Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Ferrocene-Azobenzene Derivative Showing Unprecedented Phase Transition and Better Solubility upon UV Irradiation

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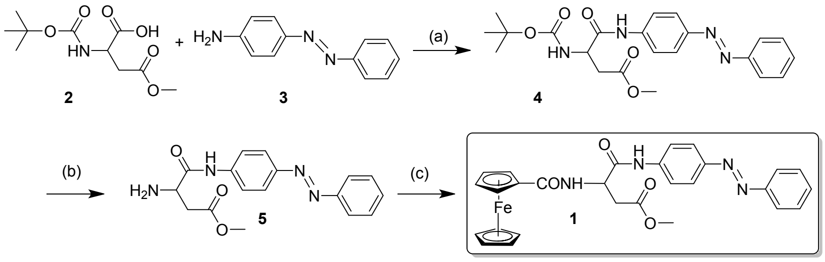
1. Materials and instruments

Reagents and solvents were purchased from various commercial sources and used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer at room temperature. Mass spectra were obtained by using Tsq quantum access max from Thermo. Scanning electron microscope (SEM) images were carried out on a Helios NanoLab 600iDual Beam FIB/FE-SEM (FEI, USA). All the samples were coated with gold before test. UV-vis absorption spectra were measured by a Shimadzu UV3100S. FT-IR spectra were recorded with Nicolet 6700, melting point data of samples were got by using microscopic X-4A. Differential scanning calorimetry (DSC) measurement was performed by DSC 200 F3. Powder X-ray diffraction (XRD) patterns were measured on a Rigaku D/max 2500 X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm) (Japan). The UV lamp we used was FC-100FA (USA). Sample temperatures were controlled by a heating/cooling stage Linkam 10033L. Photoirradiation experiments were carefully performed to minimize the heat radiation from the light source. Polarizing optical micrographs (POM) were taken by an OLYMPUS BX51 microscope equipped with a high pressure Hg lamp, optical filters and heat absorbing filters so that observation the image in situ upon photoirradiation was possible.

2. Synthetic



Scheme S1. Synthetic procedure for azobenzene derivatives **1**. Reagents and conditions : (a) HBTU, TEA, HOBt, DCM, 24 h (49%); (b) TFA, DCM, rt, 5 h (85%); (c) HBTU, HOBt, TFA, ferrocenecarboxylic acid, DCM, 24 h (96%). HOBt = 1-hydroxy-1H-benzo-triazole, HBTU=O-Benzotriazole-N,N,N,N-tetramethyl uranium -hexafluorophosphate, DCM=dichloromethane, TEA=triethylamine, TFA=trifluoro-acetic Acid.

Compound 4

Synthesis of azobenzene derivatives **4**: triethylamine agent (5 mL) was added dropwise to solution of DCM (25 mL) treated with the Boc-L-aspartic acid 4-methyl ester (2.313 g, 0.01 mmol), HOBT (1.49 g, 0.01 mmol)，and HBTU (4.17 g, 0.01 mmol) which were at room temperature for 12 h and was poured into 4-Aminoazobenzene (1.97 g, 0.01 mmol) and stirred for 12h. Compound **4** was isolated as an orange powder (2.09 g, 49%). Melting point: 163 ^{o}C. ^{1}H NMR (CDCl$_3$)：δ = 8.87 (s, 1H),7.93 –7.89 (m, 2H), 7.69 – 7.67(m, 2H),7.67 – 7.43 (m, 3H), 6.87 – 6.83 (m, 1H), 5.92 (s, 1H), 4.67 (dd, J = 8.61, 7.55 Hz, 1H), 3.72 (m, 3H), 3.09-2.99 (m, 1H), 2.85 – 2.73 (m, 1H), 1.49 – 1.45 (m, 9H), 1.25 (s, 1H). ^{13}C NMR (CDCl$_3$): δ = 172.61, 169.10, 152.66, 149.11, 140.14, 130.79, 129.08, 123.99, 122.75, 119.89, 81.6, 52.29, 51.40, 35.25, 28.30; MS: m/z calcd for $C_{22}H_{26}N_4O_5$: 425.19 $[M-H]^-$; found: 425.19; IR (KBr, cm^{-1}): 3315 (ν_{N-H}), 2990 (ν_{C-H}), 1742 ($\nu_{C=O}$ ester), 1678 (amide I), 1551 (amide II).

Compound 5

For synthesis of **5**, TFA (19 mL) was added dropwise to a DCM solution (45 mL) of compound **4** (1.72 g, 4 mmol), the mixture was stirred at room temperature overnight. After the product was purified by column chromatography with DCM as eluent, afford the product as an orange powder (1.36 g, Yield: 85%). Melting point: 126 °C. ^1H NMR ($CDCl_3$): δ = 9.87 (s, 1H), 7.96 – 7.95 (m, 2H), 7.93 – 7.91 (m, 2H), 7.79 – 7.78 (m, 2H), 7.55 – 7.48 (m, 3H), 6.90 – 6.84 (dd, J =8.20, 8.25 Hz, 1H), 3.88 – 3.86 (m, 1H), 3.76 (s, 3H), 3.74 (s, 1H), 3.08 – 2.98 (m, 1H), 2.88 – 2.83 (m, 1H). ^{13}C NMR ($CDCl_3$): δ = 172.35, 171.53, 152.70, 148.99, 140.19, 130.73, 129.08, 124.05, 122.73, 119.47, 52.37, 52.03, 38.78; HRMS: m/z calcd for $C_{17}H_{17}N_4O_3$: 325.14 $[M-H]^-$; found: 325.14; IR (KBr, cm^{-1}): 3404 (ν_{N-H}), 3267 (ν_{C-H}), 1736 ($\nu_{C=O}$ ester), 1663 (amide I), 1508 (amide II).

Compound 1

For synthesis of **1**, a mixture of compound **5** (0.40 g,1.4 mmol), ferrocenecarboxylic acid (0.52 g, 1.5 mmol) were dissolve in DCM (45 mL) and stirred at room temperature for 18 hrs. The product was purified by chromatography over silica using DCM-EtOAc (10:1) as eluent to afford **1** as orange crystal (2.10 g, Yield: 96 %). Melting point: 216 °C. ^1H NMR (DMSO-d_6): δ = 10.48 (s, 1H),7.91 – 7.87 (m, 2H), 7.87 – 7.86 (m, 2H), 7.85 – 7.84 (m, 2H), 7.60 – 7.51 (m, 3H), 5.00 – 4.94 (m, 1H), 4.86 (t, J = 1.7 Hz, 2H), 4.37 (t, J = 1.8 Hz, 2H), 4.19 (s, 5H), 3.65 (s, 3H), 2.99 – 2.94 (dd, J = 4.57, 5.69 Hz, 1H), 2.89 – 2.82 (dd, J = 8.80, 8.73 Hz, 1H), 2.93 – 2.69 (m, 1H). ^{13}C NMR (DMSO-d_6): δ = 171.17, 170.50, 169.91, 148.09, 142.54, 131.52, 129.87, 124.11, 122.80, 120.05, 79.64, 75.89, 70.70, 69.91, 68.94, 68.88, 52.08, 51.07, 35.99 ; MS: m/z calcd for $C_{28}H_{26}N_4O_4$: 537.22 $[M-H]^-$; found: 537.22; FTIR (KBr, cm^{-1}): 3226 (ν_{N-H}), 2909 (ν_{C-H}), 1719 ($\nu_{C=O}$ ester), 1644 (amide I), 1409 (amide II).

3. Differential scanning calorimetry (DSC) curve of 1

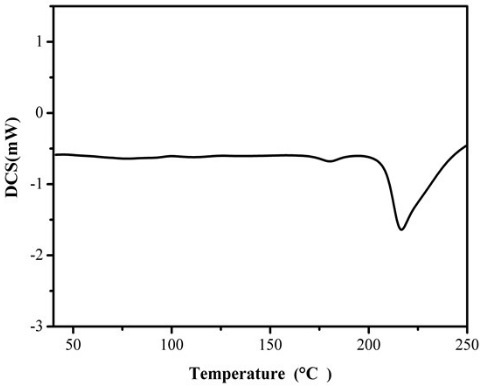


Figure S1. DSC second heating curve of **1** with rate 10 ^{o}C/min.

4. UV-vis absorption spectra of 1 in acetonitrile solution

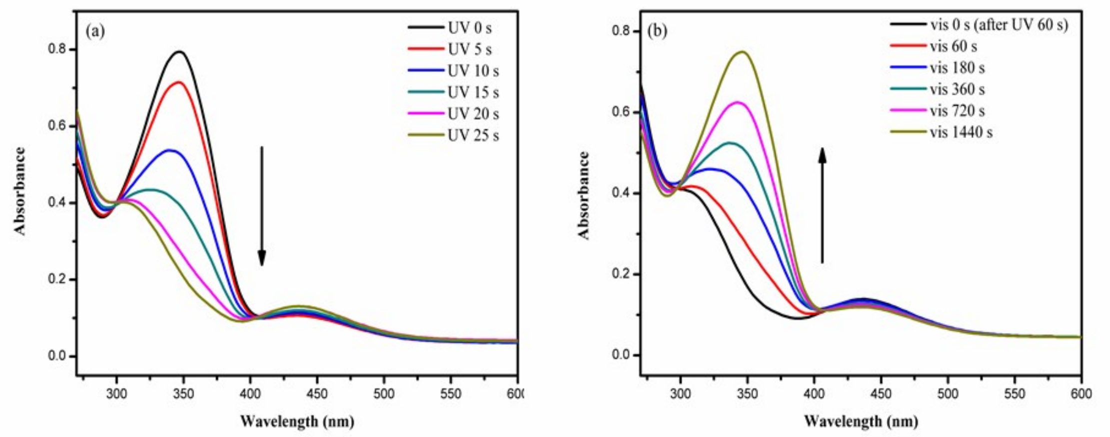
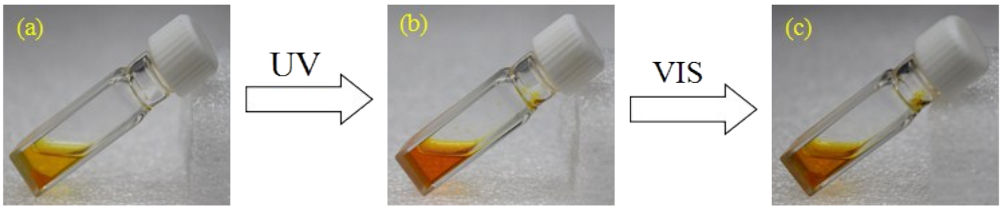


Figure S2. UV-vis absorption spectra of compound **1** (c = 0.01 mg/mL, cell is 1 cm). (a) the process from *trans*- to *cis*-isomer solution upon 365 nm irradiation; (b) the process from *cis*- to *trans*-rich solution upon visible light irradiation.

5. Photographs of 1 in organic solvents

(1)



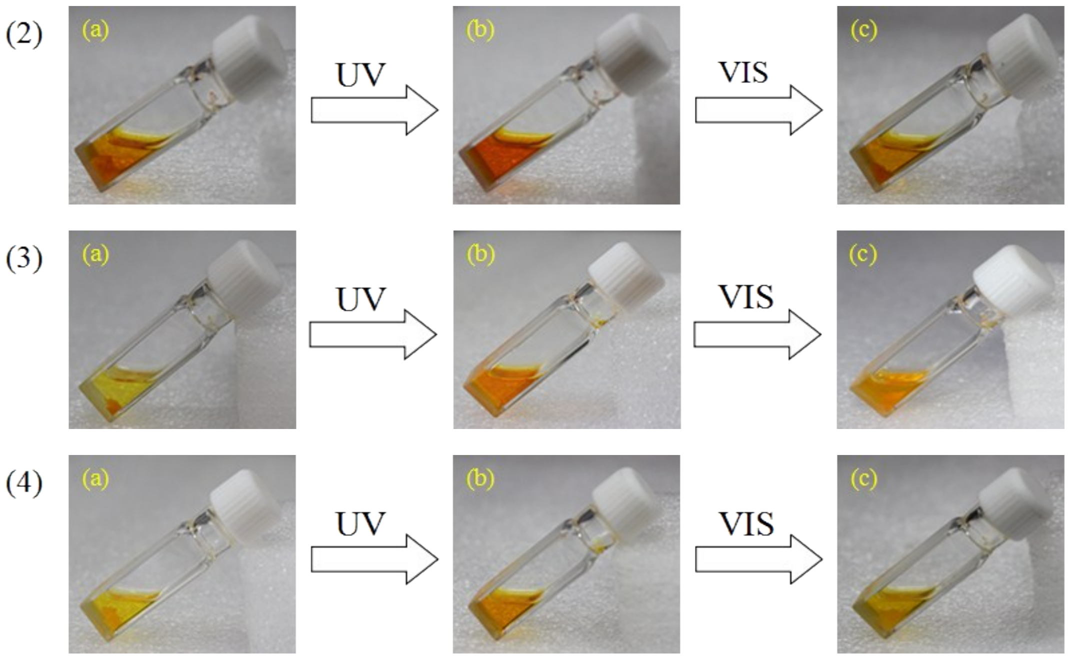


Figure S3. Representative photographic images of **1**: (1) acetonitrile/dichloromethane = 2/1, 4 mg/mL; (2) acetone, 4 mg/mL; (3) toluene, 3 mg/mL; (4) hexane, 3 mg/mL. (a) *trans*-isomer crystalline precipitate; (b) *cis*-isomer solution under 365 nm irradiation for 2 h; (c) trans-isomer reformed crystalline after visible light for 24 hours.

6. SEM images

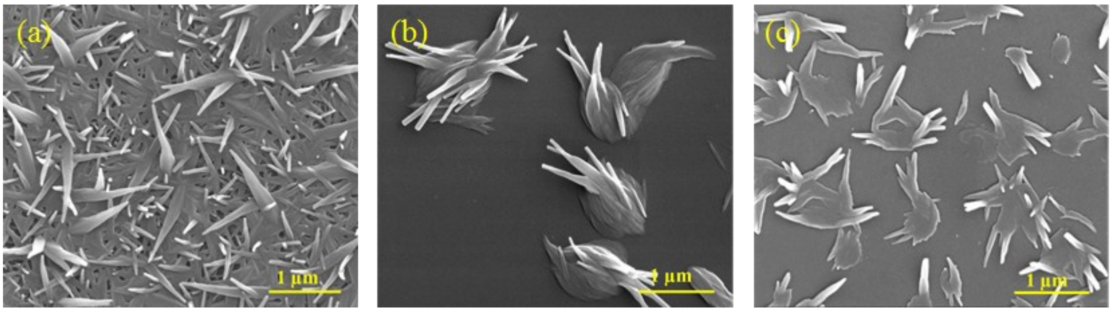


Figure S4. SEM images of **1** obtained from dichloromethane suspension (0.5 mg/mL) (a) asprepared sample; (b) irradiated upon 365 nm lamp for 2 h; (c) subsequently exposed to visible light for 24 hours.

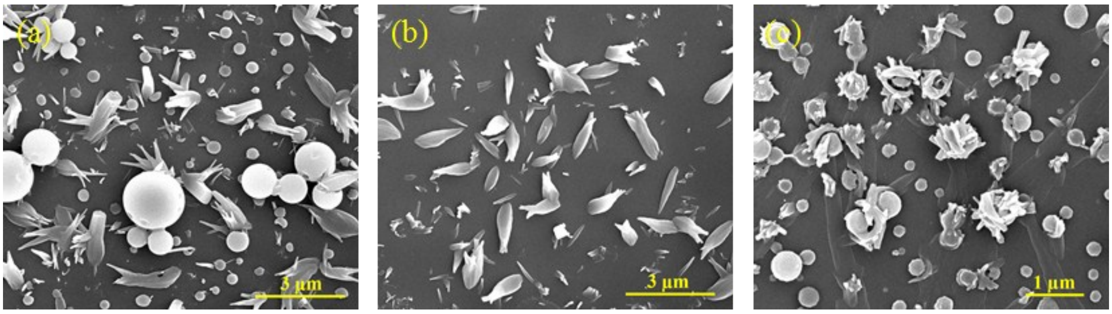


Figure S5. SEM images of **1** obtain from acetone suspension (0.5 mg/mL) (a) asprepared sample; (b) irradiation upon 365 nm lamp for 2 h; (c) subsequently exposed to visible light for 24 hours.

7. POM images

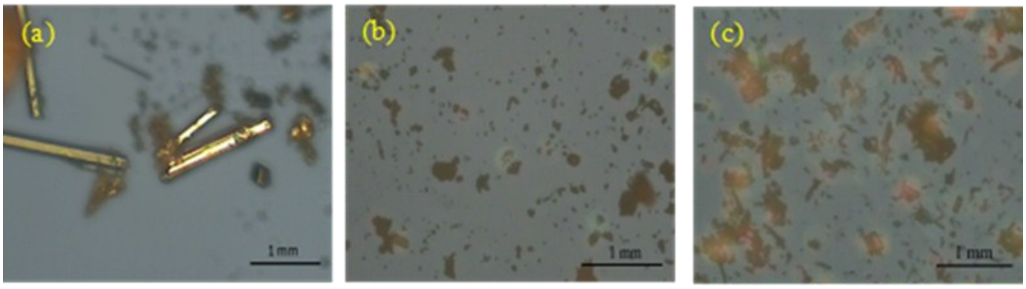


Figure S6. POM images of compound (a) **1**, (b) **4** and (c) **5**.

8. The solubility of different temperature in acetonitrile

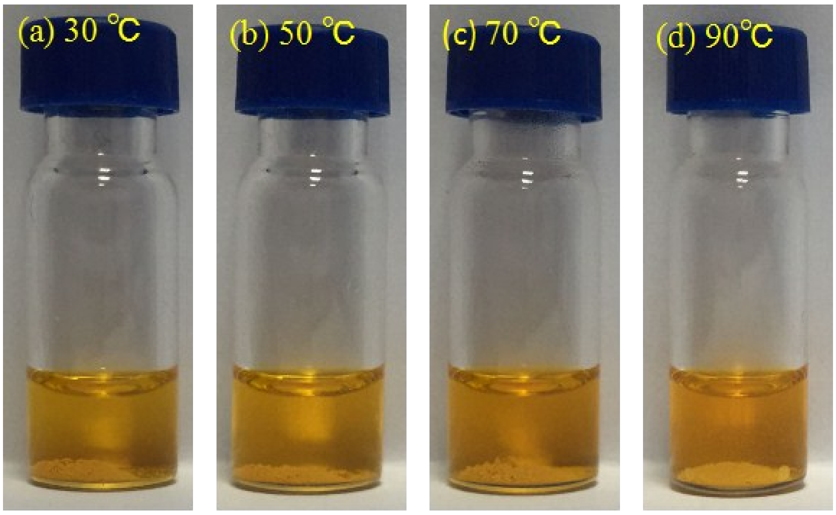


Figure S7. Optical images of the vials containing azobenzene derivatives **1** (1 mg) acetonitrile solution (0.5 mL) at different temperature.

9. ^{1}H NMR spectra of Azobenzene derivatives 1 in CD_3CN

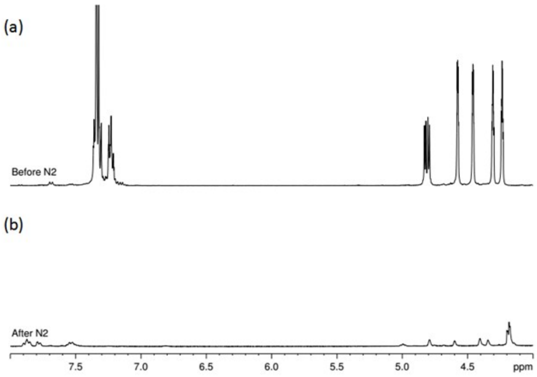


Figure S8. Azobenzene derivatives **1** in CD_3CN (a) before nitrogen to remove the solvent; (b) re-dissolve the sample after nitrogen to remove the solvent.

10. Percentage of cis and trans formed at photostationary state

Table S1. The *cis*- and *trans*- isomer percentage

	Times	Trans-isomer	Cis-isomer
^{1}H NMR	0 min	90%	10%
	60 min	81%	19%
UV	0 min	100%	0%
	24 min	92%	8%

11. FTIR spectra of compound 4, 5 and 1

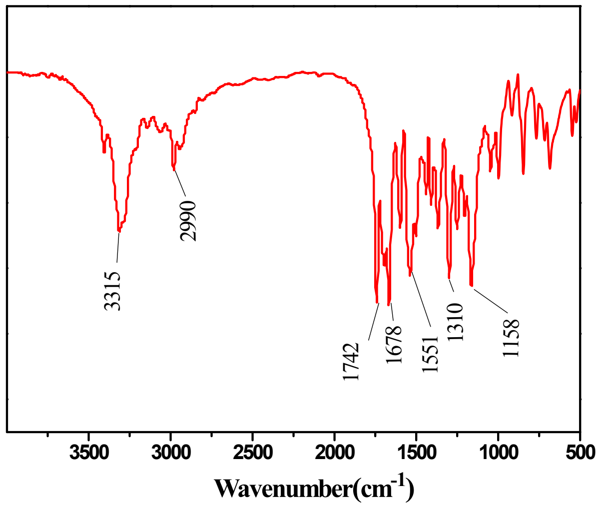


Figure S9. FTIR spectrum of compound **4**.

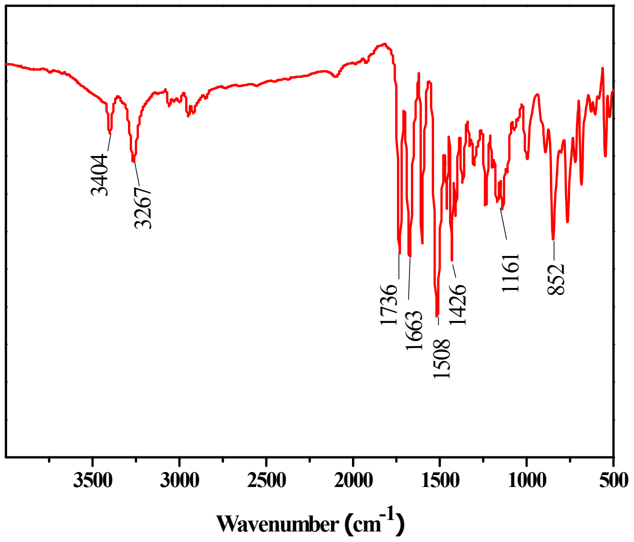


Figure S10. FTIR spectrum of compound **5**.

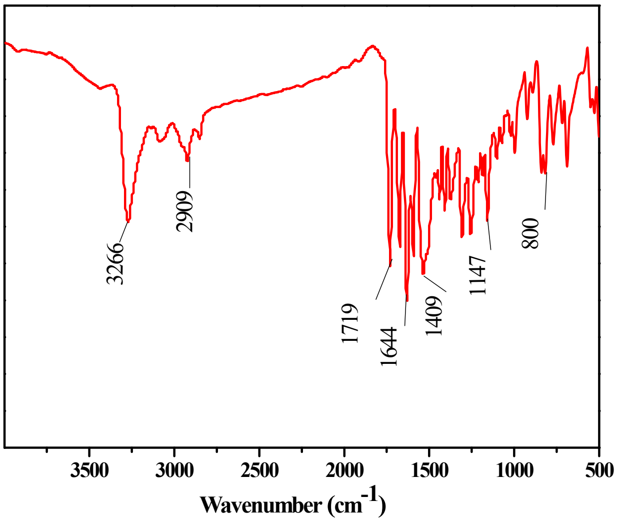


Figure S11. FTIR spectrum of compound **1**.

12. NMR spectra

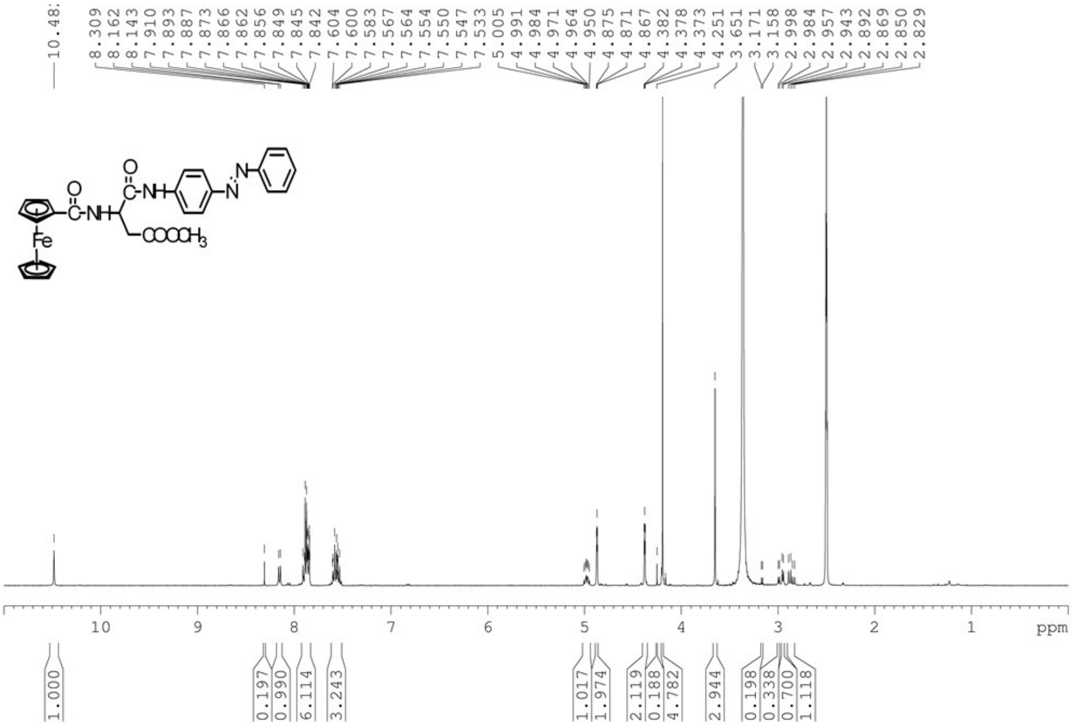


Figure S12. ^{1}H NMR spectrum of **1** in DMSO-d_6.

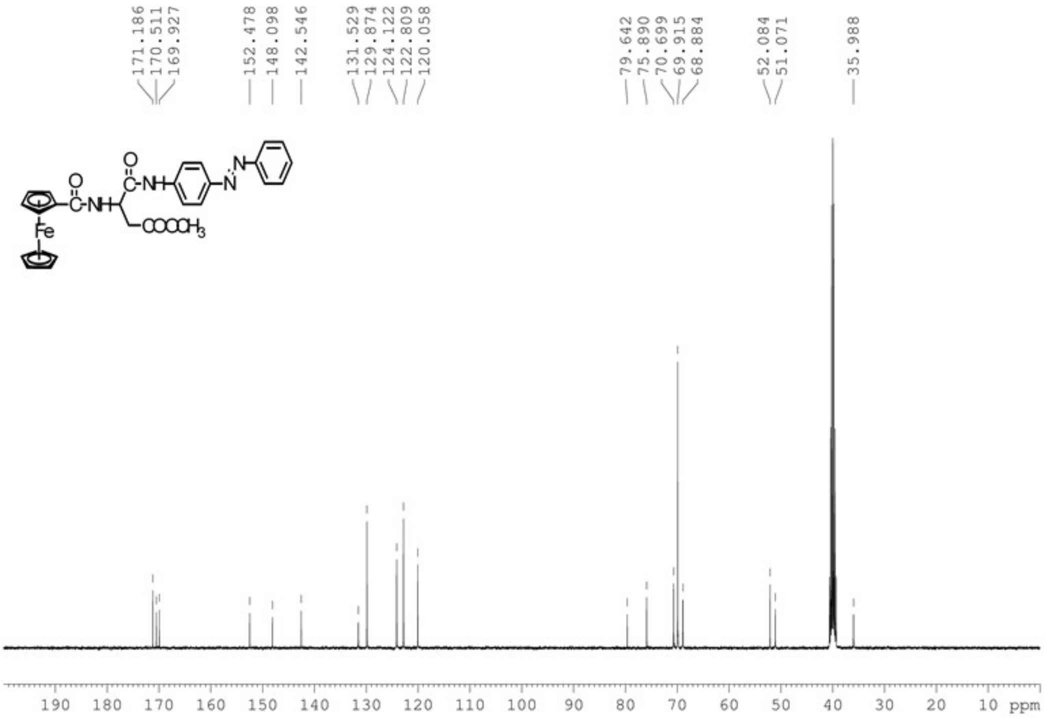


Figure S13. ^{13}C NMR spectrum of **1** in DMSO-d_6

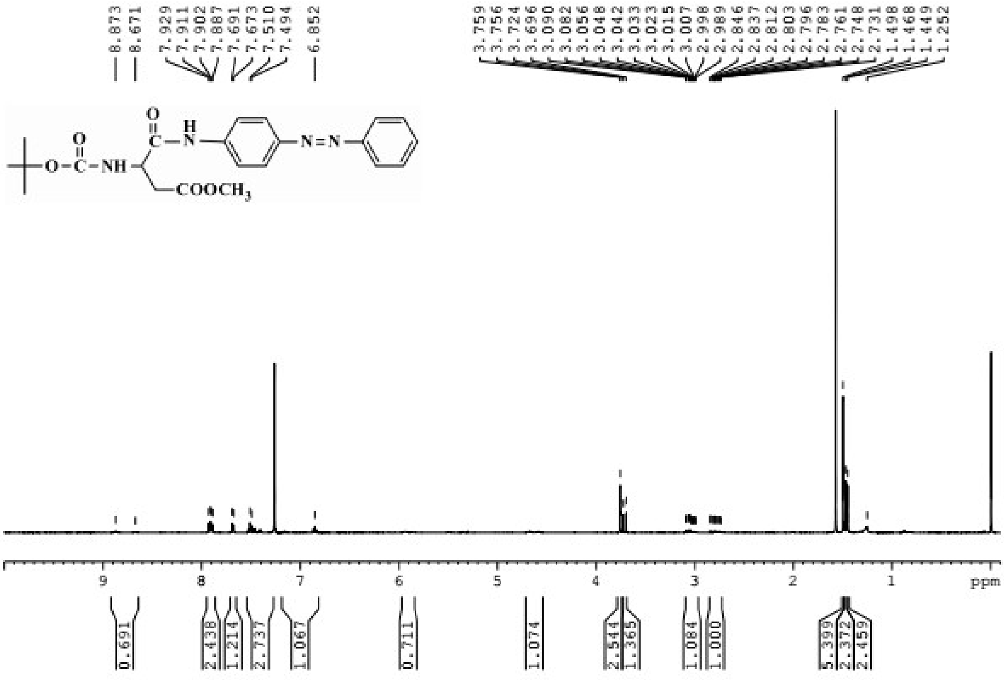


Figure S14. ^{1}H NMR spectrum of **4** in CDCl$_3$.

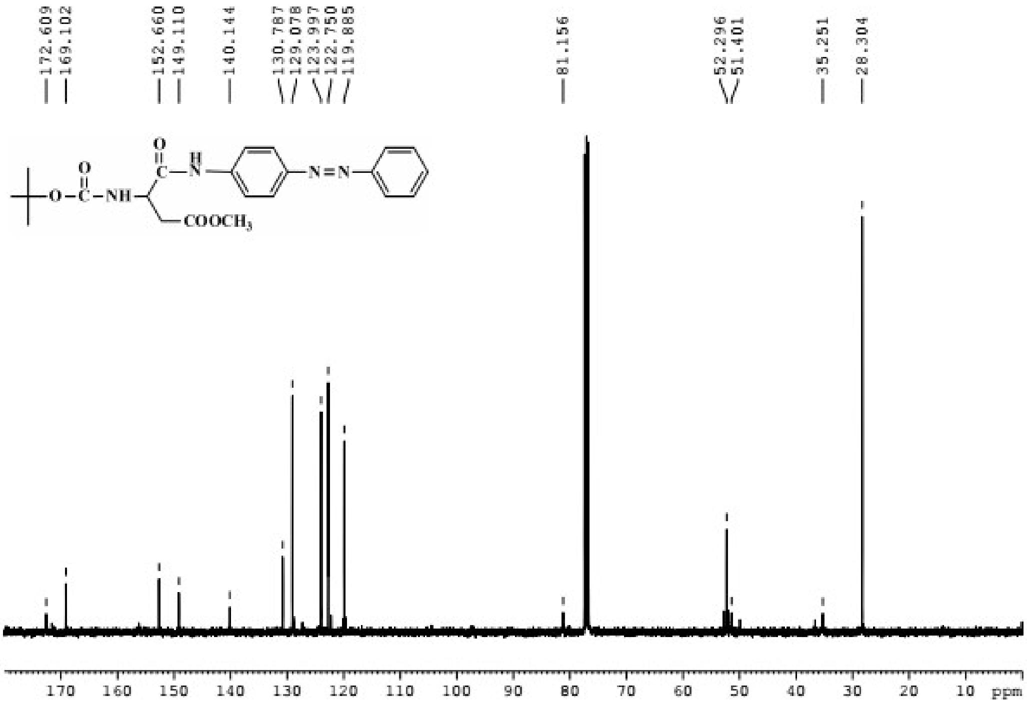


Figure S15. ^{13}C NMR spectrum of **4** in CDCl$_3$.

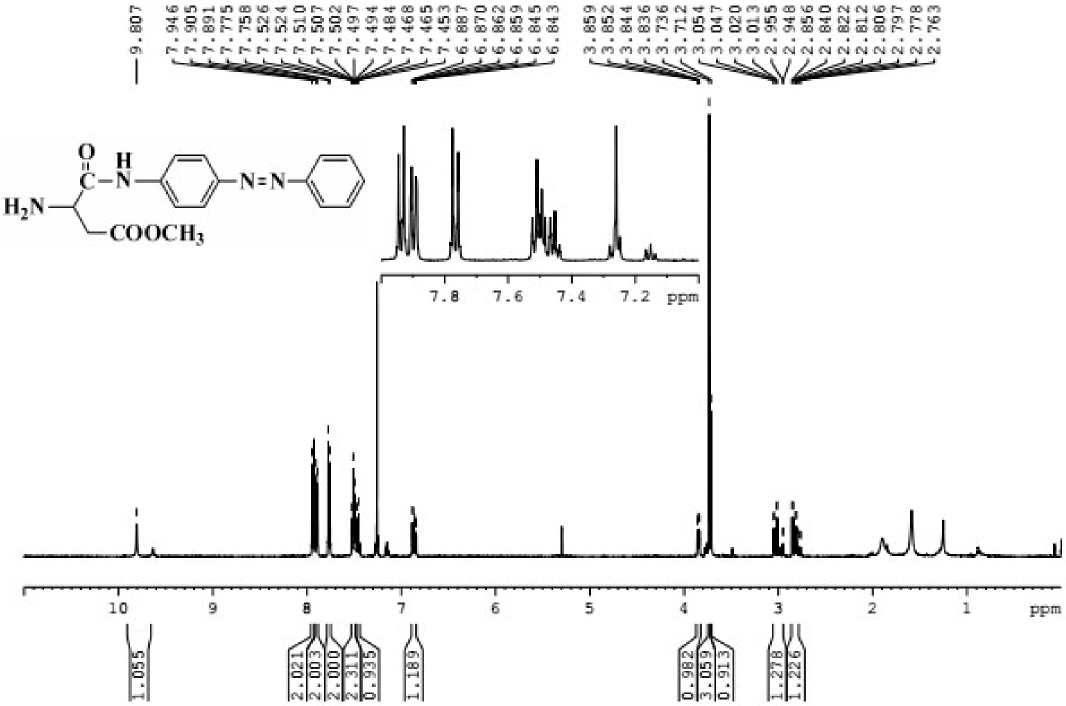


Figure S16. ^{1}H NMR spectrum of **5** in CDCl$_3$.

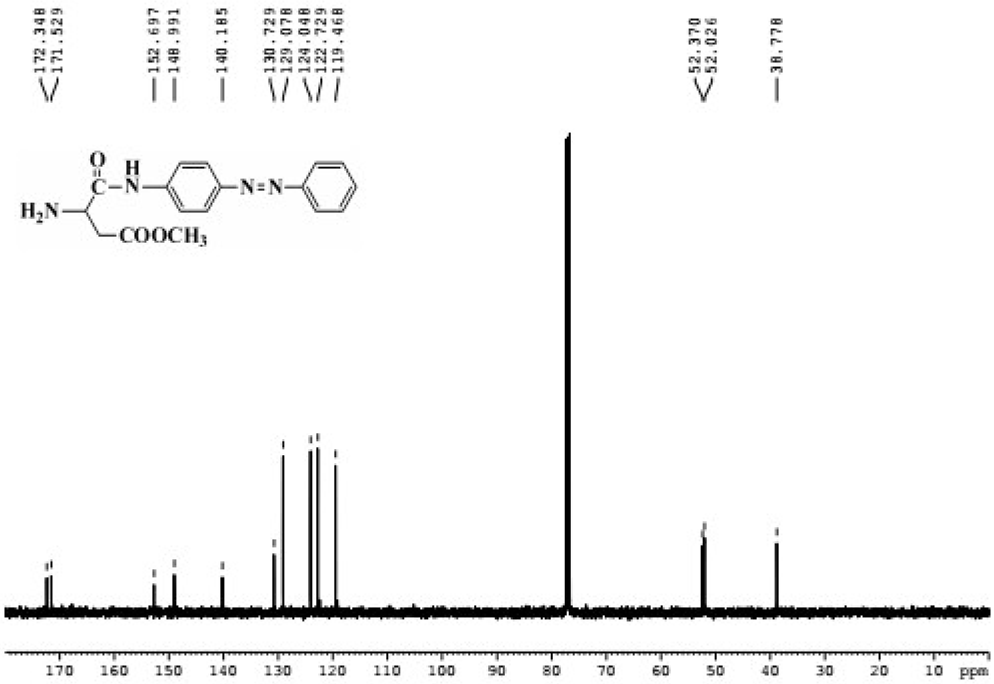


Figure S17. ^{13}C NMR spectrum of **5** in $CDCl_3$

13. Mass spectra

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Script Version
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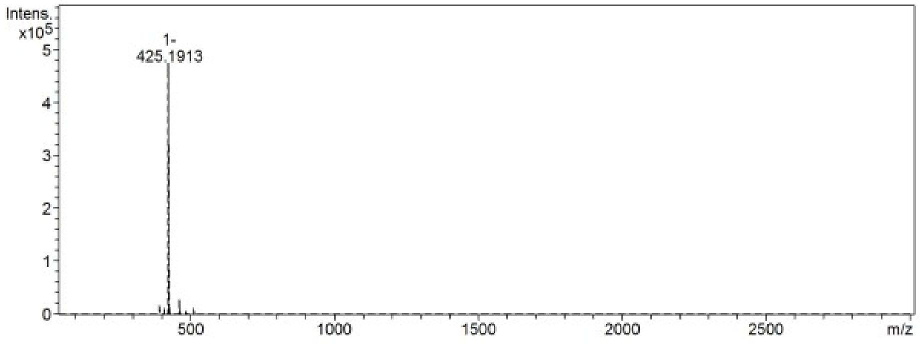

Figure S18. Mass spectrum of **4**

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Script Version
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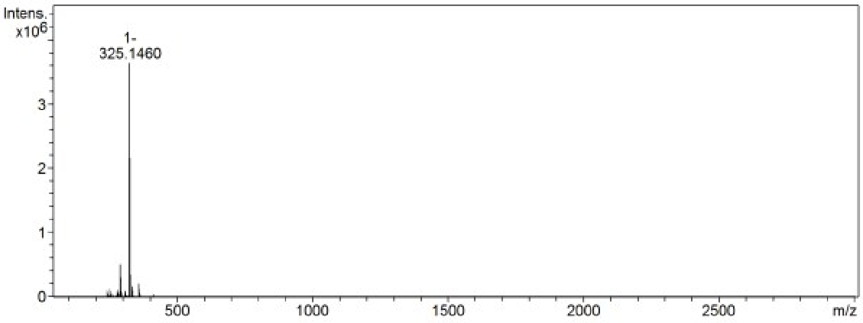

Figure S19. Mass spectrum of **5**

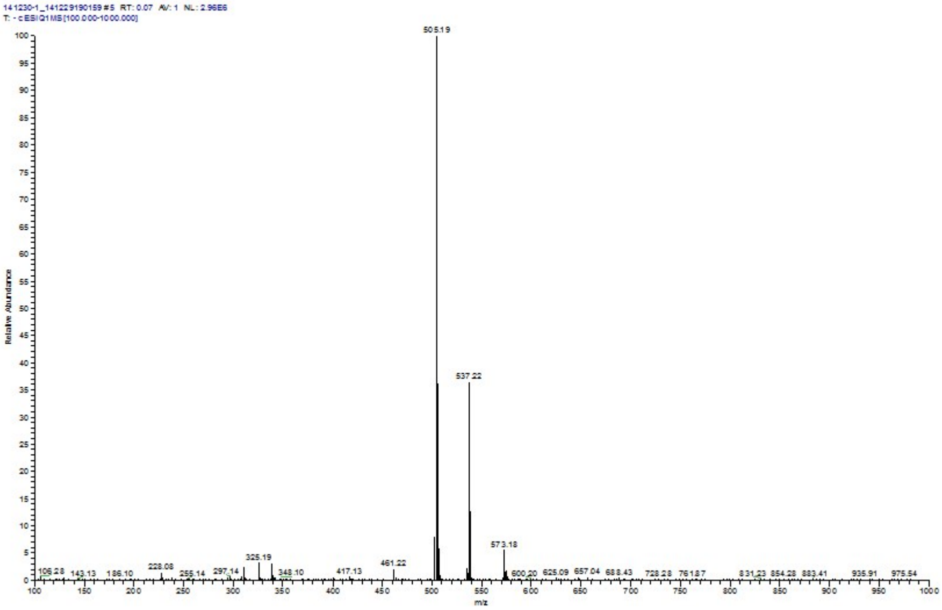

Figure S 20. Mass spectrum of **1**