Supplementary Information

Exploring Organic Photosensitizers Based on Hemicyanine Derivatives: A Sustainable Approach for Preparation of Amide Linkages

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Table S1. Comparison of C4 photocatalyst with off shelf photosensitizer for carrying out oxidative amidation of aldehydes.

Photocatalysts	**Solvent**	**Time**	**Additive**	**Reuseability/ Recyclability**	**Yield**
C4 (This Work)	**DMSO:H_2O (1:1)**	**12h**	**-**	**Yes**	**82%**
Phenazine ethosulfate	MeCN	12h	-	No	41%
$Ru(bpy)_3Cl_2$	MeCN	12h	-	No	37%
$Ru(phen)_3Cl_2$	MeCN	12h	-	No	46%
$Ru(phen)_3(PF_6)_2$	MeCN	12h	-	No	42%
$Ir(dtbpy)(ppy)_2PF_6$	MeCN	12h	-	No	44%
Nile red	MeCN	12h	-	No	29%
Rhodamine B	MeCN	12h	-	No	26%
Alizarin red S	MeCN	12h	-	No	22%
Methylene blue	MeCN	12h	-	No	16%

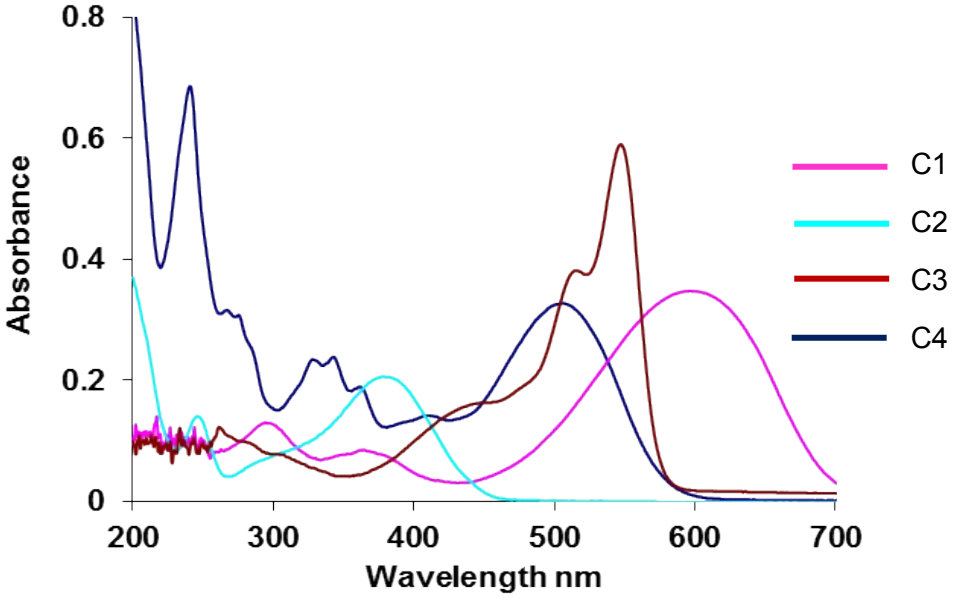

Fig. S1. Uv-vis spectra of **C1, C2, C3** and **C4** in DMSO: H_2O (1:1) solvent mixture.

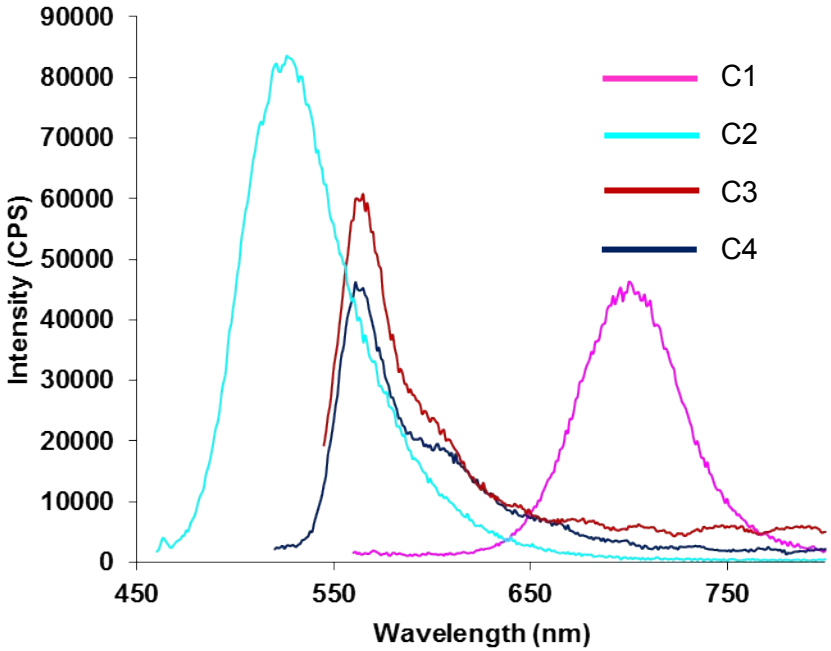

Fig. S2. Fluorescence spectra of **C1, C2, C3** and **C4** in DMSO:H_2O (1:1) solvent mixture.

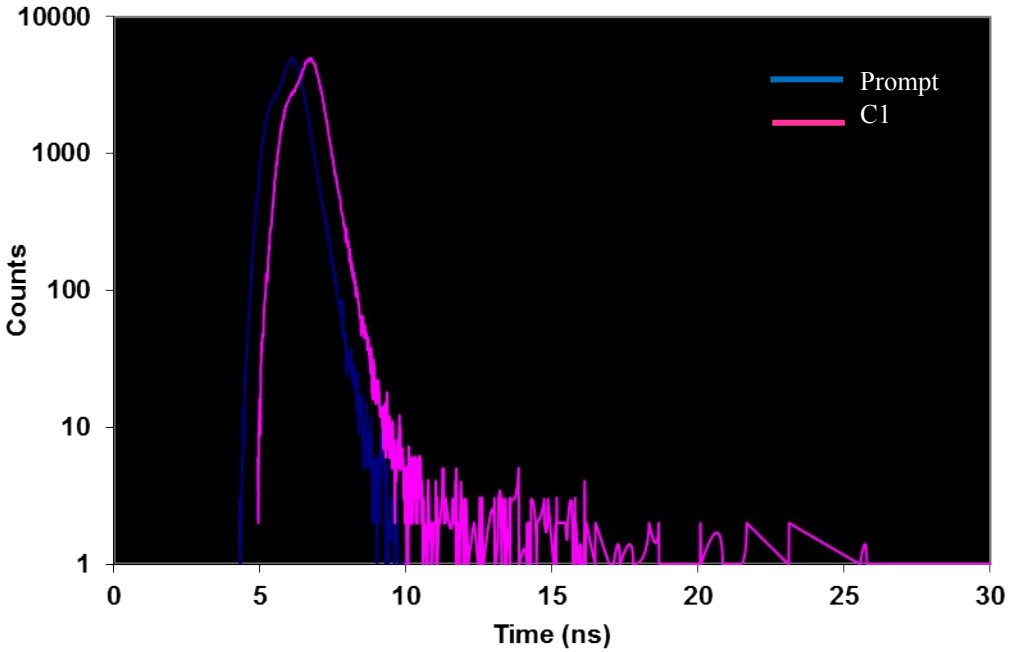

Fig. S3 Fluorescence lifetime decay profiles of **C1** in H_2O: DMSO (1:1, v/v). IRF = instrument response function. λ_{ex} = 635 nm and emission spectra are recorded at 686 nm with 32 slit width.

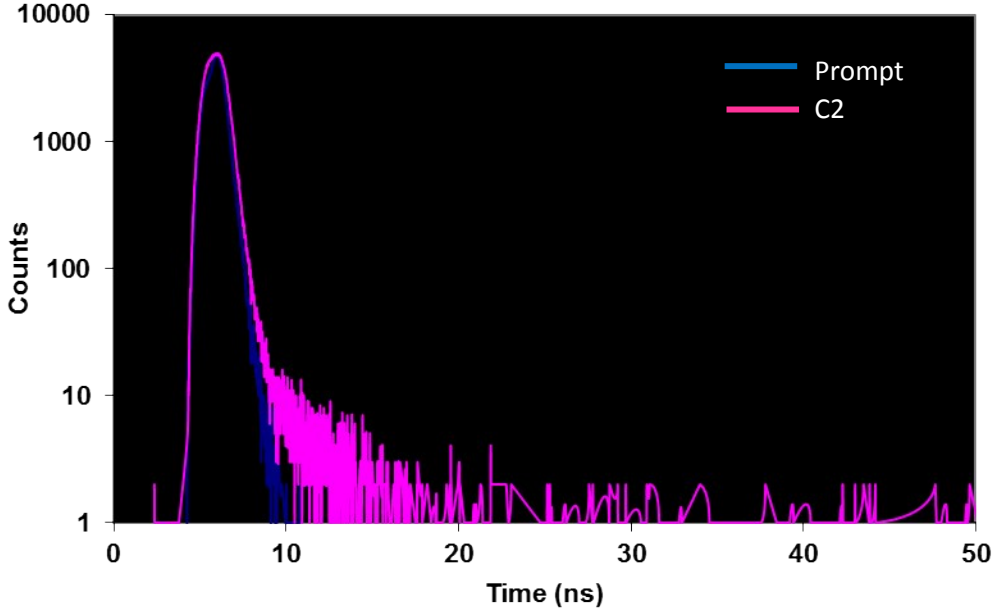

Fig. S4 Fluorescence lifetime decay profiles of **C2** in H_2O: DMSO (1:1, v/v). IRF = instrument response function. λ_{ex} = 485 nm and emission spectra are recorded at 511 nm with 32 slit width.

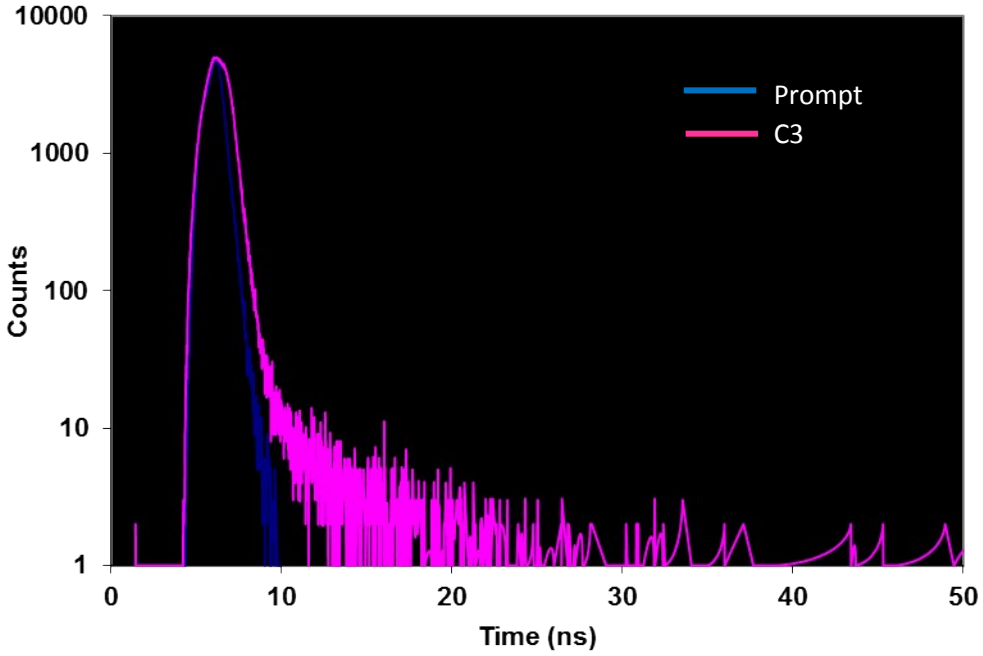

Fig. S5 Fluorescence lifetime decay profiles of **C3** in H_2O: DMSO (1:1, v/v). IRF = instrument response function. λ_{ex} = 485 nm and emission spectra are recorded at 557 nm with 32 slit width.

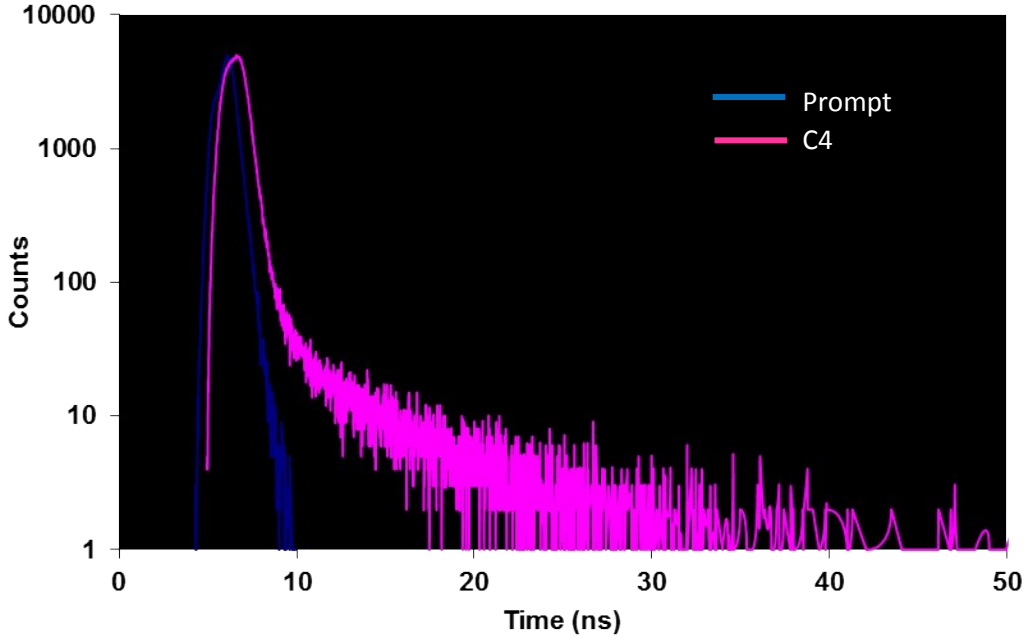

Fig. S6 Fluorescence lifetime decay profiles of **C4** in H_2O: DMSO (1:1, v/v). IRF = instrument response function. λ_{ex} = 485 nm and emission spectra are recorded at 616 nm with 32 slit width.

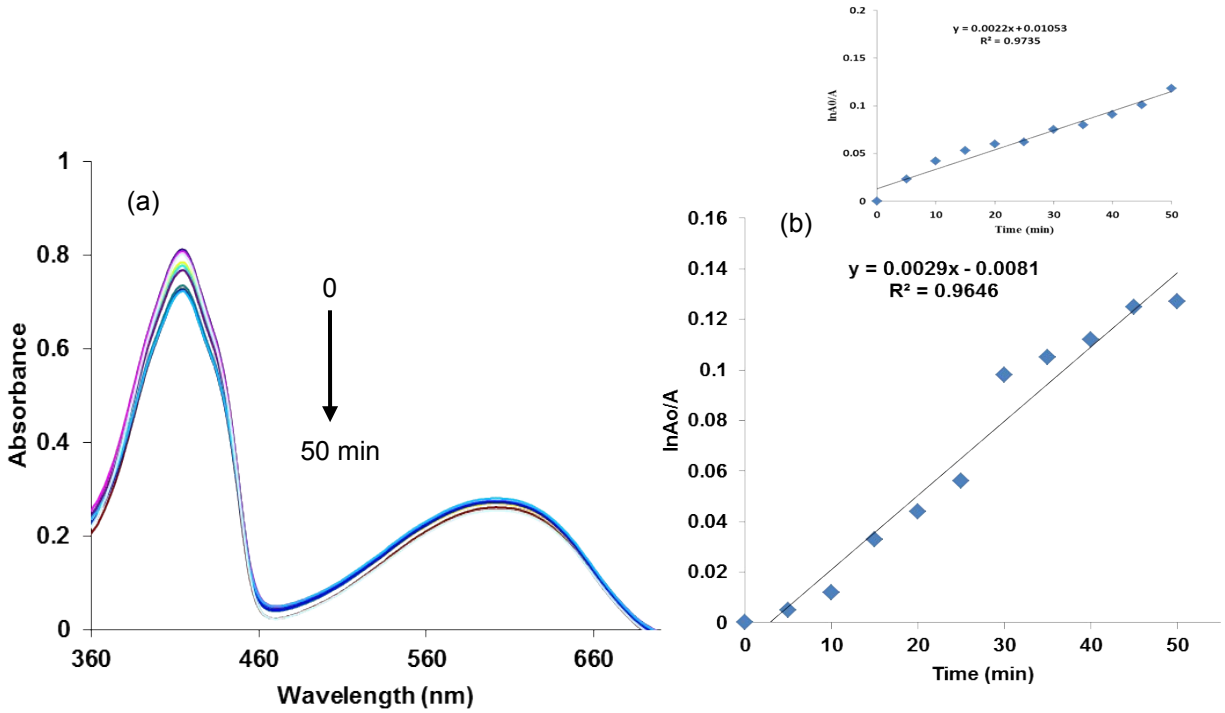

Fig. S7 (a) Decrease in absorption maxima of DPBF (50μM) at 418 nm in DMSO under illumination in the presence of 5μM **C1** for 50 min after the solution was saturated with air oxygen. (b) Semilogarithmic plots for the absorption decays of DPBF (50μM) (lnA_0/A) versus time at the same experimental conditions. inset: shows semilogarithmic plots for reference dye methylene blue under same conditions.

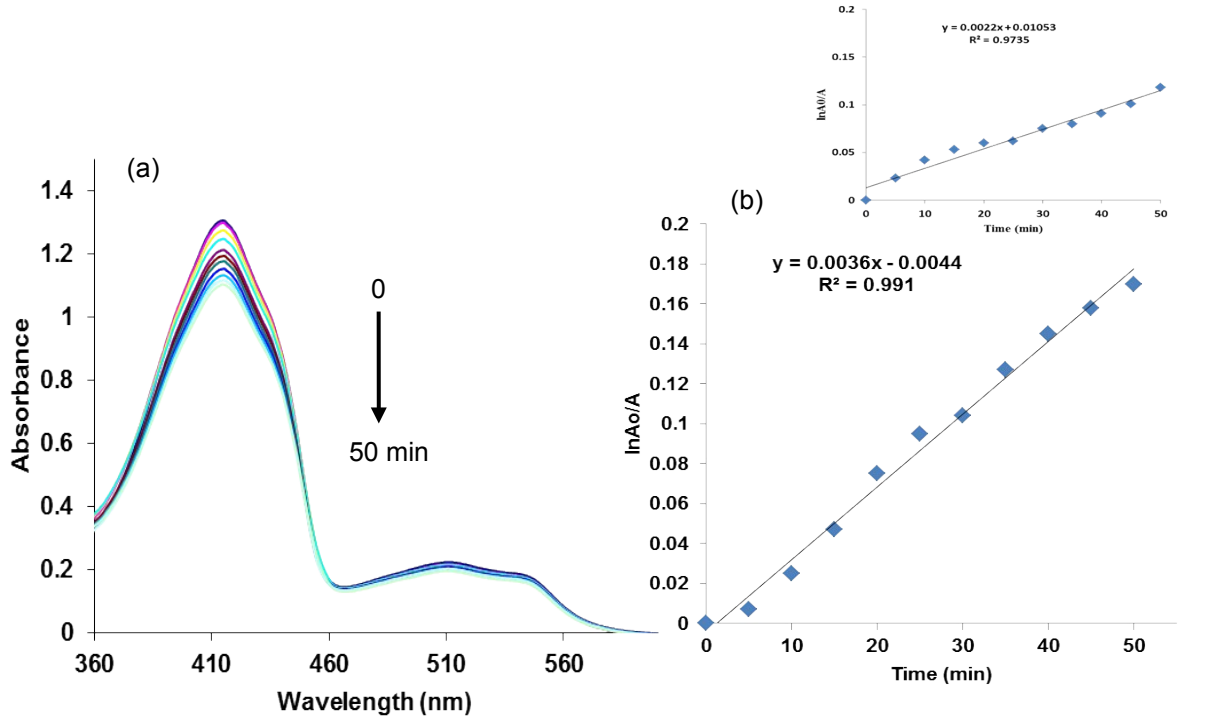

Fig. S8 (a) Decrease in absorption maxima of DPBF (50μM) at 418 nm in DMSO under illumination in the presence of 5μM **C4** for 50 min after the solution was saturated with an air oxygen. (b) Semilogarithmic plots for the absorption decays of DPBF (50μM) (lnA0/A) versus time at the same experimental conditions. inset: shows semilogarithmic plots for reference dye methylene blue under same conditions.

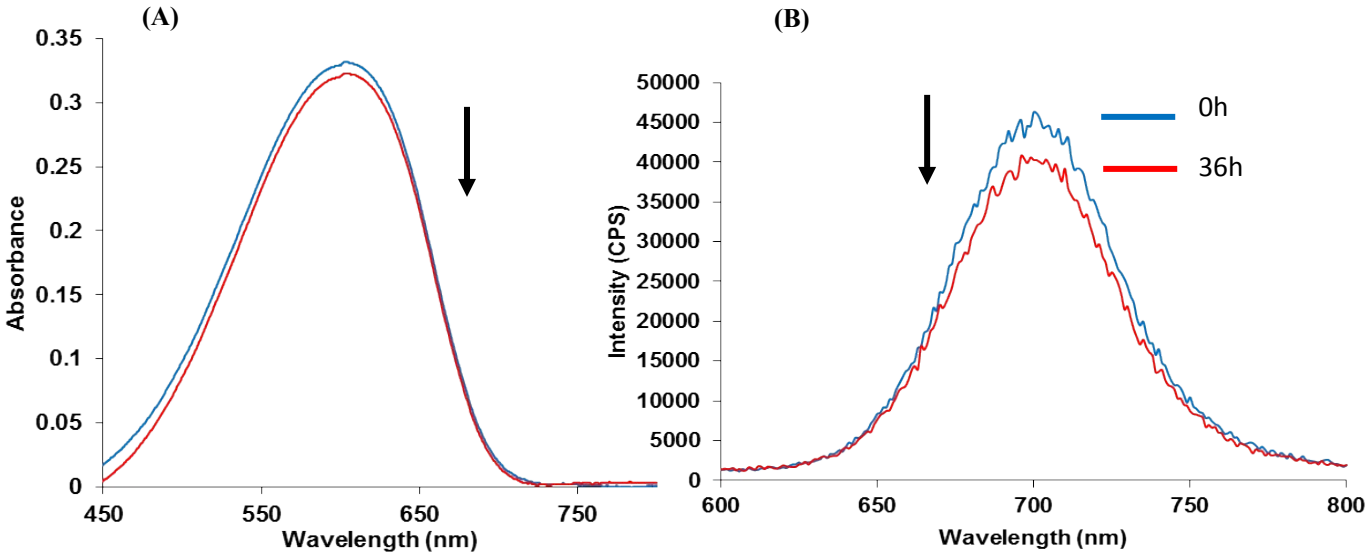

Fig. S9 (A) UV-vis and (B) fluorescence spectra of derivative **C1** after irradiation of 36h.

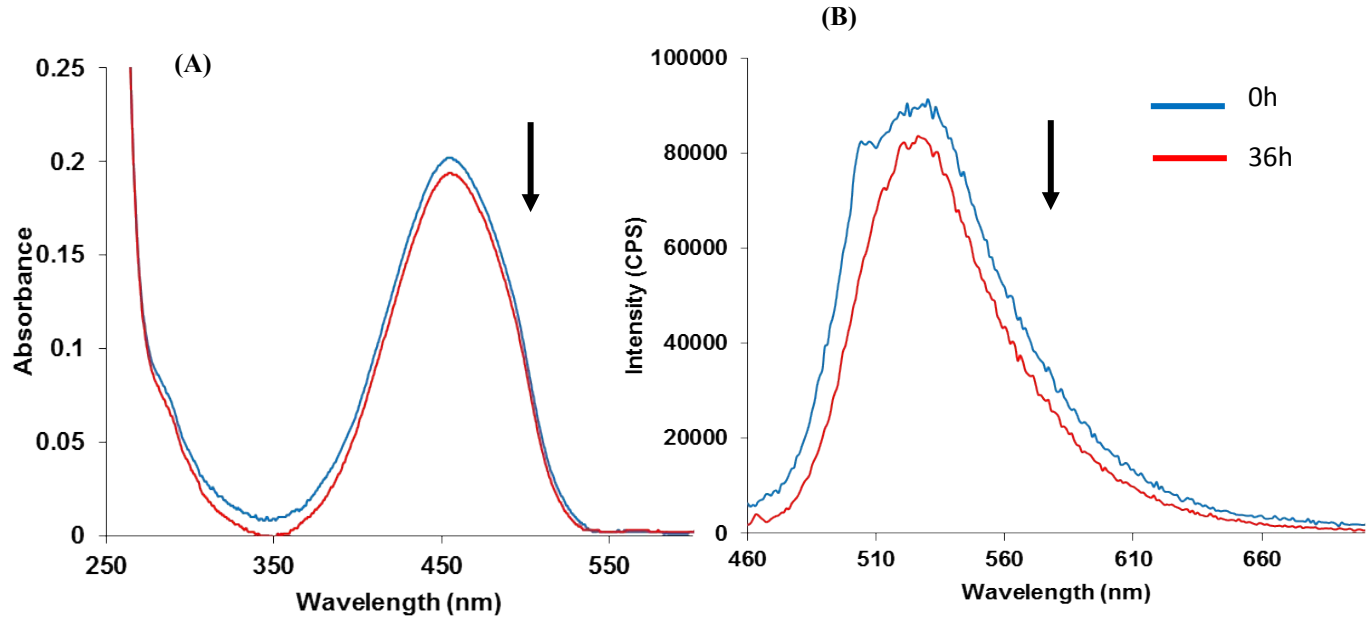

Fig. S10 (A) UV-vis and (B) fluorescence spectra of derivative **C2** after irradiation of 36h.

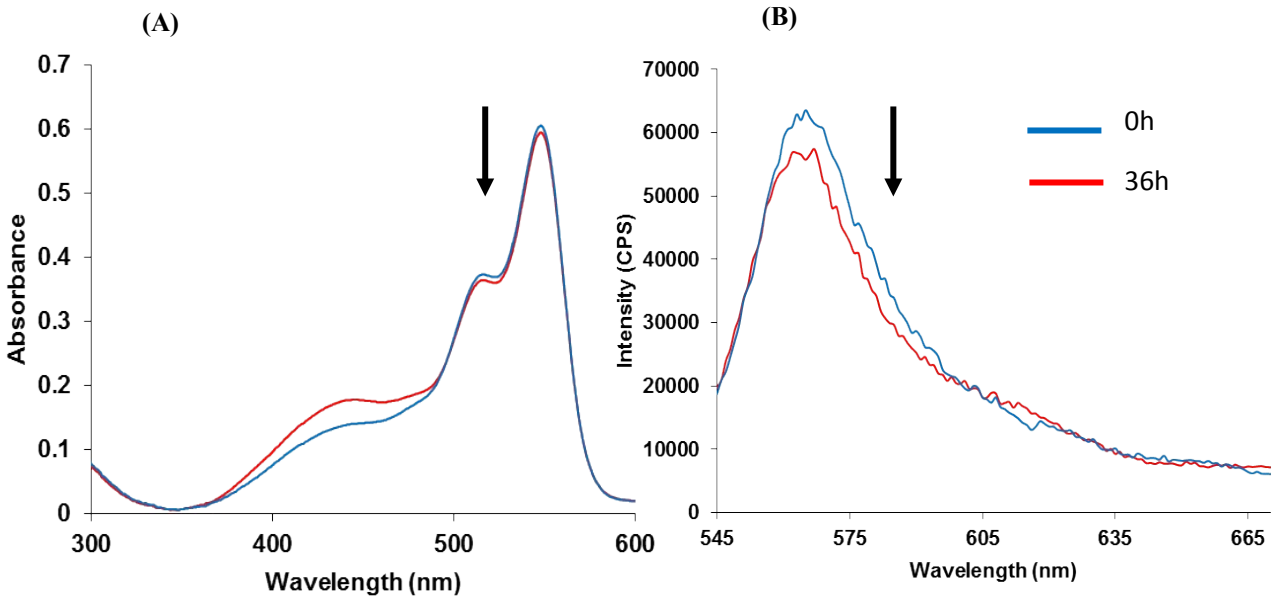

Fig. S11 (A) UV-vis and (B) fluorescence spectra of derivative **C3** after irradiation of 36h.

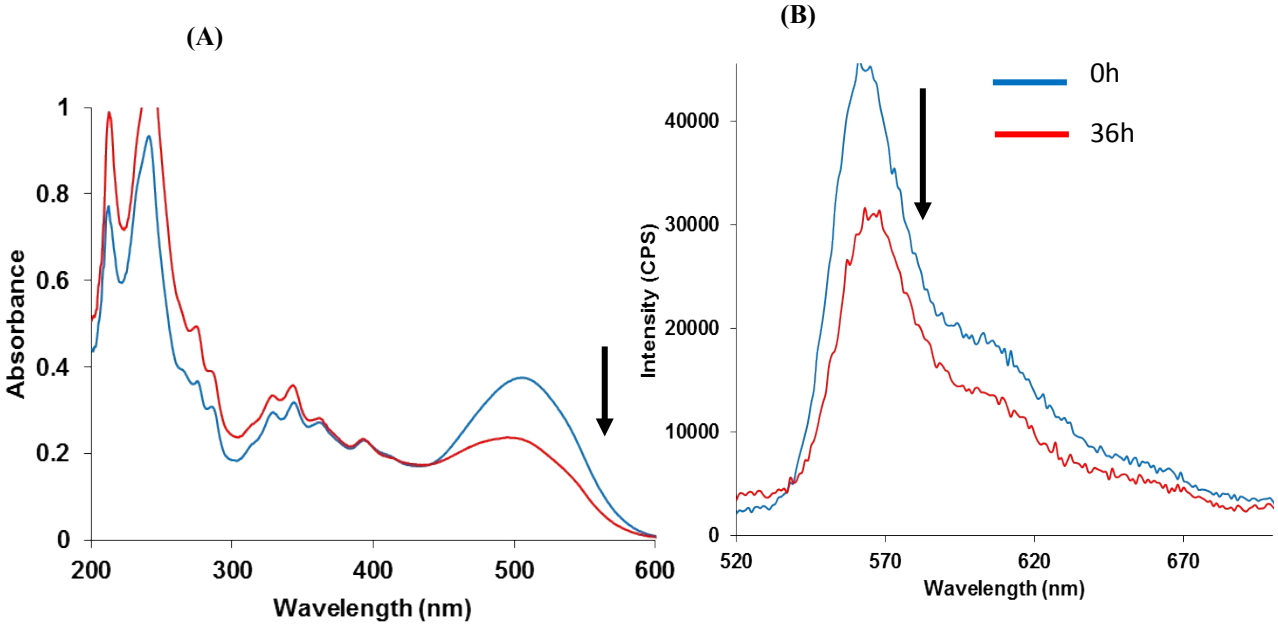

Fig. S12 (A) Uv-vis and (B) fluorescence spectra of derivative **C1** after irradiation of 36h.

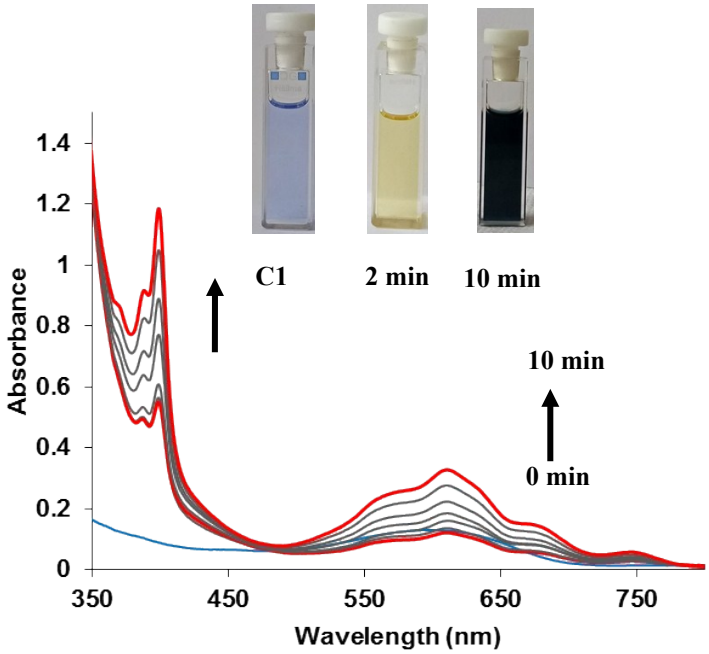

Fig. S13 Absorption spectral changes of derivative **C1** (0.02 mM) in presence of MV^{2+} (0.2 mM) and TEOA (50 mM) in DMSO under room light and inert atmosphere. inset: Photograph of solution before and after 10 min.

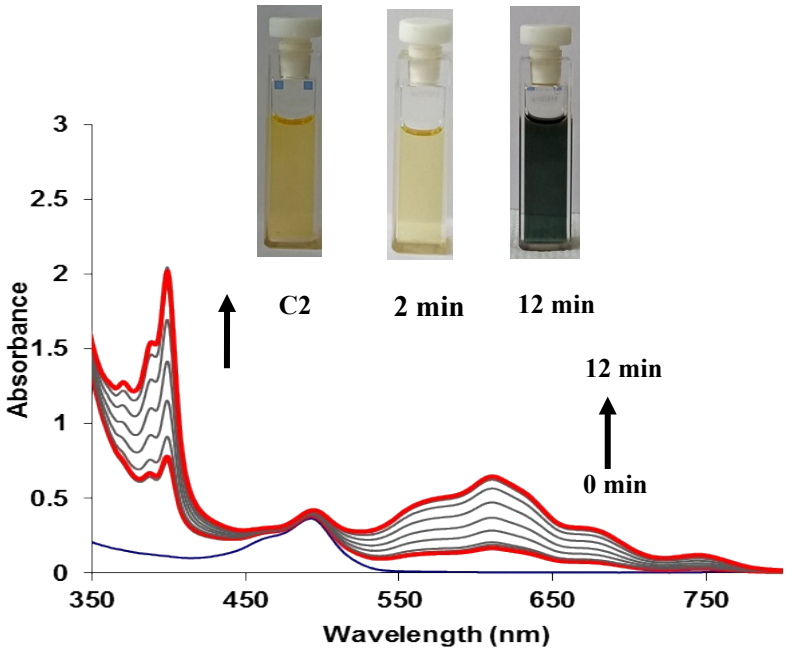

Fig. S14 Absorption spectral changes of derivative **C2** (0.02 mM) in presence of MV^{2+} (0.2 mM) and TEOA (50 mM) in DMSO under room light and inert atmosphere. inset: Photograph of solution before and after 12 min.

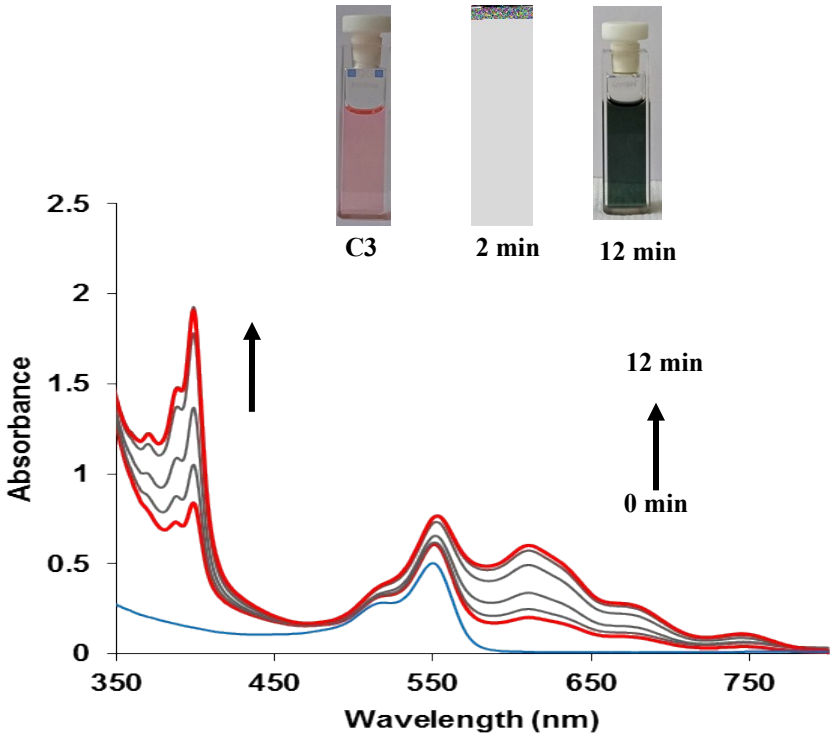

Fig. S15 Absorption spectral changes of derivative **C3** (0.02 mM) in presence of MV^{2+} (0.2 mM) and TEOA (50 mM) in DMSO under room light and inert atmosphere. inset: Photograph of solution before and after 12 min.

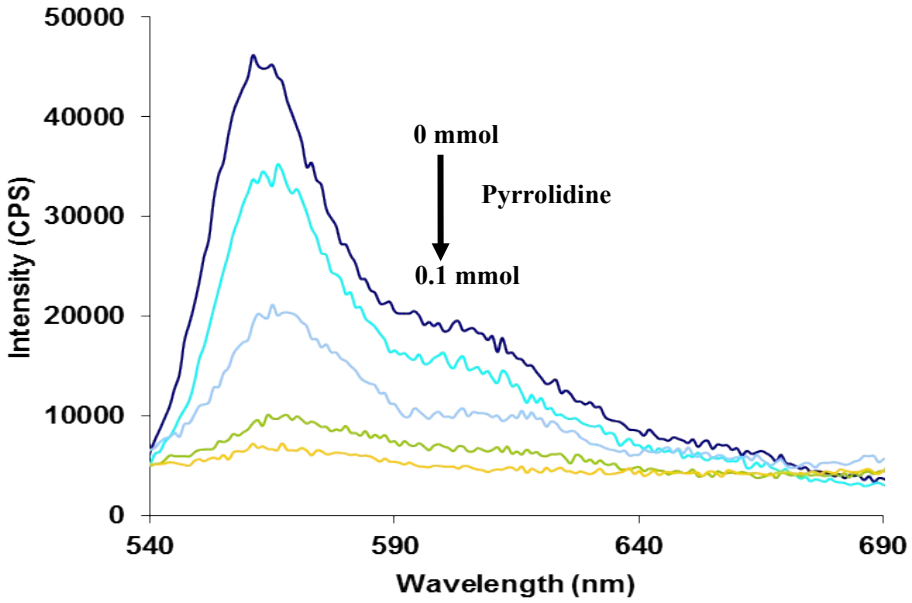

Fig. S16 Fluorescence spectra of derivative **C4** (5µM) upon addition of pyrrolidine (0.1 mmol) in DMSO:Water (1:1).

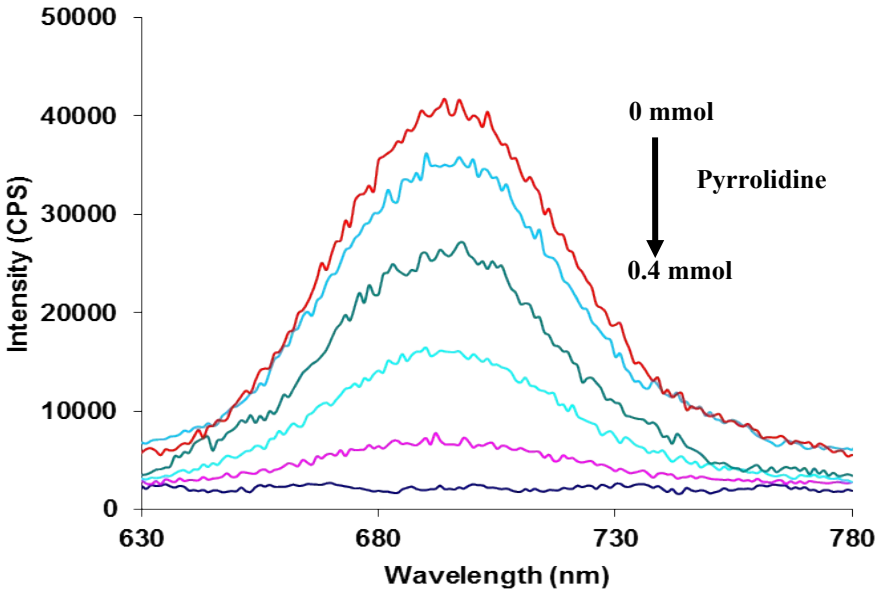

Fig. S17 Fluorescence spectra of derivative **C1** (5µM) upon addition of pyrrolidine (0.4 mmol) in DMSO:Water (1:1).

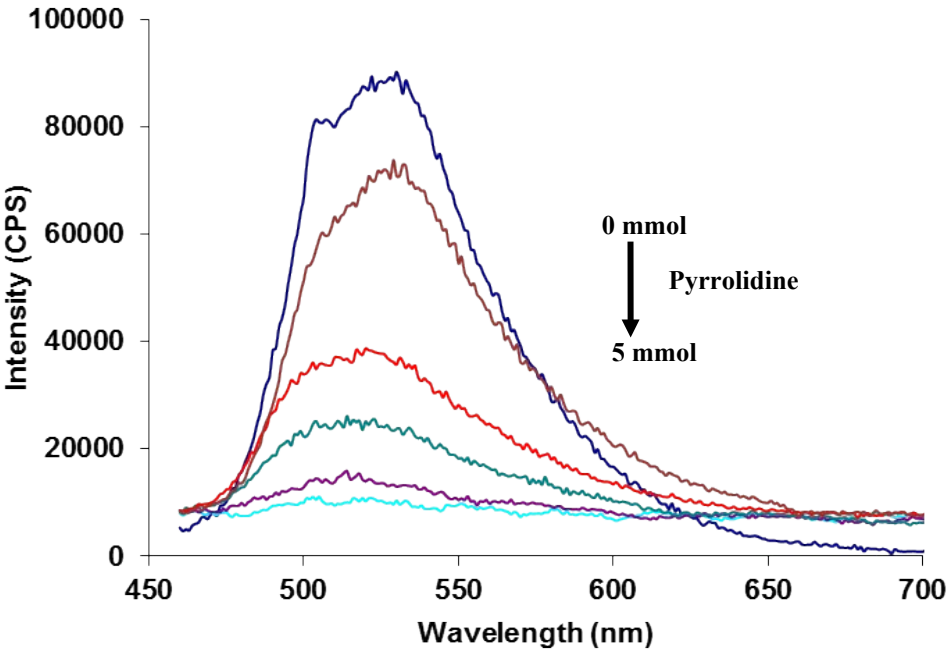

Fig. S18 Fluorescence spectra of derivative **C2** (5µM) upon addition of pyrrolidine (5 mmol) in DMSO:Water (1:1).

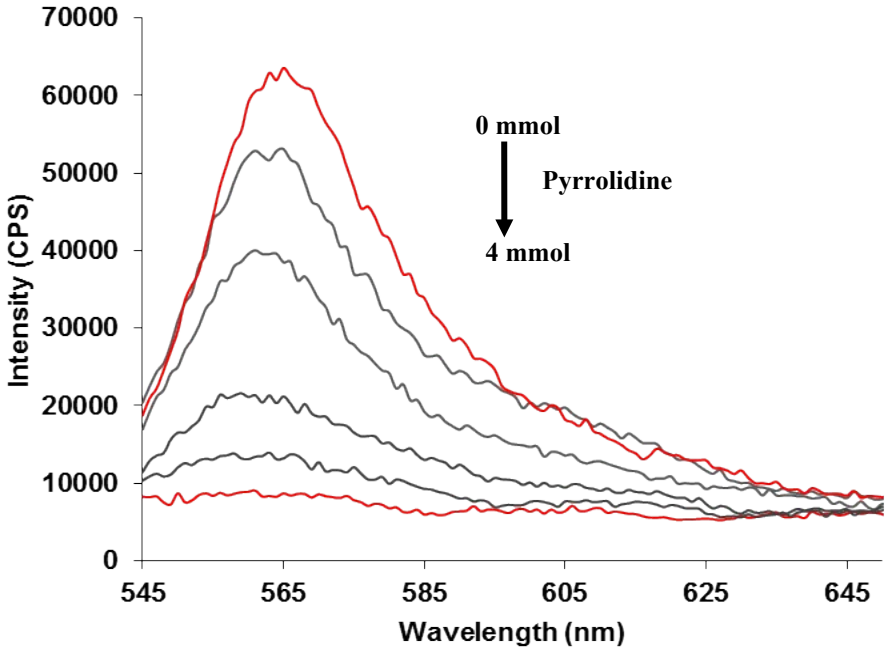

Fig. S19 Fluorescence spectra of derivative **C3** (5µM) upon addition of pyrrolidine (4 mmol) in DMSO:Water (1:1).

Fig. S20 Oxidative amidation of nitrobenzaldehyde in presence of solar light using **C4** as photosensitizer under optimized conditions.

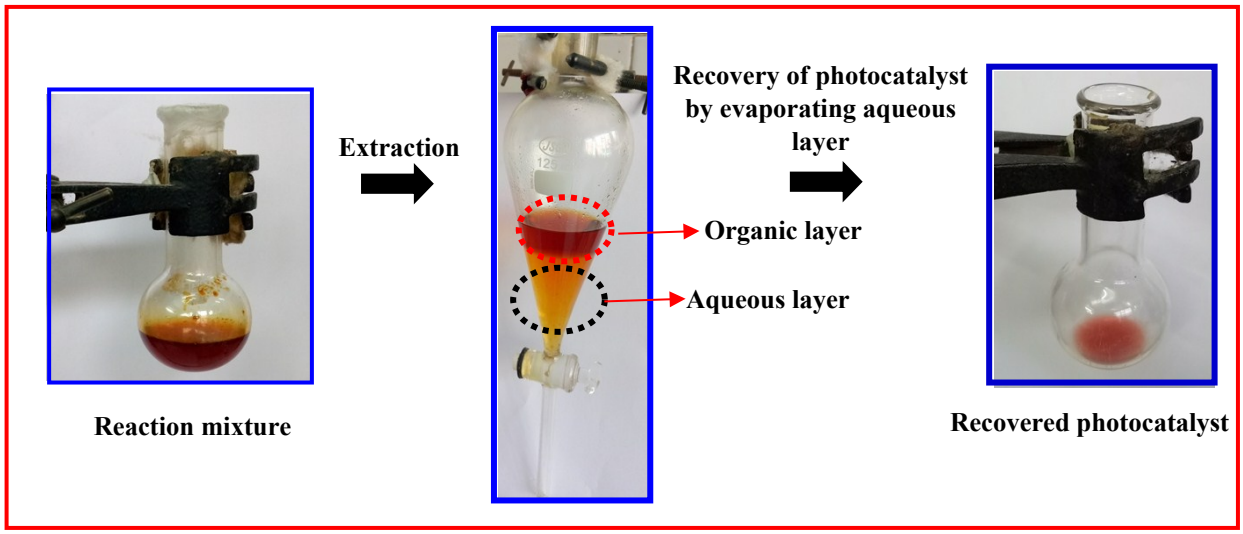

Fig. S21 Images showing the recovery of photocatalyst **C4** by usual work up.

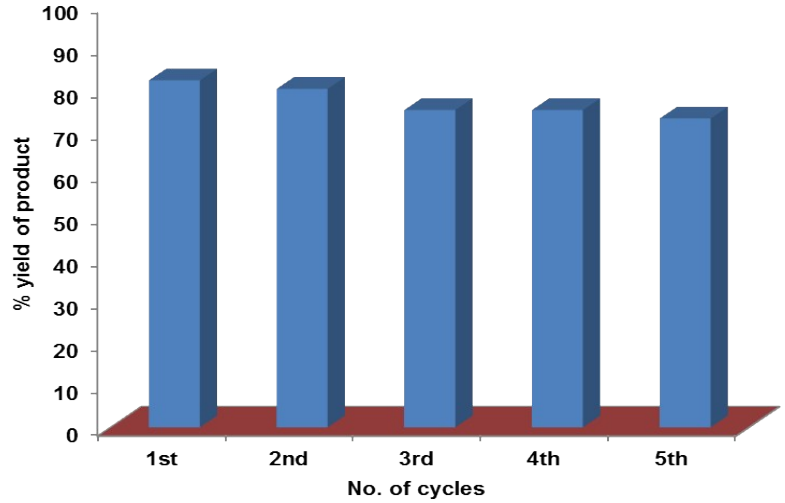

Fig. S22 Reusability of **C4** for carrying out oxidative amidation of aromatic aldehydes under visible light irradiation.

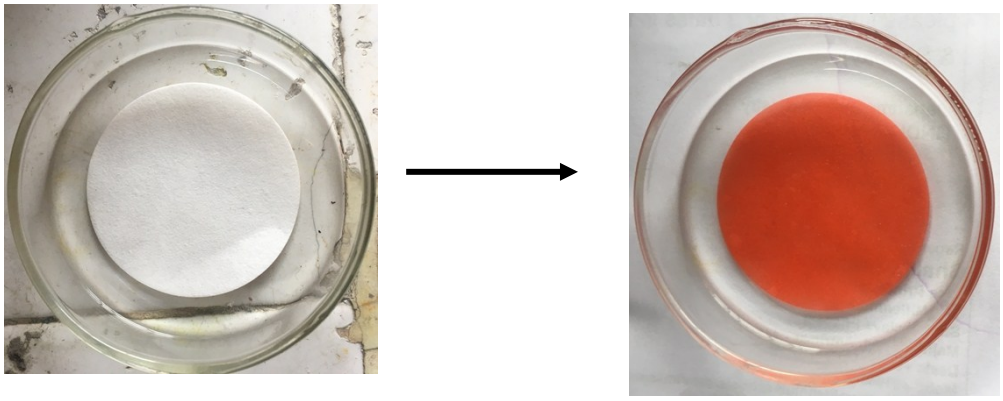

Fig. S23 (a) Whatman filter paper (b) coated with derivative C4 by dip the whatman filter paper into solution of derivative **C4** (5 μM).

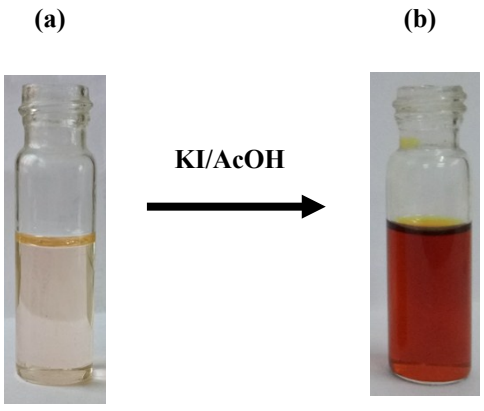

Fig. S24 (a) Reaction mixture of pyrrolidine (0.75 mmol) and **C4** (1 mol%) after irradiation of 8 h**;** (b) After addition of mixture KI (1.0×10^{-1} M), aqueous acetic acid (1.0×10^{-1} M) colour of solution changes to brown.

(4-nitrophenyl)(pyrrolidin-1-yl)methanone[1], 5a

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.27 (d, *J* = 9 Hz, 2H, Ar-H), 7.68 (d, *J* = 9 Hz, 2H, Ar-H), 3.66 (t, *J* = 6 Hz, 2H, CH_2), 3.38 (t, *J* = 6 Hz, 2H, CH_2), 2.01-1.90 (m, 4H, CH_2).

(4-methoxyphenyl)(pyrrolidin-1-yl)methanone[2], 5b

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.51 (d, *J* = 6 Hz, 2H, Ar-H), 6.92 (d, *J* = 6 Hz, 2H, Ar-H), 3.83 (s, 3H, OCH_3), 3.63 (t, *J* = 6 Hz, 2H, CH_2), 3.48 (t, *J* = 9 Hz, 2H, CH_2),1.94-1.86 (m, 4H, CH_2).

Phenyl(pyrrolidin-1-yl)methanone[1], 5c

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.51-7.50 (m, 2H, Ar-H), 7.40-7.38 (m, 3H, Ar-H), 3.64 (t, *J* = 7.5 Hz, 2H, CH_2), 3.42 (t, *J* = 7.5 Hz, 2H, CH_2), 1.98-1.93 (m, 2H, CH_2), 1.89-1.84 (m, 2H, CH_2).

(4-cyanophenyl)(pyrrolidin-1-yl)methanone[1], 5d

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.68 (d, *J* = 10 Hz, 2H, Ar-H), 7.59 (d, *J* = 10 Hz, 2H, Ar-H), 3.62 (t, *J* = 7.5 Hz, 2H, CH_2), 3.35 (t, *J* = 7.5 Hz, 2H, CH_2), 1.98-1.93 (m, 2H, CH_2), 1.91-1.86 (m, 2H, CH_2).

(4-chlorophenyl)(pyrrolidin-1-yl)methanone[1], 5e

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.43 (d, *J* = 6 Hz, 2H, Ar-H), 7.33 (d, *J* = 6 Hz, 2H, Ar-H), 3.59 (t, *J* = 6 Hz, 2H, CH_2), 3.37 (t, *J* = 6Hz, 2H, CH_2), 1.94-1.82 (m, 4H, CH_2).

(4-nitrophenyl)(piperidin-1-yl)methanone[3], 7a

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.27 (d, *J* = 8 Hz, 2H, Ar-H), 7.55 (d, *J* = 8 Hz, 2H, Ar-H), 3.73 (bs, 2H, CH_2), 3.28 (bs, 2H, CH_2), 1.79-1.52 (m, 6H, CH_2).

(4-methoxyphenyl)(piperidin-1-yl)methanone[2], 7b

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.37 (d, *J* = 9 Hz, 2H, Ar-H), 6.90 (d, *J* = 9 Hz, 2H, Ar-H), 3.83 (s, 3H, OCH_3), 3.64 (br, 2H, CH_2), 3.44 (br, 2H, CH_2), 1.66-1.58 (m, 6H, CH_2).

Phenyl (piperidin-1-yl)methanone, 7c

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.37 (m, 5H, Ar-H), 3.69 (br, 2H, CH_2), 3.33 (br, 2H, CH_2), 1.66-1.51 (m, 6H, CH_2).

(4-cyanophenyl)(piperidin-1-yl)methanone[1], 7d

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.70 (d, *J* = 6 Hz, 2H, Ar-H), 7.48 (d, *J* = 6 Hz, 2H, Ar-H), 3.71 (br, 2H, CH_2), 3.27 (br, 2H, CH_2), 1.60 (bs, 4H, CH_2), 1.53 (br, 2H, CH_2).

(4-chlorophenyl)(piperidin-1-yl)methanone[2], 7e

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.38-7.32 (m, 4H, Ar-H), 3.69 (bs, 2H, CH_2), 3.33 (bs, 2H, CH_2), 1.68-1.51 (m, 6H, CH_2).

morpholino(4-nitrophenyl)methanone[2], 8a

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.27 (d, *J* = 8 Hz, 2H, Ar-H), 7.57 (d, *J* = 8 Hz, 2H, Ar-H), 3.79-3.37 (m, 8H, CH_2).

morpholino(4-methoxyphenyl)methanone[2], 8b

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.28 (d, *J* = 9 Hz, 2H, Ar-H), 6.82 (d, *J* = 9 Hz, 2H, Ar-H), 3.72 (s, 3H, OCH_3), 3.60 (br, 8H, CH_2).

Derivative C3.

^{1}H NMR (DMSO-d_6, 400 MHz,): δ (ppm) = 10.02 (s, 1H), 8.35 (d, *J* = 6 Hz, 1H), 8.12 (d, *J* = 8 Hz, 2H), 7.83 (d, *J* = 8 Hz, 2H), 7.62-7.50 (m, 2H), 7.45 (d, *J* = 16 Hz, 2H), 6.95 (d, *J* = 8 Hz, 2H), 4.07 (s, 3H), 1.76 (s, 6H), ^{13}C NMR (DMSO-d_6, 125 MHz) δ = 163.69, 154.24, 143.65, 142.33, 134.02, 129.32, 126.46, 123.23, 116.99, 115.11, 109.76, 52.20, 34.97, 26.14; MS (ESI): m/z 278.16 $[M]^+$.

Derivative C4.

^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 9.27 (d, *J* = 16 Hz, 1H), 8.99 (d, *J* = 8 Hz, 1H), 8.74 (d, *J* = 8 Hz, 1H), 8.49-8.38 (m, 5H), 8.30 (d, *J* = 8 Hz, 1H), 8.19-8.14 (m, 1H), 7.98-7.90 (m, 3H), 7.65-7.63 (m, 2H), 4.24 (s, 3H), 1.91 (s, 6H), MS (ESI): m/z 386.48 $[M+1]^+$.

Refrences

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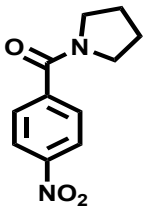
2. K. Ekoue-Kovi and C. Wolf, *Org. Lett*., 2007, **9**, 3429.

3. Y.-C. Hsu, V. C.-C. Wang, K.-C. A. Yeung, C.-Y. Tsai, C.-C. Chang, B.-C. Lin, Y.-T. Chan, C.-P. Hsu, G. P. A. Yap, T. Jurca and T.-G. Ong, *Angew. Chem. Int. Ed*., 2018, **57**, 4622.



5a

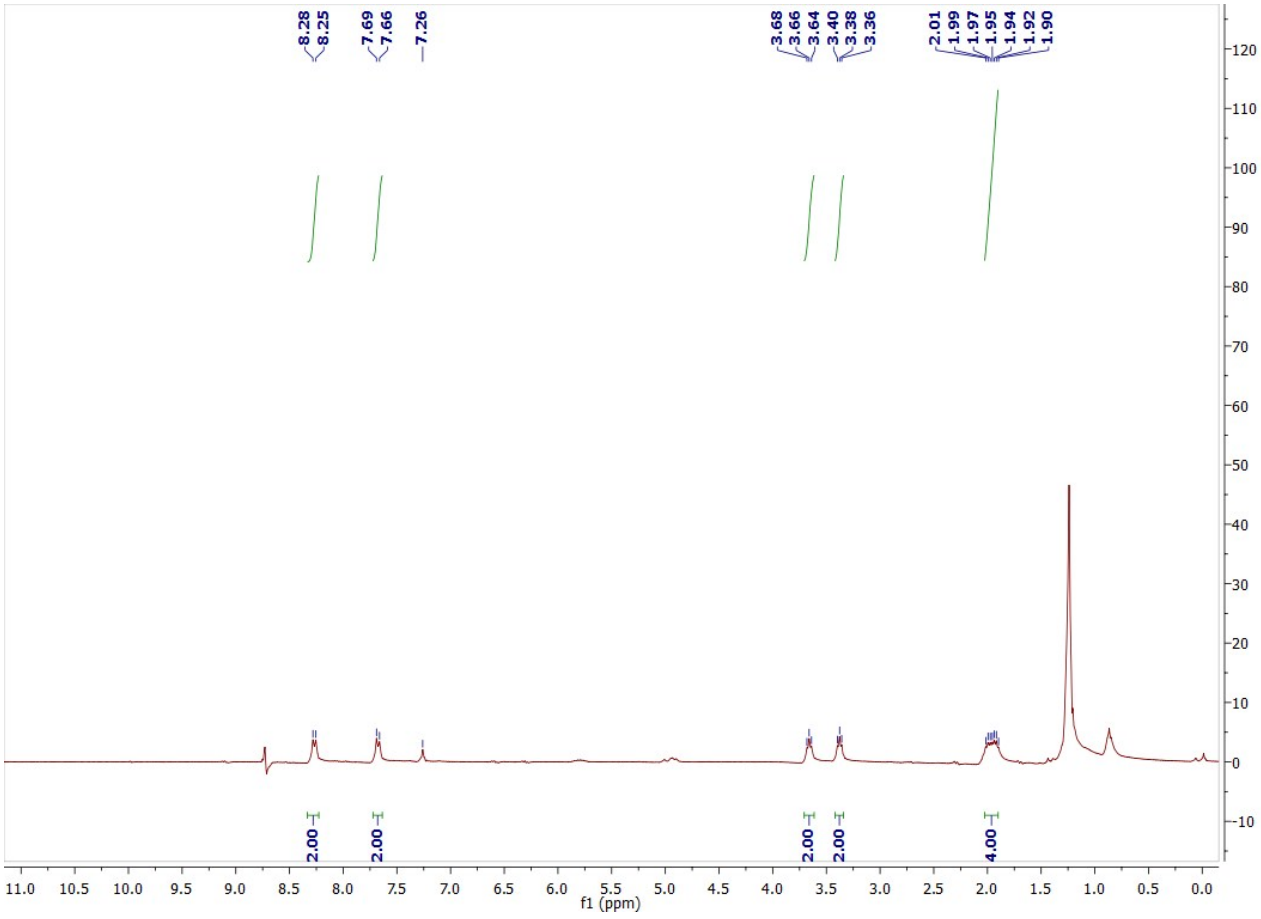
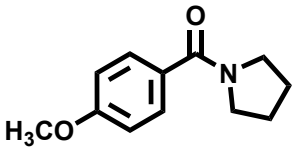


Fig. S25 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **5a**.



5b

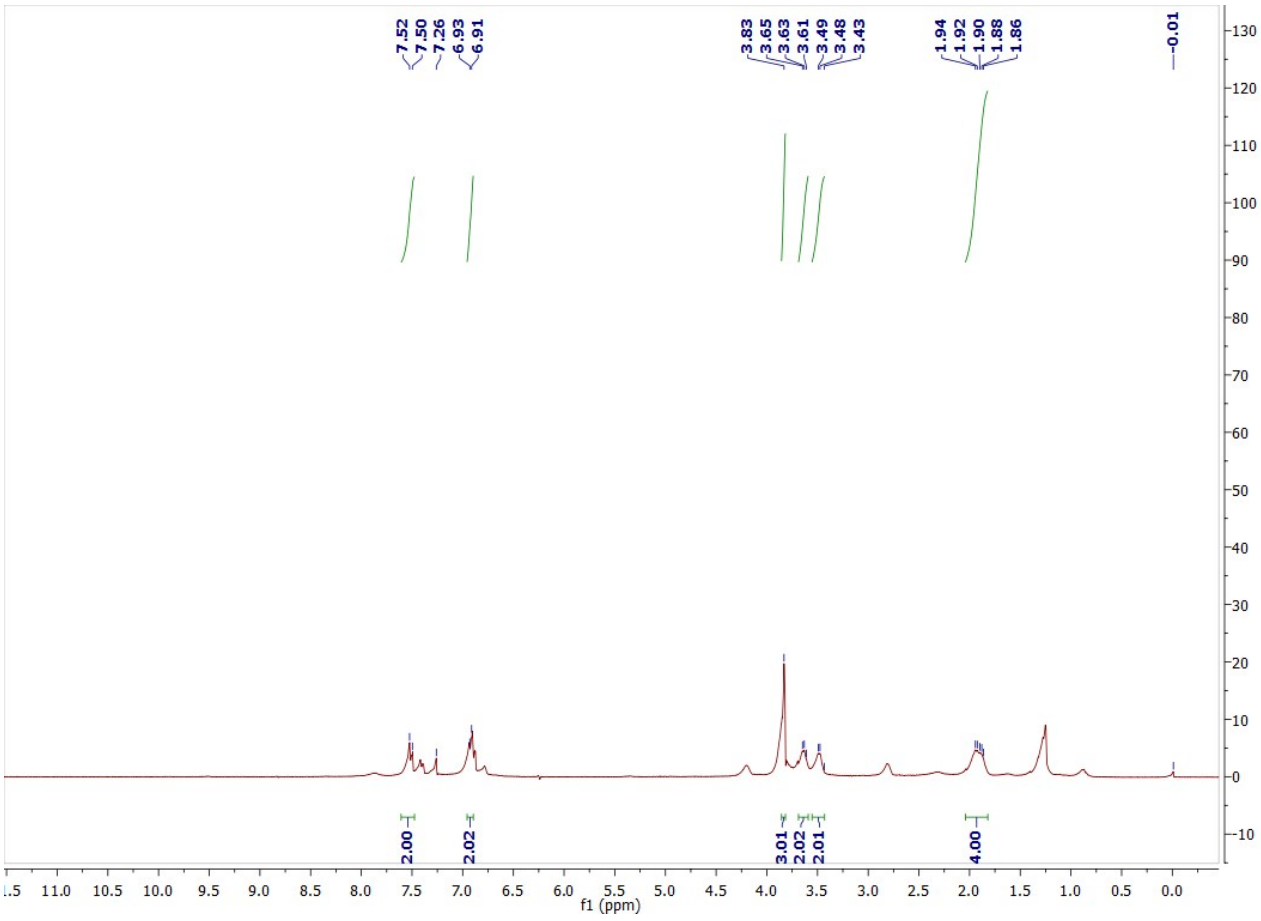
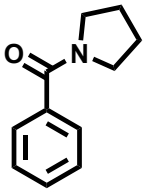


Fig. S26 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **5b**.



5c

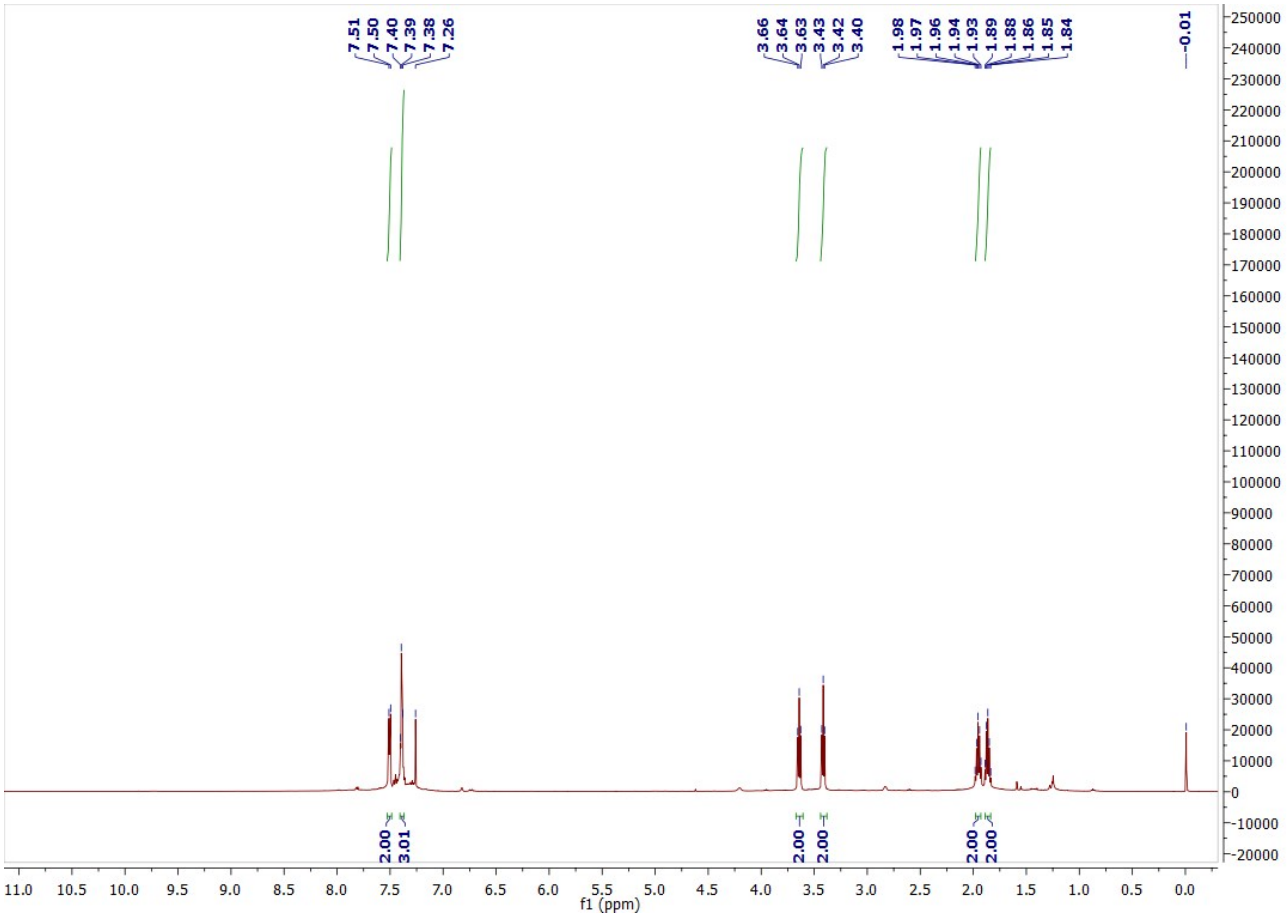
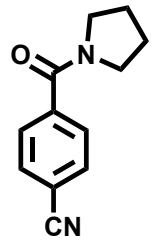


Fig. S27 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5c**.



5d

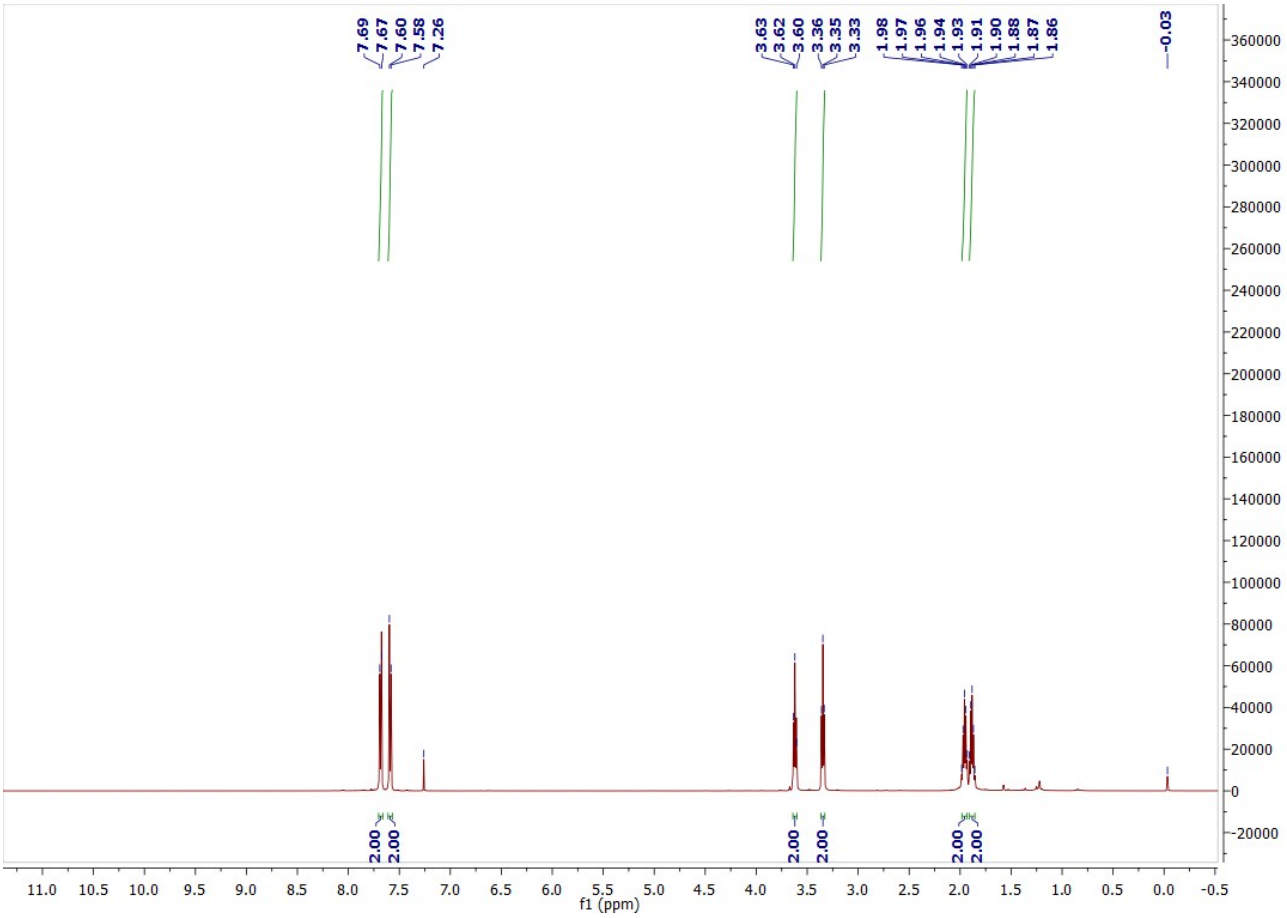
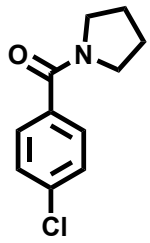


Fig. S28 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5d**.



5e

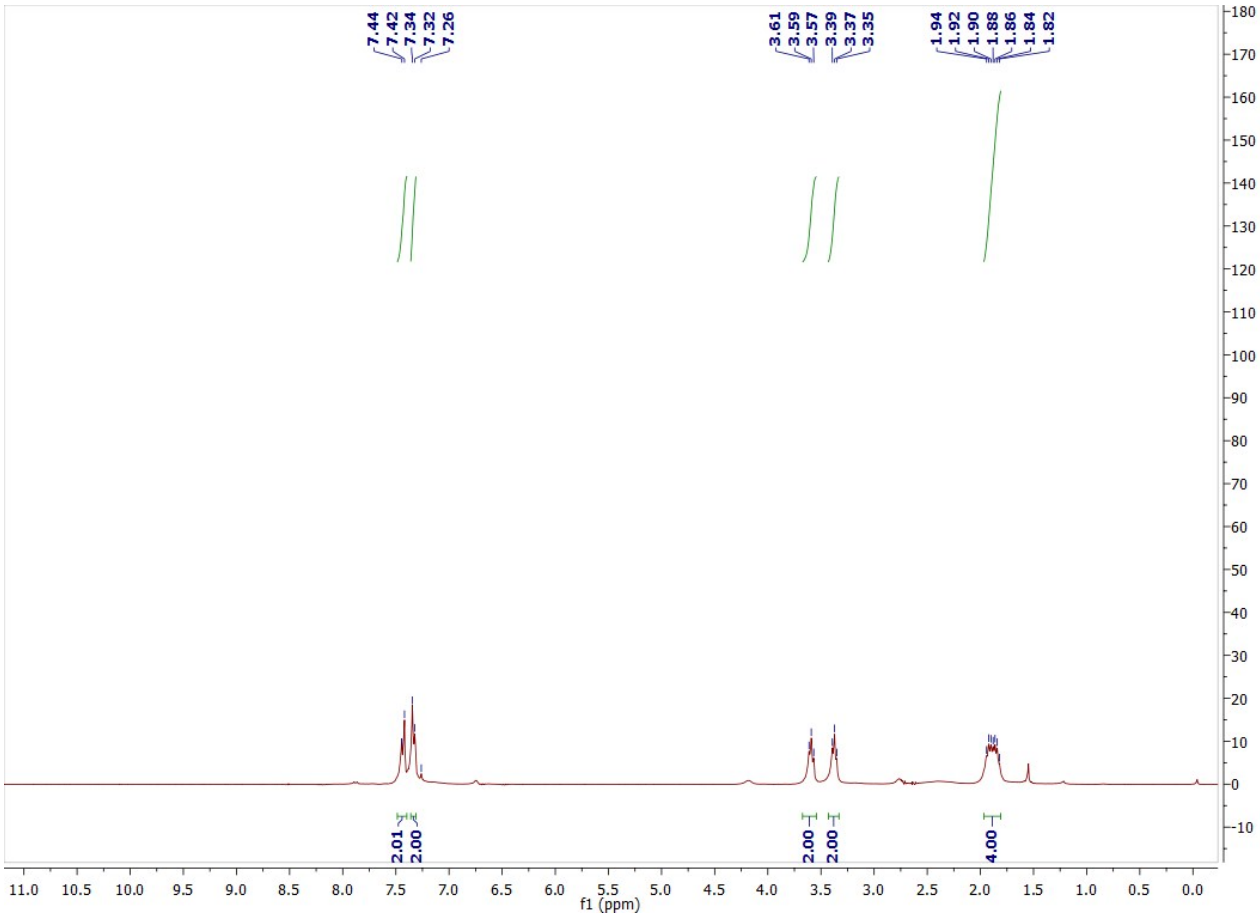


Fig. S29 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **5e**.

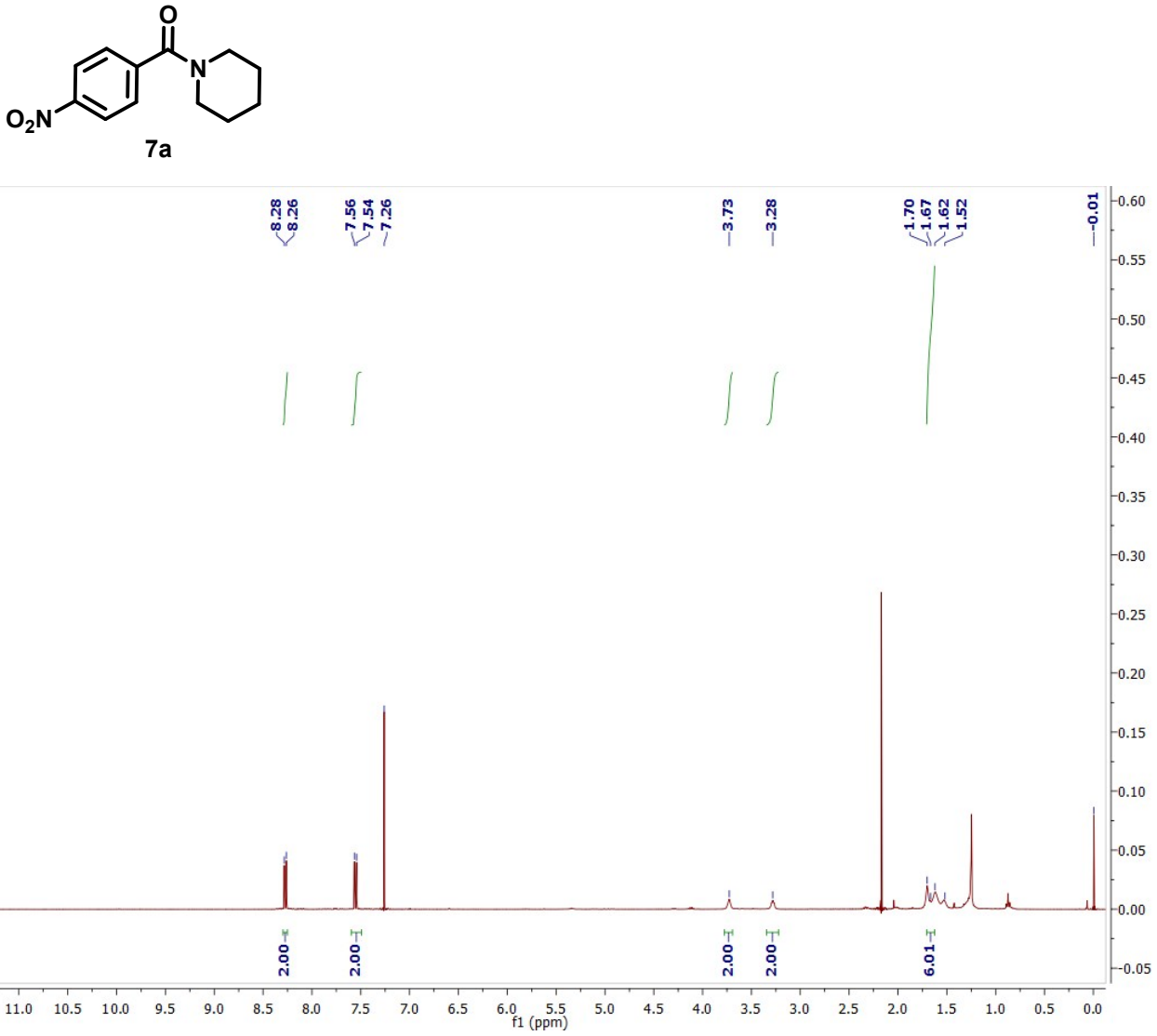
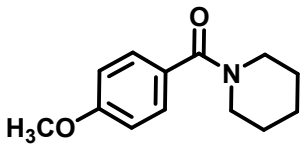


Fig. S30 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7a**.



7b

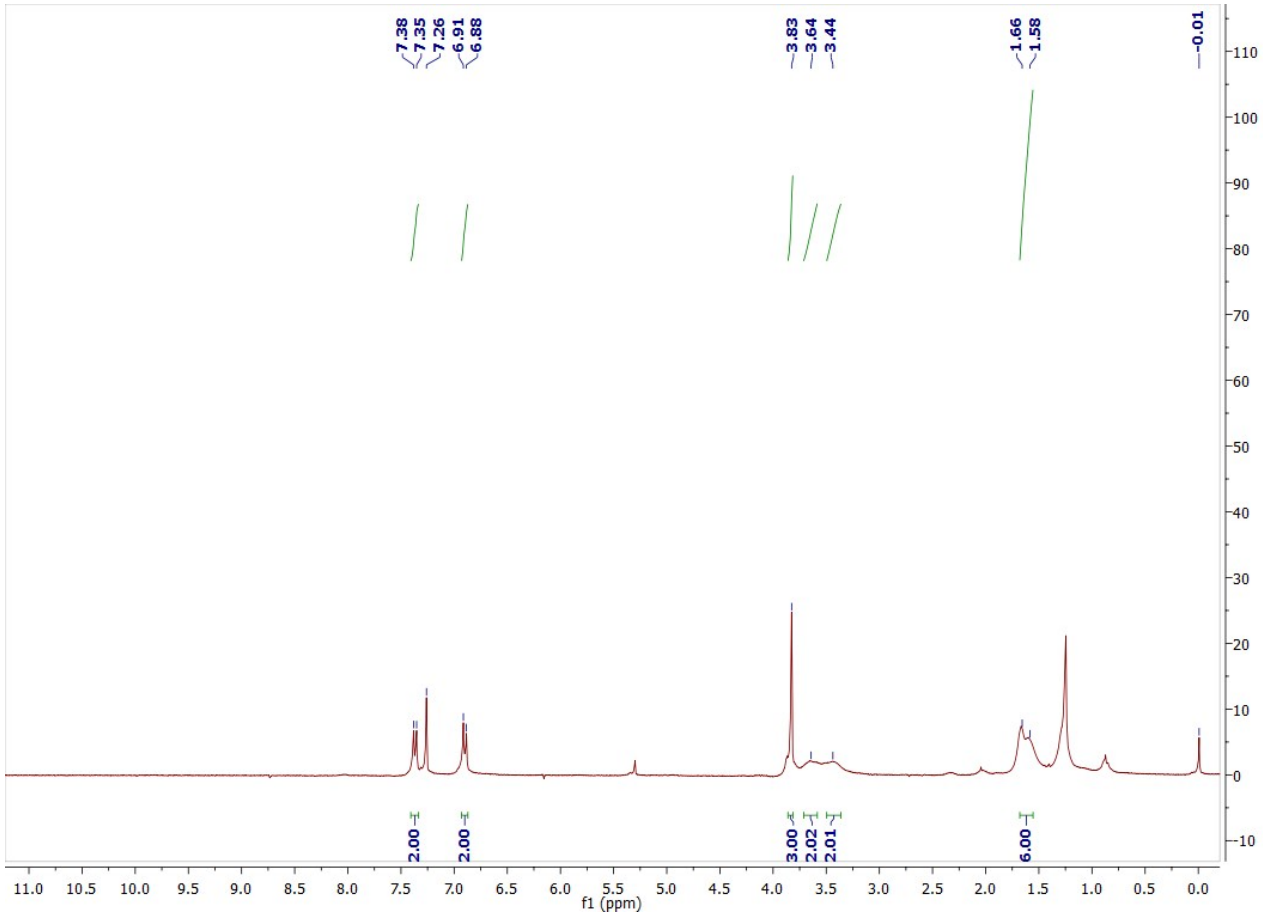
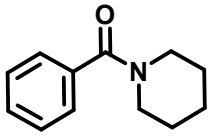


Fig. S31 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7b**.



7c

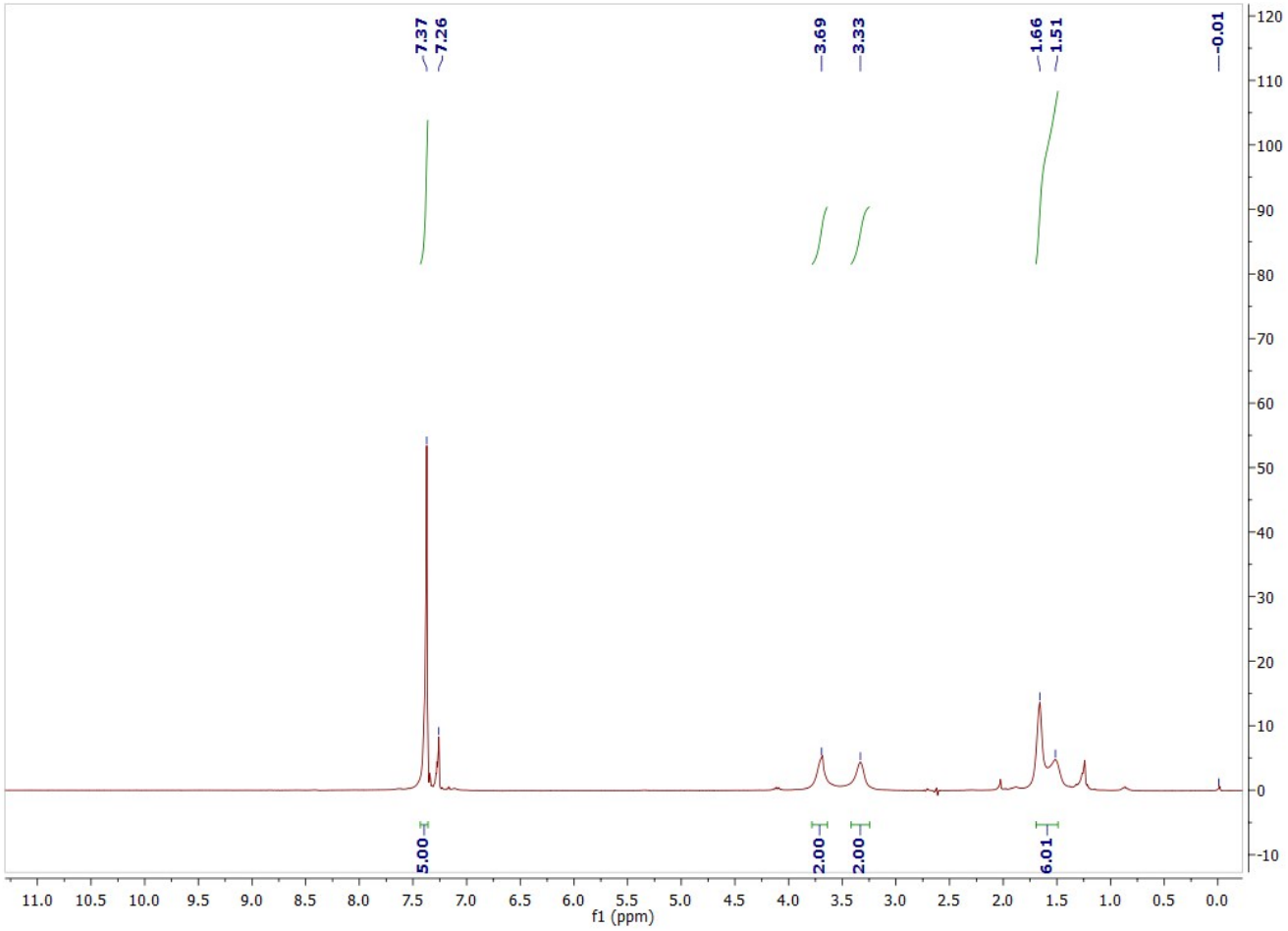
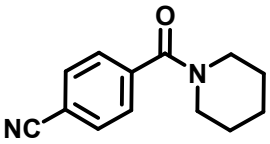


Fig. S32 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7c**.



7d

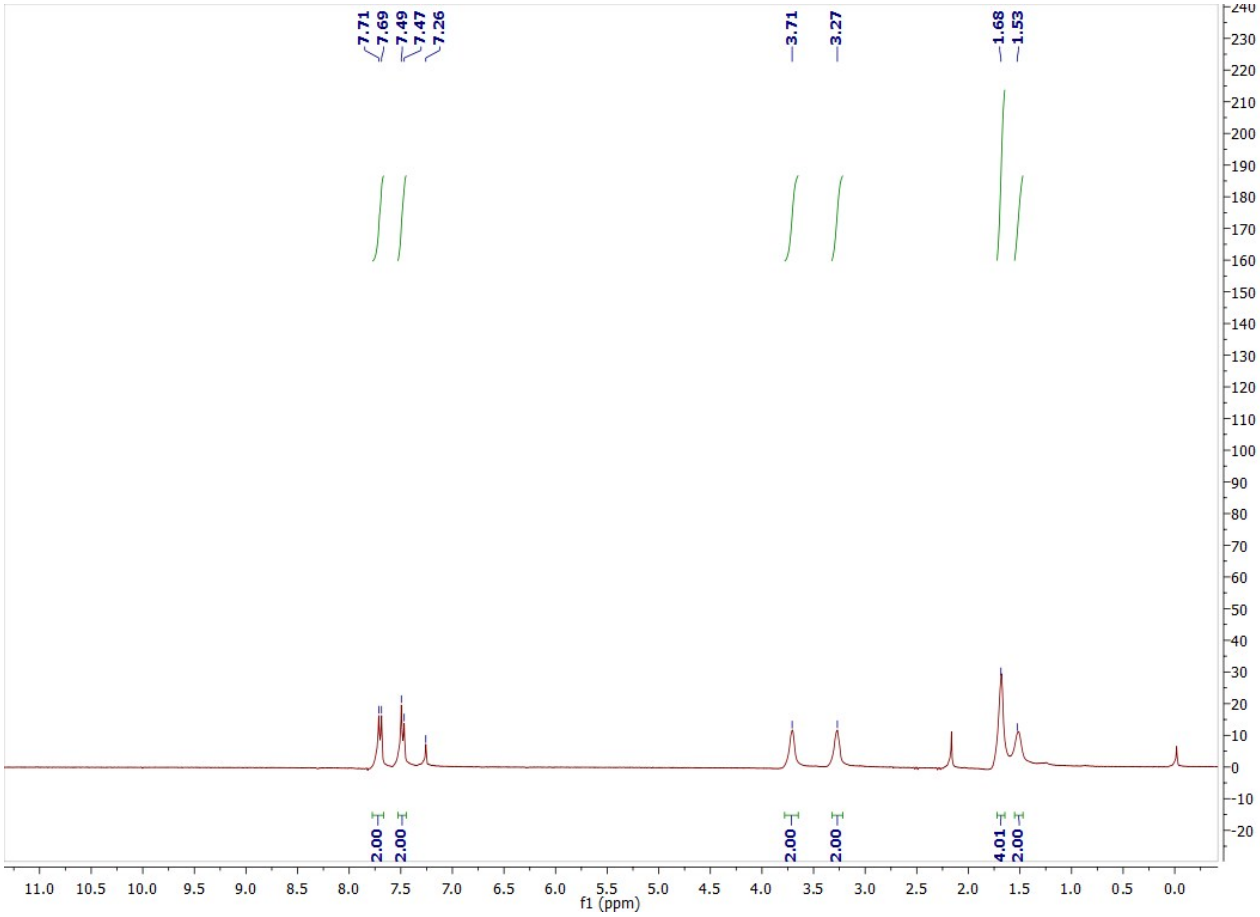
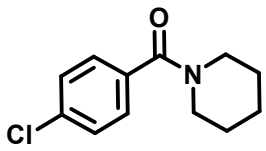


Fig. S33 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7d**.



7e

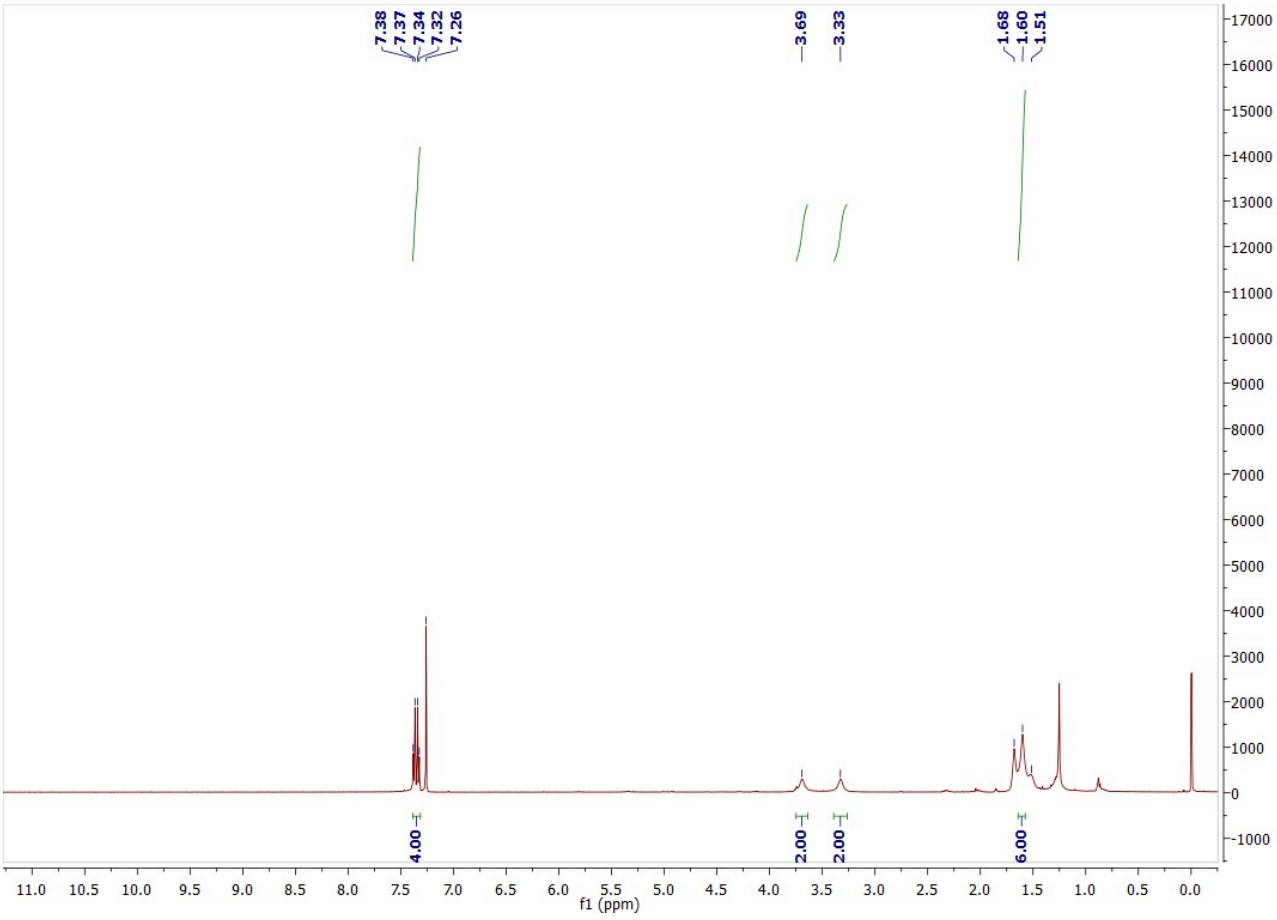
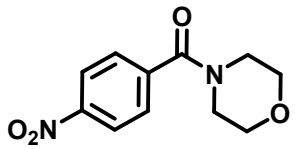


Fig. S34 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7e**.



8a

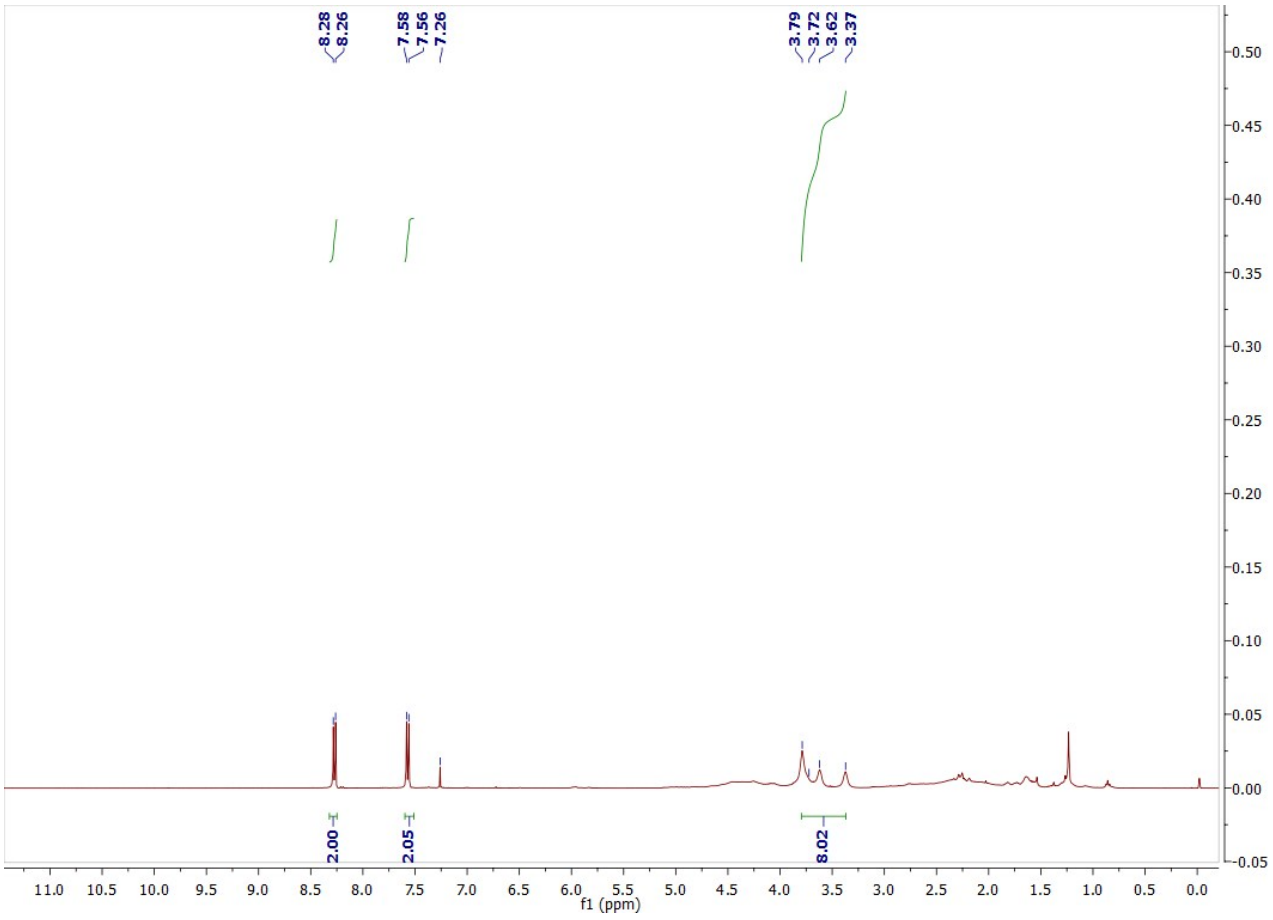
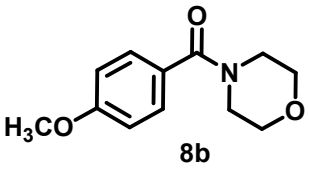


Fig. S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8a**.



8b

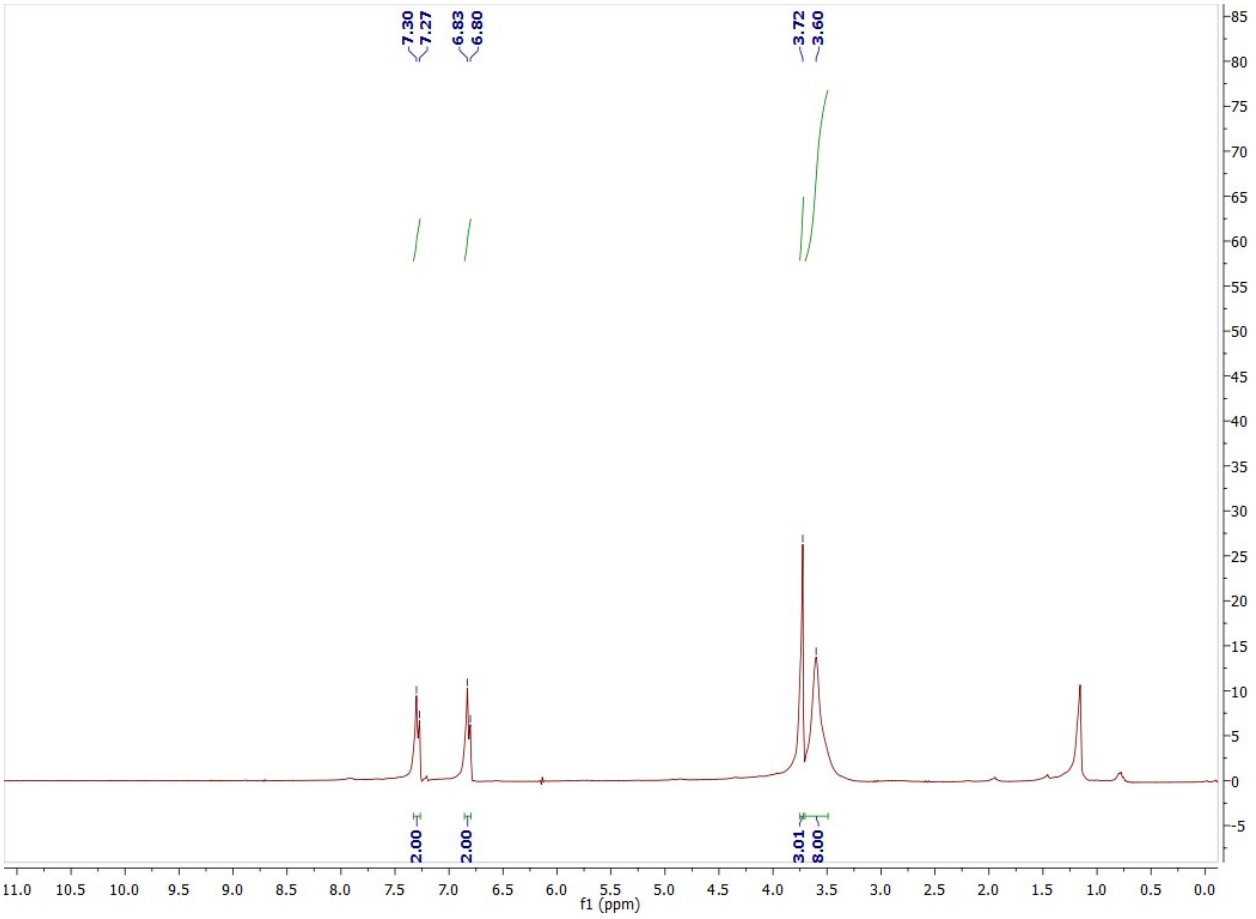
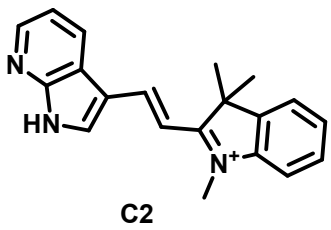


Fig. S36 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **8b**.



C2

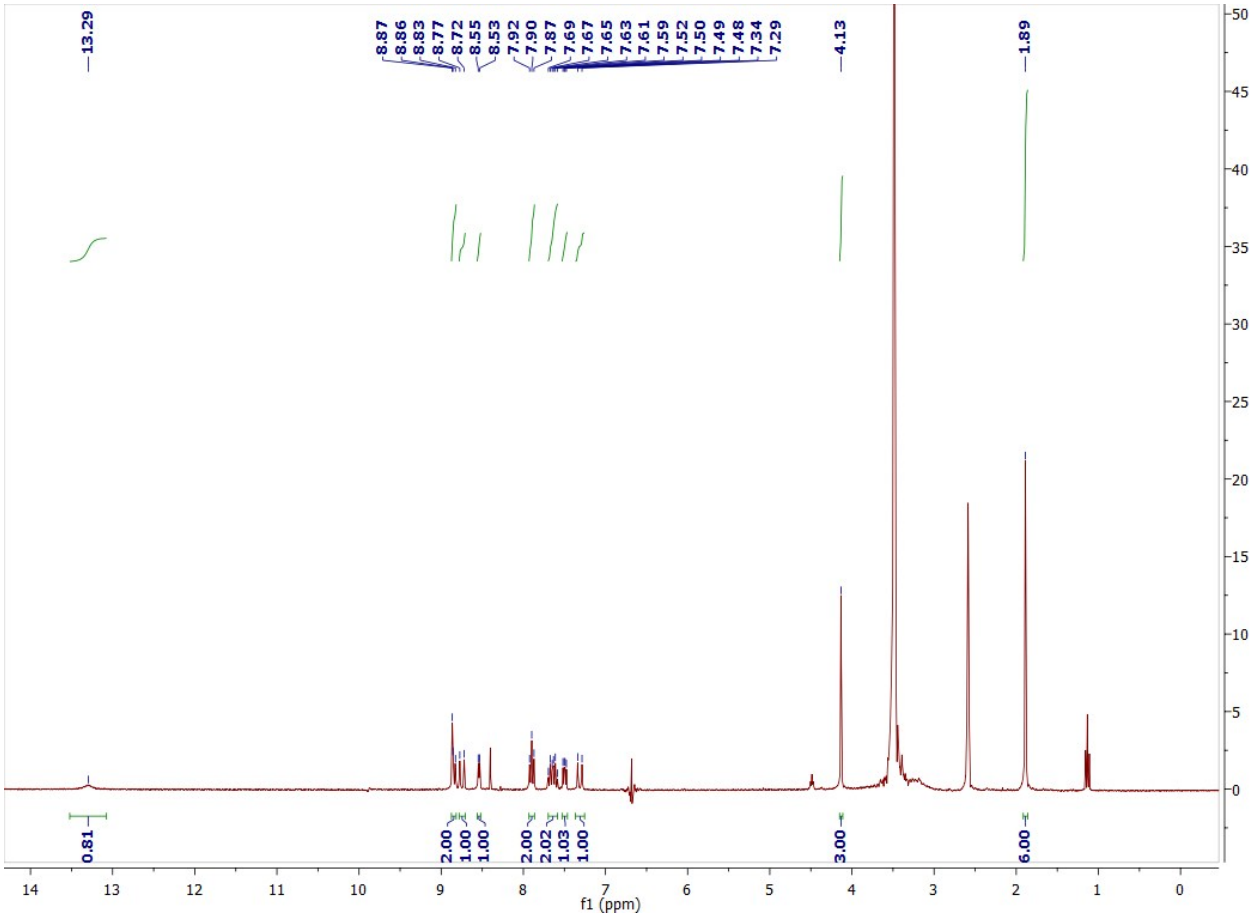


Fig. S37 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **C2**.

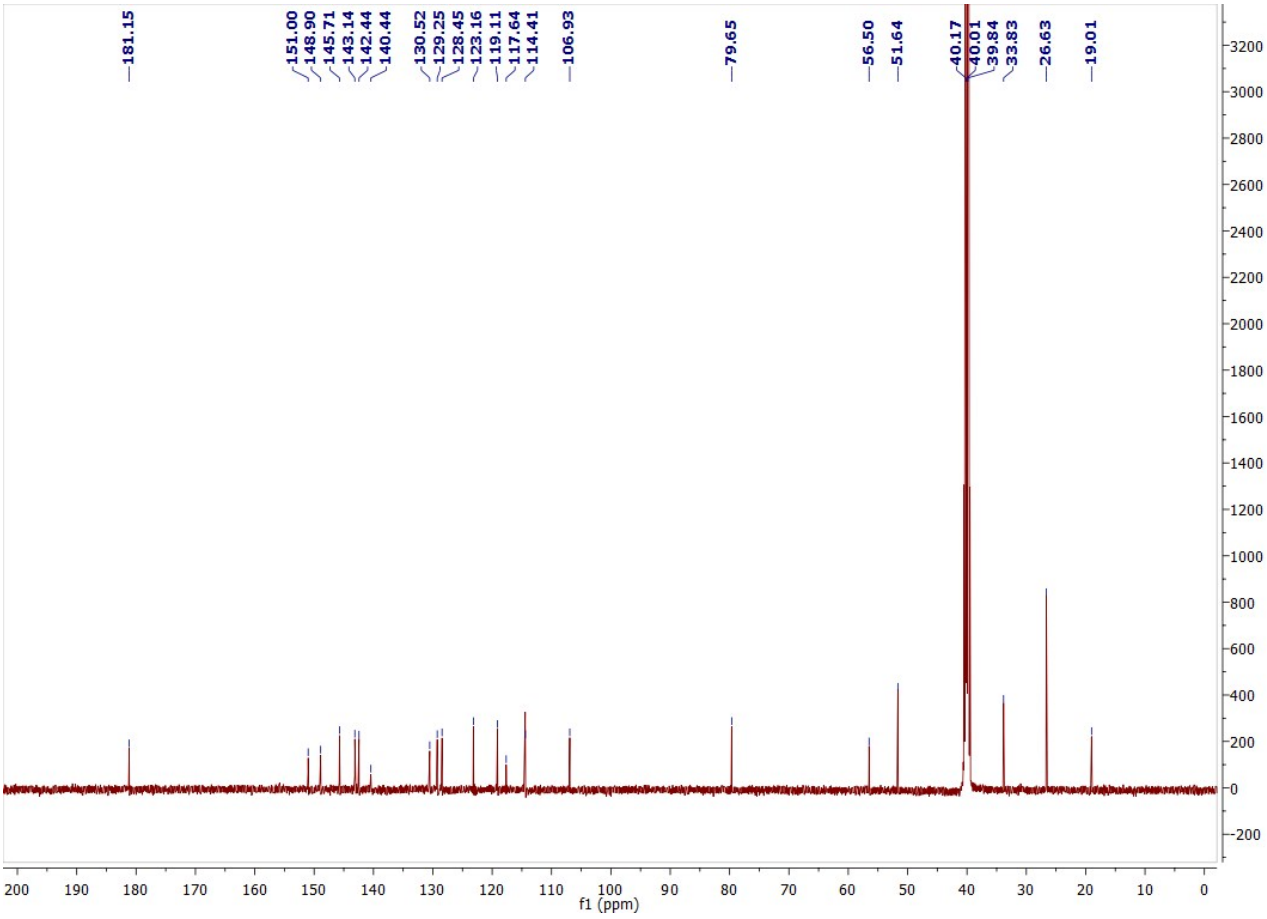


Fig. S38 ^{13}C NMR (500 MHz, $CDCl_3$) spectrum of **C2**.

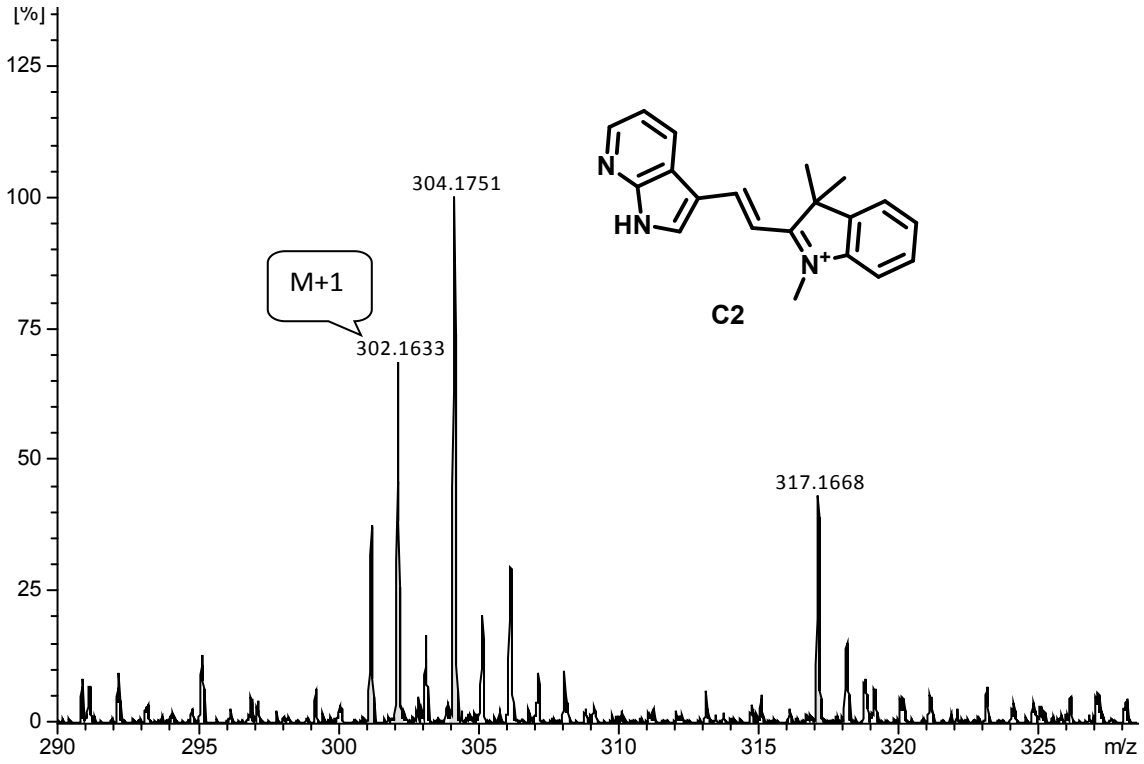
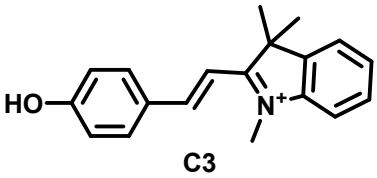


Fig. S39 Mass spectrum of **C2**.



C3

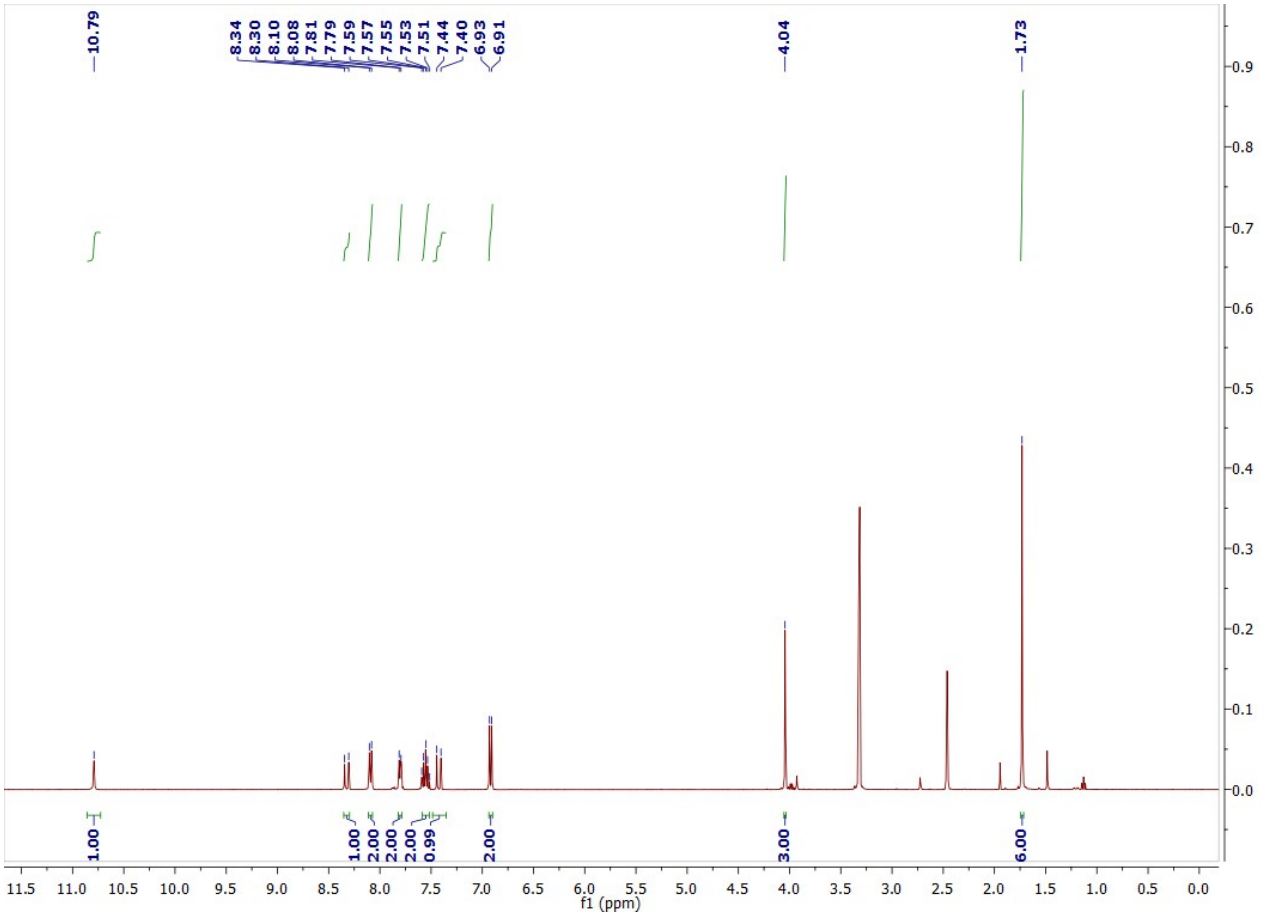


Fig. S40 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **C3**.

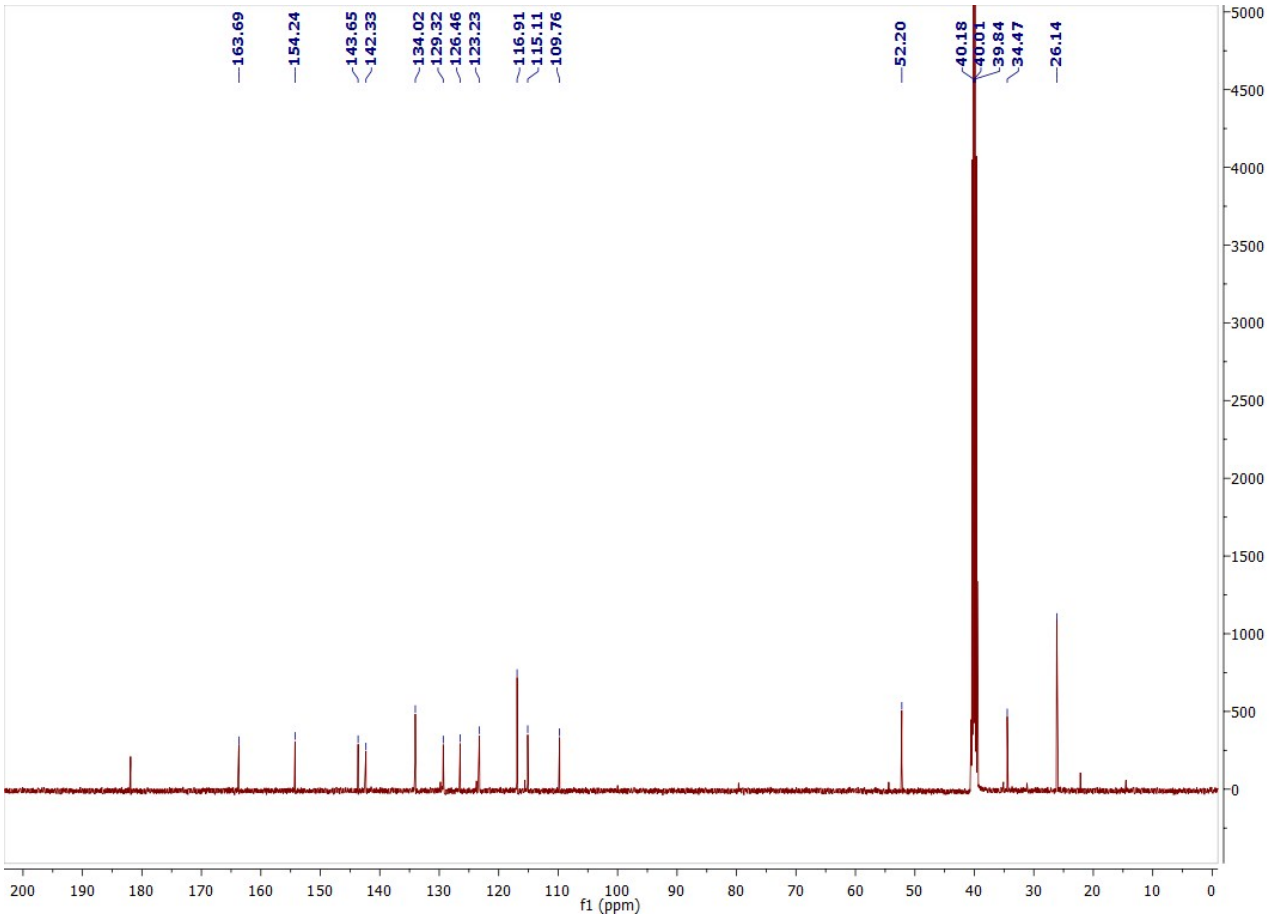


Fig. S41 ^{13}C NMR (500 MHz, DMSO-d_6) spectrum of **C3**.

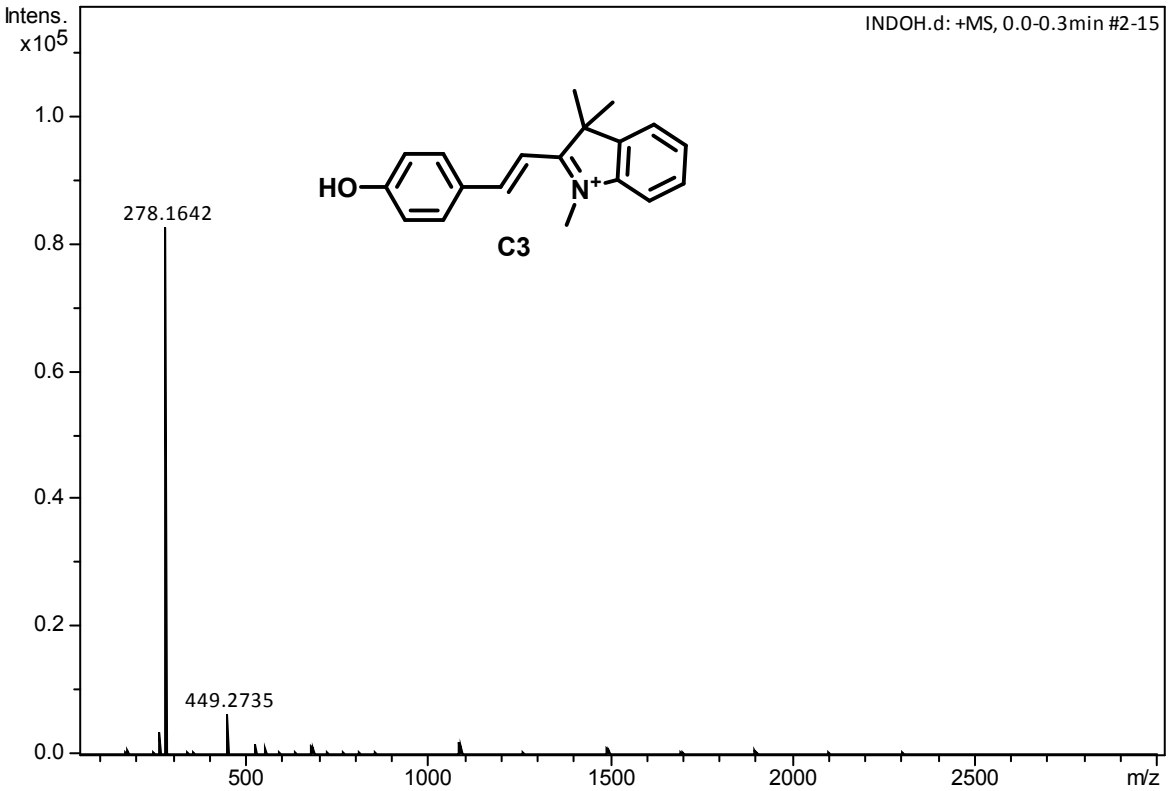


Fig. S42 Mass spectrum of **C3**.

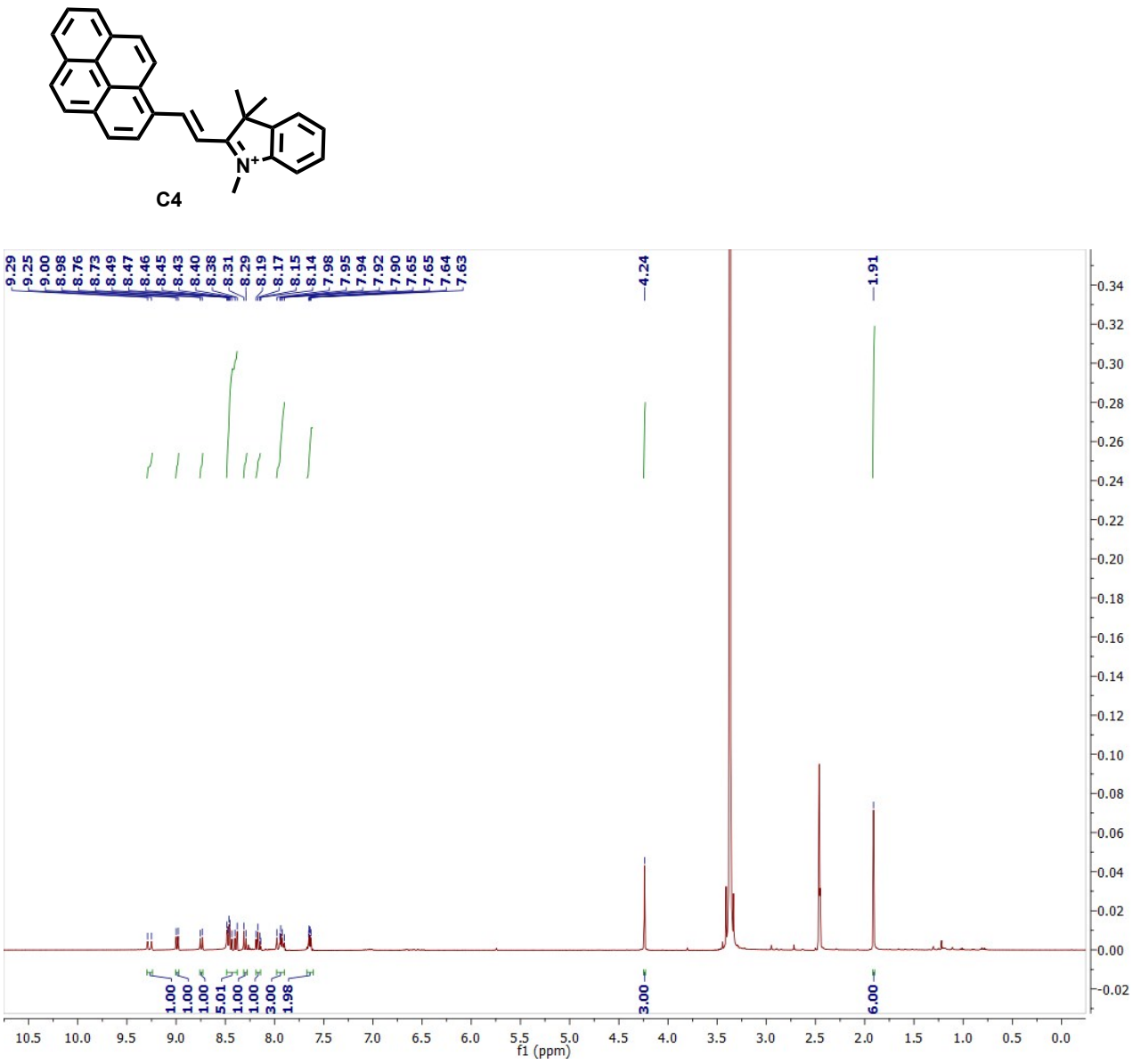


Fig. S43 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **C4**.

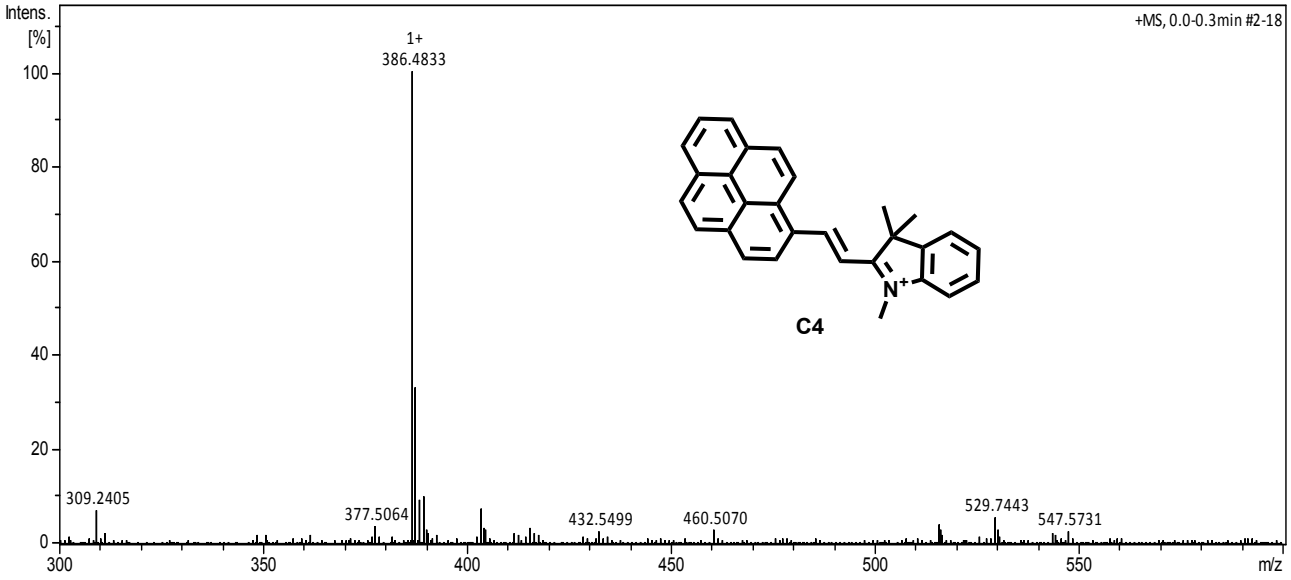


Fig. S44 Mass spectrum of **C4**.