

Diethyl (5-benzyl-2-(4-(N'-hydroxycarbamimidoyl)phenyl)-5-methyl-4,5-dihydrofuran-3-yl)phosphonate

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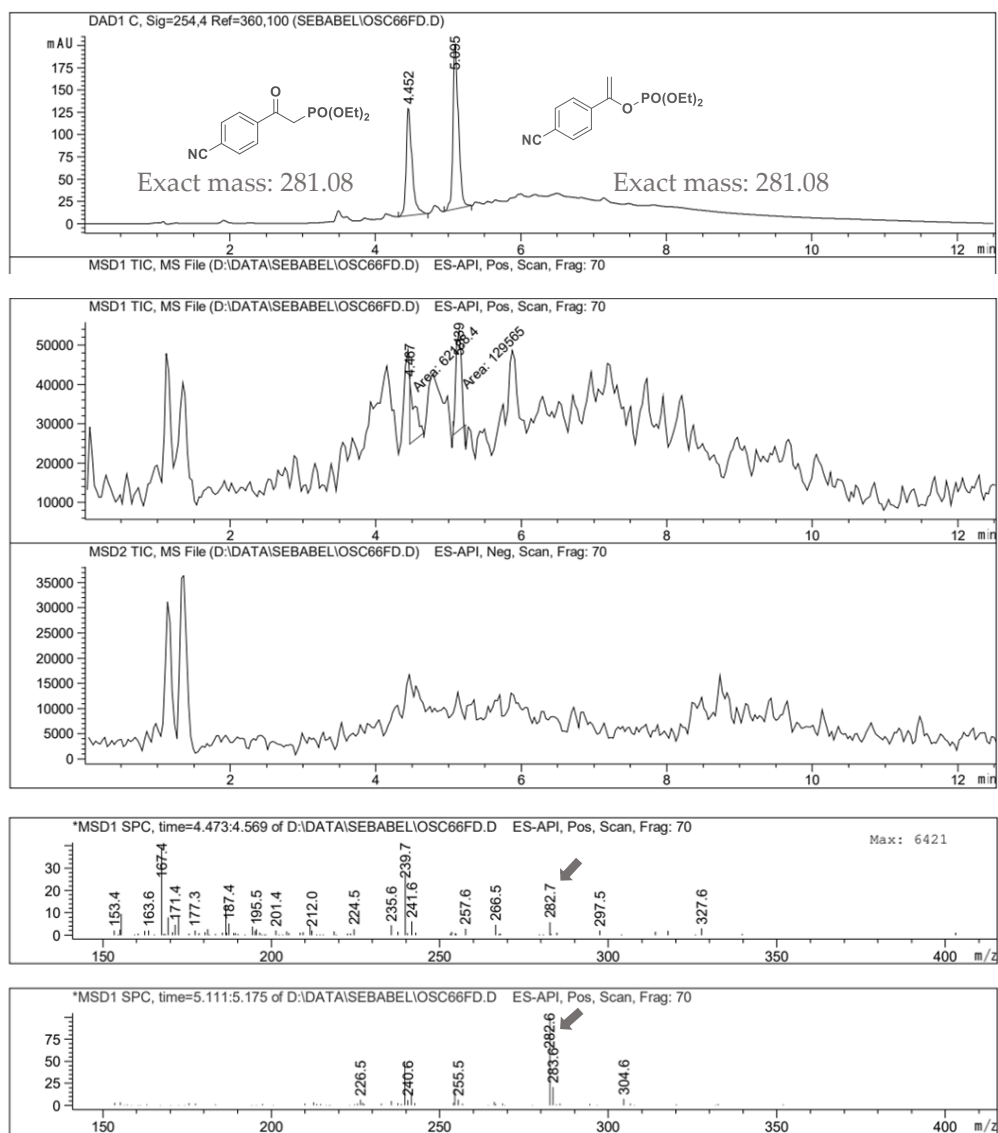


Figure S1 LC/MS of 2 and 2'

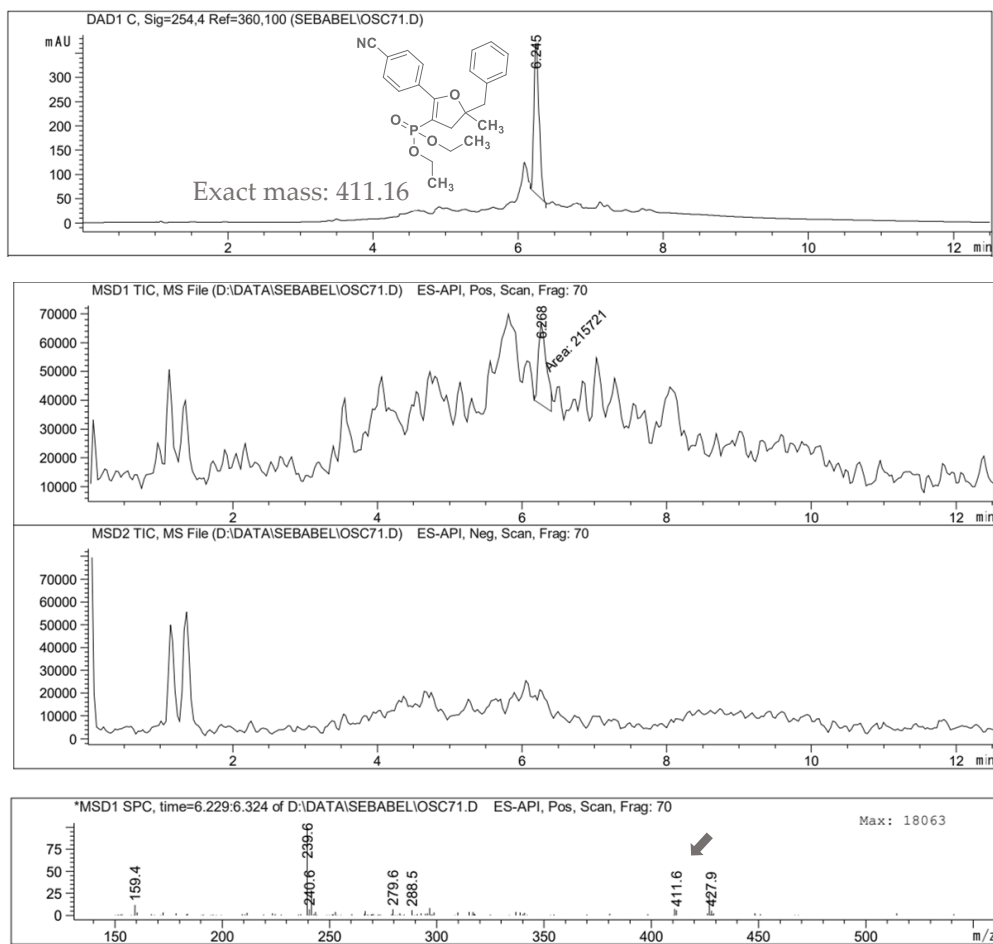


Figure S2 LC/MS of 3

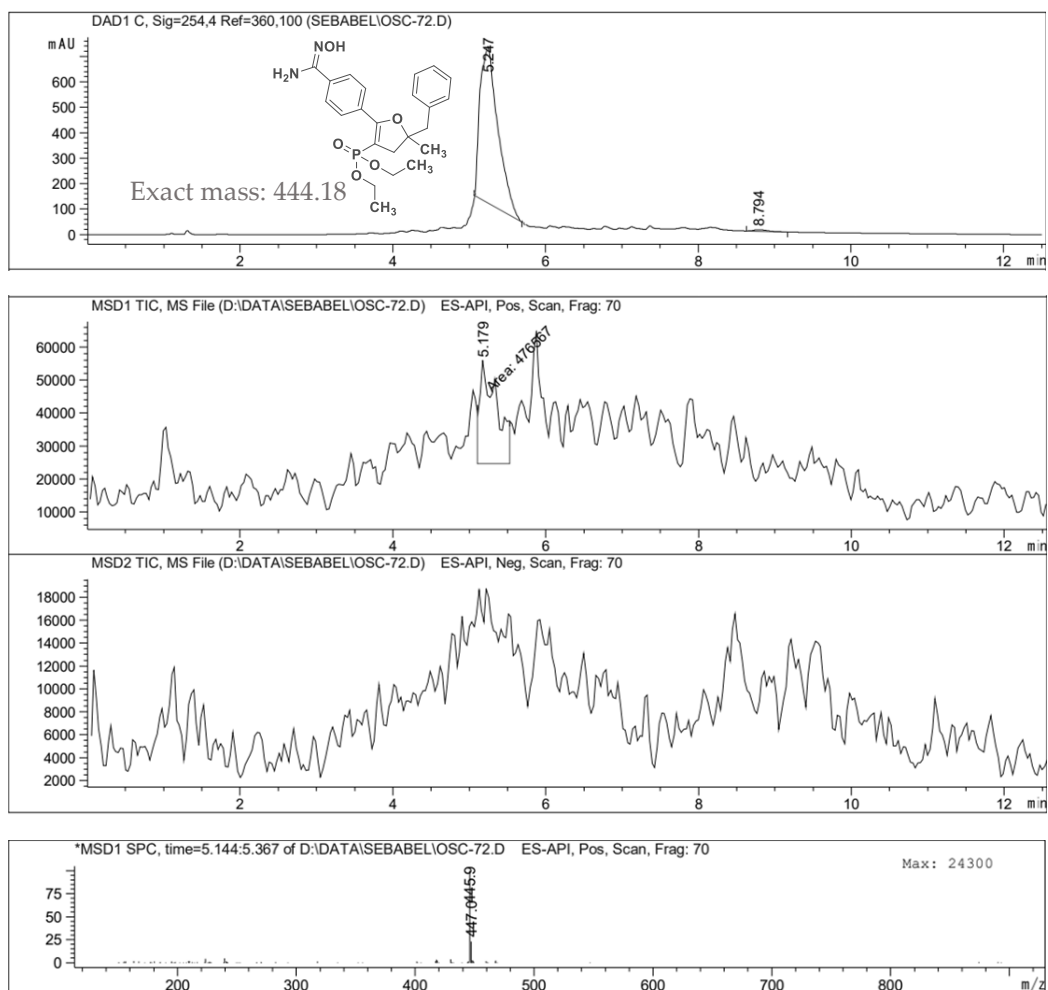


Figure S3 LC/MS of A

Osc-72_Mex2 14 (0.352)

1: TOF MS ES+
2.01e7

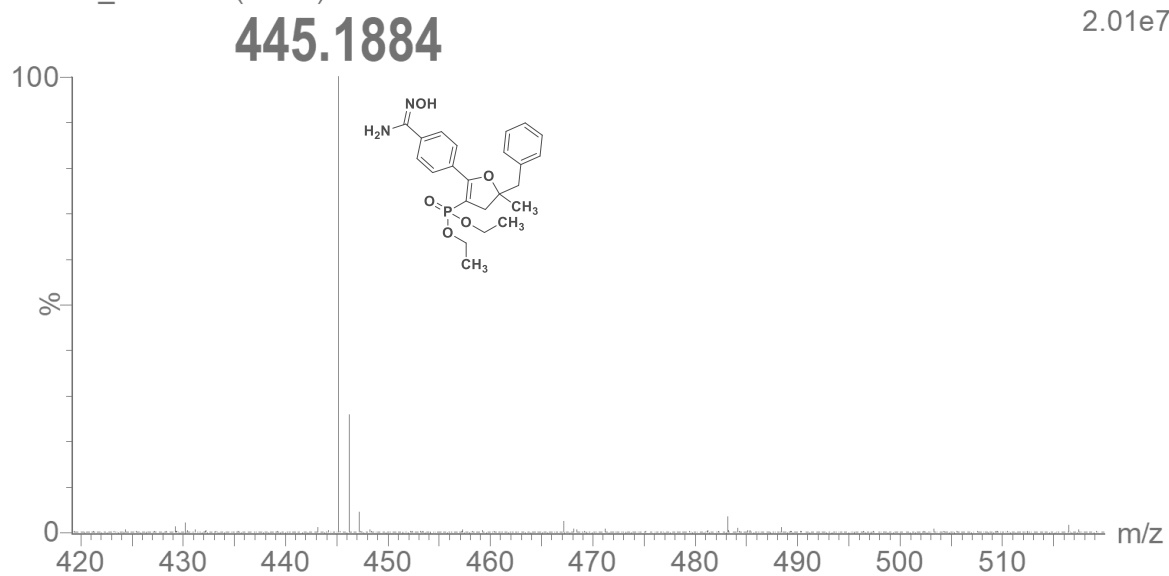


Figure S4 HRMS spectra of A

Diethyl (2-(4-cyanophenyl)-2-oxoethyl)phosphonate (**2**)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.12 (d, $^3J_{\text{H-H}} = 8.8$ Hz, 2H, 2CH_{Ar}), 7.78 (d, $^3J_{\text{H-H}} = 8.7$ Hz, 2H, 2CH_{Ar}), 4.18-4.09 (m, 4H, 2CH_2), 3.63 (d, $^3J_{\text{H-H}} = 22.9$ Hz, 2H, CH_2), 1.28 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 6H, 2CH_3).

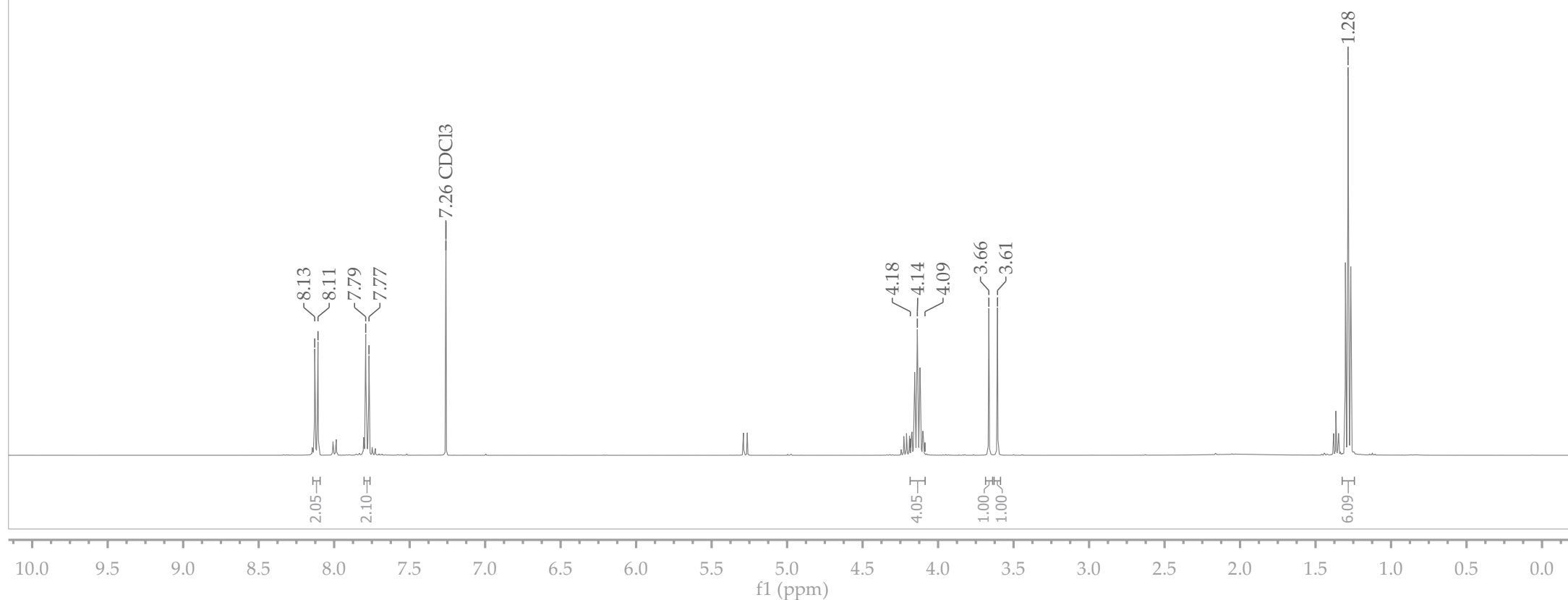
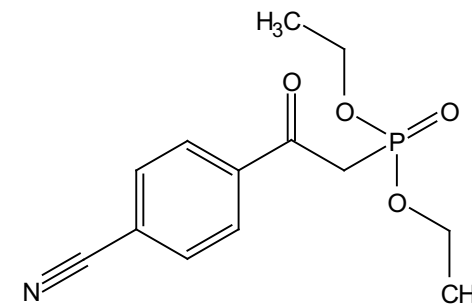


Figure S5: ^1H NMR spectra of compound **2**

1. Zhou, P.; Hu, B.; Li, L.; Rao, K.; Yang, J.; Yu, F. $\text{Mn}(\text{OAc})_3$ -Promoted Oxidative C_{sp}^3 -P Bond Formation through C_{sp}^2 - C_{sp}^2 and P-H Bond Cleavage: Access to β -Ketophosphonates. *J. Org. Chem.* **2017**, *82*, 13268–13276, doi:10.1021/acs.joc.7b02391.

2. Zhou, M.; Chen, M.; Zhou, Y.; Yang, K.; Su, J.; Du, J.; Song, Q. β -Ketophosphonate Formation via Aerobic Oxyphosphorylation of Alkynes or Alkynyl Carboxylic Acids with H-Phosphonates. *Org. Lett.* **2015**, *17*, 1786–1789, doi:10.1021/acs.orglett.5b00574.

Diethyl (2-(4-cyanophenyl)-2-oxoethyl)phosphonate (**2**)

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 190.9 (C), 139.5 (C), 132.6 (2CH_{Ar}), 129.6 (2CH_{Ar}), 117.9 (C), 117.0 (C), 63.1 (d, $J = 6.8$ Hz, 2CH_2), 39.2 (d, $J = 131.5$ Hz, CH_2), 16.3 (d, $J = 6.0$ Hz, 2CH_3).

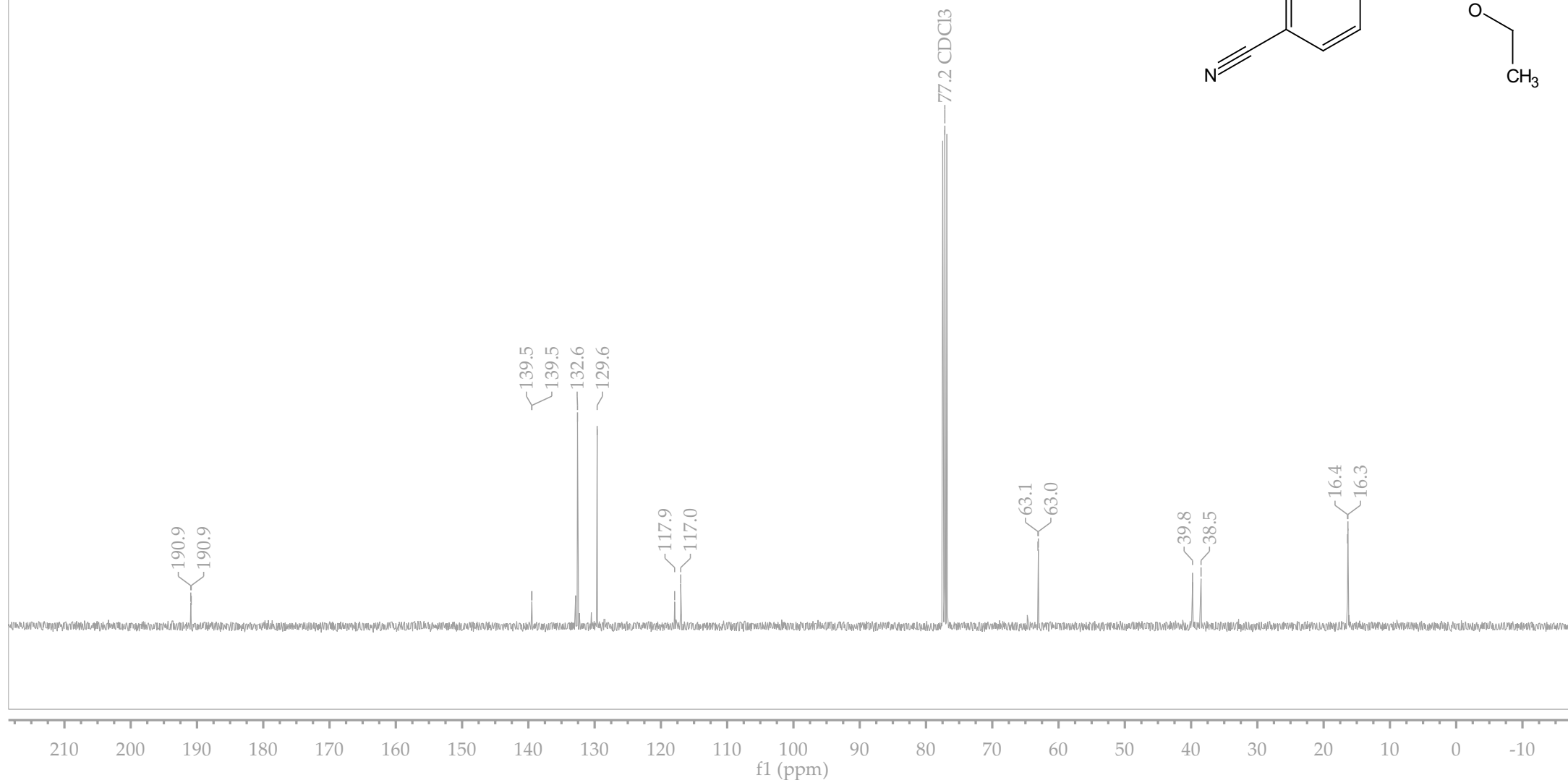
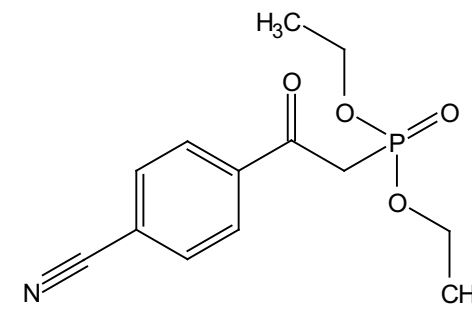


Figure S6: ^{13}C NMR spectra of compound **2**

1. Zhou, P.; Hu, B.; Li, L.; Rao, K.; Yang, J.; Yu, F. $\text{Mn}(\text{OAc})_3$ -Promoted Oxidative C_{sp}^3 -P Bond Formation through C_{sp}^2 - C_{sp}^2 and P-H Bond Cleavage: Access to β -Ketophosphonates. *J. Org. Chem.* **2017**, *82*, 13268–13276, doi:10.1021/acs.joc.7b02391.
2. Zhou, M.; Chen, M.; Zhou, Y.; Yang, K.; Su, J.; Du, J.; Song, Q. β -Ketophosphonate Formation via Aerobic Oxyphosphorylation of Alkynes or Alkynyl Carboxylic Acids with H-Phosphonates. *Org. Lett.* **2015**, *17*, 1786–1789, doi:10.1021/acs.orglett.5b00574.

1-(4-Cyanophenyl)vinyl diethyl phosphate (**2'**)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.72-7.62 (m, 4H, 4 CH_{Ar}), 5.45-5.38 (m, 2H, CH_2), 4.29-4.15 (m, 4H, 2 CH_2), 1.35 (td, $J_{\text{H-H}} = 1.2$ Hz, $J_{\text{H-H}} = 7.2$ Hz, 6H, 2 CH_3).

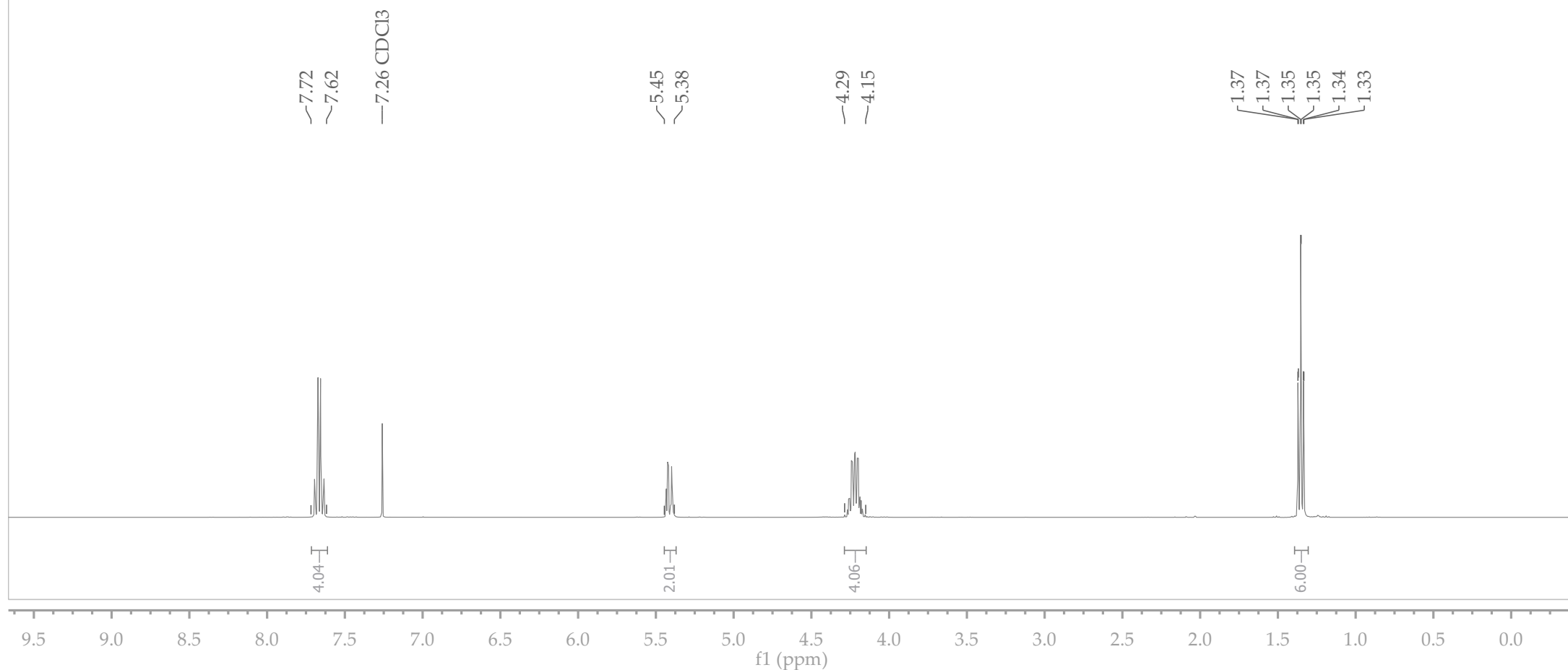
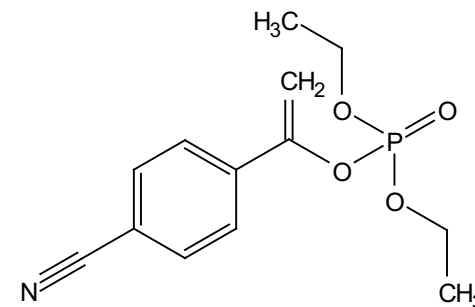


Figure S7: ^1H NMR spectra of compound **2'**

1-(4-Cyanophenyl)vinyl diethyl phosphate (2')

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 150.7 (d, $J = 7.4$ Hz, C), 138.7 (d, $J = 6.6$ Hz, C), 132.4 (2CH_{Ar}), 125.9 (2CH_{Ar}), 118.6 (C), 112.7 (C), 100.7 (d, $J = 3.7$ Hz, CH_2), 65.0 (d, $J = 6.2$ Hz, 2CH_2), 16.2 (d, $J = 6.8$ Hz, 2CH_3).

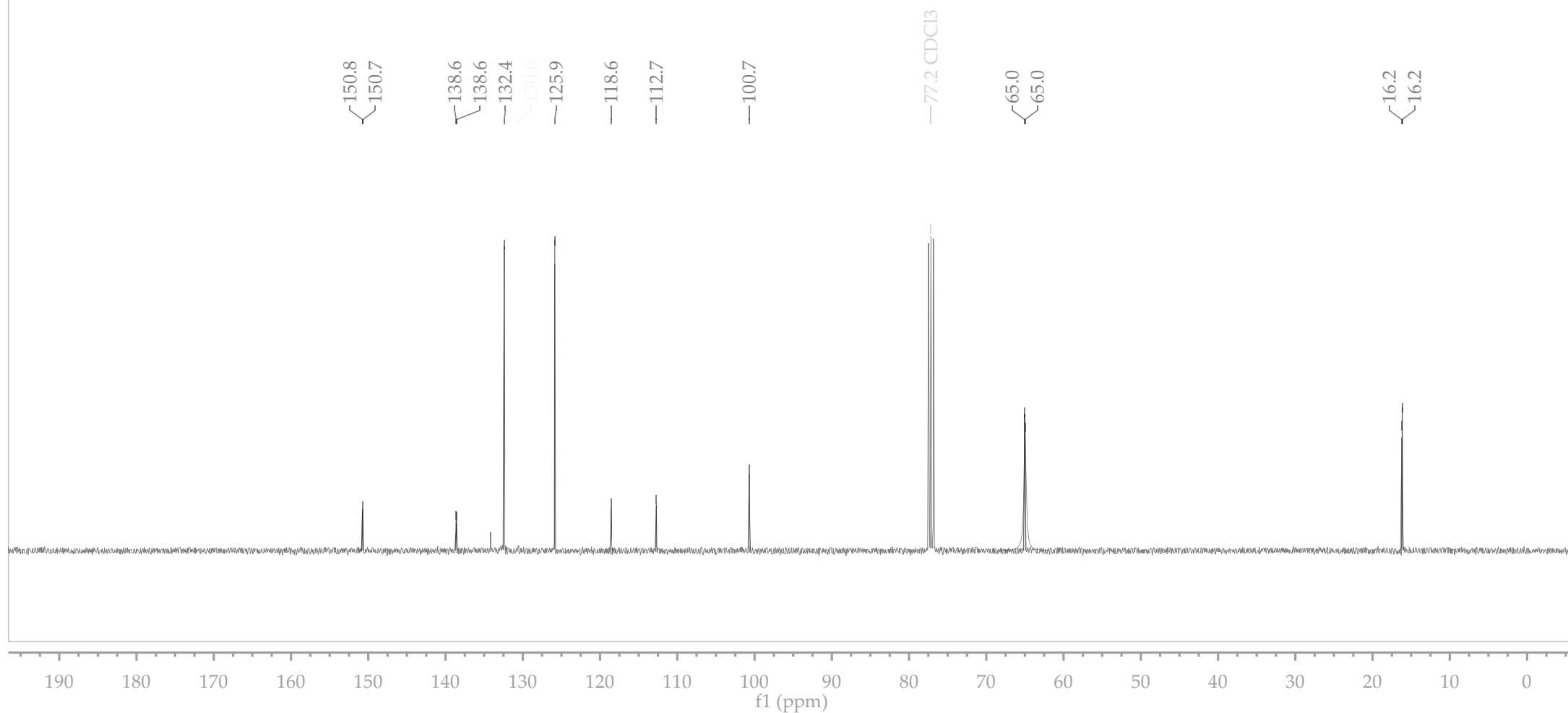
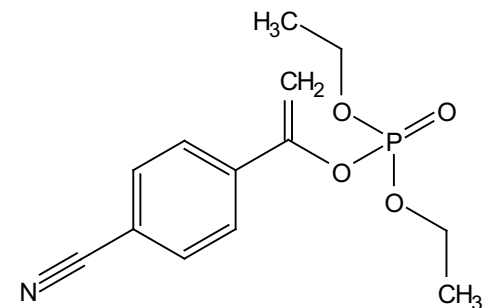


Figure S8: ^{13}C NMR spectra of compound 2'

Diethyl (5-benzyl-2-(4-(*N'*-hydroxycarbamimidoyl)phenyl)-5-methyl-4,5-dihydrofuran-3-yl)phosphonate (**3**)

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.91 (d, $^3J_{\text{H-H}} = 8.7$ Hz, 2H, 2CH_{Ar}), 7.65 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 2H, 2CH_{Ar}), 7.31-7.19 (m, 5H, CH), 3.97-3.68 (m, 4H, 2CH_2), 3.06 (dd, $^4J_{\text{H-H}} = 3.4$ Hz, $^2J_{\text{H-H}} = 15.3$ Hz, 1H, H-(CH_2)), 3.00 (dd, $^4J_{\text{H-H}} = 14.1$ Hz, $^2J_{\text{H-H}} = 40.1$ Hz, 2H, H-(CH_2)), 2.80 (dd, $^4J_{\text{H-H}} = 3.3$ Hz, $^2J_{\text{H-H}} = 15.5$ Hz, 1H, H-(CH_2)), 1.50 (s, 3H, CH_3), 1.18 (t, $^3J_{\text{H-H}} = 7.0$ Hz, 3H, CH_3), 1.13 (t, $^3J_{\text{H-H}} = 7.0$ Hz, 3H, CH_3).

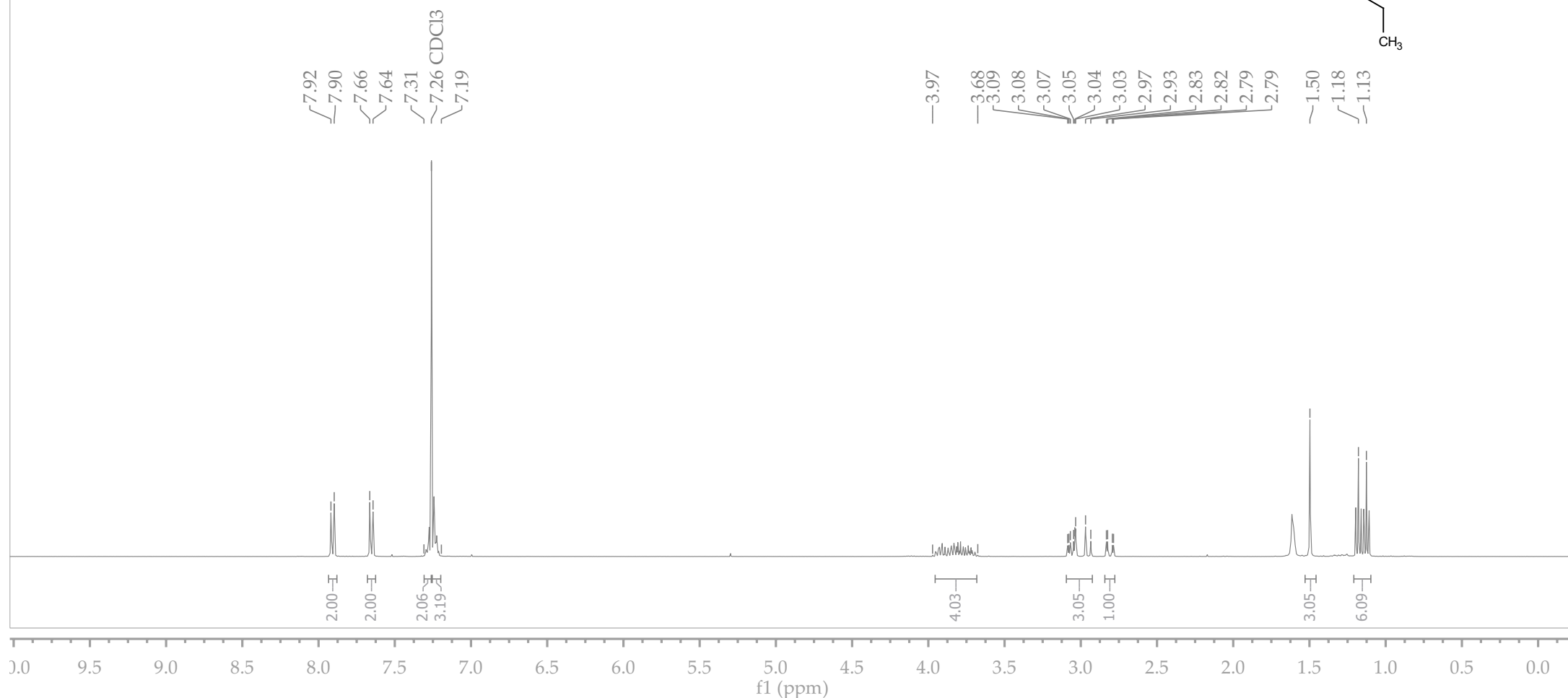
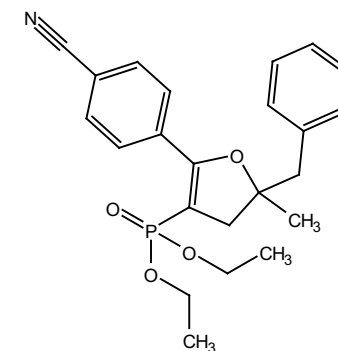


Figure S9: ^1H NMR spectra of compound **3**

Diethyl (5-benzyl-2-(4-(*N'*-hydroxycarbamimidoyl)phenyl)-5-methyl-4,5-dihydrofuran-3-yl)phosphonate (**3**)

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 161.7 (d, $J = 26.2$ Hz, C), 136.5 (C), 134.5 (C), 131.7 (2CH_{Ar}), 130.6 (2CH_{Ar}), 129.6 (2CH_{Ar}), 128.4 (2CH_{Ar}), 127.0 (CH_{Ar}), 118.7 (C), 113.6 (C), 97.3 (d, $J = 213.8$ Hz, C), 88.1 (d, $J = 11.8$ Hz, C), 61.7 (t, $J = 6.3$ Hz, 2CH_2), 46.8 (CH_2), 44.3 (d, $J = 8.6$ Hz, CH_2), 27.1 (CH_3), 16.3 (t, $J = 6.4$ Hz, 2CH_3).

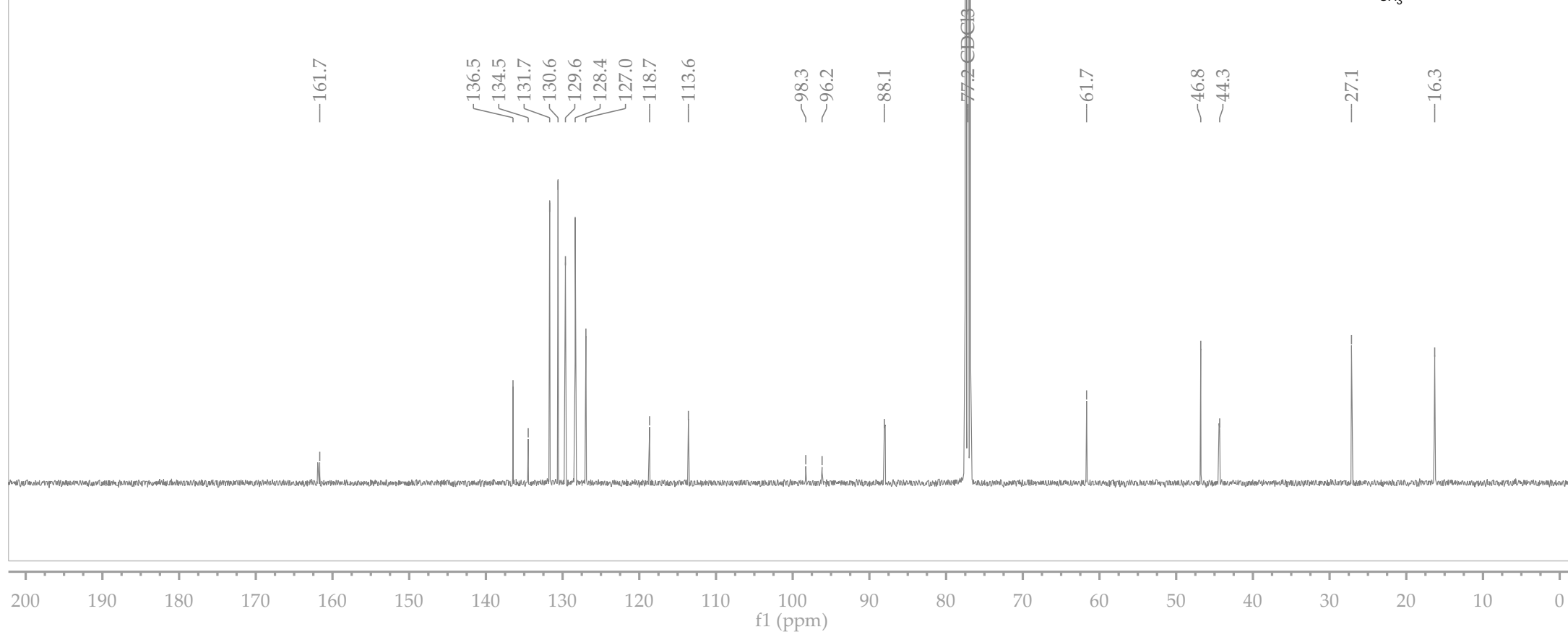
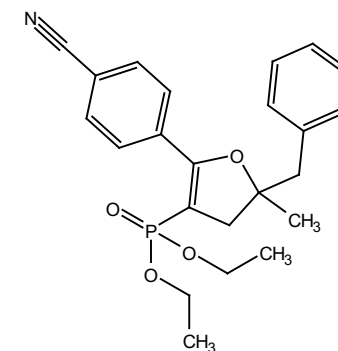


Figure S10: ^{13}C NMR spectra of compound **3**

Diethyl (5-benzyl-2-(4-(*N*'-hydroxycarbamimidoyl)phenyl)-5-methyl-4,5-dihydrofuran-3-yl)phosphonate (**A**)

^1H NMR (400 MHz, DMSO- d_6) δ (ppm) 9.82 (s, 1H, OH), 7.77-7.66 (m, 4H, 4CH_{Ar}), 7.33-7.17 (m, 5H, 5CH_{Ar}), 5.96 (br s, 2H, NH₂), 3.83-3.68 (m, 2H, CH₂), 3.65-3.54 (m, 2H, CH₂), 3.01 (q, $J_{\text{H-H}} = 16.5$ Hz, 2H, CH₂), 2.93 (dd, $^4J_{\text{H-H}} = 2.9$ Hz, $^2J_{\text{H-H}} = 15.2$ Hz, 1H, H-(CH₂)), 2.70 (dd, $^4J_{\text{H-H}} = 2.8$ Hz, $^2J_{\text{H-H}} = 15.3$ Hz, 1H, H-(CH₂)), 1.44 (s, 3H, CH₃), 1.08 (t, $^3J_{\text{H-H}} = 7.0$ Hz, 3H, CH₃), 1.01 (t, $^3J_{\text{H-H}} = 7.0$ Hz, 3H, CH₃).

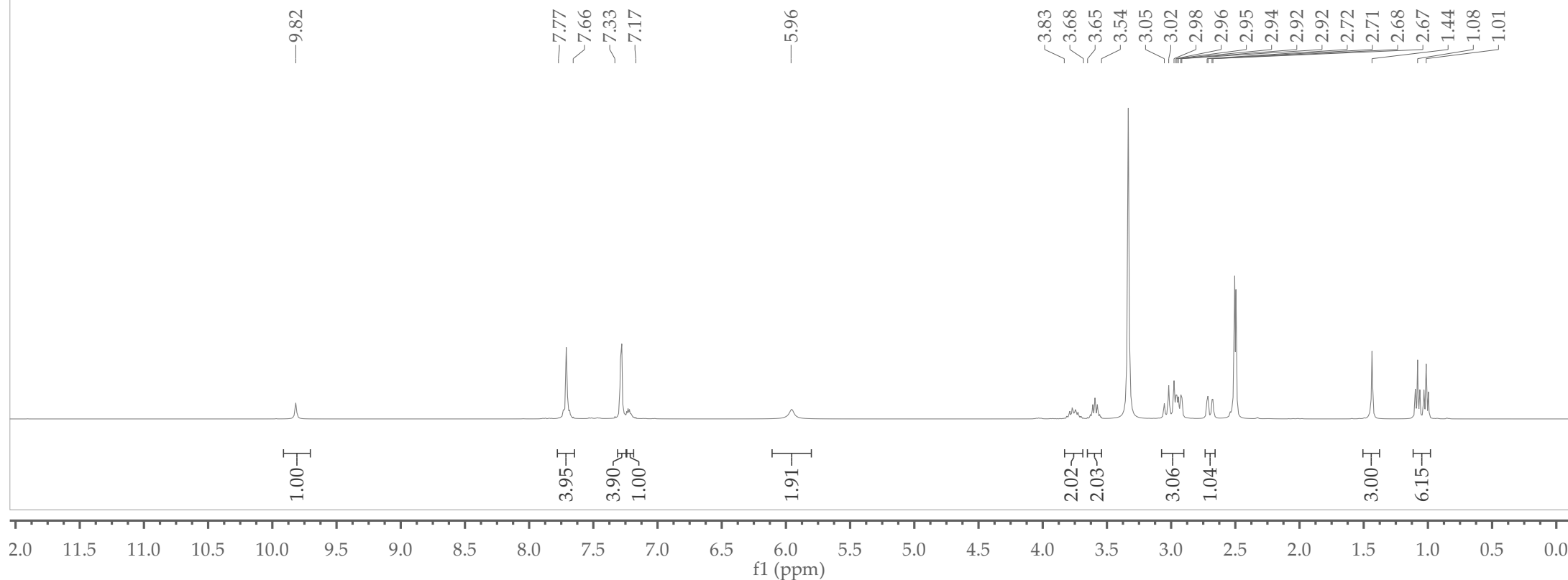
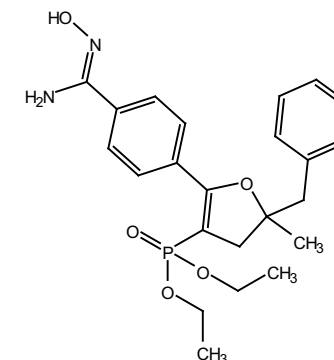


Figure S11: ^1H NMR spectra of compound A

Diethyl (5-benzyl-2-(4-(*N*'-hydroxycarbamimidoyl)phenyl)-5-methyl-4,5-dihydrofuran-3-yl)phosphonate (**A**)

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 163.5 (d, $J = 26.2$ Hz, C), 152.5 (C), 136.6 (C), 133.6 (C), 131.8 (C), 130.6 (2 CH_{Ar}), 129.2 (2 CH_{Ar}), 128.3 (2 CH_{Ar}), 126.8 (CH_{Ar}), 125.4 (2 CH_{Ar}), 94.8 ((d, $J = 214.7$ Hz, C), 87.6 (d, $J = 11.8$ Hz, C), 61.6 (t, $J = 6.3$ Hz, 2 CH_2), 46.8 (CH_2), 44.3 (d, $J = 8.6$ Hz, CH_2), 27.1 (CH_3), 16.3 (t, $J = 6.4$ Hz, 2 CH_3).

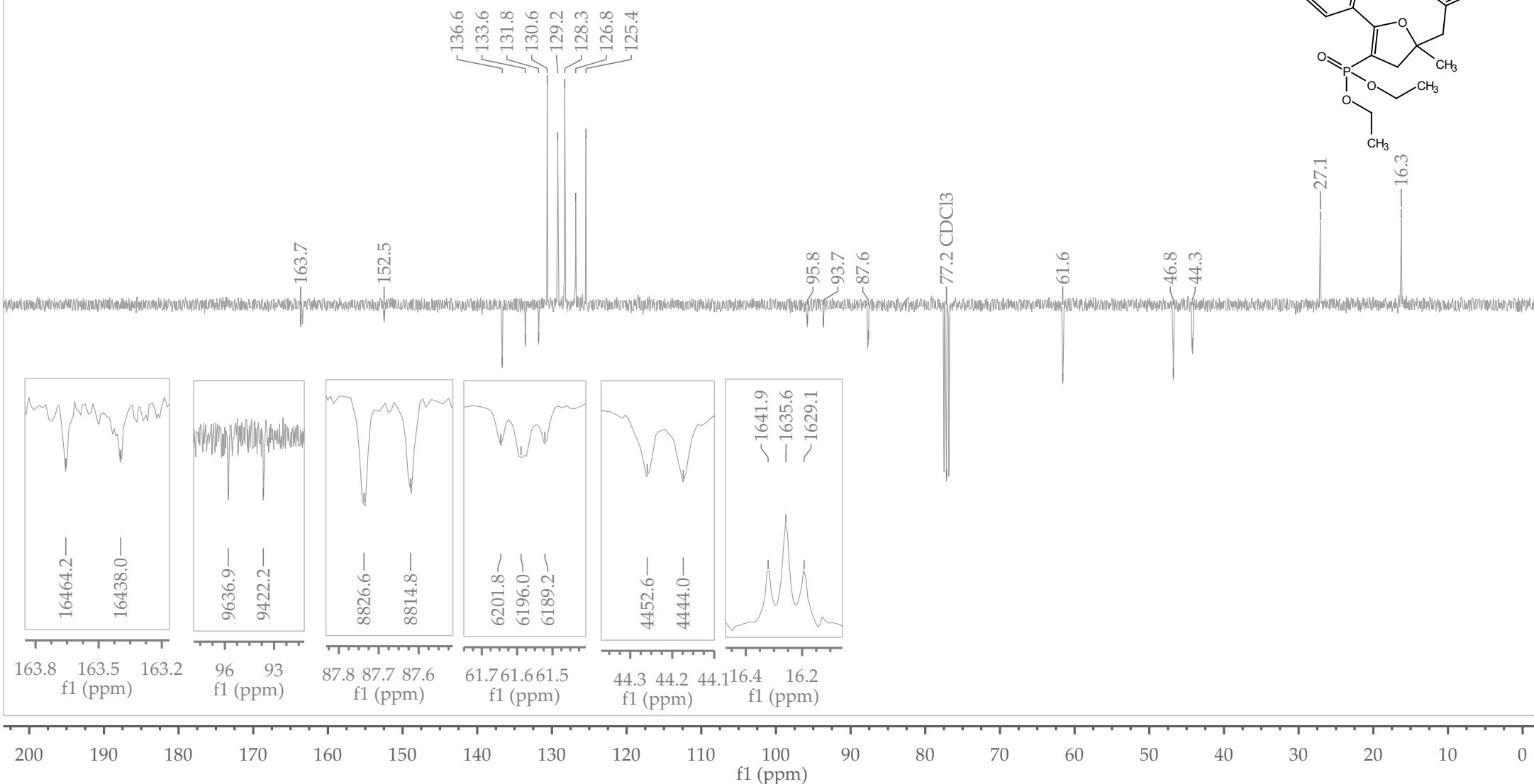
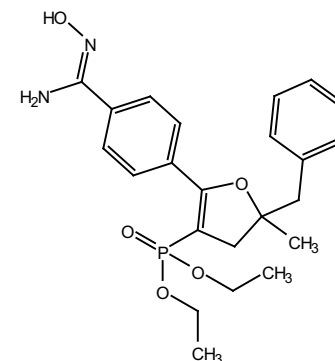


Figure S12: ^{13}C NMR spectra of compound **A**