Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information (New Journal of Chemistry)

Photochemistry of triphenylamine (TPA) in homogeneous solution and the role of transient *N*-phenyl-*4a,4b*-dihydrocarbazole. A steady-state and time-resolved investigation.

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1. Decay traces of N-phenyl-*4a,4b*-dihydrocarbazole (DHC_0) transient, reciprocal plot and kinetic parameters measured in acetonitrile under N_2 and N_2O atmospheres.

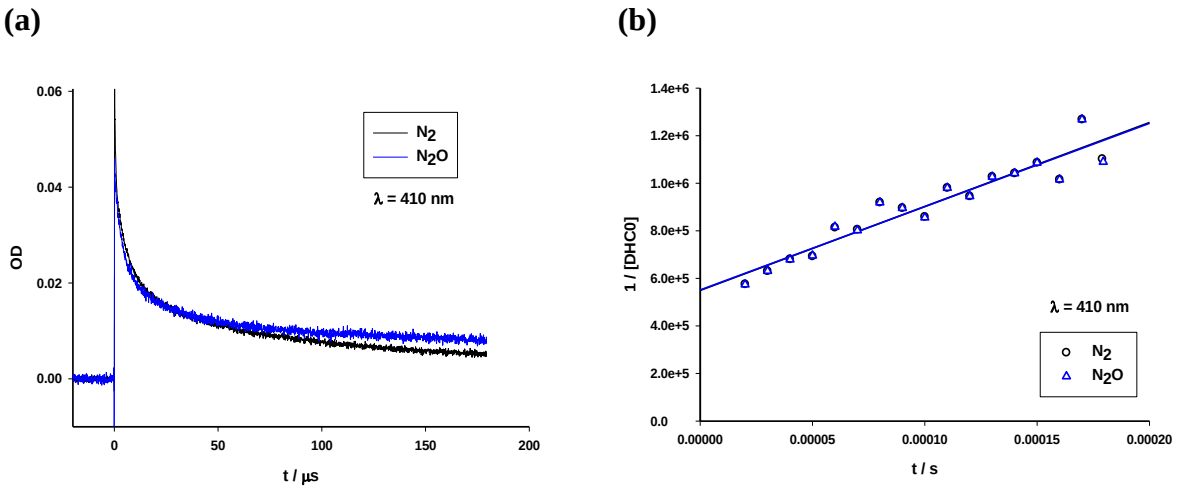

Figure S1. (a) Decay traces of N-phenyl dihydrocarbazole (DHC_0) transient in acetonitrile recorded at λ_{abs} = 410 nm after a laser pulse of 355 nm under N_2 and N_2O atmosphere; (b) Reciprocal plot of the concentration of the DHC_0 transient versus time in N_2- (○) and N_2O-saturated (Δ) acetonitrile solution recorded at 410 nm.

Table S1. Lifetime and rate constant values of DHC_0 in acetonitrile at 410 nm under different conditions.[a]

Atmosphere	τ_d / μs	k_d / s^{-1}	τ_R / μs	k_R / $M^{-1}.s^{-1}$	τ_{O2} / μs	k_{O2} / $M^{-1}.s^{-1}$
N_2	5.21±0.07	$1.9x10^5$	59.0±0.8	$1.8x10^9$	---	---
N_2O	4.71±0.09	$2.1x10^5$	45.5±0.9	$1.8x10^9$	---	---
O_2	---	---	---	---	23.9±0.3	$2.1x10^7$

[a]Irradiation of TPA in acetonitrile ($1.0x10^{-3}$ M) with a laser pulse of 355 nm. ε(410 nm) = 8903 $M^{-1}.cm^{-1}$.

2. Time-resolved UV-visible absorption spectra, decay traces and reciprocal plots of N-phenyl-*4a,4b*- dihydrocarbazole (DHC_0) transient in different homogeneous media under N_2 and O_2 atmospheres.

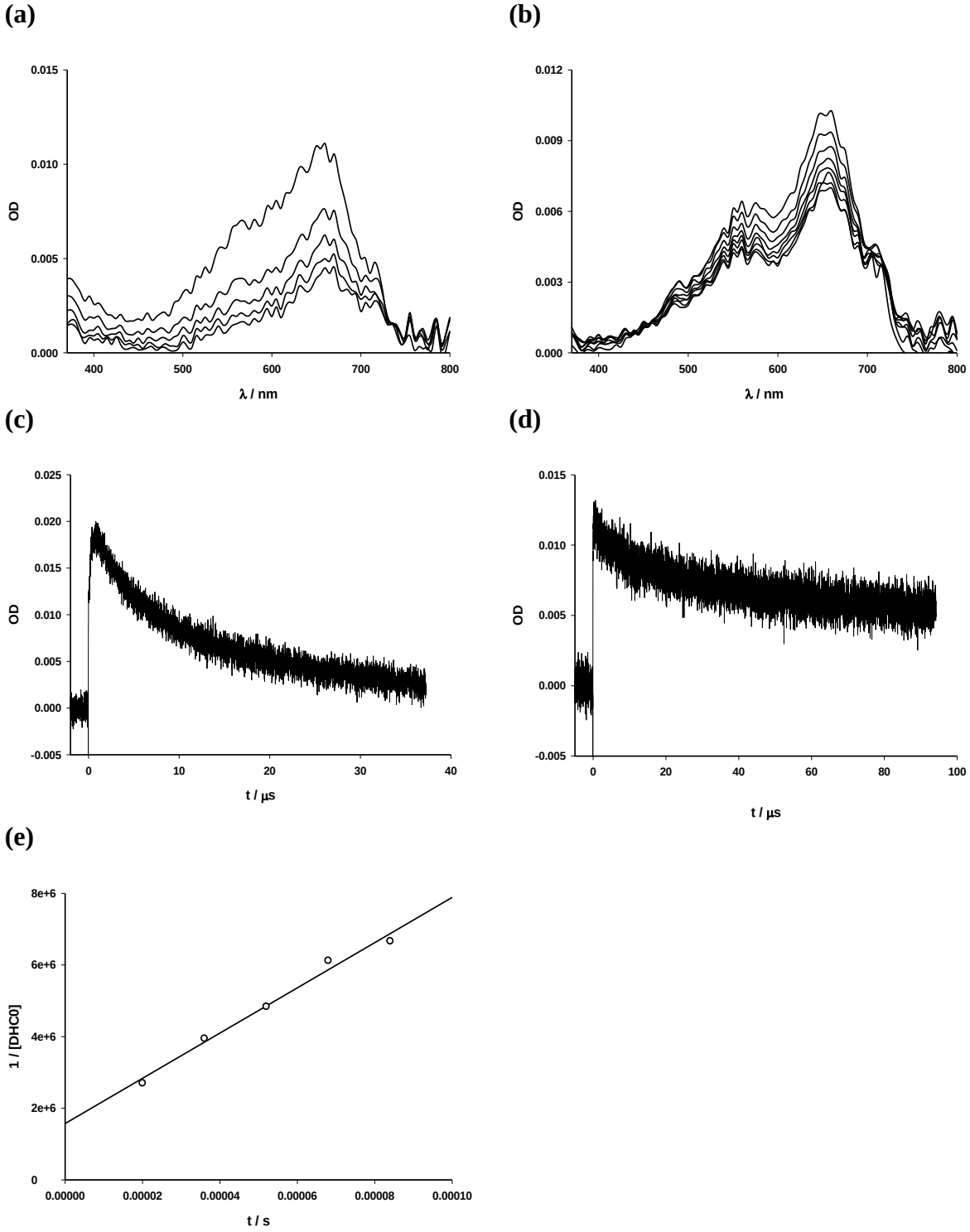

Figure S2. Time-resolved UV-visible absorption spectra of N-phenyl-*4a,4b*-dihydrocarbazole (DHC_0) transient in dichloromethane after a laser pulse of 355 nm under (a) N_2 and (b) O_2 atmospheres. Decay traces of DHC_0 transient in dichloromethane recorded at λ_{abs} = 630 nm after a laser pulse of 355 nm under (c) N_2 and (d) O_2 atmospheres. Reciprocal plot of the concentration of the DHC_0 transient versus time in N_2- (○) dichloromethane solution recorded at 630 nm.

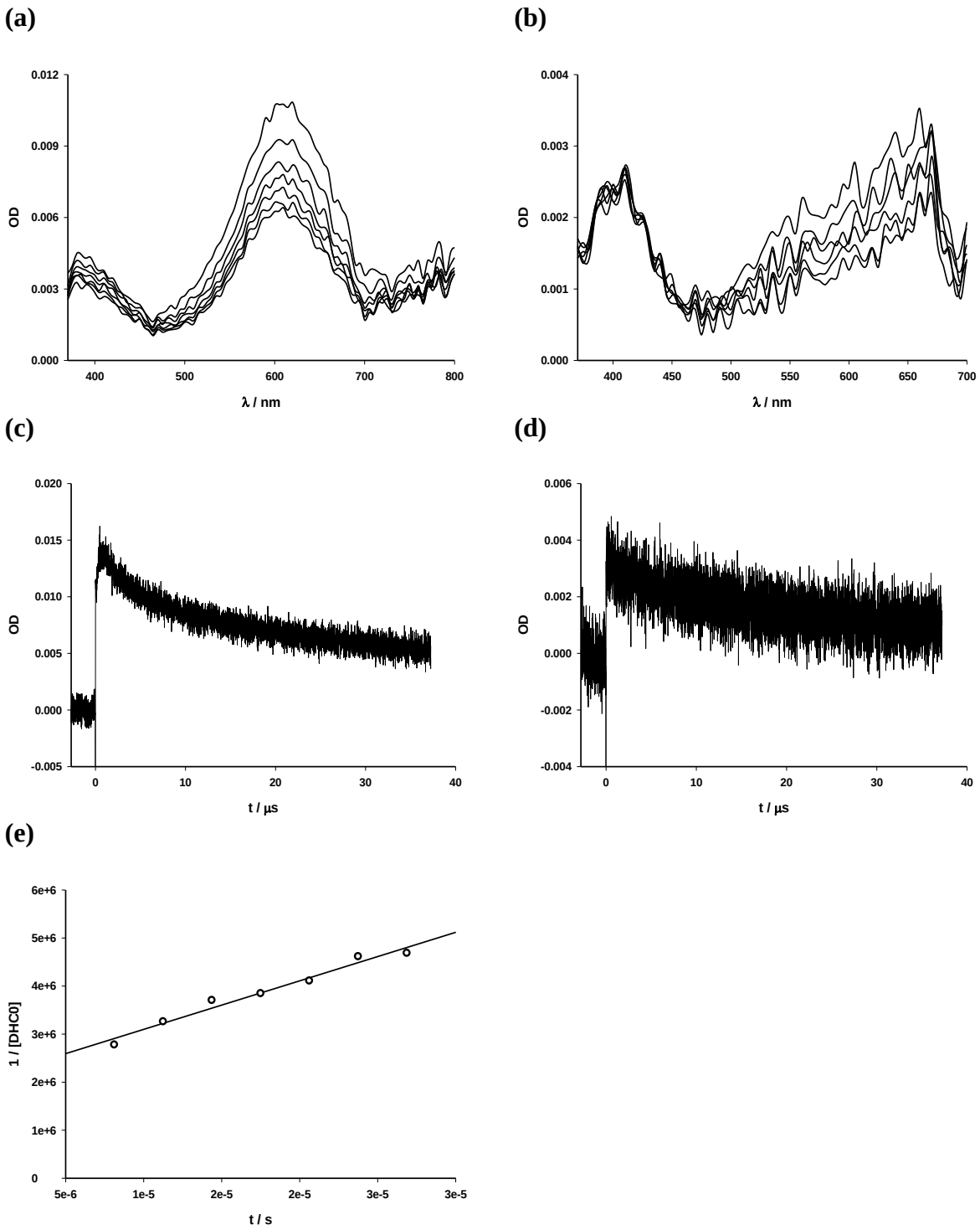

Figure S3. Time-resolved UV-visible absorption spectra of N-phenyl-*4a,4b*-dihydrocarbazole (DHC_0) transient in acetonitrile water (9:1) after a laser pulse of 355 nm under (a) N_2 and (b) O_2 atmospheres. Decay traces of N-phenyl-*4a,4b*-dihydrocarbazole (DHC_0) transient in acetonitrile water (9:1) recorded at λ_{abs} = 620 nm after a laser pulse of 355 nm under (c) N_2 and (d) O_2 atmospheres. Reciprocal plot of the concentration of the DHC_0 transient versus time in N_2- (○) acetonitrile water (9:1) solution recorded at 620 nm.

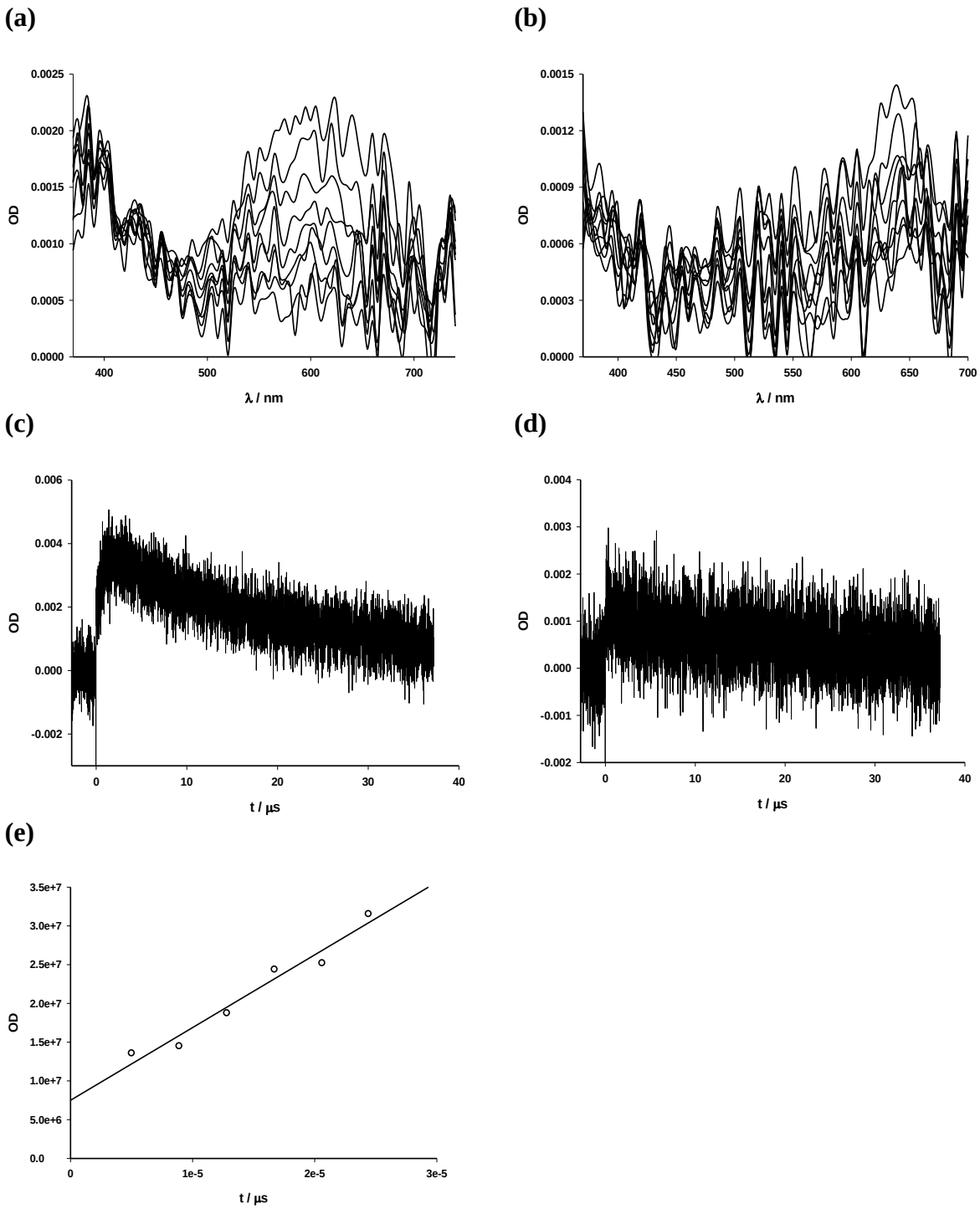

Figure S4. Time-resolved UV-visible absorption spectra of N-phenyl-*4a,4b*-dihydrocarbazole (DHC_0) transient in TFE after a laser pulse of 355 nm under (a) N_2 and (b) O_2 atmospheres. Decay traces of N-phenyl-*4a,4b*-dihydrocarbazole (DHC_0) transient in TFE recorded at λ_{abs} = 620 nm after a laser pulse of 355 nm under (c) N_2 and (d) O_2 atmospheres. Reciprocal plot of the concentration of the DHC_0 transient versus time in N_2- (○) TFE solution recorded at 620 nm.

3. Decay traces of transient DHC_0 and Intermediate I recorded in acetonitrile.

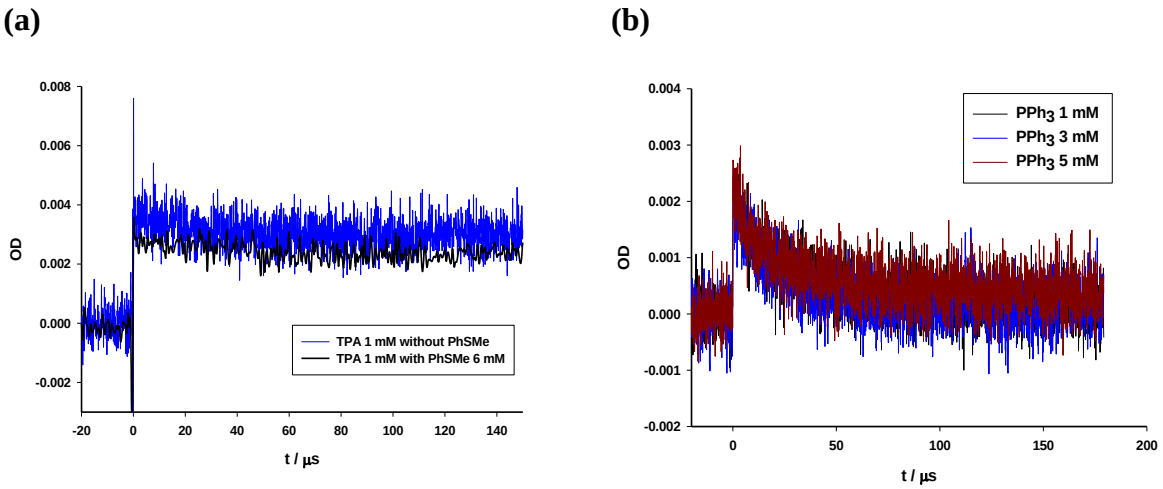

Figure S5. (a) Decay traces of intermediate I in acetonitrile recorded at λ_{abs} = 410 nm after a laser pulse of 355 nm under O_2 atmosphere in the absence (blue line) and presence (black line) of thioanisole. (b) Decay traces of transient DHC_0 in acetonitrile recorded at λ_{abs} = 625 nm after a laser pulse of 355 nm under O_2 atmosphere at different concentrations of triphenylphosphine (PPh_3).

4. ^{1}H-NMR spectra of the reaction mixture obtained after irradiation (366 nm) of TPA in different solvents under molecular oxygen.

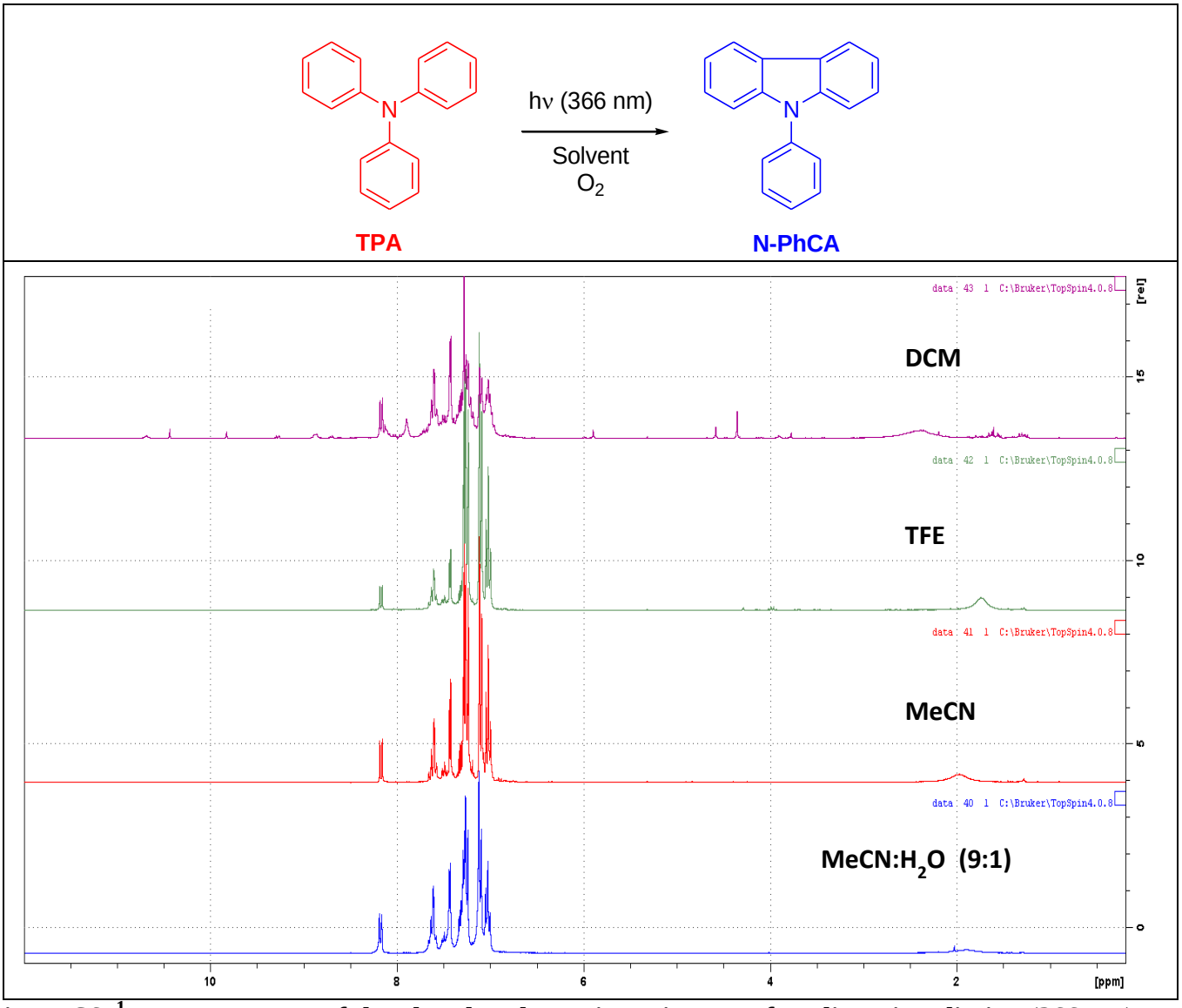

Figure S6. ^{1}H-NMR spectra of the photolyzed reaction mixtures after direct irradiation (366 nm) of triphenylamine (TPA) in different solvents under O_2 atmosphere during 6 hours.

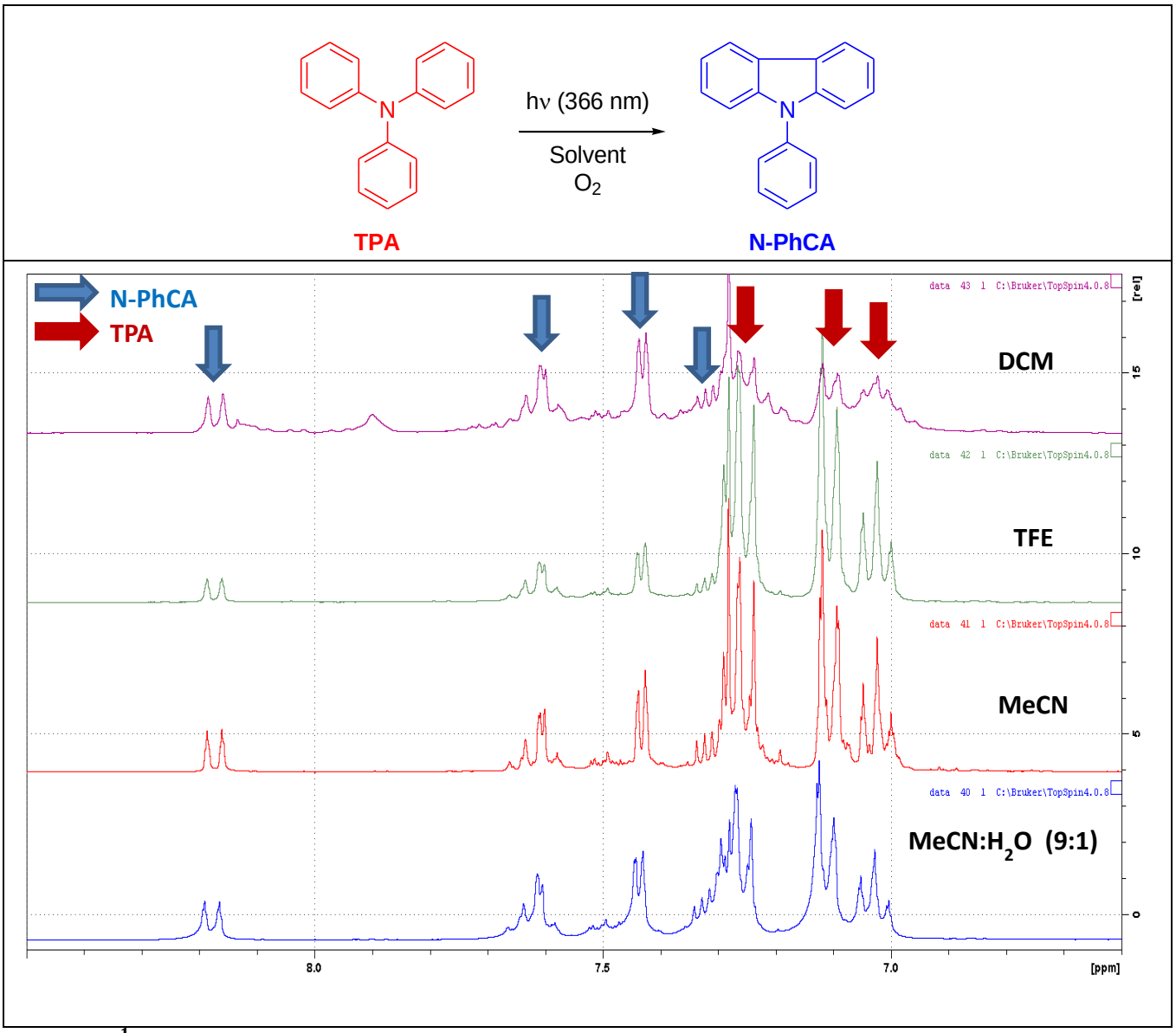

Figure S7. ^{1}H-NMR spectra (aromatic chemical shifts only) of the photolyzed reaction mixtures after direct irradiation (366 nm) of triphenylamine (TPA) in different solvents under O_2 atmosphere during 6 hours.

5. UV-visible spectrum of N-phenylcarbazole (N-PhCA) and triphenylamine (TPA).

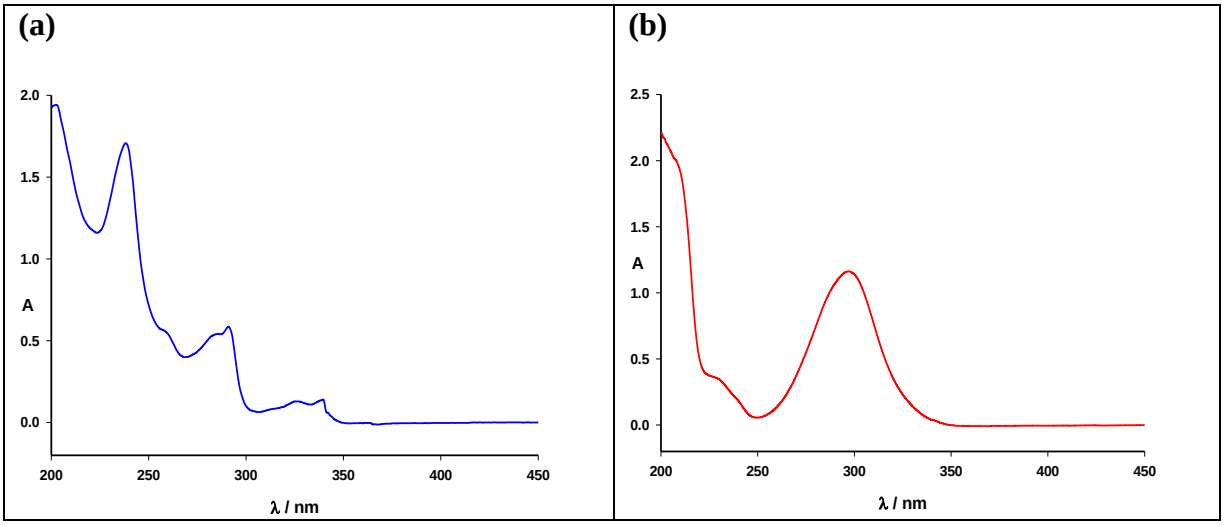

Figure S8. UV-visible spectrum of (a) N-Phenylcarbazole (N-PhCA) recorded in methanol and (b) triphenylamine (TPA) in acetonitrile at 25°C.