Supporting information

Robust Synthesis of NIR-emissive P-Rhodamine Fluorophores

Maria Sauer,[1] Veselin Nasufovic,[1] Hans-Dieter Arndt,[1*] Ivan Vilotijevic[1*]

[1]Friedrich-Schiller-Universität, Institut für Organische und Makromolekulare Chemie, Humboldtstr. 10, D-07743 Jena, Germany.

*Authors to whom correspondence should be addressed: ivan.vilotijevic@uni-jena.de hd.arndt@uni-jena.de,

Table of content

1. General information

1.1. Reagents

All reagents were purchased from Acros Chemicals, Alfa Aesar, Apollo Scientific, ABCR, Carbolution Chemicals, Carbosynth, Manchester Organics, Merck, Novabiochem, Sigma-Aldrich, TCI Europe, VWR and used without further purification. Cyanin 5.5 NHS-Ester was purchased from Lumiprobe GmbH. All solvents, if not purchased in purity or dryness suitable, were distilled using standard methods, tetrahydrofuran (THF) was distilled under a N_2 atmosphere from Na/benzophenone; dichloromethane (DCM or CH_2Cl_2) was distilled under a N_2 atmosphere from CaH_2 before use. Other solvents were passed through alumina columns (toluene) or molecular sieves columns (dimethylformamide - DMF) (Pure Solv, Innovative Technology, Inc., USA) by applying N_2 overpressure right before use. Mg turnings and LiCl were anhydrated with heating under reduced pressure before use. Phenylphosphonic dichloride and ester derivatives were distilled under reduced pressure prior use. *t*-Butyllithium was titrated with menthol in THF at 0 °C with 1,10-phenanthroline as indicator.

All solvents for flash chromatography were distilled prior to usage. All solvents used in reactions were anhydrated and that is not annotated in later described procedures additionally. Deionized water was used for all experiments.

1.2. Reaction conditions

All reactions were performed in heat dried glassware under atmosphere of N_2 if not stated otherwise.

1.3. Thin Layer Chromatography

TLC was carried out on Merck precoated silica gel plates (60F-254); compounds were visualized using ultraviolet light irradiation at 254 nm and 366 nm

1.4. Silica gel flash liquid chromatography (column chromatography)

Purifications were performed using silica gel from Macherey & Nagel (particle size 40 – 60 μm) under approximately 0.2-0.6 Bar pressure.

1.5. NMR spectroscopy

^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded using a Bruker Fourier 300 system (300 MHz, ^{1}H- and 75 MHz for ^{13}C-NMR), a Bruker Avance I 400 system (400 MHz for ^{1}H-, 101 MHz for ^{13}C-NMR and 162 MHz for ^{31}P-NMR), Spectra were referenced to appropriate residual solvent peaks ($CDCl_3$, Methanol-d_4). Spectra were recorded at 298 K, if not stated otherwise. $CDCl_3$ was stored over molecular sieves in fridge. P-rhodamines exist as mixtures of atropisomers. These spectra are reported as spectra of mixtures including H-P and C-P coupling which causes multiple peaks, especially in ^{13}C-NMR.

1.6. Mass spectrometry

ESI-MS were performed on a Finnigan LCQ spectrometer for monitoring of reaction conditions. Calculated masses were obtained using the software ChemDraw Professional 16. High resolution mass spectrometry (HR-MS) measurements were performed using LC-coupled MAXIS Impact ESI-TOF spectrometer (Bruker Daltronics, Bremen, Germany).

1.7. Fourier transform infrared spectroscopy (FT-IR)

IR spectra were measured by using a Thermo Nicolet Spectrometer FT-IR Avatar 370 filled with ATR unit. Spectra were analysed using Spectragryph v1.2.11. The following notations indicate the intensity of the absorption bands: s = strong, m = medium, w = weak.

1.8. UV-Vis and fluorescence spectroscopy

UV/Vis absorption spectra were obtained using a Jasco V-630 and solutions for determination of extinction coefficients were prepared in concentrations (1 - 6 µM) with absorptions between 0.05 and 0.5 in 1 cm square quartz cuvette using PBS-buffer (pH = 7.4) + 1% DMSO as co-solvent. PBS-buffer: (2.2 g of Na_2HPO_4; 0.2 g of NaH_2PO_4; 8.5 g of NaCl were dissolved in 1 L of water. pH was adjusted to pH = 7.4 with 1 M HCl).

Fluorescence emission spectra were recorded on Jasco FP-6500 spectrofluorometer having a cell holder thermostated at 25 °C. Relative fluorescence quantum efficiency was obtained by comparison of the area of the emission curve spectrum of the tested sample rhodamine excited at 625 nm with area of the emission curve spectrum of a solution of Cy5.5 (Cyanin 5.5 NHS-Ester, Lumiprobe) in PBS (pH 7.4)which has a quantum efficiency of 0.23.[1] For the determination of fluorescence quantum efficiency, the sample absorbance at the excitation wavelength was kept as low as possible to avoid fluorescence errors (A < 0.06). The recorded data was processed with Originlab OriginPro 2019b.

2. Syntheses

2.1. General procedures:

Amines derivatives **2a-c**[2] were prepared according to the literature known procedures.

2.1.1. General Procedure 1: Synthesis of benzoate-electrophiles

Following a modified procedure[3] the substituted acid was dissolved in DMF and K_2CO_3 (1.5 equiv.) and MeI (1.2 equiv.) were added at 0 °C. The reaction mixture was stirred at ambient temperature for 16 h and was quenched by the addition of water. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water, brine, anhydrated over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography (5% EtOAc in PE) to yield the substituted methyl ester.

2.1.2. General Procedure 2: Reaction of organolithium reagents with phenylphosphonic dichloride

A solution of 3-Bromoarylamine (2 equiv.) in anhydrous THF was cooled to –78 °C and treated dropwise with *n*-BuLi (2.5 equiv., 2.5 M in hexane). The reaction mixture was stirred for 1 h at –78 °C and was added dropwise (cannula transfer) to a –78 °C cooled solution of phenylphosphonic dichloride in anhydrous THF and stirred for 1 h. The reaction was quenched by addition of saturated ammonium chloride solution. The organic layer was separated and the aqueous fraction was extracted with dichloromethane. The combined organic layers were washed with brine, anhydrated with solid $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (100% EtOAc + 1% NEt_3) to yield the triarylphosphine oxide.

2.1.3. General Procedure 3: Bromination of Triarylphosphine oxides

To triarylphosphine oxide (1 equiv.) in acetonitrile or acetonitrile: dichloromethane (0.1 M) was added *N*-bromosuccinimide portion wise at 0 °C and stirred at this temperature for one hour. The reaction was quenched by addition of saturated sodium bicarbonate solution and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water, brine, anhydrated over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography (70% EtOAc in PE + 1% NEt_3) to yield the brominated phosphine oxides.

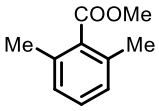
2.1.4. General Procedure 4: Synthesis of P-rhodamines

To a solution of dibromide (1 equiv.) in THF (0.1 M) was added *t*-BuLi (1.9 M in pentane, 4.2 equiv.) at –78 °C and stirred for 1 h followed by addition of substituted methyl ester (1.5 equiv.) in anhydrous THF (0.1 M). After removal of cooling bath, the reaction mixture was stirred at ambient temperature, quenched by addition of aq. hydrochloric acid and stirred 15 minutes. The reaction mixture was diluted with water and extracted with dichloromethane. The combined organic layers were anhydrated over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography (0-10% MeOH in CH_2Cl_2) to yield the P-rhodamines as dark green solids.

2.2. Synthesized molecules

2.2.1. Synthesis of benzoates

methyl 2,6-dimethylbenzoate (11e):



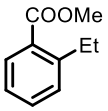
Following **General procedure 1,** 2,6-dimethylbenzoic acid (3.00 g, 19.98 mmol, 1 equiv.), K_2CO_3 (4.14g, 29.97 mmol, 1.5 equiv.), MeI (1.5 mL, 23.97 mmol, 1.2 equiv.) in DMF (23 mL) was used to yield the methyl 2,6-dimethylbenzoate **11e** (2.93 g, 89%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 7.6 Hz, 2H), 3.91 (s, 3H), 2.31 (s, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 170.62, 135.07, 133.95, 129.46, 127.67, 51.99, 19.83 ppm.

The NMR data were in accordance with published data.[3]

methyl 2-ethylbenzoate (11d):



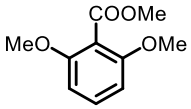
Following **General procedure 1**, 2-ethylbenzoic acid (1.00 g, 6.67 mmol, 1 equiv.), K_2CO_3 (1.38 g, 10.0 mmol, 1.5 equiv.), MeI (0.5 mL, 8.00 mmol, 1.2 equiv.) in DMF (8 mL) was used to yield the methyl 2-ethylbenzoate **11d** (765 mg, 70%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, J = 7.9, 1.4 Hz, 1H), 7.43 (td, J = 7.6, 1.5 Hz, 1H), 7.32 – 7.20 (m, 2H), 3.90 (s, 3H), 2.98 (q, J = 7.5 Hz, 2H), 1.24 (t, J = 7.5 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 168.35, 146.14, 132.14, 130.64, 130.33, 129.50, 125.80, 52.01, 27.68, 16.00 ppm.

The NMR data were in accordance with published data.[4]

methyl 2,6-dimethoxybenzoate (11c):



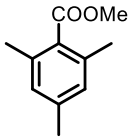
Following a modified procedure,[5] to a solution of 2,6-dimethoxybenzoic acid (3.00 g, 16.5 mmol, 1 equiv.) in methanol (62 mL) was added a precooled solution of conc. H_2SO_4 at 0 °C. The reaction mixture was stirred under reflux for 16h and concentrated under reduced pressure. Water was added and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography (5% EtOAc in PE) to yield the methyl 2,6-dimethoxybenzoate **11c** (2.98 g, 92%) as colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (t, J = 8.3 Hz, 1H), 6.58 (d, J = 8.4 Hz, 2H), 3.93 (s, 3H), 3.83 (s, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 167.18, 157.42, 131.21, 113.06, 104.00, 56.12, 52.55 ppm.

The NMR data were in accordance with published data.[5]

methyl 2,4,6-trimethylbenzoate (11f):



2,4,6-Trimethylbenzoic acid chloride (0.5 mL, 3.00 mmol, 1 equiv.), MeOH (2.4 mL, 60.0 mmol, 20 equiv.) and NEt_3 (0.63 mL, 4.50 mmol, 1.5 equiv.) was stirred at ambient temperature for 16 h. MeOH was evaporated and the residue was purified by column chromatography (5% EtOAc in PE) to yield the methyl ester **11f** (477 mg, 89%) as colorless oil.

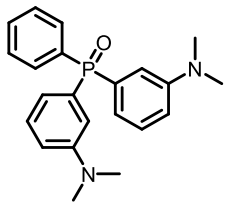
^{1}H NMR (400 MHz $CDCl_3$): δ = 6.85 (s, 2H), 3.89 (s, 3H), 2.29 (s, 6H), 2.28 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 170.74, 139.42, 135.31, 131.01, 128.51, 51.86, 21.24, 19.88 ppm.

The NMR data were in accordance with published data.[6]

2.2.2. Synthesis of phosphine oxides

bis(3-(dimethylamino)phenyl)(phenyl)phosphine oxide (12a):



Following **General procedure 2**, 3-bromo-*N*,*N*-dimethylaniline **2a** (10.6 g, 52.9 mmol, 2 equiv.) in THF (105 mL), *n*-BuLi (26 mL, 66.1 mmol, 2.5 equiv., 2.5 M in hexane) and phenylphosphonic dichloride (3.7 mL, 26.4 mmol, 1 equiv.) in THF (53 mL) were used to yield the phosphine oxide **12a** (7.62 g, 79%) as colorless solid.

TLC: R_f = 0.28 (100% EtOAc + 1% NEt_3)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.62 (m, 2H), 7.54 – 7.38 (m, 4H), 7.27 – 7.14 (m, 4H), 6.86 – 6.76 (m, 5H), 2.92 (s, 12H) ppm.

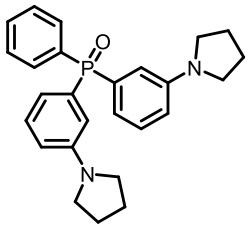
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.37 (d, J = 13.5 Hz), 133.17 (d, J = 103.3 Hz), 132.22 (d, J = 9.8 Hz), 131.61 (d, J = 2.8 Hz), 130.85 (d, J = 9.1 Hz), 128.95 (d, J = 14.5 Hz), 128.31 (d, J = 12.0 Hz), 119.97 (d, J = 10.7 Hz), 115.63 (d, J = 11.0 Hz), 115.48 (d, J = 2.7 Hz), 40.48 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 31.25 ppm.

IR (ATR): 3059 (w), 2886 (w), 2805 (w), 1585 (s), 1566 (m), 1493 (s), 1412 (m), 1350 (s), 1323 (m), 1184 (s), 1161 (s), 1115 (s), 1061 (m), 988 (s), 961 (m), 868 (m), 822 (m), 764 (s), 714 (s), 694 (s), 683 (s), 606 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{22}H_{25}N_2NaOP$ $(M+Na)^+$ 387.1602, found 387.1607.

phenylbis(3-(pyrrolidin-1-yl)phenyl)phosphine oxide (12d):



Following **General procedure 2**, 1-(3-bromophenyl)pyrrolidine **2c** (1.73 g, 7.65 mmol, 2 equiv.) in THF (25 mL), *n*-BuLi (3.8 mL, 9.56 mmol, 2.5 equiv., 2.5 M in hexane) and phenylphosphonic dichloride (0.54 mL, 3.83 mmol, 1 equiv.) in THF (13 mL) were used to yield the phosphine oxide **12d** (1.54 g, 97%) as colorless solid.

TLC: R_f = 0.24 (100% EtOAc + 1% NEt_3)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (ddt, J = 11.8, 6.9, 1.6 Hz, 2H), 7.52 – 7.44 (m, 1H), 7.40 (dddd, J = 8.3, 5.6, 2.9, 1.5 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.05 – 6.96 (m, 2H), 6.74 (ddt, J = 11.7, 7.4, 1.1 Hz, 2H), 6.66 (ddt, J = 8.3, 2.4, 1.1 Hz, 2H), 3.31 – 3.19 (m, 8H), 2.02 – 1.92 (m, 8H) ppm.

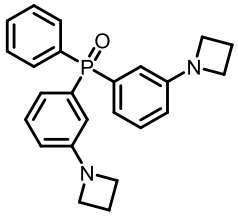
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 147.75 (d, J = 13.7 Hz), 133.77 (d, J = 102.7 Hz), 133.19 (d, J = 103.1 Hz), 132.24 (d, J = 9.8 Hz), 131.52 (d, J = 2.7 Hz), 128.94 (d, J = 14.4 Hz), 128.26 (d, J = 11.9 Hz), 118.98 (d, J = 10.6 Hz), 114.94 (d, J = 11.0 Hz), 114.75 (d, J = 2.7 Hz), 47.68, 25.56 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 35.18 ppm.

IR (ATR): 3055 (w) 2970 (w), 2832 (w), 1589 (s), 1431 (s), 1369 (s), 1180 (s), 1115 (s), 999 (m), 864 (m), 760 (m), 718 (s), 694 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{26}H_{30}N_2OP$ $(M+H)^+$ 417.2096, found 417.2095.

bis(3-(azetidin-1-yl)phenyl)(phenyl)phosphine oxide (12b):



Following **General procedure 2,** 1-(3-bromophenyl)azetidine **2b** (1.52 g, 7.15 mmol, 2 equiv.) in THF (24 mL), *n*-BuLi (3.6 mL, 8.93 mmol, 2.5 equiv., 2.5 M in hexane) and phenylphosphonic dichloride (0.51 mL, 3.57 mmol, 1 equiv.) in THF (12 mL) were used to yield the phosphine oxide **12b** (909 mg, 66%) as colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.69 – 7.58 (m, 2H), 7.53 – 7.44 (m, 1H), 7.40 (ddd, J = 8.4, 6.7, 2.9 Hz, 2H), 7.20 (td, J = 7.8, 3.7 Hz, 2H), 6.87 (dt, J = 13.3, 1.8 Hz, 2H), 6.78 (ddt, J = 11.8, 7.4, 1.2 Hz, 2H), 6.53 (ddt, J = 8.2, 2.4, 1.1 Hz, 2H), 3.84 (t, J = 7.2 Hz, 8H), 2.32 (p, J = 7.2 Hz, 4H) ppm.

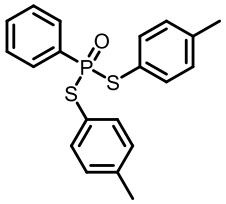
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 151.93 (d, J = 13.8 Hz), 133.31 (d, J = 103.2 Hz), 132.99 (d, J = 103.2 Hz), 132.18 (d, J = 9.6 Hz), 131.67 (d, J = 3.2 Hz), 128.74 (d, J = 14.6 Hz), 128.32 (d, J = 12.1 Hz), 120.72 (d, J = 11.2 Hz), 114.51 (d, J = 5.2 Hz), 114.44 (d, J = 2.7 Hz), 52.41, 16.97 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 34.55 ppm.

IR (ATR): 2924 (w), 2859 (m), 1736 (m), 1589 (s), 1474 (s), 1423 (s), 1350 (s), 1188 (s), 984 (m), 876 (m), 783 (m), 694 (s), 656 (w), 602 (m) cm^{-1}.

HRMS (ESI): Calcd. for $C_{24}H_{25}N_2NaOP$ $(M+Na)^+$ 411.1602, found 411.1608.

***S,S*-di-*p*-tolyl phenylphosphonodithioate (14):**



Following a procedure of Hosoya *et al*.,[7] *p*-Toluenethiol (5.62 g, 45.0 mmol, 2 equiv.) and triethylamine (9.4 mL, 68.0 mmol, 3 equiv.) were dissolved in THF (150 mL), cooled to 0 °C and treated dropwise with phenylphosphonic dichloride (3.2 mL, 23.0 mmol, 1 equiv.). The reaction mixture was stirred at 0 °C for 2 h and was quenched by addition of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ethylacetate. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography (20% EtOAc in PE) to yield the thioester **14** (8.02 g, 94%) as colorless solid.

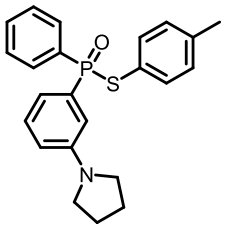
TLC: R_f = 0.42 (20% EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 – 7.73 (m, 2H), 7.53 – 7.45 (m, 1H), 7.44 – 7.36 (m, 2H), 7.34 (d, J = 2.0 Hz, 2H), 7.32 (d, J = 2.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 4H), 2.31 (s, 3H), 2.30 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ =139.74 (d, J = 3.1 Hz), 135.74 (d, J = 4.0 Hz), 133.53 (d, J = 107.4 Hz), 132.67 (d, J = 3.4 Hz), 131.80 (d, J = 10.9 Hz), 130.17 (d, J = 2.4 Hz), 128.44 (d, J = 14.3 Hz), 122.65 (d, J = 6.2 Hz), 21.37 ppm.

The NMR spectra are in accordance with published data.[7]

***S*-(*p*-tolyl) phenyl(3-(pyrrolidin-1-yl)phenyl)phosphinothioate (16):**



Following a modified procedure of Hosoya *et al*.,[7] to a suspension of magnesium turnings (1.02 g, 41.8 mmol, 2.2 equiv.) and anhydrous LiCl (1.61 g, 38.0 mmol, 2 equiv.) in THF (10 mL) was added a solution of 1-(3-bromophenyl)pyrrolidine (8.62 g, 38.0 mmol, 2 equiv.) in THF (38) and stirred after initiation at ambient temperature for 1 h. Generated Grignard reagent was added dropwise (cannula transfer) to a -40 °C cooled solution of *S,S*-di-*p*-tolyl phenylphosphonodithioate **14** (7.06 g, 19.0 mmol, 1 equiv.) in anhydrous THF (38 mL). After complete addition the reaction mixture was stirred at -40 °C for 1 h. The reaction was quenched by addition of saturated ammonium chloride solution. The organic

layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water, brine, anhydrated over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography (50% EtOAc in PE) to yield the **16** *S*-4-toluoyl-phosphinothioate (6.92 g, 93%) as colorless solid.

TLC: R_f = 0.6 (50% EtOAc in PE)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (ddt, J = 12.7, 6.9, 1.5 Hz, 2H), 7.52 – 7.44 (m, 1H), 7.42 – 7.33 (m, 4H), 7.27 (td, J = 7.9, 4.9 Hz, 1H), 7.10 – 6.98 (m, 4H), 6.69 – 6.62 (m, 1H), 3.27 (h, J = 3.2 Hz, 4H), 2.25 (d, J = 1.3 Hz, 3H), 2.05 – 1.94 (m, 4H) ppm.

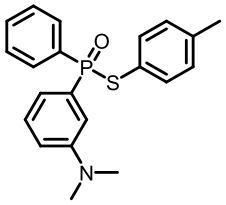
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 147.76 (d, J = 15.2 Hz), 138.98 (d, J = 2.4 Hz), 135.41 (d, J = 3.8 Hz), 133.70 (d, J = 37.8 Hz), 132.65 (d, J = 37.7 Hz), 132.03 (d, J = 3.0 Hz), 131.78 (d, J = 10.2 Hz), 129.99 (d, J = 1.8 Hz), 129.28 (d, J = 15.7 Hz), 128.39 (d, J = 13.0 Hz), 123.01 (d, J = 5.2 Hz), 118.04 (d, J = 10.9 Hz), 115.28 (d, J = 3.1 Hz), 114.42 (d, J = 11.8 Hz), 47.70, 25.57, 21.28 ppm.

^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$): δ = 46.52 ppm.

IR (ATR): 3048 (b), 2974 (w), 2828 (w), 1585 (s), 1481 (s), 1431 (s), 1373 (s), 1200 (s), 999 (m), 853 (m), 802 (s), 764 (s), 698 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{23}H_{24}NNaOPS$ $(M+Na)^+$ 416.1214, found 416.1203.

***S*-(p-tolyl) (3-(dimethylamino)phenyl)(phenyl)phosphinothioate (15):**



Following a modified procedure of Hosoya *et al*.,[7] to a suspension of magnesium turnings (1.01 g, 41.6 mmol, 2.2 equiv.) and anhydrous LiCl (1.60 g, 37.8 mmol, 2 equiv.) in THF (7.5 mL) was added a solution of 3-bromo-*N*,*N*-dimethylaniline (5.4 mL, 37.8 mmol, 2 equiv.) in THF (38 mL) and stirred after initiation at ambient temperature for 1 h. Generated Grignard reagent was added dropwise (cannula transfer) to a –40 °C cooled solution of *S*,*S*-di-*p*-tolyl phenylphosphonodithioate **14** (7.00 g, 18.9 mmol, 1 equiv.) in anhydrous THF (38 mL). After complete addition the reaction mixture was stirred at -40 °C for 1 h. The reaction was quenched by addition of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water, brine, anhydrated over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography (50% EtOAc in PE) to yield the *S*-4-toluoyl-phosphinothioate **15** (6.35 g, 91%) as colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (ddt, J = 12.7, 7.0, 1.5 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.43 – 7.36 (m, 2H), 7.35 (dd, J = 8.2, 1.7 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.19 (ddd, J = 15.0, 2.7, 1.3 Hz, 1H), 7.12 (ddt, J = 12.7, 7.4, 1.2 Hz, 1H), 7.00 (d, J = 7.9 Hz, 2H), 6.84 – 6.77 (m, 1H), 2.92 (s, 6H), 2.24 (s, 3H) ppm.

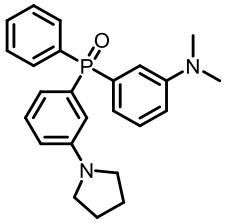
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.30 (d, J = 14.9 Hz), 138.97 (d, J = 2.6 Hz), 135.35 (d, J = 3.5 Hz), 133.64 (d, J = 19.2 Hz), 132.59 (d, J = 19.1 Hz), 132.05 (d, J = 2.7 Hz), 131.70 (d, J = 10.2 Hz), 129.94 (d, J = 1.5 Hz), 129.20 (d, J = 15.6 Hz), 128.38 (d, J = 13.0 Hz), 122.88 (d, J = 5.2 Hz), 118.97 (d, J = 11.1 Hz), 115.86 (d, J = 3.0 Hz), 115.06 (d, J = 12.0 Hz), 40.38, 21.20 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 42.57 ppm.

IR (ATR): 3055 (b), 2916 (w), 2805 (w), 1589 (s), 1493 (s), 1408 (m), 1362 (s), 1238 (m), 1184 (s), 1084 (m), 991 (m), 852 (m), 802 (s), 764 (s), 702 (s), 683 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{21}H_{22}NNaOPS$ $(M+Na)^+$ 390.1065, found 390.1057.

(3-(dimethylamino)phenyl)(phenyl)(3-(pyrrolidin-1-yl)phenyl)phosphine oxide (17):



Following a modified procedure,[7] to a suspension of magnesium turnings (407 mg, 16.8 mmol, 2.2 equiv.) and anhydrous LiCl (646 mg, 15.2 mmol, 2 equiv.) in THF (4 mL) was added a solution of 3-bromo-*N*,*N*-dimethylaniline **2a** (2.2 mL, 15.2 mmol, 2 equiv.) in THF (7.6 mL) and stirred after initiation at ambient temperature for 1 h.

Generated Grignard reagent was added dropwise (cannula transfer) to a 0 °C cooled solution of *S*-4-toluoyl-phosphinothioate **14** (3.00 g, 7.62 mmol, 1 equiv.) in THF (7.6 mL). After complete addition the reaction mixture was stirred at 0 °C for 15 minutes then at ambient temperature for 45 minutes. The reaction was quenched by addition of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water, brine, anhydrated over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography (100% EtOAc + 1% NEt_3) to yield the unsymmetrical triarylphosphine oxide oxide **17** (2.83 g, 95%) as white solid.

TLC: R_f = 0.25 (100% EtOAc)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 – 7.64 (m, 2H), 7.54 – 7.45 (m, 1H), 7.41 (tdd, J = 8.4, 2.9, 1.2 Hz, 2H), 7.26 – 7.13 (m, 4H), 6.99 (ddd, J = 13.8, 2.6, 1.4 Hz, 1H), 6.87 – 6.63 (m, 5H), 3.29 – 3.20 (m, 4H), 2.93 (s, 6H), 2.03 – 1.90 (m, 4H) ppm.

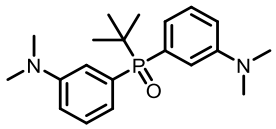
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.37 (d, J = 13.5 Hz), 147.76 (d, J = 13.8 Hz), 134.13 (d, J = 30.7 Hz), 133.37 (d, J = 59.6 Hz), 132.48 (d, J = 12.3 Hz), 132.24 (d, J = 9.9 Hz), 131.59 (d, J = 2.8 Hz), 129.06 (d, J = 4.7 Hz), 128.87 (d, J = 4.7 Hz), 128.31 (d, J = 12.0 Hz), 120.04 (d, J = 10.6 Hz), 118.95 (d, J = 10.7 Hz), 115.68 (d, J = 10.9 Hz), 115.50, 114.92 (d, J = 11.1 Hz), 114.81 (d, J = 2.9 Hz), 47.68, 40.54, 25.57 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 42.50 ppm.

IR (ATR): 3055 (bw), 2951 (w), 2897 (w), 1736 (s), 1585 (s), 1493 (s), 1431 (m), 1354 (s), 1227 (m), 1180 (s), 1115 (s), 991 (m), 868 (s), 818 (m), 760 (s), 694 (s), 606 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{24}H_{27}N_2NaOP$ $(M+Na)^+$ 413.1759, found 413.1753.

***tert*-butylbis(3-(dimethylamino)phenyl)phosphine oxide (12b):**



To 3-bromo-*N*,*N*-dimethylaniline **2a** (4.83 g, 24 mmol, 1 equiv.) in 60 ml of THF at -78 °C *n*-BuLi (10.6 mL, 26.5 mmol, 1.1 equiv.) was added and after stirring for 1 h at the same temperature *tert*-butyl-dichlorophosphine (1.9 g, 12 mmol, 0.5 equiv.) dissolved in 10 ml of anhydrous THF was added. After stirring at the same temperature for 1 h and 1 h at 25 °C, it was quenched with minimal amount of water and H_2O_2 (12.2 mL, 5 equiv.) was added at 25 °C. After 2 h of stirring at 25 °C reaction was cooled down to 0 °C, saturated solution of $NaHCO_3$ was added and residual H_2O_2 was quenched using saturated solution of Na_2SO_3. Reaction mixture was extracted with ethyl acetate (3 x 100 ml), combined organic fractions were anhydrated with solid anhydrous Na_2SO_4 and volatiles removed under reduced pressure. Residue was dissolved in toluene and molecular sieves were added. After stirring for 2 h at 25 °C, molecular sieves were filtered off and flash chromatography using EtOAc + 3% of MeOH as eluent provided 3.3 g (81%) of the product **12b** as viscose oil which amorphously solidify upon storage in freezer.

R_f = 0.12 in EtOAc

IR (ATR) $\tilde{\nu}$ = 2827.8 (m), 2361.7 (w), 2260.8 (w), 2165.6 (w), 2093.3 (w), 2048.1 (w), 1973.5 (w), 1880.2 (w), 1701.5 (w), 1535.5 (w), 1381.9 (m), 1270.4 (m), 1202.7 (s), 1025.9 (m), 894.8 (m), 837.64 (m), 750.74 (m), 652.6 (s), 606.33 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, 297 K) δ = 7.40 (ddd, *J* = 12.4, 2.8, 1.3 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.21 (ddt, *J* = 9.9, 7.6, 1.2 Hz, 2H), 6.88 – 6.81 (m, 2H), 2.99 (s, 12H), 1.27 (d, *J* = 14.6 Hz, 9H) ppm.

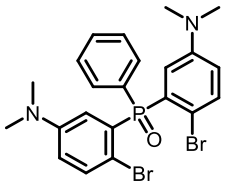
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 297 K) δ = 150.37, 150.25, 132.44, 131.55, 128.75, 128.62, 119.70, 119.61, 116.62, 116.53, 115.03, 115.01, 40.56, 34.43, 33.73, 25.63 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 297 K) δ = 40.05 ppm.

HRMS (EI^+) m/z: $[M + H]^+$, Calculated for $C_{20}H_{30}N_2OP^+$ 345.2090; Found 345.2096.

2.2.3. Synthesis of brominated phosphine oxides

bis(2-bromo-5-(dimethylamino)phenyl)(phenyl)phosphine oxide (10a):



Following **General procedure 3,** phosphine oxide **12a** (2.00 g, 5.49 mmol, 1 equiv.) and NBS (2.05 g, 11.5 mmol, 2.1 equiv.) in acetonitrile (55 mL) were used to yield brominated phosphine oxide **10a** (2.29 g, 80%) as white solid.

TLC: R_f = 0.35 (70% EtOAc in PE + 1% NEt_3)

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.89 – 7.79 (m, 2H), 7.57 – 7.50 (m, 1H), 7.49 – 7.41 (m, 4H), 7.05 (dd, J = 15.4, 3.2 Hz, 2H), 6.67 (dd, J = 8.8, 2.3 Hz, 2H), 2.84 (s, 12H) ppm.

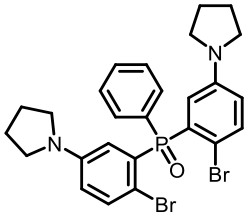
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ* = 149.26 (d, J = 12.9 Hz), 134.87 (d, J = 9.4 Hz), 132.94 (d, J = 10.0 Hz), 132.54 (d, J = 48.5 Hz), 131.90 (d, J = 2.9 Hz), 131.46 (d, J = 49.1 Hz), 128.27 (d, J = 12.7 Hz), 120.33 (d, J = 11.9 Hz), 116.74 (d, J = 2.6 Hz), 111.31 (d, J = 4.7 Hz), 40.34 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): *δ* = 36.15 ppm.

IR (ATR): 2898 (w), 2854 (w), 2808 (w), 1582 (s), 1485 (s), 1439 (s), 1393 (m), 1350 (s), 1223 (m), 1180 (s), 1119 (s), 1057 (m), 961 (w), 826 (m), 810 (m), 756 (m), 714 (s), 679 (m) cm^{-1}.

HRMS (ESI): Calcd. for $C_{22}H_{23}Br_2N_2NaOP$ $(M+Na)^+$ 542.9813, found 542.9824.

bis(2-bromo-5-(pyrrolidin-1-yl)phenyl)(phenyl)phosphine oxide (10d):



Following general **General procedure 3,** phosphine oxide **12d** (589 mg, 1.41 mmol, 1 equiv.) and NBS (529 mg, 2.97 mmol, 2.1 equiv.) in acetonitrile:dichloromethane (4:1, 14 mL) were used to yield brominated phosphine oxide **10d** (432 mg, 53%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 – 7.78 (m, 2H), 7.57 – 7.49 (m, 1H), 7.52 – 7.34 (m, 4H), 6.87 (dd, J = 15.3, 3.0 Hz, 2H), 6.50 (dd, J = 8.7, 3.0, 2H), 3.20 – 3.00 (m, 8H), 1.99 – 1.89 (m, 8H) ppm.

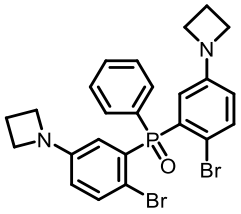
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.66 (d, J = 12.8 Hz), 134.87 (d, J = 9.6 Hz), 132.99 (d, J = 3.6 Hz), 132.24 (d, J = 69.1 Hz), 132.20 (d, J = 102.2 Hz), 131.53 (d, J = 43.0 Hz), 128.20 (d, J = 12.6 Hz), 119.61 (d, J = 11.8 Hz), 116.02 (d, J = 2.5 Hz), 110.06 (d, J = 4.5 Hz), 47.57, 25.56 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 36.09 ppm.

IR (ATR): 2967 (w), 2835 (w), 1736 (w), 1585 (s), 1547 (w), 1400 (m), 1366 (s), 1188 (s), 1161 (w), 1115 (s), 806 (s), 718 (s), 694 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{26}H_{27}Br_2N_2NaOP$, found $(M+Na)^+$ 595.0126, found 595.0129.

bis(3-(azetidin-1-yl)phenyl)(phenyl)phosphine oxide (10c):



Following **General procedure 3,** phosphine oxide **12c** (867 mg, 2.23 mmol, 1 equiv.) and NBS (814 mg, 4.58 mmol, 2.05 equiv.) in acetonitrile:dichloromethane (6:1, 22 mL) were used to yield brominated phosphine oxide **10c** (670 mg, 55%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 – 7.77 (m, 2H), 7.52 (td, J = 7.3, 1.6 Hz, 1H), 7.47 – 7.37 (m, 4H), 6.72 (dd, J = 14.7, 2.9 Hz, 2H), 6.40 (dd, J = 8.5, 2.8 Hz, 2H), 3.77 (td, J = 7.4, 1.8 Hz, 8H), 2.31 (p, J = 7.3 Hz, 4H) ppm.

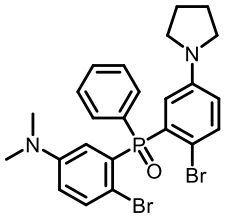
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 50.81 (d, J = 12.9 Hz), 134.75 (d, J = 8.8 Hz), 132.89 (d, J = 9.6 Hz), 132.42 (d, J = 92.8 Hz), 131.94 , 132.11 – 130.78 (m), 128.27 (d, J = 12.2 Hz), 119.14 (d, J = 11.3 Hz), 115.82 (d, J = 2.6 Hz), 112.08 (d, J = 4.4 Hz), 52.32, 16.83 ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 35.29 ppm.

IR (ATR): 3055 (w), 2916 (w), 2851 (w), 1585 (s), 1555 (w), 1458 (s), 1393 (m), 1346 (s), 1184 (s), 1150 (m), 1111 (s), 814 (m), 791 (m), 752 (m), 694 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{24}H_{23}Br_2N_2NaOP$ $(M+Na)^+$ 566.9813, found 566.9818.

(2-bromo-5-(dimethylamino)phenyl)(2-bromo-5-(pyrrolidin-1-yl)phenyl)(phenyl)phosphine oxide (18):



Following **General procedure 3,** phosphine oxide **17** (1.50 g, 3.84 mmol, 1 equiv.) and NBS (1.51 g, 7.88 mmol, 2.05 equiv.) in acetonitrile:dichloromethane (4:1, 40 mL) were used to yield brominated phosphine oxide **18** (1.45 g, 69%) as white solid.

TLC: R_f = 0.56 (100% EtOAc + 1% NEt_3)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 – 7.77 (m, 2H), 7.57 – 7.47 (m, 1H), 7.43 (tdd, J = 9.6, 7.4, 3.9 Hz, 4H), 7.05 (dd, J = 15.5, 3.2 Hz, 1H), 6.88 (dd, J = 15.3, 3.0 Hz, 1H), 6.67 (ddd, J = 8.8, 3.2, 0.9 Hz, 1H), 6.51 (ddd, J = 8.7, 3.1, 0.9 Hz, 1H), 3.14 (tt, J = 6.7, 2.2 Hz, 4H), 2.83 (s, 6H), 1.95 (dq, J = 6.7, 3.3 Hz, 4H) ppm.

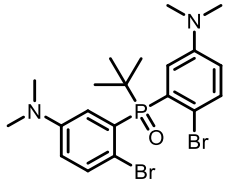
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.25 (d, J = 12.9 Hz), 146.69 (d, J = 13.1 Hz), 134.90 (d, J = 3.6 Hz), 134.81 (d, J = 3.5 Hz), 132.94 (d, J = 9.6 Hz), 132.56 (d, J = 28.5 Hz), 131.83 (d, J = 2.1 Hz), 131.48 (d, J = 29.4 Hz), 128.21 (d, J = 12.7 Hz), 120.36 (d, J = 11.5 Hz), 119.59 (d, J = 12.0 Hz), 116.70 (d, J = 2.6 Hz), 116.06 (d, J = 2.6 Hz), 111.40 (d, J = 5.0 Hz), 109.98 (d, J = 5.1 Hz), 47.57, 40.31, 25.54 ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 32.18 ppm.

IR (ATR): 2970 (w), 2940 (w), 2897 (w), 2847 (w), 1717 (s), 1585 (s), 1546 (m), 1474 (s), 1439 (s), 1354 (s), 1315 (w), 1180 (s), 1161 (s), 1114 (s), 991 (m), 868 (m), 817 (m), 760 (s), 694 (s), 671 (m), 605 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{24}H_{25}Br_2N_2NaOP$ $(M+Na)^+$ 568.9969, found 568.9965.

bis(2-bromo-5-(dimethylamino)phenyl)(*tert*-butyl)phosphine oxide (10b):



12b (3.3 g, 9.75 mmol) was dissolved in DMF (120 mL) and NBS (3.4 g, 19.5 mmol) was added at 25 °C. Reaction conversion was monitored by TLC and after 6 h DMF was removed under reduced pressure. Reaction mixture was purified by flash chromatography using EtOAc as eluent. 76% (3.7 g) of white to slight yellow solid product **10b** could be isolated.

$\mathbf{R_f}$ = 0.65 in DCM:MeOH = 9:1

IR (ATR) $\tilde{\nu}$ = 2833 (m), 2361.1 (w), 2147.6 (w), 2045.9 (w), 1969.6 (w), 1662.3 (w), 1524.4 (m), 1409.8 (s), 1276.9 (m), 1083.8 (s), 984.29 (m), 896.21 (m), 855.05 (m), 714.01 (m), 655.5 (s), 610.5 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, 297 K) δ = 7.50 (dd, *J* = 12.8, 3.2 Hz, 2H), 7.39 (dd, *J* = 8.8, 4.6 Hz, 2H), 6.68 (ddd, *J* = 8.9, 3.2, 0.8 Hz, 2H), 3.00 (s, 12H), 1.52 (d, *J* = 14.6 Hz, 9H) ppm.

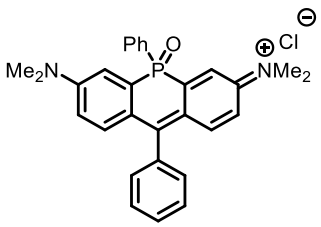
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 297 K) δ = 148.89, 148.77, 135.10, 135.02, 132.84, 131.90, 119.33, 119.23, 116.45, 116.43, 111.30, 111.26, 40.57, 36.49, 35.77, 27.14 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 297 K) δ = 42.70 ppm.

HRMS (EI^+) m/z: $[M + H]^+$, Calculated for $C_{20}H_{28}B_{r2}N_2OP^+$ 501.0301; Found 501.0302.

2.2.4. Synthesis of P-rhodamines

***N*-(7-(dimethylamino)-5-oxido-5,10-diphenyl-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium chloride (13a)**



Following **General procedure 4,** dibromide **10a** (43 mg, 0.08 mmol, 1 equiv.) in THF (0.8 mL) and *t*-BuLi (0.18 mL, 0.34 mmol, 4.1 equiv. 1.9 M in pentane) were used. Methylbenzoate **11a** (15 µL, 0.12 mmol, 1.5 equiv.) in THF (1.2 mL) was added. After removal of cooling bath, the reaction mixture was

stirred for 1 h, aq. HCl (67 µL, 0.41 mmol, 5 equiv., 6 M) was added and stirred for 1 h. The crude product was purified by column chromatography to yield **13a** (20 mg, 50%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.77 – 7.69 (m, 2H), 7.64 (tq, J = 6.5, 3.5, 3.0 Hz, 6H), 7.55 (td, J = 7.5, 3.2 Hz, 2H), 7.39 (dt, J = 7.3, 3.4 Hz, 2H), 7.25 (dd, J = 9.7, 6.0 Hz, 2H), 6.96 (dd, J = 9.6, 2.6 Hz, 2H), 3.38 (s, 11H) ppm.

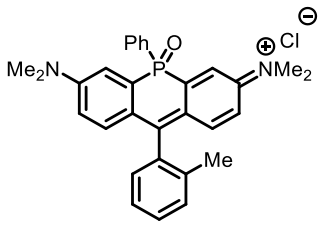
^{13}C{^{1}H} NMR (75 MHz, Methanol-d_4): δ = 165.84 (d, J = 6.8 Hz), 156.49 (d, J = 12.8 Hz), 142.09 (d, J = 8.9 Hz), 139.37 (d, J = 95.2 Hz), 137.38, 134.40 (d, J = 3.1 Hz), 133.62 (d, J = 109.7 Hz), 131.10 (d, J = 10.5 Hz), 130.78 , 130.71 (d, J = 15.5 Hz), 129.74 , 124.84 (d, J = 6.7 Hz), 121.04 (d, J = 7.4 Hz), 116.72 (d, J = 1.4 Hz), 41.49 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.25 ppm.

IR (ATR): 3364 (bw), 2924 (w), 1574 (s), 1354 (s), 1315 (s), 1246 (m), 1215 (w), 1150 (s), 895 (m), 817 (s), 748 (m), 667 (w) cm^{-1}.

HRMS (ESI): Calcd. for $C_{29}H_{28}N_2OP$ $(M)^+$ 451.1939, found 451.1941.

***N*-(7-(dimethylamino)-5-oxido-5-phenyl-10-(o-tolyl)-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium chloride (13i):**



Following **General procedure 4,** dibromide **10a** (50.0 mg, 0.096 mmol, 1 equiv.) in THF (1.0 mL) and *t*-BuLi (0.26 mL, 0.42 mmol, 4.4 equiv. 1.9 M in pentane) were used. Methyl-2-methylbenzoate **11g** (20 µL, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added. After removal of cooling bath the reaction mixture was stirred for 1 h, aq. HCl (1 mL, 1.91 mmol, 20 equiv., 2 M) was added and stirred for 15 min. The crude product was purified by column chromatography to yield **13i** (37 mg, 77%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.79 – 7.60 (m, 5H), 7.59 – 7.48 (m, 4H), 7.48 – 7.41 (m, 2H), 7.25 – 7.11 (m, 3H), 6.97 (dd, J = 9.7, 2.8 Hz, 2H), 3.40 (d, J = 6.9 Hz, 12H), 2.07 (d, J = 14.0 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (75 MHz, Methanol-d_4): δ = 156.62 (d, J = 13.1 Hz), 156.57 (d, J = 13.1 Hz), 141.26 (d, J = 9.0 Hz), 139.32 (d, J = 94.9 Hz), 139.17 (d, J = 95.3 Hz), 137.17 (d, J = 44.9 Hz), 136.91 (d, J = 22.1 Hz), 134.47 (d, J = 2.9 Hz), 134.44 (d, J = 27.9 Hz), 132.99 (d, J = 27.6 Hz), 131.72 (d, J = 6.1 Hz), 131.15 (d, J = 20.4 Hz), 131.03 (d, J = 19.0 Hz), 130.71 (d, J = 12.8 Hz), 130.61 (d, J = 12.8 Hz),

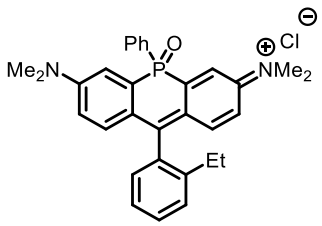
129.51, 127.17 (d, *J* = 12.4 Hz), 124.57 (d, *J* = 6.8 Hz), 124.40 (d, *J* = 6.5 Hz), 121.05 (d, *J* = 7.3 Hz), 117.06, 41.57, 19.71, 19.51 ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, Methanol-d_4): δ = 14.48, 14.22 ppm.

IR (ATR): 3287 (bw), 2920 (w), 2855 (w), 1578 (s), 1489 (m), 1439 (m), 1354 (s), 1315 (s), 1246 (w), 1146 (s), 1057 (m), 903 (s), 868 (s) cm^{-1}.

HRMS (ESI): Calcd for $C_{30}H_{30}N_2OP$ $(M)^+$ 465.2096, found 465.2100.

***N*-(7-(dimethylamino)-10-(2-ethylphenyl)-5-oxido-5-phenyl-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium chloride (13d):**



Following **General procedure 4,** dibromide **10a** (50.0 mg, 0.096 mmol, 1 equiv.) in THF (1.0 mL) and *t*-BuLi (0.21 mL, 0.40 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-ethylbenzoate **11d** (24 mg, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 1 h. After removal of cooling bath the reaction mixture was stirred for 1 h, aq. HCl (1.0 mL, 1.91 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13d** (35 mg, 71%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.79 – 7.40 (m, 10H), 7.23 – 7.14 (m, 3H), 6.98 (dd, J = 9.6, 2.8 Hz, 2H), 3.40 (d, J = 14.3 Hz, 12H), 2.33 (q, J = 7.6 Hz, 2H), 0.94 (t, J = 7.6 Hz, 3H) ppm.

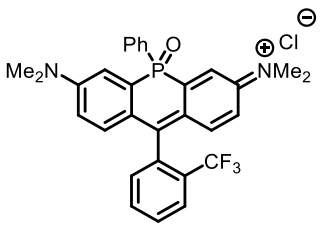
$^{13}C\{^{1}H\}$ NMR (101 MHz, Methanol-d_4): δ = 164.10 (d, J = 6.9 Hz), 155.16 (d, J = 13.0 Hz), 141.01 (d, J = 144.1 Hz), 140.15 (d, J = 8.9 Hz), 137.67 (d, J = 95.3 Hz), 133.86 (d, J = 161.1 Hz), 133.11 (d, J = 2.8 Hz), 132.04 , 129.88 (d, J = 11.1 Hz), 129.72 (d, J = 4.7 Hz), 129.22 (d, J = 12.9 Hz), 128.45 (d, J = 40.3 Hz), 127.36 (d, J = 335.6 Hz), 123.68 (d, J = 6.6 Hz), 119.56 (d, J = 7.0 Hz), 115.67 – 115.42 (m), 40.24, 26.18, 14.44 ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, Methanol-d_4): δ = 14.63, 14.22 ppm.

IR (ATR): 3406 (bw), 2967 (w), 2870 (w), 1578 (s), 1489 (m), 1439 (m), 1354 (s), 1315 (s), 1246 (m), 1215 (m), 1150 (s), 1057 (m), 957 (m), 907 (s), 818 (s), 748 (w) cm^{-1}.

HRMS (ESI): Calcd. for $C_{31}H_{32}N_2OP$ $(M)^+$ 479.2252, found 479.2262.

***N*-(7-(dimethylamino)-5-oxido-5-phenyl-10-(2-(trifluoromethyl)phenyl)-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium chloride (13l):**



Following **General procedure 4,** dibromide **10a** (50.0 mg, 0.096 mmol, 1 equiv.) in THF (1.0 mL) and *t*-BuLi (0.21 mL, 0.40 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-(trifluoromethyl)benzoate **11h** (15 µL, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 30 minutes, aq. HCl (1 mL, 1.91 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13l** (42 mg, 79%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 8.01 (dd, J = 7.5, 1.8 Hz, 1H), 7.88 (qd, J = 7.5, 1.6 Hz, 2H), 7.79 – 7.57 (m, 5H), 7.52 (tdd, J = 6.4, 3.3, 1.3 Hz, 2H), 7.48 (dd, J = 7.1, 1.6 Hz, 1H), 7.08 – 6.93 (m, 4H), 3.40 (d, J = 8.7 Hz, 12H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 156.52 (d, J = 13.0 Hz), 141.53 (d, J = 8.8 Hz), 141.37 (d, J = 8.9 Hz), 140.02 – 138.45 (m), 135.57 – 133.01 (m), 131.49 (d, J = 9.6 Hz), 131.20 (d, J = 11.0 Hz), 130.74 (d, J = 13.0 Hz), 130.49 (d, J = 13.0 Hz), 129.65 (d, J = 30.4 Hz), 127.89 (q, J = 4.9 Hz), 125.23 (d, J = 273.9 Hz), 125.18 – 124.83 (m), 121.44 (d, J = 7.2 Hz), 121.30 (d, J = 7.5 Hz), 116.96 (d, J = 8.4 Hz), 41.66 ppm.

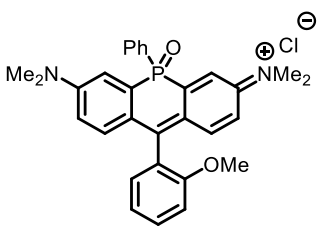
^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 10.42 ppm.

^{19}F NMR (377 MHz, Methanol-d_4): δ = -59.96 ppm.

IR (ATR): 3379 (bw), 2924 (w), 1578 (s), 1493 (m), 1439 (m), 1354 (s), 1312 (s), 1250 (m), 1219 (m), 1153 (s), 1107 (m), 910 (s), 880 (m), 818 (m) cm^{-1}.

HRMS (ESI): Calcd. for $C_{30}H_{27}F_3N_2OP$ $(M)^+$ 519.1813, found 519.1810.

***N*-(7-(dimethylamino)-10-(2-methoxyphenyl)-5-oxido-5-phenyl-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium chloride (13b):**



Following **General procedure 4,** dibromide **10a** (50.0 mg, 0.096 mmol, 1 equiv.) in THF (1.0 mL) and *t*-BuLi (0.21 mL, 0.40 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-methoxybenzoate **11b** (21 µL, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 1 h, aq. HCl (1.0 mL, 1.91 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13b** (16 mg, 32%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.87 – 7.76 (m, 2H), 7.77 – 7.67 (m, 1H), 7.65 – 7.57 (m, 4H), 7.53 (dtd, J = 8.7, 6.8, 3.4 Hz, 2H), 7.33 – 7.16 (m, 5H), 6.93 (ddd, J = 9.6, 5.6, 2.8 Hz, 2H), 3.77 (d, J = 18.7 Hz, 3H), 3.37 (d, J = 3.3 Hz, 12H) ppm.

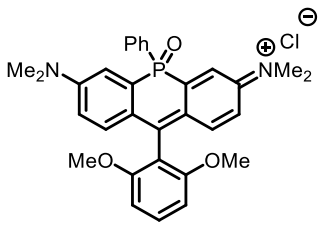
^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 158.20 (d, J = 25.1 Hz), 156.61 (d, J = 13.4 Hz), 141.74 (d, J = 9.2 Hz), 141.41 (d, J = 8.8 Hz), 139.42 (d, J = 95.2 Hz), 134.37 (d, J = 2.4 Hz), 134.25 (d, J = 3.2 Hz), 132.75 (d, J = 6.0 Hz), 131.49 (d, J = 110.2 Hz), 131.06 (d, J = 11.1 Hz), 130.68 (d, J = 12.8 Hz), 130.51 (d, J = 13.0 Hz), 128.28 (d, J = 515.0 Hz), 125.32 (d, J = 6.7 Hz), 121.78 (d, J = 9.7 Hz), 120.72 (d, J = 7.6 Hz), 120.31 (d, J = 7.2 Hz), 116.74, 112.73 (d, J = 16.9 Hz), 56.53, 56.30, 41.45 (d, J = 2.4 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.20, 14.16 ppm.

IR (ATR): 3372 (bw), 2920 (m), 2851 (m), 1578 (s), 1489 (m), 1435 (m), 1354 (s), 1323 (s), 1246 (m), 1153 (s), 1061 (m), 907 (s), 818 (s) 752 (m) cm^{-1}.

HRMS (ESI): Calcd. for $C_{30}H_{30}N_2O_2P$ $(M)^+$ 481.2045, found 481.2052.

***N*-(10-(2,6-dimethoxyphenyl)-7-(dimethylamino)-5-oxido-5-phenyl-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium chloride (13c):**



Following **General procedure 4,** dibromide **10a** (50.0 mg, 0.096 mmol, 1 equiv.) in THF (1.0 mL) and *t*-BuLi (0.21 mL, 0.40 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2,6-dimethoxybenzoate **11c** (28 mg, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 2 h, aq. HCl (1.0 mL, 1.91 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13c** (26 mg, 50%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.86 – 7.77 (m, 2H), 7.65 – 7.56 (m, 4H), 7.52 (td, J = 7.6, 3.4 Hz, 2H), 7.28 (dd, J = 9.6, 6.2 Hz, 2H), 6.96 – 6.86 (m, 4H), 3.76 (s, 3H), 3.74 (s, 3H), 3.36 (s, 12H) ppm.

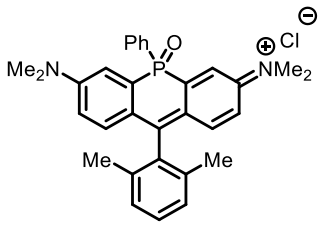
^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 163.13 (d, J = 6.9 Hz), 158.99 (d, J = 32.0 Hz), 156.68 (d, J = 13.0 Hz), 141.07 (d, J = 8.9 Hz), 139.32 (d, J = 95.2 Hz), 134.20 (d, J = 2.8 Hz), 133.78 (d, J = 108.8 Hz), 133.33 , 130.88 (d, J = 10.7 Hz), 130.48 (d, J = 13.0 Hz), 125.33 (d, J = 6.9 Hz), 119.96 (d, J = 7.3 Hz), 116.79 , 113.99 , 105.32 (d, J = 12.1 Hz), 56.80, 56.58, 41.43 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.11 ppm.

IR (ATR): 3356 (bw), 2924 (m), 2851 (m), 1717 (w), 1578 (s), 1470 (m), 1435 (m), 1354 (s), 1319 (s), 1250 (m), 1219 (w), 1150 (s), 1103 (s), 907 (s), 822 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{31}H_{32}N_2O_3P$ $(M)^+$ 511.2151, found 511.2152.

***N*-(7-(dimethylamino)-10-(2,6-dimethylphenyl)-5-oxido-5-phenyl-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium chloride (13e):**



Following **General procedure 4,** dibromide **10a** (50.0 mg, 0.096 mmol, 1 equiv.) in THF (1.0 mL) and *t*-BuLi (0.21 mL, 0.40 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2,6-dimethylbenzoate **11e** (24 mg, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 30 minutes, aq. HCl (1.0 mL, 1.91 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13e** (5 mg, 10%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.73 (d, J = 2.7 Hz, 1H), 7.69 (td, J = 3.4, 1.4 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.53 (td, J = 7.7, 3.5 Hz, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 8.0 Hz, 2H), 7.13 (dd, J = 9.6, 6.1 Hz, 2H), 6.97 (dd, J = 9.6, 2.8 Hz, 2H), 3.41 (s, 12H), 2.01 (s, 3H), 1.99 (s, 3H) ppm.

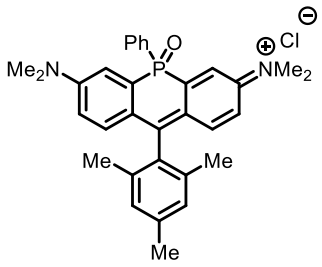
^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 156.77 (d, J = 13.6 Hz), 140.30 (d, J = 8.4 Hz), 139.20 (d, J = 94.9 Hz), 137.06 (d, J = 83.9 Hz), 134.52 (d, J = 2.9 Hz), 134.41 (d, J = 2.4 Hz), 131.33 (d, J = 10.8 Hz), 130.70 (d, J = 3.6 Hz), 130.55 , 129.04 (d, J = 6.4 Hz), 124.02 (d, J = 2.3 Hz), 123.93 (d, J = 6.9 Hz), 121.15 (d, J = 6.9 Hz), 117.43, 41.57, 19.93, 19.71 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.52 ppm.

IR (ATR): 3383 (bw), 2920 (m), 1578 (s), 1354 (s), 1319 (s), 1250 (m), 1215 (w), 1150 (s), 1057 (m), 903 (s), 818 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{31}H_{32}N_2OP$ $(M)^+$ 479.2252, found 479.2262.

***N*-(7-(dimethylamino)-10-mesityl-5-oxido-5-phenyl-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium chloride (13f):**



Following **General procedure 4,** dibromide **10a** (50.0 mg, 0.096 mmol, 1 equiv.) in THF (1.0 mL) and *t*-BuLi (0.21 mL, 0.40 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2,4,6-trimethylbenzoate **11f** (26 mg, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 3 h, aq. HCl (1.0 mL, 1.91 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13f** (10 mg, 20%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.74 – 7.58 (m, 6H), 7.52 (td, J = 7.5, 3.5 Hz, 2H), 7.20 – 7.07 (m, 4H), 6.97 (dd, J = 9.6, 2.9 Hz, 2H), 3.40 (s, 12H), 2.40 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H) ppm.

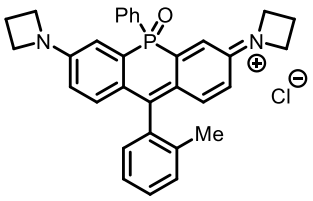
^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 156.76 (d, J = 13.9 Hz), 140.83, 140.48 (d, J = 8.7 Hz), 139.18 (d, J = 92.0 Hz), 136.90 (d, J = 84.4 Hz), 134.49 (d, J = 2.5 Hz), 133.50 (d, J = 34.5 Hz), 131.31 (d, J = 10.5 Hz), 130.60 (d, J = 12.7 Hz), 129.70 (d, J = 5.1 Hz), 124.28 (d, J = 5.5 Hz), 121.04 (d, J = 7.0 Hz), 117.37, 41.54, 21.20, 19.88, 19.65 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.50 ppm.

IR (ATR): 3364 (bw), 2920 (m), 2855 (m), 1578 (s), 1493 (m), 1439 (m), 1354 (s), 1323 (s), 1250 (m), 1215 (w), 1153 (s), 1057 (s), 907 (s), 818 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{32}H_{34}N_2OP$ $(M)^+$ 493.2413, found 493.2409.

1-(7-(azetidin-1-yl)-5-oxido-5-phenyl-10-(o-tolyl)-3*H*-acridophosphin-3-ylidene)azetidin-1-ium chloride (13j)



Following **General procedure 4,** dibromide **10c** (50.0 mg, 0.09 mmol, 1 equiv.) in THF (0.9 mL) and *t*-BuLi (0.20 mL, 0.38 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-methylbenzoate **11g** (19 µL, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 1 h, aq. HCl (0.9 mL, 1.83 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13j** (31 mg, 65%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.81 – 7.58 (m, 3H), 7.58 – 7.38 (m, 5H), 7.30 – 7.00 (m, 5H), 6.60 – 6.48 (m, 2H), 4.42 (s, 8H), 2.63 – 2.47 (m, 4H), 2.05 (d, J = 9.8 Hz, 3H) ppm.

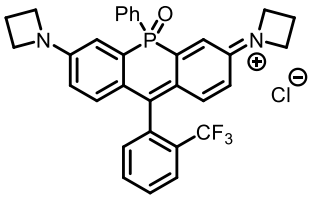
^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 155.13 (d, J = 12.2 Hz), 140.75 (d, J = 8.5 Hz), 139.45 (d, J = 13.5 Hz), 138.50 (d, J = 13.0 Hz), 137.37 (d, J = 9.5 Hz), 136.95 (d, J = 20.4 Hz), 134.56 – 134.28 (m), 133.53 – 132.18 (m), 131.76 , 131.35 (d, J = 64.4 Hz), 131.20 (d, J = 10.9 Hz), 130.79 (d, J = 2.3 Hz), 130.67 (d, J = 13.0 Hz), 130.58 (d, J = 13.0 Hz), 127.21 (d, J = 16.7 Hz), 119.13 (d, J = 6.5 Hz), 114.80, 53.78, 19.54 (d, J = 21.3 Hz), 16.78 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 13.86, 13.63 ppm.

IR (ATR): 3383 (bw) 2920 (m), 2851 (m), 1582 (s), 1366 (s), 1285 (s), 1223 (s), 1146 (s), 1026 (w), 903 (m), 749 (m) cm^{-1}.

HRMS (ESI): Calcd. for $C_{32}H_{30}N_2OP$ $(M)^+$ 489.2096, found 489.2091.

1-(7-(azetidin-1-yl)-5-oxido-5-phenyl-10-(2-(trifluoromethyl)phenyl)-3*H*-acridophosphin-3-ylidene)azetidin-1-ium chloride (13m):



Following **General procedure 4,** dibromide **10c** (50.0 mg, 0.09 mmol, 1 equiv.) in THF (0.9 mL) and *t*-BuLi (0.20 mL, 0.38 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-(trifluoromethyl)benzoate **11h** (20 µL, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred

at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 1 h, aq. HCl (0.9 mL, 1.83 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13m** (37 mg, 70%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-*d4*): δ = 8.08 – 7.95 (m, 1H), 7.86 (dp, J = 14.4, 7.3 Hz, 2H), 7.75 – 7.58 (m, 3H), 7.53 (tt, J = 7.7, 3.6 Hz, 2H), 7.48 – 7.39 (m, 1H), 7.36 – 7.19 (m, 2H), 6.87 (d, J = 41.1 Hz, 2H), 6.63 – 6.43 (m, 2H), 4.44 (s, 8H), 2.55 (p, J = 7.7 Hz, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 154.98, 140.99, 134.42 (d, J = 3.0 Hz), 133.69, 131.34, 131.16 (d, J = 11.1 Hz), 130.70 (d, J = 12.9 Hz), 130.46 (d, J = 13.2 Hz), 127.90 (d, J = 5.2 Hz), 125.23 (d, J = 273.6 Hz), 119.37, 114.71, 53.89, 16.77 ppm.

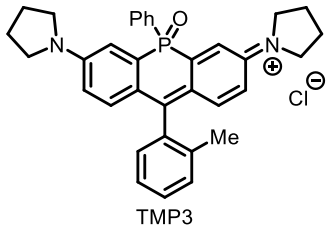
^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 13.54 ppm.

^{19}F NMR (377 MHz, Methanol-d_4): δ = -60.05 ppm.

IR (ATR): 3368 (bw) 2920 (m), 2851 (m), 1582 (s), 1369 (s), 1285 (s), 1227 (s), 1150 (m), 1034 (w), 1146 (s), 907 (m), 741 (m) cm^{-1}.

HRMS (ESI): Calcd. for $C_{32}H_{27}F_3N_2OP$ $(M)^+$ 543.1813, found 543.1817.

1-(5-oxido-5-phenyl-7-(pyrrolidin-1-yl)-10-(o-tolyl)-3*H*-acridophosphin-3-ylidene)pyrrolidin-1-ium (13k):



TMP3

Following **General procedure 4,** dibromide **10d** (40.0 mg, 0.07 mmol, 1 equiv.) in THF (0.7 mL) and *t*-BuLi (0.15 mL, 0.29 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-methylbenzoate **11g** (15 µL, 0.10 mmol, 1.5 equiv.) in THF (1.0 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 1 h, aq. HCl (0.7 mL, 1.39 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13k** (20 mg, 52%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.80 – 7.60 (m, 3H), 7.59 – 7.38 (m, 7H), 7.24 – 7.17 (m, 1H), 7.12 (ddd, J = 9.5, 7.5, 6.1 Hz, 2H), 6.81 (dd, J = 9.5, 2.6 Hz, 2H), 3.73 (d, J = 44.2 Hz, 8H), 2.13 (dq, J = 8.2, 5.1, 4.1 Hz, 8H), 2.07 (d, J = 12.5 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 165.20 (d, J = 5.0 Hz), 153.87 (d, J = 13.0 Hz), 153.83 (d, J = 13.1 Hz), 141.06 (d, J = 8.8 Hz), 139.25 (d, J = 94.4 Hz), 139.10 (d, J = 94.6 Hz), 137.36 (d, J =

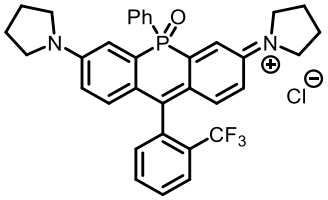
23.7 Hz), 136.93 (d, *J* = 7.0 Hz), 134.47 (d, *J* = 18.5 Hz), 134.44 (d, *J* = 3.3 Hz), 132.58 (d, *J* = 181.0 Hz), 131.77, 131.22 (d, *J* = 10.6 Hz), 130.87 (d, *J* = 7.8 Hz), 130.60 (d, *J* = 12.9 Hz), 128.41 (d, *J* = 228.7 Hz), 124.56 (d, *J* = 6.8 Hz), 124.39 (d, *J* = 6.7 Hz), 122.43 (d, *J* = 940.4 Hz), 121.97 (d, *J* = 7.0 Hz), 50.84, 26.00 (d, *J* = 8.8 Hz), 19.68, 19.47 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-*d*$_4$): δ = 14.30, 14.06 ppm.

IR (ATR): 3325 (bw) 2920 (m), 2862 (m), 1574 (s), 1373 (s), 1308 (s), 1227 (s), 1153 (s), 1103 (m), 903 (s), 849 (m), 748 (m), 718 (m), 694 (w), 629 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{34}H_{34}N_2OP$ $(M)^+$ 517.2409, found 517.2411.

1-(5-oxido-5-phenyl-7-(pyrrolidin-1-yl)-10-(2-(trifluoromethyl)phenyl)-3*H*-acridophosphin-3-ylidene)pyrrolidin-1-ium (13n):



Following **General procedure 4,** dibromide **10d** (40.0 mg, 0.07 mmol, 1 equiv.) in THF (0.7 mL) and *t*-BuLi (0.15 mL, 0.29 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-(trifluoromethyl)benzoate **11h** (15 µL, 0.10 mmol, 1.5 equiv.) in THF (1.0 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 1 h, aq. HCl (0.7 mL, 1.39 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **13n** (23 mg, 54%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-*d*$_4$): δ = 8.01 (dd, J = 7.5, 1.7 Hz, 1H), 7.92 – 7.82 (m, 2H), 7.72 – 7.65 (m, 2H), 7.62 (td, J = 7.3, 1.5 Hz, 1H), 7.57 (d, J = 2.5 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.49 – 7.45 (m, 1H), 6.98 (dd, J = 9.6, 6.0 Hz, 2H), 6.82 (dd, J = 9.5, 2.5 Hz, 2H), 3.73 (d, J = 36.7 Hz, 8H), 2.12 (dd, J = 7.1, 3.8 Hz, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Methanol-*d*$_4$): δ = 153.75 (d, *J* = 13.1 Hz), 141.17 (d, *J* = 9.0 Hz), 139.08 (d, *J* = 94.0 Hz), 135.85 – 135.54 (m), 134.41 (d, *J* = 3.2 Hz), 133.20 (d, *J* = 10.4 Hz), 132.52 (d, *J* = 228.9 Hz), 131.18 (d, *J* = 10.5 Hz), 130.49 (d, *J* = 13.0 Hz), 127.90 (d, *J* = 4.9 Hz), 125.26 (d, *J* = 273.9 Hz), 125.36 – 124.75 (m), 122.21 (d, *J* = 7.0 Hz), 117.69, 50.95, 26.02, 25.92 ppm.

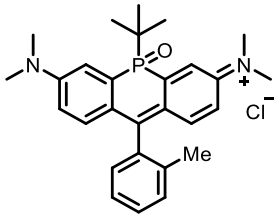
^{31}P{^{1}H} NMR (162 MHz, Methanol-*d*$_4$): δ = 14.07 ppm.

^{19}F NMR (377 MHz, Methanol-*d*$_4$): δ = -60.00 ppm.

IR (ATR): 3325 (bw) 2920 (m), 2855 (m), 1578 (s), 1373 (s), 1304 (s), 1227 (s), 1153 (s), 1099 (s), 1034 (w), 1146 (s), 907 (m), 849 (m), 748 (w), 629 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{34}H_{31}F_3N_2OP$ $(M)^+$ 571.2126, found 571.2131.

***N*-(5-(tert-butyl)-7-(dimethylamino)-5-oxido-10-(o-tolyl)-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium chloride (13g):**



Following modified **General procedure 4,** dibromide **10b** (100.0 mg, 0.2 mmol, 1 equiv.) in THF (5 mL) and *t*-BuLi (0.44 mL, 0.84 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl 2-methylbenzoate **11g** (45 µL, 0.30 mmol, 1.5 equiv.) in THF (5 mL) was added over the course of 15 min and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 1 h, letting it to warm up. After addition of aq. HCl (1 mL) reaction was stirred for 15 minutes at 25 °C. The crude product was purified by column chromatography, according to **General procedure 4, 13g** (70 mg, 73%) was obtained as dark green solid.

R_f = 0.46 in DCM:MeOH = 9:1

IR (ATR) $\tilde{\nu}$ = 2881.6 (m), 2360.5 (w), 2161.1 (w), 1951.6 (w), 1818 (w), 1641.8 (w), 1525.5 (m), 1422.4 (m), 1273.1 (s), 1195.7 (s), 1073.1 (s), 974.19 (s), 929.42 (m), 848.3 (m), 781.7 (s), 708.14 (m), 614.08 (s) cm^{-1}.

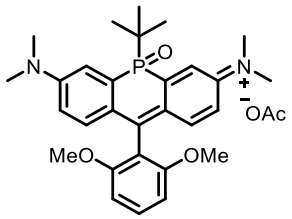
^{1}H NMR (300 MHz, Methanol-d_4, 297 K) δ = 7.66 (dd, *J* = 14.0, 2.7 Hz, 2H), 7.55 – 7.37 (m, 3H), 7.19 – 7.04 (m, 3H), 6.98 (dd, *J* = 9.7, 2.8 Hz, 2H), 3.44 (s, 9H), 2.17 (s, 3H), 1.29 (s, 5H), 1.23 (s, 4H), 1.17 (d, *J* = 3.4 Hz, 5H) ppm.

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4, 297 K) δ = 156.13, 156.01, 141.72, 141.64, 137.12, 136.91, 131.91, 131.76, 131.03, 127.23, 126.02, 122.61, 122.54, 122.53, 117.04, 41.66, 30.89, 23.15, 20.4 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4, 297 K) δ = 30.43 ppm.

HRMS (EI^+) m/z: Calcd. for $C_{28}H_{34}N_2OP^+$ (M^+) 445.2403, found 445.2409.

***N*-(5-(*tert*-butyl)-10-(2,6-dimethoxyphenyl)-7-(dimethylamino)-5-oxido-3*H*-acridophosphin-3-ylidene)-*N*-methylmethanaminium acetate (13h):**



Following modified **General procedure 4,** dibromide **10b** (80.0 mg, 0.16 mmol, 1 equiv.) in THF (5 mL) and *t*-BuLi (0.35 mL, 0.672 mmol, 4.2 equiv. 1.9 M in pentane) were used. After addition of *t*-BuLi and stirring for 30 min at -78 °C, reaction flask was transferred to cooling bath with -20 °C and methyl 2,6-dimethoxybenzoate **11g** (47 mg, 0.24 mmol, 1.5 equiv.) in THF (5.0 mL) was added over 1 h. Reaction was let to warm up to room temperature over 6 h. After addition of aq. HCl (1 mL) reaction was stirred for 15 minutes. The crude product was purified by column chromatography using DCM:MeOH from 0% MeOH to 10% of MeOH with constant 1% of AcOH. Product **13h** (47 mg, 54%) was isolated as dark green solid.

R_f = 0.28 in DCM:MeOH = 9:1

IR (ATR) $\tilde{\nu}$ = 2994 (m), 2877.2 (m), 2400.5 (w), 2359.7 (w), 2167.1 (w), 2027.8 (w), 1967.8 (w), 1931.4 (w), 1857 (w), 1820.4 (w), 1664.9 (w), 1482.4 (m), 1395.1 (s), 1269.7 (m), 1191.5 (m), 1120.1 (m), 1073.6 (m), 928 (m), 848.88 (m), 762.2 (m), 710.17 (m) cm^{-1}.

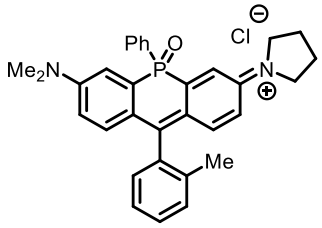
^{1}H NMR (400 MHz, Methanol-d_4, 297 K) δ = 7.83 – 7.46 (m, 3H), 7.42 – 7.18 (m, 2H), 6.93 (ddd, *J* = 37.1, 9.0, 3.5 Hz, 4H), 3.68 (d, *J* = 8.0 Hz, 5H), 3.45 (s, 6H), 1.31 (s, 6H), 1.18 (d, *J* = 16.3 Hz, 10H), 0.92 (s, 3H) ppm.

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4, 297 K) δ = 178.02, 157.92, 157.41, 154.56, 154.43, 139.81, 139.73, 134.98, 131.86, 131.82, 125.21, 120.18, 120.12, 115.22, 112.60, 103.88, 103.72, 55.09, 54.92, 40.00, 29.34, 27.73, 22.31, 21.98, 21.63 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4, 297 K) δ = 35.04 ppm.

HRMS (EI^+) m/z: Calcd. for $C_{29}H_{36}N_2O_3P^+$ $(M)^+$ 491.2458, found 491.2467.

1-(7-(dimethylamino)-5-oxido-5-phenyl-10-(o-tolyl)-3*H*-acridophosphin-3-ylidene)pyrrolidin-1-ium chloride (19a):



Following **General procedure 4,** dibromide **18** (50.0 mg, 0.09 mmol, 1 equiv.) in THF (0.9 mL) and *t*-BuLi (0.20 mL, 0.38 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-methyl benzoate **11g** (19 µL, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 1 h. After removal of cooling bath the reaction miVaxture was stirred for 1 h, aq. HCl (0.9 mL, 1.83 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **19a** (25 mg, 52%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.80 – 7.66 (m, 2H), 7.66 – 7.59 (m, 2H), 7.59 – 7.48 (m, 4H), 7.48 – 7.39 (m, 2H), 7.26 – 7.07 (m, 3H), 6.95 (dd, J = 9.6, 2.7 Hz, 1H), 6.83 (dd, J = 9.6, 2.6 Hz, 1H), 3.88 – 3.66 (m, 4H), 3.37 (d, J = 6.6 Hz, 6H), 2.18 – 2.09 (m, 5H), 2.07 (d, J = 13.1 Hz, 3H) ppm.

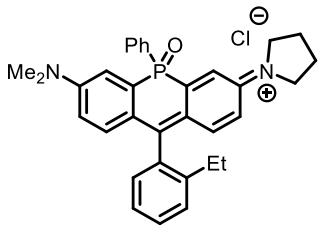
^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 165.36 (d, *J* = 6.9 Hz), 156.39 (d, *J* = 4.4 Hz), 156.26 (d, *J* = 4.4 Hz), 154.16 (d, *J* = 4.2 Hz), 154.03 (d, *J* = 4.3 Hz), 141.35 (d, *J* = 8.9 Hz), 140.95 (d, *J* = 9.4 Hz), 140.14 (d, *J* = 14.2 Hz), 139.20 (d, *J* = 14.8 Hz), 138.26 (d, *J* = 15.4 Hz), 137.31 (d, *J* = 33.1 Hz), 136.88 (d, *J* = 2.9 Hz), 134.45 (d, *J* = 3.2 Hz), 134.45 (d, *J* = 11.1 Hz), 133.60 (d, *J* = 110.1 Hz), 132.55 (d, *J* = 174.8 Hz), 131.22 (d, *J* = 10.5 Hz), 131.10 (d, *J* = 10.8 Hz), 130.89 (d, *J* = 5.2 Hz), 130.71 (d, *J* = 12.9 Hz), 130.61 (d, *J* = 12.9 Hz), 128.40 (d, *J* = 227.4 Hz), 127.10 , 124.71 (d, *J* = 6.9 Hz), 124.54 (d, *J* = 8.7 Hz), 124.38 (d, *J* = 10.1 Hz), 124.26 , 122.41 (d, *J* = 7.0 Hz), 120.80 – 120.48 (m), 118.00 (d, *J* = 4.5 Hz), 116.88 , 51.04 (d, *J* = 4.5 Hz), 41.40, 26.03, 25.91, 19.69, 19.48 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.39, 14.14 ppm.

IR (ATR): 3372 (bw), 2920 (w), 2855 (w), 1578 (s), 1366 (s), 1315 (s), 1242 (m), 1219 (w), 1153 (m), 1057 (m), 906 (m), 818 (m), 714 (w) cm^{-1}.

HRMS (ESI): Calcd. for $C_{32}H_{32}N_2OP$ $(M)^+$ 491.2252, found 491.2248.

1-(7-(dimethylamino)-10-(2-ethylphenyl)-5-oxido-5-phenyl-3*H*-acridophosphin-3-ylidene)-pyrrolidin-1-ium chloride (19b):



Following **General procedure 4,** dibromide **18** (53.0 mg, 0.097 mmol, 1 equiv.) in THF (1 mL) and *t*-BuLi (0.21 mL, 0.41 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-ethyl benzoate **11d** (24 mg, 0.15 mmol, 1.5 equiv.) in THF (1.5 mL) was added and stirred at –78 °C for 1 h. After removal of cooling bath the reaction mixture was stirred for 1 h, aq. HCl (1.0 mL, 1.94 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **19b** (25 mg, 48%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ =

7.79 – 7.39 (m, 12H), 7.21 – 7.12 (m, 3H), 6.95 (dd, *J* = 9.6, 2.8 Hz, 1H), 6.84 (dd, *J* = 9.5, 2.5 Hz, 1H), 3.84 (d, *J* = 6.6 Hz, 2H), 3.71 (t, *J* = 6.2 Hz, 2H), 3.39 (s, 7H), 2.33 (q, *J* = 7.5 Hz, 2H), 2.14 (p, *J* = 6.0 Hz, 5H), 0.94 (t, *J* = 7.6 Hz, 3H).

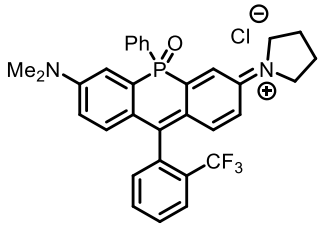
^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 165.22 (d, *J* = 7.3 Hz), 156.25 (d, *J* = 13.0 Hz), 154.02 (d, *J* = 13.1 Hz), 143.09, 141.61 (d, *J* = 9.3 Hz), 141.25, 138.97, 138.97 (d, *J* = 190.8 Hz), 136.12, 134.45 (d, *J* = 2.7 Hz), 134.00 (d, *J* = 109.3 Hz), 130.86 (d, *J* = 43.3 Hz), 130.85 (d, *J* = 67.7 Hz), 130.85 (d, *J* = 90.3 Hz), 127.06, 125.16 (d, *J* = 7.0 Hz), 124.93 (d, *J* = 6.9 Hz), 122.26 (d, *J* = 6.5 Hz), 120.51 (d, *J* = 7.5 Hz), 117.29 (d, *J* = 109.8 Hz), 51.07, 41.42, 27.54, 26.04, 25.93, 15.80 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.54, 14.14 ppm.

IR (ATR): 3379 (bw), 2924 (w), 2862 (w), 1574 (s), 1366 (m), 1312 (s), 1219 (m), 1153 (s), 1057 (m), 907 (s), 814 (m), 748 (m) cm^{-1}.

HRMS (ESI): Calcd. for $C_{33}H_{34}N_2OP$ $(M)^+$ 505.2409, found 505.2394.

1-(7-(dimethylamino)-5-oxido-5-phenyl-10-(2-(trifluoromethyl)phenyl)-3*H*-acridophosphin-3-ylidene)pyrrolidin-1-ium chloride (19c):



Following **General procedure 4,** dibromide **18** (52.0 mg, 0.095 mmol, 1 equiv.) in THF (1 mL) and *t*-BuLi (0.21 mL, 0.40 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-(trifluoromethyl)benzoate **11h** (21 µL, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 30 minutes, aq. HCl (1.0 mL, 1.90 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **19c** (30 mg, 54%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 8.01 (dd, J = 7.5, 1.7 Hz, 1H), 7.93 – 7.82 (m, 2H), 7.81 – 7.42 (m, 9H), 7.05 – 6.93 (m, 3H), 6.84 (dd, J = 9.6, 2.6 Hz, 1H), 3.88 – 3.67 (m, 4H), 3.37 (d, J = 8.0 Hz, 6H), 2.17 – 2.06 (m, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 156.22 (d, J = 13.0 Hz), 154.01 (d, J = 13.1 Hz), 141.45 (d, J = 8.2 Hz), 141.04 (d, J = 9.3 Hz), 138.65 (d, J = 97.6 Hz), 135.58 , 134.42 (d, J = 3.0 Hz), 134.03 (d, J = 48.8 Hz), 133.15 , 131.46 (d, J = 9.8 Hz), 131.18 (d, J = 10.8 Hz), 130.73 (d, J = 12.9 Hz), 130.48 (d, J = 13.0 Hz), 127.89 (q, J = 4.9 Hz), 125.23 (d, J = 273.6 Hz), 125.30 – 124.75 (m), 122.69 (d, J = 6.7 Hz), 120.84 (d, J = 7.5 Hz), 117.35 (d, J = 114.9 Hz), 51.15, 41.47, 26.01, 25.89 ppm.

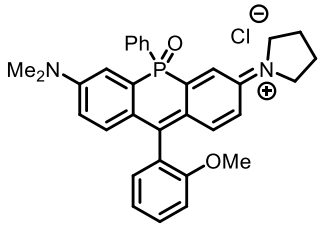
^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.15 ppm.

^{19}F NMR (377 MHz, Methanol-d_4): δ = -59.96 ppm.

IR (ATR): 3283 (bw), 2862 (w), 1578 (s), 1366 (m), 1308 (s), 1242 (m), 1223 (m), 1153 (s), 1103 (s), 1053 (m), 1030 (m), 907 (s), 814 (s), 748 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{32}H_{29}F_3N_2OP$ $(M)^+$ 545.1970, found 545.1979.

1-(7-(dimethylamino)-10-(2-methoxyphenyl)-5-oxido-5-phenyl-3*H*-acridophosphin-3-ylidene)pyrrolidin-1-ium chloride (19d):



Following **General procedure 4,** dibromide **18** (50.0 mg, 0.09 mmol, 1 equiv.) in THF (0.9 mL) and *t*-BuLi (0.20 mL, 0.38 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2-methoxybenzoate **11b** (20 µL, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 1 h, aq. HCl (0.9 mL, 1.82 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **19d** (25 mg, 51%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.87 – 7.78 (m, 2H), 7.76 – 7.68 (m, 1H), 7.67 – 7.47 (m, 6H), 7.31 – 7.18 (m, 5H), 6.92 (ddd, J = 9.6, 5.3, 2.8 Hz, 1H), 6.80 (ddd, J = 9.6, 4.6, 2.5 Hz, 1H), 3.83 – 3.61 (m, 5H), 3.34 (d, J = 3.3 Hz, 6H), 2.11 (dt, J = 7.4, 3.5 Hz, 4H) ppm.

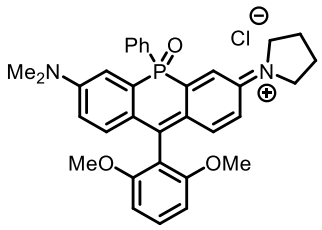
^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 164.21 (d, J = 6.9 Hz), 163.94 (d, J = 7.0 Hz), 158.19 (d, J = 25.2 Hz), 156.30 (d, J = 13.0 Hz), 154.09 (d, J = 13.0 Hz), 141.84 (d, J = 8.7 Hz), 141.50 (d, J = 9.4 Hz), 141.38 (d, J = 9.4 Hz), 141.04 (d, J = 9.4 Hz), 140.21 (d, J = 19.2 Hz), 139.34 (d, J = 4.4 Hz), 139.16 (d, J = 3.2 Hz), 138.28 (d, J = 18.1 Hz), 134.23 (d, J = 2.8 Hz), 133.54 (d, J = 161.7 Hz), 133.23 (d, J = 7.4 Hz), 132.35 (d, J = 65.2 Hz), 131.05 (d, J = 10.5 Hz), 130.88 (d, J = 11.0 Hz), 130.68 (d, J = 13.0 Hz), 130.51 (d, J = 12.7 Hz), 125.93 (d, J = 26.2 Hz), 125.43 (d, J = 6.3 Hz), 125.19 (d, J = 6.6 Hz), 125.06 (d, J = 6.2 Hz), 124.80 (d, J = 6.8 Hz), 122.04 (d, J = 7.1 Hz), 121.78 (d, J = 10.5 Hz), 121.64 (d, J = 7.0 Hz), 120.28 (d, J = 7.3 Hz), 119.87 (d, J = 7.6 Hz), 117.67 , 116.72 – 116.46 (m), 112.73 (d, J = 17.4 Hz), 56.55, 56.30, 50.93, 41.31, 26.01, 25.91 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.11, 14.03 ppm.

IR (ATR): 3375 (bw), 2920 (w), 2851 (w), 1574 (s), 1485 (m) 1366 (s), 1312 (s), 1224 (m), 1153 (s), 1061 (m), 903 (s), 814 (m), 694 (s) cm^{-1}.

HRMS (ESI): Calcd. for $C_{32}H_{32}N_2O_2P$ $(M)^+$ 507.2201, found 507.2203.

1-(10-(2,6-dimethoxyphenyl)-7-(dimethylamino)-5-oxido-5-phenyl-3*H*-acridophosphin-3-ylidene)pyrrolidin-1-ium chloride (19e):



Following **General procedure 4,** dibromide **18** (50.0 mg, 0.09 mmol, 1 equiv.) in THF (0.9 mL) and *t*-BuLi (0.20 mL, 0.38 mmol, 4.2 equiv. 1.9 M in pentane) were used. Methyl-2,6-dimethoxybenzoate **11c** (27 mg, 0.14 mmol, 1.5 equiv.) in THF (1.4 mL) was added and stirred at –78 °C for 30 minutes. After removal of cooling bath the reaction mixture was stirred for 2h, aq. HCl (0.9 mL, 1.82 mmol, 20 equiv., 2 M) was added and stirred for 15 minutes. The crude product was purified by column chromatography to yield **19e** (13 mg, 25%) as dark green solid.

^{1}H NMR (400 MHz, Methanol-d_4): δ = 7.82 (ddt, J = 12.9, 7.0, 1.4 Hz, 2H), 7.66 – 7.56 (m, 3H), 7.58 – 7.44 (m, 3H), 7.27 (ddd, J = 9.6, 6.1, 3.4 Hz, 2H), 6.91 (dt, J = 9.5, 4.1 Hz, 3H), 6.79 (dd, J = 9.5, 2.6 Hz, 1H), 3.75 (d, J = 10.7 Hz, 10H), 3.33 (s, 6H), 2.11 (s, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4): δ = 159.15, 158.83, 156.40 (d, J = 13.1 Hz), 154.21 (d, J = 13.2 Hz), 141.24 (d, J = 9.0 Hz), 140.67 (d, J = 9.3 Hz), 139.27 (d, J = 6.9 Hz), 138.29, 134.39, 134.17 (d, J = 2.8 Hz), 133.29 (d, J = 2.8 Hz), 132.15 (d, J = 94.5 Hz), 130.87 (d, J = 10.7 Hz), 130.46 (d, J = 13.0 Hz), 125.48 (d, J = 6.6 Hz), 125.17 (d, J = 6.9 Hz), 121.29 (d, J = 6.9 Hz), 119.54 (d, J = 7.4 Hz), 117.67 (d, J = 1.8 Hz), 116.60 (d, J = 1.5 Hz), 114.09, 105.29 (d, J = 13.0 Hz), 56.78, 56.56, 50.88, 41.26, 25.98 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methanol-d_4): δ = 14.12 ppm.

IR (ATR): 3387 (bw), 2924 (w), 2862 (w), 1574 (s), 1470 (m) 1366 (m), 1312 (s), 1219 (m), 1153 (s), 1099 (s), 1057 (m), 907 (s), 818 (m), 613 (m) cm^{-1}.

HRMS (ESI): Calcd. for $C_{33}H_{34}N_2O_3P$ $(M)^+$ 537.2307, found 537.2312.

3. References

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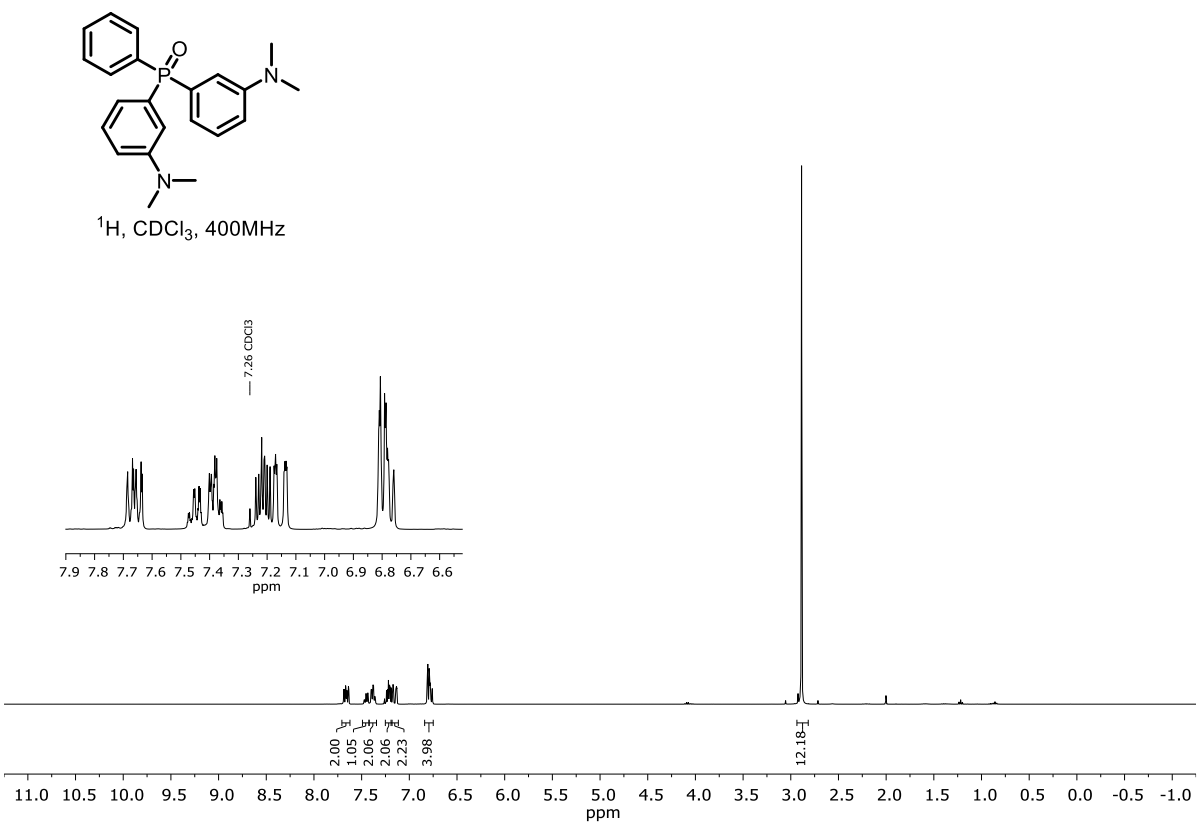
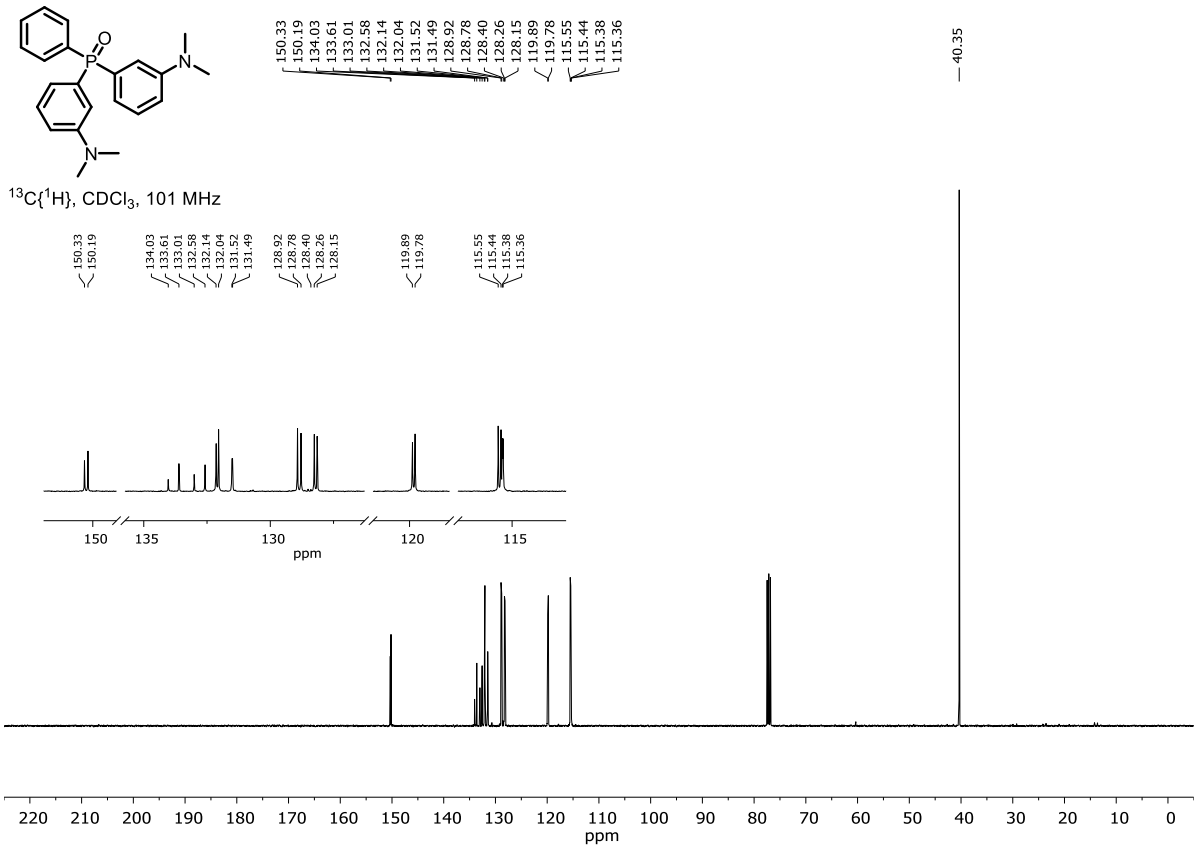
6. M. Shibuya, T. Sato, M. Tomizawa and Y. Iwabuchi, *Chem. Commun.*, 2009, 1739-1741.
7. Y. Nishiyama, Y. Hazama, S. Yoshida and T. Hosoya, *Org. Lett.*, 2017, **19**, 3899-3902

4. NMR spectra

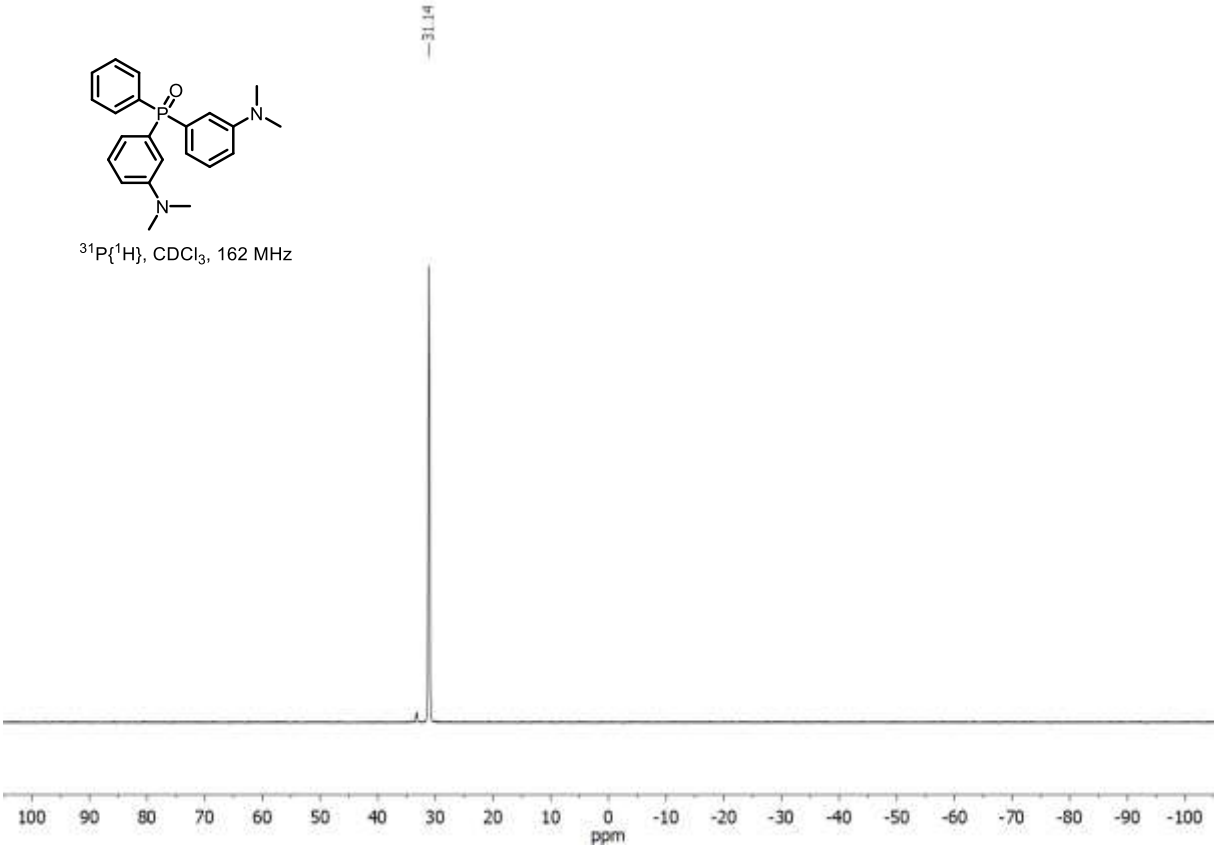
^{1}H NMR spectrum of 12a:



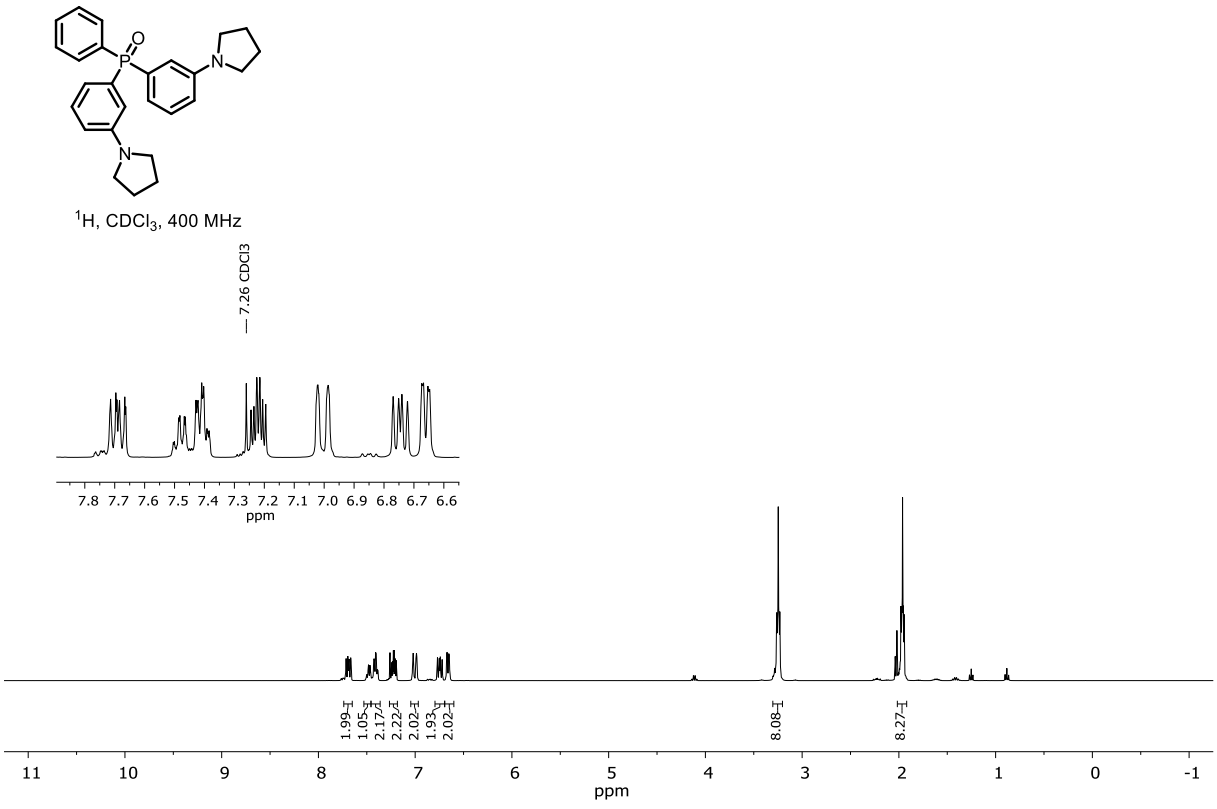
^{13}C{^{1}H} NMR spectrum of 12a:



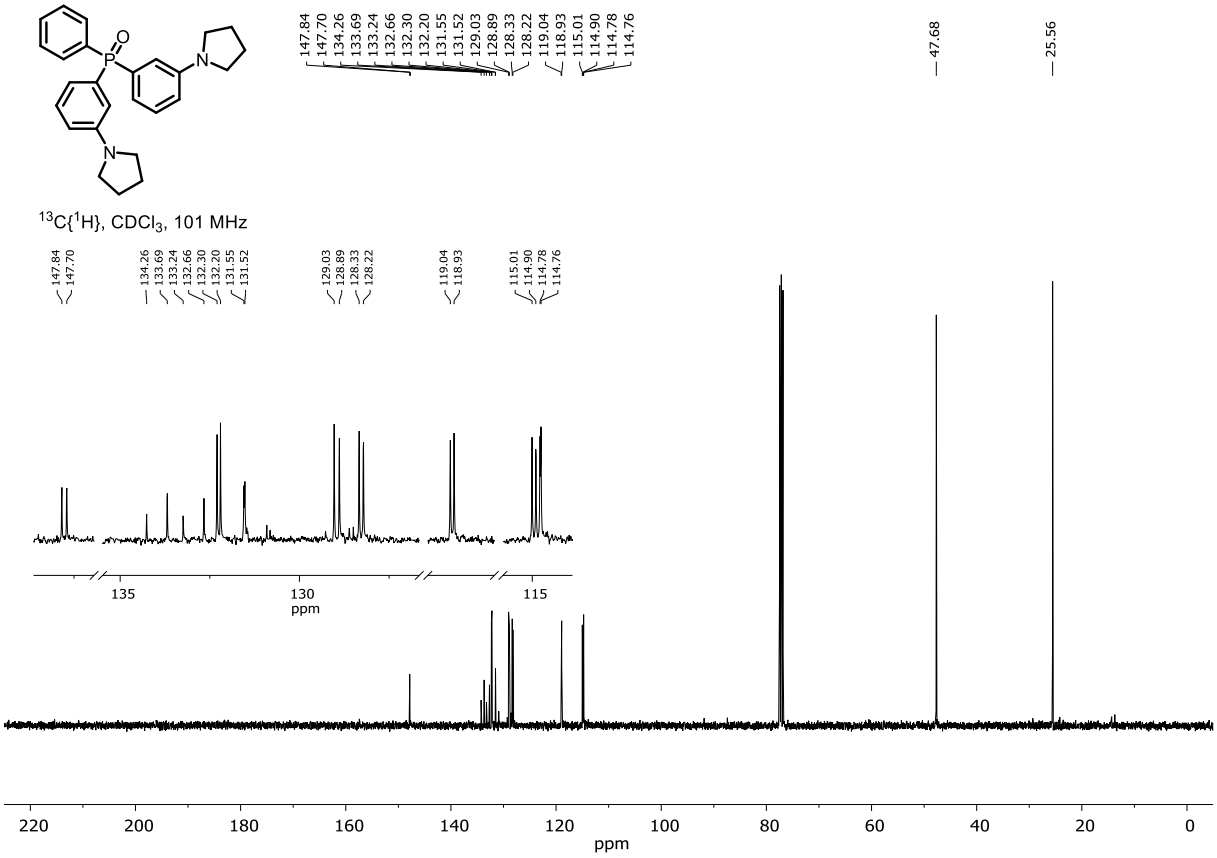
$^{31}P\{^{1}H\}$ NMR spectrum of 12a:



^{1}H NMR spectrum of 12d:

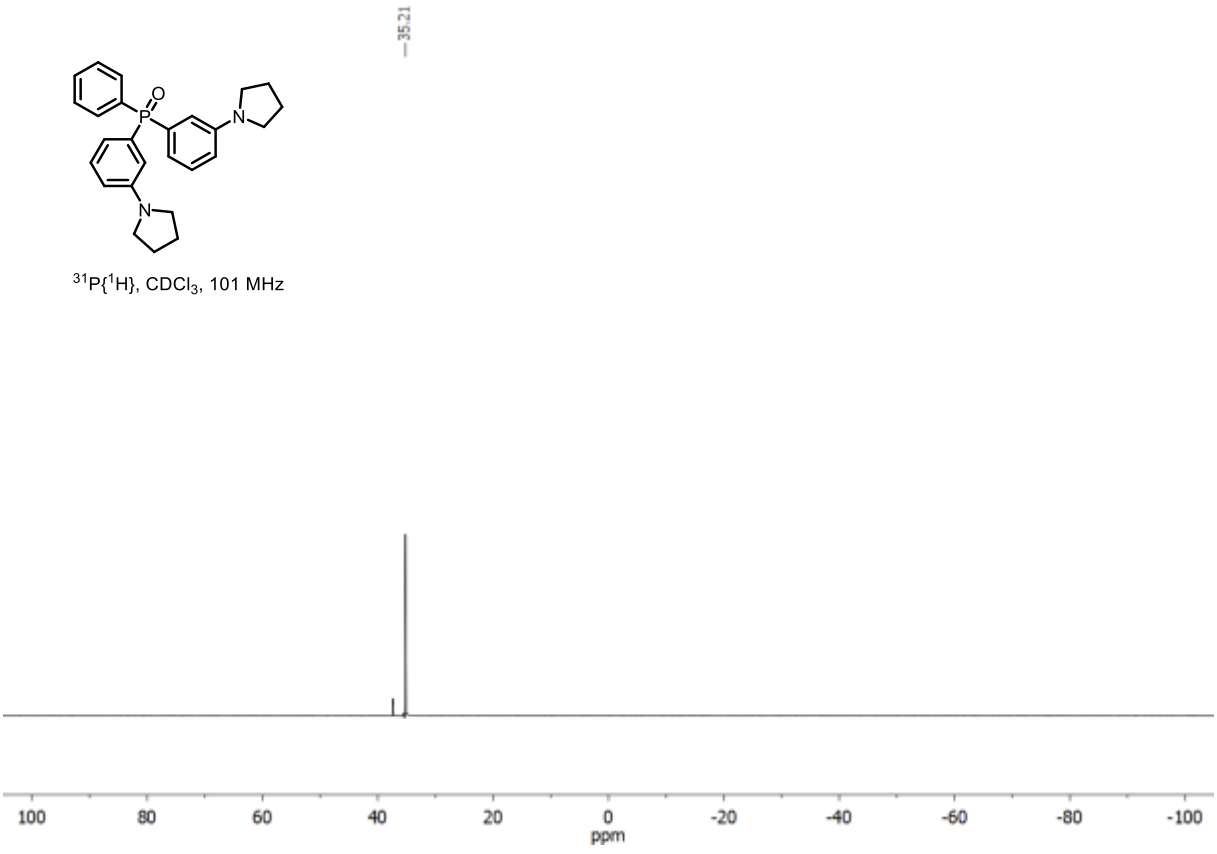


$^{13}C\{^{1}H\}$ NMR spectrum of 12d:



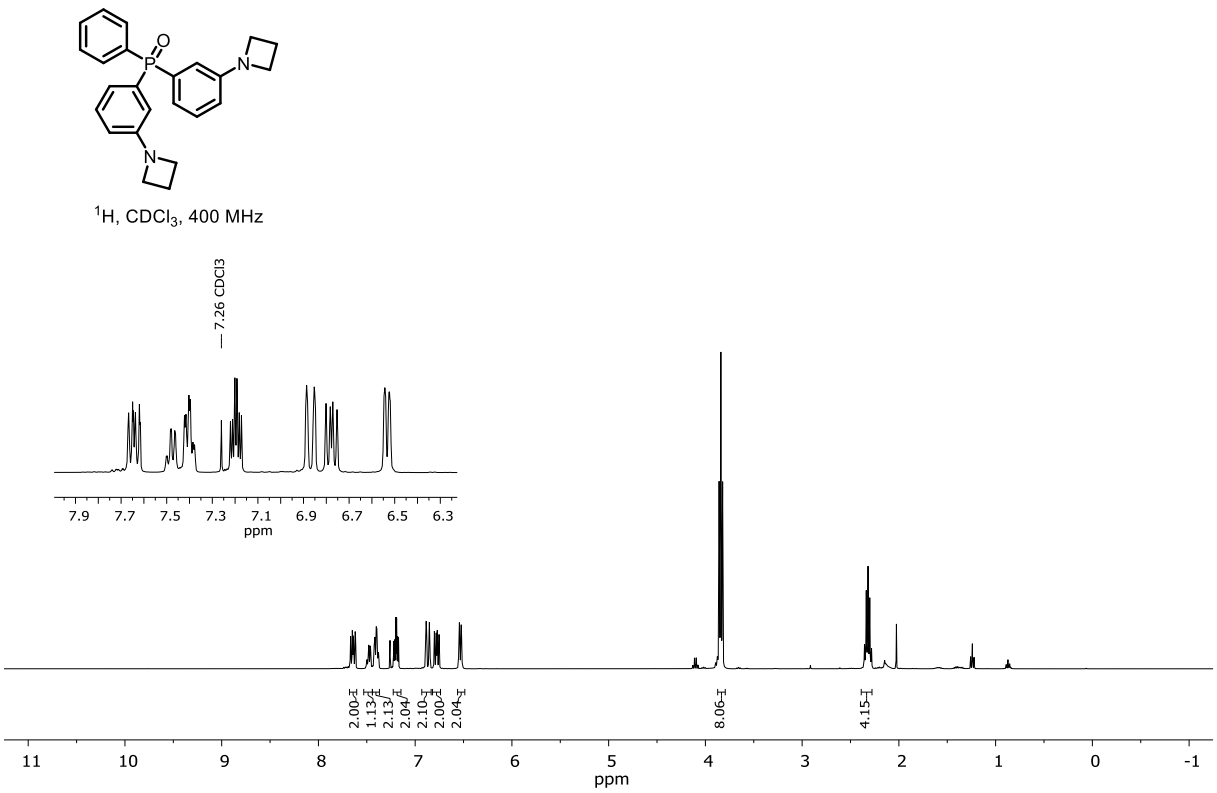
$^{13}C\{^{1}H\}$, $CDCl_3$, 101 MHz

$^{31}P\{^{1}H\}$ NMR spectrum of 12d:

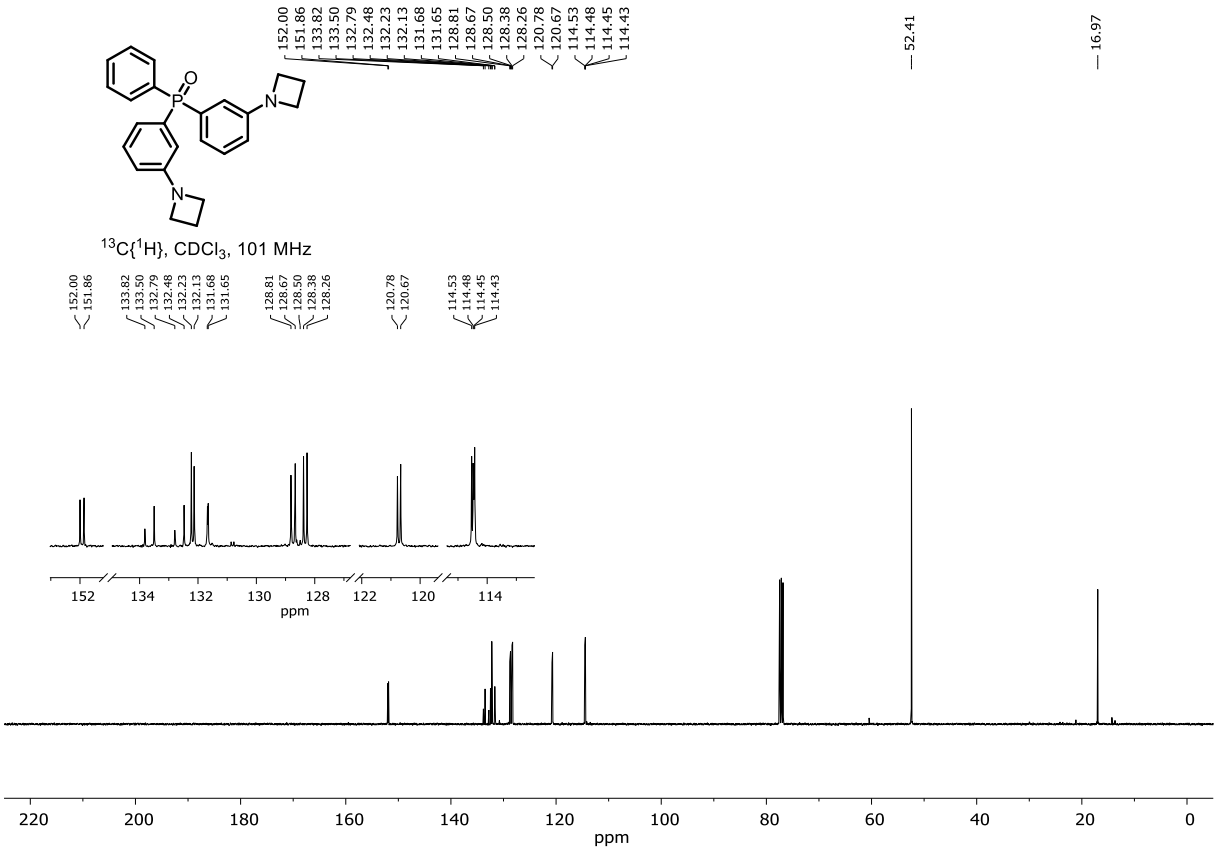


$^{31}P\{^{1}H\}$, $CDCl_3$, 101 MHz

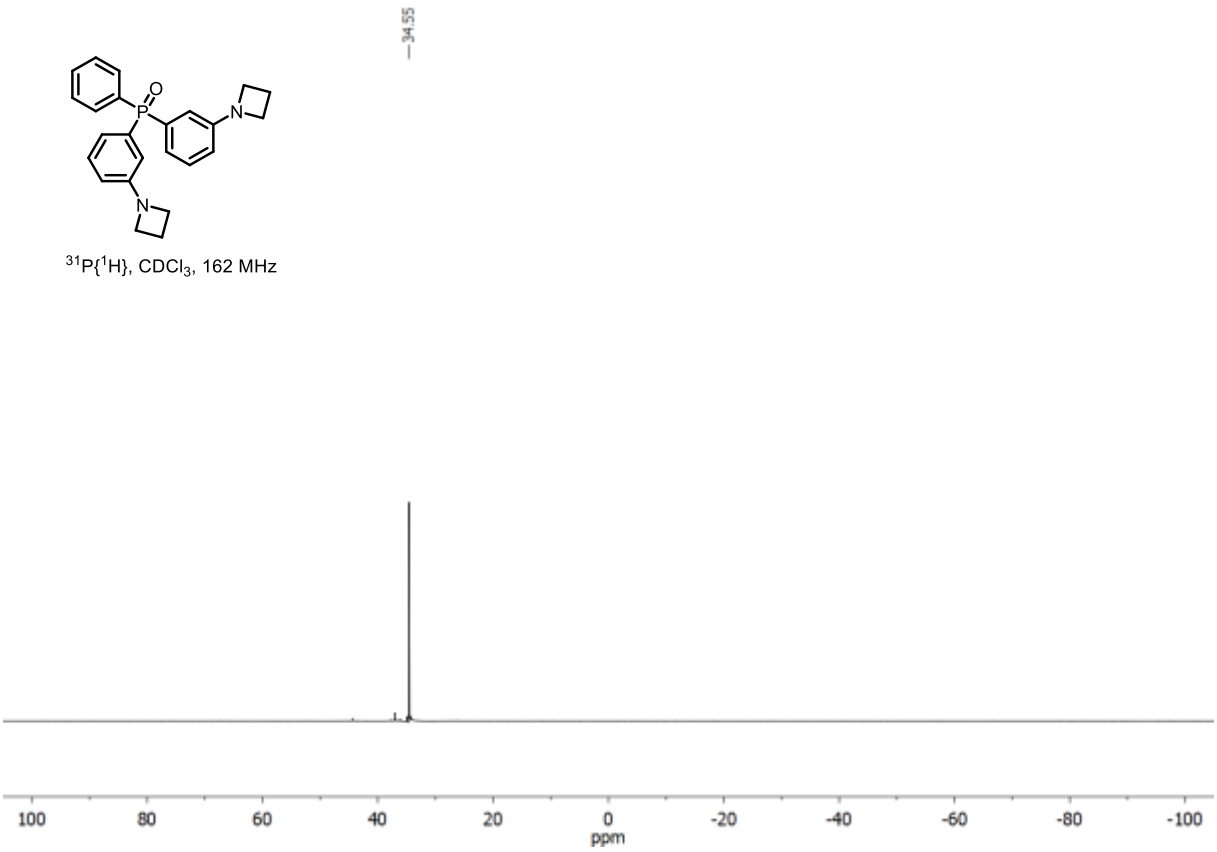
^{1}H NMR spectrum of 12c:



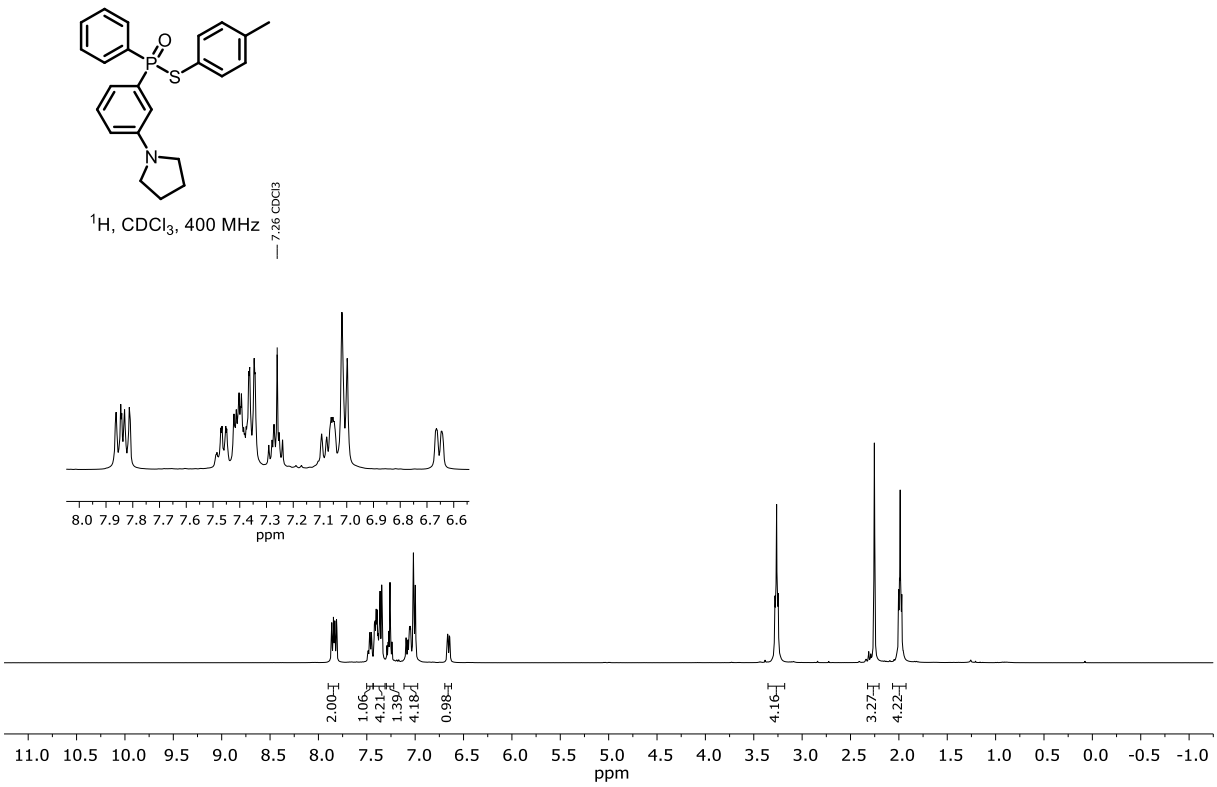
^{13}C{^{1}H} NMR spectrum of 12c:



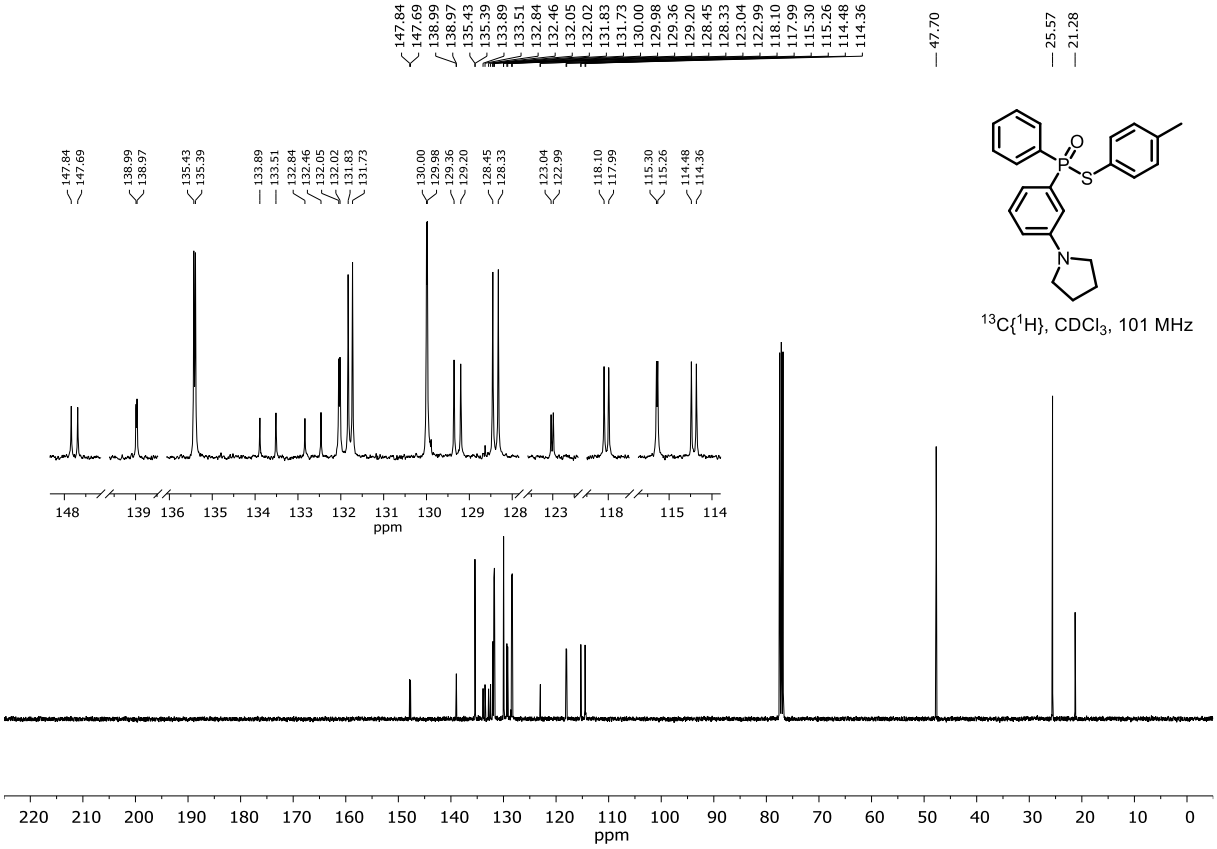
$^{31}P\{^{1}H\}$ NMR spectrum of 12c:



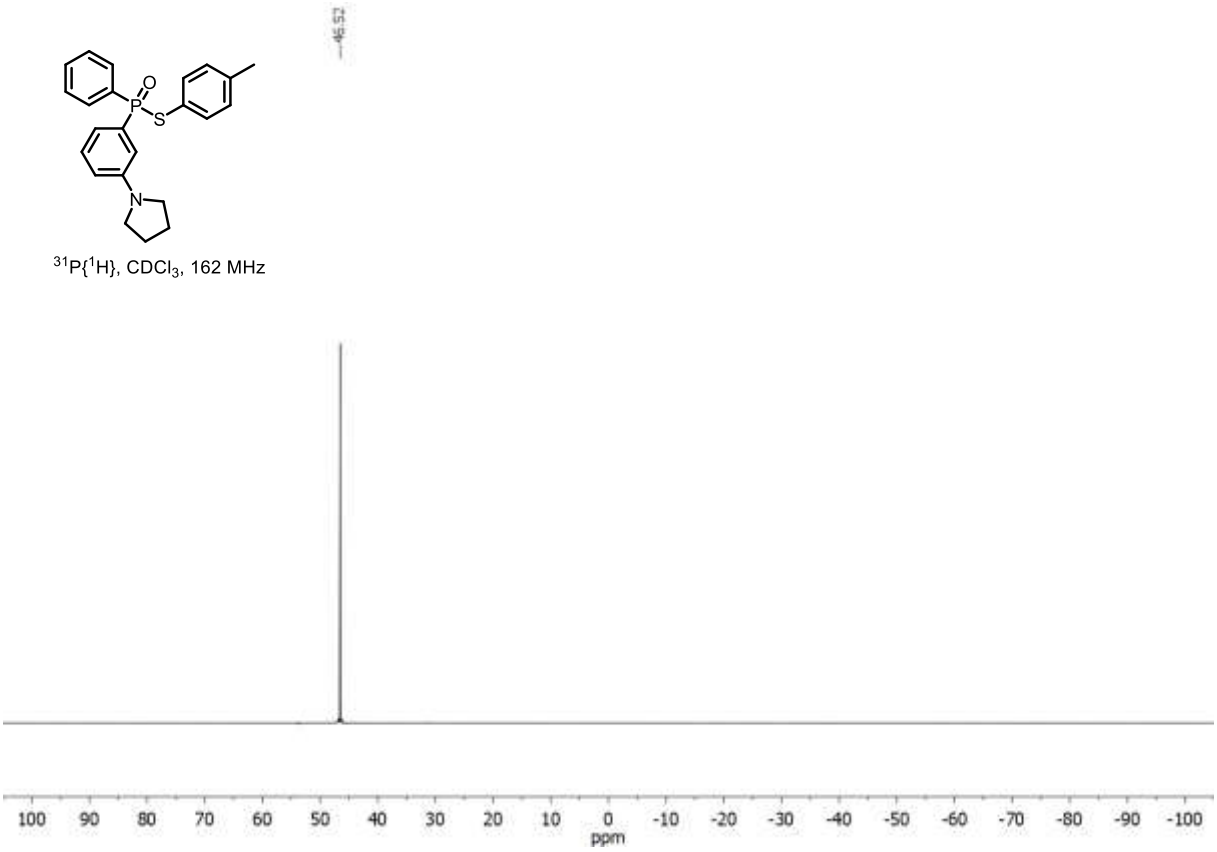
^{1}H NMR spectrum of 16:



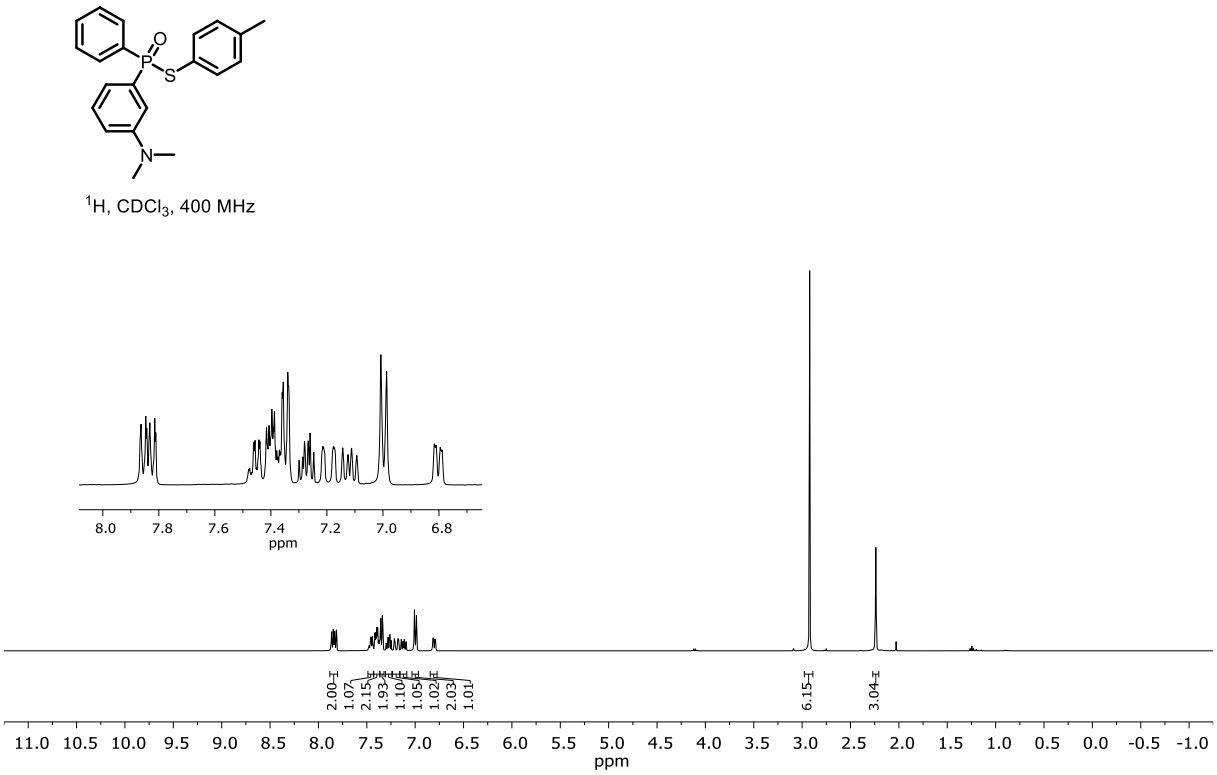
$^{13}C\{^{1}H\}$ NMR spectrum of 16:



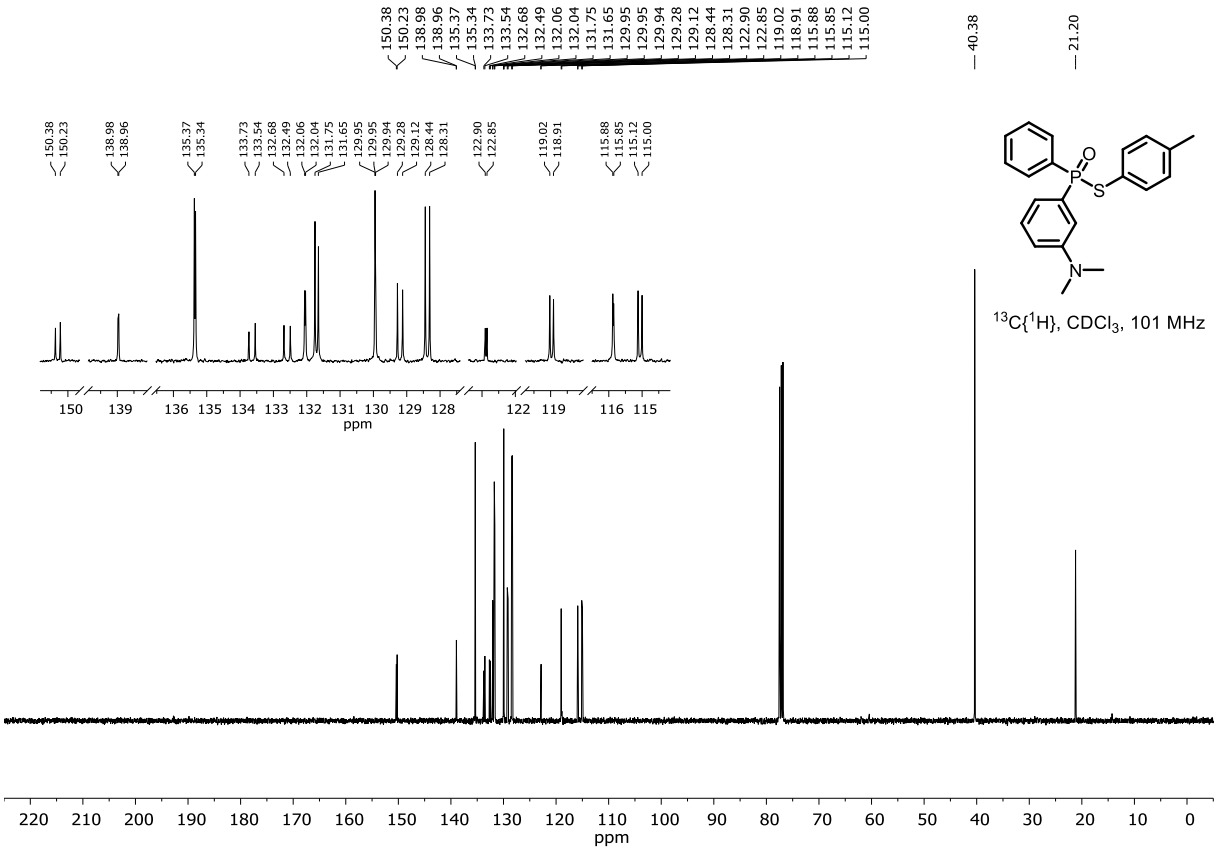
$^{31}P\{^{1}H\}$ NMR spectrum of 16:



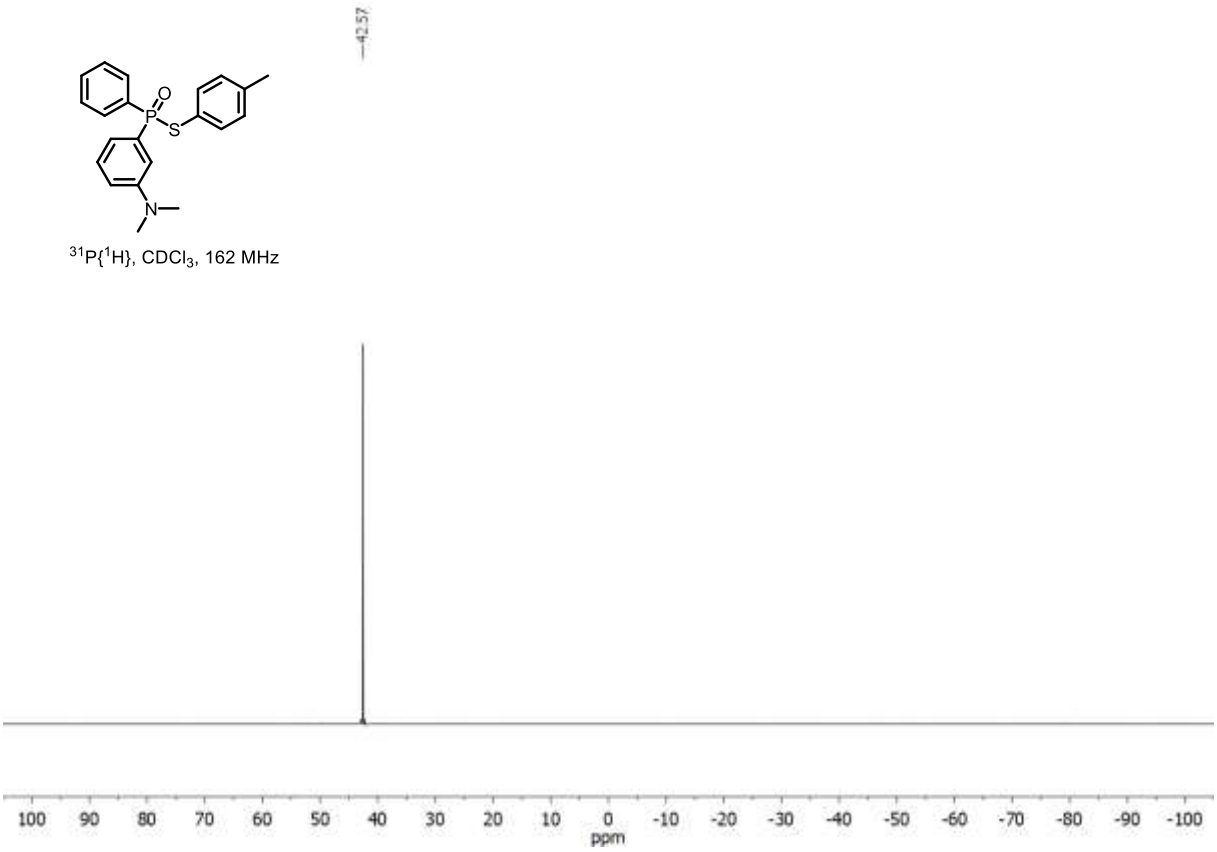
^{1}H NMR spectrum of 15:



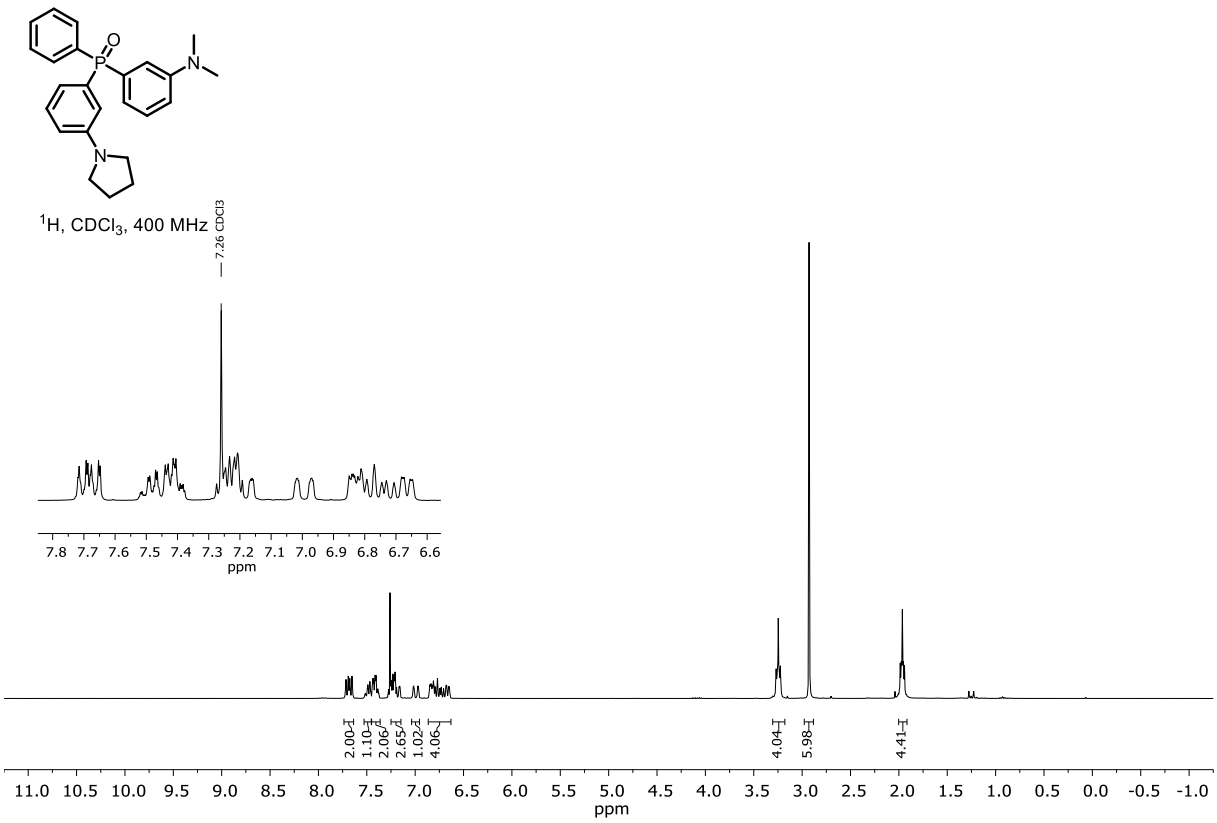
^{13}C{^{1}H} NMR spectrum of 15:



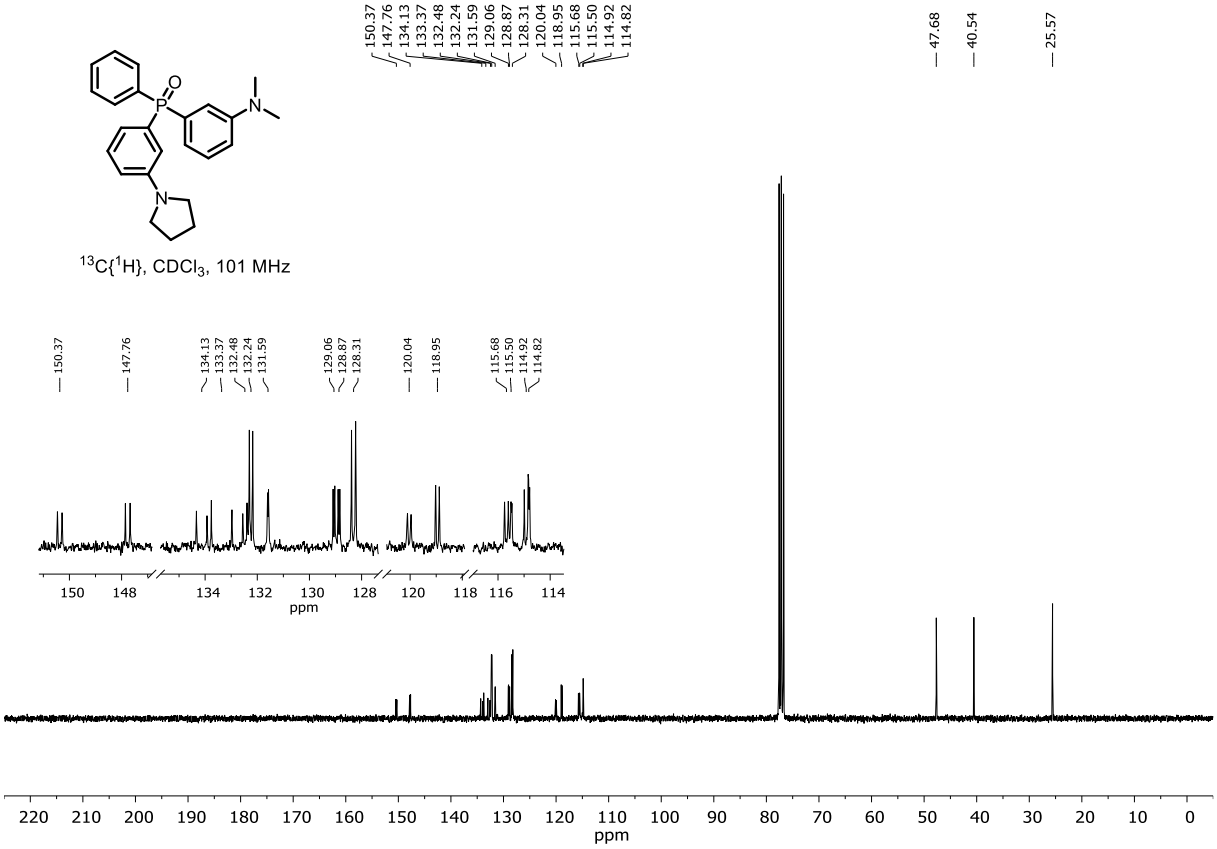
$^{31}P\{^{1}H\}$ NMR spectrum of 15:



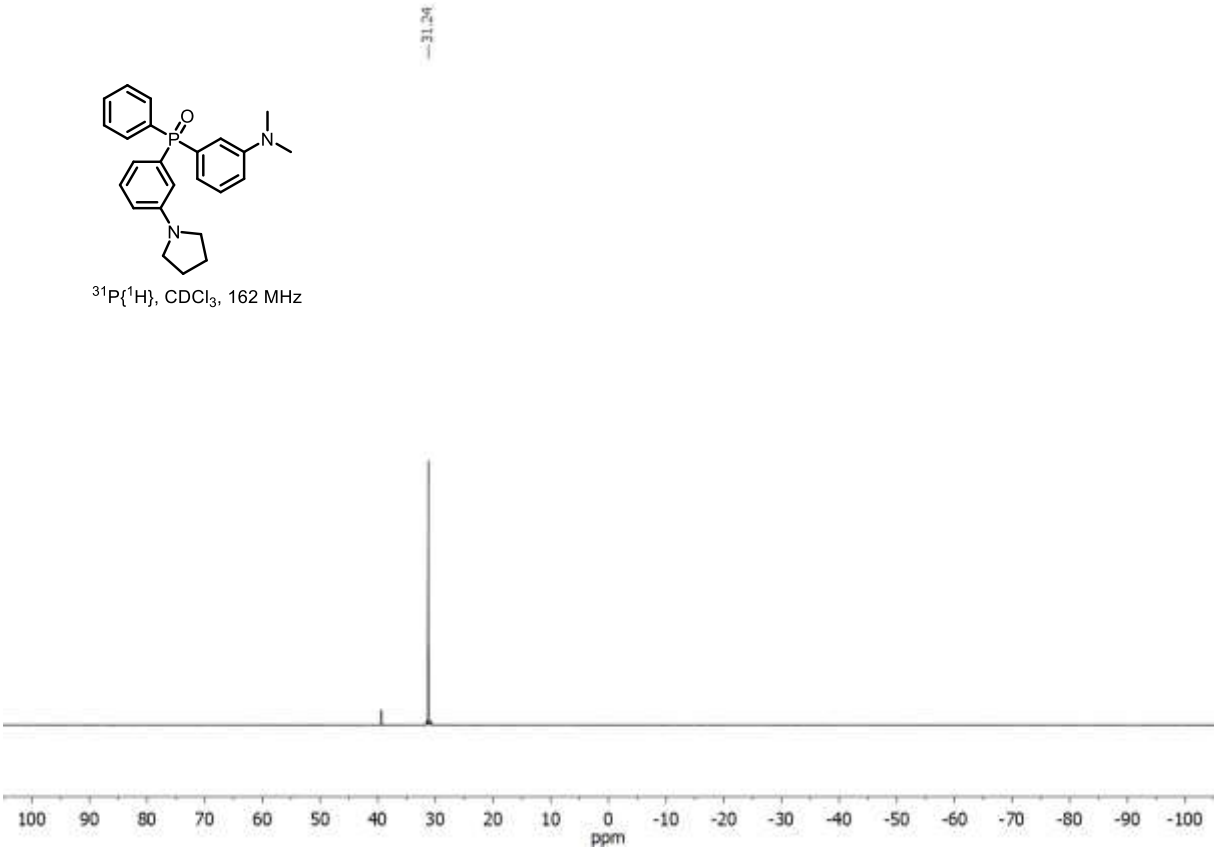
^{1}H NMR spectrum of 17:



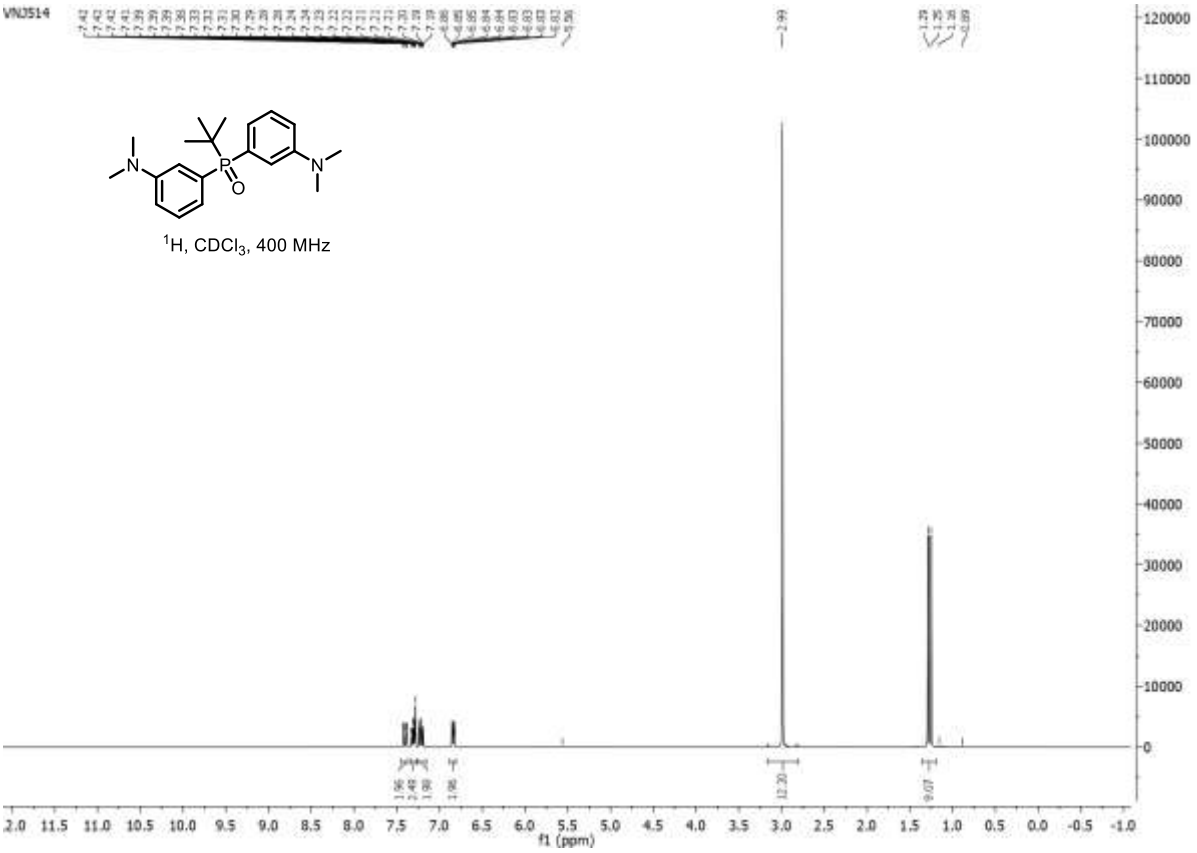
$^{13}C\{^{1}H\}$ NMR spectrum of 17:



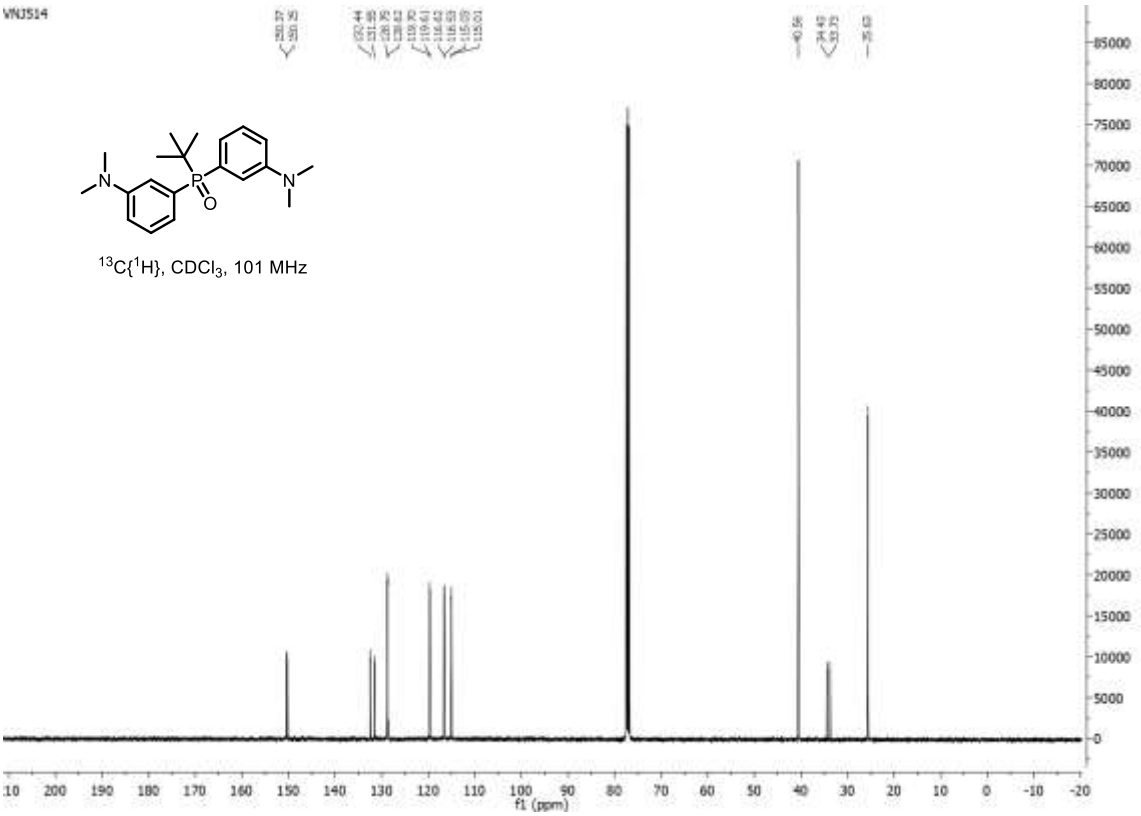
$^{31}P\{^{1}H\}$ NMR spectrum of 17:



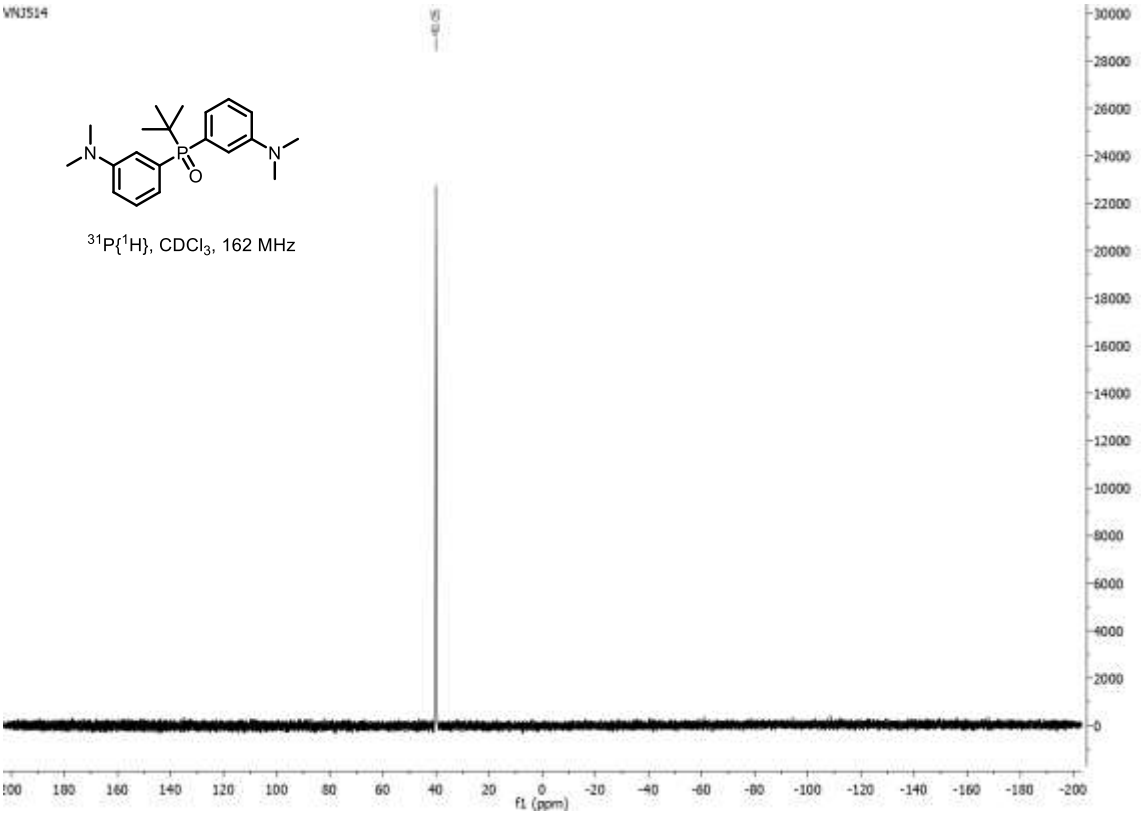
^{1}H spectrum of 12b:



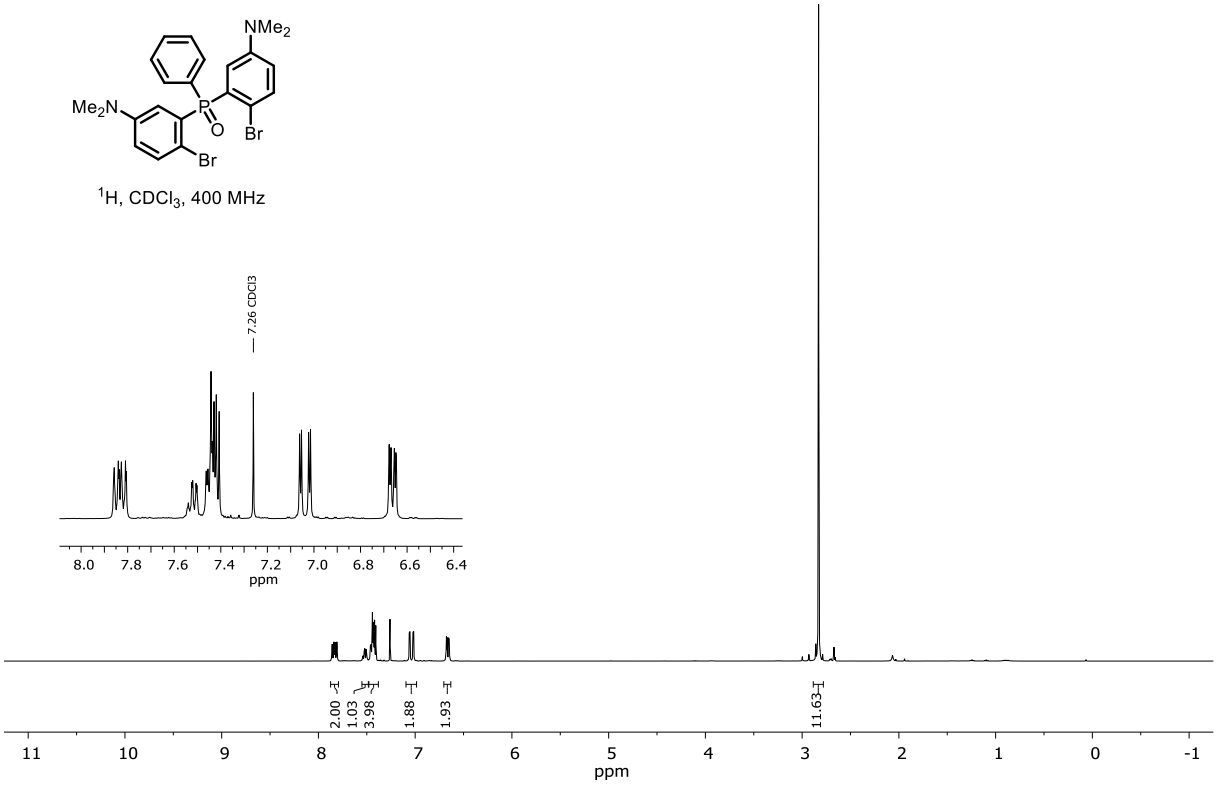
^{13}C{^{1}H} spectrum of 12b:



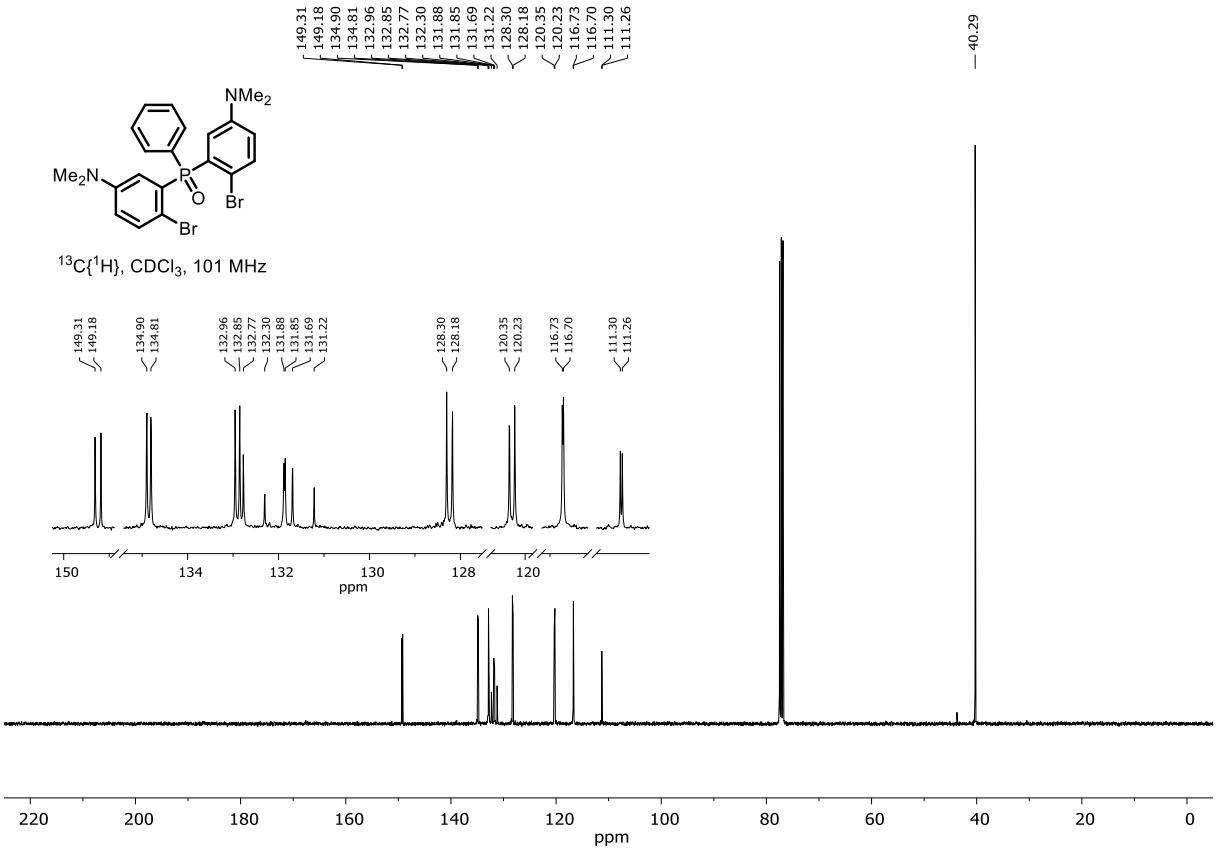
$^{31}P\{^{1}H\}$ spectrum of 12b:



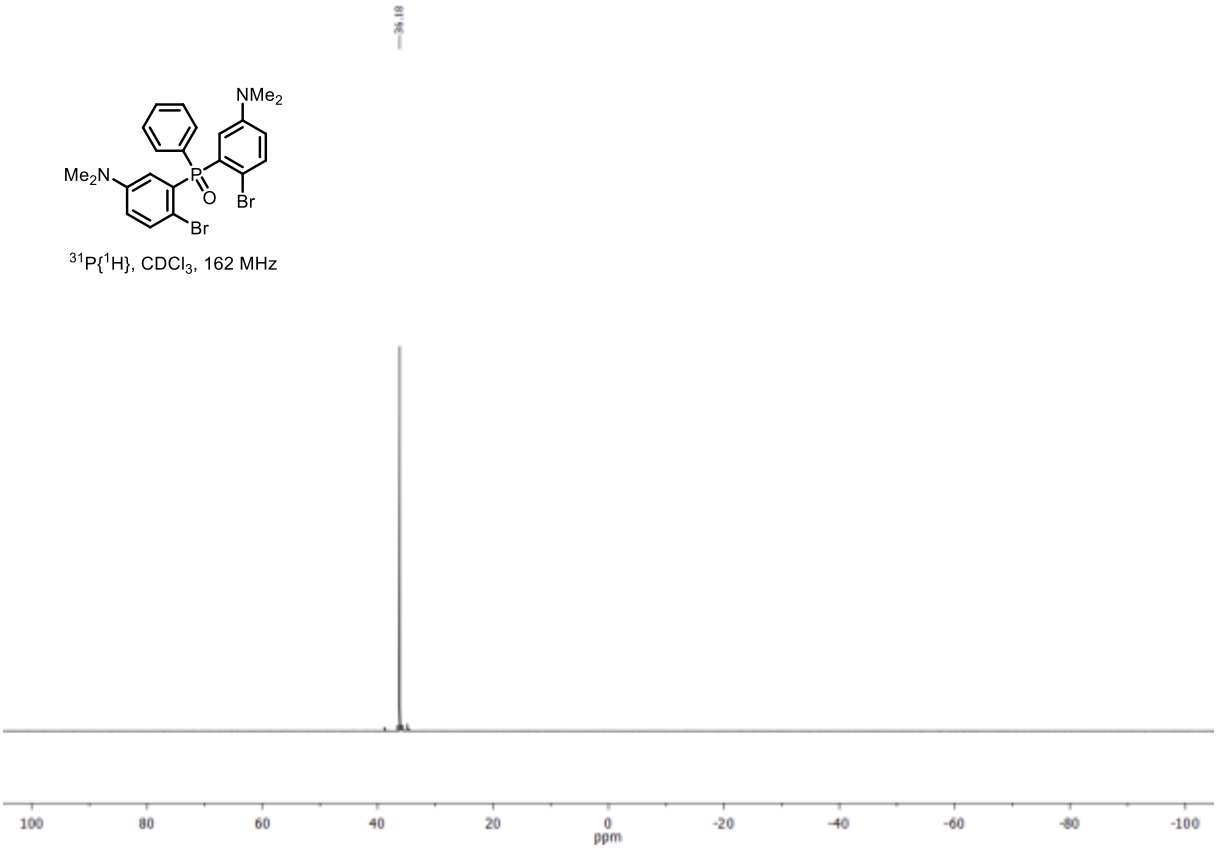
^{1}H NMR spectrum 10a:



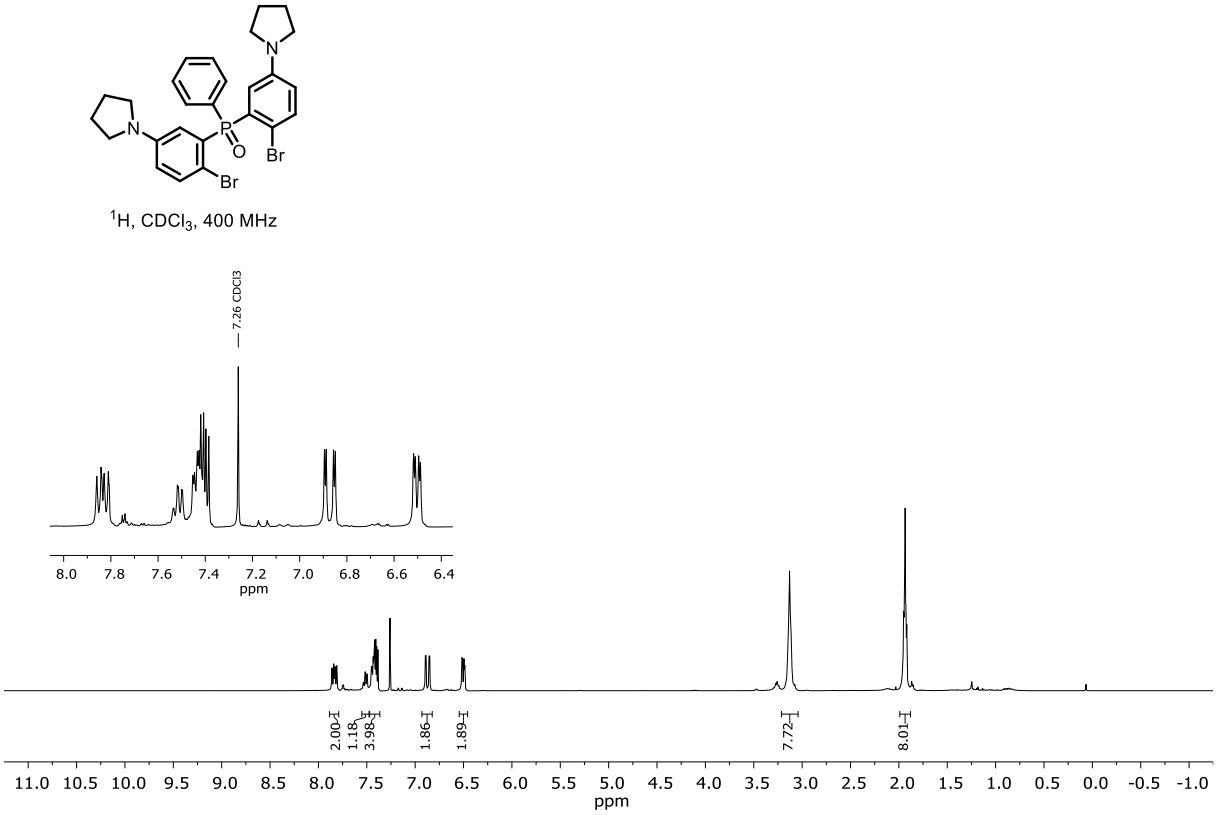
$^{13}C\{^{1}H\}$ NMR spectrum of 10a:



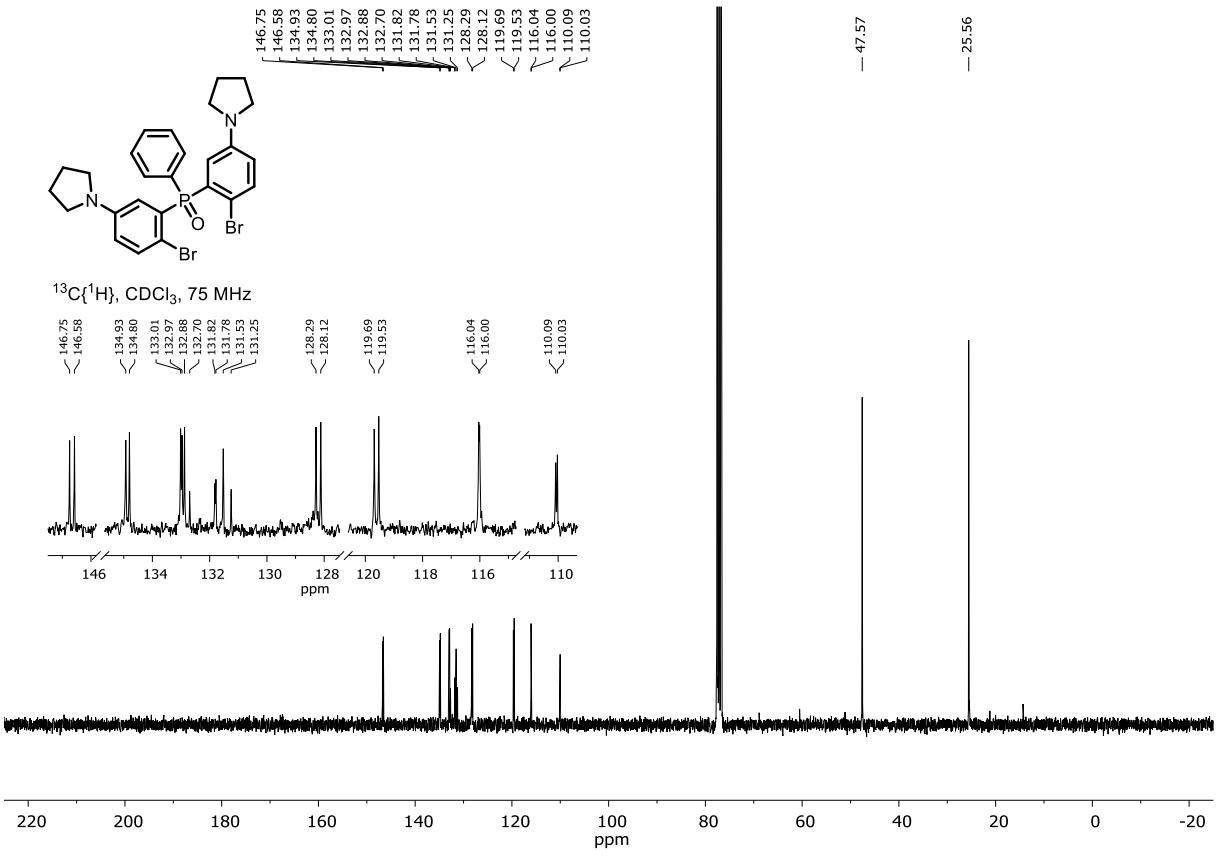
$^{31}P\{^{1}H\}$ NMR spectrum of 10a:



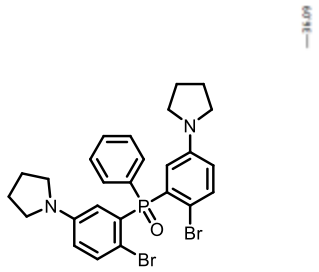
^{1}H NMR spectrum of 10d:



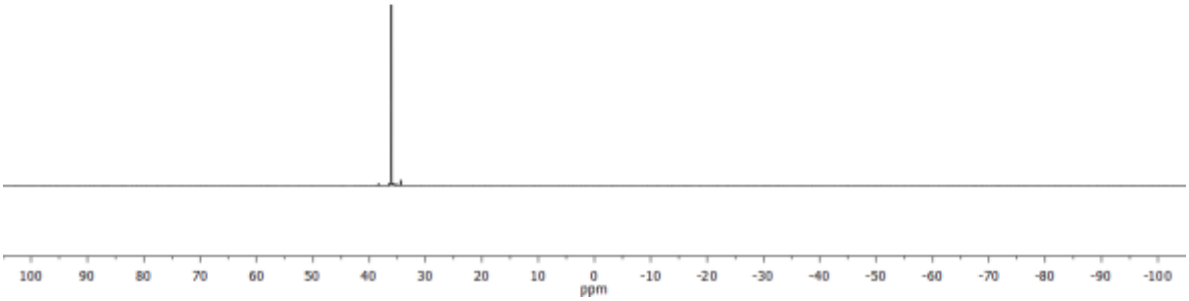
^{13}C{^{1}H} NMR spectrum of 10d:



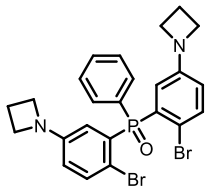
$^{31}P\{^{1}H\}$ NMR spectrum of 10d:



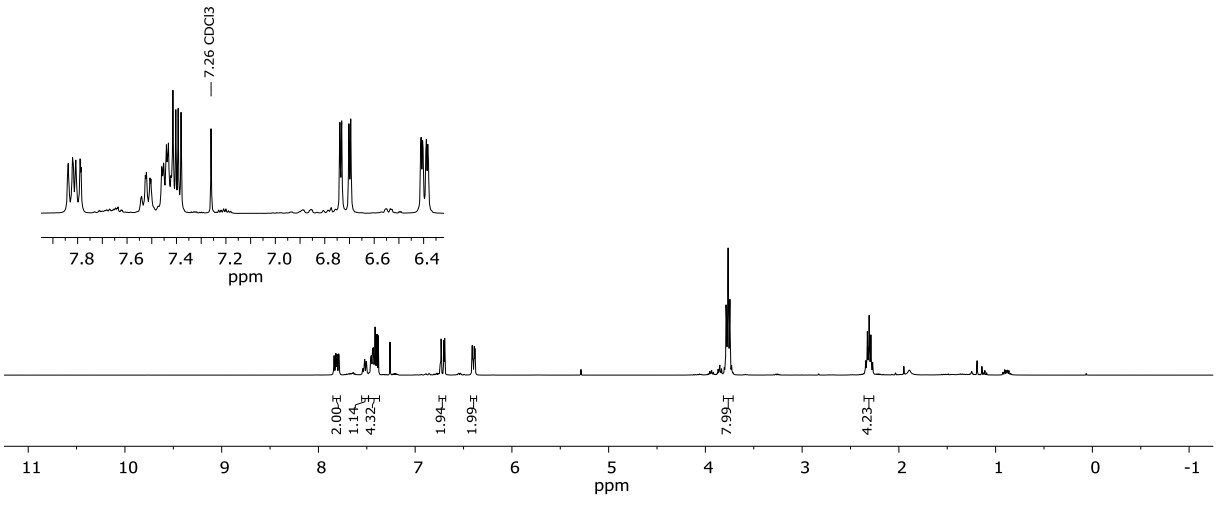
$^{31}P\{^{1}H\}$, $CDCl_3$, 162 MHz



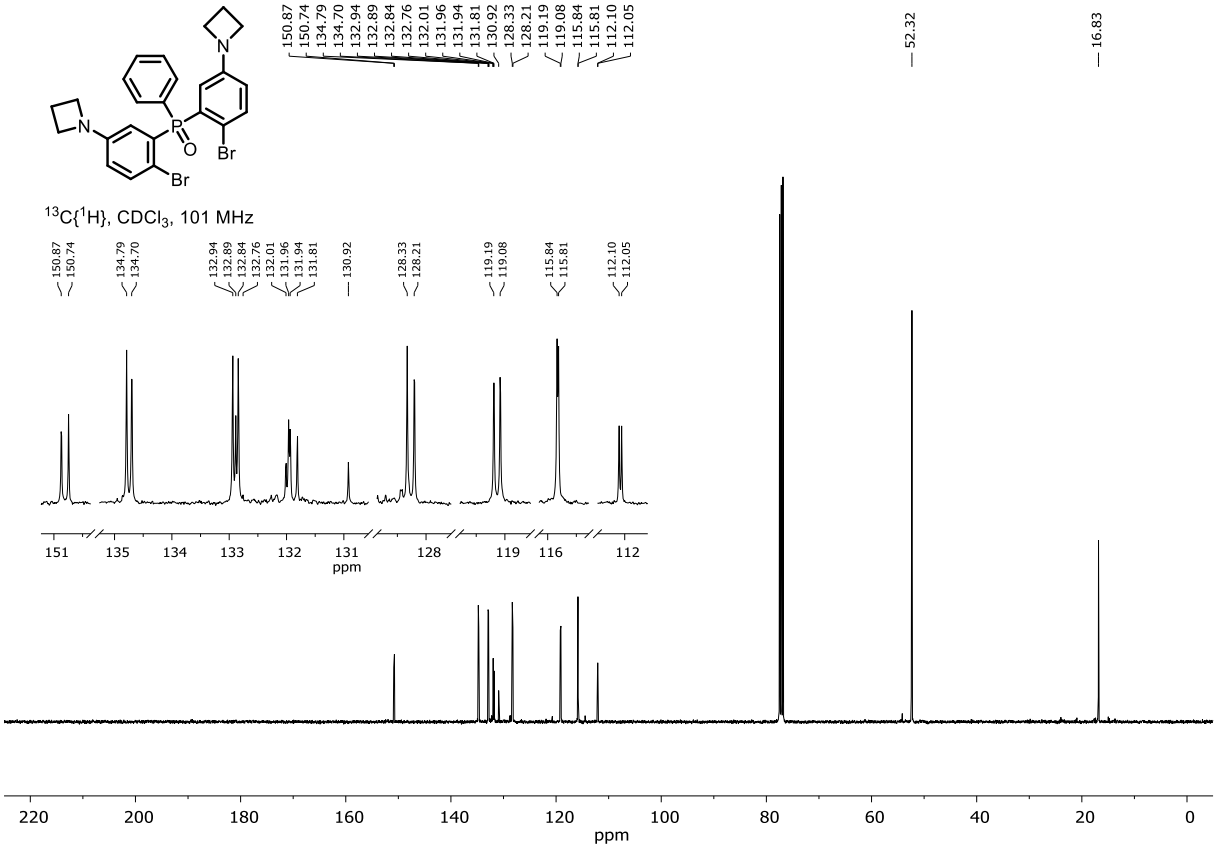
^{1}H NMR spectrum of 10c:



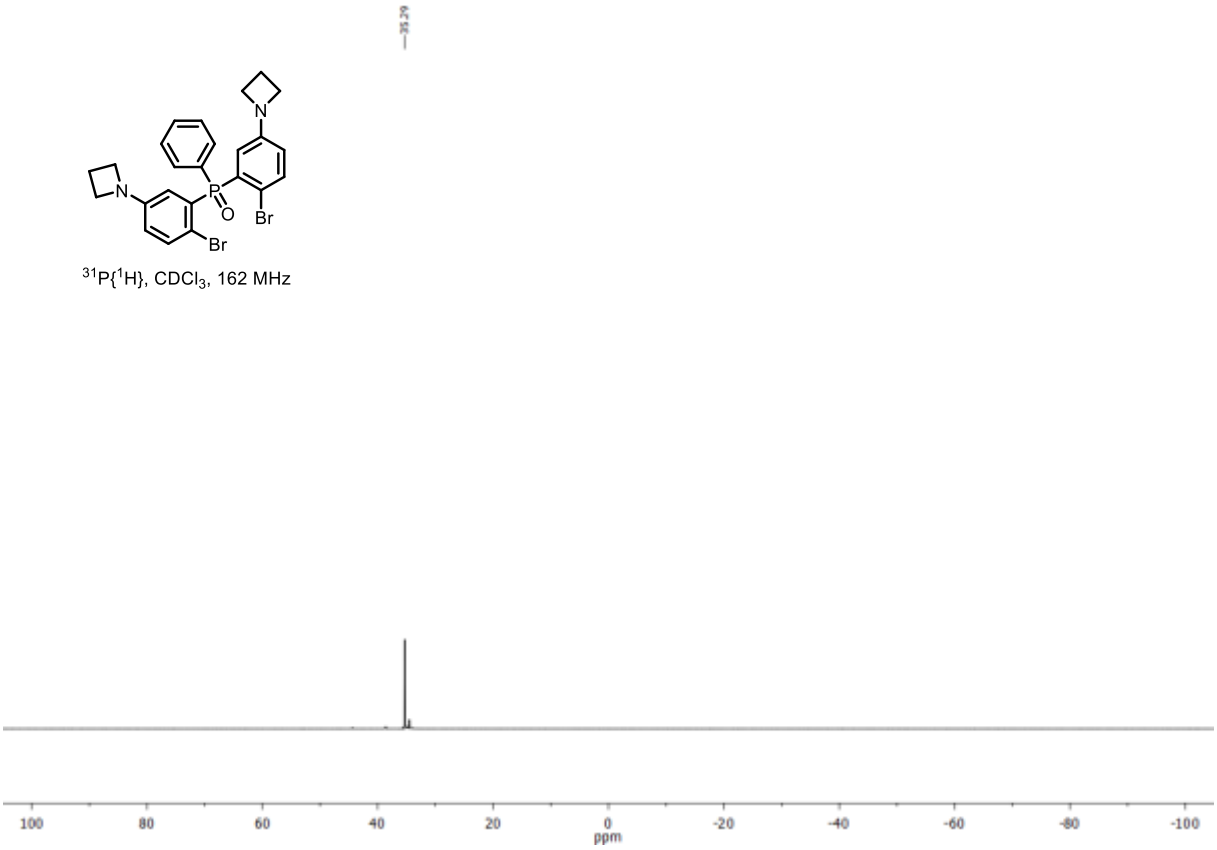
^{1}H, $CDCl_3$, 400 MHz



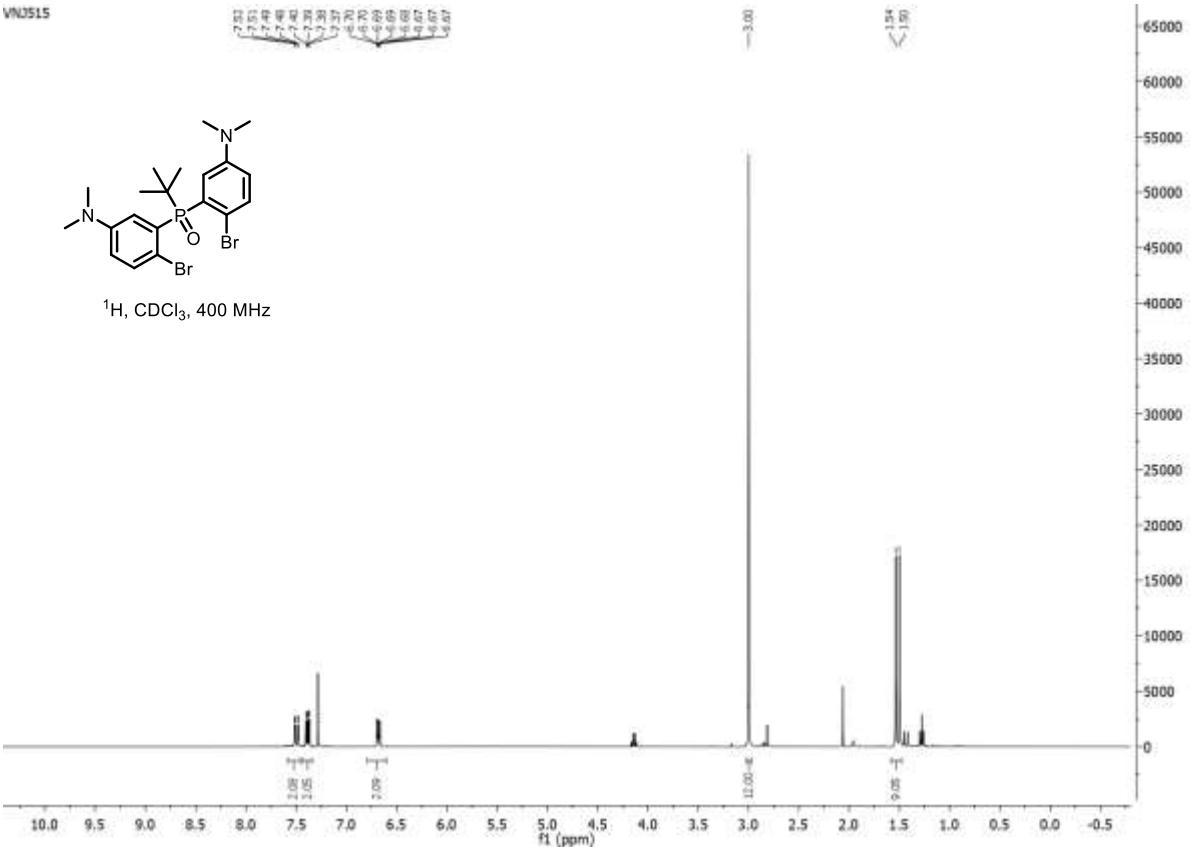
$^{13}C\{^{1}H\}$ NMR spectrum of 10c:



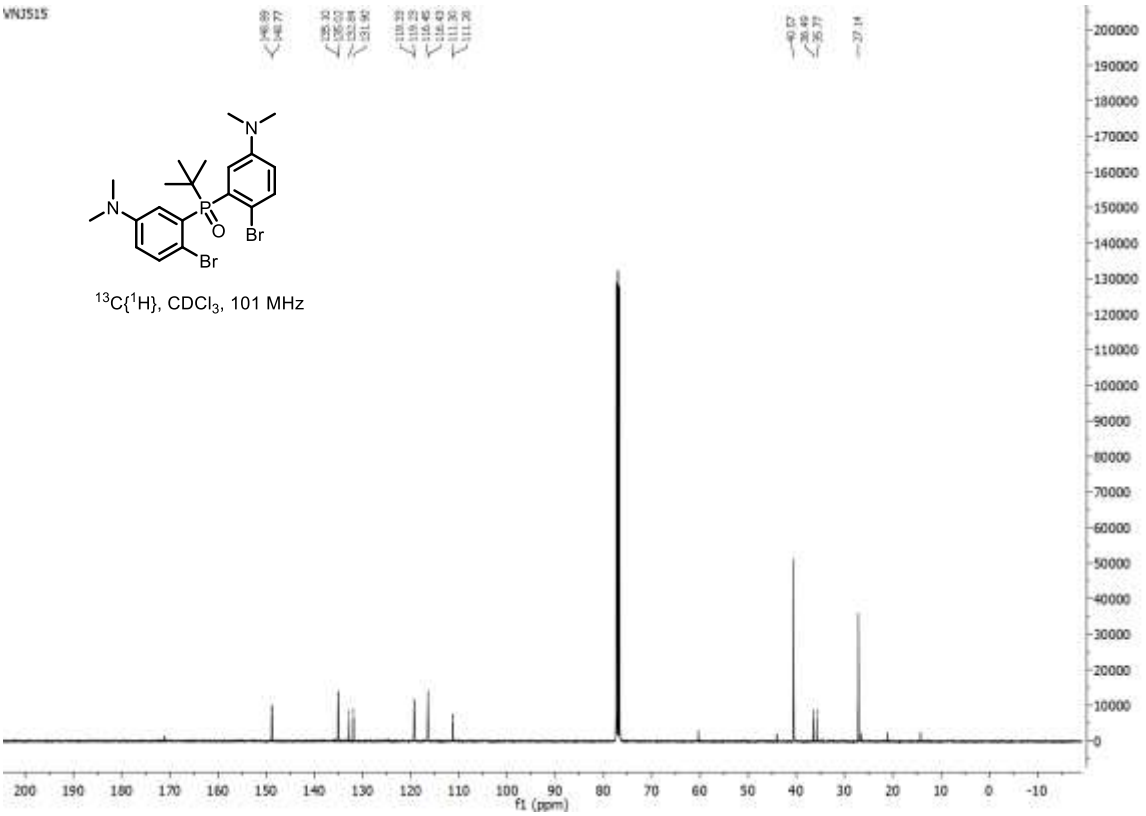
$^{31}P\{^{1}H\}$ NMR spectrum of 10c:



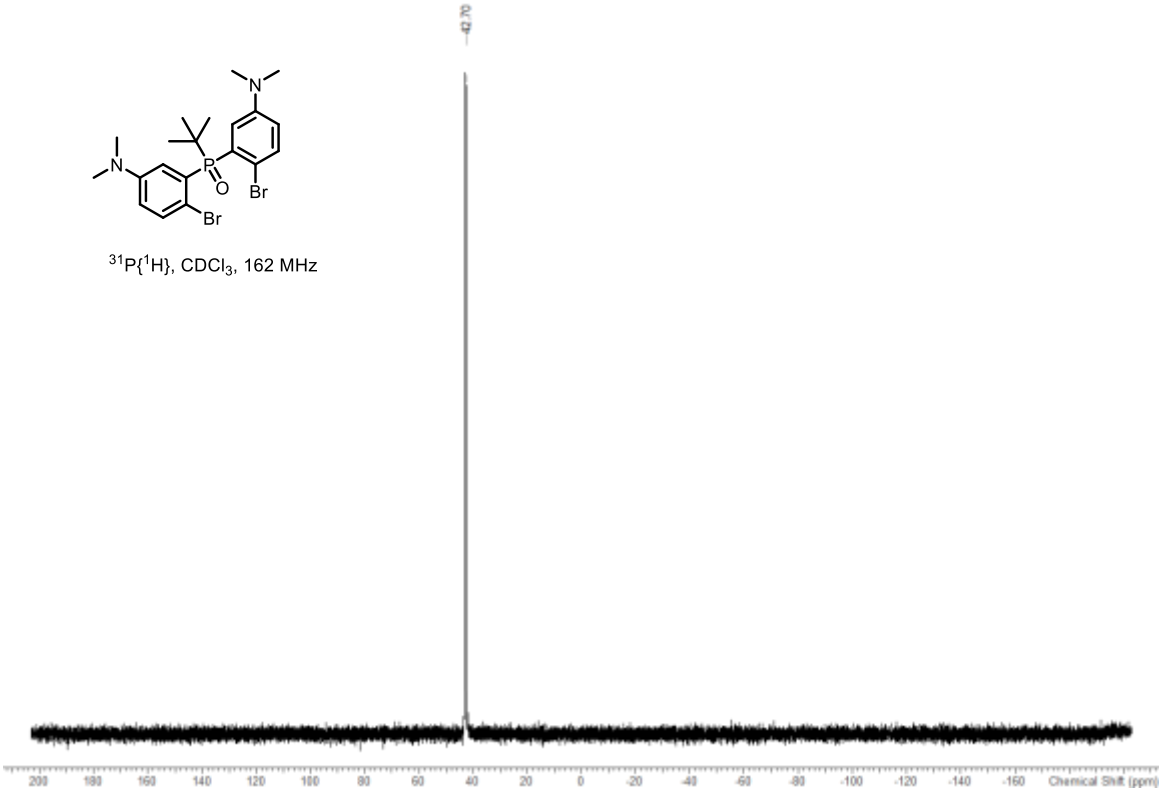
1H spectrum of 10b:



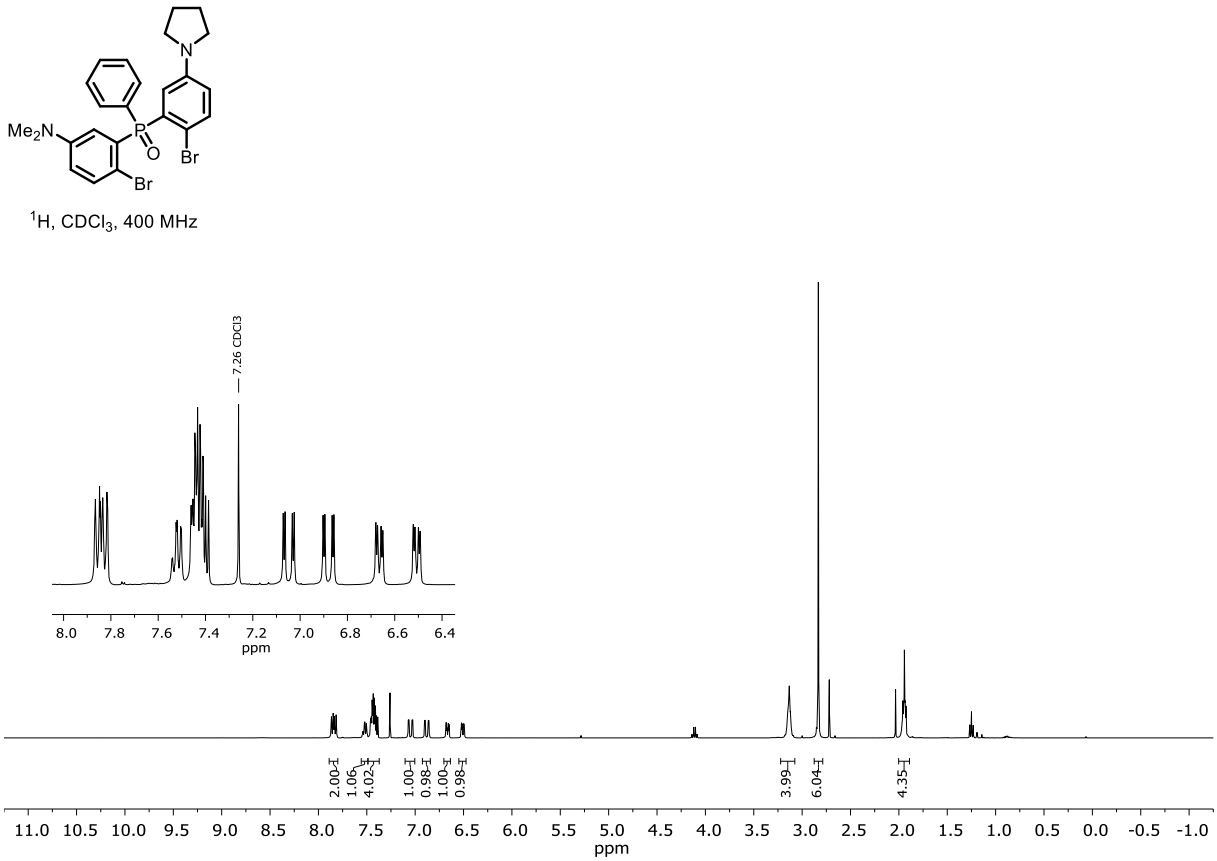
$^{13}C\{^{1}H\}$ spectrum of 10b:



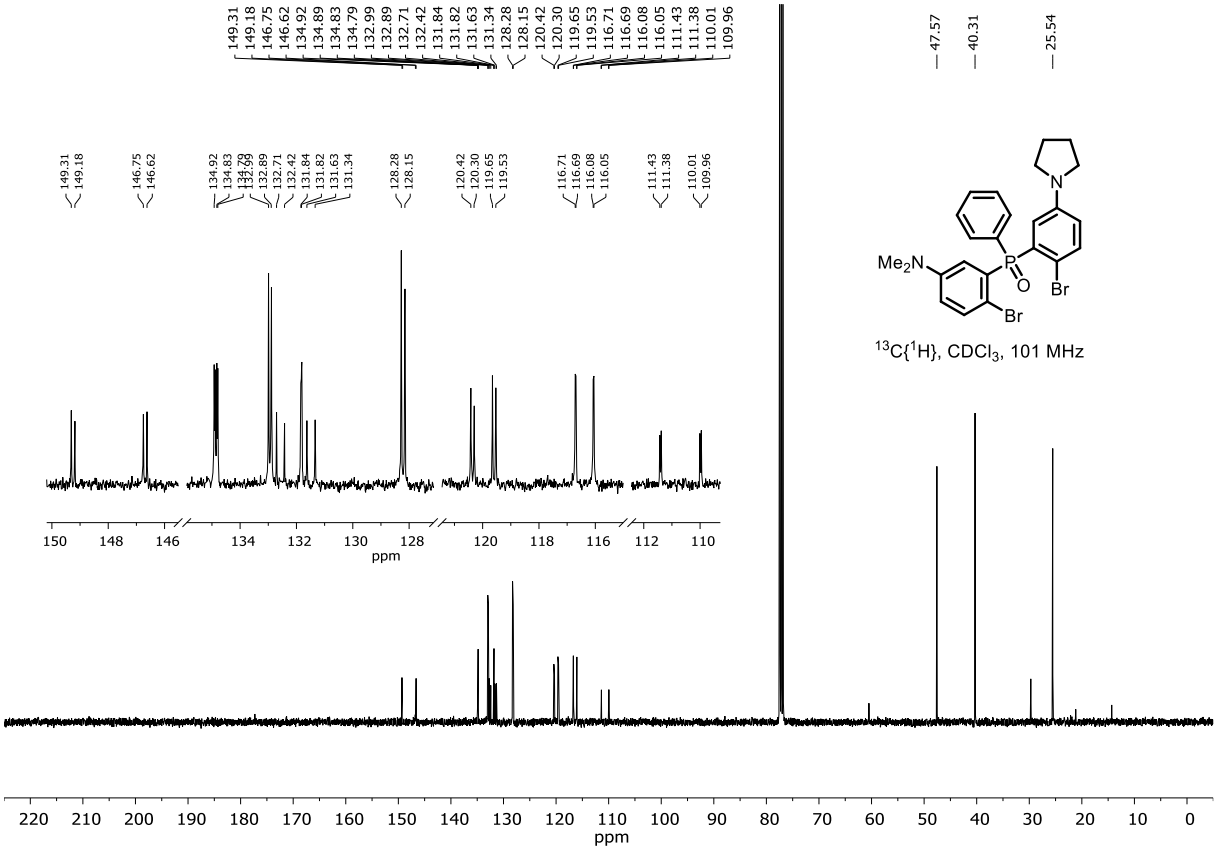
$^{31}P\{^{1}H\}$ spectrum of 10b:



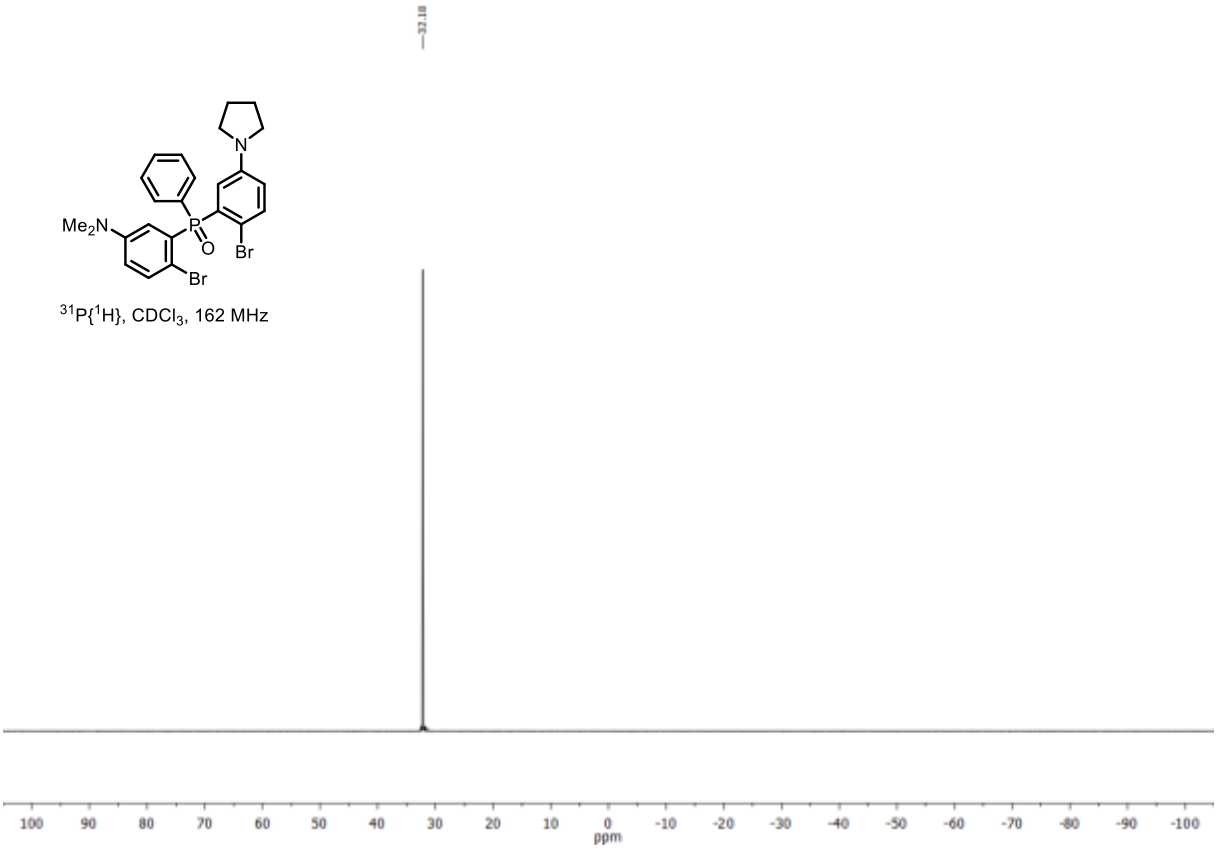
^{1}H NMR spectrum of 18:



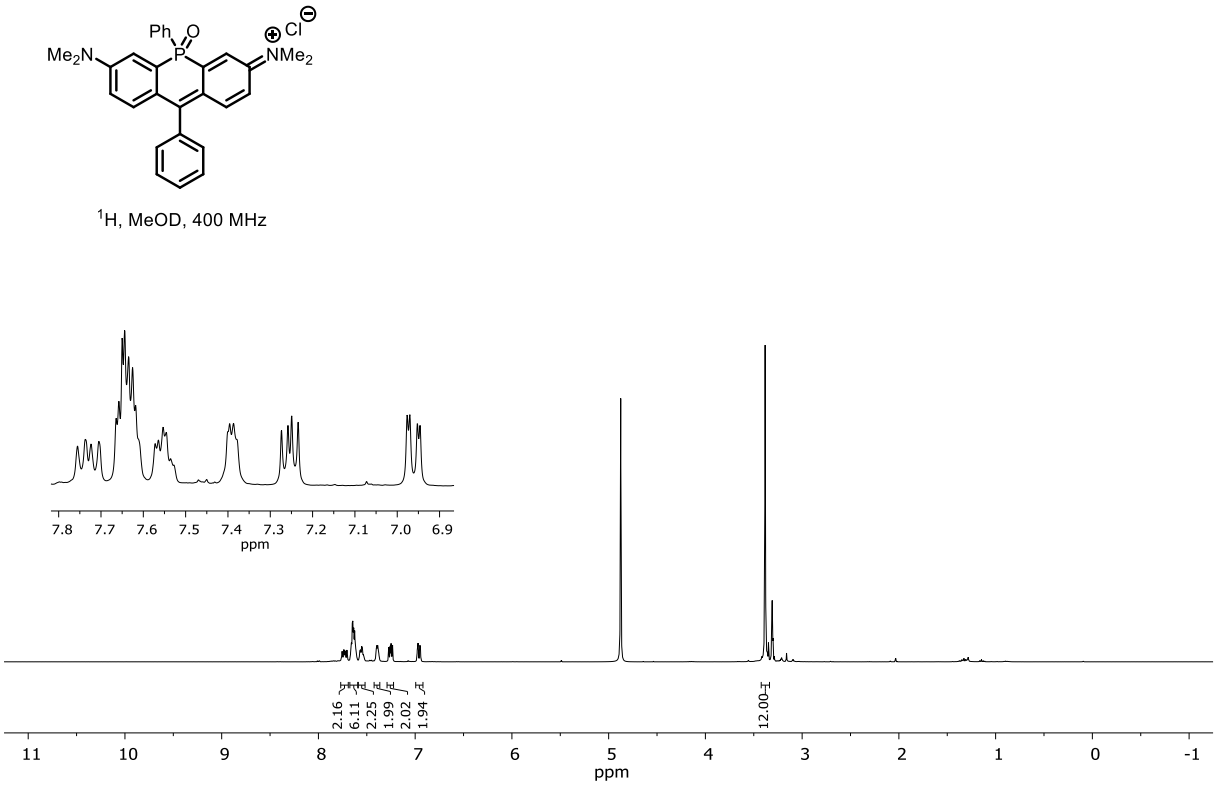
$^{13}C\{^{1}H\}$ NMR spectrum of 18:



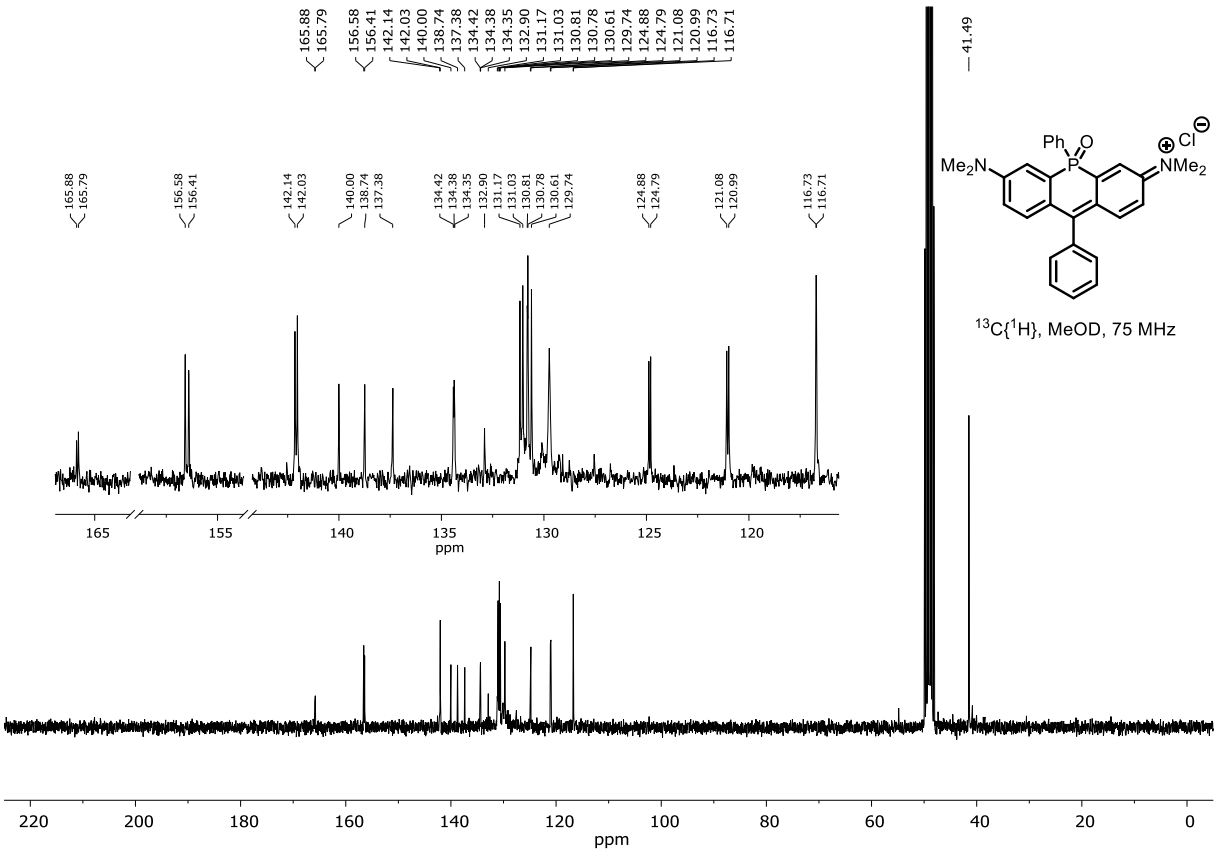
$^{31}P\{^{1}H\}$ NMR spectrum of 18:



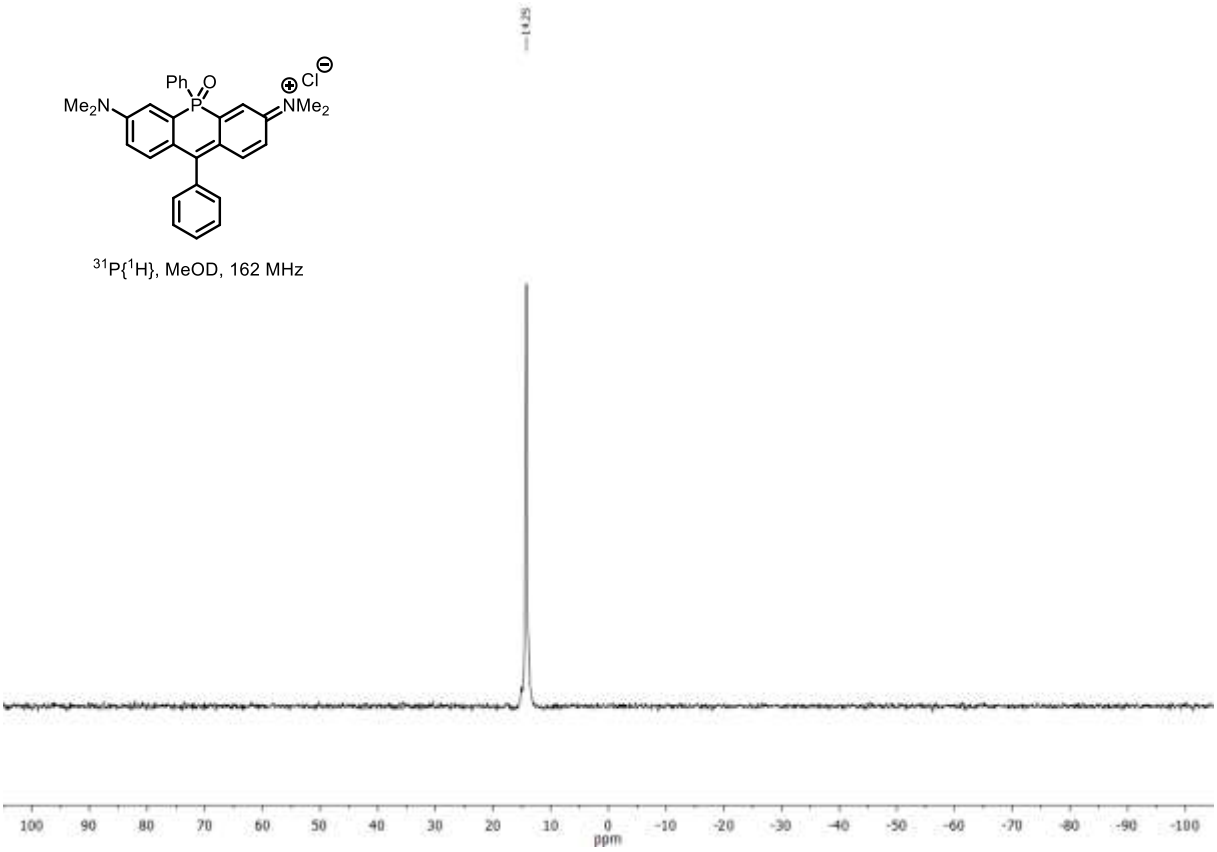
^{1}H NMR spectrum of 13a:



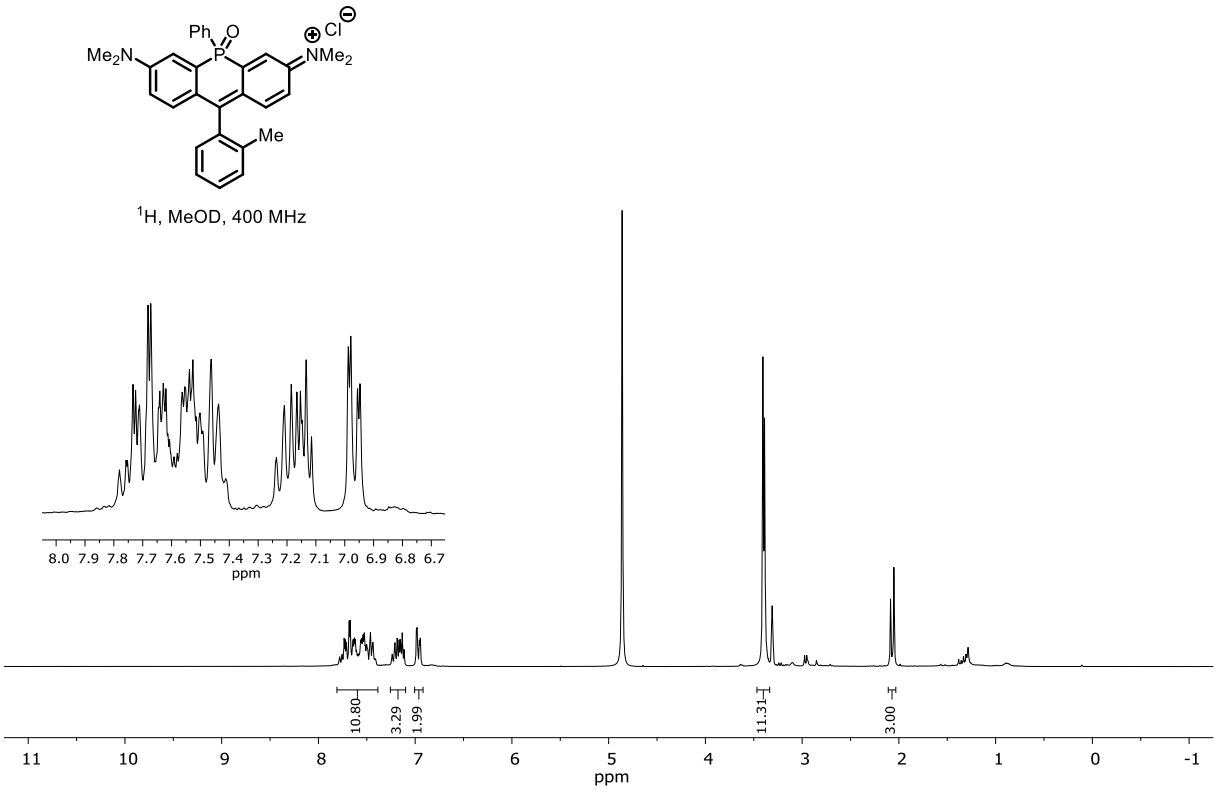
^{13}C{^{1}H} NMR spectrum of 13a:



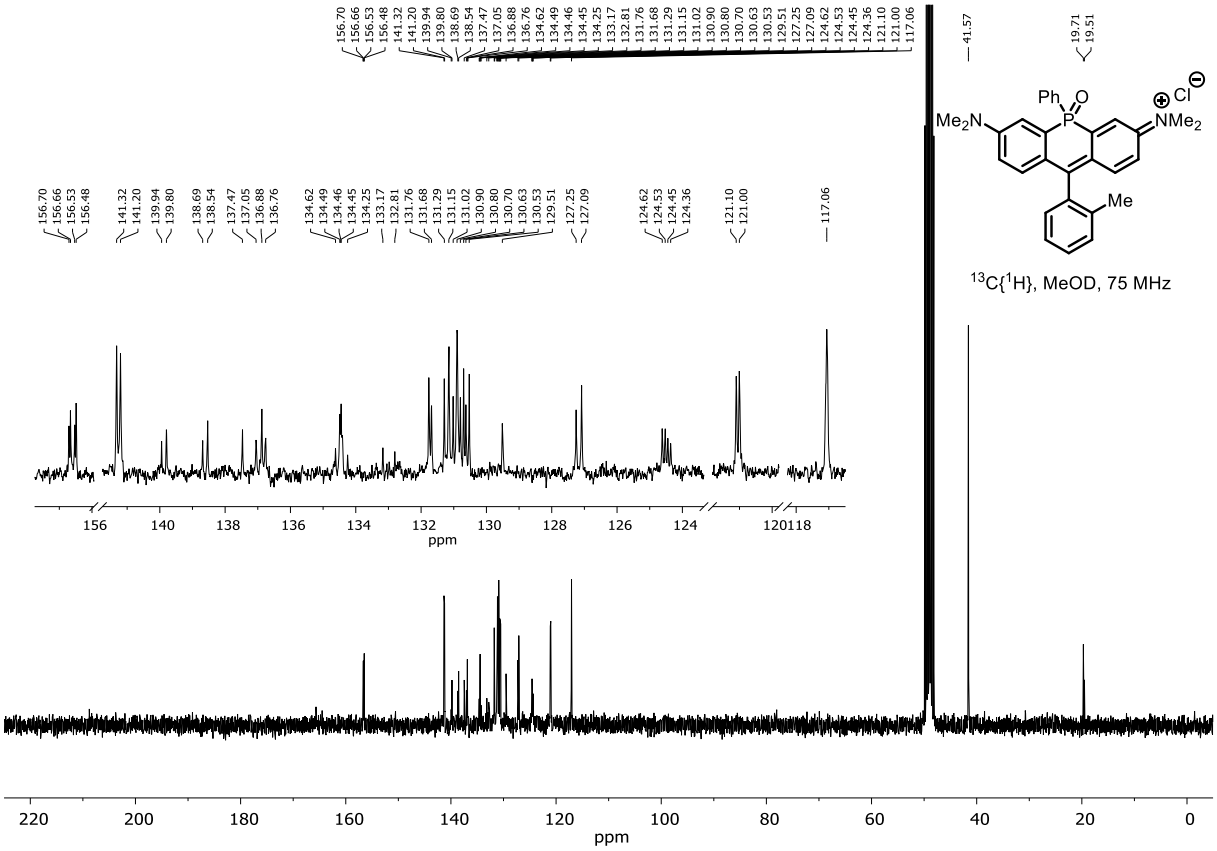
$^{31}P\{^{1}H\}$ NMR spectrum of 13a:



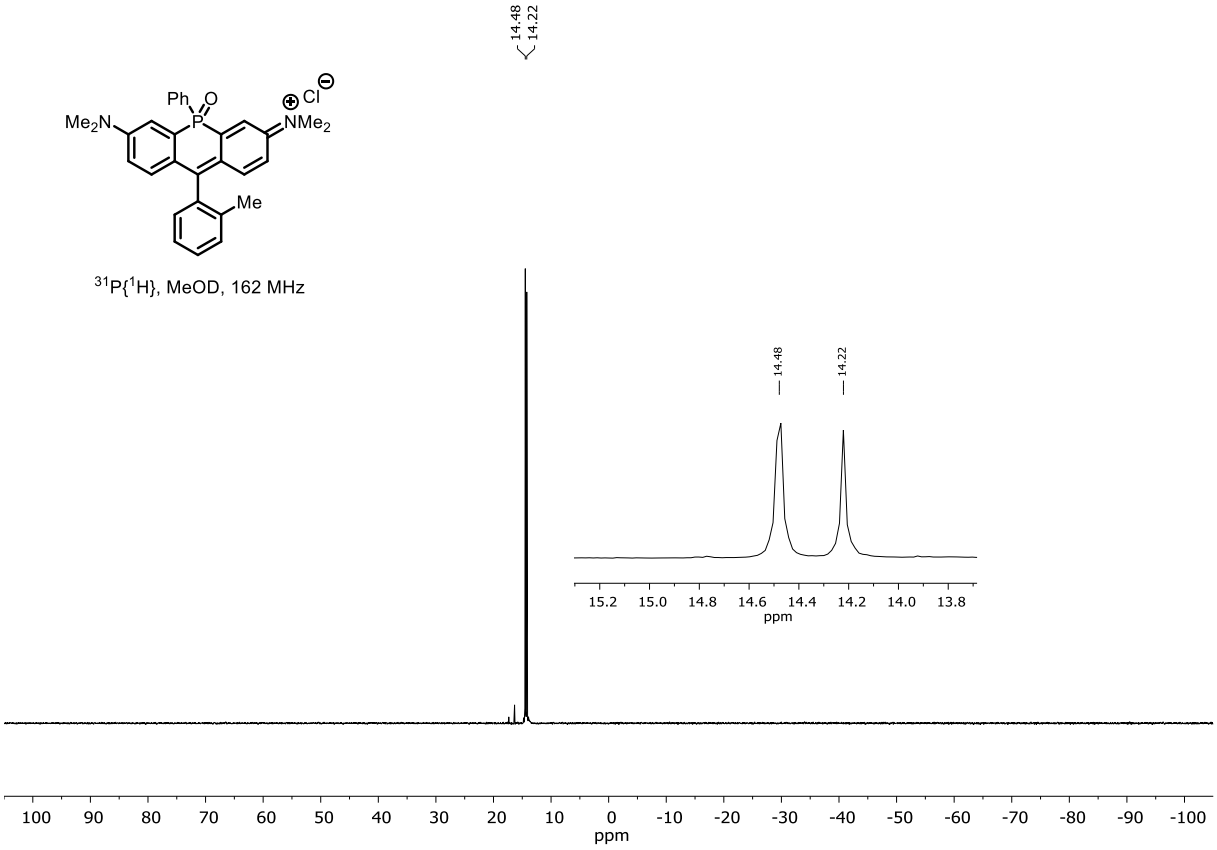
^{1}H NMR spectrum of 13i:



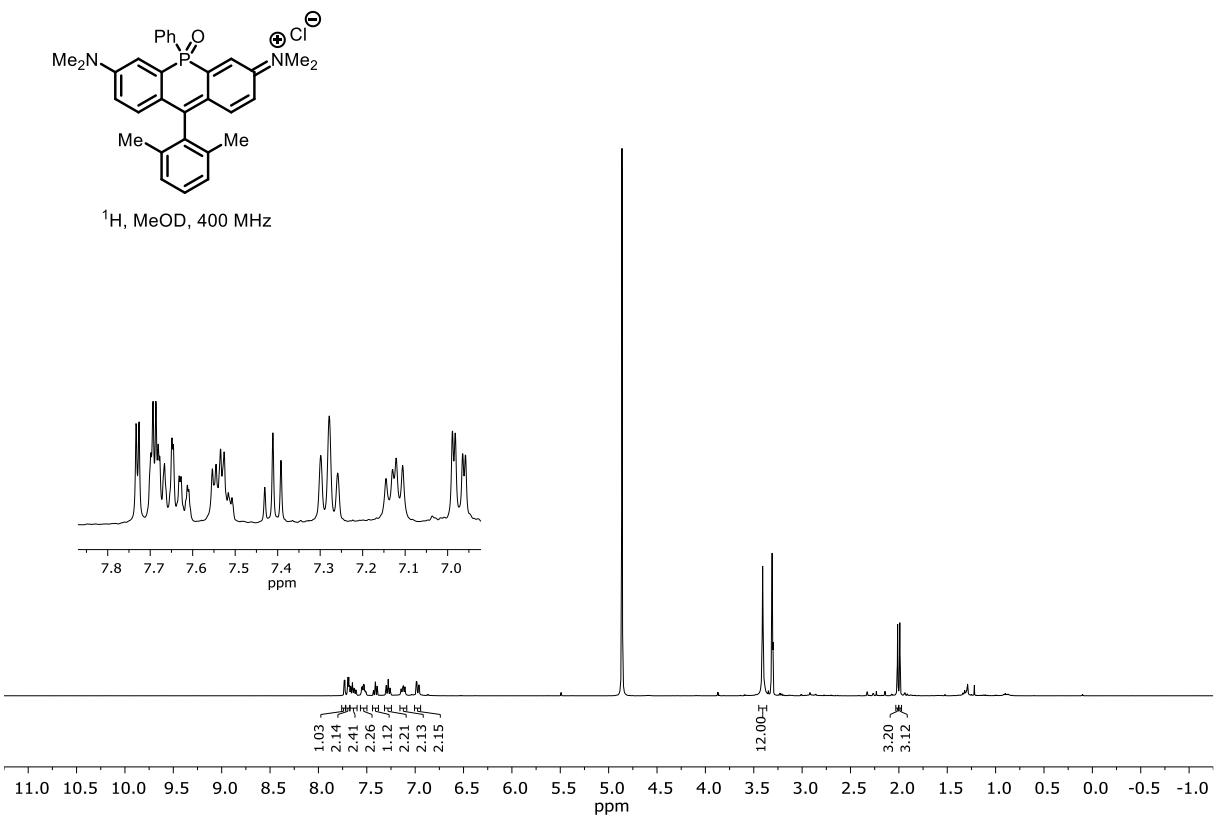
$^{13}C\{^{1}H\}$ NMR spectrum of 13i:



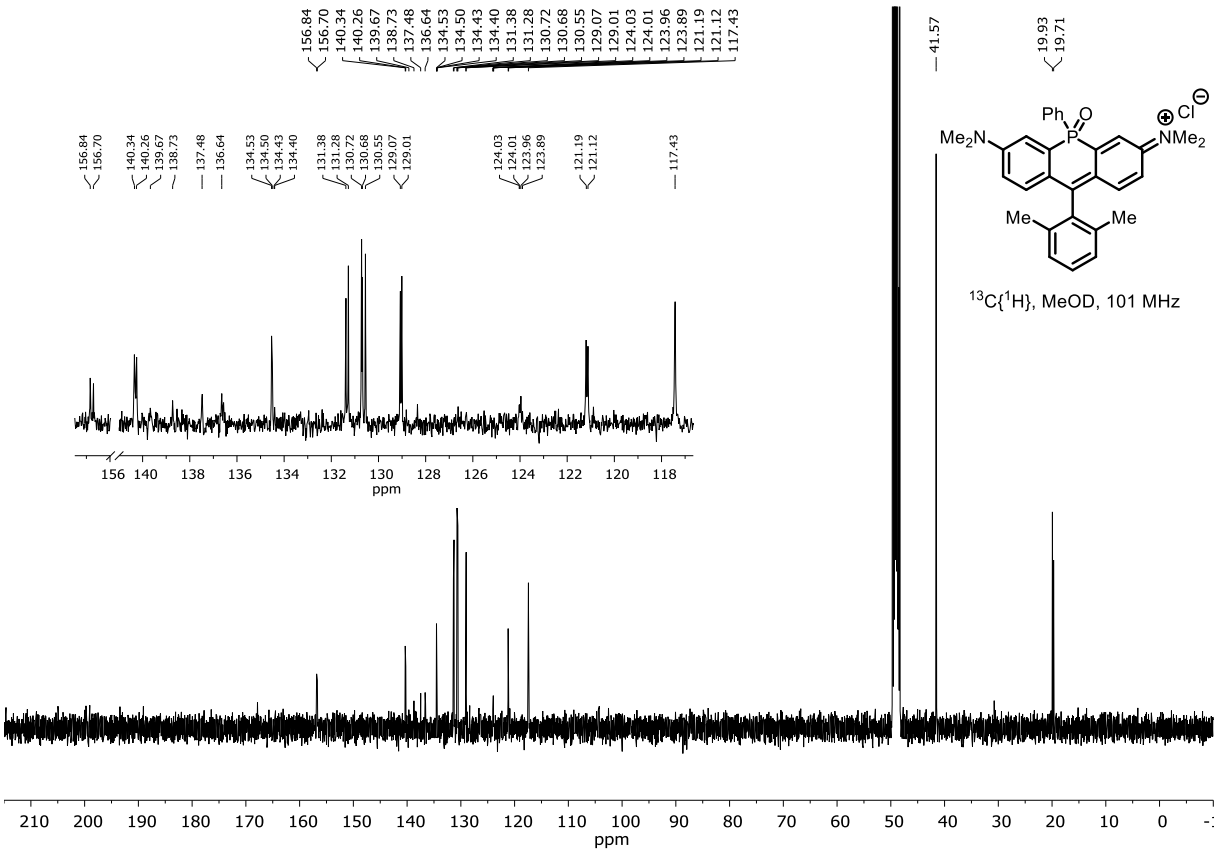
$^{31}P\{^{1}H\}$ NMR spectrum of 13i:



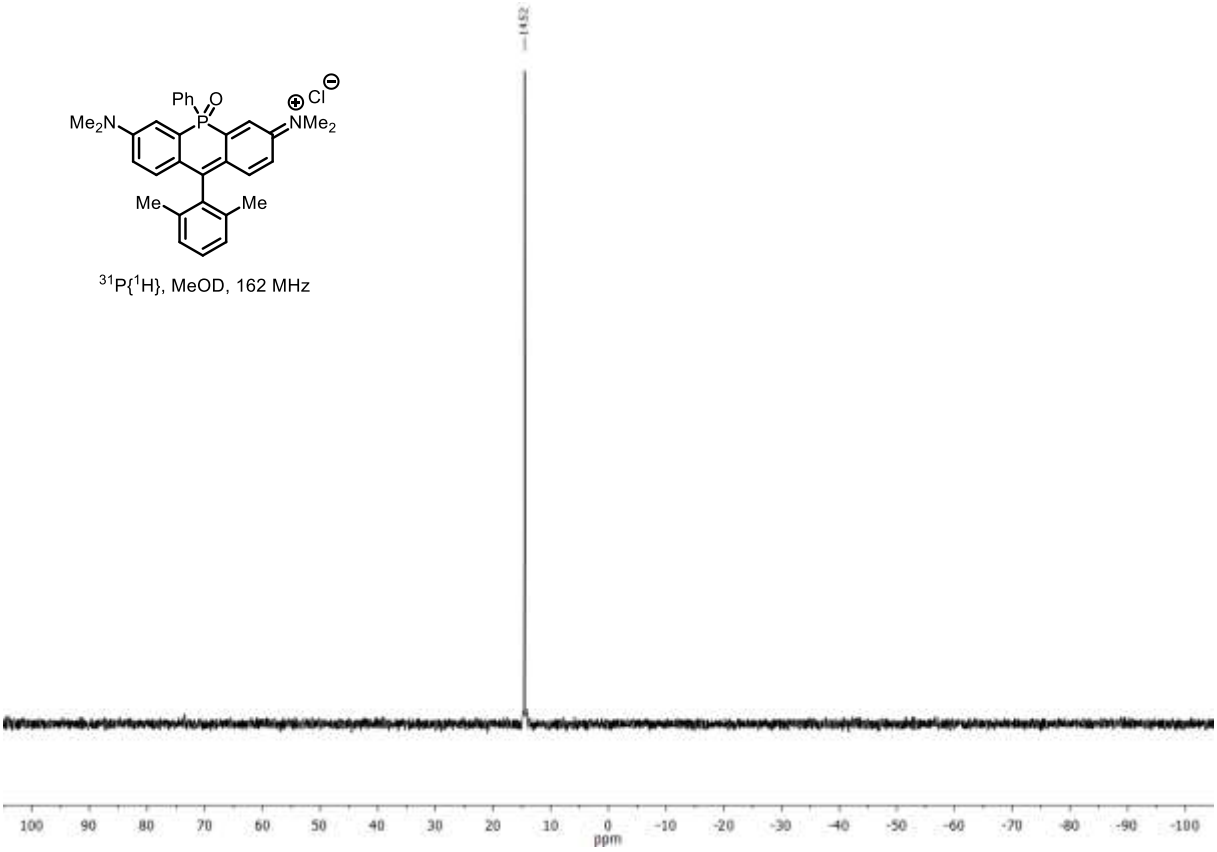
^{1}H NMR spectrum of 13e:



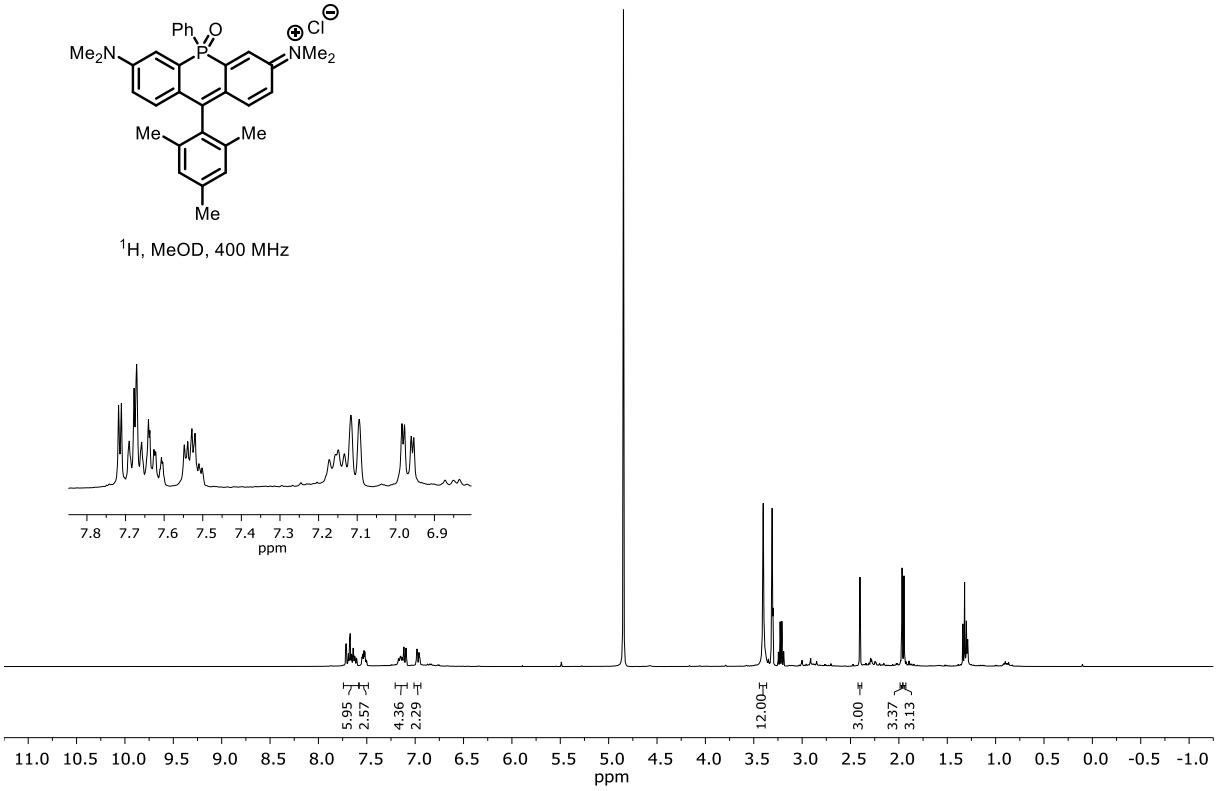
^{13}C{^{1}H} NMR spectrum of 13e:



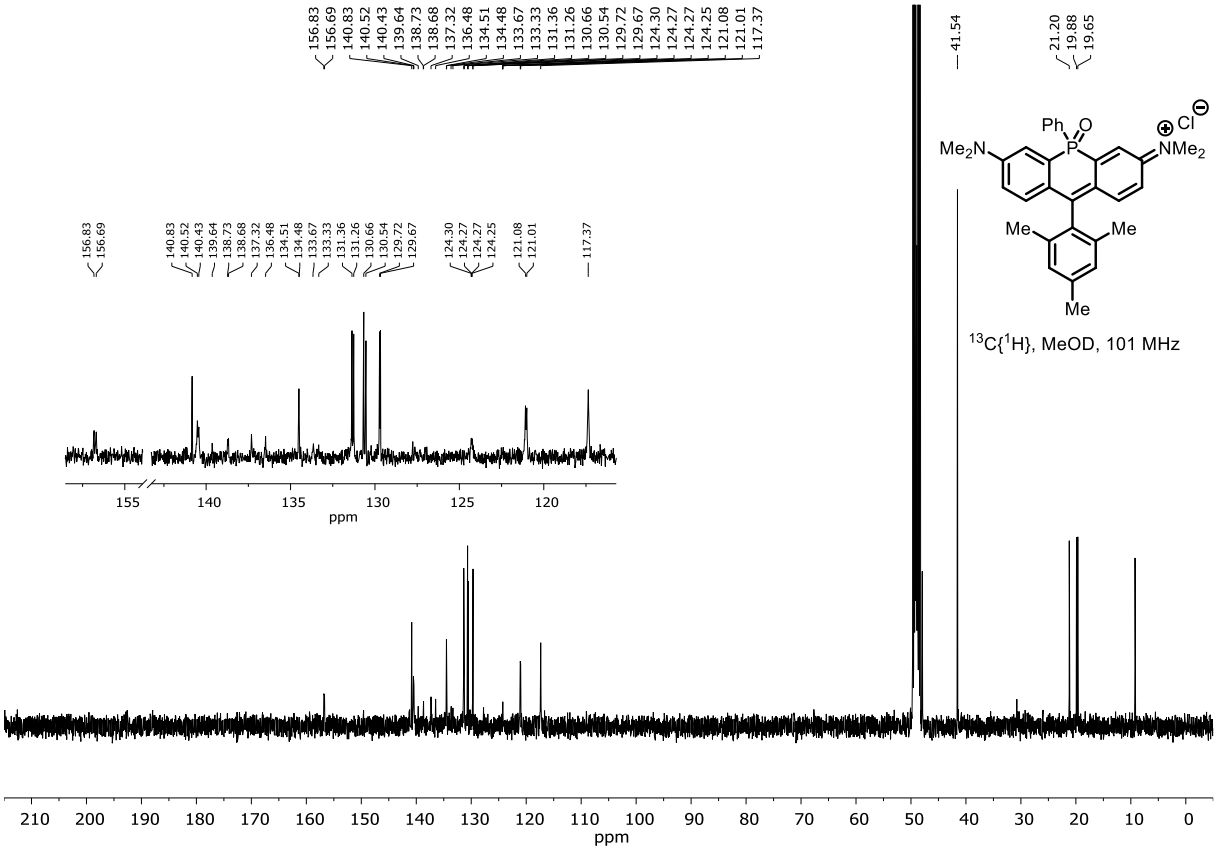
$^{31}P\{^{1}H\}$ NMR spectrum of 13e:



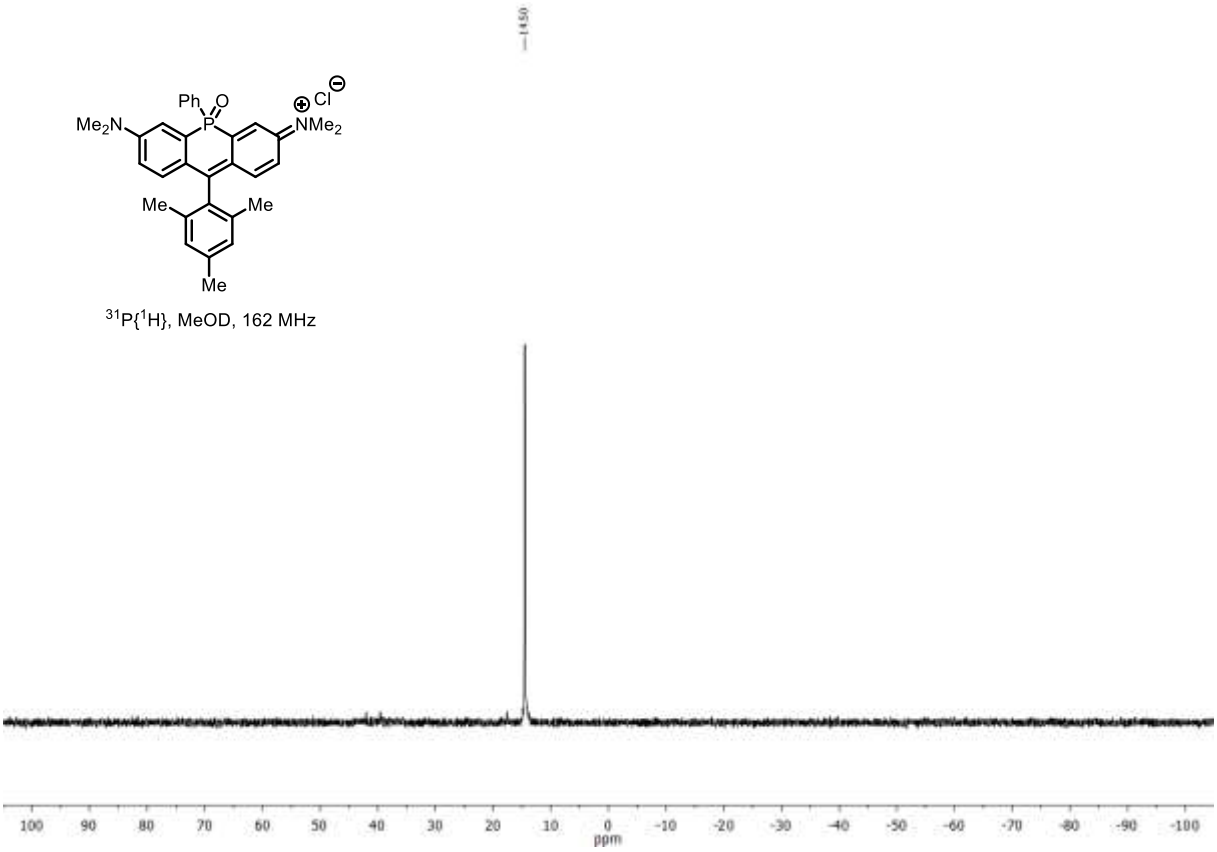
^{1}H NMR spectrum of 13f:



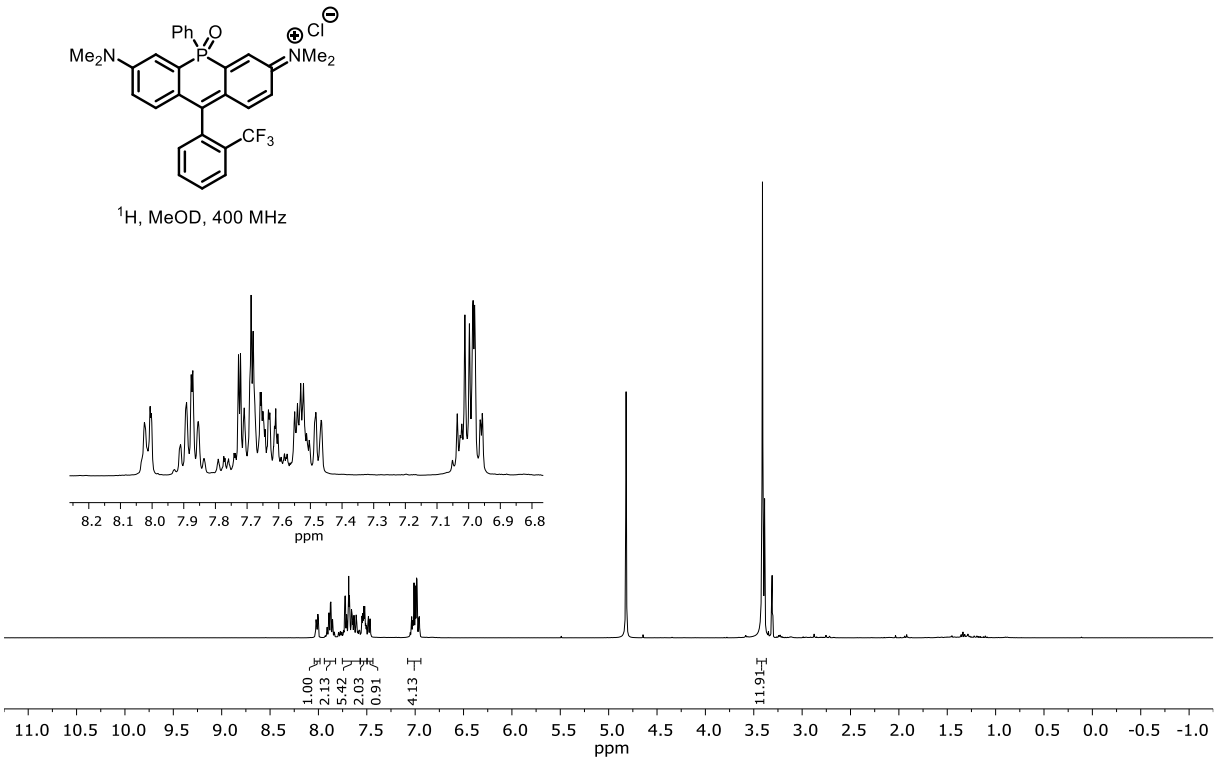
$^{13}C\{^{1}H\}$ NMR spectrum of 13f:



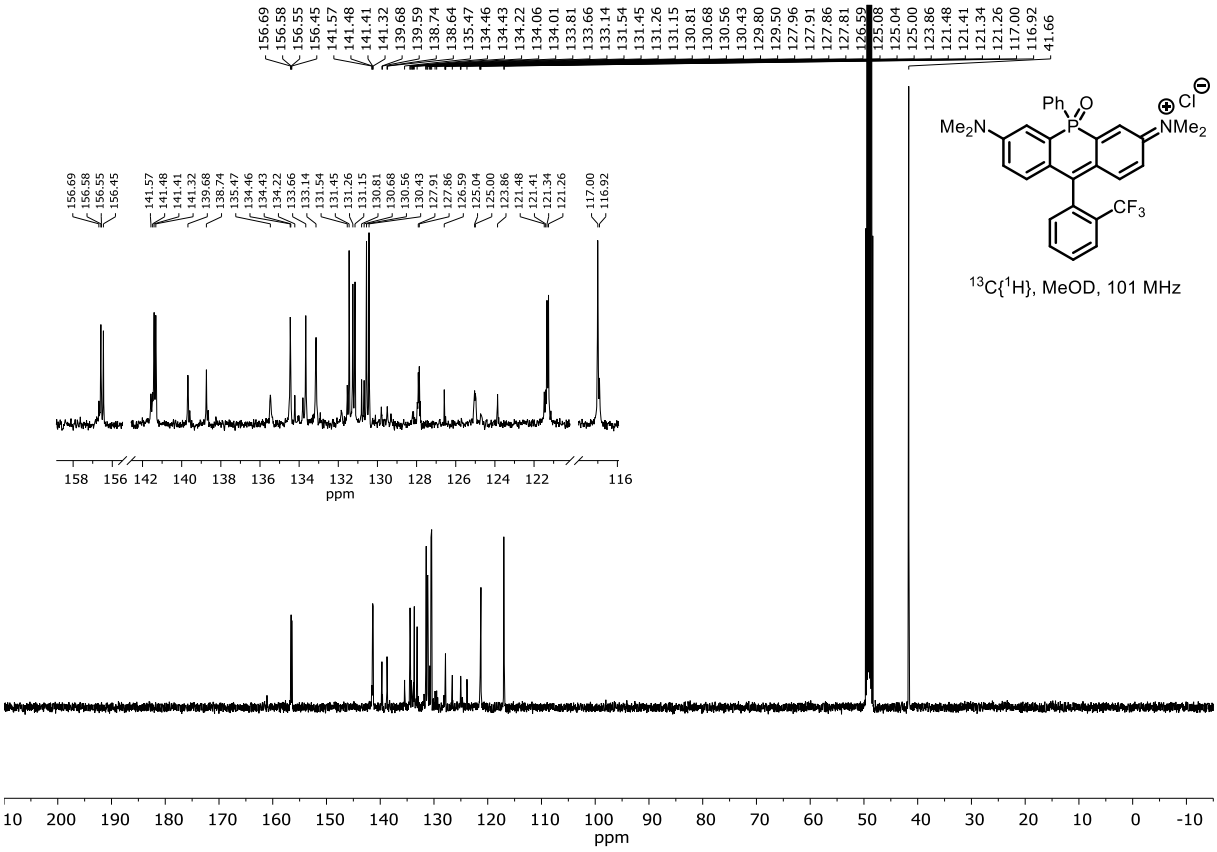
$^{31}P\{^{1}H\}$ NMR spectrum of 13f:



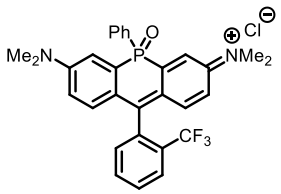
^{1}H NMR spectrum of 13l:



^{13}C{^{1}H} NMR spectrum of 13l:

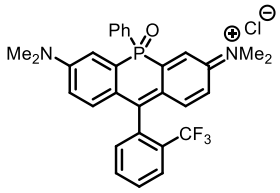


$^{31}P\{^{1}H\}$ NMR spectrum of 13l:



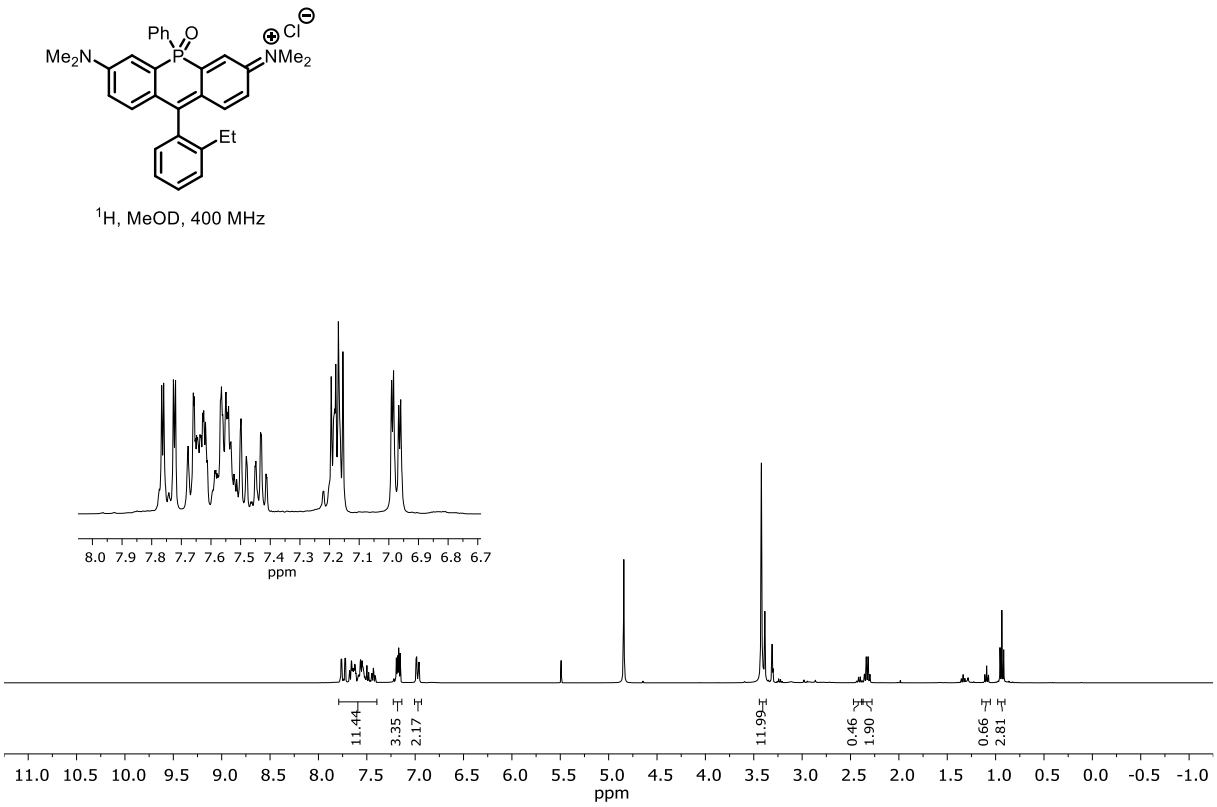
$^{31}P\{^{1}H\}$, MeOD, 162 MHz

^{19}F NMR spectrum of 13l:

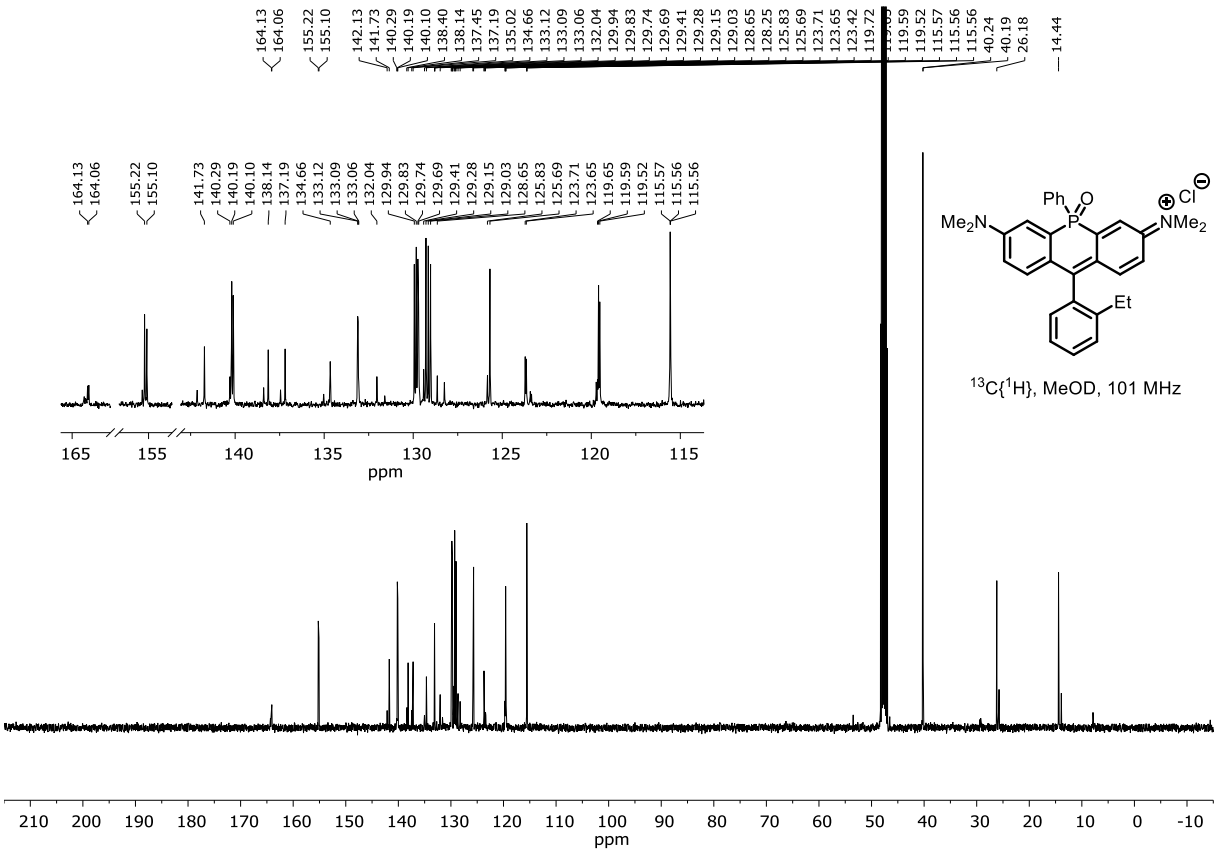


^{19}F, MeOD, 377 MHz

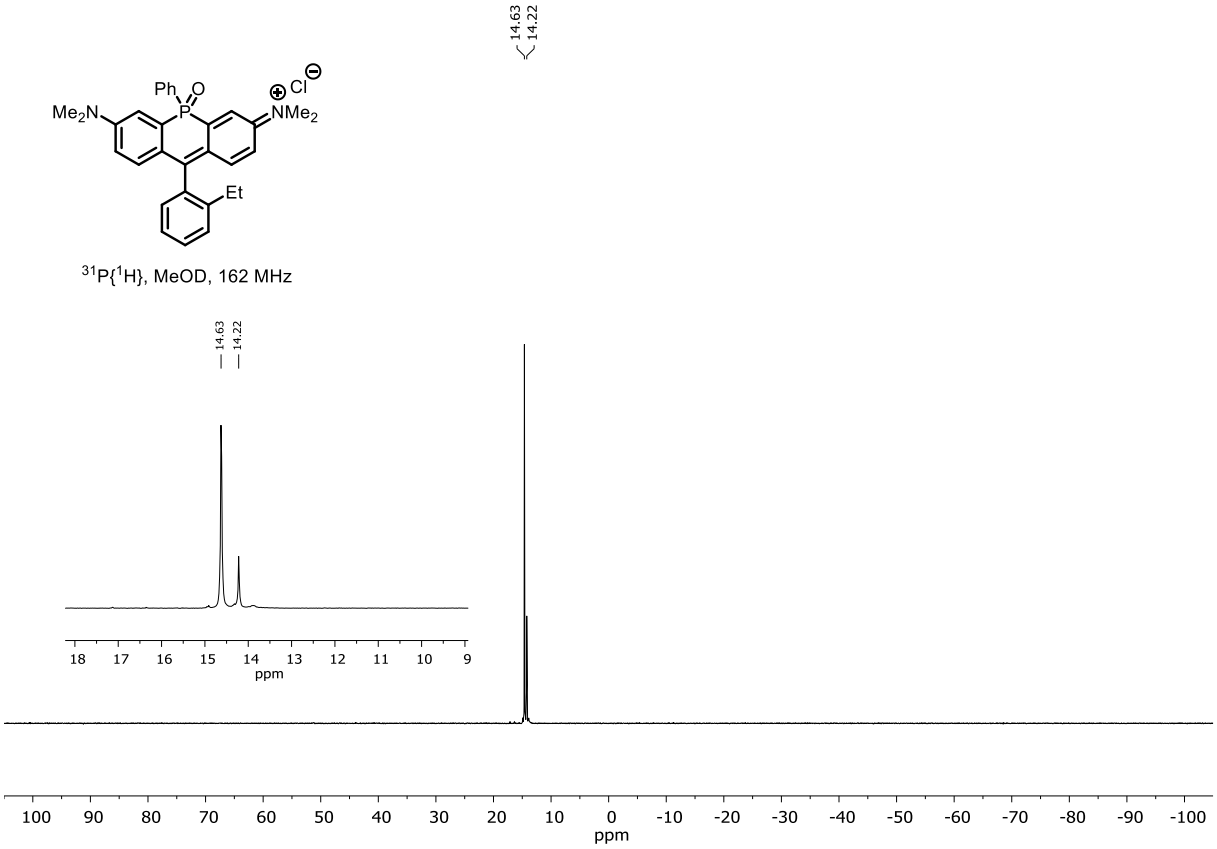
^{1}H NMR spectrum of 13d:



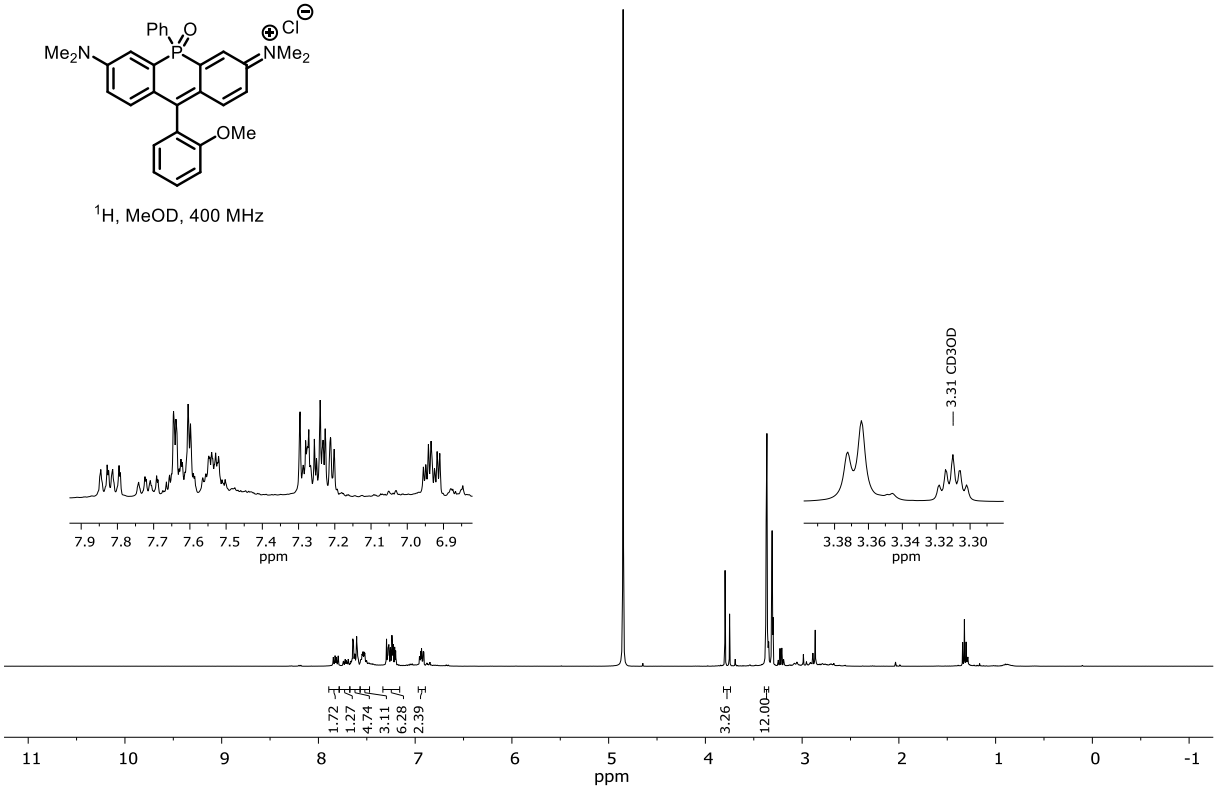
^{13}C{^{1}H} NMR spectrum of 13d:



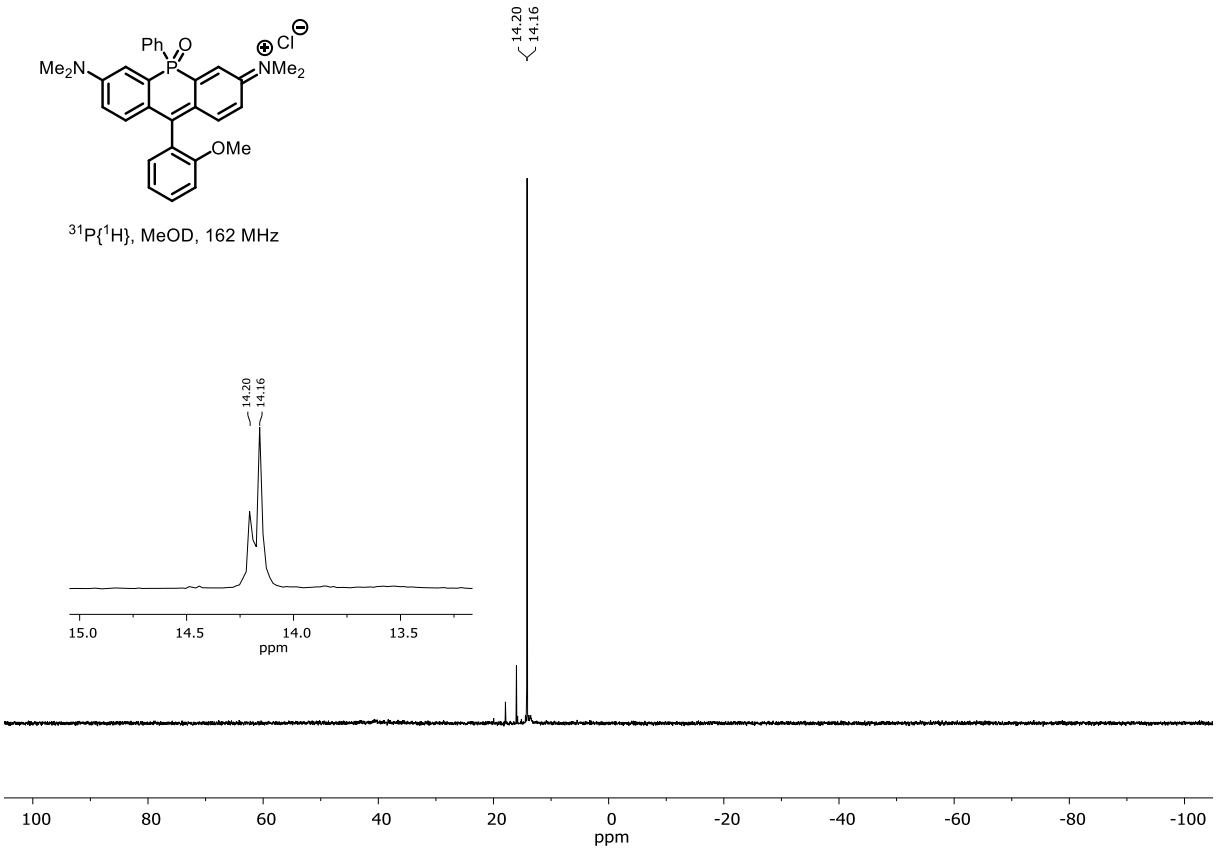
$^{31}P\{^{1}H\}$ NMR spectrum of 13d:



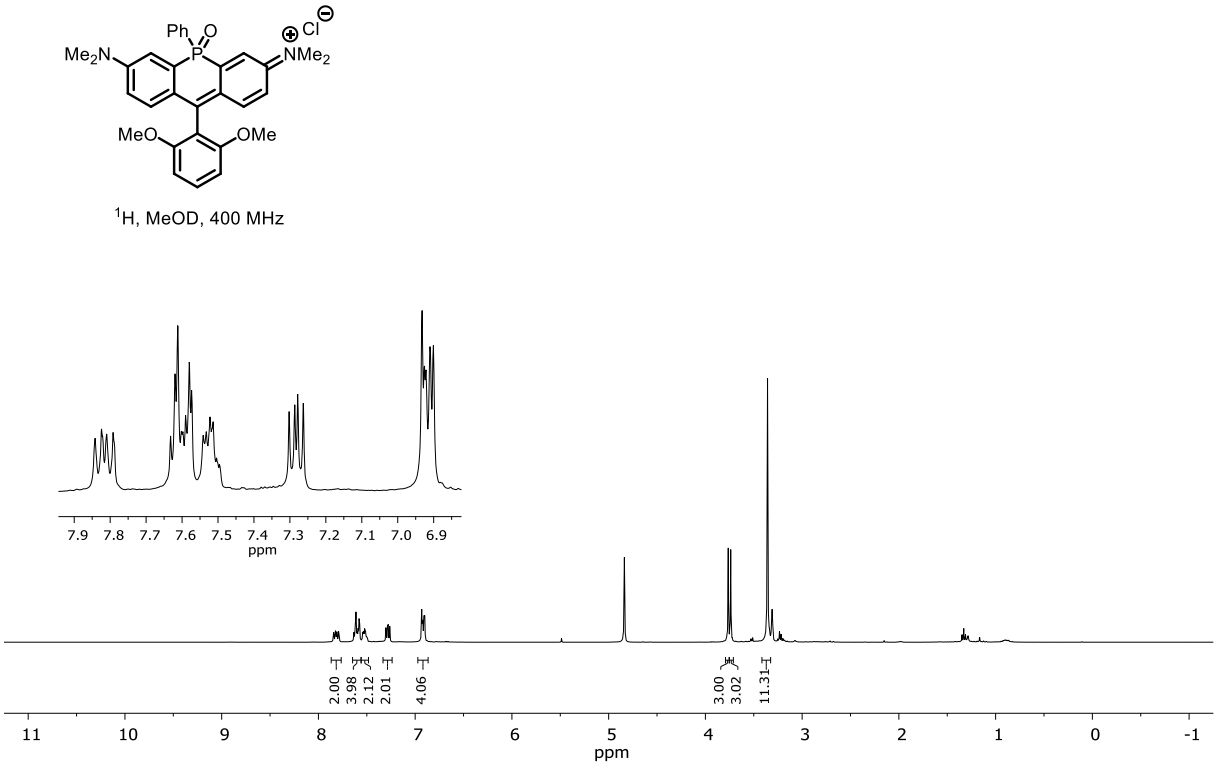
^{1}H NMR spectrum of 13b:



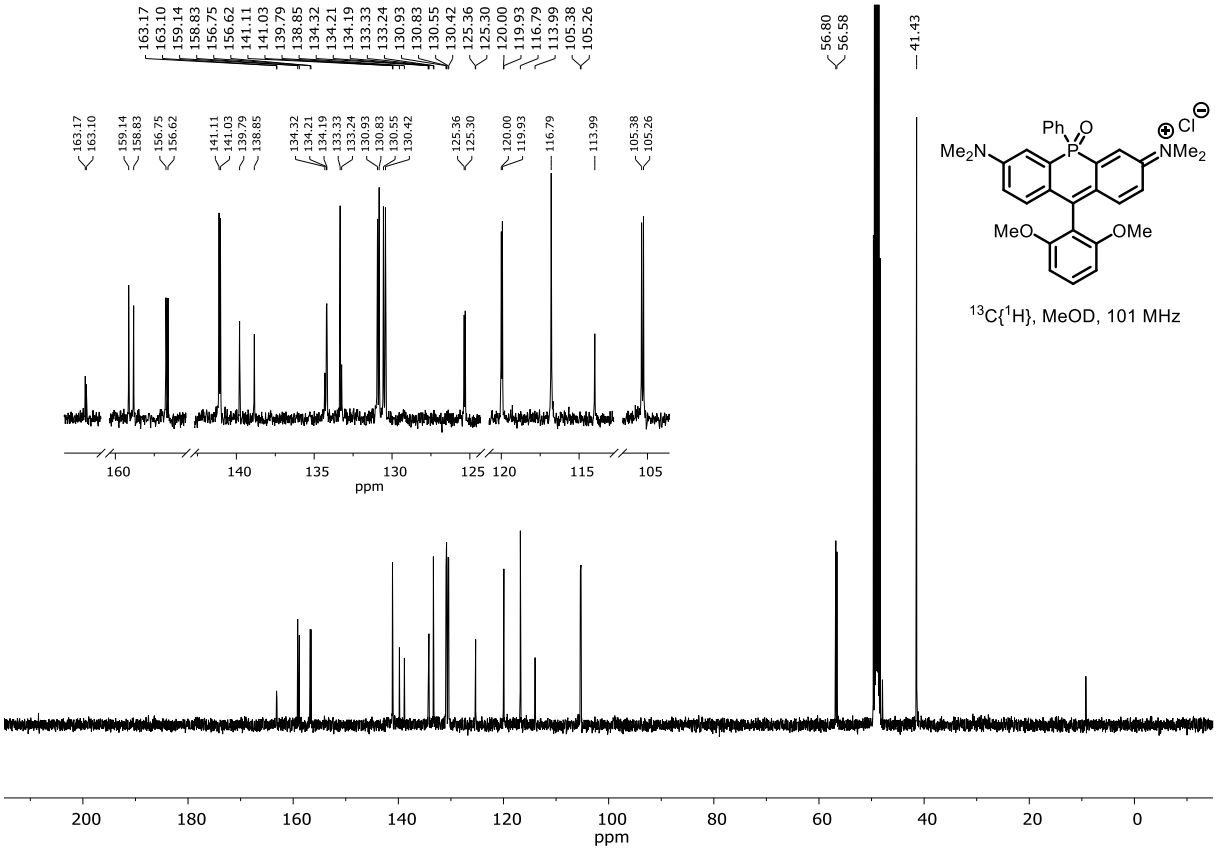
$^{31}P\{^{1}H\}$ NMR spectrum of 13b:



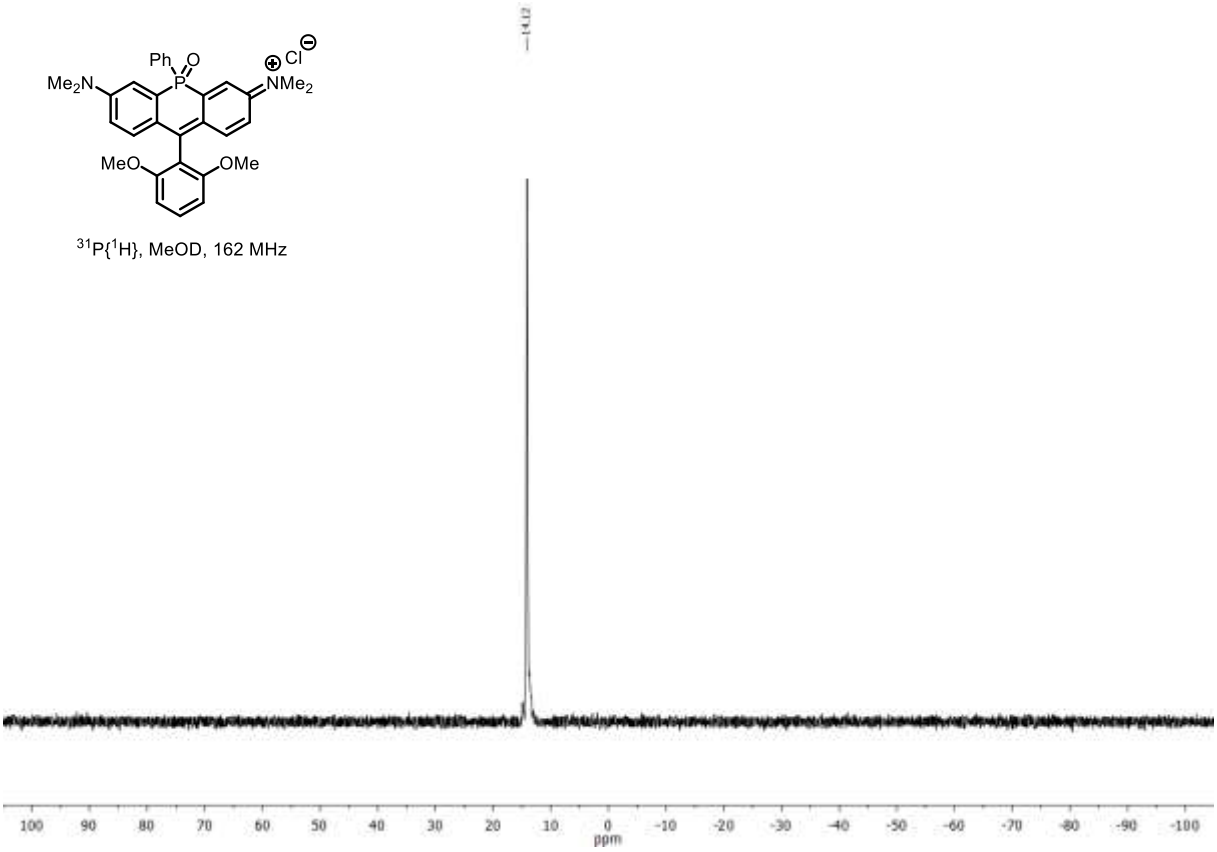
^{1}H NMR spectrum of 13c:



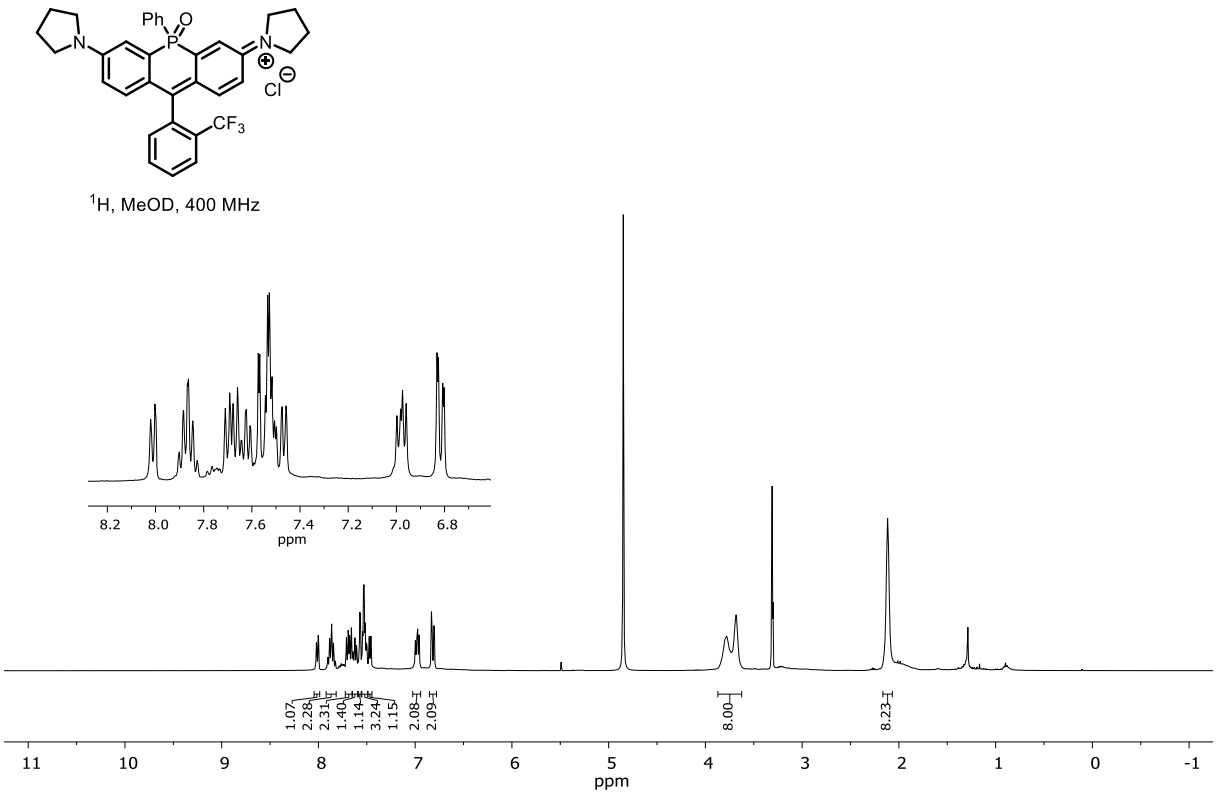
$^{13}C\{^{1}H\}$ NMR spectrum of 13c:



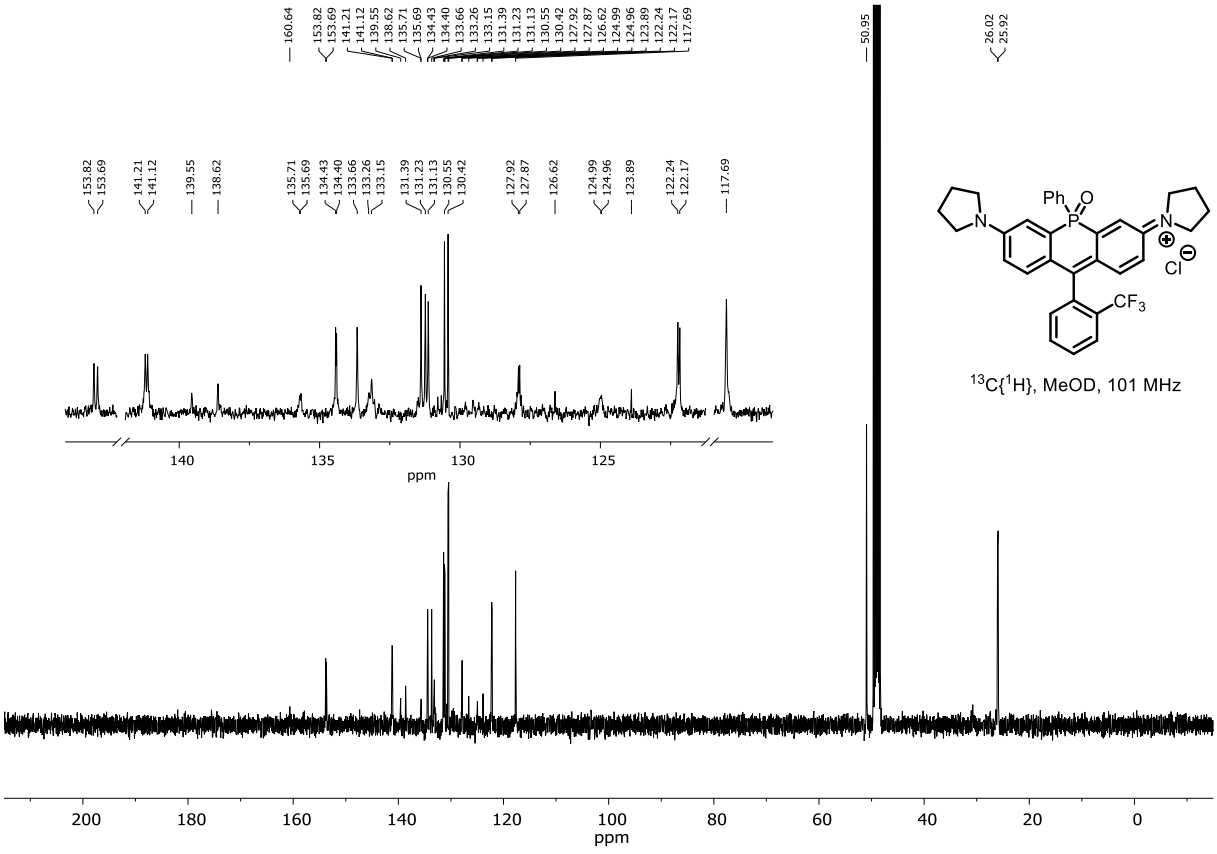
$^{31}P\{^{1}H\}$ NMR spectrum of 13c:



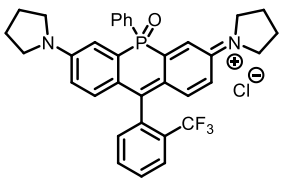
^{1}H NMR spectrum of 13n:



^{13}C{^{1}H} NMR spectrum of 13n:

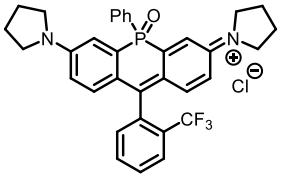


$^{31}P\{^{1}H\}$ NMR spectrum of 13n:



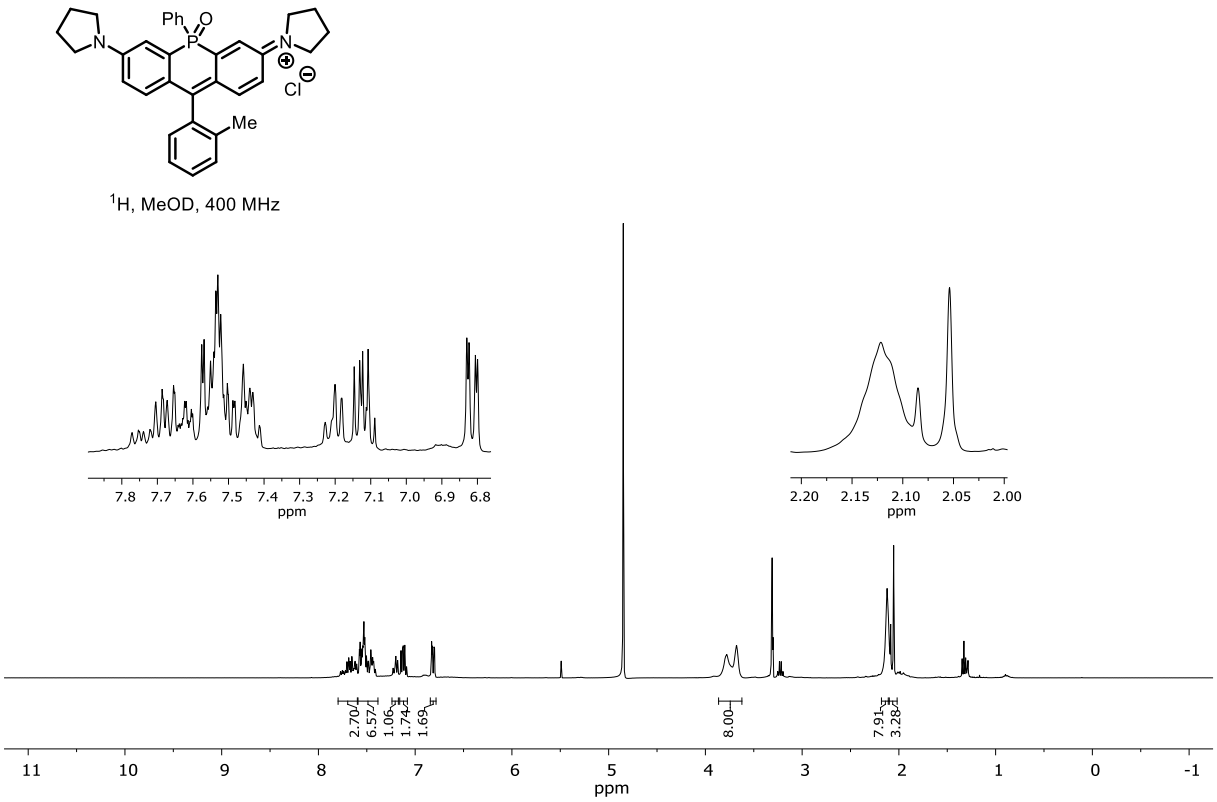
$^{31}P\{^{1}H\}$, MeOD, 162 MHz

^{19}F NMR spectrum of 13n:

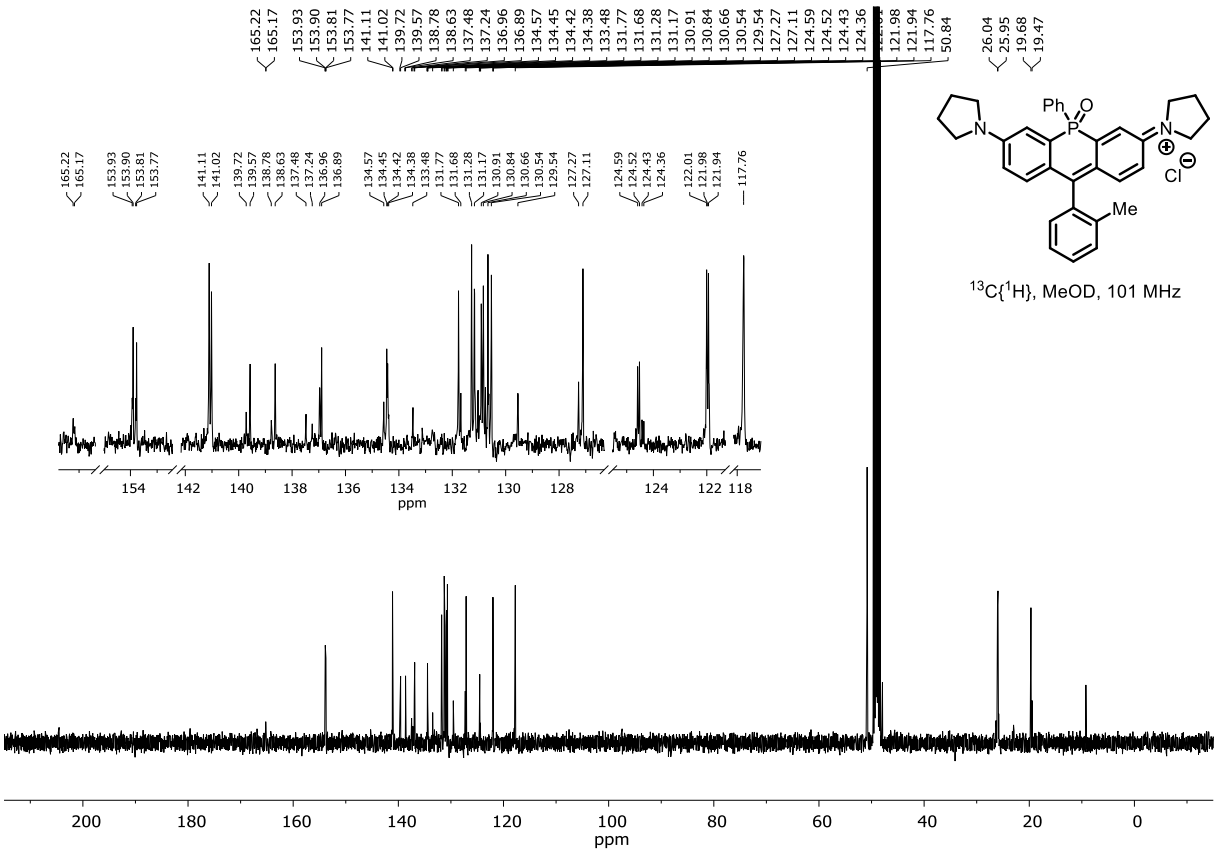


^{19}F, MeOD, 377 MHz

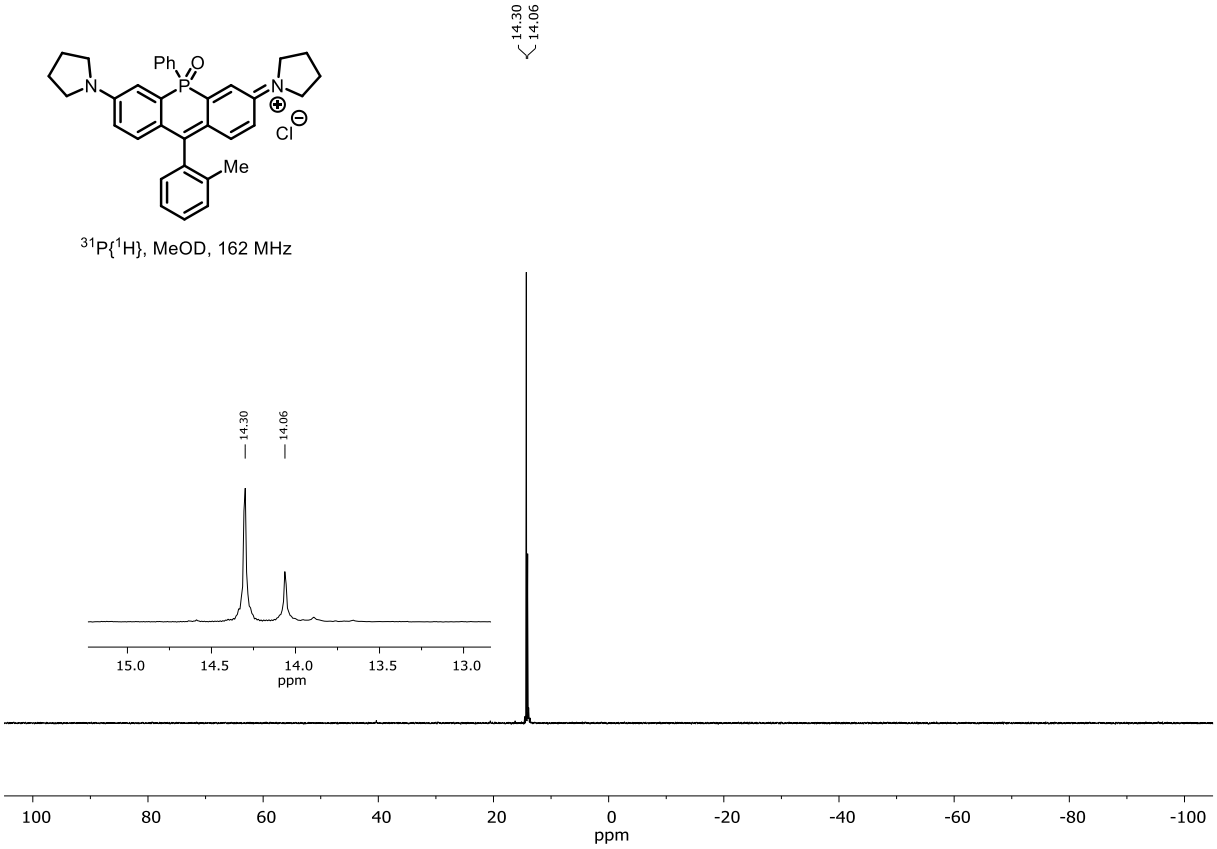
^{1}H NMR spectrum of 13k:



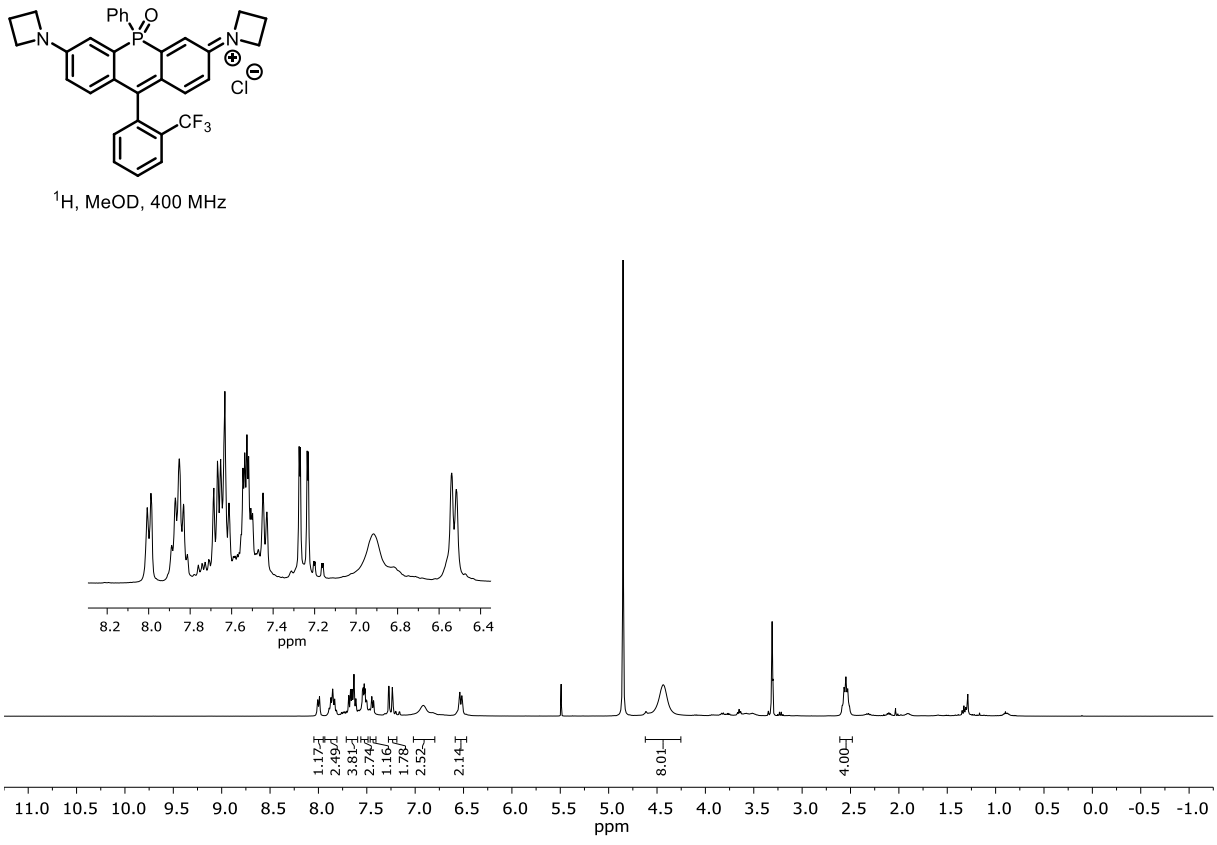
^{13}C{^{1}H} NMR spectrum of 13k:



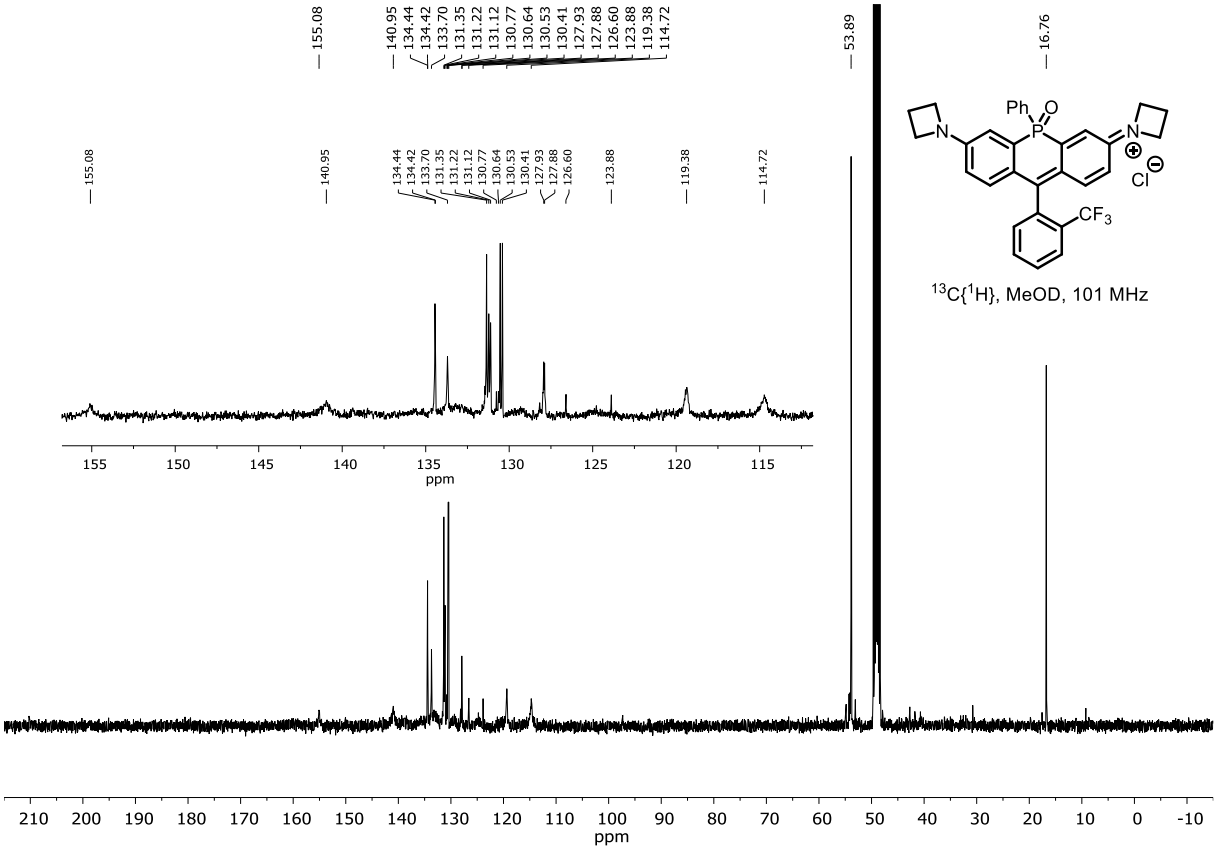
$^{31}P\{^{1}H\}$ NMR spectrum of 13k:



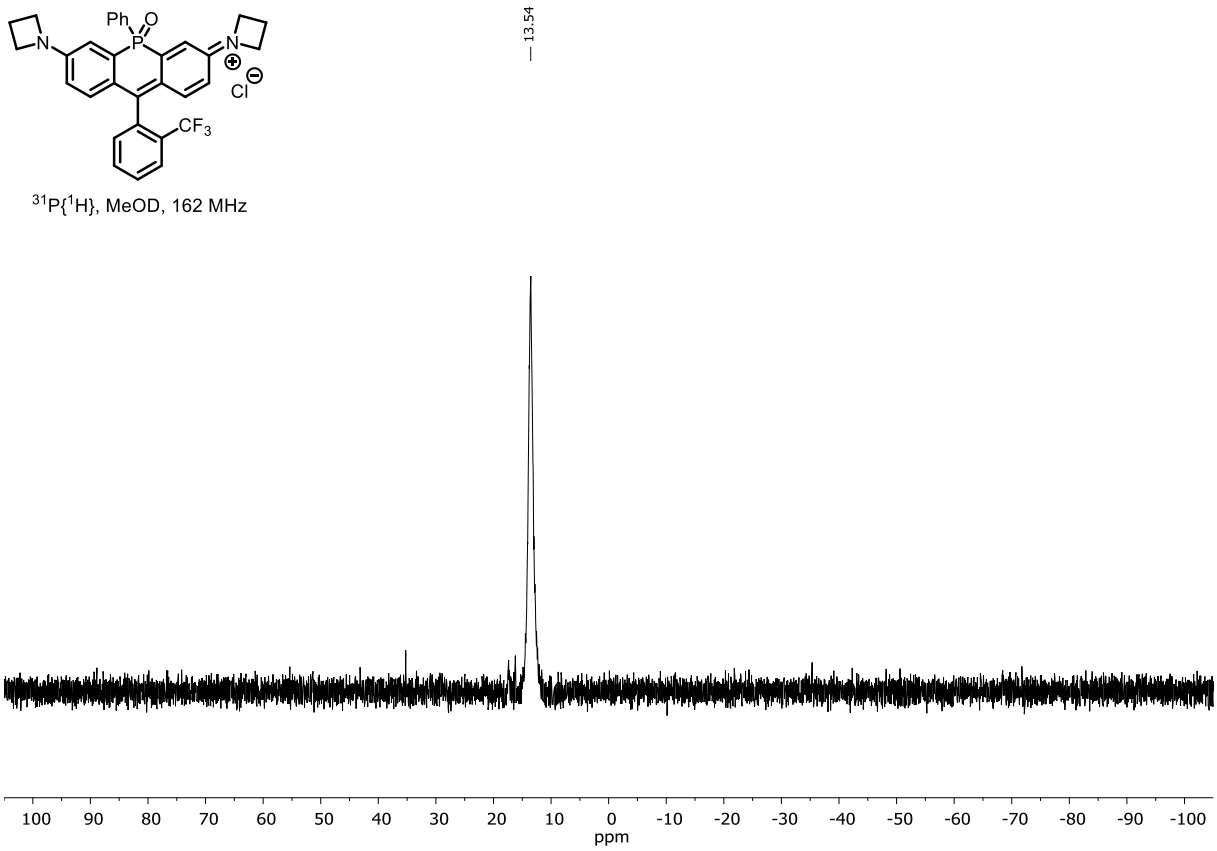
^{1}H NMR spectrum of 13m:



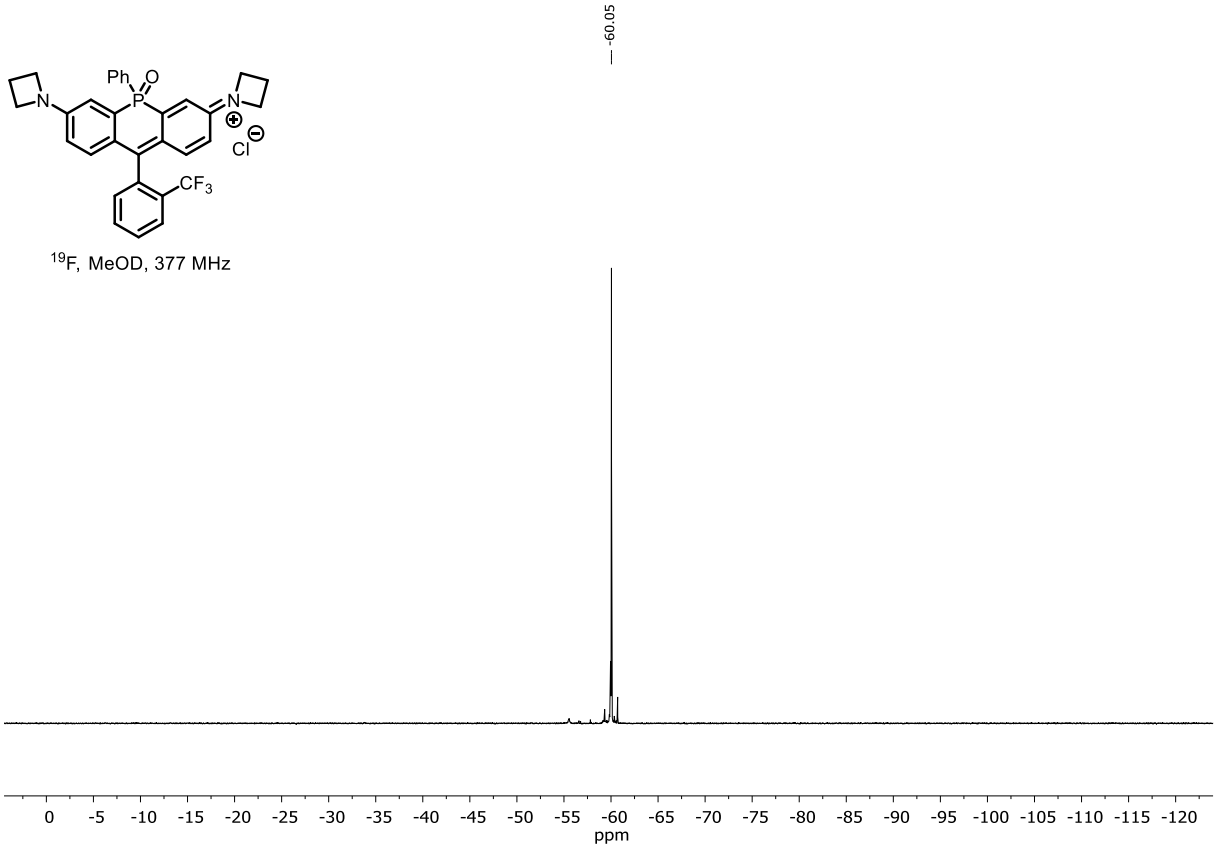
$^{13}C\{^{1}H\}$ NMR spectrum of 13m:



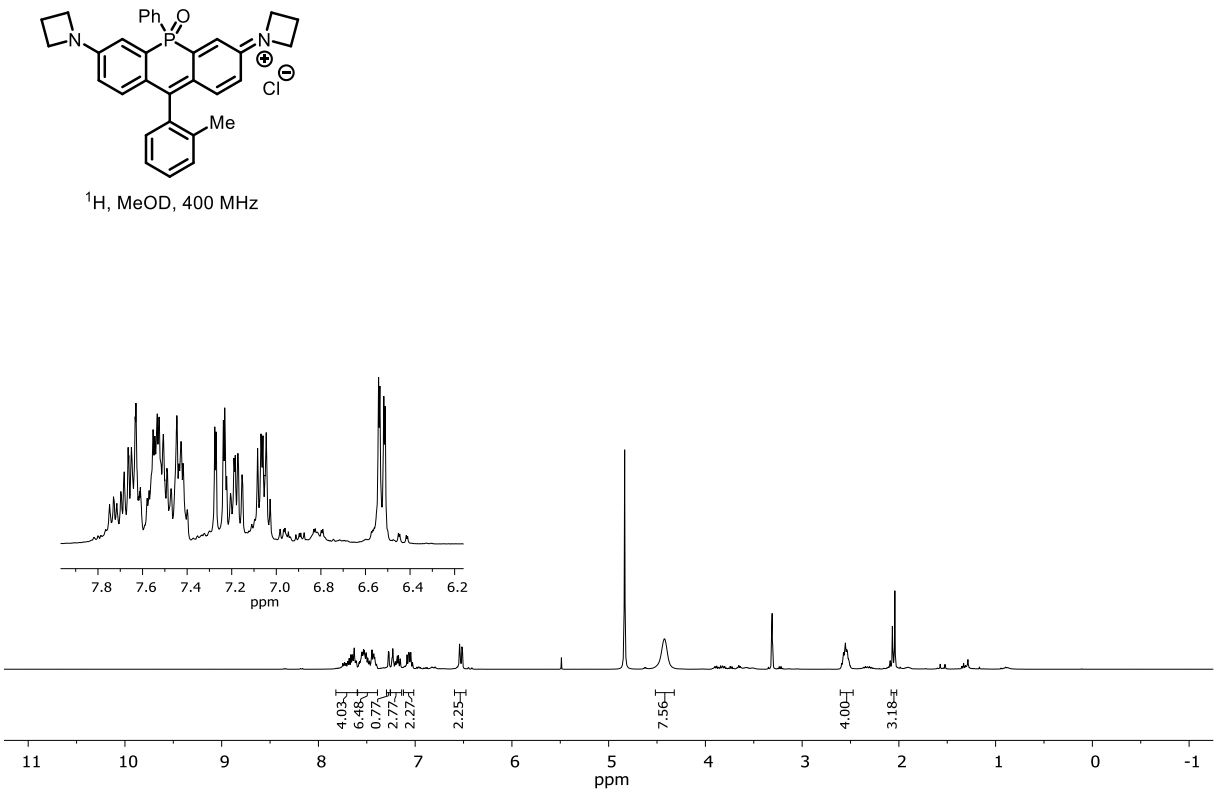
$^{31}P\{^{1}H\}$ NMR spectrum of 13m:



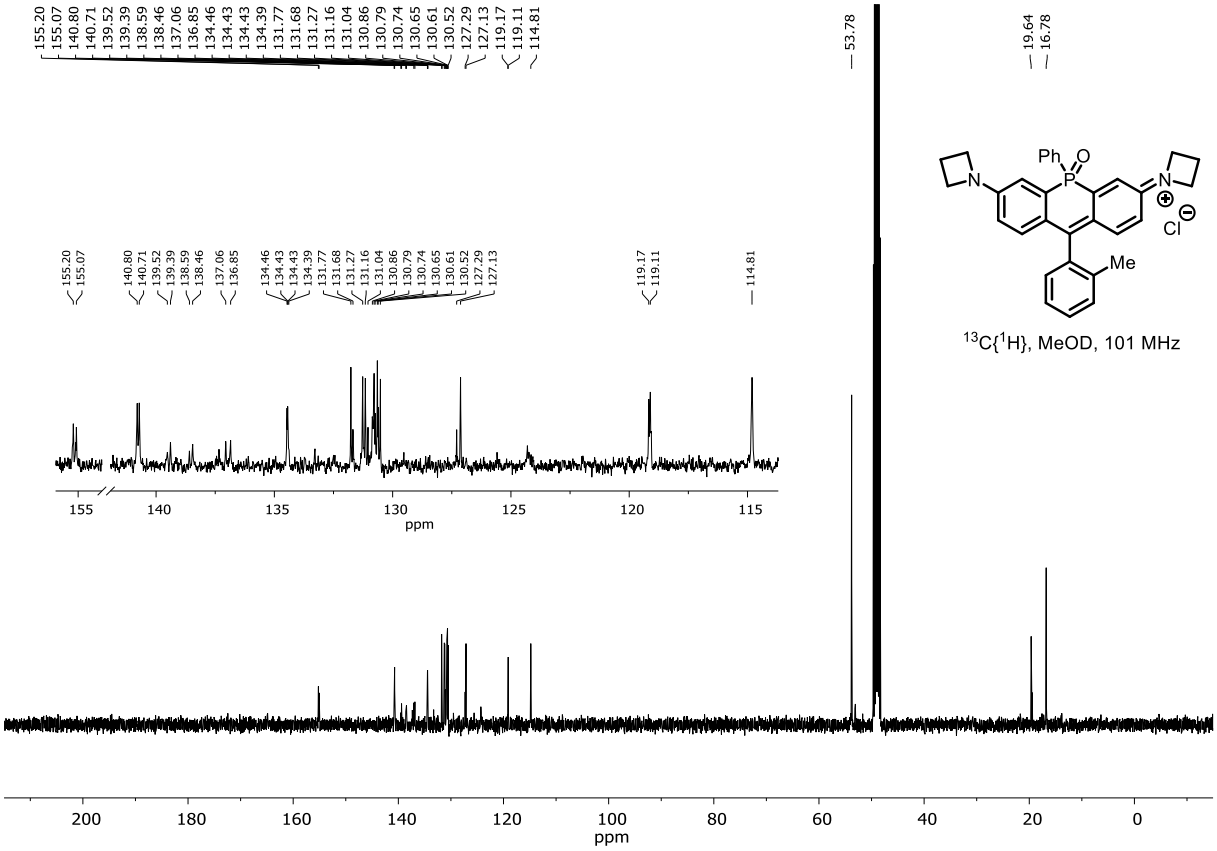
^{19}F NMR spectrum of 13m:



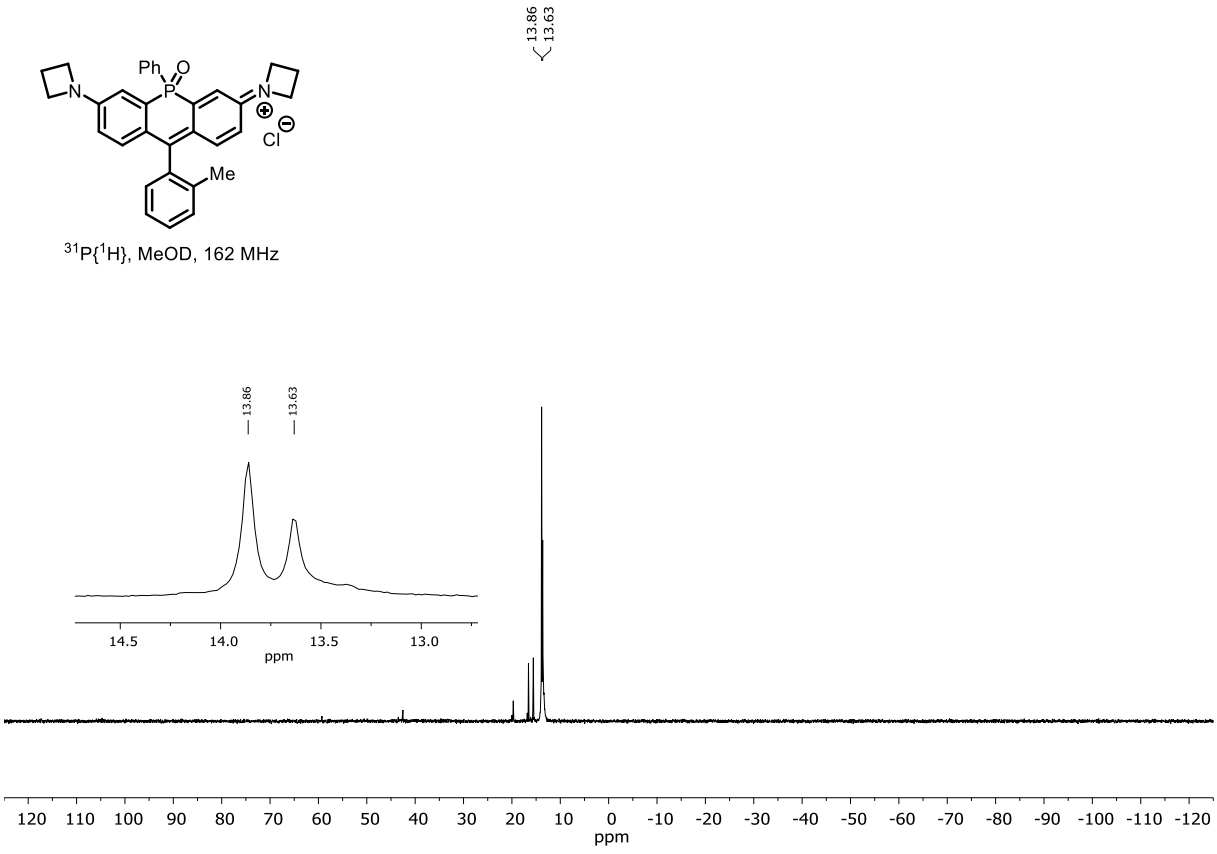
^{1}H NMR spectrum of 13j:



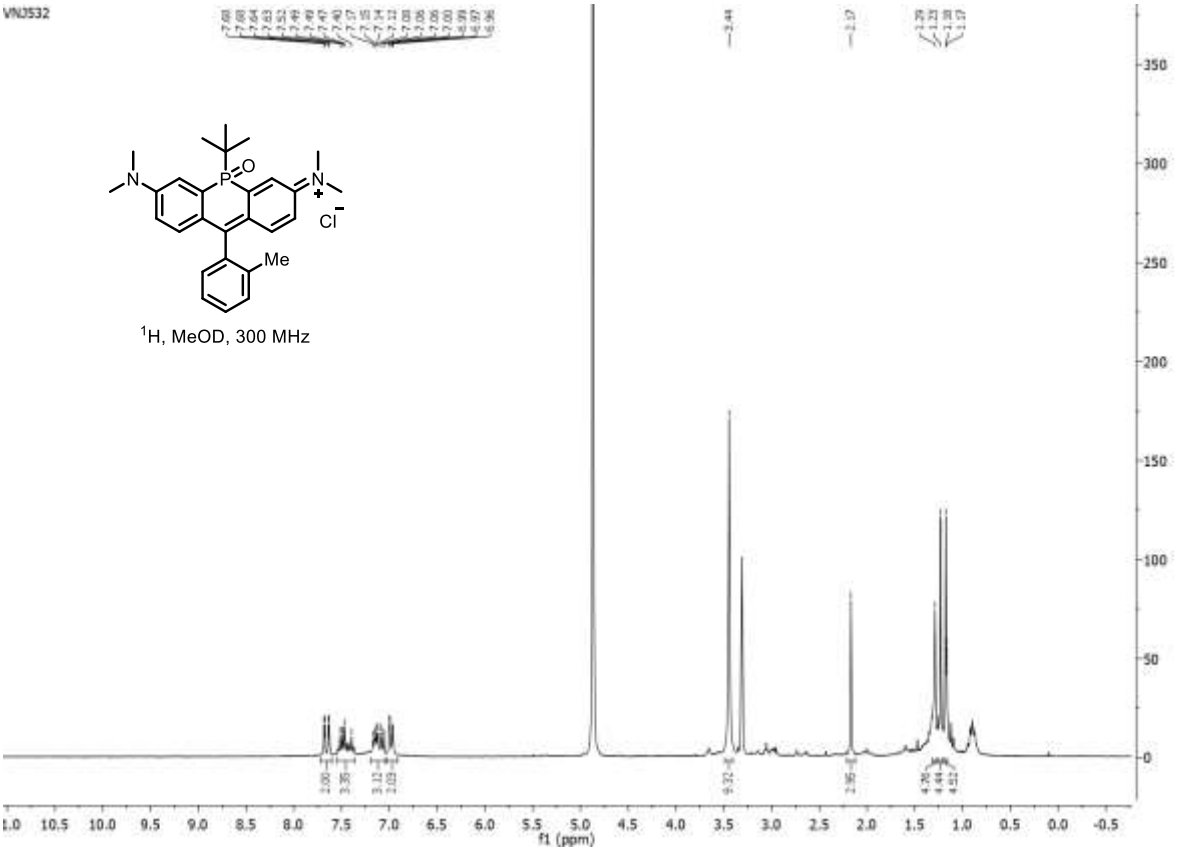
$^{13}C\{^{1}H\}$ NMR spectrum of 13j:



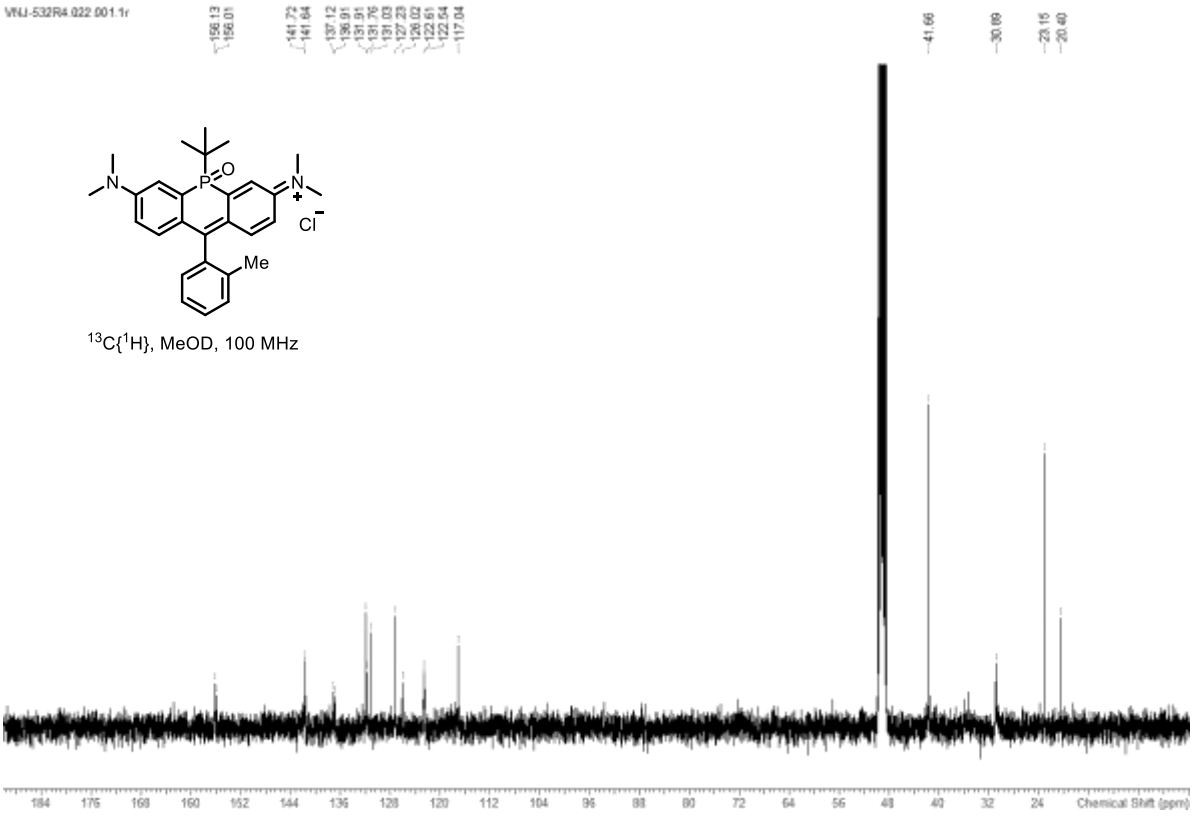
$^{31}P\{^{1}H\}$ NMR spectrum of 13j:



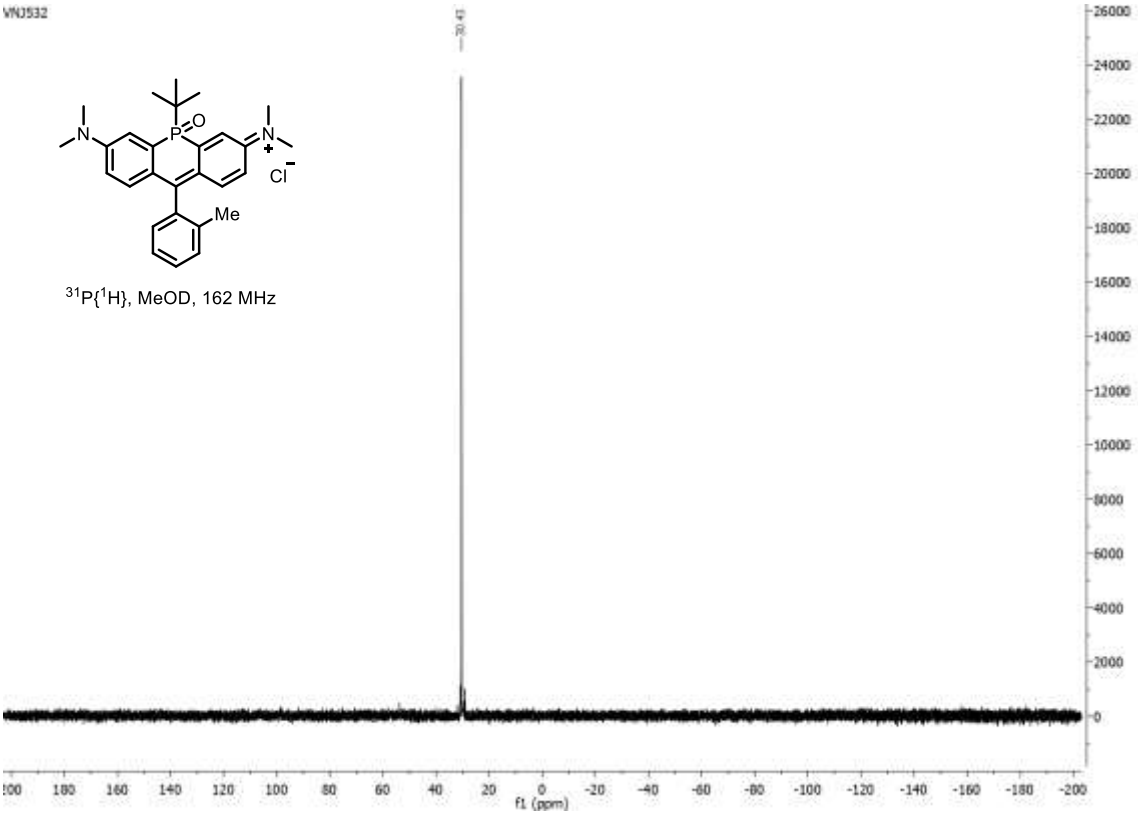
^{1}H spectrum of 13g:



^{13}C{^{1}H} spectrum of 13g:

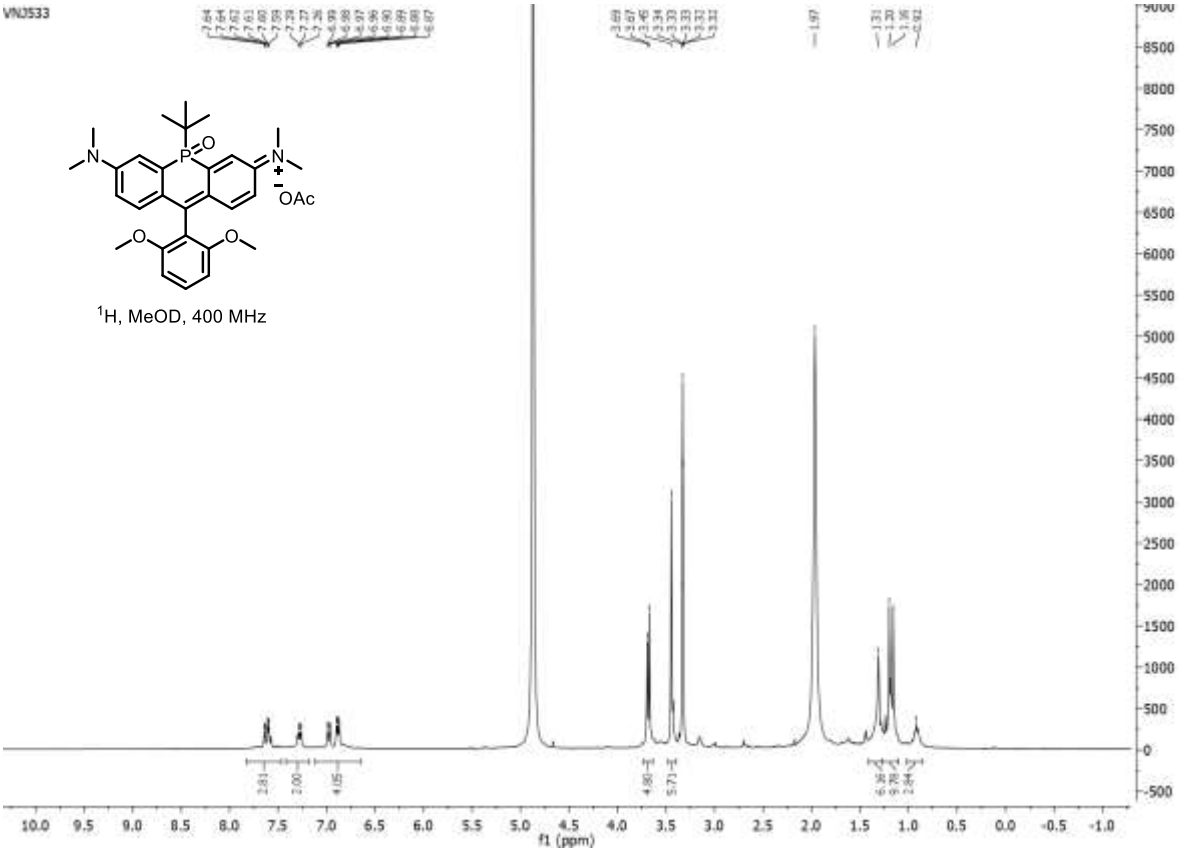


$^{31}P\{^{1}H\}$ spectrum of 13g:



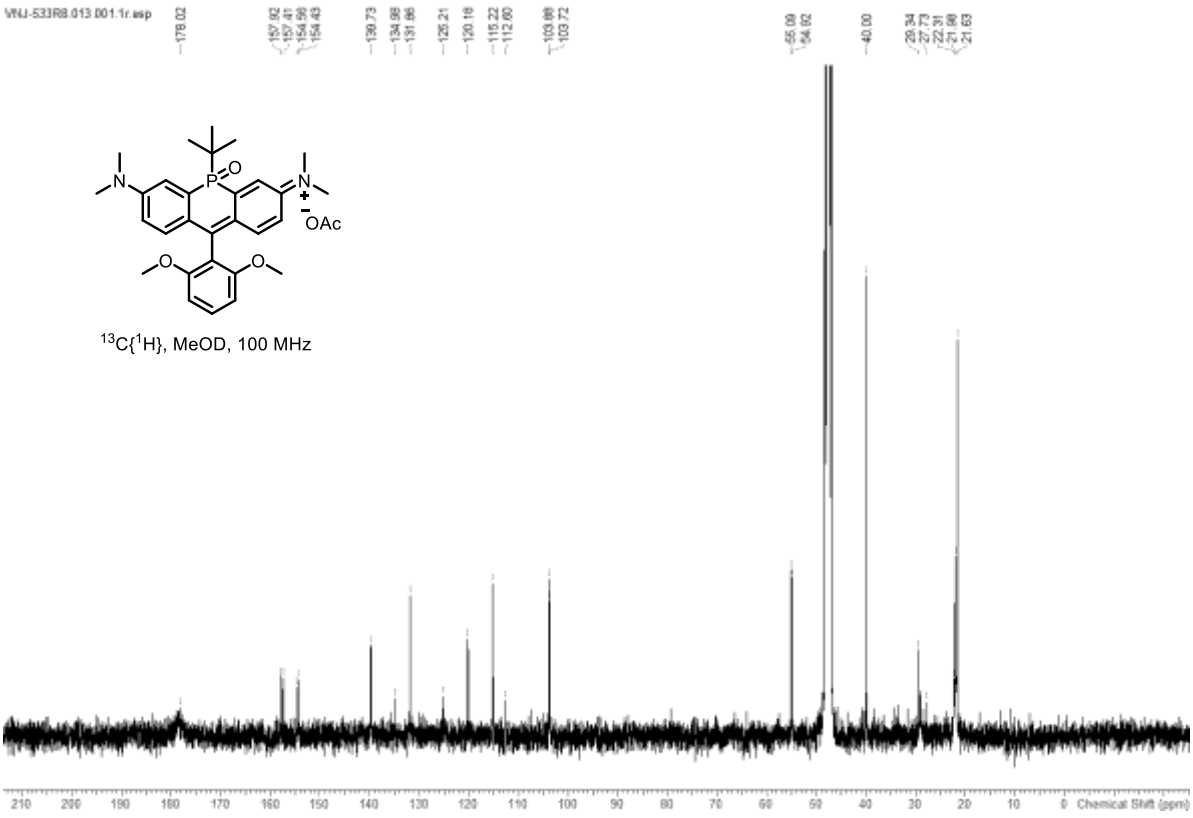
$^{31}P\{^{1}H\}$, MeOD, 162 MHz

^{1}H spectrum of 13h:



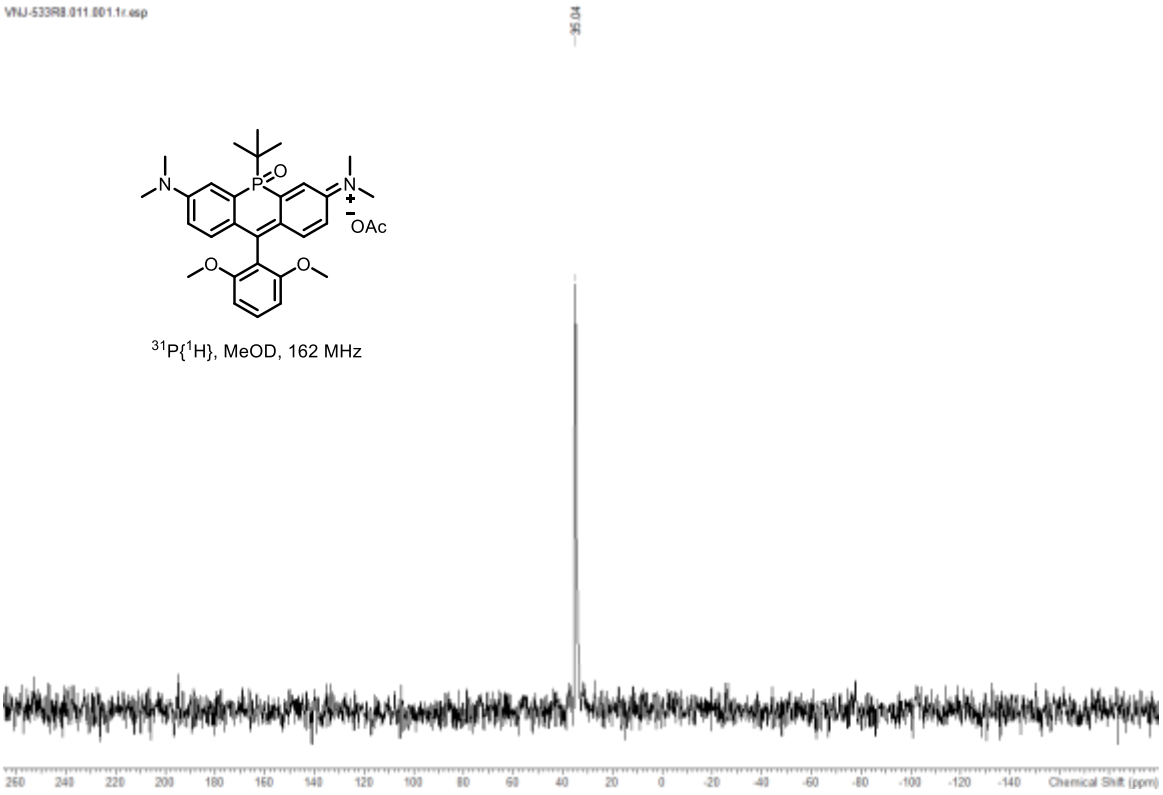
^{1}H, MeOD, 400 MHz

$^{13}C\{^{1}H\}$ spectrum of 13h:



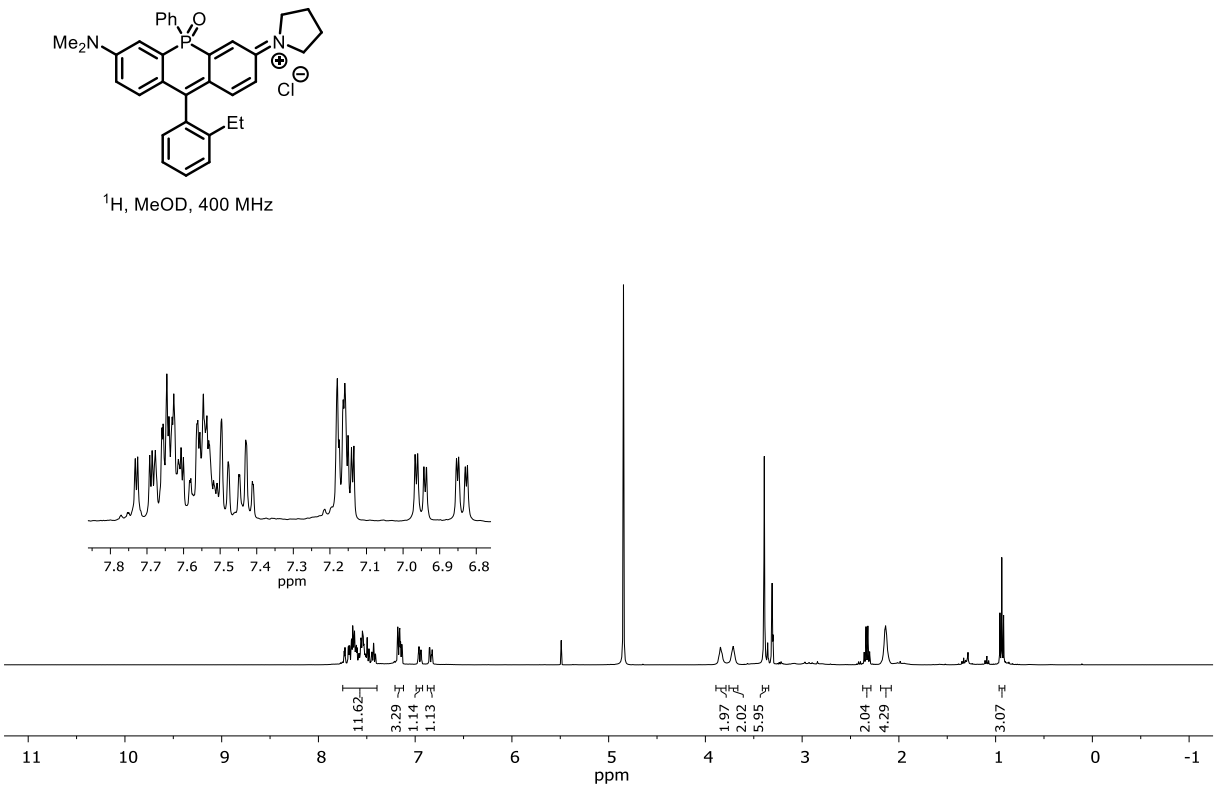
$^{13}C\{^{1}H\}$, MeOD, 100 MHz

$^{31}P\{^{1}H\}$ spectrum of 13h:

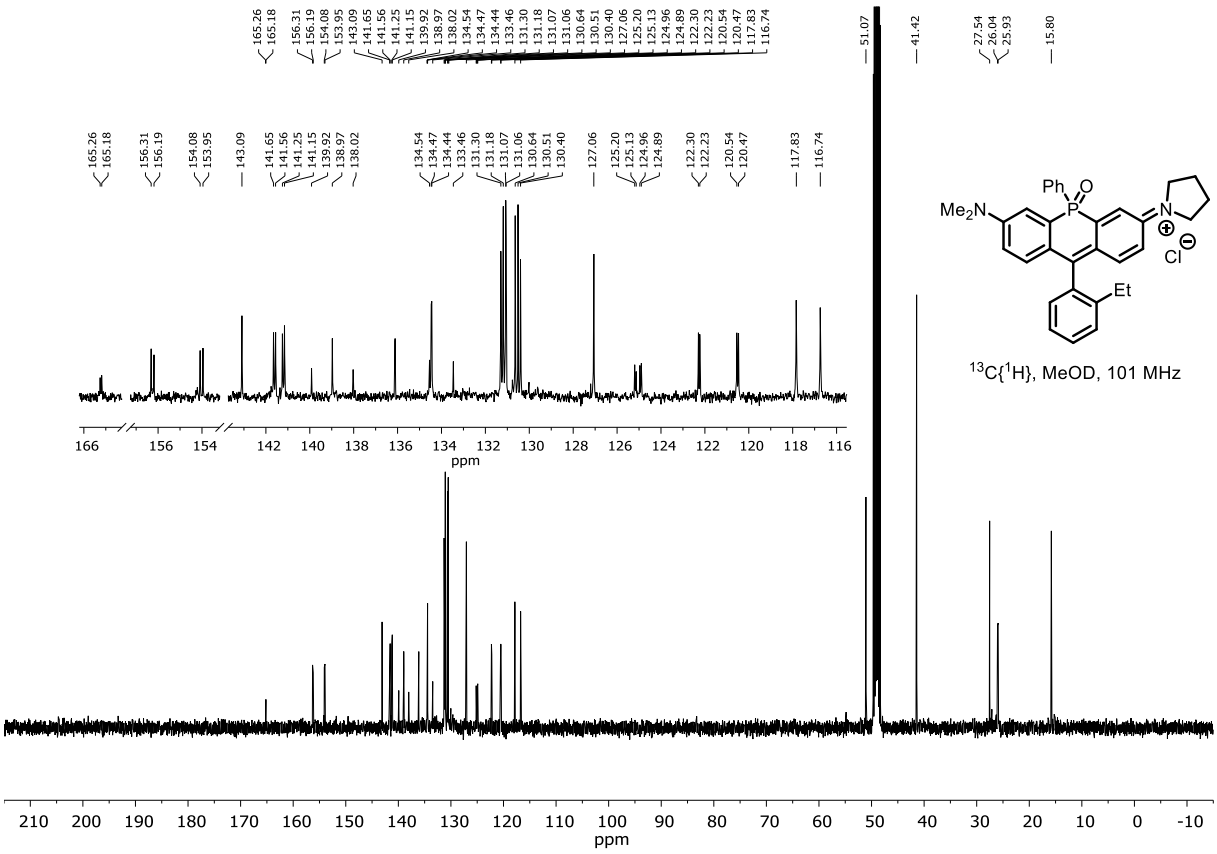


$^{31}P\{^{1}H\}$, MeOD, 162 MHz

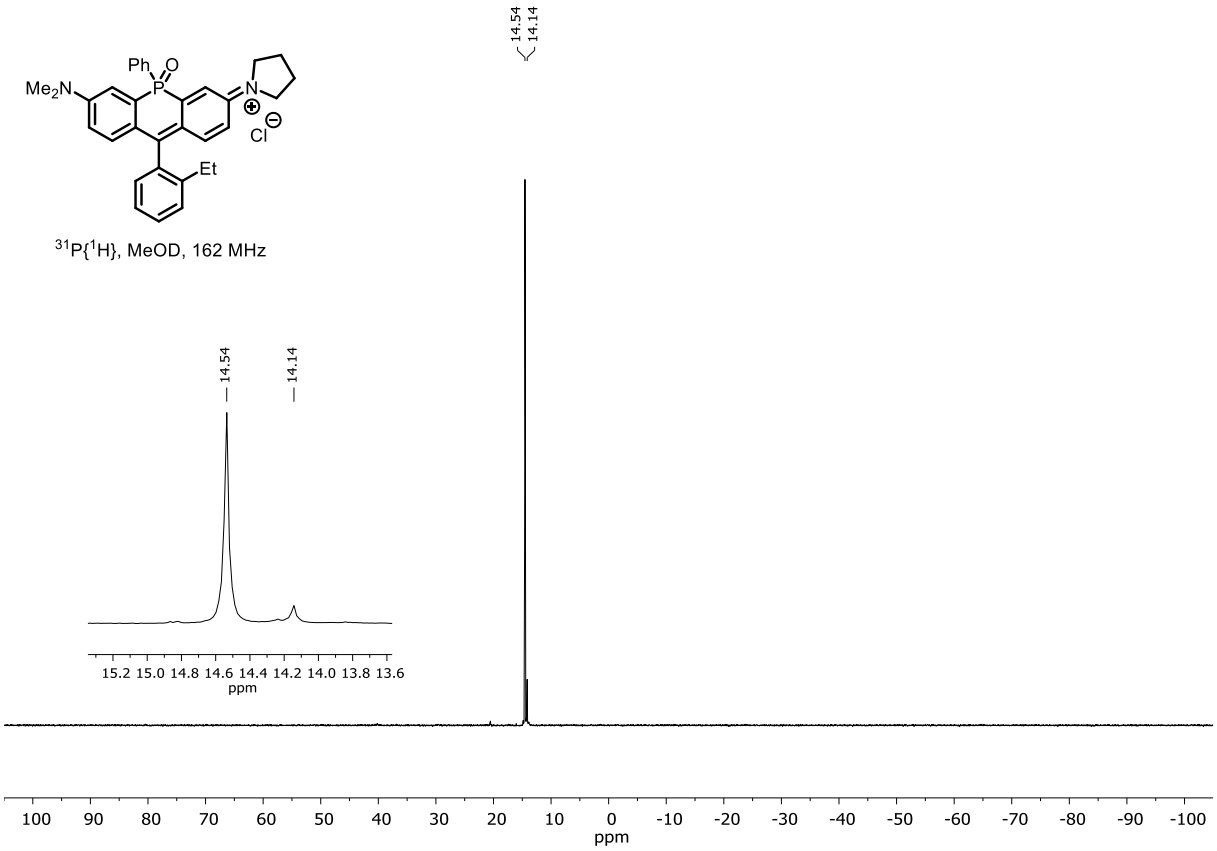
^{1}H NMR spectrum of 19b:



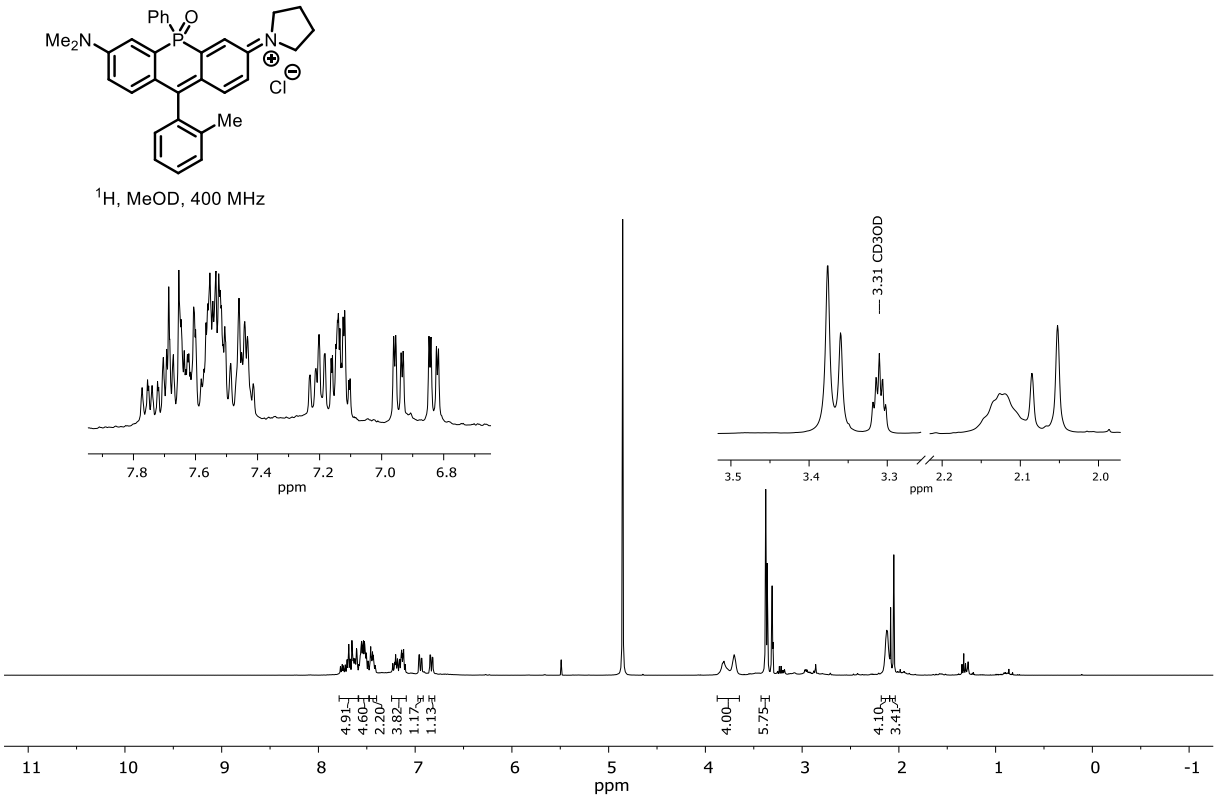
^{13}C{^{1}H} NMR spectrum of 19b:



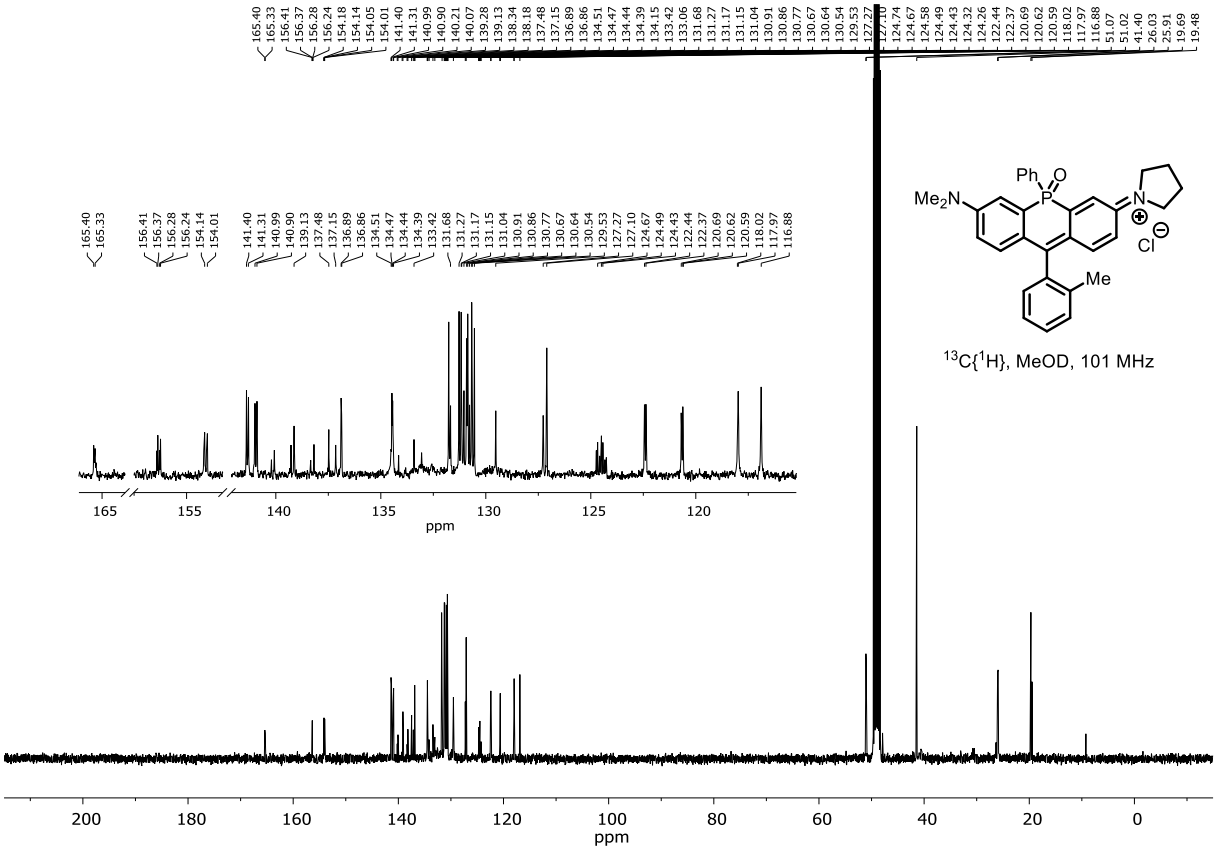
$^{31}P\{^{1}H\}$ NMR spectrum of 19b:



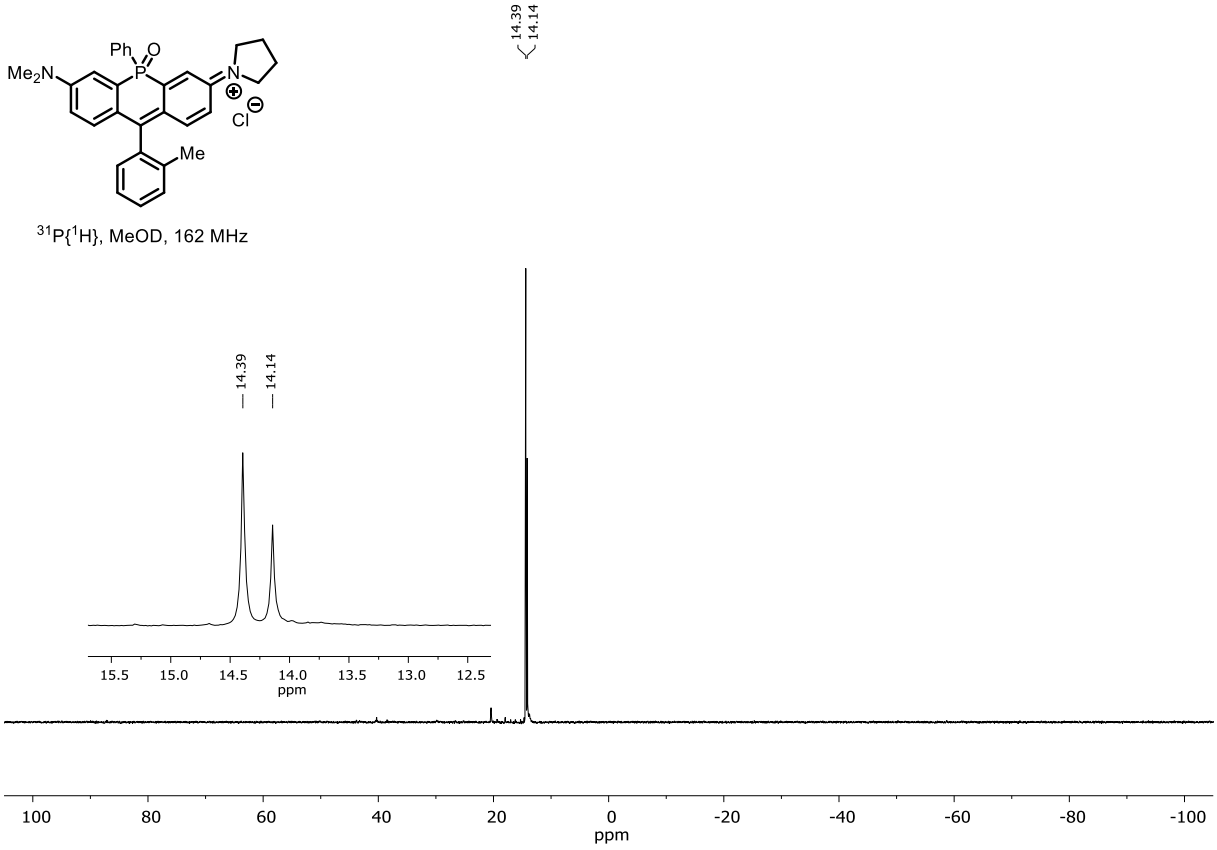
^{1}H NMR spectrum of 19a:



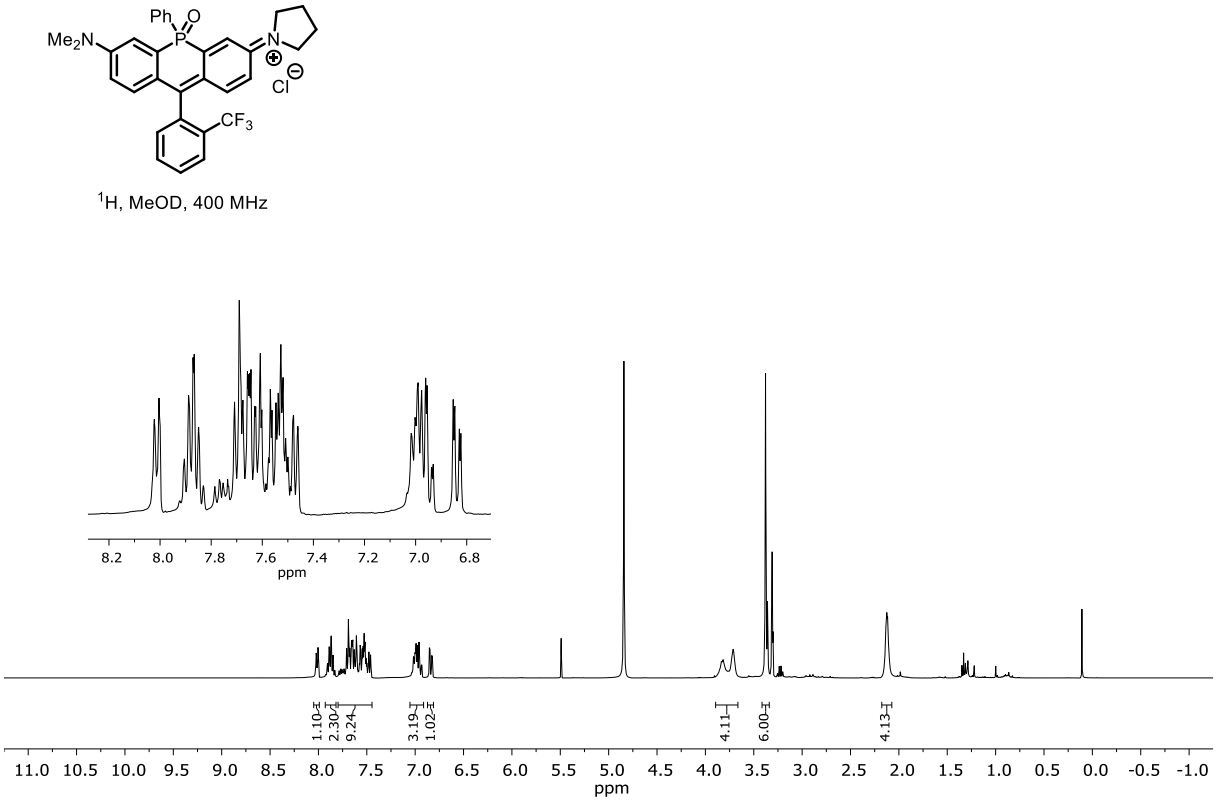
$^{13}C\{^{1}H\}$ NMR spectrum of 19a:



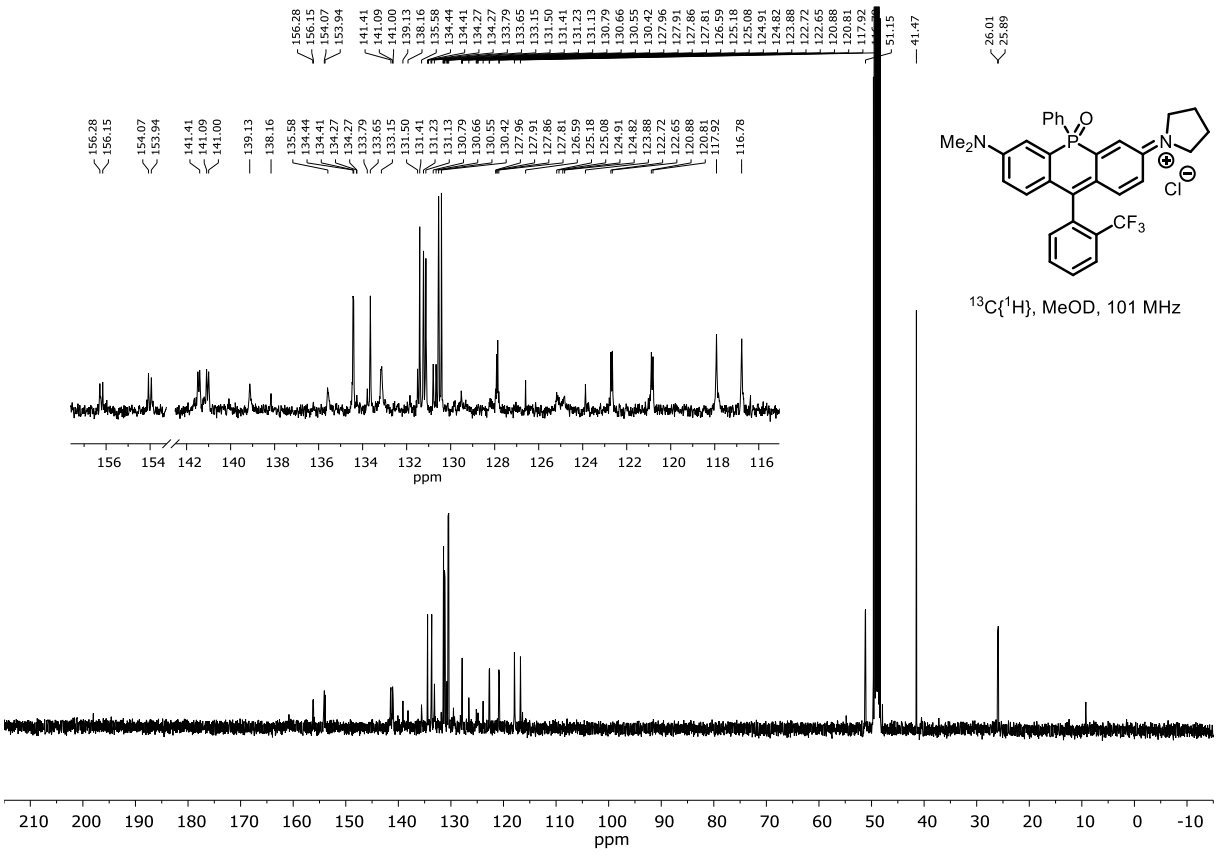
$^{31}P\{^{1}H\}$ NMR spectrum of 19a:



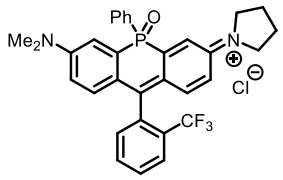
^{1}H NMR spectrum of 19c:



^{13}C{^{1}H} NMR spectrum of 19c:

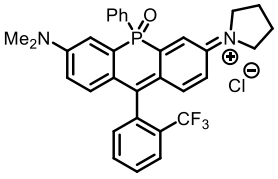


$^{31}P\{^{1}H\}$ NMR spectrum of 19c:



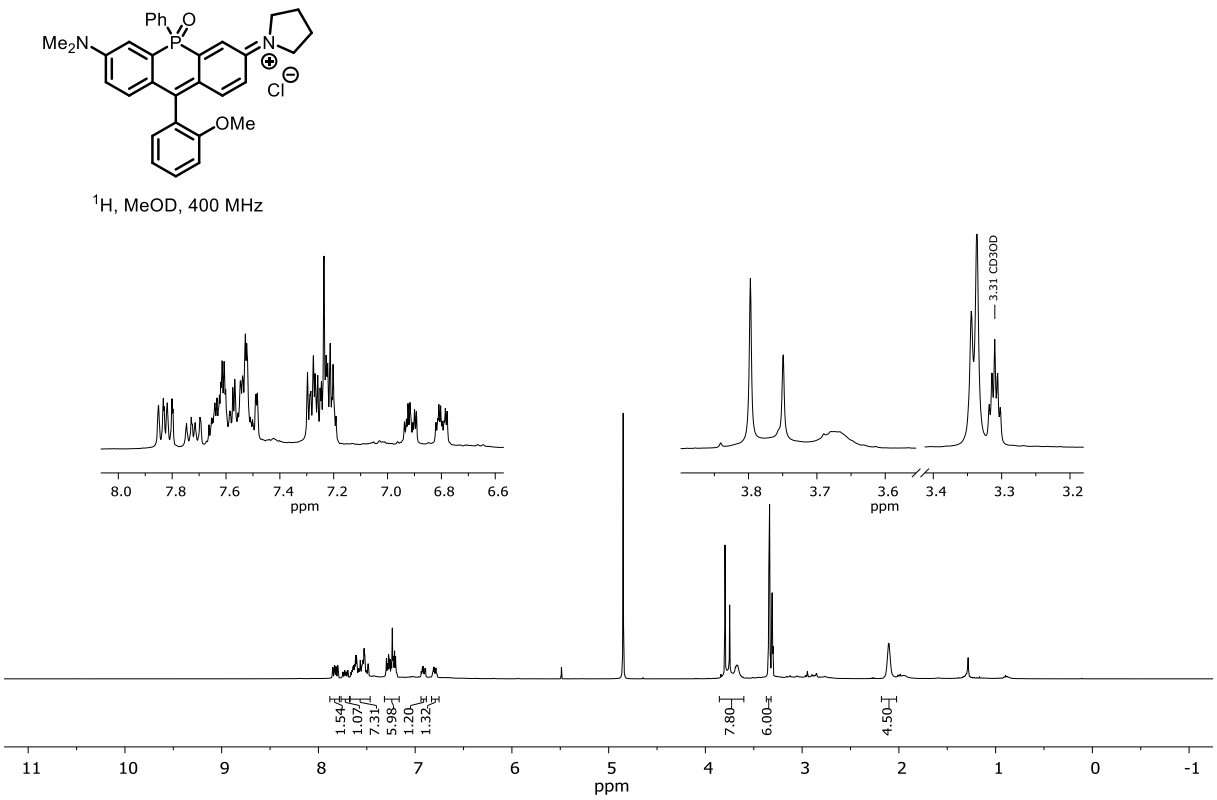
$^{31}P\{^{1}H\}$, MeOD, 162 MHz

^{19}F NMR spectrum of 19c:

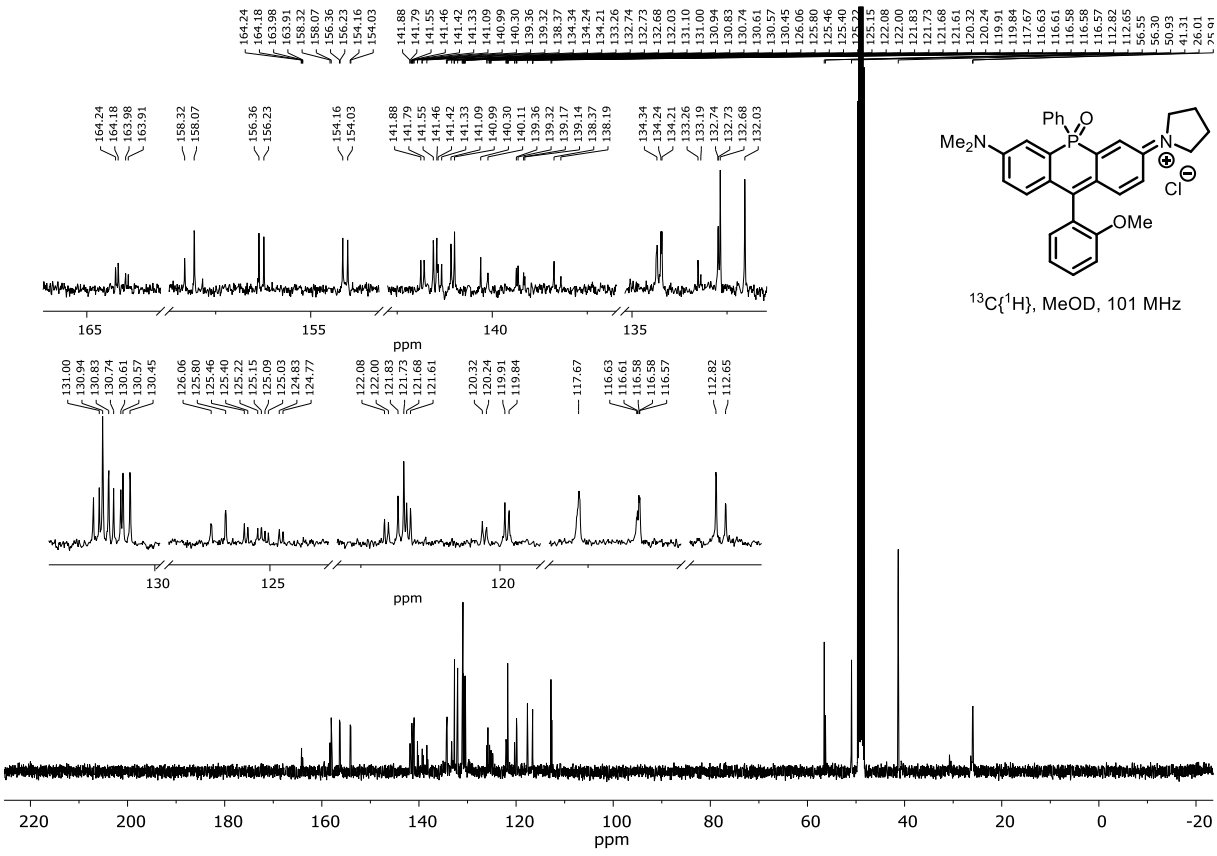


^{19}F, MeOD, 377 MHz

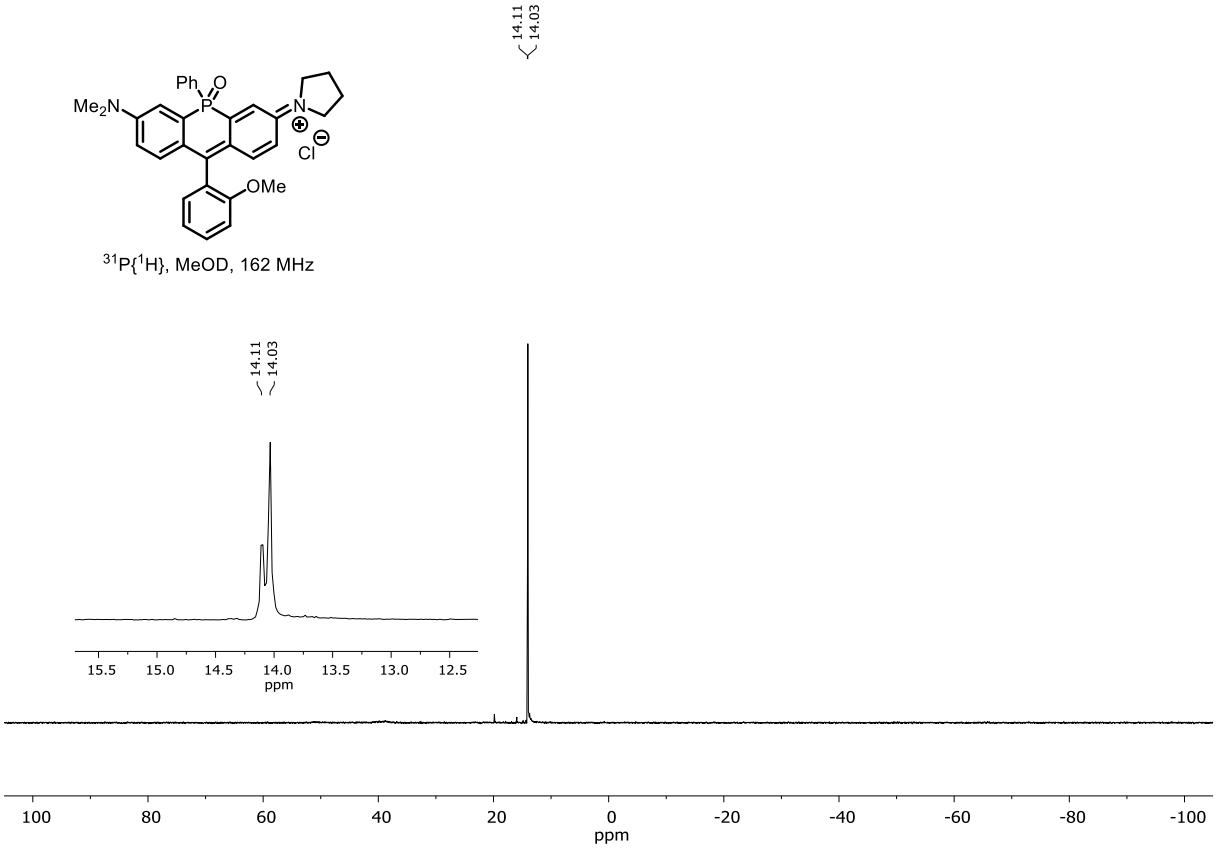
^{1}H NMR spectrum of 19d:



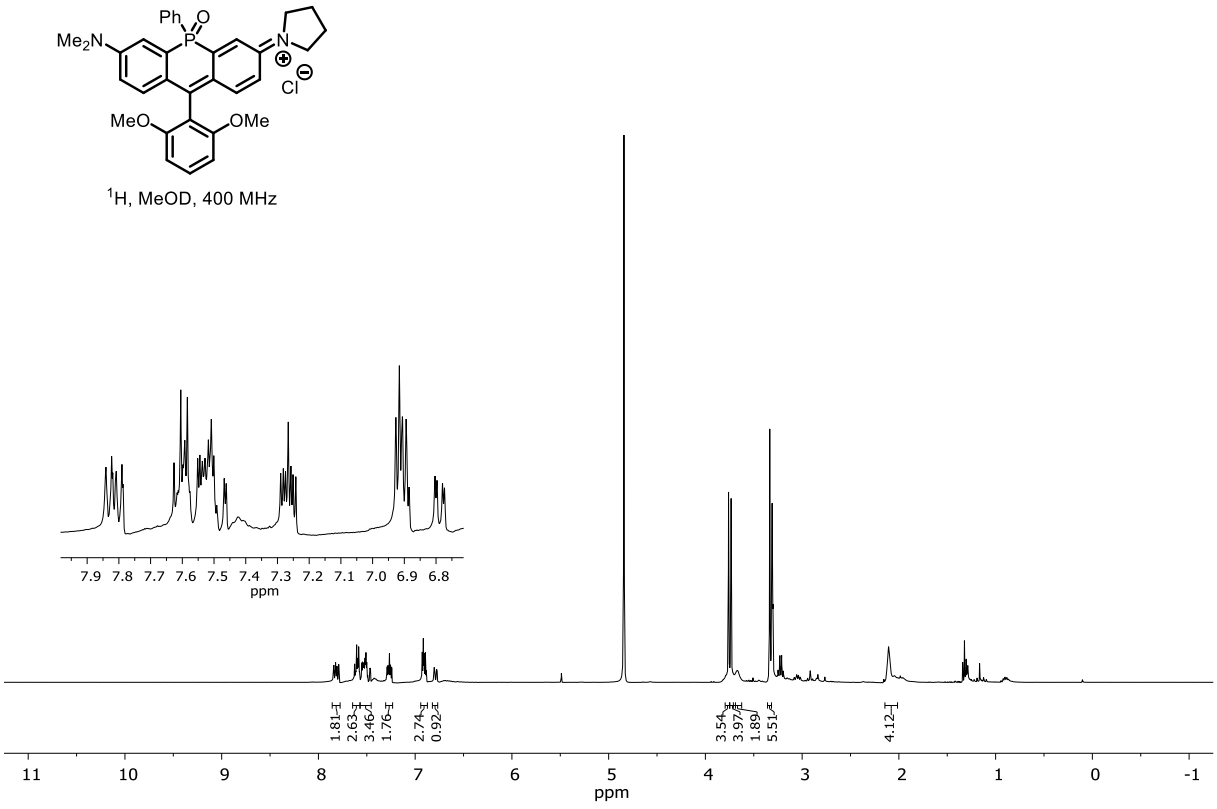
^{13}C{^{1}H} NMR spectrum of 19d:



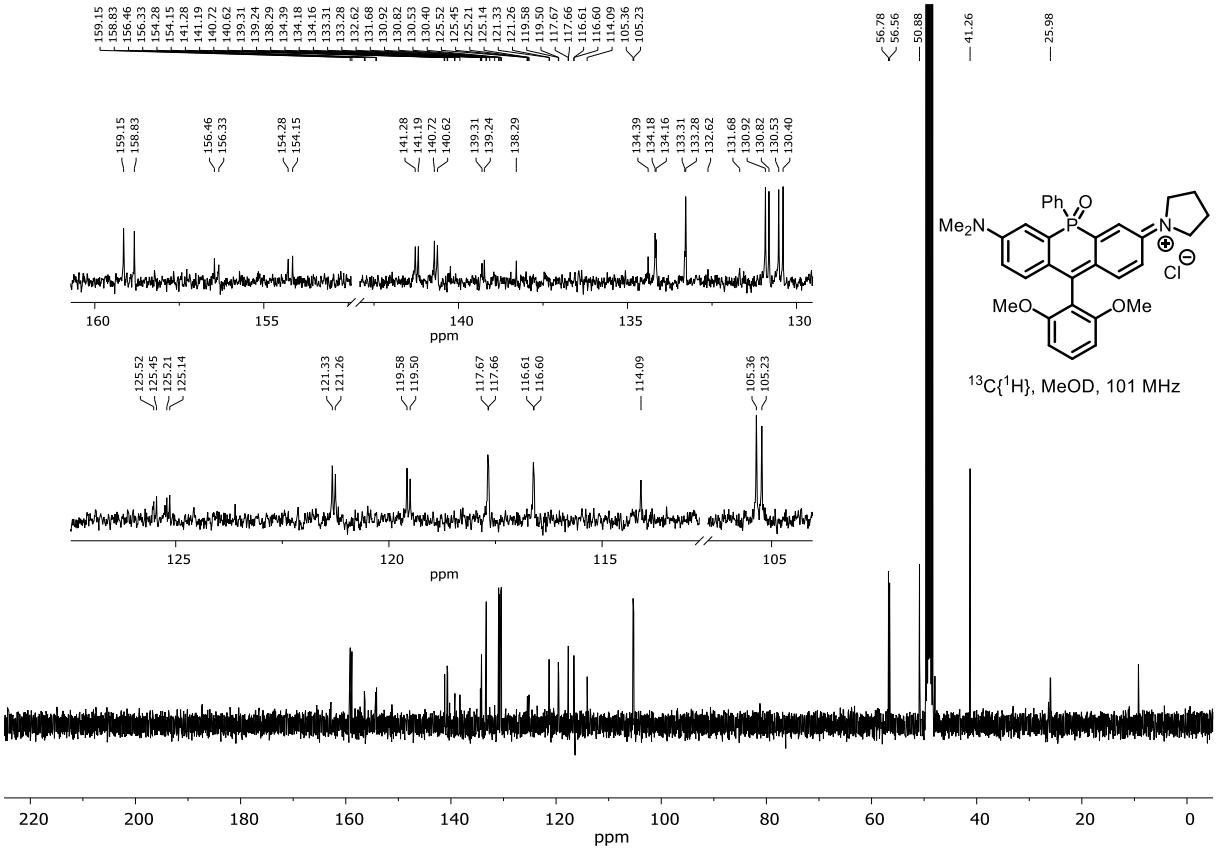
$^{31}P\{^{1}H\}$ NMR spectrum of 19d:



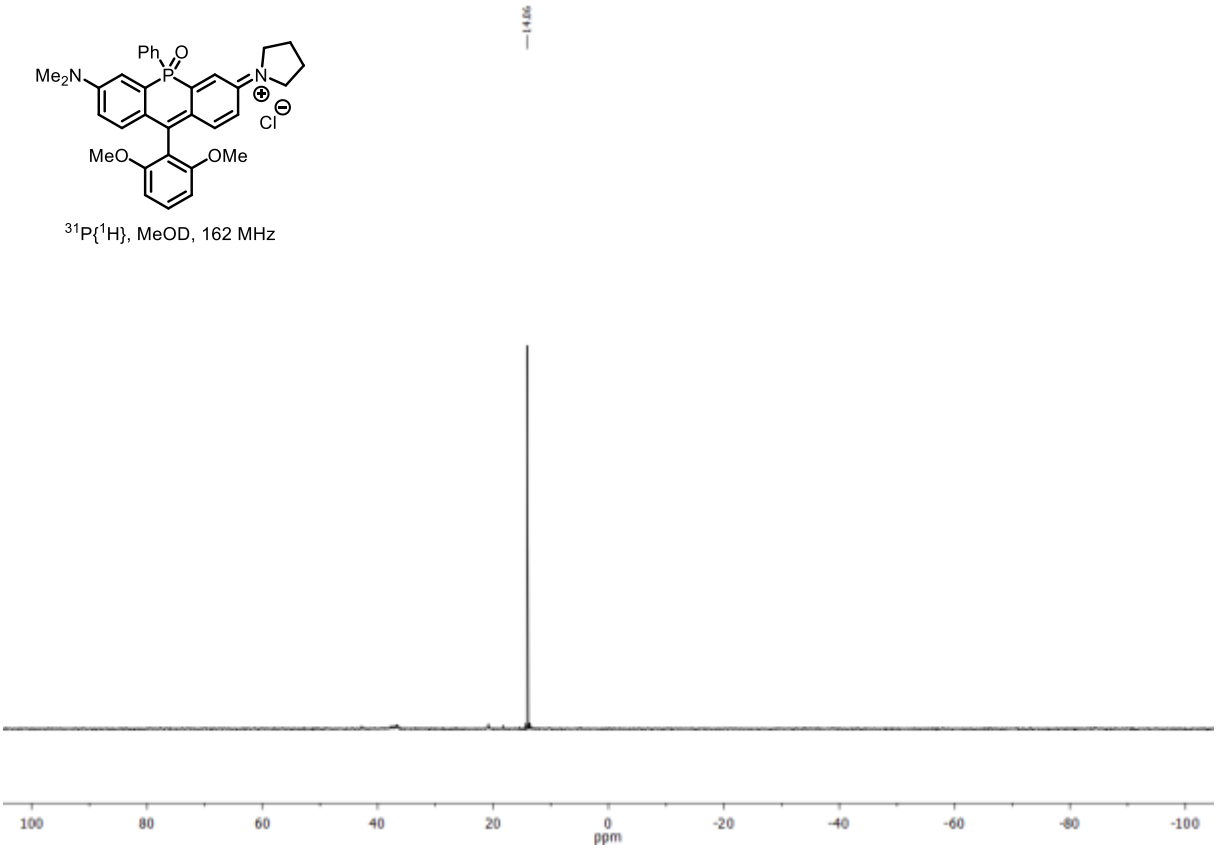
^{1}H NMR spectrum of 19e:



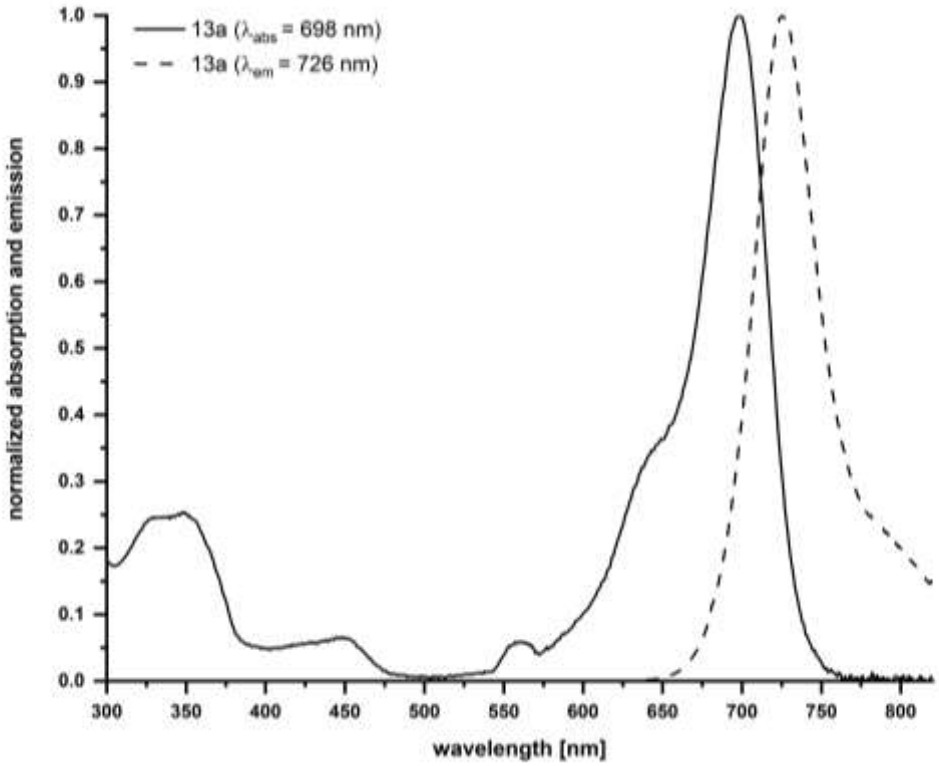
$^{13}C\{^{1}H\}$ NMR spectrum of 19e:

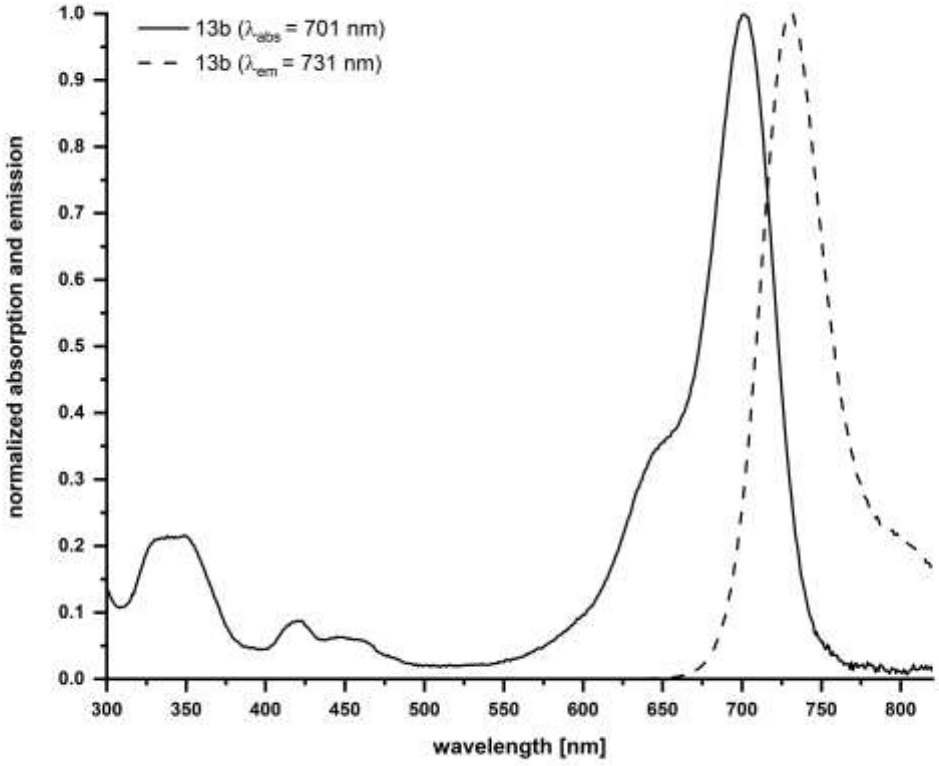


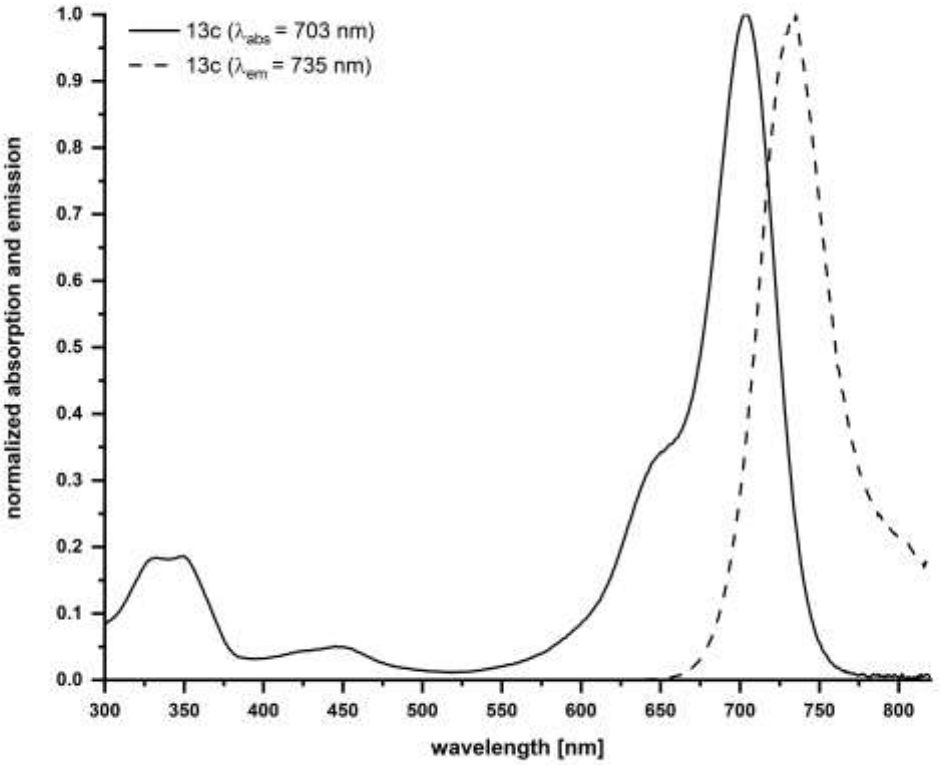
$^{31}P\{^{1}H\}$ NMR spectrum of 19e:

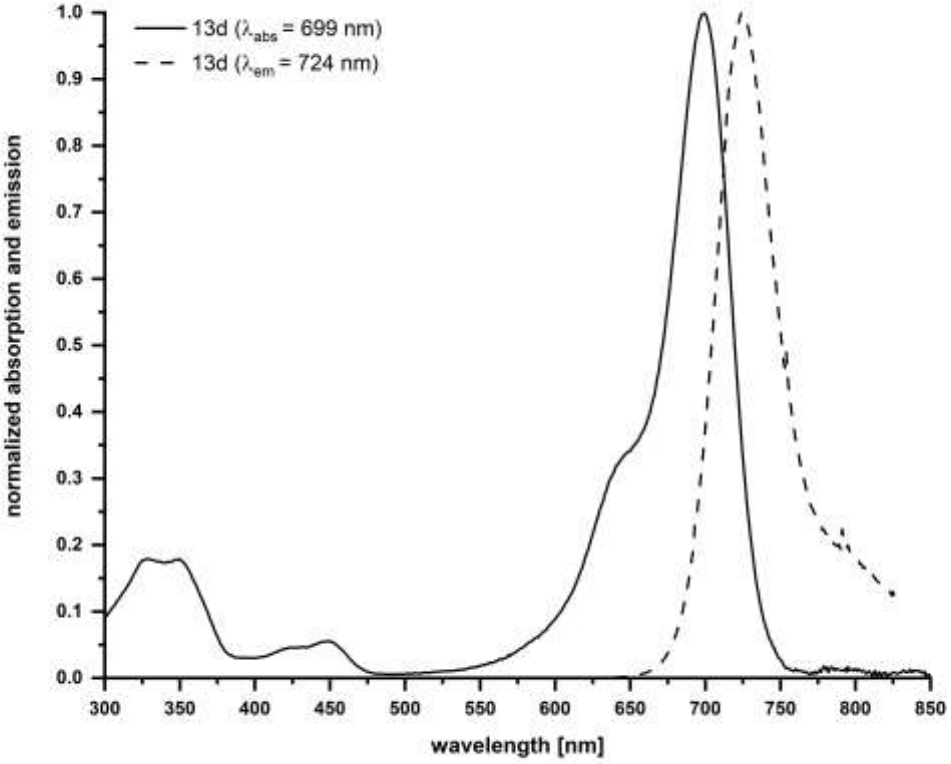


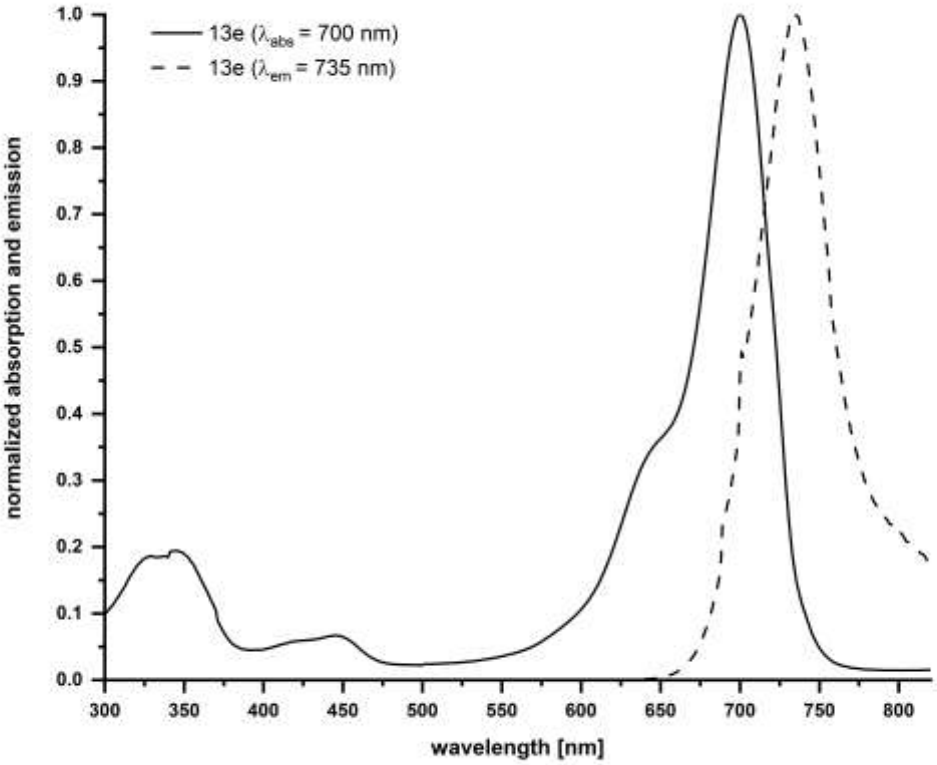
Normalized absorption and emission spectra

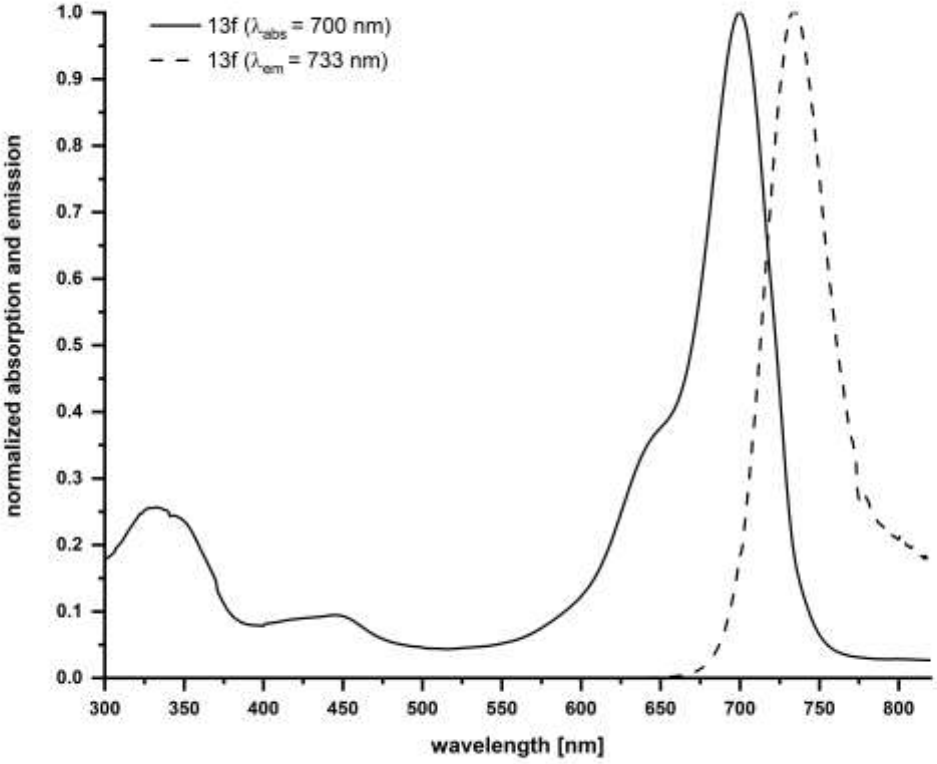


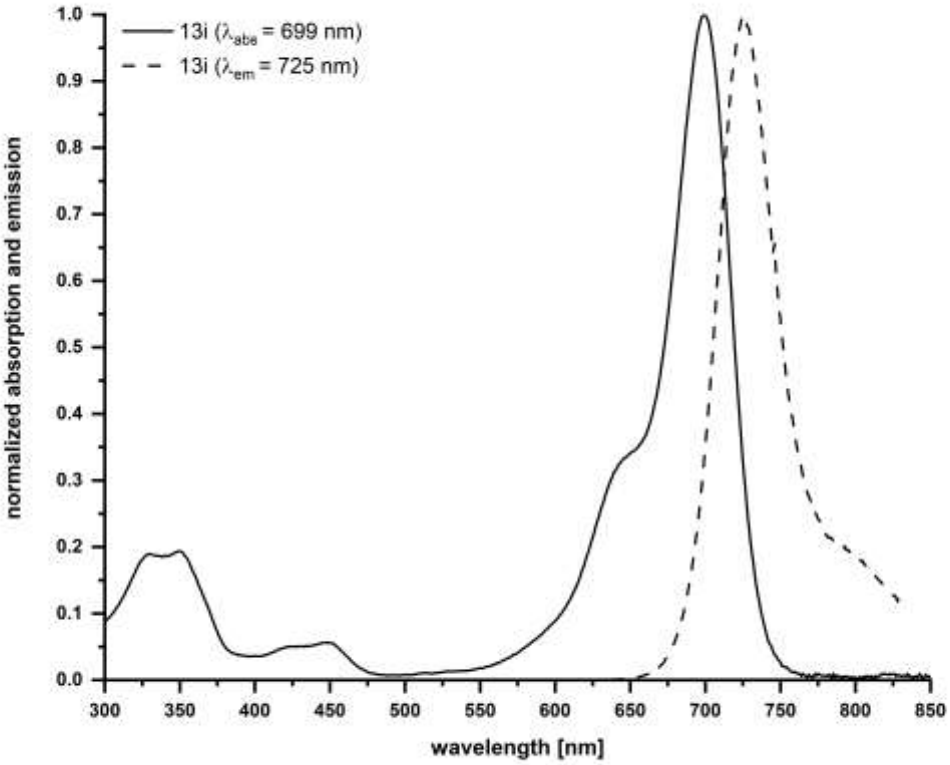


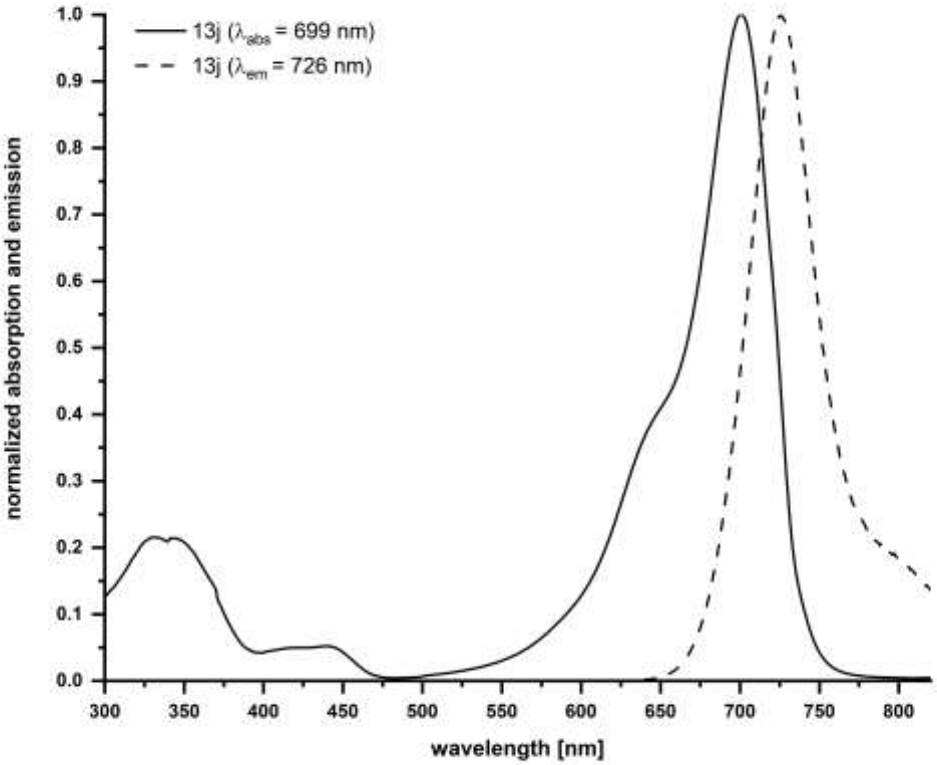

13c (λ_{abs} = 703 nm)
13c (λ_{em} = 735 nm)
normalized absorption and emission
wavelength [nm]

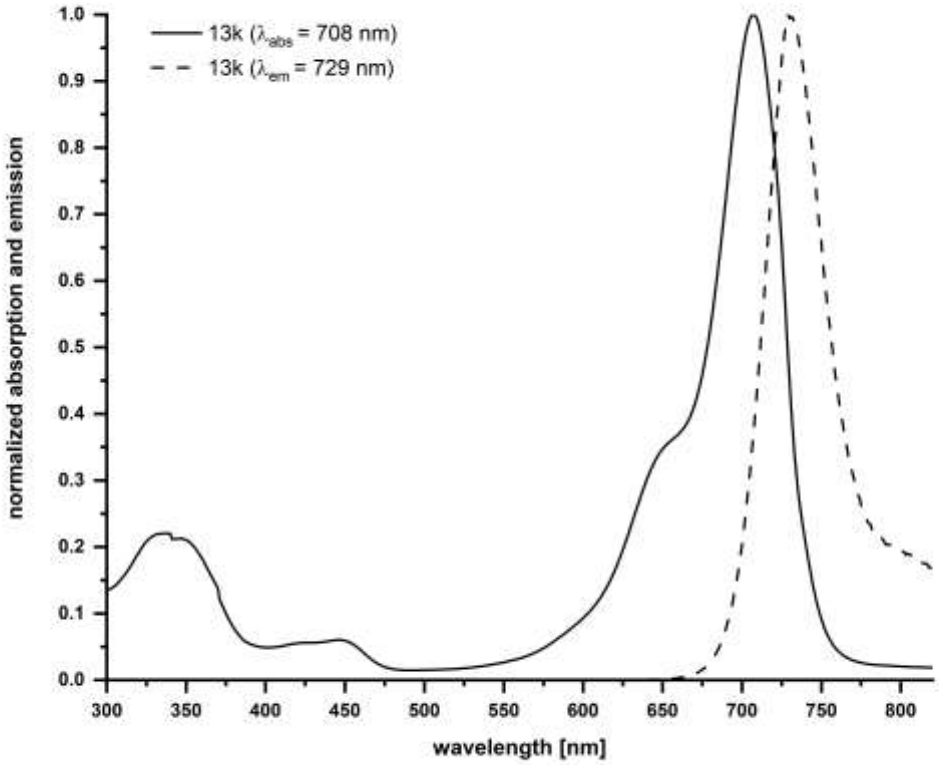

13d (λ_{abs} = 699 nm)
13d (λ_{em} = 724 nm)
normalized absorption and emission
wavelength [nm]

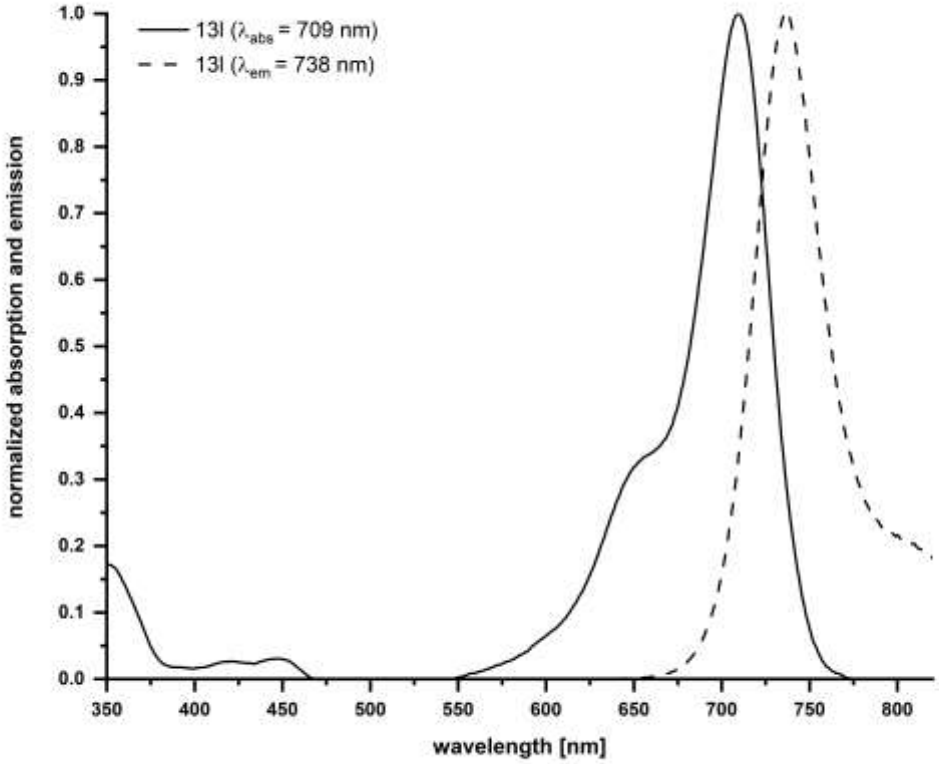

13e (λ_{abs} = 700 nm)
13e (λ_{em} = 735 nm)
normalized absorption and emission
wavelength [nm]
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
300
350
400
450
500
550
600
650
700
750
800

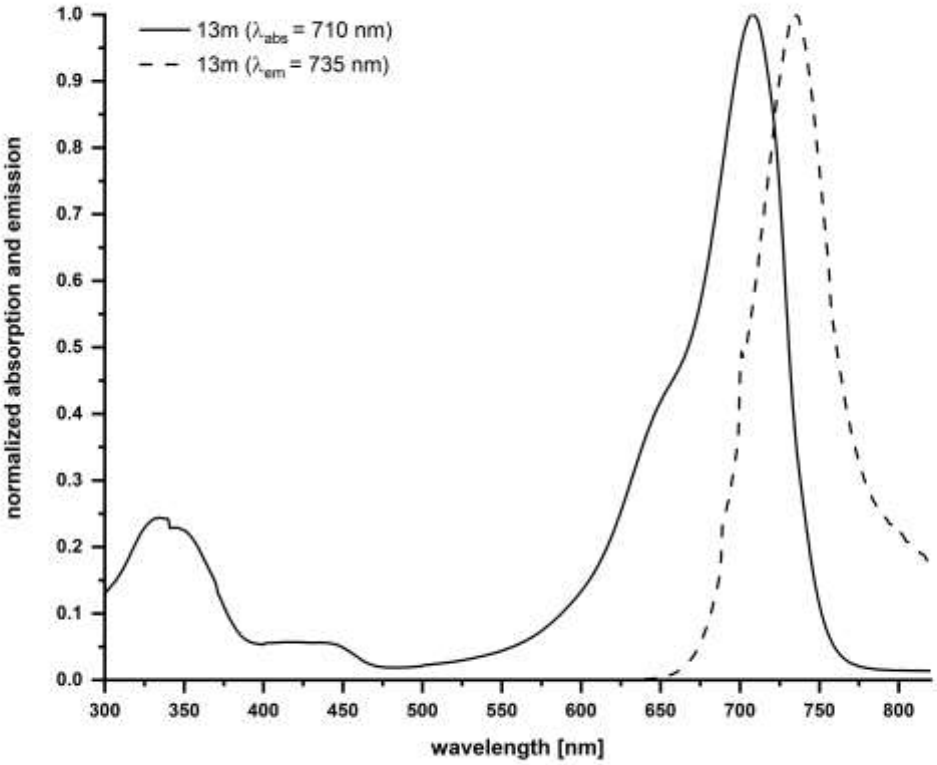

13f (λ_{abs} = 700 nm)
13f (λ_{em} = 733 nm)
normalized absorption and emission
wavelength [nm]
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
300
350
400
450
500
550
600
650
700
750
800

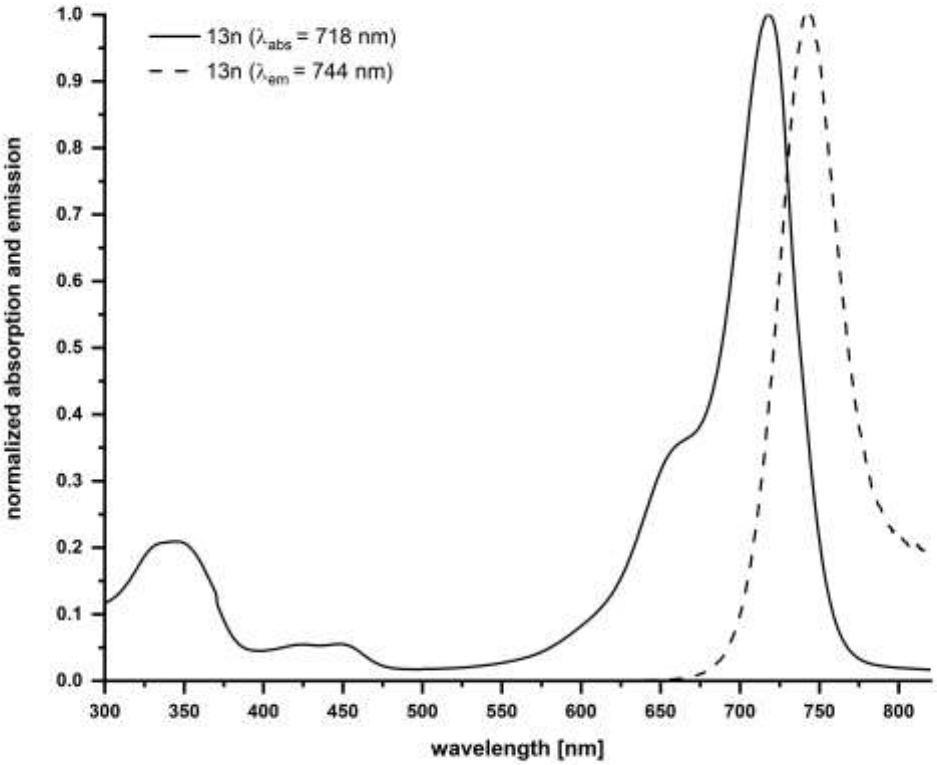

13i (λ_{abs} = 699 nm)
13i (λ_{em} = 725 nm)
normalized absorption and emission
wavelength [nm]

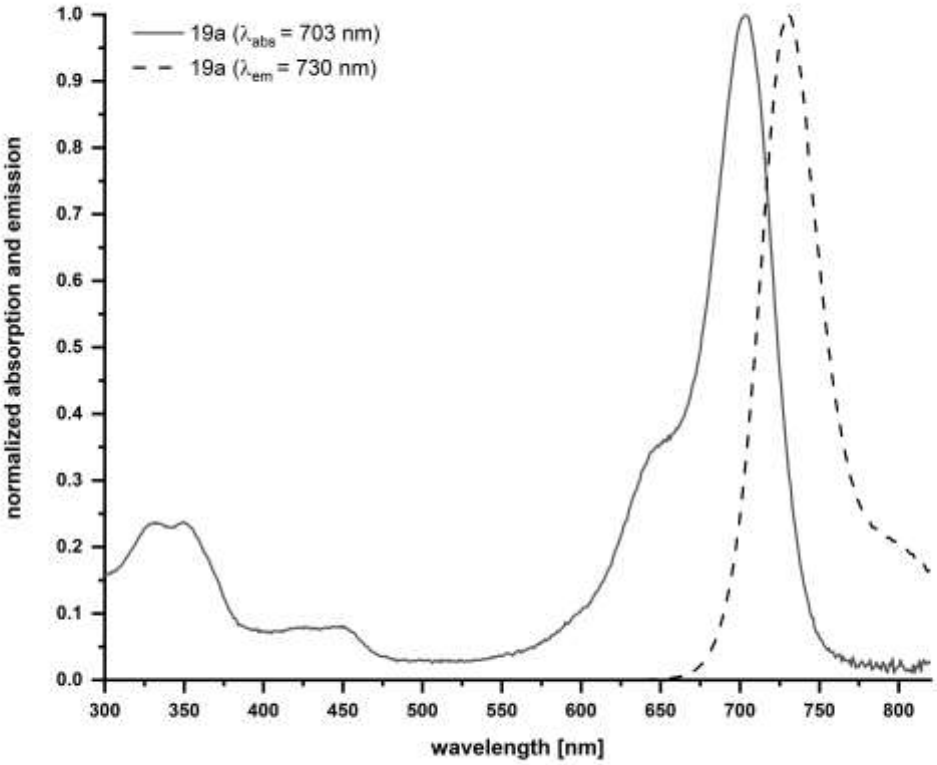

13j (λ_{abs} = 699 nm)
13j (λ_{em} = 726 nm)
normalized absorption and emission
wavelength [nm]

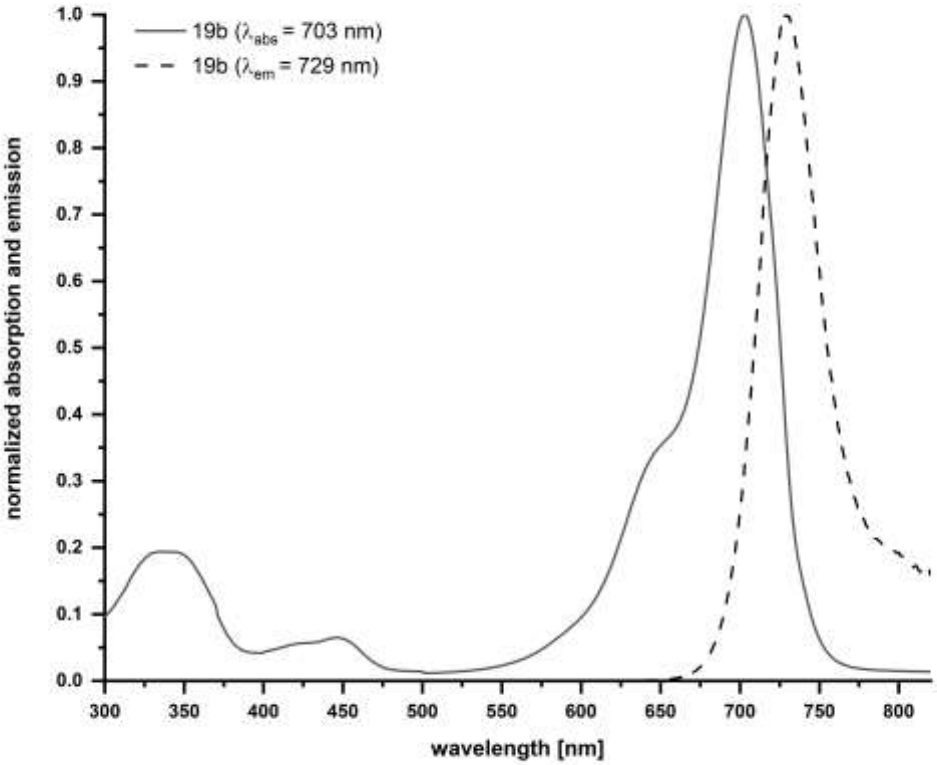

13k (λ_{abs} = 708 nm)
13k (λ_{em} = 729 nm)
normalized absorption and emission
wavelength [nm]

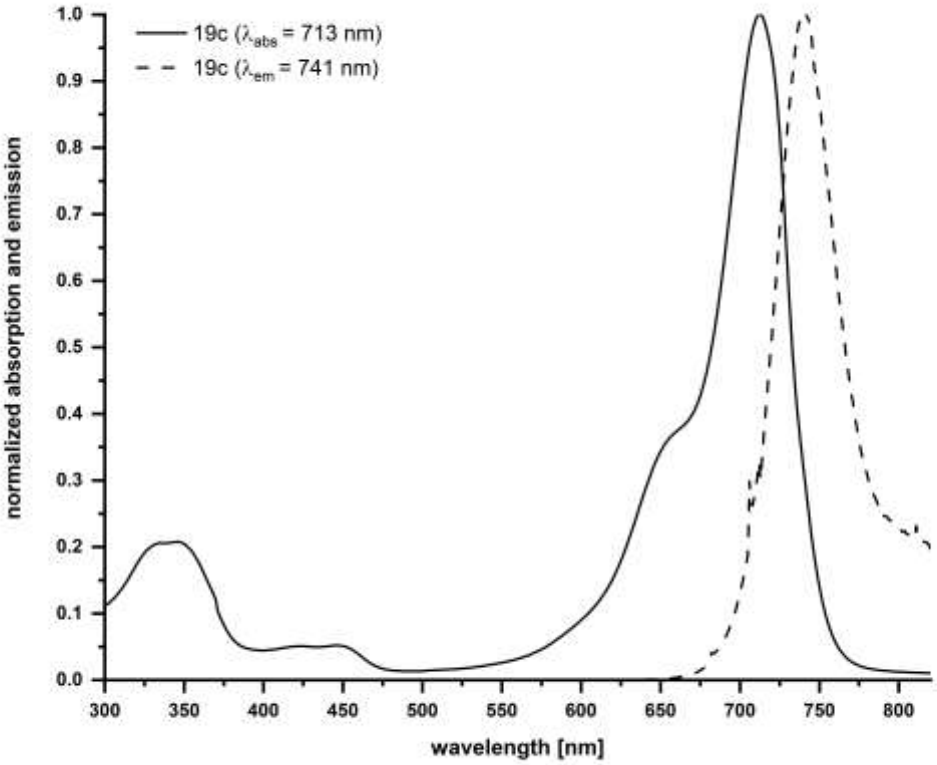

13l (λ_{abs} = 709 nm)
13l (λ_{em} = 738 nm)
normalized absorption and emission
wavelength [nm]

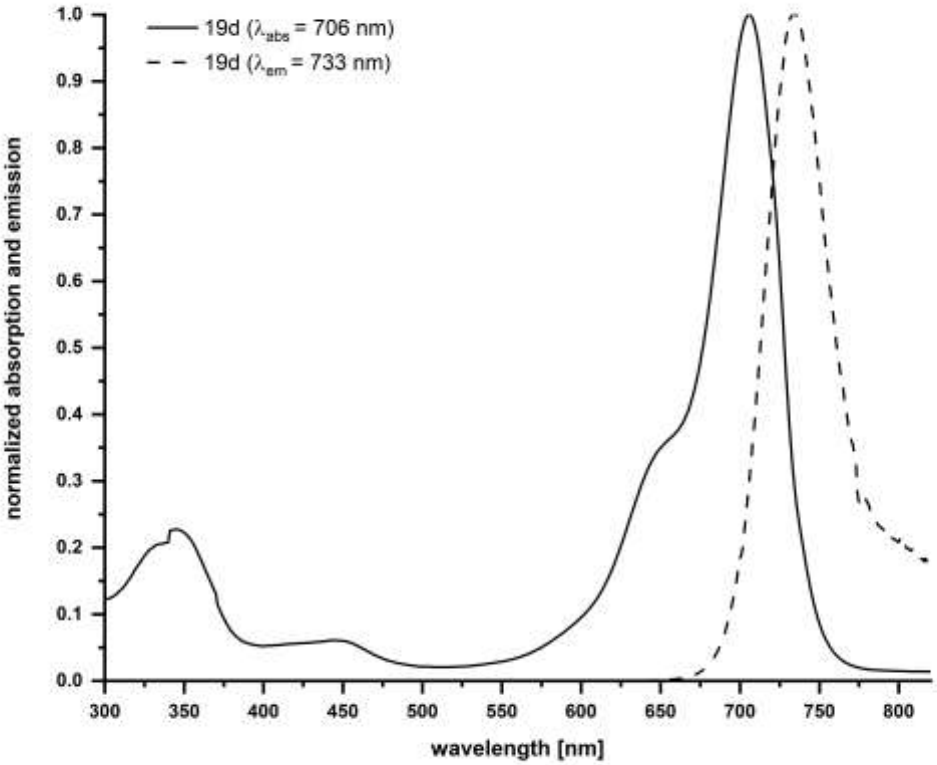

13m (λ_{abs} = 710 nm)
13m (λ_{em} = 735 nm)
normalized absorption and emission
wavelength [nm]
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
300
350
400
450
500
550
600
650
700
750
800

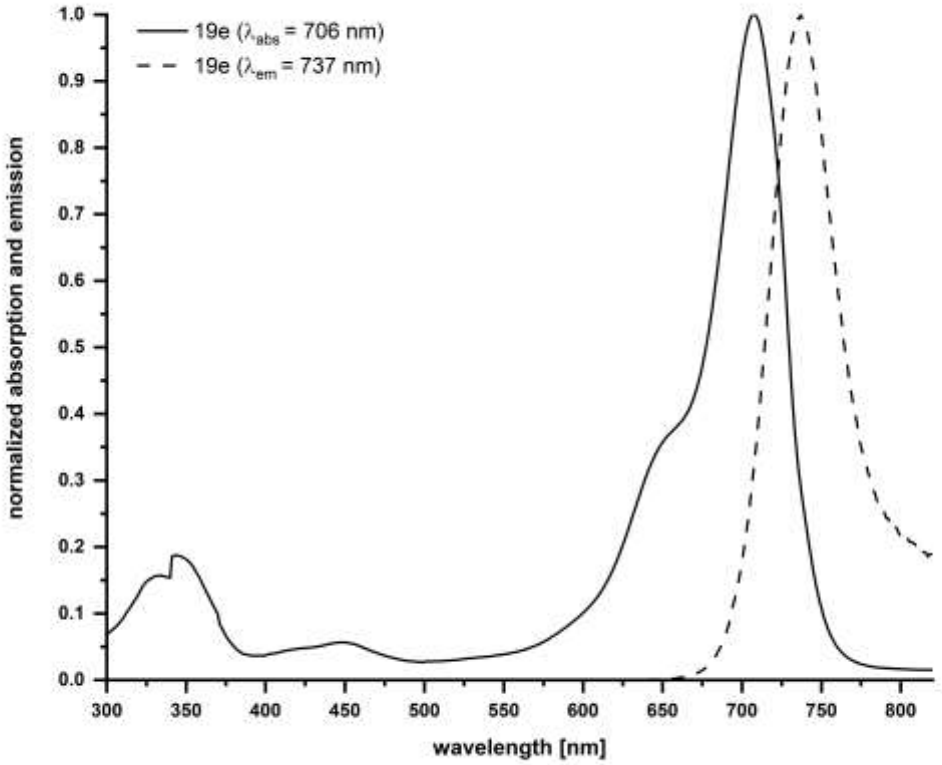

13n (λ_{abs} = 718 nm)
13n (λ_{em} = 744 nm)
normalized absorption and emission
wavelength [nm]
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
300
350
400
450
500
550
600
650
700
750
800


19a (λ_{abs} = 703 nm)
19a (λ_{em} = 730 nm)
normalized absorption and emission
wavelength [nm]


19b (λ_{abs} = 703 nm)
19b (λ_{em} = 729 nm)
normalized absorption and emission
wavelength [nm]


19c (λ_{abs} = 713 nm)
19c (λ_{em} = 741 nm)
normalized absorption and emission
wavelength [nm]


19d (λ_{abs} = 706 nm)
19d (λ_{em} = 733 nm)
normalized absorption and emission
wavelength [nm]


19e (λ_{abs} = 706 nm)
19e (λ_{em} = 737 nm)
normalized absorption and emission
wavelength [nm]
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
300
350
400
450
500
550
600
650
700
750
800