Supporting Information for

Bodipy Derivatives as Organic Triplet Photosensitizers for Aerobic Photoorganocatalytic Oxidative Coupling of Amines and Photooxidation of Dihydroxylnaphthalenes

Ling Huang, Jianzhang Zhao,* Song Guo, Caishun Zhang and Jie Ma

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, E-208 West Campus, 2 Ling-Gong Road, Dalian 116024, China

E-mail : zhaojzh@dlut.edu.cn

Group Web : http://finechem.dlut.edu.cn/photochem

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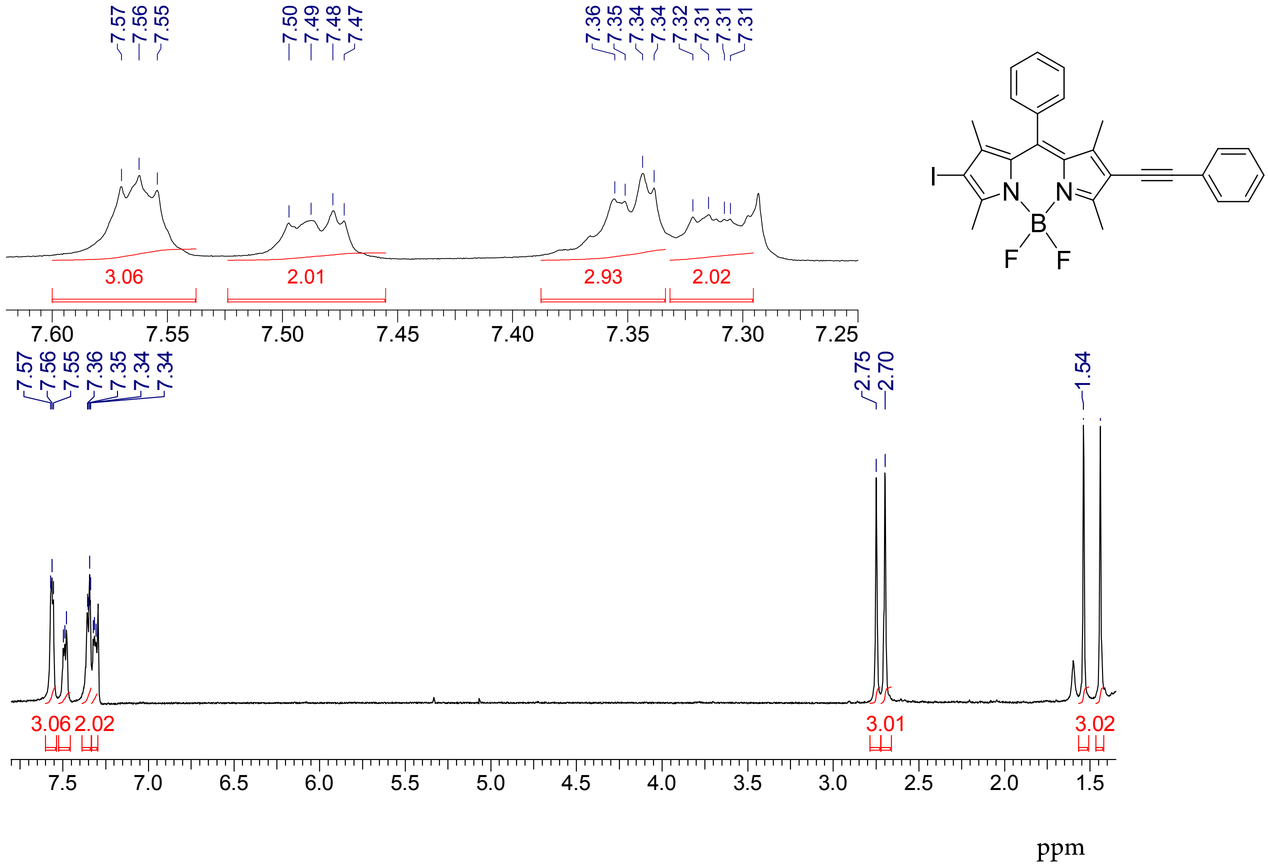


Figure S1. ^{1}H NMR of **B-3** (400 MHz, $CDCl_3$).

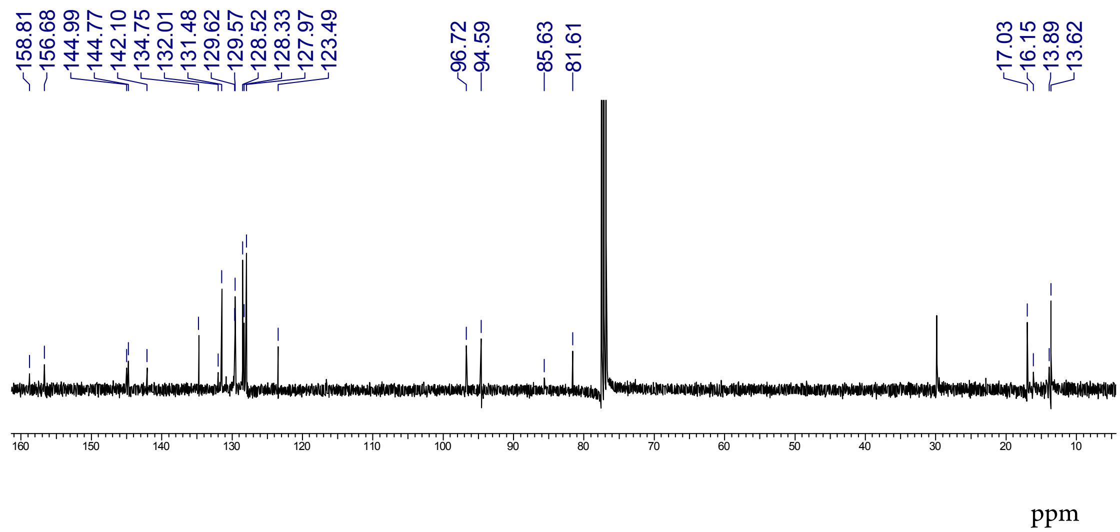


Figure S2. ^{13}C NMR of **B-3** (100 MHz, $CDCl_3$).

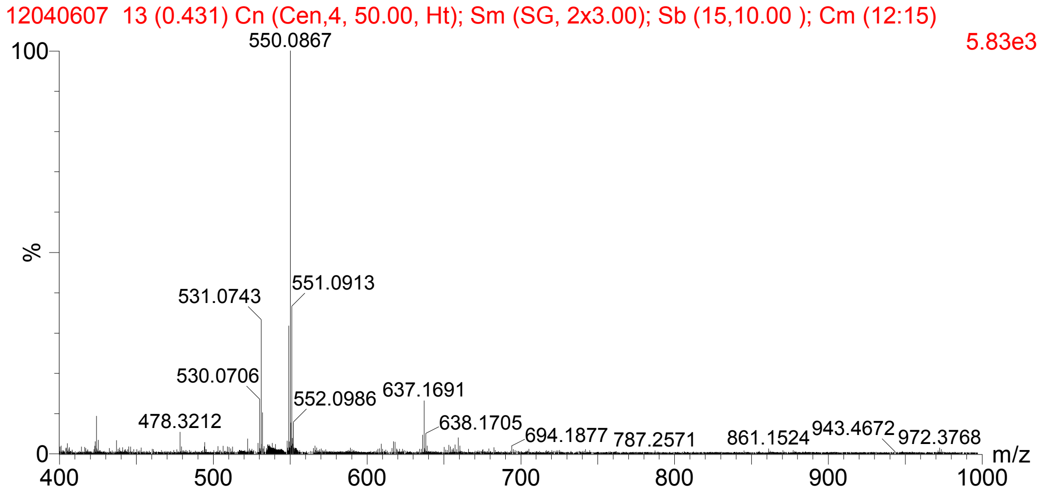


Figure S3. TOF HRMS MALDI of **B-3**.

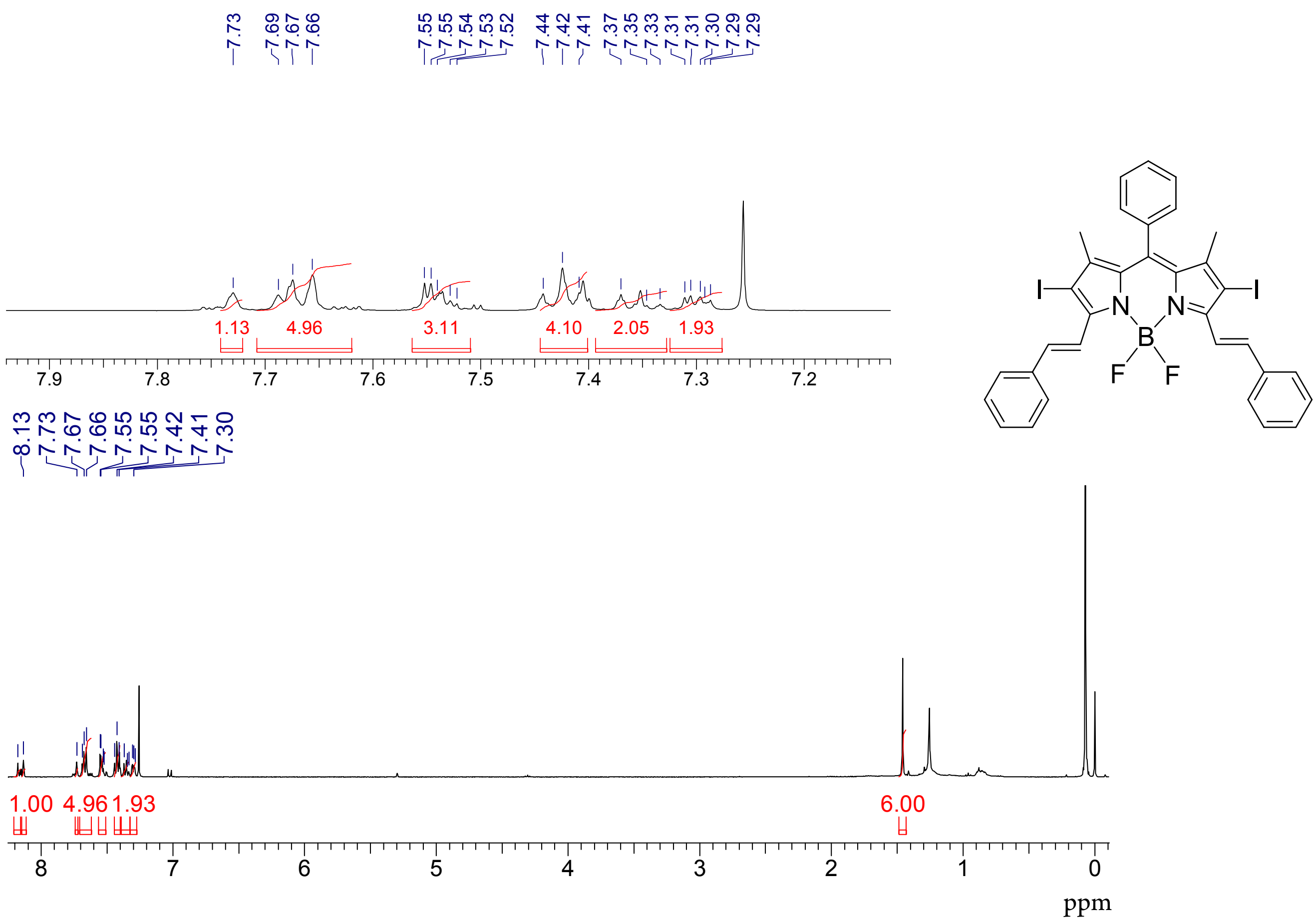


Figure S4. [1]H NMR of **B-4** (400 MHz, $CDCl_3$).

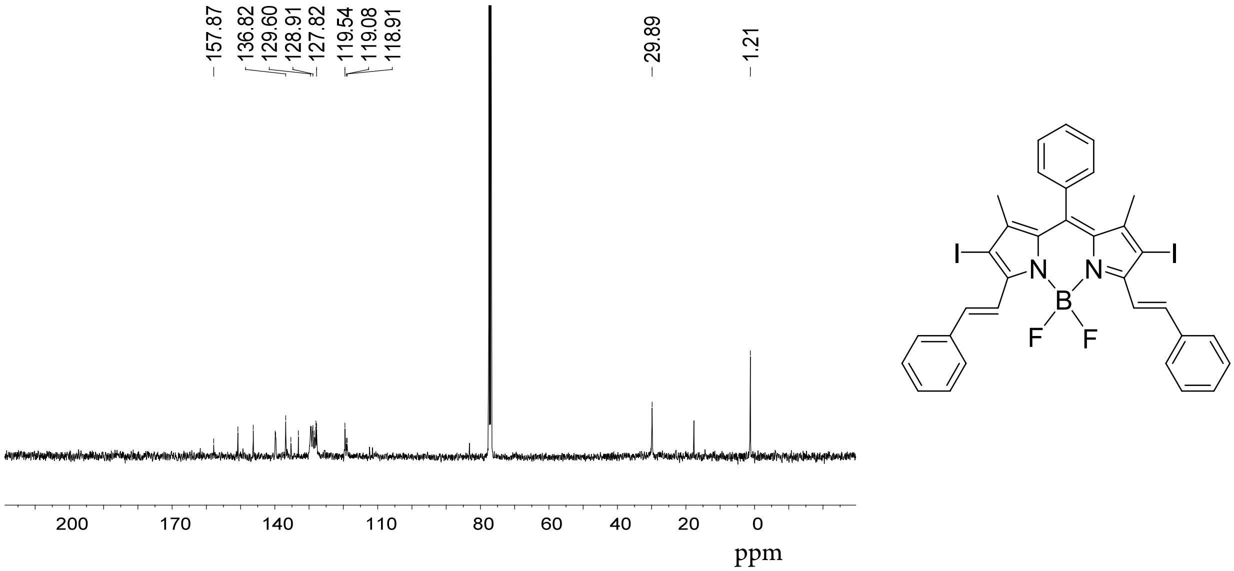


Figure S5. ^{13}C NMR of **B-4** (100 MHz, $CDCl_3$).

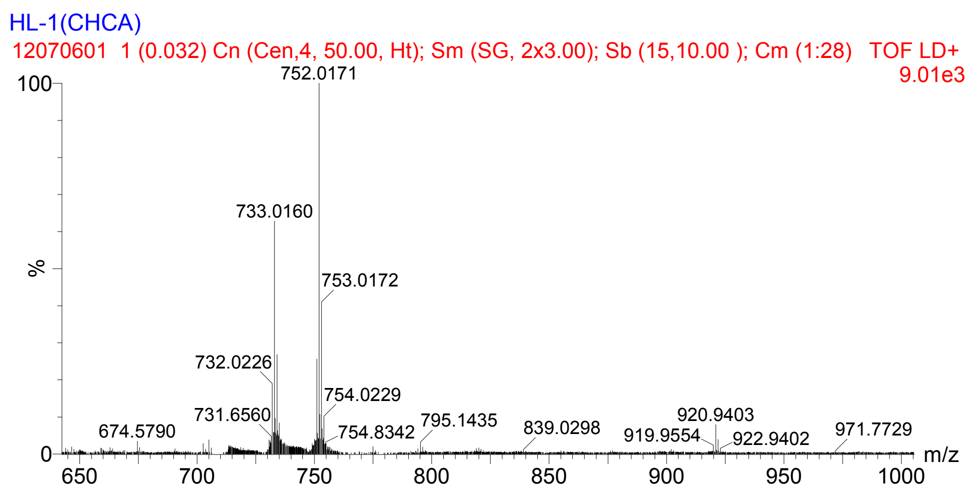
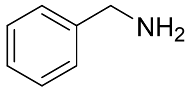
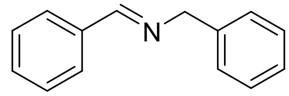
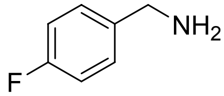
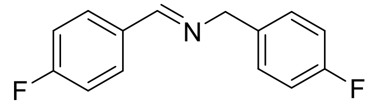
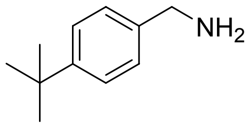
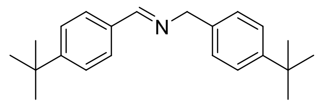
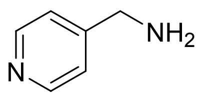
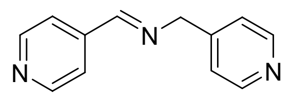
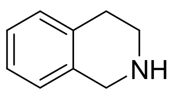
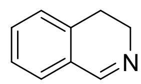
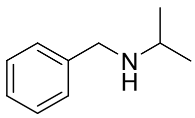
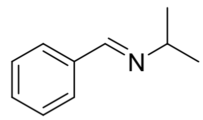


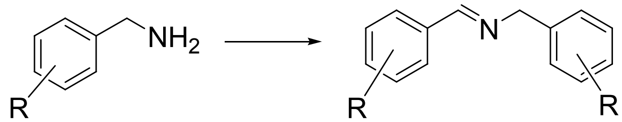
Figure S6. TOF HRMS MALDI of **B-4**.

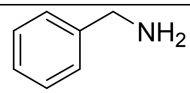
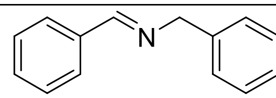
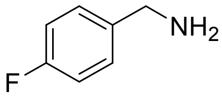
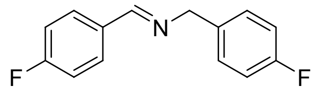
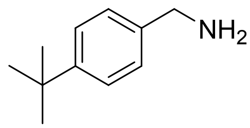
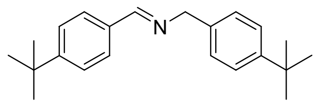
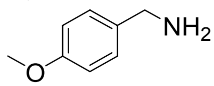
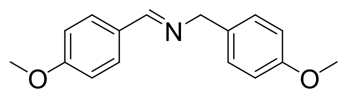
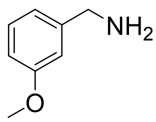
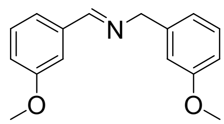
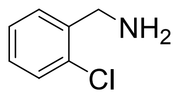
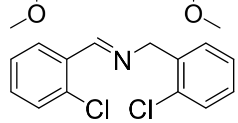
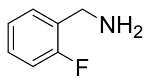
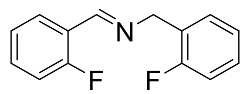
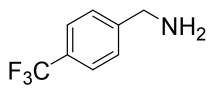
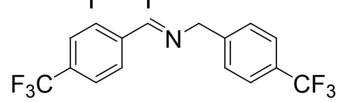
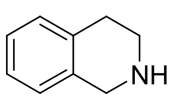
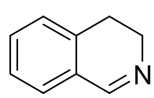
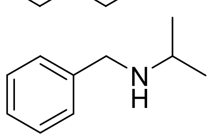
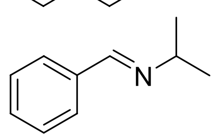
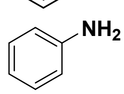
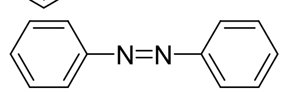
Table S1. Photocatalytic Oxidation of Various Amines Using **B-2** and **B-3** as photocatalysts [a]

Entry	Photosensitizers	Substrate	Product	t [h]	Yield[%] [b]
1	**B-2/B-3**			1.0	100/100
2	**B-2/B-3**			1.0	62/100
3	**B-2/B-3**			1.0	100/100
4	**B-2/B-3**			1.5	66/63
5	**B-2**			3.0	65
6	**B-2/B-3**			2.5	52/100

[a] Reaction conditions: amine substrate (0.5 mmol), photosensitizer (0.005 mmol, 1mol%), acetonitrile (5 mL), in air, irradiation wavelength λ >380 nm, 1 h. [b] The crude product yields were determined by ^{1}H NMR spectrum.

Table S2. Oxidation of various amines using **B-4**.[a] The general reaction is applicable to entries 1-6.



Entry	Substrate	Product	t / [h]	Yield/[%] [b]	TON
1			1.0	100	100
2			0.5	100	100
3			1.0	100	100
5			1.0	90	90
6			1.0	91	91
7			1.0	100	100
8			2.0	30	30
9			2.0	93	93
10			2.5	50	50
11			3.0	60	60
12			3.0	No Reaction	-

[a] Reaction conditions: various amines (0.5 mmol), photosensitizers catalyst **B-4** (0.005 mmol, 1%), acetonitrile/CH_2Cl_2 (5 mL, v/v = 3:2), in air saturated solution, $\lambda > 380$ nm, 1 h. [b] The crude product yields were determined by ^{1}H NMR spectrum.

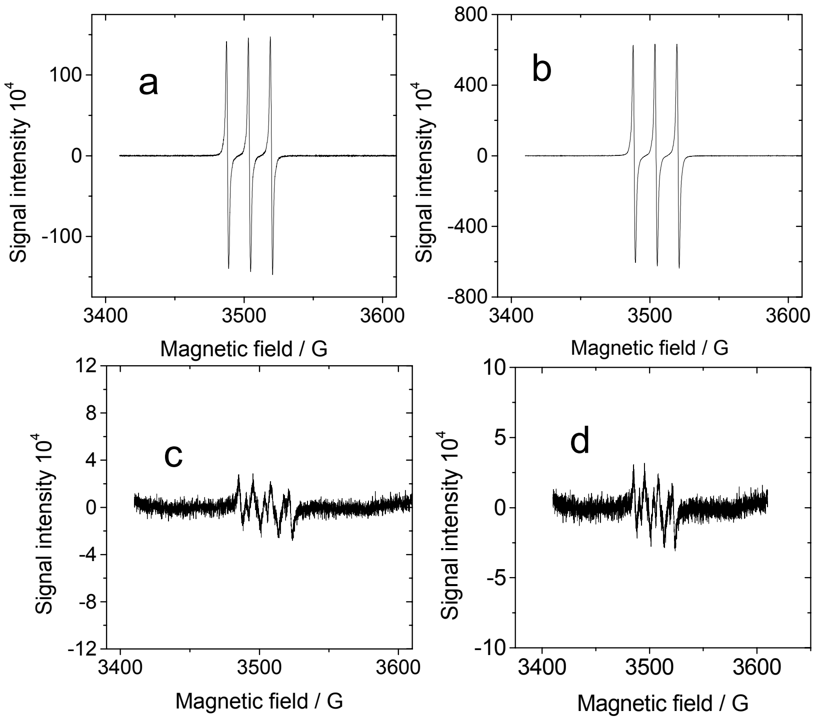


Figure S7. (a) ESR spectrum of a solution of **B-4** (1.0×10^{-4} M), benzylamine (1.5×10^{-3} M), and TEMP (0.12 M) in air-saturated CH_3CN upon irradiation for 20s by 532 nm laser 141 mW/cm^2. (b) ESR spectrum of a solution of **B-4** (1.0×10^{-4} M) and TEMP (0.12 M) in air-saturated CH_3CN upon irradiation for 60 s by 532 nm laser 141 mW/cm^2. (c) ESR spectrum of a solution of **B-4** (1.0×10^{-4} M), DMPO (2.0×10^{-2} M), benzylamine (1.5×10^{-3} M) in air-saturated CH_3CN upon irradiation for 532 nm laser 141 mW/cm^2. (d) ESR spectrum of a solution of **B-4** (1.0×10^{-4} M), DMPO (2.0×10^{-2} M), in air-saturated CH_3CN upon irradiation 60 s for 532 nm laser 141 mW/cm^2. 22 °C.

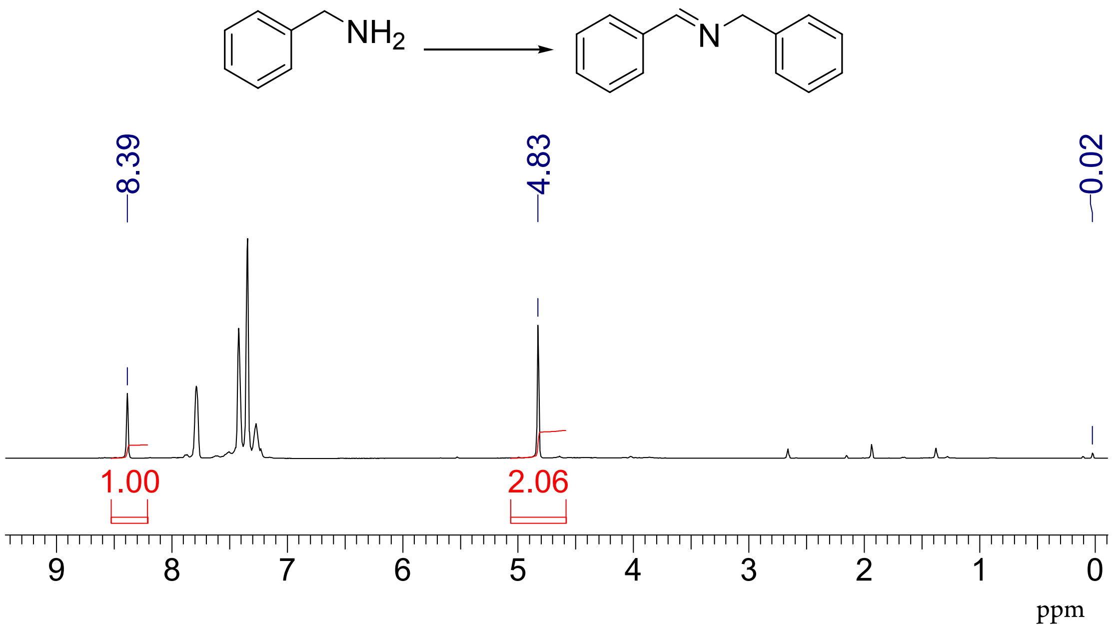


Figure S8. [1]H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with **B-1** as the photocatalyst (400 MHz, $CDCl_3$). The conversion of the reaction was calculated by integrating the singlet peak of the featured proton in the products (at about 4.87 ppm for -CH=N-C***H*₂**-) and that of the corresponding proton in the starting materials (at about 3.98 ppm as singlet for H_2N-C***H*₂**-).

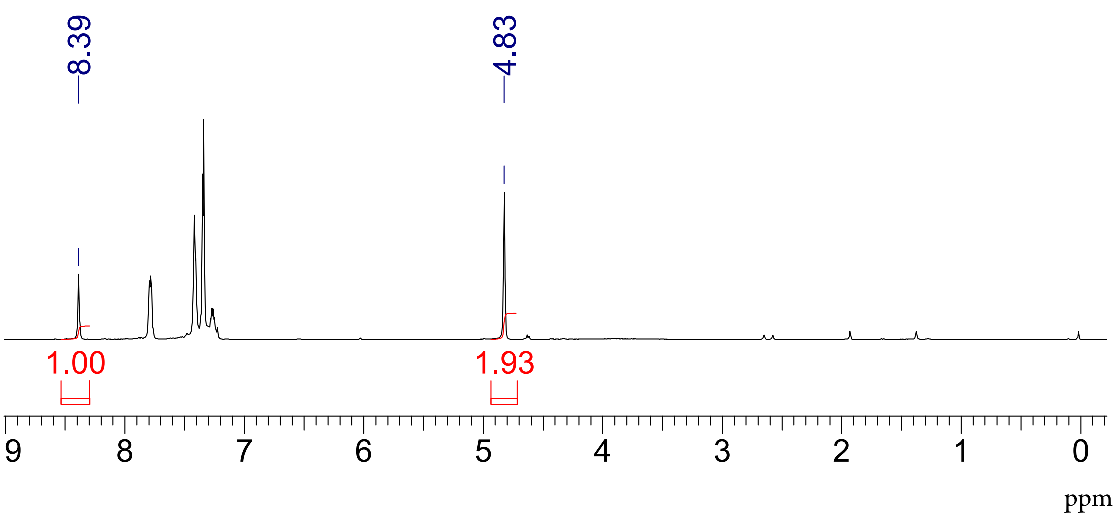


Figure S9. [1]H-NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with **B-2** as the triplet photosensitizer (400 MHz, $CDCl_3$).

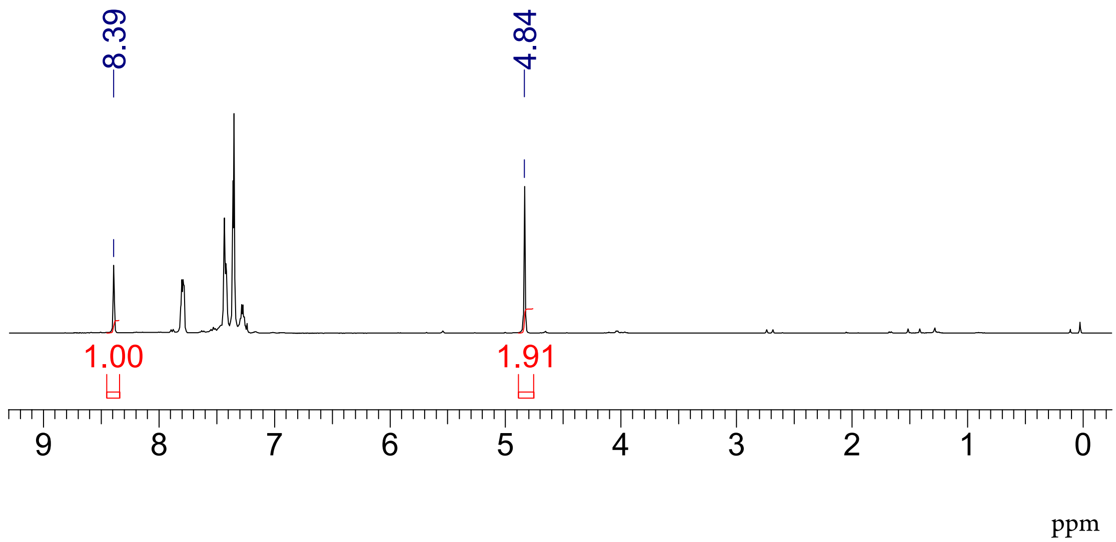


Figure S10. ¹H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with **B-3** (400 MHz, $CDCl_3$).

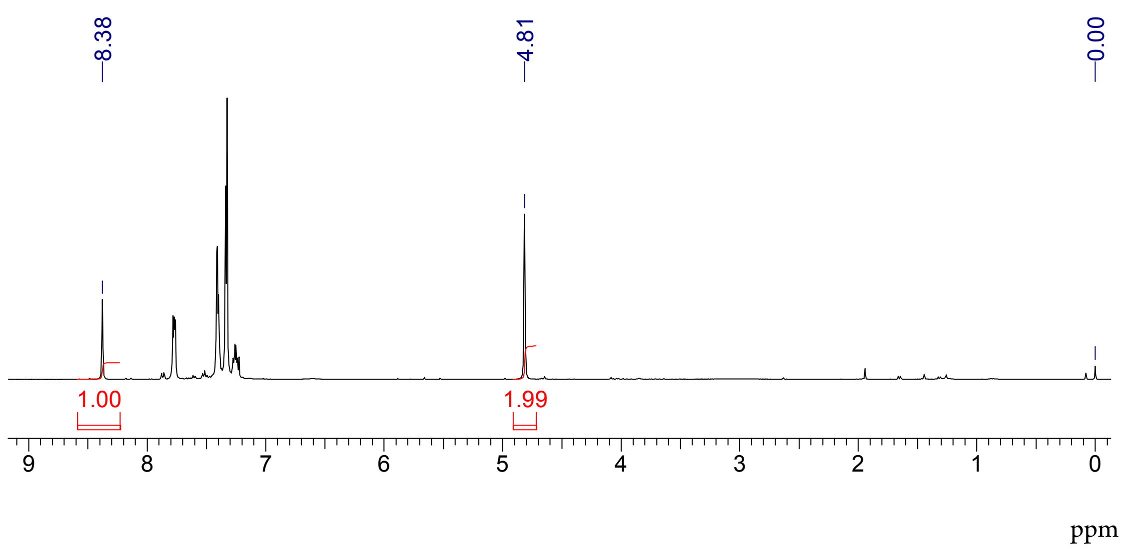


Figure S11. ¹H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with **B-4** (400 MHz, $CDCl_3$).

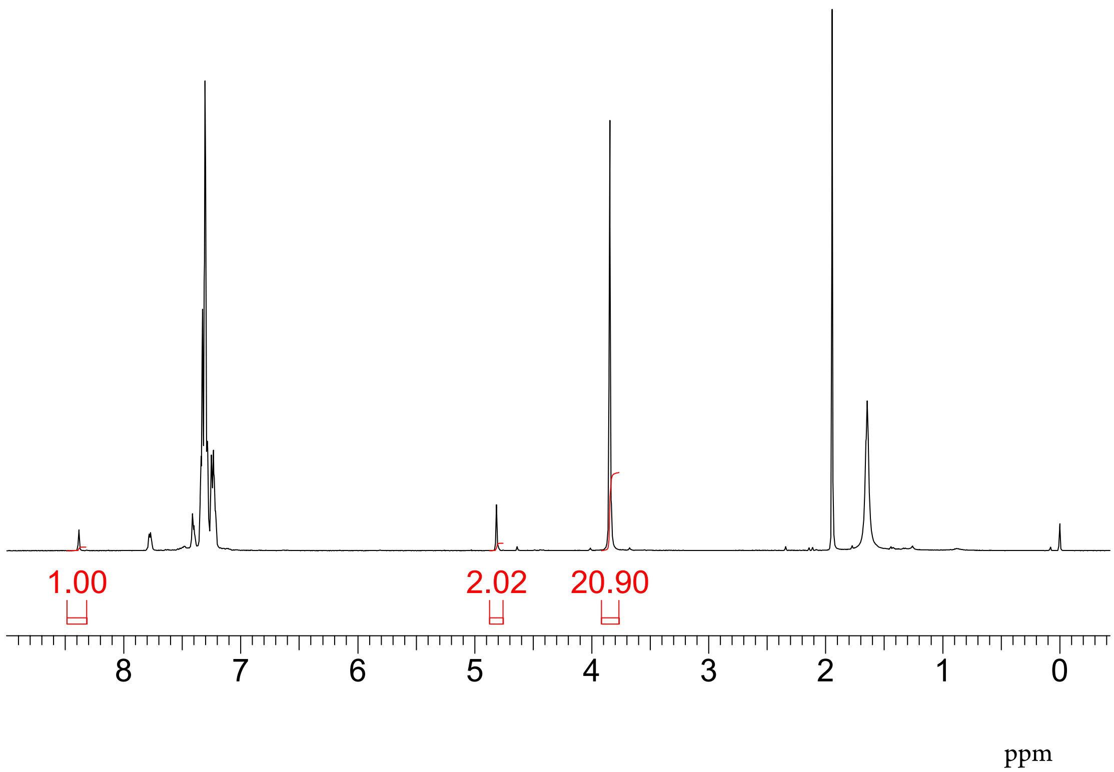


Figure S12. ¹H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with **B-5** (400 MHz, $CDCl_3$).

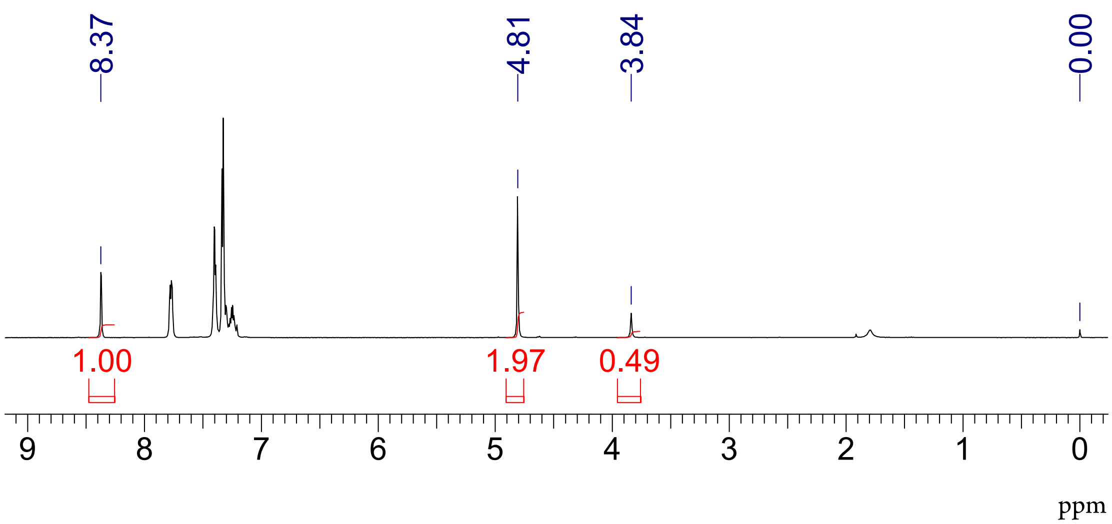


Figure S13. ¹H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with Rose Bengal (RB) (400 MHz, $CDCl_3$).

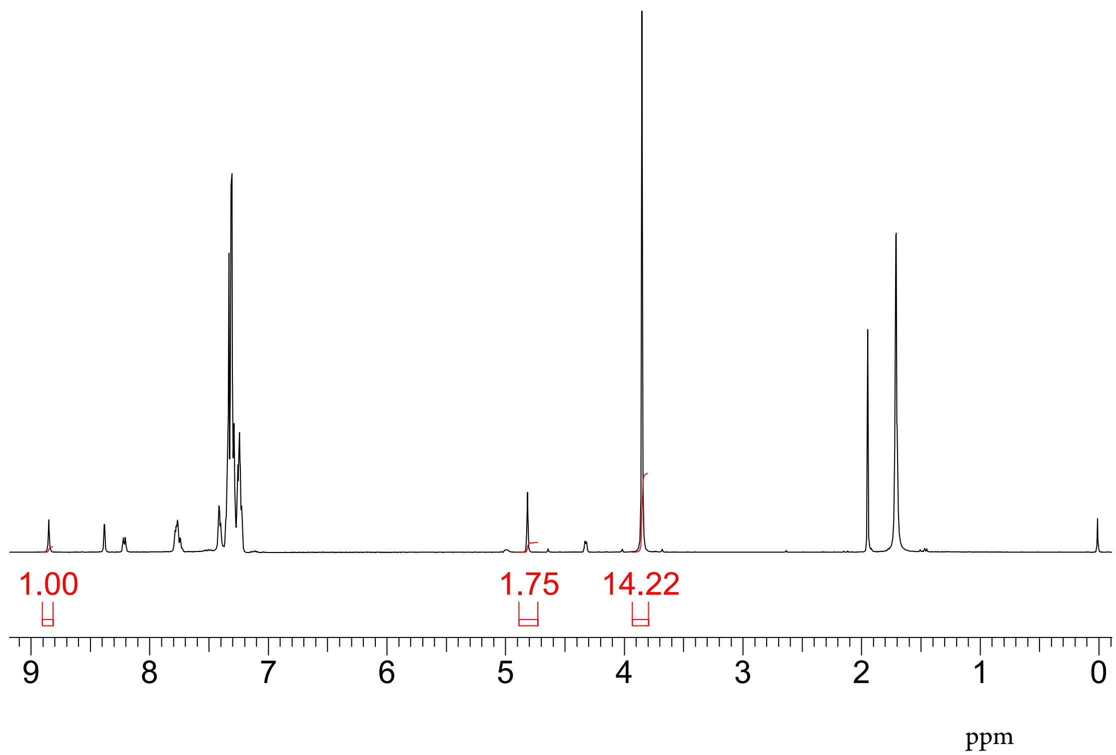


Figure S14. ^{1}H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with TPP In CH_3CN (400 MHz, $CDCl_3$).

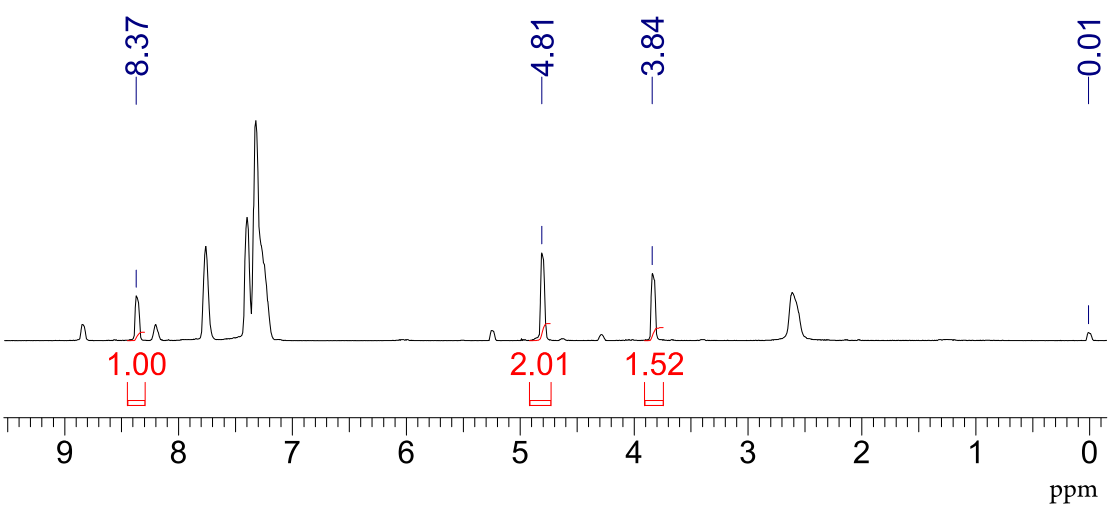


Figure S15. ^{1}H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with TPP as catalyst (400 MHz, $CDCl_3$). In CH_2Cl_2.

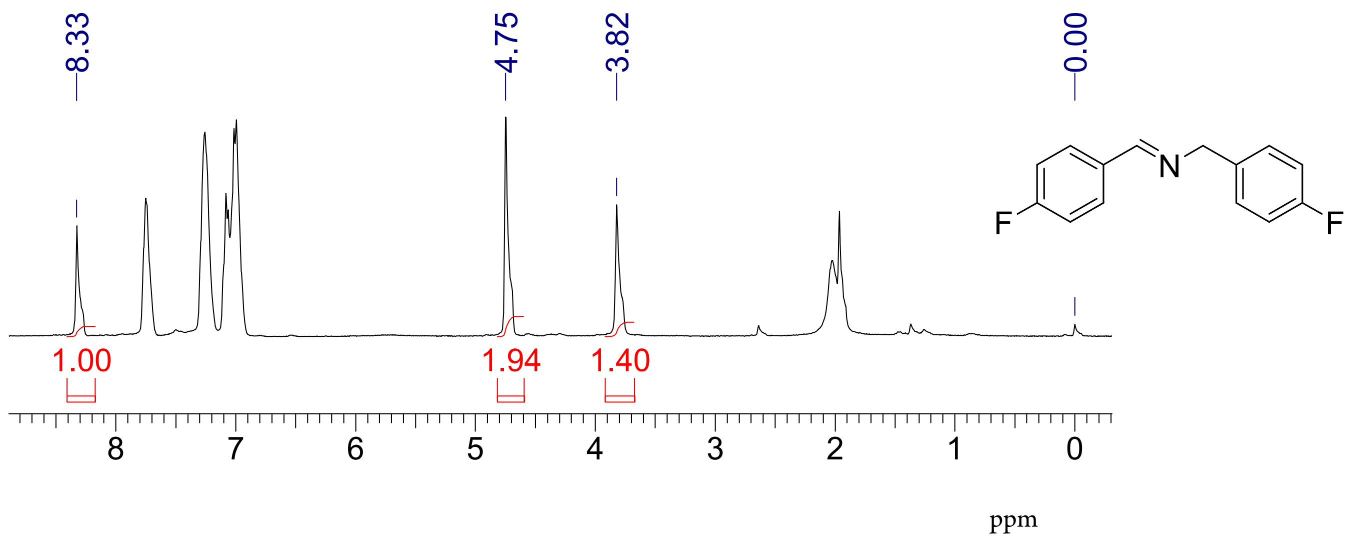


Figure S16. ^{1}H NMR spectrum of the crude product from aerobic oxidative coupling of 4-fluoro benzylamine with **B-1** (400 MHz, $CDCl_3$).

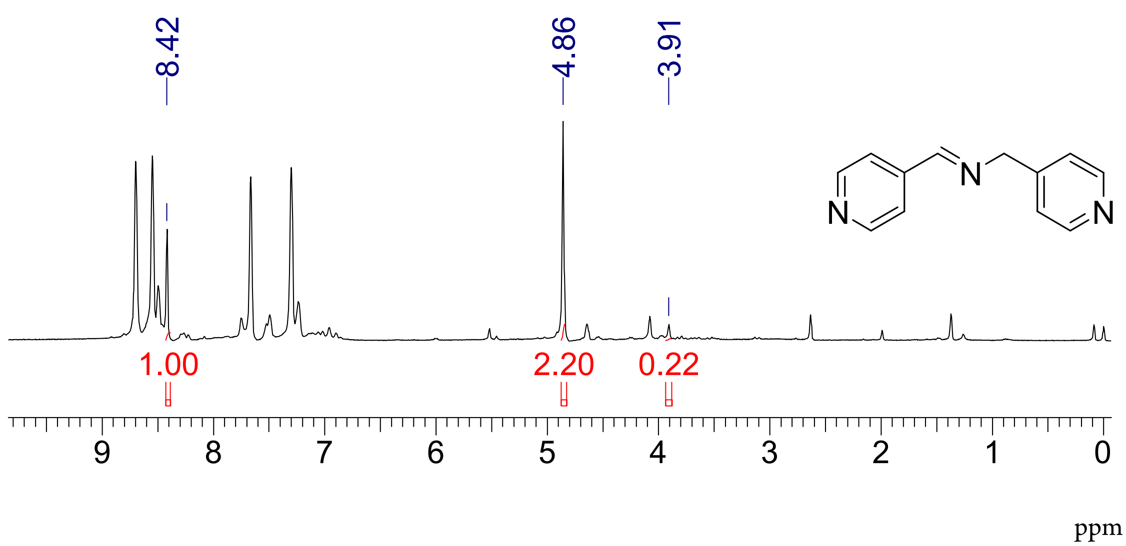


Figure S17. ^{1}H NMR spectrum of the crude product from aerobic oxidative coupling of aminmethylpyridine with **B-1** (400 MHz, $CDCl_3$)**.**

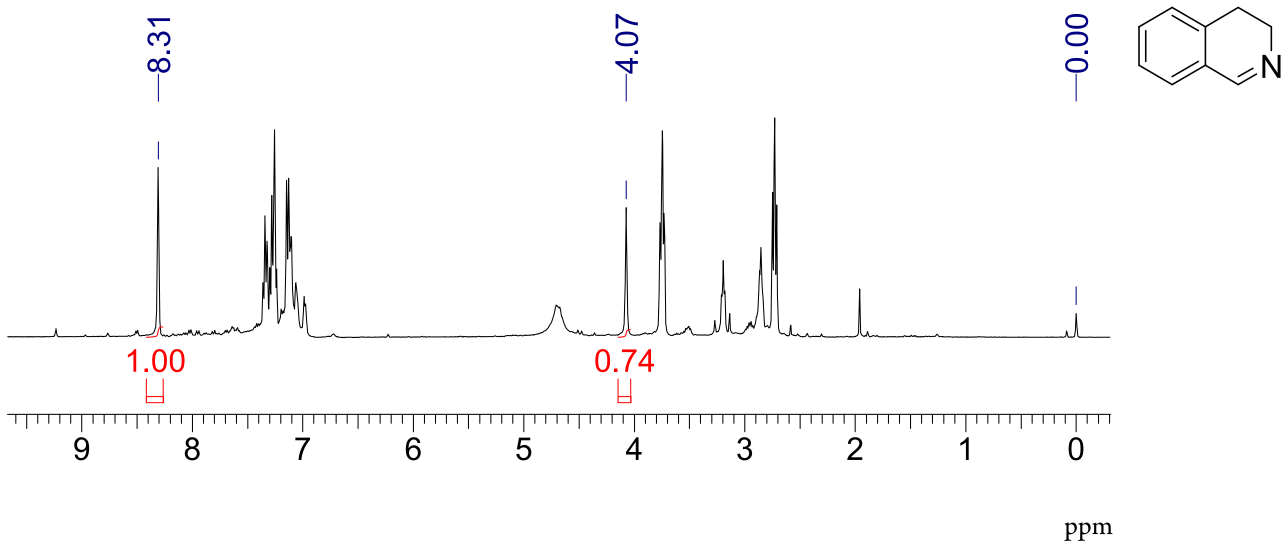


Figure S18. ^{1}H NMR spectrum of the crude product from aerobic oxidative coupling of 1,2,3,4-tetrahydroisoquinoline with **B-1** (400 MHz, $CDCl_3$).

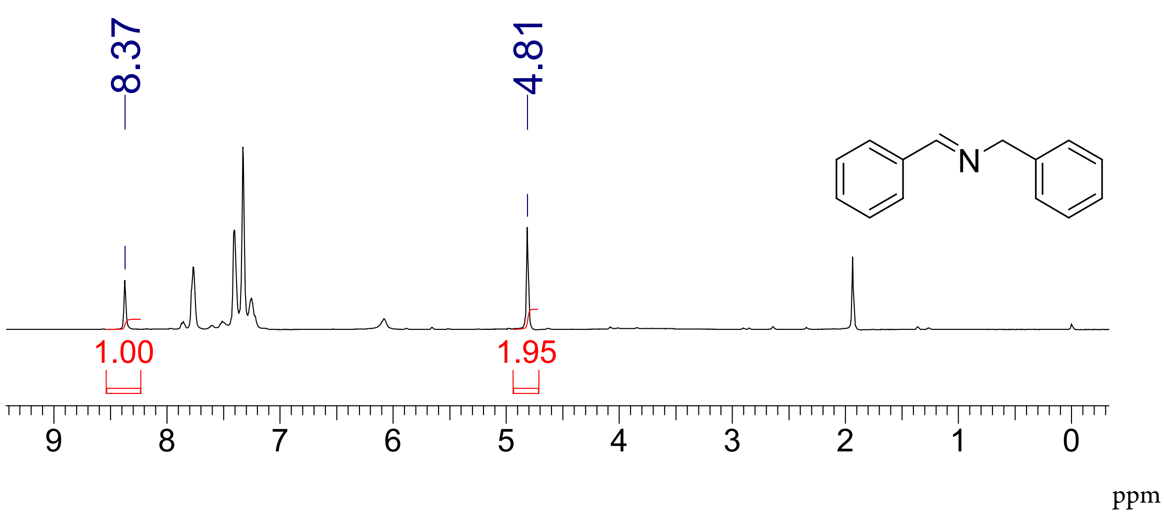


Figure S19. ^{1}H NMR spectrum of the crude product from aerobic oxidative coupling of dibenzylamine with **B-1** (400 MHz, $CDCl_3$).

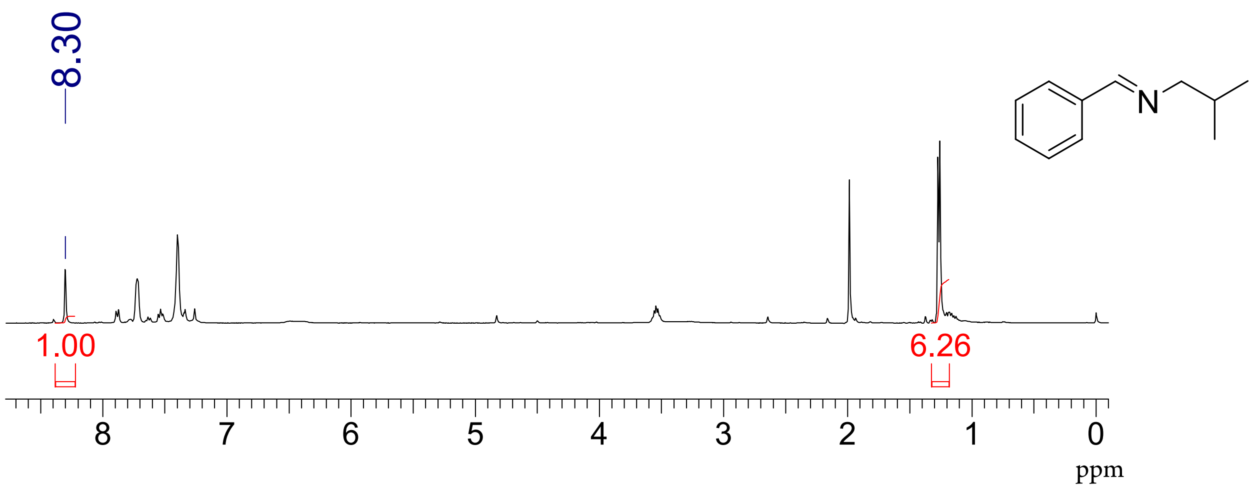


Figure S20. [1]H-NMR spectrum of the crude product from aerobic oxidative coupling of *N*-isopropylbenzylamine with **B-1** (400 MHz, $CDCl_3$).

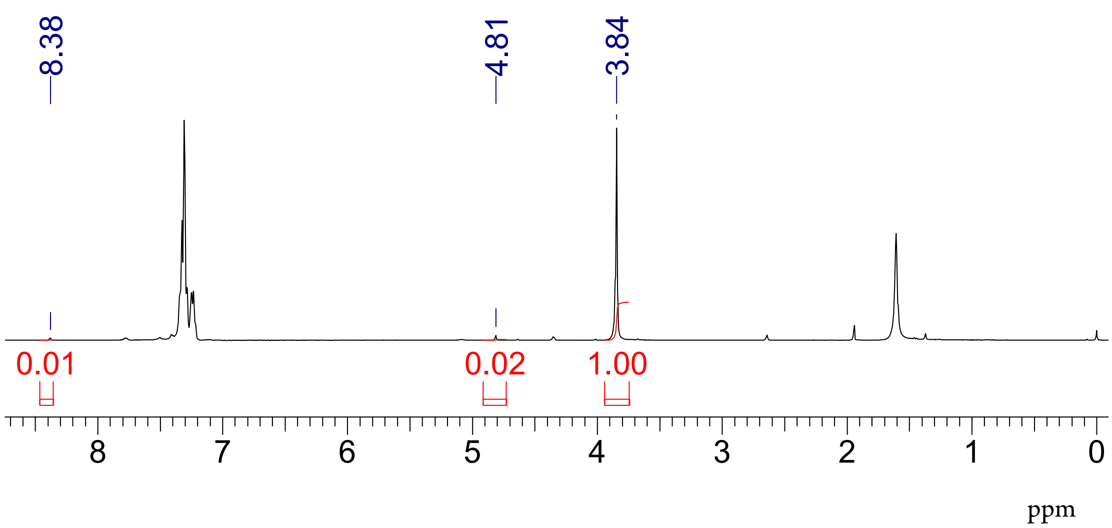


Figure S21. [1]H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with **B-1**. In N_2 saturated solution (400 MHz, $CDCl_3$).

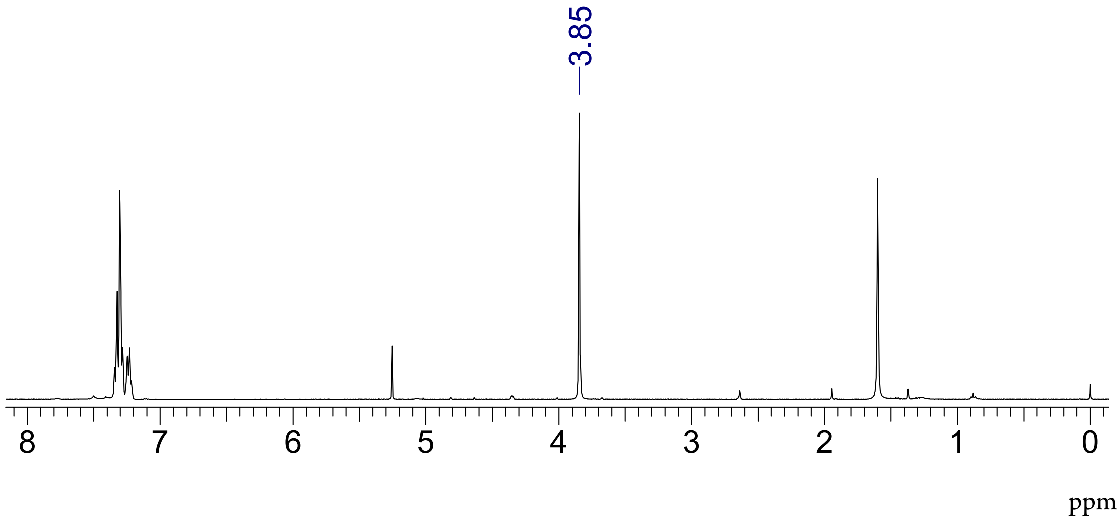


Figure S22. ^{1}H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with **B-1** as catalyst (400 MHz, $CDCl_3$). No photoirradiation.

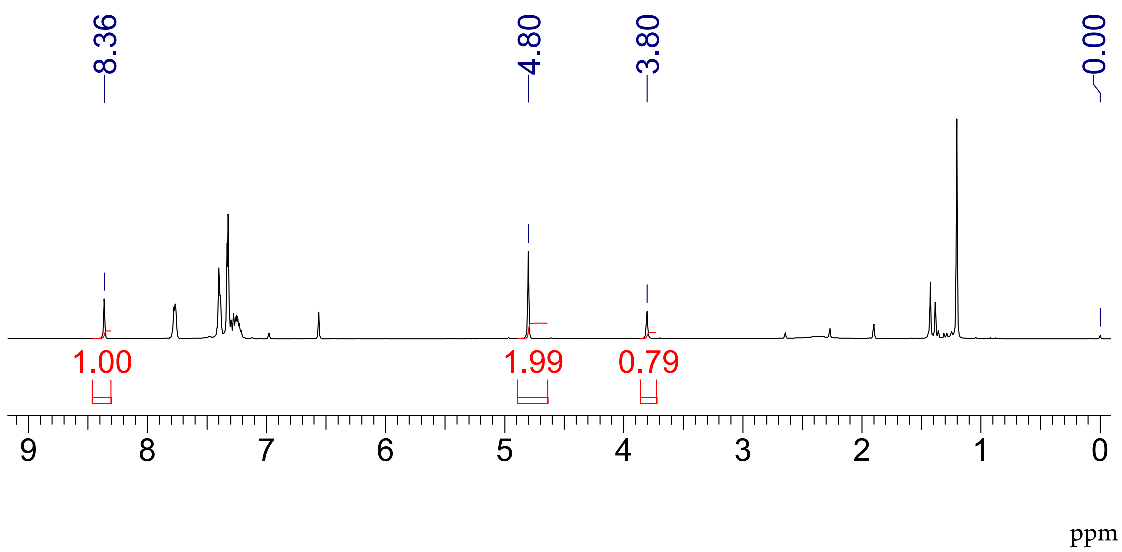


Figure S23. ^{1}H NMR spectrum of the crude product from aerobic oxidative coupling of benzylamine with **B-1** (400 MHz, $CDCl_3$), in the presence of 2,6-di-*tert*-butyl-4-methylphenol (quencher for radicals).

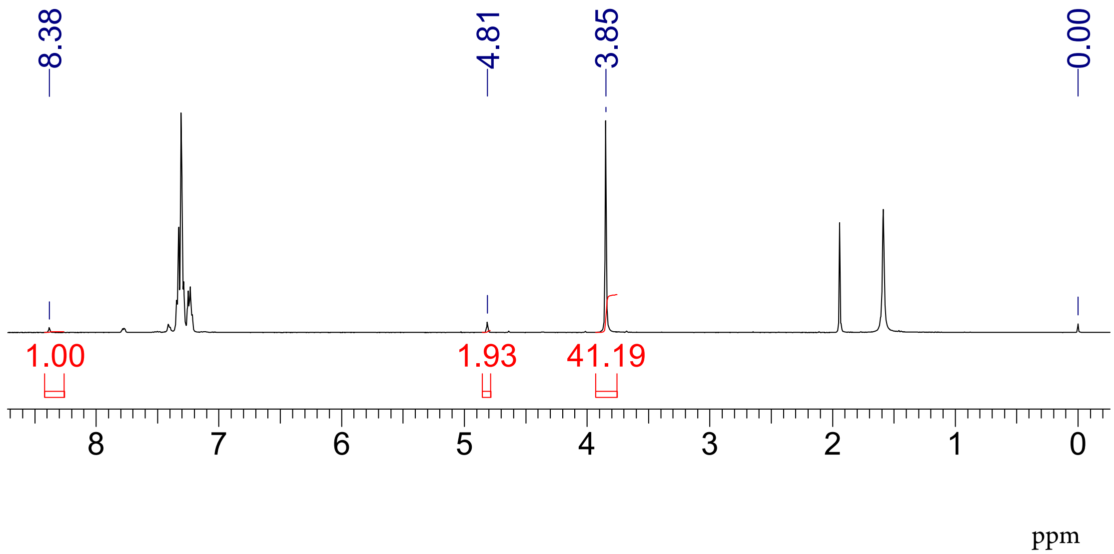


Figure S24. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of the reaction mixture of the aerobic oxidative coupling reaction of benzylamine *without* photocatalyst (**B-1)**. No reaction took place.

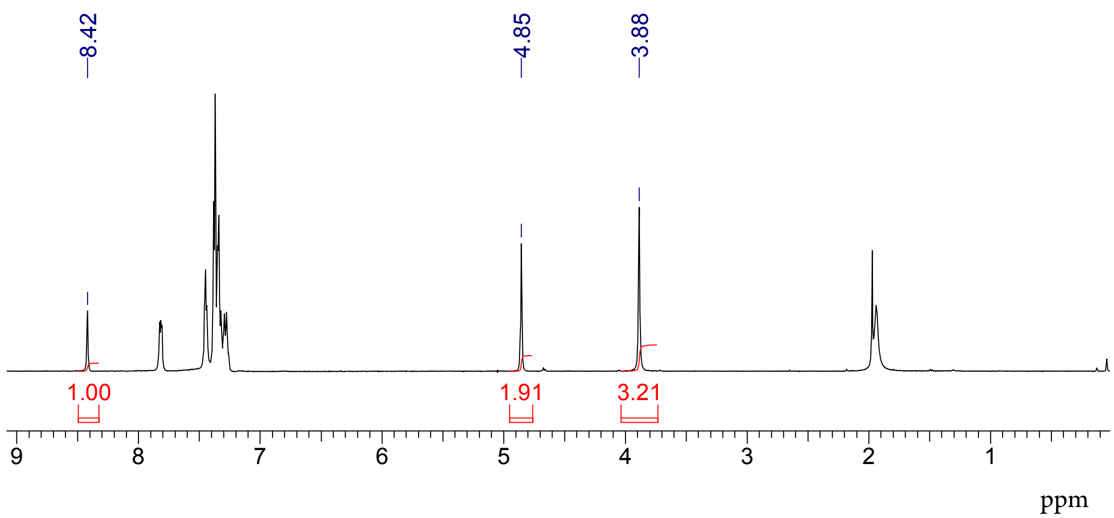


Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with $Ir(ppy)_2bpy$ as the photocatalyst.

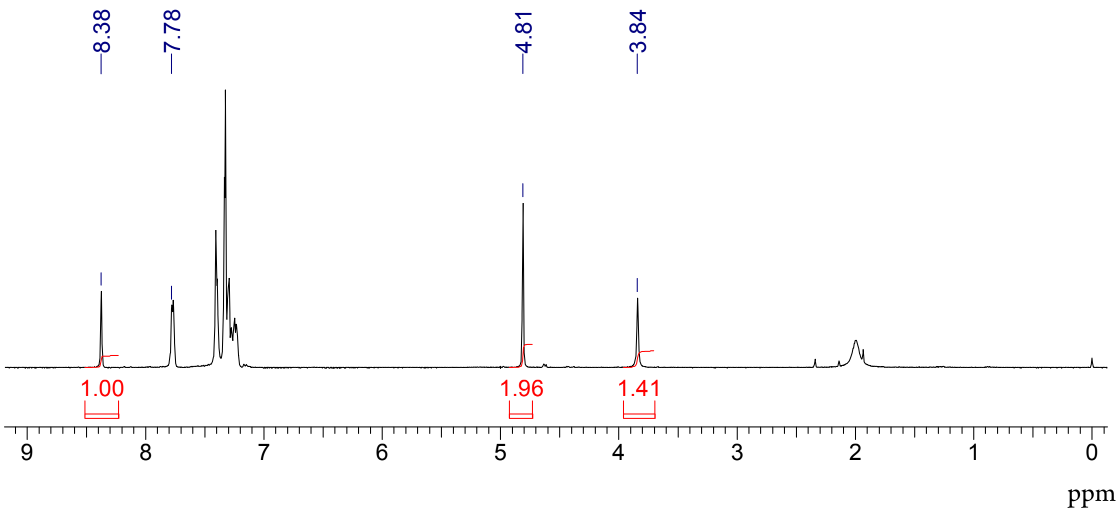


Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with **Ru-1** as the photocatalyst.

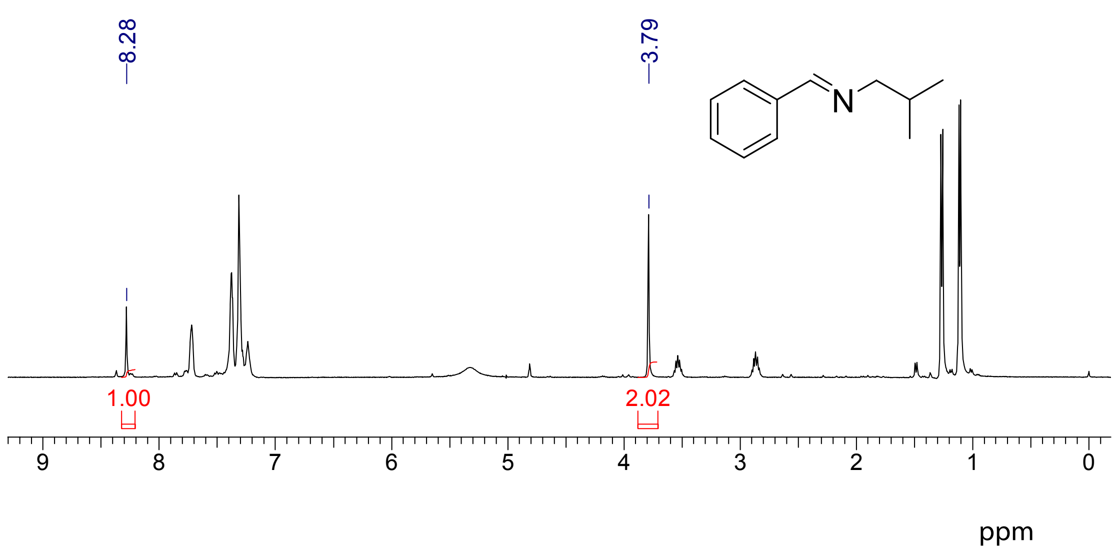


Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of *N*-isopropylbenzylamine with **B-2** as the photocatalyst.

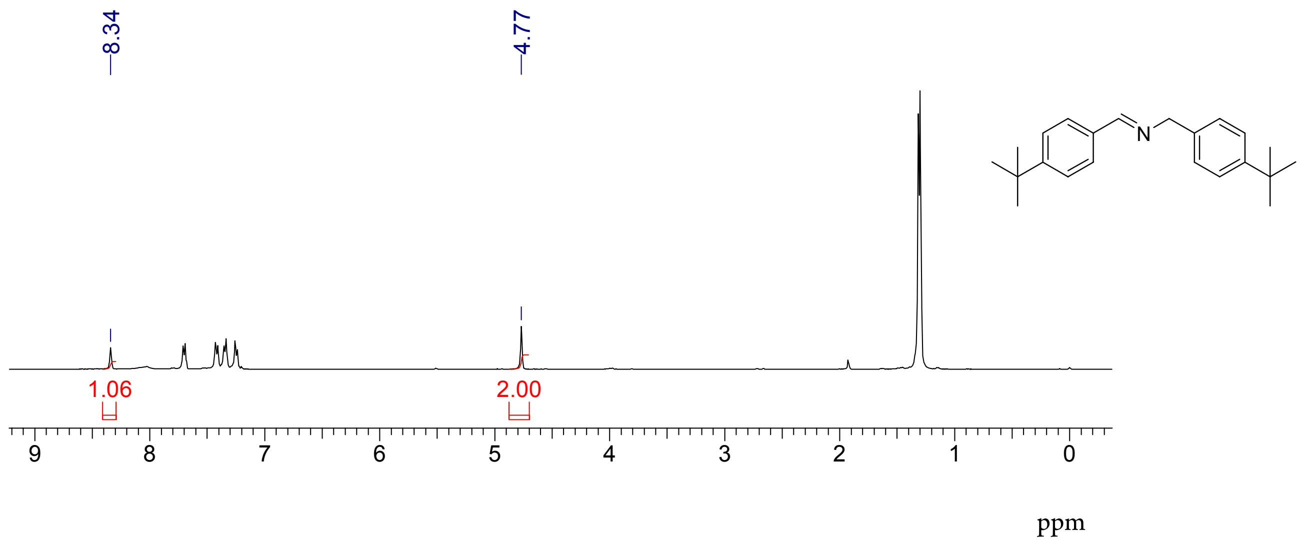


Figure S28. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 4-*tert*-butylbenzylamine with **B-3** as the photocatalyst.

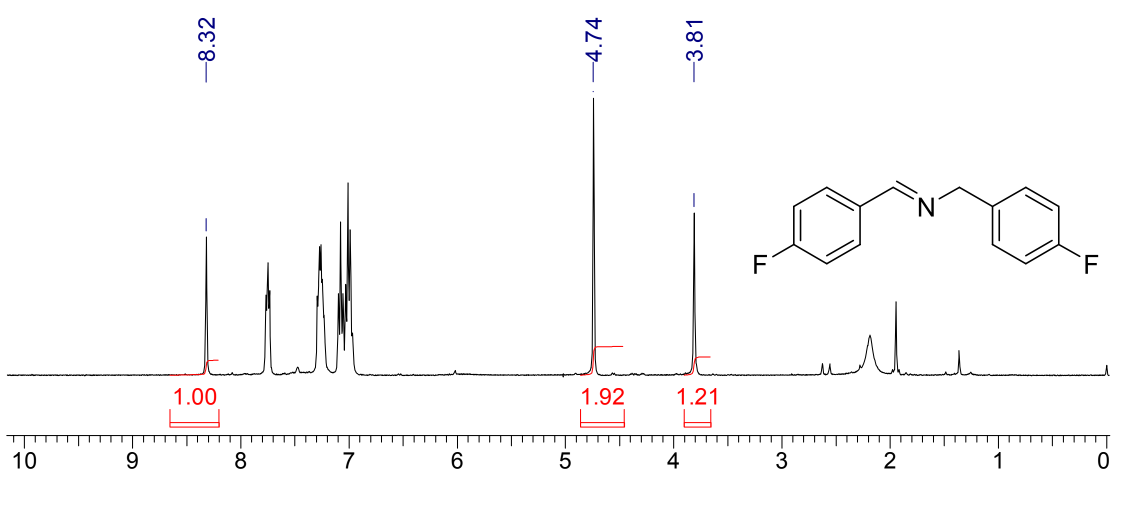


Figure S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 4-fluorobenzylamine with **B-2** as the photocatalyst.

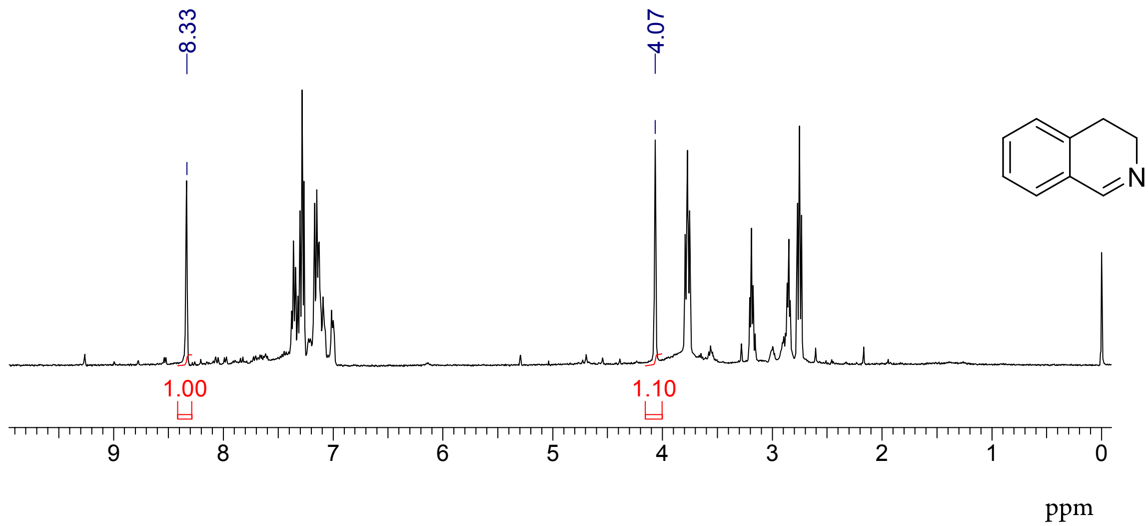


Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 1,2,3,4-tetrahydroisoquinoline with **B-2** as the photocatalyst.

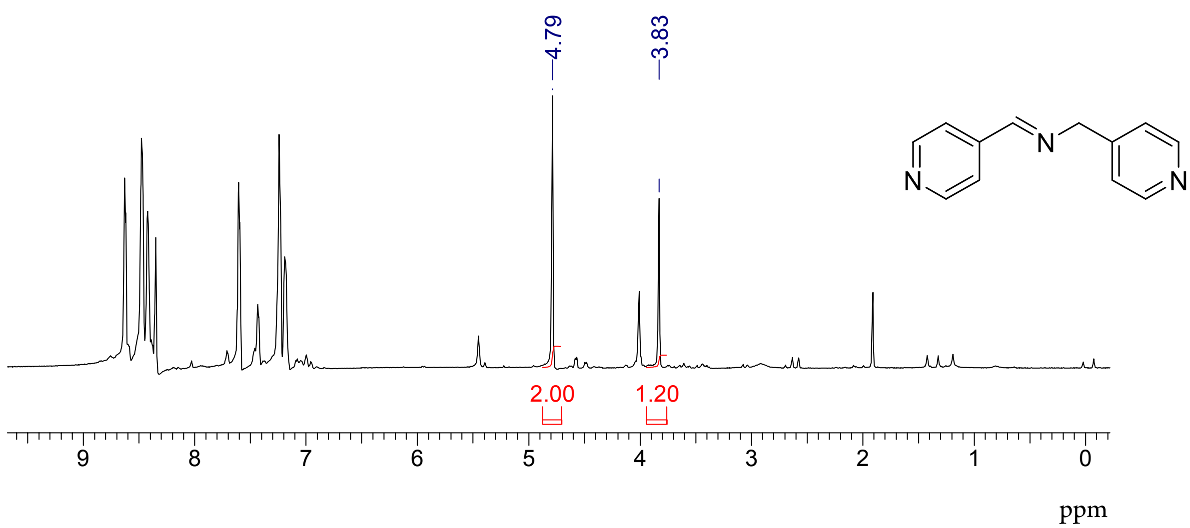


Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of aminomethylpyridine with **B-3** as the photocatalyst.

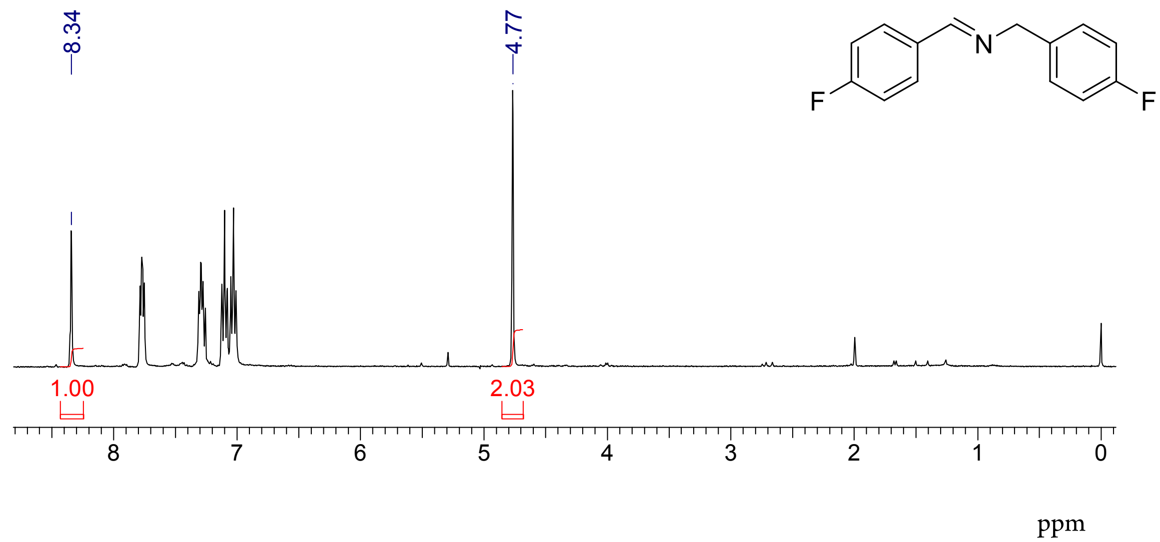


Figure S32. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 4-fluorobenzylamine with **B-3** as the photocatalyst.

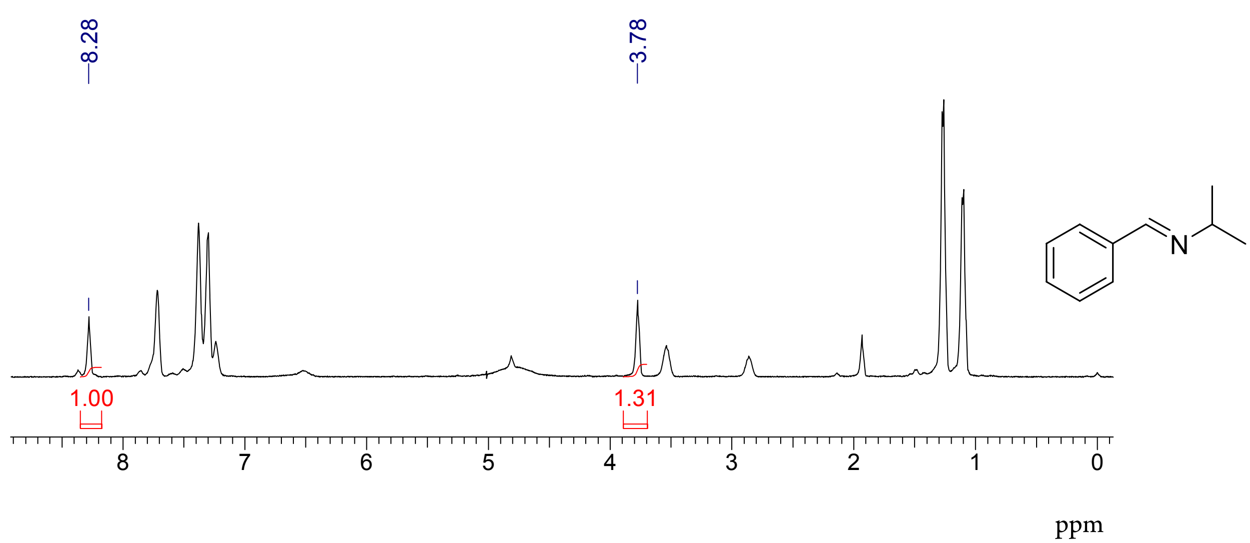


Figure S33. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of *N*-benzylisopropylamine with **B-4** as the photocatalyst.

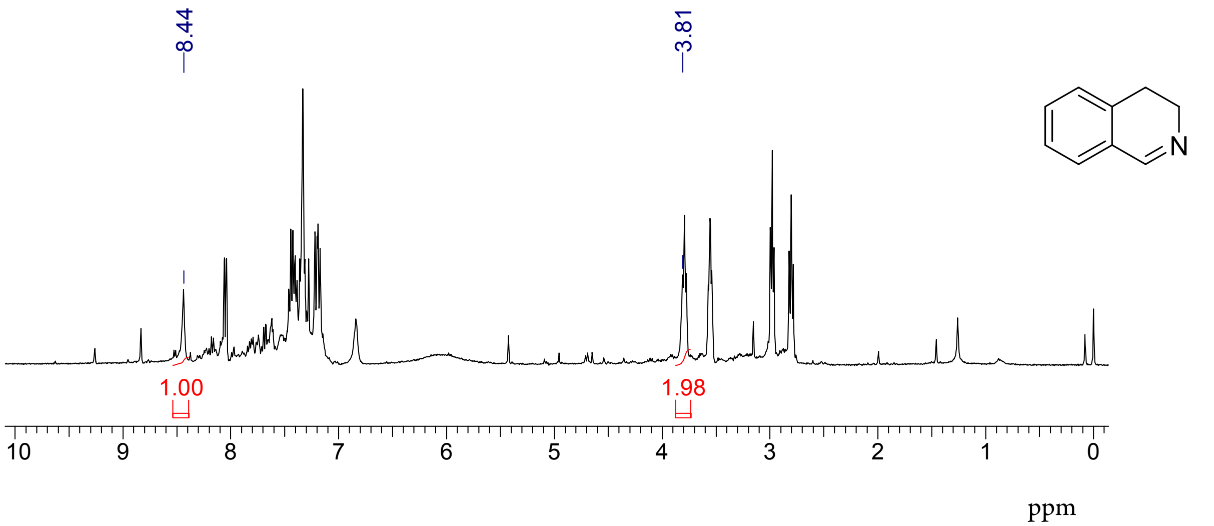


Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 1,2,3,4-tetrahydroisoquinoline with **B-4** as the photocatalyst.

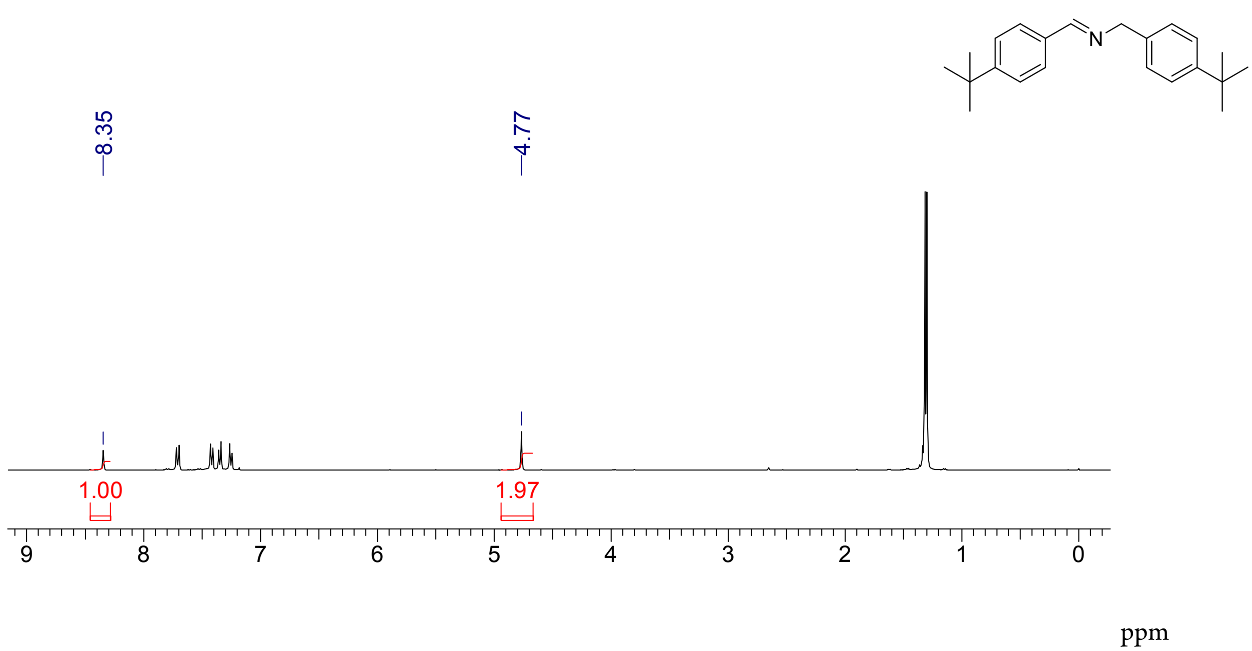


Figure S35. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$)of the crude product from aerobic oxidative coupling of 4-*tert*-butylbenzylamine with **B-1** as the photocatalyst.

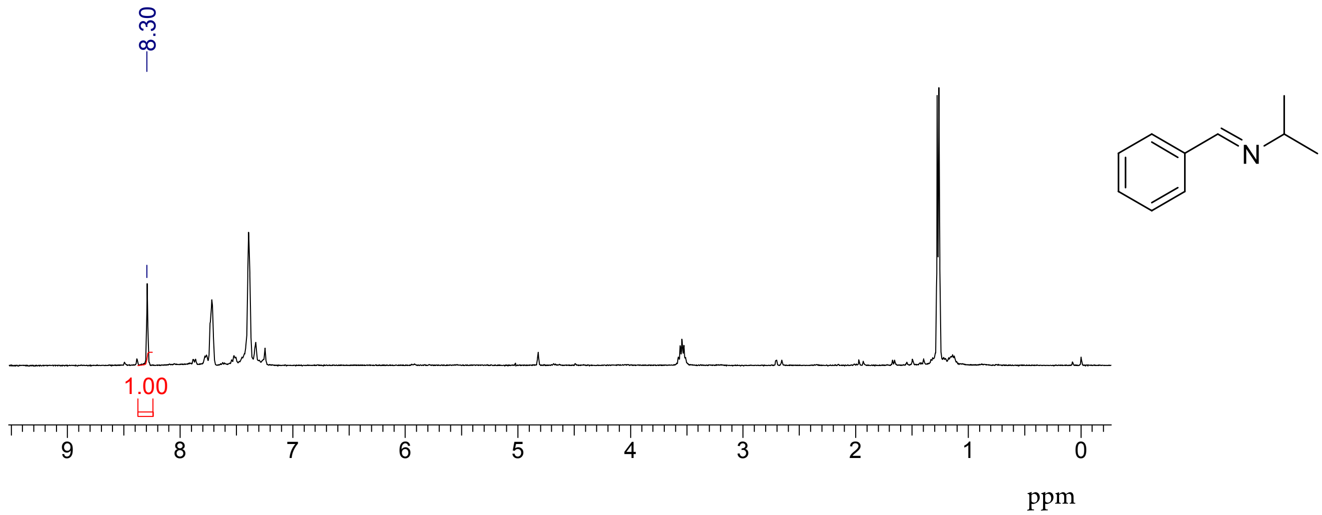


Figure S36. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of N-benzylisopropylamine with **B-3** as the photocatalyst.

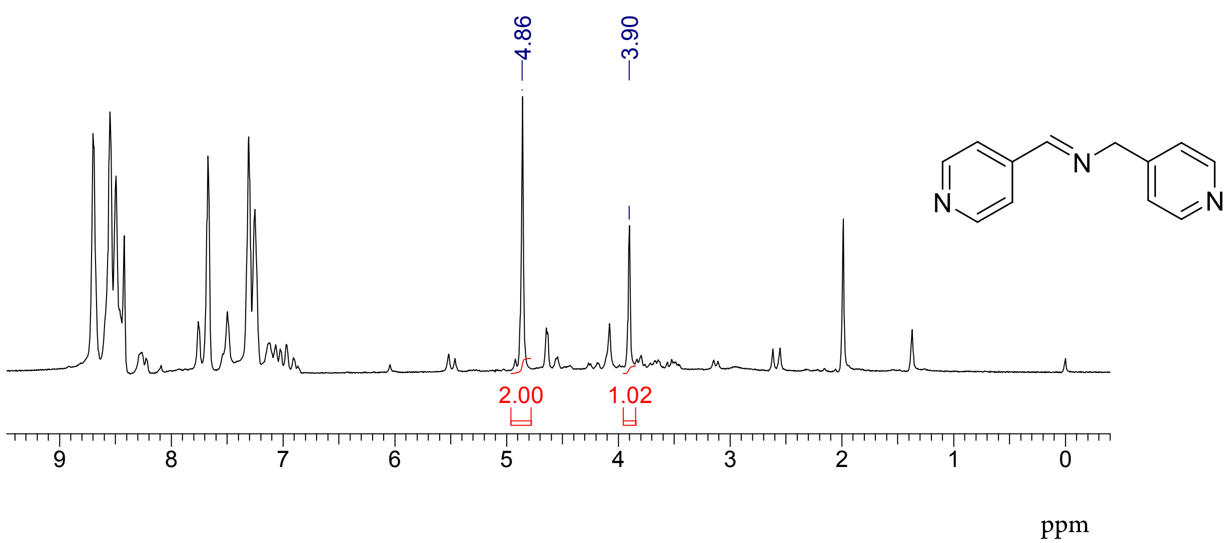


Figure S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of aminomethylpyridine with **B-1** as the photocatalyst.

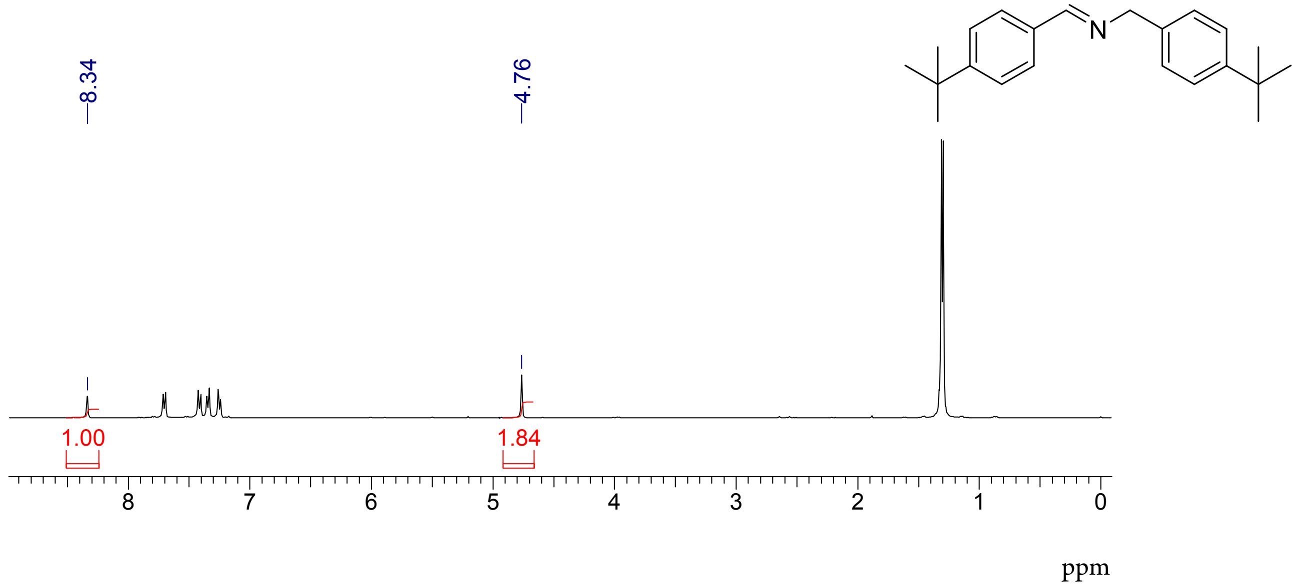


Figure S38. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 4-tert-butylbenzylamine with **B-2** as the photocatalyst.

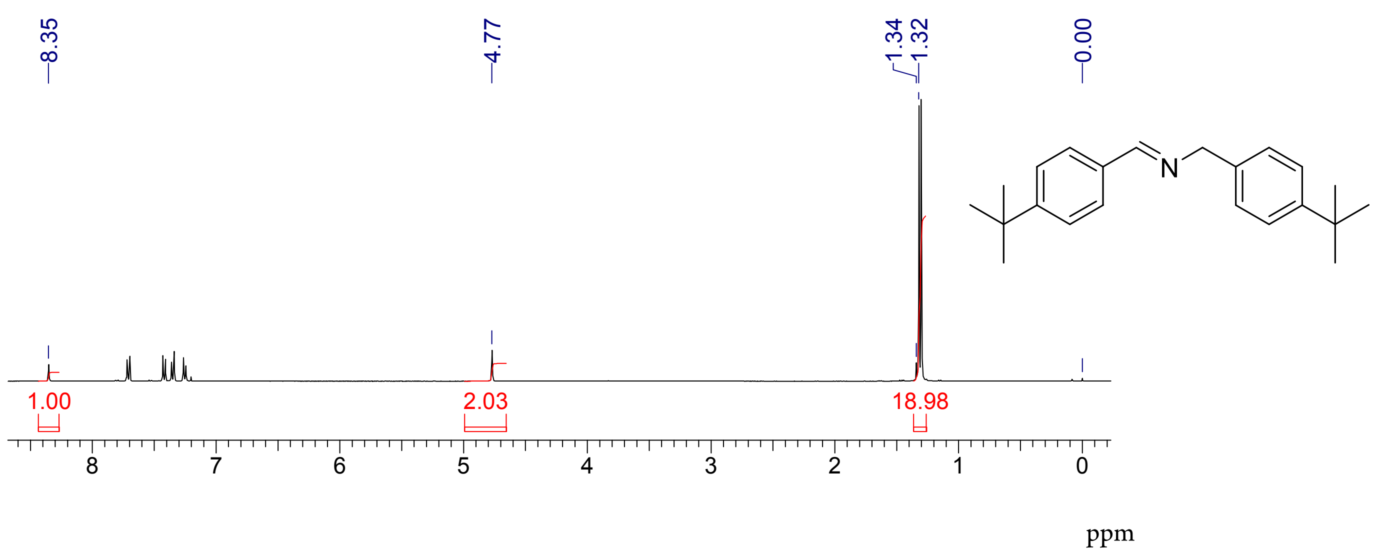


Figure S39. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 4-tert-butylbenzylamine with **B-4** as the photocatalyst.

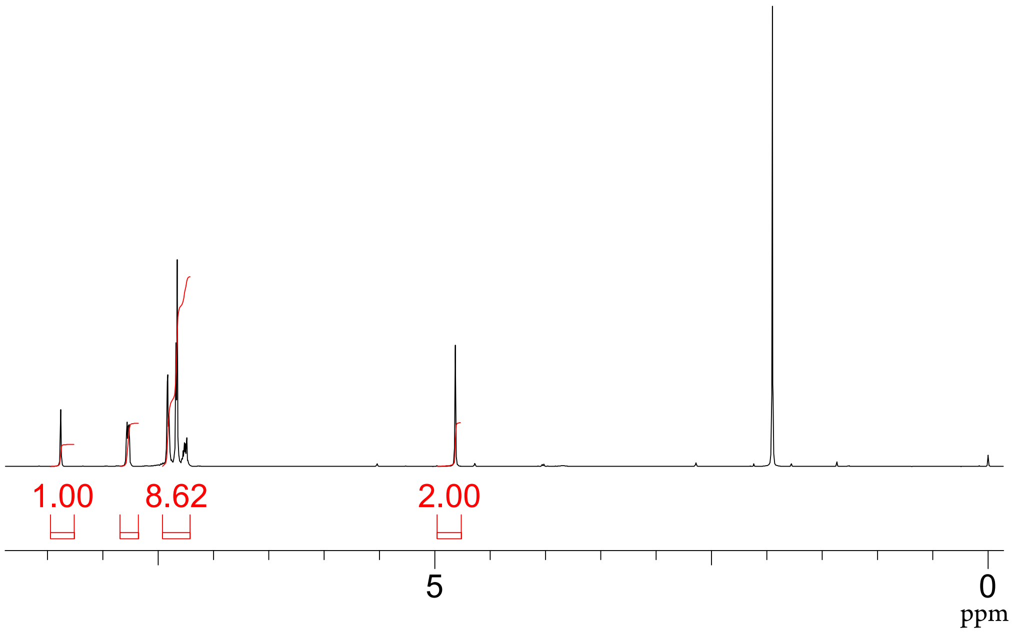


Figure S40. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine add **2 eqv. SOD** with **B-1** as the photocatalyst.

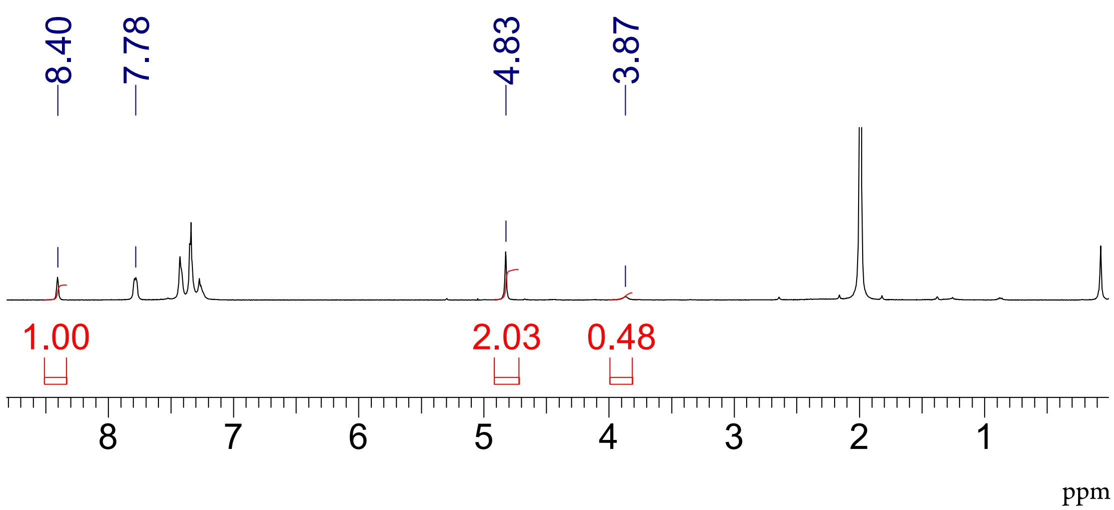


Figure S41. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with **B-1** as the photocatalyst. *No Histidine* was added.

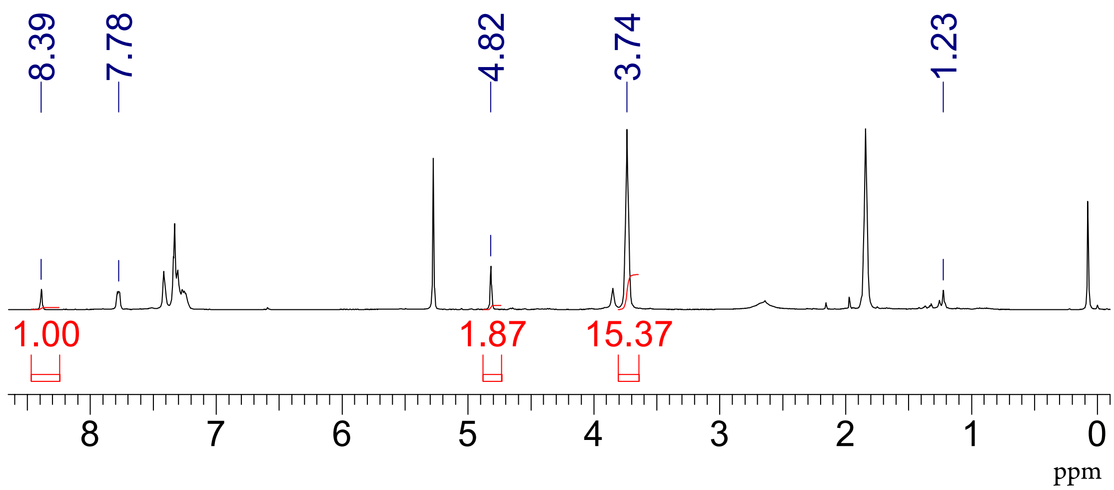


Figure S42. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with **B-1** as the photocatalyst. 2 eqv. Histidine was added.

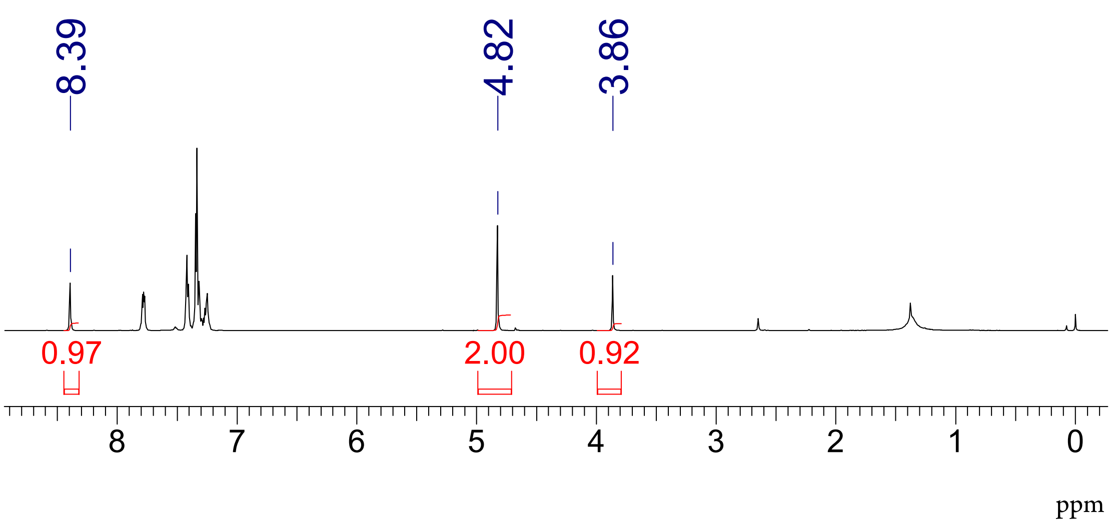


Figure S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with **B-1** as the photocatalyst. In $CDCl_3$. Reaction time was 20 min.

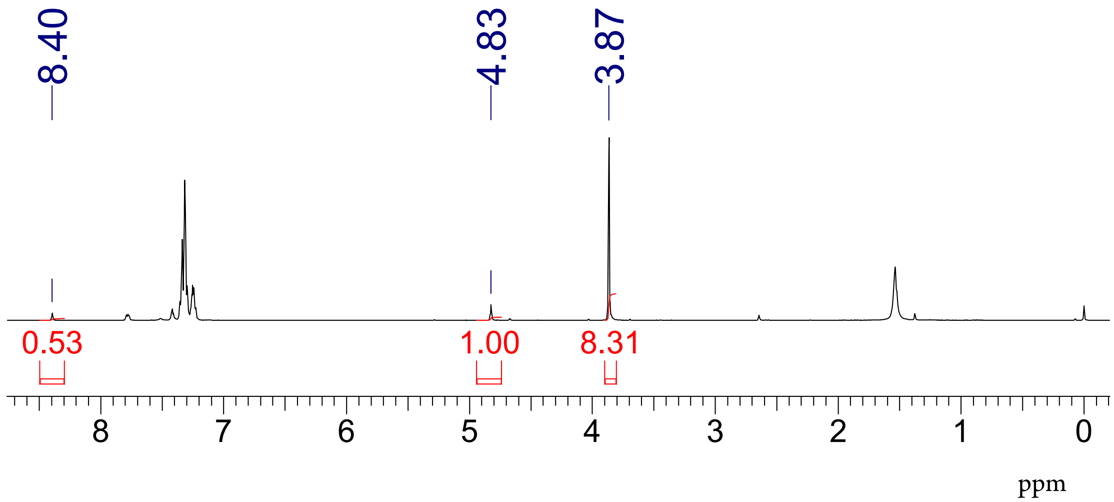


Figure S44. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with **B-1** as the photocatalyst. In $CHCl_3$. Reaction time was 20 min.

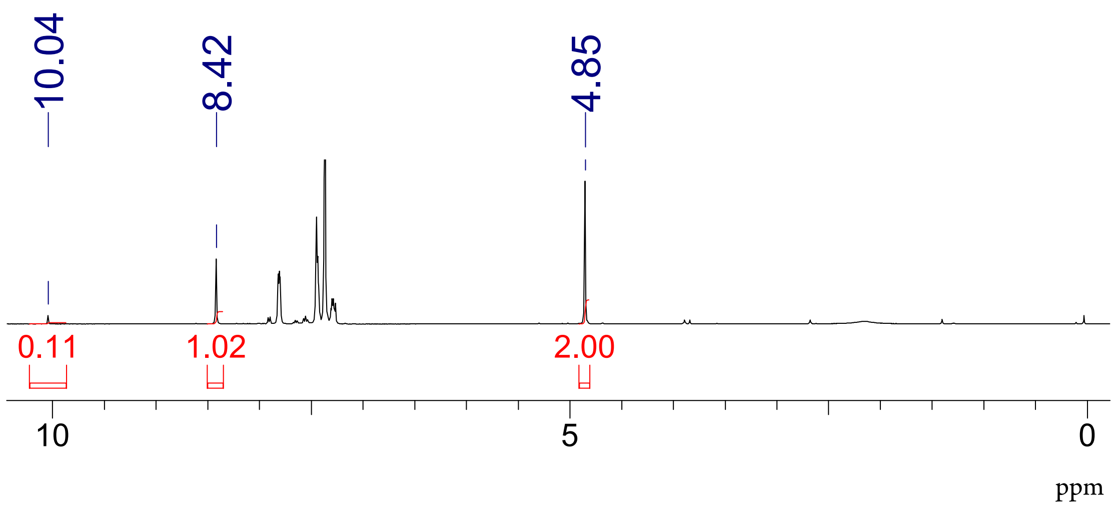


Figure S45. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of dibenzylamine with **B-1** as the photocatalyst. H_2O_2 peak at10.04 ppm was observed.

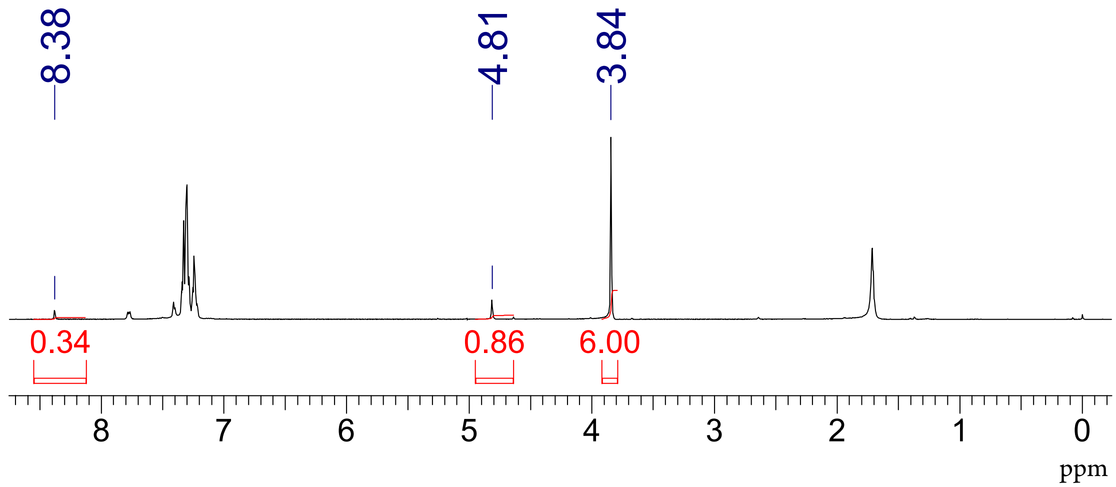
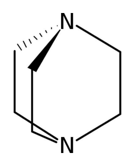


Figure S46. 1H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with B-1 as the photocatalyst. 0.0 mol % DABCO was added.



1,4-Diazabicyclo[2.2.2]octane;triethylenediamine
DABCO

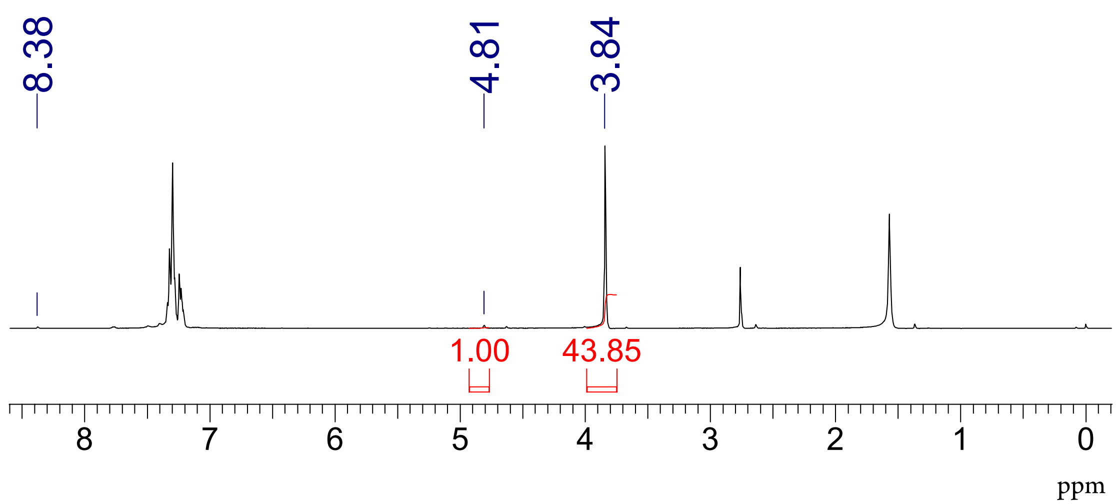


Figure S47. 1H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with B-1 as the photocatalyst. 5 mol % DABCO was added.

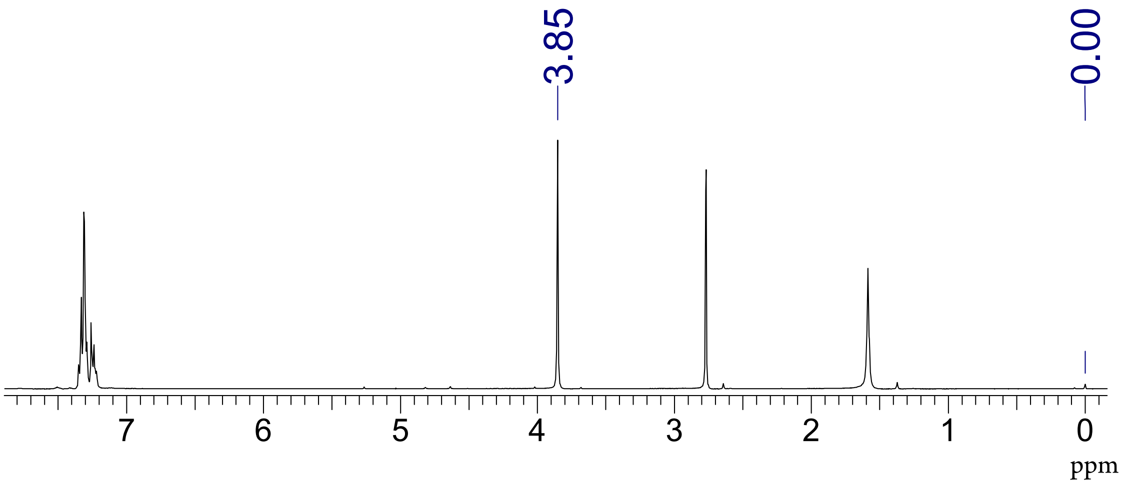
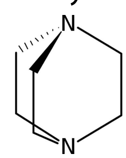


Figure S48. 1H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with B-1 as the photocatalyst. 10 mol % DABCO was added.



1,4-Diazabicyclo[2.2.2]octane;triethylenediamine
DABCO

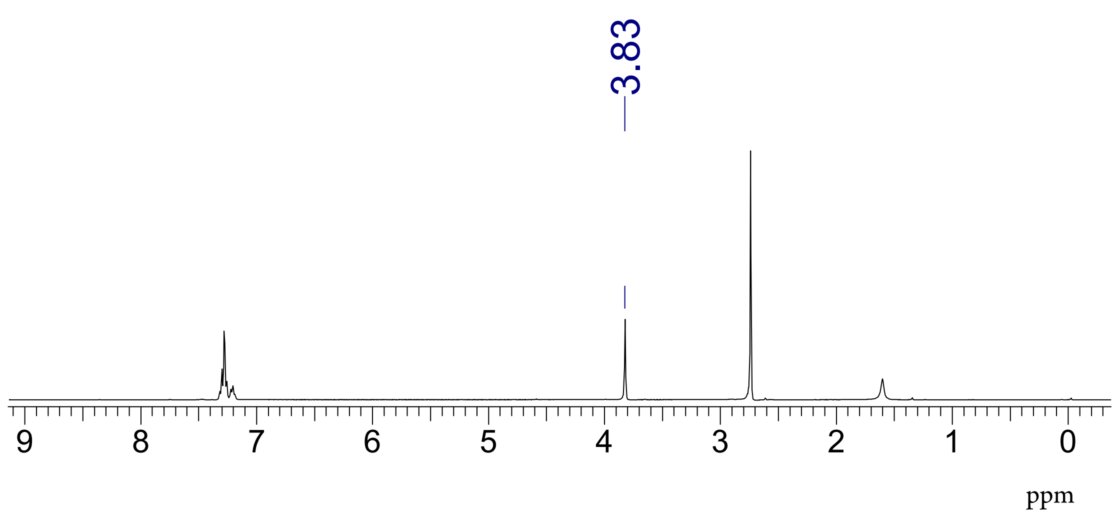


Figure S49. 1H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of benzylamine with **B-1** as the photocatalyst. 50 mol % DABCO was added.

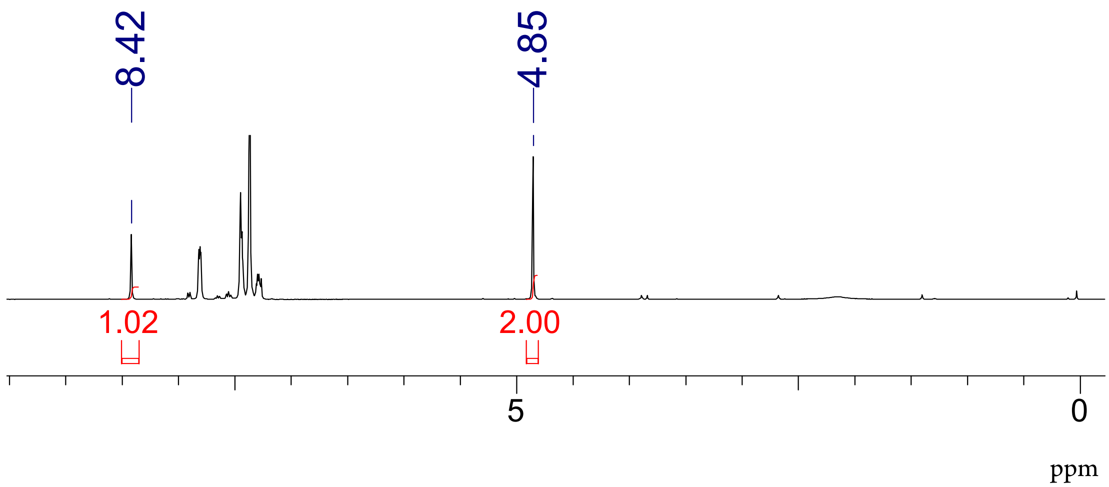


Figure S50. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of dibenzylamine with **B-1** as the photocatalyst. In $CDCl_3$. Reaction time was 120 min.

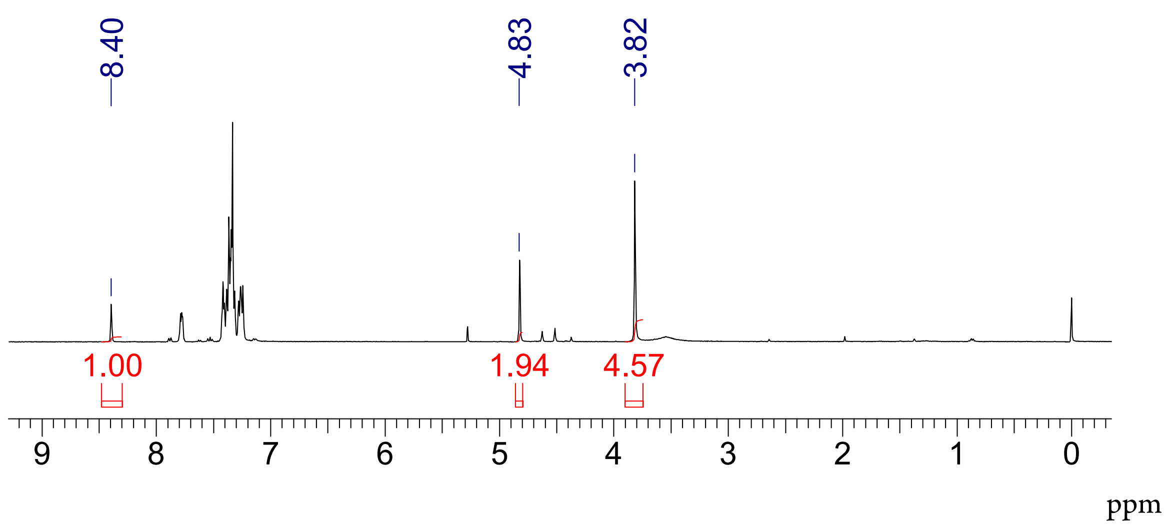


Figure S51. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of dibenzylamine with **B-1** as the photocatalyst. In $CHCl_3$. Reaction time was 180 min.

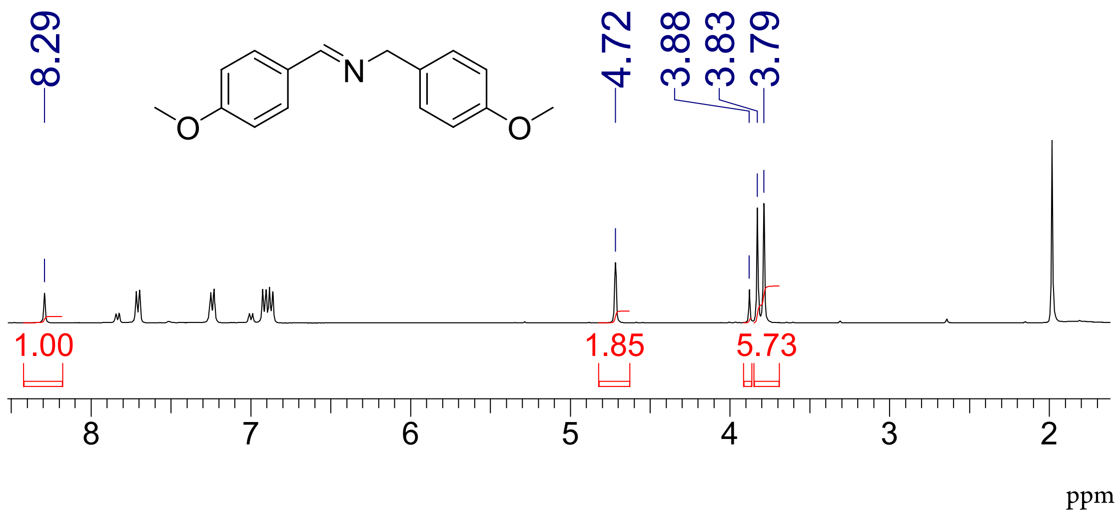


Figure S52. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 4-methoxybenzylamine with **B-1** as the photocatalyst.

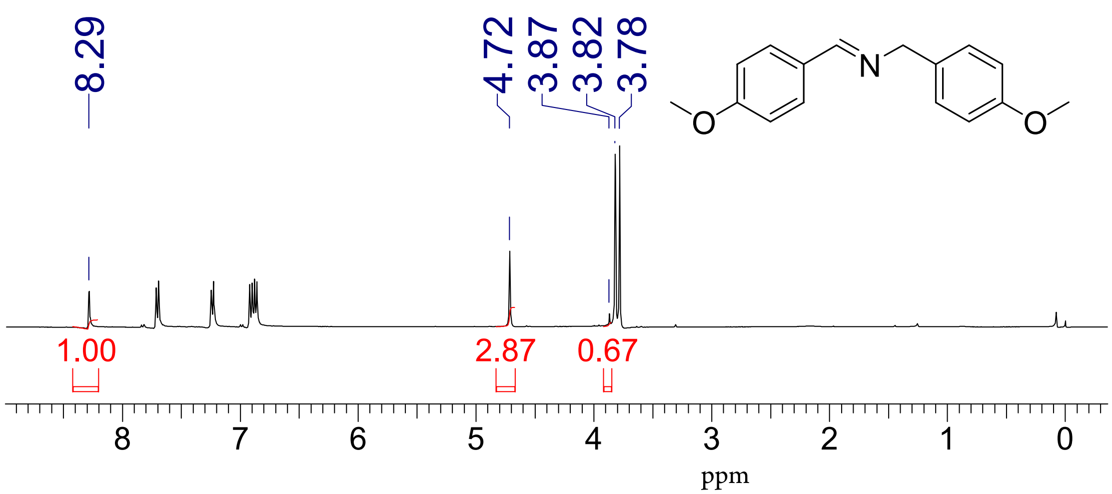


Figure S53. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 4-methoxybenzylamine with **B-4** as the photocatalyst.

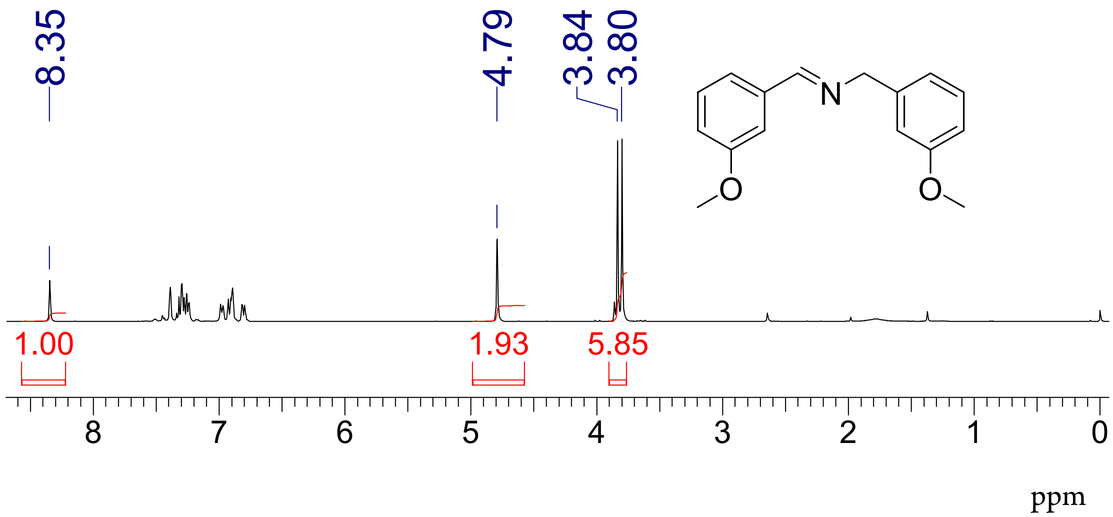


Figure S54. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 3-methoxybenzylamine with **B-1** as the photocatalyst.

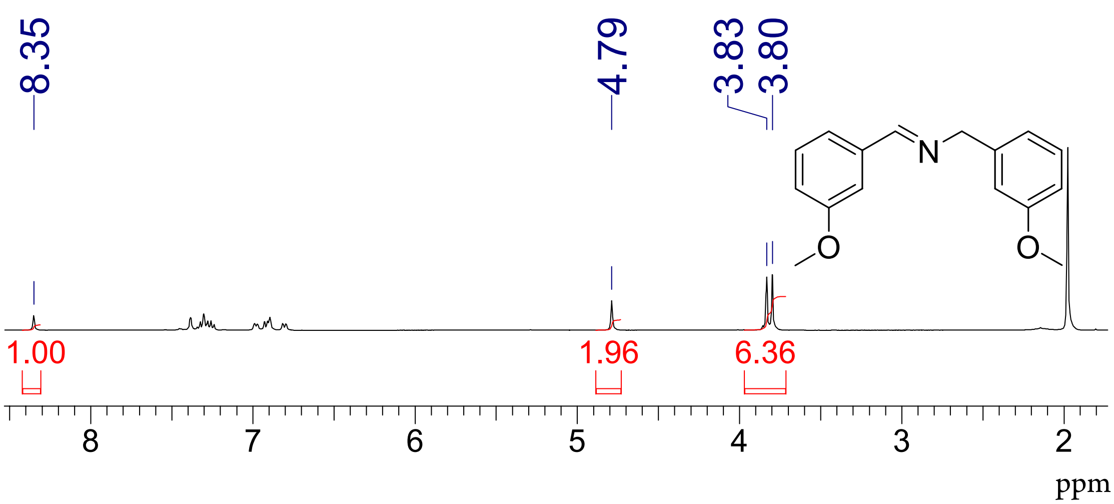


Figure S55. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 3-methoxybenzylamine with **B-4** as the photocatalyst.

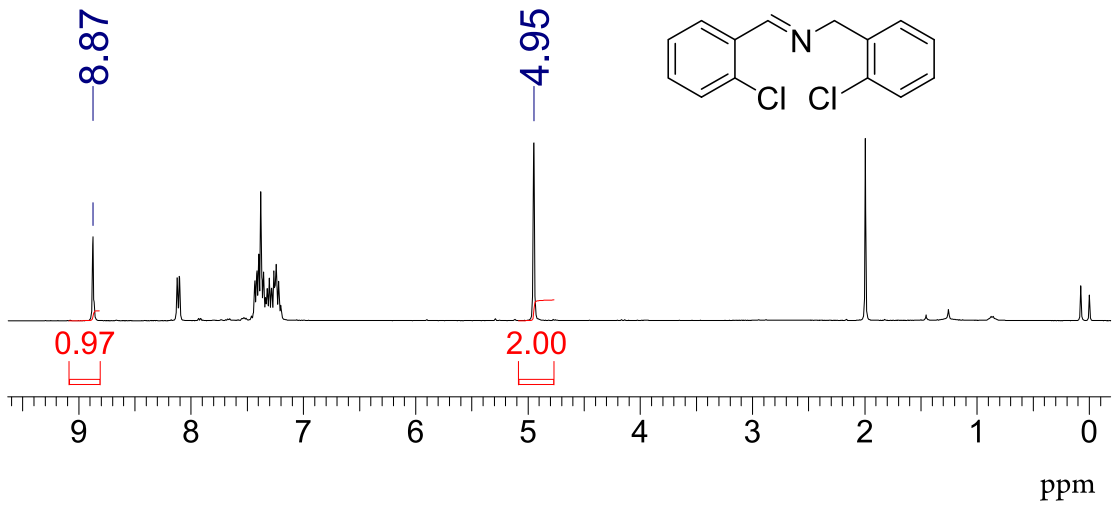


Figure S56. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 2-chlobenzylamine with **B-1** as the photocatalyst

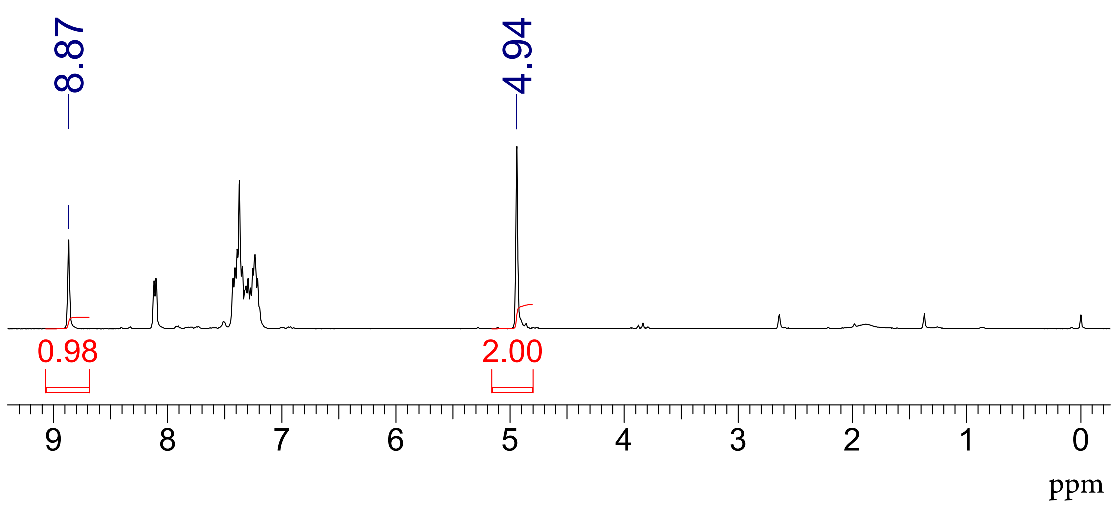


Figure S57. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 2-chlobenzylamine with **B-4** as the photocatalyst.

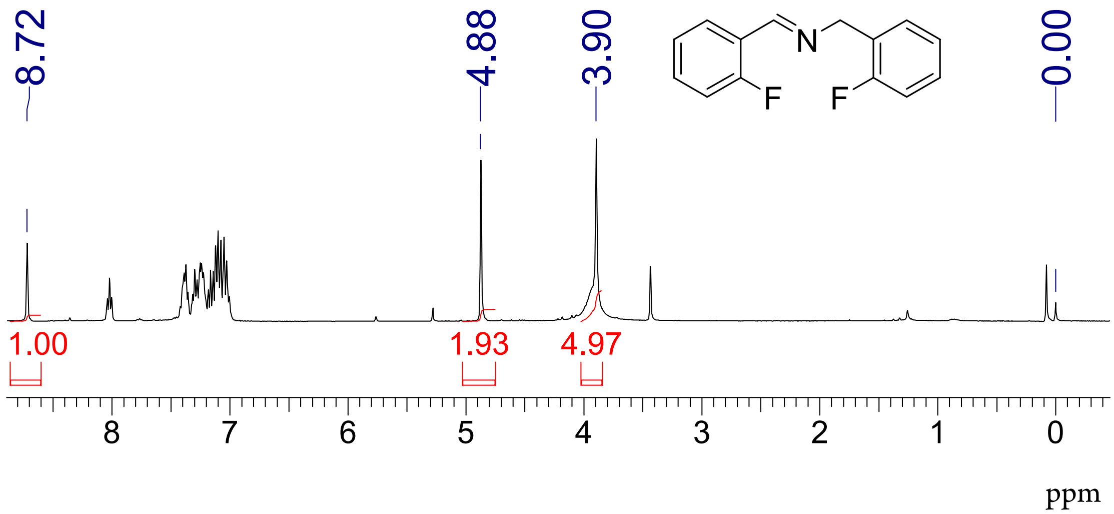


Figure S58. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 2-fluobenzylamine with **B-1** as the photocatalyst.

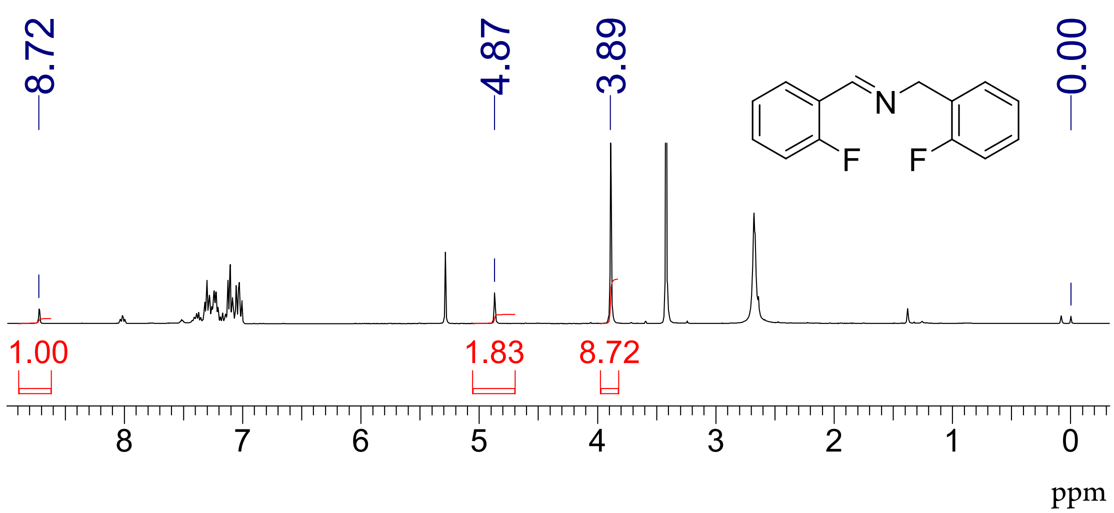


Figure S59. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 2-fluobenzylamine with **B-4** as the photocatalyst.

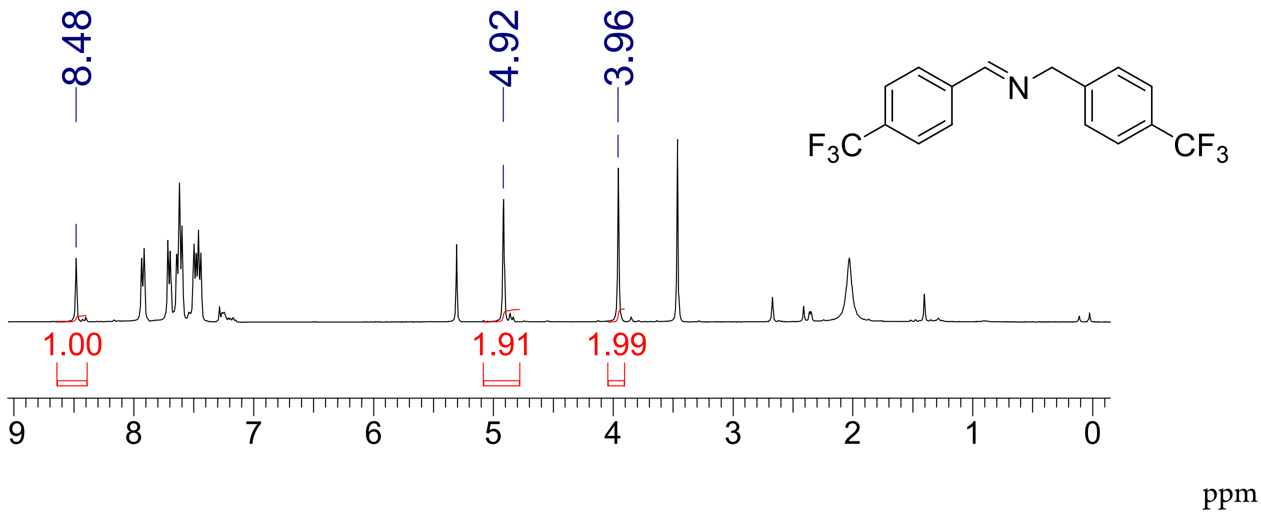


Figure S60. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 4- trifluoromethylbenzylamine with **B-1** as the photocatalyst

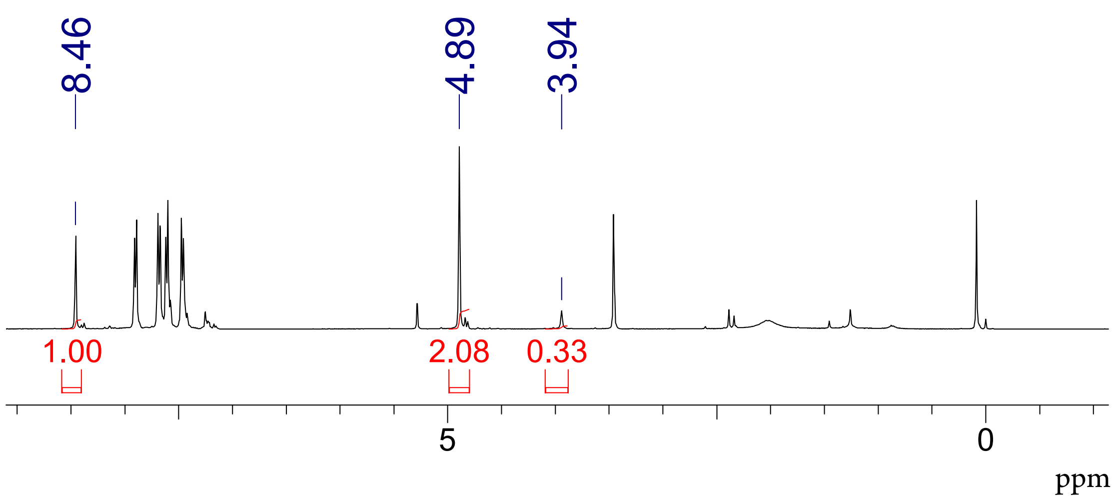


Figure S61. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude product from aerobic oxidative coupling of 4- trifluoromethylbenzylamine with **B-4** as the photocatalyst

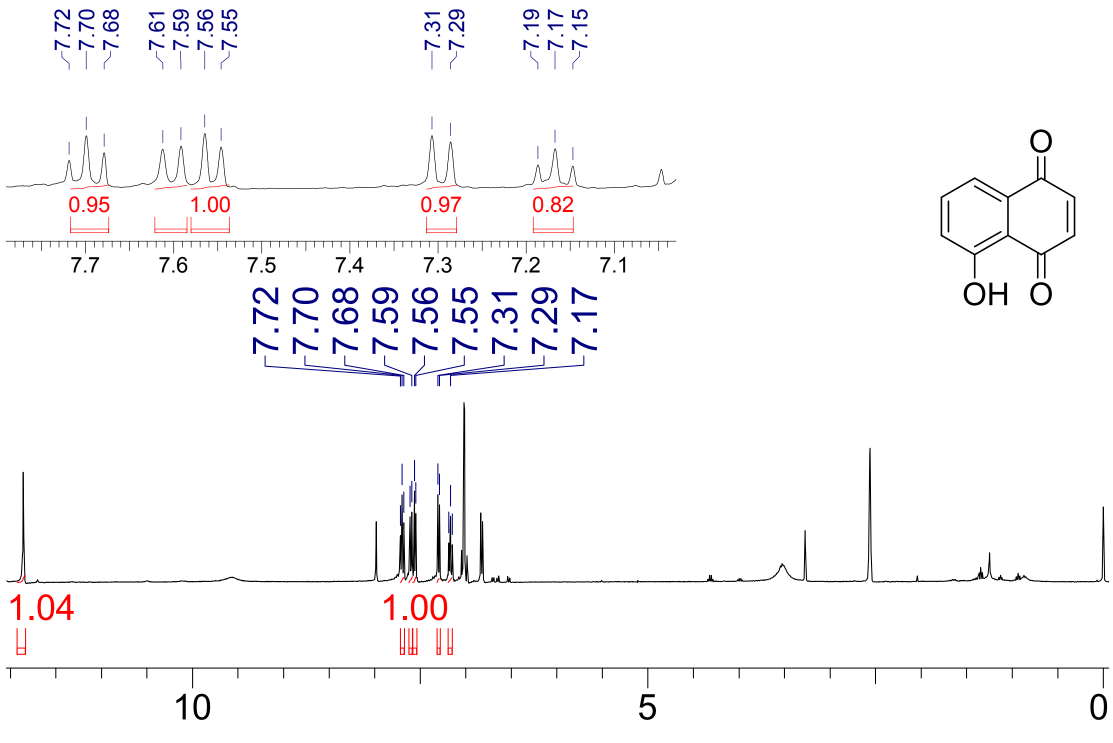
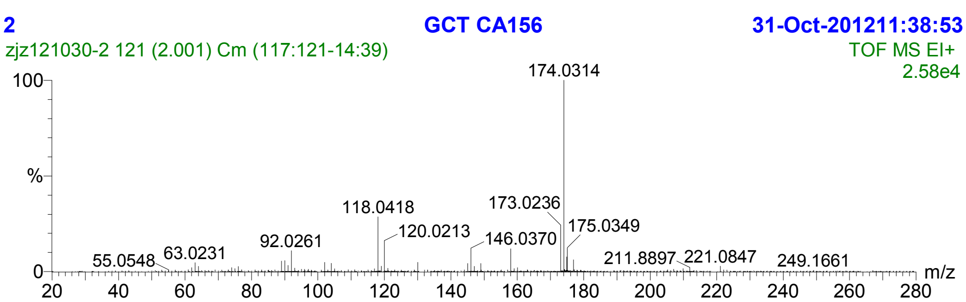


Figure S62. ^{1}H NMR spectrum of **2b**. (400 MHz, $CDCl_3/CD_3OD$).



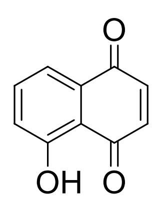


Figure S63. TOF HRMS EI$^+$ of **2b**.

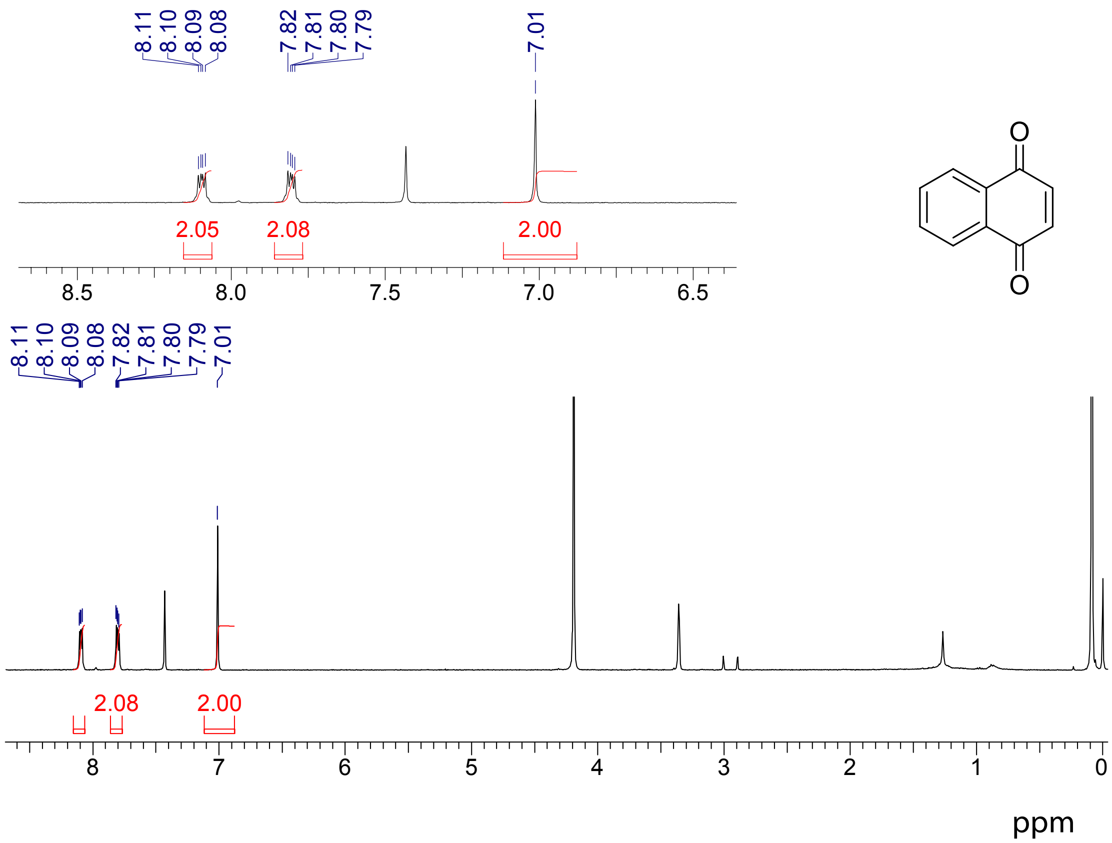


Figure S64. ^1H NMR spectrum of **2a** (400 MHz, $CDCl_3/CD_3OD$).

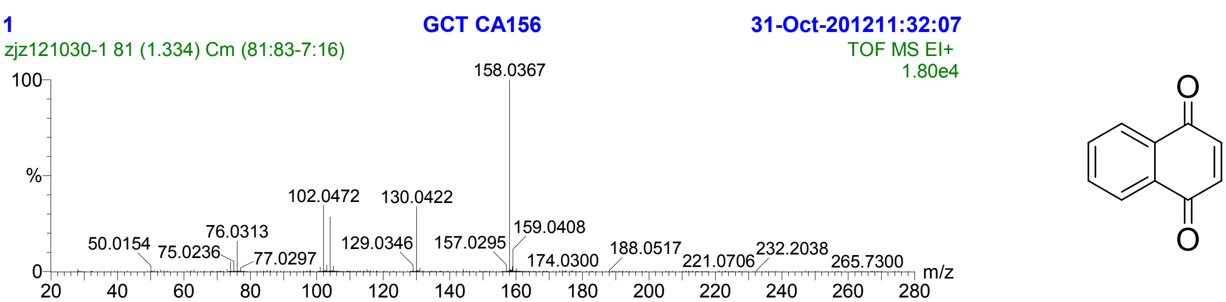


Figure S65. TOF HRMS EI^+ of **2a**.

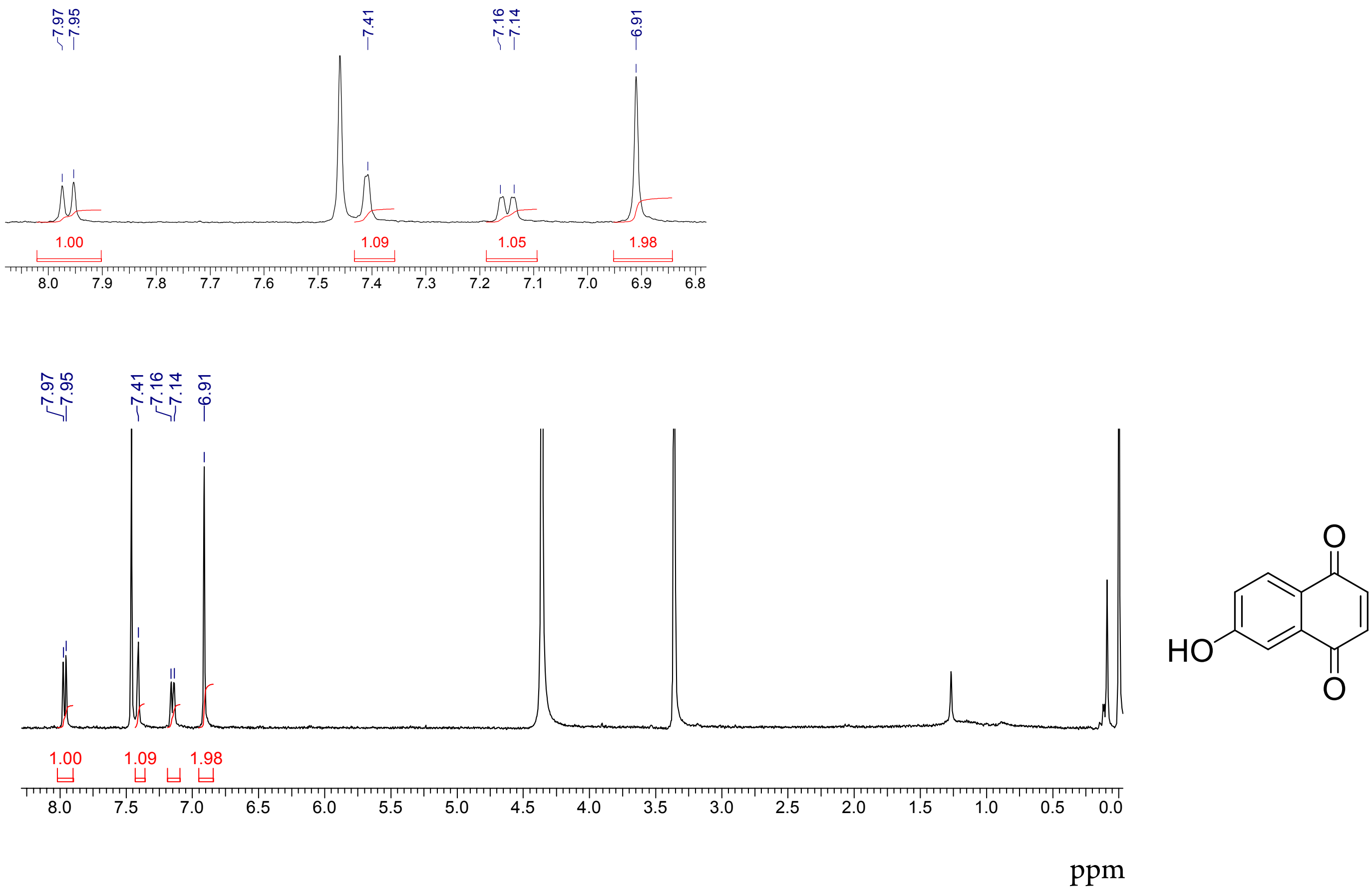


Figure S66. ^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3/CD_3OD$)**.**

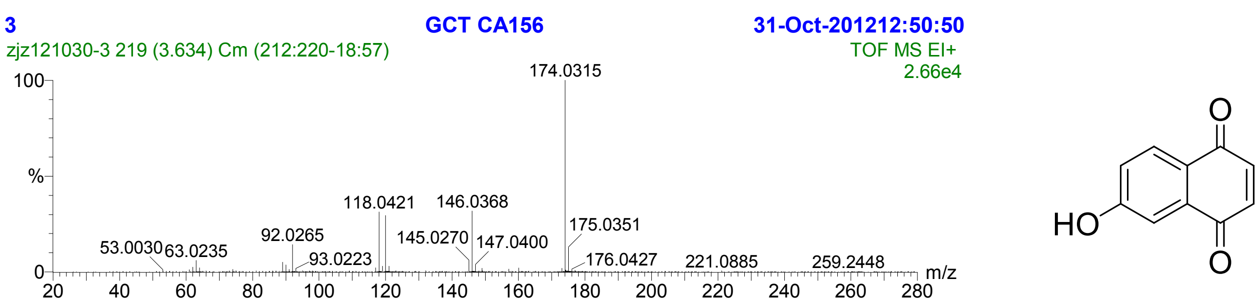


Figure S67. TOF HRMS EI^{+} of **2c**.

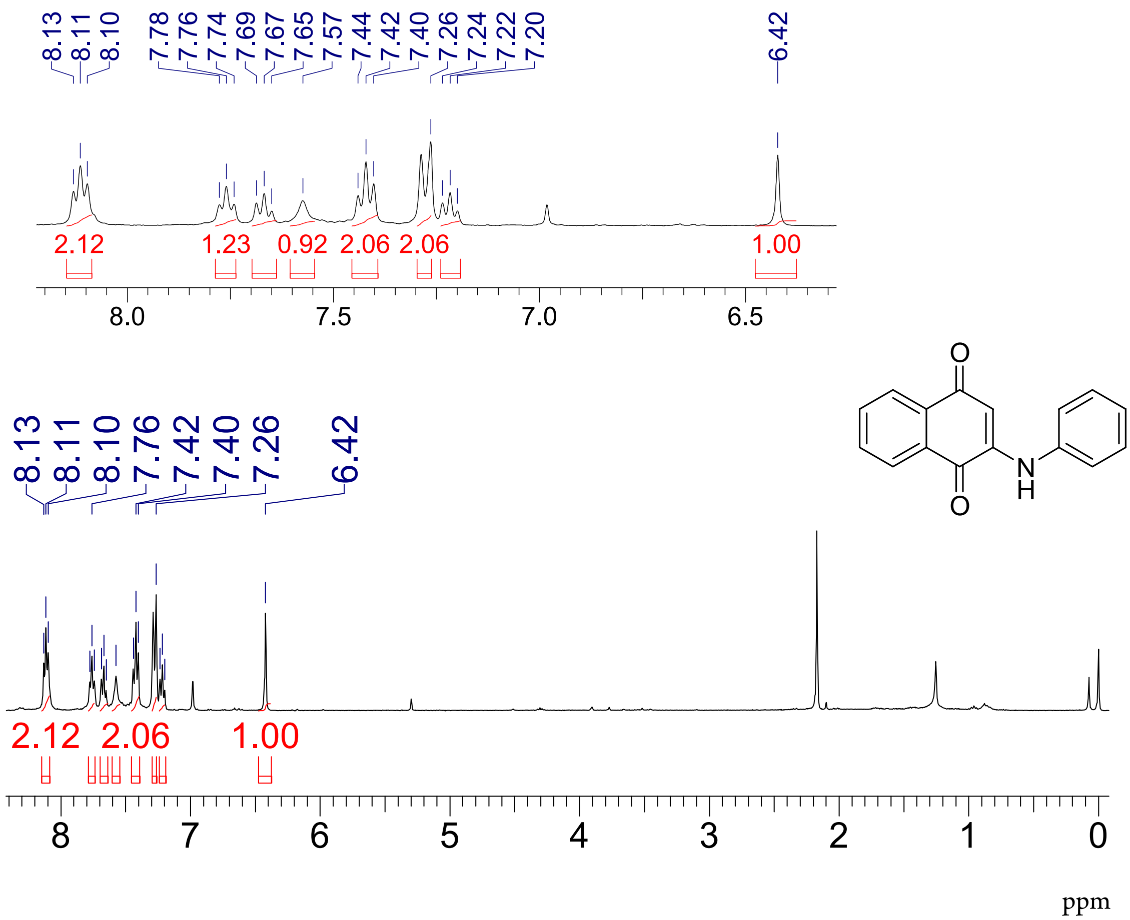


Figure S68. ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)**.**

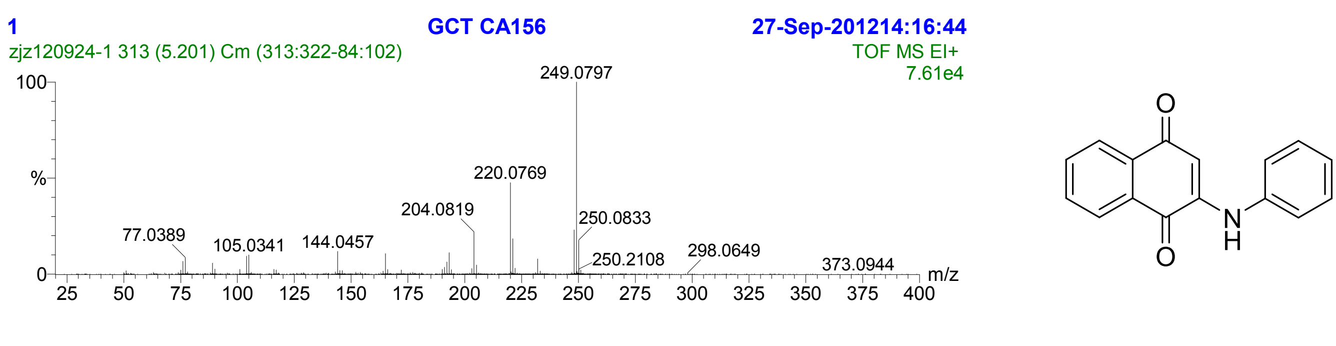


Figure S69. TOF HRMS EI^{+} of **3a**.

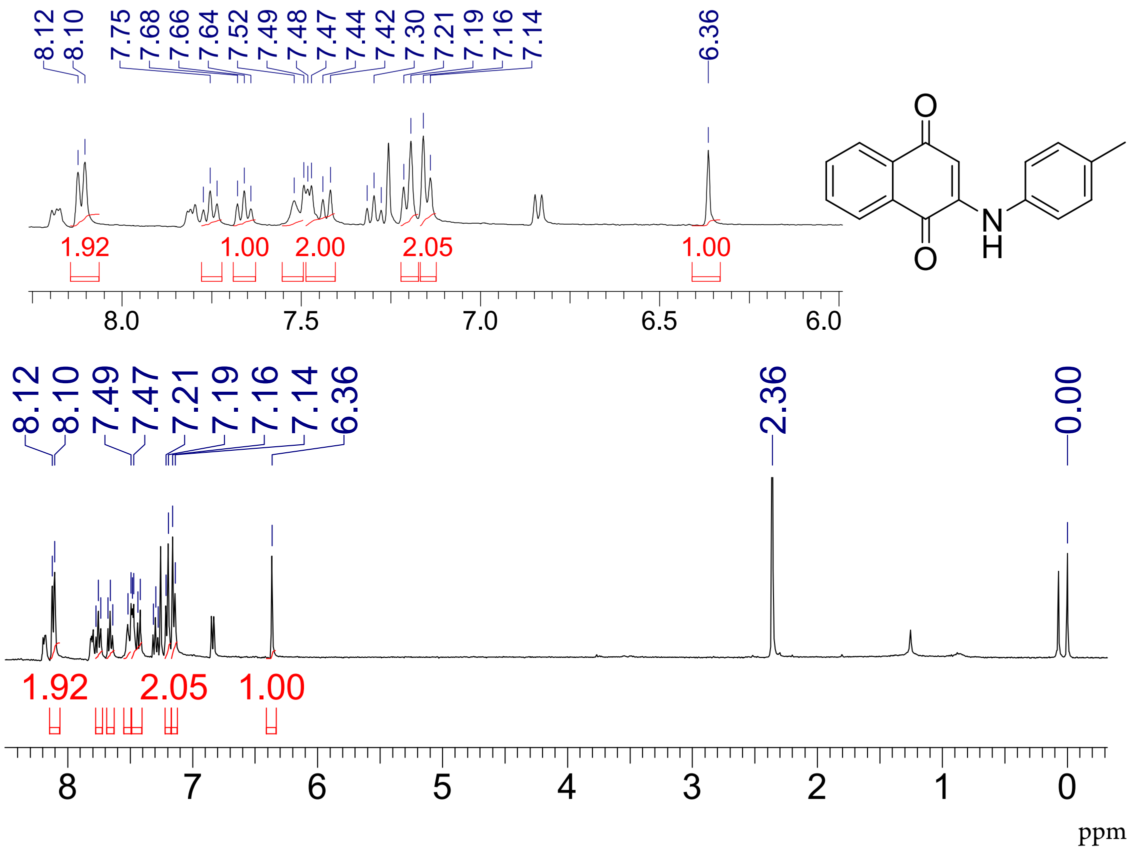


Figure S70. ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$) .

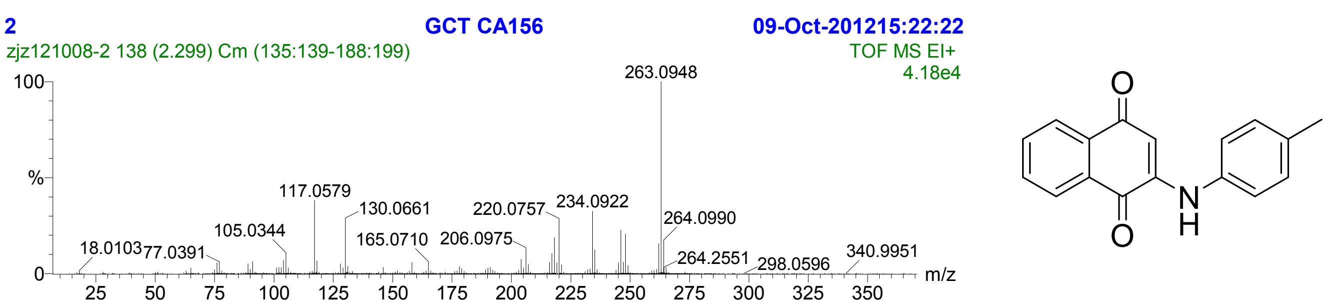


Figure S71. TOF HRMS EI+ of **3b**.

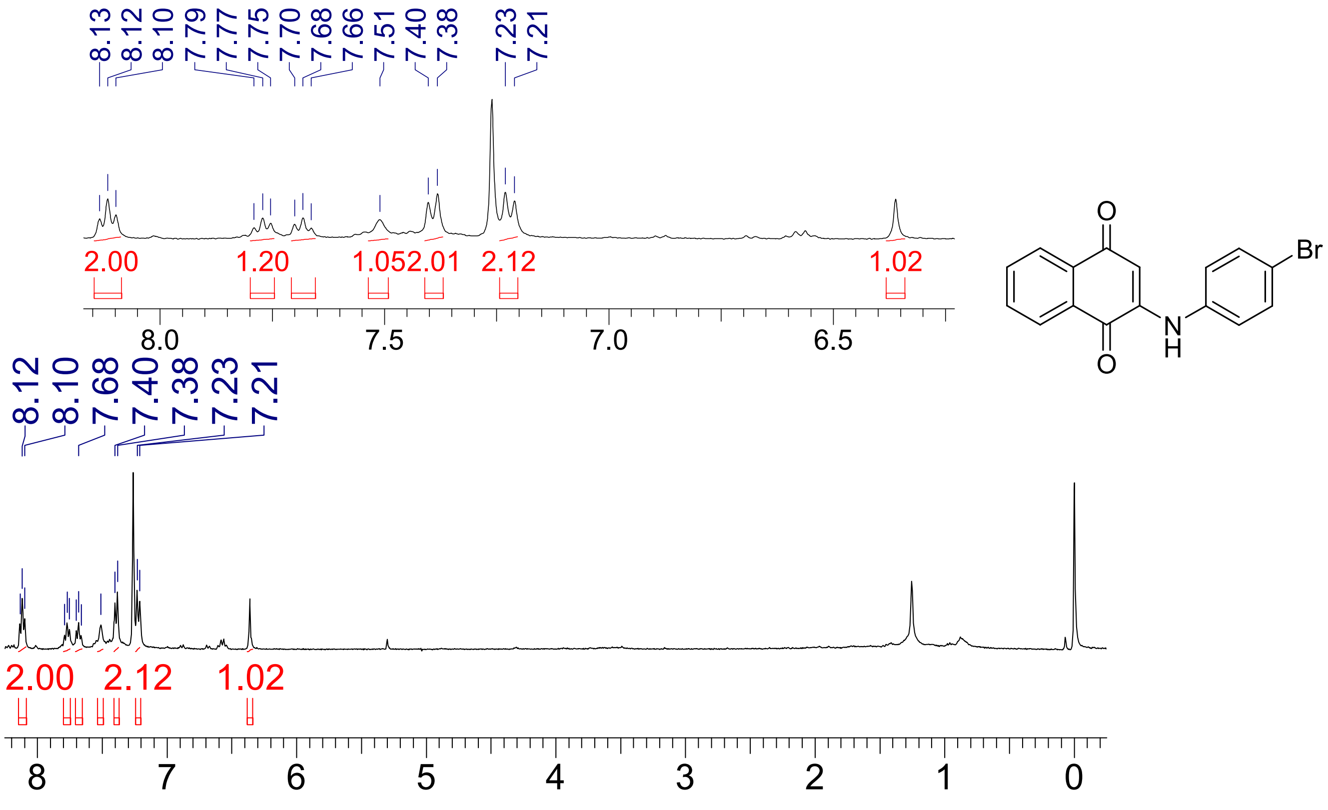


Figure S72. ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$).

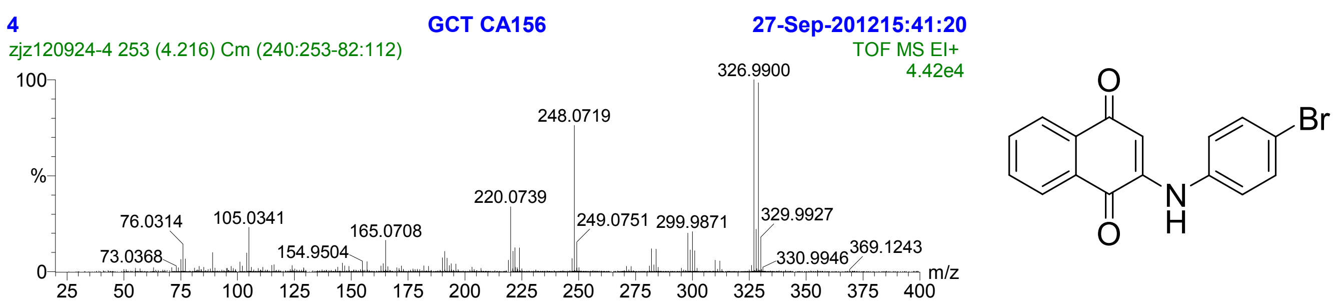


Figure S73. TOF HRMS EI$^+$ of **3c**.

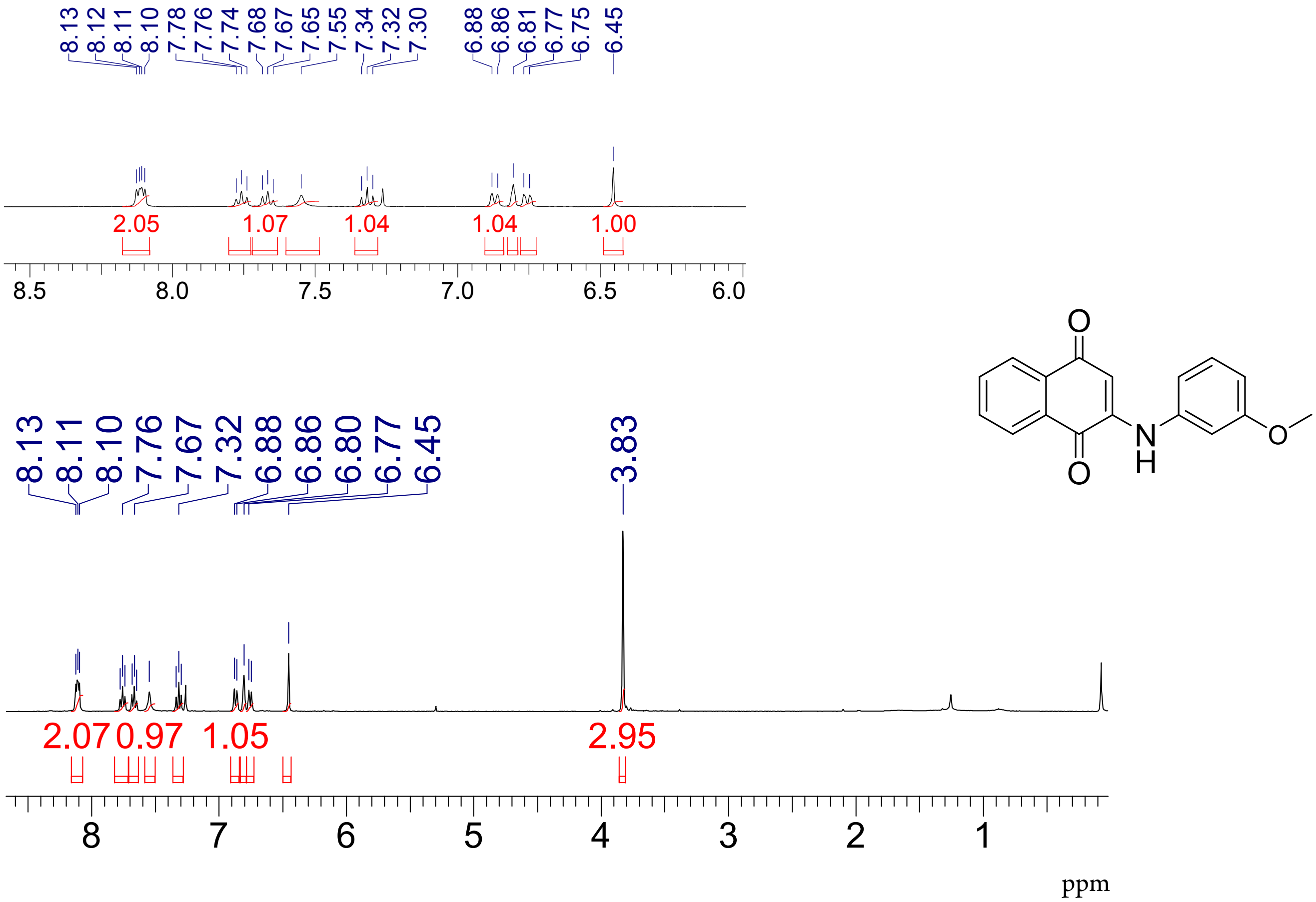


Figure S74. ^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)**.**

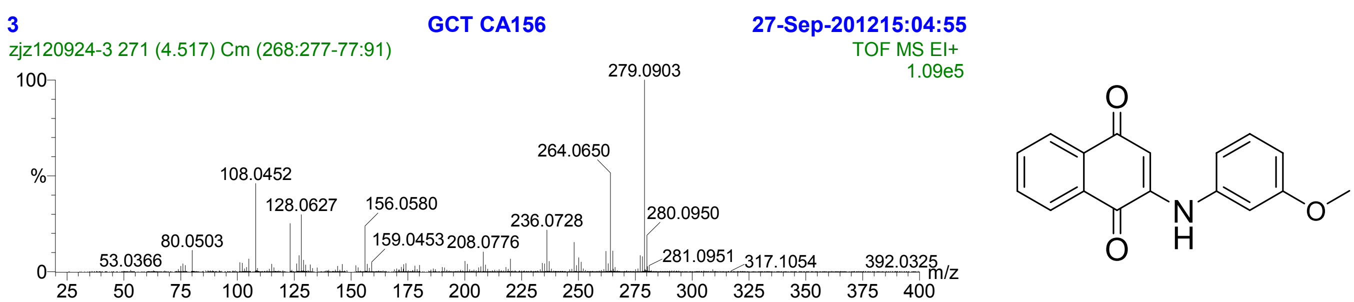


Figure S75. TOF HRMS EI$^+$ of **3d.**

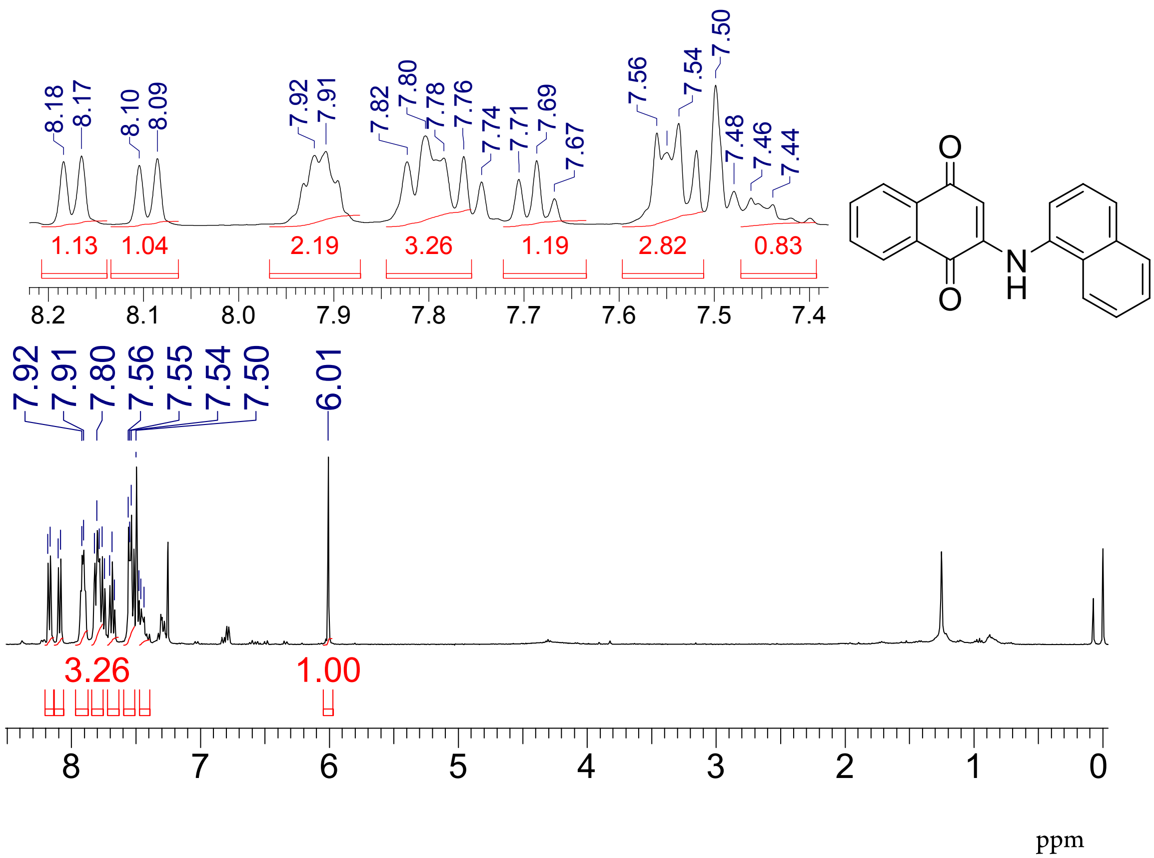


Figure S76. [1]H NMR spectrum of **3e** (400 MHz, $CDCl_3$).

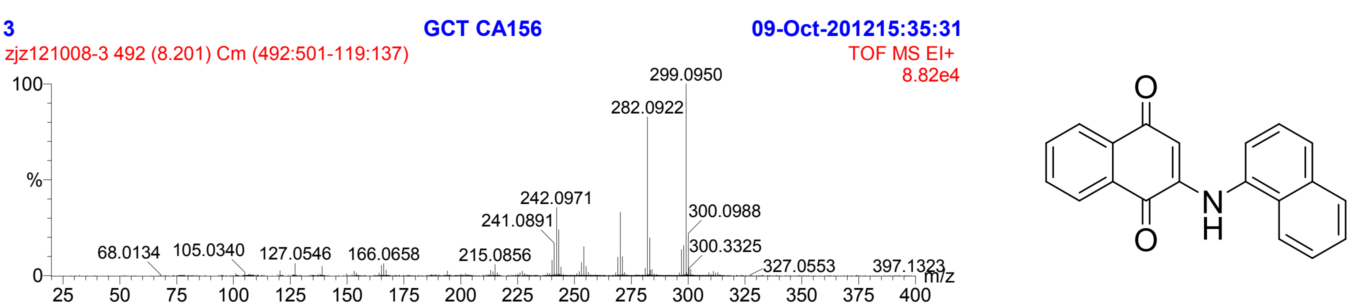


Figure S77. TOF HRMS EI^+ of **3e**

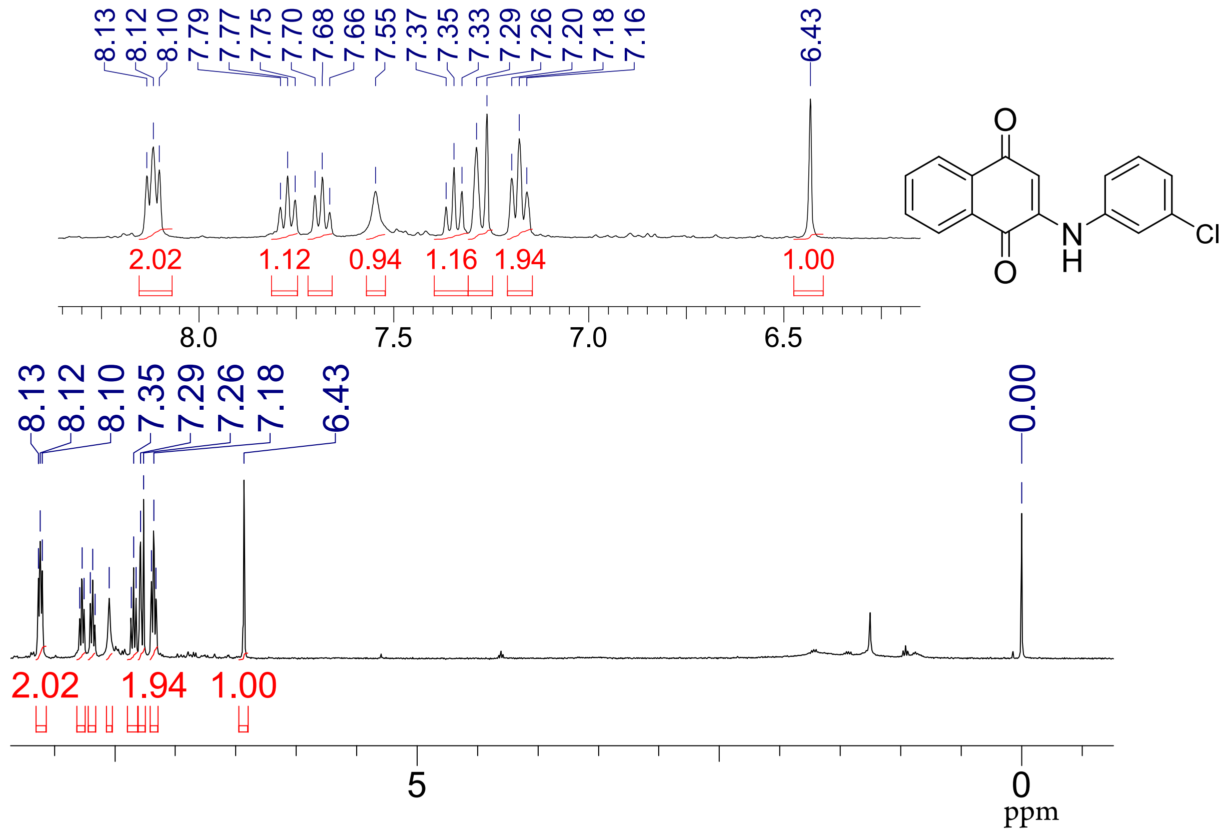


Figure S78. ^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)**.**

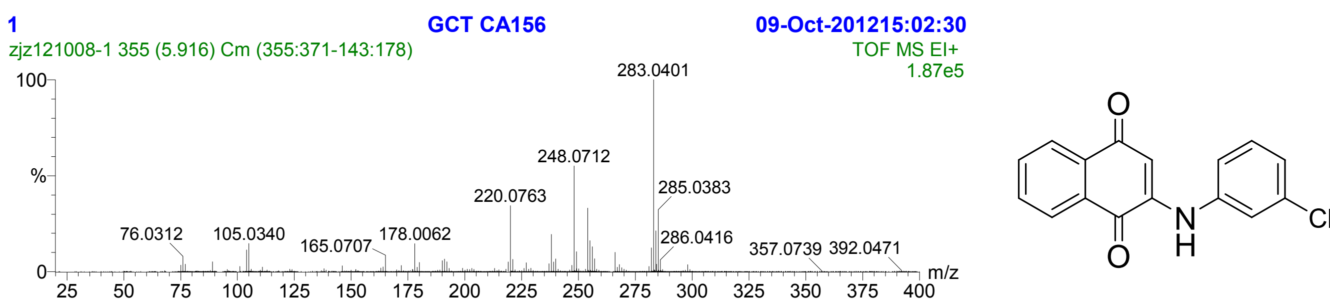


Figure S79. TOF HRMS EI^{+} of **3f.**

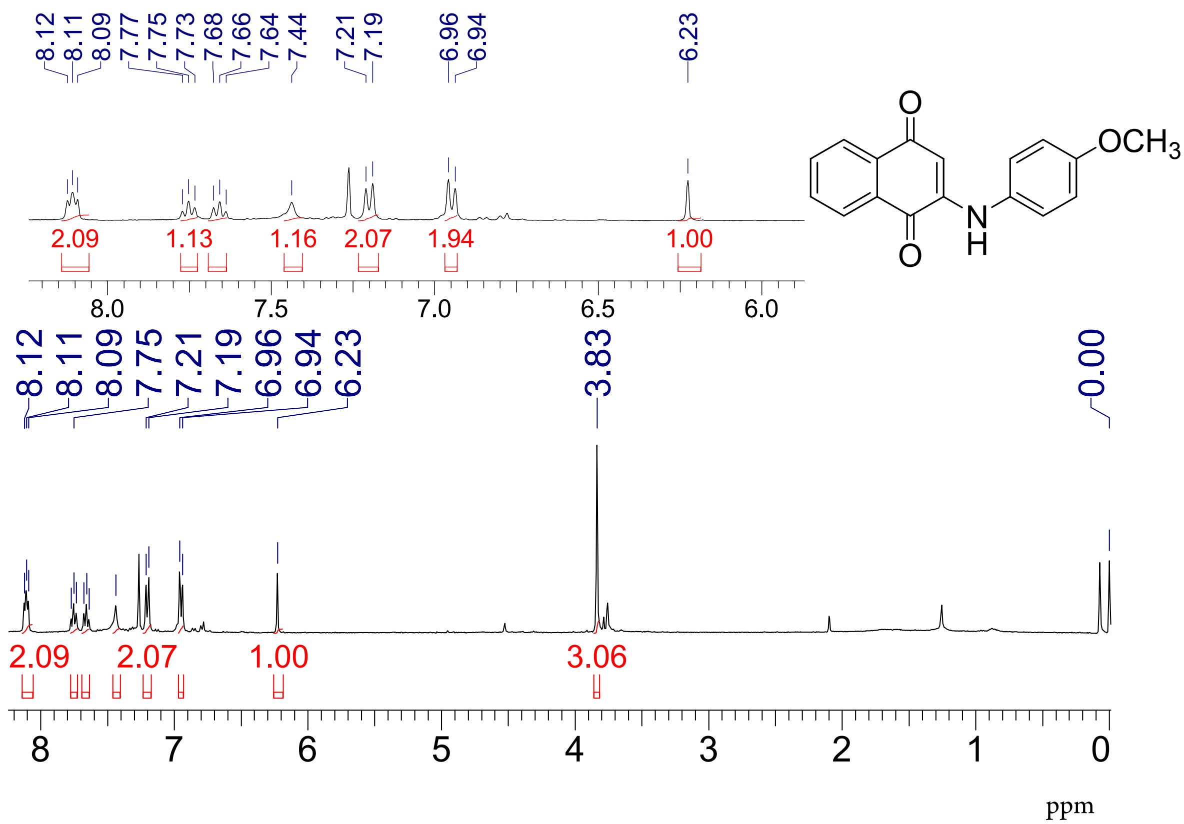


Figure S80. ^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$).

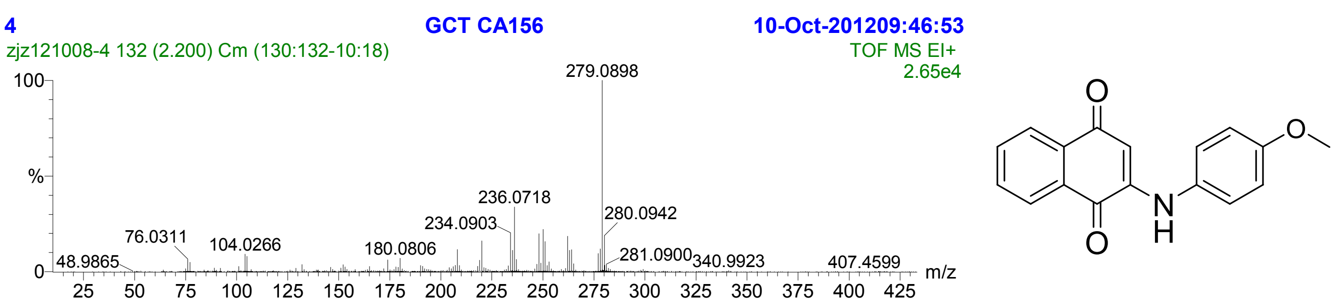


Figure S81. TOF HRMS EI^{+} of **3g.**

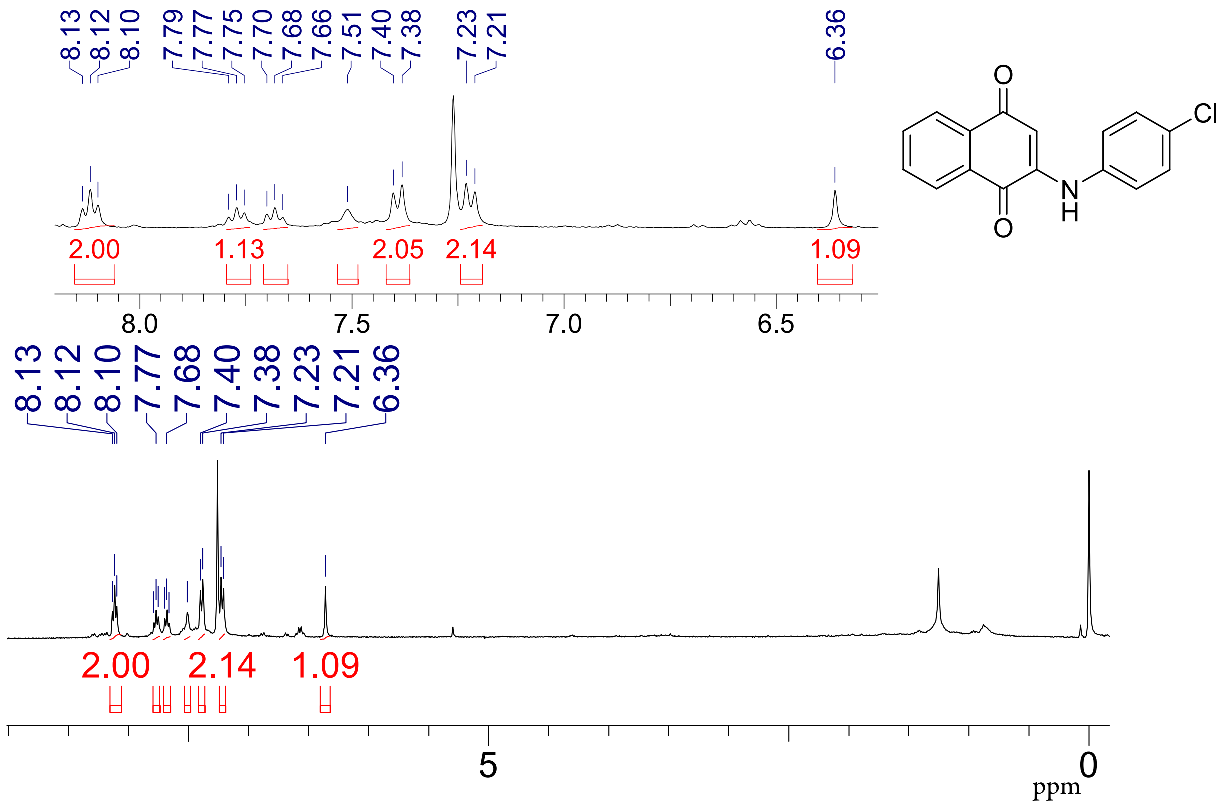


Figure S82. ^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$).

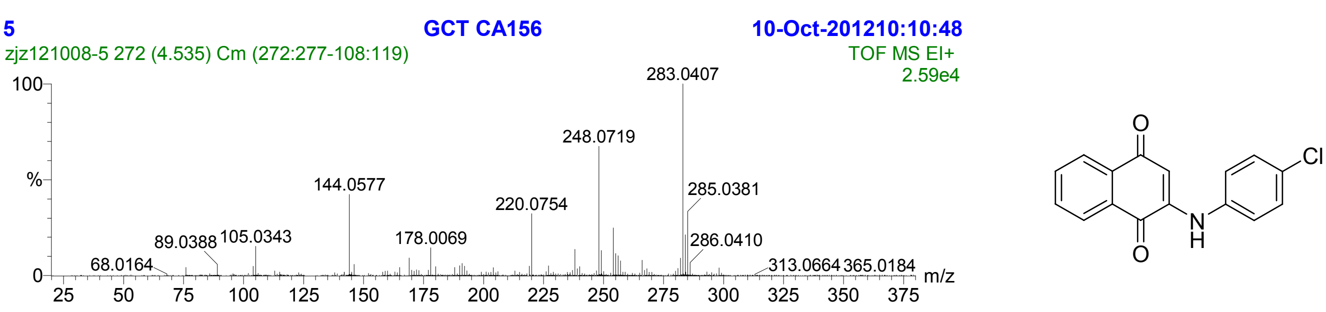


Figure S83. TOF HRMS EI^{+} of **3h.**

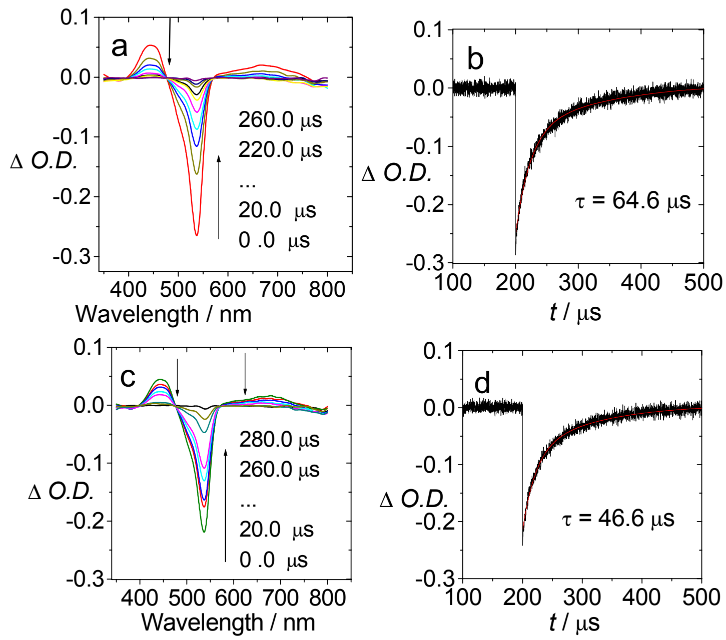
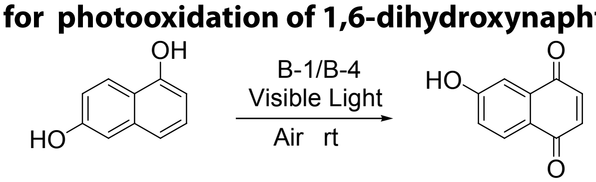


Figure S84. Nanosecond time-resolved transient difference absorption of **B-1**. (a) transient absorption difference spectra of **B-1** and (b) decay trace at 540 nm. Transient difference absorption of **B-1** in the presence of 100 eq benzylamine, (c) transient absorption difference spectra and (d) decay trace at 540 nm. In deaerated CH_3CN. 1.0 × 10^{-5} M, λ_{ex} = 532 nm, 25 °C.

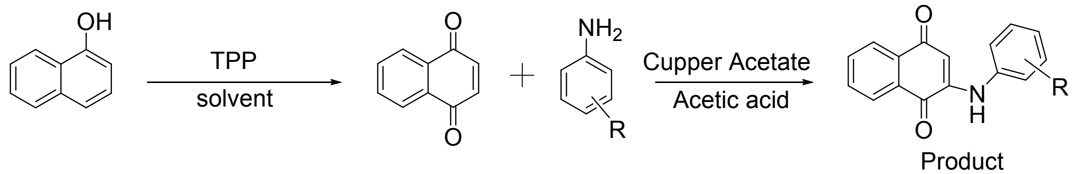
Table S3. Recycling of B-4 for photooxidation of 1,6-dihydroxynaphthalene [a]

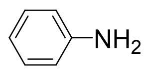
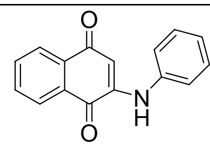
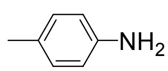
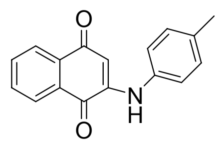
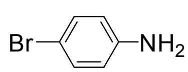
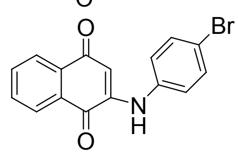
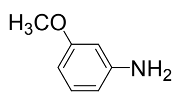
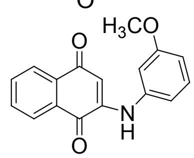
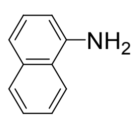
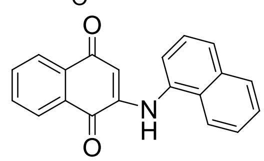
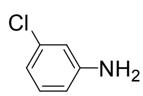
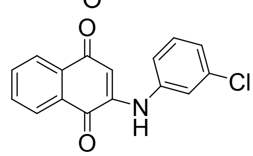
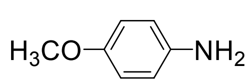
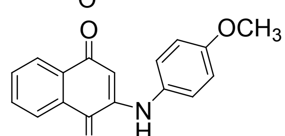
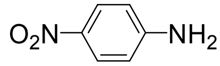
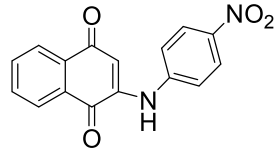


Recycle time	**1**	**2**	**3**	**4**	**5**
Yield % [b]	87	85	83	86	82

[a] Reaction conditions: 1,6-dihydroxynaphthalene (0.10 mmol), catalyst **B-4** (2 mol%), 35 W Xe light irradiation (λ> 385 nm, 30 mW/cm^2), and CH_2Cl_2/CH_3OH(5.0 mL, v/v = 4/1), reaction time 30 min, r.t.. [b] Yield of the isolated product.

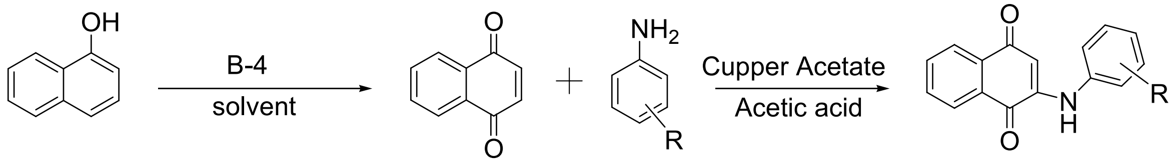
Table S4. **Photooxidation of naphthol and aniline addition oxidation with TPP** [a]



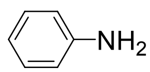
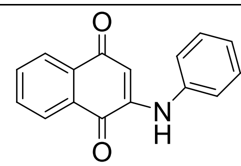
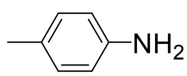
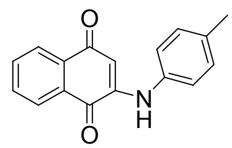
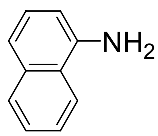
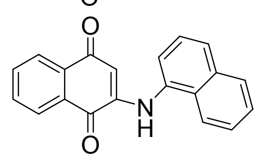
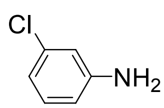
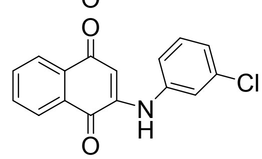
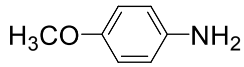
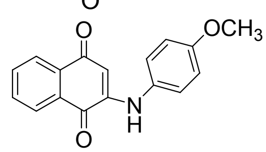
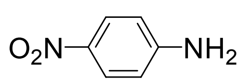
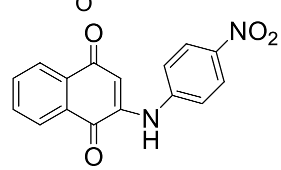
Entry	Aniline derivatives	Product	Yield%[b]
1			64
2			52
3			47
4			63
5			54
6			69
7			71
8			No reaction

[a] Step 1: Naphthol (0.5 mmol) and photosensitizer TPP (10 mol%) were mixed solvent (10 mL, $CHCl_3$/Methanol = 4/1, v/v). The mixture was irradiated with 35 W Xe lamp ($\lambda > 385$ nm), light powder density: 30 mW/cm^2. Step 2: aniline derivatives (0.6 mmol), 10 mol% $Cu(AcO)_2$ and acetic acid (10 mL) were added to the reaction mixture of the Step 1. Then the mixture was heated at 65 °C for 3 h. [b] Yield of the isolated product.

Table S5. Photooxidation of naphthol and aniline addition oxidation with B-4 [a]



Product

Entry	Aniline derivatives	Product	Yield%[b]
1			74
2			82
3			76
4			79
5			71
6			No reaction

[a] Step 1: Naphthol (0.5 mmol) and photosensitizer **B-4** (10 mol%) were mixed in solvent ($CHCl_3$/Methanol = 4/1, v/v, 10 mL), irradiated with 35 W Xe lamp (λ > 385 nm), light powder density: 30 mW/cm^2. Step 2: aniline derivatives (0.6 mmol), 10 mol% $Cu(AcO)_2$ and acetic acid (10 mL) were added to the reaction mixture of the Step 1. Then the mixture was heated at 65 °C for 3 h. [b] Yield of the isolated product.

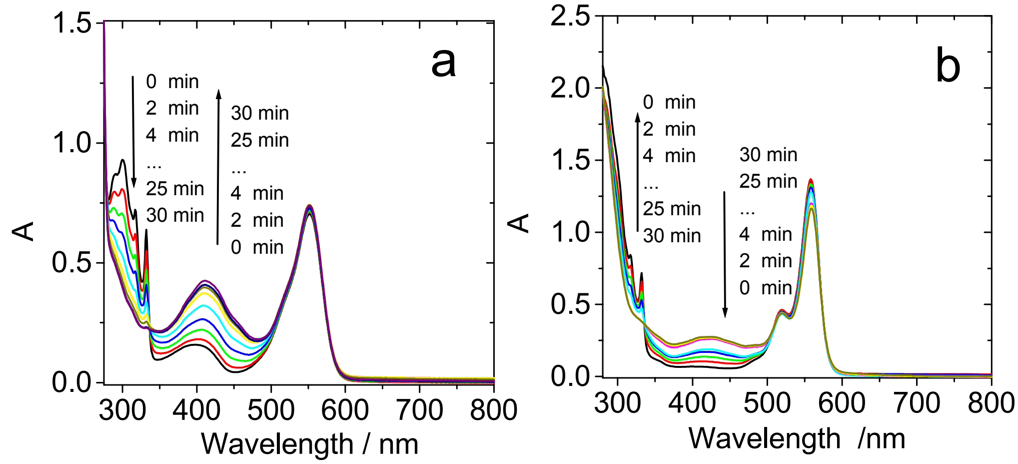


Figure S85. UV–vis absorption spectral changes for the photooxidation of DHN. (a) **B-3** as a sensitizer. (b) **B-4** as sensitizer. *c*[sensitizers] = 1.0×10^{-5} M. *c*[DHN] = 1.0×10^{-4} M. light intensity: 20 mW/cm^2 (CH_2Cl_2/MeOH, 9:1, v/v, 20 °C).

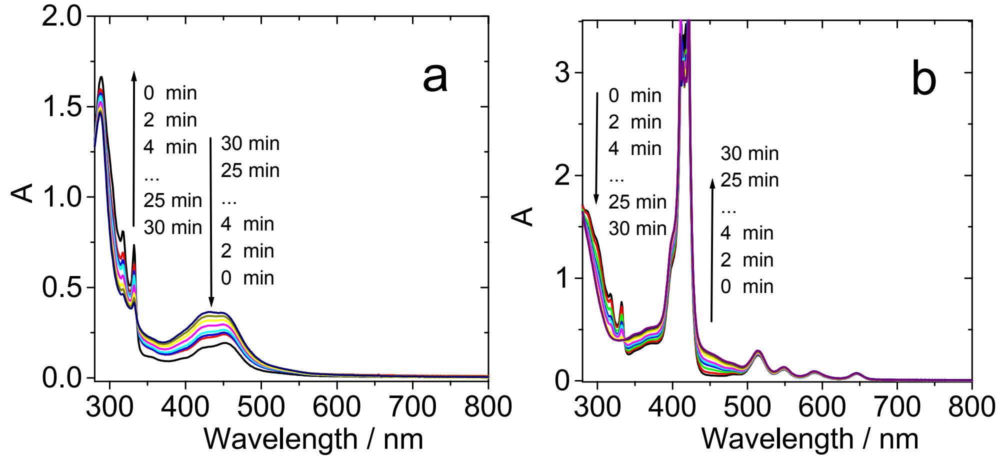


Figure S86. UV–vis absorption spectral changes for the photooxidation of DHN. (a) **Ru(bpy)$_3$[PF$_6$]$_2$** as a sensitizer. (b) **TPP** as sensitizer. *c*[sensitizers] = 1.0×10^{-5} M. *c*[DHN] = 1.0×10^{-4} M. light intensity: 20 mW/cm^2 (CH_2Cl_2/MeOH, 9:1, v/v, 20 °C).

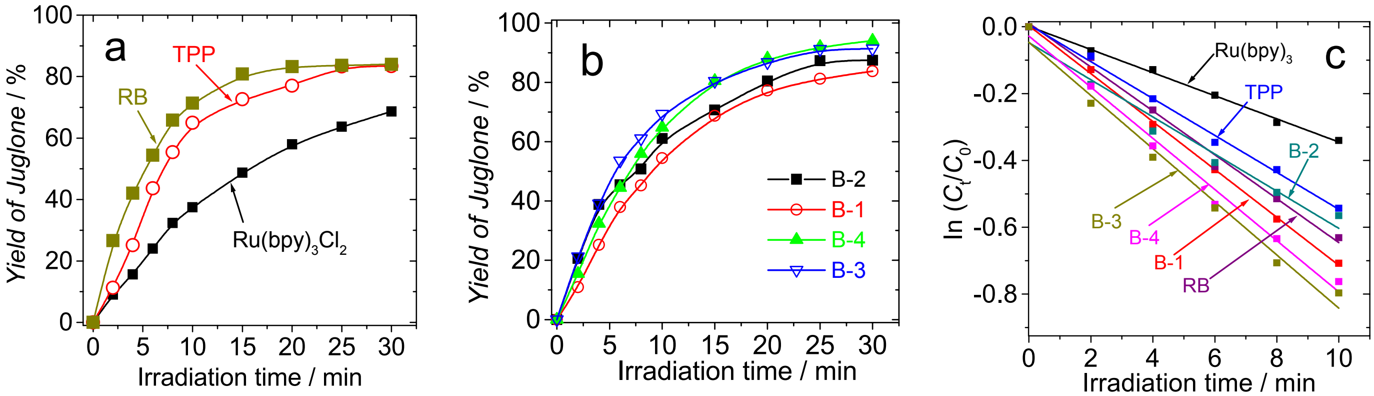


Figure S87. Photoxidation of DHN with triplet photosensitizers. (a) and (b) plots of chemical yields as a function of irradiation time. (c) Plots of ln(C_t/C_0) vs. irradiation time (*t*) for the photooxidation of DHN (CH_2Cl_2/MeOH, 9:1, v/v, 20 °C)

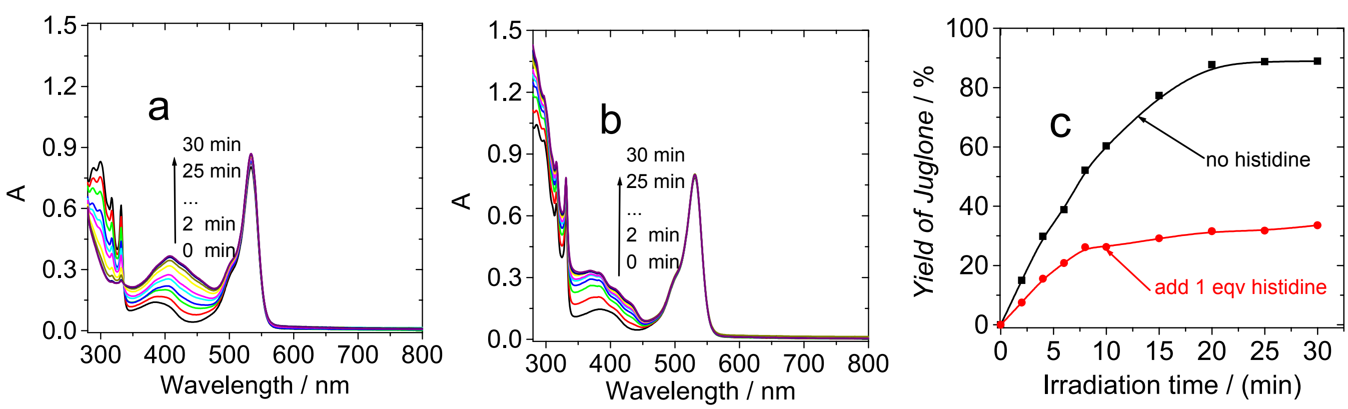


Figure S88. UV/Vis absorption spectral changes for the photooxidation of DHN. (a) **B-1** as a photocatalyst. (b) **B-1** as sensitizer, with addition of 1.0 eqv. histidine. (c) Plots of chemical yields as a function of irradiation time. *c*[sensitizers] = 1.0×10^{-5} M. *c*[DHN] = 1.0×10^{-4} M. light intensity: 20 mW/cm^2 (MeOH, 20 °C).

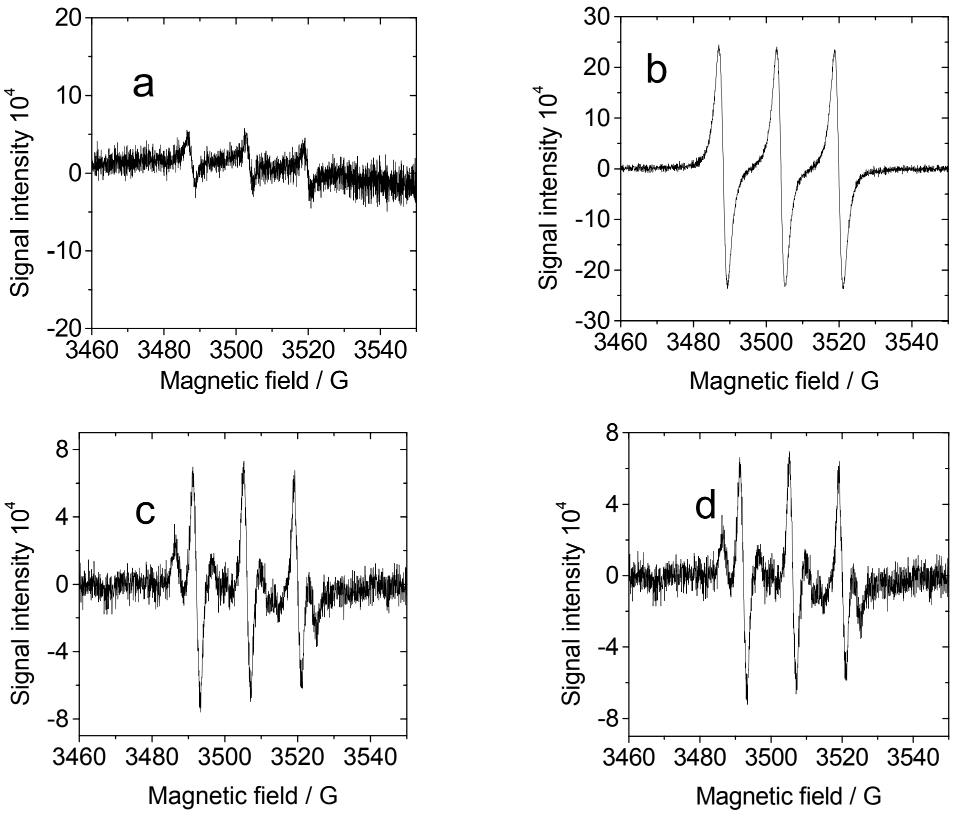
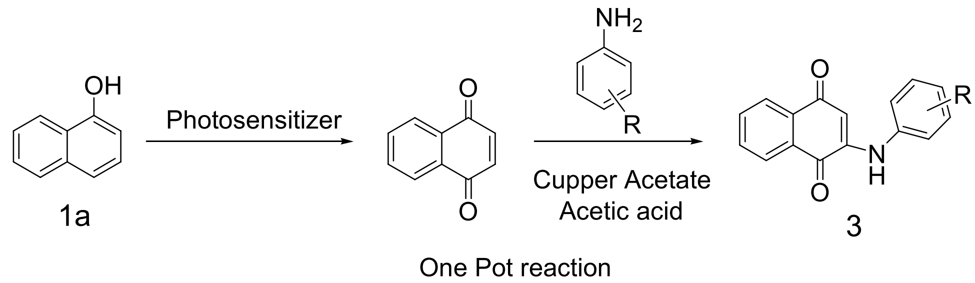


Figure S89. ESR spectrum of the mixtures in air-saturated mixed solvent (CH_2Cl_2/MeOH, 9:1,v/v) upon irradiation for 100 s by 532 nm laser 141 mW/cm^2. (a) **B-1** (1.0×10^{-4} M), DHN (1.5×10^{-3} M) and TEMP (0.12 M) (b) **B-1** (1.0×10^{-4} M) and TEMP (0.12 M). (c) **B-1** (1.0×10^{-4} M), DMPO (2.0×10^{-2} M) and DHN (1.5×10^{-3} M). (d) **B-1** (1.0×10^{-4} M) and DMPO (2.0×10^{-2} M). 20 °C.

Table S6. Photooxidation of naphthol oxidation with TPP and aniline addition to the naphthoquinones

a



Entry	Step 1 / time [h]	Step 2 / time [h]	Cupper salt	yield% [b]
1	2	6	$Cu(AcO)_2$ /10 mol%	29
2	1	6	$Cu(AcO)_2$ /10 mol%	37
3	1.5	6	$Cu(AcO)_2$ /10 mol%	59
4	1.5	3	$Cu(AcO)_2$ /10 mol%	64
5[c]	1.5	24	$Cu(AcO)_2$ /10 mol%	62
6[d]	1.5	3	$Cu(AcO)_2$ /10 mol%	12
7[e]	1.5	3	$Cu(AcO)_2$ /10 mol%	43
8	1.5	3	$Cu(AcO)_2$ /5 mol%	51
9	1.5	3	No $Cu(AcO)_2$	12
10	1.5	3	$CuSO_4$ /10 mol%	61
11	1.5	3	$CuCl_2$ /10 mol%	14
12	1.5	3	CuI /10 mol%	16
13	1.5	3	CuCl /10 mol%	61
14	1.5	3	10 mol%Cu /10 mol%	30
15	1.5	3	CuO /10 mol%	26
16	1.5	3	$AgNO_3$ /10 mol%	11

[a] Step 1: naphthol (0.5 mmol), photosensitizer TPP (10mol%), were mixed in co-solvent ($CHCl_3$/Methol=4/1, v/v). The mixture was irradiated with 35 W Xe lamp (λ>385 nm, light powder density: 30 mW/cm^2). Step 2: aniline (0.6 mmol), addition 10 ml acetic acid 10 mol% $Cu(AcO)_2$, 65 °C. [b] Overall yield of the isolated product, which were calculated based on the naphthol. [c] At room temperature, [d] No acetic acid was added. [e] Acetic acid (1 mL) was added.

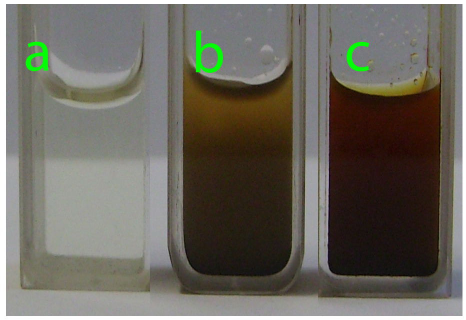
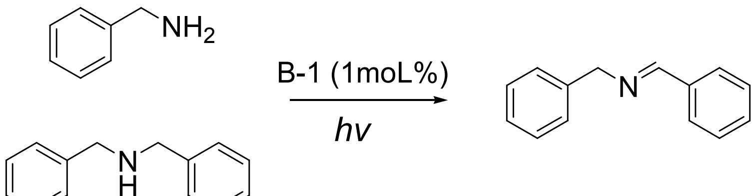
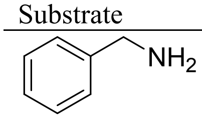
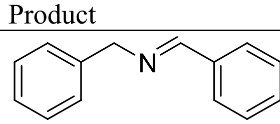
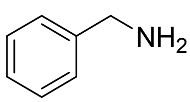
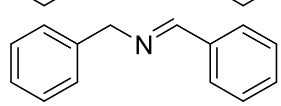
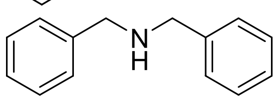
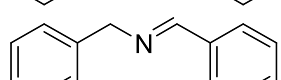
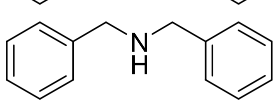
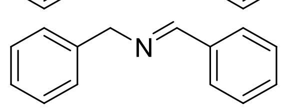


Figure S90. Detection of the H_2O_2 in the reaction mixture of photocatalytic oxidative coupling of benzylamines. (a) The picture of KI, aqueous acetic acid and starch. (b) The picture of KI, aqueous acetic acid, starch, and the benzylamine oxidation reaction liquid. (c) The picture of he picture of KI , aqueous acetic acid, starch, and the 30% H_2O_2. KI (1.0×10^{-1} M), aqueous acetic acid (1.0×10^{-1} M), starch (1.0×10^{-2} M), B-1(1 mol %), benzylamine (0.2 mmol), solvent: acetonitrile (3 mL), reaction time 1h, 20 °C.

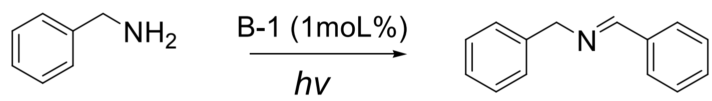
Table S7. Mechanism study of the coupling of benzylamines. Comparison of the reaction rate in $CDCl_3$ and $CHCl_3$. For the 1H NMR of the reaction mixture, please refer to Figure S43, S44, S50, S51 [a]



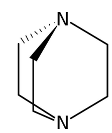
Substrate	Product	Solvent	Reaction time	Yield[%][b]
		$CDCl_3$	20 min	82
		$CHCl_3$	20 min	18
		$CDCl_3$	120 min	100
		$CHCl_3$	180 min	40

[a] Reaction conditions: benzylamine (0.2 mmol), photosensitizers catalyst (0.002 mmol, 1 mol %), solvent (3.0 mL), in air, λ > 380 nm (20 mW/cm^2), 20 °C. [b] Yield was determined with ^1H NMR.

Table S8. Mechanism study of the coupling of benzylamines. Investigation of the presence of DABCO on the reaction. DABCO is singlet oxygen ($^1O_2$) quencher. For the determination of the yields of the reaction with 1H NMR, please refer to Figure S46-S49 [a]



Entry	Add DABCO (%)	Yield[%][b]
1	0	23
2	5	1
3	10	0
4	50	0



1,4-diazabicyclo[2.2.2]octane (DABCO)

[a] Reaction conditions: benzylamine (0.2 mmol), photosensitizers catalyst (0.002 mmol, 1 mol%), : acetonitrile (3 mL) was used as solvent, in air, $\lambda > 380$ nm (20 mW/cm^2), 20 °C. [b] Yield was determined with ^{1}H NMR.

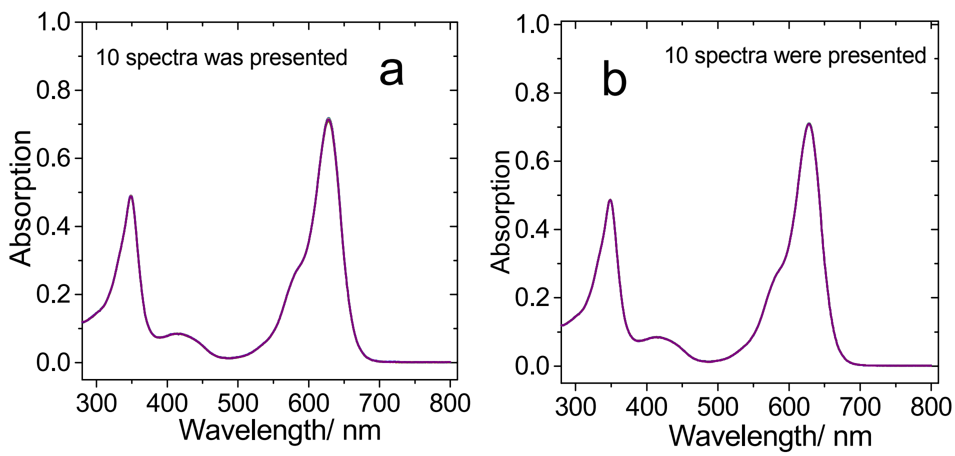
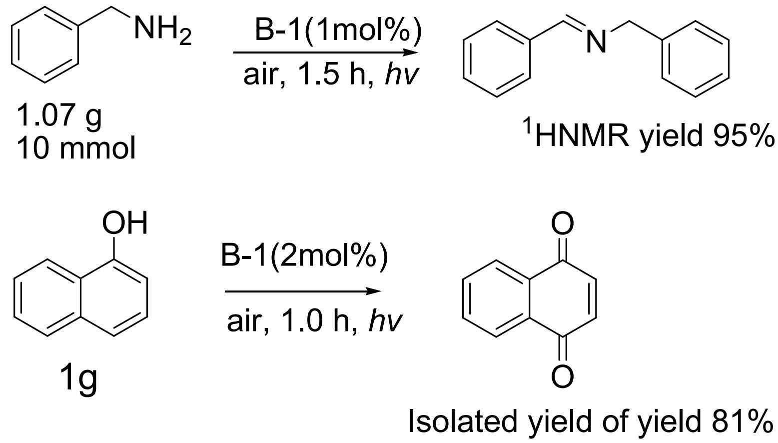


Figure S91. UV–vis spectra of **B-4** upon monochromatic light irradiation, investigation of the possible cis-trans isomerization of the styryl C=C bond in **B-4**. (a) Using 625 nm monochromatic light for the irradiation, the spectrum was measured after every 3 min of irradiation, total irradiation time was 30 min, 10 curves were presented; (b) Using 347 nm monochromatic light for the irradiation, the spectrum was measured after every 3 min of irradiation, total irradiation time was 30 min, 10 curves were presented, but no changes of the spectra were observed (in acetonitrile, $c = 1.0 \times 10^{-5}$ M, 20 °C)



Scheme S1. Scale-up of the photocatalytic reactions. Benzylamine (10 mmol), **B-1** (0.1 mmol, 1 mol %), solvent: acetonitrile (150 mL), in air, λ > 380 nm (20 mW/cm^2), 20 °C. Naphthol (7.0 mmol, 1.0 g), **B-1** (5.0 mol%), were mixed in co-solvent ($CHCl_3$/Methol=4/1, v/v). The mixture was irradiated with 35 W Xe lamp (λ>385 nm, light powder density: 30 mW/cm^2).