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Supporting Information

to the article

Photo Lewis Acid Generators: Photorelease of $B(C_6F_5)_3$ and Applications to Catalysis

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Contents

Experimetal details

An argon filled MBraun glove box was employed for manipulation and storage of all oxygen and moisture sensitive compounds. All reactions were performed on a double manifold high vacuum line using standard techniques.[1] Toluene and hexanes were dried and purified using the Grubbs/Dow purification system.[2] Other solvents as well as NMR solvents were dried by distillation from appropriate drying agents. NMR spectra were obtained using Bruker AVANCE III 400 MHz and AVANCE III 600 MHz spectrometers ^{1}H and ^{13}C chemical shifts were referenced to residual proton and naturally abundant ^{13}C resonance of the deuterated solvent, respectively. ^{19}F NMR spectra were externally referenced to C_6F_6 (δ –163.0 ppm) in C_6D_6.[3] ^{11}B NMR spectra were externally referenced to BF_3OEt_2 (δ 0 ppm) in d_6-DMSO. IR spectra were recorded in nujol using Nicolet Nexus 470 FT-IR spectrometer. UV-vis spectra were obtained with a Varian Cary 300 spectrometer using 1 cm quartz cuvettes. All UV-vis samples were prepared in a glove box using dry CH_2Cl_2. TGA/DSC analysis was performed using NETZSCH STA 409 PC/PG instrument. GC-MS analysis was obtained using an Agilent Technologies 6890N GC equipped with a 5975 mass detection unit. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Measurements were collected on a Nonius KappaCCD diffractometer by Dr. Masood Parvez; full details can be found in the independently deposited crystallography information files (cif). Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ was sublimed at 65 °C under high dynamic vacuum, dried over $Me_2Si(H)Cl$ for 4 h and re-sublimed under the same conditions after vacuum removal of volatiles. $[Ph_3S][Cl]$ and $[Ph_2I][Cl]$ were purchased from Sigma-Aldrich and used without further purification. Et_3SiH and 2,2,6,6-tetramethylpiperidine were purchased from TCI America and Sigma Aldrich, respectively. The silane was dried over and distilled from fresh $LiAlH_4$ while the amine was dried over and distilled from activated 4Å molecular sieves. Dry carbon dioxide, grade 3.0, was obtained from Praxair and used as received. Preparation, properties and reactivity of **1-Ph$_3$S** were reported previously.[4] $(Me_4C_5N)CO_2Li$ (**4**)[5] and $[K][HB(C_6F_5)_3]$ (**7-K**)[6] were synthesized according to literature procedures. **3-TMPH** was described previously.[7]

Decomposition of 1-Ph_2I to $B(C_6F_5)_3$ under ambient light

CD_3CN (65.3 μL, 1.25 mmol) was added to a solution of **1-Ph_2I** (1.4 mg, 1.25×10^{-3} mmol) in 534.7 μL of CD_2Cl_2 in a quartz NMR tube ($[\mathbf{1\text{-}Ph_2I}]_{total} = 2.1\times10^{-3}$ mol/L). No reaction was observed in dark within 30 min at room temperature. The sample was exposed to the ambient light at room temperature for 17.5 hours, followed by the NMR analysis which showed formation of a mixture of $CD_3CN{\bullet}B(C_6F_5)_3$ (41% by $^{19}F\{^1H\}$ NMR) and another unknown decomposition product (29% by $^{19}F\{^1H\}$ NMR) with 70% total conversion of **1-Ph_2I**. In the absence of acetonitrile no formation of $B(C_6F_5)_3$ from **1-Ph_2I** under ambient light was observed. Only slow (3 weeks to approx. 50% conversion) decomposition of **1-Ph_2I** to a mixture of unknown products was observed by NMR.

Decomposition of 1-Ph_2I at room temperature in dark

A solution of **1-Ph_2I** (10 mg, 9.0×10^{-3} mmol) in 0.6 mL of CD_2Cl_2 in an NMR tube was left at room temperature in dark for 24 h. NMR analysis showed approx. 37% conversion of **1-Ph_2I** to a mixture of unknown decomposition products. No $B(C_6F_5)_3$ was observed by NMR.

Reactivity of 5 with $^{13}CO_2$, TMP and $B(p\text{-}C_6F_4H)_3$

A. Treatment of 5 with $^{13}CO_2$. $^{13}CO_2$ (approx. 2.0 atm) was added *via* vacuum transfer to a solution of **5** (5.0 mg, 0.0072 mmol) in 0.5 mL of CD_2Cl_2 in a J. Young NMR tube. The reaction mixture was left at room temperature for 4 hours showing by ^{13}C NMR spectroscopy no incorporation of ^{13}C label into a carbonyl carbon position of **5**.

B. Treatment of 5 with TMP. TMP (2.0 μL, 0.012 mmol) was added in one portion at room temperature to a solution of **5** from part A (after the release of $^{13}CO_2$ pressure). The mixture was left at room temperature for 5 min and then analysed by NMR spectroscopy, which showed full conversion of **5** to **3-TMPH**.

C. Treatment of 5 with $B(p\text{-}C_6F_4H)_3$. A solution of **5** (5.0 mg, 0.0072 mmol) in 0.5 mL of CD_2Cl_2 was added in one portion at room temperature to $B(p\text{-}C_6F_4H)_3$ (3.5 mg, 0.0076 mmol). The mixture was left at room temperature for 1h showing by $^{19}F\{^1H\}$ NMR spectroscopy no release of $B(C_6F_5)_3$ and no incorporation of $B(p\text{-}C_6F_4H)_3$ into **5**.

Attempted photoinduced hydrosilylation of PhC(O)Me with Et_3SiH in the presence of 3-Ph_3S.

A: Acetophenone (17.5 μL, 0.15 mmol), Et_3SiH (24.0 μL, 0.15 mmol), and **3-Ph_3S** (1.4 mg, 0.0015 mmol) were mixed together in 0.5 mL of CD_2Cl_2 in a quartz NMR tube. The mixture was left at room temperature and ambient light for 30 min showing by NMR spectroscopy no reaction. The sample was exposed to 254 nm light for 30 min showing no hydrosilylation reaction occurring.

B: Reaction in the presence of acetonitrile. Acetophenone (17.5 μL, 0.15 mmol), Et_3SiH (24.0 μL, 0.15 mmol), **3-Ph_3S** (1.4 mg, 0.0015 mmol), and CH_3CN (0.1 μL, 0.0019 mmol) were mixed together in 0.5 mL of CD_2Cl_2 in a quartz NMR tube. The mixture was left at room temperature and ambient light for 30 min showing by NMR spectroscopy no reaction. The sample was exposed to 254 nm light for 30 min showing no hydrosilylation reaction occurring.

Decomposition of 7-Ph_3S under ambient light.

A solution of **7-Ph_3S** in CD_3CN ($2.1 \cdot 10^{-3}$ mol/L) was placed into a quartz NMR tube. The mixture was left at room temperature and ambient light for 96 hours and then analysed by NMR spectroscopy, which showed 14% conversion (by ^{19}F NMR) of **7-Ph_3S** to $CD_3CN \cdot B(C_6F_5)_3$.

Decomposition of 7-Ph_2I under ambient light.

The reaction was done analogously to 7-Ph3S. Exposure of the sample of **7-Ph_2I** in CD_3CN ($2.1 \cdot 10^{-3}$ mol/L) to ambient light for 96 hours resulted in full conversion (by ^{19}F NMR) of **7-Ph_2I** to $CD_3CN \cdot B(C_6F_5)_3$.

Thermal stability of 1-Ph_3S, 1-Ph_2I, 3-Ph_3S, 7-Ph_3S, and 7-Ph_2I

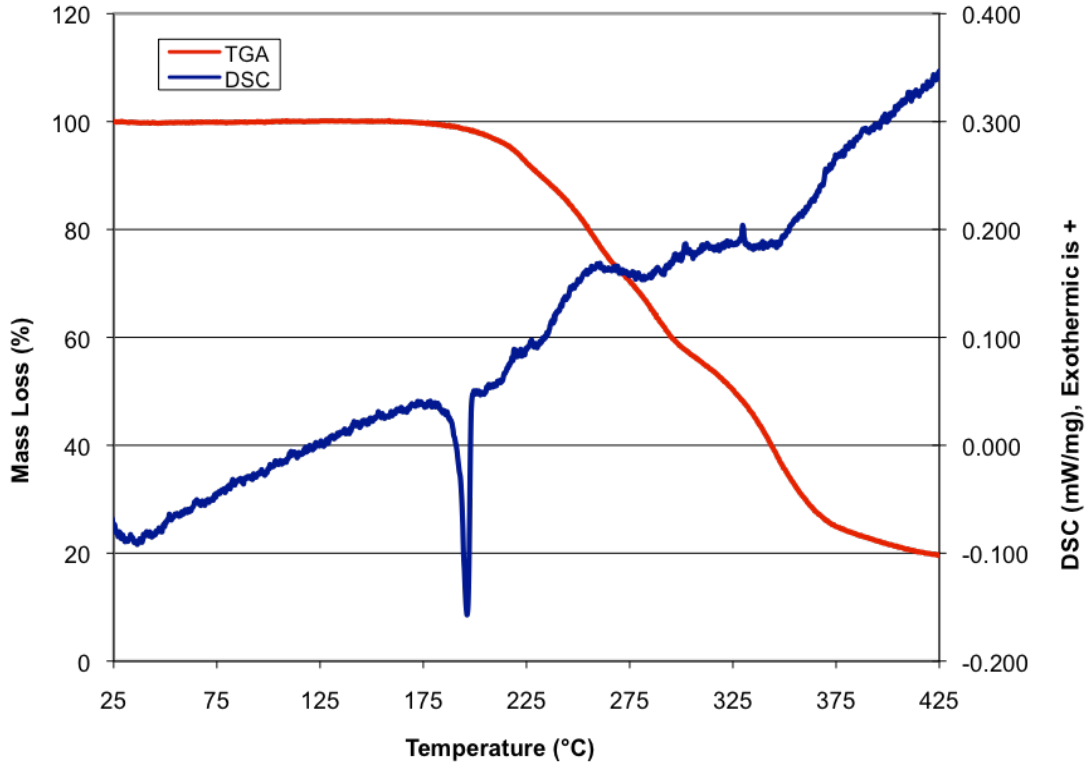

Figure S1. TGA/DSC diagram for **1-Ph_3S**.[4]

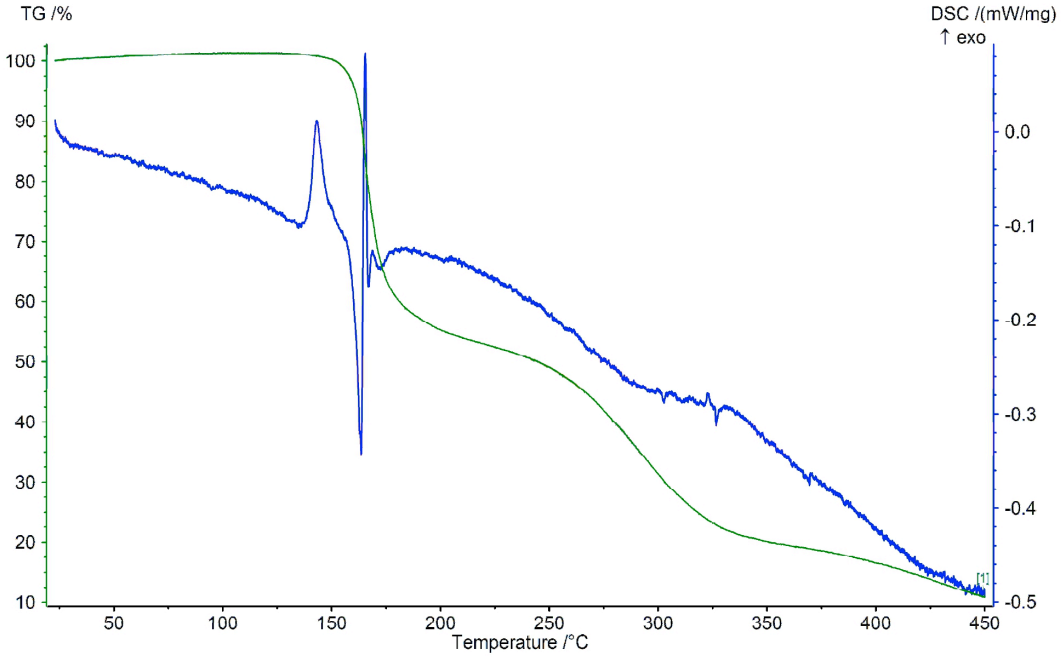

Figure S2. TGA/DSC diagram for **1-Ph_2I**.

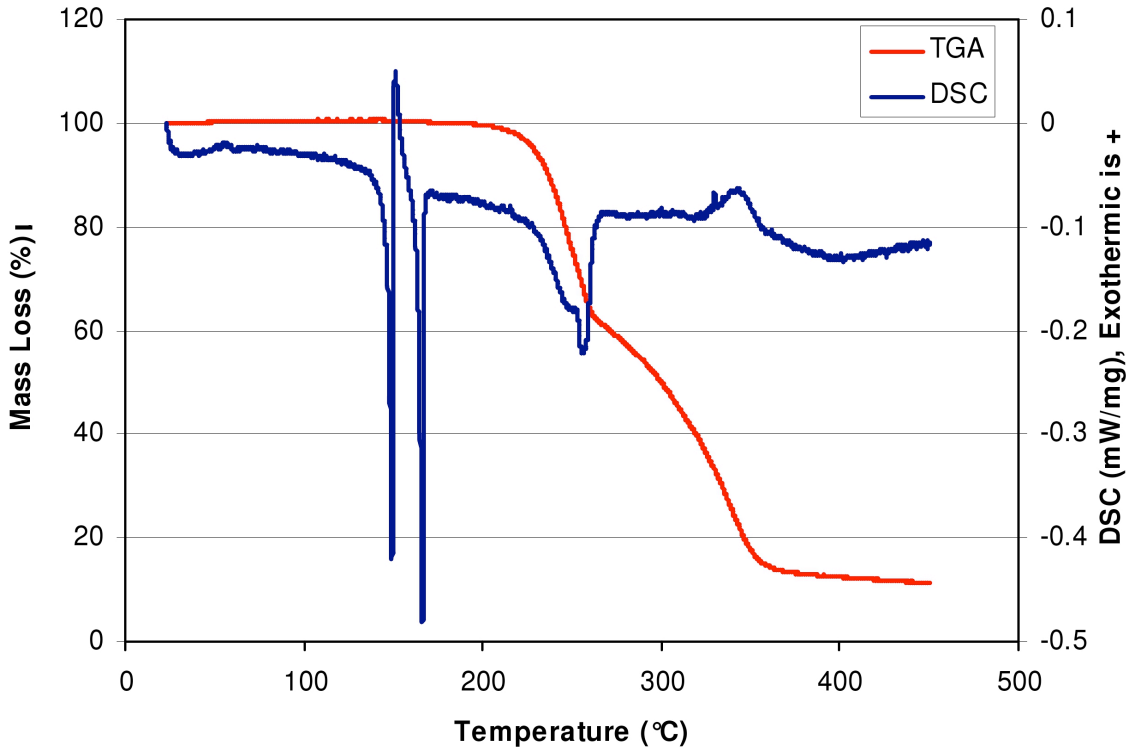

Figure S3. TGA/DSC diagram for **3-Ph_3S**

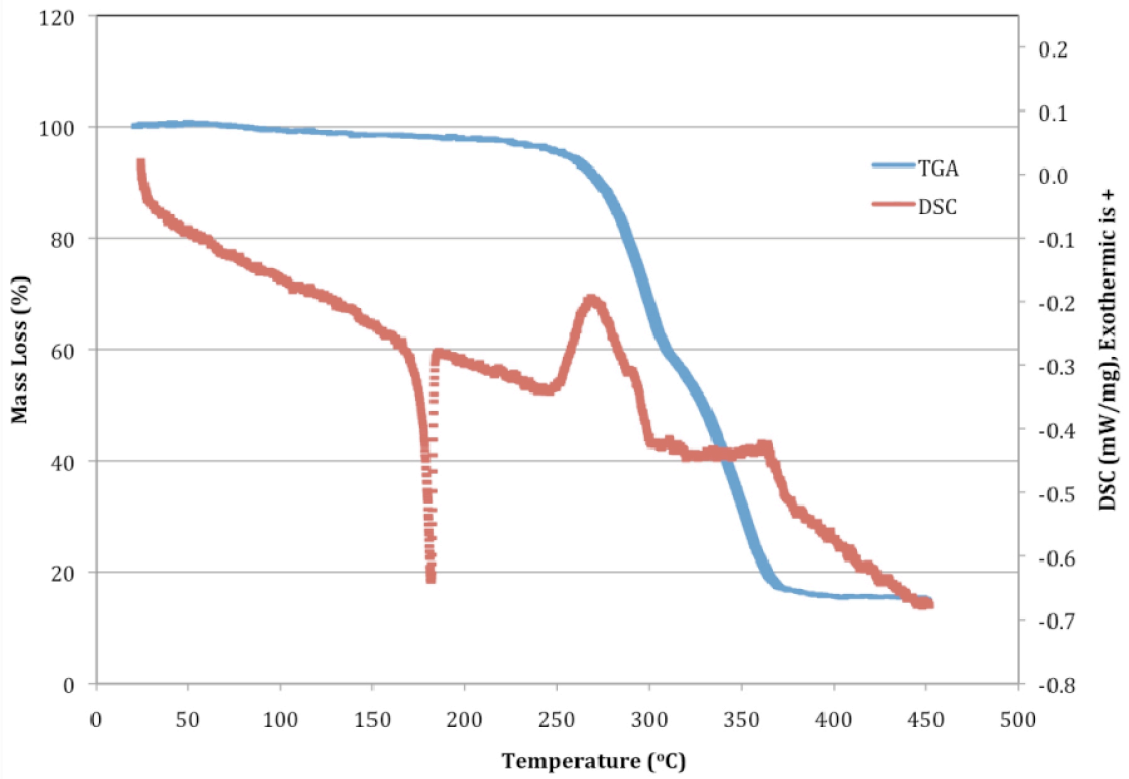

Figure S4. TGA/DSC diagram for **7-Ph_3S**.

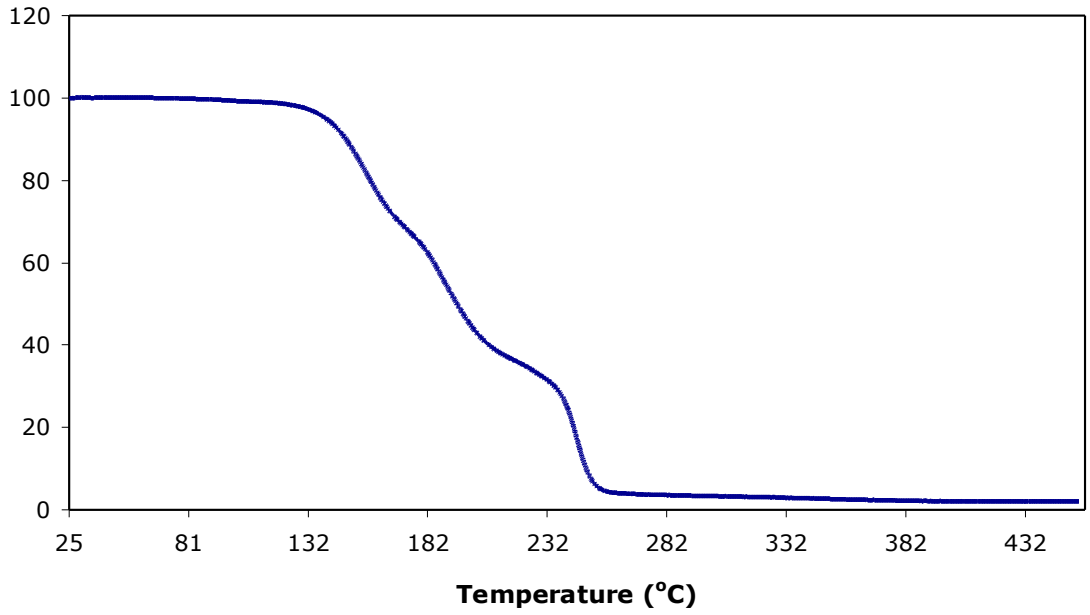

Figure S5. TGA diagram for **7-Ph_2I**.

Photolysis of PhLAGs in different solvents

Table S1. Photodecomposition of **1-Ph$_3$S**, **1-Ph$_2$I**, **3-Ph$_3$S**, **7-Ph$_3$S**, and **7-Ph$_2$I** in different solvents.

#	Comp.	Conc., mol/L	Solvent	t_{irr}, min	Conv.[a]	k_{obs}, s^{-1}
1	**1-Ph$_3$S**[4]	$2.1\cdot10^{-3}$	CD_3CN	12	58%	$(1.4\pm0.3)\cdot10^{-3}$[b]
2	**1-Ph$_3$S**[4]	$2.0\cdot10^{-3}$	CD_2Cl_2/CD_3CN (1/4)	8	74%	$(2.7\pm0.4)\cdot10^{-3}$
3	**1-Ph$_3$S**[4]	$2.1\cdot10^{-3}$	CD_2Cl_2/CD_3CN (8.7/1)	12	>99%	$(3.3\pm0.3)\cdot10^{-3}$
4	**1-Ph$_2$I**	$2.1\cdot10^{-3}$	CD_2Cl_2/CD_3CN (8.7/1)	12	>99%	$(4.4\pm0.1)\cdot10^{-3}$
5	**3-Ph$_3$S**	$2.1\cdot10^{-3}$	CD_3CN	13	46%	$(1.0\pm0.4)\cdot10^{-3}$
6	**7-Ph$_3$S**	$2.1\cdot10^{-3}$	CD_3CN	12	81%	$(2.3\pm0.2)\cdot10^{-3}$
7	**7-Ph$_2$I**	$2.1\cdot10^{-3}$	CD_3CN	12	>99%	—[c]

[a] determined by ^{1}H NMR. [b] determined at 50% conversion of **1-Ph$_3$S**. [c] k_{obs} was not determined.

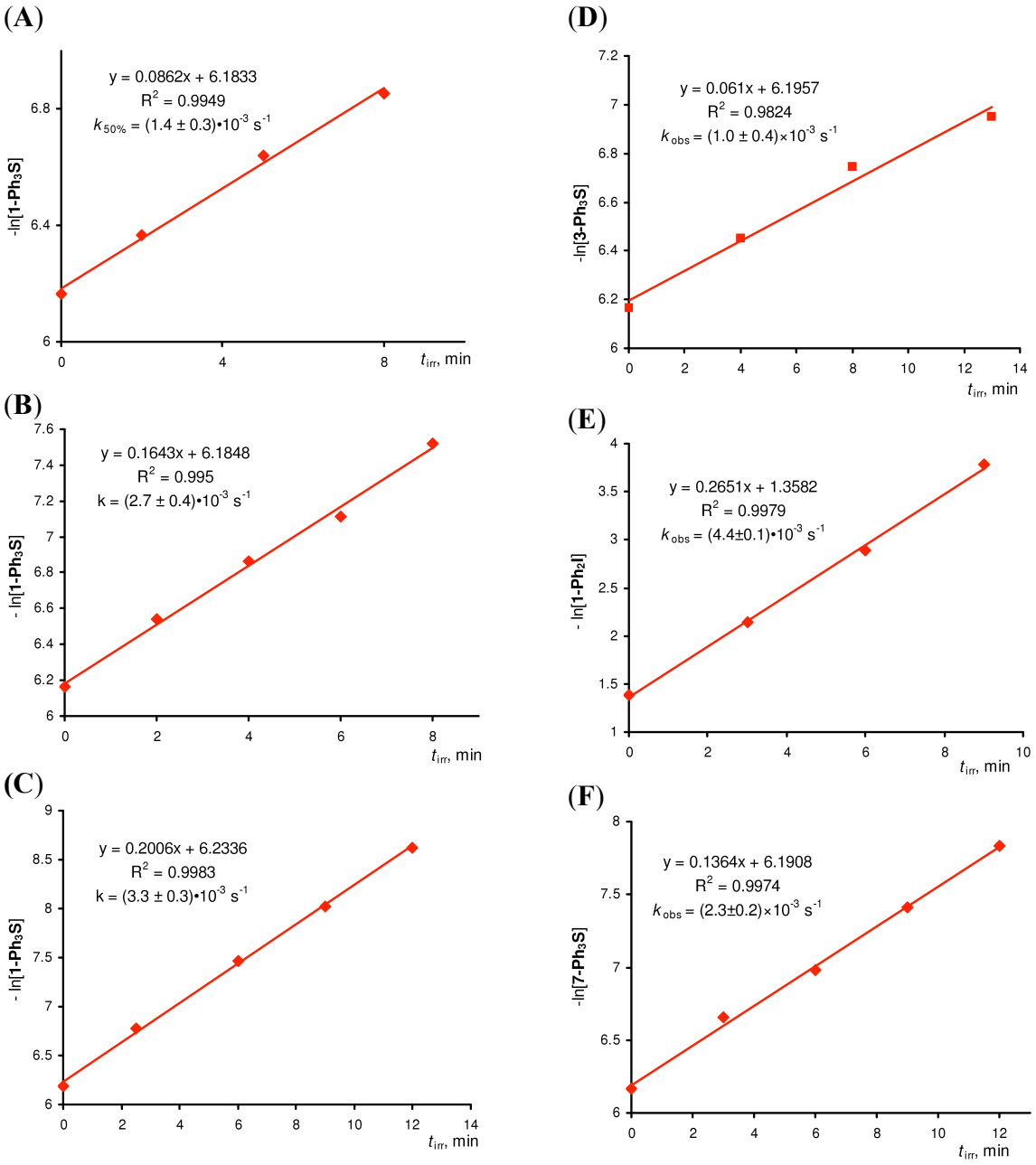

Figure S6. (**A**)**:** kinetic profile for decomposition of **1-Ph$_3$S** in CD_3CN ($2.1\cdot10^{-3}$ mol/L) to $CD_3CN\cdot B(C_6F_5)_3$ under 254 nm light; (**B**): kinetic profile for decomposition of **1-Ph$_3$S** in CD_2Cl_2/CD_3CN (1/4) ($2.0\cdot10^{-3}$ mol/L) to $CD_3CN\cdot B(C_6F_5)_3$ under 254 nm light. (**C**): kinetic profile for decomposition of **1-Ph$_3$S** in CD_2Cl_2/CD_3CN (8.7/1) ($2.1\cdot10^{-3}$ mol/L) to $CD_3CN\cdot B(C_6F_5)_3$ under 254 nm light; (**D**))**:** kinetic profile for decomposition of **3-Ph$_3$S** in CD_3CN ($2.1\cdot10^{-3}$ mol/L) to $CD_3CN\cdot B(C_6F_5)_3$ under 254 nm light; (**E**): kinetic profile for decomposition of **1-Ph$_2$I** in CD_2Cl_2/CD_3CN (8.7/1) ($2.1\cdot10^{-3}$ mol/L) to $CD_3CN\cdot B(C_6F_5)_3$ under 254 nm light; (**F**): kinetic profile for decomposition of **7-Ph$_3$S** in CD_3CN ($2.1\cdot10^{-3}$ mol/L) to $CD_3CN\cdot B(C_6F_5)_3$ under 254 nm light.

NMR spectra

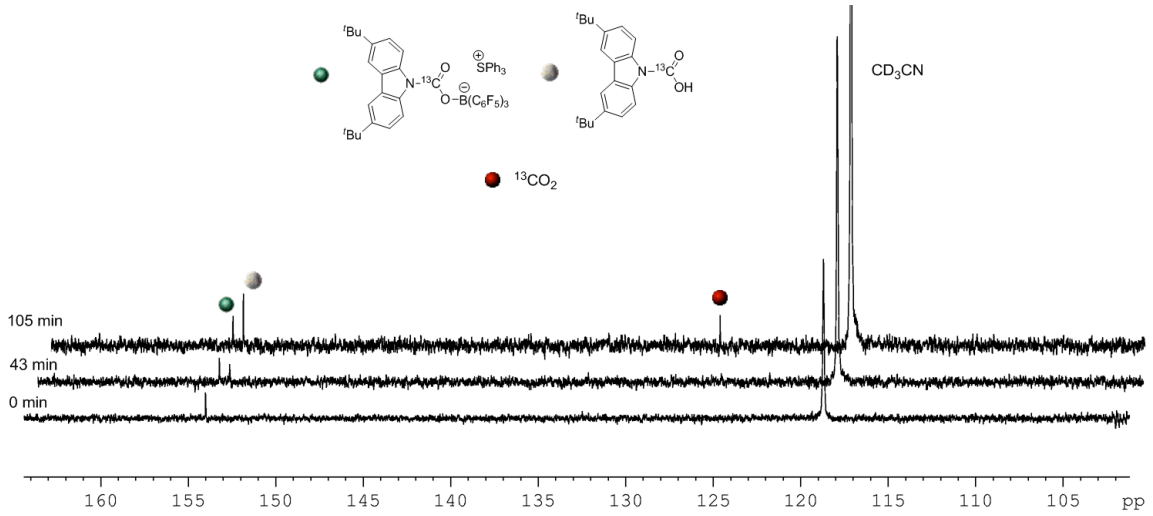

Figure S7. ^{13}C NMR spectra of the decomposition of **1-Ph$_3$S-^{13}C** under 254 nm in CD_3CN ($4.5 \cdot 10^{-3}$ mol/L). Signals at δ 154.0, 153.4, and 126.2 ppm correspond to carbonyl carbons of **1-Ph$_3$S-^{13}C**, ^{t}Bu$_2$Cab$^{13}CO_2H$, and $^{13}CO_2$, respectively.[4]

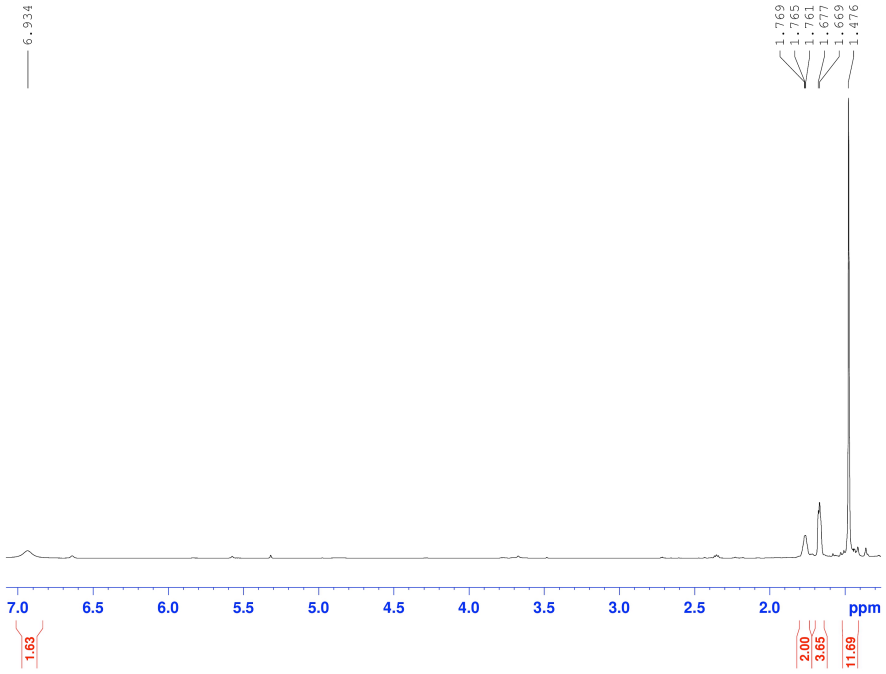

Figure S8. ^{1}H NMR spectrum of **5**. The broad resonance at δ 6.93 ppm corresponds to the *N*-bound proton.

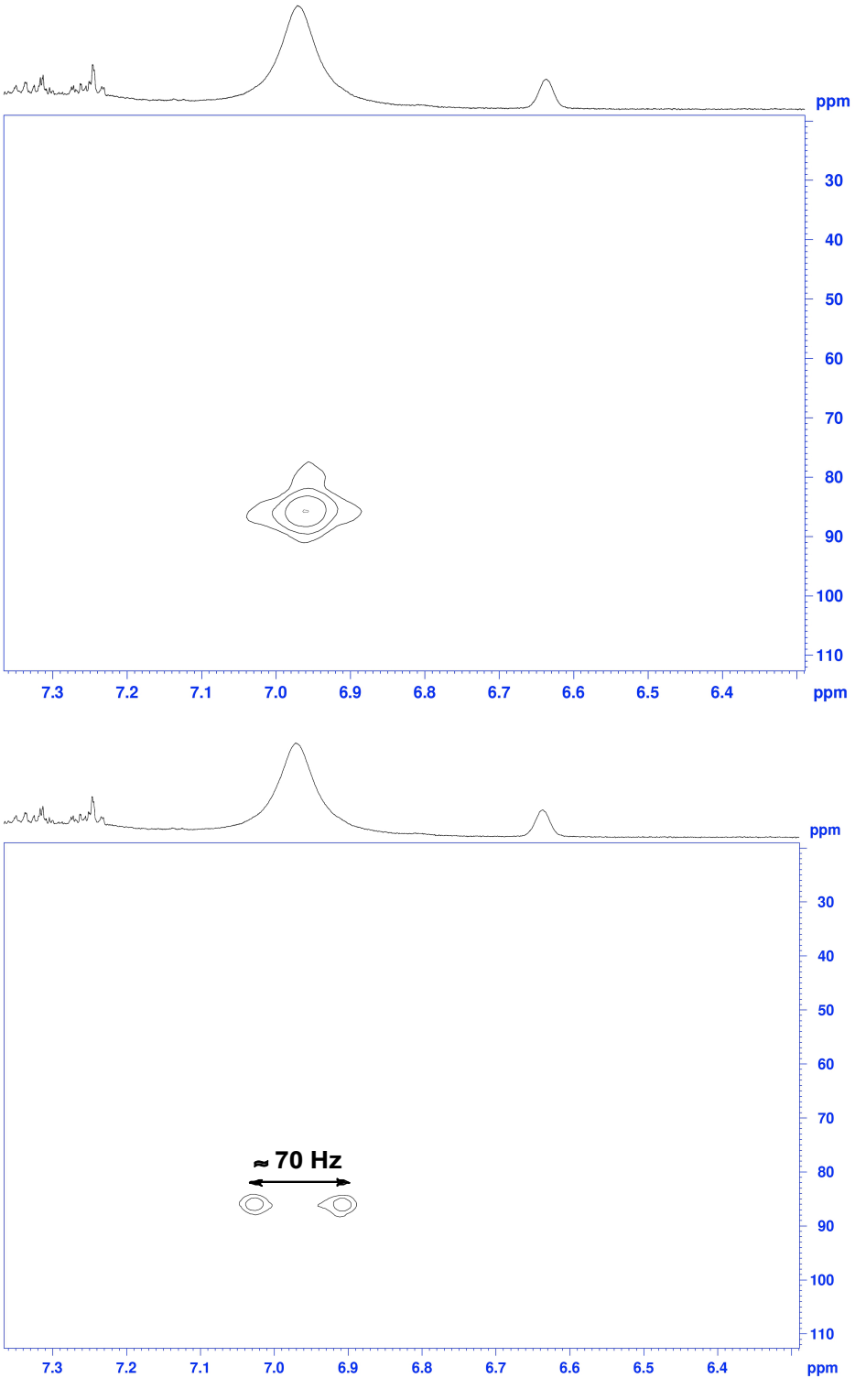

Figure S9. ^{1}H-^{15}N HMQC NMR (**A**) and ^{1}H-^{15}N HMQCND (no decoupling) NMR (**B**) spectra of **5** in CD_2Cl_2 showing coupling for *N*-bound proton (^{1}J(N-H) ≈ 70 Hz).

Catalysis by hydridoborate PhLAGs

Table S2. Photoinduced hydrosilylation with Et_3SiH and **7-Ph$_3$S** and **7-Ph$_2$I**[a]

#	Substrate	PhLAG	t_{hv}, min[b]	Conv., %[c]	Products
1	PhMeC(O)	**7-Ph$_3$S**	15	>99	PhMeCH($OSiEt_3$)
2		**7-Ph$_2$I**	10	>99	
4	PhHC(O)	**7-Ph$_3$S**	15	90	$PhCH_2(OSiEt_3)$
5		**7-Ph$_2$I**	10	>99	
7	Cyclohex-2-enone	**7-Ph$_3$S**	10	>99	
8		**7-Ph$_2$I**	5	>99	
10	PhOH	**7-Ph$_3$S**	5	>99	$PhOSiEt_3$
11		**7-Ph$_2$I**	5	>99	
13	Et_2O	**7-Ph$_3$S**	10[d]	>99	Et_3SiOEt (86%)[e]
					$Et_3SiOSiEt_3$ (12%)[e]
14		**7-Ph$_2$I**	10[d]	>99	Et_3SiOEt (91%)[e]
					$Et_3SiOSiEt_3$ (9%)[e]

[a] Conditions: [substrate] = 0.25 M, 1.0 mol % of PhLAG, substrate:Et_3SiH = 1:1, CD_2Cl_2 (solvent). [b] Time sample was irradiated at 254 nm. [c] Conversion of substrate determined by ^{1}H NMR. [d] Sample was left for 2 h at RT in the absence of light following irradiation. [e] Conversion determined by GC-MS.

Table S3. Photoinduced silylation of silanols and Piers-Rubinsztajn reactions with **7-Ph$_3$S** and **7-Ph$_2$I**[a]

#	Substrate	Hydrosilane	PhLAG	t_{hv}/t_{RT}	Products (yield, %)
1 2	Me_3SiOH	Et_3SiH	**7-Ph$_3$S** **7-Ph$_2$I**	15 min/2 h	$Me_3Si(OSiEt_3)$ (>99)[b]
4	Me_3SiOEt	Et_3SiH	**7-Ph$_3$S**	15 min/48 h	Et_3SiOEt (2)[c] $Me_3Si(OSiEt_3)$ (37)[c] $Et_3Si(OSiEt_3)$ (60)[c]
5			**7-Ph$_2$I**		Et_3SiOEt (1)[c] $Me_3Si(OSiEt_3)$ (47)[c] $Et_3Si(OSiEt_3)$ (49)[c]
7 8	Me_3SiOEt	PMHS	**7-Ph$_3$S** **7-Ph$_2$I**	15 min/10 min	$(MeHSiO)_x(MeSi(OSiMe_3)O)_y$ (>99)[b]
10 11	$Si(OMe)_4$	TMCTS[d]	**7-Ph$_3$S** **7-Ph$_2$I**	15 min/5 min	Tetra(trimethoxysiloxy)TMCTS (99)

[a] Conditions: [substrate] = 0.25 M, 1.0 mol % of PhLAG, substrate:hydrosilane = 1:1, 254 nm, CD_2Cl_2 (solvent). [b] Conversion determined by ^{1}H NMR spectroscopy. [c] Conversion determined by GC-MS. [d] TMCTS - 2,4,6,8-tetramethylcyclotetrasiloxane, Si(OMe)4/TMCTS = 4:1.

Photophysical properties

Table S4. The values of of λ_{max} (nm) and ε ($10^3 \cdot M^{-1} \cdot cm^{-1}$) for [$Ph_3S$][OTf], 3,6-di-(*t*-butyl)carbazole, lithium borate **4**, and PhLAGs **5**, **6**, **10**, **11**, **12**, **18**, **19**, and **21** summarized in **Table 1**.

Compound	Concentration, mol/L	λ_{max}, nm	ε, x$10^3 \cdot M^{-1} \cdot cm^{-1}$
[Ph_3S][OTf]	$1.1 \cdot 10^{-5}$	242	12.75
$^tBu_2$CarbH[4]	$1.1 \cdot 10^{-5}$	238	40.08
2-LiMTEDA[4]	$1.1 \cdot 10^{-5}$	233	44.18
1-Ph_3S[4]	$1.1 \cdot 10^{-5}$	234	77.84
7-Ph_3S	$1.0 \cdot 10^{-5}$	228	59.34
3-Ph_3S	$1.1 \cdot 10^{-5}$	228	23.66
1-Ph_2I	$1.1 \cdot 10^{-5}$	234	88.04
7-Ph_2I	$1.1 \cdot 10^{-5}$	226	28.64

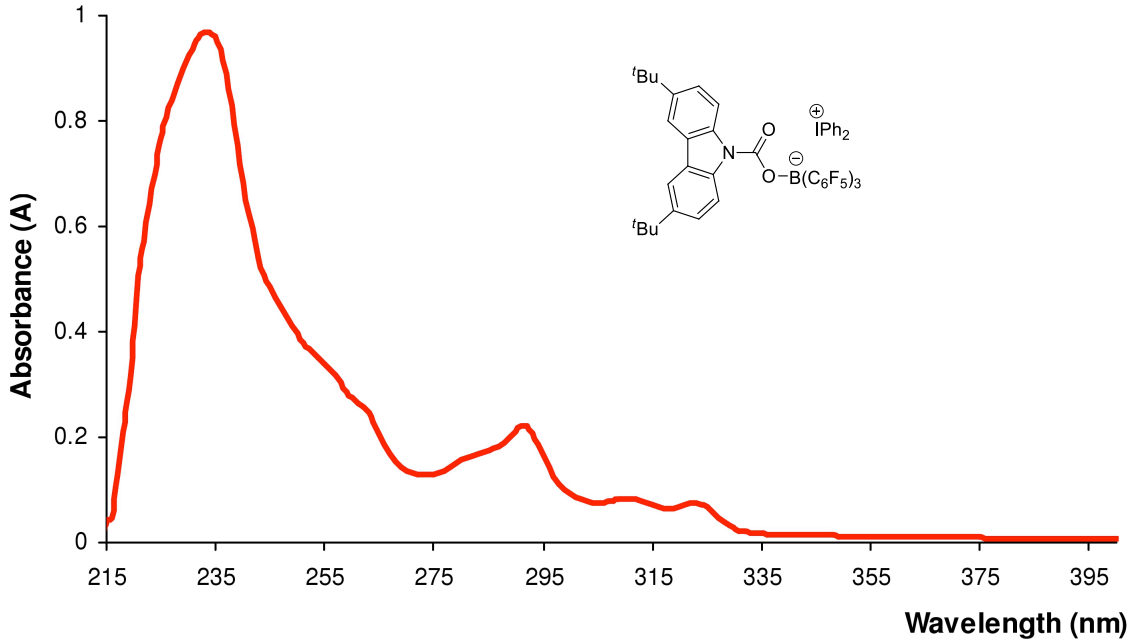

Figure S11. UV-vis spectrum of **1-Ph$_2$I** in CH_2Cl_2 ($1.1 \cdot 10^{-5}$ mol/L).

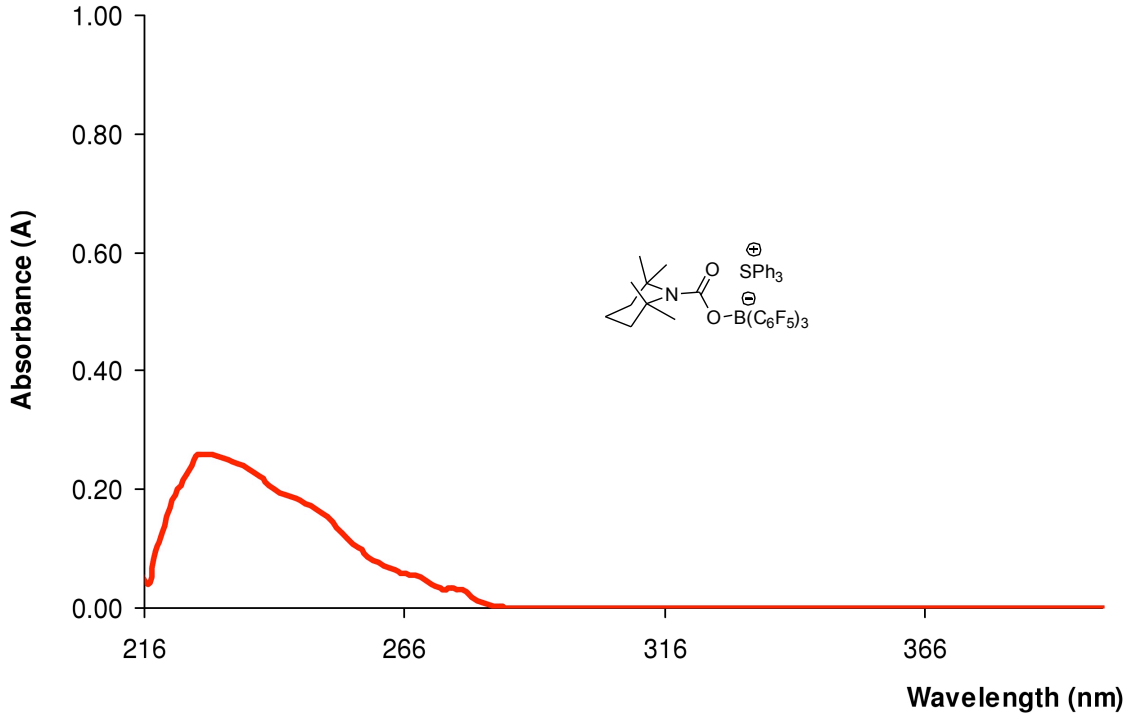

Figure S12. UV-vis spectrum of **3-Ph$_3$S** in CH_2Cl_2 ($1.1 \cdot 10^{-5}$ mol/L).

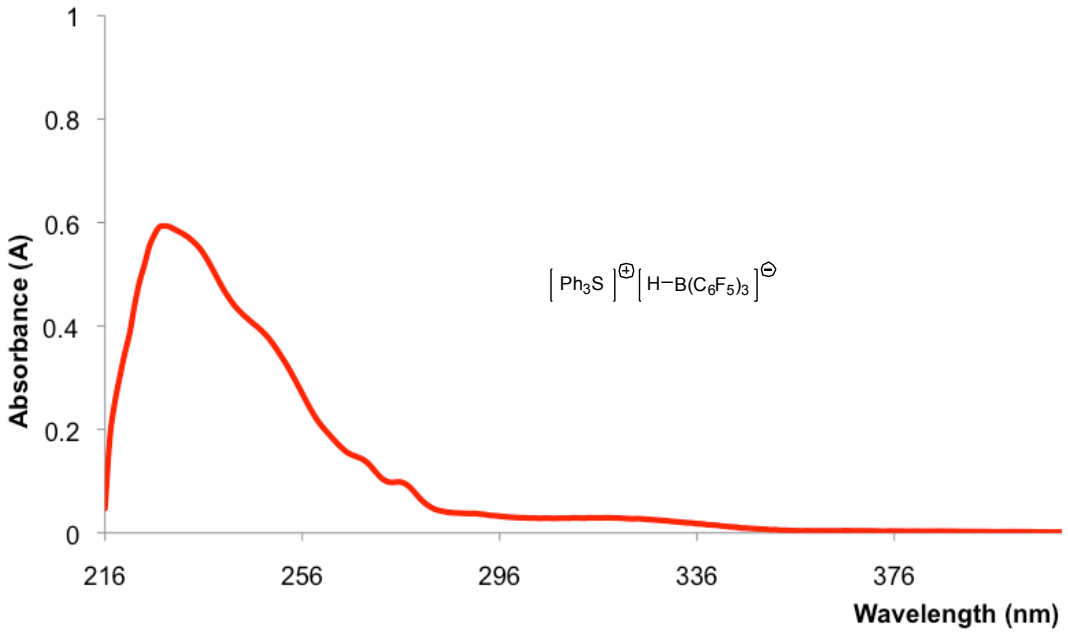

Figure S13. UV-vis spectrum of **7-Ph_3S** in CH_2Cl_2 ($1.1 \cdot 10^{-5}$ mol/L).

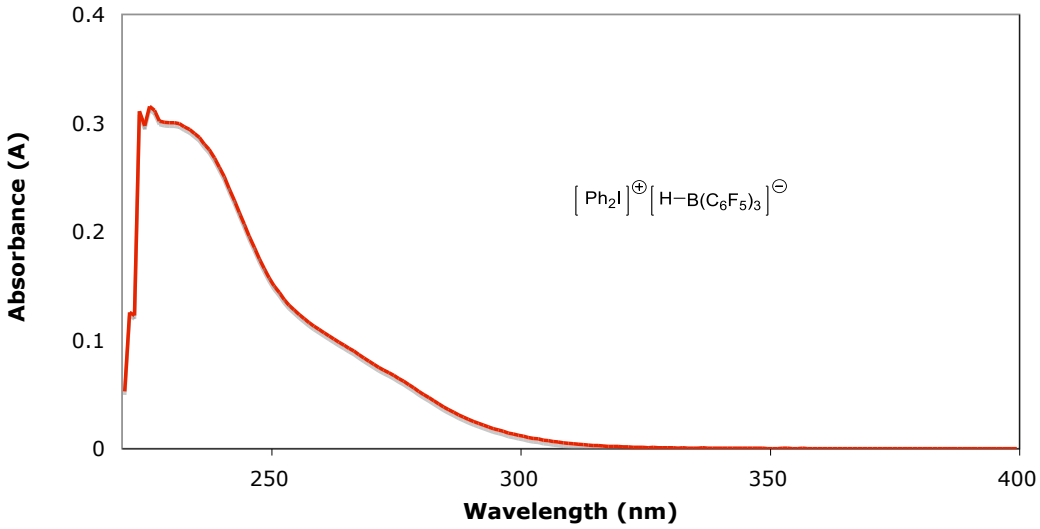

Figure S14. UV-vis spectrum of **7-Ph_2I** in CH_2Cl_2 ($1.1 \cdot 10^{-5}$ mol/L).

X-ray analysis

Single crystals of **3-Ph_3S** suitable for X-ray diffraction analysis were grown by layering toluene solution with hexanes (approx. 1:1) at -30 °C. X-ray quality crystals of **7-Ph_2I** were obtained by layering dichloromethane solution with hexanes (approx. 1:1) at -20 °C The colorless crystals were coated with polyperfluoro oil and measured on a Bruker Nonius APEX2 CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection and structure refinement details **3-Ph_3S** and **7-Ph_2I** are given in Tables S7 and S8, respectively. Structures of **3-Ph_3S** and **7-Ph_2I** are shown in Figures 1 and 2 in the main text, respectively.

Table S7. Data collection and structure refinement details for **3-Ph_3S**.

formula	$C_{46}H_{33}BF_{15}NO_2S$
formula weight	959.60
color	colorless
crystal system	monoclinic
space group	*P*2(1)/*n*
radiation wavelength, Å	0.71073
a / b / c, Å	13.388(3) / 20.097(4) / 16.261(3)
α / β / γ, deg	90.00 / 107.65(3) / 90.00
V, Å^3	4169.1(15)
Z	4
T, K	150(2)
ρ_{calc}, g/cm^3	1.529
F(000)	1952
μ, mm^{-1}	0.187
crystal size, mm^3	0.32 x 0.21 x 0.19
Θ range, deg	1.66-27.48
index ranges	$-17 \leq h \leq 17$, $-26 \leq k \leq 14$, $-21 \leq l \leq 21$
max. and min. transmission	0.9654 and 0.9427
reflections collected	9439
independent reflections	8017 [R(int) = 0.0205]
completeness to theta = 27.48°	98.7 %
absorption correction	Multi-scan
refinement method	Full-matrix least-squares on F^2
data/restrains/parameters	9439/0/595
GoF	1.204
final R indices [$I > 2\sigma(I)$]	R1 = 0.0562, *w*R2 = 0.1540
R indices (all data)	R1 = 0.0716, *w*R2 = 0.1806
largest diff. peak and hole, e/Å^3	0.502 and -0.503

Table S8. Data collection and structure refinement details for **7-Ph_2I**.

formula	$C_{30}H_{11}BF_{15}I$
formula weight	794.10
color	colorless
crystal system	monoclinic
space group	*C*2/*c*
radiation wavelength, Å	0.71073
a / b / c, Å	28.2437(7) / 10.4776(3) / 18.8072(4)
α / β / γ, deg	90.00 / 93.5440(14) / 90.00
V, Å^3	5554.9(2)
Z	8
T, K	173(2)
ρ_{calc}, g/cm^3	1.899
F(000)	3072
μ, mm^{-1}	1.276
crystal size, mm^3	0.20 x 0.18 x 0.14
Θ range, deg	2.53-27.49
index ranges	$-36 \leq h \leq 36$, $-12 \leq k \leq 13$, $-24 \leq l \leq 24$
max. and min. transmission	0.8416 and 0.7844
reflections collected	6348
independent reflections	5299 [R(int) = 0.0330]
completeness to theta = 27.49°	99.4 %
absorption correction	Multi-scan
refinement method	Full-matrix least-squares on F^2
data/restrains/parameters	6348/0/427
GoF	1.119
final R indices [$I > 2\sigma(I)$]	R1 = 0.0442, *w*R2 = 0.0891
R indices (all data)	R1 = 0.0568, *w*R2 = 0.0.0967
largest diff. peak and hole, e/Å^3	0.476 and -0.523

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