Electronic Supplementary Information for:

Synthesis of Bacteriochlorins Bearing Diverse β-Substituents

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(1) Metalation studies with BC-6

With bacteriochlorin-tetraester **BC-6** in hand, we attempted the metalation to form a Si(IV) or Al(III) bacteriochlorin. A solution of **BC-6** in THF was treated with 95% NaH followed by the addition of a metalation reagent. The reaction mixture was heated at 60–65 °C with stirring, and monitored by removal of aliquots and examination of the absorption spectrum (in CH_2Cl_2 at room temperature). The reaction monitoring relied on the expected bathochromic shift of the Q_y absorption band known to occur upon metalation of bacteriochlorins.[63] The studies are shown in Table S1.

- Attempted metalation with $AlCl_3$ (entry 1) for 24 h was followed by recovery of >90% of **BC-6**.
- When **BC-6** was treated with NaH followed by $SiCl_4$ at 55 °C, a distinct peak appeared at ~767 nm after 20 h (entry 2, Figure S1). However, after ~12 min, the absorption of the crude mixture in the glass cuvette reverted to 758 nm (Figure S2), characteristic of the starting free base bacteriochlorin.
- A similar observation occurred for Cl_2SiMe_2 (entry 3, Figure S3). A new peak at 768 nm suggested formation of a putative silicon-chelated bacteriochlorin, but the spectrum reverted to that of starting material in ~ 3 h (Figure S4).
- Treatment of **BC-6** with TFA resulted in a bathochromic shift (Figure S5) that was different from those in entries 2 and 3, suggesting the results with the metalation reagents were not due to the protonation of free base bacteriochlorin **BC-6**.

Thus, despite bathochromic shifts upon attempted siliconation, the shift was not stable, reverting to that of **BC-6**. Regardless of conditions examined, a stable metallobacteriochlorin derived from aluminum or silicon reagents was not isolated.

Table S1. Studies of Si- and Al-insertion of bacteriochlorin **BC-6**.

Entry	BC-6	Base	Reagent	T °C	Observations
1	1 mg, 4 mM	NaH (0.6 M)	$AlCl_3$ (120 mM)	60	24 h, No reaction
2	1 mg, 4 mM	NaH (0.6 M)	$SiCl_4$ (120 mM)	55	20 h, 767 nm; back to 758 nm in 12 min
3	3 mg, 4 mM	NaH (0.6 M)	Cl_2SiMe_2 (120 mM)	60–65	16 h at 60 °C, then 65 °C for 4 h, 768 nm; back to 759 nm in 2 h 47 min
4	1.0 mg, 4 mM	–	$AlCl_3$ (200 mM)	85	16 h, No reaction
5	1.0 mg, 4 mM	–	$SiCl_4$ (200 mM)	85	16 h, No reaction
6	1.0 mg, 4 mM	–	Cl_2SiMe_2 (200 mM)	85	16 h, No reaction

Experimental Procedure (entries 1–3):

(1) 100 μL of a stock solution of **BC-6** (1 mg/100 μL in CH_2Cl_2) was placed in a Schlenk flask.
(2) The aliquot was blown to dryness with a stream of argon.
(3) The film of **BC-6** was further dried under high vacuum for 1 h.
(4) The flask was charged with argon, and freshly distilled THF (360 μL) was added.
(5) The solution was deaerated by three freeze-pump-thaw cycles.
(6) A sample of NaH (95%) was added, and the mixture was stirred at rt for 30 min.
(7) A Si or Al reagent was added, and the flask was sealed immediately and heated to the indicated temperature.
(8) After the indicated time, a sample was removed, added to CH_2Cl_2, and examined by absorption spectroscopy.

Experimental Procedure (entries 4–6):

A sample of **BC-6** (1.0 mg, 1.5 μmol) in anhydrous DMF (350 μL) under argon was treated with an Al or Si reagent (72.5 μmol). The reaction mixture was stirred at 85 °C for 16 h. Samples were removed and examined by absorption spectroscopy in DMF at room temperature.

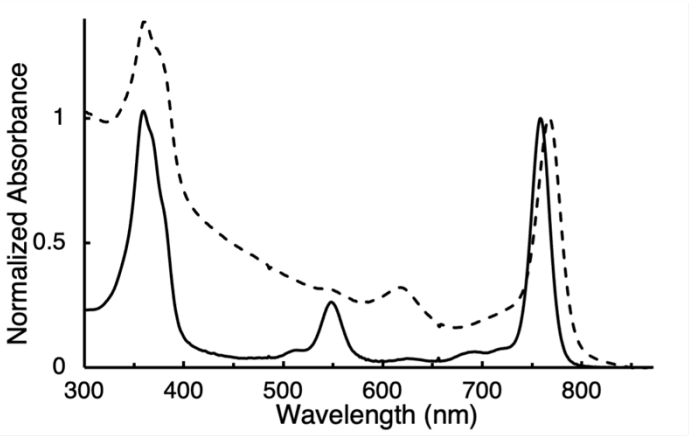

Figure S1. Absorption spectra of **BC-6** (758 nm, solid line) and crude product (767 nm, dashed line, treated with $SiCl_4$) in CH_2Cl_2 at room temperature.

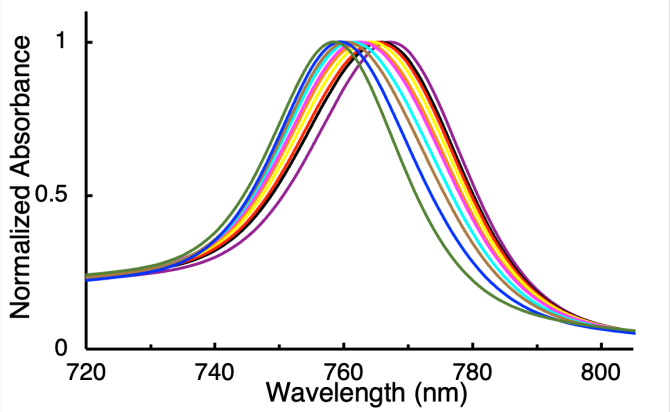

Figure S2. Absorption spectra in CH_2Cl_2 at room temperature of the crude product derived from treatment with $SiCl_4$: 767 nm (0 s, purple), 766 nm (60 s, black), 765 nm (80 s, red), 764 nm (120 s, yellow), 763 nm (180 s, orange), 762 nm (200 s, magenta), 761 nm (320 s, cyan), 760 nm (420 s, brown), 759 nm (690 s, blue), 758 nm (1080 s, green).

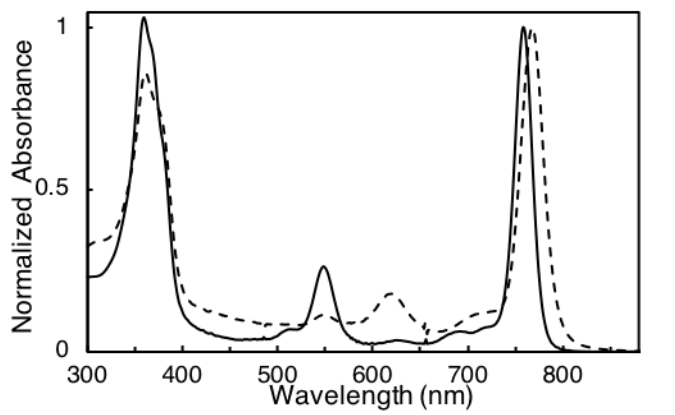

Figure S3. Absorption spectra of **BC-6** (758 nm, solid line) and crude product (768 nm, dashed line, treated with Cl_2SiMe_2) in CH_2Cl_2 at room temperature.

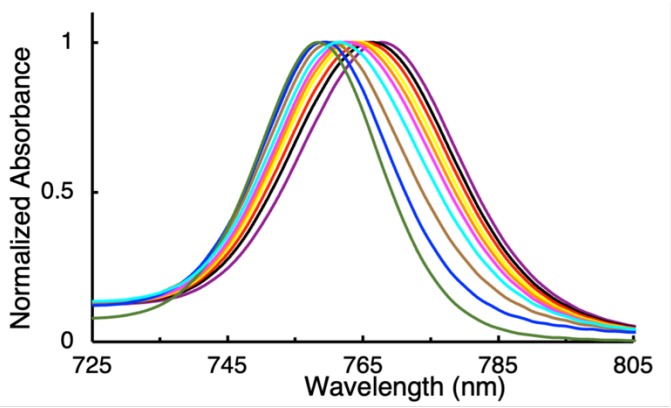

Figure S4. Absorption spectra in CH_2Cl_2 at room temperature of the crude product derived from treatment with Cl_2SiMe_2: 768 nm (0 s, purple), 766 nm (20 s, black), 765 nm (40 s, red), 764 nm (120 s, yellow), 763 nm (340 s, orange), 762 nm (660 s, magenta), 761 nm (68 min 10 s, cyan), 760 nm (108 min 10 s, brown), 759 nm (166 min 10 s, blue), 758 nm (green, starting material).

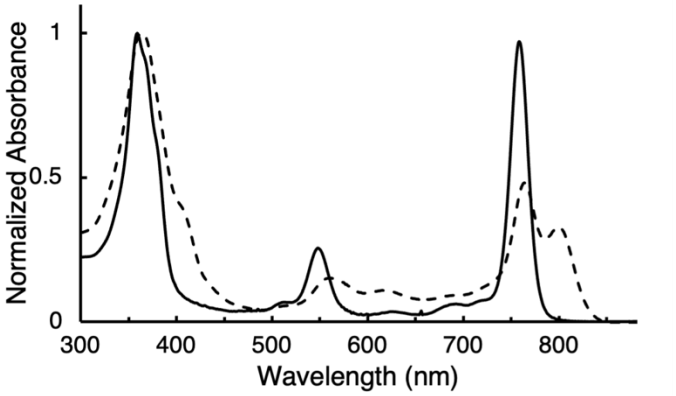

Figure S5. Absorption spectra in CH_2Cl_2 at room temperature of **BC-6** (758 nm, solid line) and upon addition of TFA (dashed line).

(2) X-ray structural data

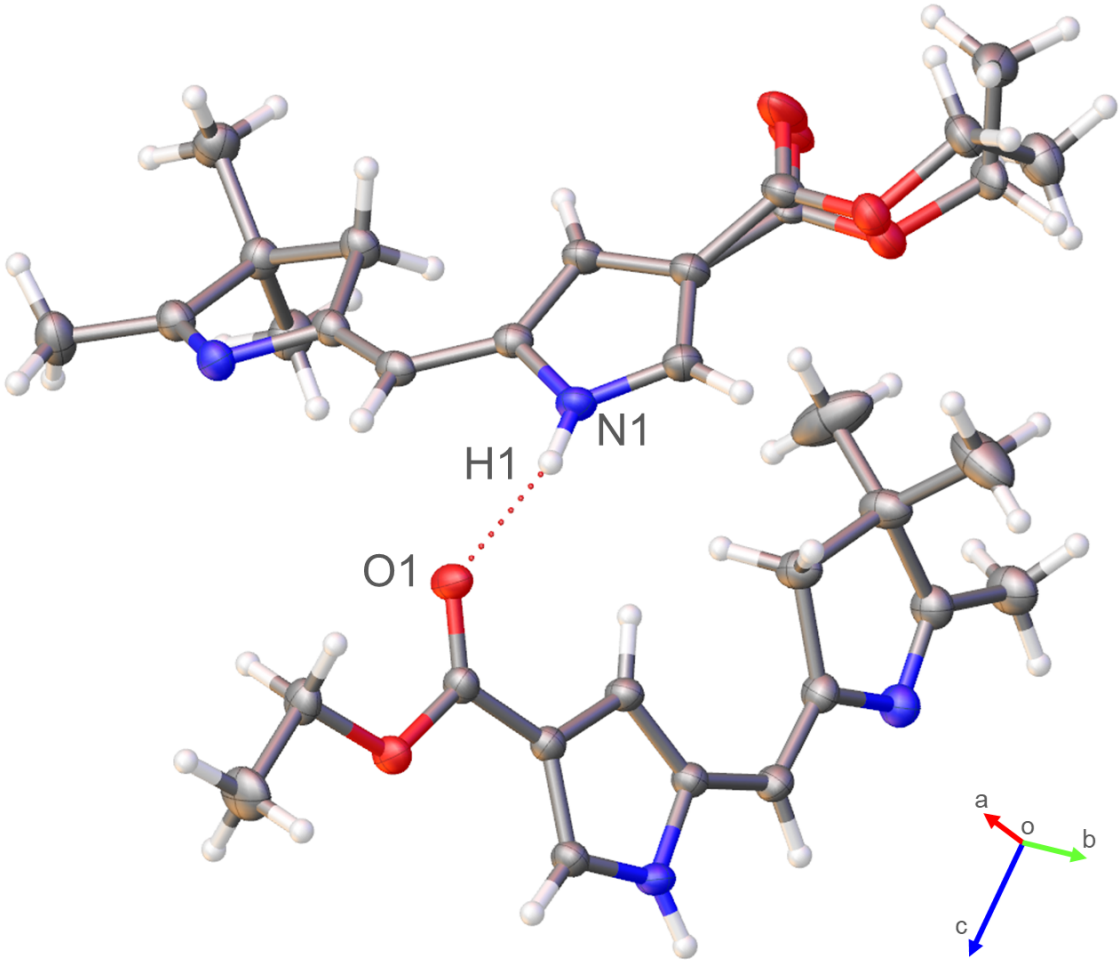

Figure S6. ORTEP diagrams of two molecules of dihydrodipyrrin **5-E** in the single-crystal X-ray structure. Ellipsoids are at the 50% probability level.

For the crystal of **5-E**, the two dihydrodipyrrin molecules in the unit cell are not positioned identically. One $-CO_2Et$ group shows disorder whereas the other $-CO_2Et$ group does not. The absence of disorder in the latter case likely stems from stabilization due to intermolecular hydrogen bonding among the two dihydrodipyrrins in the unit cell. An N–H···O bond between the pyrrole of one dihydrodipyrrin and the carbonyl unit of the other dihydrodipyrrin is illustrated by a dotted red line in the figure. The other carbonyl group may have only a weak interaction with the C–H of one of the methyl units of the gem-dimethyl group. The strong N–H···O bond can restrict the conformation and enforce the alignment of the dihydrodipyrrins in the crystal.

Table S2. Summary of Crystal Data for 5-E.

CCDC registry	2120134
Chemical formula	$C_{15}H_{20}N_2O_2$
Formula weight (g/mol)	260.33
Temperature (K)	100 (2)
Wavelength (Å)	1.54178
Crystal size (mm)	0.17 × 0.09 × 0.04
Crystal habit	pale orange plate
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions, *a* (Å)	11.1910 (2)
Unit cell dimensions, *b* (Å)	11.9815 (2)
Unit cell dimensions, *c* (Å)	21.8035 (4)
α, deg	90
β, deg	90.517 (1)
γ, deg	90
Volume (Å^3)	2923.40 (9)
Z	8
Density (calculated) (g/cm^3)	1.183
Absorption coefficient (mm^{-1})	0.634
F(000)	1120
Theta range for data collection, deg	4.05 to 74.70
Index ranges	-13<=h<=13, -14<=k<=13, -27<=l<=27
Reflections collected	52347
Independent reflections	5965 [R(int) = 0.042]
R_1	0.0376
wR_2	0.0464
R_1 (all data)	0.0939
wR_2 (all data)	0.0997
Largest diff. peak and hole (eÅ^{-3})	0.28 and -0.28
R.M.S. deviation from mean (eÅ^{-3})	0.035

Table S3. Summary of Crystal Data for 12.

CCDC registry	2125374
Chemical formula	$C_{17}H_{26}N_2O_7$
Formula weight (g/mol)	370.40
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal size (mm)	0.46 × 0.12 × 0.09
Crystal habit	colorless prism
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimension, *a* (Å)	11.7410 (18)
Unit cell dimension, *b* (Å)	11.4272 (17)
Unit cell dimension, *c* (Å)	14.676 (2)
α, deg	90
β, deg	108.466(6)
γ, deg	90
Volume (Å^3)	1867.7 (5)
Z	4
Density (calculated) (g/cm^3)	1.317
Absorption coefficient (mm^{-1})	0.091
F(000)	792
Theta range for data collection, deg	2.306 to 26.371
Index ranges	-14 <=h<= 14, -14<=k<= 14, -18<=l<=18
Reflections collected	54216
Independent reflections	3830 [R(int) = 0.065]
R_1	0.0370
wR_2	0.0880
R_1 (all data)	0.0485
wR_2 (all data)	0.0940
Largest diff. peak and hole (eÅ^3)	0.26 and −0.26
R.M.S. deviation from mean (eÅ^3)	0.050

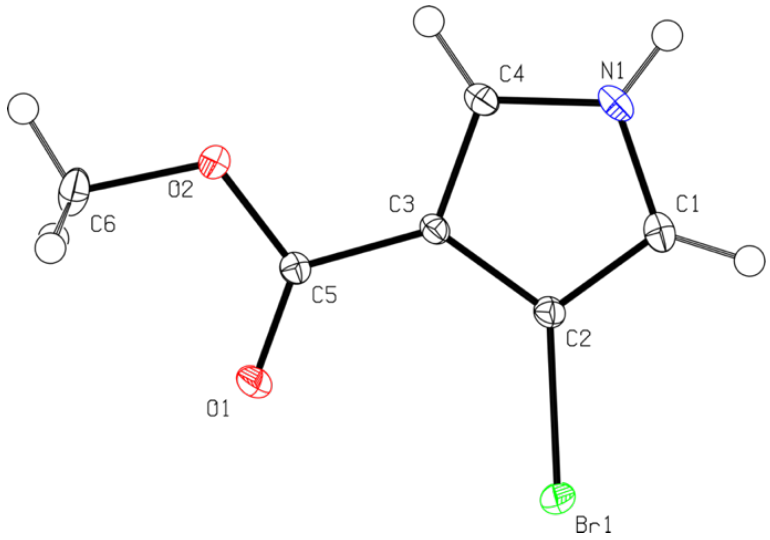

Figure S7. Single-crystal X-ray structure of pyrrole **22**.

Table S4. Summary of Crystal Data for 22.

CCDC registry	2119912
Chemical formula	$C_6H_6BrNO_2$
Formula weight (g/mol)	204.03
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal size (mm)	0.091 × 0.115 × 0.263
Crystal habit	Colorless rod
Crystal system	Monoclinic
Space group	*C*2/c
Unit cell dimensions, *a* (Å)	11.0877(9)
Unit cell dimensions, *b* (Å)	11.2881(9)
Unit cell dimensions, *c* (Å)	11.6866(10)
α, deg	90
β, deg	107.7683(18)
γ, deg	90
Volume ($Å^3$)	1392.9(2)
Z	8
Density (calculated) (g/cm^3)	1.946
Absorption coefficient (mm^{-1})	5.834
F(000)	800
Theta range for data collection, deg	2.64 to 35.06
Index ranges	-17<=h<=17, -18<=k<=18, -17<=l<=18
Reflections collected	16747
Independent reflections	3079 [R(int) = 0.0264]
R_1	0.0196
wR_2	0.0464
R_1 (all data)	0.0262
wR_2 (all data)	0.0485
Largest diff. peak and hole ($eÅ^{-3}$)	0.507 and -0.315
R.M.S. deviation from mean ($eÅ^{-3}$)	0.077

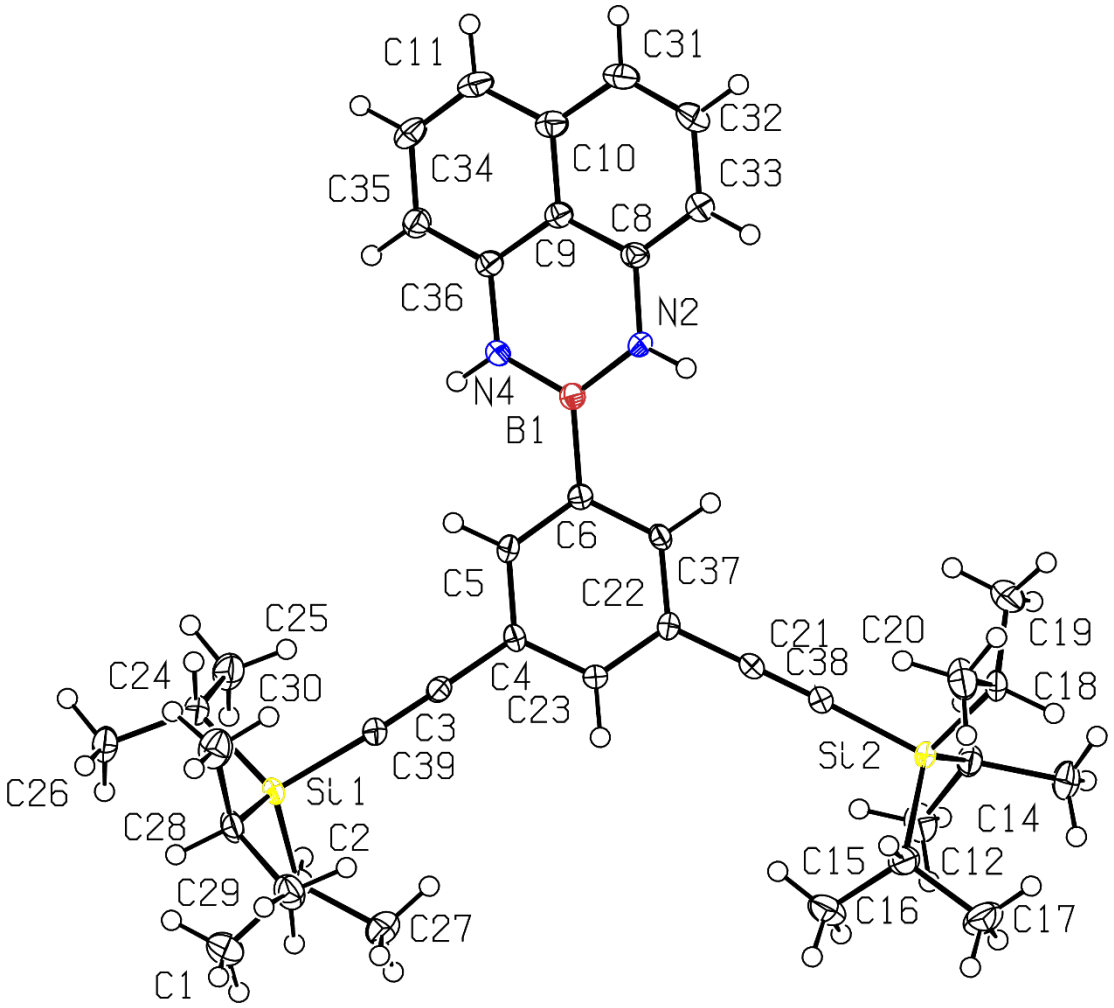

Figure S8. Single-crystal X-ray structure of **33**.

Table S5. Summary of Crystal Data for 33.

CCDC registry	2125378
Chemical formula	$C_{38}H_{53}BN_2Si_2$
Formula weight (g/mol)	604.81
Temperature (K)	100.00
Wavelength (Å)	0.71073
Crystal size (mm)	0.42 × 0.12 × 0.06
Crystal habit	Clear light colorless needle
Crystal system	Triclinic
Space group	*P*1
Unit cell dimension, *a* (Å)	7.7500(10)
Unit cell dimension, *b* (Å)	15.783(2)
Unit cell dimension, *c* (Å)	16.094(2)
α, deg	106.502(5)
β, deg	96.507(5)
γ, deg	99.230(5)
Volume (Å^3)	1836.6(4)
Z	2
Density (calculated) (g/cm^3)	1.094
Absorption coefficient (mm^{-1})	0.124
F(000)	656
Theta range for data collection, deg	4.388 to 52.744
Index ranges	-9 <=h<=9, -19<=k<=19, -20<=l<=20
Reflections collected	40609
Independent reflections	7529 [R(int) = 0.0503]
R_1	0.0382
wR_2	0.0909
R_1 (all data)	0.0507
wR_2 (all data)	0.0973
Largest diff. peak and hole (eÅ^3)	0.30 and −0.25
R.M.S. deviation from mean (eÅ^3)	0.049

Table S6. Summary of Crystal Data for BC-10.

CCDC registry	2120866
Chemical formula	$C_{24}H_{24}Br_2N_4$
Formula weight (g/mol)	528.29
Temperature (K)	173
Wavelength (Å)	0.71070
Crystal size (mm)	0.20 × 0.20 × 0.06
Crystal habit	Green prism
Crystal system	Trigonal
Space group	*R*–3
Unit cell dimension, *a* (Å)	20.0268(6)
Unit cell dimension, *b* (Å)	20.0268(6)
Unit cell dimension, *c* (Å)	14.4186(5)
α, deg	90.00
β, deg	90.00
γ, deg	120.00
Volume ($Å^3$)	5008.1(2)
Z	18
Density (calculated) (g/cm^3)	1.576
Absorption coefficient (mm^{-1})	3.661
F(000)	2394
Theta range for data collection, deg	1.84 to 28.03
Index ranges	-26 <=h<=26, -26<=k<=26, -18<=l<=19
Reflections collected	48159
Independent reflections	2699 [R(int) = 0.066]
R_1	0.0339
wR_2	0.0753
R_1 (all data)	0.0515
wR_2 (all data)	0.0827
Largest diff. peak and hole ($eÅ^3$)	1.12 and −0.50
R.M.S. deviation from mean ($eÅ^3$)	0.092

Table S7. Summary of Crystal Data for BC-12.

CCDC registry	2120288
Chemical formula	$C_{40}H_{34}N_4$
Formula weight (g/mol)	570.71
Temperature (K)	173
Wavelength (Å)	0.71070
Crystal size (mm)	0.36 × 0.28 × 0.06
Crystal habit	Green plate
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimension, *a* (Å)	9.8399 (2)
Unit cell dimension, *b* (Å)	14.8436 (3)
Unit cell dimension, *c* (Å)	10.9447 (2)
α, deg	90.00
β, deg	104.3806(11)
γ, deg	90.00
Volume (Å^3)	1548.49(5)
Z	2
Density (calculated) (g/cm^3)	1.224
Absorption coefficient (mm^{-1})	0.072
F(000)	604
Theta range for data collection, deg	2.36 to 25.05
Index ranges	-11 <=h<=11, -17<=k<=17, -12<=l<=13
Reflections collected	29745
Independent reflections	2741 [R(int) = 0.035]
R_1	0.0421
wR_2	0.1181
R_1 (all data)	0.0553
wR_2 (all data)	0.1270
Largest diff. peak and hole (eÅ^3)	0.25 and −0.19
R.M.S. deviation from mean (eÅ^3)	0.037