SUPPORTING INFORMATION

Supporting Information

Redox-Photosensitized Aminations of 1,2-Benzo-1,3-cycloalkadienes, Arylcyclopropanes, and Quadricyclane with Ammonia

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CONTENTS

Experimental General Methods and Materials	S1
¹ H and ¹³ C NMR spectra of 3e	S2-S3
¹ H and ¹³ C NMR spectra of the acetamide of 2b	S4-S5
¹ H and ¹³ C NMR spectra of the acetamide of 4b	S6-S7
¹ H and ¹³ C NMR spectra of the mixture of the acetamide of 4c and 4c'	S8-S9
¹ H and ¹³ C NMR spectra of the acetamide of 4e	S10-S11
¹ H and ¹³ C NMR spectra of the acetamide of 5a	S12-S13
Tables of X-ray data for the acetamide of 5b	S14-S19

Experimental

General Methods. Melting points were measured using open capillary tubes and are uncorrected. ¹H NMR (250 MHz) and ¹³C NMR (62.9 MHz) spectra were obtained for solutions in CDCl₃. Mass spectra were operated at an ionization voltage of 70 eV. Fluorescence spectra were measured at room temperature for argon-purged solution. The fluorescence lifetimes were measured by single-photon-counting method. Oxidation and reduction potentials were measured for an MeCN solution containing the substrate (0.01 mol dm⁻³) and Et₄NBF₄ (0.1 mol dm⁻³) at a scan rate of 0.3 V s⁻¹ at 23 °C on a cyclic voltammetry using a platinum working electrode, a platinum counter electrode, and an Ag/AgNO₃ reference electrode.

Materials. Spectral grade of MeCN was used without the further purification. 1,3,5-TPB, *m*- and *p*-TP, *m*- and *p*-DCB were used as received. Commercially available **1a**, **1b**, and **1c** were distilled under reduced pressure before use.

DATE 4-2-2

SE	250.133
SF	100.0
O1	4390.000
S1	16364
S/D	16364
SW	4000.000
HZ/Pf	.408
PW	4.0
RD	2.000
AD	2.048
RC	16
N5	297
TE	16
FV	5800
D2	150.000
Op	6SL P0
L6	0.0
C6	0.0
CX	32.00
CY	0.0
F1	9.508P0
F2	-4.988P0
HZ/CM	78.156
PW/CM	312
SR	2660.25

DATE 4-2-2

EX-100

SF 62.896
 ST 62.8
 O1 13000.000
 SI 65536
 IC 65536
 SW 16129.332
 HZ/PT .402
 P1 2.3
 RD 1.500
 RC 2.852
 NS 400
 TS 133
 TE 297
 FW 20200
 O2 4100.000
 DP 200 CPD
 LB 2.000
 CB 0.0
 CK 32.00
 CY 0.0
 F1 194.999P
 F2 -5.000P
 HZ/CM 393.008
 PPM/CM 6.250
 SR 5957.28

DATE 11-12-2
SF 250.133
SY 100.0
O1 4358.000
S1 15384
T0 16384
S4 4000.000
H2/P1 .488
P1 4.0
R0 2.000
R0 2.048
RC 10
NS 15
TE 297
F1 5000
D2 150.000
DP 63L P0
LB 0.0
GB 0.0
CX 32.00
CY 0.0
F1 9.501P
F2/CH -4.08P
PPM/CH 70.156
SR 2053.91

The acetamide of 2b

DATE 11-12-2

SF 62.896

SI 62.8

SI 13000.000

SI 65536

SI 65536

SI 16129.032

SI 482

SI 2.3

SI 1.500

SI 2.052

SI 400

SI 422

SI 297

SI 20280

SI 02 4100.000

SI 20H CPD

SI 2.000

SI 0.0

SI 32.00

SI 0.0

SI 194.999P

SI -4.993P

SI 393.003

SI 8.250

SI 5955.36

S5

DATE 4-2-2

SF 250.133

ST 100.0

SI 4350.000

ST 15384

TD 16384

SH 4000.000

HZ/P 488

PW 4.0

RO 2.000

RC 2.048

NS 4

TE 16

JE 297

FV 5000

OZ 150.000

DF 65L P0

LB 0.0

GB 0.0

CX 32.00

CY 0.00

F1 9.501P

F2 -1.498P

HZ/CM 70.156

PPM/CM 312

SR 2851.46

DATE 4-2-2

SF 62.806
 ST 62.8
 O1 13800.000
 S1 65536
 ID 65536
 SW 16129.832
 HZ/P1 .492
 PV 2.3
 RD 1.500
 RG 2.852
 RC 400
 NS 136
 TE 297
 FY 20200
 D2 4100.000
 DP 20H CPM
 LB 2.000
 GB 0.0
 CX 32.00
 CY 0.0
 F1 194.989P
 F2/CH 393.088P
 PPM/CH 6.250
 SR 5965.19

Table S1. Crystallographic Parameters of the Acetamide of 5b.

Molecular formula	C ₁₆ H ₁₆ N ₂ O
Molecular weight	250
Crystal size / mm	0.1 x 0.1 x 0.4
Crystal system	monoclinic
Space group	Cc
Z	4
a / Å	9.4078
b / Å	17.3440
c / Å	9.5395
a / °	90
b / °	118.4
g / °	90
V / Å ³	1369
Density Dx / Mg m ⁻³	1.22
Density Dm / Mg m ⁻³	1.15
θ limits	2.9-26.3
Range of h	-11 < h < 8
Range of k	0 < k < 21
Range of l	0 < l < 11
Total reflection	1790
R (unweighted)	0.0414
R (weighted)	0.0494

Table S2. Positional Parameters and their Estimated Standard Deviations of the Acetamide of **5b**.

atom	x	y	z	B(2)
C1	0.0905(5)	0.2335(2)	-0.1067(5)	5.9(1)
C2	0.1639(4)	0.1982(2)	-0.1767(4)	5.47(9)
C3	0.1696(4)	0.1134(2)	-0.1368(3)	3.91(7)
C4	0.2955(4)	0.1086(2)	0.0435(4)	3.68(7)
C5	0.2019(4)	0.1465(2)	0.1237(4)	4.14(7)
C6	0.0436(4)	0.1745(2)	-0.0189(4)	4.38(8)
C7	0.0067(3)	0.1072(2)	-0.1362(3)	3.74(7)
C8	-0.0756(3)	-0.0273(2)	-0.1770(3)	3.61(7)
C9	-0.1113(4)	-0.0987(2)	-0.1134(4)	4.90(8)
C10	0.3662(3)	0.0310(2)	0.1153(3)	3.15(6)
C11	0.322(4)	-0.0386(2)	0.0315(4)	3.73(7)
C12	0.3917(4)	-0.1072(2)	0.1048(4)	4.12(8)
C13	0.5090(3)	-0.1085(2)	0.2630(4)	3.70(7)
C14	0.5552(4)	-0.0397(2)	0.3480(4)	4.09(8)
C15	0.4841(4)	0.0281(2)	0.2738(4)	3.91(8)
C16	0.5806(4)	-0.1795(2)	0.3414(4)	4.92(9)
O1	-0.0821(3)	-0.0270(1)	-0.3098(2)	5.15(6)
N1	-0.0296(4)	0.0350(2)	-0.0833(5)	3.48(5)
N2	0.6388(4)	-0.2356(2)	0.4052(5)	7.2(1)

Table S3. Bond Distance in Angstroms of the Acetamide of **5b**.

Atom1	Atom2	Distance / Å
N1	C8	1.338(3)
N1	C7	1.449(4)
O1	C8	1.239(4)
C11	C10	1.399(4)
C11	C12	1.377(4)
C13	C12	1.382(4)
C13	C14	1.391(4)
C13	C16	1.432(4)
C8	C9	1.487(5)
C7	C3	1.638(5)
C7	C6	1.539(5)
C3	C4	1.559(4)
C3	C2	1.514(5)
C4	C10	1.512(4)
C4	C5	1.559(5)
C10	C15	1.387(4)
C5	C6	1.541(4)
C14	C15	1.372(4)
N2	C16	1.139(4)
C2	C1	1.317(7)
C6	C1	1.515(6)

Table S4. Bond Angles in Degree of the Acetamide of 5b.

Atom1	Atom2	Atom3	Angle
C8	N1	C7	121.3(2)
C10	C11	C12	121.0(2)
C12	C13	C14	119.2(3)
C12	C13	C16	121.2(3)
C14	C13	C16	119.6(2)
N1	O8	O1	121.5(3)
N1	C8	C9	117.7(3)
O1	C8	C9	120.7(3)
N1	C7	C3	117.5(2)
N1	C7	C6	114.2(3)
C3	C7	C6	94.0(2)
C7	C3	C4	103.1(3)
C7	C3	C2	98.8(3)
C4	C3	C2	104.2(2)
C3	C4	C10	119.1(2)
C3	C4	C5	102.1(2)
C10	C4	C5	112.4(3)
C11	C10	C4	124.3(2)
C11	C10	C15	117.2(2)
C4	C10	C15	118.5(2)
C11	C12	C13	120.6(3)
C4	C5	C6	103.5(3)
C13	C14	C15	119.6(2)
C13	C16	N2	179.0(3)
C10	C15	C14	122.3(3)
C3	C2	C1	106.8(4)
C7	C6	C5	101.1(2)
C7	C6	C1	97.7(3)
C5	C6	C1	106.7(3)
C2	C1	C6	109.1(3)

Table S5. Torsional Angles in Degree of the Acetamide of **5b**.

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C7	N1	C8	C1	3.2(4)
C7	N1	C8	C9	179.7(3)
C8	N1	C7	C3	-76.2(3)
C8	N1	C7	C6	175.1(3)
C12	C11	C10	C4	180.0(4)
C12	C11	C10	C15	0.8(5)
C10	C11	C12	C13	-0.8(5)
C14	C13	C12	C11	0.4(5)
C16	C13	C12	C11	179.0(4)
C12	C13	C14	C15	0.0(5)
C16	C13	C14	C15	-178.6(4)
C12	C13	C16	N2	170.9(3)
C14	C13	C16	N2	-10.6(3)
N1	C7	C3	C4	-65.8(3)
N1	C7	C3	C2	-172.8(2)
C6	C7	C3	C4	54.2(3)
C6	C7	C3	C2	-52.8(3)
N1	C7	C6	C5	65.6(3)
N1	C7	C6	C1	174.4(3)
C3	C7	C6	C5	-57.0(3)
C3	C7	C6	C1	51.8(3)
C7	C3	C4	C10	94.0(3)
C7	C3	C4	C5	-31.1(3)
C2	C3	C4	C10	-163.9(3)
C2	C3	C4	C5	71.6(3)
C7	C3	C2	C1	34.9(4)
C4	C3	C2	C1	-71.1(4)
C3	C4	C10	C11	-2.4(5)
C3	C4	C10	C15	176.7(3)
C5	C4	C10	C11	117.0(4)

(Table S5, continued)

C5	C4	C10	C15	-63.7(4)
C3	C4	C5	C6	-0.1(3)
C10	C4	C5	C6	-133.9(3)
C11	C10	C15	C14	-0.4(5)
C4	C10	C15	C14	-179.6(3)
C4	C5	C6	C7	39.4(3)
C4	C5	C6	C1	-62.2(3)
C13	C14	C15	C10	0.0(7)
C3	C2	C1	C6	-0.3(5)
C7	C6	C1	C2	-34.2(4)
C5	C6	C1	C2	69.8(4)