The Influence of the Nature of the Amino Group in Highly Fluorescent Difluoroborates Exhibiting Intramolecular Charge Transfer

Beata Jędrzejewska,[a] Agnieszka Skotnicka,[a] Adèle D. Laurent,[b] Marek Pietrzak,[a] Denis Jacquemin,[b,*] Borys Ośmiałowski [c,*]

[a] Faculty of Chemical Technology and Engineering, UTP University of Science and Technology, Seminaryjna 3, PL-85326 Bydgoszcz, Poland, [b] Laboratoire CEISAM - UMR CNRS 6230, University of Nantes, 2, rue de la Houssinière, 44322 Nantes Cedex 3, France, [c] Faculty of Chemistry, Nicolaus Copernicus University in Toruń, 7 Gagarin Street, 87-100 Toruń, Poland

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Figure S1. ^{1}H NMR spectrum (400 MHz) of **1** in $CDCl_3$.

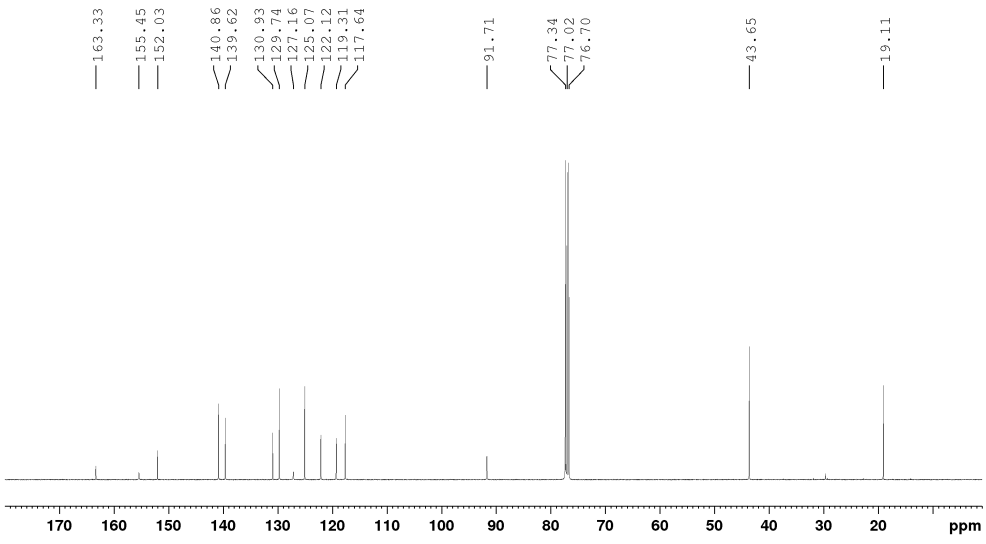


Figure S2. ^{13}C NMR spectrum (400 MHz) of **1** in $CDCl_3$.

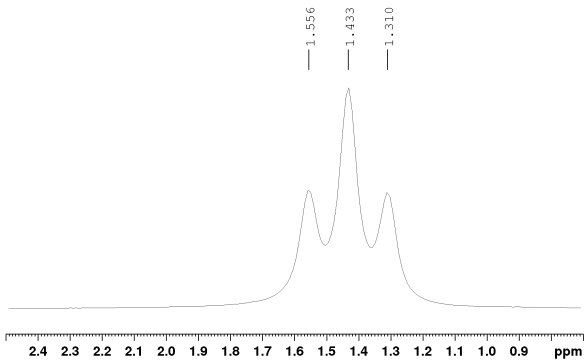


Figure S3. ^{11}B NMR spectrum (400 MHz) of **1** in $CDCl_3$.

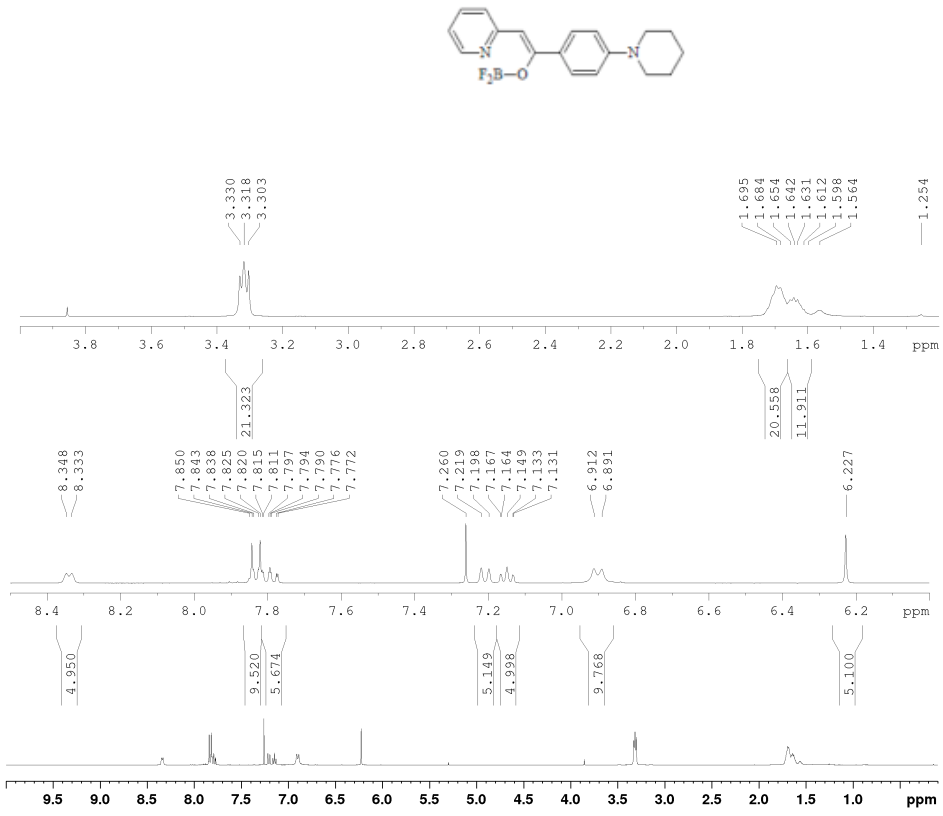


Figure S4. ^{1}H NMR spectrum (400 MHz) of **2** in $CDCl_3$.

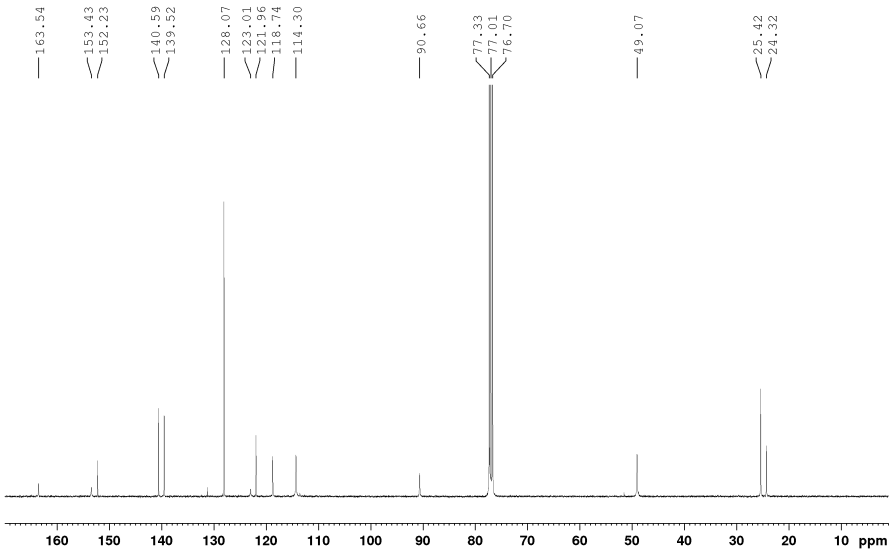


Figure S5. ^{13}C NMR spectrum (400 MHz) of **2** in $CDCl_3$.

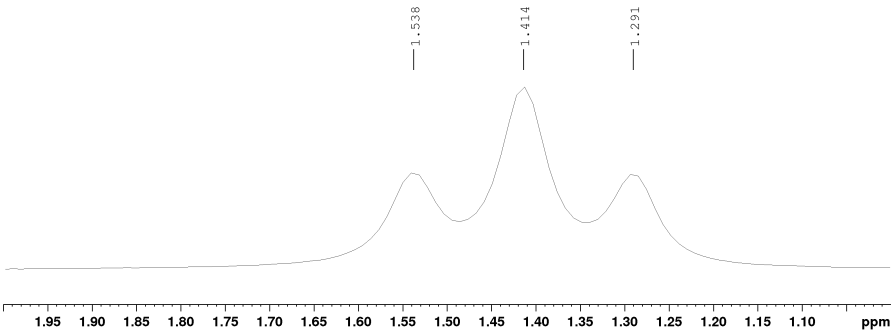


Figure S6. ^{11}B NMR spectrum (400 MHz) of **2** in $CDCl_3$.

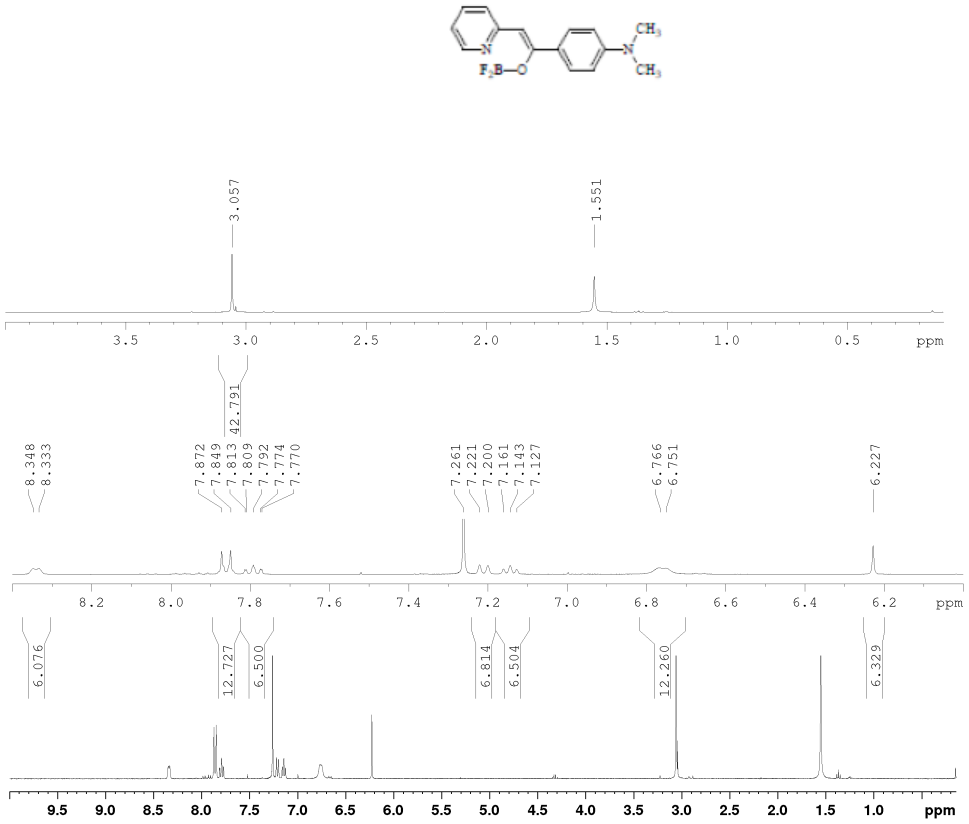


Figure S7. ^{1}H NMR spectrum (400 MHz) of **3** in $CDCl_3$.

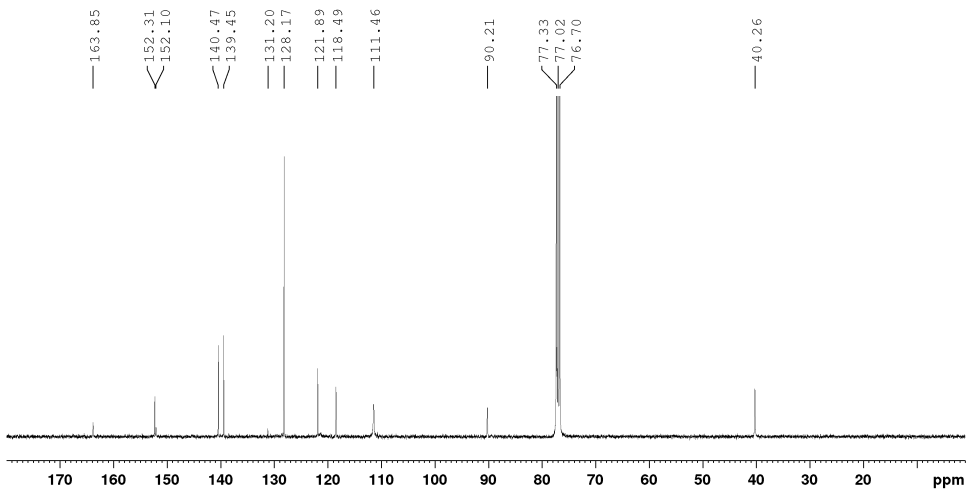


Figure S8. ^{13}C NMR spectrum (400 MHz) of **3** in $CDCl_3$.

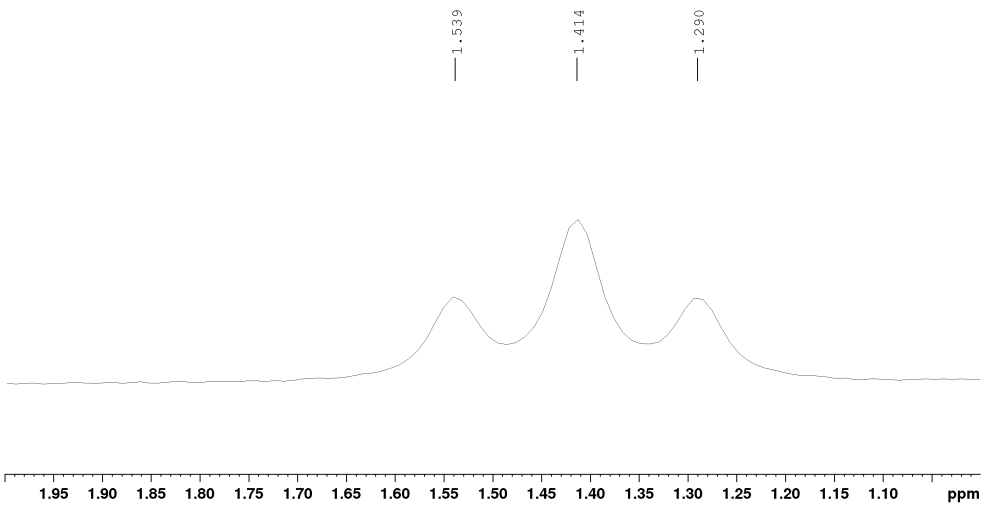


Figure S9. ^{11}B NMR spectrum (400 MHz) of **3** in $CDCl_3$.

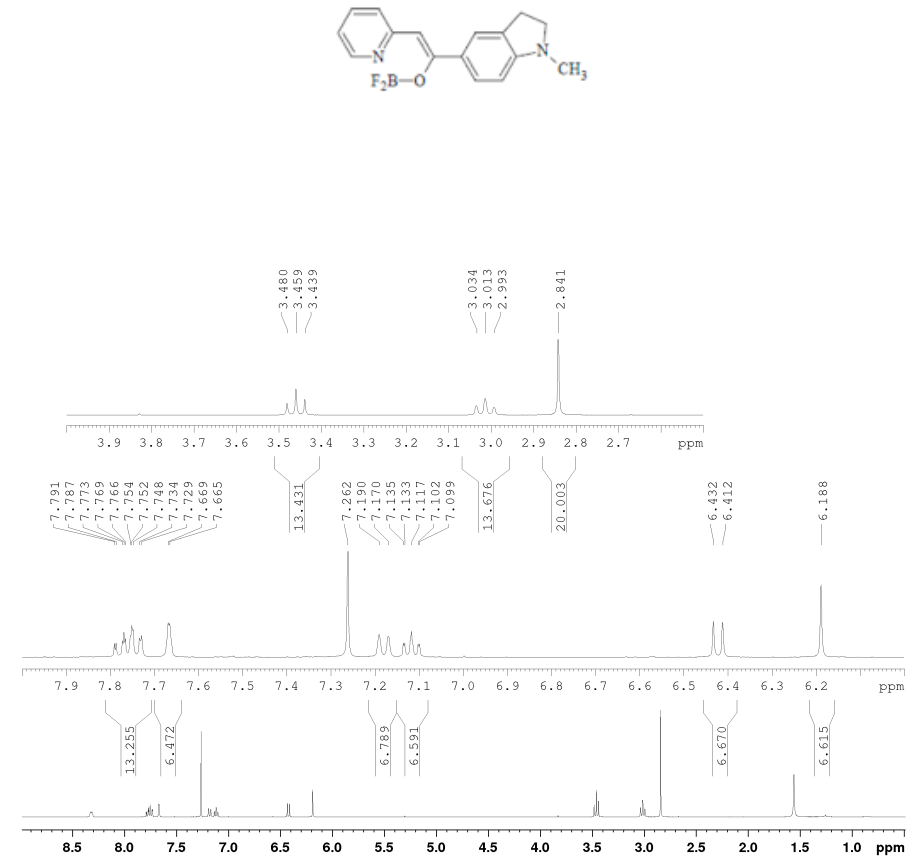


Figure S10. ^{1}H NMR spectrum (400 MHz) of **4** in $CDCl_3$.

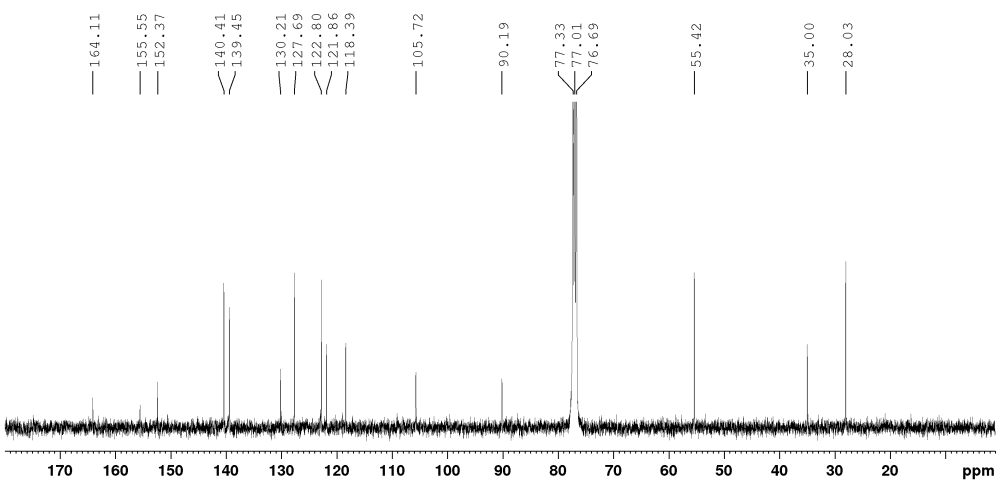


Figure S11. ^{13}C NMR spectrum (400 MHz) of **4** in $CDCl_3$.

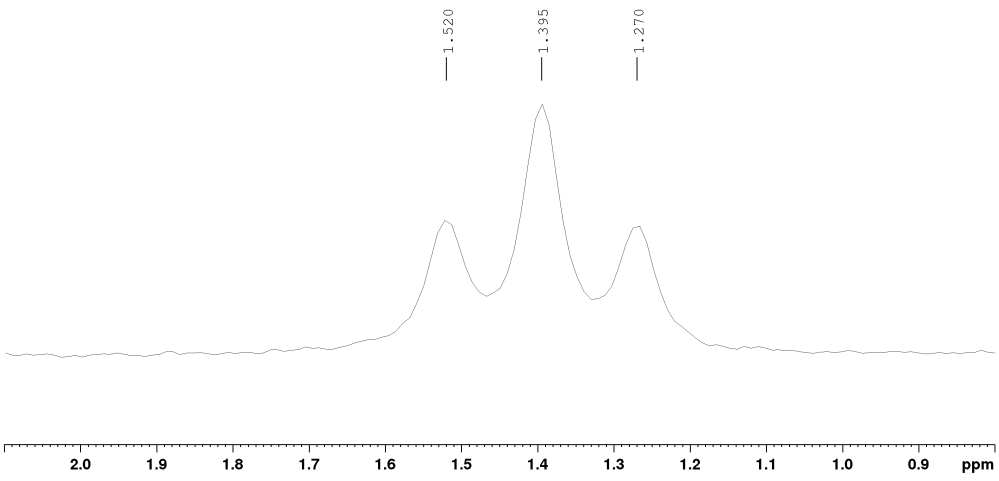


Figure S12. ^{11}B NMR spectrum (400 MHz) of **4** in $CDCl_3$.

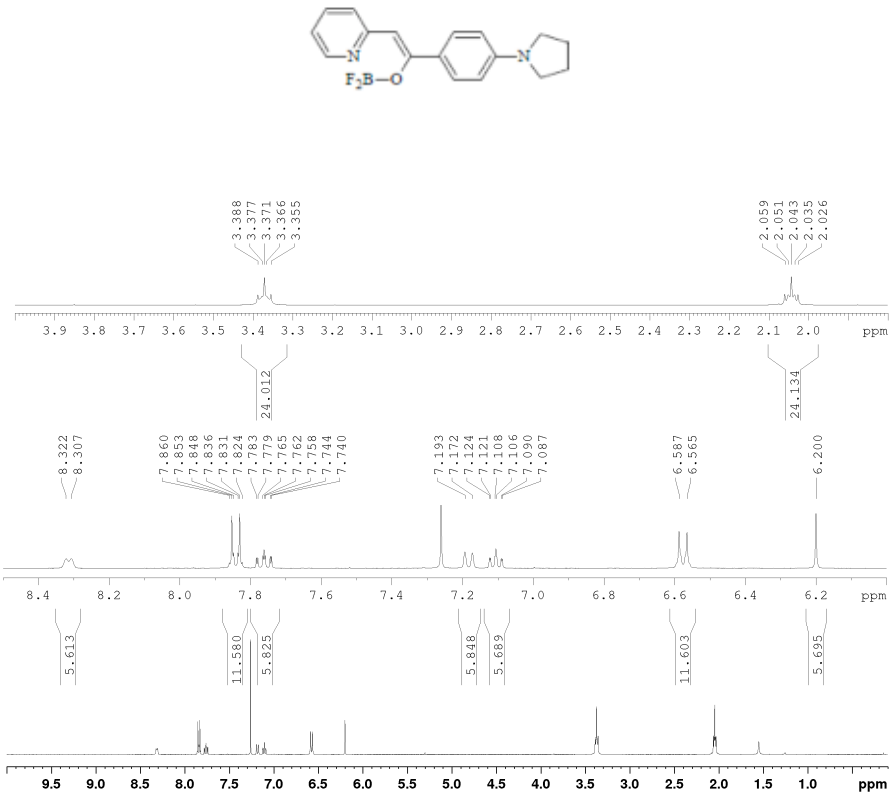


Figure S13. ^{1}H NMR spectrum (400 MHz) of **5** in $CDCl_3$.

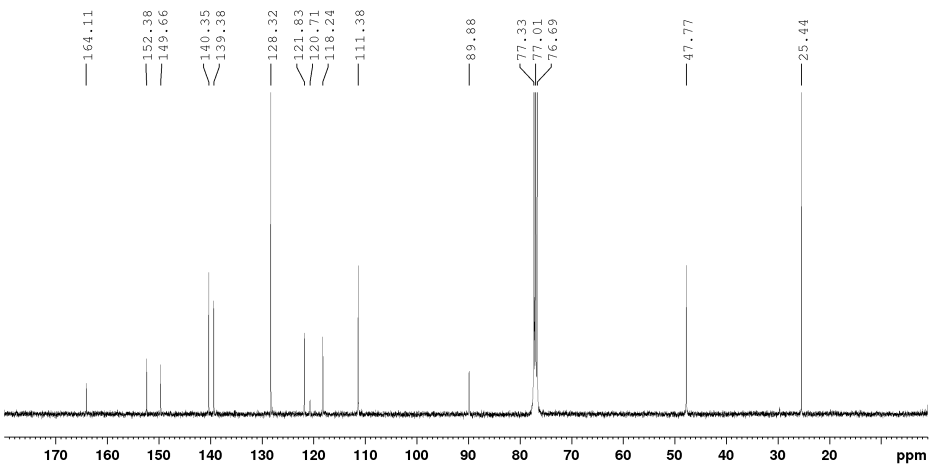


Figure S14. ^{13}C NMR spectrum (400 MHz) of **5** in $CDCl_3$.

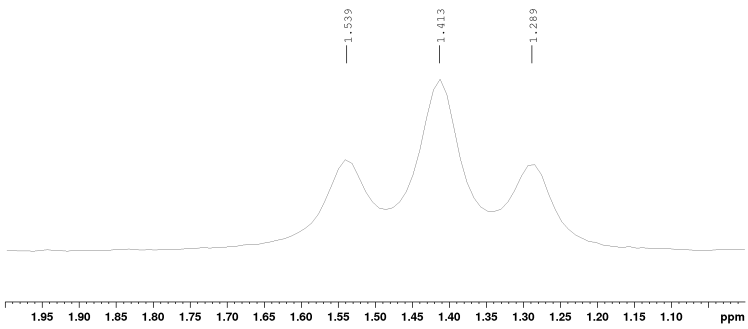


Figure S15. ^{11}B NMR spectrum (400 MHz) of **5** in $CDCl_3$.

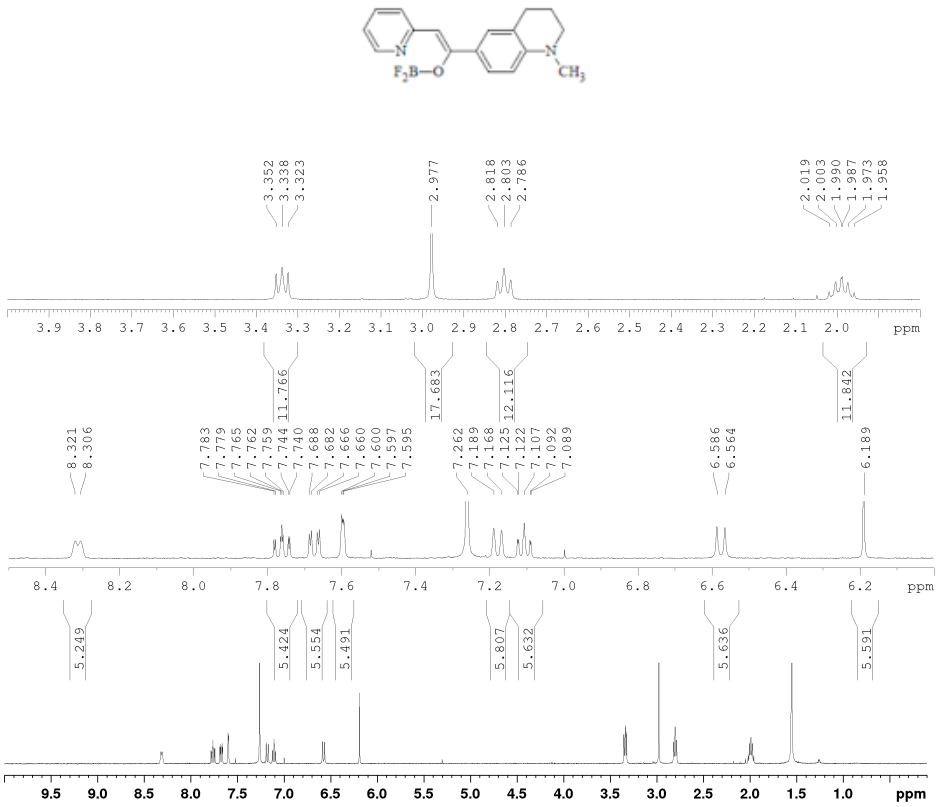


Figure S16. ^{1}H NMR spectrum (400 MHz) of **6** in $CDCl_3$.

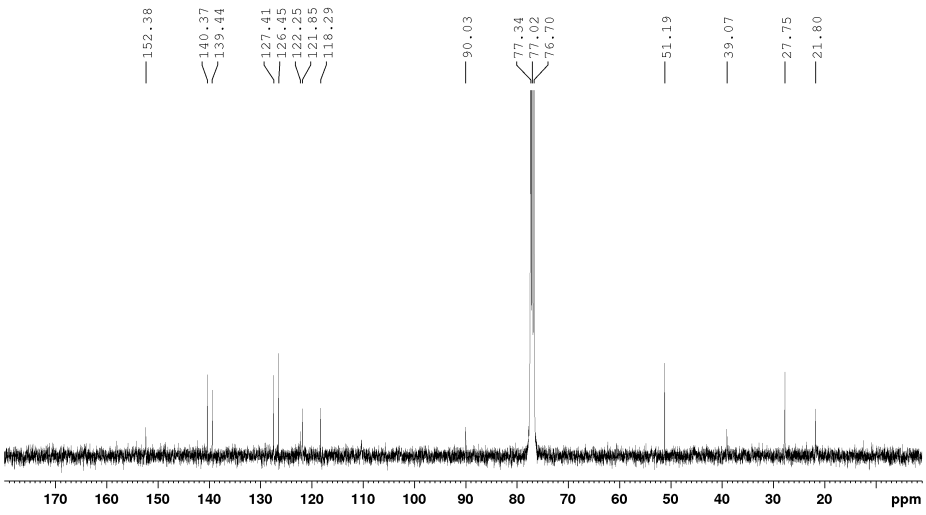


Figure S17. ^{13}C NMR spectrum (400 MHz) of **6** in $CDCl_3$.

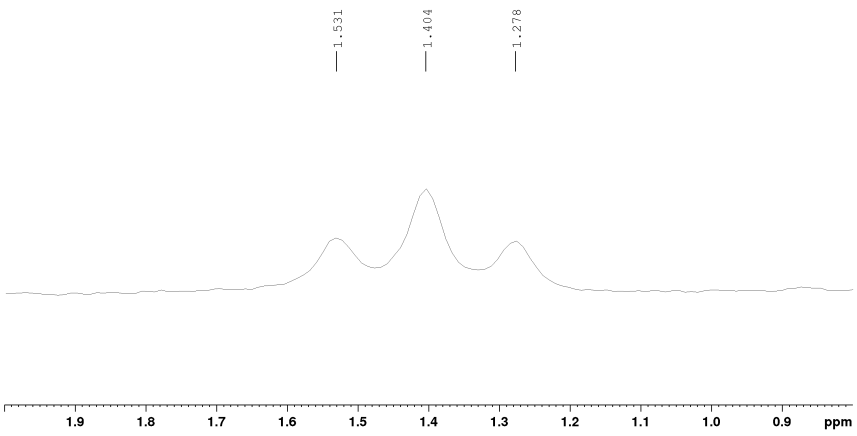


Figure S18. ^{11}B NMR spectrum (400 MHz) of **6** in $CDCl_3$.

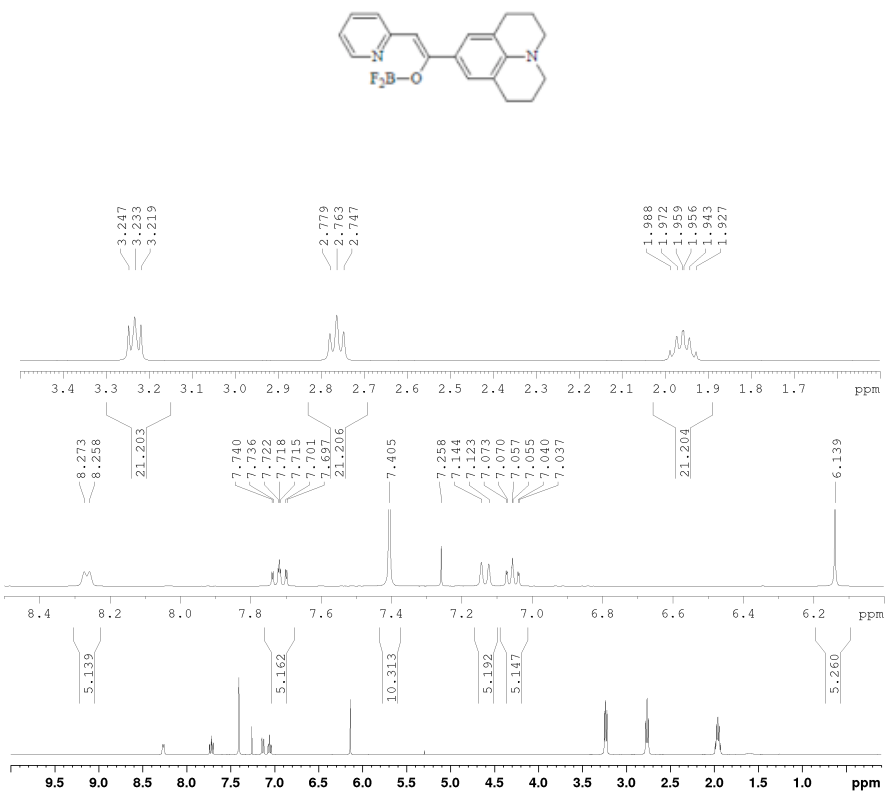


Figure S19. ^{1}H NMR spectrum (400 MHz) of **7** in $CDCl_3$.

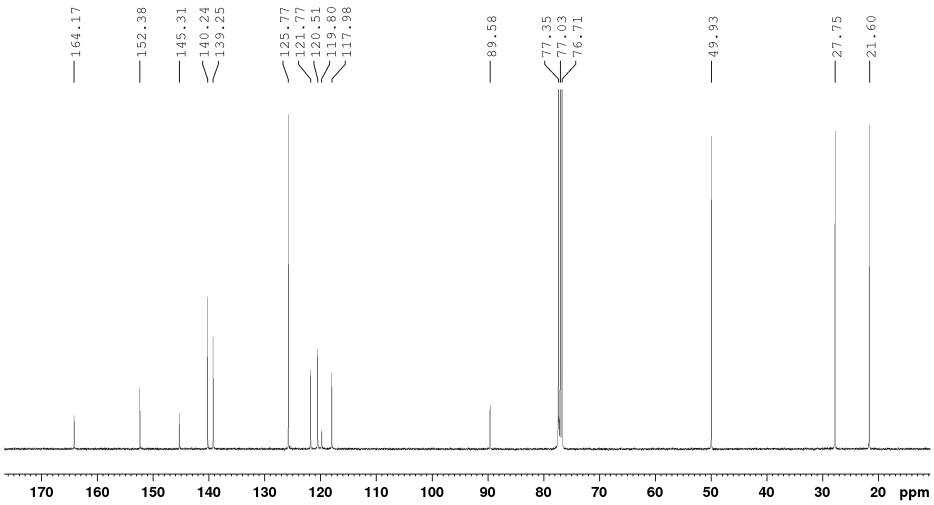


Figure S20. ^{13}C NMR spectrum (400 MHz) of **7** in $CDCl_3$.

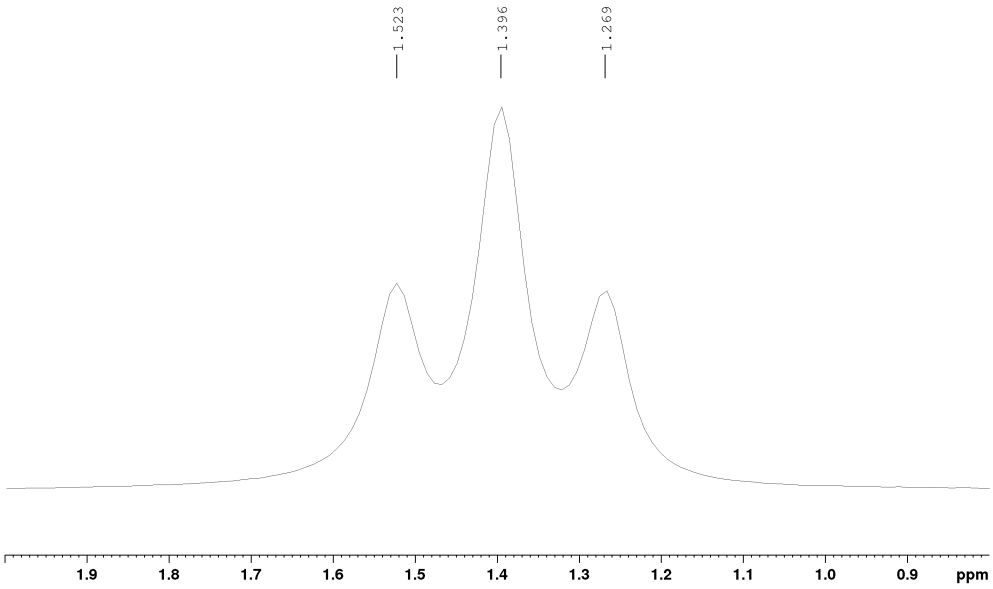


Figure S21. ^{11}B NMR spectrum (400 MHz) of **7** in $CDCl_3$.

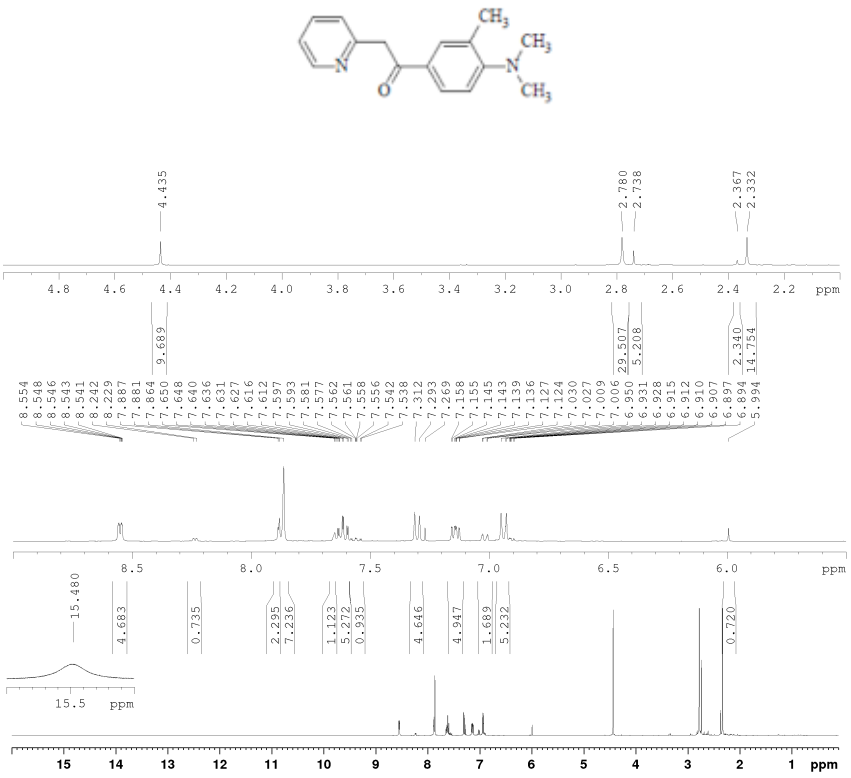


Figure S22. ^{1}H NMR spectrum (400 MHz) of precursor of **1** in $CDCl_3$.

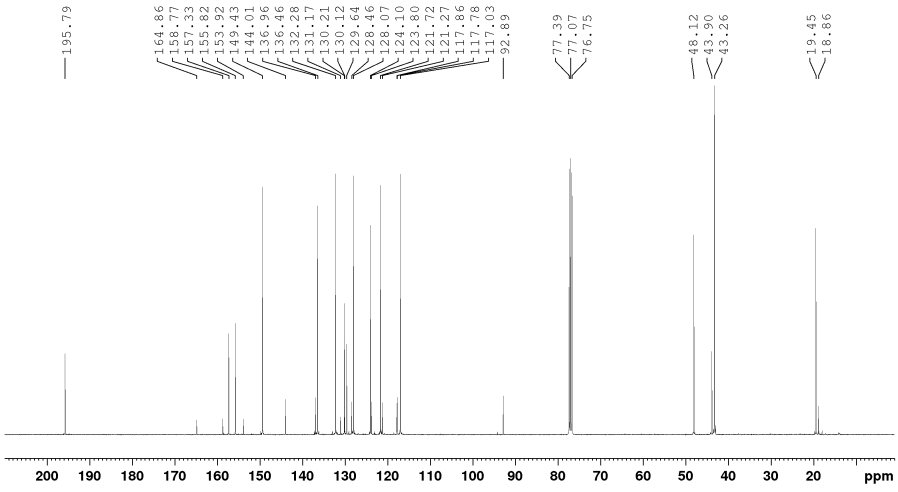


Figure S23. ^{13}C NMR spectrum (400 MHz) of precursor of **1** in $CDCl_3$.

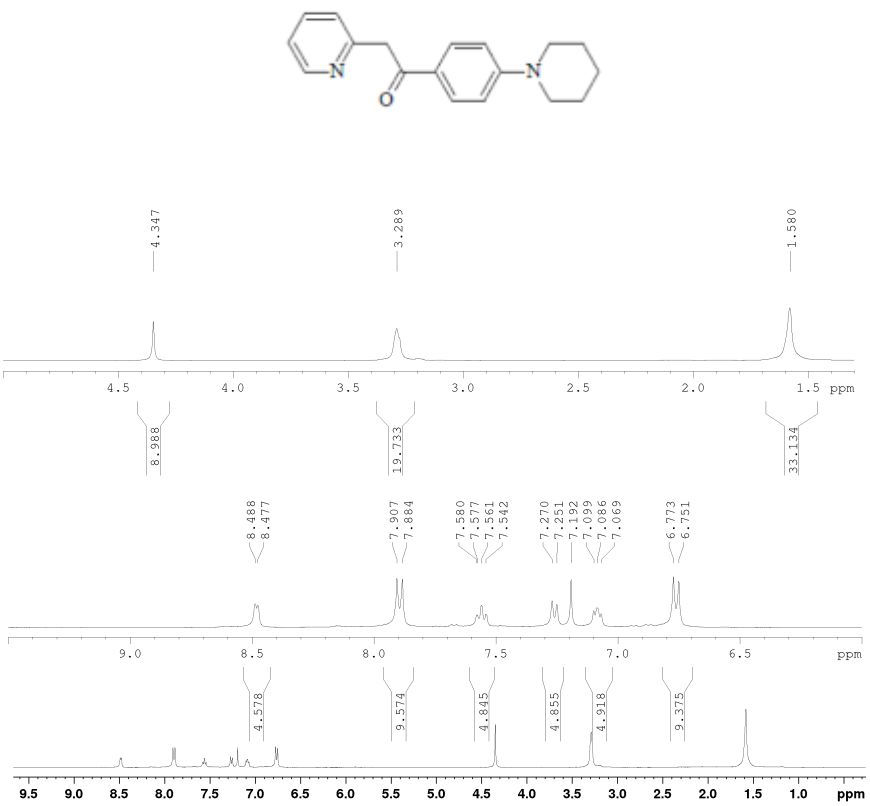


Figure S24. ^{1}H NMR spectrum (400 MHz) of precursor of **2** in $CDCl_3$.

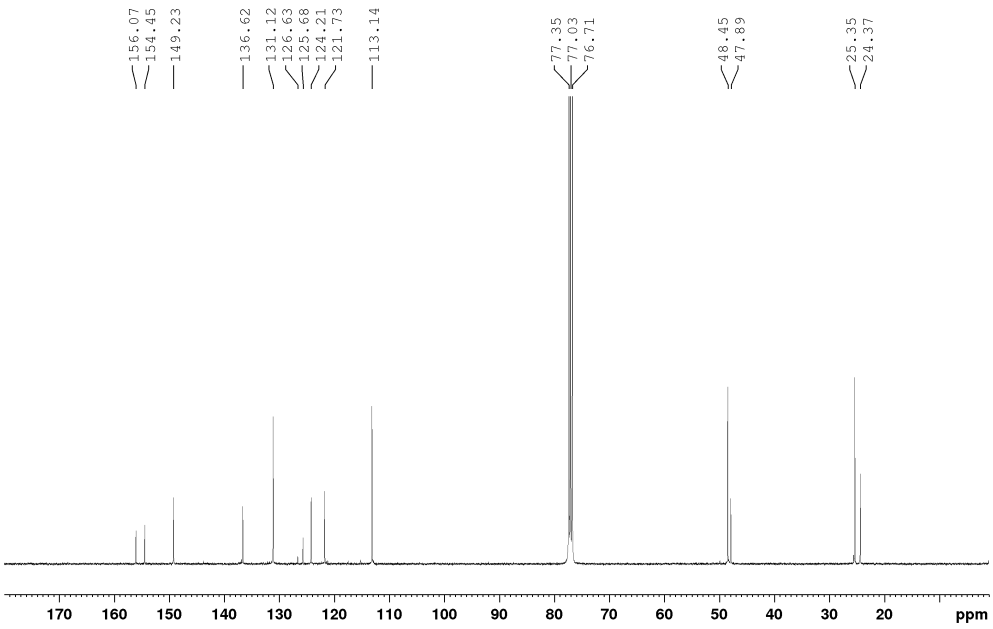


Figure S25. ^{13}C NMR spectrum (400 MHz) of precursor of **2** in $CDCl_3$.

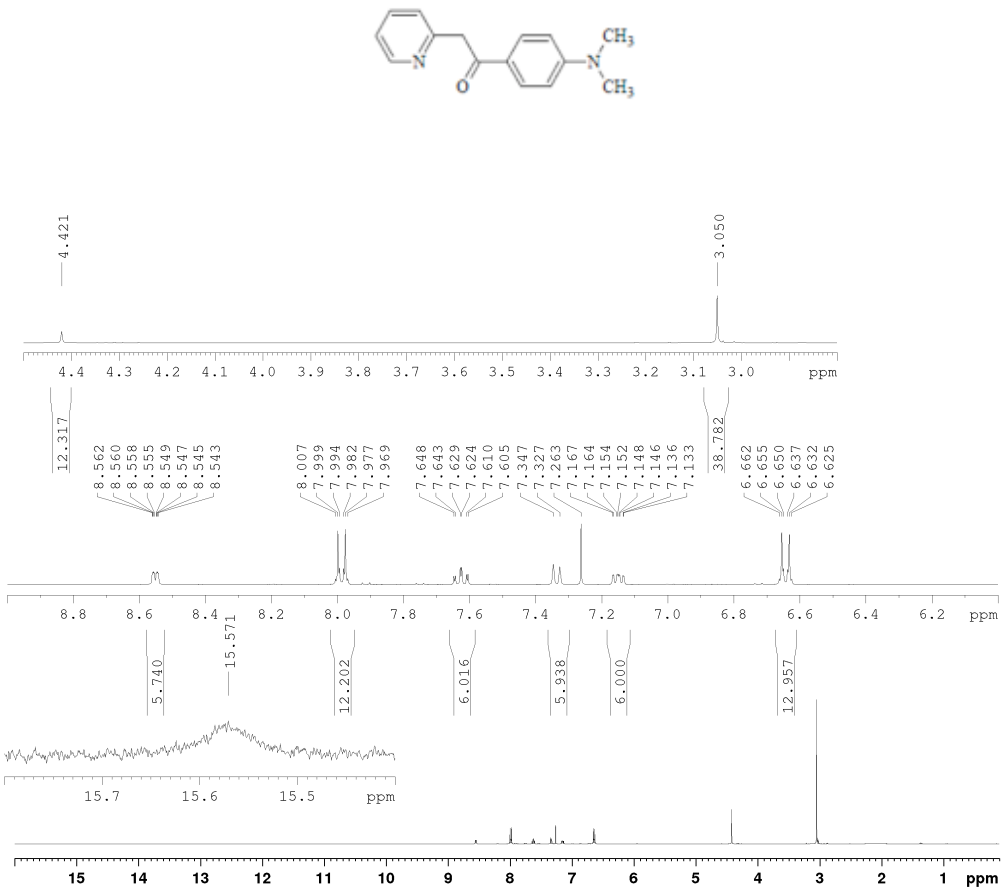


Figure S26. ^{1}H NMR spectrum (400 MHz) of precursor of **3** in $CDCl_3$.

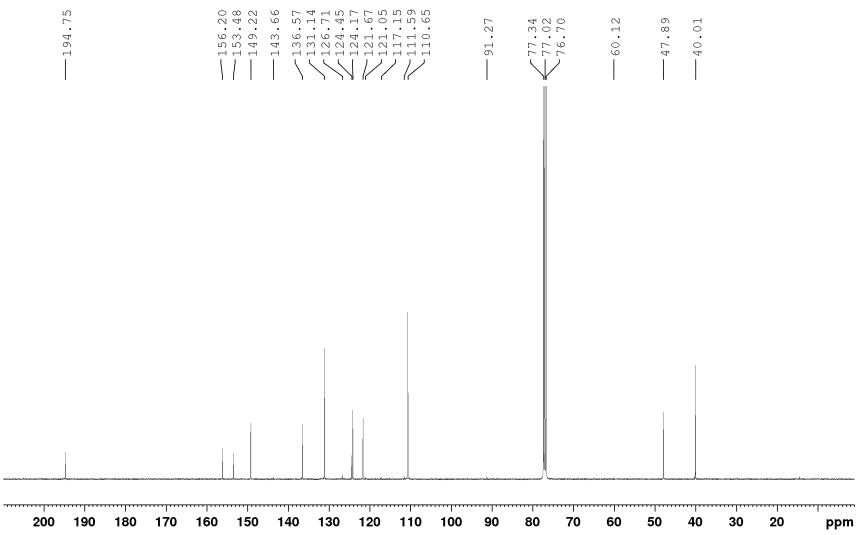


Figure S27. ^{13}C NMR spectrum (400 MHz) of precursor of **3** in $CDCl_3$.

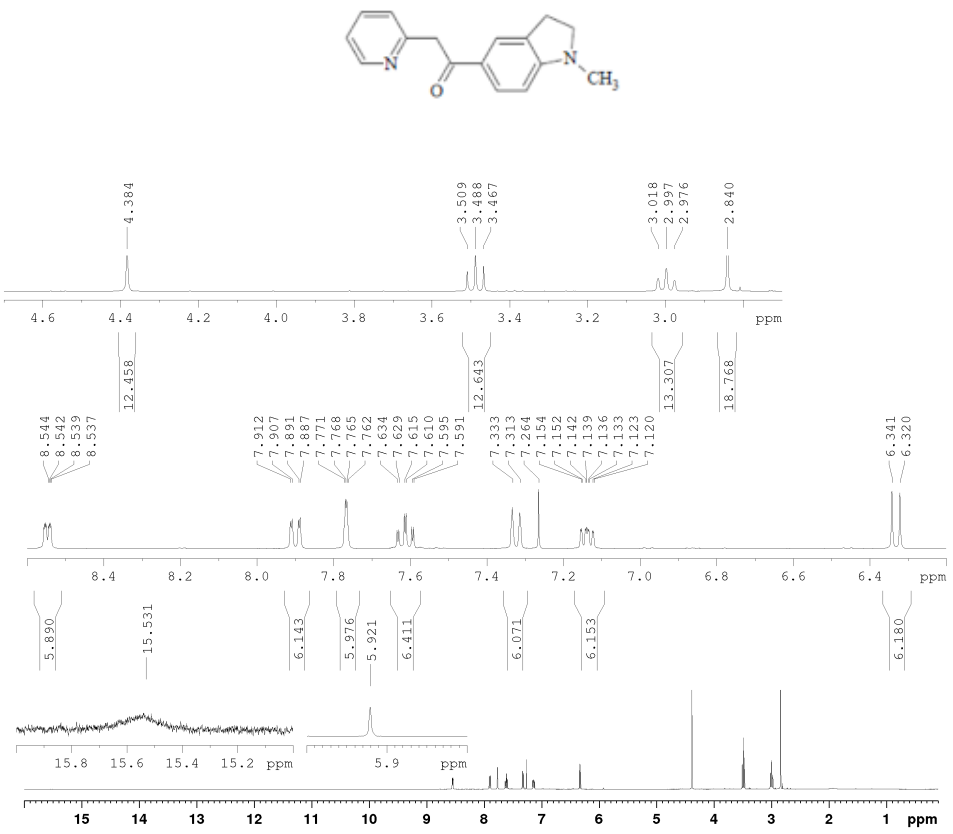


Figure S28. ^{1}H NMR spectrum (400 MHz) of precursor of **4** in $CDCl_3$.

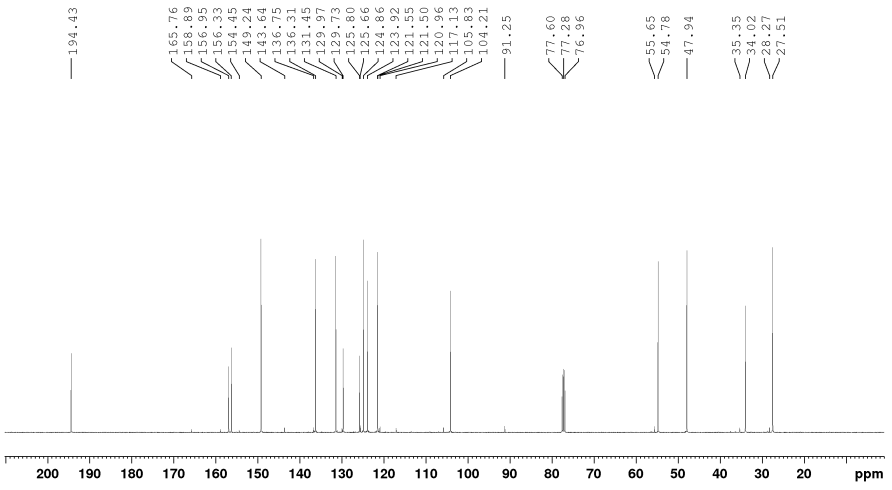


Figure S29. ^{13}C NMR spectrum (400 MHz) of precursor of **4** in $CDCl_3$.

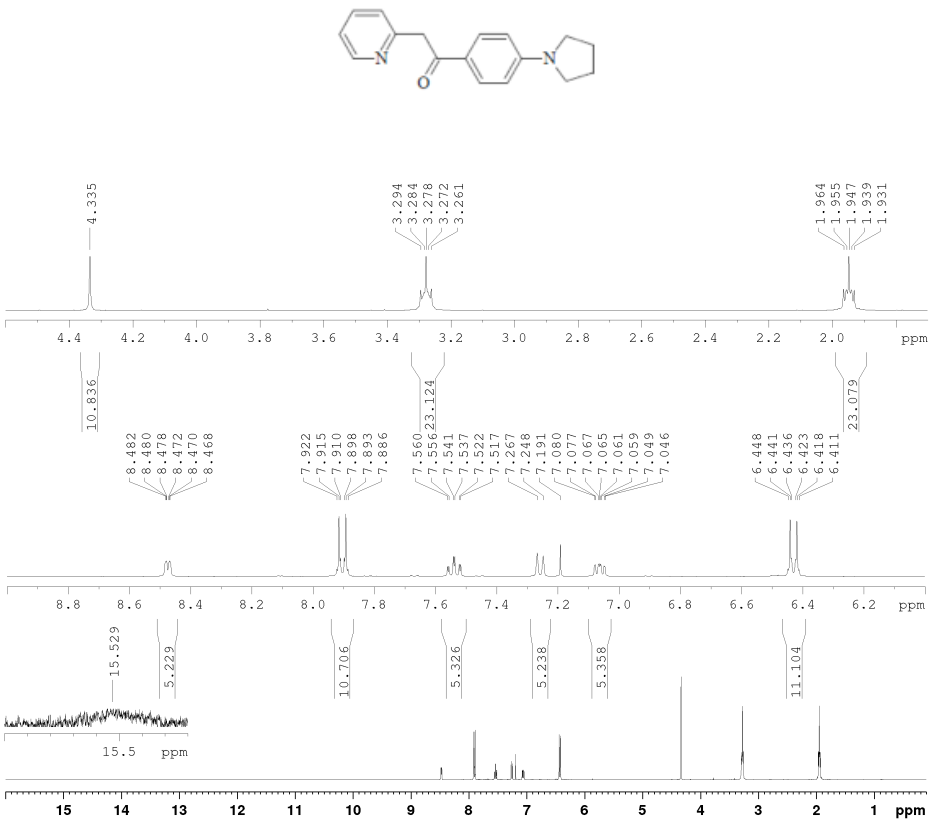


Figure S30. ^{1}H NMR spectrum (400 MHz) of precursor of **5** in $CDCl_3$.

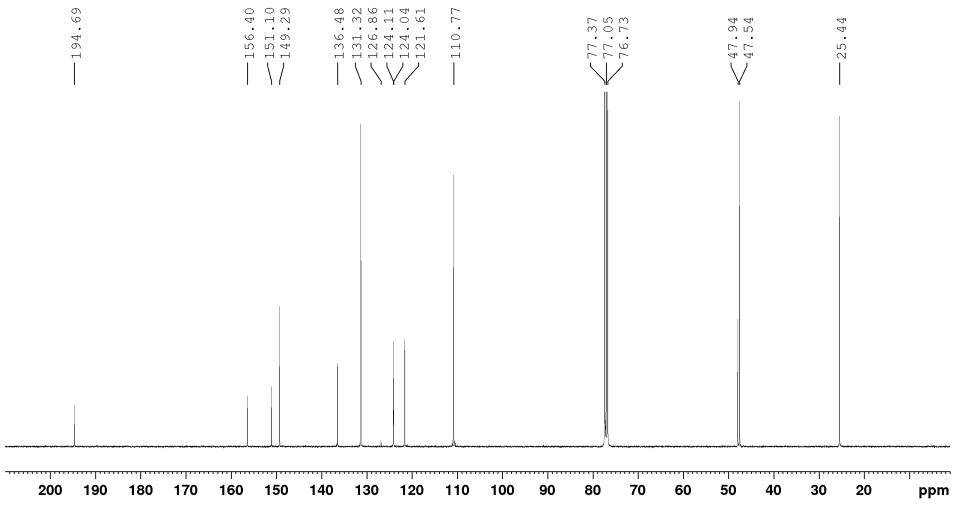


Figure S31. ^{13}C NMR spectrum (400 MHz) of precursor of **5** in $CDCl_3$.

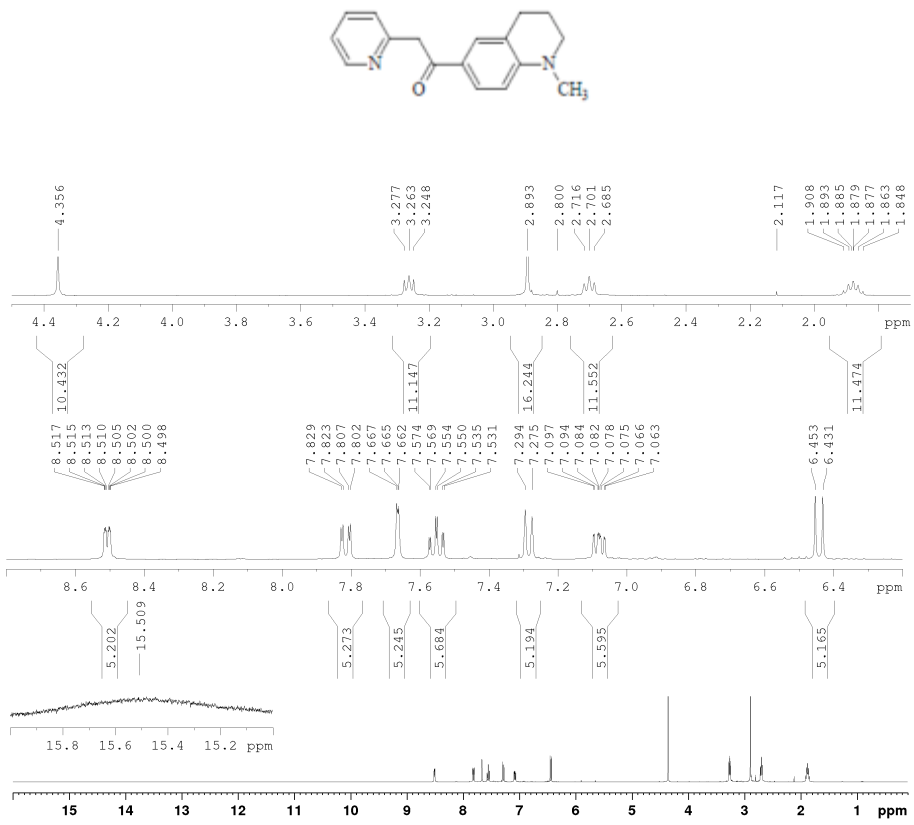


Figure S32. ^{1}H NMR spectrum (400 MHz) of precursor of **6** in $CDCl_3$.

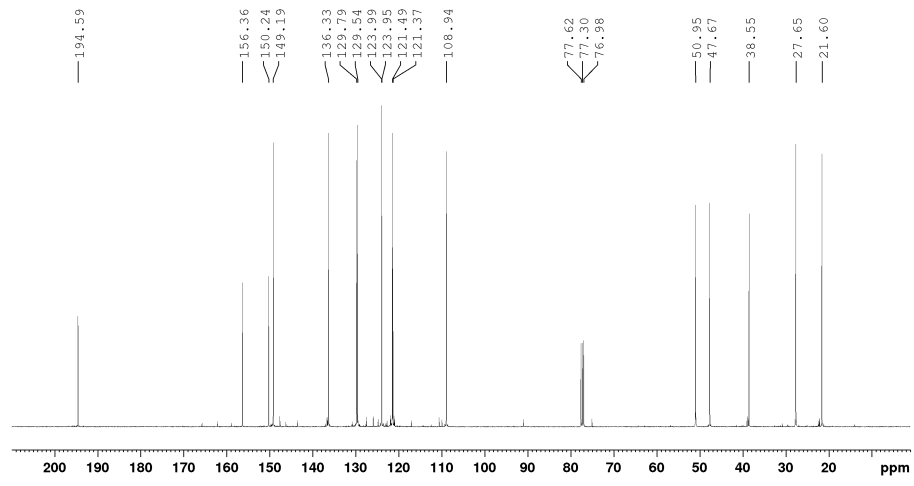


Figure S33. ^{13}C NMR spectrum (400 MHz) of precursor of **6** in $CDCl_3$.

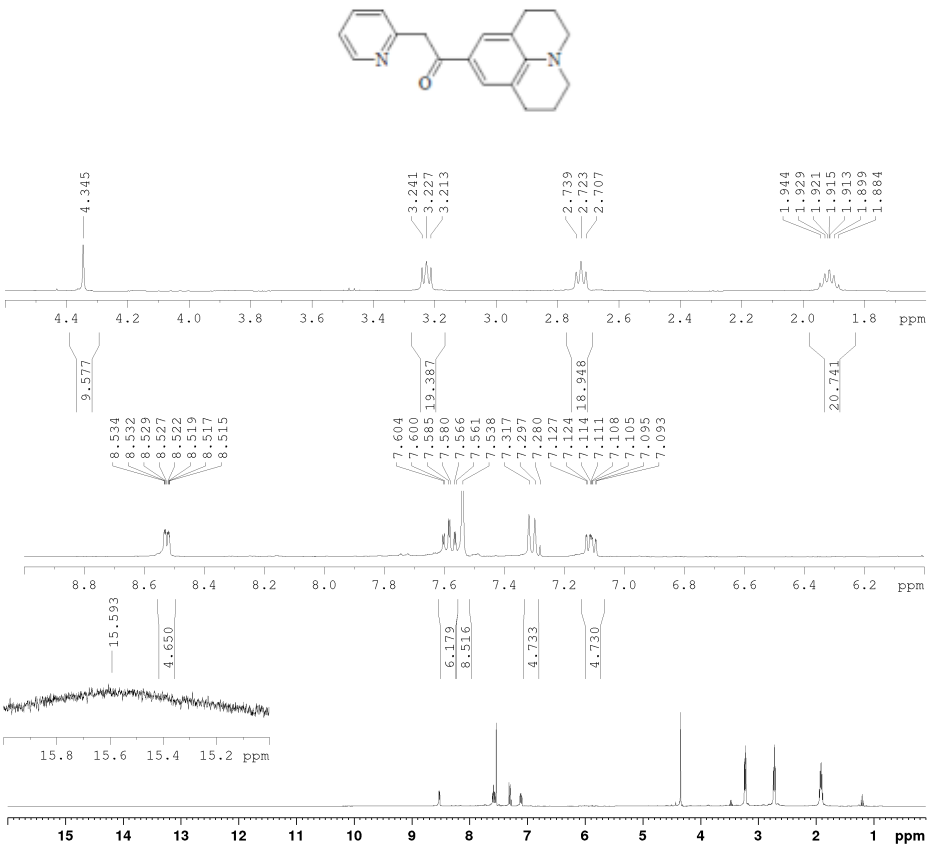


Figure S34. ^{1}H NMR spectrum (400 MHz) of precursor of **7** in $CDCl_3$.

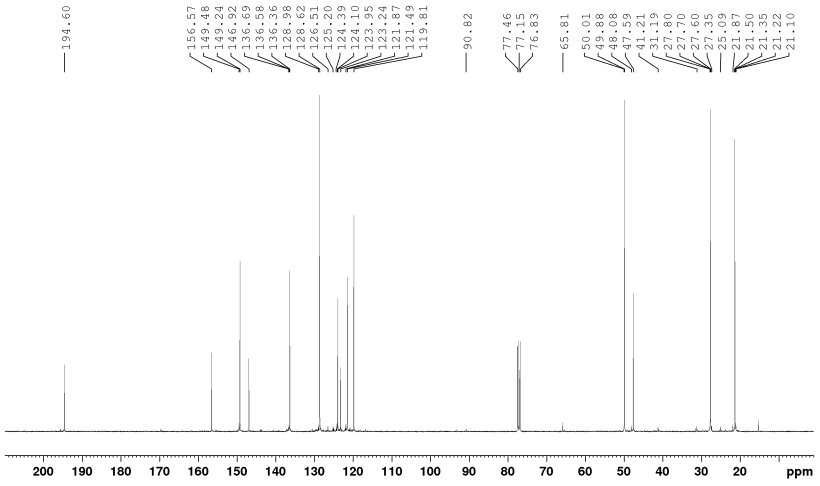
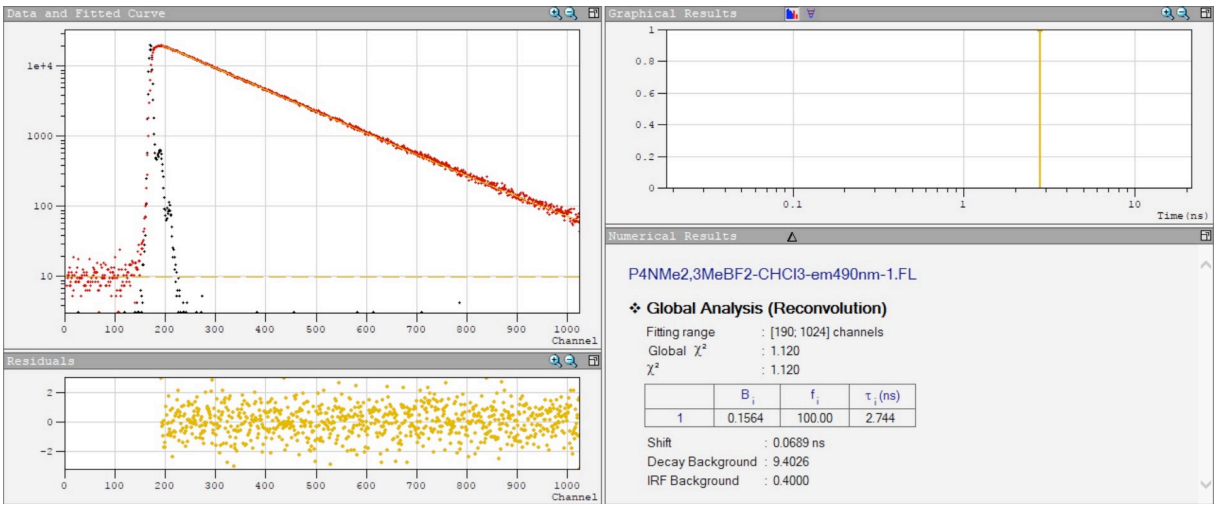
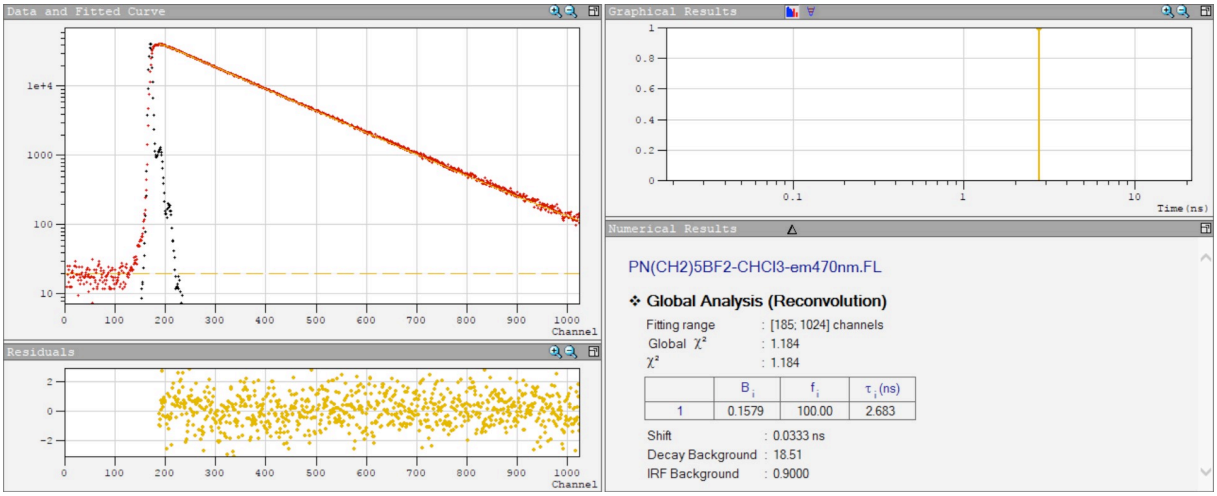


Figure S35. ^{13}C NMR spectrum (400 MHz) of precursor of **7** in $CDCl_3$.

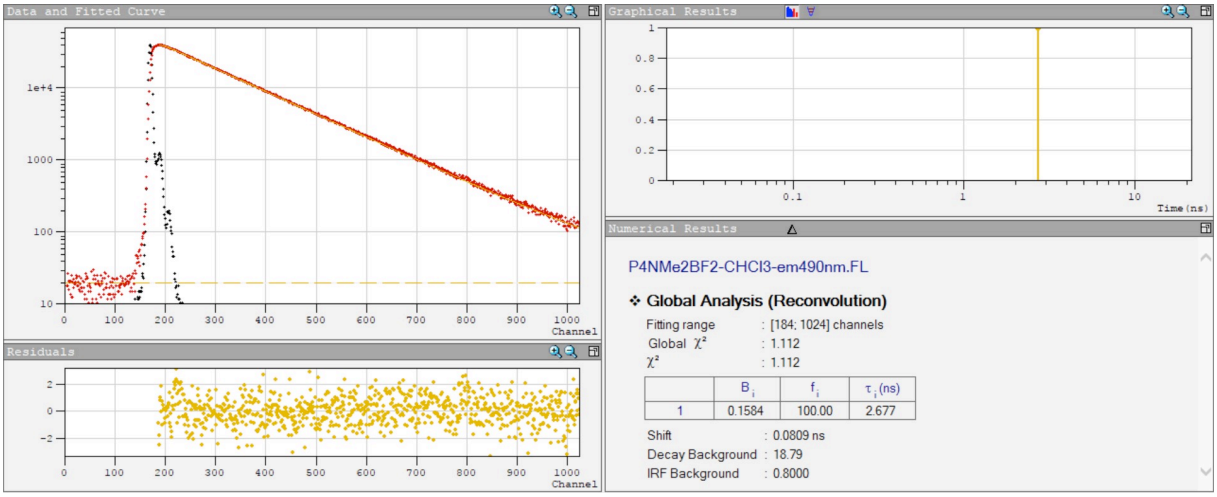
Fluorescence decay curves recorded in $CHCl_3$; Ex = 373 nm



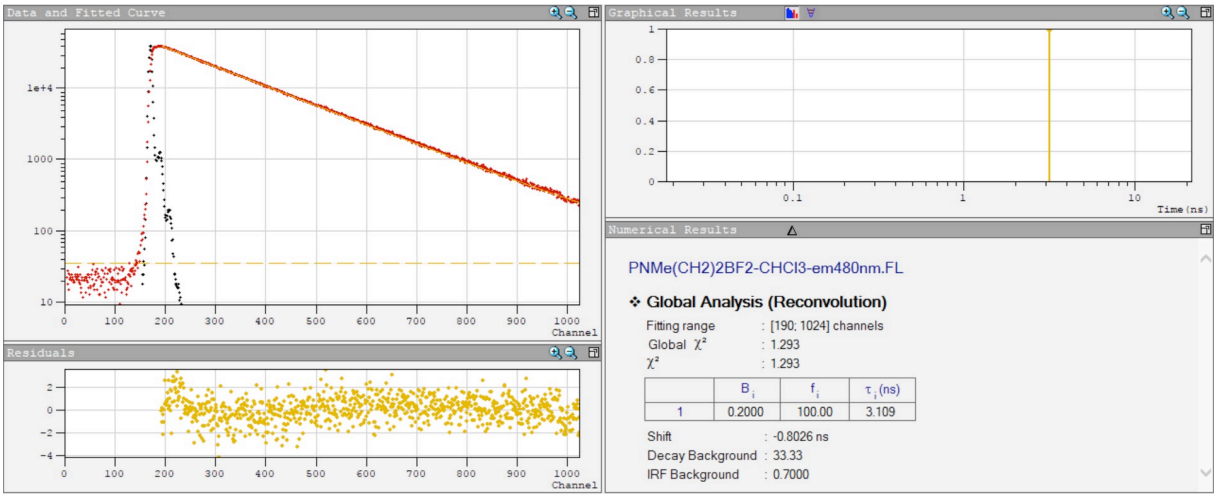
Compound **1**



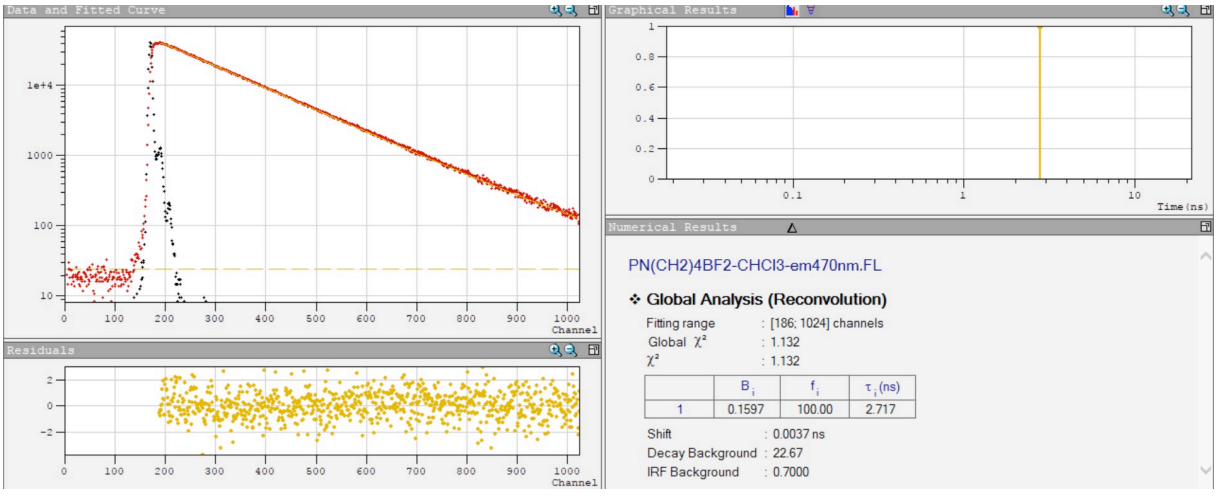
Compound **2**



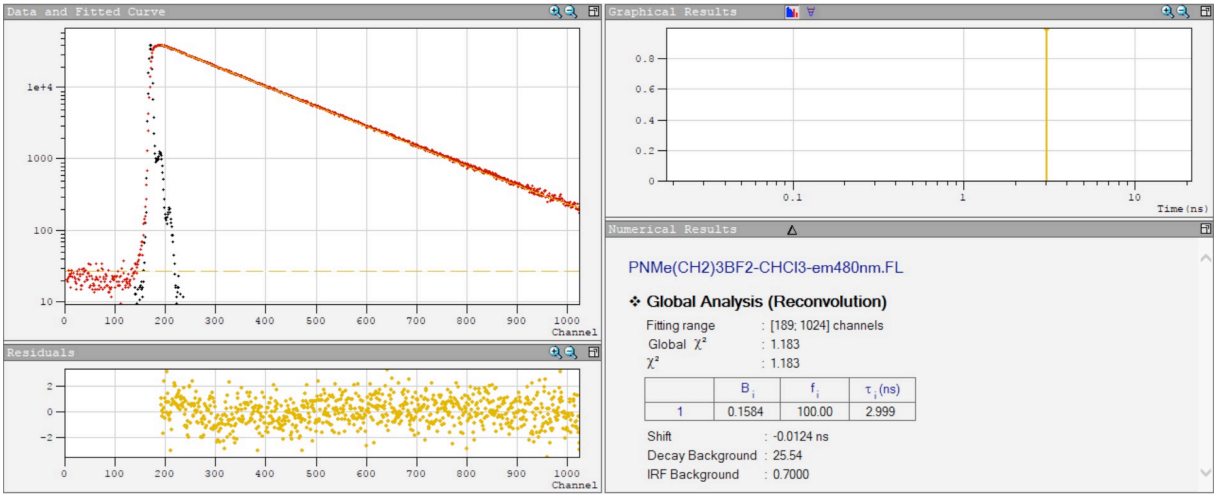
Compound **3**



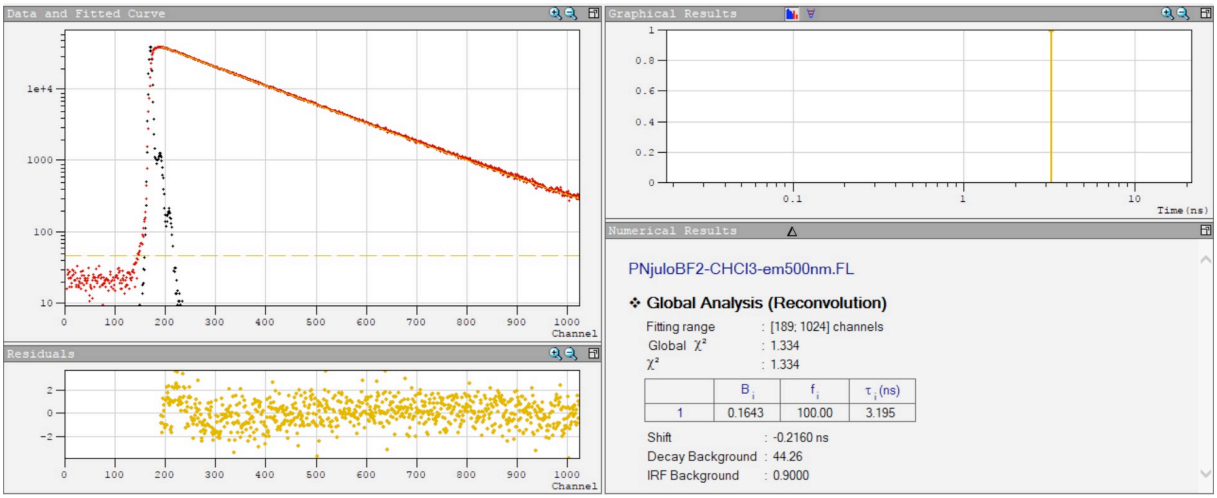
Compound **4**



Compound **5**



Compound **6**



Compound **7**

DFT Cartesian coordinates for all compounds (All data in Å).

Compound **1 (Ground-state)**

6	5.5443900	0.8142750	0.2820840
6	4.7291160	-0.2930440	0.2893670
6	2.8052680	0.9972310	-0.1635980
6	3.6036290	2.1572310	-0.1968230
6	4.9613460	2.0640230	0.0208700
1	6.6057390	0.7091730	0.4668760
1	5.0938970	-1.2969240	0.4708160
6	1.3795810	1.0256530	-0.3036190
1	3.1250970	3.1123940	-0.3801040
1	5.5766930	2.9575290	-0.0016630
6	0.6232850	-0.0668980	0.0120710
1	0.9129740	1.9618560	-0.5766830
5	2.5410170	-1.5338100	-0.0974100
7	3.4046170	-0.1994750	0.0568010
8	1.1774840	-1.2325410	0.3240030
9	2.5839730	-1.8919770	-1.4303530
9	3.0934770	-2.4923700	0.7190170
6	-0.8486170	-0.0554390	0.0618800
6	-1.5775140	1.1348700	0.1807250
6	-1.5510930	-1.2606940	0.0091870
6	-2.9660060	1.1557880	0.2139460
1	-1.0500960	2.0775660	0.3024670
6	-2.9388680	-1.2640830	0.0319380
1	-1.0033090	-2.1932980	-0.0677790
6	-3.6685140	-0.0701770	0.1166450
1	-3.4616720	-2.2117540	-0.0310670
6	-3.6833710	2.4635510	0.4327600
1	-3.0597890	3.1416790	1.0210720
1	-3.9144250	2.9723770	-0.5100250
1	-4.6259100	2.3003630	0.9622380
7	-5.0801670	-0.0643420	0.1648920
6	-5.7335620	0.5387190	-0.9940090
1	-5.6948700	-0.1280800	-1.8703400
1	-6.7822360	0.7359610	-0.7534330
1	-5.2581230	1.4817190	-1.2618000
6	-5.7207500	-1.3181540	0.5228280
1	-5.6789960	-2.0712670	-0.2814150
1	-5.2543320	-1.7333990	1.4189850
1	-6.7737270	-1.1178000	0.7395380

Compound **1 (Excited-state)**

6	-5.5724680	0.7790270	-0.2442150
6	-4.7489310	-0.3237360	-0.2050050
6	-2.8039980	1.0215590	0.0051490
6	-3.6250610	2.1769190	0.0054730
6	-4.9905950	2.0682020	-0.1172650
1	-6.6412070	0.6493860	-0.3614820
1	-5.1305220	-1.3368940	-0.2745600
6	-1.4016730	1.0644140	0.0352560
1	-3.1431840	3.1464840	0.0851860
1	-5.6141660	2.9555450	-0.1226500
6	-0.6033390	-0.0968280	-0.1275940
1	-0.9318690	2.0318720	0.1538970

5	-2.5379870	-1.5089800	0.2193920
7	-3.4134930	-0.2293830	-0.0703030
8	-1.1939210	-1.2844710	-0.3151560
9	-2.4882280	-1.6946310	1.5954180
9	-3.1195220	-2.5859930	-0.4192390
6	0.8175950	-0.0725290	-0.1396430
6	1.5848730	1.1288260	-0.0692920
6	1.5439950	-1.2937600	-0.2606590
6	2.9609160	1.1442850	-0.0549330
1	1.0775600	2.0882050	-0.0764640
6	2.9124800	-1.3039200	-0.2503640
1	0.9892520	-2.2214800	-0.3329490
6	3.6672490	-0.1040850	-0.1001480
1	3.4333250	-2.2534840	-0.2985580
6	3.6766350	2.4726980	-0.1296000
1	3.0220300	3.2138680	-0.5939480
1	3.9621250	2.8613310	0.8531460
1	4.5846360	2.3968560	-0.7345100
7	5.0354010	-0.1620960	-0.0500210
6	5.8176460	0.6508270	0.8725510
1	6.4074110	-0.0155700	1.5140800
1	6.5063150	1.3169010	0.3414390
1	5.1633820	1.2370800	1.5137200
6	5.7411060	-1.3300890	-0.5446700
1	5.7738470	-2.1402380	0.1982760
1	5.2715900	-1.6970130	-1.4583680
1	6.7685780	-1.0370740	-0.7755480

Compound **2 (Ground-state)**

6	6.3620990	0.7604000	0.4261500
6	5.5223320	-0.3229090	0.3283470
6	3.6358800	1.0445000	-0.0626480
6	4.4637600	2.1843520	0.0120020
6	5.8123260	2.0413660	0.2505890
1	7.4161790	0.6159180	0.6252390
1	5.8597540	-1.3466290	0.4378200
6	2.2187240	1.1197140	-0.2318610
1	4.0114200	3.1623340	-0.1062010
1	6.4479100	2.9188790	0.3111380
6	1.4250540	0.0239860	-0.0187360
1	1.7835960	2.0880940	-0.4353420
5	3.3159940	-1.4724800	-0.2072280
7	4.2054510	-0.1800010	0.0749740
8	1.9516270	-1.1742540	0.2113850
9	3.3791930	-1.7213460	-1.5650140
9	3.8272120	-2.5114670	0.5361630
6	-0.0399050	0.0645090	0.0111600
6	-0.7740040	-1.1266810	-0.0755760
6	-0.7584480	1.2635560	0.1270270
6	-2.1569350	-1.1278080	-0.0691680
1	-0.2393520	-2.0655000	-0.1717110
6	-2.1401540	1.2804370	0.1401760
1	-0.2312020	2.2052730	0.2461720
6	-2.8846360	0.0804110	0.0362930
1	-2.6516850	2.2257560	0.2772710

1	-2.6809610	-2.0693470	-0.1831190
6	-5.0181360	-1.1318300	0.2758370
6	-5.0034290	1.3222020	-0.1913280
6	-6.3545700	-0.7916550	0.9317390
1	-4.4431820	-1.7778700	0.9452180
1	-5.1789690	-1.6884930	-0.6609150
6	-6.3381260	0.9967570	-0.8585020
1	-5.1665610	1.8801410	0.7442770
1	-4.4164790	1.9625010	-0.8557530
6	-7.2197630	0.1067740	0.0328190
1	-6.1401880	-0.2826060	1.8781580
1	-6.8795610	-1.7182850	1.1806600
1	-6.1211660	0.4859940	-1.8033800
1	-6.8514050	1.9290130	-1.1110470
1	-7.8726900	-0.5047310	-0.5978860
1	-7.8723830	0.7245080	0.6577870
7	-4.2534680	0.0911900	0.0450840

Compound **2 (Excited-state)**

6	-6.3815740	0.7308550	-0.3665650
6	-5.5323060	-0.3464980	-0.2526780
6	-3.6282910	1.0586360	-0.0574910
6	-4.4769930	2.1898680	-0.1360170
6	-5.8361300	2.0401860	-0.2884350
1	-7.4432440	0.5673250	-0.5043080
1	-5.8866160	-1.3714590	-0.2823110
6	-2.2278240	1.1386090	0.0079760
1	-4.0216540	3.1745040	-0.0920600
1	-6.4811790	2.9095900	-0.3531300
6	-1.3980620	-0.0072040	-0.0781750
1	-1.7856130	2.1227510	0.0893650
5	-3.3046130	-1.4514100	0.2856800
7	-4.2032390	-0.2112040	-0.0884390
8	-1.9533310	-1.2188050	-0.2254110
9	-3.2875350	-1.5699540	1.6704710
9	-3.8425380	-2.5735840	-0.3135820
6	0.0219420	0.0540590	-0.0597520
6	0.7830010	-1.1525550	-0.1237210
6	0.7602850	1.2754400	0.0122930
6	2.1519180	-1.1463210	-0.1154570
1	0.2464290	-2.0931620	-0.1612400
6	2.1306320	1.2890360	0.0248580
1	0.2410800	2.2267110	0.0416240
6	2.8839320	0.0786510	-0.0398960
1	2.6435520	2.2431120	0.0420650
1	2.6814660	-2.0915120	-0.1236410
6	5.0204840	-1.0920440	-0.4090360
6	4.9936920	1.2846200	0.3606630
6	6.3524940	-0.6629320	-1.0200210
1	4.4481830	-1.6586620	-1.1464730
1	5.1842580	-1.7440400	0.4621650
6	6.3297560	0.8813960	0.9803040
1	5.1503250	1.9428610	-0.5074400
1	4.4040710	1.8371780	1.0955060
6	7.2157770	0.1185740	-0.0171850

1	6.1348840	-0.0443760	-1.8975890
1	6.8765000	-1.5521970	-1.3807620
1	6.1183470	0.2573460	1.8554530
1	6.8333320	1.7804100	1.3460170
1	7.8730530	-0.5637100	0.5301270
1	7.8620640	0.8147400	-0.5601350
7	4.2410570	0.0894440	-0.0287520

Compound **3 (Ground-state)**

6	5.3717450	0.7497490	0.3636430
6	4.5197760	-0.3284900	0.3522750
6	2.6490960	1.0242460	-0.1488000
6	3.4894690	2.1570620	-0.1645050
6	4.8363860	2.0186540	0.0862530
1	6.4241280	0.6097820	0.5745710
1	4.8457090	-1.3438330	0.5437950
6	1.2326180	1.1019460	-0.3249830
1	3.0481290	3.1275110	-0.3607370
1	5.4816440	2.8911620	0.0777430
6	0.4267450	0.0361730	-0.0260240
1	0.8085730	2.0558890	-0.6054290
5	2.3006580	-1.4936250	-0.0863840
7	3.2045430	-0.1915820	0.0873470
8	0.9389430	-1.1453970	0.3012660
9	2.3636260	-1.8591430	-1.4173930
9	2.7989320	-2.4706350	0.7445700
6	-1.0384860	0.0944950	-0.0028830
6	-1.7446550	1.3055650	0.0198380
6	-1.7838670	-1.0923970	0.0040710
6	-3.1264980	1.3378830	0.0294850
1	-1.2082530	2.2488810	0.0561910
6	-3.1667670	-1.0802920	0.0119720
1	-1.2582040	-2.0409930	-0.0039050
6	-3.8814220	0.1402200	0.0173710
1	-3.6973980	-2.0243630	0.0115040
7	-5.2498250	0.1638230	0.0156030
6	-5.9505660	1.4307430	0.0866460
1	-7.0238080	1.2454140	0.0614160
1	-5.7157850	1.9763880	1.0099770
1	-5.6966480	2.0725950	-0.7649940
6	-5.9920410	-1.0794040	0.0908750
1	-5.7771600	-1.7234420	-0.7699180
1	-5.7563800	-1.6389660	1.0053090
1	-7.0586700	-0.8575570	0.0895520
1	-3.6259680	2.2982530	0.0600710

Compound **3 (Excited-state)**

6	-5.3937590	0.7092560	-0.3002840
6	-4.5320890	-0.3640100	-0.2627740
6	-2.6428380	1.0466120	0.0153560
6	-3.5041630	2.1709320	0.0169910
6	-4.8626040	2.0165210	-0.1381510
1	-6.4543790	0.5430210	-0.4428380
1	-4.8757910	-1.3885080	-0.3589690
6	-1.2432990	1.1385540	0.0804200
1	-3.0592240	3.1553630	0.1247930

1	-5.5175290	2.8809130	-0.1414330
6	-0.4001500	0.0103450	-0.0878940
1	-0.8121970	2.1200160	0.2273080
5	-2.2877550	-1.4771020	0.1833140
7	-3.2037080	-0.2251010	-0.0974130
8	-0.9430090	-1.1924160	-0.3208550
9	-2.2553560	-1.6904150	1.5559950
9	-2.8166470	-2.5614330	-0.4883110
6	1.0187350	0.0862660	-0.0643490
6	1.7420810	1.3064320	0.1078450
6	1.7933010	-1.1024050	-0.2262800
6	3.1122440	1.3358420	0.1208840
1	1.2112970	2.2432810	0.2336220
6	3.1621580	-1.0813830	-0.2149540
1	1.2676300	-2.0408420	-0.3569700
6	3.8773510	0.1427140	-0.0402150
1	3.7027670	-2.0116370	-0.3395100
7	5.2335420	0.1686710	-0.0280030
6	5.9407110	1.4254310	0.1527400
1	7.0122780	1.2366850	0.1277630
1	5.6934690	2.1345550	-0.6455660
1	5.6897530	1.8837630	1.1162980
6	5.9923310	-1.0608720	-0.1902420
1	5.7598600	-1.7754380	0.6074590
1	5.7758340	-1.5328360	-1.1553520
1	7.0550270	-0.8295990	-0.1486530
1	3.6131820	2.2863320	0.2565080

Compound **4 (Ground-state)**

6	5.4604880	0.9227460	0.2651520
6	4.6752760	-0.2049250	0.2944080
6	2.7141610	1.0244840	-0.1756850
6	3.4832610	2.2050560	-0.2327300
6	4.8426000	2.1520190	-0.0174700
1	6.5246840	0.8497180	0.4488730
1	5.0670060	-1.1954450	0.4926280
6	1.2906590	1.0139370	-0.3135750
1	2.9791950	3.1437780	-0.4322280
1	5.4337310	3.0611550	-0.0582090
6	0.5590650	-0.0929660	0.0221200
1	0.8032030	1.9358140	-0.5978620
5	2.5194540	-1.5082230	-0.0663350
7	3.3476950	-0.1515380	0.0638530
8	1.1498340	-1.2358920	0.3534560
9	2.5691260	-1.8893210	-1.3934130
9	3.0973130	-2.4401330	0.7644310
6	-0.9085900	-0.1196550	0.0812930
6	-1.6713760	1.0673760	0.1201920
6	-1.5701590	-1.3535480	0.0912010
6	-3.0436580	0.9926420	0.1488780
1	-1.1831880	2.0374220	0.1410720
6	-2.9596390	-1.4425030	0.1209130
1	-0.9758840	-2.2598100	0.0556880
6	-3.6945660	-0.2577790	0.1588270
1	-3.4468500	-2.4116350	0.1065470

7	-5.0661380	-0.0908790	0.2209350
6	-5.3683660	1.2902500	-0.1750730
1	-5.5275050	1.3426080	-1.2644360
1	-6.2740620	1.6421490	0.3248410
6	-5.9531540	-1.1333030	-0.2457990
1	-5.8577310	-1.3069550	-1.3289170
1	-5.7426640	-2.0672350	0.2805770
1	-6.9842420	-0.8473740	-0.0253530
6	-4.1023730	2.0695950	0.2251960
1	-4.1909790	2.4441140	1.2518090
1	-3.9112760	2.9213800	-0.4307750

Compound **4 (Excited-state)**

6	-5.4923130	0.8509230	-0.2644900
6	-4.6884940	-0.2650200	-0.2188990
6	-2.7212960	1.0467560	0.0012620
6	-3.5218200	2.2153010	-0.0064940
6	-4.8884100	2.1308100	-0.1371340
1	-6.5625910	0.7396180	-0.3867650
1	-5.0867800	-1.2717090	-0.2888950
6	-1.3170610	1.0646600	0.0433990
1	-3.0236680	3.1766630	0.0741550
1	-5.4962930	3.0289460	-0.1478750
6	-0.5399820	-0.1060950	-0.1215720
1	-0.8339570	2.0248160	0.1672530
5	-2.4962220	-1.4873220	0.2082010
7	-3.3515590	-0.1938770	-0.0770670
8	-1.1521240	-1.2831260	-0.3299470
9	-2.4472420	-1.6783940	1.5846640
9	-3.0977320	-2.5546870	-0.4303110
6	0.8838210	-0.1088800	-0.1240000
6	1.6679270	1.0835190	0.0311010
6	1.5754000	-1.3523240	-0.2936390
6	3.0293160	1.0065640	0.0187650
1	1.1899570	2.0481620	0.1629830
6	2.9473500	-1.4362960	-0.3062420
1	0.9765690	-2.2483680	-0.4023560
6	3.6889480	-0.2443520	-0.1493900
1	3.4426570	-2.3948080	-0.4184920
7	5.0313330	-0.0789380	-0.1265740
6	5.3867060	1.2753580	0.3052490
1	5.7000840	1.2505910	1.3586840
1	6.2220460	1.6511230	-0.2912650
6	5.9937990	-1.1525300	-0.0812530
1	6.0812940	-1.5743290	0.9298060
1	5.6995510	-1.9455690	-0.7722370
1	6.9687100	-0.7681160	-0.3882620
6	4.0852320	2.0829840	0.1196790
1	4.1212270	2.6680840	-0.8055350
1	3.9109090	2.7756770	0.9456170

Compound **5 (Ground-state)**

6	6.0259040	0.7842300	0.3564960
6	5.1818520	-0.3000970	0.3620550
6	3.3018170	1.0299590	-0.1659660
6	4.1344730	2.1685530	-0.1995670

6	5.4816140	2.0443410	0.0562510
1	7.0788450	0.6557470	0.5718700
1	5.5146580	-1.3096270	0.5717000
6	1.8857800	1.0946380	-0.3461580
1	3.6865730	3.1322880	-0.4132430
1	6.1204690	2.9213290	0.0342310
6	1.0857900	0.0289240	-0.0285590
1	1.4567540	2.0416100	-0.6419880
5	2.9713380	-1.4877270	-0.0601550
7	3.8661370	-0.1774580	0.0923220
8	1.6075470	-1.1420610	0.3218850
9	3.0367690	-1.8747390	-1.3851390
9	3.4757390	-2.4482320	0.7863810
6	-0.3791400	0.0760150	-0.0064750
6	-1.1138820	-1.1173510	0.0545210
6	-1.0957420	1.2820350	-0.0397080
6	-2.4962230	-1.1170960	0.0659310
1	-0.5783620	-2.0597050	0.0906500
6	-2.4771630	1.3027470	-0.0297790
1	-0.5673220	2.2303050	-0.0569590
6	-3.2181690	0.0978120	0.0206500
1	-2.9941500	2.2549030	-0.0629550
1	-3.0275560	-2.0604240	0.1207130
7	-4.5790440	0.1098490	0.0303310
6	-5.3767770	1.3292880	0.1063850
6	-5.3973170	-1.0970950	-0.0282120
6	-6.7863760	0.8092820	0.3981640
1	-5.0047650	1.9887660	0.8981980
6	-6.8029680	-0.5550080	-0.2974160
1	-5.0485250	-1.7644800	-0.8238040
1	-6.9144680	0.6801510	1.4777780
1	-7.5838930	-1.2210270	0.0746010
1	-5.3511940	-1.6500180	0.9213550
1	-6.9466050	-0.4241150	-1.3748650
1	-7.5626240	1.4878360	0.0391790
1	-5.3379640	1.8845250	-0.8421940

Compound **5 (Excited-state)**

6	-6.0470850	0.7460200	-0.2814260
6	-5.1935600	-0.3339460	-0.2691640
6	-3.2930700	1.0552920	0.0401840
6	-4.1460470	2.1856550	0.0687930
6	-5.5054810	2.0450780	-0.0889660
1	-7.1090600	0.5914430	-0.4269470
1	-5.5447110	-1.3534690	-0.3885080
6	-1.8924660	1.1346280	0.1064200
1	-3.6938180	3.1639900	0.1994760
1	-6.1538020	2.9143210	-0.0715470
6	-1.0591640	0.0052700	-0.0903400
1	-1.4539700	2.1089110	0.2773920
5	-2.9564590	-1.4733430	0.1497650
7	-3.8639730	-0.2087500	-0.1014090
8	-1.6121310	-1.1882320	-0.3526390
9	-2.9225240	-1.7158430	1.5179350
9	-3.4962920	-2.5396380	-0.5424530

6	0.3606570	0.0680910	-0.0660130
6	1.1237900	-1.1243220	-0.2610390
6	1.0939940	1.2785970	0.1383140
6	2.4922810	-1.1160520	-0.2484060
1	0.5879670	-2.0519890	-0.4231090
6	2.4638420	1.2957070	0.1507270
1	0.5698820	2.2144950	0.2952760
6	3.2147990	0.0982980	-0.0407500
1	2.9817480	2.2319110	0.3244760
1	3.0335020	-2.0410770	-0.4116100
7	4.5642810	0.1113740	-0.0264720
6	5.3670910	1.3314790	0.0681930
6	5.3934780	-1.0933430	-0.0978660
6	6.7824530	0.8521690	-0.2571160
1	5.0016710	2.0848110	-0.6367460
6	6.7890420	-0.5859400	0.2678650
1	5.0233840	-1.8537440	0.5966290
1	6.9343640	0.8587670	-1.3409650
1	7.5774320	-1.2016740	-0.1684080
1	5.3665090	-1.5131260	-1.1132240
1	6.9099230	-0.5899930	1.3556260
1	7.5455580	1.4833340	0.2015470
1	5.3026330	1.7505390	1.0823000

Compound **6 (Ground-state)**

6	5.6949340	1.0099290	0.3299340
6	4.9391680	-0.1375210	0.3557590
6	2.9588220	1.0320550	-0.1836910
6	3.6985030	2.2319610	-0.2387490
6	5.0523100	2.2182560	0.0126310
1	6.7554630	0.9679920	0.5423440
1	5.3514450	-1.1143070	0.5789510
6	1.5410530	0.9817850	-0.3585530
1	3.1752990	3.1538520	-0.4657530
1	5.6202120	3.1421720	-0.0264790
6	0.8295390	-0.1391740	-0.0235630
1	1.0366310	1.8863690	-0.6678350
5	2.8281910	-1.5026760	-0.0403210
7	3.6170110	-0.1230920	0.0901900
8	1.4418880	-1.2609710	0.3402100
9	2.9226910	-1.9021170	-1.3597990
9	3.4088100	-2.4072980	0.8186980
6	-0.6352990	-0.2067920	0.0012250
6	-1.2753460	-1.4495240	0.0485970
6	-1.4421210	0.9406530	-0.0201760
6	-2.6564790	-1.5427260	0.0597720
1	-0.6756290	-2.3528760	0.0659820
6	-2.8242600	0.8804160	-0.0160520
1	-0.9818610	1.9258720	-0.0225790
6	-3.4660990	-0.3874720	0.0355810
1	-3.1112700	-2.5251740	0.0845340
7	-4.8390230	-0.4832250	0.0847440
6	-5.4694340	-1.7771970	-0.0835500
1	-5.2127560	-2.2437180	-1.0450350
1	-5.1805190	-2.4621910	0.7200570

1	-6.5513940	-1.6463970	-0.0403370
6	-5.6568190	0.6965400	-0.1649390
6	-5.0418060	1.9209170	0.4976500
1	-6.6521180	0.5033870	0.2447490
1	-5.7729260	0.8744840	-1.2465420
6	-3.6433320	2.1511190	-0.0649920
1	-5.6794640	2.7921340	0.3235590
1	-4.9913310	1.7507160	1.5787710
1	-3.1271120	2.9449530	0.4845990
1	-3.7281530	2.4934810	-1.1050030

Compound **6 (Excited-state)**

6	-5.7206700	0.9526220	-0.3221950
6	-4.9525020	-0.1882890	-0.2742690
6	-2.9521170	1.0594340	0.0098810
6	-3.7161990	2.2520260	0.0006460
6	-5.0814490	2.2114930	-0.1625330
1	-6.7906960	0.8758000	-0.4705090
1	-5.3795560	-1.1811720	-0.3678470
6	-1.5495200	1.0332320	0.0831870
1	-3.1910800	3.1964760	0.1064920
1	-5.6613410	3.1279050	-0.1742330
6	-0.8054530	-0.1598000	-0.0816320
1	-1.0385440	1.9760260	0.2280890
5	-2.8096380	-1.4833050	0.1869630
7	-3.6178340	-0.1604320	-0.1009150
8	-1.4476830	-1.3145270	-0.3182740
9	-2.7981100	-1.6914050	1.5615820
9	-3.4289780	-2.5237070	-0.4782930
6	0.6160760	-0.2064910	-0.0589160
6	1.2845150	-1.4531390	-0.2501580
6	1.4408030	0.9430750	0.1357100
6	2.6507200	-1.5405980	-0.2495980
1	0.6827650	-2.3410990	-0.4020070
6	2.8105030	0.8771510	0.1534880
1	0.9860710	1.9167840	0.2891580
6	3.4631580	-0.3844390	-0.0515620
1	3.1158320	-2.5058720	-0.4079860
7	4.8177770	-0.4775960	-0.0591880
6	5.4694950	-1.7745420	-0.1221950
1	5.1266630	-2.4271790	0.6882100
1	5.2739170	-2.2708260	-1.0797050
1	6.5445450	-1.6298920	-0.0195100
6	5.6774630	0.6919940	0.1160510
6	4.9860680	1.9689290	-0.3342560
1	6.5874190	0.5224820	-0.4663920
1	5.9719520	0.7733350	1.1735660
6	3.6518360	2.1056250	0.3913500
1	5.6396270	2.8193100	-0.1229940
1	4.8220130	1.9313810	-1.4168220
1	3.1101720	2.9961730	0.0597320
1	3.8377280	2.2256380	1.4672570

Compound **7 (Ground-state)**

6	6.0928940	0.7712370	0.3259240
6	5.2487440	-0.3131150	0.3338880

6	3.3629460	1.0210920	-0.1608080
6	4.1950570	2.1597490	-0.1964010
6	5.5453870	2.0335190	0.0416260
1	7.1483980	0.6409870	0.5272670
1	5.5840250	-1.3241810	0.5318520
6	1.9444000	1.0867570	-0.3227850
1	3.7446620	3.1249850	-0.3976840
1	6.1841820	2.9104960	0.0178000
6	1.1491560	0.0178370	-0.0061630
1	1.5097600	2.0346760	-0.6073830
5	3.0340180	-1.4984960	-0.0712330
7	3.9298720	-0.1883630	0.0813040
8	1.6736480	-1.1570670	0.3260710
9	3.0874070	-1.8764410	-1.3993210
9	3.5477900	-2.4639710	0.7640290
6	-0.3163020	0.0668350	0.0313250
6	-1.0278010	1.2723540	0.0562100
6	-1.0522270	-1.1228230	0.0425010
6	-2.4117790	1.3096920	0.0773350
1	-0.4950810	2.2197150	0.0872300
6	-2.4378570	-1.1327810	0.0596820
1	-0.5194350	-2.0690800	0.0290550
6	-3.1457100	0.0951550	0.0614880
7	-4.5295260	0.1105730	0.0201150
6	-5.2665100	-1.1165860	0.2777140
6	-4.6069480	-2.2922200	-0.4282450
1	-6.2870900	-0.9702950	-0.0896850
1	-5.3323760	-1.3163550	1.3606120
6	-3.1806580	-2.4510590	0.0864250
1	-5.1874830	-3.2023780	-0.2534080
1	-4.6013180	-2.0986530	-1.5065780
1	-2.6332470	-3.1929460	-0.5036760
1	-3.2106880	-2.8320150	1.1159560
6	-5.2432010	1.3471030	0.2967110
6	-4.5560730	2.5234090	-0.3810620
1	-5.3130140	1.5271470	1.3828820
1	-6.2639680	1.2290780	-0.0801360
6	-3.1291630	2.6405510	0.1431680
1	-4.5490900	2.3535600	-1.4633650
1	-5.1180480	3.4415930	-0.1884230
1	-2.5669810	3.3908530	-0.4222340

Compound **7 (Excited-state)**

6	-6.1179950	0.6962960	-0.2931990
6	-5.2586870	-0.3745090	-0.2069240
6	-3.3599670	1.0420640	-0.0389880
6	-4.2189430	2.1674690	-0.0898380
6	-5.5791240	2.0088710	-0.2151840
1	-7.1812650	0.5266150	-0.4092030
1	-5.6051680	-1.4020910	-0.2380580
6	-1.9583190	1.1321380	0.0023950
1	-3.7702600	3.1551830	-0.0461040
1	-6.2314890	2.8742750	-0.2587950
6	-1.1245340	-0.0033700	-0.1142220
1	-1.5226920	2.1188330	0.0891320

5	-3.0098640	-1.4682350	0.2676040
7	-3.9268970	-0.2302480	-0.0698030
8	-1.6744970	-1.2193230	-0.2705800
9	-2.9628910	-1.6054770	1.6507890
9	-3.5545570	-2.5875550	-0.3330450
6	0.2971290	0.0647110	-0.1196030
6	1.0276200	1.2875630	-0.0331950
6	1.0601880	-1.1343480	-0.2229530
6	2.3987030	1.3260440	-0.0412950
1	0.5000700	2.2335780	0.0381540
6	2.4309140	-1.1379010	-0.2333320
1	0.5249640	-2.0753280	-0.2932460
6	3.1448350	0.1036460	-0.1237070
7	4.5065550	0.1172800	-0.0802120
6	5.2862770	-1.1005170	-0.2774870
6	4.5663900	-2.3154590	0.2867040
1	6.2512020	-0.9545190	0.2155340
1	5.4826680	-1.2424960	-1.3521240
6	3.1960800	-2.4313030	-0.3694780
1	5.1684210	-3.2085940	0.1001610
1	4.4600490	-2.2009860	1.3709860
1	2.6147380	-3.2487610	0.0661370
1	3.3276600	-2.6665460	-1.4343490
6	5.2548260	1.3697670	-0.0859980
6	4.5046510	2.4651530	0.6557020
1	5.4467890	1.6798880	-1.1254590
1	6.2236230	1.1748280	0.3817780
6	3.1305510	2.6450730	0.0221130
1	4.4028580	2.1834110	1.7093970
1	5.0831350	3.3915140	0.6093010
1	2.5316700	3.3721260	0.5783490
1	3.2541810	3.0445670	-0.9936280

Order of effects upon amino group modification

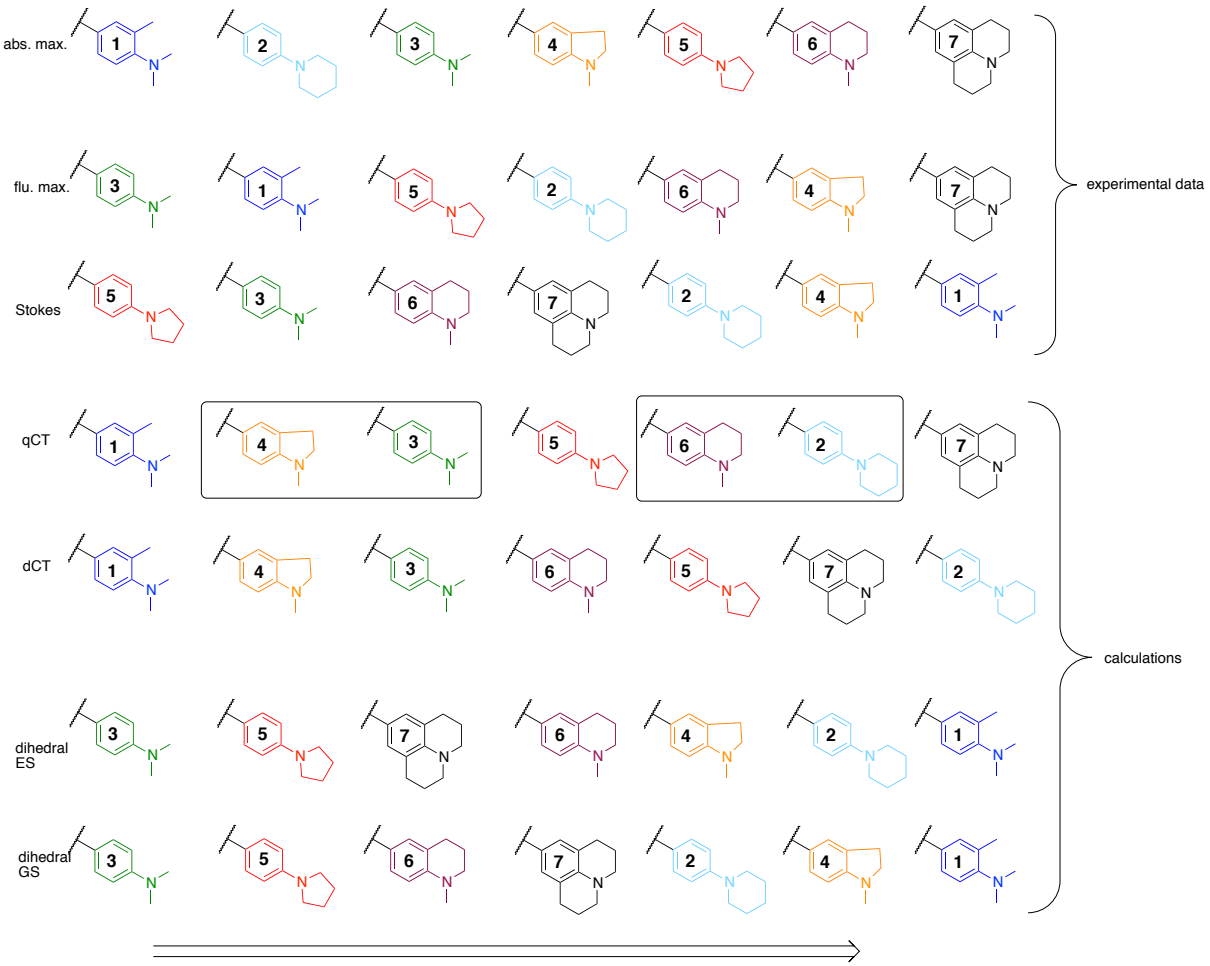


Figure S36. Ranking of various properties and parameters upon amino group modification (from the lowest to the highest). In boxes the substituents show very close values.

Based on the spectral data it was revealed that the nature of the amino group has a significant influence on the CT absorption and fluorescence. The lone electron pair of the nitrogen atom of this donor moiety is variably delocalized towards the difluoroborate core that acts as the electron acceptor. Thus, the compounds should exhibit distinctive changes in a reduction and oxidation potentials. Theoretically[1,2] the energy level of the molecule excited CT state, relative to its ground state can be expressed by eq. (1)

$$E_{CT} = E_{ox}(D) - E_{red}(A) - C \qquad (1)$$

where: $E_{ox}(D)$ and $E_{red}(A)$ are the electron oxidation and reduction potentials of the donor and acceptor and C is a constant that depends on the degree of charge separation.

As illustrated in Figure S37, the linear correlation (eq. (1)) with a coefficient (R^2=0.94) exists between the maximum of fluorescence and the difference between E_{ox}(D) and E_{red}(A) values. The results clearly show that the emission observed for tested compounds occurs from the excited CT state. Similar relationship was observed early by Verhoeven[3], for rod-shaped donor-acceptor systems.

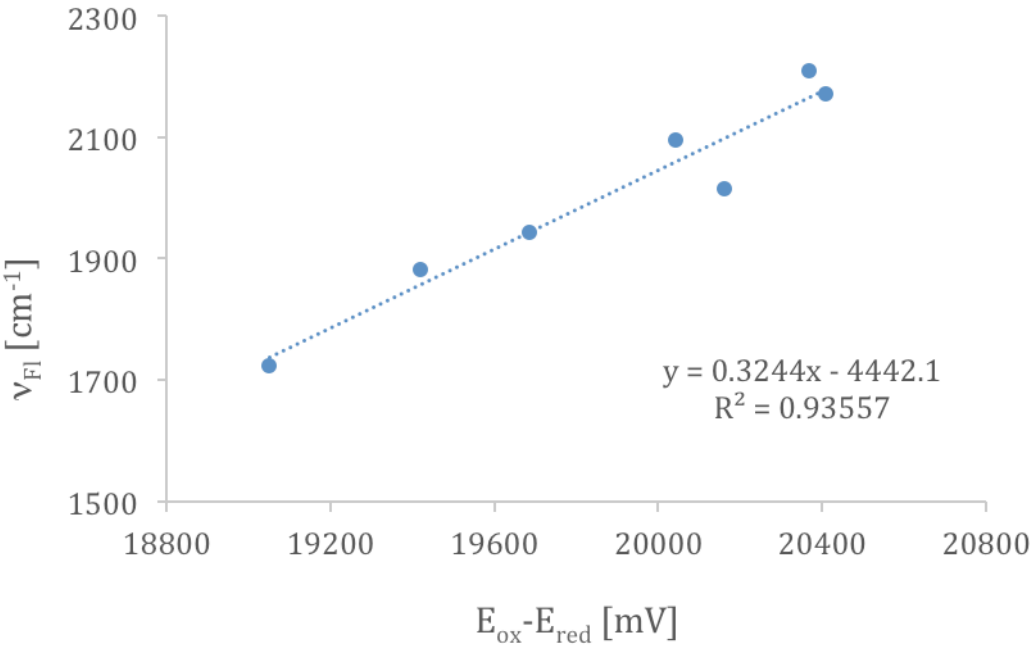


Figure S37. Fluorescence frequency of the difluoroborates tested versus E_{ox}(D) - E_{red}(A).

The cyclic voltammograms of difluoroborates (Figure S38) were recorded in acetonitrile containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The obtained oxidation and reduction potential values are listed in Table 1. Depending on the chemical substitution, the CVs feature generally one or two quasi-reversible reduction wave and one or two irreversible oxidation waves.

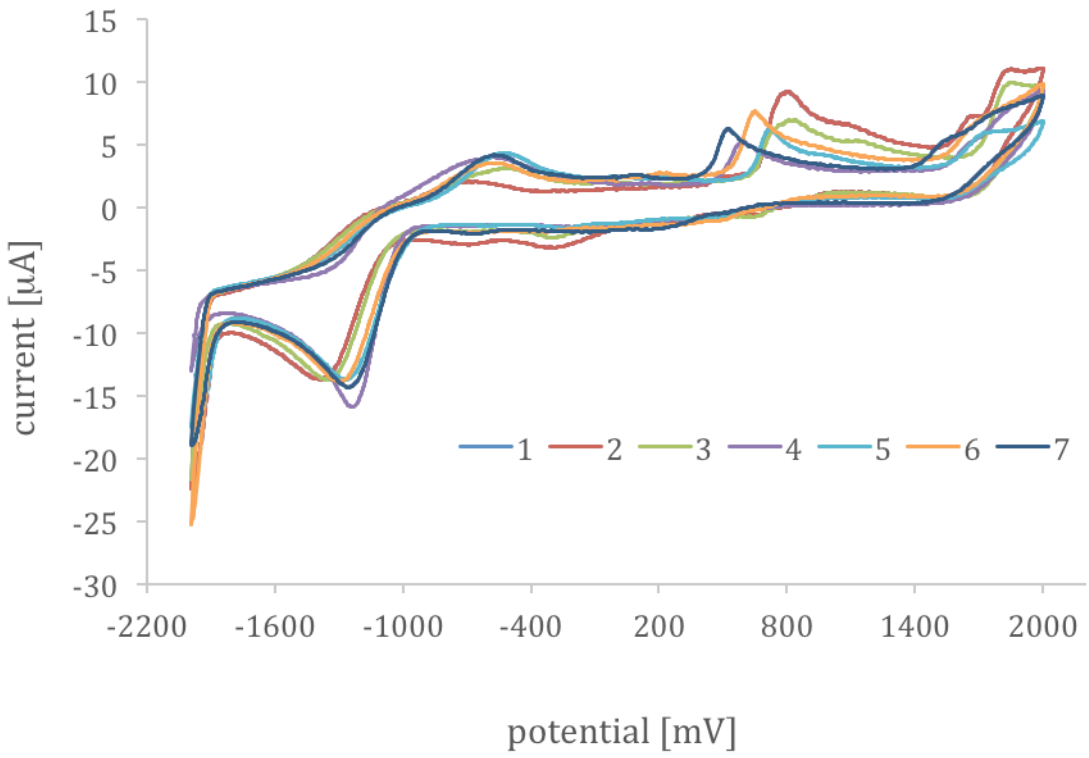


Figure S38. Cyclic voltammograms of difluoroborates tested using a platinum electrode at 400 mV s^{-1} sweep rates in anhydrous acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte.

The reduction and oxidation potential values depend on the electron donating nature of the end groups of the phenylene unit. For example, the 4-*N*,*N*-diethylamino-3-methylphenyl end-group of **1** is oxidized at 0.82 V while the oxidation of the julolidine moiety (**7**) occurs at 0.49 V. Indeed, the oxidation potential values are affected qualitatively by the electronic character of the amino group, namely, the more electron-donating the substituent, the easier the molecule is to oxidize.

Table 1. Reduction and oxidation potentials of difluoroborates tested and the substituent constants

Abbr.	σ	E_{red}(A/A$^{\cdot-}$) (V)	E_{ox}(D/D$^{\cdot+}$) (V)
1	-0.24	-1.39	0.82
2	-0.47	-1.34	0.75
3	-0.53	-1.34	0.80
4	-0.47	-1.28	0.60
5	-0.63	-1.30	0.71
6	-0.48	-1.30	0.64
7	-0.59	-1.23	0.49

In order to delineate the electronic influence of substituents of the terminal groups on electrochemical behavior of the BF_2-containing pyridine backbone dyes, we also sought to

establish whether a correlation between substituent constants and oxidation potential values could exist. For all *para*-substituted BF_2 complexes, there is a poor correlation between the oxidation potential values and the Hammett constants (R^2 = 0.35, Figure S39). However, after excluding three outlier data points for **2**, **3** and **5**, there appears to be a linear relationship with a high correlation (R^2 =0.97, Figure S39). No reasonable correlation found for all the *p*-substituted difluoroborates results from the limitation of using Hammett constants. It was shown that the use of the Hammett constants might be problematic to describe the regular influence of the substituent on electrochemical behavior. This may arise from intramolecular interaction (e.g., the steric effect, the formation of hydrogen bond bridges, tautomerism, etc.)[4] limiting its applicability and accuracy. For that reason not only the nature of the substituent in the aromatic ring at the *para*-position, but also parameters such as *a*) orientation of the aromatic ring toward the heterocyclic ring, *b*) orientation of the amino group with respect to the C-N bond, and *c*) (non)planarity of the molecule may have influence on the oxidation peak potential.[5] For example, steric interactions, which may cause the frameworks to be distorted and thereby reduced conjugation, attenuate the ability of the substituent to express its character. Another parameter, which should be considered by the interpretation of the electronic nature of the substituents on the *para*-position of the heterocyclic ring on the observed oxidation peak potentials is the stability of the species formed after the first electron detachment.[5] All that causes the lack of a good correlation between Hammett constants and oxidation potentials for the difluoroborates **1-7**. For the same reasons no linear correlation described by a large correlation coefficient is observed between the position of the absorption or fluorescence bands and the Hammett constants.

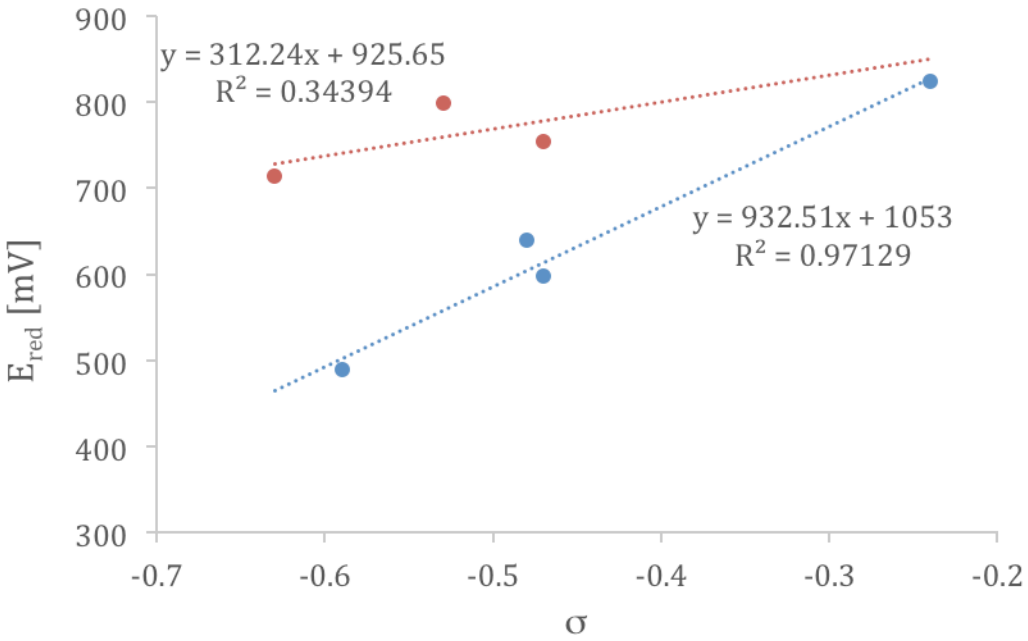


Figure S39. Correlations between oxidation potentials and Hammett constants of *para*-substituted difluoroborates.

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