# Supporting Information

# for

# From porphyrin benzylphosphoramidate conjugates to the catalytic hydrogenation of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin

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## Experimental details, characterization data for new compounds, and copies of NMR spectra

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**Experimental details**

$^{1}H$, $^{19}F$, and $^{31}P$ NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300.13, 282.38, and 121.50 MHz, respectively. $CDCl_3$ was used as the solvent. Chemical shifts are reported in ppm ($\delta$) and coupling constants (*J*) are given in Hz. Mass spectra and HRMS (ESI) were recorded on VG AutoSpec Q and M mass spectrometers. Absorption spectra were recorded on a Shimadzu UV-2501-PC spectrophotometer in $CHCl_3$ solutions. Flash chromatography was carried out with silica gel 35–70 mesh (Merck). Analytical TLC was carried out on precoated sheets with silica gel (0.2 mm thick, Merck). The aminoalkyl dibenzylphosphoramidates were synthesized in 67–75% yield from commercial dibenzylphosphonate and aliphatic diamines, as described by Souza et al in reference [1].

**General procedure for monosubstituted $TPPF_{20}$ phosphoramidates 1a–c by microwave irradiation:**

In a small vial 0.04 mmol (39.0 mg) of 5,10,15,20-tetrakispentafluorophenylporphyrin ($TPPF_{20}$) and 0.10 mmol of the aminoalkyldibenzylphosphoramidate derivatives (32.0 mg for *n* = 2; 34.8 mg for *n* = 4; 37.6 mg for *n* = 6) were dissolved in *N*-methyl-2-pyrrolidinone (NMP, 2.0 mL). The closed vial was irradiated in a microwave oven (Mileston, Microsynth, 800 W, 1 bar, 200 °C,) for 2 min intervals, until no starting material was visualized by TLC (usually 8 min). The mixture was diluted with chloroform, washed with aqueous $KHCO_3$ solution (3 x 5 mL) and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography using ethyl acetate/petroleum ether 70% as the eluent.

5-(4-{[2-(Dibenzyloxyphosphorylamino)ethyl]amino}-2,3,5,6-tetrafluorophenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (**1a**): Dark brown solid. Isolated yield 20%. $^{1}H$-NMR $\delta$ = -2.91 (s, 2H, NH), 3.23-3.39 (m, 3H, $C\underline{H_2}N\underline{H}P$), 3.69-3.73 (m, 2H, $C\underline{H_2}NHPh$), 4.80 (br s, 1H, $CH_2N\underline{H}Ph$), 5.16 (d, *J* = *8.2*, 4H, $OC\underline{H_2}Ph$), 7.35-7.47 (m, 10H, $OCH_2\underline{Ph}$), 8.85–9.01 (m, 8H, H-$\beta$). $^{19}F$-NMR $\delta$ = -185.10 to - 184.88 (m, 6F, F-*meta*), -183.86 (d, *J* = 16.9, 2F, F-*meta*), -175.10 to -174.91 (m, 3F, F-*para*), -163.95 (dd, *J* = 5.6 and 16.9, 2F, F-*ortho*), -160.00 (dd, *J* = 7.1 and 22.5, 6F, F-*ortho*), $^{31}P$-NMR $\delta$ = 10.29, HRMS (ESI) *m*/*z* calcd. for

$C_{60}H_{31}F_{19}N_6O_3P$ $[M+H]^+$: 1275.1892, found: 1275.1886, UV-vis($CHCl_3$) λmax/nm (log ε) 408 (5.06), 506 (4.01), 584 (3.52).

5-(4-{[4-(Dibenzyloxyphosphorylamino)butyl]amino}-2,3,5,6-tetrafluorophenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (**1b**): Dark brown solid. Isolated yield 42%. $^1$H-NMR δ = -2.90 (s, 2H, NH), 1.63-1.79 (m, 4H, $CH_2(C\underline{H_2})_2CH_2$), 2.84-2.90 (m, 1H, N<u>H</u>P), 2.98-3.08 (m, 2H, $C\underline{H_2}$NHP), 3.63 (t, *J* = 6.9, 2H, $C\underline{H_2}$NHPh), 5.11 (d, *J* = 7.7, 4H, $OC\underline{H_2}$Ph), 7.34-7.45 (m, 10H, $OCH_2\underline{Ph}$), 8.86–9.01 (m, 8H, H-β). $^{19}$F-NMR δ = -185.10 to -184.87 (m, 6F, F-*meta*), -184.32 (d, *J* = 16.9, 2F, F-*meta*), -175.09 to -174.91 (m, 3F, F-*para*), -164.06 (dd, *J* = 5.6 and 21.2, 2F, F-*ortho*), -160.00 (dd, *J* = *5*.6 and 24.0, 6F, F-*ortho*), $^{31}$P-NMR δ = 10.03, HRMS (ESI) *m*/*z* calcd. for $C_{62}H_{35}F_{19}N_6O_3P$ $[M+H]^+$: 1303.2205, found: 1303.2199, UV-vis($CHCl_3$) λmax/nm (log ε) 410 (5.31), 506 (4.23), 582 (3.65).

5-(4-{[6-(Dibenzyloxyphosphorylamino)hexyl]amino}-2,3,5,6-tetrafluorophenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (**1c**): Dark brown solid. Isolated yield 24%. $^1$H-NMR δ = -2.90 (s, 2H, NH), 1.40-1.58 (m, 6H, $(C\underline{H_2})_3CH_2CH_2$NHP), 1.78 (m, 2H, $C\underline{H_2}CH_2$NHP), 2.75-2.81 (m, 1H, N<u>H</u>P), 2.91-2.97 (m, 2H, $C\underline{H_2}$NHP), 3.65 (t, *J* = 6.9, 2H, $C\underline{H_2}$NHPh), 4.26 (br s, 1H, $CH_2N\underline{H}$Ph), 5.08 (d, *J* = 7.6, 4H, $OC\underline{H_2}$Ph), 7.33-7.40 (m, 10H, $OCH_2\underline{Ph}$), 8.87–9.03 (m, 8H, H-β). $^{19}$F-NMR δ = -185.10 to -184.91 (m, 6F, F-*meta*), -184.43 (d, *J* = 14.1, 2F, F-*meta*), -175.11 to -174.96 (m, 3F, F-*para*), -164.06 (dd, *J* = 5.6 and 19.7, 2F, F-*ortho*), -160.00 (dd, *J* = *5*.6 and 24.0, 6F, F-*ortho*), $^{31}$P-NMR: 10.14, HRMS (ESI) *m*/*z* calcd. for $C_{64}H_{39}F_{19}N_6O_3P$ $[M+H]^+$: 1331.2518, found: 1331.2512, UV-vis($CHCl_3$) λmax/nm (log ε) 415 (5.28), 508 (4.26), 584 (3.88).

**General procedure for hydrogenation of $TPPF_{20}$:**

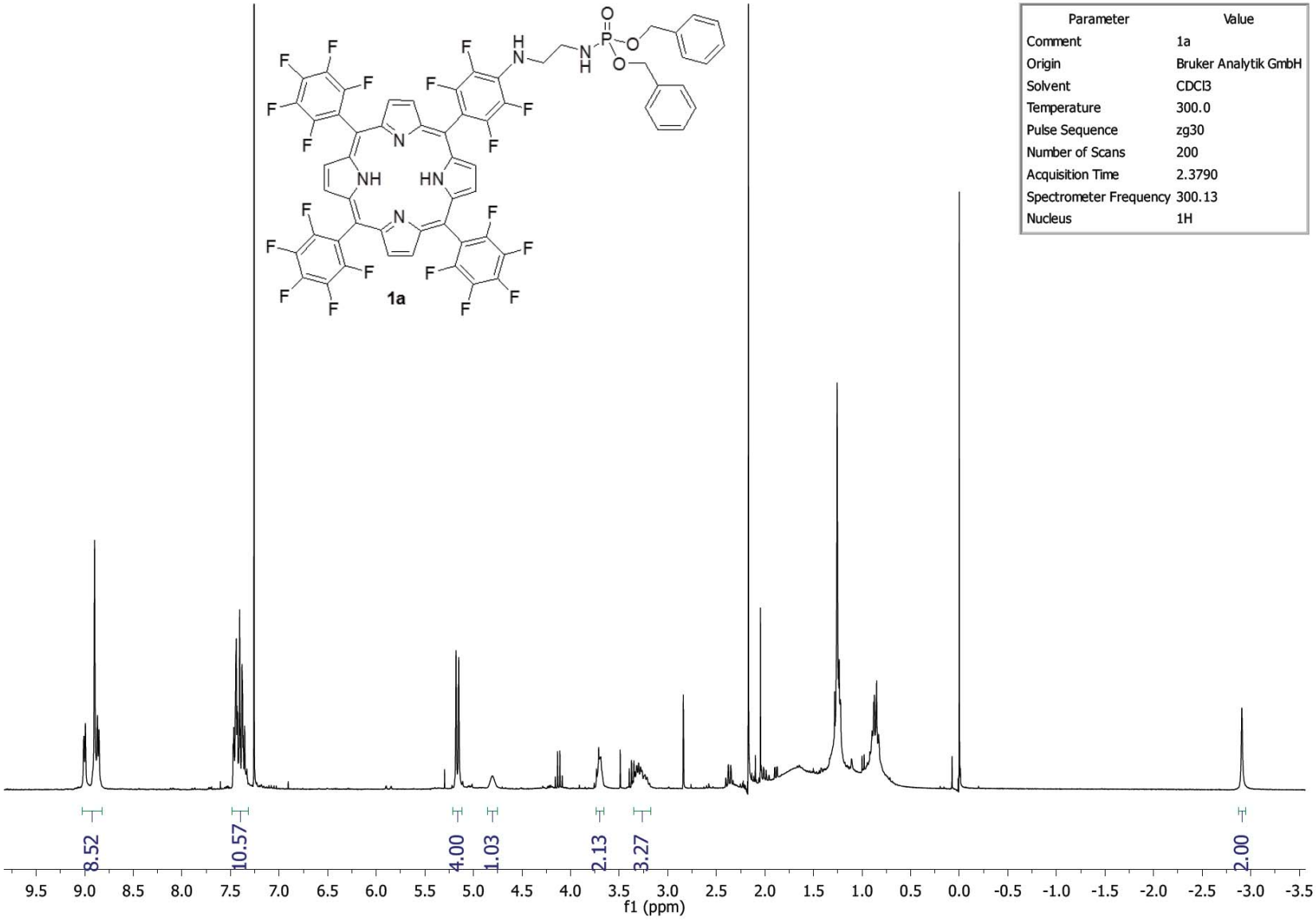
20 mg of $TPPF_{20}$ and 10 mg of Pd/C (10%) were suspended in 7 mL of the appropriate solvent and 0.7 mL of $NEt_3$, when was the case. Hydrogen was bubbled directly into the stirred suspension at room temperature (20–25 °C) and protected from light. At the end of the reaction the catalyst was filtered off and washed with chloroform, followed by evaporation of the solvents at a low temperature (<60 °C). The crude product was fractionated by preparative TLC on silica-gel plates using a mixture of petroleum ether/chloroform 4:1 as the eluent.

**$TPCF_{20}$:** $^{1}$H-NMR $\delta$ = -1.53 (s, 2H, NH), 4.31 (s, 4H, $CH_2$), 8.34 (d, *J* = 5.0, 2H, H-$\beta$), 8.45 (s, 2H, H-$\beta$), 8.67 (d, *J* = 5.0, 2H, H-$\beta$), $^{19}$F-NMR $\delta$ = -185.05 and -184.15 (2dt, *J* = 19.7 and 5.6, 8F, F-*meta*), -175.58 and -175.35 (2t, *J* = 19.7, 4F, F-*para*), -161,41 and -160.47 (2dd, *J* = 8.4 and 22.5, 8F, F-*ortho*), HRMS (ESI) *m*/*z* calcd. for $C_{44}H_{13}F_{20}N_4$ $[M+H]^+$: 977.0821, found: 977.0812, UV-vis($CHCl_3$) $\lambda$max/nm (log $\varepsilon$) 406 (5.09), 505 (4.01), 656 (4.59).

**$TPIF_{20}$:** $^{1}$H-NMR $\delta$ = 3.43 (s, 8H, $CH_2$), 4.82 (br s, 2H, NH), 6.99 (d, *J* = 4.5, 2H, H-$\beta$), 7.46 (d, *J* = 4.5, 2H, H-$\beta$), $^{19}$F-NMR $\delta$ = -185.17 to -185.03 (m, 2F, F-*meta*), -184.59 to -184.41 (m, 4F, F-*meta*), -183.45 to -183.29 (m, 2F, F-*meta*), -175.66 (t, *J* = 19.8, 2F, F-*para*), -176.18 (t, *J* = 19.8, 1F, F-*para*), -175.75 (t, *J* = 19.8, 1F, F-*para*), -162.41 (dd, *J* = 8.5 and 25.4, 2F, F-*ortho*), -162.04 (dd, *J* = 8.5 and 22.6, 4F, F-*ortho*), -161.66 (dd, *J* = *5*.6 and 22.6, 2F, F-*ortho*), HRMS (ESI) *m*/*z* calcd. for $C_{44}H_{15}F_{20}N_4$ $[M+H]^+$: 979.0977, found: 979.0967, UV-vis($CHCl_3$) $\lambda$max/nm (log $\varepsilon$) 403 (4.56), 509 (3.70), 547 (3.84), 589 (4.07).

## References


1. Souza, M. C.; Macedo, W. P.; Torres, T. S.; Pedrosa, L. F.; Alt, H. G. *Phosphorus, Sulfur Silicon Relat. Elem.* **2006,** *181,* 1885–1893. doi:10.1080/10426500500543776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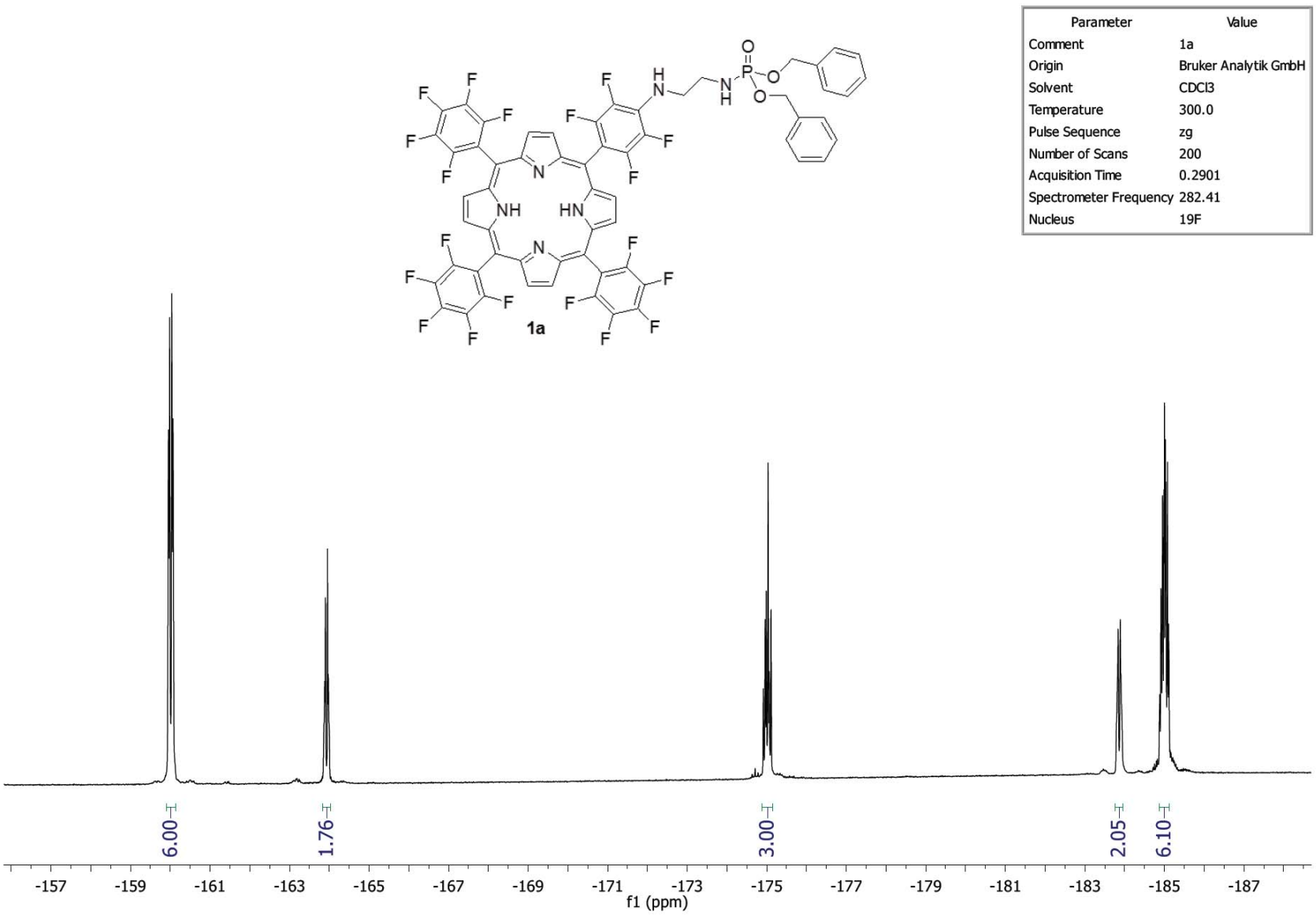
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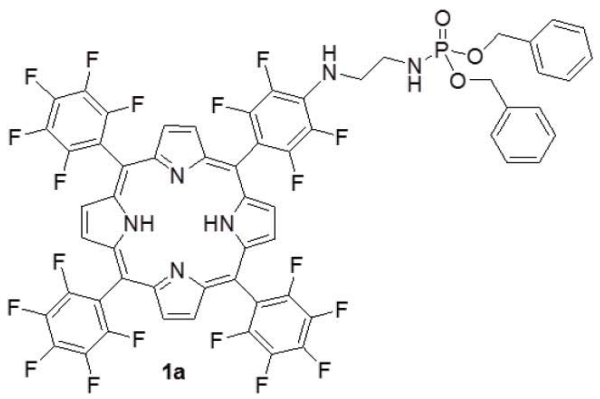


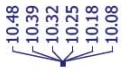


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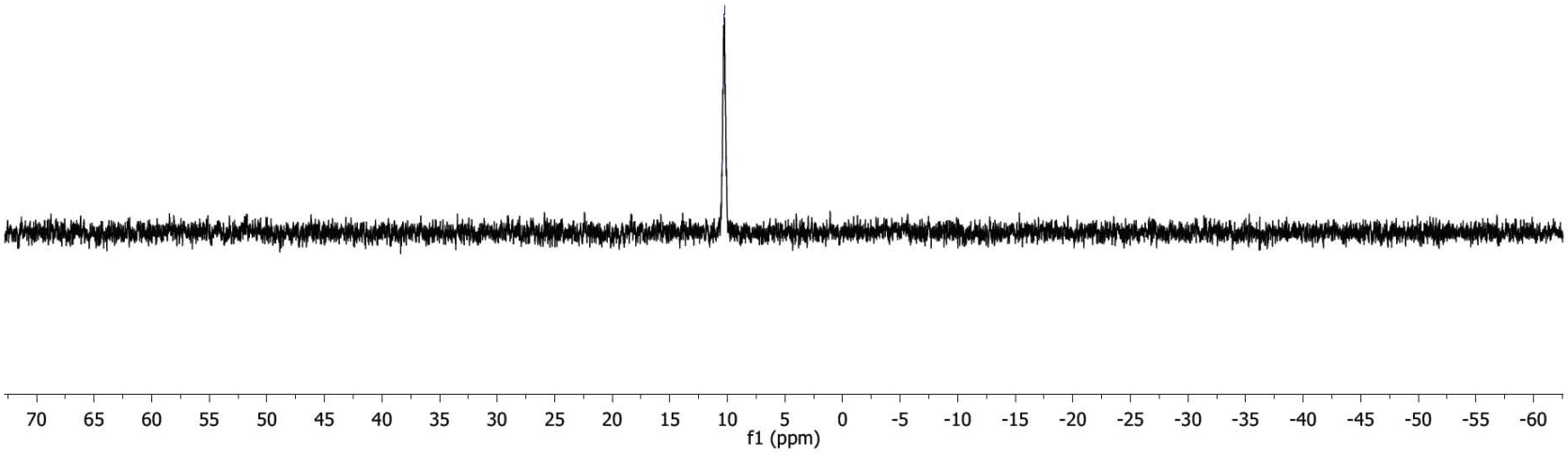

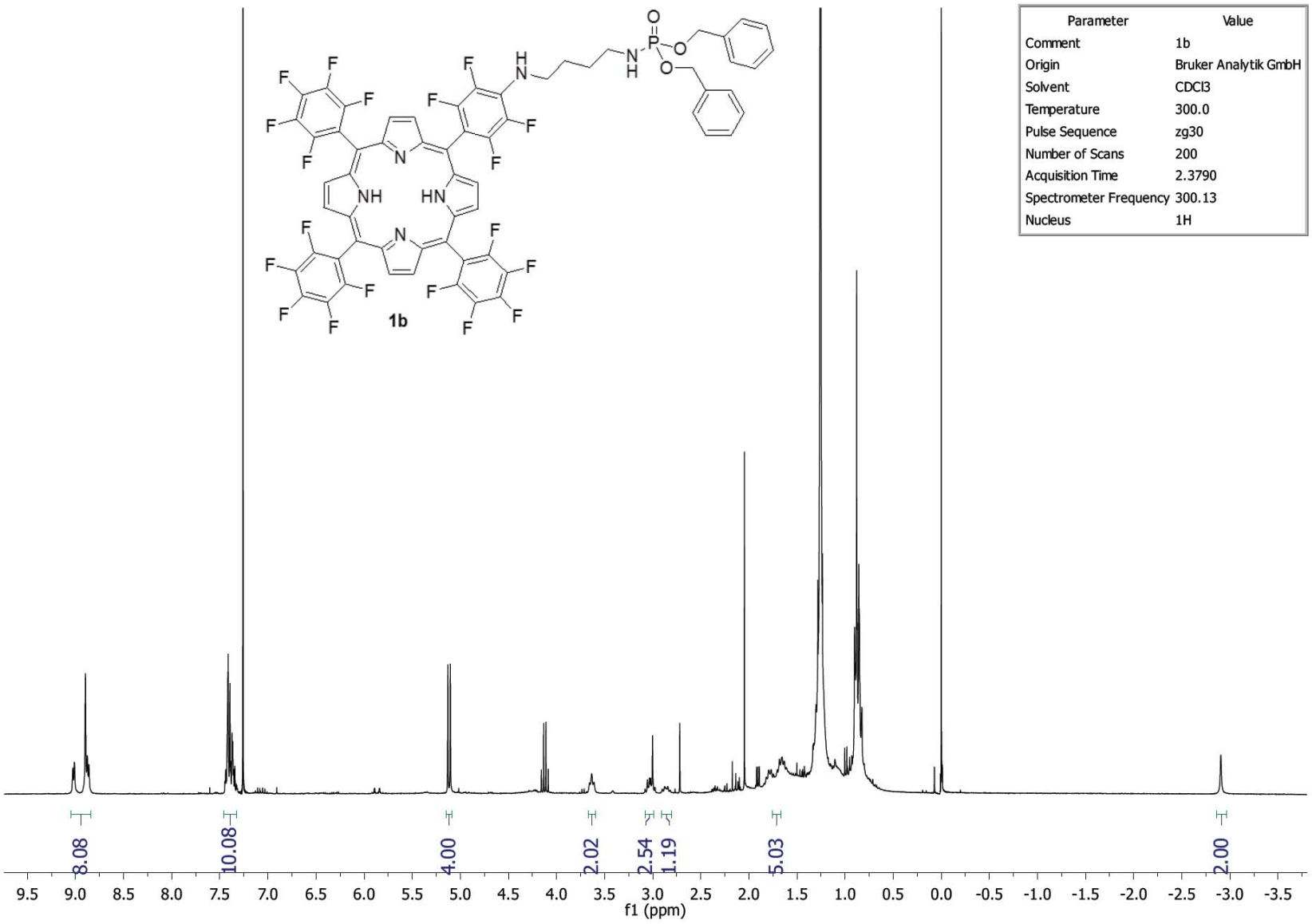
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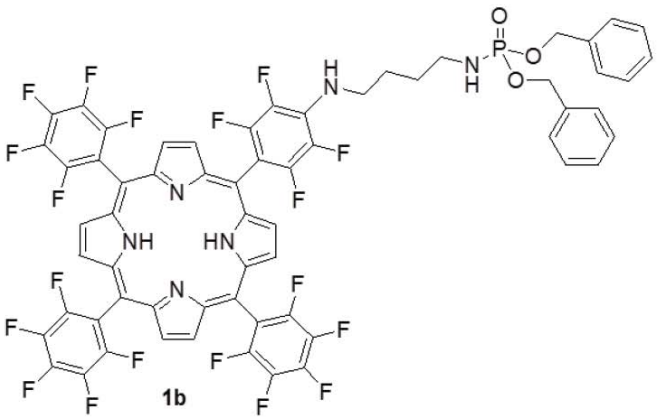


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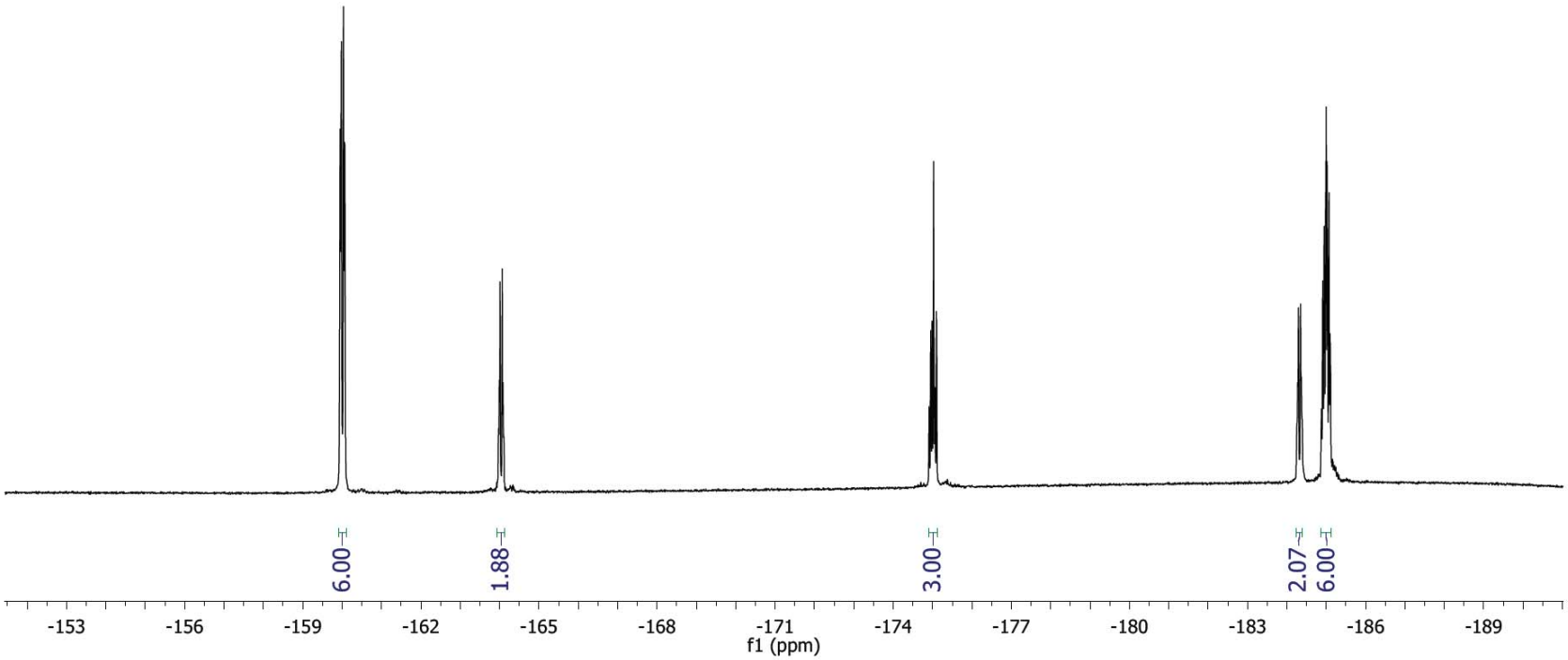

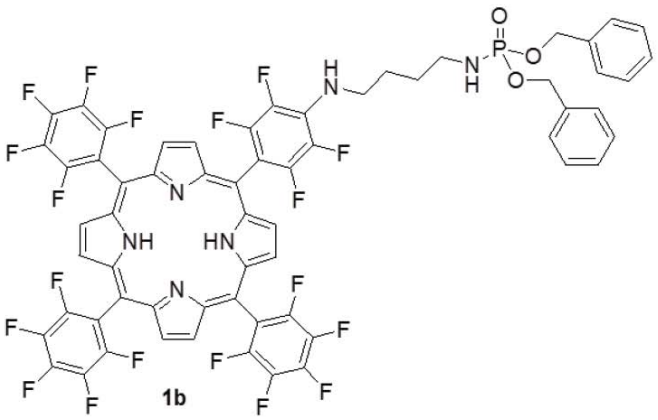



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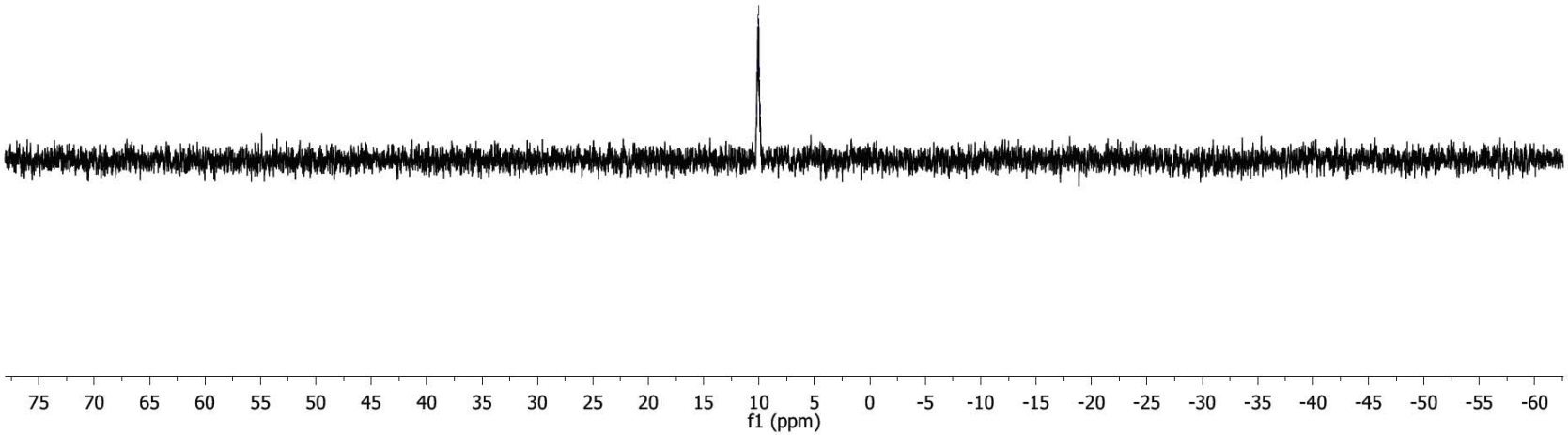

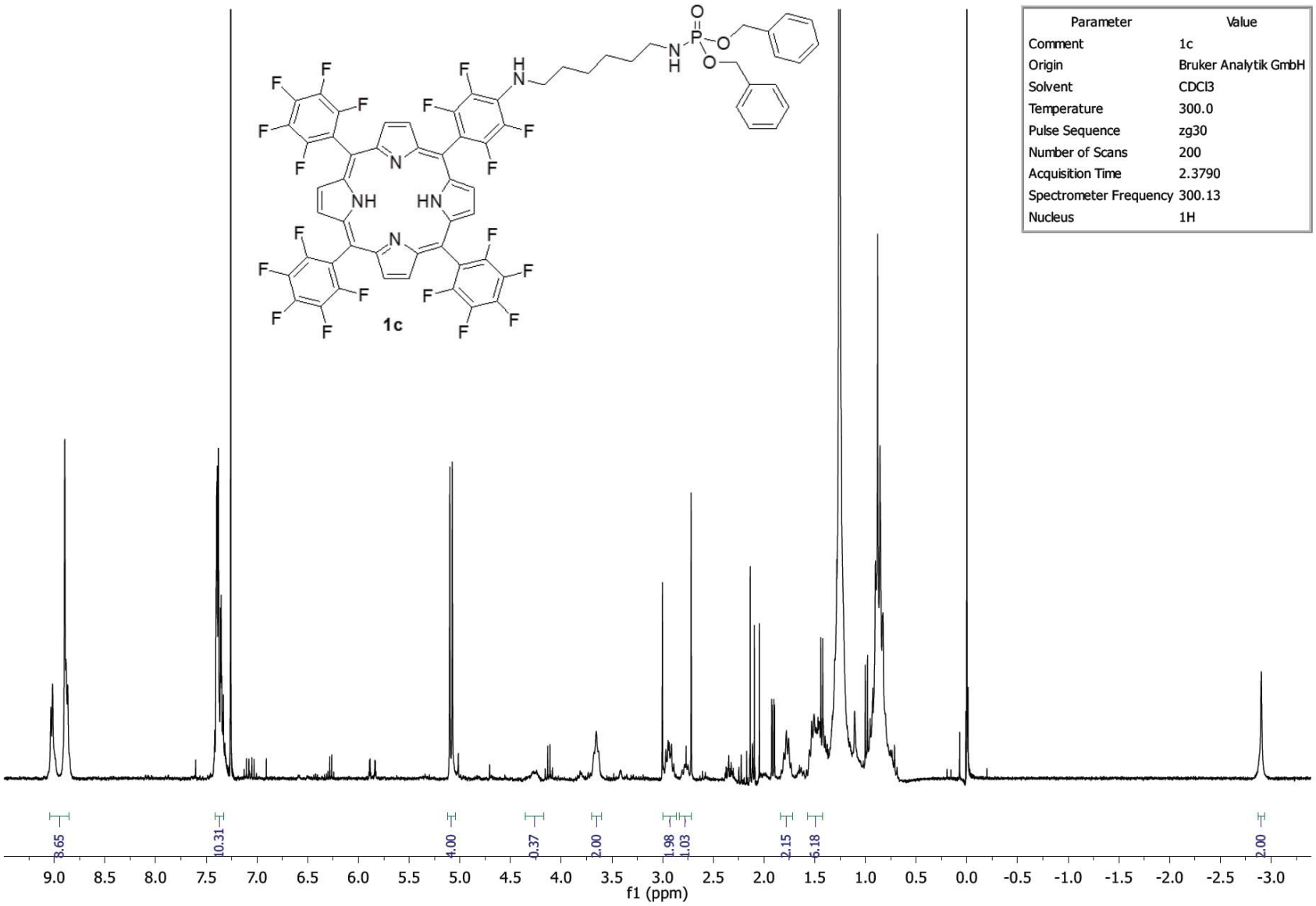
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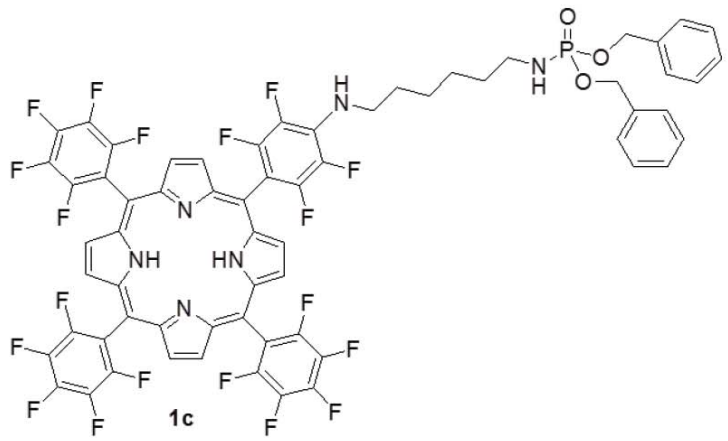


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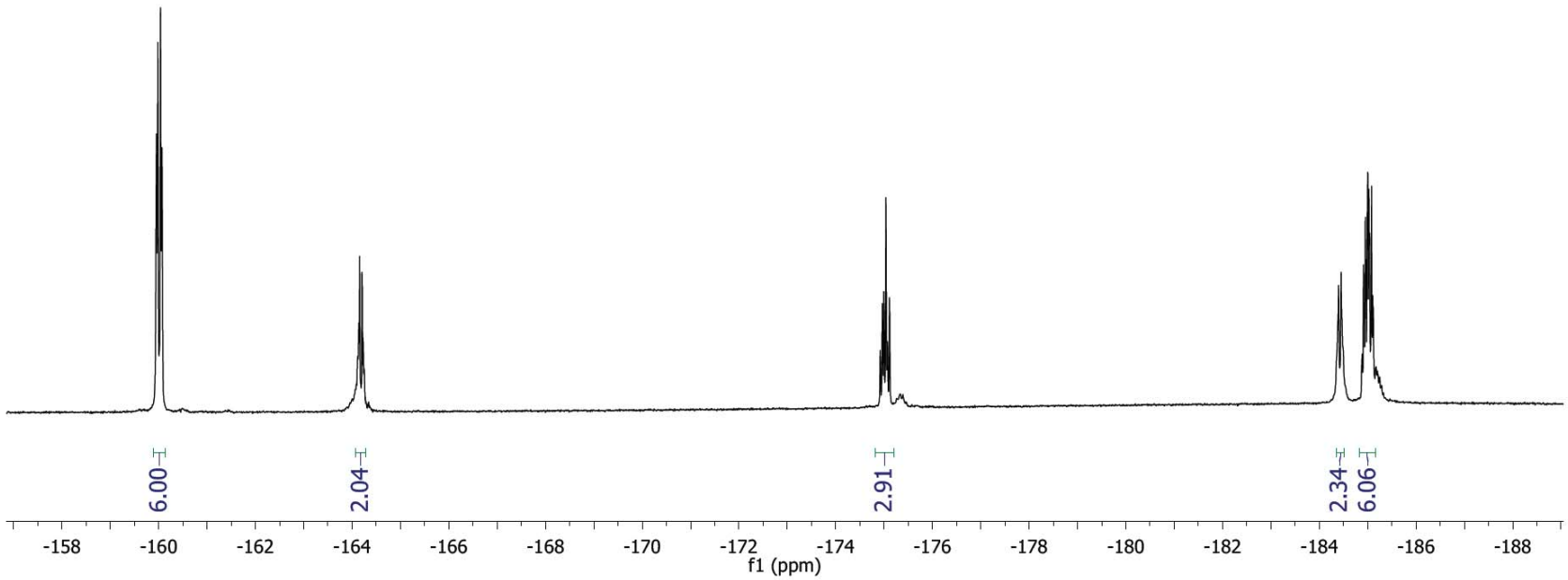

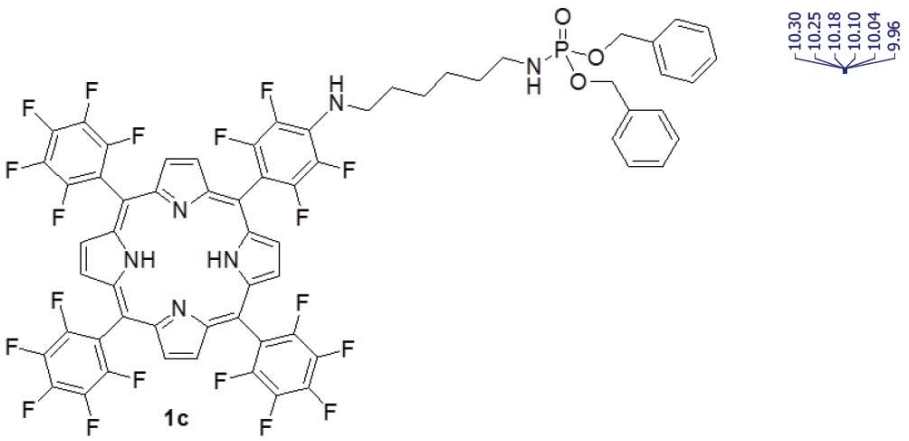


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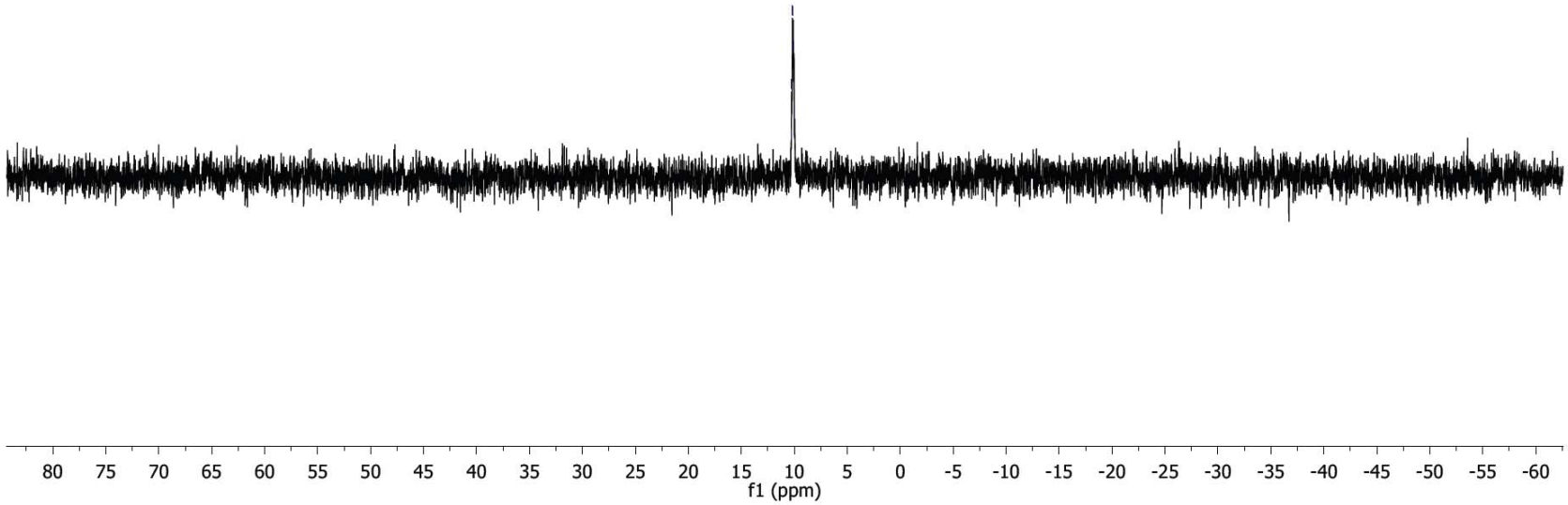

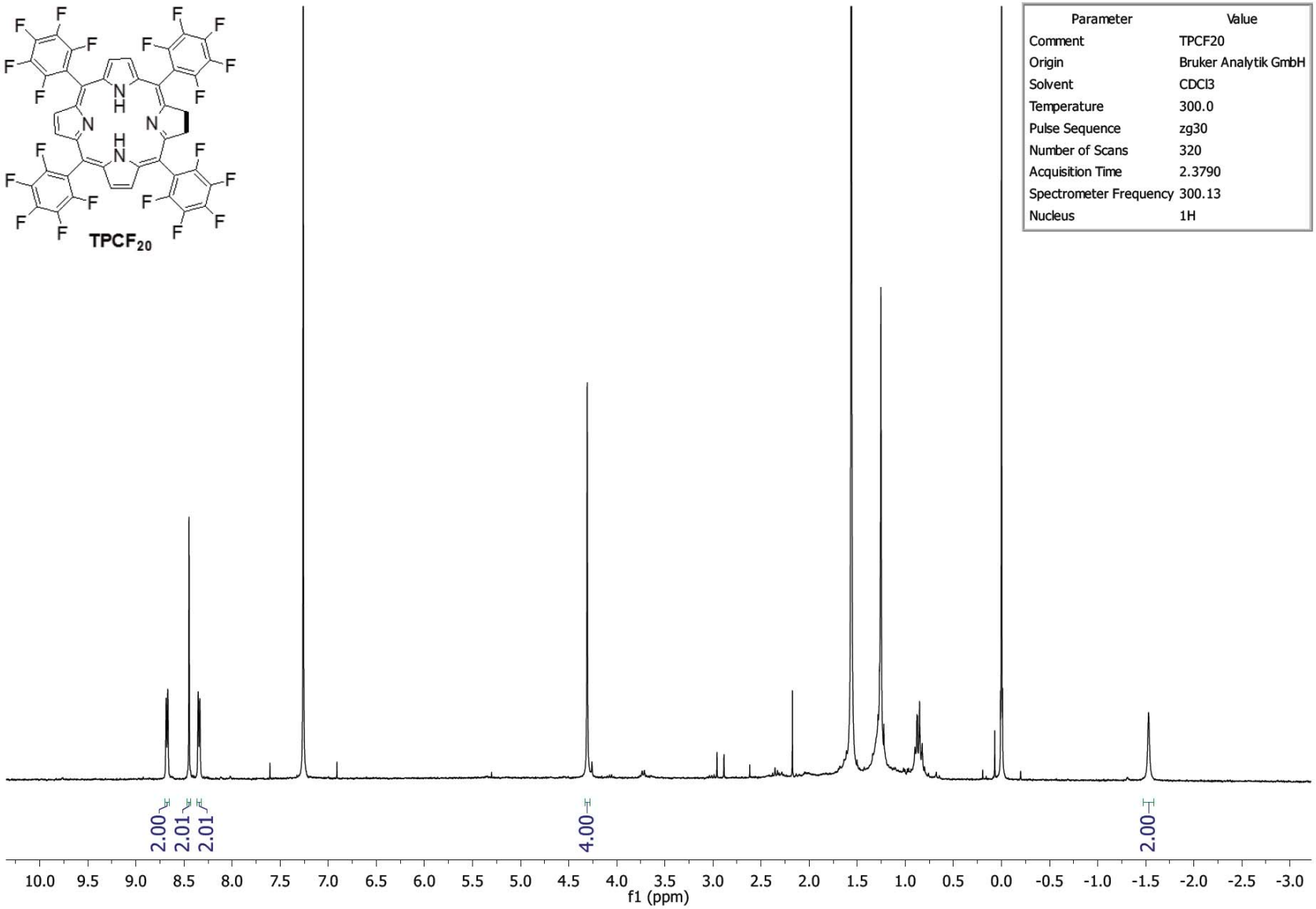
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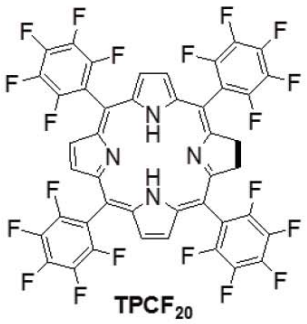


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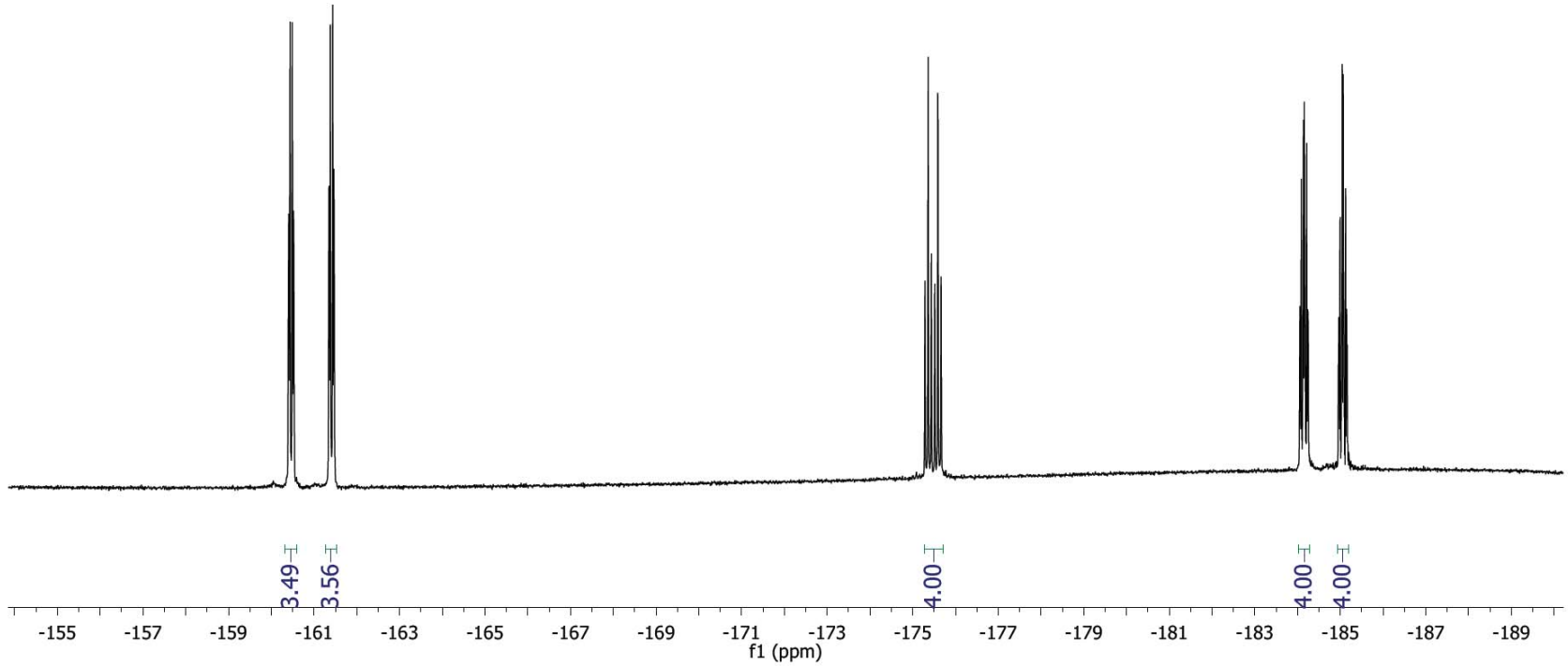

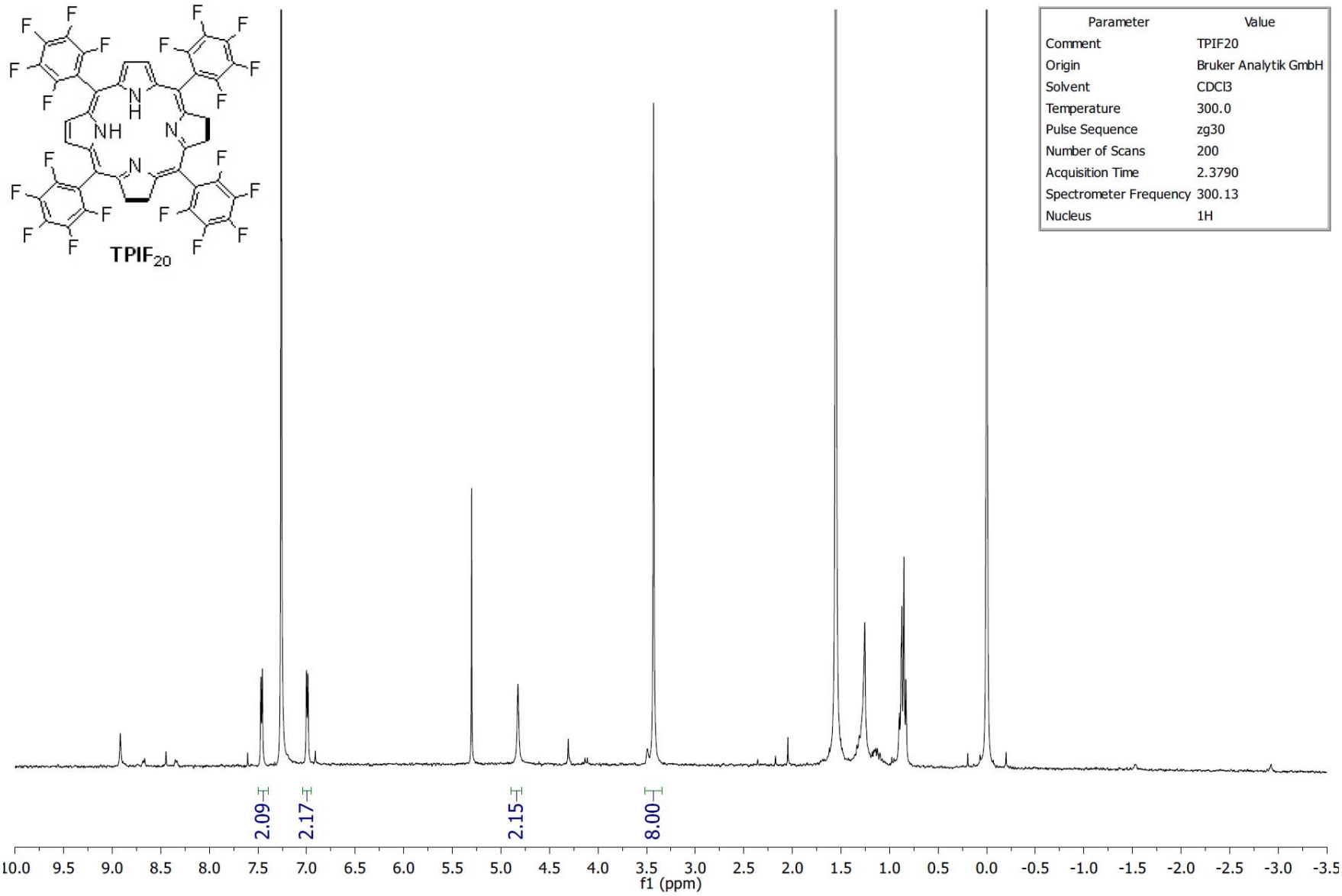
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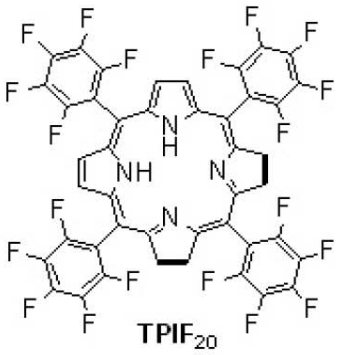


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