

Reaction of *R*-pulegone with P–H phosphonium salts

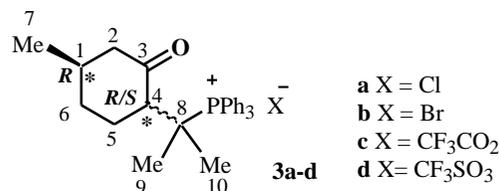
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Experimental Section

General remarks. The ^1H , ^{13}C and ^{31}P NMR spectra were recorded using a Bruker Avance-400 NMR spectrometer. Elemental analysis was accomplished with an automated EuroVector EA3000 CHNS-O elemental analyzer (Euro-Vector, Milano, Italy). MALDI mass spectra were acquired using an Ultra flex III TOF/TOF spectrometer (Bruker Daltonics, Germany). Atom numbering for interpretation of the spectra is given according to the ‘menthane’ nomenclature.



*{2-[(1R,4R)-4-Methyl-2-oxocyclohexyl]prop-2-yl}triphenylphosphonium chloride **3a**.* Yield 89% (diastereoisomer ratio is 6.4 : 1.0), colourless powder, mp 90 °C. ^{13}C NMR (100.6 MHz, CDCl₃), **3a** (*d*₁), δ_{C} : 19.06 q (br. s) (C¹⁰, $^1J_{\text{HC}}$ 126.0 Hz), 20.27 q (s) (C⁷, $^1J_{\text{HC}}$ 125.8 Hz), 25.44 m (br. s) (C⁵), 25.53 q (br. s) (C⁹, $^1J_{\text{HC}}$ 128.4 Hz), 30.15 m (s) (C⁶), 32.35 dm (s) (C¹, $^1J_{\text{HC}}$ 128.5 Hz), 38.72 d (d) (C⁸, $^1J_{\text{PC}}$ 42.1 Hz), 46.18 tm (br. s) (C², $^1J_{\text{HC}}$ 128.3 Hz), 53.80 dm (br. s) (C⁴, $^1J_{\text{HC}}$ 129.6 Hz), 118.97 dt (d) (PC_{Ph}^{ipso}, $^1J_{\text{PC}}$ 80.6 Hz, $^3J_{\text{HC}}$ 8.3 Hz), 127.07 ddd (d) (C_{Ph}^{meta}, $^1J_{\text{HC}}$ 165.6 Hz, $^3J_{\text{PC}}$ 12.0 Hz, $^3J_{\text{HC}}$ 7.35 Hz), 131.20 dm (br. s) (C_{Ph}^{para}, $^1J_{\text{HC}}$ 163.9 Hz), 132.32 dm (d) (C_{Ph}^{ortho}, $^1J_{\text{HC}}$ 162.9 Hz, $^2J_{\text{PC}}$ 8.5 Hz, $^3J_{\text{HC}}$ 7.7 Hz), 209.99 m (d) (C³, $^3J_{\text{PC}}$ 4.8 Hz); **3a** (*d*₂): 19.06 m (br. s) (C¹⁰), 20.27 m (s) (C⁷), 21.34 m (br. s) (C⁵), 22.72 m (s) (C⁶), 25.53 q (br. s) (C⁹, $^1J_{\text{HC}}$ 128.4 Hz), 25.97 m (s) (C¹), 38.82 m (d) (C⁸, $^1J_{\text{PC}}$ 41.7 Hz), 44.75 m (br. s) (C²), 54.13 m (br. s) (C⁴), 118.78 dt (d) (PC_{Ph}^{ipso}, $^1J_{\text{PC}}$ 80.5 Hz, $^3J_{\text{HC}}$ 8.1 Hz), 127.07 m (d) (C_{Ph}^{meta}, $^3J_{\text{PC}}$ 12.0 Hz), 131.20 m (s) (C_{Ph}^{para}), 132.32 m (d) (C_{Ph}^{ortho}), 210.23 m (d) (C³, $^3J_{\text{PC}}$ 4.9 Hz). ^{31}P / ^{31}P -{ ^1H } NMR (162.0 MHz, CDCl₃), δ_{P} : 41.5 m (s) (**3a**, *d*₁), 41.4 m (s) (**3a**, *d*₂). MALDI, *m/z*: calc. for C₂₈H₃₂OP⁺ [M⁺], 415.22; found 415.28. IR (KBr, cm⁻¹): 3058, 2951, 2869, 1716 (C=O), 1587, 1484, 1437, 1104, 997.

*{2-[(1R,4R)-4-Methyl-2-oxocyclohexyl]prop-2-yl}triphenylphosphonium bromide **3b**.* Yield 85% (diastereoisomer ratio is 5.5 : 1.0), colourless powder, mp 127-128 °C. ^{13}C NMR (100.6 MHz, CDCl₃), **3b** (*d*₁), δ_{C} : 19.05 q (br. s) (C¹⁰, $^1J_{\text{HC}}$ 124.8 Hz), 20.34 q (s) (C⁷, $^1J_{\text{HC}}$ 128.1 Hz), 25.48 t (s) (C⁵, $^1J_{\text{HC}}$ 127.2 Hz), 25.64 q (s) (C⁹, $^1J_{\text{HC}}$ 126.9 Hz), 30.09 m (s) (C⁶), 32.23 m (s) (C¹), 38.70 m (d) (C⁸, $^1J_{\text{PC}}$ 42.2 Hz), 46.08 m (br. s) (C², $^1J_{\text{HC}}$ 129.6 Hz), 53.63 m (s) (C⁴), 118.92 dt (d) (PC_{Ph}^{ipso}, $^1J_{\text{PC}}$ 80.7 Hz, $^3J_{\text{HC}}$ 8.2 Hz), 126.99 ddd (d) (C_{Ph}^{meta}, $^1J_{\text{HC}}$ 165.9 Hz, $^3J_{\text{PC}}$ 11.4 Hz, $^3J_{\text{HC}}$ 6.2 Hz), 131.12 dm (br. s) (C_{Ph}^{para}, $^1J_{\text{HC}}$ 163.2 Hz), 132.35 dm (d) (C_{Ph}^{ortho}, $^1J_{\text{HC}}$ 164.4 Hz, $^2J_{\text{PC}}$ 8.4 Hz), 208.70 m (d) (C³, $^3J_{\text{PC}}$ 4.7 Hz); **3b** (*d*₂): 19.05 q (br. s) (C¹⁰), 20.49 m (s) (C⁷), 21.37 m (br. s) (C⁵), 22.47 m (s) (C⁶), 25.64 m (s) (C⁹), 28.69 m (s) (C¹), 38.81 dm (d) (C⁸, $^1J_{\text{PC}}$ 41.3 Hz), 44.68 m (br. s) (C²), 53.97 d (br. s) (C⁴,

$^1J_{\text{HC}}$ 128.7 Hz), 118.73 dt (d) ($\text{PC}_{\text{Ph}}^{\text{ipso}}$, $^1J_{\text{PC}}$ 80.4 Hz, $^3J_{\text{HC}}$ 7.8 Hz), 126.80 m (m) ($\text{C}_{\text{Ph}}^{\text{meta}}$), 128.58 m (br. s) ($\text{C}_{\text{Ph}}^{\text{para}}$), 132.17 m (br. s) ($\text{C}_{\text{Ph}}^{\text{ortho}}$), 209.96 m (d) (C^3 , $^3J_{\text{PC}}$ 4.8 Hz). $^{31}\text{P} / ^{31}\text{P}\{-^1\text{H}\}$ NMR (162.0 MHz, CDCl_3), δ_{P} : 41.5 m (s) (**3b**, d_1), 41.3 m (s) (**3b**, d_2). MALDI, m/z : calc. for $\text{C}_{28}\text{H}_{32}\text{OP}^+$ [M^+], 415.22; found 415.1. IR (KBr, cm^{-1}): 3057, 2951, 1714 (C=O), 1589, 1485, 1438, 1105, 997.

{2-[(1RS,4R)-4-Methyl-2-oxocyclohexyl]prop-2-yl}triphenylphosphonium trifluoroacetate 3c. Yield 89% (diastereoisomer ratio is 6.3 : 1.0), light yellow oil. ^1H NMR (400 MHz, CDCl_3), **3c** (d_1), δ : 0.93 (d, 3H, C^7H , $^3J_{\text{HH}}$ 6.5 Hz), 1.24-1.38 (m, 1H, C^2H), 1.37 (d, 3H, C^9H , $^3J_{\text{PH}}$ 20.3 Hz), 1.62-1.75 (m, 1H, C^6H), 1.76-1.87 (m, 1H, C^5H), 1.80 (d, 3H, C^{10}H , $^3J_{\text{PH}}$ 17.9 Hz), 1.85-1.94 (m, 1H, C^1H), 1.95-2.03 (m, 1H, C^6H), 2.04-2.11 (m, 1H, C^2H), 2.22-2.30 (m, 1H, C^5H), 2.82-2.87 (m, 1H, C^4H), 7.59-7.67 (m, 15H, CH_{Ph}); **3c** (d_2): 0.90 (d, 3H, C^7H , $^3J_{\text{HH}}$ 7.2 Hz), 1.24-1.38 (m, 1H, C^2H), 1.38 d (3H, C^9H , $^3J_{\text{PH}}$ 20.2 Hz), 1.62-1.75 (m, 1H, C^6H), 1.76-1.87 (m, 1H, C^5H), 1.83 (d, 3H, C^{10}H , $^3J_{\text{PH}}$ 18.0 Hz), 1.85-1.94 (m, 1H, C^1H), 1.95-2.03 (m, 1H, C^6H), 2.04-2.11 (m, 1H, C^2H), 2.22-2.30 (m, 1H, C^5H), 2.82-2.87 (m, 1H, C^4H), 7.59-7.67 (m, 15H, CH_{Ph}). ^{13}C NMR (100.6 MHz, CDCl_3), **3c** (d_1), δ_{C} : 21.42 q (br. s) (C^{10} , $^1J_{\text{HC}}$ 126.7 Hz), 22.31 q (s) (C^7 , $^1J_{\text{HC}}$ 125.7 Hz), 27.57 q (br. s) (C^9 , $^1J_{\text{HC}}$ 130.4 Hz), 27.86 t (br. s) (C^5 , $^1J_{\text{HC}}$ 129.9 Hz), 33.05 t (s) (C^6 , $^1J_{\text{HC}}$ 127.2 Hz), 35.06 d (s) (C^1 , $^1J_{\text{HC}}$ 126.7 Hz), 41.36 d (d) (C^8 , $^1J_{\text{PC}}$ 42.4 Hz), 48.87 t (br. s) (C^2 , $^1J_{\text{HC}}$ 128.5 Hz), 57.22 d (br. s) (C^4 , $^1J_{\text{HC}}$ 126.2 Hz), 121.56 dt (d) ($\text{PC}_{\text{Ph}}^{\text{ipso}}$, $^1J_{\text{PC}}$ 80.9 Hz, $^3J_{\text{HC}}$ 8.3 Hz), 129.67 ddd (d) ($\text{C}_{\text{Ph}}^{\text{meta}}$, $^1J_{\text{HC}}$ 166.7 Hz, $^3J_{\text{PC}}$ 12.0 Hz, $^3J_{\text{HC}}$ 7.1 Hz), 134.14 dt (br. s) ($\text{C}_{\text{Ph}}^{\text{para}}$, $^1J_{\text{HC}}$ 165.7 Hz, $^3J_{\text{HC}}$ 7.7 Hz), 134.86 ddd (d) ($\text{C}_{\text{Ph}}^{\text{ortho}}$, $^1J_{\text{HC}}$ 163.9 Hz, $^2J_{\text{PC}}$ 8.4 Hz, $^3J_{\text{HC}}$ 7.7 Hz), 211.36 m (d) (C^3 , $^3J_{\text{PC}}$ 3.9 Hz); **3c** (d_2): 18.36 q (br. s) (C^{10} , $^1J_{\text{HC}}$ 126.8 Hz), 22.31 m (s) (C^7), 23.62 m (br. s) (C^5), 27.38 m (br. s) (C^9), 30.09 m (s) (C^6), 31.12 m (s) (C^1), 41.48 m (d) (C^8 , $^1J_{\text{PC}}$ 42.6 Hz), 47.36 t (s) (C^2 , $^1J_{\text{HC}}$ 126.9 Hz), 57.51 d (br. s) (C^4 , $^1J_{\text{HC}}$ 126.0 Hz), 121.43 dt (d) ($\text{PC}_{\text{Ph}}^{\text{ipso}}$, $^1J_{\text{PC}}$ 80.7 Hz, $^3J_{\text{HC}}$ 8.4 Hz), 128.88 ddd (d) ($\text{C}_{\text{Ph}}^{\text{meta}}$, $^1J_{\text{HC}}$ 162.8 Hz, $^3J_{\text{PC}}$ 12.5 Hz, $^3J_{\text{HC}}$ 7.4 Hz), 132.94 dt (br. s) ($\text{C}_{\text{Ph}}^{\text{para}}$, $^1J_{\text{HC}}$ 163.3 Hz, $^3J_{\text{HC}}$ 7.2 Hz), 134.63 m (d) ($\text{C}_{\text{Ph}}^{\text{ortho}}$), 212.49 m (d) (C^3 , $^3J_{\text{PC}}$ 3.5 Hz). $^{31}\text{P} / ^{31}\text{P}\{-^1\text{H}\}$ NMR (162.0 MHz, CDCl_3), δ_{P} : 42.3 m (s) (**3c**, d_1), 42.0 m (s) (**3c**, d_2). MALDI, m/z : calc. for $\text{C}_{28}\text{H}_{32}\text{OP}^+$ [M^+], 415.22; found 415.1. IR (film, cm^{-1}): 3066, 2961, 2876, 1713 (C=O), 1585, 1487, 1439, 1103, 999.

{2-[(1RS,4R)-4-Methyl-2-oxocyclohexyl]prop-2-yl}triphenylphosphonium triflate 3d. Yield 92% (diastereoisomer ratio is 2.8 : 1.0), light yellow powder, mp 124-126°C. ^1H NMR (400 MHz, CDCl_3), **3d** (d_1), δ : 0.95 (d, 3H, C^7H , $^3J_{\text{HH}}$ 6.4 Hz), 1.36-1.48 (m, 1H, C^2H), 1.41 (d, 3H, C^9H , $^3J_{\text{PH}}$ 20.7 Hz), 1.57-1.72 (m, 2H, C^6H , C^5H), 1.78 (d, 3H, C^{10}H , $^3J_{\text{PH}}$ 18.1 Hz), 1.72-1.86 (m, 1H, C^1H), 1.87-2.01 (m, 2H, C^6H и C^2H), 2.30-2.40 (m, 1H, C^5H), 3.25-3.33 (m, 1H, C^4H), 7.60-7.78 (m, 15H, CH_{Ph}); **3d** (d_2): 0.89 (d, 3H, C^7H , $^3J_{\text{HH}}$ 7.2 Hz), 1.36-1.48 (m, 1H, C^2H), 1.43 d (3H, C^9H , $^3J_{\text{PH}}$ 21.7 Hz), 1.57-1.72 (m, 2H, C^6H , C^5H), 1.80 (d, 3H, C^{10}H , $^3J_{\text{PH}}$ 18.0 Hz), 1.72-1.86 (m, 1H, C^1H), 1.87-2.01 (m, 2H, C^6H и C^2H), 2.30-2.40 (m, 1H, C^5H), 3.25-3.33 (m, 1H, C^4H), 7.60-7.78 (m, 15H, CH_{Ph}). ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$), **3d** (d_1), δ_{C} : 21.95 q (br. s) (C^{10} , $^1J_{\text{HC}}$ 124.3 Hz), 22.71 q (s) (C^7 , $^1J_{\text{HC}}$

127.5 Hz), 27.47 q (br. s) (C^9 , $^1J_{\text{HC}}$ 130.5 Hz), 27.77 m (d) (C^5 , $^3J_{\text{PC}}$ 7.2 Hz), 33.11 t (s) (C^6 , $^1J_{\text{HC}}$ 126.0 Hz), 34.66 d (s) (C^1 , $^1J_{\text{HC}}$ 128.3 Hz), 41.19 m (d) (C^8 , $^1J_{\text{PC}}$ 41.8 Hz), 48.94 t (s) (C^2 , $^1J_{\text{HC}}$ 129.4 Hz), 56.53 d (br. s) (C^4 , $^1J_{\text{HC}}$ 129.6 Hz), 122.08 dt (d) ($\text{PC}_{\text{Ph}}^{\text{ipso}}$, $^1J_{\text{PC}}$ 80.4 Hz, $^3J_{\text{HC}}$ 8.1 Hz), 129.98 ddd (d) ($\text{C}_{\text{Ph}}^{\text{meta}}$, $^1J_{\text{HC}}$ 165.9 Hz, $^3J_{\text{PC}}$ 11.9 Hz, $^3J_{\text{HC}}$ 7.1 Hz), 134.26 dtd (d) ($\text{C}_{\text{Ph}}^{\text{para}}$, $^1J_{\text{HC}}$ 163.9 Hz, $^3J_{\text{HC}}$ 6.4 Hz, $^4J_{\text{PC}}$ 2.7 Hz), 135.33 dd (d) ($\text{C}_{\text{Ph}}^{\text{ortho}}$, $^1J_{\text{HC}}$ 164.8 Hz, $^2J_{\text{PC}}$ 8.5 Hz), 210.96 m (d) (C^3 , $^3J_{\text{PC}}$ 5.3 Hz); **3d** (d_2): 18.89 m (br. s) (C^{10} , $^1J_{\text{HC}}$ 127.4 Hz), 22.80 m (s) (C^7), 23.91 m (d) (C^5 , $^3J_{\text{PC}}$ 7.1 Hz), 27.12 q (br. s) (C^9 , $^1J_{\text{HC}}$ 128.9 Hz), 30.15 m (s) (C^6), 31.20 d (s) (C^5 , $^1J_{\text{HC}}$ 128.5 Hz), 41.41 m (C^8 , $^1J_{\text{PC}}$ 41.3 Hz), 47.56 t (s) (C^2 , $^1J_{\text{HC}}$ 132.3 Hz), 56.85 d (br. s) (C^4 , $^1J_{\text{HC}}$ 129.9 Hz), 121.82 dt (d) ($\text{PC}_{\text{Ph}}^{\text{ipso}}$, $^1J_{\text{PC}}$ 80.0 Hz, $^3J_{\text{HC}}$ 8.0 Hz), 129.20 dm (d) ($\text{C}_{\text{Ph}}^{\text{meta}}$, $^1J_{\text{HC}}$ 163.2 Hz, $^3J_{\text{PC}}$ 11.7 Hz, $^3J_{\text{HC}}$ 7.4 Hz), 134.24 dm (d) ($\text{C}_{\text{Ph}}^{\text{para}}$, $^4J_{\text{PC}}$ 2.8 Hz), 135.39 dd (d) ($\text{C}_{\text{Ph}}^{\text{ortho}}$, $^1J_{\text{HC}}$ 165.3 Hz, $^2J_{\text{PC}}$ 8.5 Hz), 212.18 m (d) (C^3 , $^3J_{\text{PC}}$ 5.5 Hz). $^{31}\text{P} / ^{31}\text{P}\{-^1\text{H}\}$ NMR (162 MHz, CDCl_3), δ_{P} : 42.3 m (s) (**3d**, d_1), 42.1 m (s) (**3d**, d_2). MALDI, m/z : calc. for $\text{C}_{28}\text{H}_{32}\text{OP}^+$ [M^+], 415.22; found 415.28. IR (KBr, cm^{-1}): 3063, 2964, 2875, 1711 c (C=O), 1588, 1485, 1438, 1101, 997.

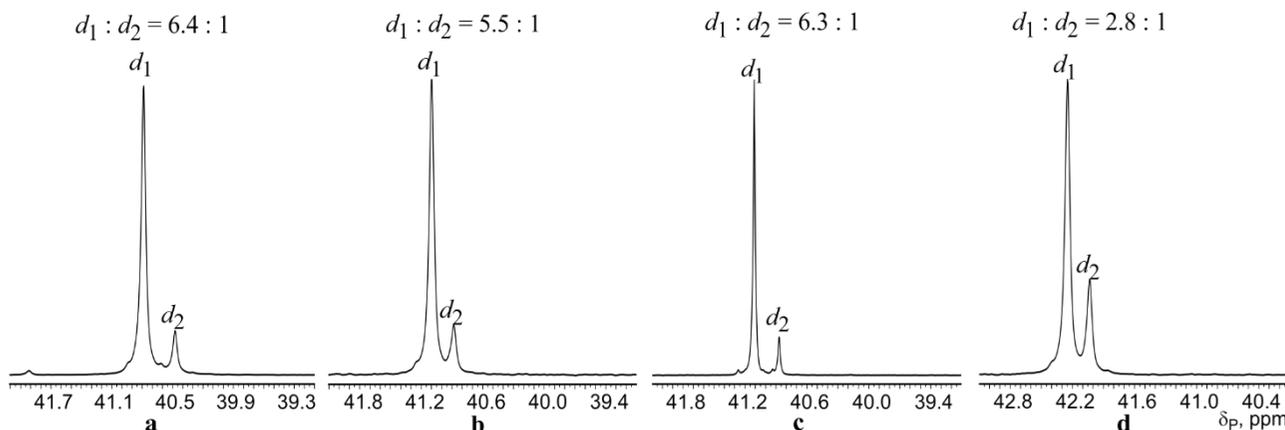


Figure S1. $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra (162.0 MHz, CDCl_3) of compounds **3a-d**.

Crystal data for **3a**·HCl. The needle crystals ($0.462 \times 0.089 \times 0.086 \text{ mm}^3$) of **3a**·HCl were prepared by slow evaporation of a petroleum ether solution at room temperature.

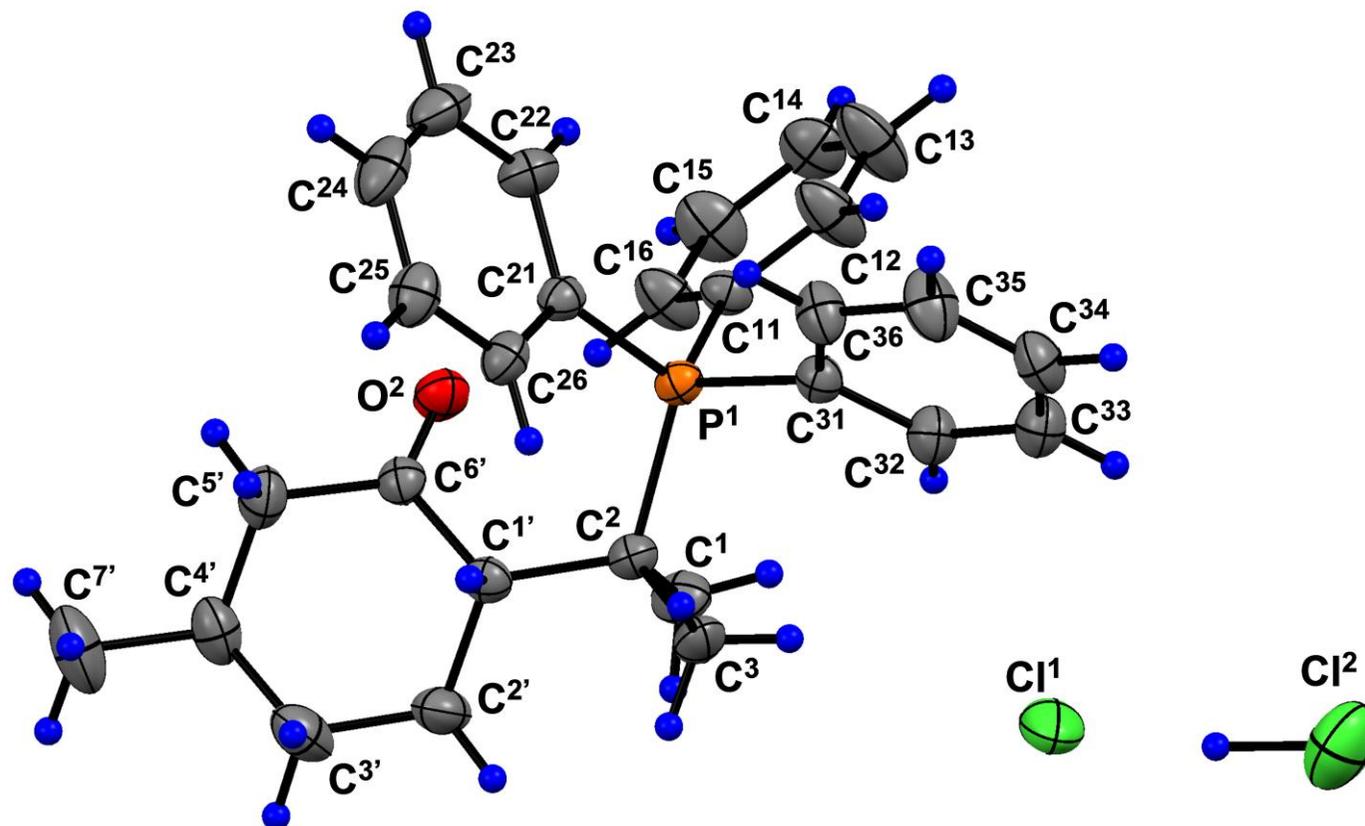


Figure S2. Geometry of compound **3a**·HCl in the crystal. Non-hydrogen atoms are shown in view of thermal ellipsoids with a probability of 30%.

Table S1. Bond lengths in the molecule of compound **3a**·HCl.

bond	<i>d</i> , Å	bond	<i>d</i> , Å	bond	<i>d</i> , Å	bond	<i>d</i> , Å	bond	<i>d</i> , Å
Cl ¹ –C ⁶	1.740(2)	C ⁹ –C ¹⁴	1.383(3)	O ⁵ –C ⁴	1.360(3)	O ^{1S} –C ^{3S}	1.427(3)	C ⁴ –C ⁵	1.385(3)
P ¹ –O ²	1.489(2)	C ⁹ –C ¹⁰	1.382(3)	O ⁵ –C ¹⁵	1.430(3)	C ¹ –C ²	1.332(3)	C ⁵ –C ⁶	1.371(3)
P ¹ –O ³	1.545(2)	C ¹⁰ –C ¹¹	1.374(4)	O ¹ –H ¹	0.77(3)	C ² –C ⁹	1.482(3)	C ⁶ –C ⁷	1.366(3)
P ¹ –O ⁴	1.536(2)	C ¹¹ –C ¹²	1.361(5)	O ³ –H ³	0.81(3)	C ² –C ³	1.501(3)	C ⁷ –C ⁸	1.382(3)
P ¹ –C ¹	1.760(2)	C ¹² –C ¹³	1.363(5)	O ⁴ –H ⁴	0.84(3)	C ³ –C ⁸	1.386(3)	–	–
O ¹ –C ⁸	1.348(3)	C ¹³ –C ¹⁴	1.378(4)	O ^{1S} –C ^{2S}	1.426(3)	C ³ –C ⁴	1.390(3)	–	–

Table S2. Bond angles in the molecule of compound **3a**·HCl.

Angle	φ (grad)	Angle	φ (grad)	Angle	φ (grad)	Angle	φ (grad)
O ² –P ¹ –O ³	110.2(1)	C ² –C ⁹ –C ¹⁴	120.3(2)	P ¹ –C ¹ –C ²	126.4(2)	O ⁵ –C ⁴ –C ⁵	124.3(2)
O ² –P ¹ –O ⁴	112.7(1)	C ² –C ⁹ –C ¹⁰	122.0(2)	C ¹ –C ² –C ³	119.1(2)	C ⁴ –C ⁵ –C ⁶	118.3(2)
O ² –P ¹ –C ¹	108.9(1)	C ⁹ –C ¹⁰ –C ¹¹	121.0(2)	C ¹ –C ² –C ⁹	123.1(2)	Cl ¹ –C ⁶ –C ⁷	118.3(2)
O ³ –P ¹ –O ⁴	107.9(1)	C ¹⁰ –C ¹¹ –C ¹²	120.2(3)	C ³ –C ² –C ⁹	117.8(2)	Cl ¹ –C ⁶ –C ⁵	118.9(2)
O ³ –P ¹ –C ¹	108.3(1)	C ¹¹ –C ¹² –C ¹³	120.0(3)	C ⁴ –C ³ –C ⁸	118.6(2)	C ⁵ –C ⁶ –C ⁷	122.8(2)
O ⁴ –P ¹ –C ¹	108.7(1)	C ¹² –C ¹³ –C ¹⁴	120.1(3)	C ² –C ³ –C ⁴	121.9(2)	C ⁶ –C ⁷ –C ⁸	118.2(2)
C ⁴ –O ⁵ –C ¹⁵	118.5(2)	C ⁹ –C ¹⁴ –C ¹³	120.9(3)	C ² –C ³ –C ⁸	119.4(2)	O ¹ –C ⁸ –C ⁷	122.7(2)
O ¹ –C ⁸ –C ³	116.0(2)	P ¹ –O ⁴ –H ⁴	113(2)	O ⁵ –C ⁴ –C ³	114.9(2)	C ³ –C ⁸ –C ⁷	121.2(2)
C ¹⁰ –C ⁹ –C ¹⁴	117.8(2)	C ^{2S} –O ^{1S} –C ^{3S}	111.1(2)	C ³ –C ⁴ –C ⁵	120.8(2)	–	–

Table S3. Torsion angles in the molecule of compound **3a**·HCl.

Angle	τ (grad)	Angle	τ (grad)	Angle	τ (grad)	Angle	τ (grad)
O ² –P ¹ –C ¹ –C ²	–169.2(2)	P ¹ –C ¹ –C ² –C ³	–0.9(3)	C ³ –C ² –C ⁹ –C ¹⁴	–5.7(3)	C ⁴ –C ³ –C ⁸ –O ¹	–178.5(2)
O ³ –P ¹ –C ¹ –C ²	–49.4(2)	P ¹ –C ¹ –C ² –C ⁹	177.4(2)	C ⁹ –C ² –C ³ –C ⁴	101.3(2)	C ⁴ –C ³ –C ⁸ –C ⁷	2.8(3)
O ⁴ –P ¹ –C ¹ –C ²	67.6(2)	C ¹ –C ² –C ³ –C ⁴	–80.3(3)	C ¹ –C ² –C ³ –C ⁸	96.1(2)	C ⁸ –C ³ –C ⁴ –O ⁵	176.0(2)
C ¹⁵ –O ⁵ –C ⁴ –C ³	162.7(2)	C ⁹ –C ² –C ³ –C ⁸	–82.3(3)	C ² –C ³ –C ⁴ –C ⁵	173.2(2)	C ⁸ –C ³ –C ⁴ –C ⁵	–3.2(3)
C ¹⁵ –O ⁵ –C ⁴ –C ⁵	–18.1(3)	C ¹ –C ² –C ⁹ –C ¹⁰	–5.5(3)	C ² –C ³ –C ⁴ –O ⁵	–7.6(3)	O ⁵ –C ⁴ –C ⁵ –C ⁶	–178.2(2)
C ^{3S} –O ^{1S} –C ^{2S} –C ^{3S_a}	57.9(3)	C ¹ –C ² –C ⁹ –C ¹⁴	175.9(2)	C ² –C ³ –C ⁸ –O ¹	5.0(3)	C ³ –C ⁴ –C ⁵ –C ⁶	0.9(3)
C ^{2S} –O ^{1S} –C ^{3S} –C ^{2S_a}	–57.7(3)	C ³ –C ² –C ⁹ –C ¹⁰	172.8(2)	C ² –C ³ –C ⁸ –C ⁷	–173.7(2)	C ⁴ –C ⁵ –C ⁶ –Cl ¹	–178.2(2)

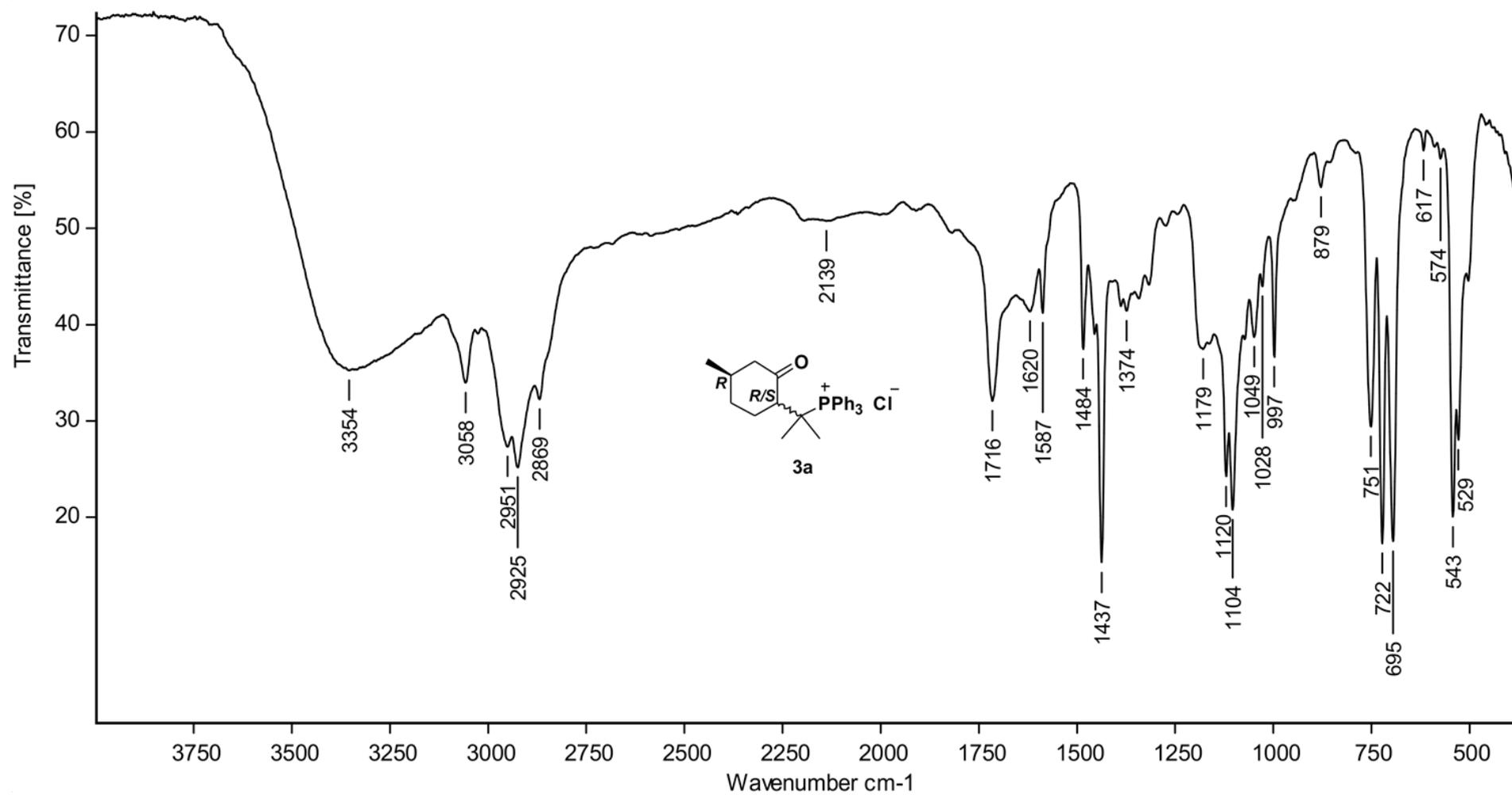


Figure S3. IR (film) spectrum of compound **3a**.

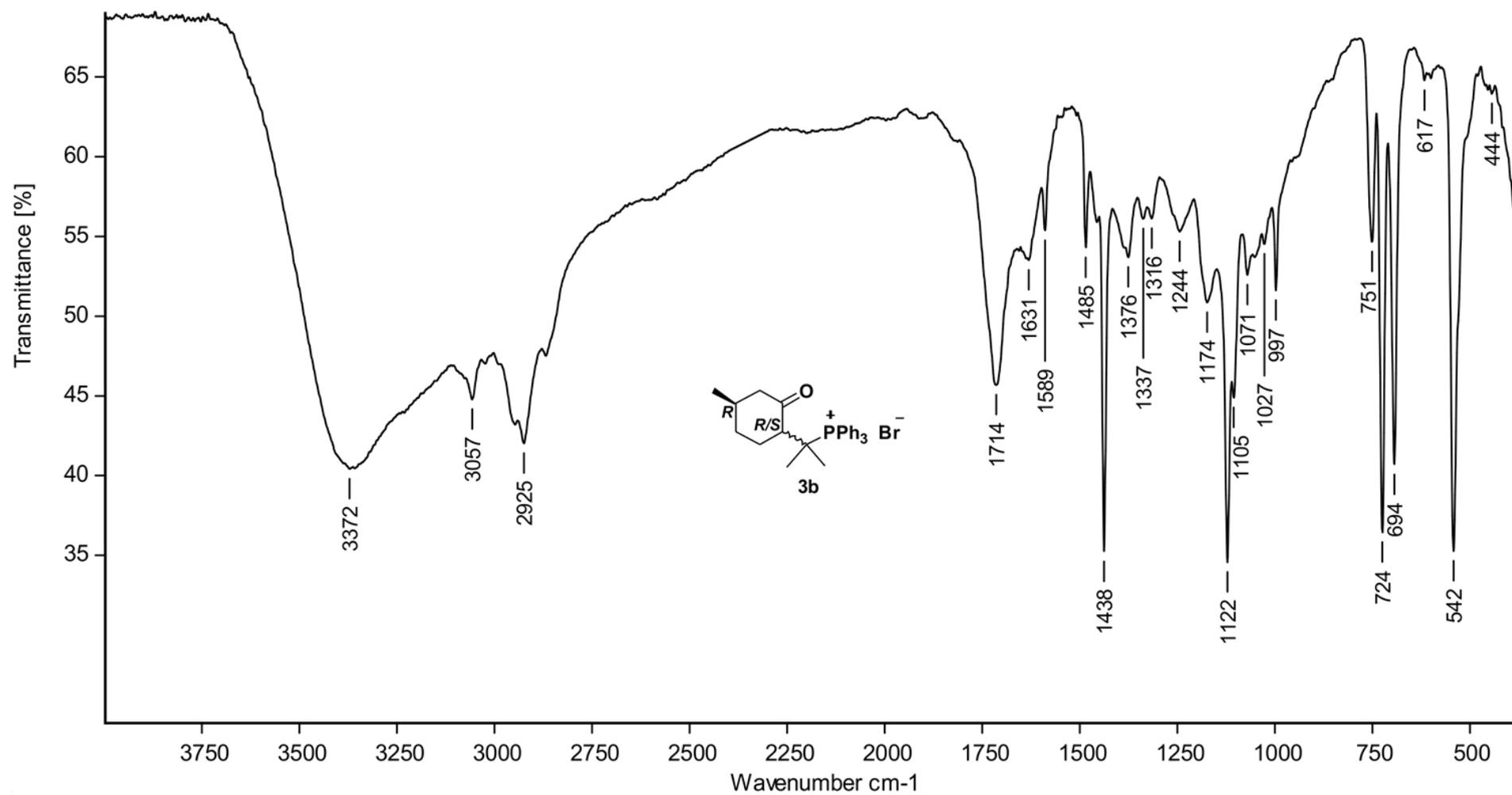


Figure S4. IR (film) spectrum of compound **3b**.

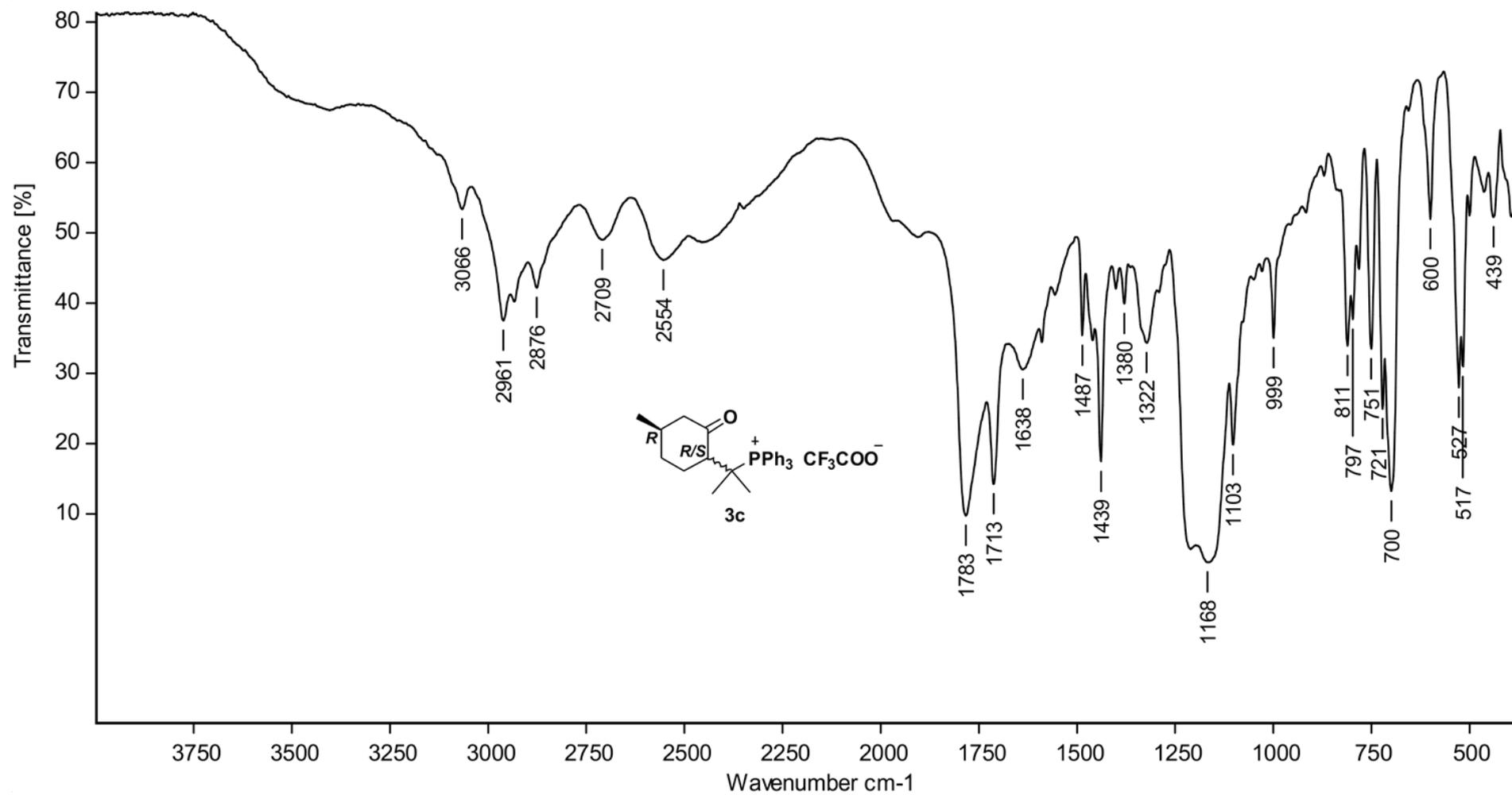


Figure S5. IR (film) spectrum of compound **3c**.

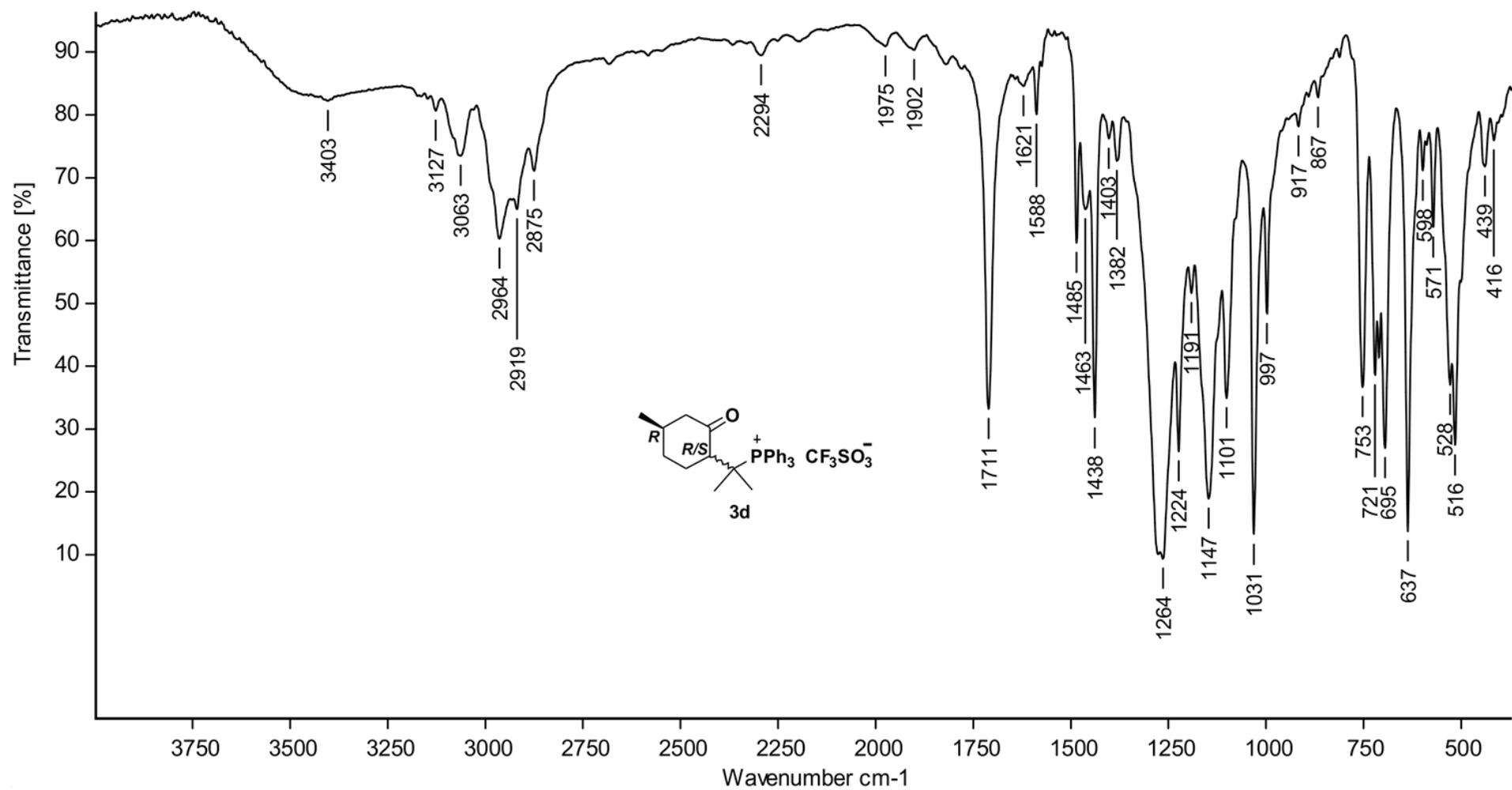


Figure S6. IR (KBr) spectrum of compound **3d**.

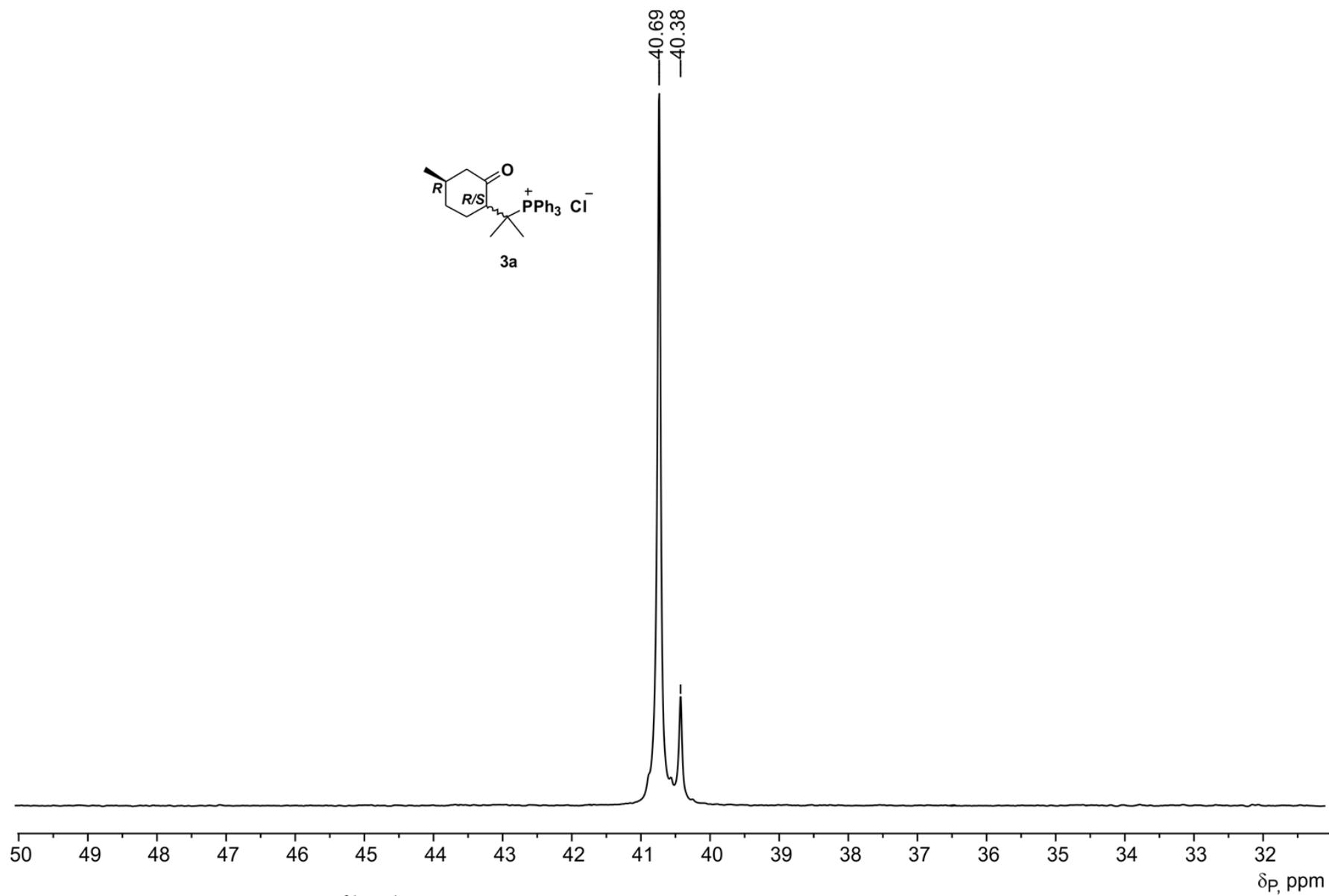


Figure S7. ^{31}P - $\{^1\text{H}\}$ NMR spectrum (162.0 MHz, CH_2Cl_2 , 25°C) of phosphonium salt (**3a**).

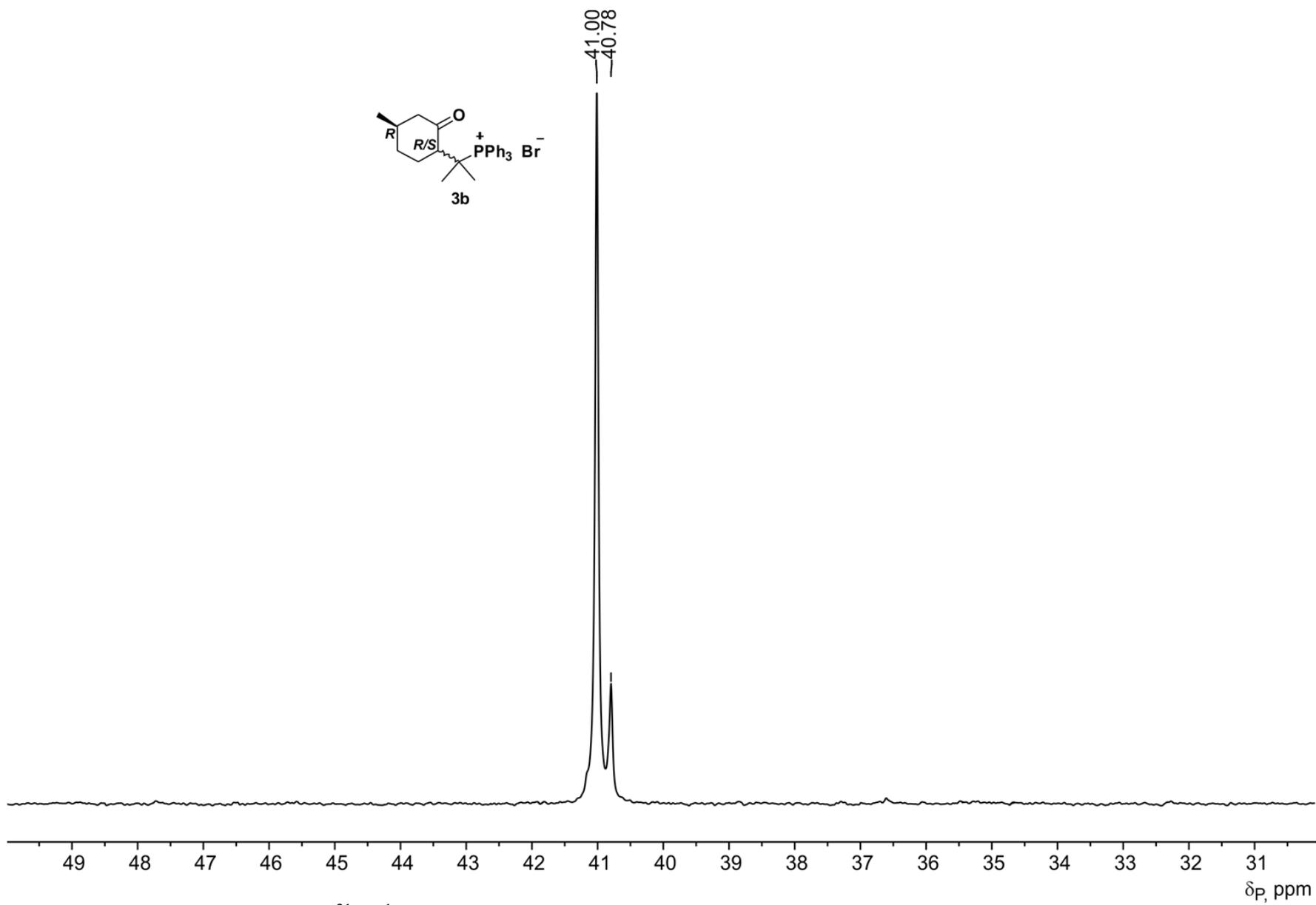


Figure S8. ^{31}P - $\{^1\text{H}\}$ NMR spectrum (162.0 MHz, CH_2Cl_2 , 25°C) of phosphonium salt (**3b**).

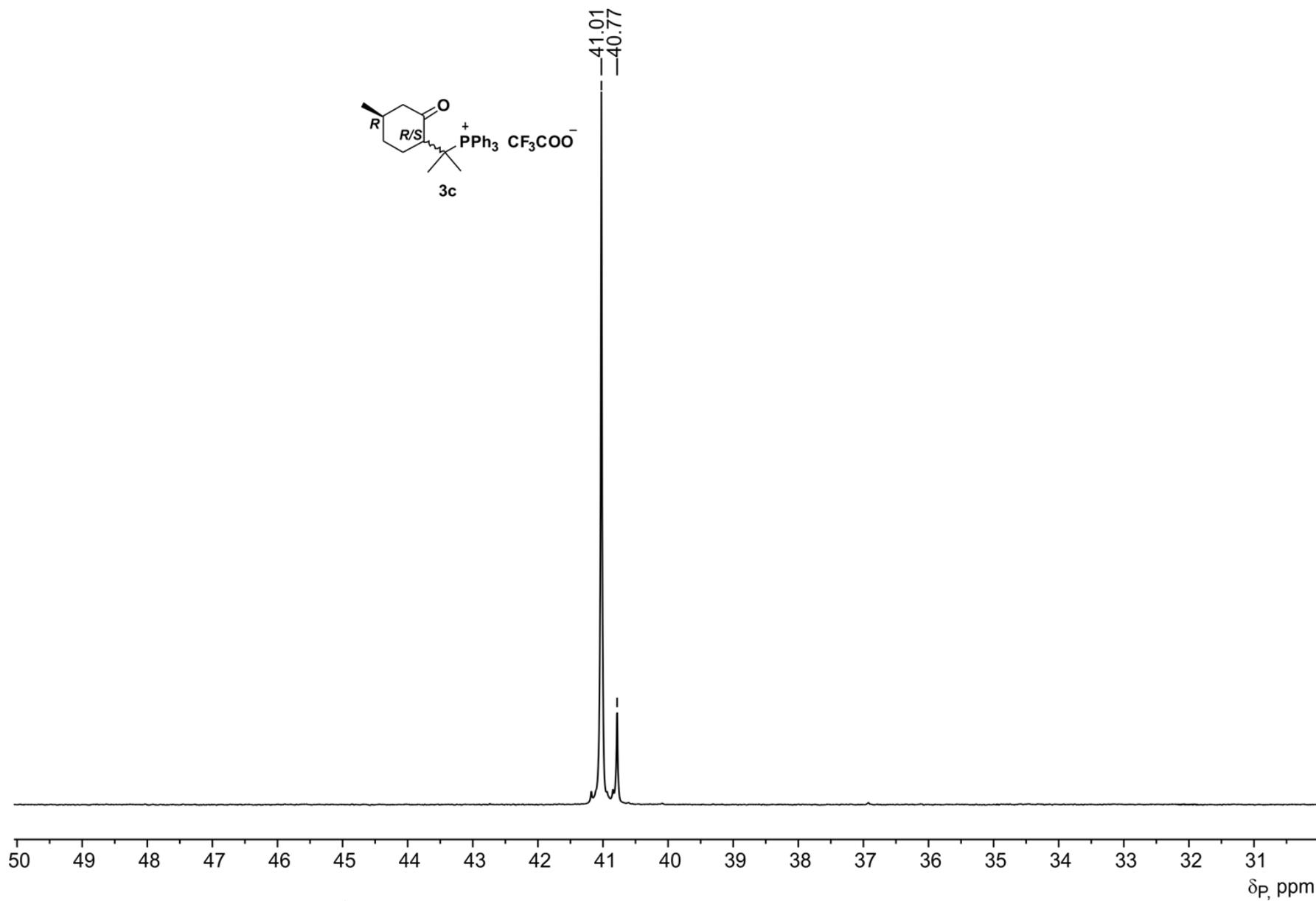


Figure S9. ^{31}P - $\{^1\text{H}\}$ NMR spectrum (162.0 MHz, CH_2Cl_2 , 25°C) of phosphonium salt (**3c**).

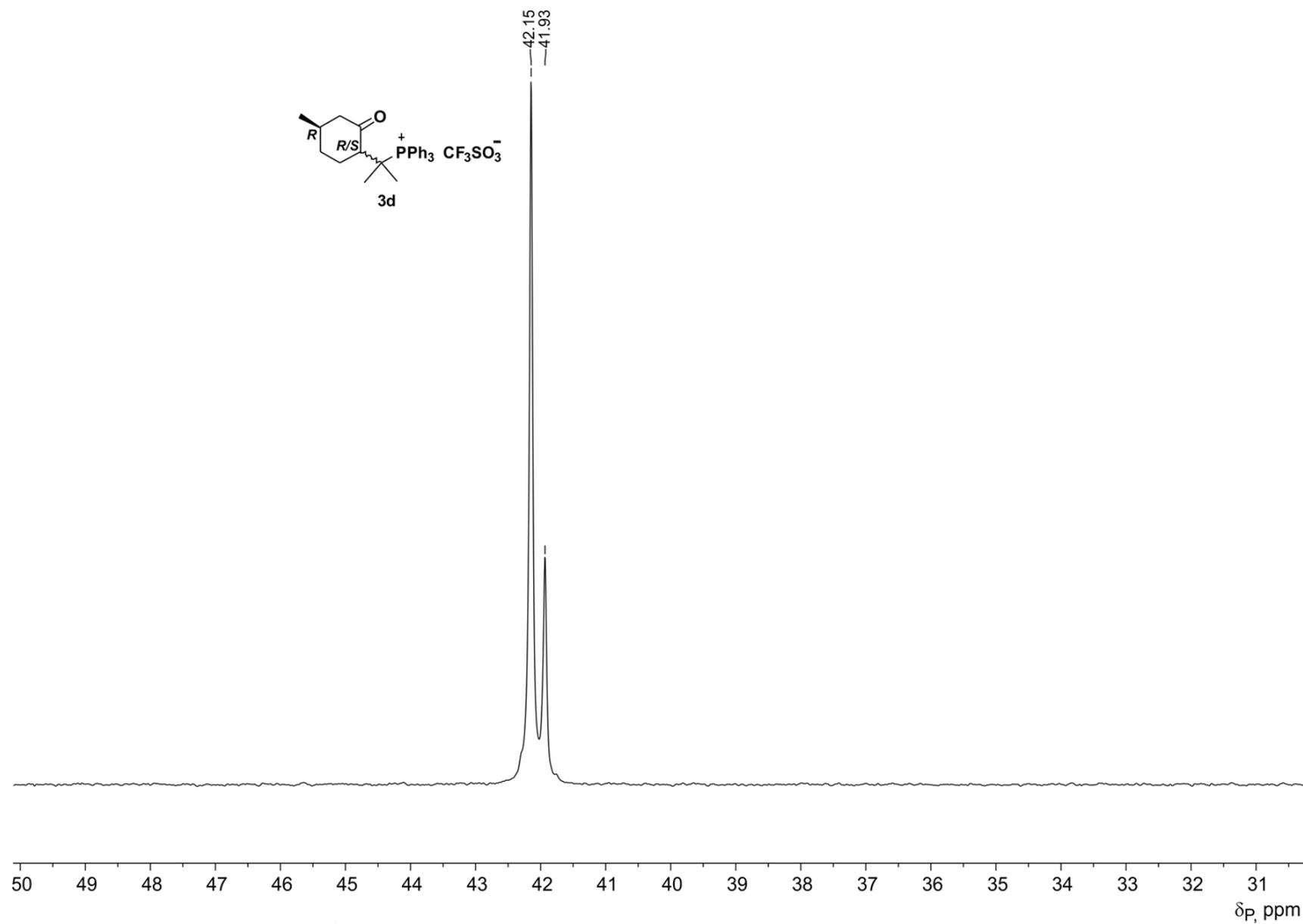


Figure S10. ^{31}P - $\{^1\text{H}\}$ NMR spectrum (162.0 MHz, CH_2Cl_2 , 25°C) of phosphonium salt (**3d**).

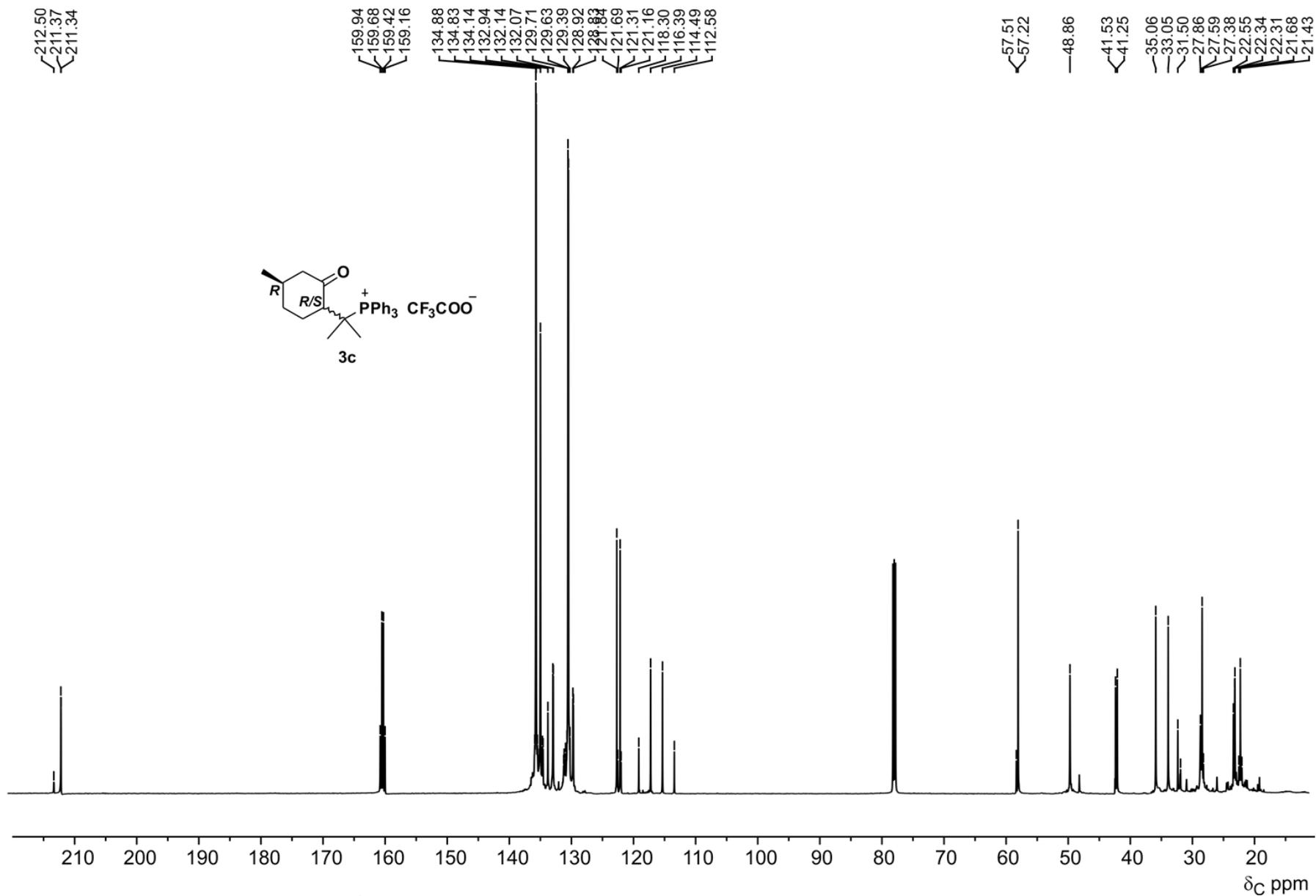


Figure S11. ^{13}C - $\{^1\text{H}\}$ NMR spectrum (100.9 MHz, CDCl_3 , 25°C) of phosphonium salt (**3c**).

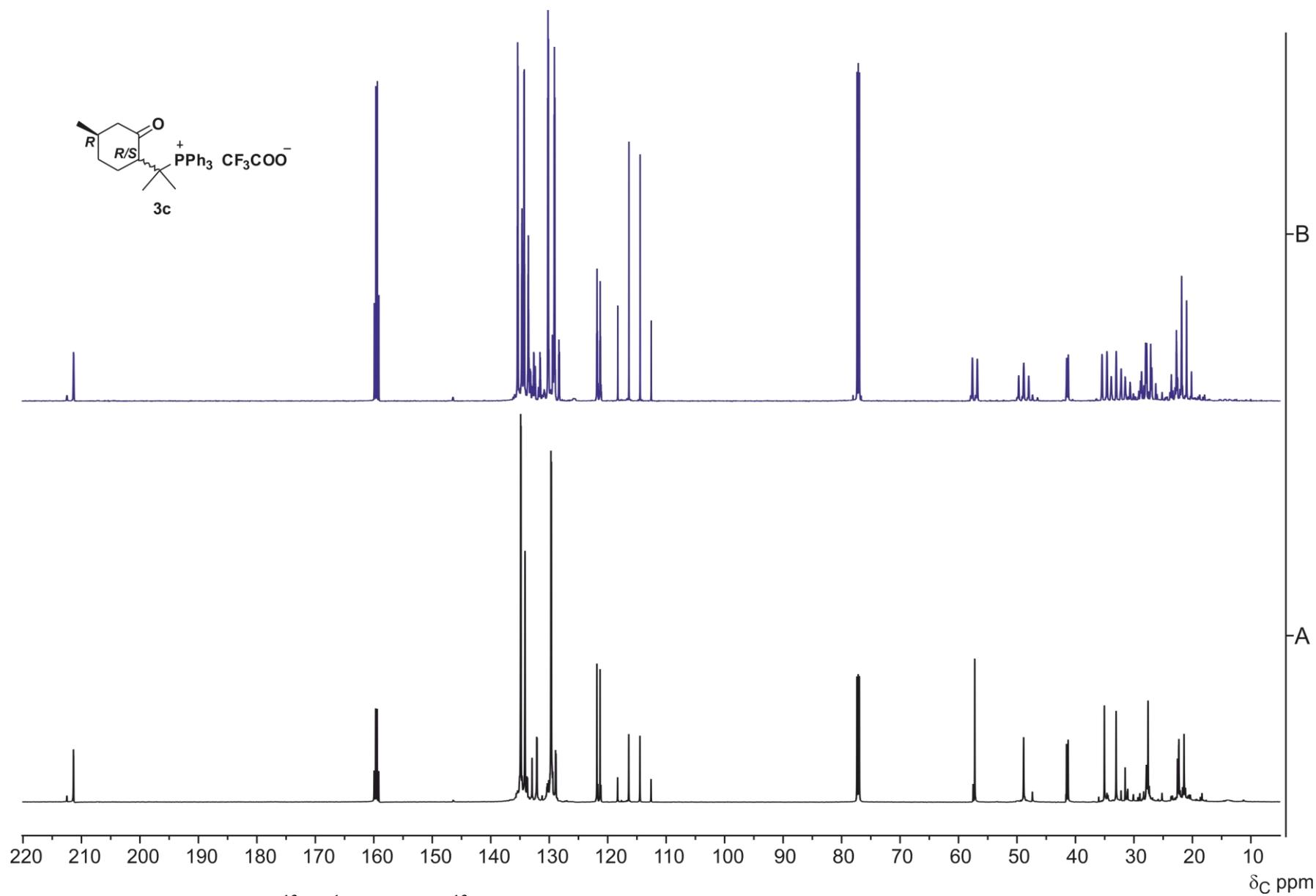


Figure S12. $^{13}\text{C}\{-^1\text{H}\}$ (A) and ^{13}C (B) NMR spectra (100.9 MHz, CDCl_3 , 25°C) of phosphonium salt (**3c**).

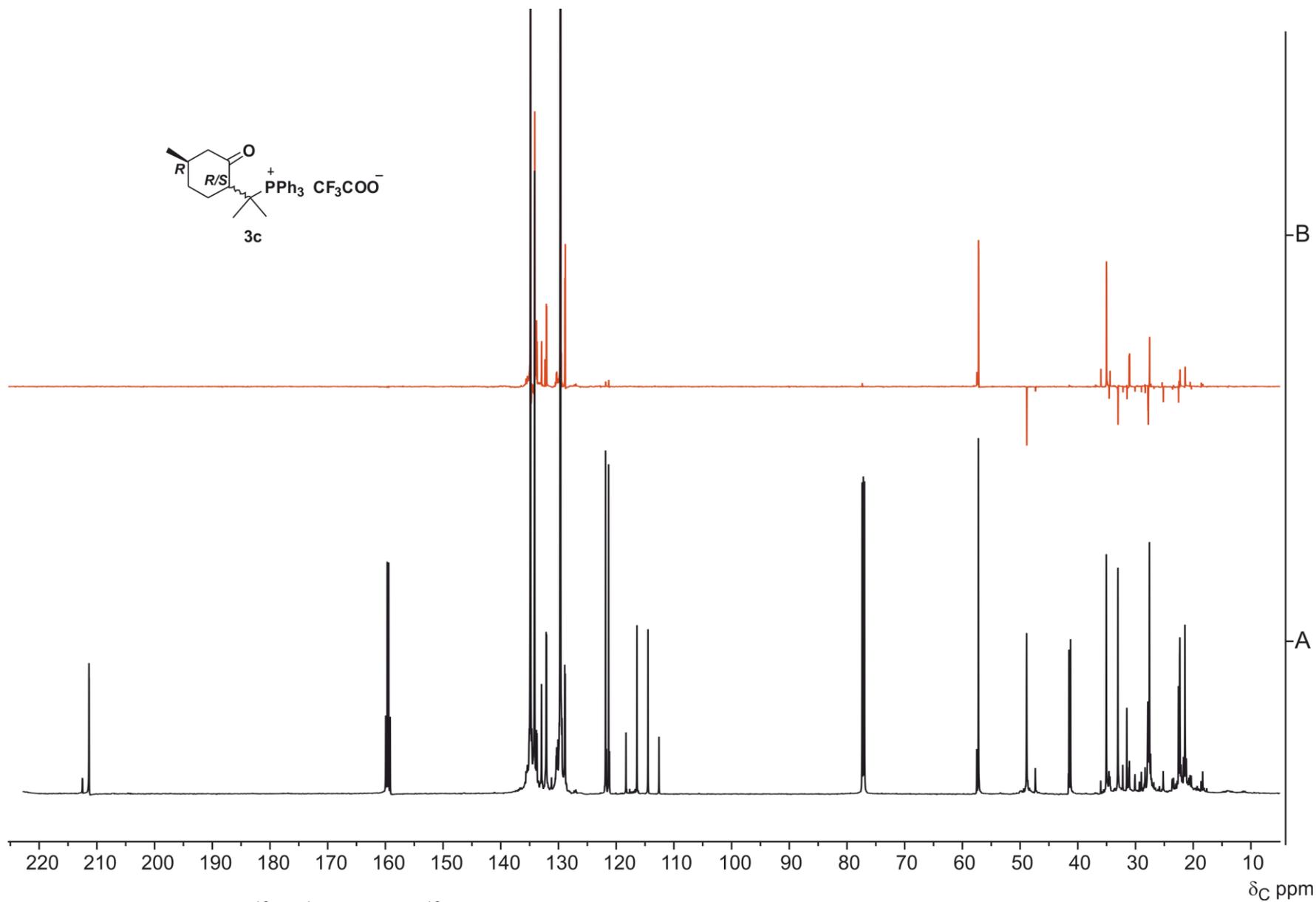
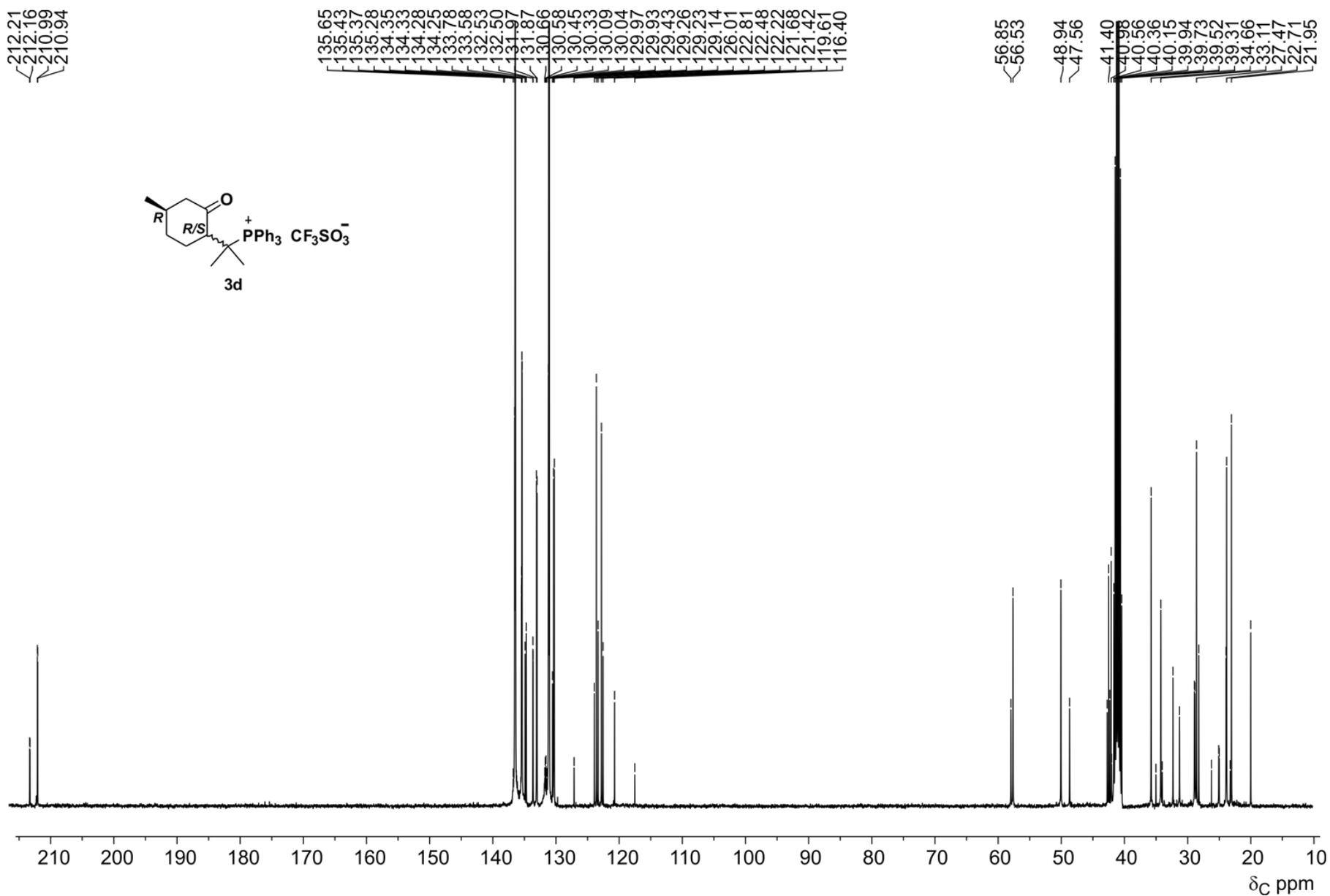


Figure S13. ¹³C-¹H (A) and ¹³C-dept (B) NMR spectra (100.9 MHz, CDCl₃, 25°C) of phosphonium salt (**3c**).



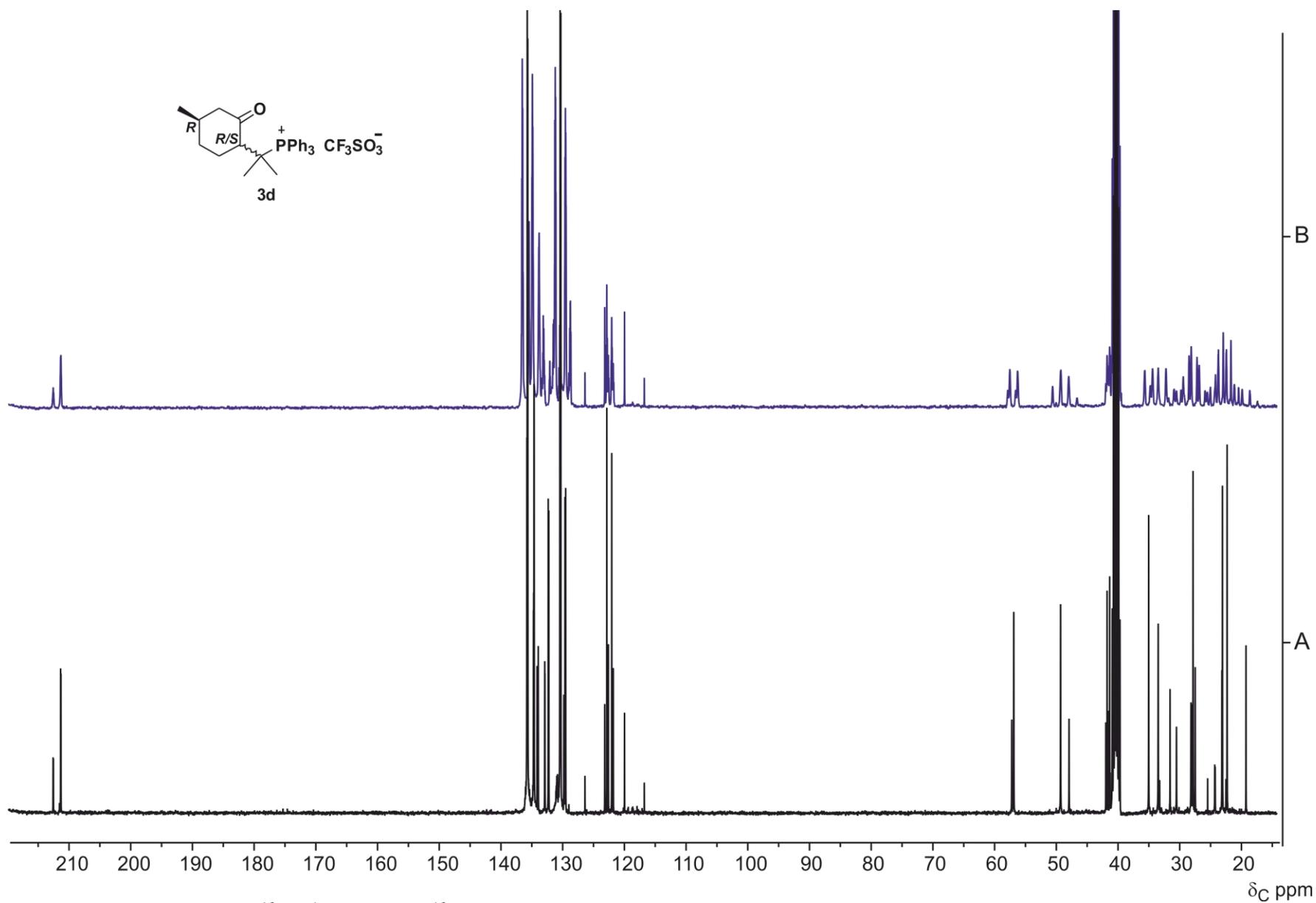


Figure S15. $^{13}\text{C}\{-^1\text{H}\}$ (A) and ^{13}C (B) NMR spectra (100.9 MHz, $\text{DMSO-}d_6$, 25°C) of phosphonium salt (**3d**).

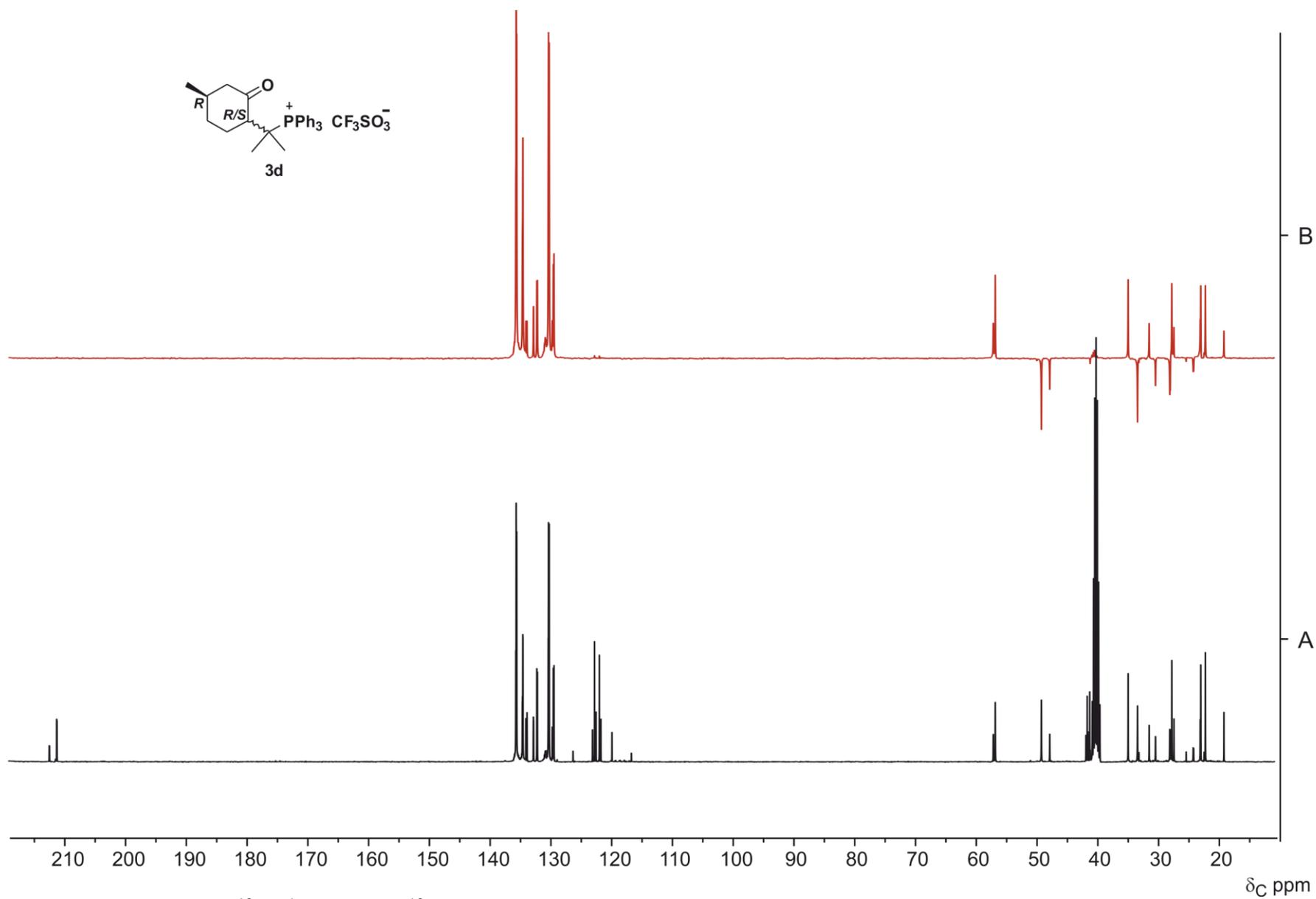


Figure S16. ^{13}C - $\{^1\text{H}\}$ (A) and ^{13}C -dept (B) NMR spectra (100.9 MHz, $\text{DMSO}-d_6$, 25°C) of phosphonium salt (**3d**).