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Dehalogenation reaction photocatalyzed by homoleptic copper(I) complexes associated with strongly reductive sacrificial donors

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I. General Chemistry: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-D_6 or THF-D_{10} at 300 and 400 MHz for ^{1}H NMR, and 50 and 75 MHz for ^{13}C NMR. Chemical shifts (δ) are given in parts per million, and coupling constants are given as absolute values expressed in hertz. High-resolution mass spectrometry (HRMS) analyses were performed using electrospray ionization (ES) and ASAP. All reactions were magnetically stirred and monitored by analytical thin layer chromatography (TLC) using UV (254 nm) for visualization. Column chromatography separations were performed using silica gel. All reagents were used without purification. All solvents were of HPLC grade or were distilled using standard drying agents prior to use. Starting chemical substrates and reagents were used as commercially provided unless otherwise indicated.

The gas chromatography measurements were performed on a Hewlett Packard HP 5 (l = 30 m, i.d.= 0.32 mm, film thickness = 0.25 mm), equipped with a FID detector (N_2 as carrier gas (1.6 mL.min^{-1}); temperature program: 80 °C for 1 min then 15 °C.min^{-1} to 320 °C).

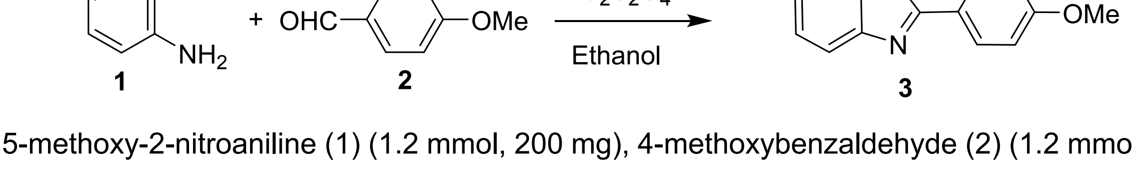
Photochemical experiments were either performed with blue (450 nm, 25 lumens, 75 mW) and green LEDs (550 nm, 75 lumens, 22 mW) purchased from Farnell, or under calibrated AM 1.5 artificial solar light (100 mW/cm², Oriel simulator).

Compound **1’** was obtained from typical procedures described in literature.[1] Copper complex **C1** ($Cu(dipp)_2PF_6$) was synthesized according to the procedure described in literature.[2]

II. Synthesis of BI_1H and BI_2H

All NMR spectra (^{1}H and ^{13}C) are available at the end of the supporting information

1. Synthesis of 5-methoxy-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3)

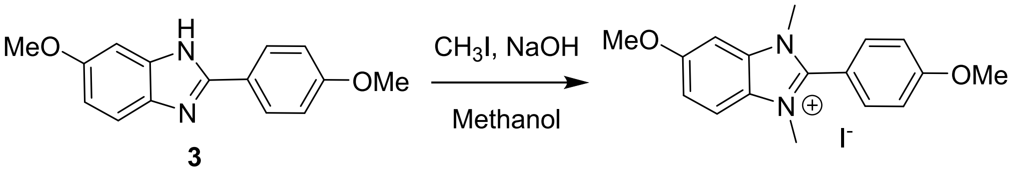


5-methoxy-2-nitroaniline (1) (1.2 mmol, 200 mg), 4-methoxybenzaldehyde (2) (1.2 mmol, 0.18 mL) and sodium dithionite $Na_2S_2O_4$ (1.78 mmol, 310 mg) were dissolved under argon in dry ethanol (16 mL). The mixture was refluxed 3 days. Then; the solution was neutralized with an aqueous solution of NH_4OH (1 M) and extracted with ethyl acetate. The organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to dryness. Purification by flash chromatography on silica (Petroleum ether 100% then Petroleum ether/EtOAc, 80/20, v/v) afforded the compound with 77% yield.

^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ= 7.95 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.7 Hz, 1H), 7.08 (s, 1H), 6.96 (d, J = 8.4 Hz, 2H), 6.90 (dd, J = 1.6 Hz, J = 8.7 Hz, 1H), 3.85 (m, 6H). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ= 161.12 (s), 156.52 (s), 127.87 (s), 122.32 (s), 114.50 (s), 112.13 (s), 55.84 (s), 55.42 (s). HRMS (ESI+) for $C_{15}H_{15}N_2O_2$ [M+H]+, m/z 255.1129 Da found, 255.1134 Da calc.

Scale-up of the reaction: the reaction was performed using (5 g, 29.76 mmol) of 5-methoxy-2-nitroaniline and the yield obtained was 66%.

2. Synthesis of 5-methoxy-2-(4-methoxyphenyl)-1,3-dimethyl-1H-benzo[d]imidazol-3-ium iodide [BI$_1^+$, I$^-$]



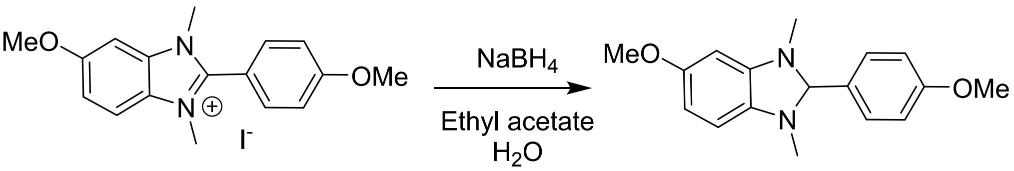
3

[BI$_1^+$, I$^-$]

In a sealed tube were introduced compound **3** (0.92 mmol, 232 mg), NaOH (1.11 mmol, 44 mg), iodomethane (2.76 mmol, 0.17 mL) and dry methanol (4 mL). The sealed tube was then heated up to 140 °C during 14 h. Then, the solution was extracted with acetone and concentrated under reduced pressure. The crude product was recrystallized in ethanol to afford [BI$_1^+$, I$^-$] with 99% yield.

^{1}H NMR spectrum (DMSO-d^6, 300 MHz) δ= 7.99 (d, J = 9.1 Hz, 1H), 7.82 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 2.2 Hz, 1H), 7.31 (m, 3H) 3.93 (s, 3H), 3.91 (s, 3H), 3.85 (s, 6H). ^{13}C NMR spectrum (DMSO-d^6, 75 MHz) δ= 162.31 (s), 158.60 (s), 149.61 (s), 132.70 (s), 132.52 (s), 125.88 (s), 116.10 (s), 114.85 (s), 114.06 (s), 112.61 (s), 95.84 (s), 56.24 (s), 55.62 (s), 32.68 (s), 32.65 (s). HRMS (ESI$^+$) for $C_{17}H_{19}N_2O_2$ [M+H]$^+$, m/z 283.1439 Da found, 283.1447 Da calc.

3. Synthesis of 5-methoxy-2-(4-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1H-benzo[d]imidazole (BI$_1$H)



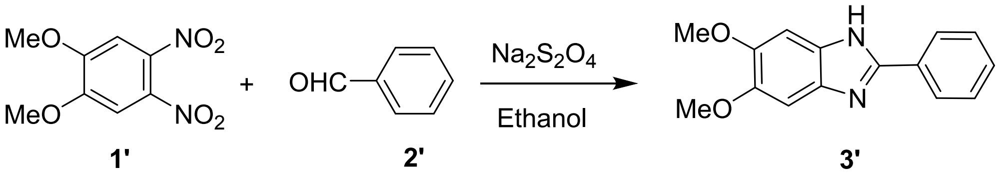
[BI$_1^+$, I$^-$]

BI$_1$H

At room temperature, in an open flask, [BI_1^+, I^-] (1.22 mmol, 500 mg) was dissolved in ethyl acetate (15 mL) and water (8 mL). $NaBH_4$ (5.28 mmol, 132 mg) was added portion-wise, then the reaction was stirred for 3 h. Finally, the ethyl acetate layer was recovered and washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure to yield a white powder (81% yield).

^1H NMR spectrum ($CDCl_3$, 300 MHz) δ: 7.49 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.32 (d, J = 8.1 Hz, 1H), 6.20 (dd, J = 2.4 Hz and 8.1 Hz, 1H), 6.11 (d, J = 2.3 Hz, 1H), 4.72 (s, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 2.52 (s, 3H), 2.51 (s, 3H). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ= 160.48 (s), 154.56 (s), 143.47 (s), 136.59 (s), 130.90 (s), 129.99 (s), 113.82 (s), 105.44 (s), 101.37 (s), 95.45 (s), 94.12 (s), 55.91 (s), 55.32 (s), 33.82 (s), 32.87(s). HRMS (ASAP) for $C_{17}H_{21}N_2O_2$ $[M+H]^+$, m/z 285.1611 Da found, 285.1603 Da calc.

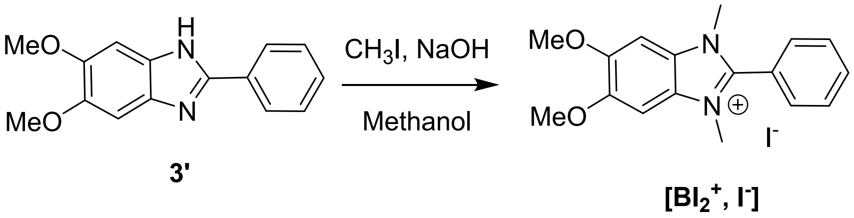
4. Synthesis of 5,6-dimethoxy-2-phenyl-1H-benzo[d]imidazole (3')



1,2-dimethoxy-4,5-dinitrobenzene (1') (22 mmol, 5.0 g) and $N_{a2}S_2O_4$ (66 mmol, 11.5 g) were dissolved under argon in dry ethanol (250 mL) and then freshly distilled benzaldehyde (34 mmol, 3.4 mL) was added dropwise. The mixture was heated up at 80 °C and followed by TLC. After 3 days the reaction was not finished, thus $Na_2S_2O_4$ (66 mmol, 11.5 g) and benzaldehyde (34 mmol, 3.4 mL) were added again. After 1 week of stirring at 80 °C the reaction seemed complete by TLC. Then; the solution was neutralized with an aqueous solution of NH_4OH (1 M) and extracted with ethyl acetate. The organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to dryness. Purification by flash chromatography on silica (Petroleum ether 100% then Petroleum ether/EtOAc, 80/20, v/v) afforded the compound with 90% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ= 8.08 (m, 2H), 7.39 (m, 3H), 7.01 (s, 2H), 3.79 (s, 6H). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ= 150.52 (s), 147.29 (s), 130.15 (s), 129.55 (s), 129.04 (s), 126.23 (s), 60.40 (s), 56.22 (s). HRMS (ESI+) for $C_{15}H_{15}N_2O_2$ [M+H]+, m/z 255.1137 Da found, 255.1134 Da calc.

Scale-up of the reaction: The reaction was performed using (5 g, 21.92 mmol) of 1,2-dimethoxy-4,5-dinitrobenzene and the yield obtained was 60%.

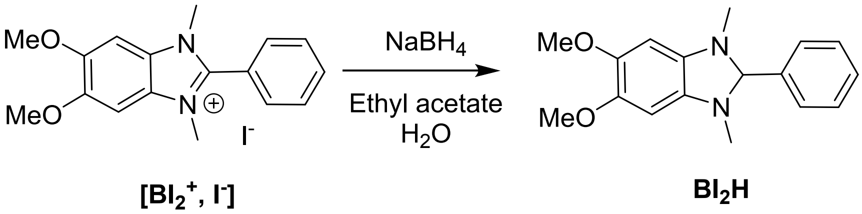
5. Synthesis of 5,6-dimethoxy-1,3-dimethyl-2-phenyl-1H-benzo[d]imidazol-3-ium iodide [BI_2^+, I^-]



In a sealed tube were introduced compound **3'** (0.39 mmol, 100 mg), NaOH (0.47 mmol, 19 mg), iodomethane (0.87 mmol, 0.06 mL) and dry methanol (3 mL). The sealed tube was then heated up to 140 °C during 14 h. Then, the solution was extracted with acetone and concentrated under reduced pressure. The crude product was recrystallized in ethanol to afford [**BI_2**$^+$, I^-] with 99% yield.

^{1}H NMR spectrum (DMSO-d^6, 300 MHz) δ: 7.86 (m, 2H), 7.79 (m, 3H), 7.69 (s, 2H), 3.95 (s, 6H), 3.86 (s, 6H). ^{13}C NMR spectrum (DMSO-d^6, 75 MHz) δ=147.38 (s), 132.48 (s), 130.72 (s), 129.29 (s), 125.51 (s), 121.35 (s), 95.37 (s), 56.50 (s), 32.76 (s). HRMS (ESI+) for $C_{17}H_{19}N_2O_2$ [M+H]+, m/z 283.1456 Da found, 283.1447 Da calc.

6. Synthesis of 5-methoxy-2-(4-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1H-benzo[d]imidazole (BI_2H)

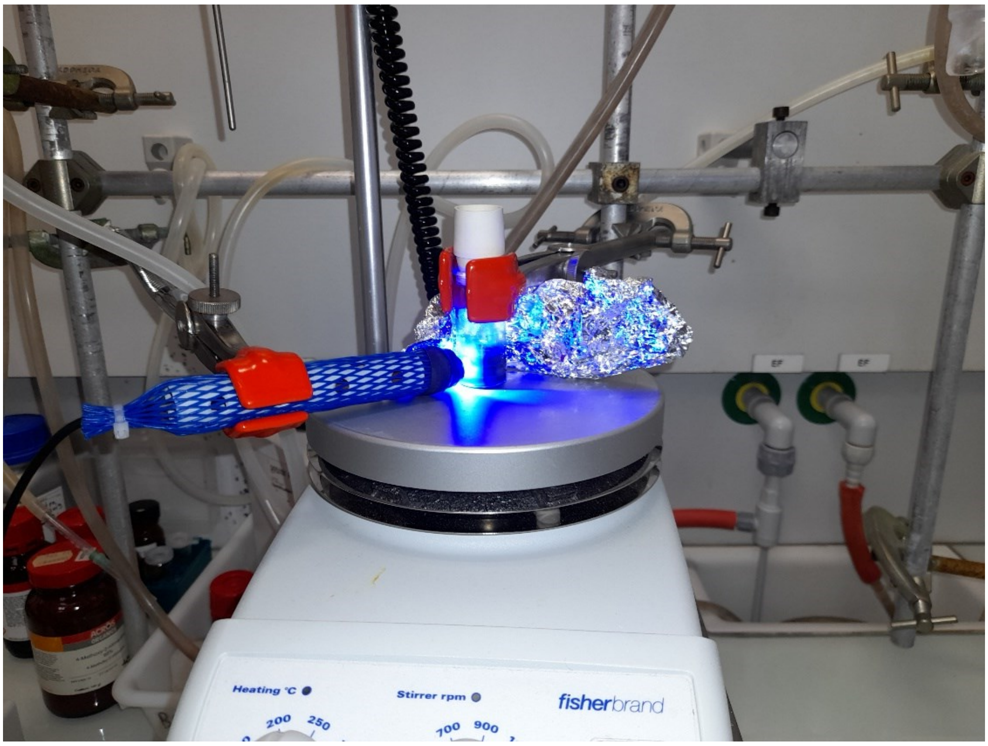


At room temperature, in an open flask, [**BI_2**$^+$, **I^-**] (0.046 mmol, 19 mg) was dissolved in ethyl acetate (1 mL) and water (0.5 mL). $NaBH_4$ (0.14 mmol, 5 mg) was added portion-wise, then the reaction was stirred for 3 h. Finally, the ethyl acetate layer was recovered, washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure to yield a white powder (99% yield).

^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ: 7.58 (m, 2H), 7.41 (m, 3H), 6.25 (s, 2H), 4.65 (s, 1H), 3.84 (s, 6H), 2.53 (s, 6H). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ= 143.03 (s), 138.91 (s), 136.08 (s), 129.33 (s), 128.91 (s), 128.42 (s), 95.99 (s), 95.32 (s), 57.69 (s), 34.09 (s). Anal. Calcd for $C_{17}H_{20}N_2O_2$. 0.7 H_2O : C, 68.76; H, 7.26; N, 9.43. Found: C, 68.44; H, 6.76; N, 9.18. HRMS (ESI+) for $C_{17}H_{21}N_2O_2$ [M+H]$^+$, m/z 285.1606 Da found, 285.1603 Da calc.

III. Typical procedure for photocatalytic reactions

An oven-dried vial was charged with BI_xH (0.2 mmol) and the corresponding 4-bromobenzophenone (0.10 mmol). The vial was sealed with a rubber septum and purged with argon (argon saturated with THF bubbling for 15 mn). Then THF (3 mL) and freshly distilled Et_3N (400 µL, 2.86 mmol) were added and the mixture was degassed for 10 min. Cu(dipp)$_2$PF$_6$ (3.6 mg, 0.005 mmol) was next added and the mixture was degassed again for 5 min. Then the reaction mixture was stirred under one blue LED irradiation for 30 min to 3 h, according to the **BI_xH** used. The distance from light source irradiation to the vial was 0.3 cm without the use of any filters (figure S0). For the trial under simulated solar light, a similar procedure was adapted (figure S0). Then for both methods, the mixture was then centrifuged (10 000 rpm, 10 min) and the filtrate was recovered and concentrated under reduced pressure. The yield of benzophenone was determined by ^{1}H NMR analysis with p-anisaldehyde (12 µL, 0.10 mmol) as internal standard. The solid was recovered, dried and characterized by ^{1}H NMR and XPS.



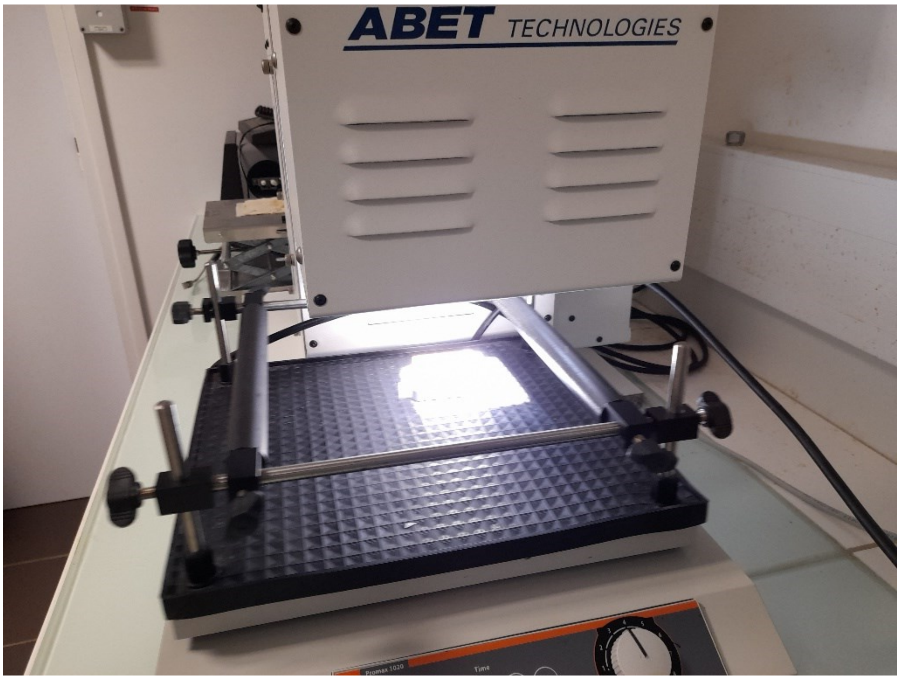


Figure S0. Pictures of the setup for photochemical reactions under LED irradiation (up) and under AM 1.5 simulated solar irriadiation.

III. Optical spectroscopy procedures

UV-visible absorption spectra were recorded on an Analytik Jena spectrophotometer, using 1 cm path length cells. The evolution of the UV-Vis spectrum of **C1** in presence of **BI$_1$H** or **BI$_2$H** under light soaking was realized by irradiating the cell (after proper argon purge of the solution for 15 mn) for 7 mn with a blue LED, under magnetic stirring.

IV. Cyclic voltammetry procedures

Oxidation potentials in MeCN were measured with cyclic voltamperometry using glassy carbon as working electrode, platinum grid for counter electrode and either a saturated calomel electrode or a Ag/AgCl in 0.1 M LiCl/Ethanol electrode were used as references. TBAPF$_6$ 0.1 M is used as a supporting electrolyte at the scan of 100 mV/s. Samples were purged with argon before measurements. The potentials are all given *vs.* SCE, $E_{vs..SCE} = E_{vs.\ Ag/AgCl} - 0.12$ V in THF+TBAPF$_6$.

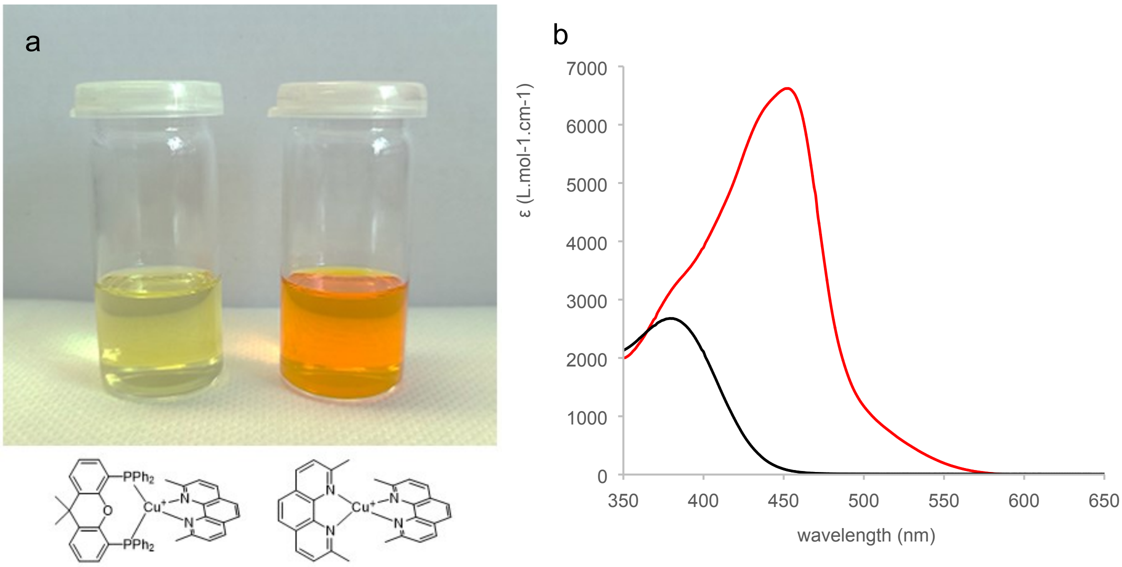


Figure S1. (a) Weakly colored but strong photo-oxidant heteroleptic *vs.* strongly colored but weakly photo-oxidant homoleptic Cu(I) complexes (0.1 mM solutions in dichloromethane). In this picture, complexes with G = methyl (left: **C2**: [Cu(xantphos)(dmp)]$^+$, dmp = 2,9-dimethyl-1,10-phenanthroline. Right: [Cu(dmp)$_2$]$^+$) have been chosen to illustrate the color differences. (b) Absorption spectra of [Cu(XantPhos)(dmp)]$^+$ and [Cu(dipp)$_2$]$^+$ (**C1**) in THF.

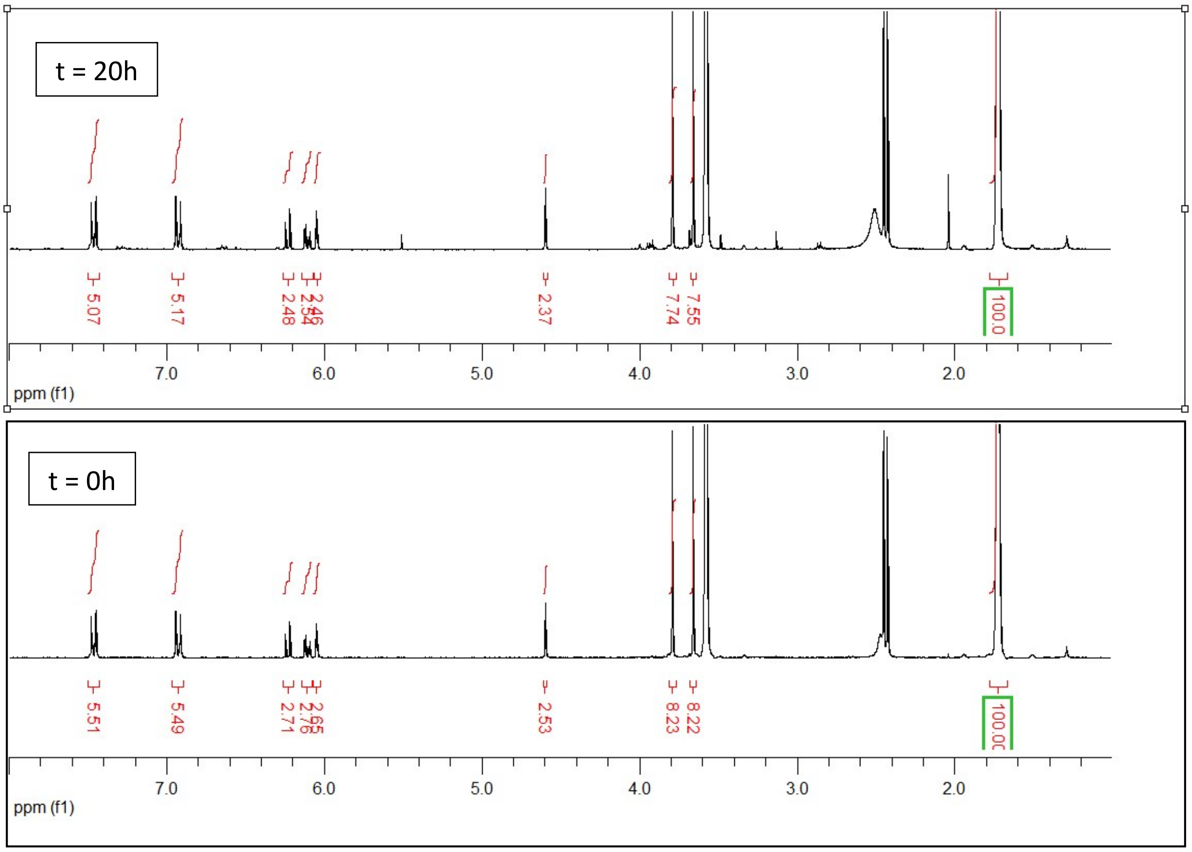


Figure S2. ^{1}H NMR spectra of **BI$_1$H** in deuterated aerated THF over 20 hours. Stability estimated by arbitrarily pinning THF residual proton signal (1.73 ppm) at 100 integration. 92% of **BI$_1$H** is estimated to remain after 20 hours in THF.

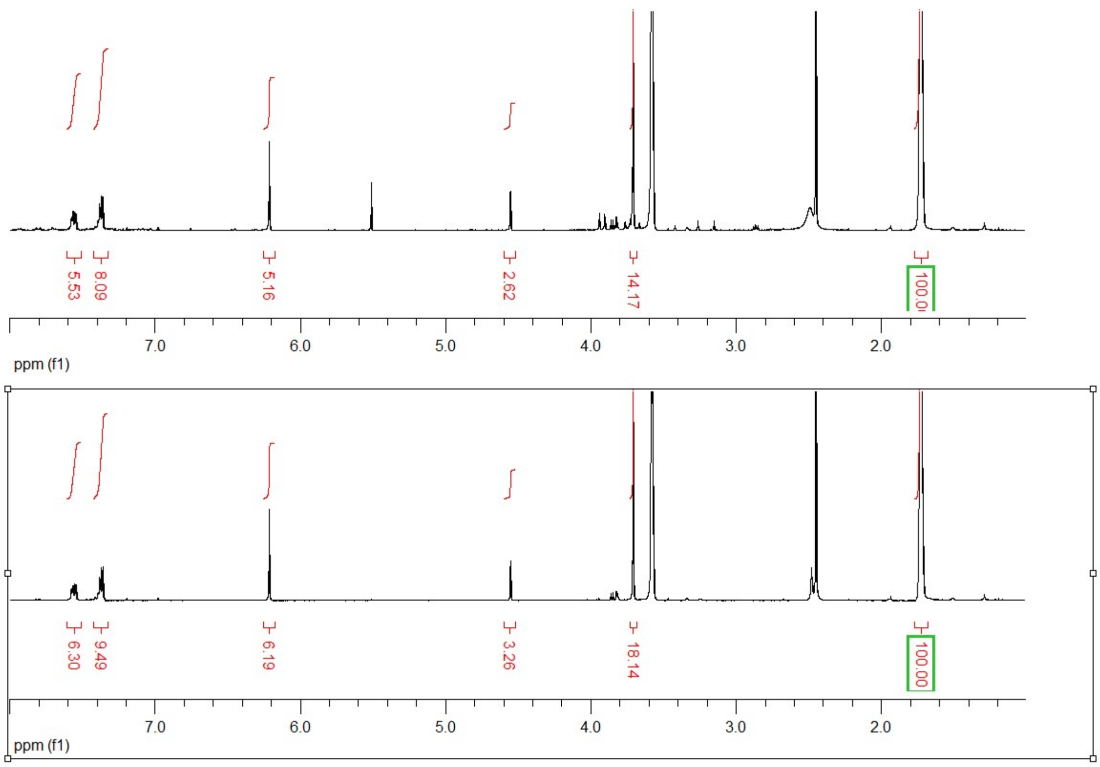


Figure S3. ^{1}H NMR spectra of **BI$_2$H** in deuterated aerated THF over 20 hours. Stability estimated by arbitrarily pinning THF residual proton signal (1.73 ppm) at 100 integration. 83% of **BI$_1$H** is estimated to remain after 20 hours in THF.

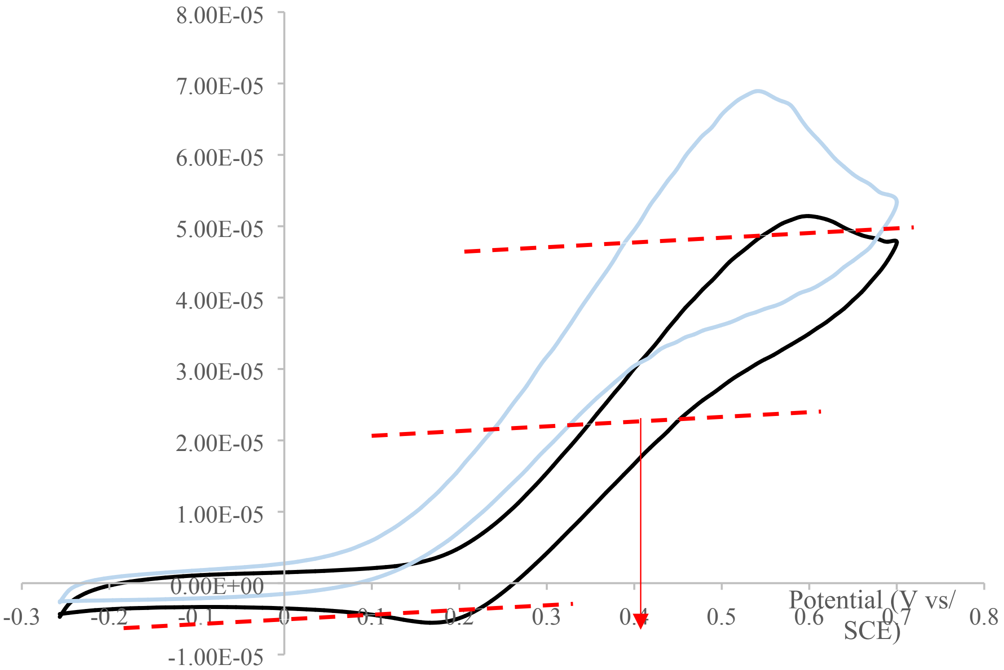


Figure S4. Cyclic voltamperometry of **BI$_1$H** in THF (black line) and in presence of 1 equivalent of TEA (blue line) with glassy carbon as working electrode, platinum grid for counter electrode and SCE for the reference electrode.

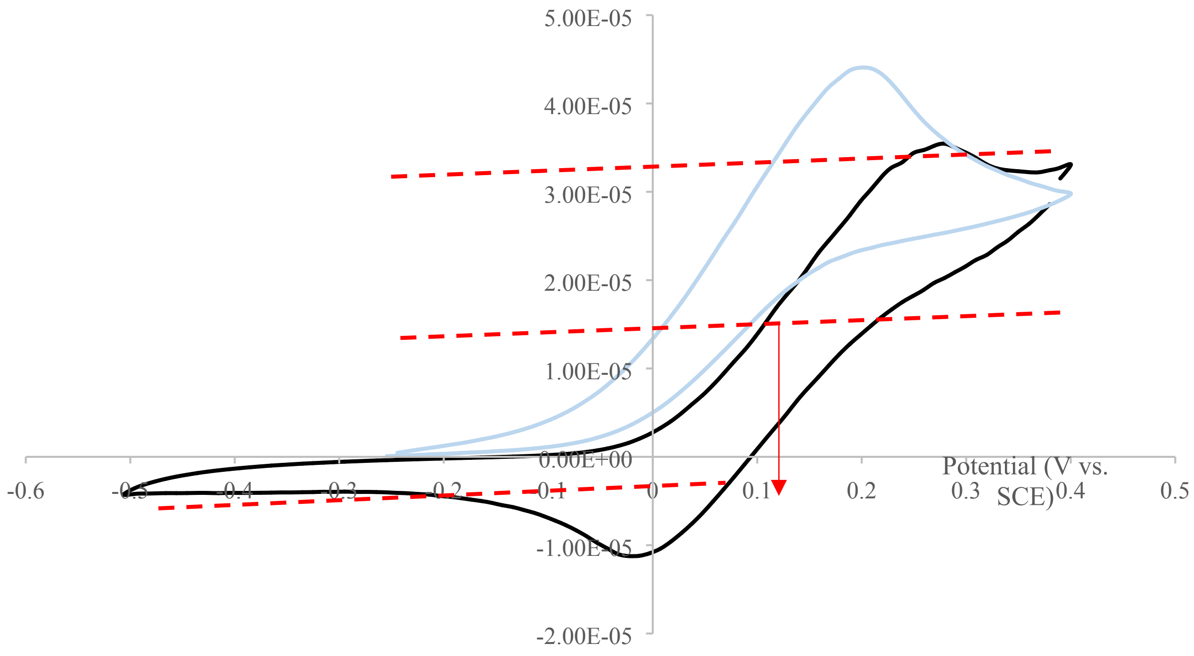


Figure S5. Cyclic voltamperometry of **BI$_2$H** in THF (black line) and in presence of 1 equivalent of TEA (blue line) with glassy carbon as working electrode, platinum grid for counter electrode and SCE for the reference electrode.

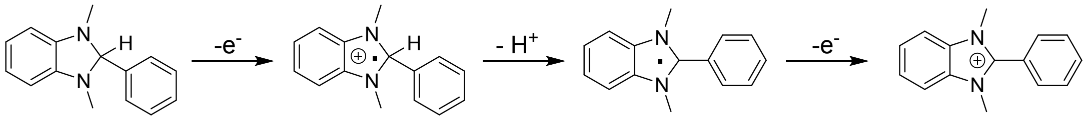


Figure S6. Series of electron transfers following one electron oxidation of benchmark **BIH** electron donor in presence of base.

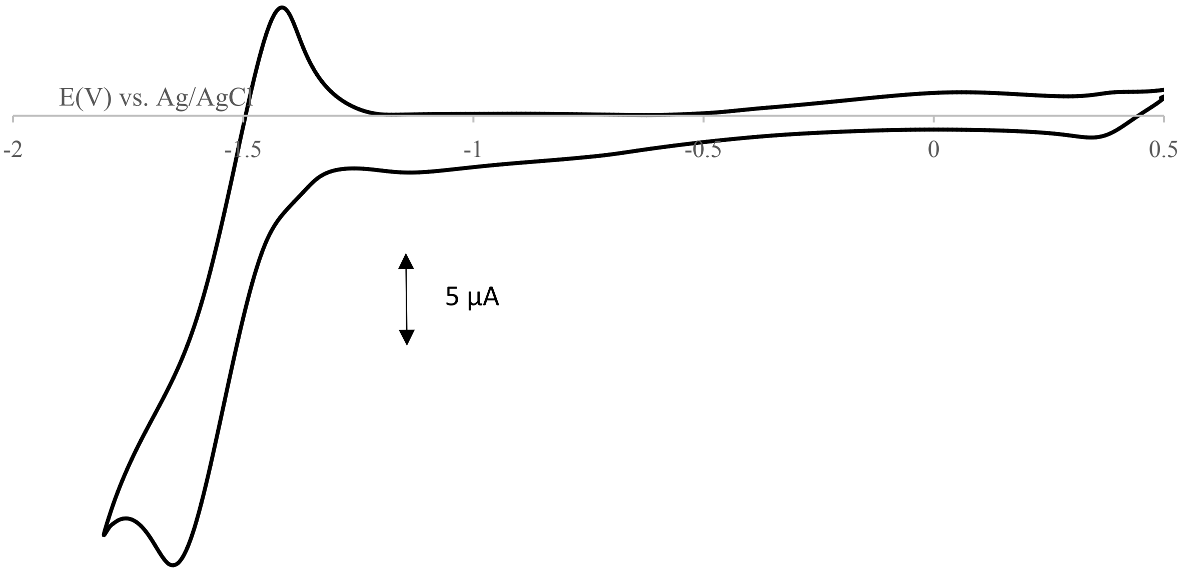


Figure S7. Cyclic voltamperometry of **C1** in THF + TBAP 0.1 M. Working electrode: platinum disc; reference electrode: Ag/AgCl in EtOH/LiCl; counter electrode: platinum foil.

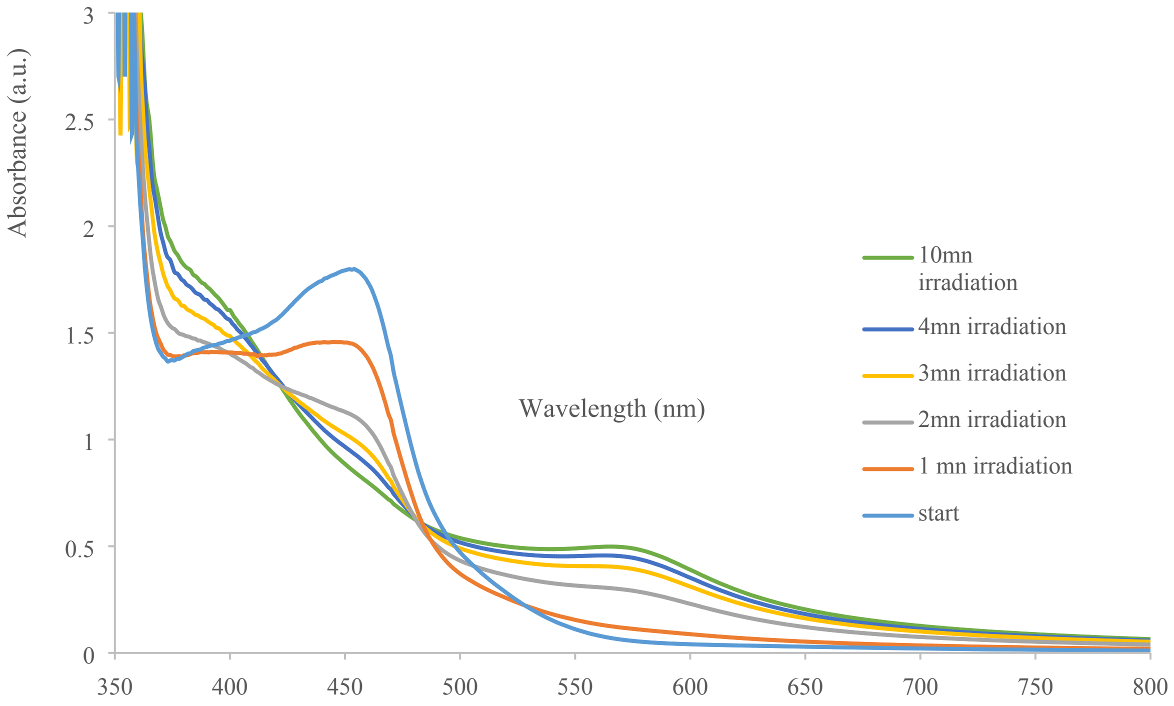


Figure S8. Evolution of the UV-Vis spectra of **C1**, **BI$_1$H** and TEA in deaerated acetonitrile under irradiation at 450 nm (blue LED).

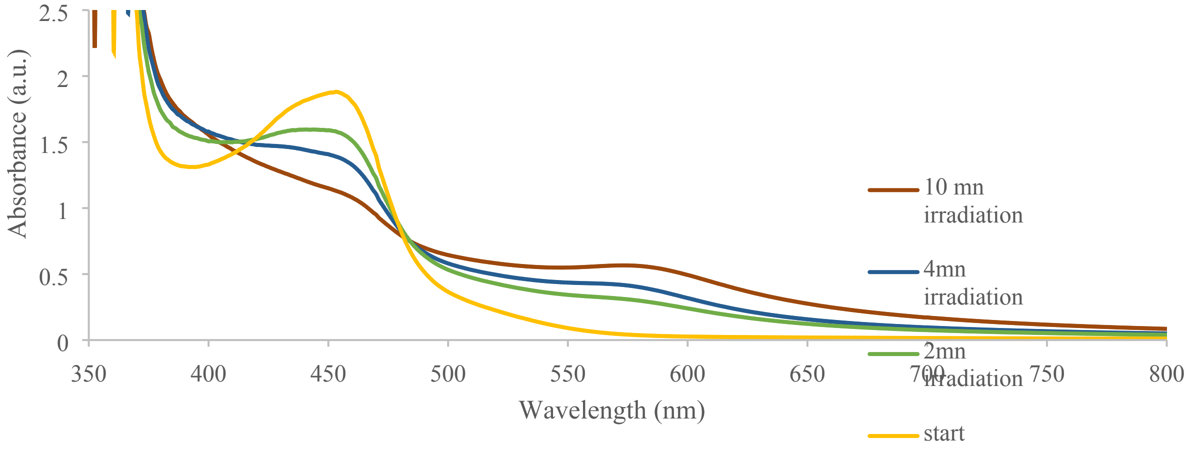


Figure S9. Evolution of the UV-Vis spectra of **C1**, **BI_2H** and TEA in deaerated acetonitrile under irradiation at 450 nm (blue LED).

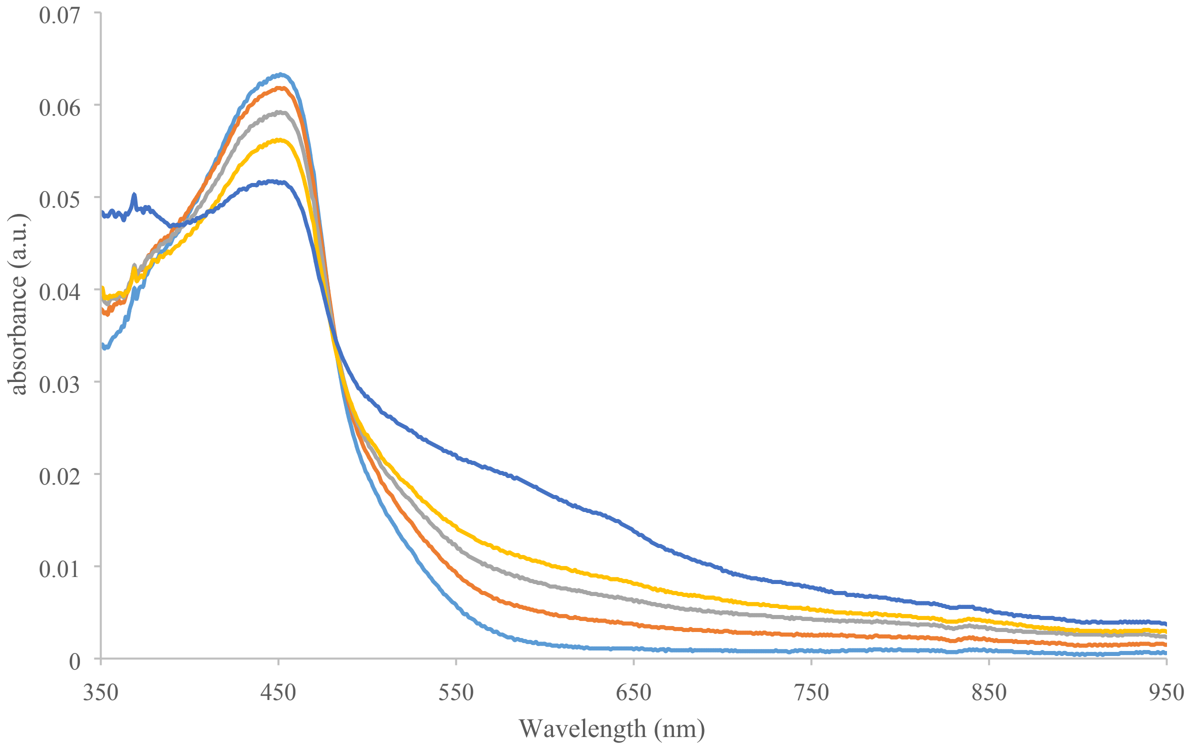


Figure S10. Evolution of the UV-Vis spectra of **C1** in THF upon reduction (supporting electrolyte: tetrabutylammonium hexafluorophosphate 0.1 M).

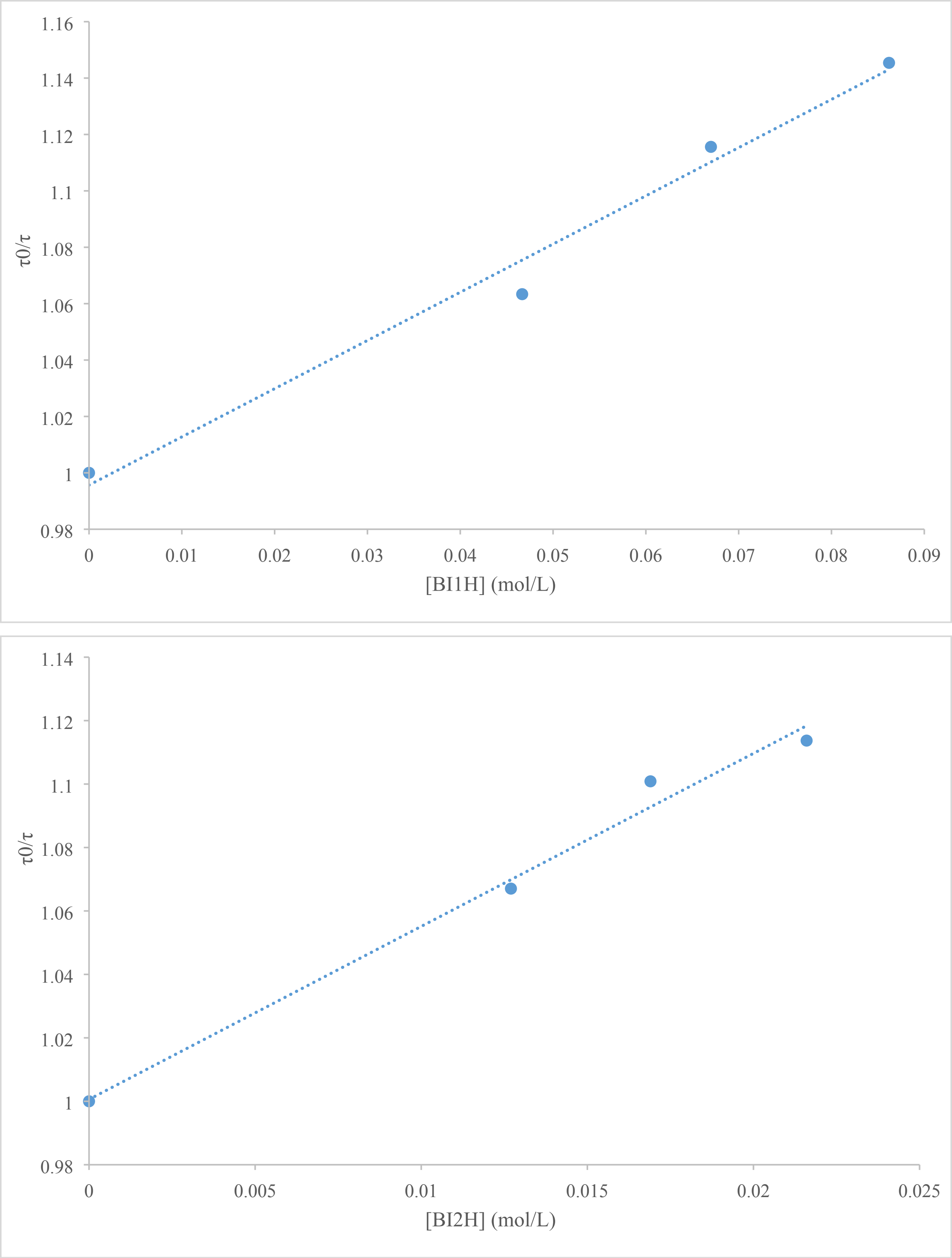


Figure S11. Stern-Volmer plots obtained in acetonitrile to monitor reductive quenching of C1's excited state by BI_1H (up) and BI_2H (bottom). Concentration in C1: ca. 0.17 mM.

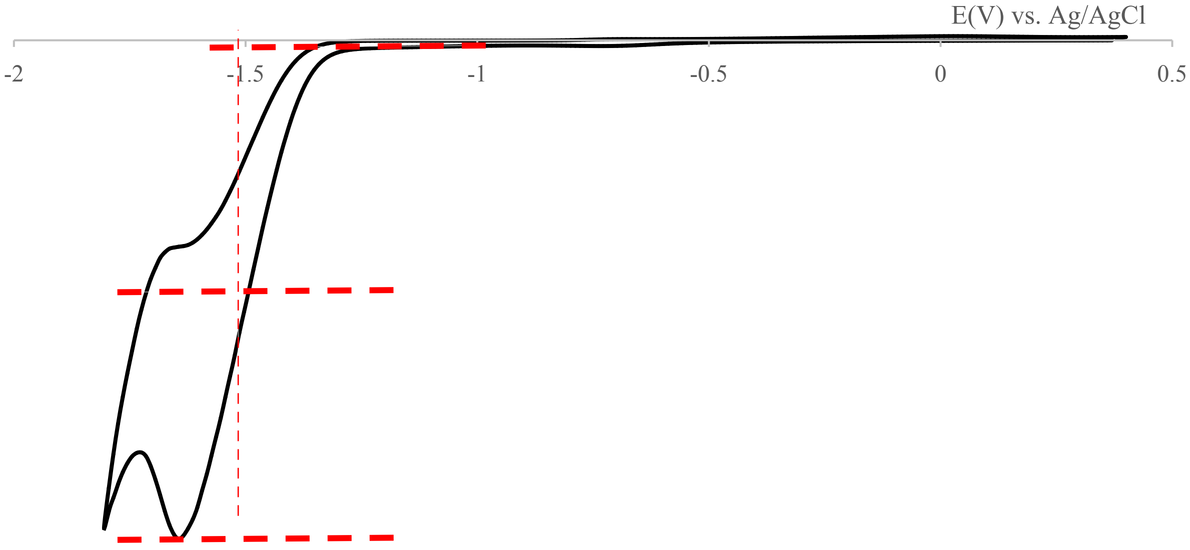


Figure S12. Cyclovoltammogram of **Bzp-Br** in ACN+TBAP 0.1 M. *Nota bene*: no signal could be observed in THF+TBAP, probably because of the large resistivity of the solvent. $E_{p/2}$ = -1.50 V *vs.* Ag/AgCl, recalibrated at -1.62 V *vs.* SCE.

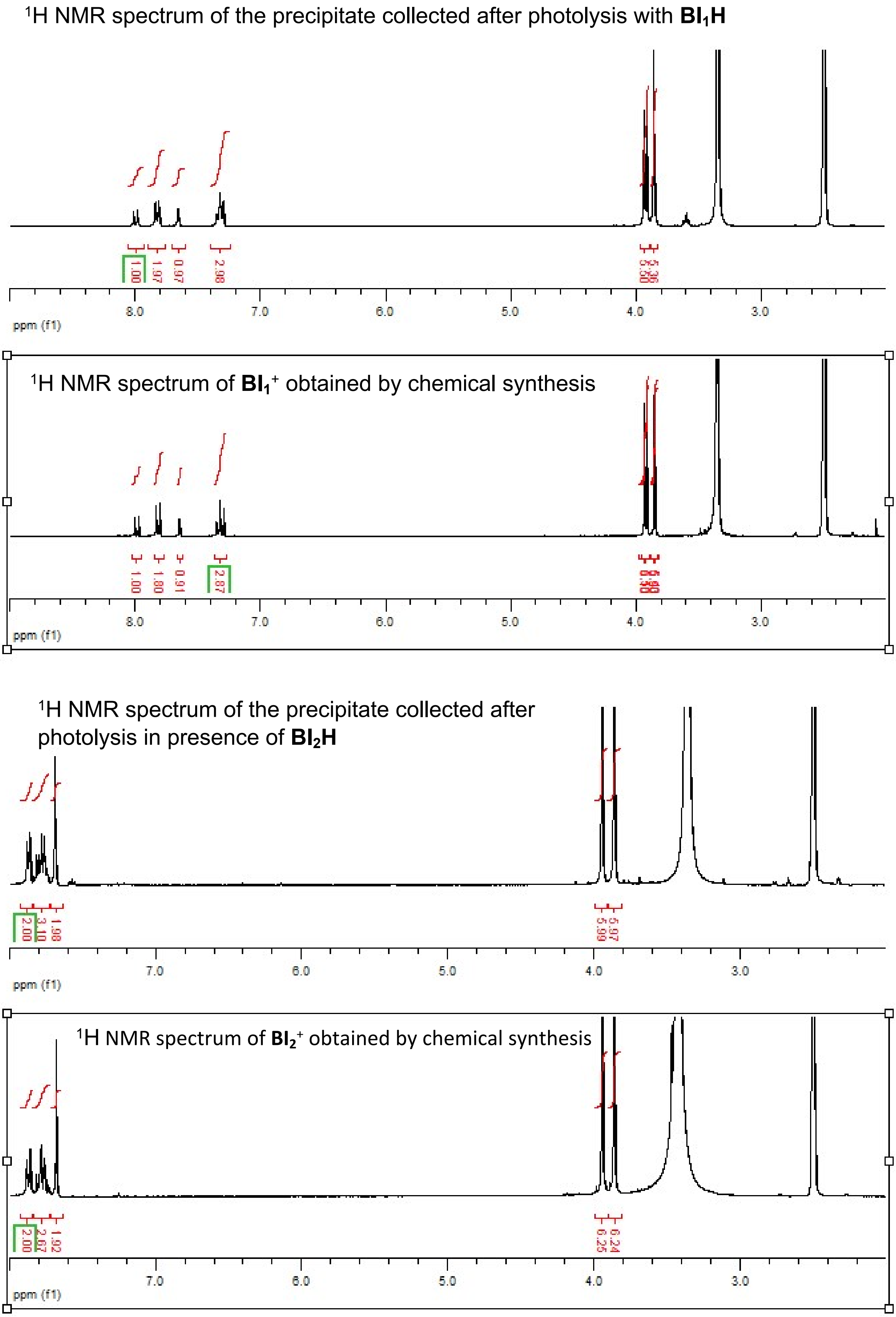


Figure S13. ^{1}H NMR spectra of collected powders precipitating during photolysis experiments (deuterated DMSO).

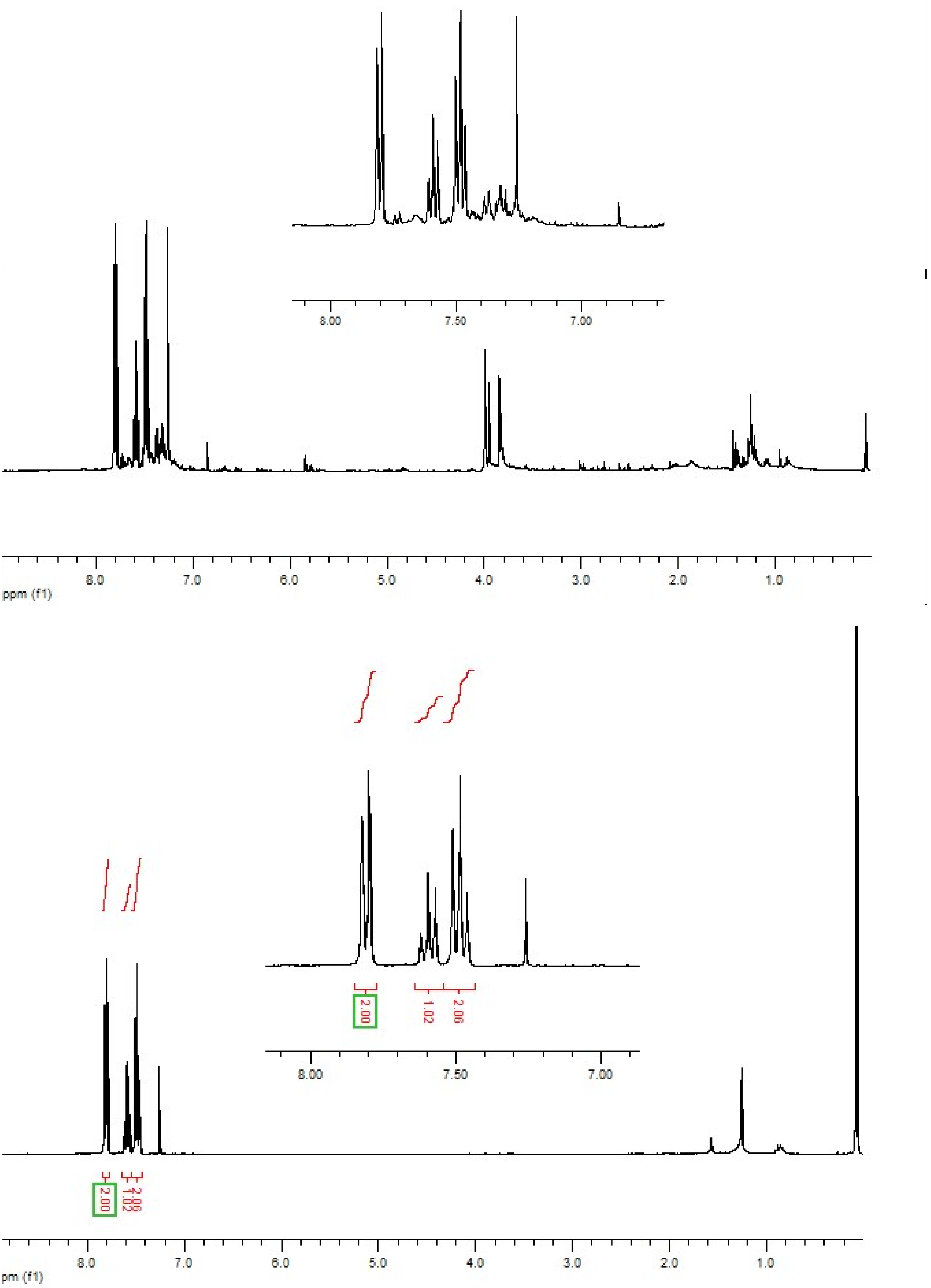


Figure S14. ^{1}H NMR spectra ($CDCl_3$) for photo-produced Bzp-H from Bzp-Br. Top: crude. Bottom: same batch after purification on silica chromatography.

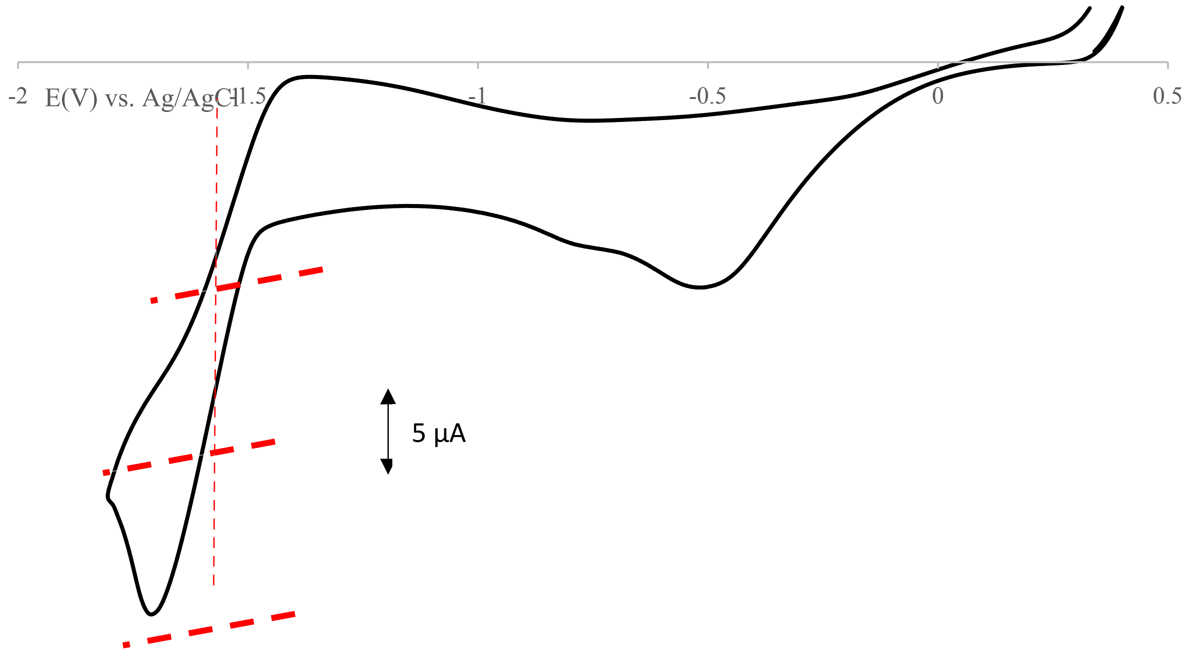
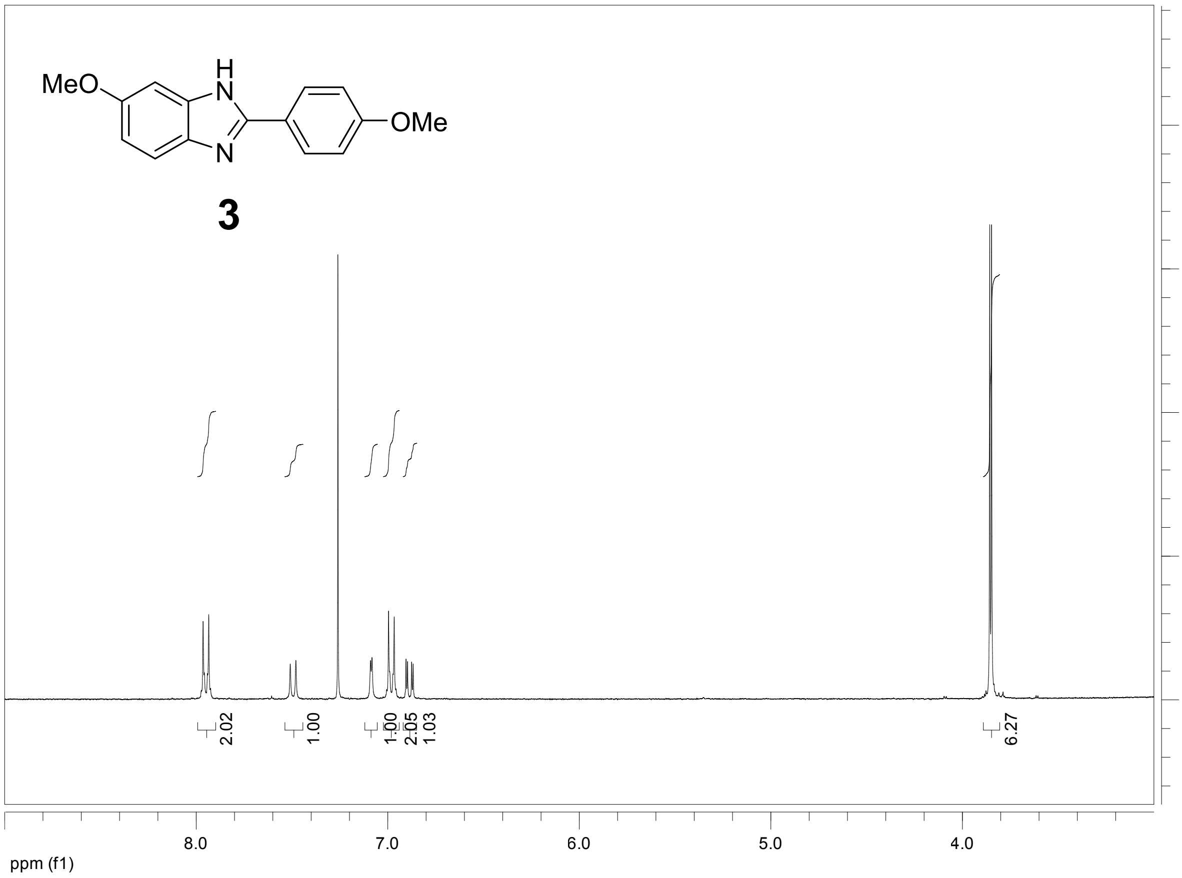
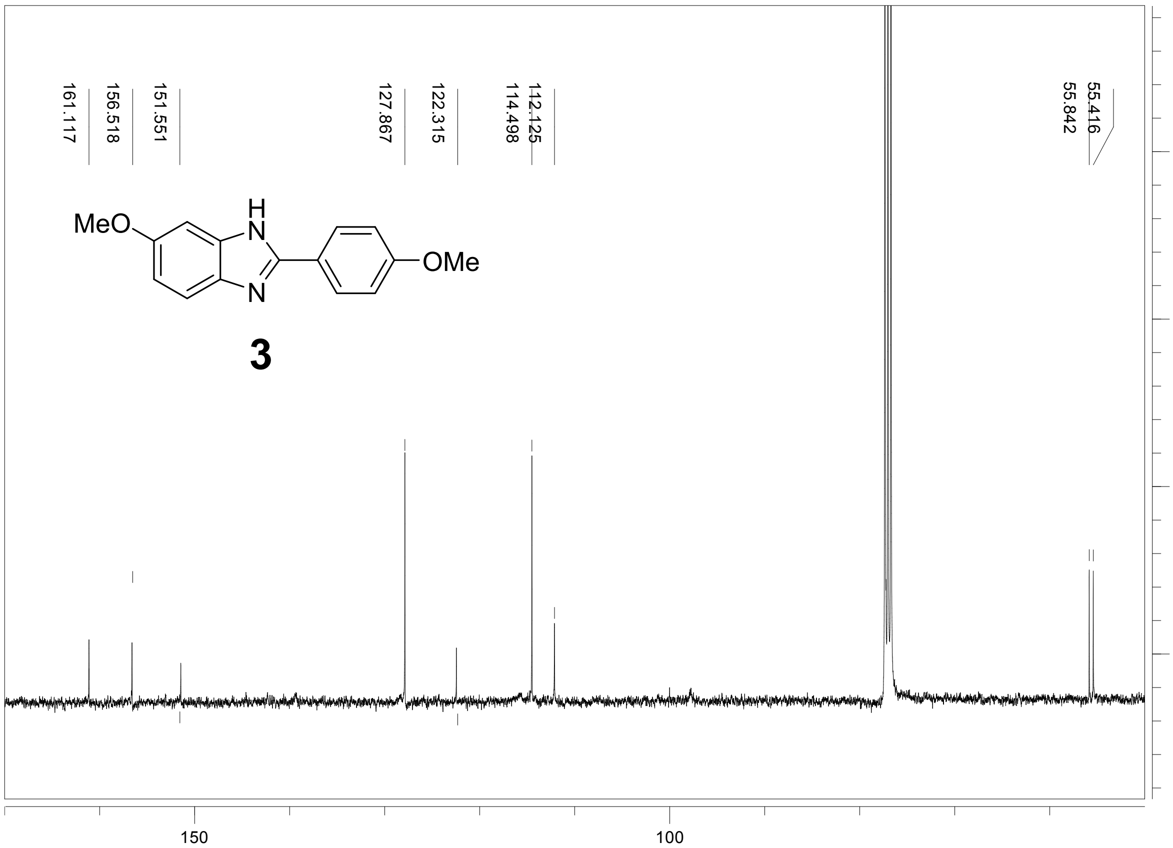


Figure S15. Cyclovoltammogram of **BI$_2^+$** in THF+TBAP 0.1 M. Glassy carbon as working electrode, platinum grid for counter electrode and SCE for the reference electrode. $E_{p/2}$ = -1.58 V vs. Ag/AgCl, recalibrated at -1.7 vs. SCE).



3

MeO
H
N
N
OMe
2.02
1.00
1.00
2.05
1.03
6.27
400
300
200
100
0
8.0
7.0
6.0
5.0
4.0
ppm (f1)



3

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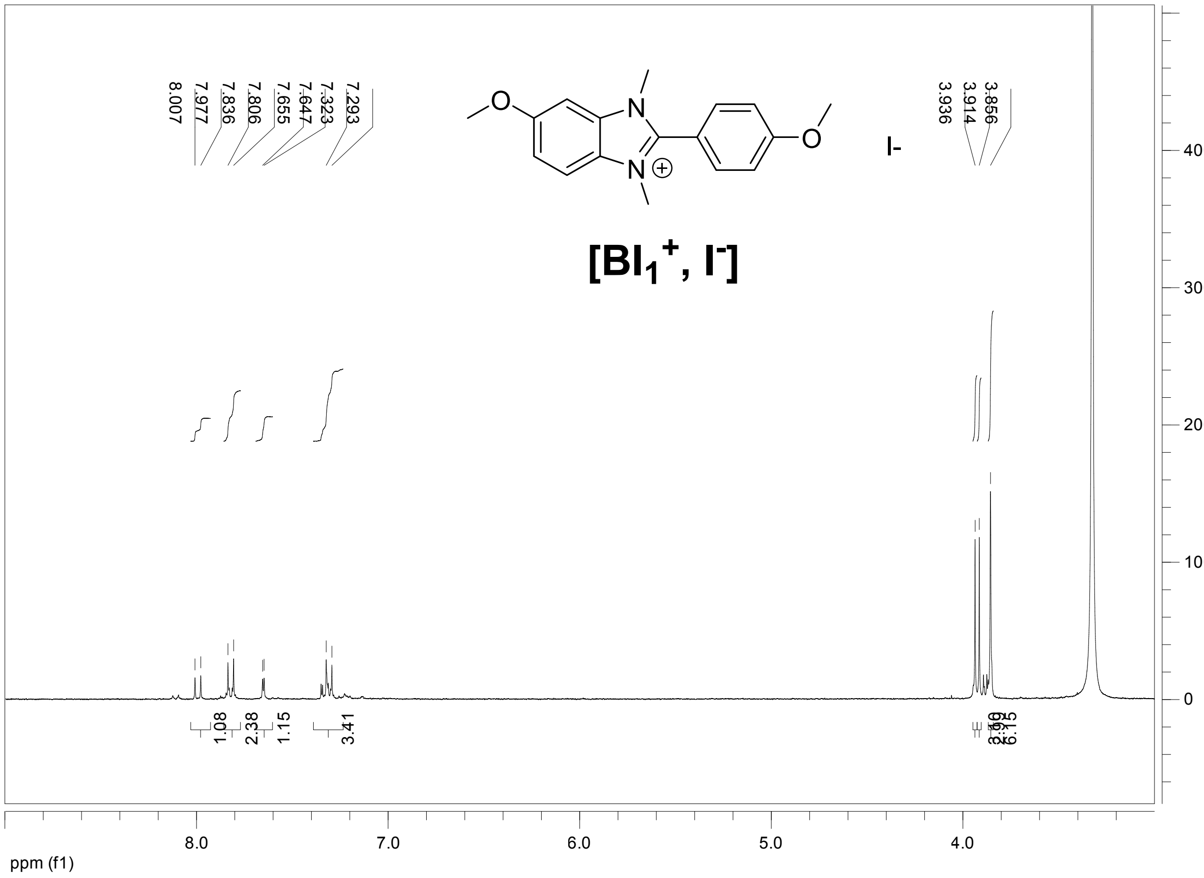
156.518
151.551
127.867
122.315
114.498
112.125
55.416
55.842
MeO
H
N
N
OMe
1500
1000
500
0
150
100
ppm (f1)


8.007
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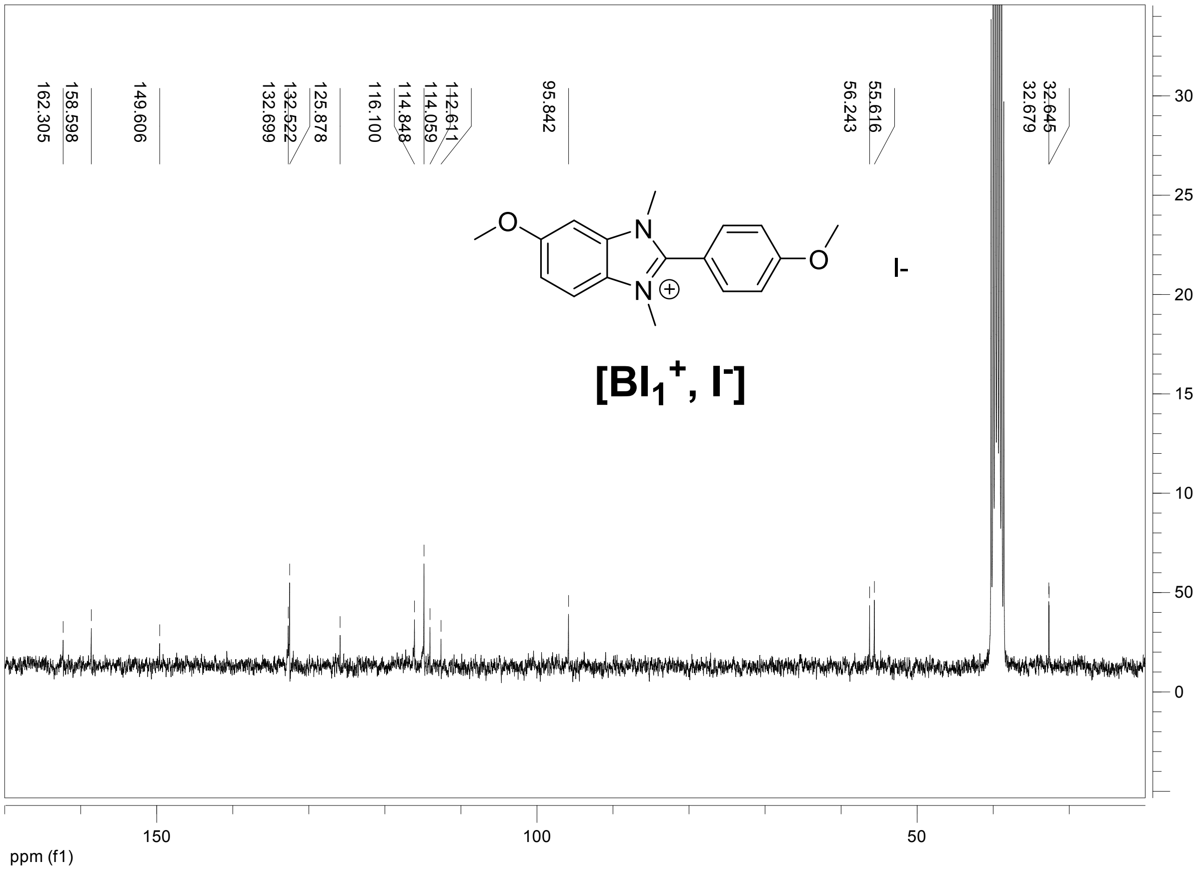
7.655
7.647
7.323
7.293
3.936
3.914
3.856
I-
[BI$_1^+$, I$^-$]
1.08
2.38
1.15
3.41
3.09
2.96
6.15
400
300
200
100
0
8.0
7.0
6.0
5.0
4.0
ppm (f1)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32.679
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[BI$_1^+$, I$^-$]
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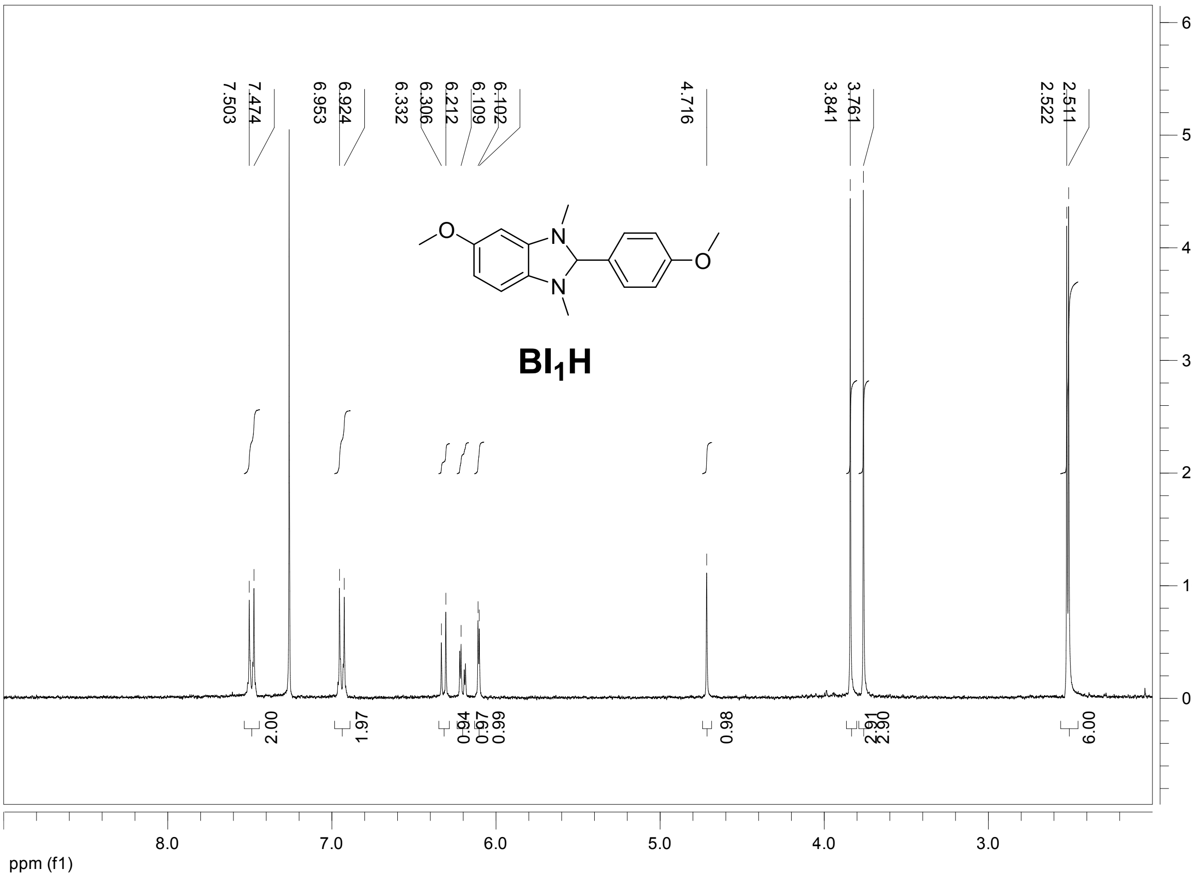
1000
500
0
150
100
50
ppm (f1)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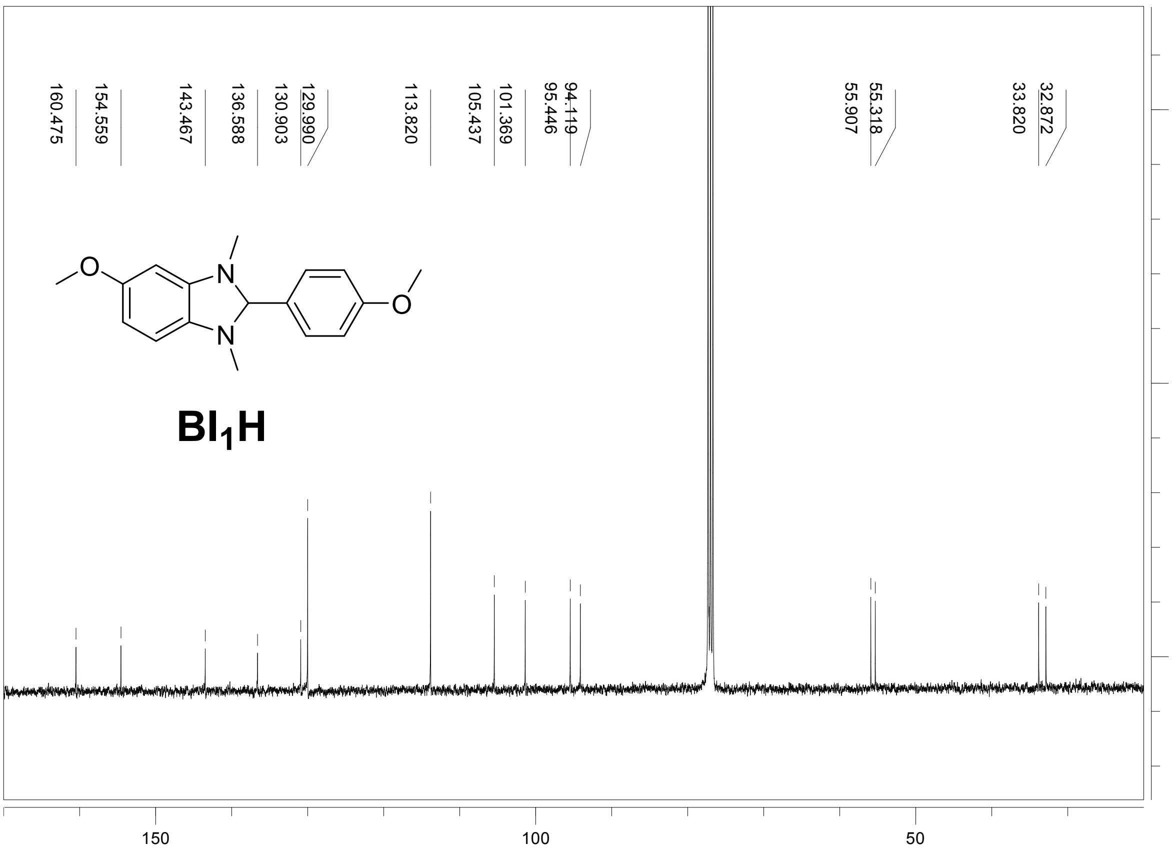
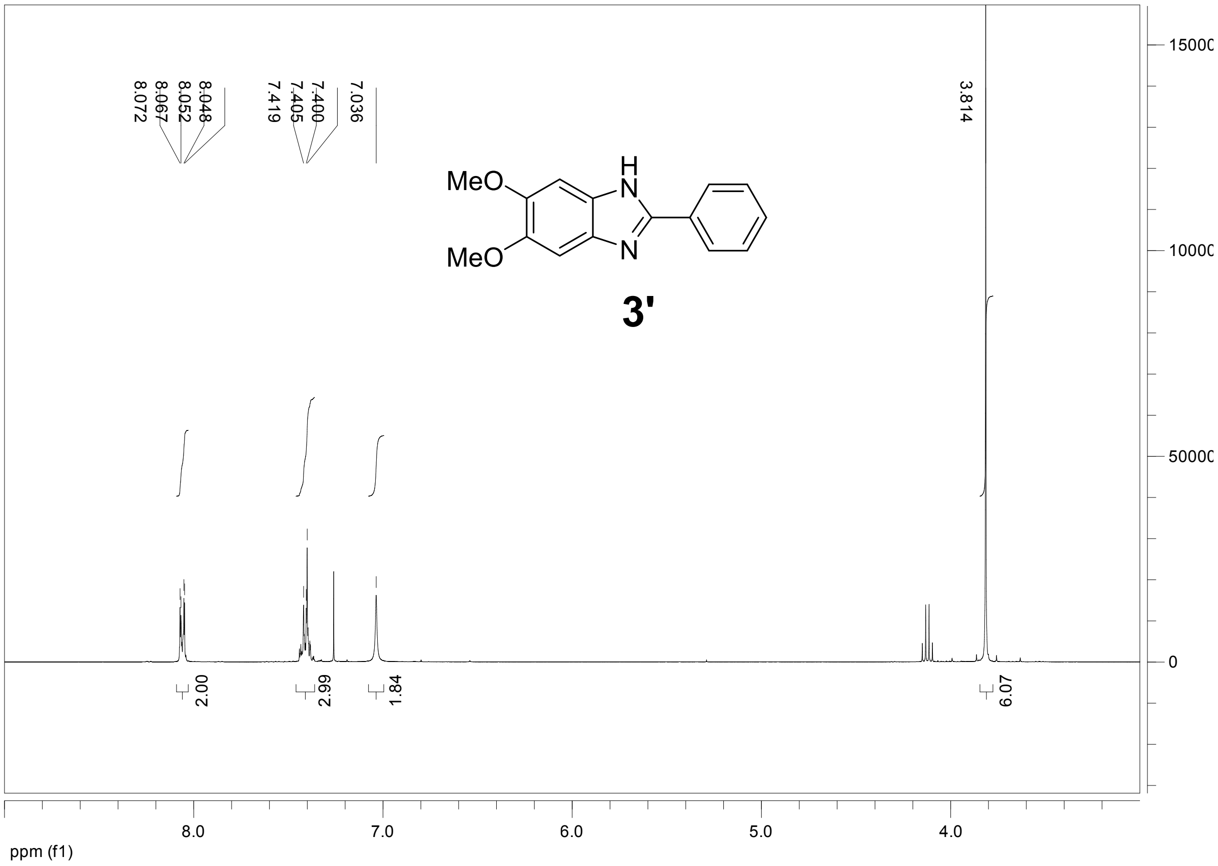
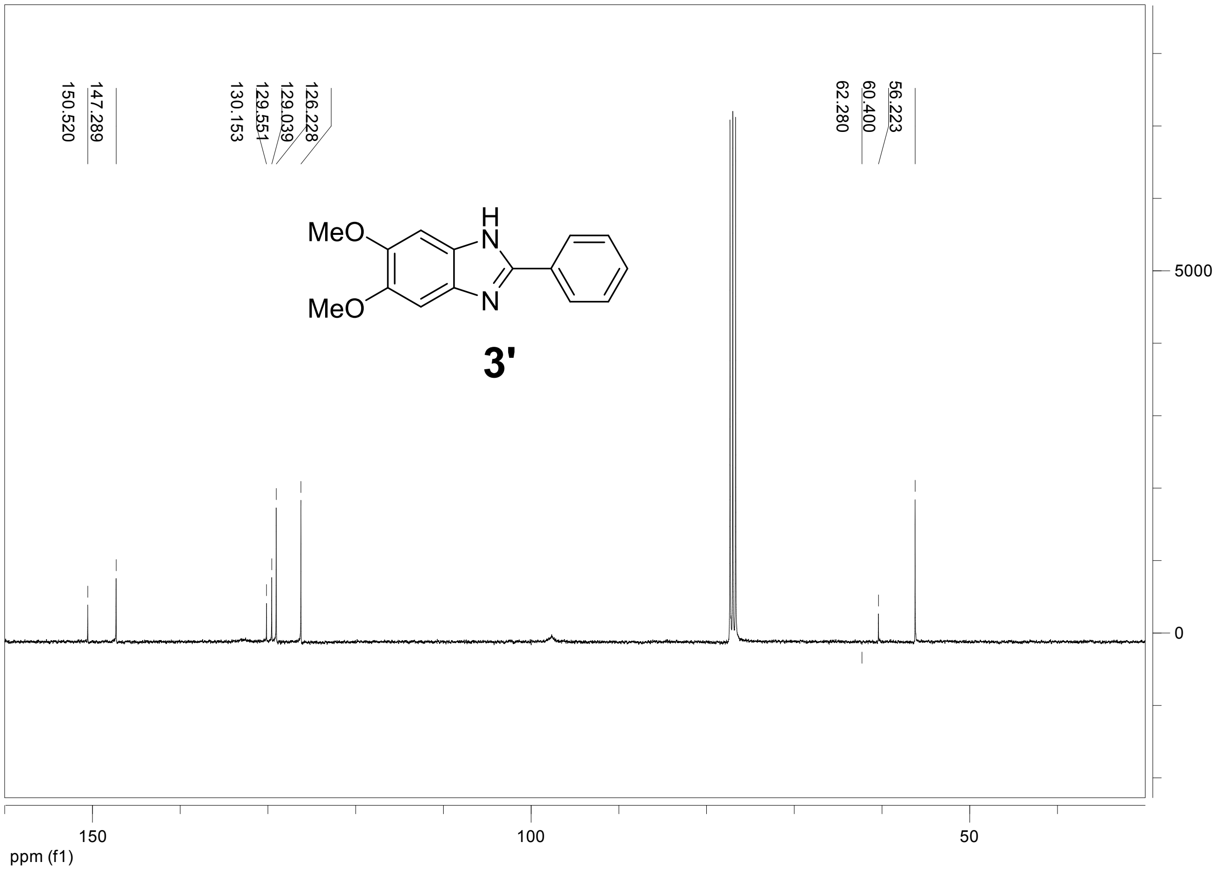
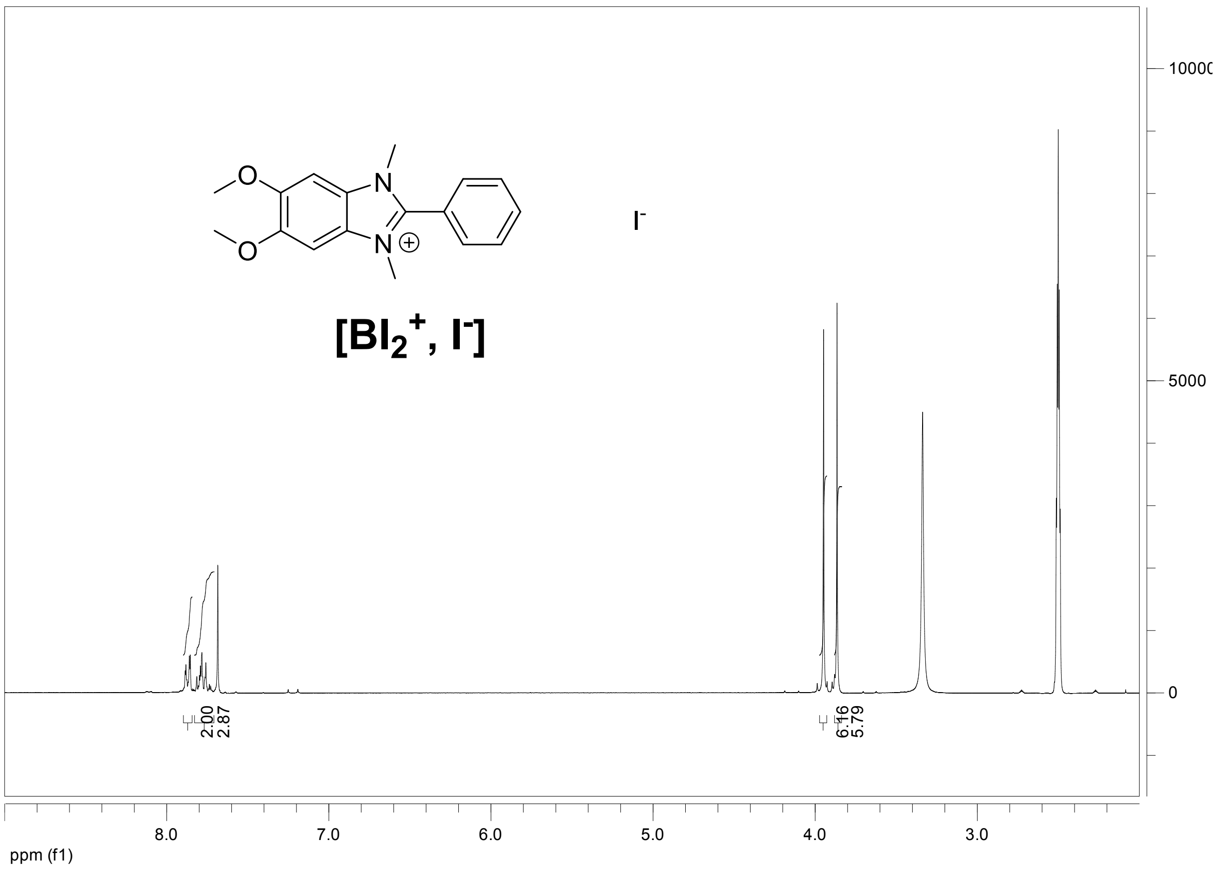
6.953
6.924
6.332
6.306
6.212
6.109
6.102
4.716
3.841
3.761
2.522
2.511
BI$_1$H
2.00
1.67
0.94
0.97
0.99
0.98
2.91
2.90
6.00
600
500
400
300
200
100
0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)

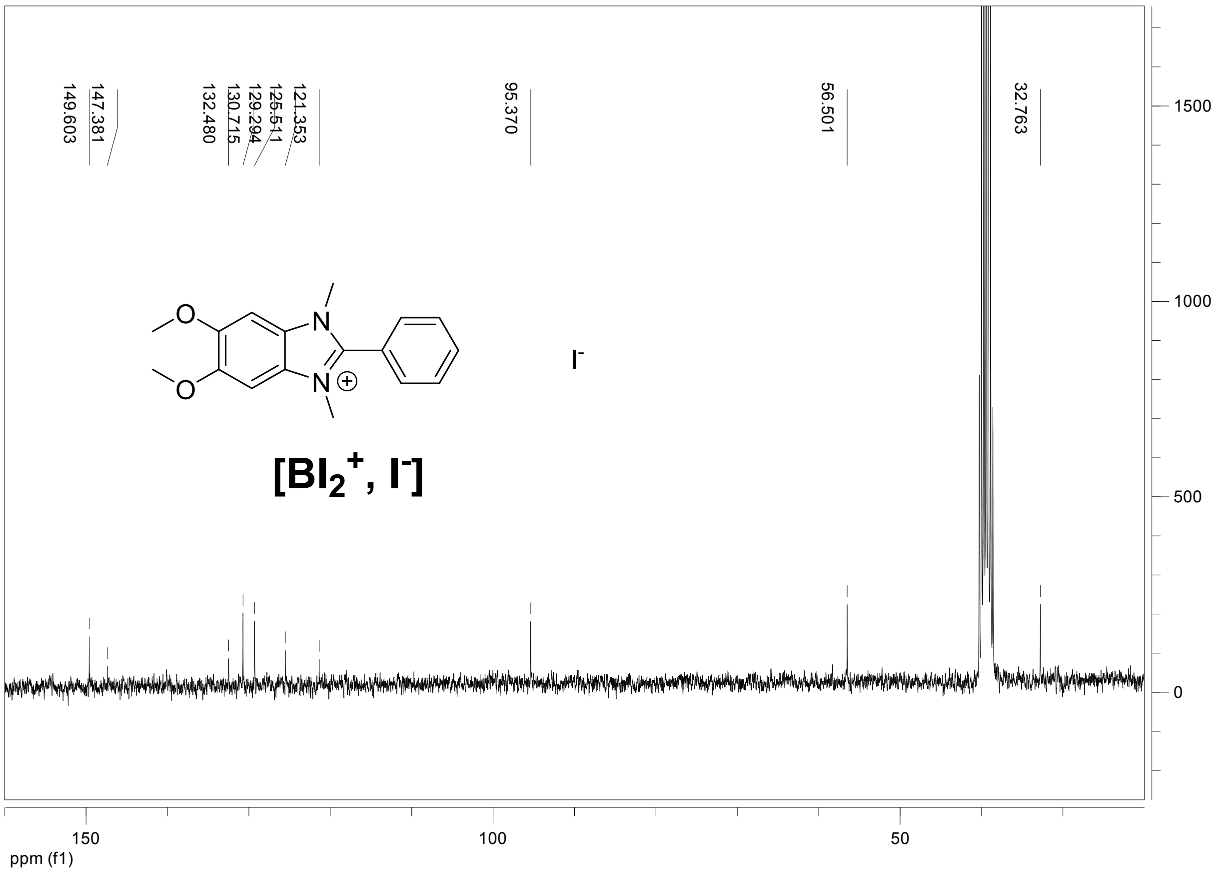

160.475
154.559
143.467
136.588
130.903
129.990
113.820
105.437
101.369
95.446
94.119
55.907
55.318
33.820
32.872
BI$_1$H
1000
500
0
150
100
50
ppm (f1)


8.072
8.067
8.052
8.048
7.419
7.405
7.400
7.036
3.814
MeO
MeO
H
N
N
3'
2.00
2.99
1.84
6.07
15000
10000
50000
0
8.0
7.0
6.0
5.0
4.0
ppm (f1)

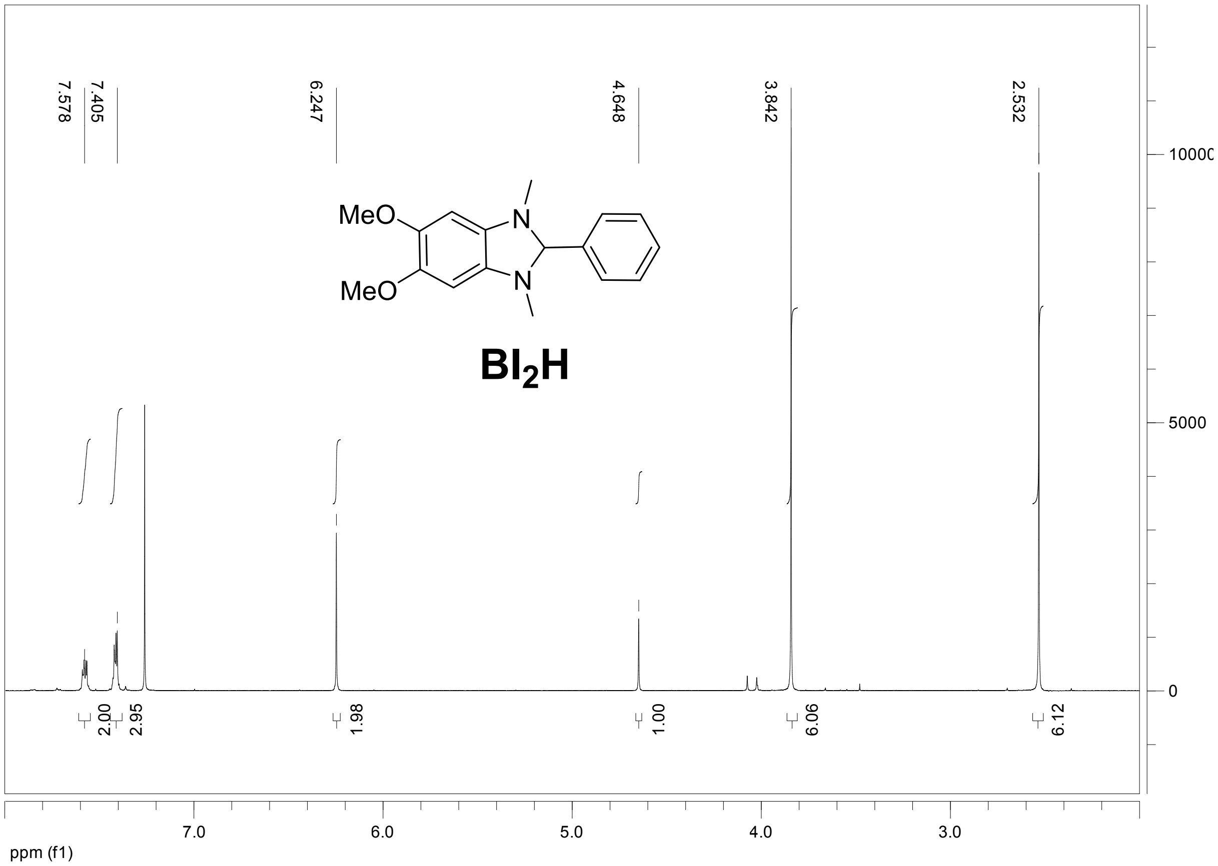

150.520
147.289
130.153
129.551
129.039
126.228
62.280
60.400
56.223
MeO
MeO
H
N
N
3'
5000
0
150
100
50
ppm (f1)

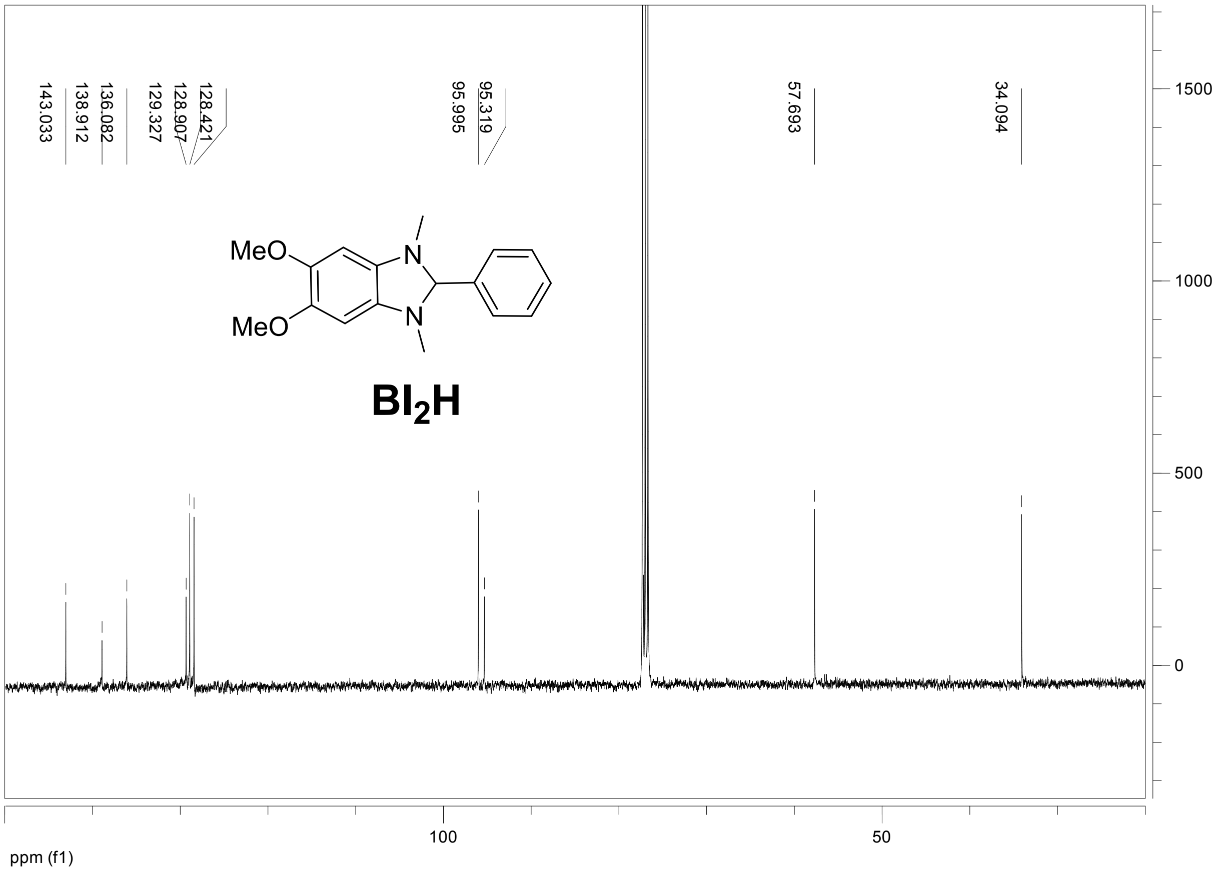


O
O
N
N
⊕
I-
[BI2+, I-]
2.00
2.87
6.16
5.79
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)



149.603
147.381
132.480
130.715
129.294
125.511
121.353
95.370
56.501
32.763
O
O
N
N
⊕
I-
[BI2+, I-]
1500
1000
500
0
150
100
50
ppm (f1)


7.578
7.405
6.247
4.648
3.842
2.532
MeO
MeO
N
N
BI$_2$H
2.00
2.95
1.98
1.00
6.06
6.12
10000
5000
0
7.0
6.0
5.0
4.0
3.0
ppm (f1)


143.033
138.912
136.082
129.327
128.907
128.421
95.995
95.319
57.693
34.094
MeO
MeO
N
N
BI$_2$H
1500
1000
500
0
100
50
ppm (f1)

References

1. “Stable highly oxidizing cobalt complexes of macrocyclic ligands”
T.J. Collins, R.D. Powell, C.Slebodnick, E.S. Uffelman *J. Am. Chem. Soc.* **1991**, *113*, 8419-8425

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S. Garakyaraghi, P. D. Crapps, C. E. McCusker, F. N. Castellano Inorg. Chem. 2016, 55, 10628-10636