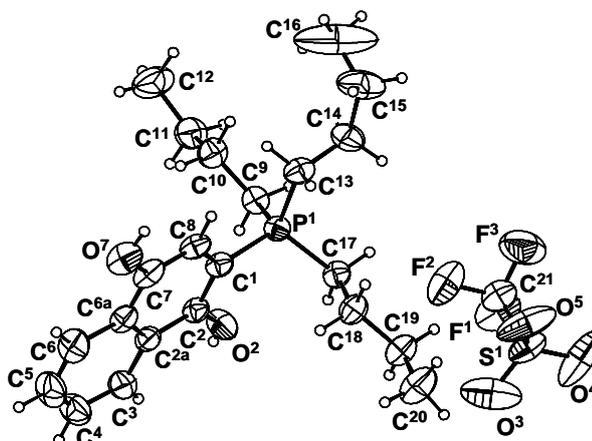


**Phosphonium salts with a dihydroxynaphthyl substituent:
versatile synthesis and evaluation of antimicrobial activity**

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General remarks

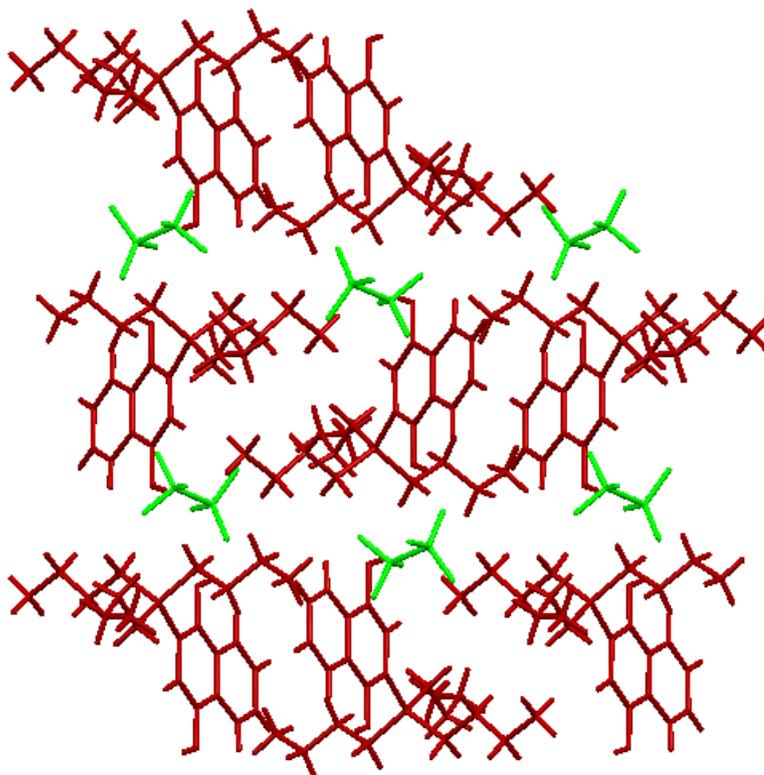
NMR experiments were carried out with Bruker spectrometer AVANCE-400 (400.1 MHz (^1H), 162.0 MHz, (^{31}P), 100.6 MHz (^{13}C)) or AVANCE-600 (600.1 MHz (^1H), 242.9 MHz, (^{31}P), 150.9 MHz (^{13}C)). Chemical shifts are reported in the δ (ppm) scale relative to the residual ^1H and ^{13}C signals of CHCl_3 or DMSO, or the external standard – H_3PO_4 (^{31}P). IR spectra were measured with Bruker Vector-22 spectrometer as suspensions in nujol. Melting points were measured with a Stuart digital SMP10 apparatus and uncorrected. Elemental analyses for C, H and N were performed using a EuroVector 2000 CHNS-3 analyzer, Italy, phosphorus content was determined by pyrolysis in oxygen stream. All the manipulations were performed in argon atmosphere. All the solvents were obtained anhydrous according to standard methods. The starting materials were used immediately after the distillation or recrystallization.

Table S1 Crystal parameters of compound **7** and X-ray crystallographic experimental conditions.

Parameter	7
Color, shape	Yellow, prismatic
Chemical formula	$C_{23}H_{34}F_3O_5PS$
Molecular weight	510.53
Crystal symmetry	Monoclinic
Space group	$P2_1/n$
Unit cell parameters: $a, b, c, \text{\AA}; \beta, \text{deg}$	$a = 10.340(3)$ $b = 14.387(4)$ $c = 17.856(5)$ $\beta = 102.409(4)$
Volume, \AA^3 ;	2594.3(13)
Z	4
Density (calc.), g/cm^3	1.307
Absorption coefficient $\mu_{\text{Mo}}, \text{cm}^{-1}$	0.238
Absorption correction	none
$F(000)$	1080
Measured reflections, $R(\text{int})$	5079, 0.0544
Observed reflections with $I > 2\sigma(I)$	2616
$R_1 (I > 2\sigma(I)) / wR_2$ (over all reflections)	0.0777 / 0.2729
Fitting parameter (goodness of fit)	1.047
Number of refined parameters	298
θ range, deg	$1.835 < \theta < 26.000$
Ranges of measurement indices	$-8 \leq h \leq 8, -16 \leq k \leq 17, -15 \leq l \leq 15$
Maximum and minimum peaks, $e \text{\AA}^{-3}$	0.633 and -0.387

Table S2 H-bonds in crystal of compound 7.

H-bond	symmetry transformation	D-H, Å	H...A, Å	D...A, Å	D-H...A, °
O ² -H ² ...O ⁵	$-1/2 + x, 3/2 - y, -1/2 + z$	0.82	1.99	2.710(7)	147
O ⁷ -H ⁷ ...O ³	$x, y, -1 + z$	0.82	1.84	2.656(8)	170
C ³ -H ³ ...O ⁵	$-1/2 + x, 3/2 - y, -1/2 + z$	0.93	2.57	3.462(7)	160
C ⁶ -H ⁶ ...O ⁷	intramolecular	0.93	2.46	2.776(7)	100
C ⁹ -H ⁹¹ ...O ²	intramolecular	0.97	2.52	3.115(5)	119
C ¹⁴ -H ¹⁴² ...O ⁴	$1 - x, 2 - y, 1 - z$	0.97	2.49	3.365(8)	149
C ⁹ -H ⁹² ...O ⁷	$1/2 + x, 3/2 - y, 1/2 + z$	0.97	2.44	3.407(5)	173
C ¹⁷ -H ¹⁷¹ ...O ²	intramolecular	0.97	2.56	3.064(6)	112

**Figure S1** Molecular packing in the crystal of compound 7.

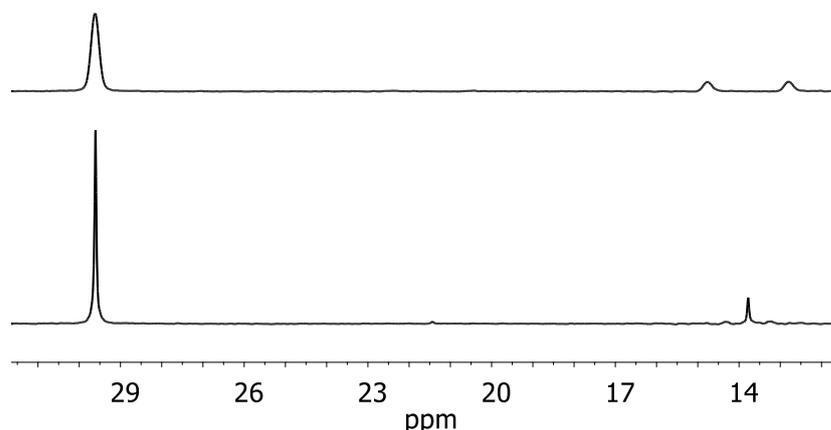


Figure S2 ^{31}P - $\{^1\text{H}\}$, ^{31}P spectra (242.9 MHz, CH_2Cl_2) of the P-H-phosphonium salt **6** and quinone **2** reaction mixture after 48 h.

‡ (1,4-Dihydroxynaphthalen-2-yl)triphenylphosphonium trifluoromethylsulphonate **4**. IR (nujol) (ν_{max} , cm^{-1}): 3250, 1622, 1591, 1440, 1358, 1292, 1238, 1163, 1106, 1075, 1028, 998, 871, 772, 749, 723, 691, 637, 600. NMR ^1H (600 MHz, CDCl_3) δ : 8.8 br. s (OH), 8.23 d (H^5 , 1H, $^3J_{\text{HCCH}}$ 8.6 Hz), 8.06 d (H^8 , 1H, $^3J_{\text{HCCH}}$ 8.1 Hz), 7.60 t (H^{12} , 3H, $^3J_{\text{HCCH}}$ 6.6 Hz), 7.51 m (H^{10} , H^{11} , 12H), 7.42 m (H^7 , 1H), 7.33 dd (H^6 , 1H, $^3J_{\text{HCCH}}$ 7.1-7.6 Hz), 6.48 d (H^3 , 1H, $^3J_{\text{PCCH}}$ 11.8 Hz). NMR ^{13}C / ^{13}C - $\{^1\text{H}\}$ (150.9 MHz, CDCl_3) δ_{C} : 152.80 br. m (s) (C^1), 148.21 br. d (d) (C^4 , $^3J_{\text{PCCC}}$ 16.3 Hz), 134.36 br. ddd (s) (C^{12} , $^1J_{\text{HC}}$ 165.3 Hz), 133.92 dddd (d) (C^{10} , $^1J_{\text{HC}}$ 164.6 Hz, $^2J_{\text{PCC}}$ 10.5 Hz, $^3J_{\text{HCCC}}$ 8.0 Hz, $^3J_{\text{HCCC}}$ 7.3 Hz), 129.94 dddd (d) (C^{11} , $^1J_{\text{HC}}$ 166.0 Hz, $^3J_{\text{PCCC}}$ 13.0 Hz, $^3J_{\text{HCCC}}$ 7.3 Hz, $^3J_{\text{HCCC}}$ 6.9 Hz), 129.93 br. m (C^{4a} , overlaps with C^{11} signal, $^3J_{\text{HCCC}}$ 6.2 Hz), 129.09 dd (s) (C^6 , $^1J_{\text{HC}}$ 161.3 Hz, $^3J_{\text{HCCC}}$ 8.0 Hz), 127.22 dd (s) (C^7 , $^1J_{\text{HC}}$ 162.4 Hz, $^3J_{\text{HCCC}}$ 8.4 Hz), 125.93 dd (d) (C^{8a} , $^3J_{\text{PCCC}}$ 9.9 Hz, $^3J_{\text{HCCC}}$ 8.0-8.4 Hz), 123.18 dd (s) (C^8 , $^1J_{\text{HC}}$ 163.1 Hz, $^3J_{\text{HCCC}}$ 6.5 Hz), 123.01 dd (s) (C^5 , $^1J_{\text{HC}}$ 164.5 Hz, $^3J_{\text{HCCC}}$ 6.5 Hz), 120.21 q (q) (C^{13} , $^1J_{\text{FC}}$ 319.8 Hz), 119.57 ddd (d) (C^9 , $^1J_{\text{PC}}$ 92.0 Hz, $^3J_{\text{HCCC}}$ 8.4 Hz, $^3J_{\text{HCCC}}$ 8.0 Hz), 108.24 dd (d) (C^3 , $^1J_{\text{HC}}$ 163.1 Hz, $^2J_{\text{PCC}}$ 10.8 Hz), 96.79 d (d) (C^2 , $^1J_{\text{PC}}$ 95.1 Hz). NMR ^{31}P / ^{31}P - $\{^1\text{H}\}$ (242.9 MHz, CDCl_3) δ_{P} : 22.4 br. s (s). Found (%): C 61.00, H 3.85, S 5.63, P 5.42. Calcd. for $\text{C}_{29}\text{H}_{22}\text{O}_5\text{F}_3\text{PS}$ (%): C 61.05, H 3.86, S 5.61, P 5.44.

(1,4-Dihydroxy-3-methylnaphthalen-2-yl)triphenylphosphonium trifluoromethylsulfonate **5**. IR (nujol) (ν_{max} , cm^{-1}): 3423, 3060, 1579, 1442, 1297, 1241, 1225, 1173, 1155, 1101, 1030, 770, 751, 727, 717, 691, 640, 575, 537, 526, 513, 499. NMR ^1H (400 MHz, $\text{DMSO}-d_6$) δ : 9.14 (OH), 8.29 d (H^5 , 1H, $^3J_{\text{HCCH}}$ 8.3 Hz), 8.15 d (H^7 , 1H, $^3J_{\text{HCCH}}$ 8.4 Hz), 7.82 m (H^{10} , H^{12} , 9H), 7.72 ddd (H^{11} , 6H, $^3J_{\text{HCCH}}$ 7.8 Hz, $^3J_{\text{HCCH}}$ 7.4 Hz, $^4J_{\text{HCCC}}$ 3.8 Hz), 7.6 m (H^6 , H^7 , OH, 3H, $^3J_{\text{HCCH}}$ 7.8 Hz, $^3J_{\text{HCCH}}$ 7.3 Hz), 1.65 s (CH_3 , 3H). NMR $^{13}\text{C}/^{13}\text{C}$ - $\{^1\text{H}\}$ (100.6 MHz, $\text{DMSO}-d_6$) δ_{C} : 154.62 br. d (d) (C^1 , $^2J_{\text{PCC}}$ 1.1 Hz), 145.03 dm (d) (C^4 , $^3J_{\text{PCCC}}$ 15.0 Hz, $^3J_{\text{HCCC}}$ 5.1 Hz, $^3J_{\text{HCCC}}$ 4.8

Hz), 134.54 ddt (d) (C^{13} , $^1J_{HC}$ 164.7 Hz, $^2J_{HCC}$ 1.5 Hz, $^3J_{HCCC}$ 8.1 Hz, $^4J_{PCCCC}$ 2.9 Hz), 134.12 dm (d) (C^{11} , $^1J_{HC}$ 164.7 Hz, $^2J_{PCC}$ 10.3 Hz), 130.49 m (d) (C^{4a} , overlap with C^6 signal, $^4J_{PCCCC}$ 2.2 Hz), 130.49 dddd (d) (C^{12} , $^1J_{HC}$ 166.2 Hz, $^3J_{PCCC}$ 12.8 Hz, $^3J_{HCCC}$ 7.7 Hz, $^3J_{HCCC}$ 7.3 Hz), 130.20 br. dd (s) (C^4 , $^1J_{HC}$ 154.4 Hz, $^3J_{HCCC}$ 8.8 Hz), 126.70 dd (s) (C^7 , $^1J_{HC}$ 164.0 Hz, $^3J_{HCCC}$ 8.8 Hz), 124.44 m (d) (C^{8a} , $^3J_{PCCC}$ 9.5 Hz), 123.66 dm (d) (C^8 , $^1J_{HC}$ 161.0 Hz, $^4J_{PCCCC}$ 1.5 Hz), 123.23 dd (s) (C^5 , $^1J_{HC}$ 164.7 Hz, $^3J_{HCCC}$ 7.3-7.7 Hz), 122.74 ddd (d) (C^{10} , $^1J_{PC}$ 89.9 Hz, $^3J_{HCCC}$ 8.4 Hz, $^3J_{HCCC}$ 8.1 Hz), 120.73 q (q) (C^{14} , $^1J_{FC}$ 322.4-322.0 Hz), 119.80 dq (d) (C^3 , $^2J_{PCC}$ 8.4 Hz, $^2J_{HCC}$ 6.2 Hz), 98.33 dq (d) (C^2 , $^1J_{PC}$ 95.0 Hz, $^3J_{HCCC}$ 4.0-4.4 Hz), 15.88 dq (d) (C^9 , $^1J_{HC}$ 128.4-128.7 Hz, $^3J_{PCCC}$ 4.4 Hz). NMR ^{31}P / ^{31}P - $\{^1H\}$ (162.0 MHz, DMSO- d_6) δ_P : 17.8 br. s (s). Found (%): C 61.61, H 4.12, S 5.51, P 5.29. Calcd. for $C_{30}H_{24}O_5F_3PS$ (%): C 61.64, H 4.11, S 5.48, P 5.31.

(1,4-Dihydroxynaphthalen-2-yl)tributylphosphonium trifluoromethylsulphonate **7**. IR (nujol) (ν_{max} , cm^{-1}): 3285, 1597, 1579, 1365, 1291, 1244, 1225, 1162, 1091, 1073, 1030, 914, 805, 760, 727, 640, 613, 593. NMR 1H (600 MHz, $CDCl_3$ /DMSO- d_6 (3:1)) δ : 8.23 d (H^5 , 1H, $^3J_{HCCH}$ 9.0 Hz), 8.18 d (H^8 , 1H, $^3J_{HCCH}$ 8.6 Hz), 7.6 dd (H^7 , 2H, overlap with H^5 signal, $^3J_{HCCH}$ 7.6 Hz, $^3J_{HCCH}$ 7.1 Hz), 7.57 dd (H^6 , 2H, overlaps with H^7 signal, $^3J_{HCCH}$ 7.1 Hz, $^3J_{HCCH}$ 7.1 Hz), 6.72 d (H^3 , 1H, $^3J_{PCCH}$ 11.4 Hz), 2.49 m (CH_2 , 6H), 1.44 m (CH_2 , 12H), 0.88 t (CH_3 , 9H, $^3J_{HCCH}$ 6.6 Hz). NMR ^{13}C / ^{13}C - $\{^1H\}$ (150.9 MHz, $CDCl_3$ /DMSO- d_6 = 3 : 1) δ_C : 151.96 dd (s) (C^1 , $^3J_{HCCC}$ 8.0 Hz, $^3J_{HCCC}$ 8.0 Hz), 148.33 br. dm (d) (C^4 , $^2J_{PCC}$ 14.4 Hz), 129.22 m (s) (C^{4a} , overlaps with C^6 signal, $^3J_{HCCC}$ 6.5 Hz), 128.59 dd (s) (C^6 , $^1J_{HC}$ 161.3 Hz, $^3J_{HCCC}$ 8.0 Hz), 127.06 dd (s) (C^7 , $^1J_{HC}$ 161.7-162.0 Hz, $^3J_{HCCC}$ 8.4-8.7 Hz), 126.14 dd (d) (C^{8a} , $^3J_{PCCC}$ 9.4 Hz, $^3J_{HCCC}$ 7.3-7.6 Hz), 123.06 dd (s) (C^8 , $^1J_{HC}$ 164.2 Hz, $^3J_{HCCC}$ 7.3-7.6 Hz), 123.03 dd (s) (C^4 , $^1J_{HC}$ 161.3 Hz, $^3J_{HCCC}$ 7.3 Hz), 120.95 q (q) (C^{13} , $^1J_{FC}$ 321.2-321.5 Hz), 106.22 dd (d) (C^3 , $^1J_{HC}$ 160.6 Hz, $^2J_{PCC}$ 7.2 Hz), 97.38 d (d) (C^2 , $^1J_{PC}$ 83.7 Hz), 23.83 tm (s) (C^{11} , $^1J_{HC}$ 129.3 Hz), 23.77 tm (d) (C^{10} , $^1J_{HC}$ 129.3 Hz, $^2J_{PCC}$ 16.03 Hz), 19.52 dt (d) (C^9 , $^1J_{HC}$ 131.5 Hz, $^1J_{PC}$ 50.6 Hz), 13.53 q (s) (C^{12} , $^1J_{HC}$ 124.9-125.3 Hz). NMR ^{31}P / ^{31}P - $\{^1H\}$ (242.9 MHz, $CDCl_3$ /DMSO- d_6 (3:1)) δ_P : 29.6 br. s (s). Found (%): C 54.13, H 6.67, S 6.37, P 6.01. Calcd. for $C_{23}H_{34}O_5F_3PS$ (%): C 54.17, H 6.66, S 6.27, P 6.07.

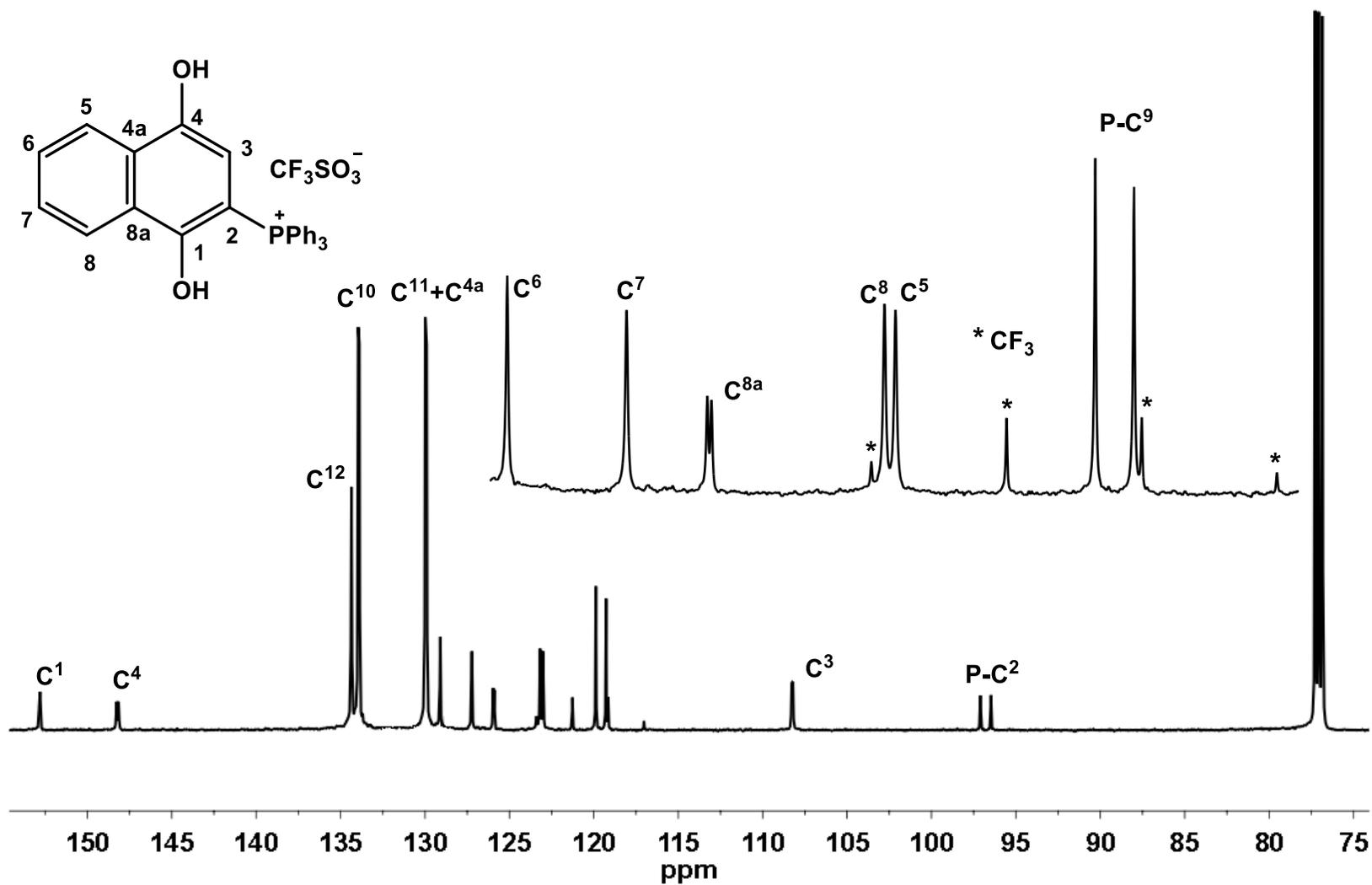


Figure S3 NMR ^{13}C - $\{^1\text{H}\}$ spectrum of phosphonium salt 4 (150.9 MHz, CDCl_3).

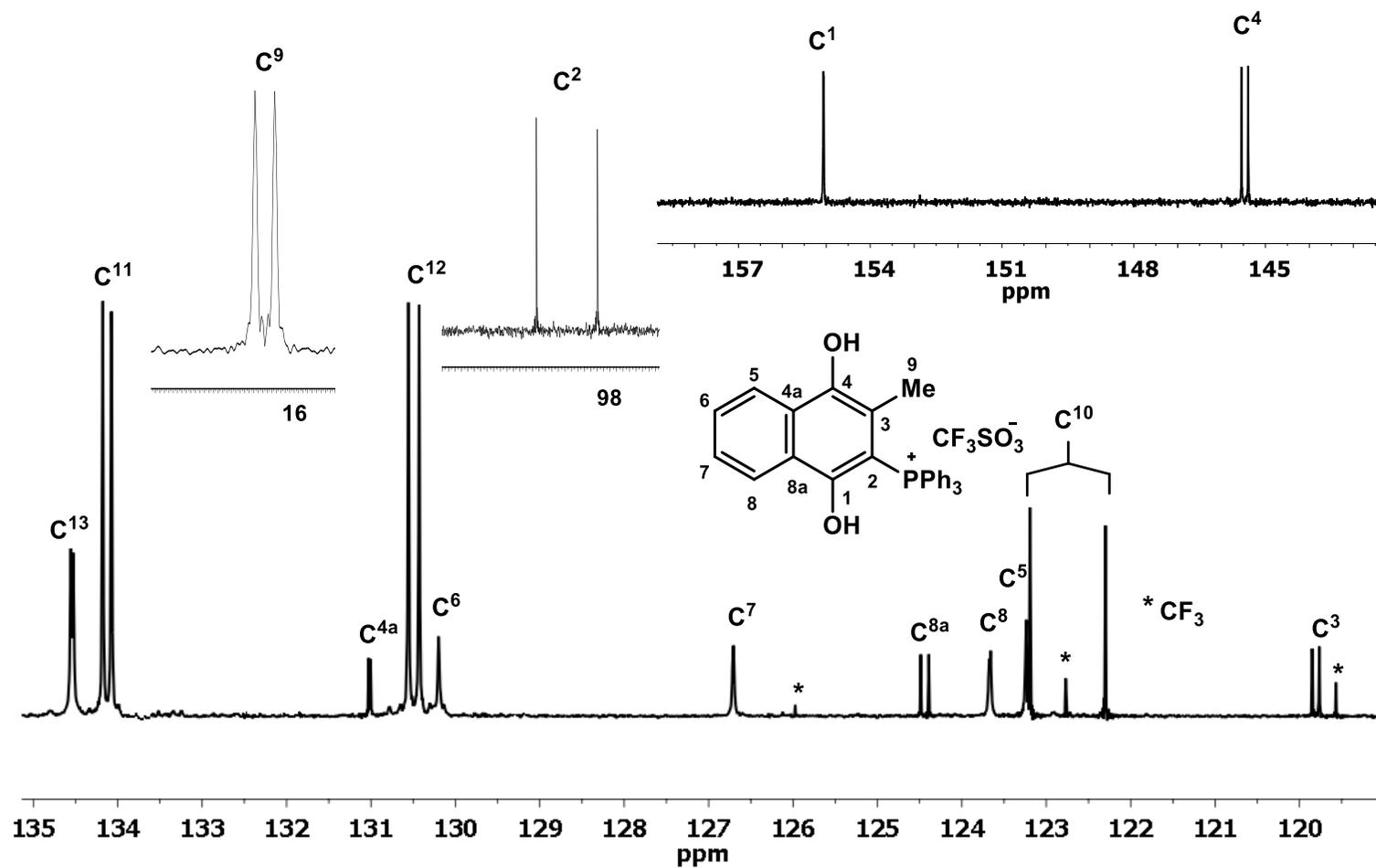


Figure S4 NMR ^{13}C - $\{^1\text{H}\}$ spectrum of phosphonium salt **5** (100.6 MHz, $\text{DMSO-}d_6$).

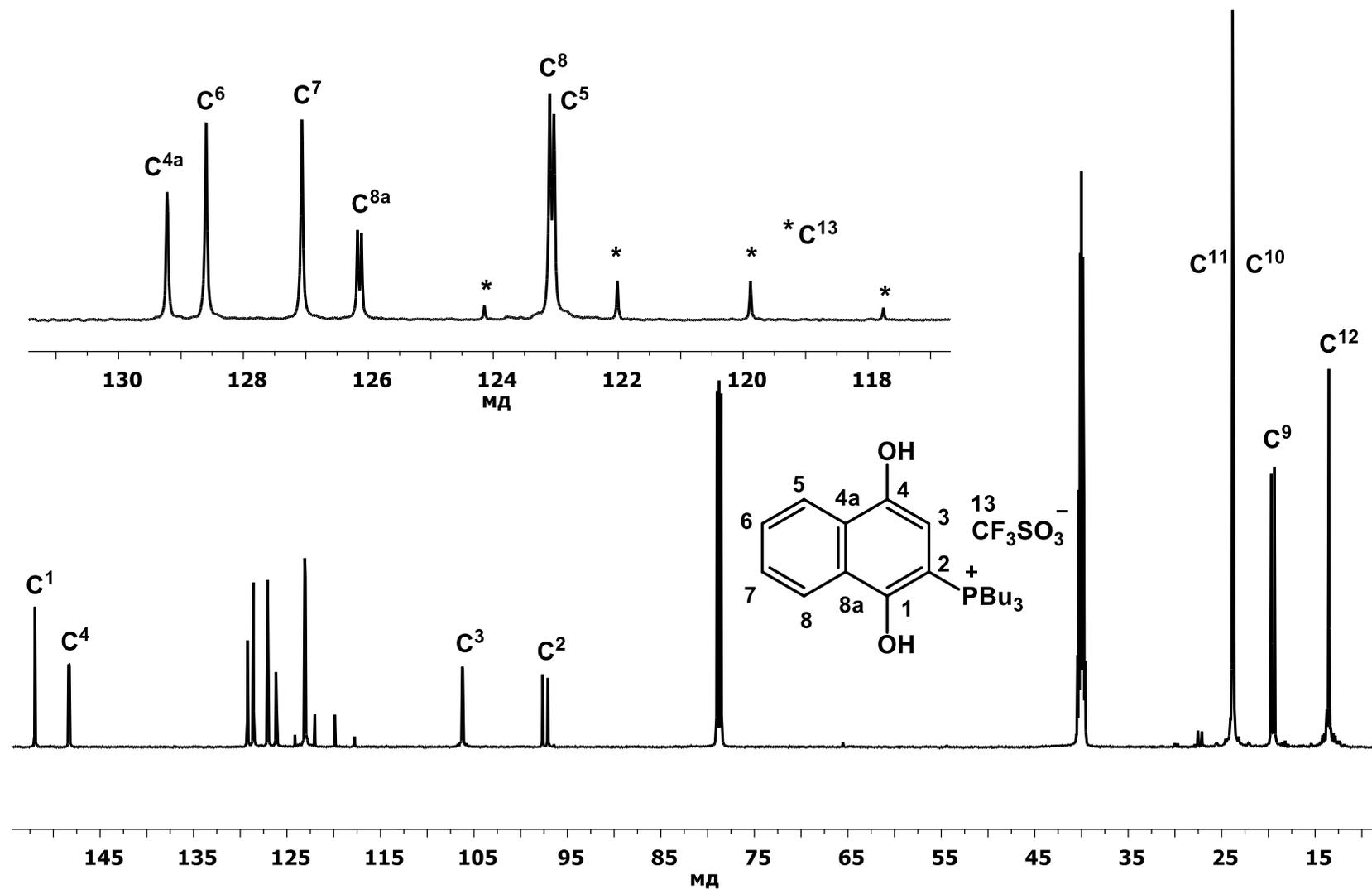
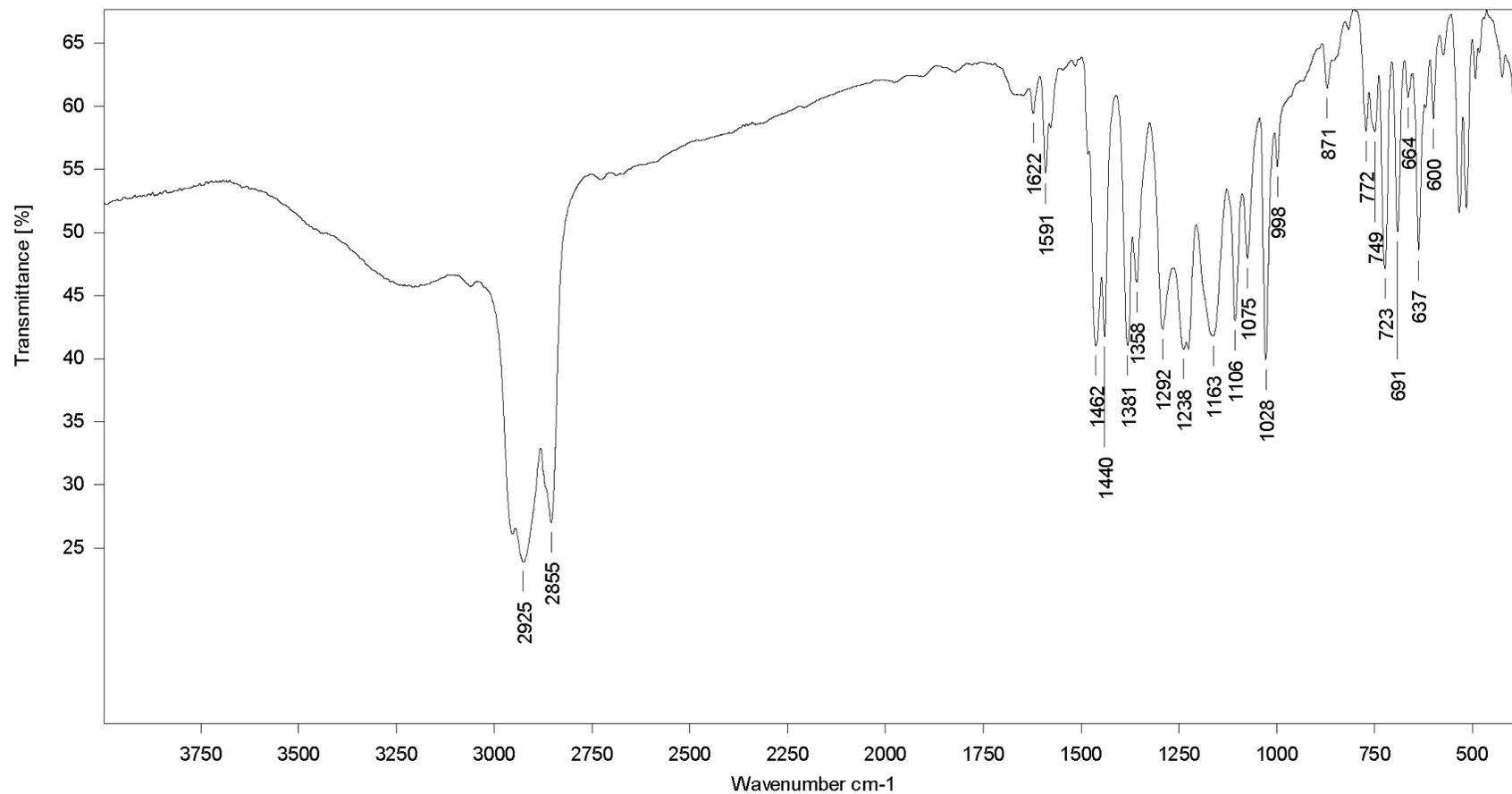


Figure S5 NMR ^{13}C - $\{^1\text{H}\}$ spectrum of phosphonium salt **7** (150.9 MHz, $\text{CDCl}_3/\text{DMSO-}d_6 = 3 : 1$).



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Filename C-A-12.0

Operator Name Sasha

Date of Measurement 20/04/2016

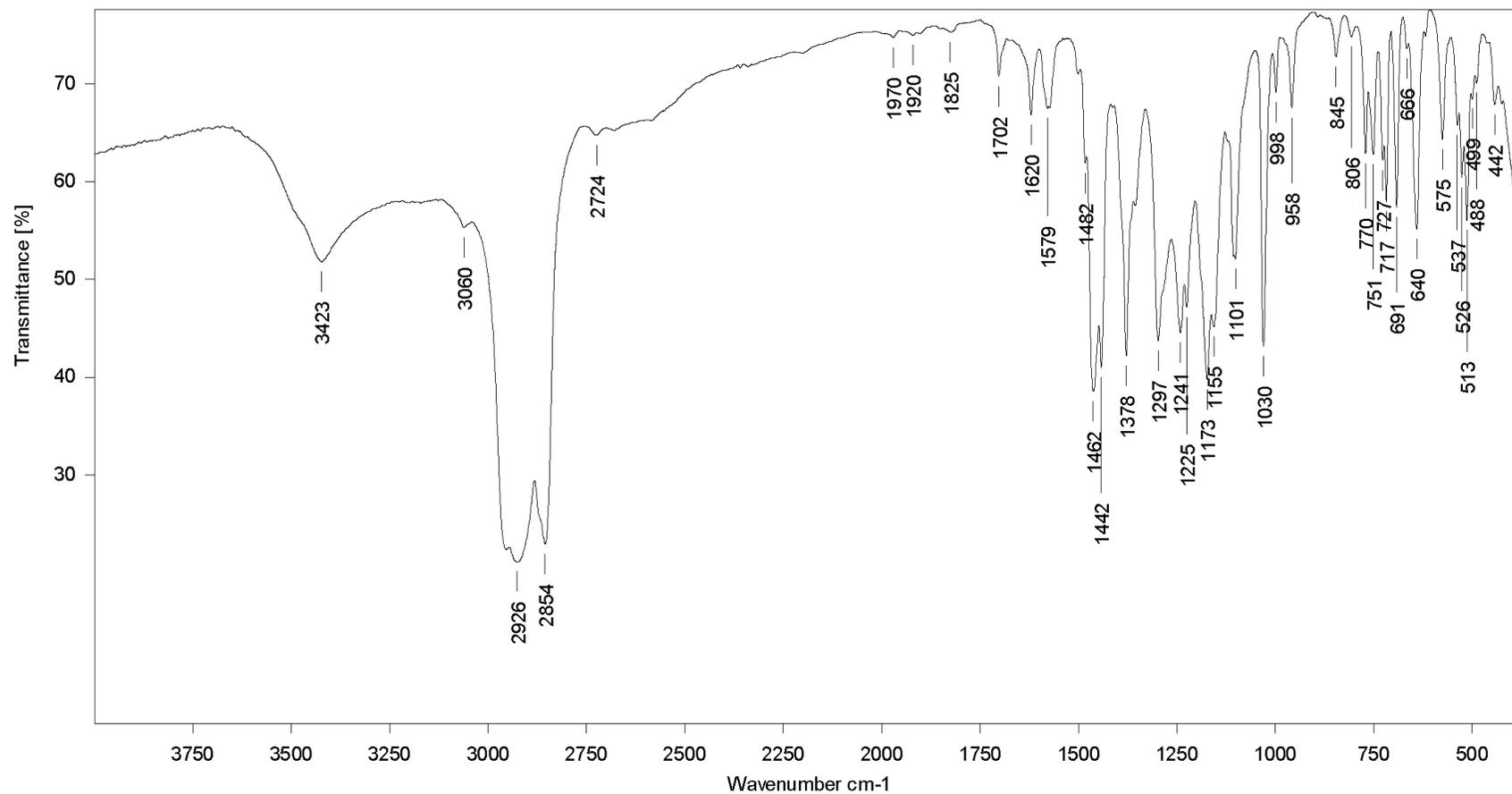
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Resolution 4

Time of Measurement 1:09:16 PM

Figure S6 IR spectrum of phosphonium salt **4** (Nujol).



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Filename KHA-260-1.2

Operator Name Sasha

Date of Measurement 15/12/2015

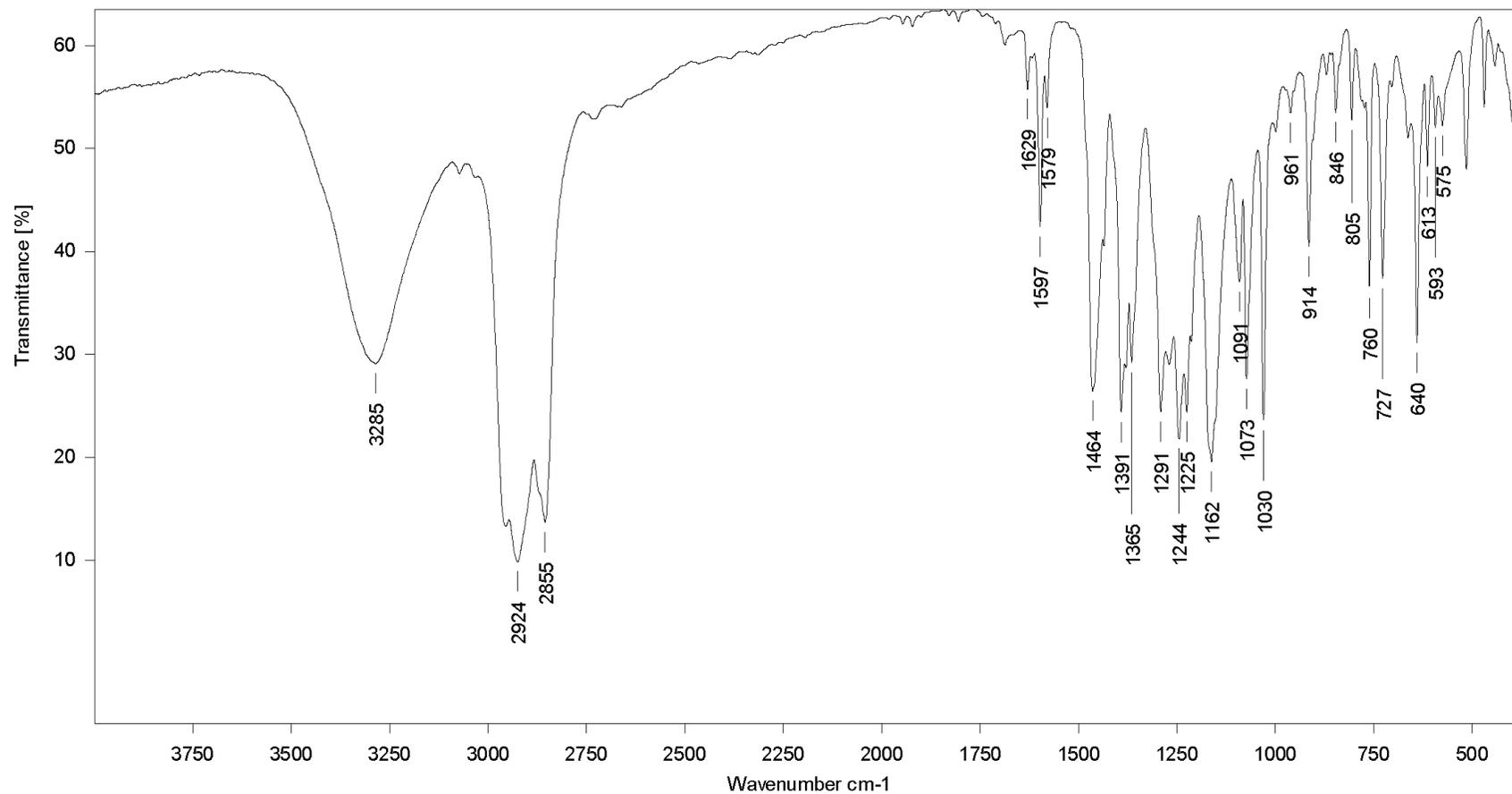
Instrument Type Tensor 27

Sample Form vaselin

Resolution 4

Time of Measurement 1:30:46 PM

Figure S7 IR spectrum of phosphonium salt **5** (Nujol).



Sample Name C-A-13

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Filename C-A-13.0

Operator Name Sasha

Date of Measurement 20/04/2016

Instrument Type Tensor 27

Sample Form vaselin

Resolution 4

Time of Measurement 1:04:24 PM

Figure S8 IR spectrum of phosphonium salt **7** (Nujol).