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The inverted solvatochromism of protonated ferrocenylethenyl-pyrimidines: the first example of the solvatochromic reversal of a hybrid organic/inorganic dye

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1 UV-VIs measurement procedure

UV–vis spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer in the range of 350–700 nm at room temperature (25 ± 1 °C). The molar concentration of each dye during the measurements were set to 1×10^{-5} mol.L^{-1}. The protonated dyes **2a**–**e** were generated in situ by the addition of 1-5 µL of trifluoroacetic acid in each solvent where the spectrum of each was recorded.

2 Solvatochromic plots of neutral dyes 1b–e

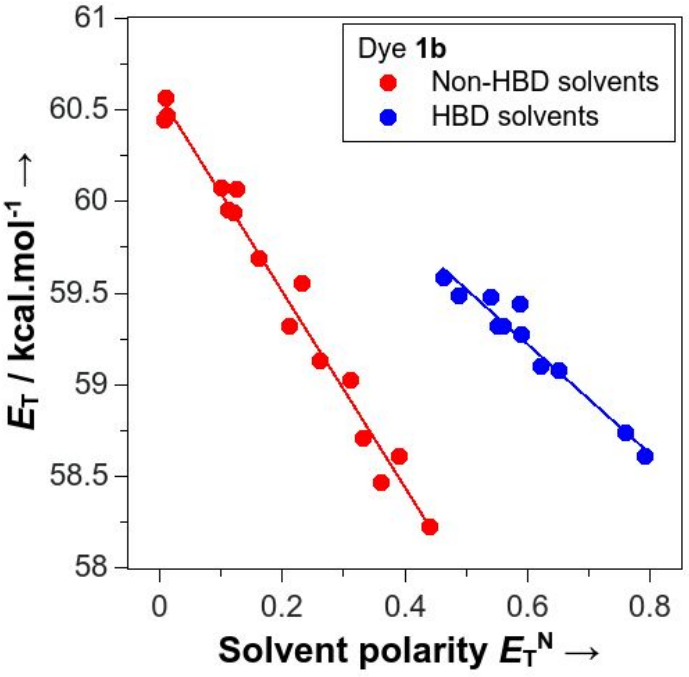


Figure SF.1. Variations of the electronic transition energy E_T of dyes **1b** as a function of normalized solvent polarity values E_T^N in HBD-(blue) and non-HBD-solvents (red). The linear regression coefficients obtained are: r^2(HBD) = 0.946; and r^2(Non-HBD) = 0.979.

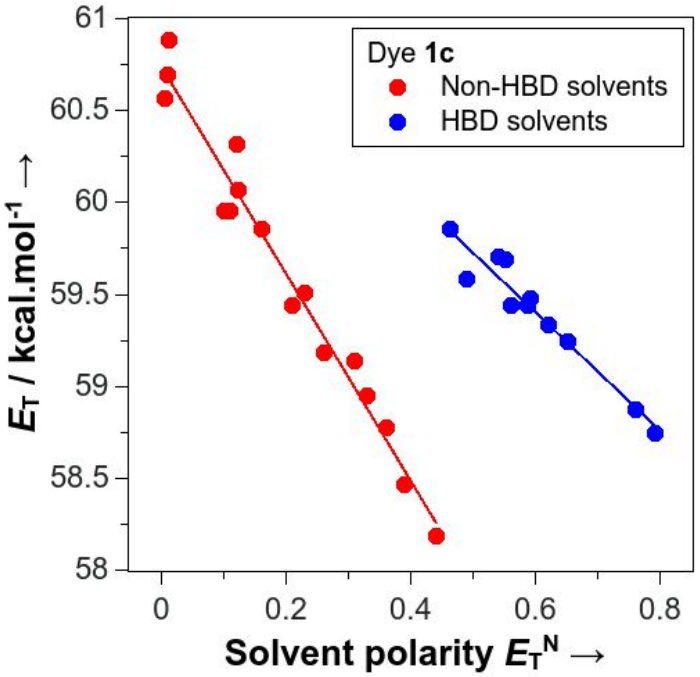


Figure SF.2. Variations of the electronic transition energy E_T of dyes **1c** as a function of normalized solvent polarity values E_T^N in HBD-(blue) and non-HBD-solvents (red). The linear regression coefficients obtained are: r^2(HBD) = 0.938; and r^2(Non-HBD) = 0.972.

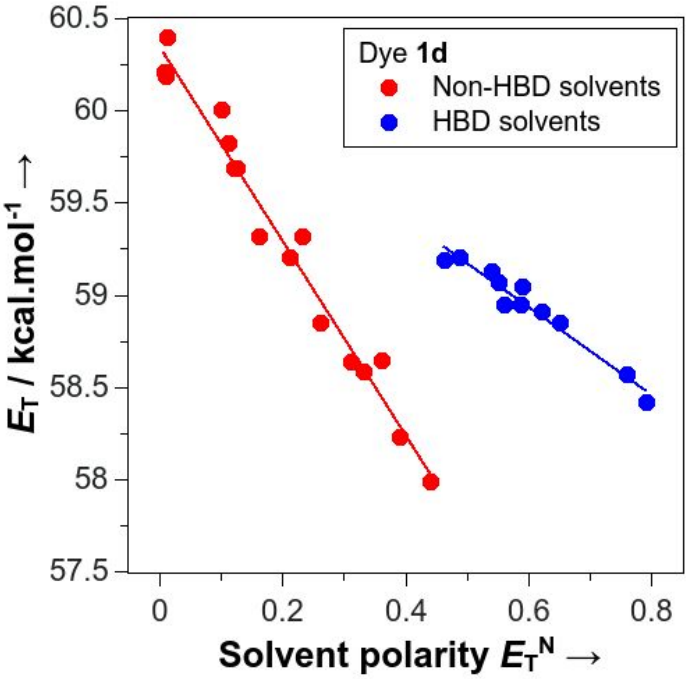


Figure SF.3. Variations of the electronic transition energy E_T of dyes **1d** as a function of normalized solvent polarity values E_T^N in HBD-(blue) and non-HBD-solvents (red). The linear regression coefficients obtained are: r^2(HBD) = 0.935; and r^2(Non-HBD) = 0.975.

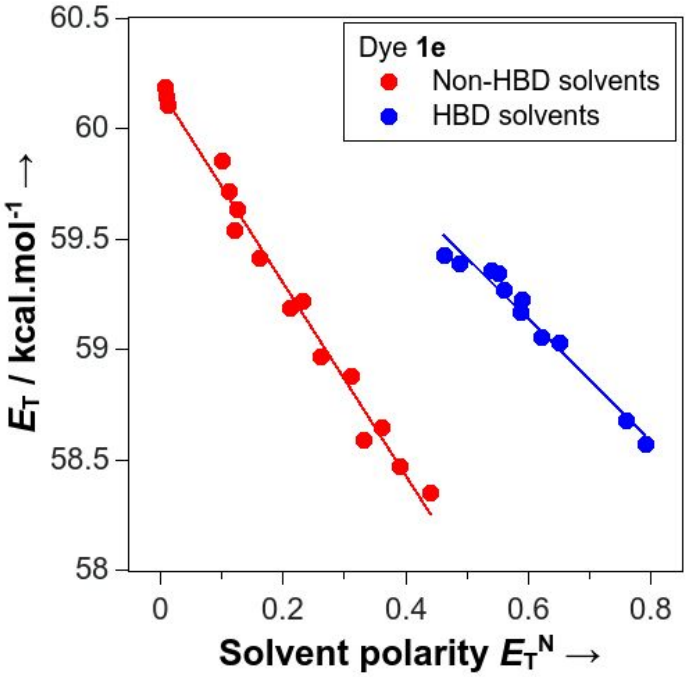


Figure SF.4. Variations of the electronic transition energy E_T of dyes **1e** as a function of normalized solvent polarity values E_T^N in HBD-(blue) and non-HBD-solvents (red). The linear regression coefficients obtained are: r^2(HBD) = 0.966; and r^2(Non-HBD) = 0.986.

3 Solvatochromic plots of protonated dyes 2b–e

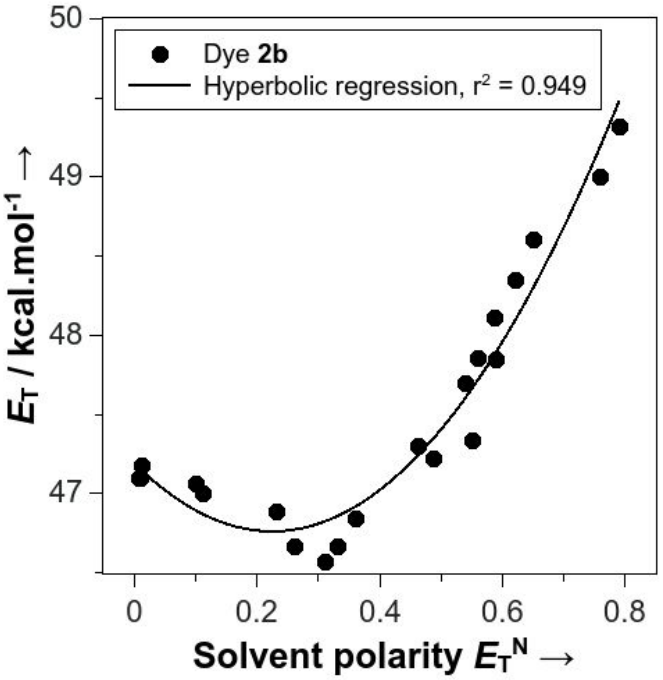


Figure SF.5. Variations of the electronic transition energy E_T of dyes **2b** as a function of normalized solvent polarity values E_T^N in twenty-one solvents.

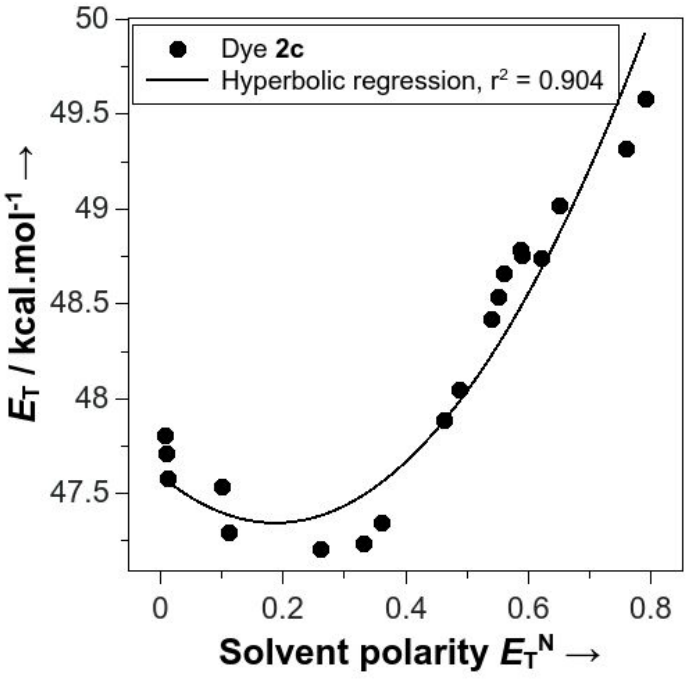


Figure SF.6. Variations of the electronic transition energy E_T of dyes **2c** as a function of normalized solvent polarity values E_T^N in twenty-one solvent.

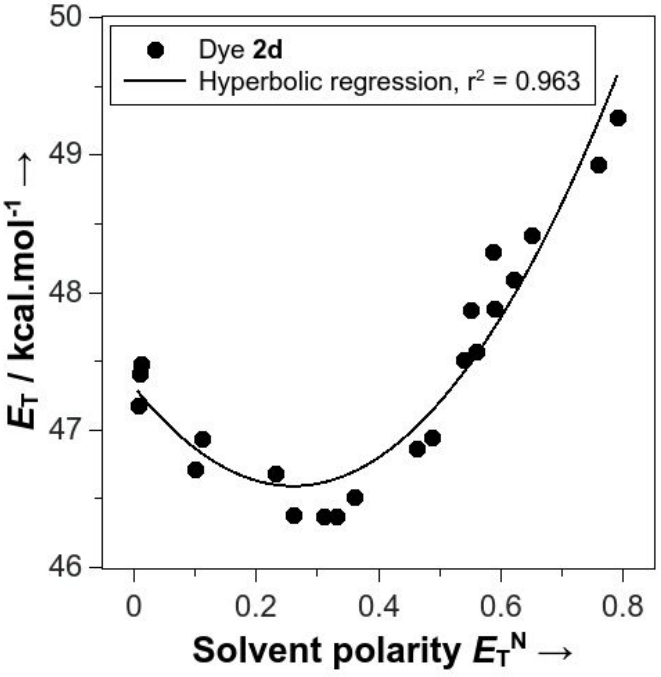


Figure SF.7. Variations of the electronic transition energy E_T of dyes **2d** as a function of normalized solvent polarity values E_T^N in twenty-one solvent.

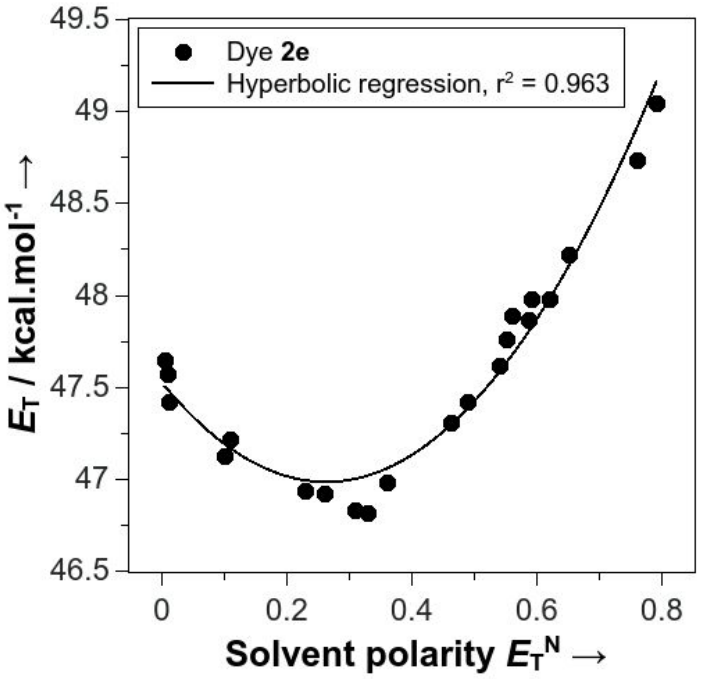


Figure SF.8. Variations of the electronic transition energy E_T of dyes **2e** as a function of normalized solvent polarity values E_T^N in twenty-one solvent.

4 Stability experiments

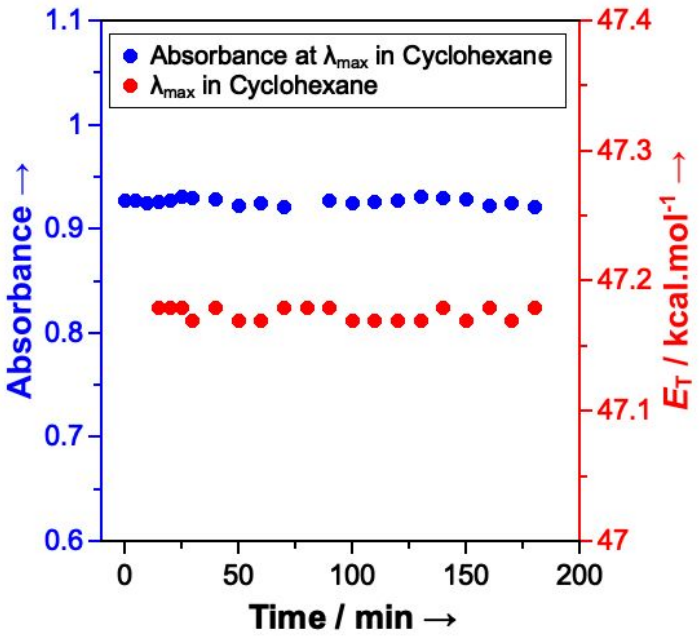


Figure SF.9. Variations of the electronic transition energy E_T of dyes **2a** (red) and the absorbance of 2a at λ_{max} in cyclohexane as a function of the time in minutes.

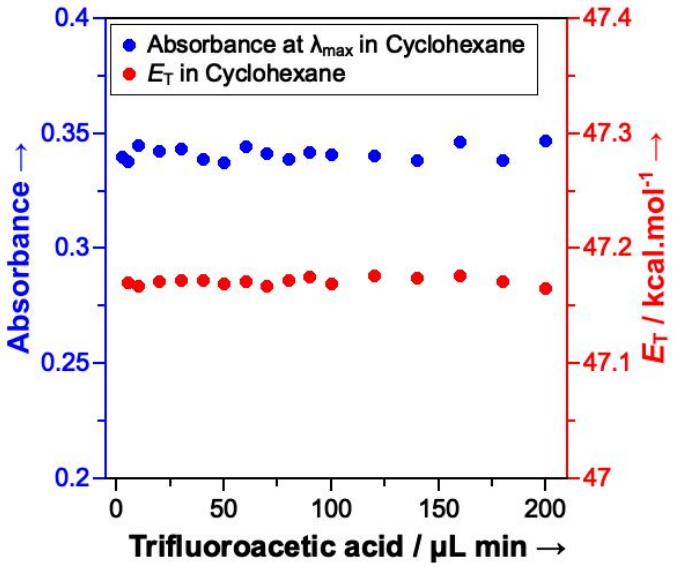


Figure SF.10. Variations of the electronic transition energy E_T of dyes **2a** (red) and the absorbance of 2a at λ_{max} in cyclohexane as a function of the increasing amount of TFA.

5 Synthetic experimental procedures

General methods

NMR spectra were recorded with a Bruker Avance 400 MHz instrument. IR spectra were recorded with a Spectrum Two FT-IR (ATR) Perkin Elmer spectrophotometer HRMS was per- formed with Varian Ionspec QFT-7 (ESI-FT ICRMS) and Agilent 6210 ESI-TOF instruments. Melting points were recorded with a Microthermal capillary melting-point apparatus and were not corrected. All reagents were reagent grade and were used without further purification. TLC was performed on TLC plates (silica gel 60, fluorescence indicator F254, 0.25 mm layer thickness). Products were purified by column chromatography on silica gel 60.

Pyrimidines **4a-d** were obtained according to literature.[1,2]

Synthesis of 4-(9,9-dimethyl-9*H*-fluoren-2-yl)-6-methyl-2-phenylpyrimidine 4e

A 10-mL microwave vial was charged with the 4-pyrimidyl tosylate **3** (200 mg, 0.588 mmol), the 9,9-Dimethyl-9*H*-fluorene-2-yl-2-boronic acid (168 mg, 0.705 mmol), tetrakis(triphenylphosphine)palladium (33.5 mg, 0.029 mmol), powdered potassium carbonate (81 mg, 0.588 mmol) and water (5 mL). The resulting reaction mixture was irradiated for 1 h at 100 °C. The reaction mixture was then extracted three times with dichloromethane (*ca.* 15 mL each). The combined organic phases were dried with anhydrous sodium sulfate and filtered. The filtrate was rotary evaporated and the obtained crude product was purified by column chromatography (silica gel, *n*-hexane:EtOAc, 10:1) to obtain a light-yellow oil; yield: 185 mg (87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 – 8.59 (m, 2H), 8.27 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.54 – 7.42 (m, 5H), 7.35 – 7.30 (m, 2H), 2.62 (s, 3H), 1.56 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ

= 167.7, 164.4, 164.0, 154.5, 154.3, 141.9, 138.5, 138.4, 136.4, 130.5, 128.6, 128.5, 128.1, 127.2, 126.6, 122.8, 121.5, 120.6, 120.4, 114.0, 47.1, 27.3, 24.7; FT-IR (ATR) *v*: 3070, 2920, 1683, 1589, 1572 cm^{-1}; HRMS (ESI-TOF): *m*/*z* [M + H^+] calcd for $C_{26}H_{23}N_2^+$: 363.1856; found: 363.1863.

General procedure for the synthesis of the 2-(ferrocen-2-yl)ethenyl]pyrimidine dyes (1a–e).

A sealed tube was charged with ferrocenecarboxaldehyde (100 mg, 0.47 mmol), Aliquat 336 (25 mg), the corresponding 2-methylpyrimidine **4a**–**e** (0.45 mmol) and an aqueous solution of sodium hydroxide (5 mL, 5 mol/L). The resulting mixture was heated to 150 ºC for 16 hours. After completion of the reaction, the mixture was cooled to room temperature and then extracted three times with dichloromethane (*ca.* 15 mL each). The collection of the organic phases were dried over anhydrous sodium sulfate. After evaporation of the volatile components the product was purified by column chromatography (hexanes:EtOAc, 20:1 → 5:1).

(*E*)-2,4-diphenyl-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine 1a.

Brown-reddish, 87% yield (185 mg), mp 165-167 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.72 – 8.62 (m, 2H), 8.30 – 8.22 (m, 2H), 7.91 (d, *J* = 15.7 Hz, 1H), 7.64 – 7.45 (m, 7H), 6.83 (d, *J* = 15.7 Hz, 1H), 4.65 – 4.60 (m, 2H), 4.46 – 4.39 (m, 2H), 4.21 (s, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 164.7, 164.7, 163.8, 138.8, 138.0, 137.3, 131.0, 130.9, 129.3, 128.8, 127.6, 124.4, 111.7, 81.4, 70.7, 70.0, 68.5; FT-IR (ATR) *v*: 3060, 2920, 1630, 1565, 1520, 1365, 1105, 745, 695; HRMS (ESI-TOF): *m*/*z* [M^+] calcd for $C_{30}H_{29}FeN_2^+$: 473.1675; found 473.1681.

(*E*)-2-phenyl-4-(4-methylphenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine 1b.

Red-brown solid, 85% yield (186 mg), mp 180-182 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (d, J = 7.3 Hz, 2H), 8.17 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 15.6 Hz, 1H), 7.59 – 7.49 (m, 3H), 7.49 (s, 1H), 7.35 (d, J = 7.8 Hz, 2H), 6.82 (d, J = 15.6 Hz, 1H), 4.68 – 4.59 (m, 2H), 4.49 – 4.40 (m, 2H), 4.29 – 4.15 (m, 5H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.7, 163.6, 141.3, 139.0, 137.0, 135.2, 130.8, 130.0, 128.9, 128.8, 127.5, 111.3, 81.5, 70.6, 69.9, 68.5, 21.9; FT-IR (ATR) v: 3050, 2920, 1630, 1565, 1510, 1365, 1270, 1190, 830, 735; HRMS (ESI-TOF): m/z [M^+] calcd for $C_{31}H_{31}FeN_2^+$: 487.1831; found 487.1836.

(*E*)-2-phenyl-4-(4-methoxyphenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine 1c.

Orange solid, 91% yield (206 mg), mp 179-180 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 – 8.60 (m, 2H), 8.28 – 8.17 (m, 2H), 7.89 (d, J = 15.7 Hz, 1H), 7.60 – 7.48 (m, 3H), 7.45 (s, 1H), 7.09 – 7.01 (m, 2H), 6.80 (d, J = 15.7 Hz, 1H), 4.63 – 4.59 (m, 2H), 4.45 – 4.39 (m, 2H), 4.20 (s, 5H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.6, 164.2, 163.5, 162.2, 139.0, 136.9, 130.7, 130.5, 129.1, 128.8, 128.8, 124.6, 114.6, 110.8, 81.6, 70.6, 69.9, 68.5, 55.8; FT-IR (ATR) v: 2920, 2850, 1735, 1570, 1515, 1370, 1265, 1040, 830, 755; HRMS (ESI-TOF): m/z [M^+] calcd for $C_{31}H_{31}FeN_2O^+$: 503.1780; found 503.1787.

(*E*)-2-phenyl-4-(4-fluorophenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine 1d.

Orange solid, 75% yield (165 mg), mp 148-149 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 – 8.62 (m, 2H), 8.31 – 8.22 (m, 2H), 7.91 (d, J = 15.7 Hz, 1H), 7.60 – 7.48 (m, 3H), 7.46 (s, 1H), 7.29 – 7.19 (m, 2H), 6.81 (d, J = 15.7 Hz, 1H), 4.64 – 4.58 (m, 2H), 4.46 – 4.41 (m, 2H), 4.20 (s, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.7, 163.9, 163.6, 138.7, 137.5, 130.9, 129.6,

129.6, 128.8, 124.2, 116.4, 116.1, 111.3, 81.4, 70.7, 70.0, 68.5; FT-IR (ATR) *v*: 3050, 2920, 2850, 1630, 1570, 1515, 1370, 1265, 1180, 965, 830, 735; HRMS (ESI-TOF): *m*/*z* [M^+] calcd for $C_{30}H_{28}FFeN_2^+$: 491.1580; found 491.1588.

(*E*)-2-phenyl-4-(4-fluorophenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine 1e.

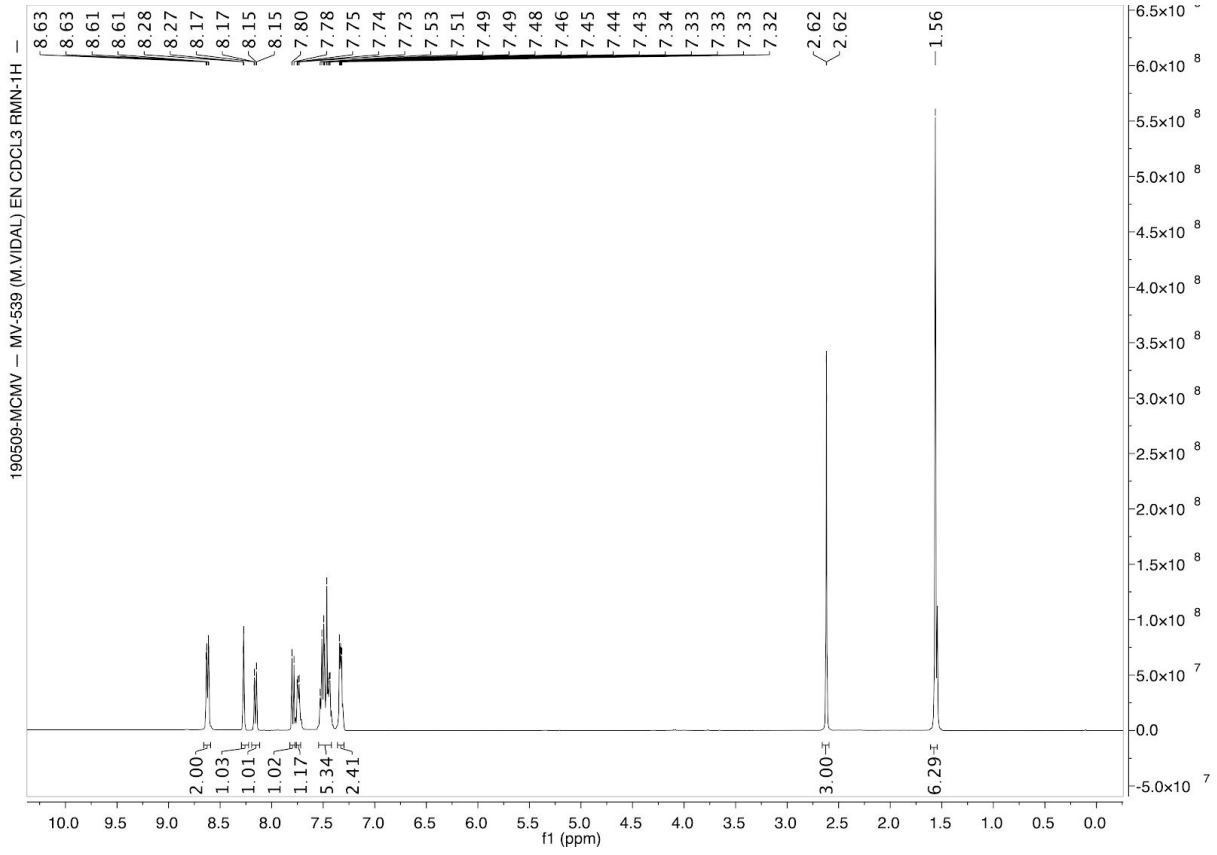
Brown-reddish solid, 54% yield (136 mg), mp 198-199 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 – 8.67 (m, 2H), 8.32 (d, *J* = 1.6 Hz, 1H), 8.25 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.95 (d, *J* = 15.7 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.63 – 7.47 (m, 5H), 7.43 – 7.34 (m, 2H), 6.86 (d, *J* = 15.7 Hz, 1H), 4.64 (s, 2H), 4.44 (s, 2H), 4.23 (s, 5H), 1.62 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.0, 164.7, 163.6, 142.2, 138.9, 137.2, 137.0, 130.9, 128.9, 128.9, 128.4, 127.6, 126.9, 124.4, 123.2, 121.8, 121.0, 120.7, 111.9, 81.5, 70.7, 70.0, 68.5, 47.5, 27.6; FT-IR (ATR) *v*: 3050, 2920, 2860, 1630, 1565, 1515, 1370, 1265, 1175, 824, 735; HRMS (ESI-TOF): *m*/*z* [M^+] calcd for $C_{39}H_{37}FeN_2^+$: 589.2301; found 589.2307.

6 References

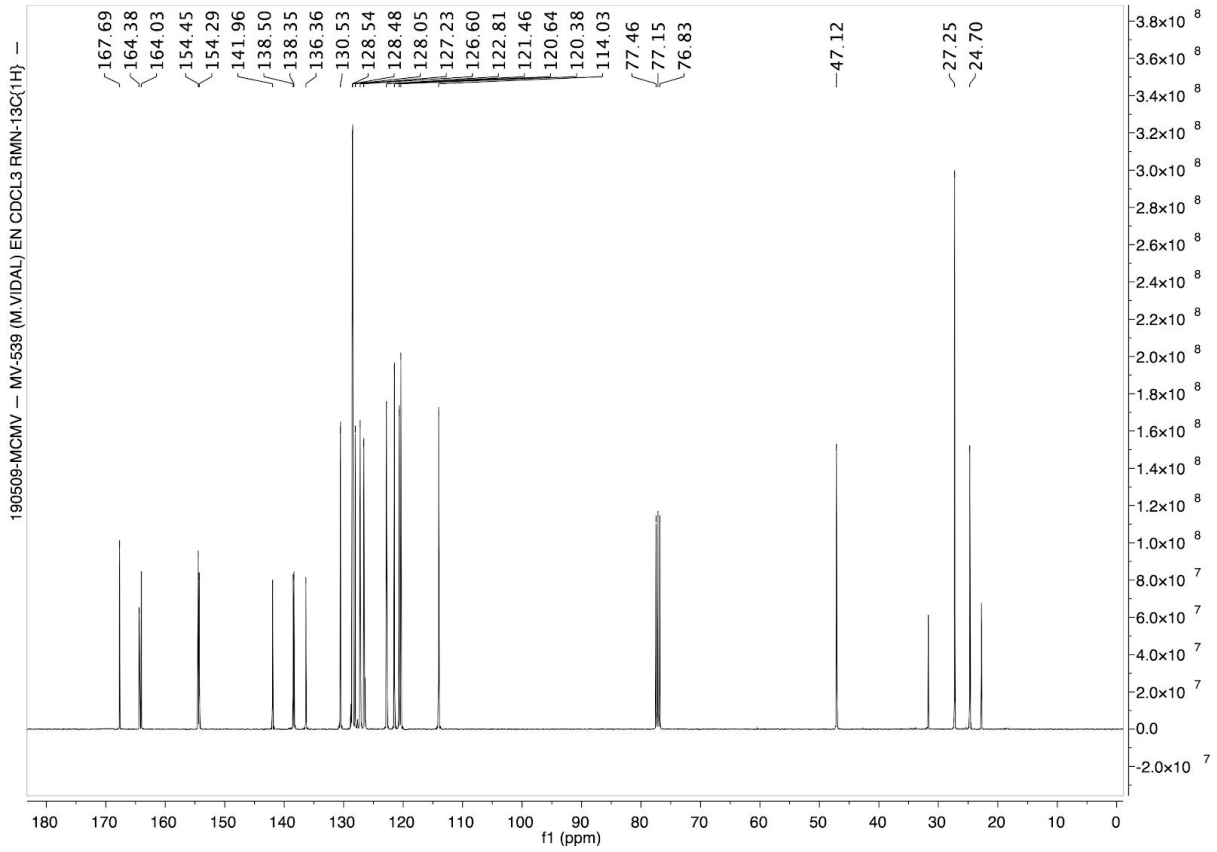
1 J. Rodríguez-Aguilar, B. Ordóñez, M. Vidal, M. C. Rezende and M. Domínguez, *SynOpen*, 2017, **01**, 0024–0028.

2 M. Vidal, M. García-Arriagada, M. C. Rezende and M. Domínguez, *Synthesis* , 2016, **48**, 4246–4252.

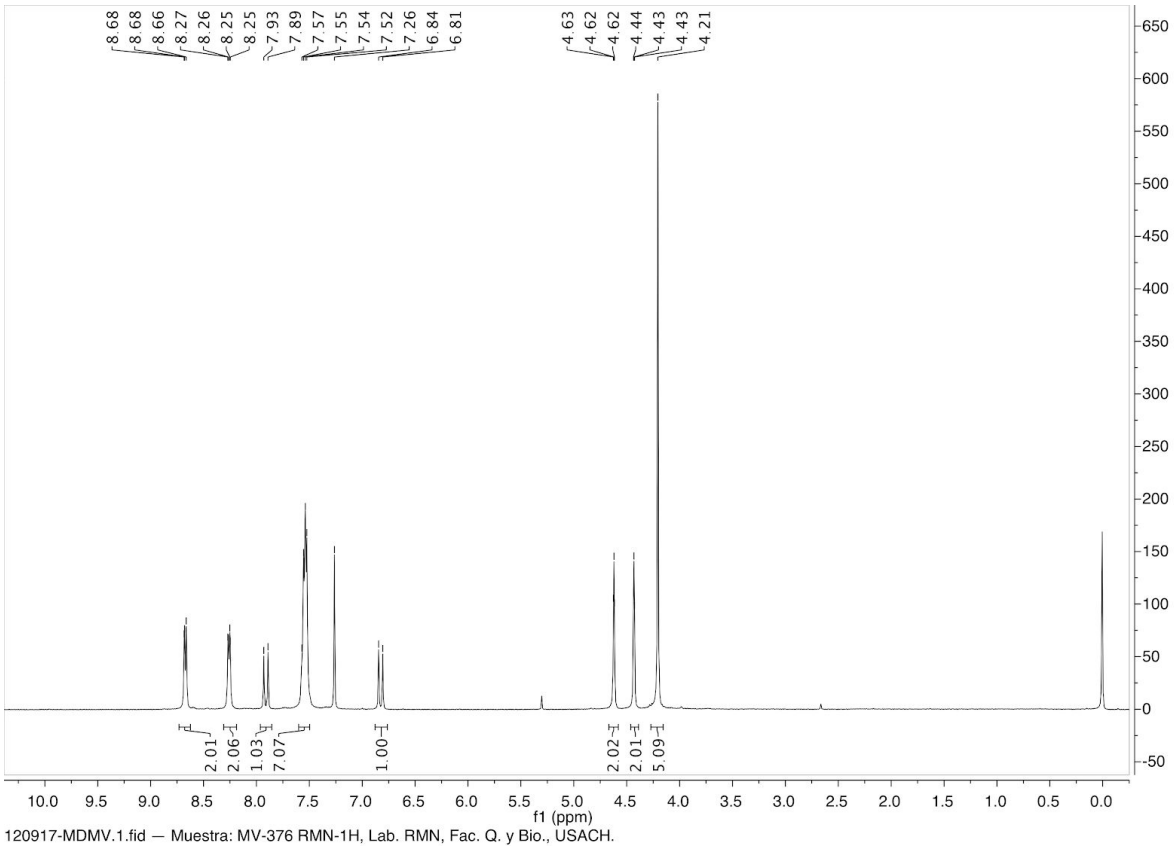
7 ^{1}H NMR and ^{13}C NMR of new compounds 4e and 1a–e



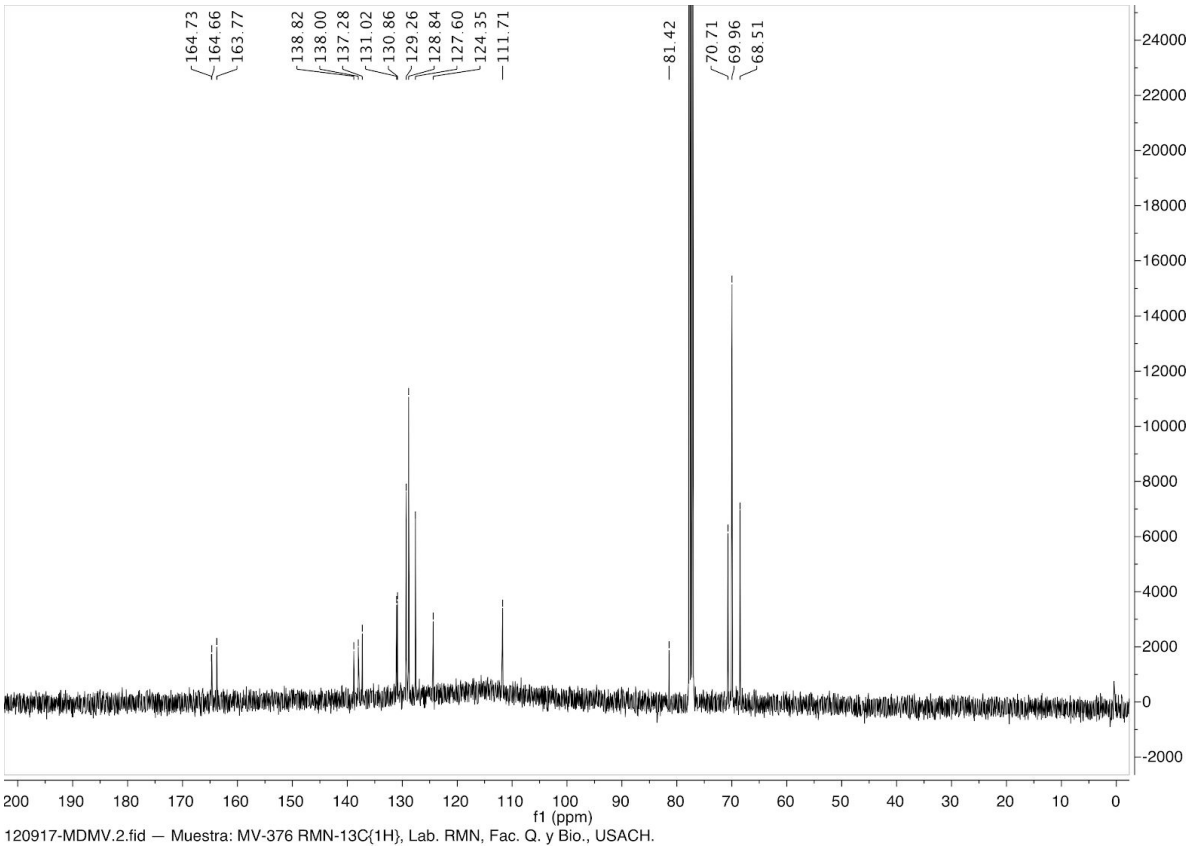
^{1}H NMR Spectrum of the 4-(9,9-dimethyl-9*H*-fluoren-2-yl)-6-methyl-2-phenylpyrimidine **4e**



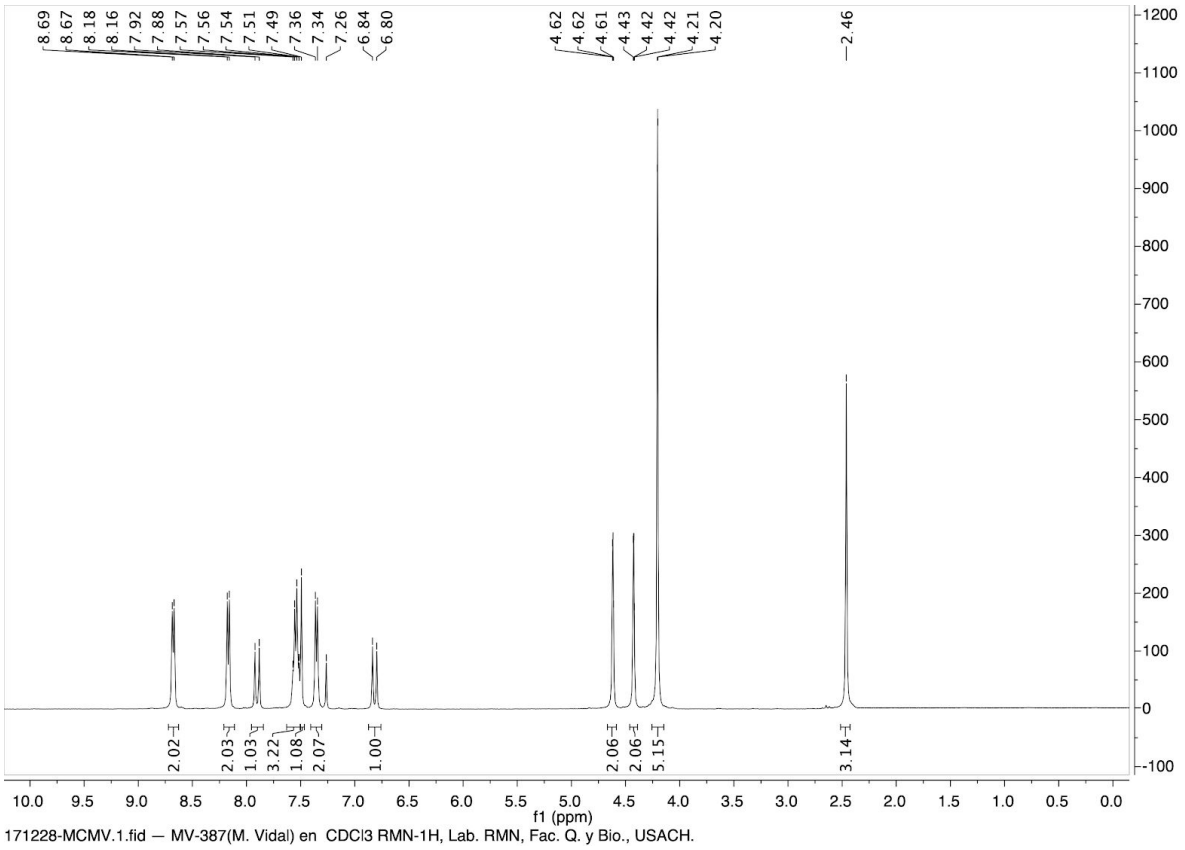
^{13}C NMR Spectrum of the 4-(9,9-dimethyl-9*H*-fluoren-2-yl)-6-methyl-2-phenylpyrimidine **4e**



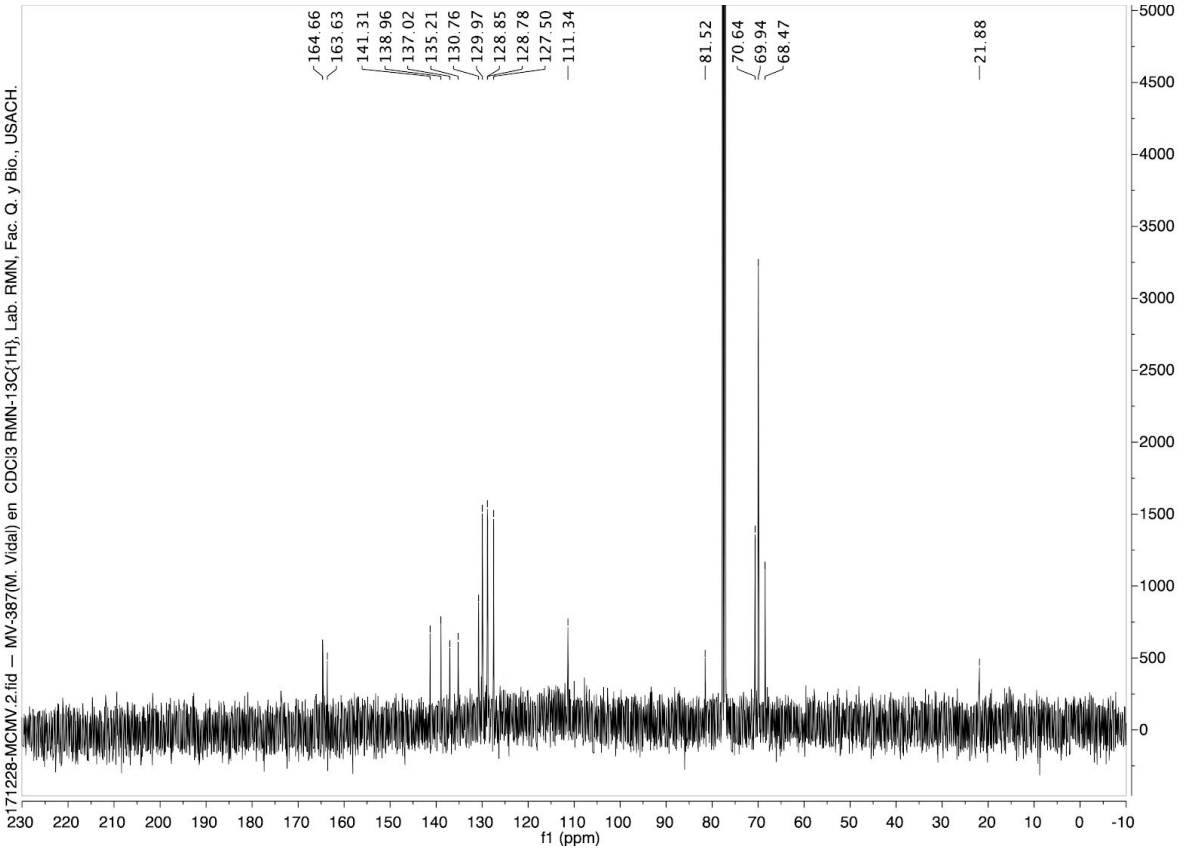
^{1}H NMR Spectrum of the (*E*)-2,4-diphenyl-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1a**



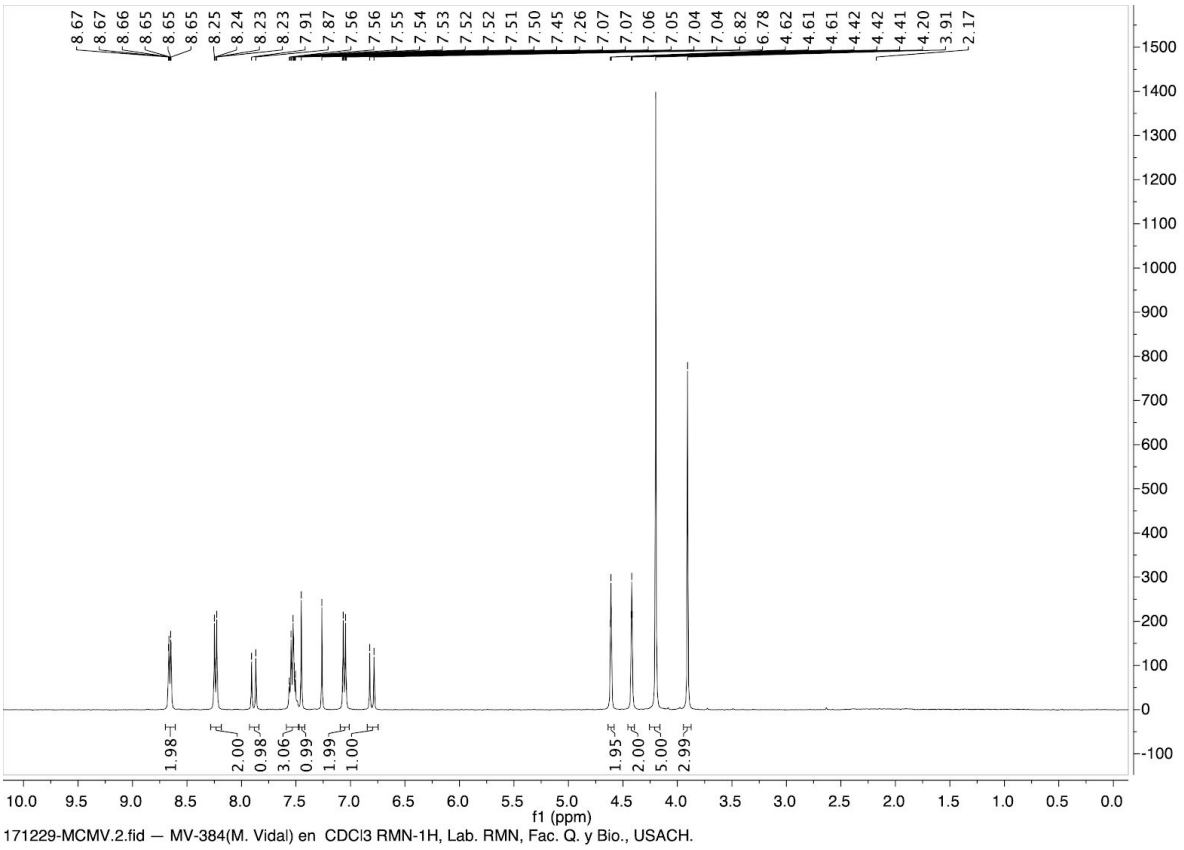
^{13}C NMR Spectrum of the (*E*)-2,4-diphenyl-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1a**



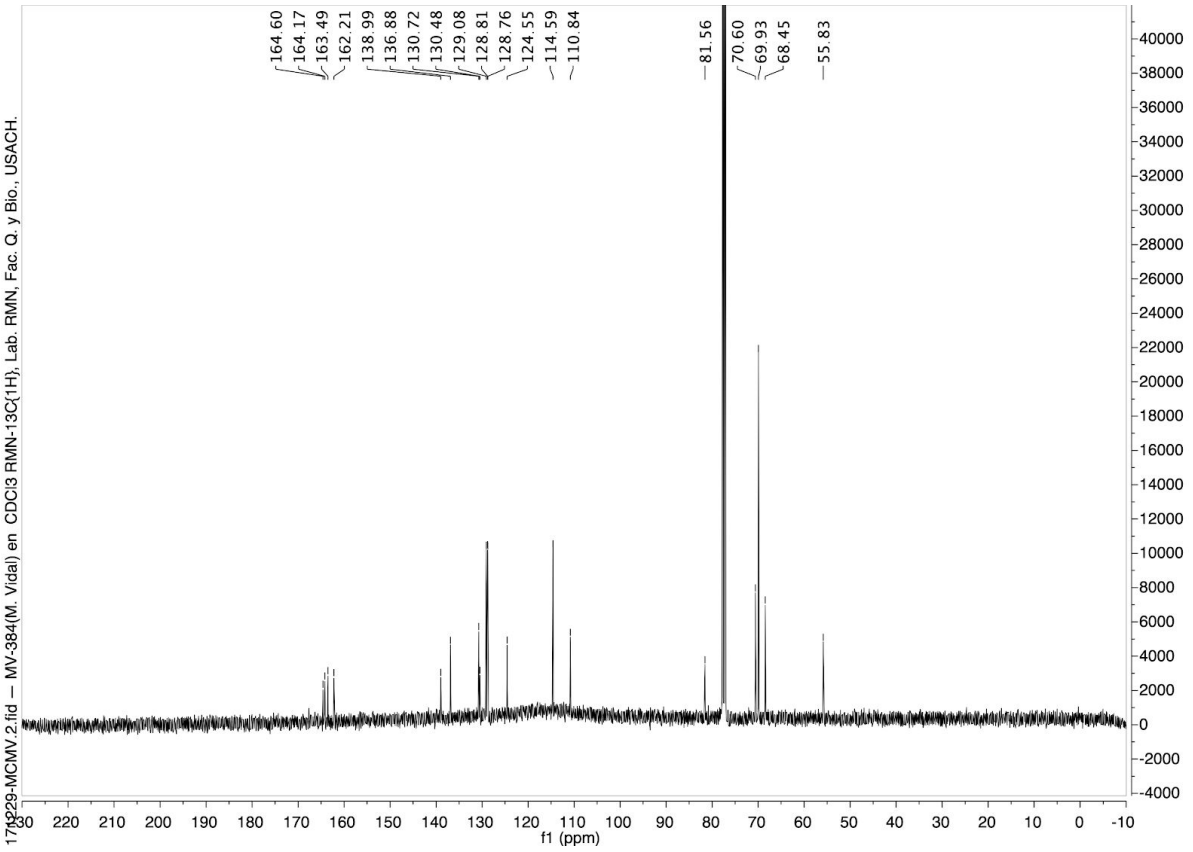
^{1}H NMR Spectrum of the (*E*)-2-phenyl-4-(4-methylphenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1b**



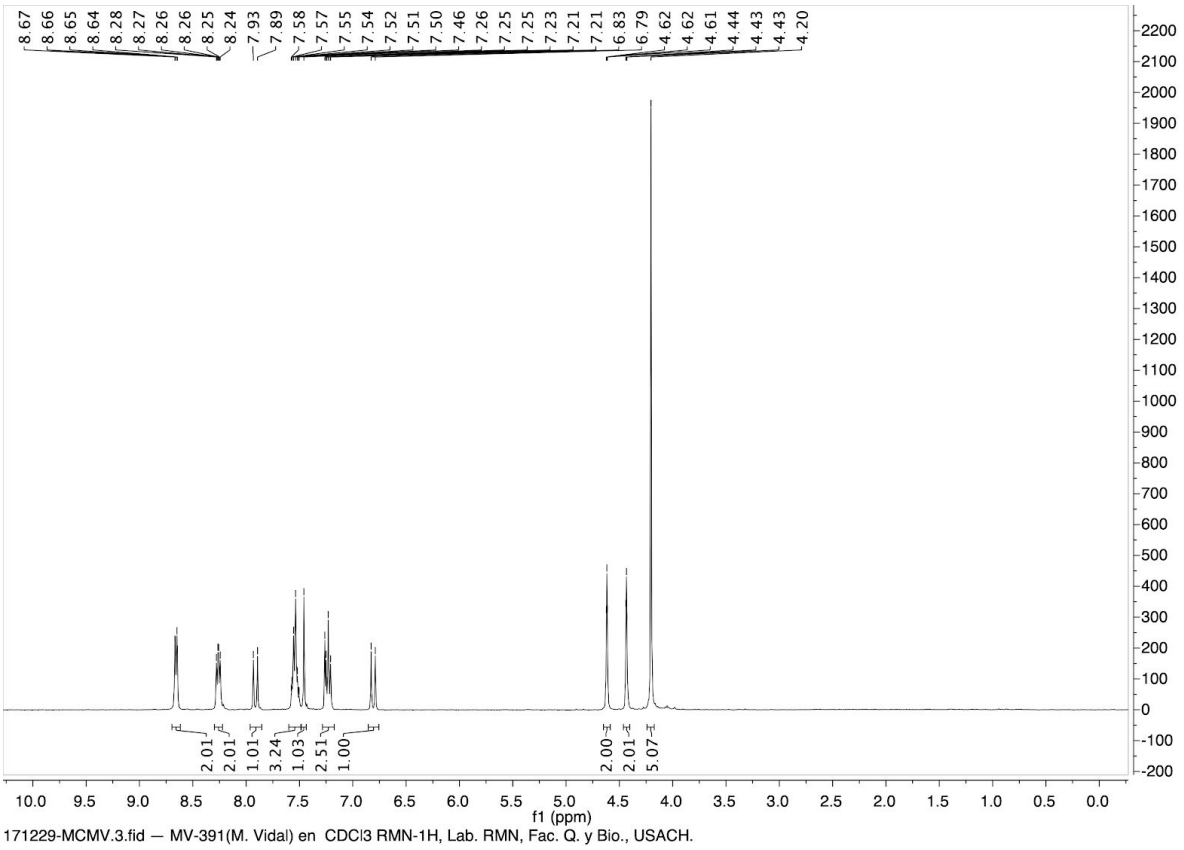
^{13}C NMR Spectrum of the (*E*)-2-phenyl-4-(4-methylphenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1b**



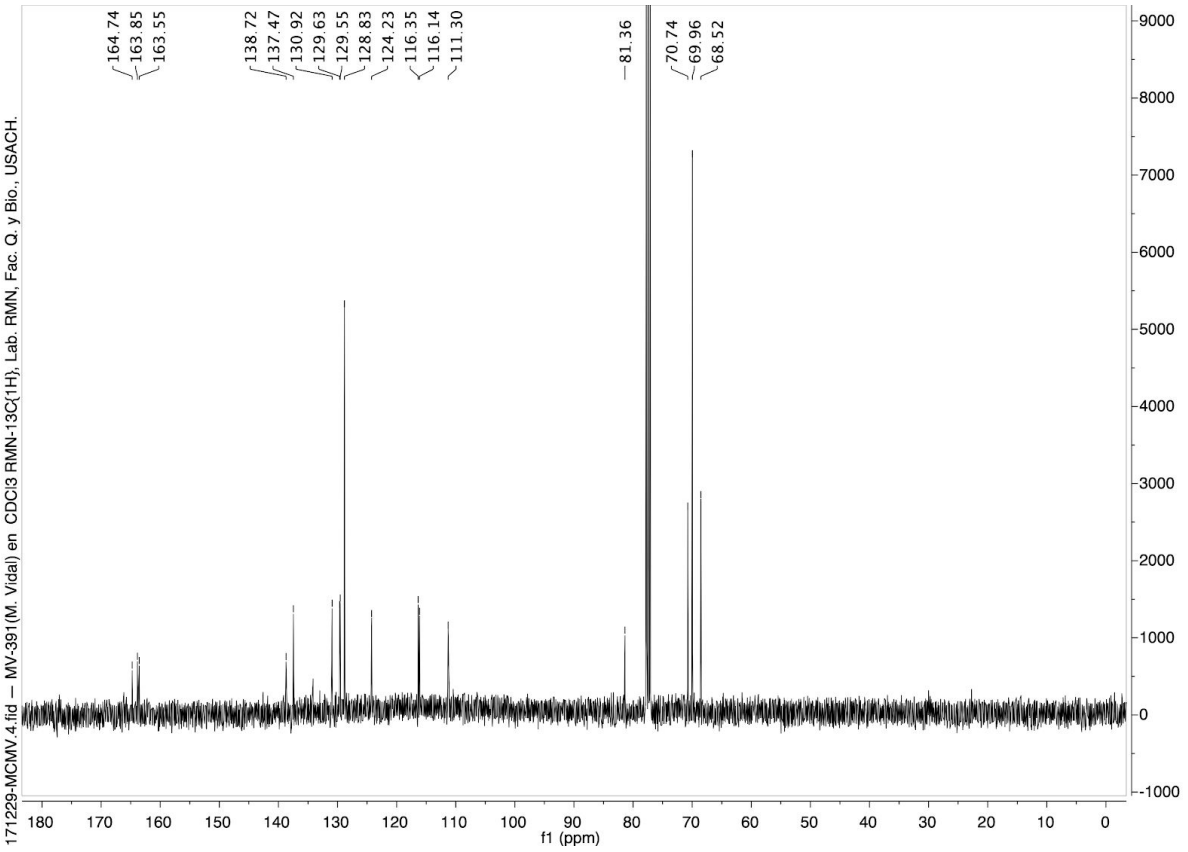
^{1}H NMR Spectrum of the (*E*)-2-phenyl-4-(4-methoxyphenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1c**



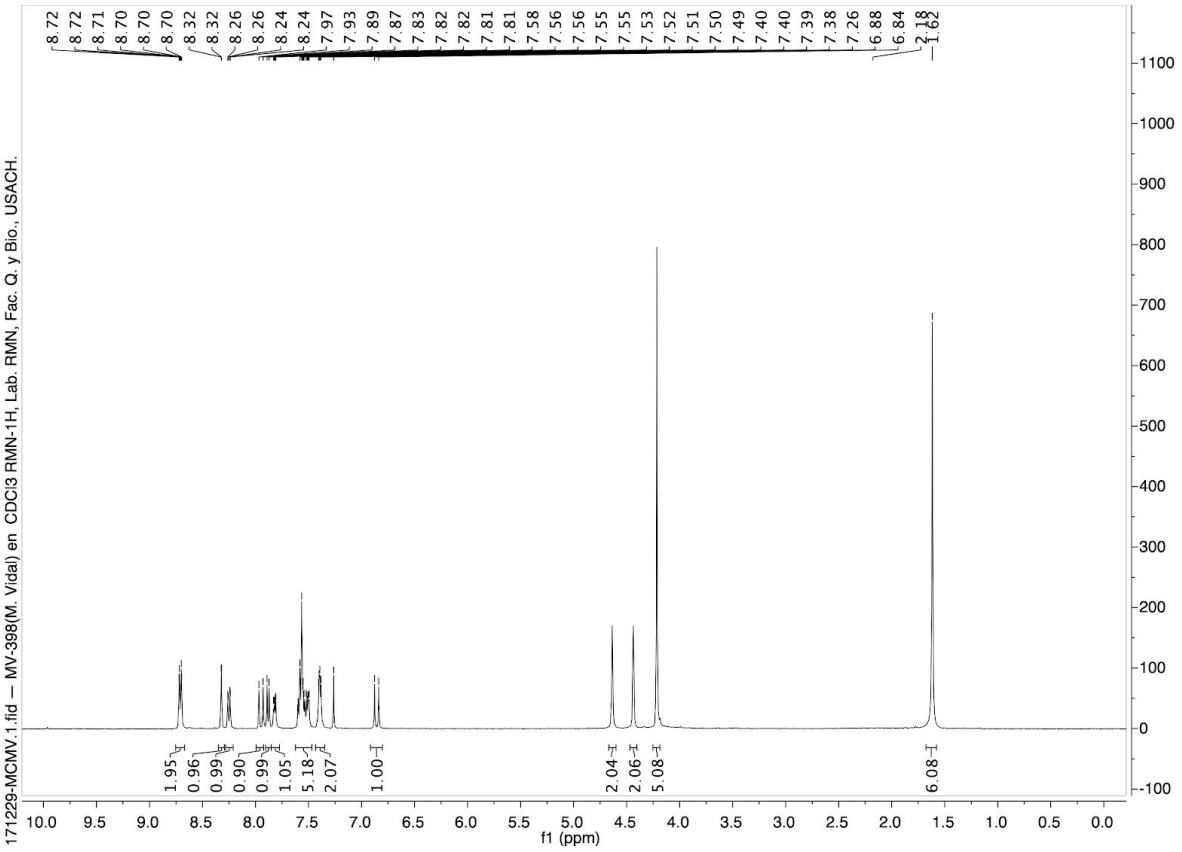
^{13}C NMR Spectrum of the (*E*)-2-phenyl-4-(4-methoxyphenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1c**



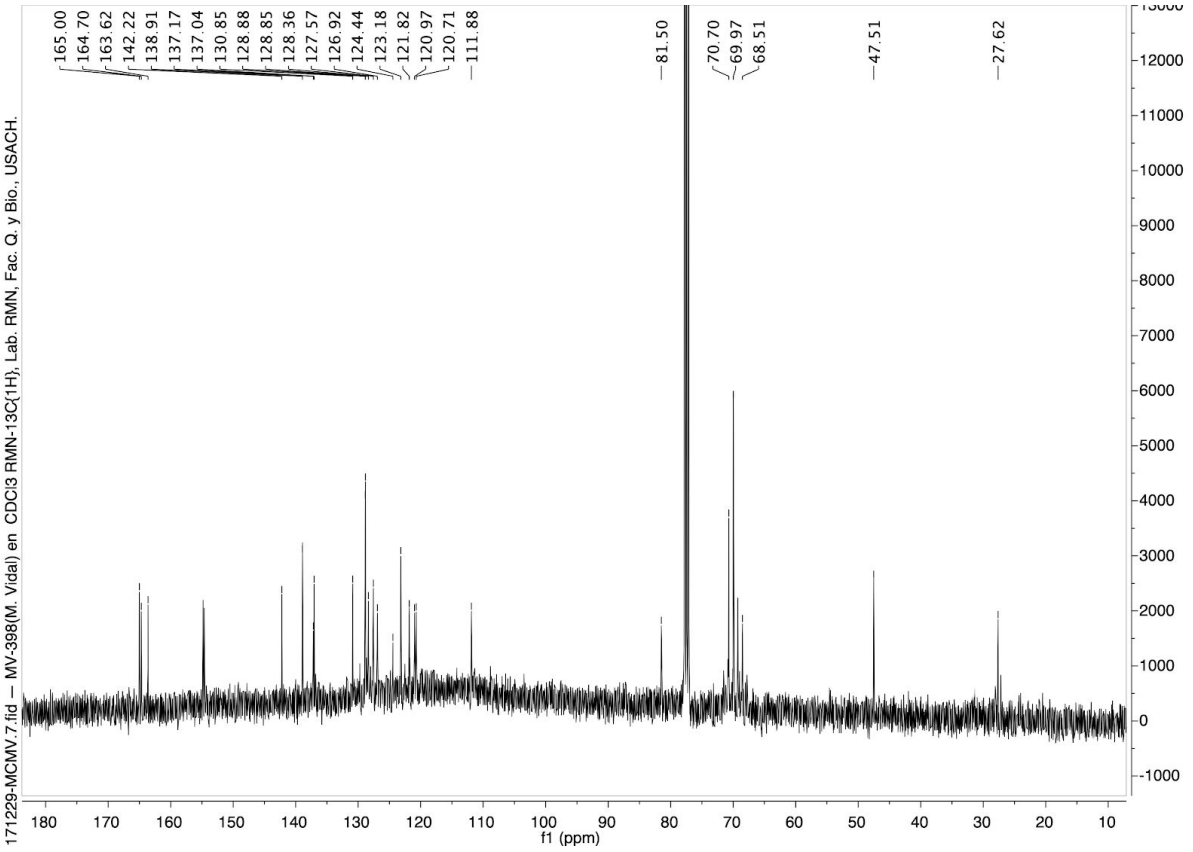
^{1}H NMR Spectrum of the (*E*)-2-phenyl-4-(4-fluorophenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1d**



^{13}C NMR Spectrum of the (*E*)-2-phenyl-4-(4-fluorophenyl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1d**



^{1}H NMR Spectrum of the (*E*)-2-phenyl-4-(9,9-Dimethyl-9*H*-fluorene-2-yl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1e**



^{13}C NMR Spectrum of the (*E*)-2-phenyl-4-(9,9-Dimethyl-9*H*-fluorene-2-yl)-6-[2-(ferrocen-2-yl)ethenyl]pyrimidine **1e**

8 Cartesian coordinates of the optimized structures

Cartesian coordinates of the optimized structure of dye 1a

C	-1.83875781703369	-0.17076104193317	0.44851675425561
N	-0.49856809712199	-0.16507291670093	0.46918731211750
C	0.12808346022909	0.92542210448413	-0.03440287291820
C	-0.61634199554560	1.99581492414607	-0.55941763361859
C	-2.01121285203789	1.89619581507656	-0.55559792466922
N	-2.62313989558064	0.80755883547067	-0.04294600620362
H	-0.10496493756782	2.87878125069290	-0.93978313751010
C	-2.88322550320829	2.96712603527715	-1.09290592434378
C	-4.22994164768272	3.03814921065403	-0.69349223592870
C	-2.39598898411712	3.92222220795682	-2.00304050753716
C	-5.06367996139962	4.04275028223026	-1.18353358462511
H	-4.60652979072880	2.29826166793216	0.01233493714733
C	-3.23337529392278	4.92217686189497	-2.49851620527963
H	-1.36217375441428	3.87381142624928	-2.34665001558867
C	-4.56910944811513	4.98829774139152	-2.08857165124070
H	-6.10408953497248	4.08983548536677	-0.85801210816014
H	-2.84310339572505	5.64908724390436	-3.21225633652714
H	-5.22241070812649	5.77207405019892	-2.47491541114350
C	-2.52422873791634	-1.36560558673409	1.01188406604750
C	-1.77962464485774	-2.42126633430645	1.56635567360422
C	-3.92698207937026	-1.45691293360475	0.99857730719969

C	-2.42317089339731	-3.54011130445674	2.09543485360413
H	-0.69252395375964	-2.35017762499001	1.57538547058659
C	-4.56871985552670	-2.57682072578356	1.52802706923409
H	-4.50292514837814	-0.63953042720857	0.56590838685983
C	-3.81997548450723	-3.62263156289965	2.07870221627873
H	-1.83288261123291	-4.35233305348294	2.52288162853055
H	-5.65825055892516	-2.63463366941420	1.51121055328806
H	-4.32260308948416	-4.49848717716690	2.49218508202561
C	1.58078758739697	0.97525411900696	-0.02555913762913
C	2.36384169756903	-0.01234193784283	0.47546903972880
H	2.03226271883442	1.86892266738581	-0.46297206561444
H	1.87038468764848	-0.88100636503442	0.91995144788874
C	3.80664535347306	-0.02665105801603	0.47568341598635
C	4.61806288739306	-1.04413318745913	1.11042103644800
C	4.70888157280341	0.84880806029047	-0.23914417874670
C	5.98948653747741	-0.77733311549741	0.81209294563102
H	4.23435610684547	-1.87002907192607	1.70400611897574
C	6.04526029409602	0.38841625949008	-0.02110467786311
H	4.42152541289566	1.69602534989271	-0.85552178034127
H	6.83995203162018	-1.37502880151783	1.12921423180634
H	6.94523353204370	0.82500215817302	-0.44611090565149
Fe	4.90093457042876	-1.07027222272610	-0.90720433893729
C	6.00601419217031	-2.07788700120872	-2.32184191409633
C	5.15526344967647	-2.98689322176487	-1.61115257739069

C	5.17642857854175	-1.08753776585654	-2.94352572297419
H	7.09177500760581	-2.11259327042235	-2.35480208712146
C	3.79967511098111	-2.55792379009515	-1.79151235446112
H	5.48318353117462	-3.83209948177525	-1.01172030901622
C	3.81281037864001	-1.38202276632662	-2.61491868172563
H	5.52394702407155	-0.24051550923873	-3.52909995537903
H	2.91952923354638	-3.02136357084581	-1.35396305279879
H	2.94434571749321	-0.79743726092983	-2.90697425220337

Cartesian coordinates of the optimized structure of dye 2a

C	-1.76376563821827	-0.21489607354152	0.44853448339976
N	-0.45009911681336	-0.15958835673421	0.46230757498158
C	0.17820050776639	0.94338508604129	-0.04907438640403
C	-0.57756240076413	2.01166929074757	-0.59374556682768
C	-1.95640011857573	1.94374820819777	-0.58779013478108
N	-2.51535053688650	0.81131958729687	-0.05570665979077
H	-0.07583920805592	2.89726715415844	-0.97703698148675
C	-2.85725646740995	2.98888148564955	-1.07965084123816
C	-4.14537931548339	3.14579201876375	-0.53323715529619
C	-2.43670779048096	3.85137702760361	-2.10905445519466
C	-4.99234314928999	4.14491379894137	-1.00868519937911
H	-4.47944206943966	2.51946137701701	0.29622768349327
C	-3.29009234749372	4.84466101726300	-2.58306363383951

H	-1.45179990571587	3.72489837791335	-2.55881017343682
C	-4.56855278792306	4.99436791246571	-2.03534005728620
H	-5.98298809110870	4.26670773891832	-0.57010149581310
H	-2.95958099347150	5.50017859313659	-3.38912389921707
H	-5.23404688286670	5.77398436629491	-2.40748592724566
C	-2.46870635371926	-1.39377991549246	0.97750179563884
C	-1.77609129671863	-2.26788338098929	1.83428916614652
C	-3.80770076013417	-1.66888983405033	0.64552186717427
C	-2.41650612962949	-3.38826140842082	2.35719345064161
H	-0.74021035076496	-2.04791292801677	2.08871282365274
C	-4.44157609815502	-2.79482315400714	1.16776143139766
H	-4.36006632120888	-1.03514482536138	-0.05059236763120
C	-3.74960669320445	-3.65422419579156	2.02663969709108
H	-1.87548686810827	-4.05662921609826	3.02774480996084
H	-5.47608096781297	-3.00642894786367	0.89640833943927
H	-4.24875233182014	-4.53383914249531	2.43483402154787
C	1.60639697958938	1.00437733770514	-0.02210289602611
C	2.38622686789419	0.01616806268114	0.51590309417940
H	2.06450308940063	1.89230888668804	-0.46090731294774
H	1.88222890212953	-0.84233250609331	0.96679277114609
C	3.81631119036501	0.00260303729436	0.54565121773483
C	4.60831764125244	-1.06192686284449	1.13458740435666
C	4.72819681206477	0.85449539297923	-0.19181981144365
C	5.97442609667092	-0.83667505857601	0.79572990868476

H	4.21438152236182	-1.88157947364582	1.72936457040570
C	6.04771789934004	0.33831667029863	-0.02104290599302
H	4.45712739454807	1.72410098604197	-0.78318648834576
H	6.81145766971156	-1.47244811280986	1.07021632948752
H	6.95001799591167	0.74280958237442	-0.47125156057255
Fe	4.80387272963463	-1.06125361577087	-0.89158156065329
C	5.87220135102285	-2.07809335697473	-2.33768572657344
C	5.00953868764914	-2.97794801104806	-1.63206862065414
C	5.06091676151180	-1.06178388250622	-2.93842056820563
H	6.95651737235103	-2.13392031536955	-2.37767860539941
C	3.66482206311288	-2.51560509341540	-1.78910764942675
H	5.32572612847632	-3.83688636822044	-1.04656581037173
C	3.69698570755374	-1.32682843640419	-2.59772694197441
H	5.42331562182395	-0.21479419510914	-3.51437576740680
H	2.77905046972135	-2.96817921282975	-1.35208925455887
H	2.83964630031437	-0.71921195591524	-2.87460210372294
H	-3.53133253090481	0.73062145992374	-0.03985679141607