Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 759–761

Phosphonium and arsonium salts based on alantolactone

Mariya E. Shemakhina, Andrey V. Nemtarev, Denis V. Chachkov, Sergei A. Pukhov and Vladimir F. Mironov

Table of Contents

Experimental Section.

General remarks. The NMR spectra were recorded at 25 °C using a Bruker Avance-400 NMR spectrometer (400.0 MHz, ^{1}H; 100.6 MHz, ^{13}C; 162 MHz, ^{31}P) in $CDCl_3$. Chemical shifts are referenced to the residual solvent peak and reported in ppm (δ scale) and all coupling constant (*J*) values are given in Hz. IR spectra were recorded using a Bruker Vector 22 spectrometer for samples in KBr pellets. MALDI mass spectra were acquired on a Bruker MALDI-TOF Ultraflex III spectrometer (Bruker Daltonik, Bremen, Germany). 2,5-Dihydroxybenzoic acid (5 mg/mL in methanol) was used as a matrix. Positively charged ions were registered. Elemental analysis was accomplished with an automated EuroVector EA3000 CHNS elemental analyzer (Euro-Vector, Italy). The progress of reactions and the purity of products were monitored by TLC on Sorbfil plates (IMID Ltd., Russian Federation). The TLC plates were visualized by UV. Solvents were purified and dried by standard protocols. Alantolactone isolated from the roots of elecampane (*Inula helenium L.*) according to [S1].

Quantum-chemical calculations were performed using the B3PW91 hybrid density functional theory (DFT) method [S2,S3] and the extended split valence basis set TZVP [S4] with full optimization of all geometric parameters. The correspondence of the found stationary points to the energy minima was proved by calculating the second derivatives of the energy to the coordinates of the atoms, wherein all the equilibrium structures that corresponded to the minimum points on the potential energy surfaces had only positive frequency values. The calculation was carried out using the GAUSSIAN 09 software package [S5]. The calculations were carried out on the MVS-10P (MVS-10P) computing cluster of the Interdepartmental Supercomputer Center of the Russian Academy of Sciences (www.jscc.ru).

References

S1. A. V. Semakov and S. G. Klochkov, *Khim. Rastit. Syr'ya* (*Chem. Plant Raw Mater.*), 2020, no. 3, DOI: 10.14258/jcprm.2020034681 (in Russian).

S2. A. D. Becke. *J. Chem. Phys.*, 1993, **98**, 5648.

S3. J. P. Perdew, K. Burke and Y. Wang. *Phys. Rev. B*, 1996, **54**, 16533.

S4. A. Schaefer, C. Huber and R. Ahlrichs. *J. Chem. Phys.*, 1994, **100**, 5829.

S5. 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, H. 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, 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 09, Revision A.01*, Gaussian, Wallingford, CT, 2009.

General procedure for the synthesis of 2 and 3. Triphenylphosphine or triphenylarsine (1 mmol) was added to a solution of a trifluoromethanesulfonic acid (1 mmol) in CH_2Cl_2 (5 ml). The resulting mixture was stirred for 0.5 h. Then a solution of alantolactone **1** (1 mmol) in CH_2Cl_2 (3 ml) was added dropwise with stirring to the reaction mixture. The mixture was stirred for 1 h under argon atmosphere. The solvent was removed under reduced pressure (15 Torr). The residue was washed with ether and dissolved in CH_2Cl_2 (2 ml). The product was precipitated with ether and dried in vacuo (15 Torr).

Atom numbering in NMR assignment does not coincide with systematic and relates to terpenoid numbering given in Schemes and Figures.

(Eudesm-5-en-12,8-olid-13-yl)(triphenyl)phosphonium triflate, [(3RS,3aR,5S,8aR,9aR)-(5,8a-dimethyl-2-oxo-2,3,3a,5,6,7,8,8a,9,9a-decahydronaphtho[2,3-b]furan-3-yl)methyl]-(triphenyl)phosphonium triflate **2**. Yield: 0.60 g (97%) (ratio of diastereomers d_1 : d_2 = 1.00 : 0.14); light yellow powder; mp 94 °C. ^{1}H NMR (400 MHz, CD_3OD), **2** (d_1), δ: 1.08 (d, 1H, C^{1}H, $^3J_{HH}$ 10.0 Hz), 1.13 (s, 3H, C^{14}H), 1.15 (br. s, 3H, C^{15}H), 1.36 (dm, 1H, C^{2}H, $^3J_{HH}$ 13.7 Hz), 1.44 (dm, 1H, C^{9}H, $^3J_{HH}$ 15.4 Hz), 1.46-1.60 (m, 3H, C^{1}H, C^{3}H), 1.73-1.88 (m, 1H, C^{2}H), 1.98 (dd, 1H, C^{9}H, $^3J_{HH}$ 14.9 Hz, $^2J_{HH}$ 3.0 Hz), 2.43-2.54 (m, 1H, C^{4}H), 2.64-2.73 (m, 1H, C^{11}H), 3.27 (br. s, 1H, C^{7}H), 3.46-3.63 (m, 1H, C^{13}H), 3.75-3.90 (m, 1H, C^{13}H), 4.77 (s, 1H, C^{8}H, overlapped with H_2O), 5.10 (s, 1H, C^{6}H), 7.68-7.95 (m, 15H, CH_{Ph}); **2** (d_2), δ: 1.01 (d, 3H, C^{15}H, $^3J_{HH}$ 7.6 Hz), 1.10 (s, 3H, C^{14}H), 1.21-1.29 (m, 2H, C^{9}H), 1.42-1.61 (m, 5H, C^{1}H, C^{2}H, C^{3}H, overlapped with C^{1}H, C^{3}H diastereomer d_1), 1.73-1.88 (m, 1H, C^{2}H, overlapped with C^{2}H diastereomer d_1), 1.93-2.03 (m, 1H, C^{9}H, overlapped with C^{9}H diastereomer d_1), 2.17-2.31 (m, 1H, C^{4}H), 2.58-2.67 (m, 1H, C^{11}H), 3.27 (m, 1H, C^{7}H, overlapped with C^{7}H diastereomer d_1), 3.46-3.63 (m, 1H, C^{13}H, overlapped with C^{13}H diastereomer d_1), 3.95-4.08 (m, 1H, C^{13}H), 4.66 (d, 1H, C^{8}H, $^3J_{HH}$ 2.1 Hz), 5.15 (br. s, 1H, C^{6}H), 7.47-7.64 (m, 15H, CH_{Ph}). ^{13}C–{^{1}H} NMR (100.6 MHz, CD_3OD), **2** (d_1), δ_C: 17.86 s (C^2), 19.92 d (C^{13}, $^1J_{PC}$ 56.9 Hz), 23.52 s (C^{15}), 29.29 s (C^{14}), 33.99 s (C^3), 34.26 s (C^{10}), 39.72 d (C^{11}, $^2J_{PC}$ 4.1 Hz), 39.82 s (C^4), 42.09 d (C^7, $^3J_{PC}$ 2.2 Hz), 43.41 s (C^1), 43.50 s (C^9), 79.40 s (C^8), 114.87 s (C^6), 119.76 d (PC_{Ph}^{ipso}, $^1J_{PC}$ 87.2 Hz), 120.65 q (CF_3, $^1J_{FC}$ 320.6 Hz), 131.67 d (C_{Ph}^{meta}, $^3J_{PC}$ 12.8 Hz), 134.98 d (C_{Ph}^{ortho}, $^2J_{PC}$ 10.1 Hz), 136.54 d (C_{Ph}^{para},

$^4J_{PC}$ 2.6 Hz), 154.20 s (C^5), 177.81 d (C^{12}, $^3J_{PC}$ 11.4 Hz); **2** (d_2), δ_C: 17.86 s (C^2, overlapped with C^2 diastereomer d_1), 22.91 s (C^{15}), 24.14 d (C^{13}, $^1J_{PC}$ 53.9 Hz), 29.29 s (C^{14}, overlapped with C^{14} diastereomer d_1), 33.99 s (C^3, overlapped with C^3 diastereomer d_1), 34.26 s (C^{10} overlapped with C^{10} diastereomer d_1), 39.44 s (C^4), 39.72 d (C^{11}, overlapped with C^{11} diastereomer d_1), 43.20 s (C^1), 43.41 s (C^9, overlapped with C^1 diastereomer d_1), 44.11 d (C^7, $^3J_{PC}$ 4.0 Hz), 79.95 s (C^8), 114.87 s (C^6, overlapped with C^6 diastereomer d_1), 119.38 d (PC_{Ph}^{ipso}, $^1J_{PC}$ 87.0 Hz), 130.06 d (C_{Ph}^{meta}, $^3J_{PC}$ 12.2 Hz), 133.10 d (C_{Ph}^{ortho}, $^2J_{PC}$ 10.0 Hz), 133.86 br. s (C_{Ph}^{para}), 151.50 s (C^5), 178.19 d (C^{12}, $^3J_{PC}$ 10.2 Hz). ^{31}P / ^{31}P-{^1H} NMR (162.0 MHz, $CDCl_3$), δ_P: 24.6 m (s) (**2**, d_1), 23.6 m (s) (**2**, d_2). Elemental analysis, calc. for $C_{34}H_{36}F_3O_5PS$: C, 63.34; H, 5.63; F, 8.84; P, 4.80; S, 4.97; found C, 63.17; H, 5.79; F, 8.78; P, 4.57; S, 4.79. MALDI, *m/z*: calc. for $C_{33}H_{36}O_2P^+$ $[M - CF_3SO_3]^+$, 495.3; found 495.4. IR (KBr, cm^{-1}): 2930, 1764 (C=O), 1440, 1262, 1157, 1112, 1030, 997.

(Eudesm-5-en-12,8-olid-13-yl)(triphenyl)arsonium triflate, [(3RS,3aR,5S,8aR,9aR)-(5,8a-dimethyl-2-oxo-2,3,3a,5,6,7,8,8a,9,9a-decahydronaphtho[2,3-b]furan-3-yl)methyl]-(triphenyl)arsonium triflate **3**. Yield: 0.51 g (74%) (ratio of diastereomers d_1 : d_2 = 1.00 : 0.70); dark brown powder; mp 61 °C. ^1H NMR (400 MHz, $CDCl_3$), **3** (d_1), δ: 1.20 (d, 3H, $C^{15}H$, $^3J_{HH}$ 7.6 Hz), 1.21-1.26 (m, 1H, C^1H, overlapped with $C^{14}H$), 1.23 (s, 3H, $C^{14}H$), 1.35-1.48 (m, 1H, C^2H), 1.48-1.55 (m, 1H, C^9H), 1.54-1.66 (m, 3H, C^1H, C^3H), 1.74-1.92 (m, 1H, C^2H), 2.06 (dm, 1H, C^9H, $^3J_{HH}$ 15.1 Hz), 2.54-2.70 (m, 1H, C^4H), 3.11-3.23 (m, 1H, $C^{11}H$), 3.53-3.62 (m, 2H, $C^{13}H$, C^7H), 3.92-4.09 (m, 1H, $C^{13}H$), 4.84 (br. s, 1H, C^8H), 5.40 (br. s, 1H, C^6H), 7.60-7.81 (m, 15H, CH_{Ar}); **3** (d_2), δ: 1.04 (d, 3H, $C^{15}H$, $^3J_{HH}$ 7.6 Hz), 1.13 (s, 3H, $C^{14}H$), 1.21-1.26 (m, 1H, C^2H, overlapped with C^2H, $C^{14}H$ diastereomer d_1), 1.35-1.48 (m, 1H, C^2H, overlapped with C^2H diastereomer d_1), 1.48-1.55 (m, 1H, C^9H, overlapped with C^9H diastereomer d_1), 1.54-1.66 (m, 3H, C^1H, C^3H, overlapped with C^1H, C^3H diastereomer d_1), 1.74-1.92 (m, 1H, C^2H, overlapped with C^2H diastereomer d_1), 2.06 (m, 1H, C^9H, overlapped with C^9H diastereomer d_1), 2.31-2.40 (m, 1H, C^4H), 3.11-3.23 (m, 1H, $C^{11}H$, overlapped with $C^{11}H$ diastereomer d_1), 3.53-3.62 (m, 2H, $C^{13}H$, C^7H, overlapped with $C^{13}H$, C^7H diastereomer d_1), 3.92-4.09 (m, 1H, $C^{13}H$, overlapped with $C^{13}H$ diastereomer d_1), 5.00 (d, 1H, C^8H, $^3J_{HH}$ 3.2 Hz), 5.26 (m, 1H, C^6H), 7.60-7.81 (m, 15H, CH_{Ar}, overlapped with CH_{Ar} diastereomer d_1). ^{13}C NMR (100.6 MHz, $CDCl_3$), **3** (d_1), δ_C: 16.93 tm (s) (C^2, $^1J_{HC}$ 125.8 Hz), 23.49 qm (s) (C^{15}, $^1J_{HC}$ 120.8 Hz), 24.49 t (s) (C^{13}, $^1J_{HC}$ 139.0 Hz), 28.96 q (s) (C^{14}, $^1J_{HC}$ 127.0 Hz), 32.94 tm (s) (C^3, $^1J_{HC}$ 125.4 Hz), 33.22 br. s (s) (C^{10}), 38.51 d (s) (C^4, $^1J_{HC}$ 128.6 Hz), 39.40 dm (s) (C^{11}, $^1J_{HC}$ 137.8 Hz), 42.00 d (s) (C^7, $^1J_{HC}$ 137.8 Hz), 42.27 t (s) (C^1, $^1J_{HC}$ 126.4 Hz), 42.50 t (s) (C^9, $^1J_{HC}$ 128.5 Hz), 79.12 dm (s) (C^8, $^1J_{HC}$ 154.0 Hz), 114.04 d (s) (C^6, $^1J_{HC}$ 155.8 Hz), 120.43 q (q) (CF_3, $^1J_{FC}$ 319.6 Hz), 123.09 dd (s) (C_{Ph}^{ipso}, $^2J_{HC}$ 8.8 Hz), 130.70 dd (s) (C_{Ph}^{ortho}, $^1J_{HC}$ 165.3 Hz, $^2J_{HC}$ 7.1 Hz), 132.86 ddd (s) (C_{Ph}^{meta},

$^{1}J_{HC}$ 164.8 Hz, $^{2}J_{HC}$ 6.7 Hz), 133.88 ddd (s) (C_{Ph}^{para}, $^{1}J_{HC}$ 163.2 Hz, $^{2}J_{HC}$ 6.6 Hz), 152.99 br. s (s) (C^{5}), 177.86 br. s (s) (C^{12}); **3** (d_2), δ_C: 16.93 tm (s) (C^{2}, overlapped with C^{2} diastereomer d_1), 22.55 m (s) (C^{15}, overlapped with C^{15}, C^{13} diastereomer d_1), 25.87 m (s) (C^{13}, overlapped with C^{13} diastereomer d_1), 28.81 m (s) (C^{14}, overlapped with C^{14} diastereomer d_1), 32.79 tm (s) (C^{3}, overlapped with C^{3} diastereomer d_1), 33.22 br. s (s) (C^{10}, overlapped with C^{10} diastereomer d_1), 37.98 d (s) (C^{4}, $^{1}J_{HC}$ 127.2 Hz), 39.40 d. m (s) (C^{11}, overlapped with C^{11} diastereomer d_1), 42.11 m (s) (C^{1}, overlapped with C^{7}, C^{1}, C^{9} diastereomer d_1), 42.32 t (s) (C^{9}, $^{1}J_{HC}$ 126.8 Hz), 44.02 d (s) (C^{7}, $^{1}J_{HC}$ 136.9 Hz), 78.53 dm (s) (C^{8}, $^{1}J_{HC}$ 154.1 Hz), 115.66 d (s) (C^{6}, $^{1}J_{HC}$ 156.2 Hz), 120.43 q (q) (CF_3, $^{1}J_{FC}$ 319.6 Hz), 121.46 dd (s) (C_{Ph}^{ipso}, $^{2}J_{HC}$ 8.8 Hz), 130.92 ddd (s) (C_{Ph}^{ortho}, $^{1}J_{HC}$ 166.0 Hz, $^{2}J_{HC}$ 7.5 Hz), 132.86 m (s) (C_{Ph}^{meta}, overlapped with C_{Ph}^{meta} diastereomer d_1), 134.25 ddd (s) (C_{Ph}^{para}, $^{1}J_{HC}$ 162.8 Hz, $^{2}J_{HC}$ 6.9 Hz), 150.26 br. s (s) (C^{5}), 177.11 br. s (s) (C^{12}). Elemental analysis, calc. for $C_{34}H_{36}AsF_3O_5S$: C, 59.30; H, 5.27; As, 10.88; F, 8.28; S, 4.66; found C, 59.10; H, 5.52; As, 10.72; F, 8.18; S, 4.46. MALDI, *m/z*: calc. for $C_{33}H_{36}O_2As^{+}$ [M – CF_3SO_3]$^{+}$, 539.2; found 539.0. IR (KBr, cm^{-1}): 2929, 1762 (C=O), 1441, 1259, 1225, 1161, 1030, 998.

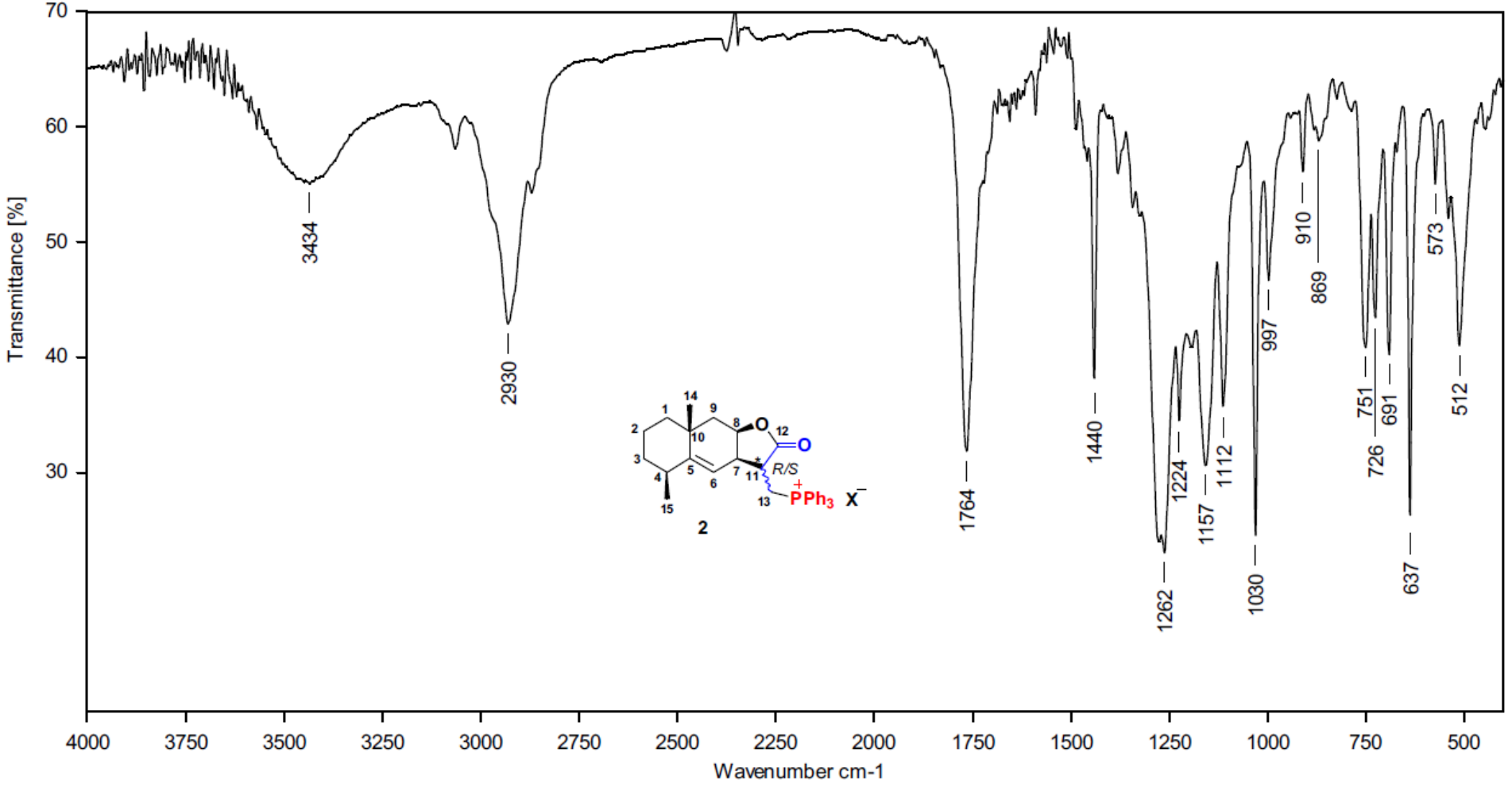


Figure S1. IR (KBr) spectrum of phosphonium salt **2.**

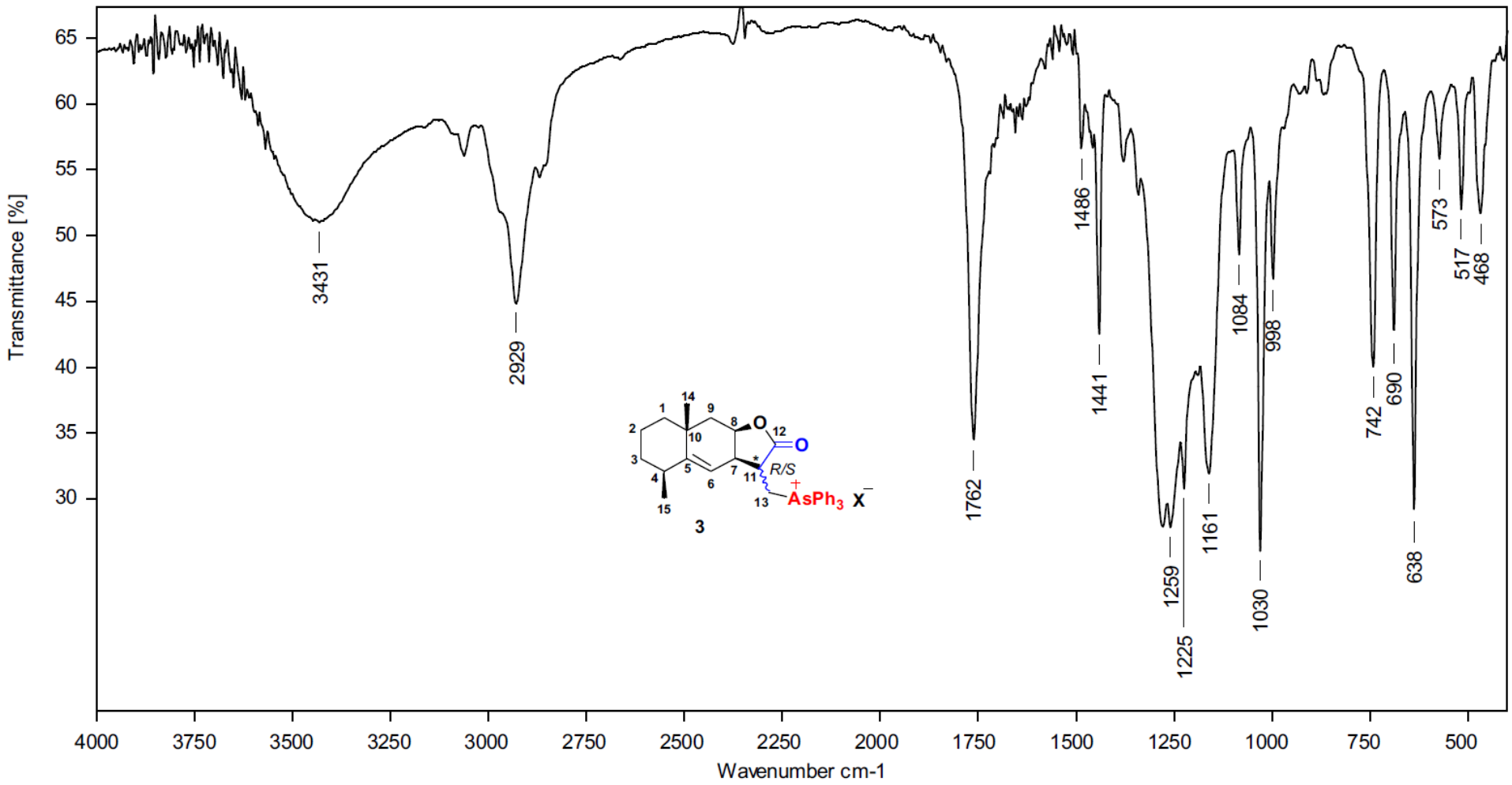


Figure S2. IR (KBr) spectrum of arsonium salt **3.**

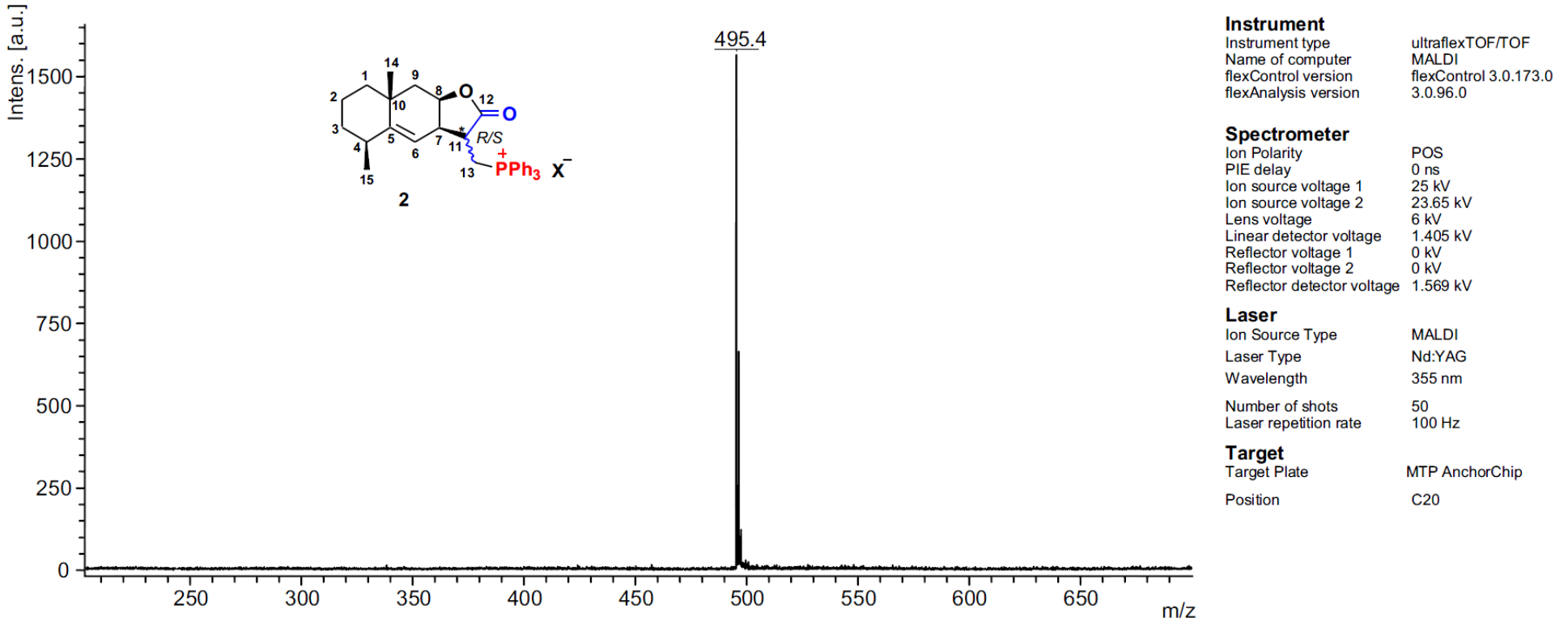


Figure S3. MALDI MS spectrum of phosphonium salt **2.**

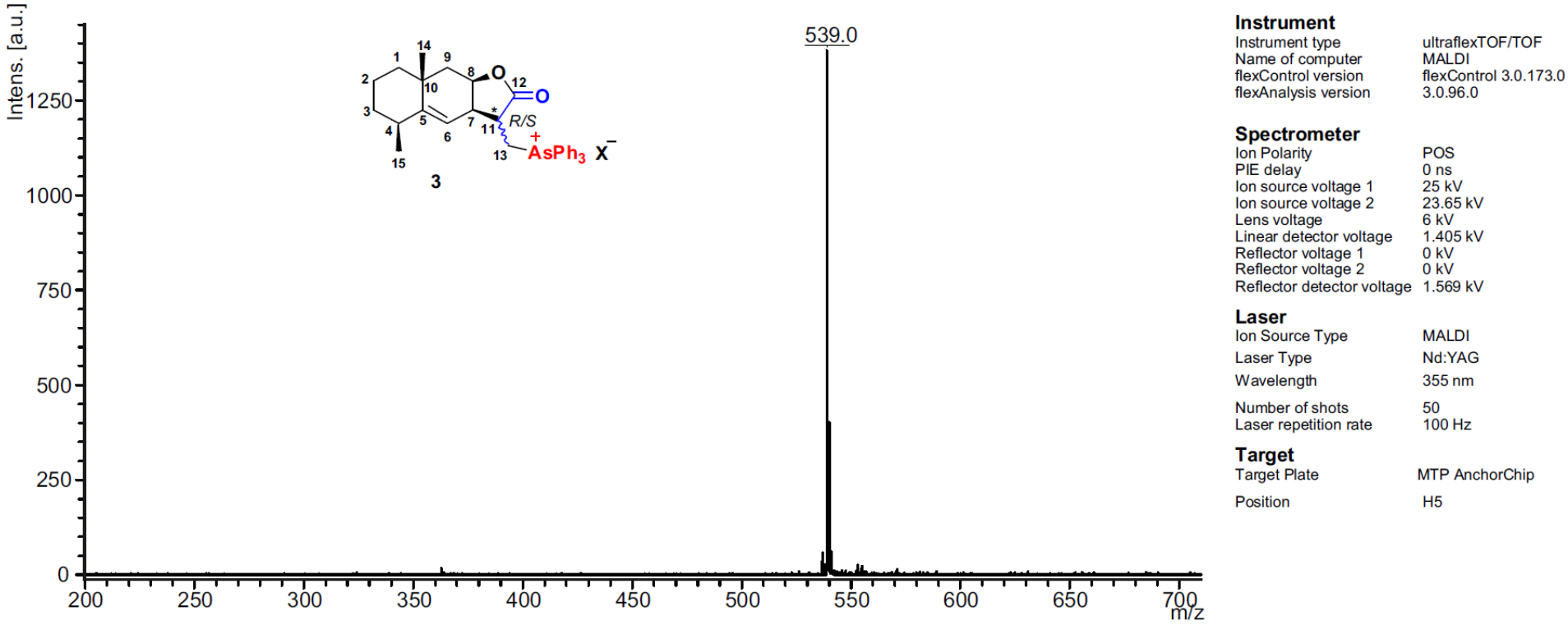


Figure S4. MALDI MS spectrum of arsonium salt **3.**

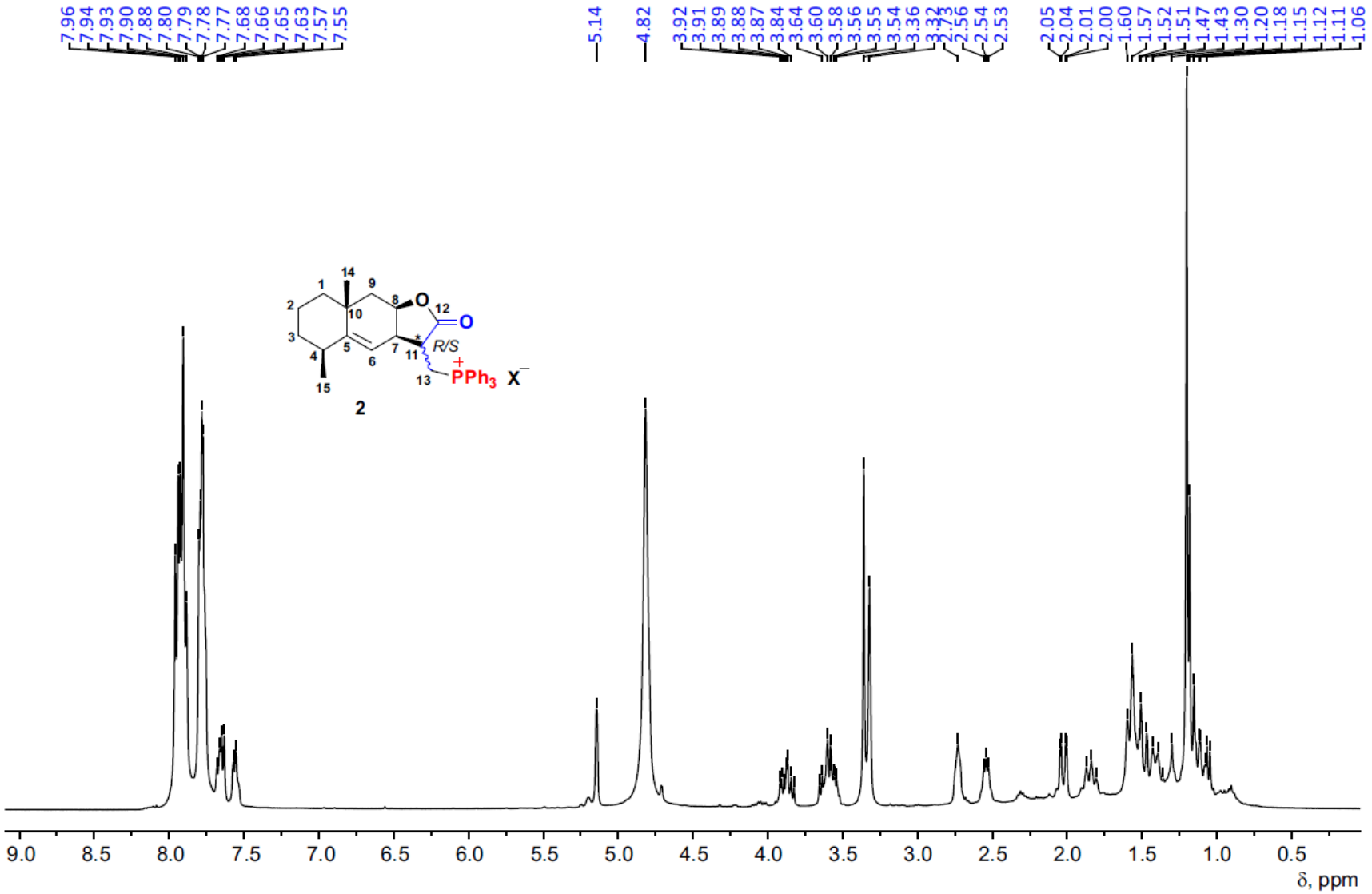


Figure S5. ^{1}H NMR (CD_3OD, 400 MHz) spectrum of phosphonium salt **2.**

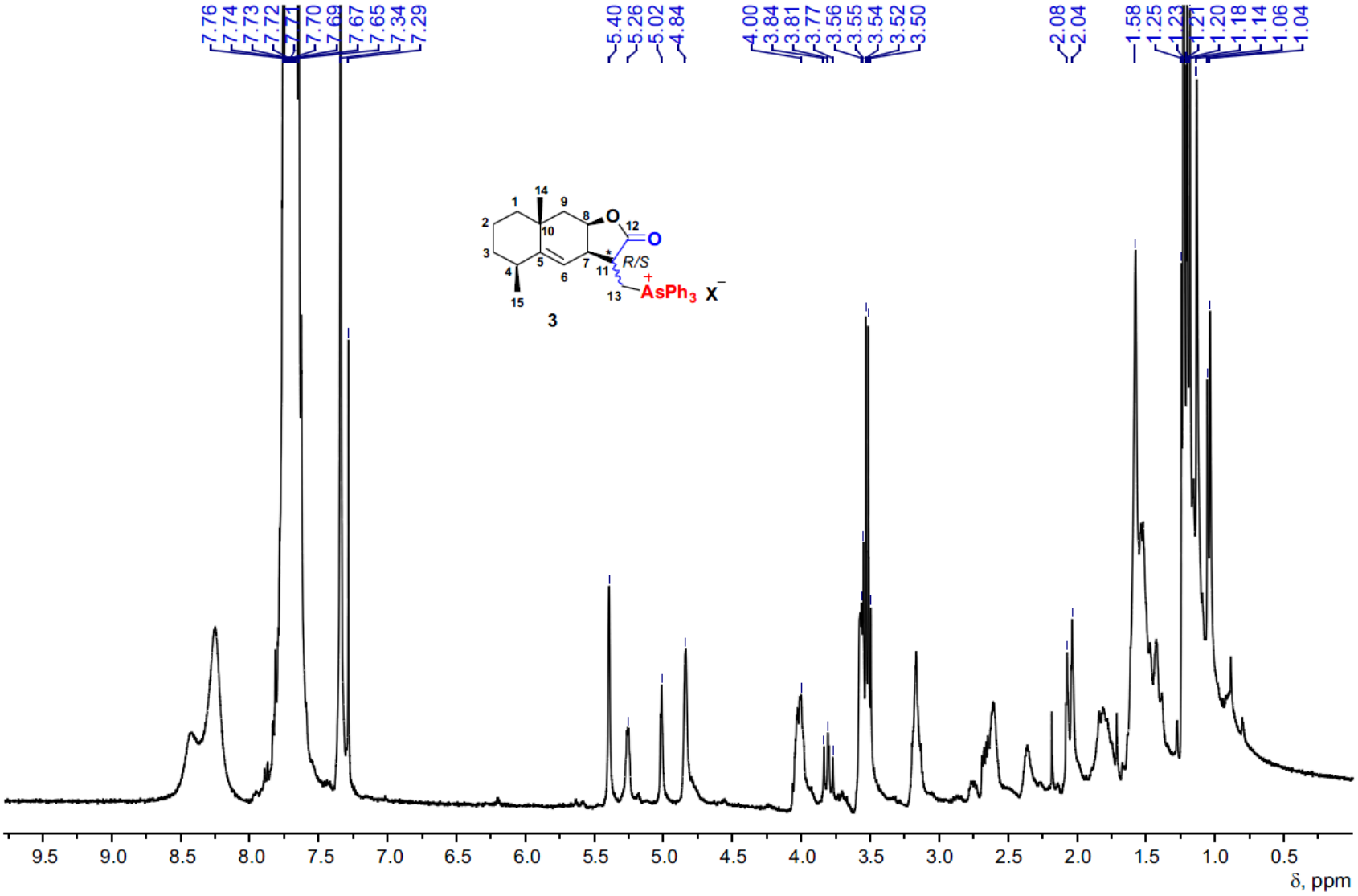


Figure S6. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of arsonium salt **3.**

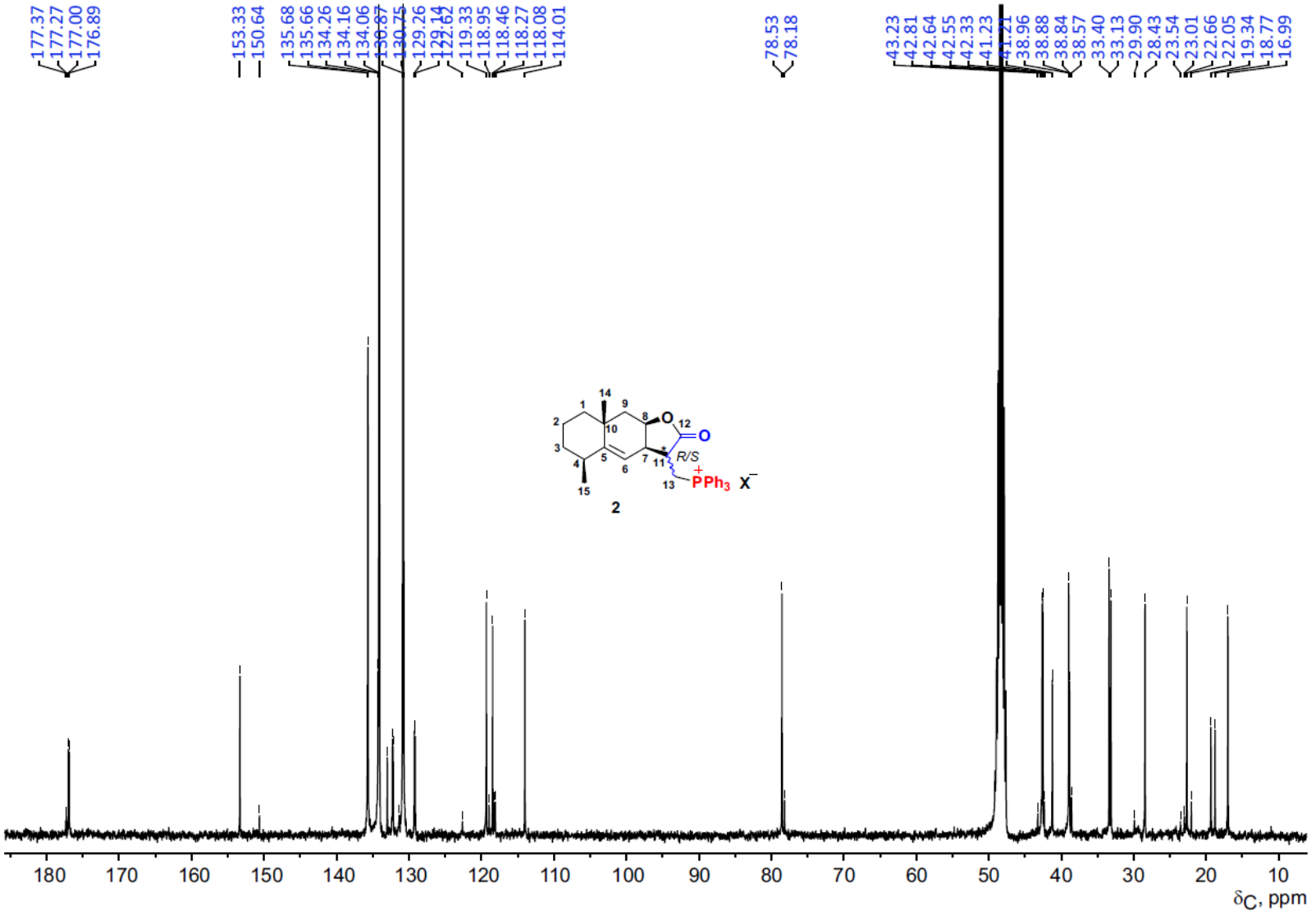


Figure S7. $^{13}C–\{^{1}H\}$ NMR (CD_3OD, 100.6 MHz) spectrum of phosphonium salt **2.**

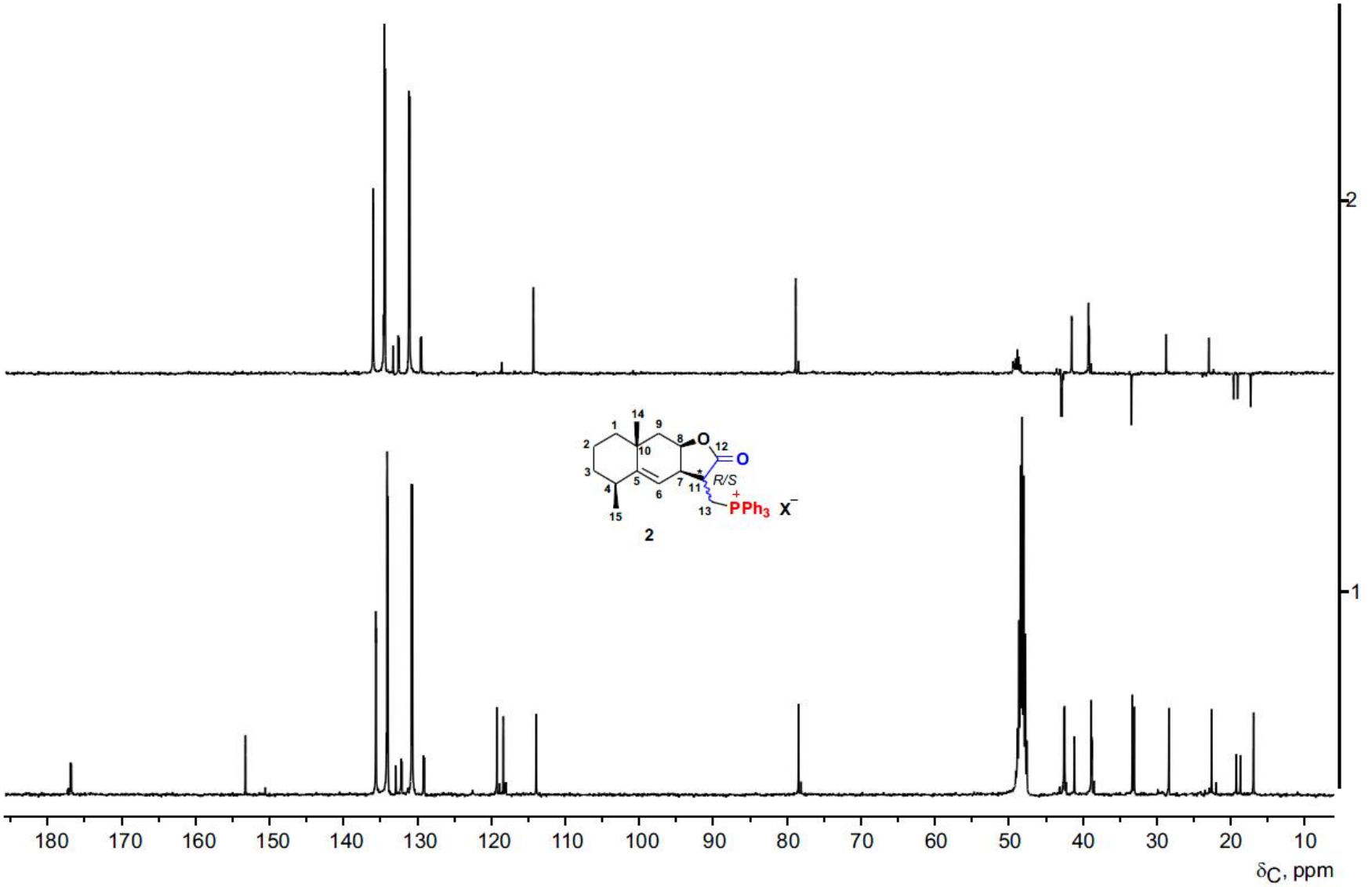


Figure S8. $^{13}C–\{^{1}H\}$ (1) and ^{13}C DEPT (2) NMR (CD_3OD, 100.6 MHz) spectra of phosphonium salt **2.**

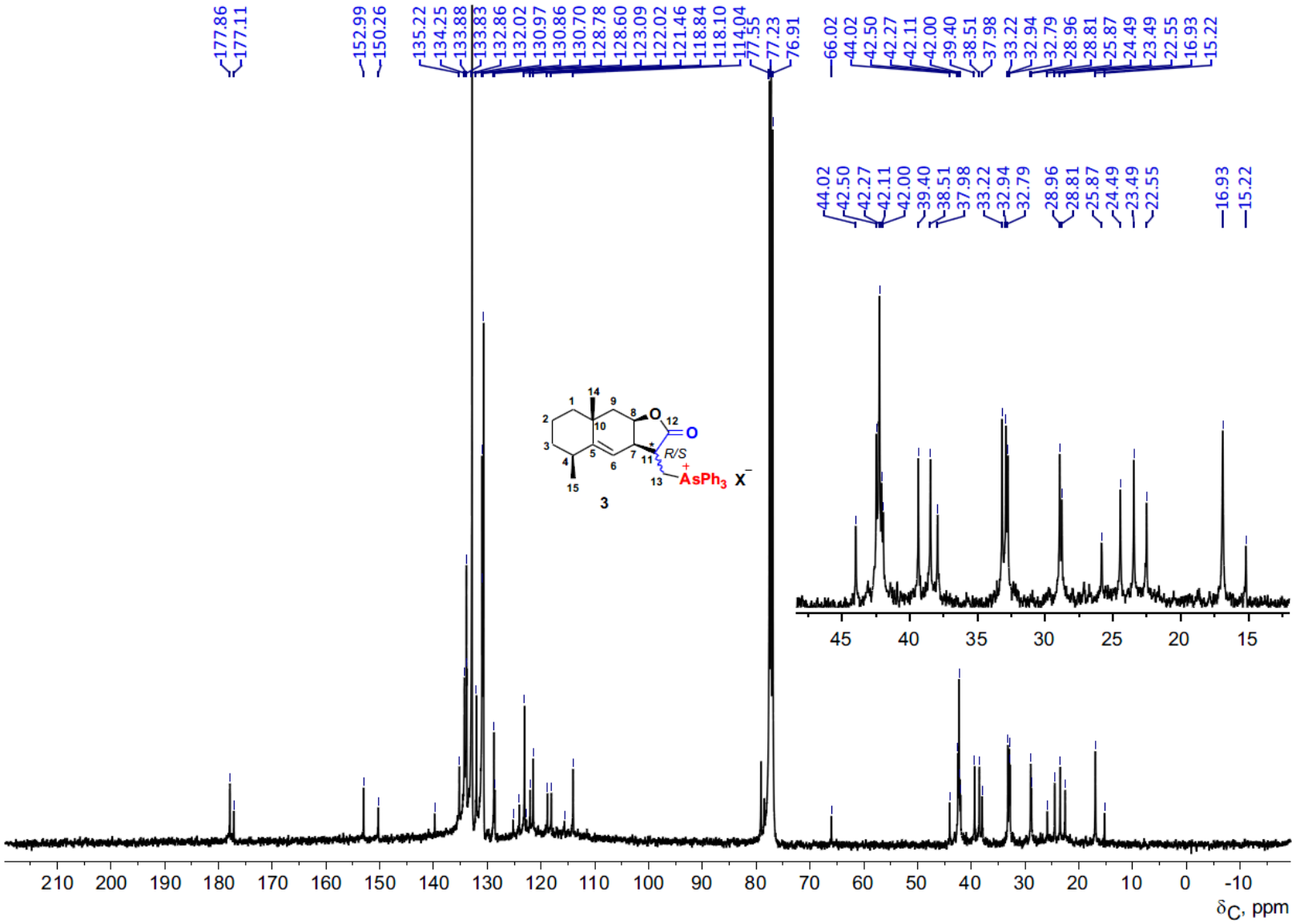


Figure S9. $^{13}C–\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz) spectrum of arsonium salt **3.**

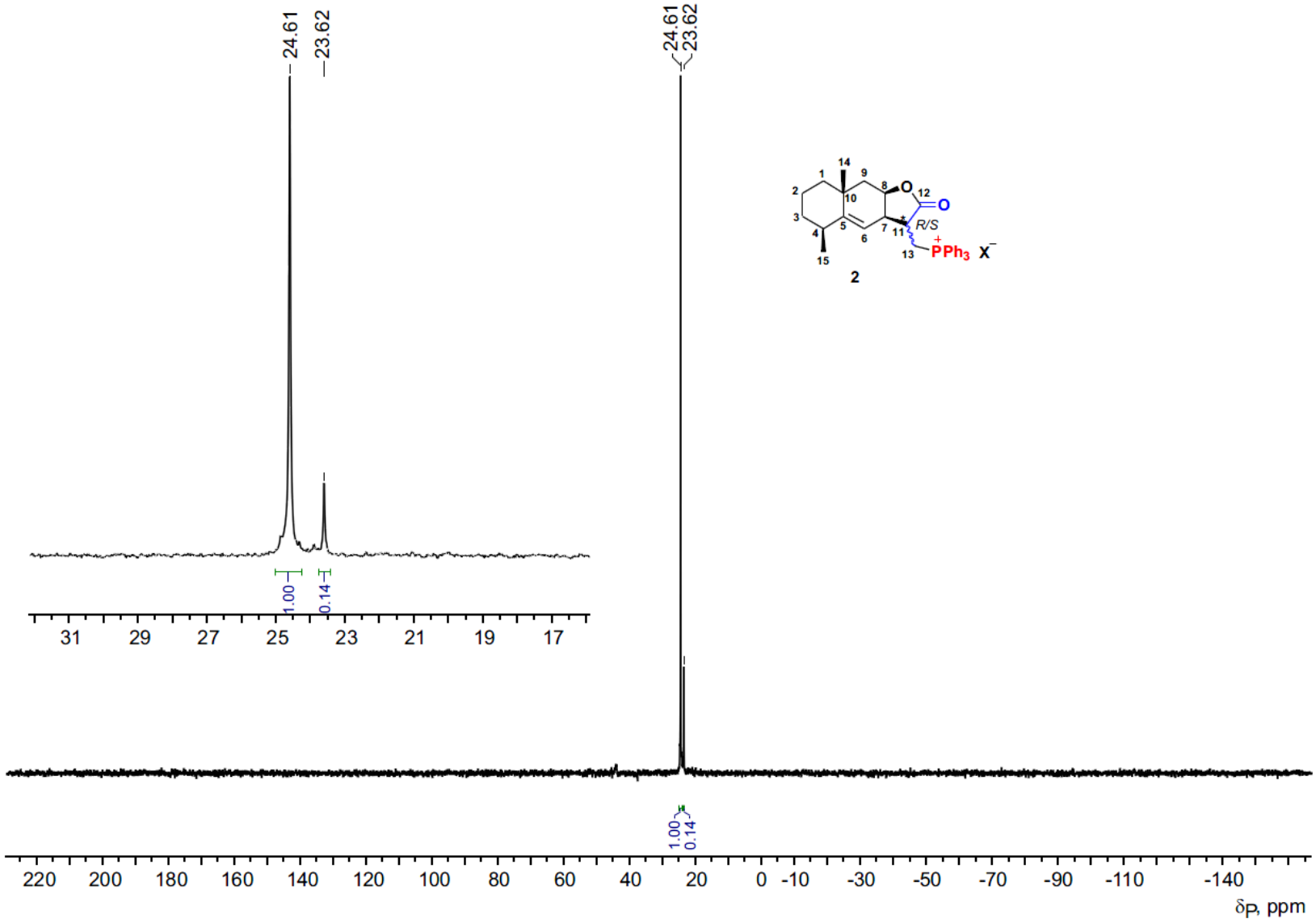
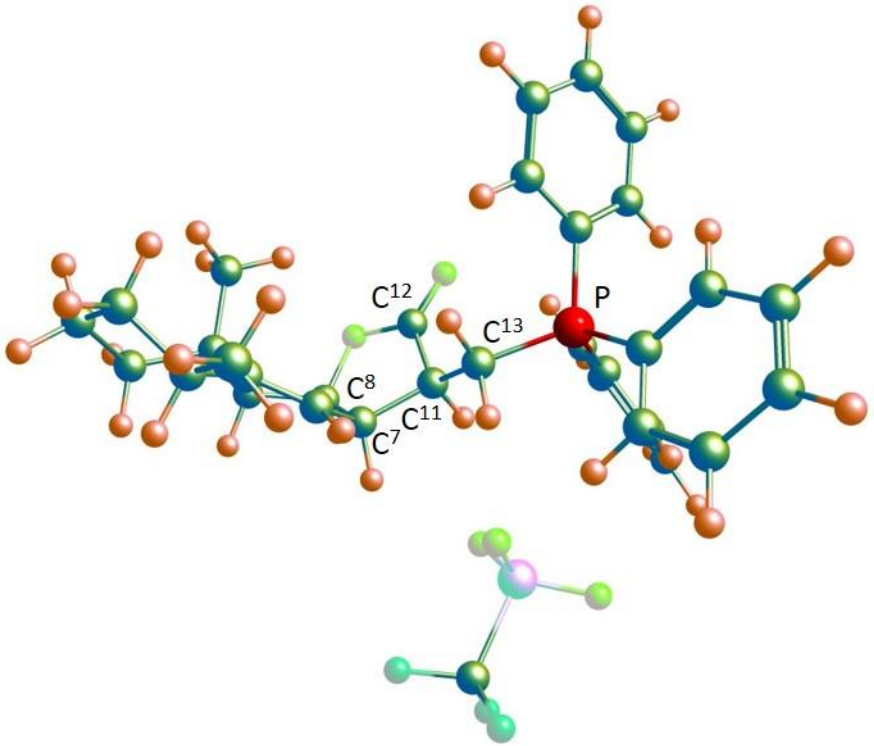
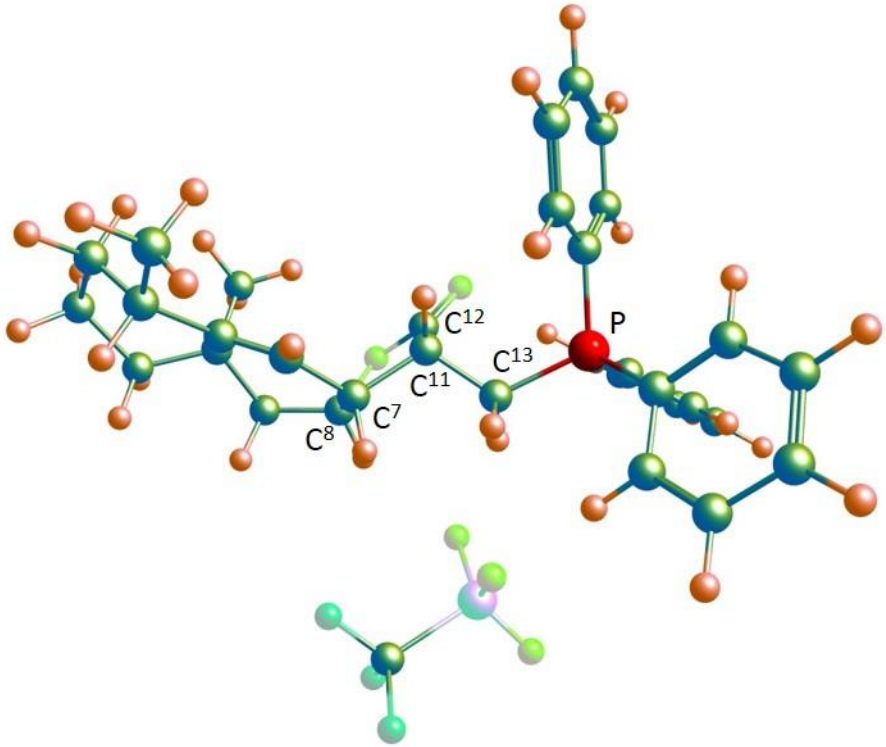


Figure S10. $^{31}P–\{^{1}H\}$ NMR (CH_2Cl_2, 162 MHz) spectrum of phosphonium salt **2.**



(11*S*)-**2**

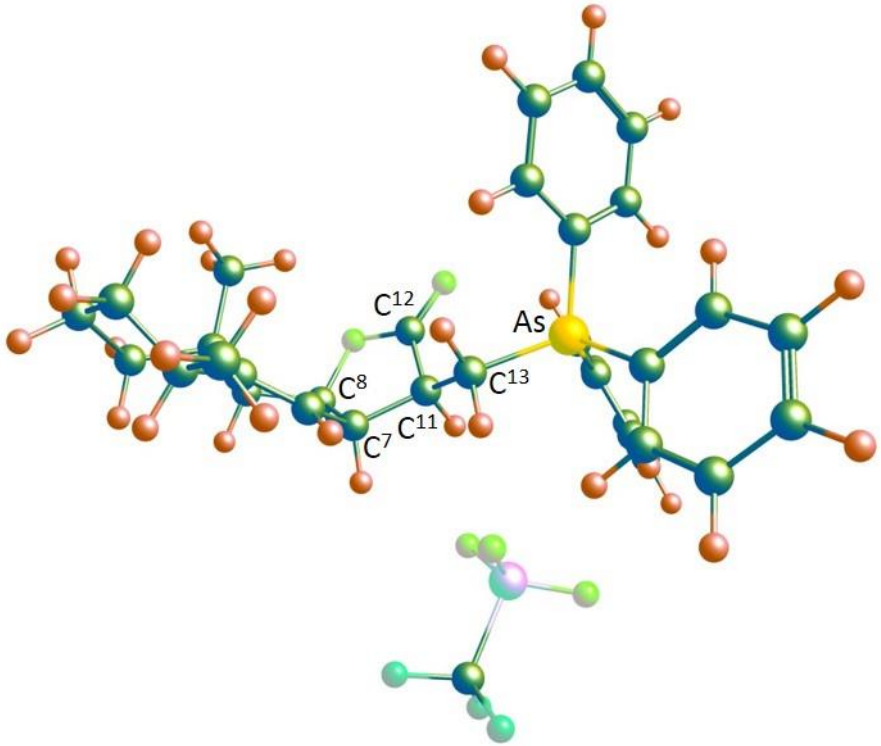
selected dihedral angles (°): C(12)–C(11)–C(13)–P –9.1127; =O–C(12)–C(11)–C(13) 24.7762; C(7)–C(11)–C(13)–P 171.519; C(8)–C(7)–C(11)–C(12) 34.4583; C(6)–C(7)–C(11)–C(12) –86.9963; C(9)–C(8)–O–C(12) 140.0175; O–C(8)–C(7)–C(11) –31.7398



(11*R*)-**2**

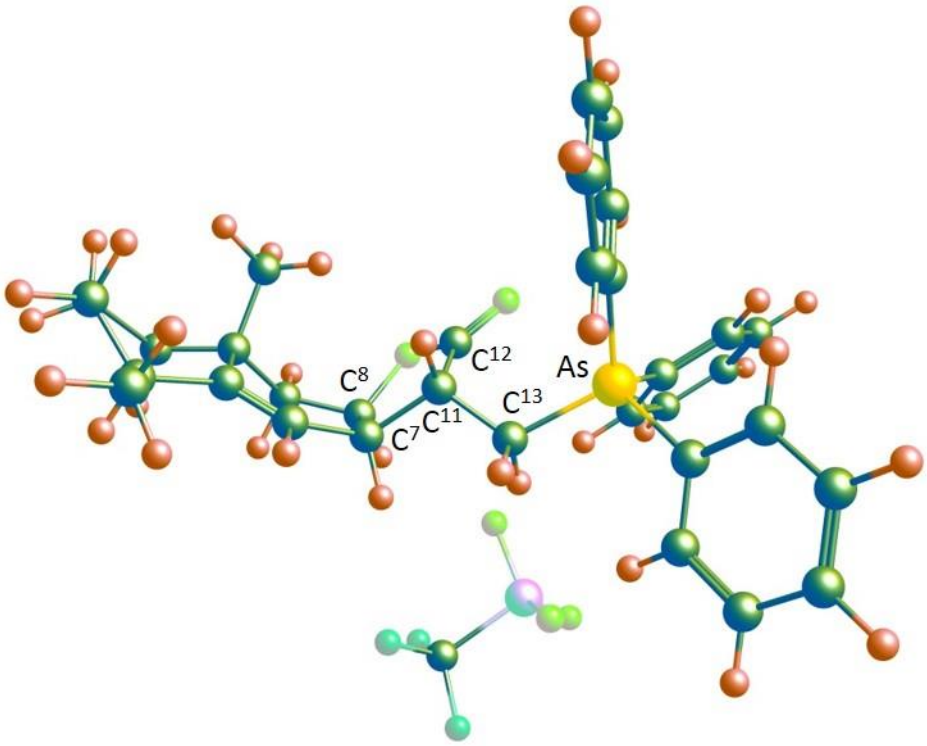
selected dihedral angles (°): C(12)–C(11)–C(13)–P 34.3109; =O–C(12)–C(11)–C(13) –43.7006; C(7)–C(11)–C(13)–P 160.6175; C(8)–C(7)–C(11)–C(12) –3.26; C(6)–C(7)–C(11)–C(12) –127.6133; C(9)–C(8)–O–C(12) 131.3811; O–C(8)–C(7)–C(11) –0.6735

Figure S11. The possible conformers of (11*S*)-**2** and (11*R*)-**2** according to DFT B3PW91 method.



(11*S*)-**3**

selected dihedral angles (°): C(12)–C(11)–C(13)–P –68.0663; =O–C(12)–C(11)–C(13) 34.6101; C(7)–C(11)–C(13)–P 171.2261; C(8)–C(7)–C(11)–C(12) 26.8451; C(6)–C(7)–C(11)–C(12) –97.0933; C(9)–C(8)–O–C(12) 140.3371; O–C(8)–C(7)–C(11) –26.2465



(11*R*)-**3**

selected dihedral angles (°): C(12)–C(11)–C(13)–P 54.607; =O–C(12)–C(11)–C(13) –55.352; C(7)–C(11)–C(13)–P 172.9989; C(8)–C(7)–C(11)–C(12) 4.9021; C(6)–C(7)–C(11)–C(12) –120.3052; C(9)–C(8)–O–C(12) 138.7467; O–C(8)–C(7)–C(11) –10.5336

Figure S12. The possible conformers of (11*S*)-**3** and (11*R*)-**3** according to DFT B3PW91 method.