Electronic supporting information

Substituents para-to-ortho positioning effect driving the photoreactivity of a dibenzothiophene-based oxalate series used as LEDs excitable free radical photoinitiators

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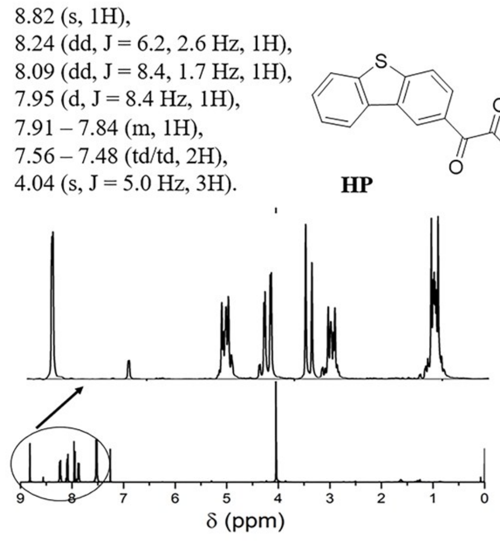
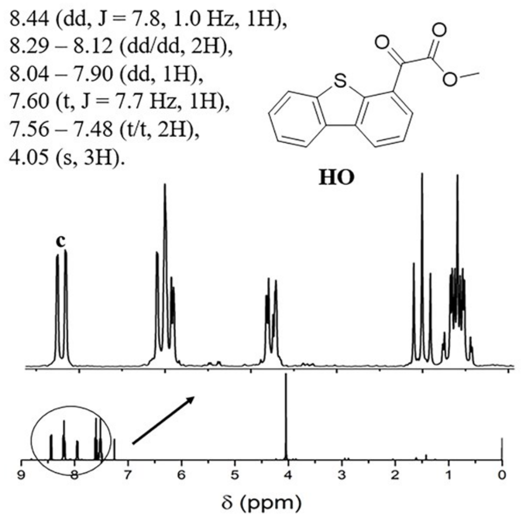
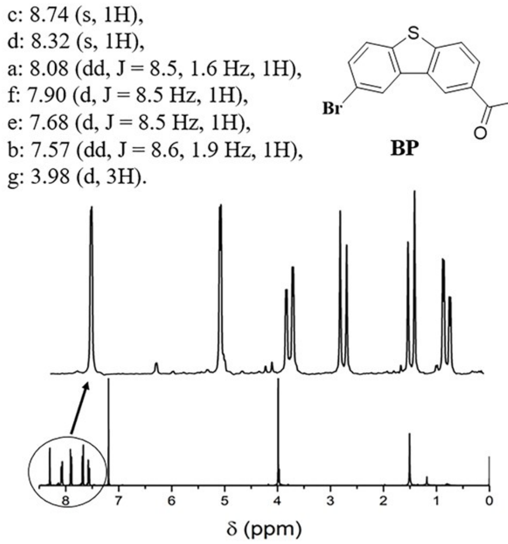


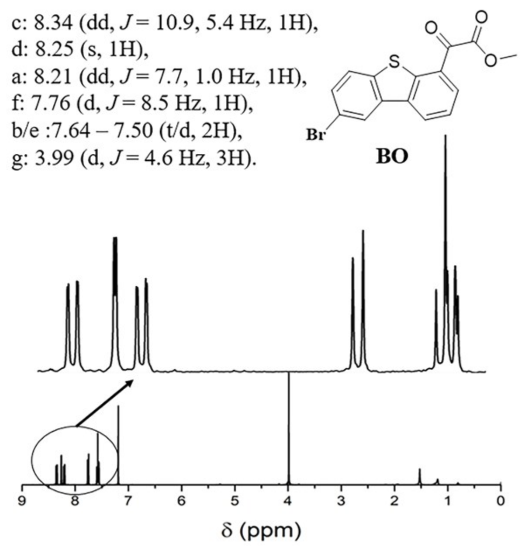
(a) ^{1}H NMR spectra of HP in $CDCl_3$



(b) ^{1}H NMR spectra of HO in $CDCl_3$

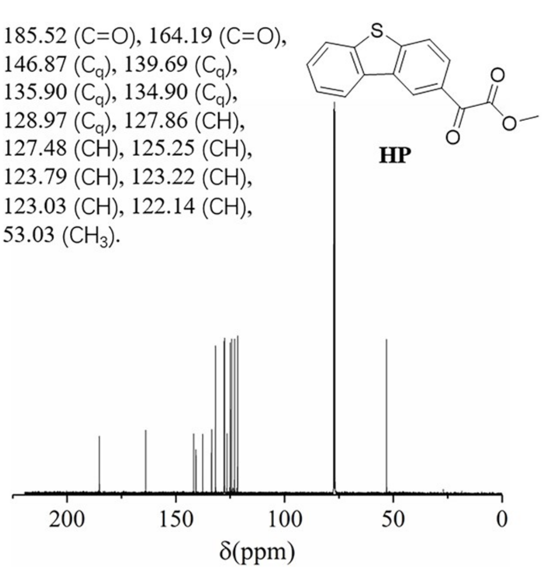


(c) ^{1}H NMR spectra of BP in $CDCl_3$

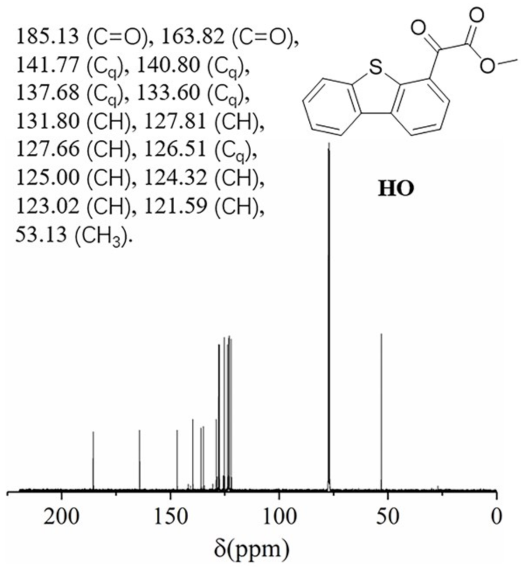


(d) ^{1}H NMR spectra of BO in $CDCl_3$

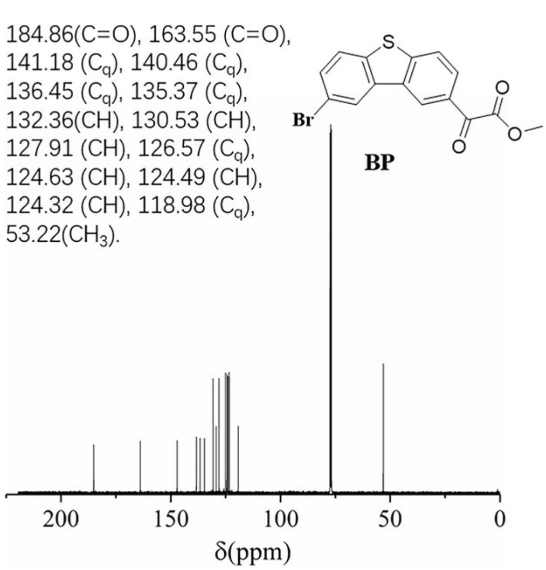
Figure S1. The ^{1}H NMR spectra of four compounds in $CDCl_3$.



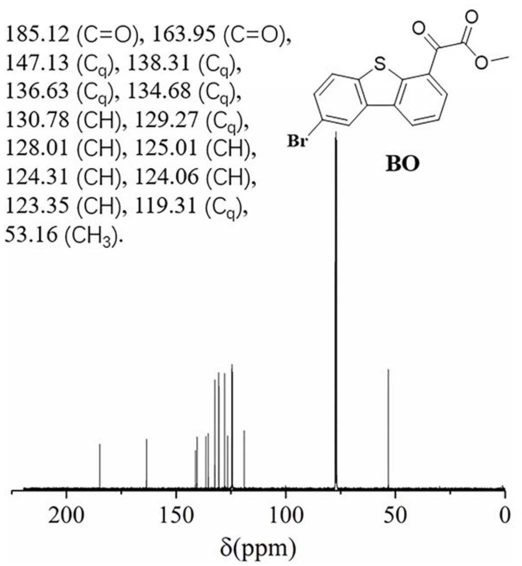
(a) ^{13}C NMR spectra of HP in $CDCl_3$



(b) ^{13}C NMR spectra of HO $CDCl_3$



(c) ^{13}C NMR spectra of BP in $CDCl_3$



(d) ^{13}C NMR spectra of BP $CDCl_3$

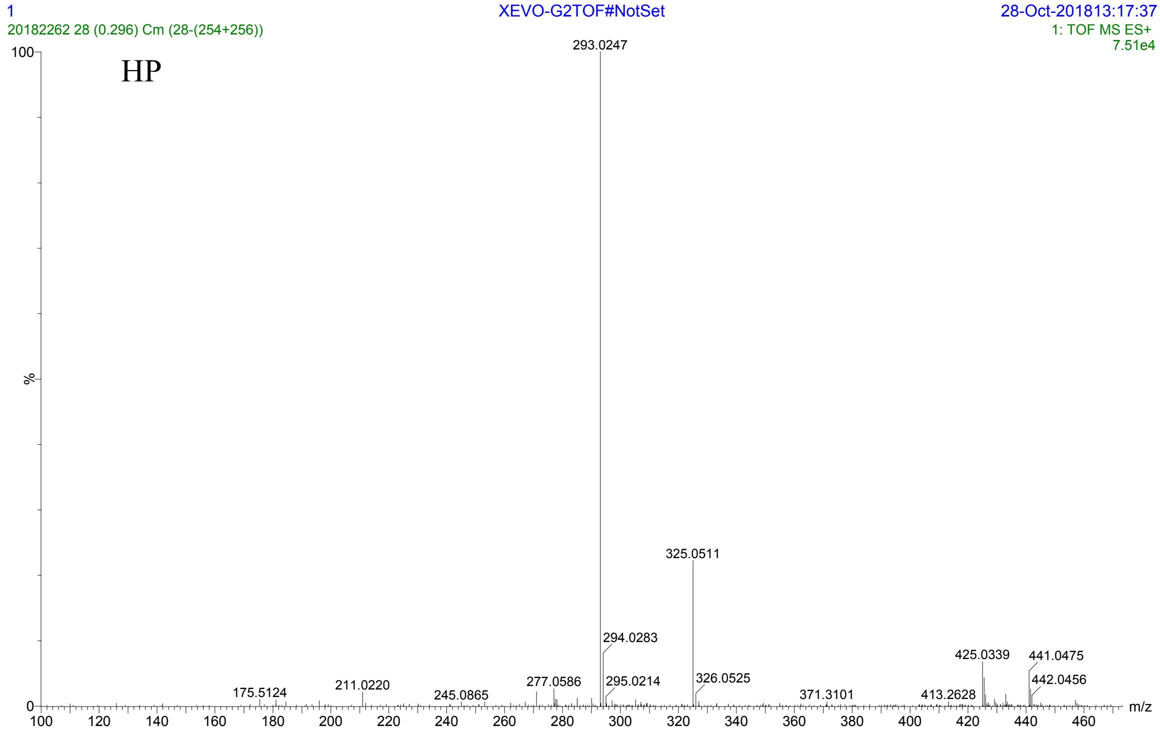
Figure S2. The ^{13}C NMR spectra of four compounds in $CDCl_3$.

HP. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.82 (s, 1H), 8.24 (dd, J = 6.2, 2.6 Hz, 1H), 8.09 (dd, J = 6.2, 2.6 Hz, 1H), 7.95 (d, J = 8.4 Hz 1H), 7.91–7.84 (m, 1H), 7.56–7.48 (td/td, 2H), 4.04 (s, J = 8.4 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 185.52 (C=O), 164.19 (C=O), 146.87 (C_q), 139.69 (C_q), 135.90 (C_q), 134.90 (C_q), 128.97 (C_q), 127.86 (CH), 127.48 (CH), 125.25 (CH), 123.79 (CH), 123.22 (CH), 123.03 (CH), 122.14 (CH), 53.03 (CH_3). HRMS (TOF MS ESI): m/z 293.0247 (M + Na^+) (Calcd: 270.0351).

HO. ^{1}H NMR ($CDCl_3$) ı (ppm): 8.44 (dd, J = 7.8, 1.0 Hz, 1H), 8.29–8.12 (dd/dd, 2H), 8.04–7.90 (dd, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.56–7.48 (t/t, 2H), 4.05 (s, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 185.13 (C=O), 163.82 (C=O), 141.77 (C_q), 140.80 (C_q), 137.68 (C_q), 133.60 (C_q), 131.80 (CH), 127.81 (CH), 127.66 (CH), 126.51 (C_q), 125.00 (CH), 124.32 (CH), 123.02 (CH), 121.59 (CH), 53.13 (CH_3). HRMS (TOF MS ESI): m/z 293.0247 (M + Na^+) (Calcd: 270.0351).

BP. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.74 (s, 1H), 8.32 (s, 1H), 8.08 (dd, J = 8.5, 1.6 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.57 (dd, J = 8.6, 1.9 Hz, 1H), 3.98 (d, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 184.86(C=O), 163.55 (C=O), 141.18 (C_q), 140.46 (C_q), 136.45 (C_q), 135.37 (C_q), 132.36(CH), 130.53 (CH), 127.91 (CH), 126.57 (C_q), 124.63 (CH), 124.49 (CH), 124.32 (CH), 118.98 (C_q), 53.22(CH_3). HRMS (TOF MS ESI): m/z 370.9355 (M + Na^+) (Calcd: 347.9456).

BO. 1H NMR (CDCl3) δ (ppm): 8.34 (dd, J = 10.9, 5.4 Hz, 1H), 8.25 (s, 1H), 8.21 (dd, J = 7.7, 1.0 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.64 – 7.50 (t/d, 2H), 3.99 (d, J = 4.6 Hz, 3H). 13C NMR (CDCl3) δ (ppm): 185.12 (C=O), 163.95 (C=O), 147.13 (Cq), 138.31 (Cq), 136.63 (Cq), 134.68 (Cq), 130.78 (CH), 129.27 (Cq), 128.01 (CH), 125.01 (CH), 124.31 (CH), 124.06 (CH), 123.35 (CH), 119.31 (Cq), 53.16 (CH3). HRMS (TOF MS ESI): m/z 386.0710 (M + K+) (Calcd: 347.9456).



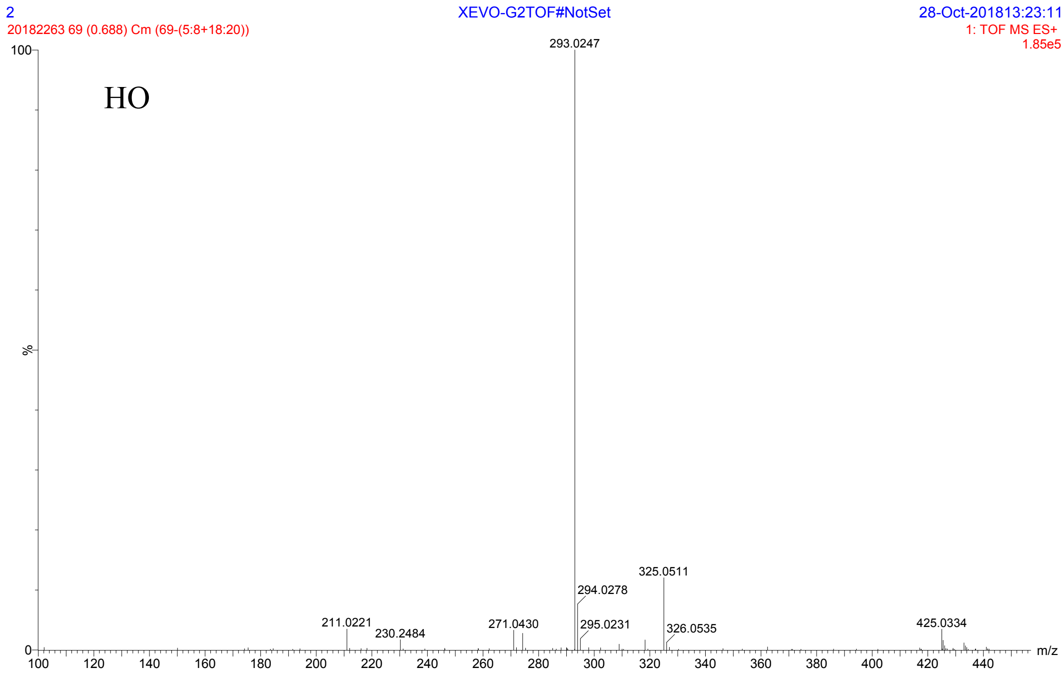


Figure S3. The Mass spectra of HO and HP.

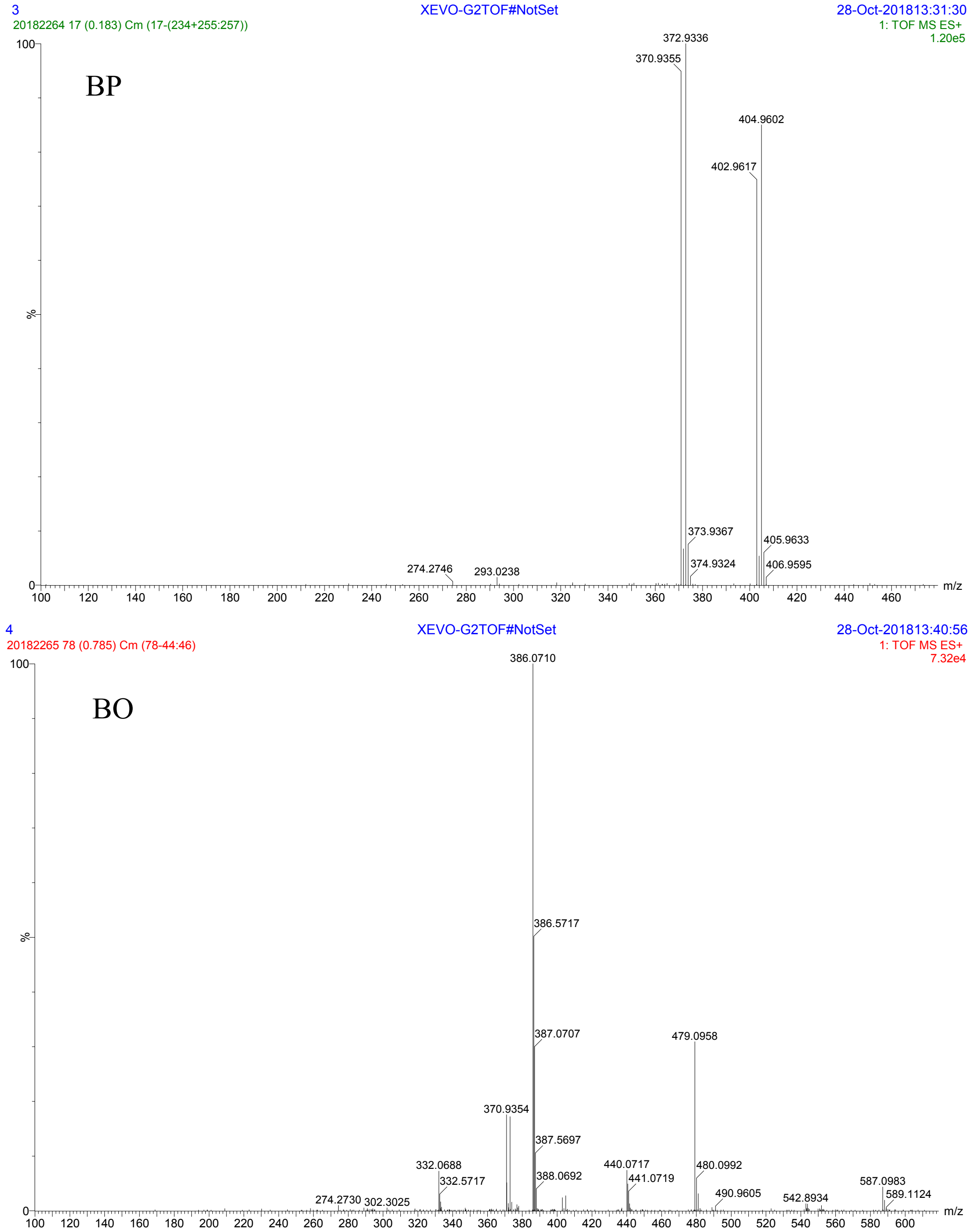


Figure S4. The Mass spectra of BO and BP.

Table S1. hfc (hyperfine coupling constants) for the detected spin adduct of PBN in toluene of four PIs.

PIs	Radical 1	Radical 2	PBNox
HP	a_N = 13.5 G ; a_H = 1.8 G ; (53.3%)	a_N = 14.0 G ; a_H = 5.1 G ; (44.3%)	(3.4%)
HO	a_N = 13.5 G ; a_H = 1.8 G ; (56.2%)	a_N = 14.0 G ; a_H = 5.1 G ; (42.0%)	(1.8%)
BP	a_N = 13.6 G ; a_H = 1.8 G ; (47.8%)	a_N = 14.0 G ; a_H = 5.1 G ; (50.2%)	(2.0%)
BO	a_N = 13.6 G ; a_H = 1.8 G ; (59.3%)	a_N = 14.0 G ; a_H = 5.1 G ; (39.2%)	(1.5%)

Table S2. Complete photopolymerization results using distinctive LEDs sources and upon irradiance in the 30-80 mW cm^{-2} range

Monomer	LEDs (λ_{irr}) / (mW·cm^{-2})	Photoinitiator	concentration of Photoinitiator	R_p / [M] s^{-1}	Conversion at t = 60 s (%)
TPGDA	365/27	**HP**	3 wt%	26	92
		HO		11	91
		BP		30	93
		BO		22	95
TMPTA		**HP**	1 wt%	5.6	41
		HO		3.7	43
		BP		4.4	40
		BO		3.2	51
HDDA		**HP**	1 wt%	9.3	85
		HO		4.3	82
		BP		6.9	78
		BO		4.1	70
TPGDA	385/48	**HP**	3 wt%	24	92
		HO		16	92
		BP		25	94
		BO		20	95
TMPTA		**HP**	1 wt%	5.3	44
		HO		4.6	48
		BP		3.6	36
		BO		4.2	41
HDDA		**HP**	1 wt%	6.5	83
		HO		3.5	82
		BP		5.7	82
		BO		3.5	76
TPGDA	405/77	**HP**	3 wt%	25	89
		HO		25	89
		BP		24	87
		BO		24	90
TMPTA		**HP**	1 wt%	1.5	31
		HO		3.1	46
		BP		1.5	34
		BO		2.2	32
HDDA		**HP**	1 wt%	1.0	59
		HO		1.7	79
		BP		1.2	62
		BO		2.4	70
TPGDA	425/37	**HP**	3 wt%	6.7	88
		HO		9.2	88
		BP		5.4	82
		BO		6.5	86
TMPTA		**HP**	1 wt%	0.1	17
		HO		0.5	28
		BP		0.04	14
		BO		0.1	20
HDDA		**HP**	1 wt%	0.5	46
		HO		0.7	66
		BP		0.8	41
		BO		0.9	70