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Supporting Information

for

Substituent-controlled construction of A_4B_2-hexaphyrins and A_3B-porphyrins: a mechanistic evaluation

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Analytical data and copies of spectra

Table of contents

1. Experimental section

*5,10,15-Tris(pentafluorophenyl)-20-phenylporphyrin (**3a**)*. Purple solid (8 mg, 15%); UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 413.0 (5.393), 508.5 (4.207), 537.0 (3.629), 583.0 (3.741), 638.5 (3.092); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.82 (s, 2H), 7.80 – 7.88 (m, 3H), 8.24 (d, *J*= 6.6 Hz, 2H), 8.85 (d, *J*= 3.9 Hz, 2H), 8.92 (s, 4H), 9.00 (d, *J*= 4.2 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.55 (dd, J_1= 23.9 Hz, J_2= 8.4 Hz, 2F), -136.62 (dd, J_1= 23.4 Hz, J_2= 8.4 Hz, 4F), -151.72 (m, 3F), -161.59 (m, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{44}H_{16}F_{15}N_4$ $[M+H]^+$: 885.1130, found: 885.1151.

*5,10,15-Tris(pentafluorophenyl)-20-(2,4,6-trimethylphenyl)porphyrin (**3b**)*. Purple solid (10 mg, 17%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 415(5.678), 510(4.528), 586(4.138); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.80 (s, 2H), 1.83 (s, 6H), 2.65 (s, 3H), 7.31 (s, 2H), 8.77 (s, 2H), 8.82 (s, 2H), 8.89 (s, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.52 (td, J_1= 24.7 Hz, J_2= 8.0 Hz, 6F), -151.72 (m, 3F), -161.58 (qd, J_1= 23.8 Hz, J_2= 8.0 Hz, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{47}H_{22}F_{15}N_4$ $[M+H]^+$: 927.1605, found: 927.1610.

*5,10,15-Tris(pentafluorophenyl)-20-(2,6-dichlorophenyl)porphyrin (**3c**)*. Purple solid (8 mg, 13%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 414(5.311), 509(4.067), 590(4.021); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.82 (s, 2H), 7.74 – 7.79 (m, 1H), 7.83-7.85 (m, 2H), 8.81 – 8.84 (m, 4H), 8.89 (s, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.34 (dd, J_1= 23.8 Hz, J_2= 8.5 Hz, 4F), -136.51 (dd, J_1= 23.8 Hz, J_2= 8.0 Hz, 2F), -151.53 (m, 3F), -161.51 (m, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{44}H_{14}Cl_2F_{15}N_4$ $[M+H]^+$: 953.0350, found: 953.0364.

*5,10,15-Tris(pentafluorophenyl)-20-(4-fluorophenyl)porphyrin (**3d**)*. Purple solid (10 mg, 17%), UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 413.5 (5.798), 509.0 (4.648), 540.0 (3.952), 584.0 (4.164), 639.0 (3.499); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.96 (s, 2H), 7.40 – 7.45 (m, 2H), 8.11

(bs, 2H), 8.76 (s, 2H), 8.82 (s, 4H), 8.87 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -113.58 (s, 1F), -136.51 (dd, J_1= 23.7 Hz, J_2= 8.0 Hz, 2F), -136.65 (dd, J_1= 23.4 Hz, J_2= 8.3 Hz, 4F), -151.63 (m, 3F), -161.56 (m, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{44}H_{15}F_{16}N_4$ $[M+H]^+$: 903.1036, found: 903.1013.

*5,10,15-Tris(pentafluorophenyl)-20-(4-chlorophenyl)porphyrin (**3e**).* Purple solid (6 mg, 9%), UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 414.0 (5.607), 509.0 (4.405), 539.5 (3.778), 584.5 (3.936), 639.0 (3.304); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.89 (s, 2H), 7.79 (d, *J*= 8.1 Hz, 2H), 8.15 (d, *J*= 8.1 Hz, 2H), 8.83 (d, *J*= 4.8 Hz, 2H), 8.90 (s, 4H), 8.95 (d, *J*= 4.8 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.51 (dd, J_1= 24.4 Hz, J_2= 9.3 Hz, 2F), -136.65 (dd, J_1= 24.2 Hz, J_2= 8.7 Hz, 4F), -151.64 (m, 3F), -161.58 (m, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{44}H_{15}ClF_{15}N_4$ $[M+H]^+$: 919.0740, found: 919.0720.

*5,10,15-Tris(pentafluorophenyl)-20-(4-bromophenyl)porphyrin (**3f**).* Purple solid (10 mg, 16%), UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 413.5 (5.670), 508.5 (4.471), 540.0 (3.825), 583.0 (4.009), 639.0 (3.400); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.88 (s, 2H), 7.94 (d, *J*= 8.3 Hz, 2H), 8.09 (d, *J*= 8.1 Hz, 2H), 8.83 (s, 2H), 8.89 (s, 4H), 8.94 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.51 (dd, J_1= 23.6 Hz, J_2= 8.7 Hz, 2F), -136.65 (dd, J_1= 23.8 Hz, J_2= 8.1 Hz, 4F), -151.64 (m, 3F), -161.56 (m, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{44}H_{15}BrF_{15}N_4$ $[M+H]^+$: 963.0235, found: 963.0239.

*5,10,15-Tris(pentafluorophenyl)-20-(4-trifluoromethylphenyl)porphyrin (**3g**).* Purple solid (9 mg, 13%); UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 413.0 (5.631), 508.0 (4.465), 537.0 (3.907), 582.5 (4.063), 638.0 (3.639); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.88 (s, 2H), 8.08 (d, *J*= 7.9 Hz, 2H), 8.35 (d, *J*= 7.5 Hz, 2H), 8.84 (s, 2H), 8.90 (s, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.10 (s, 3F), -136.50 (dd, J_1= 23.5 Hz, J_2= 7.9 Hz, 2F), -136.64 (dd, J_1= 23.6 Hz, J_2= 7.9 Hz, 4F), -151.44 (m, 3F), -161.43 (m, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{45}H_{15}F_{18}N_4$ $[M+H]^+$: 953.1004, found: 953.0982.

*5,10,15-Tris(pentafluorophenyl)-20-(4-methoxyphenyl)porphyrin (**3h**).* Purple solid (14 mg, 22%); UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 416.0 (5.032), 510.5 (3.813), 543.0 (3.121), 586.0 (3.335), 641.0 (2.653); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.83 (s, 2H), 4.11 (s, 3H), 7.32 (d, *J*= 8.4 Hz, 2H), 8.12 (d, *J*= 8.4 Hz, 2H), 8.81 (d, *J*= 4.0 Hz, 2H), 8.88 (s, 4H), 9.01 (d, *J*= 4.3 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.49 (dd, J_1= 23.7 Hz, J_2= 8.3 Hz, 2F), -136.62 (dd, J_1= 23.6 Hz, J_2= 8.2 Hz, 4F), -151.78 (m, 3F), -161.62 (m, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{45}H_{18}F_{15}N_4O$ $[M+H]^+$: 915.1241, found: 915.1244.

*5,10,15-Tris(pentafluorophenyl)-20-(2-thienyl)porphyrin (**3j**).* Purple solid (6 mg, 10%), UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 415.0 (5.495), 510.5 (4.276), 585.0 (3.802); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.85 (s, 2H), 7.53 – 7.55 (m, 1H), 7.92 (d, *J*= 5.2 Hz, 1H), 7.96 (d, *J*= 3.2 Hz, 1H), 8.83 (d, *J*= 4.3 Hz, 2H), 8.88 (s, 4H), 9.19 (d, *J*= 4.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.48 (dd, J_1= 23.4 Hz, J_2= 8.1 Hz, 2F), -136.60 (dd, J_1= 23.6 Hz, J_2= 8.1 Hz, 4F), -151.62 (m, 3F), -161.52 (m, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{42}H_{14}F_{15}N_4S$ $[M+H]^+$: 891.0694, found: 891.0674.

*5,10,15-Tris(pentafluorophenyl)-20-(3-indolyl)porphyrin (**3k**).* Purple solid (14 mg, 22%); UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 415.0 (5.279), 514.5 (4.387), 542.0 (4.152), 588.0 (4.074), 644.0 (3.821); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.68 (s, 2H), 7.19 (t, *J*= 7.6 Hz, 1H), 7.44 (t, *J*= 7.7 Hz, 1H), 7.53 (d, *J*= 8.0 Hz, 1H), 7.76 (d, *J*= 8.3 Hz, 1H), 8.02 (s, 1H), 8.75 (d, *J*= 4.1 Hz, 2H), 8.87 (s, 4H), 8.91 (s, 1H), 9.16 (d, *J*= 4.5 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.44 (m, 6F), -151.93 (m, 3F), -161.65 (m, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{46}H_{17}F_{15}N_5$ $[M+H]^+$: 924.1239, found: 924.1248.

*5,20-Bis(2,4,6-trimethylphenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (**4b**).* Purple solid (11 mg, 17%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 572.5(4.779), 722(4.066), 901(3.878), 1035(3.825); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.77 (s, 4H), 2.02 (s, 12H), 2.71 (s, 6H), 7.42 (s, 4H), 9.08 (d, *J*= 4.7 Hz, 4H), 9.38 (d, *J*= 4.6 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.91 (m, 8F), -153.59 (m, 4F), -163.44 (m, 8F); HRMS (ESI-TOF) m/z calcd. for $C_{72}H_{37}F_{20}N_6$ $[M+H]^+$: 1365.2755, found: 1365.2748. Inner NH signal was not observed.

*5,20-Bis(2,6-dichlorophenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (**4c**).* Purple solid (10 mg, 16%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 572.5(4.919), 716.5(4.052), 896.5(3.662), 1025.5(3.562); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.62 (s, 4H), -2.37 (bs, 2H), 7.86-7.89 (m, 2H), 7.93-7.96 (m, 4H), 9.04 (d, *J*= 4.8 Hz, 4H), 9.41 (d, *J*= 4.8 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.74 (d, *J*= 21.1 Hz, 8F), -153.34 (t, *J*= 20.0 Hz, 4F), -163.27 (t, *J*= 19.5 Hz, 8F); HRMS (ESI-TOF) m/z calcd. for $C_{66}H_{21}Cl_4F_{20}N_6$ $[M+H]^+$: 1417.0257, found: 1417.0244.

*5,20-Bis(4-fluorophenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (**4d**).* Purple solid (10 mg, 18%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 572.5(4.675), 721(3.780), 782.5(3.631), 900(3.487), 1023(3.302); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.67 (s, 4H), -2.24 (bs, 2H), 7.54 – 7.58 (m, 4H), 8.27 – 8.30 (m, 4H), 9.10 (d, *J*= 4.2 Hz, 4H), 9.33 (d, *J*= 4.1 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.57 (s, 2F), -137.03 (d, *J*= 20.9 Hz, 8F), -153.25 (m, 4F), -

163.24 (m, 8F); HRMS (ESI-TOF) m/z calcd. for $C_{66}H_{23}F_{22}N_6$ $[M+H]^+$: 1317.1627, found: 1317.1638.

*5,20-Bis(4-chlorophenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (**4e**)*. Purple solid (4 mg, 7%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 573.5(4.672), 714.5(4.041), 896.5(3.794); HRMS (ESI-TOF) m/z calcd. for $C_{66}H_{23}Cl_2F_{20}N_6$ $[M+H]^+$: 1349.1036, found: 1349.1015.

*5,20-Bis(4-bromophenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (**4f**)*. Purple solid (6 mg, 10%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 573.5(4.627), 716.5(3.926), 901(3.548); HRMS (ESI-TOF) m/z calcd. for $C_{66}H_{23}Br_2F_{20}N_6$ $[M+H]^+$: 1437.0026, found: 1436.9979.

*5,20-Bis(4-trifluoromethylphenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26] hexaphyrin (**4g**)*. Purple solid (7 mg, 10%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 571.5(4.301), 718(3.337), 903(3.113); HRMS (ESI-TOF) m/z calcd. for $C_{68}H_{23}F_{26}N_6$ $[M+H]^+$: 1417.1564, found: 1417.1558.

*5,20-Bis(2-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (**4j**)*. Purple solid (10 mg, 17%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 616.5(4.889), 898(3.939), 1050(3.810); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.55 (d, *J*= 3.7 Hz, 2H), 4.92 (t, *J*= 4.6 Hz, 2H), 5.35 (d, *J*= 4.8 Hz, 2H), 7.39 (s, 4H), 7.73 (s, 4H), 8.16 (d, *J*= 4.5 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -136.95 (dd, J_1= 23.7 Hz, J_2= 7.3 Hz, 4F), -137.53 (d, *J*= 24.1 Hz, 4F), -151.59 (t, *J*= 20.7 Hz, 4F), -160.68 (td, J_1= 22.3 Hz, J_2= 7.8 Hz, 4F), -160.88 (td, J_1= 22.5 Hz, J_2= 7.8 Hz, 4F); HRMS (ESI-TOF) m/z calcd. for $C_{62}H_{21}F_{20}N_6S_2$ $[M+H]^+$: 1293.0944, found: 1293.0939. Data is convenient with the literature [1] findings.

*5,10-Bis(4-trifluoromethylphenyl)tripyrromethane (**5**)*. Black solid (800 mg, 20%); R_f = 0.13 (1:6, EtOAc:hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 5.43 (s, 2H), 5.74 (d, *J*= 2.6 Hz, 2H), 5.85 (s, 2H), 6.13 – 6.16 (m, 2H), 6.71 (s, 2H), 7.29 (d, *J*= 8.2 Hz, 4H), 7.56 (d, *J*= 8.2 Hz, 4H), 7.81 (bs, 1H), 7.96 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 43.9, 107.6, 107.9, 108.6, 117.7, 124.1 (q, *J*= 273 Hz), 125.6 (q, *J*= 3.7 Hz), 128.7, 129.4 (q, *J*= 30.9 Hz), 131.3, 131.8, 146.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm: -62.18 (s, 6F); HRMS (ESI): *m/z* for $C_{28}H_{20}F_6N_3$ $[M-H]^-$ calcd: 512.1567; found: 512.1547.

*5,10,15-Tris(4-trifluoromethylphenyl)-20-(2,6-dichlorophenyl)porphyrin (**6a**)*. Purple solid (9 mg, 13%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 418(5.503), 513(4.099), 543(3.686); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.76 (s, 2H), 7.73 – 7.77 (m, 1H), 7.82 – 7.84 (m, 2H), 8.04 (d, *J*= 7.8 Hz, 6H), 8.32 – 8.37 (m, 6H), 8.72 (d, *J*= 4.6 Hz, 2H), 8.79 (s, 4H), 8.82 (d, *J*= 4.4 Hz, 2H);

^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.01 (s, 9F); HRMS (ESI-TOF) m/z calcd. for $C_{47}H_{26}Cl_2F_9N_4$ $[M+H]^+$: 887.1385, found: 887.1354.

5,10,15-Tris(4-trifluoromethylphenyl)-20-(4-fluorophenyl)porphyrin ***(6b)***. Purple solid (17.0 mg, 28%), UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 416.0 (5.809), 512.5 (4.577), 547.0 (4.210), 588.0 (4.102), 644.0 (3.821); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.82 (s, 2H), 7.48 – 7.52 (m, 2H), 8.07 (d, *J*= 7.9 Hz, 6H), 8.17 – 8.20 (m, 2H), 8.37 (d, *J*= 7.6 Hz, 6H), 8.83 (s, 6H), 8.88 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.01 (s, 9F), -114.27 (d, *J*= 47.1 Hz, 1F); HRMS (ESI-TOF) m/z calcd. for $C_{47}H_{27}F_{10}N_4$ $[M+H]^+$: 837.2071, found: 837.2070.

5,10,15-Tris(4-trifluoromethylphenyl)-20-(4-bromophenyl)porphyrin ***(6c)***. Purple solid (10.0 mg, 15%), UV–vis ($CHCl_3$): λ_{max}[nm] (logε)= 418.5 (5.375), 513.0 (4.076), 546.0 (3.602), 592.0 (3.329), 645.0 (3.176); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.92 (s, 2H), 7.84 (d, *J*= 8.0 Hz, 2H), 7.97 – 8.02 (m, 8H), 8.35 (d, *J*= 7.7 Hz, 6H), 8.73 (s, 6H), 8.79 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.02 (s, 9F); HRMS (ESI-TOF) m/z calcd. for $C_{47}H_{27}BrF_9N_4$ $[M+H]^+$: 897.1270, found: 897.1270.

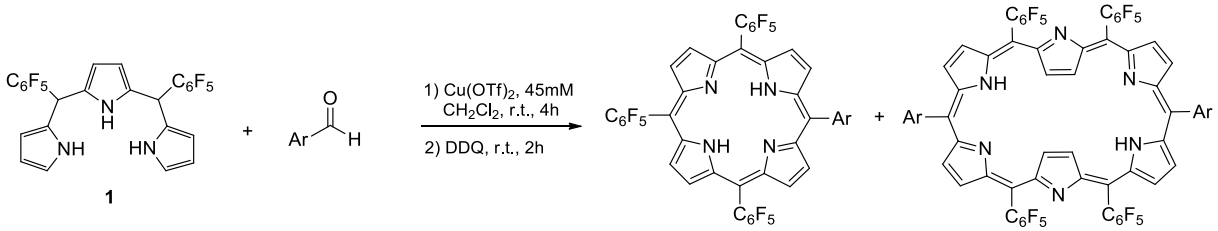
5,10,15-Tris(4-trifluoromethylphenyl)-20-(4-methoxyphenyl)porphyrin ***(6d)***. Purple solid (13 mg, 21%); UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 418.0 (5.395), 514.5 (4.039), 549.0 (3.560), 589.0 (3.664), 645.0 (3.197); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.90 (s, 2H), 4.03 (s, 3H), 7.23 (d, *J*= 8.4 Hz, 2H), 7.96 (d, *J*= 7.7 Hz, 6H), 8.05 (d, *J*= 8.4 Hz, 2H), 8.26 (d, *J*= 7.7 Hz, 6H), 8.72 (s, 6H), 8.85 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.01 (s, 9F); HRMS (ESI-TOF) m/z calcd. for $C_{48}H_{30}F_9N_4O$ $[M+H]^+$: 849.2270, found: 849.2238.

5,10,15-Tris(4-trifluoromethylphenyl)-20-(4-hydroxyphenyl)porphyrin ***(6e)***. Purple solid (7.5 mg, 12%); UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 418.0 (5.744), 514.0 (4.428), 549.0 (4.067), 589.0 (3.949), 645.0 (3.768); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.82 (s, 2H), 8.03 – 8.09 (m, 10H), 8.34 (d, *J*= 7.8 Hz, 6H), 8.80 (s, 6H), 8.93 (d, *J*= 4.5 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.00 (s, 9F); HRMS (ESI-TOF) m/z calcd. for $C_{47}H_{28}F_9N_4O$ $[M+H]^+$: 835.2119, found: 835.2098.

5,10,15-Tris(4-trifluoromethylphenyl)-20-(pentafluorophenyl)porphyrin ***(6f)***. Purple solid (8 mg, 12%); UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 414.5 (5.450), 510.5 (4.204), 543.0 (3.715), 587.0 (3.742), 642.0 (3.314); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.84 (s, 2H), 8.07 (d, *J*= 7.6 Hz, 6H), 8.35 (d, *J*= 7.3 Hz, 6H), 8.81 (s, 6H), 8.89 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.05 (d, *J*= 8.1 Hz, 9F), -136.85 (m, 2F), -151.74 (m, 1F), -161.64 (m, 2F); HRMS (ESI-TOF) m/z calcd. for $C_{47}H_{23}F_{14}N_4$ $[M+H]^+$: 909.1694, found: 909.1698.

*5,15-Bis(4-trifluoromethylphenyl)-10,20-bis(4-methoxyphenyl)porphyrin (**7d**)*. Purple solid (6 mg, 10%); UV–vis (CH_2Cl_2): λ_{max}[nm] (logε)= 419.5 (5.431), 516.0 (4.091), 552.0 (3.814), 592.0 (3.623), 647.0 (3.504); ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.77 (s, 2H), 4.13 (s, 6H), 7.33 (d, *J*= 8.2 Hz, 4H), 8.06 (d, *J*= 7.8 Hz, 4H), 8.15 (d, *J*= 8.2 Hz, 4H), 8.37 (d, *J*= 7.6 Hz, 4H), 8.81 (s, 4H), 8.93 (s, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -61.99 (s, 6F); HRMS (ESI-TOF) m/z calcd. for $C_{48}H_{33}F_6N_4O_2$ $[M+H]^+$: 811.2502, found: 811.2486.

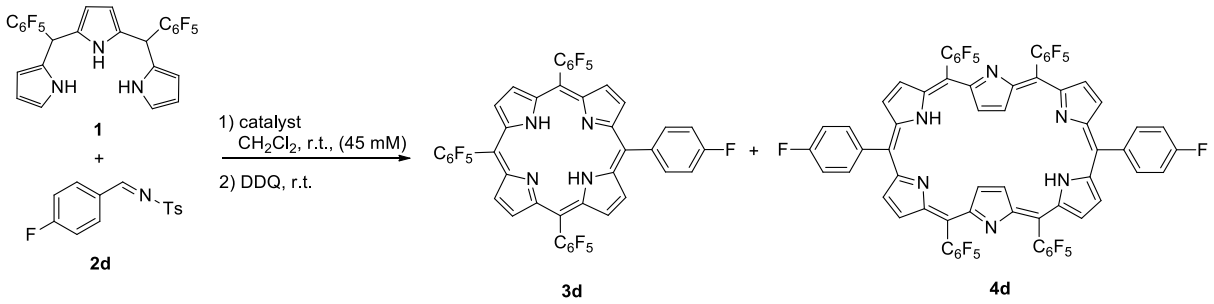
2. Table S1. Reaction of tripyrrane 1 and aldehydes



Entry	Aldehyde	Ar	Yield[a] (%) **3a–h,j,k**	Yield[a] (%) **4a–g,j**
1	**a**	C_6H_5	5	7
2	**b**	$2,4,6(CH_3)_3C_6H_2$	10	11
3	**c**	$2,6\text{-}Cl_2\text{-}C_6H_3$	9	9
4	**d**	$4\text{-}FC_6H_4$	8	20
5	**e**	$4\text{-}ClC_6H_4$	10	12
6	**f**	$4\text{-}BrC_6H_4$	11	12
7	**g**	$4\text{-}CF_3C_6H_4$	9	10
8	**h**	$4\text{-}(OCH_3)C_6H_4$	11	-
9	**i**	$4\text{-}(OH)C_6H_4$	-	-
10	**j**	2-Thiophenyl	13	10
11	**k**	3-Indolyl	13	-

[a] isolated yields after flash column chromatography

3. Table S2. Catalyst effect on the product formation of reaction of 1 and 2d



Entry	Catalyst	% Yield 3d	% Yield 4d
1	$Zn(OTf)_2$	8	10
2	$Gd(OTf)_3$	trace	trace
3	$Yb(OTf)_3$	10	13

4. NMR spectra

Peaks between 0.5–2 ppm in ^{1}H NMR spectra are due to solvent residue [2].

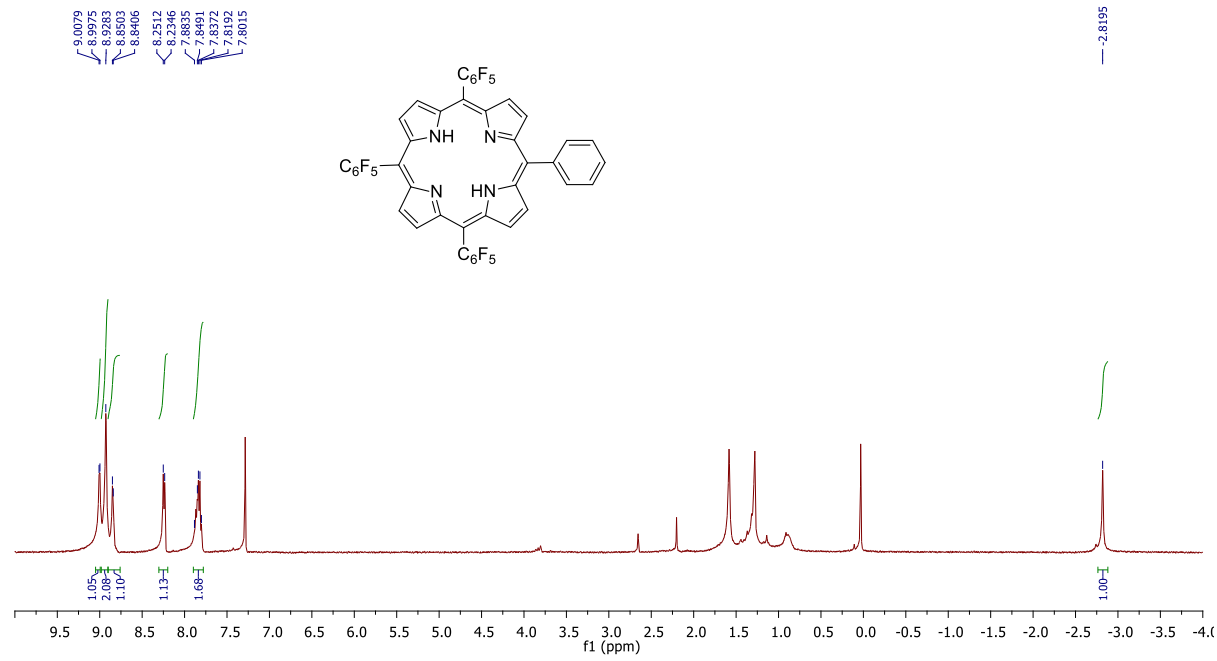


Figure S1. ^{1}H NMR of 3a ($CDCl_3$)

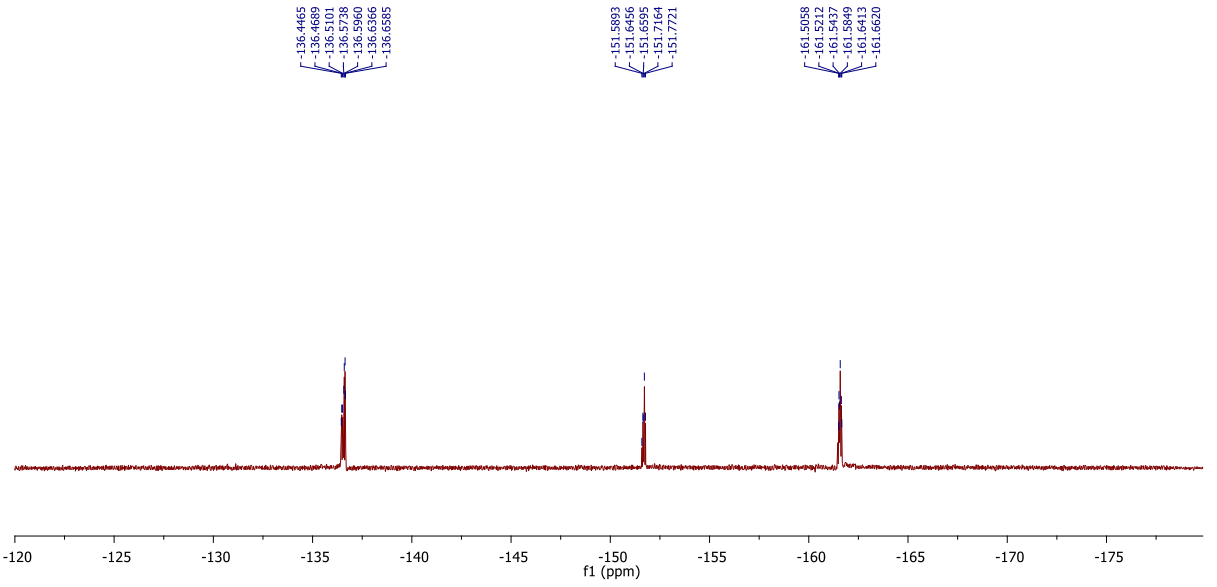


Figure S2. ^{19}F NMR of 3a ($CDCl_3$)

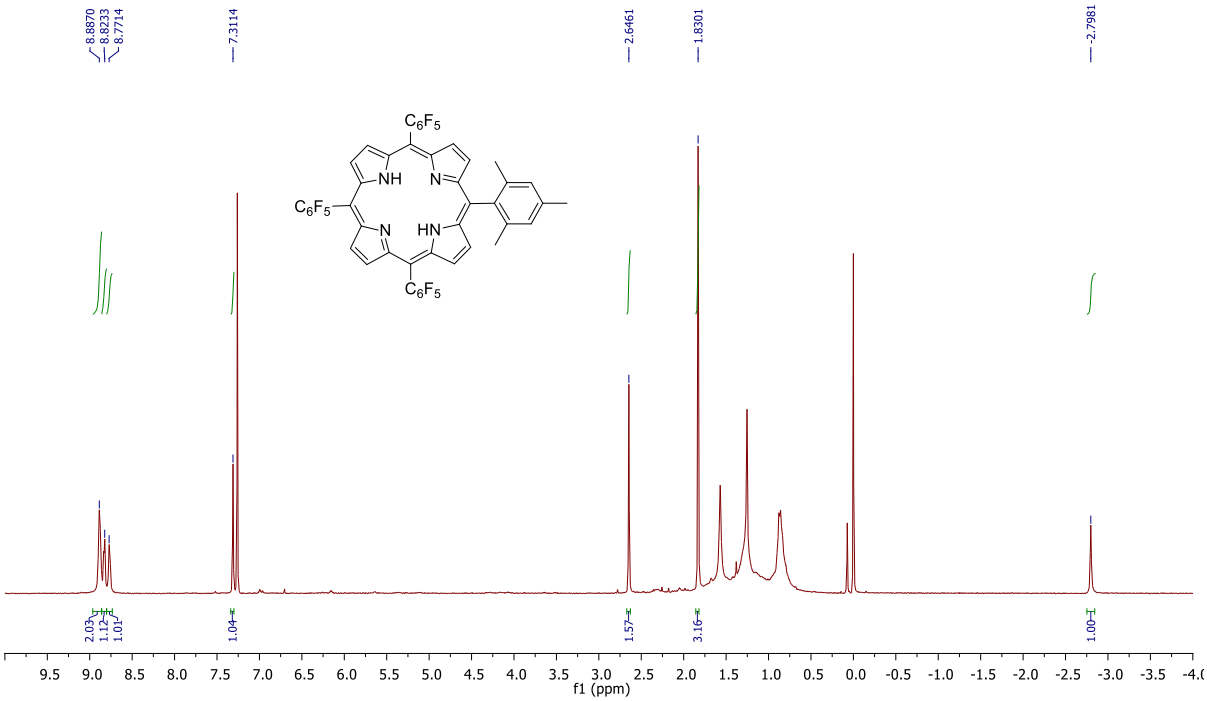


Figure S3. ^{1}H NMR of 3b ($CDCl_3$)

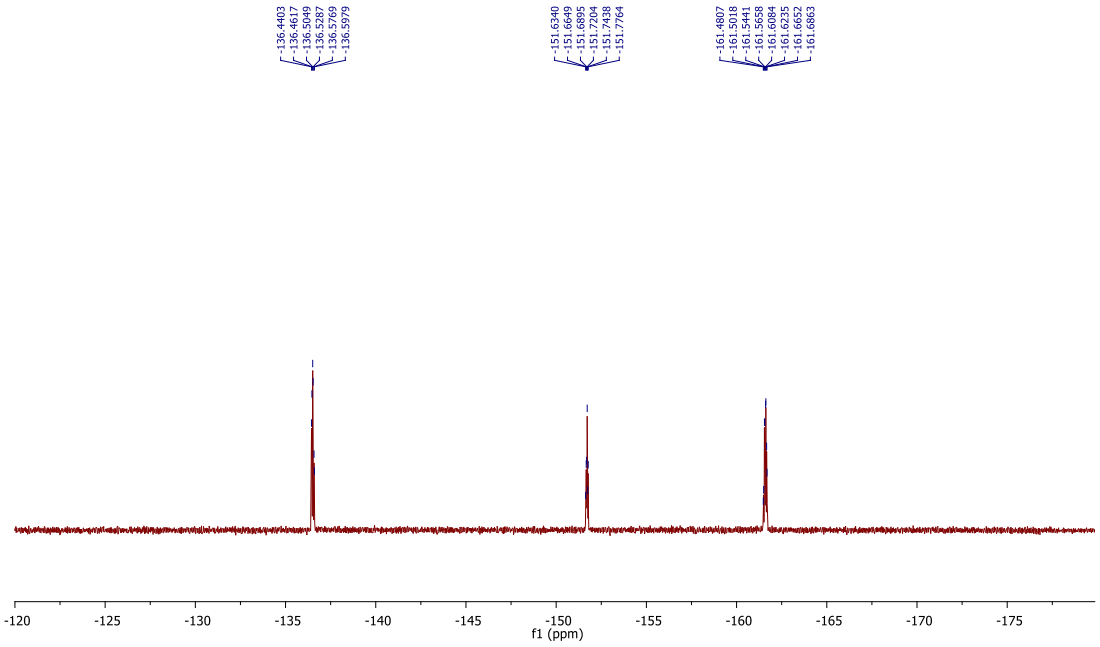


Figure S4. ^{19}F NMR of 3b ($CDCl_3$)

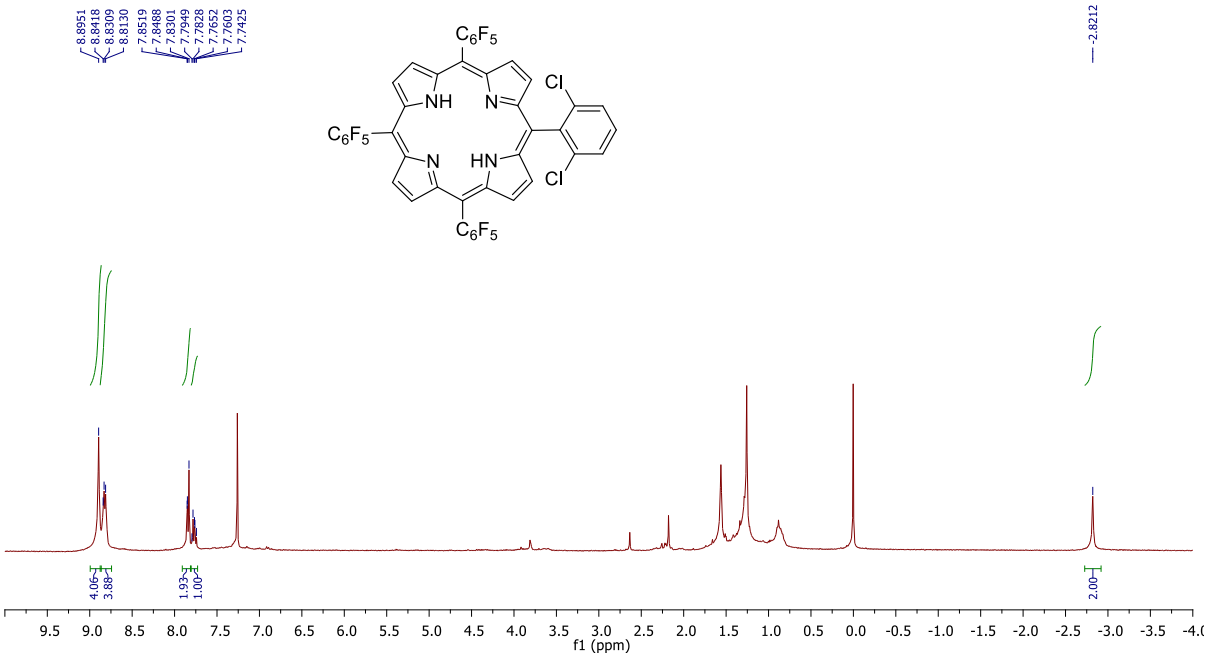


Figure S5. ^{1}H NMR of 3c ($CDCl_3$)

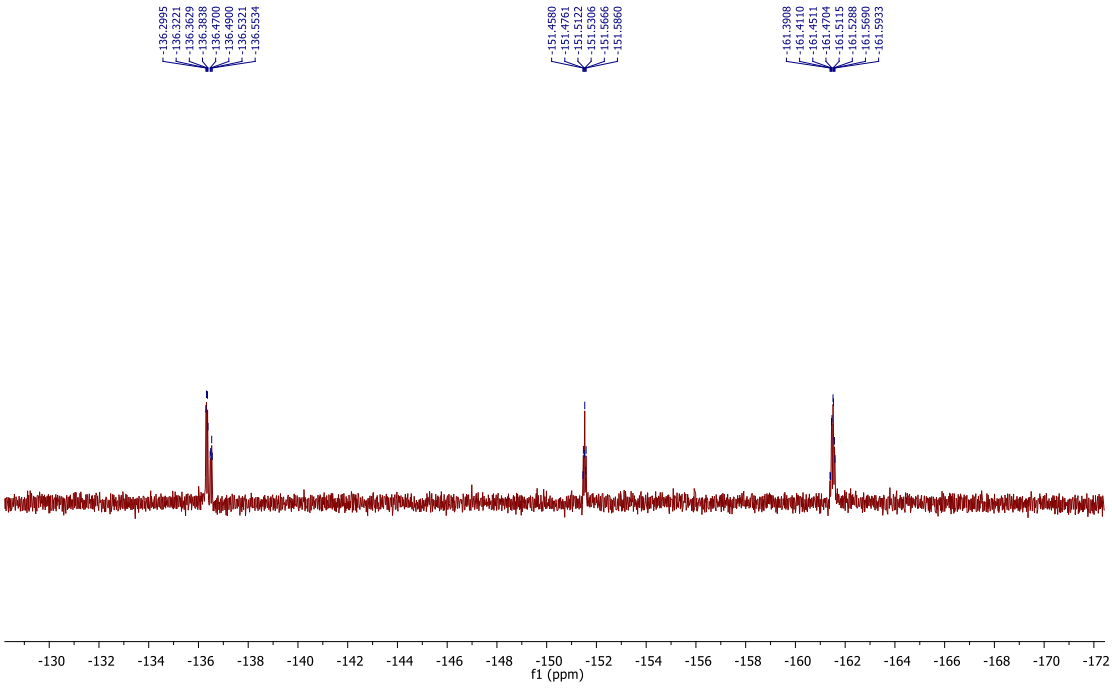


Figure S6. ^{19}F NMR of 3c ($CDCl_3$)

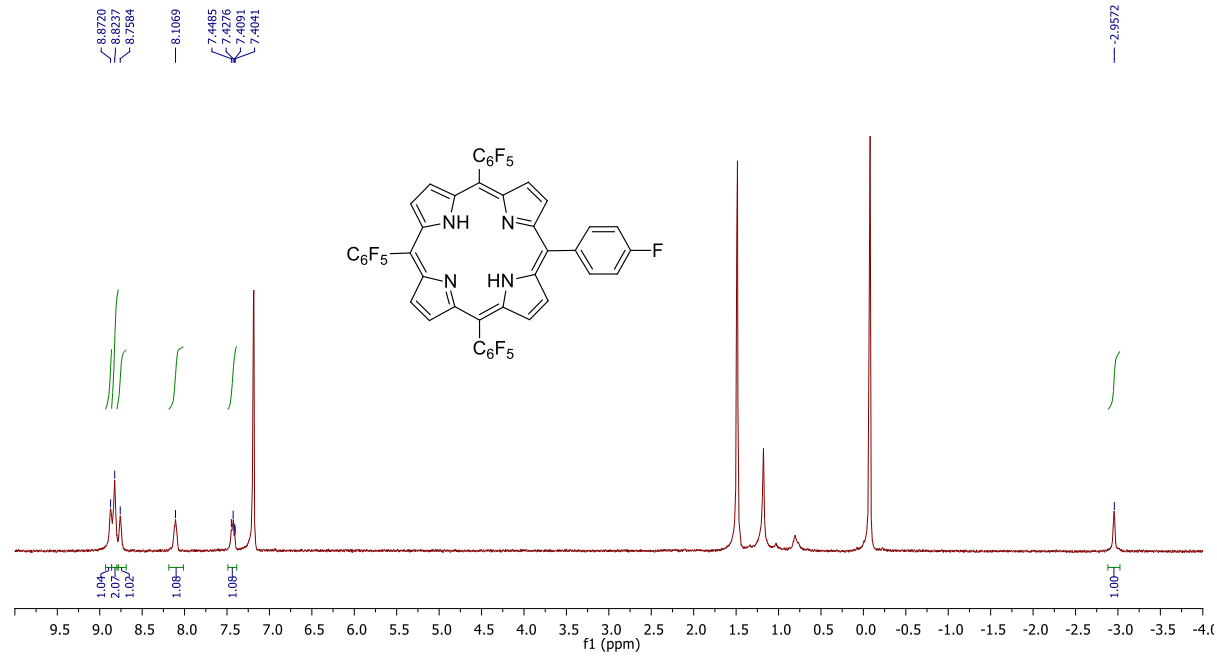


Figure S7. ^{1}H NMR of 3d ($CDCl_3$)

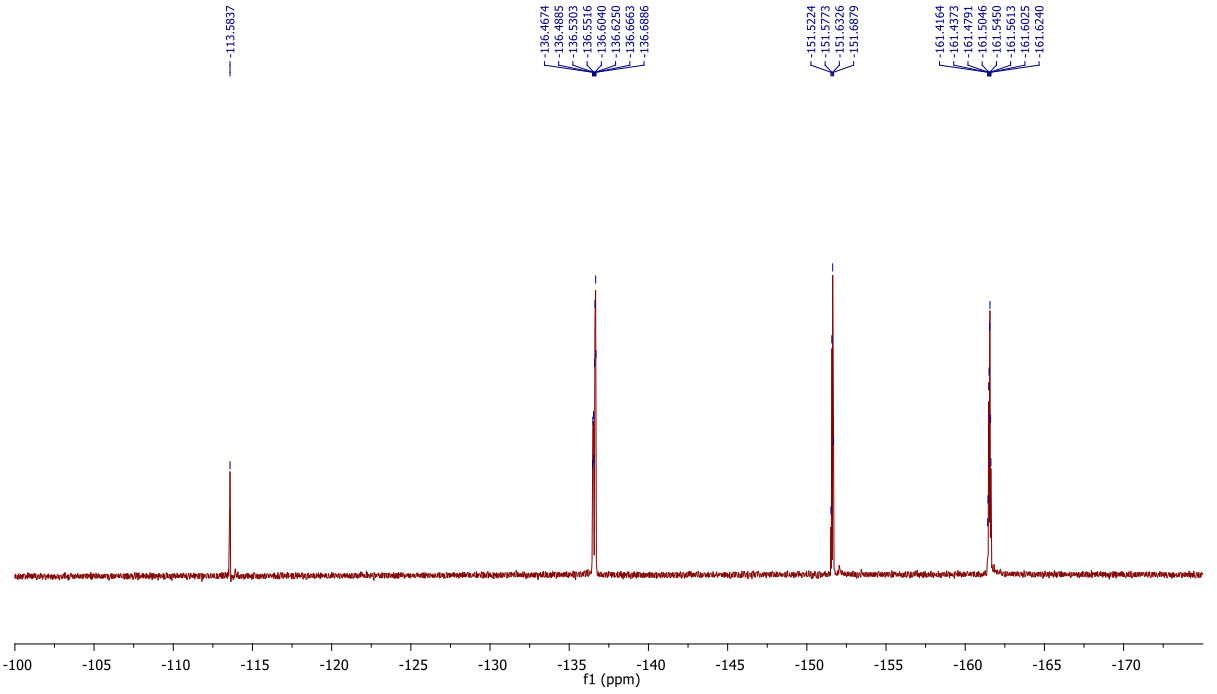


Figure S8. ^{19}F NMR of 3d ($CDCl_3$)

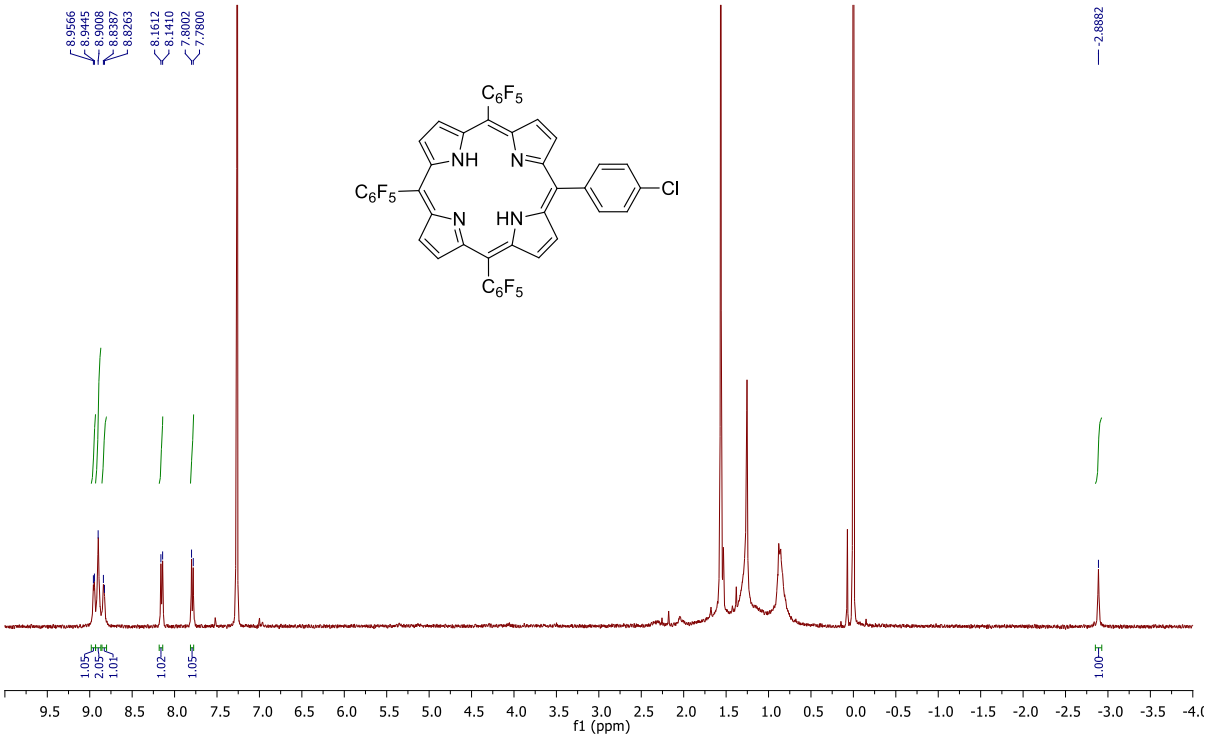


Figure S9. ^{1}H NMR of 3e ($CDCl_3$)

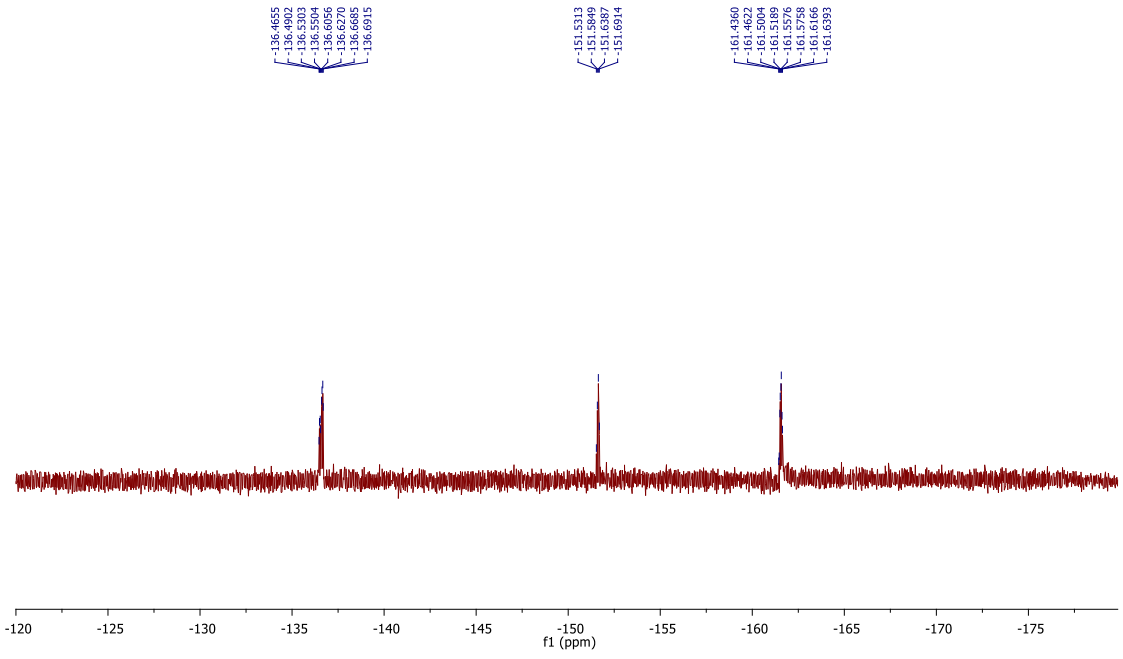


Figure S10. ^{19}F NMR of 3e ($CDCl_3$)

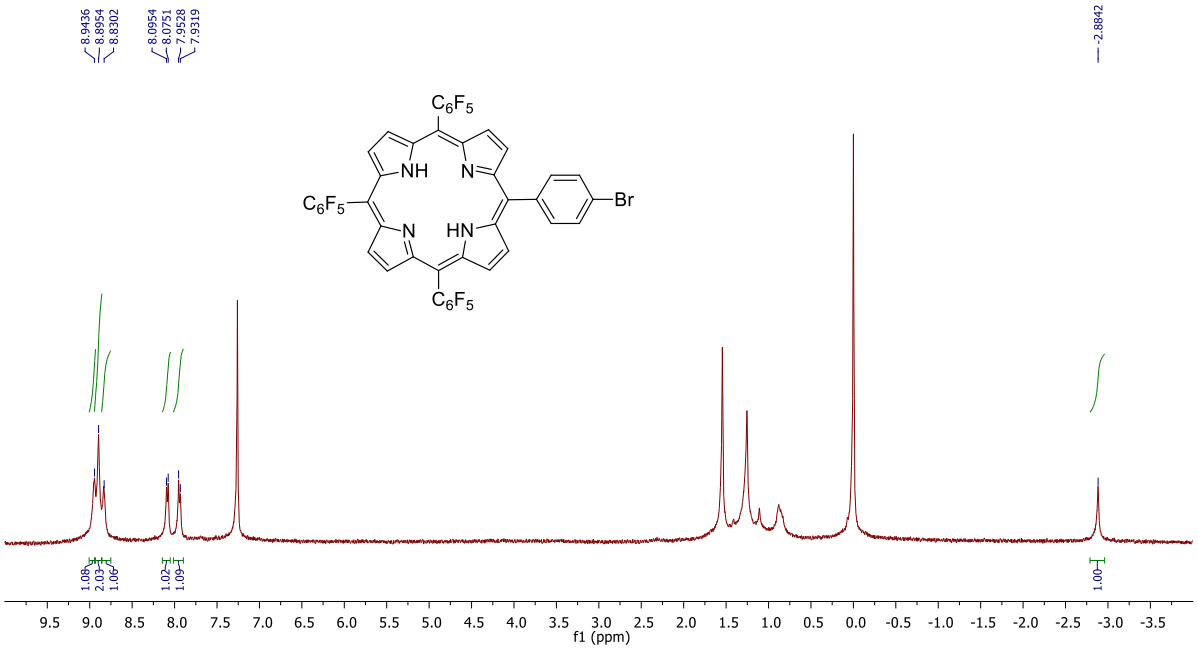


Figure S11. ^{1}H NMR of 3f ($CDCl_3$)

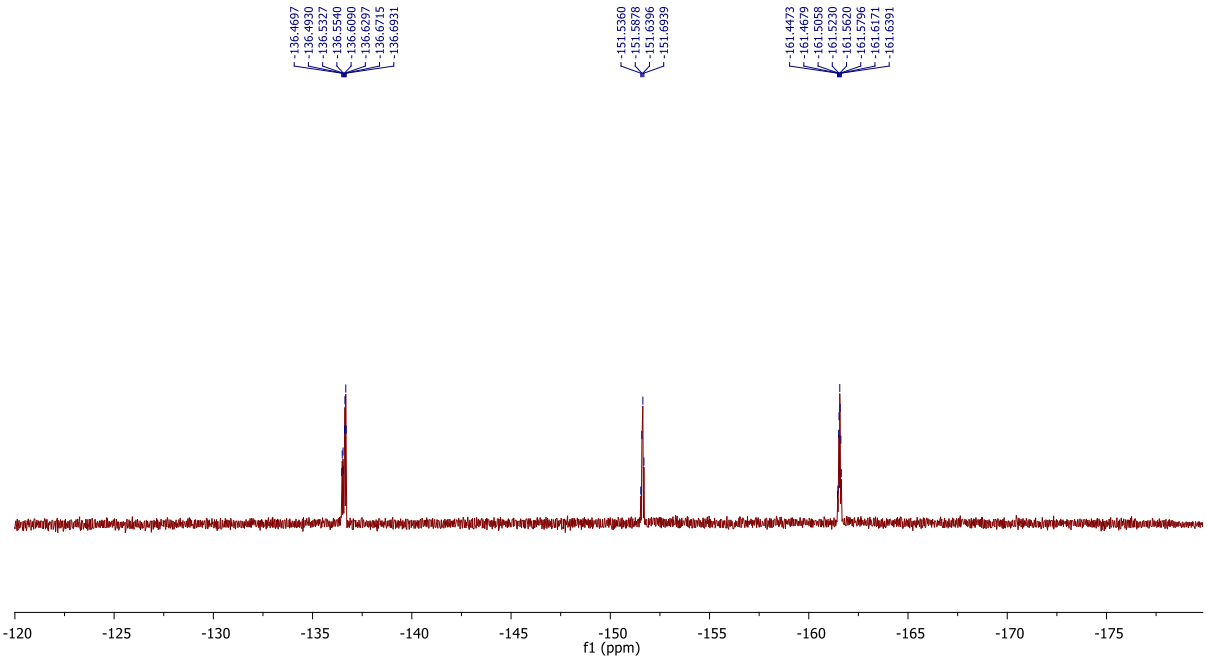


Figure S12. ^{19}F NMR of 3f ($CDCl_3$)

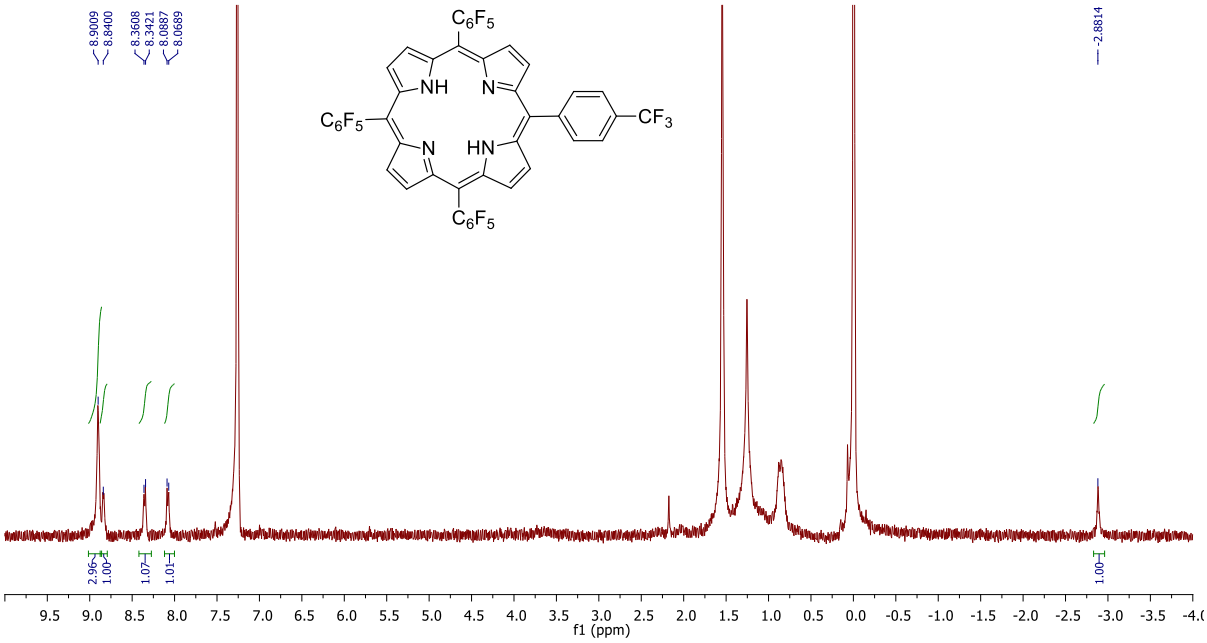


Figure S13. ^{1}H NMR of 3g ($CDCl_3$)

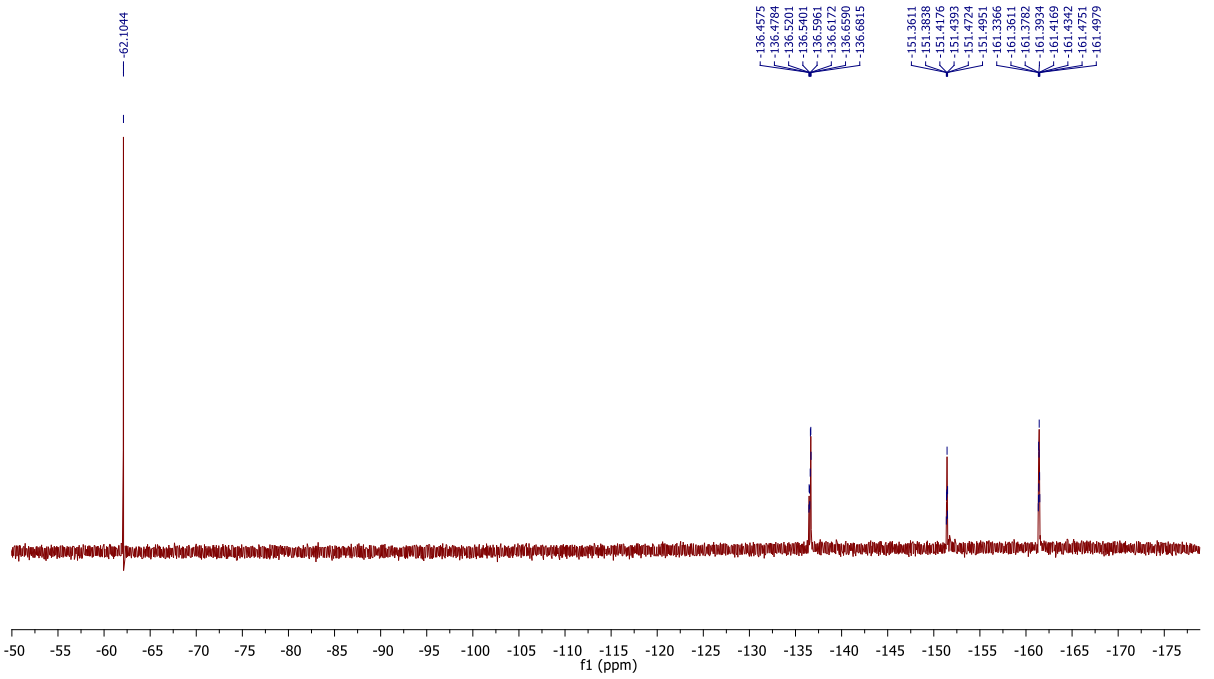


Figure S14. ^{19}F NMR of 3g ($CDCl_3$)

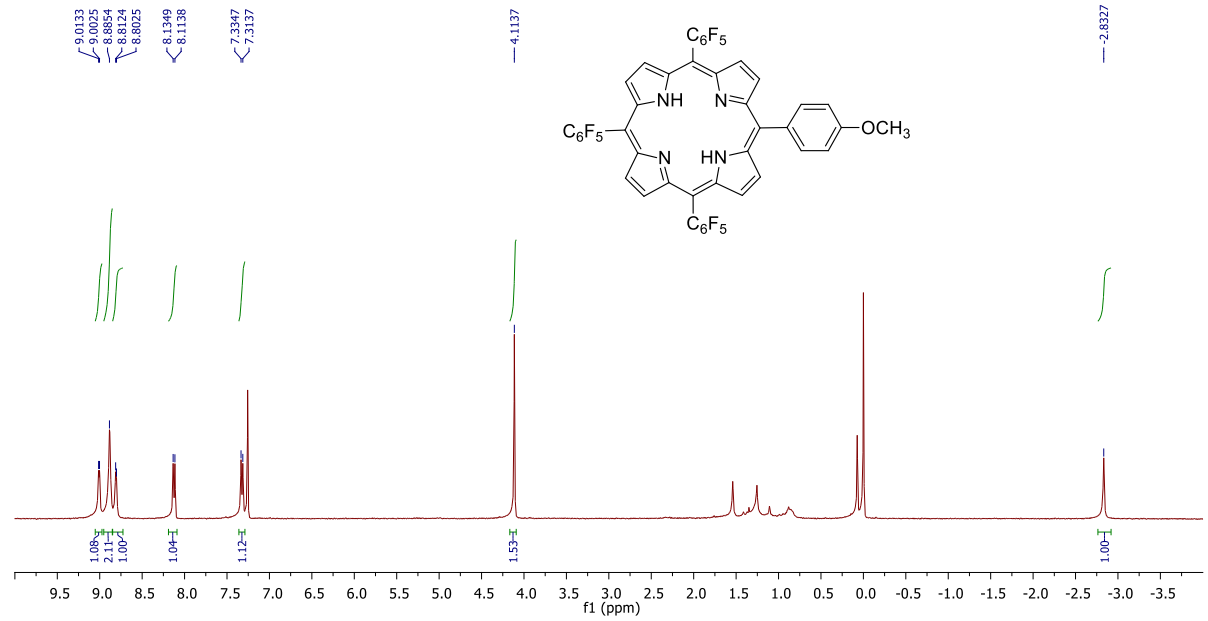


Figure S15. ^{1}H NMR of 3h ($CDCl_3$)

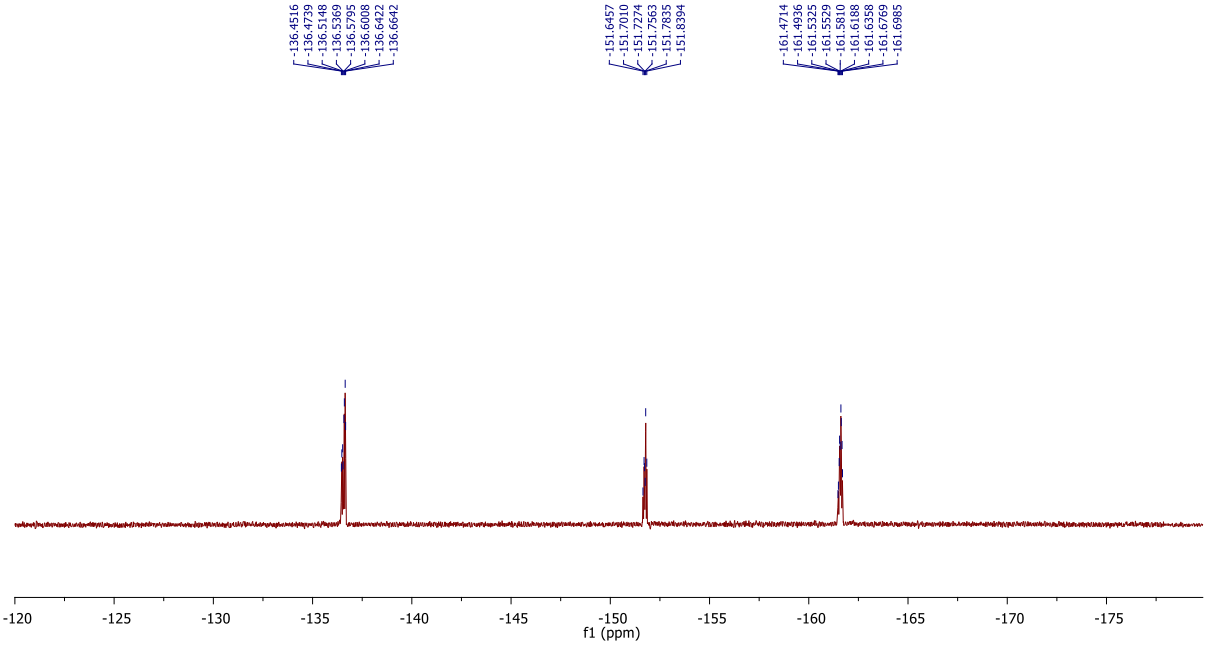


Figure S16. ^{19}F NMR of 3h ($CDCl_3$)

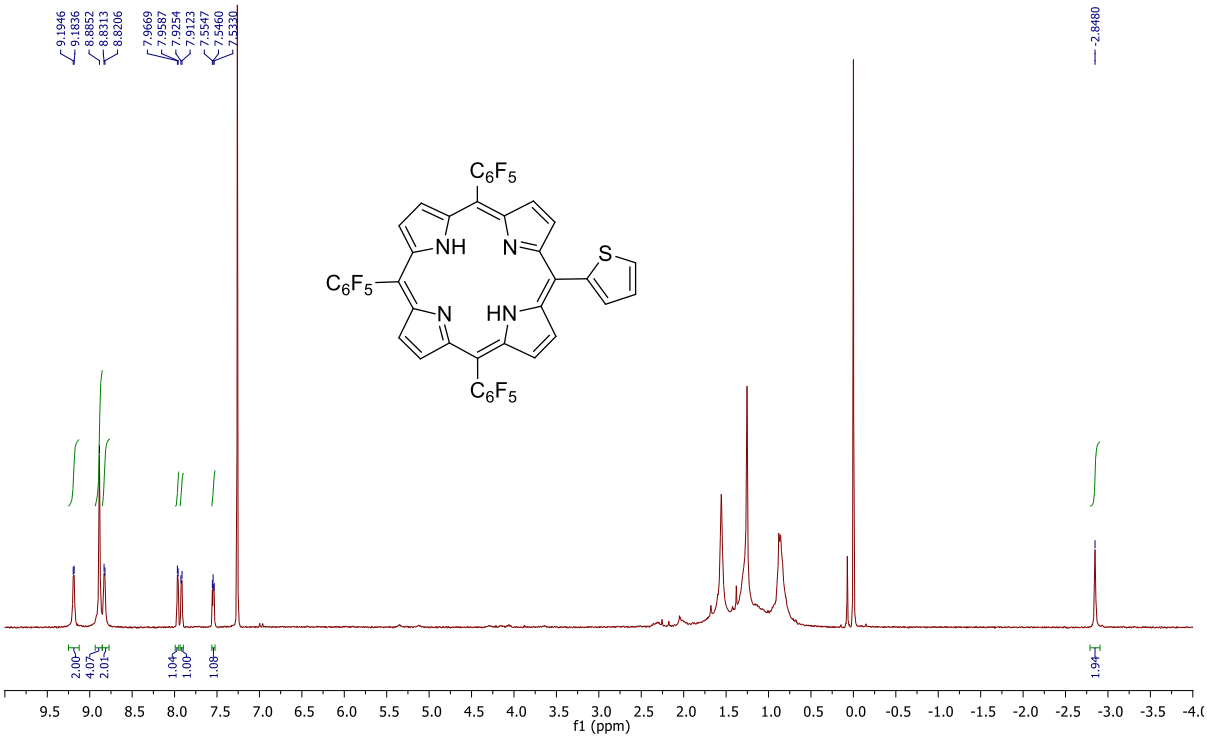


Figure S17. ^{1}H NMR of 3j ($CDCl_3$)

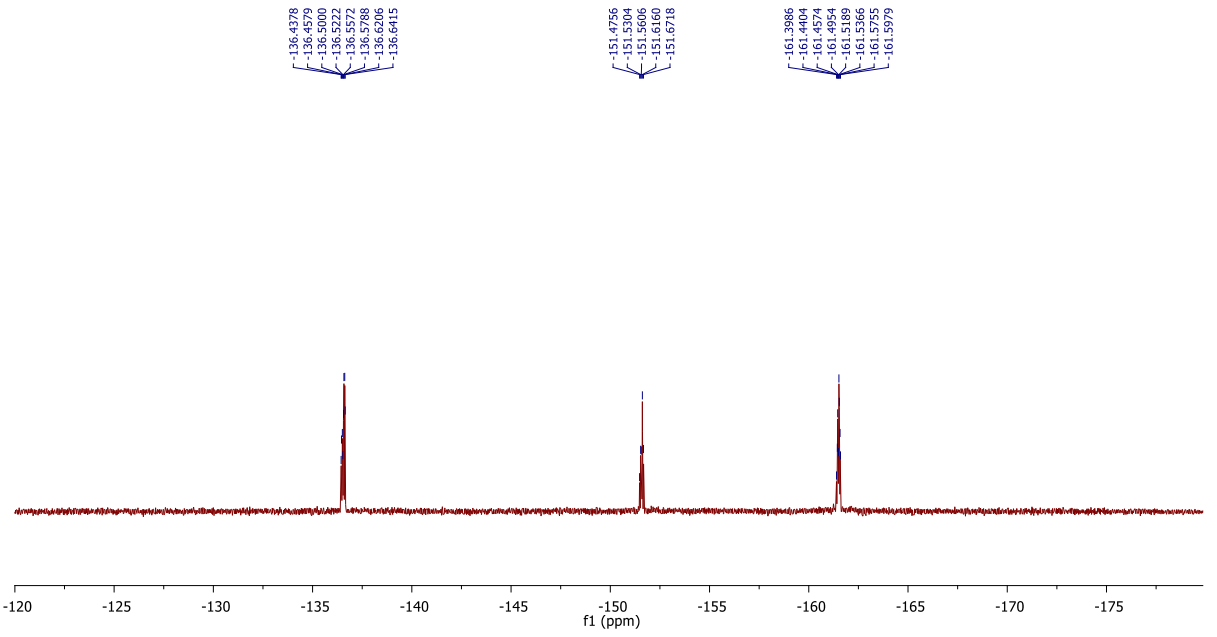


Figure S18. ^{19}F NMR of 3j ($CDCl_3$)

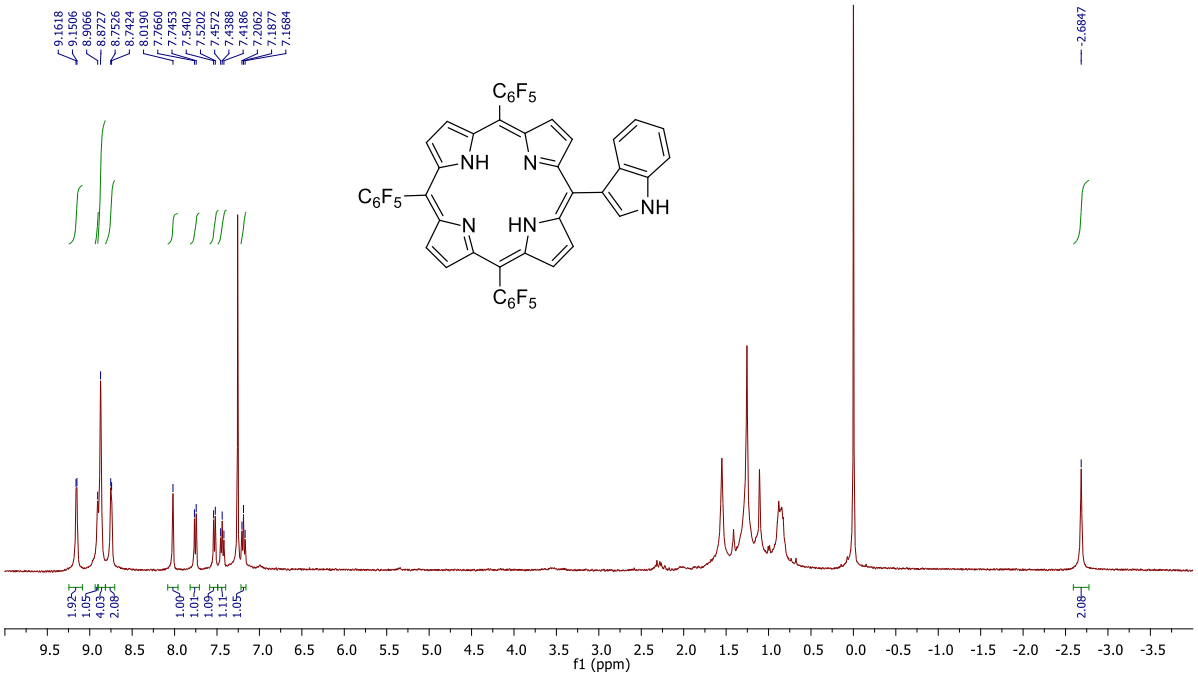


Figure S19. ^{1}H NMR of 3k ($CDCl_3$)

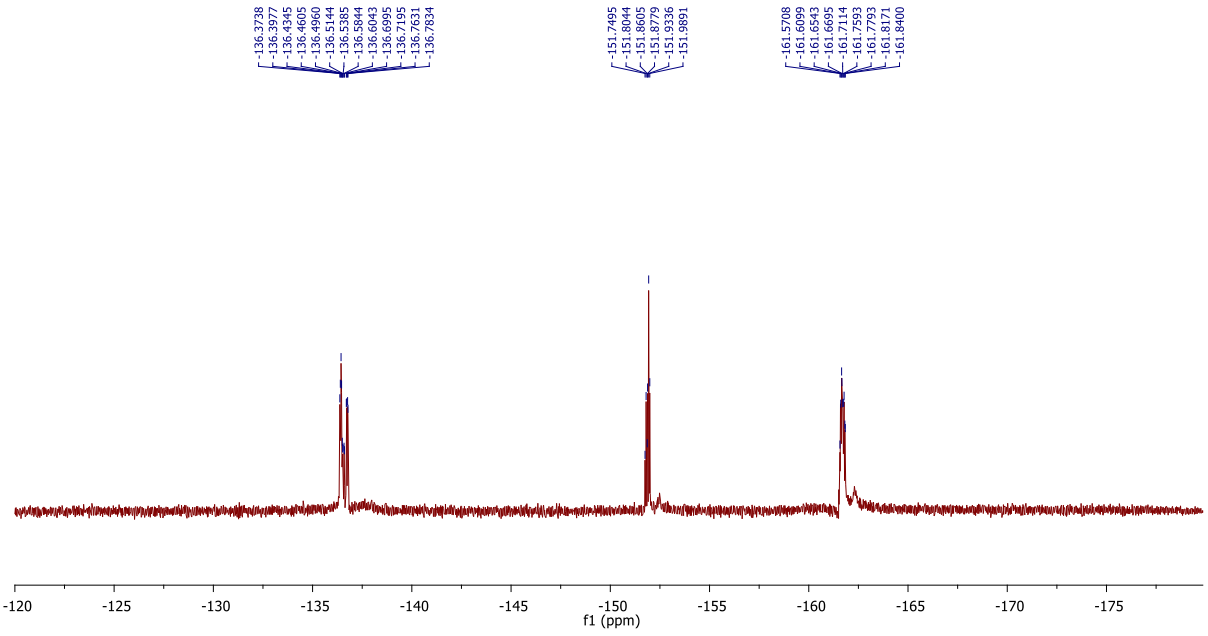


Figure S20. ^{19}F NMR of 3k ($CDCl_3$)

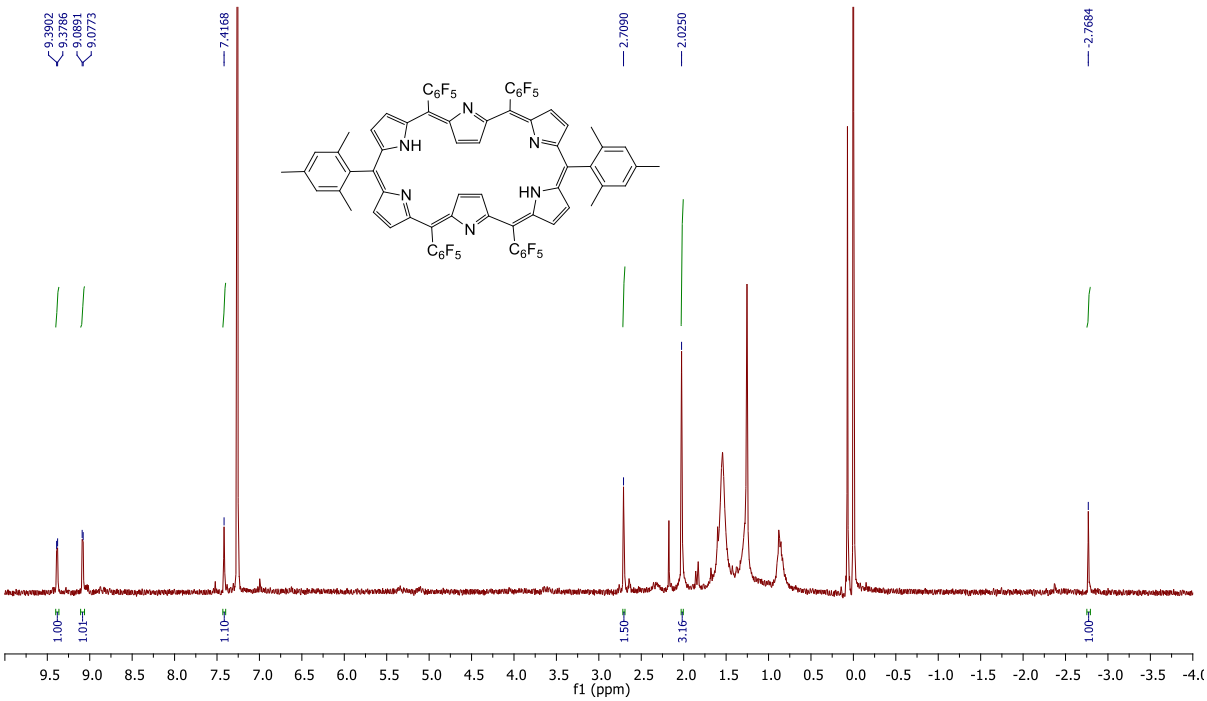


Figure S21. ^{1}H NMR of 4b ($CDCl_3$)

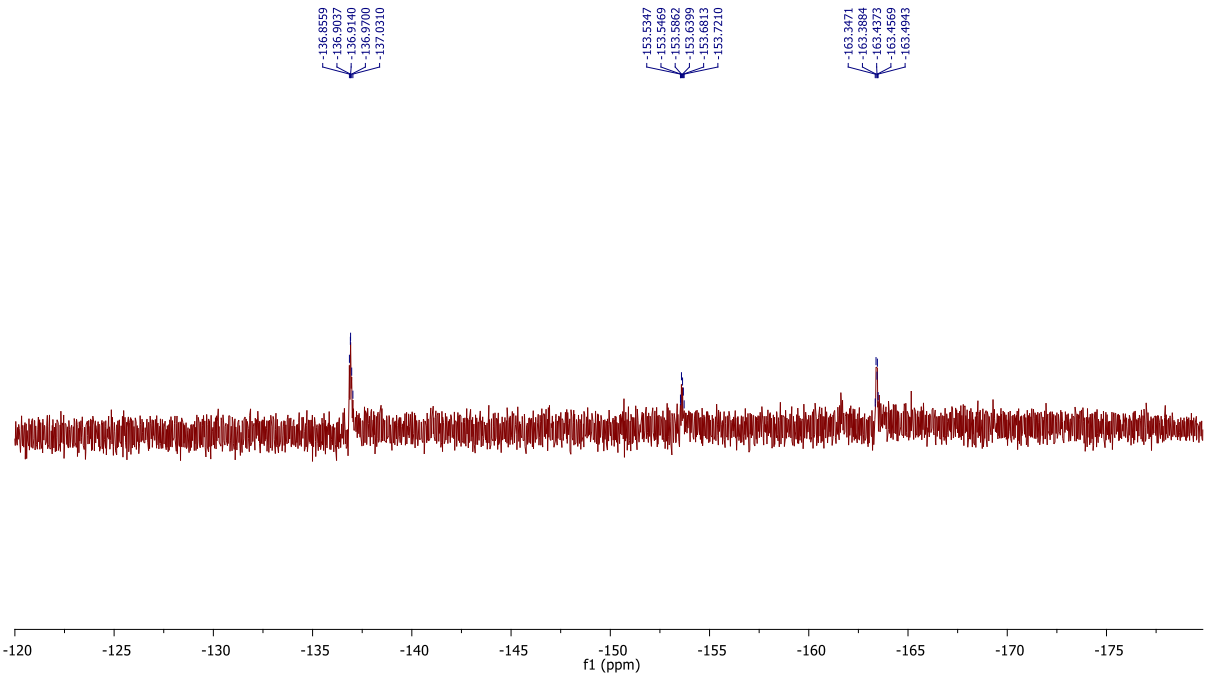


Figure S22. ^{19}F NMR of 4b ($CDCl_3$)

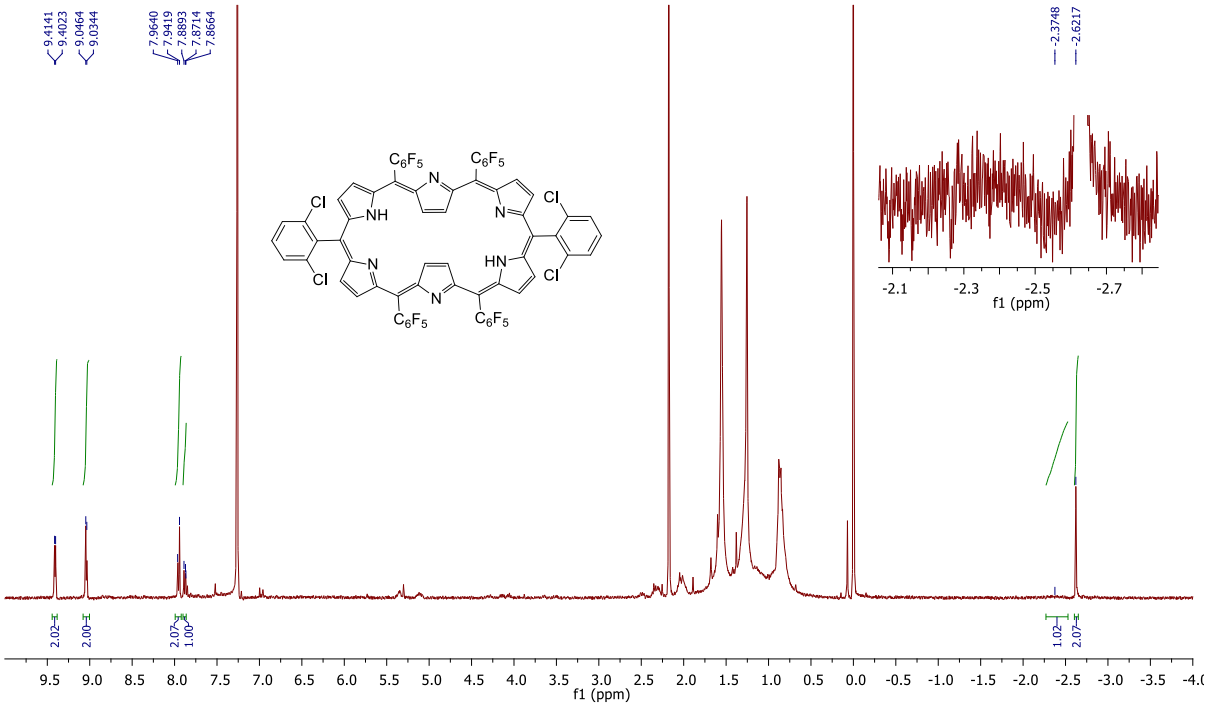


Figure S23. ^{1}H NMR of 4c ($CDCl_3$)

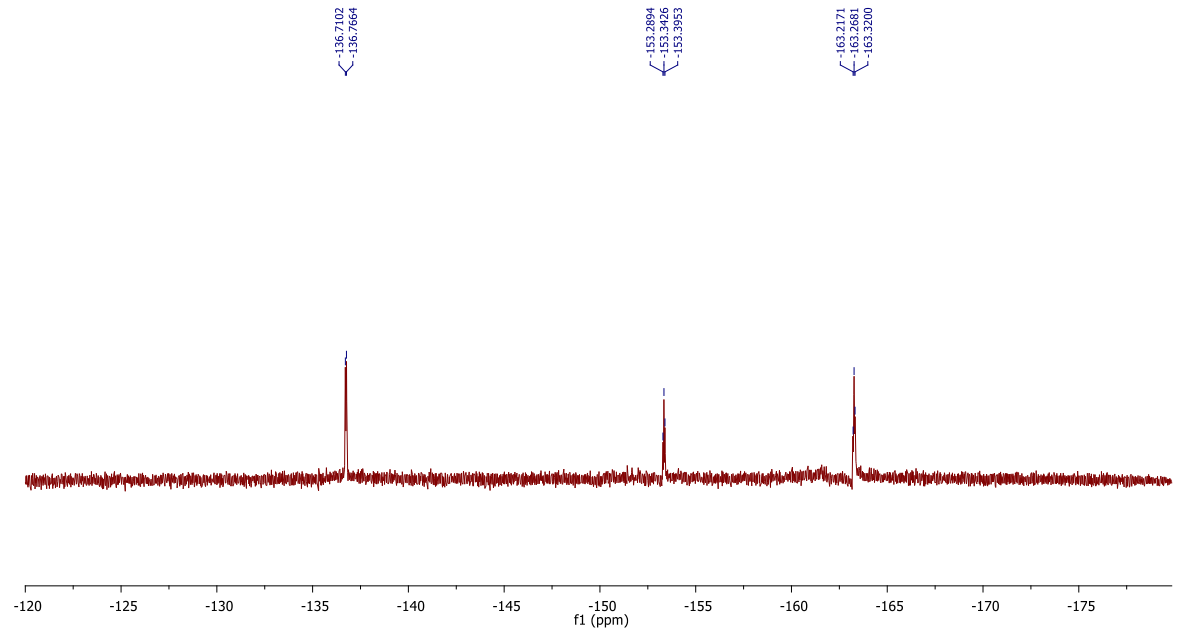


Figure S24. ^{19}F NMR of 4c ($CDCl_3$)

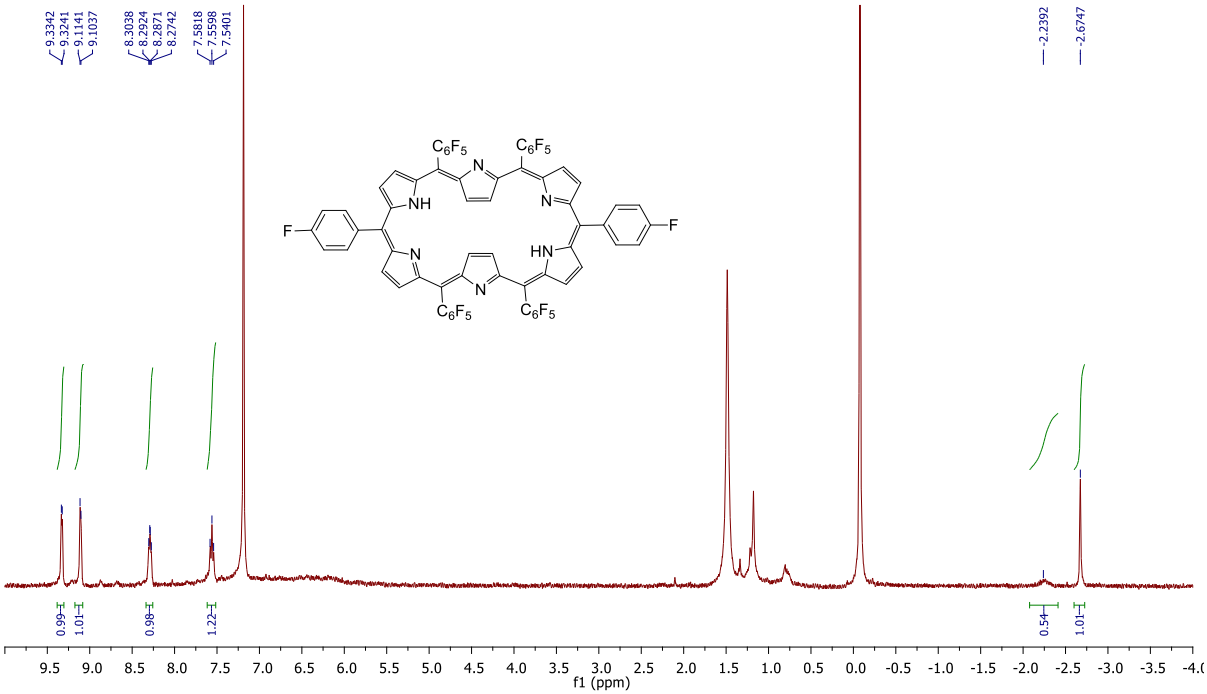


Figure S25. ^{1}H NMR of 4d ($CDCl_3$)

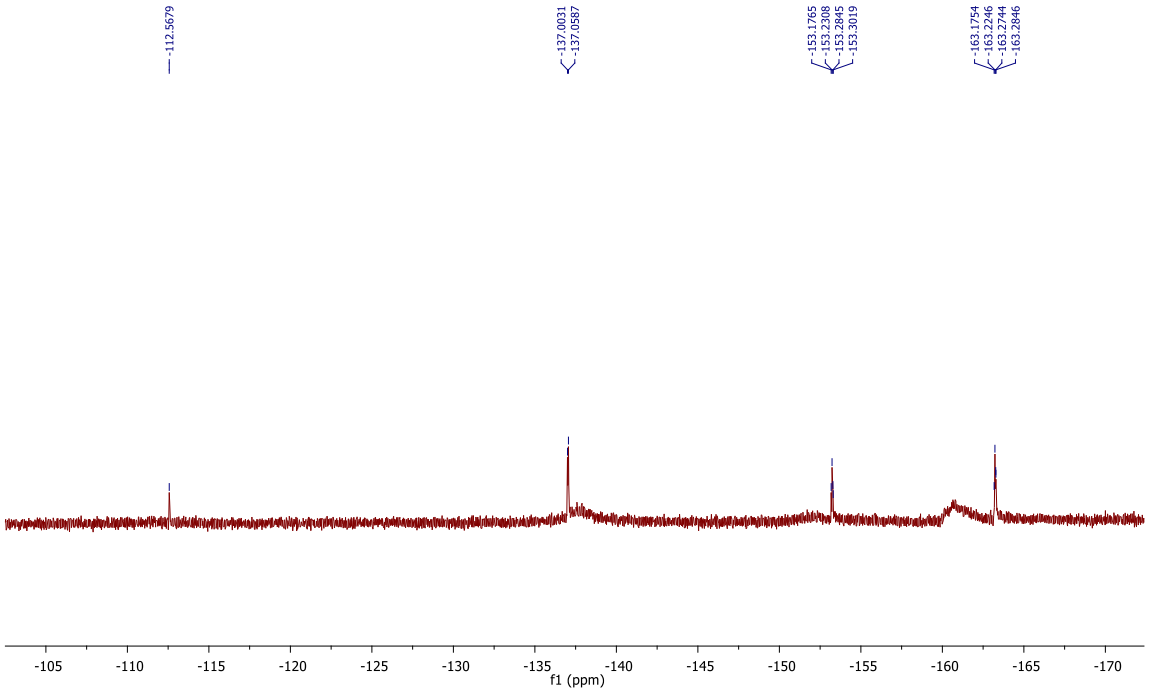


Figure S26. ^{19}F NMR of 4d ($CDCl_3$)

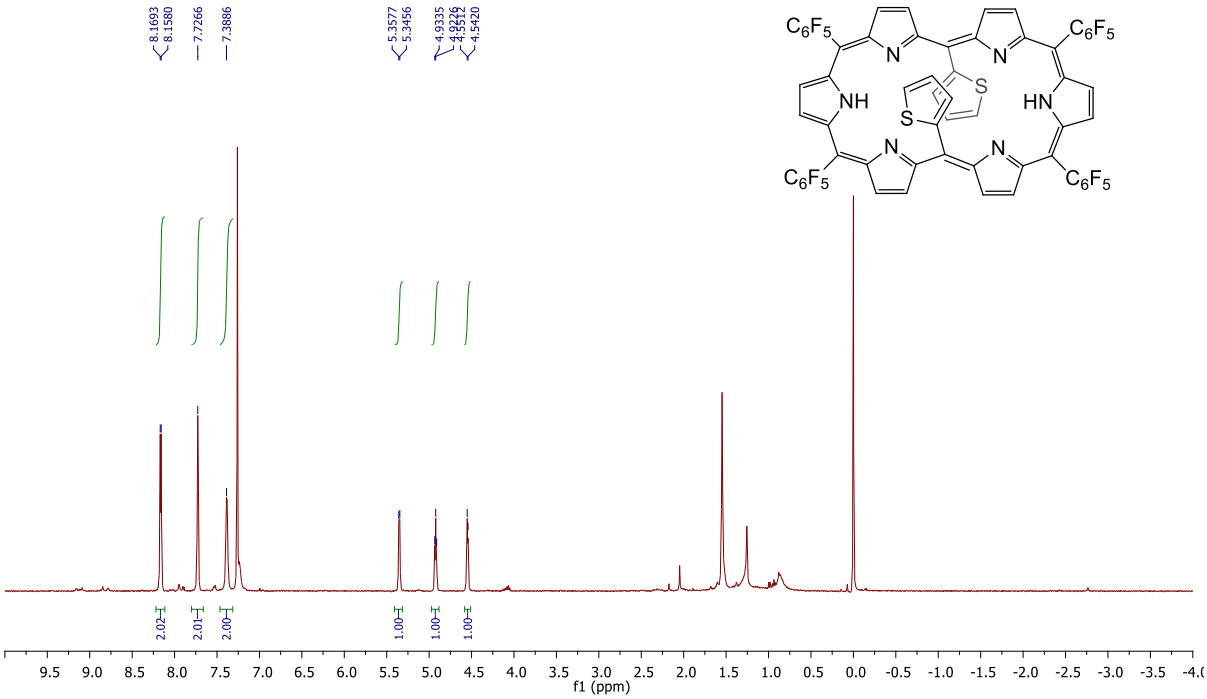


Figure S27. ^{1}H NMR of 4j ($CDCl_3$)

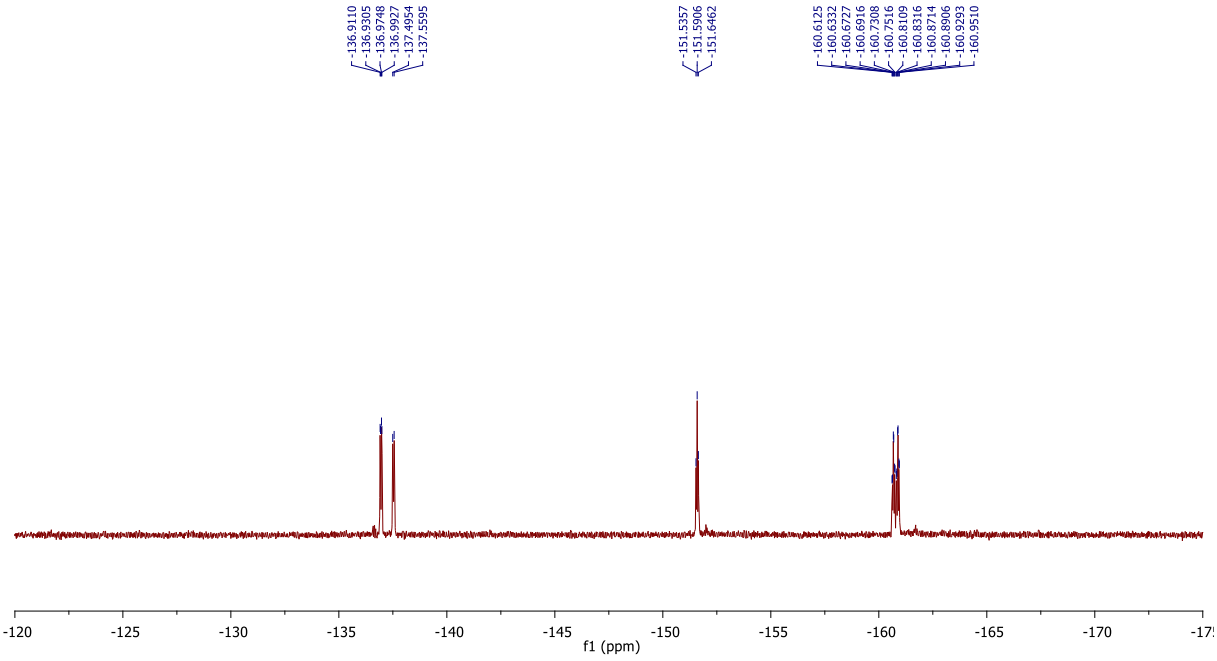


Figure S28. ^{19}F NMR of 4j ($CDCl_3$)

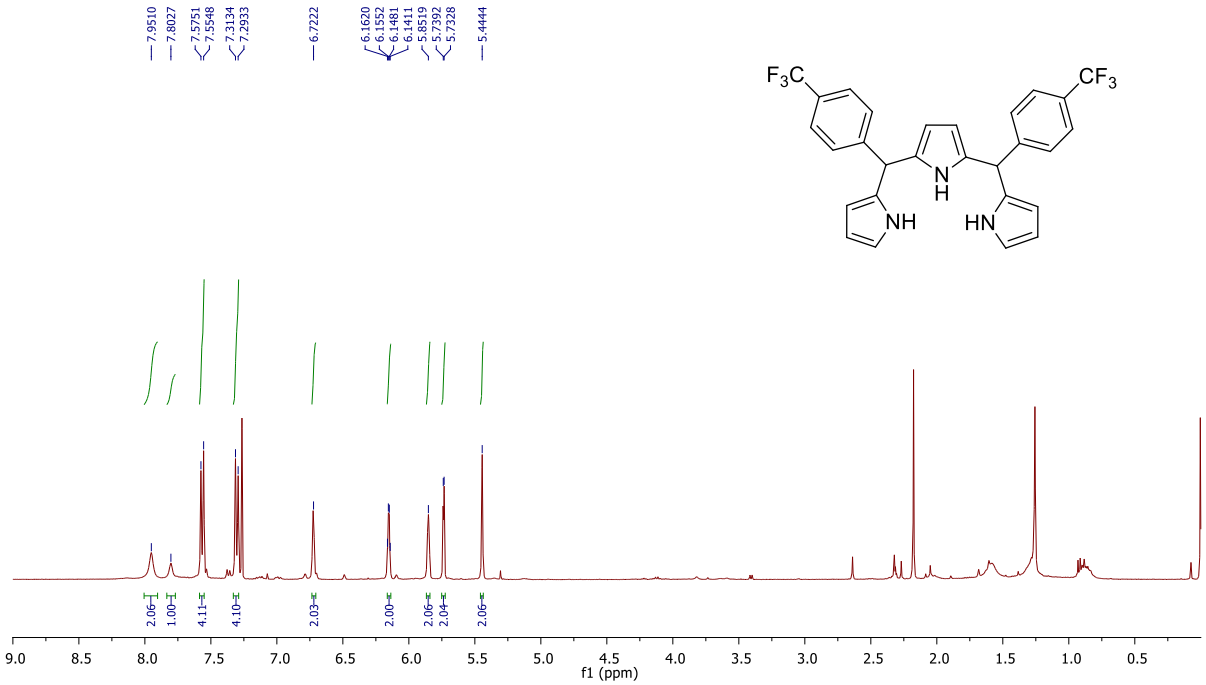


Figure S29. ^{1}H NMR of 5 ($CDCl_3$)

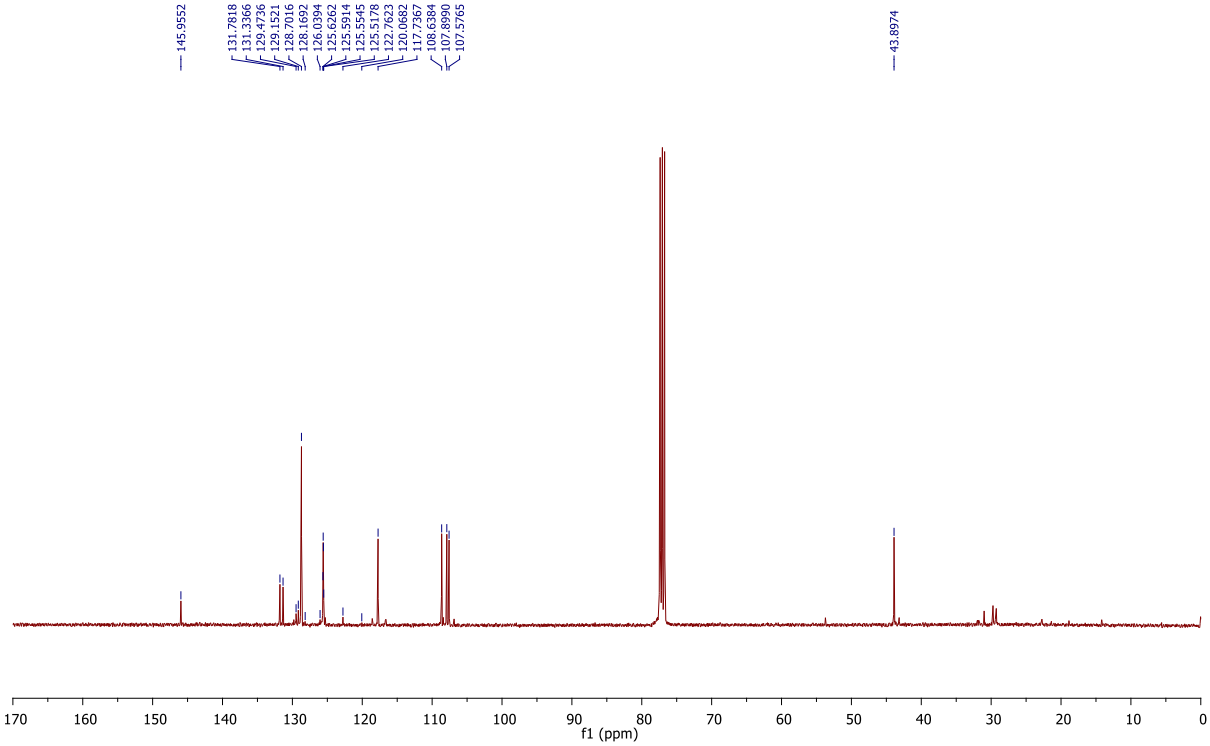


Figure S30. ^{13}C NMR of 5 ($CDCl_3$)

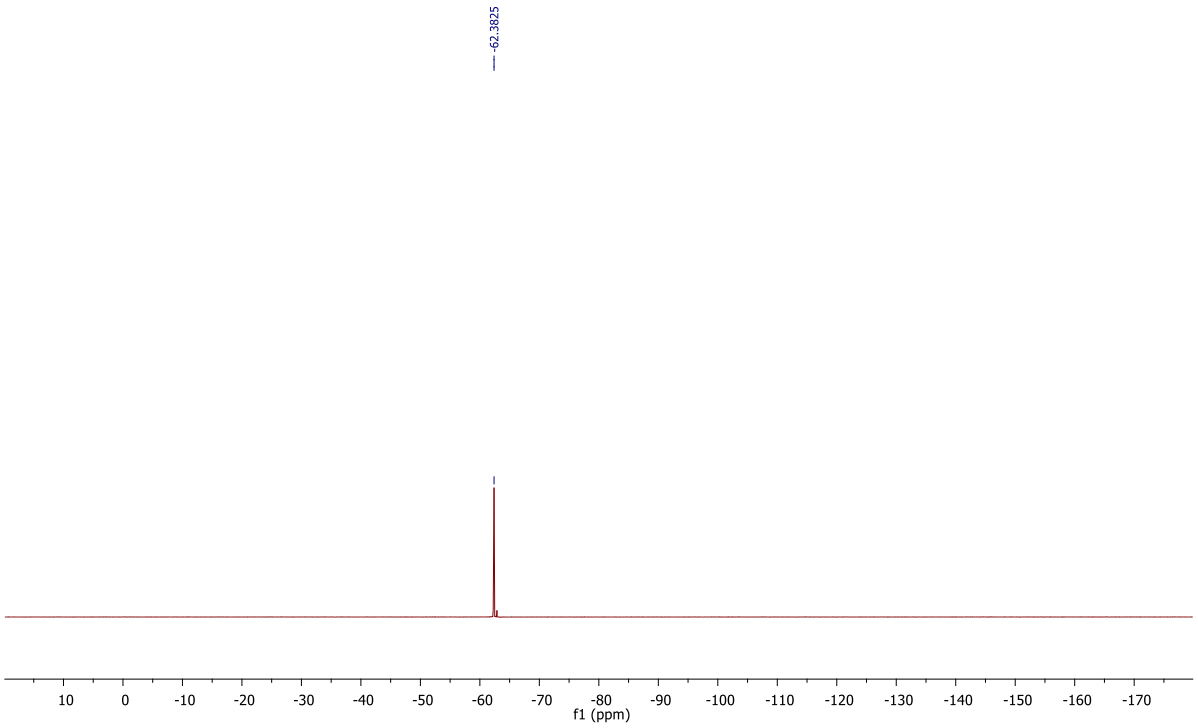


Figure S31. ^{19}F NMR of 5 ($CDCl_3$)

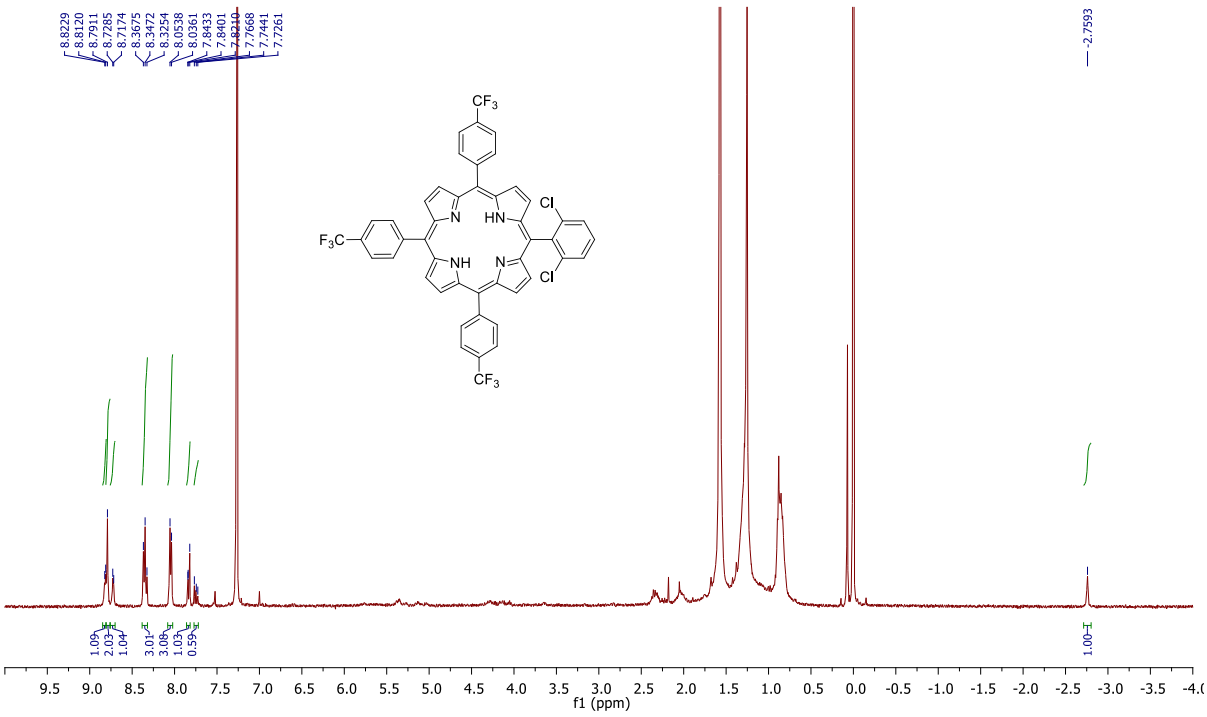


Figure S32. ^{1}H NMR of 6a ($CDCl_3$)

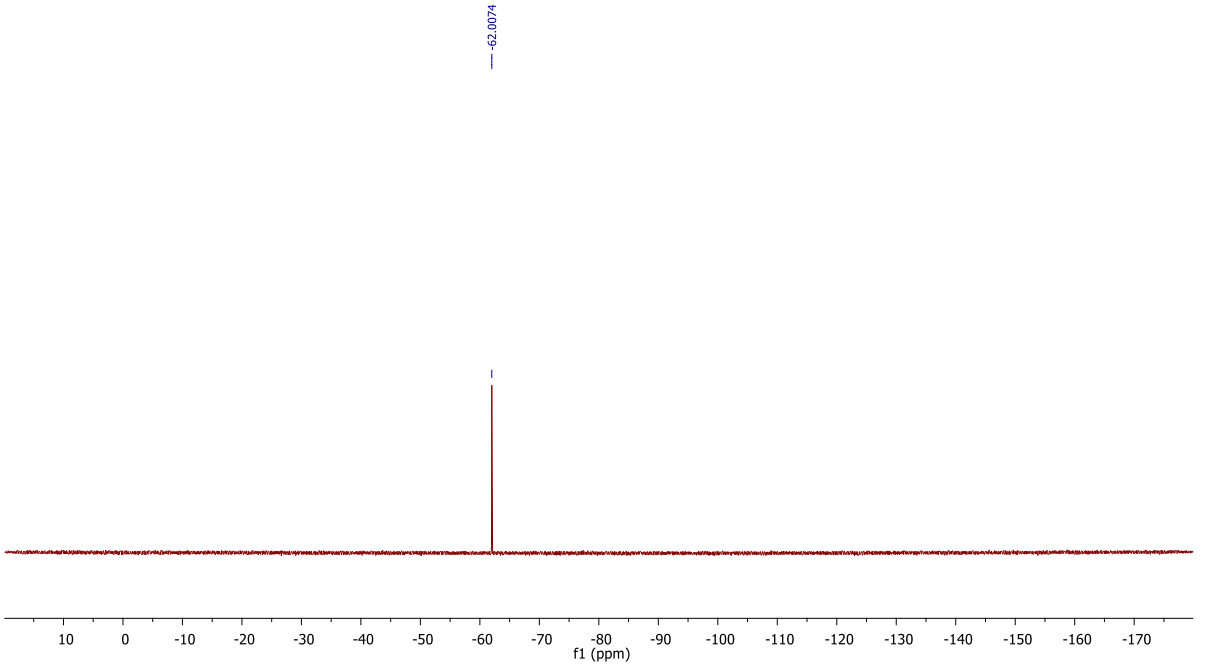


Figure S33. ^{19}F NMR of 6a ($CDCl_3$)

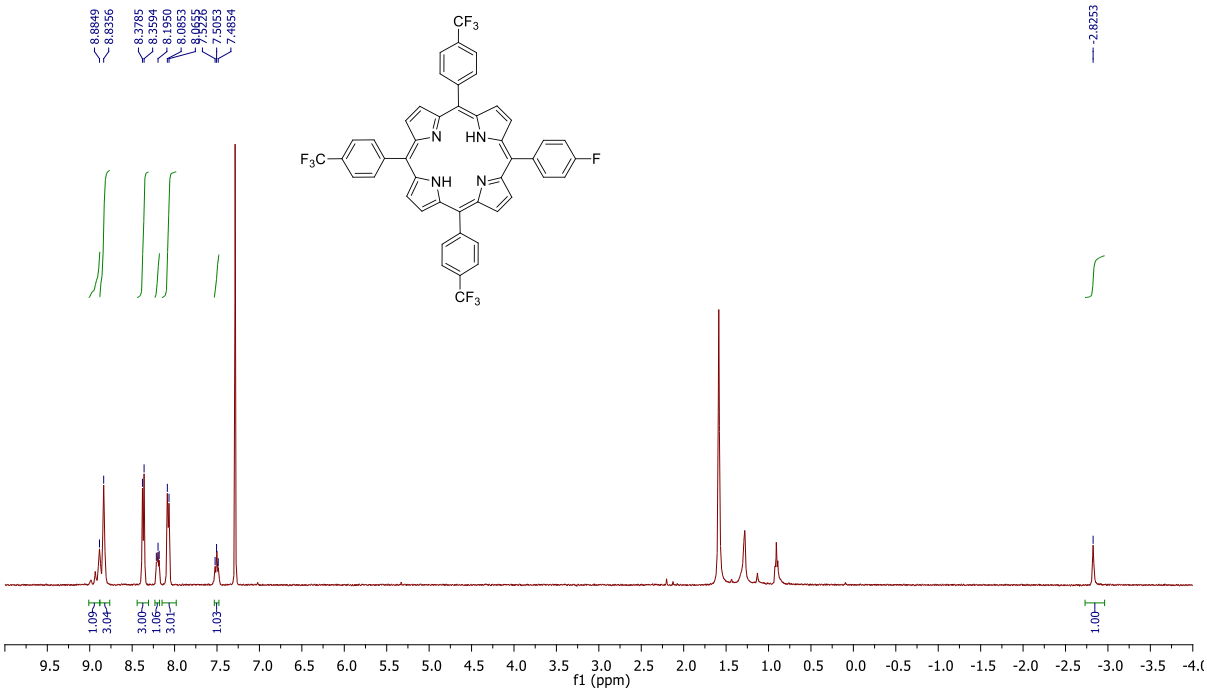


Figure S34. ^{1}H NMR of 6b ($CDCl_3$)

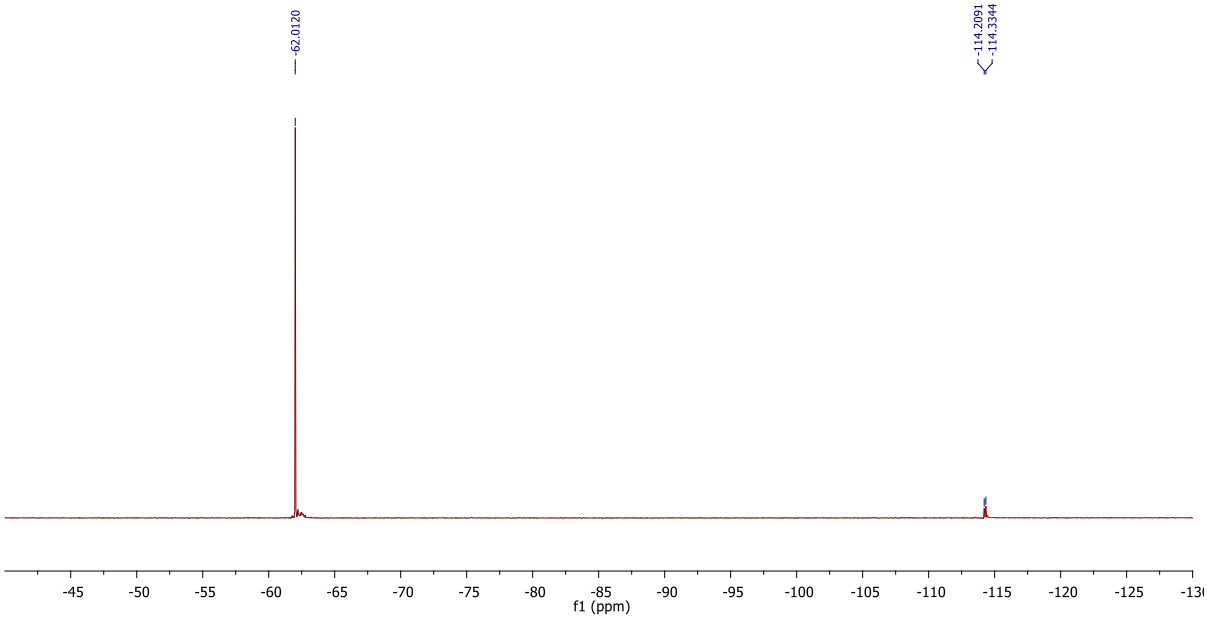


Figure S35. ^{19}F NMR of 6b ($CDCl_3$)

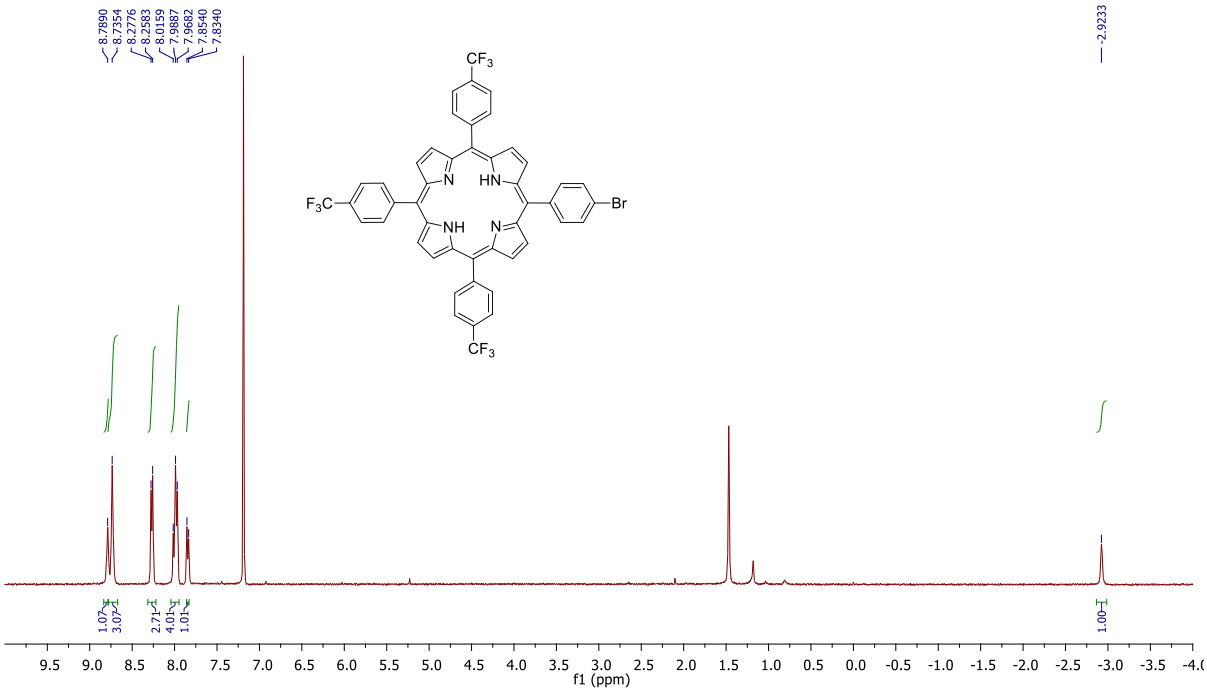


Figure S36. ^{1}H NMR of 6c ($CDCl_3$)

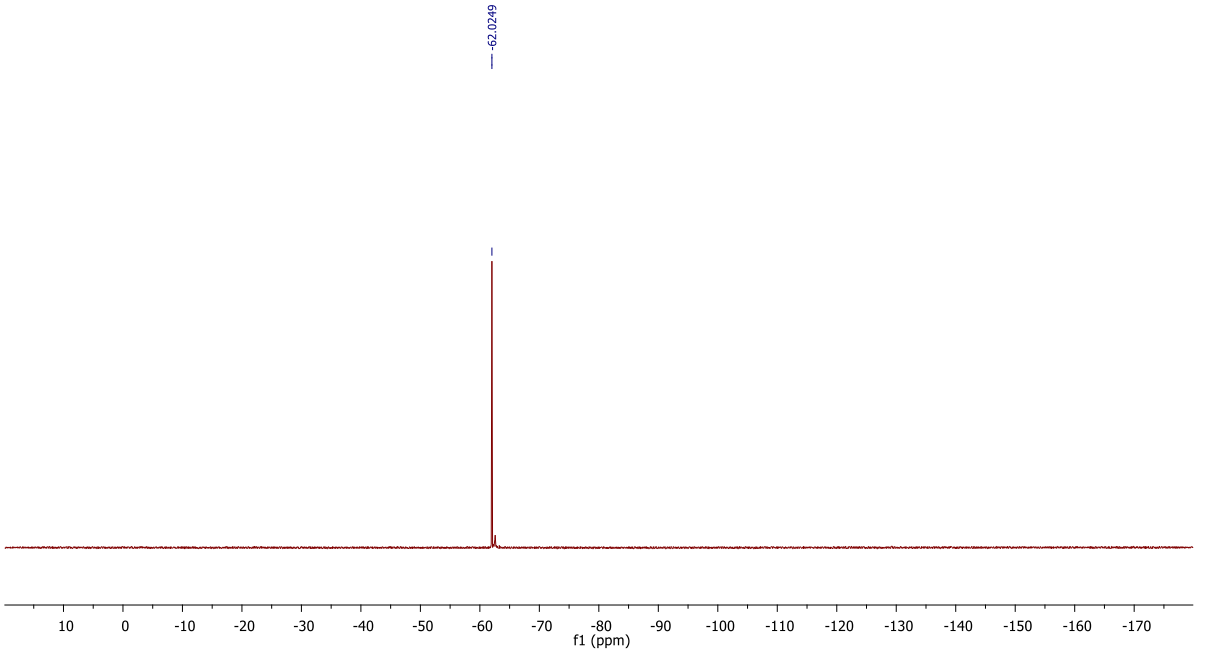


Figure S37. ^{19}F NMR of 6c ($CDCl_3$)

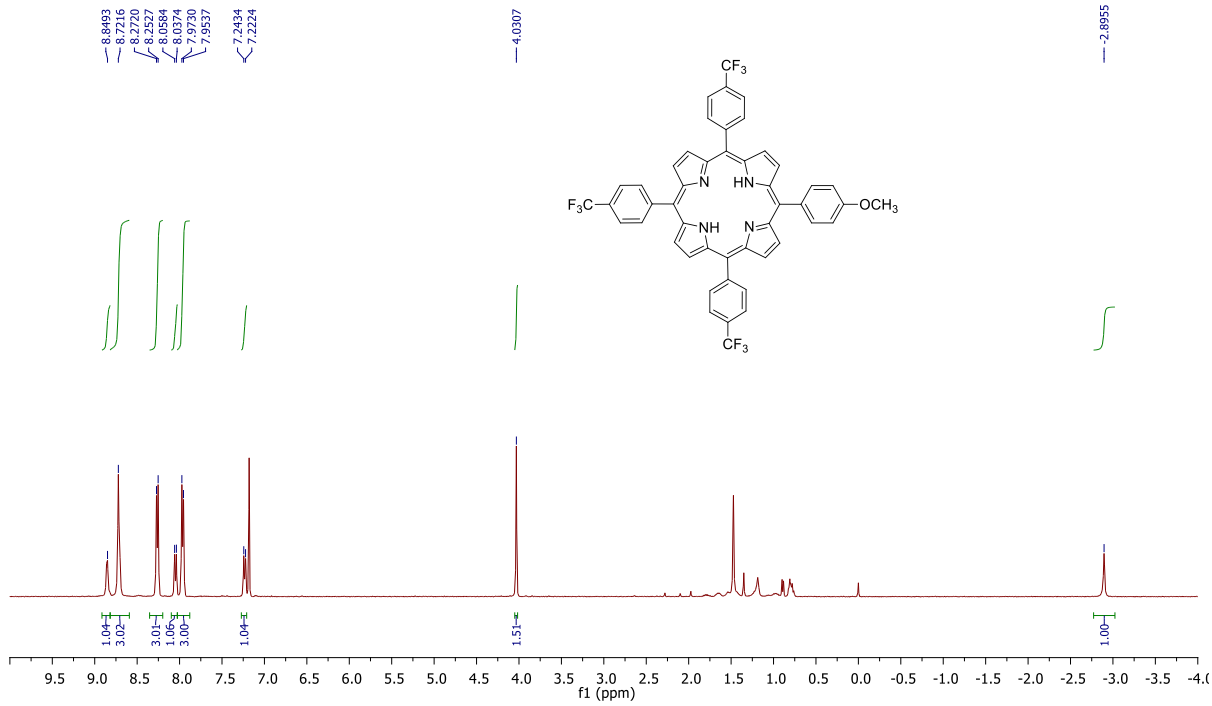


Figure S38. ^{1}H NMR of 6d ($CDCl_3$)

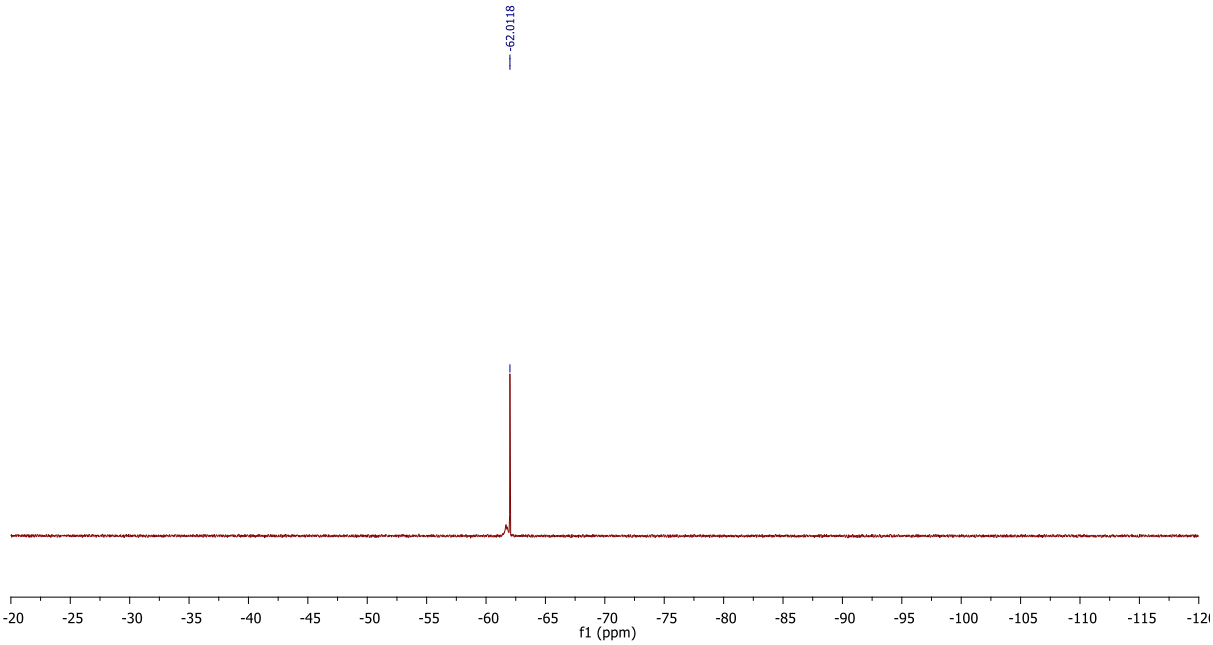


Figure S39. ^{19}F NMR of 6d ($CDCl_3$)

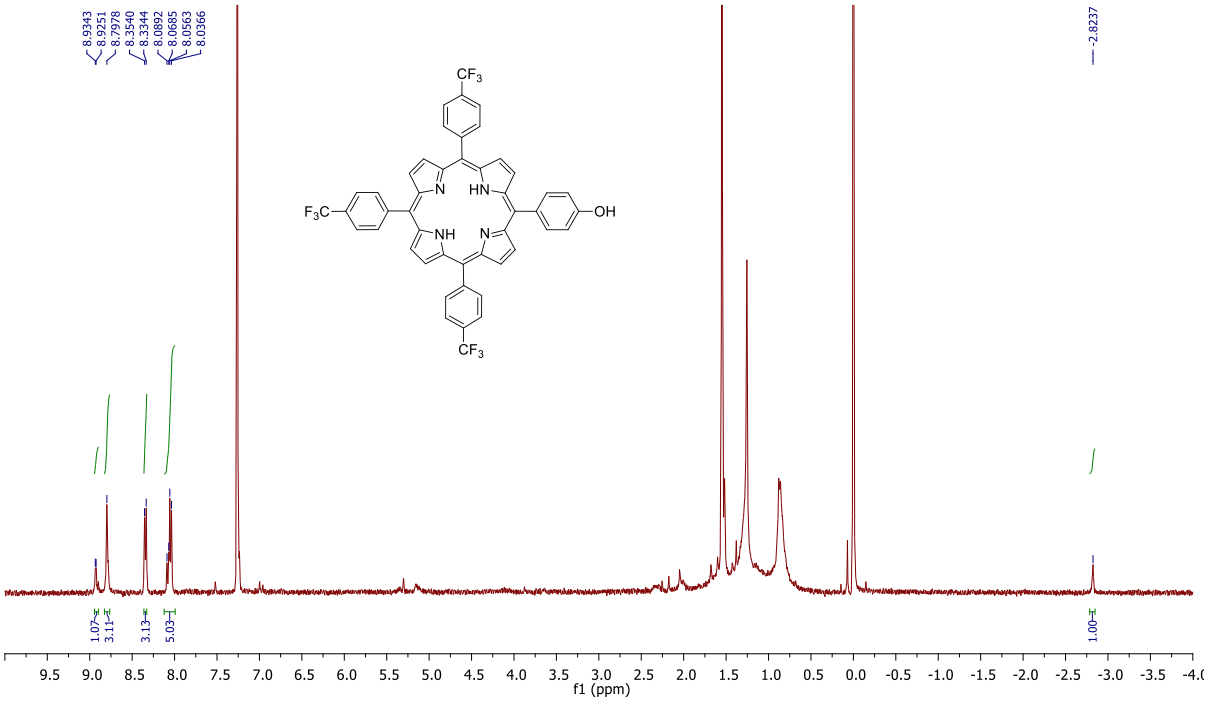


Figure S40. ^{1}H NMR of 6e ($CDCl_3$)

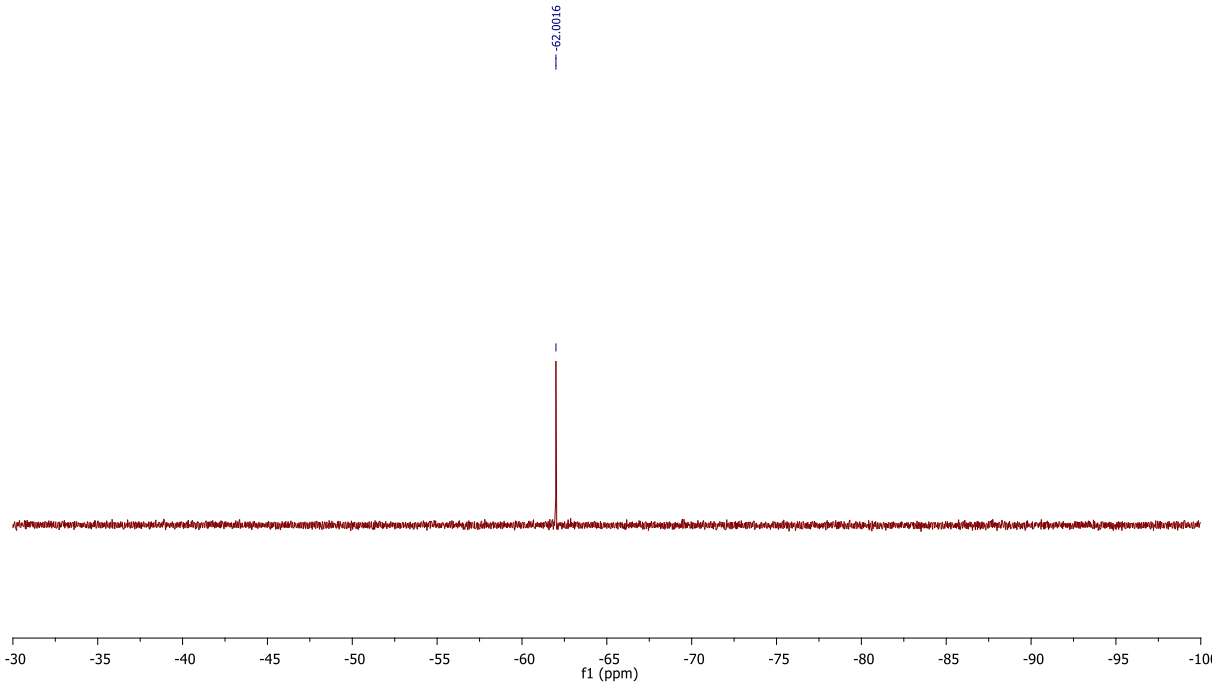


Figure S41. ^{19}F NMR of 6e ($CDCl_3$)

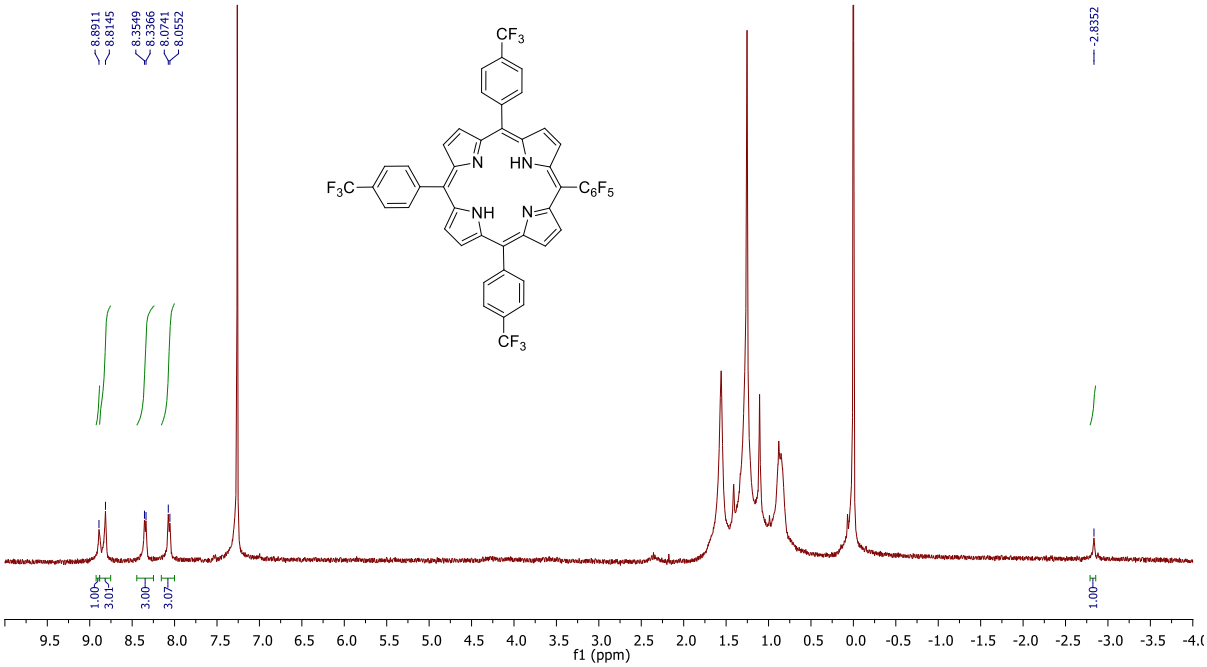


Figure S42. ^{1}H NMR of 6f ($CDCl_3$)

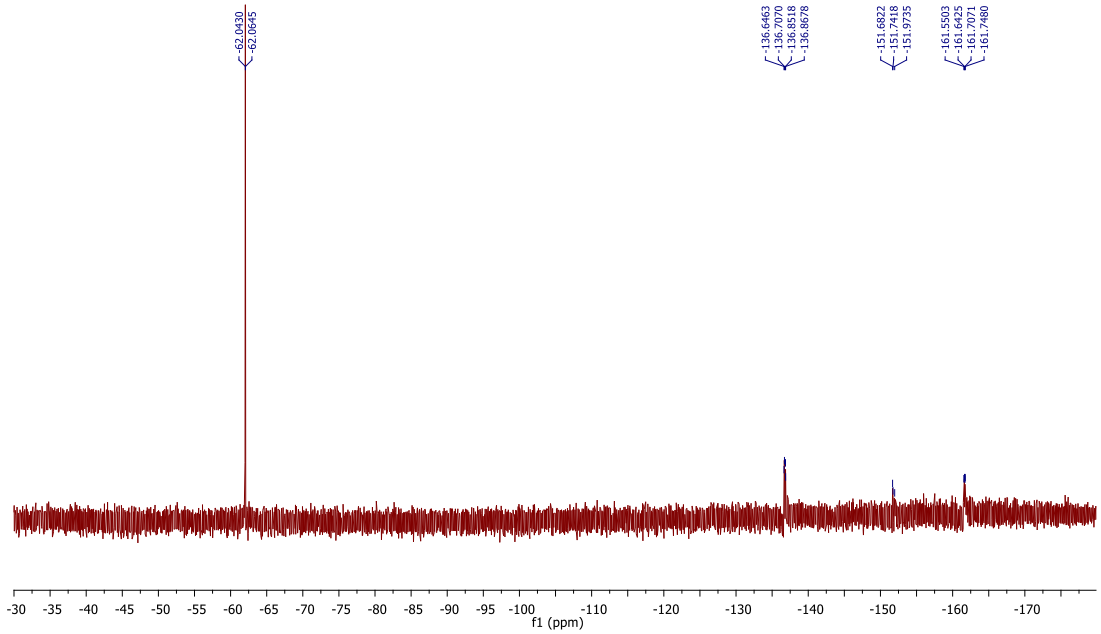


Figure S43. ^{19}F NMR of 6f ($CDCl_3$)

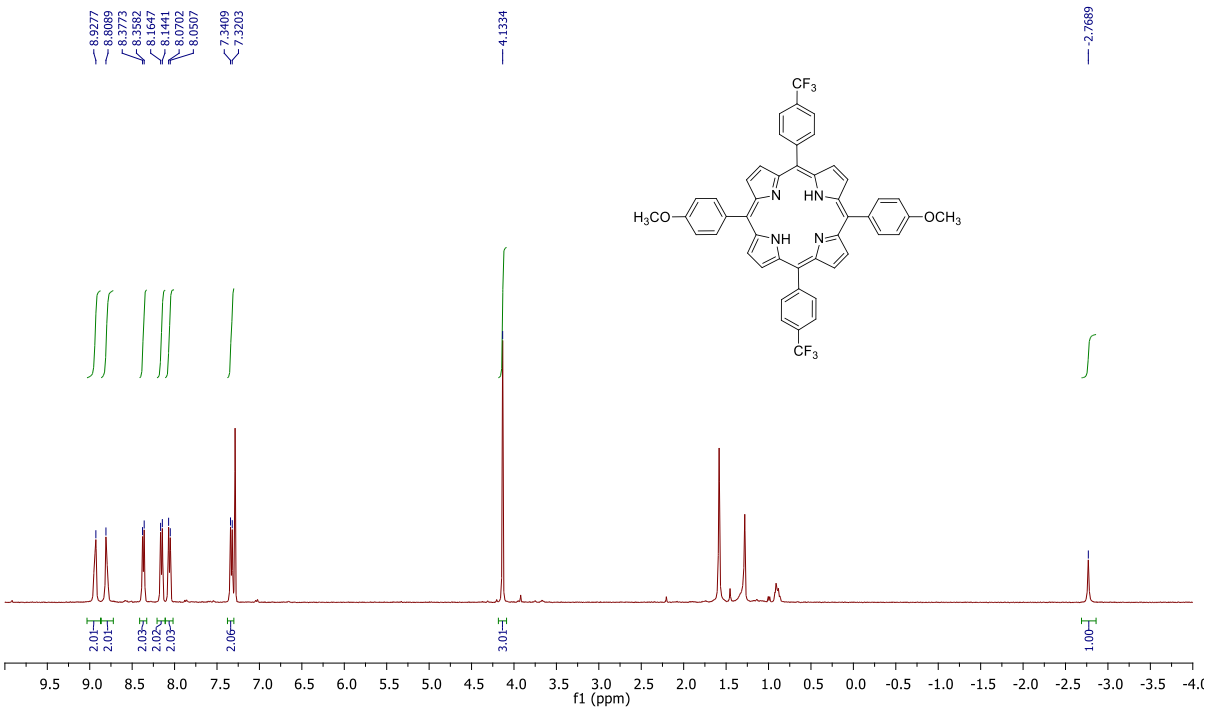


Figure S44. ^{1}H NMR of 7d ($CDCl_3$)

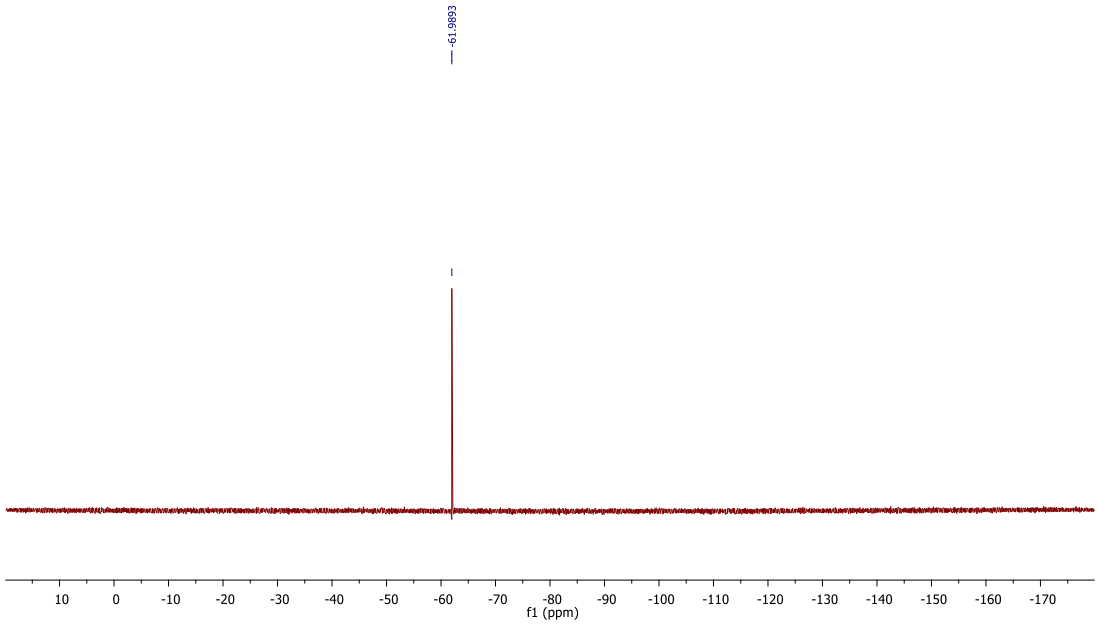


Figure S45. ^{19}F NMR of 7d ($CDCl_3$)

5. LC MS-TOF (ESI) spectra of reaction intermediates

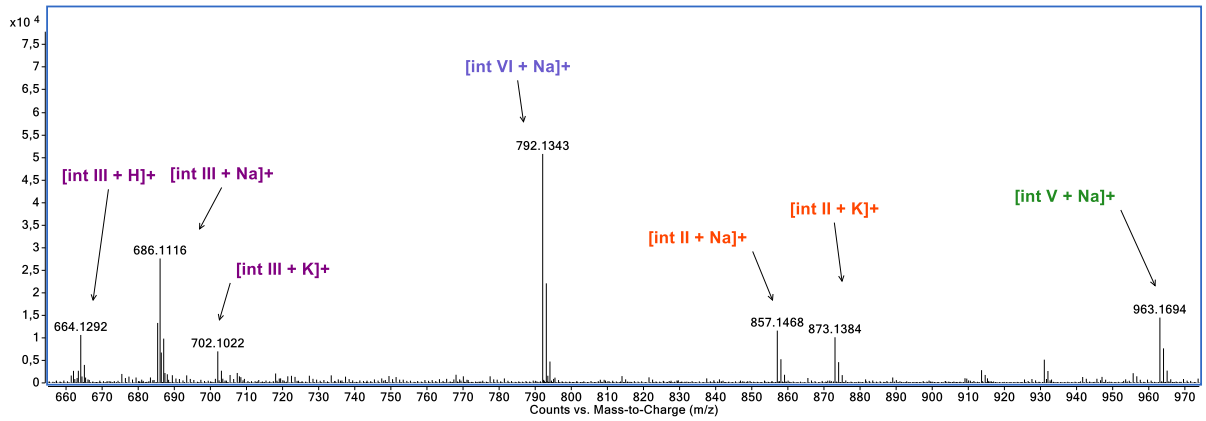


Figure S46. Intermediates **II**, **III**, **V** and **VI** in **1** and **2d** reaction mixture at 0 °C for 2 hours

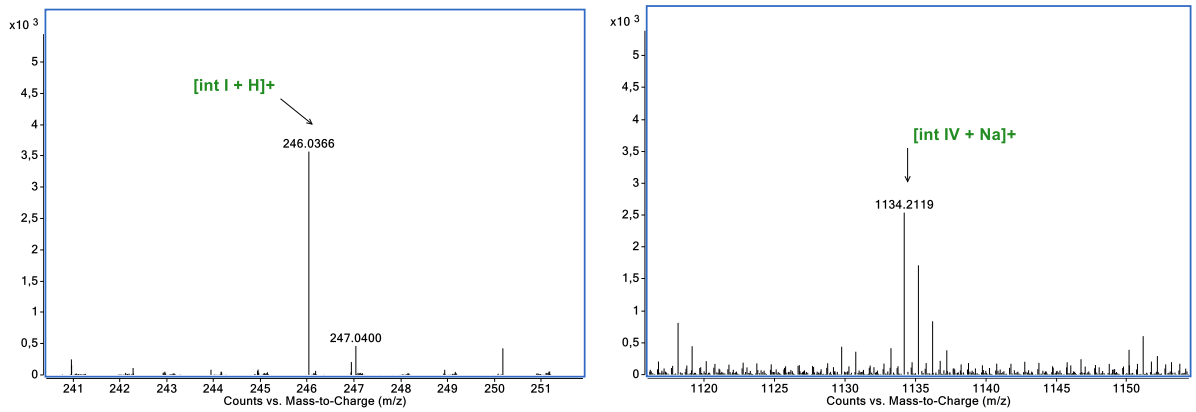


Figure S47. Intermediates **I** and **IV** in **1** and **2d** reaction mixture at 0 °C for 2 hours

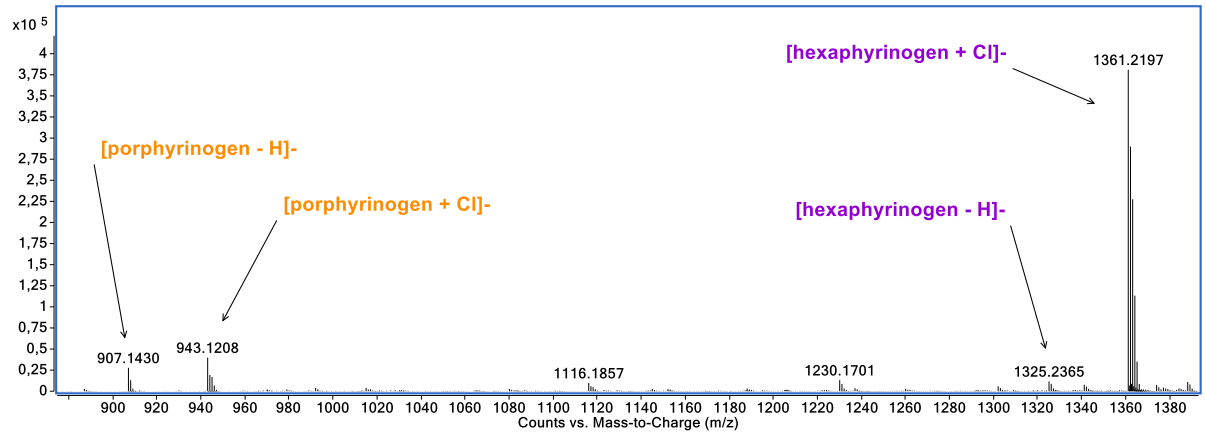


Figure S48. Porphyrinogen and hexaphyrinogen of **1** and **2d** reaction mixture at r.t. for 1 hour

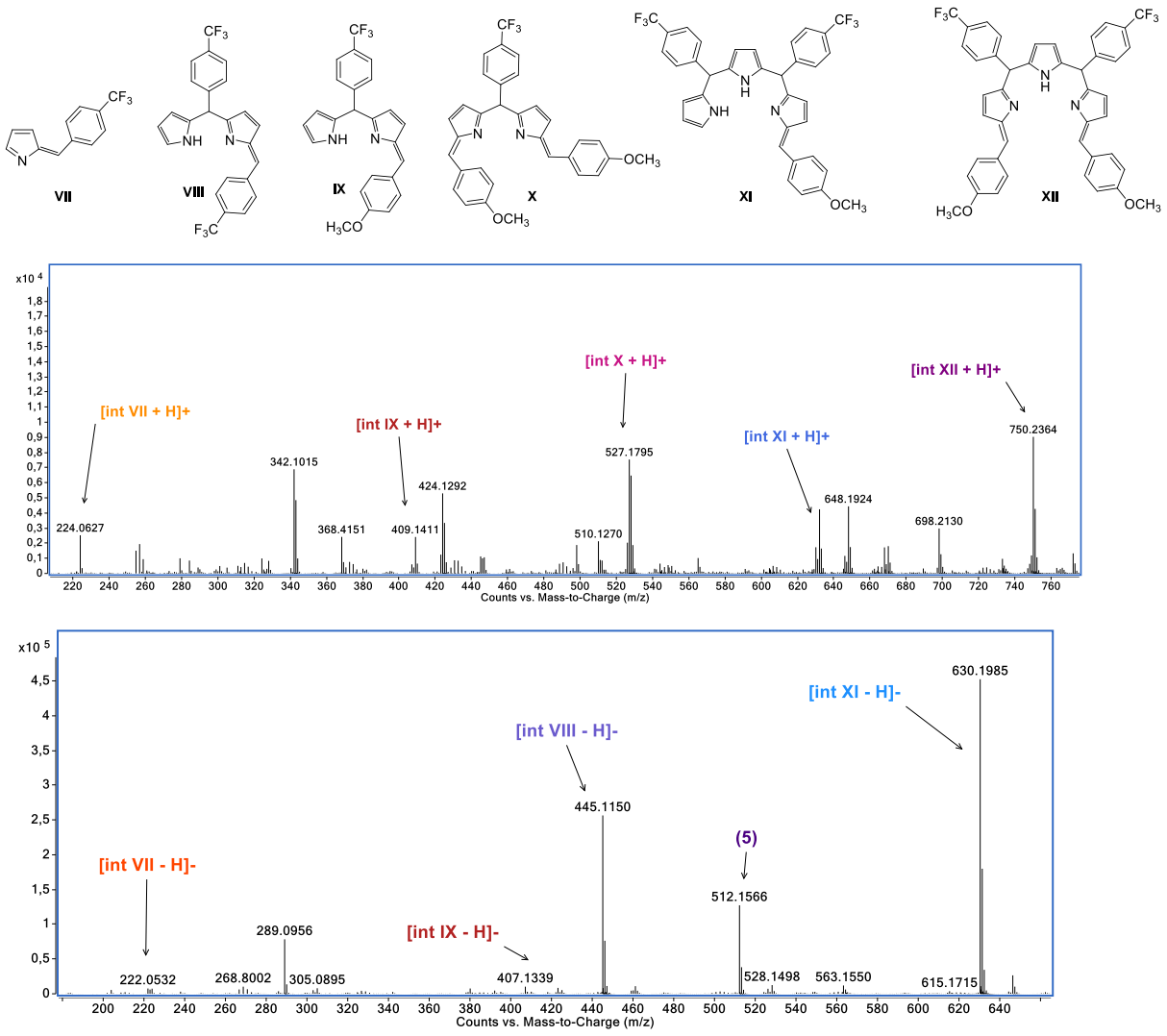


Figure S49. Intermediates **VII** - **XII** in **5** and **2h** reaction mixture at 0 °C for 30 min.

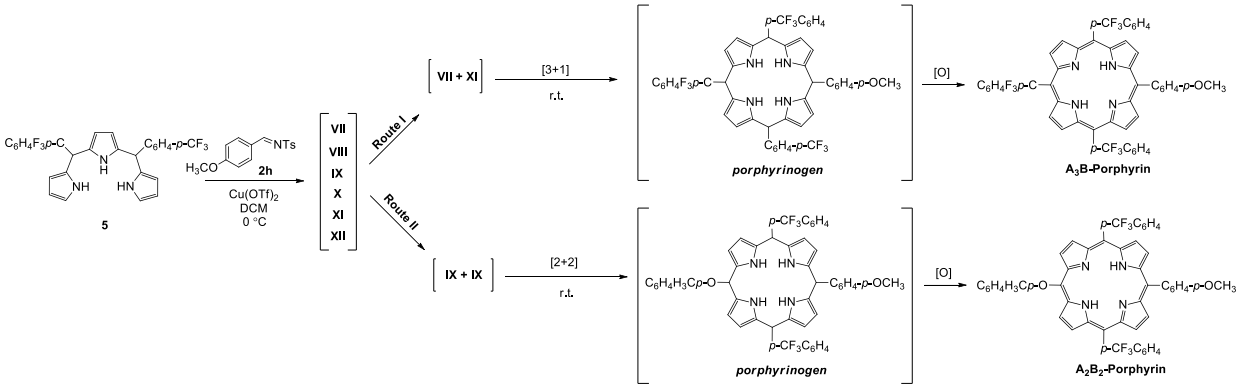


Figure S50. A suggested reaction pathway for the formation of A_3B-porphyrins and A_2B_2-porphyrins

6. LC MS-TOF (ESI) spectra of compounds

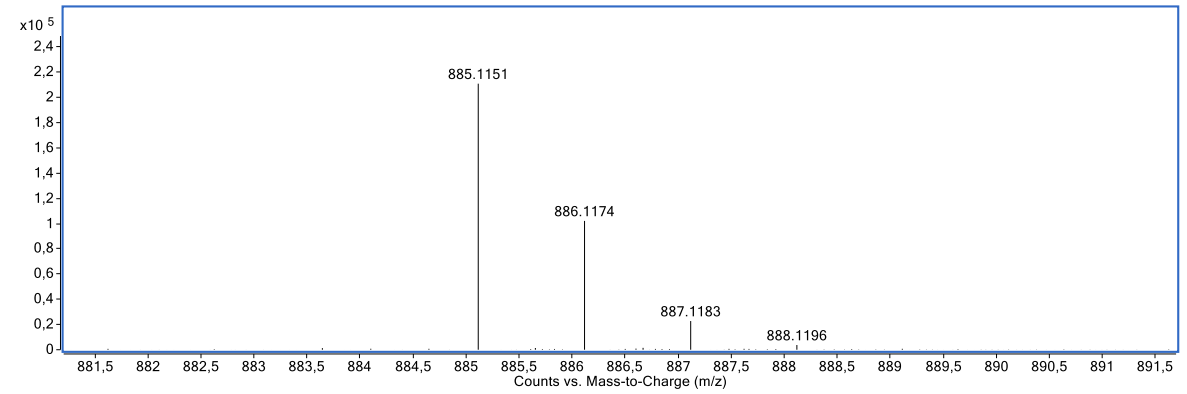


Figure S51. ESI-TOF mass spectrum of **3a**.

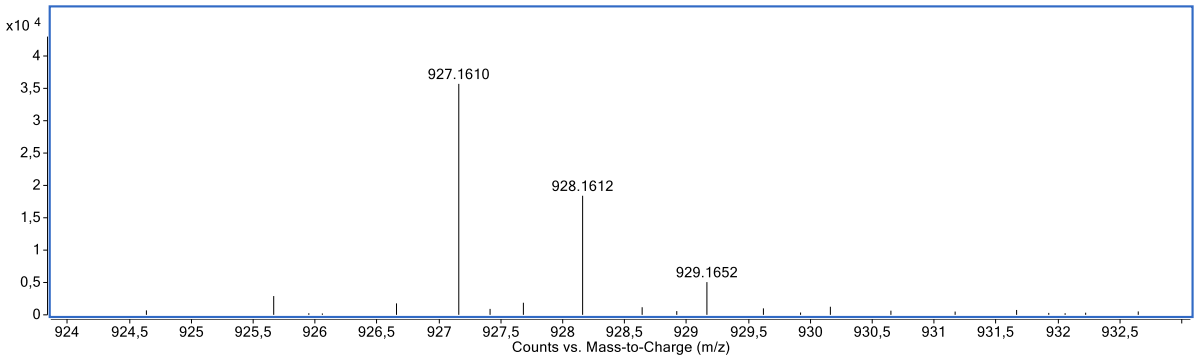


Figure S52. ESI-TOF mass spectrum of **3b**.

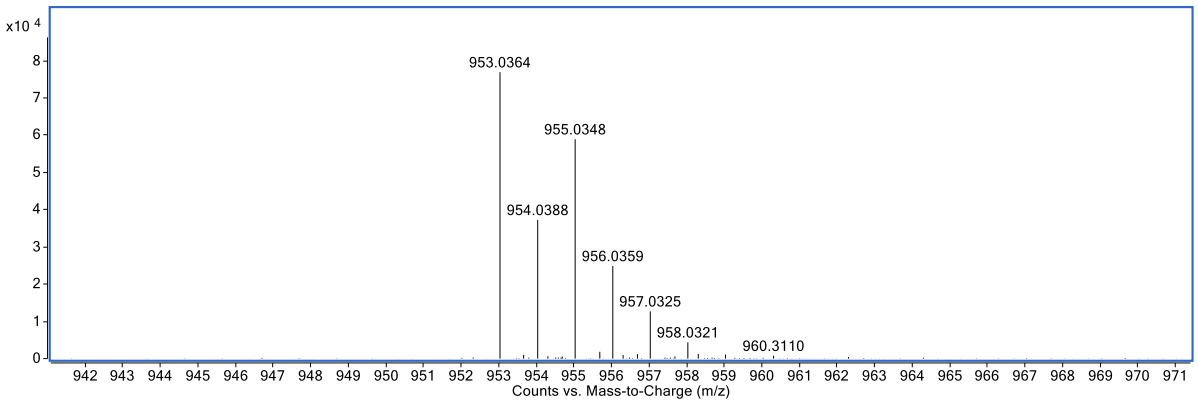


Figure S53. ESI-TOF mass spectrum of **3c**.

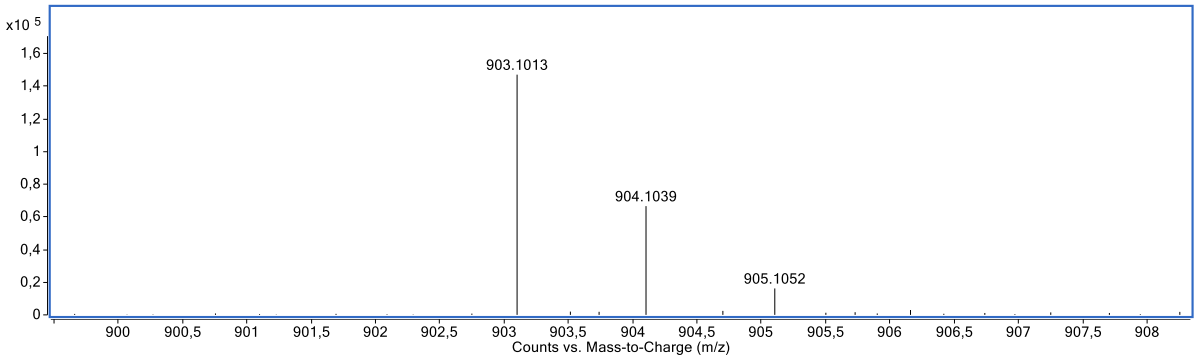


Figure S54. ESI-TOF mass spectrum of **3d**.

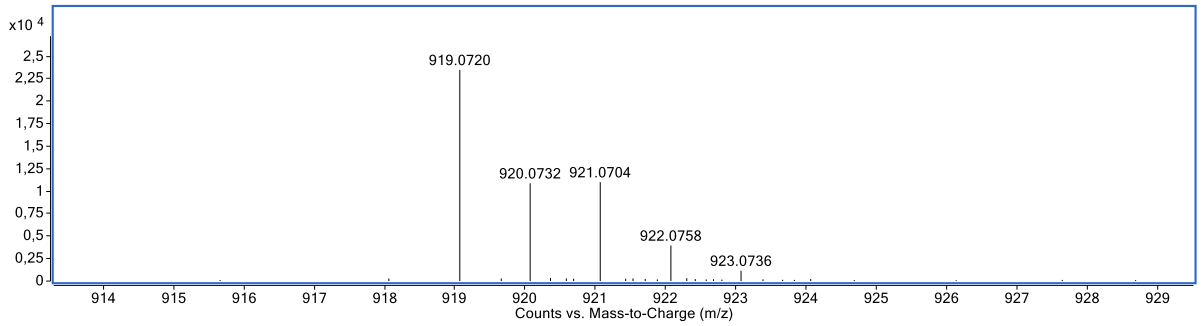


Figure S55. ESI-TOF mass spectrum of **3e**.

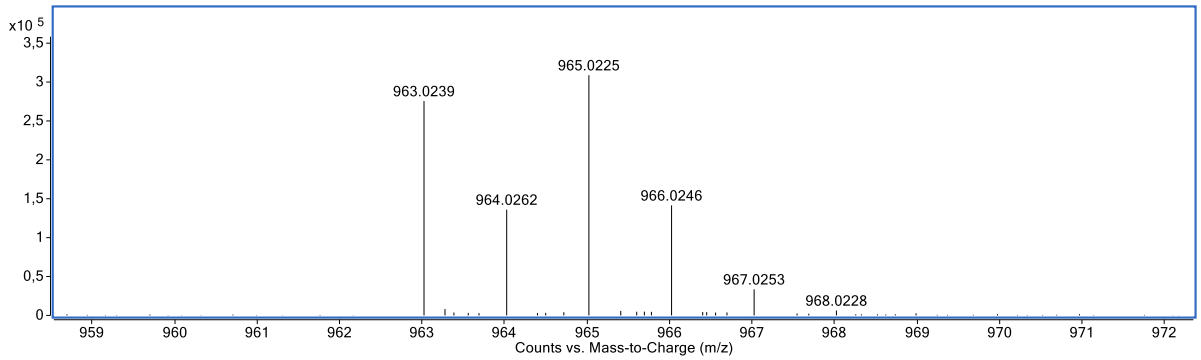


Figure S56. ESI-TOF mass spectrum of **3f**.

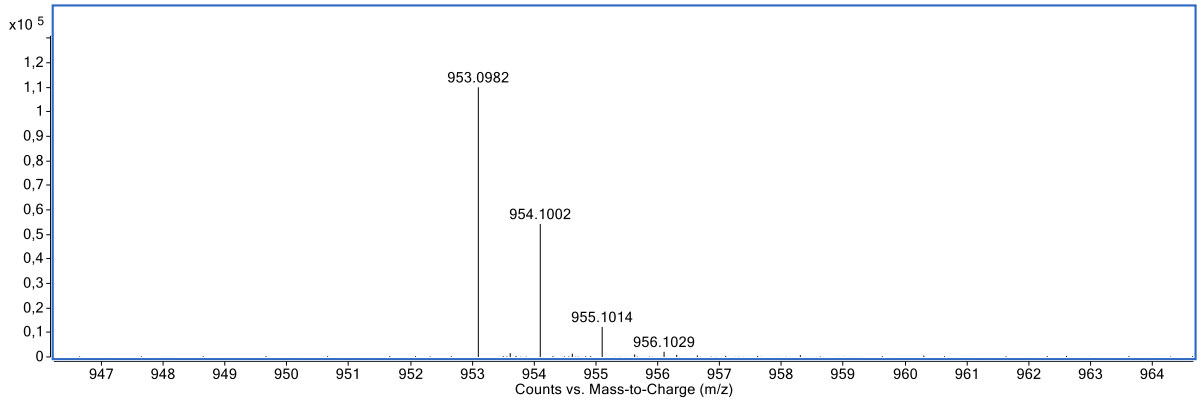


Figure S57. ESI-TOF mass spectrum of **3g**.

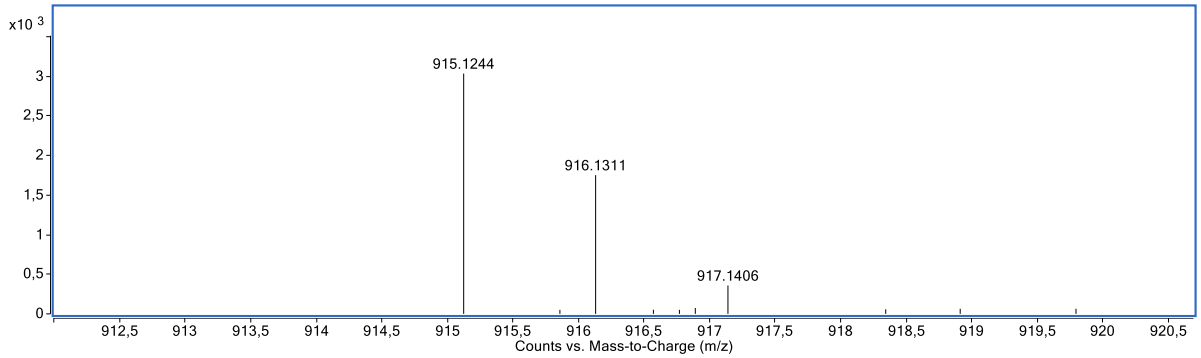


Figure S58. ESI-TOF mass spectrum of **3h**.

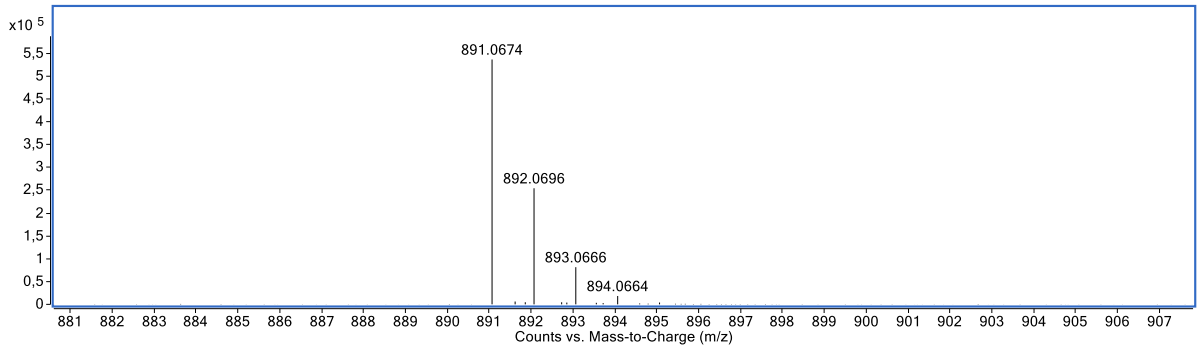


Figure S59. ESI-TOF mass spectrum of **3j**.

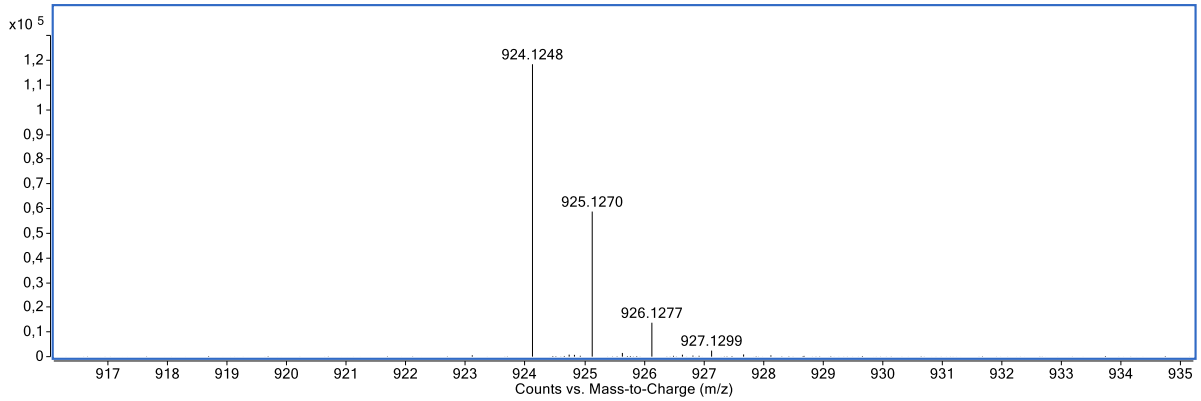


Figure S60. ESI-TOF mass spectrum of **3k**.

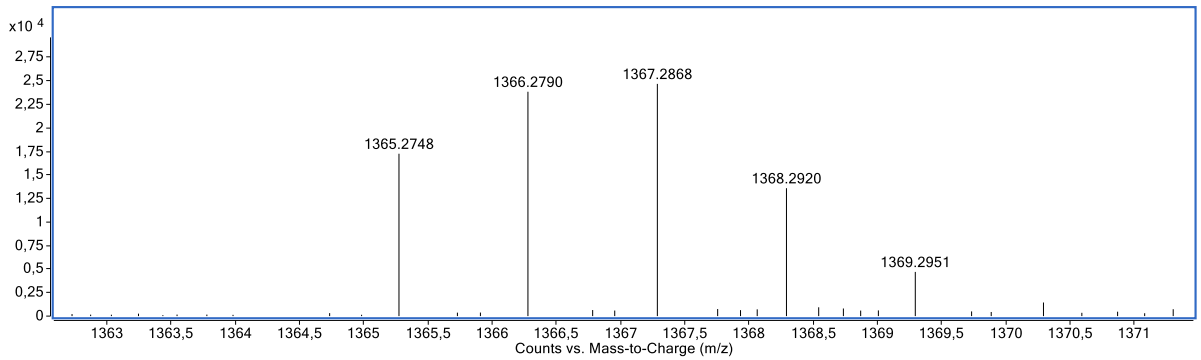


Figure S61. ESI-TOF mass spectrum of **4b**.

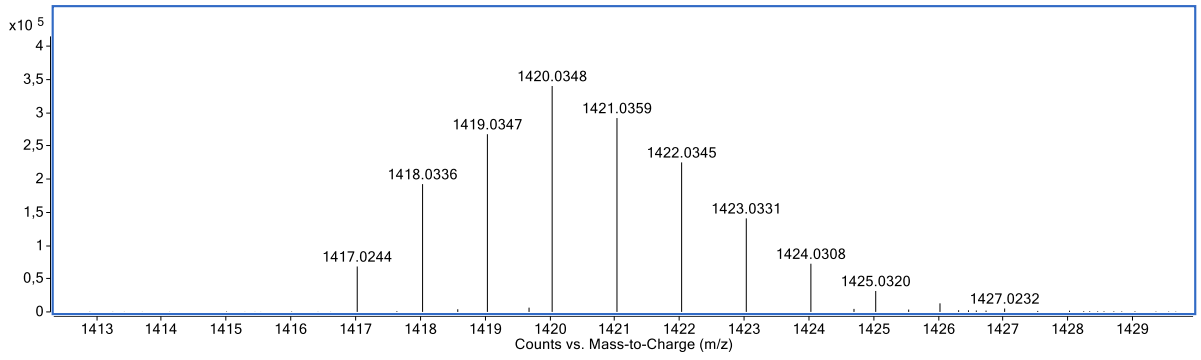


Figure S62. ESI-TOF mass spectrum of **4c**.

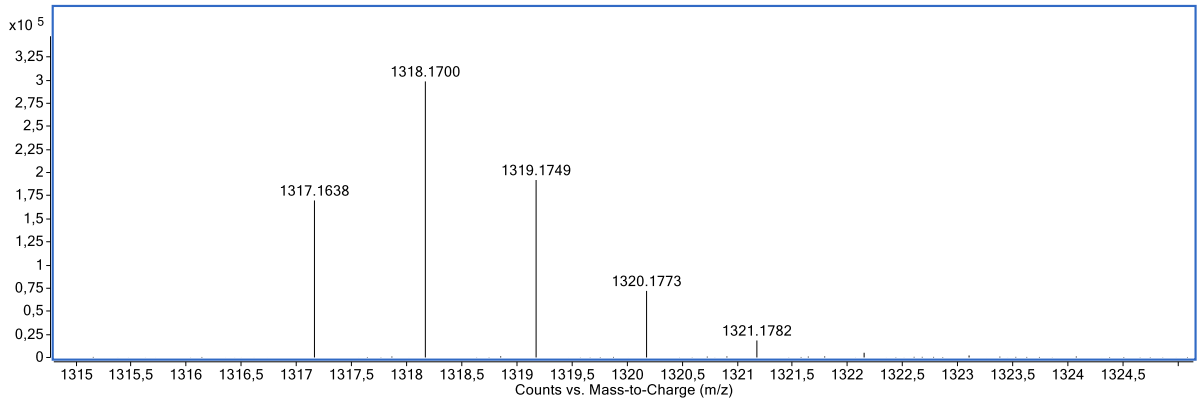


Figure S63. ESI-TOF mass spectrum of **4d**.

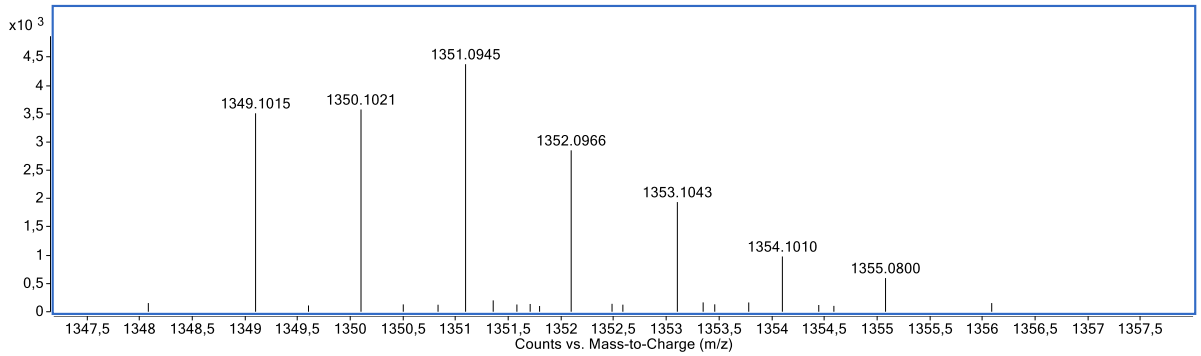


Figure S64. ESI-TOF mass spectrum of **4e**.

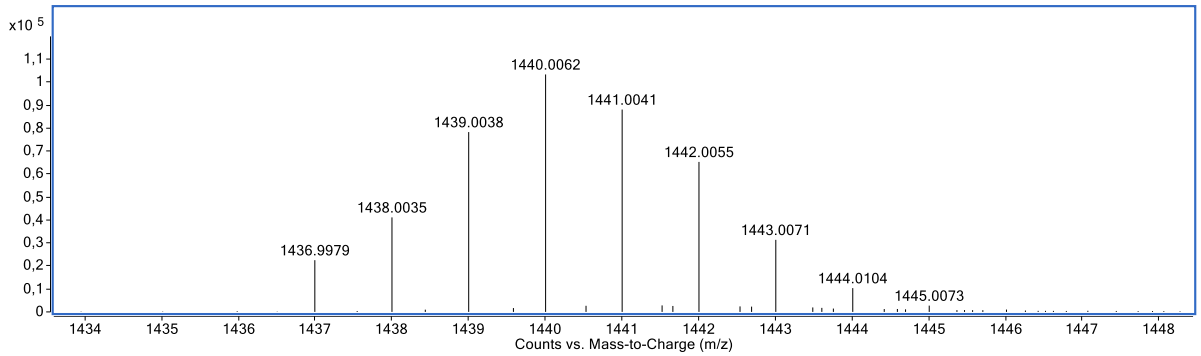


Figure S65. ESI-TOF mass spectrum of **4f**.

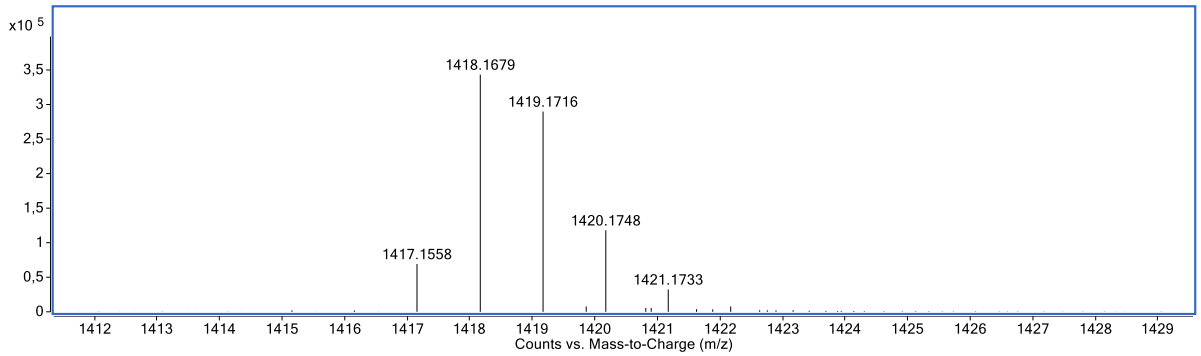


Figure S66. ESI-TOF mass spectrum of **4g**.

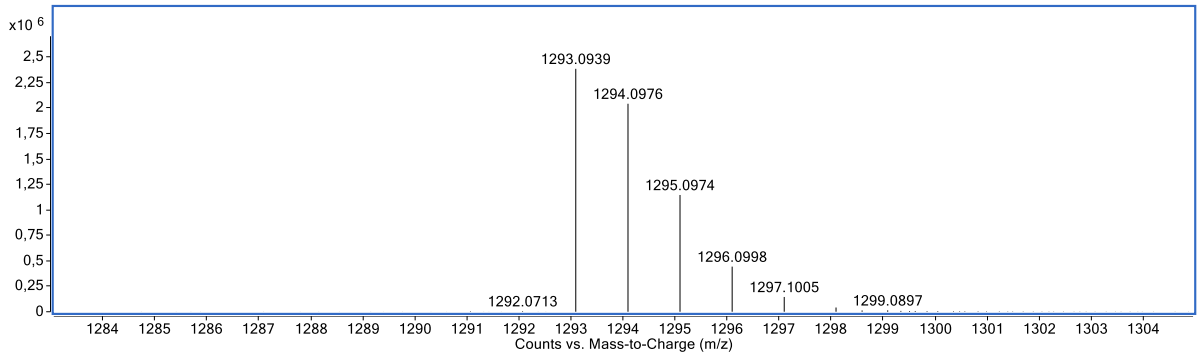


Figure S67. ESI-TOF mass spectrum of **4j**.

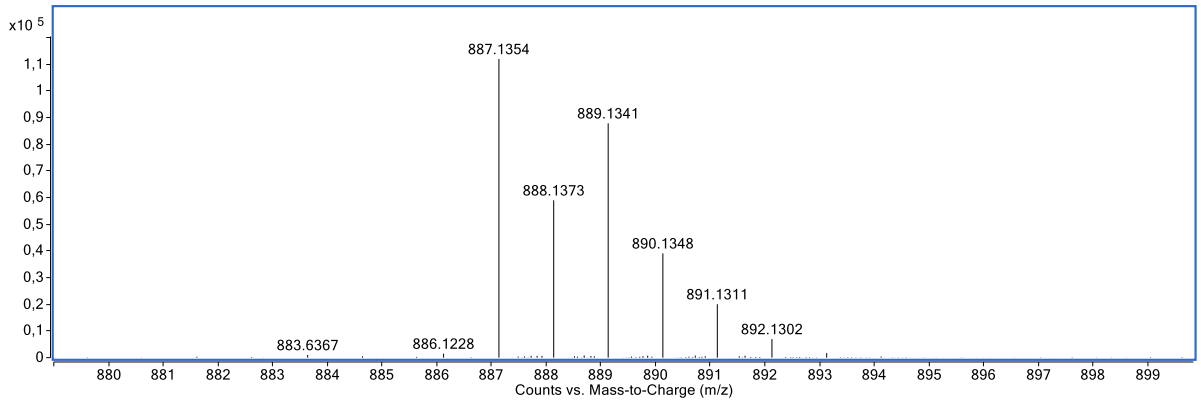


Figure S68. ESI-TOF mass spectrum of **6a**.

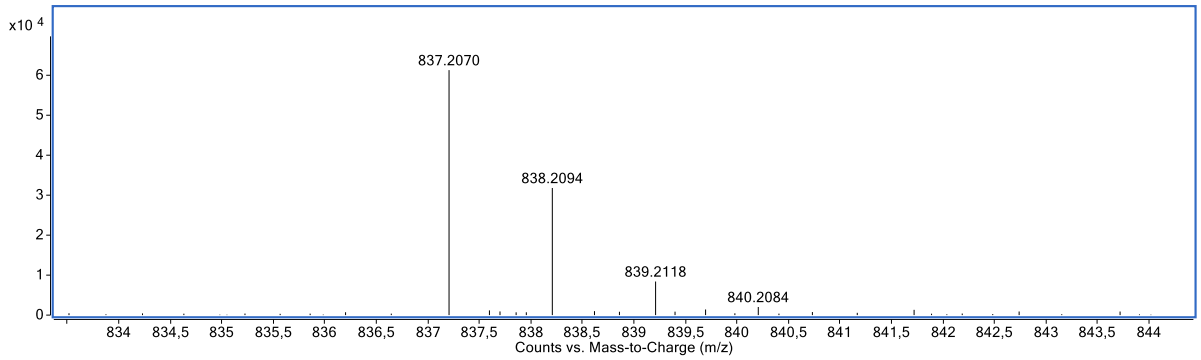


Figure S69. ESI-TOF mass spectrum of **6b**.

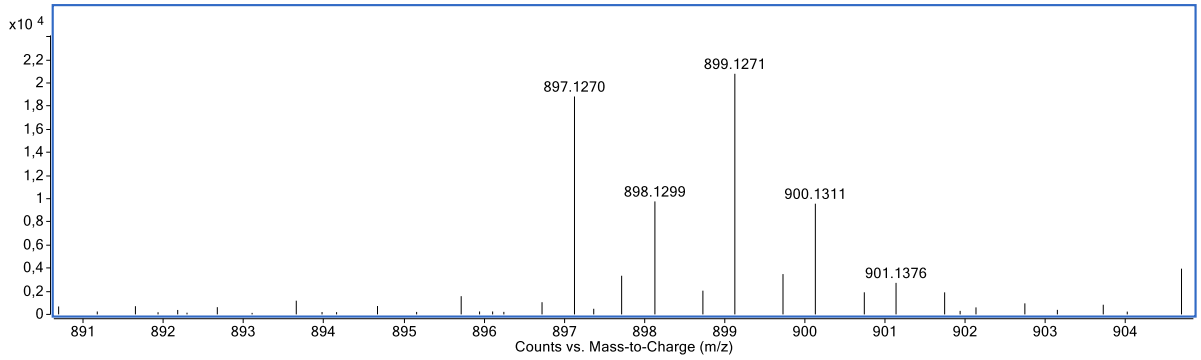


Figure S70. ESI-TOF mass spectrum of **6c**.

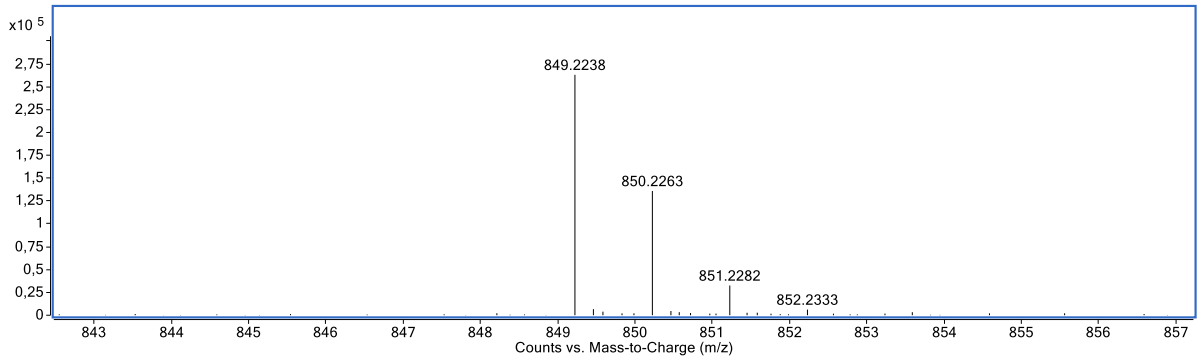


Figure S71. ESI-TOF mass spectrum of **6d**.

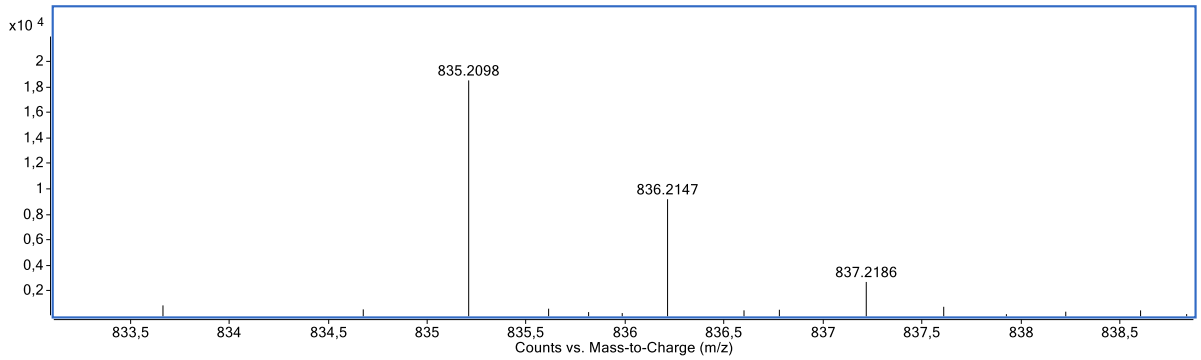


Figure S72. ESI-TOF mass spectrum of **6e**.

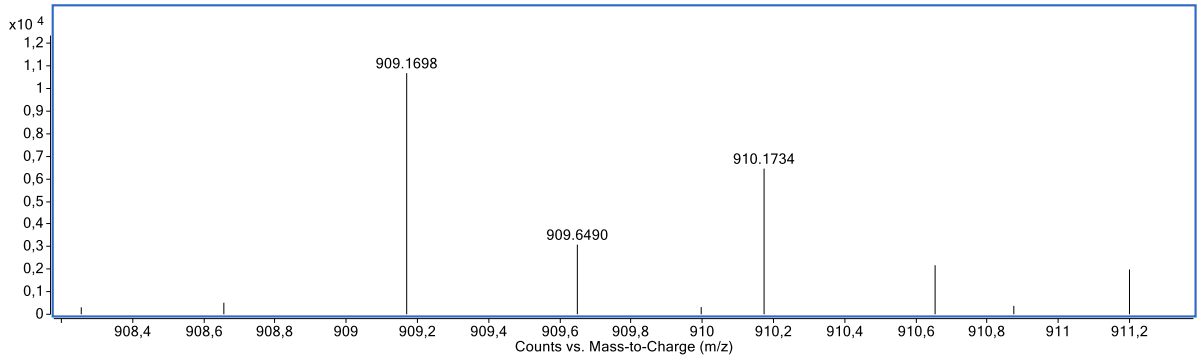


Figure S73. ESI-TOF mass spectrum of **6f**.

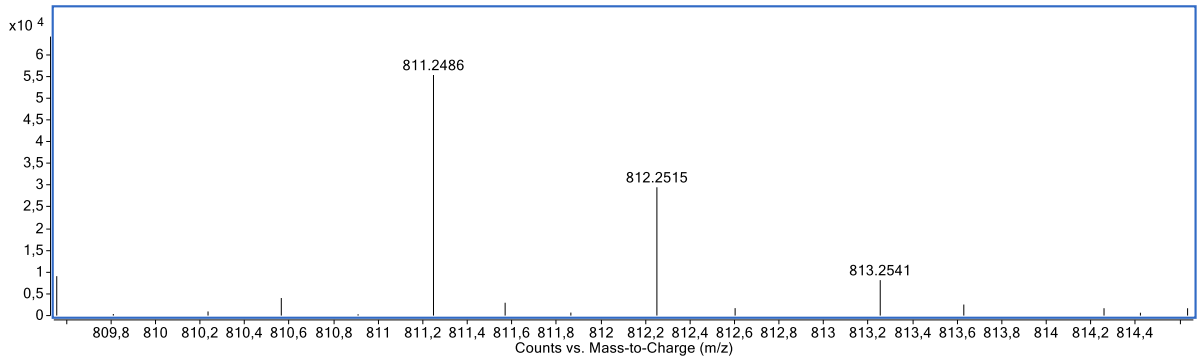


Figure S74. ESI-TOF mass spectrum of **7d**.

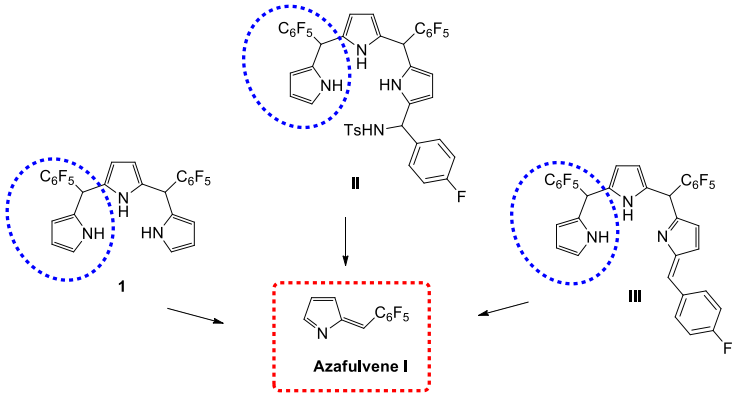


Figure S75. Possible fragmentation for the formation of azafulvene

References

[1] M. Suzuki, A. Osuka, *Chem. Eur. J.* **2007**, *13*, 196 – 202.

[2] G. R. Fulmer, A. J. M. Miller, N. H. Sherdan, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *J. Org. Chem.* **1997**, *62*, 7512 – 7515.