Supporting Information

Structure and isomerization behavior relationship of new push–pull azo-pyrrole photoswitches

D. Gallardo-Rosas,[a] J. M. Guevara-Vela,[b] T. Rocha-Rinza,[b] R. A. Toscano,[b] J. G. López-Cortés,[b] and M. C. Ortega-Alfaro*[a]

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1. General Information

The synthesis of the palladium complex used in the cross-coupling reactions was conducted under argon atmosphere with standard Schlenk techniques as reported elsewhere.[i] All temperature given for reaction conditions are externally measured. All reactions were monitored by TLC.

2. Materials

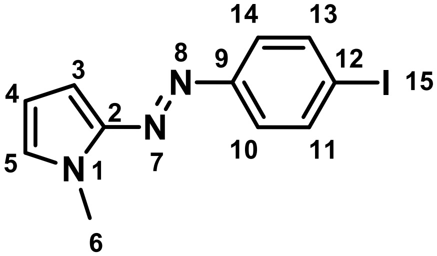
Commercial materials were used as received: CH_2Cl_2 purchased from Sigma-Aldrich in anhydrous form. $CHCl_3$, Methanol were purchased from Sigma-Aldrich in HPLC and/or spectrophotometric quality. ASTM type 1 ultra-pure water (Millipore-Q system, 18.2 M Ωcm) was used as solvent for the aggregation studies. HCl, $NaNO_2$, *N*-methylpyrrole, pyridine, 4-Iodoaniline, $Cr(CO)_6$, Et_3OBF_4, S_8, $NaBH_4$, $PdCl_2$, and K_2CO_3 were purchased from Sigma-Aldrich. Analytical thin layer chromatography was performed on DC-Fertigfolien ALUGRAM® Xtra SIL G/UV254 MACHEREY-NAGEL. Column chromatography was performed on Silica 60, 0.063-0.2 mm MACHEREY-NAGEL.

3. Methods

Melting points were obtained on a Stuart Melting Point Apparatus SMP10 and they are uncorrected. All compounds were characterized by IR spectra, recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer provide with an ATR polarization attachment and all data are expressed in wave numbers (cm^{-1}). NMR spectra were measured on a Bruker Avance 300 Spectrometer, at an operating frequency of 300 MHz for ^{1}H and 75 MHz for ^{13}C, using tetramethylsilane (TMS) as internal reference and $CDCl_3$ as solvent; chemical shifts values are given in parts per million (ppm), relative to TMS. Mass spectrometry analyses were obtained on a JEOL SX102A (EI^+ and FAB^+) and on an AccuTOF JMS-T100LC (DART), the values of the signals are expressed in mass/charge units (m/z), followed by the relative intensity with reference to a 100% base peak. UV-Vis absorption spectra were recorded at 298 K on a Thermo-Scientific Evolution 60S UV-Vis spectrophotometers, using spectrophotometric grade solvents purchased from Sigma-Aldrich Co. and 1 cm quartz cell. The solvatochromic study was performed using 10^{-5} M to 10^{-4} M solutions of azopyrrole dyes in several solvents at room temperature. The aggregation study was carried out using $5x10^{-5}$ M solutions of azopyrrole dyes at different MeOH: H_2O ratios, from 100:0 to 20:80 at room temperature.

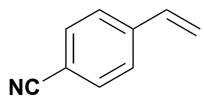
Synthesis of compound 1: In a 100 mL round-flask, 4-Iodoaniline (2.51 g, 11.2 mmol) and *N*-methylpyrrole (1 mL, 11.2 mmol), were dissolved in 6 mL of MeOH, then HCl [1M] (10 mL, 0.01 mol) was added and the mixture was cooled at mixed at 0 °C. Then, an aqueous solution of sodium nitrite (0.93 g, 13.4 mmol in the minimum quantity of water) was added dropwise. The mixture was stirred for 10 minutes at 0 °C and then for 30 more minutes at room temperature. A solution of 10% NaOH was added until pH=10 and then, the mixture was extracted with CH_2Cl_2 and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel with hexane. The spectroscopic data agreed with those reported in the literature.[ii]

2-(4'-Iodophenyl-azo)-N-methyl pyrrole (**1a**).

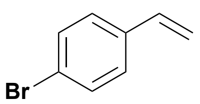


Orange solid. Yield (80 %). mp 98 °C. **^{1}H NMR** (300 MHz, $CDCl_3$, ppm): δ 3.95 (s, 3H, H6), 6.30 (t, 1H, H4), 6.72 (d, 1H, H-3), 6.96 (t, 1H, H-5), 7.79, 7.76 (m, 2H, H-11,13), 7.55, 7.52 (m, 2H, H-10,14). **^{13}C NMR** (75 MHz, $CDCl_3$, ppm): δ 33.4 (C-6), 95.03 (C-12), 100.6 (C-4), 110.57 (C-3), 123.7 (C-10,14), 127.5 (C-5), 138.1 (C-11,13), 146.4 (C-2), 153 (C-9). **HR-MS** (FAB+) m/z for $C_{11}H_{10}N_3I$: calculated 310.9919, found 310.9923.

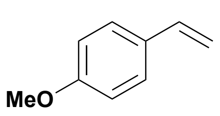
Synthesis of vinyl arenes. In a 100 mL round flask were added 1 g of the corresponding aldehyde, 1.2 equiv. of methyl triphenylphosphonium bromide and 2 equiv. of K_2CO_3 in 40 mL of THF. The mixture reaction was refluxed for 12 h. Afterward, the solvent was removed via a reduced pressure distillation and the crude was redissolved in 20 mL of dichloromethane, washed with water (2 x 20 mL) and dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel with hexane. All vinyl arenes synthesized were characterized by NMR and their data agreed with the literature.[iii]



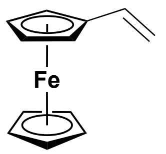
4-Vinyl benzonitrile. Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.45 (d, *J* = 10.9 Hz, 1H). **^{13}C** NMR (75 MHz, $CDCl_3$, ppm): δ 141.9, 135.4, 132.4, 126.7, 117.7, 111.1.



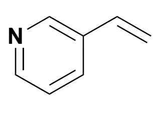
4-Bromo styrene. Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.63 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H). **^{13}C** NMR (75 MHz, $CDCl_3$, ppm): δ 136.5, 135.8, 131.7, 127.8, 121.6, 114.6.



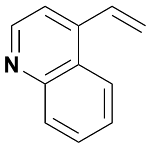
1-Methoxy-4-vinylbenzene. Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.34 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.60 (d, *J* = 17.6 Hz, 1H), 5.11 (d, *J* = 10.9 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 159.4, 136.2, 130.5, 127.4, 113.9, 111.6, 55.3.



Vinyl ferrocene. Orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ d 6.52 (dd, *J* = 16.6, 11.0 Hz, 1H), 4.81 (dd, *J* = 17.3, 1.2 Hz, 1H), 4.61 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.18 (s, 2H), 4.12 (s, 2H), 4.09 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 135.1, 111.4, 83.9, 69.6, 69.1, 67.1.



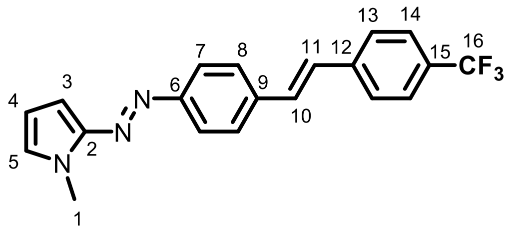
3-Vinylpiridine. Colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.35 (d, *J* = 11.0 Hz, 1H), 5.80 (d, *J* = 17.6 Hz, 1H), 6.68 (dd, *J* = 17.6, 11.0 Hz, 1H), 7.22 (dd, *J* = 7.9, 4.9 Hz 1H), 7.70 (dd, *J* = 7.9, 2.3, 1.6 Hz, 1H), 8.46 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.73 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 116.2, 123.4, 132.6, 133.0, 133.5, 148.3, 148.9.



4-Vinyl quinoline. Pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.89-7.50 (m, 6 H), 7.45 (q, *J* = 23.0, 14.4 Hz, 1 H), 6.01 (q, *J* = 23.0, 14.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 150.4, 148.6, 143.8, 132.3, 130.1, 129.5, 126.8, 126.4, 123.7, 121.0, 117.6.

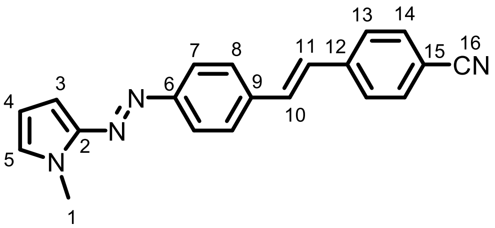
Synthesis of Stilbenyl-azopyrroles 2a-d and 3a-d. A 10 mL vial was filled with compound **1** (0.5 mmol), triethylamine (0.75 mmol), the corresponding vinyl arene (0.6 mmol), 5 mL of DMF as solvent and 0.1% mol of the palladium complex.[i] The vial was introduced into a stainless-steel reactor and placed in an oil bath at 160 °C. After the reaction is completed, the reactor was cooled to room temperature, the system was decompressed, and the mixture of reaction was diluted with 30 mL of water and extracted with hexane (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was afterwards evaporated under vacuum. The crude was purified by chromatography on silica gel using Hexane-AcOEt.

1-methyl-2-((*E*)-(4-((*E*)-4-(trifluoromethyl)styryl)phenyl)diazenyl) pyrrole (**2a**).



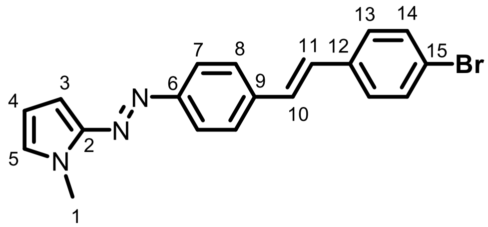
Orange solid. Yield (71 %) mp 161 ^{o}C, **IR** (cm^{-1}) 3123 (C-H pyrrole), 1611 (C=C), 1356 (C-F),1319 (N=N), 1319 (CF$_3$) **^{1}H NMR** (300 MHz, CDCl$_3$, ppm): δ 7.76 (d, *J* = 9 Hz, 2H, H8), δ 7.54 (m, 6H, H7,13 y 14), 7.16 (d, *J* = 15 Hz, 1H, H10), 7.09 (d, *J* =15, 1H, H11), 6.88 (m, 1H, H5), 6.66 (dd *J* = 3.0, 1.5 Hz, 1H, H3), 6.24 (dd, *J* = 3.0, 2.4 Hz, 1H, H4), 3.90 (s, 2H, H1). **^{13}C NMR** (75 MHz, CDCl$_3$, ppm): δ 153.41 (C6), 146.73 (C2), 140.68 (C9), 137.52 (C12), 130.60 (C10), 129.59 (q, J_{C-F} = 32.25 Hz, C15), 127.72 (C11), 127.45 (C7), 127.26 (C5), 126.67 (C13), 125.26 (q, J_{C-F} = 269 Hz, C16), 125.69 (q, J_{C-F} = 3.75 Hz, C14), 122.55 (C8), 110.48 (C4), 100.24 (C3), 33.45 (C1). MS (DART$^+$ m/z): 356 [M$^+$]. **HR-MS** (ESI+ *m/z*) for C$_{20}$H$_{17}$F$_3$N$_3$: calculated 356.13746, found 356.13658 [M$^+$+1].

4-((*E*)-4-((*E*)-(1-methyl-1H-pyrrol-2-yl)diazenyl)styryl)benzonitrile (**2b**).



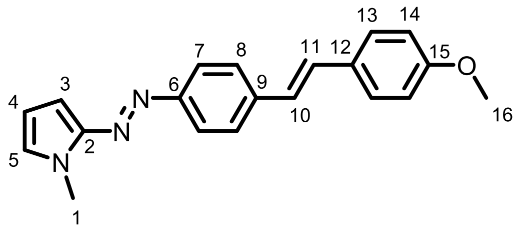
Orange-red solid. Yield (73 %) mp 161-164 ^{o}C, **IR** (cm^{-1}) 1600 (C=C), 3127 (C-H pyrrole), 2222 (C≡N), 1329 (N=N)**.** **^{1}H NMR** (300 MHz, CDCl$_3$, ppm): δ 7.86 (d, *J* = 9 Hz, 2H, H8), 7.68-7.60 (m, 6H, H7,13 y 14), 7.28 (d, *J* = 15 Hz, 1H, H11), 7.16 (d, *J* = 15 Hz, 1H, H10), 6.99 (m, 1H, H5), 6.76 (dd, *J* = 4.2, 1.5 Hz, 1H, H3), 6.34 (dd, *J* = 4.2, 2.7 Hz, 1H, H4) 4 (s, 3H, H1). **^{13}C NMR** (300 MHz, CDCl$_3$, ppm) δ 153.62 (C6), 146.74 (C2), 141.72 (C12), 137.11 (C9), 132.53 (C14), 131.78 (C10), 127.62 (C8), 127.43 (C11), 127.26 (C5), 126.94 (C13), 122.58 (C7), 119.05 (C16), 110.67 (C15), 110.57 (C4), 100.41 (C3), 33.47 (C1). MS (DART$^+$ m/z): 313 [M$^+$]. **HR-MS** (ESI+ *m/z*) for C$_{20}$H$_{17}$N$_4$: calculated 313.14532, found 313.14422 [M$^+$+1].

2-((*E*)-(4-((*E*)-4-bromostyryl)phenyl)diazenyl)-1-methylpyrrole (**2c**).



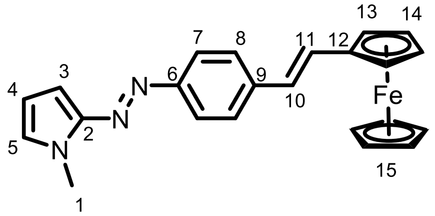
Orange solid. Yield (58%) mp 148 °C decomposition. **IR** (cm^{-1}) 1616 (C=C), 1323 (N=N), 1070 (Ar-*p*-Br). **^{1}H NMR** (300 MHz, $CDCl_3$, ppm): δ 7.84 (d, *J* = 8.4 Hz, 2H, H8), 7.61 (d, *J* = 8.4 Hz, 2H, H7), 7.52 (d, *J* = 8.4 Hz, 2H, H13), 7.42 (d, *J* = 8.4 Hz, 2H, H14), 7.17 (d, *J* = 15 Hz, 1H, H11), 7.11 (d, *J* = 15 Hz, 1H, H10), 6.98 (m, 1H, H5), 6.75 (m, 1H, H3), 6.33 (m, 1H, H4), 4 (s, 3H, H1). **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 153.15 (C6), 146.72 (C2), 137.92 (C9), 136.17(C12), 131.85 (C13), 128.82 (C11), 128.07 (C10, C14), 127.20 (C8), 127.11 (C5), 122.54 (C7), 121.55 (C15), 110.41 (C4), 100.10 (C3), 33.45 (C1). MS (EI$^+$ *m/z*): 365 [M$^+$], 367 [M$^+$+2]. **HR-MS** (ESI+ *m/z*) for $C_{19}H_{17}BrN_3$: calculated: 366.06058, found 366.05991 [M$^+$ + 1].

2-((*E*)-(4-((*E*)-4-methoxystyryl)phenyl)diazenyl)-1-methylpyrrole (**2d**).



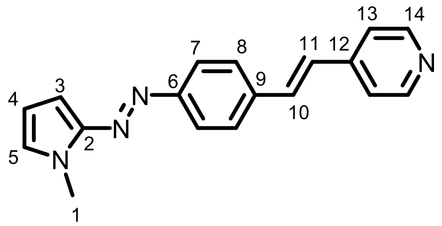
Orange solid. Yield (58%) mp 148 °C decomposition. **IR** (cm^{-1}) 1601 (C=C), 3115 (Ar-C-H), 1248 (N=N). **^{1}H NMR** (300 MHz, $CDCl_3$, ppm): δ 7.8 (d, *J* = 8.7 Hz, 2H, H8), 7.57 (d, *J* = 8.4 Hz, 2H, H7), 7.48 (d, *J* = 8.7, 2H, H13), 7.14 (d, *J* = 16.5 Hz, 1H, H11), 7.00 (d, *J* = 16.5 Hz, 1H, H10), 6.94 (m, 1H, H5), 6.91 (d, *J* = 9 Hz, 2H, H14), 6.70 (m, 1H, H3), 6.30 (m, 1H, H4), 3.97 (s, 3H, H1), 3.84 (s, 3H, H16). **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 159.51 (C15), 152.73 (C6), 146.72 (C2), 138.78 (C9), 130.04 (C12), 129.04 (C11), 127.89 (C13), 126.82 (C5 y C7), 126.03 (C10), 122.51 (C8), 114.21 (C14), 110.28 (C4), 99.86 (C3), 55.35 (C16), 33.39 (C1). **EM** (DART$^+$ *m/z*): 318 [M$^+$+1]. **HR-MS** (ESI+ *m/z*) for $C_{20}H_{20}N_3O$: calculated 318.16061, found 318.15981 [M$^+$ + 1].

2-((*E*)-(4-((*E*)-2-(ferrocenyl)phenyl)diazenyl)-1-methylpyrrole (**3a**).



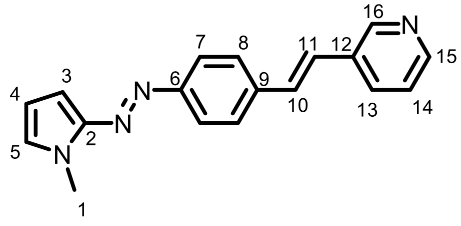
Black solid. Yield (69 %) mp 148 °C decomposition. **IR** (cm^{-1}) 1625 (C=C), 1323 (N=N). **^{1}H NMR** (300 MHz, $CDCl_3$, ppm): δ 7.78 (d, *J* = 8.4 Hz, 2H, H8), 7.50 (d, *J* = 8.4 Hz, 2H, H7), 6.95 (d, *J* = 15 Hz, 1H, H 11), 6.92 (m, 1H, H5), 6.73 (d, *J* = 15 Hz, 1H, H10), 6.70 (m, 1H, H3), 6.29 (m, 1H, H4), 4.48 (m, 2H, H13), 4.31 (m, 2H, H14), 4.15 (s, 5H, H15), 3.96 (s, 3H, H1). **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 152.40 (C6), 146.77 (C2), 139.05 (C9), 128.23 (C11), 126.73 (C5), 126.31 (C7), 125.49 (C10), 122.58 (C8), 110.28 (C4), 99.73 (C3), 83.19 (C12), 69.32 (C14 y C15), 67.05 (C13), 33.43 (C1). **EM** (DART$^+$ *m/z*): 396 [M$^+$+1]. **HR-MS** (ESI+ *m/z*) for $C_{23}H_{21}FeN_3$: calculated 395.108485, found 396.11673 [M$^+$ + 1].

4-((*E*)-4-((*E*)-(1-methyl-1H-pyrrol-2-yl)diazenyl)styryl)pyridine (**3b**).



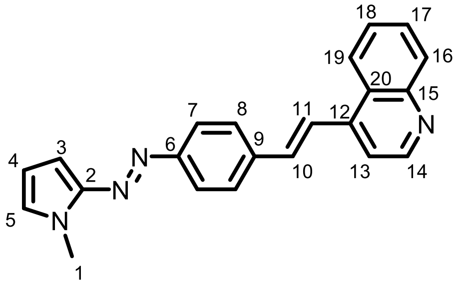
Red solid. Yield (73 %). mp 168 ^{o}C. **IR** (cm^{-1}) 1626 (C=C), 1324 (N=N). **^{1}H NMR** (300 MHz, CDCl3, ppm) δ 8.59 (d, *J* = 6 Hz, 2H, H14), 7.83 (d, *J* = 6 Hz, 2H, H8), 7.62 (d, *J* = 6 Hz, 2H, H7), 7.38 (d, *J* = 6 Hz, 2H, H13), 7.34 (d, *J* = 15 Hz, 1H, H10), 7.07 (d, *J* = 15 Hz, 1H, H11), 6.96 (m, 1H, H5), 6.74 (m, 1H, H3), 6.32 (m, 1H, H4), 3.97 (s, 3H, H1). **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 153.71 (C6), 150.25 (C14), 146.74 (C2), 144.49 (C12), 136.95 (C9), 132.56 (C11), 127.73 (C8), 127.43 (C5), 126.52 (C10), 122.56 (C7), 120.88 (C13), 110.56 (C4), 100.43 (C3), 33.47 (C1). **EM** (EI$^+$ *m/z*): 288 [M$^+$]. **HR-MS** (ESI+ *m/z*) for $C_{18}H_{16}N_4$: calculated 288.137496, found 289.14580 [M$^+$ + 1].

3-((*E*)-4-((*E*)-(1-methyl-1H-pyrrol-2-yl)diazenyl)styryl)pyridine (**3c**).



Orange solid. Yield (53%). mp 126 ^{o}C. **IR** (cm^{-1}) 1660 (C=C), 1322 (N=N). **^{1}H NMR** (300 MHz, CDCl3, ppm) δ 8.76 (s, 1H, H16), 8.52 (m, 1H, H15), 7.85 (m, 3H, H8, H13), 7.63 (d, *J* = 9 Hz, 2H, H7), 7.32 (m, 1H, H14), 7.23 (d, *J* = 15 Hz, 1H, H10), 7.14 (d, *J* = 15 Hz, 1H, H11), 6.97 (s, 1H, H5), 6.76 (m, 1H, H3), 6.33 (m, 1H, H4), 3.99 (s, 3H, H1) **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 153.35 (C6), 148.69 (C16), 148.65 (C15), 146.71 (C2), 137.53 (C9), 132.91 (C12), 132.70 (C13), 130.20 (C11), 127.33 (C7), 127.24 (C5), 125.50 (C10), 123.60 (C14), 122.55 (C8), 110.46 (C4), 100.25 (C3), 33.45 (C1). **EM** (DART$^+$ *m/z*): 289 [M$^+$ +1]. **HR-MS** (ESI+ *m/z*) for $C_{18}H_{16}N_4$: calculated 288.137496, found 289.14442 [M$^+$ + 1].

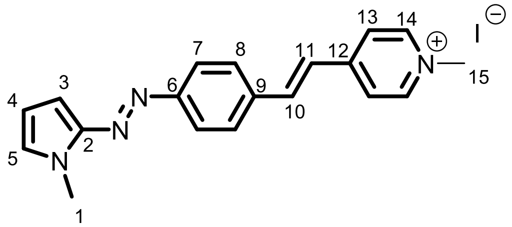
4-((*E*)-4-((*E*)-(1-methyl-1H-pyrrol-2-yl)diazenyl)styryl)quinoline (**3d**).



Red solid. Yield (95%). mp 198 ^{o}C decomposition. **IR** (cm^{-1}) 1621 (C=C) 1342 (N=N). **^{1}H NMR** (300 MHz, CDCl$_3$, ppm): δ 8.92 (d, *J* = 5 Hz, 1H, H14), 8.25 (d, *J* = 8 Hz, 1H, H16), 8.15 (d, *J* = 8 Hz, 1H, H19), 7.89 (m, 3H, H8, H11), 7.73 (m, 3H, H7, H17), 7.62 (m, 2H, H13, H18), 7.39 (d, *J* = 15 Hz, 1H, H10), 6.98 (m, 1H, H5), 6.75 (m, 1H, H3), 6.32 (m, 1H, H5), 3.99 (s, 3H, H1). **^{13}C NMR** (75 MHz, CDCl$_3$, ppm) δ 151.68 (C6), 150.09 (C15), 149.38 (C14), 146.59 (C2), 134.67 (C9), 131.67 (C12), 130.92 (C11), 129.43 (C16), 128.86 (C17) 127.88 (C7), 127.47 (C5), 126.68 (C10), 125.84 (C20), 123.46 (C18), 123.33 (C19), 122.64 (C8), 117.03 (C13), 110.59 (C4), 100.51 (C3), 33.48 (C1). **MS** (DART$^+$ *m/z*): 339 [M$^+$ +1]. **HR-MS** (ESI+ *m/z*) for $C_{22}H_{19}N_4$: calculated 339.16102, found 339.15982 [M$^+$ + 1].

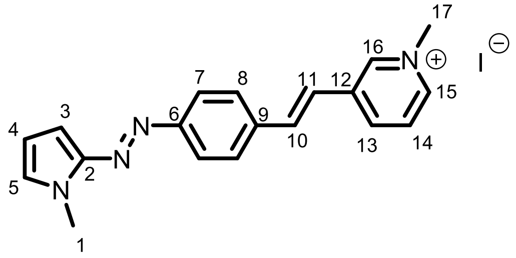
Synthesis of compounds 4b-d. In a 50 mL round-flask were added 0.5 mmol of the compound **3** and 5 equiv of MeI in 10 mL of acetonitrile. The mixture was stirred for 24h yielding a dark red solid. The solvent was eliminated by distillation under vacuo and the remanent solid was washed at least three times with diethyl ether, recovered by decantation.

1-methyl-4-((*E*)-4-((*E*)-(1-methyl-1H-pyrrol-2-yl)diazenyl)styryl) pyridin-1-ium iodide (**4b**).



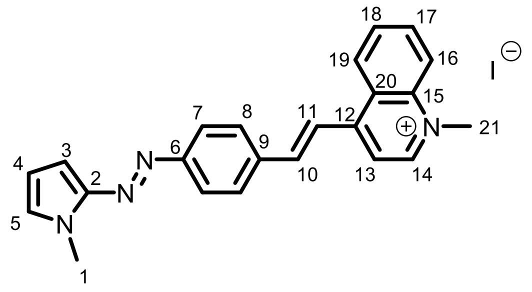
Brown solid. Yield (90 %). mp 180 ^{o}C decomposition. IR (cm^{-1}) 2999 (C(sp^{3})-H), 1613 (C=C). **^{1}H NMR** (300 MHz, (CD$_3$)$_2$SO, ppm) δ 8.89 (d, *J* = 9 Hz, 2H, H14), 8.26 (dd, *J* = 9 Hz, 2H, H13), 8.08 (d, *J* = 15 Hz, 1H, H10), 7.88 (m, 4H, H7, H8), 7.60 (d, *J* = 15 Hz, 2H, H11), 7.38 (m, 1H, H5), 6.67 (m, 1H, H3), 6.35 (dd, *J* = 4 Hz, 1H, H4), 4.27 (s, 3H, H15), 3.96 (s, 3H, H1). **^{13}C NMR** (75 MHz, (CD$_3$)$_2$SO, ppm) δ 154.47 (C6), 152.74 (C12), 146.73 (C2), 145.59 (C14), 140.23 (C10), 136.39 (C9), 130.03 (C5), 129.70 (C8), 124.31 (C11), 124.06 (C13), 122.80 (C7), 111.26 (C4), 101.17 (C3), 47.44 (C15), 33.65 (C1). **MS** (FAB+ *m/z*): 303 [M$^+$]. **HR-MS** (ESI+ *m/z*) for $C_{19}H_{19}N_4$: calculated 303.16097, found 303.16042 [M$^+$].

1-methyl-3-((*E*)-4-((*E*)-(1-methyl-1H-pyrrol-2-yl)diazenyl)styryl) pyridin-1-ium iodide (**4c**).



Orange solid. Yield (82%). mp 125 °C. **IR** (cm^{-1}) 3000 (C(sp^3)-H), 1625 (C=C), 1327 (N=N). **^{1}H NMR** (300 MHz, $(CD_3)_2SO$, ppm) δ 9.31 (s, 1H, H16), 8.86 (d, *J* = 6 Hz, 1H, H15), 8.78 (d, *J* = 9 Hz, 1H, H13), 8.14 (t, 1H, H14), 7.80 (m, 5H, H7, H8 y H10), 7.49 (d, *J* = 15 Hz, 1H, H11), 7.36 (m, 1H, H5), 6.66 (m, 1H, H3), 6.34 (m, 1H, H4), 4.38 (s, 3H, H17), 3.96 (s, 3H, H1) **^{13}C NMR** (75 MHz, $(CD_3)_2SO$, ppm) δ 153.83 (C6), 146.62 (C2), 143.80 (C16), 143.72 (C15), 141.43 (C13), 137.50 (C12), 136.89 (C10), 134.99 (C9), 129.62 (C5), 128.70 (C8), 128.03 (C14), 122.80 (C7), 122.62 (11), 111.06 (C4), 100.83 (C3), 48.59 (C17), 33.62 (C1). **MS** (FAB+ *m/z*): 303 [M^+]. **HR-MS** (ESI+ *m/z*) for $C_{19}H_{19}N_4$: calculated 303.16097, found 303.16121 [M^+].

1-methyl-4-((E)-4-((E)-(1-methyl-1H-pyrrol-2-yl)diazenyl)styryl)quinolin-1-ium iodide (**4d**).



Black solid. Yield (76%). mp 280 °C decomposition. IR (cm^{-1}) 3005 (C(sp^3)-H), 1614 (C=C), 1319 (N=N). **^{1}H NMR** (300 MHz, $(CD_3)_2SO$, ppm) δ 9.39 (d, *J* = 6 Hz, 1H, H14), 9.09 (d, *J* = 6 Hz, 1H, H16), 8.54 (d, *J* = 6 Hz, 1H, H19), 8.47 (d, *J* = 9 Hz, 1H, H13), 8.40 (d, *J* = 15 Hz, 1H, H11), 8.23 (m, 2H, H10, H17), 8.14 (d, *J* = 9 Hz, 2H, H8), 8.08 (t, 1H, H18), 7.88 (d, *J* = 9 Hz, 2H, H7), 7.39 (m, 1H, H5), 6.68 (m, 1H, H3), 6.36 (m, 1H, H4), 4.56 (s, 3H, H21), 3.97 (s, 3H, H1). **^{13}C NMR** (75 MHz, $(CD_3)_2SO$, ppm) δ 154.64 (C6), 152.77 (C12), 148.59 (C14), 146.77 (C2), 142.47 (C10), 139.24 (C15), 136.74 (C9), 135.50 (C17), 130.48 (C8), 130.14 (C5), 129.81 (C18), 127.00 (C20), 126.87 (C16), 122.67 (C7), 120.90 (C11), 119.88 (C13), 116.85 (C19), 111.32 (C4), 101.24 (C3), 45.25 (C21), 33.66 (C1). **MS** (FAB+ *m/z*): 353 [M^+]. **HR-MS** (ESI+ *m/z*) for $C_{23}H_{21}N_4$: calculated 353.17662, found 353.17747 [M^+].

^{1}H and ^{13}C NMR Spectra.

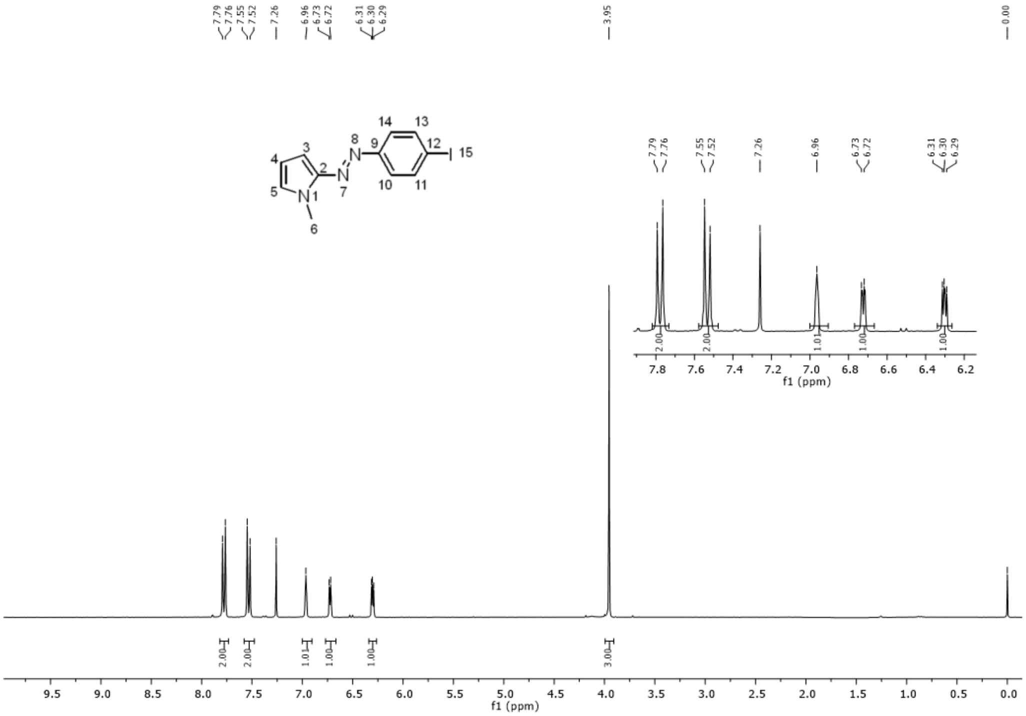


Figure S 1 ^{1}H NMR spectrum (300 MHz, CDCl$_3$) of compound **1a**

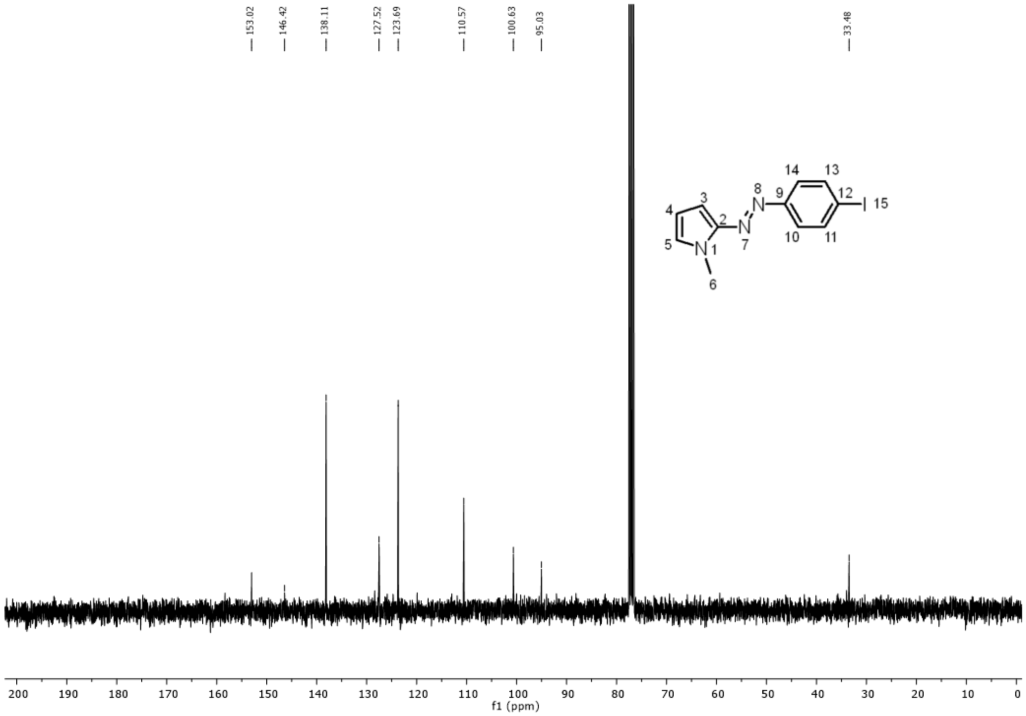


Figure S 2 ^{13}C NMR spectrum (75 MHz, CDCl$_3$) of compound **1a**

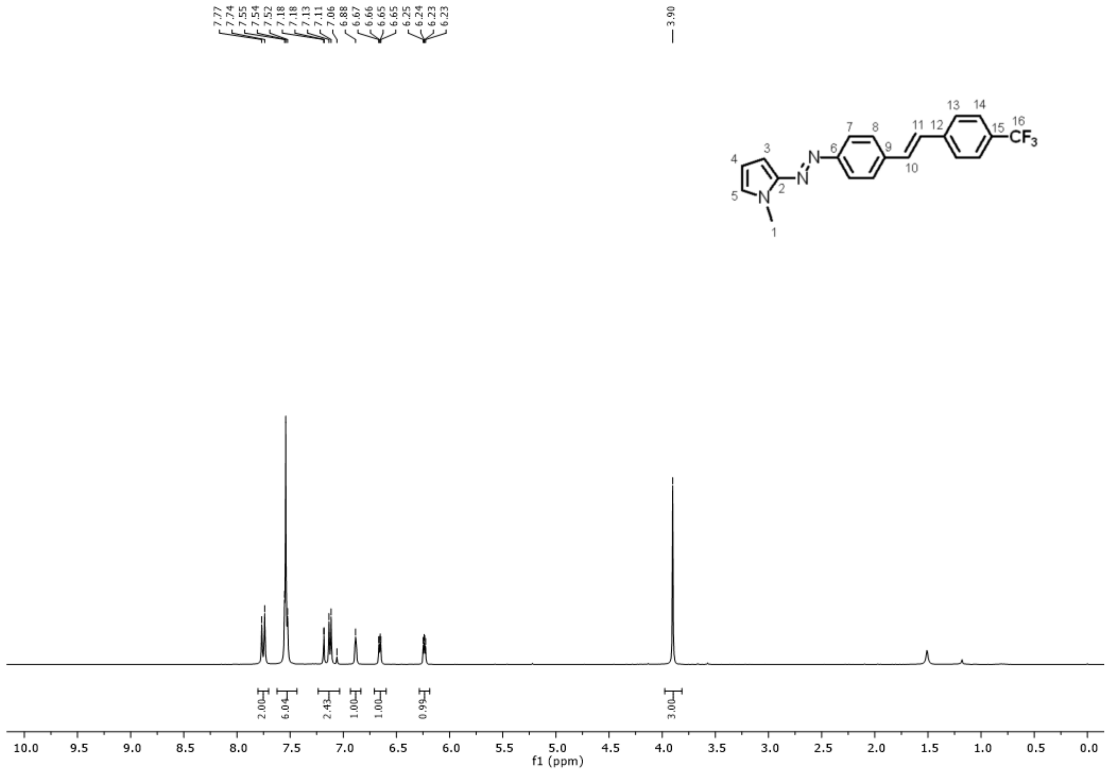


Figure S 3 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **2a**

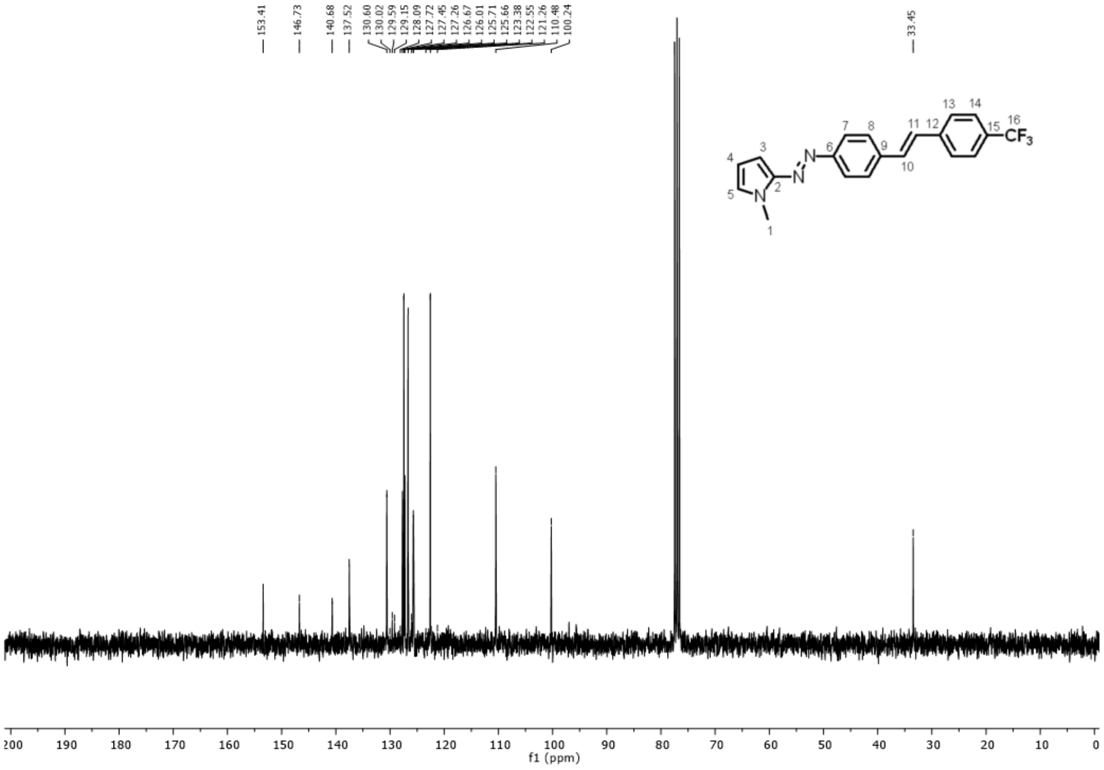


Figure S 4 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **2a**

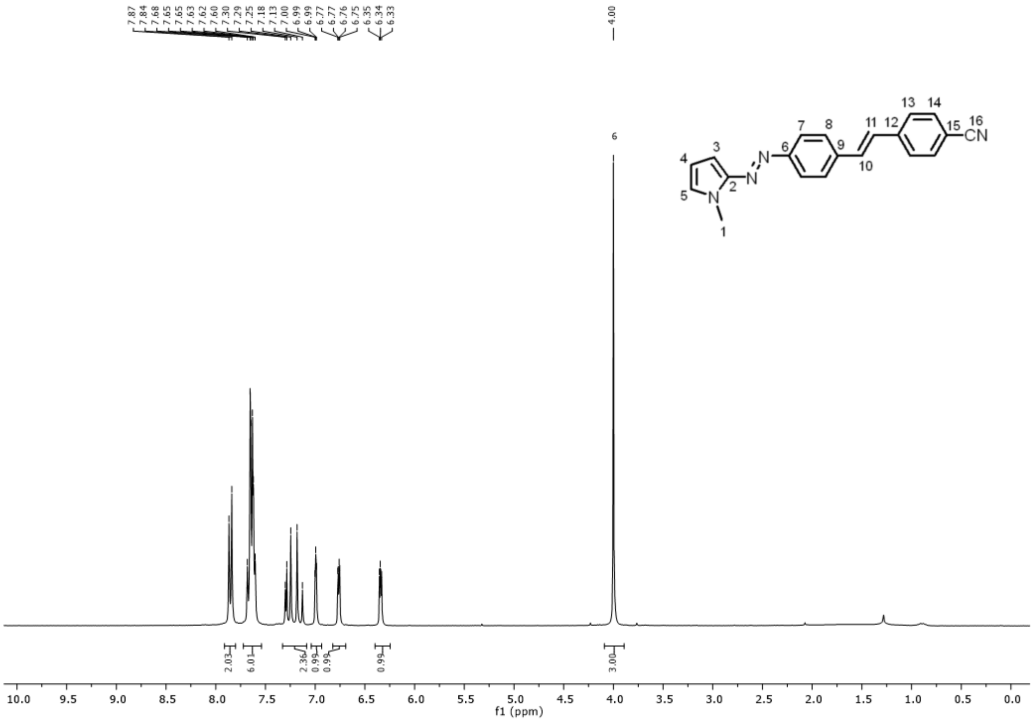


Figure S 5 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **2b**

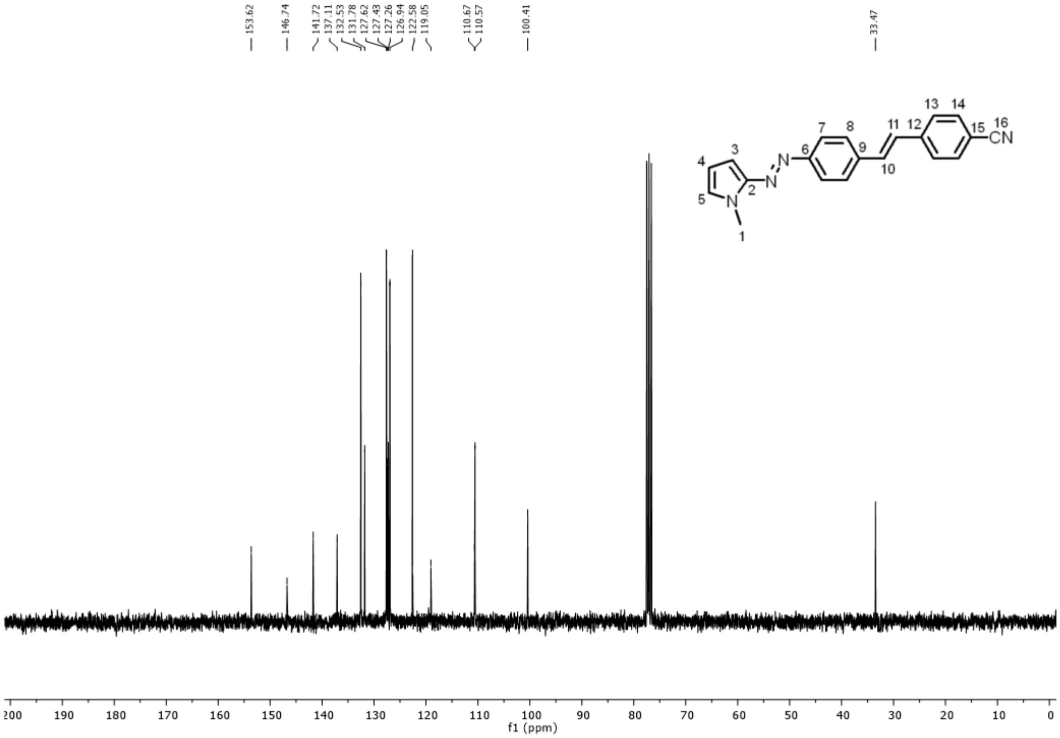


Figure S 6 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **2b**

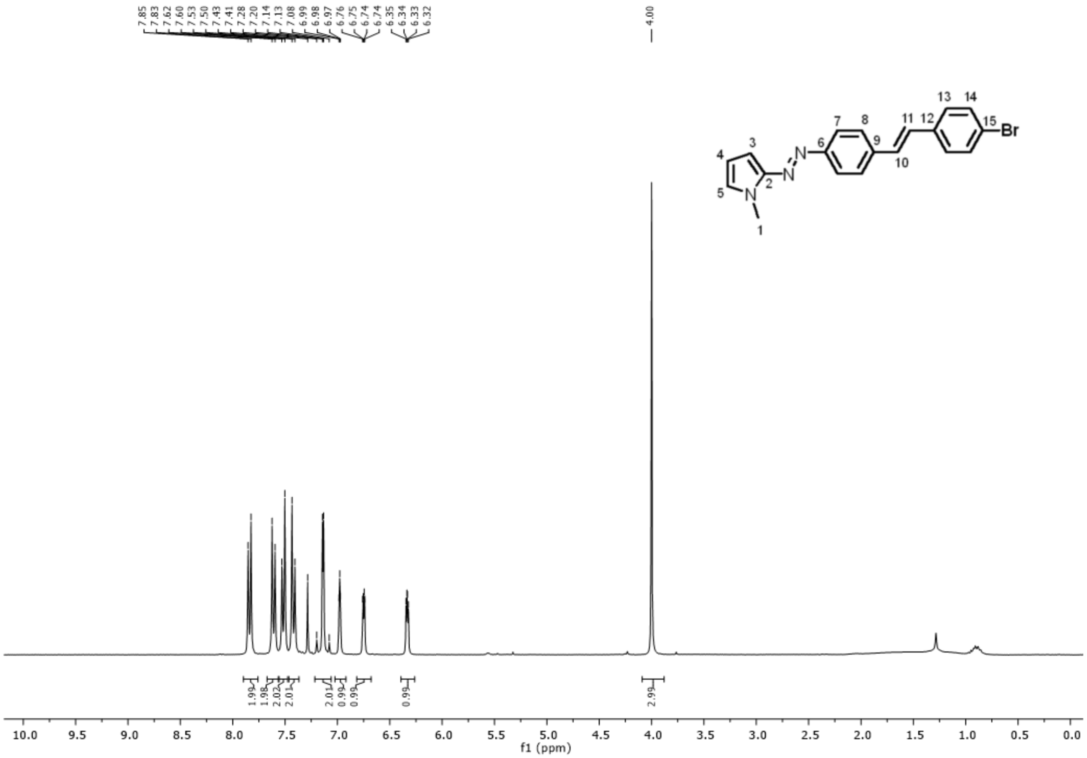


Figure S 7 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **2c**

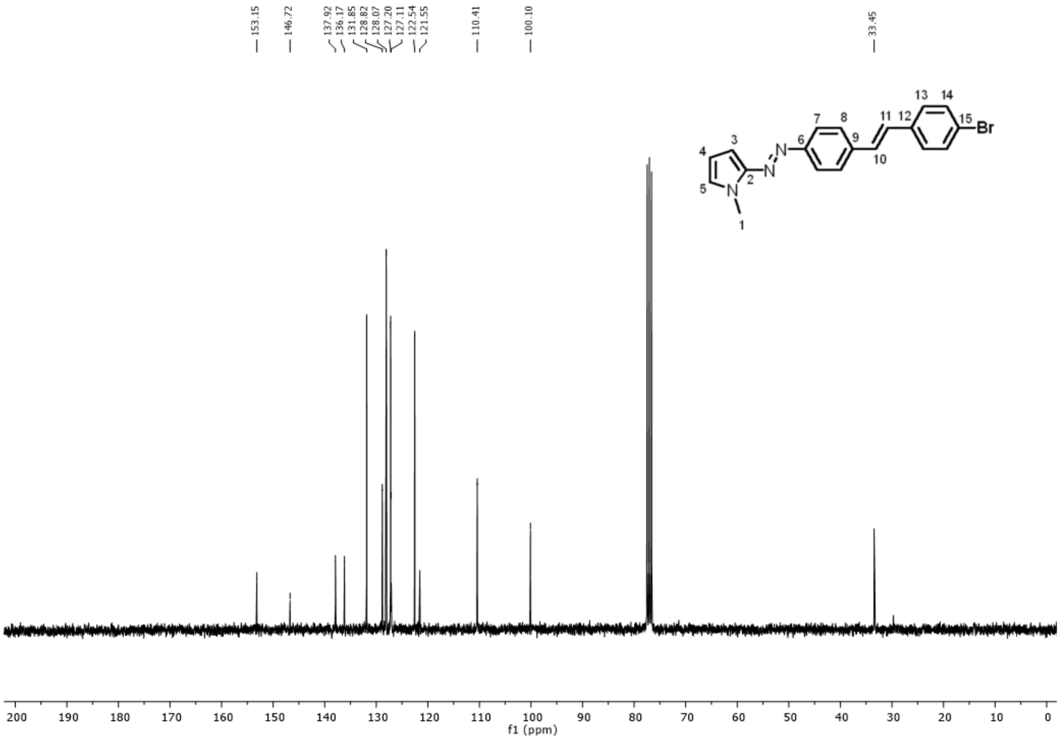


Figure S 8 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **2c**

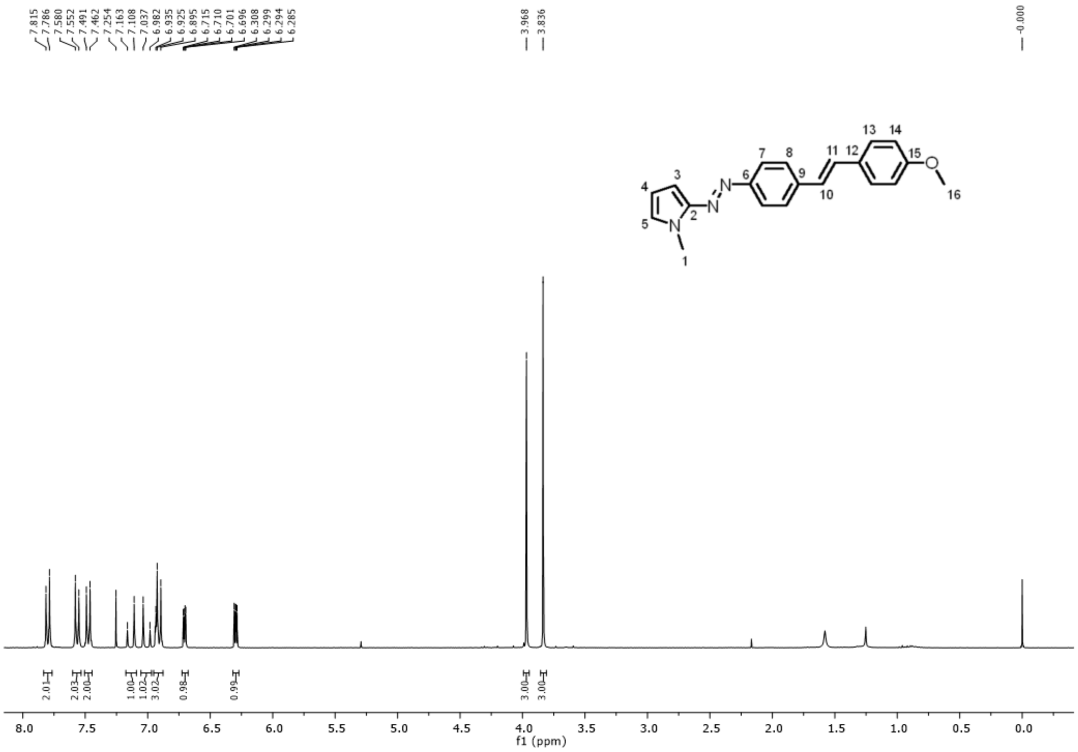


Figure S 9 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **2d**

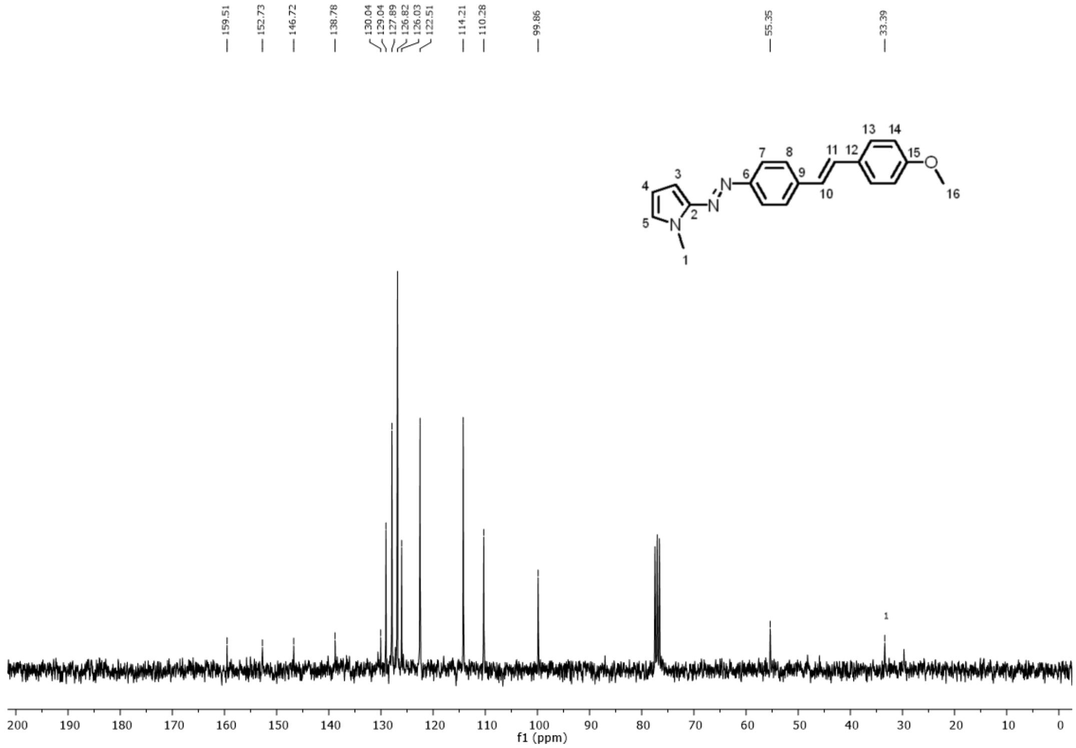


Figure S 10 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **2d**

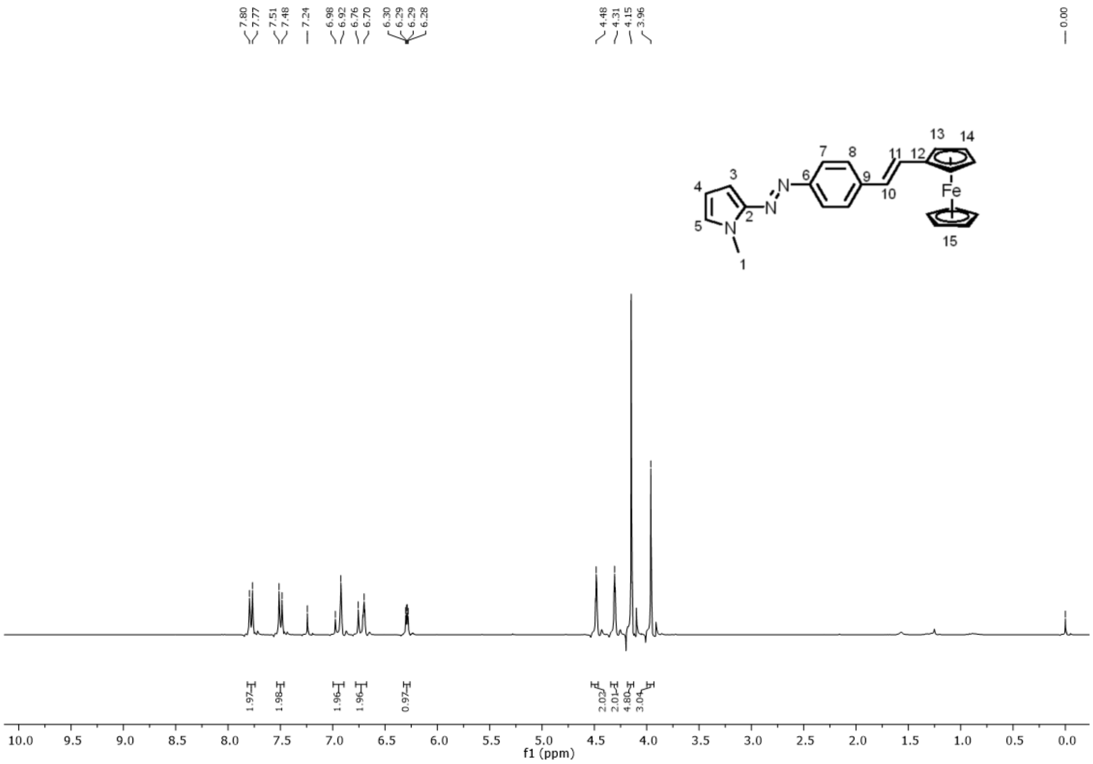


Figure S 11 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **3a**

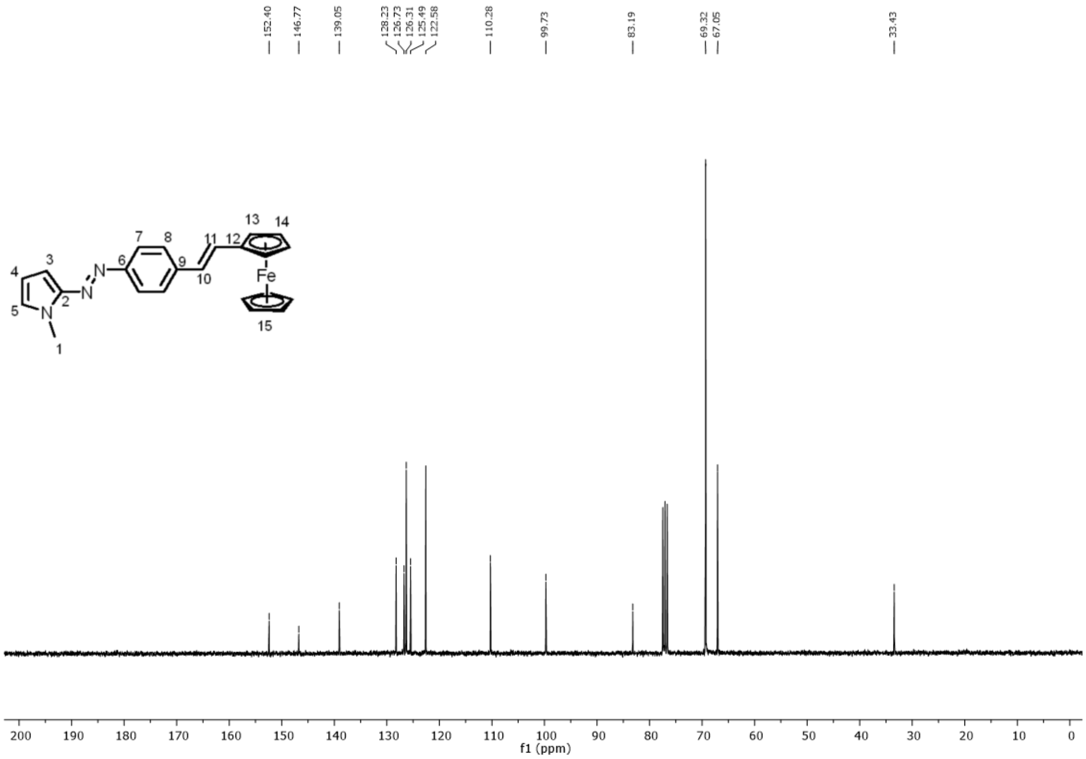


Figure S 12 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **3a**

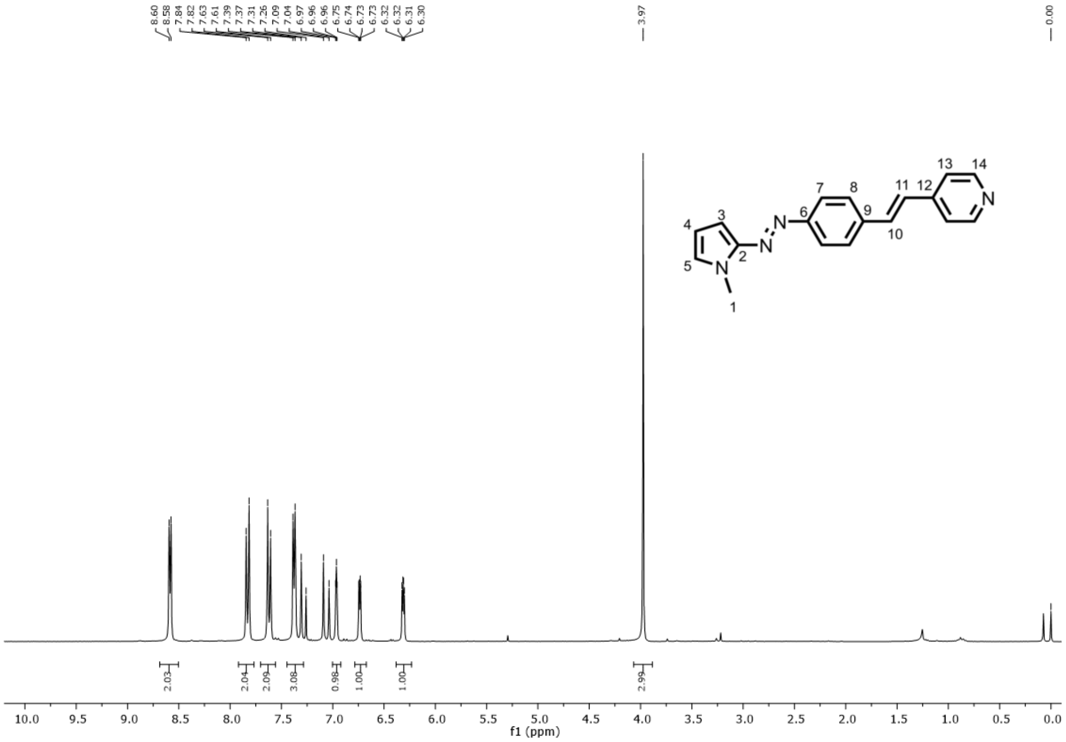


Figure S 13 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **3b**

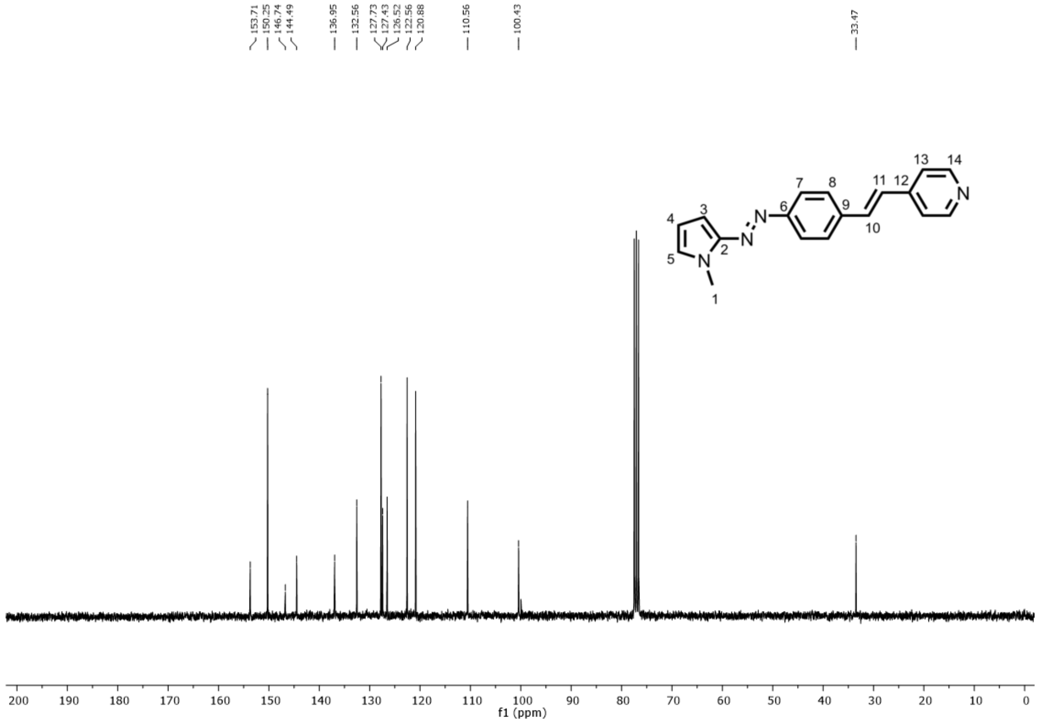


Figure S 14 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **3b**

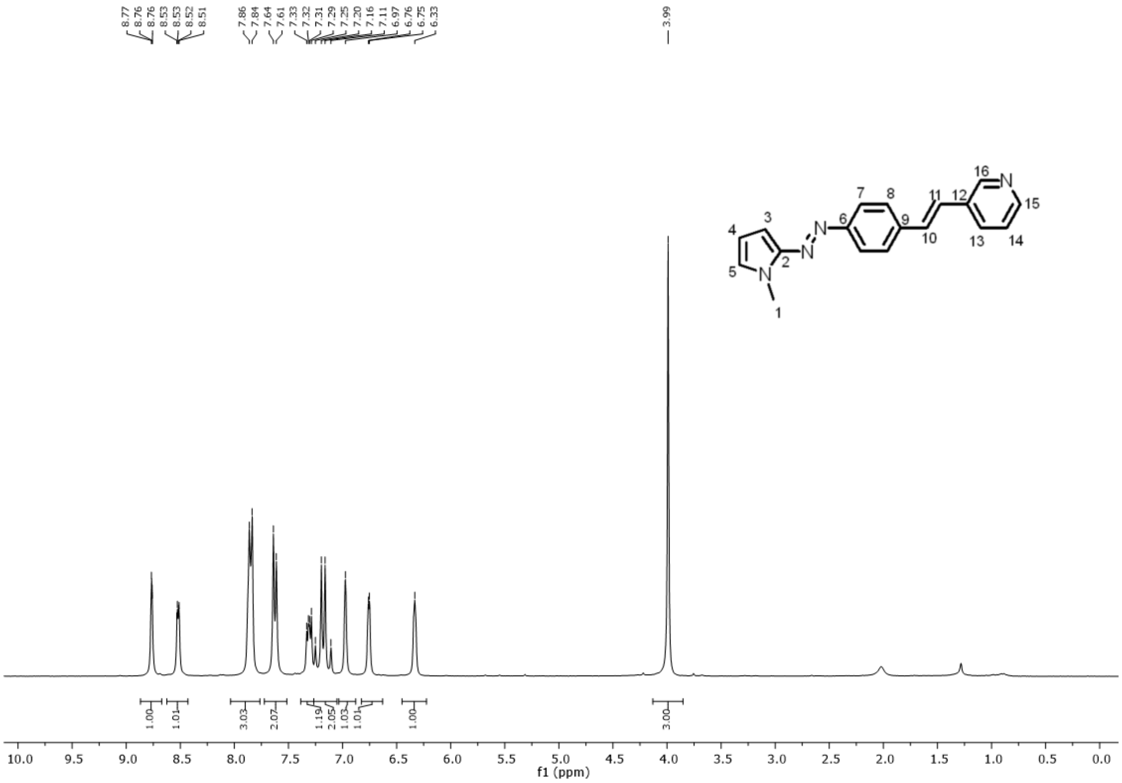


Figure S 15 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **3c**

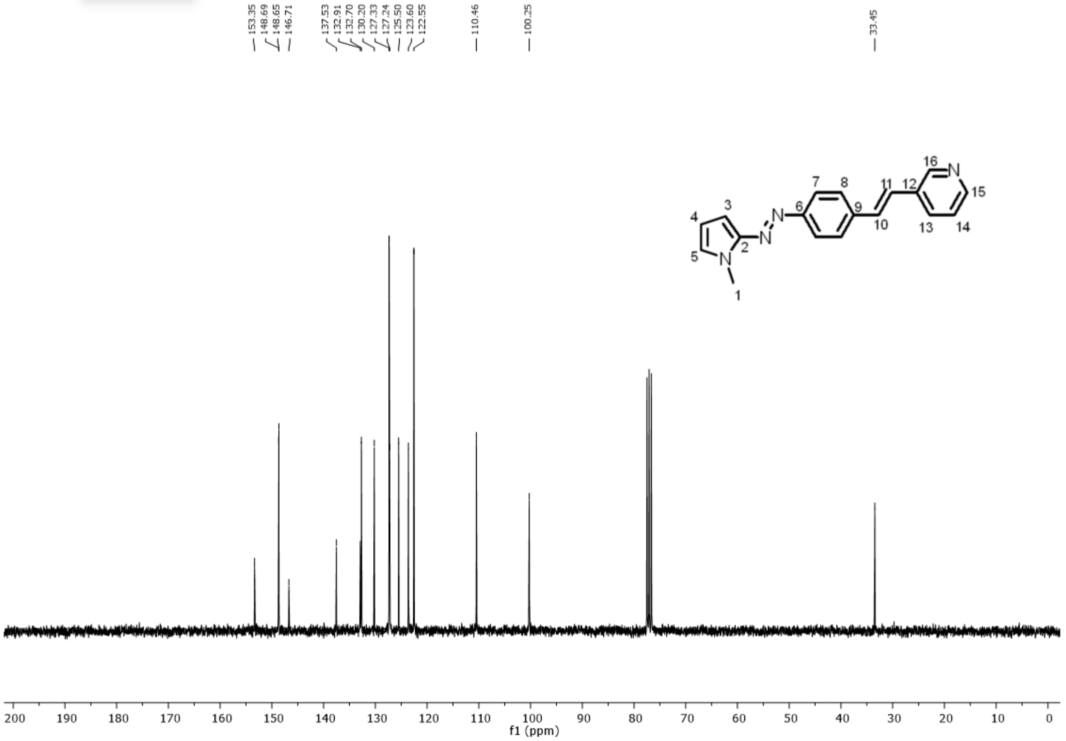


Figure S 16 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **3c**

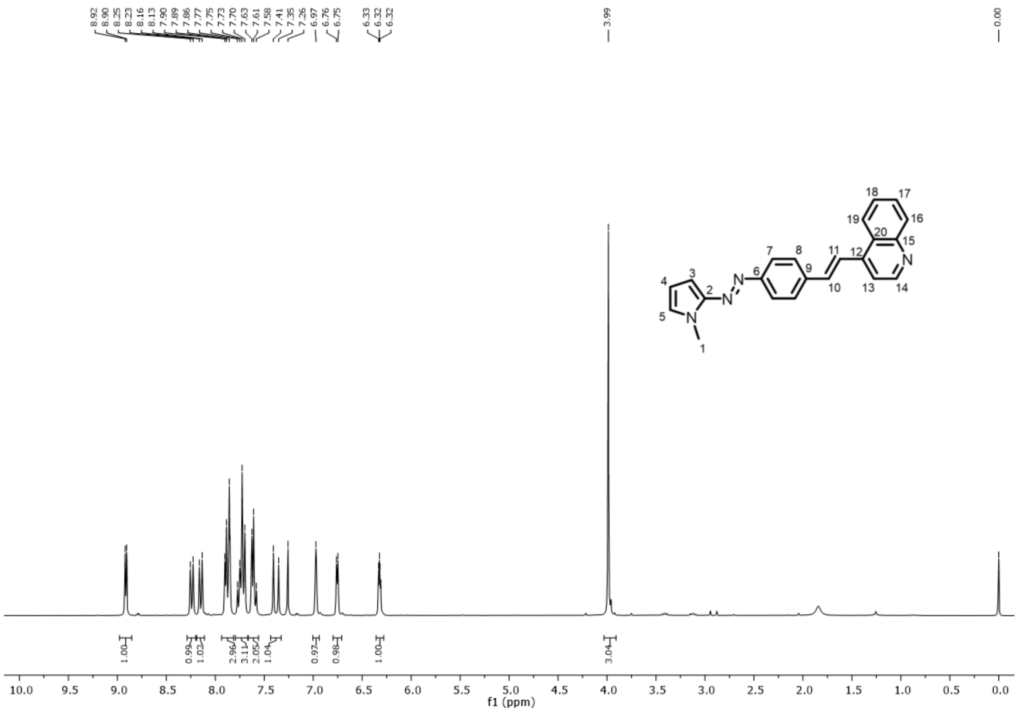


Figure S 17 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **3d**

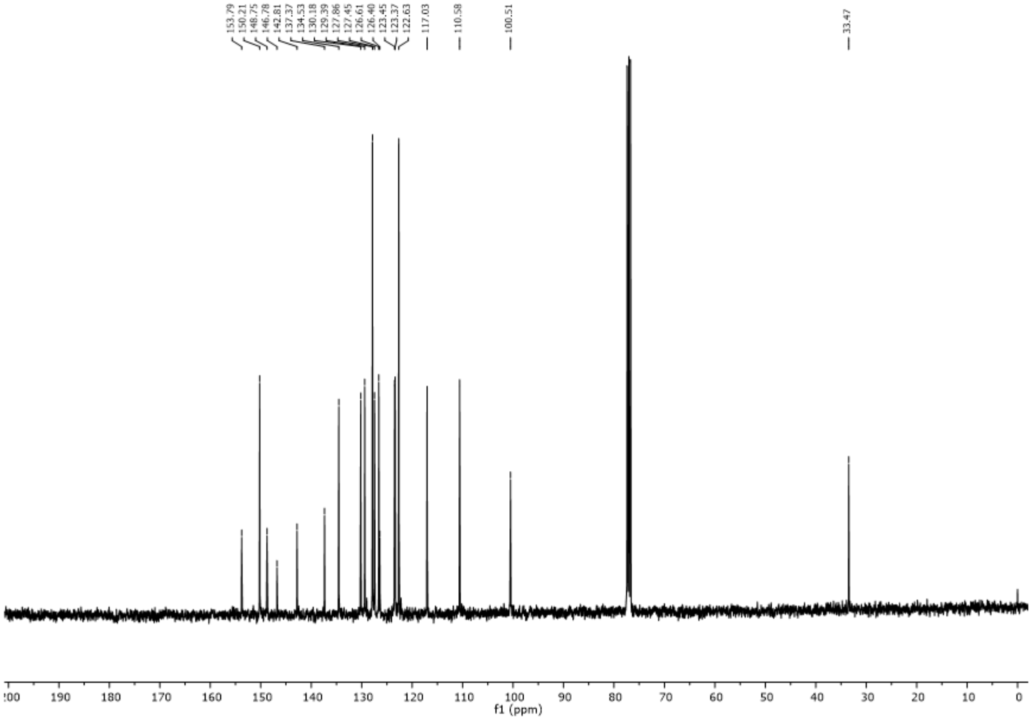


Figure S 18 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **3d**

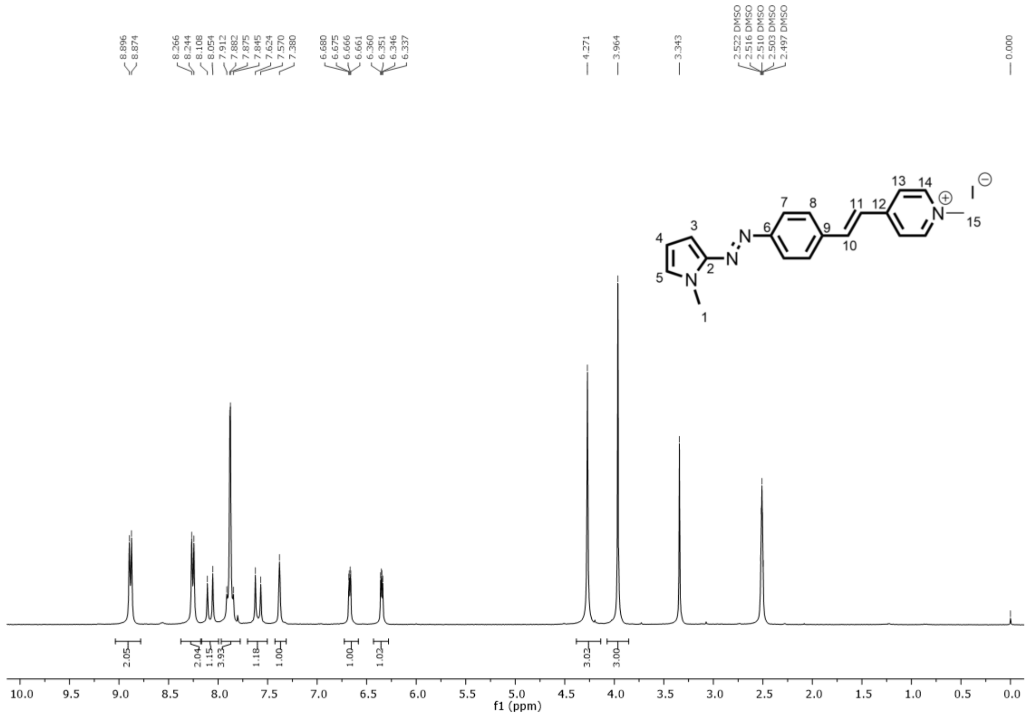


Figure S 19 ^{1}H NMR spectrum (300 MHz, DMSO-d$_6$) of compound **4b**

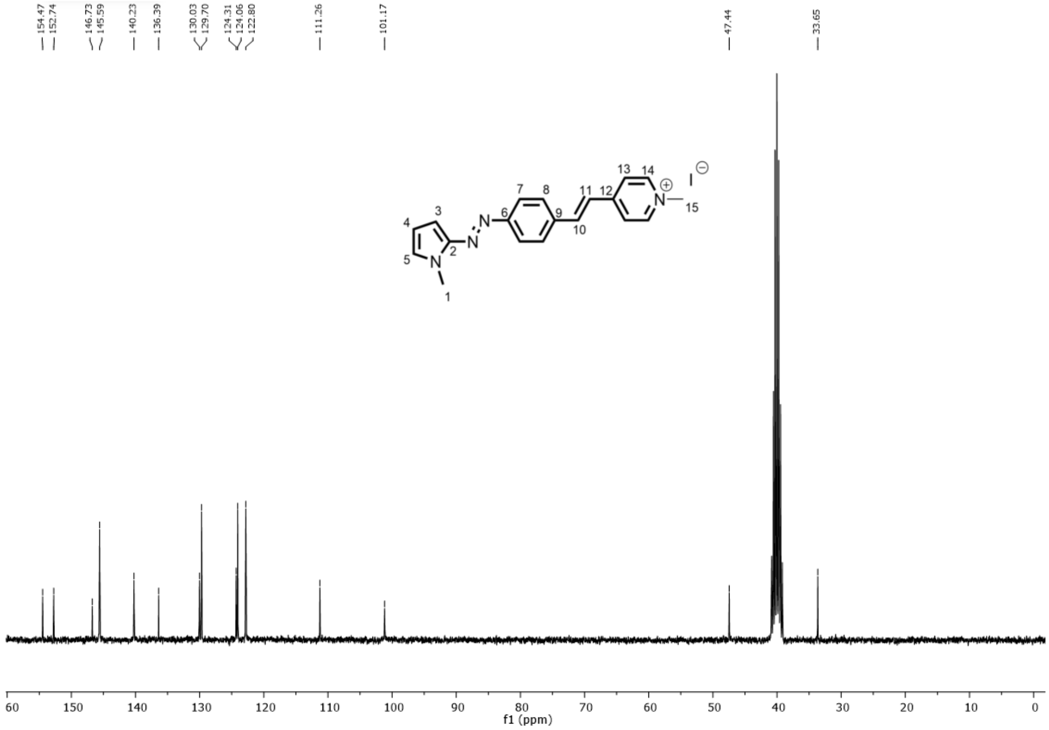


Figure S 20 ^{13}C NMR spectrum (75 MHz, CDCl$_3$) of compound **4b**

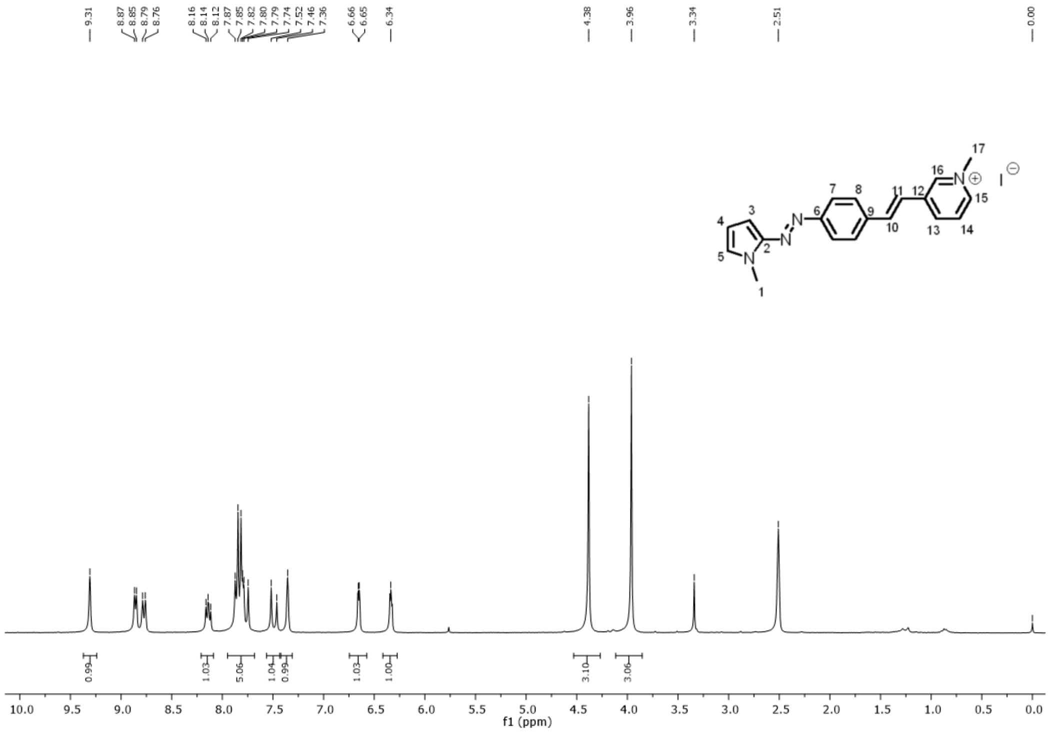


Figure S 21 ^1H NMR spectrum (300 MHz, DMSO-d_6) of compound **4c**

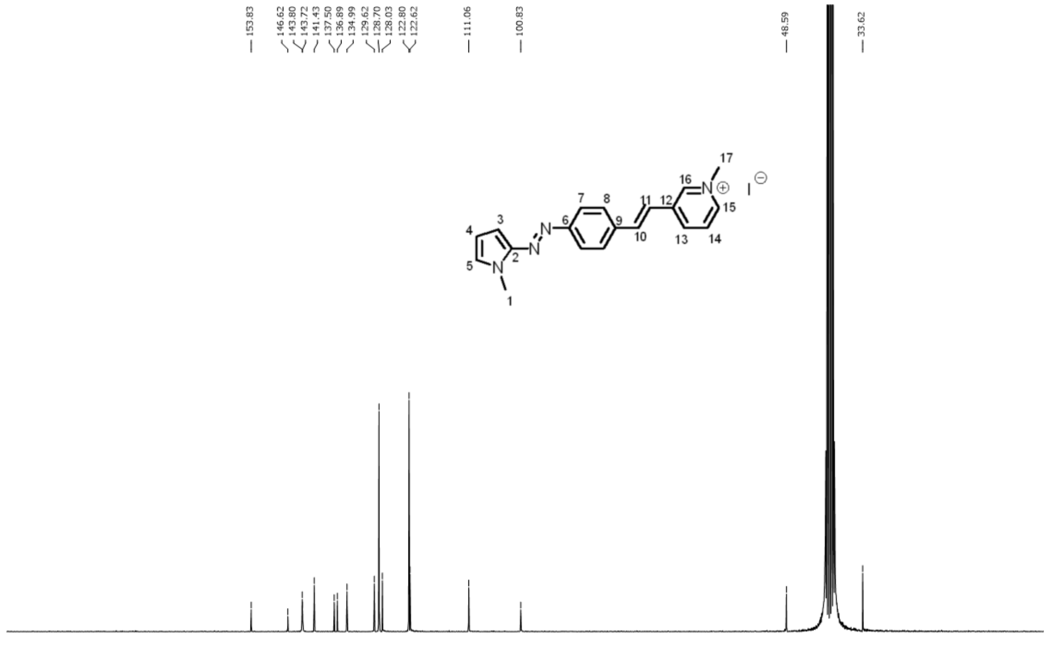


Figure S 22 ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of compound **4c**

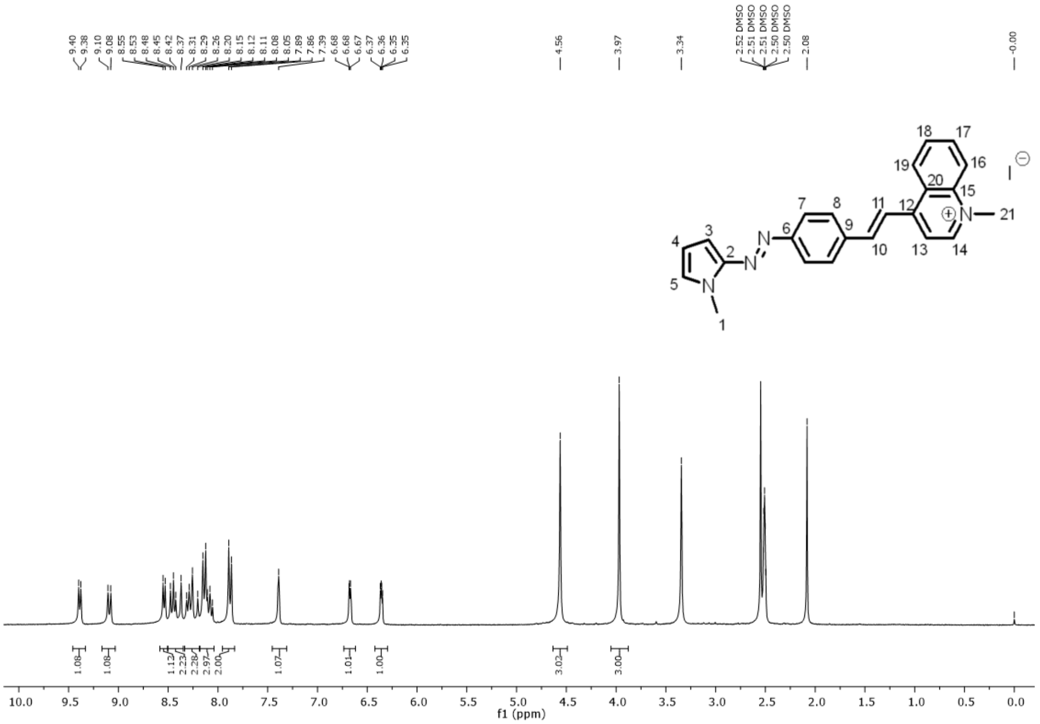


Figure S 23 ^{1}H NMR spectrum (300 MHz, DMSO-d$_6$) of compound **4d**

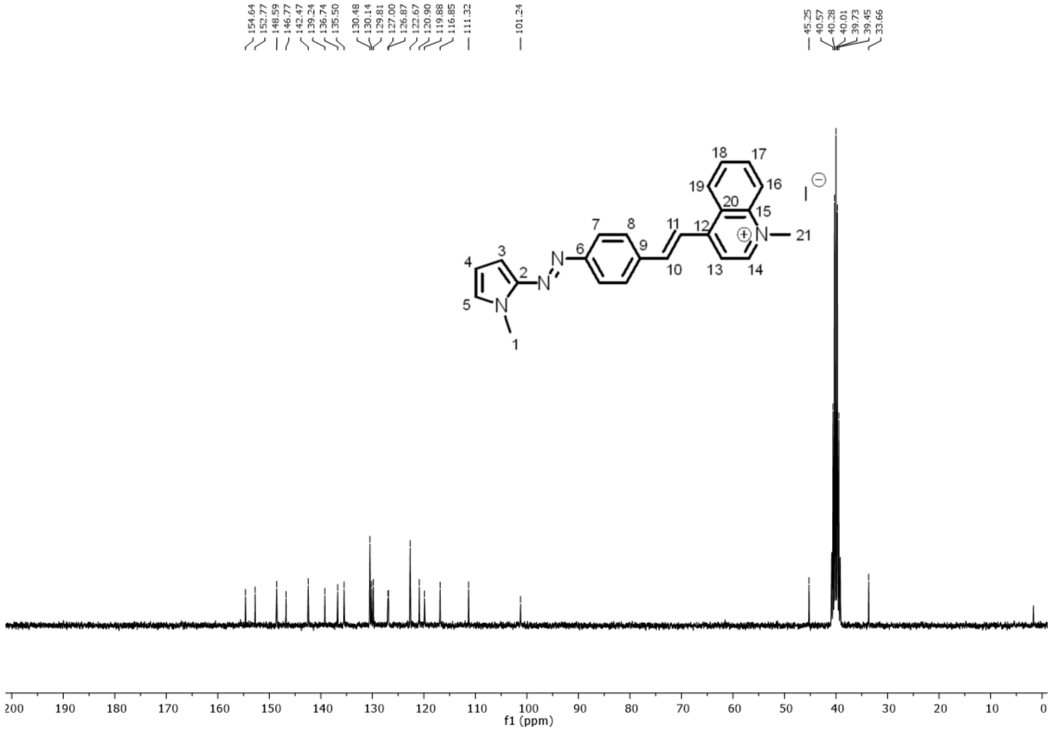


Figure S 24 ^{13}C NMR spectrum (75 MHz, DMSO-d$_6$) of compound **4d**

8. Structure determination by X-ray crystallography

Suitable X-ray quality crystals of **3b** were grown by slow evaporation of chloroform at room temperature. Crystals of each compound were mounted on a glass fiber at room temperature, and then placed on a Bruker Smart Apex CCD, equipped with Mo-K α radiation; decay was negligible in both cases. Details of crystallographic data collected for this compound are provided Table S1. Systematic absences and intensity statistics were used in space group determination. The structure was solved using direct methods.[iv] Anisotropic structure refinements were achieved using full matrix, least-squares technique on all nonhydrogen atoms. All hydrogen atoms were placed in idealized positions, based on hybridization, with isotropic thermal parameters fixed at 1.2 times the value of the attached atom. Structure solutions and refinements were performed using SHELXTL V6.10.[v]

Table S1. X-ray Data Collection and Structure Refinement Details for **3b**

Compound	**3b**
Empirical formula	$C_{18}H_{16}N_4$
Formula weight (g mol^{-1})	288.35
Crystal size (nm)	0.41 x 0.27 x 0.096
Color	Orange
Crystal system	Monoclinic
Space group	P-2_1
a (Å)	11.0543(16)
b (Å)	7.6061(11)
c (Å)	18.348(3)
α (°)	90
β (°)	97.582(3)
γ (°)	90
V (Å^3)	1529.3(4)
Z	4
Temperature (ºK)	298
D_{calc} (g/cm^3)	1.252
Number of collected reflections	27079
Number of independent reflections (R_{int})	8576, R_{int} = 0.0683
Maximum and minimum transmission	0.898 and 0.609
Data/parameters	8576 / 400
Final R indices	R = 0.0604
[$I>2\sigma(I)$]	wR_2 = 0.1570
R indices (all data)	R = 0.1417, wR_2 = 0.1186
GoF(F^2)	1.000
Absorption correction method	Multi-scan

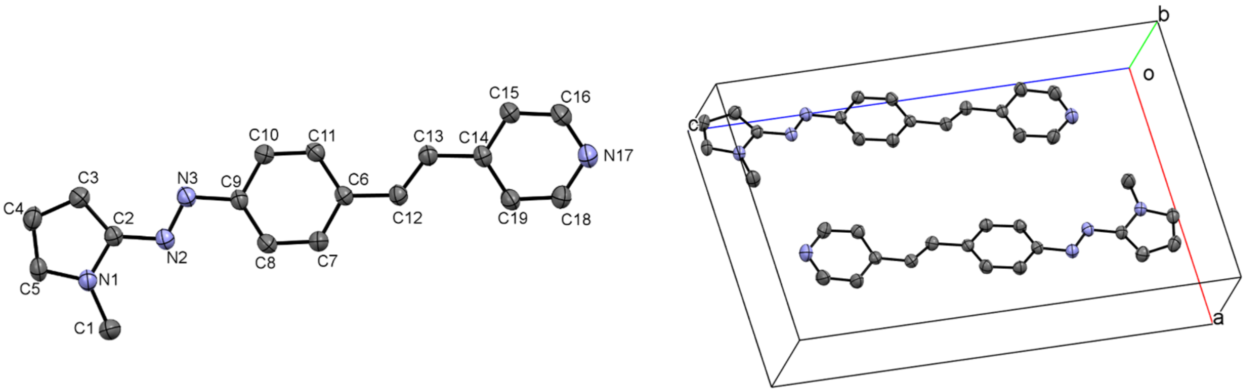


Figure S 25 ORTEP view of **3b** with thermal ellipsoids at 30% probability level. Selected bond lengths (Å) and angles (°): N(1)-C(1) 1.452(4), N(1)-C(2) 1.378(3), N(1)-C(5) 1.350(4), N(2)-N(3) 1.273(3), N(2)-C(2) 1.385(3), N(3)-C(9) 1.419(3), C(2)-C(3) 1.375(4), C(3)-C(4) 1.383(4), C(4)-C(5) 1.365(4), C(6)-C(12) 1.461(3), C(12)-C(13) 1.321(3), C(13)-C(14) 1.467(4), C(14)-C(15) 1.380(3), C(14)-C(19) 1.391(3), C(15)-C(16) 1.381(4), C(16)-N(17) 1.322(4), N(17)-C(18) 1.323(4), C(18)-C(19) 1.367(4).

X. UV-Visible studies

X.1 UV-Visible studies of compound **2a**

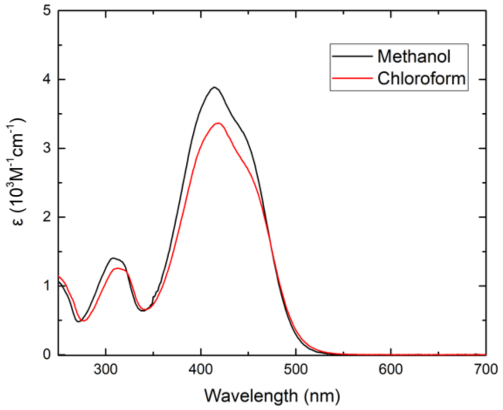


Figure S 26 UV-Visible spectra of compound **2a** in different solvents.

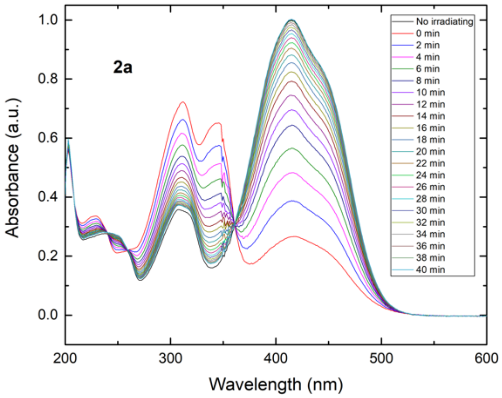
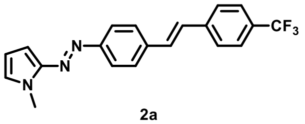


Figure S 27 UV-vis spectra for **2a** (2.5x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	**Methanol**	**Chloroform**
 2a	λ max = 415 ε = 39381	λ max = 419 ε = 33677

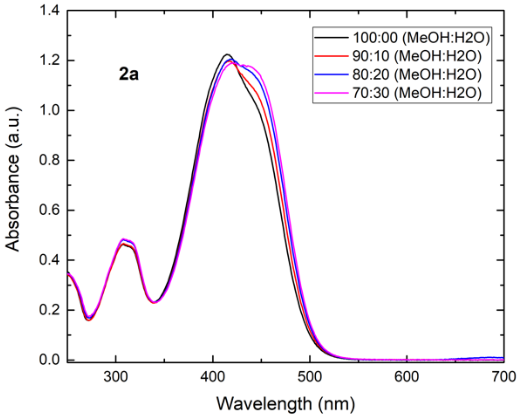


Figure S 28 UV-visible spectra of compound **2a** in different ratios MeOH/H2O.

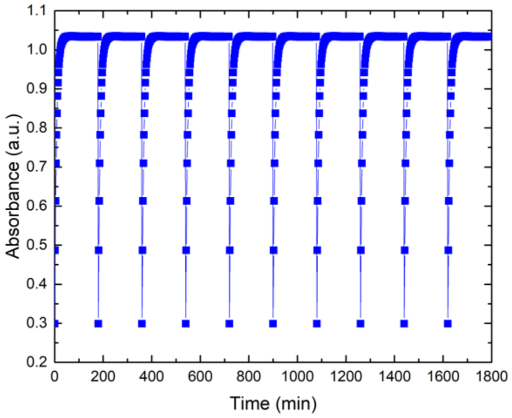
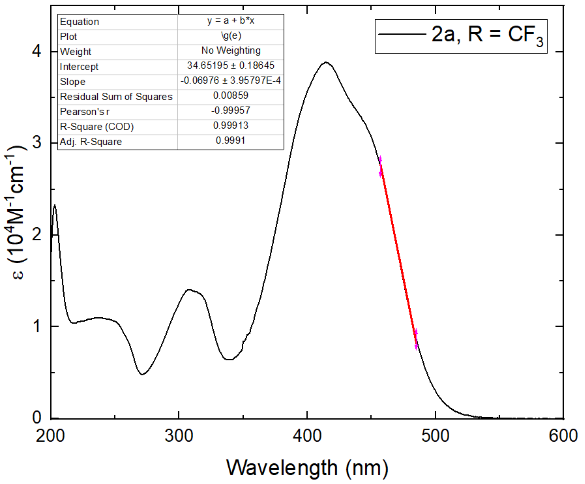


Figure S 29 **2a** was irradiated ten times for 2 minutes.



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	34.65195 ± 0.18645
Slope	-0.06976 ± 3.95797E-4
Residual Sum of Squares	0.00859
Pearson's r	-0.99957
R-Square (COD)	0.99913
Adj. R-Square	0.9991

Figure S30. Estimation of Optical GAP for **2a**

X.1 UV-Visible studies of compound **2b**

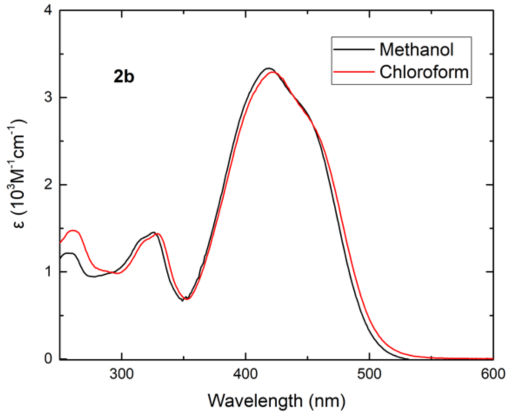


Figure S 31 UV-Visible spectra of compound **2b** in different solvents.

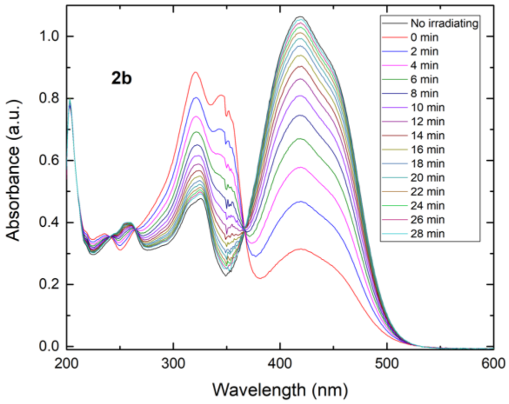
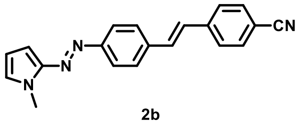


Figure S 32 UV-vis spectra for **2b** (3.1x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	Methanol	Chloroform
 2b	λ max = 419 ε = 34210	λ max = 423 ε = 33059

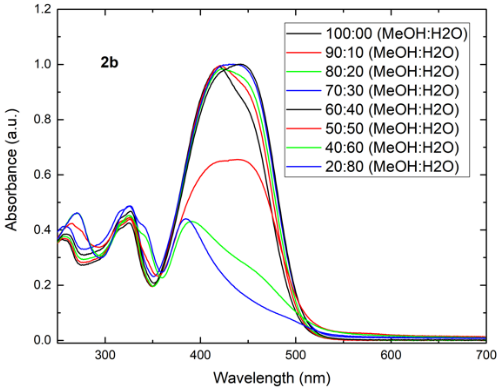


Figure S 33 UV-visible spectra of compound **2b** in different ratios MeOH/H2O.

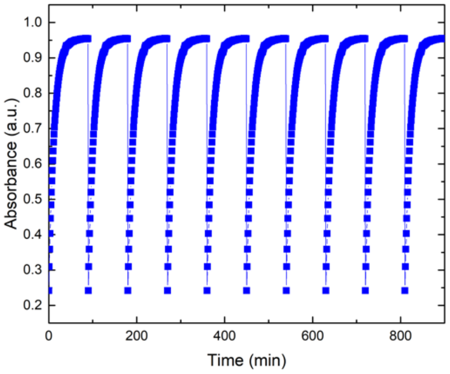
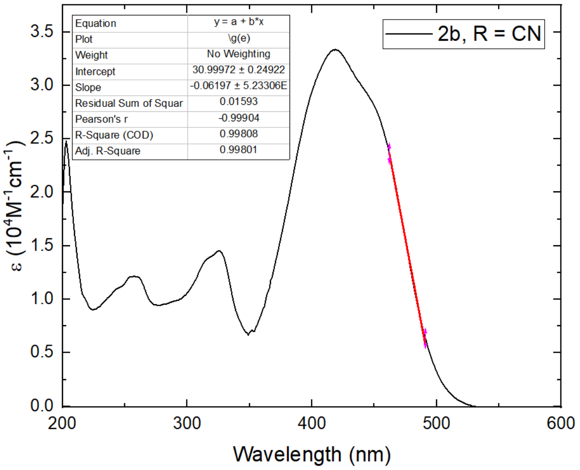


Figure S 34 2b was irradiated ten times for 2 minutes.



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	30.99972 ± 0.24922
Slope	-0.06197 ± 5.23306E
Residual Sum of Squar	0.01593
Pearson's r	-0.99904
R-Square (COD)	0.99808
Adj. R-Square	0.99801

Figure S35. Estimation of Optical GAP for **2b**

X.1 UV-Visible studies of compound **2c**

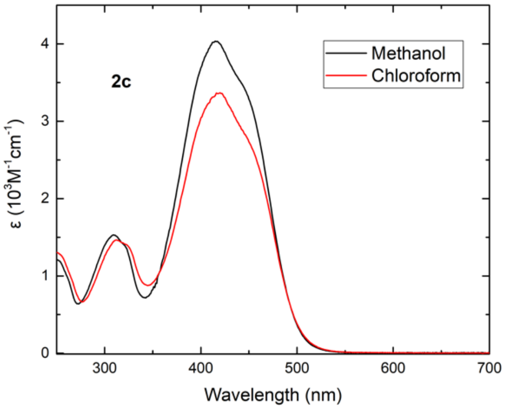


Figure S 36 UV-Visible spectra of compound **2c** in different solvents.

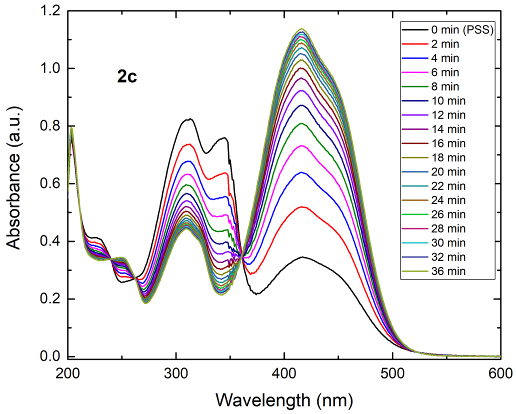
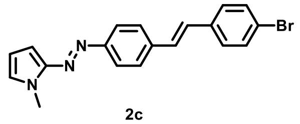


Figure S 37 UV-vis spectra for **2c** (2.8x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	**Methanol**	**Chloroform**
 2c	λ max = 415 ε = 40787	λ max = 420 ε = 35366

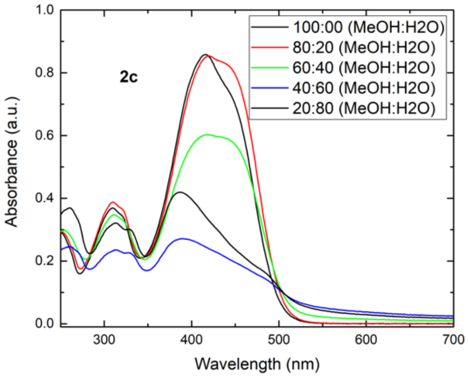


Figure S 38 UV-visible spectra of compound 2c in different ratios MeOH/H2O.

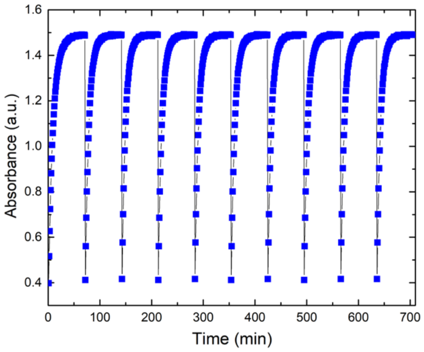
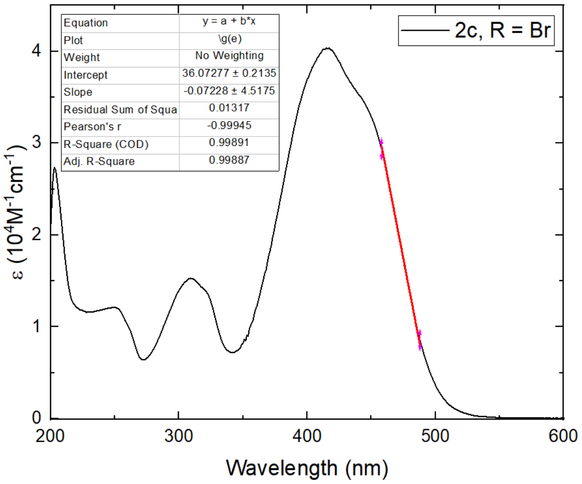


Figure S 39 2c was irradiated ten times for 2 minutes.



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	36.07277 ± 0.2135
Slope	-0.07228 ± 4.5175
Residual Sum of Squa	0.01317
Pearson's r	-0.99945
R-Square (COD)	0.99891
Adj. R-Square	0.99887

Figure S 40. Estimation of Optical GAP for **2c.**

X.1 UV-Visible studies of compound **2d**

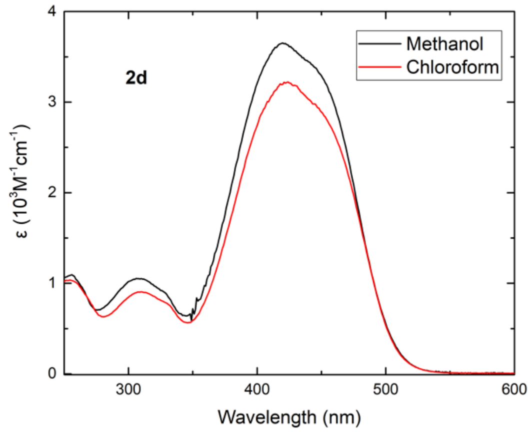


Figure S 41 UV-Visible spectra of compound **2d** in different solvents.

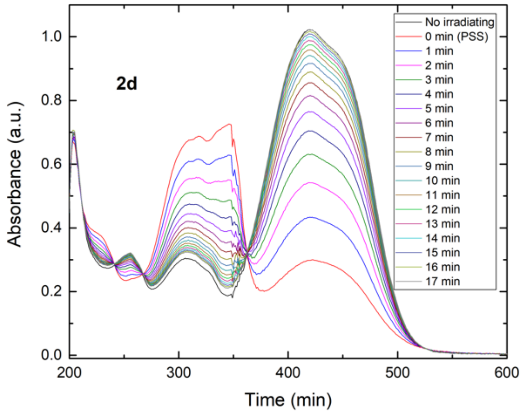
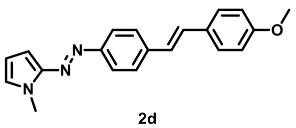


Figure S 42 UV-vis spectra for **2d** (2.7x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	Methanol	Chloroform
 **2d**	λ max = 421 ε = 37326	λ max = 424 ε = 32511

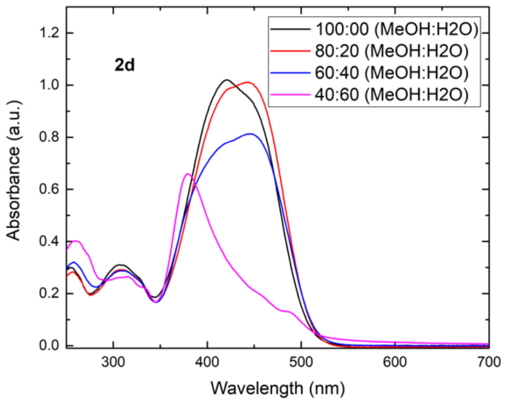


Figure S 43 UV-visible spectra of compound **2d** in different ratios MeOH/H2O.

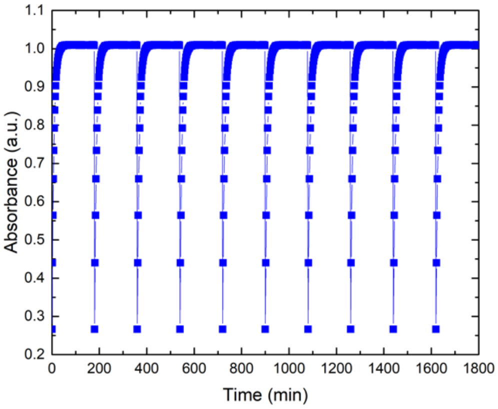
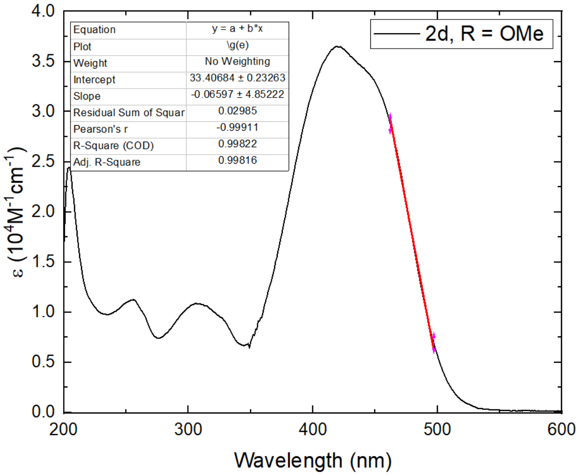


Figure S 44 **2d** was irradiated ten times for 2 minutes.



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	33.40684 ± 0.23263
Slope	-0.06597 ± 4.85222
Residual Sum of Squar	0.02985
Pearson's r	-0.99911
R-Square (COD)	0.99822
Adj. R-Square	0.99816

Figure S 45. Estimation of Optical GAP for **2d.**

X.1 UV-Visible studies of compound **3a**

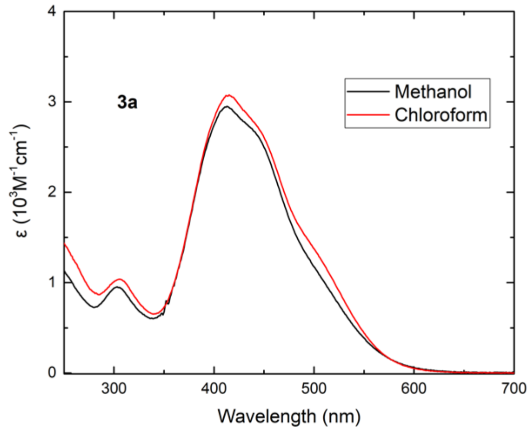


Figure S 46 UV-Visible spectra of compound **3a** in different solvents.

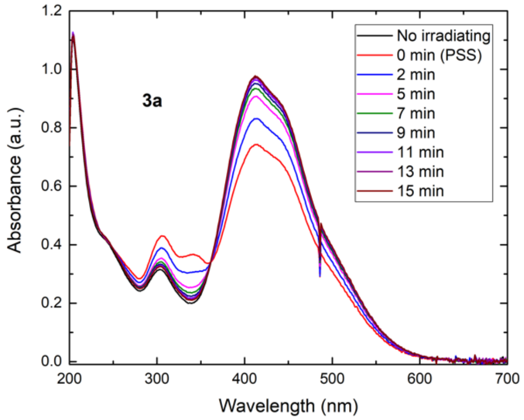
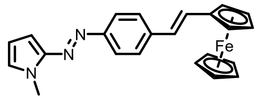


Figure S 47 UV-vis spectra for **3a** (3.2x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	Methanol	Chloroform
 **3a**	λ max = 413 ε = 30038	λ max = 415 ε = 31226

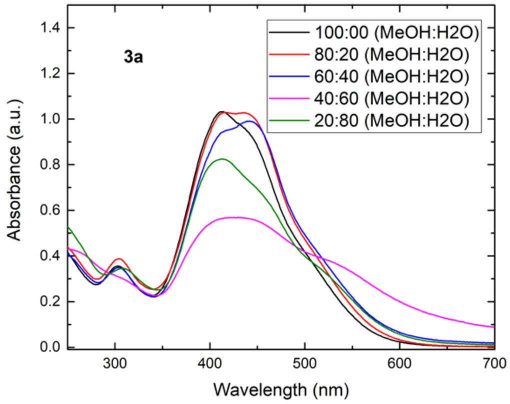


Figure S 48 UV-visible spectra of compound **3a** in different ratios MeOH/H2O.

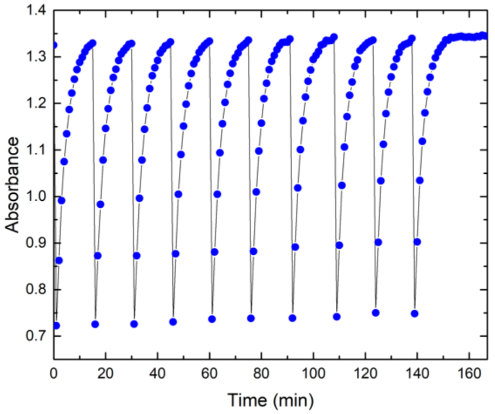
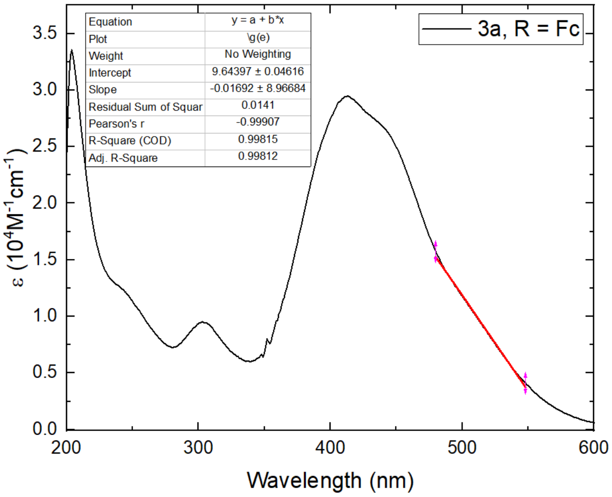


Figure S 49 **3a** was irradiated ten times for 2 minutes



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	9.64397 ± 0.04616
Slope	-0.01692 ± 8.96684
Residual Sum of Squar	0.0141
Pearson's r	-0.99907
R-Square (COD)	0.99815
Adj. R-Square	0.99812

Figure S 50. Estimation of Optical GAP for **3a**

X.1 UV-Visible studies of compound 3b

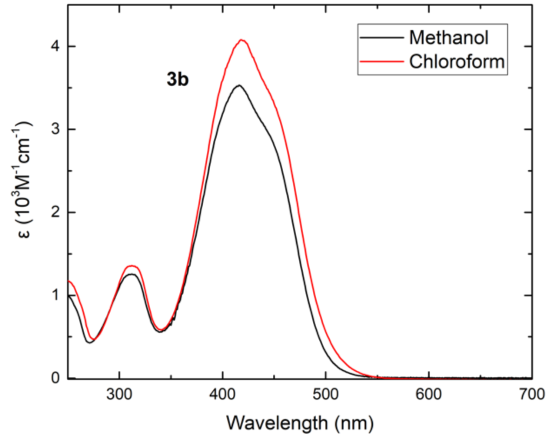


Figure S 51 UV-Visible spectra of compound **3b** in different solvents.

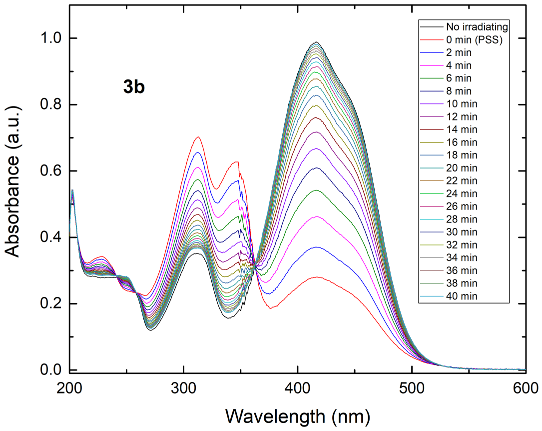
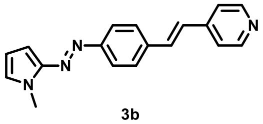


Figure S 52 UV-vis spectra for **3b** (2.7x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	**Methanol**	**Chloroform**
 **3b**	λ max = 416 ε = 36146	λ max = 418 ε = 41052

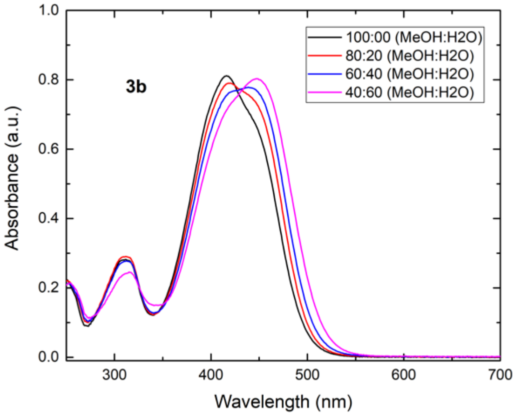


Figure S 53 UV-visible spectra of compound **3b** in different ratios MeOH/H2O.

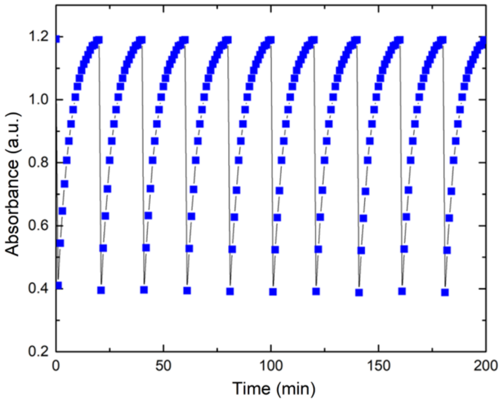
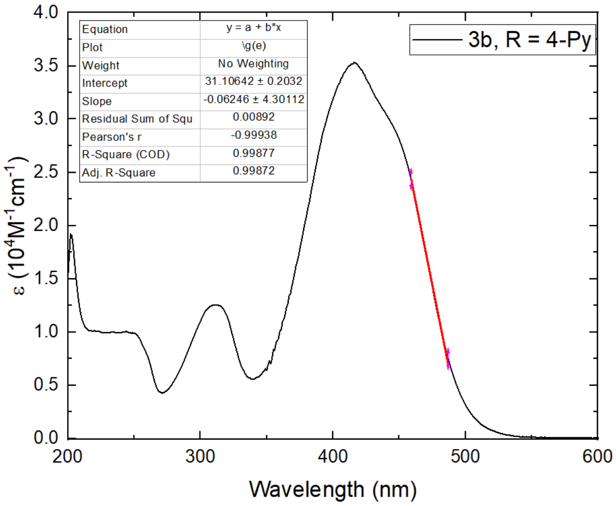


Figure S 54 **3b** was irradiated ten times for 2 minutes



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	31.10642 ± 0.2032
Slope	-0.06246 ± 4.30112
Residual Sum of Squ	0.00892
Pearson's r	-0.99938
R-Square (COD)	0.99877
Adj. R-Square	0.99872

Figure S 55. Estimation of Optical GAP for **3b**

X.1 UV-Visible studies of compound **3c**

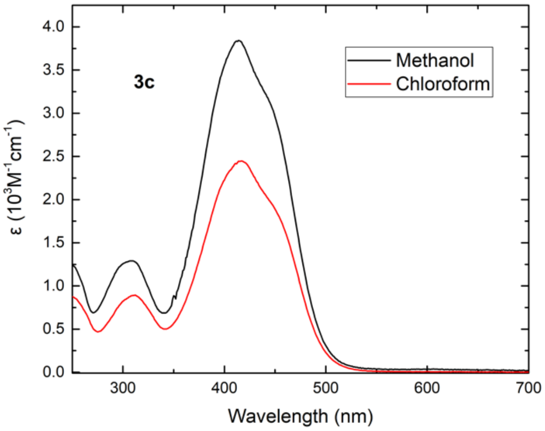


Figure S 56 UV-Visible spectra of compound **3c** in different solvents.

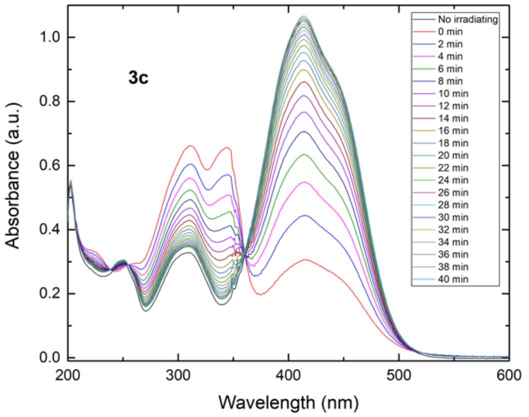
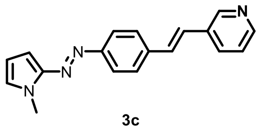


Figure S 57 UV-vis spectra for **3c** (2.7x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	Methanol	Chloroform
 3c	λ max = 416 ε = 39100	λ max = 417 ε = 25315

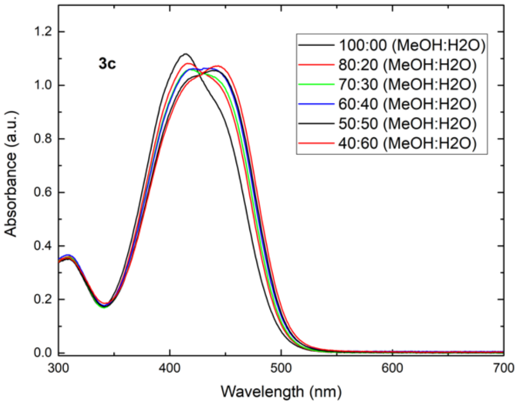


Figure S 58 UV-visible spectra of compound **3c** in different ratios MeOH/H2O.

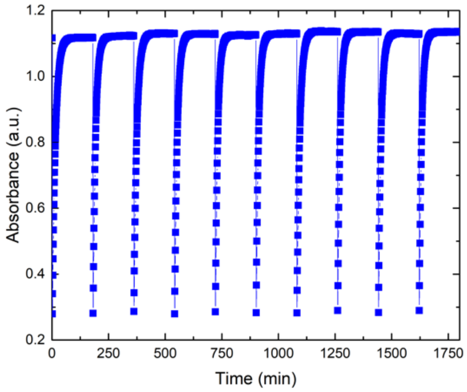
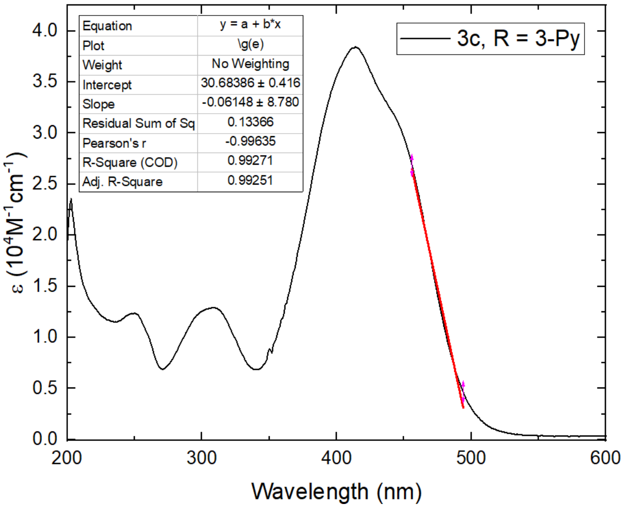


Figure S 59 3c was irradiated ten times for 2 minute



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	30.68386 ± 0.416
Slope	-0.06148 ± 8.780
Residual Sum of Sq	0.13366
Pearson's r	-0.99635
R-Square (COD)	0.99271
Adj. R-Square	0.99251

Figure S 60. Estimation of Optical GAP for **3c**

X.1 UV-Visible studies of compound **3d**

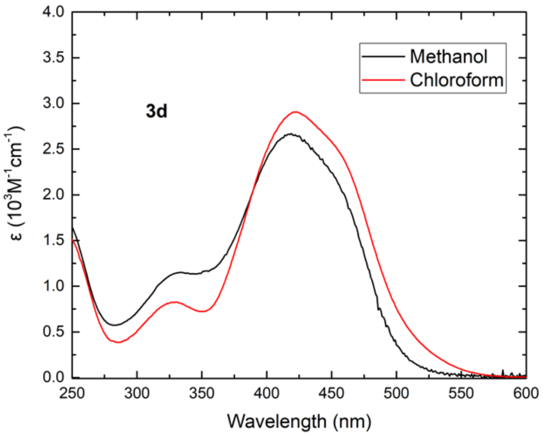


Figure S 61 UV-Visible spectra of compound **3d** in different solvents.

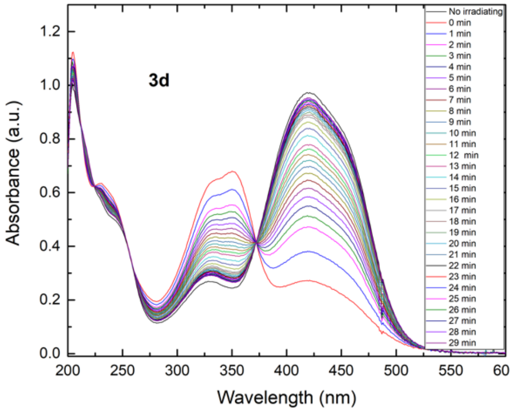
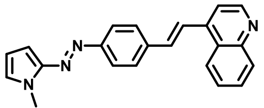


Figure S 62 UV-vis spectra for **3d** (3.8x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	Methanol	Chloroform
 3d	λ max = 418 ε = 25264	λ max = 423 ε = 30749

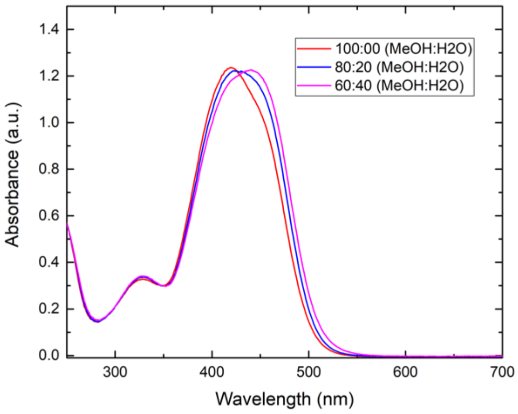


Figure S 63 UV-visible spectra of compound **3d** in different ratios MeOH/H2O.

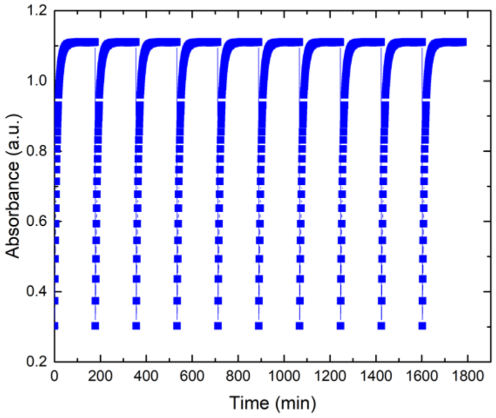
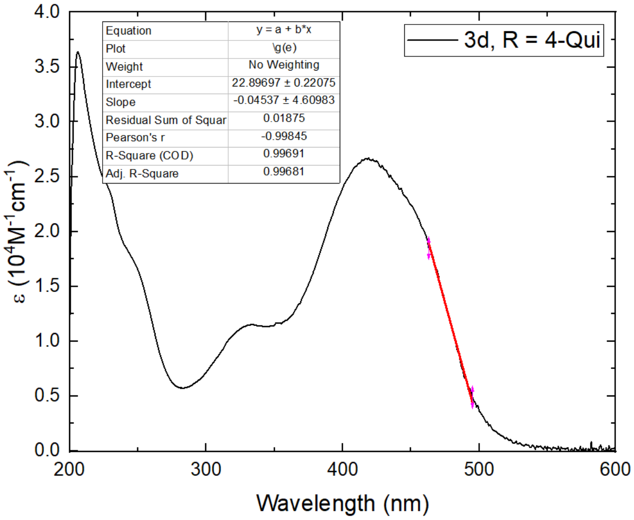


Figure S 64 3d was irradiated ten times for 2 minute



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	22.89697 ± 0.22075
Slope	-0.04537 ± 4.60983
Residual Sum of Squar	0.01875
Pearson's r	-0.99845
R-Square (COD)	0.99691
Adj. R-Square	0.99681

Figure S 65. Estimation of Optical GAP for **3d**

.1 UV-Visible studies of compound **4b**

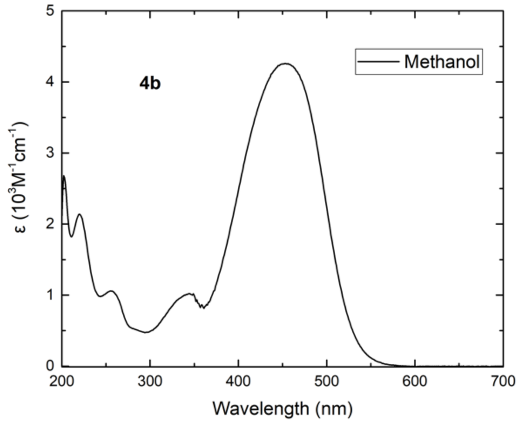


Figure S 66 UV-Visible spectra of compound **4b** in different solvents.

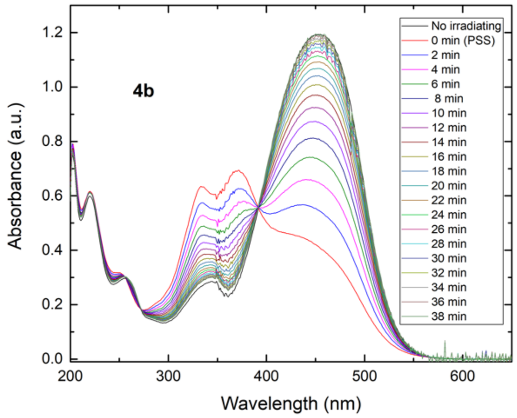
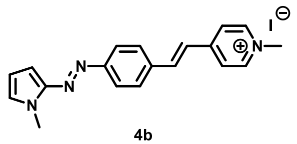


Figure S 67 UV-vis spectra for **4b** ($3x\ 10^{-5}M$, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	Methanol
 **4b**	λ max = 454 ε = 39843

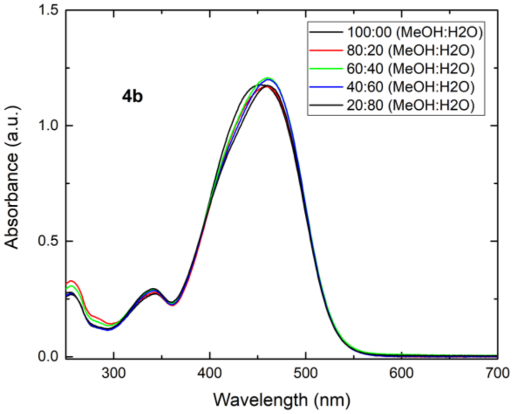


Figure S 68 UV-visible spectra of compound **4b** in different ratios MeOH/H2O.

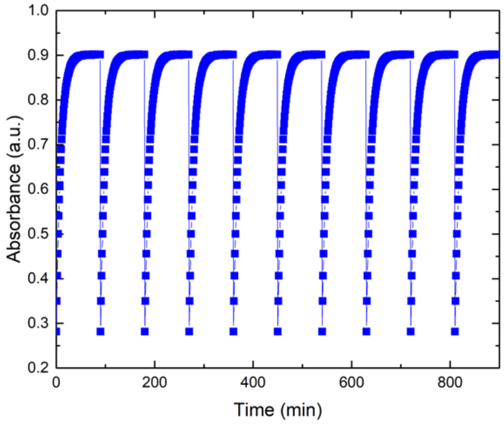
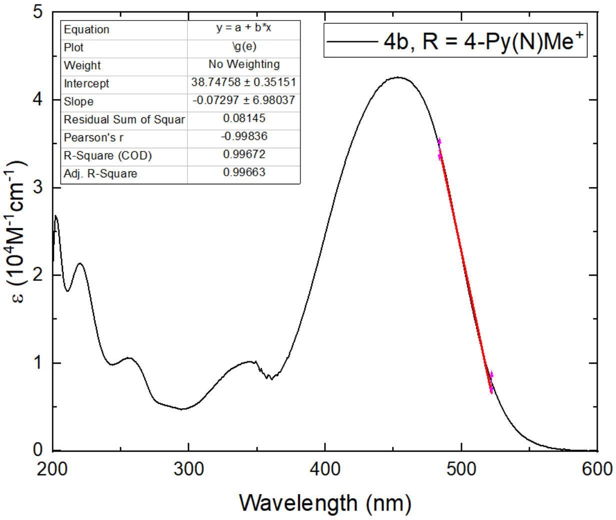


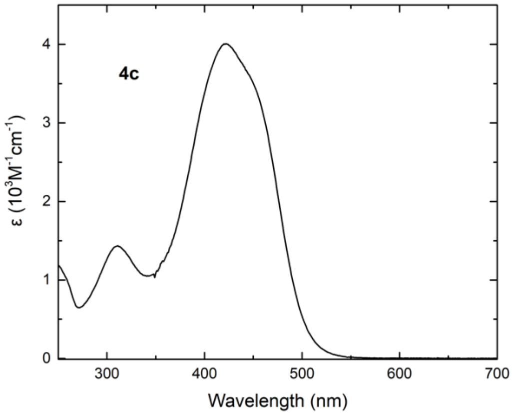
Figure S 69 4b was irradiated ten times for 2 minute



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	38.74758 ± 0.35151
Slope	-0.07297 ± 6.98037
Residual Sum of Squar	0.08145
Pearson's r	-0.99836
R-Square (COD)	0.99672
Adj. R-Square	0.99663

Figure S 70. Estimation of Optical GAP for **4b**

X.1 UV-Visible studies of compound 4c



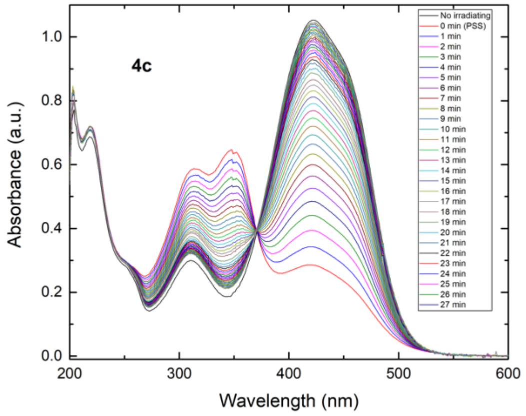
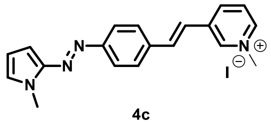
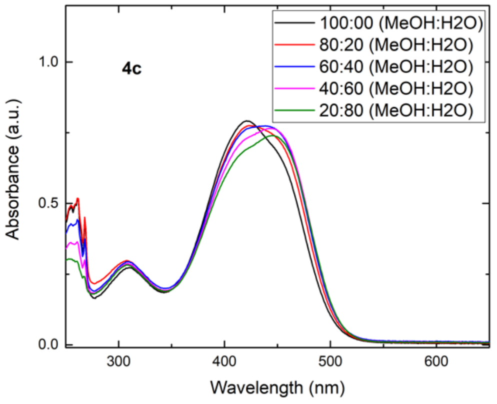


Figure S 71 UV-Visible spectra of compound **3c** in different solvents.

Figure S 72 UV-vis spectra for **4c** (2.6x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	Methanol
 **4c**	λ max = 422 ε = 40425



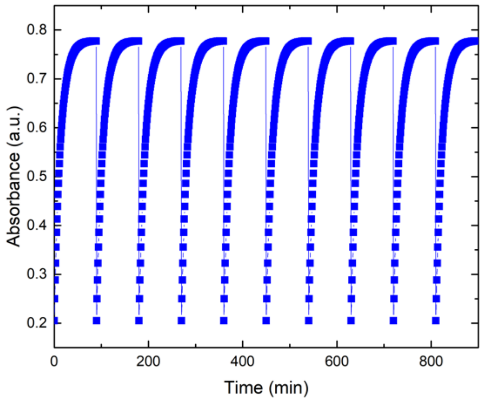
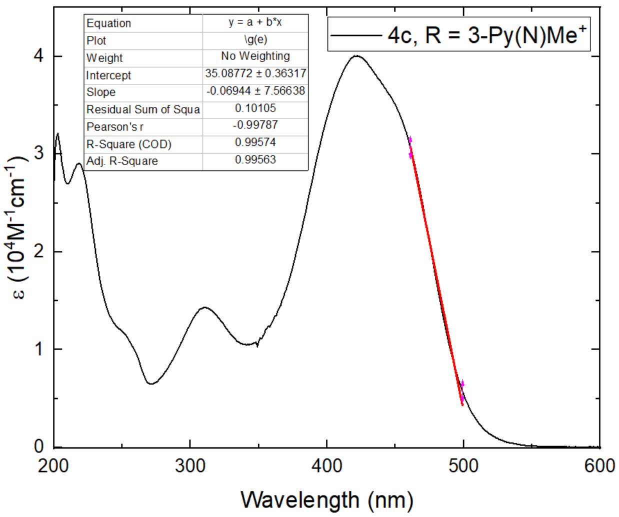


Figure S 73 UV-visible spectra of compound **4c** in different ratios MeOH/H$_2$O.

Figure S 74 **4c** was irradiated ten times for 2 minutes.



Equation	y = a + b*x
Plot	\g(e)
Weight	No Weighting
Intercept	35.08772 ± 0.36317
Slope	-0.06944 ± 7.56638
Residual Sum of Squa	0.10105
Pearson's r	-0.99787
R-Square (COD)	0.99574
Adj. R-Square	0.99563

Figure S 75. Estimation of Optical GAP for **4c**

X.1 UV-Visible studies of compound **4d**

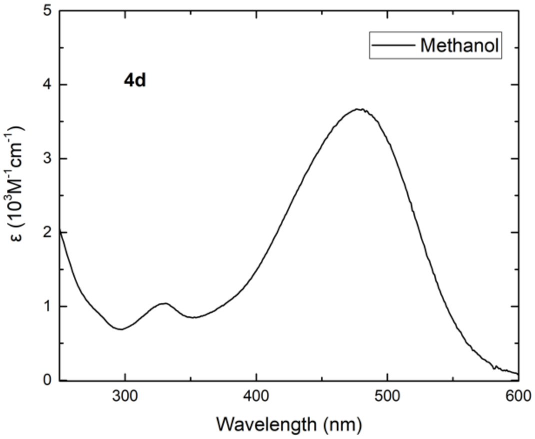


Figure S 76 UV-Visible spectra of compound **4d** in different solvents.

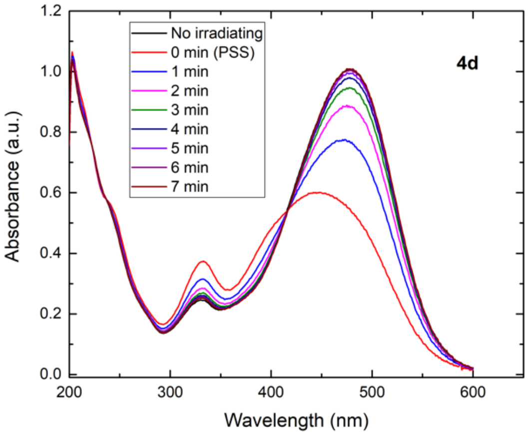
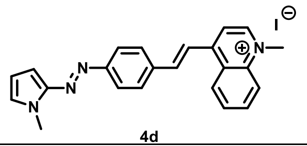
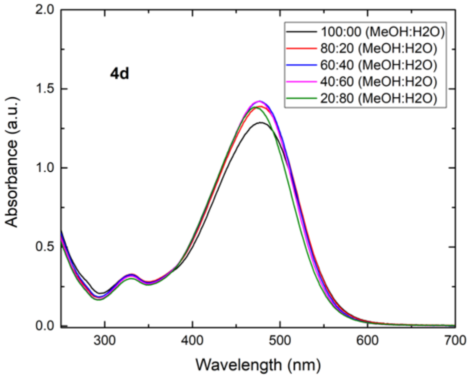


Figure S 77 UV-vis spectra for **4d** (2.7x 10^{-5}M, MeOH) after white light irradiation (PSS) and cis-trans return.

Compound	Methanol
 4d	λ max = 476 ε = 37570



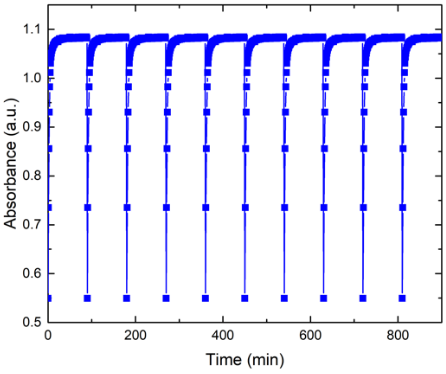


Figure S 78 UV-visible spectra of compound **4d** in different ratios MeOH/H2O.

Figure S 79 4d was irradiated ten times for 2 minute

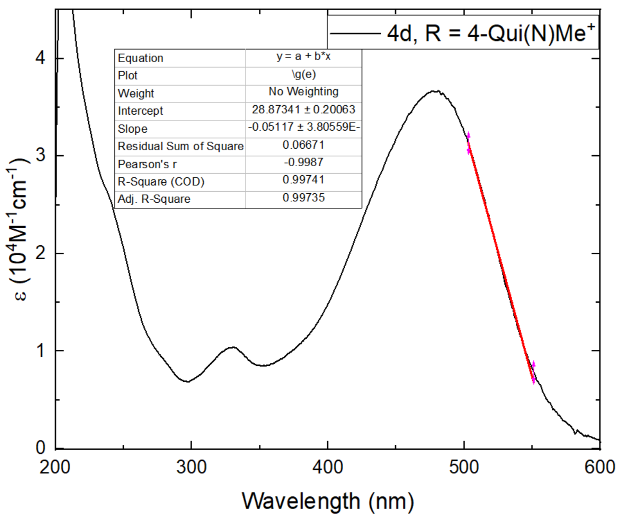


Figure S 80. Estimation of Optical GAP for **4d**

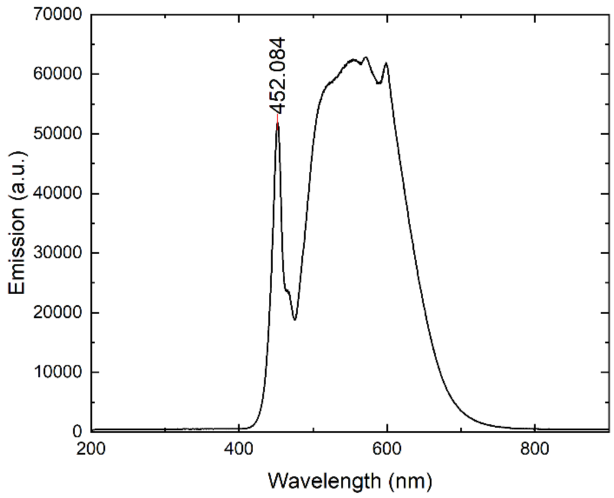


Figure S 81. Emission spectrum of the white led used in the photoisomerization processes.

X.2 **Computational studies**

In this link

https://www.dropbox.com/scl/fi/fks2387g3gz1np386p75z/xyz.zip?rlkey=qp4jzhuub2el6dqojv5entvmm&dl=0

the interested reader can download the xyz files of the local minima of the compounds **2a**-**2g**, **3a**-**3d** and **4b**-**4d** optimized in gas phase, in chloroform and in methanol.

Table S2. Values of $\Delta Q(\Omega_A)$ (equation (4) in the main body of the manuscript) for the QTAIM basins within compounds **2a**-**2g** addressed in this investigation. The atom numbering can be found in the xyz files attached to this document. The atoms for which

$|\Delta Q(\Omega_A)| < 5 \times 10^{-3}$ are not reported. Atomic units are used throughout.

2a		**2b**		**2c**		**2d**		**2e**		**2f**		**2g**	
Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$
N2	0.02	N2	0.02	N2	0.02	N2	0.02	N2	0.02	N2	0.02	N2	0.02
N3	0.02	N3	0.02	N3	0.02	N3	0.02	N3	0.02	N3	0.02	N3	0.02
H5	-0.01	H5	-0.01	H5	-0.01	H5	-0.01	H5	-0.01	H5	-0.01	H5	-0.01
H6	0.01	H6	0.01	H6	0.01	H6	0.01	H6	0.01	H6	0.01	H6	0.01
H7	-0.01	H7	-0.01	H7	-0.01	H7	-0.01	H7	-0.01	H7	-0.01	H7	-0.01
C8	0.01	C8	0.01	C8	0.01	C8	0.01	C8	0.01	C8	0.01	C8	0.01
H10	-0.02	H10	-0.02	H10	-0.02	H10	-0.02	H10	-0.02	H10	-0.02	H10	-0.02
C13	-0.01	C13	-0.01	C13	-0.01	C13	-0.01	C13	-0.01	C13	-0.01	C13	-0.01
C16	0.01	C16	0.01	C16	0.01	C16	0.01	C16	0.01	C16	0.01	C16	0.01
H17	0.01	H17	0.01	H17	0.01	H17	0.01	H17	0.01	H17	0.01	H17	0.01
C18	0.01	C18	0.01	C18	0.01	C18	0.01	C18	0.01	C18	0.01	C18	0.01
H19	-0.02	H19	-0.02	H19	-0.02	H19	-0.02	H19	-0.02	H19	-0.02	H19	-0.02
C20	0.01	C20	0.01	C20	0.01	C20	0.01	C20	0.01	C20	0.01	C20	0.01
C21	0.01	H22	-0.01	C21	0.01	C21	0.01	C21	0.01	H22	-0.01	C21	0.01
H22	-0.01			H22	-0.01	H22	-0.01	H22	-0.01			H22	-0.01

Table S3. Values of $\Delta Q(\Omega_A)$ (equation (4) in the main body of the manuscript) for the QTAIM basins within compounds **3a**-**3d** addressed in this investigation. The atom numbering can be found in the xyz files attached to this document. . The atoms for which $|\Delta Q(\Omega_A)| < 5 \times 10^{-3}$ are not reported. Atomic units are used throughout.

3a		**3b**		**3c**		**3d**	
Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$
C30	-0.01	N2	0.03	N2	0.02	N2	0.02
C32	-0.01	N3	0.02	N3	0.02	N3	0.02
C35	-0.01	H5	-0.01	H5	-0.01	H5	-0.01
C37	-0.01	H6	0.01	H6	0.01	H6	0.01
Fe38	0.09	H7	-0.01	H7	-0.01	H7	-0.01
C39	-0.01	C8	0.01	C8	0.01	C8	0.01
C40	-0.01	H10	-0.02	H10	-0.02	H10	-0.02
C43	-0.01	C13	-0.01	C13	-0.01	C13	-0.01
C44	-0.01	C16	0.01	C16	0.01	C16	0.01
C47	-0.01	H17	0.01	H17	0.01	H17	0.01
		C18	0.01	C18	0.01	C18	0.01
		H19	-0.02	H19	-0.02	H19	-0.02
		C20	0.01	C20	0.01	C20	0.01
		H22	-0.01	H22	-0.01	C21	0.01
		H28	-0.01	H28	-0.01	H22	-0.01

Table S4. Values of $\Delta Q(\Omega_A)$ (equation (4) in the main body of the manuscript) for the QTAIM basins within compounds **4b, 4c** and **4d** addressed in this investigation. The atom numbering can be found in the xyz files attached to this document. The atoms for which

$|\Delta Q(\Omega_A)| < 5 \times 10^{-3}$ are not reported. Atomic units are used throughout.

4b		**4c**		**4d**	
Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$	Átomo	$\Delta Q(\Omega_A)$
N3	0.02	N3	0.02	N3	0.02
C4	-0.01	C4	-0.01	C4	-0.01
H5	0.01	H5	0.01	H5	0.01
H6	0.01	H6	0.01	H6	0.01
H7	0.01	H7	0.01	H7	0.01
C8	0.02	C8	0.03	C8	0.03
C9	0.01	C9	0.01	C9	0.01
H10	0.02	H10	0.02	H10	0.02
C11	0.01	C11	0.02	C11	0.02
H12	0.02	H12	0.02	H12	0.02
C13	0.02	C13	0.02	C13	0.02
H14	0.02	H14	0.02	H14	0.03
C15	0.01	C15	0.01	C15	0.01
H17	0.01	C16	0.01	C16	0.01
C25	-0.02	H17	0.01	H17	0.01
H26	-0.01	H24	0.01	H24	0.01
H28	-0.01	C25	-0.02	C25	-0.02
C29	-0.01	H26	-0.01	H26	-0.01
C30	-0.01	H28	-0.01	C27	0.01
H31	-0.02	C29	-0.01	H28	-0.01
C32	-0.02	C30	-0.02	C29	-0.01
H33	-0.02	H31	-0.03	C30	-0.01
C35	-0.01	C32	-0.01	H31	-0.02
H36	-0.02	H33	-0.02	C32	-0.03
C37	-0.01	C34	-0.04	H33	-0.02
H38	-0.01	H36	-0.02	H36	-0.02
C39	0.01	H38	-0.02	C38	-0.01
H40	-0.01	C39	0.01	C39	-0.01
H41	-0.01	H40	-0.01	C40	-0.01
H42	-0.01	H41	-0.01	H41	-0.02
		H42	-0.01	C42	-0.01
				H43	-0.01
				H44	-0.02
				C45	0.01
				H46	-0.01
				H47	-0.01
				H48	-0.01

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