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Synthesis of bis-phosphonium salts from 6-bromo-1,2-naphthoquinone and α,ω-bis(diphenylphosphino)alkanes

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^{1}H, ^{13}C, ^{13}C-{^{1}H}, ^{31}P, and ^{31}P-{^{1}H} NMR spectra were recorded on Bruker Avance 400 (100.6 MHz, ^{13}C) and Bruker CXP-100 instruments (36.48 MHz, ^{31}P) (20 °C, δ scale with reference to TMS) with signals for the residual protons of the deuterated solvent or the carbon nuclei as the internal standards (^{1}H and ^{13}C) and with H_3PO_4 as the external standard (^{31}P). IR spectra were recorded on a Bruker Vector 22 FTIR spectrometer in Nujol. The EI mass spectra were obtained on a TRACE MS Finnigan MAT instrument; the energy of ionizing electrons was 70 eV, the temperature of the ion source was 200 °C. The samples were introduced into the ion source using a direct inlet system. Heating of the ampoule was carried out in a programmed mode within the temperatures range of 35–150 °C at a rate of 35 K min^{-1}. The MS data were processed using the 'Xcalibur' system program.

*(Pentane-1,5-diyl)bis[(7-bromo-3-hydroxy-4-oxonaphthalen-1(4*H*)-ylidene)(diphenyl)phosphorane]* **7**. To the boiling suspension of 0.54 g (2.27 mmol) quinone **1** in 20 ml of benzene a solution of 0.50 g (1.13 mmol) 1,5-bis(diphenylphosphino)pentane **3** in 10 ml of benzene was added dropwise with permanent bubbling of argon. The reaction mixture became black and a light-green precipitate was gradually formed. The reaction mixture acquired a green-brown tinge during 10-15 min. The precipitate was filtered off, washed with 5 ml of benzene and dried under reduced pressure (12 Torr). IR, ν/cm^{-1}: 1597, 1537, 1344, 1211, 1156, 1110, 1074, 996, 967, 821, 744, 721, 693, 529, 479. ^{1}H NMR (400 MHz, DMF-d$_7$) δ: 7.25 (d, H^2, $^3J_{PCCH}$ 14.7 Hz), 7.32 (br. s, H^8), 8.31 (dd, H^6, $^3J_{HCCH}$ 8.8 Hz, $^4J_{HCCCH}$ 1.5 Hz), 7.28 (dd, H^5, $^3J_{HCCH}$ 8.6 Hz, $^5J_{PCCCCH}$ 1.7 Hz), 8.03 (m, H^{10}, H^{11}), 8.20 (dt, H^{12}, $^3J_{HCCH}$ 6.9 Hz, overlaps with H^5 signal), 3.43 (m, H^{13}), 1.72 (m, H^{14}), 2.38 (m, H^{15}). ^{31}P / ^{31}P-{^{1}H} NMR (DMF-d$_7$) δ_P: 19.1 m (s). Found (%): C, 64.25; H, 4.41; Br, 17.41; P, 6.37. Calc. for $C_{49}H_{40}Br_2O_4P_2$ (%): C, 64.33; H, 4.37; Br, 17.50; P, 6.78.

(Butane-1,4-diyl)bis[(7-bromo-3,4-dihydroxy-1-naphthyl)(diphenyl)phosphonium] dibromide **8**: IR (ν/cm^{-1}): 3560–3564 (OH), 1620, 1595, 1562, 1341, 1210, 1163, 1113, 1080, 1028, 984, 963, 919, 848, 819, 743, 721, 690, 529, 502, 484. ^{1}H NMR (DMSO-d$_6$) δ: 8.18 (dd, H^6, $^3J_{HCCH}$ 9.0 Hz, $^4J_{HCCCH}$ 1.8 Hz), 7.83 (dt, H^{12}, $^3J_{HCCH}$ 7.2 Hz, $^5J_{PCCCCH}$ 0.9–1.3 Hz), 7.78 (dd, H^{10}, $^3J_{PCCH}$ 12.6–13.0 Hz, $^3J_{HCCH}$

7.6 Hz), 7.73 (d, H^{2}, $^{3}J_{PCCH}$ 16.6 Hz), 7.69 (ddd, H^{11}, $^{3}J_{HCCH}$ 7.6 Hz, $^{3}J_{HCCH}$ 7.2 Hz, $^{4}J_{PCCCH}$ 3.1 Hz), 7.50 (dd, H^{5}, $^{3}J_{HCCH}$ 9.0 Hz, $^{5}J_{PCCCCH}$ 1.8 Hz), 7.31 (br. s, H^{8}), 2.49 (m, H^{13}), 1.83 (m, H^{14}). ^{13}C NMR (DMSO-d$_{6}$) δ: 146.71 [m (d), C^{4}, $^{3}J_{HCCC}$ 6.1 Hz, $^{4}J_{PCCCC}$ 2.5 Hz], 140.31 [dd (d), C^{3}, $^{3}J_{PCCC}$ 17.8 Hz, $^{2}J_{HCC}$ 3.5 Hz], 134.57 [dt (br. s), C^{12}, $^{1}J_{HC}$ 160.8 Hz, $^{3}J_{HCCC}$ 8.1 Hz, $^{2}J_{HCC}$ 2.5 Hz], 133.05 [ddd (d), C^{10}, $^{1}J_{HC}$ 165.1 Hz, $^{2}JP_{CC}$ 10.2 Hz, $^{3}J_{HCCC}$ 6.6 Hz], 130.18 [ddd (d), C^{11}, $^{1}J_{HC}$ 167.33 Hz, $^{3}J_{PCCC}$ 12.7 Hz, $^{3}J_{HCCC}$ 7.1 Hz], 129.61 [m (d), C^{8a}, $^{2}J_{PCC}$ 8.1 Hz, overlaps with C^{11} signal], 129.59 [dd (d), C^{2}, $^{1}J_{HC}$ 161.4 Hz, $^{2}J_{PCC}$ 11.7 Hz], 128.59 [dd (s), C^{6}, $^{1}J_{HC}$ 169.4 Hz, $^{3}J_{HCCC}$ 5.6 Hz], 126.02 [ddd (d), C^{8}, $^{1}J_{HC}$ 163.3 Hz, $^{3}J_{PCCC}$ 6.6 Hz, $^{3}J_{HCCC}$ 5.6 Hz], 125.30 [d (br. s), C^{5}, $^{1}J_{HC}$ 166.3 Hz], 125.13 [dd (d), C^{4a}, $^{3}JP_{CCC}$ 11.7 Hz, $^{3}J_{HCCC}$ 4.1 Hz], 119.37 [ddd (s), C^{7}, $^{3}J_{HCCC}$ 13.2 Hz, $^{2}J_{HCC}$ 6.6 Hz, $^{2}J_{HCC}$ 5.1 Hz], 119.25 [dt (d), C^{9}, $^{1}J_{PC}$ 85.8 Hz, $^{3}J_{HCCC}$ 8.1 Hz], 97.97 [br. d (d), C^{1}, $^{1}J_{PC}$ 92.1 Hz], 23.44 [tdm (d), C^{14}, $^{1}J_{HC}$ 131.7 Hz, ^{2}J+ 21.9 Hz], 22.37 [tdm (d), C^{13}, $^{1}J_{HC}$ 131.7 Hz, $^{1}J_{PC}$ 51.8 Hz]. ^{31}P / ^{31}P-{^{1}H} NMR [36.48 MHz, CDCl$_{3}$–DMSO-d$_{6}$ (1:3)] d: 22.2 [m (s)]. Found (%): C, 54.25; H, 3.41; Br, 30.41; P, 5.37. Calc. for $C_{48}H_{40}Br_{4}O_{4}P_{2}$ (%): C, 54.23; H, 3.76; Br, 30.13; P, 5.84.

(Pentane-1,5-diyl)bis[(7-bromo-3,4-dihydroxy-1-naphthyl)(diphenyl)phosphonium] ditriflate **10**. To solution of compound **7** (0.47 g, 0.51 mmol) in 10 ml of $CH_{2}Cl_{2}$ under argon bubbling 0.09 ml (1.03 mmol) of triflic acid was added dropwise. The reaction mixture turned maroon. After 24 h, the mixture was concentrated at reduced pressure (14 Torr) to a brown glassy substance, which was triturated with dry Et$_{2}$O (15 ml). The colorless crystals that formed were filtered off, washed with dry Et$_{2}$O (5 ml) and dried at reduced pressure (12 Torr). IR, ν/cm^{-1}: 3339 (OH), 1725, 1669, 1625, 1595 (C=C$_{arom}$), 1564, 1502, 1342 (C–F), 1224, 1162 (ν_{as} SO$_{2}$), 1109, 1078, 1026 (ν_{as} SO$_{2}$), 980, 960, 818, 723, 638, 512. ^{1}H NMR (CDCl$_{3}$) δ: 8.24 (d, H^{2}, $^{3}J_{PCCH}$ 15.9 Hz), 7.74 (br. s, H^{8}, overlaps with the signal of H^{12}), 8.20 (dd, H^{6}, $^{3}J_{HCCH}$ 9.1 Hz, $^{4}J_{HCCCH}$ 1.8 Hz), 7.50 (dd, H^{5}, $^{3}J_{HCCH}$ 9.0 Hz, $^{5}J_{PCCCCH}$ 1.5 Hz), 7.71 (br. d, H^{10}, $^{2}J_{PCCH}$ 12.6 Hz, $^{3}J_{HCCH}$ 7.6 Hz), 7.66 (dd, H^{11}, $^{3}J_{HCCH}$ 7.6 Hz, $^{4}J_{PCCCH}$ 3.2-3.6 Hz), 7.75 (dd, H^{12}, overlaps with the signal of H^{5}, $^{3}J_{HCCH}$ 7.7 Hz, $^{5}J_{PCCCCH}$ 1.5 Hz), 3.23 (br. dt, H^{13}, $^{2}J_{PCH}$ 12.1 Hz, $^{3}J_{HCCH}$ 3.9 Hz), 1.69 (m, H^{14}, $^{3}J_{PCCH}$ 5.5 Hz), 2.06 (m, H^{15}). ^{13}C NMR (CDCl$_{3}$) δ_{C}: 146.55 [d (d), C^{4}, $^{4}J_{PCCCC}$ 2.6 Hz], 139.97 [dd (d), C^{3}, $^{3}J_{PCCC}$ 17.9 Hz, $^{2}J_{HCC}$ 3.3 Hz], 127.38 [dd (d), C^{2}, $^{1}J_{HC}$ 161.0 Hz, $^{2}J_{PCC}$ 12.1 Hz], 98.71 [d (d), C^{1}, $^{1}J_{PC}$ 92.1 Hz], 130.18 [m (d), C^{8a}, $^{2}J_{PCC}$ 7.7 Hz, overlaps with C^{11} signal], 127.47 [ddd (d), C^{8}, $^{1}J_{HC}$ 162.5 Hz, $^{3}J_{PCCC}$ 6.6 Hz, $^{3}J_{HCCC}$ 5.1 Hz], 120.42 [dd (s), C^{7}, $^{3}J_{HCCC}$ 12.1 Hz, $^{2}J_{HCC}$ 4.4 Hz], 129.38 [dd (s), C^{6}, $^{1}J_{HC}$ 169.1 Hz, $^{3}J_{HCCC}$ 5.5 Hz], 124.97 [d (s), C^{5}, $^{1}J_{HC}$ 166.9 Hz], 124.01 [m (d), C^{4a}, $^{3}J_{PCCC}$ 11.7 Hz, overlaps with C^{5} signal], 118.75 [dt (d), C^{9}, $^{1}J_{PC}$ 84.7 Hz, $^{3}J_{HCCC}$ 8.1 Hz], 132.95 [ddd (d), C^{10}, $^{1}J_{HC}$ 164.7 Hz, $^{2}J_{PCC}$ 10.3 Hz, $^{3}J_{HCCC}$ 7.3 Hz], 130.43 [ddd (d), C^{11}, $^{1}J_{HC}$ 166.2 Hz, $^{3}J_{PCCC}$ 12.8 Hz, $^{3}J_{HCCC}$ 7.3 Hz], 134.71 [br. dd (d), C^{12}, $^{1}J_{HC}$ 164.7 Hz, $^{4}J_{PCCCC}$ 1.5 Hz], 25.51 [td (d), C^{13}, $^{1}J_{HC}$ 132.4 Hz, $^{1}J_{PC}$ 53.9 Hz], 22.64 [br. ddd (dd), C^{14}, $^{1}J_{HC}$ 128.7 Hz, $^{2}J_{PCC}$ 3.9 Hz,

$^4J_{PCCCC}$ 2.0 Hz], 31.30 [ddm (dd), C^{15}, $^1J_{HC}$ 126.9 Hz, $^3J_{PCCC}$ 17.9-18.2 Hz], 120.89 [q (q), C^{16}, $^1J_{FC}$ 321.0 Hz]. ^{31}P / ^{31}P-{^{1}H} NMR (CDCl$_3$) δ_P: 25.6 m (s). Found (%): Br, 13.90; P, 5.04; S, 5.23. Calc. for $C_{51}H_{42}Br_2O_{10}P_2F_6S_2$ (%): Br, 13.17; P, 5.10; S 5.27.

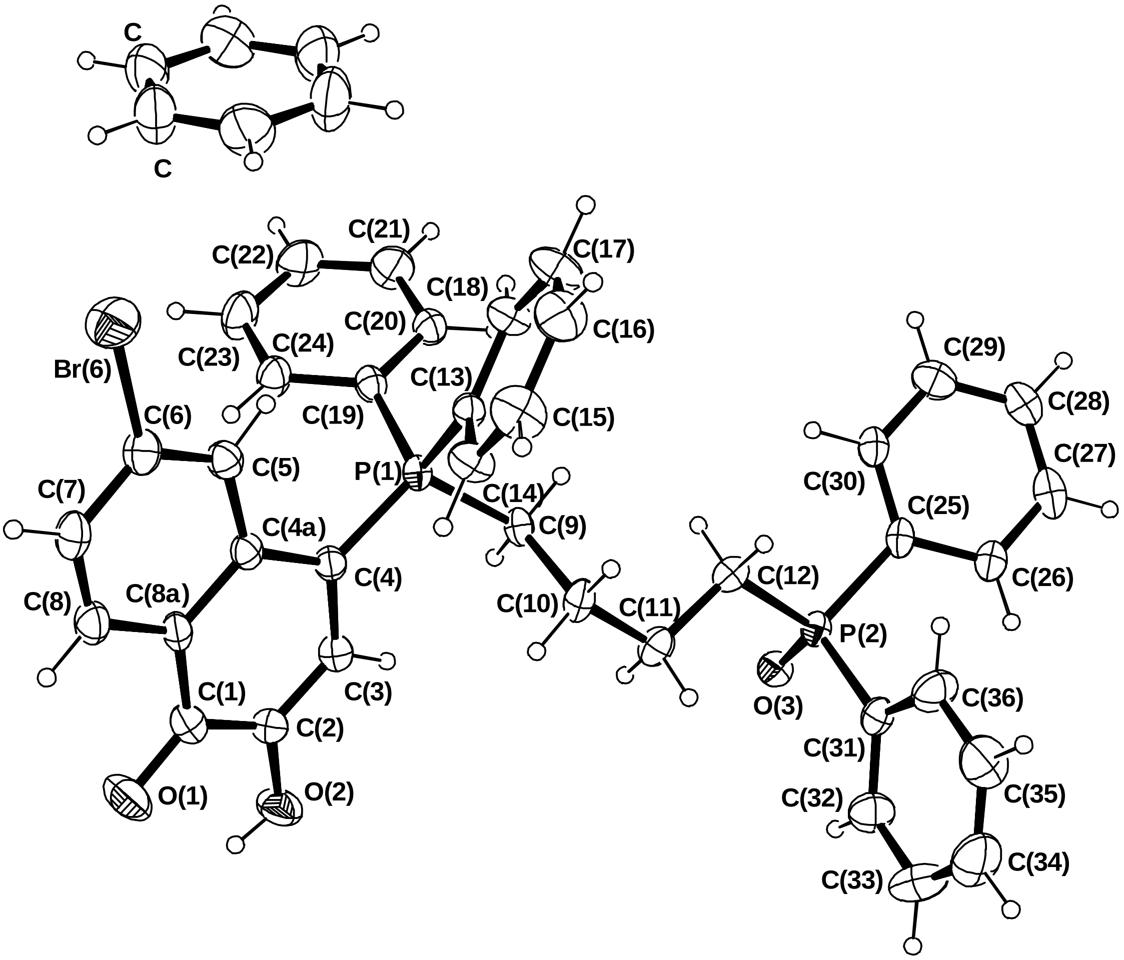

Figure S1 Molecular structure and atom-labeling scheme for **5** (solvate with three benzene molecules, one benzene molecule is shown for clarity).

Table S1 Bond Distances (Å) for **5**.

Br6–C6	1.895(4)	C2–C3	1.391(4)
S50–O52	1.425(3)	C3–C4	1.378(5)
S50–C50	1.783(6)	C4–C4A	1.435(4)
S50–O50	1.399(4)	C4A–C8A	1.420(4)
S50–O51	1.427(3)	C4A–C5	1.399(5)
S60–C60	1.804(6)	C5–C6	1.369(4)
S60–O63	1.417(3)	C6–C7	1.395(4)
S60–O61	1.422(4)	C7–C8	1.344(6)
S60–O62	1.438(3)	C8–C8A	1.420(5)
P1–C15	1.803(3)	C9–C14	1.383(5)
P1–C21	1.811(3)	C9–C10	1.386(5)
P1–C9	1.793(3)	C10–C11	1.365(5)
P1–C4	1.790(3)	C11–C12	1.365(6)
F51–C50	1.283(8)	C12–C13	1.366(6)
F52–C50	1.286(8)	C13–C14	1.382(5)
F53–C50	1.323(7)	C15–C16	1.378(5)
F61–C60	1.288(7)	C15–C20	1.383(5)
F62–C60	1.306(7)	C16–C17	1.373(6)
F63–C60	1.317(7)	C17–C18	1.367(7)
O1–C1	1.356(4)	C18–C19	1.355(7)
O2–C2	1.362(4)	C19–C20	1.400(5)
O1–H1	0.88(4)	C21–C22	1.530(4)
O2–H2	0.88(4)	C22–C22_a	1.522(5)
O70–H74	0.93(4)	O70–H72	0.94(5)
O70–H73	0.90(4)	C1–C2	1.378(4)
C1–C8A	1.404(5)		

Table S2 Bond Angles (^{o}) for **5**.

O50–S50–C50	104.7(3)	O2–C2–C3	123.2(3)
O50–S50–O51	116.6(3)	C2–C3–C4	121.8(3)
O50–S50–O52	113.6(3)	P1–C4–C4A	121.7(2)
O52–S50–C50	103.9(2)	P1–C4–C3	118.3(2)
O51–S50–O52	112.3(2)	C3–C4–C4A	120.0(3)
O51–S50–C50	104.0(2)	C4–C4A–C5	123.7(3)
O62–S60–O63	112.9(2)	C4–C4A–C8A	117.6(3)
O63–S60–C60	106.1(2)	C5–C4A–C8A	118.6(3)
O61–S60–O62	113.0(2)	C4A–C5–C6	120.5(3)
O62–S60–C60	102.3(2)	C5–C6–C7	121.5(3)
O61–S60–C60	104.6(3)	Br6–C6–C7	118.9(3)
O61–S60–O63	116.2(2)	Br6–C6–C5	119.6(2)
C4–P1–C15	110.4(1)	C6–C7–C8	119.0(3)
C4–P1–C9	109.4(1)	C7–C8–C8A	122.2(3)
C15–P1–C21	106.9(1)	C1–C8A–C8	121.7(3)
C4–P1–C21	109.9(1)	C1–C8A–C4A	120.1(3)
C9–P1–C15	113.9(2)	C4A–C8A–C8	118.2(3)
C9–P1–C21	106.2(1)	P1–C9–C14	122.9(3)
C1–O1–H1	110(3)	C10–C9–C14	119.2(3)
C2–O2–H2	115(3)	P1–C9–C10	117.7(2)
H73–O70–H74	104(5)	C9–C10–C11	120.3(3)
H72–O70–H73	81(4)	C10–C11–C12	120.2(4)
H72–O70–H74	120(5)	C11–C12–C13	120.5(4)
O1–C1–C2	120.4(3)	C12–C13–C14	120.1(4)
C2–C1–C8A	121.2(3)	C9–C14–C13	119.7(3)
O1–C1–C8A	118.4(3)	P1–C15–C20	123.6(2)
O2–C2–C1	117.6(3)	P1–C15–C16	116.9(3)
C1–C2–C3	119.3(3)	C16–C15–C20	119.5(3)

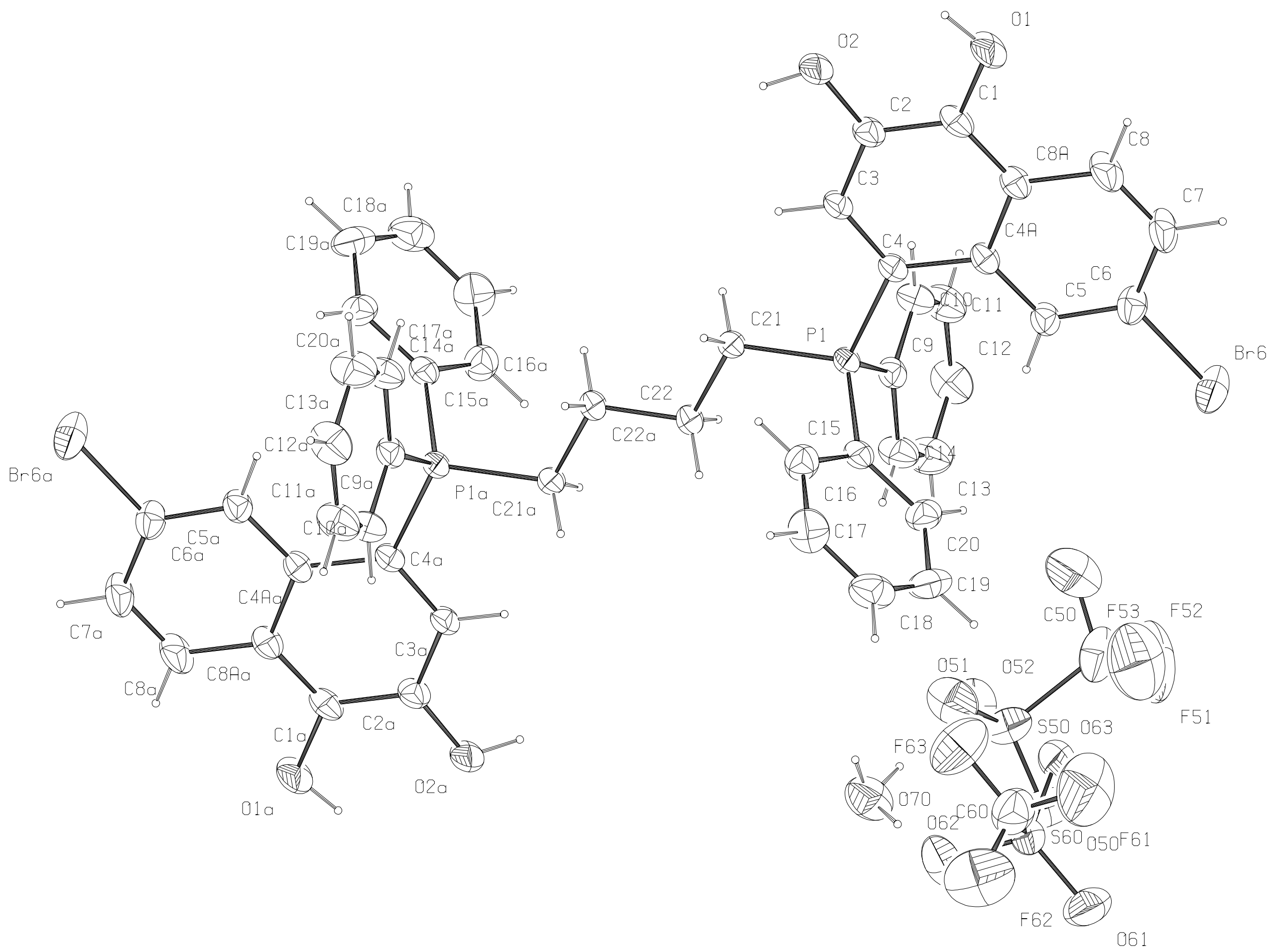

Figure S2 Molecular structure and atom-labeling scheme for **9** **[**$(C_{48}H_{40}Br_2O_4P_2)^{2+} \cdot 2(H_3O^+) \cdot 4(CF_3SO_3^-)$**]** (two trifluoromethane sulfonate anions and one hydroxonium cation are omitted for clarity).

Table S3 Bond Distances (Å) for **9**.

Br6–C6	1.912(4)	C15–C16	1.361(9)
P1–C4	1.759(5)	C16–C17	1.350(8)
P1–C9	1.814(3)	C17–C18	1.372(7)
P1–C13	1.813(4)	C19–C24	1.388(6)
P1–C19	1.818(4)	C19–C20	1.399(6)
P2–C12	1.811(4)	C20–C21	1.380(7)
P2–C25	1.829(5)	C21–C22	1.358(9)
P2–C31	1.788(4)	C22–C23	1.366(7)
O1–C1	1.286(6)	C23–C24	1.391(7)
O2–C2	1.400(6)	C25–C26	1.380(5)
O2–H2	0.86(4)	C25–C30	1.388(5)
C1–C8A	1.459(6)	C26–C27	1.387(7)
C1–C2	1.413(6)	C27–C28	1.379(7)
C2–C3	1.359(7)	C28–C29	1.366(7)
C3–C4	1.424(5)	C29–C30	1.386(8)
C4–C4A	1.456(5)	C31–C36	1.399(7)
C4A–C5	1.421(5)	C31–C32	1.408(6)
C4A–C8A	1.423(6)	C32–C33	1.367(7)
C5–C6	1.358(6)	C33–C34	1.390(8)
C6–C7	1.408(8)	C34–C35	1.374(10)
C7–C8	1.340(5)	C35–C36	1.356(8)
C8–C8A	1.415(5)	C3–H3	0.9300
C9–C10	1.515(5)	C5–H5	0.9300
C10–C11	1.526(5)	C7–H7	0.9300
C11–C12	1.551(6)	C8–H8	0.9300
C13–C14	1.380(5)	C9–H9A	0.9700
C13–C18	1.400(6)	C9–H9B	0.9700
C14–C15	1.378(6)	C10–H10A	0.9700

Table S4 Bond Angles (^{o}) for **9**.

C4–P1–C9	110.2(2)	C7–C8–C8A	121.7(4)
C4–P1–C13	112.9(2)	C1–C8A–C4A	122.1(4)
C4–P1–C19	112.5(2)	C4A–C8A–C8	119.7(3)
C9–P1–C13	105.8(2)	C1–C8A–C8	118.2(4)
C9–P1–C19	105.9(2)	P1–C9–C10	116.3(3)
C13–P1–C19	109.2(2)	C9–C10–C11	113.2(3)
C12–P2–C25	105.1(2)	C10–C11–C12	113.0(3)
C12–P2–C31	105.6(2)	P2–C12–C11	112.3(3)
C25–P2–C31	107.0(2)	P1–C13–C14	119.6(3)
C2–O2–H2	101(2)	C14–C13–C18	117.6(4)
O1–C1–C2	120.8(4)	P1–C13–C18	122.7(3)
O1–C1–C8A	123.1(4)	C13–C14–C15	120.6(4)
C2–C1–C8A	116.1(5)	C14–C15–C16	120.5(4)
O2–C2–C1	118.2(5)	C15–C16–C17	120.1(5)
O2–C2–C3	119.2(4)	C16–C17–C18	120.6(5)
C1–C2–C3	122.6(4)	C13–C18–C17	120.6(4)
C2–C3–C4	123.2(4)	P1–C19–C20	119.0(3)
P1–C4–C3	118.2(3)	P1–C19–C24	120.4(3)
P1–C4–C4A	124.6(3)	C20–C19–C24	120.6(4)
C3–C4–C4A	117.1(4)	C19–C20–C21	118.0(5)
C4–C4A–C5	124.2(4)	C20–C21–C22	121.9(5)
C4–C4A–C8A	118.8(3)	C21–C22–C23	120.1(5)
C5–C4A–C8A	116.8(3)	C22–C23–C24	120.5(5)
C4A–C5–C6	121.2(4)	C19–C24–C23	118.9(4)
Br6–C6–C7	118.5(3)	P2–C25–C26	121.5(3)
C5–C6–C7	121.4(4)	C26–C25–C30	118.1(4)
Br6–C6–C5	120.2(4)	P2–C25–C30	120.2(3)
C6–C7–C8	119.1(4)	C25–C26–C27	121.8(4)

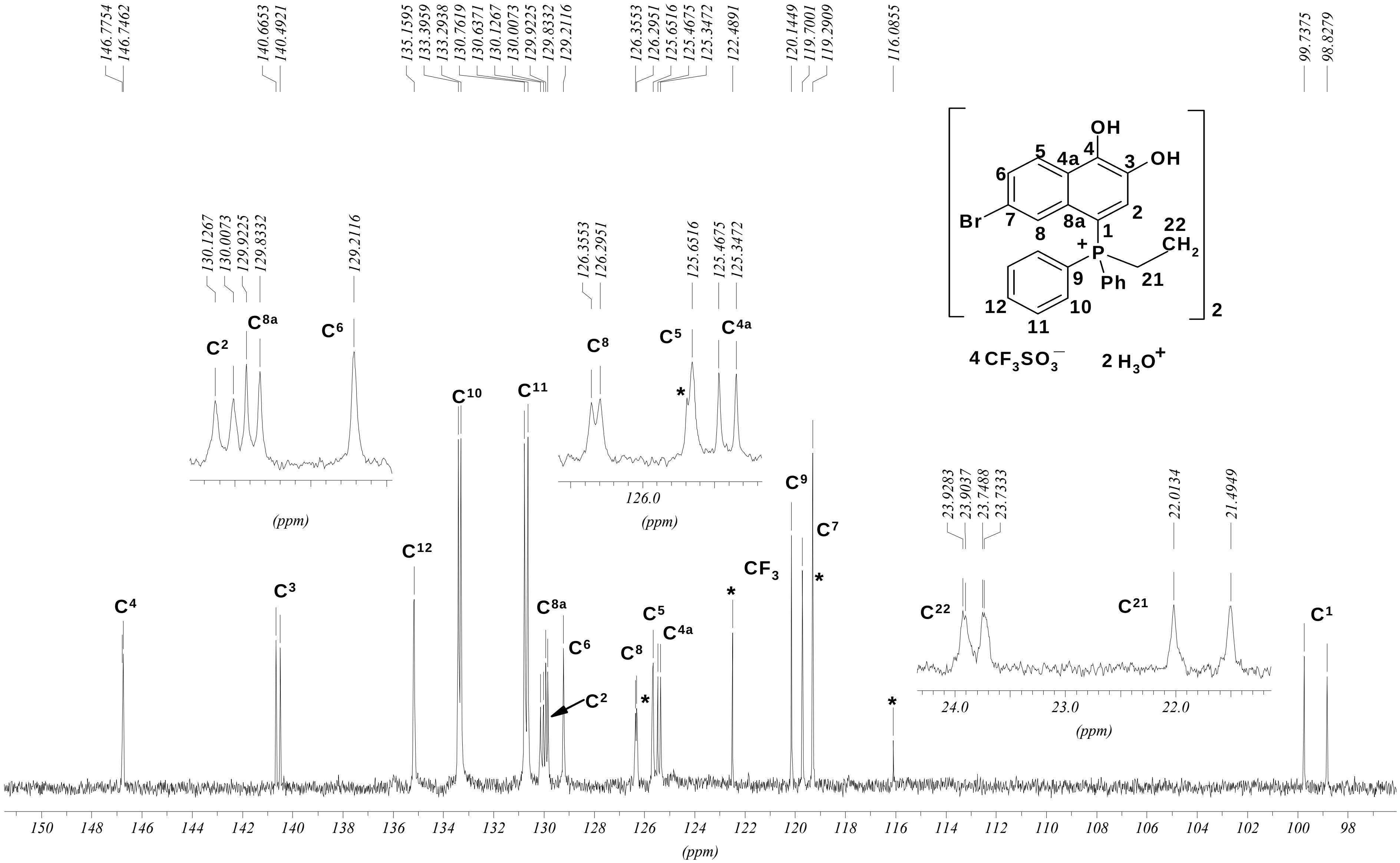

Figure S3 ^{13}C-{^{1}H} NMR spectrum (DMSO-D$_6$) of compound **9**.

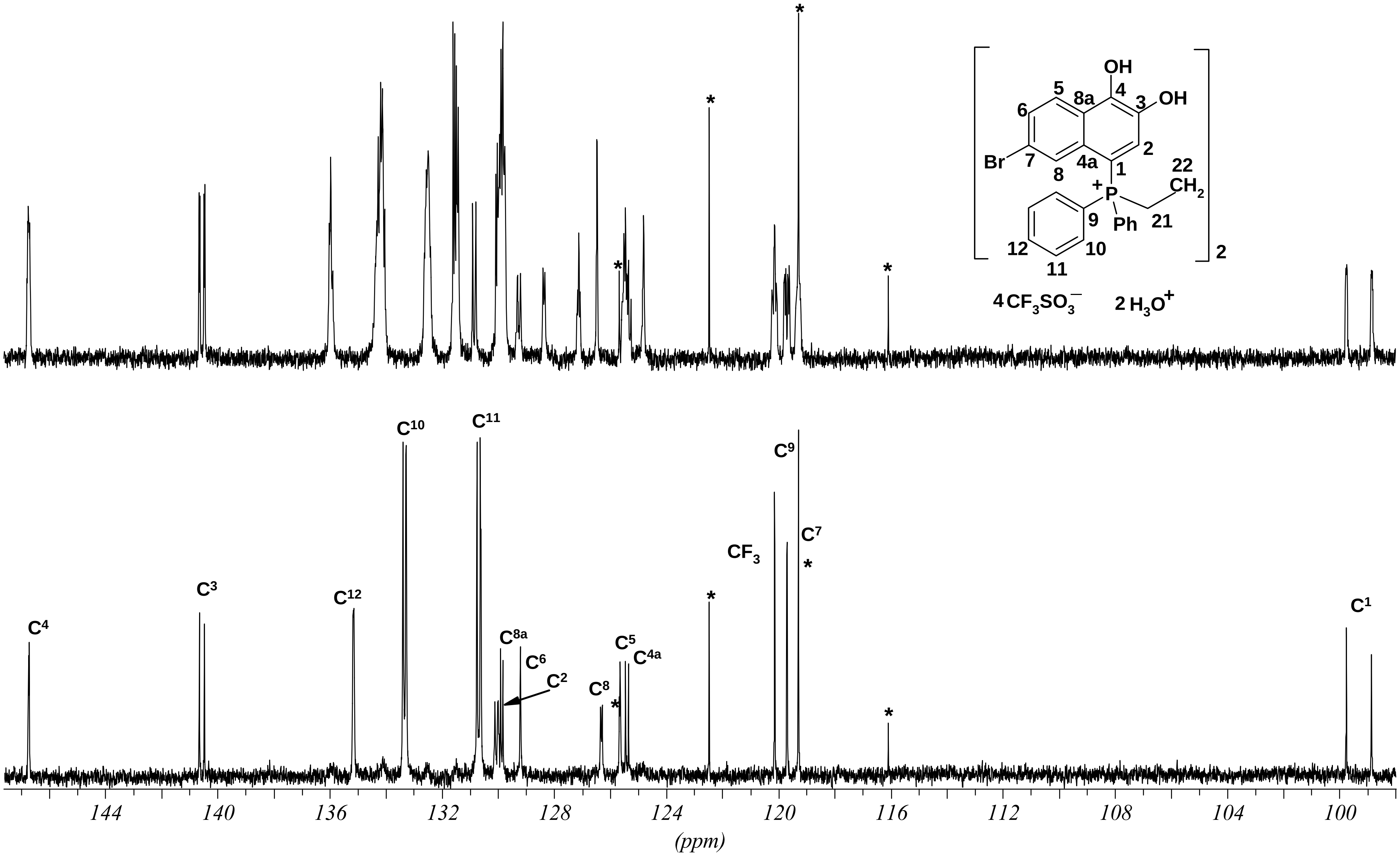

Figure S4 Downfield parts of ^{13}C and ^{13}C-{^{1}H} NMR spectra (DMSO-D$_6$) of compound **9**.

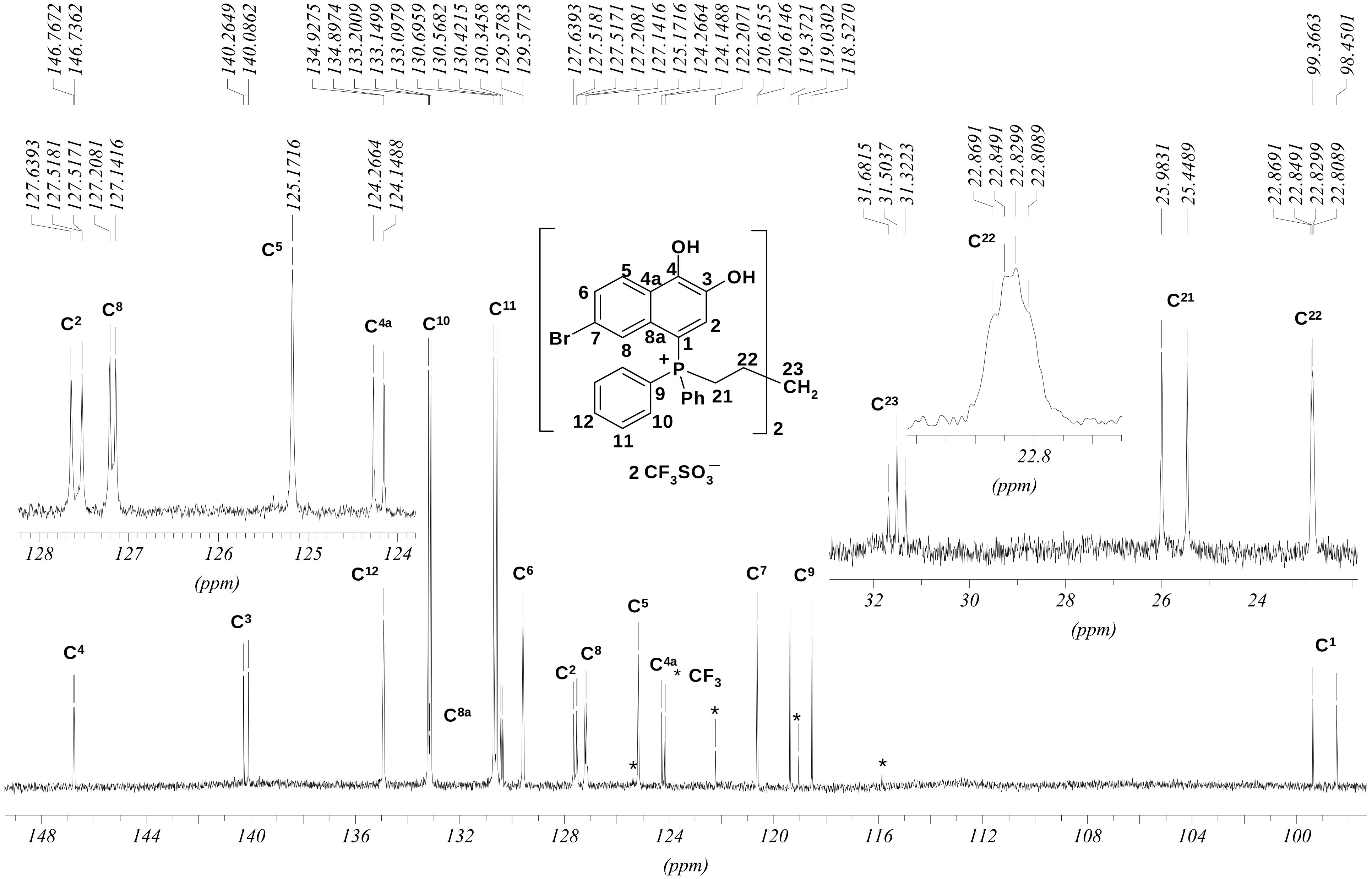

Figure S5 Downfield part of $^{13}C-\{^1H\}$ NMR spectrum (DMSO-D_6) of compound **10**.

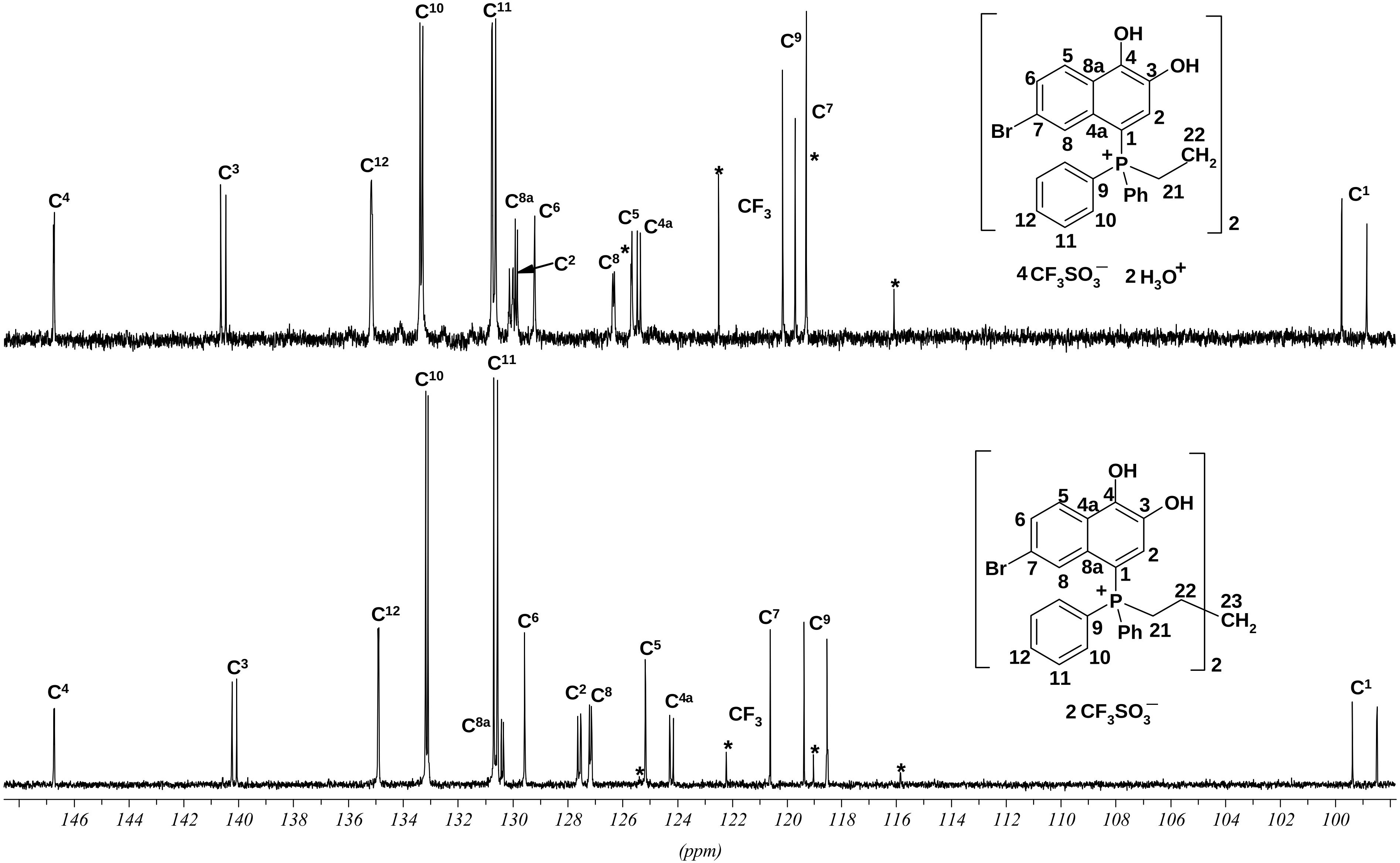

Figure S6 Downfield parts of $^{13}C-\{^1H\}$ NMR spectra (DMSO-D$_6$) of compounds **9** and **10**.