Electronic Supplementary Material (ESI) for ChemComm.

Phosphate linkers with traceable cyclic intermediates for self-immolation detection and monitoring

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Supporting Information

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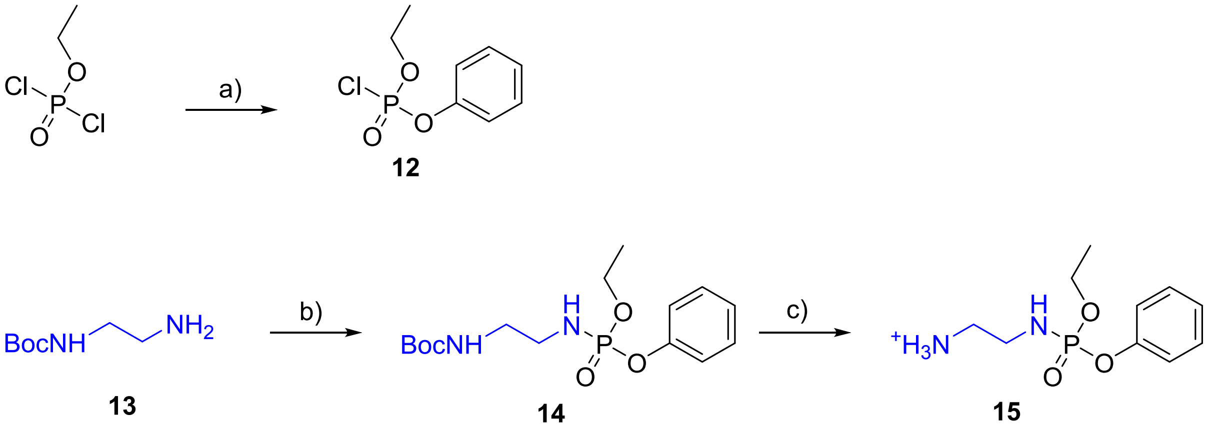
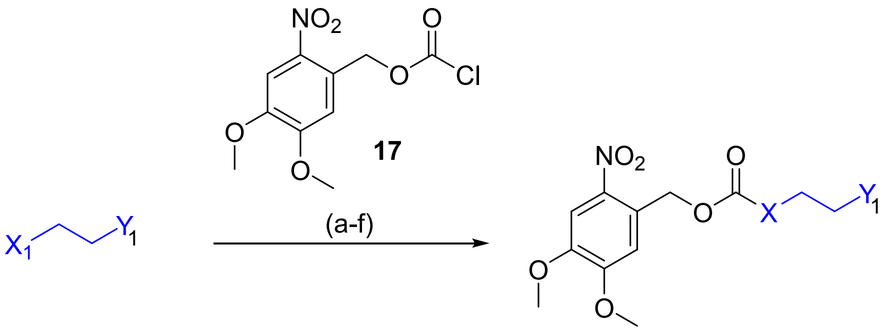
1 Synthesis



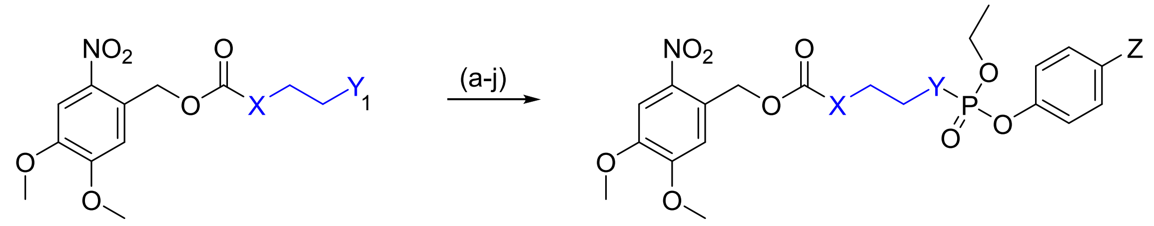
Scheme 1. Reaction conditions: a) phenol, triethylamine, DCM, −78 °C to 25 °C, 2 h; b) compound **12**, triethylamine, DCM, −78 °C to 25 °C, 12 h; c) CF_3COOH, DCM, 25 °C, 2 h.



18: X_1 = OH, Y_1 = *NH*-Boc
19: X_1 = Y_1 = OH
20: X_1 = NH_2, Y_1 = OH
21: X_1 = SH, Y_1 = OH
22: X_1 = Y_1 = NH_2
23: X_1 = SH, Y_1 = *NH*-Boc

a) **24**: X = O, Y_1 = *NH*-Boc
b) **25**: X = O, Y_1 = OH
c) **26**: X = NH, Y_1 = OH
d) **27**: X = S, Y_1 = OH
e) **28**: X = NH, Y_1 = NH_2
f) **29**: X = S, Y_1 = *NH*-Boc

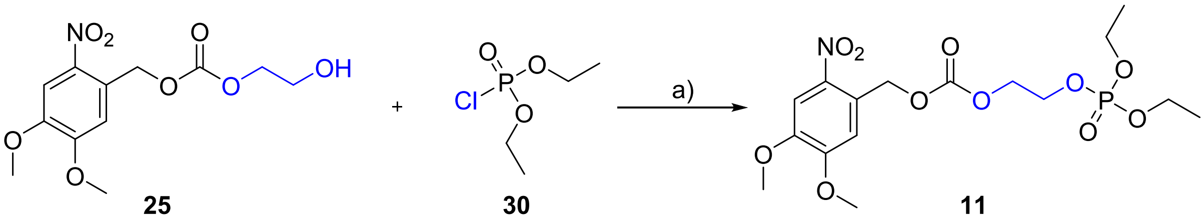
Scheme 2. Reaction conditions: a) compound **18**, pyridine, DCM, 0 °C to 25 °C, 12 h; b) compound **19**, Pyridine, THF, 0 °C to 25 °C, 12 h; or toluene, c) compound **20**, triethylamine, DCM, −78 °C to 25 °C, 12 h; d) compound **21**, DCM, triethylamine, −78 °C to 25 °C, 1 h; e) compound **22**, DCM, 25 °C, 12 h; f) compound **23**, triethylamine, DCM, −78 °C to 25 °C, 12 h.



24: X = O, Y_1 = *NH*-Boc
25: X = O, Y_1 = OH
26: X = NH, Y_1 = OH
27: X = S, Y_1 = OH
28: X = NH, Y_1 = NH_2
29: X = S, Y_1 = *NH*-Boc

a) **1**: X = O, Y = NH, Z = H
b) **2**: X = Y = O, Z = H
c) **3**: X = NH, Y = O, Z = H
d) **4**: X = S, Y = O, Z = H
e) **5**: X = Y = NH, Z = H
f) **6**: X = S, Y = NH, Z = H
g) **7**: X = Y = O, Z = OCH_3
h) **8**: X = Y = O, Z = CH_3
i) **9**: X = Y = O, Z = F
j) **10**: X = Y = O, Z = NO_2

Scheme 3. Reaction conditions: a) 1. compound **24**, CF_3COOH, DCM, 25 °C, 2 h. 2. triethylamine, DCM, **12**, –78 °C to 25 °C, 12 h; b) compound **25**, triethylamine, DCM, **12**, –78 °C to 25 °C, 12 h; c) Compound **26**, triethylamine, DCM, **12**, –78 °C to 25 °C, 12 h; d) compound **27**, triethylamine, DCM, **12**, –78 °C to 25 °C, 12 h; e) compound **28**, triethylamine, DCM, –78 °C to 25 °C, 12 h; f) 1. compound **29**, CF_3COOH, DCM, 25 °C, 2h. 2. triethylamine, DCM, **12**, –78 °C to 25 °C, 12 h; g) compound **25**, triethylamine, toluene, ethyl dichlorophosphate, 4-methoxyphenol, DCM, 25 °C, 24 h; compound **25**, triethylamine, toluene, ethyl dichlorophosphate, 4-methylphenol, DCM, 25 °C, 24 h; i) compound **25**, triethylamine, toluene, ethyl dichlorophosphate, 4-fluorophenol, DCM, 25 °C, 24 h; j) compound **25**, triethylamine, toluene, ethyl dichlorophosphate, 4-nitrophenol, DCM, 25 °C, 24 h.



25 **30** **11**

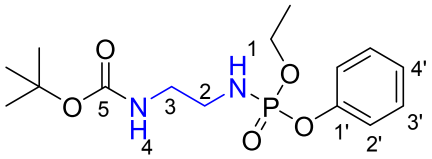
Scheme 4. Reaction conditions: a) triethylamine, 25 °C, 12 h.

Experimental Section

General. All reagents were purchased from commercial suppliers and used as received. 4,5-Dimethoxy-2-nitrobenzyl chloroformate was purchased from Fluorochem Ltd. (United Kingdom). All reactions were performed under an inert atmosphere of argon. Thin layer chromatography (TLC) and preparative TLC was performed on TLC aluminium sheets (silica-gel 60 F_{254}; Merck). Reaction progress was monitored using TLC and/or ^{31}P NMR in $CDCl_3$. Flash-column chromatography was performed on Compact (ECOM s.r.o.) chromatography system using silica-gel or C18 silica-gel 230–400 mesh, 60 Å (Merck KGaA, Germany). HPLC analyses were performed on Agilent 1100 HPLC System (with G1311A quaternary pump, G1314A UV VWD detector) using LiChrospher®100, RP-18 column (Endcapped 5mm, 4 mm, 250 mm) in isocratic mode 55% MeCN/ water (v/v, modified with 0.1% phosphoric acid, 1.0 mL/min, l = 350 nm). Final products were recovered by solvent evaporation and freeze-drying. All products were viscous oils, semi-solids or non-crystalline solids. The reaction conditions were not optimized for the highest possible yields.

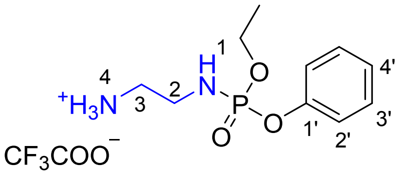
*Ethyl phenyl phosphorochloridate (**12**)* was prepared in accordance to the previously published procedure.[1] Phenol (94 µL, 0.95 mmol, 0.95 eq.) and TEA (138 µL, 0.95 mmol, 0.95 eq.) were dissolved in DCM (3 mL). The solution was cooled down to –78 °C and ethyl phosphorodichloridate (119 µL, 1 mmol, 1 eq.) was added dropwise. The mixture was stirred at –78 °C for 15 min. and then allowed to warm up to 25 °C and stirred for 2 h. The crude reaction mixture of **12** was stored under argon and directly used in the next reaction steps in the amount required for phosphorylation. $[M+H]^+$ 221.09.

*Tert-butyl (2-((ethoxy(phenoxy)phosphoryl)amino)ethyl)carbamate (**14**)*



Tert-butyl (2-aminoethyl)carbamate **13** (152 µL, 0.95 mmol, 0.95 eq.) and triethylamine (132 µL, 0.95 mmol, 0.95 eq.) were dissolved in DCM (3 mL) and cooled down at –78 °C. The solution of ethyl phenyl phosphorochloridate **12** (220 mg, 1.00 mmol, 1.00 eq.) in DCM (2 ml) and triethylamine (138 µL, 1.00 mmol, 1.00 eq.) were added. The mixture was stirred at –78 °C for 5 min., allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was washed with water (20 mL), brine (20 mL) and dried over sodium sulfate. The title compound was purified using C18 chromatography (water – acetonitrile gradient). Volatiles were evaporated and title compound was dried in high vacuum. Yield **14** (156 mg, 45%) of a white semisolid. ^{1}H NMR (400 MHz, DMSO-*d$_6$*) *δ* 7.36 (m, 2H, 3’), 7.20–7.16 (m, 3H, 2’, 4’), 6.76 (t, 1H $J_{4\text{-}3}$ = 5.3, 4), 5.34 (td, 1H, $J_{1\text{-}P}$ = 12.5, $J_{1\text{-}2}$ = 6.8, 1), 4.03 (m, 2H, O-**CH$_2$**-CH$_3$), 2.94 (m, 2H, 3), 2.82 (m, 2H, 2), 1.36 (s, 9H, *t*Bu), 1.25 ppm (dt, 3H, $J_{CH3\text{-}CH2}$ = 7.1, $J_{CH3\text{-}P}$ = 0.7, O-CH$_2$-**CH$_3$**). ^{13}C NMR (100 MHz, DMSO-*d$_6$*) *δ* 155.71 (5), 151.11 (d, $J_{1'\text{-}P}$ = 6.4, 1’), 129.80 (3’), 124.53 (4’), 120.33 (d, $J_{2'\text{-}P}$ = 4.6, 2’), 77.85 (**C**-*t*Bu), 62.23 (d, $J_{CH2\text{-}P}$ = 5.5, O-**C**H$_2$-CH$_3$), 41.51 (d, $J_{3\text{-}P}$ = 6.1, 3), 40.85 (2), **C**H$_3$-*t*Bu), 16.21 ppm (d, $J_{CH3\text{-}P}$ = 6.4, O-CH$_2$-**C**H$_3$). ^{31}P NMR (161 MHz, DMSO-*d$_6$*) *δ* 5.38 ppm. HRMS (ES$^+$) calcd for $C_{15}H_{25}O_5N_2NaP$ = 367.13933, found [M+Na]$^+$ 367.13941.

*2-((Ethoxy(phenoxy)phosphoryl)amino)ethan-1-aminium trifluoroacetate (**15**).*

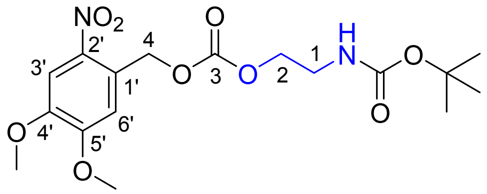


Tert-butyl (2-((ethoxy(phenoxy)phosphoryl)amino)ethyl)carbamate **14** (25 mg, 0.07 mmol) was dissolved in DCM-trifluoroacetic acid mixture (1 mL, 1:1) and stirred at 25 °C for 2 h. Reaction mixture was evaporated to dryness, co-evaporated with DCM (3x10 mL) and dried in high vacuum. Yield **15** (17 mg, 96%) of a white solid. ^{1}H NMR (400 MHz, DMSO-*d$_6$*) *δ* 7.76 (bs, 3H, NH$_3^+$), 7.39 (m, 2H, 3’), 7.21–7.17 (m, 3H, 2’, 4’), 5.56 (td, 1H, $J_{1\text{-}P}$ = 11.7, $J_{1\text{-}2}$ = 6.9, 1), 4.07 (m, 2H, O-**CH$_2$**-CH$_3$), 3.05 (m, 2H, 2), 2.80 (m, 2H, 3), 1.26 ppm (t, 3H, $J_{CH3\text{-}CH2}$ = 7.1, O-CH$_2$-**CH$_3$**). ^{13}C NMR (100 MHz, DMSO-*d$_6$*) *δ* 158.24 (d, $J_{C\text{-}F}$ = 32, CF**C**OO$^-$), 150.94 (d, $J_{1'\text{-}P}$ = 6.7, 1’), 129.93 (3’), 124.80 (4’), 120.34 (d, $J_{2'\text{-}P}$ = 4.6, 2’), 117.23 (q, $J_{C\text{-}F}$ = 300, **C**FCOO$^-$), 62.69 (d, $J_{CH2\text{-}P}$ = 5.5, O-**C**H$_2$-CH$_3$), 39.9 (3), 38.54 (2), 16.21 ppm (d, $J_{CH3\text{-}P}$ = 6.4, O-CH$_2$-

CH$_3$). ^{31}P NMR (161 MHz, DMSO-d_6) δ 5.05 ppm. HRMS (ES$^+$) calcd for $C_{10}H_{18}O_3N_2P$ = 245.10496, found [M+H]$^+$ 245.10498.

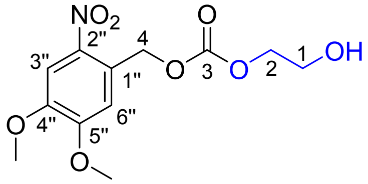
DMNBC PhotoArms *(24 – 29).*

*4, 5-Dimethoxy-2-nitrobenzyl (2-(tert-butyloxycarbonylamino)ethyl) carbonate (**24**)***.**



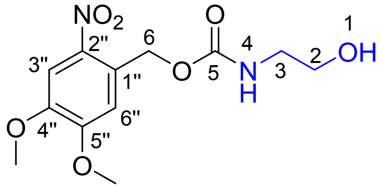
Tert-butyl (2-hydroxyethyl)carbamate **18** (161 µL, 1.00 mmol, 1.00 eq.) and pyridine (242 µL, 3.00 mmol, 3.00 eq.) were dissolved in DCM (2 mL). The solution was cooled down at 0 °C and 4, 5-dimethoxy-2-nitrobenzyl chloroformate **17** (303 mg, 1.10 mmol, 1.10 eq.) was added dropwise. The mixture was stirred at 0 °C for 5 min and then allowed to warm up at 25 °C and stirred for 12 hours. The reaction mixture was evaporated to dryness *in vacuo*. The title compound was purified using silica-gel chromatography (DCM – acetone gradient). Yield **24** (288 mg, 72%) of white-yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 1H, 3'), 7.19 (s, 1H, 6'), 6.98 (t, 1H, $J_{NH\text{-}1}$ = 5.5, NH), 5.44 (s, 2H, 4), 4.10 (t, 2H, $J_{2\text{-}1}$ = 5.6, 2), 3.91 and 3.88 (s, 3H, 4''-O-CH$_3$) and 3.88 (s, 3H, 5''-O-CH$_3$), 3.19 (q, 2H, $J_{1\text{-}NH}$ = 5.5, $J_{1\text{-}2}$ = 5.6, 1), 1.36 ppm (s, 9H, *t*Bu). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.81 (NH-CO), 154.31 (3), 153.32 and 148.38 (4' and 5'), 140.05 (2'), 125.45 (1'), 111.87 (6'), 108.44 (3'), 78.02 (O-C-*t*Bu), 66.82 (2), 66.02 (4), 59.00 (1), 56.46 and 56.31 (4'-O-CH$_3$ and 5'-O-CH$_3$), 38.8 (1), 28.33 ppm (*t*Bu). HRMS (ES$^+$) calcd for $C_{17}H_{25}O_9N_2$ 401.1555, found [M+H]$^+$ 401.1554.

*4, 5-Dimethoxy-2-nitrobenzyl (2-hydroxyethyl) carbonate (**25**)***.**



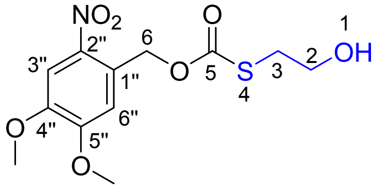
Ethylene glycol **19** (2 mL, 35.77 mmol, 9.85 eq.) and pyridine (350 µL, 4.35 mmol, 1.20 eq.) were dissolved in THF (12 mL). The solution was cooled down at 0 °C and 4, 5-dimethoxy-2-nitrobenzyl chloroformate **17** (1 g, 3.63 mmol, 1 eq.) was added in one portion. The mixture was stirred at 0 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was evaporated to dryness *in vacuo*, methanol (10 mL) was added and final product precipitated from the mixture. The title compound was filtered off, washed with methanol and dried in high vacuum. Yield **25** (800 mg, 73%) of a bright yellow solid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) *δ* 7.71 (s, 1H, 3''), 7.19 (s, 1H, 6''), 5.44 (s, 2H, 4), 4.89 (t, 1H, J_{OH-1} = 5.5, OH), 4.14 (m, 2H, 2), 3.90 (s, 3H, 4''-O-C**H$_3$**), 3.88 (s, 3H, 5''-O-C**H$_3$**), 3.59 ppm (m, 2H, 1). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) *δ* 154.53 (3), 153.34 (4''), 148.37 (5''), 140.03 (2''), 125.53 (1''), 111.83 (6''), 108.45 (3''), 69.89 (2), 65.98 (4), 59.00 (1), 56.46 and 56.32 ppm (5''-O-CH$_3$ and 4''-O-CH$_3$). HRMS (ES$^+$) calcd for $C_{12}H_{15}O_8NNa$ 324.0690, found [M+Na]$^+$ 324.0688.

*4, 5-dimethoxy-2-nitrobenzyl (2-hydroxyethyl)carbamate (**26**)***.**



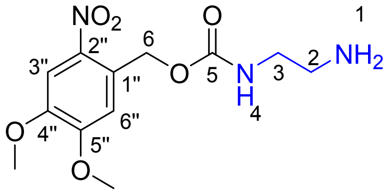
2-Aminoethanol **20** (31 µL, 0.51 mmol, 1.00 eq.) and triethylamine (70 µL, 0.51 mmol, 1.00 eq.) were dissolved in DCM (2 mL). The solution was cooled down at –78 °C and solution of 4, 5-dimethoxy-2-nitrobenzyl chloroformate **17** (140 mg, 0.51 mmol, 1.00 eq.) in DCM (2 mL) was added dropwise. The mixture was stirred at –78 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was evaporated to dryness *in vacuo* and product was purified using silica-gel flash chromatography (DCM – methanol gradient). The title compound was isolated after evaporation of volatiles and dried in high vacuum. Yield **26** (79 mg, 52%) of an off-white semi-solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70 (s, 3'), 7.43 (t, J_{NH-2} = 5.6, NH), 7.21 (s, 6'), 5.32 (s, 2H, 4), 4.66 (t, J_{OH-1} = 5.5, OH), 3.90 (s, 3H, 5'-O-Me), 3.87 (s, 3H, 4'-O-Me), 3.41 (m, 2H, 1), 3.08 (m, 2H, 2). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.96 (3), 153.56 (5'), 147.84 (4'), 139.39 (2'), 128.20 (1'), 110.66 (6'), 108.30 (3'), 62.46 (4), 60.09 (1), 56.42 (5'-O-Me), 56.27 (4'-O-Me), 43.25 (2). HRMS (ES$^+$) calcd for $C_{12}H_{16}O_7N_2Na$ 323.08497, found [M+Na]$^+$ 323.08488.

*4, 5-Dimethoxy-2-nitrobenzyl (2-hydroxyethyl)thiocarbonate (**27**)***.**



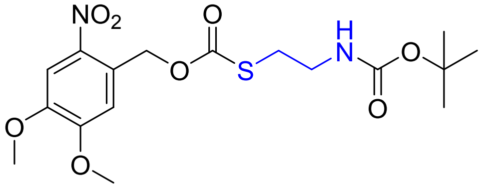
2-Mercaptoethanol **21** (35 µL, 0.48 mmol, 1.00 eq.) and triethylamine (68 µL, 0.48 mmol, 1.00 eq.) were dissolved in DCM (2 mL). The solution was cooled down at –78 °C and solution of 4, 5-dimethoxy-2-nitrobenzyl chloroformate **17** (135 mg, 0.48 mmol, 1 eq.) was added dropwise. The mixture was stirred at –78 °C for 50 min. and then allowed to warm up at 25 °C and stirred for 1 hour. The reaction mixture was evaporated to dryness *in vacuo*, final product was isolated using preparative TLC (2% methanol in chloroform). Volatiles were evaporated and the title compound was dried in high vacuum. Yield **27** (110 mg, 72%) of a yellowish solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70 (s, 1H, 3''), 7.19 (s, 1H, 6''), 5.53 (s, 2H, 4), 5.02 (t, 1H, J_{OH-1} = 5.5, OH), 3.90 (s, 3H, 5''-O-CH$_3$), 3.88 (s, 3H, 4''-O-CH$_3$), 3.56 (m, 2H, 1), 2.97 ppm (t, 2H, J_{2-1} = 6.5, 2). ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.22 (3), 153.26 (5''), 148.52 (4''), 140.20 (2''), 125.06 (1''), 112.46 (6''), 108.53 (3''), 65.78 (4), 60.0 (1), 56.46 and 56.33 (4''-O-CH$_3$ and 5''-O-CH$_3$), 33.63 ppm (2). HRMS (ES$^+$) calcd for $C_{12}H_{15}O_7NNaS$ 340.04614, found [M+Na]$^+$ 340.04624.

*4, 5-Dimethoxy-2-nitrobenzyl (2-aminoxyethyl)carbamate (**28**)***.**



Ethylenediamine **22** (670 µL, 10.00 mmol, 10.00 eq.) was dissolved in DCM (15 mL) and the solution of 4, 5-dimethoxy-2-nitrobenzyl chloroformate **17** (276 mg, 1.00 mmol, 1.00 eq.) was added in dropwise. The mixture was stirred at 25 °C for 12 h. The reaction mixture was washed with distilled water (20 mL), brine (20 mL), dried over sodium sulfate and evaporated to dryness. The title compound was isolated using silica-gel chromatography (DCM – methanol 0 – 20% gradient), evaporated and dried in high vacuum. Yield **28** (238 mg, 80%) of a white-yellow solid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) *δ* 7.69 (s, 1H, 3’’), 7.42 (t, 1H, $J_{4\text{-}3}$ = 5.6, 4), 7.19 (s, 6’’), 5.32 (s, 2H, 6), 3.90 (s, 3H, 5’’-O-CH$_3$), 3.87 (s, 3H, 4’’-O-CH$_3$), 3.01 (m, 2H, 3), 2.58 ppm (m, 2H, 2). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) *δ* 155.98 (5), 153.50 (5’’), 147.88 (4’’), 139.50 (2’’), 128.11 (1’’), 110.80 (6’’), 108.32 (3’’), 62.44 (6), 56.41 (5’’-O-CH$_3$), 56.27 (4’’-O-CH$_3$), 44.12 (3), 41.70 ppm (2). HRMS (ES$^+$) calcd for $C_{12}H_{18}$ O_6N_3 300.1190, found [M+H]$^+$ 300.1193.

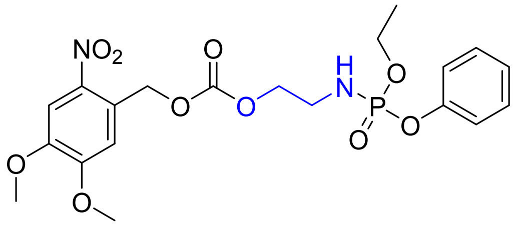
*4, 5-Dimethoxy-2-nitrobenzyl (2-(tert-butyloxycarbonylamino)ethyl)thiocarbonate (**29**)***.**



Tert-butyl (2-mercaptoethyl)carbamate **23** (84 µL, 0.50 mmol, 1.00 eq.) and triethylamine (69 µL, 0.50 mmol, 1.00 eq.) were dissolved in DCM (2 mL). The solution was cooled down at –78 °C and solution of 4, 5-dimethoxy-2-nitrobenzyl chloroformate **17** (138 mg, 0.50 mmol, 1.00 eq.) in DCM (2 mL) was added dropwise. The mixture was stirred at –78 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was evaporated to dryness in *vacuo* and product was purified using silica-gel flash chromatography (DCM – methanol gradient) or reverse phase flash chromatography (water – methanol gradient). The title compound was isolated after evaporation of volatiles and dried in high vacuum. Yield **29** (123 mg, 59%) of almost white semi-solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 1H, 3''), 7.19 (s, 1H, 6''), 7.04 (t, 1H, J_{NH-1} = 5.6, NH), 5.53 (s, 2H, 4), 3.90 (s, 3H, 5''-O-C**H₃**), 3.88 (s, 3H, 4''-O-C**H₃**), 3.15 (m, 2H, 1), 2.93 (t, 2H, J_{2-1} = 6.6, 2), 1.36 ppm (s, 9H, *t*Bu). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.91 (3), 155.67 (5), 153.25 (5''), 148.51 (4''), 140.19 (2''), 125.02 (1''), 112.42 (6''), 108.53 (3''), 78.01 (O-**C**-*t*Bu), 65.80 (4), 56.46 and 56.33 (4''-O-**C**H$_3$ and 5''-O-**C**H$_3$), 39.79 (1), 30.72 (2), 28.35 ppm (*t*Bu). HRMS (ES$^+$) calcd for $C_{17}H_{24}O_8N_2NaS$ 439.11456, found [M+Na]$^+$ 439.11441.

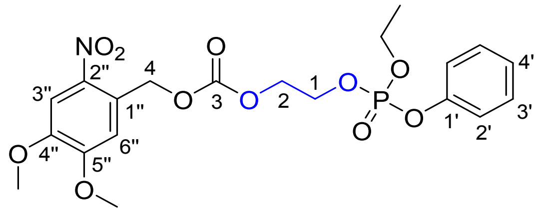
DMNBC Phosphate Self-immolative linkers *(1 – 11).*

*4, 5-Dimethoxy-2-nitrobenzyl (2-((ethoxy(phenoxy)phosphoryl)amino)ethyl) carbonate (**1**).*



4, 5-Dimethoxy-2-nitrobenzyl (2-(*tert*-butyloxycarbonylamino)ethyl) carbonate **24** (280 mg, 0.68 mmol, 1.00 eq.) was dissolved in DCM (3 mL) and solution was cooled down at 0 °C. Trifluoroacetic acid (3 mL) was added dropwise and mixture was stirred at 0 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 2 h. The reaction mixture was evaporated to dryness in *vacuo*, co-evaporated with DCM (3 x 5 mL) and dried in high vacuum. This crude deprotected amine was dissolved in DCM (3 mL), triethylamine (187 µL, 1.35 mmol, 2.00 eq.) and solution was cooled down at –78 °C. Solution of ethyl phenyl phosphorochloridate **12** (141 mg, 0.64 mmol, 0.94 eq.) in DCM (3 ml) was added dropwise. The mixture was stirred at –78 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was evaporated to dryness *in vacuo* and purified using preparative TLC chromatography (hexane – ethyl acetate 1:1). The title compound was extracted to DCM (5 mL), evaporated and dried in high vacuum. Yield **1** (50 mg, 16%) of a yellowish semisolid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 1H, 3''), 7.34 (m, 2H, 3'), 7.13 (s, 1H, 6''), 7.17 (m, 2H, 2'), 7.14 (m, 1H, 4'), 5.57 (dt, 1H, $J_{\text{NH-P}}$ = 12.5, $J_{\text{NH-2}}$ = 6.9, NH), 5.43 (s, 2H, 5), 4.08 (t, 2H, $J_{3\text{-}2}$ = 5.6, 3), 4.03 (m, 2H, O-**CH$_2$**-CH$_3$), 3.88 (s, 3H, 5''-O-C**H$_3$**), 3.87 (s, 3H, 4''-O-C**H$_3$**), 3.11 (m, 2H, 2), 1.23 ppm (t, 3H, $J_{\text{CH3-CH2}}$ = 7.0, O-CH$_2$-C**H$_3$**). ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.29 (4), 153.31 (5''), 151.05 (d, $J_{1'\text{-P}}$ = 6.3, 1'), 148.40 (4''), 140.05 (2''), 129.75 (3'), 125.41 (1''), 124.53 (4'), 120.30 (d, $J_{2'\text{-P}}$ = 4.9, 2'), 111.92 (6''), 108.44 (3''), 68.04 (d, $J_{3\text{-P}}$ = 5.2, 3), 66.06 (5), 62.31 (d, $J_{\text{CH2-P}}$ = 5.5, O-**CH$_2$**-CH$_3$), 56.45 and 56.31 (5''-O-CH$_3$, 4''-O-CH$_3$), 39.86 (2), 16.13 ppm (d, $J_{\text{CH3-P}}$ = 6.9, O-CH$_2$-**CH$_3$**). ^{31}P NMR (161 MHz, DMSO-d_6) δ 5.19 ppm. HRMS (ES$^+$) calcd for $C_{20}H_{26}O_{10}N_2P$ 485.13196, found [M+H]$^+$ 485.13194.

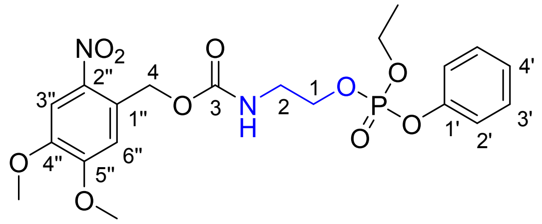
*4, 5-dimethoxy-2-nitrobenzyl (2-((ethoxy(phenoxy)phosphoryl)oxy)ethyl) carbonate (**2**).*



4, 5-Dimethoxy-2-nitrobenzyl (2-hydroxyethyl) carbonate **25** (301 mg, 1.00 mmol, 1.00 eq.) was dissolved in DCM (4 mL). The solution was cooled down at –78 °C and solution of ethyl phenyl phosphorochloridate **12** (220 mg, 1.00 mmol, 1.00 eq.) in DCM (2 ml) followed by addition of triethylamine (138 µL, 1.00 mmol, 1.00 eq.). The mixture was stirred at –78 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was evaporated to dryness *in vacuo* and purified using preparative TLC chromatography (hexane – ethyl acetate 1:1). The title compound was extracted to DCM (5 mL), evaporated and dried in high vacuum. Yield **2** (12 mg, 2%) of a yellowish semisolid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 1H, 3''), 7.38 (m, 2H, 3'), 7.23–7.18 (m, 4H, 6'', 4', 2'), 5.45 (s, 2H, 4), 4.38-4.30 (m, 4H, 1, 2), 4.15 (m, 2H, O-C**H$_2$**-CH$_3$), 1.24 ppm (dt, 3H, $J_{\text{CH3-CH2}}$ = 7.1, $J_{\text{CH3-P}}$ = 1.0, O-CH$_2$-C**H$_3$**). ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.17 (3), 153.30 (5'' or 4''), 150.31 (d, $J_{1'\text{-P}}$ = 7.1, 1'), 148.44 (4'' or 5''), 140.11 (2''), 130.08 (3'), 125.38 (4'), 125.23 (1''), 120.07 (d, $J_{2'\text{-P}}$ =

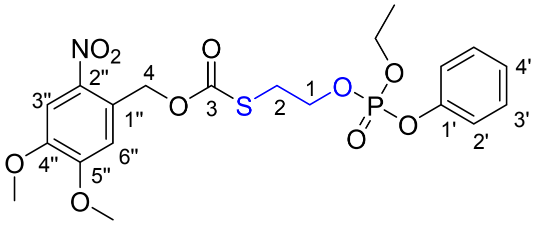
4.5, 2’), 112.01 (6’’), 108.46 (3’’), 66.87 (d, $J_{2\text{-P}}$ = 6.8, 2), 66.26 (4), 65.92 (d, $J_{1\text{-P}}$ = 5.6, 1), 64.75 (d, $J_{CH2\text{-P}}$ = 6.3, O-C**H₂**-CH₃), 56.42 and 56.32 (5’’-O-CH₃ and 4’’-O-CH₃), 15.98 ppm (d, $J_{CH3\text{-P}}$ = 6.4, O-CH₂-C**H₃**). ^{31}P NMR (161 MHz, DMSO-*d₆*) *δ* –3.77 ppm. HRMS (ES$^+$) calcd for $C_{20}H_{24}O_{11}NNaP$ 508.0979, found [M+H]$^+$ 508.0983.

*4, 5-Dimethoxy-2-nitrobenzyl (2-((ethoxy(phenoxy)phosphoryl)oxy)ethyl)carbamate (**3**).*



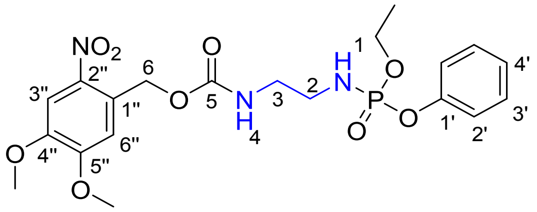
4, 5-dimethoxy-2-nitrobenzyl (2-hydroxyethyl)carbamate **26** (104 mg, 0.35 mmol, 1.00 eq.) was dissolved in DCM (4 mL). The solution was cooled down at –78 °C and solution of ethyl phenyl phosphorochloridate **12** (84 mg, 0.38 mmol, 1.1 eq.) in DCM (2 ml) was followed by addition of triethylamine (53 µL, 0.35 mmol, 1.00 eq.). The mixture was stirred at –78 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was evaporated to dryness *in vacuo* and purified using preparative TLC chromatography (hexane – ethyl acetate 1:1). The title compound was extracted to DCM (5 mL), evaporated and dried in high vacuum. Yield **3** (15 mg, 9%) of a yellowish semisolid. ^{1}H NMR (400 MHz, DMSO-*d₆*) *δ* 7.70 (t, $J_{NH\text{-}2}$ = 5.8, NH), 7.69 (s, 3’’), 7.38 (m, 2H, 3’), 7.23-7.14 (4H, 2’, 4’, 6’’), 5.34 (s, 2H, 4), 4.18-4.08 (m, 4H, 1, O-**CH₂**-CH₃), 3.38 and 3.86 (2 x s, 2 x 3H, 5’’-O-CH₃, 4’’-O-CH₃), 3.31-3.27 (m, 2H, 2), 1.23 (t, 3H, $J_{CH3\text{-}CH2}$ = 7.1, O-CH₂-**CH₃**). ^{13}C NMR (100 MHz, DMSO-*d₆*) *δ* 156.01 (3), 153.51 (5’’ or 4’’), 150.42 (d, $J_{1'\text{-P}}$ = 7.0, 1’), 147.93 (5’’ or 4’’), 139.51 (2’’), 130.07 (3’), 127.85 (1’’), 125.32 (4’), 120.10 (d, $J_{2'\text{-P}}$ = 4.7, 2’), 110.81 (6’’), 108.33 (3’’), 66.56 (d, $J_{1\text{-P}}$ = 6.5, 1), 64.64 (d, $J_{CH2\text{-P}}$ = 6.1, O-**CH₂**-CH₃), 62.65 (4), 56.38 and 56.27 (5’’-O-CH₃ and 4’’-O-CH₃), 40.81 (d, $J_{2\text{-P}}$ = 7.8, 2), 16.01 (d, $J_{CH3\text{-P}}$ = 6.5, O-CH₂-**CH₃**). ^{31}P NMR (161 MHz, DMSO-*d₆*) *δ* –6.36 ppm. HRMS (ES$^+$) calcd for $C_{20}H_{26}O_{16}N_2P$ = 485.13196, found [M+H]$^+$ 485.13167.

*4, 5-Dimethoxy-2-nitrobenzyl (2-((ethoxy(phenoxy)phosphoryl)oxy)ethyl)thiocarbonate (**4**).*



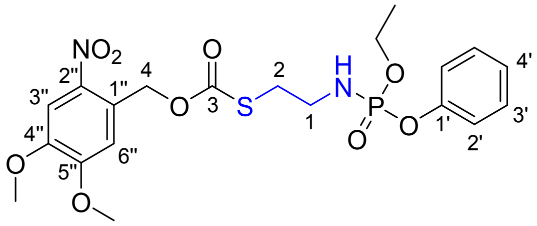
4, 5-Dimethoxy-2-nitrobenzyl (2-hydroxyethyl)thiocarbonate **4** (100 mg, 0.32 mmol, 1.00 eq.) was dissolved in DCM (4 mL). The solution was cooled down at –78 °C and solution of ethyl phenyl phosphorochloridate **12** (70 mg, 0.32 mmol, 1.00 eq.) in DCM (2 ml) followed by addition of triethylamine (44 µL, 0.32 mmol, 1.00 eq.). The mixture was stirred at –78 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was evaporated to dryness in *vacuo* and purified using preparative TLC chromatography (cyclohexane – ethyl acetate 1:1). The title compound was extracted to DCM (5 mL), volatiles were evaporated and product was dried in high vacuum. Yield **4** (24 mg, 15%) of yellowish semisolid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 3''), 7.40 (m, 2H, 3'), 7.25–7.18 (m, 4H, 4', 6'', 2'), 5.55 (s, 2H, 4), 4.25 (m, 2H, 1), 4.16 (m, 2H, O-**CH$_2$**-CH$_3$), 3.89 and 3.88 (2 x s, 2 x 3H, 5''-O-CH$_3$, 4''-O-CH$_3$), 3.22 (td, 2H, $J_{2\text{-}1}$ = 6.3, $J_{2\text{-P}}$ = 0.7, 2), 1.25 ppm (dt, 3H, $J_{\text{CH3-CH2}}$ = 7.1, $J_{\text{CH3-P}}$ = 0.9, O-CH$_2$-**CH$_3$**). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.51 (3), 153.25 (5'' or 4''), 150.35 (d, $J_{1'\text{-P}}$ = 6.9, 1'), 148.59 (4'' or 5''), 140.27 (2''), 130.12 (3'), 125.41 (4'), 124.78 (1''), 120.08 (d, $J_{2'\text{-P}}$ = 4.6, 2'), 112.63 (6''), 108.55 (3''), 66.16 (d, $J_{1\text{-P}}$ = 5.8, 1), 66.13 (4), 64.81 (d, $J_{\text{CH2-P}}$ = 6.2, O-**CH$_2$**-CH$_3$), 56.45 and 56.34 (5''-O-CH$_3$, 4''-O-CH$_3$), 30.96 (d, $J_{\text{CH2-P}}$ = 8.1, 2), 16.03 ppm (d, $J_{\text{CH3-P}}$ = 6.1, O-CH$_2$-**CH$_3$**). ^{31}P NMR (161 MHz, DMSO-d_6) δ –6.76 ppm. HRMS (ES$^+$) calcd for $C_{20}H_{25}O_{10}NPS$ 502.09313, found [M+H]$^+$ 502.09270.

*4, 5-Dimethoxy-2-nitrobenzyl (2-((ethoxy(phenoxy)phosphoryl)amino)ethyl)carbamate (**5**).*



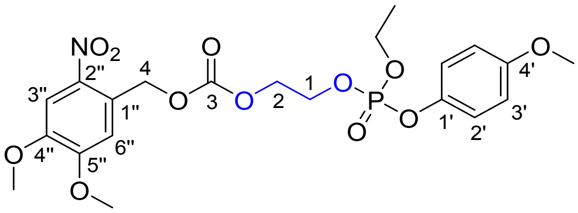
4, 5-Dimethoxy-2-nitrobenzyl (2-aminoxyethyl)carbamate **28** (238 mg, 0.80 mmol, 1.00 eq.) was dissolved in DCM (3 mL) and added dropwise to the solution of ethyl phenyl phosphorochloridate **12** (220 mg, 1.00 mmol, 1.25 eq.) in DCM (2 ml) cooled down at –78 °C. After addition of triethylamine (138 µL, 1.00 mmol, 1.25 eq.), reaction mixture was stirred at –78 °C for 5 min., allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was evaporated to dryness *in vacuo* and purified using reverse-phase chromatography (water – acetonitrile gradient). Volatiles were evaporated and title compound was dried in high vacuum. Yield **5** (100 mg, 21%) of an off-white semisolid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (s, 1H, 3’’), 7.42 (t, 1H, $J_{4\text{-}3}$ = 5.7, 4), 7.35 (m, 2H, 3’), 7.19–7.11 (m, 4H, 6’’, 2’, 4’), 5.39 (m, 1H, 1), 5.31 (s, 2H, 6), 4.03 (m, 2H, PO**CH$_2$**-CH$_3$), 3.89 (s, 3H, 5’’-O-CH$_3$), 3.87 (s, 3H, 4’’-O-CH$_3$), 3.04 (m, 2H, 3), 2.88 (m, 2H, 2), 1.23 ppm (t, 3H, $J_{\mathrm{CH3\text{-}CH2}}$ = 7.1, PO-CH$_2$-**CH$_3$**). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.89 (5), 153.47 (5’’), 151.08 (d, $J_{1'\text{-}\mathrm{P}}$ = 6.4, 1’), 147.93 (4’’), 142.83 (2’’ or 1’’), 129.79 (3’), 127.84 (1’’ or 2’’), 124.54 (4’), 120.29 (d, $J_{2'\text{-}\mathrm{P}}$ = 4.8, 2’), 110.91 (6’’), 108.34 (3’’), 62.57 (6), 62.28 (d, $J_{\mathrm{P\text{-}CH2}}$ = 5.4, PO-**C**H$_2$), 56.39 (5’’-O-**C**H$_3$), 56.28 (4’’-O-**C**H$_3$), 41.89 (d, $J_{3\text{-}\mathrm{P}}$ = 6.1, 3), 40.72 (2), 16.17 ppm (d, $J_{\mathrm{CH3\text{-}P}}$ = 6.8, O-CH$_2$-**C**H$_3$). ^{31}P NMR (202 MHz, DMSO-d_6) δ 5.37 ppm. HRMS (ES$^+$) calcd for $C_{20}H_{27}O_9N_3P$ 484.1479, found [M+H]$^+$ 484.1480.

*4, 5-Dimethoxy-2-nitrobenzyl (2-((ethoxy(phenoxy)phosphoryl)amino)ethyl)thiocarbonate (**6**).*



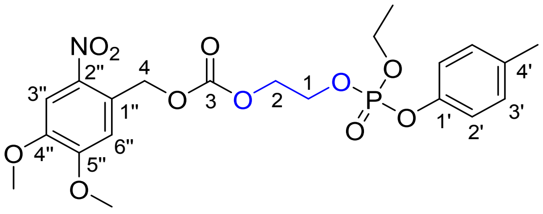
4, 5-Dimethoxy-2-nitrobenzyl (2-(*tert*-butyloxycarbonylamino)ethyl)thiocarbonate **29** (100 mg, 0.24 mmol, 1.00 eq.) was dissolved in DCM (3 mL) and solution was cooled down at 0 °C. Trifluoroacetic acid (3 mL) was added dropwise and mixture was stirred at 0 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 2 h. The reaction mixture was evaporated to dryness *in vacuo*, co-evaporated with DCM (3x5 mL), co-evaporated with toluene (5 mL) and dried in high vacuum. This crude deprotected amine was dissolved in DCM (3 mL), triethylamine (80 µL, 0.58 mmol, 2.42 eq.) and solution was cooled down at 0 °C. Solution of ethyl phenyl phosphorochloridate **12** (57 mg, 0.26 mmol, 1.08 eq.) in DCM (3 ml) was added dropwise. The mixture was stirred at 0 °C for 5 min. and then allowed to warm up at 25 °C and stirred for 12 h. The reaction mixture was evaporated to dryness *in vacuo* and purified using preparative TLC chromatography (cyclohexane – ethyl acetate 3:2) (or reverse phase flash chromatography (water – methanol gradient)). The title compound was extracted to DCM (5 mL), evaporated and dried in high vacuum. Yield **6** (83 mg, 69%) of a pale-yellowish semisolid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 1H, 3’’), 7.36 (m, 2H, 3’), 7.14–7.20 (m, 4H, 6’’, 2’, 4’), 5.64 (dt, 1H, J_{NH-1} = 6.7, J_{NH-P} = 12.6, NH), 5.53 (s, 2H, 4), 4.04 (m, 2H, O-**CH$_2$**-CH$_3$), 3.89 (s, 3H, 5’’-O-CH$_3$), 3.88 (s, 3H, 4’’-O-CH$_3$), 3.05 (m, 2H, 1), 2.90 (m, 2H, 2), 1.24 ppm (dt, 3H, $J_{CH3-CH2}$ = 7.1, J_{CH3-P} = 0.6, O-CH$_2$-**CH$_3$**). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.87 (3), 153.22 (5’’), 151.03 (d, 1’, $J_{1'-P}$ = 6.2), 148.55 (4’’), 140.26 (2’’), 129.79 (3’), 124.90 (1’’), 124.56 (4’), 120.29 (d, 2’, $J_{2'-P}$ = 4.7), 112.59 (6’’), 108.53 (3’’), 65.87 (4), 62.37 (d, O-**C**H$_2$-CH$_3$, J_{CH2-P} = 5.2), 56.45 and 56.33 (4’’-O-**C**H$_3$ and 5’’-O-**C**H$_3$), 40.91 (1), 32.09 (d, 2, J_{2-P} = 5.8, 16.16 ppm (d, O-CH$_2$-**C**H$_3$ J_{CH3-P} = 6.6). ^{31}P NMR (161 MHz, DMSO-d_6) δ 4.81 ppm. HRMS (ES$^+$) calcd for $C_{20}H_{26}O_9N_2PS$ 501.10911, found [M+H]$^+$ 501.10885.

*4, 5-Dimethoxy-2-nitrobenzyl (2-((ethoxy(4-methoxyphenoxy)phosphoryl)oxy)ethyl) carbonate (**7**)***.**



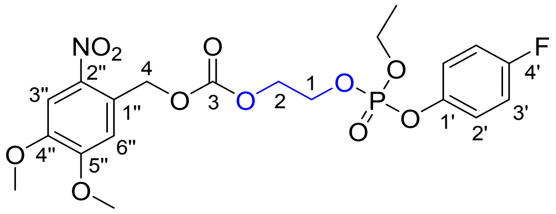
4, 5-Dimethoxy-2-nitrobenzyl (2-hydroxyethyl) carbonate **25** (120 mg, 0.40 mmol, 1.00 eq.) was suspended in toluene (4 mL) and ethyl dichlorophosphate (50 µL, 0.40 mmol, 1.00 eq.) and triethylamine (100 µL, 0.72 mmol, 1.80 eq.) were added at 25 °C. The mixture was stirred for 12 h, evaporated to dryness in *vacuo* and dissolved in dichloromethane (4 mL). 4-Methoxyphenol (50 mg, 0.40 mmol, 1.00 eq.) and triethylamine (100 µL, 0.72 mmol, 1.80 eq.) were added and reaction mixture was stirred at 25 °C for 12 h. The title product was isolated after evaporation of volatiles using normal-phase flash chromatography (DCM – methanol gradient on silica-gel) and followed by reverse-phase flash chromatography (water – acetonitrile gradient on C18 silica-gel). Yield **7** (18 mg, 9%) of almost white semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.74 (s, 1H, 3’’), 7.13 (m, 2H, 2’), 7.07 (s, 1H, 6’’), 6.82 (m, 2H, 3’), 5.61 (d, 1H, J_{GEM} = 14.6, 4a), 5.58 (d, 1H, J_{GEM} = 14.6, 4b), 4.42 (m, 2H, 2), 4.37 (m, 2H, 1), 4.22 (m, 2H, O-**CH$_2$**-CH$_3$), 3.98 (s, 3H, 5’’-O-C**H$_3$**), 3.97 (s, 3H, 4’’-O-C**H$_3$**), 3.77 (s, 3H, 4’-O-C**H$_3$**), 1.35 ppm (dt, 3H, $J_{CH3\text{-}CH2}$ = 7.1, $J_{CH3\text{-}P}$ = 1.1, O-CH$_2$-C**H$_3$**). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 156.76 (4’), 154.41 (3), 153.71 (5’’), 148.28 (4’’), 143.99 (d, $J_{1'\text{-}P}$ = 7.0, 1’), 139.53 (2’’), 126.48 (1’’), 120.81 (d, $J_{2'\text{-}P}$ = 4.6, 2’), 114.59 (3’), 109.76 (6’’), 108.10 (3’’), 66.62 (d, $J_{2\text{-}P}$ = 7.0, 2), 66.51 (4), 65.42 (d, $J_{1\text{-}P}$ = 5.4, 1), 64.90 (d, $J_{CH2\text{-}P}$ = 6.1, O-C**H$_2$**-CH$_3$), 56.51 and 56.36 (5’’-O-CH$_3$ and 4’’-O-CH$_3$), 55.53 (4’-O-CH$_3$), 16.01 ppm (d, $J_{CH3\text{-}P}$ =6.6, O-CH$_2$-**CH$_3$**). ^{31}P NMR (161 MHz, $CDCl_3$) *δ* –5.84 ppm. HRMS (ES$^+$) calcd for $C_{21}H_{27}O_{12}NP$ 516.12654, found [M+H]$^+$ 516.12646.

*4, 5-dimethoxy-2-nitrobenzyl (2-((ethoxy(4-methylphenoxy)phosphoryl)oxy)ethyl) carbonate (**8**).*



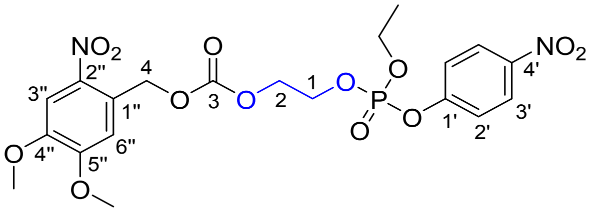
4, 5-Dimethoxy-2-nitrobenzyl (2-hydroxyethyl) carbonate **25** (120 mg, 0.40 mmol, 1.00 eq.) was suspended in toluene (3 mL) and ethyl dichlorophosphate (50 µL, 0.40 mmol, 1.00 eq.) and triethylamine (100 µL, 0.72 mmol, 1.80 eq.) were added at 25 °C. The mixture was stirred for 12 h, evaporated to dryness *in vacuo* and dissolved in dichloromethane (3 mL). 4-Methylphenol (45 mg, 0.42 mmol, 1.05 eq.) and triethylamine (100 µL, 0.72 mmol, 1.80 eq.) were added and reaction mixture was stirred at 25 °C for 12 h. The title product was isolated after evaporation of volatiles using normal-phase flash chromatography (n-hexane – ethyl acetate gradient on silica-gel) and followed by reverse-phase flash chromatography (water – acetonitrile gradient on C18 silica-gel). Yield **8** (21 mg, 11) of almost white semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H, 3’’), 7.09–7.13 (m, 4H, 2’, 3’), 7.08 (s, 1H, 6’’), 5.61–5.62(m, 2H, 4), 4.35–4.49 (m, 4H, 1, 2), 4.24 (m, 2H, O-$\mathbf{CH_2}$-CH_3), 3.98 and 3.98 (s, 3H, 5’’-O-CH_3) and (s, 3H, 4’’-O-CH_3), 2.32 (s, 3H, 4’-CH_3), 1.36 ppm (dt, 3H, $J_{\mathrm{CH3\text{-}CH2}}$ = 7.1, $J_{\mathrm{CH3\text{-}P}}$ = 1.1, O-CH_2-$\mathbf{CH_3}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.46 (3), 153.77 (5’’), 148.31 (4’’), 148.25 (1’), 139.56 (2’’), 134.82 (4’), 130.17 (3’), 126.58 (1’’), 119.65 (d, $J_{2'\text{-P}}$ = 4.6, 2’), 109.74 (6’’), 108.14 (3’’), 66.66 (d, $J_{2\text{-P}}$ = 7.0, 2), 66.55 (4), 65.43 (d, $J_{1\text{-P}}$ = 5.4, 1), 64.93 (d, $J_{\mathrm{CH2\text{-}P}}$ = 6.2, O-$\mathbf{CH_2}$-CH_3), 56.55 and 56.41 (5’’-O-CH_3 and 4’’-O-CH_3), 20.68 (4’-CH_3), 16.04 ppm (d, $J_{\mathrm{CH3\text{-}P}}$ =6.3, O-CH_2-$\mathbf{CH_3}$). ^{31}P NMR (161 MHz, $CDCl_3$) δ –6.14 ppm. HRMS (ES$^+$) calcd for $C_{21}H_{27}O_{11}NP$ 500.13162, found $[M+H]^+$ 500.13157.

*4, 5-Dimethoxy-2-nitrobenzyl (2-((ethoxy(4-fluorophenoxy)phosphoryl)oxy)ethyl) carbonate (**9**).*



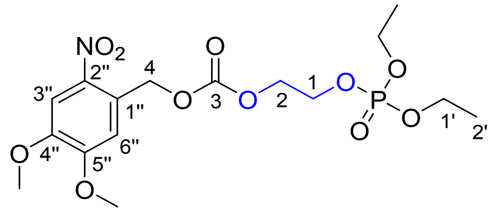
4, 5-Dimethoxy-2-nitrobenzyl (2-hydroxyethyl) carbonate **25** (120 mg, 0.40 mmol, 1.00 eq.) was suspended in toluene (3 mL) and ethyl dichlorophosphate (50 µL, 0.40 mmol, 1.00 eq.) and triethylamine (100 µL, 0.72 mmol, 1.80 eq.) were added at 25 °C. The mixture was stirred for 12 h, evaporated to dryness *in vacuo* and dissolved in dichloromethane (3 mL). 4-Fluorophenol (45 mg, 0.40 mmol, 1.00 eq.) and triethylamine (100 µL, 0.72 mmol, 1.80 eq.) were added and reaction mixture was stirred at 25 °C for 12 h. The title product was isolated after evaporation of volatiles using normal-phase flash chromatography (n-hexane – ethyl acetate gradient on silica-gel) and followed by reverse-phase flash chromatography (water – acetonitrile gradient on C18 silica-gel). Yield **9** (18 mg, 9%) of almost white semisolid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (s, 1H, 3’’), 7.19 (m, 2H, 2’), 7.07 (s, 1H, 6’’), 7.01 (m, 2H, 3’), 5.61 (s, 2H, 4), 4.35–4.45 (m, 4H, 2, 1), 4.25 (m, 2H, O-**CH$_2$**-CH$_3$), 3.99 (s, 3H, 5’’-O-CH$_3$), 3.98 (s, 3H, 4’’-O-CH$_3$), 1.36 ppm (dt, 3H, $J_{\text{CH3-CH2}}$ = 7.1, $J_{\text{CH3-P}}$ = 1.1, O-CH$_2$-**CH$_3$**). ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.75 (d, $J_{4'\text{-F}}$ = 243.6, 4’), 154.44 (3), 153.71 (5’’), 148.39 (4’’), 146.34 (dd, $J_{1'\text{-P}}$ = 6.6, $J_{1'\text{-F}}$ = 2.3, 1’), 139.67 (2’’), 126.34 (1’’), 121.41 (dd, $J_{2'\text{-P}}$ = 4.6, $J_{2'\text{-F}}$ = 8.5, 2’), 116.29 (d, $J_{3'\text{-F}}$ = 23.7, 3’), 109.94 (6’’), 108.18 (3’’), 66.62 (4), 66.57 (d, $J_{2\text{-P}}$ = 7.2, 2), 65.60 (d, $J_{1\text{-P}}$ = 5.4, 1), 65.13 (d, $J_{\text{CH2-P}}$ = 6.2, O-**CH$_2$**-CH$_3$), 56.53 and 56.41 (5’’-O-CH$_3$ and 4’’-O-CH$_3$), 16.03 ppm (d, $J_{\text{CH3-P}}$ = 6.7, O-CH$_2$-**CH$_3$**). ^{31}P NMR (161 MHz, CDCl$_3$) δ –6.16 ppm. HRMS (ES$^+$) calcd for $C_{20}H_{24}O_{11}NFP$ 504.10655, found [M+H]$^+$ 504.10645.

*4, 5-Dimethoxy-2-nitrobenzyl (2-((ethoxy(4-nitrophenoxy)phosphoryl)oxy)ethyl) carbonate (**10**).*



4, 5-Dimethoxy-2-nitrobenzyl (2-hydroxyethyl) carbonate **25** (100 mg, 0.33 mmol, 1.00 eq.) was suspended in toluene (5 mL) and ethyl dichlorophosphate (50 µL, 0.40 mmol, 1.20 eq.) and triethylamine (100 µL, 0.72 mmol, 2.20 eq.) were added at 25 °C. The mixture was stirred for 12 h, evaporated to dryness *in vacuo* and dissolved in dichloromethane (3 mL). 4-Nitrophenol (40 mg, 0.29 mmol, 0.88 eq.) and triethylamine (50 µL, 0.36 mmol, 1.09 eq.) were added and reaction mixture was stirred at 25 °C for 12 h. The title product was isolated after evaporation of volatiles using normal-phase flash chromatography (DCM – methanol gradient on silica-gel) and followed by reverse-phase flash chromatography (water – acetonitrile gradient on C18 silica-gel). Yield **10** (12 mg, 8%) of almost white semisolid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22 (m, 2H, 3’), 7.74 (s, 1H, 3’’), 7.38 (m, 2H, 2’), 7.04 (s, 1H, 6’’), 5.60 (d, 1H, J_{GEM} = 14.7, 4a), 5.56 (d, 1H, J_{GEM} = 14.7, 4b), 4.40–4.46 (m, 4H, 2, 1), 4.28 (m, 2H, O-**CH_2**-CH_3), 3.99 and 3.98 (s, 3H, 5’’-O-C**H_3**) and (s, 3H, 4’’-O-C**H_3**), 1.38 ppm (dt, 3H, $J_{CH3\text{-}CH2}$ = 7.1, $J_{CH3\text{-}P}$ = 1.1, O-CH_2-C**H_3**). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.17 (d, $J_{1'\text{-}P}$ = 6.2, 1’), 154.37 (3), 153.61 (5’’ or 4’’), 148.49 (5’’ or 4’’), 144.74 (4’), 139.80 (2’’), 125.92 (1’’), 125.62 (3’), 120.56 (d, $J_{2'\text{-}P}$ = 5.4, 2’), 110.25 (6’’), 108.20 (3’’), 66.72 (4), 66.37 (d, $J_{2\text{-}P}$ = 6.9, 2), 65.98 (d, $J_{1\text{-}P}$ = 5.4, 1), 65.59 (d, $J_{CH2\text{-}P}$ = 6.2, O-**CH_2**-CH_3), 56.50 and 56.39 (5’’-O-CH_3 and 4’’-O-CH_3), 15.99 ppm (d, $J_{CH3\text{-}P}$ = 6.9, O-CH_2-**CH_3**). ^{31}P NMR (161 MHz, $CDCl_3$) δ –7.19 ppm. HRMS (ES$^+$) calcd for $C_{20}H_{24}O_{13}N_2P$ 531.10105, found [M+H]$^+$ 531.10120.

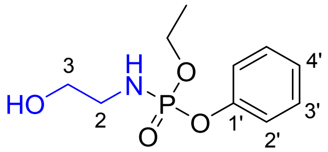
*4, 5-Dimethoxy-2-nitrobenzyl (2-((diethoxyphosphoryl)oxy)ethyl) carbonate (**11**)***.**



4, 5-Dimethoxy-2-nitrobenzyl (2-hydroxyethyl) carbonate **25** (120 mg, 0.40 mmol, 1.00 eq.) was dissolved in DCM (3 mL) and diethyl chlorophosphate **30** (60 µL, 0.41 mmol, 1.04 eq.) and triethylamine (100 µL, 0.72 mmol, 1.80 eq.) were added at 25 °C. The mixture was stirred at 25 °C for 12 h, evaporated to dryness in *vacuo*. The title product was isolated after evaporation of volatiles using normal-phase flash chromatography (cyclohexane – ethyl acetate gradient on silica-gel) and followed by reverse-phase flash chromatography (water – acetonitrile gradient on C18 silica-gel). Yield **11** (12 mg, 7%) of almost white oily solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H, 3’’), 7.09 (s, 1H, 6’’), 5.62 (s, 2H, 4), 4.43 (m, 2H, 2), 4.29 (m, 2H, 1), 4.15 (m, 4H, 1’), 4.02 (s, 3H, 5’’-O-C**H_3**), 3.98 (s, 3H, 4’’-O-C**H_3**), 1.35 ppm (dt, 6H, $J_{2'\text{-}1'}$ = 7.1, $J_{2'\text{-}P}$ = 1.0, 2’). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.50 (3), 153.74 (5’’), 148.35 (4’’), 139.62 (2’’), 126.51 (1’’), 109.84 (6’’), 108.17 (3’’), 66.81 (d, $J_{2\text{-}P}$ = 7.0, 2), 66.54 (4), 66.54 (4), 64.72 (d, $J_{1\text{-}P}$ = 5.4, 1), 64.04 (d, $J_{1'\text{-}P}$ = 6.0, 1’), 56.56 (5’’-O-CH_3), 56.40 (4’’-O-CH_3), 16.06 ppm (d, $J_{1'\text{-}P}$ =6.9, 1’). ^{31}P NMR (161 MHz, $CDCl_3$) δ –1.03 ppm. HRMS (ES$^+$) calcd for $C_{16}H_{25}O_{11}NP$ 438.11597, found [M+H]$^+$ 438.11566.

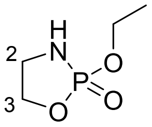
Intermediates (***1-I, 1-cyc-I, 1-P, 2-I, 2-cyc-I, 2-P, 2-cyc-P, 3-I, 3-P*** *and* ***4-P, 6-I).***

*Ethyl phenyl (2-hydroxyethyl)phosphoramidate (**1-I**).*



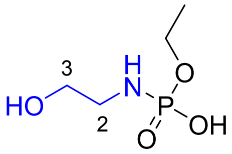
^{1}H NMR (500 MHz, 50% CACO/DMSO, indirectly from HMBC) δ 7.32 (3'), 7.11 (2'), 7.10 (4'), 4.02 (O-$\mathbf{CH_2}$-CH_3), 3.37 (3), 2.88 (2), 1.18 ppm (O-CH_2-$\mathbf{CH_3}$). ^{13}C NMR (125 MHz, 50% CACO/DMSO) δ 151.77 (d, $J_{1'\text{-}P}$ = 6.8, 1'), 131.60 (3'), 126.85 (4'), 121.76 (d, $J_{2'\text{-}P}$ = 4.6, 2'), 65.11 (d, $J_{CH2\text{-}P}$ = 5.8, O-$\mathbf{CH_2}$-CH_3), 62.99 (d, $J_{3\text{-}P}$ = 6.0, 3), 44.36 (2), 17.24 ppm (d, $J_{CH3\text{-}P}$ = 6.9, O-CH_2-$\mathbf{CH_3}$). ^{31}P NMR (202 MHz, 50% CACO/DMSO) δ 6.34ppm.

*2-Ethoxy-1,3,2-oxazaphospholidine 2-oxide (**1-cyc-I**).*



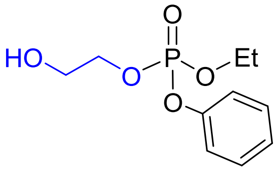
^{13}C NMR (125 MHz, 50% CACO/DMSO) δ 68.81 (d, $J_{3\text{-}P}$ = 4.3, 3), 65.35 (d, $J_{3\text{-}P}$ = 6.8, O-$\mathbf{CH_2}$-CH_3), 43.40 (d, $J_{2\text{-}P}$ = 10.0, 2), 17.3 ppm (O-CH_2-$\mathbf{CH_3}$). ^{31}P NMR (202 MHz, 50% CACO/DMSO) δ 26.93 ppm.

*Ethyl hydrogen (2-hydroxyethyl)phosphoramidate (**1-P**).*



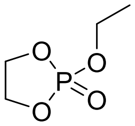
^{1}H NMR (500 MHz, 50% CACO/DMSO) δ 3.64 (m, 2H, O-$\mathbf{CH_2}$-CH_3), 3.38 (t, 2H, $J_{3\text{-}2}$ = 5.8, 3), 2.74 (dt, 2H, $J_{2\text{-}3}$ = 5.8, $J_{2\text{-}P}$ = 10.0, 2), 1.06 ppm (t, 3H, $J_{CH3\text{-}CH2}$ = 7.1, O-CH_2-$\mathbf{CH_3}$). ^{13}C NMR (125 MHz, 50% CACO/DMSO) δ 63.95 (d, $J_{3\text{-}P}$ = 6.4, 3), 61.58 (d, $J_{CH2\text{-}P}$ = 5.2, O-$\mathbf{CH_2}$-CH_3), 44.73 (2), 17.66 ppm (d, $J_{CH3\text{-}P}$ = 7.3, O-CH_2-$\mathbf{CH_3}$). ^{31}P NMR (202 MHz, 50% CACO/DMSO) δ 7.91 ppm.

*Ethyl (2-hydroxyethyl) phenyl phosphate (**2-I**).*



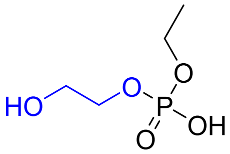
^{31}P NMR (202 MHz, 50% CACO/DMSO) δ –6.13 ppm.

*2-Ethoxy-1,3,2-dioxaphospholane 2-oxide (**2-cyc-I**)*



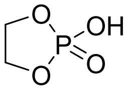
^{31}P NMR (202 MHz, 50% CACO/DMSO) δ 18.05 ppm.

*Ethyl (2-hydroxyethyl) hydrogen phosphate (**2-P**)*



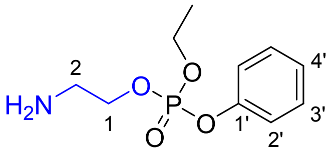
^{1}H NMR (500 MHz, 50% CACO/DMSO) δ 4.76 (m, 2H, O-**CH$_2$**-CH$_3$), 4.73 (m, 2H, 3), 4.57 (m, 2H, 2), 2.13 ppm (dt, 3H, $J_{CH3\text{-}CH2}$ = 7.1, $J_{CH3\text{-}P}$ = 0.7, O-CH$_2$-**CH$_3$**). ^{13}C NMR (125 MHz, 50% CACO/DMSO) δ 67.74 (d, $J_{3\text{-P}}$ = 5.8, 3), 62.74 (d, $J_{2\text{-P}}$ = 5.6, 2), 62.64 (d, $J_{CH2\text{-P}}$ = 7.7, O-**CH$_2$**-CH$_3$), 17.54 ppm (d, $J_{CH3\text{-P}}$ = 7.2, O-CH$_2$-**CH$_3$**). ^{31}P NMR (202 MHz, 50% CACO/DMSO) δ 0.02 ppm.

*2-Hydroxy-1,3,2-dioxaphospholane 2-oxide (**2-cyc-P**).*



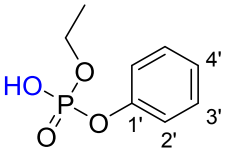
^{1}H NMR (500 MHz, 50% CACO/DMSO) δ 5.06 ppm (d, $J_{CH2\text{-P}}$ = 10.3, O-CH$_2$). ^{13}C NMR (125 MHz, 50% CACO/DMSO) δ 66.02 ppm (d, $J_{CH2\text{-P}}$ = 1.8, O-CH$_2$). ^{31}P NMR (202 MHz, 50% CACO/DMSO) δ 17.59 ppm.

*2-Aminoethyl ethyl phenyl phosphate (**3-I**).*



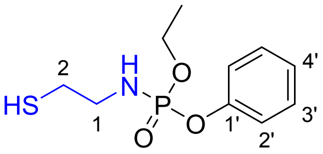
^{1}H NMR (500 MHz, 50% CACO/DMSO,) *δ* 7.32 (m, 2H, 3’), 7.20 (m, 1H, 4’), 7.13 (m, 2H, 2’), 4.10–4.20 (m, 4H, 1, O-**CH$_2$**-CH$_3$), 2.90 (m, 2H, 2), 1.21 ppm (t, 3H, $J_{CH3\text{-}CH2}$ = 7.0, O-CH$_2$-**CH$_3$**), NH$_2$ was not detected. ^{13}C NMR (125 MHz, 50% CACO/DMSO) *δ* 151.23 (d, $J_{1'\text{-}P}$ = 7.5, 1’), 131.80 (3’), 127.48 (4’), 121.44 (d, $J_{2'\text{-}P}$ = 4.6, 2’), 69.43 (1), 67.42 (d, $J_{CH2\text{-}P}$ = 6.2, O-**CH$_2$**-CH$_3$), 41.67 (d, $J_{2\text{-}P}$ = 7.6, 2), 17.12 ppm (d, $J_{CH3\text{-}P}$ = 6.4, O-CH$_2$-**CH$_3$**). ^{31}P NMR (202 MHz, 50% CACO/DMSO) *δ* –6.30 ppm.

*Ethyl phenyl hydrogen phosphate (**3-P** = **4-P**).*



^{1}H NMR (500 MHz, 50% CACO/DMSO,) *δ* 7.23 (m, 2H, 3’), 7.04 (m, 2H, 2’), 7.00 (m, 1H, 4’), 3.79 (m, 2H, O-**CH$_2$**-CH$_3$), 1.06 ppm (t, 3H, $J_{CH3\text{-}CH2}$ = 7.0, O-CH$_2$-**CH$_3$**). ^{13}C NMR (125 MHz, 50% CACO/DMSO) *δ* 153.91 (d, $J_{1'\text{-}P}$ = 6.9, 1’), 130.99 (3’), 124.91 (4’), 121.59 (d, $J_{2'\text{-}P}$ = 4.5, 2’), 63.23 (d, $J_{CH2\text{-}P}$ = 5.7, O-**CH$_2$**-CH$_3$), 17.47 ppm (d, $J_{CH3\text{-}P}$ = 7.1, O-CH$_2$-**CH$_3$**). ^{31}P NMR (202 MHz, 50% CACO/DMSO) *δ* –5.40 ppm.

*Ethyl phenyl (2-mercaptoethyl)phosphoramidate (**6-I**).*



^{1}H NMR (500 MHz, 50% CACO/DMSO,) *δ* 7.31 (m, 2H, 3’), 7.14 (m, 1H, 4’), 7.10 (m, 2H, 2’), 5.2 (NH), 4.02 (m, 2H, O-**CH$_2$**-CH$_3$), 3.06 (m, 2H, 1), 2.59 (m, 2H, 2), 1.19 ppm (t, 3H, $J_{CH3\text{-}CH2}$ = 7.1, O-CH$_2$-**CH$_3$**). ^{13}C NMR (125 MHz, 50% CACO/DMSO) *δ* 151.76 (d, $J_{1'\text{-}P}$ = 6.9, 1’), 131.55 (3’), 126.80 (4’), 121.64 (d, $J_{2'\text{-}P}$ = 4.5, 2’), 65.09 (d, $J_{CH2\text{-}P}$ = 5.5, O-**CH$_2$**-CH$_3$), 41.52 (1), 40.0 (2), 17.26 ppm (d, $J_{CH3\text{-}P}$ = 6.4, O-CH$_2$-**CH$_3$**). ^{31}P NMR (202 MHz, 50% CACO/DMSO) *δ* 5.58 ppm.

2 Photochemical activation

The photolysis quantum yield (Φ) was calculated as the concentration change in initial compound divided by the absorbed light intensity of the initial compound (at low photoconversion) and the overall procedure was described in detail in our previous article.[2] The concentration change was determined using HPLC chromatography (Agilent 1100 HPLC System; G1311A quaternary pump, G1314A UV VWD detector; conditions: LiChrospher®100, RP-18 Endcapped 5μm, 4 mm × 250 mm, 55% MeCN in water containing 0.1% phosphoric acid, 1.0 mL/min, λ = 350 nm). The corresponding absorbed light intensity I_a during the photolysis (irradiation wavelengths of 340 nm; three LED341W diodes Thorlabs) was determined using an Ocean Optics HR4000CG-UV-NIR spectrophotometer (the incident light intensity was determined by ferrioxalate actinometry).

Table S1. Intensity of absorption, photolysis quantum yield, photolytic efficiency, and reaction rate of direct photolysis for the studied compounds **1**–**6**.[a]

Cpd	ε_A	Φ	$\varepsilon_A \times \Phi$	k_a	k_p
1	4560	0.0051±0.0002	23.2 ± 1.1	4.6×10^{-3}	2.3×10^{-5}
2	5510	0.0088±0.0007	49.0 ± 3.9	3.8×10^{-3}	3.4×10^{-5}
3	7750	0.0190±0.0010	155.0 ± 7.6	2.9×10^{-3}	5.9×10^{-5}
4	4980	0.0047±0.0001	23.9 ± 0.5	5.1×10^{-3}	2.4×10^{-5}
5	6710	0.0159±0.0011	106.7 ± 7.1	2.7×10^{-3}	4.2×10^{-5}
6	6470	0.0026±0.0001	17.2 ± 0.1	3.4×10^{-3}	9.0×10^{-6}

[a] Molar absorption coefficient ε_A [M^{-1} cm^{-1}], photolysis quantum yield Φ, photolytic efficiency $\varepsilon_A \times \Phi$ [M^{-1} cm^{-1}], specific rate of light absorption k_a ($k_a = I_a/c$; I_a – absorbed light intensity, c – concentration) [mol of photons/ (mol of cpd × s)], first-order rate constant k_p ($k_p = \Phi \times k_a$) [s^{-1}].

It is worth noting that the imaginary frequencies for the hydrogen abstraction process (ESHT) were well over 1500 cm^{-1} for all of the model compounds **1**, **2** / **4**, **6** / **3**, **5** bearing X = O / S / N, respectively (see Fig. 4 in the main text). Such high imaginary frequency strongly suggests that quantum tunneling is an important process in the photo-induced ESHT of the compounds presented herein.[3]

Because the high activation barrier of ESHT in *o*-nitrobenzenes allows efficient population transfer to the triplet state by intersystem crossing (ISC),[4] we have also calculated the magnitude of the spin-orbit coupling (SOC) for all three groups of model compounds bearing X = O / S / N (Fig. 4 in the main text). The SOC (S_1-T_2) was not influenced by the heteroatom significantly and had the same value (38 cm^{-1}) for all three groups. This is approximately half of the value reported for the simpler *o*-nitrotoluene derivatives.[4]

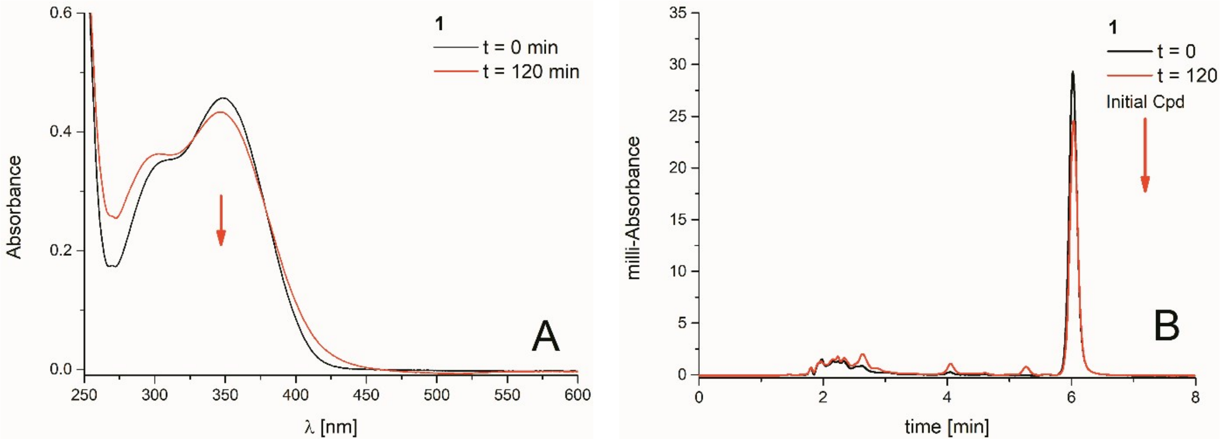


Figure S1. (A) UV–vis absorption spectral changes during photolysis of **1** (340 nm) in 50% CACO/DMSO and (B) corresponding HPLC trace.

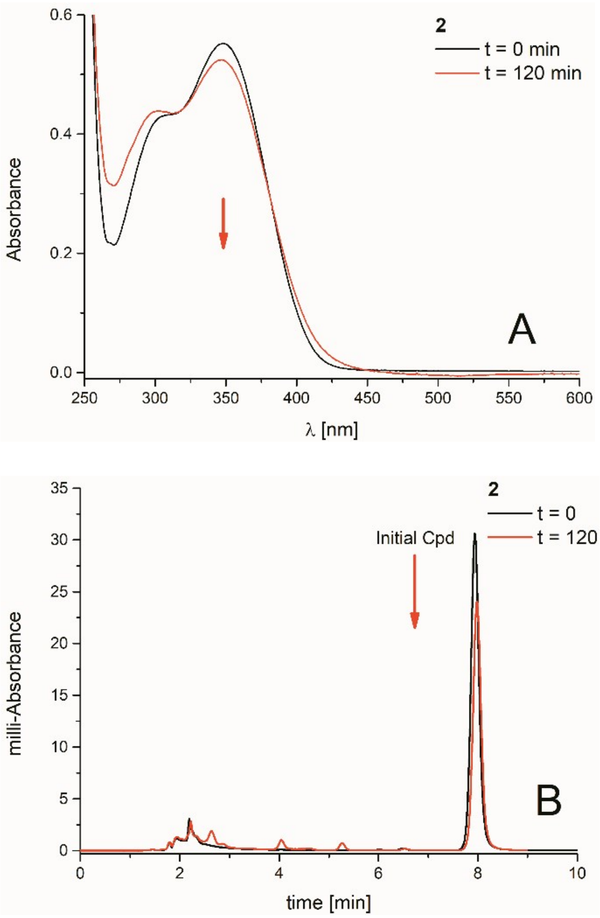


Figure S2. (A) UV–vis absorption spectral changes during photolysis of **2** (340 nm) in 50% CACO/DMSO and (B) corresponding HPLC trace.

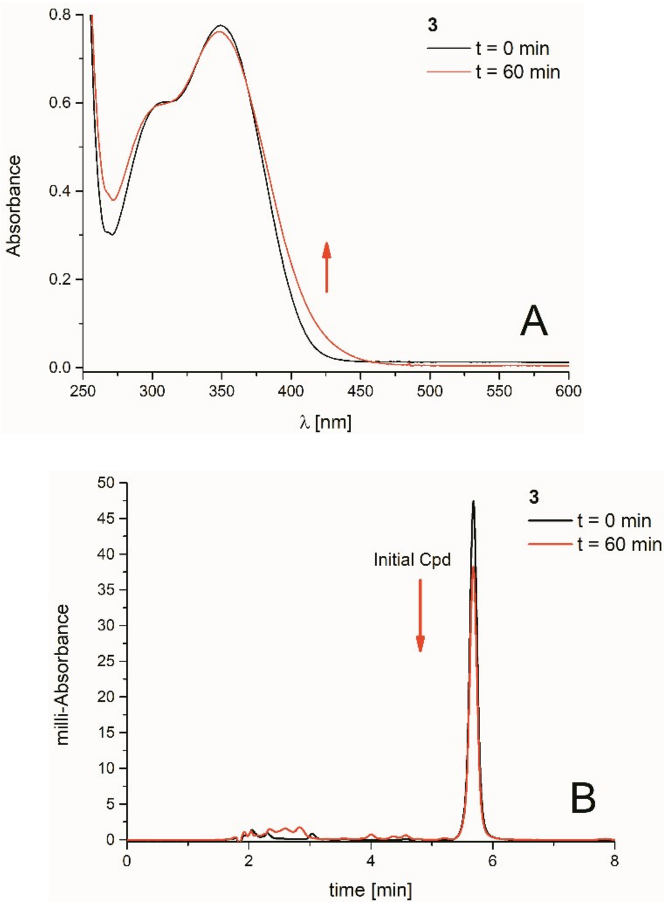


Figure S3. (A) UV–vis absorption spectral changes during photolysis of **3** (340 nm) in 50% CACO/DMSO and (B) corresponding HPLC trace.

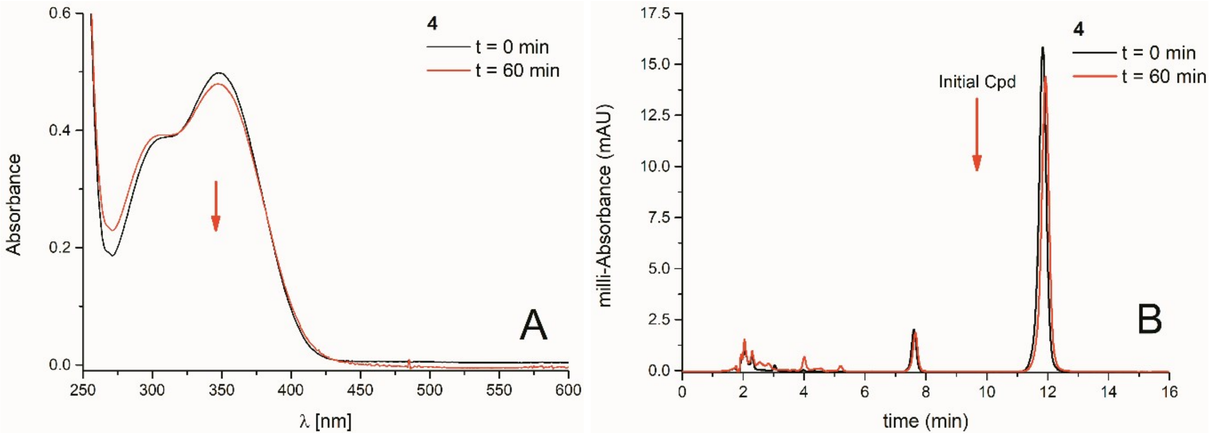


Figure S4. (A) UV–vis absorption spectral changes during photolysis of **4** (340 nm) in 50% CACO/DMSO and (B) corresponding HPLC trace.

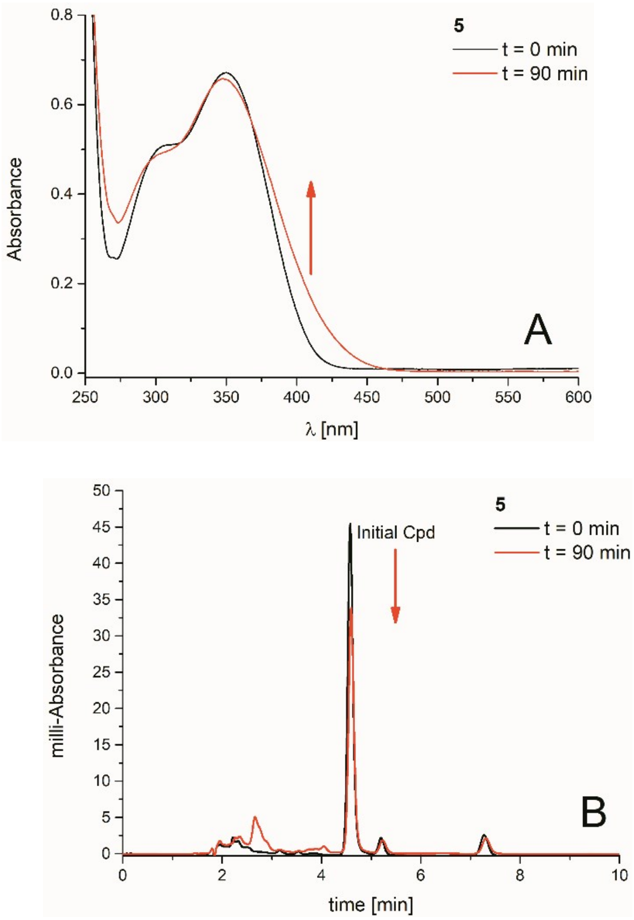


Figure S5. (A) UV–vis absorption spectral changes during photolysis of **5** (340 nm) in 50% CACO/DMSO and (B) corresponding HPLC trace.

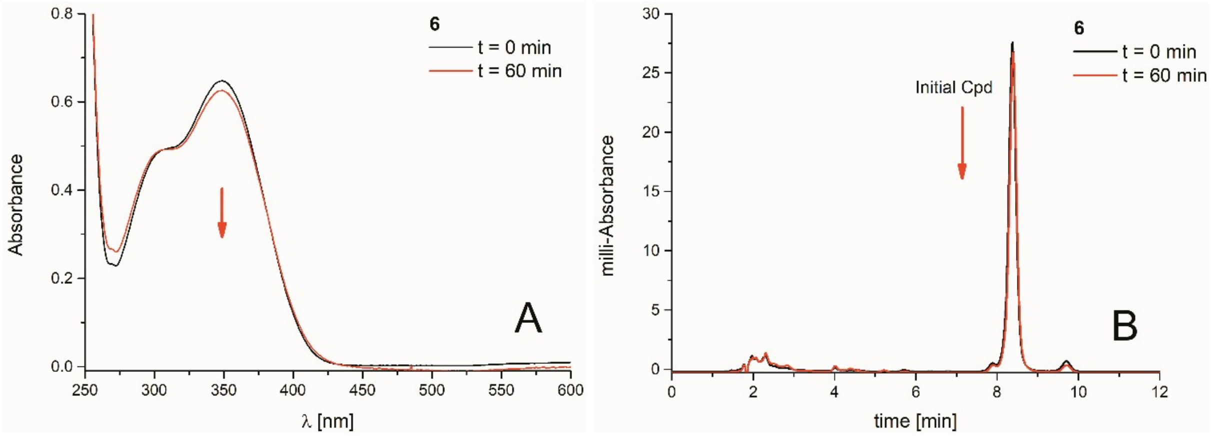


Figure S6. (A) UV–vis absorption spectral changes during photolysis of **6** (340 nm) in 50% CACO/DMSO and (B) corresponding HPLC trace.

3 NMR spectroscopy

General. All NMR irradiation experiments (including *in situ* or *ex situ* irradiation) were performed under previously optimized conditions[2] in the mixture of 1/1, Cacodylate buffer (CACO, pH 7.4, 0.1M)/DMSO-d_6, *v/v.*[2] We selected the sodium cacodylate (dimethyl arsinic acid sodium salt, CAS Number 6131-99-3) as an equivalent substitute for the phosphate buffer which could hinder important ^{31}P NMR signals. The ratio of solvent composition 50% CACO/DMSO-d_6 was also optimized before to balance sample solubility, photo-activation and self-immolation reaction rates.[2] For the *in situ* and *ex situ* irradiation experiments we used 0.5 mM and 5 mM sample concentration, respectively.

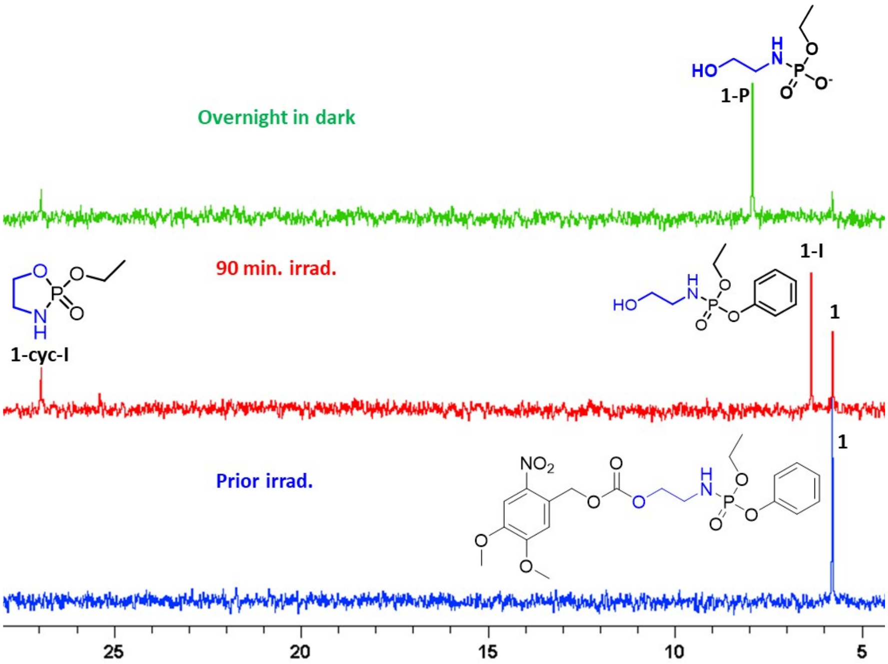


Figure S7. A series of ^{31}P NMR spectra after photoactivation of compound **1** (δ_P 5.8 ppm) into the intermediate **1**-**I** (6.33 ppm), through cyclic intermediate **1**-**cyc**-**I** (26.9 ppm). The final product **1**-**P** with ^{31}P chemical shift 7.9 ppm was detected overnight.

To confirm the structure of the cyclic intermediates, we performed irradiation experiment at higher concentration (5 mM, ex situ irradiation) and the same reaction pathway was found (Figure S8). The first traces of the cyclic intermediate **1**-**cyc**-**I** (δ_P 26.9 ppm) were obtained after 10 min. of *ex situ* irradiation. We irradiated longer (30 min.) to accumulate sufficient amount of **1**-**cyc**-**I** for recording high-quality ^{13}C spectra in order to assign ^{13}C signals and the corresponding interaction constants with phosphorus atom $^2J_{CP}$ (Figure S9). The experimentally obtained *J*-couplings in the cyclic forms were significantly different from the values found in the acyclic intermediates and the final product. They were in a good agreement with the DFT calculated values (Table S1).

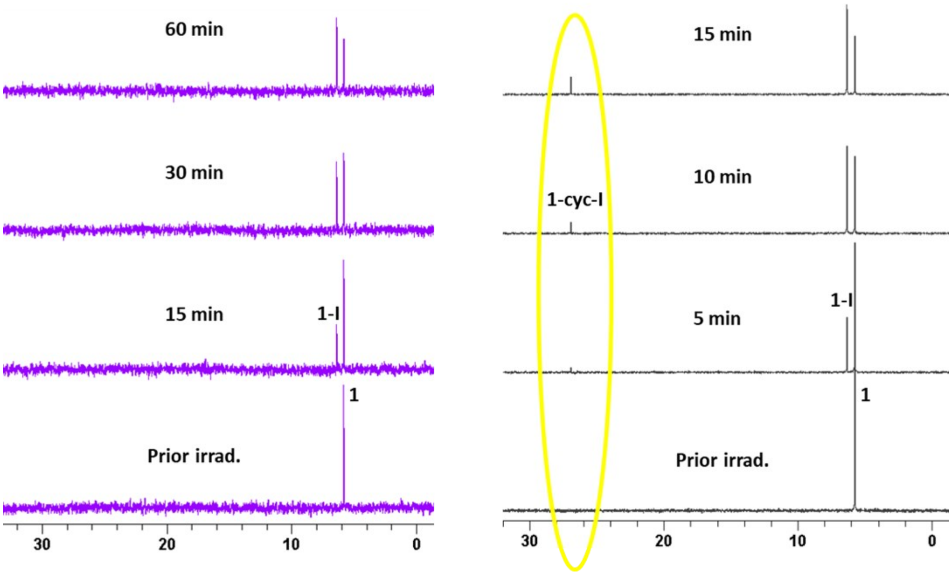


Figure S8. A series of ^{31}P NMR spectra of compound **1** measured during *in situ* (left) and after *ex situ* (right) irradiation by UV light (365 nm). The 0.5 mM (left) and 5 mM (right) concentration of compound **1** was used in 400 µL of a solvent mixture 50% CACO/DMSO-d_6 at room temperature (25 °C).

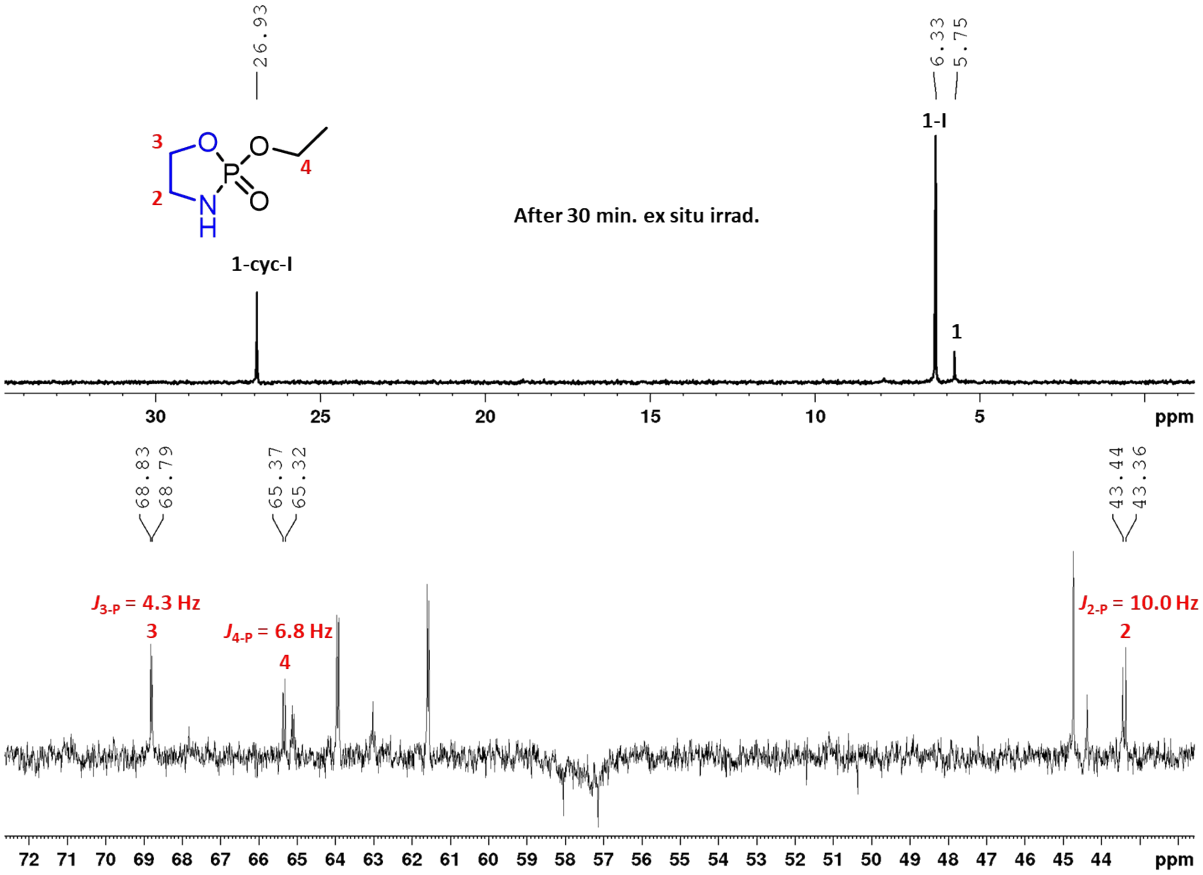


Figure S9. NMR signal assignment of the cyclic intermediate **1-cyc-I** prepared by *ex situ* irradiation (365 nm, 30 min.) of **1** (5 mM) in 50% CACO/DMSO-d_6. ^{31}P NMR spectrum recorded after 30 min. of *ex situ* irradiation (top). A part of aliphatic region of ^{13}C APT spectrum with the assignment of the signals corresponding to the cyclic intermediate **1-cyc-I** (bottom).

The photoactivated intermediate **2-I** (δ_P –6.1 ppm) is spontaneously converted into the intermediate (δ_P 18.1 ppm) consequently slowly transformed (within an hour) into the stable final product **2-P** (δ_P 0.01 ppm). To collect high-quality ^{13}C spectra for structure determination, we irradiated higher initial concentration of **2** (5 mM) in 50% CACO/DMSO-d_6 *ex situ*. We followed the same reaction pathway, however, new signal at 17.6 ppm appeared and did not change at all. To characterize both stable products with δ_P 17.6 and 0.01 ppm, we prepared a mixture of them by 40-min *ex situ* irradiation of **2** (Figure S10–11) and collected ^{13}C spectrum from this mixture. Although the 0-ppm signal may indicate release of free phosphate, ^{13}C spectra clearly revealed the structure of the desired final product **2-P**. All four carbon signals, three O-CH$_2$ groups above 60 ppm and CH$_3$ group below 20 ppm, are split by the spin-spin interaction ($J_{C\text{-}P}$) with phosphorus atom (Figure S11). The aromatic signals are not split, which clearly indicates that phenol released. The ^{31}P chemical shift 17.6 ppm indicates a cyclic structure **2-cyc-P** as is close to the published value of 17 ppm found in cyclic intermediates.[5] Furthermore, this product provided only one doublet ^{13}C signal at 66.0 ppm, indicating O-CH_2 group attached to the phosphorus core and points out a symmetrical molecule when providing just one ^{13}C signal. It also corresponds to the traces of ethanol found in ^{1}H spectra. The significantly different molecular geometry became evident as an enormous change in $^{2}J_{C\text{-}P}$ coupling. While in the final product the interaction constant $^{2}J_{C2\text{-}P}$ is 5.6 Hz, the cyclic product displayed $J_{C\text{-}P}$ 1.8 Hz.

The second unusually high chemical shift at 18.1 ppm might correspond to the cyclic intermediate **2-cyc-I**, where the ethyl group is still attached. It was not possible to determine the structure *in situ* as this compound is not a major component in the reaction mixture. However, from the 18.1 ppm signal, the final stable product at 0 ppm is formed, as visible in a series of *in situ* irradiation experiments. Based on the ^{31}P chemical shift very close to the cyclic product (17.6 ppm), we concluded that there must be only a small structural change compared to **2-cyc-P**, such as a presence of ethyl substituent. This hypothesis was confirmed by DFT calculations (Table S2).

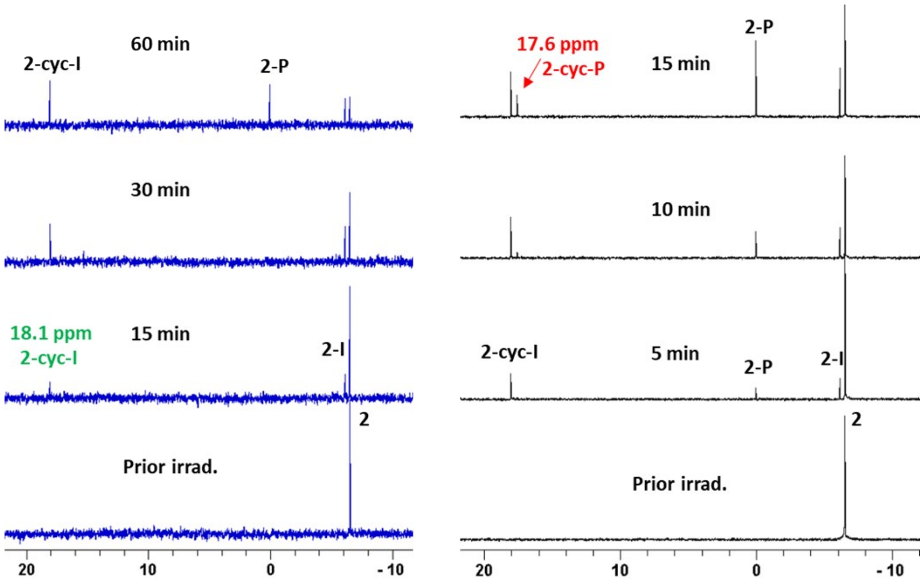


Figure S10. A series of ^{31}P NMR spectra of compound **2** measured during *in situ* (left) and after *ex situ* (right) irradiation by UV light (365 nm). 0.5 mM (*in situ*, left) and 5 mM (*ex situ*, right) concentration of compound **2** was used in 400 µL of a solvent mixture 50% CACO/DMSO-d_6 at room temperature (25 °C).

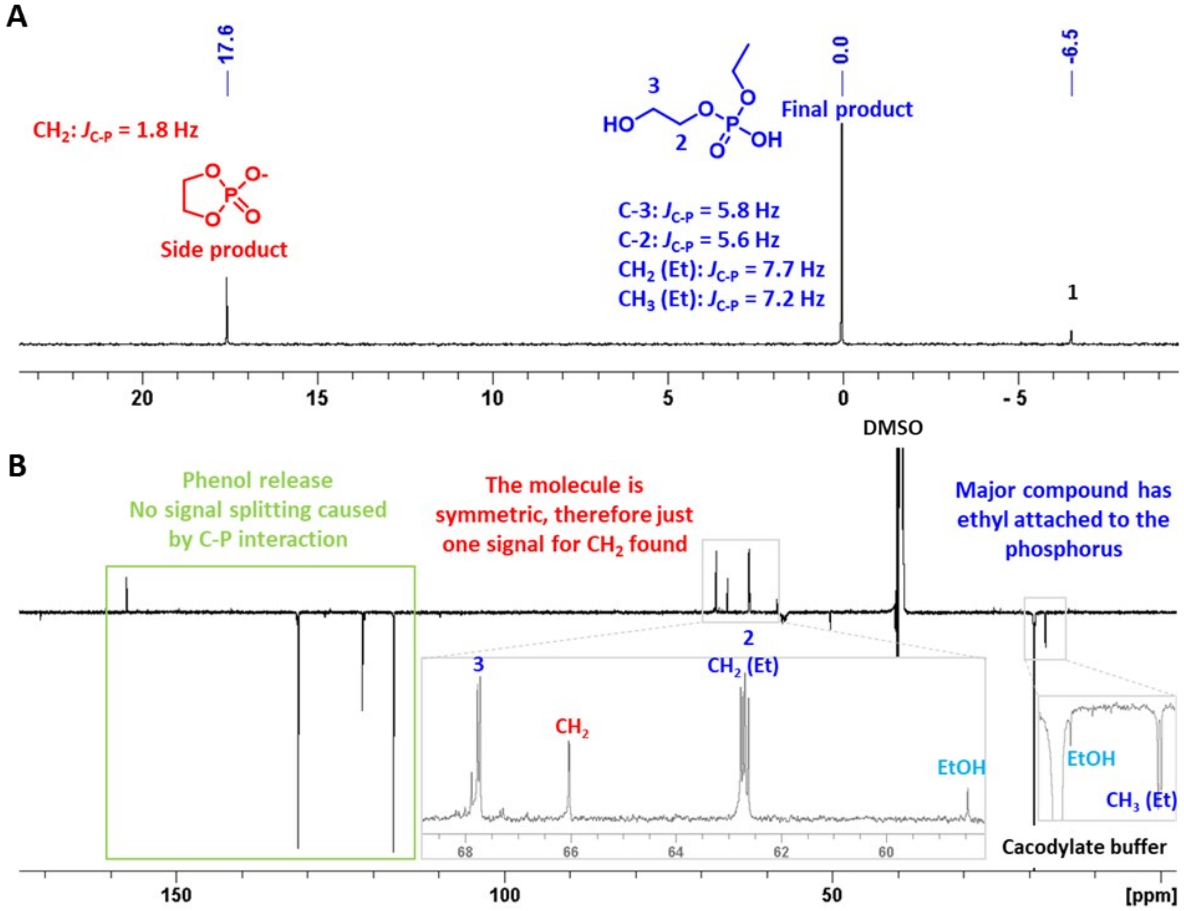
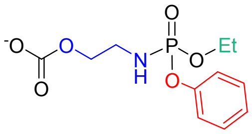
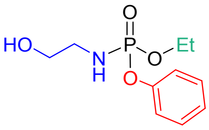
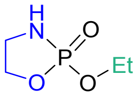
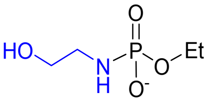
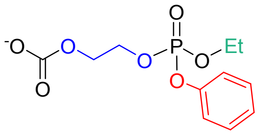
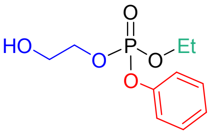
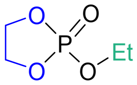
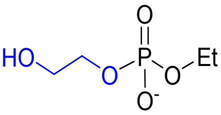
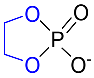


Figure S11. NMR signal assignment of the two stable products **2**-**cyc**-**P** and **2**-**P** (17.6 and 0.01 ppm, respectively) formed by *ex situ* irradiation (365 nm, 40 minutes) of derivative **2** (5 mM) in 50% cacodylate buffer in DMSO-d_6. (A) ^{31}P NMR spectrum recorded after 40 minutes of *ex situ* irradiation. (B) ^{13}C APT spectra of the same sample from which the ^{31}P spectrum was recorded. Phenol and traces of ethanol have been found as another two side-products not detectable in ^{31}P spectrum.

Table S2. Experimental and theoretical (B3LYP/IGLO-III/PCM=water) ^{31}P chemical shifts and ^{2}J-couplings (C-P) of the products of the SI process of compounds **1** and **2**. Chemical shifts in ppm, couplings in Hz.

Compound	**Structure**	δ_{exp}	δ_{calc}	$^{2}J_{CP,exp}$	$^{2}J_{CP,calc}$
Not observed experimentally		-	2.2	-	
1-I		6.3	6.6	0	-
1-cyc-I		26.9	29.4	10	12
1-P		7.9	10.9	0	-
Not observed		-	−9.5	-	
2-I		−6.1	−4.8	0	
2-cyc-I		18.1	21.3	0	-
2-P		0.01	3.5	(−)5.6	−8.0
2-cyc-P		17.6	21.8	1.8	2.0

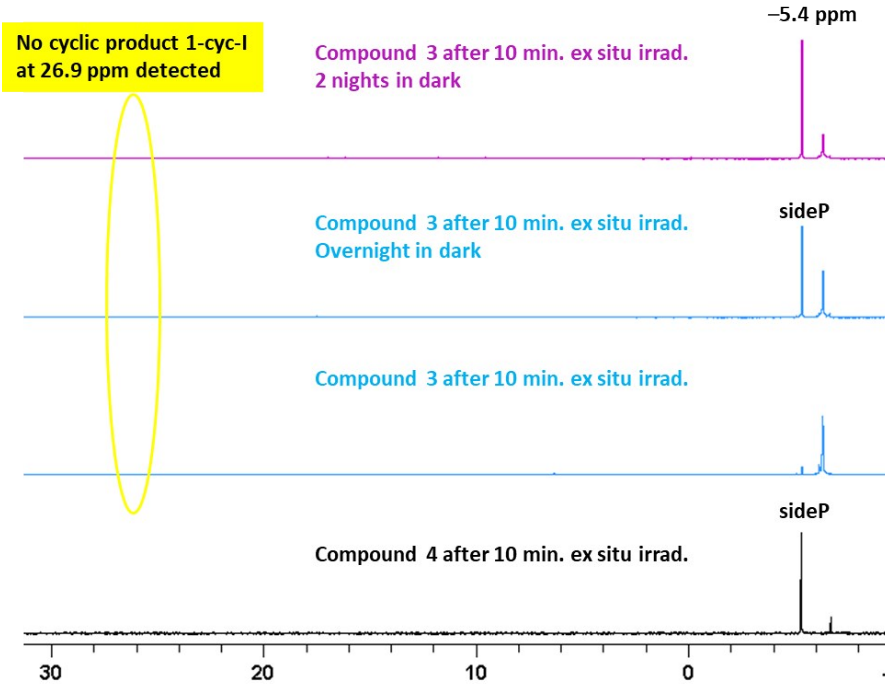


Figure S12. A comparison of the ^{31}P NMR spectra of compounds **3** and **4** after 10 min. of *ex situ* irradiation (365 nm). The same undesired final product **sideP** with δ_P –5.4 ppm was detected in both cases. Cyclization of **3**-**I** should lead to **1**-**cyc**-**I** with δ_P 26.9 ppm.

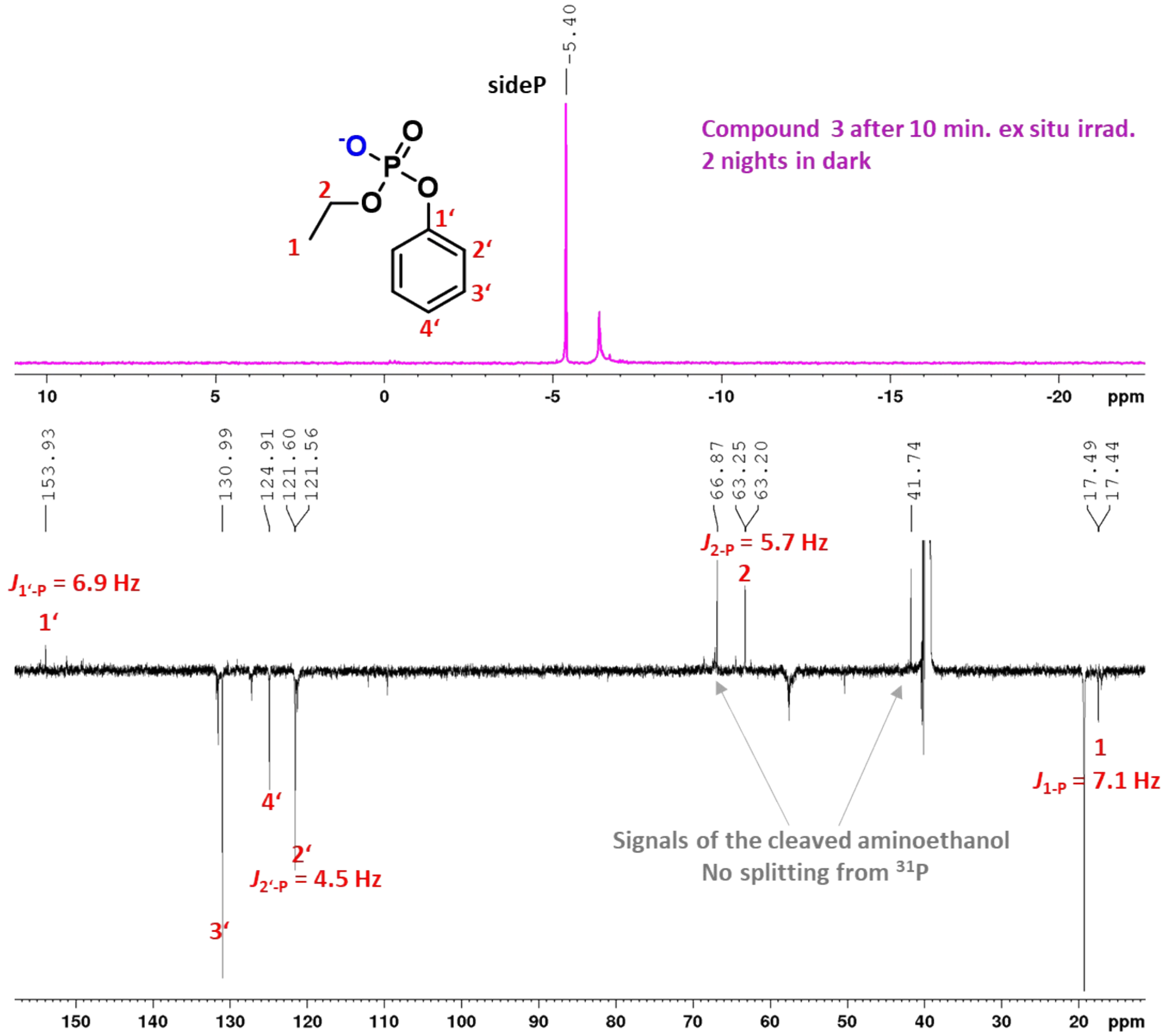


Figure S13. NMR signal assignment of the side product **sideP** formed after 10 min. of *ex situ* irradiation of compound **3** (5 mM) in 50% CACO/ DMSO-d_6.

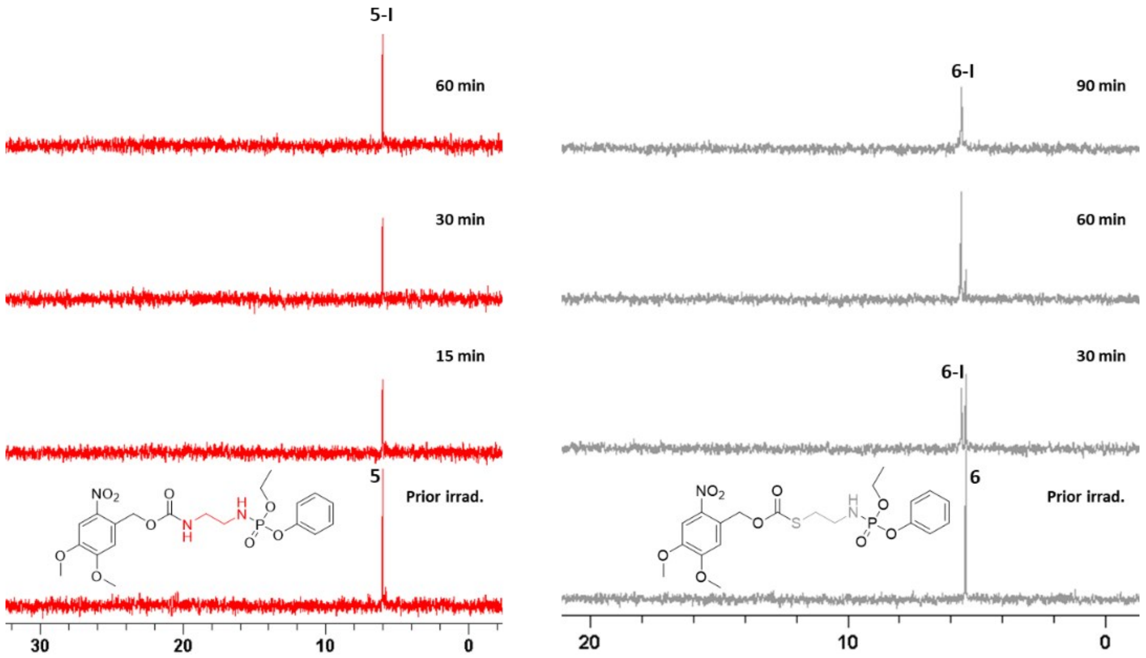


Figure S14. A series of ^{31}P NMR spectra of compounds **5** (left) and **6** (right) measured during *in situ* irradiation by UV light (365 nm). The 0.5 mM concentration was used in 400 µL of a solvent mixture 50% CACO/DMSO-d_6 at room temperature (25 °C). Both compounds yielded stable intermediates **5-I** and **6-I**, respectively.

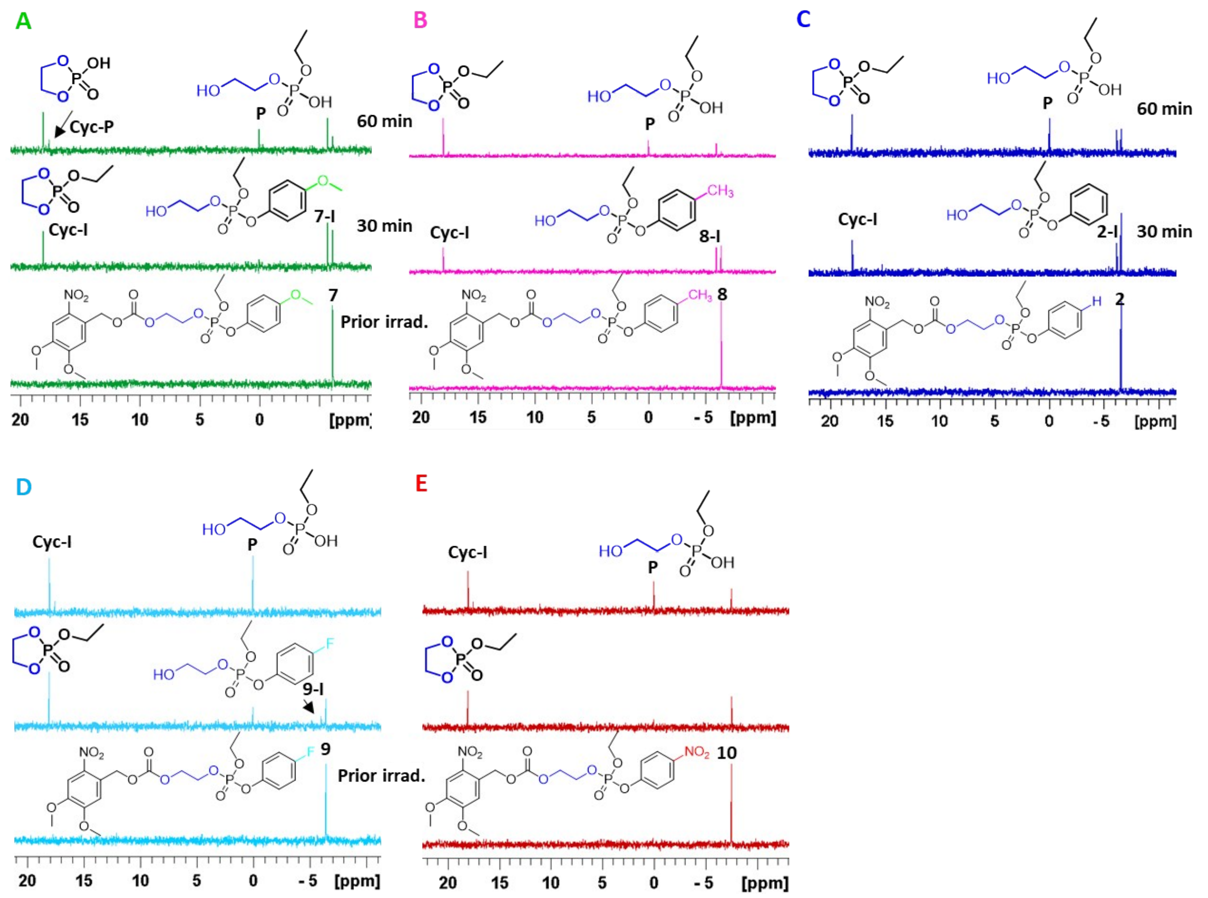


Figure S15. A series of ^{31}P NMR spectra of compounds **7**–**10** measured as 0.5 mM solutions in 50% CACO/DMSO at room temperature. The data to compound **2** (C) are added as a standard for direct comparison.

To emphasize the importance of sufficiently low electron density of the attacked phosphorus atom, we also studied structural analogue of **2**, compound **11**, where phenol as a good leaving group was substituted by ethyl (Figure S16). Compound **11** is cleaved off immediately after photoactivation process and no **2-cyc-I** was detected. Only traces of diethyl phosphate were found overnight. The linker self-cleavage can be explained by the fact that ethylene glycol spacer has slightly lower pK_a than ethanol (pK_a 15.1 *vs* 15.9, respectively), hence, is a better leaving group.

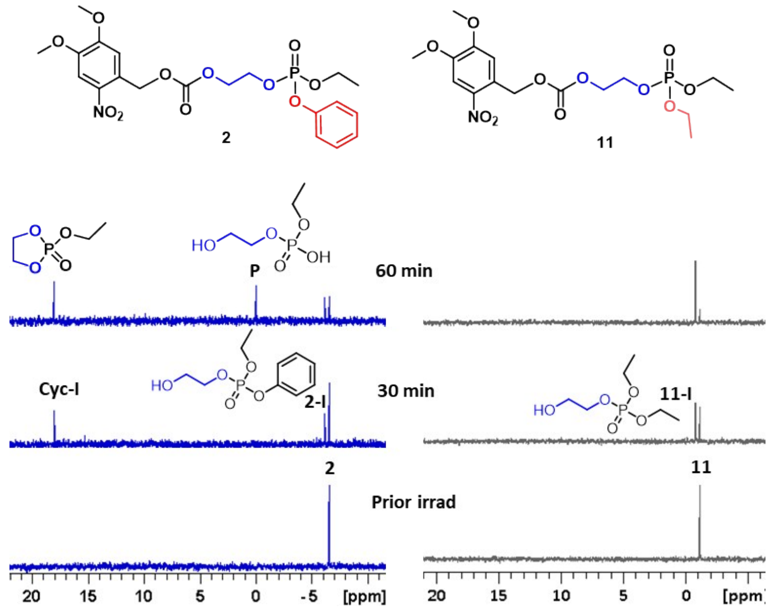


Figure S16. A series of ^{31}P NMR spectra of compounds **2** (left) and **11** (right) measured as 0.5 mM solutions in 50% CACO/DMSO at room temperature. No cyclic intermediate **cyc-I** was found after photoactivation of **11**.

4 DFT Calculations

Photochemical activation

The DFT and TD-DFT calculations were performed with Gaussian 16[6] and Orca 4.2.1[7] electronic-structure program packages. Geometry optimization of minima and the transition states involved for ground states as well as for the excited states were performed at M062X level of theory and 6-31G(d) basis set. All the calculations were performed in vacuo. Frequency calculations were performed on the minima in order to ascertain the type of stationary point as well as to obtain zero-point vibrational energies. Thermodynamic properties were calculated at 298 Kelvin. A quasiharmonic correction was applied during the entropy calculation by setting all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}.[8] Transition state geometries were optimized using the same method, verifying each time that only one imaginary vibrational frequency is present in the transition state. IRC calculations were used to check whether the transition states connected the desired energy minima. Single point energy calculations were done using M062X level of theory and 6-311+G(d,p) basis set. Spin-orbit coupling between S1-T2 and S1-T1 was calculated using Orca program package. Corresponding spin-orbit matrix elements were evaluated as the parameter influencing the rate of intersystem crossing.

The reaction mechanism of self-immolation process

The lowest energy conformers of **1-I**, **2-I**, **1-I-O$^-$** and **2-I-O$^-$** were used as starting structures. The reaction coordinate was constructed by first approaching the P atom by linker's terminal O^- to reach **I1** via **TS1** and then pulling the P–OPh bond to reach **cyc-P** via **TS2**, see Fig. 5 in manuscript. All minima and transition states were confirmed via calculations of harmonic vibrational modes. The B3LYP density functional together with def2TZVP basis set were as implemented in Gaussian 16[9] code were used. The SI process in **1** and **2** requires nucleofilic attack of terminal alcoholate. The formation of alcoholate from I–OH presents an energy penalty for deprotonation, that can be evaluated as 1.3*pKa (in kcal/mol). Free energy of deprotonation, ΔGdeprot(AH), was calculated as:

ΔGdeprot(AH) = G(A-) + G(H3O+) – G(AH) – G(H2O)

In order to minimize the error, a free energy of deprotonation of ethylene glycole (with known pK_a of 15.1) was used as a reference for obtaining pK_a estimates of S1 and S2. For $\Delta G_{deprot}(AH)$ obtained in kcal/mol this leads to:

$$pKa\ (AH) = \frac{\Delta G(AH) - \Delta G(ethylenglycole)}{1.365} + 15.1$$

This led to estimates of pK_a (**1**) = 20.4 and pK_a (**2**) = 15.2. Free energy of a species was calculated using was calculated using COSMO-RS [6,9] method (conductor-like screening model for realistic solvation) as implemented in COSMOthermX19, employing “BP_TZVPD_FINE_19.ctd” parametrization file, FINE cavities ($cosmo_isorad keyword) with ε_r = ∞ (ideal conductor). The underlying input files were obtained using Becke-Perdew 86 (BP86) exchange-correlation functional[7,8] with def2-TZVPD[10,11] basis set and the D3 empirical dispersion correction with zero-damping as implemented in TurboMole 7.4 program suite.[12]

The calculations of NMR parameters

Only the lowest energy isomers/conformers were evaluated to identify observed compounds. The methods were selected following previous experience,[13] in which the B3LYP density functional with IGLO-III basis set was found to perform well for ^{31}P NMR parameters.

5 Compound characterization: ^{1}H, ^{13}C and ^{31}P NMR spectra

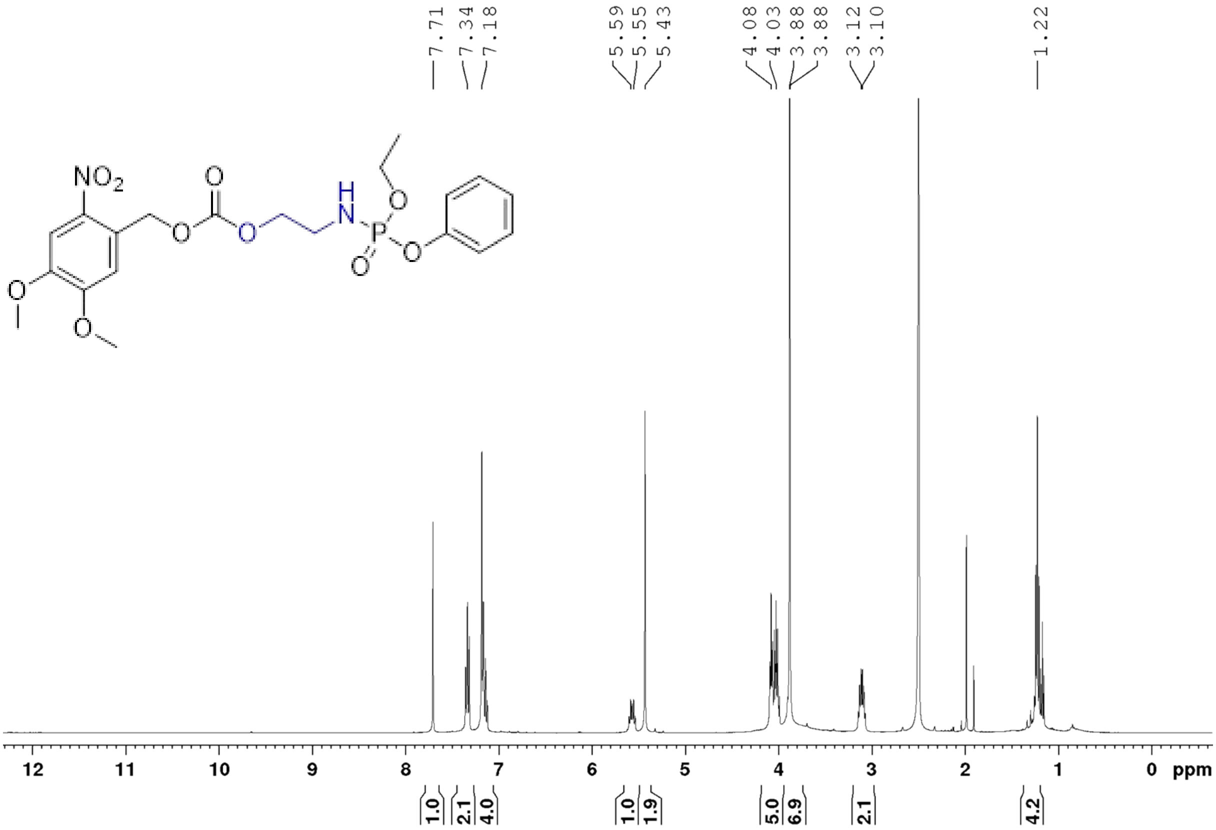


Figure SX. ^{1}H spectrum of **1** in DMSO-d_6 measured at room temperature.

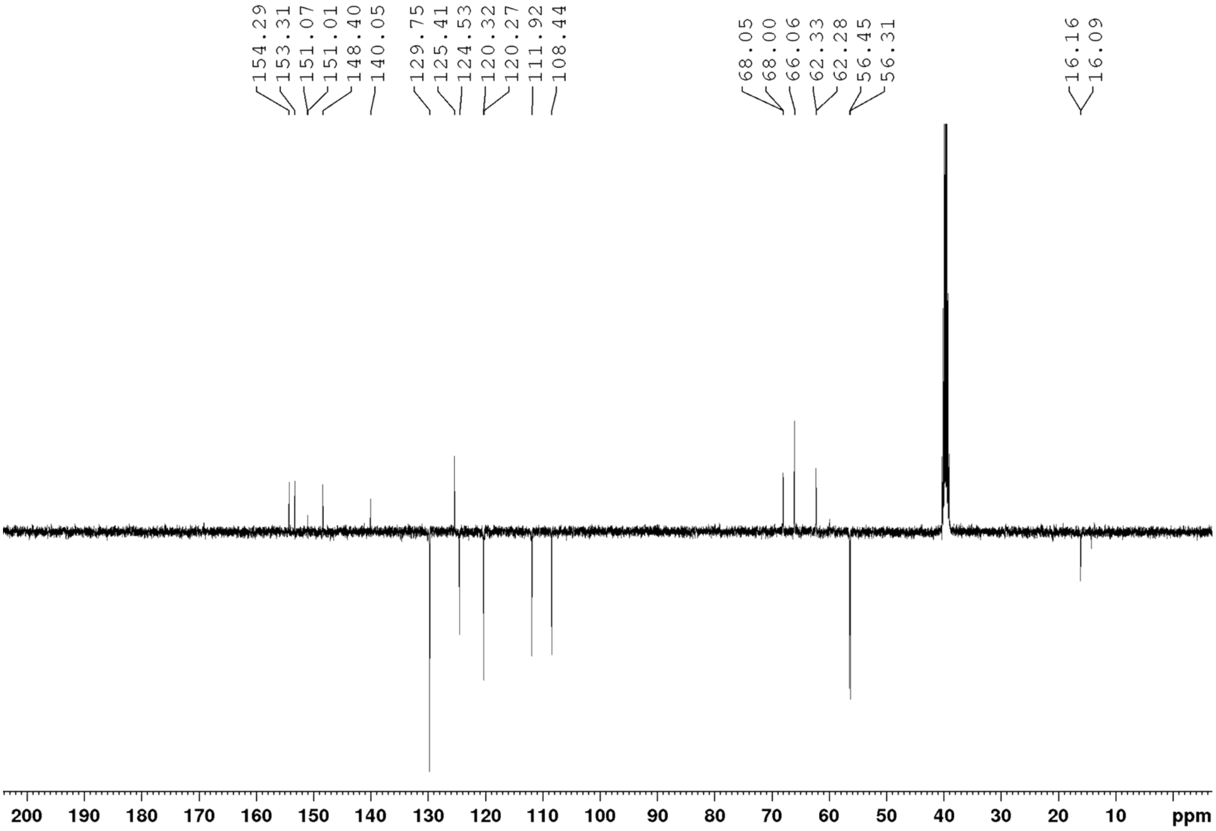


Figure SX. ^{13}C APT spectrum of **1** in DMSO-d_6 measured at room temperature.

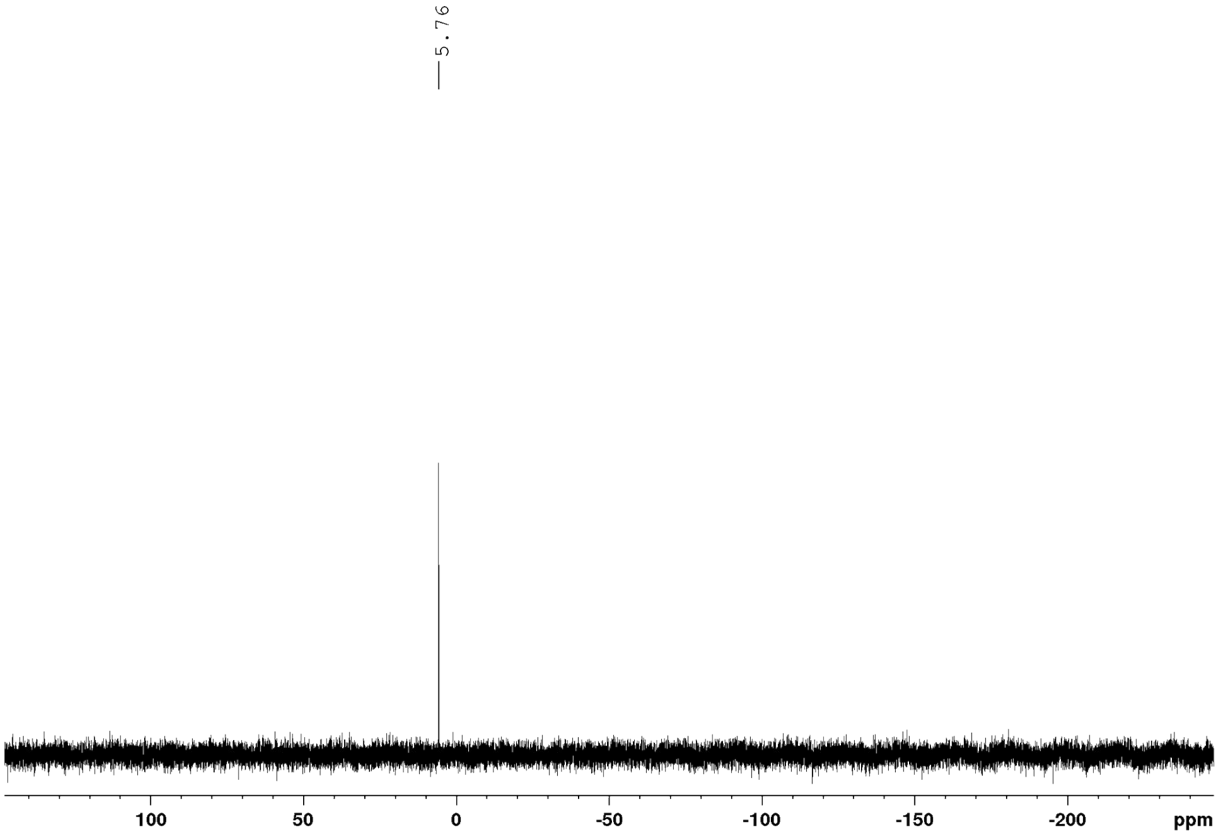


Figure SX. ^{31}P spectrum of **1** in 50% CACO/DMSO-d_6 measured at room temperature.

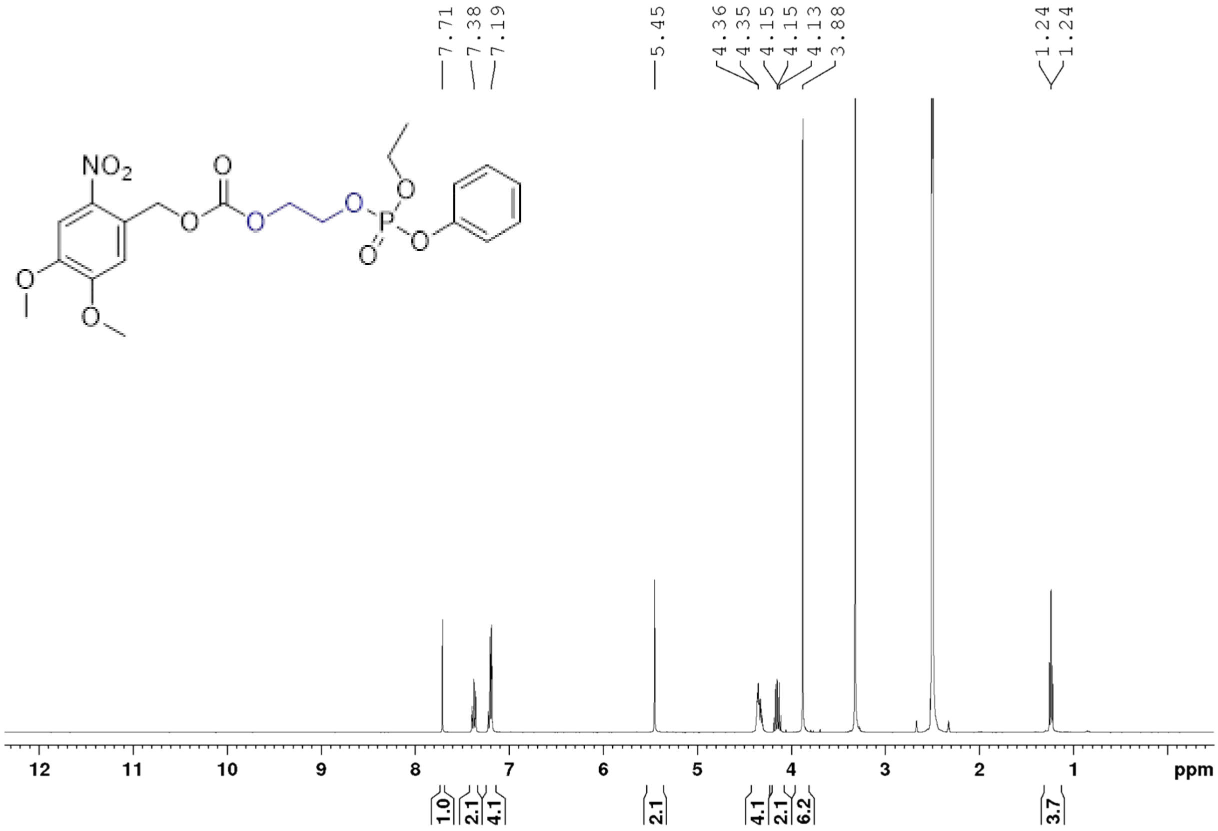


Figure SX. ^{1}H spectrum of **2** in DMSO-d_6 measured at room temperature.

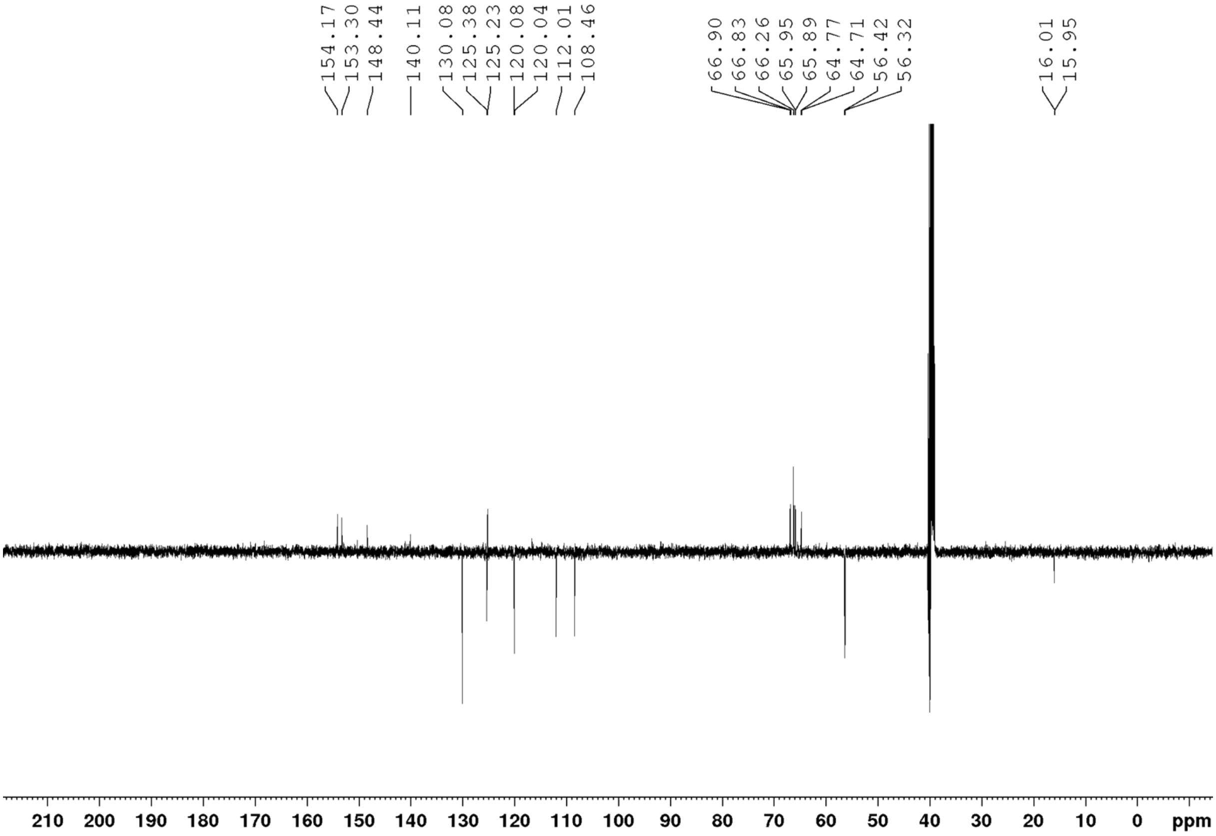


Figure SX. ^{13}C APT spectrum of **2** in DMSO-*d*$_6$ measured at room temperature.

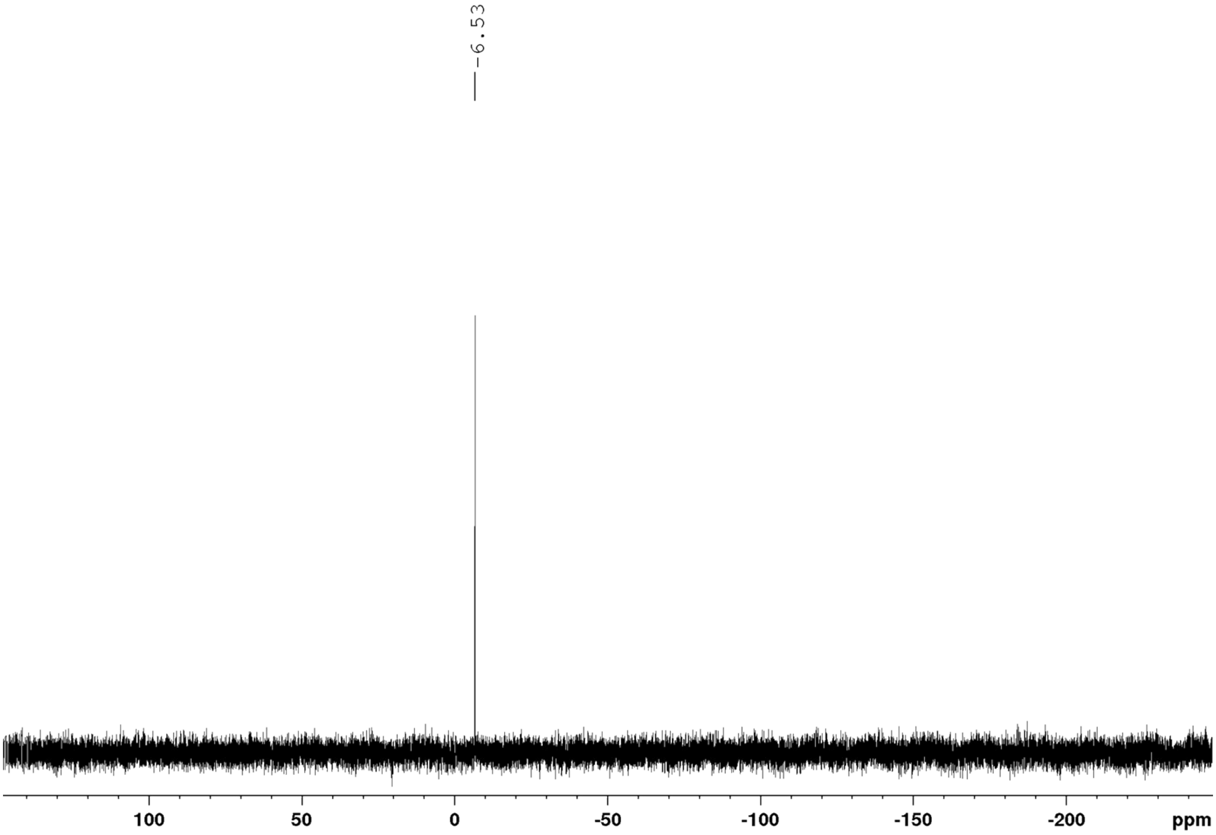


Figure SX. ^{31}P spectrum of **2** in 50% CACO/DMSO-*d*$_6$ measured at room temperature.

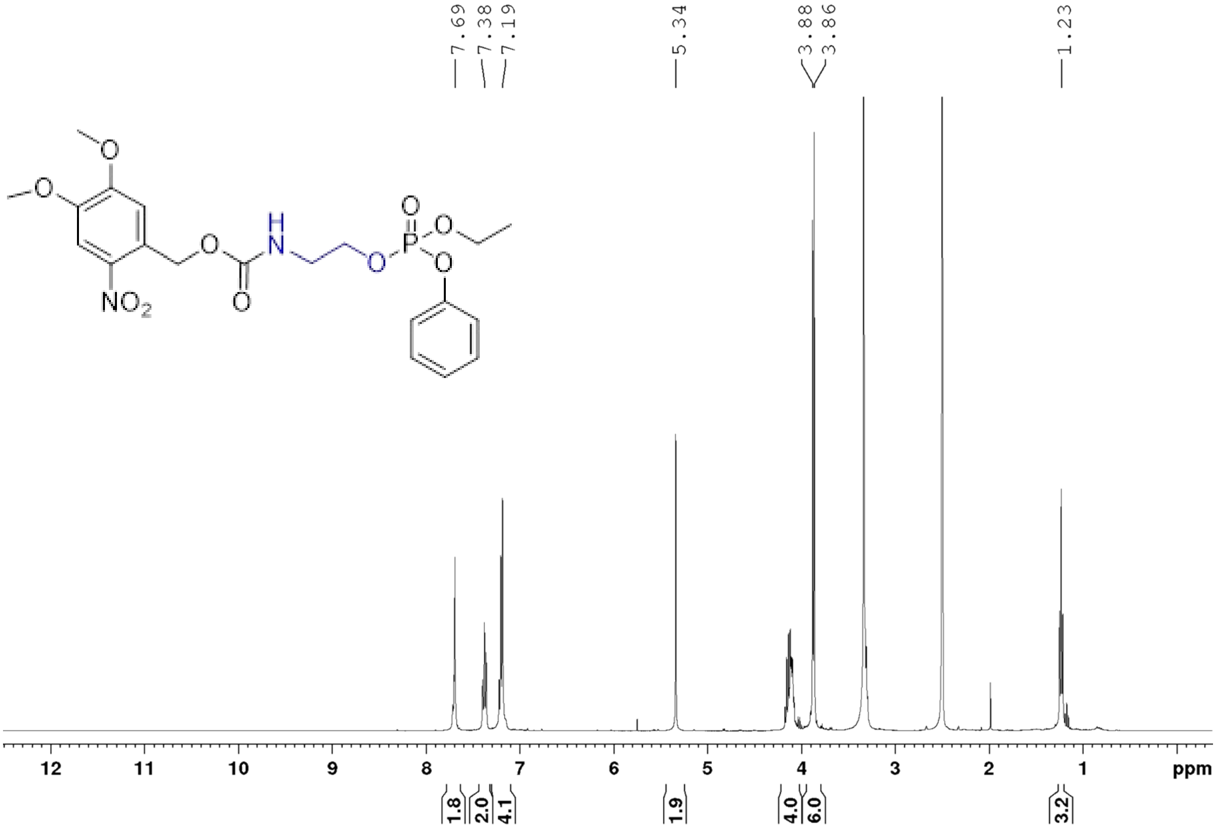


Figure SX. ^{1}H spectrum of **3** in DMSO-d_6 measured at room temperature.

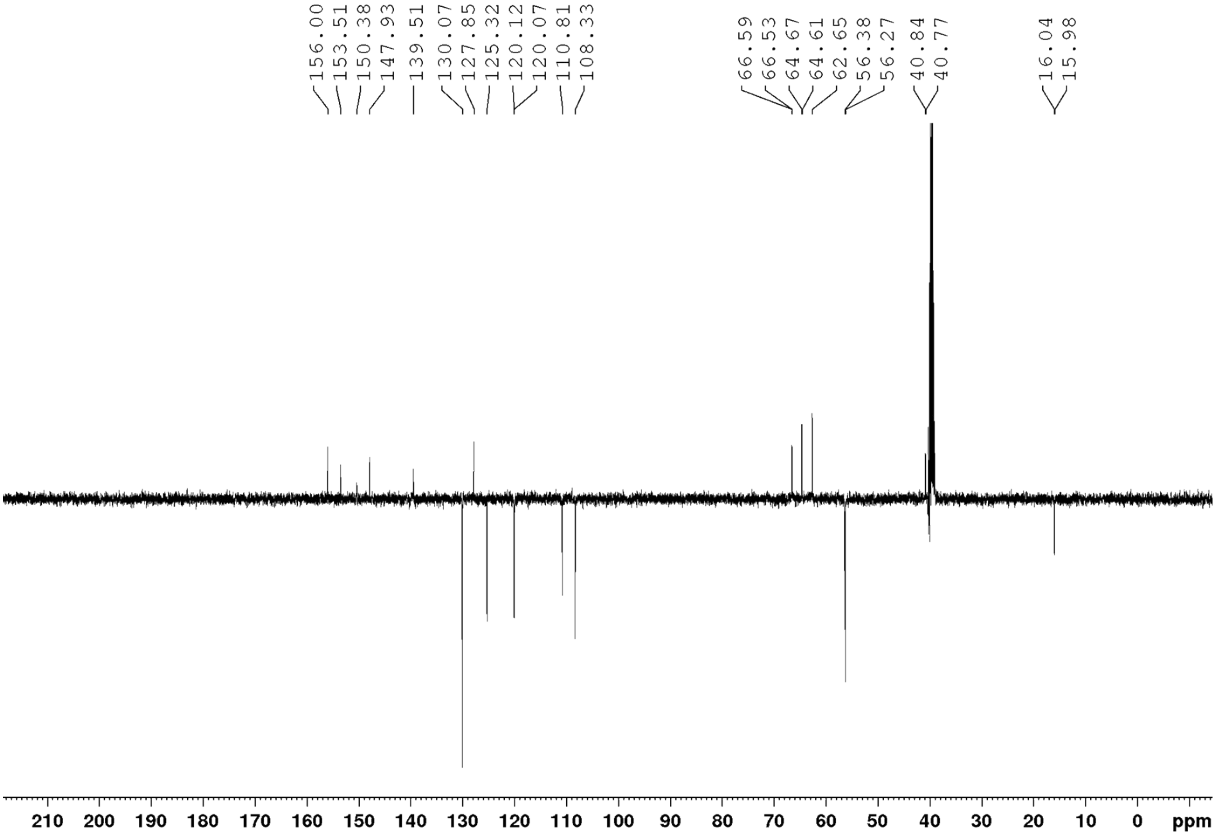


Figure SX. ^{13}C APT spectrum of **3** in DMSO-d_6 measured at room temperature.

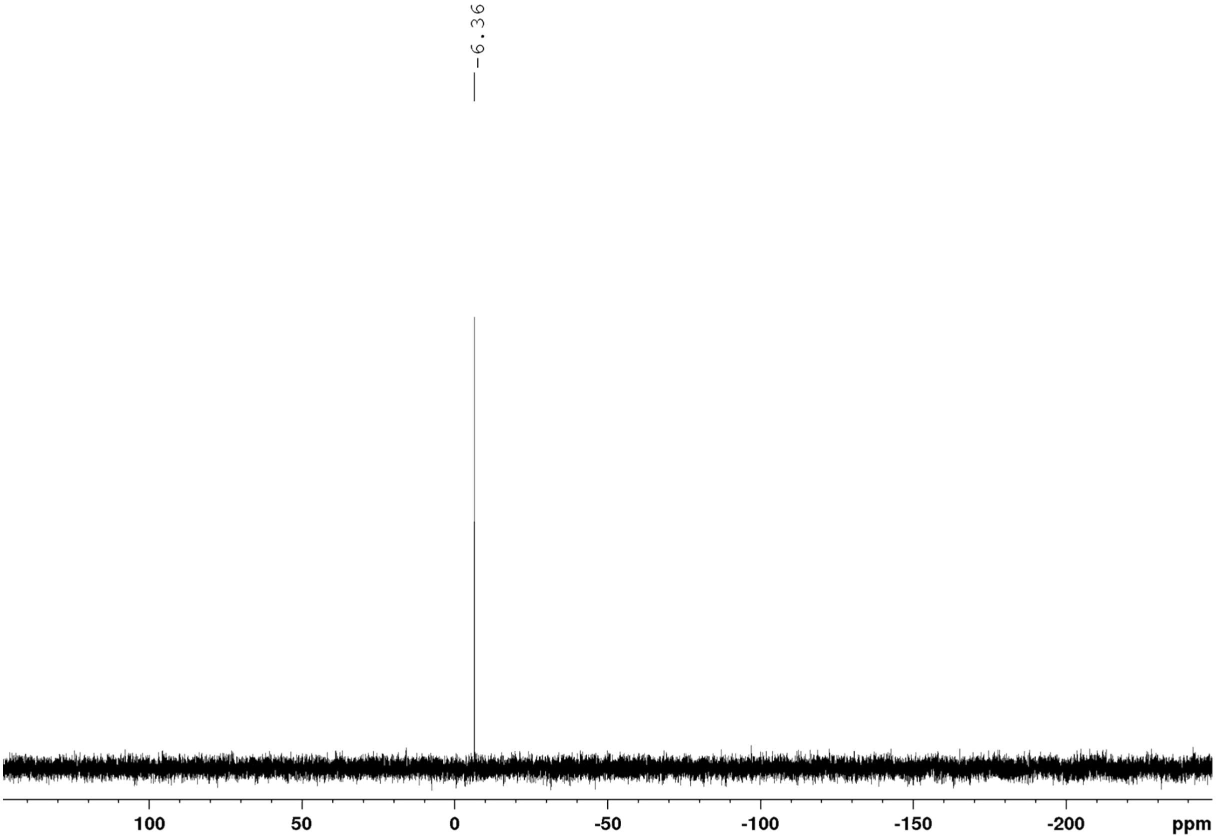


Figure SX. ^{31}P spectrum of **3** in 50% CACO/DMSO-d_6 measured at room temperature.

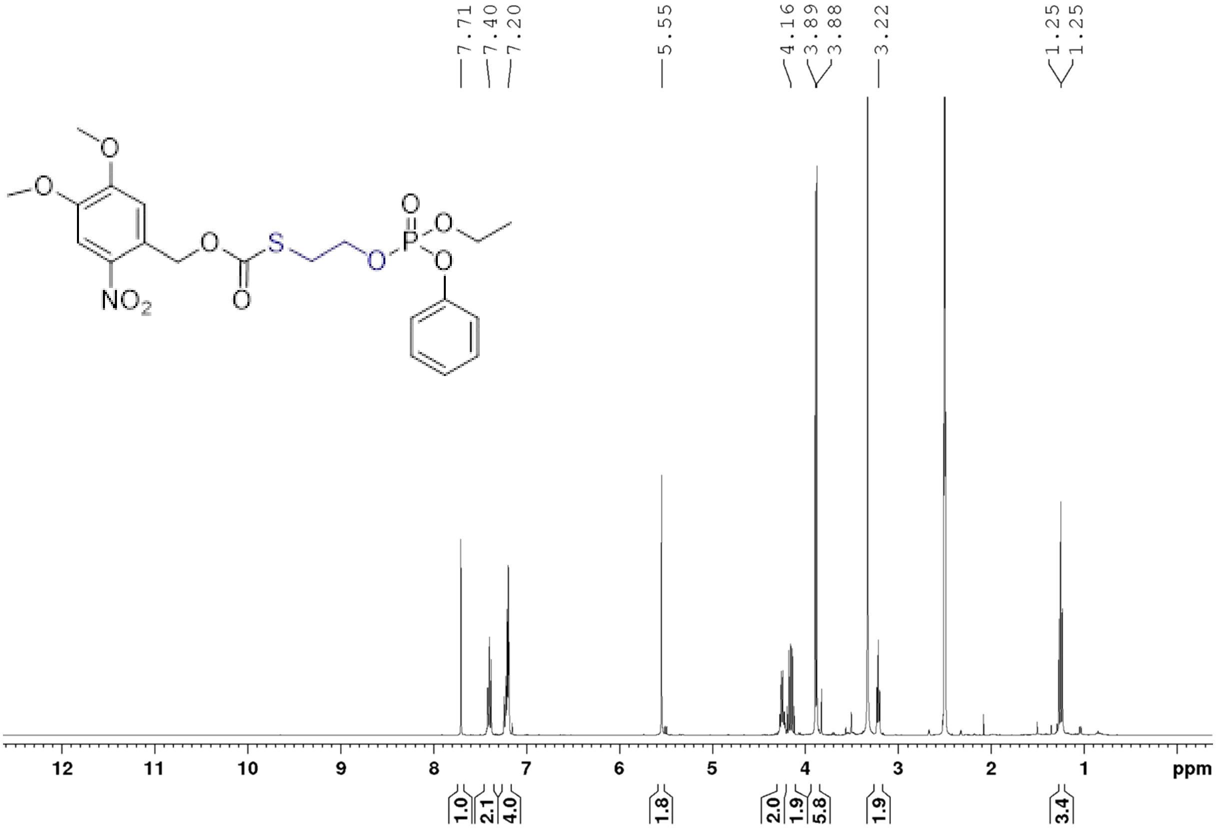


Figure SX. ^1H spectrum of **4** in DMSO-d_6 measured at room temperature.

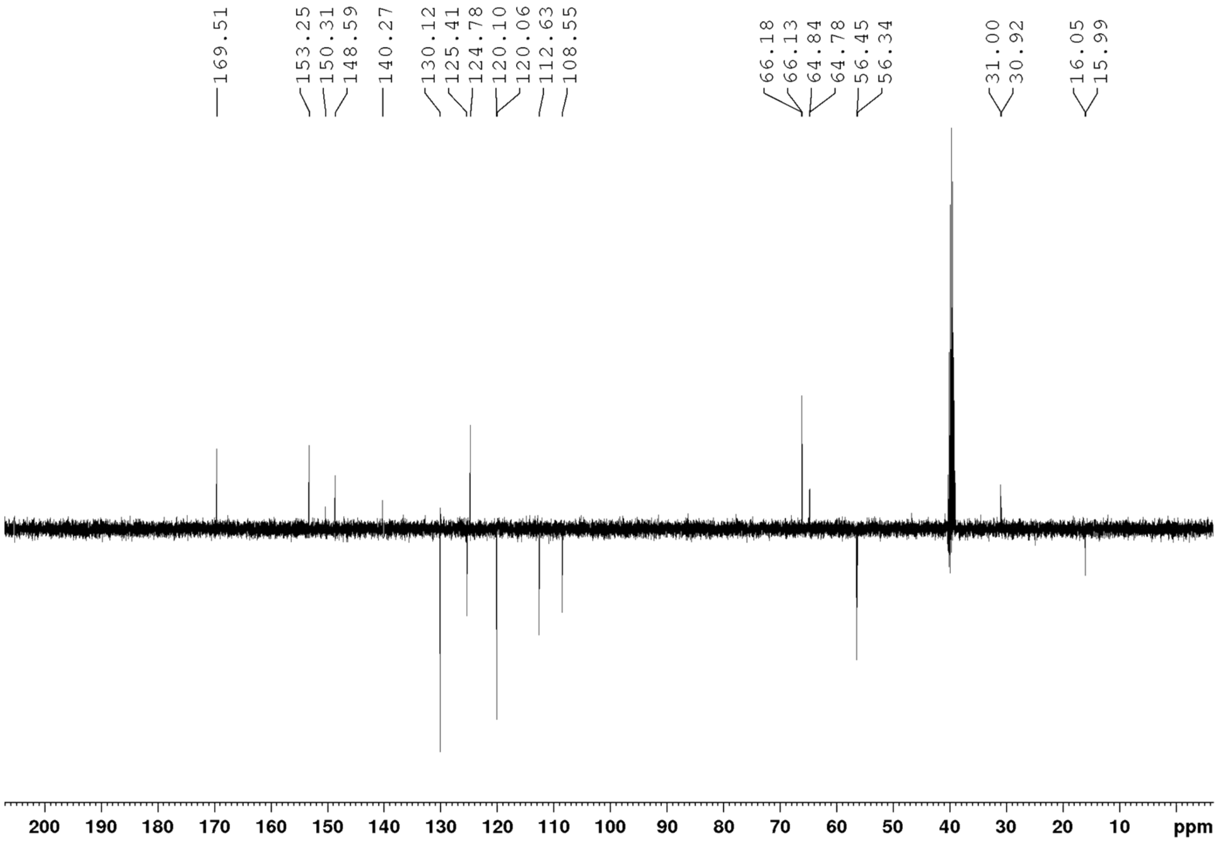


Figure SX. ^{13}C APT spectrum of **4** in DMSO-*d₆* measured at room temperature.

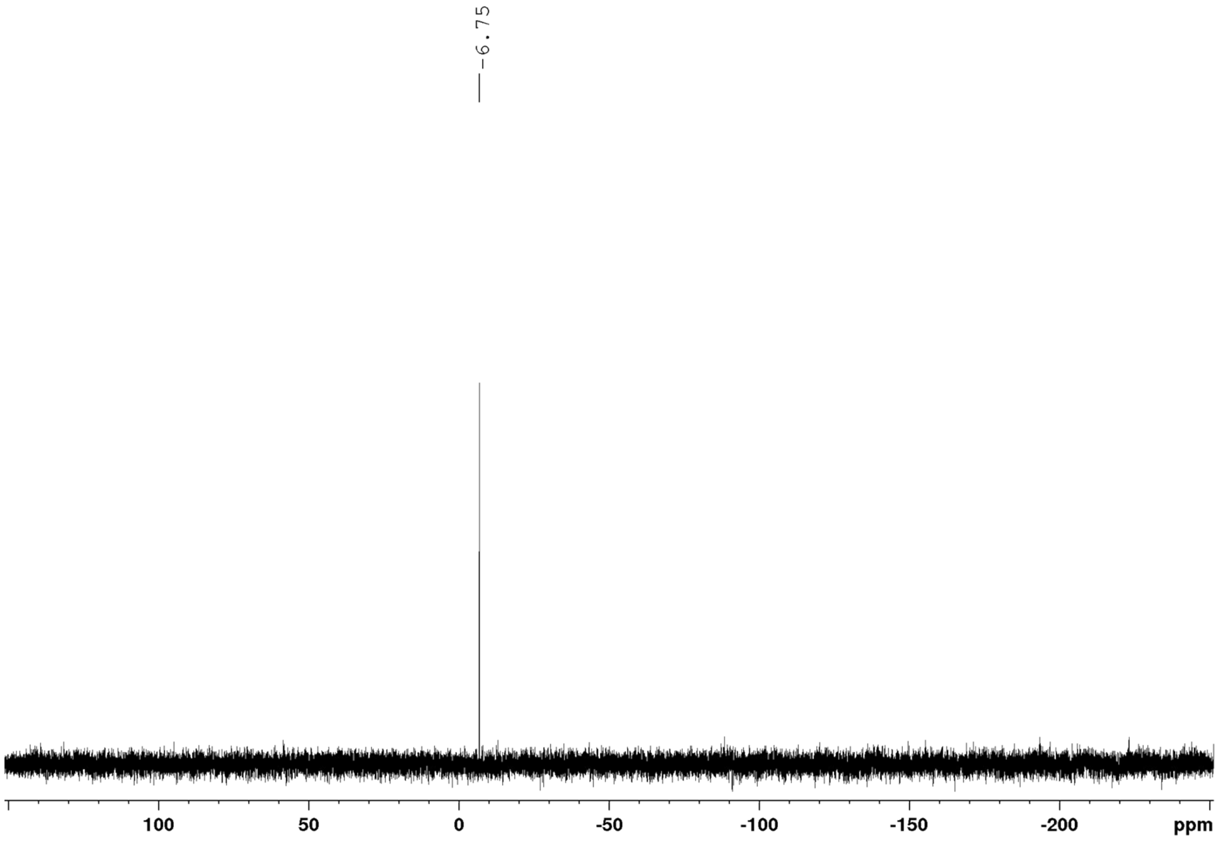


Figure SX. ^{31}P spectrum of **4** in 50% CACO/DMSO-*d₆* measured at room temperature.

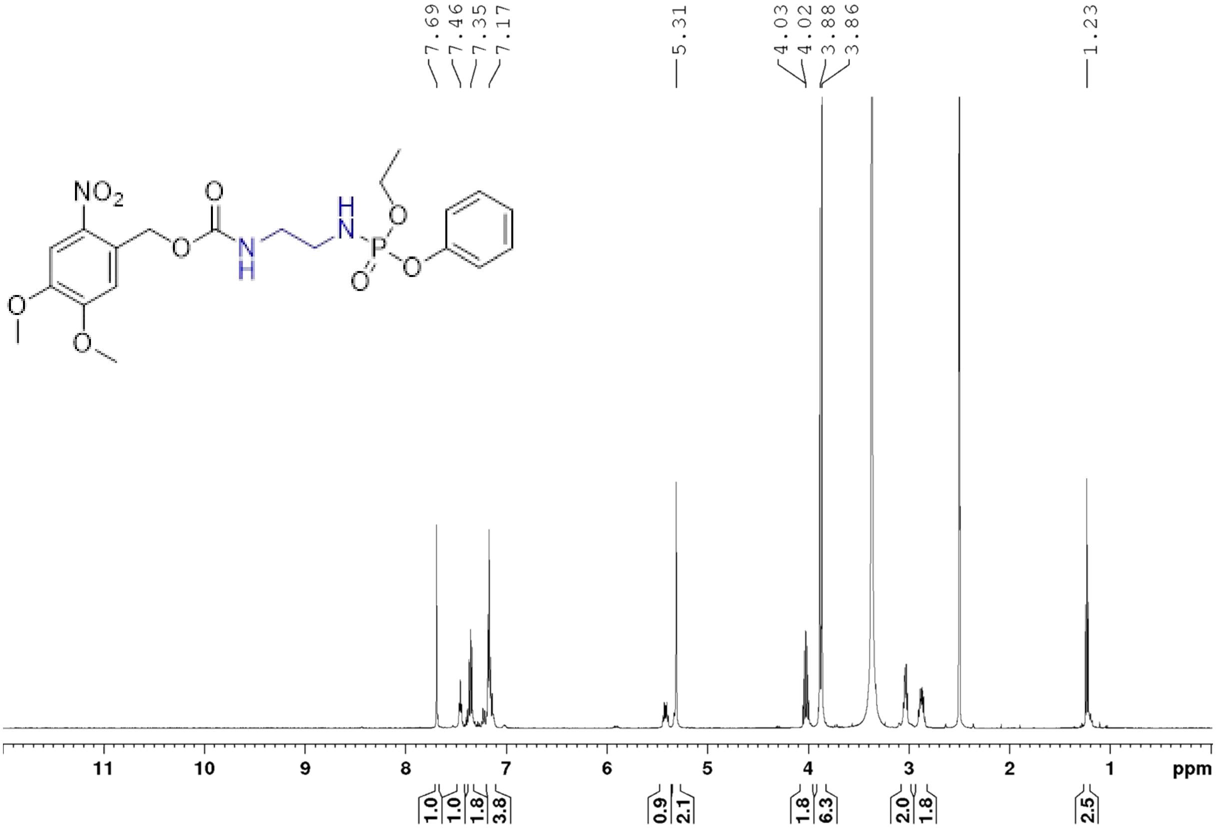


Figure SX. ^{1}H spectrum of **5** in DMSO-d_6 measured at room temperature.

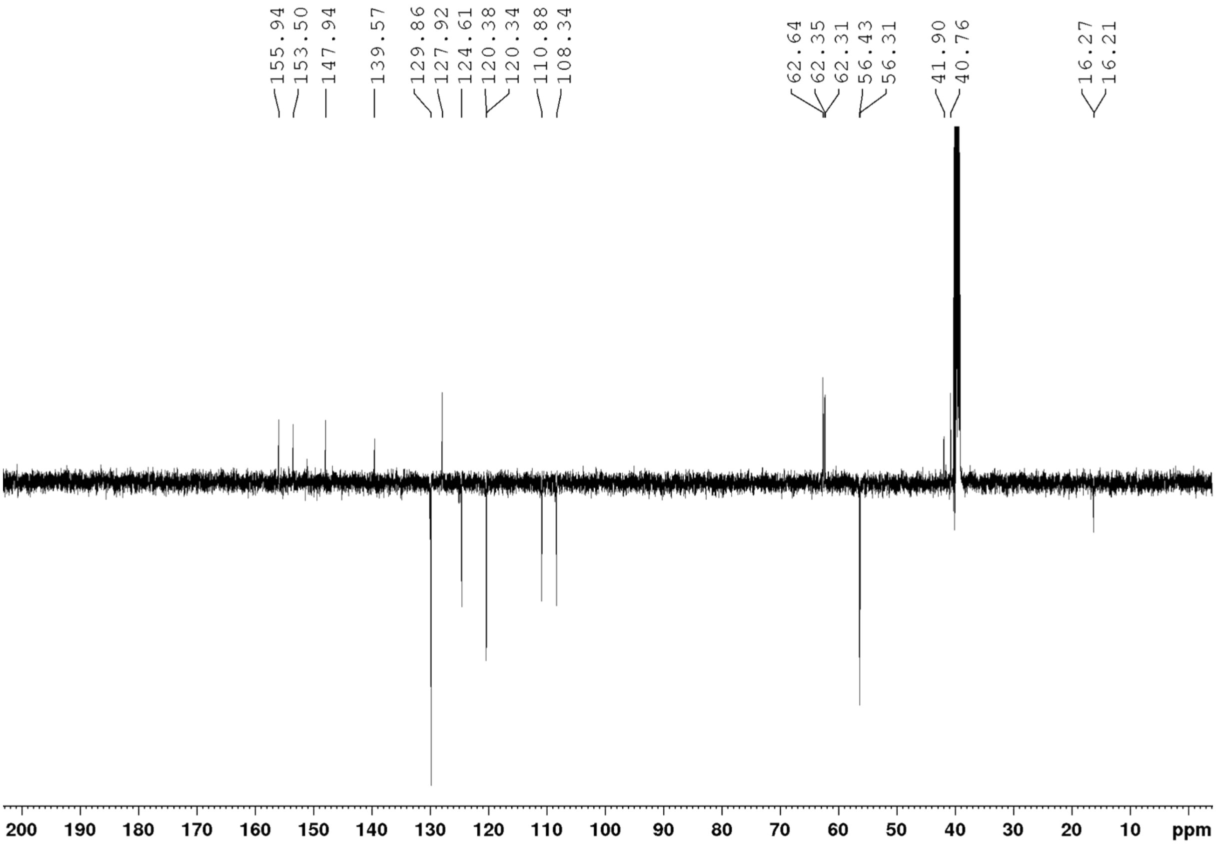


Figure SX. ^{13}C APT spectrum of **5** in DMSO-d_6 measured at room temperature.

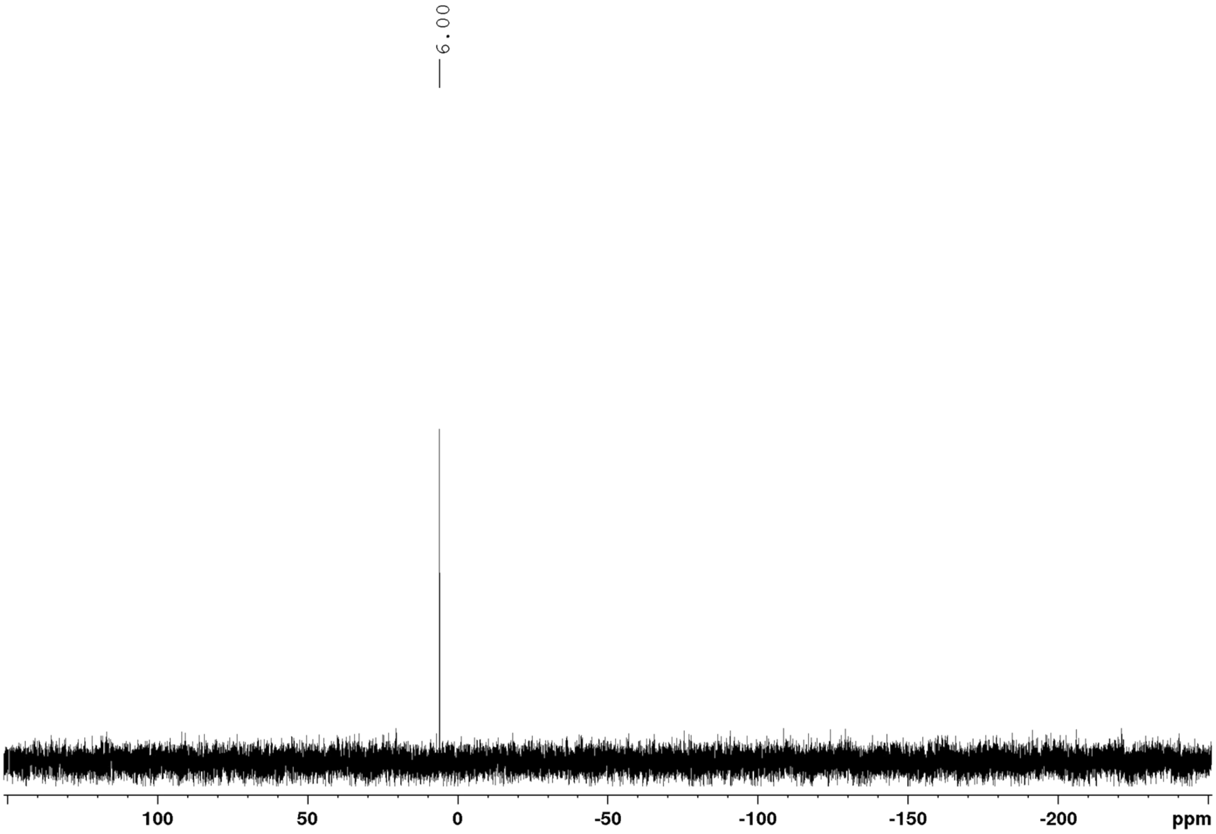


Figure SX. ^{31}P spectrum of **5** in 50% CACO/DMSO-d_6 measured at room temperature.

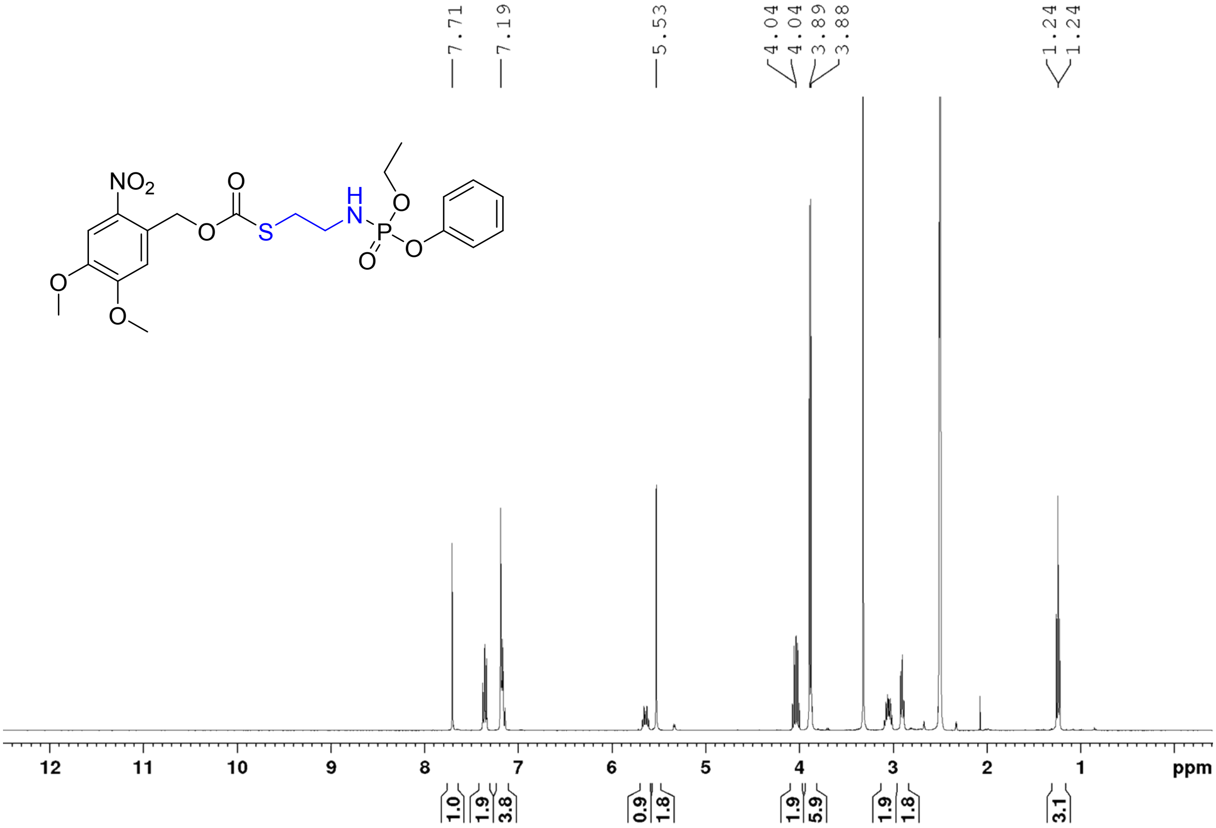


Figure SX. ^{1}H spectrum of **6** in DMSO-d_6 measured at room temperature.

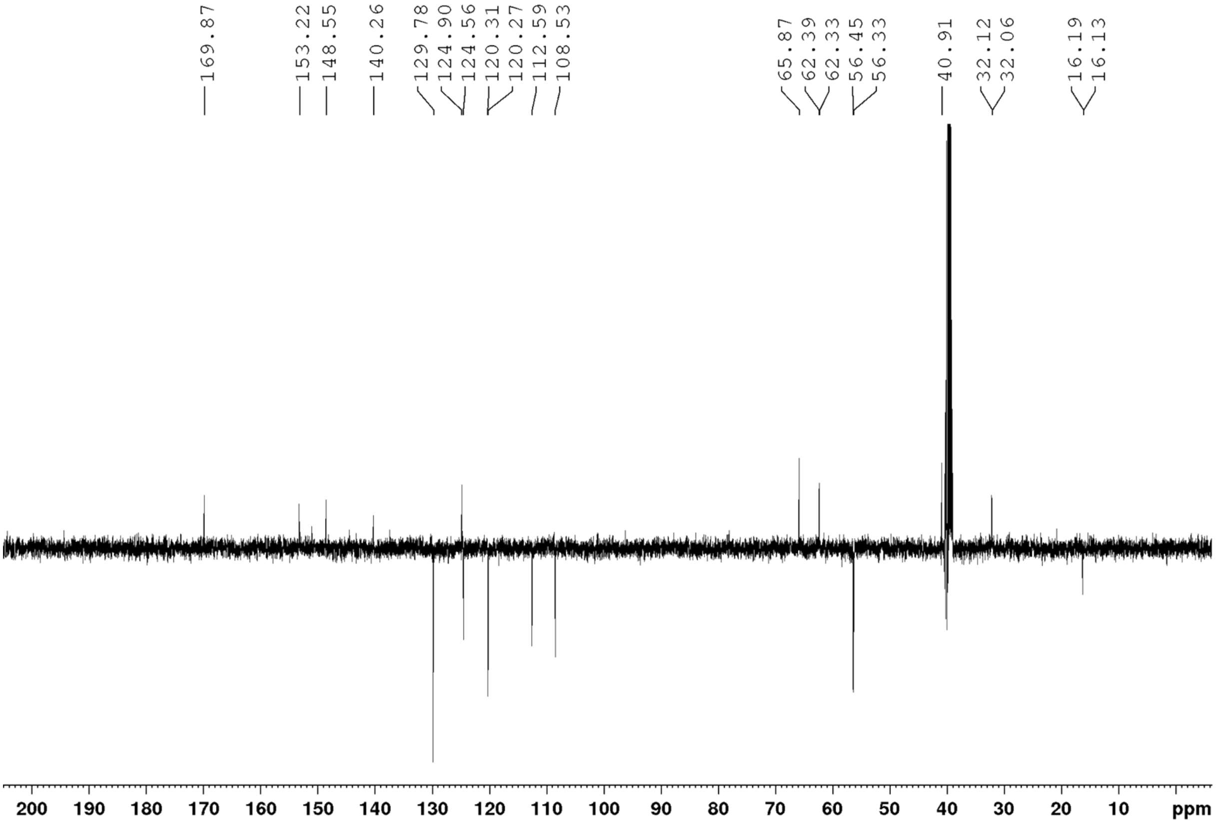


Figure SX. ^{13}C APT spectrum of **6** in DMSO-d_6 measured at room temperature.

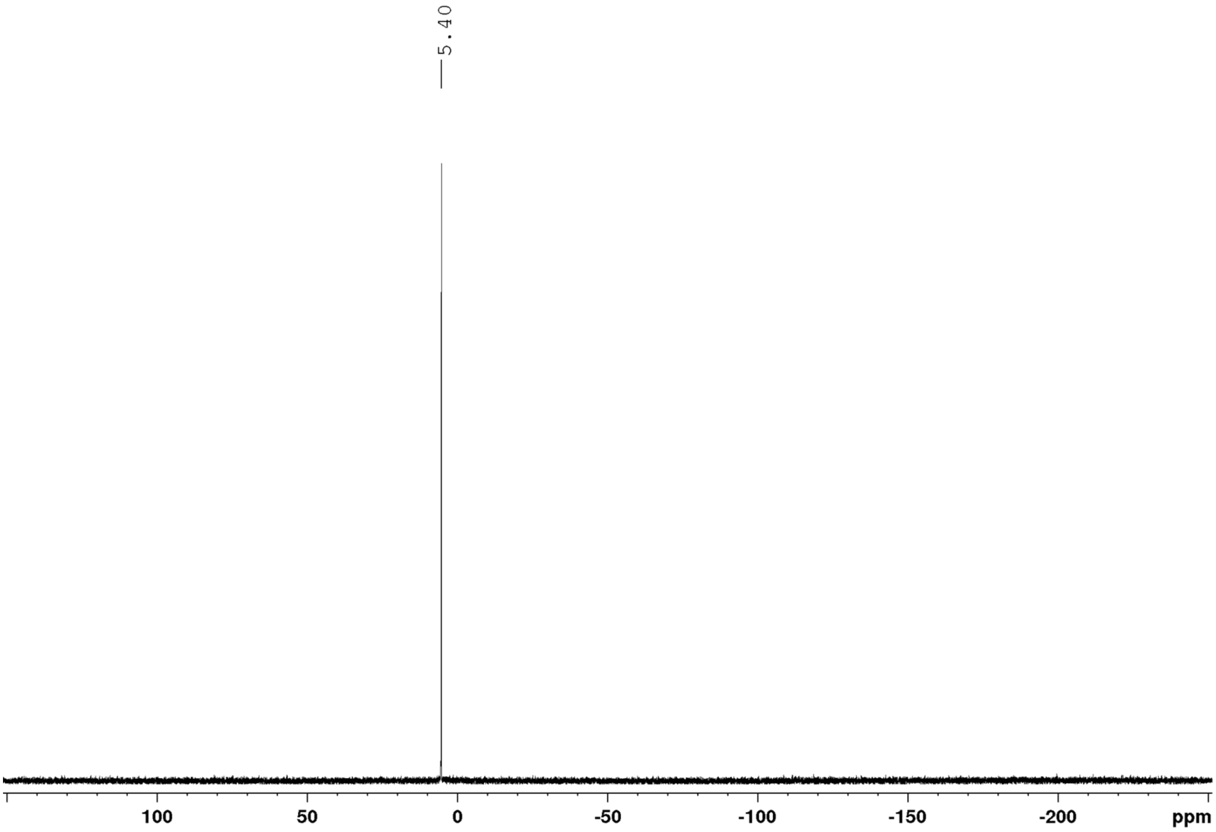


Figure SX. ^{31}P spectrum of **6** in 50% CACO/DMSO-d_6 measured at room temperature.

6 Compound characterization: HR-MS spectra

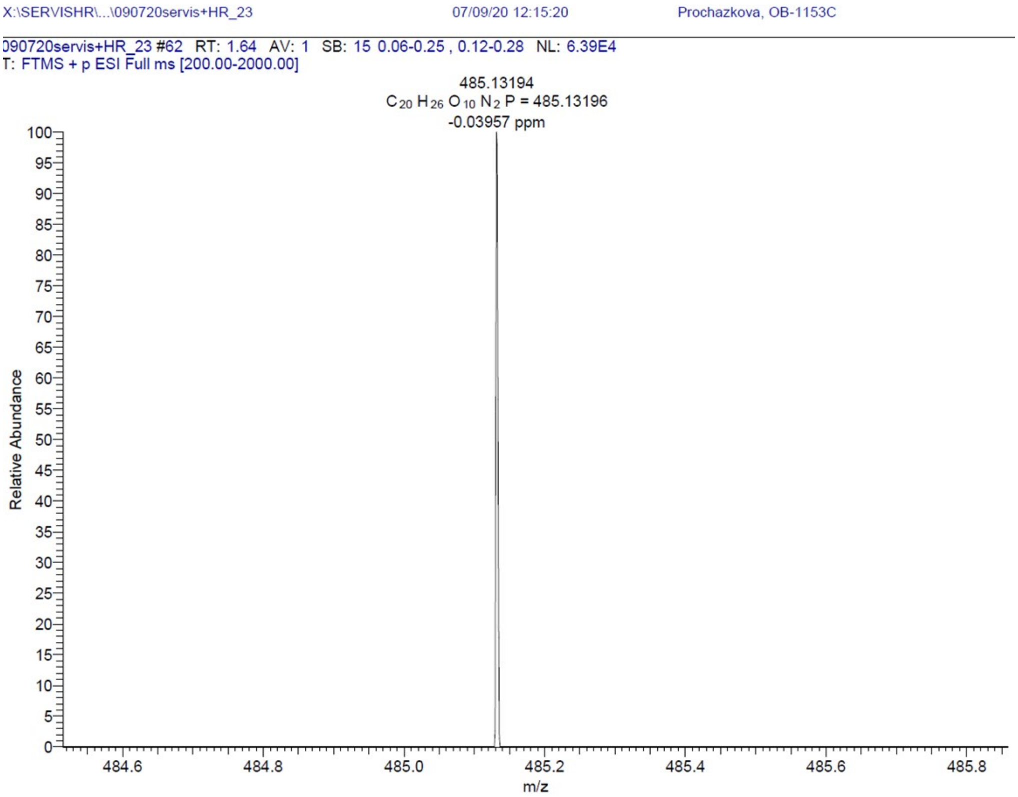


Figure SX. HR-MS spectrum of **1**.

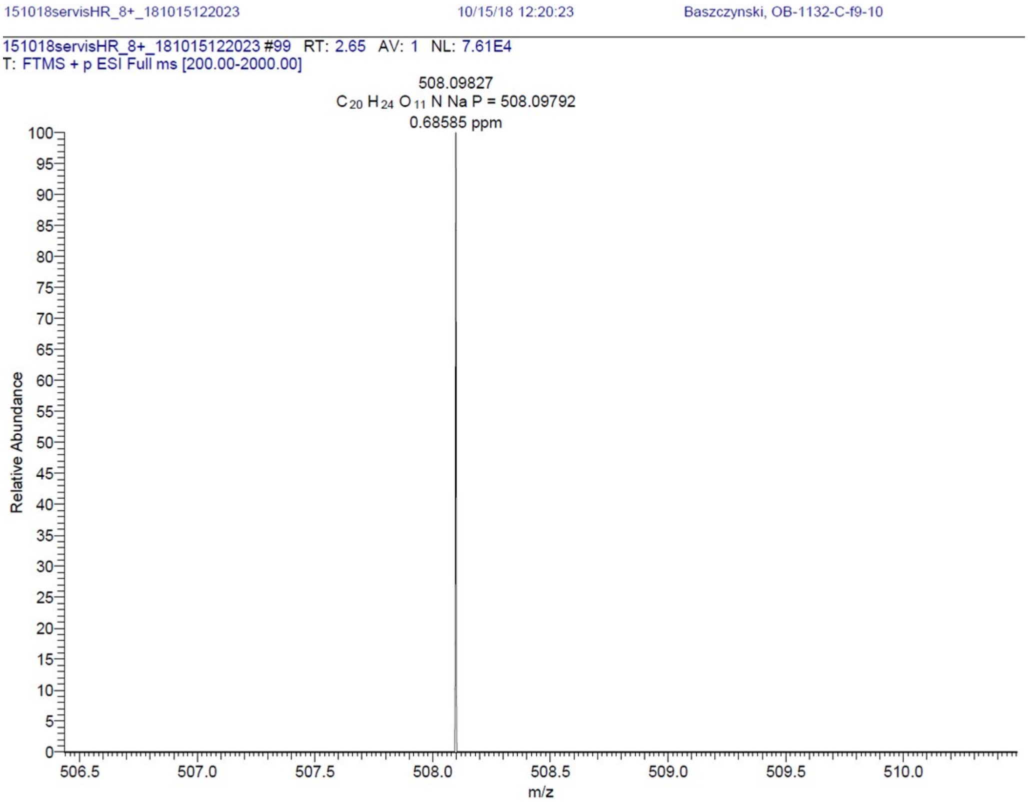


Figure SX. HR-MS spectrum of **2**.

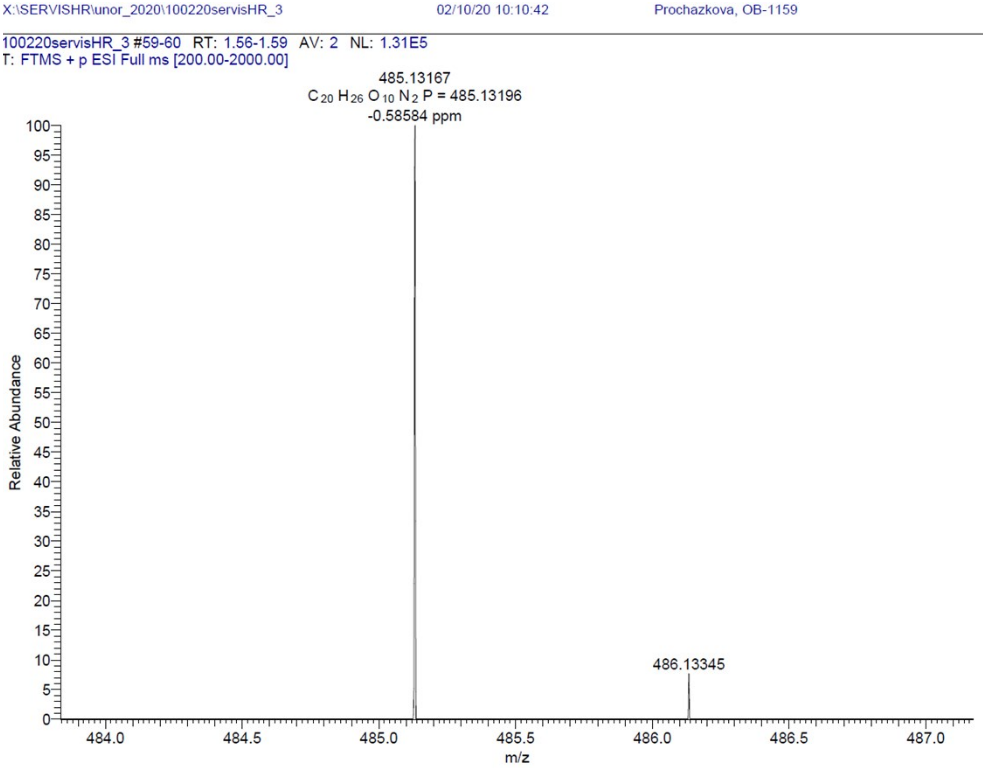


Figure SX. HR-MS spectrum of **3**.

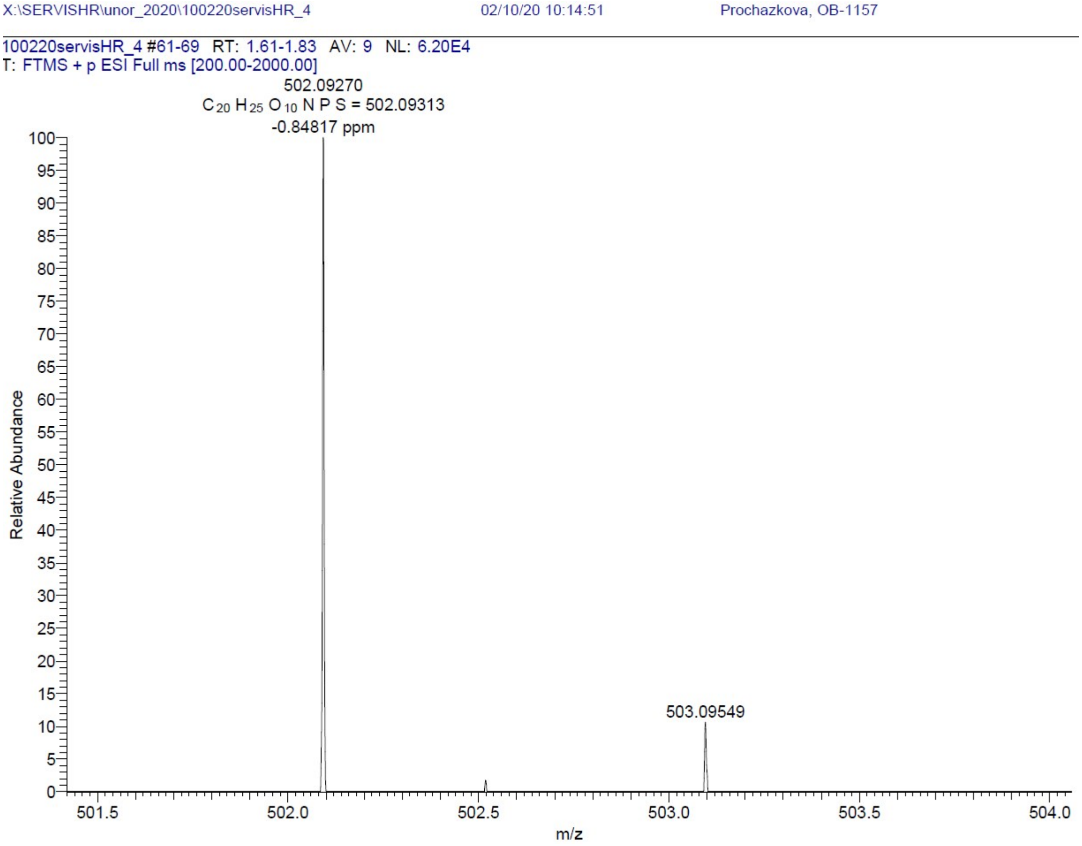


Figure SX. HR-MS spectrum of **4**.

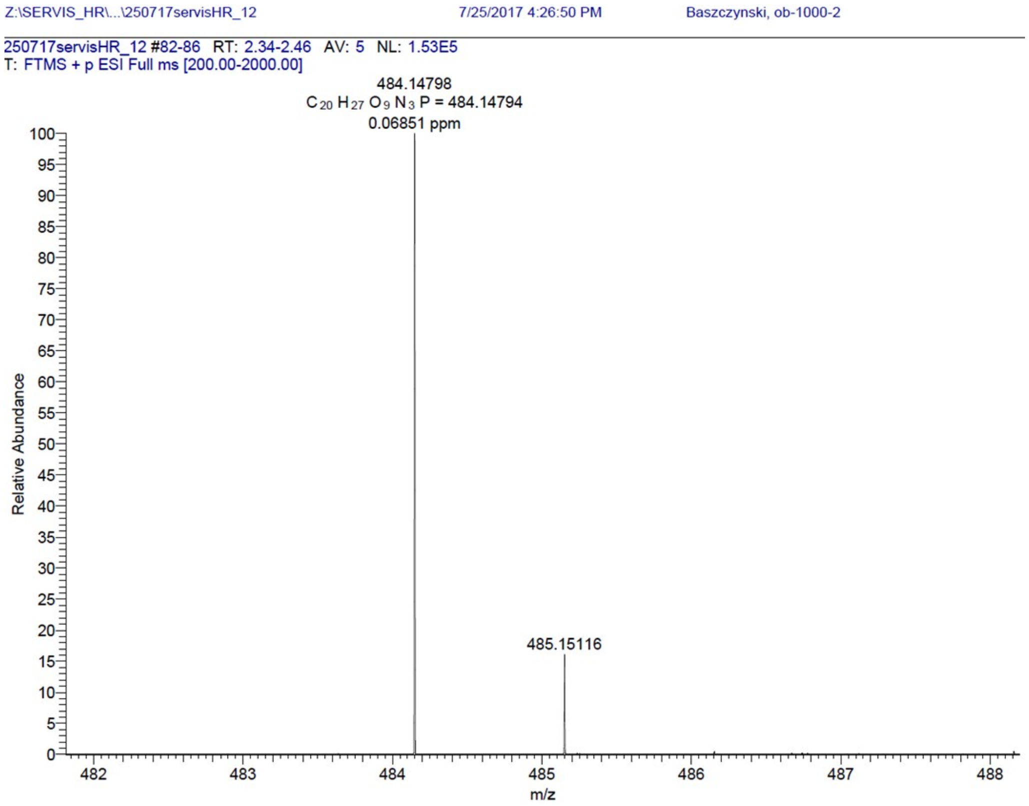


Figure SX. HR-MS spectrum of **5**.

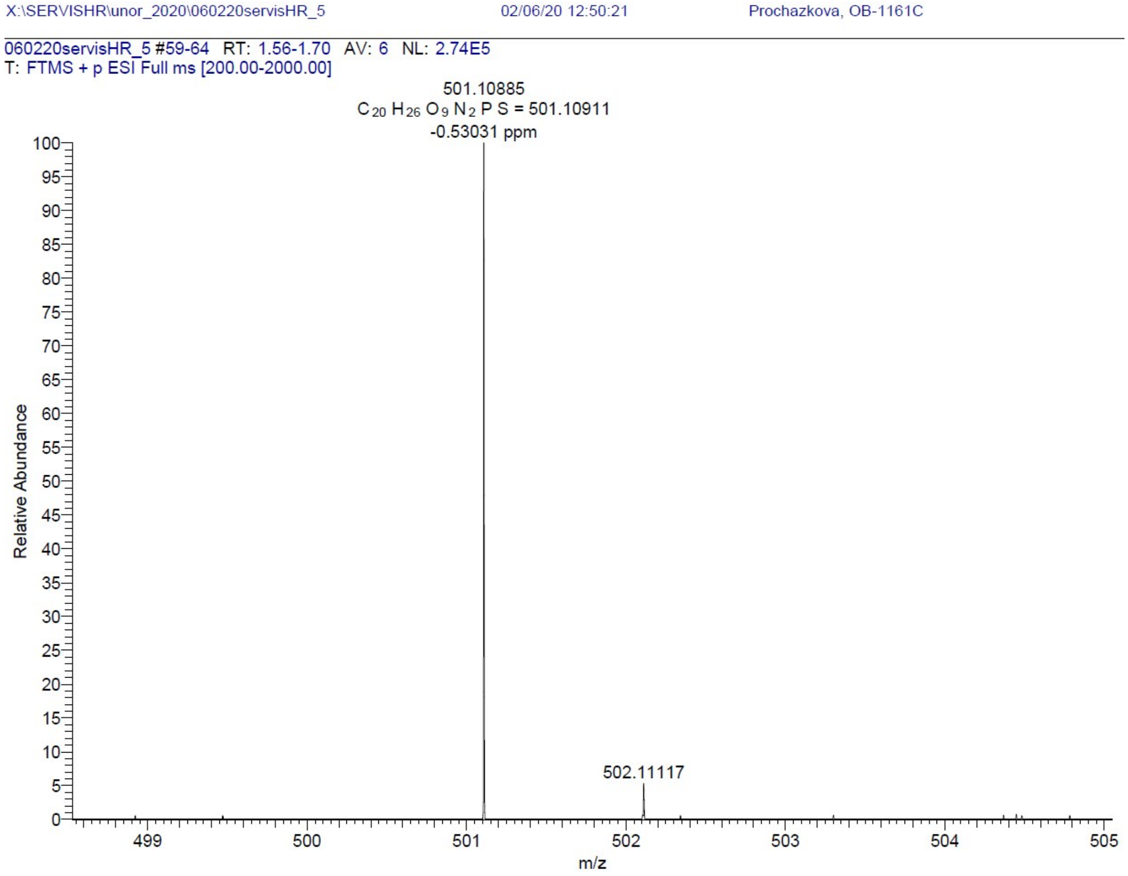


Figure SX. HR-MS spectrum of **6**.

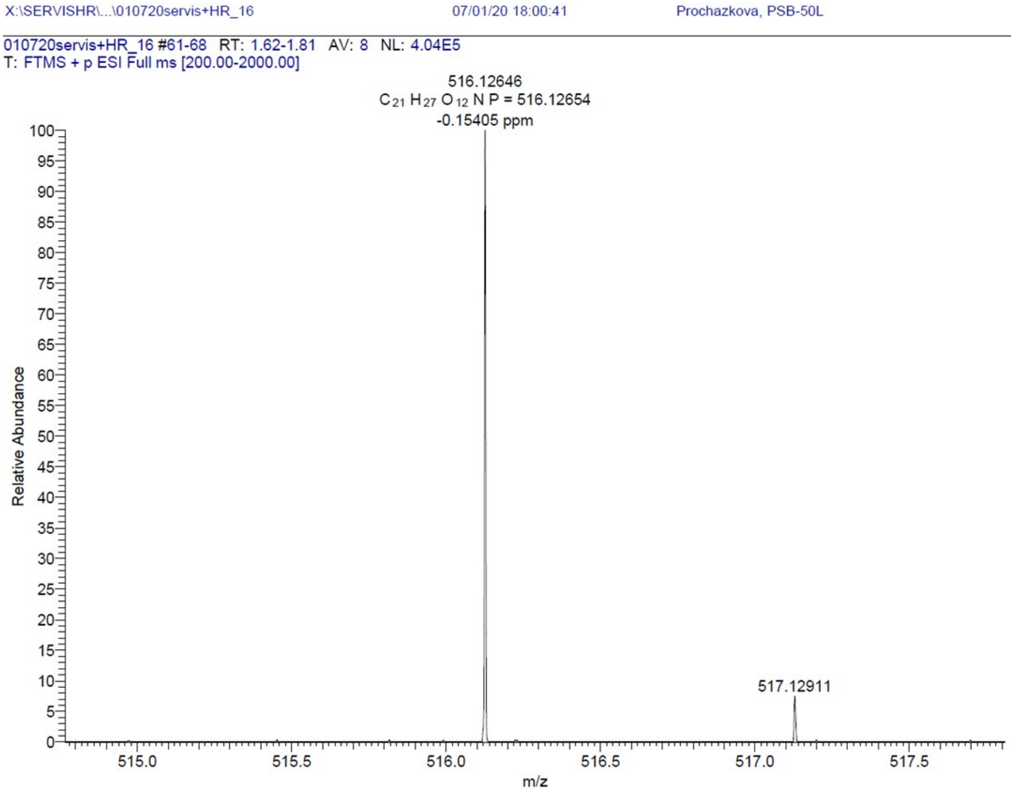


Figure SX. HR-MS spectrum of **7**.

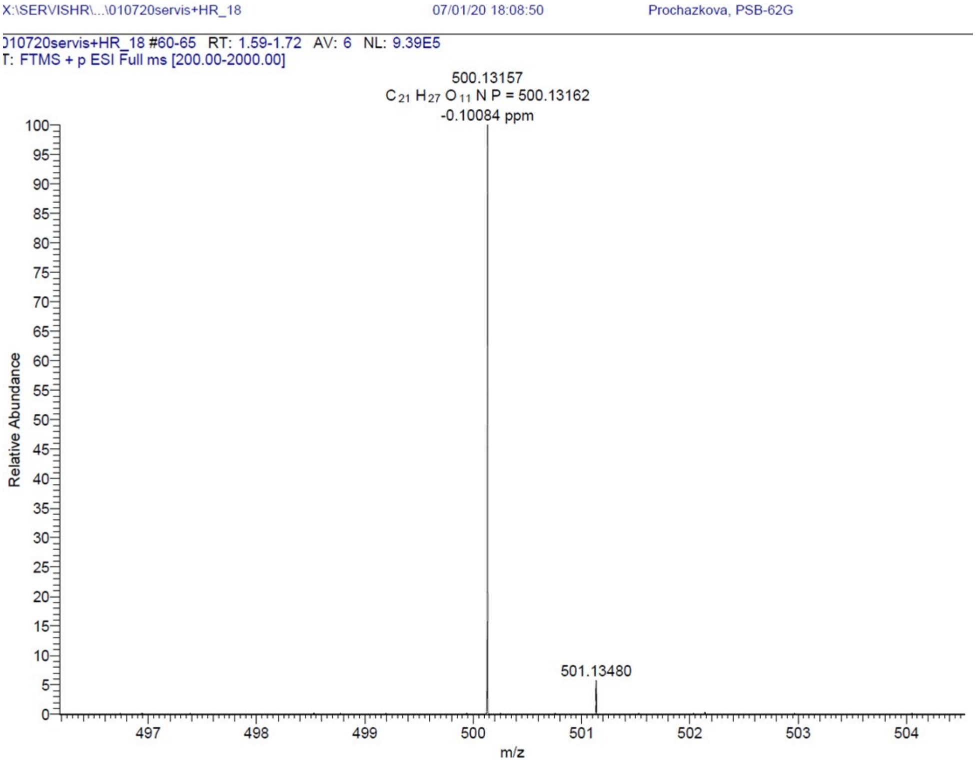


Figure SX. HR-MS spectrum of **8**.

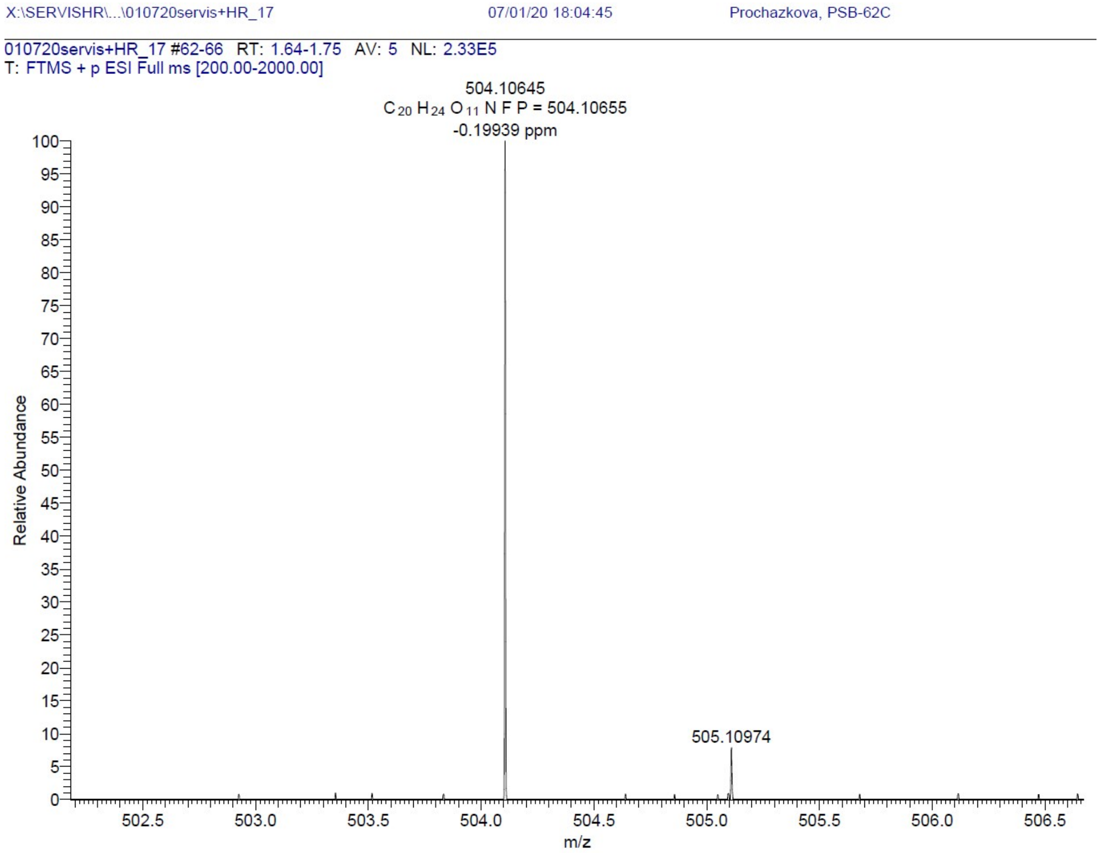


Figure SX. HR-MS spectrum of **9**.

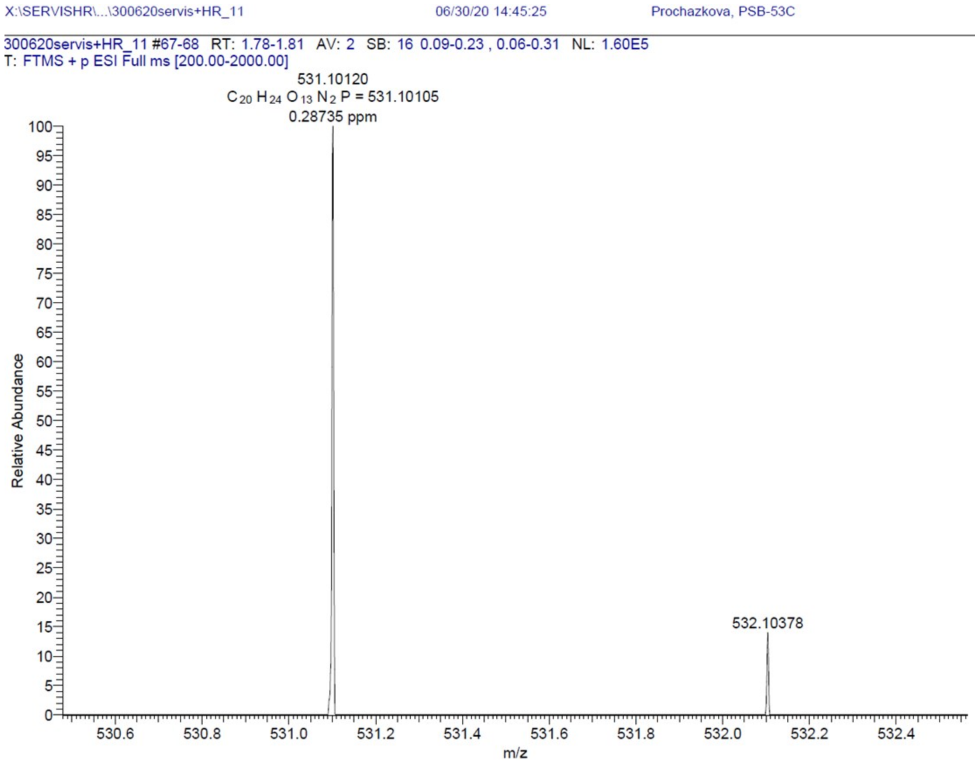


Figure SX. HR-MS spectrum of **10**.

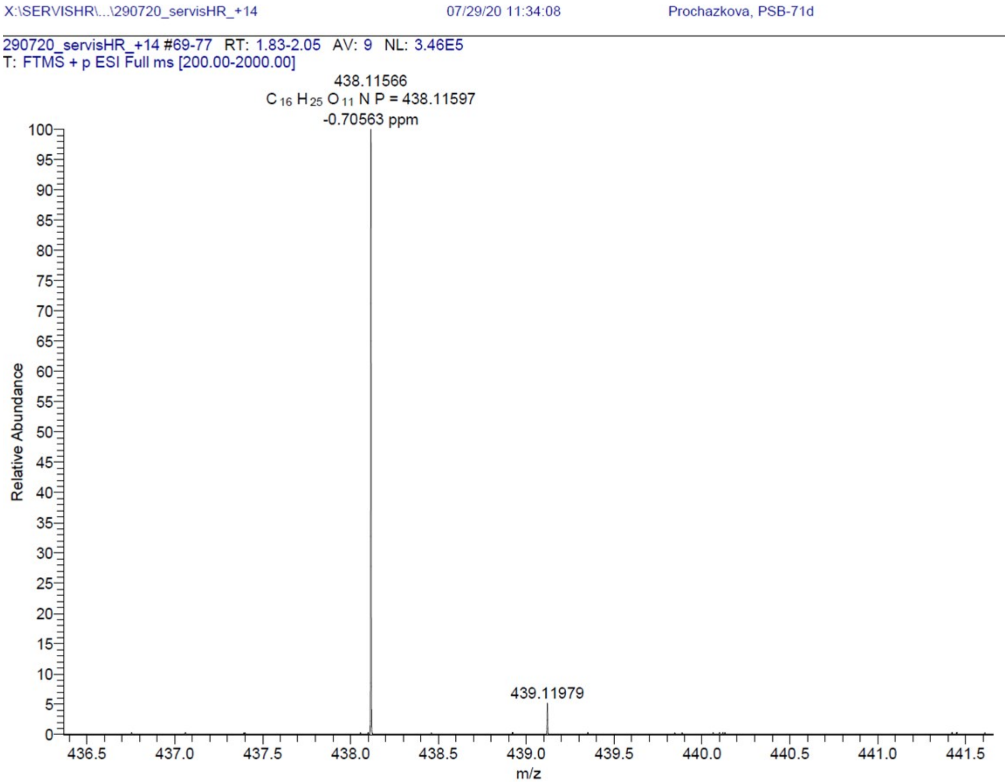


Figure SX. HRMS spectrum of **11**.

7 X, Y, Z Coordinates

Phenolate

Ph-O(-)

C	-0.05783	-0.00000	-0.03333
C	0.01025	-0.00000	1.39983
C	1.21618	-0.00000	2.08560
C	2.43890	0.00000	1.40805
C	2.41432	-0.00000	0.01046
C	1.21739	-0.00000	-0.69084
H	-0.92848	0.00000	1.94554
H	1.20712	-0.00000	3.17159
H	3.37660	0.00000	1.94934
H	3.35023	0.00000	-0.54046
H	1.22062	-0.00000	-1.77663
O	-1.16809	0.00000	-0.67465

Compound 1

1-OH

C	-1.57389	1.32681	0.30663
C	-0.99677	0.08063	0.53208
C	-0.22935	-0.53053	-0.45430
C	-0.04362	0.12934	-1.66199
C	-0.61211	1.37090	-1.90617
C	-1.38258	1.96786	-0.91388
O	0.69796	-0.45489	-2.69165
P	2.24836	-0.83726	-2.52317
O	2.59995	-1.26564	-4.00064
C	2.46929	-0.35624	-5.12997
C	3.06984	-1.02903	-6.34077
N	2.95950	0.57375	-2.10438
C	4.13508	0.70989	-1.23298
C	3.80794	0.64511	0.25496
O	3.54698	-0.67276	0.72654
O	2.56418	-1.94063	-1.59114
H	2.97821	-0.36988	-7.20561
H	2.55093	-1.96263	-6.56119
H	4.12686	-1.24343	-6.17905
H	2.99047	0.57269	-4.88971
H	1.40966	-0.13954	-5.27316
H	4.86148	-0.06625	-1.47994
H	4.59833	1.67080	-1.45924
H	4.66442	1.02108	0.82060
H	2.95453	1.30560	0.45790
H	-0.44758	1.85307	-2.86057
H	-1.83004	2.93624	-1.09647
H	-2.17166	1.79510	1.07753
H	-1.14439	-0.42366	1.47831
H	0.22477	-1.49835	-0.29501
H	3.10666	-1.17952	0.01941
H	2.47595	1.43022	-2.32500

1-O(-)

C	-3.72514	1.57488	-1.87322
C	-4.00589	2.42111	-2.94208
C	-3.29333	2.29114	-4.13082
C	-2.30064	1.32454	-4.25158
C	-2.03091	0.48920	-3.17553
C	-2.73837	0.60037	-1.98419
O	-1.06806	-0.49768	-3.34508
P	0.28851	-0.56782	-2.46286
O	0.97880	-1.80633	-3.17110
C	1.59708	-1.68181	-4.48779
C	2.08828	-3.05123	-4.89421
N	0.99489	0.86565	-2.79421
C	2.14759	1.42488	-2.06897
C	3.45766	1.36220	-2.88189
O	3.90578	0.11661	-3.15050
O	0.10667	-0.84060	-1.02537
H	2.55720	-2.99333	-5.87853
H	1.26759	-3.76892	-4.94531
H	2.82981	-3.41888	-4.18277
H	2.42059	-0.96864	-4.38294
H	0.84707	-1.30947	-5.19067
H	1.91579	2.46374	-1.80040
H	2.26792	0.85628	-1.14533
H	4.17032	1.99707	-2.28709
H	3.25517	1.98788	-3.79725
H	-2.50764	-0.06451	-1.16377
H	-4.27794	1.66824	-0.94711
H	-4.77680	3.17507	-2.85025
H	-3.50674	2.94415	-4.96739
H	-1.73469	1.20956	-5.16654
H	0.91816	1.18780	-3.74976

1-TS1

C	-3.60937	1.54003	-1.74388
C	-4.05406	2.31011	-2.81544
C	-3.44879	2.16347	-4.06046
C	-2.40513	1.26051	-4.23161
C	-1.96375	0.49423	-3.15462
C	-2.57019	0.62964	-1.90579
O	-0.96584	-0.41916	-3.38402
P	0.47840	-0.45129	-2.53015
O	1.01565	-1.71324	-3.34984
C	1.75589	-1.55954	-4.57404
C	2.15933	-2.93536	-5.05531
N	0.93020	1.07941	-2.95512
C	2.08574	1.78361	-2.40099
C	3.30754	0.85759	-2.44034
O	2.93399	-0.37033	-1.98713
O	0.18939	-0.75278	-1.11137
H	2.72152	-2.85165	-5.98741
H	1.28234	-3.55914	-5.23636
H	2.79080	-3.42863	-4.31447
H	2.62845	-0.94057	-4.36820
H	1.12573	-1.05754	-5.31513
H	2.22202	2.71113	-2.96327
H	1.86975	2.04596	-1.36029

H	4.11498	1.34607	-1.84819
H	3.68355	0.85518	-3.49590
H	-2.21263	0.02935	-1.08167
H	-4.07659	1.64438	-0.77227
H	-4.86502	3.01450	-2.68224
H	-3.78609	2.75551	-4.90220
H	-1.92356	1.13777	-5.19344
H	0.63453	1.37191	-3.87332

1-cycP(OPh)

C	2.94404	1.26714	3.27592
C	2.12620	1.26418	2.14995
C	1.47560	2.44309	1.73668
C	1.68393	3.60795	2.50044
C	2.50058	3.59646	3.62168
C	3.14238	2.42476	4.02181
O	0.66438	2.54052	0.67887
P	0.35910	1.36800	-0.70048
O	-0.69377	2.26789	-1.27583
N	2.01433	1.44137	-0.98218
C	2.62320	0.49207	-1.89461
C	1.52328	-0.55264	-2.07361
O	0.31612	0.16587	-1.96692
O	-0.16047	0.22353	0.36171
C	-1.10452	0.51905	1.39529
C	-1.83323	-0.76216	1.74893
H	-2.37394	-1.15285	0.88499
H	-2.55016	-0.57761	2.55213
H	-1.12820	-1.52424	2.08727
H	-1.80498	1.28113	1.04587
H	-0.58714	0.91601	2.27218
H	3.53522	0.06259	-1.47280
H	2.87706	0.95922	-2.85435
H	1.18593	4.51755	2.18710
H	2.63922	4.51058	4.18738
H	3.78101	2.41604	4.89572
H	3.43001	0.34478	3.57312
H	1.97584	0.35298	1.59131
H	1.59816	-1.32165	-1.28972
H	1.57394	-1.04731	-3.04622
H	2.61697	1.97059	-0.38044

1-TS2

H	1.72789	-2.08103	-6.32735
H	3.15448	-3.01725	-5.85037
C	2.18110	-2.65252	-5.51525
H	-2.93068	0.11797	-5.14323
H	1.54506	-3.51406	-5.30331
H	2.98639	-0.93298	-4.49915
H	-5.01421	1.32921	-4.60611
C	2.34737	-1.79179	-4.27849
C	-3.03021	0.64340	-4.20072
C	-4.19720	1.32686	-3.89339
H	2.81809	-2.35676	-3.47194
O	-0.84897	-0.04302	-3.69252
O	1.04736	-1.34959	-3.88093
H	0.27087	1.91386	-3.28825

C	-1.93707	0.61196	-3.30723
N	1.04695	1.32315	-3.04690
H	2.58926	2.75761	-2.94563
H	3.73080	0.66785	-3.13906
C	-4.32626	2.00836	-2.68296
H	-5.23660	2.54268	-2.44305
P	0.73146	-0.29513	-2.67687
C	2.16566	1.94004	-2.35884
C	-2.08226	1.30073	-2.08400
C	3.13523	0.77288	-2.22073
C	-3.25874	1.98349	-1.79009
O	2.33235	-0.36694	-2.00158
H	1.88592	2.33256	-1.37192
H	-1.27798	1.27226	-1.36492
O	0.00934	-0.85722	-1.48693
H	3.82271	0.90197	-1.38139
H	-3.33934	2.50256	-0.84138

1-P

H	-3.58299	-0.42845	-4.59415
C	-3.05738	0.31033	-4.00237
H	-2.36569	-1.09326	-2.52629
H	-3.56572	1.96456	-5.27984
C	-2.37057	-0.05410	-2.84140
C	-3.04132	1.65558	-4.38054
C	-1.69532	0.88704	-2.07786
C	-2.37043	2.60833	-3.62808
H	-1.17341	0.58412	-1.17667
H	-2.37663	3.64917	-3.93505
C	-1.66321	2.27462	-2.42879
H	-4.45756	4.88153	-2.17216
O	-1.06101	3.15616	-1.71108
O	-4.81338	3.37275	-0.81087
C	-4.07572	4.56844	-1.20388
H	-3.02161	4.30156	-1.28874
H	-5.23557	6.18646	-0.31368
O	-6.46852	2.97608	1.15015
P	-5.08338	3.30335	0.76511
H	-2.42184	2.45904	0.17480
C	-4.32780	5.61044	-0.11035
H	-3.48673	6.29969	-0.03450
N	-4.45890	4.80471	1.11192
O	-4.12193	2.19789	1.37154
C	-2.67428	2.26009	1.21656
H	-2.30670	3.08656	1.82723
H	-4.79444	5.28185	1.93503
H	-2.48638	0.12192	1.05673
C	-2.10522	0.93760	1.67230
H	-1.01806	0.95853	1.57754
H	-2.35808	0.74064	2.71533

COMPOUND 2

2-OH

C	-0.95188	2.13935	0.09824
C	-1.38766	0.82866	-0.07251
C	-0.65142	-0.06150	-0.84815

C	0.52117	0.38267	-1.44032
C	0.97328	1.68375	-1.28439
C	0.22646	2.56449	-0.50902
O	1.25315	-0.48275	-2.26469
P	2.22643	-1.59787	-1.68277
O	2.86373	-2.21378	-2.97676
C	3.56969	-1.40363	-3.96913
C	4.31745	-2.34210	-4.88342
O	3.31648	-0.71657	-0.95468
C	4.38686	-1.26008	-0.12578
C	3.92309	-1.56688	1.28507
O	3.22356	-2.79443	1.41419
O	1.59612	-2.63244	-0.84188
H	4.84296	-1.76268	-5.64426
H	3.62960	-3.02518	-5.38288
H	5.05009	-2.92467	-4.32395
H	4.24579	-0.72647	-3.44582
H	2.82603	-0.81614	-4.50806
H	4.80452	-2.14908	-0.60218
H	5.14119	-0.47549	-0.11148
H	4.81150	-1.64213	1.91596
H	3.32480	-0.72134	1.64774
H	1.89340	1.98993	-1.76269
H	0.56855	3.58313	-0.38012
H	-1.52958	2.82793	0.70086
H	-2.30423	0.49453	0.39603
H	-0.97166	-1.08371	-0.99374
H	2.51256	-2.81302	0.74643

2-O(-)

C	-3.97342	2.40919	-2.72866
C	-3.21394	2.39018	-3.89537
C	-2.23090	1.42321	-4.07669
C	-2.01984	0.47739	-3.08261
C	-2.77087	0.47933	-1.91414
C	-3.74896	1.45391	-1.74156
O	-1.07075	-0.51597	-3.30432
P	0.35868	-0.51398	-2.55647
O	1.04530	-1.72890	-3.28014
C	1.69429	-1.59157	-4.58105
C	2.07172	-2.97520	-5.05244
O	0.95480	0.84212	-3.07659
C	1.99991	1.60791	-2.39036
C	3.38431	1.23167	-2.91692
O	3.75630	-0.03828	-2.64622
O	0.28411	-0.69129	-1.09757
H	2.56845	-2.90573	-6.02213
H	1.19112	-3.61043	-5.16065
H	2.75886	-3.44647	-4.34777
H	2.56851	-0.95953	-4.41962
H	0.99747	-1.11226	-5.27187
H	1.74902	2.65296	-2.58773
H	1.92423	1.40322	-1.32084
H	4.04851	2.02603	-2.47586
H	3.35834	1.48555	-4.01047
H	-2.58075	-0.26982	-1.15830
H	-4.33788	1.46239	-0.83329

H	-4.73731	3.16327	-2.59054
H	-3.38378	3.13000	-4.66713
H	-1.62626	1.39340	-4.97297

2-TS1

C	-2.03747	1.31974	-2.07814
C	-3.09991	2.20433	-1.91645
C	-4.07268	2.34258	-2.90102
C	-3.97560	1.58127	-4.06324
C	-2.91907	0.69710	-4.23827
C	-1.94528	0.56266	-3.24728
O	-0.95031	-0.34006	-3.50267
P	0.43525	-0.54792	-2.61197
O	0.05197	-0.96744	-1.25155
O	1.00682	-1.68130	-3.55599
C	1.90164	-1.40222	-4.65677
C	2.23899	-2.71592	-5.32324
O	0.99161	0.91263	-2.89271
C	1.99463	1.53699	-2.05201
C	3.24072	0.65631	-2.06861
O	2.86988	-0.63384	-1.85597
H	2.91380	-2.53920	-6.16291
H	1.34030	-3.20693	-5.69995
H	2.73378	-3.38611	-4.61838
H	2.78785	-0.92146	-4.24584
H	1.40583	-0.72161	-5.35378
H	2.14137	2.53472	-2.46883
H	1.58651	1.61593	-1.04097
H	3.93768	1.08302	-1.31019
H	3.74553	0.82811	-3.05257
H	-1.29478	1.20947	-1.30230
H	-3.16364	2.78838	-1.00655
H	-4.89550	3.03229	-2.76498
H	-4.72445	1.67563	-4.83985
H	-2.83125	0.10207	-5.13817

2-cycP(OPh)

C	-4.38954	1.72046	-2.42560
C	-4.25027	1.15189	-3.69076
C	-3.03389	0.62212	-4.09759
C	-1.90765	0.64249	-3.25215
C	-2.05753	1.21796	-1.97681
C	-3.28273	1.74467	-1.58108
O	-0.78282	0.11362	-3.73525
P	0.76693	-0.10509	-2.82924
O	1.23232	-0.82942	-4.21639
C	2.32845	-1.75039	-4.28900
C	2.19494	-2.52215	-5.58631
O	0.83846	1.54688	-2.91653
C	2.03061	2.16775	-2.43375
C	3.08992	1.08369	-2.53102
O	2.39232	-0.08588	-2.18214
O	0.18535	-0.91871	-1.71280
H	3.02470	-3.22467	-5.68970
H	2.21018	-1.84383	-6.44151
H	1.26018	-3.08504	-5.60889
H	2.30639	-2.42710	-3.43189

H	3.27546	-1.20788	-4.25798
H	2.23652	3.04189	-3.05237
H	1.88222	2.48373	-1.39645
H	3.91993	1.24759	-1.84049
H	3.49349	1.02970	-3.55377
H	-1.21556	1.24199	-1.30317
H	-3.36985	2.18208	-0.59280
H	-5.33769	2.13386	-2.10640
H	-5.09630	1.12014	-4.36769
H	-2.92525	0.17990	-5.08076

2-TS2

H	2.28335	-1.90235	-6.10375
H	0.99792	-3.10367	-5.91177
H	0.60404	-1.37300	-5.86315
C	1.34662	-2.12060	-5.58721
H	-2.49424	-0.33232	-5.17161
H	-4.73064	0.56797	-4.65898
C	1.54377	-2.11273	-4.08835
H	2.28334	-2.85749	-3.78307
O	2.05900	-0.82544	-3.68391
C	-2.66886	0.18982	-4.23688
O	-0.40662	-0.15587	-3.66247
C	-3.92544	0.69862	-3.94311
H	4.00523	1.46994	-3.25419
H	0.60943	-2.30635	-3.56793
C	-1.56839	0.32990	-3.34294
H	2.33802	3.23185	-3.28052
O	1.21353	1.54947	-2.91087
P	1.48917	0.01533	-2.45440
C	3.48107	1.63101	-2.30521
C	-4.16632	1.37422	-2.74508
C	2.23439	2.47963	-2.50021
H	-5.14732	1.77198	-2.51783
O	2.97498	0.40336	-1.79717
C	-1.84253	1.01845	-2.12729
H	4.17385	2.06273	-1.58349
O	0.80755	-0.68829	-1.34513
C	-3.10685	1.52141	-1.84876
H	1.92368	2.95697	-1.56772
H	-1.04092	1.13697	-1.41264
H	-3.26980	2.04075	-0.90952

2-cycP

C	0.91437	1.60348	2.93635
H	1.95572	1.27961	2.96280
H	0.56472	1.72487	3.96348
H	0.85827	2.57063	2.43528
C	0.05404	0.58255	2.22749
H	0.12271	-0.39672	2.69918
H	-0.99046	0.88772	2.19410
O	0.45606	0.46618	0.82967
P	1.42899	-0.65718	0.30151
O	2.04157	-1.47463	1.35602
O	0.62811	-1.49268	-0.80579
O	2.40018	0.13528	-0.69222
C	2.25514	-0.32782	-2.06002

C	0.85579	-0.94196	-2.12736
H	0.09094	-0.19234	-2.33532
H	0.78719	-1.75234	-2.84821
H	3.03340	-1.06442	-2.26117
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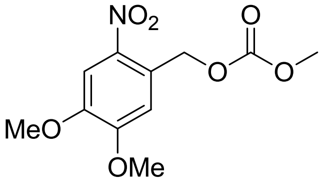
S1 excited state geometries:



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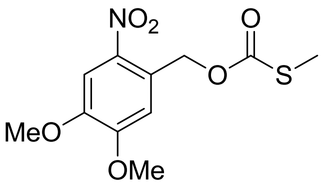
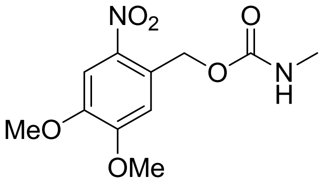
C	-0.40200700	-0.87152600	-0.03831800
C	0.00370200	0.46305100	-0.02512900
C	-0.99423600	1.44518900	-0.10258100
C	-2.35125200	1.10670100	-0.19534500
C	-2.73048900	-0.21931600	-0.21526400
H	0.36410400	-1.63299500	0.01365100
H	-3.11070900	1.87716100	-0.25760700
O	-4.04823800	-0.53638700	-0.35412000
O	-2.20067900	-2.50070500	-0.17862000
C	-4.64513800	-1.09410200	0.81192300
H	-4.58000200	-0.38856000	1.64839600
H	-5.69210400	-1.26821200	0.56271800
H	-4.16868300	-2.03917200	1.08543300
C	-1.24133900	-3.53944200	-0.15762400
H	-0.66116600	-3.52510800	0.77215700
H	-1.80598900	-4.46874900	-0.22181500
H	-0.56024600	-3.46330300	-1.01253400
N	-0.67581900	2.79741800	-0.13035600
O	-1.52831200	3.76252200	-0.14392700
O	0.44258900	3.34530000	0.19584700
C	1.46822600	0.82417700	0.06290300
H	1.76616200	1.49513700	-0.74867100
H	1.70303400	1.33358800	1.00250400
O	2.22313900	-0.38488200	-0.02006800
C	3.54733800	-0.21599900	0.06004700
O	4.12385400	-1.41396800	-0.02788800
C	5.54991800	-1.37716900	0.04018200
H	5.87255400	-2.41298100	-0.04739100
H	5.95385900	-0.77661000	-0.77721800
H	5.87408900	-0.95094700	0.99163100
O	4.11541700	0.83720200	0.18908800



C	-1.92672800	-1.28090200	-0.13118100
C	-0.61547800	-0.82014300	-0.02877500
C	-0.31567400	0.54214700	-0.01986000
C	-1.38741600	1.44245300	-0.10343700
C	-2.71318700	0.99817600	-0.19914600
C	-2.98734200	-0.35357600	-0.21554200
H	0.20675500	-1.52010100	0.02850000
H	-3.53051300	1.70656500	-0.26578500
O	-4.27557200	-0.77293800	-0.35714800
O	-2.27969500	-2.58609700	-0.16871000
C	-4.83073700	-1.37488500	0.80771300
H	-4.82144700	-0.66654200	1.64426900
H	-5.86083500	-1.62800700	0.55601600
H	-4.28440500	-2.28098200	1.08220000
C	-1.24215500	-3.54680600	-0.14072900
H	-0.66814700	-3.48381800	0.79087000
H	-1.73234600	-4.51753600	-0.20276500
H	-0.56656500	-3.42092900	-0.99414500
N	-1.17559300	2.81571000	-0.13547700
O	-2.10182300	3.71006900	-0.15895900
O	-0.10849200	3.45055400	0.20528400
C	1.11412700	1.02076000	0.07044500
H	1.35799700	1.71705400	-0.73763000
H	1.30909300	1.54012700	1.01359000
O	1.97009100	-0.12369500	-0.02031600
C	3.28102800	0.14768400	0.06248300
O	3.75415100	1.24275000	0.19984100
S	4.20141800	-1.36642700	-0.06309400
C	5.85359900	-0.63333300	0.08319200
H	5.95373100	-0.11695500	1.03754600
H	6.56522200	-1.45801100	0.02709800
H	6.02840700	0.06740400	-0.73282300



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C	-1.02275100	1.43848600	-0.12575600
C	-2.37466000	1.07719900	-0.20809000
C	-2.73262300	-0.25474700	-0.21445300
H	0.38625600	-1.61341400	0.00877000
H	-3.14683700	1.83489900	-0.27048400
O	-4.04601900	-0.59586300	-0.34145800

O	-2.16740500	-2.52701500	-0.15439600
C	-4.62666000	-1.14196500	0.83799100
H	-4.56752400	-0.42093900	1.66161300
H	-5.67231000	-1.33731400	0.59901700
H	-4.13331200	-2.07442500	1.12517200
C	-1.19366300	-3.54957100	-0.11567800
H	-0.61063700	-3.50825200	0.81183300
H	-1.74359700	-4.48894200	-0.15944200
H	-0.51644600	-3.48093200	-0.97475800
N	-0.73086000	2.79741500	-0.15806300
O	-1.60389400	3.74415700	-0.16835200
O	0.37505100	3.36883800	0.16982400
C	1.45213700	0.85926900	0.03113500
H	1.71241300	1.58865200	-0.74257900
H	1.69296700	1.31865100	0.99437300
O	2.23595500	-0.31728800	-0.14460400
C	3.56091700	-0.14973900	0.11170300
C	5.66625900	-1.38522200	-0.01501000
H	6.13959800	-1.38482400	-1.00259600
H	6.00292200	-0.50692600	0.53565400
H	5.96773400	-2.28488300	0.52694400
O	4.04985900	0.88925900	0.49275900
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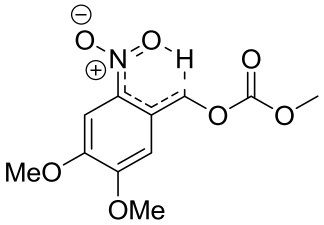
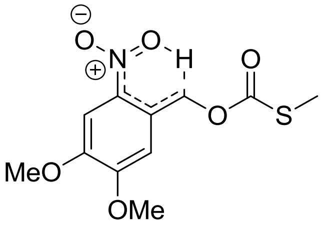
S1 transition state geometries:



C	-2.26704600	0.26670800	0.53157800
C	-1.46981100	1.38917600	0.52377700
C	-0.24222600	1.36345500	-0.15842900
C	0.16454800	0.21803500	-0.84511800
C	-0.65191800	-0.91846300	-0.83127700
C	-1.86045600	-0.91102300	-0.14767100
N	0.54282000	2.50922100	-0.13364300
O	0.19434200	3.60600100	0.36583600
C	1.46506600	0.21911400	-1.57856400
O	1.68456200	2.58047300	-0.80903300
H	-1.77736900	2.28066000	1.05643100
H	-0.31162000	-1.80554700	-1.35419400
H	1.87156600	1.35037900	-1.33291200
H	1.39829100	0.14307500	-2.66460100
O	2.39292800	-0.74721400	-1.17413400
O	-3.43124200	0.27700400	1.24013300
O	-2.70865200	-1.96473300	-0.05601600
C	-2.31605500	-3.16670400	-0.68348800
H	-1.37166300	-3.53800600	-0.26836800
H	-3.10967400	-3.88537300	-0.48245400
H	-2.20850300	-3.03300700	-1.76675500

C	-4.60550900	0.29398700	0.43644900
H	-4.67044100	-0.60227500	-0.18672400
H	-5.44711600	0.32161300	1.12898600
H	-4.62183900	1.18925800	-0.19598900
C	2.78626200	-0.68020300	0.12019300
O	3.54560300	-1.73956700	0.36588500
C	4.06705100	-1.78256900	1.69744400
H	4.66206900	-2.69217300	1.74632600
H	4.68556000	-0.90368200	1.88833500
H	3.25056400	-1.81276200	2.42120800
O	2.50133200	0.19731400	0.88693400



C	-2.49651900	0.05097600	0.57112100
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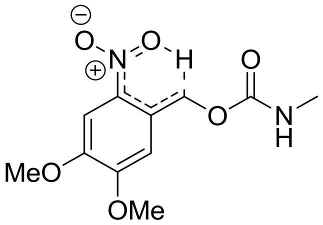
C	-0.66222900	1.43014200	-0.14420300
C	-0.13604400	0.37353100	-0.88983200
C	-0.79273900	-0.86222800	-0.89021600
C	-1.96350600	-1.03922300	-0.16504400
N	-0.03158400	2.66674600	-0.09759000
O	-0.49740100	3.68913100	0.46008900
C	1.12044900	0.57462200	-1.67007500
O	1.06994300	2.90901800	-0.80075200
H	-2.25656500	2.09295800	1.15713900
H	-0.35823600	-1.67865200	-1.45656900
H	1.38927500	1.73997700	-1.38466300
H	1.01926500	0.53757400	-2.75545900
O	2.18230300	-0.28194200	-1.34473700
O	-3.62335800	-0.11792300	1.31857300
O	-2.65897500	-2.19957500	-0.08256400
C	-2.12605500	-3.32161800	-0.75373100
H	-1.12555900	-3.56637800	-0.37815100
H	-2.80536200	-4.14768800	-0.54673500
H	-2.07621500	-3.15085500	-1.83593600
C	-4.81978500	-0.22981600	0.55613800
H	-4.78988200	-1.10467500	-0.09921900
H	-5.63033900	-0.33842500	1.27713300
H	-4.97833900	0.67655900	-0.03973300
C	2.61781100	-0.23473400	-0.05709800
O	2.24853600	0.56219200	0.75623900
S	3.80862400	-1.51690900	0.19371300
C	4.17433300	-1.13371100	1.92838000
H	3.27201400	-1.22497100	2.53247800
H	4.92025400	-1.85914800	2.25514100
H	4.57265500	-0.12291900	2.01336300



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C	-1.52766000	1.35878900	0.53406900
C	-0.29816400	1.37256200	-0.14448200
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N	0.44992100	2.54336900	-0.11484700
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C	1.44657700	0.28537900	-1.56796700
O	1.58674400	2.65505700	-0.79010500
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H	1.37011500	0.22841100	-2.65517000
O	2.39863400	-0.66064600	-1.18774400
O	-3.45751500	0.18479500	1.24227300
O	-2.66249800	-2.03019400	-0.05654100
C	-2.22900200	-3.21772200	-0.68228100
H	-1.27556800	-3.55969000	-0.26219700
H	-3.00045800	-3.96173700	-0.48656400
H	-2.11926400	-3.08035300	-1.76506300
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H	3.86347200	-2.25252100	-0.38062300
C	4.28167800	-1.78540400	1.66889800
H	5.33883200	-1.51053200	1.59809900
H	3.78849000	-1.11201600	2.36982300
H	4.19936900	-2.81042800	2.03734900

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