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Intense Absorption of Azulene Realized by Molecular Orbital Inversion

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General Experimental Considerations

^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE-III-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) or Bruker AVANCE-III-600 (600 MHz for ^{1}H, 150 MHz for ^{13}C). Spectra are reported (in δ) referenced to internal Me_4Si. Mass spectra were recorded on Thermo S cientific, Exactive Plus Orbitrap Mass Spectrometer for electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), or ITQ 700 GC/MS for electronic impact ionization (EI). IR spectra were recorded on JASCO FT/IR-610 Spectrometer. Melting points were determined with Yanaco melting point apparatus. Absorption spectra were recorded on Shimadzu UV-3600 spectrometer. Square wave voltammetry (SWV) and cyclic voltammetry (CV) measurements were performed on BAS Electrochemical Analyzer (Model 630E).

Single-Crystal X-ray Diffraction

Data of **2a**, **2b**, **2a-Br$_2$** and **2a-Br$_2$** were collected using a Rigaku HyPix-600 diffractometer with Cu Kα radiation (λ = 1.54187 Å). Single crystals were mounted on MiTeGen Dual-Thickness MicroMounts using a trace of mineral oil. Frames were collected, reflections were indexed and processed, and the files were scaled and corrected for absorption using Rigaku CrysAlis^{Pro} program. The space groups were assigned, and the structures were solved by direct methods using *XPREP* within the *SHELXTL* suite of programs and refined by full-matrix least-squares against F^2 with all reflections using *SHELXL-2018* with the graphical interface *SHELXLE*. CCDC 2254119 for **2a**, CCDC 2254124 for **2b**, CCDC 2254133 for **2a-Br$_2$** and CCDC 2254134 for **2b-Br$_2$** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Thin film fabrication and characterization

The thin films of **2a**, **2a-Br$_2$** and **2b** were prepared by the spin-coating of the solution of each compound (10 mg/mL in chlorobenzene) at 1000 rpm for 60 s. UV-Vis absorption spectra were recorded with Shimadzu UV-3600 Plus spectrometer. Atomic force microscope (AFM) images were obtained with a Molecular Imaging Picoscan Plus instrument operating in AC mode with Nanoworld NCSTR probes. Photoelectron yield spectroscopy (PYS) measurements were carried out using a BUNKOUKEIKI BIP-KV201 (accuracy: ± 0.02 eV, extraction voltage = 10 V) under vacuum ($<10^{-2}$ Pa).

Synthetic procedures and characterization data

Synthesis of 2,6-bis(diarylamino)azulene (2)

A mixture of 2,6-dibromoazulene (285 mg, 1.00 mmol), diarylamine (3.00 mmol), palladium(II) acetate (12 mg, 0.05 mmol), potassium *t*-butoxide (1.57 g, 14.0 mmol) and tri-*t*-butylphosphonium tetrafluoroborate (3.0 mg, 0.01 mmol) was dissolved in toluene (30 mL), and the whole was refluxed for 2 −3 h under argon atmosphere. Thereafter, the resultant mixture was diluted with toluene and H_2O and filtered through celite. The toluene layer was dried pover sodium sulfate, and the solution was concentrated using a rotary evaporator. The obtained crude product was purified by recrystallization from chloroform/hexane to yield as brown solids of **2a** (80%) and **2b** (82%).

2a: m.p. 237−239 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (d, *J* = 14.4 Hz, 2H), 7.33 (d, *J* = 6.4 Hz, 8H), 7.28 (dd, *J* = 12.4, 11.1 Hz, 4H), 7.15 (quint, *J* = 6.4 Hz, 2H), 7.09 (dd, *J* = 12.9, 11.1 Hz, 4H), 7.01 (tt, *J* = 11.1, 1.7 Hz, 2H), 6.94 (d, *J* = 14.4 Hz, 2H), 6.70 (s, 2H); ^{1}H NMR (600 MHz, acetone-d_6): δ 7.73 (d, *J* = 11.0 Hz, 2H), 7.41 (dd, *J* = 8.5, 7.4 Hz, 4H), 7.33 (dd, *J* = 8.5, 1.2 Hz, 4H), 7.31 (dd, 8.7, 7.4 Hz, 4H), 7.22 (tt, *J* = 7.4, 1.2 Hz, 2H), 7.09 (dd, *J* = 8.7, 1.2 Hz, 4H), 7.07 (tt, *J* = 7.4, 1.2 Hz, 2H), 6.92 (d, *J* = 11.0 Hz, 2H) 6.66 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.1, 151.1, 148.2, 147.0, 137.7, 129.4, 129.3, 129.3, 125.4, 124.6, 124.6, 123.2, 123.0, 107.4; IR (KBr): ν_{max} 3032, 1585, 1486, 1455, 1310, 836, 753 cm^{-1}; UV−Vis (THF) λ_{max} (ε): 479 (31500), 365 (8610), 320 (50600) nm; HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{34}H_{27}N_2$ $[M + H]^+$: 463.2174, Found 463.2169.

2b: m.p. 232−235 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 11.2 Hz, 2H), 7.25 (d, *J* = 8.9 Hz, 4H), 7.02 (d, *J* = 9.0 Hz, 4H), 6.87 (d, *J* = 9.0 Hz, 4H), 6.83 (d, *J* = 11.2 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 4H), 6.55 (s, 2H), 3.82 (s, 6H), 3.79 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.6, 155.8,154.3, 151.7, 141.7, 140.4, 137.0, 128.8, 126.8, 126.4, 121.0, 114.7, 114.6, 106.1, 55.5; IR (KBr): ν_{max} 3037, 2996, 2949, 2832, 1605, 1463, 1440, 1359 cm^{-1}; UV−Vis (THF) λ_{max} (ε): 488 (31700), 382 (8110), 323 (50800), 287 (21000) nm; HRMS (ESI-orbitrap) *m*/*z* : $C_{38}H_{35}N_2O_4$ $[M + H]^+$: 583.2597, Found 583.2591. Anal. Calcd for $C_{38}H_{34}N_2O_4$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.41; H, 5.70; N, 4.86.

Synthesis of 1,3-dibromo-2,6-bis(diarylamino)azulene (2-Br_2)

To a dichloromethane (5 mL) solution of **2** (0.45 mmol) was slowly dropped a dichloromethane (15 mL) solution of *N*-bromosuccinimide (165 mg, 0.93 mmol) at –78 °C under argon. After completion of the dropwise addition, the mixture was stirred for 2 hours. Thereafter, a saturated aqueous solution of sodium hydrogen carbonate was added, and the dichloromethane layer was washed with brine. After the dichloromethane solution was dried over sodium sulfate. The resultant solution was filtered through aluminium oxide. After concentration with a rotary evaporator, reddish-orange solids of **2a-Br_2** (82%) and **2b-Br_2** (84%) were obtained.

2a-Br_2: m.p. 236–239 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (d, *J* = 11.3 Hz, 2H), 7.35 (dd, *J* = 8.7, 7.2 Hz, 4H), 7.23 (dd, *J* = 8.7, 7.3 Hz, 4H), 7.21–7.18 (m, 6H), 7.06 (dd, *J* = 8.7, 1.1 Hz, 4H), 6.98 (tt, *J* = 7.3, 1.1 Hz, 2H), 6.95 (d, *J* = 11.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.7, 146.7, 146.2, 144.2, 133.3, 131.3, 129.9, 128.9, 126.5, 125.6, 122.2, 122.1, 119.0, 102.1; IR (KBr): ν_{max} 3034, 1575, 1488, 1451, 1318, 695 cm^{-1}; UV–Vis (THF) λ_{max} (ε): 299 (28500), 349 (41400), 492 (28300); HRMS (ESI-orbitrap) *m/z* : $C_{34}H_{25}Br_2N_2$ $[M + H]^+$: 619.0384, Found 619.0359; Anal. Calcd for $C_{34}H_{24}Br_2N_2$; C, 65.83; H, 3.90; N, 4.52. Found: C, 65.56; H, 3.78; N, 4.59.

2b-Br_2: m.p. 230–232 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 11.1 Hz, 2H), 7.12 (d, *J* = 7.4 Hz, 4H), 6.96 (d, *J* = 7.6 Hz, 4H), 6.89 (d, *J* = 7.4 Hz, 4H), 6.82 (d, *J* = 11.1 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 4H), 3.82 (s, 6H), 3.77 (s, 6H); ^{13}C NMR (150 MHz $CDCl_3$) δ 157.8, 157.6, 154.8, 140.5, 139.5, 135.2, 132.8, 130.5, 128.0, 123.4, 116.9, 115.2, 114.2,101.4, 55.5, 55.5; IR (KBr): ν_{max} 3037, 2996, 2931, 2833, 2361, 1583, 1505, 1398, 1320, 1287, 1241, 1034, 870, 828, 721, 552cm^{-1}; UV–Vis (THF) λ_{max} (ε): 313 (43200), 372 (47900), 516 (34600); HRMS (ESI-orbitrap) m/z calcd.for $C_{38}H_{32}N_2O_4Br_2$ $[M + H]^+$: 739.0807, Found 739.0801.

Synthesis of 1,3-dimethoxy-2,6-bis(diarylamino)azulene (3)

To a mixture of **2-Br$_2$** (0.24 mmol), copper(I) bromide (38 mg, 0.27 mmol) in *N*,*N*-dimethylformamide (7.5 mL) and methanol (5 mL), methanol (10 mL) solution of sodium methoxide (4.8 g, 88.8 mmol) was added, and the mixture was stirred for 1 week at 100 °C under argon. Thereafter, water was added to the resultant mixture, and the mixture was filtered through celite. After extraction with ethyl acetate, the organic layer was dried over sodium sulfate, and the solution was concentrated using a rotary evaporator. The obtained crude product was purified by preparative gel permeation chromatography with chloroform to obtain yellowish-brown solids of **3a** (74%) and reddish-brown solids of **3b** (58%). The tailing phenomena were appeared for the performing thin layer chromatography (TLC) on the compounds.

3a: m.p. 238–241 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 11.2 Hz, 2H), 7.31–7.24 (m, 8H), 7.17–7.14 (m, 8H), 7.09 (tt, *J* = 7.4, 1.2 Hz, 2H), 7.02 (tt, *J* = 7.3, 1.2 Hz, 2H), 6.57 (d, *J* = 11.2 Hz, 2H), 3.62 (s, 6H); ^{13}C NMR (150 MHz $CDCl_3$) δ 156.3, 147.7, 146.0, 140.5, 129.6, 129.4, 129.2, 129.0, 125.7, 124.0, 122.7, 121.8, 117.6, 117.1. 62.2; IR (KBr): ν_{max} 3033, 2956, 2924, 2853, 1937, 1729, 1587, 1572, 1488, 1392, 1290, 1274, 1060, 1033, 753, 696; UV–Vis (THF) λ_{max} (ε): 297 (30600), 342 (42400), 353 (42500), 494 (31000); HRMS (ESI-orbitrap) *m*/*z* calcd.for $C_{36}H_{30}N_2O_2$ M^+: 522.2307, Found 522.2307.

3b: m.p. 235–236 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 11.1 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 4H), 7.05 (d, *J* = 8.9 Hz, 4H), 6.84 (d, *J* = 8.9 Hz, 4H), 6.80 (d, *J* = 8.9 Hz, 4H), 6.46 (d, 11.1, 2H) 3.81(s, 6H), 3.79 (s,6H), 3.60 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 156.6, 155.2, 141.0, 140.2, 140.2, 129.4, 128.7, 127.6, 123.0, 116.9, 114.9, 114.9, 114.4, 62.4, 55.6, 55.6; IR (KBr): ν_{max} 2939, 2929, 2833, 1582, 1502, 1397, 1287, 1242, 1034, 827, 555 cm^{-1}; UV–Vis (THF) λ_{max} (ε): 283 (42298), 344 (55978), 347 (55978), 506 (37308); HRMS (ESI-orbitrap) *m*/*z* calcd. for $C_{40}H_{38}N_2O_6$ M^+: 642.2729, Found 642.2725.

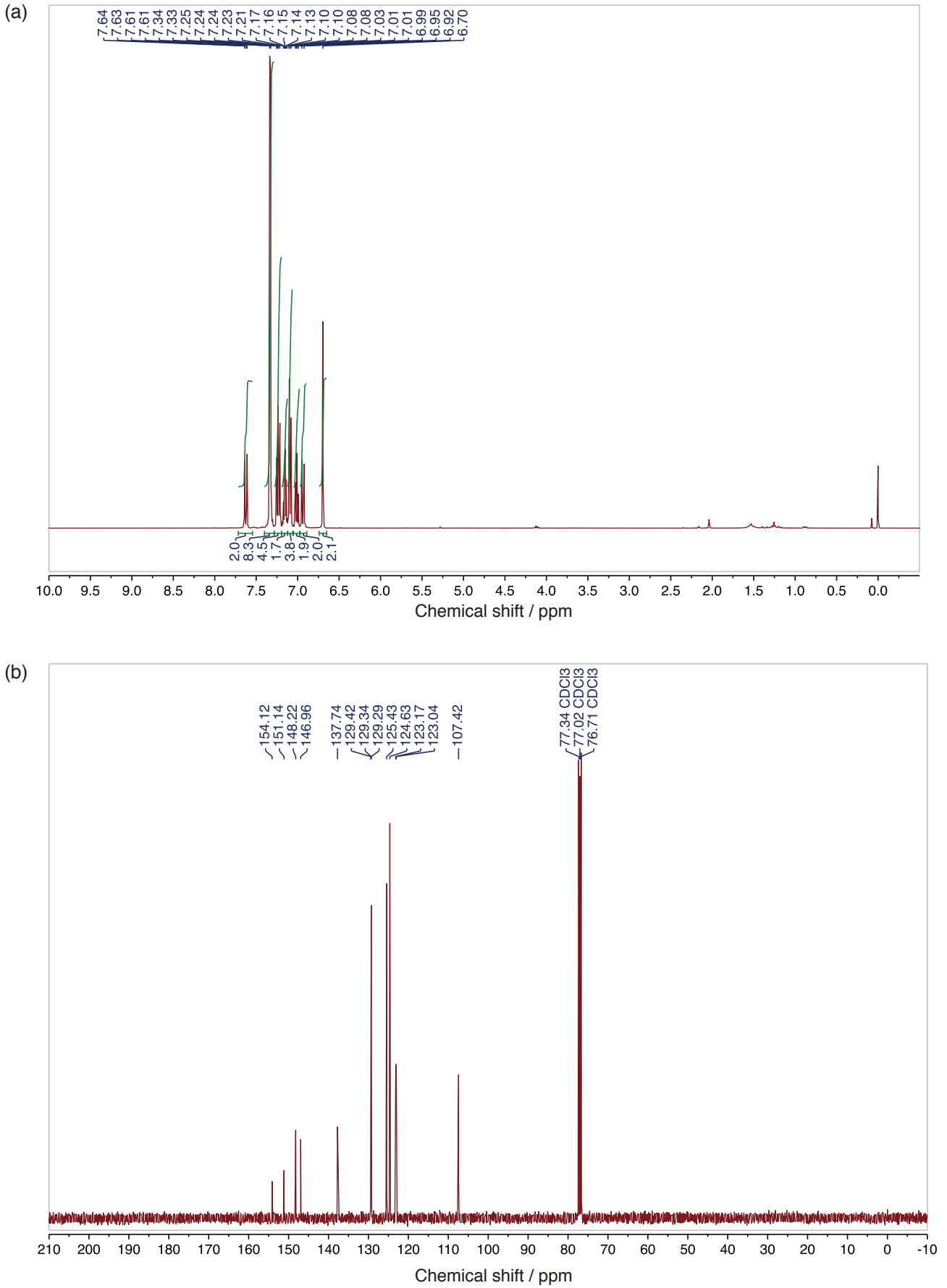


Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra of **2a**.

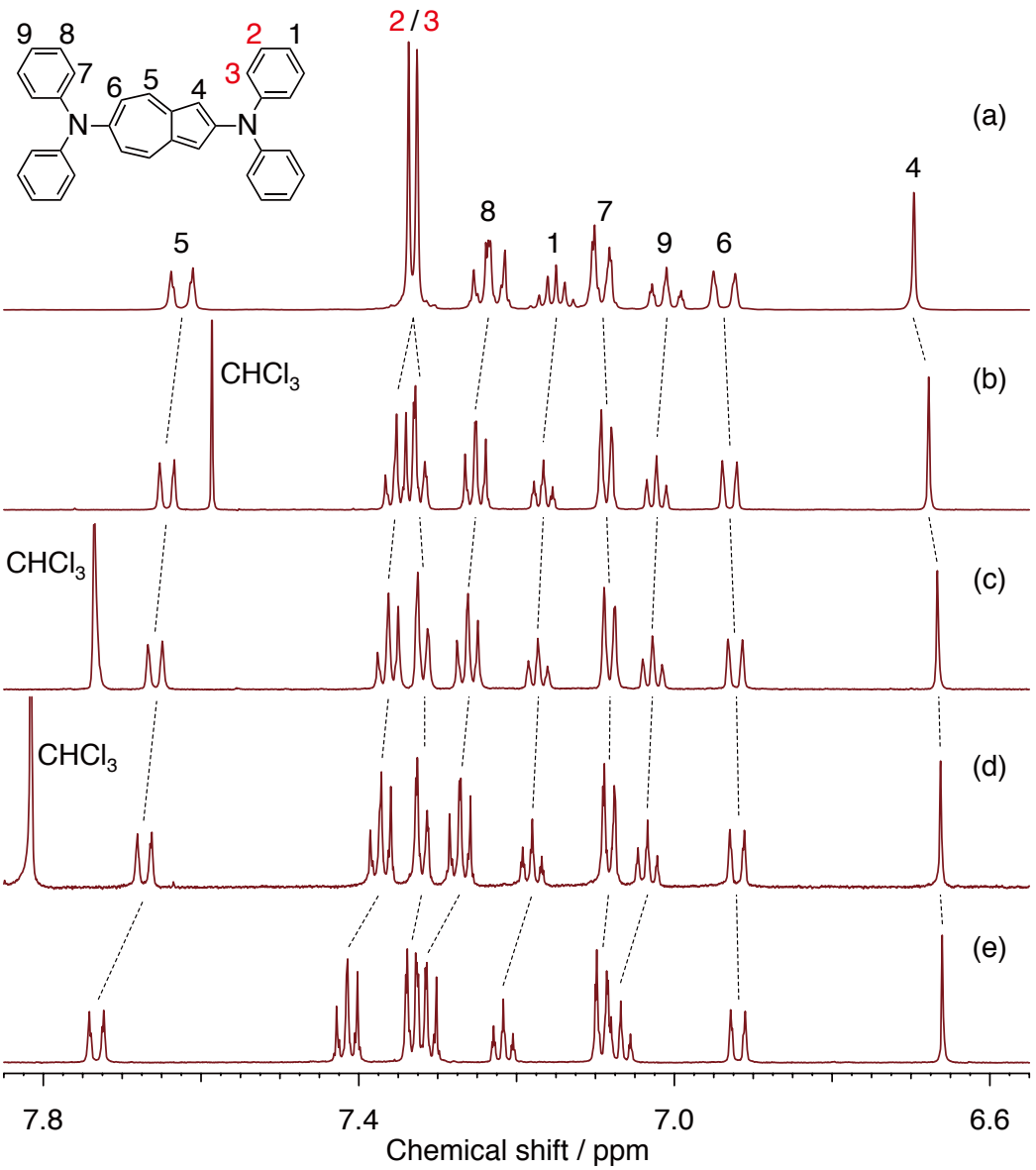


Figure S2. ^{1}H NMR spectra of **2a** in (a) $CDCl_3$, (b) $CDCl_3$ / acetone-d_6 = 2:1, (c) $CDCl_3$ / acetone-d_6 = 1:1, (d) $CDCl_3$ / acetone-d_6 = 1:2 and (e) acetone-d_6.

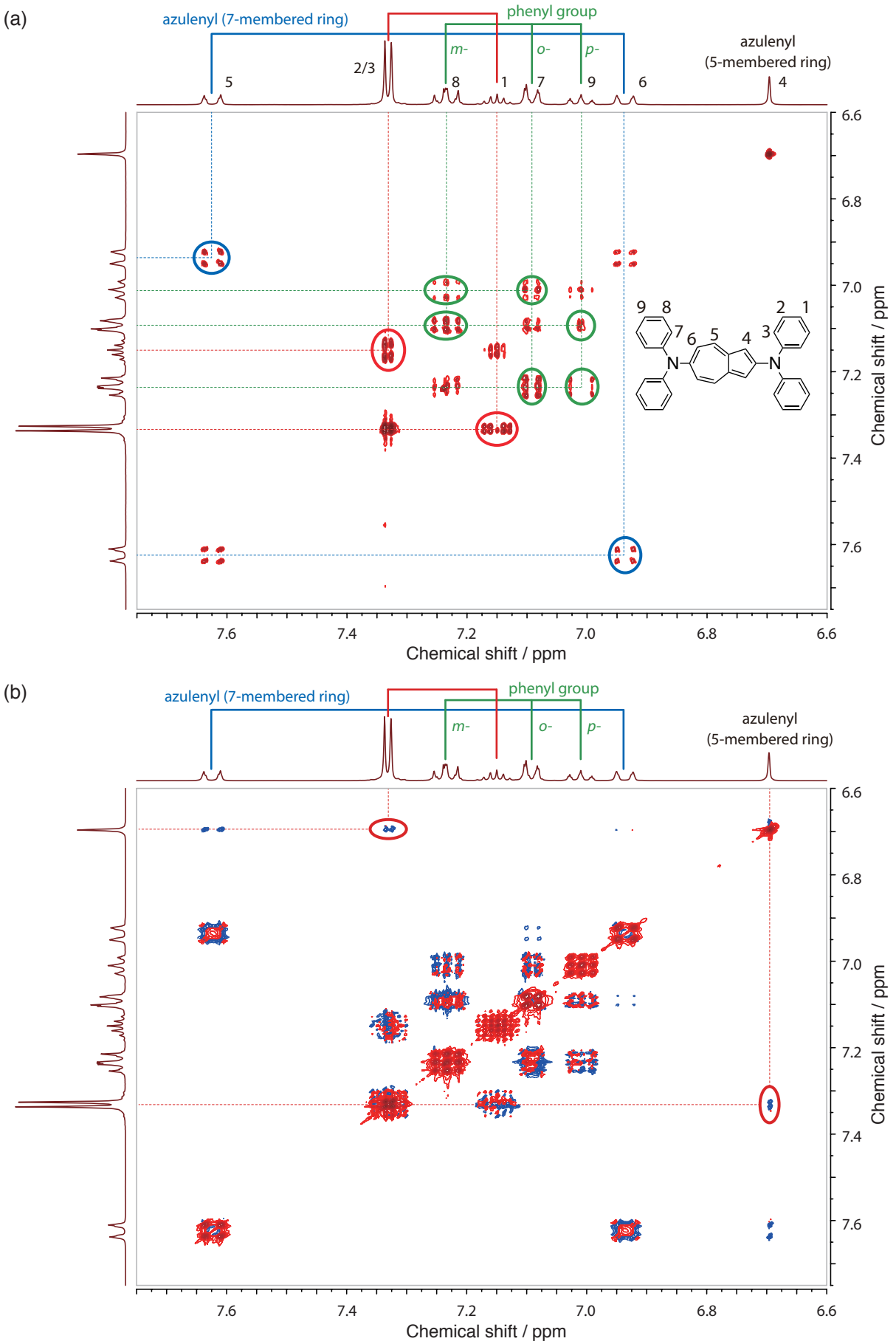


Figure S3. (a) ^{1}H-^{1}H COSY and (b) NOESY NMR spectra of **2a**.

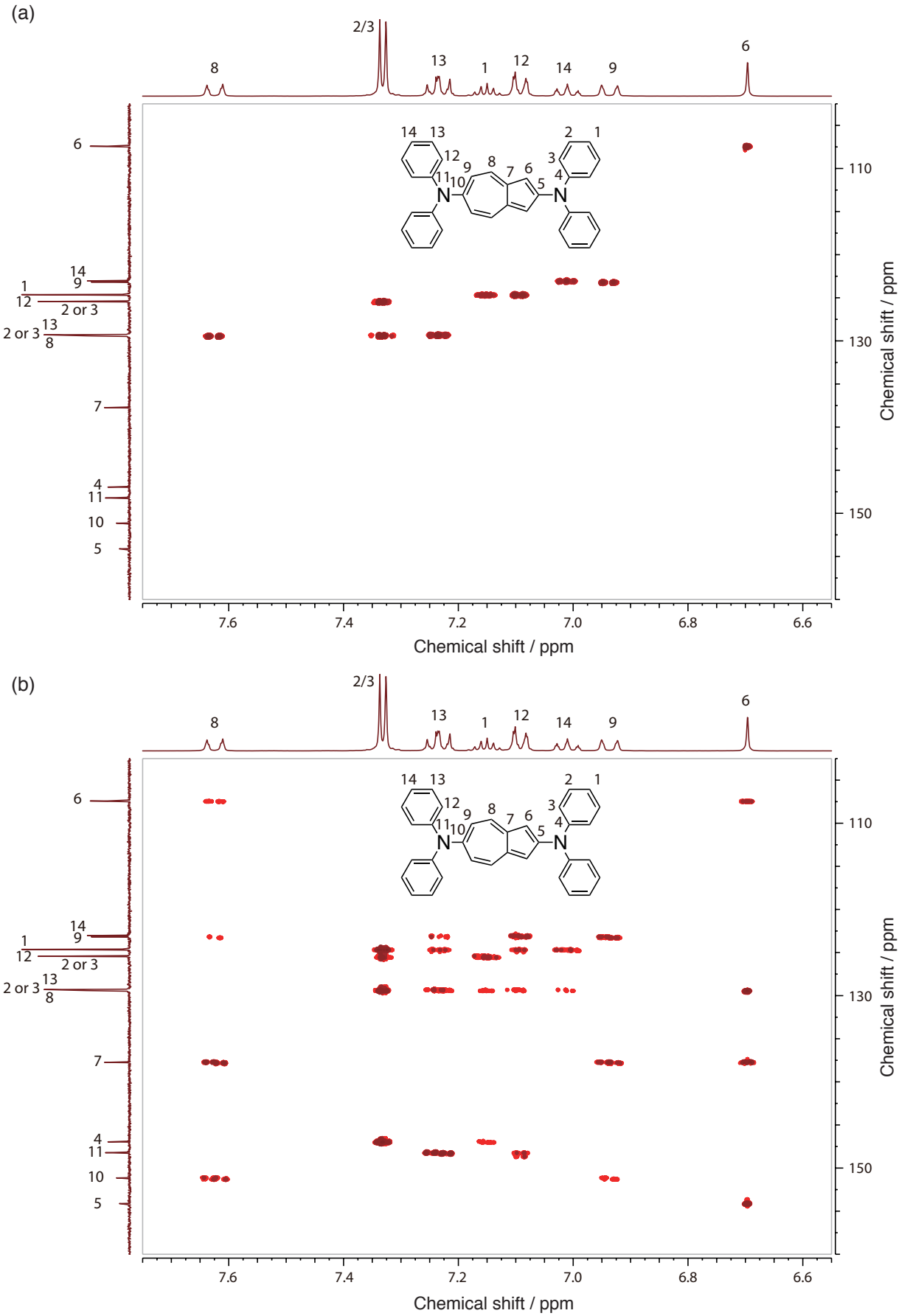


Figure S4. (a) HSQC and (b) HMBC NMR spectra of **2a**.

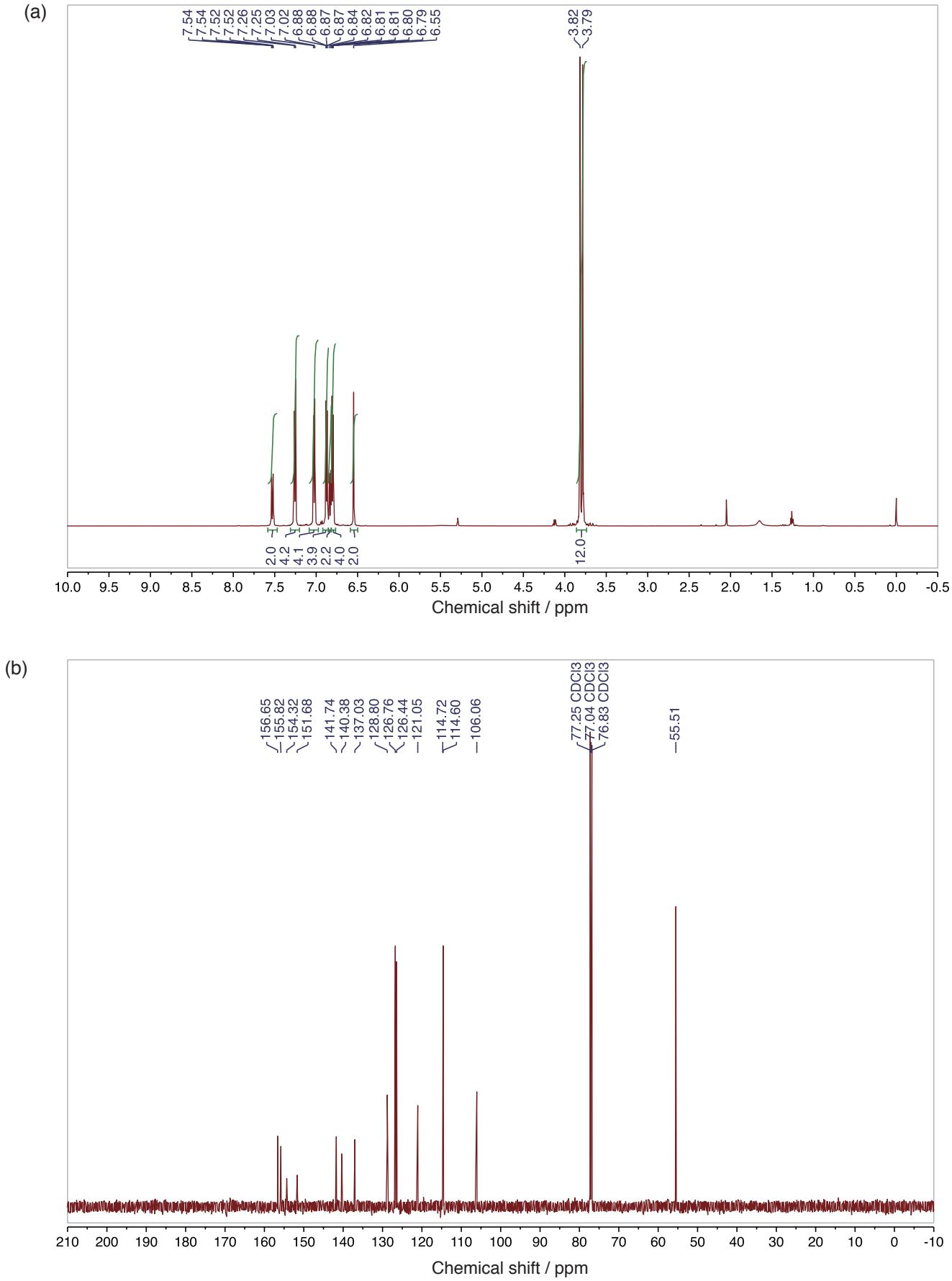


Figure S5. (a) ^{1}H and (b) ^{13}C NMR spectra of **2b**.

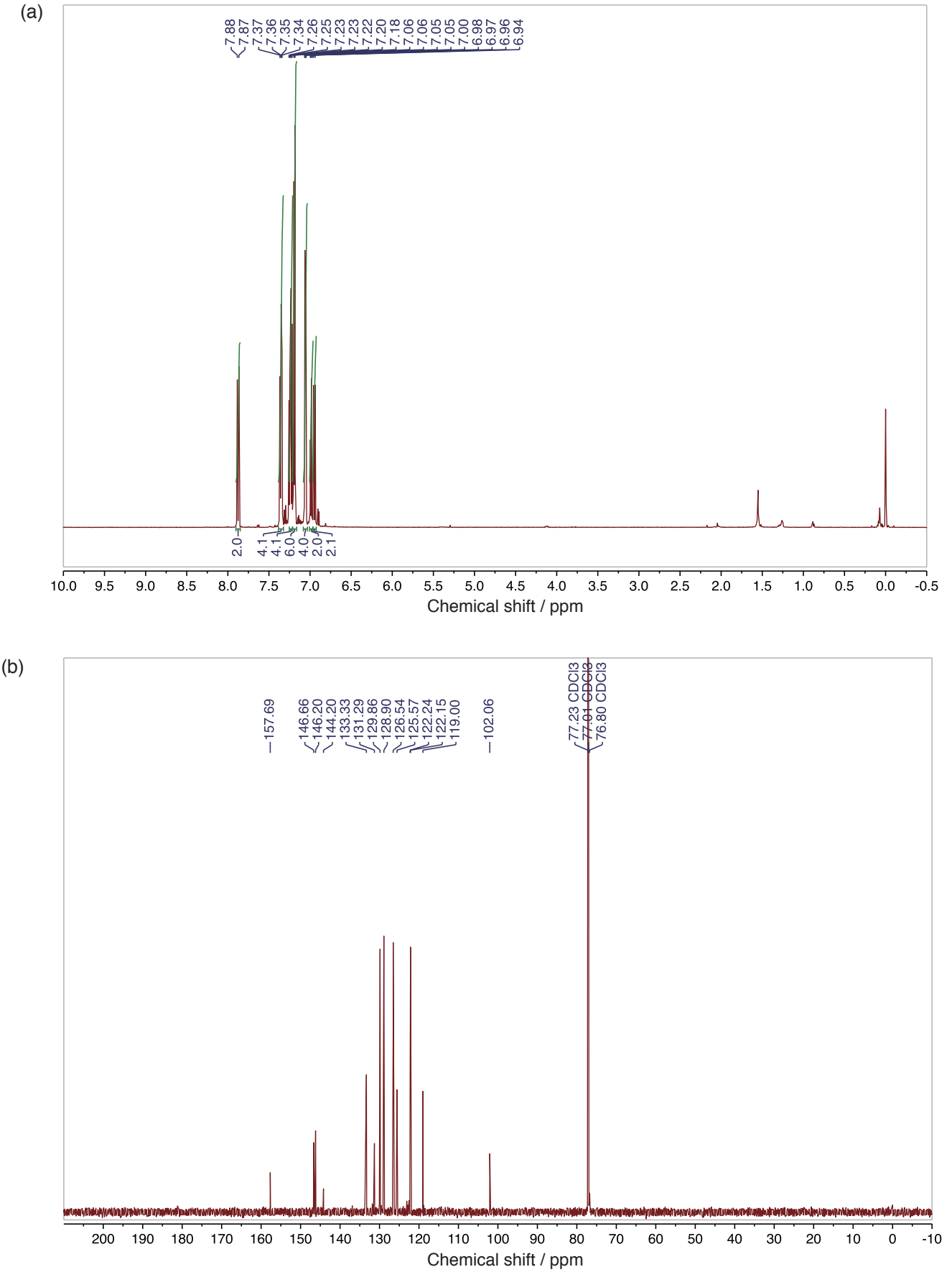


Figure S6. (a) ^{1}H and (b) ^{13}C NMR spectra of **2a-Br$_2$**.

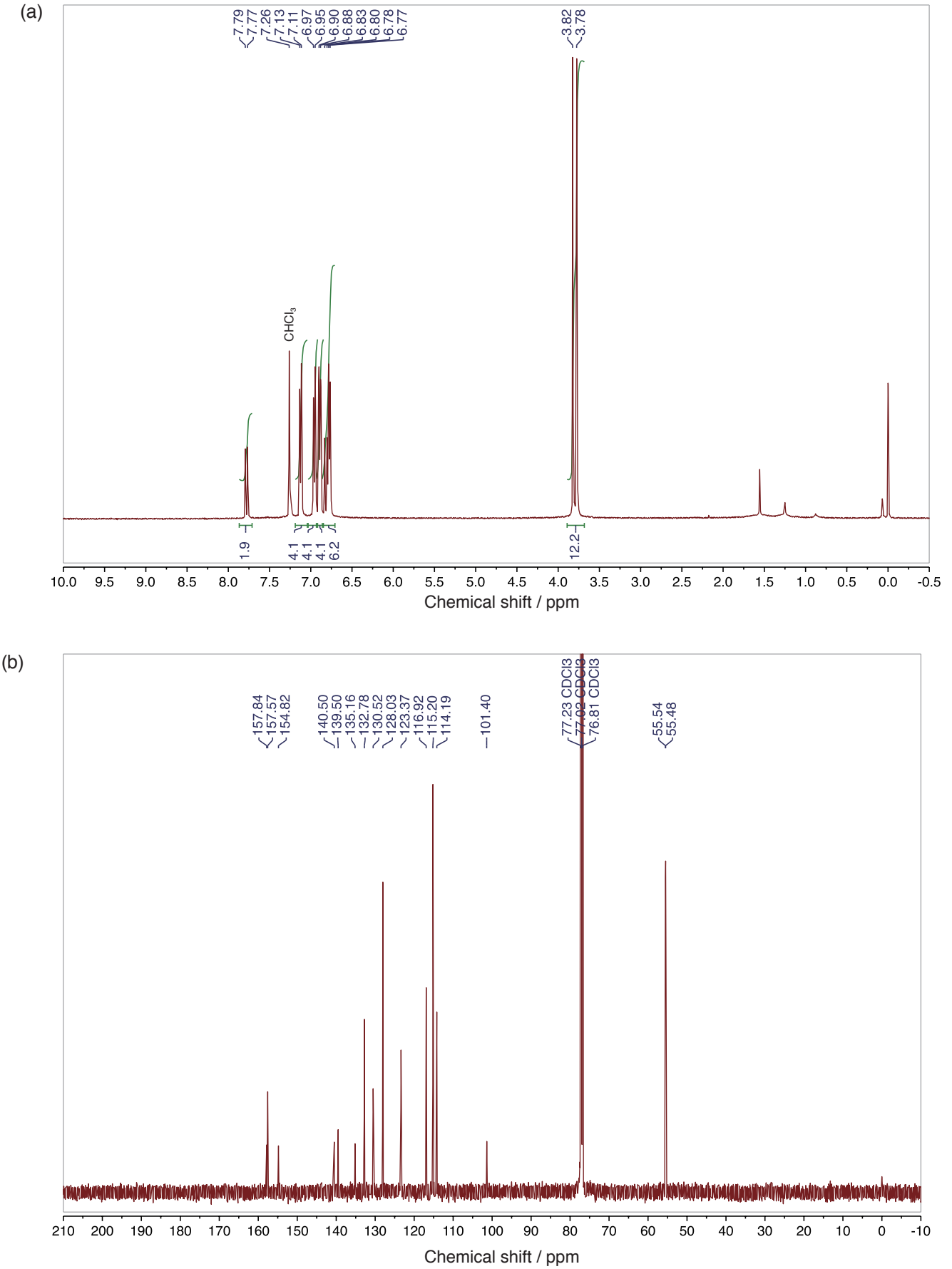


Figure S7. (a) ^{1}H and (b) ^{13}C NMR spectra of **2b-Br$_2$**.

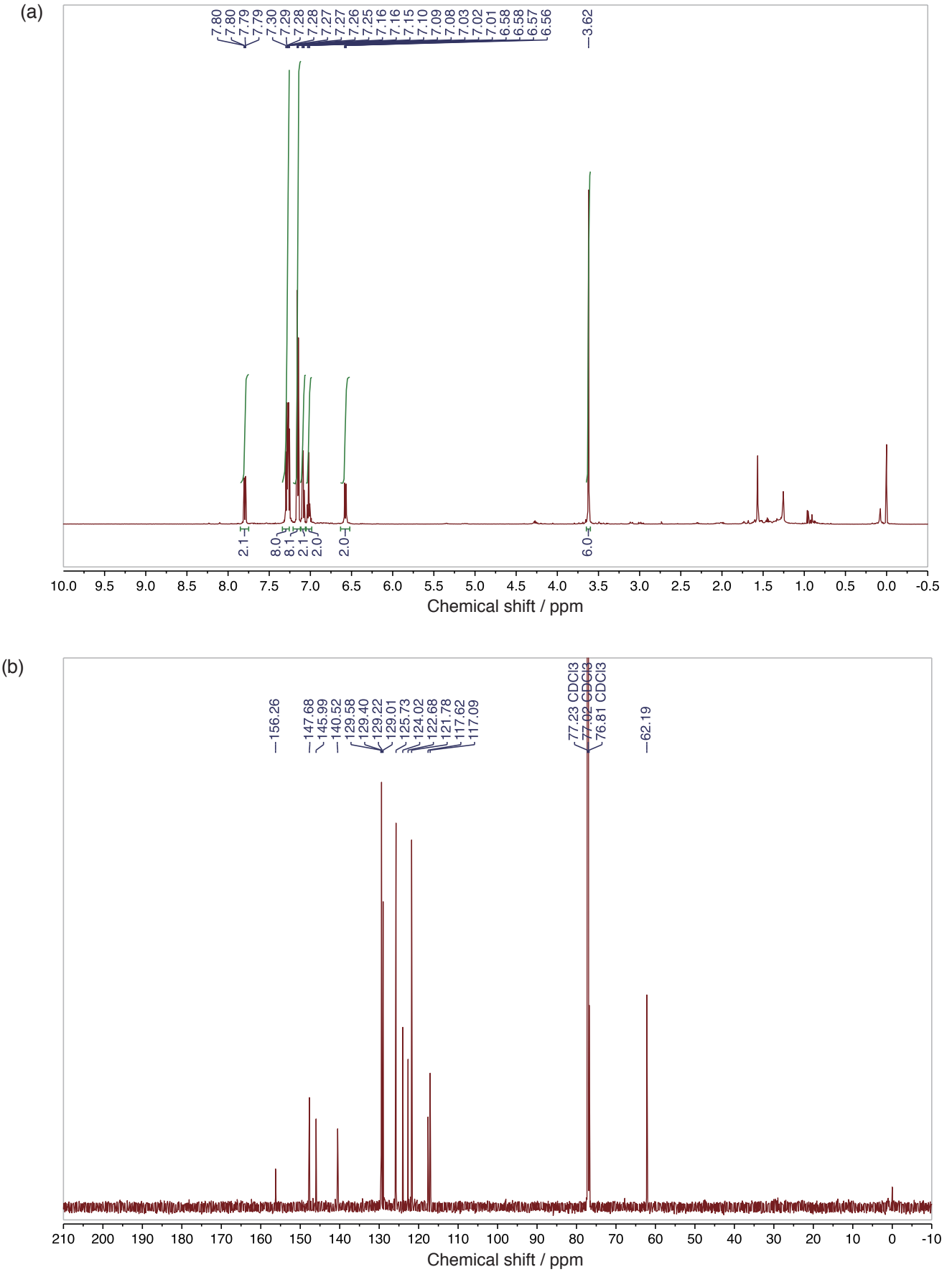


Figure S8. (a) ^{1}H and (b) ^{13}C NMR spectra of **3a**.

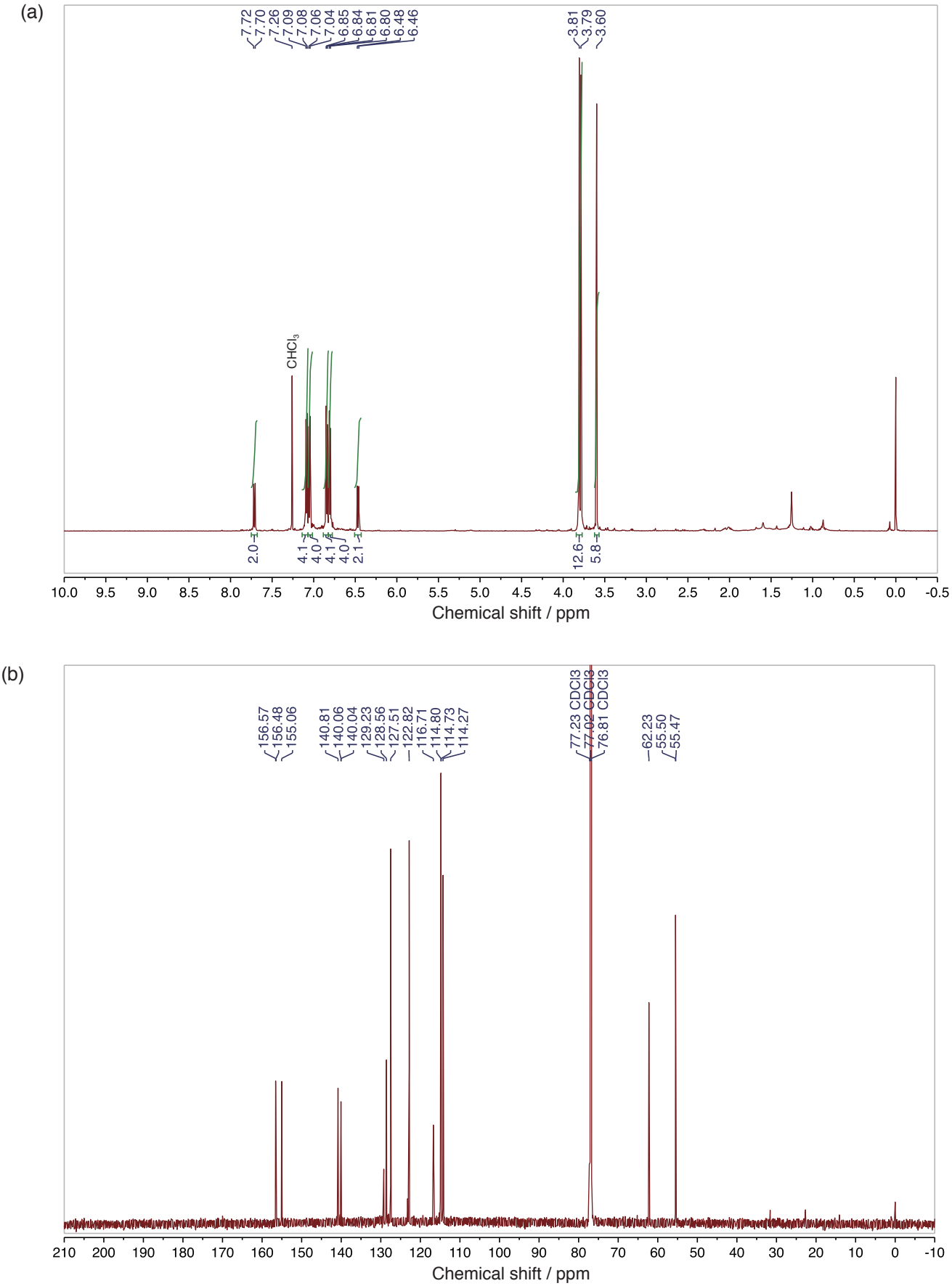


Figure S9. (a) ^{1}H and (b) ^{13}C NMR spectra of **3b**.

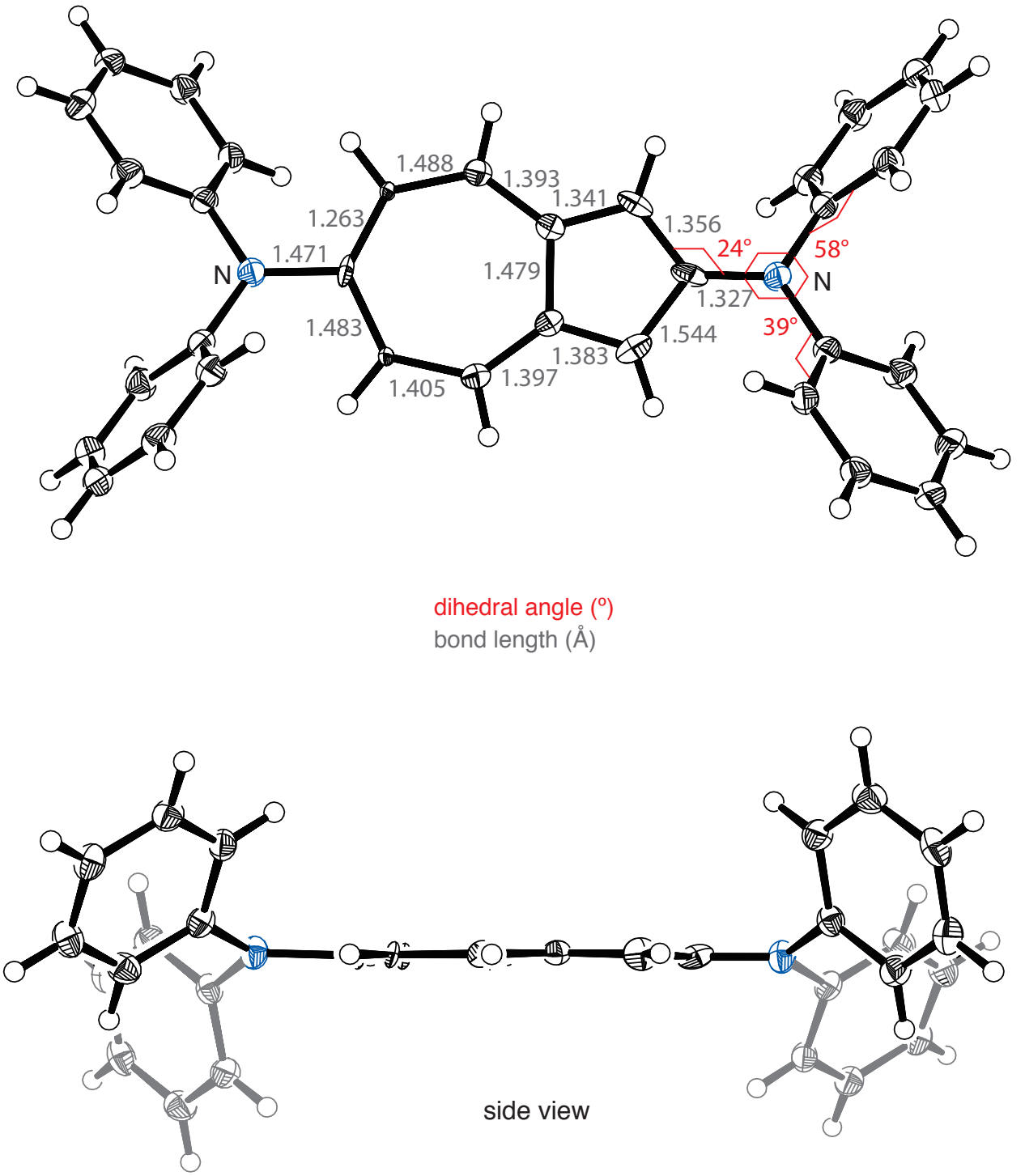


Figure S10. *ORTEP* drawings of **2a**.

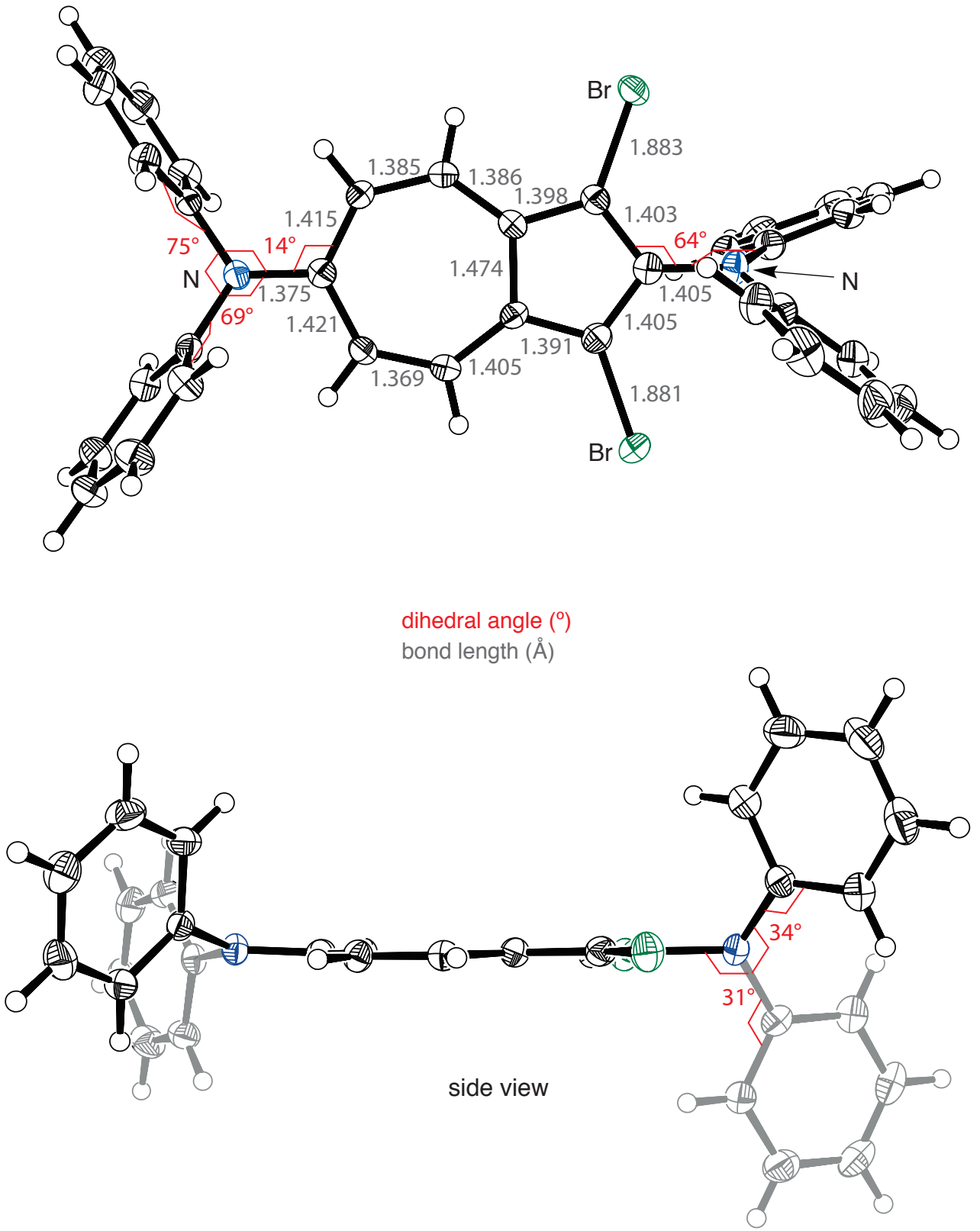


Figure S11. *ORTEP* drawings of **2a-Br$_2$**.

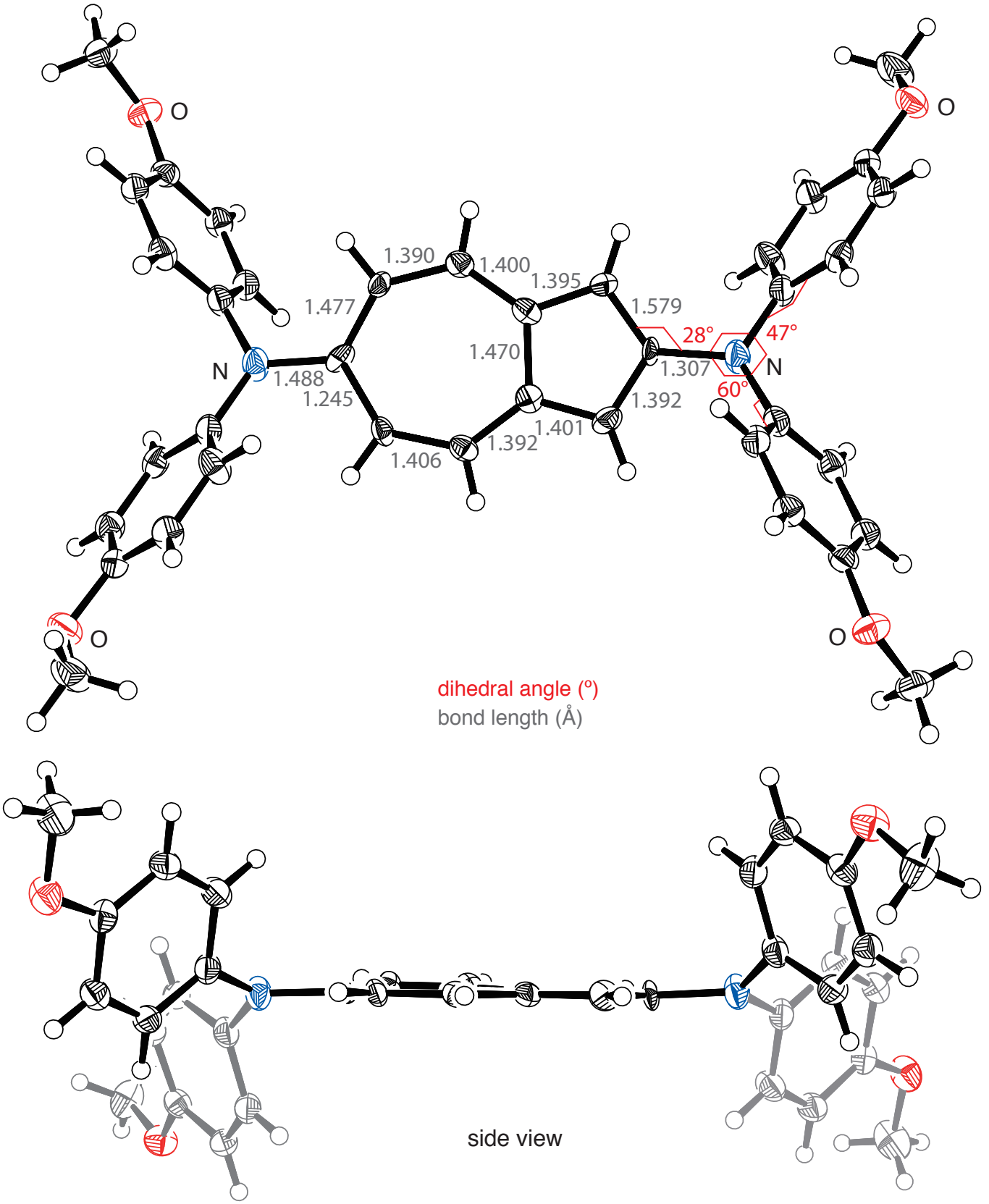


Figure S12. *ORTEP* drawings of **2b**.

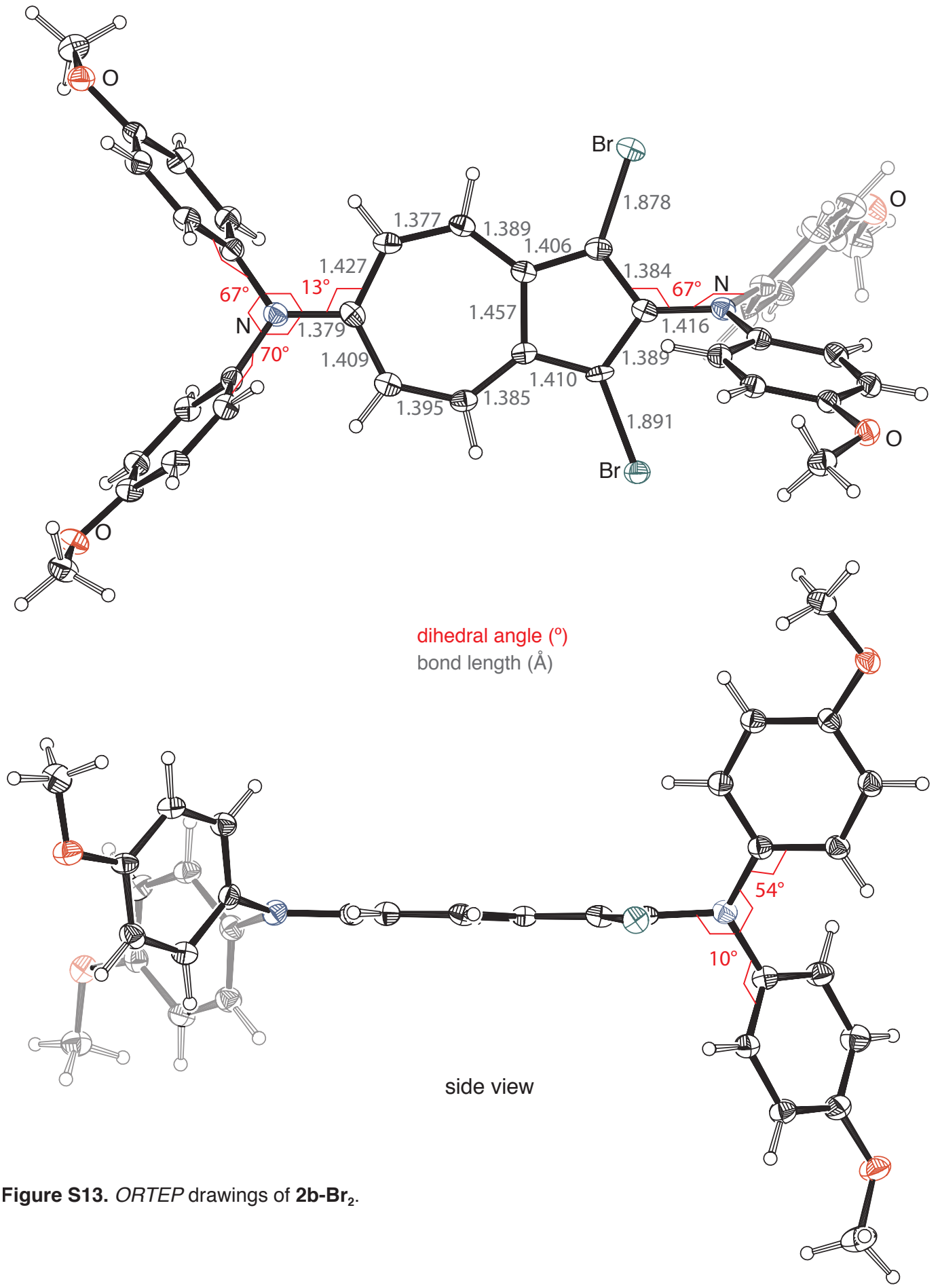
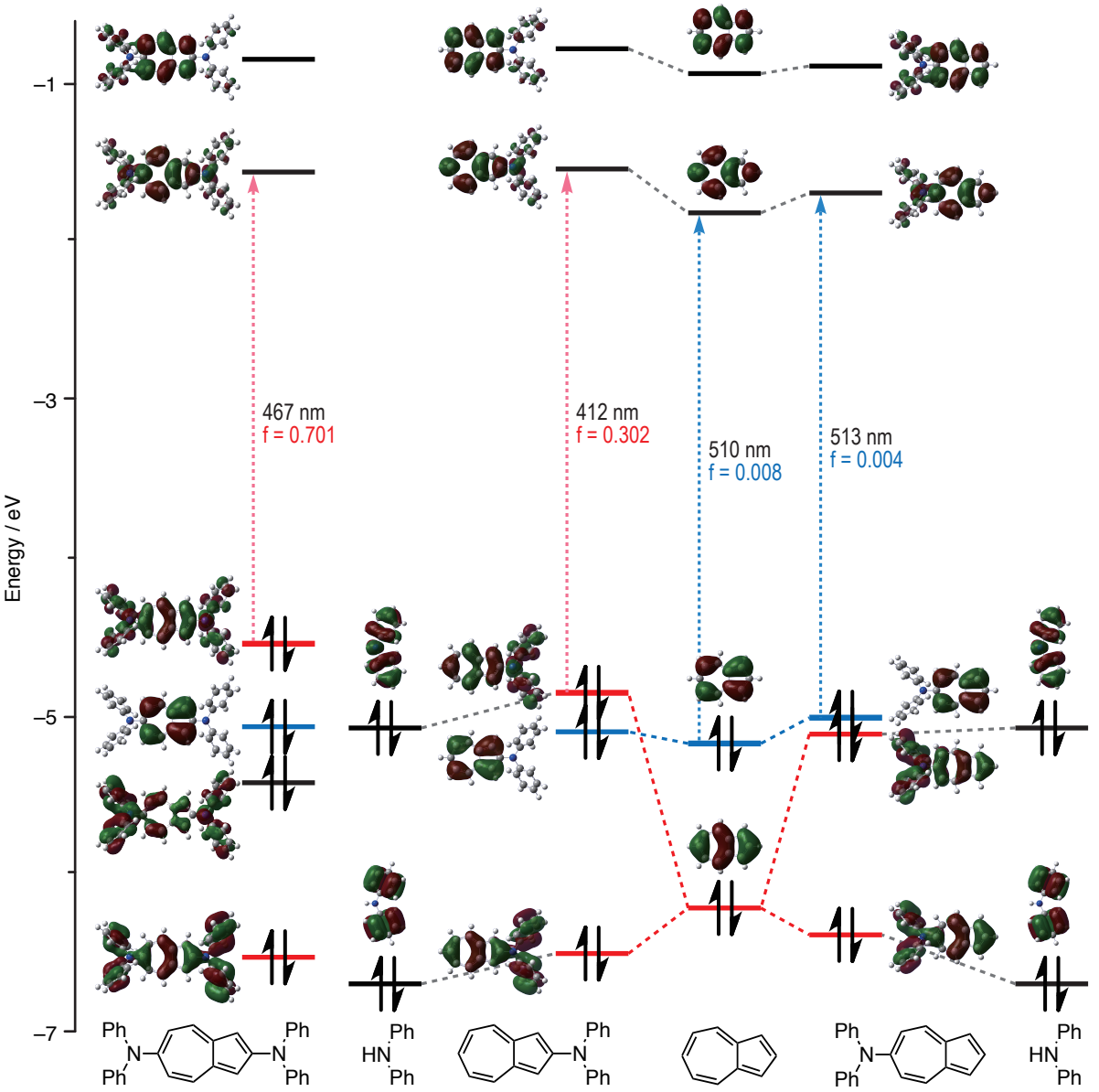


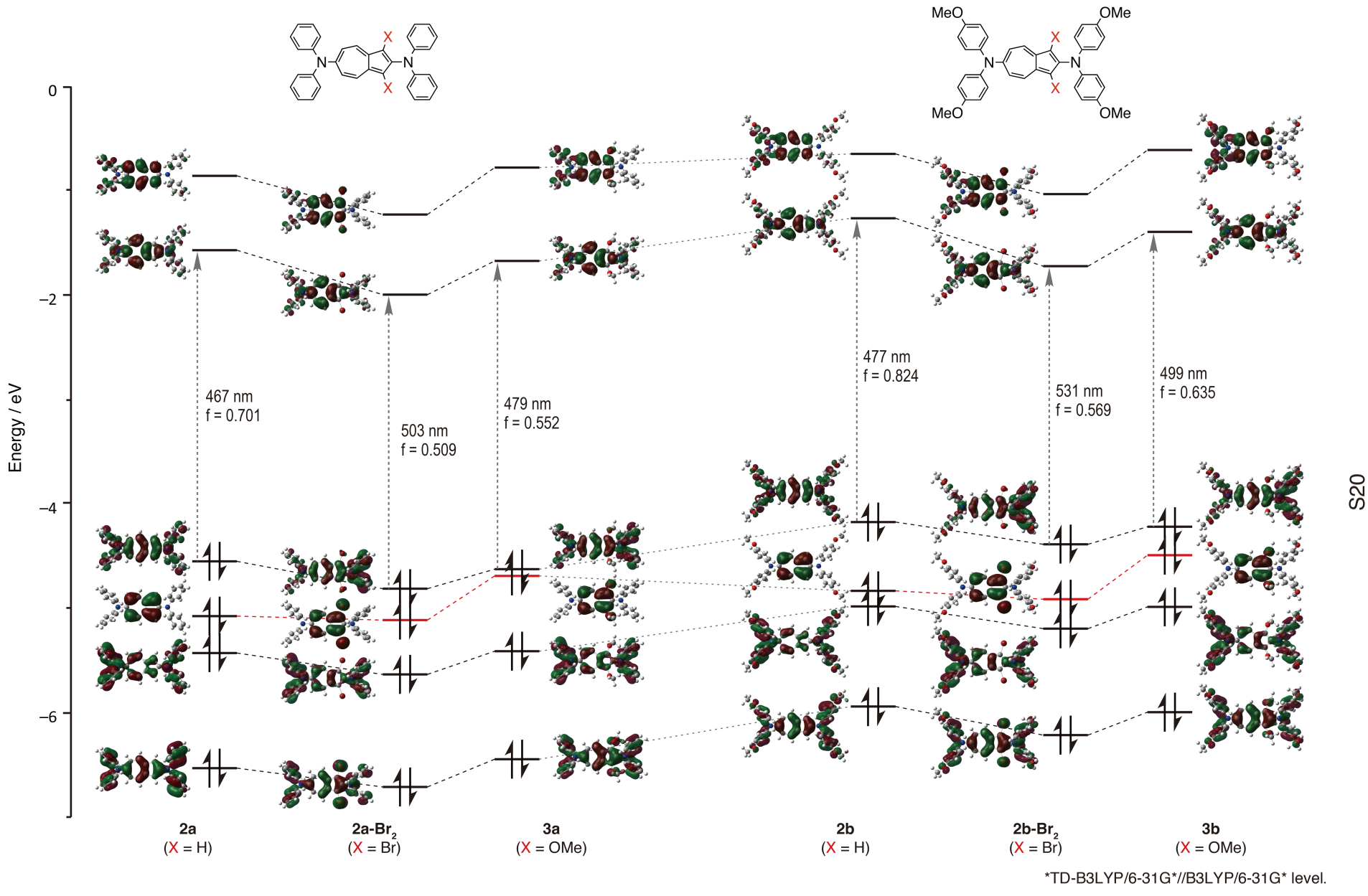
Figure S13. *ORTEP* drawings of **2b-Br$_2$**.



TD-B3LYP/6-31G//B3LYP/6-31G* level.

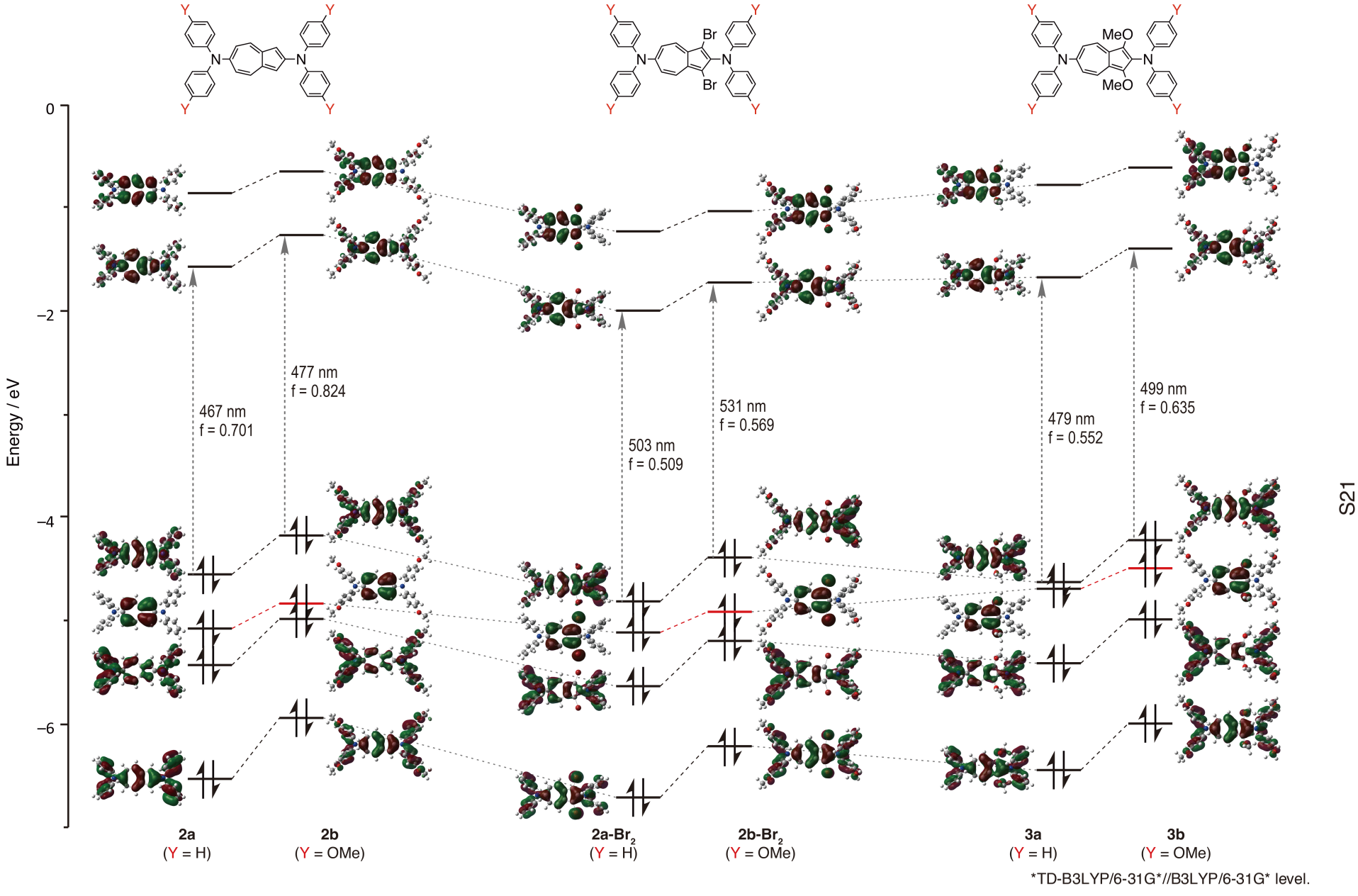
The introduction of a diphenylamino group to the 6-position of azulene exhibits weaker interaction between the LUMO of azulene and the HOMO of diphenylamine, and the MO energy level inversion is not exhibited unlike **2** and 2-(diphenylamino)azulene.

Figure S14. MO diagrams of **2**, 2- and 6-(diphenylamino)azulene, azulene, and diphenylamine. The HOMO of azulene and its derived molecular orbitals are indicated as blue lines, and the HOMO–1 of azulene and its derived molecular orbitals are indicated as red lines.



The doubly bromine-substituted **2-Br$_2$** exhibits lower-lying energy levels than **2**, whereas the doubly methoxy-substituted **3** shows similar energy levels to **2**. The methoxy groups exhibit both an inductive electron-withdrawing effect and a mesomeric electron-donating effect, and tend to gently perturb each orbital of **2** individually. Exceptionally, the HOMO–1 of **2**, which has large coefficients at the 1- and 3-positions, is more strongly perturbed by the electron-donating effect and raised by the introduction of the bromines and especially methoxy groups at these positions.

Figure S15. MO diagrams of **2**, **2-Br$_2$** and **3** disposed to compare the substituent effect at 1,3-positions of azulene skeleton.



Although introduction of methoxy groups to the *para*-positions of the diphenylamino groups leads to an overall energy increase in the MO levels, HOMO–1 is not significantly affected. Its orbital node is located at 2- and 6-positions of the azulene skeleton. Therefore, it is considered to be less sensitive to substituent effects at these positions.

Figure S16. MO diagrams of **2**, **2-Br$_2$** and **3** disposed to compare the substituent effect at *para*-positions of diphenylamino groups.

Table S1. Atomic coordinates of optimized structure of **1**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.018456	0.746688	1.578692
2	6	0	0.018456	-0.746688	1.578692
3	6	0	0.000000	-1.150421	0.220593
4	6	0	0.000000	0.000000	-0.587986
5	6	0	0.000000	1.150421	0.220593
6	6	0	-0.081606	1.590809	2.680922
7	6	0	-0.089241	1.262835	4.041273
8	6	0	0.000000	0.000000	4.634110
9	6	0	0.089241	-1.262835	4.041273
10	6	0	0.081606	-1.590809	2.680922
11	7	0	-0.014983	2.486829	-0.251910
12	6	0	-1.025798	2.862277	-1.178565
13	6	0	-0.732106	3.655833	-2.300177
14	6	0	-1.739023	4.000408	-3.199969
15	6	0	-3.047759	3.550614	-3.013601
16	6	0	-3.340245	2.752576	-1.905641
17	6	0	-2.344299	2.415105	-0.991834
18	6	0	1.061575	3.358473	0.059753
19	6	0	2.358558	2.855174	0.252059
20	6	0	3.403936	3.711762	0.592559
21	6	0	3.185583	5.083181	0.734910
22	6	0	1.898007	5.588096	0.539048
23	6	0	0.842404	4.739330	0.213787
24	7	0	0.014983	-2.486829	-0.251910
25	6	0	-1.061575	-3.358473	0.059753
26	6	0	-2.358558	-2.855174	0.252059
27	6	0	-3.403936	-3.711762	0.592559
28	6	0	-3.185583	-5.083181	0.734910
29	6	0	-1.898007	-5.588096	0.539048
30	6	0	-0.842404	-4.739330	0.213787
31	6	0	1.025798	-2.862277	-1.178565
32	6	0	2.344299	-2.415105	-0.991834
33	6	0	3.340245	-2.752576	-1.905641
34	6	0	3.047759	-3.550614	-3.013601
35	6	0	1.739023	-4.000408	-3.199969
36	6	0	0.732106	-3.655833	-2.300177
37	1	0	0.000000	0.000000	-1.671727
38	1	0	-0.127216	2.653166	2.449365
39	1	0	-0.159595	2.103985	4.726935
40	1	0	0.000000	0.000000	5.723243
41	1	0	0.159595	-2.103985	4.726935
42	1	0	0.127216	-2.653166	2.449365
43	1	0	0.284911	3.996529	-2.464345
44	1	0	-1.491508	4.613538	-4.062849
45	1	0	-3.827214	3.816779	-3.721795
46	1	0	-4.354425	2.397135	-1.742015
47	1	0	-2.579247	1.805735	-0.124843
48	1	0	2.539360	1.791953	0.132646
49	1	0	4.400159	3.300956	0.735944
50	1	0	4.004300	5.747769	0.995433
51	1	0	1.706391	6.652056	0.653511
52	1	0	-0.157166	5.139755	0.078408
53	1	0	-2.539360	-1.791953	0.132646
54	1	0	-4.400159	-3.300956	0.735944
55	1	0	-4.004300	-5.747769	0.995433
56	1	0	-1.706391	-6.652056	0.653511
57	1	0	0.157166	-5.139755	0.078408
58	1	0	2.579247	-1.805735	-0.124843
59	1	0	4.354425	-2.397135	-1.742015
60	1	0	3.827214	-3.816779	-3.721795
61	1	0	1.491508	-4.613538	-4.062849
62	1	0	-0.284911	-3.996529	-2.464345

Method: B3LYP/6-31G(d)
Key word: opt=tight freq scf=tight
E (RB3LYP): -1420.73376210 hartree

Table S2. Atomic coordinates of optimized structure of **2a**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.031471	0.518026	1.835213
2	6	0	0.000000	0.000000	2.657300
3	6	0	1.031471	-0.518026	1.835213
4	6	0	0.666483	-0.330353	0.498029
5	6	0	-0.666483	0.330353	0.498029
6	6	0	1.418543	-0.695635	-0.622725
7	6	0	1.137560	-0.545347	-1.976827
8	6	0	0.000000	0.000000	-2.605620
9	6	0	-1.137560	0.545347	-1.976827
10	6	0	-1.418543	0.695635	-0.622725
11	7	0	0.000000	0.000000	-4.032588
12	7	0	0.000000	0.000000	4.053197
13	6	0	0.408150	-1.160281	-4.746259
14	6	0	0.000000	-2.435365	-4.321835
15	6	0	0.407605	-3.571379	-5.018096
16	6	0	1.210776	-3.458142	-6.155084
17	6	0	1.611147	-2.190923	-6.584186
18	6	0	1.223656	-1.049852	-5.884230
19	6	0	-0.408150	1.160281	-4.746259
20	6	0	-1.223656	1.049852	-5.884230
21	6	0	-1.611147	2.190923	-6.584186
22	6	0	-1.210776	3.458142	-6.155084
23	6	0	-0.407605	3.571379	-5.018096
24	6	0	0.000000	2.435365	-4.321835
25	6	0	-1.225601	0.061628	4.779507
26	6	0	-2.312812	-0.748274	4.418502
27	6	0	-3.506460	-0.678565	5.135257
28	6	0	-3.628703	0.181941	6.228246
29	6	0	-2.543170	0.980109	6.595678
30	6	0	-1.351253	0.928464	5.875578
31	6	0	1.225601	-0.061628	4.779507
32	6	0	1.351253	-0.928464	5.875578
33	6	0	2.543170	-0.980109	6.595678
34	6	0	3.628703	-0.181941	6.228246
35	6	0	3.506460	0.678565	5.135257
36	6	0	2.312812	0.748274	4.418502
37	1	0	-1.942531	0.987766	2.181235
38	1	0	1.942531	-0.987766	2.181235
39	1	0	2.385535	-1.147182	-0.402202
40	1	0	1.912874	-0.889536	-2.655173
41	1	0	-1.912874	0.889536	-2.655173
42	1	0	-2.385535	1.147182	-0.402202
43	1	0	-0.635696	-2.526724	-3.446865
44	1	0	0.081994	-4.550247	-4.675806
45	1	0	1.520526	-4.345696	-6.699395
46	1	0	2.242496	-2.087001	-7.462831
47	1	0	1.549132	-0.068326	-6.213847
48	1	0	-1.549132	0.068326	-6.213847
49	1	0	-2.242496	2.087001	-7.462831
50	1	0	-1.520526	4.345696	-6.699395
51	1	0	-0.081994	4.550247	-4.675806
52	1	0	0.635696	2.526724	-3.446865
53	1	0	-2.214484	-1.426975	3.577716
54	1	0	-4.340054	-1.312384	4.844208
55	1	0	-4.558465	0.229038	6.788128
56	1	0	-2.626083	1.657894	7.441254
57	1	0	-0.512773	1.558211	6.155790
58	1	0	0.512773	-1.558211	6.155790
59	1	0	2.626083	-1.657894	7.441254
60	1	0	4.558465	-0.229038	6.788128
61	1	0	4.340054	1.312384	4.844208
62	1	0	2.214484	1.426975	3.577716

Method: B3LYP/6-31G(d)
Key word: opt=tight freq scf=tight
E (RB3LYP): -1420.74296549 hartree

Table S3. Atomic coordinates of optimized structure of **2b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.648261	0.362803	0.498648
2	6	0	-0.648261	-0.362803	0.498648
3	6	0	-1.381032	-0.762791	-0.623817
4	6	0	-1.109505	-0.599145	-1.977712
5	6	0	0.000000	0.000000	-2.610936
6	6	0	1.109505	0.599145	-1.977712
7	6	0	1.381032	0.762791	-0.623817
8	6	0	1.003913	0.569155	1.835986
9	6	0	0.000000	0.000000	2.659557
10	6	0	-1.003913	-0.569155	1.835986
11	7	0	0.000000	0.000000	-4.033605
12	6	0	0.434652	1.147707	-4.755564
13	6	0	-0.434652	-1.147707	-4.755564
14	7	0	0.000000	0.000000	4.052389
15	6	0	-1.211576	-0.190417	4.781738
16	6	0	1.211576	0.190417	4.781738
17	6	0	1.268821	1.108296	5.834862
18	6	0	2.440795	1.288282	6.572379
19	6	0	3.587387	0.554392	6.247948
20	6	0	3.538769	-0.364490	5.189140
21	6	0	2.364698	-0.551091	4.472727
22	6	0	-1.268821	-1.108296	5.834862
23	6	0	-2.440795	-1.288282	6.572379
24	6	0	-3.587387	-0.554392	6.247948
25	6	0	-3.538769	0.364490	5.189140
26	6	0	-2.364698	0.551091	4.472727
27	6	0	1.291751	1.024597	-5.854836
28	6	0	1.701660	2.145305	-6.580607
29	6	0	1.272313	3.420491	-6.196933
30	6	0	0.420649	3.553533	-5.090020
31	6	0	0.000000	2.433946	-4.387070
32	6	0	0.000000	-2.433946	-4.387070
33	6	0	-0.420649	-3.553533	-5.090020
34	6	0	-1.272313	-3.420491	-6.196933
35	6	0	-1.701660	-2.145305	-6.580607
36	6	0	-1.291751	-1.024597	-5.854836
37	8	0	-4.787718	-0.654609	6.894588
38	6	0	-4.892836	-1.574605	7.967685
39	8	0	4.787718	0.654609	6.894588
40	6	0	4.892836	1.574605	7.967685
41	8	0	1.617301	4.584289	-6.826392
42	6	0	2.483008	4.506133	-7.945812
43	8	0	-1.617301	-4.584289	-6.826392
44	6	0	-2.483008	-4.506133	-7.945812
45	1	0	-2.325253	-1.260727	-0.403573
46	1	0	-1.869801	-0.979560	-2.653597
47	1	0	1.869801	0.979560	-2.653597
48	1	0	2.325253	1.260727	-0.403573
49	1	0	0.385114	1.687551	6.084136
50	1	0	2.447738	2.008543	7.382641
51	1	0	4.432873	-0.933914	4.954782
52	1	0	2.332544	-1.272505	3.662623
53	1	0	-0.385114	-1.687551	6.084136
54	1	0	-2.447738	-2.008543	7.382641
55	1	0	-4.432873	0.933914	4.954782
56	1	0	-2.332544	1.272505	3.662623
57	1	0	1.638864	0.039881	-6.151992
58	1	0	2.363179	2.009419	-7.428723
59	1	0	0.087781	4.547559	-4.807729
60	1	0	-0.669610	2.547170	-3.540247
61	1	0	0.669610	-2.547170	-3.540247
62	1	0	-0.087781	-4.547559	-4.807729
63	1	0	-2.363179	-2.009419	-7.428723
64	1	0	-1.638864	-0.039881	-6.151992
65	1	0	-5.918064	-1.493256	8.333840
66	1	0	-4.197267	-1.328810	8.781561
67	1	0	-4.707352	-2.605456	7.636928
68	1	0	5.918064	1.493256	8.333840
69	1	0	4.197267	1.328810	8.781561
70	1	0	4.707352	2.605456	7.636928
71	1	0	2.626181	5.533127	-8.287249
72	1	0	2.042095	3.912839	-8.758464
73	1	0	3.456745	4.075601	-7.675663
74	1	0	-2.626181	-5.533127	-8.287249
75	1	0	-2.042095	-3.912839	-8.758464
76	1	0	-3.456745	-4.075601	-7.675663
77	1	0	1.890208	1.084811	2.181114
78	1	0	-1.890208	-1.084811	2.181114

Method: B3LYP/6-31G(d)
Key word: opt=tight freq scf=tight
E (RB3LYP): -1878.82986742 hartree

Table S4. Atomic coordinates of optimized structure of **2a-Br$_2$**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.067838	0.388849	-1.326819
2	6	0	0.000000	0.000000	-2.171568
3	6	0	1.067838	-0.388849	-1.326819
4	6	0	0.693524	-0.257617	0.017913
5	6	0	-0.693524	0.257617	0.017913
6	6	0	1.476763	-0.545678	1.137657
7	6	0	1.182954	-0.440450	2.490461
8	6	0	0.000000	0.000000	3.126639
9	6	0	-1.182954	0.440450	2.490461
10	6	0	-1.476763	0.545678	1.137657
11	7	0	0.000000	0.000000	4.540314
12	7	0	0.000000	0.000000	-3.570497
13	6	0	1.178145	0.337367	5.272612
14	6	0	1.925295	1.474729	4.930177
15	6	0	3.070086	1.803135	5.653807
16	6	0	3.474200	1.017194	6.735428
17	6	0	2.725154	-0.108630	7.083697
18	6	0	1.587964	-0.454203	6.355365
19	6	0	-1.178145	-0.337367	5.272612
20	6	0	-1.587964	0.454203	6.355365
21	6	0	-2.725154	0.108630	7.083697
22	6	0	-3.474200	-1.017194	6.735428
23	6	0	-3.070086	-1.803135	5.653807
24	6	0	-1.925295	-1.474729	4.930177
25	6	0	-0.385148	1.177466	-4.272572
26	6	0	0.000000	2.437350	-3.792661
27	6	0	-0.387314	3.592786	-4.468998
28	6	0	-1.144392	3.510786	-5.638641
29	6	0	-1.520518	2.254809	-6.121441
30	6	0	-1.154408	1.094987	-5.443248
31	6	0	0.385148	-1.177466	-4.272572
32	6	0	1.154408	-1.094987	-5.443248
33	6	0	1.520518	-2.254809	-6.121441
34	6	0	1.144392	-3.510786	-5.638641
35	6	0	0.387314	-3.592786	-4.468998
36	6	0	0.000000	-2.437350	-3.792661
37	1	0	2.466607	-0.935686	0.907509
38	1	0	1.971598	-0.765968	3.160914
39	1	0	-1.971598	0.765968	3.160914
40	1	0	-2.466607	0.935686	0.907509
41	1	0	1.603549	2.095022	4.099374
42	1	0	3.639687	2.686567	5.378269
43	1	0	4.363013	1.280473	7.301587
44	1	0	3.032187	-0.730774	7.920068
45	1	0	1.012114	-1.335255	6.620670
46	1	0	-1.012114	1.335255	6.620670
47	1	0	-3.032187	0.730774	7.920068
48	1	0	-4.363013	-1.280473	7.301587
49	1	0	-3.639687	-2.686567	5.378269
50	1	0	-1.603549	-2.095022	4.099374
51	1	0	0.605216	2.503115	-2.894050
52	1	0	-0.082101	4.562114	-4.083511
53	1	0	-1.438625	4.412984	-6.167366
54	1	0	-2.118134	2.175124	-7.025875
55	1	0	-1.467238	0.123177	-5.810457
56	1	0	1.467238	-0.123177	-5.810457
57	1	0	2.118134	-2.175124	-7.025875
58	1	0	1.438625	-4.412984	-6.167366
59	1	0	0.082101	-4.562114	-4.083511
60	1	0	-0.605216	-2.503115	-2.894050
61	35	0	-2.771073	0.940915	-1.924090
62	35	0	2.771073	-0.940915	-1.924090

Method: B3LYP/6-31G(d)
Key word: opt=tight freq scf=tight
E (RB3LYP): -6562.95012330 hartree

Table S5. Atomic coordinates of optimized structure of **2b-Br$_2$**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.738844	-0.146812
2	6	0	0.000000	-0.738844	-0.146812
3	6	0	0.002203	-1.572448	0.974886
4	6	0	-0.000884	-1.261820	2.327208
5	6	0	0.000000	0.000000	2.967746
6	6	0	0.000884	1.261820	2.327208
7	6	0	-0.002203	1.572448	0.974886
8	6	0	-0.007641	1.135350	-1.491411
9	6	0	0.000000	0.000000	-2.339392
10	6	0	0.007641	-1.135350	-1.491411
11	7	0	0.000000	0.000000	4.377606
12	6	0	-0.665274	1.027330	5.115206
13	6	0	0.665274	-1.027330	5.115206
14	7	0	0.000000	0.000000	-3.735650
15	6	0	0.944718	0.797335	-4.443816
16	6	0	-0.944718	-0.797335	-4.443816
17	6	0	-0.568421	-1.510609	-5.594796
18	6	0	-1.494517	-2.281214	-6.281234
19	6	0	-2.817940	-2.379419	-5.825339
20	6	0	-3.198993	-1.680794	-4.675603
21	6	0	-2.267420	-0.887852	-4.001882
22	6	0	0.568421	1.510609	-5.594796
23	6	0	1.494517	2.281214	-6.281234
24	6	0	2.817940	2.379419	-5.825339
25	6	0	3.198993	1.680794	-4.675603
26	6	0	2.267420	0.887852	-4.001882
27	6	0	-0.014089	1.691790	6.158465
28	6	0	-0.668044	2.673759	6.905464
29	6	0	-1.990343	3.016593	6.599890
30	6	0	-2.647834	2.356831	5.549722
31	6	0	-1.997588	1.369118	4.824759
32	6	0	1.997588	-1.369118	4.824759
33	6	0	2.647834	-2.356831	5.549722
34	6	0	1.990343	-3.016593	6.599890
35	6	0	0.668044	-2.673759	6.905464
36	6	0	0.014089	-1.691790	6.158465
37	1	0	-0.018990	-2.636278	0.744951
38	1	0	-0.031619	-2.116098	2.995393
39	1	0	0.031619	2.116098	2.995393
40	1	0	0.018990	2.636278	0.744951
41	1	0	0.457627	-1.459415	-5.944206
42	1	0	-1.209670	-2.835000	-7.170526
43	1	0	-4.214775	-1.731277	-4.300211
44	1	0	-2.573804	-0.334011	-3.119964
45	1	0	-0.457627	1.459415	-5.944206
46	1	0	1.209670	2.835000	-7.170526
47	1	0	4.214775	1.731277	-4.300211
48	1	0	2.573804	0.334011	-3.119964
49	1	0	1.014199	1.435341	6.394107
50	1	0	-0.133776	3.166779	7.709483
51	1	0	-3.676043	2.626577	5.330169
52	1	0	-2.517659	0.855163	4.022233
53	1	0	2.517659	-0.855163	4.022233
54	1	0	3.676043	-2.626577	5.330169
55	1	0	0.133776	-3.166779	7.709483
56	1	0	-1.014199	-1.435341	6.394107
57	8	0	3.646616	3.174706	-6.568861
58	8	0	-3.646616	-3.174706	-6.568861
59	8	0	-2.722099	3.962781	7.256575
60	8	0	2.722099	-3.962781	7.256575
61	6	0	4.992791	3.309072	-6.148250
62	1	0	5.518249	2.344317	-6.156696
63	1	0	5.466465	3.982424	-6.865407
64	1	0	5.061424	3.745012	-5.142266
65	6	0	-4.992791	-3.309072	-6.148250
66	1	0	-5.518249	-2.344317	-6.156696
67	1	0	-5.466465	-3.982424	-6.865407
68	1	0	-5.061424	-3.745012	-5.142266
69	6	0	-2.106417	4.664954	8.324589
70	1	0	-1.229149	5.230555	7.983556
71	1	0	-2.859735	5.360091	8.699451
72	1	0	-1.805004	3.986113	9.133536
73	6	0	2.106417	-4.664954	8.324589
74	1	0	1.229149	-5.230555	7.983556
75	1	0	2.859735	-5.360091	8.699451
76	1	0	1.805004	-3.986113	9.133536
77	35	0	-0.088584	2.927127	-2.084958
78	35	0	0.088584	-2.927127	-2.084958

Method: B3LYP/6-31G(d)
Key word: opt=tight freq scf=tight
E (RB3LYP): -7021.03778041 hartree

Table S6. Atomic coordinates of optimized structure of **3a**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.741465	-0.201796
2	6	0	0.000000	-0.741465	-0.201796
3	6	0	-0.011544	-1.582576	0.908516
4	6	0	-0.016897	-1.265612	2.264116
5	6	0	0.000000	0.000000	2.890440
6	6	0	0.016897	1.265612	2.264116
7	6	0	0.011544	1.582576	0.908516
8	6	0	-0.007906	1.147881	-1.544338
9	6	0	0.000000	0.000000	-2.384847
10	6	0	0.007906	-1.147881	-1.544338
11	7	0	0.000000	0.000000	4.312768
12	6	0	-0.795688	0.934506	5.035118
13	6	0	0.795688	-0.934506	5.035118
14	7	0	0.000000	0.000000	-3.789335
15	6	0	0.858025	0.891624	-4.494810
16	6	0	-0.858025	-0.891624	-4.494810
17	6	0	-0.432065	-1.509053	-5.682365
18	6	0	-1.281067	-2.377085	-6.366214
19	6	0	-2.557533	-2.657915	-5.874874
20	6	0	-2.977826	-2.053731	-4.688382
21	6	0	-2.142378	-1.173066	-4.005177
22	6	0	0.432065	1.509053	-5.682365
23	6	0	1.281067	2.377085	-6.366214
24	6	0	2.557533	2.657915	-5.874874
25	6	0	2.977826	2.053731	-4.688382
26	6	0	2.142378	1.173066	-4.005177
27	6	0	-0.270312	1.603885	6.151281
28	6	0	-1.059537	2.504184	6.864928
29	6	0	-2.373644	2.763573	6.470186
30	6	0	-2.895901	2.104158	5.355072
31	6	0	-2.120328	1.189472	4.645749
32	6	0	2.120328	-1.189472	4.645749
33	6	0	2.895901	-2.104158	5.355072
34	6	0	2.373644	-2.763573	6.470186
35	6	0	1.059537	-2.504184	6.864928
36	6	0	0.270312	-1.603885	6.151281
37	6	0	-1.176302	2.940886	-2.544000
38	6	0	1.176302	-2.940886	-2.544000
39	1	0	-0.048190	-2.644893	0.672784
40	1	0	-0.057831	-2.112793	2.941532
41	1	0	0.057831	2.112793	2.941532
42	1	0	0.048190	2.644893	0.672784
43	1	0	0.561407	-1.302825	-6.067099
44	1	0	-0.934426	-2.845299	-7.283947
45	1	0	-3.214247	-3.339651	-6.407780
46	1	0	-3.968429	-2.261047	-4.292103
47	1	0	-2.475826	-0.703986	-3.085261
48	1	0	-0.561407	1.302825	-6.067099
49	1	0	0.934426	2.845299	-7.283947
50	1	0	3.968429	2.261047	-4.292103
51	1	0	2.475826	0.703986	-3.085261
52	1	0	0.754832	1.413639	6.452758
53	1	0	-0.638031	3.015079	7.726640
54	1	0	-2.983875	3.470505	7.025034
55	1	0	-3.919682	2.290464	5.041398
56	1	0	-2.533150	0.667237	3.788449
57	1	0	2.533150	-0.667237	3.788449
58	1	0	3.919682	-2.290464	5.041398
59	1	0	2.983875	-3.470505	7.025034
60	1	0	0.638031	-3.015079	7.726640
61	1	0	-0.754832	-1.413639	6.452758
62	1	0	-1.007297	3.998485	-2.760070
63	1	0	-2.026648	2.835883	-1.857368
64	1	0	-1.397822	2.413880	-3.479018
65	1	0	1.007297	-3.998485	-2.760070
66	1	0	2.026648	-2.835883	-1.857368
67	1	0	1.397822	-2.413880	-3.479018
68	1	0	3.214247	3.339651	-6.407780
69	8	0	0.026538	2.458593	-1.940351
70	8	0	-0.026538	-2.458593	-1.940351

Method: B3LYP/6-31G(d)
Key word: opt=tight freq scf=tight
E (RB3LYP): -1649.77084668 hartree

Table S7. Atomic coordinates of optimized structure of **3b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.740129	-0.342261
2	6	0	0.000000	-0.740129	-0.342261
3	6	0	-0.015942	-1.579977	0.770272
4	6	0	-0.022409	-1.264998	2.125344
5	6	0	0.000000	0.000000	2.757098
6	6	0	0.022409	1.264998	2.125344
7	6	0	0.015942	1.579977	0.770272
8	6	0	-0.009640	1.146925	-1.684499
9	6	0	0.000000	0.000000	-2.528308
10	6	0	0.009640	-1.146925	-1.684499
11	7	0	0.000000	0.000000	4.174300
12	6	0	-0.702473	1.002367	4.906534
13	6	0	0.702473	-1.002367	4.906534
14	7	0	0.000000	0.000000	-3.930232
15	6	0	0.817825	0.925043	-4.642439
16	6	0	-0.817825	-0.925043	-4.642439
17	6	0	-0.355483	-1.539732	-5.820190
18	6	0	-1.155819	-2.436224	-6.514245
19	6	0	-2.435108	-2.762006	-6.041994
20	6	0	-2.900570	-2.165199	-4.865872
21	6	0	-2.098469	-1.249087	-4.183361
22	6	0	0.355483	1.539732	-5.820190
23	6	0	1.155819	2.436224	-6.514245
24	6	0	2.435108	2.762006	-6.041994
25	6	0	2.900570	2.165199	-4.865872
26	6	0	2.098469	1.249087	-4.183361
27	6	0	-0.092159	1.668737	5.973876
28	6	0	-0.783638	2.629837	6.714672
29	6	0	-2.103027	2.952600	6.378418
30	6	0	-2.719477	2.293840	5.303509
31	6	0	-2.032832	1.325824	4.585303
32	6	0	2.032832	-1.325824	4.585303
33	6	0	2.719477	-2.293840	5.303509
34	6	0	2.103027	-2.952600	6.378418
35	6	0	0.783638	-2.629837	6.714672
36	6	0	0.092159	-1.668737	5.973876
37	6	0	-1.192014	2.940705	-2.662475
38	6	0	1.192014	-2.940705	-2.662475
39	1	0	-0.055649	-2.642392	0.534856
40	1	0	-0.069935	-2.114271	2.799399
41	1	0	0.069935	2.114271	2.799399
42	1	0	0.055649	2.642392	0.534856
43	1	0	0.636016	-1.305100	-6.193923
44	1	0	-0.801575	-2.910321	-7.424443
45	1	0	-3.884152	-2.395956	-4.472644
46	1	0	-2.469976	-0.789329	-3.273262
47	1	0	-0.636016	1.305100	-6.193923
48	1	0	0.801575	2.910321	-7.424443
49	1	0	3.884152	2.395956	-4.472644
50	1	0	2.469976	0.789329	-3.273262
51	1	0	0.934688	1.430177	6.233232
52	1	0	-0.278965	3.123527	7.537313
53	1	0	-3.746304	2.547698	5.059290
54	1	0	-2.521825	0.812485	3.763249
55	1	0	2.521825	-0.812485	3.763249
56	1	0	3.746304	-2.547698	5.059290
57	1	0	0.278965	-3.123527	7.537313
58	1	0	-0.934688	-1.430177	6.233232
59	1	0	-1.030048	3.999700	-2.878306
60	1	0	-2.032300	2.831096	-1.964035
61	1	0	-1.425848	2.415938	-3.595929
62	1	0	1.030048	-3.999700	-2.878306
63	1	0	2.032300	-2.831096	-1.964035
64	1	0	1.425848	-2.415938	-3.595929
65	8	0	0.020152	2.460000	-2.078563
66	8	0	-0.020152	-2.460000	-2.078563
67	8	0	3.137514	3.663677	-6.794928
68	8	0	-3.137514	-3.663677	-6.794928
69	8	0	-2.870053	3.878837	7.027061
70	8	0	2.870053	-3.878837	7.027061
71	6	0	4.429894	4.037688	-6.351046
72	1	0	5.111877	3.177084	-6.314817
73	1	0	4.801610	4.759453	-7.081128
74	1	0	4.397035	4.509756	-5.359689
75	6	0	-4.429894	-4.037688	-6.351046
76	1	0	-5.111877	-3.177084	-6.314817
77	1	0	-4.801610	-4.759453	-7.081128
78	1	0	-4.397035	-4.509756	-5.359689
79	6	0	-2.296401	4.573086	8.122105
80	1	0	-1.420106	5.159924	7.815416
81	1	0	-3.071558	5.248866	8.488248
82	1	0	-2.004279	3.886409	8.928090
83	6	0	2.296401	-4.573086	8.122105
84	1	0	1.420106	-5.159924	7.815416
85	1	0	3.071558	-5.248866	8.488248
86	1	0	2.004279	-3.886409	8.928090

Method: B3LYP/6-31G(d)
Key word: opt=tight freq scf=tight
E (RB3LYP): -2107.85752492 hartree

Complete list of authors of Gaussian 09

Gaussian 09, revision B.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, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Table S8 Redox Potentials (V)[a] and HOMO and LUMO levels (eV)[b] of azulene, **2**, **2-Br$_2$** and **3**

Compd	$^{ox}E_1^{c}$	$^{red}E_1^{c}$	$^{ox}E_{1\ (onset)}^{c}$	$^{red}E_{1\ (onset)}^{c}$	HOMO[b]	LUMO[b]
azulene	0.50	–2.15	0.32	–2.02	–5.12	–2.78
2a	0.03	–2.16	–0.11	–2.03	–4.69	–2.77
2b	–0.12	–2.28	–0.29	–2.15	–4.51	–2.65
2a-Br$_2$	0.36	–1.82	0.24	–1.69	–5.04	–3.11
2b-Br$_2$	0.10	–1.94	–0.02	–1.81	–4.78	–2.99
3a	–0.07	–2.08	–0.20	–1.96	–4.60	–2.84
3b	–0.14	–2.16	–0.26	–2.04	–4.54	–2.76

[a] *Vs.* ferrocene/ferrocenium (Fc/Fc$^+$) couple. [b] Conversion potential of ferrocene as Ip = –4.8 eV.[ref.] [c] Conditions: solvent, PhCN; supporting electrolyte, ^{n}Bu$_4$NPF$_6$; reference electrode, Ag/Ag+; counter electrode, Pt; working electrode, Pt wire.

ref.: M. M.-Olvera, R. A.-Ramos, M. M.-Domínguez, L. Salmon, G. Molnár, A. Bousseksou, M. P. C.-Castro, *New J. Chem.*, 2022, **46**, 4992-5001.

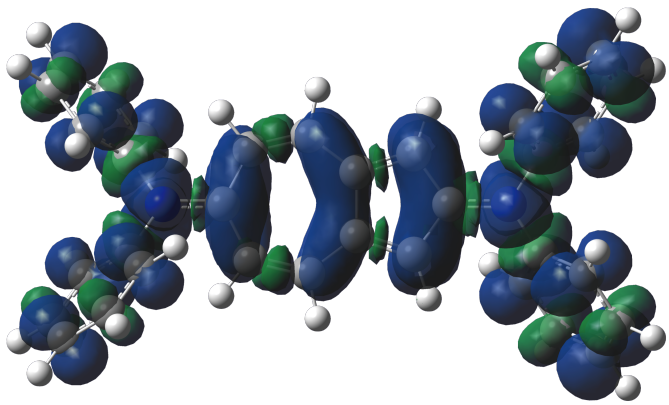


Figure S17. Spin density plot of radical cation of **2a** calculated at B3LYP/6-31G* level.

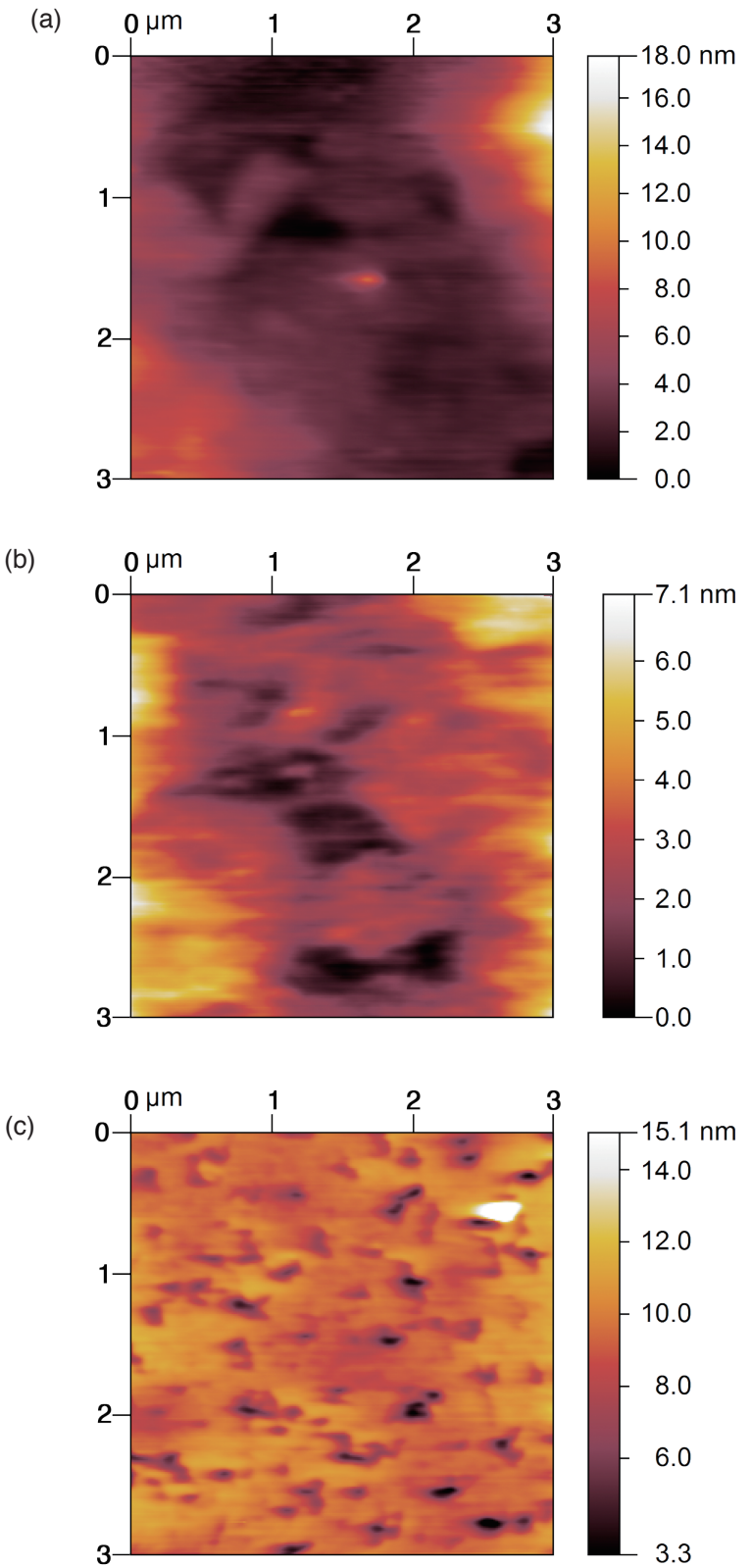


Figure S18. AFM images of (a) **2a**, (b) **2a-Br$_2$** and (c) **2b** thin films.