Electronic supplementary information for

Synthesis and structure of 1,4,5,8-tetraethynylnaphthalene derivatives

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1. Experimental detail

General methods.

All reactions were performed under an inert atmosphere (N_2 or Ar) unless otherwise noted. Commercially available reagents and solvents were used as received except for the dry solvents. Dry Et_3N was prepared by distillation from NaOH. Dry THF was purchased and purified through a Glass Contour solvent system. 5,8-Dibromo-1,4-naphthoquinone and 5,8-diiodo-1,4-naphthoquinone were prepared following the published procedures[S1] from 1,4-dibromonaphthalene and 1,4-diiodonaphthalene, respectively. Chemical shifts (δ) are expressed in ppm referred to residual nondeuterated solvent as the internal standard ($CDCl_3$; ^{1}H 7.26 ppm, ^{13}C 77.0 ppm). GPC was performed using JAIGEL-1H and 2H GPC column (600 mm × 20 mm) with $CHCl_3$ as the eluent.

Preparation of 5,8-dibromo-1,4-bis[(trimethylsilyl)ethynyl]-1,4-dihydronaphthalene-1,4-diol (6).

To a solution of (trimethylsilyl)acetylene (1.80 mL, 12.7 mmol) in THF (50 mL) was added *n*-BuLi (1.67 M in hexane, 5.70 mL, 9.52 mmol) at −78 °C. The mixture was stirred at −78 °C for 45 min and then, 5,8-dibromo-1,4-naphthoquinone (1.00 g, 3.17 mmol) was added at this temperature. The mixture was warmed gradually to rt and stirred for 20 h. Saturated aqueous solution of NH_4Cl was added and the mixture was extracted with ether. The combined organic layer was washed with brine and then dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude product was purified by silica gel column chromatography ($CHCl_3$/hexane = 1/1→1/0) to give two diastereomers of 5,8-dibromo-1,4-bis[(trimethylsilyl)ethynyl]-1,4-dihydronaphthalene-1,4-diol (**6**) (major diastereomer: brown amorphous solid, 1.22 g, 75%; minor diastereomer: orange solid, 265 mg, 16%). The stereochemistry of each diastereomer was not determined. The major diastereomer was used for the next reaction.

Data for major diastereomer: Mp 93–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.49 (s, 2H), 6.03 (s, 2H), 4.17 (br s, 2H), 0.15 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 136.3, 135.7, 127.2, 122.9, 103.7, 91.5, 64.4, −0.4; IR (KBr) 3426, 3063, 2959, 2898, 2171, 1429, 1326, 1251, 1156, 1036, 974, 843, 778, 760 cm^{-1}; HR-MS (EI) calcd for $C_{20}H_{23}O_2{}^{79}Br_2Si_2$ [$(M-H)^+$] *m/z* 508.9603, found 508.9602.

Data for minor diastereomer: Mp 70–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.52 (s, 2H), 6.10 (s, 2H), 3.97 (s, 2H), 0.14 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 137.2, 136.1, 128.0, 123.2, 104.5, 92.7, 65.1, −0.1; IR (KBr) 3529, 3495, 3439, 3056, 2959, 2898, 2171, 1432, 1387, 1364, 1310, 1249, 1224, 1175, 1159, 1045, 996, 863, 842, 795, 777, 760, 699, 649, 618, 521 cm^{-1}; HR-MS (EI)

calcd for $C_{20}H_{21}O^{81}Br_2Si_2$ $[(M-H_2O-H)^+]$ *m/z* 494.9457, found 494.9440.

Preparation of 5,8-dibromo-1,4-bis[(trimethylsilyl)ethynyl]naphthalene (7).

To a solution of **6** (major isomer, 811 mg, 1.58 mmol) in EtOH (4 mL) was added $SnCl_2 \cdot 2H_2O$ (714 mg, 3.17 mmol). The mixture was stirred at 60 °C for 1 h. The resulting precipitates were filtered and washed with EtOH to give 5,8-dibromo-1,4-bis[(trimethylsilyl)ethynyl]naphthalene (**7**) (697 mg, 92%) as an orange solid. Mp 144–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.75 (s, 2H), 7.63 (s, 2H), 0.27 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 136.1, 134.2, 132.8, 122.5, 121.0, 108.1, 104.5, −0.6; IR (KBr) 2955, 2896, 2143, 1368, 1248, 864, 839, 807, 757, 632 cm^{-1}; HR-MS (EI) calcd for $C_{20}H_{22}{}^{79}Br_2Si_2$ (M^+) *m/z* 475.9627, found 475.9626.

Preparation of 1,4,5,8-tetrakis[(trimethylsilyl)ethynyl]naphthalene (4b).

To an argon purged solution of **7** (513 mg, 1.07 mmol), $Pd(PPh_3)_2Cl_2$ (173 mg, 246 mmol), CuI (92 mg, 483 μmol) in Et_3N (30 mL) was added (trimethylsilyl)acetylene (900 μL, 6.37 mmol). The mixture was stirred at rt for 10 min then stirred at 80 °C for 60 min. The mixture was cooled to rt and then diluted with saturated aqueous solution of NH_4Cl and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. Combined organic layer was washed with saturated aqueous solution of NH_4Cl and brine and then dried over $MgSO_4$. After evaporation of solvent under reduced pressure, the crude product was purified by silica gel column chromatography (hexane/AcOEt = 100/1) twice followed by GPC to give 1,4,5,8-tetrakis[(trimethylsilyl)ethynyl] naphthalene (**4b**) (311 mg, 57%) as a yellow solid. Mp 139–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.66 (s, 4H), 0.30 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 135.8, 131.2, 121.9, 106.5, 105.1, 0.1; IR (KBr) 2958, 2898, 2139, 1392, 1247, 944, 890, 840, 758, 697, 677, 654, 631, 458, 422 cm^{-1}; HR-MS (EI) calcd for $C_{30}H_{40}Si_4$ (M^+) *m/z* 512.2207, found 512.2206.

Preparation of 1,4-bis[(trimethylsilyl)ethynyl]-5,8-bis[(triisopropylsilyl)ethynyl]naphthalene (4c).

To an argon purged solution of **7** (610 mg, 1.28 mmol), $Pd(PPh_3)_2Cl_2$ (268 mg, 382 mmol), CuI (122 mg, 641 μmol) in Et_3N (30 mL) was added (triisopropylsilyl)acetylene (850 μL, 3.82 mmol). The mixture was stirred at 80 °C for 3 h. The mixture was cooled to rt and then diluted with saturated aqueous solution of NH_4Cl and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. Combined organic layer was washed with saturated aqueous solution of NH_4Cl and brine and then dried over $MgSO_4$. After evaporation of solvent under reduced pressure, the crude product was purified by silica gel column chromatography (hexanes) twice to give 1,4-bis[(trimethylsilyl)ethynyl]-5,8-bis[(triisopropylsilyl)ethynyl]naphthalene (**4c**) (623 mg, 73%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.69 (s, 2H) 7.66 (s, 2H), 1.20–1.15 (m, 42H),

0.27 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 136.0, 135.9, 131.1, 122.0, 107.1, 106.9, 105.8, 104.3, 18.9, 11.6, 0.0; IR (KBr) 2958, 2944, 2894, 2865, 2137, 1545, 1463, 1432, 1389, 1249, 1072, 1016, 996, 941, 884, 841, 782, 760, 678, 592 cm^{-1}; HR-MS (FAB) calcd for $C_{42}H_{64}Si_4$ (M^+) *m/z* 680.4085, found 680.4084.

Preparation of 5,8-diiodo-1,4-bis(phenylethynyl)-1,4-dihydronaphthalene-1,4-diol (9).

To a solution of phenylacetylene (700 μL, 7.32 mmol) in THF (40 mL) was added *n*-BuLi (1.63 M in hexane, 3.70 mL, 6.03 mmol) at −78 °C. The mixture was stirred at −78 °C for 1 h. To the resulting solution was added 5,8-diiodo-1,4-napthoquinone (1.00 g, 2.44 mmol) at this temperature. The mixture was allowed to warm rt and stirred for 16 h. Saturated aqueous solution of NH_4Cl was added and the mixture was extracted with ehter. Combined organic layer was washed with brine, then dried over $MgSO_4$. After evaporation of solvent under reduced pressure, the crude product was purified by silica gel column chromatography ($CHCl_3$/hexane = 2/1→1/0) to give two diastereomers of 5,8-diiodo-1,4-bis(phenylethynyl)-1,4-dihydronaphthalene-1,4-diol (**9**) (major diastereomer: pale yellow solid 1.21 g, 81%. minor diastereomer: pale yellow solid 26.6 mg, 1.8%). Stereochemistry of the diastereomers was not determined. Major diastereomer was used for the next reaction.

Data for major diastereomer: Mp 173–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.70 (s, 2H), 7.48–7.44 (m, 4H), 7.34–7.28 (m, 6H) 6.27 (s, 2H), 3.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 143.7, 138.5, 131.7, 128.8, 128.3, 127.4, 122.1, 97.6, 89.1, 88.0, 66.2; IR (KBr) 3483, 3392, 3050, 2223, 1596, 1570, 1488, 1442, 1422, 1398, 1365, 1302, 1248, 1214, 1173, 1145, 1118, 1071, 1060, 1033, 1020, 996, 978, 961, 916, 808, 789, 756, 722, 689, 671, 584, 546, 525, 475, 465 cm^{-1}; HR-MS (EI) calcd for $C_{26}H_{16}O_2I_2$ (M^+) *m/z* 613.9240, found 613.9232.

Data for minor diastereomer: Mp 89–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.71 (s, 2H), 7.47–7.43 (m, 4H), 7.32–7.27 (m, 6H) 6.24 (s, 2H), 3.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 144.1, 138.4, 132.1, 129.1, 128.5, 127.4, 122.5, 97.9, 88.6, 87.6, 66.1; IR (KBr) 3354, 3078, 3052, 3032, 2955, 2925, 2852, 2219, 1597, 1572, 1488, 1442, 1423, 1316, 1257, 1176, 1145, 1069, 1017, 996, 957, 916, 811, 755, 688, 620, 585, 544, 526, 479 cm^{-1}; MS (FAB) *m/z* 597([M-OH]$^+$).

Preparation of 5,8-diiodo-1,4-bis(phenylethynyl)naphthalene (10).

To a solution of **9** (major isomer, 1.16 g, 1.89 mmol) in EtOH (6 mL) was added $SnCl_2 \cdot 2H_2O$ (868 mg, 3.78 mmol). The mixture was stirred at 60 °C for 1 h. The resulting precipitates were filtered and washed with EtOH to give 5,8-diiodo-1,4-bis(phenylethynyl)naphthalene (**10**) (1.08 g, 99%) as a yellow solid. Mp 156–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.90 (s, 2H), 7.87 (s, 2H), 7.66–7.62 (m, 4H) 7.41–7.38 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 143.3, 134.8, 133.6,

130.8, 128.8, 128.5, 124.5, 123.6, 104.5, 94.2, 89.1; IR (KBr) 3051, 2200, 1970, 1954, 1904, 1890, 1681, 1595, 1566, 1544, 1489, 1439, 1374, 1341, 1259, 1197, 1181, 1069, 1018, 993, 918, 852, 831, 798, 755, 692, 665, 643, 577, 529 cm^{-1}; HR-MS (EI) calcd for $C_{26}H_{14}I_2$ (M^+) *m/z* 579.9185, found 579.9200.

Preparation of 1,4,5,8-tetrakis(phenylethynyl)naphthalene (4a).

To a mixture of **10** (972 mg, 1.68 mmol), $Pd(PPh_3)_4$ (196 mg, 170 μmol) and CuI (132 mg, 693 μmol) in THF/Et_3N (1:1, 40 mL) was added phenylacetylene (500 μL, 4.55 mmol). The mixture was stirred at rt for 15 h and then diluted with $CHCl_3$ and saturated aqueous solution of NH_4Cl. Aqueous layer was separated and extracted with $CHCl_3$. Combined organic layer was washed with brine and then dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the resulting crude product was purified by silica gel column chromatography ($CHCl_3$/hexane = 1/4) followed by GPC to give 1,4,5,8-tetrakis(phenylethynyl)naphthalene (**4a**) (623 mg, 70%) as a yellow solid. Mp 142–144 °C (decomp.); ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.84 (s, 4H), 7.38–7.34 (m, 8H), 7.24–7.19 (m, 4H), 7.16–7.11 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 134.3, 132.5, 131.6, 128.1, 128.0, 123.6, 122.0, 99.6, 89.9; IR (KBr) 3077, 3053, 3033, 3017, 1594, 1546, 1489, 1440, 1408, 1390, 1156, 1068, 1024, 985, 933, 918, 843, 754, 689, 640, 541, 528, 512, 468 cm^{-1}; HR-MS (FAB) calcd for $C_{42}H_{24}$ (M^+) *m/z* 528.1878, found 528.1842.

X-ray crystallographic structure analysis

A single crystal of **4a** suitable for X-ray diffraction was obtained from benzene/MeCN. Data collection was conducted with a Rigaku Mercury CCD area detector with graphite monochromated MoKα radiation. The structure was solved by direct method[S2] and expanded using Fourier techniques. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares method using SHELXL-97.[S3] Hydrogen atoms were placed at calculated positions and refined "riding" on their corresponding carbon atoms. In the subsequent refinement, the function $\Sigma w(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively.

Computational methods.

DFT calculations were perfomed with the Gaussian 09 program package.[S4] The geometries were optimized using the B3LYP method with the 6-31G* basis set. The natures of the stationary points were assessed by means of vibration frequency analysis. The single point calculations of Mol-A and Mol-B were conducted using the Cartesian coordinates of each structure obtained by the X-ray crystal structure analyses, except for those of hydrogen atoms which were optimized.

2. UV-vis and fluorescence spectra of 4a in $CHCl_3$

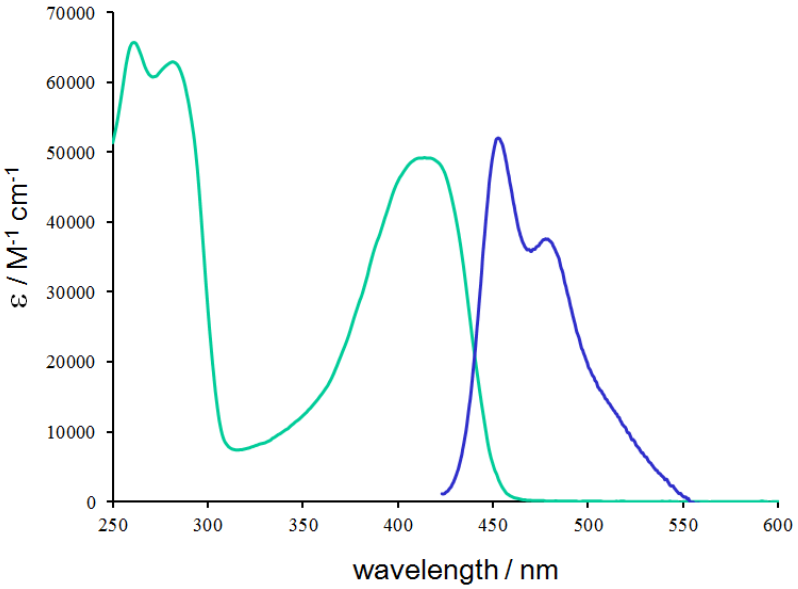


Fig. S1 UV-vis (light green) and fluorescence (blue, arbitrary scale, excited at 414 nm) spectra of **4a** in $CHCl_3$.

3. Overlays of the structures of 4a in crystal and optimized structure

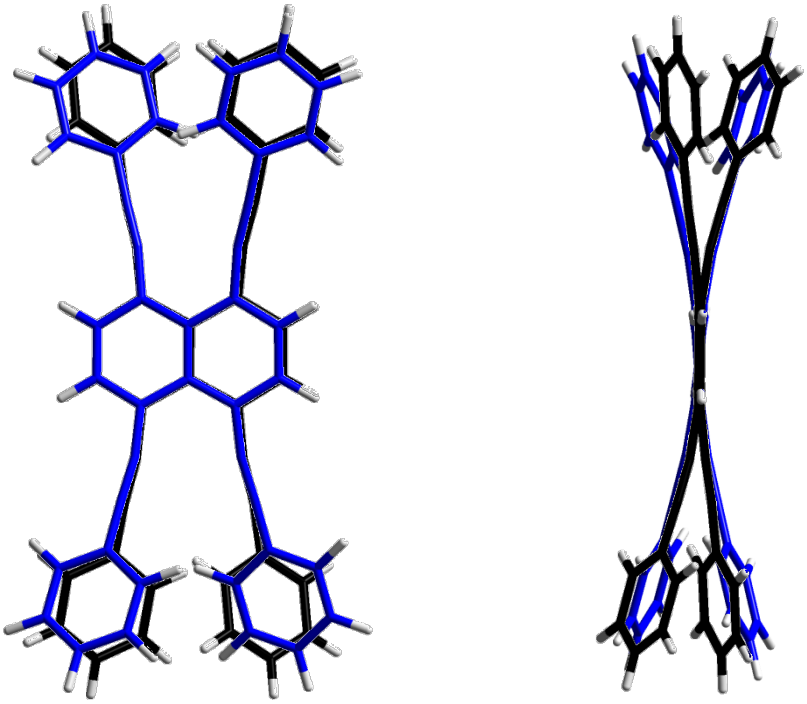


Fig. S2 Overlays of Mol-A in the crystal (black) and optimized structure (blue).

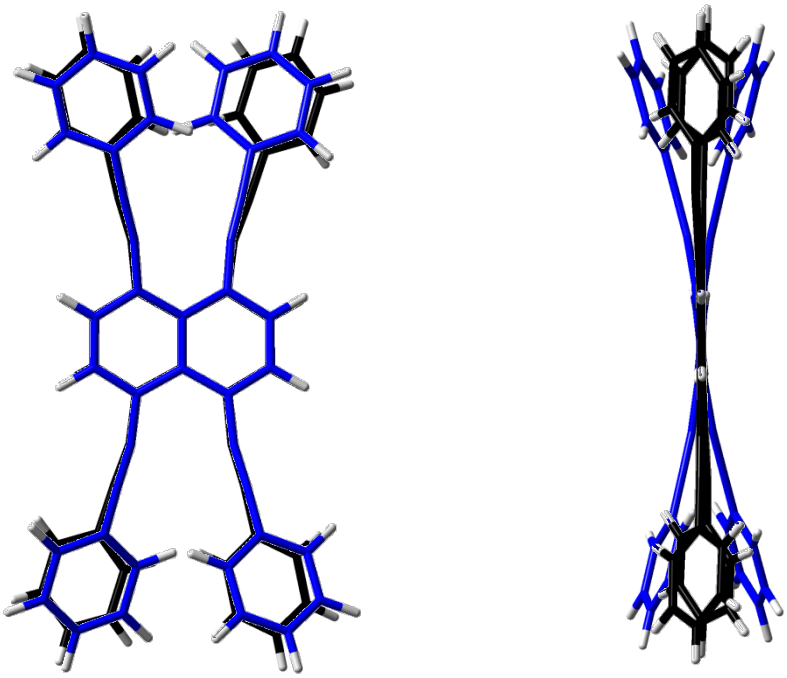


Fig. S3 Overlays of Mol-B in the crystal (black) and optimized structure (blue).

4. Molecular arrangement of 4a in the crystal

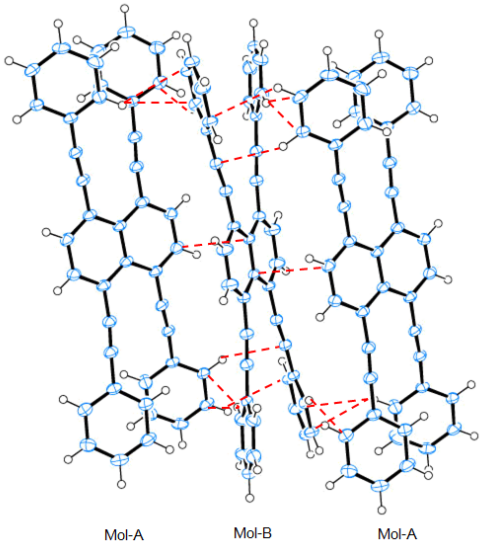
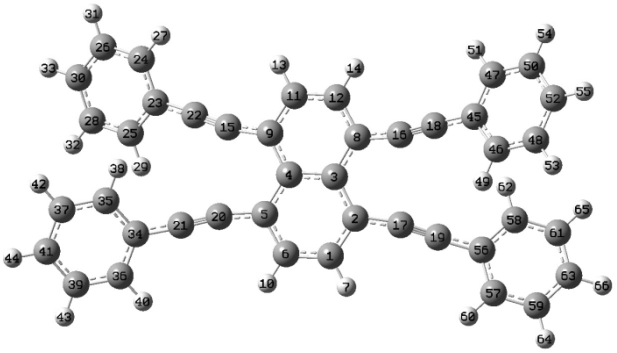


Fig. S4 Molecular arrangement of **4a** in crystal. Red dotted lines show short contacts (< vDW radius) between neighboring molecules. Displacement ellipsoids are drawn at the 50% probability level. Short contacts between molecules located behind and in front of the plane were omitted for clarity.

5. Cartesian coordinates of optimized structure of 4a



SCF Done: E(RB3LYP) = -1614.72626404 A.U. after 6 cycles

Number of imaginary frequencies: 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.692651	-2.446865	-0.065297
2	6	0	1.419518	-1.256744	-0.099893
3	6	0	0.721879	-0.000052	-0.000003
4	6	0	-0.721866	-0.000064	-0.000021
5	6	0	-1.419485	-1.256766	0.099840
6	6	0	-0.692611	-2.446878	0.065141
7	1	0	1.229510	-3.386524	-0.141029
8	6	0	1.419486	1.256660	0.099888
9	6	0	-1.419500	1.256634	-0.099908
10	1	0	-1.229462	-3.386546	0.140806
11	6	0	-0.692652	2.446757	-0.065244
12	6	0	0.692610	2.446769	0.065223
13	1	0	-1.229518	3.386412	-0.140967
14	1	0	1.229462	3.386433	0.140927
15	6	0	-2.819145	1.390161	-0.318941
16	6	0	2.819131	1.390235	0.318884
17	6	0	2.819169	-1.390293	-0.318842
18	6	0	3.960157	1.716021	0.594654
19	6	0	3.960208	-1.716058	-0.594586

20	6	0	-2.819127	-1.390329	0.318859
21	6	0	-3.960168	-1.716044	0.594656
22	6	0	-3.960167	1.715918	-0.594764
23	6	0	-5.303893	2.046983	-0.928391
24	6	0	-5.777873	3.364362	-0.757398
25	6	0	-6.180111	1.070365	-1.445719
26	6	0	-7.088736	3.690718	-1.092344
27	1	0	-5.106516	4.119895	-0.360652
28	6	0	-7.489407	1.407153	-1.777887
29	1	0	-5.820086	0.055693	-1.579017
30	6	0	-7.948931	2.715147	-1.603452
31	1	0	-7.440791	4.709637	-0.955045
32	1	0	-8.154317	0.644722	-2.174551
33	1	0	-8.971543	2.973222	-1.865006
34	6	0	-5.303902	-2.046991	0.928360
35	6	0	-6.179986	-1.070360	1.445889
36	6	0	-5.778026	-3.364304	0.757232
37	6	0	-7.489287	-1.407066	1.778112
38	1	0	-5.819854	-0.055738	1.579288
39	6	0	-7.088896	-3.690580	1.092239
40	1	0	-5.106773	-4.119852	0.360339
41	6	0	-7.948955	-2.714993	1.603537
42	1	0	-8.154095	-0.644625	2.174926
43	1	0	-7.441052	-4.709450	0.954838
44	1	0	-8.971576	-2.972993	1.865132
45	6	0	5.303872	2.047143	0.928264
46	6	0	6.180153	1.070594	1.445609
47	6	0	5.777779	3.364548	0.757225
48	6	0	7.489443	1.407463	1.777728
49	1	0	5.820186	0.055907	1.578960
50	6	0	7.088634	3.690985	1.092126
51	1	0	5.106369	4.120032	0.360477
52	6	0	7.948895	2.715473	1.603234
53	1	0	8.154401	0.645081	2.174403
54	1	0	7.440626	4.709921	0.954791
55	1	0	8.971504	2.973604	1.864751

56	6	0	5.303933	-2.047115	-0.928217
57	6	0	5.777829	-3.364549	-0.757348
58	6	0	6.180223	-1.070504	-1.445418
59	6	0	7.088688	-3.690947	-1.092265
60	1	0	5.106405	-4.120083	-0.360718
61	6	0	7.489519	-1.407334	-1.777553
62	1	0	5.820268	-0.055796	-1.578638
63	6	0	7.948964	-2.715369	-1.603224
64	1	0	7.440673	-4.709903	-0.955062
65	1	0	8.154489	-0.644902	-2.174112
66	1	0	8.971578	-2.973464	-1.864751

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6. ^{1}H and ^{13}C NMR spectra of new compounds

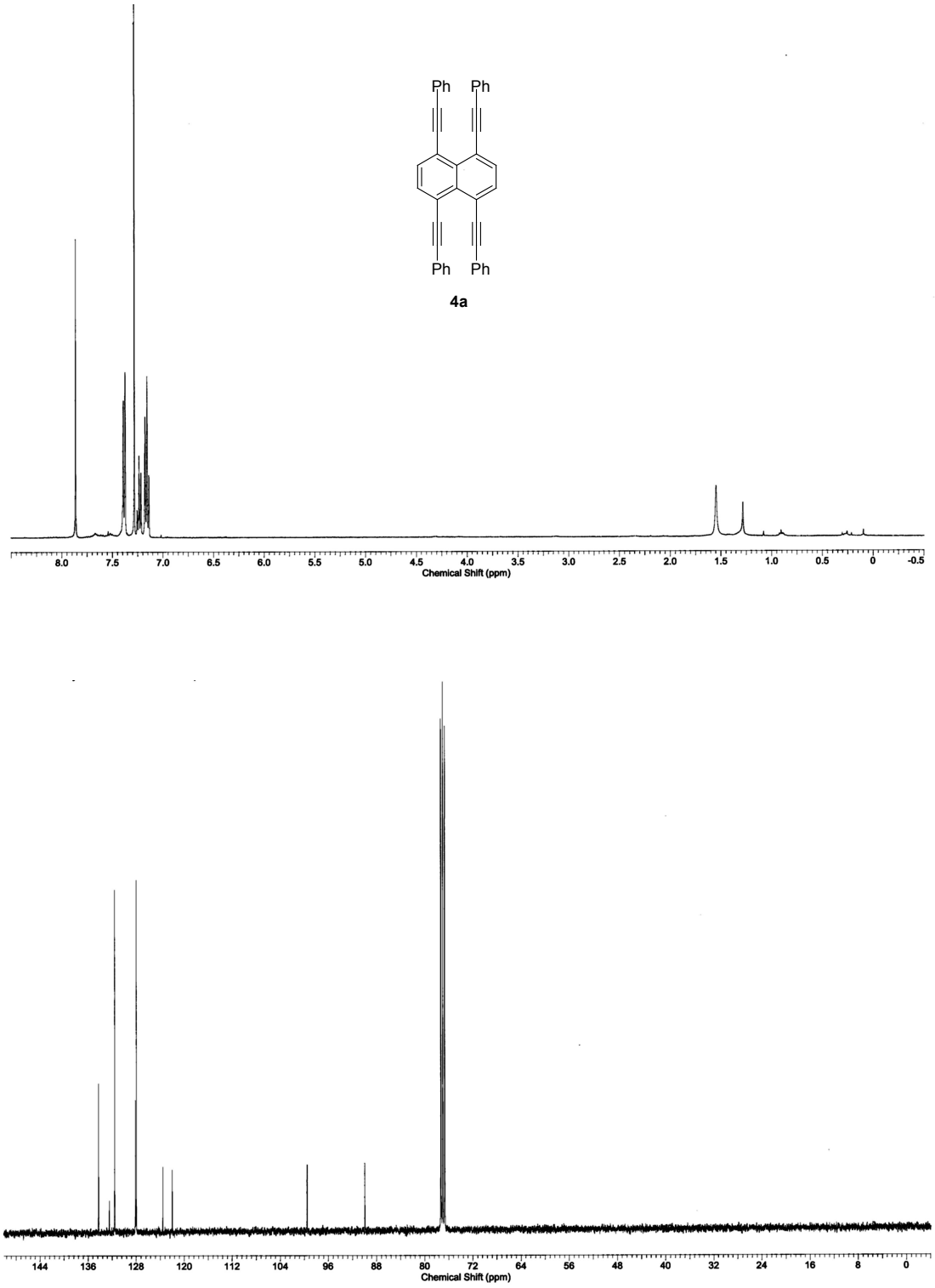

Figure S5 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4a**.

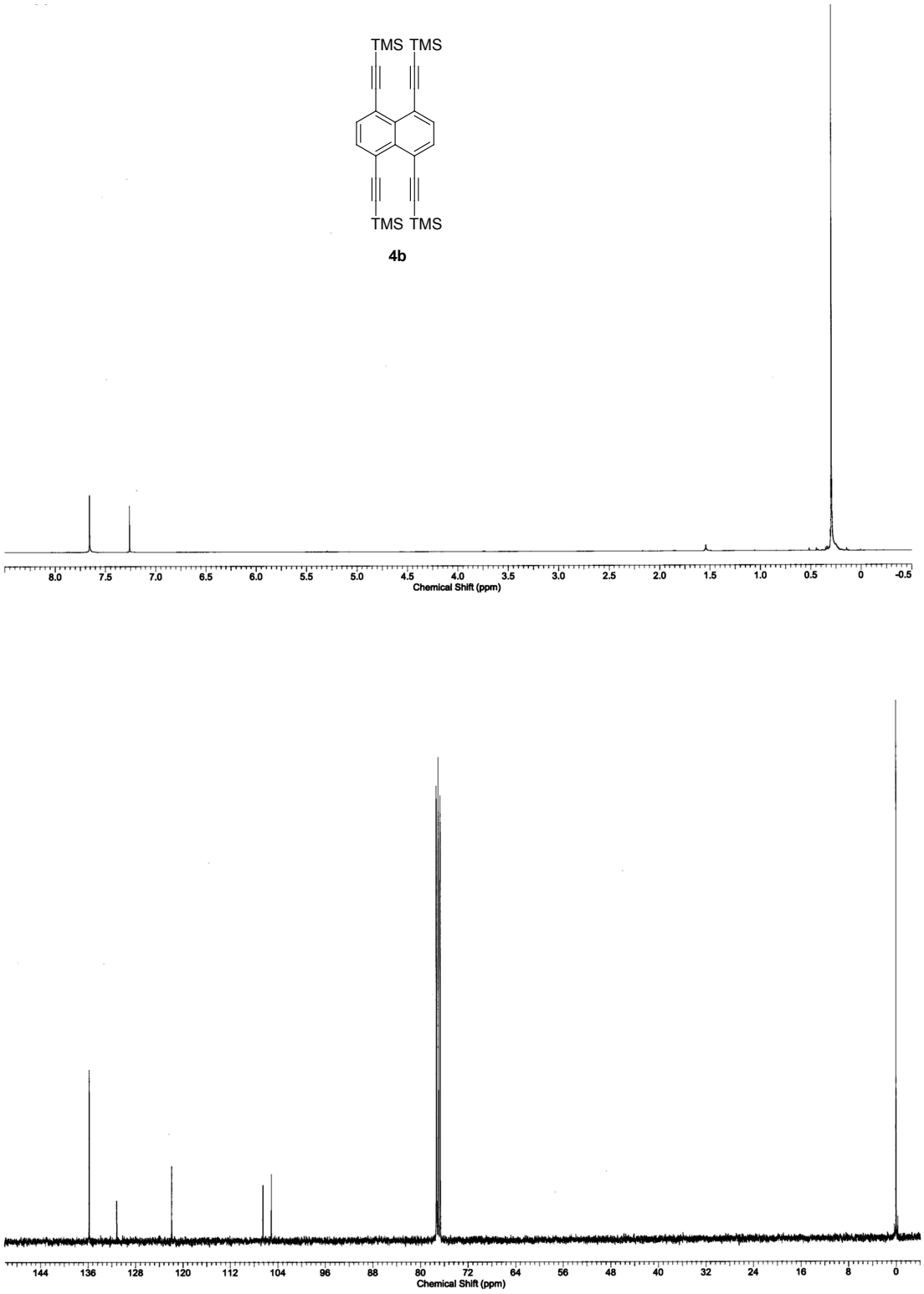

Figure S6 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4b**.

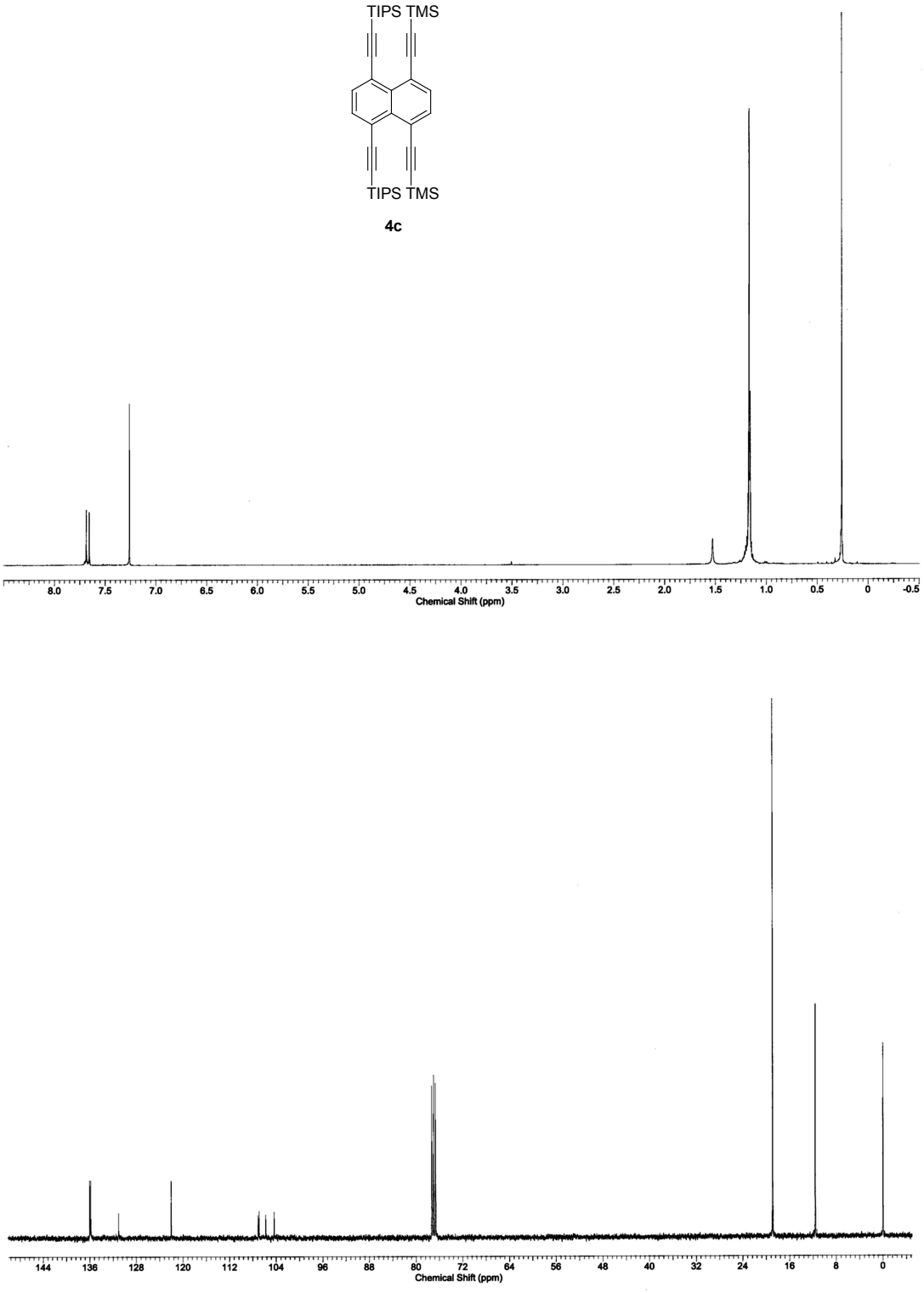

Figure S7 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4c**.

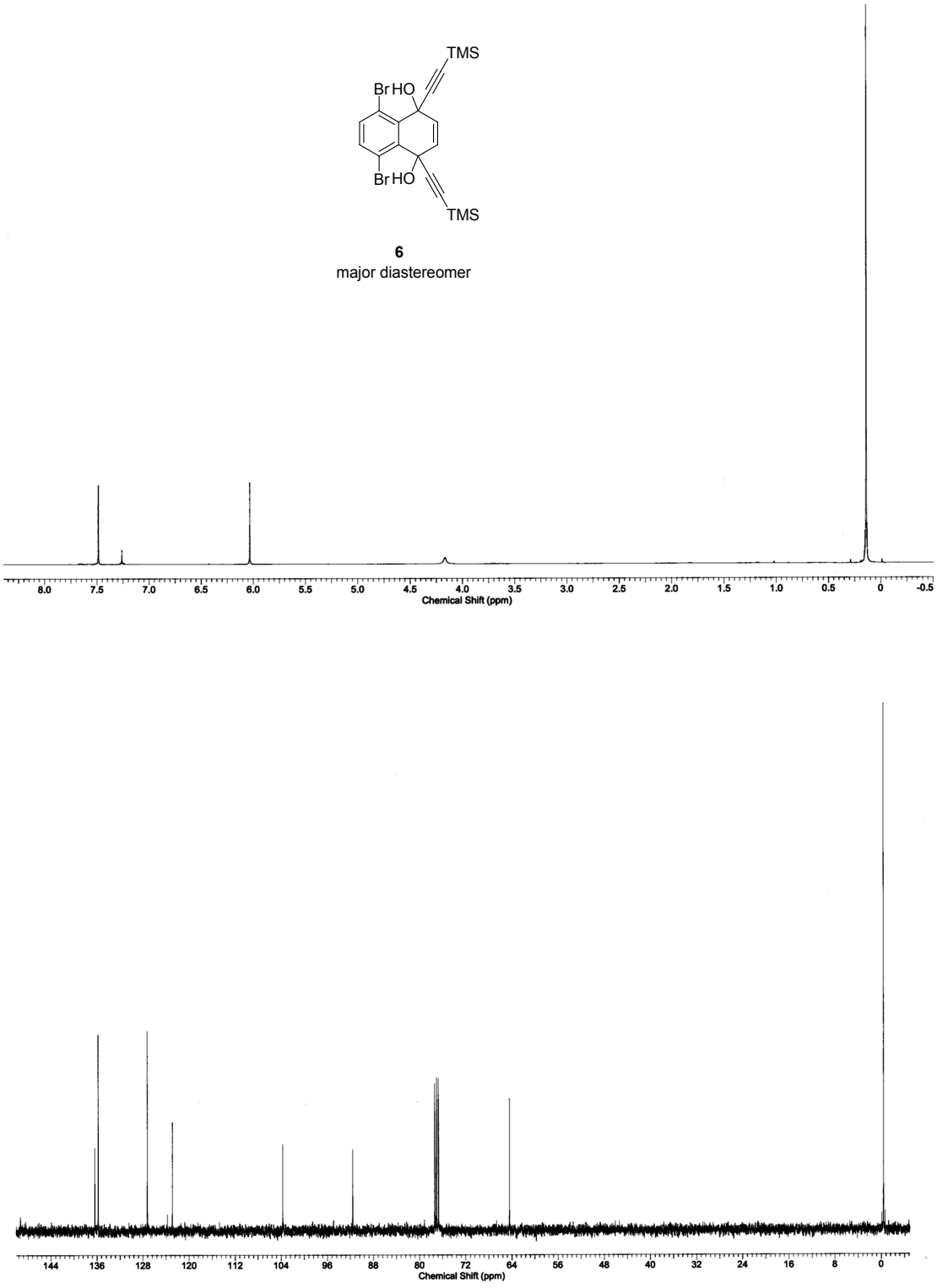

Figure S8 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **6** (major diastereomer).

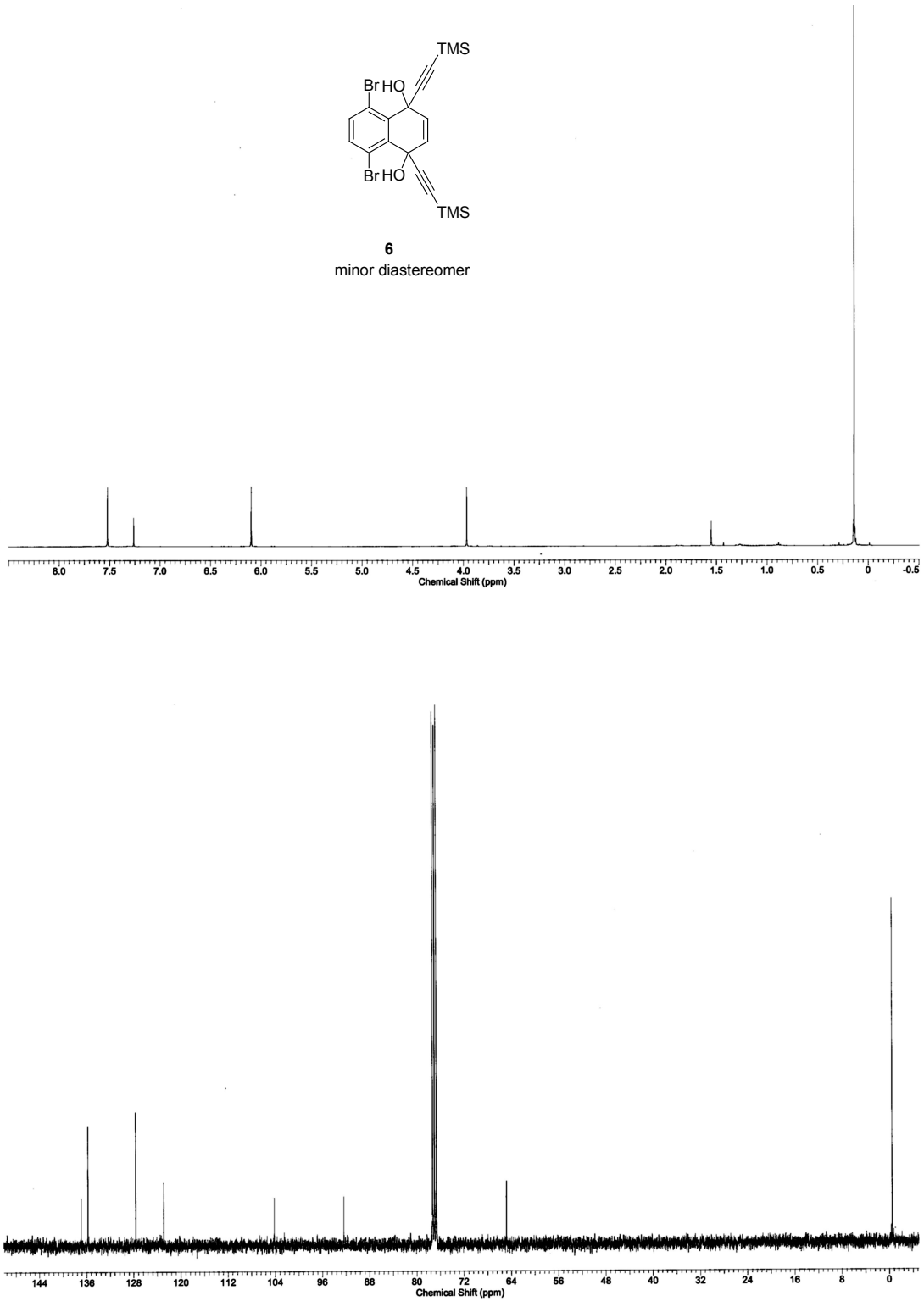

Figure S9 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **6** (minor diastereomer).

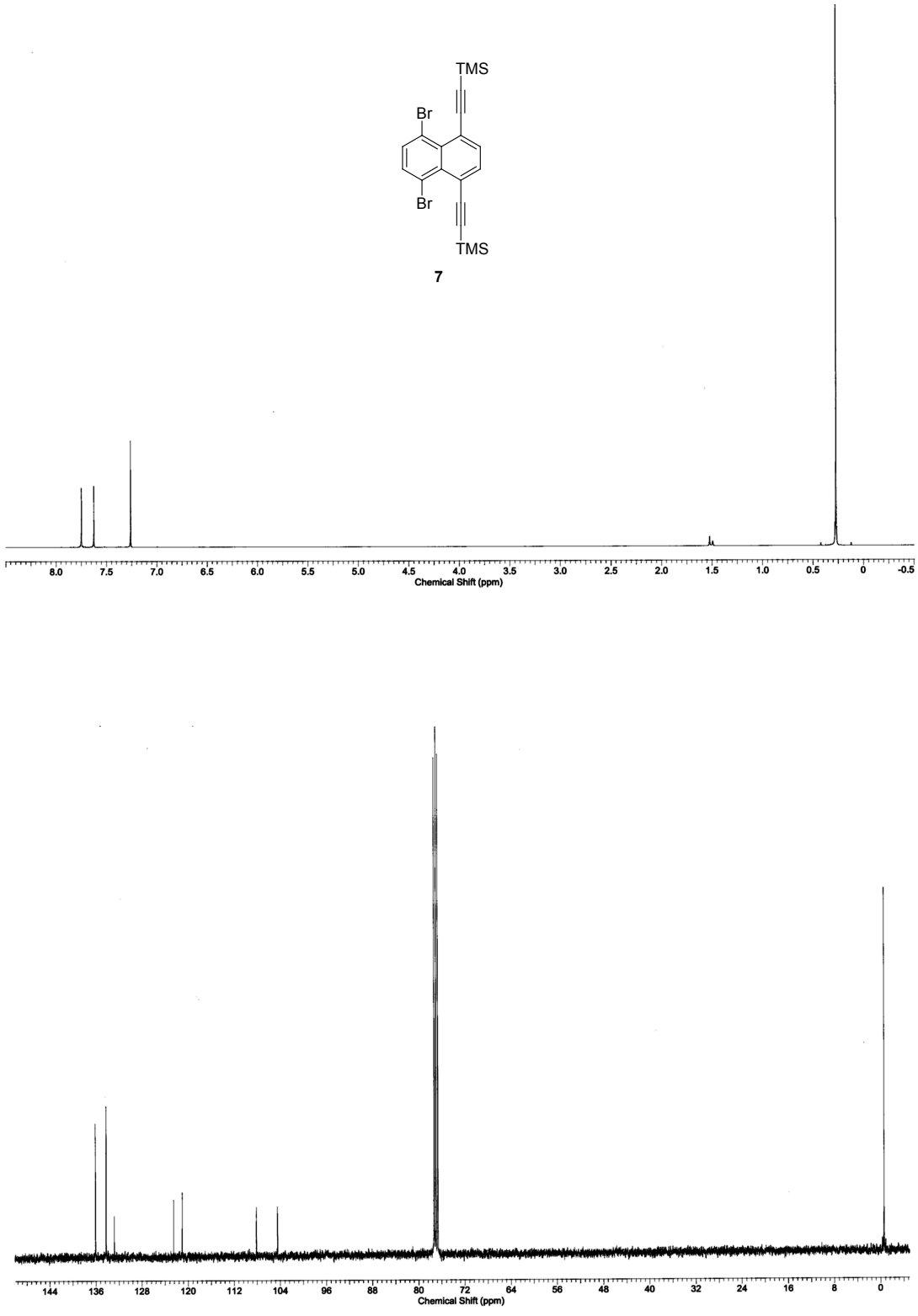

Figure S10 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **7**.

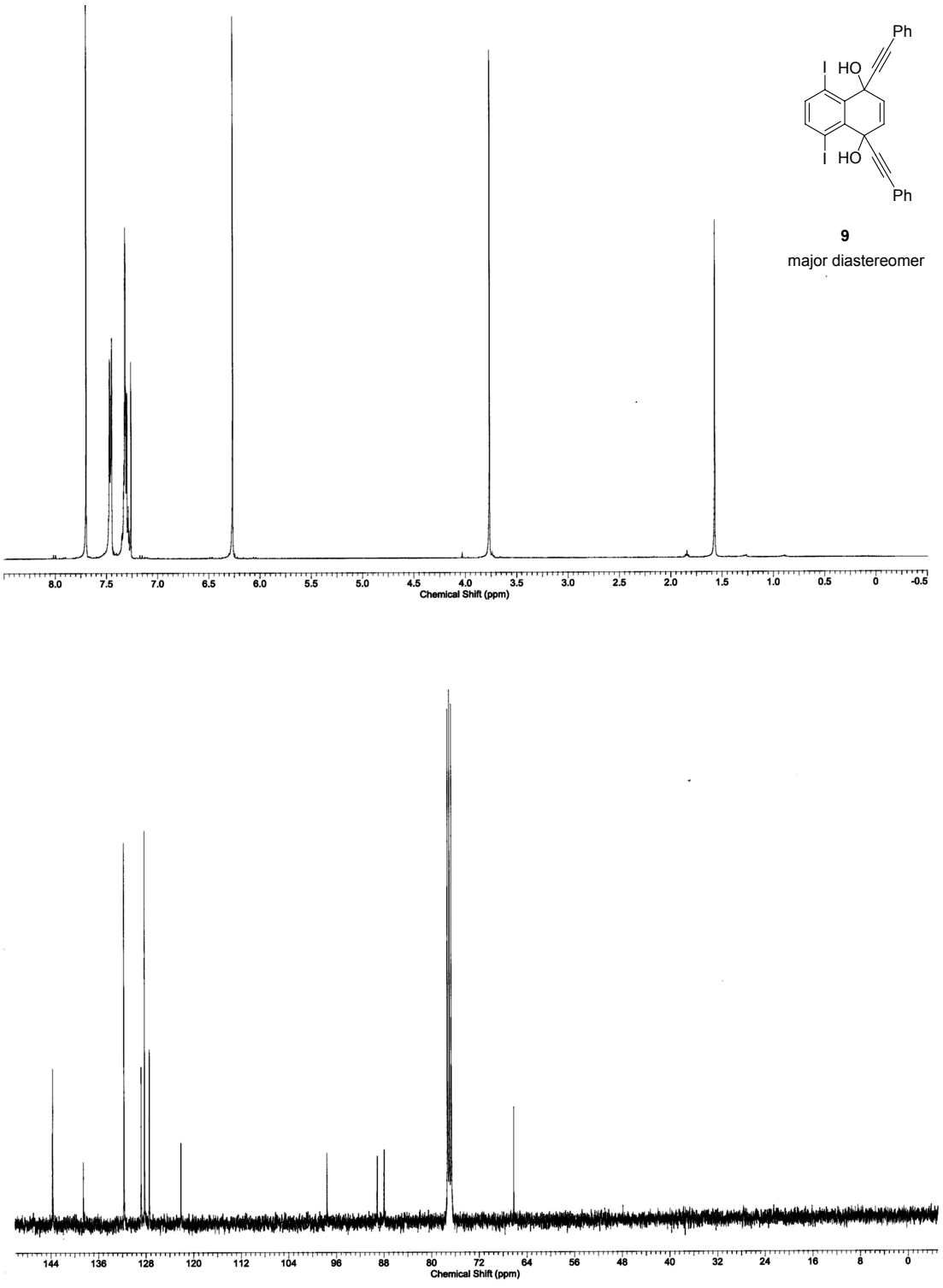

Figure S11 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **9** (major diastereomer).

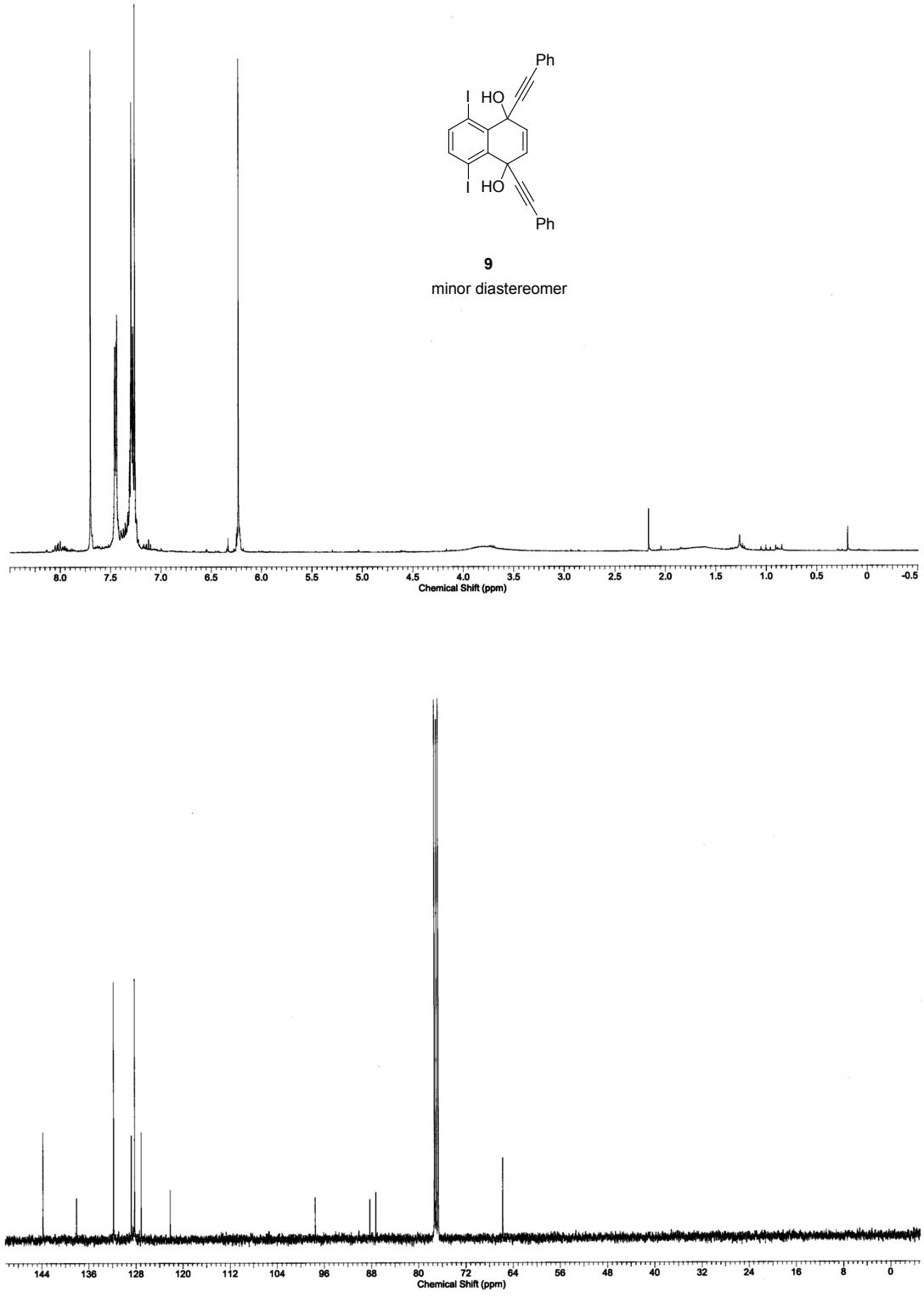

Figure S12 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **9** (minor diastereomer).

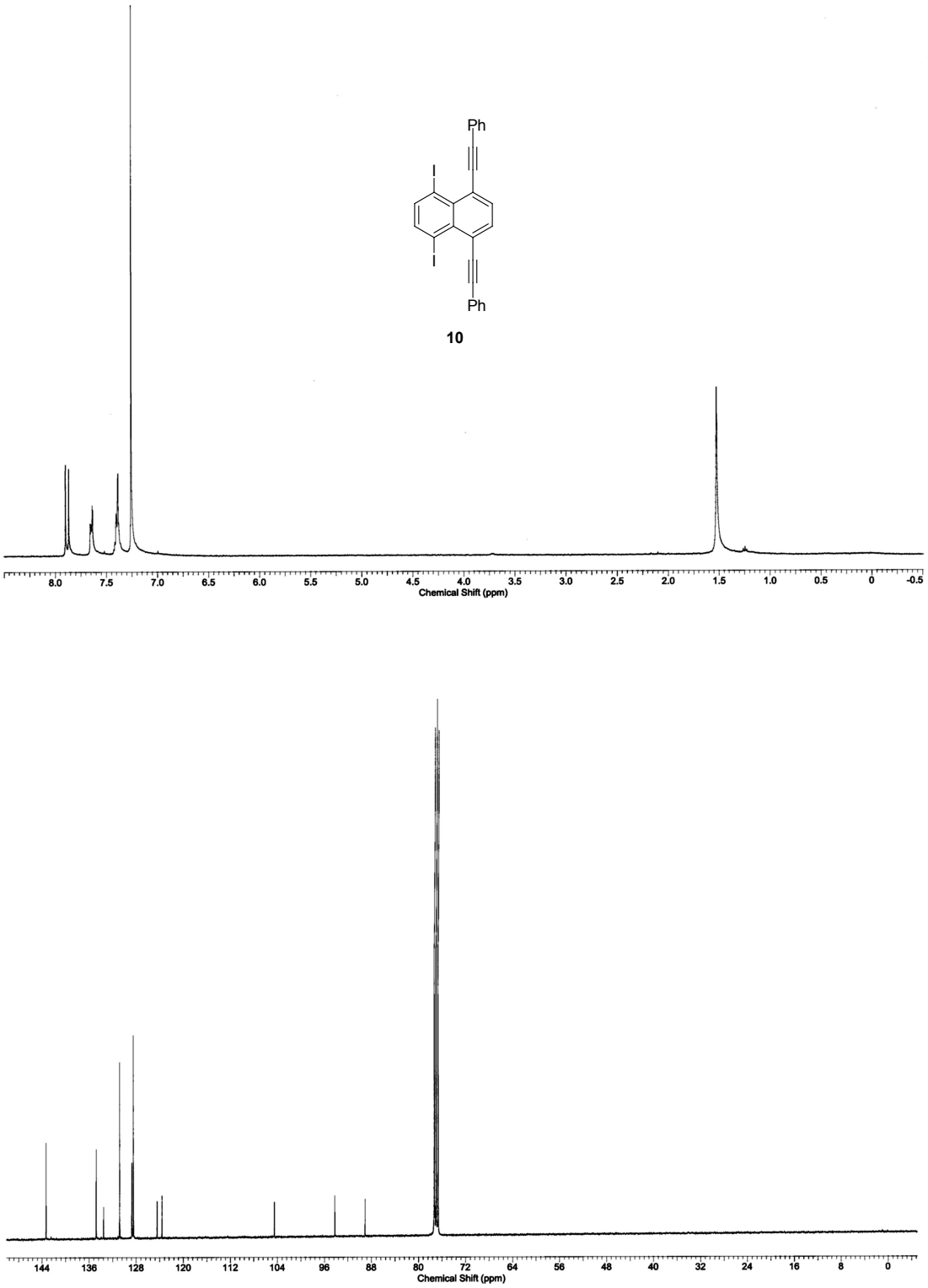

Figure S13 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **10**.

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