Heterocycles

Synthesis and Photophysical Property of Methanobenzo[10]annulene-2,3:8,9-bis(dicarboximide) Derivatives

Supporting Information

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1. [1]H, [13]C NMR, IR and mass spectra

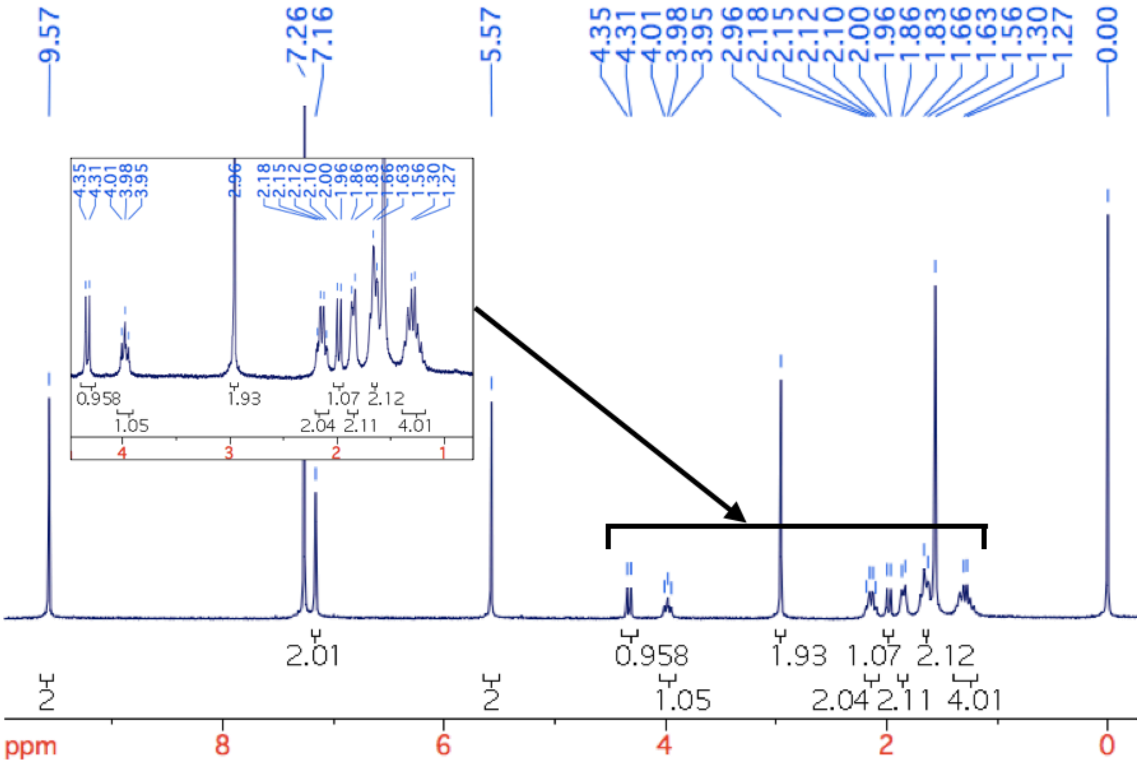

Figure S1. ^{1}H NMR spectra of **11** (400 MHz, $CDCl_3$, r.t.).

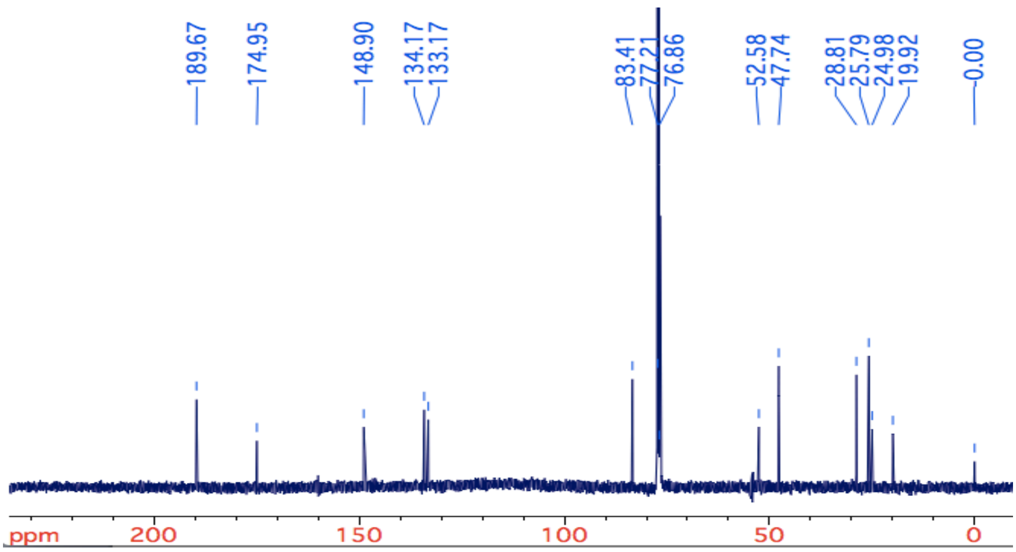

Figure S2. ^{13}C NMR spectra of **11** (100 MHz, $CDCl_3$, r.t.).

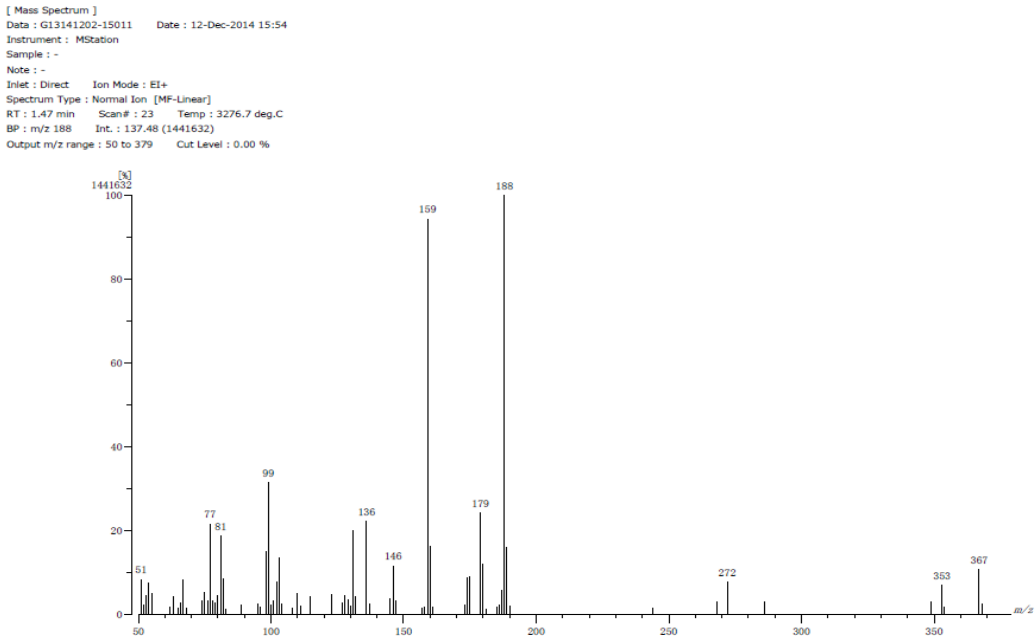

Figure S3. Mass spectra of **11**.

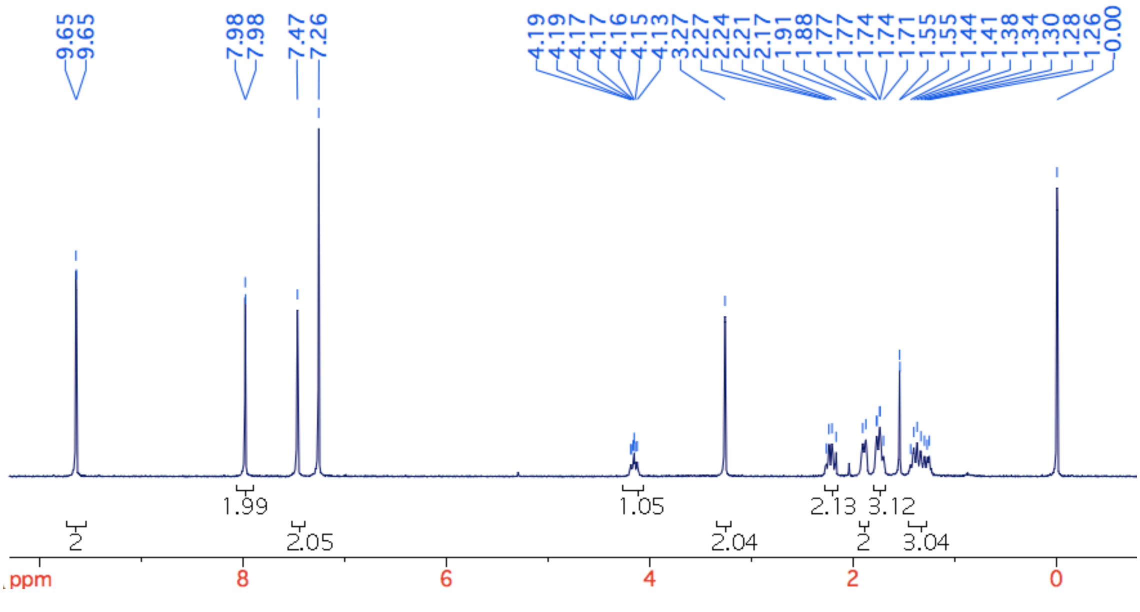

Figure S4. ^{1}H NMR spectra of **12** (400 MHz, $CDCl_3$, r.t.).

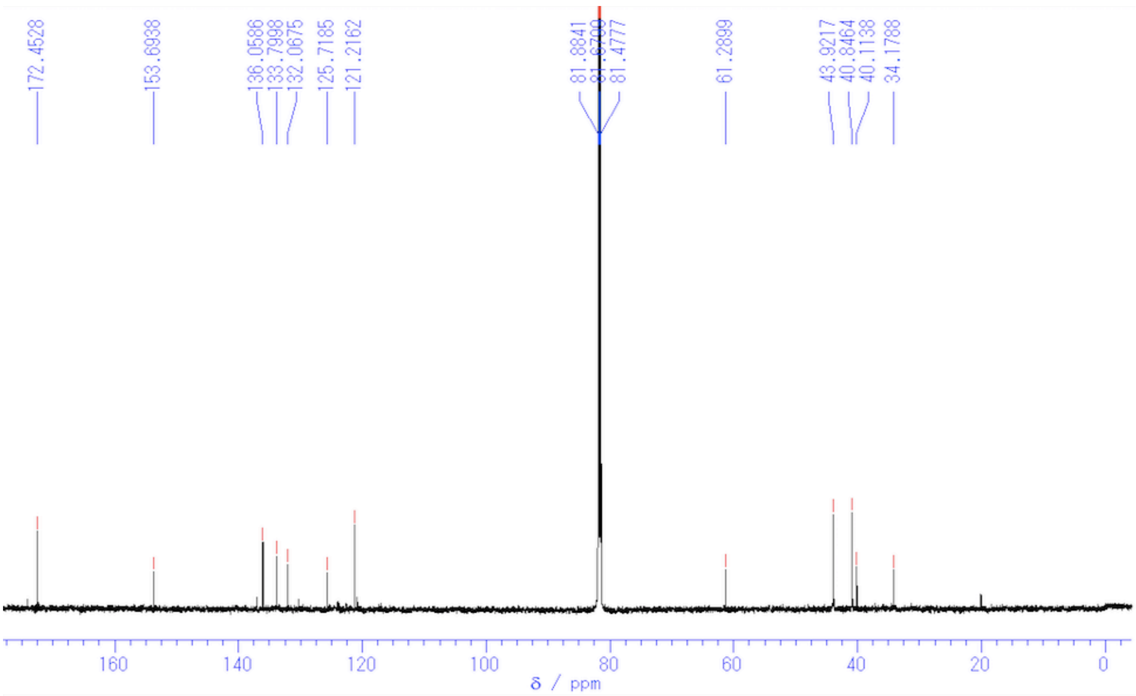

Figure S5. ^{13}C NMR spectra of **12** (126 MHz, $CDCl_3$, r.t.).

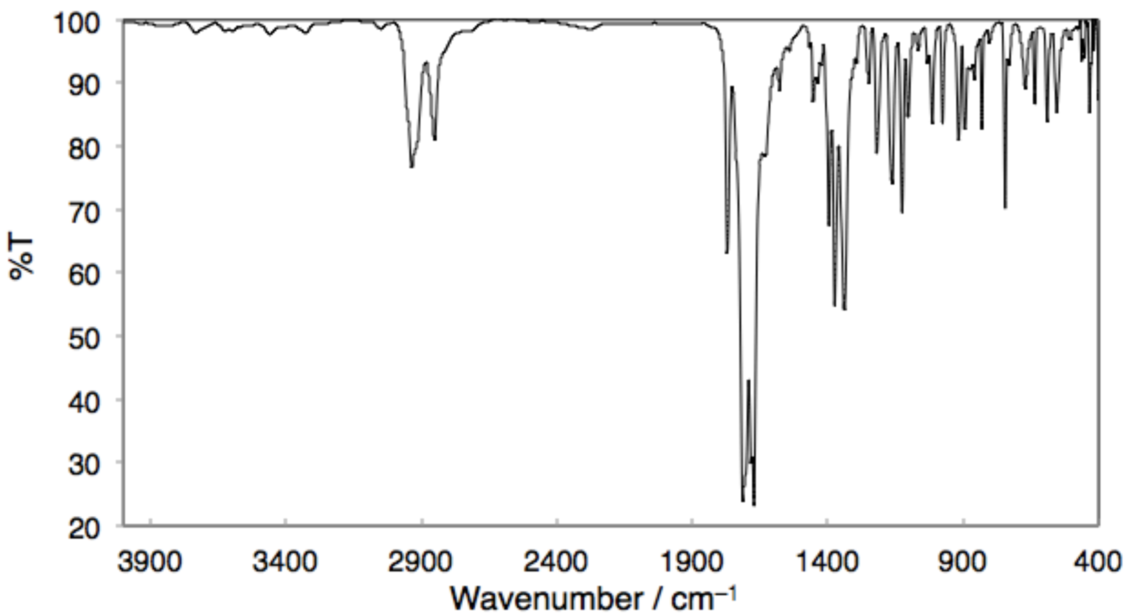

Figure S6. IR spectra of **12** (KBr).

IR (KBr): ν = 2936m, 2859m, 1770m, 1714vs, 1683s, 1672vs, 1631m, 1577w, 1454w, 1436w, 1424w, 1395m, 1374s, 1339s, 1298w, 1293w, 1248w, 1219m, 1162m, 1125m, 1103w, 1032w, 1014w, 976w, 917w, 895w, 879w, 859w, 831w, 745m, 730w, 671w, 635w, 590w, 554w, 463w, 452w, 433w, 426w cm^{-1}.

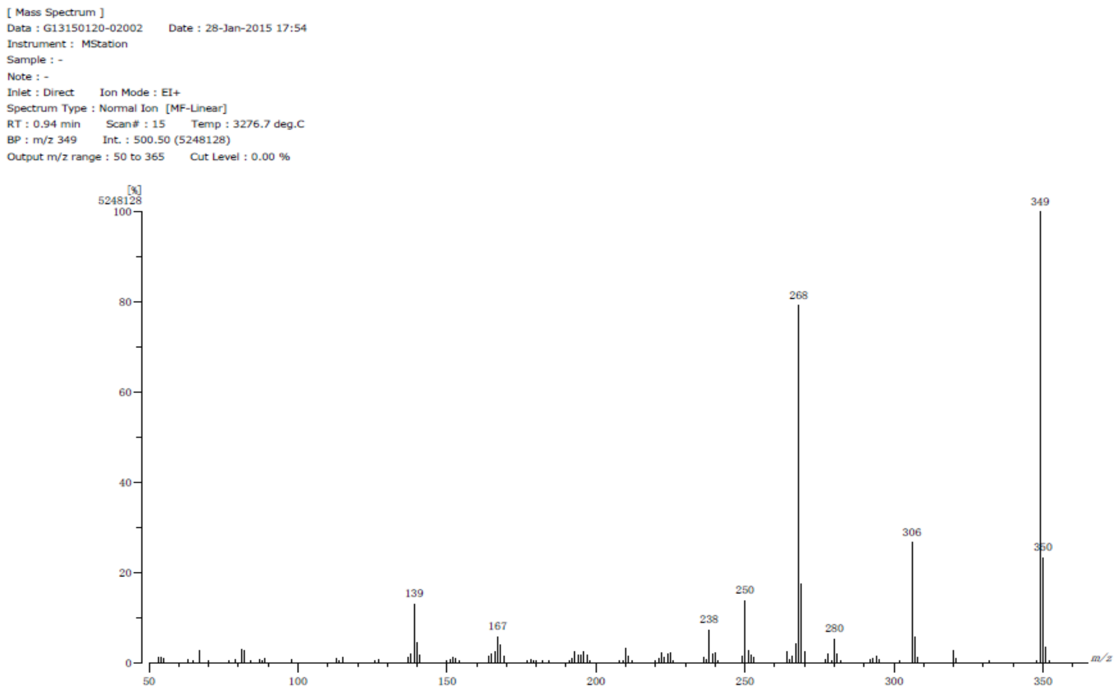

Figure S7. Mass spectra of **12**.

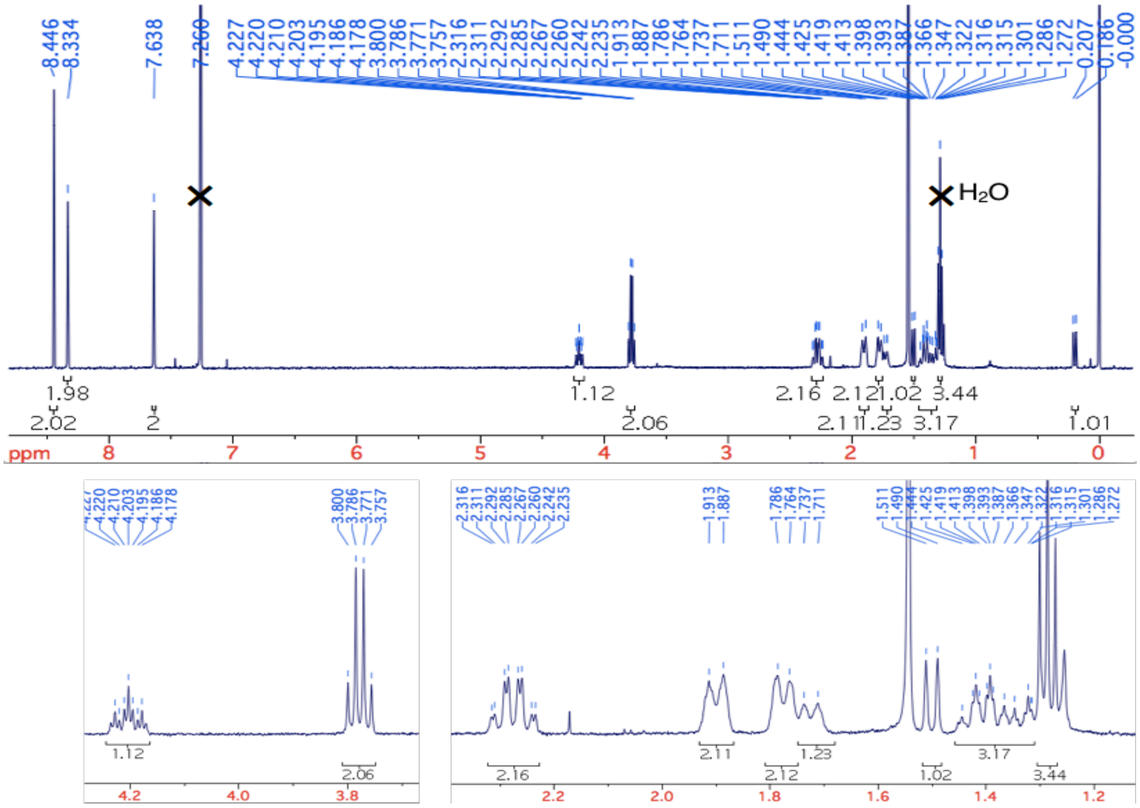

Figure S8. ^{1}H NMR spectra of **8a** (500 MHz, $CDCl_3$, r.t.).

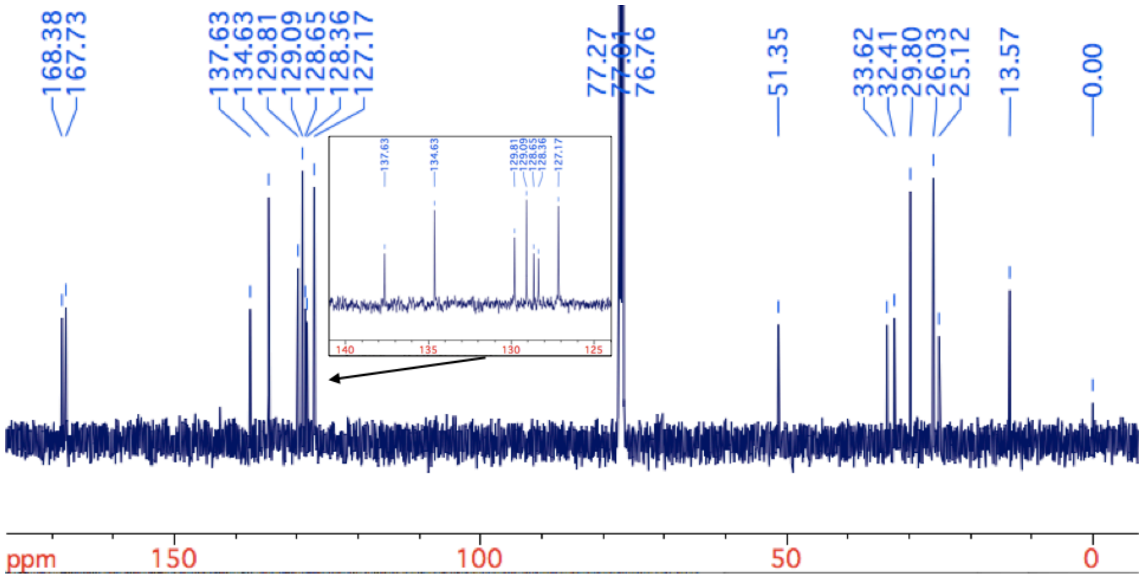

Figure S9. ^{13}C NMR spectra of **8b** (126 MHz, $CDCl_3$, r.t.).

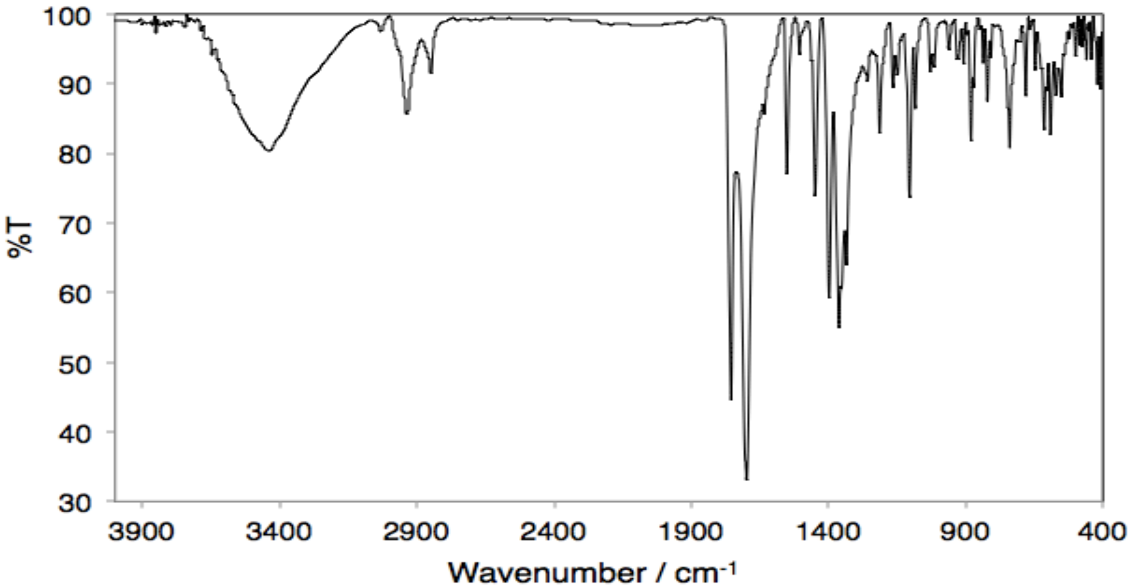

Figure S10. IR spectra of **8b** (KBr).

IR (KBr): ν = 3647w, 3442m, 2934m, 2847w, 1755vs, 1698vs, 1634m, 1551m, 1506w, 1448m, 1398s, 1362s, 1335s, 1257w, 1214m, 1166w, 1148w, 1105m, 1084m, 1029w, 1015w, 928w, 907w, 881m, 872w, 836w, 821w, 808w, 740m, 682w, 647w, 625w, 614m, 605w, 591m, 570w, 552w, 499w, 460w, 442w, 420w, 409w, 401w cm^{-1}.

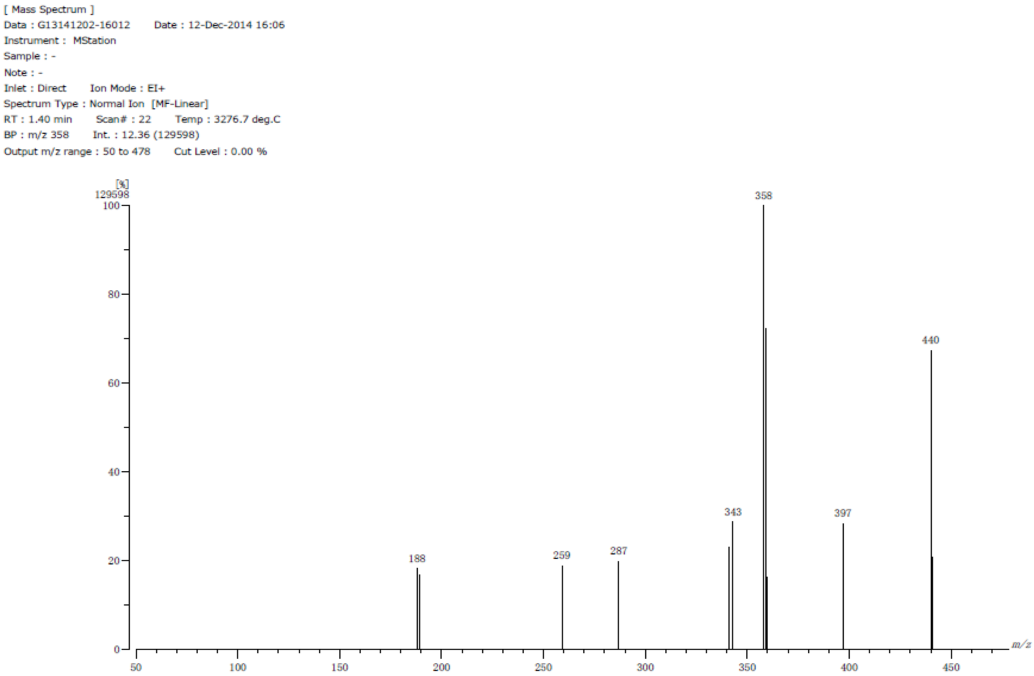

Figure S11. Mass spectra of **8b**.

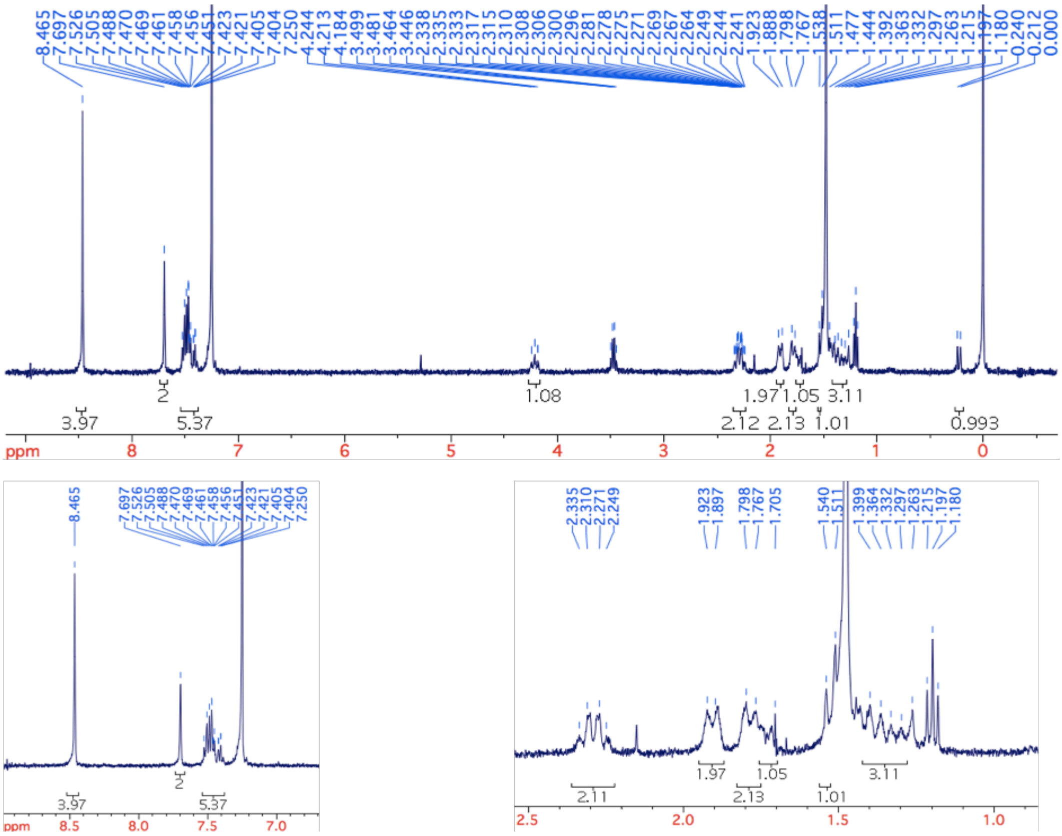

Figure S12 ^{1}H NMR spectra of **8c** (400 MHz, $CDCl_3$, r.t.).

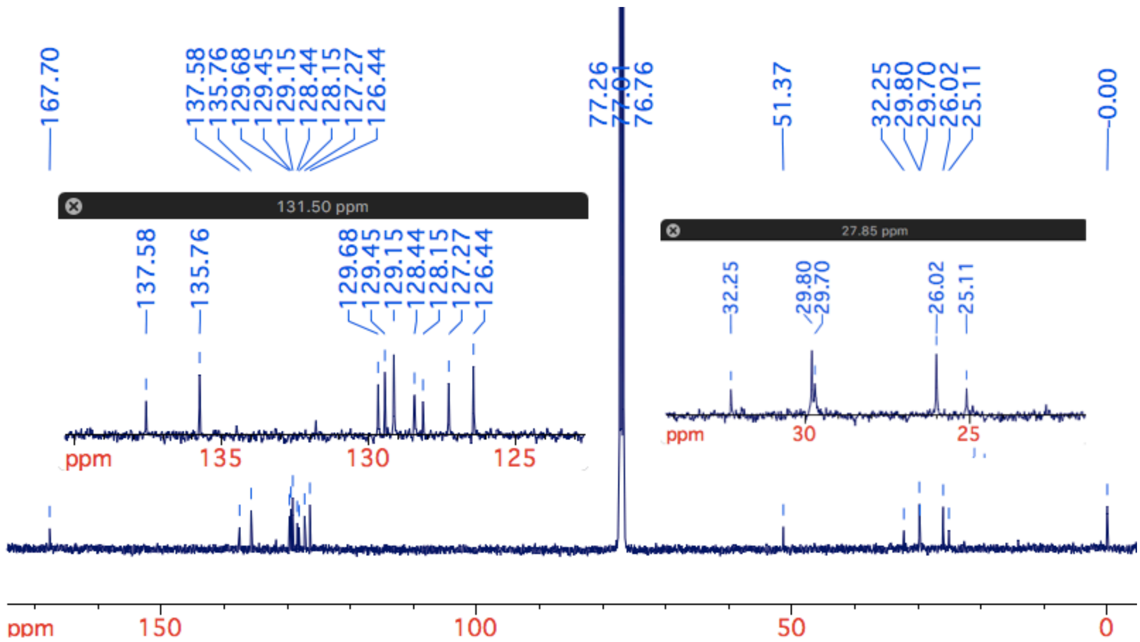

Figure S13. ^{13}C NMR spectra of **8c** (100 MHz, $CDCl_3$, r.t.).

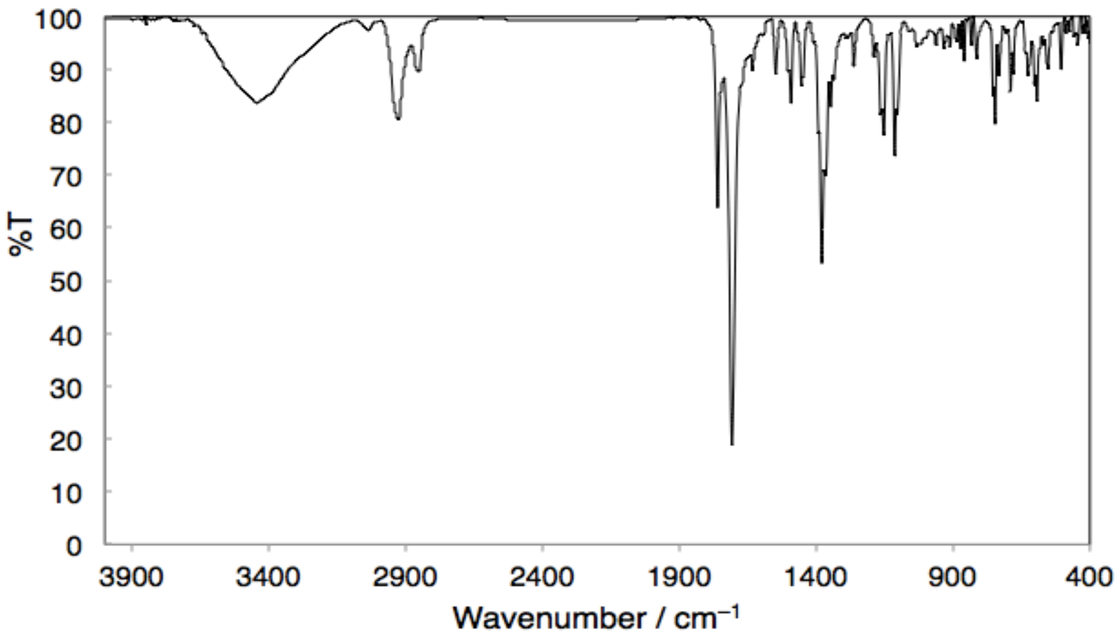

Figure S14. IR spectra of **8c** (KBr).

IR (KBr): ν = 3445w, 2926m, 2851w, 1761s, 1709vs, 1673w, 1633w, 1549w, 1503w, 1493w, 1455w, 1448w, 1391m, 1380s, 1366m, 1347w, 1336w, 1263w, 1188w, 1165m, 1153m, 1114m, 1104m, 1033w, 1017w, 961w, 933w, 910w, 873w, 859w, 834w, 814w, 754w, 746m, 733w, 689w, 680w, 634w, 626w, 602w, 593w, 569w, 553w, 505, 444w cm^{-1}.

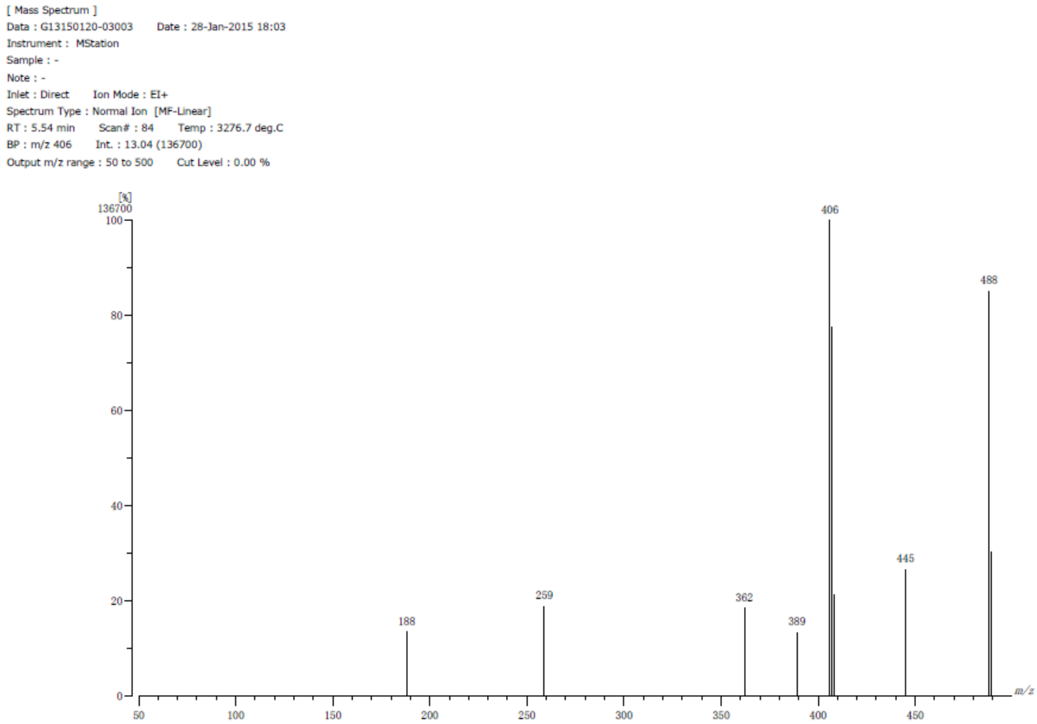

Figure S15. Mass spectra of **8c**.

2. UV-Vis absorption and normalized fluorescence spectra of 7a, 7b.

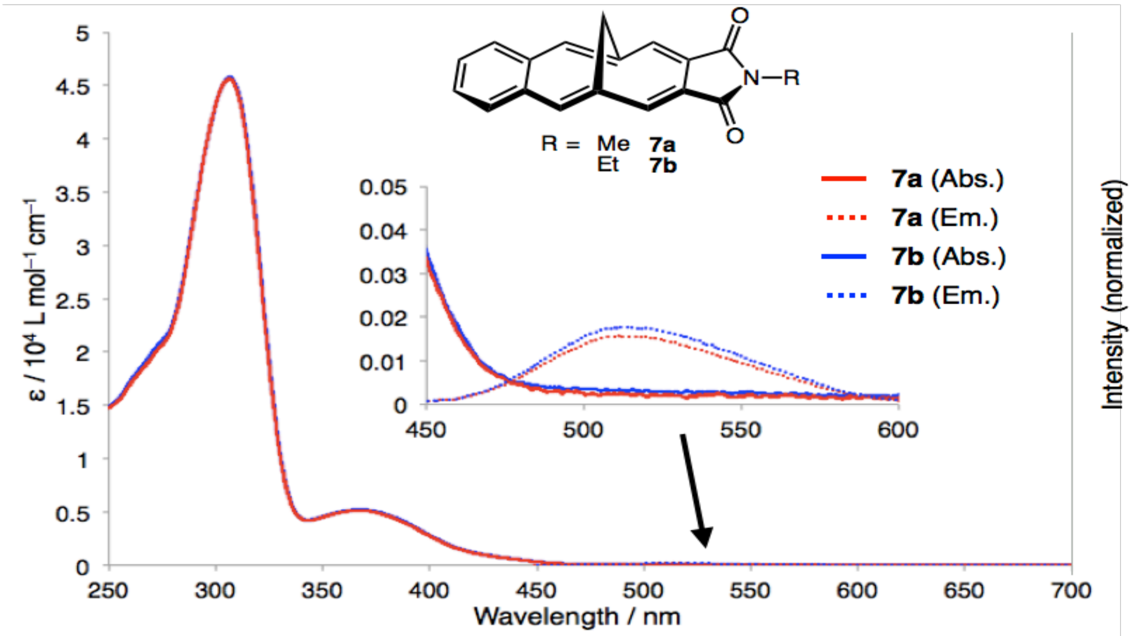

Figure S16. UV-Vis absorption and normalized fluorescence spectra of **7** (**7a**: 3.9×10^{-5} M; **7b**: 3.6×10^{-5} M).

3. Detail for theoretical calculations.

Theoretical calculations were performed using Gaussian 09 rev. D.01 program package [S1] and B3LYP/6-31G(d,p) basis sets were used for the optimization. The S_0 state minima have been confirmed by determination of the vibrational frequencies. Time-dependent density functional theory (TD-DFT) calculations were performed by using B3LYP/6-311+G(d,p) basis sets.

Table S1. Electronic transitions for **7b**, **8a**, **8b**, and **1Ph** in the lowest excited states.

Compounds	Experimental λ_{abs} /nm (log ε)	Computed λ_{abs} /nm (strength)	Composition of band (amplitude)	Electronic transitions
7b	436 (2.81)	400.11 (0.0314)	HOMO–1→LUMO+1 (0.14337)	π(An)[1]→π*(An)
			HOMO→LUMO (0.68661)	π(An)→π*(An)
8b	420 (3.53)	413.11 (0.1256)	HOMO–1→LUMO (0.31956)	π(An)→π*(An)
			HOMO→LUMO+1 (0.62224)	π(An)→π*(An)
8c	437 (3.48)	416.61 (0.0645)	HOMO–1→LUMO (0.26385)	π(Ph)[2]→π*(An)
			HOMO–3→LUMO (0.24948)	π(An)→π*(An)
			HOMO→LUMO+1 (0.59672)	π(An)→π*(An)
1Ph	356[3]	352.80 (0.0052)	HOMO→LUMO (0.69519)	π(Ph)→π*(An)

[1] 1,6-Methano[10]annulene skeleton. [2] *N*-Phenyl group. [3] Taken from reference S2.

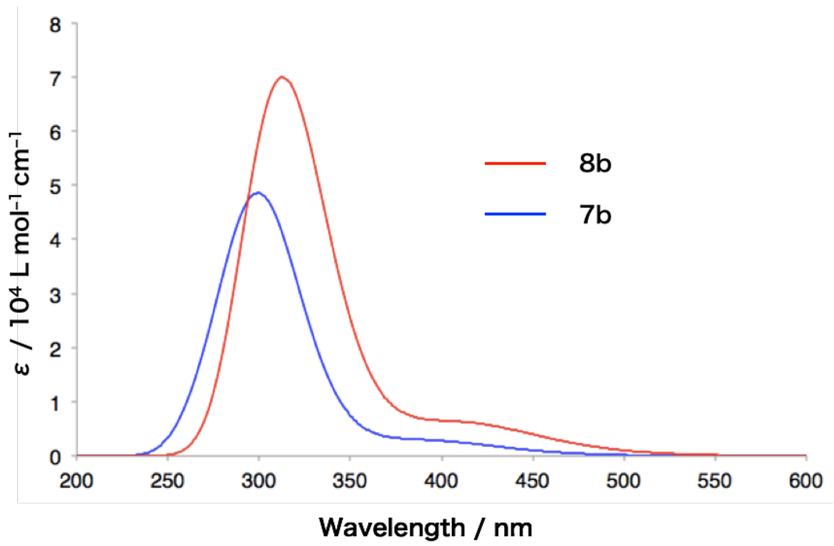

Figure S17. Simulated UV-Vis absorption spectra of **8b** and **7b** at the TD-B3LYP/6-311+G(d,p) level.

The molecular extinction coefficients ε increased by annulation to bis(dicarboximide).

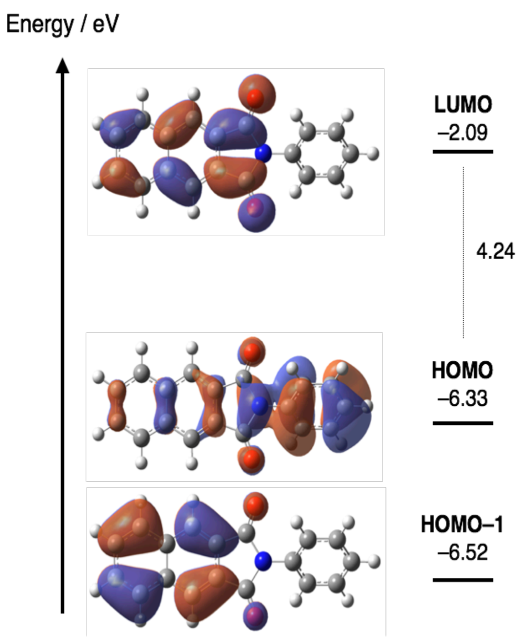

Figure S18. Frontier Kohn-Sham orbitals of **1Ph** at the B3LYP/6-31G(d,p) level.

References

[S1] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford, Connecticut, USA (2013).

[S2] V. Wintgens, P. Valat, J. Kossanyi, A. Demeter, L. Biczóc, and T. Bérces, *J. Photochem. Photobiol. A,* 1996, **93**, 109.