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Supporting information

Electrochemical trifluoromethylation of 2-isocyanobiaryls using CF₃SO₂Na: Synthesis of 6-(trifluoromethyl)phenanthridines

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1. Cyclic voltammetry

Cyclic voltammetry experiments were conducted in a 4-neck flask that contained the analytes dissolved in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile. A glassy carbon disc (Ø 3 mm), a Pt wire (Ø 0.5 mm), and Ag/AgCl electrode were used as a working electrode, a counter electrode, and a pseudo-reference electrode, respectively. The voltage was measured by PalmSens4 potentiostat in the presence of ferrocene as an external standard, at a scan rate of 0.1V/s (Fig. S1 and S2).



Fig. S1 Cyclic voltammetry experiment set up.



Fig. S2 Cyclic voltammograms of Blank, 1a, 2, and 3a.

2. Faradaic calculation

$$Faradaic \ efficiency = \frac{Q \ experimental}{Q \ theoretical} \times 100$$

$$Faradaic \ efficiency = \frac{z \times n \times F}{Q \ theoretical} \times 100$$

With z = number of electron required for the reaction used = 2

n = mol of product obtained = (maybe use the number in moles here and list the mass in parentheses) 0.0447

g (88%, MW. of product = 247.2202 g/mol)

F = Faradaic constant (96485 C/mol)

Q theoretical = I (current, Ampere) × t (reaction time, second)

$$Faradaic \ efficiency = \frac{2 \times (\frac{0.0447 \ g}{247.2202 \ g. \ mol}) \times 96485}{0.005 \ \text{A} \times 7200 \ \text{second}} \times 100$$

Faradaic efficiency = 94%





Scheme S1 Synthesis of 2-isocyanobiphenyls 1

4. General procedure B (Synthesis of phenanthridines 3)



Scheme S2 Synthesis of phenanthridines 3.

5. Radical trapping experiment



30% Recovery of **1a** Detec (Isolated yield)

4, 45% Detected by ¹⁹F-NMR

Scheme S3 Radical trapping experiment.

6. Picture of experiment set up





Fig. S3 Reactors set up and electrode.

7. NMR spectra of 2-isocyanobiphenyls 1a-1s

¹H NMR spectrum of **1a** (400 MHz, CDCl₃)



 $^{^{13}\}text{C}$ NMR spectrum of 1a (100 MHz, CDCl_3)



 ^1H NMR spectrum of 1b (400 MHz, CDCl_3)



¹H NMR spectrum of **1c** (400 MHz, CDCl₃)





¹H NMR spectrum of **1d** (400 MHz, CDCl₃)



 $^{19}\mathsf{F}$ NMR spectrum of 1d (376 MHz, CDCl_3)



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¹H NMR spectrum of **1g** (400 MHz, CDCl₃)



¹H NMR spectrum of **1h** (400 MHz, CDCl₃)



¹H NMR spectrum of **1i** (400 MHz, CDCl₃)



¹H NMR spectrum of **1j** (400 MHz, CDCl₃)







¹H NMR spectrum of **1I** (400 MHz, CDCl₃)





¹H NMR spectrum of **1n** (400 MHz, CDCl₃)



¹⁹F NMR spectrum of **1n** (470 MHz, CDCl₃)

1.485 1.469 1. -0.003 7.485 7.469 7.441 7.435 7.370 7.355 7.355 7.355 7.355 7.355 7.355 QМе 7.086 ,OMe NC 10 ΛA 6]<u>;</u> 66 00.1 5.00 7.5 7.2 7.4 7.3 7.1 7.0 ppm 6.01 1.05 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm ^{13}C NMR spectrum of 1o (125 MHz, CDCl_3) Alternative
 Alter 166.367 55.993 251 997 743 776. OMe OMe NC 10 mah w month 149 ppm ppm 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ò ppm

¹H NMR spectrum of **1o** (500 MHz, CDCl₃)









¹H NMR spectrum of **1r** (400 MHz, CDCl₃)



¹H NMR spectrum of **1s** (400 MHz, CDCl₃)



8. NMR spectra of 6-(trifluoromethyl)phenanthridines 3a-3s

¹H NMR spectrum of **3a** (400 MHz, CDCl₃)









¹H NMR spectrum of **3c** (400 MHz, CDCl₃)









¹H NMR spectrum of **3e** (400 MHz, CDCl₃)



 $F_{3}C \xrightarrow{V_{2}}{V_{2}} F_{3}C \xrightarrow{V_{2}}{V_{2$

1.96⊣ |0.96∃ € 00 ₽ 40 6.0 5.5 5.0 f1 (ppm) 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ¹³C NMR spectrum of **3f** (125 MHz, CDCl₃) F₃C $\overbrace{76.742}^{77.250}$



¹H NMR spectrum of **3f** (400 MHz, CDCl₃)

-0.068

8.051 8.049 8.034 8.034 8.034 8.034 8.034 7.893 7.893 7.875 7.875 7.875 7.877 7.875 7.857

0.96

7.9

7.8

-96

8.0

8.1

f1 (ppm)



$^{19}\mathsf{F}$ NMR spectrum of 3f (376 MHz, CDCl_3)

651 630 532 532 533 539 371 371 371 964 945 945 945 945 945 925 811 772 772 772 725 8.651 7.7811 7.791 7.772 7.772 8.391 .964 .945 8.284 111 CI CF₃ N 3g 19]<mark>:</mark>[)<u>8</u>)<u>s</u>(0.91)<u>ē</u> ()<u>ē</u> (8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 8.6 ppm MILIA 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 2.5 1.0 0.5 4.0 3.5 3.0 2.0 1.5 ppm ¹³C NMR spectrum of **3g** (100 MHz, CDCl₃) 77.316 76.999 76.680 130.237 -123.566 -123.409 -123.055 -122.455 -121.670 -121.255 147 114 081 047 813 -126.147 -126.114 -126.081 -126.047 117.536 126.1 126.1 126.0 126.0 N/T Ĩ Ĩ CI CF₃ Ν 3g Nh ppm 120 ppm 130 128 126 124 122 ppm

90 80 70 60 50

40 30

20 10

ppm

¹H NMR spectrum of **3g** (400 MHz, CDCl₃)

170 160 150 140 130 120 110 100



¹H NMR spectrum of **3h** (400 MHz, CDCl₃) -2.636-0.076 7.802 7.797 7.797 7.779 7.779 7.777 7.777 7.777 7.772 7.775 7.775 7.754 7.747 Me CF₃ M Ν 3h 2.11-0.95-3.06--00. 8.2 8.1 f1 (ppm) 8.6 8.5 8.3 8.1 8.0 7.8 7.7 8.4 7.9 2.11 ^J 0.95 ^H 1.00 ^J 3.06 _U 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1 (ppm) ¹³C NMR spectrum of **3h** (100 MHz, CDCl₃) 146.652 146.522 146.323 146.570 141.435 138.233 138.233 138.233 138.233 138.233 138.131 131.034 123.133 125.270 125.250 125.27 -77.318 -77.000 -76.682 -21.926---0.023 126.090 125.270 125.236 125.204 123.337 122.377 121.946 120.583 -117.828Me CF₃ mon 3h mon howwww 147.0 146.5 146.0 145.5 145.0 f1 (ppm) ò 160 110 100 90 80 70 50 40 30 10 150 140 130 60 20

f1 (ppm)

120

















---0.003 7.965 7.947 7.947 7.944 7.928 7.929 7.919 7.915 7.915 7.915 7.915 7.878 7.881 8.366 8.363 8.345 8.345 8.343 -8.125 -8.121 -8.103 -8.103 CN Ν CF_3 31 0.90-0.85 .81 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 f1 (ppm) 1.00 0.95 0.95 0.95 月 1.81 月 6.0 5.5 5.0 f1 (ppm) 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ^{13}C NMR spectrum of **3I** (100 MHz, CDCl₃) 77.318 76.683 -125.540-124.005 122.786 -121.177 -117.966 -117.277 -120.031 CN Ν CF_3 126 125 124 123 122 121 120 119 118 117 f1 (ppm) 31 131.552 131.336 131.305 131.271 131.234 131.192 -146.283-145.942-145.269-145.606146.5 146.0 145.5 145.0132.0 131.5 131.0 f1 (ppm) f1 (ppm) ΰ 160 80 f1 (ppm) 150 140 130 120 110 100 70 40 30 10 90 60 50 20

¹H NMR spectrum of **3I** (400 MHz, CDCl₃)





ò

¹H NMR spectrum of **3m** (400 MHz, CDCl₃)





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¹H NMR spectrum of **3n** (500 MHz, CDCl₃)





¹⁹F NMR spectrum of **3n** (470 MHz, CDCl₃)

454 445 435 435 435 243 248 248 224 917 744 775 772 772 630 630 630 260 4.154 œ œ œ QМе OMe 8.454 8.445 8.441 8.441 8.435 8.248 8.243 8.241 8.238 8.238 8.238 7.917 754 741 733 733 733 726 722 7722 630 627 SV/V CF₃ Ν 30 M 66.0 8 0.95 35 1.00 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 ppm 3.05 0.95 2.02 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm ^{13}C NMR spectrum of 3o (125 MHz, CDCl_3) $\bigwedge^{77.250}_{76.996}$ 56.123
 56.020
 56.020
 128.584 -121.557 -121.064 -118.861 -117.180 -123.266 OMe 184 927 666 408 OMe 145. 144. 144. 144. °CF₃ Ń 30 145 ppm 128 126 124 122 120 ppm 170 160 150 140 130 120 110 100 80 70 40 30 20 10 90 60 50 ppm

¹H NMR spectrum of **3o** (500 MHz, CDCl₃)





¹H NMR spectrum of **3p** (400 MHz, CDCl₃)





¹H NMR spectrum of **3q** (400 MHz, CDCl₃)



¹H NMR spectrum of **3r** (400 MHz, CDCl₃)





8:926 8:778 8:778 8:776 8:477 8:455 8:455 8:455 8:455 8:455 8:455 8:455 8:427 8:455 8:427 8:425 8:427 8:425 8:427 ---0.003 ~2.795 8.457 8.458 8.455 8.455 8.427 ~8.225 -7.730 -7.727 -7.709 -7.706 0 Ме Me CF_3 1.05-Ν 0.96 0.95--66.0 3s 8.1 f1 (ppm) 8.5 8.3 8.2 7.9 7.8 7.7 8.4 8.0 3.01 2.89 4 **1**-66.0 1.05 88 -96 6.0 5.5 5.0 f1 (ppm) 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ^{13}C NMR spectrum of 3s (100 MHz, CDCl_3) 146.083 145.752 145.419 140.926 136.529 135.879 132.383 130.996 122.422 127.050 127.024 127.008 124.332 124.332 124.332 124.332 124.332 121.394 122.292 121.394 146.415 120.470 -196.92177.318 -26.612 76.682 -127.050 -127.024 -127.008 -125.976 -146.415 -146.083 -145.752 -145.419 123.194 123.194 122.292 121.394 120.470 124.332 -117.7170 Ме Me N 128 127 126 125 124 123 122 121 120 119 118 117 f1 (ppm) Ń CF₃ 146.5 146.0 145.5 f1 (ppm) 3s 110 100 f1 (ppm) 210 200 190 180 170 160 150 140 130 120 90 80 70 60 40 30 20 10 Ó 50

¹H NMR spectrum of **3s** (400 MHz, CDCl₃)



¹H NMR spectrum of **4** (400 MHz, CDCl₃)



