

Supporting Information

Regioselective synthesis of spiroxindolopyrrolidine: A one step cycloaddition reaction twists inherent optical and fluorescence property of Ferrocene-Anthracene dyad

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1. Experimental Section

General Considerations. All melting points are uncorrected. IR spectra were recorded on a SHIMADZU IR-8300 series FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on BRUKER 300 MHz instrument in CDCl_3 solvent with TMS as a standard. Mass spectra were recorded by ESI Q-ToF Mass Spectrometer (Micromass). Elemental analysis was carried out using Perkin-Elmer CHNS 2400 instrument. Column chromatography was performed on silica gel (ACME, 100-200 mesh). Routine monitoring of the reaction was done using thin layer chromatography developed on glass plates coated with silica gel-G (ACME) of 25 mm thickness and visualized with iodine. The organic extracts of crude products were dried over anhydrous Na_2SO_4 . Solvents were reagent grade and were purified according to standard procedures. The starting materials isatin and sarcosine were purchased commercially and used as such.

Proceducre for the synthesis of ferrocene based dipolarophiles 1:

A solution of 9-anthraldehyde (1.1 mmol), acetylferrocene (1mmol), powdered KOH (2mmol) in ethanol (10mL) were stirred at room temperature. After the completion of the reaction as evidenced by TLC, the solid obtained was filtered and washed with chilled ethanol. The crude product was recrystallized in ethanol.

1-ferrocenyl-3-anthracenyl-prop-2-ene-1-one (1)

^1H NMR (CDCl_3 /300 MHz) : δ 4.29 (s, 5H), 4.61(s, 2H), 4.91(s, 2H), 7.10 (d, $J = 15.9$ Hz, 1H), 7.49-8.48 (m, 9H), 8.72 (d, $J = 15.9$ Hz, 1H)

General procedure for the synthesis of ferrocene based spiro-cycloadduct:

A solution of the dipolarophile **1** derived from ferrocene (1mmol), isatin (1mmol) and sarcosine (1mmol) were refluxed in 10 mL toluene until completion of the reaction as evidenced by TLC (8 hours). The solvent was removed under reduced pressure and the crude product was subjected to column chromatography using petroleum ether: ethyl acetate (4:1) as eluent. The product was then recrystallized from methanol.

Thus were prepared:

1-N-Methyl-spiro-[2.3']oxindole-3-ferrocenyl-4-anthracenylpyrrolidine (4a): Following General Procedure, reaction of dyad **1** (100 mg, 0.24 mmol) with isatin **2a** (35.34 mg, 0.24 mmol) and sarcosine (21.38 mg, 0.24 mmol) in toluene (10 mL) yielded after column chromatography (Hexane/AcOEt 4/1) **4a** as a orange solid (115 mg, 81.15%). M.p.: 242 °C; IR (KBr) : 1668, 1706 cm^{-1} ; ^1H NMR ($\text{CDCl}_3/300$ MHz) : δ 2.28 (s, 3H), 2.87 (s, 5H), 3.70 (t, $J = 9.6$ Hz, 1H), 4.12-4.18 (m, 3H), 4.39 (s, 1H), 4.51 (s, 1H), 5.18 (d, $J = 10.5$ Hz, 1H), 6.33 (q, $J = 13.5$ Hz, 1H), 6.72 (d, $J = 7.2$ Hz, 1H), 6.92-9.67 (m, 13H), 8.63 (s, 1H); ^{13}C NMR ($\text{CDCl}_3/75$ MHz) : 35.4, 38.8, 68.4, 68.8, 69.5, 72.6, 76.6, 78.7, 109.8, 112.3, 118.1, 124.0, 124.9, 125.8, 126.3, 128.0, 129.0, 129.9, 138.6, 149.1, 159.2, 182.9, 199.6 ppm; Mass spectrum m/z : 591.20 ($\text{M}+\text{H}^+$); CHN Analysis calculated for $\text{C}_{37}\text{H}_{30}\text{FeN}_2\text{O}_2$: C, 75.26; H, 5.12; N, 4.74 %.; Found : C, 75.23; H, 5.15; N, 4.79 %.

1-N-Methyl-spiro-[2.3']-N-allyl-oxindole-3-ferrocenoyl-4-anthracenylpyrrolidine(4b):

Following General Procedure, reaction of dyad **1** (100 mg, 0.24 mmol) with N-allylisatin **2b** (44.92 mg, 0.24 mmol) and sarcosine (21.38 mg, 0.24 mmol) in toluene (10 mL) yielded after

column chromatography (Hexane/AcOEt 4/1) **4b** as a orange solid (119 mg, 78.63 %). M.p.: 238 °C; IR (KBr) : 1656, 1720 cm⁻¹; ¹H NMR (CDCl₃/300 MHz) : δ 2.22 (s, 3H), 2.86 (s, 5H), 3.71 (t, *J* = 9.6 Hz, 1H), 4.11-4.45 (m, 7H), 4.96-5.05 (m, 2H), 5.18 (d, *J* = 10.5 Hz, 1H), 5.28 - 5.65 (m, 1H), 6.36 (q, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 7.12-8.03 (m, 10H), 8.37 (s, 1H), 8.95 (d, *J* = 9.3 Hz, 1H), 9.71 (d, *J* = 9 Hz, 1H); ¹³C NMR (CDCl₃/75 MHz) : 35.4, 38.3, 42.4, 59.8, 61.5, 68.4, 69.7, 72.2, 72.6, 76.0, 78.7, 109.0, 117.7, 122.7, 124.8, 124.9, 125.0, 125.4, 125.9, 126.2, 126.4, 127.2, 127.9, 128.9, 129.0, 129.8, 131.0, 131.2, 131.6, 132.2, 133.3, 142.2, 176.9, 199.5 ppm. ; Mass spectrum *m/z*: 631.34 (M+H)⁺; CHN Analysis, Calculated for C₄₀H₃₄FeN₂O₂ : C, 76.19; H, 5.43; N, 4.44 %. Found : C, 76.22; H, 5.49; N, 4.42 %.

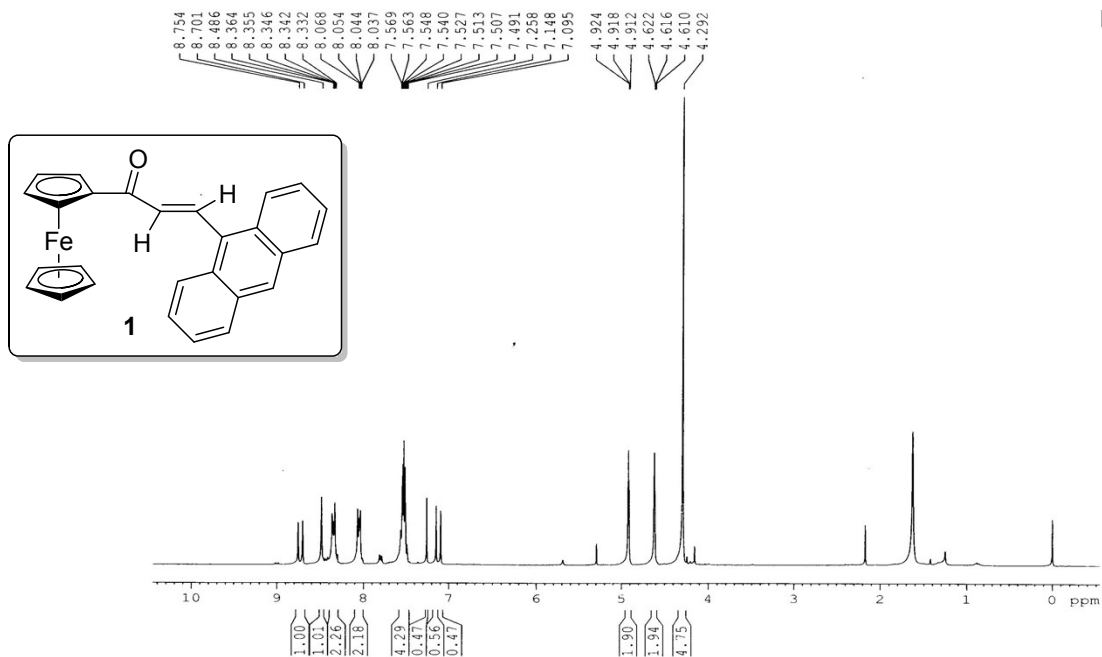
1-*N*-Methyl-spiro-[2.3']-*N*-methyl-oxindole-3-ferrocenoyl-4-anthracenyl pyrrolidine (4c):

Following General Procedure, reaction of dyad **1** (100 mg, 0.24 mmol) with *N*-methyl isatin **2c** (38.67 mg, 0.24 mmol) and sarcosine (21.38 mg, 0.24 mmol) in toluene (10 mL) yielded after column chromatography (Hexane/AcOEt 4/1) **4c** as a orange solid (117 mg, 80.64%). M.p. : 260 °C; IR (KBr) : 1667, 1702 cm⁻¹; ¹H NMR (CDCl₃/300 MHz) : δ 2.24 (s, 3H), 2.88 (s, 5H), 3.14 (s, 3H), 3.70 (t, *J* = 9.45, 1H), 4.06-4.19 (m, 3H), 4.37 (d, *J* = 13.2 Hz, 1H), 5.152 (d, *J* = 10.2 Hz, 1H), 6.31-6.34 (m, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 7.11-8.03 (m, 10H), 8.36 (s, 1H), 8.96 (d, *J* = 9 Hz, 1H), 9.71 (d, *J* = 9 Hz, 1H); ¹³C NMR (CDCl₃/75 MHz) : 26.19, 35.37, 38.34, 59.76, 61.69, 68.36, 69.17, 72.22, 72.49, 78.75, 107.99, 122.79, 124.92, 125.07, 125.66, 125.91, 126.23, 126.53, 127.09, 127.91, 129.03, 129.82, 131.29, 131.68, 132.20, 133.15, 143.05, 177.47, 199.58 ppm. Mass spectrum *m/z*: 606.43 (M+H)⁺; CHN Analysis, Calculated for C₃₈H₃₃FeN₂O₂: C, 75.37; H, 5.49; N, 4.63 %. Found : C, 75.41; H, 5.57; N, 4.54 %.

1-*N*-Methyl-spiro-[2.3']-*N*-benzyl-oxindole-3-ferrocenoyl-4-anthracenylpyrrolidine (4d):

Following General Procedure, reaction of dyad **1** (100 mg, 0.24 mmol) with *N*-benzylisatin **2d** (56.94 mg, 0.24 mmol) and sarcosine (21.38 mg, 0.24 mmol) in toluene (10 mL) yielded after column chromatography (Hexane/AcOEt 4/1) **4d** as a orange solid (126 mg, 77.19%). M.p.: 248 °C; IR (KBr) : 1667, 1702 cm⁻¹; ¹H NMR (CDCl₃/300 MHz) : δ 2.23 (s, 3H), 2.86 (s, 5H), 3.72 (t, *J* = 9.6 Hz, 1H), 4.10-4.22 (m, 3H), 4.46 (d, *J* = 18 Hz, 1H), 4.83 (d, *J* = 15.9 Hz, 1H),

4.46 (d, $J=15.6$ Hz, 1H), 5.25 (d, $J=10.2$ Hz, 1H), 6.35 (q, $J=6.9$ Hz, 1H), 6.53-6.56 (m, 1H), 7.04-8.05 (m, 15H), 8.38 (s, 1H), 8.95 (d, $J=9.3$ Hz, 1H), 9.74 (d, $J=9$ Hz, 1H); ^{13}C NMR ($\text{CDCl}_3/75$ MHz) : 35.4, 38.4, 44.0, 59.8, 61.3, 68.5, 68.7, 69.9, 72.4, 72.7, 78.8, 109.2, 122.7, 124.8, 125.3, 126.0, 126.3, 126.4, 127.1, 127.2, 127.4, 127.9, 128.6, 129.0, 129.8, 131.2, 131.7, 132.2, 133.3, 135.4, 142.3, 177.2, 199.6 ppm.; Mass spectrum m/z : 681.41 (M+H) $^+$; CHN Analysis calculated for $\text{C}_{44}\text{H}_{36}\text{FeN}_2\text{O}_2$: C, 77.65; H, 5.33; N, 4.12 %. Found : C, 77.59; H, 5.47; N, 4.24 %.



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PROCNO   1

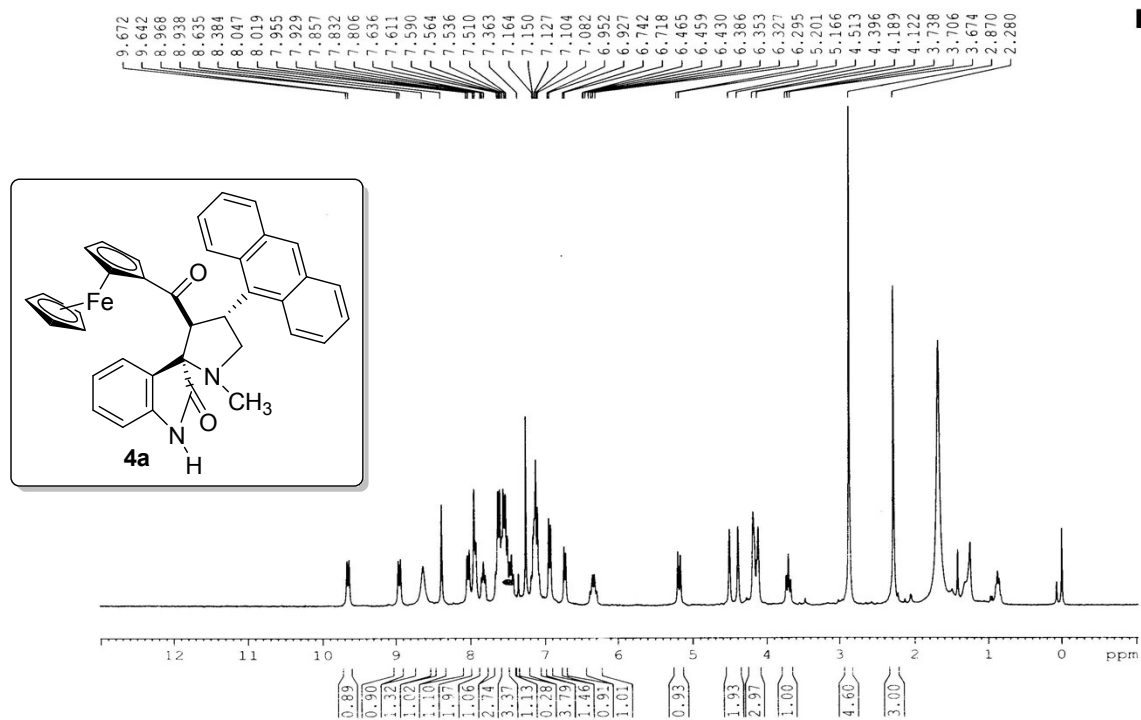
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RG       322.5
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Figure S1. ¹H NMR Spectrum of 1



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PL1      0.00 dB
SFO1     300.1318534 MHz

F2 - Processing parameters
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Figure S2. ¹H NMR Spectrum of 4a

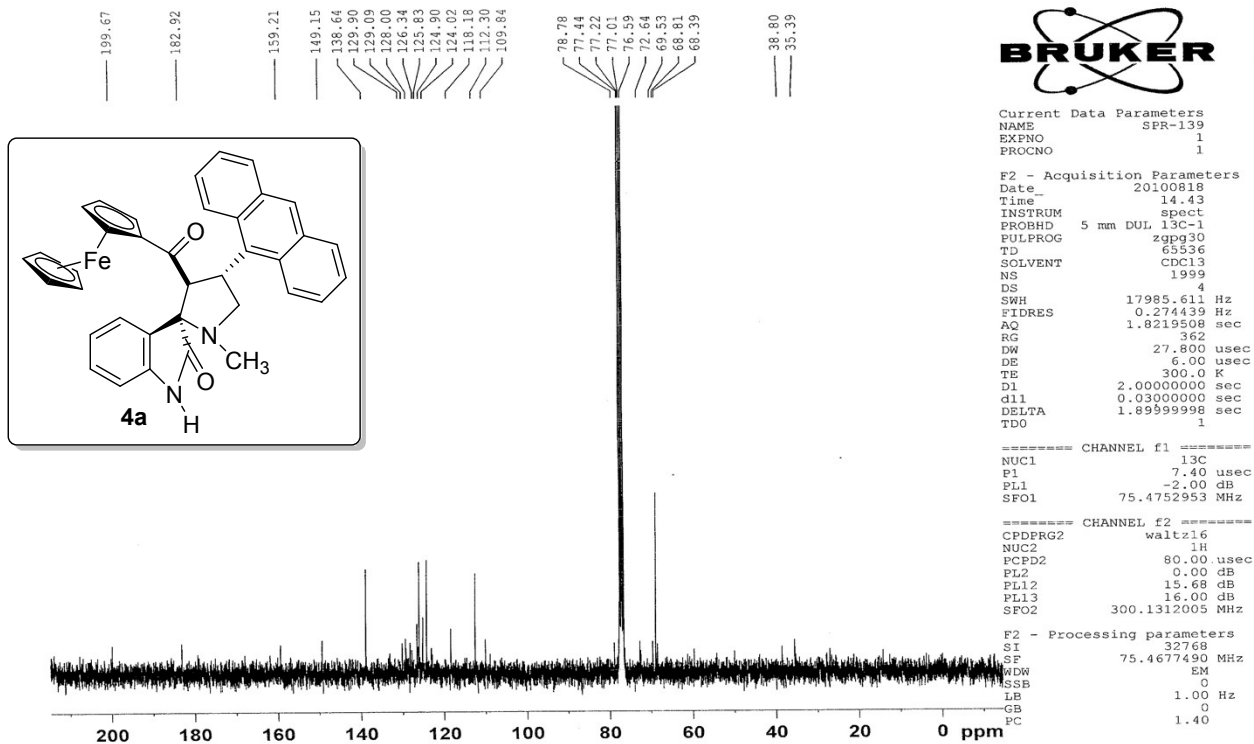


Figure S3. ¹³C NMR Spectrum of 4a

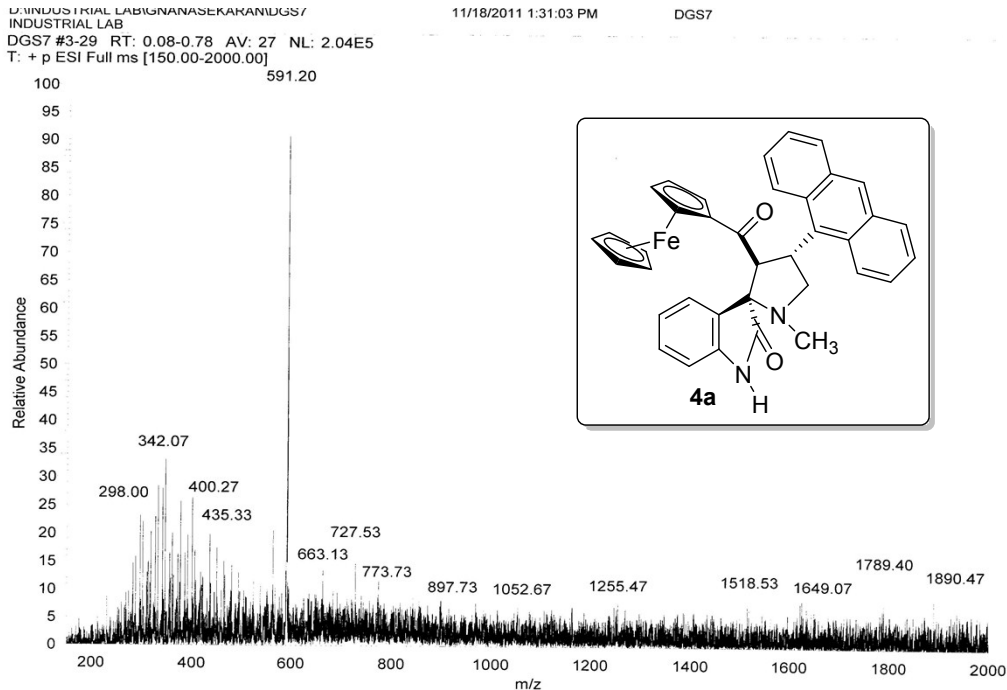


Figure S4. Mass Spectrum of 4a

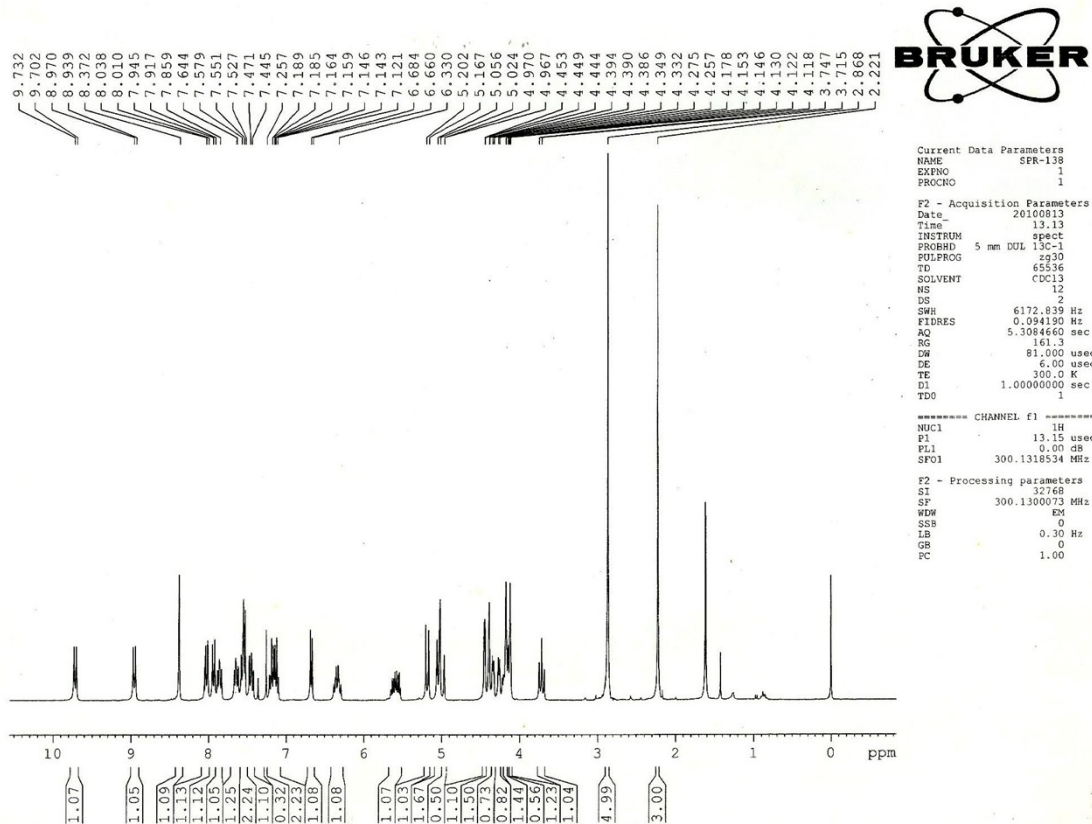


Figure S5. ¹H NMR Spectrum of 4b

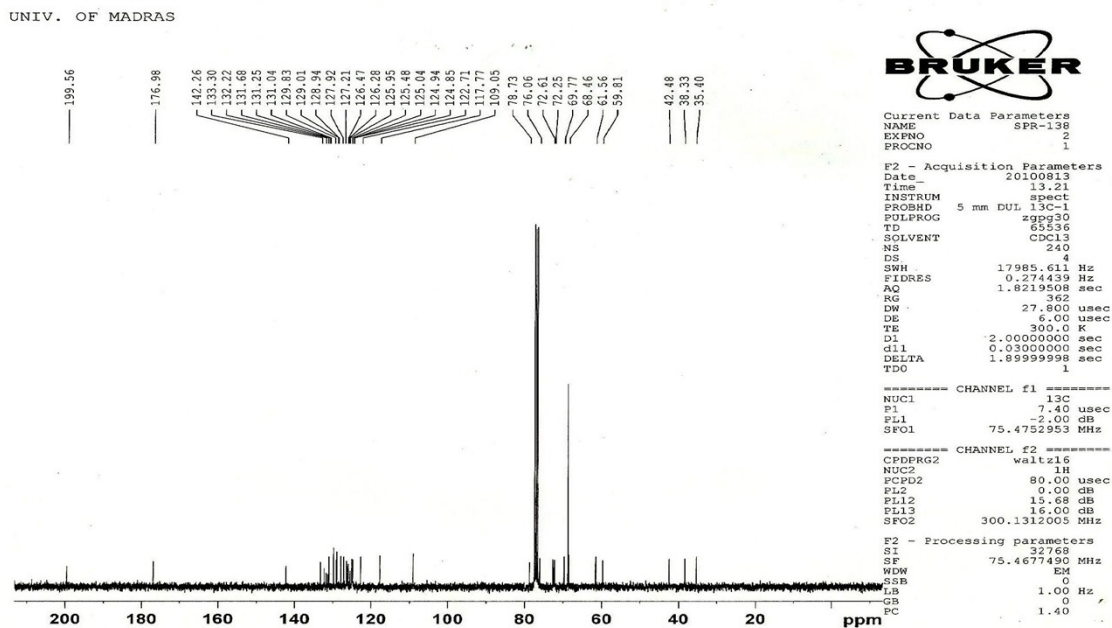
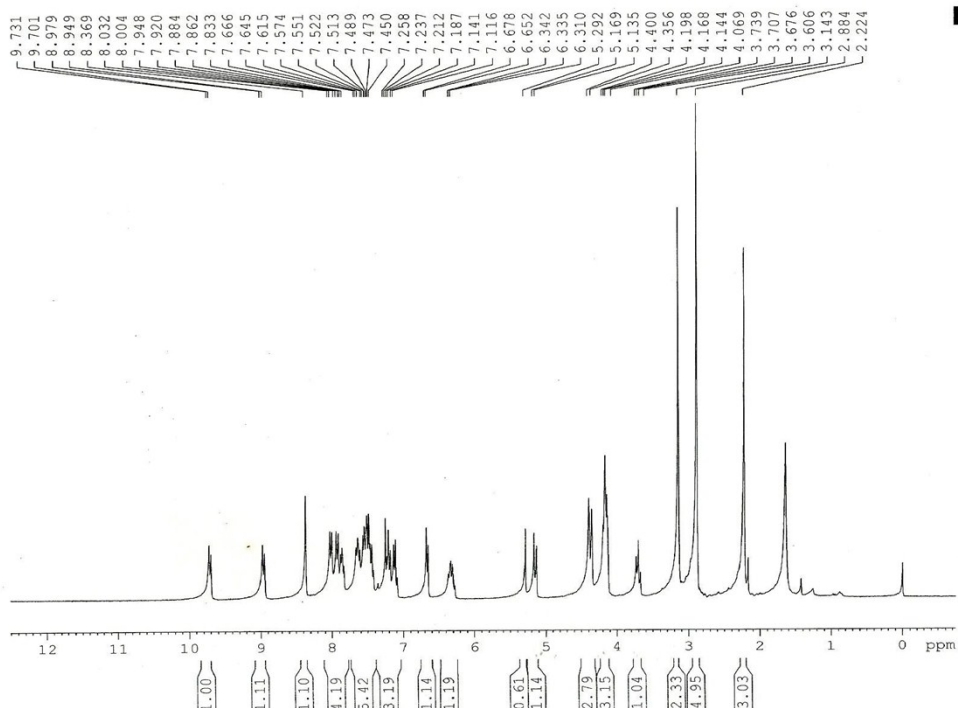


Figure S6. ¹³C NMR Spectrum of 4b



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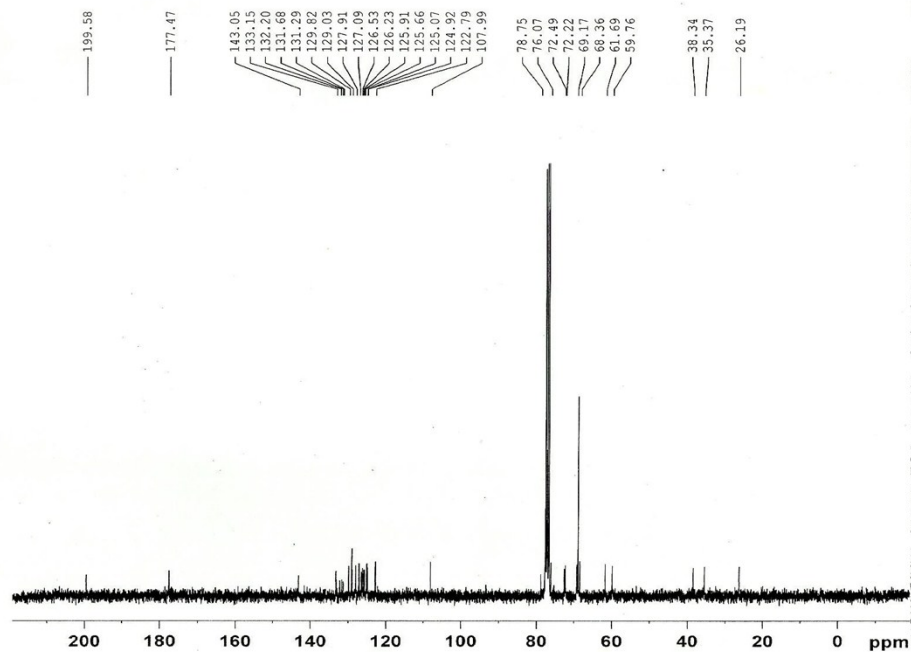
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FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG            181
DW            81.000 usec
DE            6.00 usec
TE            300.0 K
D1            1.00000000 sec
D11           1
D12           1
D13           1
D14           1
D15           1
D16           1
D17           1
D18           1
D19           1
D20           1

----- CHANNEL f1 -----
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PL1           0.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
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WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
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Figure S7. ¹H NMR Spectrum of 4c

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Current Data Parameters
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PROCNO        1

F2 - Acquisition Parameters
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TE            300.0 K
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d11           0.03000000 sec
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TD0           1

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PL1           -2.00 dB
SFO1          75.4752953 MHz

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NUC2          1H
PCPD2         80.00 usec
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PL12          15.68 dB
PL13          16.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
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SF            75.4677490 MHz
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GB            0
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Figure S8. ¹³C NMR Spectrum of 4c

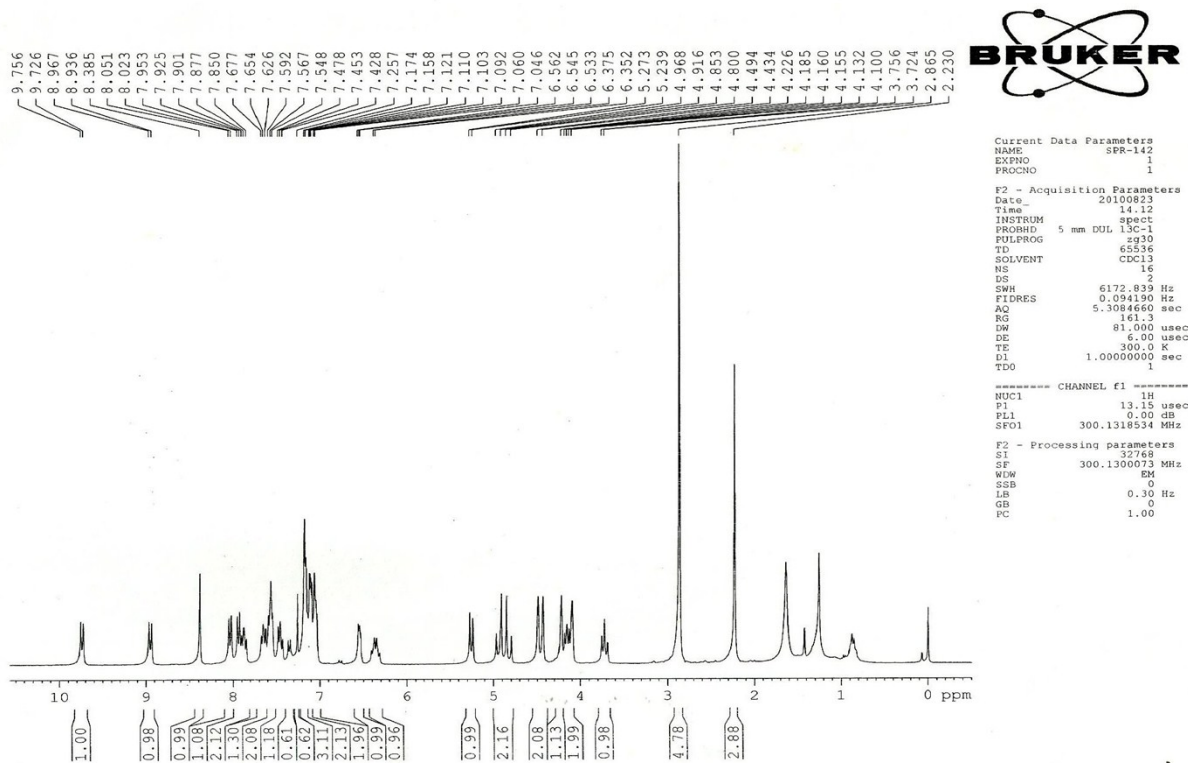


Figure S9. ¹H NMR Spectrum of 4d

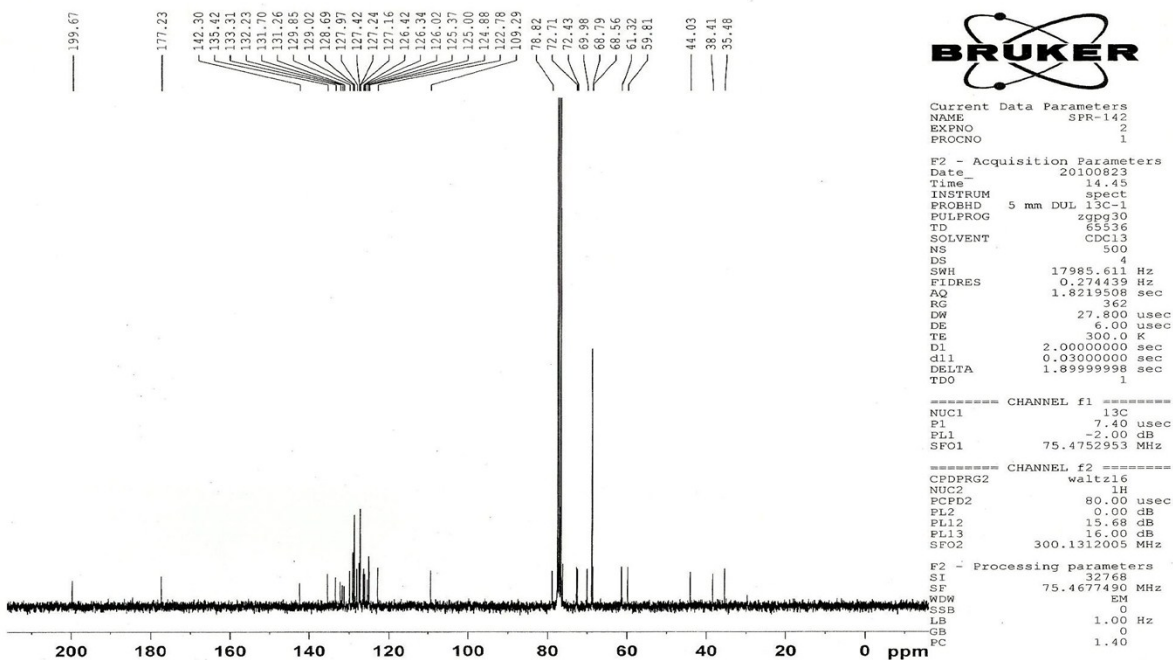


Figure S10. ¹³C NMR Spectrum of 4d

3. Single crystal X-ray studies:

The compound crystallizes in centrosymmetric space group and in monoclinic crystal system with the space group $C2/c$. The pyrrolidine ring [N1/C12-C15] makes the dihedral angle of $88.43(2)^\circ$ with anthracene (C31-C44) system. The Fe–centroid distance to the substituted cyclopentadienyl ring is $1.6488(3) \text{ \AA}$ [$1.6474(14) \text{ \AA}$ for the unsubstituted ring] and the $Cg3$ —Fe1— $Cg4$ angle is $178.72(6)^\circ$ where $Cg3$ and $Cg4$ are the centroids of the substituted and unsubstituted cyclopentadienyl (Cp) rings, respectively. The five-membered [N1/C12-C15] ring adopts an envelope conformation with C15, the envelope flap, lying $-0.251(3) \text{ \AA}$ from the plane defined by atoms N1, C12, C13 and C14. The asymmetry parameter $\Delta C_s[C15]$ is $0.036(2)$ and puckering parameters q_2 and φ_2 are $0.400(3) \text{ \AA}$ and $151.10(4)^\circ$, respectively. The crystal packing of the molecule is stabilized by C-H...O, C-H... π and $\pi \dots \pi$ types of intra and intermolecular interactions in addition to van der Waals forces. The C-H...O hydrogen bonds link the molecules into dimers. Here, atoms C3 and C28 at (x, y, z) donate one proton each to atoms $O_2(1/2-x, -1/2-y, 2-z)$ and $O_1(1/2-x, 1/2-y, 2-z)$ which connects the molecules forming a cyclic centrosymmetric $R_2^2(18)$, $R_2^2(22)$ dimers, respectively.

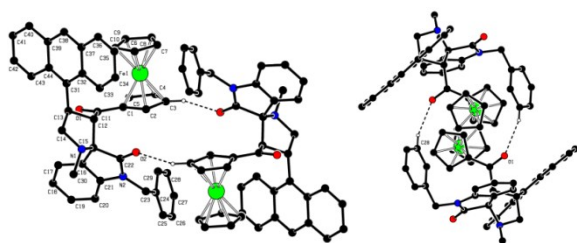


Figure S11. Formation of $R_2^2(18)$ and $R_2^2(22)$ centrosymmetric dimer.

The C-H... π inter and intra molecular interactions are observed by C-H... π [C10-H10... $Cg7$ (distance of $3.569(4) \text{ \AA}$) and C14-H14B... $Cg7$ (distance of $3.546(4) \text{ \AA}$), where $Cg7$ is the centroid of the ring defined by the atoms C31/C32/C37/C38/C39/C44] interactions exist. In the

π - π [Cg3...Cg4 (x, y, z) distance of 3.295(3) Å) interactions, Cg3 and Cg4 are the centroids of the Cp rings defined by the atoms C1-C5 and C6-C10 respectively].

Table 1. Hydrogen bonding (C-H... π and π ... π) table shows intra and intermolecular interactions [Å and °]

COMPOUND	D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
Cycloadduct 4d	C3 --H3...O2 ⁱ	0.98	2.40	3.318(4)	155
	C28 --H28...O1 ⁱⁱ	0.93	2.46	3.341(5)	158
	C45 --H45...O2 ⁱⁱⁱ	0.98	2.45	3.340(5)	151
	C2 -H2 ...O2	0.98	2.52	3.337(4)	140
	C10-H10...Cg7	0.98	2.77	3.569(4)	140
	C14-H14B...Cg7 ^{iv}	0.97	2.76	3.546(4)	138
	C6 -H6...Cg8	0.98	2.84	3.675(5)	144
	Cg3... Cg4	-	-	3.294(2)	-

Symmetry codes: (i) 1/2-x, -1/2-y, 2-z (ii) 1/2-x, 1/2-y, 2-z (iii) x, 1+y, -1+z (iv) 1-x, y, 5/2-z

Cg3, g4 centroids of the rings are (C1-C5) and (C6-C10).

Cg7, Cg8 centroids of the rings are (C31/C32/C37/C38/C39/C34) and (C32-C37).

4. UV-Vis & Fluorescence Spectrum

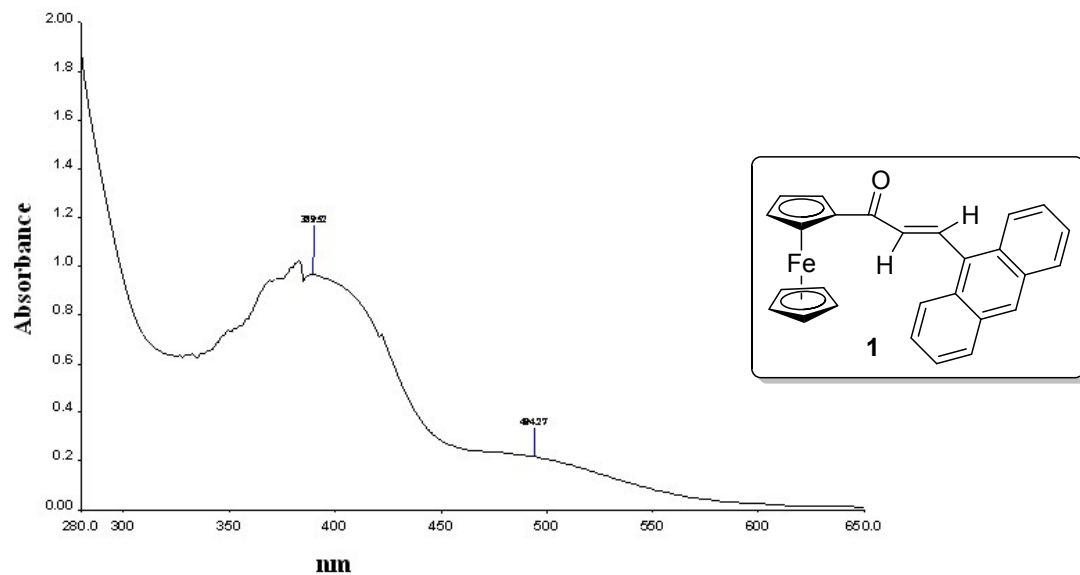


Figure S12. UV-VIS. Spectrum of 1

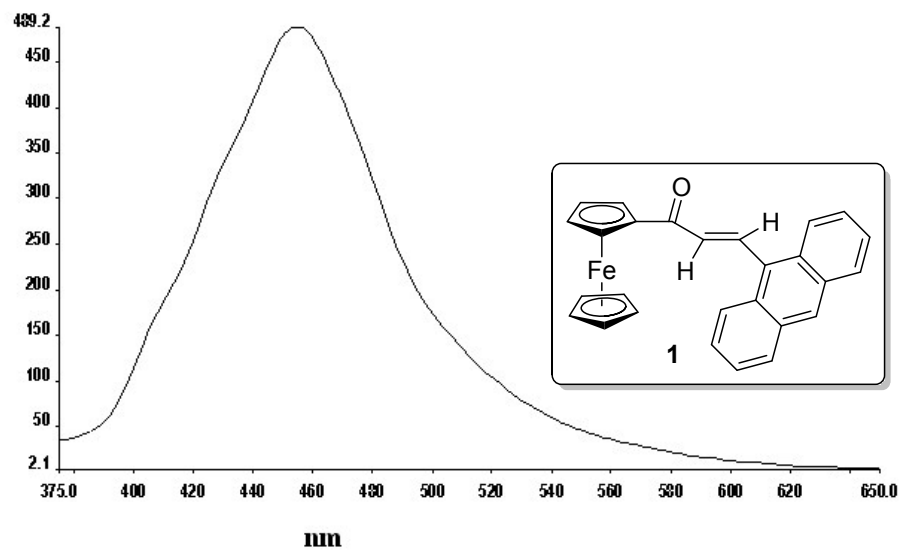


Figure S13. Fluorescence Spectrum of 1

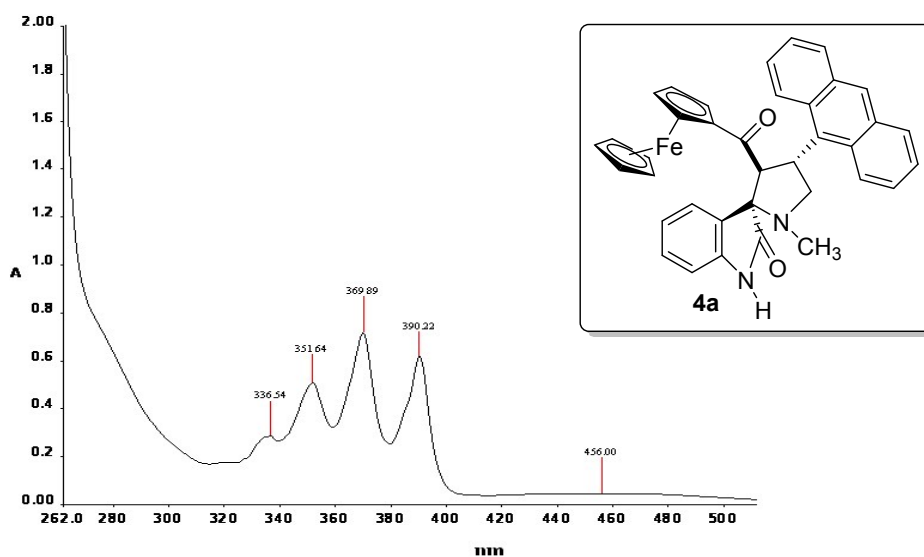


Figure S14. UV-VIS. Spectrum of **4a**

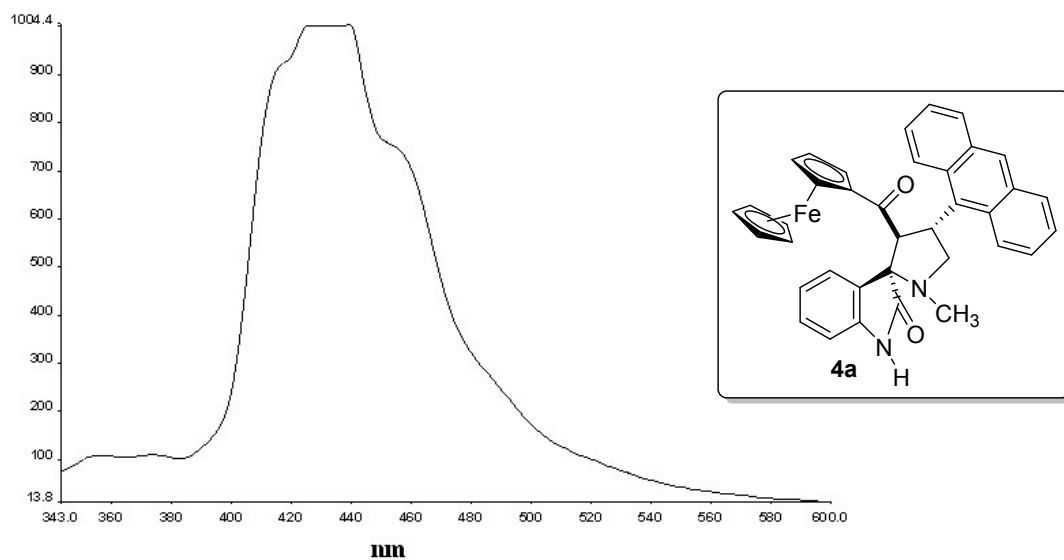


Figure S15. Fluorescence Spectrum of **4a**

5. Life-time Fluorescence Studies:

Time-resolved fluorescence decays were obtained by the time-correlated single-photon-counting (TCSPC) method. A diode-pumped Millennia VCW laser (Spectra Physics, 532 nm) was used to pump the Ti-Sapphire rod in a Tsunami picosecond-mode locked laser system (Spectra

Physics). The 750 nm (85 MHz) beam from the Ti-Sapphire laser was passed through a pulse picker (Spectra Physics, 3980 2S) to generate 4 MHz pulses. The second harmonic output (375 nm) was generated by a flexible harmonic generator (Spectra Physics, GWU 23PS). A vertically polarized 375 nm laser was used to excite the sample. The fluorescence emission at the magic angle (54.78) was counted by an MCP PMT apparatus (Hamamatsu R3809U) after being passed through the monochromator and was processed through a constant fraction discriminator (CFD), a time-to-amplitude converter (TAC) and a multichannel analyzer (MC). The instrument response function for this system is ≈ 52 ps. The fluorescence decay was obtained and was further analyzed by using IBH (UK) software (DAS-6).

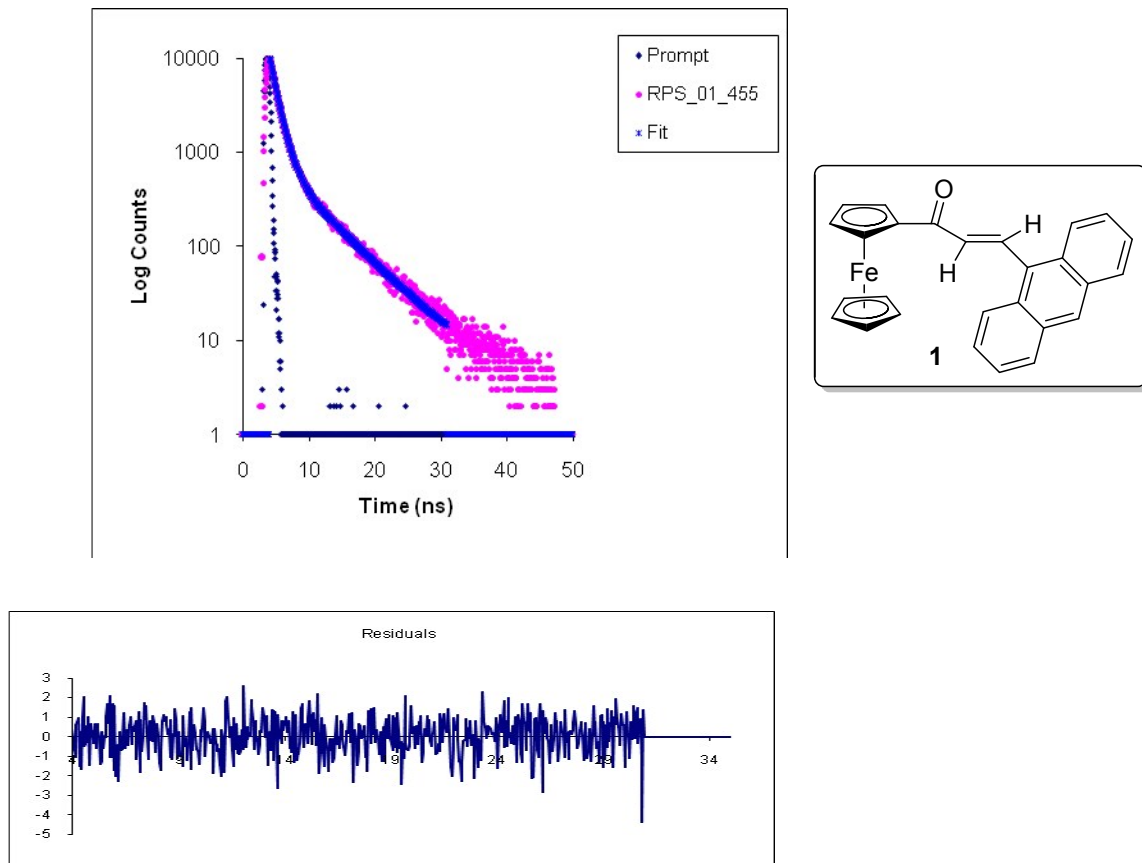


Figure S16. Life-time Fluorescence of (1)

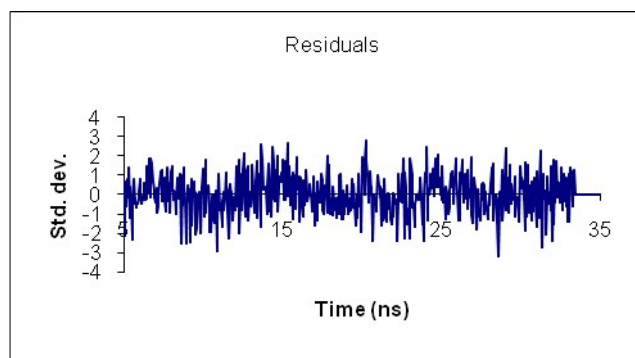
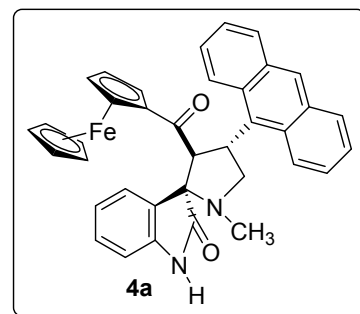
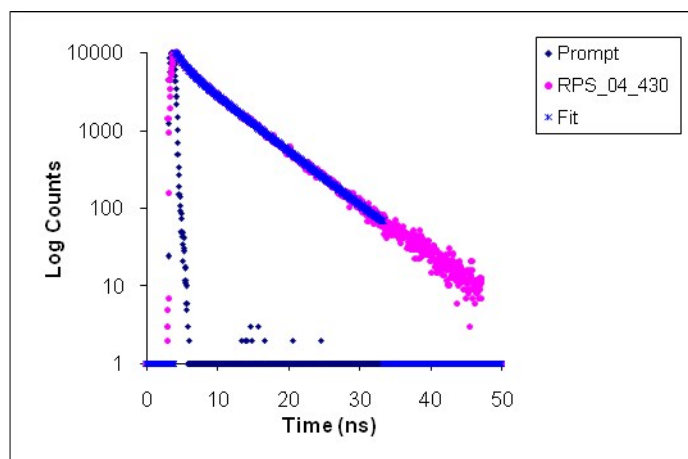


Figure S17. Life-time Fluorescence of (4a) at 430