Supporting Information

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1. MATERIALS AND INSTRUMENTS

Reactions were carried out using oven-dried glassware in argon atmosphere unless stated otherwise. Dry dichloromethane, acetonitrile, and methanol were obtained by distillation over calcium hydride.[1] All other solvents were used as received without further purification. Thin layer chromatography was conducted using aluminum-backed SiliaPlates with F_{254} indicator, visualized under a UV lamp and/or staining with 5% sulfuric acid solution in ethanol. Flash chromatography was conducted using SiliaFlash P60 gel with 40-63 μm particle size (230-400 mesh). ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{31}P NMR spectra were recorded on a Bruker Avance Spectrospin DRX500 spectrometer or a Bruker Avance Spectrospin DPX200 spectrometer using either the non-deuterated residual solvent peaks or tetramethyl silane peak (TMS, δ 0 ppm) as references. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Scientific). HRMS analyses were performed at University of Illinois at Urbana Champaign Mass Spectroscopy facility. Elemental analyses were performed by Galbraith Laboratories, Inc. MALDI-TOF MS was performed using a Waters Micromass instrumentation. MALDI samples were prepared following the reported protocol on BSA analysis with MALDI.[2] Microscopy was performed using an Olympus FV300 microscope. Flow Cytometry analysis was carried out at the University of Massachusetts Medical School Flow Core Lab.

2. KINETIC STUDIES

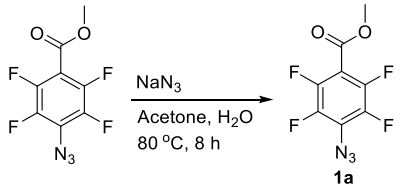
Stock solutions of PFAA (5 mM) and phosphine (5 mM) were prepared in the selected solvent. Time-dependent measurements (n = 2-5) were initiated upon mixing the two solutions (0.3 mL each), after which NMR spectra were acquired every 1-2 min over a period of 30-45 min. Rate constants were estimated through nonlinear regression using R (version 3.3.2),[3] with packages minpack.lm (version 1.2-1), and deSolve (version 1.14) for solving differential equations using the LSODA integrator.[4,5] Either first order, second order or coupled reaction models (for compound **3ab**) were applied, depending on the rate-limiting step.[6]

3. PRODUCT STABILITY

Stability studies were performed using compound **3aa** (5 mM) or **3ab** (5 mM) in CD_3CN or CD_3CN/D_2O (for hydrolysis study). For the aza-ylide reaction, excess CS_2 or *p*-anisaldehyde was added into the solution of **3aa** or **3ab** in CD_3CN. The reaction mixture was monitored by ^{1}H NMR and spectra were recorded every week.

4. SYNTHESIS OF PFAAS 1, PHOSPHINES 2, AND IMINOPHOSPHORANES 3

Methyl 4-azido-2,3,5,6-tetrafluorobenzoate (1a)

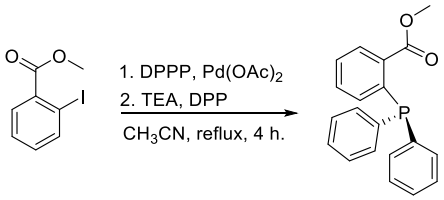


1a

Synthesized following our previously reported protocol.[7-15] Methyl 2,3,4,5,6-pentafluorobenzoate (6.0 g, 27 mmol) was added to solution of sodium azide (1.8 g, 27 mmol) in 44 mL acetone/water (8:3) mixture. The solution was refluxed for 8 h. The mixture was cooled and diluted with 50 mL of water and diethyl ether (50 mL). The organic layer was washed with distilled water (3 × 100 mL), brine (100 mL) and dried with magnesium sulfate. Collected solution was concentrated by

aspirator and the white solid was obtained. The crude product was then purified by flash chromatography using hexanes:ethyl acetate as eluent (40:1) to obtain white crystalline product (5.8 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) 3.97 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 146.3, 144.3, 141.5, 139.5, 123.4, 107.6, 53.2; ^{19}F NMR (188 MHz, $CDCl_3$), (external ref., trifluoroacetic acid, -76.5 ppm) δ -142.1 – -142.4 (m, 2F), -151.8 – -151.9 (m, 2F).

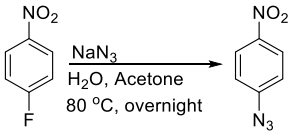
Methyl 2-(diphenylphosphanyl)benzoate (2a)



2a

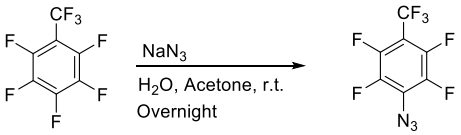
A published method was followed.[6] Methyl 2-iodobenzoate (4.90 g, 18.7 mmol), palladium (II) acetate (0.042 g, 0.19 mol), and 1,3-bis(diphenylphosphino)propane (DPPP) (0.077 g, 0.19 mmol) was added in an oven-dried 100-mL round-bottom flask. Freshly distilled anhydrous acetonitrile (15 mL) was added and the reaction mixture was stirred for 10 min at room temperature. A solution of triethylamine (TEA) (2.1 g, 21 mmol) and diphenylphosphine (DPP) (3.35 g, 18.0 mmol) in anhydrous acetonitrile (5 mL) was then added, and the mixture was refluxed for 4 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo* to yield a light brown solid. The crude product was purified by flash column chromatography using 1:9 EtOAc/hexanes to yield a white solid (R_f = 0.4 on TLC plate using the same solvent). The product was further purified by recrystallization from anhydrous methanol to give a colorless crystalline solid (4.6 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) 8.07 – 8.04 (br, 1H), 7.40 – 7.27 (m, 12H), 6.95 – 6.93 (br, 1H), 3.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2 (d, *J* = 2.2 Hz), 140.4 (d, *J* = 26.6 Hz), 137.8 (d, *J* = 11.0 Hz), 134.2, 134.2 (d, *J* = 18.9 Hz), 133.8 (d, *J* = 20.8 Hz), 131.9, 130.6, 128.6, 128.4 (d, *J* = 7.2 Hz), 128.1, 52.0; ^{31}P NMR (81 MHz, $CDCl_3$), (external ref.: 85% phosphoric acid at 0 ppm) δ -4.85.

1-Azido-4-nitrobenzene (1b)



Synthesized following a similar synthetic protocol as for compound **1a** at room temperature. Purified using column chromatography using hexanes:ethyl acetate (40:1) as the eluent to give the product as yellow solid (400 mg, 35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 9.0 Hz, 2H), 7.17 (d, J = 9.0 Hz, 2H).

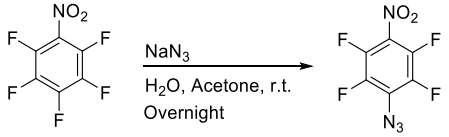
1-Azido-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (1c)



1c

Synthesized following a similar synthetic protocol as for compound **1a**. In brief, 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene (283 mg, 1.2 mmol) was dissolved in acetone/water (8/3 v/v, 6 mL). To this solution, sodium azide (78 mg, 1.2 mmol) in acetone/water (8/3 v/v, 5 mL) was added. The solution was stirred overnight at room temperature. Afterwards, diethyl ether (20 mL) was added and the product was extracted using diethyl ether (3 ×). The organic layer was washed with brine (3 ×), followed by drying over sodium sulfate. The solvent was then removed under vacuum. The compound was purified by column chromatography using hexanes:ethyl acetate (40:1) as the eluent to give the product as a clear liquid (200 mg, 64%). ^{19}F NMR (188 MHz, $CDCl_3$) δ -59.4 (t, *J* = 21.1 Hz, 3F), -138.2 – -146.0 (m, 2F), -153.6 (dd, *J* = 17.5, 6.6 Hz, 2F). ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.9 – 147.0 (m), 143.8 – 143.1 (m), 142.7 – 141.8 (m), 139.1 – 138.1 (m), 123.8, 118.4, 32.0, 30.1, 23.0, 14.4.

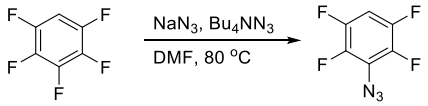
1-Azido-2,3,5,6-tetrafluoro-4-nitrobenzene (1d)



1d

Synthesized following a similar synthetic protocol as for compound **1c.** The product was obtained as a pale yellow liquid (200 mg, 71%). ^{19}F NMR (188 MHz, d_6- $CDCl_3$) δ -150.1 – -150.9 (m, 2F), -153.4 – -153.8 (m, 2F). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.2 (dd, *J* = 4.5, 2.1 Hz), 143.9 (dd, *J* = 4.6, 2.2 Hz), 143.6 – 143.3 (m), 143.2 (dd, *J* = 8.3, 3.3 Hz), 139.0 (dd, *J* = 4.7, 2.2 Hz), 138.7 (dd, *J* = 4.7, 2.2 Hz), 138.3 (dd, *J* = 8.3, 3.6 Hz), 138.2 – 137.9 (m), 126.5, 125.5 (tt, *J* = 11.9, 2.5 Hz).

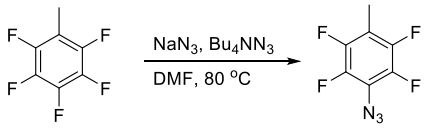
3-Azido-1,2,4,5-tetrafluorobenzene (1e)



1e

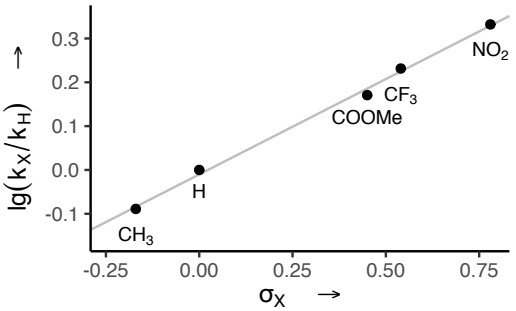
Synthesized following a reported procedure.[16] In brief, NaN_3 (773 mg, 11.9 mmol) was added into a solution of 1,2,3,4,5-pentafluorobenzene (1.0 g, 6.0 mmol) and Bu_4NN_3 (169 mg, 0.6 mmol) in DMF (5 mL). The reaction mixture was stirred at 80 ºC overnight. Water (50 mL) was then added, and the compound was extracted using diethyl ether (3 × 20 mL). The organic layer was then washed with water (3 ×), brine (3 ×), and dried over sodium sulfate. The compound was further purified using column chromatography using hexane:EtOAc (1:5) to obtain a yellow viscous liquid (456 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (m, 1H). ^{19}F NMR (188 MHz, $CDCl_3$) δ -135.9 (m, 2F), -149.0 (m, 2F).

1-Azido-2,3,5,6-tetrafluoro-4-methylbenzene (1f)



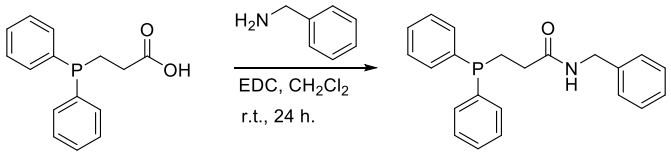
1f

Synthesized following a similar synthetic protocol as for compound **1e** to yield a pale yellow liquid (76.1 mg, 7%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.24 (t, J = 2.1 Hz, 3H). ^{19}F NMR (188 MHz, $CDCl_3$) δ -147.5 (m, 2F), -157.3 (m, 2F).



Graph S1. Hammett Analysis of para substituted PFAA, ρ ~ 0.43; conditions: $[PFAA]_0$ = 2.5 mM, $[2a]_0$ = 2.5 mM, CD_3CN, 25 °C.

***N*-Benzyl-3-(diphenylphosphanyl)propanamide (2d)**

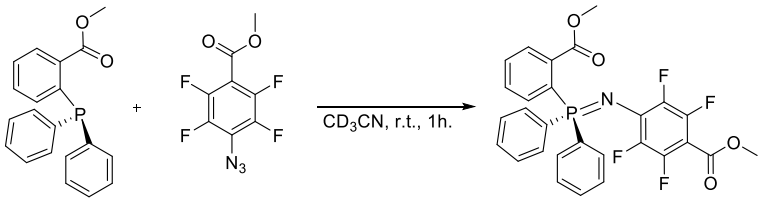


2d

To a solution of 3-(diphenylphosphanyl)propanoic acid (1 g, 3.87 mmol) in CH_2Cl_2 (5 mL), benzyl amine (1.2 g, 11.6 mmol) was added. After stirring for 30 min, *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide (826 mg, 4.3 mmol) was added.

The reaction was continuously stirred for 24 h. CH_2Cl_2 (50 mL) and water (50 mL) were added, and the reaction mixture was stirred for an additional 30 min. The organic layer was then washed with water (3 ×), brine (3 ×), and dried over sodium sulfate. The solvent was then removed under vacuum. The crude product was purified using column chromatography using hexanes:ethyl acetate (3:2) to obtain white solid product (0.9 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 4H), 7.31 – 7.25 (m, 8H), 7.24 – 7.18 (m, 3H), 5.96 (s, 1H), 4.33 (d, *J* = 5.7 Hz, 2H), 2.39 – 2.34 (m, 2H), 2.27 – 2.21 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1 (d, *J* = 13.6 Hz), 138.3 (s), 137.9 (d, *J* = 12.7 Hz), 132.8 (d, *J* = 18.6 Hz), 128.7 (dd, *J* = 23.5, 11.1 Hz), 127.9 (s), 127.5 (s), 43.7 (s), 32.8 (d, *J* = 18.3 Hz), 23.5 (d, *J* = 11.9 Hz). ^{31}P NMR (81 MHz, $CDCl_3$), (external ref., 85 % phosphoric acid, 0 ppm) δ -20.22 (s).

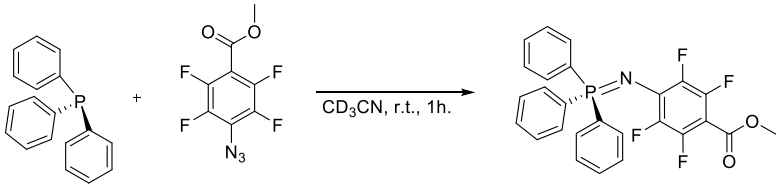
Methyl 2,3,5,6-tetrafluoro-4-(((2-(methoxycarbonyl)phenyl)diphenyl-λ^5-phosphanylidene)amino)benzoate (3aa)



3aa

Phosphine **2a** (0.5 g, 1.56 mmol) was dissolved in acetonitrile (20 mL), and the solution was purged with argon. A solution of **1a** (0.4 g, 1.6 mmol) in acetonitrile (20 mL) was injected at room temperature and the resulting mixture was stirred. Immediately, the solution turned pale yellow and gas started to evolve. After a few minutes, the solution became colorless and stopped bubbling. The solution was continued to stir under argon for an additional 1 h. The solvent was removed by evaporation, and the solid was purified by flash column chromatography (1:4 EtOAc/hexanes) to yield the product as a white solid (0.835 g, 99%), TLC: R_f = 0.4 (1:4 EtOAc/hexanes). Crystals were grown from methanol at -5 °C. ^{1}H NMR (500 MHz, CD_3CN, ppm) 7.92 – 7.88 (m, 1 H), 7.78 – 7.74 (m, 5 H), 7.68 – 7.64 (m, 3 H), 7.58 – 7.52 (m, 5 H), 3.85 (s, 3 H), and 3.30 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2 (d, *J* = 2.2 Hz), 140.4 (d, *J* = 26.6 Hz), 137.8 (d, *J* = 11.0 Hz), 134.2 (d, *J* =15 Hz), 133.8 (d, *J* = 20.8 Hz), 131.9, 130.6, 128.6, 128.4 (d, *J* = 7.2 Hz), 128.1; ^{31}P NMR (81 MHz, $CDCl_3$), (external ref., 85% phosphoric acid, 0 ppm) δ 12.27 (t, *J* =4.0); ^{19}F NMR (188 MHz, $CDCl_3$, ppm), (external ref., trifluoroacetic acid, -76.5 ppm) δ -137.4 – -137.6 (m, 2F), -149.7 – -149.9 (m, 2F); Elemental Anal. Calcd for $C_{28}H_{20}F_4NO_4P$: C, 62.1; H, 3.7; N, 2.6. Found: C, 62.0; H, 3.8; N, 2.6.

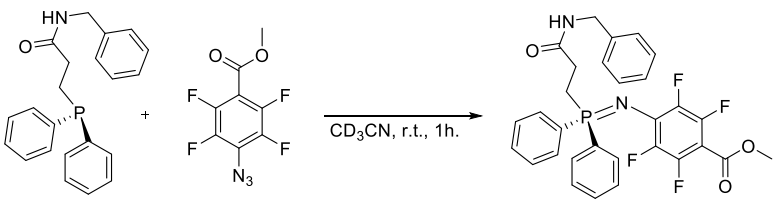
Methyl 2,3,5,6-tetrafluoro-4-((triphenyl-λ^5-phosphanylidene)amino)benzoate (3ab)



3ab

Phosphine **2b** (0.105 g, 0.40 mmol) was dissolved in acetonitrile (5 mL), and the solution was purged with argon. A solution of **1a** (0.1 g, 0.40 mmol) in acetonitrile (5 mL) was injected at room temperature and the resulting mixture was stirred for 1 h. The solvent was removed by evaporation, and the solid was purified by flash column chromatography (1:3 EtOAc/hexanes) to yield the product as solid (0.184 g, 95%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.75 – 7.68 (m, 3H), 7.65 – 7.58 (m, 3H), 7.54 – 7.48 (m, 3H), 3.79 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.6 – 161.1 (m), 150.5 – 148.0 (m), 146.2 – 143.6 (m), 141.1 – 139.7 (m), 136.4 – 135.2 (m), 133.5 – 132.6 (m), 132.6 (d, *J* = 3.0 Hz), 131.9 (s), 129.9 (s), 129.2 (d, *J* = 12.5 Hz), 98.3 (t, *J* = 14.0 Hz), 52.6 (s); ^{31}P NMR (81 MHz, $CDCl_3$), (external ref., 85% phosphoric acid, 0 ppm) δ 5.92 (t, *J* = 4.5 Hz); ^{19}F NMR (188 MHz, DMSO), (external ref., trifluoroacetic acid, -76.5 ppm) δ -147.2 (d, *J* = 17.0 Hz), -156.6 – -157.0 (m); HRMS (ESI) $C_{26}H_{19}NO_2F_4P$ [M-H] $^+$ 484.190; found 484.193.

Methyl 4-(((3-(benzylamino)-3-oxopropyl)diphenyl-λ^5-phosphanylidene)amino)-2,3,5,6-tetrafluorobenzoate (3ad)



3ad

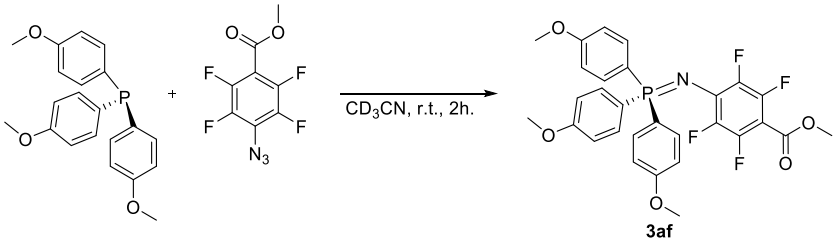
Phosphine **2d** (0.1 g, 0.28 mmol) was dissolved in acetonitrile (5 mL), and the solution was purged with argon. A solution of **1a** (66 mg, 0.28 mmol) in acetonitrile (5 mL) was injected at room temperature and the resulting mixture was stirred for 1 h. The solvent was removed by evaporation, and the solid was purified by flash column chromatography (1:3 EtOAc/hexanes) to yield the product as a white solid (0.1 g, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.66 (m, 4H), 7.59 – 7.37 (m, 6H), 7.33 – 7.13 (m, *J* = 25.0, 14.9, 4.2 Hz, 5H), 6.24 (s, 1H), 4.33 (d, *J* = 5.6 Hz, 2H), 3.86 (s, 3H), 2.90 (dd, *J* = 16.2, 9.7 Hz, 2H), 2.51 – 2.35 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.0, 170.7, 138.3, 132.8 (d, *J* = 2.9 Hz), 131.7, 131.5, 131.1, 129.6, 129.3, 129.1, 128.2, 128.0, 52.7, 44.3, 28.7 (d, *J* = 2.9 Hz), 26.4. ^{31}P NMR (81 MHz, $CDCl_3$) (external ref., 85% phosphoric acid, 0 ppm) δ 11.45 (t, *J* = 4.8 Hz, 1P). ^{19}F NMR (188 MHz, $CDCl_3$), (external ref., trifluoroacetic acid, -76.5 ppm) δ -140.4 (d, *J* = 15.8 Hz, 2F), -151.8 (d, *J* = 18.0 Hz, 2F). HRMS (ESI) $C_{30}H_{26}N_2O_3F_4P$ $[M-H]^+$ 569.217; found 569.222.

Methyl 2,3,5,6-tetrafluoro-4-((tri-p-tolyl-λ^5-phosphanylidene)amino)benzoate (3ae)

3ae

Phosphine **2e** (0.110 g, 0.40 mmol) was dissolved in acetonitrile (5 mL) and the solution was purged with argon. A solution of **1a** (0.100 g, 0.40 mmol) in acetonitrile (5 mL) was injected at room temperature and the resulting mixture was stirred for 1 h. The solvent was removed by evaporation, and the solid was purified by flash column chromatography (1:3 EtOAc/hexanes) to yield a white solid (0.191 g, 99%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.65 (dd, *J* = 11.9, 8.8 Hz, 6H), 7.05 (dd, *J* = 8.8, 2.3 Hz, 6H), 3.85 (s, 9H), 3.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 – 160.7 (m), 147.6 (ddd, *J* = 12.4, 8.5, 3.8 Hz), 146.1 – 145.1 (m), 141.8 – 141.2 (m), 136.1 – 135.6 (m), 132.4 (d, *J* = 10.5 Hz), 129.4 (d, *J* = 12.9 Hz), 128.0 (s), 127.1 (s), 97.5 (t, *J* = 14.0 Hz), 52.1 (s), 21.6 (s); ^{31}P NMR (81 MHz, CD_3CN), (external ref., 85% phosphoric acid, 0 ppm) δ 7.85 (t, *J* = 4.8 Hz); ^{19}F NMR (188 MHz, CD_3CN), (external ref., trifluoroacetic acid, -76.5 ppm) δ -148.2 (d, *J* = 15.0 Hz), -157.8 (d, *J* = 20.0 Hz); HRMS (ESI) $C_{29}H_{25}NO_2F_4P$ $[M-H]^+$ 526.159; found 526.158.

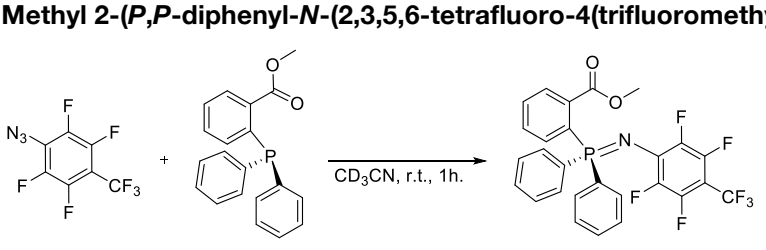
Methyl 2,3,5,6-tetrafluoro-4-((tris(4-methoxyphenyl)- λ^5-phosphanylidene)amino)benzoate (3af)



3af

Phosphine **2f** (0.128 g, 0.40 mmol) was dissolved in acetonitrile (5 mL) and the solution was purged with argon. A solution of **1a** (0.100 g, 0.40 mmol) in acetonitrile (5 mL) was injected at room temperature and the resulting mixture was stirred for 2 h. The solvent was removed by evaporation, and the solid was purified by flash column chromatography (1:3 EtOAc/hexanes) to yield the product as a white solid (0.213 g, 99%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.65 (dd, *J* = 11.9, 8.8 Hz, 6H), 7.05 (dd, *J* = 8.8, 2.3 Hz, 6H), 3.85 (s, 9H), 3.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6 (d, *J* = 2.9 Hz), 162.2 – 162.0 (m), 147.9 – 147.6 (m), 145.8 – 145.5 (m), 143.7 – 143.3 (m), 141.8 – 141.5 (m), 136.2 – 135.8 (m), 122.6 (s), 121.7 (s), 114.3 (d, *J* = 13.5 Hz), 97.4 (t, *J* = 13.8 Hz), 55.5 (s), 52.2 (s); ^{31}P NMR (81 MHz, CD_3CN), (external ref., 85% phosphoric acid, 0 ppm) δ 7.18 (t, *J* = 4.6 Hz); ^{19}F NMR (188 MHz, CD_3CN), (external ref., trifluoroacetic acid, -76.5 ppm) δ -148.2 (d, *J* = 15.6 Hz), -158.0 (d, *J* = 20.1 Hz); HRMS (ESI) $C_{29}H_{25}NO_5F_4P$ $[M-H]^+$ 563.137; found 563.139.

Methyl 2-(*P*,*P*-diphenyl-*N*-(2,3,5,6-tetrafluoro-4(trifluoromethyl)phenyl) phosphorimidoyl) benzoate (3ca)

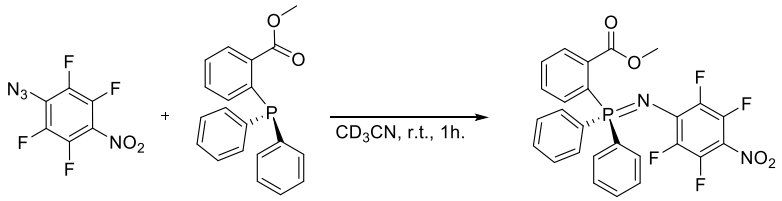


3ca

Phosphine **2a** (0.100 g, 0.31 mmol) was dissolved in acetonitrile (5 mL) and the solution was purged with argon. A solution of **1c** (80.9 mg, 0.31 mmol) in acetonitrile (5 mL) was injected at room temperature and the resulting mixture was

stirred for 1 h. The solvent was removed by evaporation, and the solid was purified by flash column chromatography (1:3 EtOAc/hexanes) to yield the product as a viscous transparent oil (169 mg, 99%).[1]H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.5, 4.0 Hz, 1H), 7.78 – 7.59 (m, 5H), 7.59 – 7.40 (m, 8H), 3.30 (s, 3H). [13]C NMR (50 MHz, $CDCl_3$) δ 167.6 (d, J = 2.6 Hz), 136.1 (d, J = 6.0 Hz), 135.5 (d, J = 11.1 Hz), 132.8, 132.6, 132.3, 132.1, 131.8, 131.6, 131.4, 131.2, 130.6, 129.1 (d, J = 13.0 Hz), 52.5. [31]P NMR (81 MHz, $CDCl_3$) (external ref., 85% phosphoric acid, 0 ppm) δ 6.76 (s). [19]F NMR (188 MHz, $CDCl_3$), (external ref., trifluoroacetic acid, -76.5 ppm) δ -52.0 (t, J = 21.0 Hz), -140.1 – -146.8 (m), -150.1 (d, J = 16.9 Hz). HRMS (ESI) $C_{27}H_{18}NO_2F_7P$ $[M-H]^+$ 552.163; found 552.172.

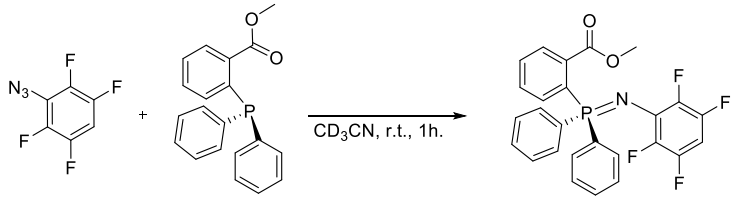
Methyl 2-(*P*,*P*-diphenyl-*N*-(2,3,5,6-tetrafluoro-4-nitrophenyl)phosphorimidoyl)benzoate (3da)



3da

Phosphine **2a** (0.100 g, 0.31 mmol) was dissolved in acetonitrile (5 mL) and the solution was purged with argon. A solution of **1d** (73.2 mg, 0.31 mmol) in acetonitrile (5 mL) was injected at room temperature and the resulting mixture was stirred for 1 h. The solvent was removed by evaporation, and the solid was purified by flash column chromatography (1:3 EtOAc/hexanes) to yield the product as a yellow solid (162 mg, 99%). [1]H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 1H), 7.79 – 7.67 (m, 1H), 7.64 – 7.57 (m, 1H), 7.57 – 7.48 (m, 1H), 3.36 (s, 1H). [13]C NMR (50 MHz, $CDCl_3$) δ 167.4 (d, *J* = 2.7 Hz), 136.1 (d, *J* = 6.2 Hz), 135.6 (d, *J* = 10.9 Hz), 132.9 (d, *J* = 2.2 Hz), 132.6 (d, *J* = 2.9 Hz), 132.3, 132.1, 132.0, 131.9 – 131.1 (m), 129.8, 129.2 (d, *J* = 13.1 Hz), 52.6. [31]P NMR (81 MHz, $CDCl_3$) (external ref., 85% phosphoric acid, 0 ppm) δ 8.56 (t, *J* = 4.1 Hz). [19]F NMR (188 MHz, $CDCl_3$) (external ref., trifluoroacetic acid, -76.5 ppm) δ -147.8 (d, *J* = 17.8 Hz), -150.1 (d, *J* = 21.8 Hz). HRMS (ESI) $C_{26}H_{18}N_2O_4F_4P$ $[M-H]^+$ 529.140; found 529.146.

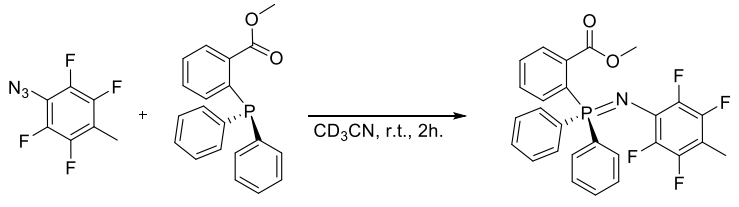
Methyl 2-(*P*,*P*-diphenyl-*N*-(2,3,5,6-tetrafluorophenyl)phosphorimidoyl)benzoate (3ea)



3ea

Phosphine **2a** (0.100 g, 0.31 mmol) was dissolved in acetonitrile (5 mL) and the solution was purged with argon. A solution of **1e** (59.2 mg, 0.31 mmol) in acetonitrile (5 mL) was injected at room temperature and the resulting mixture was stirred for 1 h. The solvent was removed by evaporation, and the solid was purified by flash column chromatography (1:3 EtOAc/hexanes) to yield the product as a yellow viscous liquid (148 mg, 99%). [1]H NMR (200 MHz, $CDCl_3$) δ 8.00 – 7.84 (m, 2H), 7.84 – 7.67 (m, 7H), 7.67 – 7.31 (m, 16H), 6.45 – 6.10. [13]C NMR (126 MHz, $CDCl_3$) δ 167.2, 135.6 (d, *J* = 6.3 Hz), 135.2 (d, *J* = 10.7 Hz), 132.5, 132.1 – 131.5 (m), 131.4 – 131.0 (m), 130.8 (d, *J* = 8.3 Hz), 128.5 (d, *J* = 12.8 Hz), 93.1, 92.9, 92.7, 51.9. [31]P NMR (81 MHz, $CDCl_3$) (external ref., 85% phosphoric acid, 0 ppm) δ 5.10 (t, *J* = 4.6 Hz). [19]F NMR (188 MHz, $CDCl_3$) (external ref., trifluoroacetic acid, -76.5 ppm) δ -140.1 – -140.8 (m), -149.0 – -150.0 (m). HRMS (ESI) $C_{26}H_{18}NOF_4P$ $[M-H]^+$ 484.190; found 484.196.

Methyl 2-(*P*,*P*-diphenyl-*N*-(2,3,5,6-tetrafluoro-4-methylphenyl)phosphorimidoyl)benzoate (3fa)

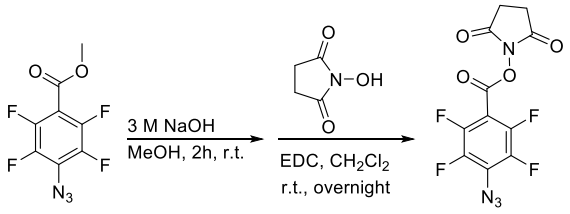


3fa

Phosphine **2a** (0.100 g, 0.31 mmol) was dissolved in acetonitrile (5 mL) and the solution was purged with argon. A solution of **1f** (63.6 mg, 0.31 mmol) in acetonitrile (5 mL) was injected at room temperature and the resulting mixture was stirred for 1 h. The solvent was removed by evaporation, and the solid was purified by flash column chromatography (1:3 EtOAc/hexanes) to yield the product as a white solid (153 mg, 99%). [1]H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.3, 4.2 Hz, 1H), 7.80 – 7.73 (m, 4H), 7.62 – 7.55 (m, 2H), 7.55 – 7.47 (m, 3H), 7.44 (td, *J* = 7.4, 3.0 Hz, 4H), 3.22 (s, 3H), 2.08 (s, 3H). [13]C NMR (126 MHz, $CDCl_3$) δ 167.3 (d, *J* = 2.3 Hz), 146.4 (s), 144.5 (s), 143.7 (s), 141.8 (s), 135.6 (d, *J* = 6.2 Hz),

135.2 (d, *J* = 10.6 Hz), 132.6 (s), 132.1 – 131.4 (m), 131.2 (d, *J* = 11.7 Hz), 130.7 (d, *J* = 8.3 Hz), 128.5 (d, *J* = 12.8 Hz), 102.5 (s), 51.9 (s), 6.7 (s). ^{19}F NMR (188 MHz, $CDCl_3$) (external ref., trifluoroacetic acid, -76.5 ppm) δ -145.3 – -145.7 (m), -150.3 – -150.5 (m). ^{31}P NMR (81 MHz, $CDCl_3$) (external ref., 85% phosphoric acid, 0 ppm) δ 4.94 (t, *J* = 4.3 Hz). HRMS (ESI) $C_{27}H_{21}NO_2F_4P$ $[M-H]^+$ 498.1246; found 498.1246.

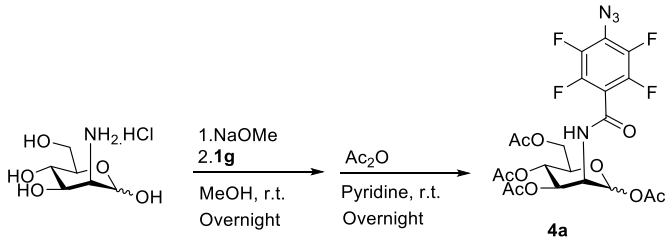
_N_-Succinimidyl-4-azido-2,3,5,6-tetrafluorobenzoate (1e)



1e

Synthesized according to a reported procedure.[7-15] Briefly, compound **1a** (3 g, 12 mmol) was dissolved in methanol (20 mL), after which NaOH solution (3 M, 10 mL) was added and the reaction mixture was stirred for 2 h. The solution was acidified by addition of aqueous HCl (1 M) until pH < 1, followed by addition of water (20 mL). The product was extracted with chloroform (3 × 100 mL) and the organic layer was washed with distilled water (100 mL) and brine (3 × 100 mL). The organic phase was dried over sodium sulfate, and the solvent removed by evaporation. The obtained white solid and *N*-hydroxysuccinimide (1.6 g, 13.9 mmol) were dissolved in dichloromethane (30 mL). After stirring for 30 min, *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide (EDC, 2.7 g, 13.9 mmol) was added, and the reaction mixture was stirred overnight. The mixture was diluted with dichloromethane (70 mL) and water (100 mL), and was stirred for 1 h. Following washing with water (3 × 100 mL) and brine (3 × 100 mL), the solution was dried over sodium sulfate, and purified using a short column of silica gel (CH_2Cl_2) to obtain the product as a white solid (1.6 g, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.88 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 155.3 – 155.1 (m), 147.6 – 147.2 (m), 145.5 – 145.1 (m), 141.5 (ddd, *J* = 7.2, 5.2, 3.0 Hz), 139.5 (ddd, *J* = 8.5, 5.0, 3.0 Hz), 126.4 (tt, *J* = 11.7, 3.3 Hz), 101.9 (t, *J* = 13.9 Hz), 25.6; ^{19}F NMR (188 MHz, $CDCl_3$) δ -261.0 – -261.6 (m), -276.8 – -277.8 (m).

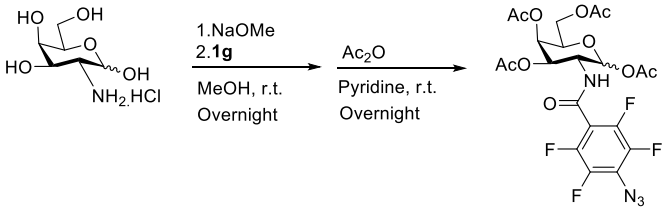
1,3,4,6-Tetra-O-acetyl-*N*-5-(4-azido-2,3,5,6-tetrafluorobenzoyl) mannosamine (4a)



4a

Synthesized following a reported procedure.[17] In brief, mannosamine hydrochloride (215 mg, 1 mmol) was added into a solution of NaOMe (55 mg, 1 mmol) in methanol (10 mL). The mixture was stirred for 1 h until the solid was completely dissolved. A solution of **1g** (332 mg, 1 mmol) in methanol (5 mL) was then added, and after stirring for 24 h at room temperature, the solvent was removed by evaporation. The residue was redissolved in pyridine (3 mL), and acetic anhydride (3 mL) was added. After stirring for 24 h, water (5 mL) was added and the mixture was stirred for 1 h. Dichloromethane (100 mL) was added to the solution, which was stirred for 1 h. The organic phase was washed with aqueous HCl solution (1 M, 3 × 100 mL), saturated $NaHCO_3$ (3 × 100 mL), distilled water (100 mL), and brine (100 mL). The organic phase was further dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (dichloromethane/ethyl acetate 10:1) to afford the product as a white solid **7** (100 mg, 17%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.31 (d, *J* = 8.8 Hz, 1H), 6.15 (s, 1H), 5.40 (dd, *J* = 10.2, 4.3 Hz, 1H), 5.26 (t, *J* = 10.1 Hz, 1H), 4.83 (ddd, *J* = 9.1, 4.3, 1.8 Hz, 1H), 4.26 (dd, *J* = 12.4, 4.5 Hz, 1H), 4.11 – 4.03 (m, 2H), 2.22 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 170.2, 169.6, 168.0, 157.9, 145.3, 143.4, 141.5 (d, *J* = 16.8 Hz), 139.5 (d, *J* = 18.7 Hz), 122.8, 110.1 (t, *J* = 16.6 Hz), 91.1, 70.2, 68.8, 65.1, 61.9, 50.0, 20.8, 20.6, 20.6, 20.6; ^{19}F NMR (188 MHz, $CDCl_3$), (external ref., trifluoroacetic acid, -76.5 ppm) δ -138.8 (td, *J* = 12.3, 3.9 Hz), -148.6 (td, *J* = 12.6, 4.2 Hz); HRMS (ESI) $C_{21}H_{20}N_4O_{10}F_4$ $[M-H]^-$ 563.137; found 563.139.

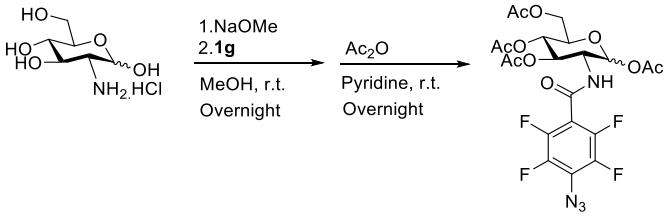
1,3,4,6-Tetra-*O*-acetyl-*N*-5-(4-azido-2,3,5,6-tetrafluorobenzoyl)galactosamine (4b)



4b

Synthesized using D-galactosamine hydrochloride in analogy to compound **4a**. White solid (150 mg, 27%). ^{1}H (500 MHz, $CDCl_3$) δ 6.37 (d, *J* = 3.2 Hz, 1H), 6.09 (d, *J* = 8.5 Hz, 1H), 5.46 (s, 1H), 5.31 (dd, *J* = 11.4, 2.8 Hz, 1H), 4.90 – 4.83 (m, 1H), 4.29 (t, *J* = 6.0 Hz, 1H), 4.17 – 4.05 (m, 2H), 2.21 (s, 3H), 2.17 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H); ^{13}C (126 MHz, $CDCl_3$) δ 170.4, 170.1, 168.6, 157.8, 145.1, 143.0, 141.5 (d, *J* = 19.1 Hz), 139.5 (dd, *J* = 14.7, 5.1 Hz), 122.6, 110.2 (t, *J* = 16.6 Hz), 90.6, 77.7, 77.3, 76.9 (d, *J* = 32.0 Hz), 68.7, 67.5, 66.6, 61.2, 47.9, 20.8, 20.7, 20.6, 20.6; ^{19}F (188 MHz, $CDCl_3$), (external ref., trifluoroacetic acid, -76.5 ppm) δ -139.8 (td, *J* = 12.4, 3.9 Hz), -148.4 (td, *J* = 12.3, 3.9 Hz); HRMS (ESI) $C_{21}H_{20}N_4O_{10}F_4$ $[M-H]^-$ 563.137; found 563.136.

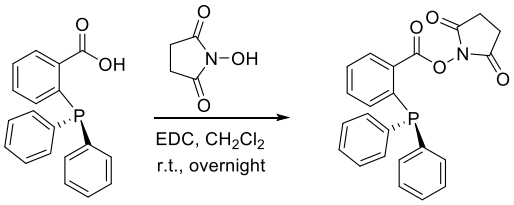
1,3,4,6-Tetra-*O*-acetyl-*N*-5-(4-azido-2,3,5,6-tetrafluorobenzoyl)glucosamine (4c)



4c

Synthesized using D-glucosamine hydrochloride in analogy to compound **4a**. White solid (170 mg, 30%). ^{1}H (500 MHz, $CDCl_3$) δ 6.35 (p, *J* = 3.6 Hz, 1H), 6.14 (d, *J* = 8.4 Hz, 1H), 5.37 – 5.30 (m, 1H), 5.26 (t, *J* = 9.8 Hz, 1H), 4.63 (ddd, *J* = 10.9, 8.6, 3.7 Hz, 1H), 4.29 (dd, *J* = 12.3, 4.1 Hz, 1H), 4.09 (dd, *J* = 12.5, 2.3 Hz, 1H), 4.05 (ddd, *J* = 10.2, 4.0, 2.6 Hz, 1H), 2.19 (s, *J* = 7.5 Hz, 3H), 2.11 (s, *J* = 3.8 Hz, 3H), 2.08 (s, *J* = 2.9 Hz, 3H), 2.06 (s, *J* = 2.0 Hz, 3H). ^{13}C (126 MHz, $CDCl_3$) δ 171.8, 170.7, 169.1, 168.4, 157.6, 145.0, 143.0, 141.4 (d, *J* = 16.1 Hz), 139.4 (d, *J* = 15.5 Hz), 122.6 (t, *J* = 11.4 Hz), 110.2 (t, *J* = 18.1 Hz), 89.9, 70.2, 69.8, 67.3, 61.5, 51.9, 20.7, 20.7, 20.5, 20.5. ^{19}F (188 MHz, $CDCl_3$), (external ref., trifluoroacetic acid, -76.5 ppm) δ -139.7 (td, *J* = 12.6, 4.2 Hz), -148.3 (td, *J* = 12.6, 4.2 Hz).HRMS (ESI) $C_{21}H_{20}N_4O_{10}F_4$ $[M-H]^-$ requires 563.137; found 563.136.

***N*-Succinimidyl 2-(diphenylphosphino)benzoate (2g)**



2g

Synthesized following a reported procedure.[18] In brief, 2-(diphenylphosphanyl)benzoic acid (300 mg, 0.98 mmol) and *N*-hydroxysuccinimide (169 mg, 1.47 mmol) were dissolved in dichloromethane (5 mL). After stirring for 30 min, *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide (EDC, 227 mg, 1.18 mmol) was added to the solution. The reaction was stirred for 24 h under argon. The reaction mixture was diluted with dichloromethane (50 mL) followed by washing with water (3 × 100 mL), brine (100 mL), and dried over sodium sulfate. The solvent was removed under vacuum and the yellowish residue was purified by column chromatography with 30% ethyl acetate in hexanes as the eluent to obtain the product as a yellow solid (297 mg, 0.73 mmol, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33-8.31 (m, 1H), 7.51-7.45 (m, 2H), 7.33-7.32 (m, 6H), 7.25-7.22 (m, 4H), 7.02-6.99 (m, 1H), 2.81 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ169.0 (d, *J* = 2.1 Hz), 160.9 (d, *J* = 1.9 Hz), 143.2 (d, *J* = 30.5 Hz), 136.8 (d, *J* = 11.1 Hz), 134.8, 133.9 (d, *J* = 20.8 Hz), 131.7, 128.9, 128.6 (d, *J* = 7.2 Hz), 128.5, 25.6.

5. SYNTHESIS OF LABELING AGENTS (P_{2G}-BSA-FITC AND P_{2H}-BSA-FITC)

BSA labeling was performed according to the reported method.[19] BSA (10 mg) was dissolved in carbonate buffer solution (pH 10, 10 mL) containing fluorescein isothiocyanate (FITC, 1 mg). The buffer was prepared by mixing of

aqueous K_2CO_3 (0.1 M, 60 mL) and aqueous $NaHCO_3$ (0.1 M, 40 mL). The solution was stirred for 24 h at room temperature in the dark. Afterwards, the solution was dialyzed against carbonate buffer (pH 10) for 3 d and the buffer was changed every 24 h. A solution of *N*-succinimidyl 3-(diphenyl phosphino)benzoate **2g** (1.0 mg, 2.8 μmol) or *N*-succinimidyl 3-(diphenylphosphino)propionate **2h** (1.0 mg, 2.8 μmol) in DMSO (1 mL) was added to the purified solution, which was stirred for 24 h. Purification by dialysis against PBS buffer for 3 d, changing the solution every 24 h, yielded **P_{2g}-BSA-FITC** or **P_{2h}-BSA-FITC** as a yellow solution.

6. CELL CULTURE

A549 cells (human lung carcinoma epithelial cells, ATCC) were cultured in high glucose Dulbecco's Modified Eagle's Medium (DMEM, ATCC), supplemented with fetal bovine serum (FBS, 10%, ATCC) and penicillin-streptomycin solution (1%, Sigma-Aldrich) in a humidified incubator in CO_2-containing (5%) atmosphere at 37 °C.

7. CELL TREATMENT WITH PFAA-DERIVATIZED CARBOHYDRATES

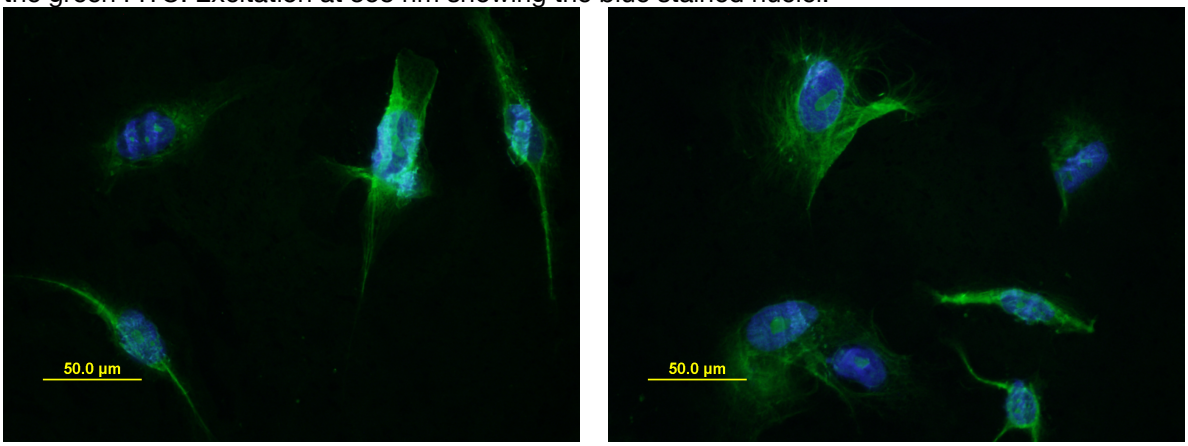
A solution of peracetylated PFAA-derivatized carbohydrate (22 mM) in ethanol (0, 50, 100, or 150 μL) was added into culture medium (2 mL) with cell density of at least 10^6 cells/mL (as determined by cell counter). The cells were incubated for 3 d with gentle shaking at 150 rpm in a humidified incubator in CO_2-containing (5%) atmosphere at 37 °C. For visualization study by fluorescence microscopy, the cells were seeded on cover glass slides placed inside a 6-well plate.

8. CELL LABELING

After cell growth for 3 d, cells from each well were washed with PBS buffer (pH = 7.4, 3 ×) to remove residual sugar, after which fresh PBS buffer (2 mL) was added to each well. Reagent **P_{2g}-BSA-FITC** or **P_{2h}-BSA-FITC** (100 μL, 1 mg/mL) was then added to each well, and the cells were incubated for 30 min at 4 °C in the dark. The cells were subsequently washed with PBS buffer (3 ×) to remove excess labeling agent. The cells were detached from the wells using trypsin, pelleted by centrifugation (3500 rpm, 3 min), and re-suspended in high glucose Dulbecco's Modified Eagle's Medium (DMEM, 200 μL) for flow cytometry analysis. For microscopy studies, the cells that were seeded on glass slides were examined under a confocal fluorescence microscope (Olympus FV300) without detachment from the glass slide.

9. ADDITIONAL CELL LABELING IMAGES

Figure S1. Zoomed-in fluorescence overlay images of A549 cells treated for 3 days with 0.3 mM of **4a** followed by 1 μM of **P_{2h}-BSA-FITC** at 4 °C for 30 min. The cell nuclei were stained with Hoechst 33342 dye. Excitation at 488 nm showing the green FITC. Excitation at 358 nm showing the blue stained nuclei.



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11. SPECTRA

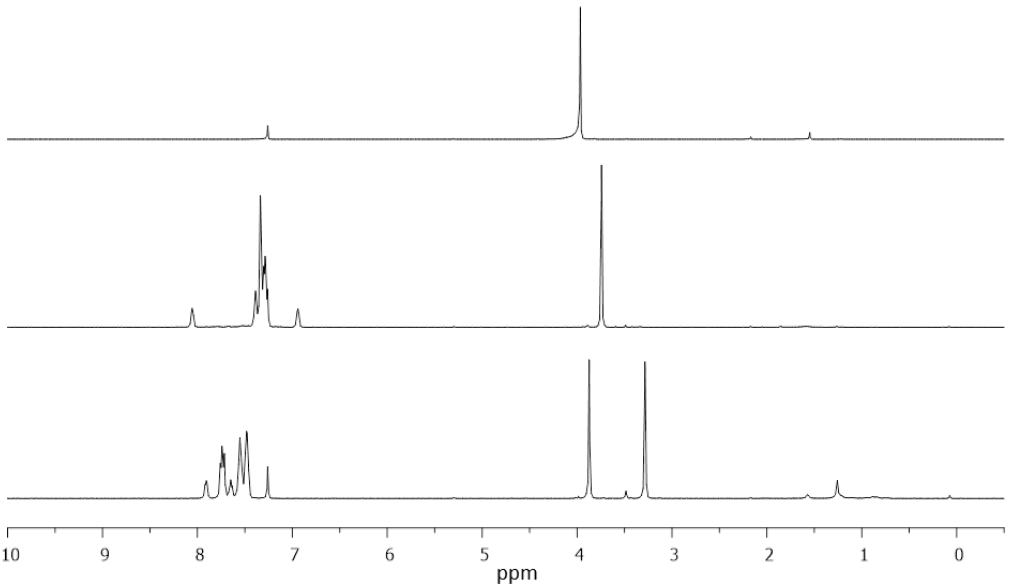

*Figure S1. ^{1}H NMR spectra of compound **1a** (top), compound **2a** (middle), and compound **3aa** (bottom) in $CDCl_3$.*

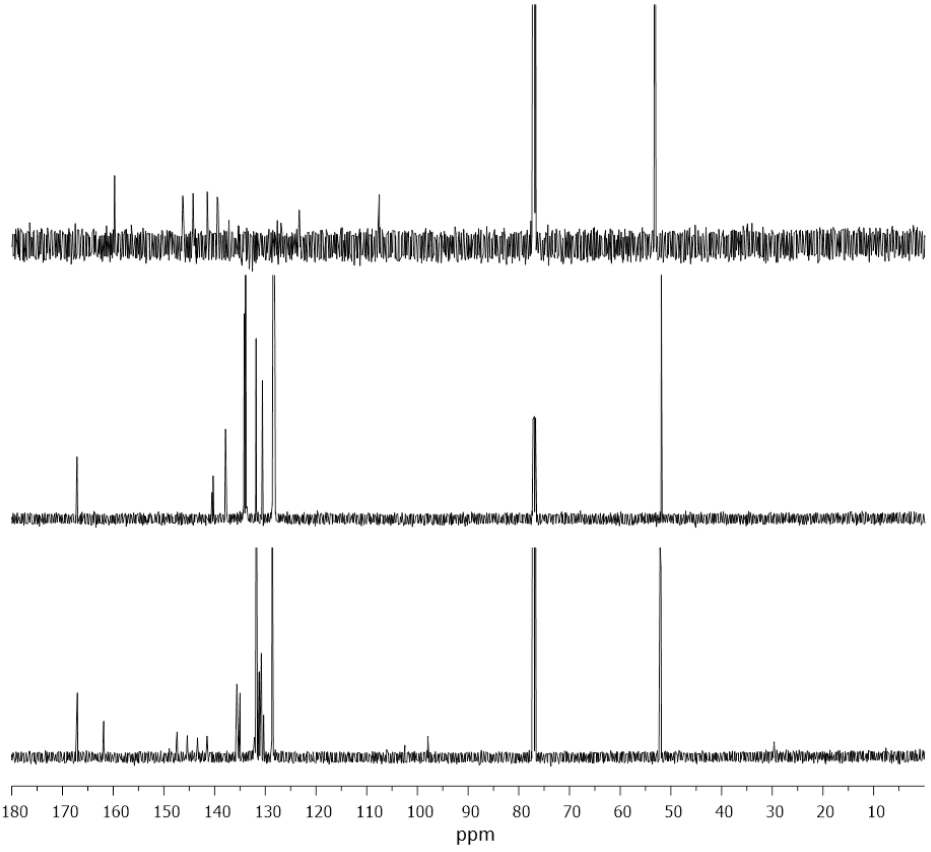

*Figure S2. ^{13}C NMR spectra of compound **1a** (top), compound **2a** (middle), and compound **3aa** (bottom) in $CDCl_3$.*

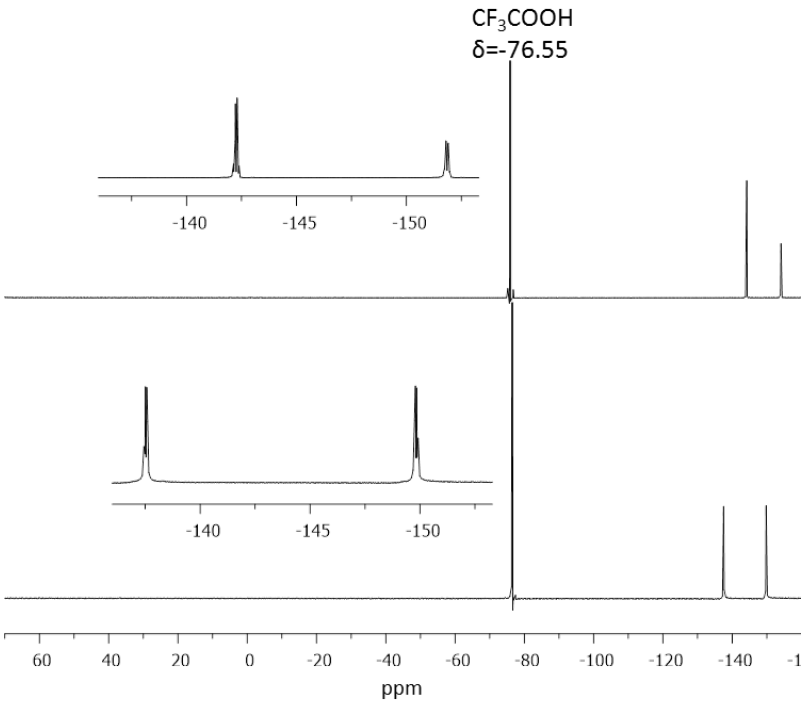

*Figure S3.^{19}F NMR spectra of (top) compound **1a** and (bottom) compound **3aa**. Trifluoroacetic acid (-76.55 ppm) used as external standard reference (capillary).*

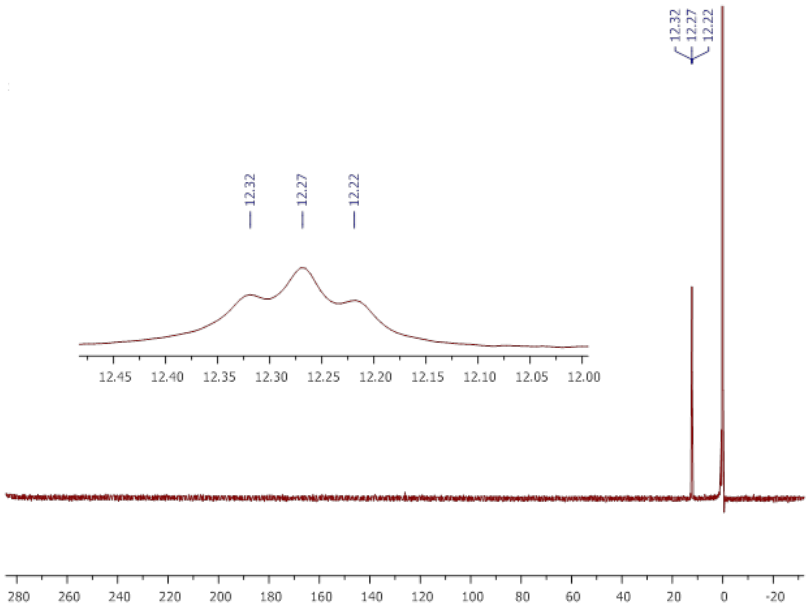

*Figure S4. ^{31}P NMR spectrum of compound **3aa**. Phosphoric acid (85%) used as reference (0 ppm, capillary).*

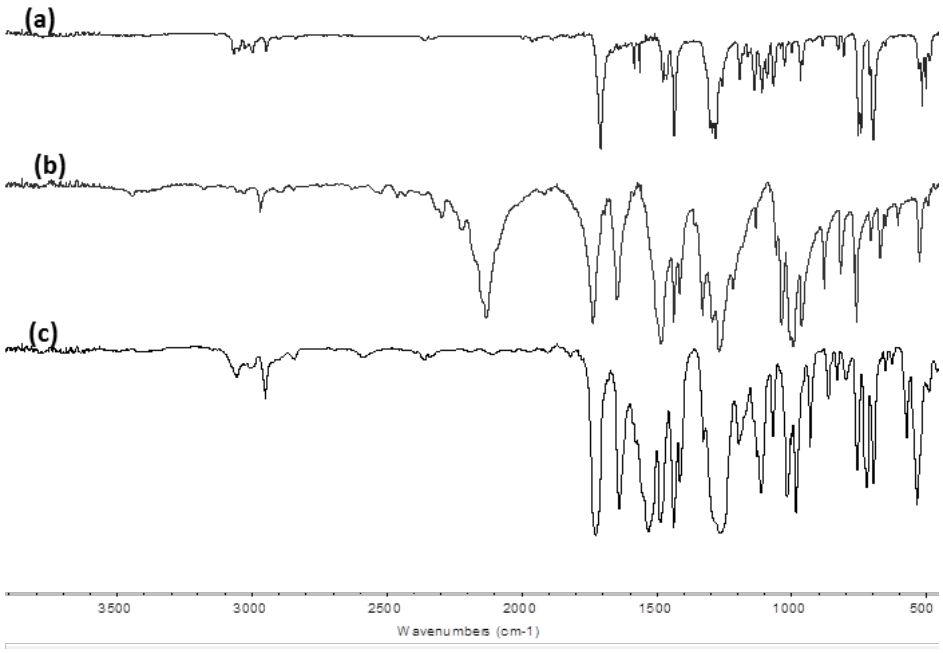

*Figure S5. IR spectra of compound **2a** (a), compound **1a** (b), and compound **3aa** (c).*

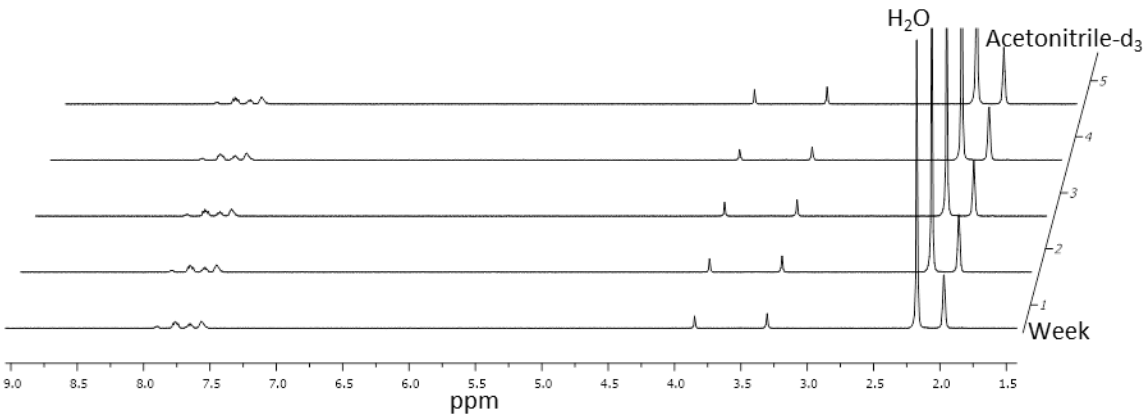

***Figure S6.** ^{1}H NMR spectra of compound **3aa** after storage at ambient conditions. Spectra were recorded weekly for 5 w.*

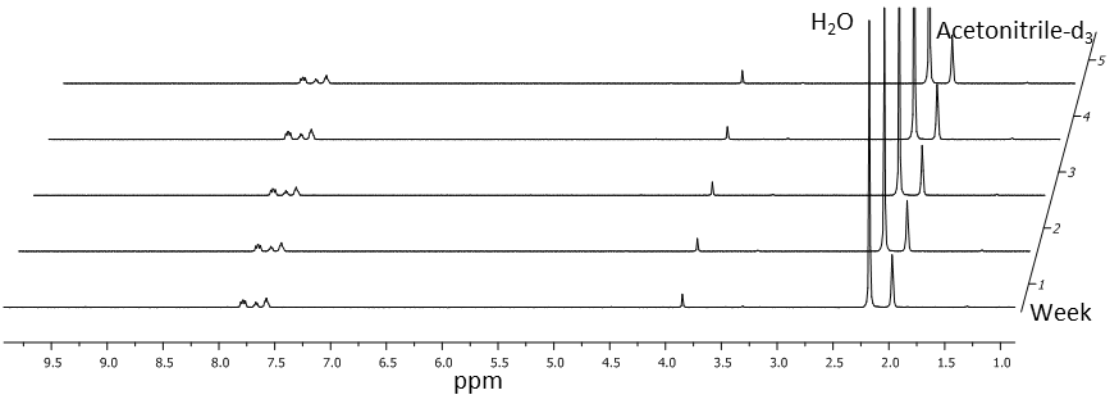

Figure S7. *^{1}H NMR spectra of compound **3ab** after storage at ambient conditions. Spectra were recorded weekly for 5 w.*

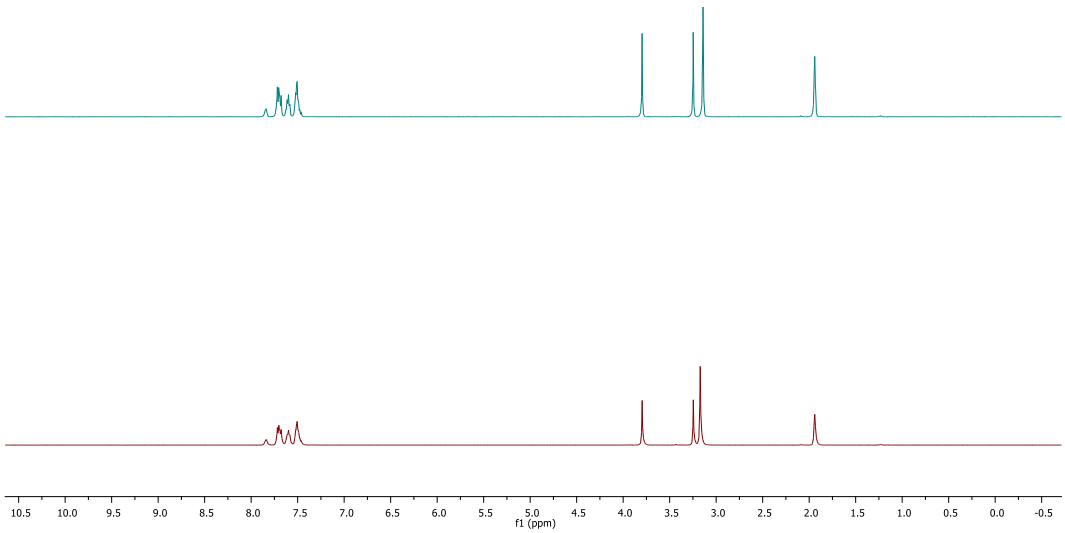

Figure S8. *^{1}H NMR spectra monitoring the stability of compound **3aa** in D_2O/CD_3CN (1:9 v/v) before (bottom) and after (top) 35 d.*

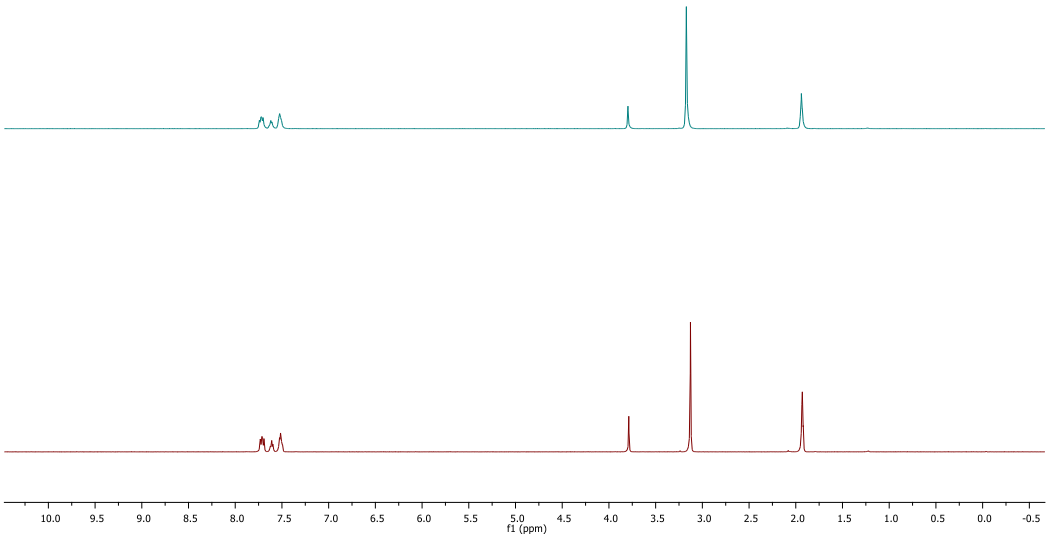

Figure S9. *^{1}H NMR spectra monitoring the stability of compound **3ab** in D_2O/CD_3CN (1:9 v/v) before (bottom) and after (top) 35 d at ambient conditions.*

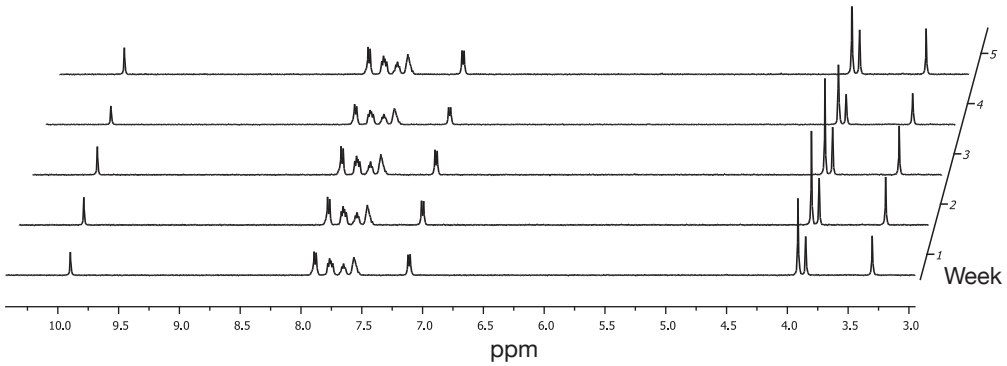

Figure S10. *[1]H NMR spectra of compound **3aa (**2.5 mg, 0.005 mmol**)** and p-anisaldehyde (1 mg, 0.0075 mmol) in CD_3CN (0.6 mL) at ambient conditions over the course of 35 d. Spectra were recorded weekly for 5 w.*

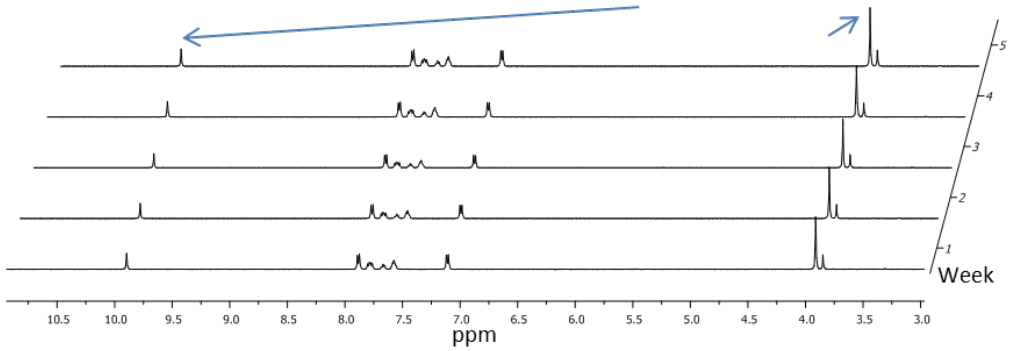

Figure S11. *[1]H NMR spectra of compound **3ab (**2.5 mg, 0.005 mol**)** and p-anisaldehyde (1 mg, 0.0075 mmol) in CD_3CN (0.6 mL) at ambient conditions over the course of 35 d. Spectra were recorded weekly for 5 w.*

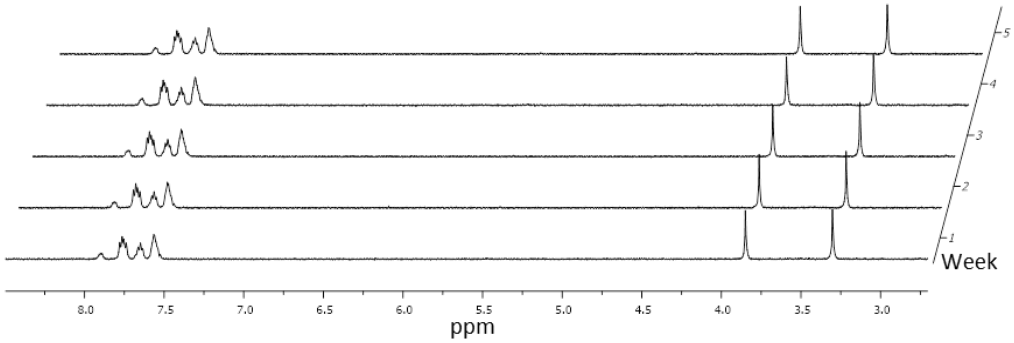

Figure S12. *[1]H NMR spectra of compound **3aa (**2.5 mg, 0.005 mmol**)** and CS_2 (0.5 mg, 0.0075 mmol) in CD_3CN (0.6 mL) at ambient conditions over the course of 35 d. Spectra were recorded weekly for 5 w.*

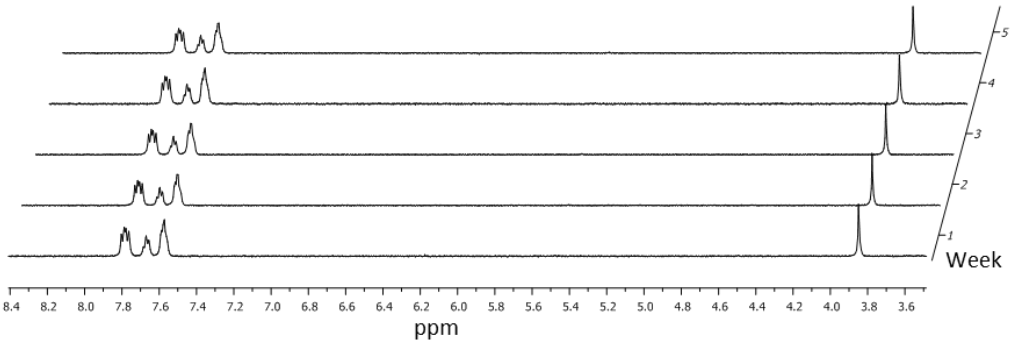

Figure S13. *[1]H NMR spectra of compound **3aa (**2.5 mg, 0.005 mmol**)** and CS_2 (0.5 mg, 0.0075 mmol) in CD_3CN (0.6 mL) at ambient conditions over the course of 35 d. Spectra were recorded weekly for 5 w.*

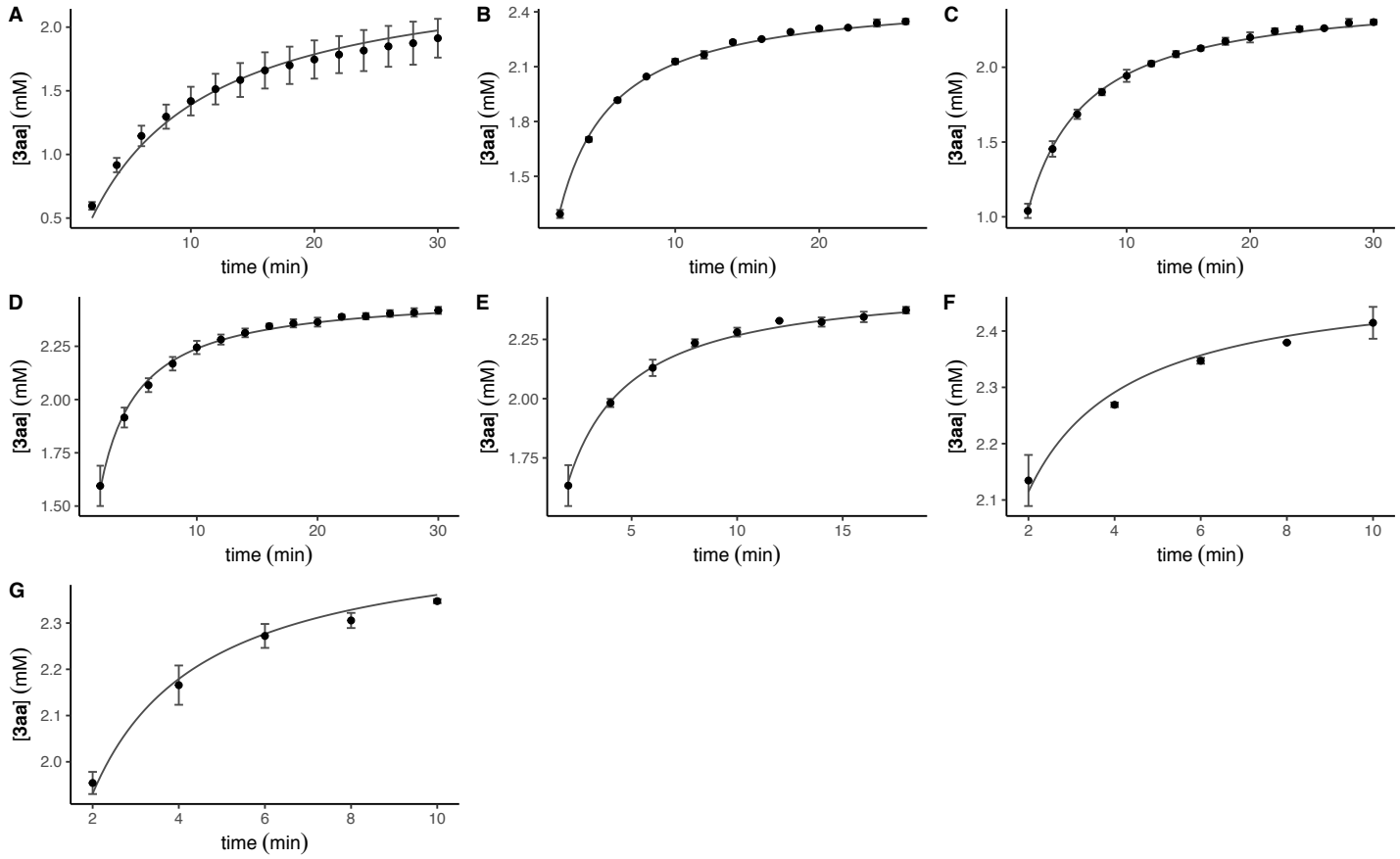

*Figure S14. Solvent effect on the kinetics of the reaction between compounds **1a** and **2a** (initial concentrations 2.5 mM) at 298 K. Recorded by NMR spectroscopy. (A) $CDCl_3$, (B) CD_3CN, (C) acetone-d_6, (D) CD_3OD, (E) CD_3CN/D_2O (5/1), (F) CD_3CN/D_2O (1/1), and (G) CD_3OD/D_2O (5/1). Each data point: mean ± SD (n = 3 (A-E, G); n = 2 (F)).*

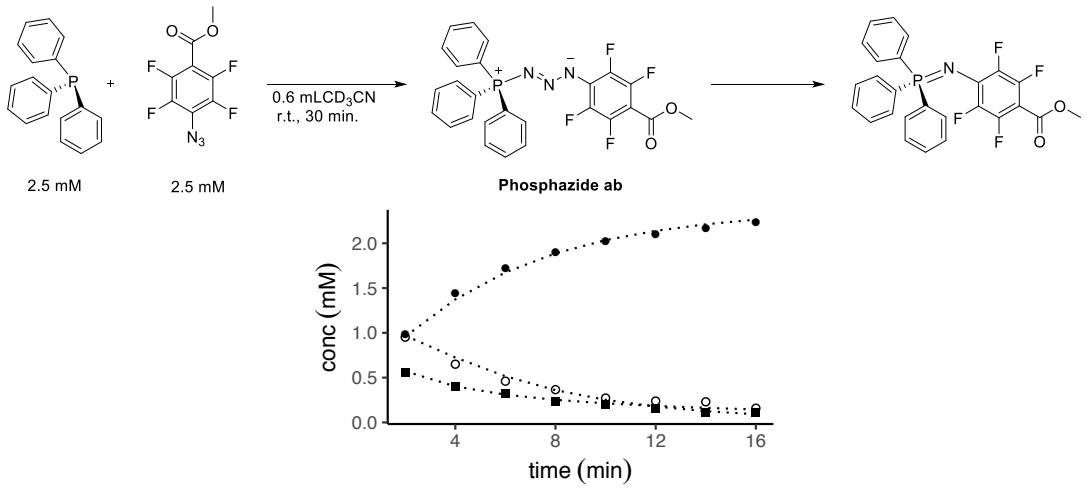

*Figure S15. Kinetics of the reaction between compounds **1a** and **2b** (initial concentrations 2.5 mM) in CD_3CN (0.6 mL) at 298 K. Recorded by NMR spectroscopy. **phosphazide ab**; **phosphazide ab**. Each data point: mean ± SD (n = 3).*

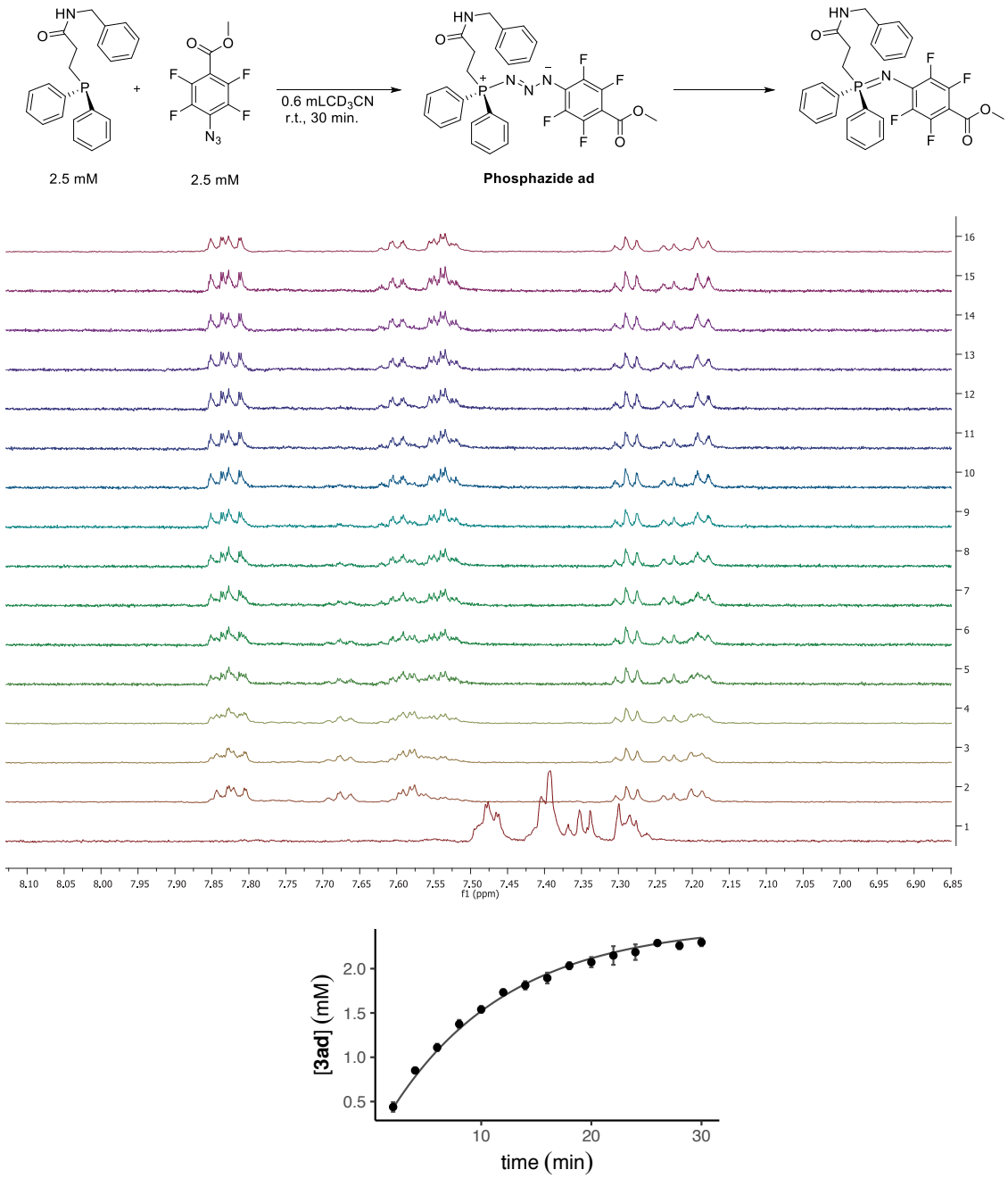

Figure S16. (***A***) *^{1}H NMR spectra monitoring the reaction between compounds* ***1a*** *and* ***2d*** *(initial concentrations 2.5 mM) at 298 K over the course of 30 min. (****B****) First order kinetic analysis. Each data point: mean ± SD (n = 5).*

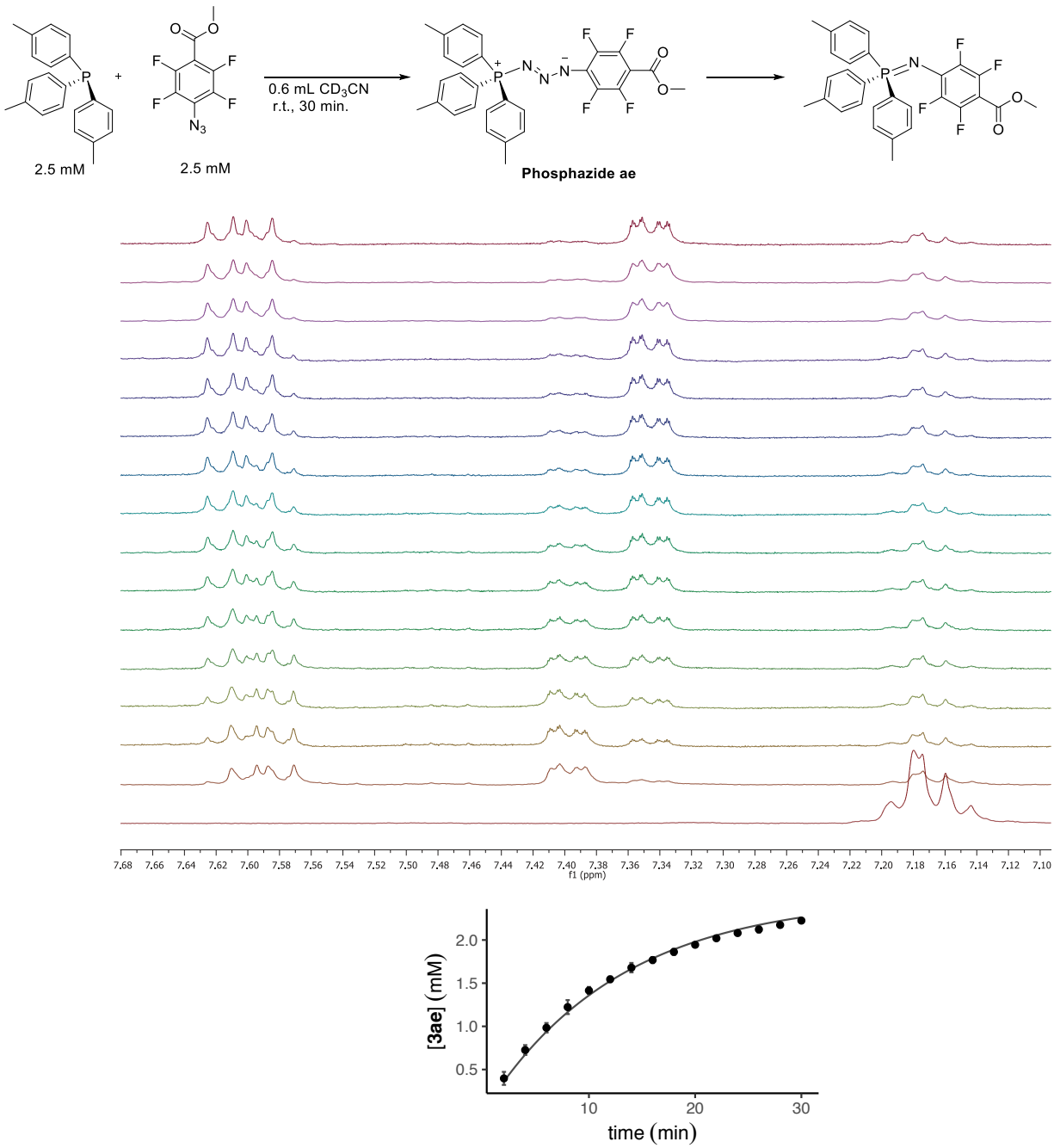

Figure S17. (***A***) *^{1}H NMR spectra monitoring the reaction between compounds* ***1a*** *and* ***2e*** *(initial concentrations 2.5 mM) at 298 K over the course of 30 min. (****B****) First order kinetic analysis. Each data point: mean ± SD (n = 3).*

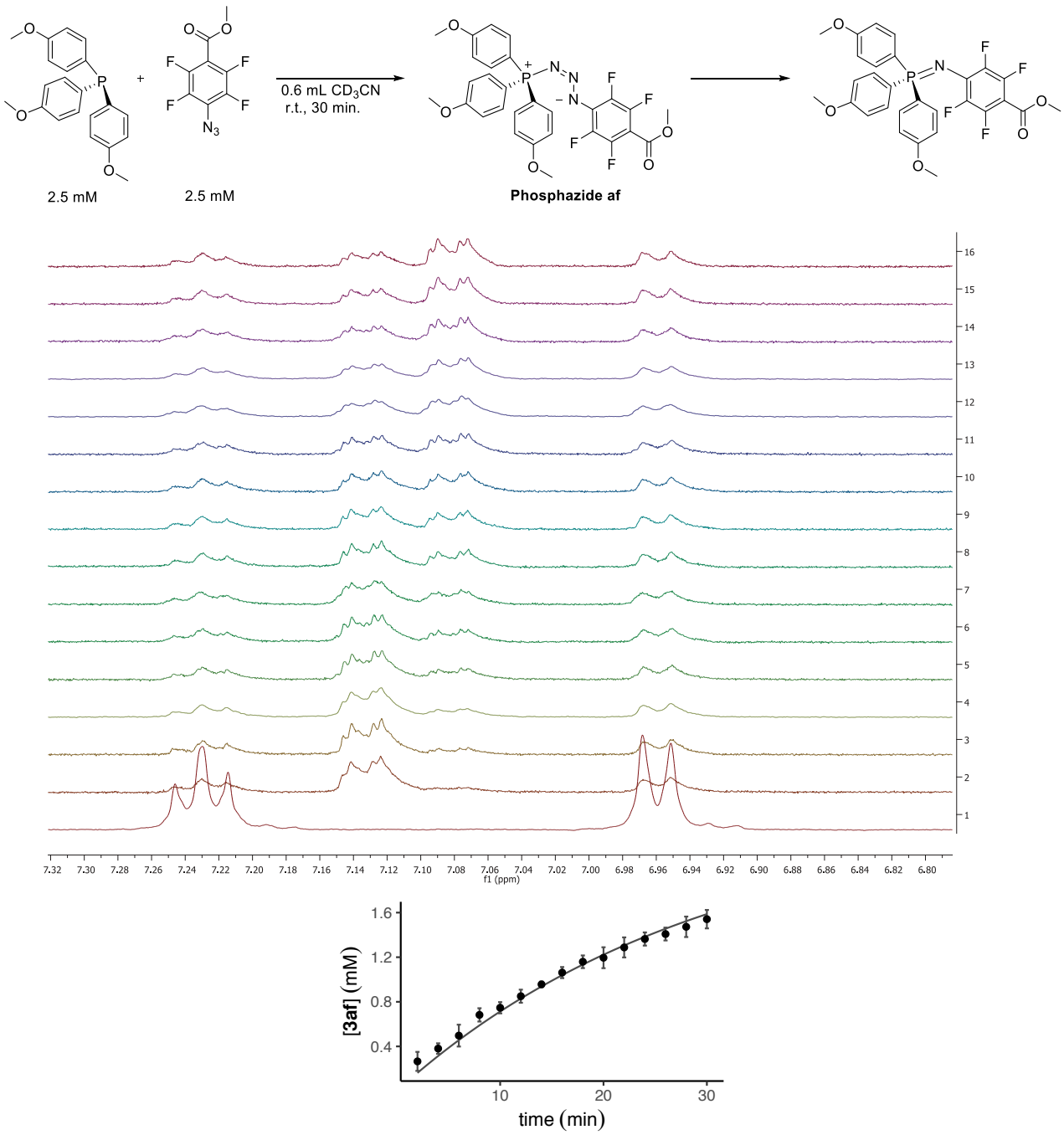

Figure S18. (***A***) [1]*H NMR spectra monitoring the reaction between compounds* ***1a*** *and* ***2f*** *(initial concentrations 2.5 mM) at 298 K over the course of 30 min. (****B****) First order kinetic analysis. Each data point: mean ± SD (n = 3).*

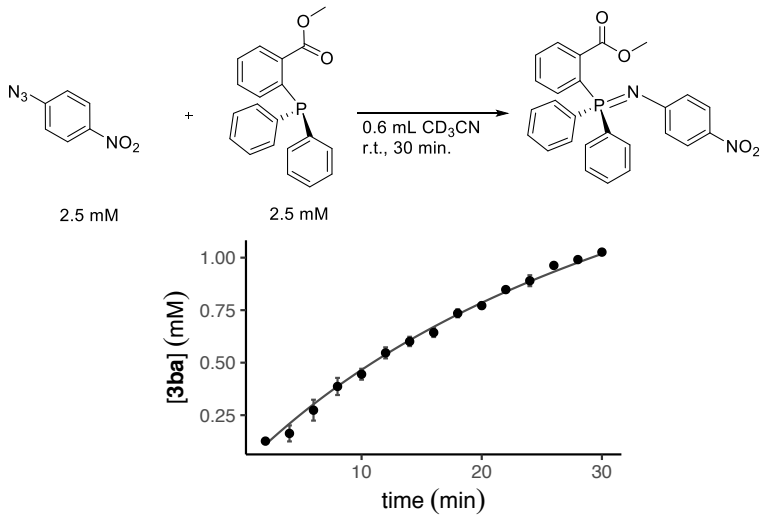

***Figure S19**. Kinetic analyses of the reaction between compounds **1b** and **2a** (initial concentrations 2.5 mM) in CD_3CN (0.6 mL) at 298 K. Recorded by NMR spectroscopy. Each data point: mean ± SD (n = 3).*

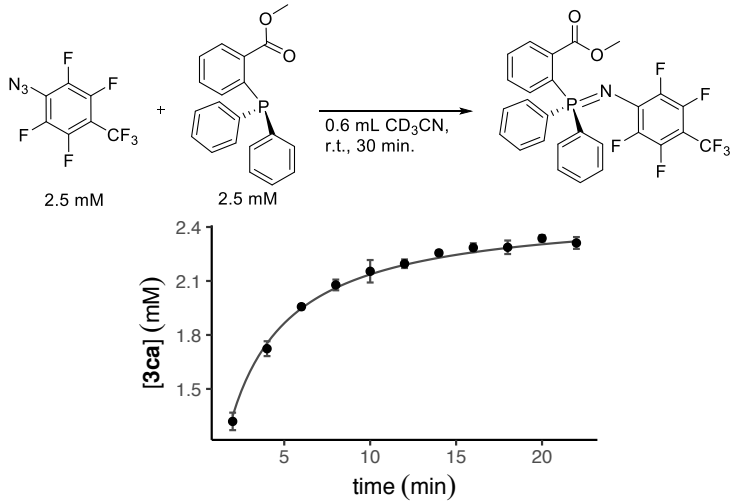

***Figure S20**. Kinetic analyses of the reaction between compounds **1c** and **2a** (initial concentrations 2.5 mM) in CD_3CN (0.6 mL) at 298 K. Recorded by NMR spectroscopy. Each data point: mean ± SD (n = 3).*

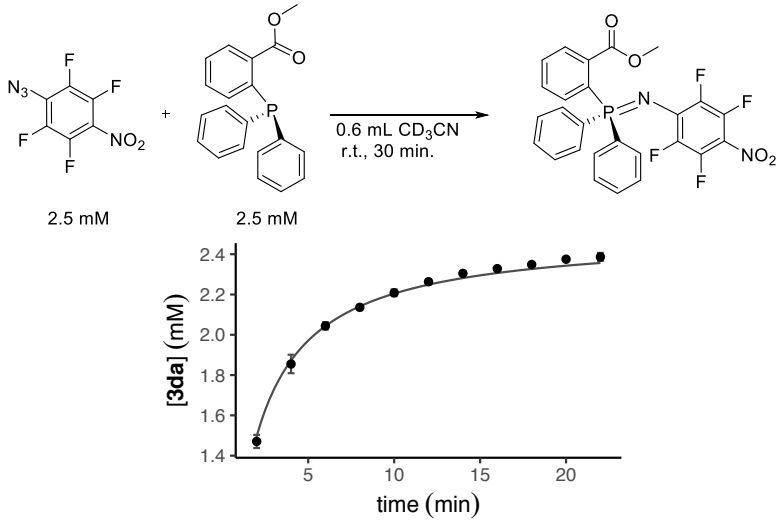

***Figure S21**. Kinetic analyses of the reaction between compounds **1d** and **2a** (initial concentrations 2.5 mM) in CD_3CN (0.6 mL) at 298 K. Recorded by NMR spectroscopy. Each data point: mean ± SD (n = 3).*

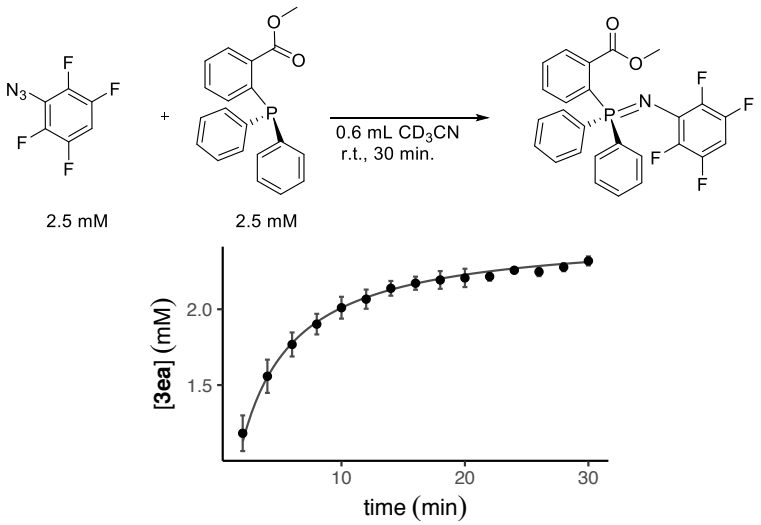

***Figure S22**. Kinetic analyses of the reaction between compounds **1e** and **2a** (initial concentrations 2.5 mM) in CD_3CN (0.6 mL) at 298 K. Recorded by NMR spectroscopy. Each data point: mean ± SD (n = 4).*

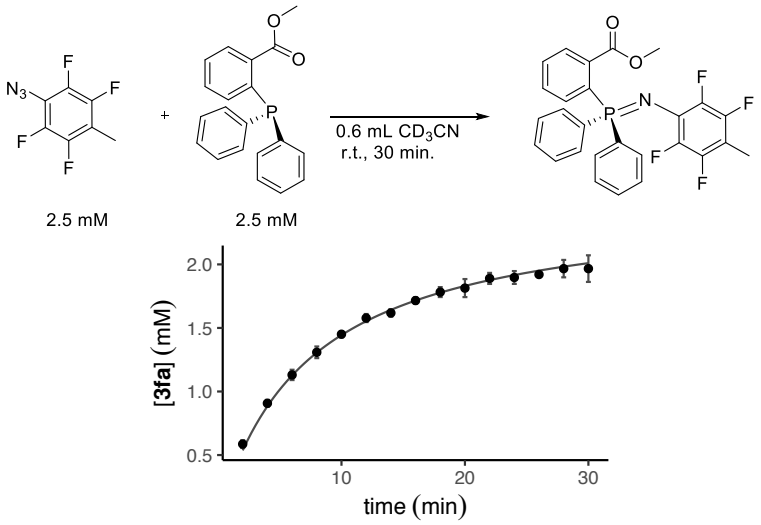

***Figure S23**. Kinetic analyses of the reaction between compounds **1f** and **2a** (initial concentrations 2.5 mM) in CD_3CN (0.6 mL) at 298 K. Recorded by NMR spectroscopy. Each data point: mean ± SD (n = 3).*

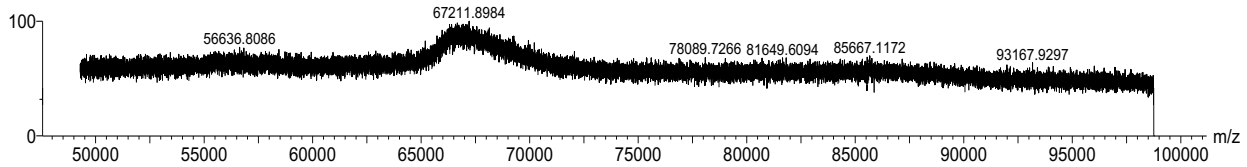

***Figure S24**. MALDI-TOF MS spectrum of agent **P_{2g}-BSA-FITC**.*

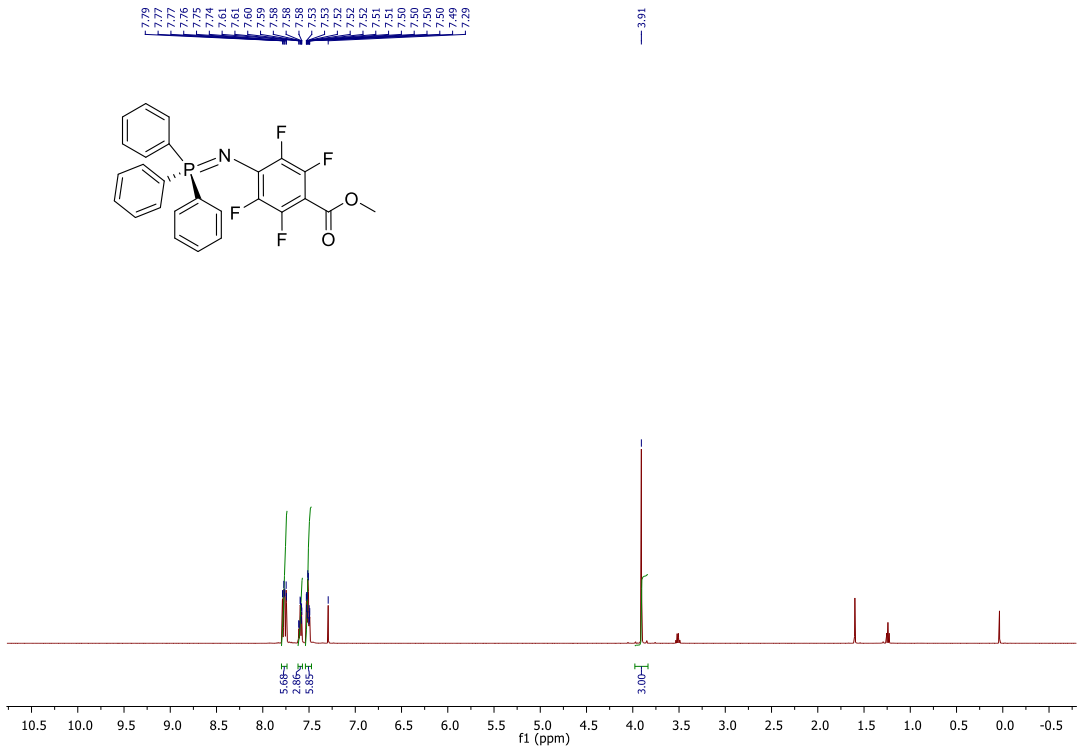

Figure S25. *^{1}H NMR spectrum of compound **3ab** in $CDCl_3$.*

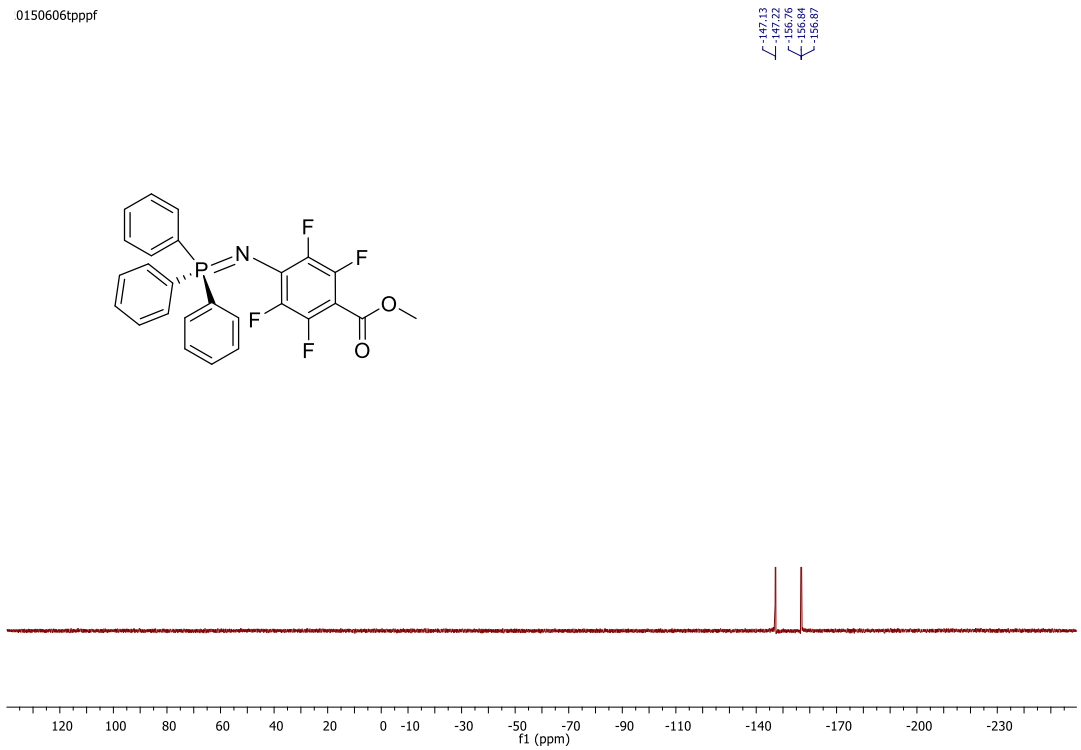

Figure S26. *^{19}F spectrum of compound **3ab** in $CDCl_3$. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

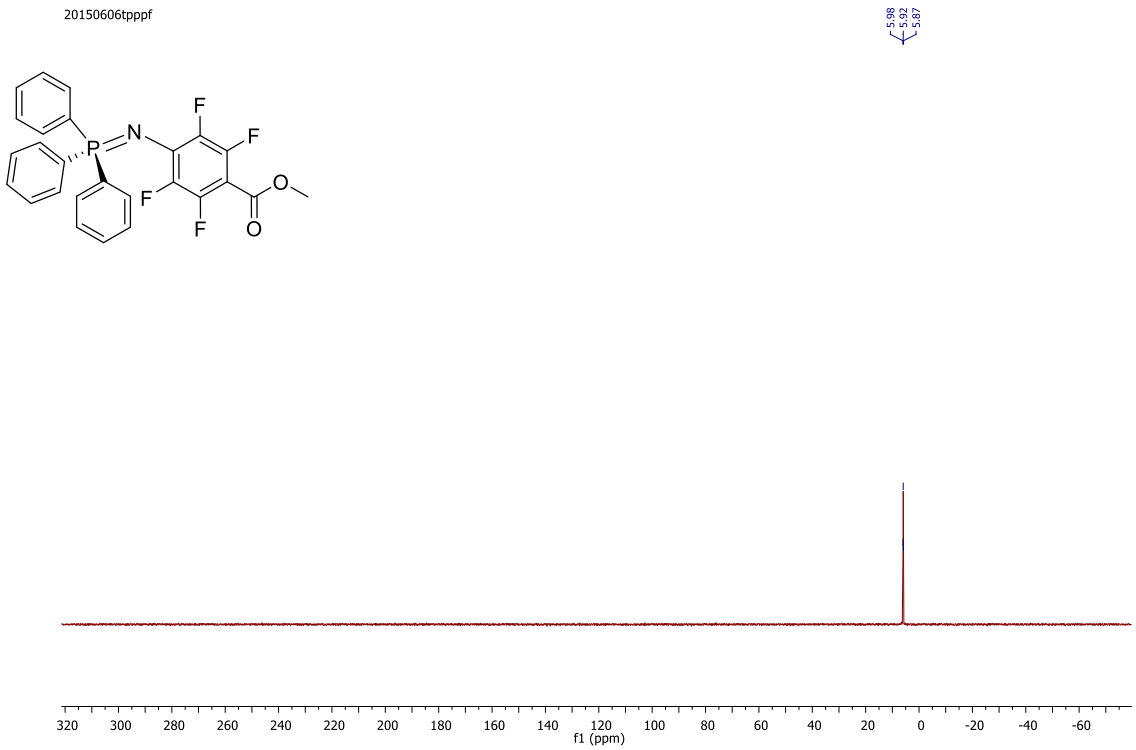

Figure S27. *^{31}P spectrum of compound **3ab** in $CDCl_3$. Phosphoric acid (85%) used as external reference (0 ppm).*

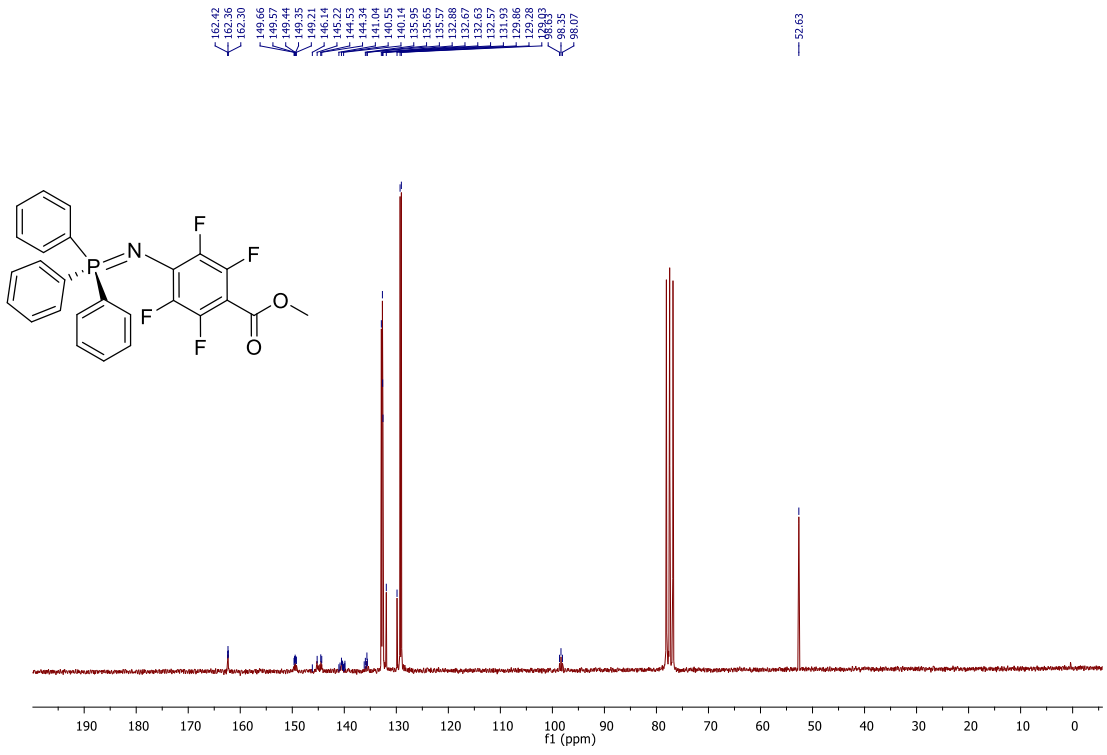

Figure S28. *^{13}C NMR spectrum of compound **3ab** in $CDCl_3$.*

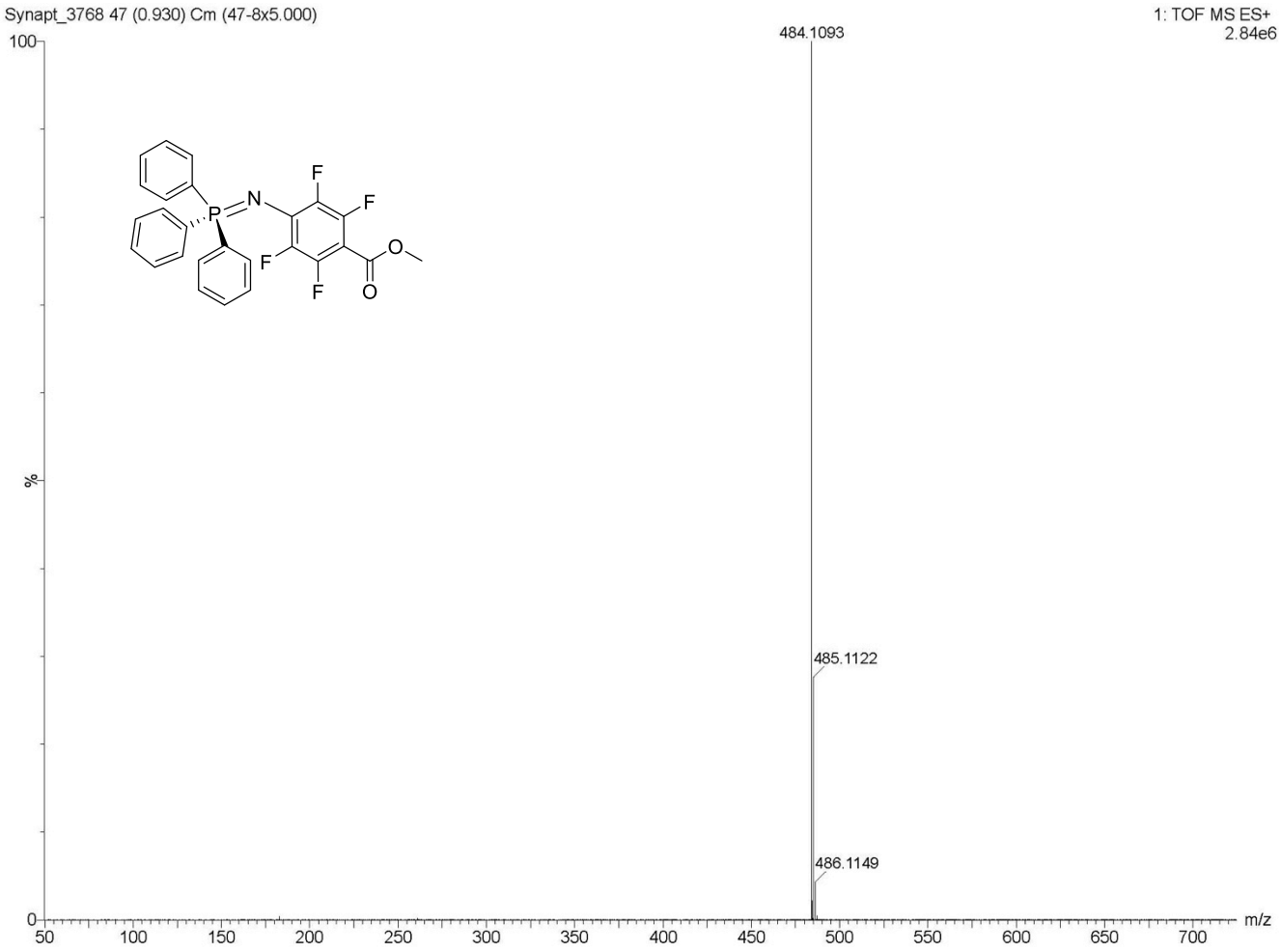

***Figure S29**. HRMS spectrum of compound **3ab**.*

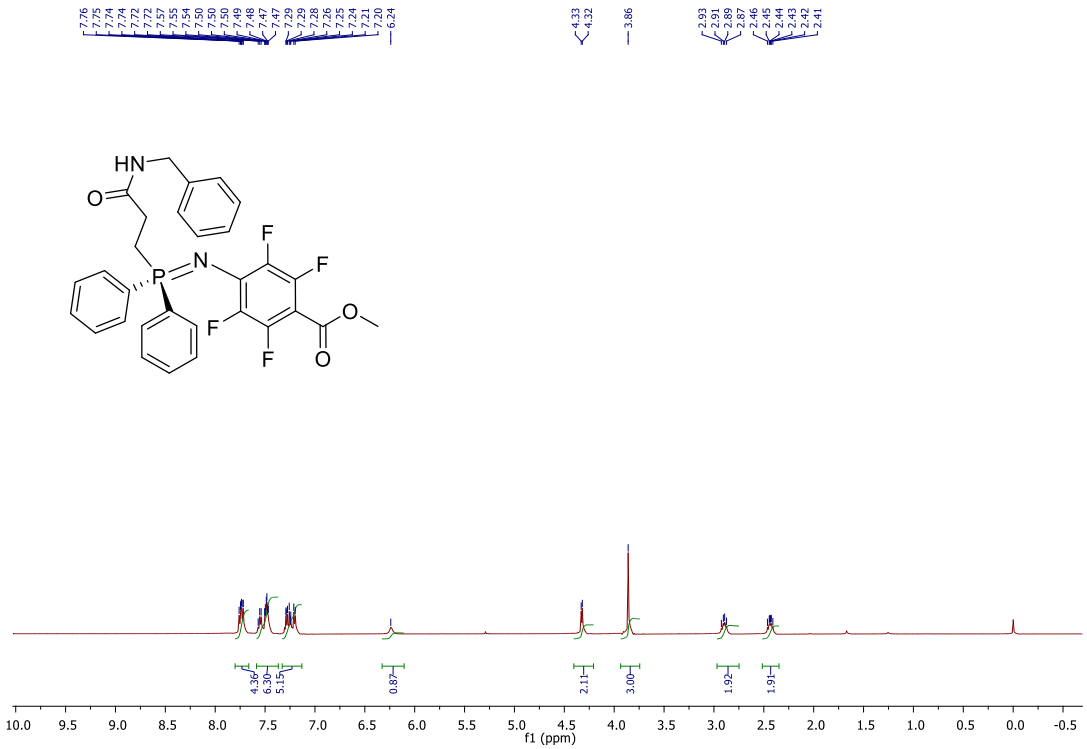

***Figure S30**. ^{1}H NMR spectrum of compound **3ad** in $CDCl_3$.*

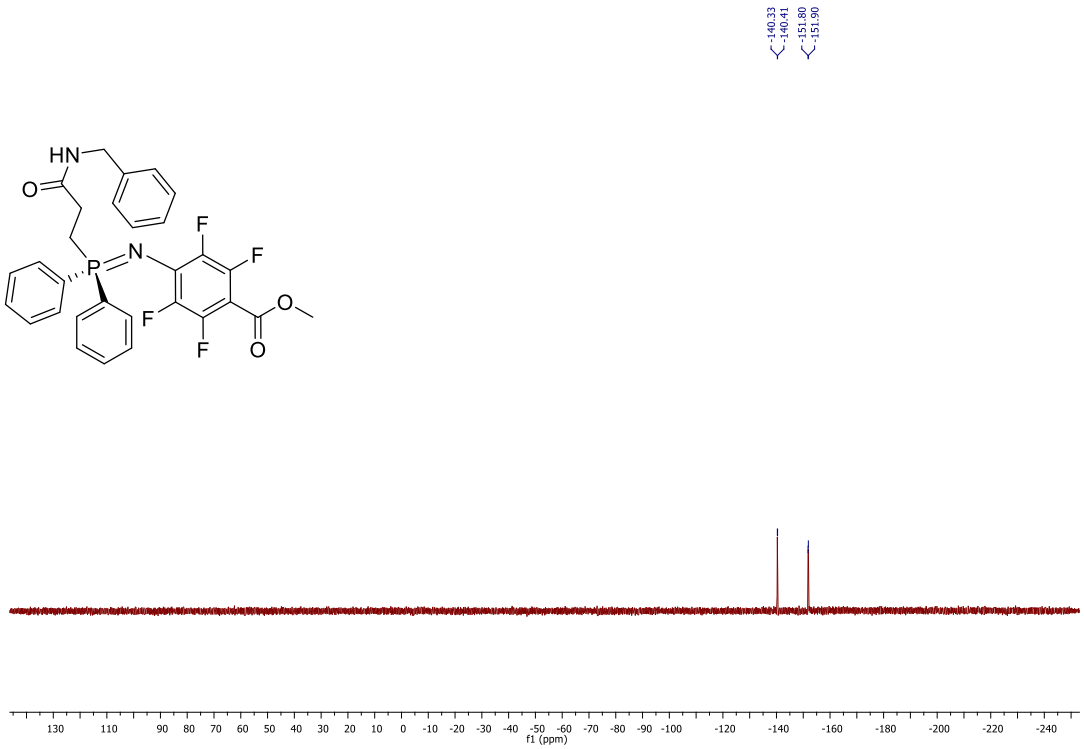

Figure S31. *^{19}F NMR spectrum of compound **3ad** in $CDCl_3$. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

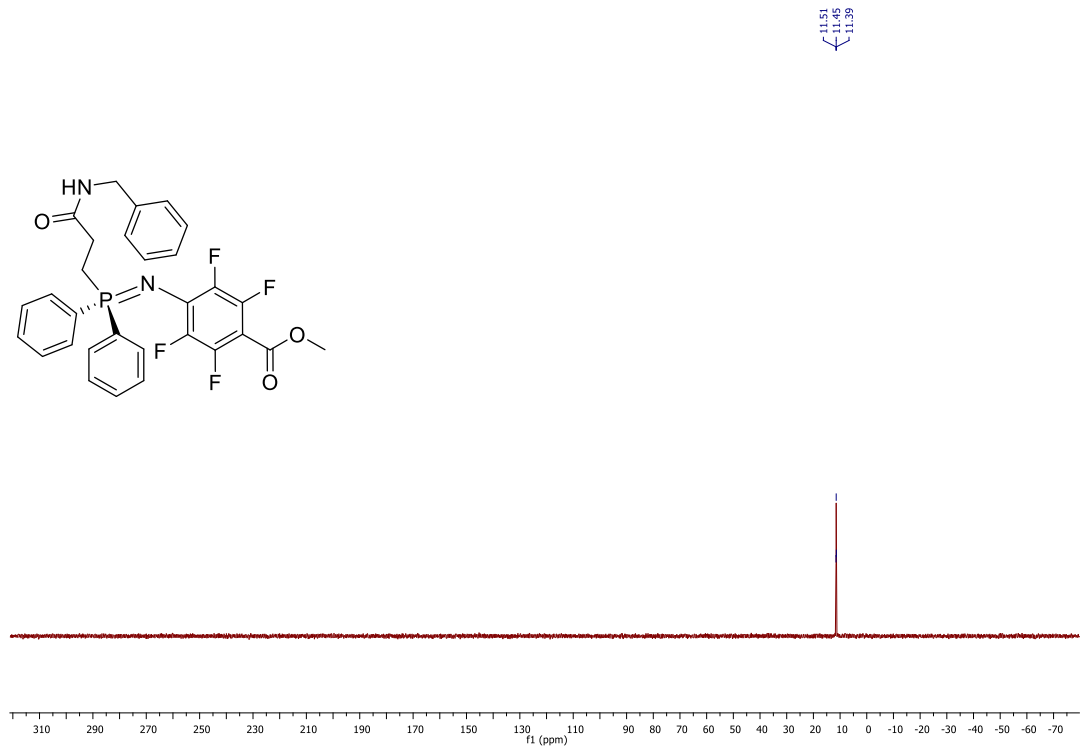

Figure S32. *^{31}P NMR spectrum of compound **3ad** in $CDCl_3$. Phosphoric acid (85%) used as external reference (0 ppm).*

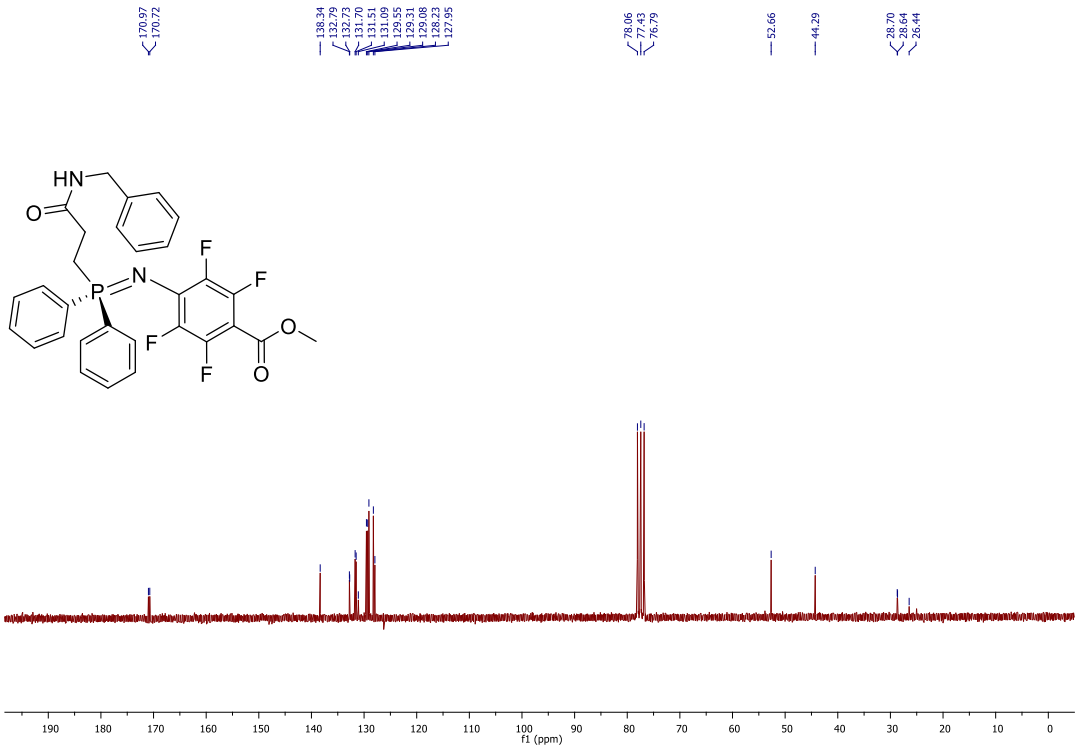

Figure S33. *^{13}C NMR spectrum of compound **3ad** in $CDCl_3$.*

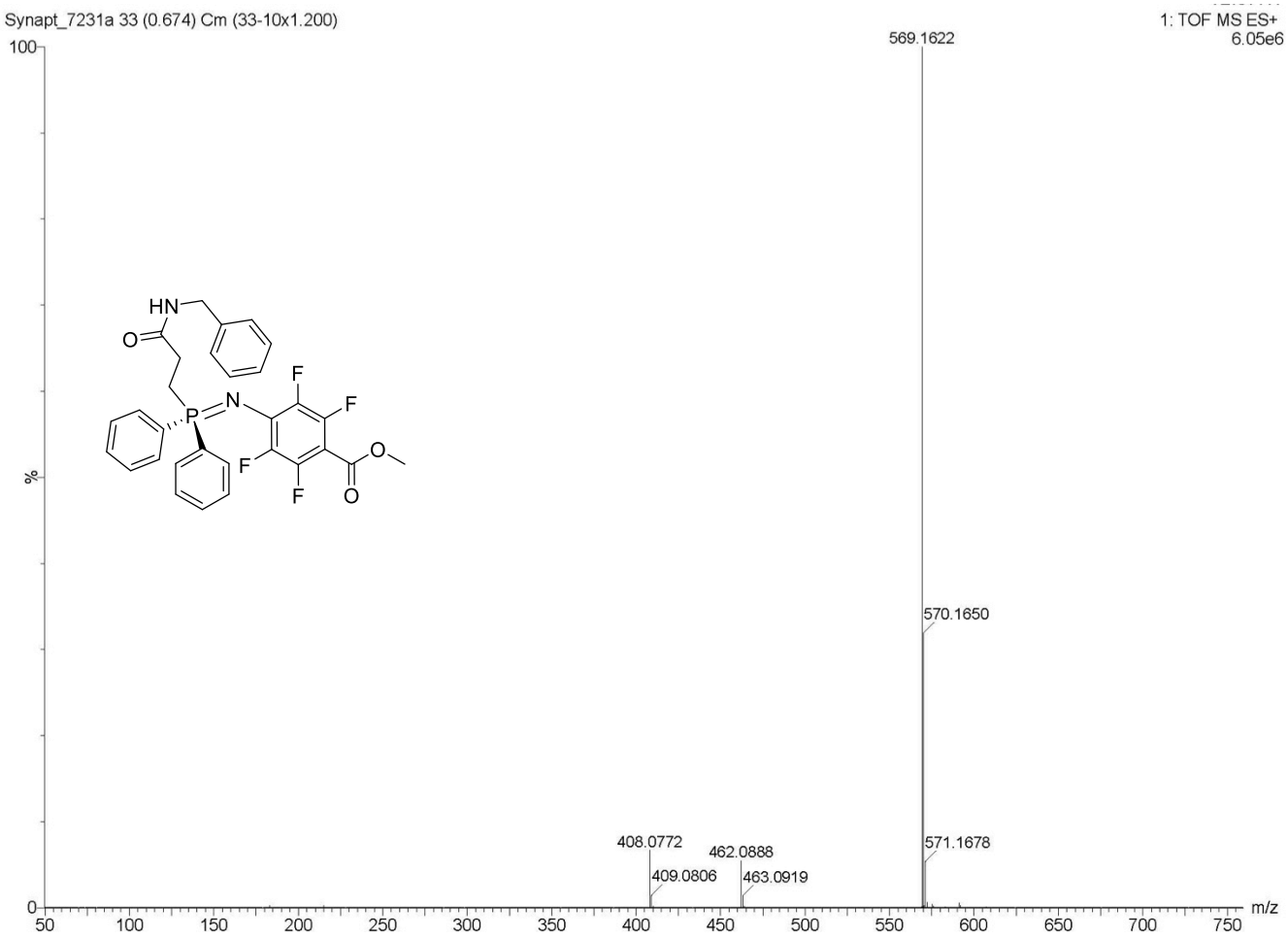

Figure S34. *HRMS spectrum of compound **3ad**.*

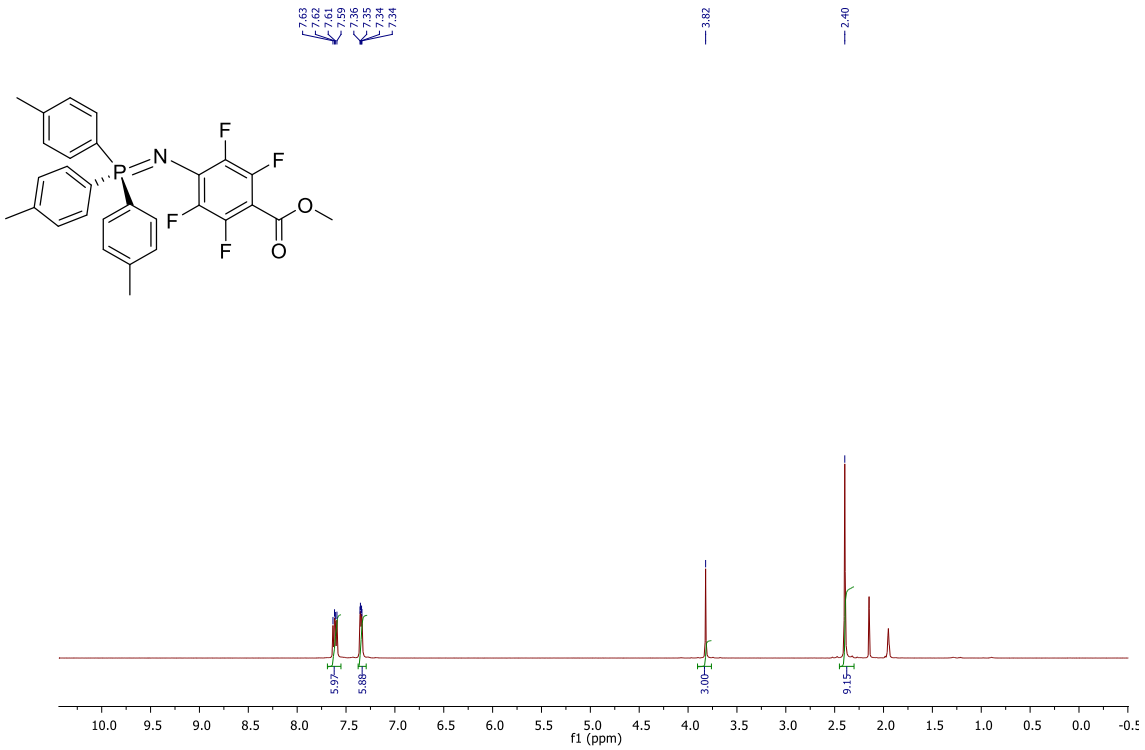

Figure S35. *^{1}H NMR spectrum of compound **3ae** in CD_3CN.*

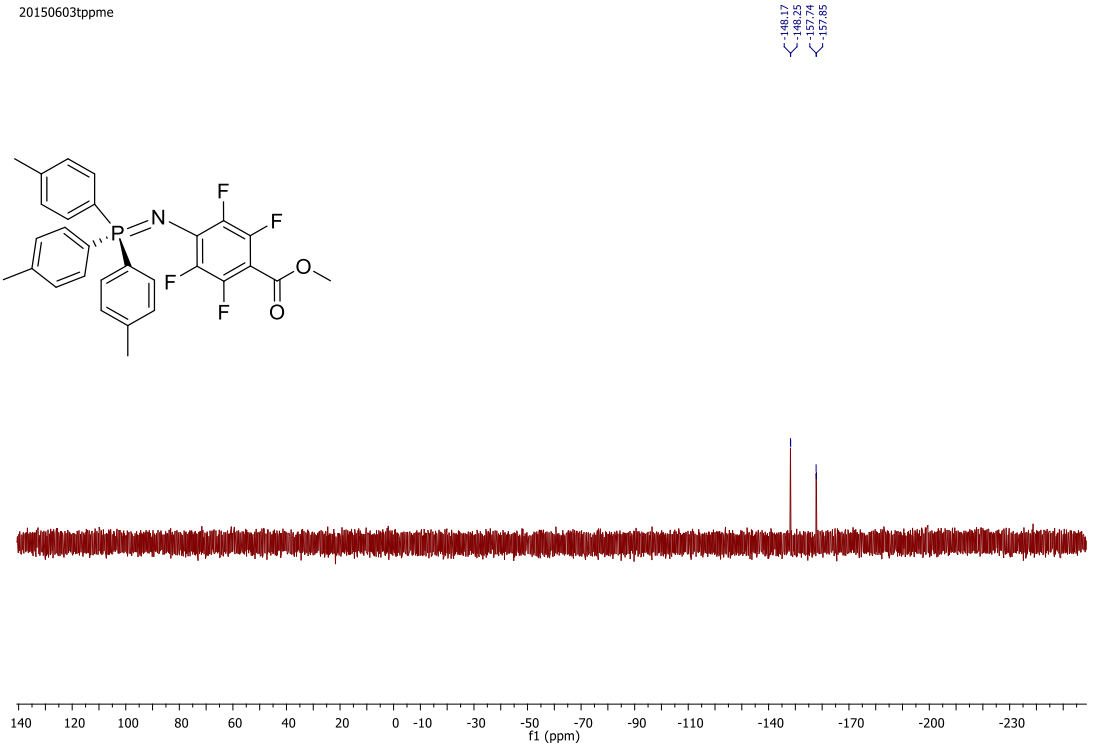

Figure S36. *^{19}F NMR spectrum of compound **3ae** in CD_3CN. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

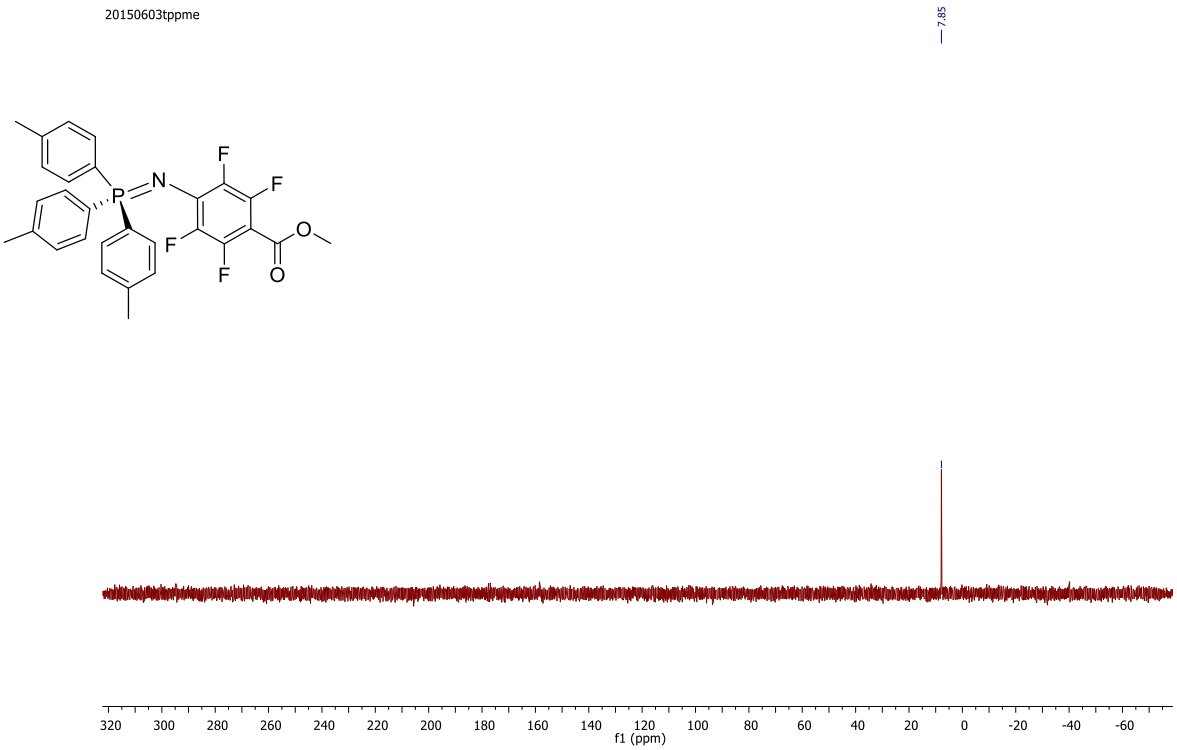

Figure S37. *^{31}P NMR spectrum of compound **3ae** in CD_3CN. Phosphoric acid (85%) used as external reference (0 ppm).*

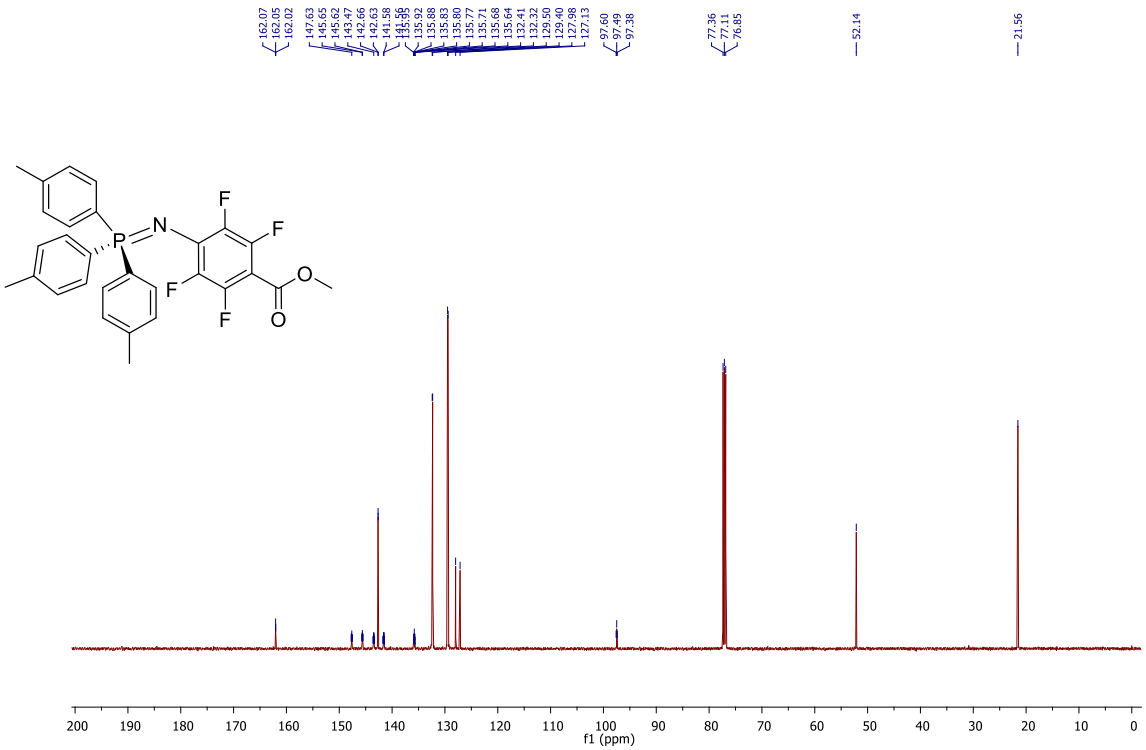

Figure S38. *^{13}C NMR spectrum of compound **3ae** in CD_3CN.*

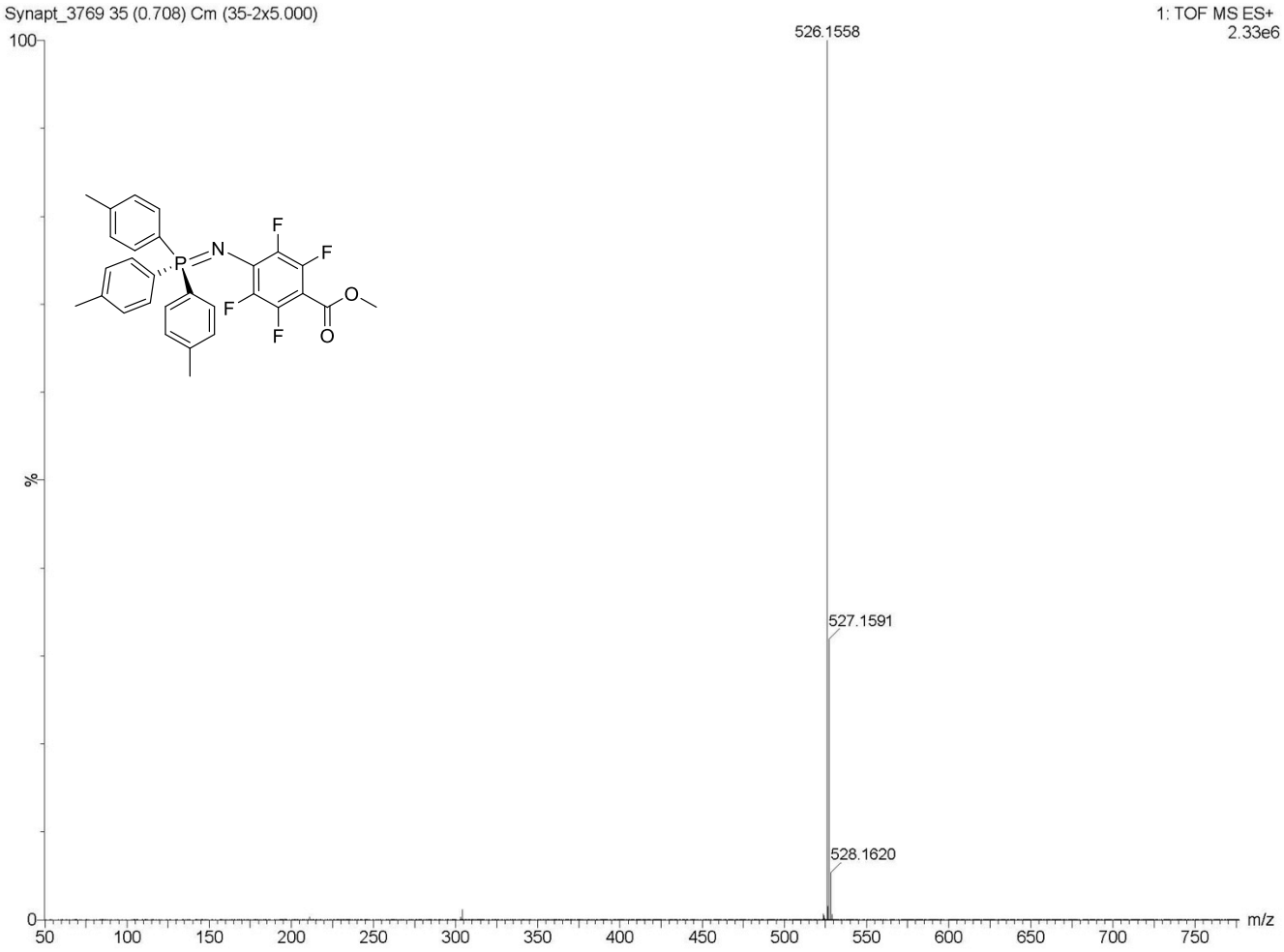

***Figure S39**. HRMS spectrum of compound **3ae**.*

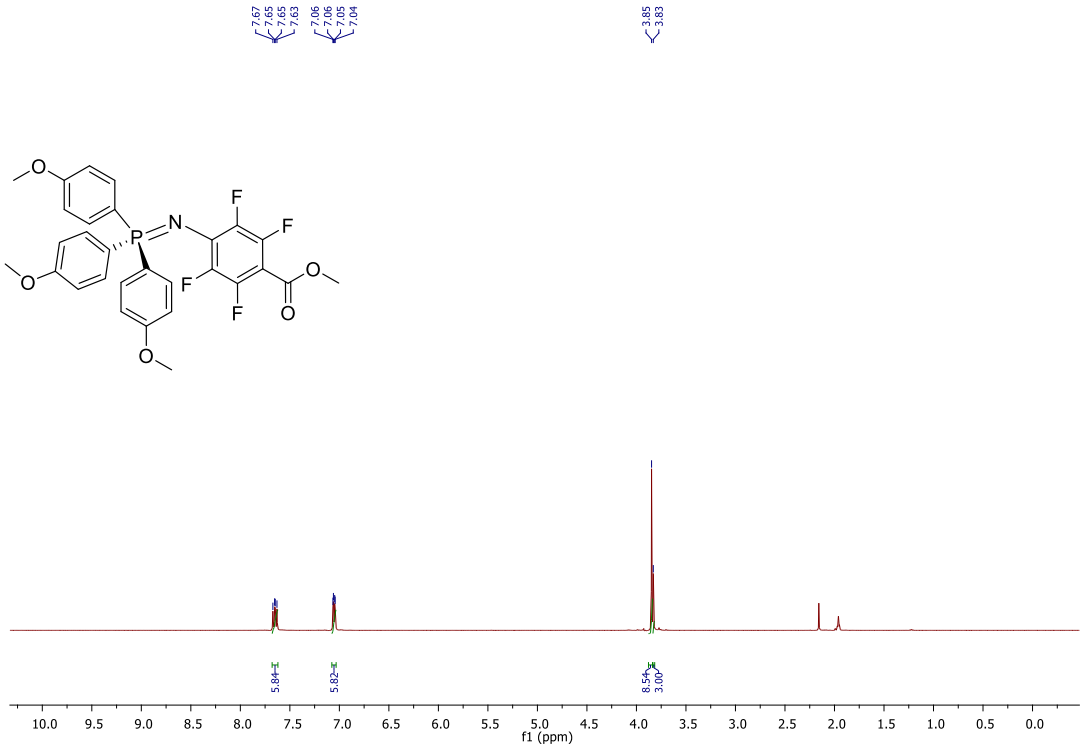

***Figure S40**. ^1H NMR spectrum of compound **3af** in CD_3CN.*

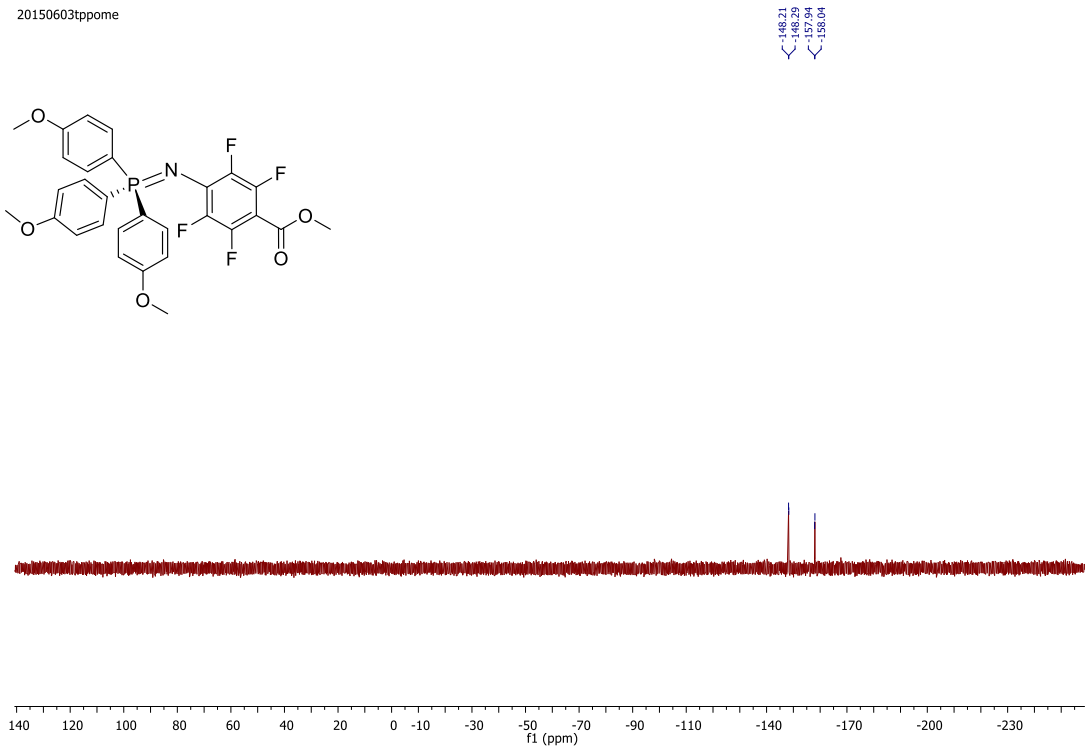

Figure S41. *^{19}F NMR spectrum of compound **3af** in CD_3CN. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

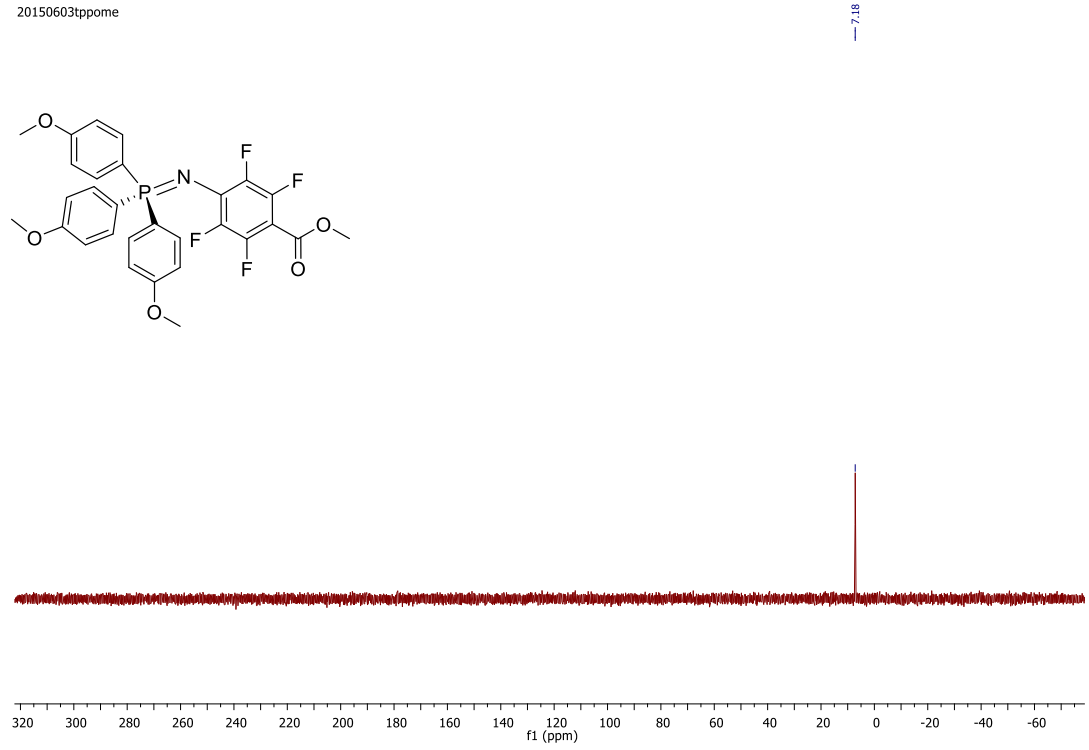

Figure S42. *^{31}P NMR spectrum of compound **3af** in CD_3CN. Phosphoric acid (85%) used as external reference (0 ppm).*

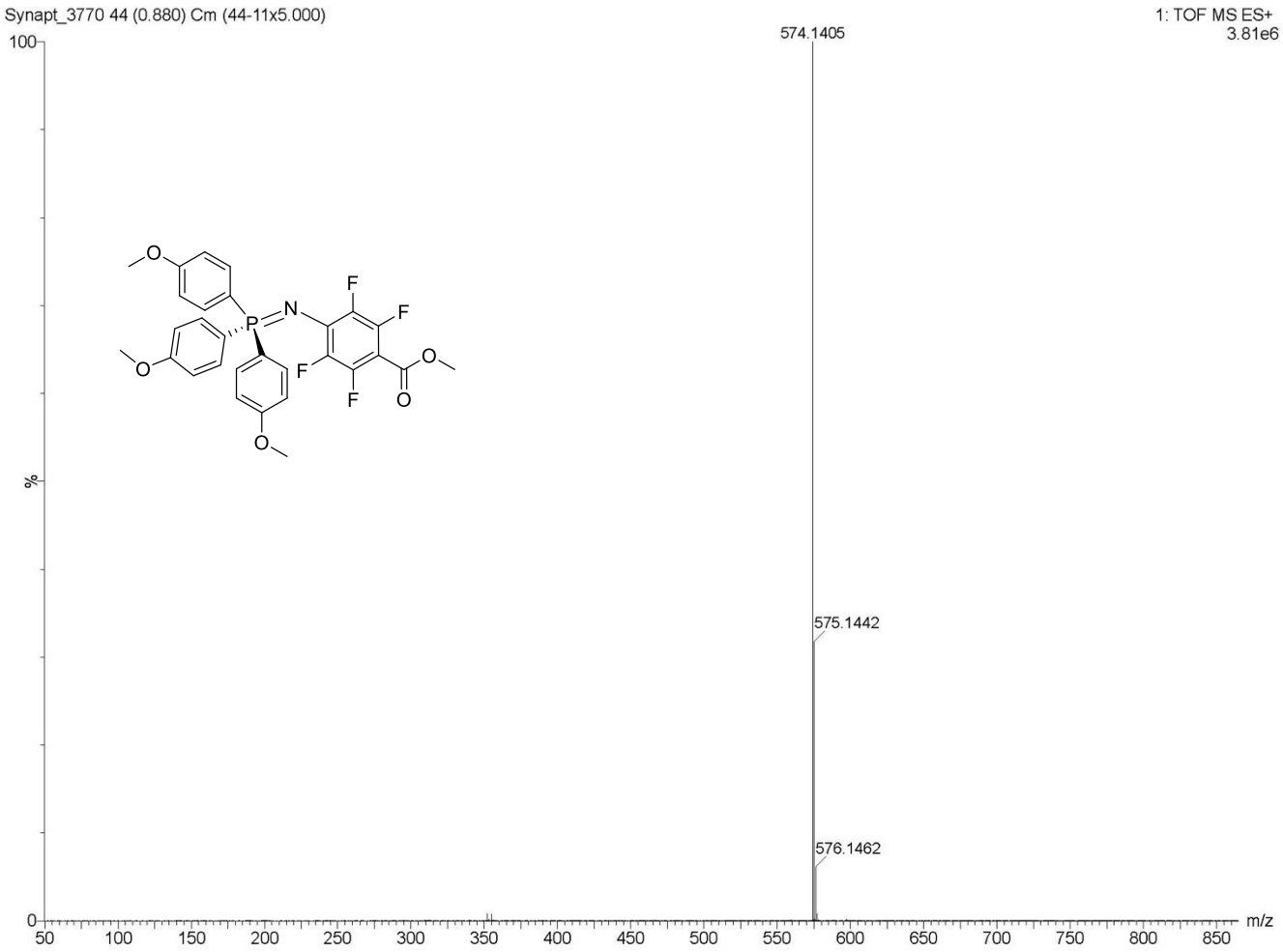

Figure S43**. HRMS spectrum of compound **3af.

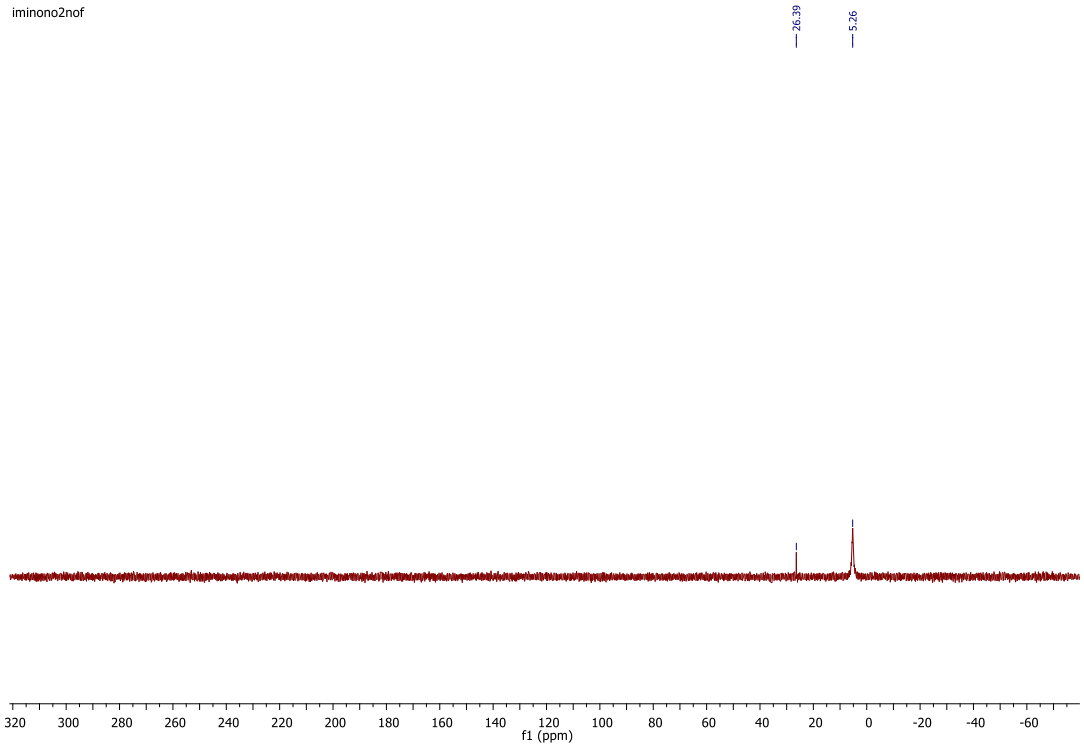

***Figure S44**. ^{31}P NMR spectrum of compound **3ba** in $CDCl_3$. Phosphoric acid (85%) used as external reference (0 ppm).*

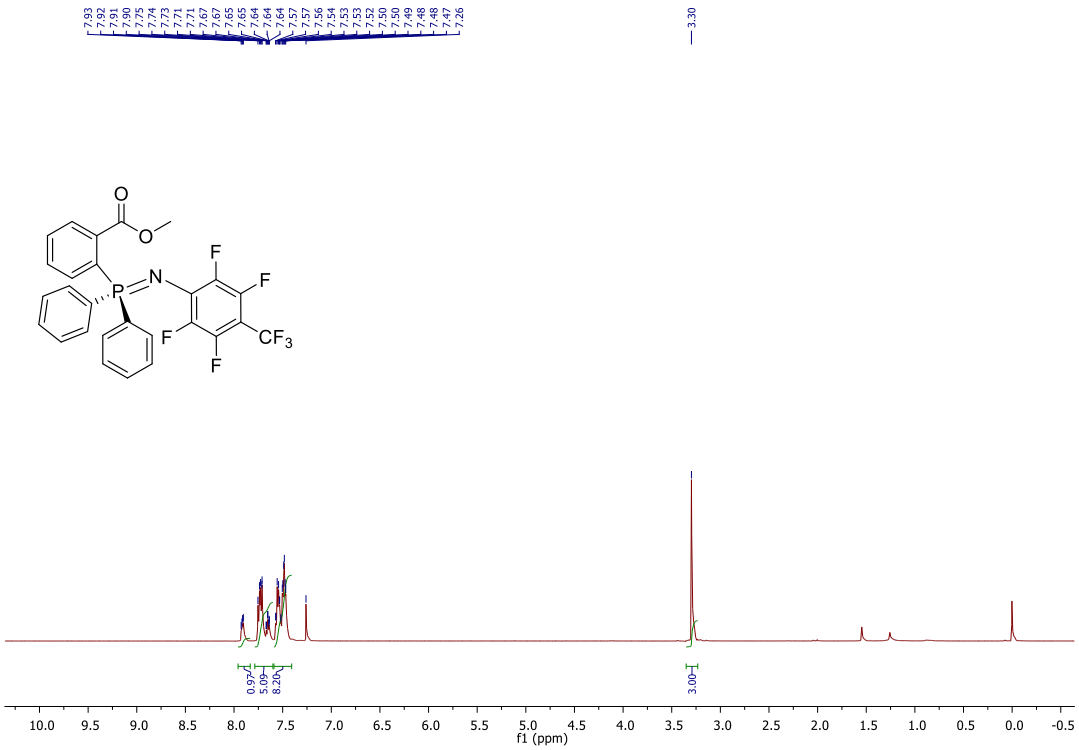

Figure S45. *^{1}H NMR spectrum of compound **3ca** in $CDCl_3$.*

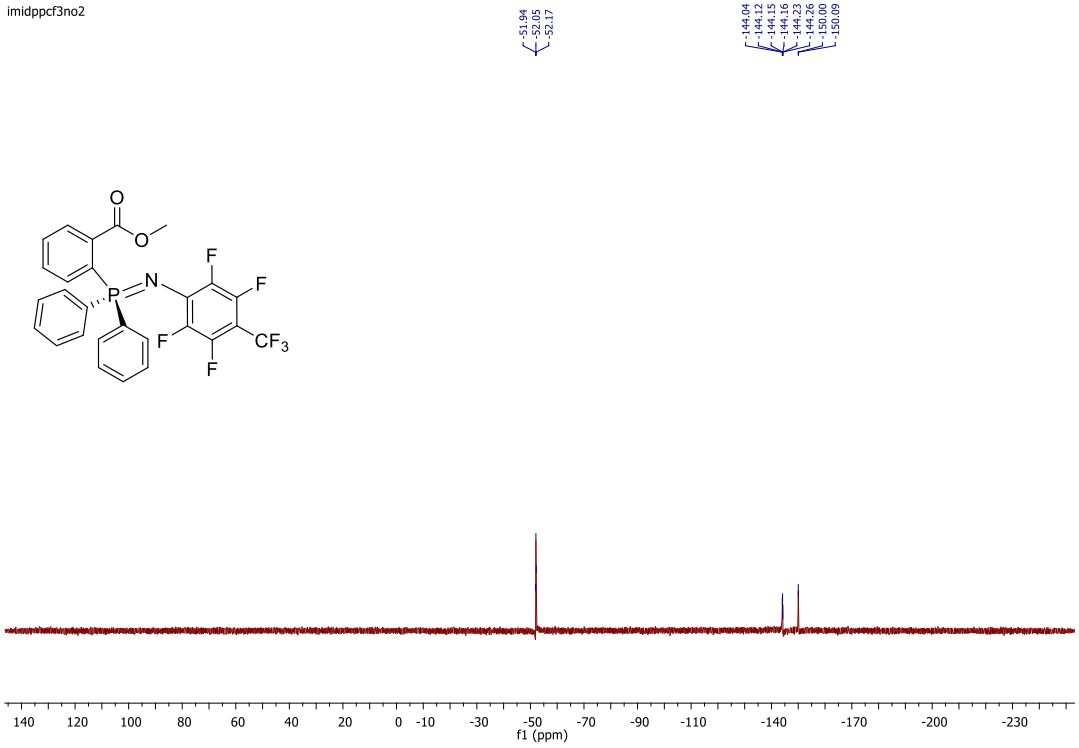

Figure S46. *^{19}F NMR spectrum of compound **3ca** in $CDCl_3$. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

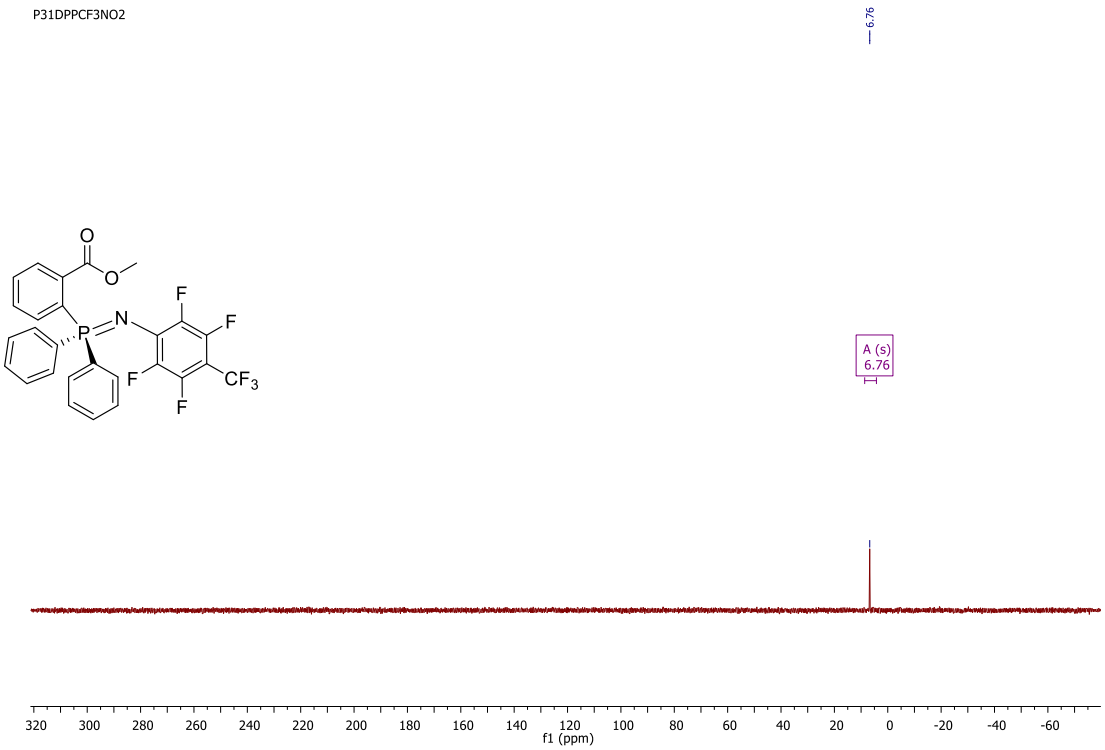

Figure S47. *^{31}P NMR spectrum of compound **3ca** in $CDCl_3$. Phosphoric acid (85%) used as external reference (0 ppm).*

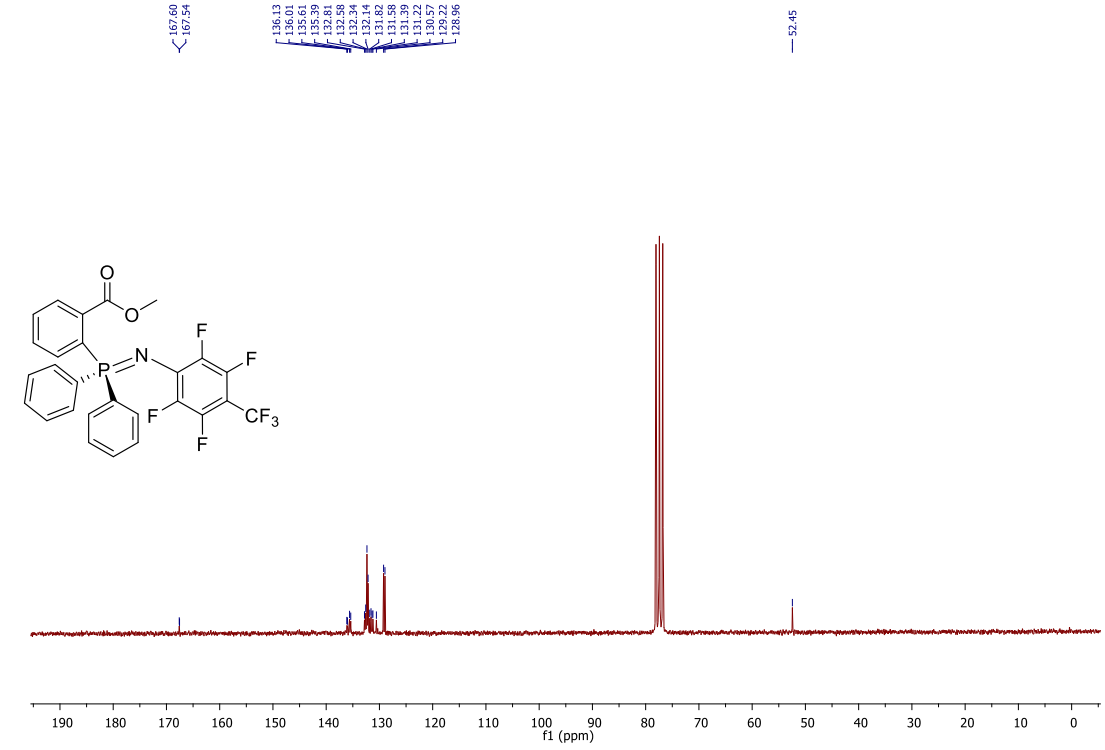

Figure S48. *^{13}C NMR spectrum of compound **3ca** in $CDCl_3$.*

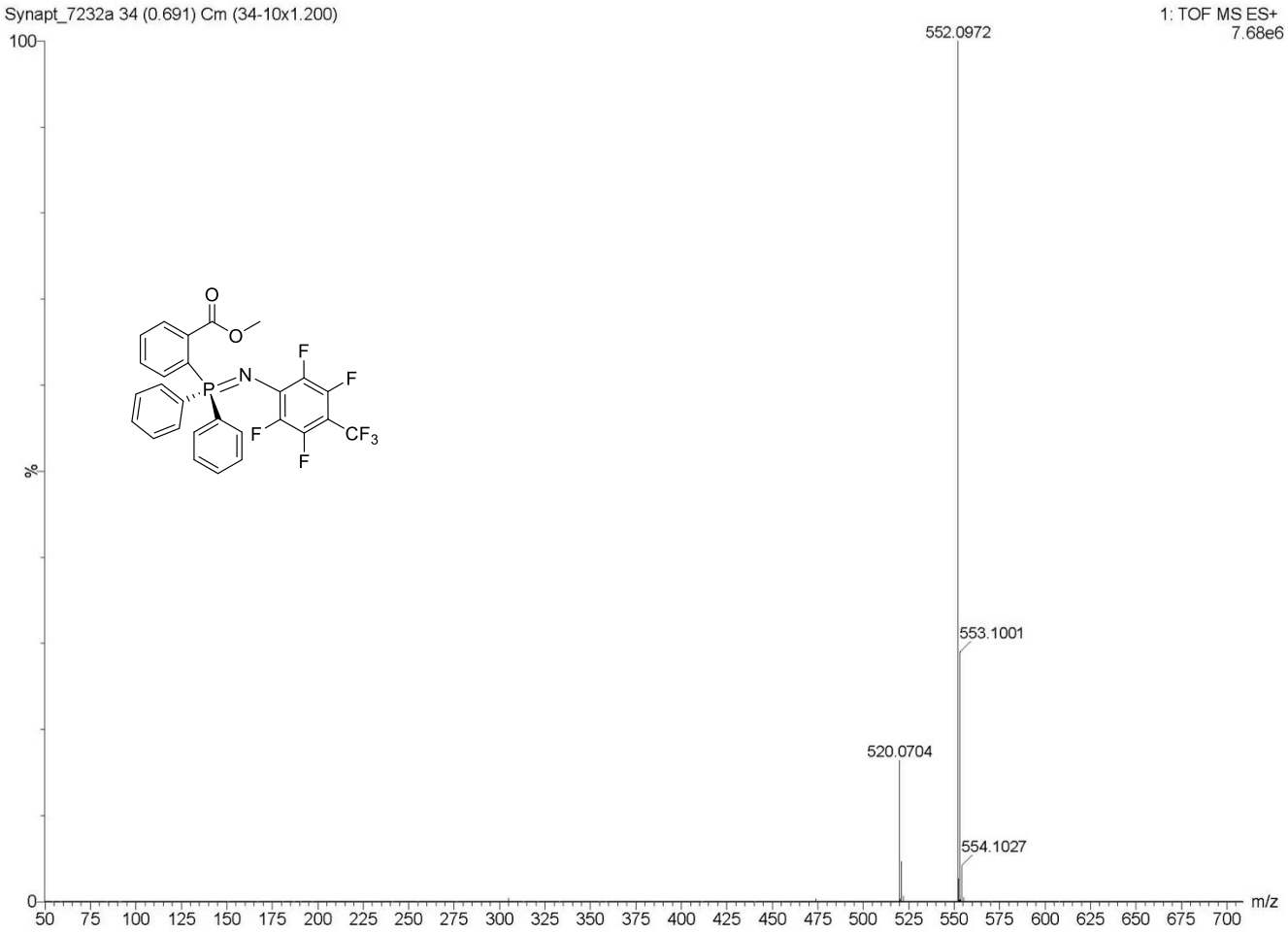

Figure S49**. HRMS spectrum of compound **3ca.

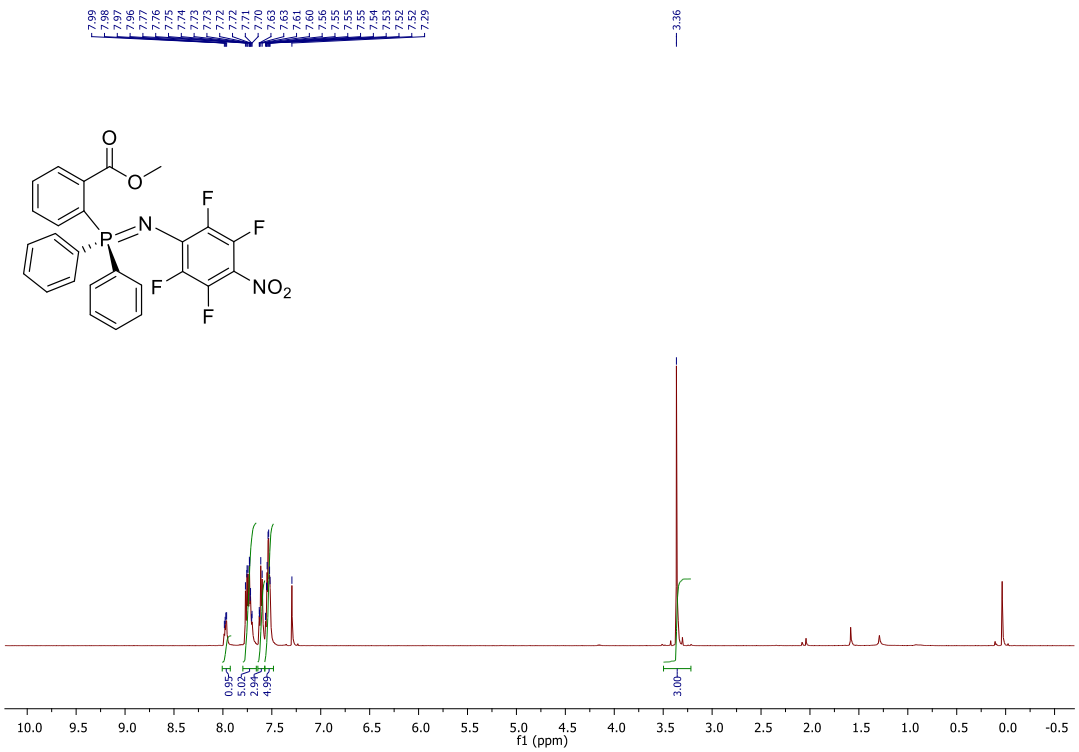

***Figure S50**. ^{1}H NMR spectrum of compound **3da** in $CDCl_3$.*

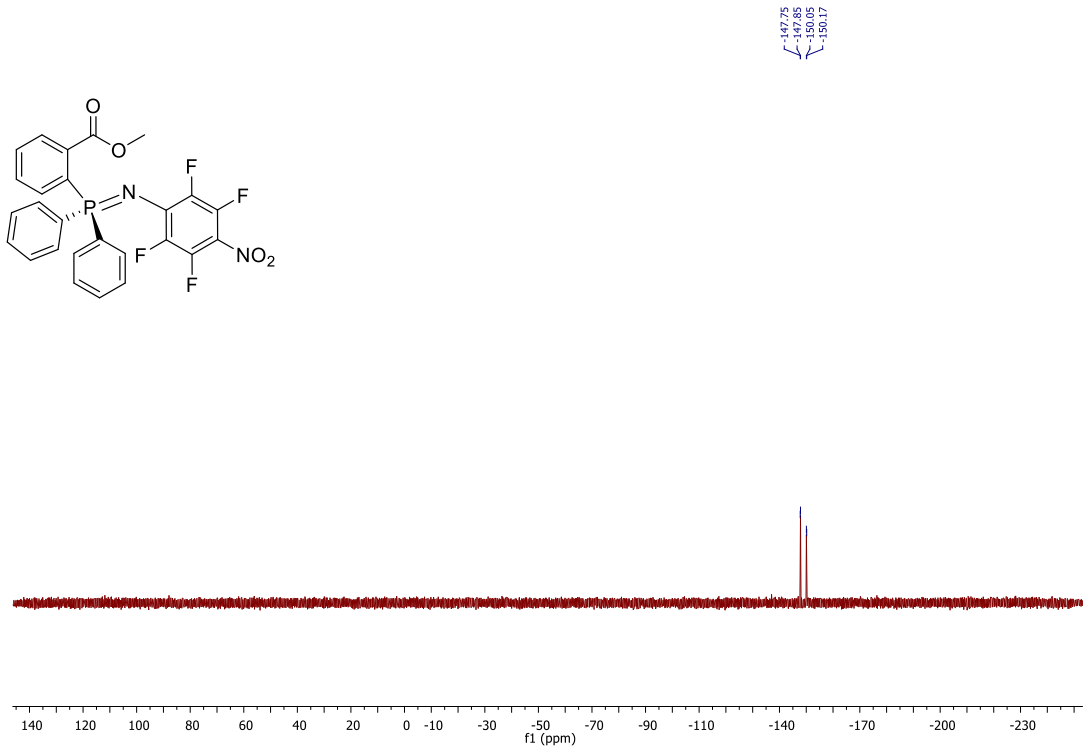

Figure S51. *^{19}F NMR spectrum of compound **3da** in $CDCl_3$. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

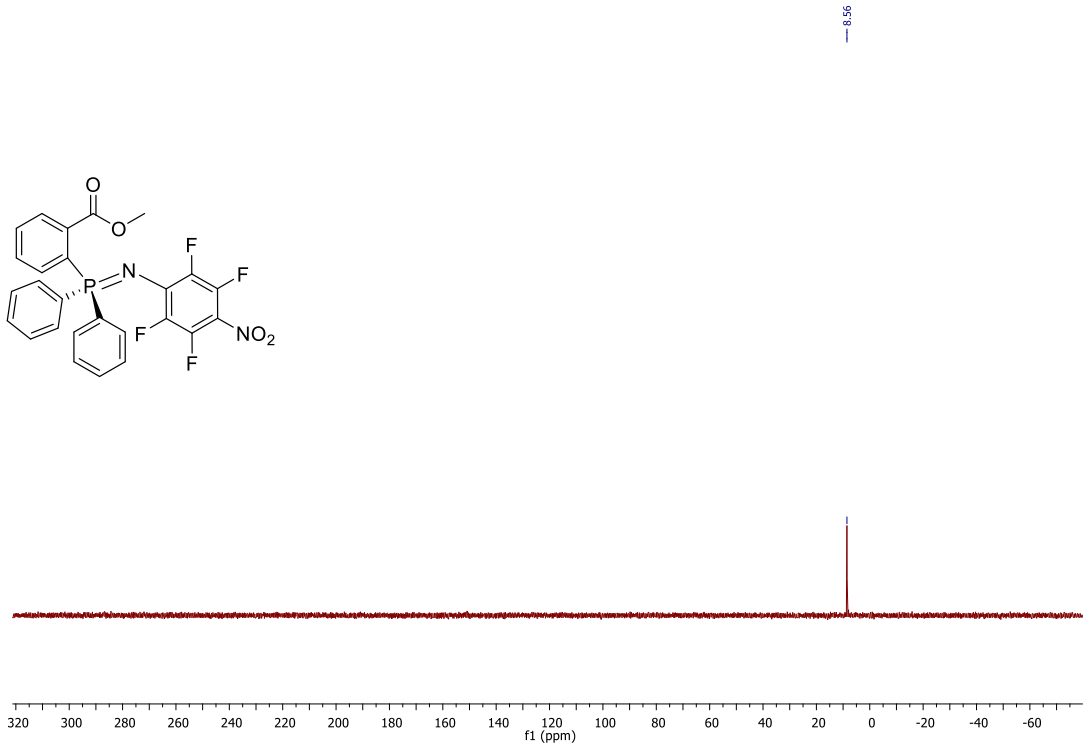

Figure S52. *^{31}P NMR spectrum of compound **3da** in $CDCl_3$. Phosphoric acid (85%) used as external reference (0 ppm).*

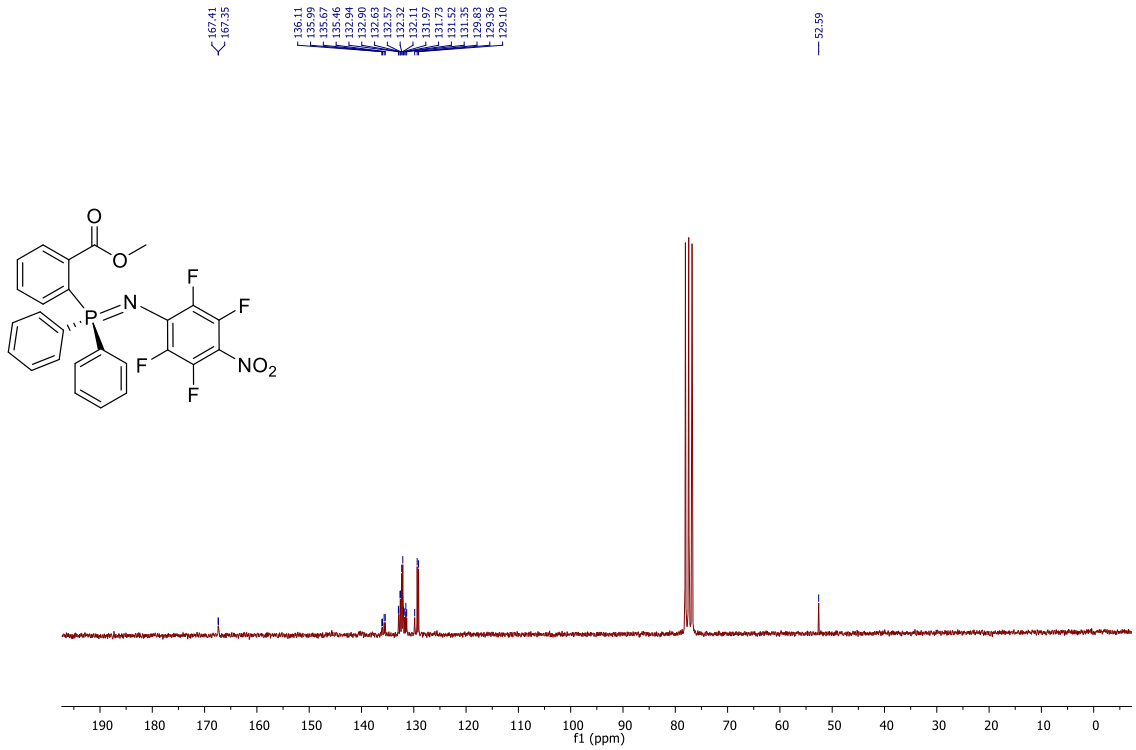

Figure S53. *^{13}C NMR spectrum of compound **3da** in $CDCl_3$.*

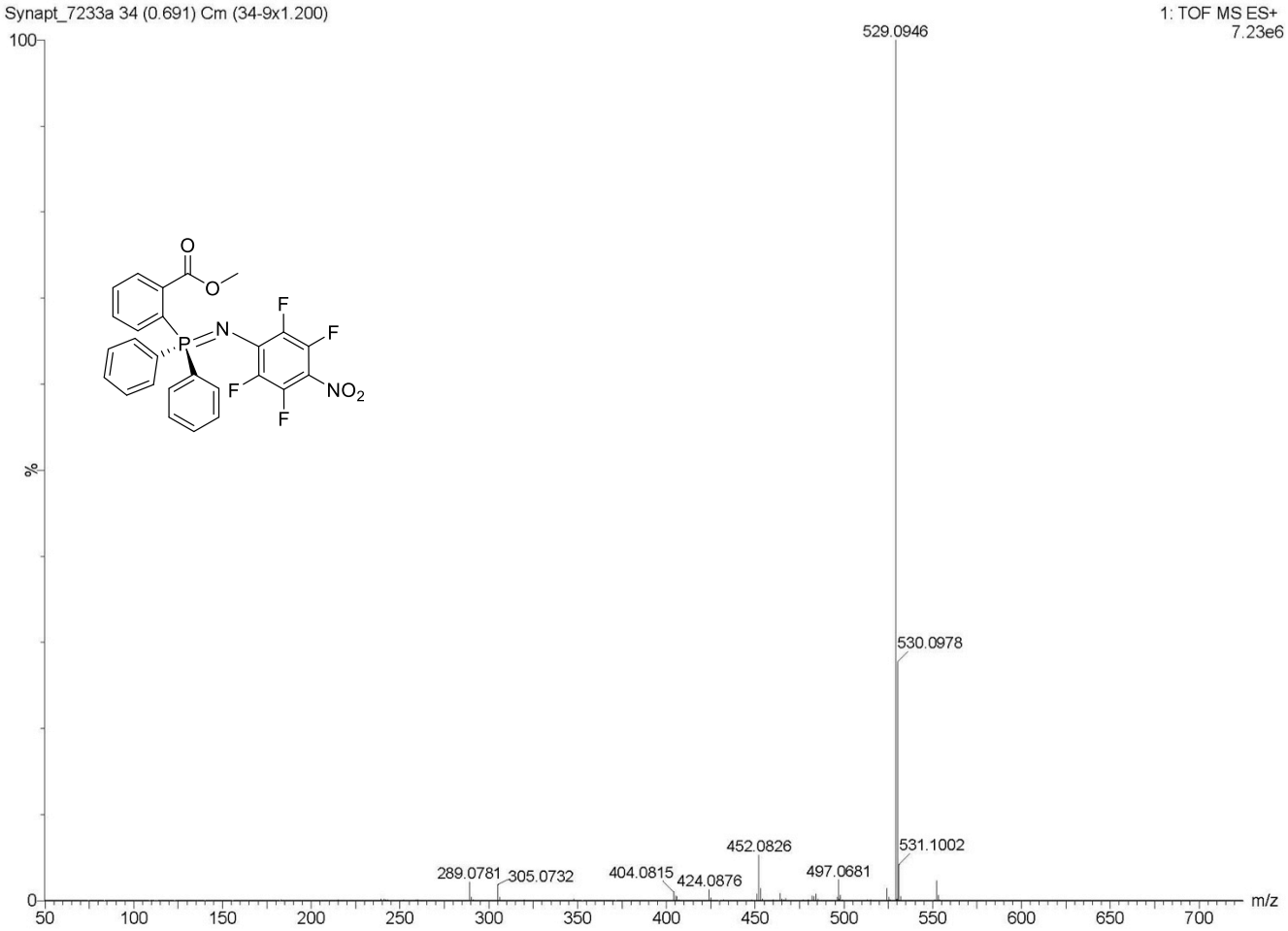

Figure S54. *HRMS spectrum of compound **3da**.*

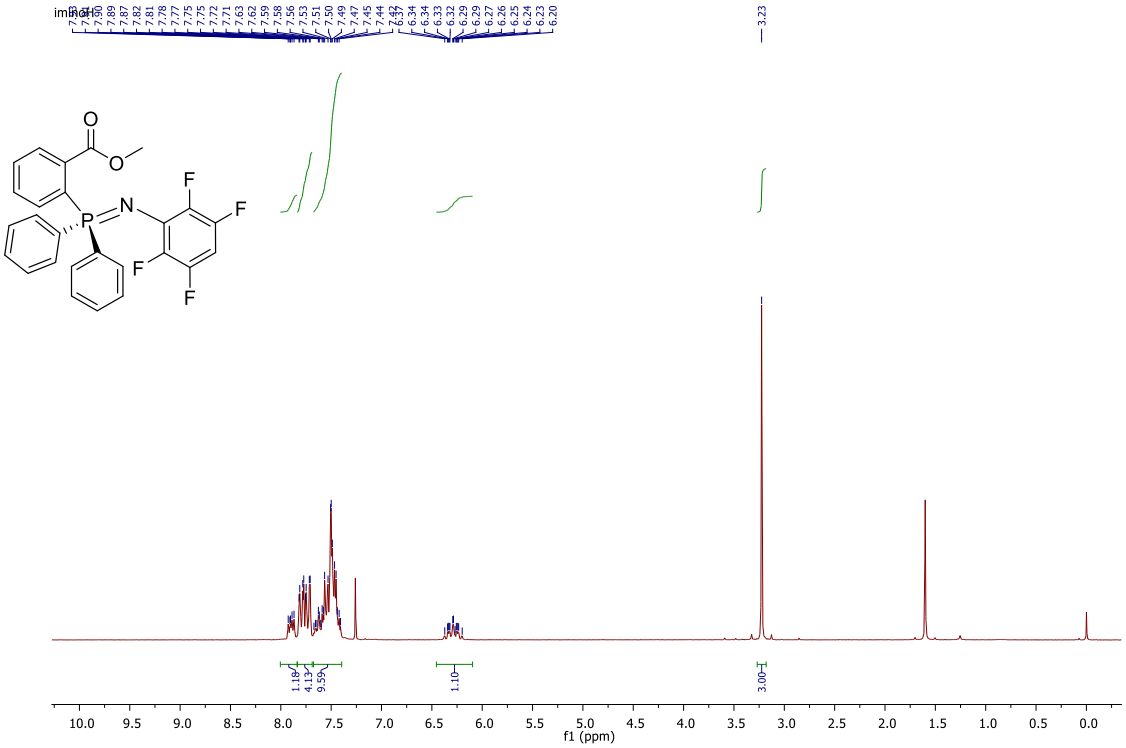

Figure S55. *^{1}H NMR spectrum of compound **3ea** in $CDCl_3$.*

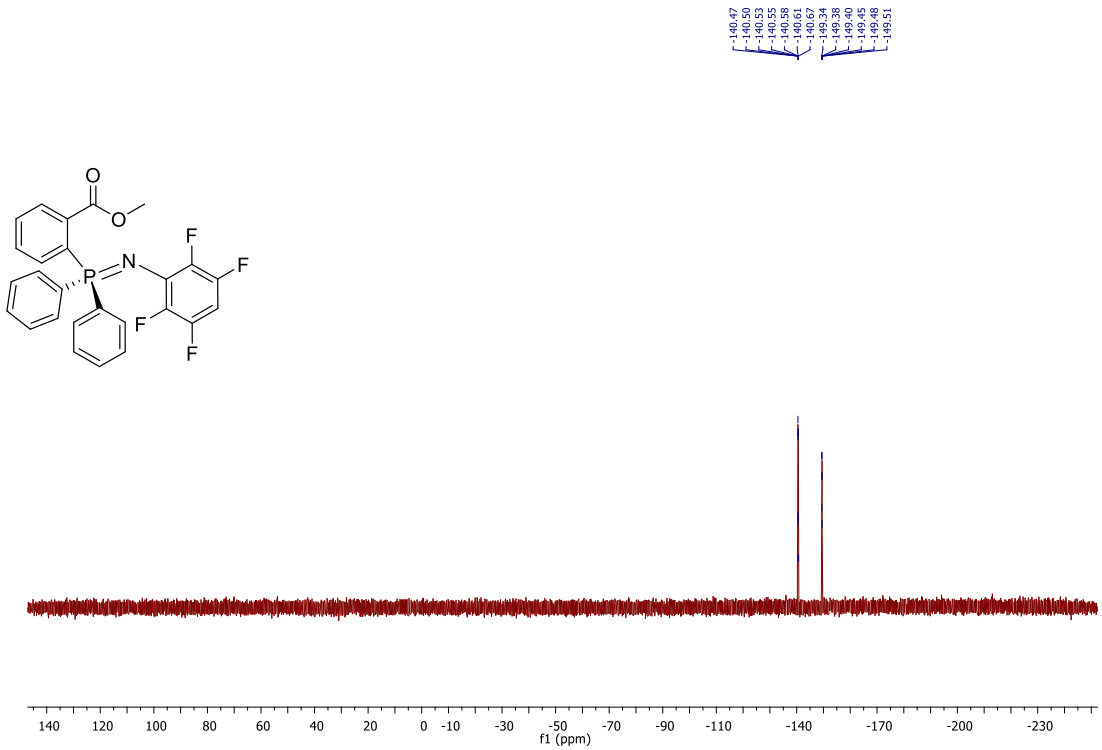

Figure S56. *^{19}F NMR spectrum of compound **3ea** in $CDCl_3$. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

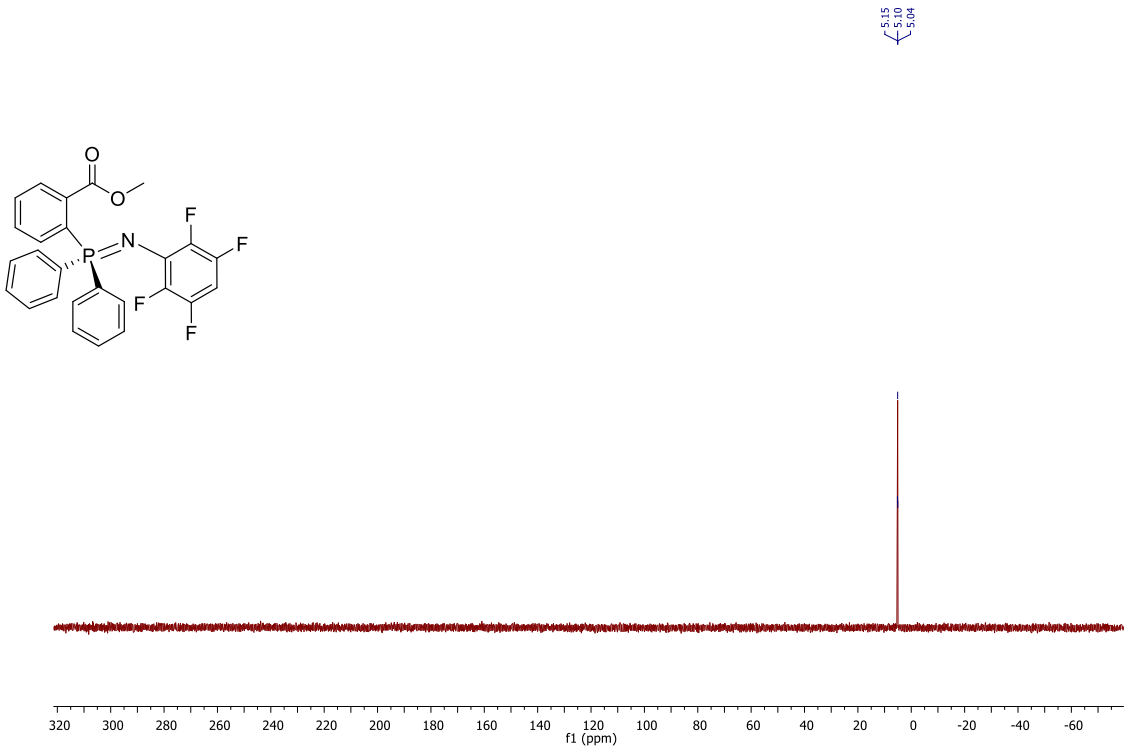

Figure S57. *^{31}P NMR spectrum of compound **3ea** in $CDCl_3$. Phosphoric acid (85%) used as the external reference (0 ppm).*

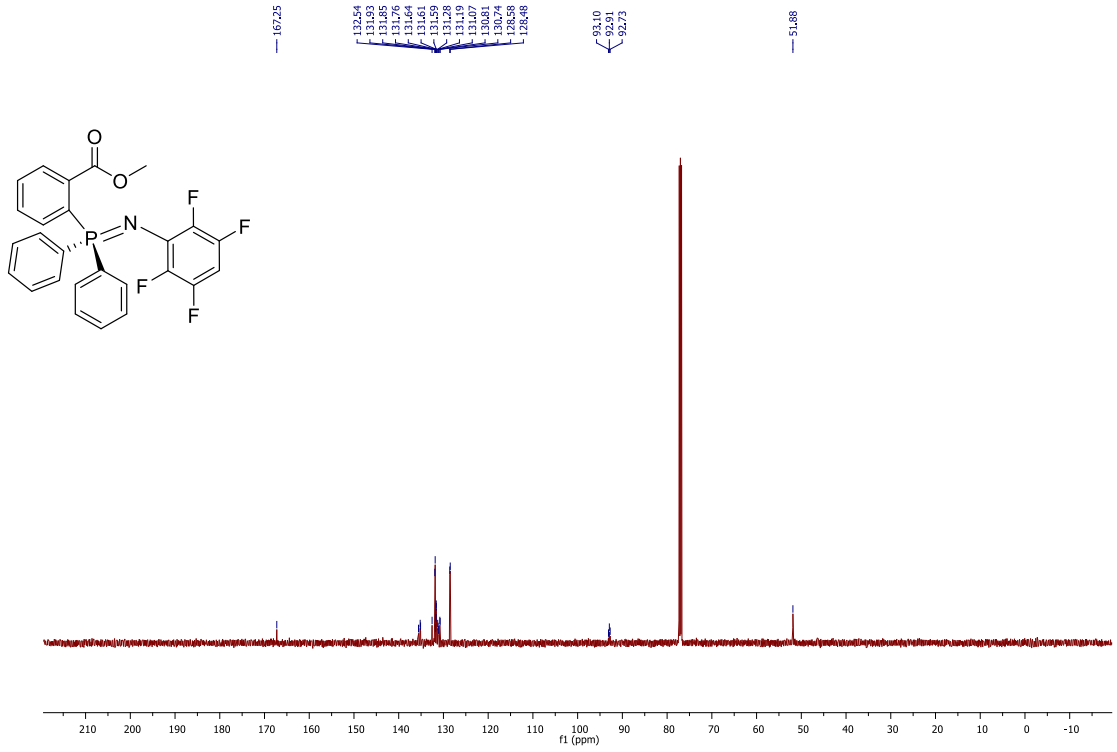

Figure S58. *^{13}C NMR spectrum of compound **3ea** in $CDCl_3$.*

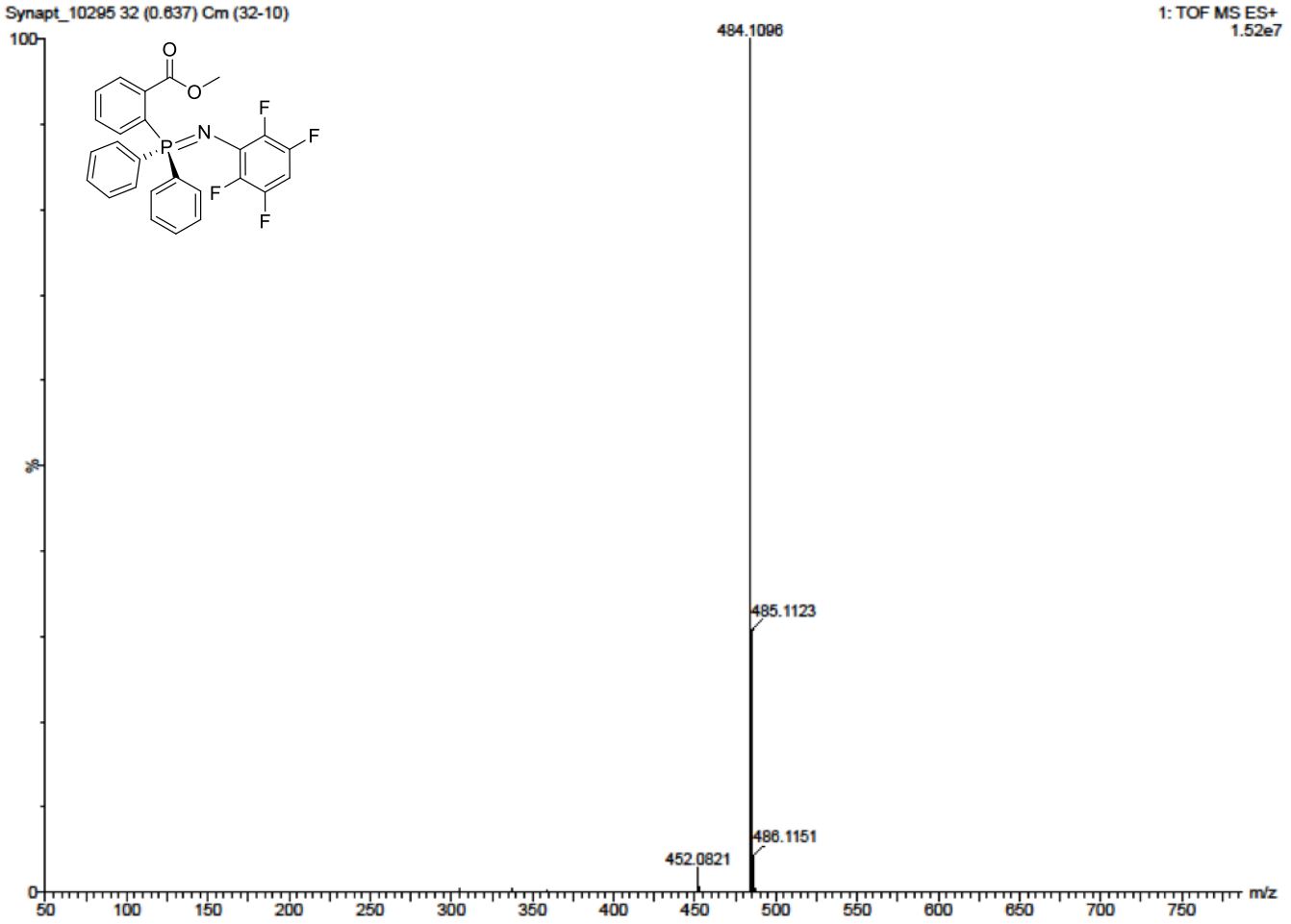

Figure S59**. HRMS spectrum of compound **3ea.

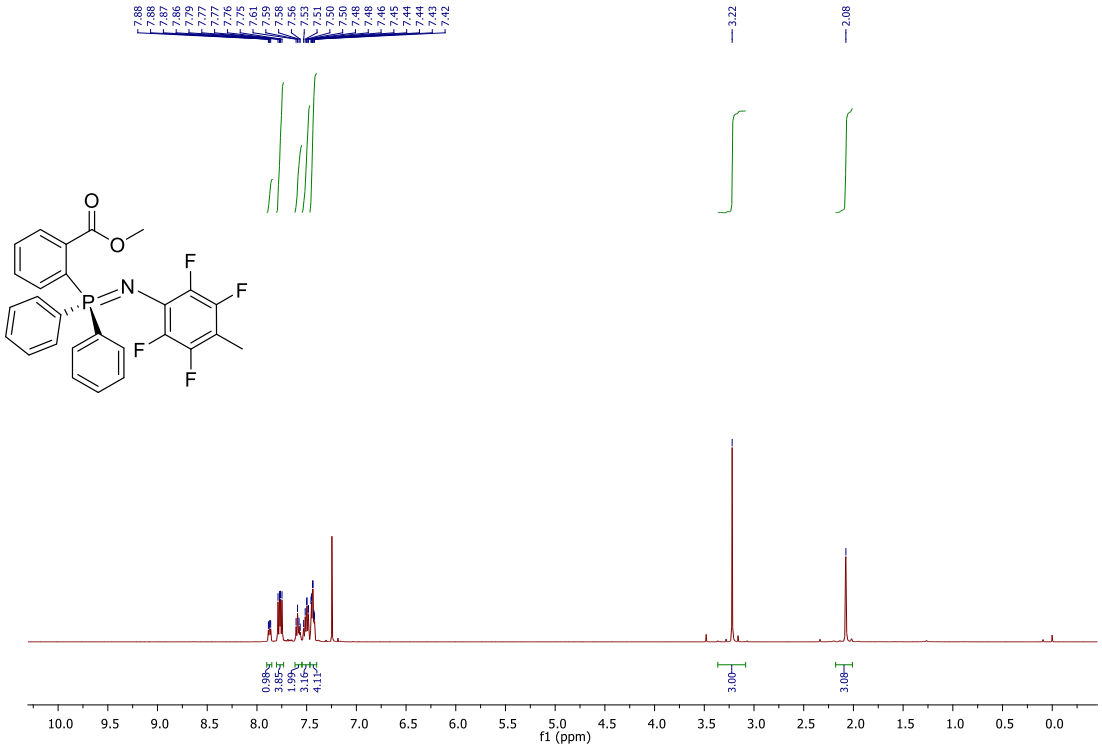

***Figure S60**. ^{1}H NMR spectrum of compound **3fa** in $CDCl_3$.*

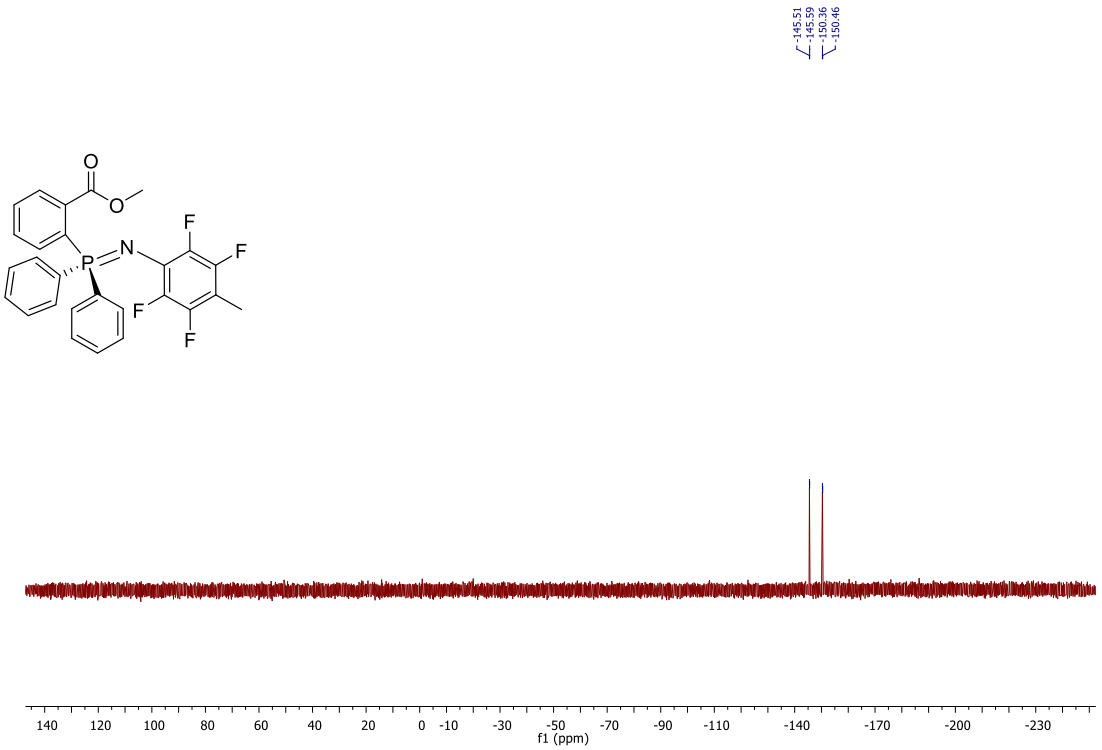

Figure S61. *^{19}F NMR spectrum of compound **3fa** in $CDCl_3$. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

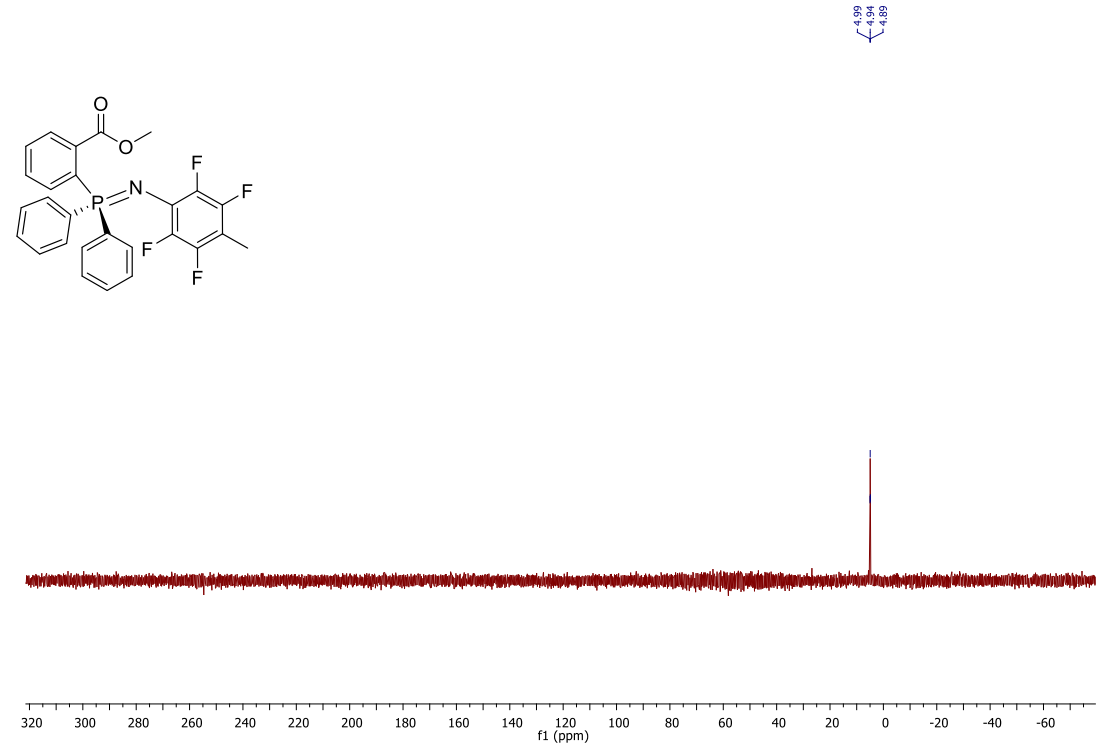

Figure S62. *^{31}P NMR spectrum of compound **3fa** in $CDCl_3$. Phosphoric acid (85%) used as external reference (0 ppm).*

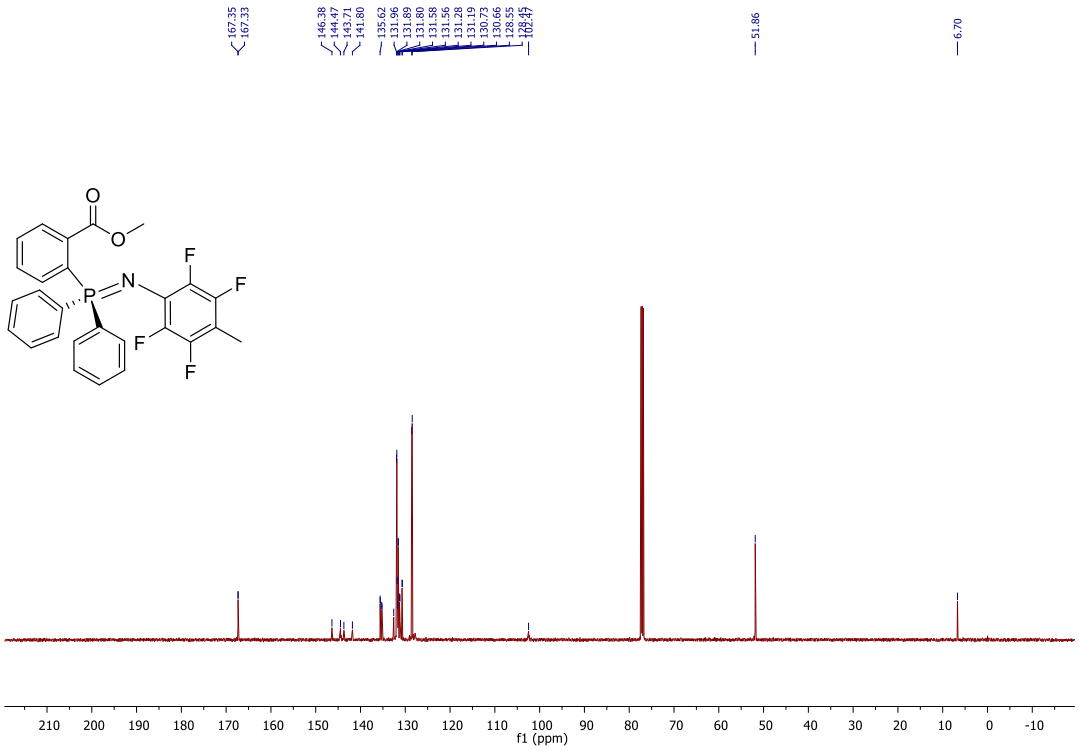

Figure S63. *^{13}C NMR spectrum of compound **3fa** in $CDCl_3$.*

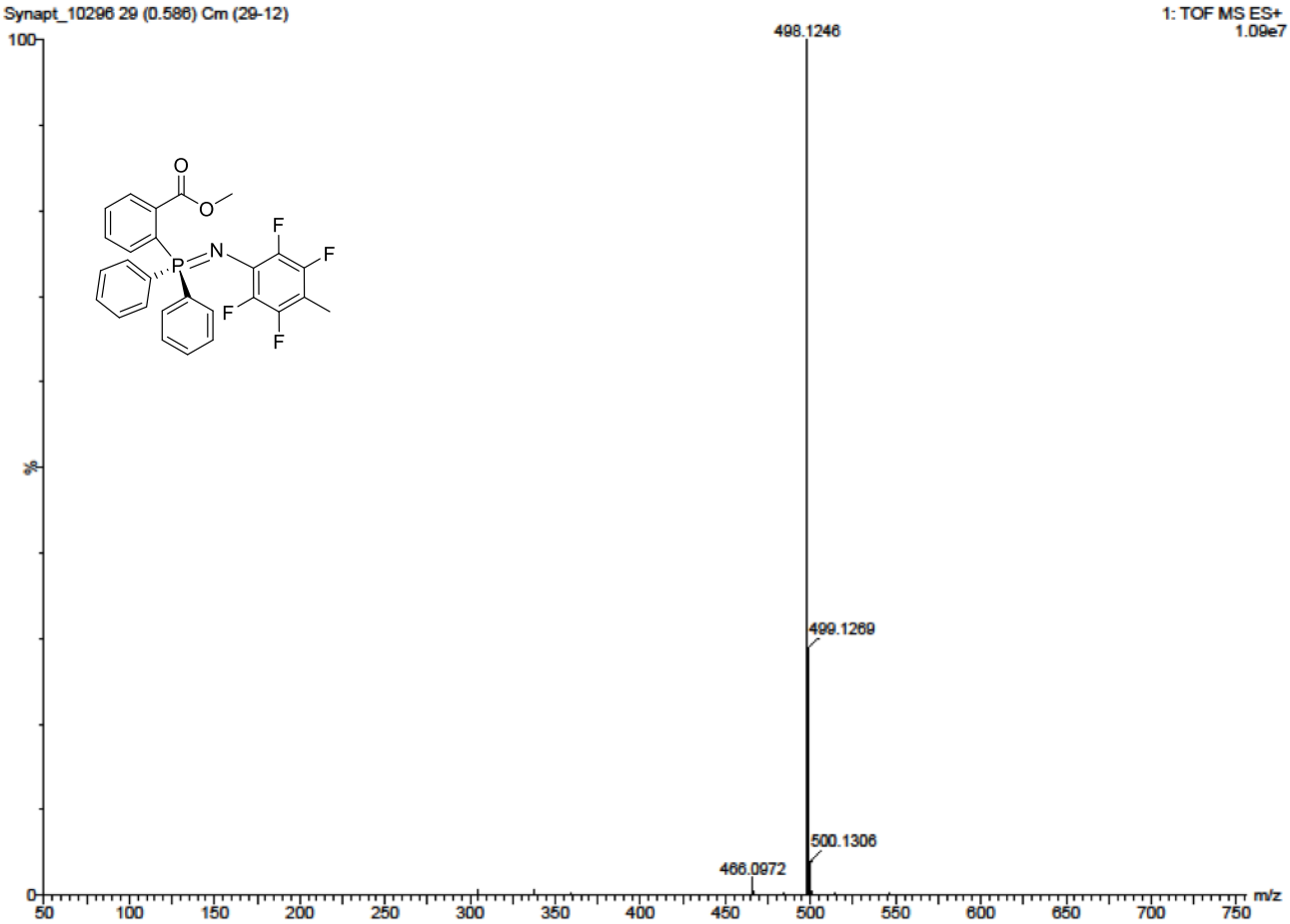

Figure S64. *HRMS spectrum of compound **3fa**.*

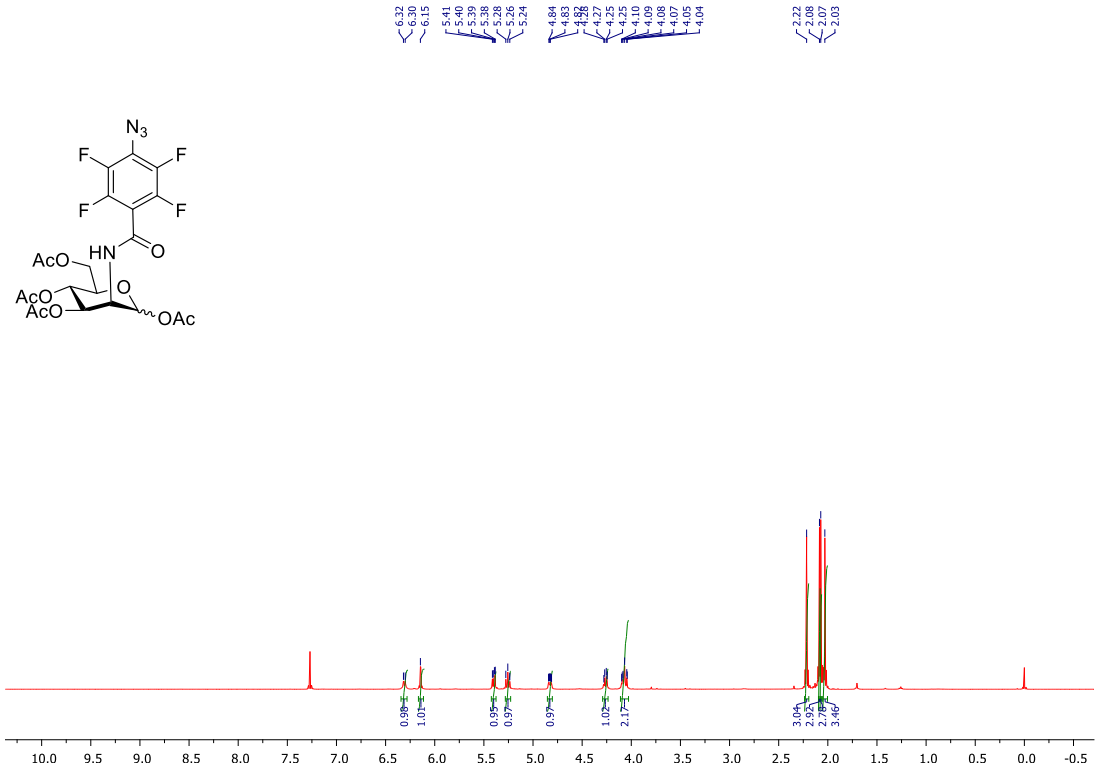

Figure S65. *^{1}H NMR spectrum of compound **4a** in $CDCl_3$.*

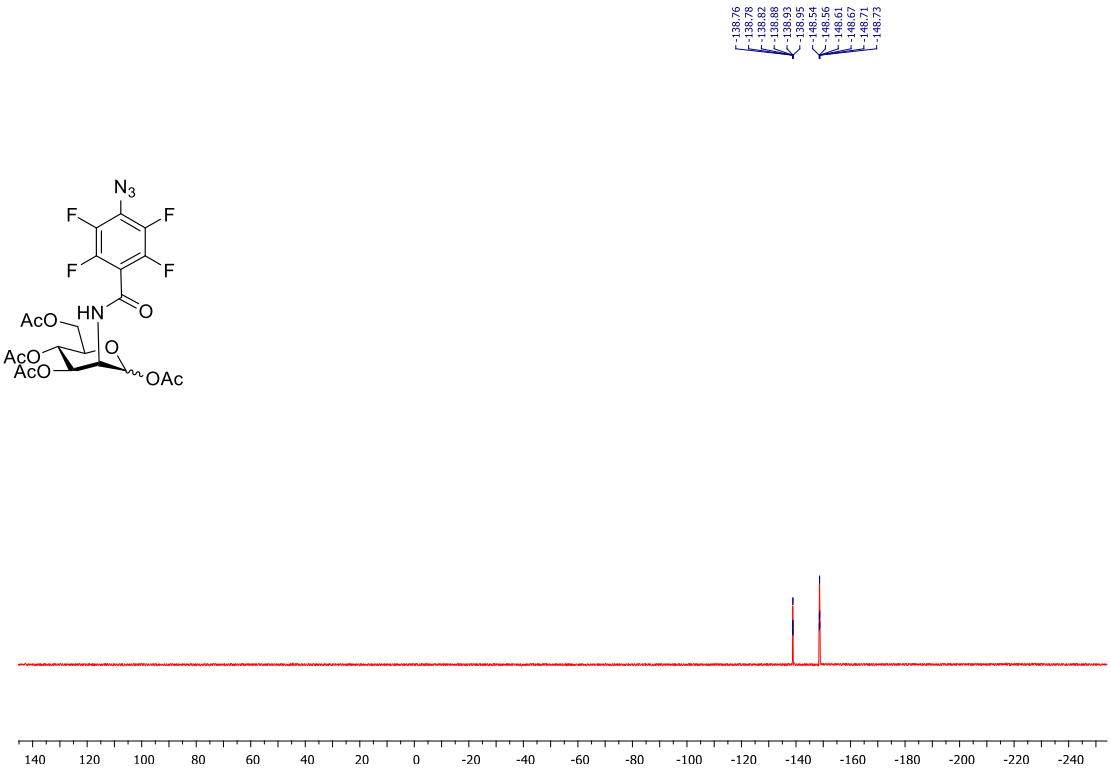

Figure S66. *^{19}F NMR spectrum of compound **4a** in $CDCl_3$. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

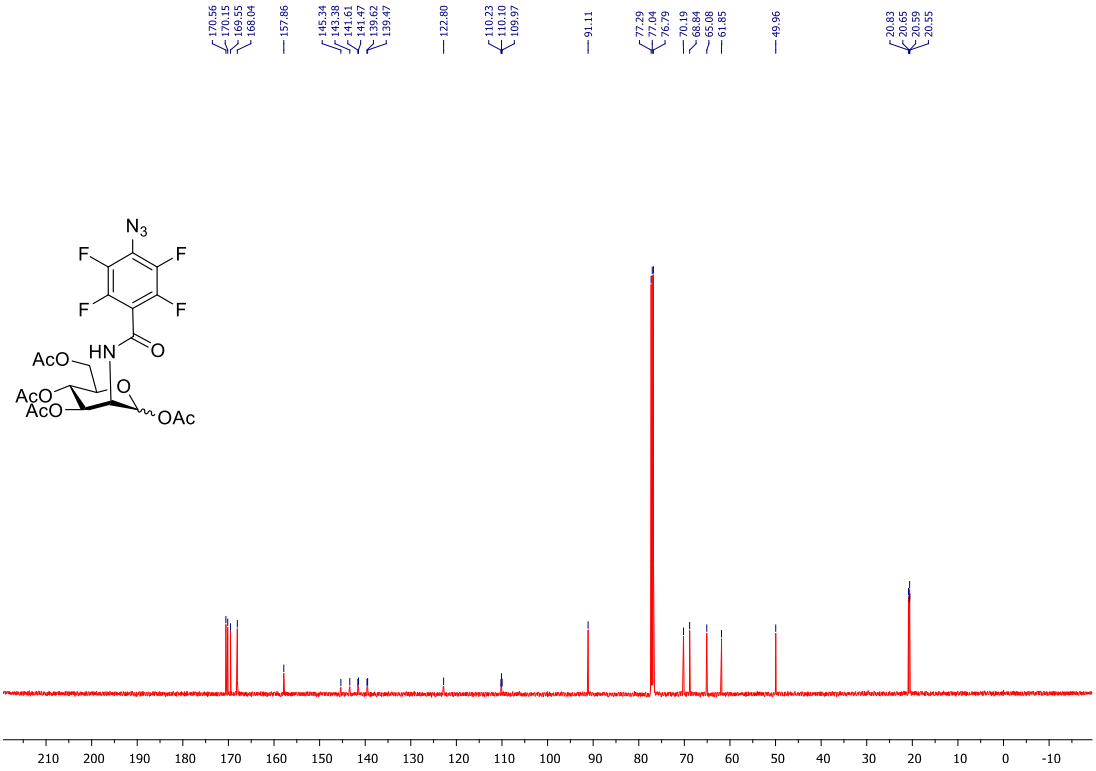

Figure S67. *^{13}C NMR spectrum of compound **4a** in $CDCl_3$.*

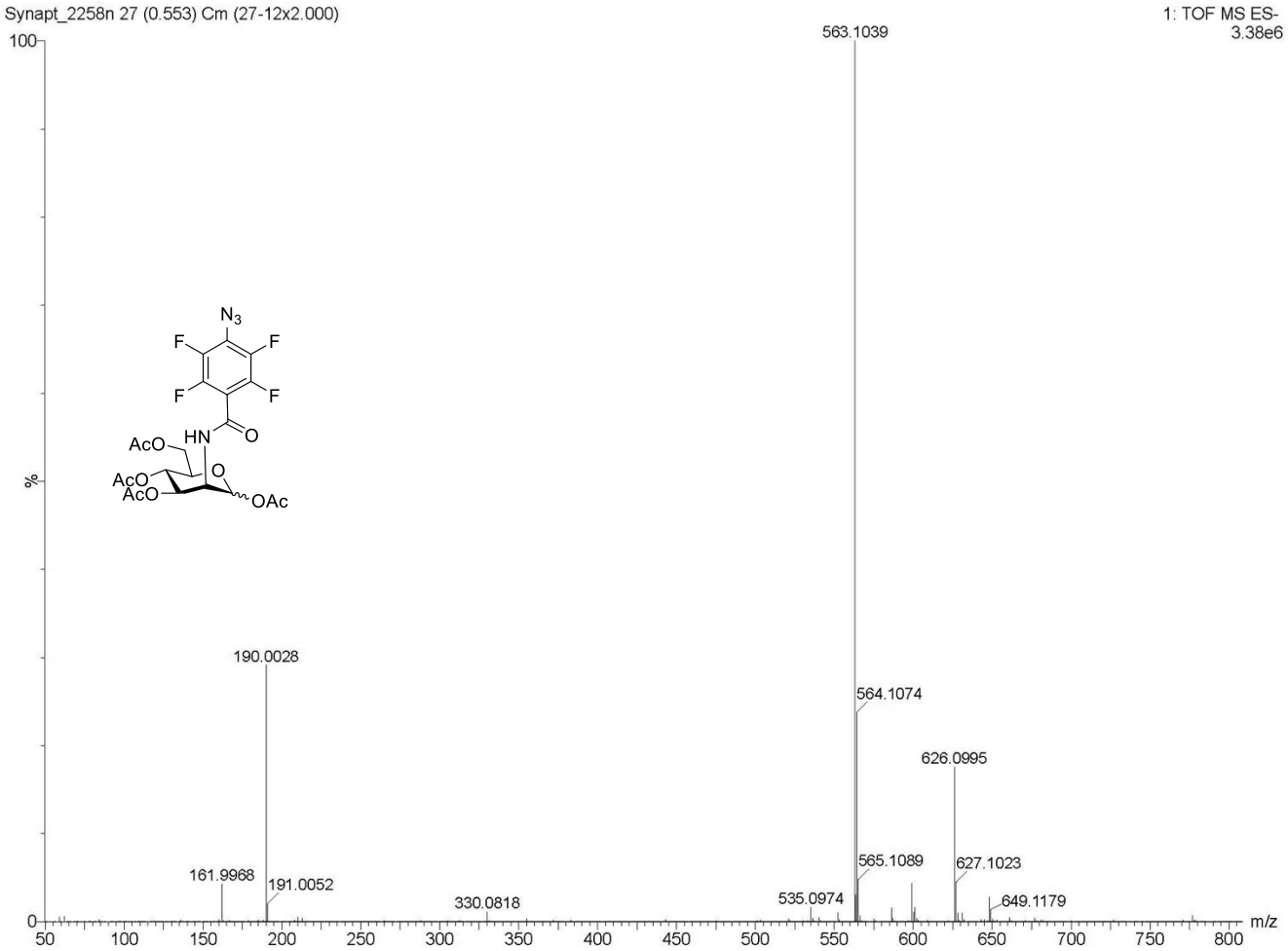

Figure S68. *HRMS spectrum of compound **4a**.*

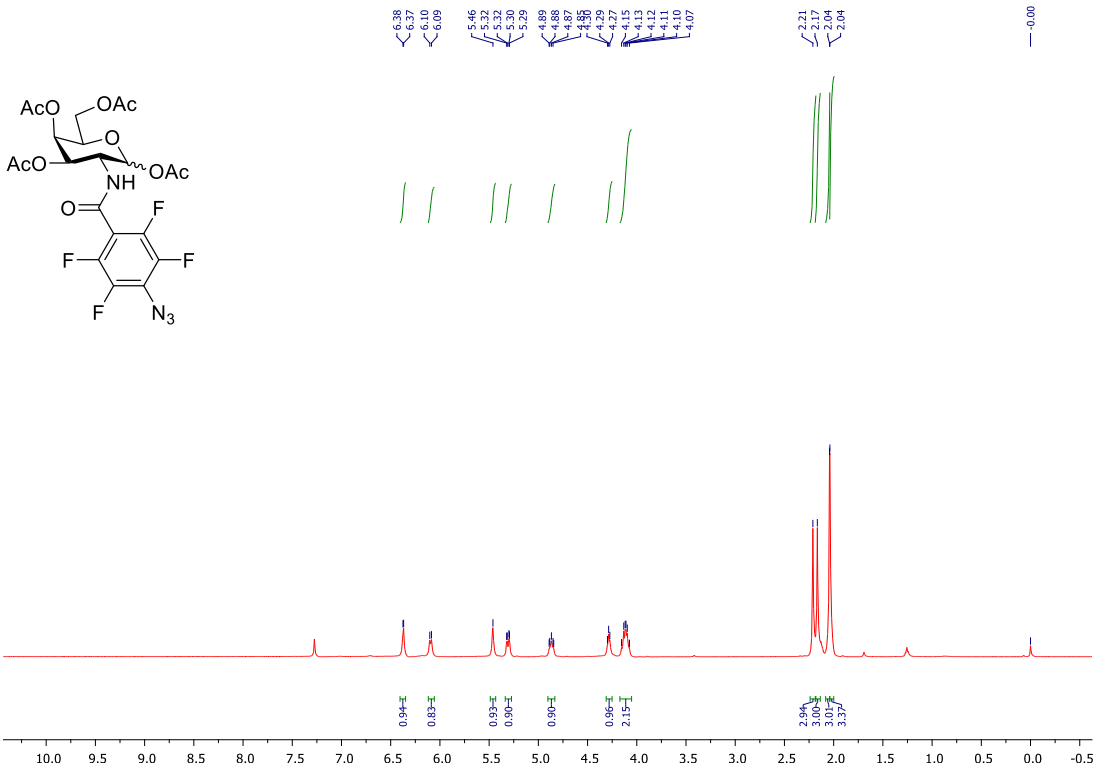

Figure S69. *^{1}H NMR spectrum of compound **4b** in $CDCl_3$.*

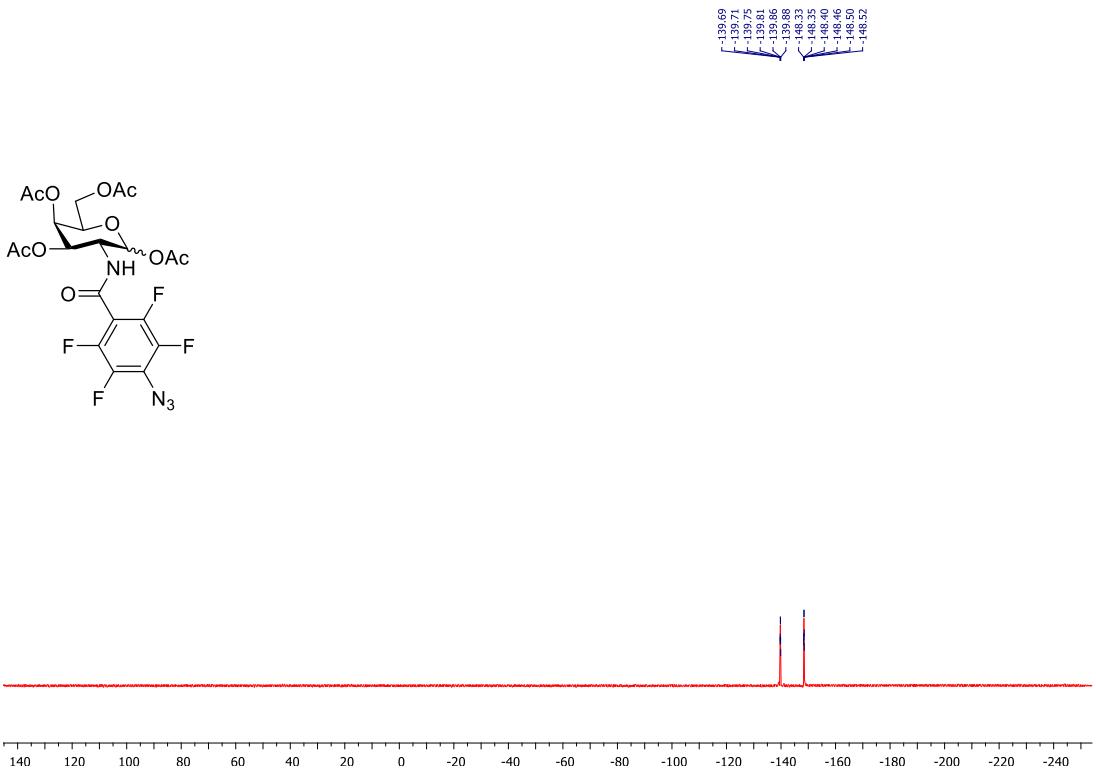

Figure S70. *^{19}F NMR spectrum of compound **4b** in $CDCl_3$. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

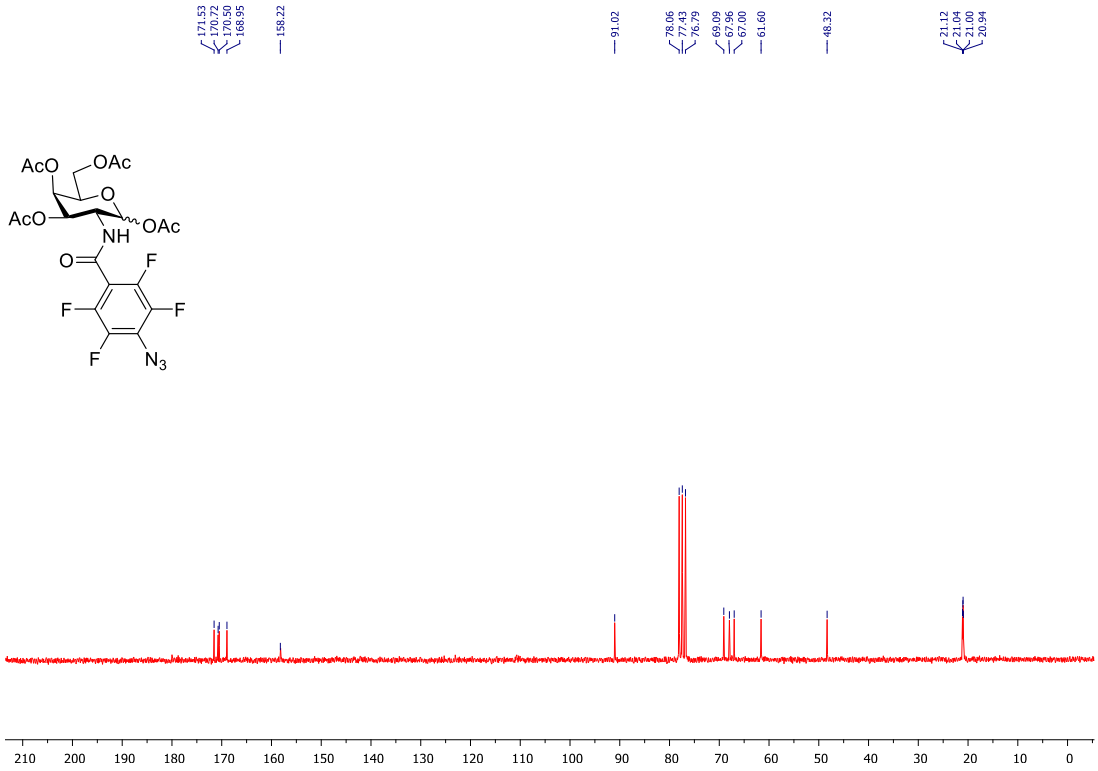

Figure S71. *^{13}C NMR spectrum of compound **4b** in $CDCl_3$.*

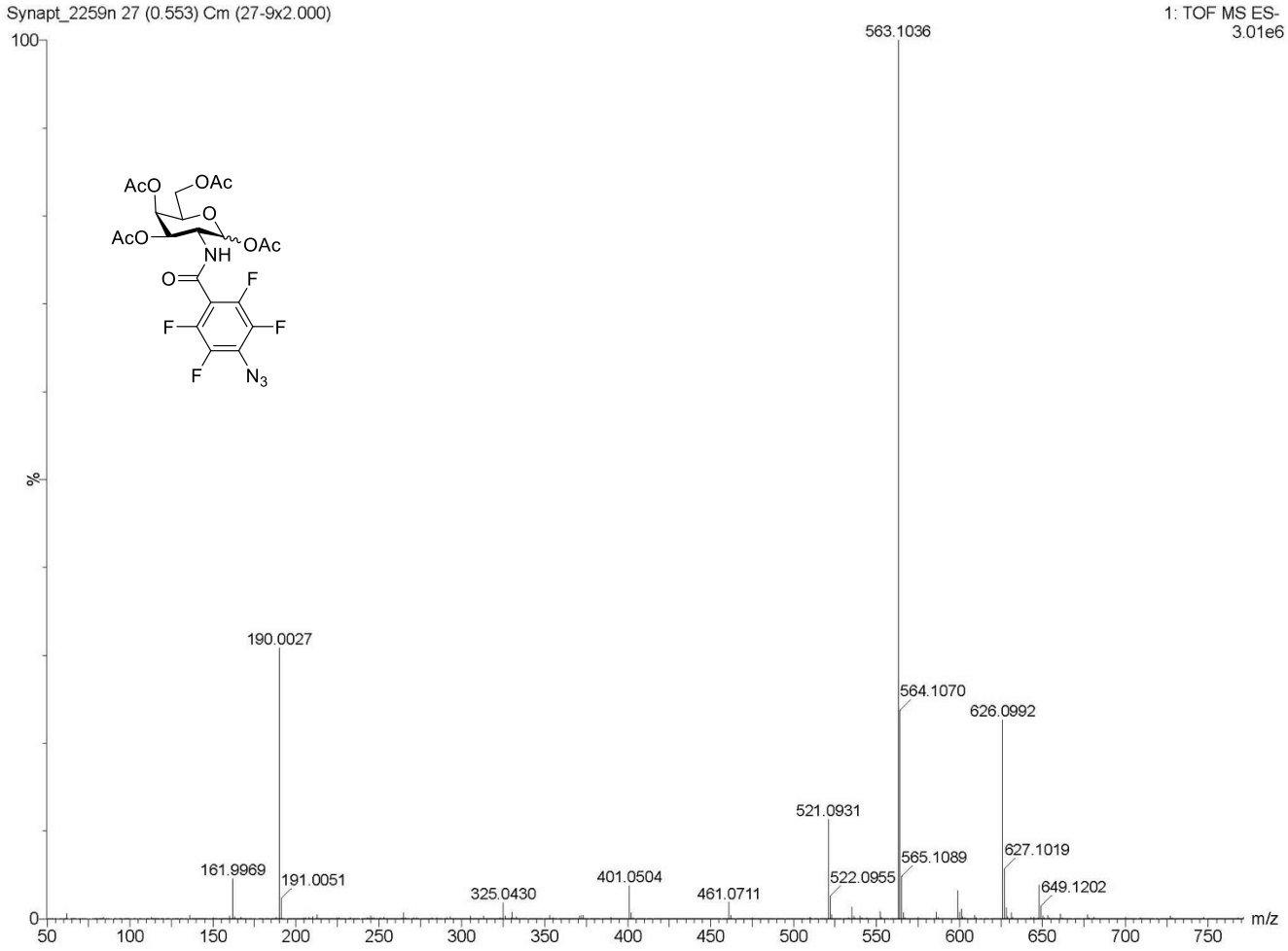

Figure S72. *HRMS spectrum of compound **4b**.*

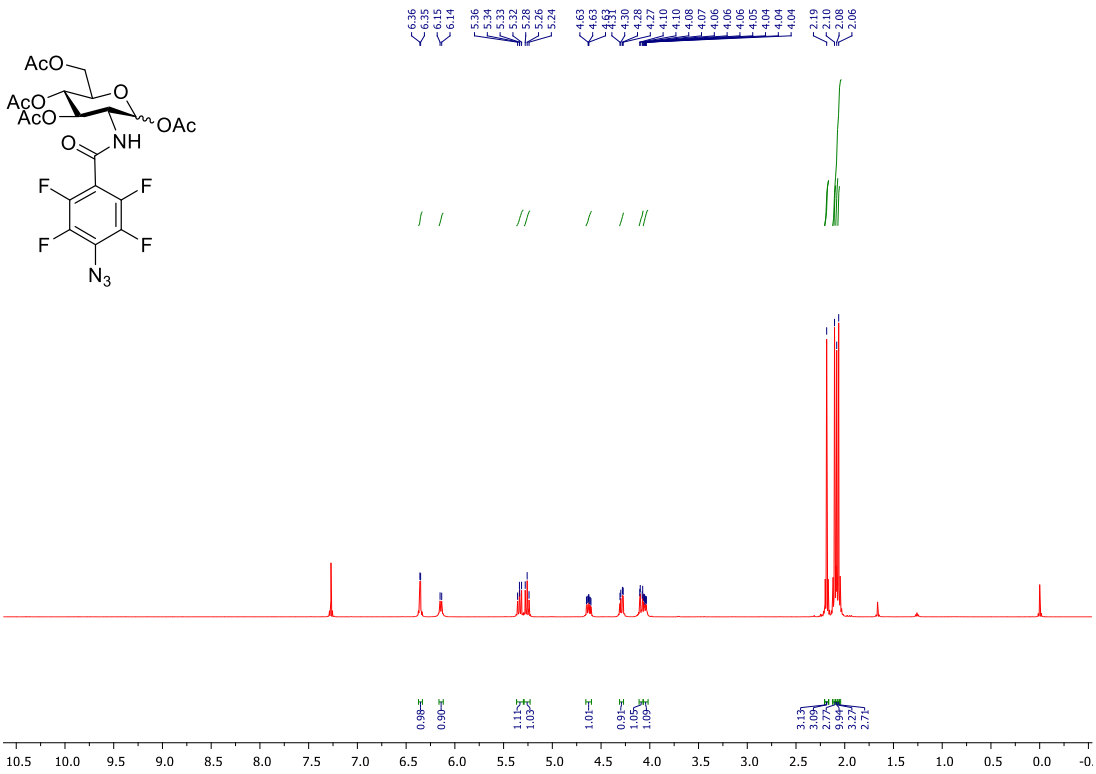

Figure S73. *^{1}H NMR spectrum of compound **4c** in $CDCl_3$.*

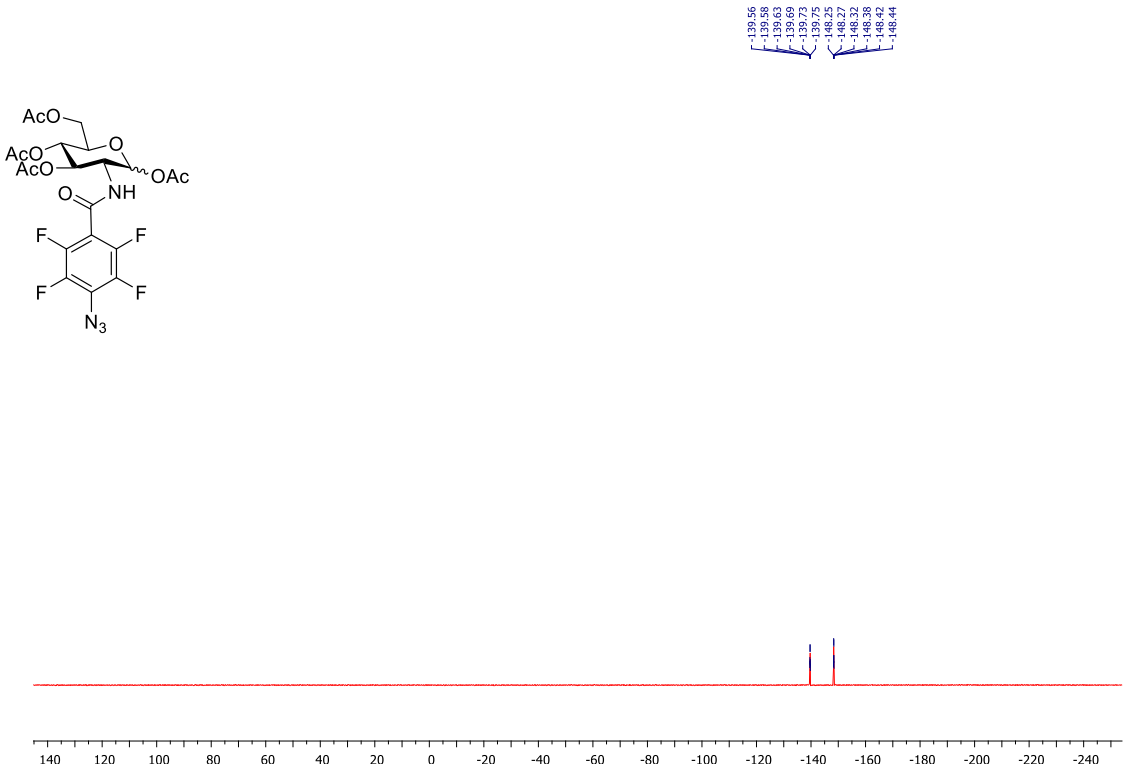

Figure S74. *^{19}F NMR spectrum of compound **4c** in $CDCl_3$. Trifluoroacetic acid (-76.55 ppm) used as external reference.*

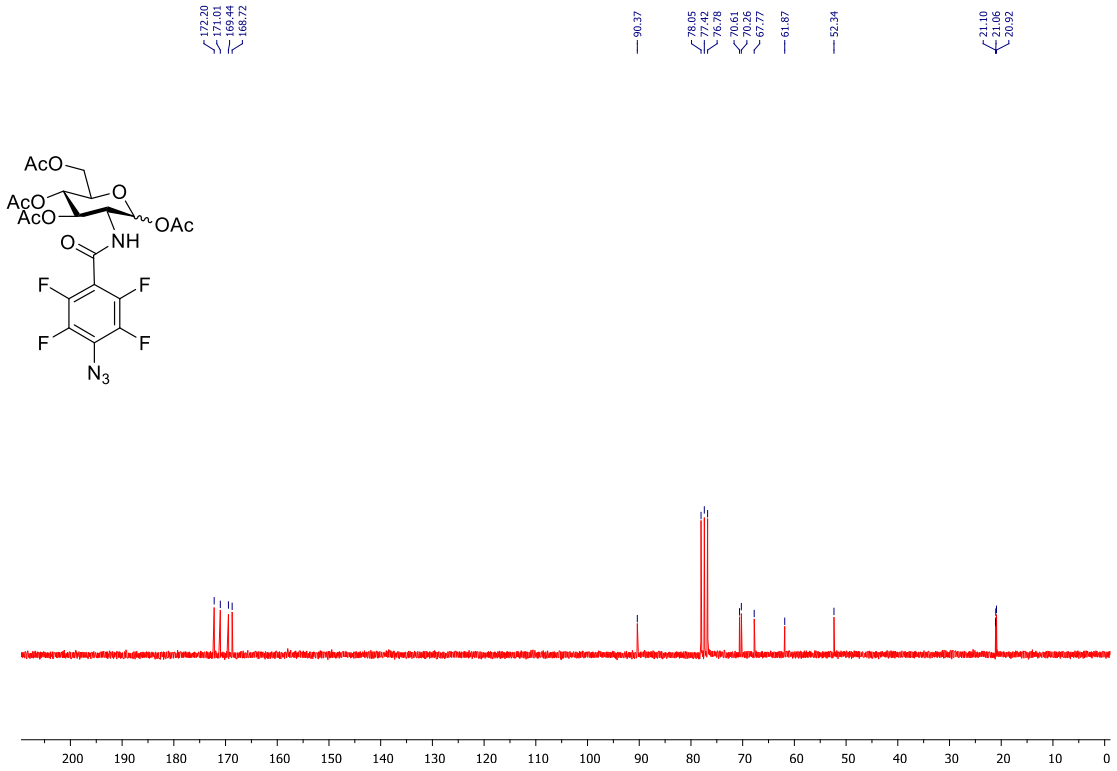

***Figure S75**. [13]C NMR spectrum of compound **4c** in $CDCl_3$.*

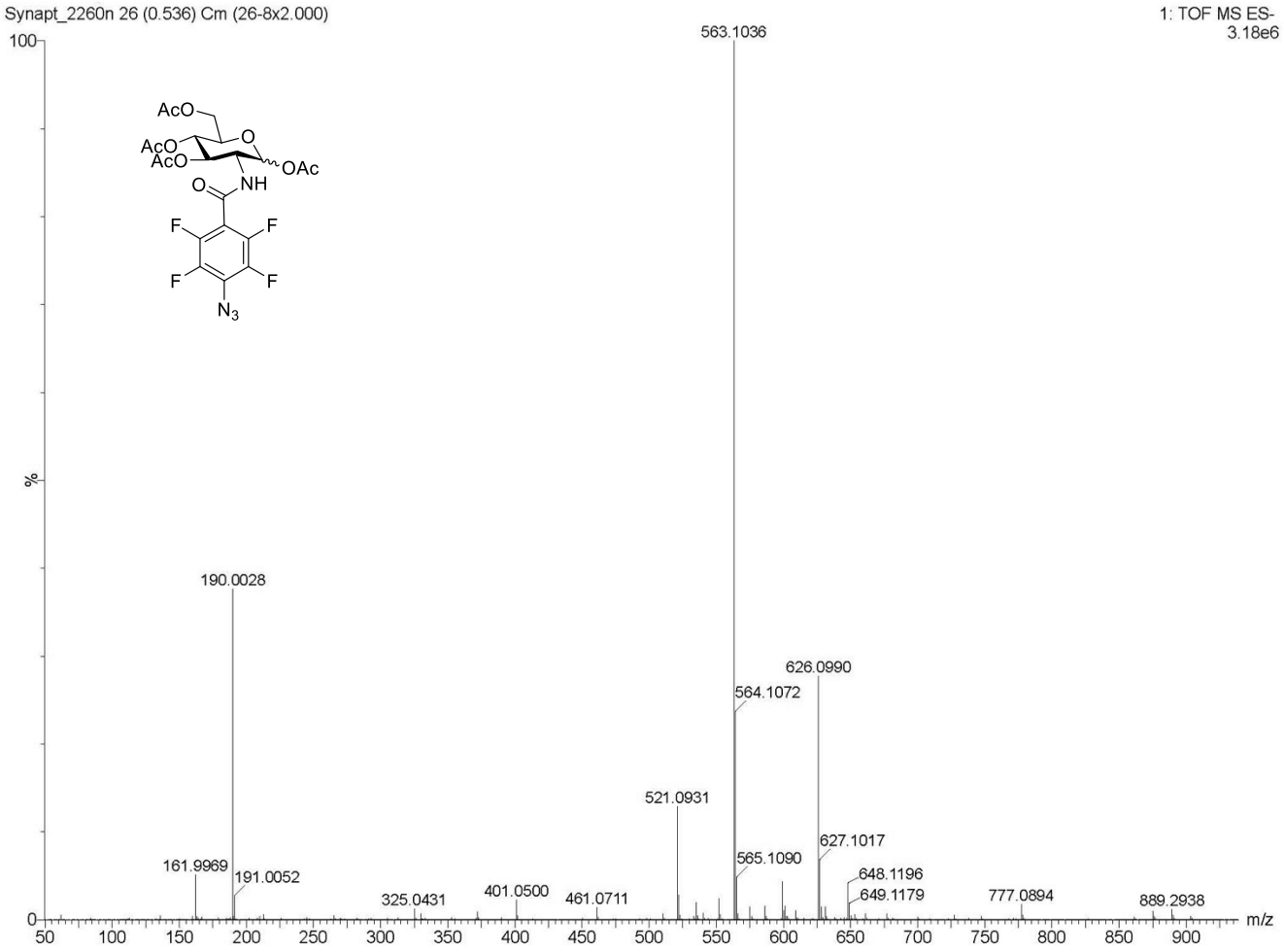

***Figure S76**. HRMS spectrum of compound **4c**.*