

## **Iminosemiquinone radical ligand enables access to well-defined redox-active Cu<sup>II</sup>–CF<sub>3</sub> complex**

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## General information

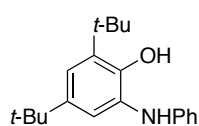
All reactions were performed under argon atmosphere, in flame dried glassware with magnetic stirring using standard Schlenk techniques, unless mentioned otherwise. Ethyl acetate was distilled over calcium hydride, dichloromethane and acetonitrile were used from solvent dispensers. All solvents were sparged with argon prior to use. All other commercially available reagents were used without purification, unless otherwise noted. CuCl (97% purity) and 5-(trifluoromethyl)dibenzothiophenium triflate were purchased from Sigma Aldrich. Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel and visualized with a UV lamp (254 nm).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at room temperature unless otherwise required on Bruker Avance 300 MHz, Bruker Avance 400 MHz. Shifts ( $\delta$ ) are given in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). IR spectra were measured using Tensor 27 (ATR Diamond) Bruker spectrometer, and JASCO FT/IR-4100 for KBr pellets. IR data are reported as characteristic bands ( $\text{cm}^{-1}$ ). UV spectra were recorded using JASCO V-530. Wavelengths ( $\lambda$ ) are given in nanometer (nm) and molar extinction coefficients ( $\epsilon$ ) are given in  $\text{M}^{-1}\cdot\text{cm}^{-1}$ . X-band EPR spectra were recorded on a Bruker ELEXSYS 500 spectrometer equipped with an Oxford Instrument continuous-flow liquid-helium cryostat and a temperature control system. Cyclic voltammograms were recorded using Autolab PGSTAT 100, and were performed in dichloromethane solutions containing 0.1 M  $[\text{N}(n\text{-Bu})_4]\text{PF}_6$  as the supporting electrolyte at a glassy carbon working electrode, a KCl saturated calomel reference electrode, and a platinum wire as a counter electrode. Pulsed-EPR experiments were carried out at X-band (9.64 GHz) with a Bruker ELEXSYS E580 FT spectrometer. The spectrometer was equipped with a Bruker CryoFree system for FlexLine for low temperature measurements (5 K). A spin echo was generated by a series of  $\pi/2$  and  $\pi$  microwave pulses ( $\pi/2$  and  $\pi$  represent the rotation angles of electron magnetization), with controlled time delays between pulses. By varying these time delays, the echo intensity exhibits modulations at the frequencies of the hyperfine interactions. One-dimensional spectroscopy was carried out with the standard three-pulse electron spin echo envelope modulation (3P-ESEEM) sequence ( $\pi/2$ - $\tau$ - $\pi/2$ - $t_1$ - $\pi/2$ -echo), whereby an echo is generated at time  $\tau+T$  after the last  $\pi/2$  pulse. The lengths of the  $\pi/2$  was 14 ns,  $\tau$  was fixed in a typical value of 136 ns and 512 points were collected, varying  $t_1$  with a step of 20 ns. Fourier transform of the time-domain echo envelope leads to a hyperfine spectrum in the frequency domain similar to the corresponding ENDOR spectrum. Two-dimensional techniques were also carried out using the hyperfine sublevel correlation spectroscopy (HYSCORE) from the four-pulse sequence  $\pi/2$ - $\tau$ - $\pi/2$ - $t_1$ - $\pi$ - $t_2$ - $\pi/2$ - $\tau$ -echo, and a 16-step cycle. At time  $\tau$  after the last  $\pi/2$  pulse, an echo is generated and measured at each  $t_1$  and  $t_2$  value, which are incremented by steps of 16 ns from their initial value. This two-dimensional set of

echoes gives, after Fourier transform along  $t_1$  and  $t_2$ , a two-dimensional HYSORE spectrum. The lengths of the  $\pi/2$  and  $\pi$  pulses were 12 and 32 ns, respectively, and a delay of  $\tau = 136$  ns between the first two  $\pi/2$  pulses gave the best sensitivity and resolution for the detection of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$  and  $^{19}\text{F}$  peaks, with no blind-spot effect. HYSORE spectra were recorded with  $256 \times 256$  data points for both  $t_1$  and  $t_2$  time domains. Prior to Fourier transform of the HYSORE data, the background decay was removed using a polynomial fit and apodized with a Hamming function.

### General procedure for ligands synthesis

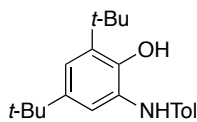
To a pale brown solution of 3,5-di-*tert*-butylcatechol (5.72 g, 25.7 mmol, 1 equiv.) in heptane (30 mL), were added dropwise the corresponding aniline (25.7 mmol, 1 equiv.) and triethylamine (358  $\mu$ L, 2.57 mmol, 0.1 equiv.). The resulting dark brown mixture was refluxed for 5 h under air. After cooling down to room temperature, the desired product precipitated as a white powder, which was filtered and washed with cold heptane.

**2-anilino-4,6-di-*tert*-butylphenol.** This compound was synthesized according to the general procedure in 68 % yield. The characterization data were identical to those previously reported.<sup>1</sup>



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 1.29 (s, 9H), 1.47 (s, 9H), 5.00 (bs, 1H), 6.45 (bs, 1H), 6.69 (d,  $J$  = 7.7 Hz, 2H), 6.87 (t,  $J$  = 7.3 Hz, 1H), 7.06 (d,  $J$  = 2.2 Hz, 1H), 7.20-7.26 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  = 29.7, 31.7, 34.5, 35.2, 115.3, 119.9, 121.6, 122.1, 127.9, 129.5, 135.5, 142.3, 146.9, 149.5.

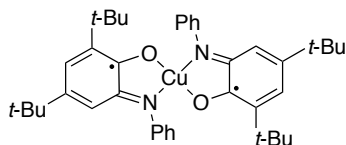
**2-(4-methylanilino)-4,6-di-*tert*-butylphenol (6).** This compound was synthesized according to the general procedure in 72 % yield. The characterization data were identical to those previously reported.<sup>2</sup>



<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta$  = 1.28 (s, 9H), 1.46 (s, 9H), 2.25 (s, 3H), 4.96 (bs, 1H), 6.56 (bs, 1H), 6.57 (d,  $J$  = 8.2 Hz, 2H), 7.01 (d,  $J$  = 8.2 Hz, 2H), 7.04 (d,  $J$  = 2.4 Hz, 1H), 7.23 (d,  $J$  = 2.4 Hz, 1H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz):  $\delta$  = 21.0, 30.2, 32.2, 35.1, 35.7, 116.1, 122.1, 122.5, 129.4, 130.0, 130.6, 135.9, 143.0, 145.4, 150.2.

### Preparation of [Cu<sup>II</sup>(L<sub>sq</sub>)<sub>2</sub>] [1]

To a colorless solution of 2-anilino-4,6-di-*tert*-butylphenol (1.06 g, 3.56 mmol, 2 equiv.) in acetonitrile (40 mL), were added at 40 °C, CuCl (176 mg, 1.78 mmol, 1 equiv.) and triethylamine (992  $\mu$ L, 7.12 mmol, 4 equiv.). The resulting dark green mixture was refluxed for 2 h under air. After cooling down to room temperature, the dark green complex formed was filtered and washed with cold acetonitrile. Yield : 789 mg (68%). The characterization data were identical to those previously reported.<sup>1</sup>



ESI-MS (MeOH/MeCN):  $m/z$  653 [M]<sup>+</sup>.

IR (KBr, cm<sup>-1</sup>): 2961-2866s, 1582m, 1485s, 1464s, 1442m, 1386m, 1356m, 1334m, 1256s, 1203m, 1179m, 1105m, 1026m, 994m, 860m, 764m, 701m,

<sup>1</sup> P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, **123**, 2213.

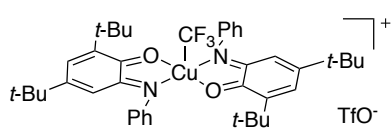
<sup>2</sup> O. I. Shadyro, V. L. Sorokin, G. A. Ksendzova, G. I. Polozov, S. N. Nikolaeva, N. I. Pavlova, O. V. Savinova and E. I. Boreko, *Pharm. Chem. J.*, 2003, **37**, 399. Translated from *Khim. Pharm. Zh.*, 2003, **37**, 5.

692m.

UV-vis [ $\text{CH}_2\text{Cl}_2$ ;  $\lambda$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\cdot\text{cm}^{-1}$ ): 307 (21000), 460 (4610), 795 (7470).

### Preparation of $[\text{Cu}^{\text{II}}(\text{L}_{\text{BQ}})_2\text{CF}_3]\text{OTf}$ [3]

Into a Schlenk flask under an argon atmosphere, were introduced complex [1] (602 mg, 0.92 mmol, 1 equiv.) and 5-(trifluoromethyl)dibenzothiophenium triflate (370 mg, 0.92 mmol, 1 equiv.). Degassed dichloromethane was added (22 mL) and the resulting solution was stirred at room temperature overnight. After evaporation of the solvent, the residue was triturated with hexane and filtered to afford a red-brown solid. Yield : 567 mg (69 %).



ESI+ (MeOH):  $m/z$  722  $[\text{M}]^+$ , 653  $[\text{M} - \text{CF}_3]^+$ .

ESI- (MeCN):  $m/z$  149  $\text{TfO}^-$ .

IR (KBr,  $\text{cm}^{-1}$ ): 2961-2870s, 1648s, 1623s, 1590m, 1481m, 1382m,

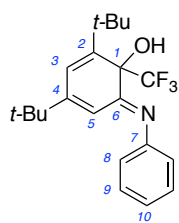
1369m, 1258s, 1171s, 1032s, 701m, 653m.

UV-vis [ $\text{CH}_2\text{Cl}_2$ ;  $\lambda$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\cdot\text{cm}^{-1}$ ): 502 (4250).

### Reactivity of $[\text{Cu}^{\text{II}}(\text{L}_{\text{BQ}})_2\text{CF}_3]\text{OTf}$ [3]

#### $[\text{Cu}^{\text{II}}(\text{L}_{\text{BQ}})_2\text{CF}_3]\text{OTf}$ without any substrate at room temperature (Table S1, Entry 1)

Into a Schlenk flask under an argon atmosphere, was introduced complex [3] (77 mg, 0.088 mmol, 1 equiv.). Degassed acetonitrile (1 mL) was added and the resulting solution was stirred at room temperature for 18 h. The reaction was quenched with a saturated aqueous  $\text{NH}_4\text{Cl}$  solution and extracted with dichloromethane. The combined organic layers were washed with brine and dried over  $\text{MgSO}_4$ . After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (pentane/dichloromethane 99:1 to 80:20) to afford **4** (10 mg, 35 %).



$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz):  $\delta$  = 1.05 (s, 9H, t-Bu), 1.31 (s, 9H, t-Bu), 5.78 (s, 1H, OH), 5.88 (s, 1H, **H5**), 6.34 (s, 1H, **H3**), 6.85 (d,  $J$  = 8.1 Hz, 2H, **H8**), 7.14 (t,  $J$  = 7.6 Hz, 1H, **H10**), 7.34 (t,  $J$  = 7.7 Hz, 2H, **H9**).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 101 MHz):  $\delta$  = 28.7 ( $(\text{CH}_3)_3\text{C}$ -), 31.4 ( $(\text{CH}_3)_3\text{C}$ -), 36.3 ( $(\text{CH}_3)_3\text{C}$ -), 38.7 ( $(\text{CH}_3)_3\text{C}$ -), 79.4 (q,  $^2J$  = 28 Hz, **C1**), 108.9 (**C5**), 121.9 (**C8**), 124.1 (**C3**), 124.9 (q,  $^1J$  = 293.9 Hz,  $\text{CF}_3$ ), 125.9 (**C10**), 129.8 (**C9**), 148.6 (**C7**), 152.0 (**C2** or **C4**),

160.5 (**C2** or **C4**), 168.0 (**C6**).  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 376 MHz):  $\delta$  = -75.6.

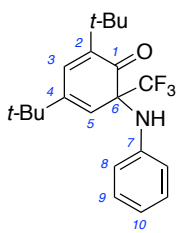
ESI-MS (MeOH):  $m/z$  388  $[\text{MNa}]^+$ , 366  $[\text{MH}]^+$ .

IR : 3230-3344b, 2964m, 1638m, 1615m, 1594m, 1368m, 1216s, 1172s, 1149s, 948m, 741m, 720m,

696m.

***[Cu<sup>II</sup>(L<sub>BQ</sub>)<sub>2</sub>CF<sub>3</sub>]OTf without any substrate at 70 °C (Table S1, Entry 2)***

Into a Schlenk flask under an argon atmosphere, was introduced complex **[3]** (66 mg, 0.076 mmol, 1 equiv.). Degassed acetonitrile (0.9 mL) was added and the resulting solution was stirred at 70 °C for 9 h. The reaction was quenched with a saturated aqueous NH<sub>4</sub>Cl solution and extracted with dichloromethane. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (pentane/dichloromethane 99:1 to 70:30) to afford **5** (15 mg, 54 %).



<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ = 1.16 (s, 9H, t-Bu), 1.21 (s, 9H, t-Bu), 4.90 (bs, 1H, NH), 6.05 (d, *J* = 2.4 Hz, 1H, **H5**), 6.59 (d, *J* = 8.0 Hz, 2H, **H8**), 6.82 (t, *J* = 7.4 Hz, 1H, **H10**), 7.06 (d, *J* = 2.4 Hz, 1H, **H3**), 7.10 (t, *J* = 7.9 Hz, 2H, **H9**). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 101 MHz): δ = 28.9 ((CH<sub>3</sub>)<sub>3</sub>C-), 29.6 ((CH<sub>3</sub>)<sub>3</sub>C-), 35.7 ((CH<sub>3</sub>)<sub>3</sub>C-), 35.9 ((CH<sub>3</sub>)<sub>3</sub>C-), 67.9 (q, <sup>2</sup>*J* = 25 Hz, **C6**), 118.8 (**C8**), 121.8 (**C10**), 124.0 (q, <sup>1</sup>*J* = 288 Hz, **CF<sub>3</sub>**), 125.8 (**C5**), 129.8 (**C9**), 137.4 (**C3**), 145.3 (**C7**), 147.2 (**C2** or **C4**), 149.0 (**C2** or **C4**), 197.4 (**C1**). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 376 MHz): δ = -76.7.

ESI-MS (MeOH): *m/z* 388 [MNa]<sup>+</sup>.

IR : 2958s, 2868m, 1682m, 1603m, 1583m, 1500s, 1477s, 1445sh, 1421s, 1363m, 1228s, 1201s, 1157s, 744s, 693m.

Entry	Solvent	T, t	Yield of 4	Yield of 5
1	MeCN	r.t., 18 h	35 %	traces
2	MeCN	70 °C, 9 h	-	54 %

Table S1

***Reaction of [Cu<sup>II</sup>(L<sub>BQ</sub>)<sub>2</sub>CF<sub>3</sub>]OTf with N-benzylidene methylamine (Table S2, Entry 1)***

To a solution of complex **[3]** (52 mg, 0.060 mmol, 1 equiv.) in ethyl acetate (600 μL) was added at room temperature N-benzylidene methylamine (15 μL, 0.119 mmol, 2 equiv.). The resulting solution was stirred at 70 °C for 9 h. The reaction was quenched with a saturated aqueous NaHCO<sub>3</sub> solution and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (pentane/dichloromethane 99:1 to 70:30) to afford a mixture of **5** (54 %) and benzaldehyde, resulting from hydrolysis of the starting material (16 %).

***Reaction of [Cu<sup>II</sup>(L<sub>BQ</sub>)<sub>2</sub>CF<sub>3</sub>]OTf with 4-chlorobenzaldehyde (Table S2, Entry 2)***

Into a Schlenk flask under an argon atmosphere, were introduced complex **[3]** (80 mg, 0.092 mmol, 1 equiv.) and 4-chlorobenzaldehyde (13 mg, 0.092 mmol, 1 equiv.). Degassed ethyl acetate (1.1 mL) was added and the resulting solution was stirred at room temperature for 18 h. The reaction was quenched with a saturated aqueous NH<sub>4</sub>Cl solution and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (pentane/dichloromethane 99:1 to 70:30) to afford **4** (15 mg, 45 %). The starting material was totally recovered.

Entry	Substrate	Solvent	T, t	Yield of 4	Yield of 5
1	N-benzylidene methylamine	AcOEt	70 °C, 9 h	-	54 %
2	4-chlorobenzaldehyde	AcOEt	r.t., 18 h	45 %	traces

Table S2

**Reaction of [Cu<sup>II</sup>(L<sub>BQ</sub>)<sub>2</sub>CF<sub>3</sub>]OTf with 4-iodoanisole (Table S3, Entry 1)**

Into a Schlenk flask under an argon atmosphere, were introduced complex **[3]** (86 mg, 0.099 mmol, 1 equiv.) and 4-iodoanisole (37 mg, 0.158 mmol, 1.6 equiv.). Degassed ethyl acetate (1.1 mL) was added and the resulting solution was stirred at 70 °C for 9 h. The reaction was quenched with a saturated aqueous NH<sub>4</sub>Cl solution and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (pentane/dichloromethane 99:1 to 70:30) to afford **5** (7 mg, 19 %). The starting material was totally recovered.

**Reaction of [Cu<sup>II</sup>(L<sub>BQ</sub>)<sub>2</sub>CF<sub>3</sub>]OTf with benzyl bromide (Table S3, Entry 2)**

To a solution of complex **[3]** (70 mg, 0.080 mmol, 1 equiv.) in ethyl acetate (900 μL) was added at room temperature benzyl bromide (20 μL, 0.160 mmol, 2 equiv.). The resulting solution was stirred at room temperature for 18 h. The reaction was quenched with a saturated aqueous NH<sub>4</sub>Cl solution and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (pentane/dichloromethane 99:1 to 80:20) to afford **4** (13 mg, 44 %). The starting material was totally recovered.

Entry	Substrate	Solvent	T, t	Yield of 4	Yield of 5
1	4-iodoanisole	AcOEt	70 °C, 9 h	-	19 %
2	Benzyl bromide	AcOEt	r.t., 18 h	44 %	-

Table S3

**Reaction of  $[\text{Cu}^{\text{II}}(\text{L}_{\text{BQ}})_2\text{CF}_3]\text{OTf}$  with potassium phenyltrifluoroborate at room temperature (Table S4, Entry 1)**

Into a Schlenk flask under an argon atmosphere, were introduced complex **[3]** (89 mg, 0.102 mmol, 1 equiv.) and potassium phenyltrifluoroborate (19 mg, 0.102 mmol, 1 equiv.). Degassed acetonitrile (1.1 mL) was added and the resulting solution was stirred at room temperature for 18 h. The reaction was quenched with a saturated aqueous  $\text{NH}_4\text{Cl}$  solution and extracted with dichloromethane. The combined organic layers were washed with brine and dried over  $\text{MgSO}_4$ . After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (pentane/dichloromethane 99:1 to 80:20) to afford **4** (8 mg, 22 %).

**Reaction of  $[\text{Cu}^{\text{II}}(\text{L}_{\text{BQ}})_2\text{CF}_3]\text{OTf}$  with potassium phenyltrifluoroborate at 70 °C (Table S4, Entry 2)**

Into a Schlenk flask under an argon atmosphere, were introduced complex **[3]** (72 mg, 0.083 mmol, 1 equiv.) and potassium phenyltrifluoroborate (15 mg, 0.083 mmol, 1 equiv.). Degassed acetonitrile (1 mL) was added and the resulting solution was stirred at 70 °C for 9 h. The reaction was quenched with a saturated aqueous  $\text{NH}_4\text{Cl}$  solution and extracted with dichloromethane. The combined organic layers were washed with brine and dried over  $\text{MgSO}_4$ . After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (pentane/dichloromethane 99:1 to 70:30) to afford **5** (21 mg, 69 %).

Entry	Substrate	Solvent	T, t	Yield of <b>4</b>	Yield of <b>5</b>
<b>1</b>	$\text{PhBF}_3\text{K}$	MeCN	r.t., 18 h	22 %	traces
<b>2</b>	$\text{PhBF}_3\text{K}$	MeCN	70 °C, 9 h	-	69 %

Table S4

**Reaction of  $[\text{Cu}^{\text{II}}(\text{L}_{\text{BQ}})_2\text{CF}_3]\text{OTf}$  with TEMPO**

Into a Schlenk flask under an argon atmosphere, was introduced complex **[3]** (38 mg, 0.044 mmol, 1 equiv.) and TEMPO (8 mg, 0.052 mmol, 1.2 equiv.). Degassed 1,2-dichloroethane (500  $\mu\text{L}$ ) was added and the resulting solution was stirred at 70 °C for 6 h. No trace of  $\text{TEMPO-CF}_3$ <sup>3,4</sup> could be observed in <sup>19</sup>F NMR.

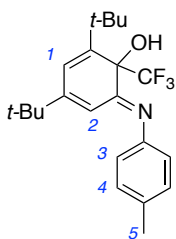
<sup>3</sup> X. Wang, Y. Ye, S. Zhang, J. Feng, Y. Xu, Y. Zhang and J. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 16410.

<sup>4</sup> S. Mizuta, O. Galicia-Lopez, K. M. Engle, S. Verhoog, K. Wheelhouse, G. Rassias and V. Gouverneur, *Chem. Eur. J.*, 2012, **18**, 8583.

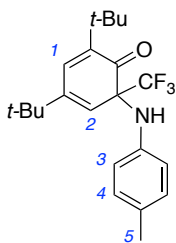


### Reaction with an exogenous ligand

Into a 10 mL round bottom flask, were added complex **[1]** (28 mg, 0.043 mmol, 20 %), 2-(4-methylanilino)-4,6-di-*tert*-butylphenol **6** (67 mg, 0.216 mmol, 1 equiv.) and 5-(trifluoromethyl)dibenzothiophenium triflate (87 mg, 0.216 mmol, 1 equiv.). Ethyl acetate (2.5 mL) and triethylamine (60  $\mu$ L, 0.432 mmol, 2 equiv.) were added and the resulting solution was stirred at 70 °C for 2 h. The reaction was quenched with a saturated aqueous NH<sub>4</sub>Cl solution and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (pentane/dichloromethane 99:1 to 70:30) to afford a mixture of **4** (1.4 mg, 2 %) and **7** (6.8 mg, 8 %) and a mixture of **5** (7 mg, 8 %) and **8** (22 mg, 27 %).



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.09 (s, 9H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 2.36 (s, 3H, **H5**), 5.86 (bs, 1H, OH), 5.94 (d,  $J$  = 1.4 Hz, 1H, **H2**), 6.32 (d,  $J$  = 1.4 Hz, 1H, **H1**), 6.79 (d,  $J$  = 8.0 Hz, 2H, **H3**), 7.15 (d,  $J$  = 8.0 Hz, 2H, **H4**). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz):  $\delta$  = -75.7.



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.17 (s, 9H, *t*-Bu), 1.23 (s, 9H, *t*-Bu), 2.22 (s, 3H, **H5**), 4.81 (bs, 1H, NH), 6.06 (d,  $J$  = 2.2 Hz, 1H, **H2**), 6.55 (d,  $J$  = 8.4 Hz, 2H, **H3**), 6.92 (d,  $J$  = 8.6 Hz, 2H, **H4**), 7.01 (d,  $J$  = 2.2 Hz, 1H, **H1**). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz):  $\delta$  = -76.3.

## Electrochemical studies

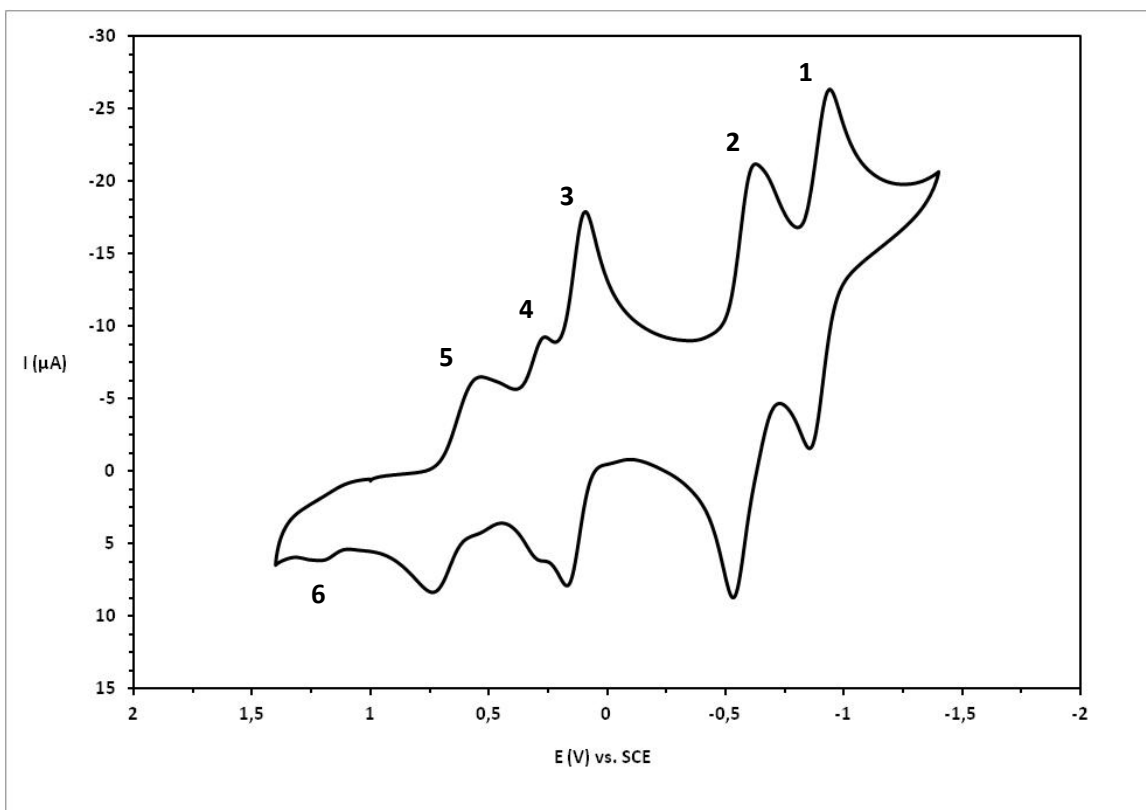


Figure S1

Table S5. Summary of the redox potentials for the various waves of the CV of complex [3]

Wave	$E_{p(\text{red})}$ V/SCE	$E_{p(\text{ox})}$ V/SCE	$E_{p(\text{ox})} - E_{p(\text{red})}$	$\frac{1}{2}(E_{p(\text{ox})} + E_{p(\text{red})})$ V/SCE	$\frac{1}{2}(E_{p(\text{ox})} + E_{p(\text{red})})$ V/ $E_{\text{Fc}^+/\text{Fc}}$ <sup>a</sup>	$E_{1/2}$ ([Cu(LSO) <sub>2</sub> ]) <sup>b</sup>
1	-0.940	-0.854	86 mV	-0.897	-1.35	-1.32
2	-0.627	-0.532	106 mV	-0.579	-1.04	-1.02
3	0.092	0.171	79 mV	0.132	-0.33	-0.26
4	0.262	~0.290	~28 mV	0.276	-0.18	
5	0.532	0.736	200mV	0.634	0.17	0.37
6		1.216	irrev			

<sup>a</sup>  $E_{\text{Fc}^+/\text{Fc}}$  taken as +0.46V / SCE in DCM 0.1M TBABF<sub>4</sub> according to N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877. (data for TBPf<sub>6</sub> since TBABF<sub>4</sub> was not used).

<sup>b</sup> P. Chaudhuri, C. Nazari Verani, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, **123**, 2213.

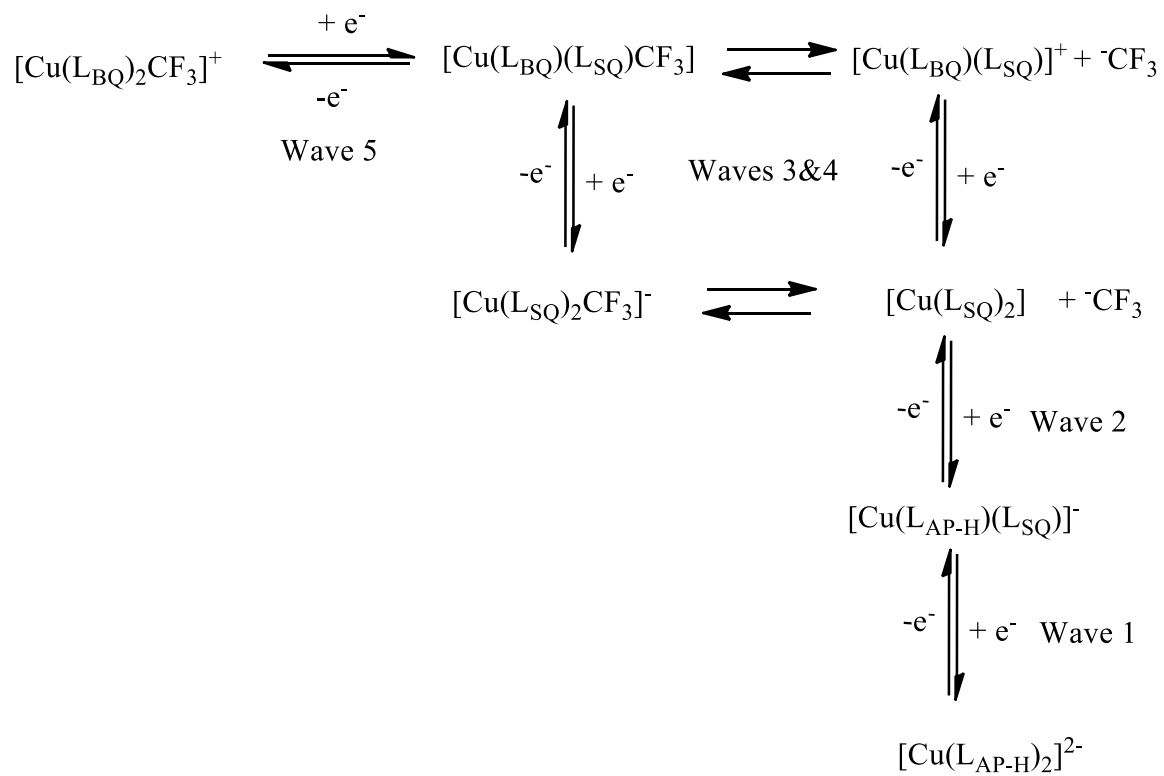
Figure S1 (figure 2 in the main text) shows the cyclic voltammogram of  $[\text{Cu}(\text{L}_{\text{BQ}})_2\text{CF}_3]^+$  in a 0.1M TBABF<sub>4</sub> /dichloromethane electrolyte, recorded with SCE as reference. The data are summarized in table S5.

The resting potential is at 0.8V/SCE, before the first wave in reduction (labeled **5**). During the cathodic scan, several reduction processes are observed.

At 0.634 V/SCE, the first reducing process of our trifluoromethylated complex is clearly different from that of the known  $[\text{Cu}(\text{L}_{\text{BQ}})_2]^{2+}$  complex, which occurs at an estimated 0.83V/SCE (0.37V/ferrocene). It is, however, very close to that of the first reduction of the  $[\text{Cu}(\text{L}_{\text{BQ}})_2\text{Br}_2]$  system, which occurs at an estimated 0.56 V/SCE (no precise potential was given in the literature for this process). Thus, this is an agreement with the presence of an additional anionic ligand onto the copper in our product.

Moreover, as was observed in the case of  $[\text{Cu}(\text{L}_{\text{BQ}})_2\text{Br}_2]$ , the two most negative waves (labeled **1** & **2**) are quasi reversible and their potentials correspond to the reversible process of couple  $[\text{Cu}(\text{L}_{\text{SQ}}) (\text{L}_{(\text{AP-H})})]^- / [\text{Cu}(\text{L}_{(\text{AP-H})})_2]^{2-}$  (AP = amidophenolate) (wave **1**) and the reversible process of couple  $[\text{Cu}(\text{L}_{\text{SQ}})_2] / [\text{Cu}(\text{L}_{\text{SQ}}) (\text{L}_{(\text{AP-H})})]^-$  (wave **2**) ; the slight differences in potential can be attributed to the estimated correction of potential between SCE and Ferrocene references. As proposed for the dibromo system, this suggests the loss of the CF<sub>3</sub> ligand upon the first reducing processes (waves **3**, **4** and **5**, overall 2e<sup>-</sup> reduction).

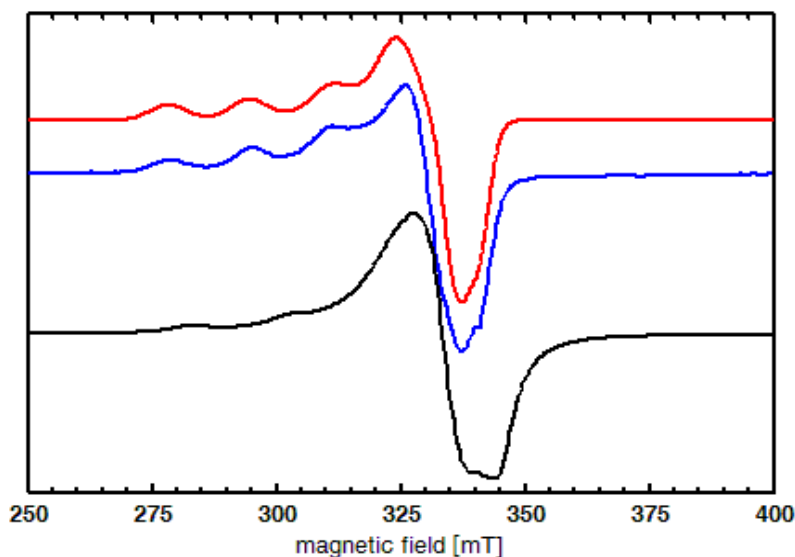
This led us to suggest the EC mechanism for the first two reduction processes, yielding a complicated CV with at least three observable waves, and associated with the various following reactions upon successive reductions:



**Scheme 1**

Finally, the small irreversible oxidation process at 1.216 V/SCE could be related to irreversible copper oxidation.

## EPR studies



**Figure S2.** X-band EPR spectra of  $\text{Cu}(\text{L}_{\text{SO}})_2$  (bottom),  $[\text{Cu}(\text{L}_{\text{BO}})_2\text{CF}_3]\text{OTf}$  (middle)  $10^{-3}\text{M}$  in frozen  $\text{CH}_2\text{Cl}_2$  at 10 K, and simulation<sup>5</sup> of the latter (top) with  $g_i=2.225, 2.065, 2.000$  and  $A_i^{\text{Cu}} = (182, 13.5, 9.5) \times 10^{-4}\text{cm}^{-1}$ .

### Pulsed-EPR experiments

The electron spin echo envelope modulation (ESEEM) effect is induced by nuclei hyperfine-coupled to the unpaired electron spin. These couplings manifest themselves in a periodic modulation of the electron spin echo intensity as a function of the pulse separation time.<sup>6</sup> For nuclei coupled to the electron spin via an anisotropic hyperfine interaction, 1D-pulsed ESEEM experiments have proven to be powerful tools to examine these interactions, especially for weak couplings and for nuclei with a small Zeeman splitting. Hyperfine sublevel correlation (HYSCORE)<sup>7</sup> is a two-dimensional pulsed EPR technique which allows for the measurement of the quadrupolar and hyperfine couplings of the electronic spin with the surrounding nuclei, which appear as spots and ridges distributed in two different quadrants (+,+) and (-,+). (+,+) corresponds to  $\omega_1 > 0, \omega_2 > 0$ , whereas (-,+) to  $\omega_1 < 0, \omega_2 > 0$ . Nuclear modulations in the (+,+) quadrant correspond to the “weak coupling case” characterized by  $|A_{\text{iso}}| < 2|v_i|$ , where  $A$  and  $v_i$  are the hyperfine interaction and the nuclear Zeeman frequency, respectively, of the interacting nucleus. The (-,+) quadrant corresponds to the “high coupling case”, with  $|A_{\text{iso}}| > 2|v_i|$ .<sup>8</sup> The 3P-ESEEM spectrum recorded

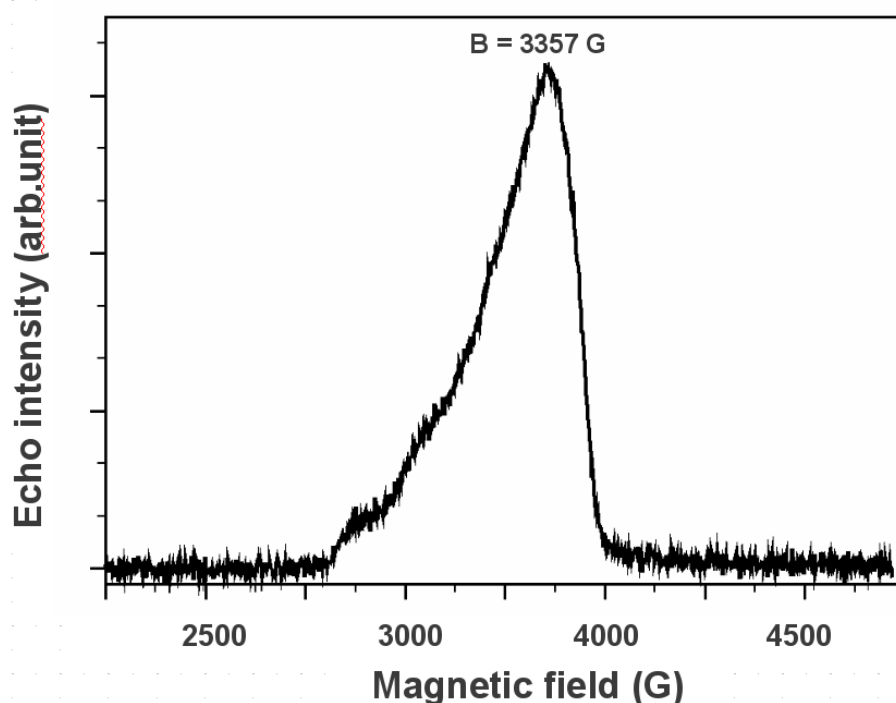
<sup>5</sup> S. Stoll and A. Schweiger, **EasySpin, a comprehensive software package for spectral simulation and analysis in EPR**, *J. Magn. Reson.*, 2006, **178**, 42.

<sup>6</sup> T. Prisner, M. Rohrer and F. MacMillan, *Annu. Rev. Phys. Chem.*, 2001, **52**, 52279.

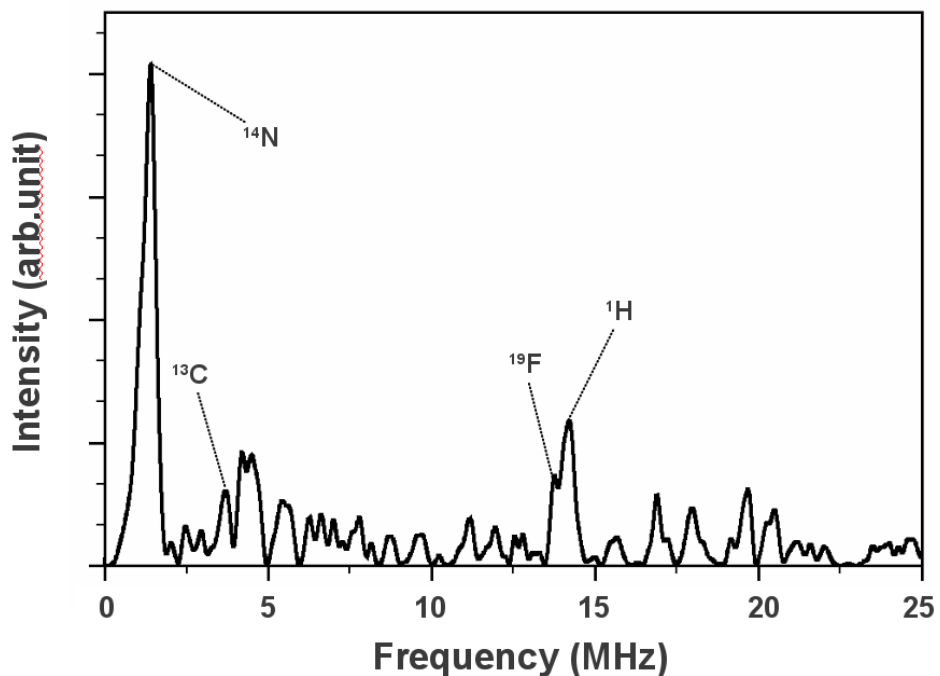
<sup>7</sup> P. Höfer, A. Grupp, H. Nebenführ and M. Mehring, Hyperfine sublevel correlation (HYSCORE) spectroscopy: a 2D ESR investigation of the squaric acid radical, *Chem. Phys. Lett.*, 1986, **132**, 279.

<sup>8</sup> A. G. Maryasov and M. K. Bowman, Hyperfine sublevel correlation (HYSCORE) spectra of paramagnetic centers with nuclear spin  $I=1$  having isotropic hyperfine interactions, *J. Phys. Chem. B.*, 2004, **108**, 9412.

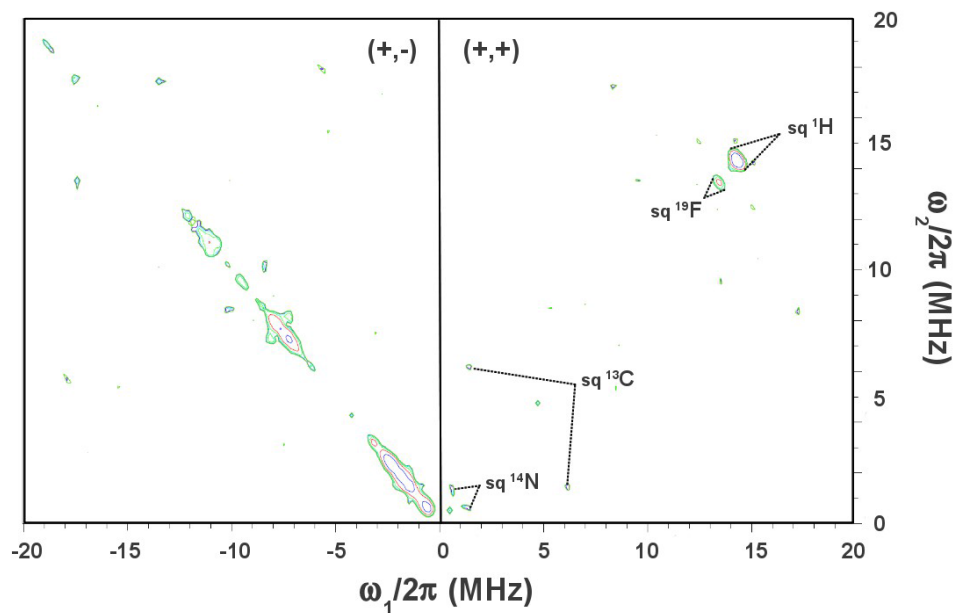
on a frozen  $\text{CH}_2\text{Cl}_2$  sample of complex **[3]** is shown in Figure S4. The ESEEM spectrum reveals four main peaks (1.06, 3.70, 13.76 and 14.24 MHz) attributed to the basic frequency of  $^{14}\text{N}$  ( $I=1$ ,  $\nu = 1.32$  MHz),  $^{13}\text{C}$  ( $I=1/2$ ,  $\nu = 3.67$  MHz),  $^{19}\text{F}$  ( $I=1/2$ ,  $\nu = 13.70$  MHz) and  $^1\text{H}$  ( $I=1/2$ ,  $\nu = 14.60$  MHz) nuclei. These data also demonstrate the interaction between the  $^{13}\text{C}$  from the  $\text{CF}_3$  group with the metal centre, in agreement with a direct coordination of the  $\text{CF}_3$  group to the copper ion in **[3]**. It also shows that nitrogen and proton centers are present in the surroundings of the unpaired electron of the system as detected by HYSCORE experiments. The 2D HYSCORE spectrum of complex **[3]** recorded at 4 K at a different time delay ( $\tau = 136$  ns) is shown in Figure S5. It is also characterized by four pairs of crosspeaks centered at the  $^{14}\text{N}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^1\text{H}$  Larmor nuclear frequencies ( $\nu = 1.0$ , 3.7, 13.4 and 14.3 MHz, respectively). These symmetric cross-peaks appear in the (+,+) quadrant, indicating weak hyperfine isotropic couplings that are estimated at 0.7, 4.7, 1.0 and 2.0 MHz, respectively. These couplings are attributed to distant protons, nitrogens and carbons while it emphasizes the interaction between the  $^{19}\text{F}$  centers with the paramagnetic center of the complex. Similarly, we observe specific features in the (-,+) quadrant indicating a strong hyperfine coupling from the  $^{13}\text{C}$  nuclei that is estimated at 19 MHz from the antidiagonal peak. These results support the  $\text{CF}_3$  group as being as ligand of **[3]**.



**Figure S3.** Electron Spin Echo (ESE) detected field sweep spectra of complex **[3]**. Experimental conditions: frozen  $\text{CH}_2\text{Cl}_2$  sample of **[3]**,  $T = 5\text{K}$ . The magnetic field position of the 3PESEEM and HYSCORE experiments is indicated.



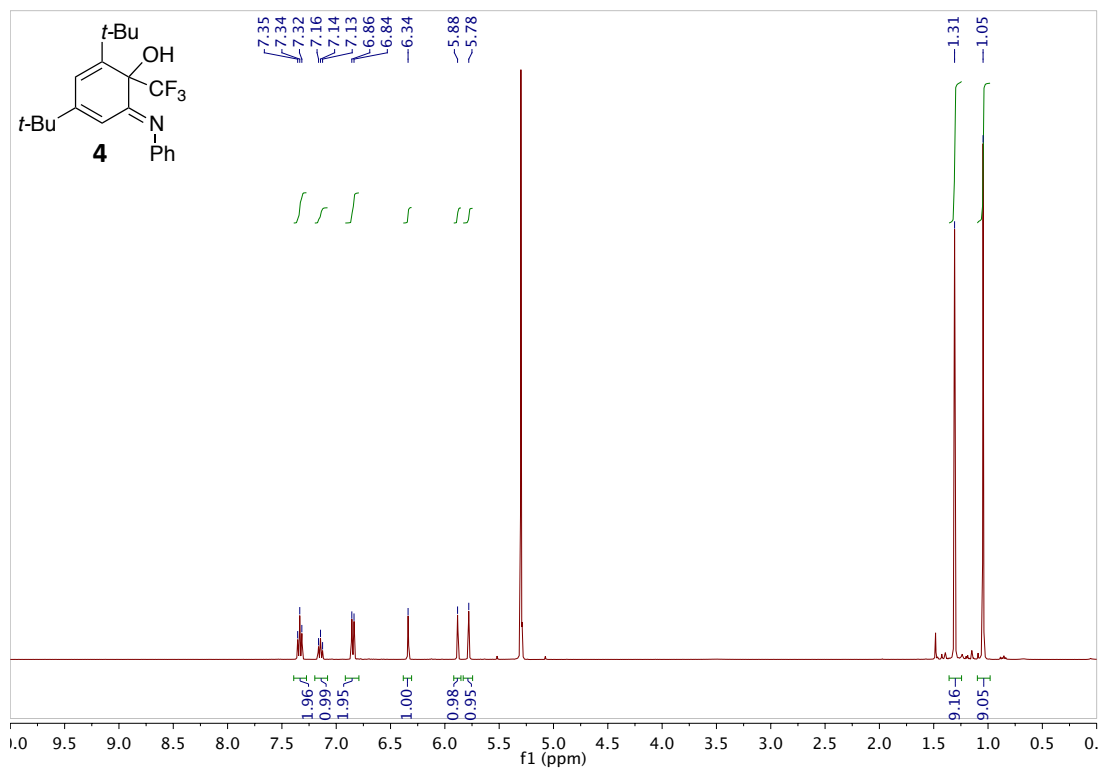
**Figure S4.** 3P-ESEEM spectrum of complex **[3]**. Experimental conditions: frozen  $\text{CH}_2\text{Cl}_2$  sample of **[3]**,  $T = 5\text{K}$ . Spectrum recorded for the  $B = 3357\text{ G}$  value of the ESE detected field sweep spectrum. The time delay was set to 136 ns and a pulse length of 16 ns was used for  $\pi/2$  pulses.



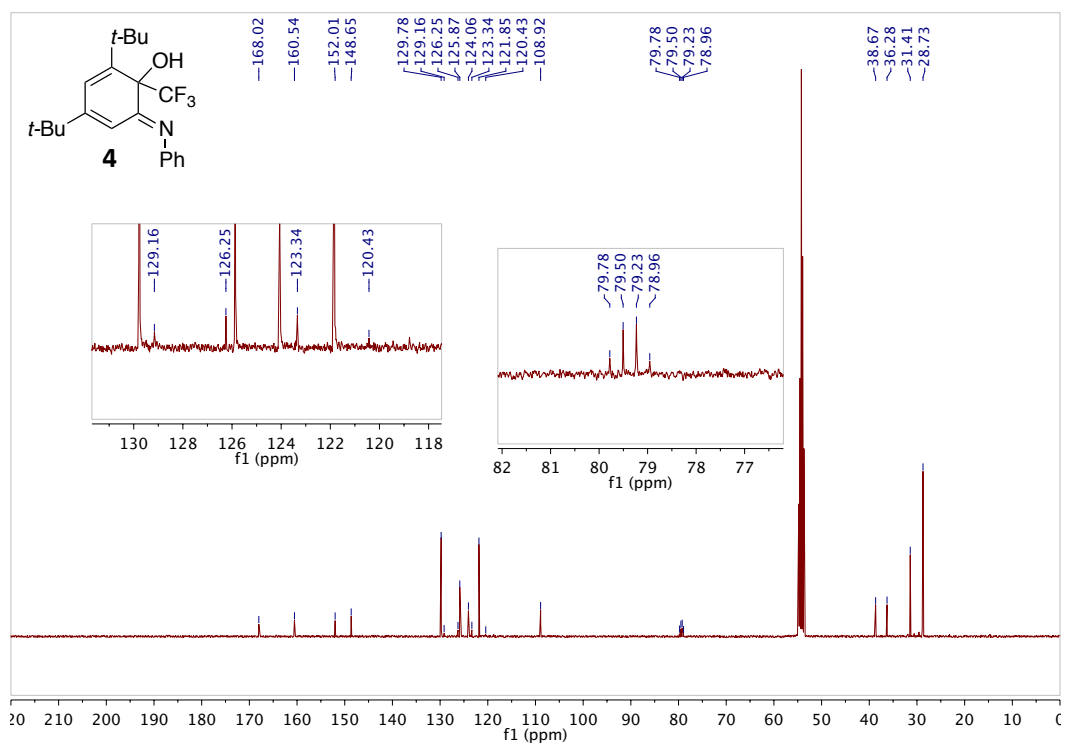
**Figure S5.** 2D-HYSCORE spectra of complex **[3]**. Experimental conditions: frozen  $\text{CH}_2\text{Cl}_2$  sample of **[3]**,  $T = 5\text{K}$ . Spectrum recorded for the  $B = 3357\text{ G}$  value of the ESE detected field sweep spectrum. The time delay was set to 200 ns and a pulse length of 12 ns was used for  $\pi/2$  pulses with  $256 \times 256$  points along  $t_1$  and  $t_2$  directions.

## NMR spectra

<sup>1</sup>H NMR

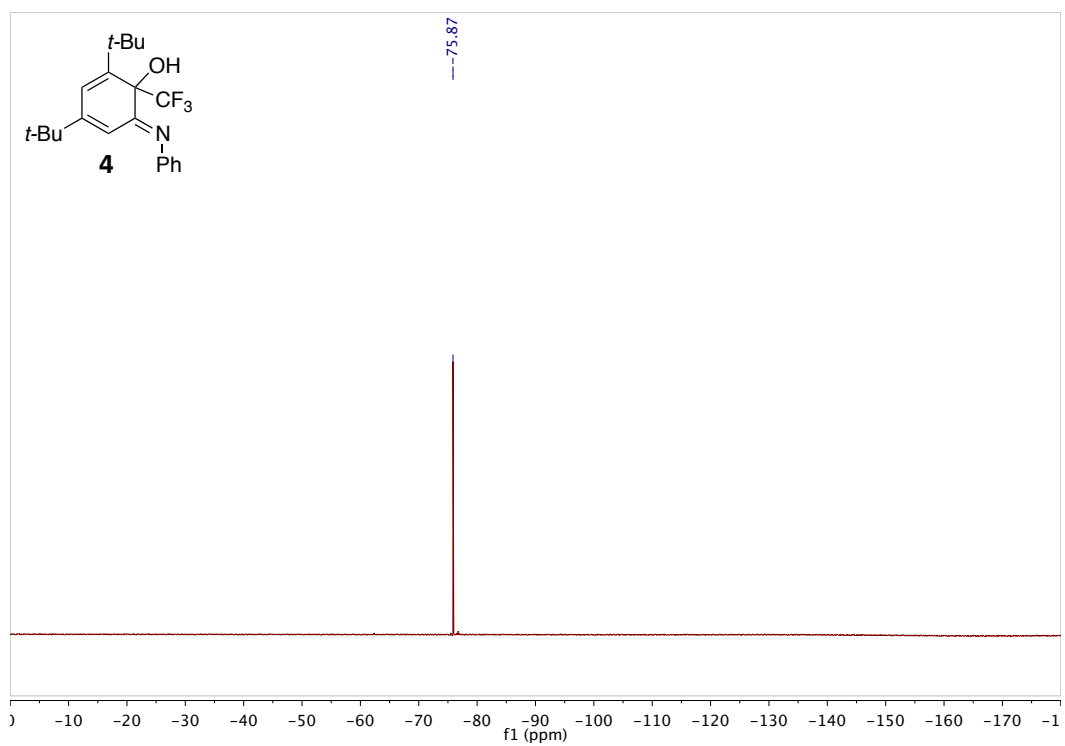


<sup>13</sup>C NMR

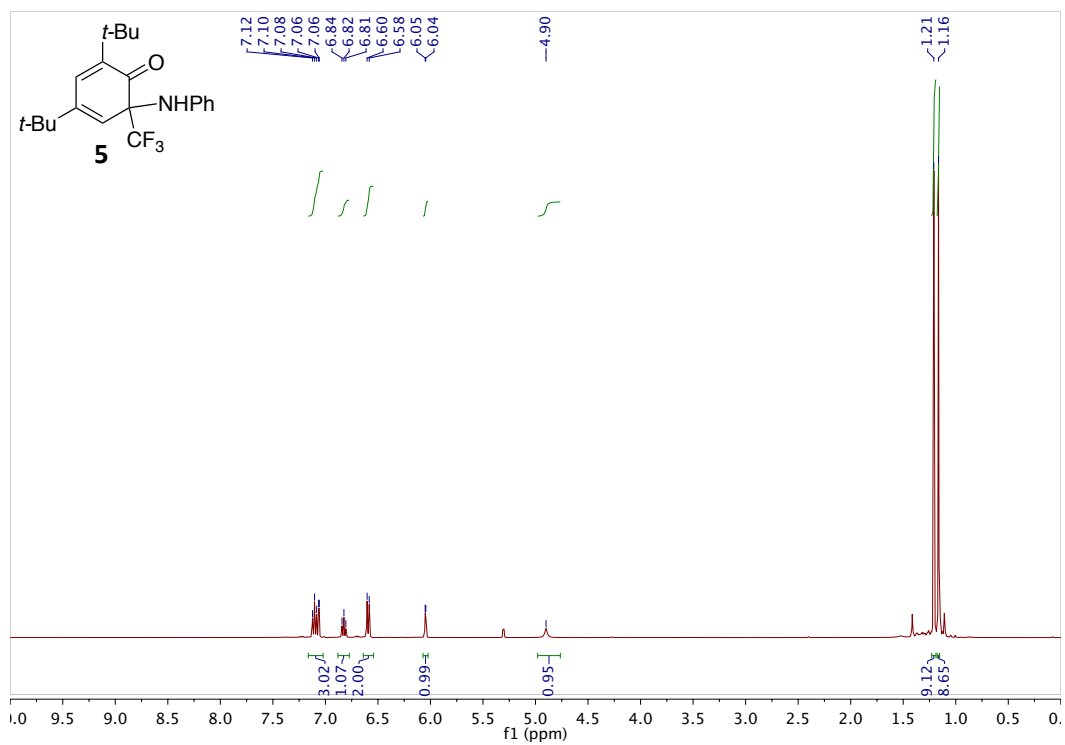




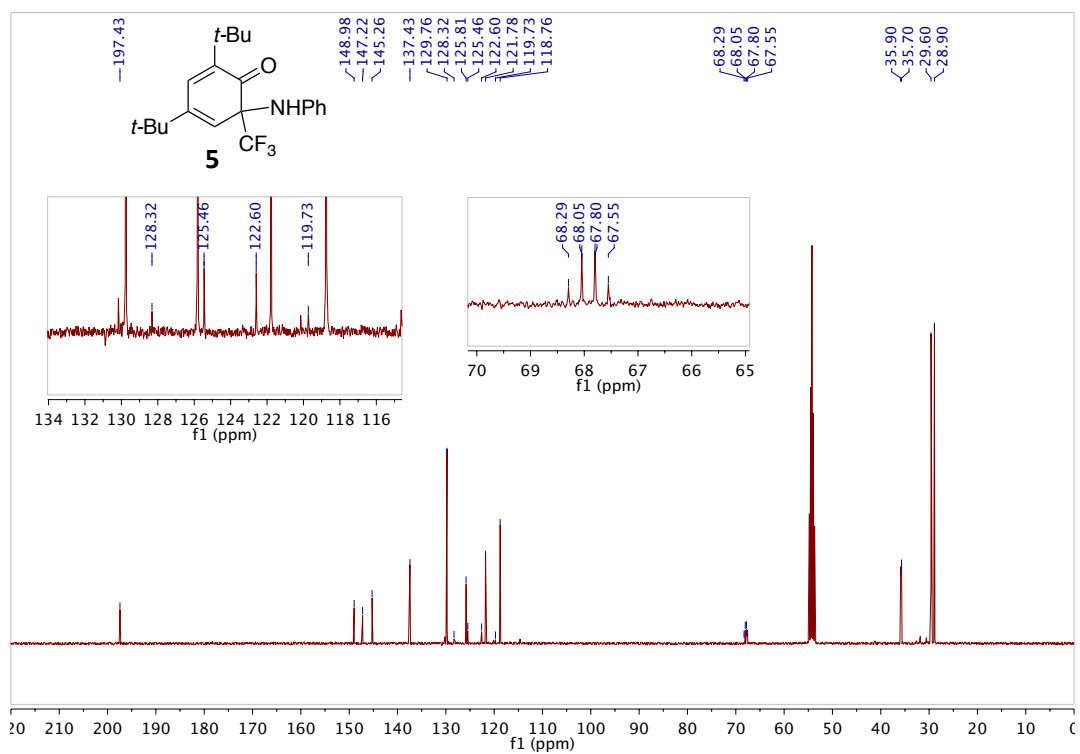
<sup>19</sup>F NMR



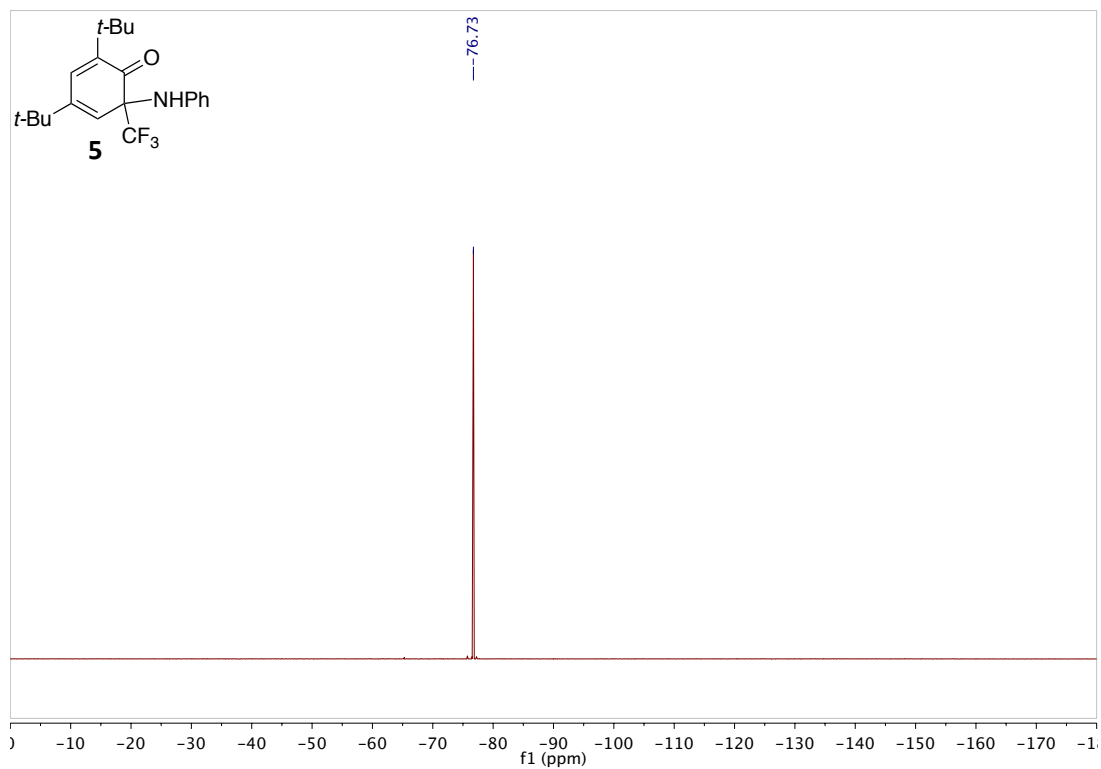
<sup>1</sup>H NMR



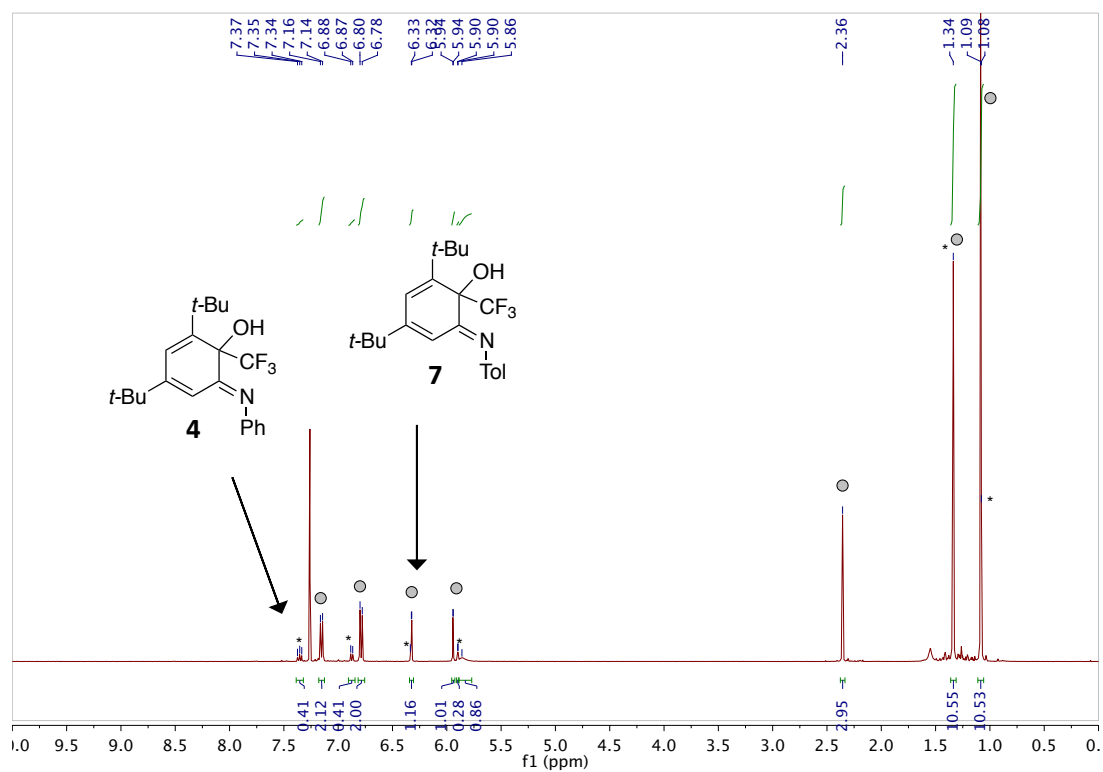
<sup>13</sup>C NMR



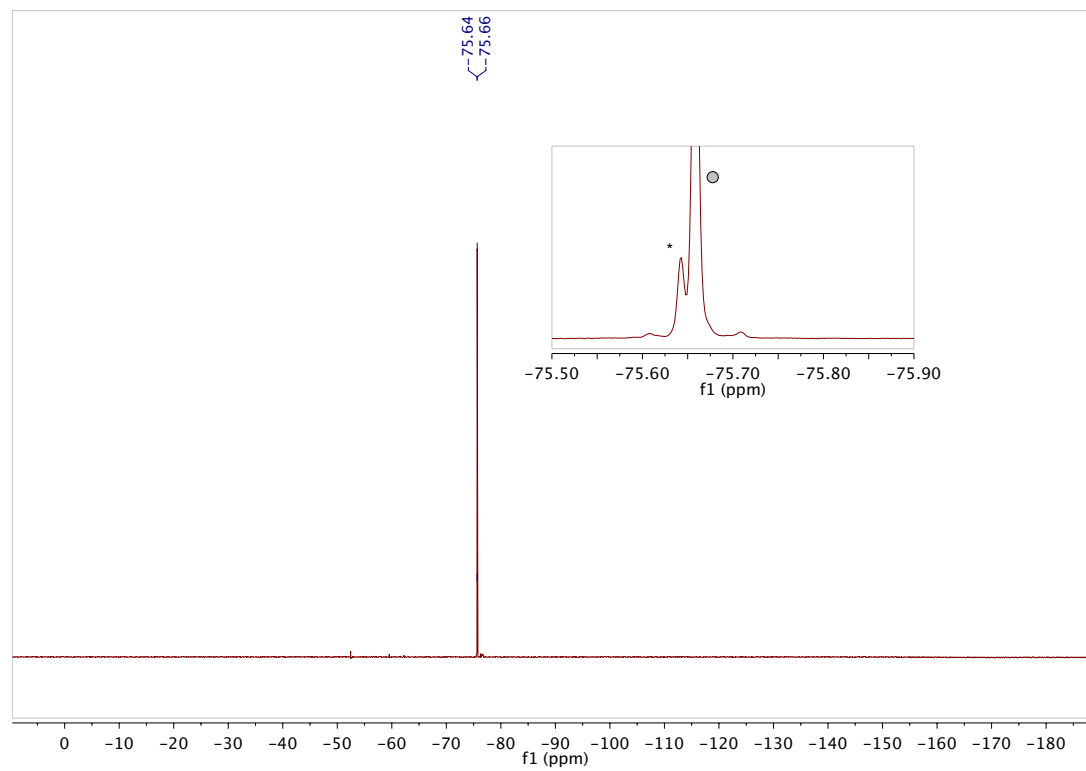
<sup>19</sup>F NMR



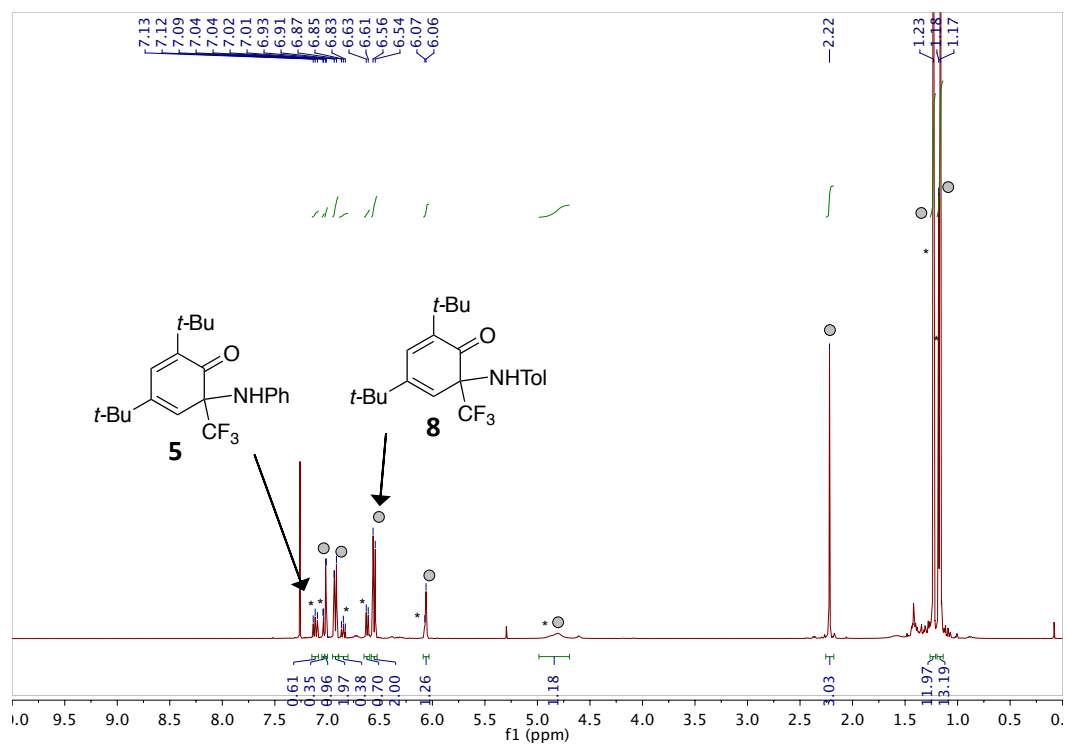
<sup>1</sup>H NMR: Mixture of **4** and **7**



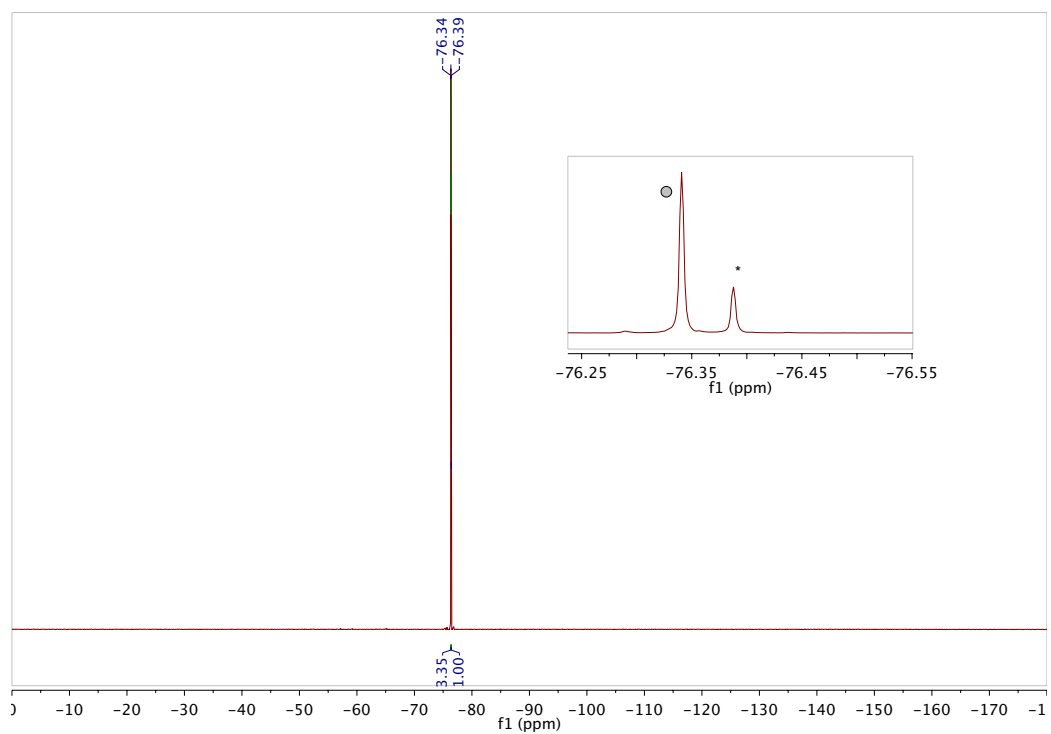
<sup>19</sup>F NMR: Mixture of **4** and **7**



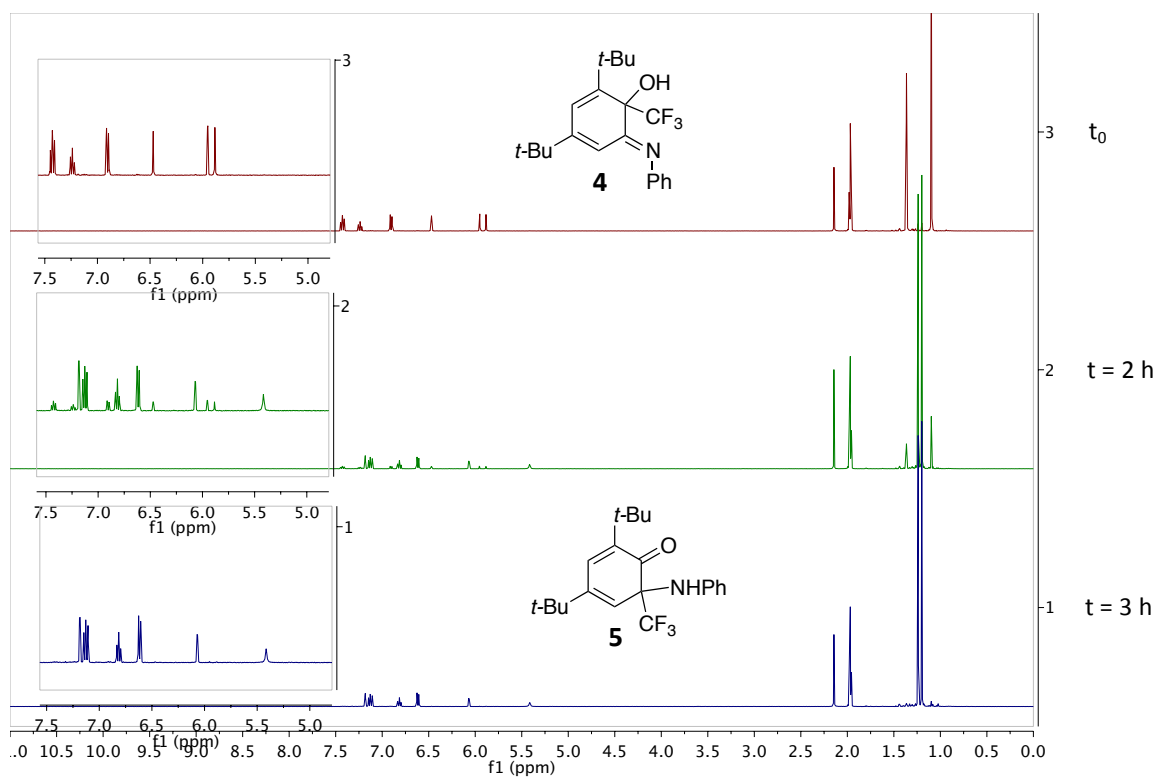
<sup>1</sup>H NMR: Mixture of **5** and **8**



<sup>19</sup>F NMR: Mixture of **5** and **8**



$^1\text{H}$  NMR: Conversion of **4** into **5** upon heating at 70°C in MeCN- $d_3$



$^{19}\text{F}$  NMR: Conversion of **4** into **5** upon heating at 70°C in MeCN- $d_3$

