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Supporting Information for:

Highly efficient one-pot multi-component synthesis of α-aminophosphonates and bis-α–aminophosphonates catalyzed by heterogeneous reusable silica supported dodecatungstophosphoric acid (DTP/SiO_2) at ambient temperature and their antitubercular evaluation against *Mycobactrium Tuberculosis*

Shafeek A. R. Mulla*[a], Mohsinkhan Y. Pathan[a] Santosh S. Chavan[a], Suwarna P. Gample[b], Dhiman Sarkar[b]

[a]Chemical Engineering & Process Development Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India.
[b]Combi. Chem. Bio. Resource Center, Organic Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India.
*Corresponding author Tel: +91 20 25902316
Fax: +91 20 25902676
E-mail: sa.mulla@ncl.res.in

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1. General experimental details

All chemicals and reagents required for the reactions were procured from Sigma-Aldrich with purity >98% and used without further purification. All reactions were monitored by TLC. TLC was performed on 0.25 mm E. Merck pre-coated silica gel plates (60F254). Column chromatography was performed on silica gel, Merck grade 60–120 mesh size. The products were characterized using ^{1}HNMR, ^{13}C NMR and mass spectra. NMR spectra were recorded on Bruker AC-200 spectrometers. Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Mass spectra were recorded by MALDI TOF/ TOF and Electron Spray Ionization (ESI).

2. General Procedure for the preparation of DTP/SiO_2

DTP impregnated SiO_2 (20% DTP/SiO_2) catalyst was prepared by a incipient wetness technique[1] as follows.

2 g of dry dodecatungstophosphoric acid (DTP) was weighed accurately. This was dissolved in 8 ml of methanol. The solution was added in small aliquots of 1 ml each time to the silica with constant stirring with a glass rod properly. The solution was added at time intervals of 2 min. Initially on addition of the DTP solution, silica was in a powdery form but on complete addition it formed a paste. The paste on further kneading for 10 min resulted in a free flowing powder. The performed catalyst was dried at 120 ^{o}C for removal of water and other occluded volatiles and subsequently calcined at 285 ^{o}C for 3 h.

3. General experimental procedure for 20% DTP/SiO_2 mediated synthesis of α-aminophosphonates

The reaction mixture of aldehyde (10 mmol), amine (10 mmol) and Di/Tri alkyl phosphite (10 mmol) were stirred in 10 ml round bottom flask containing 5 ml acetonitrile solvent in the presence of 50 mg (0.35 mol%) 20% DTP/SiO_2 catalyst at room temperature for 1 h. The completion of the reaction was monitored by TLC. After completion of reaction, reaction mixture was diluted with ethyl acetate (10 ml) and catalyst was recovered by filtration. The filtrate was washed with aqueous $NaHCO_3$ and then with water followed by separation of aqueous layer and organic layer. The organic layer is dried over anhydrous Na_2SO_4 and concentrate in vacuum to gives the crude product. The crude product was purified by silica gel column chromatography using 70:30 ratio of pet ether/ethyl acetate to afford the pure α-amino phosphonates.

4. Antitubercular testing using XTT Reduction menadione assay protocol

M. *tuberculosis* H37Ra (ATCC 25177) were grown to logarithmic phase ($O.D._{595}$~1.0) in a defined medium *(M. pheli* medium). The stock culture was maintained at -70 ^{0}C and sub-cultured once in *M. pheli* medium before inoculation into experimental culture. Isoniazid, ethambutol and pyrazinamide were procured from Sigma. Drugs were solubilized in dimethyl sulfoxide (DMSO) and stored in aliquots at -20 °C. XTT sodium salt powder (Sigma) was prepared as a 1.25 mM stock solution in sterile Ix PBS and used immediately. Menadione (Sigma) was always freshly prepared as a 6 mM solution in DMSO before use. Compounds were screened for their inhibitory effect on MTB by following XTT Reduction Menadione Assay (XRMA) protocol published earlier. Briefly,

2.5 µl of these inhibitor solutions were added in a total volume of 250 µl of *M. pheli* medium consisting of 1x 10^6 bacilli. The incubation was terminated on the 8th day for MTB cultures. The XRMA was then carried out to estimate viable cells present in different wells of the assay plate. For that, in all wells of assay plate 200 µM XTT was added as a final concentration and incubated at 37 ^{0}C for 20 minutes. Then 60 µM Menadione was added as a final concentration and incubated at 37 ^{0}C for 40 minutes. The optical density was read on a micro plate reader (Spectramax plus 384 plate reader, Molecular Devices Inc) at 490 nm filter against a blank prepared from cell-free wells. Absorbance given by cells treated with the vehicle alone was taken as 100% cell growth. All experiments were performed in triplicates and the quantitative value was expressed as the average ± standard deviation and IC_{50} values were calculated from their dose response curves. For details: Sarkar D., Sing U., *J. Micro. Methods*, **211**, 84, 202.

5. Cytotoxicity evaluation using MTT Reduction menadione assay protocol :

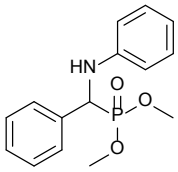
Cytotoxicity of compounds was tested for their inhibitory effect on THP-1 (Acquired from NCCS). In case of THP-1, cells were grown in RPMI medium. About 10,000 cells were taken per well in 96-well tissue culture plates and treated with different concentrations of test samples for 72 h. Vehicle control [dimethyl sulfoxide (DMSO), 1%] were run simultaneously. Cell viability was assessed with 10 ml from 5 mg/ml stock solution of tetrazolium salt (MTT) dissolved in cell culture medium and subsequently incubated for additional 1 h at 37 °C, 5% of CO_2 and 95% humidity in incubator. The violet colored formazan crystals formed were solubilized in 200 ml of isopropanol and incubated for another 4 h. The optical density was read on a micro plate reader at 49 nm

filter against a blank prepared from cell-free wells.

All experiments were out in triplicate, and the quantitative value was expressed as the average+ standard deviation.

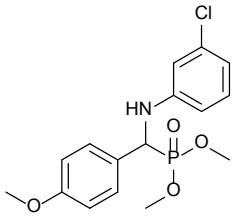
6. Spectral data for the products

Dimethyl phenyl(phenylamino)methylphosphonate[2a] (4a)



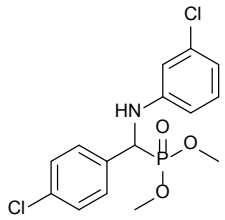
White solid; mp: 91-93 °C; ^{1}H NMR (200 MHz, Acetone d_6): δ= 7.37-7.36 (m, 2H), 7.24-7.19 (m, 3H), 6.97-6.93 (m 2H), 6.56-6.45 (m, 3H), 4.80 (br s, 1H), 4.72 (d, *J*=24 Hz, 1H), 3.68 (d, *J*=10 Hz, 3H), 3.34 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, Acetone d_6): δ= 148.5, 138.1, 130.1, 129.5, 128.8, 118.7, 115.0, 57.4, 54.3.

Dimethyl (((3-chlorophenyl)amino)(4-methoxyphenyl)methylphosphonate (4b)



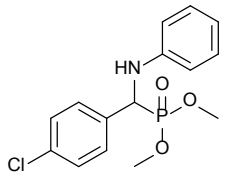
Yellow solid; mp: 92-94 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.45-7.27 (m, 4H), 6.66-6.49 (m, 4H), 4.70 (d, *J*=24 Hz, 1H), 4.25 (br s, 1H), 3.75 (d, *J*=10 Hz, 3H), 3.65 (s, 3H), 3.45 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 153.4, 140.8, 140.4, 136.4, 136.3, 129.2, 128.6, 128.5, 128.4, 115.9, 115.3, 58.7, 55.9, 54.2.; MALDI TOF/TOF m/z calcd for $C_{16}H_{19}ClNO_4P$ [M+] 355.07, observed 354.91.

Dimethyl ((4-chlorophenyl)(3-chlorophenyl)amino)methyl)phosphonates[2a] (4c)



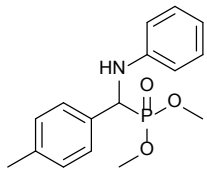
Yellow solid; mp: 134-136 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.41-7.40 (m, 1H), 7.39-7.30 (m, 2H), 7.10-7.05 (m, 2H), 6.70-6.56 (m, 1H), 6.56-6.50 (m, 2H), 4.80 (br s, 1H), 4.69 (s, 1H), 3.78 (d, *J*=10 Hz, 3H), 3.54 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 151.9, 151.7, 137.0, 134.0, 127.6, 127.2, 127.1, 126.9, 124.7, 111.3, 54.9, 52.8, 52.6.

Dimethyl (4-chlorophenyl) (phenylamino)methylphosphonate[2a] (4d)



White solid; mp: 112-114 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.42-7.28 (m, 4H), 7.08-7.04 (m, 2H), 6.69 (t, *J*=7.02 Hz, 1H), 6.55-6.50 (m, 2H), 4.78 (br s, 1H), 4.67 (d, *J*=21 Hz, 1H), 3.79 (d, *J*=10 Hz, 3H), 3.55 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 145.9, 134.3, 129.3, 129.2, 129.0, 118.9, 113.9, 56.8, 53.8.

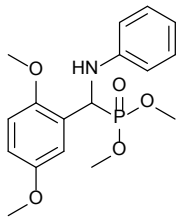
Dimethyl (phenylamino)(p-tolyl)methylphosphonate)[2b] (4e)



White solid; mp: 122-124 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.34-7.30 (m, 2H), 7.14-7.03 (m, 4H), 6.69-6.52 (m, 3H), 4.79 (s, 1H), 4.77 (d, *J*=21 Hz, 1H), 3.75 (d, *J*=10 Hz,

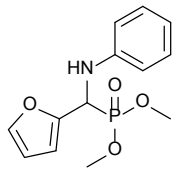
3H), 3.45 (*d*, *J*=10 Hz, 3H), 2.32 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 146.0, 137.6, 132.6, 129.5, 129.2, 127.8, 118.6, 113.9, 57.0, 53.8, 21.3; MALDI TOF/TOF m/z calcd for $C_{16}H_{20}NO_3P$ [M + K^+] 344.12, observed 344.02.

Dimethyl (2,5-dimethoxy phenyl)(phenylamino)methylphosphonate[2c] (4f)



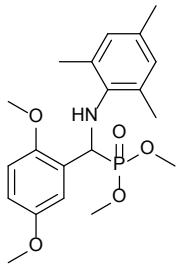
White solid; mp: 134-136 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.11-7.01 (m, 3H) 6.79-6.55 (m, 5H) 5.40 (d, *J*=24 Hz, 1H), 4.78 (br s, 1H), 3.90 (s, 3H), 3.84 (d, *J*=10 Hz, 3H), 3.71 (s, 3H), 3.46 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 146.2, 145.90, 135.7, 129.0, 128.6, 127.8, 118.4, 113.7, 57.1, 54.1, 53.5; MALDI TOF/TOF m/z calcd for $C_{17}H_{22}NO_5P$ [M + K^+] 390.12, observed 390.02.

Dimethyl (furan-2-yl)(phenylamino)methylphosphonate)[2a] (4g)



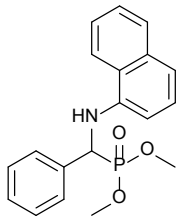
Black solid; mp: 102-105 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.30 (s, 1H), 7.04-6.67 (m, 2H), 6.64-6.54 (m, 3H), 6.31-6.22 (m, 2H), 4.88 (d, *J*=24 Hz, 1H), 4.54 (br s, 1H), 3.75 (d, *J*=10 Hz, 3H), 3.55 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 149.1, 145.7, 142.4, 129.1, 118.9, 133.8, 110.7, 108.9, 53.7, 53.4, 51.3, 48.1.

Dimethyl (mesitylamino)(2,5-dimethoxyphenyl)methylphosphonate[2d] (4h)



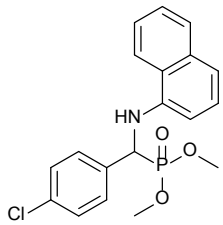
White solid; mp: 109-111 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 6.82-6.72 (m, 5H), 5.01 (d, *J*=23 Hz, 1H), 4.29 (br s, 1H), 3.86-3.67 (m, 9H), 3.46 (d, *J*=10 Hz, 3H), 2.24-2.14 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 153.8, 141.9, 130.5, 129.5, 128.9, 128.3, 114.4, 112.2, 56.4, 55.5, 29.8, 20.6, 18.6.

Dimethyl (napthalen-1-ylamino)(phenyl)methylphosphonate[2d] (4i)



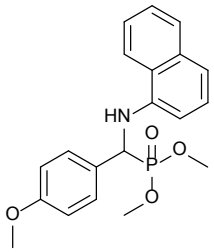
White solid; mp: 128-130 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 8.00-7.52 (m, 1H), 7.56-7.49 (m,1H), 7.48-7.47 (m, 4H), 7.33-7.29 (m, 3H), 7.18-7.13 (m, 2H), 6.36 (d, *J*=8 Hz, 1H), 5.00 (d, *J*=24 Hz, 1H), 3.82 (d, *J*=10 Hz, 3H), 3.52 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 159.5, 141.3, 134.3, 128.7, 126.9, 126.2, 125.8, 125.1, 124.1, 120.1, 118.8, 114.2, 106.6, 56.8, 55.00.

Dimethyl (4-chlorophenyl)(naphthalene-1-ylamino)methylphosphonate (4j)



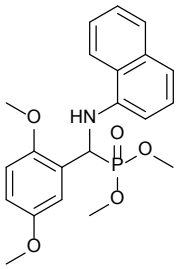
White solid; mp: 127-129 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.96 (d, *J*=7 Hz, 1H), 7.78-7.74 (m, 1H), 7.44-7.42 (m, 4H), 7.32-7.13 (m, 4H), 6.32 (d, *J*=7 Hz, 1H), 5.40 (s, 1H), 4.94 (d, *J*=24 Hz, 1H), 3.80 (d, *J*=10 Hz, 3H), 3.58 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 140.7, 134.1, 129.0, 128.9, 128.8, 125.9, 125.3, 124.1, 119.9, 119.2, 106.7, 57.1, 54.1; MALDI TOF/TOF m/z calcd for $C_{19}H_{19}ClNO_3P$ [M +] 375.07, observed 375.02.

Dimethyl (4-methoxyphenyl)(naphthalene-1-ylamino)methylphosphonate[2e] (4k)



White solid; mp: 113-115 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.98-7.91 (m, 1H), 7.76-7.12 (m, 1H), 7.53-7.38 (m, 4H), 7.25-7.09 (m, 2H), 6.83 (d, *J*=8 Hz, 2H), 6.38 (d, *J*=8 Hz, 1H), 4.90 (d, *J*=23 Hz, 1H), 3.78 (d, *J*=10 Hz, 3H), 3.75 (s, 3H), 3.51 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 159.5, 141.3, 134.3, 128.7, 126.9, 126.2, 125.8, 125.1, 124.1, 120.1, 118.8, 114.2, 106.6, 56.8, 55.0, 53.7.

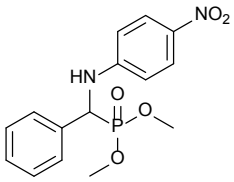
Dimethyl (2,5-dimethoxyphenyl)(naphthalene-1-ylamino)methylphosphonate[2e] (4l)



White solid; mp: 130-132 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 8.03-7.91 (m, 1H), 7.77-

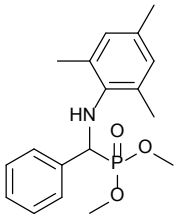
7.72 (m, 1H), 7.55-7.40 (m, 2H), 7.20-7.05 (m, 3H), 6.88-6.70 (m, 2H), 6.48-6.43 (m, 1H), 5.55 (d, *J*=24 Hz, 1H), 3.94 (s, 3H), 3.87 (d, *J*=10 Hz, 3H), 3.65 (s, 3H), 3.49 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 154.1, 151.5, 141.0, 134.3, 128.6, 126.4, 125.7, 125.0, 123.9, 120.2, 118.6, 114.1, 113.5, 111.8, 105.9, 56.4, 55.4, 53.7, 49.9, 46.8.

Dimethyl (4-nitrophenylamino)(phenyl)methylphosphonate[2f] (4m)



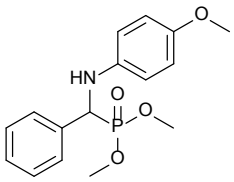
Yellow solid; mp: 124-126 °C; ^{1}H NMR (200 MHz, $CDCl_3$+DMSO d_6): δ= 7.90 (d, *J*=9 Hz, 2H), 7.45-7.20 (m, 5H), 6.70 (d, *J*=9 Hz, 2H), 4.90 (dd, 1H), 4.40 (br s, 1H), 3.69 (d, *J*=10 Hz, 3H), 3.46 (d, *J*=10 Hz, 3H); ^{13}C NMR (50MHz, $CDCl_3$+DMSO d_6): δ= 151.9, 137.1, 133.9, 127.6, 127.1, 124.7, 111.3, 54.9, 52.7, 51.9.

Dimethyl (mesitylamino)(phenyl)methylphosphonate (4n)



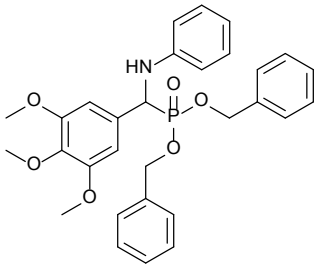
Yellow solid; mp: 93-95 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.44-7.30 (m, 2H), 7.25-7.17-7.19 (m, 3H), 6.61 (s, 2H), 4.73 (s, 1H), 4.37 (d, *J*=22 Hz, 1H), 3.74 (d, *J*=10 Hz, 3H), 3.34 (d, *J*=10 Hz, 3H), 2.09 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 141.4, 136.9, 131.1, 130.1, 129.6, 129.1, 128.4, 60.8, 57.8, 53.8, 29.7, 20.6, 18.7; MALDI TOF/TOF m/z calcd for $C_{18}H_{24}NO_3P$ [M + K^+] 372.14, observed 372.03.

Dimethyl (4-methoxyphenylamino)(phenyl)methylphosphonate[2g] (4o)



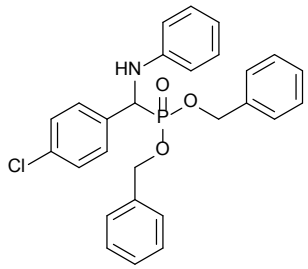
White solid; mp: 85-87 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.45-7.23 (m, 5H), 6.64 (d, *J*=9 Hz, 2H), 6.51 (d, *J*=9 Hz, 2H), 4.75 (d, *J*=24 Hz, 1H), 4.22 (br s, 1H), 3.79 (d, *J*=10 Hz, 3H), 3.65 (s, 3H), 3.47 (d, *J*=10 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 152.7, 139.8, 135.8, 128.6, 128.0, 127.9, 127.8, 115.2, 114.7, 58.1, 55.3, 53.6; MALDI TOF/TOF m/z calcd for $C_{16}H_{20}NO_4P$ [M +] 321.11, observed 321.04.

Dibenzyl (phenylamino)(3,4,5-trimethoxyphenyl)methylphosphonate (4p)



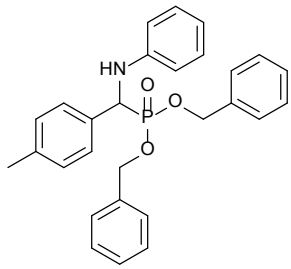
White solid; mp: 103-105 °C; ^{1}HNMR (200 MHz, $CDCl_3$): δ= 7.34-7.29 (m, 8H), 7.17-7.10 (m, 4H), 6.74 (t, *J*=7 Hz, 1H), 6.64 (d, *J*=2 Hz, 2H), 6.60 (d, *J*=7 Hz, 2H), 5.09-5.04 (m, 2H), 4.93 (dd, *J*=7 Hz, 1H), 4.77-4.65 (m, 2H), 3.85 (s, 3H), 3.76 (s, 6H); ^{13}CNMR (50 MHz, $CDCl_3$): δ= 153.4, 146.2, 131.1, 129.2, 128.6, 128.5, 128.2, 127.9, 118.8, 113.9, 104.8, 104.6, 68.6, 60.7, 58.2, 55.9; MALDI TOF/TOF m/z calcd for $C_{30}H_{32}NO_6P$ [M + K^+] 572.19, observed 572.06.

Dibenzyl (4-chlorophenyl)(phenylamino)methylphosphonate (4q)



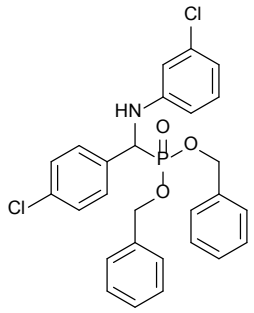
Yellow solid; mp: 131-133 °C; ^{1}HNMR (200 MHz, $CDCl_3$): δ= 7.37-7.26 (m, 12H), 7.11-7.07 (m, 4H), 6.73 (t, *J*=7 Hz, 1H), 6.50 (d, *J*=7 Hz, 2H), 5.07-4.68 (m, 5H); ^{13}CNMR (50 MHz, $CDCl_3$):δ= 145.9, 134.3, 129.2, 128.8, 128.6, 128.2, 128.1, 118.8, 113.9, 68.9, 57.3, 54.3; MALDI TOF/TOF m/z calcd for $C_{27}H_{25}ClNO_3P$ [M + K^+] 516.12, observed 515.98.

Dibenzyl (phenylamino)(p-tolyl)methylphosphonate (4r)



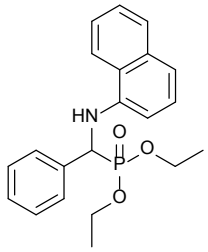
Greenish solid; mp: 137-139 °C; ^{1}HNMR (200 MHz, $CDCl_3$): δ= 7.38-7.30 (m, 10H), 7.18-7.07 (m, 6H), 6.73 (t, *J*=7 Hz, 1H), 6.58 (d, *J*=7 Hz, 2H), 5.07-4.58 (m, 5H), 2.37(s, 3H); ^{13}CNMR (50 MHz, $CDCl_3$):δ= 146.1, 137.5, 136.1, 132.6, 129.4, 129.1, 128.5, 127.9, 127.8, 118.5, 113.9, 68.5, 57.5, 54.5, 21.3; MALDI TOF/TOF m/z calcd for $C_{28}H_{28}NO_3P$ [M + K^+] 496.18, observed 496.05.

Dibenzyl ((4-chlorophenyl)((3-chlorophenyl)amino)methyl)phosphonates (4s)



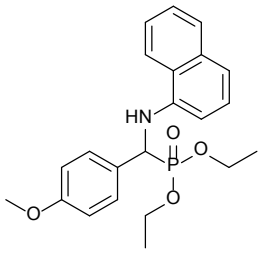
Yellow solid; mp: 99-101 °C; ^{1}HNMR (200 MHz, $CDCl_3$): δ= 7.30-7.32 (m, 11H), 7.21-7.18 (m, 3H), 7.17-6.90 (m, 1H), 6.52-6.39 (m, 3H), 4.99 (br, s 1H), 4.95-4.55 (m, 5H); ^{13}CNMR (125 MHz, $CDCl_3$): δ= 147.0, 135.4, 134.8, 133.6, 130.1, 129.1, 128.9, 128.6, 128.1, 128.0, 127.8, 118.7, 113.7, 111.9, 68.8, 56.3, 54.8; MALDI TOF/TOF m/z calcd for $C_{27}H_{24}Cl_2NO_3P$ [M + K^+] 550.08, observed 549.98.

Diethyl (naphthalene-1-ylamino)(phenyl)methylphosphonate[2h] (4t)



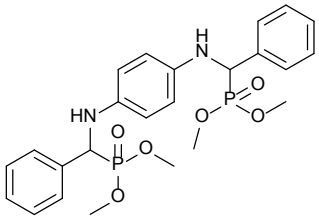
White solid; mp: 114-116 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.96-6.99 (m, 11H), 6.25 (dd, *J*=7 Hz, 1H), 5.39 (br s, 1H), 4.87 (d, *J*=24 Hz, 1H), 3.53-4.12 (m, 4H), 1.20 (t, *J*=7 Hz, 3H), 1.05 (t, *J*=7 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 159.4, 141.5, 134.4, 128.7, 127.4, 126.2, 125.7, 125.0, 124.1, 120.1, 118.6, 114.0, 106.6, 63.2, 57.2, 54.9, 54.2, 16.5.

Diethyl (4-methoxyphenyl)(phenylamino)methylphosphonate[2e] (4u)



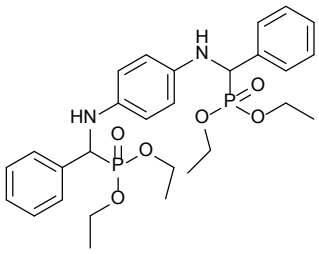
White solid; mp: 96-98 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.92 (d, *J*=7 Hz, 1H), 7.67-7.62 (m, 1H), 7.40-7.29 (m, 4H), 7.08-7.04 (m, 2H), 6.75 (d, *J*=8 Hz, 2H), 6.31 (dd, *J*=7 Hz, 1H), 4.78 (d, *J*=23 Hz, 1H), 4.10-3.83 (m, 4H), 3.67 (s, 3H), 1.22 (t, *J*=7 Hz, 3H), 1.09 (t, *J*=7 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 141.4, 135.7, 134.4, 128.6, 127.9, 127.7, 126.1, 125.7, 125.0, 124.1, 120.1, 118.7, 106.5, 63.2, 57.8, 54.8, 16.5.

Tetramethyl((1,4-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonates) (4v)



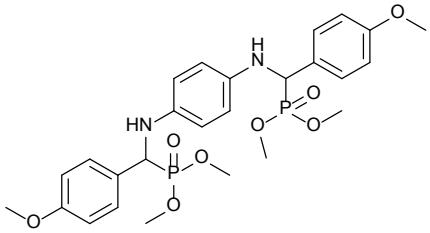
Brown solid; mp: 178-180 °C; ^{1}H NMR (200 MHz, $CDCl_3$+DMSO d_6): δ= 7.38-7.20 (m, 10H), 6.38 (s, 4H), 4.62 (d, *J*=24 Hz, 2H), 3.65 (d, *J*=10 Hz, 6H), 3.38 (d, *J*=10 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$+DMSO d_6): δ= 132.7, 128.4, 124.3, 117.7, 112.7, 53.3, 52.7, 49.2, 28.7; MALDI TOF/TOF m/z calcd for $C_{24}H_{30}N_2O_6P_2$ [M + K^+] 543.15, observed 543.07.

Tetraethyl ((1,4-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonates)[2i] (4w)



White solid; mp: 152-154 °C; ^{1}H NMR (200 MHz, $CDCl_3$+DMSO d_6): δ= 7.34-7.17 (m, 10H), 6.28 (s, 4H), 4.44 (d, *J*=24 Hz, 2H), 4.03 (s, 2H), 4.01-3.56 (m, 8H), 1.19 (t, *J*=7 Hz, 6H), 1.01 (t, *J*=7 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$+DMSO d_6): δ= 158.7, 128.7, 127.5, 114.9, 113.4, 54.5, 52.7, 29.1.

Tetramethyl ((1,4-phenylenebis(azanediyl))bis((4-methoxyphenyl)methylene)) bis(phosphonate[2e] (4x)



White solid; mp: 161-163 °C; ^{1}H NMR (200 MHz, $CDCl_3$+DMSO d_6): δ= 7.32-7.26 (m, 4H), 6.80-6.76 (m, 4H), 6.40 (s, 4H), 4.62 (d, *J*=24 Hz, 2H), 4.23 (br s, 2H), 3.73 (s, 6H), 3.67 (d, *J*=10 Hz, 6H), 3.46 (d, *J*=10 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$+DMSO d_6): δ= 136.4, 128.5, 128.0, 127.9, 115.5, 62.9, 16.5, 16.4, 16.3.

Reference

[1] G. D. Yadav, H. G. Manyar, *Microporous and Mesoporous Materials*, **2003**, *63*, 85.

[2] (a) S. Bhagat, A. K. Chakraborti, *J. Org. Chem.,* **2007**, *72*, 1263-1270; (b) V. H. Tillu, D. K. Dumbre, R. D. Wakharkar, V. R. Choudhary, *Tetrahedron Lett.,* **2011**, *52*, 863-866; (c) A. Manjula, B. V. Rao, P. Neelakantan, *Synth. Commun.,* **2003**, *33*, 2963-2969; (d) Xue-Jun Mu, Mao-Yi Lei, Jian-Ping Zou, W. Zhang, *Tetrahedron Lett.,* **2006**, *47*, 1125-1127; (e) B. P. Lugoykin, *Zhurnal obshchei khimii,* **1970**, *40*, 2391-2392; (f) S. D.

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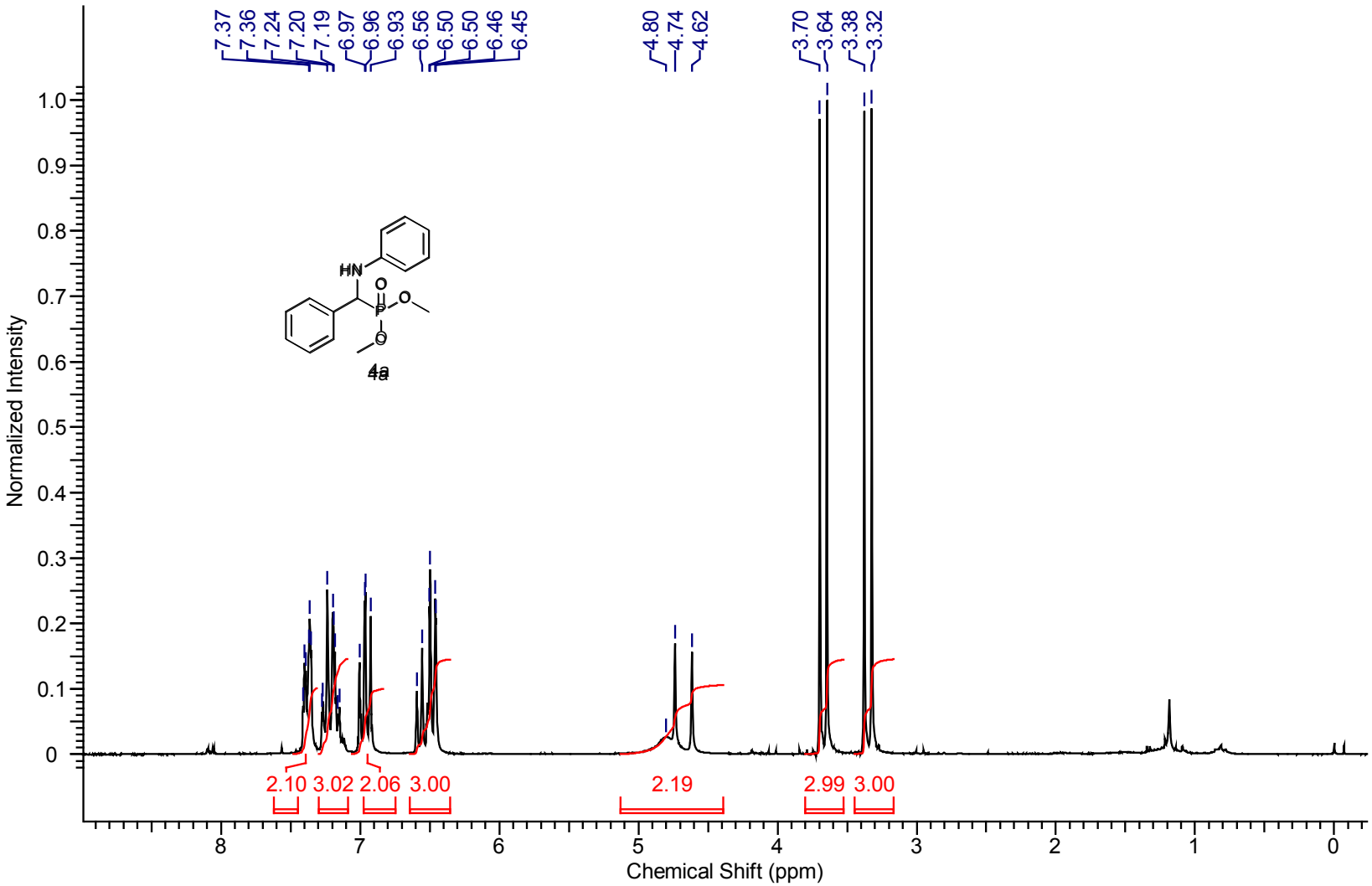
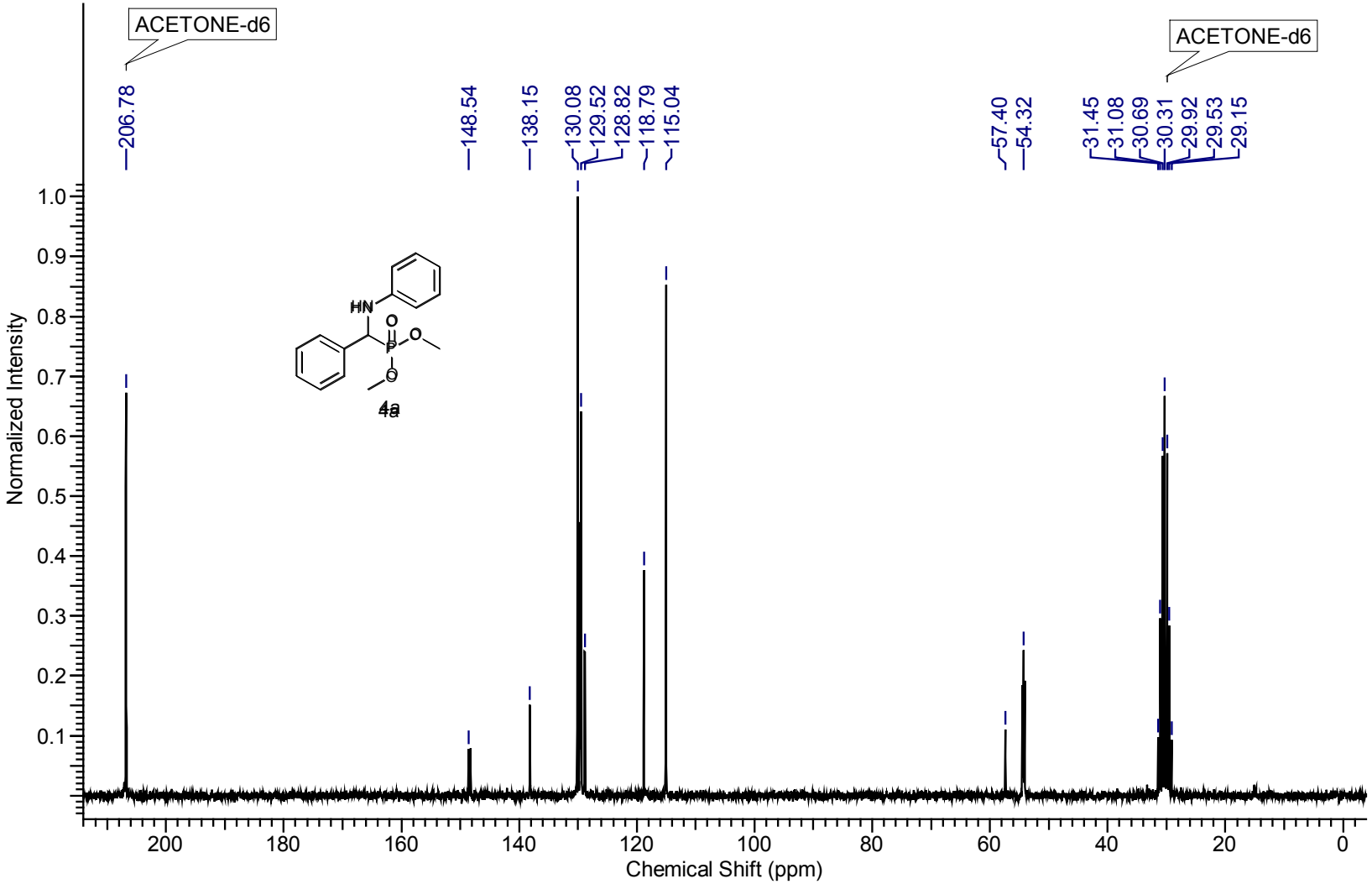
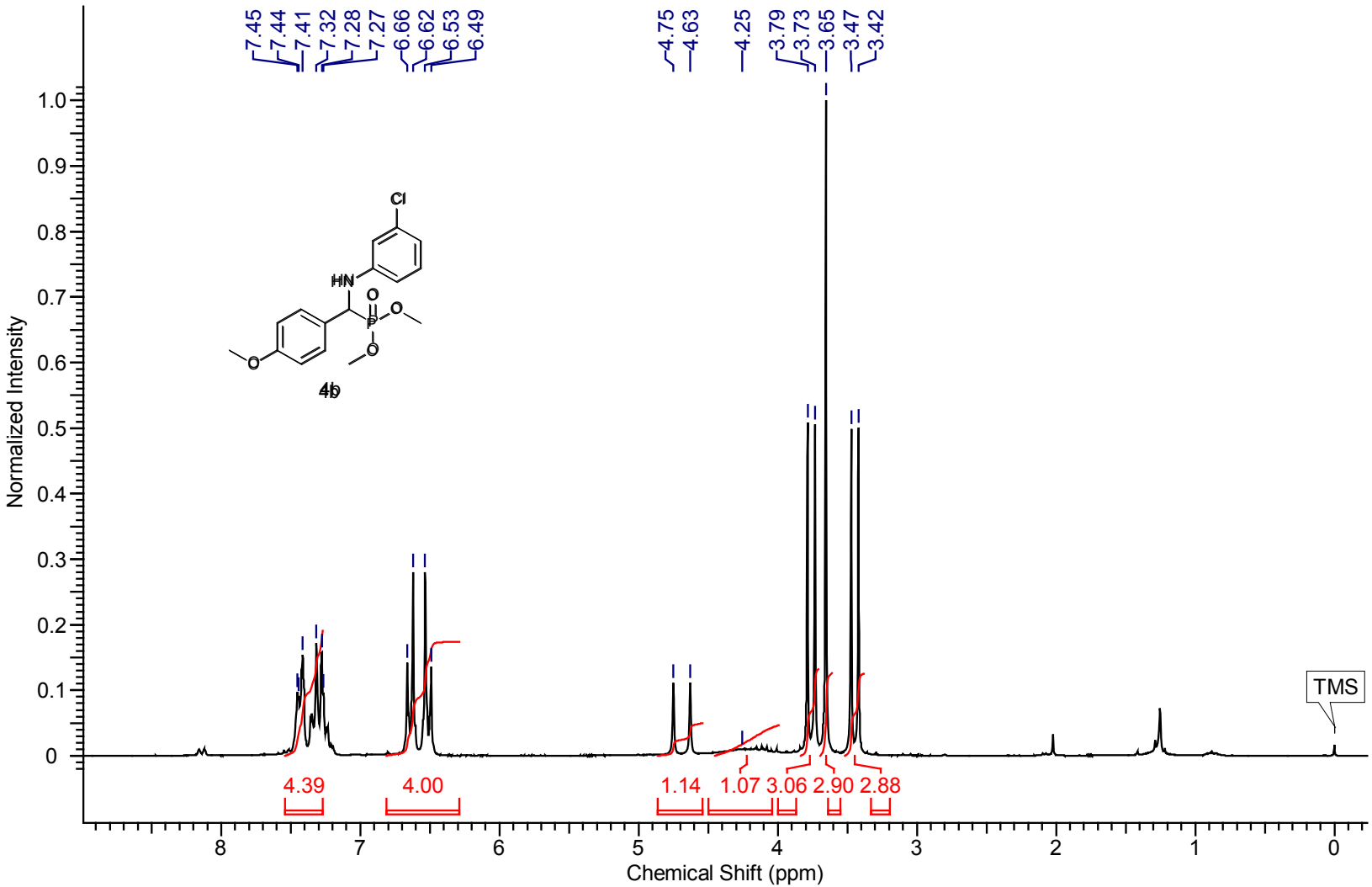
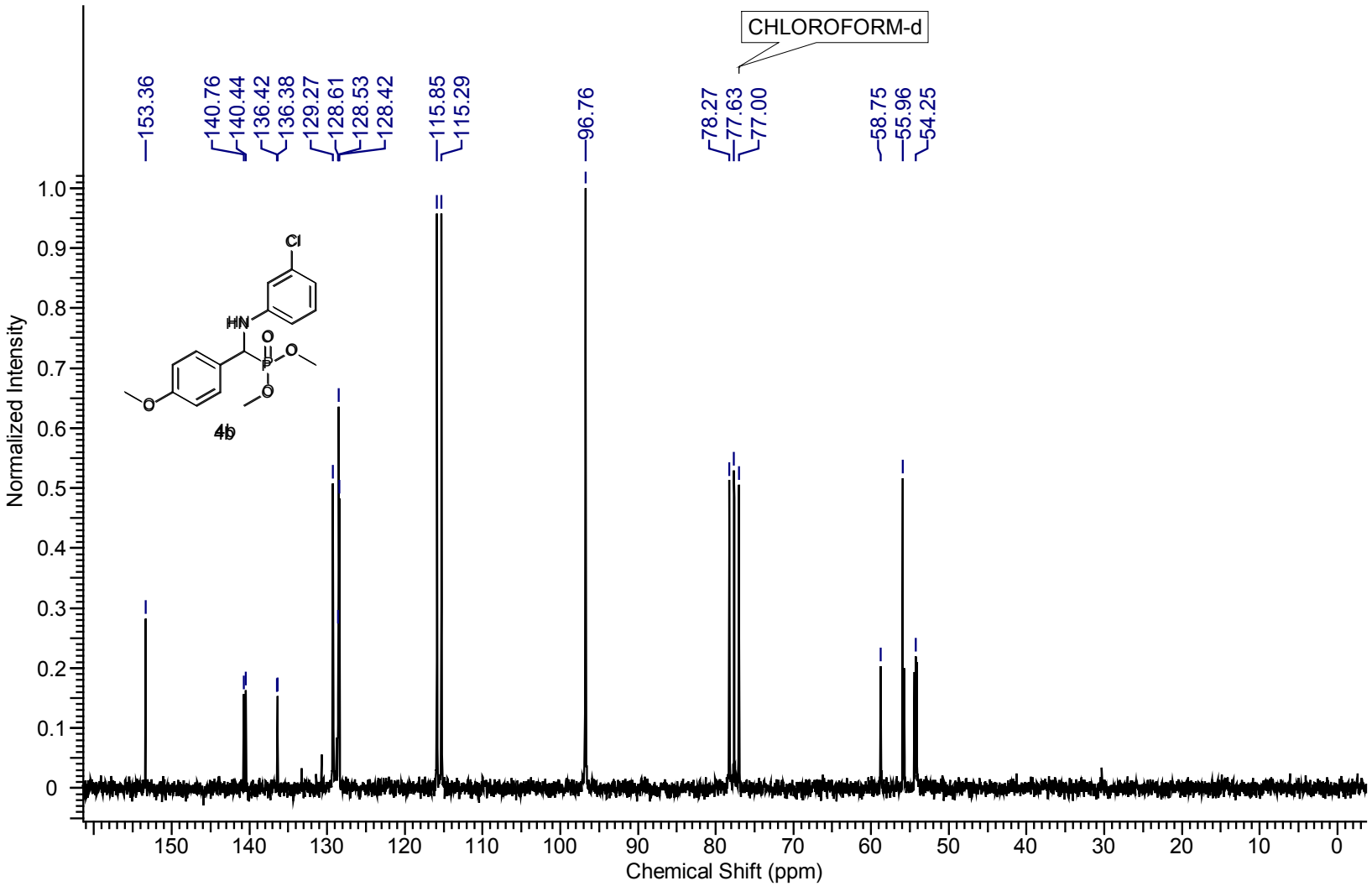
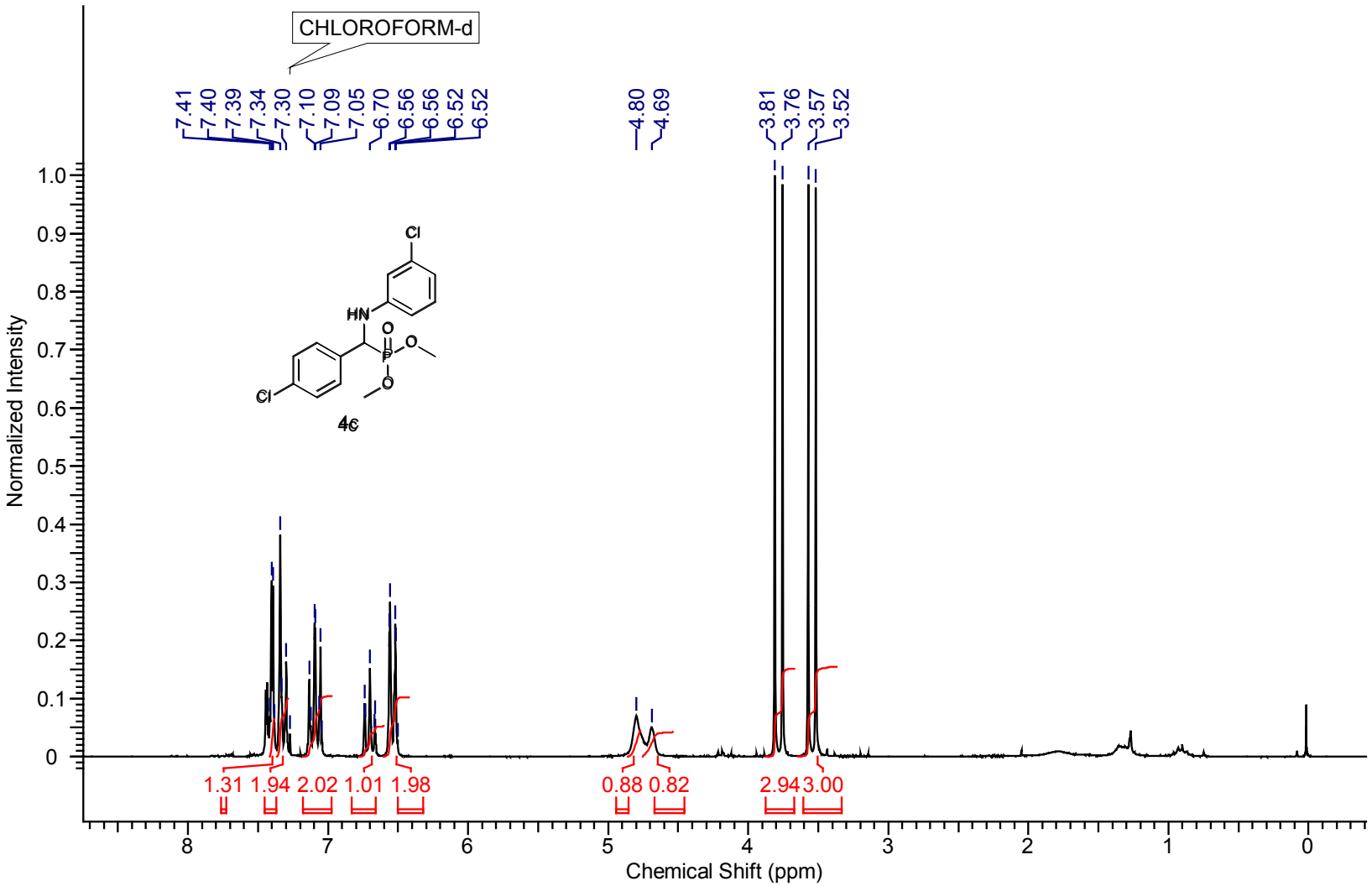

7.37
7.36
7.24
7.20
7.19
6.97
6.96
6.93
6.56
6.50
6.50
6.46
6.45
4.80
4.74
4.62
3.70
3.64
3.38
3.32
HN
O
P
O
O
4a
Normalized Intensity
Chemical Shift (ppm)
2.10
3.02
2.06
3.00
2.19
2.99
3.00


ACETONE-d6
ACETONE-d6
206.78
148.54
138.15
130.08
129.52
128.82
118.79
115.04
57.40
54.32
31.45
31.08
30.69
30.31
29.92
29.53
29.15
HN
O
P
O
O
4a
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.45
7.44
7.41
7.32
7.28
7.27
6.66
6.62
6.53
6.49
4.75
4.63
4.25
3.79
3.73
3.65
3.47
3.42
Cl
HN
O
P
O
O
O
4b
TMS
4.39
4.00
1.14
1.07
3.06
2.90
2.88
Normalized Intensity
Chemical Shift (ppm)


CHLOROFORM-d
153.36
140.76
140.44
136.42
136.38
129.27
128.61
128.53
128.42
115.85
115.29
96.76
78.27
77.63
77.00
58.75
55.96
54.25
Cl
HN
O
P
O
O
O
4b
Normalized Intensity
Chemical Shift (ppm)


CHLOROFORM-d
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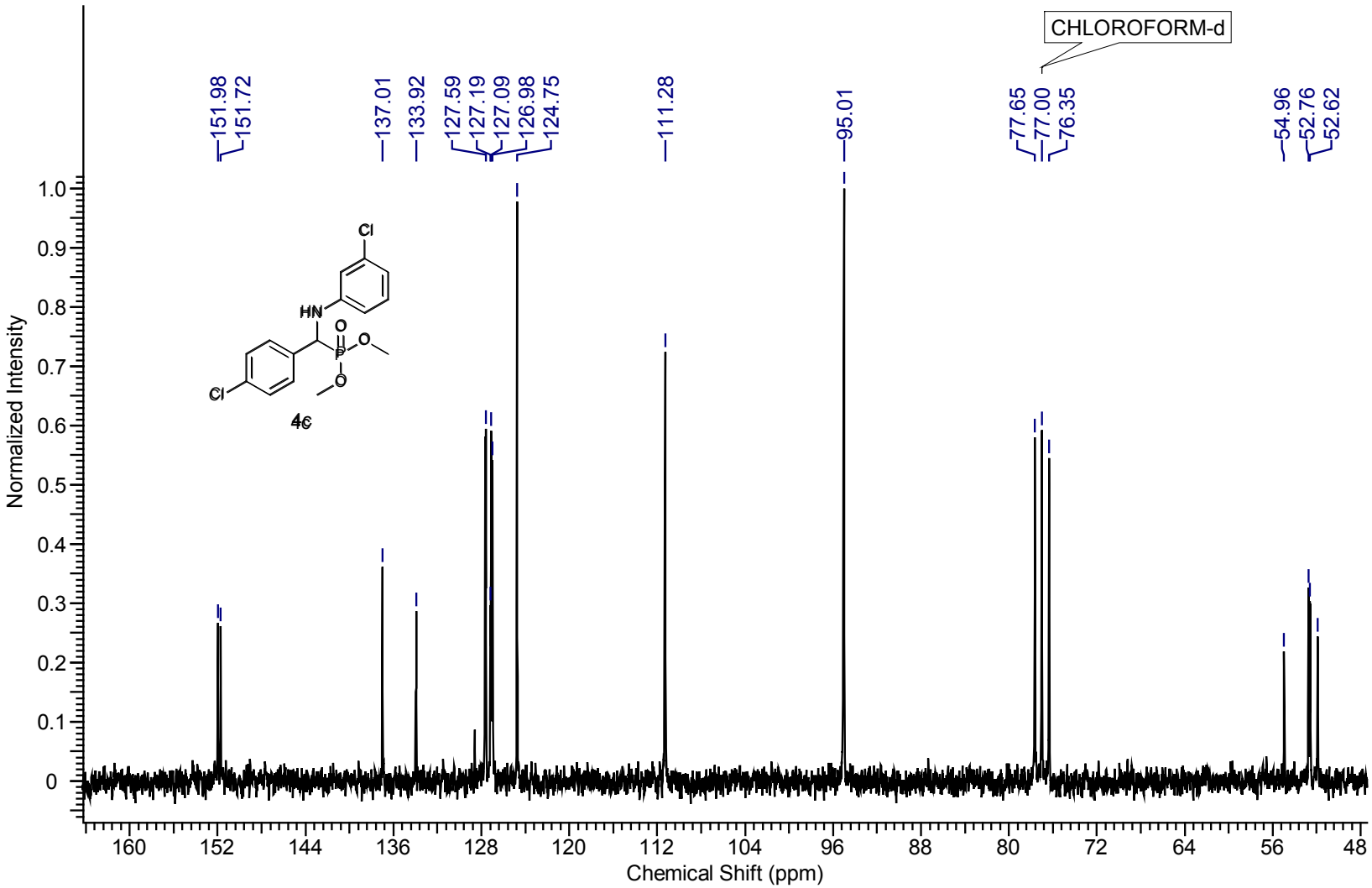
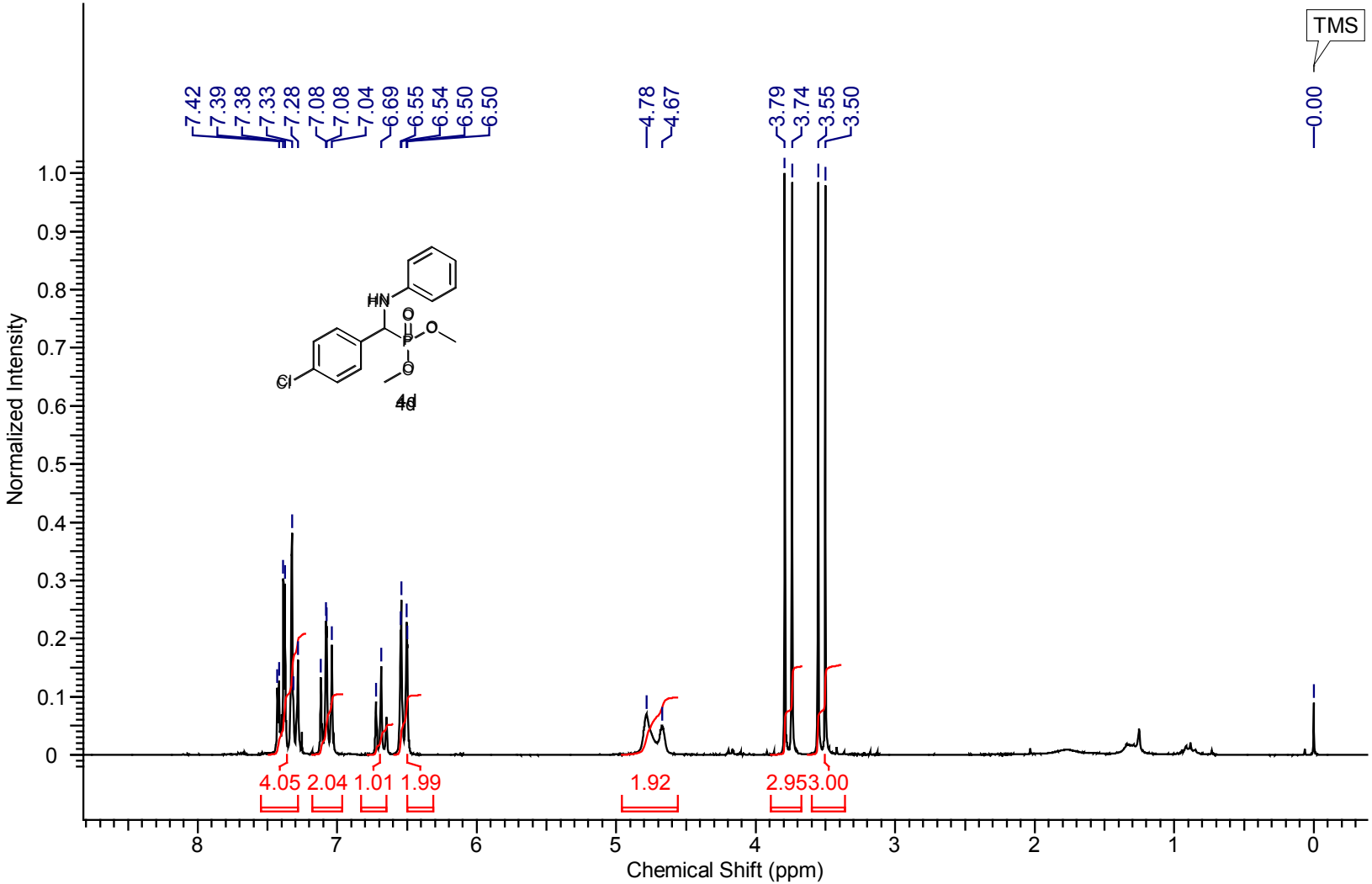
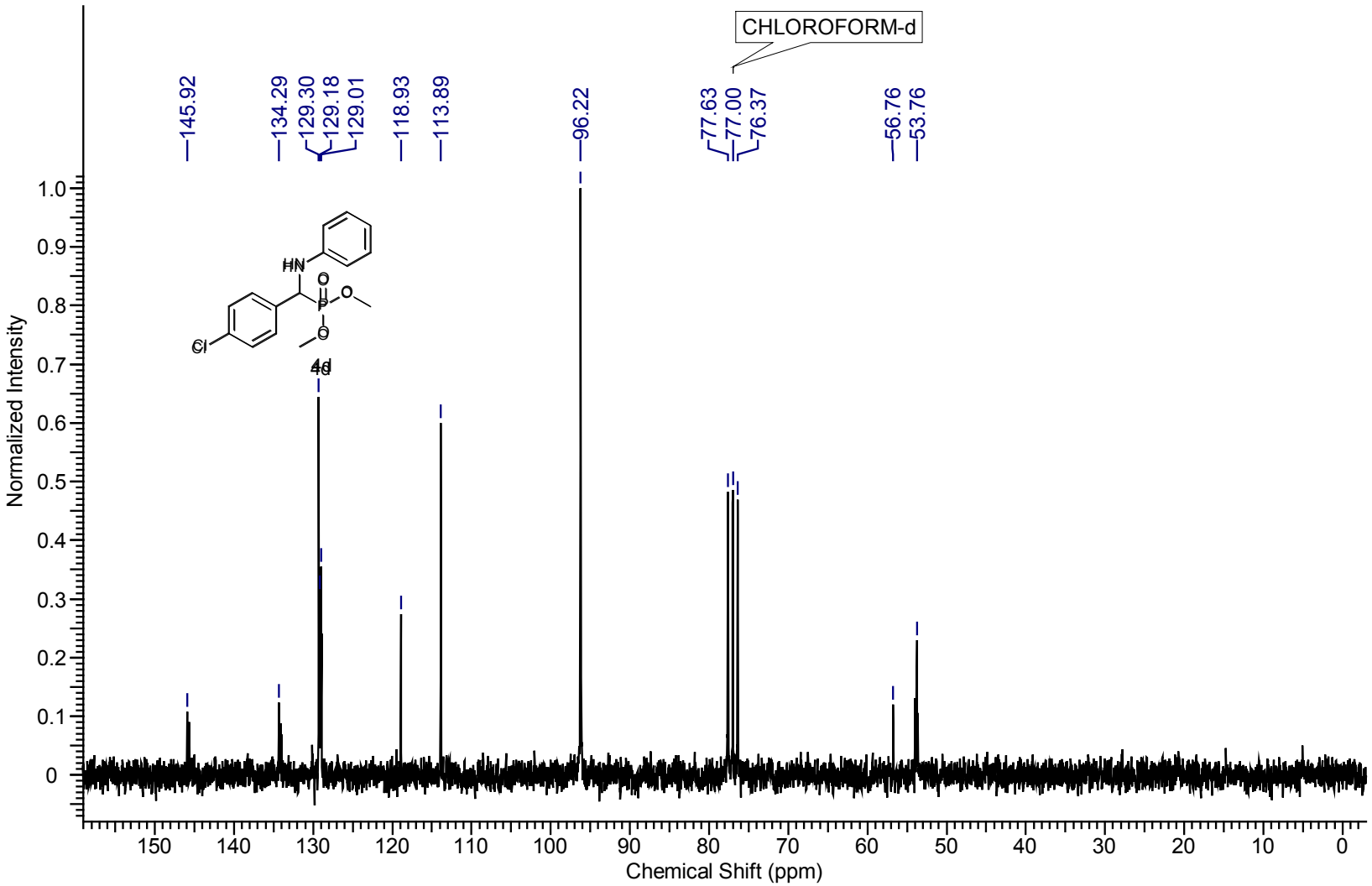
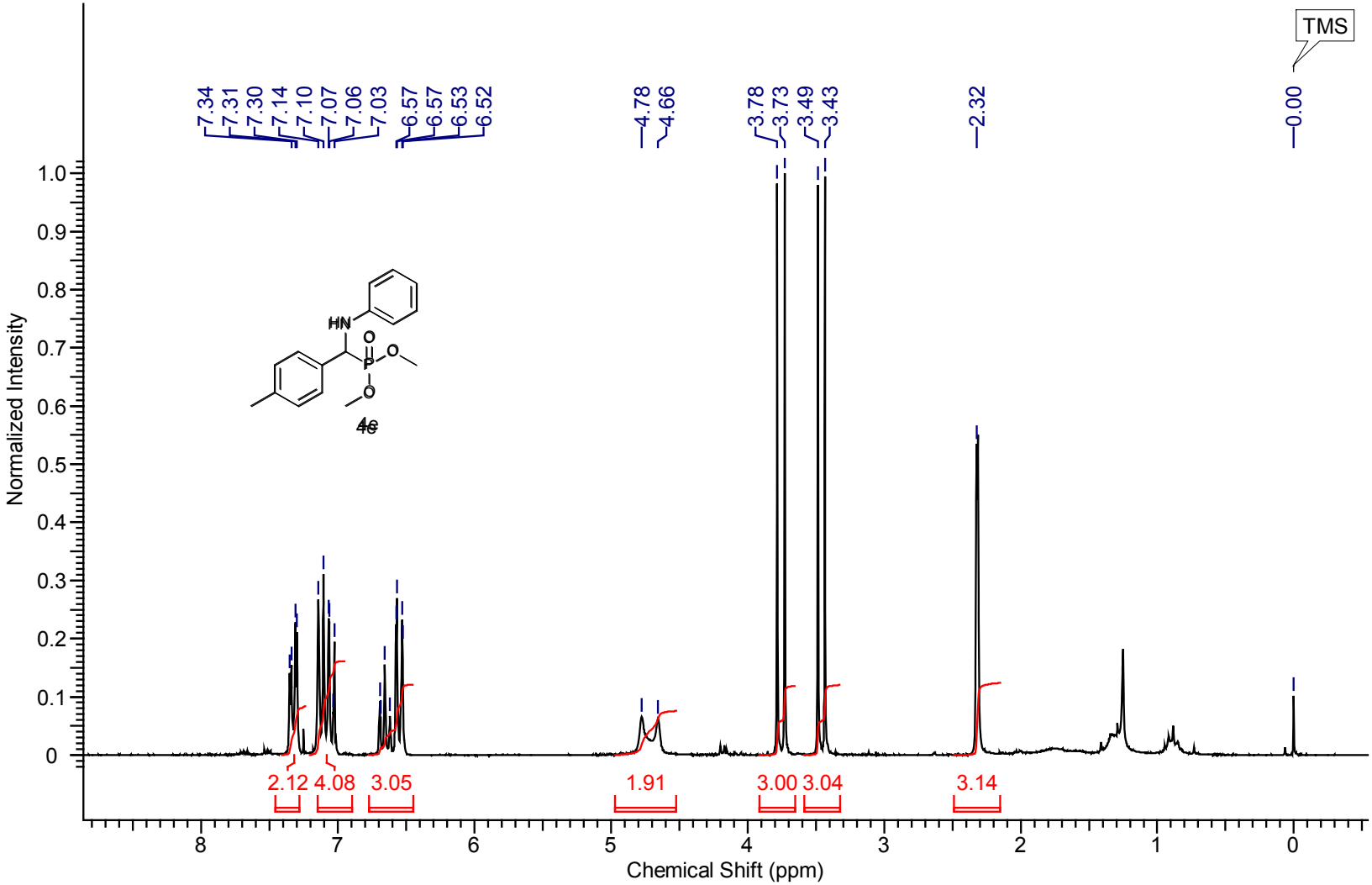
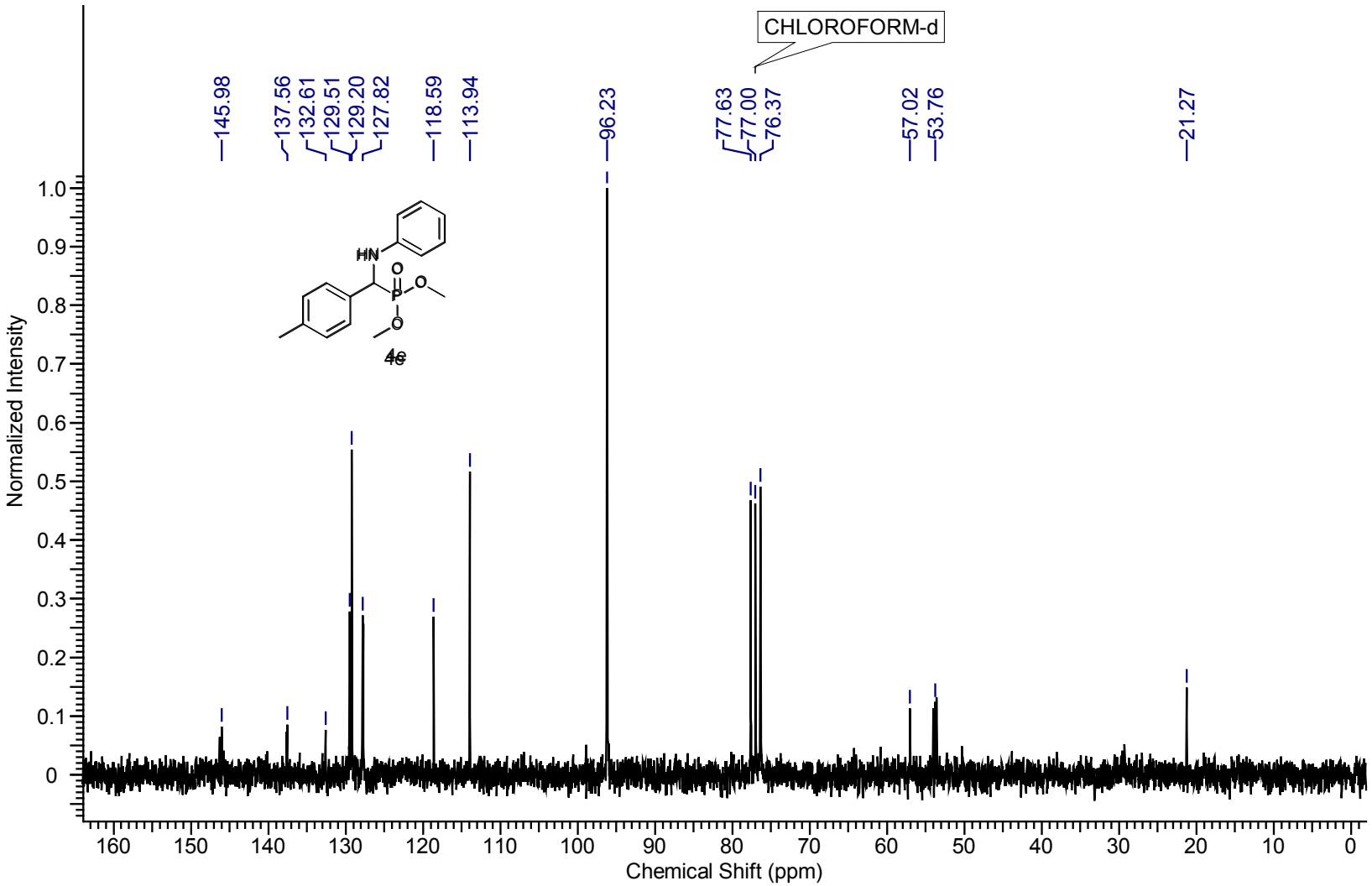
7.40
7.39
7.34
7.30
7.10
7.09
7.05
6.70
6.56
6.56
6.52
6.52
4.80
4.69
3.81
3.76
3.57
3.52
Cl
HN
O
P
O
O
Cl
4c
1.31 1.94 2.02 1.01 1.98
0.88 0.82
2.94 3.00
Normalized Intensity
Chemical Shift (ppm)

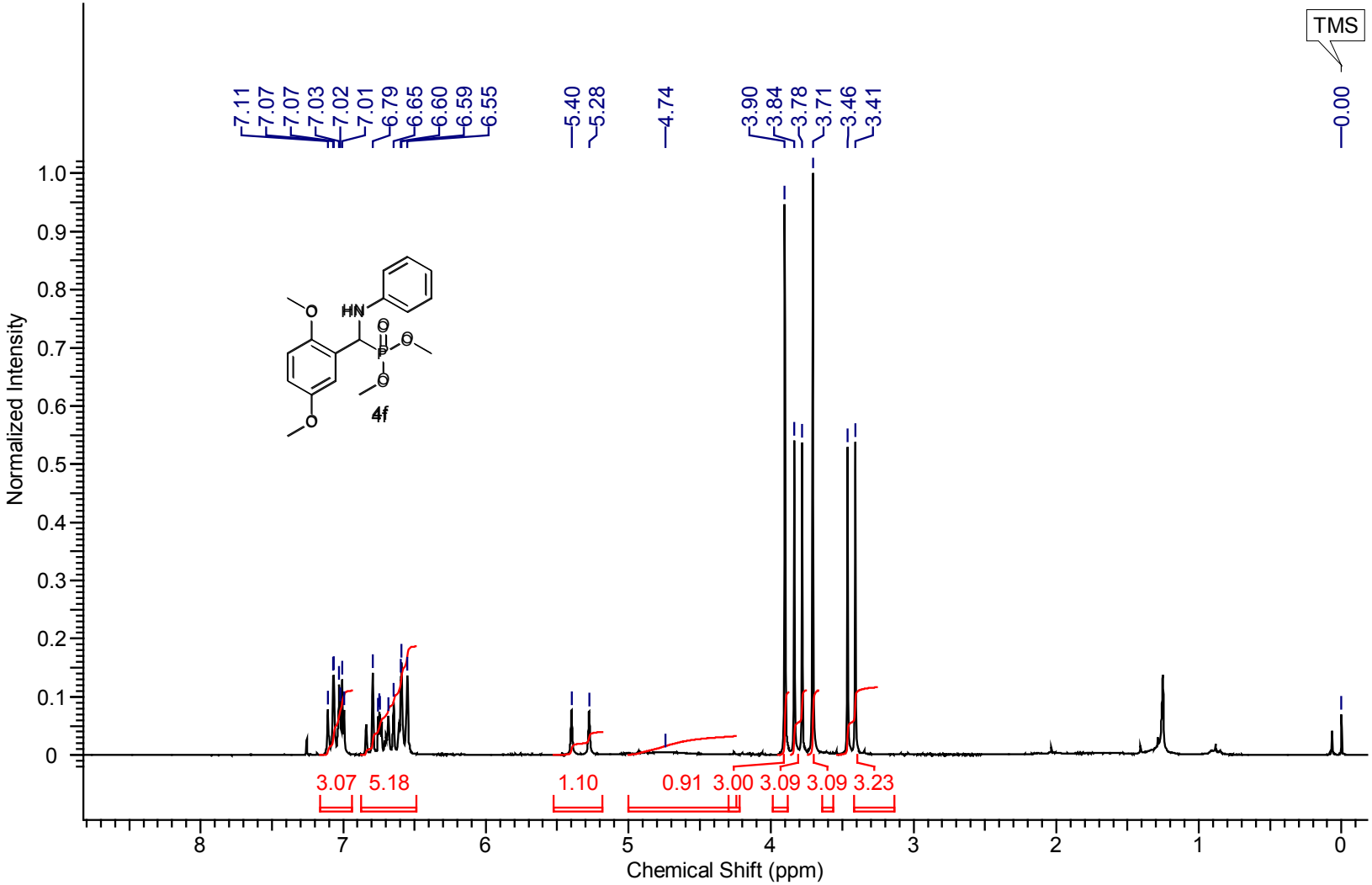

CHLOROFORM-d
151.98
151.72
137.01
133.92
127.59
127.19
127.09
126.98
124.75
111.28
95.01
77.65
77.00
76.35
54.96
52.76
52.62
Cl
HN
O
P
O
O
Cl
4c
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
Chemical Shift (ppm)


TMS
7.42
7.39
7.38
7.33
7.28
7.08
7.08
7.04
6.69
6.55
6.54
6.50
6.50
4.78
4.67
3.79
3.74
3.55
3.50
0.00
HN
O
P
O
O
Cl
4d
Normalized Intensity
Chemical Shift (ppm)
4.05
2.04
1.01
1.99
1.92
2.95
3.00


CHLOROFORM-d
145.92
134.29
129.30
129.18
129.01
118.93
113.89
96.22
77.63
77.00
76.37
56.76
53.76
HN
O
P
O
O
O
Cl
4d
Normalized Intensity
Chemical Shift (ppm)


TMS
7.34
7.31
7.30
7.14
7.10
7.07
7.06
7.03
6.57
6.57
6.53
6.52
4.78
4.66
3.78
3.73
3.49
3.43
2.32
0.00
HN
O
P
O
O
4e
2.12
4.08
3.05
1.91
3.00
3.04
3.14
Normalized Intensity
Chemical Shift (ppm)


CHLOROFORM-d
145.98
137.56
132.61
129.51
129.20
127.82
118.59
113.94
96.23
77.63
77.00
76.37
57.02
53.76
21.27
HN
O
P
O
O
4c
Normalized Intensity
Chemical Shift (ppm)


TMS
7.11
7.07
7.07
7.03
7.02
7.01
6.79
6.65
6.60
6.59
6.55
5.40
5.28
4.74
3.90
3.84
3.78
3.71
3.46
3.41
0.00
HN
O
P
4f
Normalized Intensity
Chemical Shift (ppm)
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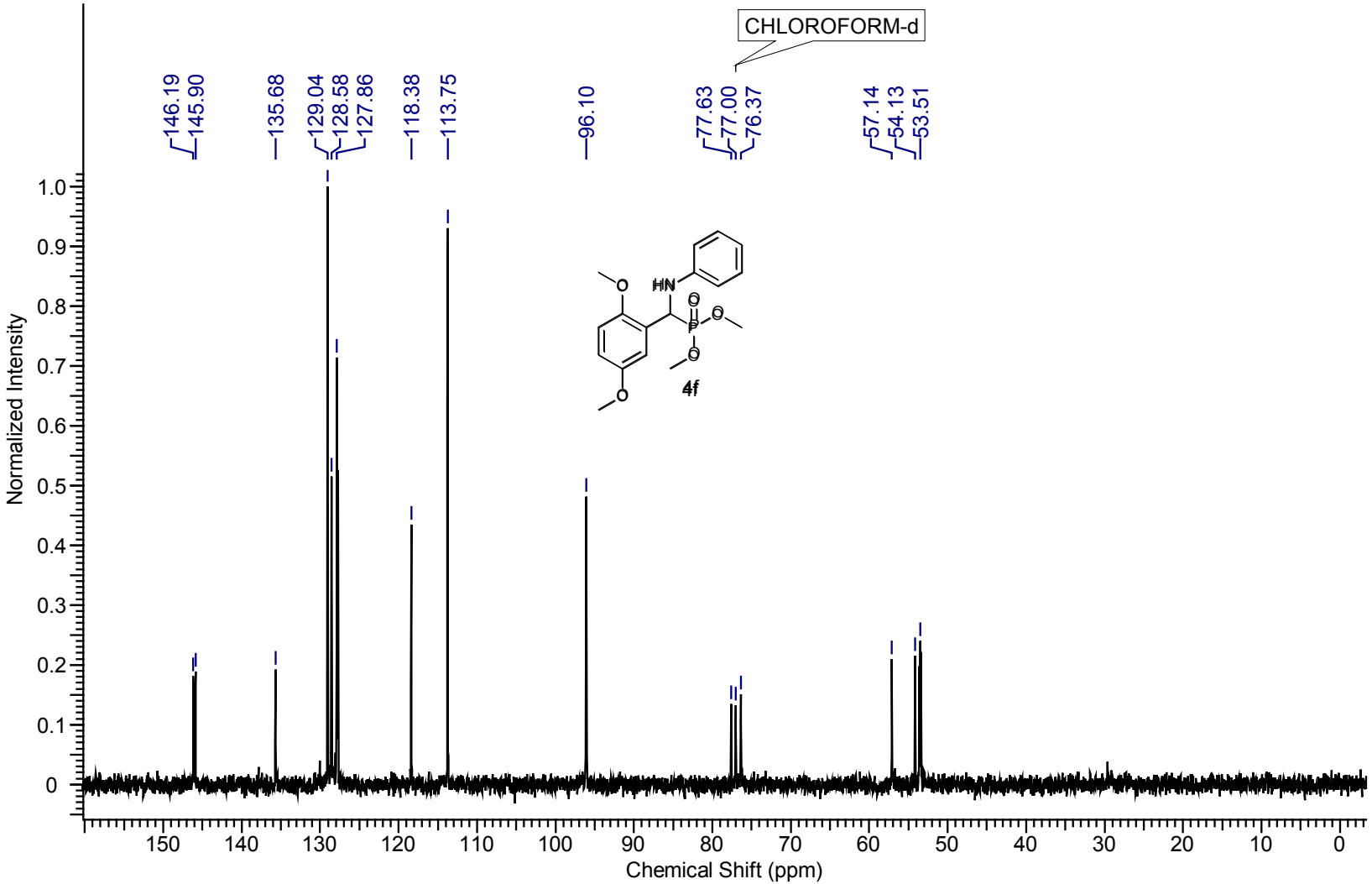
5.18
1.10
0.91
3.00
3.09
3.09
3.23


CHLOROFORM-d
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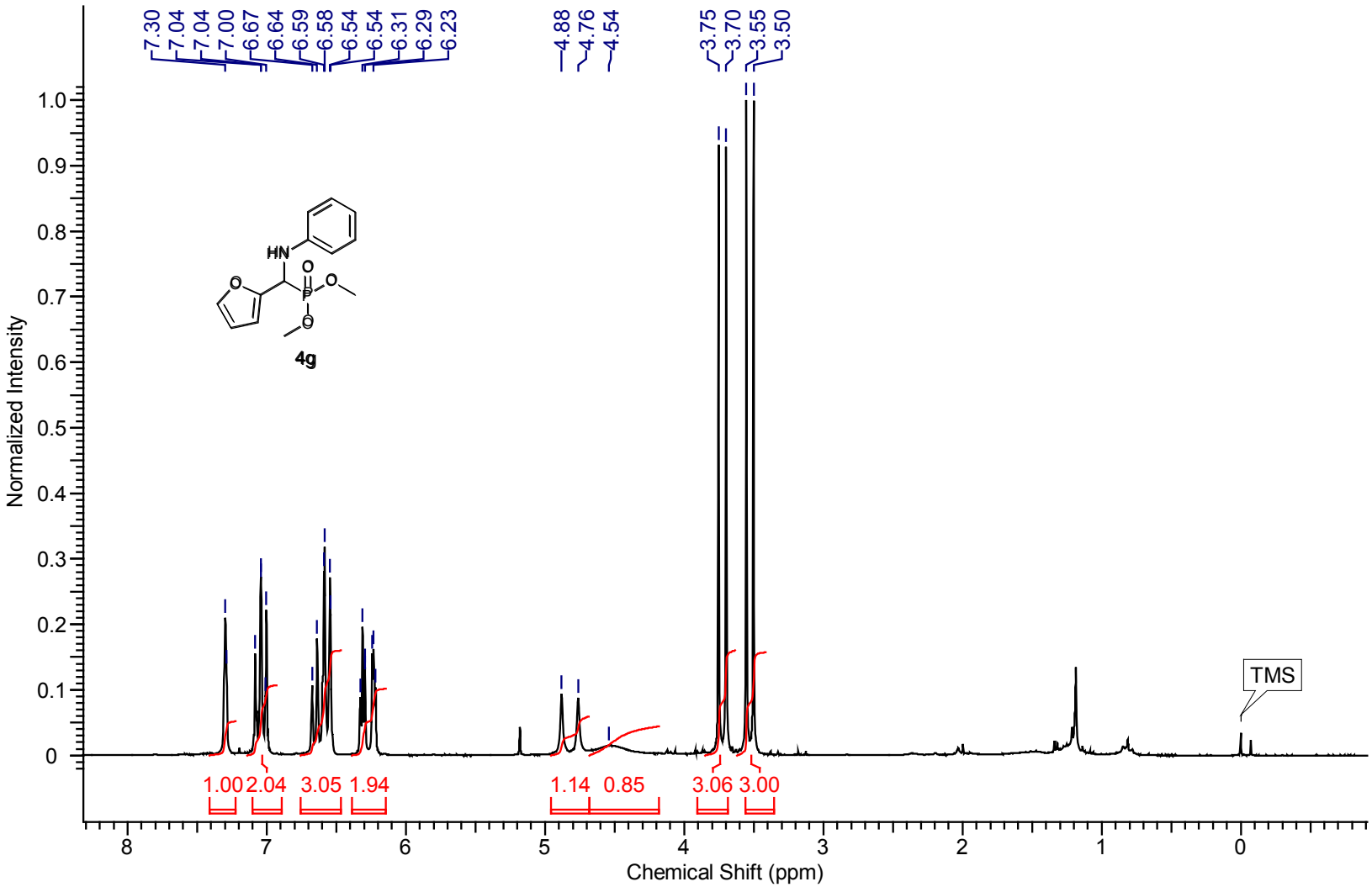
127.86
118.38
113.75
96.10
77.63
77.00
76.37
57.14
54.13
53.51
HN
O
P
4f
Normalized Intensity
Chemical Shift (ppm)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7.04
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6.58
6.54
6.54
6.31
6.29
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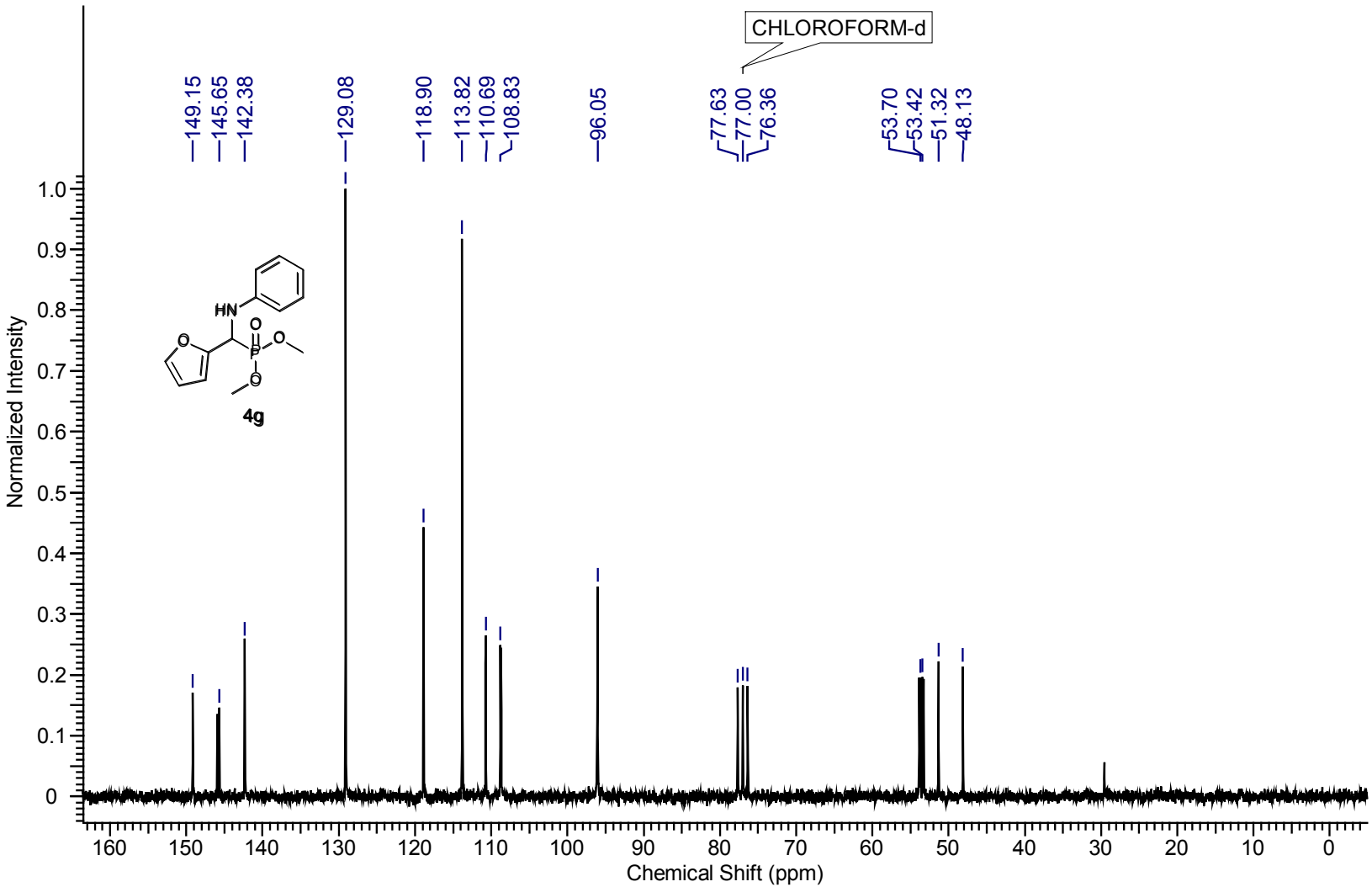
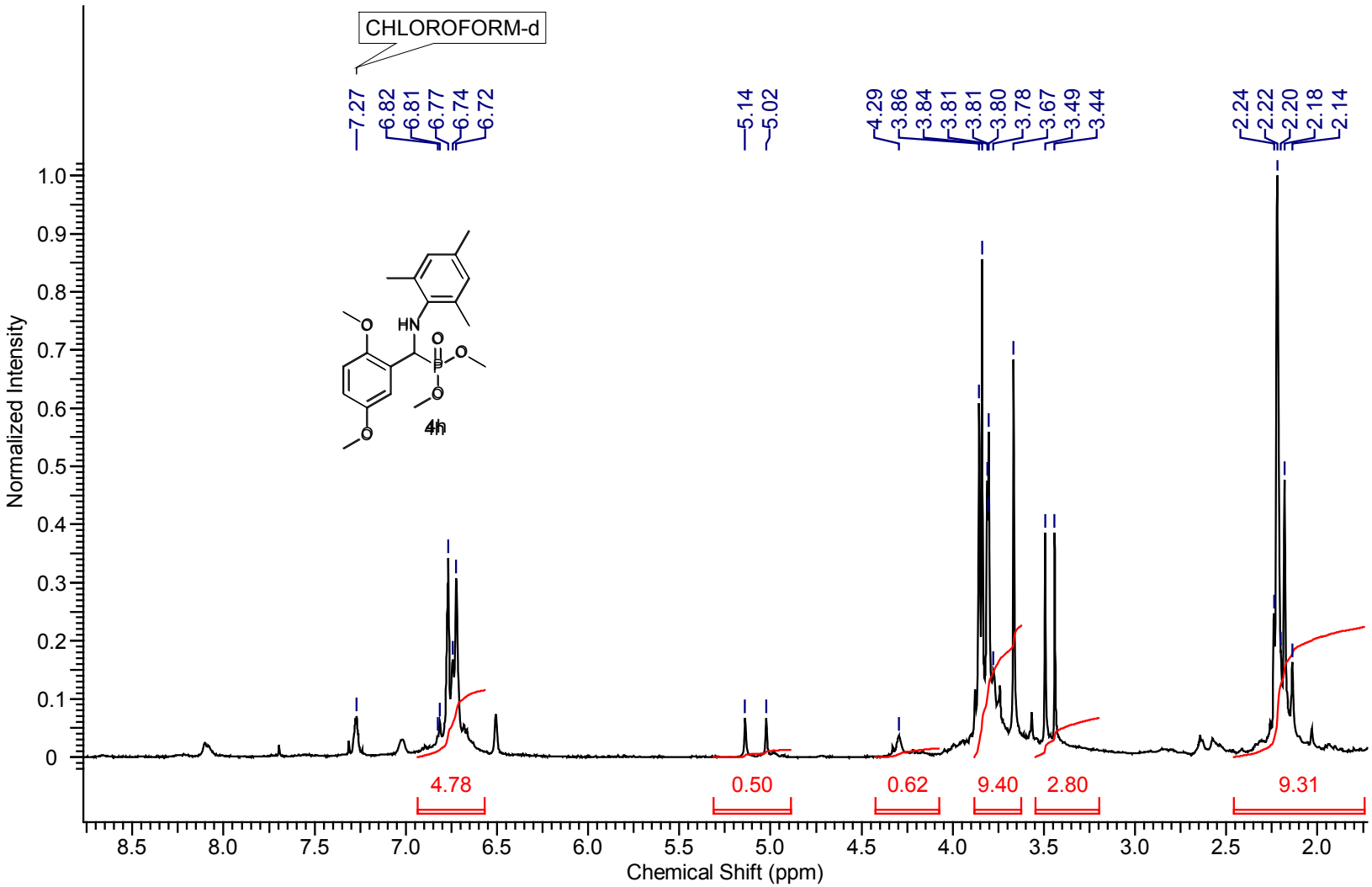
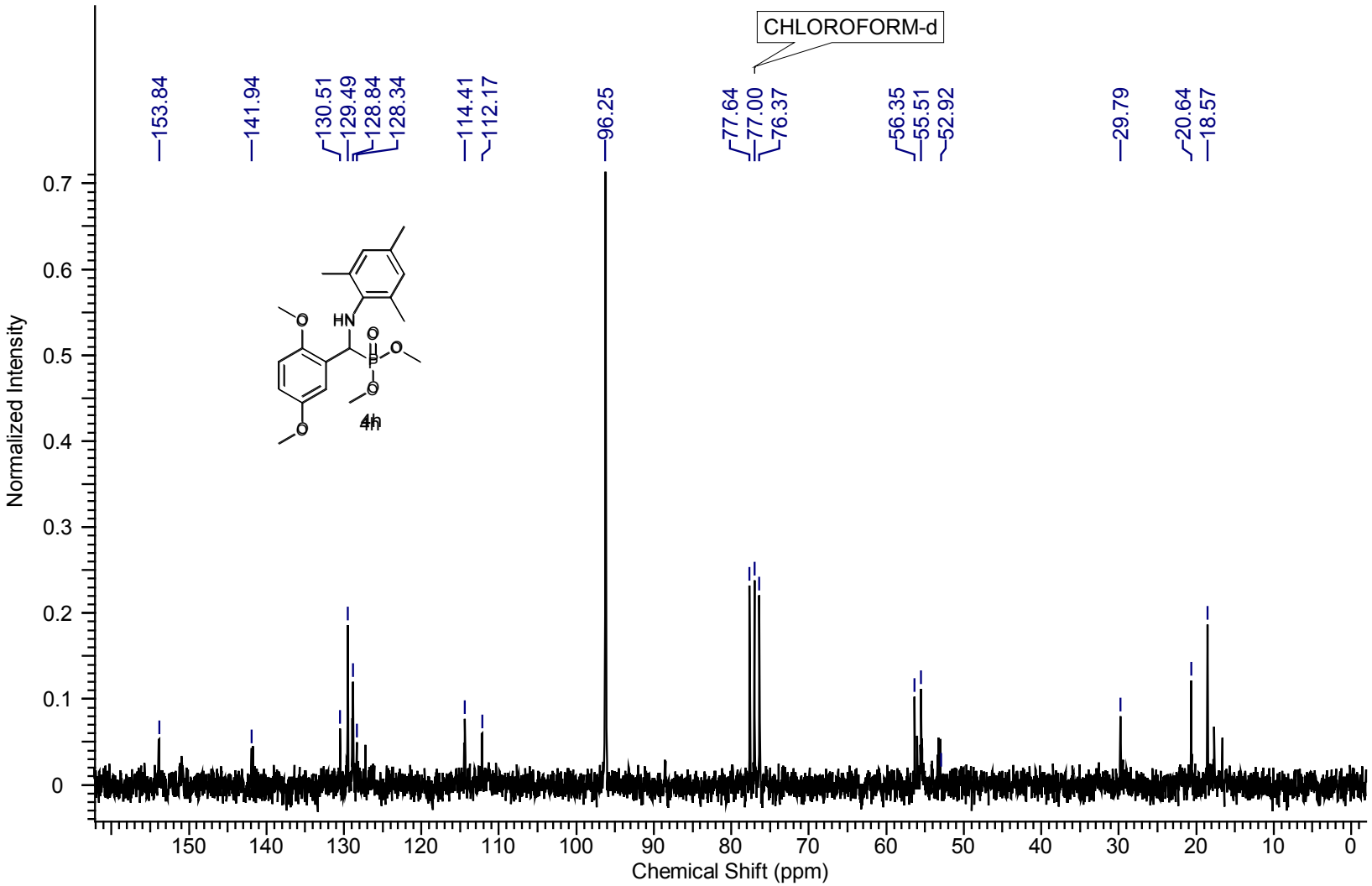
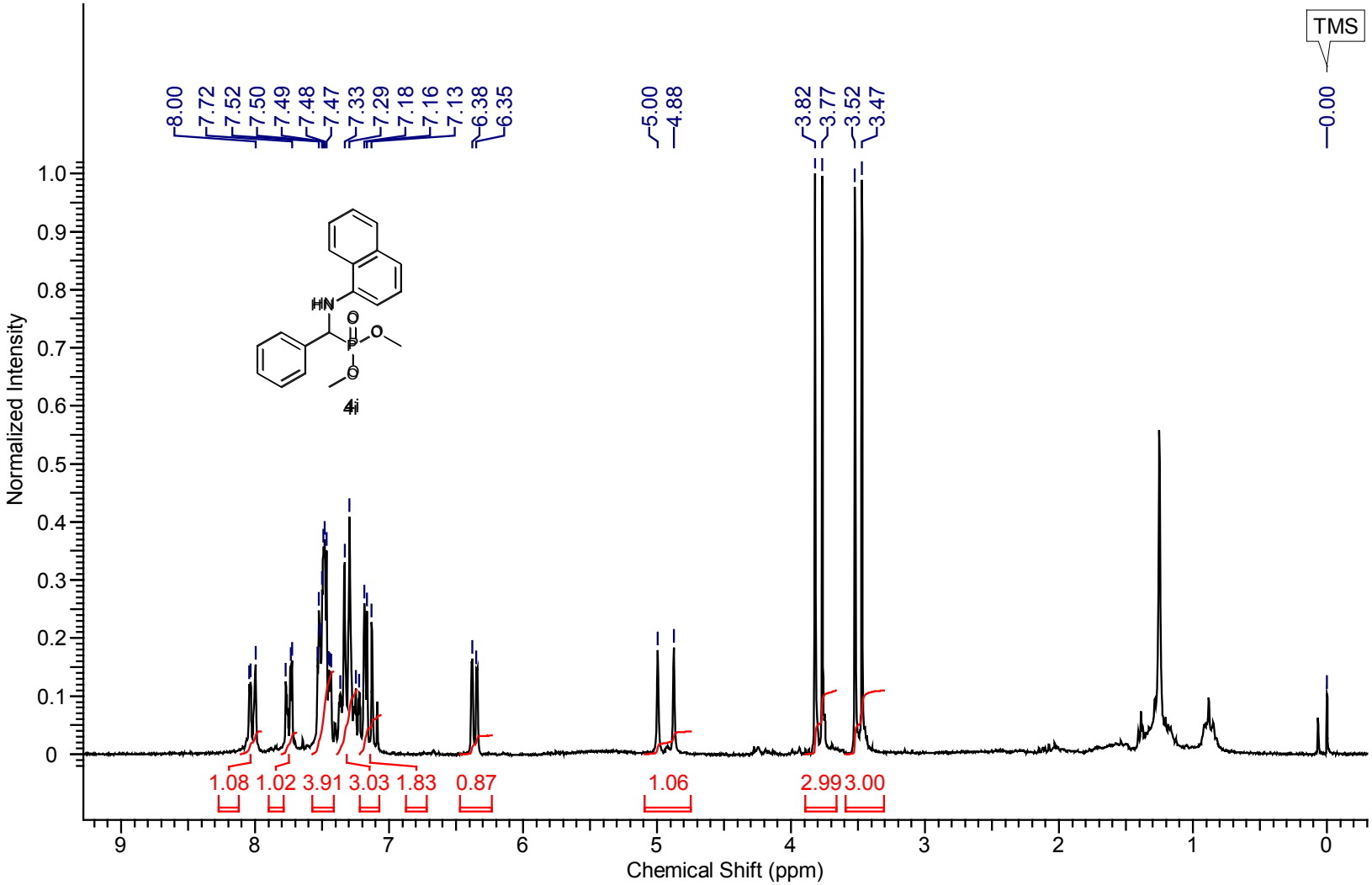
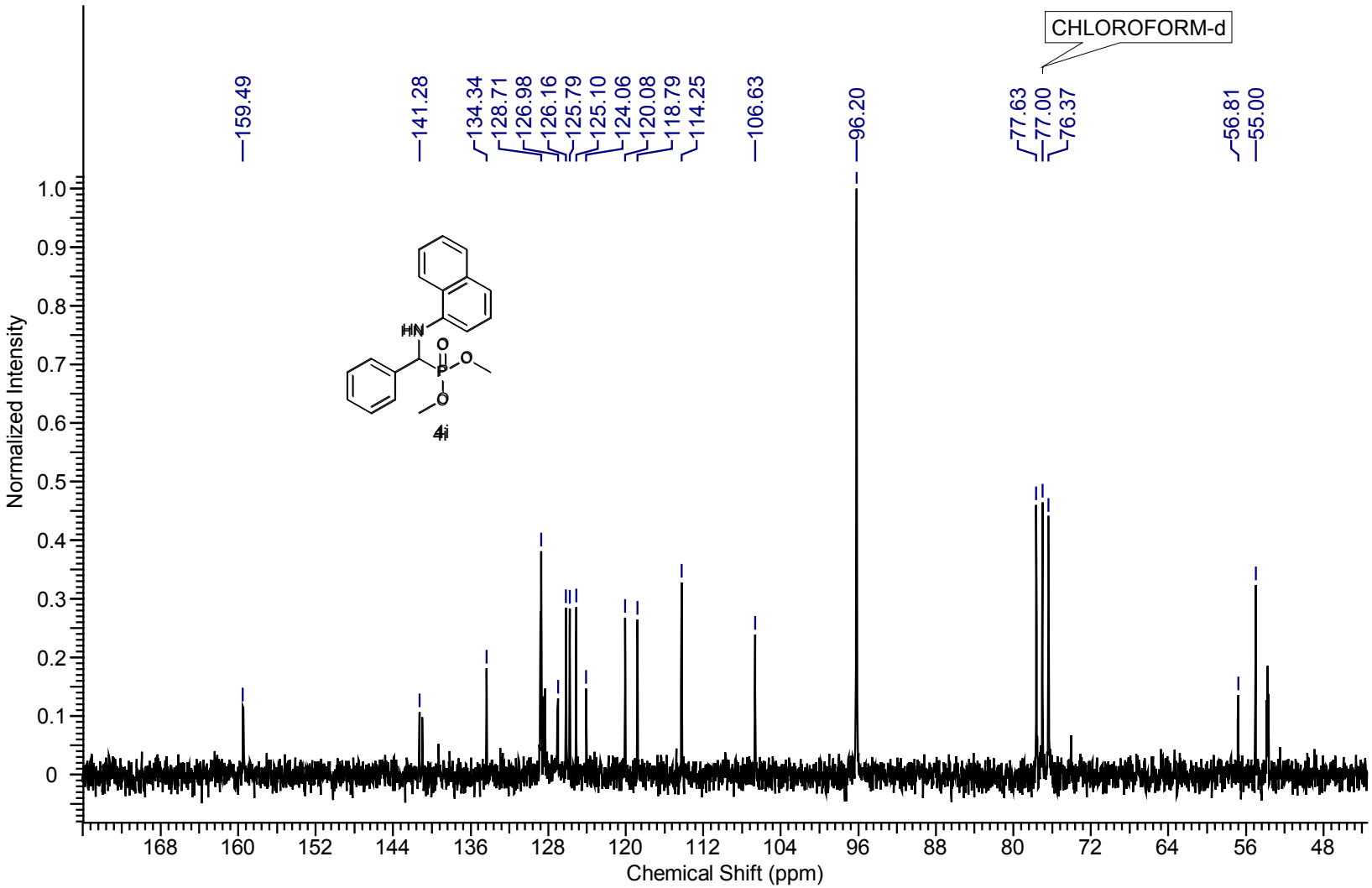
4.76
4.54
3.75
3.70
3.55
3.50
HN
O
P
O
O
O
4g
TMS
1.00
2.04
3.05
1.94
1.14
0.85
3.06
3.00
Normalized Intensity
Chemical Shift (ppm)

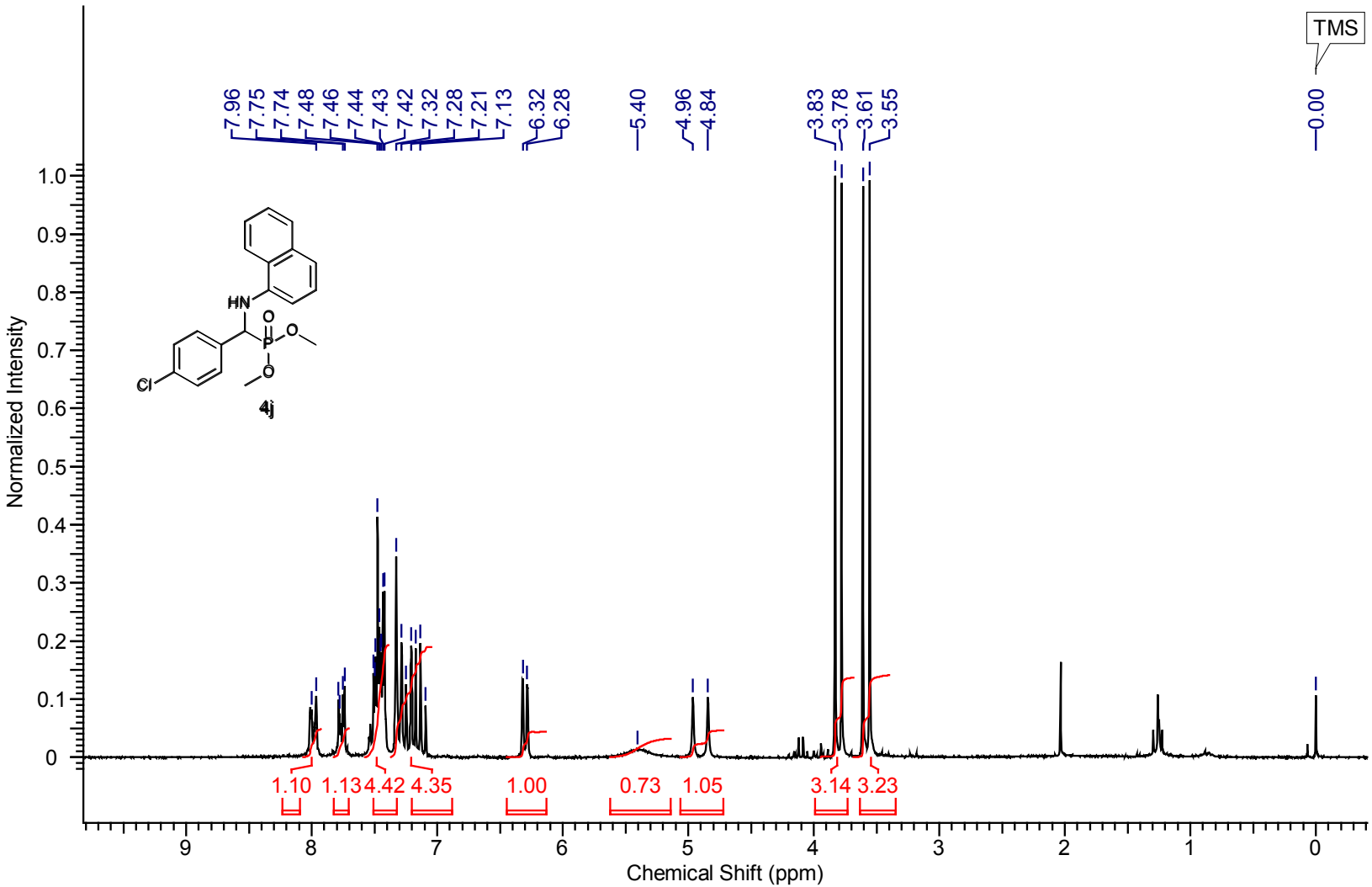

CHLOROFORM-d
149.15
145.65
142.38
129.08
118.90
113.82
110.69
108.83
96.05
77.63
77.00
76.36
53.70
53.42
51.32
48.13
HN
O
P
O
O
O
4g
Normalized Intensity
Chemical Shift (ppm)

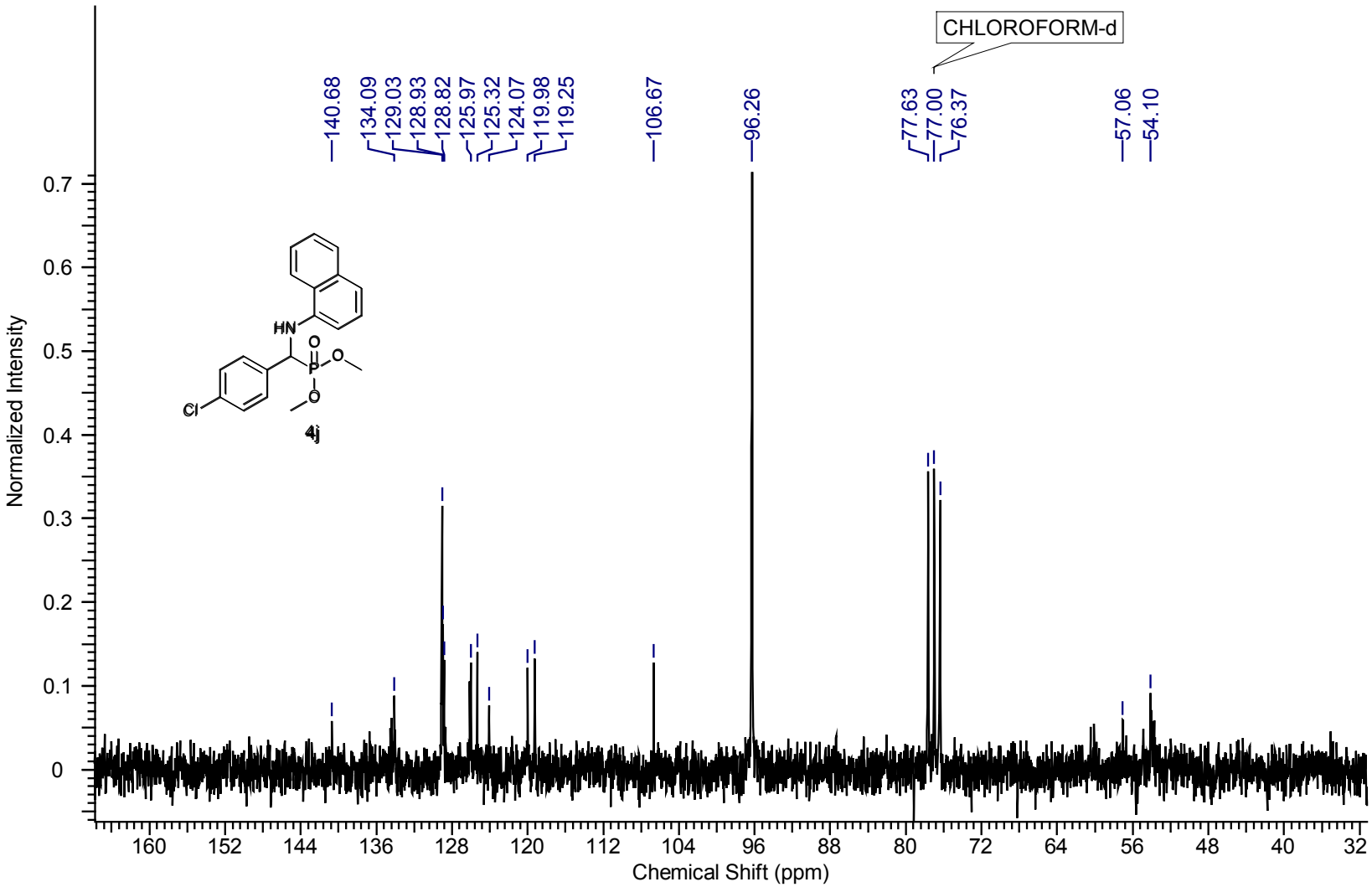

CHLOROFORM-d
7.27
6.82
6.81
6.77
6.74
6.72
5.14
5.02
4.29
3.86
3.84
3.81
3.81
3.80
3.78
3.67
3.49
3.44
2.24
2.22
2.20
2.18
2.14
HN
O
P
4h
Normalized Intensity
Chemical Shift (ppm)
4.78
0.50
0.62
9.40
2.80
9.31

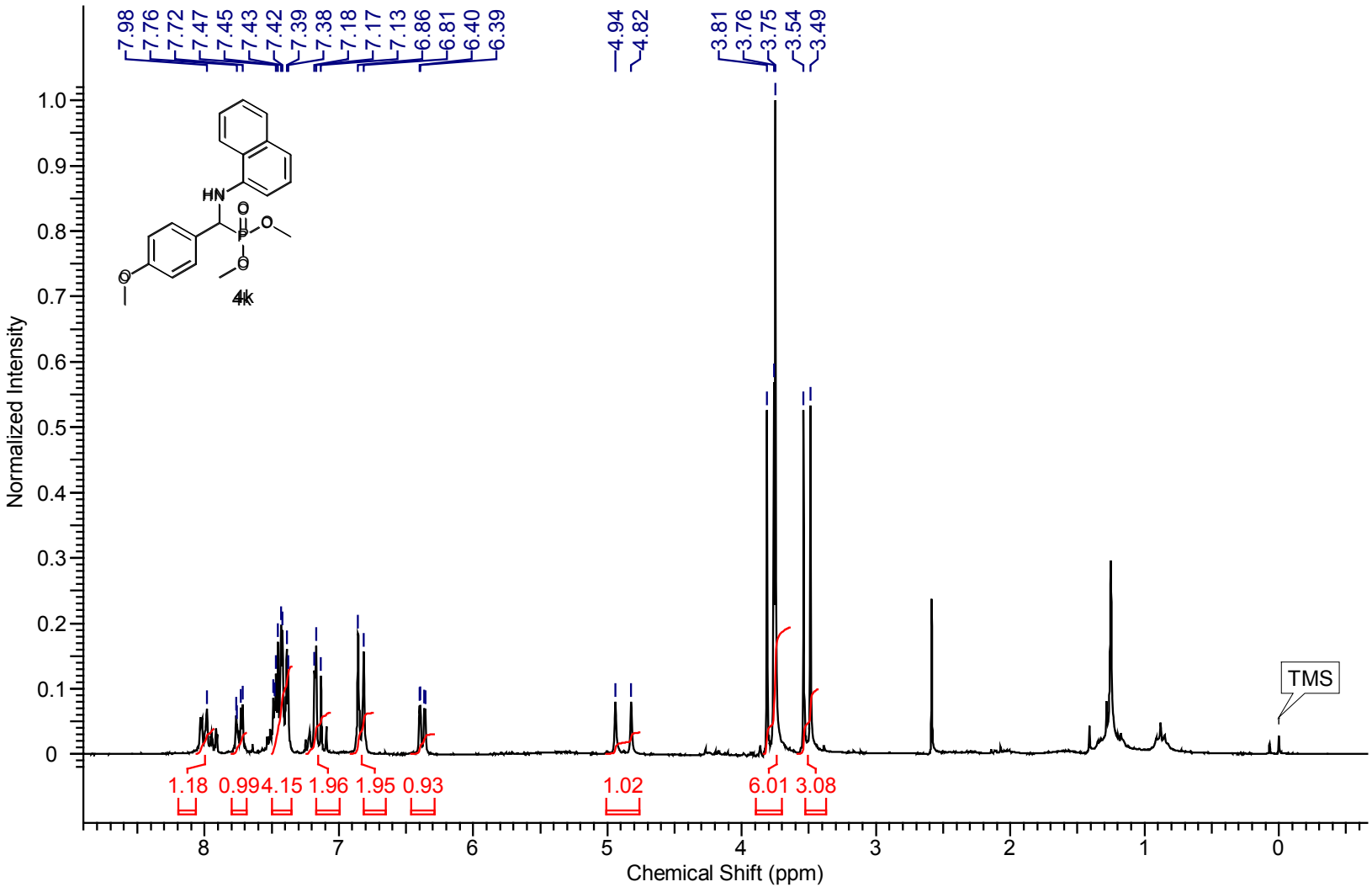

CHLOROFORM-d
153.84
141.94
130.51
129.49
128.84
128.34
114.41
112.17
96.25
77.64
77.00
76.37
56.35
55.51
52.92
29.79
20.64
18.57
HN
O
P
4h
Normalized Intensity
Chemical Shift (ppm)

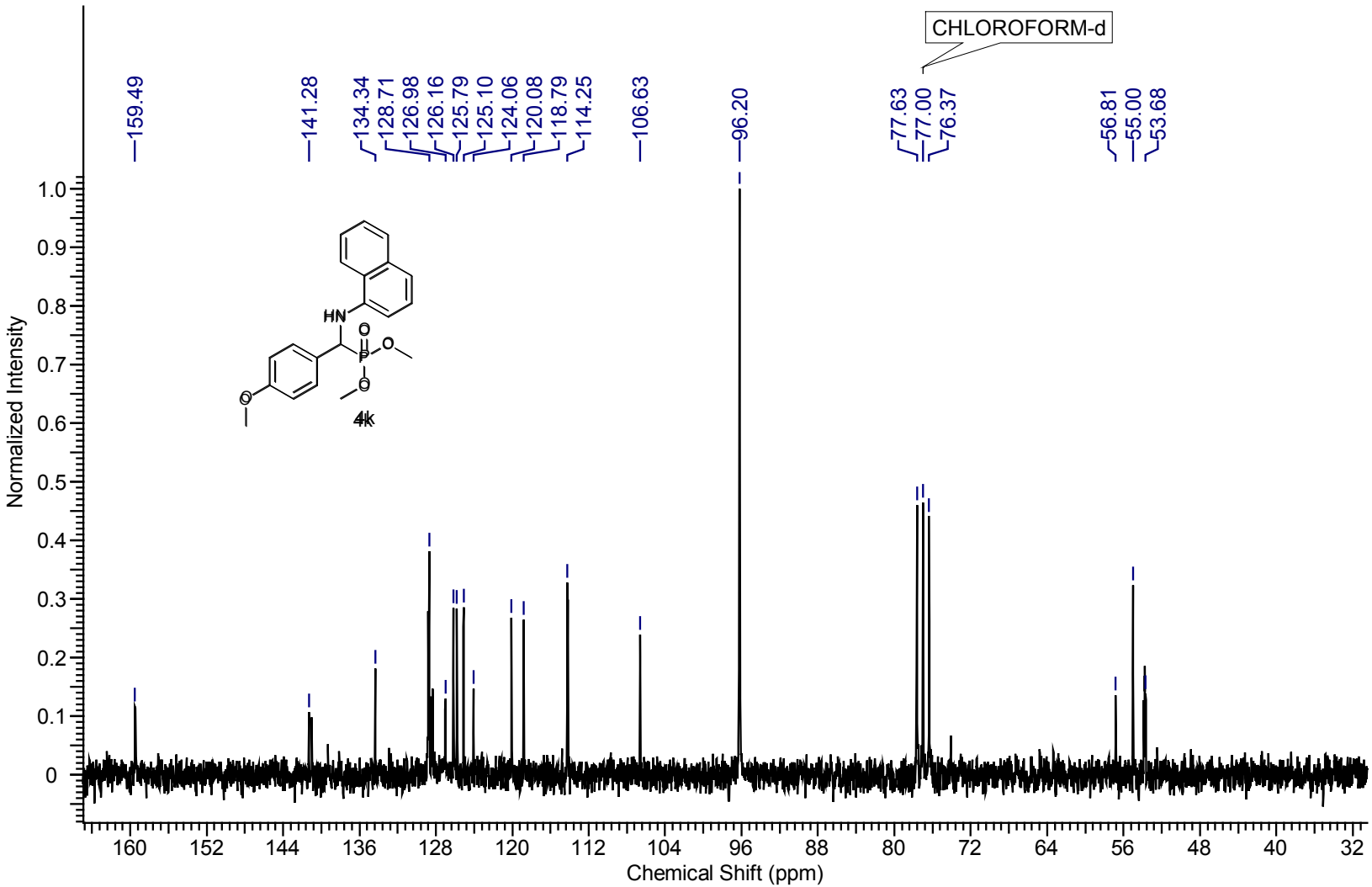

TMS
8.00
7.72
7.52
7.50
7.49
7.48
7.47
7.33
7.29
7.18
7.16
7.13
6.38
6.35
5.00
4.88
3.82
3.77
3.52
3.47
0.00
HN
O
P
O
O
4i
1.08
1.02
3.91
3.03
1.83
0.87
1.06
2.99
3.00
Normalized Intensity
Chemical Shift (ppm)

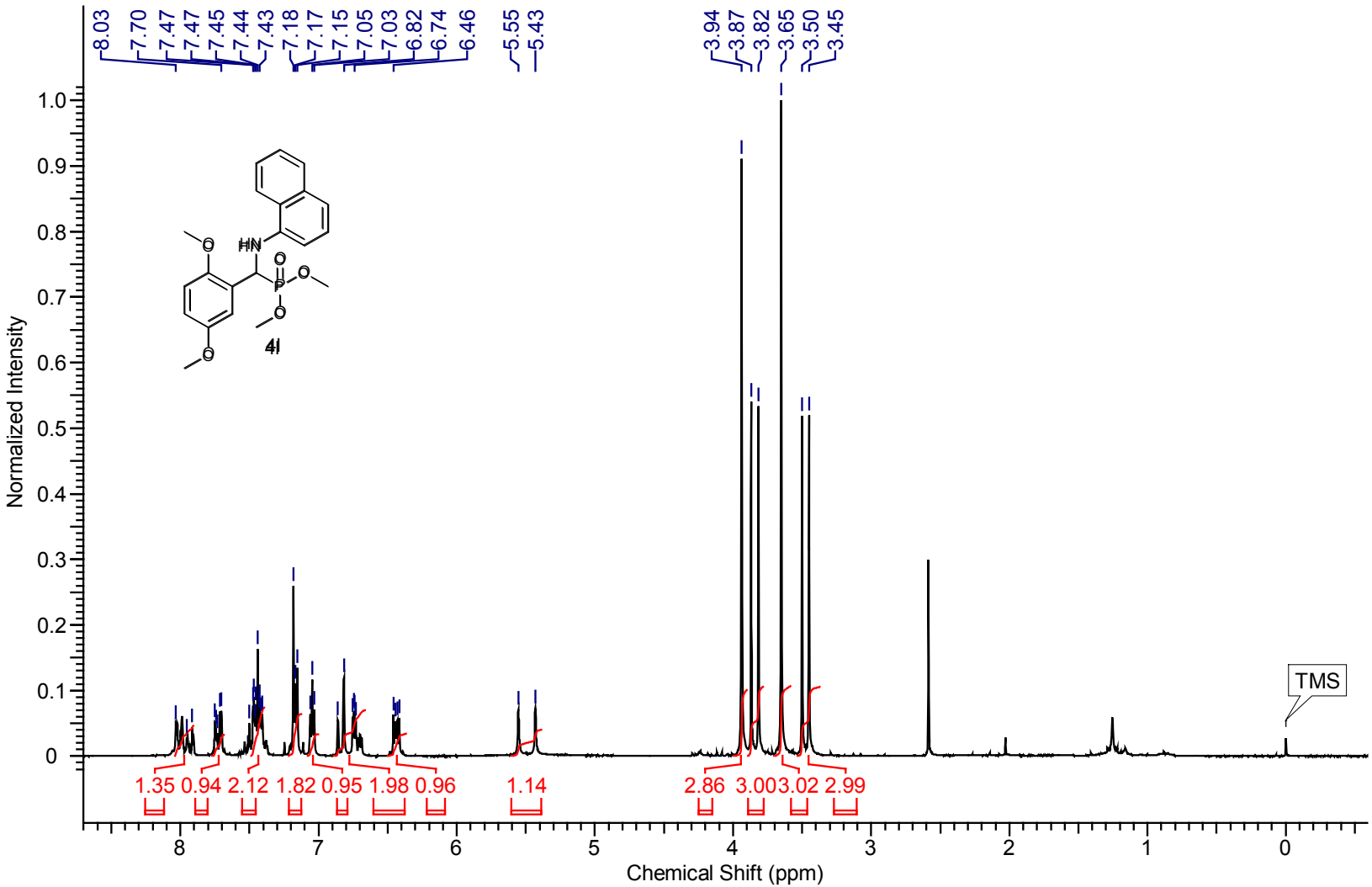

CHLOROFORM-d
159.49
141.28
134.34
128.71
126.98
126.16
125.79
125.10
124.06
120.08
118.79
114.25
106.63
96.20
77.63
77.00
76.37
56.81
55.00
HN
O
P
O
O
4i
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
Chemical Shift (ppm)

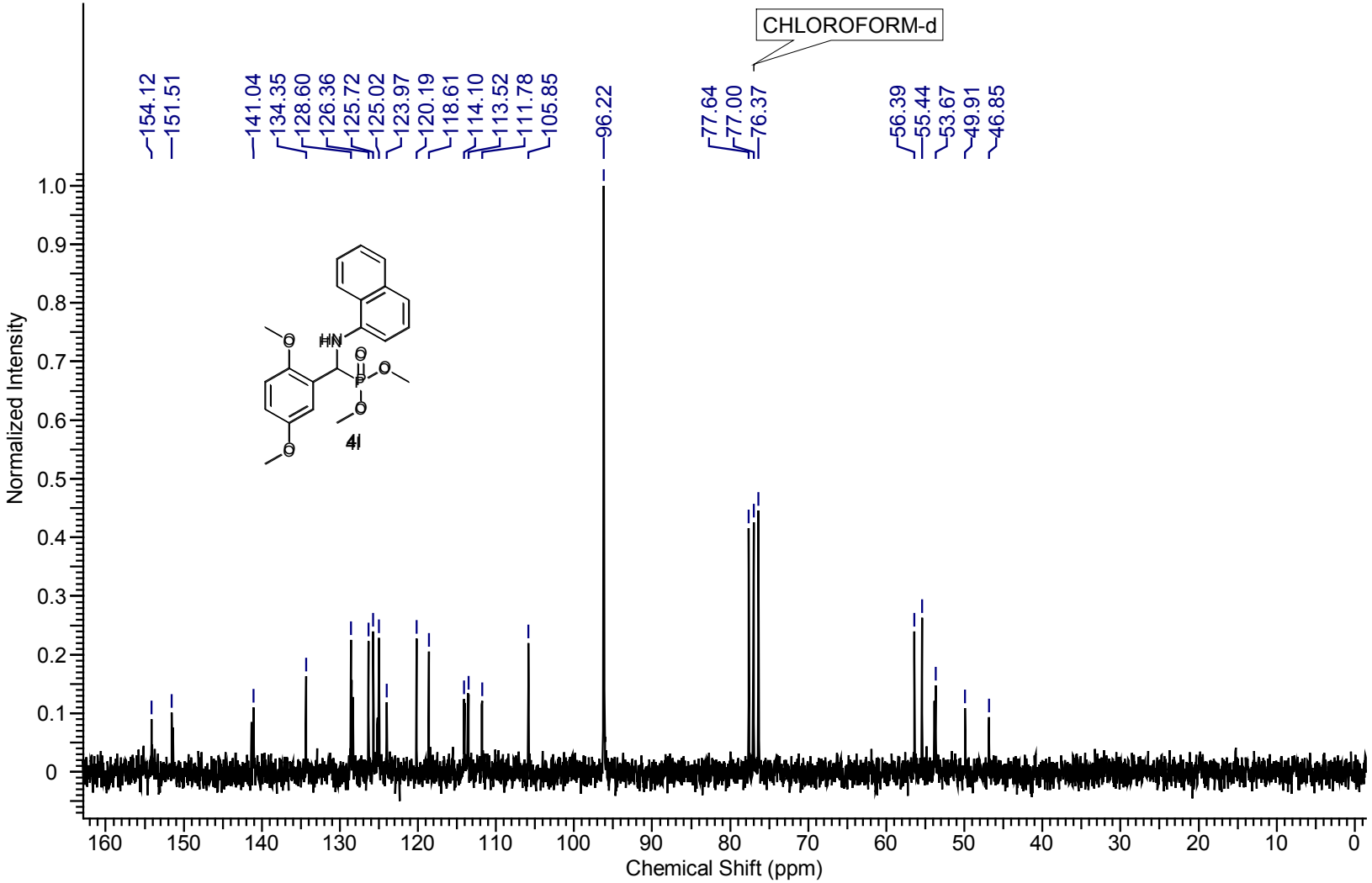

TMS
7.96
7.75
7.74
7.48
7.46
7.44
7.43
7.42
7.32
7.28
7.21
7.13
6.32
6.28
5.40
4.96
4.84
3.83
3.78
3.61
3.55
0.00
HN
O
P
O
O
Cl
4j
1.10
1.13
4.42
4.35
1.00
0.73
1.05
3.14
3.23
Normalized Intensity
Chemical Shift (ppm)

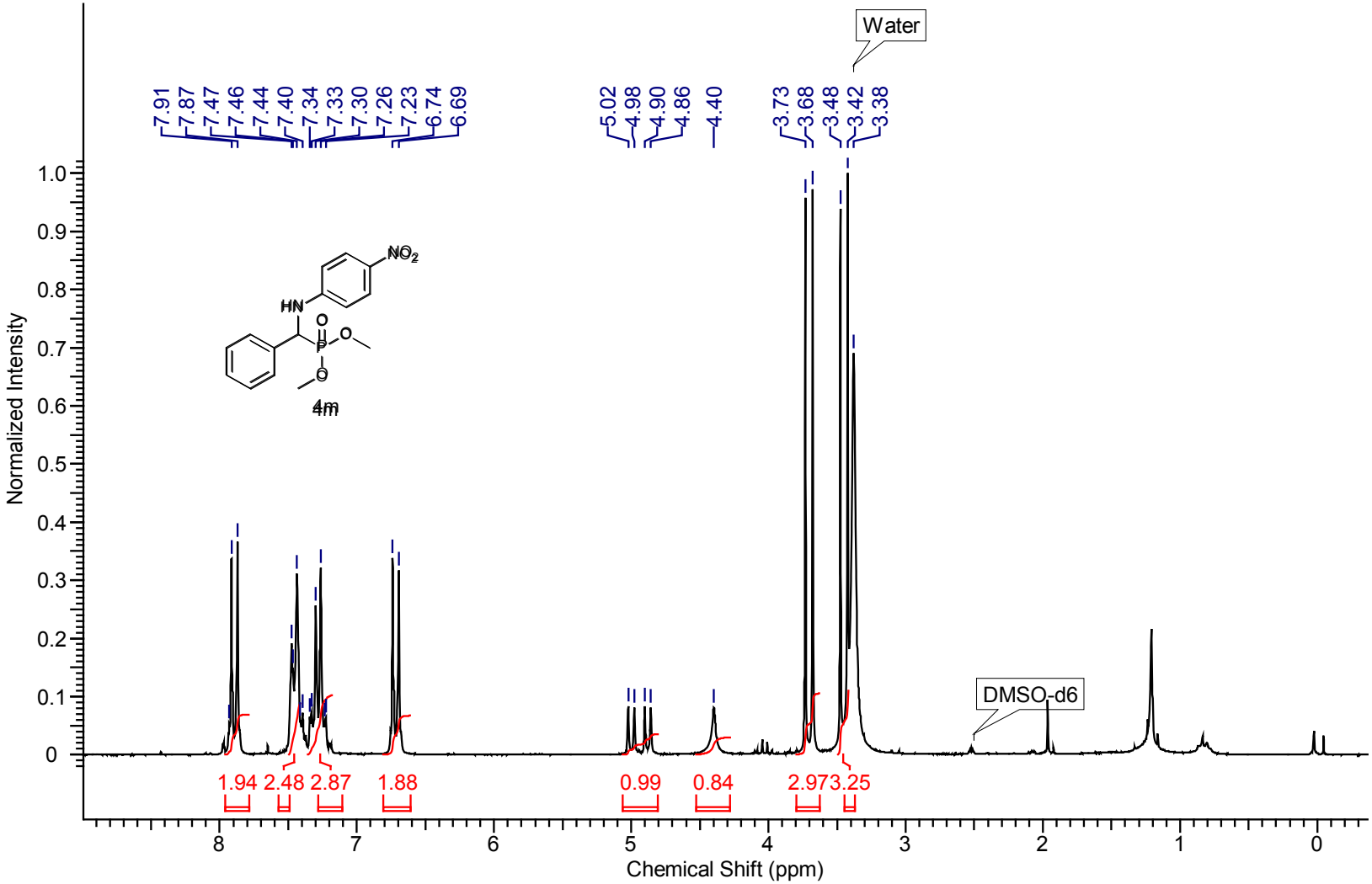

CHLOROFORM-d
140.68
134.09
129.03
128.93
128.82
125.97
125.32
124.07
119.98
119.25
106.67
96.26
77.63
77.00
76.37
57.06
54.10
HN
O
P
O
O
Cl
4j
Normalized Intensity
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
Chemical Shift (ppm)

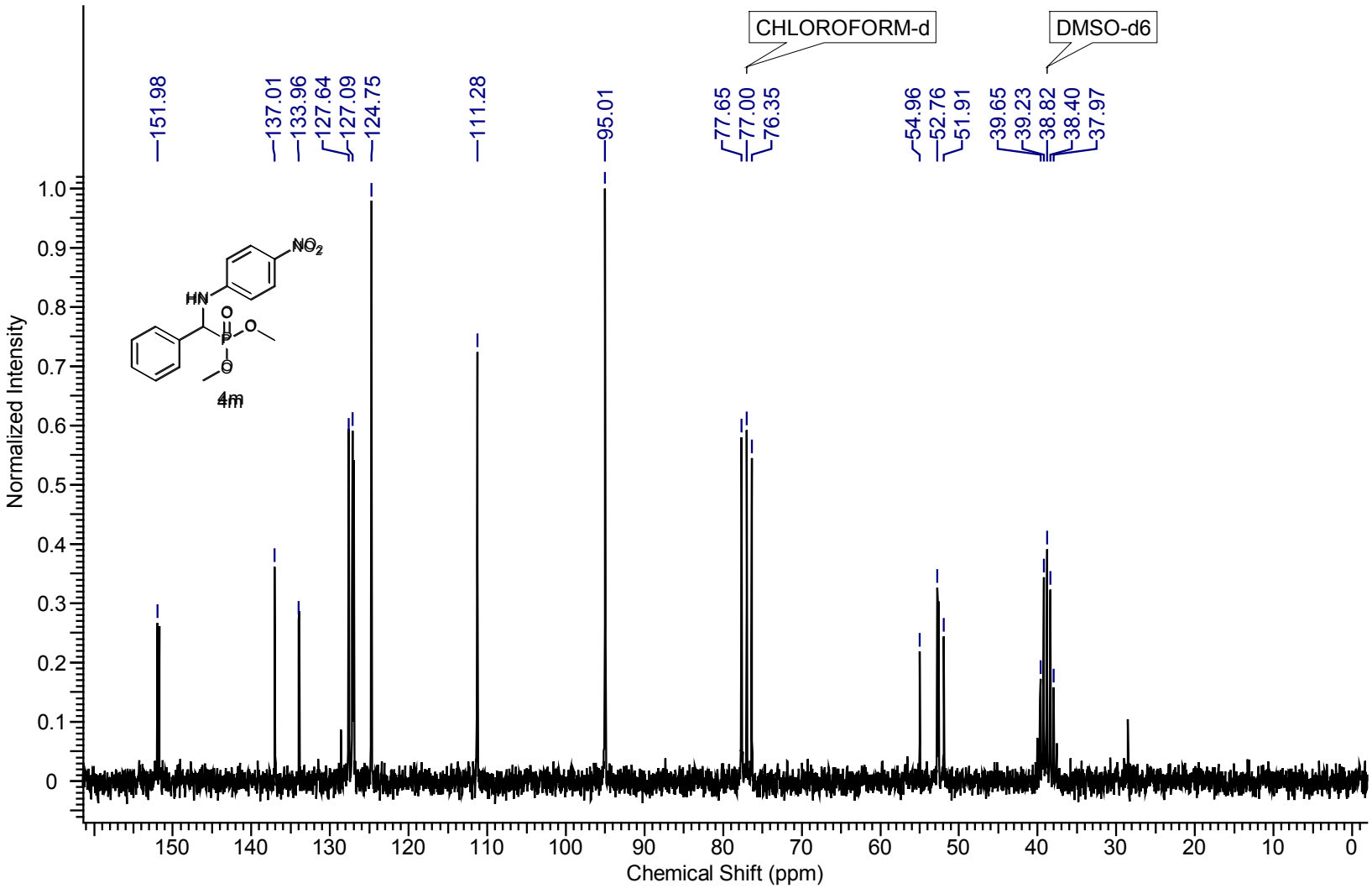

7.98
7.76
7.72
7.47
7.45
7.43
7.42
7.39
7.38
7.18
7.17
7.13
6.86
6.81
6.40
6.39
4.94
4.82
3.81
3.76
3.75
3.54
3.49
HN
O
P
O
O
O
O
4k
TMS
1.18
0.99
4.15
1.96
1.95
0.93
1.02
6.01
3.08
Normalized Intensity
Chemical Shift (ppm)

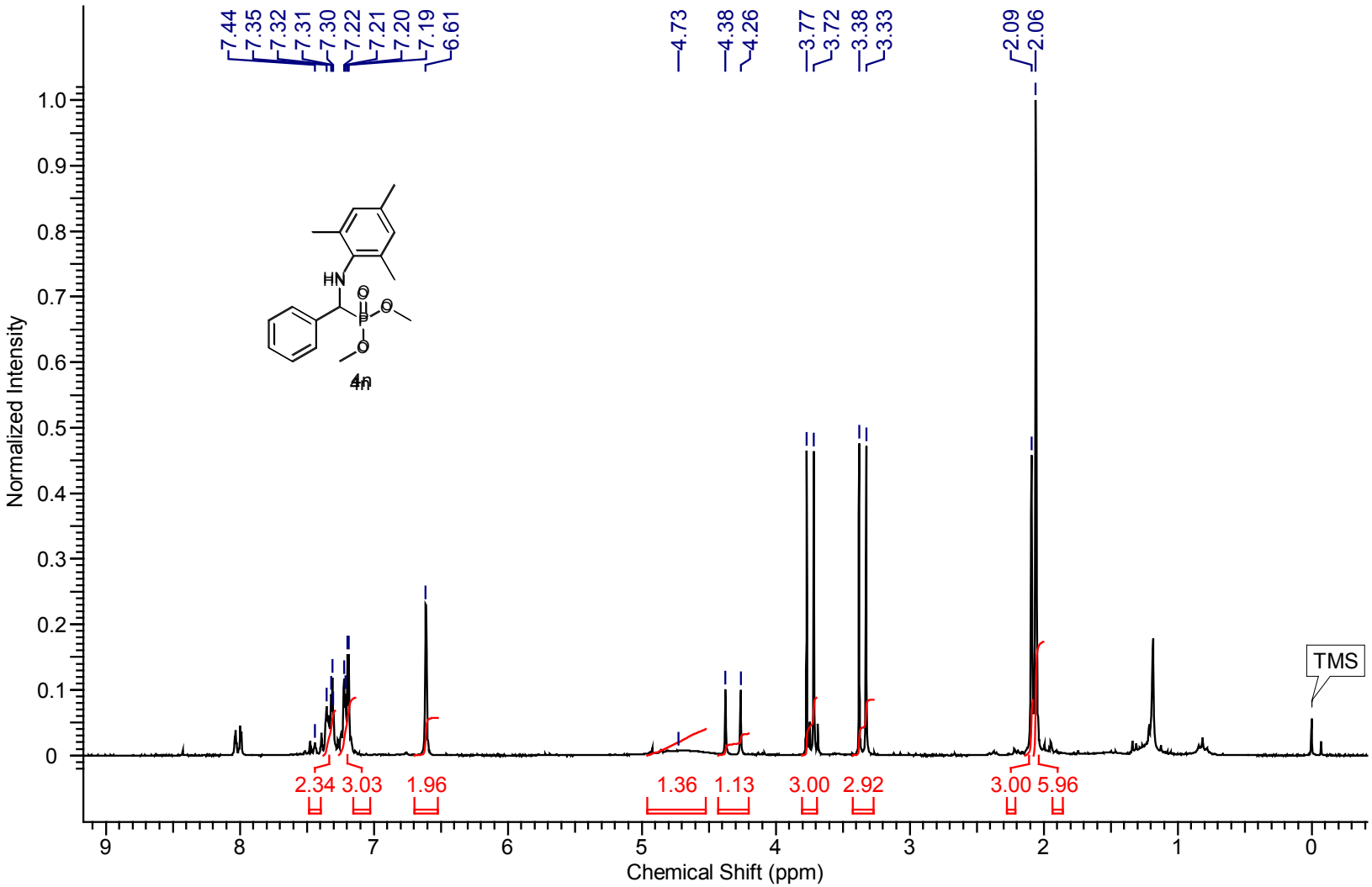

CHLOROFORM-d
159.49
141.28
134.34
128.71
126.98
126.16
125.79
125.10
124.06
120.08
118.79
114.25
106.63
96.20
77.63
77.00
76.37
56.81
55.00
53.68
HN
O
P
O
O
O
4k
Normalized Intensity
Chemical Shift (ppm)

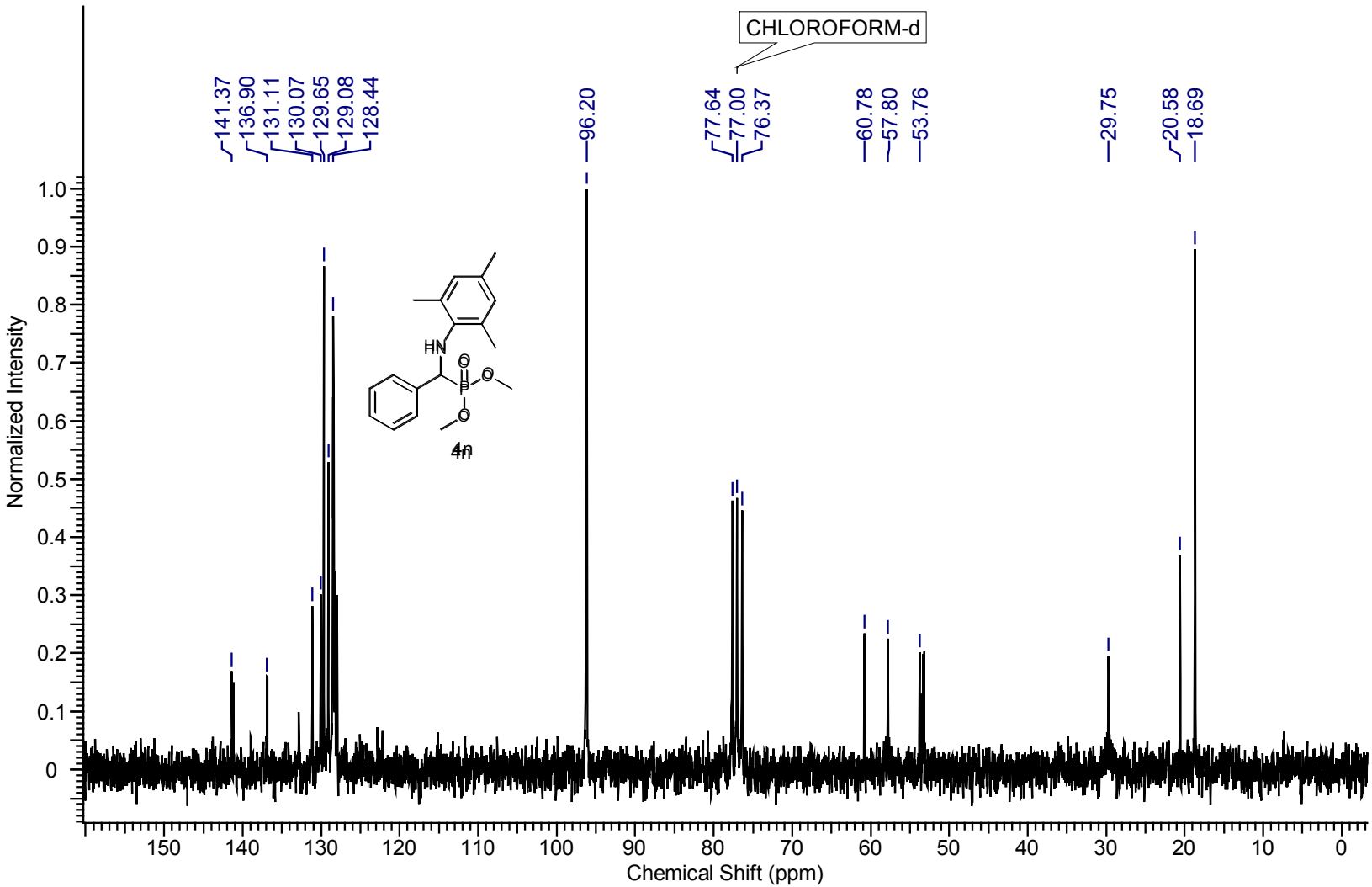

8.03
7.70
7.47
7.47
7.45
7.44
7.43
7.18
7.17
7.15
7.05
7.03
6.82
6.74
6.46
5.55
5.43
3.94
3.87
3.82
3.65
3.50
3.45
Normalized Intensity
Chemical Shift (ppm)
TMS
1.35 0.94 2.12 1.82 0.95 1.98 0.96
1.14
2.86 3.00 3.02 2.99
4l

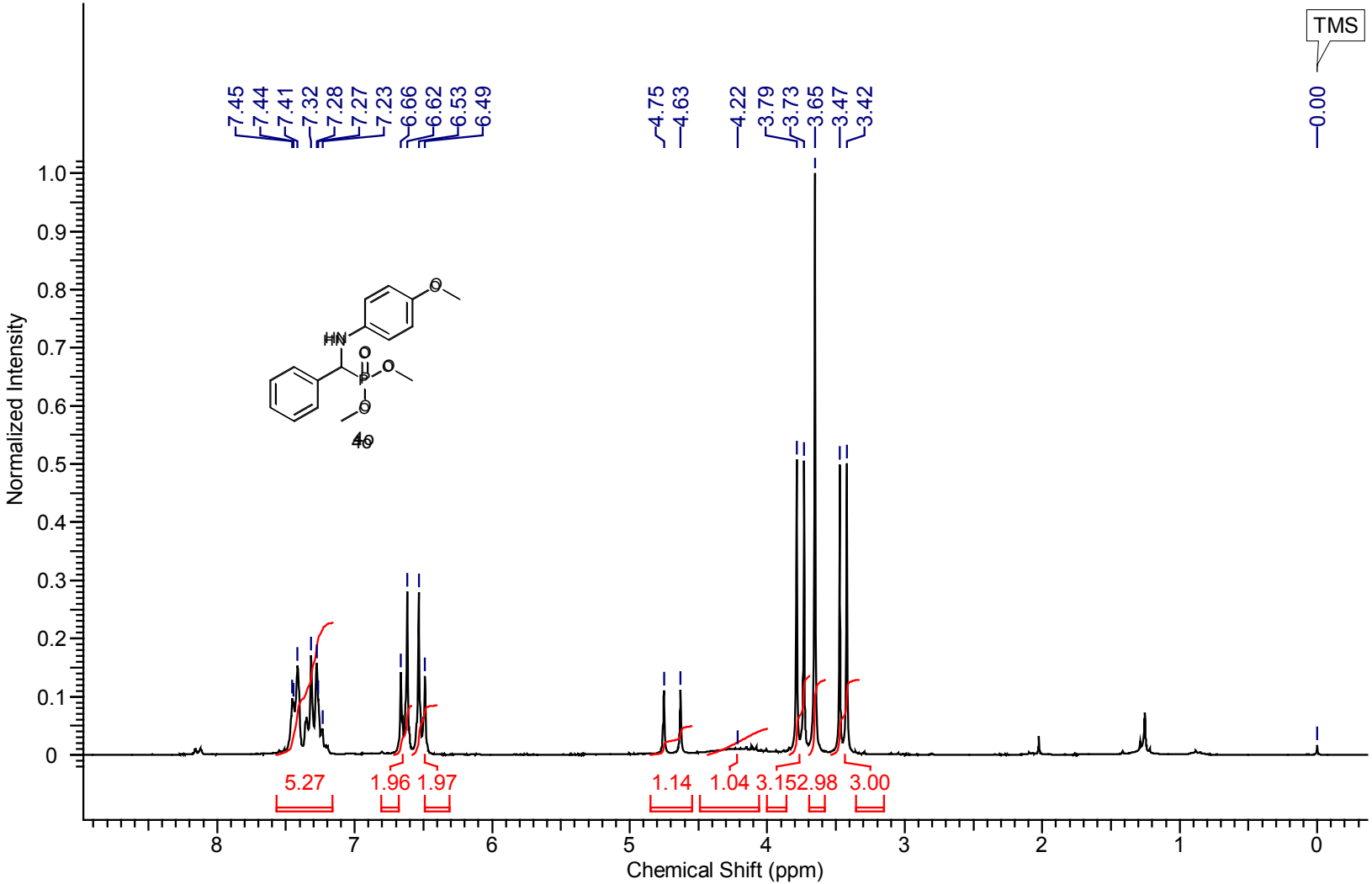

CHLOROFORM-d
154.12
151.51
141.04
134.35
128.60
126.36
125.72
125.02
123.97
120.19
118.61
114.10
113.52
111.78
105.85
96.22
77.64
77.00
76.37
56.39
55.44
53.67
49.91
46.85
Normalized Intensity
Chemical Shift (ppm)
4l

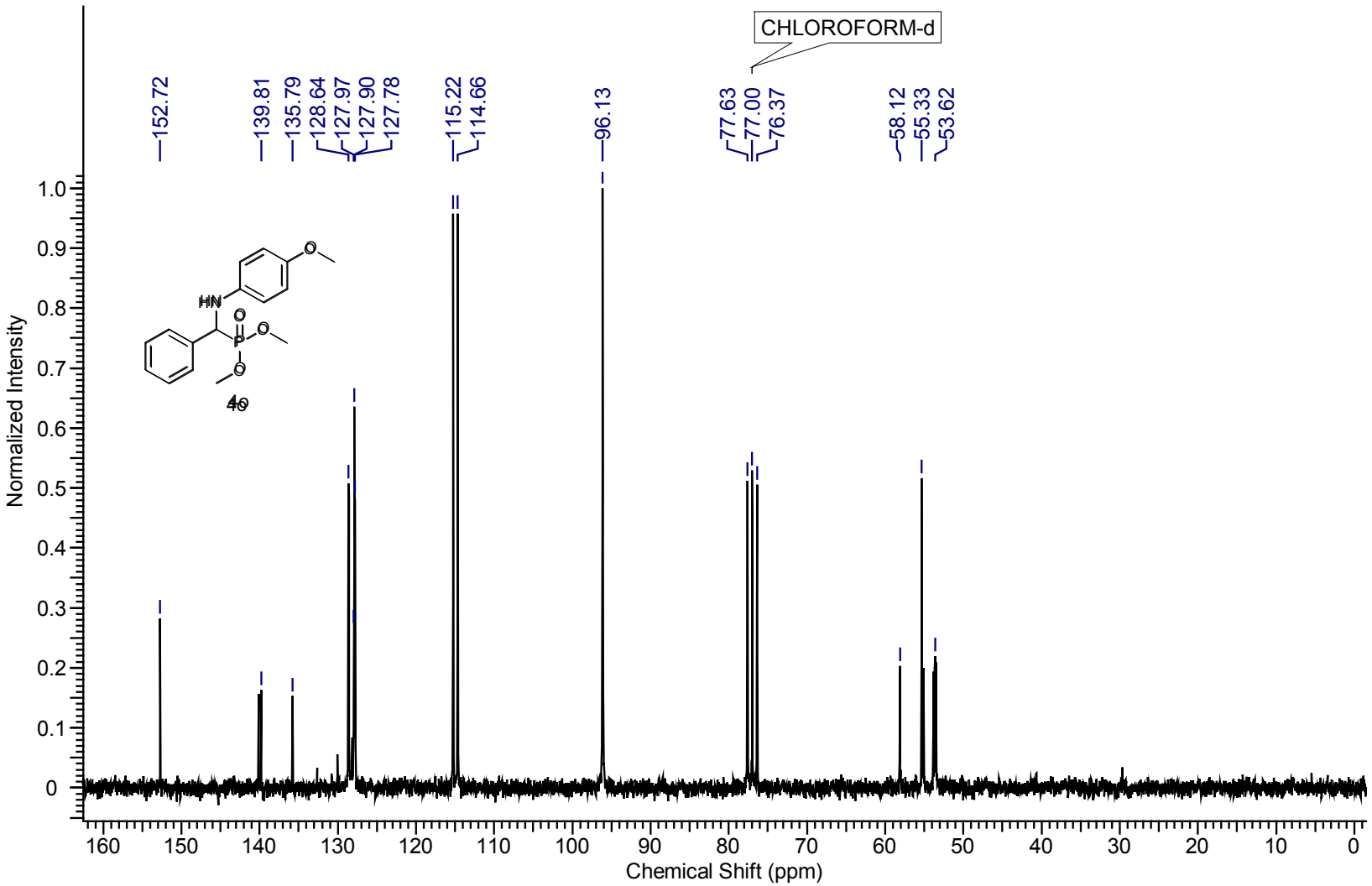

Water
7.91
7.87
7.47
7.46
7.44
7.40
7.34
7.33
7.30
7.26
7.23
6.74
6.69
5.02
4.98
4.90
4.86
4.40
3.73
3.68
3.48
3.42
3.38
NO2
HN
O
P
O
O
4m
DMSO-d6
1.94
2.48
2.87
1.88
0.99
0.84
2.97
3.25
Normalized Intensity
Chemical Shift (ppm)

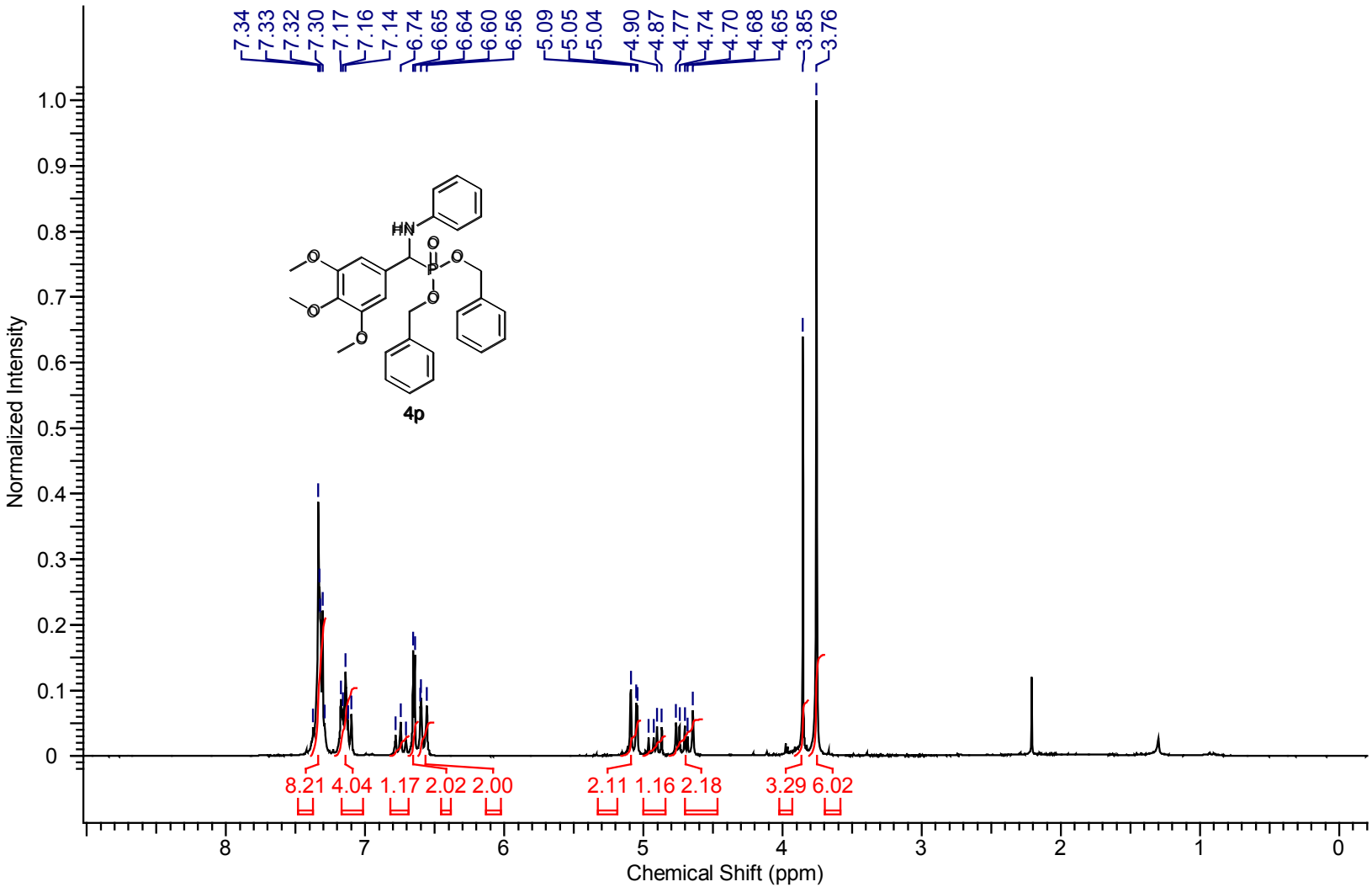

CHLOROFORM-d
DMSO-d6
151.98
137.01
133.96
127.64
127.09
124.75
111.28
95.01
77.65
77.00
76.35
54.96
52.76
51.91
39.65
39.23
38.82
38.40
37.97
NO2
HN
O
P
O
O
4m
Normalized Intensity
Chemical Shift (ppm)

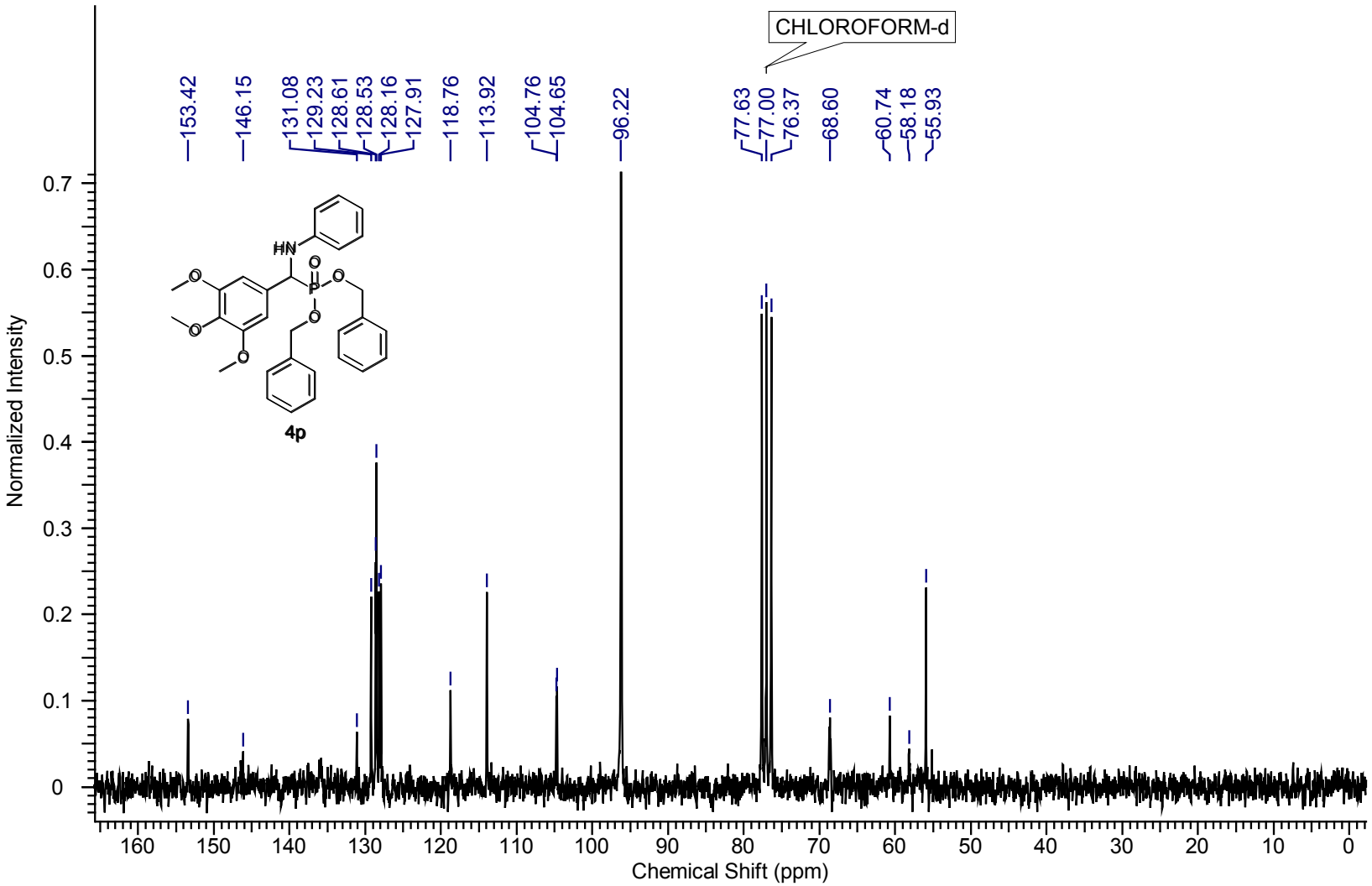

7.44
7.35
7.32
7.31
7.30
7.22
7.21
7.20
7.19
6.61
4.73
4.38
4.26
3.77
3.72
3.38
3.33
2.09
2.06
HN
O
P
O
O
O
4n
TMS
2.34
3.03
1.96
1.36
1.13
3.00
2.92
3.00
5.96
Normalized Intensity
Chemical Shift (ppm)

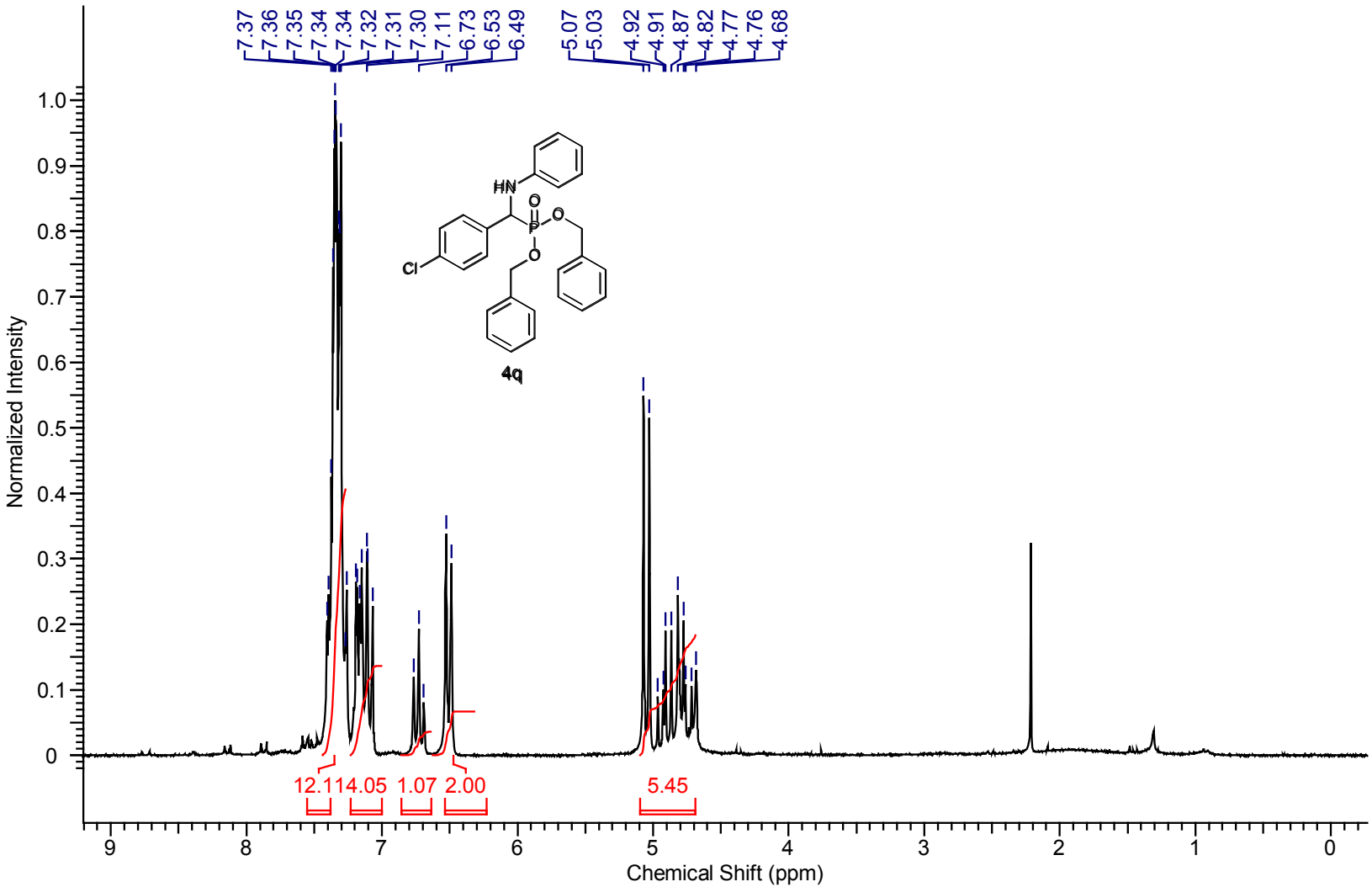

CHLOROFORM-d
141.37
136.90
131.11
130.07
129.65
129.08
128.44
96.20
77.64
77.00
76.37
60.78
57.80
53.76
29.75
20.58
18.69
HN
O
P
O
O
4n
Normalized Intensity
Chemical Shift (ppm)

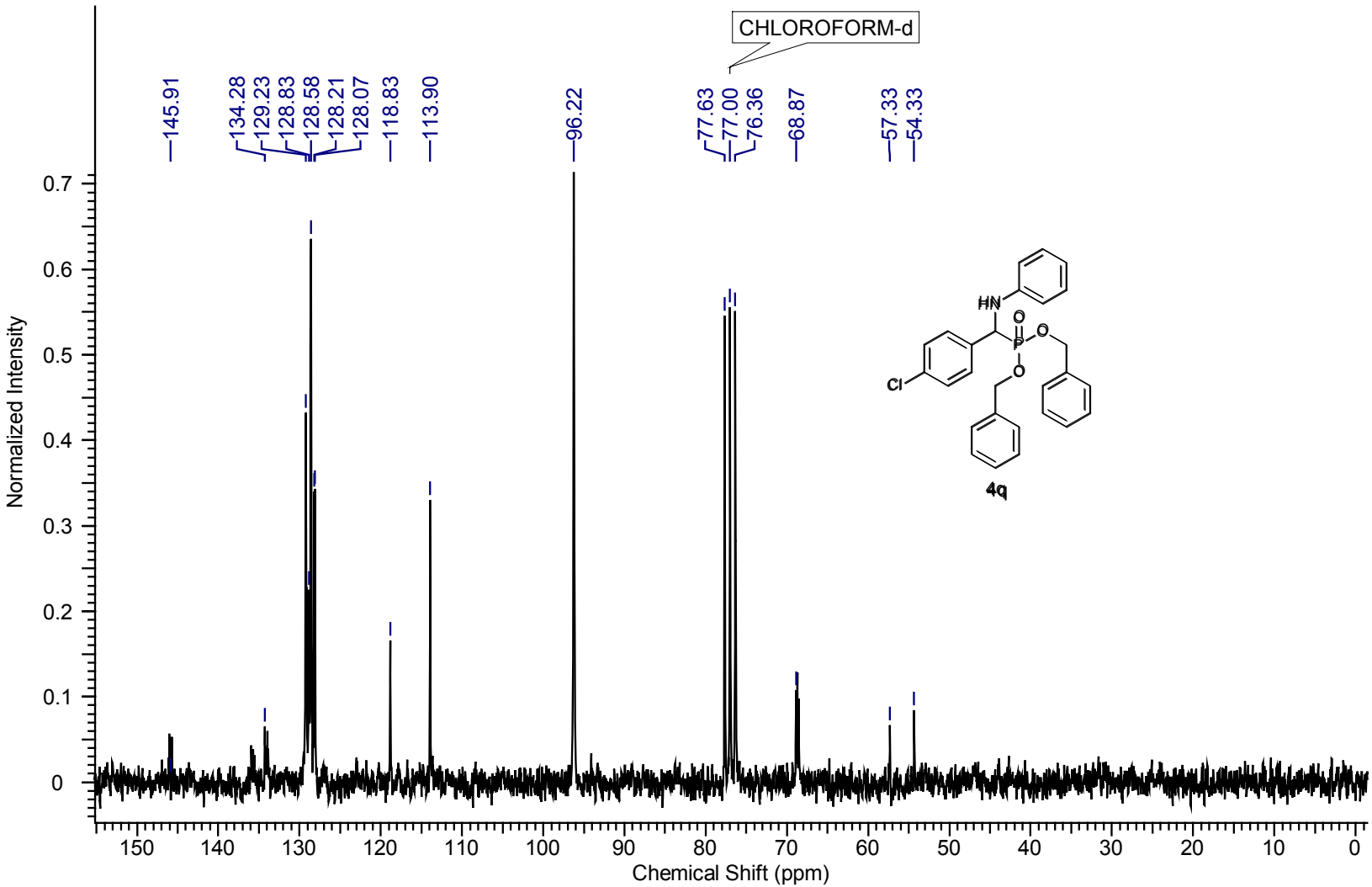

TMS
7.45
7.44
7.41
7.32
7.28
7.27
7.23
6.66
6.62
6.53
6.49
4.75
4.63
4.22
3.79
3.73
3.65
3.47
3.42
0.00
Normalized Intensity
Chemical Shift (ppm)
5.27
1.96
1.97
1.14
1.04
3.15
2.98
3.00
HN
O
P
40

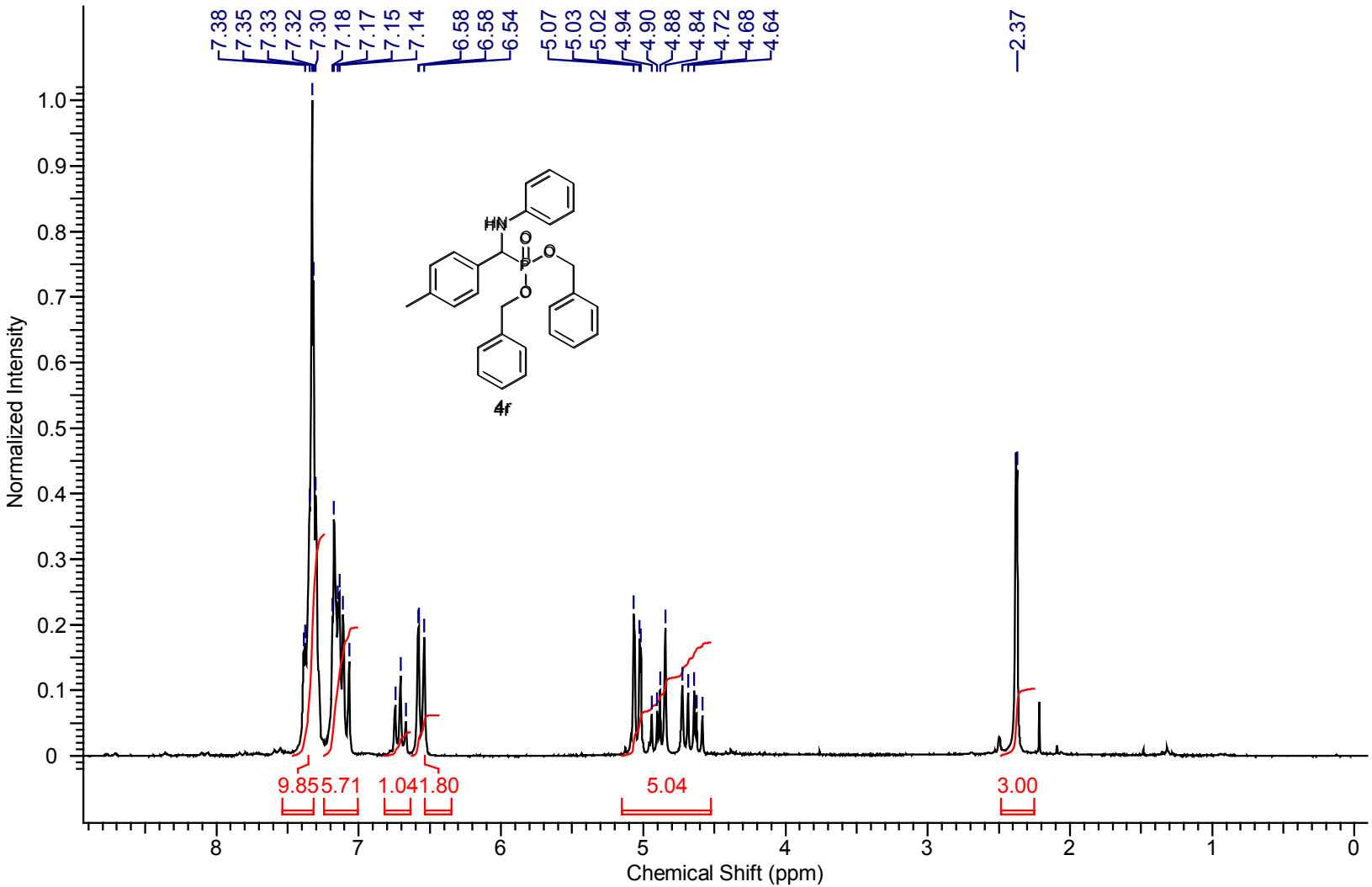

CHLOROFORM-d
152.72
139.81
135.79
128.64
127.97
127.90
127.78
115.22
114.66
96.13
77.63
77.00
76.37
58.12
55.33
53.62
HN
O
P
40
Normalized Intensity
Chemical Shift (ppm)

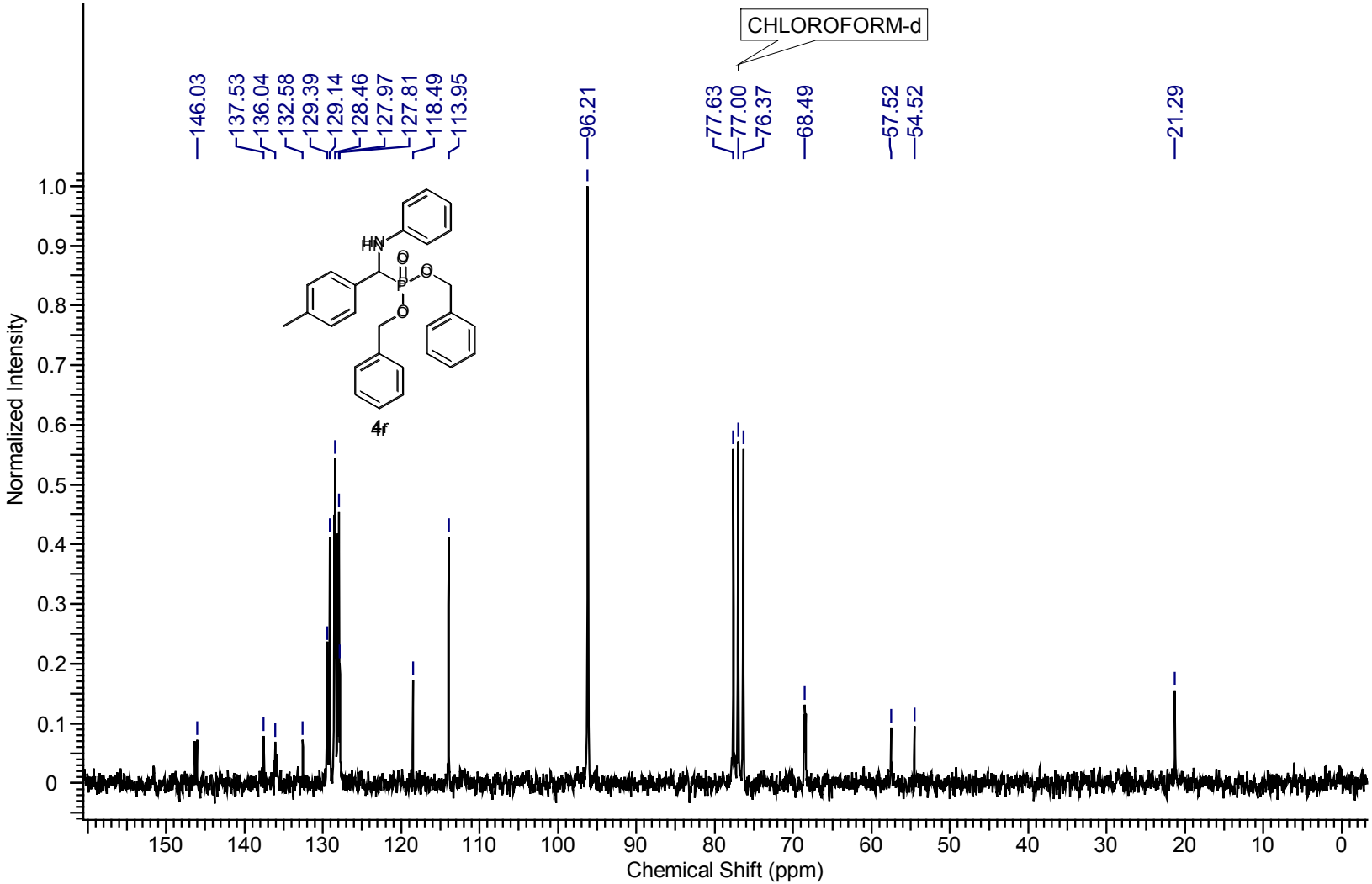

7.34
7.33
7.32
7.30
7.17
7.16
7.14
6.74
6.65
6.64
6.60
6.56
5.09
5.05
5.04
4.90
4.87
4.77
4.74
4.70
4.68
4.65
3.85
3.76
HN
O
P
O
O
O
O
O
4p
8.21
4.04
1.17
2.02
2.00
2.11
1.16
2.18
3.29
6.02
Normalized Intensity
Chemical Shift (ppm)

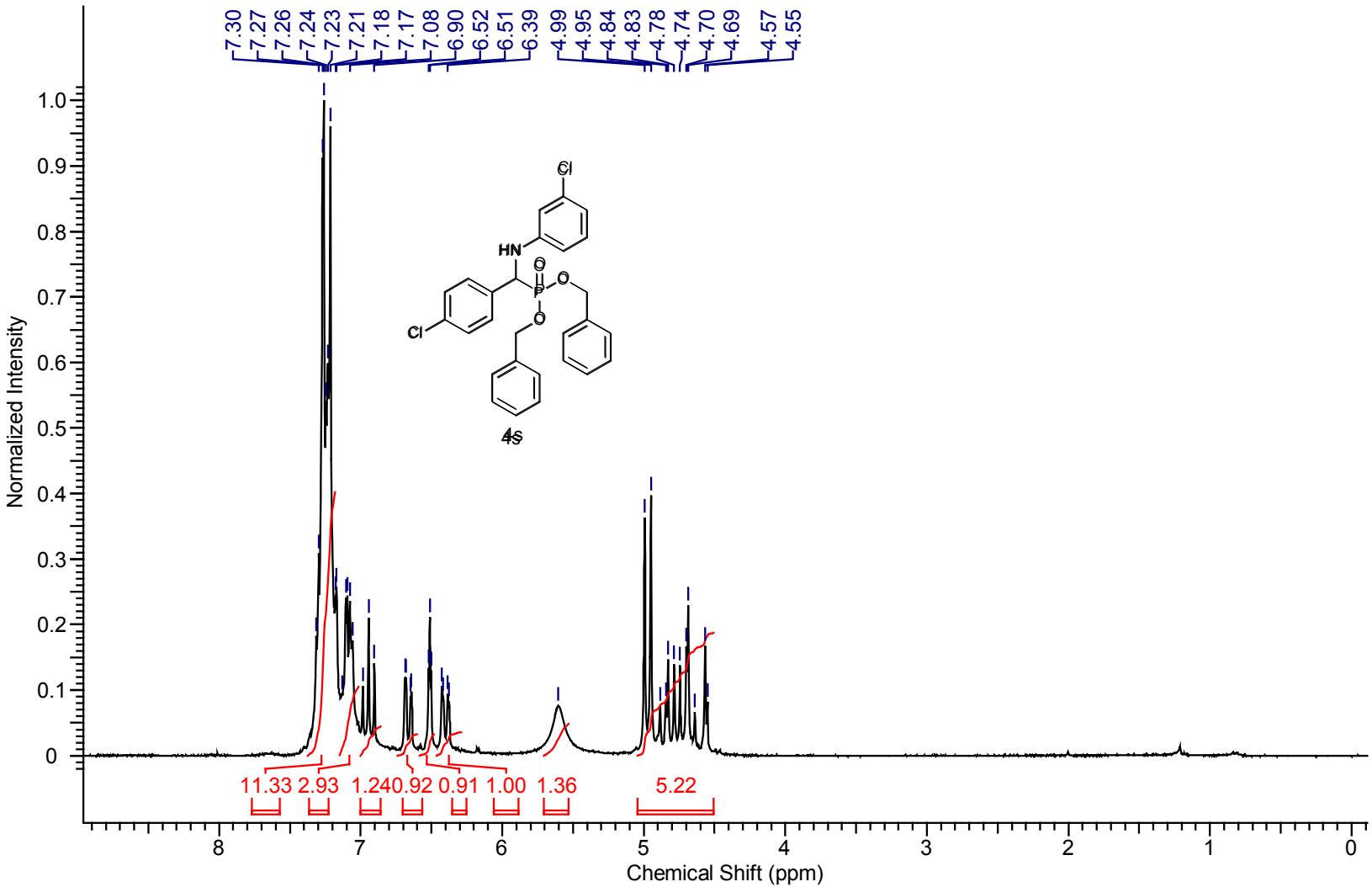

CHLOROFORM-d
153.42
146.15
131.08
129.23
128.61
128.53
128.16
127.91
118.76
113.92
104.76
104.65
96.22
77.63
77.00
76.37
68.60
60.74
58.18
55.93
HN
O
P
O
O
O
O
O
4p
Normalized Intensity
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

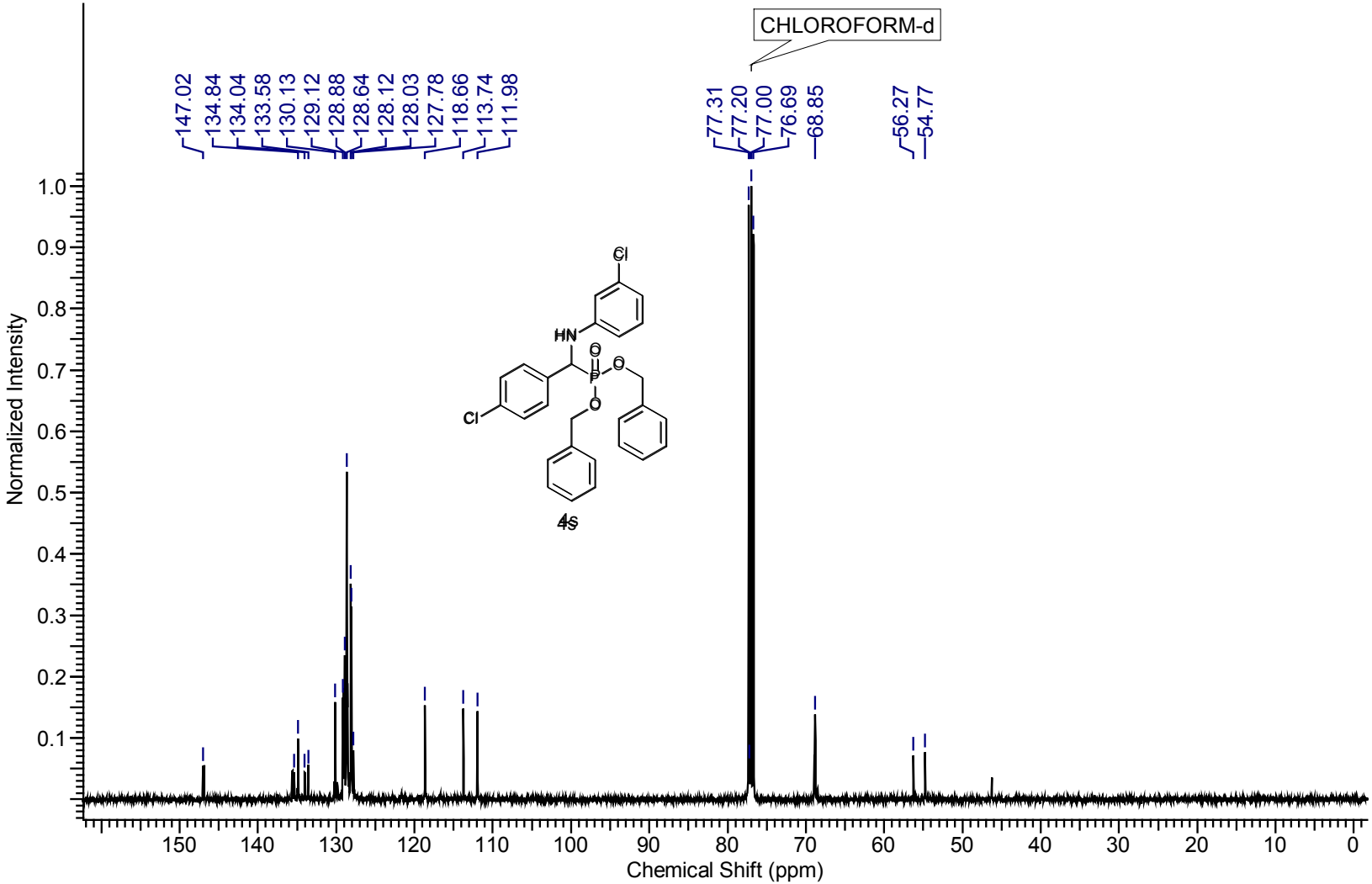

7.37
7.36
7.35
7.34
7.34
7.32
7.31
7.30
7.11
6.73
6.53
6.49
5.07
5.03
4.92
4.91
4.87
4.82
4.77
4.76
4.68
HN
O
P
O
O
Cl
4q
12.11
4.05
1.07
2.00
5.45
Normalized Intensity
Chemical Shift (ppm)

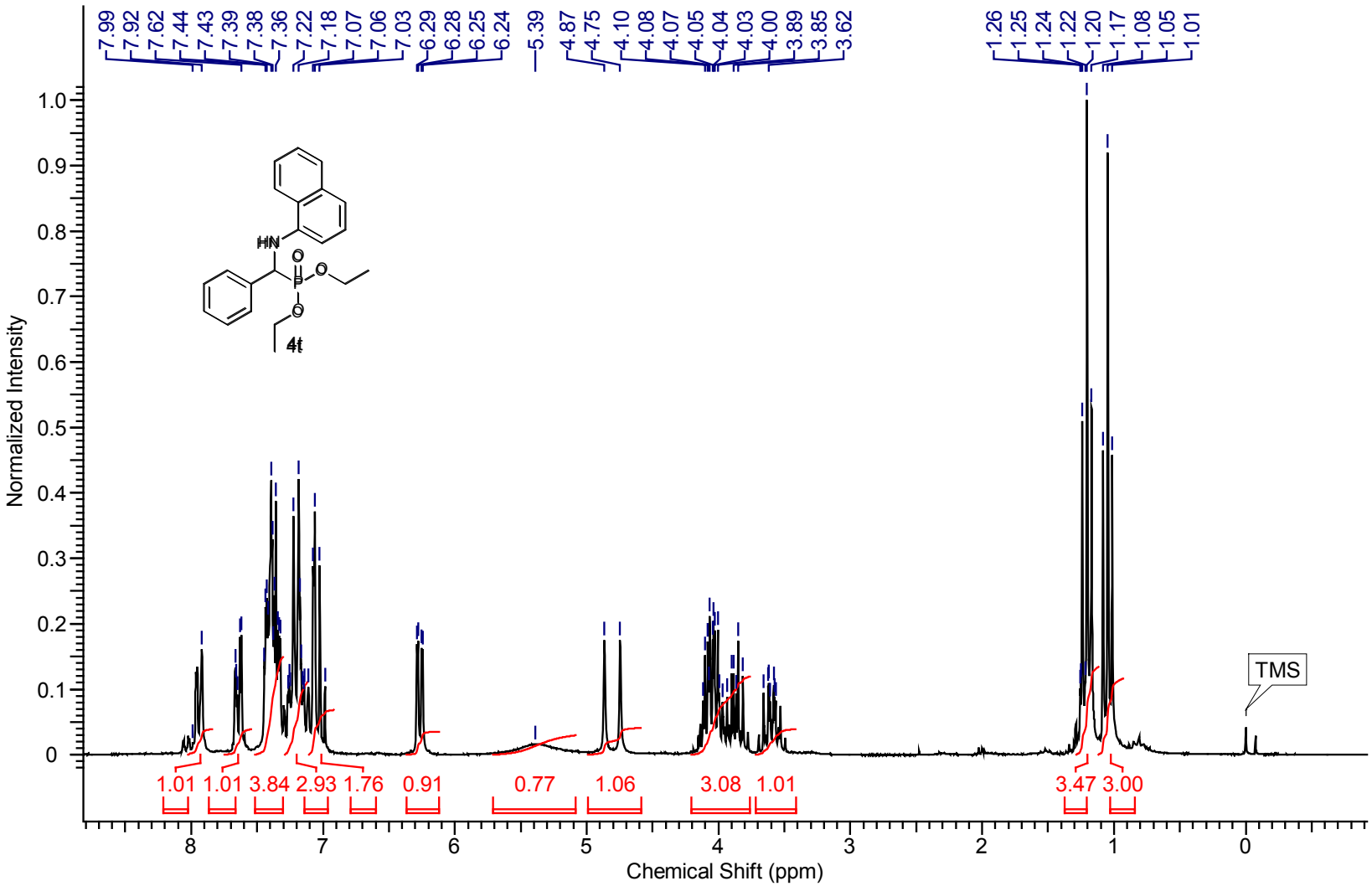

CHLOROFORM-d
145.91
134.28
129.23
128.83
128.58
128.21
128.07
118.83
113.90
96.22
77.63
77.00
76.36
68.87
57.33
54.33
Normalized Intensity
Chemical Shift (ppm)
HN
O
P
O
O
Cl
4q

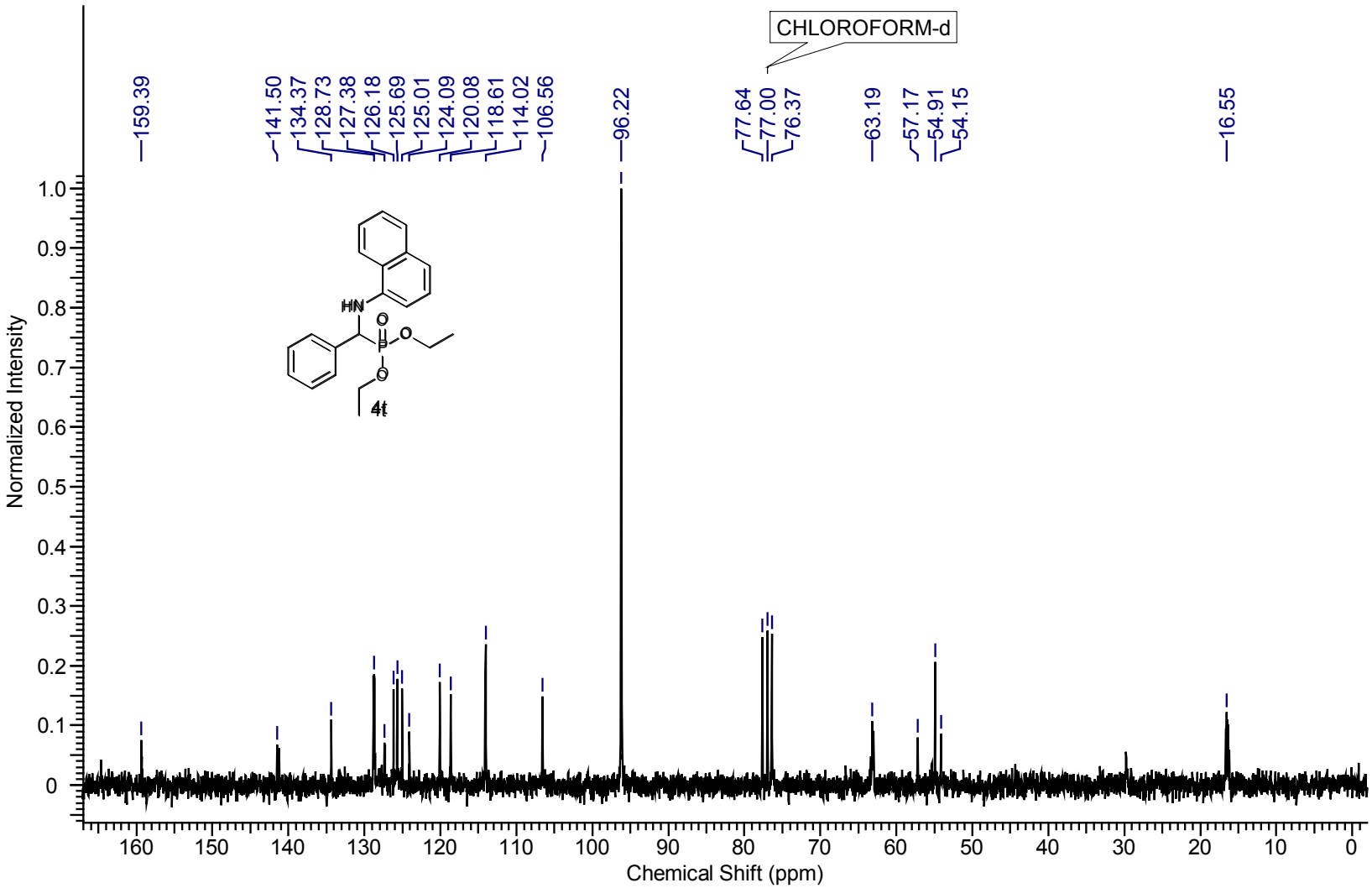

7.38
7.35
7.33
7.32
7.30
7.18
7.17
7.15
7.14
6.58
6.58
6.54
5.07
5.03
5.02
4.94
4.90
4.88
4.84
4.72
4.68
4.64
2.37
HN
O
P
O
O
4f
9.85
5.71
1.04
1.80
5.04
3.00
Normalized Intensity
Chemical Shift (ppm)

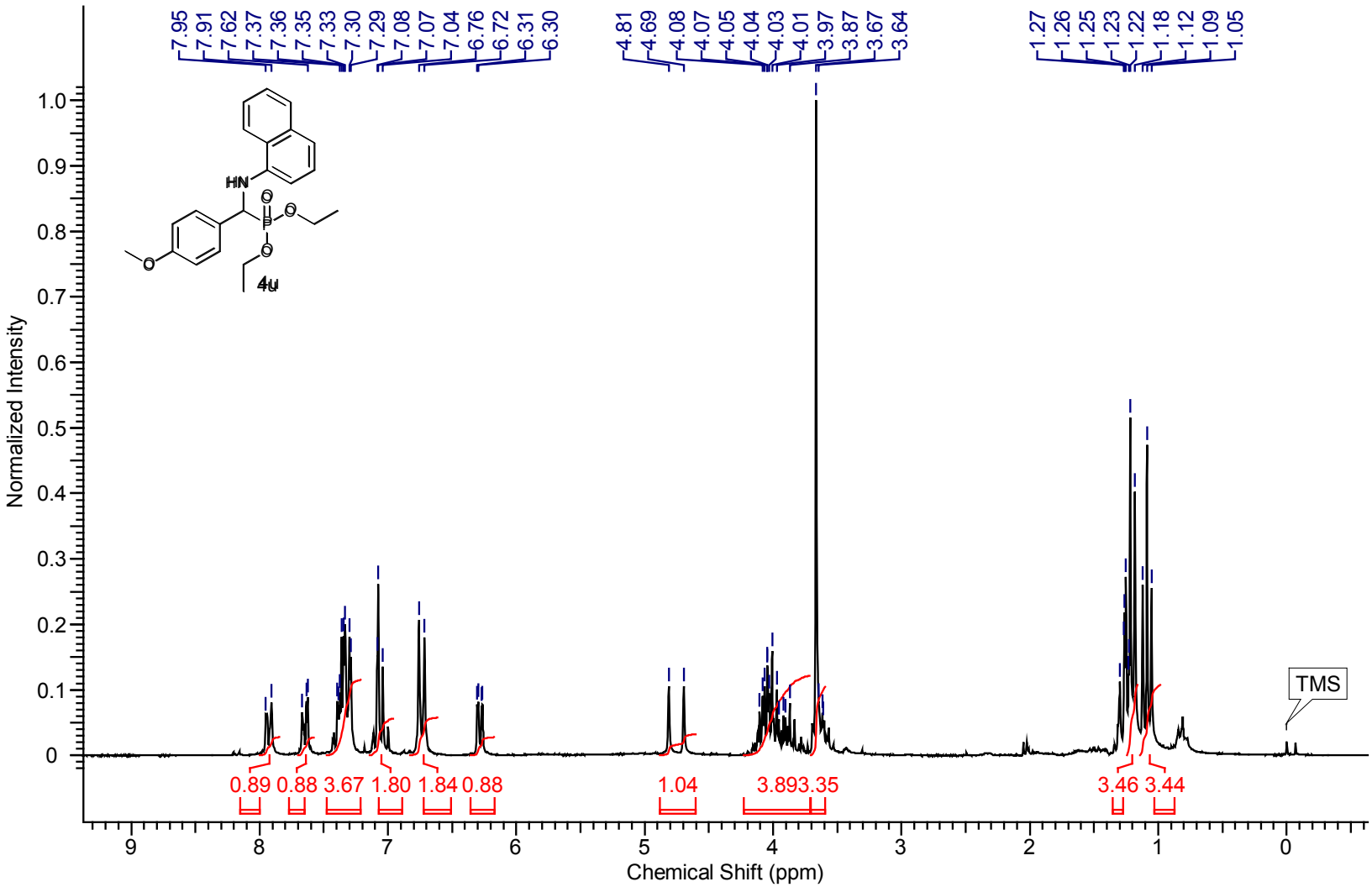

CHLOROFORM-d
146.03
137.53
136.04
132.58
129.39
129.14
128.46
127.97
127.81
118.49
113.95
96.21
77.63
77.00
76.37
68.49
57.52
54.52
21.29
HN
O
P
O
O
4f
Normalized Intensity
Chemical Shift (ppm)

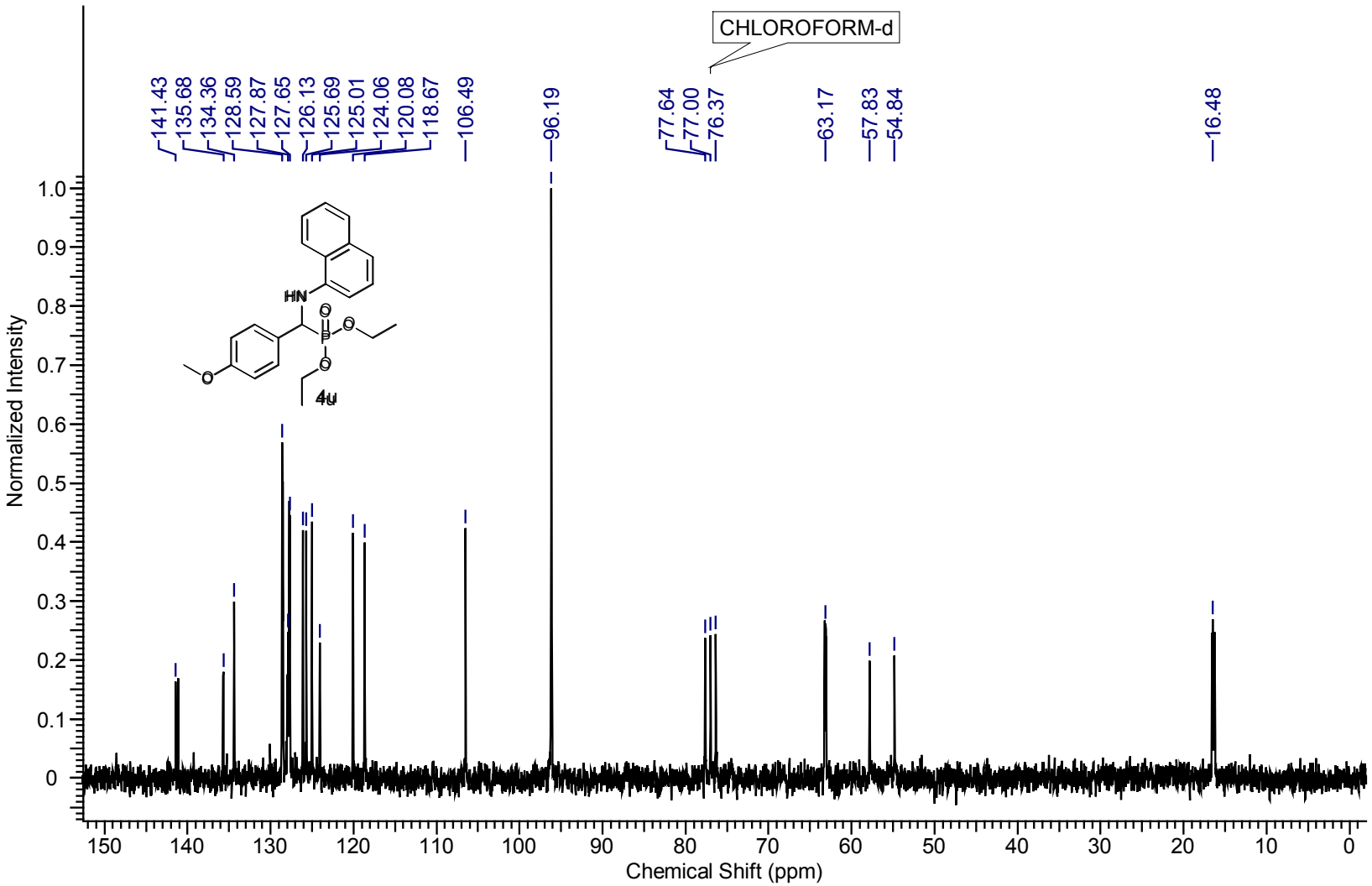

7.30
7.27
7.26
7.24
7.23
7.21
7.18
7.17
7.08
6.90
6.52
6.51
6.39
4.99
4.95
4.84
4.83
4.78
4.74
4.70
4.69
4.57
4.55
Cl
HN
O
P
O
O
Cl
4s
11.33
2.93
1.24
0.92
0.91
1.00
1.36
5.22
Normalized Intensity
Chemical Shift (ppm)

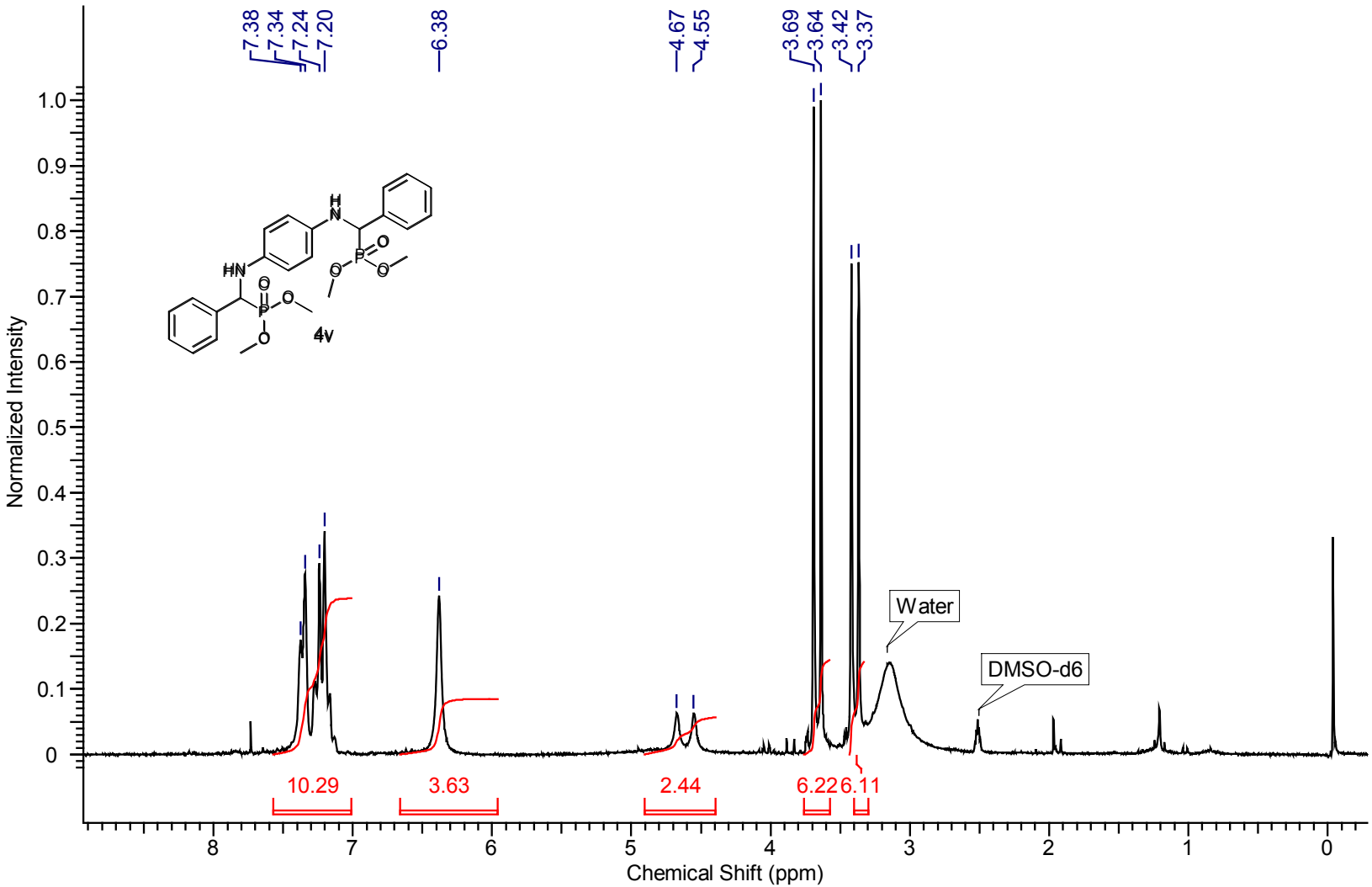

CHLOROFORM-d
147.02
134.84
134.04
133.58
130.13
129.12
128.88
128.64
128.12
128.03
127.78
118.66
113.74
111.98
77.31
77.20
77.00
76.69
68.85
56.27
54.77
Cl
HN
O
P
O
O
O
Cl
4s
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

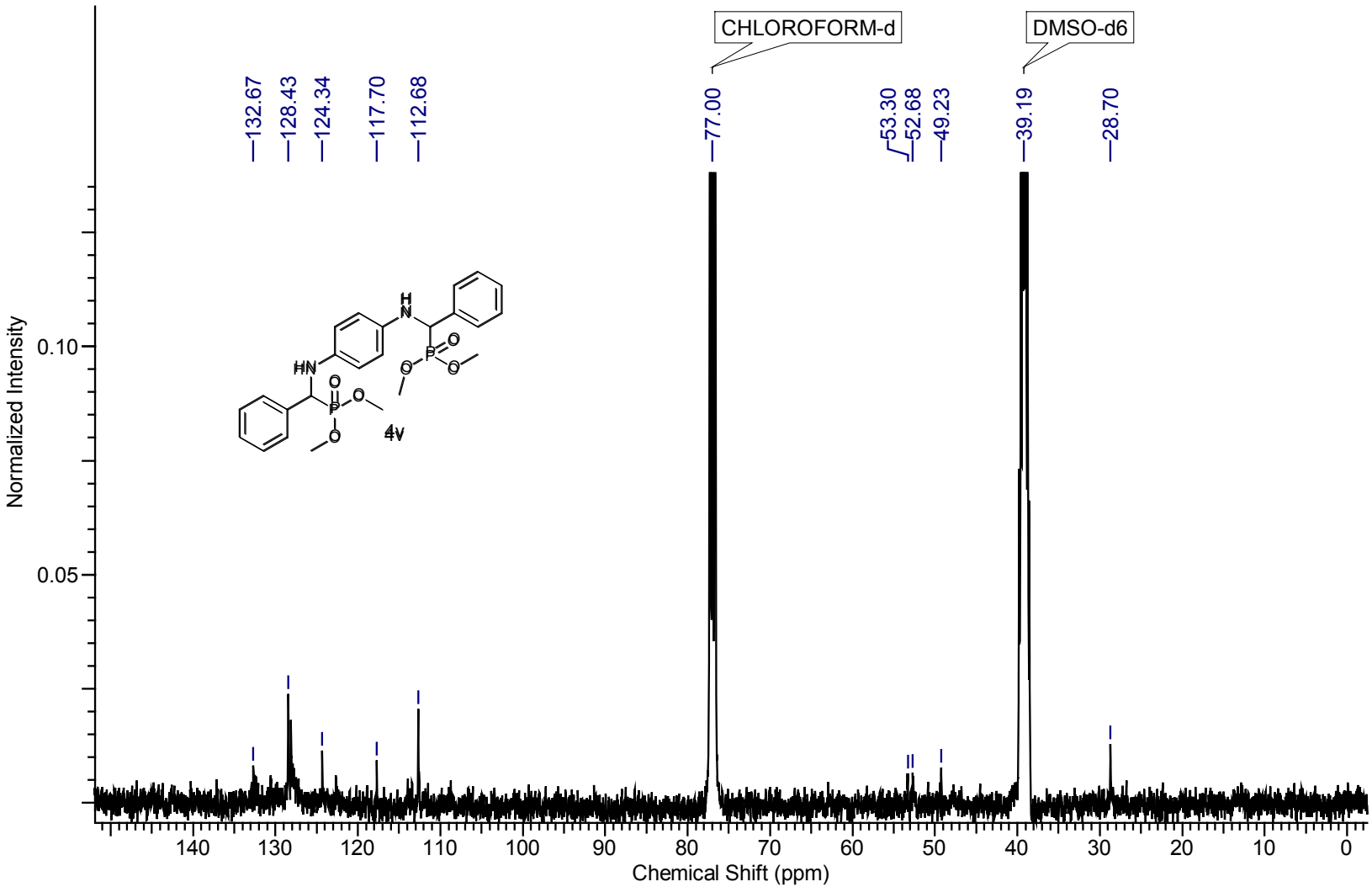

7.99
7.92
7.62
7.44
7.43
7.39
7.38
7.36
7.22
7.18
7.07
7.06
7.03
6.29
6.28
6.25
6.24
5.39
4.87
4.75
4.10
4.08
4.07
4.05
4.04
4.03
4.00
3.89
3.85
3.62
1.26
1.25
1.24
1.22
1.20
1.17
1.08
1.05
1.01
HN
O
P
O
O
O
4t
TMS
1.01
1.01
3.84
2.93
1.76
0.91
0.77
1.06
3.08
1.01
3.47
3.00
Normalized Intensity
Chemical Shift (ppm)

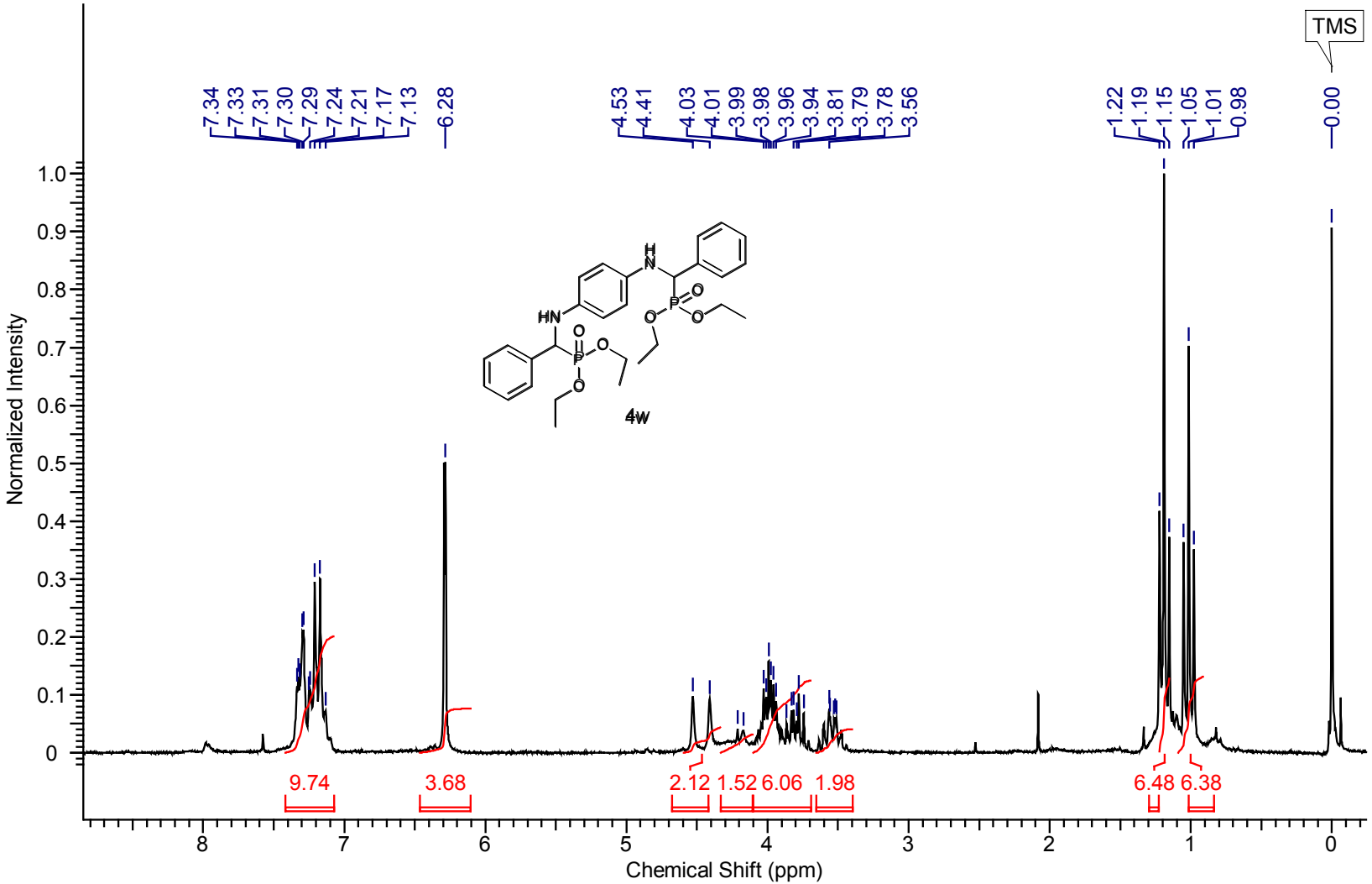

CHLOROFORM-d
159.39
141.50
134.37
128.73
127.38
126.18
125.69
125.01
124.09
120.08
118.61
114.02
106.56
96.22
77.64
77.00
76.37
63.19
57.17
54.91
54.15
16.55
HN
O
P
O
O
4t
Normalized Intensity
Chemical Shift (ppm)

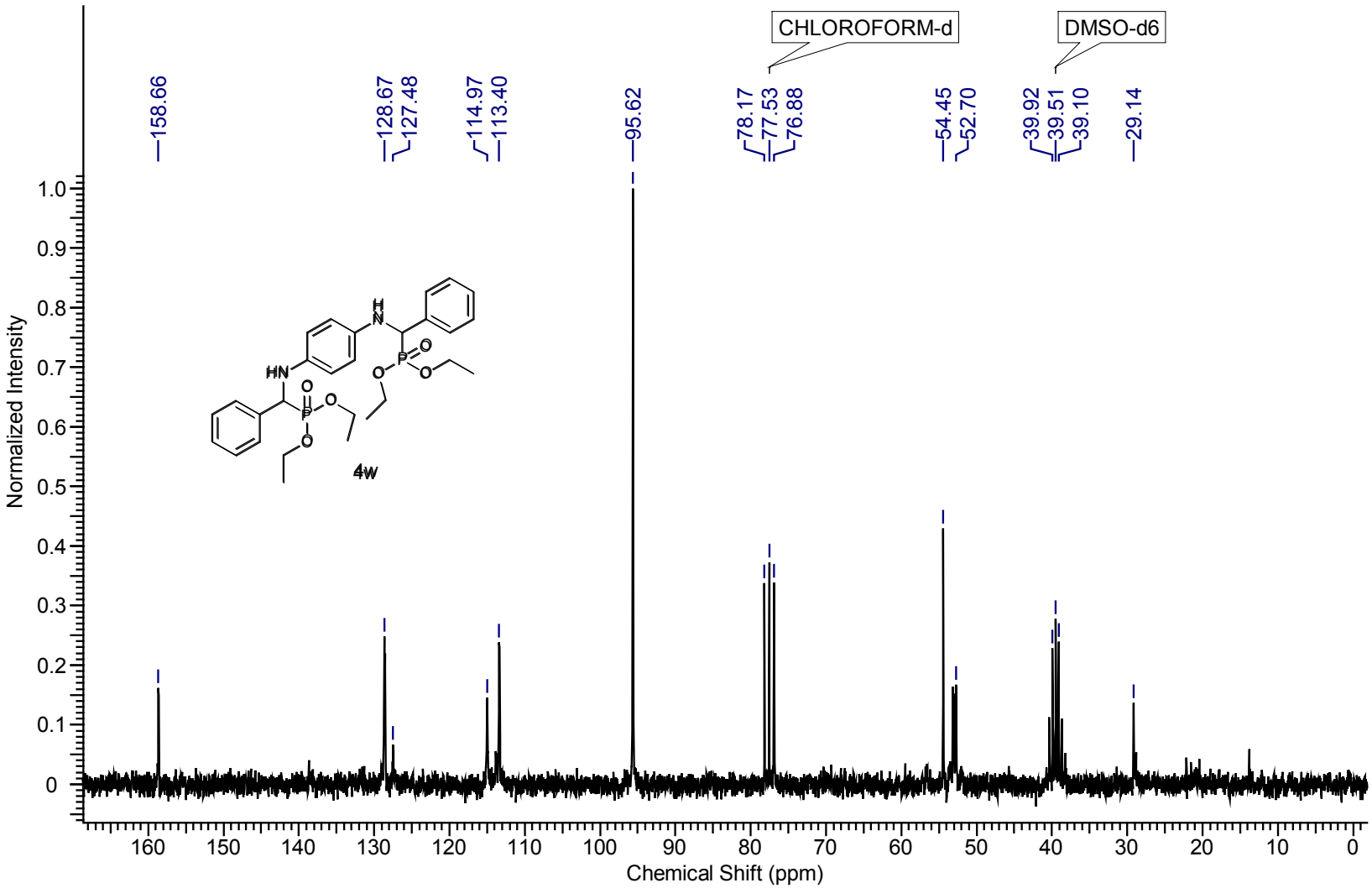

7.95
7.91
7.62
7.37
7.36
7.35
7.33
7.30
7.29
7.08
7.07
7.04
6.76
6.72
6.31
6.30
4.81
4.69
4.08
4.07
4.05
4.04
4.03
4.01
3.97
3.87
3.67
3.64
1.27
1.26
1.25
1.23
1.22
1.18
1.12
1.09
1.05
HN
O
P
O
O
O
O
4u
TMS
0.89 0.88 3.67 1.80 1.84 0.88
1.04
3.893.35
3.46 3.44
Normalized Intensity
Chemical Shift (ppm)

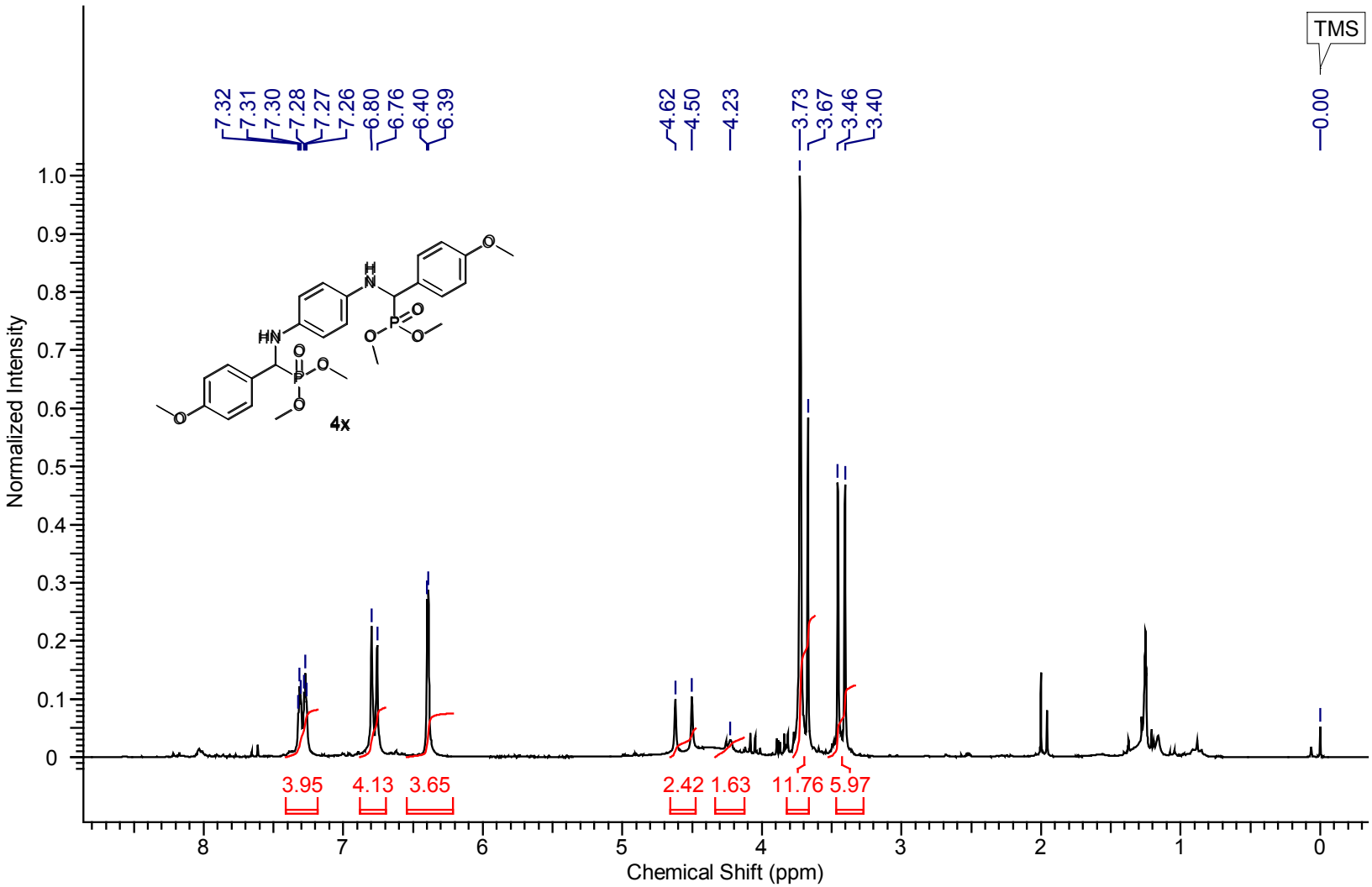

CHLOROFORM-d
141.43
135.68
134.36
128.59
127.87
127.65
126.13
125.69
125.01
124.06
120.08
118.67
106.49
96.19
77.64
77.00
76.37
63.17
57.83
54.84
16.48
HN
O
P
O
O
O
O
4u
Normalized Intensity
Chemical Shift (ppm)

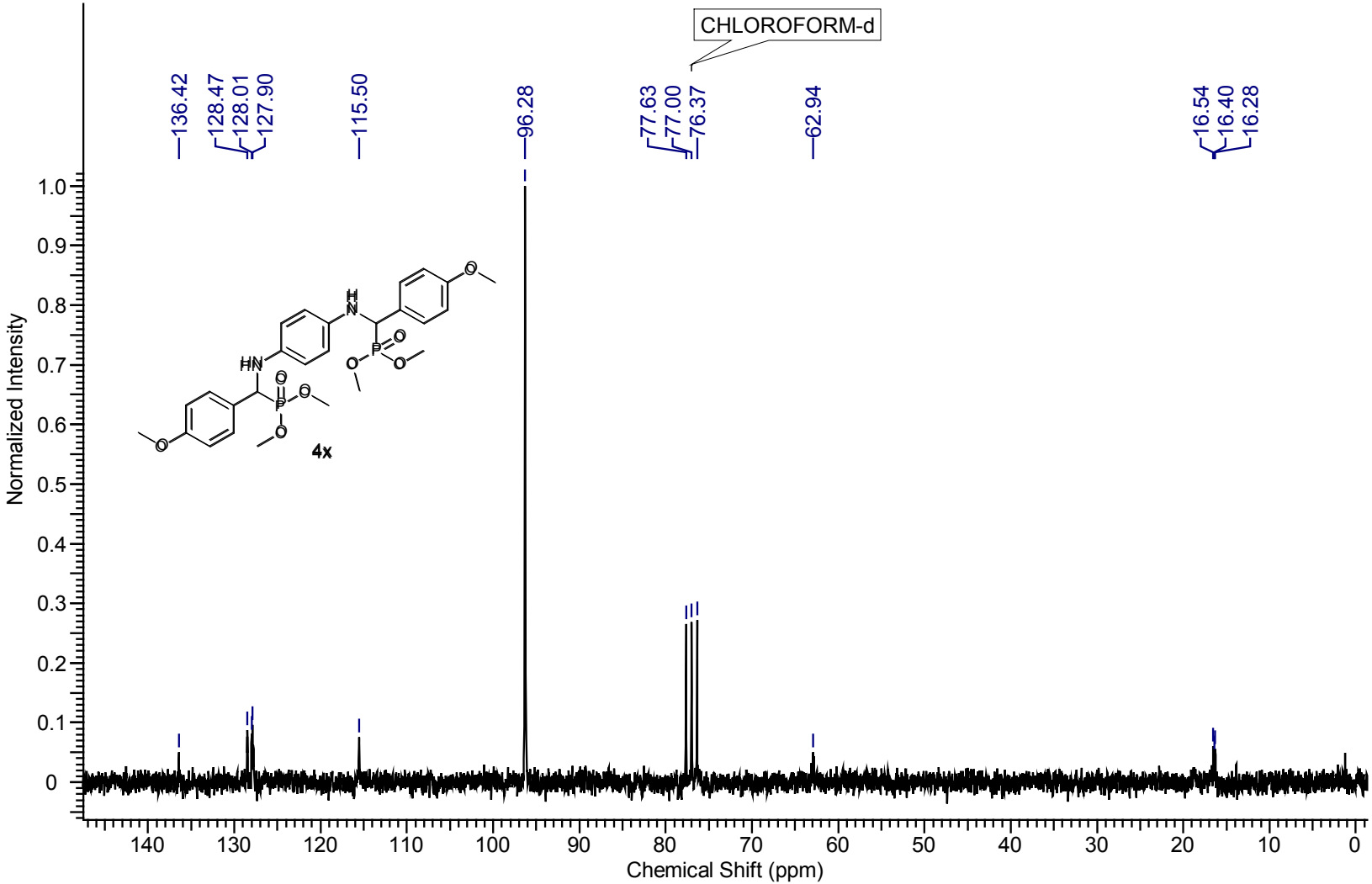

7.38
7.34
7.24
7.20
6.38
4.67
4.55
3.69
3.64
3.42
3.37
4v
Water
DMSO-d6
10.29
3.63
2.44
6.22
6.11
Normalized Intensity
Chemical Shift (ppm)


CHLOROFORM-d
DMSO-d6
132.67
128.43
124.34
117.70
112.68
77.00
53.30
52.68
49.23
39.19
28.70
4v
Normalized Intensity
0.10
0.05
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


TMS
7.34
7.33
7.31
7.30
7.29
7.24
7.21
7.17
7.13
6.28
4.53
4.41
4.03
4.01
3.99
3.98
3.96
3.94
3.81
3.79
3.78
3.56
1.22
1.19
1.15
1.05
1.01
0.98
0.00
4w
9.74
3.68
2.12
1.52
6.06
1.98
6.48
6.38
Normalized Intensity
Chemical Shift (ppm)


CHLOROFORM-d
DMSO-d6
158.66
128.67
127.48
114.97
113.40
95.62
78.17
77.53
76.88
54.45
52.70
39.92
39.51
39.10
29.14
Normalized Intensity
Chemical Shift (ppm)
4w


TMS
7.32
7.31
7.30
7.28
7.27
7.26
6.80
6.76
6.40
6.39
4.62
4.50
4.23
3.73
3.67
3.46
3.40
0.00
4x
3.95
4.13
3.65
2.42
1.63
11.76
5.97
Normalized Intensity
Chemical Shift (ppm)


CHLOROFORM-d
136.42
128.47
128.01
127.90
115.50
96.28
77.63
77.00
76.37
62.94
16.54
16.40
16.28
4x
Normalized Intensity
Chemical Shift (ppm)