

Supporting Information

Structure-Property Relationship of Phenylene-Based Self-Assembled-Monolayers for Record Low Work Function of Indium Tin Oxide

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1. General remarks

Reagents and solvents for synthesis

All reagents were obtained from commercial suppliers and were used without further purification if not otherwise stated. Deuterated solvents were purchased from Sigma-Aldrich Laborchemikalien GmbH (Seelze, Germany). All reactions requiring exclusion of oxygen and moisture were carried out in heat-gun dried glassware under a dry and oxygen free nitrogen or argon atmosphere using Schlenk and glovebox techniques.

Column chromatography

Column chromatography was performed using silica gel from Macherey, Nagel & Co. KG (Düren, Germany) (particle size: 0.040 - 0.063 mm). For TLC Polygram Sil G/UV 254 plates from Macherey, Nagel & Co. KG (Düren, Germany) were used and examined under UV-light irradiation (254 nm and 365 nm). Before column chromatography the crude product was mixed with Celite 545 and DCM to make a slurry. The solvent was removed by rotary evaporation to get a dry powder.

¹H-NMR, ¹³C-NMR, ¹⁹F-NMR and ³¹P-NMR spectra

All spectra were recorded at room temperature on a Bruker Avance III 300 (¹H: 300 MHz, ¹³C: 100 MHz, ¹⁹F: 283 MHz), on a Bruker Avance III 500 (¹H: 500 MHz, ¹³C: 126 MHz, ³¹P: 202 MHz, ¹⁹F: 471 MHz) or on a Bruker Avance III 600 (¹H: 600 MHz, ¹³C: 151 MHz, ³¹P: 243 MHz). ¹³C-NMR, ¹⁹F-NMR and ³¹P-NMR spectra were measured proton decoupled, decoupled if not stated otherwise. NMR spectra were integrated and processed using the Software ACD/Spectrus Processor (ACD/Labs). For calibration the residual solvent peaks were referenced.¹ Chemical shifts δ are reported in ppm and coupling constants J in Hz. The following abbreviations describe the observed multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dd = doublet of doublet of doublet, dt = doublet of triplet, td = triplet of doublet, bs = broad singlet, m = multiplet.

UV reactions

UV reactions were carried out in a Rayonet RPR-200 Photochemical Reactor from Southern New England Ultraviolet Company.

Mass spectrometry

The mass spectra were recorded using the following instruments: JEOL JMS-700 magnetic sector (EI); Bruker ApexQehybrid 9.4 T FT-ICR (ESI, DART); Finnigan LCQquadrupole ion trap (DART).

Melting points

Melting points were determined in open glass capillaries with a Stuart Digital Melting Point Apparatus from Cole-Parmer Ltd (SMP10).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed, using a TGA/DSC1 STARe from METTLER – TOLEDO. All measurements were performed under nitrogen atmosphere.

Elemental analysis

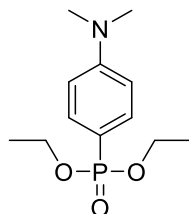
Elemental analyses were provided by the Microanalytical Laboratory of the University of Heidelberg using a Vario MICRO cube machine.

Crystal structure analysis

Crystal structure analysis was accomplished on a Bruker Smart CCD or a Bruker APEX diffractometer with Mo K α radiation, $\lambda = 0.71073$ Å. Supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic DataCentre via www.ccdc.cam.ac.uk/data_request/cif.

2. Synthesis

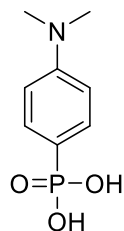
Diethyl (4-(dimethylamino)phenyl)phosphonate (2)



4-Bromo-*N,N*-dimethylaniline (4.00 g, 20.0 μ mol, 1 eq.) diethyl phosphite (5.52 g, 5.15 ml, 40.0 μ mol, 2.00 eq.), trimethylamine (2.23 g, 3.05 ml, 22.0 mmol, 1.10 eq.) and palladium acetate (224 mg, 997 μ mol, 5 mol%) were combined and degassed by freeze-pump-thaw for three times in a schlenk tube. The mixture was then transferred in a microwave vial under argon atmosphere. The reaction mixture was irradiated at 150 °C for 20 min. The excess of diethyl phosphite was removed under reduced pressure. The product was obtained by column chromatography (EA) as a colorless liquid (2.73 g, 1.00 mmol, 53%). The NMR spectra is in accordance with the literature.²

¹H-NMR (500 MHz, CDCl₃): δ [ppm] = 1.28 (t, J = 7.1 Hz, 6 H), 3.00 (s, 6 H) 3.93 - 4.17 (m, 4 H), 6.68 (dd, J = 8.9, 3.4 Hz, 2 H), 7.62 (dd, J = 12.6, 8.9 Hz, 2 H).

(4-(Dimethylamino)phenyl)phosphonic acid (PhPA)



In a dried flask diethyl (4-(dimethylamino)phenyl)phosphonate (537 mg, 3.89 μmol , 1.00 eq.) was dissolved in 6 ml of dry DCM under argon atmosphere. TMS-Br (957 mg, 820 μl , 6.26 mmol, 3.00 eq.), was added dropwise and the reaction mixture was stirred for 16 h. The solvent was removed under reduced pressure, followed by the addition of 9 ml methanol and 1 ml of water. The mixture was stirred for 1 h and the solvents were removed at reduced pressure. Washing the residue with DCM, EA, acetone and PE yielded the title compound (286 mg, 1.42 μmol , 68%) as colorless solid.

$^1\text{H}\{\text{P}\}$ -NMR (500 MHz, D_2O): δ [ppm] = 3.26 (s, 6 H), 7.59 (d, J = 8.2 Hz, 2 H), 7.83 (d, J = 8.2 Hz, 2 H).

$^{13}\text{C}\{\text{H}\}$ -NMR (126 MHz, D_2O): δ [ppm] = 46.1, 120.3 (d, J = 15.0 Hz), 132.4 (d, J = 10.4 Hz), 137.2 (d, J = 177.4 Hz), 143.6 (d, J = 3.5 Hz).

$^{31}\text{P}\{\text{H}\}$ -NMR (202 MHz, D_2O): δ [ppm] = 10.99.

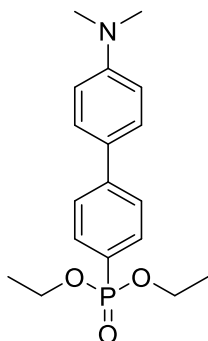
IR: ν [cm^{-1}] = 3301, 2620, 1602, 1118, 917, 433.

HR-MS (ESI (-)): calc.: for $\text{C}_8\text{H}_{11}\text{NO}_3\text{P}$ $[\text{M}-\text{H}]^-$: 200.0482, found: 200.0481.

Elemental analysis: calc.: for C, 47.77%; H, 6.01%; N, 6.96%; O, 23.86%; P, 15.40%, found: C, 41.50%; H, 5.83%; N, 6.02%.

Melting point: 170 $^\circ\text{C}$ (decomposition).

Diethyl (4'-(dimethylamino)-[1,1'-biphenyl]-4-yl)phosphonate (4)



4-(Dimethylamino)phenylboronic acid and 4-bromo-4'-(dimethylamino)biphenyl were synthesized according to literature.³

In a dried flask 4-Bromo-4'-(dimethylamino)biphenyl (700 mg, 2.72 μ mol, 1.00 eq.), diethylphosphite (413 mg, 380 μ l, 2.99 μ mol, 1.10 eq.) and trimethylamine (302 mg, 41.0 μ l, 2.99 μ mol, 1.10 eq.) were dissolved in 5 ml of dry toluene. The mixture was degassed by freeze-thaw technique in 3 cycles. Tetrakis(triphenylphosphane)palladium(0) (78.0 mg, 68 μ mol, 3 mol%) was added and degassed once again. The mixture was heated at 90 °C for 1 d. The product was isolated by column chromatography (EA) and crystalized from PE. The product was obtained as a colorless solid (616 mg, 1.85 mmol, 68%).

¹H{P}-NMR (500 MHz, CDCl₃): δ [ppm] = 1.35 (t, J = 7.1 Hz, 6 H), 3.02 (s, 6 H), 3.99 - 4.24 (m, 4 H), 6.82 (br d, J = 7.2 Hz, 2 H), 7.55 (d, J = 7.2 Hz, 2 H), 7.65 (d, J = 8.2 Hz, 2 H), 7.83 (d, J = 8.2 Hz, 2 H).

¹³C{H,P}-NMR (151 MHz, CDCl₃): δ [ppm] = 16.3, 40.3, 61.9, 112.5, 124.9, 125.9, 127.3, 127.8, 132.2, 145.1, 150.4.

³¹P{H}-NMR (202 MHz, CDCl₃): δ [ppm] = 19.68.

IR: ν [cm⁻¹] = 2979, 2900, 1240, 1220, 1017, 956, 803, 514.

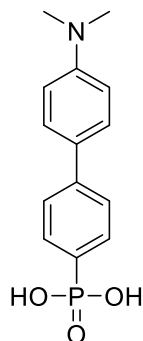
HR-MS (DART (+)): calc.: for C₁₈H₂₅NO₃P⁺ [M+H]⁺: 334.1567, found: 334.1567.

Melting point: 126 °C.

Elemental analysis: calc.: C, 64.85%; H, 7.26%; N, 4.20%; O, 14.40%; P, 9.29%, found: C, 64.89%; H, 7.28%; N, 3.95%.

R_f (EA): 0.40.

(4'-(Dimethylamino)-[1,1'-biphenyl]-4-yl)phosphonic acid (XPA)



In a dried flask diethyl (4'-(dimethylamino)-[1,1'-biphenyl]-4-yl)phosphonate (250 mg, 750 μmol , 1.00 eq.) was dissolved in 6 ml of dry DCM under argon atmosphere. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and TMS-Br (344 mg, 2.97 μl , 2.25 mmol, 3 eq.) was added dropwise. The reaction was stirred for 16 h and was allowed to warm up overnight. The solvent was removed under reduced pressure and was then cooled with an ice bath. Then 9 ml methanol and 1 ml of water was added and the reaction was stirred for another 16 h, while it was allowed to warm up to room temperature. The solvents were removed under reduced pressure and the final product was obtained without further purification as a colorless solid (95.0 mg, 342 μmol , 46%).

$^1\text{H}\{\text{P}\}$ -NMR (600 MHz, methanol- d_4) as hydro chloride: δ [ppm] = 3.36 (s, 6 H), 7.82 (d, J = 8.4 Hz, 2 H), 7.86 (d, J = 8.4 Hz, 2 H), 7.92 (m, 4 H).

$^{13}\text{C}\{\text{H,P}\}$ -NMR (151 MHz, methanol- d_4) as hydro chloride: δ [ppm] = 47.5, 122.7, 128.4, 130.5, 132.4, 132.9, 143.5, 143.8, 143.9.

$^{31}\text{P}\{\text{H}\}$ -NMR (243 MHz, methanol- d_4) as hydrochloride: δ [ppm] = 16.55.

IR: ν [cm^{-1}] = 3026, 2962, 1597, 1487, 1132, 809, 524.

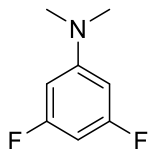
HR-MS (ESI (-)): calc.: for $\text{C}_{14}\text{H}_{15}\text{NO}_3\text{P}^-$ [M-H]: 276.0795, found: 276.0794.

Melting point: $180\text{ }^{\circ}\text{C}$ (decomposition).

Elemental analysis: calc.: C, 60.65%; H, 5.82%; N, 5.05%; O, 17.31%; P, 11.17%. found: C, 54.33%; H, 6.59%; N, 3.58%.

R_f (EA): 0.00.

3,5-Difluoro-*N,N*-dimethylaniline (6)



3,5-Difluoro-aniline (2.46 g, 19.0 mmol, 1.00 eq.) was dissolved in degassed trimethyl phosphate (1.18 g, 1.50 ml, 12.9 μ mol, 0.67 eq.) and heated for 2 h at 200 °C. After cooling to room temperature, 20 ml of an aqueous NaOH solution (5 M) was added and then heated for 1 h at 100 °C. After cooling to room temperature, the reaction was extracted with EA and the combined organic layers were dried with Na₂SO₄. The product was isolated via column chromatography (EA/PE 1:80) as a colorless liquid (1.26 g, 8.04 mmol, 43%).

¹H{F}-NMR (500 MHz, CDCl₃): δ [ppm] = 2.95 (s, 6 H), 6.12 - 6.19 (m, 3 H).

¹³C{H,F}-NMR (126 MHz, CDCl₃): δ [ppm] = 40.2, 91.2, 94.8, 152.2, 164.1.

¹⁹F{H}-NMR (471 MHz, CDCl₃): δ [ppm] = -110.54.

IR: ν [cm⁻¹] = 2962, 1636, 1257, 1011, 794.

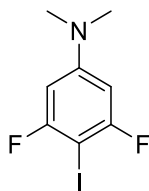
HR-MS (EI(+)): calc.: for C₈H₉F₂N [M]⁺: 157.0698, found: 157.0684.

Refractive index: n_D^{20} : 1.513.

Elemental analysis: calc.: C, 61.14%; H, 5.77%; F, 24.18%; N, 8.91%, found: C, 60.80%; H, 5.98%; N, 9.04%.

R_f (EA/PE 1:80): 0.44.

3,5-Difluoro-4-iodo-*N,N*-dimethylaniline (7)



3,5-Difluoro-*N,N*-dimethylaniline (1.68 g, 10.67 mmol, 1.00 eq.) was dissolved in 150 ml of dry THF and cooled to -78 °C. Then *n*-BuLi in *n*-hexane (5.20 ml, 2.5 M, 12.8 mmol, 1.20 eq.) was added dropwise and stirred for 30 min. Iodine (4.06 g, 16.01 mmol, 1.50 eq.) was added and the reaction was allowed to warm up to room temperature overnight. The reaction was quenched with an aqueous solution of saturated sodium thiosulfate. THF was removed under reduced pressure and the aqueous solution was extracted with EA. The combined organic layers were dried with Na₂SO₄. No further purification was required. The target compound was isolated as a pale yellow solid (2.74 g, 9.69 mmol, 91%).

¹H{F}-NMR (500 MHz, CDCl₃): δ [ppm] = 2.95 (s, 6 H), 6.22 (s, 2 H).

¹³C{H,F}-NMR (126 MHz, CDCl₃): δ [ppm] = 40.2, 52.0, 95.4, 152.1, 163.1.

¹⁹F{H}-NMR (471 MHz, CDCl₃): δ [ppm] = -94.48.

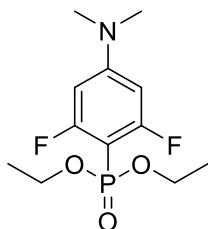
IR: ν [cm⁻¹] = 3099, 2904, 2826, 1612, 1014, 807.

HR-MS (DART (+)): calc.: for C₈H₉F₂IN [M+H]⁺: 283.9742, found: 283.9751.

Melting point: 58 °C.

Elemental analysis: calc.: C, 33.95%; H, 2.85%; F, 13.42%; I, 44.83%; N, 4.95%, found: C, 34.08%; H, 3.11%; N 4.85%.

Diethyl (4-(dimethylamino)-2,6-difluorophenyl)phosphonate (8)



3,5-Difluoro-4-iodo-*N,N*-dimethylaniline (2.00 g, 7.07 mmol, 1.00 eq.) was dissolved in degassed triethyl phosphite (39.3 ml, 267 mmol, 32.0 eq.). The mixture was irradiated for 1 d in a photoreactor (16 bulbs, 350 nm). The excess of triethyl phosphite was removed under reduced pressure (5 - 40 mbar) at 50 °C. The title compound was obtained via column chromatography (EA/DCM 1:5) as a colorless liquid (1.05 g, 3.59 mmol, 51%).

¹H{F}-NMR (301 MHz, CDCl₃): δ [ppm] = 1.33 (t, *J* = 7.0 Hz, 6 H), 2.99 (s, 6 H), 4.11 – 4.22 (m, 4 H), 6.14 (d, *J* = 4.5 Hz, 2 H).

¹³C{H,P}-NMR 151 MHz, CDCl₃): δ [ppm] = 16.2, 39.9, 62.1, 90.6 (t, *J* = 21.9 Hz), 94.7 (d, *J* = 30.9 Hz), 154.5 (t, *J* = 14.6 Hz), 165.1 (dd, *J* = 249.9, 12.0 Hz).

¹³C{H,F}-NMR 126 MHz, CDCl₃): δ [ppm] = 16.2 (d, *J* = 6.9 Hz), 39.9, 62.1 (d, *J* = 5.2 Hz), 90.6 (d, *J* = 198.3 Hz), 94.7 (d, *J* = 6.9 Hz), 154.5 (d, *J* = 1.2 Hz), 165.1 (d, *J* = 1.7 Hz).

³¹P{H}-NMR 122 MHz, CDCl₃): δ [ppm] = 10.80 (t, *J* = 3.4 Hz).

¹⁹F{H}-NMR 283 MHz, CDCl₃): δ [ppm] = -102.00 (d, *J* = 3.9 Hz).

IR: ν [cm⁻¹] = 3308, 2985, 2938, 1629, 1248, 1034, 1017, 519.

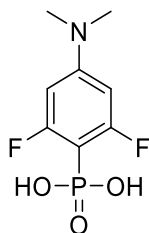
HR-MS (DART (+)): calc.: for C₁₂H₁₉F₂NO₃P [M+H]⁺: 294.1065, found: 294.1059.

Refractive index: n_D²⁰: 1.520.

Elemental analysis: calc.: C, 49.15%; H, 6.19%; F, 12.96%; P 10.56%; N, 4.95%, found: C, 48.93%; H, 6.48%; N, 5.03%.

R_f (EA): 0.45.

(4-(Dimethylamino)-2,6-difluorophenyl)phosphonic acid (PhFPA)



In a dried flask diethyl diethyl (4-(dimethylamino)-2,6-difluorophenyl)phosphonate (175 mg, 597 μmol , 1.00 eq.) was dissolved in 6 ml of dry DCM under argon atmosphere. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and TMS-Br (274 mg, 236 μl , 1.79 mmol, 3 eq.) was added dropwise. The reaction was stirred for 16 h and was allowed to warm up overnight to room temperature. The solvent was removed under reduced pressure and was then cooled with an ice bath. Then 10 ml methanol and 1 ml of water was added and the reaction was stirred for another 16 h, while it was allowed to warm up to room temperature. The solvents were removed under reduced pressure and the final product was obtained without further purification as a colorless solid (81.0 mg, 341 μmol , 57%).

$^1\text{H}\{\text{F},\text{P}\}$ -NMR (500 MHz, DMSO): δ [ppm] = 2.93 (s, 6 H), 6.29 (s, 2 H), 10.60 (br s, 2 H).

$^{13}\text{C}\{\text{H},\text{P}\}$ -NMR (151 MHz, DMSO): δ [ppm] = 39.6, 94.1 - 95.1 (m), 95.7 (t, $J = 23.2$ Hz), 153.5 (t, $J = 14.6$ Hz), 163.9 (dd, $J = 246.2, 13.2$ Hz).

$^{19}\text{F}\{\text{H},\text{P}\}$ -NMR (471 MHz, DMSO): δ [ppm] = -102.66.

$^{31}\text{P}\{\text{H},\text{F}\}$ -NMR (202 MHz, DMSO): δ [ppm] = 4.04.

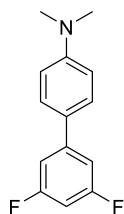
IR: ν [cm^{-1}] = 2927, 2317, 1625, 1104, 994, 916, 647, 469.

HR-MS (ESI(-)): calc.: for $\text{C}_8\text{H}_9\text{F}_2\text{NO}_3\text{P}^-$ $[\text{M}-\text{H}]^-$: 236.0294, found: 236.0295.

Elemental analysis: calc.: C, 40.52%; H, 4.25%; F, 16.02%; N, 5.91%; O, 20.24%; P, 13.06%, found: C, 40.42%; H, 4.52%; N, 5.95%.

Melting point: $130\text{ }^{\circ}\text{C}$ (decomposition).

3',5'-Difluoro-*N,N*-dimethyl-[1,1'-biphenyl]-4-amine (10)



In 30 ml of degassed THF 4-bromo-*N,N*-dimethylaniline (3.50 g, 17.5 mmol, 1.00 eq.), (3,5-difluorophenyl)boronic acid (4.14 g, 26.2 mmol, 1.50 eq.) and XPhos Pd G3 (150 mg, 350 μ mol, 2 mol%) were dissolved. Then 70 ml of a degassed aqueous solution of 500 mM potassium phosphate was added. After stirring for 4 d at room temperature the organic layer was removed under reduced pressure and the aqueous phase extracted with EA and the combined organic layers were dried with Na₂SO₄. After purification via column chromatography (EA/PE 1:50) the targeted compound was isolated as a colorless solid (2.84 g, 12.2 mmol, 70%).

¹H{F}-NMR (500 MHz, CDCl₃): δ [ppm] = 3.03 (s, 6 H), 6.70 (t, J = 1.8 Hz, 1 H), 6.80 (d, J = 8.7 Hz, 2 H), 7.09 (d, J = 1.8 Hz, 2 H), 7.49 (d, J = 8.7 Hz, 2 H).

¹³C{H,F}-NMR (126 MHz, CDCl₃): δ [ppm] = 40.3, 100.9, 108.5, 112.4, 126.4, 127.5, 144.5, 150.6, 163.3.

¹⁹F{H}-NMR (471 MHz, CDCl₃): δ [ppm] = -110.47.

IR: ν [cm⁻¹] = 3100, 2901, 1588, 1112, 983, 810, 511.

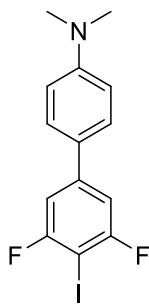
HR-MS (ESI(-)): calc.: for C₁₄H₁₄F₂N [M+H]⁺: 234.0189, found: 234.1091.

Elemental analysis: calc.: C, 72.09%; H, 5.62%; F, 16.29%; N, 6.00%, found: C, 71.89%; H, 5.63%; N, 6.12%.

Melting point: 120 °C.

R_f (EA/PE 1:50): 0.23

3',5'-Difluoro-4'-iodo-*N,N*-dimethyl-[1,1'-biphenyl]-4-amine (11)



In 150 ml of dry THF 3',5'-difluoro-*N,N*-dimethyl-[1,1'-biphenyl]-4-amine (2.50 g, 10.7 mmol, 1.00 eq.) was dissolved and cooled to -78 °C. Then *n*-butyllithium in *n*-hexane (5.14 ml, 2.50 M, 12.9 mmol, 1.20 eq.) was added and stirred for 30 min. Iodine (4.08 g, 16.1 mmol, 1.50 eq.) was added and the reaction was allowed to warm up to room temperature overnight. The reaction was quenched with a solution of saturated sodium thiosulfate. THF was removed under reduced pressure and the aqueous phase was extracted with EA and dried with Na₂SO₄. The solvent was removed under reduced pressure. The title compound was purified via column chromatography (EA/PE 20:1) and obtained as a pale yellow solid (3.48 g, 10.7 mmol, 91%).

¹H{F}-NMR (500 MHz, CDCl₃): δ [ppm] = 3.03 (s, 6 H), 6.78 (d, *J* = 8.9 Hz, 2 H), 7.10 (s, 2 H), 7.47 (d, *J* = 8.9 Hz, 2 H).

¹³C{H,F}-NMR (126 MHz, CDCl₃): δ [ppm] = 40.3, 66.6, 108.6, 112.4, 125.4, 127.4, 144.5, 150.7, 162.9.

¹⁹F{H}-NMR (471 MHz, CDCl₃): δ [ppm] = -93.57.

IR: ν [cm⁻¹] = 2886, 2803, 1575, 1018, 813, 566.

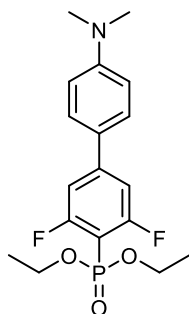
HR-MS (DART (+)): calc.: for C₁₄H₁₃F₂IN [M+H]⁺: 360.0055, found: 360.0060.

Melting point: 119 °C.

Elemental analysis: calc.: C, 46.82%; H, 3.37%; F, 10.58%; I, 35.33%; N, 3.90%, found: C, 47.04%; H, 3.47%; N, 3.93%.

R_f (EA/PE 1:20): 0.40.

Diethyl (4'-(dimethylamino)-3,5-difluoro-[1,1'-biphenyl]-4-yl)phosphonate (12)



3',5'-difluoro-4'-iodo-*N,N*-dimethyl-[1,1'-biphenyl]-4-amine (2.00 g, 5.57 mmol, 1.00 eq.) was dissolved in degassed triethyl phosphite (31.0 ml, 179 mmol, 32.0 eq.). The mixture was irradiated for 2 d in a photoreactor (16 bulbs, 350 nm). The excess of triethyl phosphite was removed under reduced pressure (5 - 40 mbar) at 50 °C. The title compound was obtained via column chromatography (EA/DCM 1:5), followed by recrystallization from PE as colorless flakes (2.06 g, 5.57 mmol, 41%).

¹H{F,P}-NMR (500 MHz, CDCl₃): δ [ppm] = 1.39 (t, J = 7.1 Hz, 6 H), 3.03 (s, 6 H) 4.09 - 4.31 (m, 4 H), 6.78 (br d, J = 8.5 Hz, 2 H), 7.14 (s, 2 H), 7.50 (d, J = 8.5 Hz, 2 H).

¹³C{H}-NMR (151 MHz, CDCl₃): δ [ppm] = 16.3 (d, J = 6.6 Hz), 40.3, 62.7 (d, J = 5.7 Hz), 102.3 (dt, J = 189.2, 21.3 Hz), 108.5 - 109.2 (m), 112.4, 124.84, 127.67, 148.41 (td, J = 10.4, 1.4 Hz), 151.1, 164.1 (ddd, J = 253.8, 8.9, 2.4 Hz).

¹⁹F{H,P}-NMR (471 MHz, CDCl₃): δ [ppm] = -102.01.

³¹P{H,F} NMR (202 MHz, CDCl₃): δ [ppm] = 8.93.

IR: ν [cm⁻¹] = 2984, 2903, 1606, 1253, 1016, 806, 509.

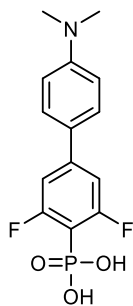
HR-MS (DART (+)): calc.: for C₁₈H₂₃F₂NO₃P [M+H]⁺: 370.1378, found: 370.1382.

Melting point: 82 °C.

Elemental analysis: calc.: C, 58.53%; H, 6.00%; F, 10.29%; N, 3.79%; O, 13.00%; P, 8.39%, found: C, 58.68%; H, 5.93%; N, 3.59%.

R_f (EA/DCM 1:5): 0.42.

(4'-(Dimethylamino)-3,5-difluoro-[1,1'-biphenyl]-4-yl)phosphonic acid (XFPA)



In a dried flask diethyl (4'-(dimethylamino)-3,5-difluoro-[1,1'-biphenyl]-4-yl)phosphonate (150 mg, 406 μmol , 1.00 eq.) was dissolved in 6 ml of dry DCM under argon atmosphere. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and TMS-Br (1.87 mg, 1.16 ml, 1.22 mmol, 3 eq.) was added dropwise. The reaction was stirred for 16 h and was allowed to warm up overnight. The solvent was removed under reduced pressure and the remaining product was cooled with an ice bath. Then 10 ml methanol and 1 ml of water were added and the reaction was stirred for another 16 h, while it was allowed to warm up. The solvents were removed under reduced pressure and the final product was obtained without further purification as a colorless solid (83.0 mg, 265 μmol , 65%).

$^1\text{H}\{\text{F,P}\}$ -NMR (500 MHz, DMSO): δ [ppm] = 2.98 (s, 6 H), 6.83 (br d, J = 8.5 Hz, 2 H), 7.36 (s, 2 H), 7.67 (br d, J = 8.5 Hz, 2 H), 10.67 (br s, 2 H).

$^{13}\text{C}\{\text{H,F}\}$ -NMR (126 MHz, DMSO): δ [ppm] = 40.2, 107.3 (d, J = 176.9 Hz), 108.2 (d, J = 6.4 Hz), 112.7, 124.2, 127.6, 145.8, 150.5, 163.1 (d, J = 1.7 Hz).

$^{13}\text{C}\{\text{H,P}\}$ -NMR (151 MHz, DMSO): δ [ppm] = 40.2, 107.3 (t, J = 22.4 Hz), 108.1 (d, J = 28.1 Hz), 112.7, 124.2, 127.6, 145.8 (t, J = 10.8 Hz), 150.6, 163.1 (dd, J = 250.0, 10.4 Hz).

$^{19}\text{F}\{\text{H,P}\}$ -NMR (471 MHz, DMSO): δ [ppm] = -102.29.

$^{31}\text{P}\{\text{H,F}\}$ -NMR (202 MHz, DMSO): δ [ppm] = 1.95.

IR: ν [cm^{-1}] = 3391, 2655, 1620, 1130, 1016, 825, 526.

HR-MS (DART (+)): calc.: for $\text{C}_{14}\text{H}_{15}\text{F}_2\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 314.0752, found: 314.0752.

Melting point: $220\text{ }^{\circ}\text{C}$ (decomposition).

Elemental analysis: calc.: C, 53.68%; H, 4.51%; F, 12.13%; N, 4.47%; O, 15.32%; P, 9.89%, found: C, 53.14%; H, 4.80%; N, 4.33%.

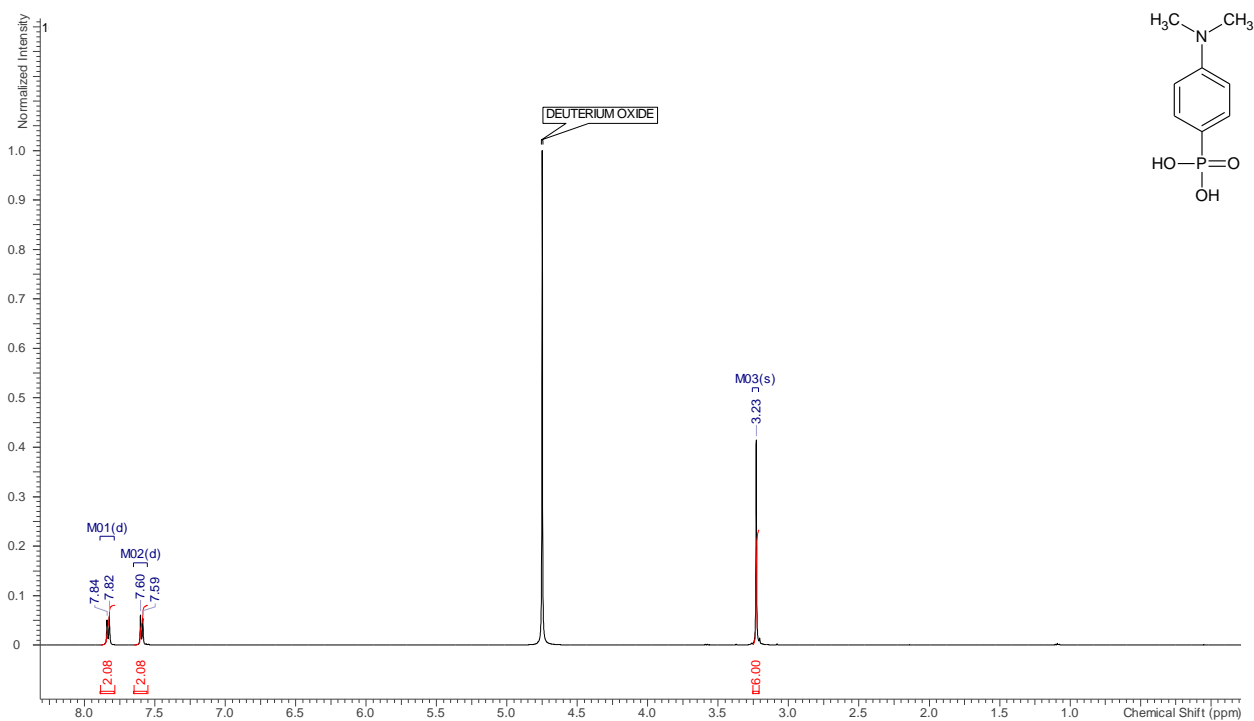


Figure S1. $^1\text{H}\{\text{P}\}$ -NMR of PhPA in D_2O (500 MHz, 298 K).

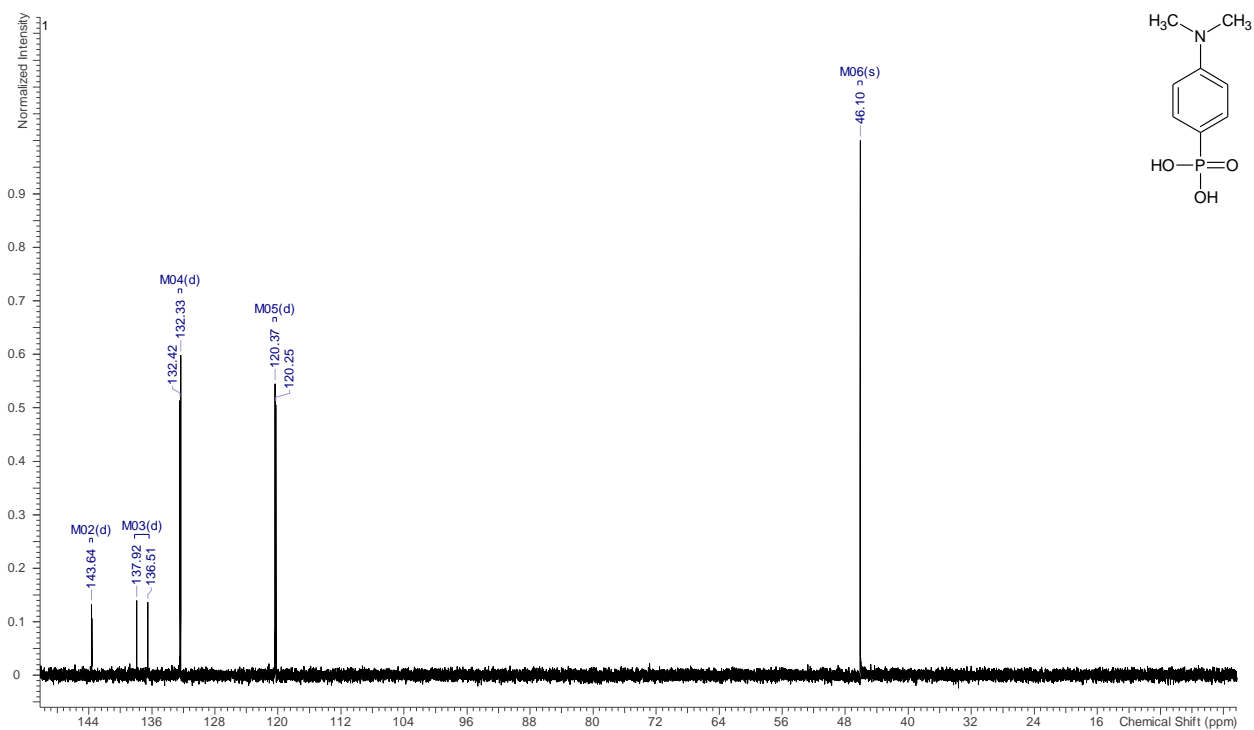


Figure S2. $^{13}\text{C}\{\text{H}\}$ -NMR of PhPA in D_2O (126 MHz, 298 K).

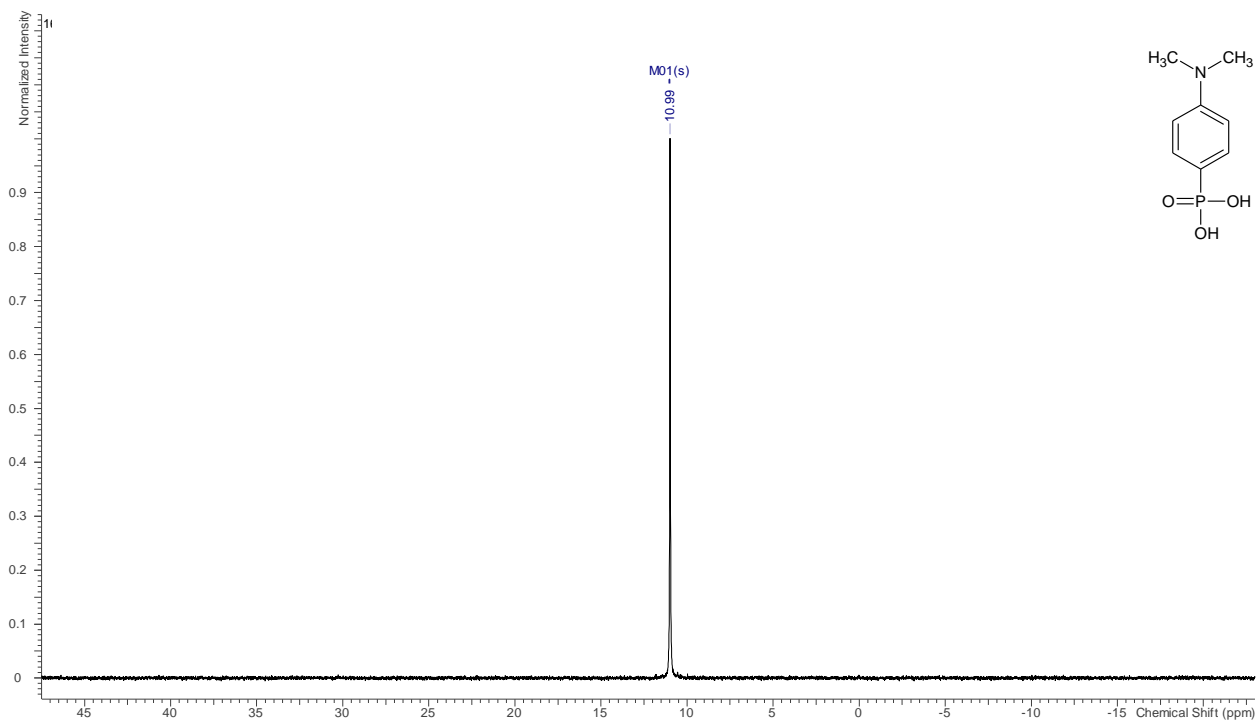


Figure S3. $^{31}\text{P}\{\text{H}\}$ -NMR of PhPA in D_2O (202 MHz, 298 K).

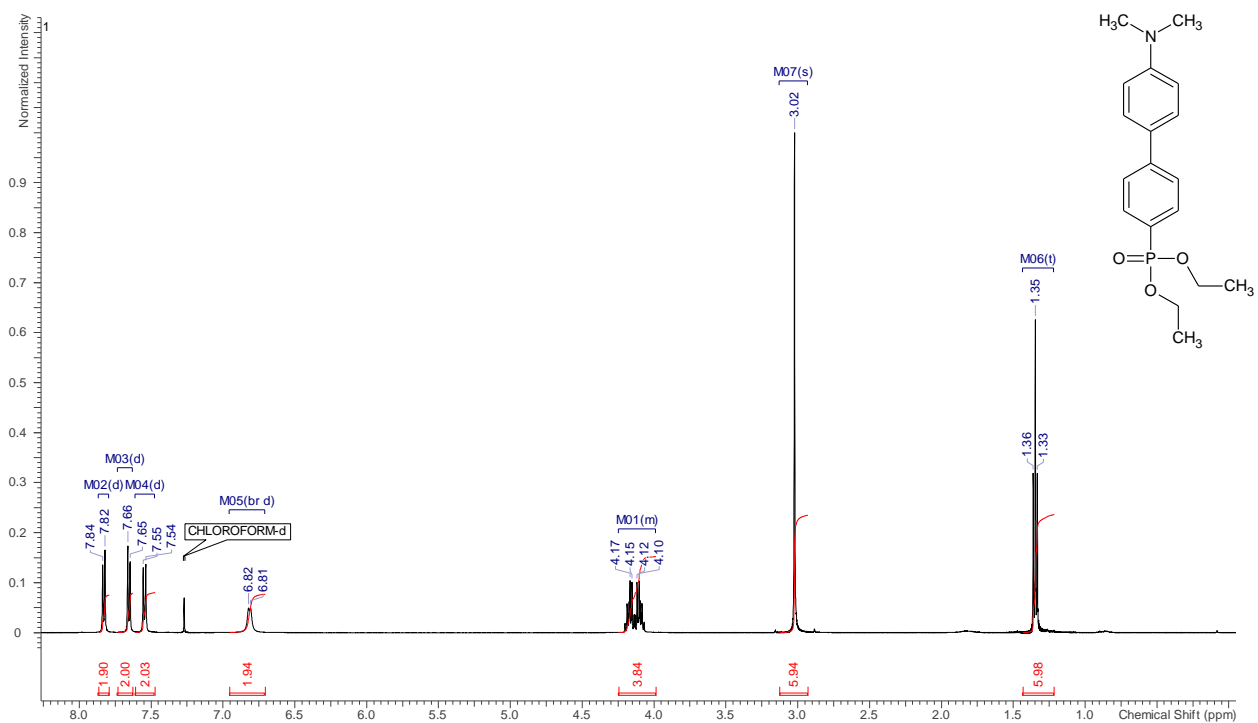


Figure S4. $^1\text{H}\{\text{P}\}$ -NMR of compound 4 in CDCl_3 (500 MHz, 298 K).

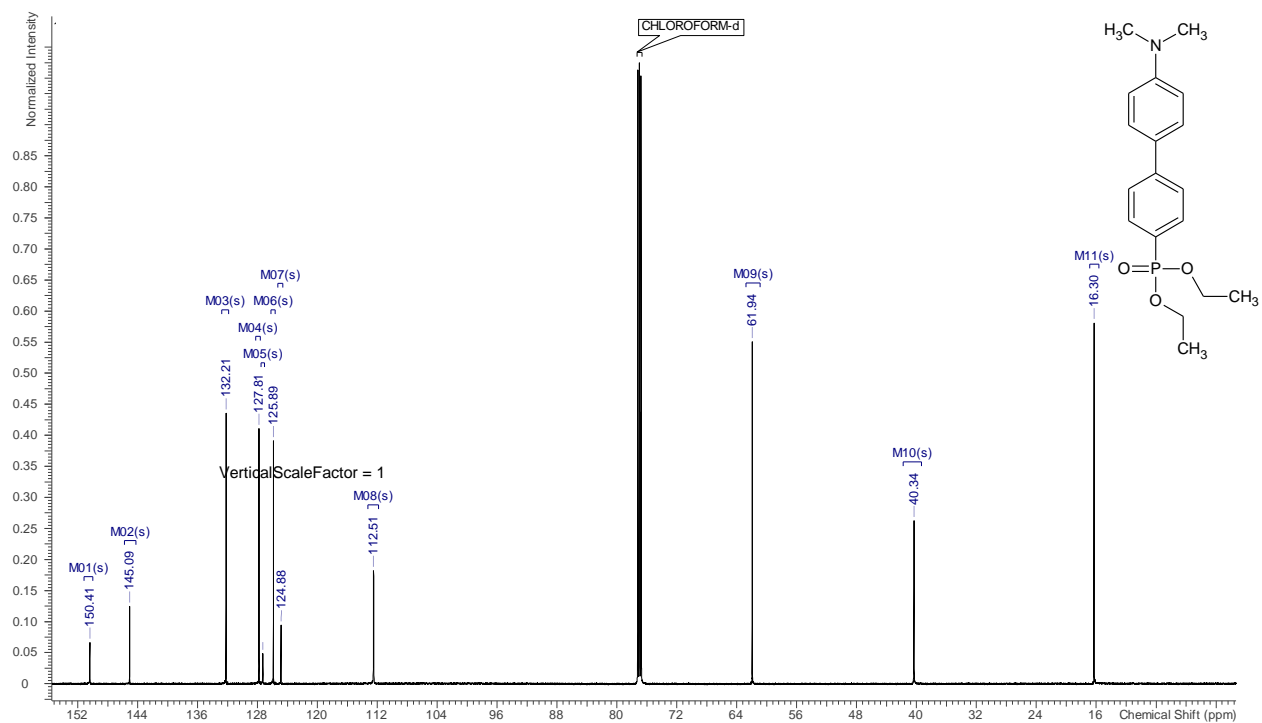


Figure S5. $^{13}\text{C}\{\text{H,P}\}$ -NMR of compound 4 in CDCl_3 (151 MHz, 298 K).

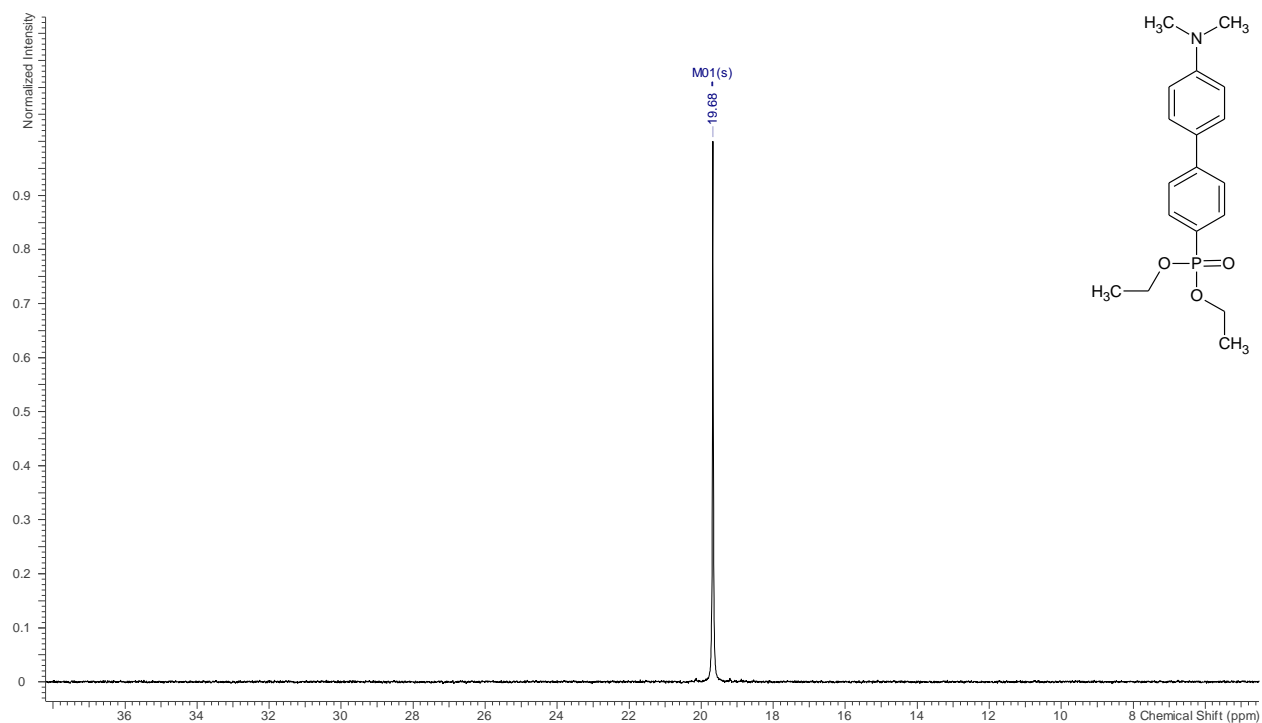


Figure S6. $^{31}\text{P}\{\text{H}\}$ -NMR of compound 4 in CDCl_3 (202 MHz, 298 K).

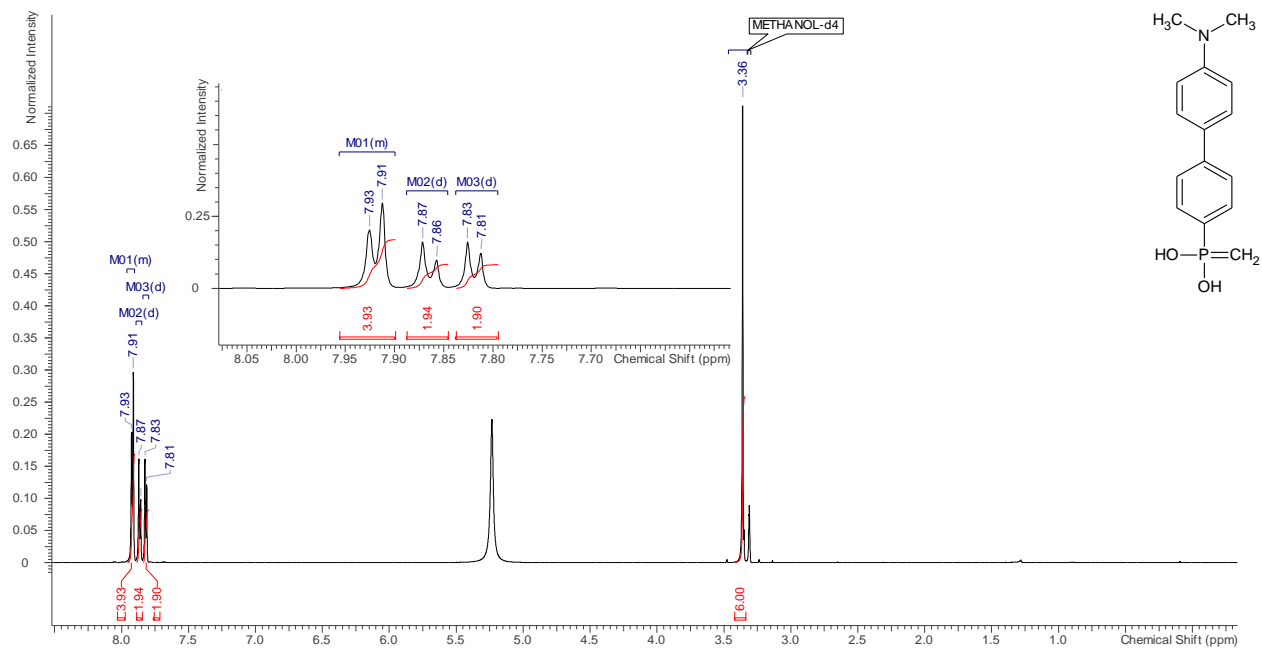


Figure S7. ¹H{P}-NMR of XPA in methanol-*d*₄ (600 MHz, 298 K).

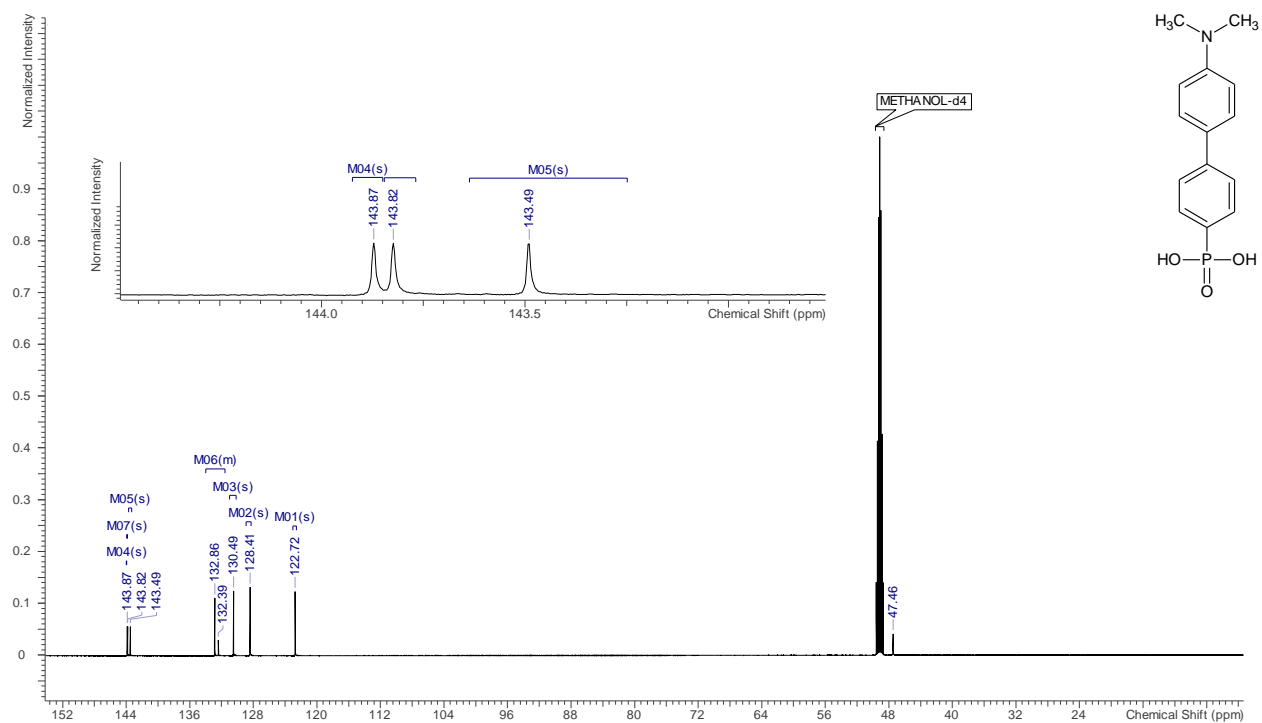


Figure S8. ¹³C{H,P}-NMR of XPA in methanol-*d*₄ (151 MHz, 298 K).

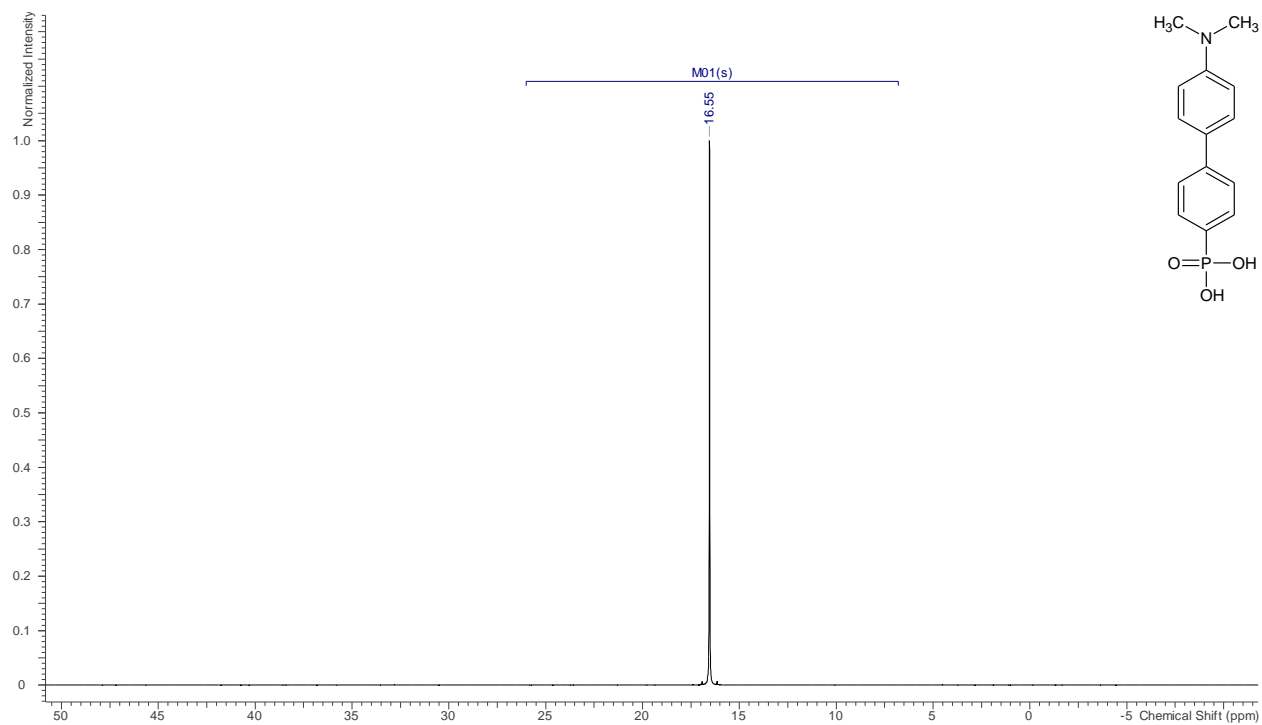


Figure S9. $^{31}\text{P}\{\text{H}\}$ -NMR of XPA in methanol- d_4 (243 MHz, 298 K).

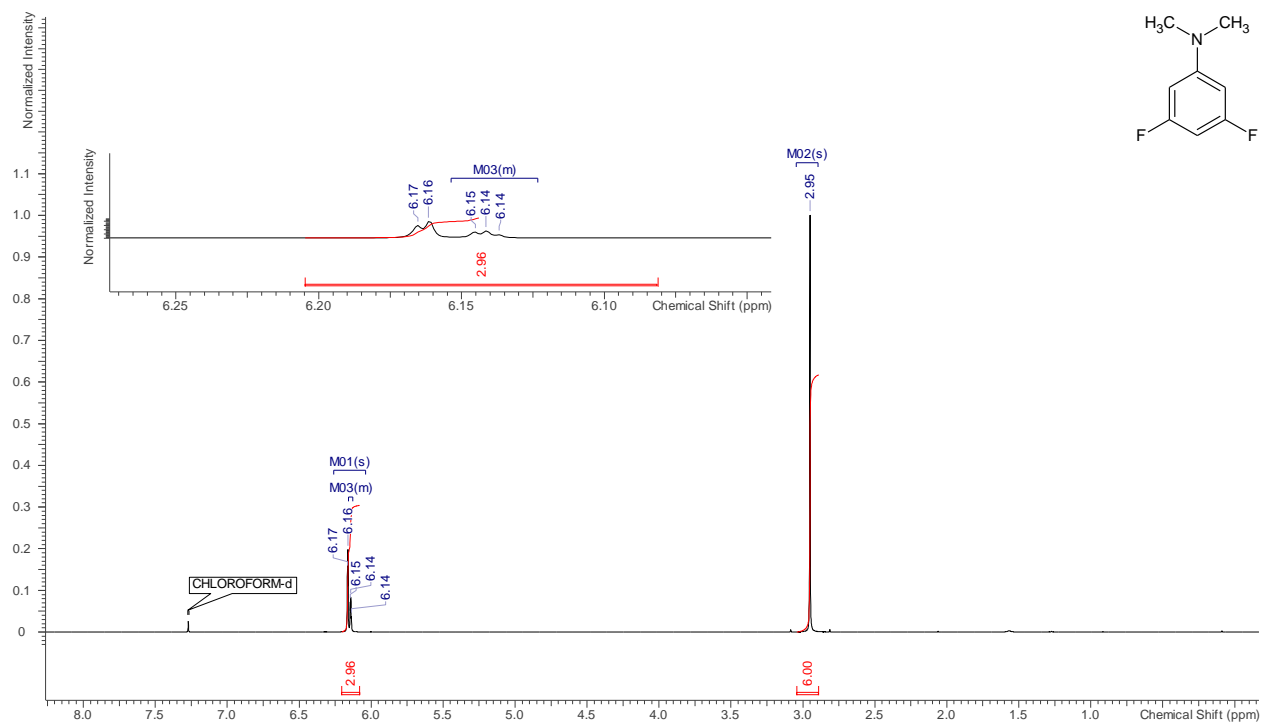


Figure S10. $^1\text{H}\{\text{F}\}$ -NMR of compound 6 in CDCl_3 (500 MHz, 298 K).

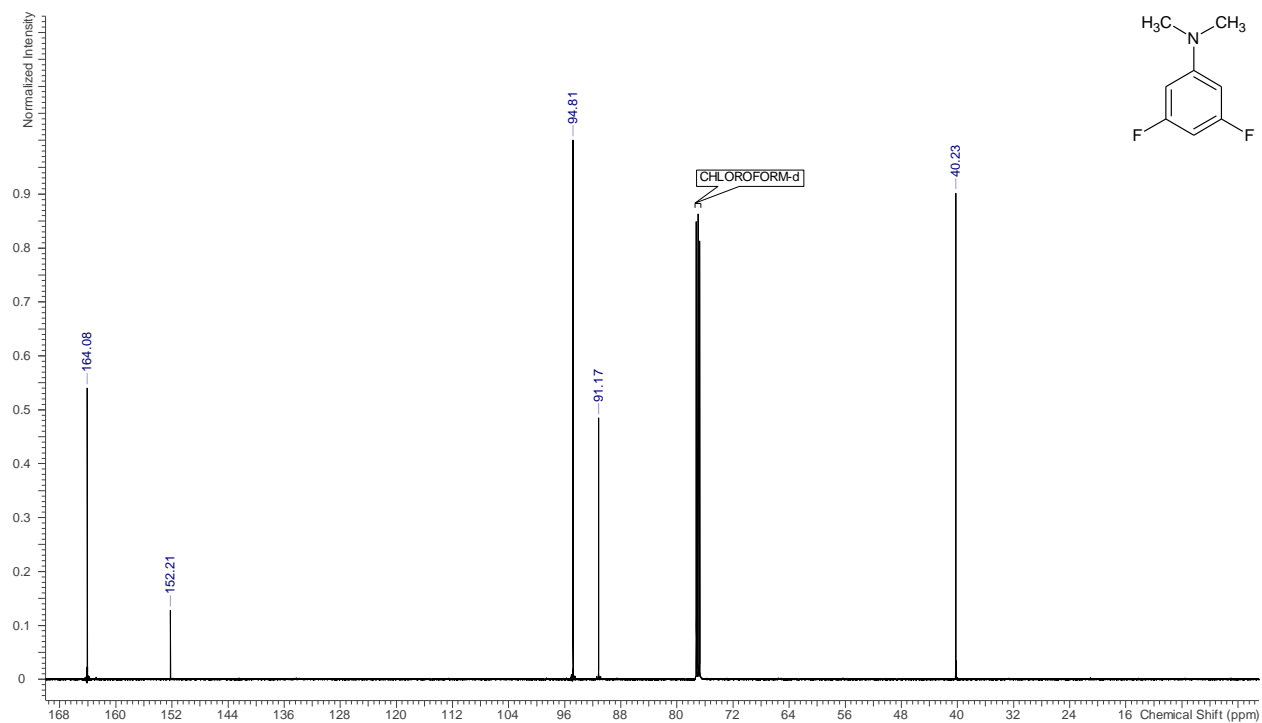


Figure S11. $^{13}\text{C}\{\text{H},\text{F}\}$ -NMR of compound 6 in CDCl_3 (126 MHz, 298 K).

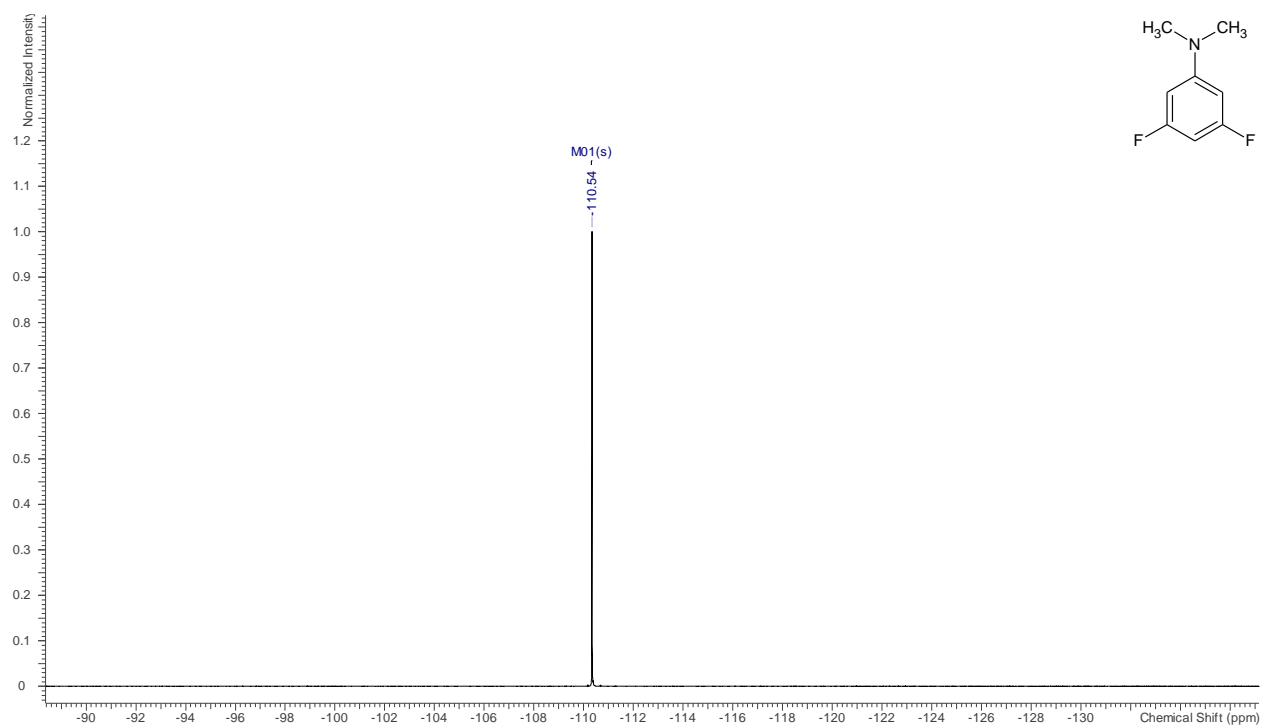


Figure S12. $^{19}\text{F}\{\text{H}\}$ -NMR of compound 6 in CDCl_3 (471 MHz, 298 K).

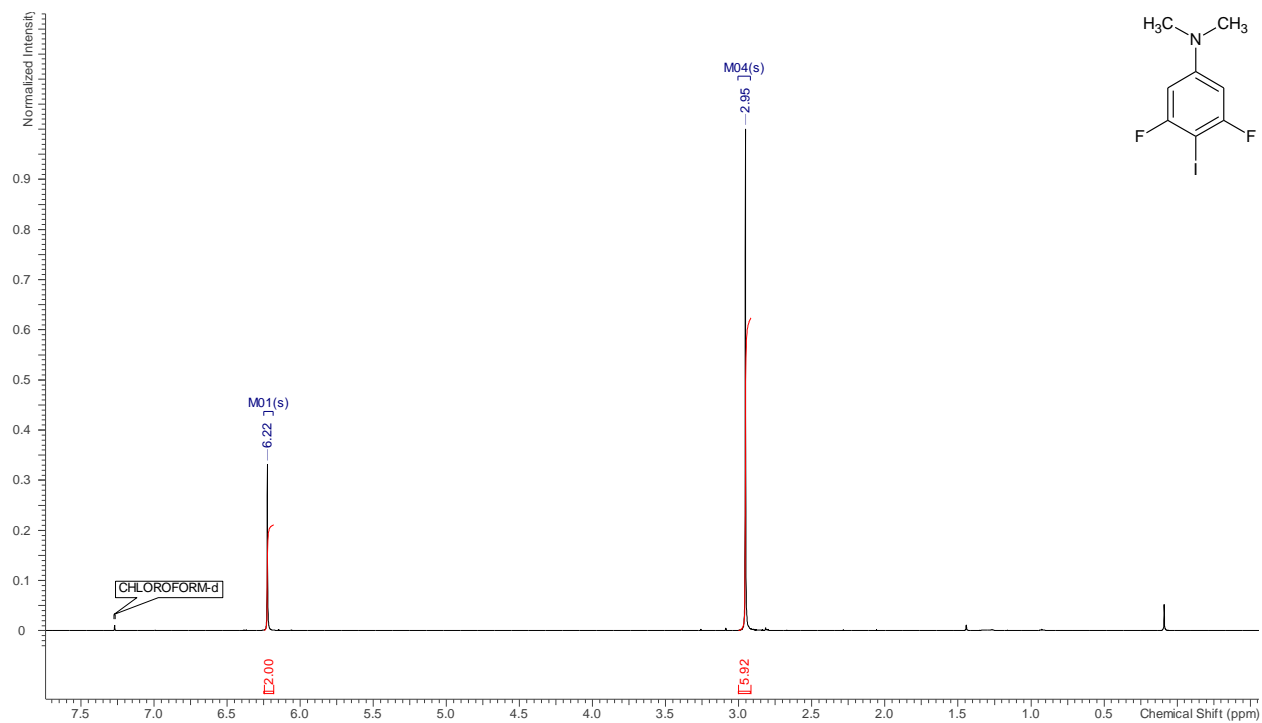


Figure S13. $^1\text{H}\{\text{F}\}$ -NMR of compound 7 in CDCl_3 (500 MHz, 298 K).

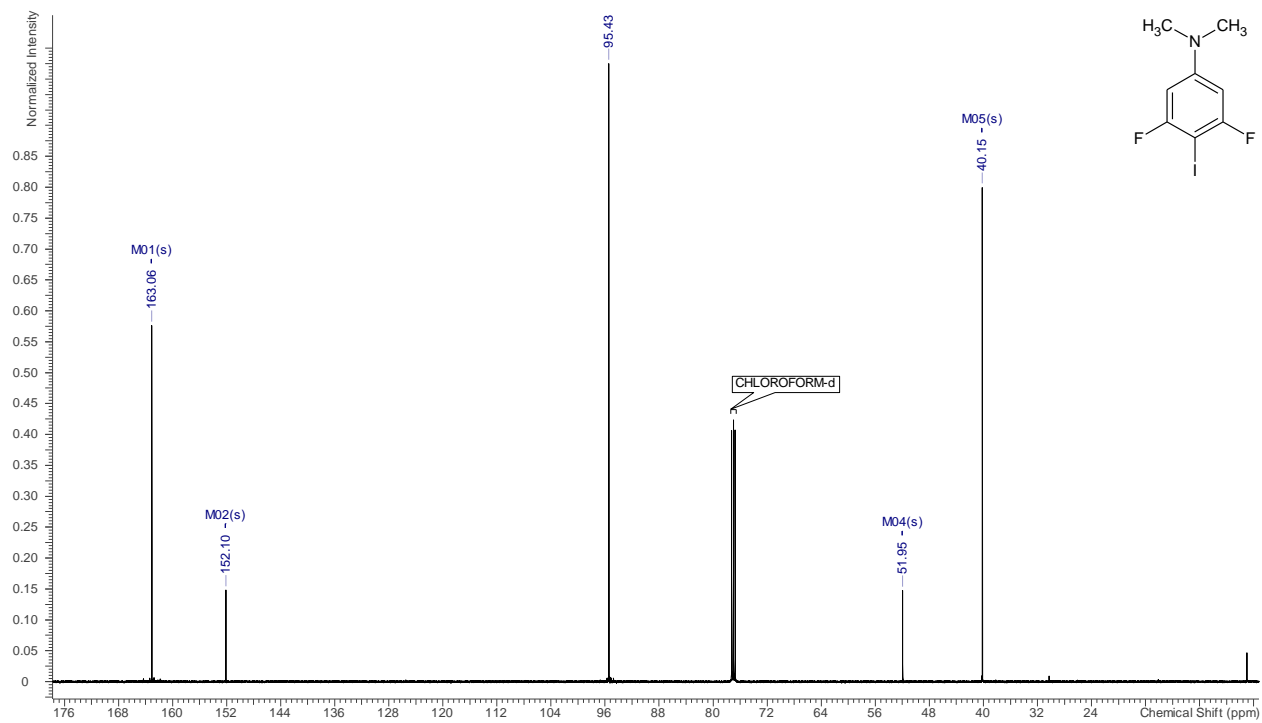


Figure S14. $^{13}\text{C}\{\text{H},\text{F}\}$ -NMR of compound 7 in CDCl_3 (126 MHz, 298 K).

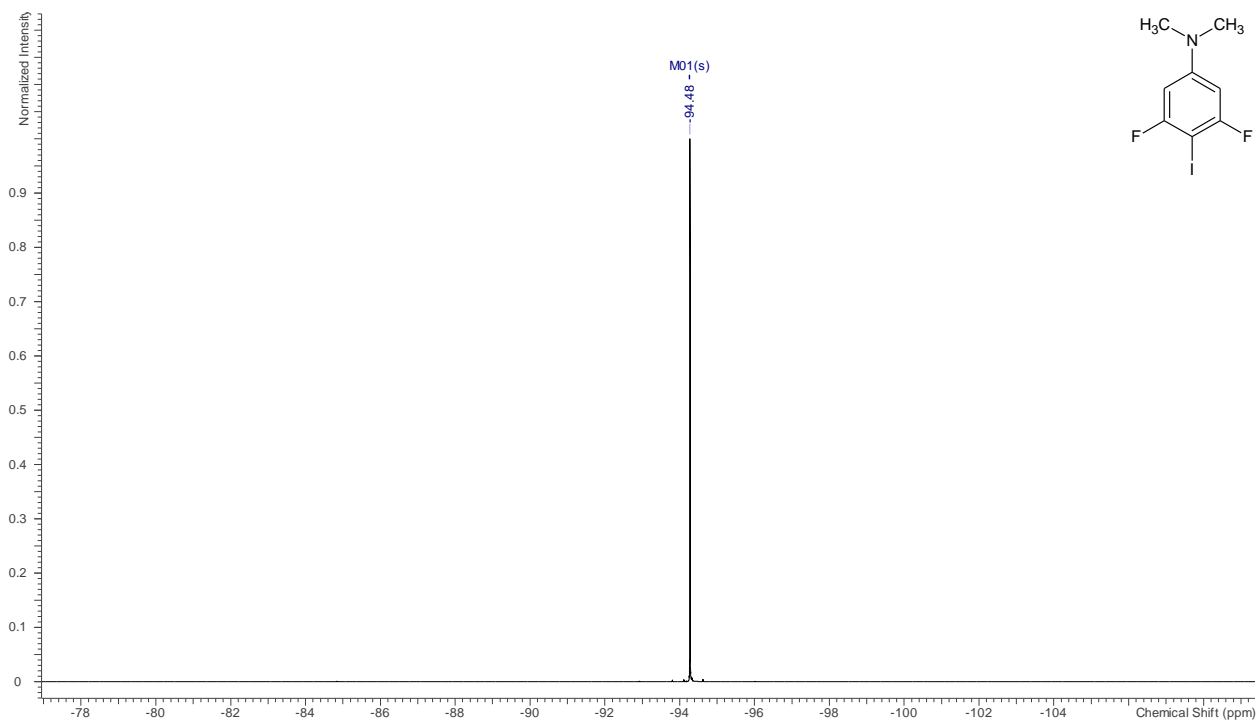


Figure S15. $^{19}\text{F}\{\text{H}\}$ -NMR of compound 7 in CDCl_3 (471 MHz, 298 K).

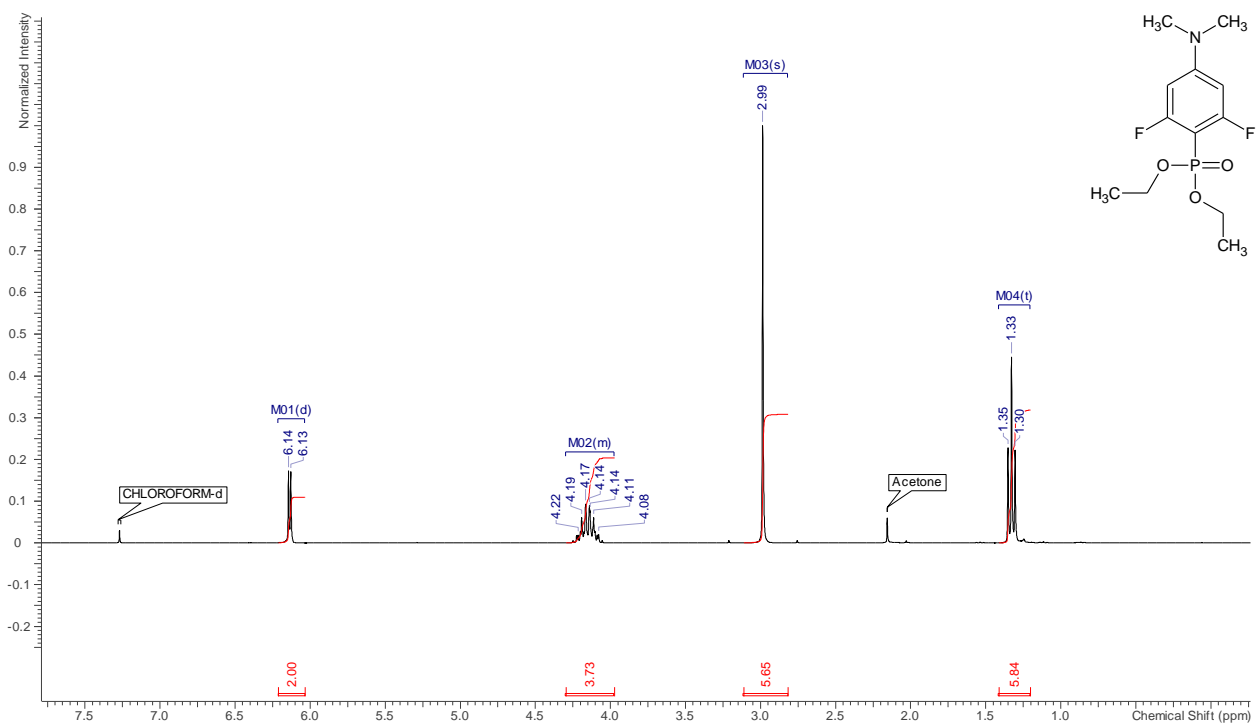


Figure S16. $^1\text{H}\{\text{F}\}$ -NMR of compound 8 in CDCl_3 (301 MHz, 298 K).

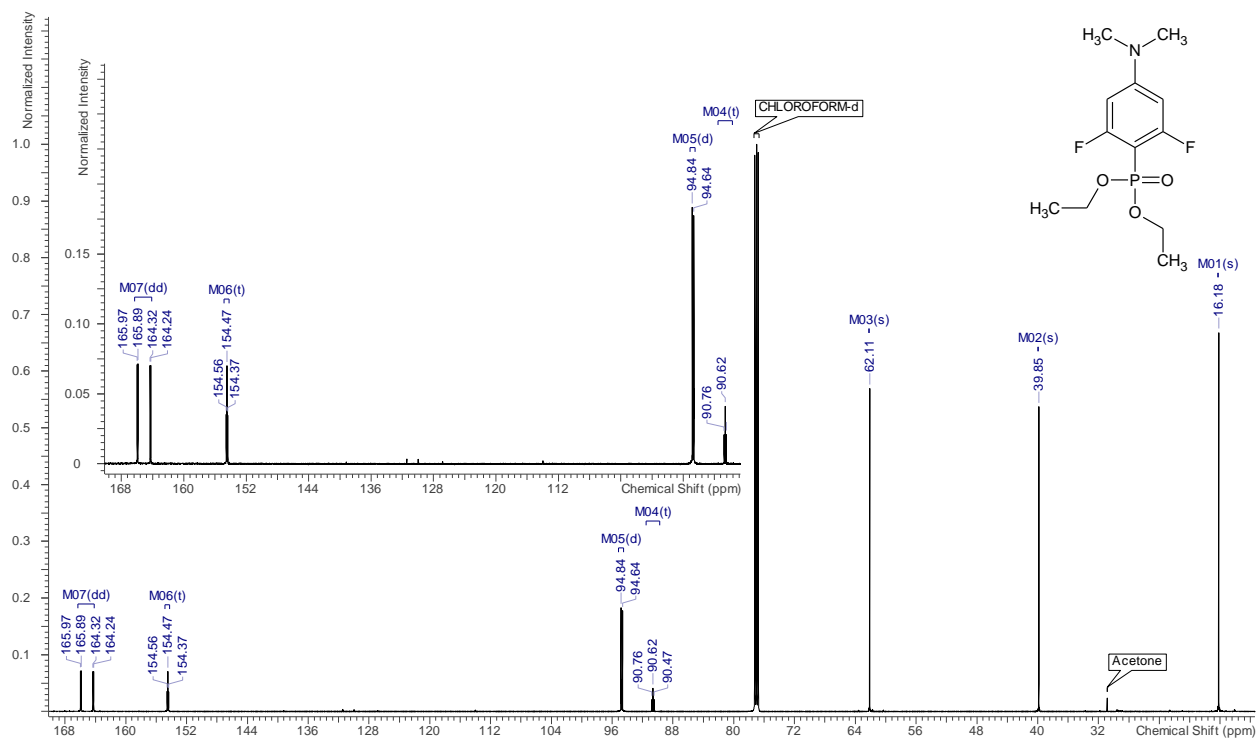


Figure S17. $^{13}\text{C}\{\text{H,P}\}$ -NMR of compound 8 in CDCl_3 (151 MHz, 298 K).

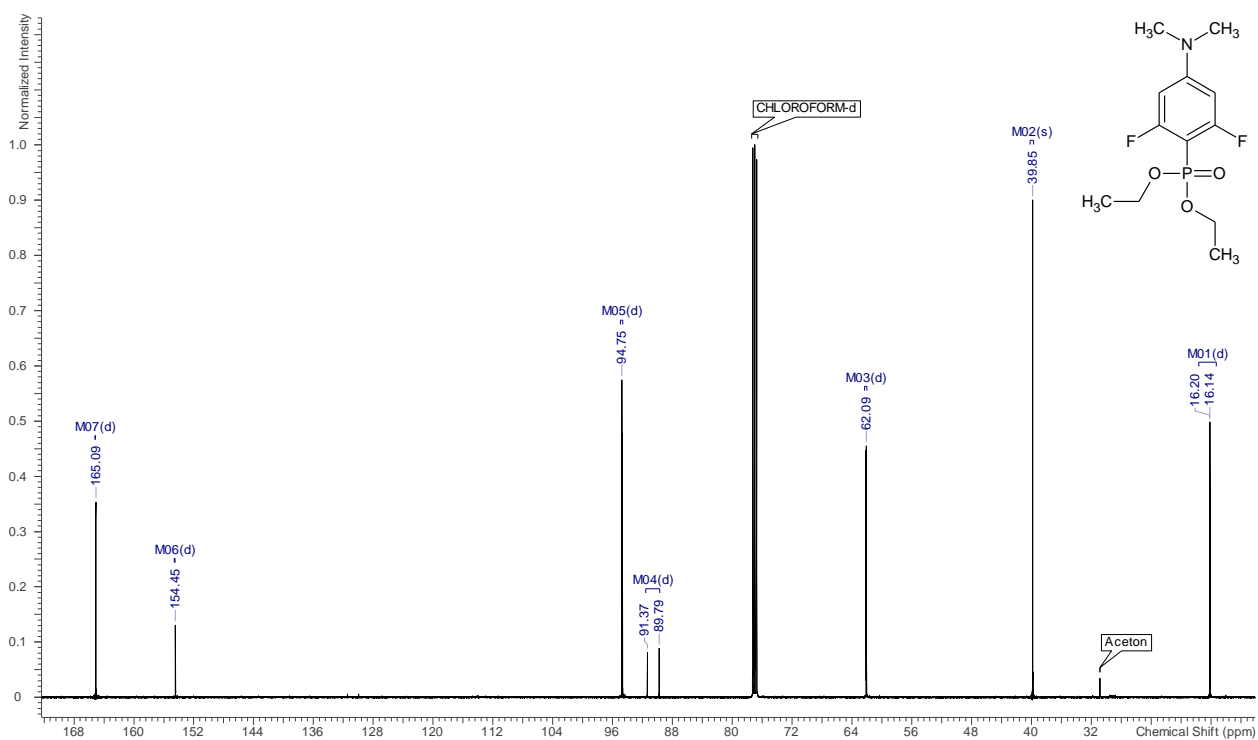


Figure S18. $^{13}\text{C}\{\text{H,F}\}$ -NMR of compound 8 in CDCl_3 (126 MHz, 298 K).

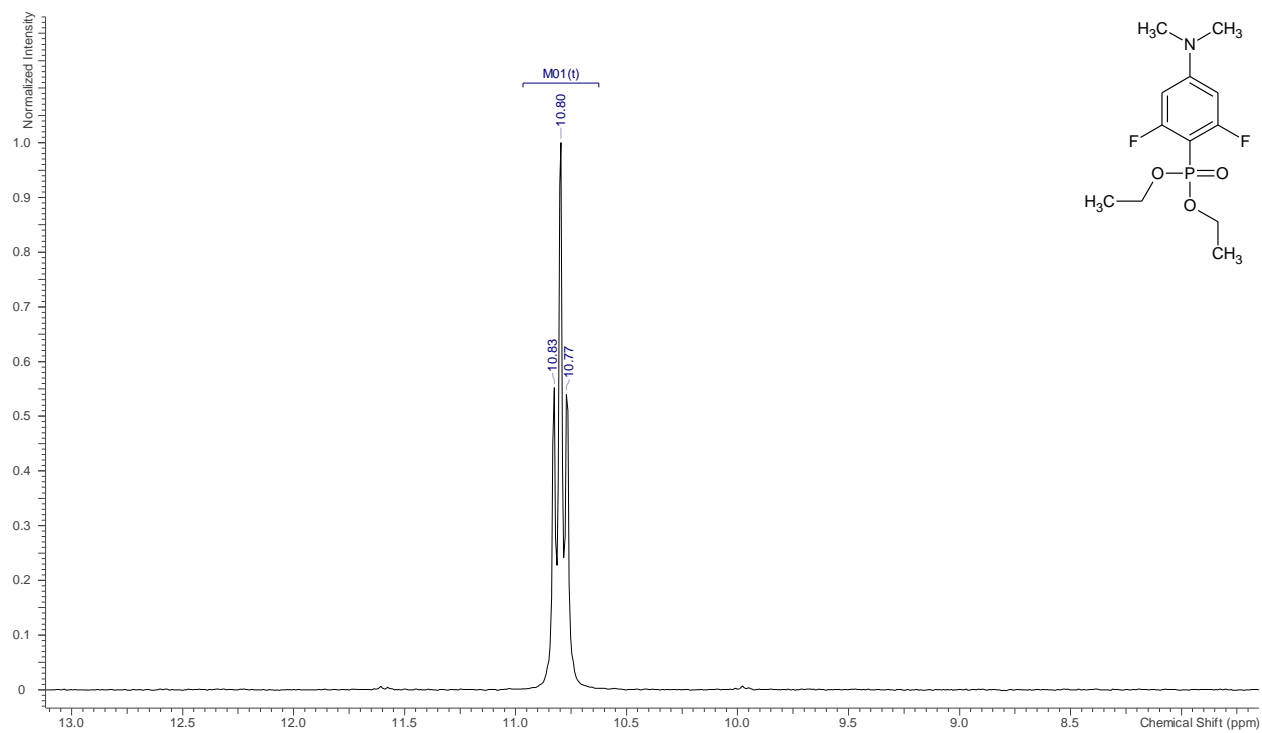


Figure S19. $^{31}\text{P}\{^1\text{H}\}$ -NMR of compound 8 in CDCl_3 (122 MHz, 298 K).

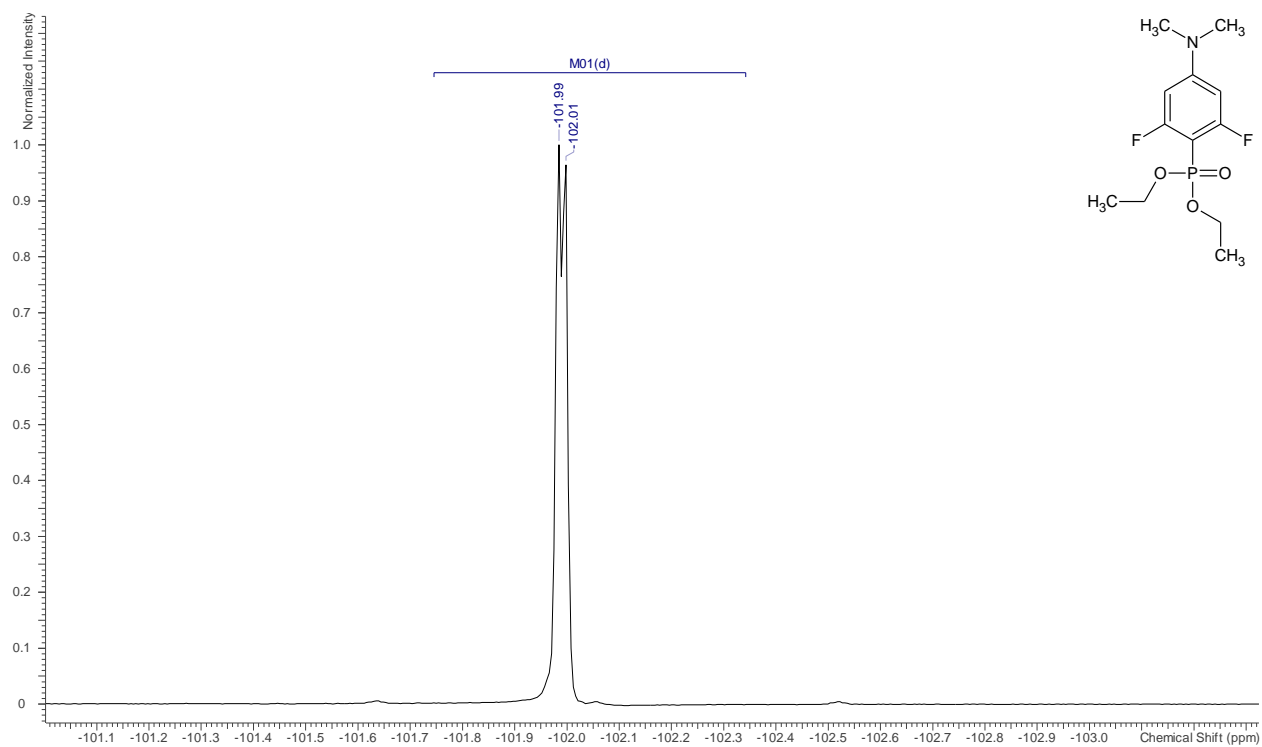


Figure S20. $^{19}\text{F}\{^1\text{H}\}$ -NMR of compound 8 in CDCl_3 (283 MHz, 298 K).

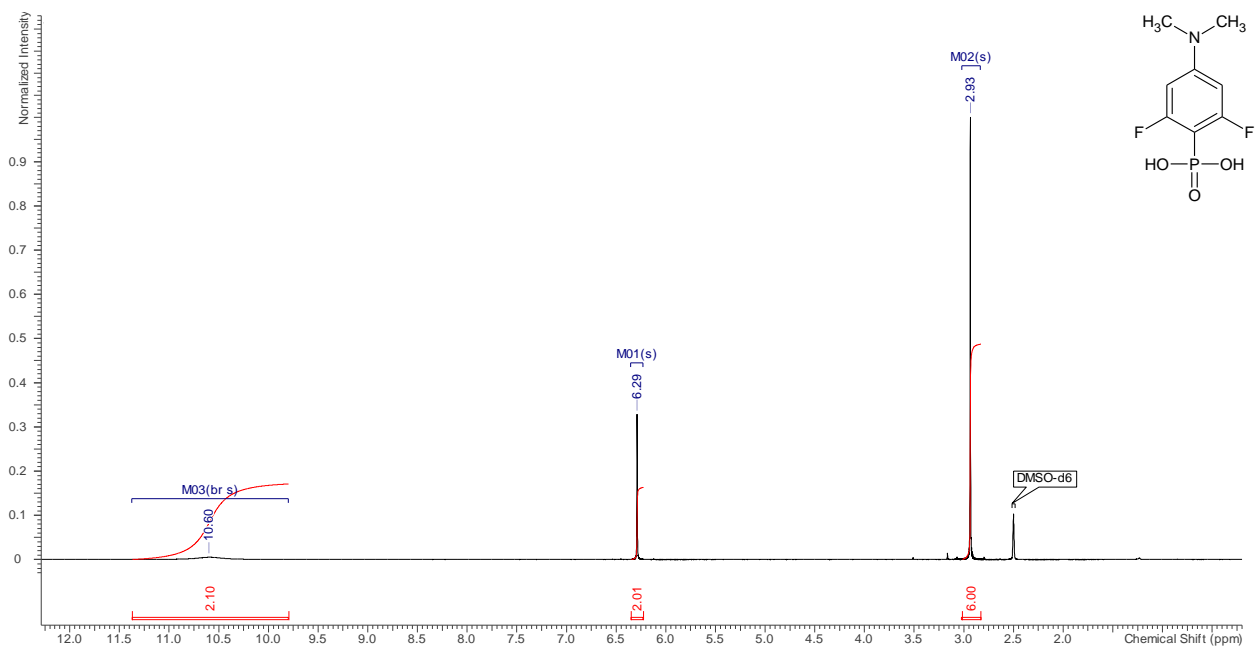


Figure S21. $^1\text{H}\{\text{P},\text{F}\}$ -NMR of PhFPA in DMSO (500 MHz, 298 K).

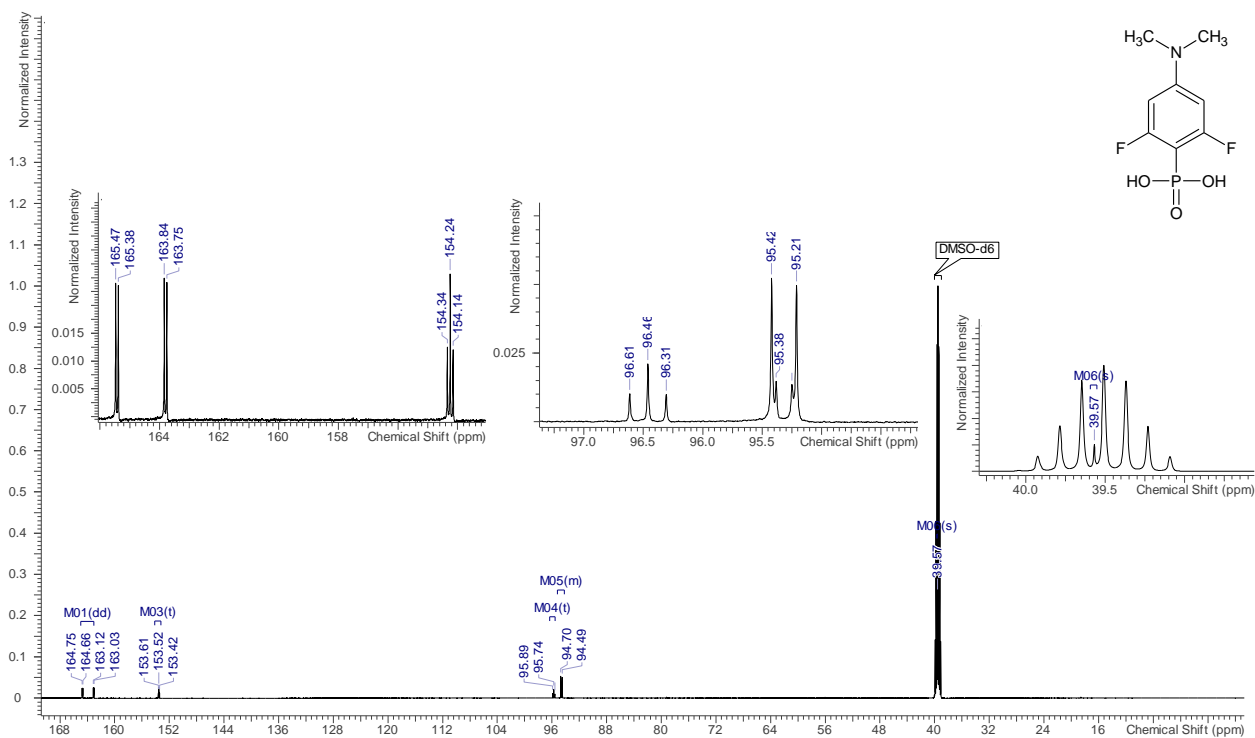


Figure S22. $^{13}\text{C}\{\text{H},\text{P}\}$ -NMR of PhFPA in DMSO (151 MHz, 298 K).

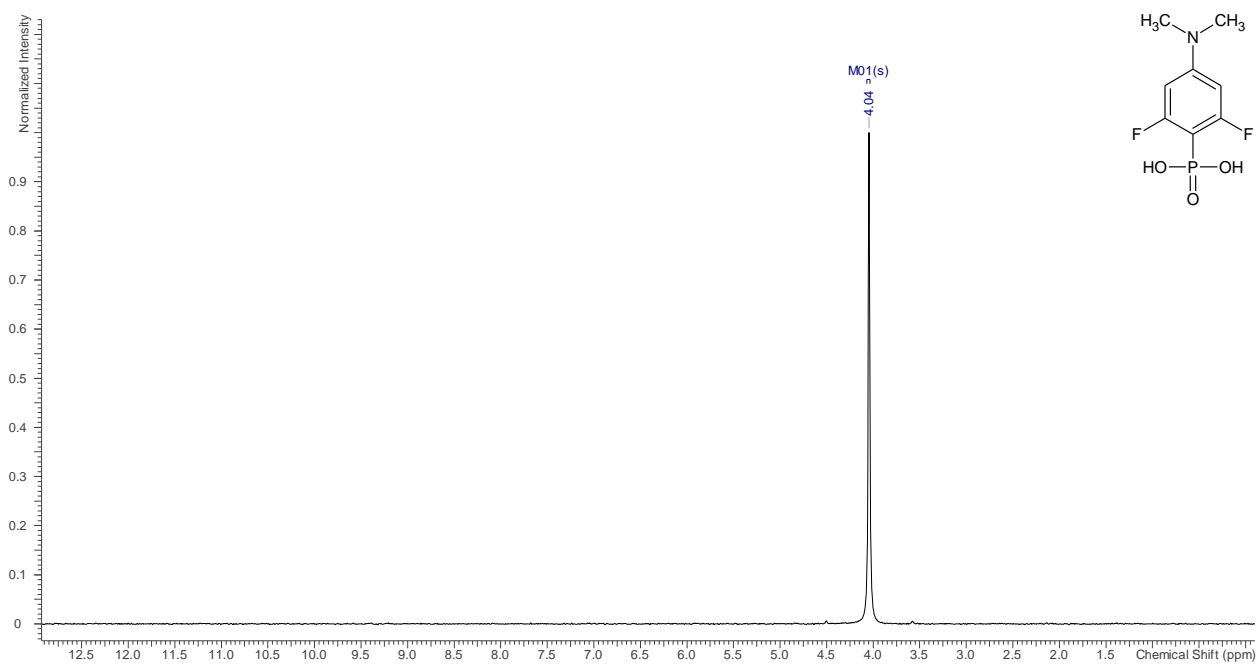


Figure S23. $^{31}\text{P}\{\text{H},\text{F}\}$ -NMR of PhFPA in DMSO (202 MHz, 298 K).

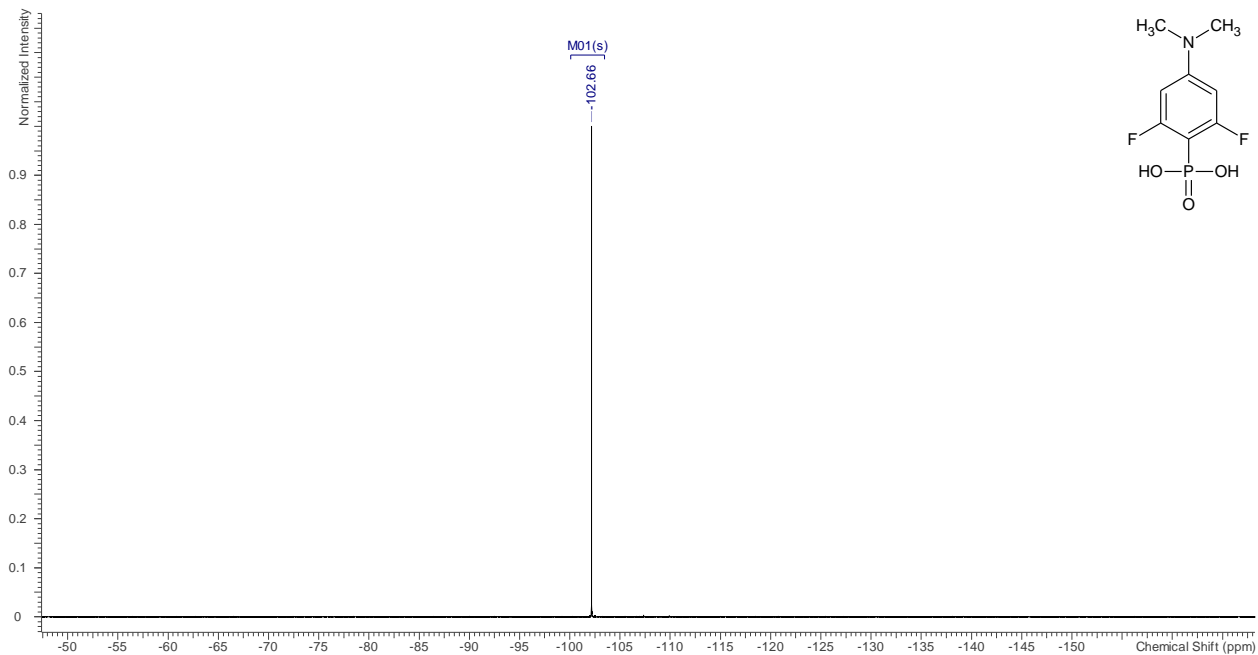


Figure S24. $^{19}\text{F}\{\text{H},\text{P}\}$ -NMR of PhFPA in DMSO (471 MHz, 298 K).

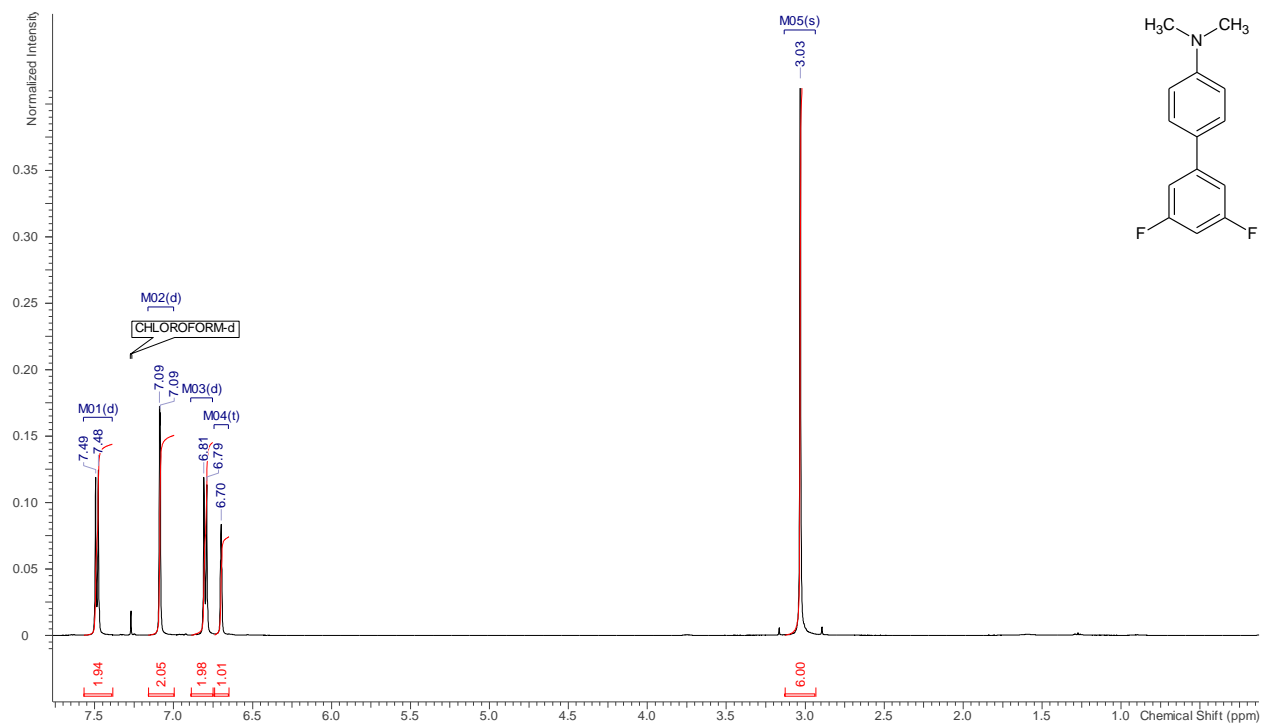


Figure S25. $^1\text{H}\{\text{F}\}$ -NMR of compound 10 in CDCl_3 (500 MHz, 298 K).

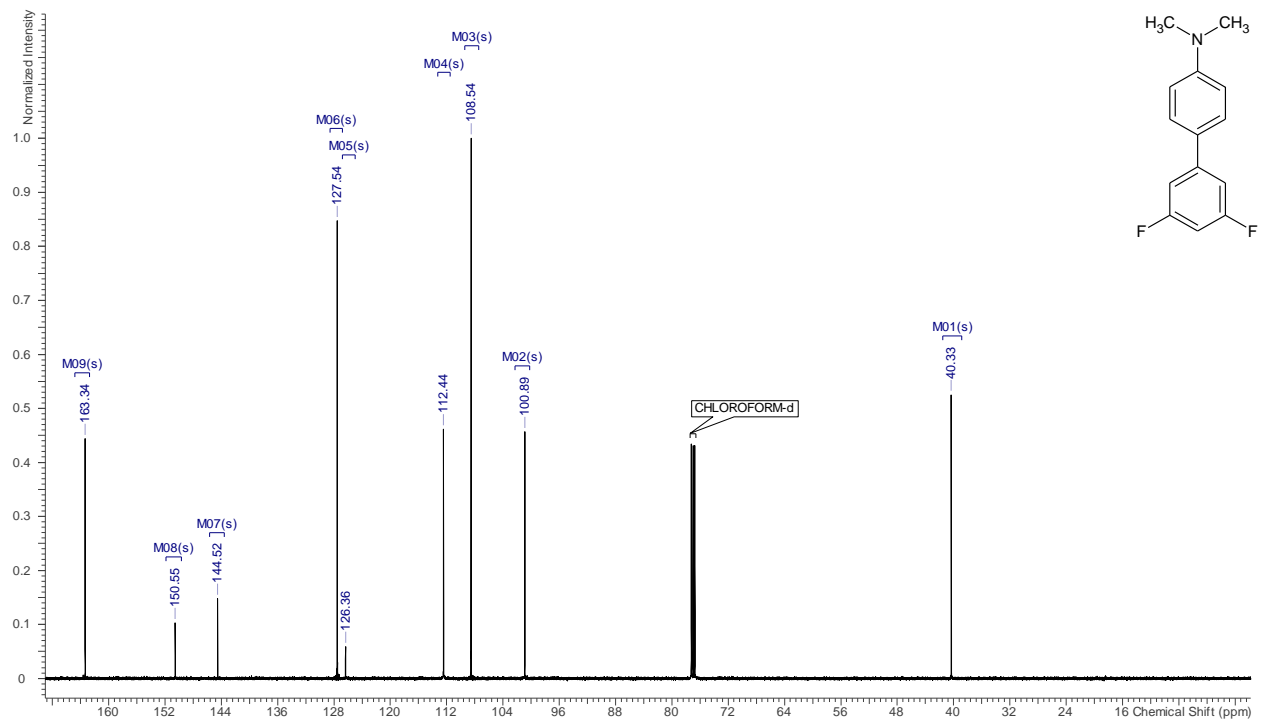


Figure S26. $^{13}\text{C}\{\text{H},\text{F}\}$ -NMR of compound 10 in CDCl_3 (126 MHz, 298 K).

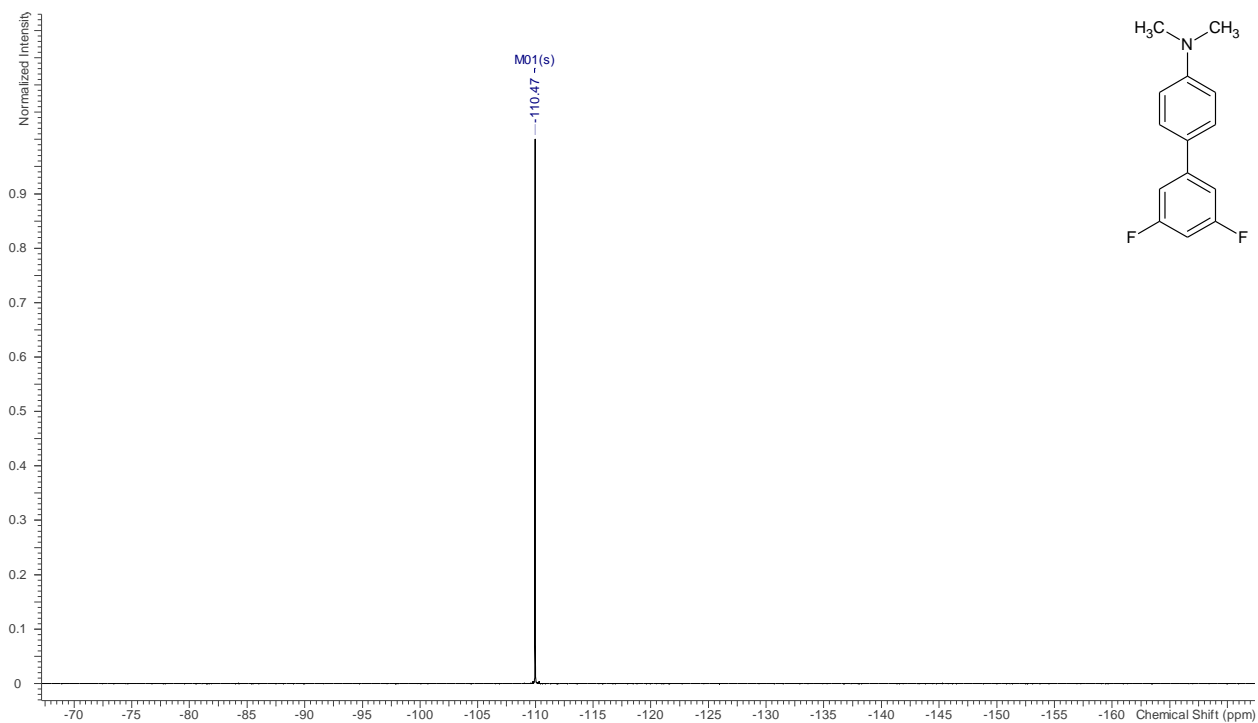


Figure S27. ^{19}F -NMR of compound 10 in CDCl_3 (471 MHz, 298 K).

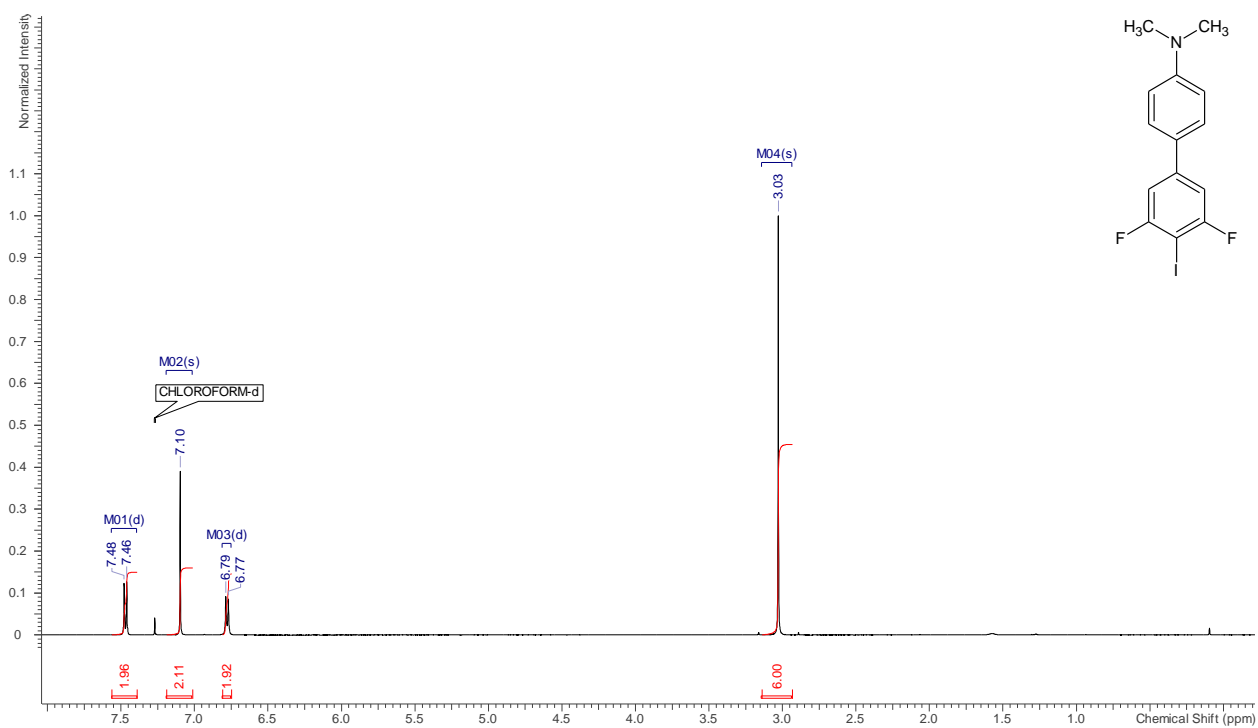


Figure S28. ^1H -NMR of compound 11 in CDCl_3 (500 MHz, 298 K).

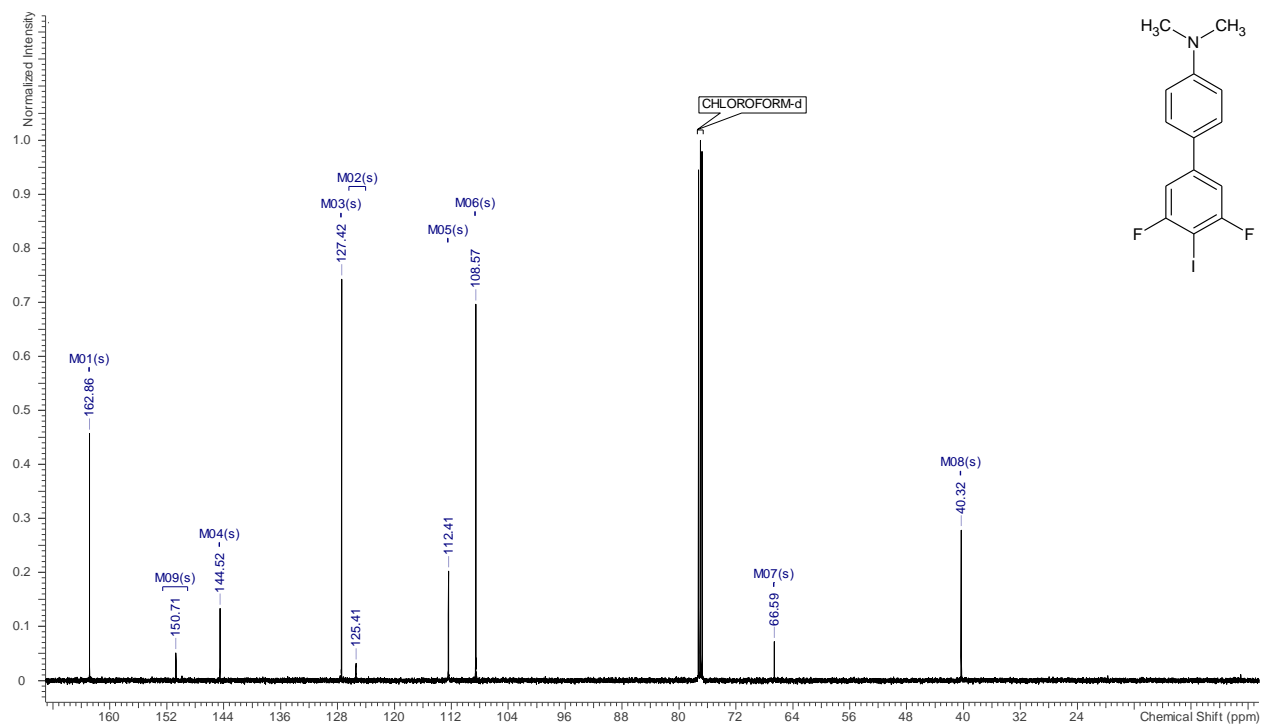


Figure S29. ¹³C{H,F}-NMR of compound 11 in CDCl₃ (126 MHz, 298 K).

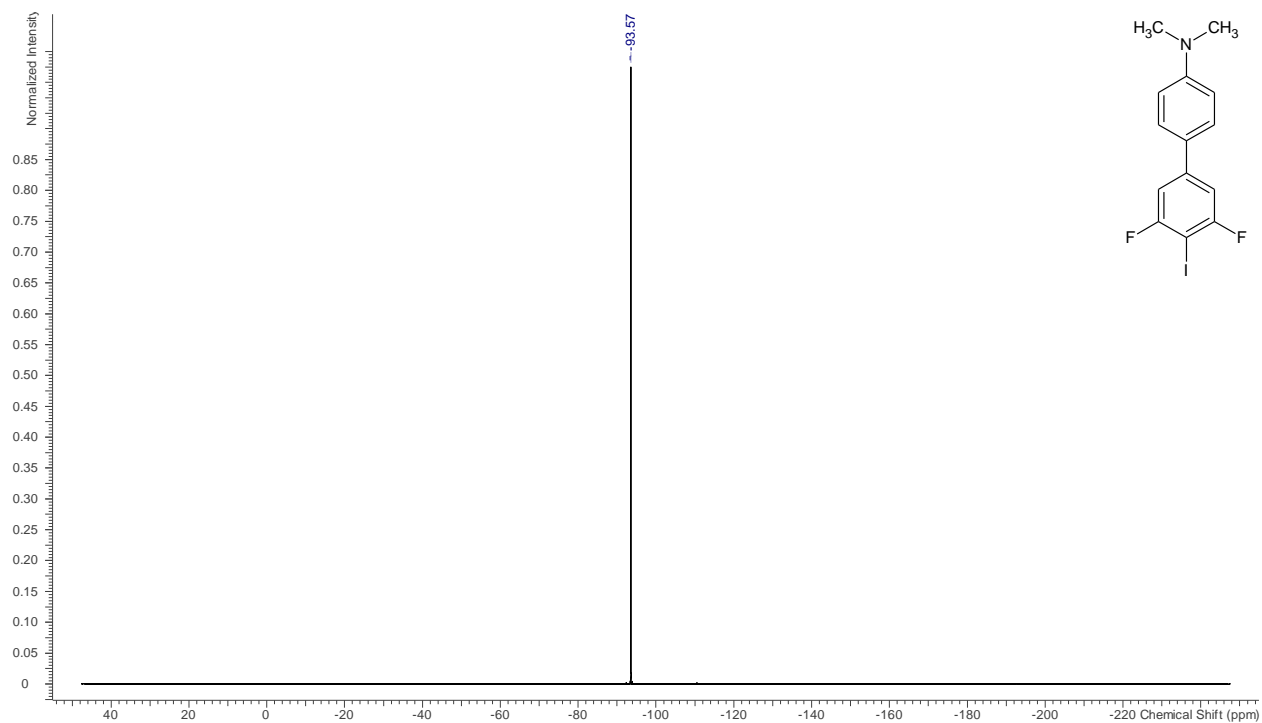


Figure S30. ¹⁹F{H}-NMR of compound 11 in CDCl₃ (471 MHz, 298 K).

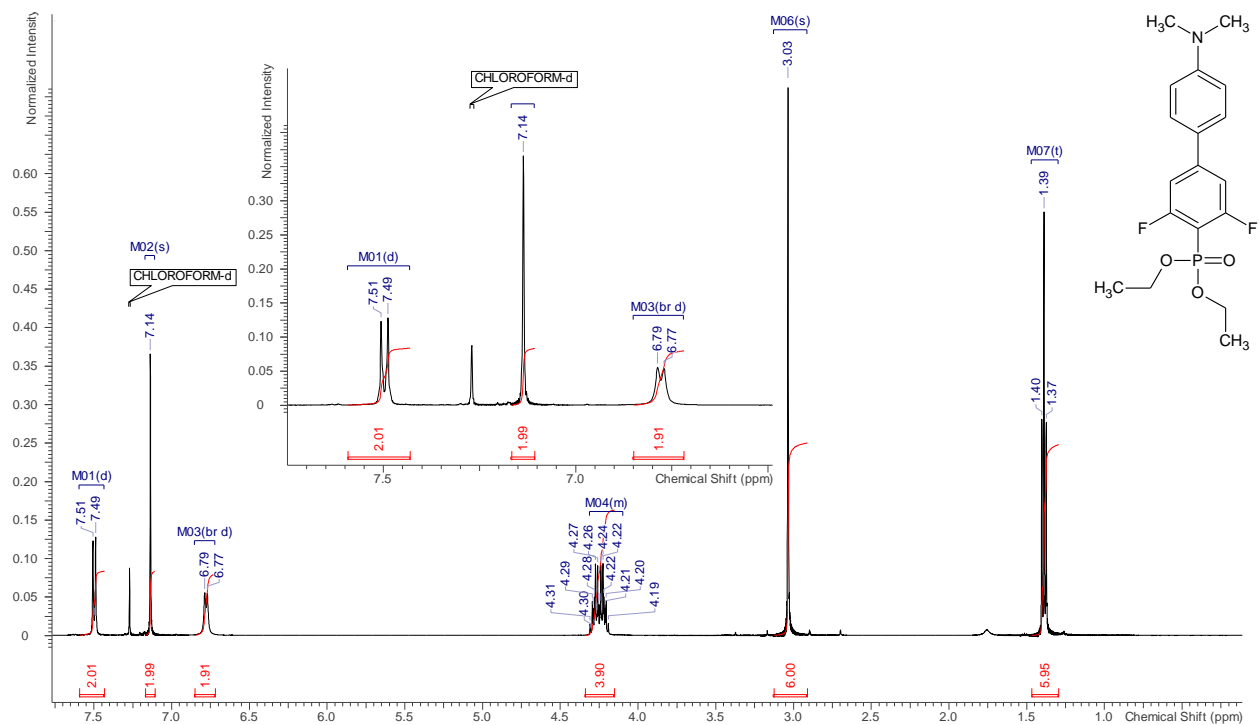


Figure S31. $^1\text{H}\{\text{F,P}\}$ -NMR of compound 12 in CDCl_3 (500 MHz, 298 K).

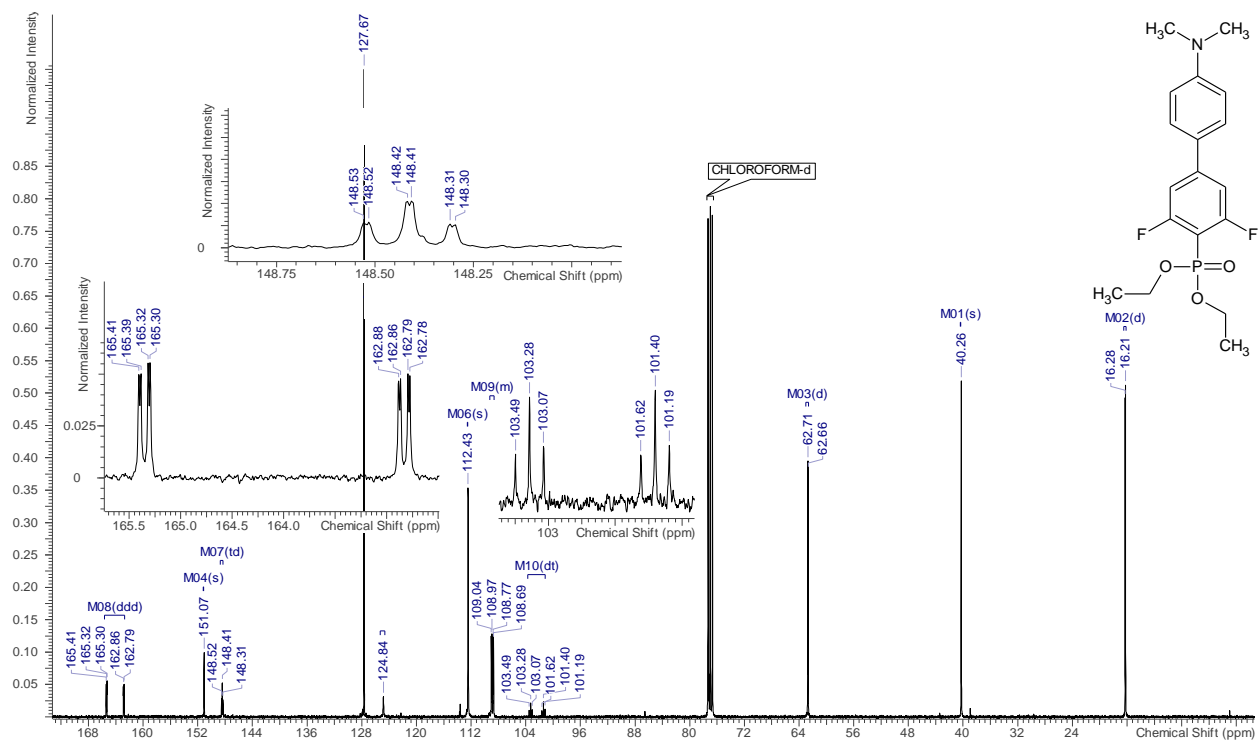


Figure S32. $^{13}\text{C}\{\text{H}\}$ -NMR of compound 12 in CDCl_3 (151 MHz, 298 K).

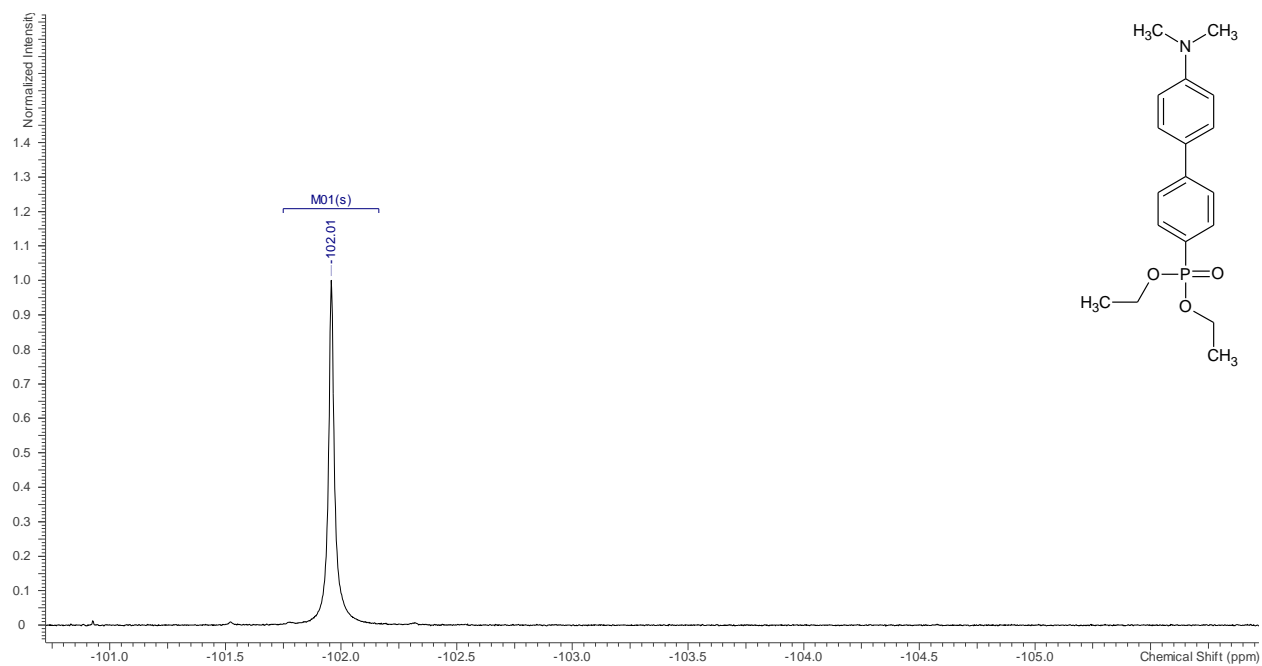


Figure S33. $^{19}\text{F}\{\text{H,P}\}$ -NMR of compound 12 in CDCl_3 (471 MHz, 298 K).

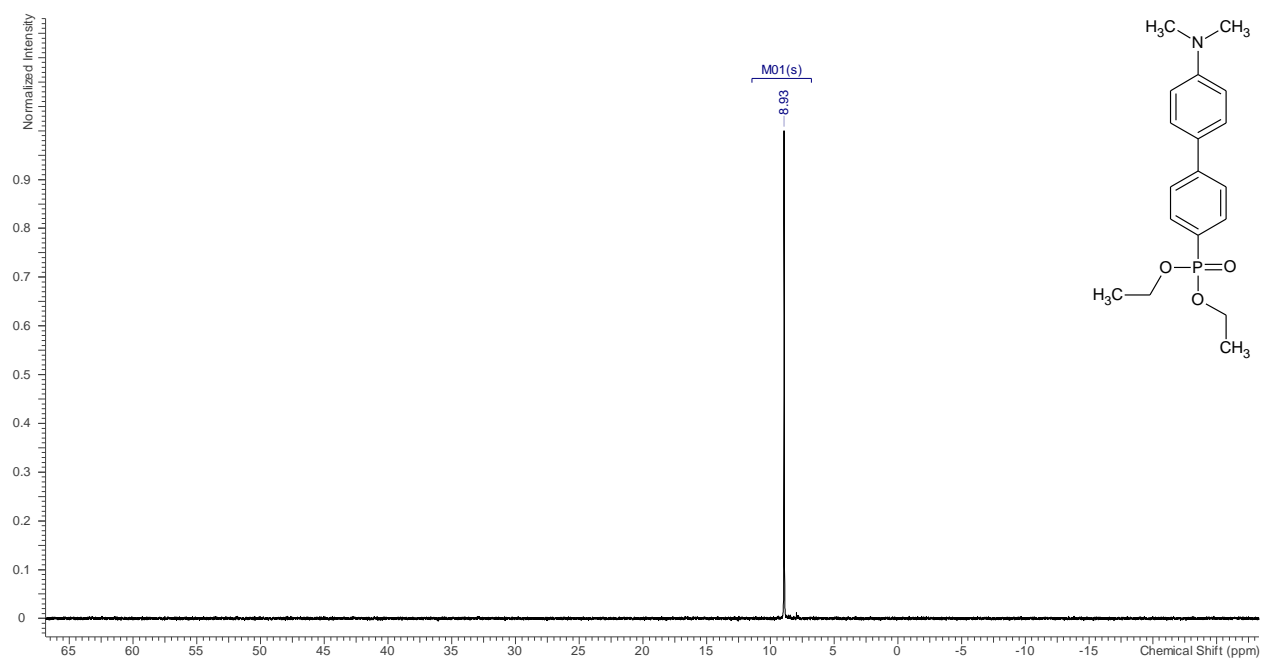


Figure S34. $^{31}\text{P}\{\text{H,F}\}$ -NMR of compound 12 in CDCl_3 (202 MHz, 298 K).

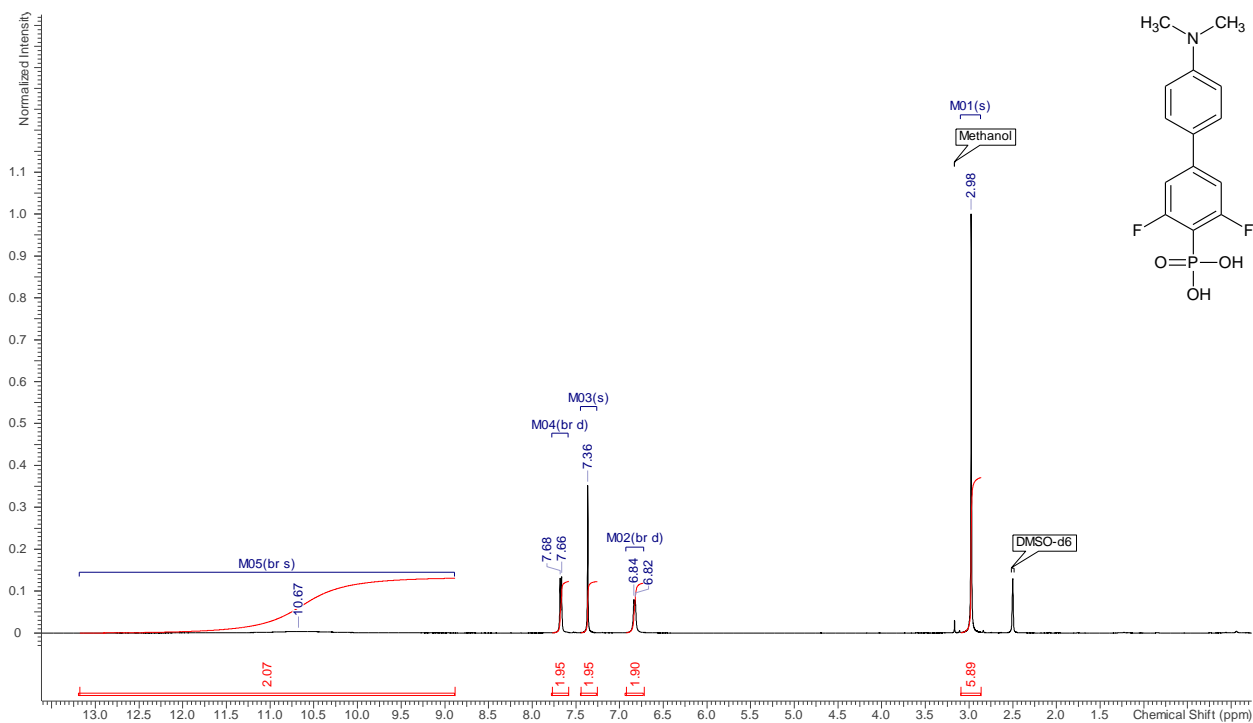


Figure S35. $^1\text{H}\{\text{F},\text{P}\}$ -NMR of XFPA in DMSO (500 MHz, 298 K).

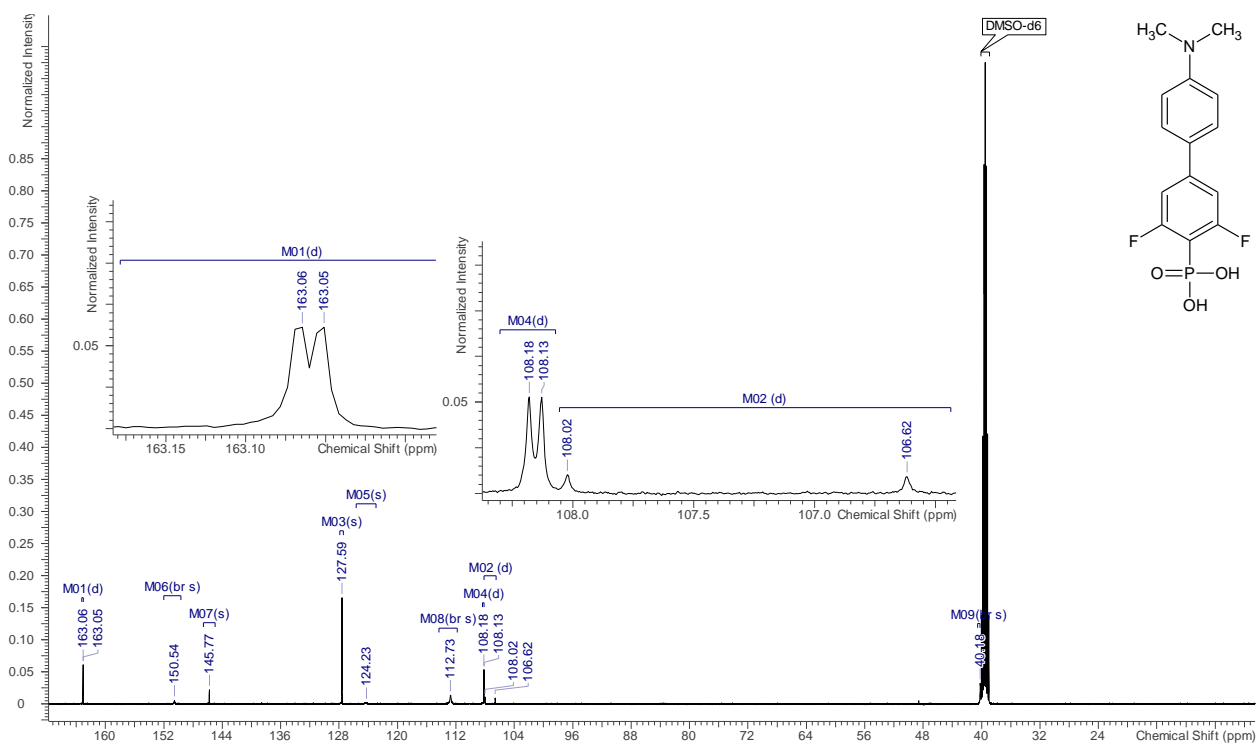


Figure S36. $^{13}\text{C}\{\text{H},\text{F}\}$ -NMR of XFPA in DMSO (126 MHz, 298 K).

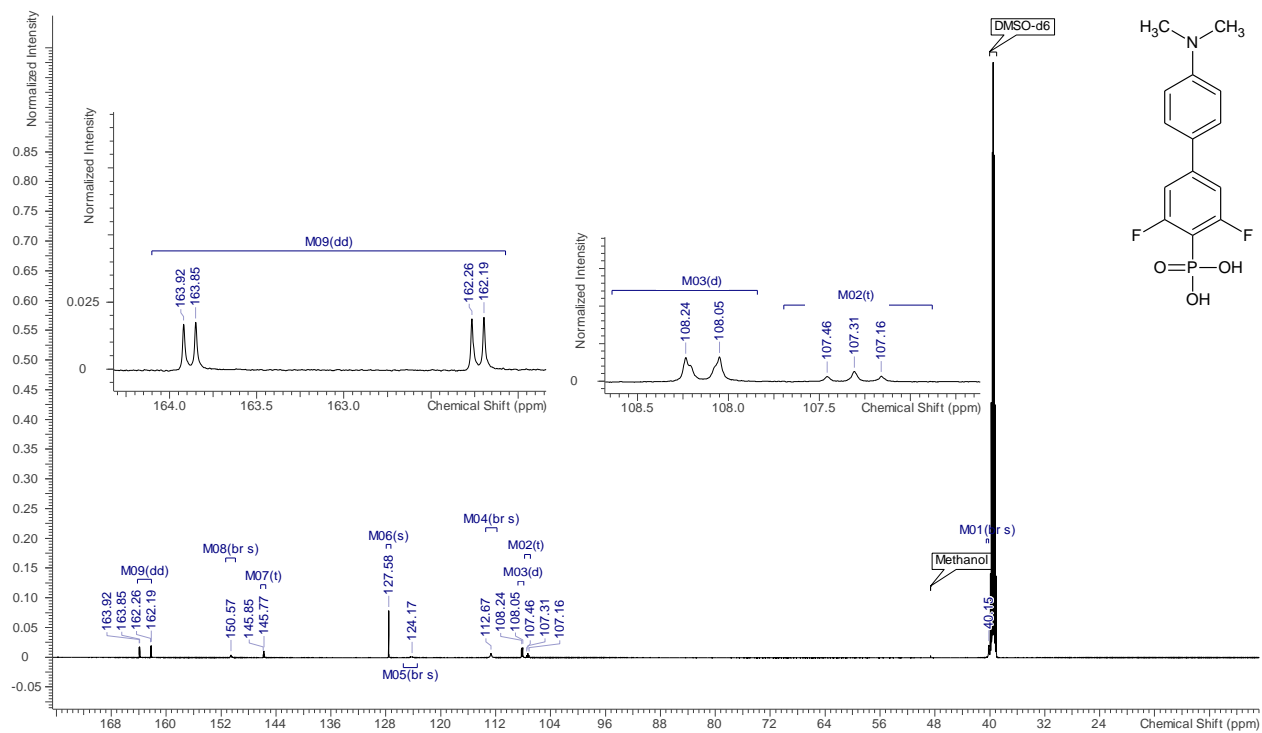


Figure S37. $^{13}\text{C}\{\text{H,P}\}$ -NMR of XFPA in DMSO (151 MHz, 298 K).

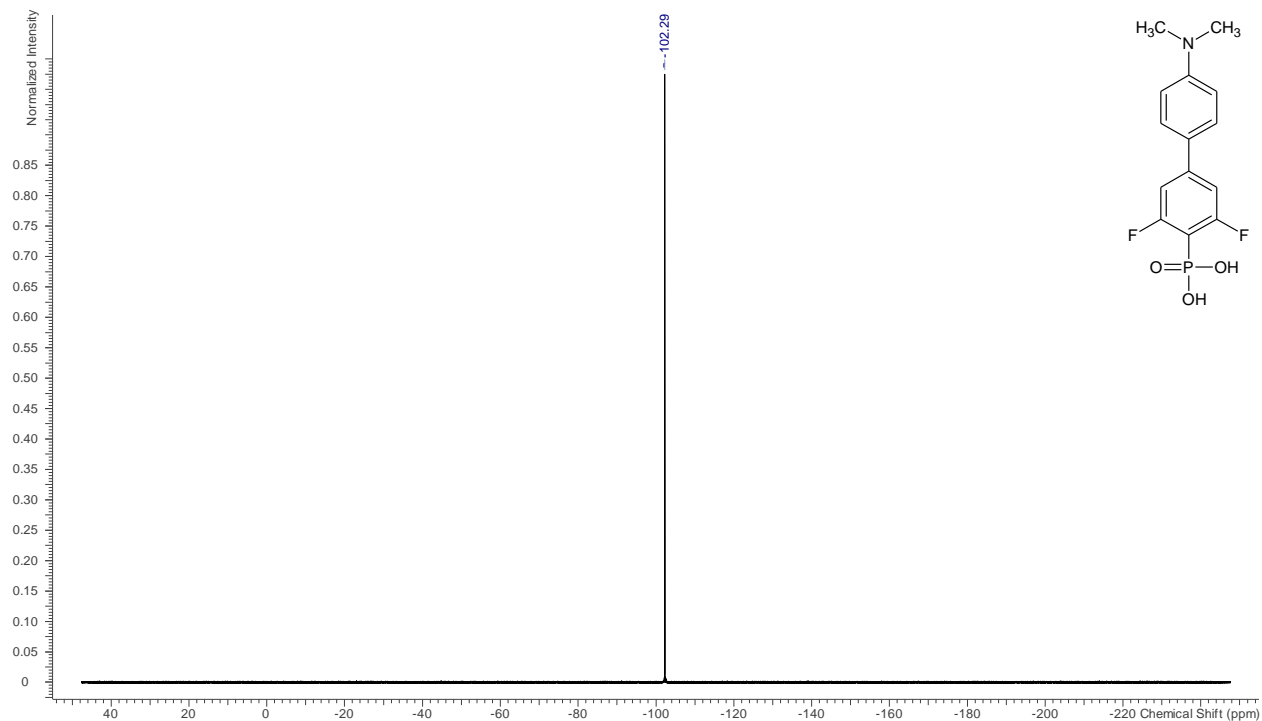


Figure S38. $^{19}\text{F}\{\text{H,P}\}$ -NMR of XFPA in DMSO (471 MHz, 298 K).

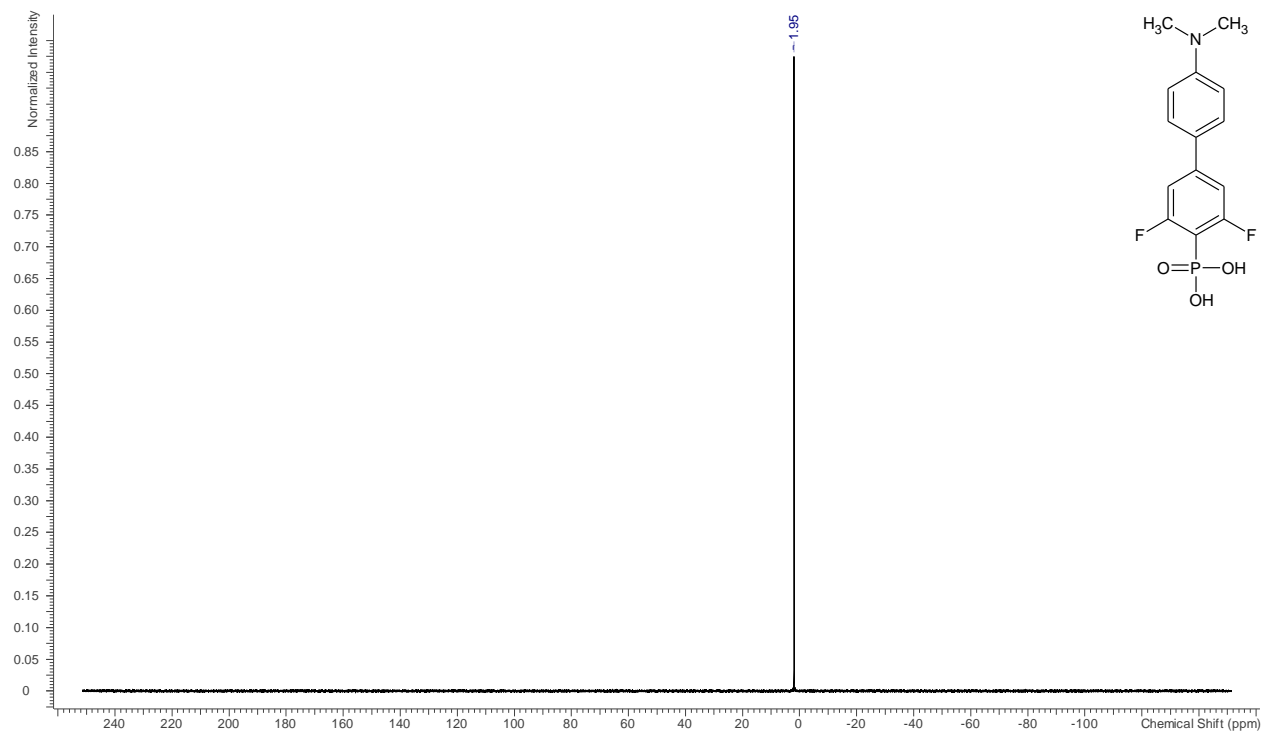


Figure S39. $^{31}\text{P}\{\text{H},\text{F}\}$ -NMR of XFPA in DMSO (202 MHz, 298 K).

3. Crystal structures

PhPA



Figure S40. Crystal structure of PhPA. PhPA was crystalized from ethanol.

Table S1: Crystal data and structure refinement for PhPA.

CCDC	1837997	
Empirical formula	$C_8H_{12.67}NO_{3.33}P$	
Formula weight	207.16	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	12	
Unit cell dimensions	$a = 10.8345(6)$ Å	$\alpha = 90$ deg.
	$b = 28.9272(15)$ Å	$\beta = 104.0195(14)$ deg.
	$c = 9.4951(5)$ Å	$\gamma = 90$ deg.
Volume	$2887.2(3)$ Å ³	
Density (calculated)	1.43 g/cm ³	
Absorption coefficient	0.26 mm ⁻¹	
Crystal shape	"stick-plate"	
Crystal size	$0.275 \times 0.105 \times 0.038$ mm ³	
Crystal colour	colourless	
Theta range for data collection	1.9 to 26.4 deg.	
Index ranges	$-10 \leq h \leq 13$, $-34 \leq k \leq 36$, $-11 \leq l \leq 11$	
Reflections collected	20056	
Independent reflections	5891 ($R(\text{int}) = 0.0517$)	
Observed reflections	4124 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.90	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5891 / 0 / 399	
Goodness-of-fit on F^2	1.02	
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.047$, $wR2 = 0.100$	
Largest diff. peak and hole	0.39 and -0.39 eÅ ⁻³	

XPA



Figure S41. Crystal structure of XPA. XPA was crystalized from DMSO.

Table S2. Crystal data and structure refinement for XPA.

CCDC	1837999
Empirical formula	C ₁₆ H ₂₂ NO ₄ PS
Formula weight	355.37
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	Cc
Z	8
Unit cell dimensions	a = 39.0162(12) Å α = 90 deg. b = 11.0877(5) Å β = 92.212(3) deg. c = 7.7507(3) Å γ = 90 deg.
Volume	3350.5(2) Å ³
Density (calculated)	1.41 g/cm ³
Absorption coefficient	2.79 mm ⁻¹
Crystal shape	long plate
Crystal size	0.360 x 0.060 x 0.020 mm ³
Crystal colour	colourless
Theta range for data collection	2.3 to 75.4 deg.
Index ranges	-48 ≤ h ≤ 47, -13 ≤ k ≤ 13, -4 ≤ l ≤ 9
Reflections collected	10009
Independent reflections	3701 (R(int) = 0.0385)
Observed reflections	3424 (I > 2σ (I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.85 and 0.25
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	3701 / 158 / 460
Goodness-of-fit on F ²	1.04
Final R indices (I > 2σ(I))	R1 = 0.049, wR2 = 0.134
Absolute structure parameter	0.02(2)
Largest diff. peak and hole	0.83 and -0.37 eÅ ⁻³

PhFPA

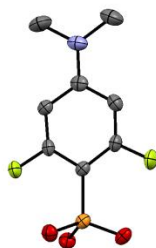


Figure S42: Crystal structure of PhFPA. PhFPA was crystallized from ethanol.

Table S3. Crystal data and structure refinement for PhFPA.

CCDC	1837998
Empirical formula	C ₈ H ₁₀ F ₂ NO ₃ P
Formula weight	237.14
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pbcm
Z	4
Unit cell dimensions	a = 8.8398(12) Å α = 90 deg. b = 15.936(2) Å β = 90 deg. c = 6.8655(9) Å γ = 90 deg.
Volume	967.2(2) Å ³
Density (calculated)	1.63 g/cm ³
Absorption coefficient	0.30 mm ⁻¹
Crystal shape	irregular
Crystal size	0.150 x 0.100 x 0.060 mm ³
Crystal colour	colourless
Theta range for data collection	2.3 to 28.7 deg.
Index ranges	-11 ≤ h ≤ 11, -20 ≤ k ≤ 21, -9 ≤ l ≤ 9
Reflections collected	7585
Independent reflections	1359 (R(int) = 0.0691)
Observed reflections	930 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.87
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1359 / 0 / 94
Goodness-of-fit on F ²	1.07
Final R indices (I > 2σ(I))	R1 = 0.043, wR2 = 0.093
Largest diff. peak and hole	0.32 and -0.35 eÅ ⁻³

XFPA

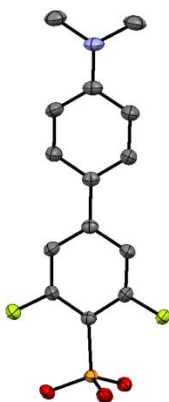


Figure S43. Crystal structure of XFPA. XFPA was crystalized from DMSO/acetone.

Table S4. Crystal data and structure refinement for XFPA.

CCDC	1837996
Empirical formula	$C_{16.50}H_{20}F_2NO_4PS_{0.50}$
Formula weight	381.33
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Z	4
Unit cell dimensions	$a = 8.1179(4) \text{ Å}$ $\alpha = 91.3174(12) \text{ deg.}$ $b = 8.4131(4) \text{ Å}$ $\beta = 92.7441(12) \text{ deg.}$ $c = 25.6661(13) \text{ Å}$ $\gamma = 95.1251(12) \text{ deg.}$
Volume	$1743.24(15) \text{ Å}^3$
Density (calculated)	1.45 g/cm^3
Absorption coefficient	0.26 mm^{-1}
Crystal shape	"plate-needle"
Crystal size	$0.251 \times 0.059 \times 0.050 \text{ mm}^3$
Crystal colour	colourless
Theta range for data collection	0.8 to 26.5 deg.
Index ranges	$-10 \leq h \leq 10, -10 \leq k \leq 10, -32 \leq l \leq 32$
Reflections collected	24656
Independent reflections	7196 ($R(\text{int}) = 0.0540$)
Observed reflections	4891 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.90
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7196 / 110 / 490
Goodness-of-fit on F^2	1.05
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.048, wR2 = 0.117$
Largest diff. peak and hole	0.46 and -0.60 eÅ^{-3}

4. TGA

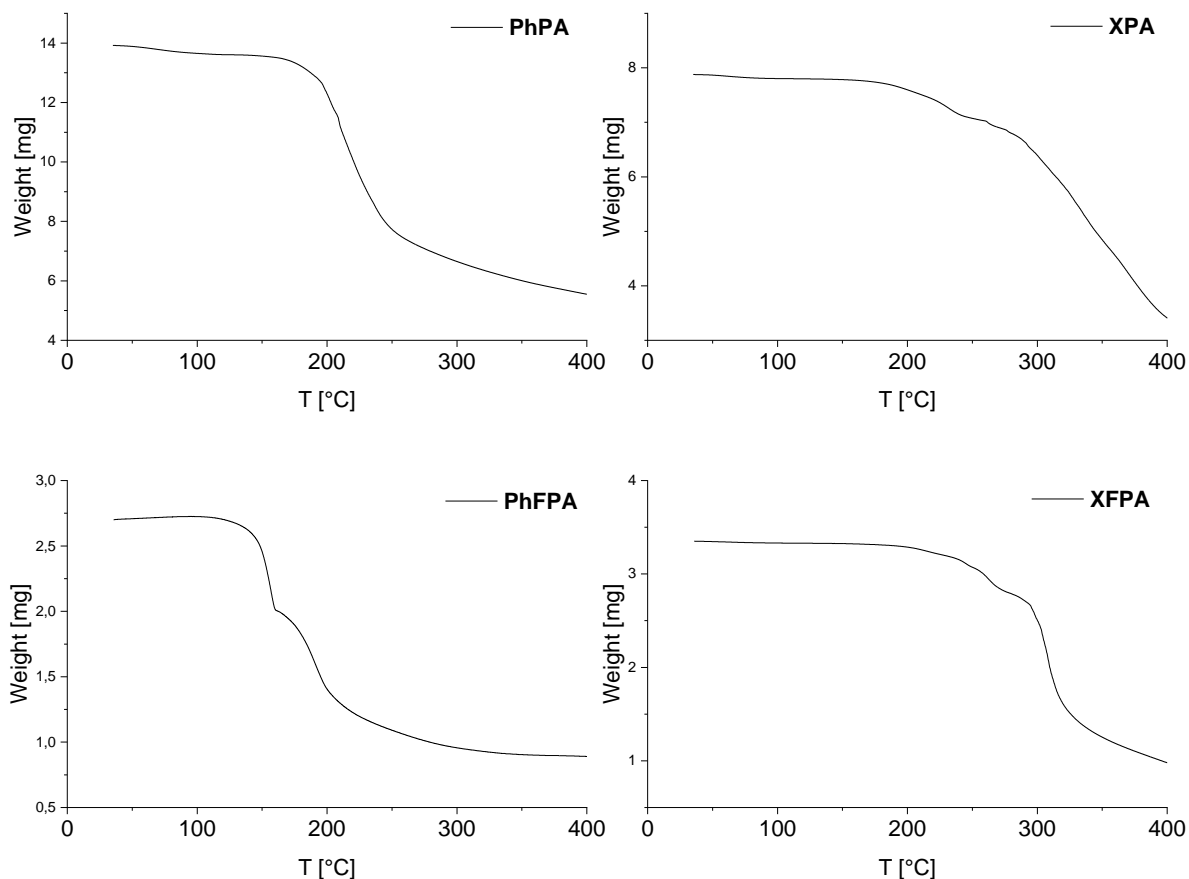


Figure S44. TGA curves of PhPA, XPA, PhFPA, XFPA. The heating rates were 10 K per minute for PhPA, XPA and XFPA and 5 K per minute for PhFPA, respectively.

The TGA measurements show, that PhPA starts to decompose at roughly 170 °C, while the same can be seen for XPA at 180 °C. For the fluorinated derivatives decomposition for PhFPA can be seen at a temperature of 130 °C while this is true for XFPA at 220 °C.

5. SAM preparation

The ITO substrates were detergent/solvent cleaned (DSC) with acetone and isopropanol in the ultrasonic bath for 15 min each. The cleaned substrates were transferred into a N₂ glovebox and immersed into 0.2 mM solution of the corresponding molecules in ethanol for 16 h at 50 °C. The immersion was followed up by a heating the substrates on a hotplate for 3 h at 140 °C for PhPA, XPA and XFPA and 100 °C for PhFPA (see TGA in the SI). Subsequent ultrasonic bath treatment in ambient conditions in ethanol for 20 min eliminated multilayer formation. To avoid water and solvent adsorption in the SAMs one last heating step at the hotplate in the glovebox for 10 min at 100 °C was performed before the SAMs were characterized by the following techniques.

6. IR measurements

Infrared reflection-absorption spectroscopy (IRRAS) was performed using a Vertex 80v (Bruker) Fourier-transform (FT) IR spectrometer equipped with a liquid nitrogen cooled MCT detector. The samples were positioned in a customized reflection unit inside the sample compartment of the spectrometer that was evacuated to about 3 mbar. The spectra were obtained using p-polarized light with an angle of incidence of 75° with respect to the surface normal. All spectra are the average of 600 scans with a resolution of 1 cm^{-1} . Each SAM measurement was divided by background spectrum of an ITO DSC substrate, thus giving the relative reflectance R of the monolayer.

The IRRAS spectra of the SAM on ITO for PhPA, PhFPA and XPA in addition to Figure 1 are shown in Figure S45. In comparison to these spectra the corresponding simulated IRRAS spectra based on DFT calculations are plotted as well as the ATR spectra of the isotropic/bulk material. The ATR spectra were recorded with a Jasco FT/IR-4100. Modes marked with vertical lines and numbers can be found in Table S5 where they are assigned to the vibrational modes and transition dipole moment (TDM) orientation in the molecule. The thicker lines with o and p indicate the modes for the tilt angle calculations. The grey range in the spectra is influenced by the longitudinal mode of the glass substrate beneath the ITO. This is due to the fact that for IRRAS a reference sample of ITO DSC has to be measured. The electronic properties like plasma frequency and damping of the ITO are changed by the applied SAM and thus lead to different reflection properties compared to the reference.⁴ This range is therefore excluded in the spectral analysis of the SAMs.

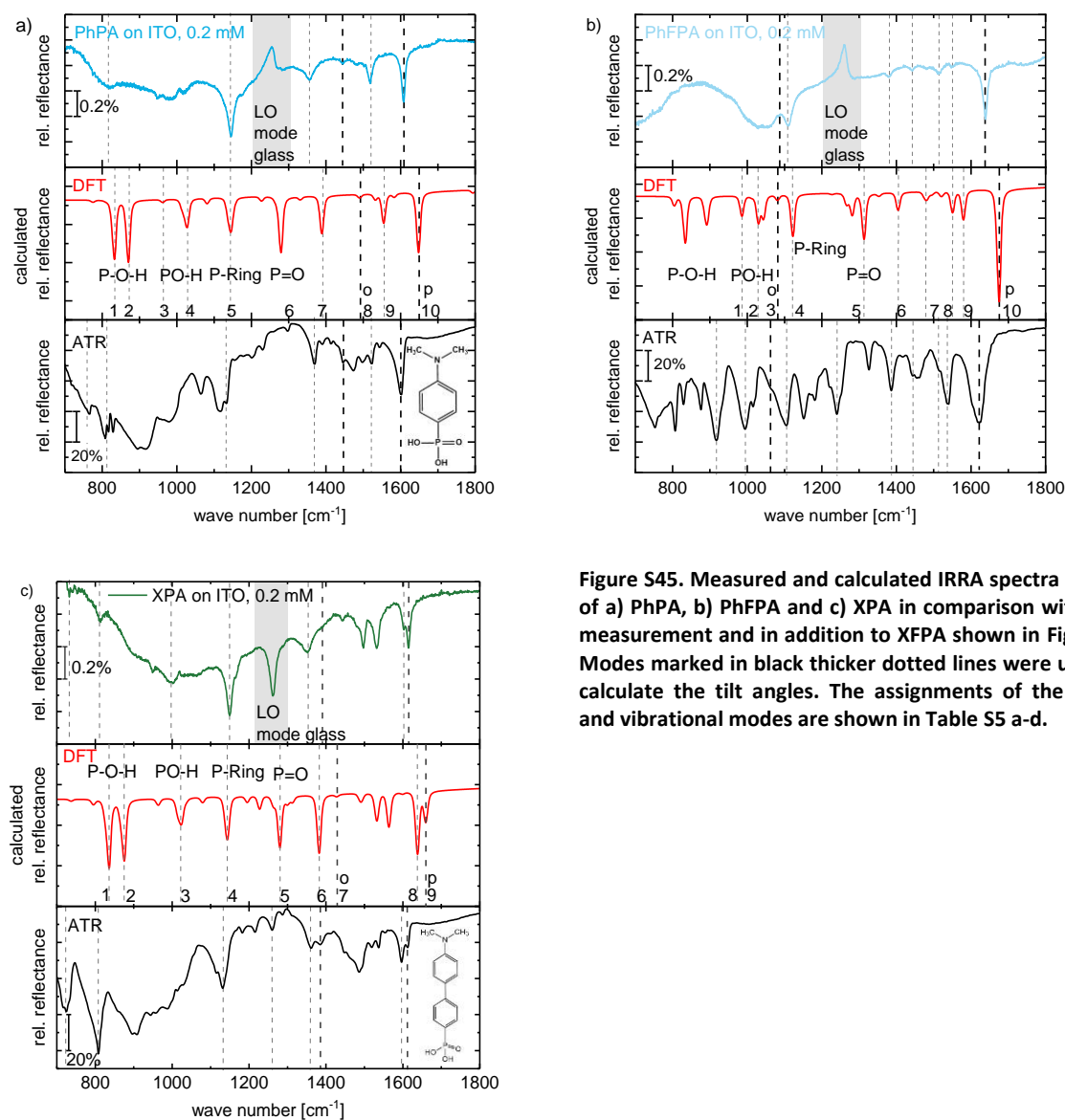


Figure S45. Measured and calculated IRRA spectra on ITO of a) PhPA, b) PhFPA and c) XPA in comparison with ATR measurement and in addition to XFPA shown in Figure 1. Modes marked in black thicker dotted lines were used to calculate the tilt angles. The assignments of the peaks and vibrational modes are shown in Table S5 a-d.

The tilt angle calculation is an estimation for an average tilt angle and the error is mainly influenced by the base line of the spectra, the strength of the oscillators as well as the exact orientation of the TDM. The highlighted vibrational modes (in gray in Table S5 and with thicker dashed lines in Figure S45) used for the tilt angle calculation are visualized in the 3D molecular structures in Figure S47. The orthogonal mode in the case of PhPA is the one which deviates the most from an orthogonal orientation relative to the molecular axis, its offset is roughly 30°. In

terms of the angle calculation this means that in the case of angles $< 60^\circ$ the calculated angle is overestimated, the value is larger than in reality. The other o modes show an angle of mainly 90° relative to the molecular axis. Speaking of PhPA and PhFPA the difference in the tilt angles is therefore real and considering the challenge in tilt angle determination as described above the difference could be larger but not smaller. In the case of XPA and XFPA the orientation of the o and p modes is very similar and the tilt angle difference can be trusted.

In general it can be added that in the tilt angle determination a resulting angle between $45^\circ - 50^\circ$ is the magic angle which does not allow to clarify whether the molecules on the surface are completely disordered or all perfectly aligned. The exact value depends on the distance between the vibrational modes (ν_o/ν_p). However, the calculated tilt angles are all below this magic angle and thus indicate an ordering within the monolayers.

Table S5 a-d. Mode assignment for all four molecules for SAM, bulk and DFT spectra. The modes for the tilt angle calculation are marked in gray.

a)

Mode	Position [cm^{-1}]			Assignment	Orientation
	PhPA SAM	Bulk	DFT		
1	broad	765	833	ν P-OH, breathing ring	p
2	--	808	870	ν P-O-H	o
3	--	--	962	ω CH ₃	p
4	--	--	1028	PO-H, δ ring	o
5	1145	1133	1145	P-Ring	p
6	--	--	1279	ν P=O	p
7	1356	1369	1382	δ aniline	p
8	1443	1445	1491	CH ₃	o
9	1518	1522	1555	ν_s C=C, CN	p
10	1608	1602	1648	ν_{as} C=C	p

b)

Mode	Position [cm^{-1}]	Assignment	Orientation
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	PhFPA SAM	Bulk	DFT		
1	--	915	984	PO-H	p
2	--	992	1030	PO-H, δ ring	o
3	1085	1063	1080	ω CH ₃	o
4	1106	1103	1120	P-Phenyl	p
5	--	1240	1312	P=O	p
6	1379	1387	1404	CH ₃ , δ ring, CF	p
7	1440	1441	1481	CH ₃	p
8	1513	1512	1550	wagging CH ₃ , CN	p
9	1548	1538	1579	ν_{as} C=C	p
10	1639	1622	1673	ν_s C=C	p

c)

Mode	Position [cm ⁻¹]			Assignment	Orientation
	XPA SAM	Bulk	DFT		
1	732	724	834	ν_s P-OH, breathing ring	o
2	811	808	876	ν_{as} P-OH, delta ring	o
3	broad	--	1022	PO-H	p
4	1149	1133	1143	ν P-Ring	p
5	--	1260	1280	ν P=O	o,p
6	1354	1360	1382	δ anilin, CN	p
7	1400	1386	1427	δ benzylring	o
8	1601	1596	1638	ν C=C (benzyl)	p
9	1614	1613	1660	ν C=C (anilin)	p

d)

Mode	Position [cm ⁻¹]			Assignment	Orientation
	XFPA SAM	Bulk	DFT		
1	816	760	831	ν_s P-OH	o
2	888	823	890	ν_{as} P-OH	o
3	--	904	1011	PO-H	o
4	--	925	1030	PO-H	p
5	1149	1133	1141	P-Ring	p
6	--	1280	1292	ν P=O, δ ring	o,p
7	1530	1523	1565	δ anilin, CN	p
8	1549	1548	1572	δ ring	o
9	1614	1604	1649	ν C=C	p
10	1628	1621	1663	ν_{as} C=C	p

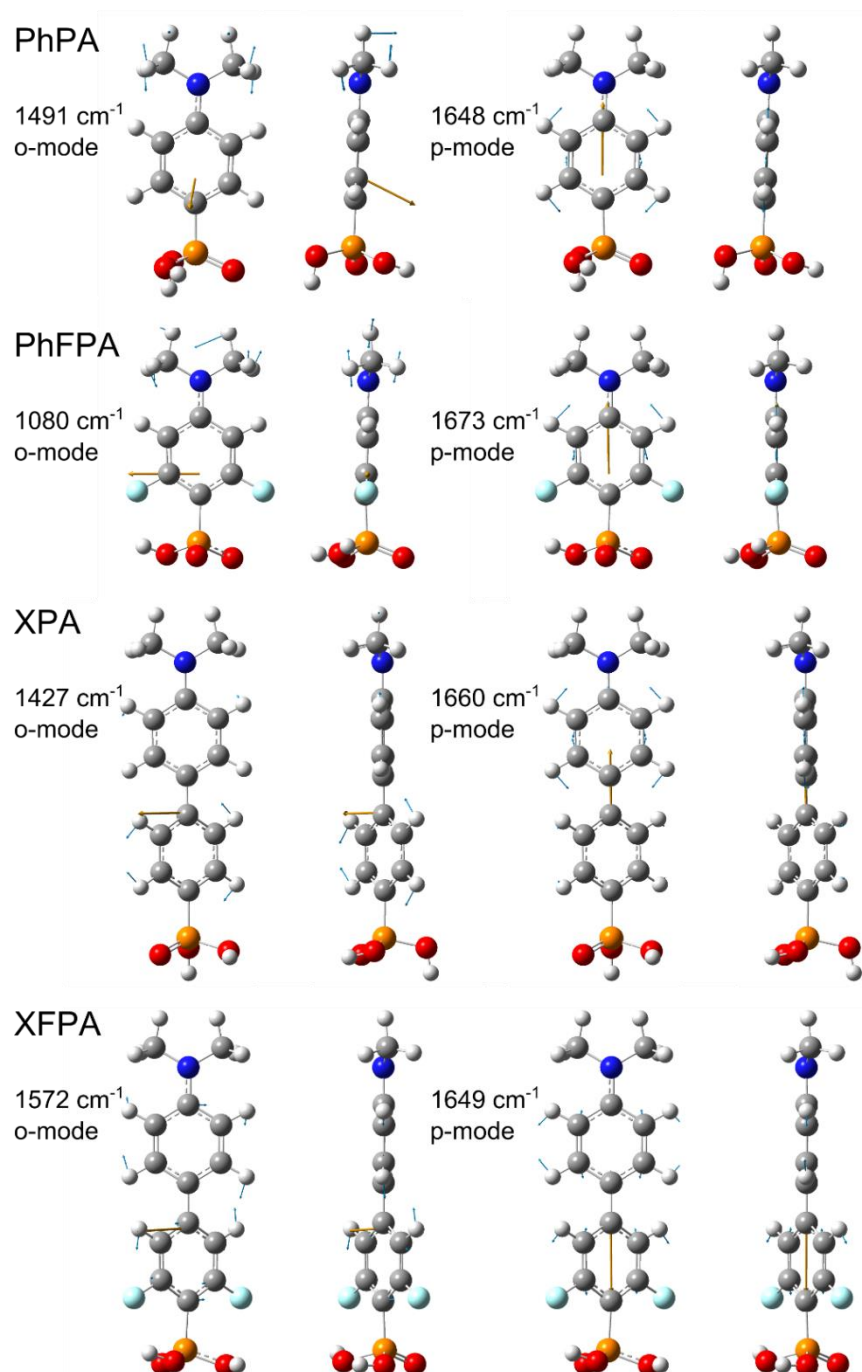


Figure S46 Visualization in the 3D molecular structure of the vibrational modes used for the tilt angle calculations based on the DFT calculation described later on. For each molecule the o and p modes are shown. The resulting transition dipole moments are indicated with yellow arrows, the atomic displacement is depicted with blue arrows. The hydrogen atoms are colored white, carbon is gray, nitrogen blue, phosphor orange, oxygen red and fluorine light blue.

7. Contact angle measurements

Contact angles were measured with a Krüss DSA 100 goniometer. Water droplets with a volume of 1 μL were disposed onto the center of the samples used for spectroscopy and analyzed within the software. The static contact angle was then extracted via a Young-Laplace fit.

8. XPS

The XPS data presented in this work has been measured with a PHI5000 Versa Probe spectrometer from ULVAC-PHI Inc equipped with a concentric hemispherical analyzer for the measurement of kinetic electron energies. A monochromatic aluminum K_{α} X-ray source was employed, generating focused X-ray beams at photon energy of 1486.6 eV in an angle of 54.7° w.r.t. the analyzer. For the XPS core level spectra the illuminated spot on the sample's surface was approximately 200 μm in diameter. Survey spectra were recorded with a pass energy of 187.85 eV, detail spectra of the core level lines were measured with 11.75 eV, valence bands were taken with 23.5 eV and for the secondary electron cutoff 2.95 eV were chosen. The spectra are referenced in binding energy with respect to the Fermi edge and the core level lines of in-situ cleaned Ag, Au and Cu foils. Differing from this, the C 1s spectra displayed in Figure 2a were referenced to their respective main peaks. Secondary electron edges were measured with XPS with a bias of 7 V and calibrated via the work function of in-situ sputter-cleaned Ag foil determined by ultraviolet photoelectron spectroscopy (UPS). Here, the Ag UP spectrum was referenced to its Fermi level position. The base pressure of the measuring chamber during all experiments was kept in the 10^{-9} mbar regime. The take-off angle was 90° .

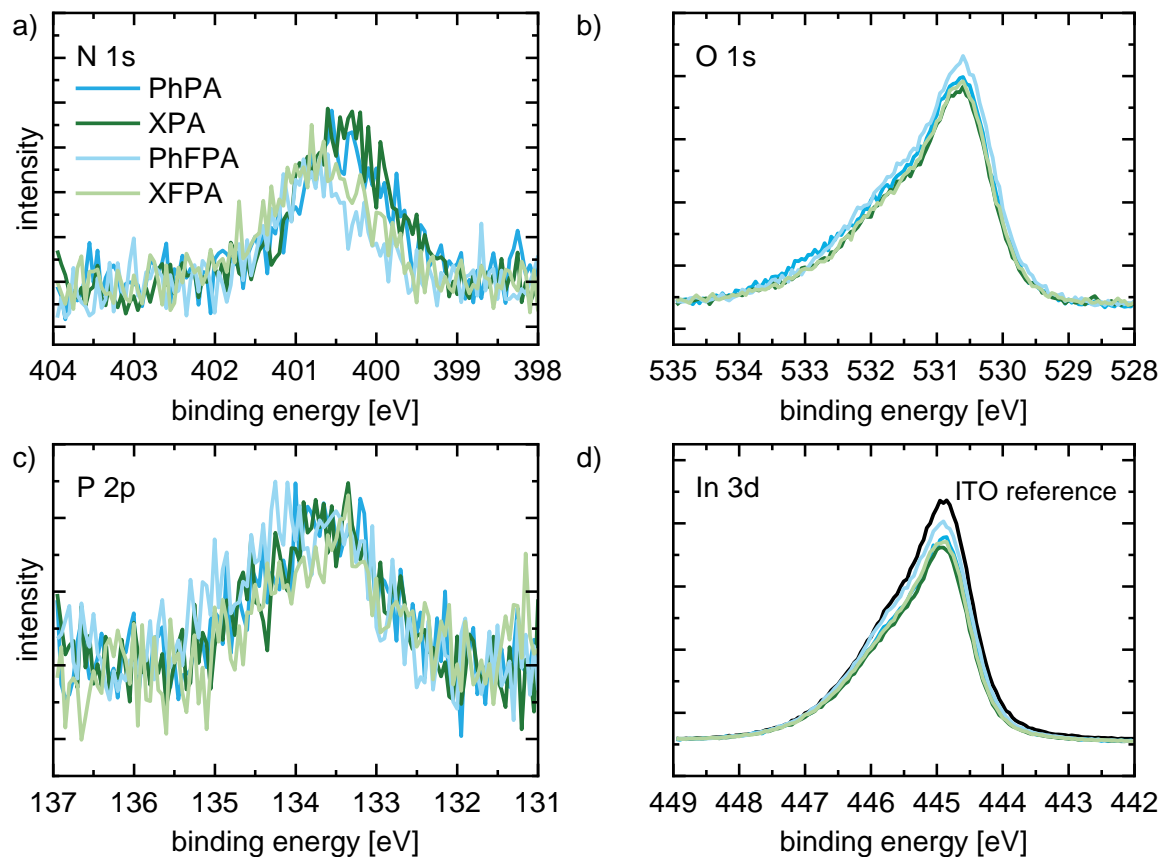


Figure S47. XPS core level detail spectra of the four molecules on ITO. In all four cases a Shirley background⁵ was subtracted. The integrals of the N 1s peaks are 233, 244, 147 and 200 for PhPA, XPA, PhFPA and XFPA, respectively.

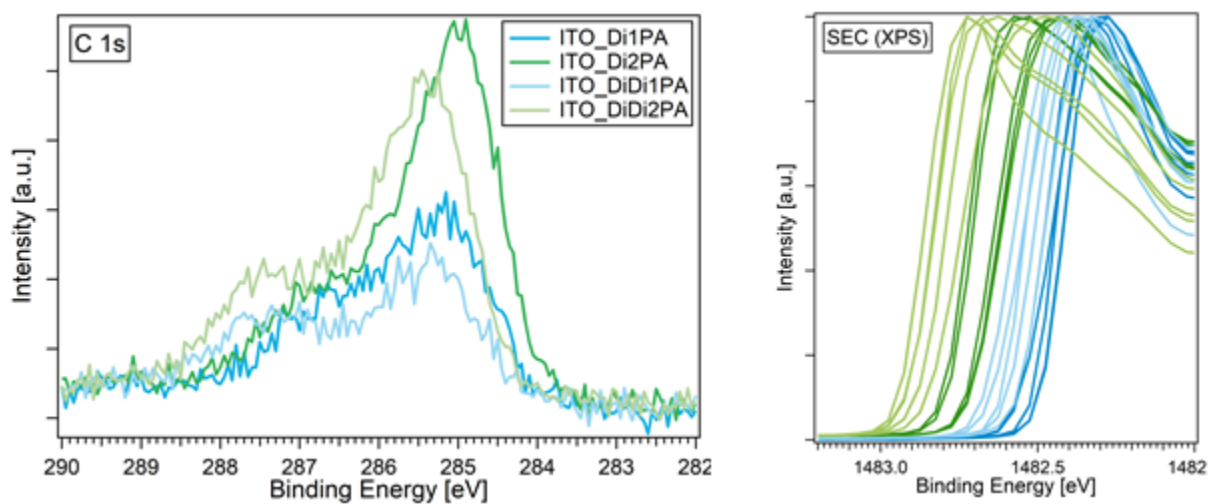


Figure S48. C 1s spectra regularly calibrated and diagram showing all SECs.

Layer thicknesses:

The nominal layer thicknesses d of the molecules on ITO was calculated via the integrated C 1s signal I and the following formula:

$$d = -\lambda \cdot \ln(1 - I/I_{\infty})$$

Here, λ is the inelastic mean free path of electrons in the adsorbate and was calculated to a value of 3.2 nm for the backbones of all four molecules using the TPP-2M formula.⁶ I_{∞} is the theoretical signal intensity of an infinitely thick layer of the molecules backbone. This value was extracted by measurements of a similar molecule (4-cyanophenyl-phosphonic acid) on several NiO_x films.⁷ Here, the nominal layer thicknesses have been calculated via the damping of the clean substrate signal. For each layer thickness the respective C 1s signal was measured. Using an exponential fit the I_{∞} value was extracted.

This typically used direct way of estimating the layer thickness by the attenuation of the substrate was not feasible in this work, as even after intense cleaning of the ITO substrates residual carbon contamination was detected. Thus, it was not possible to measure the undisturbed intensity of a pure substrate as reference.

The results are presented in Table S6.

Table S6. Nominal layer thicknes and molecular length of PhPA, XPA, PhFPA and XFPA.

molecule	PhPA	XPA	PhFPA	XFPA
nominal layer thickness [Å]	6.1	8.3	5.0	8.4
molecular length [Å]	8	12	8	12

9. DFT calculations for IR and dipole moment

Dipole moments:

Dipole moments were calculated using Spartan'10 (Wavefunction Inc.) employing density functional theory (DFT) with B3LYP as functional and 6-311+G** as basis set in vacuum.

IR spectra:

Calculations of vibrational modes of the four molecules for comparison with the measured IR spectra employ density functional theory (DFT) and have been carried out with the program Gaussian09.⁸ We used the B3LYP functional with the 6-311+G(d,p) basis set in this work for geometry optimizations and calculation of harmonic frequencies. The equilibrium structures of the molecules as well as vibrational frequencies and oscillator strengths have been calculated for isolated molecules, i.e. effects of the environment are neglected. Vibrational frequencies have been calculated in the harmonic approximation, thus higher-order effects like Fermi resonances are not reproduced by the calculations. Based on the calculated oscillator parameters a dielectric function has been simulated.⁹ For the dielectric background, we used $\epsilon_{\infty} = 2.9$,^{10,11} the oscillators were described as Brendel oscillators with a damping of 4 cm^{-1} and a Gaussian broadening of 4 cm^{-1} . With such dielectric functions, we calculated the reflectance spectra of a thin film on ITO. The ITO was described by a dielectric model with a surface and bulk Drude layer as described elsewhere.⁴ The chosen values for damping and Gaussian broadening resulted in a total FWHM of 10 cm^{-1} , corresponding to the width of the narrowest absorption bands in the measured spectrum. The assignment is shown in Figure S46 and the modes are listed with the corresponding number in Table S5.

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