Electronic Supporting Information

Visible-Light-Controlled Homo- and Copolymerization of Styrenes by Bichromophoric Ir-Pd Catalyst

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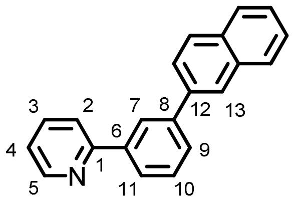
Experimental Details and Spectral Data

General Procedures.

Standard Schlenk and vacuum line techniques under a nitrogen atmosphere were employed for the reactions. Dichloromethane (CaH_2) and Acetone (K_2CO_3) were treated with appropriate drying agents and distilled. MeOH and EtOH were dehydrated by Mg with I_2, and distilled. 5,5'-dibromo-2,2'-bipyrimidine (bpm^{Br}) and [Pd(cod)MeCl] were prepared according to the published procedures [ref]. Other chemicals were purchased and used as received. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-JMN-LA500, JEOL-JMS-ECS400, and Bruker AVANCE-400 spectrometers. ESI-MS spectra were recorded on a ThermoQuest Finnigan LCQ Duo mass spectrometer. UV-vis spectra were obtained by a JASCO V-670 spectrometer.

Preparation of 2-[3-(2-naphthyl)phenyl]pyridine (ppy^{naph}).



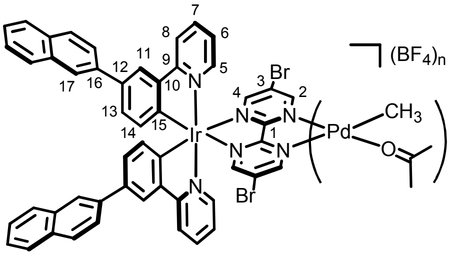
3-(2-Naphthyl)phenylboronic acid (1.20 g, 0.00484 mol), Na_2CO_3 (2.89 g, 0.0272 mol) and $Pd(PPh_3)_4$ (132 mg, 0.000114 mol) were dissolved with toluene (20 mL) , EtOH (20 mL) and H_2O (4 mL) in a 200 mL 2-necked flask. Then 2-bromopyridine (0.352 mL, 0.00369 mol) was added and refluxed for 12 h under N2. The reaction mixture was extracted with CH_2Cl_2 (3 times), washed with brine (3 times), and the collected organic layer was dried over $MgSO_4$. After removal of the solvent, the crude product was purified by silica-gel column chromatography (CH_2Cl_2 / hexane = 1 / 1) to yield the target compound as a pale yellow oil (0.570 g, 0.00203 mol, 41.9%). ^{1}H NMR (400 MHz, r.t., $CDCl_3$, δ / ppm) : δ 8.79 (d, 1 H, J = 4.8 Hz, H5), 8.43 (s, 1 H, H7), 8.17 (s, 1 H, H13), 8.02 (d, 1 H, J = 7.6 Hz, H11), 7.97 – 7.79 (m, 6 H, H2, H9, *naphthyl*), 7.77 (dd, 1 H, J = 7.2 Hz, 7.2 Hz, H3), 7.61 (dd, 1 H, J = 7.6 Hz, 7.6 Hz, H10), 7.55 – 7.51 (m, 2 H, *naphthyl*), 7.26 (dd, 1 H, J = 7.2 Hz, 4.8 Hz, H4). ^{13}C NMR (133 MHz, r.t., $CDCl_3$, δ / ppm) : δ 157.4 (s, C1), 149.8 (d, J_{CH} = 180.3 Hz, C5), 141.7 (s, C8), 140.1 (s, C6), 138.4 (s, C12), 136.9 (d, J_{CH} = 161.5 Hz, C3), 133.8 (s, *naphthyl*), 132.8 (s, *naphthyl*), 129.4 (d, J_{CH} = 160.6 Hz, C10), 128.5 (d, J_{CH} = 158.9 Hz, *naphthyl*), 128.3 (d, J_{CH} = 157.0 Hz, *naphthyl*), 128.1 (d, J_{CH} = 159.7 Hz, *naphthyl*), 127.7 (d, J_{CH} = 165.1 Hz, C9), 126.4 (d, J_{CH} = 158.7 Hz, *naphthyl*), 126.1 (d, J_{CH} = 157.5 Hz, C7), 126.1 (d, J_{CH} = 157.5 Hz, C13 or *naphthyl*), 126.0 (d, J_{CH} = 157.5 Hz, C11 or C13 or *naphthyl*), 126.0 (d, J_{CH} = 157.5 Hz, C11 or *naphthyl*), 125.7 (d, J_{CH} = 158.3 Hz, *naphthyl*), 122.3 (d, J_{CH} = 158.4 Hz, C4), 120.8 (d, J_{CH} = 153.9 Hz, C2). EI-MS : m/z = 281 $[M]^+$. HR-MS (EI) : m/z = 281.1210 (calcd for $[C_{21}H_{15}N]^+$: 281.1204).

Electronic Supporting Information

Preparation of [Ir(ppy^{naph})$_2$(bpm^{Br})PdMe(Me$_2$CO)](BF$_4$)$_2$ (1).

[Ir(ppy^{naph})(bpm^{Br})](BF$_4$) was prepared in a similar fashion to the published procedure for the synthesis of [Ir(C^N)$_2$(N^N)]$^+$.[1]

$IrCl_3 \cdot 3H_2O$ (0.357 g, 1.01 mmol) and 3-(2-naphthyl)-2-pyridyl benzene (0.570 g, 2.03 mmol) were dissolved in 2-ethoxyethanol (15 mL) and H_2O (5 mL), and refluxed under N_2 for 24 h. The precipitate was filtered, washed with H_2O and EtOH, and then dried up to afford [Ir(ppy^{naph})$_2$Cl]$_2$ as a yellow solid (0.732 g, 0.464 mmol, 91.9%). ^{1}H NMR (400 MHz, r.t., $CDCl_3$, δ / ppm) : δ 9.39 (d, J = 5.2 Hz, 4 H, H5), 8.08 (d, J = 8.0 Hz, 4 H, H8), 7.89 – 7.78 (m, 24 H, H7, H11, H17, *naphthyl*), 7.62 (dd, J = 8.4 Hz, 2.0 Hz, 4 H, *naphthyl*), 7.45 – 7.38 (m, 8 H, *naphthyl*), 7.99 (d, J = 8.0 Hz, 4 H, H13), 7.90 (dd, J = 6.0 Hz, 5.2 Hz, 4 H, H6), 6.16 (d, J = 8.0 Hz, 4 H, H14).



[Ir(ppy^{naph})$_2$Cl]$_2$ (0.409 g, 0.259 mmol) and 5,5'-dibromo-2,2'-bipyrimidine (0.196 g, 0.620 mmol) were dissolved in CH_2Cl_2 (20 mL) and MeOH (10 mL), and refluxed under N_2 for 5 h. The mixture was concentrated under vacuum and stirred with an excess amount of NH_4BF_4 at ambient temperature for 5 h. The precipitate was filtered and washed with EtOH, water, and Et_2O. The resulting solid was purified by column chromatography packed with neutral aluminum oxide (CH_2Cl_2 / hexane = 3 : 1). The eluted pale orange band was collected and dried up under vacuum. The obtained solid was dissolved in CH_2Cl_2 and a slow diffusion of hexane yielded [Ir(ppy^{naph})$_2$(bpm^{Br})](BF$_4$) as a dark-red solid (0.238 g, 0.206 mmol, 79.5%). ^{1}H NMR (400 MHz, CD_3CN, r.t., δ / ppm) : δ 9.27 (d, J = 2.8 Hz, 2 H, H2), 8.61 (d, J = 2.4 Hz, 2 H, H4), 8.31 (d, J = 8.0 Hz, 2 H, H8), 8.27 (d, J = 1.6 Hz, 2 H, H11), 8.11 (s, 2 H, H17), 8.01 – 7.85 (m, 12 H, H5, H7, *naphthyl*), 7.79 (dd, J = 8.8 Hz, 2.0 Hz, 2 H, *naphthyl*), 7.52 – 7.46 (m, 4 H, *naphthyl*), 7.36 (dd, J = 8.0 Hz, 1.6 Hz, 1 H, H13), 7.18 (dd, J = 7.6 Hz, 6.0 Hz, 1 H, H6), 6.51 (d, J = 8.0 Hz, 1 H, H14). ^{13}C NMR (100 MHz, CD_3CN, r.t., δ / ppm) : δ 162.8 (s, C1), 156.6 (d, J_{CH} = 192.2 Hz, C2), 156.0 (s, C9), 154.4 (d, J_{CH} = 198.3 Hz, C4), 145.9 (d, J_{CH} = 183.1 Hz, C5), 142.1 (s, C15), 141.0 (s, C10), 135.1 (d, J_{CH} = 159.9 Hz, C7), 134.0 (s, C12), 131.9 (s, C16), 129.7 (s, *naphthyl*), 128.4 (s, *naphthyl*), 128.2 (d, J_{CH} = 157.6 Hz, C14), 125.2 (d, J_{CH} = 170.1 Hz, C13), 124.3 (d, J_{CH} = 163.2 Hz, *naphthyl*), 123.9 (d, J_{CH} = 160.5 Hz, *naphthyl*), 123.4 (d, J_{CH} = 157.8 Hz, *naphthyl*), 122.3 (d, J_{CH} = 159.2 Hz, *naphthyl*), 121.8 (d, J_{CH} = 167.9 Hz, *naphthyl*), 120.9 (d, J_{CH} = 151.7 Hz, *naphthyl*), 120.6 (d, J_{CH} = 169.1 Hz, C17), 120.4 (s, C3), 119.9 (d, J_{CH} = 161.6 Hz, C6), 119.4 (d, J_{CH} = 162.9 Hz, C11), 116.3 (d, J_{CH} = 165.5 Hz, C8). ESI-MS (CH_3CN) : m/z = 1069 [M – BF$_4$]$^+$. Anal. Found (calcd for $C_{50}H_{32}BBr_2F_4IrN_6$ + (2 H_2O)): C, 50.04 (50.39); H, 3.02 (3.04); N, 6.87 (7.05).

Electronic Supporting Information

Palladation of [Ir(ppy^{naph})(bpm^{Br})](BF$_4$) was implemented in a similar fashion to the published procedure for the synthesis of the Ru-Pd complex.[2]

[Ir(ppy^{naph})$_2$(bpm^{Br})](BF$_4$) (188 mg, 0.163 mmol) and [PdMeCl(cod)] (47.4 mg, 0.179 mmol) was dissolved in CH_2Cl_2 (8 mL) and stirred at ambient temperature for 3 h. The solvent was removed under reduced pressure and the resulting solid was precipitated with CH_2Cl_2 - Et_2O, which yielded [Ir(Ph^{naph}py)$_2$(bpm^{Br})PdMeCl](BF$_4$)$_2$ as a brownish-red solid (201 mg, 0.153 mmol, 93.9%). ^{1}H NMR (400 MHz, r.t., CD_3NO_2, δ / ppm) : δ 9.29 (br, 2 H, H2), 8.78 (br, 2 H, H4), 8.35 (d, J = 8.0 Hz, 2 H, H8), 8.15 (d, J = 2.0 Hz, 2 H, H11), 8.11 (s, 2 H, H17), 8.05 – 7.86 (m, 10 H, H5, H7, *naphthyl*), 7.83 (dd, J = 8.8 Hz, 2.0 Hz, 2 H, *naphthyl*), 7.53 – 7.46 (m, 4 H, *naphthyl*), 7.42 (dd, J = 8.0 Hz, 2.0 Hz, 2 H, H13), 7.21 (dd, J = 7.6 Hz, 6.0 Hz, 2 H, H6), 6.49 (d, J = 8.0 Hz, 2 H, H14), 1.17 (s, 3 H, Pd-CH_3). ESI-MS (acetone) : m/z = 1225 $[M - BF_4]^+$.

[Ir(Ph^{naph}py)$_2$(bpm^{Br})PdMeCl](BF$_4$)$_2$ (194 mg, 0.148 mmol) was dissolved in acetone (8 mL) and acetone (4 mL) solution of $AgBF_4$ (28.8 mg, 0.148 mmol) was added. The mixture was stirred at ambient temperature for 1 h. The resulting solution was filtered through Celite and the filtrate was concentrated under vacuum. Then a slow addition of Et_2O gave the target compound **1** as a brownish-red solid (202 mg, 0.142 mmol, 96.0%). ^{1}H NMR (400 MHz, CD_3CN, r.t., δ / ppm) : δ 9.28 (br, 2 H, H2), 8.30 (br, 2 H, H4), 8.29 (d, J = 8.0 Hz, 2 H, H8), 8.23 (d, J = 2.0 Hz, 2 H, H11), 8.13 (s, 2 H, H17), 8.00 (ddd, J = 8.0 Hz, 6.4 Hz, 1.2 Hz, 2 H, H7), 7.92 – 7.84 (m, 10 H, H5, *naphthyl*), 7.79 (dd, J = 8.8 Hz, 1.6 Hz, 2 H, *naphthyl*), 7.52 – 7.45 (m, 4 H, *naphthyl*), 7.33 (dd, J = 7.6 Hz, 2.0 Hz, 2 H, H13), 7.21 (dd, J = 6.4 Hz, 6.0 Hz, 2 H, H6), 6.38 (dd, J = 7.6, 2.8 Hz, 2 H, H14), 1.07 (br, 3 H, Pd-CH_3). ^{13}C NMR (100 MHz, CD_3CN, r.t., δ / ppm) : δ 167.7 (s, C1), 161.6 (d, J_{CH} = 189.8 Hz, C2), 160.9 (s, C9), 159.4 (d, J_{CH} = 200.4 Hz, C4), 151.6 (d, J_{CH} = 183.8 Hz, C5), 146.9 (s, C15), 146.0 (s, C10), 140.2 (d, J_{CH} = 165.7 Hz, C7), 139.0 (s, C12), 137.0 (s, C16), 134.8 (s, *naphthyl*), 133.5 (s, *naphthyl*), 133.2 (d, J_{CH} = 157.7 Hz, C14), 130.3 (d, J_{CH} = 158.7 Hz, C13), 129.4 (d, J_{CH} = 159.4 Hz, *naphthyl*), 129.0 (d, J_{CH} = 158.3 Hz, *naphthyl*), 128.5 (d, J_{CH} = 160.2 Hz, *naphthyl*), 127.4 (d, J_{CH} = 153.7 Hz, *naphthyl*), 126.9 (d, J_{CH} = 164.8 Hz, *naphthyl*), 126.1 (d, J_{CH} = 156.5 Hz, *naphthyl*), 125.9 (d, J_{CH} = 156.8 Hz, C17), 125.9 (s, C3), 125.1 (d, J_{CH} = 169.1 Hz, C6), 124.6 (d, J_{CH} = 148.8 Hz, C11), 121.6 (d, J_{CH} = 168.8 Hz, C8), -3.13 (br, Pd-CH_3), The proton and carbon signals of a coordinating solvent were each overlapped with the residual proton signals and the carbon signals of CD_3CN, respectively. Anal. Found (calcd for $C_{53}H_{38}B_2Br_2F_4IrN_7Pd$ + (2 H_2O)): C, 44.31 (44.18); H, 3.27 (2.94); N, 6.67 (6.80).

Photochemical Reaction.

A CD_3NO_2 solution (0.4 mL) of styrene (0.5 mol/l) with a catalytic amount of the catalyst **1** (2 mol%) was prepared in a 5ϕ NMR glass tube under nitrogen atmosphere. For visible-light irradiation, the tube was put in a water bath (25 °C) and placed at a distance of 70 mm from a light source (150 W Xe lamp with a L42 cut-off filter ($\lambda_{\mathrm{irr.}}$ > 420 nm)). For the dark condition, the tube was foiled with an aluminum sheet and placed in a water bath (25 °C / 60 °C). Reactions were followed by ^{1}H NMR spectroscopy after appropriate time intervals.

For copolymerization of styrene and 2,2,2-trifluoroethyl vinyl ether, a CD_3NO_2 solution (0.4 mL) of both substrates (50 equiv/cat, each) with a catalytic amount of the Ir-Pd complex (1 mol%) was prepared, then irradiated or kept dark, under the same condition.

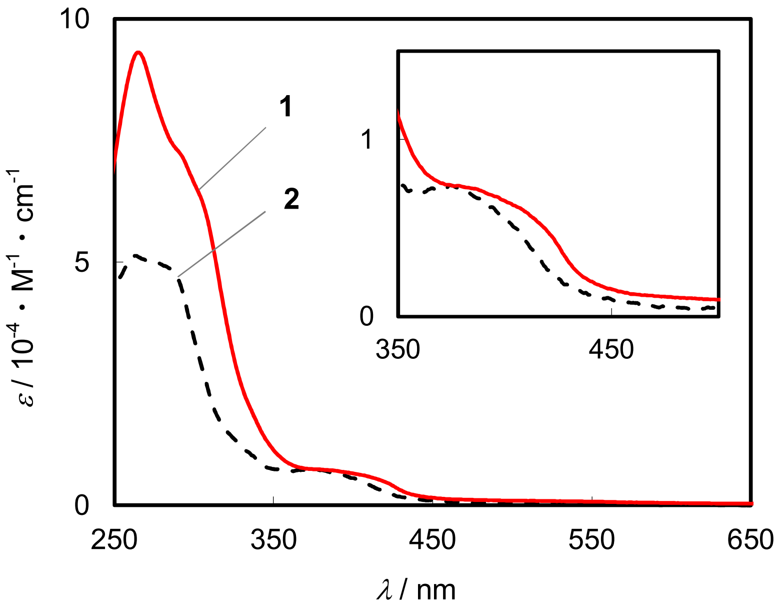


Figure S1. UV-vis absorption spectrum of **1** (solid line) and **2** (dashed line) in deaerated CH_3CN (r.t.)

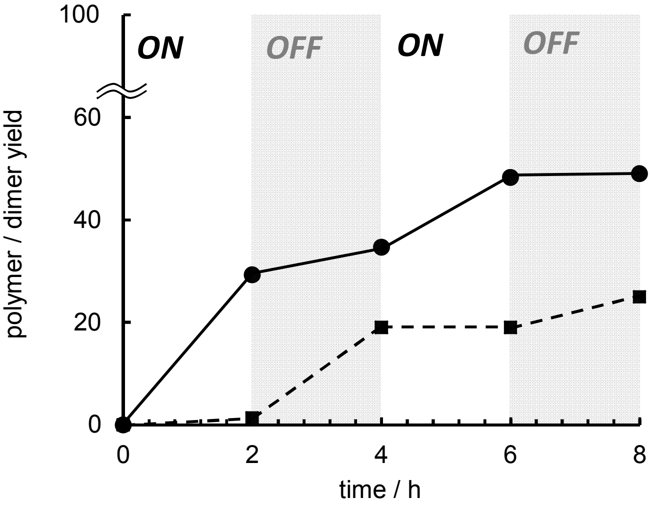


Figure S2. UV-vis absorption spectrum of **1** (solid line) and **2** (dashed line) in deaerated CH_3CN (r.t.)

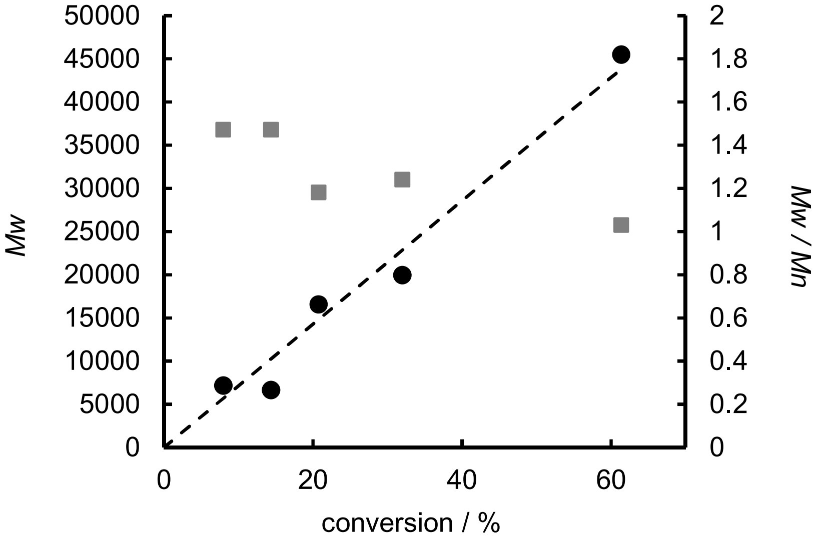


Figure S3. Molecular weight (M_w, circle) and molecular weight distribution (M_w/M_n, square) plotted against conversion during photocatalytic reactions of 4-fluorostyrene ($\lambda_{irr} > 420$ nm, cat. 2 mol%, CD_3NO_2, r.t.)

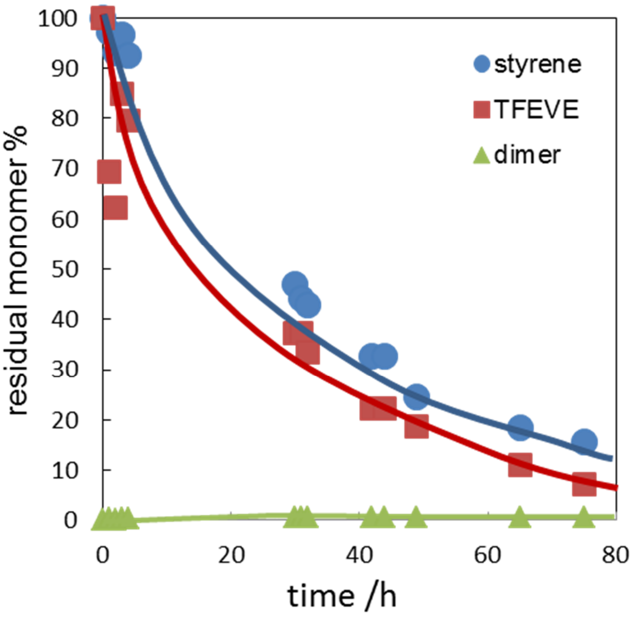


Figure S4. Copolymerization of Styrene and TFEVE by **1** under irradiation (ON)

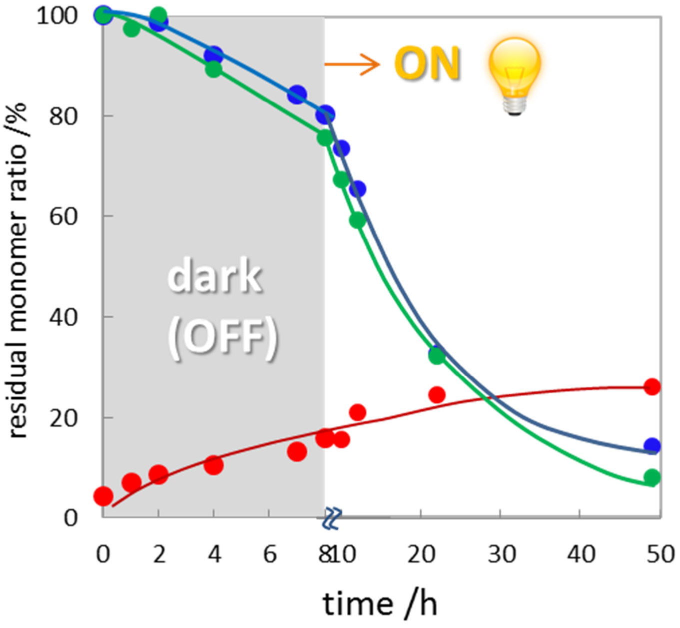
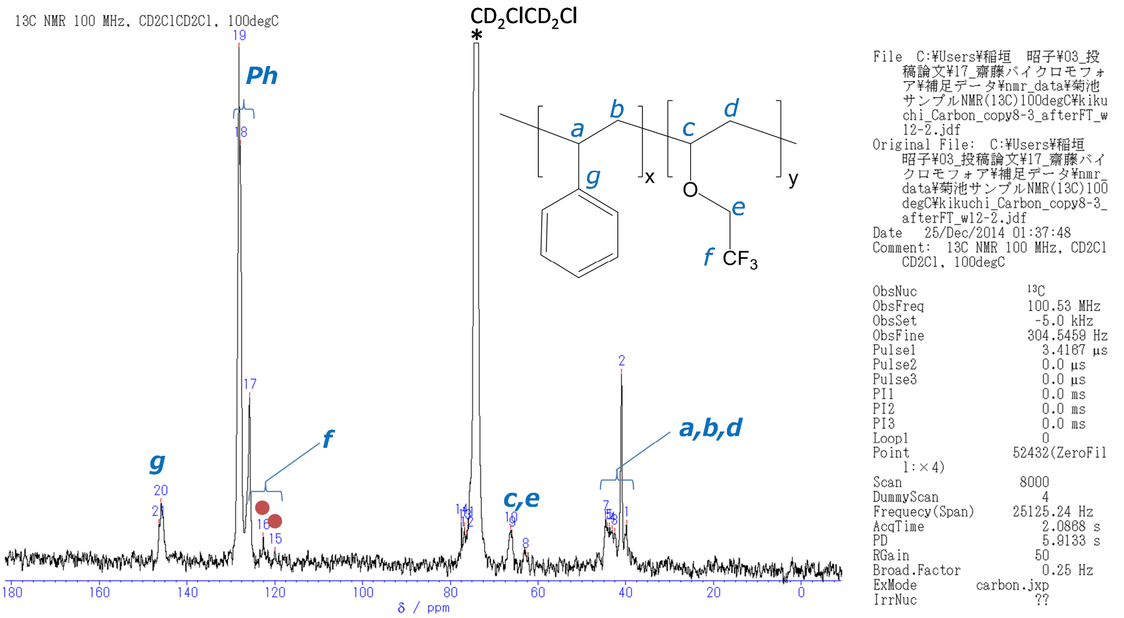


Figure S5. Copolymerization of Styrene and TFEVE by **1** under OFF → ON irradiation

a) ^{13}C NMR spectra (100 MHz, CD_2ClCD_2Cl, 100ºC)



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b) ^{1}H NMR spectra (100 MHz, CD_2ClCD_2Cl, 100ºC)

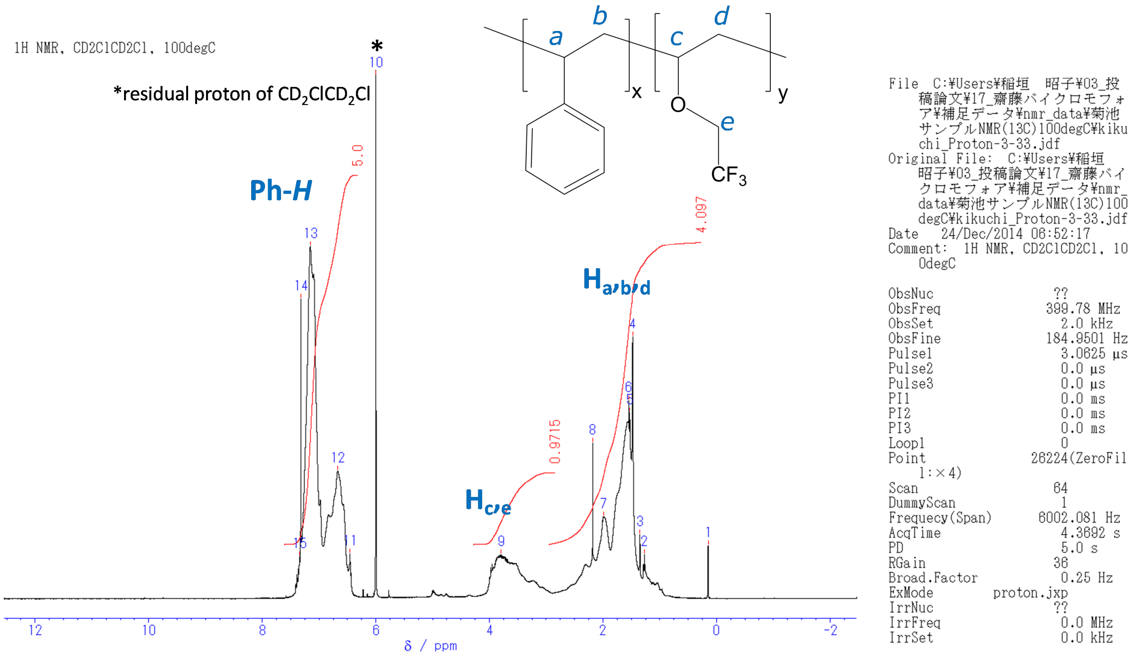

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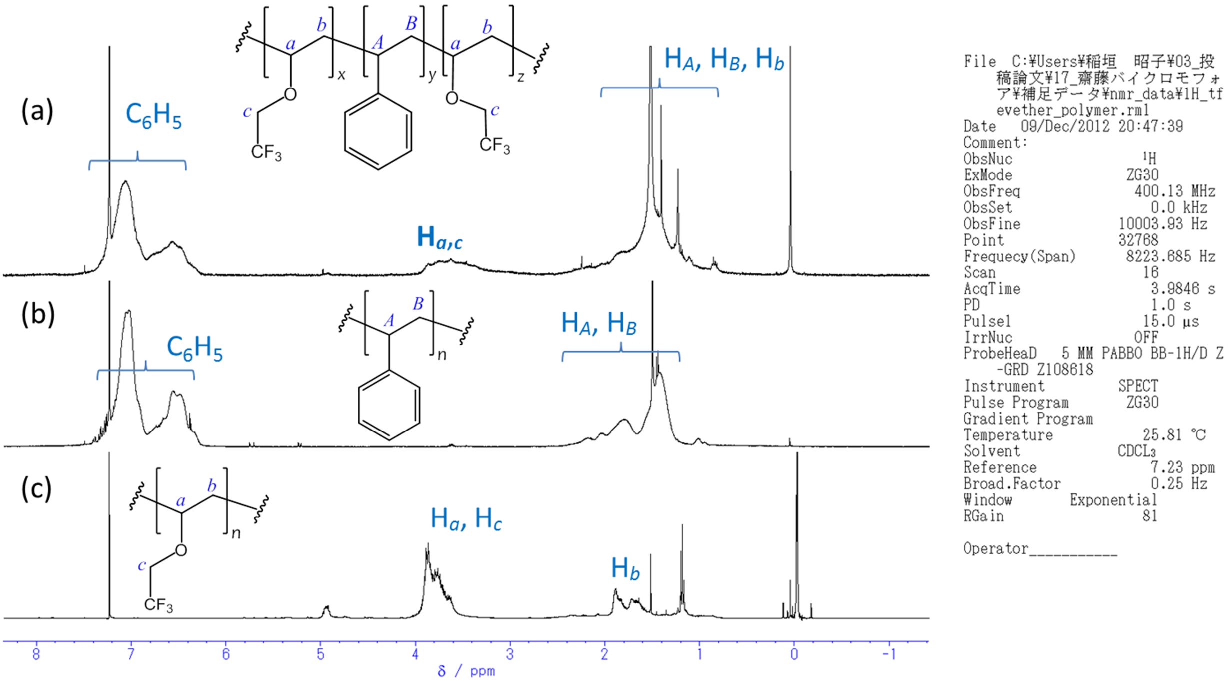
Figure S6. ^{1}H, ^{13}C, NMR spectra of TFEVE / styrene copolymer (M_W = 5786, M_n = 4209, M_W/M_n = 1.37)



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Operator___________
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Figure S7. Comparison of ^{1}H NMR spectra of copolymer with styrene and TFEVE homopolymers

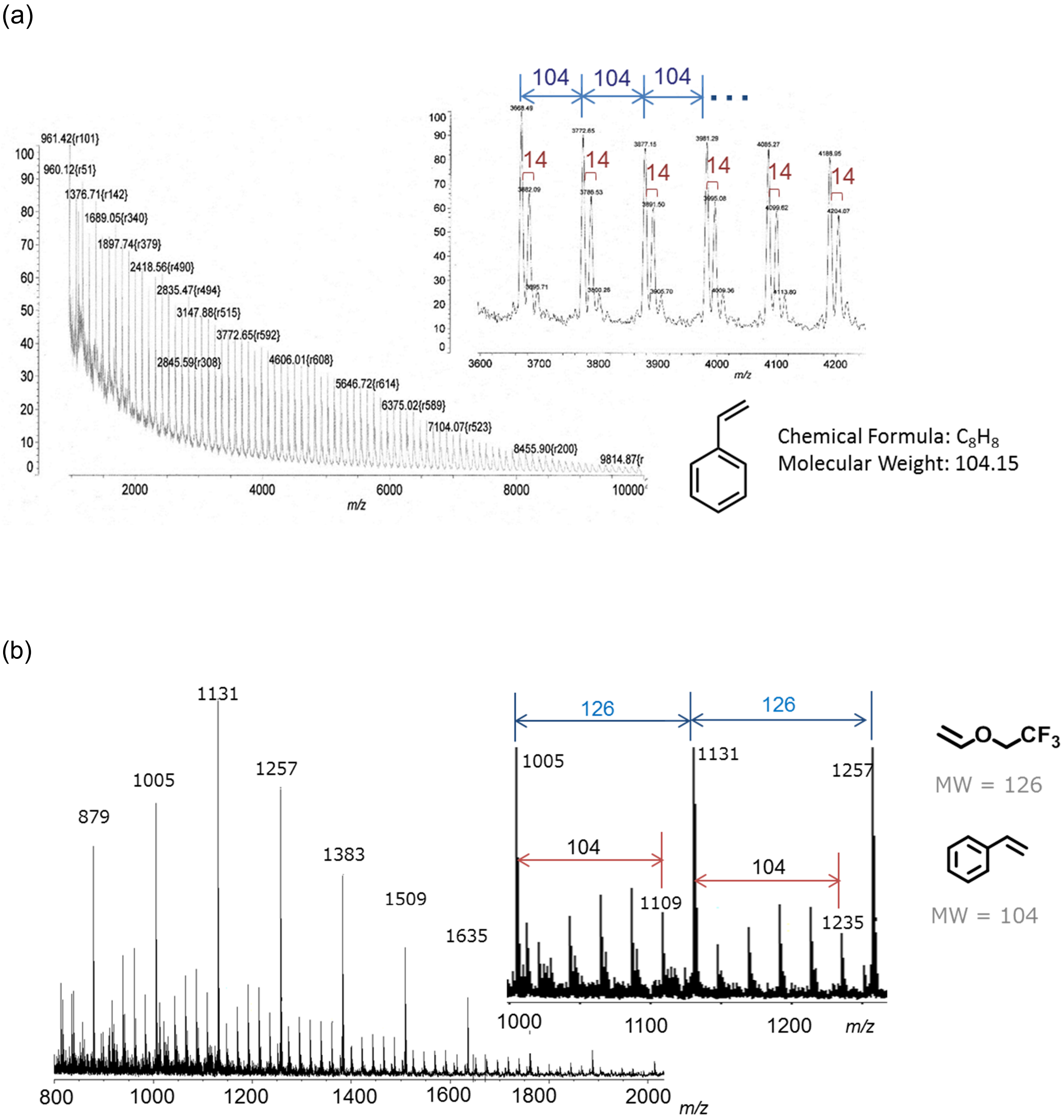


Figure S8. MALDI-TOF-MS spectra of (a) polystyrene catalyzed by **1** (2 mol%, CD_3NO_2, irradiated at λ > 420 nm), (b) TFEVE / styrene copolymer catalyzed by **1** (1 mol%, CD_3NO_2, irradiated at λ > 420 nm). Matrix: dithranol

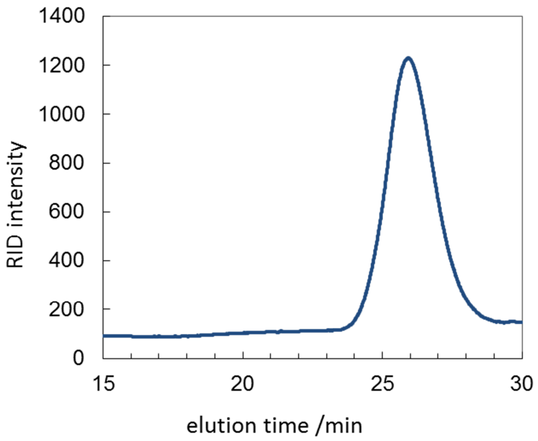
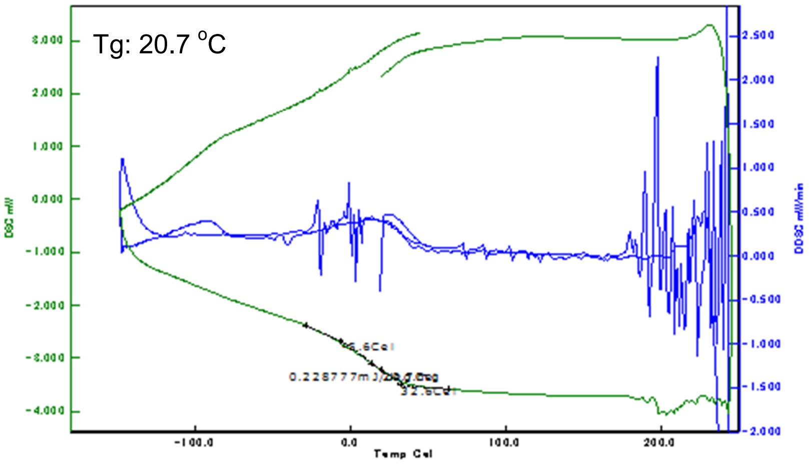
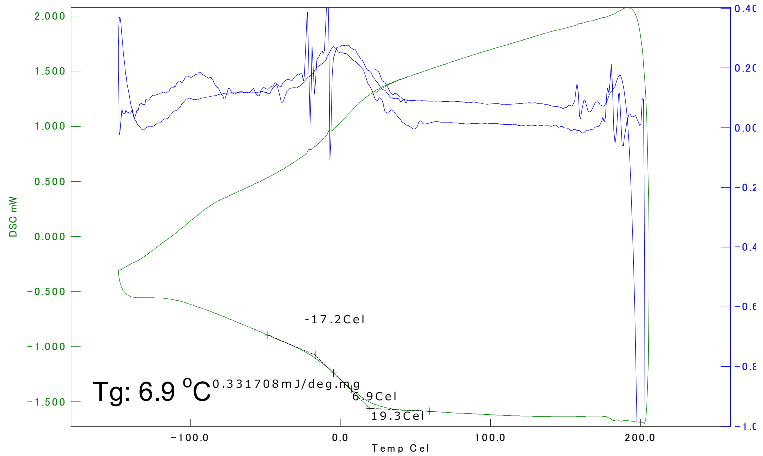


Figure S9. GPC chart of TFEVE / styrene copolymer (M_{W} = 5786, M_{n} = 4209, $M_{\mathrm{W}}/M_{\mathrm{n}}$ = 1.37)

a) DSC curve of the TFEVE / styrene copolymer (Table 2, entry 1)



b) DSC curve of the TFEVE / styrene copolymer (Table 2, entry 2)



c) DSC curve of the TFEVE / styrene copolymer (Table 2, entry 3)

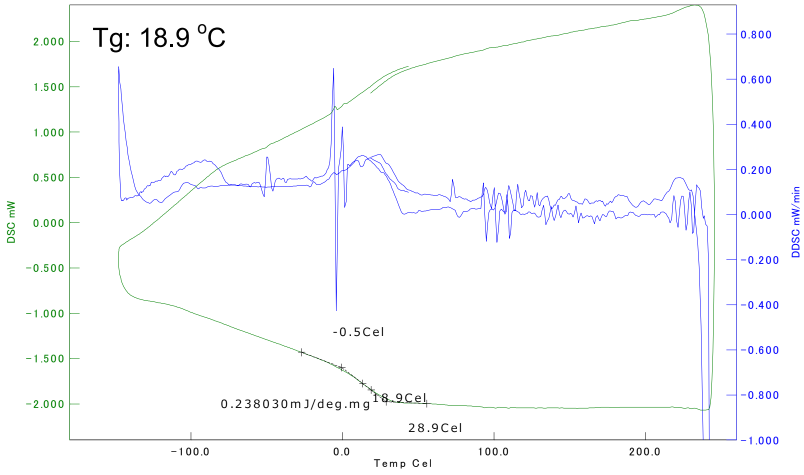


Figure S10. DSC curves of the TFEVE / styrene copolymer

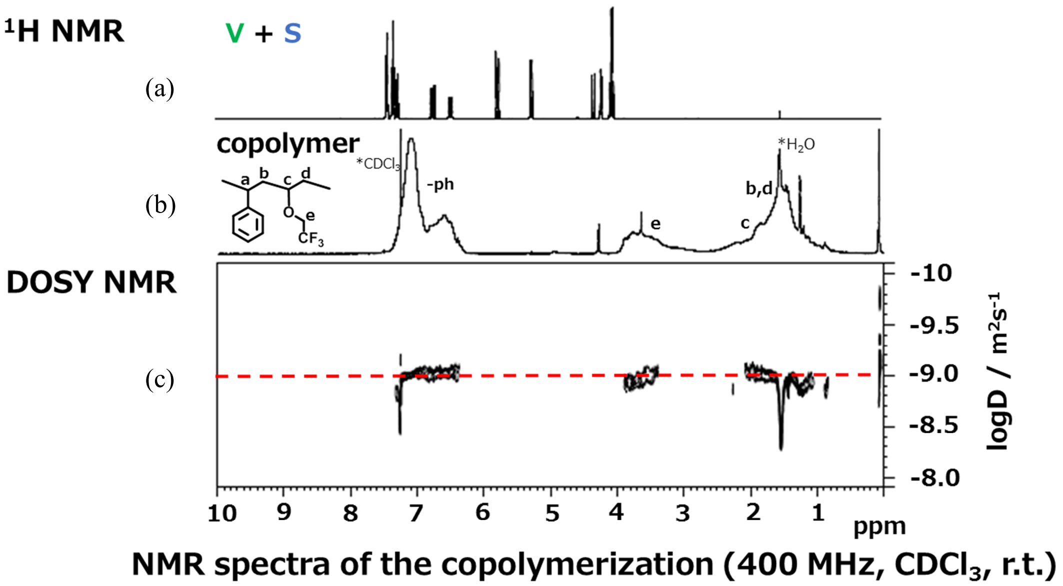


Figure S11. ^{1}H, ^{13}C, DOSY NMR spectra of TFEVE / styrene copolymer

(a) ^{1}H NMR spectra of (a) 2,2,2-trifluoroethyl vinyl ether (V) and styrene (S),

(b) copolymer of V and S, (c) DOSY NMR spectrum of the V-S copolymer.

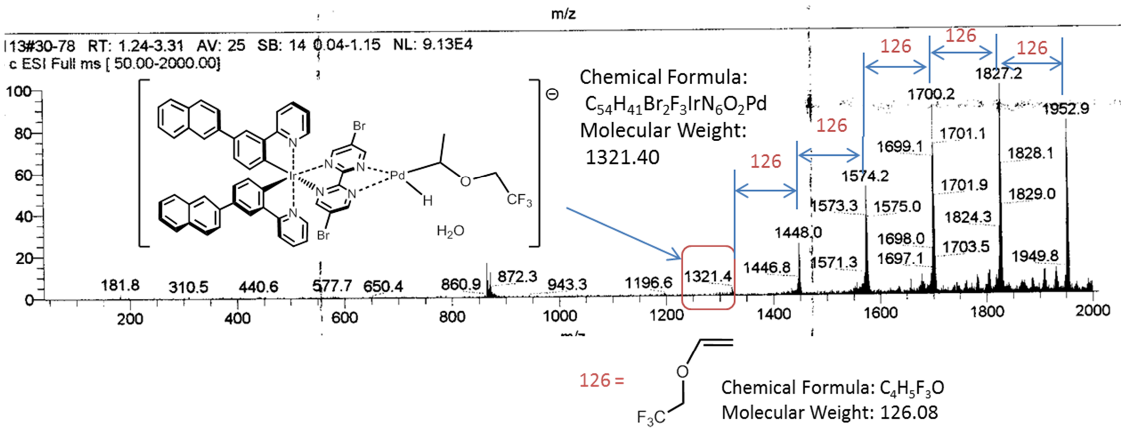


Figure S12. ESI-MS spectra of the reaction mixture of the catalytic copolymerization with TFEVE and styrene

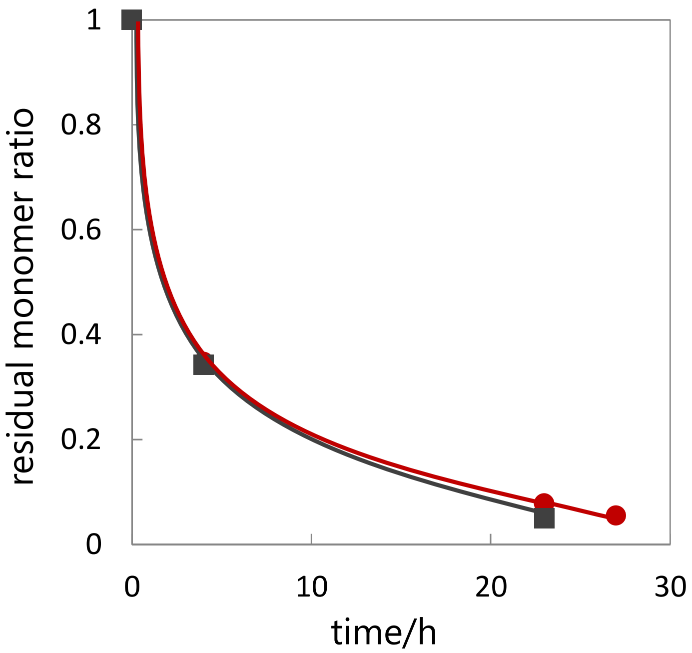


Figure S13. Consumption rate of TFEVE under dark (square) or irradiated (circle) condition (with 1 mol% of catalyst **1**).

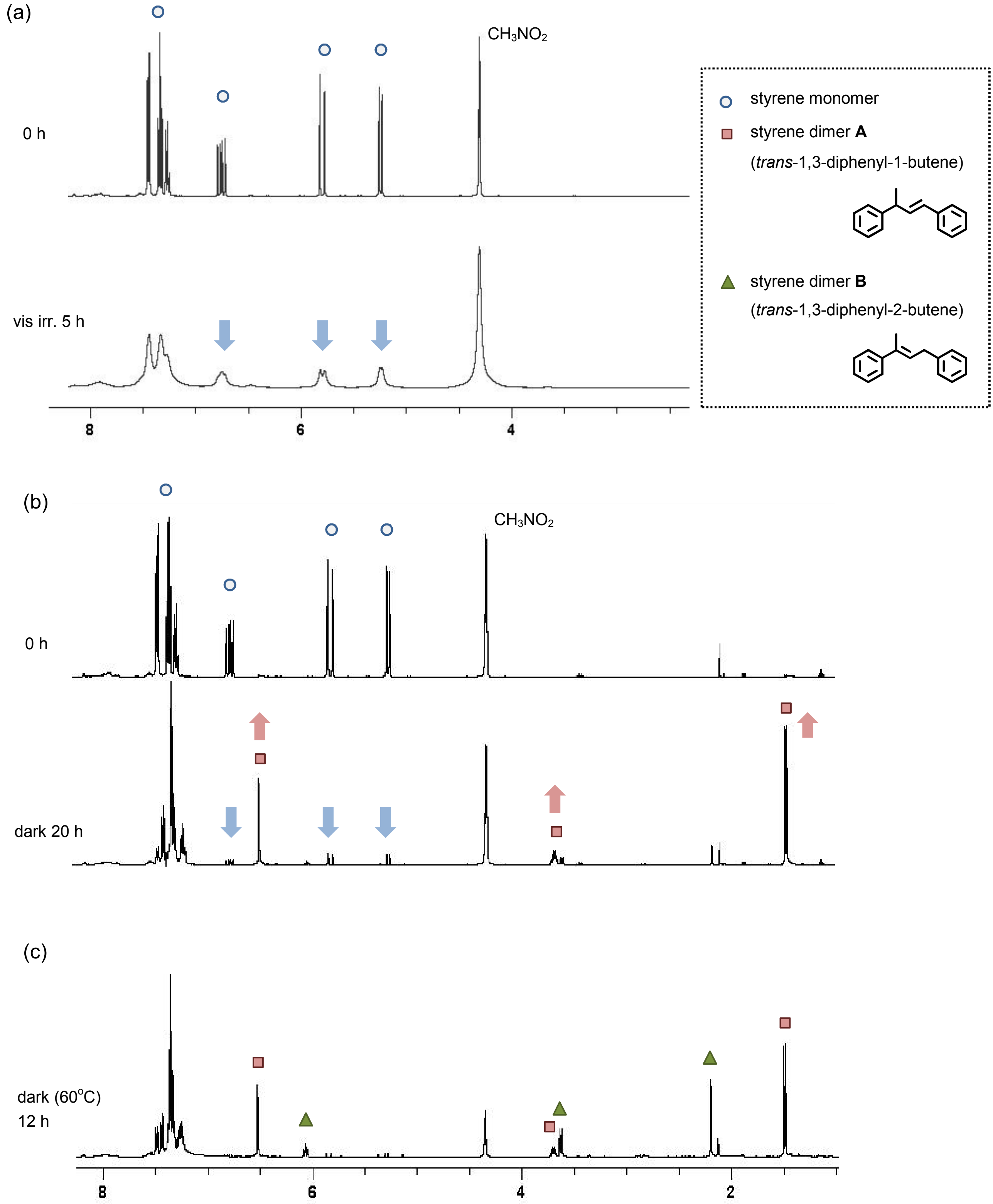


Figure S14. ^{1}H NMR spectra during the photocatalytic polymerization of styrene by **1** in different conditions (400 MHz, CD3NO2, r.t.) (a) visible-light irradiation (l > 420 nm, r.t.) (b) dark (r.t.), (c) dark (60 ^{o}C)

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