

Facile Synthesis of Unsymmetrical Acridines and Phenazines by a Rhodium(III)-Catalyzed Amination, Cyclization and Aromatization Cascade

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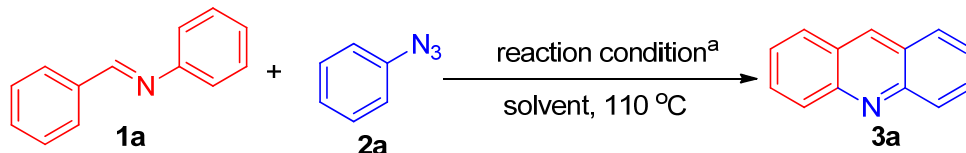
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I. General Information

Unless noted, all catalytic reactions were set up inside an inert atmosphere (N_2) glovebox utilizing glassware that was oven-dried ($150\text{ }^\circ\text{C}$) and evacuated while hot prior to use, whereas the work-up and isolation of the products from the catalytic reactions were conducted on the bench-top using standard techniques. Dioxane, THF and other solvents were passed through a column of activated alumina under nitrogen and were stored in a glovebox over activated 4 Å molecular sieves prior to use. Chloroform- d_1 (Cambridge Isotopes) was used as received. All aldehydes were freshly distilled or purified by flash column chromatography before use. Acetic acid was distilled in a flame-dried apparatus under N_2 atmosphere by adding 5 %v/v acetic anhydride with 2.0 g of CrO_3 per 100 mL and heating to $100\text{ }^\circ\text{C}$ for 2 h before fractionally distilling under ambient pressure. Unless otherwise noted, all other reagents and materials were obtained from commercial suppliers and used without further purification. $[\text{Cp}^*\text{RhCl}_2]_2$,¹ $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3(\text{SbF}_6)_2]$,¹ imines,² azobenzenes,³ aromatic azides⁴ and $\text{AgBC}_{24}\text{F}_{20}$ ⁵ were synthesized according to published procedures. Chromatography was performed on Merck 60 230-240 mesh silica gel. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR characterization data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1 and 125.8 MHz (respectively) with chemical shifts reported in parts per million relative to CHCl_3 (^1H NMR; 7.26 ppm, $^{13}\text{C}\{^1\text{H}\}$ NMR; 77.00 ppm). IR spectra were recorded on a Nicolet 6700 FTIR spectrometer and only partial data are provided. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Mass spectra (HRMS) were obtained by the Keck Center of Yale University using a Bruker 9.4 TAPEXQe FT-ICR mass spectrometer.

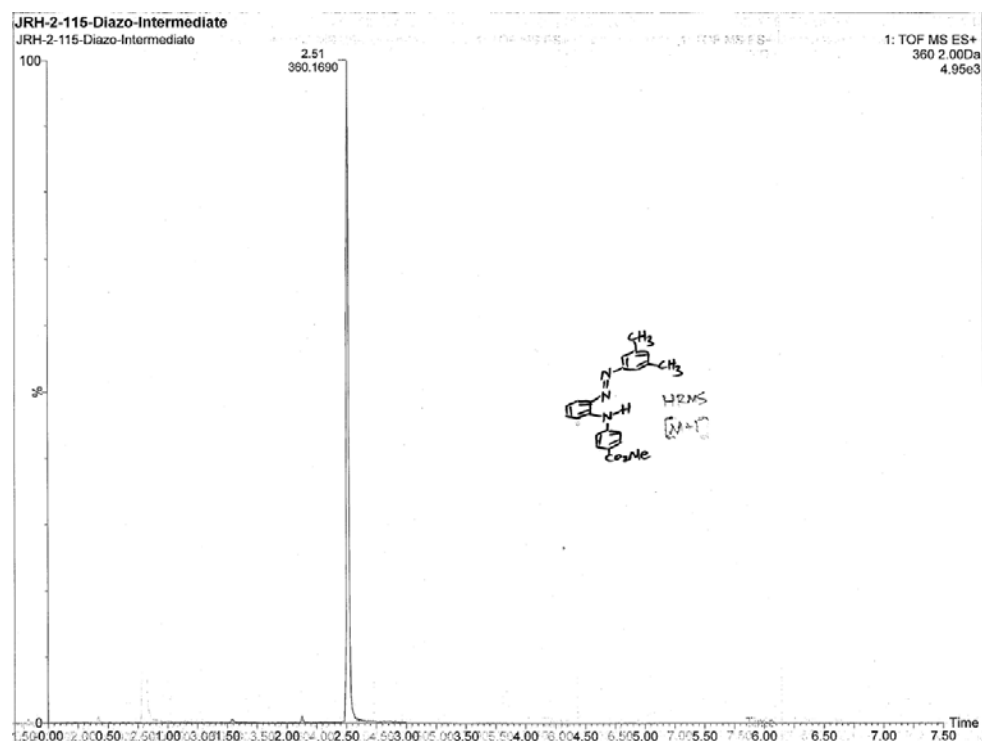
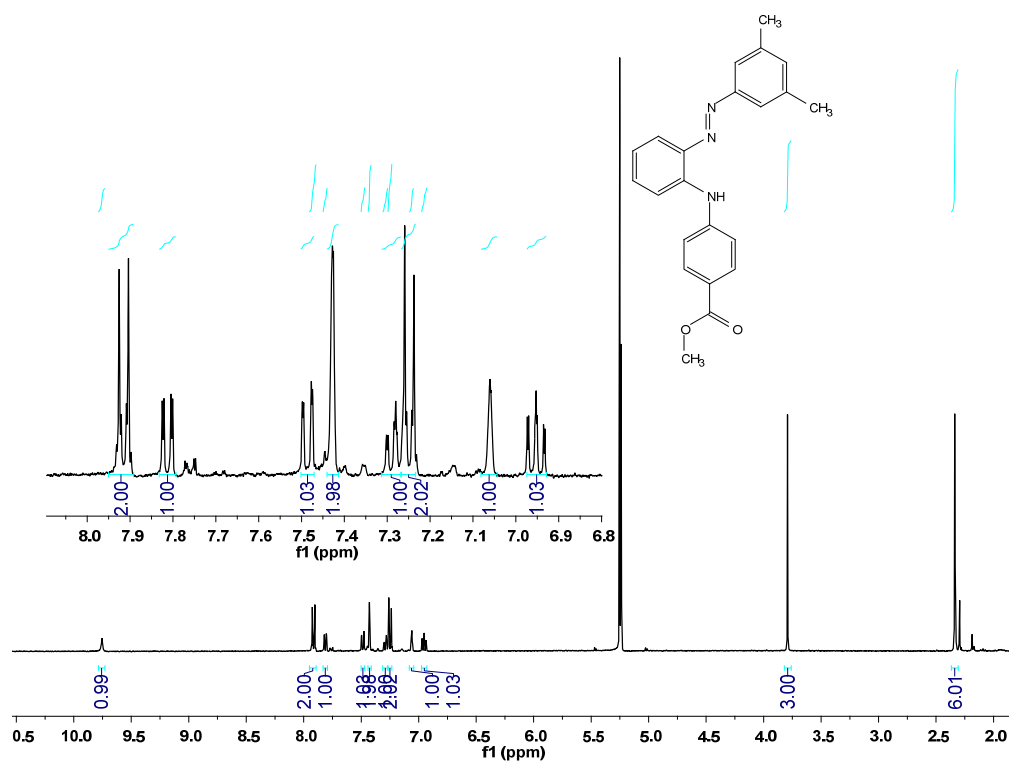
II. Optimization of Reaction Conditions for Equation 1



entry	solvent	catalyst	catalyst loading (mol%)	additive	yield ^b
1	DCE	[(Cp*RhCl ₂) ₂], AgSbF ₆	5	--	57
2	THF	[(Cp*RhCl ₂) ₂], AgSbF ₆	5	--	18
3	Dioxane	[(Cp*RhCl ₂) ₂], AgSbF ₆	5	--	25
4	EtOAc	[(Cp*RhCl ₂) ₂], AgSbF ₆	5	--	16
5	HOAc	[(Cp*RhCl ₂) ₂], AgSbF ₆	10	--	0
6	DCE	Cp*Rh(CH ₃ CN) ₃ (SbF ₆) ₂	10	--	56
7	DCE	Cp*Rh(CH ₃ CN) ₃ (SbF ₆) ₂	10	2.0 equiv. CF ₃ CO ₂ CH ₂ CF ₃	71
8	DCE	Cp*Rh(CH ₃ CN) ₃ (SbF ₆) ₂	10	2.0 equiv. Ac ₂ O	77
9	DCE	[(Cp*RhCl ₂) ₂]	5	--	0
10	DCE	AgSbF ₆	20	--	0

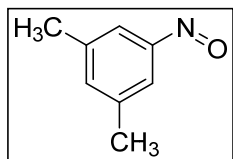
^a Conditions: **1a** (0.10 mmol), **2a** (0.20 mmol) in 1.0 mL of solvent for 20 h. ^b Determined by ¹H NMR relative to 2,6-dimethoxytoluene as external standard.

III. ¹H NMR and LCMS of uncyclized diarylamine 13 derived from 7b and 2b

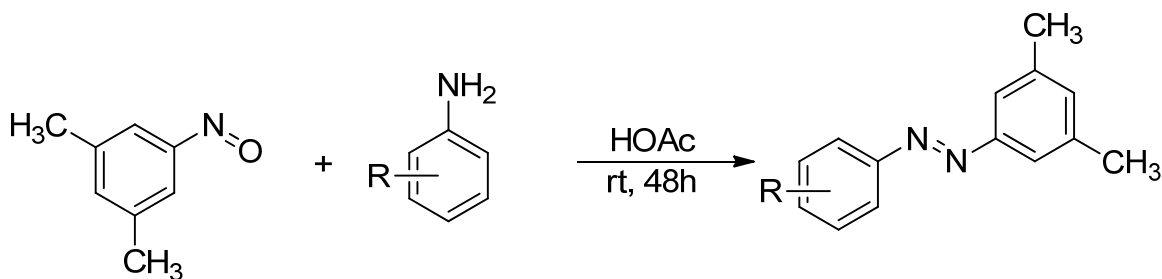


HRMS (ESI/[M+H]⁺) calcd. for C₂₂H₂₂N₃O₂: 360.1707. Found 360.1690.

IV. Preparation of Starting Materials

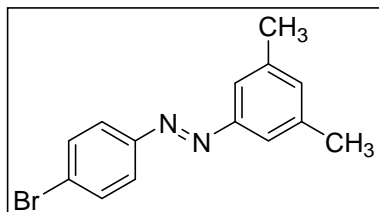


Procedure for 1,3-dimethyl-5-nitrosobenzene formation (S1)⁶: In a three-necked round bottom flask equipped with a thermometer adapter and magnetic stirring bar was added the Ph₂Se₂ catalyst (1.436 g, 4.600 mmol, 5 mol %) and 3,5-dimethylaniline (11.149 g, 92.002 mmol, 1.0 equiv) in 115 mL of CHCl₃. The flask was covered with aluminum foil and placed into a water bath. Following this, a 30% aqueous H₂O₂ solution (27.68 mL, 277.1 mmol, 3.0 equiv) was added dropwise over ca. 0.5 h [note that slow addition is necessary because the reaction is exothermic]. The reaction mixture was then stirred at room temperature for 2 h. At this time the reaction mixture was transferred to a separatory funnel, and the aqueous phase was extracted with CHCl₃ (3 × 60 mL). The combined organic phases were dried (MgSO₄) and concentrated at 0 °C. Purification by silica gel column chromatography using pentane/Et₂O (20:1) as the eluent provided the product, which eluted as a green band. This material was triturated with a minimal amount of pentane to afford product **S1** 2.603 g (21%) as an off-white solid (mp: 59-60 °C). IR (film): 3046, 2197, 1615, 1589, 1469, 1396, 1368, 1278, 1266, 1153, 1048, 978, 913, 858 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.51 (s, 2H), 7.37 (s, 1H), 2.46 (s, 6H); ¹³C {¹H} NMR (CDCl₃) δ 166.7, 139.2, 137.0, 119.0, 21.0.



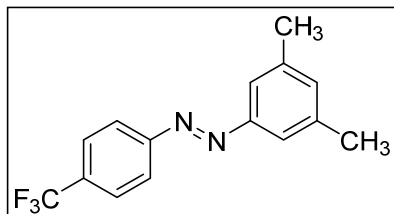
General Procedure for the Preparation of Azobenzenes: To a round bottom flask equipped with a stir bar was combined the indicated aniline (6.00 mmol, 1.2 equiv) and 3,5-dimethylnitrosobenzene **S1** (0.676 g, 5.00 mmol, 1.0 equiv) in glacial acetic acid (50 mL, 0.1 M) as solvent. The flask was covered with aluminum foil, and the reaction solution was stirred at room temperature for 48 h. The reaction solution was diluted with hexanes and was transferred to a separatory funnel with water (250 mL). The organic layer was collected and washed with water

(150 mL). The organic layer was dried with MgSO₄, and concentrated. Purification by flash column chromatography with hexanes/ethyl acetate (30:1) afforded the azobenzene.



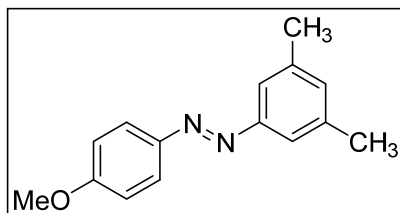
(E)-1-(4-Bromophenyl)-2-(3,5-dimethylphenyl)diazene (7c):

From 4-bromoaniline (0.413 g, 2.40 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (30:1) as eluent the product **7c** (0.278 g, 48% yield) was obtained as an orange powder (mp: 58-59 °C). IR (film) 1610, 1573, 1468, 1396, 1373, 1284, 1262, 1152, 1123, 1097, 1060, 1004, 907, 878, 854, 831 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.78 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.54 (s, 2H), 7.14 (s, 1H), 2.42 (s, 6H); ¹³C NMR (CDCl₃) δ 152.7, 151.4, 138.8, 133.0, 132.3, 125.1, 124.2, 120.7, 21.2; HRMS (ESI/[M+H]⁺) calcd. for C₁₄H₁₄BrN₂: 289.0335. Found 289.0333.



(E)-1-(3,5-Dimethylphenyl)-2-(4-(trifluoromethyl)phenyl)diazene (7d):

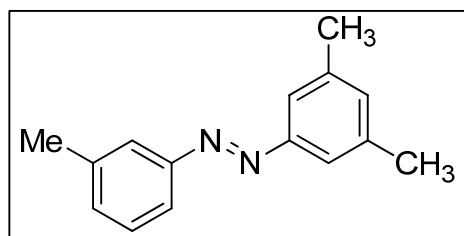
From 4-(trifluoromethyl)aniline (0.387 g, 2.40 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (30:1) as eluent the product **7d** (0.220 g, 39% yield) was obtained as an orange powder (mp: 30-31 °C). IR (film) 3010, 2926, 1611, 1456, 1410, 1318, 1285, 1263, 1164, 1101, 1061, 1010, 900, 881, 845 cm⁻¹; ¹H NMR (CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.58 (s, 2H), 7.17 (s, 1H), 2.43 (s, 6H); ¹³C {¹H} NMR (CDCl₃) δ 154.5, 152.7, 138.9, 133.5, 132.0 (q, *J* = 32.3 Hz), 126.2 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 273.0 Hz), 122.9, 121.0, 21.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.57; HRMS (ESI/[M+H]⁺) calcd. for C₁₅H₁₄F₃N₂: 279.1104. Found 279.1101.



(E)-1-(3,5-Dimethylphenyl)-2-(4-methoxyphenyl)diazene (7e):

From *p*-anisidine (0.296 g, 2.40 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (30:1) as eluent the product **7e** (0.294 g, 61% yield) was obtained as a red oil. IR (film) 1599, 1500, 1462, 1295, 1247, 1180, 1143, 1102, 1028, 852, 834 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.91 (d, *J* = 9.0 Hz, 2H), 7.51 (s, 2H), 7.09 (s, 1H),

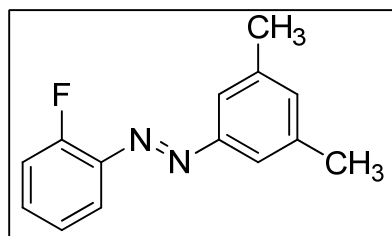
7.02 (d, $J = 9.0$ Hz, 2H), 3.89 (s, 3H), 2.41 (s, 6H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 161.9, 153.0, 147.1, 138.7, 132.1, 124.6, 120.3, 114.2, 55.6, 21.2; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}$: 241.1335. Found 241.1333.



(E)-1-(3,5-Dimethylphenyl)-2-(m-tolyl)diazene (7f):

From *m*-toluidine (0.257 g, 2.40 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (30:1) as eluent the product **7f** (0.289 g, 64% yield) was obtained as a red powder. (mp: 40-41 °C)

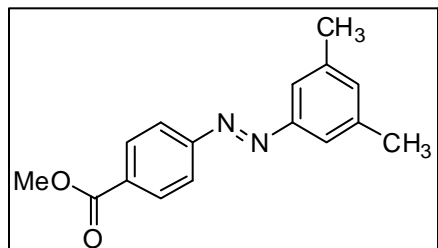
IR (film): 2919, 1607, 1465, 1285, 1139, 1078, 1040, 913, 878, 855 cm^{-1} ; ^1H NMR (CD_2Cl_2) δ 7.72 (s, 1H), 7.70 (d, $J = 7.6$ Hz, 1H), 7.53 (s, 2H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.15 (s, 1H), 2.46 (s, 3H), 2.42 (s, 6H); ^{13}C $\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 153.5, 153.4, 139.8, 139.5, 133.2, 132.2, 129.4, 123.5, 121.1, 120.7, 21.7, 21.6; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_2$: 225.1386. Found 225.1384.



(E)-1-(3,5-Dimethylphenyl)-2-(2-fluorophenyl)diazene (7g):

From 2-fluoroaniline (0.267 g, 2.40 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (30:1) as eluent the product **7g** (0.297 g, 65% yield) was obtained as a red powder (mp: 30-31 °C). IR (film):

1589, 1481, 1374, 1286, 1260, 1220, 1123, 1101, 855 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.74 (td, $J = 7.8$, 1.7 Hz, 1H), 7.58 (s, 2H), 7.42-7.48 (m, 1H), 7.17-7.30 (m, 2H), 7.15 (s, 1H), 2.42 (s, 6H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 160.0 (d, $J = 257.2$ Hz), 153.0, 140.8 (d, $J = 6.9$ Hz), 138.8, 133.2, 132.2 (d, $J = 8.3$ Hz), 124.3 (d, $J = 3.8$ Hz), 120.9, 117.8, 117.0 (d, $J = 19.9$ Hz), 21.2; ^{19}F NMR (376 MHz, CDCl_3) δ -125.77; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{14}\text{H}_{14}\text{FN}_2$: 229.1136. Found 229.1120.



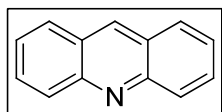
(E)-Methyl 4-((3,5-dimethylphenyl)diazenyl)benzoate (7h):

From methyl 4-aminobenzoate (0.907 g, 6.00 mmol, 1.2 equiv) with purification by silica gel column chromatography using hexane/EtOAc (20:1) as eluent the

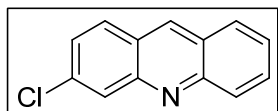
product **7h** (0.785 g, 59% yield) was obtained as a red powder (mp: 104-105 °C). IR 1723, 1601, 1439, 1404, 1274, 1190, 1107, 916, 860 (film) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 8.19 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 8.8 Hz, 2H), 7.57 (s, 2H), 7.15 (s, 1H), 3.95 (s, 3H), 2.42 (s, 6H); ^{13}C { ^1H } NMR (CDCl_3) δ 166.7, 155.4, 152.9, 139.0, 133.5, 131.7, 130.7, 122.6, 121.1, 52.4, 21.3; HRMS (ESI/[M+H] $^{+}$) calcd. for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_2$: 269.1285. Found 269.1283.

V. Rh(III)-catalyzed Acridines Synthesis by Reaction with Aldehydes and Azides

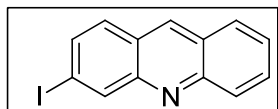
General Procedure: In a N_2 -filled glovebox, $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3(\text{SbF}_6)_2]$ (16.8 mg, 0.0200 mmol, 0.10 equiv), MgSO_4 (100 mg), benzylamine (8.6 mg, 0.080 mmol, 0.4 equiv), the indicated aldehyde (0.200 mmol, 1.0 equiv) and azide (0.300 mmol, 1.5 equiv) were added to a screw-capped conical vial with a stir bar followed by addition of DCE (4.0 mL, aldehyde = 0.050 M). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath at 110 °C. After 20 h of stirring, the vial was removed from the oil bath and was cooled to ambient temperature. The mixture was filtered through a pad of celite, washed with CH_2Cl_2 , and the solvent was removed under reduced pressure. The crude residue was loaded onto a silica gel column for chromatographic purification.



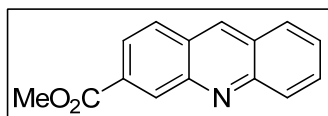
Acridine (3a): Derived from benzaldehyde (**4a**) (21.3 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexane/ethyl acetate (4/1) as eluent afforded the product **3a** (27.3 mg, 76% yield) as a yellowish powder. ^1H NMR (CDCl_3): δ 8.77 (s, 1H), 8.25 (dd, J = 8.8, 0.8 Hz, 2H), 8.01 (dm, J = 8.4 Hz, 2H), 7.79 (ddd, J = 8.8, 6.6, 1.4 Hz, 2H), 7.54 (ddd, J = 8.4, 6.6, 0.8 Hz, 2H); ^{13}C { ^1H } NMR (CDCl_3): δ 149.1, 136.1, 130.3, 129.4, 128.2, 126.6, 125.7. The analytical data for this compound are consistent with previously reported data.⁷



3-Chloroacridine (3b): Derived from 4-chlorobenzaldehyde (28.2 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3b** (35.1 mg, 82% yield) as a yellowish powder (mp: 131-133 °C). IR (film): 3053, 1612, 1554, 1509, 1453, 1304, 1059, 960, 910, 898, 786 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.72 (s, 1H), 8.23 (d, $J = 1.9$ Hz, 1H), 8.20 (dd, $J = 8.8, 0.7$ Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.92 (d, $J = 9.0$ Hz, 1H), 7.80 (ddd, $J = 9.0, 6.8, 1.4$ Hz, 1H), 7.54 (ddd, $J = 8.2, 6.8, 0.8$ Hz, 1H), 7.46 (dd, $J = 9.0, 2.0$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 149.6, 148.9, 136.3, 136.1, 130.9, 129.44, 129.37, 128.2, 128.0, 127.1, 126.5, 126.0, 124.8; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{13}\text{H}_9\text{ClN}$: 214.0418. Found 214.0413.

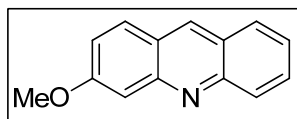


3-Iodoacridine (3c): Derived from 4-Iodobenzaldehyde (46.4 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexanes/ethyl acetate (10/1) as eluent afforded the product **3c** (40.3 mg, 66% yield) as a yellowish powder (mp: 131-133 °C). IR (film): 1603, 1550, 1446, 1423, 1387, 1153, 1039, 963, 926, 910, 787, 740 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.69 (m, 1H), 8.66 (m, 1H), 8.19 (dd, $J = 8.8, 0.8$ Hz, 1H), 7.94 (dm, $J = 8.4$ Hz, 1H), 7.78 (ddd, $J = 8.8, 6.6, 1.4$ Hz, 1H), 7.72 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.65 (d, $J = 8.8$ Hz, 1H), 7.53 (ddd, $J = 8.3, 6.9, 1.2$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 149.23, 149.19, 138.5, 136.1, 134.2, 130.8, 129.5, 129.0, 128.2, 126.7, 126.1, 125.2, 97.1; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{13}\text{H}_9\text{IN}$: 305.9774. Found 305.9778.

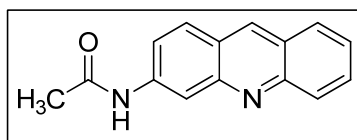


Methyl acridine-3-carboxylate (3d): Derived from methyl 4-formylbenzoate (32.9 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3d** (42.7 mg, 90% yield) as a yellowish powder (mp: 150-152 °C). IR (film): 1710, 1558, 1314, 1229, 1085, 911, 806, 734 cm^{-1} ; ^1H NMR (CDCl_3): δ 9.00 (s, 1H), 8.78 (s, 1H), 8.26 (d, $J = 8.8$ Hz, 1H), 8.09 (dd, $J = 8.8, 1.5$ Hz, 1H), 8.04 (d, $J = 8.8$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 7.81 (ddd, $J = 8.8, 6.8, 1.4$ Hz, 1H), 7.58 (ddd, $J = 8.4, 6.8, 0.8$ Hz, 1H), 4.02 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 166.8, 149.8, 148.1, 135.7, 132.8, 131.5, 130.7, 129.8, 128.5, 128.2, 128.1, 127.4, 126.8, 124.5, 52.5; HRMS

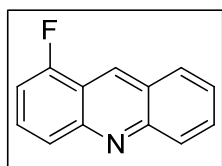
(ESI/[M+H]⁺) calcd. for C₁₅H₁₂NO₂: 238.0863. Found 238.0858.



3-Methoxyacridine (3e): Derived from 4-anisaldehyde (27.3 mg) and phenylazide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3e** (25.1 mg, 60% yield) as a yellowish powder (mp: 89-91 °C). IR (film): 2970, 1633, 1482, 1433, 1274, 1204, 1169, 1026, 914, 862 cm⁻¹; ¹H NMR (CDCl₃): δ 8.64 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.75 (ddd, *J* = 8.8, 6.8, 1.4 Hz, 1H), 7.44-7.50 (m, 2H), 7.20 (dd, *J* = 9.2, 2.4 Hz, 1H), 4.00 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 161.5, 150.8, 149.1, 135.7, 130.3, 129.3, 128.7, 128.3, 125.5, 124.7, 122.9, 121.2, 105.1, 55.6; HRMS (ESI/[M+H]⁺) calcd. for C₁₄H₁₂NO: 210.0913. Found 210.0910.

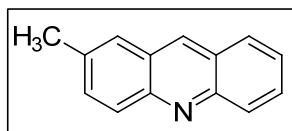


N-(acridin-3-yl)acetamide (3f): Derived from *N*-(4-formylphenyl)acetamide (32.7 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using ethyl acetate as eluent afforded the product **3f** (30.3 mg, 64% yield) as a yellowish powder (mp: 236-238 °C). IR (film): 2922 (br), 1694, 1616, 1484, 1439, 1309, 1018, 906 cm⁻¹; ¹H NMR (CD₃OD): δ 8.80 (s, 1H), 8.53 (s, 1H), 8.05 (dd, *J* = 8.8, 0.7 Hz, 1H), 7.99 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.95 (d, *J* = 9.1 Hz, 1H), 7.77 (ddd, *J* = 8.8, 6.6, 1.4 Hz, 1H), 7.61 (dd, *J* = 9.1, 1.9 Hz, 1H), 7.50 (ddd, *J* = 8.4, 6.6, 1.0 Hz, 1H), 2.22 (s, 3H); ¹³C{¹H} NMR (CD₃OD): δ 172.3, 150.6, 150.1, 142.4, 138.3, 132.3, 130.4, 129.9, 128.6, 127.5, 126.5, 125.4, 122.3, 115.4, 24.3; HRMS (ESI/[M+H]⁺) calcd. for C₁₅H₁₃N₂O: 237.1022. Found 237.1016.

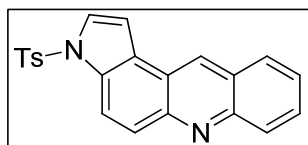


1-Fluoroacridine (3g): Derived from 1-fluorobenzaldehyde (24.9 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3g** (32.7 mg, 83% yield) as a yellowish powder (mp: 108-110 °C). IR (film): 3049, 1643, 1555, 1520, 1468, 1310, 1215, 1133, 1020, 907, 808, 725 cm⁻¹; ¹H NMR (CDCl₃): δ 9.04 (s, 1H), 8.23 (dd, *J* = 8.8, 0.7 Hz, 1H), 8.04 (d, *J* = 8.9 Hz, 2H), 7.82 (ddd, *J* = 8.4, 6.6, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.9, 7.5, 6.2 Hz, 1H), 7.57 (ddd, *J* = 8.4, 6.8, 0.8 Hz,

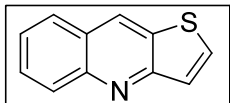
1H), 7.17 (dd, $J = 8.9, 7.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 157.9 (d, $J = 257.1$ Hz), 149.4, 149.3 (d, $J = 2.5$ Hz), 131.0, 129.9 (d, $J = 4.2$ Hz), 129.5, 129.3 (d, $J = 9.0$ Hz), 128.5, 126.23, 126.17 (d, $J = 2.5$ Hz), 125.4 (d, $J = 4.2$ Hz), 118.4 (d, $J = 17.2$ Hz), 107.9 (d, $J = 19.1$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -122.52; HRMS (ESI/[M+H] $^{+}$) calcd. for $\text{C}_{13}\text{H}_9\text{FN}$: 198.0714. Found 198.0710.



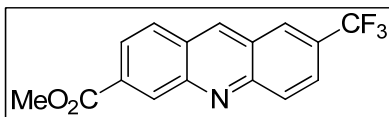
2-Methylacridine (3h): Derived from *m*-tolualdehyde (24.1 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3h** (30.5 mg, 79% yield) as a yellowish powder (mp: 131-133 °C). IR (film): 3052, 2910, 1515, 1404, 1149, 975, 920, 821 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.62 (s, 1H), 8.22 (dd, $J = 8.8, 0.8$ Hz, 1H), 8.13 (d, $J = 8.9$ Hz, 1H), 7.96 (dm, $J = 8.4$ Hz, 1H), 7.74 (ddd, $J = 8.0, 6.6, 1.4$ Hz, 1H), 7.71 (s, 1H), 7.61 (dd, $J = 8.9, 1.9$ Hz, 1H), 7.61 (ddd, $J = 8.9, 8.0, 1.0$ Hz, 1H), 2.56 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 148.6, 148.1, 135.4, 134.8, 133.2, 129.7, 129.4, 129.1, 128.1, 126.7, 126.7, 126.2, 125.5, 21.8; HRMS (ESI/[M+H] $^{+}$) calcd. for $\text{C}_{14}\text{H}_{12}\text{N}$: 194.0964. Found 194.0960.



3-Tosyl-3H-pyrrolo[3,2-a]acridine (3i): Derived from 1-tosyl-1H-indole-4-carbaldehyde (59.9 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3i** (31.3 mg, 42% yield) as a yellowish powder (mp: 239-240 °C). IR (film): 3134, 3021, 1365, 1294, 1183, 1121, 1005, 821, 726, 704 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.96 (s, 1H), 8.44 (d, $J = 9.5$ Hz, 1H), 8.24 (d, $J = 8.7$ Hz, 1H), 8.08 (d, $J = 9.5$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.74-7.90 (m, 2H), 7.56 (t, $J = 7.8$ Hz, 1H), 7.29 (d, $J = 3.5$ Hz, 1H), 7.24 (d, $J = 8.4$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 148.0, 147.4, 145.4, 135.7, 130.8, 130.4, 130.1, 129.7, 129.4, 127.8, 126.8, 126.7, 126.4, 126.0, 125.60, 125.55, 121.3, 118.9, 107.6, 21.5; HRMS (ESI/[M+H] $^{+}$) calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$: 373.1005. Found 373.1019.

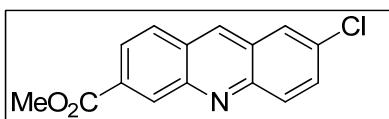


Thieno[3,2-b]quinoline (3j): Derived from benzaldehyde (21.3 mg) and 3-azidothiophene (37.6 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3j** (25.2 mg, 68% yield) as a yellowish powder (mp: 105-106 °C). IR (film): 3058, 2921, 1614, 1582, 1544, 1506, 1393, 1364, 1303, 1225, 1081, 1018, 903, 793, 742 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.67 (s, 1H), 8.20 (dd, $J = 8.6, 0.7$ Hz, 1H), 7.93 (d, $J = 5.7$ Hz, 1H), 7.91 (dm, $J = 8.2$ Hz, 1H), 7.75 (ddd, $J = 8.4, 5.3, 1.4$ Hz, 1H), 7.64 (dd, $J = 5.7, 0.8$ Hz, 1H), 7.55 (ddd, $J = 8.1, 6.7, 1.1$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 157.6, 147.0, 134.6, 131.0, 129.7, 129.21, 129.17, 127.4, 125.7, 125.0, 124.7; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{11}\text{H}_8\text{NS}$: 186.0372. Found 186.0370.



Methyl 7-(trifluoromethyl)acridine-3-carboxylate (3k): Derived from methyl 4-formylbenzoate (32.9 mg) and 1-azido-4-(trifluoromethyl)benzene (56.2 mg, 0.300 mmol, 1.5 equiv).

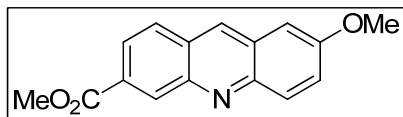
Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3k** (45.2 mg, 74% yield) as a yellowish powder (mp: 196-198 °C). IR (film): 1725, 1475, 1437, 1330, 1260, 1236, 1138, 1056, 925, 846, 757 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.96 (s, 1H), 8.85 (s, 1H), 8.33 (d, $J = 9.2$ Hz, 1H), 8.31 (s, 1H), 8.12 (dd, $J = 8.8, 1.5$ Hz, 1H), 8.04 (d, $J = 8.8$ Hz, 1H), 7.91 (dd, $J = 9.1, 1.9$ Hz, 1H), 4.03 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 166.4, 149.7, 149.4, 137.3, 132.7, 132.6, 131.3, 128.6, 128.4 (q, $J = 32.5$ Hz), 128.3, 126.5 (q, $J = 4.8$ Hz), 125.8 (q, $J = 2.8$ Hz), 125.6, 125.4, 123.8 (q, $J = 272.2$ Hz), 52.6; ^{19}F NMR (376 MHz, CDCl_3) δ -63.97; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{16}\text{H}_{11}\text{F}_3\text{NO}_2$: 306.0736. Found 306.0730.



Methyl 7-chloroacridine-3-carboxylate (3l): Derived from methyl 4-formylbenzoate (32.9 mg) and 1-azido-4-chlorobenzene (46.1 mg, 0.300 mmol, 1.5 equiv). Purification

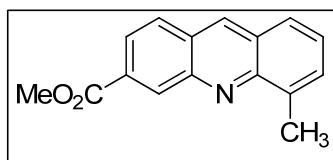
by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3l** (45.7 mg, 84% yield) as a yellowish powder (mp: 203-205 °C). IR (film): 1717, 1557, 1509, 1300, 1191, 1087, 1068, 920, 752 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.92 (s, 1H), 8.62 (s, 1H), 8.16 (d, $J = 9.2$ Hz, 1H), 8.07 (dd, $J = 8.8, 1.5$ Hz, 1H), 7.98 (d, $J = 8.8$ Hz, 1H), 7.94 (d, $J = 2.3$

Hz, 1H), 7.69 (dd, $J = 9.3, 2.3$ Hz, 1H), 4.02 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 166.6, 148.1, 147.9, 134.6, 132.8, 132.6, 131.9, 131.7, 131.5, 128.3, 128.2, 127.4, 126.2, 125.2, 52.5; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{15}\text{H}_{11}\text{ClNO}_2$: 272.0473. Found 272.0466.



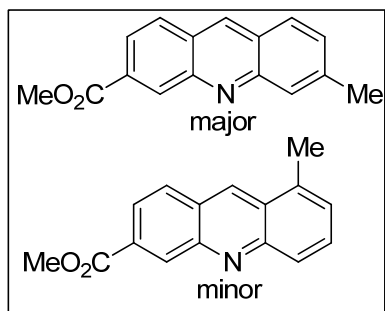
Methyl 7-methoxyacridine-3-carboxylate (3m): Derived from methyl 4-formylbenzoate (32.9 mg) and 1-azido-4-methoxybenzene (44.8 mg, 0.300 mmol, 1.5 equiv).

Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3m** (41.2 mg, 77% yield) as a yellowish powder (mp: 208-210 °C). IR (film): 1707, 1634, 1477, 1300, 1197, 1090, 1022, 915, 868, 839 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.93 (t, $J = 0.6$ Hz, 1H), 8.55 (s, 1H), 8.12 (d, $J = 9.5$ Hz, 1H), 8.05 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.94 (d, $J = 8.8$ Hz, 1H), 7.47 (dd, $J = 9.5, 2.8$ Hz, 1H), 7.10 (d, $J = 2.8$ Hz, 1H), 4.01 (s, 3H), 3.97 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 166.9, 157.8, 147.0, 146.4, 133.1, 132.8, 131.3, 130.3, 128.5, 128.4, 127.8, 126.1, 124.7, 102.9, 55.6, 52.4; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{16}\text{H}_{14}\text{NO}_3$: 268.0968. Found 268.0962.



Methyl 5-methylacridine-3-carboxylate (3n): Derived from methyl 4-formylbenzoate (32.9 mg) and 2-azidotoluene (40.0 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column

chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **3n** (42.7 mg, 85% yield) as a yellowish powder (mp: 103-105 °C). IR (film): 2948, 1710, 1566, 1431, 1316, 1289, 1239, 1204, 1092, 921, 740 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.99 (t, $J = 0.6$ Hz, 1H), 8.65 (s, 1H), 8.04 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.97 (d, $J = 8.7$ Hz, 1H), 7.80 (d, $J = 8.5$ Hz, 1H), 7.80 (dm, $J = 8.5$ Hz, 1H), 7.44 (dd, $J = 8.4, 6.7$ Hz, 1H), 4.02 (s, 3H), 2.93 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 166.9, 149.2, 147.3, 137.7, 135.5, 133.3, 130.9, 129.8, 128.2, 127.9, 127.4, 126.6, 126.1, 124.3, 52.4, 18.3; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{16}\text{H}_{14}\text{NO}_2$: 252.1019. Found 252.1012.

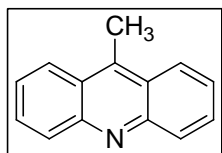


Methyl 6-methylacridine-3-carboxylate (30): Derived from methyl 4-formylbenzoate (32.9 mg) and 3-azidotoluene (40.0 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using hexanes/ethyl acetate (4/1) as eluent afforded the product **31** (38.2 mg, 76% yield) as an inseparable mixture of two isomers in 7:1 ratio and as a yellowish powder. IR (film): 2953, 1707, 1556, 1434, 1315, 1234, 1145, 1089, 910,

752 cm^{-1} ; Major isomer: ^1H NMR (CDCl_3): δ 8.95 (s, 1H), 8.67 (s, 1H), 8.04 (dd, $J = 8.7, 1.6$ Hz, 1H), 8.00 (s, 1H), 7.98 (d, $J = 8.8$ Hz, 1H), 7.87 (d, $J = 8.6$ Hz, 1H), 7.40 (dd, $J = 8.6, 1.5$ Hz, 1H), 4.03 (s, 3H), 2.62 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 166.9, 150.0, 148.1, 141.2, 135.2, 132.6, 131.2, 129.6, 128.4, 127.9, 127.71, 127.69, 125.8, 124.0, 52.4, 22.3; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{16}\text{H}_{14}\text{NO}_2$: 252.1019. Found 252.1010.

VI. Rh(III)-catalyzed Acridine Synthesis from Imines

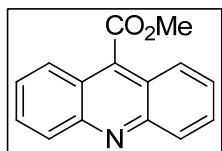
General procedure: In a N_2 -filled glovebox, $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3(\text{SbF}_6)_2]$ (16.8 mg, 0.0200 mmol, 0.10 equiv), Ac_2O (40.9 mg, 0.400 mmol, 2.0 equiv), the indicated imine (0.200 mmol, 1.0 equiv) and azide (0.300 mmol, 1.5 equiv) were added to a screw-capped conical vial with a stir bar followed by addition of DCE (2.0 mL, [imine] = 0.10 M). The vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath at 110 $^\circ\text{C}$. After stirring for 20 h, the vial was removed from the oil bath and was cooled to ambient temperature. The solvent was removed under reduced pressure. The crude residue was loaded onto a silica gel column for chromatographic purification.



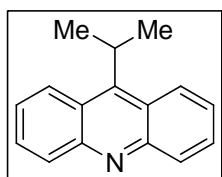
9-Methylacridine (6a): Derived from (*E*)-*N*-(1-phenylethylidene)aniline (39.1 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/ Et_2O (2/1)

as eluent afforded the product **6a** (33.6 mg, 87% yield) as a yellowish powder. ^1H NMR

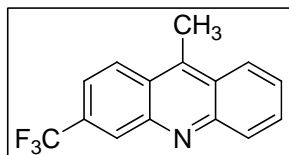
(CDCl₃): δ 8.20-8.26 (m, 4H), 7.76 (ddd, J = 7.8, 6.6, 1.2 Hz, 2H), 7.54 (dd, J = 8.4, 6.9 Hz, 2H), 3.10 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 148.4, 142.1, 130.3, 129.7, 125.5, 125.4, 124.5, 13.6. The analytical data for this compound are consistent with previously reported data.⁸



Methyl acridine-9-carboxylate (6b): Derived from (*Z*)-methyl 2-phenyl-2-(phenylimino)acetate (47.9 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O (2/1) as eluent afforded the product **6b** (37.5 mg, 79% yield) as a yellowish powder. ¹H NMR (CDCl₃): δ 8.27 (dt, J = 8.8, 0.7 Hz, 2H), 8.01 (ddd, J = 8.7, 1.2, 0.7 Hz, 2H), 7.80 (ddd, J = 8.8, 6.6, 1.3 Hz, 2H), 7.60 (ddd, J = 8.7, 6.6, 1.2 Hz, 2H), 4.21 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 168.0, 148.7, 136.8, 130.3, 130.0, 127.1, 125.1, 122.4, 52.9. The analytical data for this compound are consistent with previously reported data.⁹

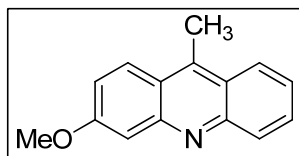


9-Isopropylacridine (6c): Derived from (*E*)-*N*-(2-methyl-1-phenylpropylidene)aniline (44.7 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O (2/1) as eluent afforded the product **6c** (38.9 mg, 88% yield) as a yellowish oil. ¹H NMR (CDCl₃): δ 8.43 (d, J = 8.9 Hz, 2H), 8.25 (d, J = 8.7 Hz, 2H), 7.73 (ddd, J = 8.6, 6.5, 1.1 Hz, 2H), 7.50 (ddd, J = 8.8, 6.5, 1.2 Hz, 2H), 4.52 (hept, J = 7.3 Hz, 1H), 1.75 (d, J = 7.3 Hz, 6H); ¹³C{¹H} NMR (CDCl₃): δ 151.8, 149.0, 130.8, 129.3, 124.9 (2C), 124.5, 28.4, 22.7. The analytical data for this compound are consistent with previously reported data.¹⁰

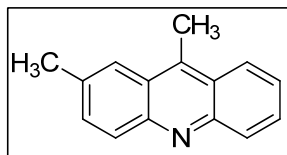


9-Methyl-3-(trifluoromethyl)acridine (6d): Derived from (*E*)-*N*-(1-(4-(trifluoromethyl)phenyl)ethylidene)aniline (52.7 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O (2/1) as eluent afforded the product **6d** (43.4 mg, 83% yield) as a yellowish powder. ¹H NMR (CDCl₃): δ 8.51 (s, 1H), 8.30 (d, J = 9.1 Hz, 1H), 8.20 (dd, J = 8.2, 7.8 Hz, 2H), 7.79 (ddd, J = 8.8, 6.5, 1.2 Hz, 1H), 7.63 (dd, J = 9.1, 1.7 Hz, 1H), 7.58 (ddd, J = 8.7, 6.5, 1.1 Hz, 1H), 3.09 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 149.2, 146.9, 142.6, 131.1 (q, J = 32.6 Hz), 130.5 (2C), 128.4 (q, J = 4.7 Hz), 126.5, 126.2,

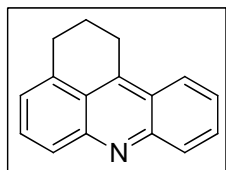
126.13, 126.07, 124.5, 124.0 (q, $J = 272.4$ Hz), 120.4 (q, $J = 2.9$ Hz), 13.7; ^{19}F NMR (376 MHz, CDCl_3) δ -64.28. The analytical data for this compound are consistent with previously reported data.⁸



3-Methoxy-9-methylacridine (6e): Derived from (*E*)-*N*-(1-(4-methoxyphenyl)ethylidene)aniline (45.1 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/ Et_2O (1/1) as eluent afforded the product **6e** (27.7 mg, 62% yield) as a yellowish powder. ^1H NMR (CDCl_3): δ 8.13 (tm, $J = 9.4$ Hz, 2H), 8.06 (d, $J = 9.5$ Hz, 1H), 7.71 (tm, $J = 7.8$ Hz, 1H), 7.46 (tm, $J = 7.8$ Hz, 1H), 7.41 (d, $J = 2.5$ Hz, 1H), 7.18 (dd, $J = 9.5, 2.6$ Hz, 1H), 3.98 (s, 3H), 3.00 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 160.8, 150.3, 142.0, 129.7, 129.5, 125.8, 124.5, 124.54, 124.49, 124.4, 121.6, 120.6, 105.7, 55.5, 13.5. The analytical data for this compound are consistent with previously reported data.¹¹

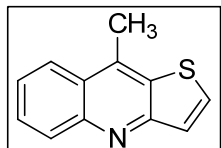


2,9-Dimethylacridine (6f): Derived from (*E*)-*N*-(1-(*m*-tolyl)ethylidene)aniline (41.9 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/ Et_2O (2/1) as eluent afforded the product **6f** (32.4 mg, 78% yield) as a yellowish powder. ^1H NMR (CDCl_3): δ 8.16-8.21 (m, 2H), 8.10 (d, $J = 8.9$ Hz, 1H), 7.94 (s, 1H), 7.71 (ddd, $J = 8.7, 6.5, 1.3$ Hz, 1H), 7.58 (dd, $J = 8.9, 1.8$ Hz, 1H), 7.51 (ddd, $J = 8.7, 6.5, 1.2$ Hz, 1H), 3.05 (s, 3H), 2.59 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 147.9, 147.3, 140.8, 135.0, 132.5, 130.2, 129.9, 129.2, 125.6, 125.5, 125.2, 124.4, 122.7, 22.2, 13.5. The analytical data for this compound are consistent with previously reported data.⁸

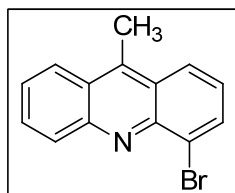


2,3-Dihydro-1H-benzo[kl]acridine (6g): Derived from (*E*)-*N*-(3,4-dihydronaphthalen-1(2H)-ylidene)aniline (44.3 mg) and phenyl azide (**2a**) (35.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/ Et_2O (2/1) as eluent afforded the product **6g** (13.9 mg, 32% yield) as a yellowish viscous oil. IR (film): 3045, 2935, 1685, 1566, 1525, 1464, 1141, 1061, 945, 813, 742 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.21 (dm, $J = 8.7$ Hz, 1H), 8.18 (dm, $J = 8.7$ Hz, 1H), 8.04 (dd, J

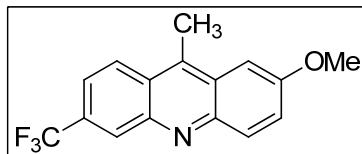
= 8.8, 0.7 Hz, 1H), 7.76 (ddd, J = 8.7, 6.6, 1.4 Hz, 1H), 7.66 (dd, J = 8.8, 6.7 Hz, 1H), 7.53 (ddd, J = 8.6, 6.6, 1.2 Hz, 1H), 7.24 (dq, J = 6.7, 1.2 Hz, 1H), 3.58 (t, J = 8.0 Hz, 2H), 3.19 (t, J = 8.0 Hz, 2H), 2.26 (pent. J = 8.0 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 148.8, 148.2, 144.0, 136.9, 130.1, 129.9, 129.7, 127.4, 125.1, 124.0, 123.8, 123.5, 122.5, 30.5, 26.5, 22.7. HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{16}\text{H}_{14}\text{N}$: 220.1121. Found 220.1117.



9-Methylthieno[3,2-b]quinoline (6h): Derived from (*E*)-*N*-(1-phenylethylidene)aniline (39.1 mg) and 3-azidothiophene (37.6 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/ Et_2O (2/1) as eluent afforded the product **6h** (34.7 mg, 87% yield) as a yellowish powder (mp: 75-77 °C). IR (film): 3325, 3068, 1579, 1553, 1493, 1369, 1258, 1136, 1081, 1015, 738 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.17 (dm, J = 8.6 Hz, 1H), 8.03 (dm, J = 9.1 Hz, 1H), 7.84 (d, J = 5.7 Hz, 1H), 7.71 (ddd, J = 8.3, 6.8, 1.5 Hz, 1H), 7.58 (d, J = 5.7 Hz, 1H), 7.52 (ddd, J = 8.3, 6.8, 1.5 Hz, 1H), 2.88 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 156.7, 147.1, 137.8, 133.6, 131.6, 129.7, 128.7, 125.5, 125.2, 124.1, 122.9, 17.1; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{12}\text{H}_{10}\text{NS}$: 200.0528. Found 200.0520.

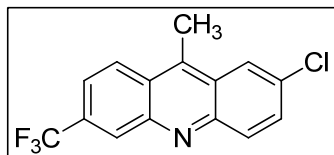


4-Bromo-9-methylacridine (6i): Derived from (*E*)-*N*-(1-phenylethylidene)aniline (39.1 mg) and 1-azido-2-bromobenzene (59.4 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/ Et_2O (2/1) as eluent afforded the product **6i** (47.4 mg, 87% yield) as a yellowish powder (mp: 127-129 °C). IR (film): 1624, 1603, 1510, 1454, 1420, 1119, 1052, 864, 750, 731 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.32 (d, J = 8.7 Hz, 1H), 8.16 (d, J = 8.7 Hz, 1H), 8.14 (dd, J = 8.8, 1.1 Hz, 1H), 8.09 (dd, J = 7.1, 1.0 Hz, 1H), 7.77 (ddd, J = 8.5, 6.6, 1.1 Hz, 1H), 7.54 (ddd, J = 8.5, 6.6, 1.1 Hz, 1H), 7.31 (dd, J = 8.7, 7.2 Hz, 1H), 3.04 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 148.6, 144.9, 143.0, 133.1, 130.9, 130.0, 126.3, 126.1, 125.9, 125.6, 125.1, 124.5, 124.3, 13.9; HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{14}\text{H}_{11}\text{BrN}$: 272.0069. Found 272.0068.



2-Methoxy-9-methyl-6-(trifluoromethyl)acridine (6j): Derived from (*E*)-*N*-(1-(4-(trifluoromethyl)phenyl)ethylidene)aniline (52.7 mg) and 1-azido-4-methoxybenzene (44.8 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using

pentane/Et₂O (2/1) as eluent afforded the product **6j** (53.1 mg, 91% yield) as a yellowish powder (mp: 149-151 °C). IR (film): 2940, 1619, 1484, 1420, 1320, 1262, 1211, 1143, 1114, 1039, 920, 809 cm⁻¹; ¹H NMR (CDCl₃): δ 8.42 (s, 1H), 8.14 (d, *J* = 9.1 Hz, 1H), 8.03 (d, *J* = 9.4 Hz, 1H), 7.56 (dd, *J* = 9.1, 1.7 Hz, 1H), 7.42 (dd, *J* = 9.4, 2.7 Hz, 1H), 7.11 (d, *J* = 2.6 Hz, 1H), 3.95 (s, 3H), 2.88 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 157.6, 146.2, 145.1, 139.3, 131.9, 129.9 (d, *J* = 32.5 Hz), 128.2 (d, *J* = 4.7 Hz), 127.0, 126.2, 125.54, 125.47, 124.1 (d, *J* = 272.2 Hz), 120.4 (d, *J* = 2.9 Hz), 99.7, 55.4, 13.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -64.07; HRMS (ESI/[M+H]⁺) calcd. for C₁₆H₁₃F₃NO: 292.0944. Found 292.0932.

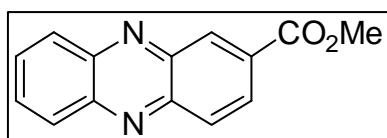


2-Chloro-9-methyl-6-(trifluoromethyl)acridine (6k): Derived from (*E*)-*N*-(1-(4-(trifluoromethyl)phenyl)ethylidene)aniline (52.7 mg) and 1-azido-4-chlorobenzene (46.1 mg, 0.300 mmol, 1.5 equiv).

Purification by silica gel column chromatography using pentane/Et₂O (2/1) as eluent afforded the product **6k** (30.2 mg, 51% yield) as a yellowish powder (mp: 137-139 °C). IR (film): 1613, 1556, 1516, 1414, 1314, 1249, 1171, 1113, 906, 888, 811, 720 cm⁻¹; ¹H NMR (CDCl₃): δ 8.48 (s, 1H), 8.29 (d, *J* = 9.1 Hz, 1H), 8.18 (d, *J* = 2.1 Hz, 1H), 8.13 (d, *J* = 9.2 Hz, 1H), 7.70 (dd, *J* = 9.2, 2.2 Hz, 1H), 7.67 (dd, *J* = 9.2, 1.8 Hz, 1H), 3.05 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 147.4, 147.0, 141.7, 132.6, 132.2, 131.7, 131.5 (d, *J* = 32.7 Hz), 128.5 (d, *J* = 4.7 Hz), 126.5, 126.4, 126.0 123.9 (d, *J* = 272.5 Hz), 123.2, 121.1 (d, *J* = 2.9 Hz), 13.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -64.36; HRMS (ESI/[M+H]⁺) calcd. for C₁₅H₁₀ClF₃N: 296.0448. Found 296.0444.

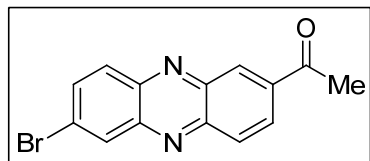
VII. Rh(III)-catalyzed Phenazine Synthesis by Reaction with Azobenzenes

General procedure: In a N₂-filled glovebox, [Cp*RhCl₂]₂ (6.2 mg, 0.010 mmol, 0.05 equiv), AgB(C₆F₅)₄ (41.2 mg, 0.0400 mmol, 0.20 equiv, 23.6 %w/w toluene), the indicated diazobenzene (0.200 mmol, 1.0 equiv) and aryl azide (0.300 mmol, 1.5 equiv) were added to a 10-20 mL microwave vial with a stir bar followed by addition of distilled HOAc (4.0 mL, 0.05 M) [use of glacial acetic acid without distillation results in a reduced yield]. The vial was sealed and was removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath at 110 °C. After stirring for 24 h, the vial was removed from the oil bath and was cooled to ambient temperature. The mixture was diluted with CH₂Cl₂ and filtered through a pad of celite with CH₂Cl₂, and the solvent was removed under reduced pressure. The crude residue was loaded onto a silica gel column for chromatographic purification.



Methyl phenazine-2-carboxylate (8a): Derived from (*E*)-1,2-diphenyldiazene (**7a**) (36.4 mg, 0.200 mmol, 1.0 equiv) and methyl 4-azidobenzoate (53.2 mg, 0.300 mmol, 1.5 equiv).

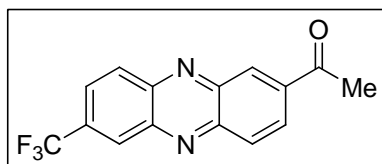
Purification by silica gel column chromatography using pentane/Et₂O/CH₂Cl₂ (6:3:1) as eluent afforded the product **8a** (29.2 mg, 61% yield) as a yellow solid (mp: 153-154 °C). IR (film): 3053, 3016, 2961, 1721, 1512, 1441, 1361, 1315, 1292, 1244, 1196, 1146, 1093, 973, 945, 906, 850, 808 cm⁻¹; ¹H NMR (CDCl₃): δ 8.94 (d, *J* = 1.9 Hz, 1H), 8.35 (dd, *J* = 9.1, 1.9 Hz, 1H), 8.22 (m, 3H), 7.85 (m, 2H), 4.02 (s, 3H). ¹³C NMR (CDCl₃) δ 166.2, 144.6, 144.3, 144.1, 142.5, 132.9, 131.6, 131.5, 130.9, 130.0, 129.9, 129.7, 129.2, 52.7. HRMS (ESI/[M+H]⁺) calcd. for C₁₄H₁₁N₂O₂: 239.0815. Found 239.0809.



1-(7-Bromophenazin-2-yl)ethanone (8b): Derived from (*E*)-1-(4-bromophenyl)-2-(3,5-dimethylphenyl)diazene (**7c**) (57.9 mg, 0.200 mmol, 1.0 equiv) and 1-(4-azidophenyl)ethanone (48.4 mg,

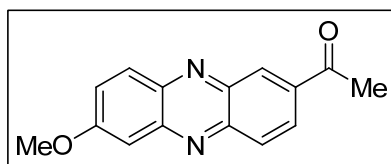
0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O/CH₂Cl₂ (6:3:1) as eluent afforded the product **8b** (38.8 mg, 64% yield) as a yellow

solid (mp: 197-199 °C). IR (film): 1673, 1594, 1415, 1354, 1276, 1221, 1181, 1131, 1042, 915, 878, 816 cm⁻¹; ¹H NMR (CDCl₃): δ 8.76 (d, *J* = 1.8 Hz, 1H), 8.43 (d, *J* = 2.1 Hz, 1H), 8.38 (dd, *J* = 9.1, 1.9 Hz, 1H), 8.23 (d, *J* = 9.1 Hz, 1H), 8.10 (d, *J* = 9.2 Hz, 1H), 7.90 (dd, *J* = 9.2, 2.1 Hz, 1H), 2.81 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 197.0, 145.1, 144.4, 142.8, 142.6, 138.1, 134.8, 132.1, 131.7, 131.0, 130.1, 128.5, 126.5, 26.6; HRMS (ESI/[M+H]⁺) calcd. for C₁₄H₁₀BrN₂O: 300.9971. Found 300.9991.



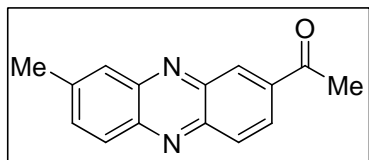
1-(7-(Trifluoromethyl)phenazin-2-yl)ethanone (8c): Derived from (E)-1-(3,5-dimethylphenyl)-2-(4-(trifluoromethyl)phenyl)diazene (**7d**) (55.7 mg, 0.200 mmol, 1.0

equiv) and 1-(4-azidophenyl)ethanone (48.4 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O/CH₂Cl₂ (9:1:1) as eluent afforded the product **8c** (38.9 mg, 67% yield) as a yellow solid (mp: 129-131 °C). IR (film): 1676, 1477, 1424, 1325, 1256, 1194, 1161, 1118, 1049, 929, 892, 829 cm⁻¹; ¹H NMR (CDCl₃): δ 8.81 (d, *J* = 1.7 Hz, 1H), 8.57 (s, 1H), 8.42 (dd, *J* = 9.1, 1.9 Hz, 1H), 8.37 (d, *J* = 9.1 Hz, 1H), 8.29 (d, *J* = 9.1 Hz, 1H), 7.99 (dd, *J* = 9.1, 1.9 Hz, 1H), 2.83 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 196.9, 145.5, 144.3, 143.9, 142.9, 138.9, 132.9 (q, *J* = 33.2 Hz), 132.0, 131.4, 130.4, 128.7, 128.2 (q, *J* = 4.6 Hz), 126.1 (q, *J* = 2.8 Hz), 123.4 (q, *J* = 272.8 Hz), 26.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -64.43; HRMS (ESI/[M+H]⁺) calcd. for C₁₅H₁₀F₃N₂O: 291.0740. Found 291.0723.

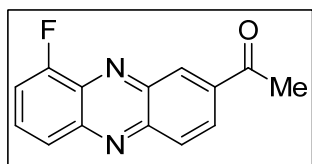


1-(7-Methoxyphenazin-2-yl)ethanone (8d): Derived from (E)-1-(3,5-dimethylphenyl)-2-(4-methoxyphenyl)diazene (**7e**) (48.1 mg, 0.200 mmol, 1.0 equiv) and 1-(4-azidophenyl)ethanone

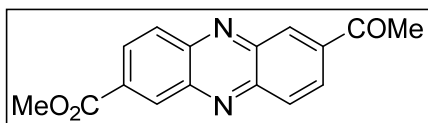
(48.4 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O/CH₂Cl₂ (3:3:1) as eluent afforded the product **8d** (15.3 mg, 30% yield) as a yellow solid (mp: 204-206 °C). IR (film): 2924, 1670, 1603, 1468, 1415, 1362, 1297, 1237, 1216, 1187, 1117, 1005, 814 cm⁻¹; ¹H NMR (CDCl₃): δ 8.80 (d, *J* = 1.6 Hz, 1H), 8.37 (dd, *J* = 9.1, 1.9 Hz, 1H), 8.19 (dd, *J* = 9.1, 0.6 Hz, 1H), 8.12 (d, *J* = 9.5 Hz, 1H), 7.55 (dd, *J* = 6.6, 2.8 Hz, 1H), 7.42 (d, *J* = 2.7 Hz, 1H), 4.05 (s, 3H), 2.81 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 197.3, 162.4, 146.2, 145.0, 141.6, 141.0, 136.7, 132.2, 130.9, 129.4, 128.0, 127.2, 104.5, 56.1, 26.6; HRMS (ESI/[M+H]⁺) calcd. for C₁₅H₁₃N₂O₂: 253.0972. Found 253.0977.



1-(8-Methylphenazin-2-yl)ethanone (8e): Derived from (*E*)-1-(3,5-dimethylphenyl)-2-(*m*-tolyl)diazene (**7f**) (44.7 mg, 0.200 mmol, 1.0 equiv) and 1-(4-azidophenyl)ethanone (48.4 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O/CH₂Cl₂ (6:3:1) as eluent afforded the product **8e** (31.9 mg, 67% yield) as a yellow solid (mp: 164-166 °C). IR (film): 1671, 1485, 1429, 1355, 1300, 1228, 1143, 1009, 951, 830 cm⁻¹; ¹H NMR (CDCl₃): δ 8.74 (d, *J* = 1.7 Hz, 1H), 8.30 (dd, *J* = 9.1, 1.9 Hz, 1H), 8.20 (d, *J* = 9.1 Hz, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.95 (s, 1H), 7.69 (dd, *J* = 8.9, 1.8 Hz, 1H), 2.78 (s, 3H), 2.64 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 197.2, 144.4, 144.2, 143.2, 142.7, 141.9, 137.7, 134.7, 132.0, 130.1, 129.2, 127.8, 127.2, 26.6, 22.2; HRMS (ESI/[M+H]⁺) calcd. for C₁₅H₁₃N₂O: 237.1022. Found 237.1016.

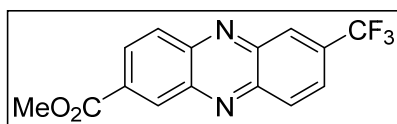


1-(9-Fluorophenazin-2-yl)ethanone (8f): Derived from (*E*)-1-(3,5-dimethylphenyl)-2-(2-fluorophenyl)diazene (**7g**) (45.7 mg, 0.200 mmol, 1.0 equiv) and 1-(4-azidophenyl)ethanone (48.4 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O/CH₂Cl₂ (6:3:1) as eluent afforded the product **8f** (42.5 mg, 88% yield) as a yellow solid (mp: 198-200 °C). IR (film): 1672, 1610, 1521, 1361, 1287, 1230, 1060, 837 cm⁻¹; ¹H NMR (CDCl₃): δ 8.92 (d, *J* = 1.6 Hz, 1H), 8.41 (dd, *J* = 9.1, 1.9 Hz, 1H), 8.26 (dd, *J* = 9.1, 0.6 Hz, 1H), 8.08 (dt, *J* = 8.9, 1.0 Hz, 1H), 7.84 (m, 1H), 7.55 (ddd, *J* = 9.8, 7.6, 1.1 Hz, 1H), 2.81 (s, 3H); ¹³C{¹H} NMR (CDCl₃): δ 197.0, 157.1 (d, *J* = 264.0 Hz), 145.2, 144.9, 142.3 (d, *J* = 1.9 Hz), 138.3, 135.7 (d, *J* = 13.4 Hz), 132.4, 130.7 (d, *J* = 8.2 Hz), 130.1, 128.7, 125.8 (d, *J* = 5.1 Hz), 113.5 (d, *J* = 18.4 Hz), 26.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -124.42; HRMS (ESI/[M+H]⁺) calcd. for C₁₄H₁₀FN₂O: 241.0772. Found 241.0750.



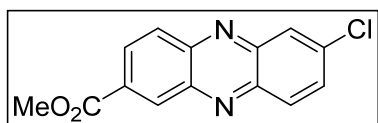
Methyl 7-acetylphenazine-2-carboxylate (8g): Derived from methyl (*E*)-4-((3,5-dimethylphenyl)diazenyl)benzoate (**7h**) (53.7 mg, 0.200 mmol, 1.0 equiv) and 1-(4-azidophenyl)ethanone (48.4 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O/CH₂Cl₂ (2:1:1) as eluent afforded the product **8g** (39.2 mg, 70% yield) as a yellow solid (mp: 256-258 °C). IR (film): 3043, 2962, 1721, 1680, 1469, 1435,

1360, 1312, 1283, 1245, 1185, 1091, 973, 949, 906, 885, 838, 808 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 9.00 (d, $J = 1.6$ Hz, 1H), 8.83 (d, $J = 1.6$ Hz, 1H), 8.42 (m, 2H), 8.31 (dd, $J = 9.2$, 1.6 Hz, 2H), 4.06 (s, 3H), 2.83 (s, 3H). ^{13}C NMR (CDCl_3) δ 197.1, 166.0, 145.5, 145.2, 143.8, 143.6, 138.8, 133.0, 132.7, 132.0, 130.5, 130.2, 130.0, 128.4, 52.8, 26.7; HRMS (ESI/[M+H] $^{+}$) calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_3$: 281.0921. Found 281.0918.



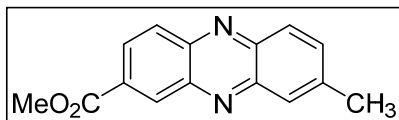
Methyl 7-(trifluoromethyl)phenazine-2-carboxylate (8h):

Derived from methyl (*E*)-4-((3,5-dimethylphenyl)diazenyl)benzoate (**7h**) (53.7 mg, 0.200 mmol, 1.0 equiv) and 1-azido-4-(trifluoromethyl)benzene (56.2 mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/ Et_2O / CH_2Cl_2 (6:3:1) as eluent afforded the product **8h** (34.4 mg, 56% yield) as a yellow solid (mp: 273-274 $^{\circ}\text{C}$). IR (film): 3019, 2956, 1723, 1515, 1479, 1323, 1254, 1196, 1163, 1121, 1092, 1049, 925, 896, 831 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 8.96 (d, $J = 1.9$ Hz, 1H), 8.56 (s, 1H), 8.41 (dd, $J = 9.1$, 1.9 Hz, 1H), 8.37 (d, $J = 9.1$ Hz, 1H), 8.28 (d, $J = 9.1$ Hz, 1H), 7.98 (dd, $J = 9.1$, 1.9 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (CDCl_3) δ 165.8, 145.2, 144.3, 143.6, 142.8, 133.0, 132.9 (q, $J = 33.1$ Hz), 132.8, 131.6, 130.2, 130.1, 128.1 (q, $J = 4.6$ Hz), 126.0 (q, $J = 2.8$ Hz), 123.4 (q, $J = 272.9$ Hz), 52.8; ^{19}F NMR (376 MHz, CDCl_3) δ -64.51; HRMS (ESI/[M+H] $^{+}$) calcd. for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_2$: 307.0689. Found 307.0686.



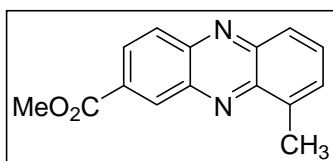
Methyl 7-chlorophenazine-2-carboxylate (8i): Derived from methyl (*E*)-4-((3,5-dimethylphenyl)diazenyl)benzoate (**7h**) (53.7 mg, 0.200 mmol, 1.0 equiv) and 1-azido-4-chlorobenzene (46.1

mg, 0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/ Et_2O / CH_2Cl_2 (6:3:1) as eluent afforded the product **8i** (26.1 mg, 48% yield) as a yellow solid (mp: 207-208 $^{\circ}\text{C}$). IR (film): 1718, 1599, 1433, 1306, 1240, 1179, 1090, 1059, 973, 949, 825, 808 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 8.94 (d, $J = 1.9$ Hz, 1H), 8.38 (dd, $J = 9.1$, 1.9 Hz, 1H), 8.21 (m, 3H), 7.78 (dd, $J = 9.1$, 2.3 Hz, 1H), 4.04 (s, 3H); ^{13}C NMR (CDCl_3) δ 166.0, 145.0, 144.2, 142.5, 142.4, 137.9, 133.0, 132.4, 131.8, 131.2, 129.9, 129.9, 128.1, 52.8; HRMS (ESI/[M+H] $^{+}$) calcd. for $\text{C}_{14}\text{H}_{10}\text{ClN}_2\text{O}_2$: 273.0425. Found 273.0424.



Methyl 8-methylphenazine-2-carboxylate (8j): Derived from methyl (*E*)-4-((3,5-dimethylphenyl)diazenyl)benzoate (**7h**) (53.7 mg, 0.200 mmol, 1.0 equiv) and 3-azidotoluene (40.0 mg,

0.300 mmol, 1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O/CH₂Cl₂ (6:3:1) as eluent afforded the product **8j** (29.1 mg, 58% yield) as a yellow solid (mp: 157-158 °C). IR (film): 1718, 1436, 1312, 1241, 1182, 1147, 1095, 973, 847, 819 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 8.92 (s, 1H), 8.32 (d, *J* = 9.2 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.96 (s, 1H), 7.68 (d, *J* = 9.2 Hz, 1H), 4.02 (s, 3H), 2.63 (s, 3H); ¹³C NMR (CDCl₃) δ 166.3, 144.2, 144.2, 143.2, 142.4, 141.7, 134.7, 132.8, 131.3, 129.9, 129.1, 128.6, 127.9, 52.6, 22.2; HRMS (ESI/[M+H]⁺) calcd. for C₁₅H₁₃N₂O₂: 253.0972. Found 253.0970.



Methyl 9-methylphenazine-2-carboxylate (8k): Derived from methyl (*E*)-4-((3,5-dimethylphenyl)diazenyl)benzoate (**7h**) (53.7 mg, 0.200 mmol, 1.0 equiv) and 2-azidotoluene (40.0 mg, 0.300 mmol,

1.5 equiv). Purification by silica gel column chromatography using pentane/Et₂O/CH₂Cl₂ (6:3:1) as eluent afforded the product **8k** (31.1 mg, 62% yield) as a yellow solid (mp: 155-156 °C). IR (film): 1720, 1430, 1313, 1299, 1243, 1198, 1148, 1089, 969, 857, 845 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 8.99 (dd, *J* = 1.9, 0.7 Hz, 1H), 8.35 (dd, *J* = 9.0, 1.9 Hz, 1H), 8.23 (dd, *J* = 9.0, 0.7 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.75 (dd, *J* = 8.8, 6.8 Hz, 1H), 7.65 (d, *J* = 6.8 Hz, 1H), 4.03 (s, 3H), 2.91 (s, 3H); ¹³C NMR (CDCl₃) δ 166.3, 144.5, 144.3, 143.8, 141.6, 138.4, 133.3, 131.7, 131.1, 129.9, 129.6, 129.0, 127.5, 52.6, 17.6; HRMS (ESI/[M+H]⁺) calcd. for C₁₅H₁₃N₂O₂: 253.0972. Found 253.0970.

VIII. Reference:

1. White, C.; Thompson S. J.; Maitlis P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 17, 1654.
2. Kuninobu, Y.; Yu, P.; Takai, K. *Org. Lett.* **2010**, 12, 4274.
3. Lian, Y.; Bergman, R. B.; Lavis, L. D.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, 135, 7122
4. (a) Cheng, H.; Wan, J.; Lin, M.; Liu, Y.; Lu, X.; Liu, J.; Xu, Y.; Chen, J.; Tu, Z.; Cheng, Y. E.; Ding, K. *J. Med. Chem.* **2012**, 55, 2144. (b) Wilkening, I.; del Signore, G.; Hackenberger, C. P. R. *Chem. Commun.* **2011**, 47, 349. (c) Berger, O.; Kaniti, A., Tran van Ba, C.; Vial, H.; Ward, S. A.; Biagini, G. A.; Bray, P. G.; O'Neill, P. M. *Chem Med Chem.* **2011**, 6, 2094. (d) *Org. Lett.*, **2008**, 10, 2409.
5. Kuprat, M.; Lehmann, M.; Schuiz, A.; Villinger, A. *Organometallic* **2010**, 29, 1421.
6. Johansson, M.; Backvall, J.-E. *Eur. J. Org. Chem.* **2007**, 26, 4431.
7. Kuninobu, Y.; Tatsuzaki, T.; Matsuki, T.; Takai, K. *J. Org. Chem.* **2011**, 76, 7005.
8. Tevelikhovsky D.; Buchwald, S. *J. Am. Chem. Soc.* **2010**, 132, 14048.
9. Adamczyk, M.; Chen, Y.; Mattingly, P. G.; Pan, Y.; Rege, S. *J. Org. Chem.* **1998**, 63, 5636.
10. Hyodo, I.; Tobisu, M.; Chatani, N. *Chem. Commun.* **2012**, 48, 308.
11. Huang, Z.-X.; Yang, Y.; Xiao, Q.; Zhang, Y.; Wang, J.-B. *Eur. J. Org. Chem.* **2012**, 6586.

