Supporting Information

for

Synthesis of Phosphate Stabilized Iodanes and their Application in Intramolecular Aryl Migrations

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1. General Information

All chemicals were purchased from commercial suppliers and used as received. Unless otherwise noted, all reactions were carried out under air. Reactions with chemicals sensitive to moisture or oxygen were carried out under an argon atmosphere using standard Schlenk techniques. Anhydrous diethyl ether (Et_2O) was obtained from an Inert PS-MD-6 solvent purification system. All other solvents were dried using standard methods if necessary. [1]

Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (Macherey-Nagel, POLYGRAM SIL G/UV254) and visualized by UV light (254 nm). Flash column chromatography was performed on silica gel (40 – 63 μm) with the solvents given in the procedures.

NMR spectra were recorded on a Bruker AVANCE NEO 600 MHz spectrometer with BBO probe head and a Bruker AVANCE NEO 600 MHz spectrometer with TXI probe head at 25 °C. Chemical shifts for ^{1}H-NMR spectra are reported as δ (parts per million) relative to the residual proton signal of $CDCl_3$ at 7.26 ppm (s), DMSO-d_6 at 2.50 ppm (quint) or MeOH-d_4 at 3.31 ppm (quint). Chemical shifts for ^{13}C-NMR spectra are reported as δ (parts per million) relative to the signal of $CDCl_3$ at 77.0 ppm (t), DMSO-d_6 at 39.5 ppm (sept) or MeOH-d_4 at 49.0 ppm (sept). Chemical shifts for ^{19}F-NMR spectra are reported as δ (parts per million) relative to the signal of $Si(CH_3)_4$ at 0.0 ppm. The following abbreviations are used to describe splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet. Coupling constants J are given in Hz.

ESI and APCI mass spectra were recorded on an Advion Expression CMSL via ASAP probe or direct inlet. Low resolution EI mass spectra were recorded on an Agilent 5977A Series GC/MSD system. High resolution (HR) EI mass spectra were recorded on a double focusing mass spectrometer ThermoQuest MAT 95 XL from Finnigan MAT. HR-ESI mass spectra were recorded on a Bruker Impact II. All Signals are reported with the quotient from mass to charge *m/z*.

IR spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer with a diamond ATR unit. The absorption bands are reported in cm^{-1}.

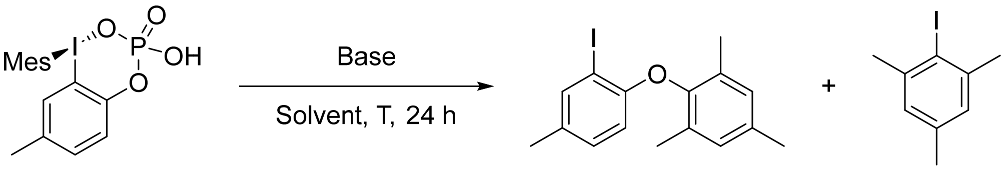
Melting points of solids were measured on a Büchi M-5600 Melting Point apparatus and are uncorrected. The measurements were performed with a heating rate of 2 °C/min and the melting point temperatures T are reported in °C.

Reactions that required heating were either heated using an oil bath, if the reaction was performed in a flask or in a heating block, if the reaction was performed in a screw cap vial.

Single crystals were grown from MeOH-solutions by slow Et_2O diffusion. Intensity data of suitable single crystals were collected on a Bruker D8 Venture CMOS diffractometer at 100 K with Mo-Kα (0.71073 Å) radiation. All structures were solved by direct methods and refined based on F2 by use of the SHELX program package as implemented in Olex 2.2. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a rigid model. Figures were created using Diamond 4.0. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk)

2. Optimisation of Reaction Conditions

*Table 1: Optimization of the aryl migration from **9a** to **10a** in an aqueous medium.*



9a **10a** **12**

Entry[a]	Base	eq.	Solvent	T (°C)	Yield **10a**	Yield **12**
1	Cs_2CO_3	1.10	MeCN	80	98%[b]	-
2	Cs_2CO_3	1.10	**H_2O**	80	45%[b]	54%
3	**CsOH**	1.10	H_2O	80	5%	75%
4	**NaOH**	1.10	H_2O	80	4%	73%
5	**NaOAc**	1.10	H_2O	80	7%	77%
6	**K_3PO_4**	1.10	H_2O	80	21%	7%
7	**$Ca(OH)_2$**	1.10	H_2O	80	72%	-
8	$Ca(OH)_2$	**2.00**	H_2O	80	83%	-
9	$Ca(OH)_2$	2.00	H_2O	**40**	84%	-
10	$Ca(OH)_2$	2.00	H_2O	**rt**	12%	-
11	**$Mg(OH)_2$**	2.00	H_2O	40	1%	2%
12	**$Ba(OH)_2$**	2.00	H_2O	40	3%	4%
13	**no base**	-	H_2O	80	traces	-

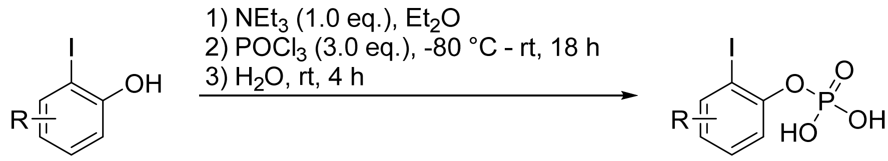
[a] General reaction conditions: **9a** (50.0 µmol), solvent (0.05 M), addition of base, stirring at the given temperature for 24 h, yield was determined via ^1H NMR using dinitrobenzene as an internal standard. [b] isolated yield.

3. General Procedures and Literature known Starting Materials

3.1. 2-Iodo phenols and trimethylsilyl arenes

Except of 2-iodophenol all iodinated phenols were prepared as mentioned in the literature.[2] Furthermore trimethyl(*p*-tolyl)silane [3], (4-(*tert*-butyl)phenyl)triethylsilane [3], trimethyl(4-chlorophenyl)silane [4], trimethyl(4-fluorophenyl)silane [5], trimethyl(naphthalen-1-yl)silane [3] and trimethyl(4-(trifluoromethyl)phenyl)silane [6] were synthesised according to literature.

3.2. General Procedure for Phosphorylation of Phenols (GP1)

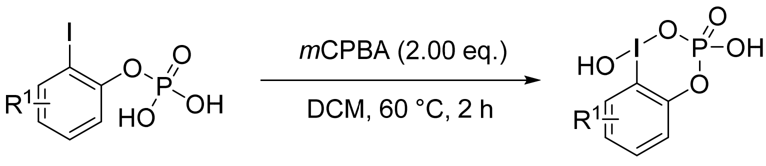


S1 **11**

*Scheme 1: General Scheme for the Phosphorylation of 2-iodo phenols into **7**.*

To a solution of $POCl_3$ (3.00 eq.) in Et_2O (0.6 M) was added a solution of the phenol derivative (1.00 eq.) and NEt_3 (1.00 eq.) in Et_2O (0.2 M) at -80 °C over a period of 30 min. The resulting mixture was slowly warmed to rt and stirred for 18 h. After complete conversion (^{1}H-NMR in $CDCl_3$), water (10 mL/mmol) was added, and the solution was stirred for further 4 h. The resulting phases were separated, and the aqueous phase was extracted with Et_2O (5 x 20 mL/mmol). The combined organic phases were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was triturated several times with *n*-pentane (5 mL/mmol) until the product **11** was solidified.

3.3. General Procedure for Oxidation into cyclic Hydroxy-Iodanes (GP2)

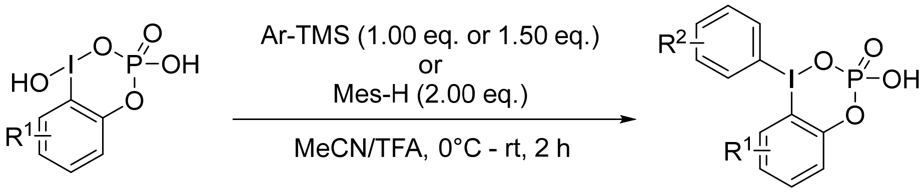


S2 **8**

*Scheme 2: General Scheme for the oxidation of phosphate derivatives (**11**) into hydroxy iodanes (**8**).*

To a suspension of **11** (1.00 eq.) in DCM (0.2 M) was added *m*CPBA (70%, 2.00 eq.) and the mixture was stirred at 60 °C for 2 h. After complete consumption of the starting material the mixture was concentrated under reduced pressure and suspended in Et_2O (5 mL/mmol). The precipitate was washed with Et_2O (2 x 5 mL/mmol) and dried *in vacuo* to obtain **8**.

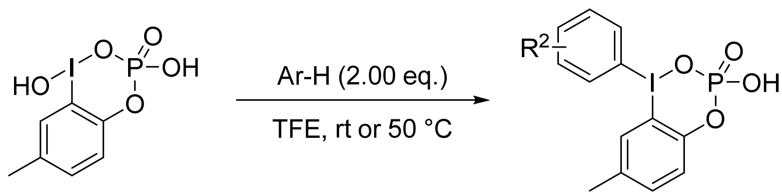
3.4. General Procedure for Arylation of 8 into 9 in MeCN/TFA (GP3)



*Scheme 3: General Scheme for the arylation of **8** with less electron-rich aromatic systems.*

To an ice-cooled solution of **8** (1.00 eq.) in MeCN/TFA (1:1, 0.1 M) was slowly added Ar-TMS (1.00 eq. or 1.50 eq.) or mesitylene (2.00 eq.) and the solution was stirred at rt for 2 h. The solvent was removed under reduced pressure, the residue was suspended in Et_2O (10 mL/mmol), and the resulting precipitate was washed with Et_2O (2 x 10 mL/mmol). Afterwards the solid was repeatedly suspended in water (5 mL/mmol), which was then removed by lyophilization, until the TFA was completely removed, to obtain phosphate-stabilised diaryliodanes **9**.

3.5. General Procedure for Arylation of 8 into 9 in TFE (GP4)

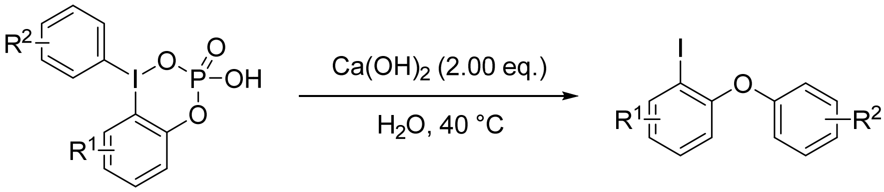


*Scheme 4: General Scheme for the arylation of **8** with electron-rich aromatic systems.*

To a solution of **8** (1.00 eq) in TFE (0.1 M) was added the electron rich arene (2.00 eq.) and the mixture was stirred at rt or 50 °C. After complete conversion, the solvent was removed under reduced pressure and the residue was suspended in Et_2O (10 mL/mmol). The precipitate was washed with Et_2O (2 x 10 mL/mmol) and dried *in vacou* to obtain **9**.

Note: Due to the low solubility of some substrates in DMSO-d_6 the NMR-sample was mixed with a few drops of TFA to obtain a complete solution.

3.6. General Procedure for Aryl Migration into Iodo-Diaryl Ethers (GP6)



9 10

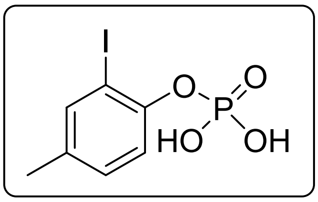
*Scheme 5: General Scheme for the aryl migration of **9** into diaryl ethers **10**.*

To a suspension of **9** (100 µmol, 1.00 eq.) in water (0.05 M, 2 mL) was added $Ca(OH)_2$ (200 µmol, 14.8 mg, 2.00 eq.) and the mixture was stirred at 40 °C. After complete conversion, EtOAc (10 mL) was added, the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography to obtain diaryl ethers **10**.

4. Experimental Data

4.1. Synthesis of 2-Iodoaryl dihydrogen phosphates

2-Iodo-4-methylphenyl dihydrogen phosphate (11a)

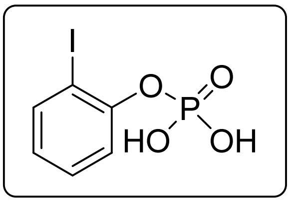


Following GP1, the reaction of 2-iodo-4-methylphenol (2.34 g, 10.0 mmol) with NEt_3 (1.39 mL, 10.0 mmol) in Et_2O (50 mL) and $POCl_3$ (2.80 mL, 30.0 mmol) in Et_2O (50 mL) gave the product **11a** (3.09 g, 9.84 mmol, 98%) as an off-white solid.

^{1}H NMR (601 MHz, DMSO-*d$_6$*) δ 7.66 – 7.60 (m, 1H), 7.25 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, DMSO-*d$_6$*) δ 149.5 (d, *J* = 5.4 Hz), 139.3, 135.0, 129.9, 119.5 (d, *J* = 2.5 Hz), 89.5 (d, *J* = 8.5 Hz), 19.6. HRMS(ESI): *m/z* $[M-H]^-$ calculated for $C_7H_7IO_4P^-$: 312.9132; found 312.9124. IR (ATR) $\tilde{\nu}$ = 2921, 2849, 2360, 1480, 1223, 1094, 989. Mp = 134-136 °C.

*Note: The two protons of the phosphoric acid cannot be integrated in the ^{1}H-NMR which leaded to a widening and shift of the water-signal. This is also present in the following spectra of **S2.***

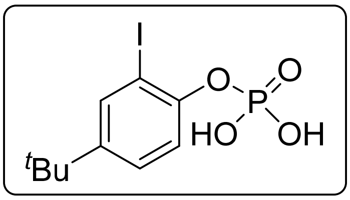
2-Iodophenyl dihydrogen phosphate (11b)



Following GP1, the reaction of 2-iodophenol (2.20 g, 10.0 mmol) with NEt_3 (1.39 mL, 10.0 mmol) in Et_2O (50 mL) and $POCl_3$ (2.80 mL, 30.0 mmol) in Et_2O (50 mL) gave the product **11b** (2.86 g, 9.55 mmol, 95%) as an off-white solid.

^{1}H NMR (601 MHz, DMSO-*d$_6$*) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.33 (m, 2H), 6.90 (td, *J* = 7.4, 1.7 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-*d$_6$*) δ 151.6 (d, *J* = 5.1 Hz), 139.3, 129.5, 125.7, 119.9 (d, *J* = 2.5 Hz), 89.8 (d, *J* = 8.7 Hz). HRMS(ESI): *m/z* $[M-H]^-$ calculated for $C_6H_5IO_4P^-$: 298.8976; found 298.8970. IR (ATR) $\tilde{\nu}$ = 2916, 2849, 2359, 2331, 1458, 1216, 1021, 976. Mp = 114-116 °C.

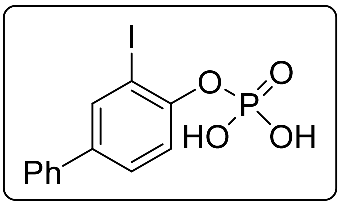
4-(*Tert*-butyl)-2-iodophenyl dihydrogen phosphate (11c)



Following GP1, the reaction of 4-(*tert*-butyl)-2-iodophenol (828 mg, 3.00 mmol) with NEt_3 (418 µL, 3.00 mmol) in Et_2O (15 mL) and $POCl_3$ (841 µL, 9.00 mmol) in Et_2O (15 mL) gave the product **11c** (987 mg, 2.77 mmol, 92%) as a pink solid.

^{1}H NMR (600 MHz, DMSO-*d$_6$*) δ 7.74 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 1.25 (s, 9H). ^{13}C NMR (151 MHz, DMSO-*d$_6$*) δ 149.4 (d, *J* = 5.3 Hz), 148.2, 135.7, 126.5, 119.3 (d, *J* = 2.5 Hz), 89.6 (d, *J* = 8.4 Hz), 33.9, 31.1. HRMS(ESI): *m/z* $[M-H]^-$ calculated for $C_{10}H_{13}IO_4P^-$: 354.9602; found 354.9589. IR (ATR) $\tilde{\nu}$ = 2955, 2901, 2864, 2324, 1491, 1478, 1227, 1026, 974. Mp = 150-152 °C.

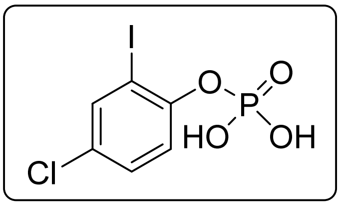
3-Iodo-[1,1'-biphenyl]-4-yl dihydrogen phosphate (11d)



Following GP1, the reaction of 3-iodo-[1,1'-biphenyl]-4-ol (888 mg, 3.00 mmol) with NEt_3 (418 µL, 3.00 mmol) in Et_2O (15 mL) and $POCl_3$ (841 µL, 9.00 mmol) in Et_2O (15 mL) gave the product **11d** (758 mg, 2.02 mmol, 67%) as an off-white solid.

^{1}H NMR (600 MHz, DMSO-*d$_6$*) δ 8.07 (d, *J* = 2.3 Hz, 1H), 7.67 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-*d$_6$*) δ 151.2 (d, *J* = 5.2 Hz), 138.1, 137.6, 137.0, 129.0, 127.8, 127.6, 126.6, 119.9 (d, *J* = 2.4 Hz), 90.4 (d, *J* = 8.7 Hz). HRMS(ESI): *m/z* $[M-H]^-$ calculated for $C_{12}H_9IO_4P^-$: 374.9289; found 374.9278. IR (ATR) $\tilde{\nu}$ = 3058, 3025, 2653, 2356, 2119, 1472, 1196, 1027, 998. Mp = 144-146 °C.

4-Chloro-2-iodophenyl dihydrogen phosphate (11e)

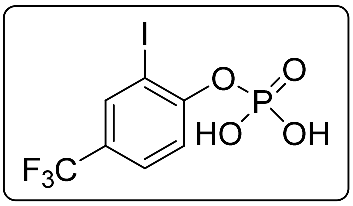


Following GP1, the reaction of 4-chloro-2-iodophenol (1.02 g, 4.00 mmol) with NEt_3 (558 µL, 4.00 mmol) in Et_2O (20 mL) and $POCl_3$ (1.12 mL, 12.0 mmol) in Et_2O (20 mL) gave the product **11e** (1.31 g, 3.92 mmol, 98%) as an off-white solid.

^{1}H NMR (601 MHz, DMSO-*d$_6$*) δ 7.88 (d, *J* = 2.6 Hz, 1H), 7.46 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-*d$_6$*) δ 150.9 (d, *J* = 5.2 Hz), 138.0, 129.2, 128.3, 120.7 (d, *J* = 2.5 Hz), 91.0 (d, *J* = 8.8 Hz). HRMS(ESI): *m/z* $[M-H]^-$ calculated for $C_6H_4IO_4P^-$: 332.8586; found 332.8576. IR (ATR) $\tilde{\nu}$ = 3083, 2615, 2119, 1570, 1462, 1193, 981. Mp = 164-166 °C.

2-Iodo-4-(trifluoromethyl)phenyl dihydrogen phosphate (11f)

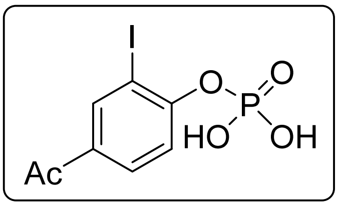
Following GP1, the reaction of 2-iodo-4-(trifluoromethyl)phenol (1.15 g, 4.00 mmol) with NEt_3 (558 µL, 4.00 mmol) in Et_2O (20 mL) and $POCl_3$ (1.12 mL, 12.0 mmol) in Et_2O (20 mL) gave the product **11f** (1.38 g, 3.75 mmol, 94%) as an off-white solid.



^1H NMR (600 MHz, DMSO-d_6) δ 8.14 (d, J = 2.3 Hz, 1H), 7.78 (dd, J = 8.7, 2.3 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.0 (d, J = 4.7 Hz), 136.1 (d, J = 3.7 Hz), 126.9 (d, J = 3.7 Hz), 125.7 (q, J = 32.5 Hz), 123.2 (q, J = 272.2 Hz) 119.8 (d, J = 2.5 Hz), 90.5 (d, J = 9.2 Hz). ^{19}F NMR (565 MHz, DMSO-d_6) δ -60.4 (s). IR (ATR) $\tilde{\nu}$ = 3110, 2753, 1601, 1487, 1314, 1176, 1028, 970. HRMS(ESI): m/z $[M-H]^-$ calculated for $C_7H_4F_3IO_4P^-$ 366.8850; found 366.8810. IR (ATR) $\tilde{\nu}$ = 3110, 3085, 1601, 1487, 1314, 1176, 1117, 970. Mp = 140-142 °C

4-Acetyl-2-iodophenyl dihydrogen phosphate (11g)

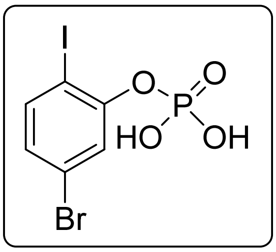
Following GP1, the reaction of 1-(4-hydroxy-3-iodophenyl)ethan-1-one (232 mg, 885 mmol) with NEt_3 (123 µL, 885 µmol) in Et_2O (4.4 mL) and $POCl_3$ (248 µL, 2.66 mmol) in Et_2O (4.4 mL) gave the product **11g** (264 mg, 773 µmol, 87%) as an off-white solid.



^1H NMR (601 MHz, DMSO-d_6) δ 8.34 (d, J = 1.3 Hz, 1H), 7.98 (dd, J = 8.6, 2.2 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 195.8, 155.3 (d, J = 4.9 Hz), 139.3, 133.9, 129.9, 119.1 (d, J = 2.4 Hz), 90.0 (d, J = 9.1 Hz), 26.7. HRMS(ESI): m/z $[M-H]^-$ calculated for $C_8H_7IO_5P^-$: 340.9081; found 340.9068. IR (ATR) $\tilde{\nu}$ = 2923, 1628, 1581, 1251, 1215, 1098, 1037, 961, 915. Mp = 176-178 °C (decomp.).

5-Bromo-2-iodophenyl dihydrogen phosphate (11h)

Following GP1, the reaction of 5-bromo-2-iodophenol (897 mg, 3.00 mmol) with NEt_3 (418 µL, 3.00 mmol) in Et_2O (15 mL) and $POCl_3$ (841 µL, 9.00 mmol) in Et_2O (15 mL) gave the product **11h** (1.11 g, 2.93 mmol, 98%) as an off-white solid.

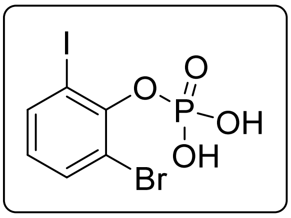


^1H NMR (601 MHz, DMSO-d_6) δ 7.77 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 1.3 Hz, 1H), 7.12 (dd, J = 8.4, 2.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 152.6 (d, J = 5.2 Hz), 140.6, 128.4, 122.4 (d, J = 2.6 Hz), 121.4, 88.9 (d, J = 8.9 Hz). HRMS(ESI): m/z $[M-H]^+$

calculated for $C_6H_4BrIO_4P^+$: 376.8081; found 376.8068. IR (ATR) $\tilde{\nu}$ = 3079, 2699, 2319, 1561, 1456, 1378, 1178, 975. Mp = 174-176 °C.

2-Bromo-6-iodophenyl dihydrogen phosphate (11i)

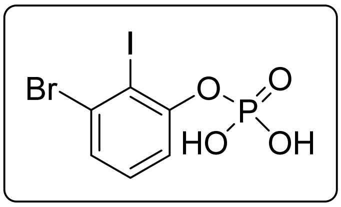
Following GP1, the reaction of 2-bromo-6-iodophenol (299 mg, 1.00 mmol) with NEt_3 (139 µL, 1.00 mmol) in Et_2O (5 mL) and $POCl_3$ (280 µL, 3.00 mmol) in Et_2O (5 mL) gave the product **11i** (368 mg, 970 µmol, 97%) as an off-white solid.



^{1}H NMR (601 MHz, DMSO-d_6) δ 7.83 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.64 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.84 (td, *J* = 7.9, 1.3 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 149.9 (d, *J* = 7.1 Hz), 139.1, 133.6, 127.6, 115.7 (d, *J* = 3.6 Hz), 92.6 (d, *J* = 4.2 Hz). HRMS(ESI): *m/z* [M-H]$^-$ calculated for $C_6H_4BrIO_4P^-$: 376.8081; found 376.8069. IR (ATR) $\tilde{\nu}$ = 2849, 1560, 1421, 1127, 1043, 973, 762, 702. Mp = 172-174 °C.

3-Bromo-2-iodophenyl dihydrogen phosphate (11j)

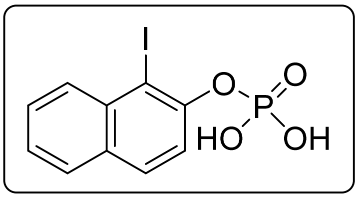
Following GP1, the reaction of 3-bromo-2-iodophenol (149 mg, 500 µmol) with NEt_3 (69.7 µL, 500 µmol) in Et_2O (2.5 mL) and $POCl_3$ (140 µL, 1.50 mmol) in Et_2O (2.5 mL) gave the product **11j** (165 mg, 437 µmol, 87%) as an off-white solid.



^{1}H NMR (600 MHz, DMSO-d_6) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.29 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.5 (d, *J* = 5.1 Hz), 130.5, 130.2, 127.8, 118.1 (d, *J* = 2.6 Hz), 98.9 (d, *J* = 8.8 Hz). HRMS(ESI): *m/z* [M-H]$^-$ calculated for $C_6H_4BrIO_4P^-$: 376.8081; found 376.8065. IR (ATR) $\tilde{\nu}$ = 2953, 2918, 2850, 2359, 2339, 1558, 1433, 1409, 1244, 1190, 1042, 784. Mp = 146-148 °C. Mp = 146-148 °C

1-Iodonaphthalen-2-yl dihydrogen phosphate (11k)

Following GP1, the reaction of 1-iodonaphthalen-2-ol (540 mg, 2.00 mmol) with NEt_3 (279 µL, 2.00 mmol) in Et_2O (10 mL) and $POCl_3$ (561 µL, 6.00 mmol) in Et_2O (10 mL) gave the product **11k** (659 mg, 1.99 mmol, 99%) as a brown solid.

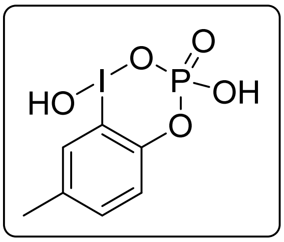


^{1}H NMR (601 MHz, DMSO-d_6) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ

150.7 (d, J = 5.3 Hz), 134.9, 131.3, 130.6, 129.9, 128.5 (2xC), 125.7, 119.7, 92.3 (d, J = 8.9 Hz). HRMS(ESI): m/z $[M-H]^-$ calculated for $C_{10}H_7IO_4P^-$: 348.9132; found 348.9128. IR (ATR) $\tilde{\nu}$ = 3047, 2305, 1591, 1499, 1353, 1212, 1108, 1033, 1014, 968. Mp = 169-171 °C.

4.2. Syntheses of Iodosoarylphosphoric Acids

1,3-Dihydroxy-7-methyl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (8a)

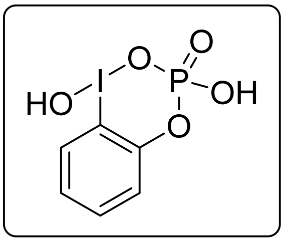


Following GP2, the reaction of **11a** (1.56 g, 5.00 mmol) with *m*CPBA (2.47 g, 10.0 mmol) in DCM (25 mL) gave the product **8a** (1.47 g, 4.45 mmol, 89%) as a colourless solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.48 (s, 1H), 7.70 (s, 1H), 7.35 (dd, J = 8.3, 2.0 Hz, 1H), 7.12 (dd, J = 8.2, 1.3 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 148.9 (d, J = 8.1 Hz), 135.2, 133.3, 130.9, 122.4 (d, J = 4.0 Hz), 116.9 (d, J = 3.5 Hz), 20.2. HRMS(ESI): *m/z* $[M+Na]^+$ calculated for $C_7H_8INaO_4P^+$: 336.9097; found 336.9096. IR (ATR) $\tilde{\nu}$ = 3364, 3075, 2927, 2479, 2278, 2114, 1667, 1482, 1227, 1129, 1040, 906. Mp = 94-96 °C (decomp.).

*Note: Only one signal of one hydroxy group is visible in the ^{1}H-NMR. This is also present in the following spectra of **8**.*

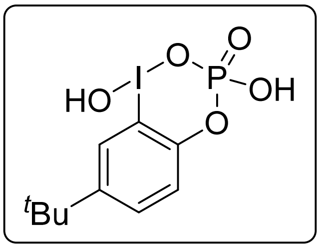
1,3-Dihydroxy-1*H*-1λ³-benzo[e][1,2,4,3]iodadioxaphosphinine 3-oxide (8b)



Following GP2, the reaction of **11b** (600 mg, 2.00 mmol) with *m*CPBA (986 mg, 4.00 mmol) in DCM (10 mL) gave the product **8b** (628 mg, 1.99 µmol, 99%) as a colourless solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.56 (s, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.1 (d, J = 8.1 Hz), 132.8, 131.2, 125.70, 122.8 (d, J = 4.1 Hz), 117.3 (d, J = 3.5 Hz). MS(ESI): *m/z* = 301.0 $[M+H]^+$. IR (ATR) $\tilde{\nu}$ = 2927, 2522, 1634, 1464, 1227, 1117, 907, 772. Mp = 115-117 °C (decomp.). The analytical data is in accordance with the literature data.[7]

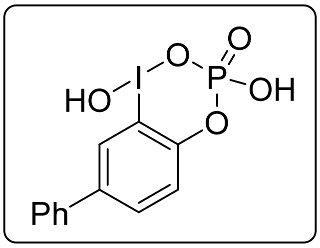
7-(*Tert*-butyl)-1,3-dihydroxy-1*H*-1λ^3-benzo[e][1,2,4,3]iodadioxaphosphinine 3-oxide (8c)



Following GP2, the reaction of **11c** (178 mg, 500 µmol) with *m*CPBA (148 mg, 600 µmol, 1.20 eq.) in DCM (2.5 mL) at room temperature gave the product **8c** (111 mg, 298 µmol, 60%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-*d*$_6$) δ 8.60 (s, 1H), 7.92 (d, *J* = 2.3 Hz, 1H), 7.58 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.19 – 7.13 (m, 1H), 1.30 (s, 9H). ^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 148.8 (d, *J* = 8.2 Hz), 148.4, 129.8, 127.7, 122.2, 117.0 (d, *J* = 3.2 Hz), 34.7, 31.0. HRMS(ESI): *m/z* [M-H_2O+Na+MeO]$^+$ calculated for $C_{11}H_{16}INaO_5P^+$: 408.9672; found 408.9670. IR (ATR) $\tilde{\nu}$ = 2961, 2869, 2359, 1484, 1387, 1261, 1143, 1037, 947, 902. Mp = 100 -102 °C (decomp.).

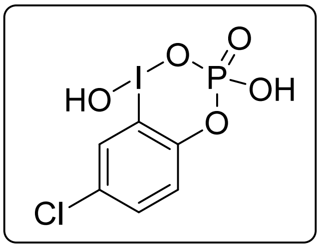
1,3-Dihydroxy-7-phenyl-1*H*-1λ^3-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (8d)



Following GP2, the reaction of **11d** (188 mg, 500 µmol) with *m*CPBA (247 mg, 1.00 mmol) in DCM (2.5 mL) gave the product **8d** (191 mg, 488 µmol, 98%) as a colourless solid.

^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.64 (s, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 150.6 (d, *J* = 7.9 Hz), 138.2, 137.7, 130.9, 129.2, 129.2, 128.0, 126.7, 123.1 (d, *J* = 4.1 Hz), 117.8 (d, *J* = 3.3 Hz). HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{13}H_{12}INaO_5P^+$: 428.9359; found 428.9357. IR (ATR) $\tilde{\nu}$ = 3429, 2917, 2359, 2327, 1694, 1474, 1383, 1235, 1131, 1073, 763. Mp = 88-90 °C (decomp.).

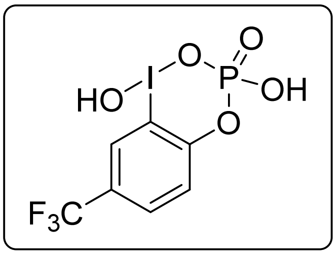
7-Chloro-1,3-dihydroxy-1*H*-1λ^3-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (8e)



Following GP2, the reaction of **11e** (134 mg, 400 µmol) with *m*CPBA (197 mg, 800 µmol) in DCM (2 mL) gave the product **8e** (89.1 mg, 254 µmol, 64%) as a colourless solid.

^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.73 (s, 1H), 7.93 (d, *J* = 2.5 Hz, 1H), 7.63 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.26 (dd, *J* = 8.6, 1.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 150.3 (d, *J* = 8.0 Hz), 132.7, 130.5, 129.0, 124.1 (d, *J* = 4.2 Hz), 117.8 (d, *J* = 3.3 Hz). HRMS(ESI): *m/z* [M-H_2O+Na+MeO]$^+$ calculated for $C_7H_7ClINaO_5P^+$: 386.8657; found 386.8662. IR (ATR) $\tilde{\nu}$ = 3445, 3340, 3094, 2498, 1645, 1465, 1121, 1022, 974. Mp = 102-104 °C (decomp.).

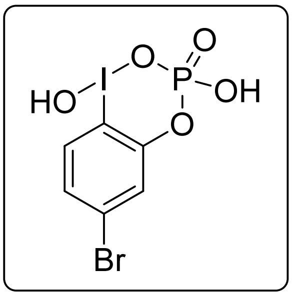
1,3-Dihydroxy-7-(trifluoromethyl)-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (8f)



Following GP2, the reaction of **11f** (147 mg, 400 µmol) with *m*CPBA (197 mg, 800 µmol) in DCM (2 mL) gave the product **8f** (122 mg, 318 µmol, 79%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-*d₆*) δ 8.87 (s, 1H), 8.27 (d, *J* = 2.2 Hz, 1H), 7.95 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-*d₆*) δ 154.4 (d, *J* = 7.5 Hz), 130.0, 128.8, 125.9 (q, *J* = 32.7 Hz), 123.7 (d, *J* = 4.3 Hz), 123.4 (q, *J* = 272.4 Hz), 117.6. ^{19}F NMR (565 MHz, DMSO-*d₆*) δ -60.53 (s). HRMS(ESI): *m/z* $[M\text{-}H_2O+2Na+MeO]^+$ calculated for $C_8H_6F_3INa_2O_5P^+$: 442.8740; found 442.8737. IR (ATR) $\tilde{\nu}$ = 3094, 3073, 1604, 1489, 1315, 1272, 1114, 1023, 967, 902. Mp = 94-96 °C (decomp.).

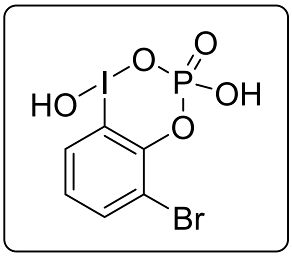
6-Bromo-1,3-dihydroxy-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (8h)



Following GP2, the reaction of **11h** (189 mg, 500 µmol) with *m*CPBA (148 mg, 1.00 mmol) in DCM (2.5 mL) gave the product **8h** (181 mg, 459 µmol, 92%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-*d6*) δ 8.71 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.47 (dd, *J* = 2.1, 1.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-*d₆*) δ 152.0 (d, *J* = 7.7 Hz), 140.6, 132.8, 128.6, 125.5 (d, *J* = 4.4 Hz), 116.4 (d, *J* = 3.4 Hz). HRMS(ESI): *m/z* $[M\text{-}OH+Na+MeO]^+$ calculated for $C_7H_7BrINaO_5P^+$: 430.8151; found 430.8148. IR (ATR) $\tilde{\nu}$ = 3085, 2997, 2480, 1570, 1557, 1456, 1385, 1123, 1039, 928, 804. Mp = 113-115 °C (decomp.).

5-Bromo-1,3-dihydroxy-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (8i)



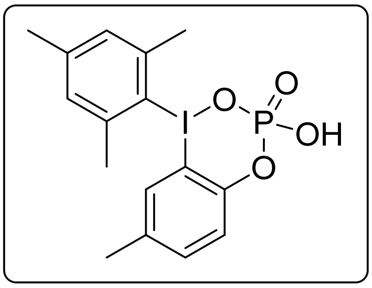
Following GP2, the reaction of **11i** (189 mg, 500 µmol) with *m*CPBA (247 mg, 1.00 mmol) in DCM (2.5 mL) gave the product **8i** (154 mg, 390 µmol, 78%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-*d₆*) δ 8.76 (s, 1H), 7.91 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.86 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.27 (td, *J* = 8.0, 0.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-*d₆*) δ 148.5 (d, *J* = 7.7 Hz), 136.4, 131.3, 127.1, 119.0 (d, *J* = 3.6 Hz), 116.3 (d, *J* = 4.5 Hz). HRMS(ESI): *m/z* $[M\text{-}OH+Na+MeO]^+$ calculated for

$C_7H_7BrINaO_5P^+$: 430.8151; found 430.8150. IR (ATR) $\tilde{\nu}$ = 2919, 2360, 1557, 1441, 1430, 1144, 1084, 946, 897. Mp = 114-116 °C (decomp.).

4.3. Synthesis of 1-Aryliodoarylphosphonic Acids

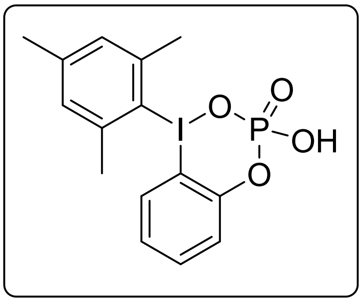
3-Hydroxy-1-mesityl-7-methyl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9a)



Following GP4, the reaction of **8a** (330 mg, 1.00 mmol) with mesitylene (278 µL, 2.00 mmol) in TFE (10 mL) at 50 °C for 16 h gave the product **9a** (379 mg, 877 µmol, 88%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-d_6 + TFA) δ 7.70 (d, *J* = 2.0 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.17 (s, 2H), 2.59 (s, 6H), 2.28 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6 + TFA) δ 148.6 (d, *J* = 5.4 Hz), 143.1, 142.1, 136.6, 136.2, 134.6, 129.8, 122.3, 121.1, 107.5 (d, *J* = 7.7 Hz), 26.4, 20.6, 19.9. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{16}H_{18}INaO_4P^+$: 454.9880; found 454.9879. IR (ATR) $\tilde{\nu}$ = 2922, 2359, 1485, 2337, 1185, 1103, 912, 886. Mp = 154-156 °C (decomp.).

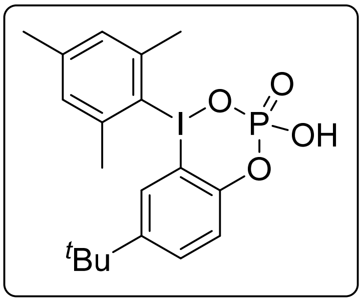
3-Hydroxy-1-mesityl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9b)



Following GP3, the reaction of **8b** (158 mg, 500 µmol) with mesitylene (139 µL, 1.00 mmol) in MeCN/TFA (1:1, 5 mL) gave the product **9b** (159 mg, 380 µmol, 76%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-d_6 + TFA) δ 7.54 (td, *J* = 7.9, 1.5 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.18 (s, 2H), 7.10 (td, *J* = 7.8, 1.5 Hz, 1H), 2.53 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6 + TFA) δ 151.9 (d, *J* = 6.3 Hz), 142.7, 141.6, 134.2, 133.2, 129.5, 126.3, 123.1, 122.9, 109.9 (d, *J* = 3.0 Hz), 26.0, 20.6. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{15}H_{16}INaO_4P^+$: 440.9723; found 440.9715. IR (ATR) $\tilde{\nu}$ = 2972, 2917, 2360, 2340, 1465, 1261, 1177, 1100, 926, 885. Mp = 141- 143 °C (decomp.).

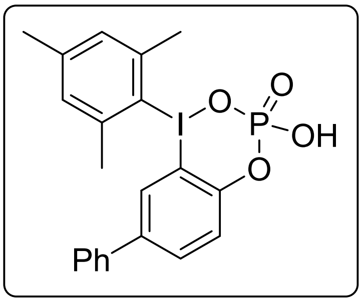
7-(*Tert*-butyl)-3-hydroxy-1-mesityl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9c)



Following GP3, the reaction of **8c** (93.0 mg, 250 µmol) with mesitylene (69.6 µL, 500 µmol) in MeCN/TFA (1:1, 2.5 mL) gave the product **9c** (92.2 mg, 194 µmol, 78%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-d_6) δ 7.56 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.18 (s, 2H), 2.56 (s, 6H), 2.28 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 149.5 (d, *J* = 6.0 Hz), 148.5, 142.6, 141.7, 131.2, 130.2, 129.4, 123.1, 121.9, 108.9 (d, *J* = 5.6 Hz), 34.3, 30.7, 26.0, 20.5. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{19}H_{24}INaO_4P^+$: 497.0349; found 497.0342. IR (ATR) $\tilde{\nu}$ = 2961, 2868, 2359, 2342, 1772, 1489, 1245, 1170, 1139, 1014, 906. Mp = 149-151 °C (decomp.).

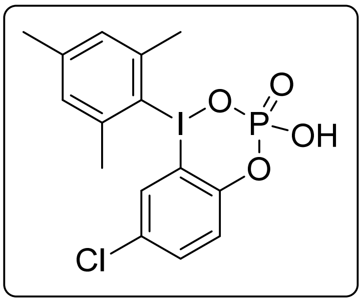
3-Hydroxy-1-mesityl-7-phenyl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9d)



Following GP3, the reaction of **8d** (118 mg, 300 µmol) with mesitylene (83.5 µL, 600 µmol) in MeCN/TFA (1:1, 3 mL) gave the product **9d** (112 mg, 226 µmol, 75%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-d_6) δ 7.81 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.47 – 7.39 (m, 5H), 7.38 – 7.33 (m, 1H), 7.17 (s, 2H), 2.57 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.7 (d, *J* = 6.6 Hz), 142.6, 141.6, 137.8, 131.6, 131.3, 129.4, 129.2, 129.0, 128.0, 126.5, 123.6, 123.1, 111.1 (d, *J* = 5.2 Hz), 26.0, 20.5. HRMS(ESI): m/z [M+Na]$^+$ calculated for $C_{21}H_{20}INaO_4P^+$: 517.0036; found 517.0026. IR (ATR) $\tilde{\nu}$ = 3030, 2977, 2918, 2359, 2325, 1662, 1474, 1178, 940, 892. Mp = 134-136 °C (decomp.).

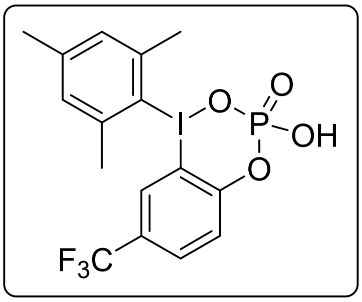
7-Chloro-3-hydroxy-1-mesityl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9e)



Following GP3, the reaction of **8e** (175 mg, 500 µmol) with mesitylene (139 µL, 1.00 mmol) in MeCN/TFA (1:1, 5 mL) gave the product **9e** (158 mg, 349 µmol, 70%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-d_6) δ 7.60 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.40 (d, *J* = 2.5 Hz, 1H), 7.32 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.19 (s, 2H), 2.52 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.8 (d, *J* = 6.8 Hz), 142.8, 141.6, 132.9, 132.5, 129.6, 128.8, 124.3, 123.5, 111.3, 26.0, 20.6. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{15}H_{15}INaO_4P^+$: 474.9333; found 474.9330. IR (ATR) $\tilde{\nu}$ = 3074, 2923, 1578, 1462, 1379, 1232, 1175, 1093, 936, 884, 764. Mp = 134-136 °C (decomp.).

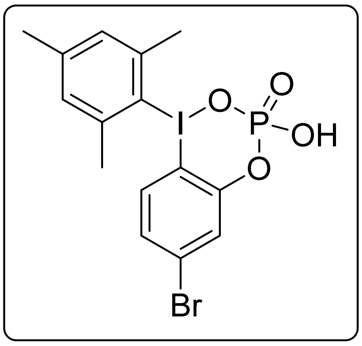
3-Hydroxy-1-mesityl-7-(trifluoromethyl)-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9f)



Following GP3, the reaction of **8f** (192 mg, 500 µmol) with mesitylene (139 µL, 1.00 mmol) in MeCN/TFA (1:1, 5 mL) gave the product **9f** (236 mg, 485 µmol, 97%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-d_6+TFA) δ 7.90 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.69 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.18 (s, 2H), 2.53 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6+TFA) δ 156.3 (d, *J* = 6.3 Hz), 142.8, 141.6, 130.9, 130.2, 129.5, 125.3 (q, *J* = 33.1 Hz), 123.8, 123.0 (q, *J* = 273.9 Hz), 116.8, 111.1 (d, *J* = 4.5 Hz), 25.9, 20.6. ^{19}F NMR (565 MHz, DMSO-d_6) δ -60.54 (s). HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{16}H_{15}F_3INaO_4P^+$: 508.9597; found 508.9588. IR (ATR) $\tilde{\nu}$ = 2922, 1604, 1489, 1317, 1265, 1119, 1073, 887. Mp = 126-128 °C (decomp.).

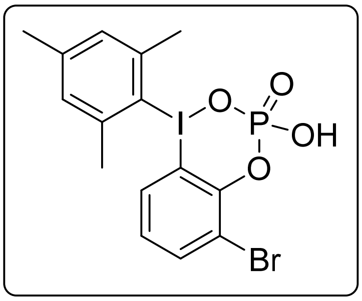
6-Bromo-3-hydroxy-1-mesityl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9g)



Following GP3, the reaction of **8h** (118 mg, 300 µmol) with mesitylene (83.5 µL, 600 µmol) in MeCN/TFA (1:1, 3 mL) gave the product **9g** (111 mg, 223 µmol, 74%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-*d6* + TFA) δ 7.89 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 2.2 Hz, 1H), 7.42 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.18 (s, 2H), 2.58 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, DMSO-*d6* + TFA) δ 148.1 (d, *J* = 7.0 Hz), 143.3, 141.5, 136.8, 133.1, 129.8, 128.6, 124.4, 117.0 (d, *J* = 4.2 Hz), 111.4, 26.0, 20.6. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{15}H_{15}BrINaO_4P^+$: 518.8828; found 518.8824. IR (ATR) $\tilde{\nu}$ = 2917, 1733, 1564, 1456, 1385, 1196, 1098, 900. Mp = 165-167 °C (decomp.).

5-Bromo-3-hydroxy-1-mesityl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9h)

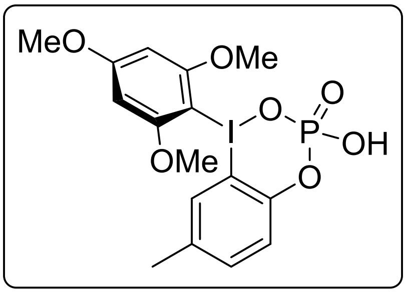


Following GP3, the reaction of **8i** (98.7 mg, 250 µmol) with mesitylene (69.6 µL, 500 µmol) in MeCN/TFA (1:1, 2.5 mL) gave the product **9h** (117 mg, 235 µmol, 94%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-*d6*) δ 7.87 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.35 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.22 (s, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, DMSO-*d6*) δ 148.5 (d, *J* = 7.0 Hz), 143.7, 141.9, 137.2, 133.5, 130.2, 129.0, 124.8, 117.4 (d, *J* = 4.2 Hz), 111.8, 26.4, 21.0. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{15}H_{15}BrINaO_4P^+$: 518.8828; found 518.8825. IR (ATR) $\tilde{\nu}$ = 2918, 2360, 1435, 1178, 1109, 930, 873, 754. Mp = 147-149 °C (decomp.).

3-Hydroxy-7-methyl-1-(2,4,6-trimethoxyphenyl)-1*H*-1λ^3-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9i)

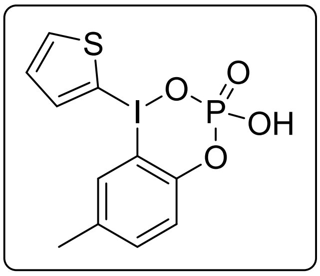
Following GP4, the reaction of **8a** (165 mg, 500 µmol) with 1,3,5-trimethoxy benzene (168 mg, 1.00 mmol) in TFE (5 mL) at room temperature for 18 h gave the product **9i** (220 mg, 458 µmol, 92%) as a colourless solid.



^{1}H NMR (601 MHz, DMSO-d_6 + TFA) δ 7.59 – 7.54 (m, 1H), 7.42 – 7.33 (m, 2H), 6.42 (s, 2H), 3.90 (s, 6H), 3.85 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6 + TFA) δ 166.5, 160.0, 148.3 (d, *J* = 5.2 Hz), 136.5, 135.7, 134.2, 120.9, 109.4 (d, *J* = 7.6 Hz), 92.1, 86.8, 57.4, 56.2, 20.0. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{16}H_{18}INaO_7P^+$: 502.9727; found 502.9727. IR (ATR) $\tilde{\nu}$ = 2949, 2359, 1580, 1341, 1206, 1097, 812. Mp = 165-167 °C (decomp.).

3-Hydroxy-7-methyl-1-(thiophen-2-yl)-1*H*-1λ^3-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9j)

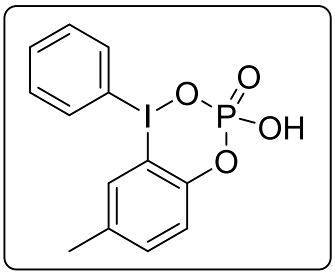
Following GP4, the reaction of **8a** (165 mg, 500 µmol) with thiophene (80.1 µL, 1.00 mmol) in TFE (5 mL) at room temperature for 18 h gave the product **9j** (220 mg, 458 µmol, 92%) as a colourless solid.



^{1}H NMR (601 MHz, DMSO-d_6 + TFA) δ 8.12 – 8.03 (m, 1H), 8.00 (d, *J* = 3.7 Hz, 1H), 7.94 (d, *J* = 5.3 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.15 (dd, *J* = 5.3, 3.8 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6 + TFA) δ 148.0 (d, *J* = 5.3 Hz), 140.7, 137.3, 136.4, 136.1, 134.9, 129.6, 120.6, 112.5, 100.6, 20.0. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{11}H_{10}INaO_4PS^+$: 418.8974; found 418.8973. IR (ATR) $\tilde{\nu}$ = 3112, 2924, 2356, 1488, 1227, 1191, 1101, 905, 720. Mp = 160-162 °C (decomp.).

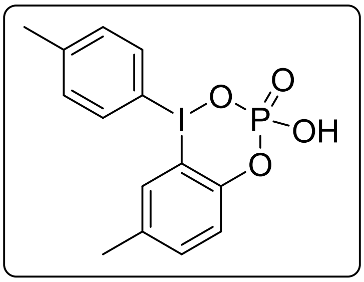
3-Hydroxy-7-methyl-1-phenyl-1*H*-1λ^3-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9k)

Following GP3, the reaction of **8a** (165 mg, 500 µmol) with trimethyl(phenyl)silane (129 µL, 750 µmol, 1.50 eq.) in MeCN/TFA (1:1, 5 mL) gave the product **9k** (143 mg, 367 µmol, 73%) as a colourless solid.



^{1}H NMR (601 MHz, DMSO-d_6) δ 8.19 (d, *J* = 7.9 Hz, 2H), 7.71 – 7.62 (m, 2H), 7.51 (t, J = 7.7 Hz, 2H), 7.35 – 7.26 (m, 2H), 2.20 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 149.6 (d, *J* = 6.3 Hz), 135.8, 135.3, 134.7, 133.9, 131.8, 131.5, 121.9, 117.0, 111.1 (d, *J* = 5.7 Hz), 19.9. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{13}H_{12}INaO_4P^+$: 412.9410; found 412.9407. IR (ATR) $\tilde{\nu}$ = 2925, 1661, 1485, 1250, 1174, 896, 816. Mp = 146-148 °C (decomp.).

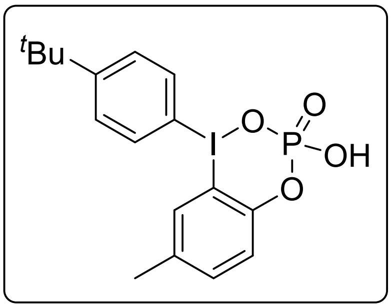
3-Hydroxy-7-methyl-1-(*p*-tolyl)-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9l)



Following GP3, the reaction of **8a** (165 mg, 500 µmol) with trimethyl(*p*-tolyl)silane (142 µL, 750 µmol, 1.50 eq.) in MeCN/TFA (1:1, 5 mL) gave the product **9l** (126 mg, 323 µmol, 65%) as a colourless solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.67 (s, 1H), 7.35 – 7.26 (m, 4H), 2.34 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 149.5 (d, *J* = 6.2 Hz), 142.2, 135.7, 135.3, 134.6, 133.8, 132.1, 121.9, 113.3, 111.1 (d, *J* = 5.6 Hz), 20.9, 19.9. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{14}H_{14}INaO_4P^+$: 426.9567; found 426.9561. IR (ATR) $\tilde{\nu}$ = 2923, 2359, 2341, 1661, 1484, 1273, 1159, 1117, 927, 901. Mp = 164-166 °C (decomp.).

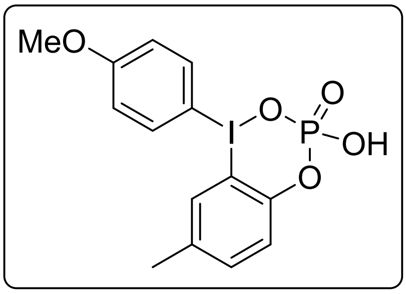
1-(4-(*Tert*-butyl)phenyl)-3-hydroxy-7-methyl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9m)



Following GP3, the reaction of **8a** (165 mg, 500 µmol) with (4-(*tert*-butyl)phenyl)trimethylsilane (155 mg, 750 µmol, 1.50 eq.) in MeCN/TFA (1:1, 5 mL) gave the product **9m** (177 mg, 396 µmol, 79%) as a colourless solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.10 (d, *J* = 8.6 Hz, 2H), 7.78 (s, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 1.3 Hz, 2H), 2.22 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.0, 149.4 (d, *J* = 6.0 Hz), 135.5, 135.3, 135.1, 134.0, 128.6, 121.7, 113.2, 110.7 (d, *J* = 6.1 Hz), 34.9, 30.7, 19.9. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{17}H_{20}INaO_4P^+$: 469.0036; found 469.0031. IR (ATR) $\tilde{\nu}$ = 2963, 2866, 2360, 2340, 1483, 1233, 1183, 1118, 937, 834. Mp = 152-154 °C (decomp.).

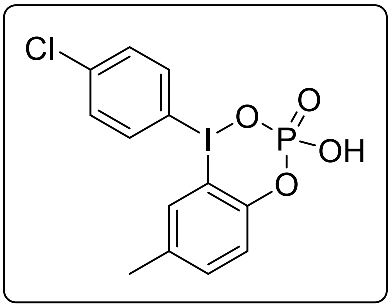
3-Hydroxy-1-(4-methoxyphenyl)-7-methyl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9n)



Following GP4, the reaction of **8a** (330 mg, 1.00 mmol) with anisole (217 µL, 2.00 mmol) in TFE (10 mL) at 50 °C for 16 h gave the product **9n** (273 mg, 650 µmol, 65%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-*d₆*) δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (151 MHz, DMSO-*d₆*) δ 161.8, 150.1 (d, *J* = 6.7 Hz), 138.0, 134.9, 133.4, 133.3, 122.9, 117.1, 112.1 (d, *J* = 4.2 Hz), 106.5, 55.6, 20.0. HRMS(ESI): *m/z* [M+Na]⁺ calculated for $C_{14}H_{14}INaO_5P^+$: 442.9516; found 442.9514. IR (ATR) $\tilde{\nu}$ = 2841, 1572, 1484, 1250, 1174, 1020, 893, 820. Mp = 144-146 °C (decomp.).

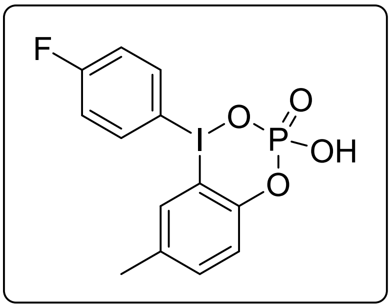
1-(4-Chlorophenyl)-3-hydroxy-7-methyl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9o)



Following GP3, the reaction of **8a** (165 mg, 500 µmol) with (4-chlorophenyl)trimethylsilane (92.4 µL, 500 µmol, 1.00 eq.) in MeCN/TFA (1:1, 5 mL) gave the product **9o** (158 mg, 372 µmol, 74%) as a colourless solid.

^{1}H NMR (600 MHz, DMSO-*d₆*) δ 8.18 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.53 (m, 3H), 7.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (151 MHz, DMSO-*d₆*) δ 149.9 (d, *J* = 6.7 Hz), 137.7, 137.0, 135.2, 134.1, 133.7, 131.4, 122.5 (d, *J* = 2.7 Hz), 115.4, 111.8 (d, *J* = 4.8 Hz), 19.9. HRMS(ESI): *m/z* [M+Na]⁺ calculated for $C_{13}H_{11}ClINaO_4P^+$: 446.9020; found 446.9013. IR (ATR) $\tilde{\nu}$ = 2924, 1659, 1485, 1389, 1238, 1174, 1086, 997, 900. Mp = 128-130 °C (decomp.).

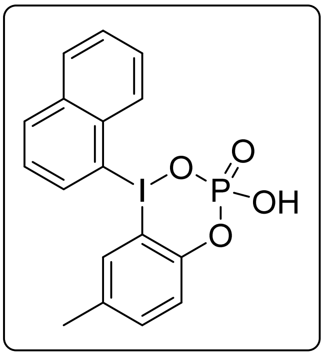
1-(4-Fluorophenyl)-3-hydroxy-7-methyl-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9p)



Following GP3, the reaction of **8a** (99.0 mg, 300 μmol) with (4-fluorophenyl)trimethylsilane (53.1 μL, 300 μmol, 1.00 eq.) in MeCN/TFA (1:1, 3 mL) gave the product **9p** (101 mg, 247 μmol, 83%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-d_6+TFA) δ 8.32 – 8.18 (m, 2H), 7.53 (d, *J* = 2.1 Hz, 1H), 7.38 (t, *J* = 8.9 Hz, 2H), 7.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.23 (dd, *J* = 8.2, 1.1 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6+TFA) δ 164.7, 163.0, 149.9 (d, *J* = 6.8 Hz), 138.8 (d, *J* = 8.7 Hz), 135.2, 133.9, 133.6, 122.6, 118.8 (d, *J* = 22.5 Hz), 111.9, 20.0. ^{19}F NMR (565 MHz, DMSO-d_6+TFA) δ -107.11 (s). HRMS(ESI): m/z [M+Na]$^+$ calculated for $C_{13}H_{11}FINaO_4P^+$: 430.9316; found 430.9313. IR (ATR) $\tilde{\nu}$ = 2926, 2358, 1653, 1576, 1482, 1399, 1232, 1161, 942, 901, 825. Mp = 122-124 °C (decomp.).

3-Hydroxy-7-methyl-1-(naphthalen-1-yl)-1*H*-1λ³-benzo[*e*][1,2,4,3]iodadioxaphosphinine 3-oxide (9r)

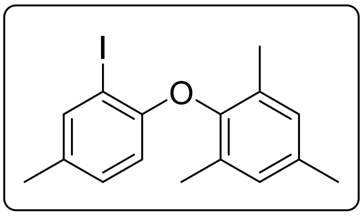


Following GP3, the reaction of **8a** (165 mg, 500 μmol) with trimethyl(naphthalen-1-yl)silane (152 μL, 750 μmol, 1.50 eq.) in MeCN/TFA (1:1, 5 mL) gave the product **9r** (155 mg, 351 μmol, 70%) as a colourless solid.

^{1}H NMR (601 MHz, DMSO-d_6 + TFA) δ 8.71 (d, *J* = 7.4 Hz, 1H), 8.27 (dd, *J* = 8.4, 4.6 Hz, 2H), 8.11 (s, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.34 (m, 1H), 2.21 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6 + TFA) δ 148.5 (d, *J* = 4.9 Hz), 137.9, 136.4, 136.0, 134.6, 134.2, 133.5, 131.1, 129.8, 129.4, 129.1, 128.0, 127.5, 120.2, 118.9, 109.2 (d, *J* = 8.3 Hz), 19.8. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{17}H_{14}INaO_4P^+$: 462.9567; found 462.9565. IR (ATR) $\tilde{\nu}$ = 2926, 2359, 1683, 1484, 1249, 1172, 1121, 893. Mp = 146-148 °C (decomp.).

4.4. Syntheses of Diaryl Ethers

2-(2-Iodo-4-methylphenoxy)-1,3,5-trimethylbenzene (10a)



Method in MeCN with Cs_2CO_3:

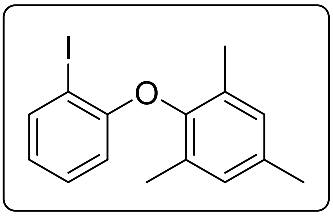
A suspension of **9a** (21.6 mg, 50.0 µmol, 1.00 eq.) and Cs_2CO_3 (17.9 mg, 55.0 µmol, 1.10 eq.) in MeCN (1 mL) was stirred for 24 h at 80 °C. After cooling to room temperature EtOAc (10 mL) was added, the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The product **10a** (17.2 mg, 48.8 µmol, 98%) was obtained as a colourless solid.

Method in H_2O with $Ca(OH)_2$:

Following GP5, the reaction of **9b** (43.2 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **101** (28.4 mg, 80.6 µmol, 81%) as a colourless solid.

^{1}H NMR (601 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 2.0, 0.9 Hz, 1H), 6.92 – 6.88 (m, 3H), 6.19 (d, *J* = 8.3 Hz, 1H), 2.30 (s, 3H), 2.25 (s, 3H), 2.08 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 149.4, 140.1, 134.8, 132.6, 130.9, 130.0, 129.7, 112.6, 84.9, 20.9, 20.1, 16.4. HRMS(ESI): *m/z* $[M+Na]^+$ calculated for $C_{16}H_{17}INaO^+$: 375.0216; found 375.0212. IR (ATR) $\tilde{\nu}$ = 3032, 2948, 2916, 2853, 1472, 1225, 1210, 1145, 1035, 855, 804. Mp = 68-71 °C.

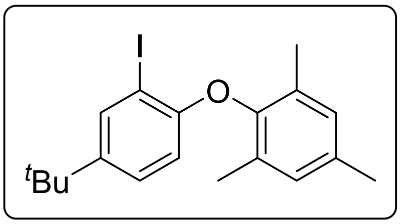
2-(2-Iodophenoxy)-1,3,5-trimethylbenzene (10b)



Following GP5, the reaction of **9b** (41.8 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10b** (26.2 mg, 78.7 µmol, 79%) as a colourless solid.

^{1}H NMR (601 MHz, $CDCl_3$ δ 7.84 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.15 – 7.09 (m, 1H), 6.91 (s, 2H), 6.72 (td, *J* = 7.6, 1.4 Hz, 1H), 6.31 (dd, *J* = 8.3, 1.4 Hz, 1H), 2.31 (s, 3H), 2.08 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6, 149.2, 139.8, 135.0, 130.9, 129.7, 129.5, 123.1, 113.0, 85.2, 21.0, 16.4. MS(ESI): *m/z* = 339.0 $[M+H]^+$. IR (ATR) $\tilde{\nu}$ = 2918, 2853, 2359, 1580, 1462, 1435, 1228, 1221, 1141, 1017, 859, 738. Mp = 68-70 °C. The analytical data is in accordance with literature data. [8]

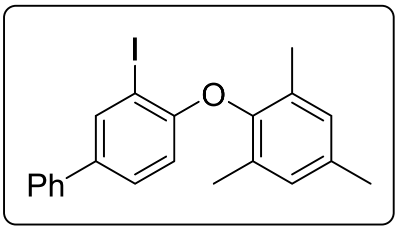
2-(4-(*tert*-Butyl)-2-iodophenoxy)-1,3,5-trimethylbenzene (10c)



Following GP5, the reaction of **9c** (47.4 mg) gave after a reaction time of 48 h and column chromatography (cyclohexane) the product **10c** (28.7 mg, 72.8 µmol, 73%) as a colourless oil.

^{1}H NMR (601 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.3 Hz, 1H), 7.11 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.90 (s, 2H), 6.21 (d, *J* = 8.6 Hz, 1H), 2.30 (s, 3H), 2.08 (s, 6H), 1.27 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 149.5, 146.1, 136.7, 134.8, 131.0, 129.7, 126.4, 112.4, 84.9, 34.2, 31.6, 21.0, 16.5. HRMS(EI): *m/z* $[M]^{\cdot+}$ calculated for $C_{19}H_{23}IO^+$: 394.0794; found 394.0791. IR (ATR) $\tilde{\nu}$ 3006, 2959, 2920, 2860, 2734, 1476, 1280, 1034.

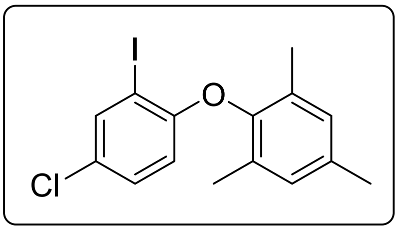
3-Iodo-4-(mesityloxy)-1,1'-biphenyl (10d)



Following GP5, the reaction of **9d** (49.4 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10d** (28.8 mg, 69.5 µmol, 70%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.30 (m, 2H), 6.94 (s, 2H), 6.37 (d, *J* = 8.5 Hz, 1H), 2.32 (s, 3H), 2.12 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 149.3, 139.5, 138.4, 136.5, 135.1, 130.9, 129.8, 129.0, 128.2, 127.3, 126.9, 113.1, 85.5, 21.0, 16.4. HRMS(ESI): *m/z* $[M+Na]^+$ calculated for $C_{21}H_{19}INaO^+$: 437.0373; found 437.0372. IR (ATR) $\tilde{\nu}$ = 3027, 2918, 2853, 1592, 1465, 1233, 1199, 1034, 1015, 854, 755.

2-(4-Chloro-2-iodophenoxy)-1,3,5-trimethylbenzene (10e)



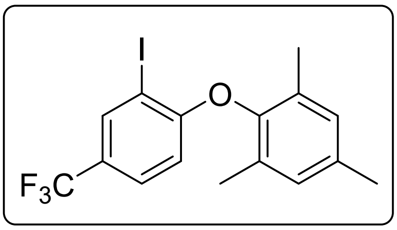
Following GP5, the reaction of **9e** (45.3 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10e** (28.7 mg, 77.0 µmol, 77%) as a colourless solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.4 Hz, 1H), 7.09 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.91 (s, 2H), 6.22 (d, *J* = 8.8 Hz, 1H), 2.30 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 149.1, 138.9, 135.3, 130.7, 129.9, 129.4, 127.0, 113.4, 85.2, 20.9, 16.3. HRMS(ESI): *m/z*

[M+Na]$^+$ calculated for $C_{15}H_{14}ClINaO^+$: 394.9670; found 394.9662. IR (ATR) $\tilde{\nu}$ = 2951, 2914, 2851, 2360, 2342, 1458, 1270, 1232, 1194, 1031, 816. Mp = 77-78 °C.

2-(2-Iodo-4-(trifluoromethyl)phenoxy)-1,3,5-trimethylbenzene (10f)

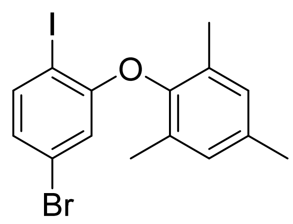
Following GP5, the reaction of **9f** (48.6 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10f** (20.6 mg, 50.7 µmol, 51%) as a colourless oil.



^{1}H NMR (601 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.39 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.93 (s, 2H), 6.36 (d, *J* = 8.6 Hz, 1H), 2.31 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 148.8, 137.1 (d, *J* = 3.8 Hz), 135.6, 130.6, 130.0, 127.0 (d, *J* = 3.8 Hz), 125.3 (q, *J* = 33.2 Hz), 123.3 (q, *J* = 271.9 Hz), 112.6, 84.8, 21.0, 16.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ -61.67 (s). HRMS(EI): *m/z* [M]$^{\cdot+}$ calculated for $C_{16}H_{14}F_3IO^+$: 406.0041; found 406.0034. IR (ATR) $\tilde{\nu}$ = 2951, 2919, 2859, 2360, 2342, 1601, 1478, 1316, 1120, 1036, 824.

2-(5-Bromo-2-iodophenoxy)-1,3,5-trimethylbenzene (10g)

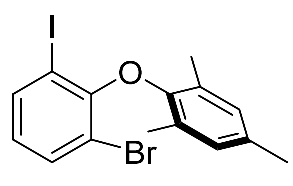
Following GP5, the reaction of **9g** (49.7 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10g** (29.0 mg, 69.5 µmol, 70%) as a colourless solid.



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 1H), 6.92 (s, 2H), 6.88 (dd, J = 8.3, 2.2 Hz, 1H), 6.41 (d, J = 2.1 Hz, 1H), 2.31 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 148.8, 140.6, 135.4, 130.6, 130.0, 126.4, 123.1, 116.2, 83.5, 21.0, 16.3. HRMS(EI): *m/z* [M]$^{\cdot+}$ calculated for $C_{15}H_{14}BrIO^+$: 415.9273; found 415.9266. IR (ATR) $\tilde{\nu}$ = 2914, 2859, 2360, 2342, 1587, 1464, 1386, 1306, 1218, 813, 700. Mp = 84-86 °C.

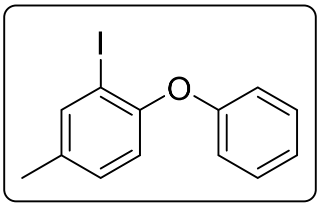
2-(2-bromo-6-iodophenoxy)-1,3,5-trimethylbenzene (10h)

Following GP5, the reaction of **9h** (49.7 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10h** (20.2 mg, 50.8 µmol, 51%) as a colourless solid.



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, J = 7.8, 1.6 Hz, 1H), 7.49 (dd, J = 8.0, 1.5 Hz, 1H), 6.80 (s, 2H), 6.66 (t, J = 7.9 Hz, 1H), 2.26 (s, 3H), 2.04 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.6, 150.7, 139.5, 134.7, 133.1, 130.0, 128.4, 125.5, 113.1, 90.1, 20.7, 17.9. HRMS(ESI): *m/z* [M+Na]$^+$ calculated for $C_{15}H_{14}IO^+$: 438.9165; found 438.9160. IR (ATR) $\tilde{\nu}$ = 2951, 2920, 2852, 2360, 2342, 1464, 1418, 1225, 1134, 857, 755. Mp = 97-99 °C.

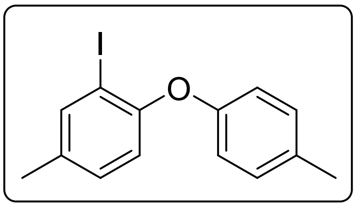
2-Iodo-4-methyl-1-phenoxybenzene (10i)



Following GP5, the reaction of **9k** (39.0 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10i** (28.3 mg, 91.3 µmol, 91%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.12 – 7.06 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 154.2, 140.2, 135.6, 130.5, 129.9, 123.2, 119.9, 118.0, 89.3, 20.4. MS(ESI): *m/z* = 311.0 [M+H]$^+$. IR (ATR) $\tilde{\nu}$ = 3038, 2920, 2852, 2360, 1587, 1475, 1236, 1198, 1037, 744, 688. The analytical data is in accordance with literature data.[8]

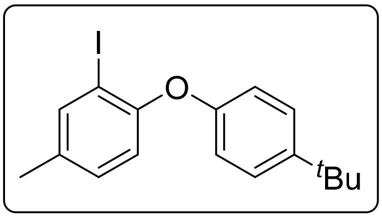
2-Iodo-4-methyl-1-(*p*-tolyloxy)benzene (10j)



Following GP5, the reaction of **9l** (40.4 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10j** (21.2 mg, 65.4 µmol, 65%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.1 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.09 – 7.05 (m, 1H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 154.6, 140.1, 135.2, 132.8, 130.4, 130.3, 119.3, 118.1, 88.9, 20.8, 20.3. MS(ESI): *m/z* = 325.3 [M+H]$^+$. IR (ATR) $\tilde{\nu}$ = 3027, 2919, 2861, 2733, 2361, 1505, 1476, 1237, 1199, 1036, 808. The analytical data is in accordance with literature data. [9]

1-(4-(Tert-butyl)phenoxy)-2-iodo-4-methylbenzene (10k)

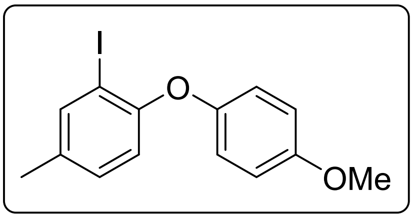


Following GP5, the reaction of **9m** (44.6 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10k** (20.0 mg, 54.6 µmol, 55%) as a colourless solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.37 – 7.28 (m, 2H), 7.11 – 7.03 (m, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 1H), 2.31 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.9, 154.5, 146.0, 140.0, 135.1, 130.3, 126.5, 119.3, 117.5, 88.8, 34.3, 31.5, 20.2.

HRMS(ESI): *m/z* $[M+Na]^+$ calculated for $C_{17}H_{19}INaO^+$: 389.0373; found 389.0364. IR (ATR) $\tilde{\nu}$ = 2958, 2934, 2855, 2360, 1896, 1591, 1478, 1238, 1104, 1035, 813. Mp = 83-85 °C.

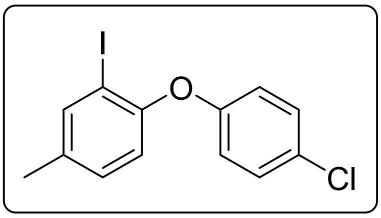
2-Iodo-1-(4-methoxyphenoxy)-4-methylbenzene (10l)



Following GP5, the reaction of **9n** (42.0 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane/EtOAc 100:1) the product **10l** (4.7 mg, 14 µmol, 14%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 9.1 Hz, 2H), 6.86 (d, *J* = 9.1 Hz, 2H), 6.69 (d, *J* = 8.3 Hz, 1H), 3.79 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 155.4, 150.8, 140.1, 134.8, 130.3, 120.0, 118.3, 115.0, 88.2, 55.8, 20.3. HRMS(ESI): m/z $[M+Na]^+$ calculated for $C_{14}H_{13}INaO_2^+$: 362.9853; found 362.9845. IR (ATR) $\tilde{\nu}$ = 2922, 2852, 2833, 2360, 1502, 1476, 1226, 1195, 1035, 828.

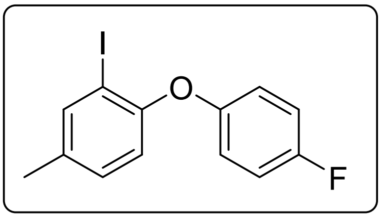
1-(4-Chlorophenoxy)-2-iodo-4-methylbenzene (10m)



Following GP5, the reaction of **9o** (42.5 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10m** (32.3 mg, 93.7 µmol, 94%) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.29 – 7.24 (m, 2H), 7.14 – 7.09 (m, 1H), 6.88 – 6.81 (m, 3H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 153.7, 140.4, 136.2, 130.6, 129.8, 128.1, 120.2, 119.0, 89.3, 20.4. HRMS(ESI): m/z $[M+Na]^+$ calculated for $C_{13}H_{10}ClINaO^+$: 366.9357; found 366.9350. IR (ATR) $\tilde{\nu}$ = 3023, 2920, 2853, 2361, 1585, 1474, 1237, 1089, 884, 820.

1-(4-Fluorophenoxy)-2-iodo-4-methylbenzene (10n)

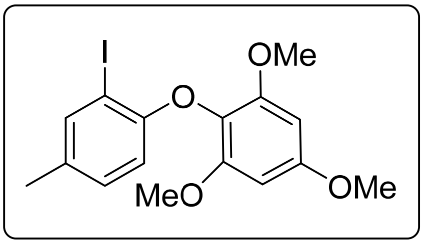


Following GP5, the reaction of **9p** (40.8 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane) the product **10n** (17.0 mg, 51.8 µmol, 52%) as a colourless oil.

^{1}H NMR (601 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.12 – 7.07 (m, 1H), 7.03 – 6.98 (m, 2H), 6.93 – 6.88 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8 (d, *J* =

241.3 Hz), 154.5, 153.3 (d, J = 2.6 Hz), 140.3, 135.6, 130.5, 119.5 (d, J = 8.2 Hz), 119.3, 116.4 (d, *J* = 23.4 Hz), 88.8, 20.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ -120.54 (tt, *J* = 8.3, 4.4 Hz). HRMS(EI): m/z [M]$^{•+}$ calculated for $C_{13}H_{10}OFI^+$: 327.9760; found 327.9755. IR (ATR) $\tilde{\nu}$ = 2922, 2853, 1499, 1476, 1248, 1217, 1187, 1037.

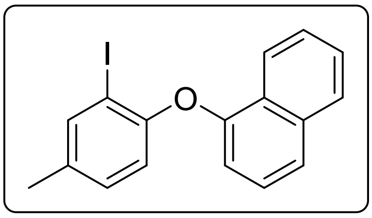
2-(2-Iodo-4-methylphenoxy)-1,3,5-trimethoxybenzene (10o)



Following GP5, the reaction of **9i** (48.0 mg) gave after a reaction time of 24 h and column chromatography (DCM/MeOH 10:1) the product **10o** (28.0 mg, 70.0 µmol, 70%) as a brown solid.

^{1}H NMR (601 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 6.26 – 6.22 (m, 3H), 3.92 (s, 3H), 3.84 (s, 6H), 2.11 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 161.4, 161.0, 132.7, 124.8, 124.0, 116.3, 116.1, 91.5, 78.1, 56.8, 56.0, 20.7. HRMS(ESI): *m/z* [M+H]$^+$ calculated for $C_{16}H_{18}IO_4^+$: 401.0244; found 401.0240. IR (ATR) $\tilde{\nu}$ = 3007, 2939, 2841, 2360. 2342, 1577, 1466, 1341, 1226, 1205, 1118, 808. Mp = 113-116 °C.

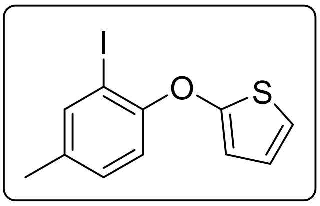
1-(2-Iodo-4-methylphenoxy)naphthalene (10p)



Following GP5, the reaction of **9r** (44.0 mg) gave after a reaction time of 24 h and column chromatography (cyclohexane/EtOAc 4:1) the product **10p** (34.4 mg, 95.5 µmol, 96%) as a colourless oil.

^{1}H NMR (601 MHz, $CDCl_3$) δ 8.33 – 8.23 (m, 1H), 7.92 – 7.84 (m, 1H), 7.78 – 7.71 (m, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.84 – 6.75 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 153.1, 140.3, 135.5, 135.1, 130.5, 127.8, 126.8, 126.4, 126.1, 125.8, 123.2, 122.4, 119.4, 111.9, 88.8, 20.4. HRMS(ESI): m/z [M+Na]$^+$ calculated for $C_{17}H_{13}INaO^+$: 382.9903; found 382.9896. IR (ATR) $\tilde{\nu}$ = 3051, 2919, 1595, 1574, 1477, 1388, 1258, 1235, 1079, 1043, 766.

2-(2-Iodo-4-methylphenoxy)thiophene (10q)



Following GP5, the reaction of **9j** (39.6 mg) gave after a reaction time of 24 h and column chromatography (DCM/MeOH 10:1) the product **10q** (19.4 mg, 61.4 µmol, 61%) as a colourless solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (dd, J = 5.3, 1.1 Hz, 1H), 7.64 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.14 (dd, *J* = 5.3, 3.6 Hz, 1H), 7.03 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 6.49 (s, 1H), 2.13 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 140.3, 136.0, 133.7, 129.9, 126.3, 125.3, 121.0, 116.1, 94.9, 20.7. HRMS(ESI): *m/z* $[M+H]^+$ calculated for $C_{11}H_{10}IOS^+$: 316.9492; found 316.9489. IR (ATR) $\tilde{\nu}$ = 2915, 2852, 1566, 1455, 1383, 1222, 1197, 1017, 888, 793. Mp = 103-105 °C.

5. References

1 W. L. F. Armarego, *Purification of Laboratory Chemicals*, Elsevier Science & Technology, Jordan Hill, 6th edn., 2009.
2 M. Damrath, L. D. Caspers, D. Duvinage and B. J. Nachtsheim, *Org. Lett.*, 2022, **24**, 2562–2566.
3 J. H. Kuhlmann, M. Uygur and O. García Mancheño, *Org. Lett.*, 2022, **24**, 1689–1694.
4 M. J. Harper, E. J. Emmett, J. F. Bower and C. A. Russell, *J. Am. Chem. Soc.*, 2017, **139**, 12386–12389.
5 H. Bloux, A. Dahiya, A. Hébert, F. Fabis, F. Schoenebeck and T. Cailly, *Chem. Eur. J.*, 2023, **29**, e202203366.
6 I. Mosiagin, A. J. Fernandes, A. Budinská, L. Hayriyan, K. E. O. Ylijoki and D. Katayev, *Angew. Chem. Int. Ed.*, 2023, **62**, e202310851.
7 J. E. Leffler and H. Jeffe, *J. Org. Chem.*, 1973, **38**, 2719–2721.
8 H. Chen, J. Han and L. Wang, *Angew. Chem. Int. Ed.*, 2018, **57**, 12313–12317.
9 L. F. Tietze, B. Waldecker, D. Ganapathy, C. Eichhorst, T. Lenzer, K. Oum, S. O. Reichmann and D. Stalke, *Angew. Chem. Int. Ed.*, 2015, **54**, 10317–10321.

6. NMR-Spectra

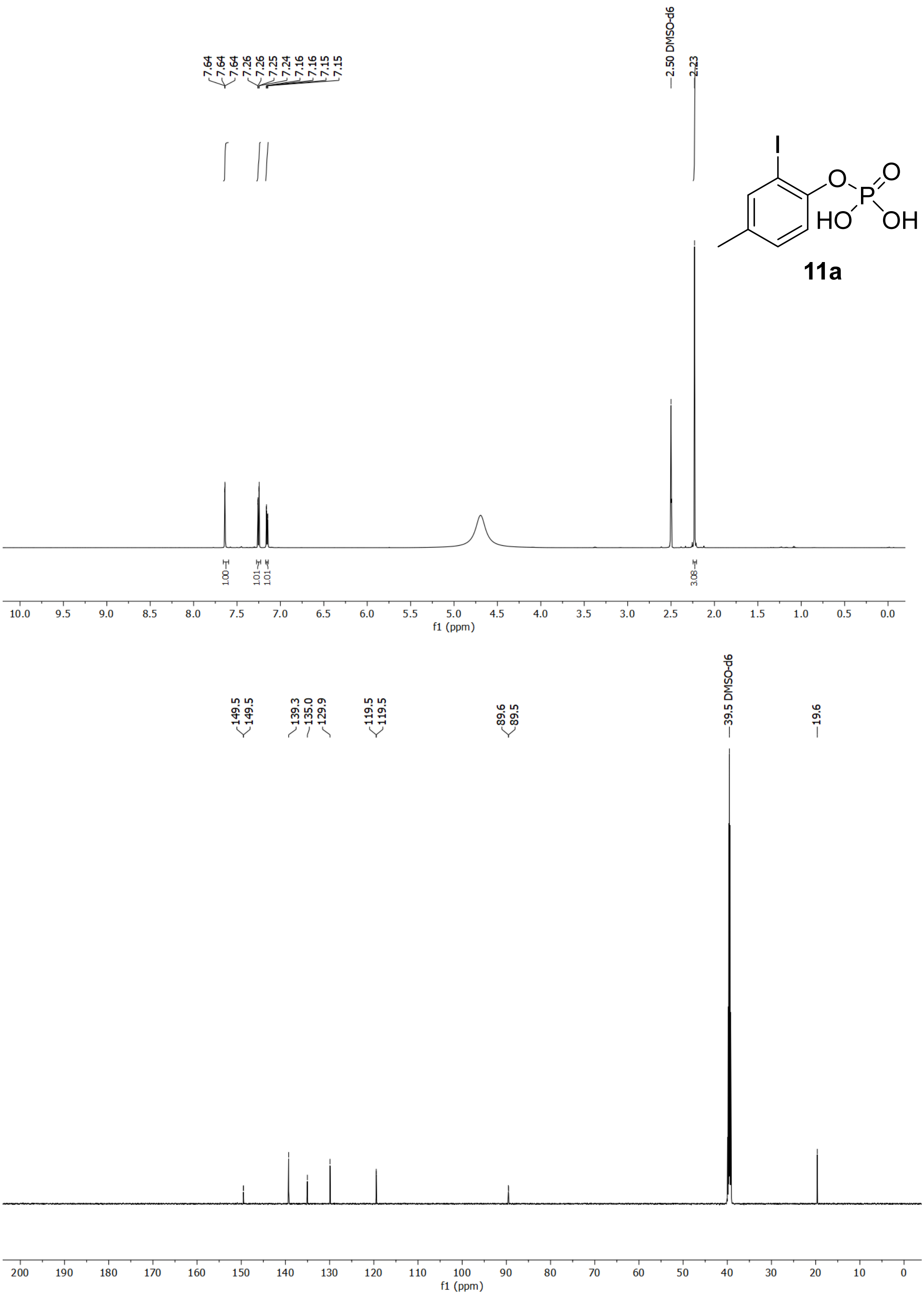


Figure 1: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectra of **11a** in DMSO-*d6*.

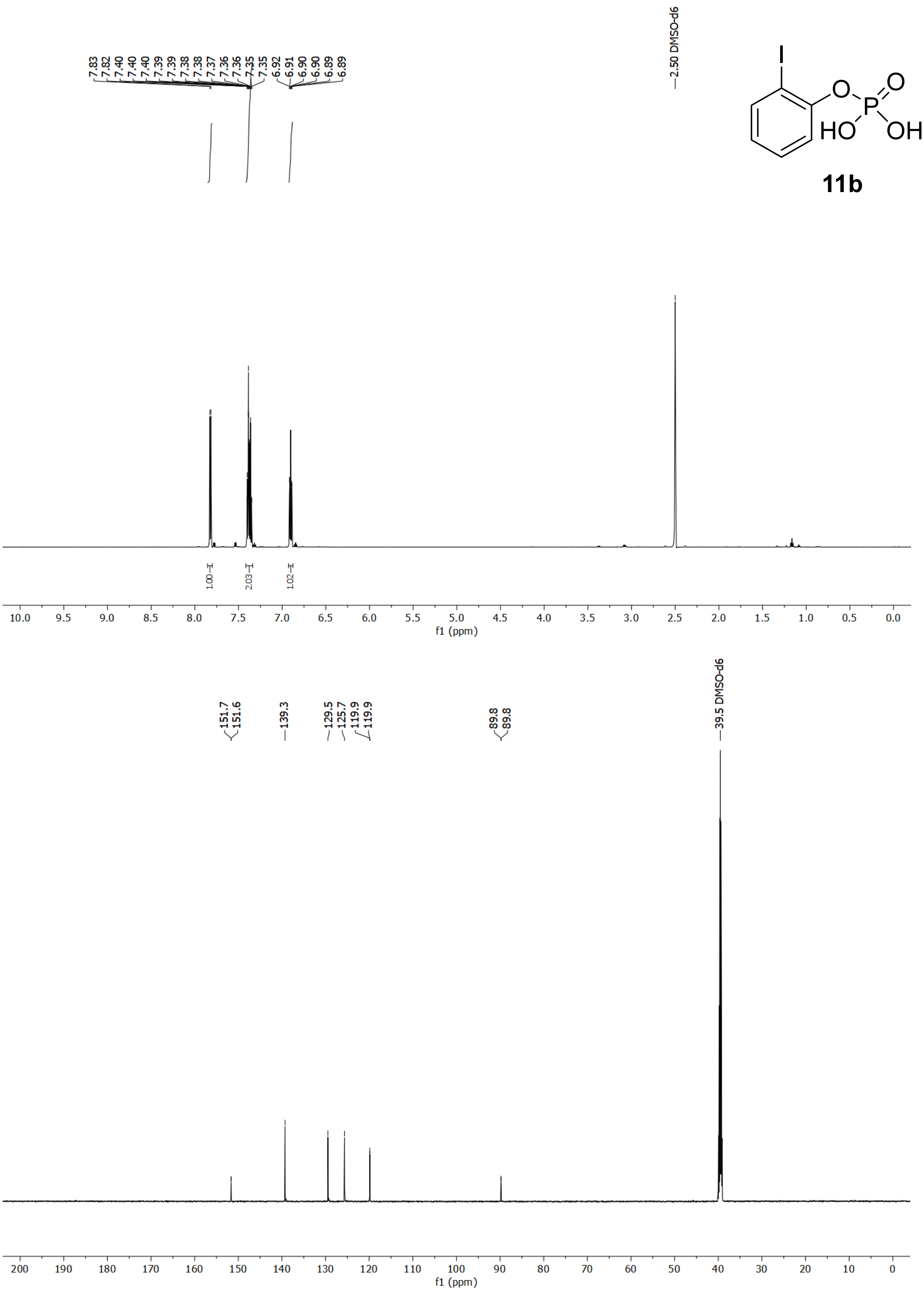


Figure 2: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **11b** in DMSO-*d6*.

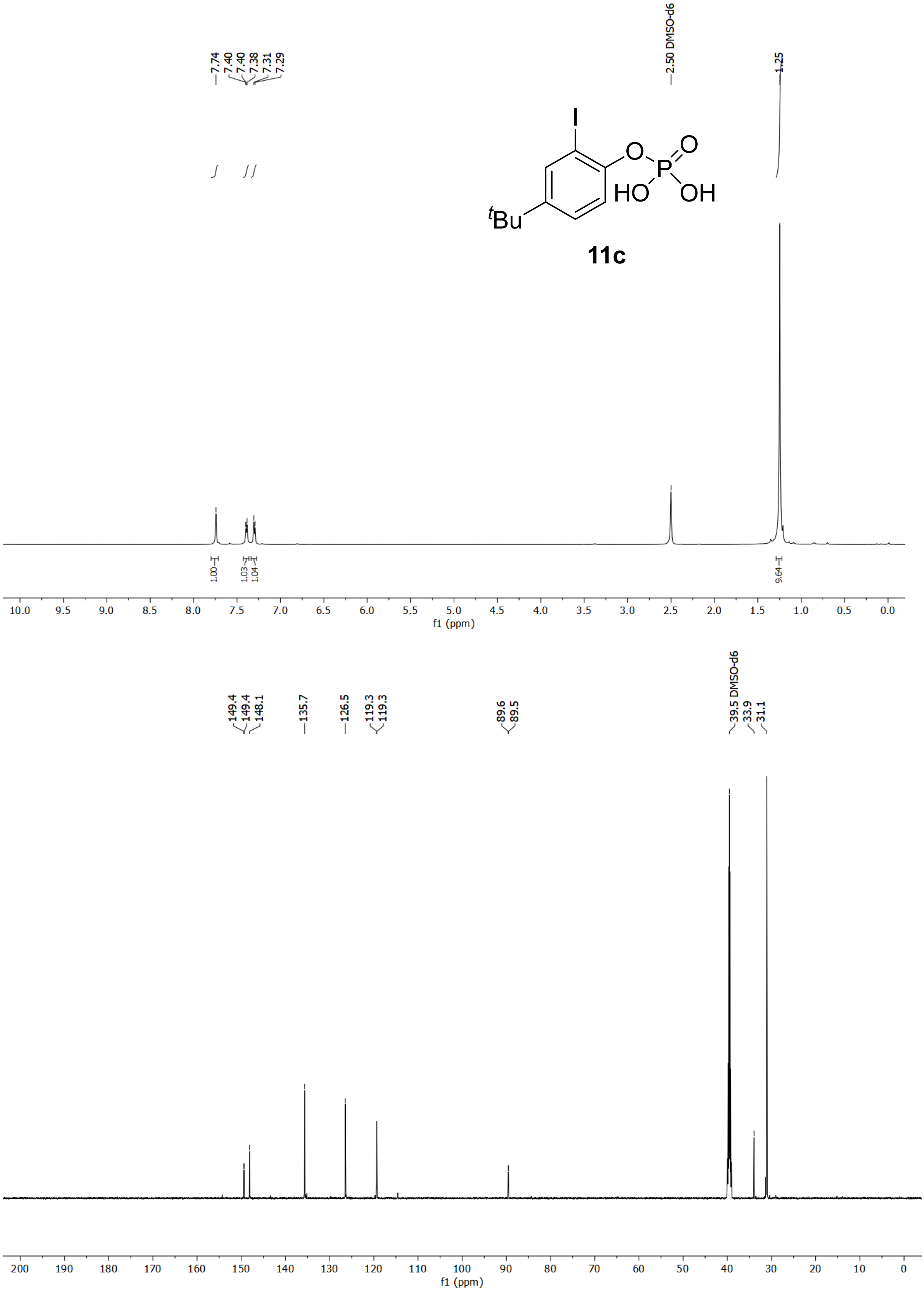
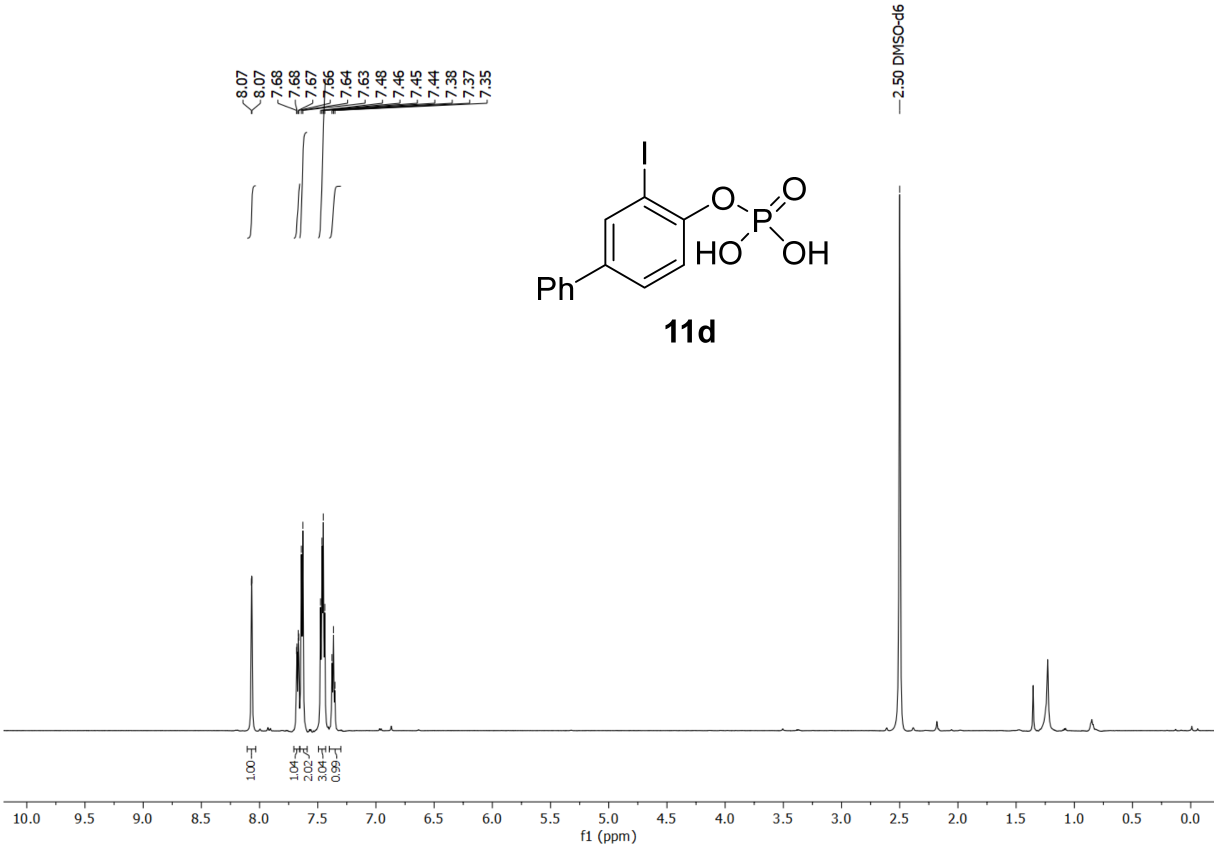


Figure 3: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectra of **11c** in DMSO-*d6*.



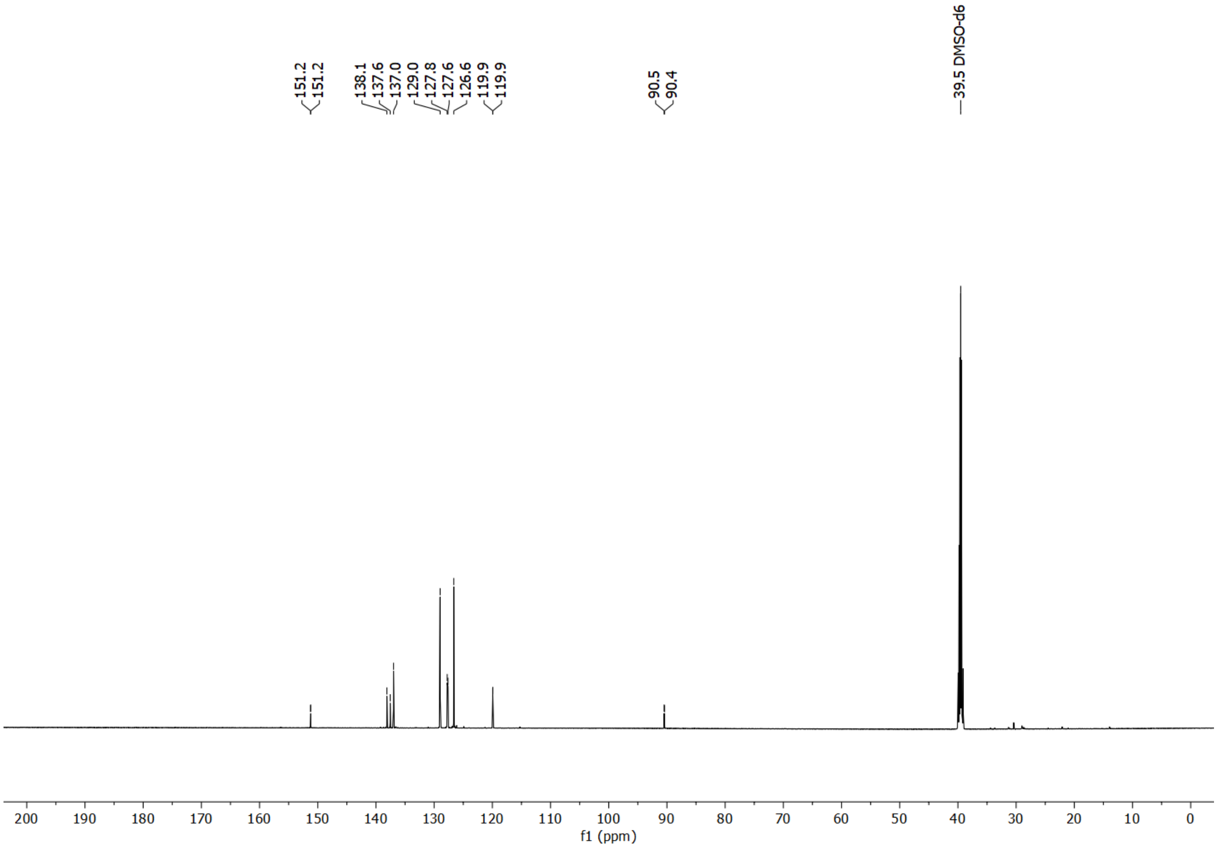


Figure 4: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **11d** in DMSO-*d6.*

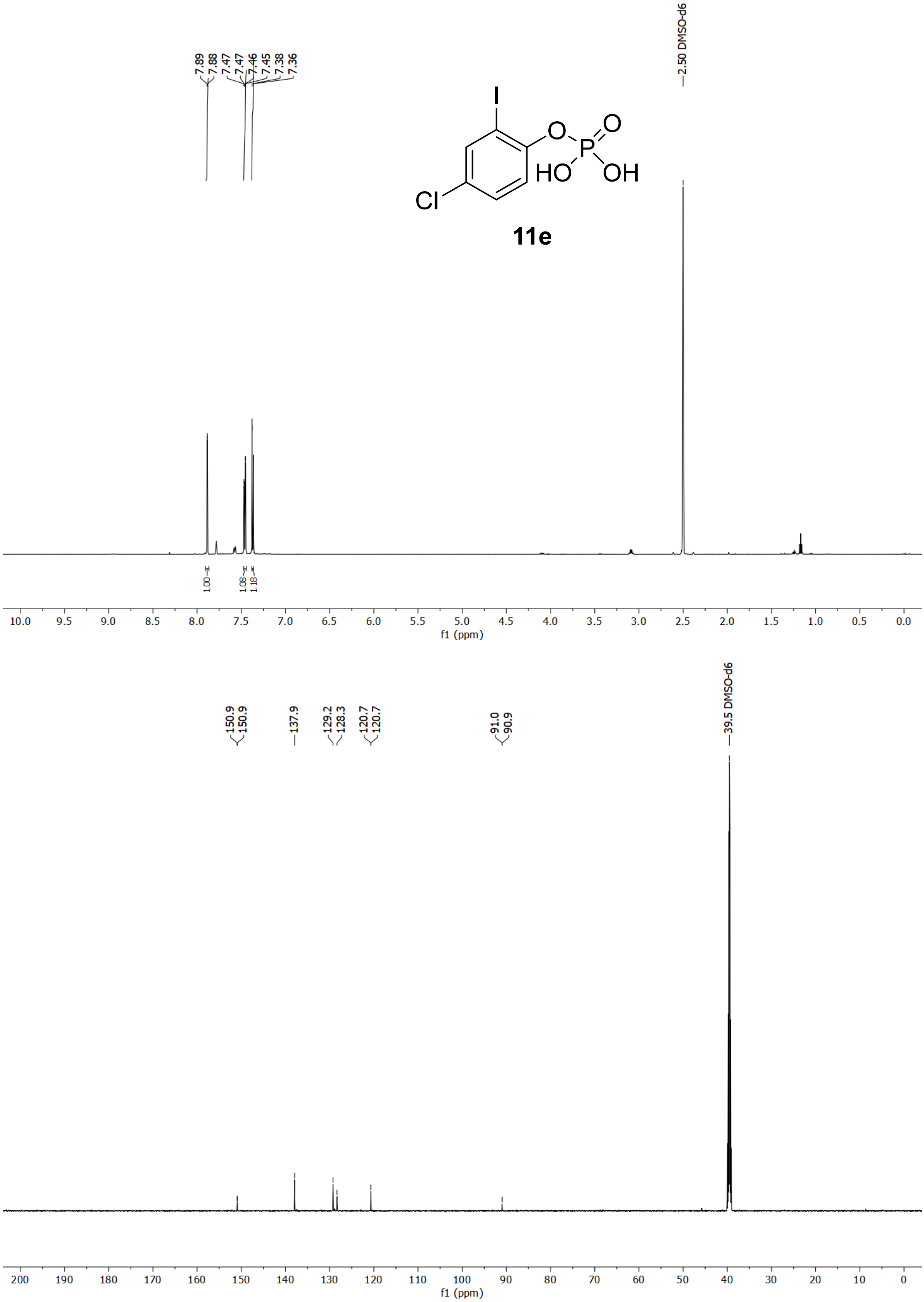


Figure 5: 601 MHz [1]H- and 151 MHz [13]C-NMR-spectrum of **11e** in DMSO-*d6.*

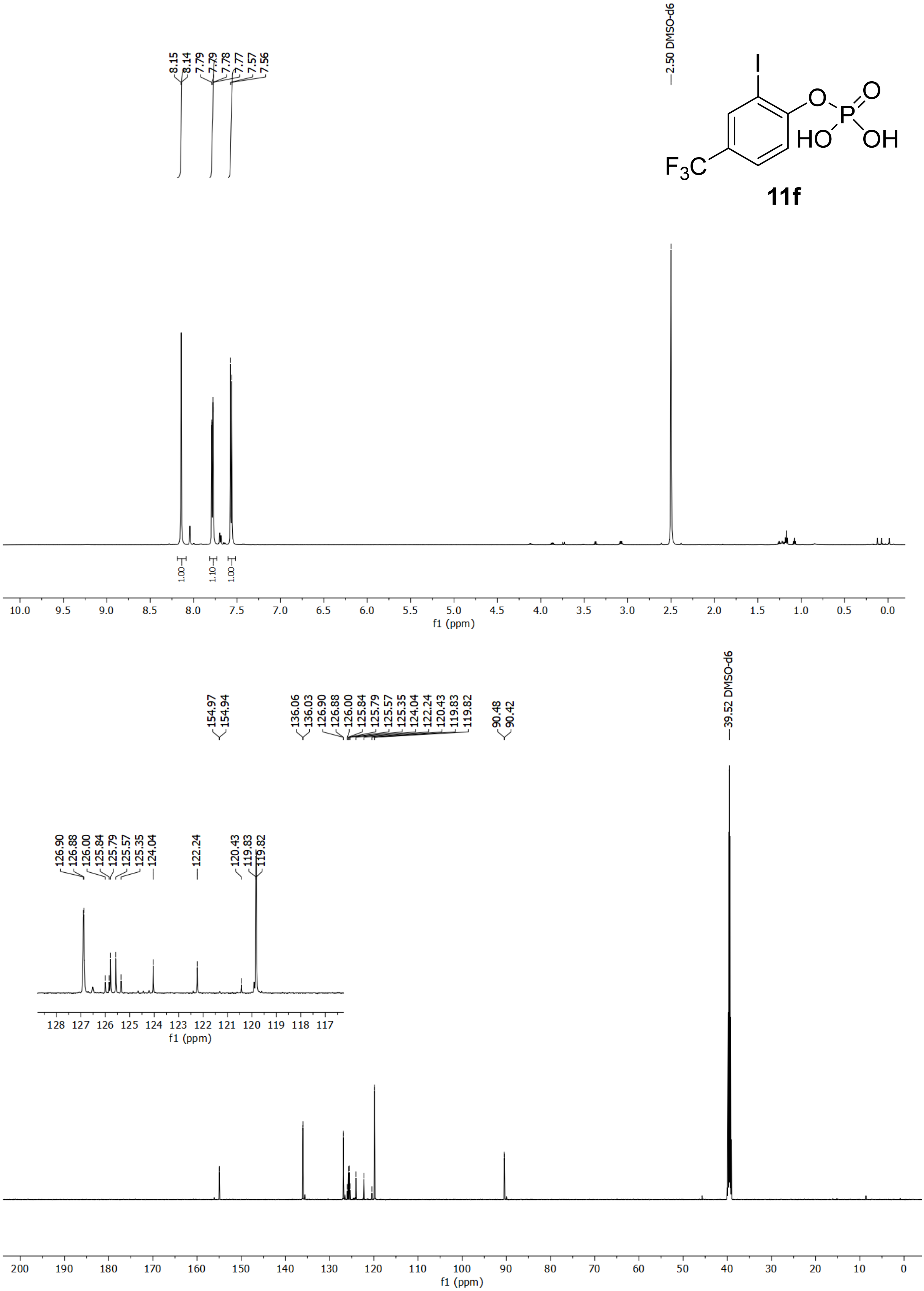


Figure 6: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **11f** in DMSO-*d6*.

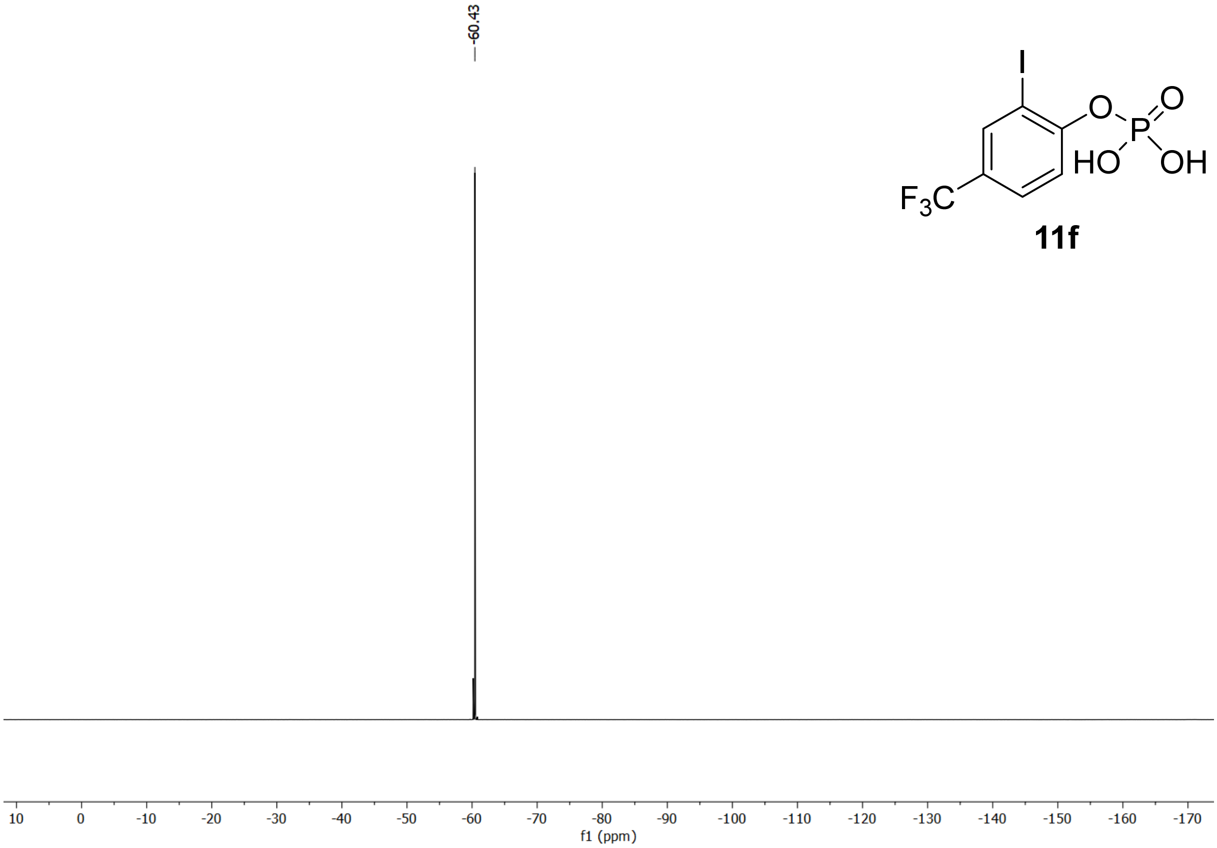
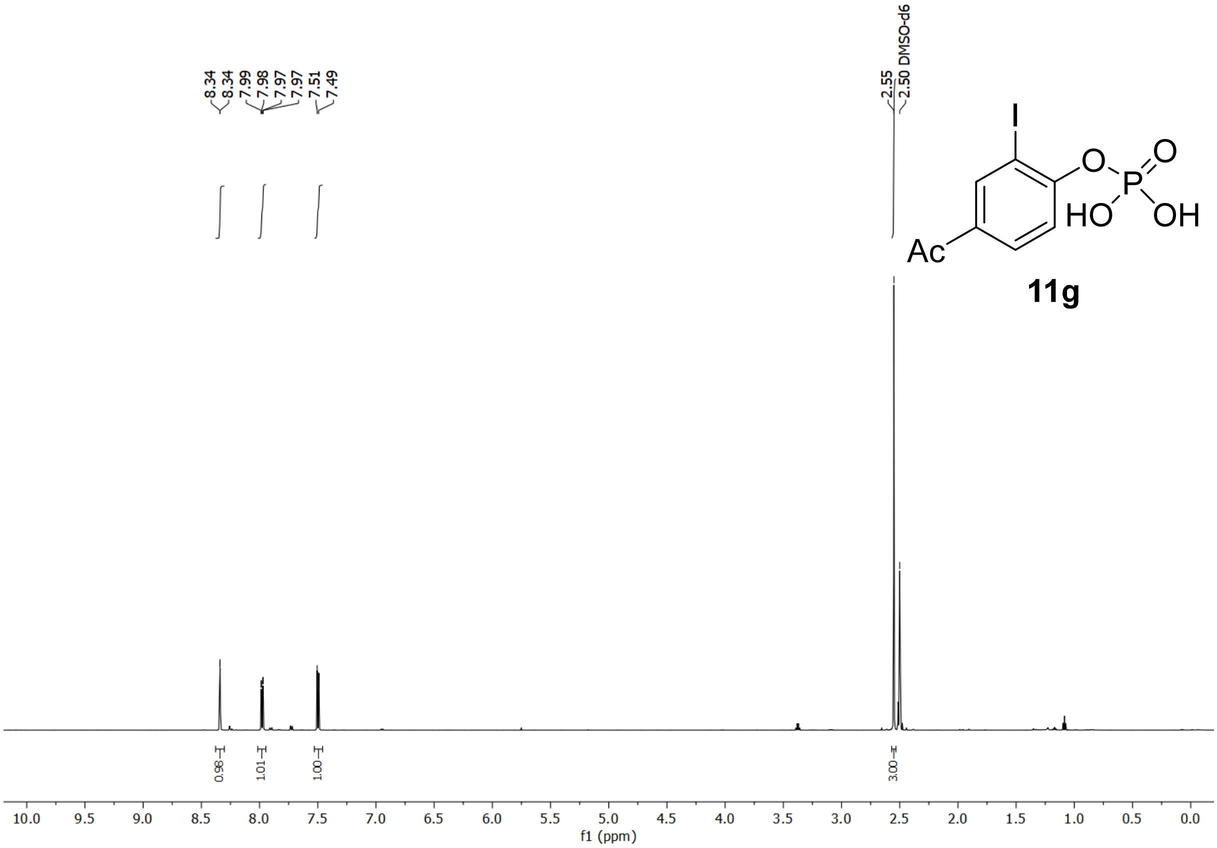


Figure 7: 565 MHz 19F-NMR-spectrum of **11f** in DMSO-*d*6.



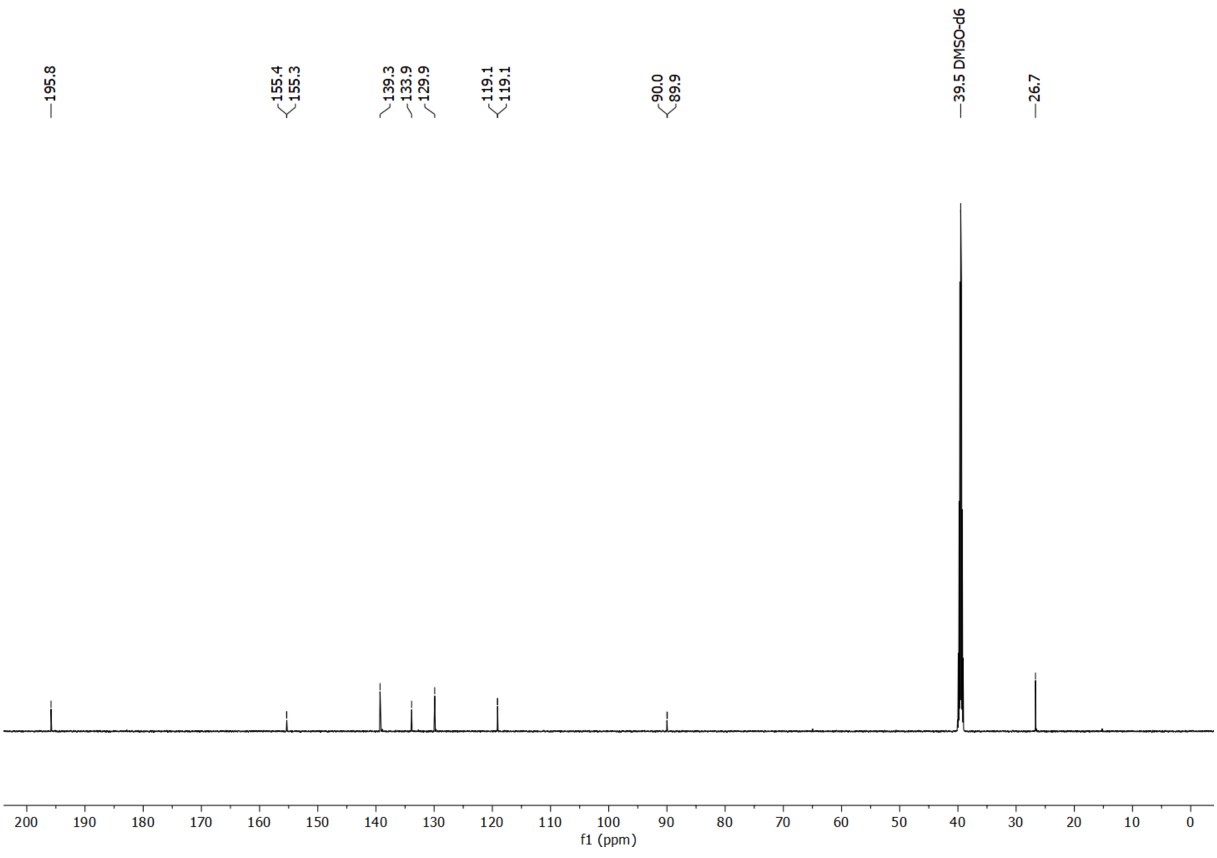
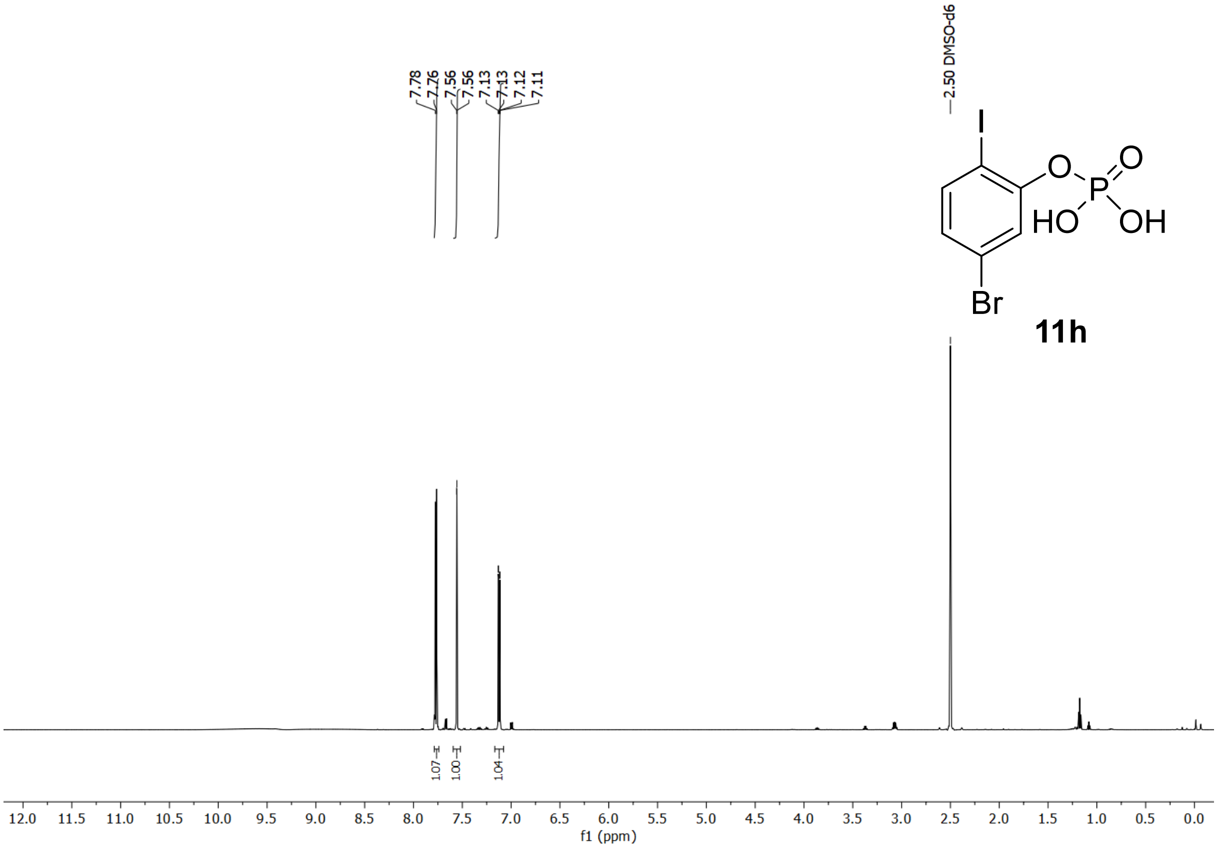


Figure 8: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **11g** in DMSO-*d6.*



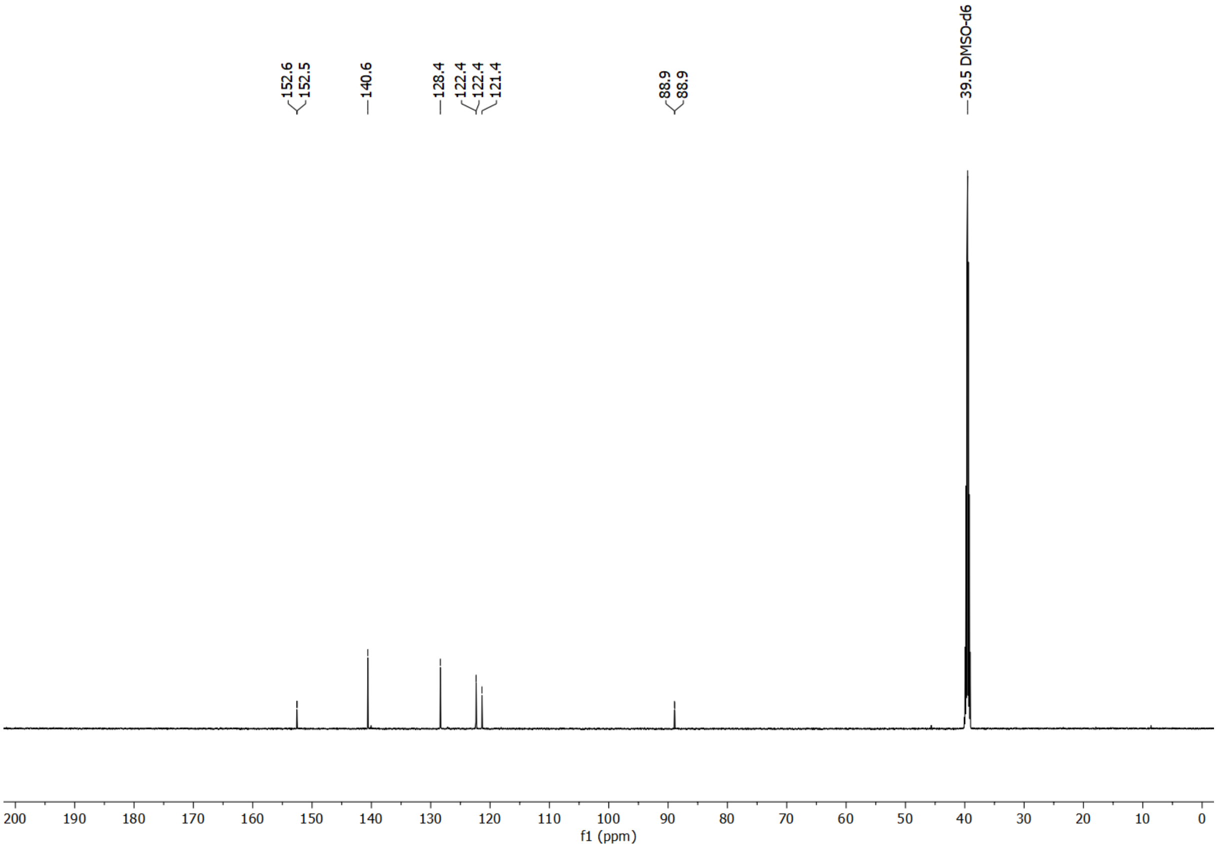


Figure 9: 601 MHz [1]H- and 151 MHz [13]C-NMR-spectrum of **11h** in DMSO-*d6.*

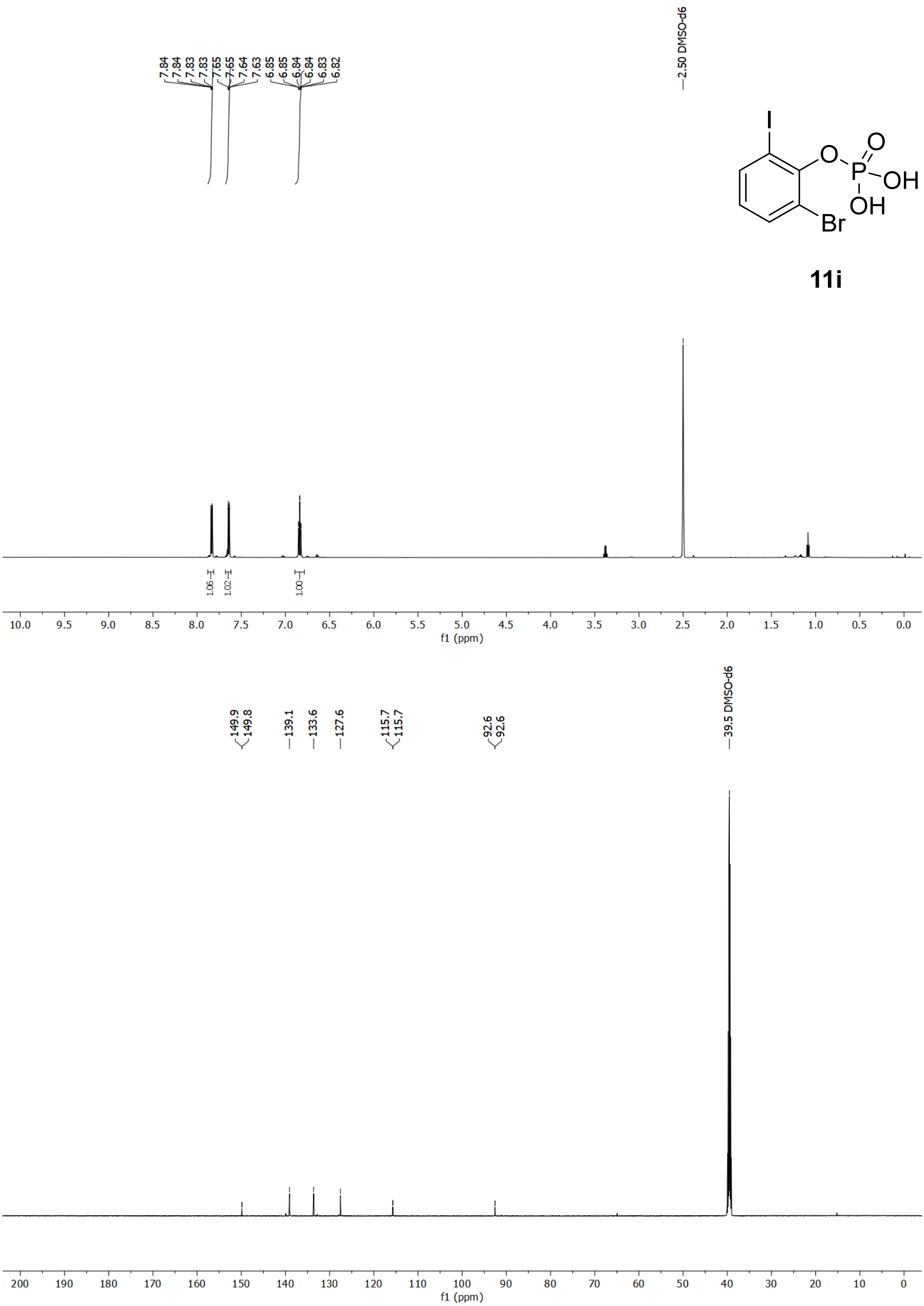


Figure 10: 600 MHz ¹H- and 151 MHz ¹³C-NMR-spectrum of **11i** in DMSO-*d6*.

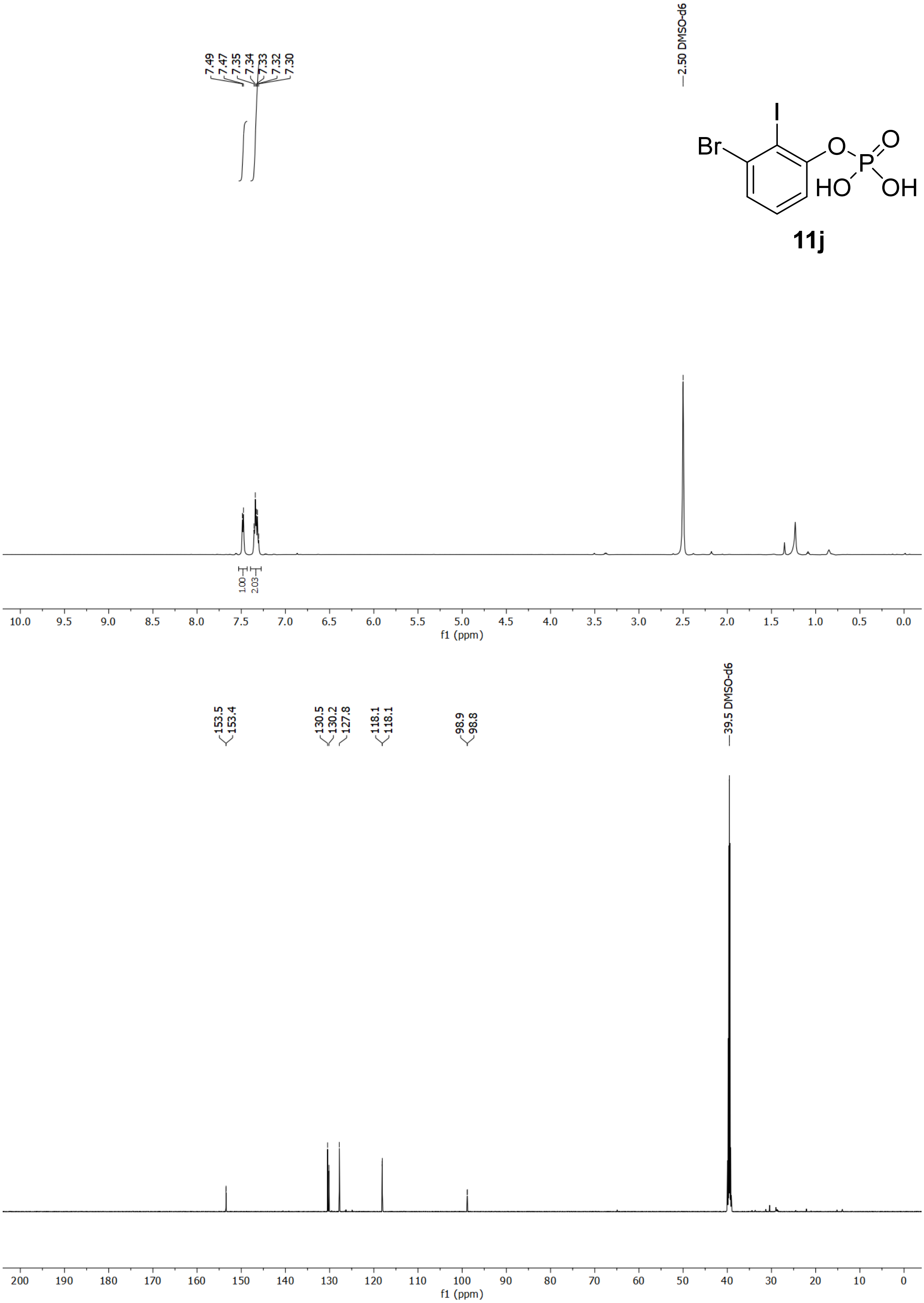


Figure 11: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **11j** in DMSO-*d6.*

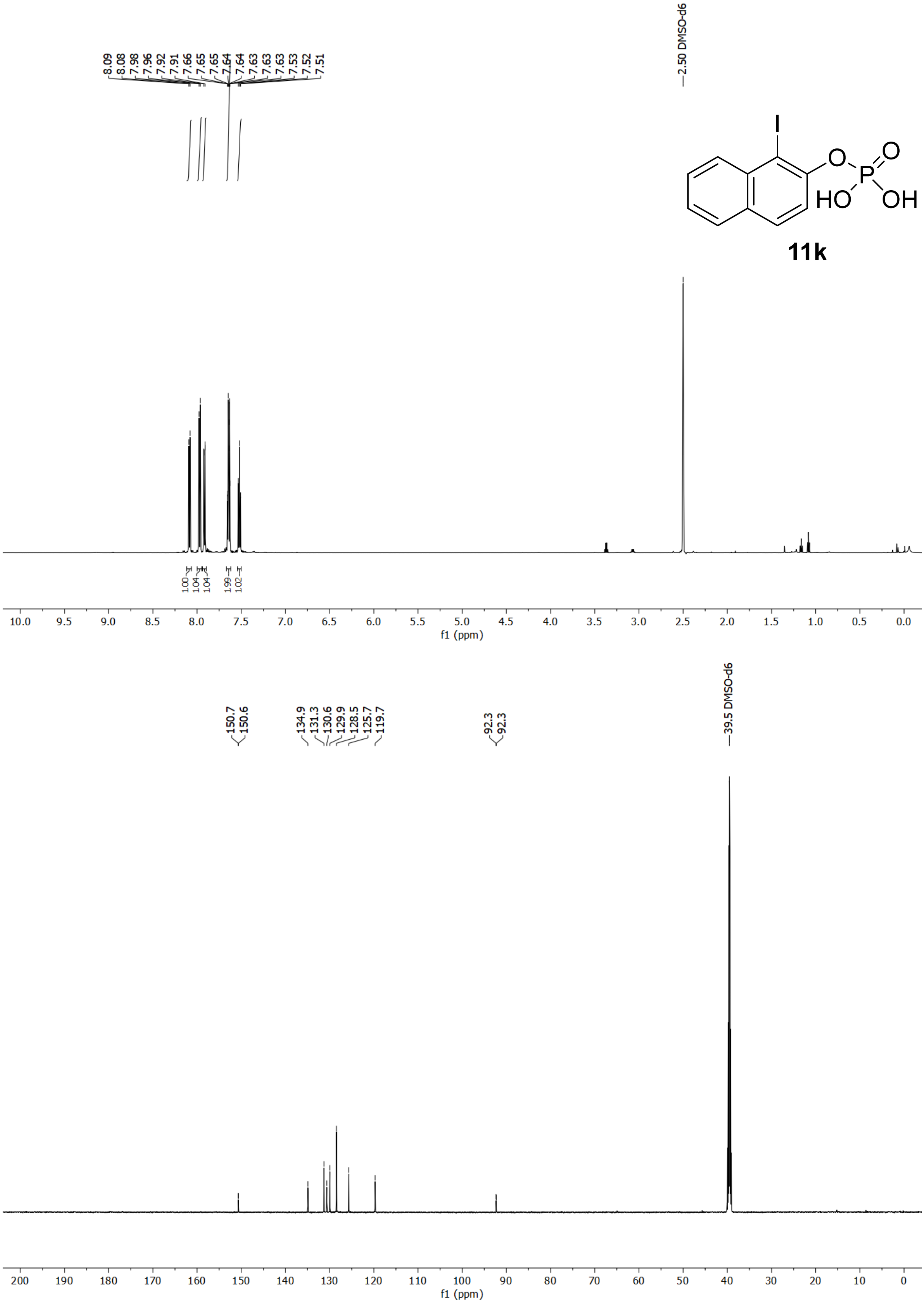


Figure 12: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **11k** in DMSO-*d6.*

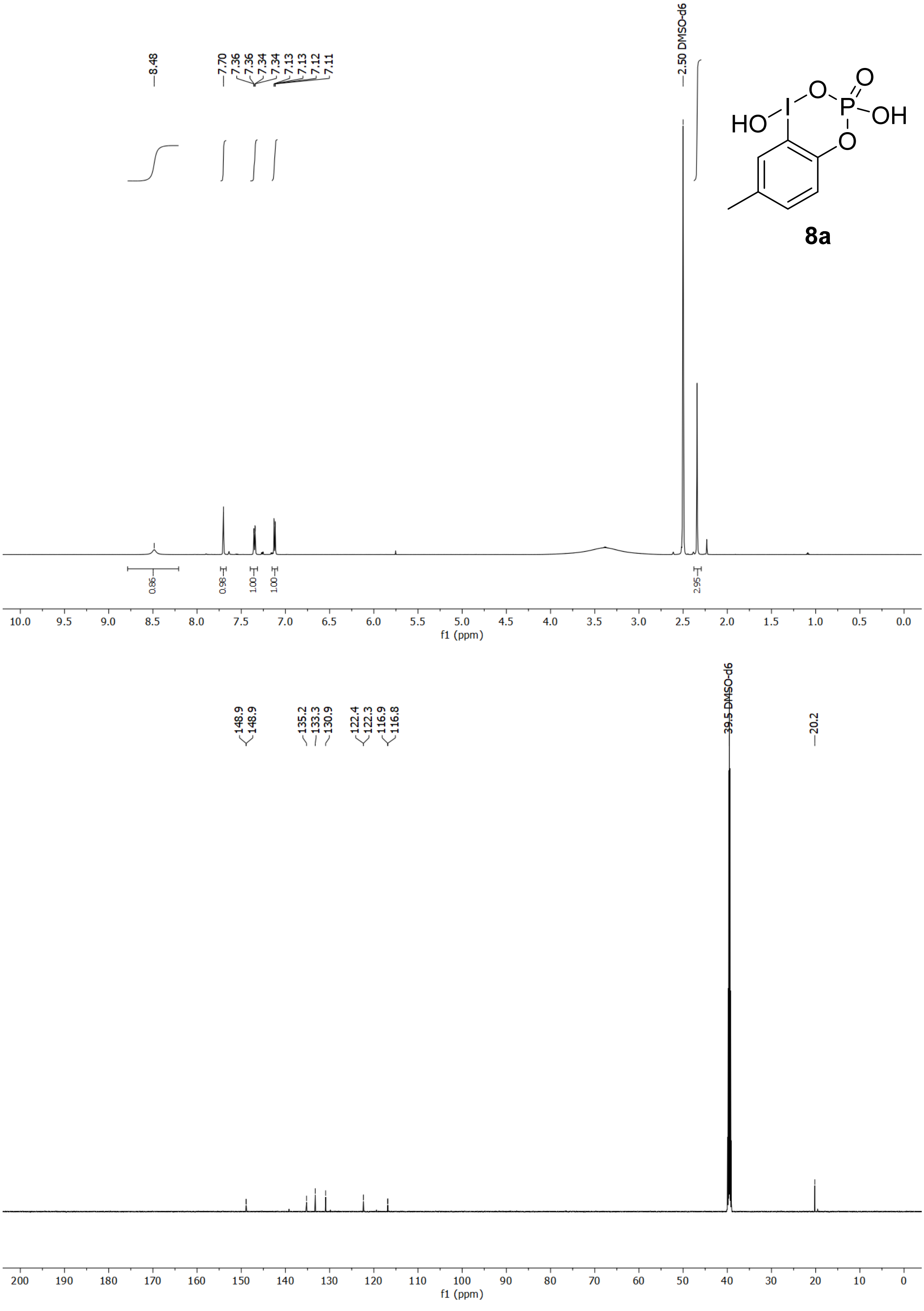
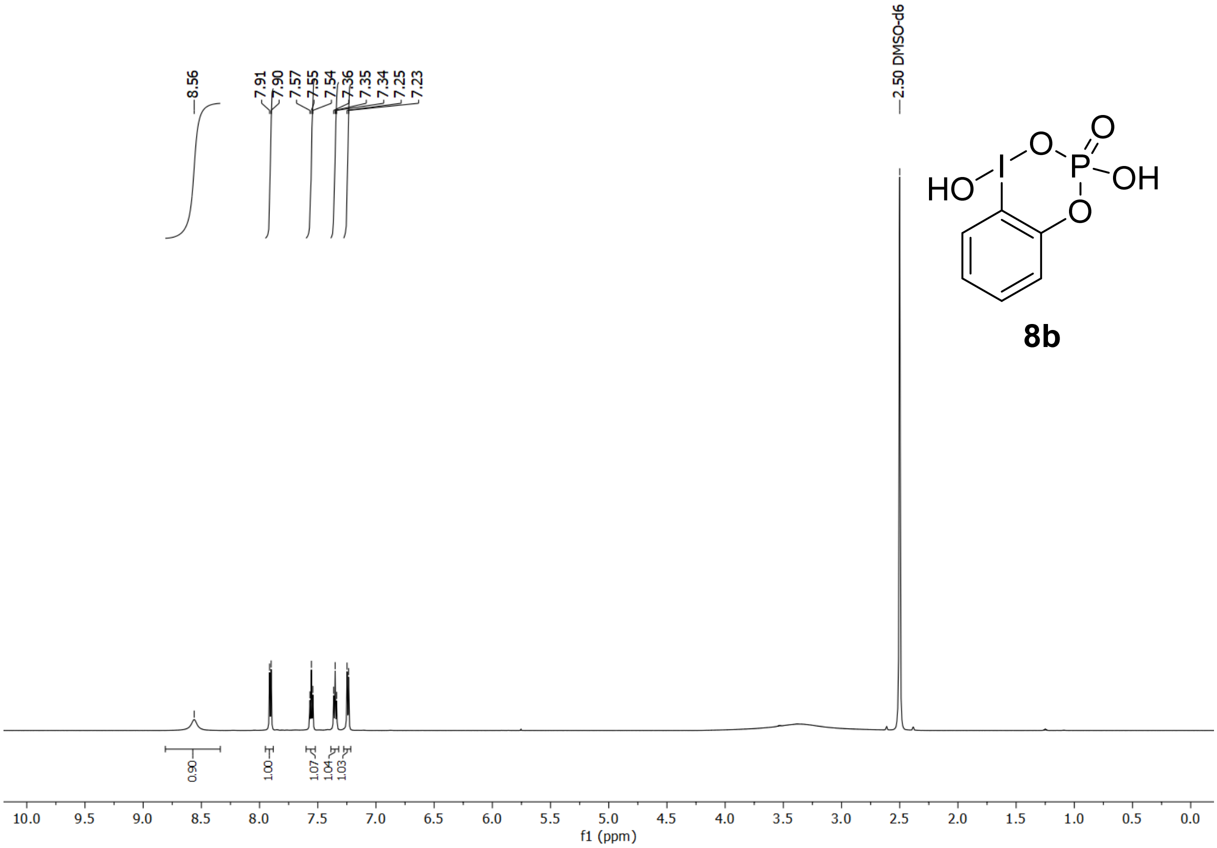


Figure 13: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **8a** in DMSO-*d6.*



8b

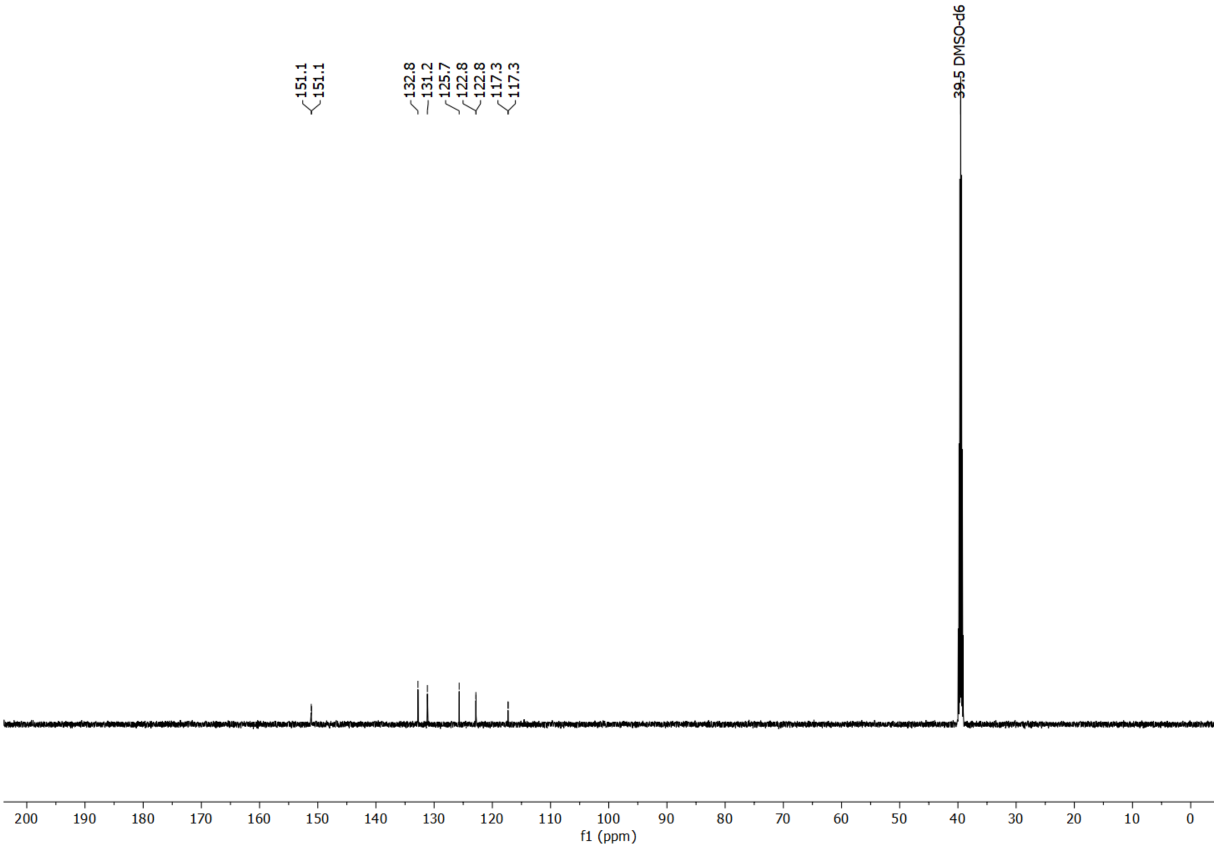


Figure 14: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **8b** in DMSO-*d6*.

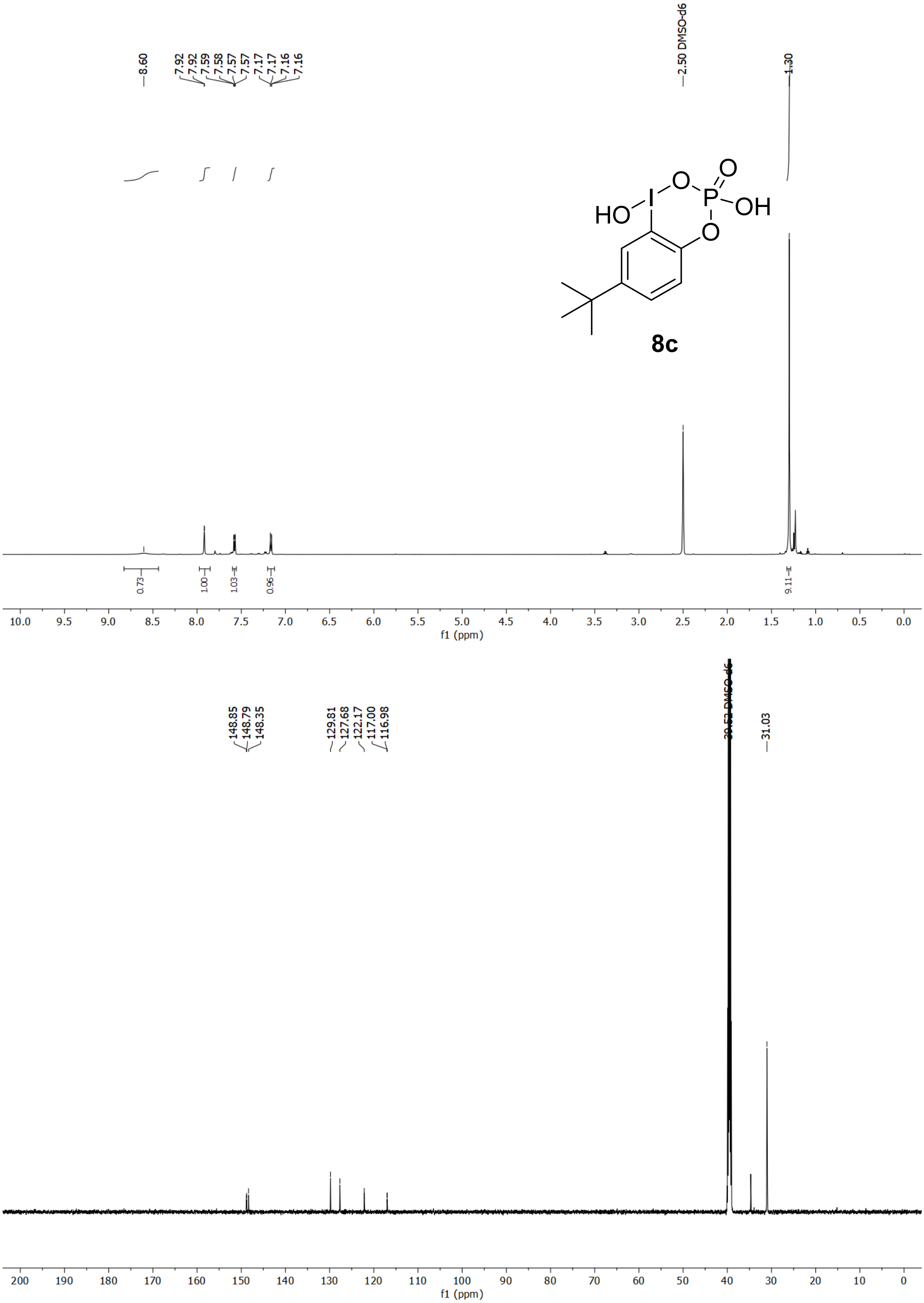


Figure 15: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **8c** in DMSO-*d6.*

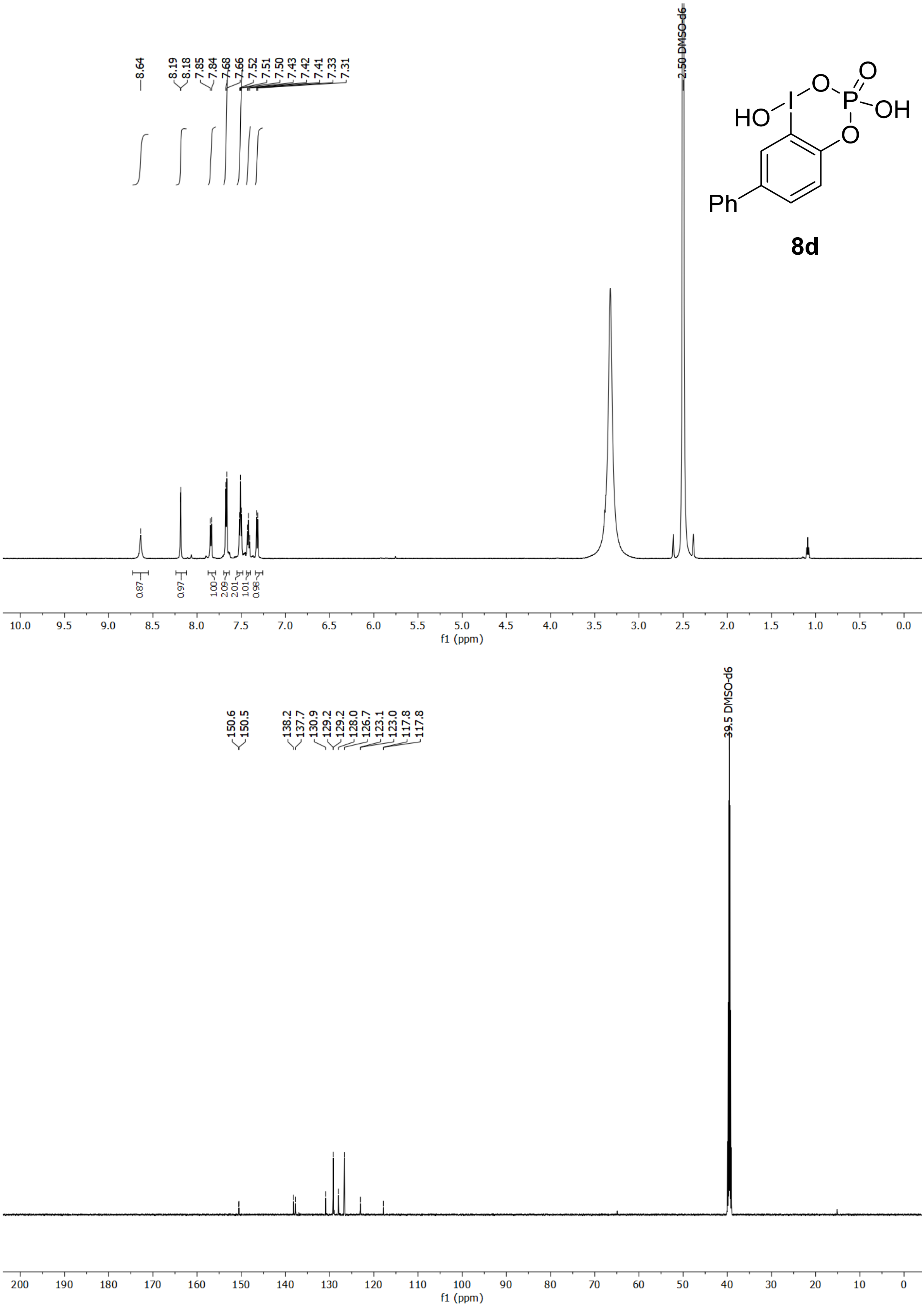


Figure 16: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **8d** in DMSO-*d6.*

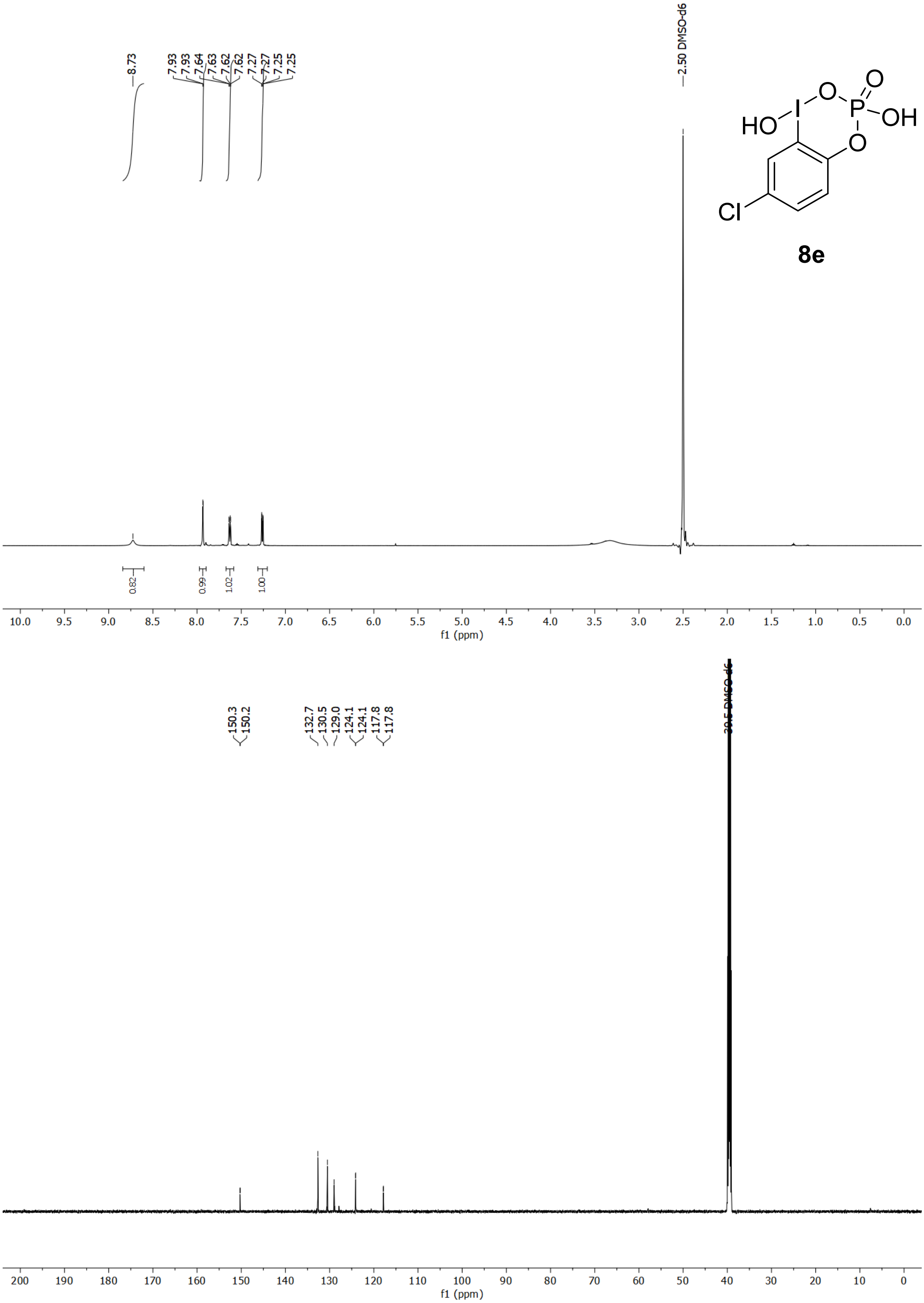


Figure 17: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **8e** in DMSO-*d6.*

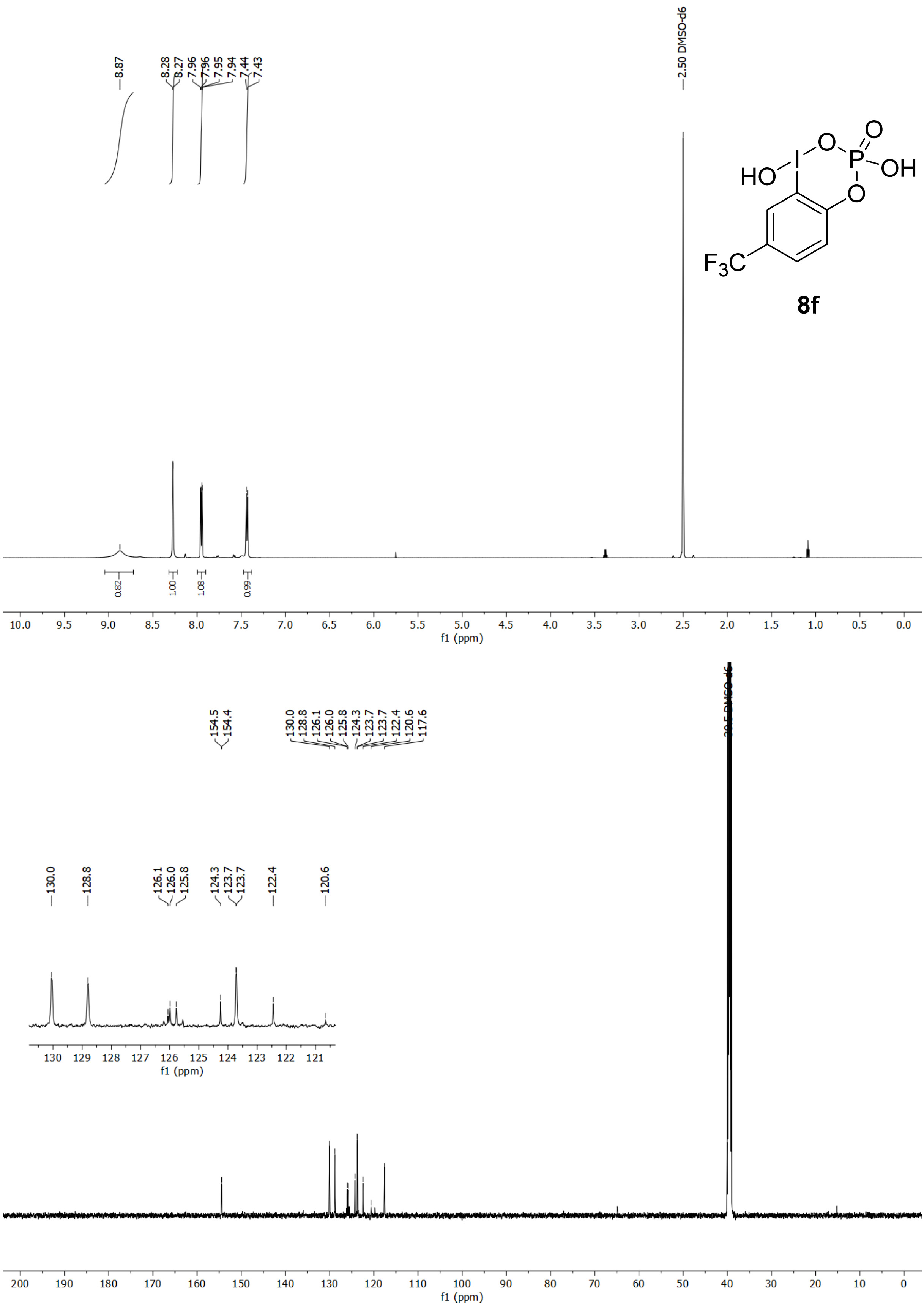


Figure 18: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **8f** in DMSO-*d6*.

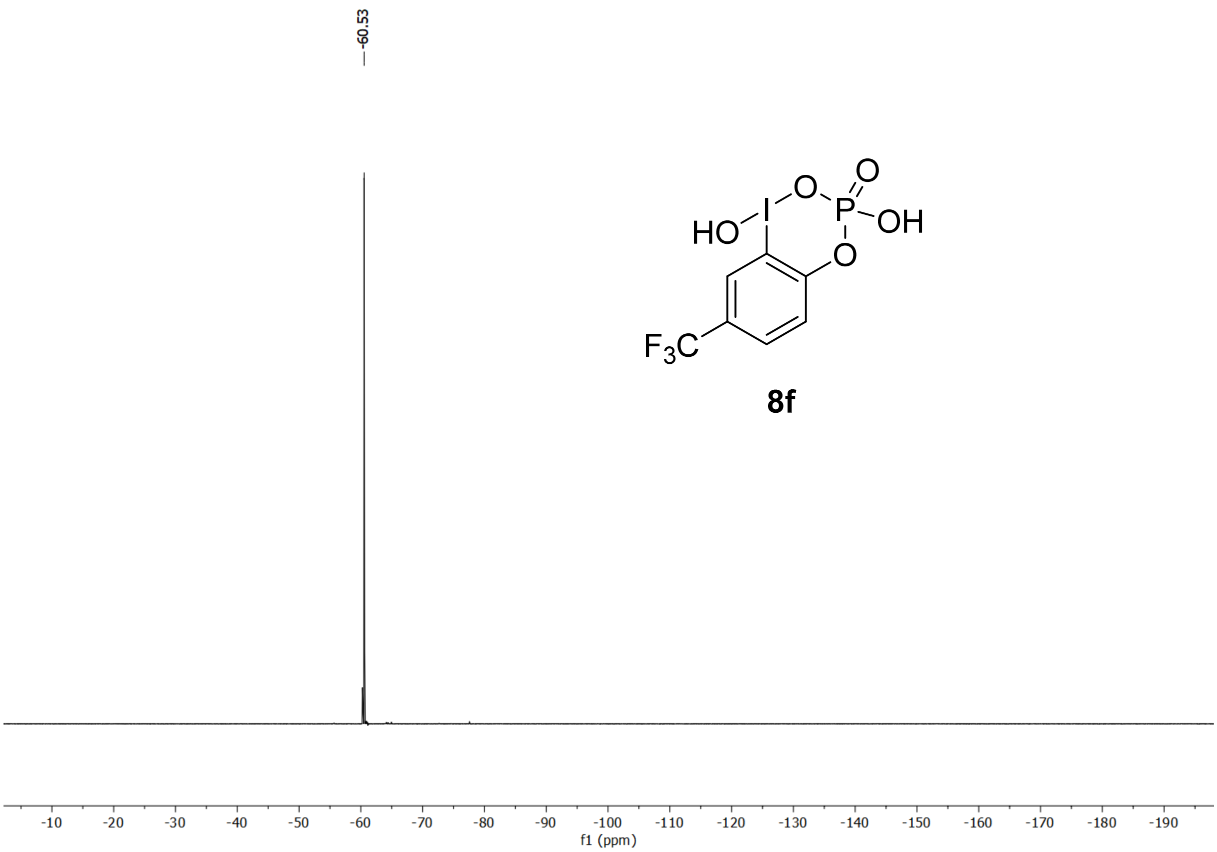
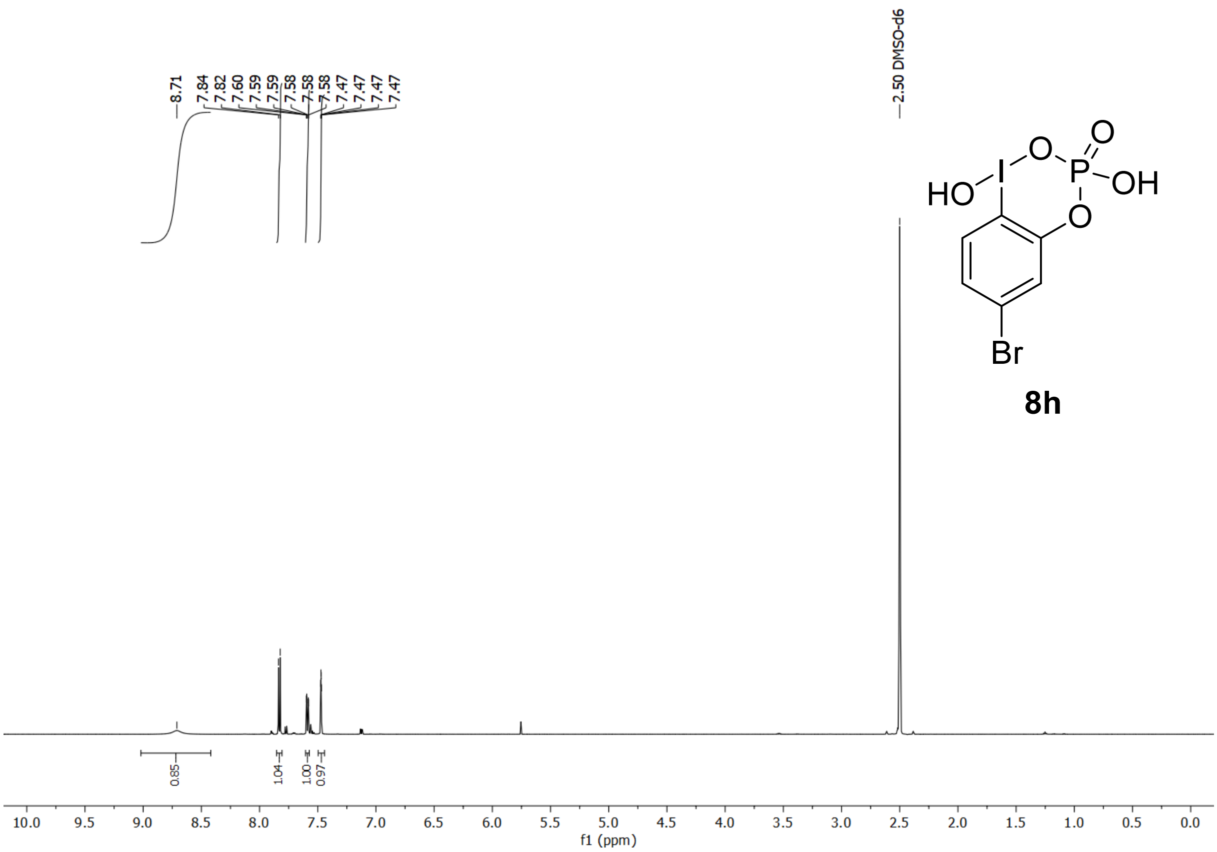


Figure 19: 565 MHz ^{19}F-NMR-spectrum of **8f** in DMSO-*d6*.



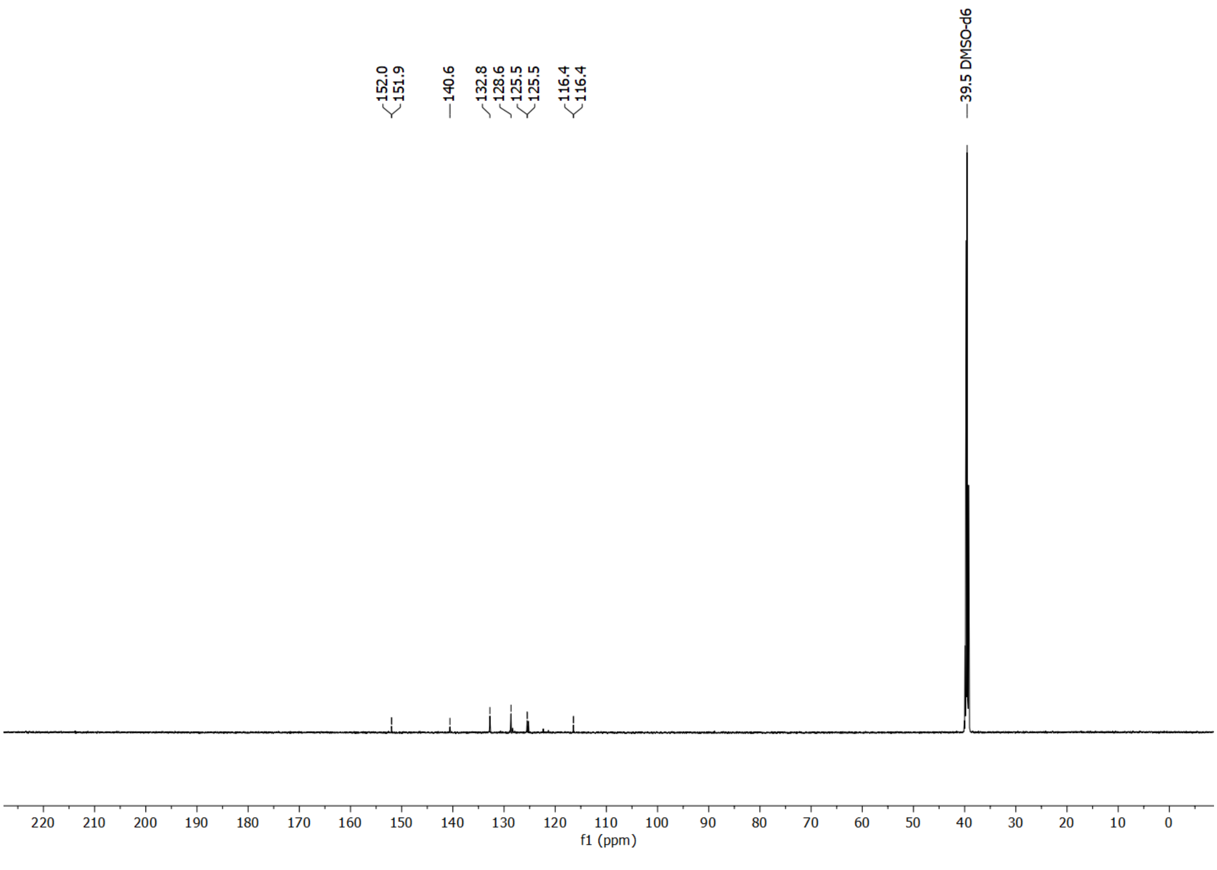


Figure 20: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **8h** in DMSO-*d6.*

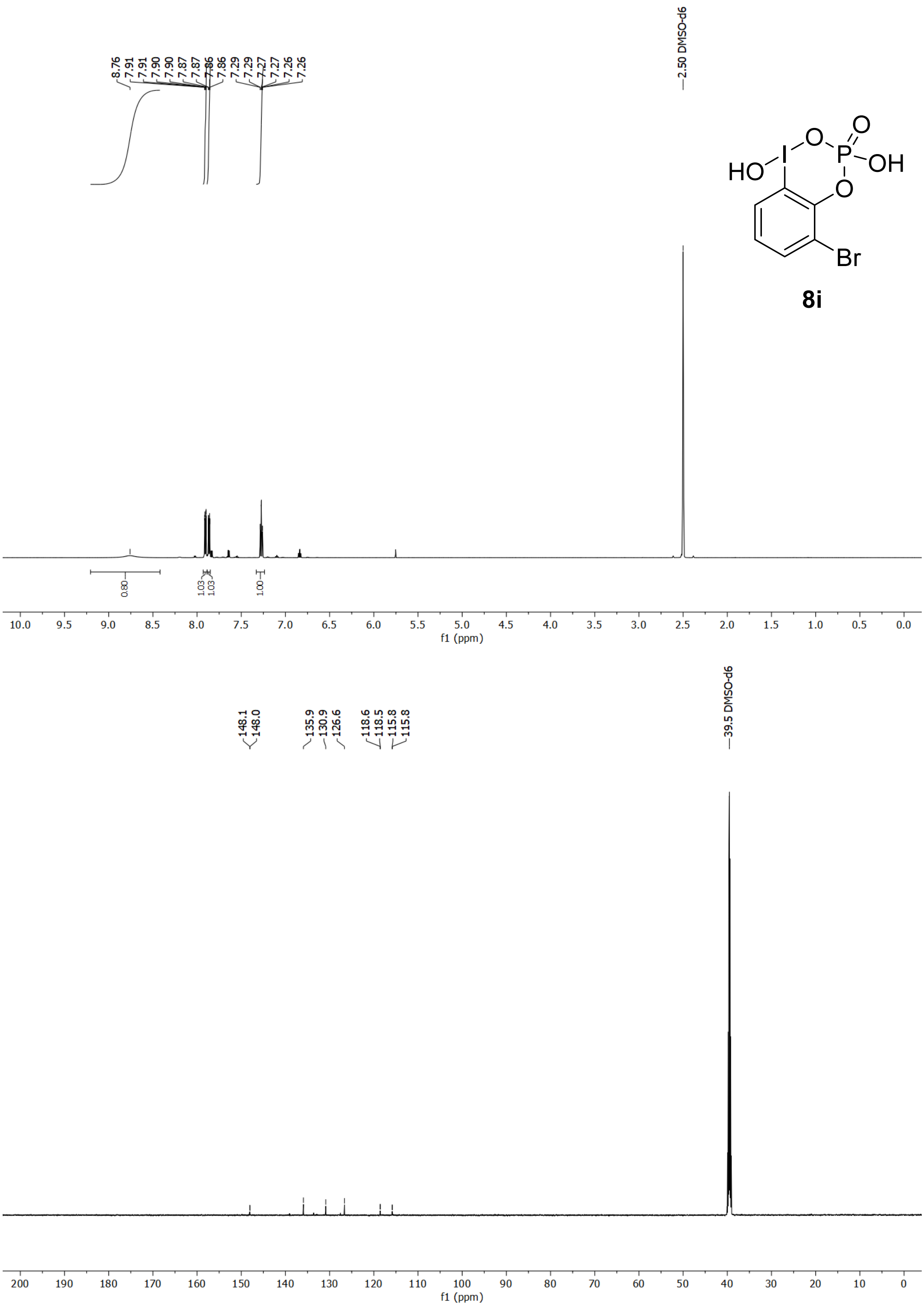


Figure 21: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **8i** in DMSO-*d6.*

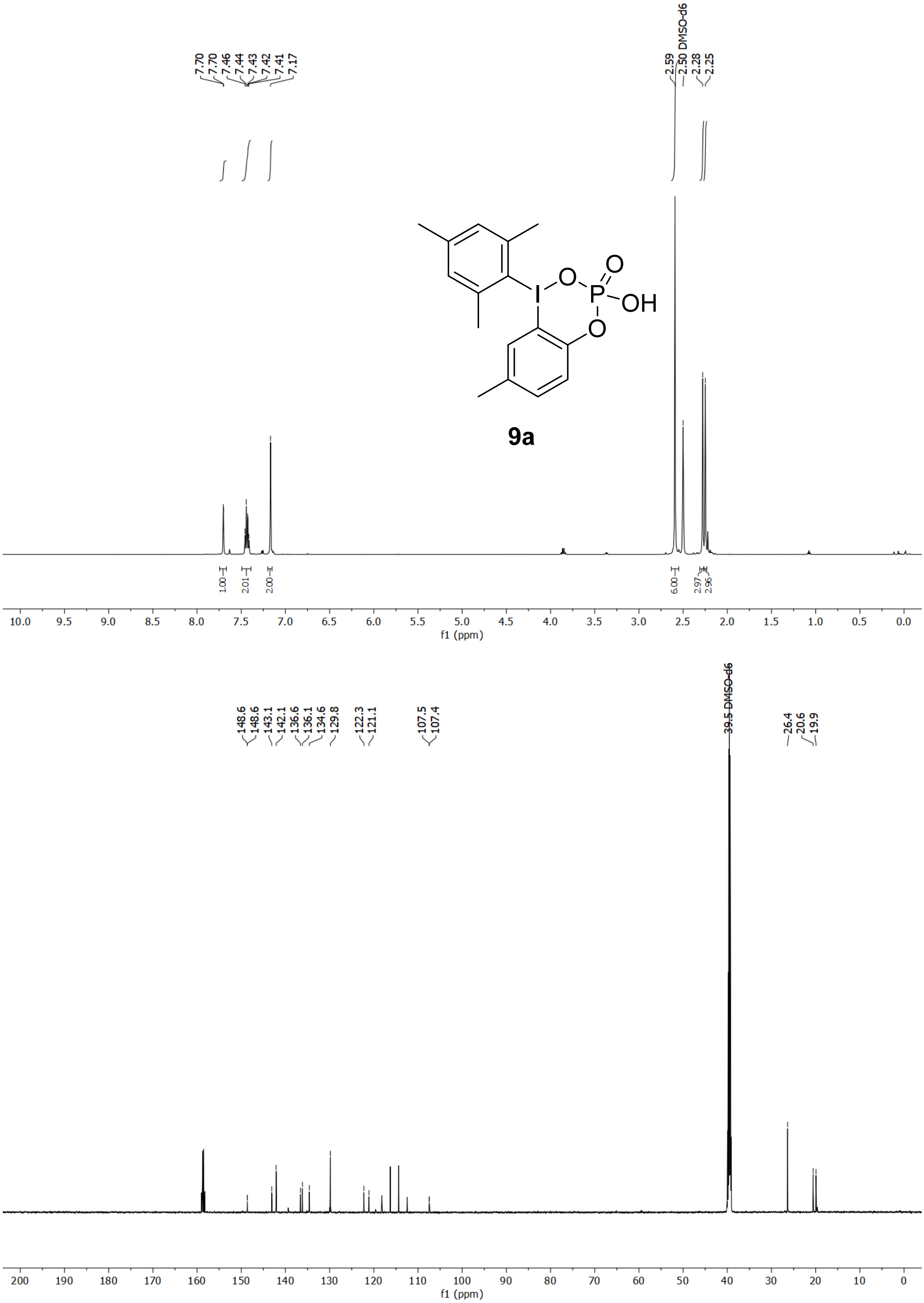


Figure 22: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9a** in DMSO-*d6*+TFA.

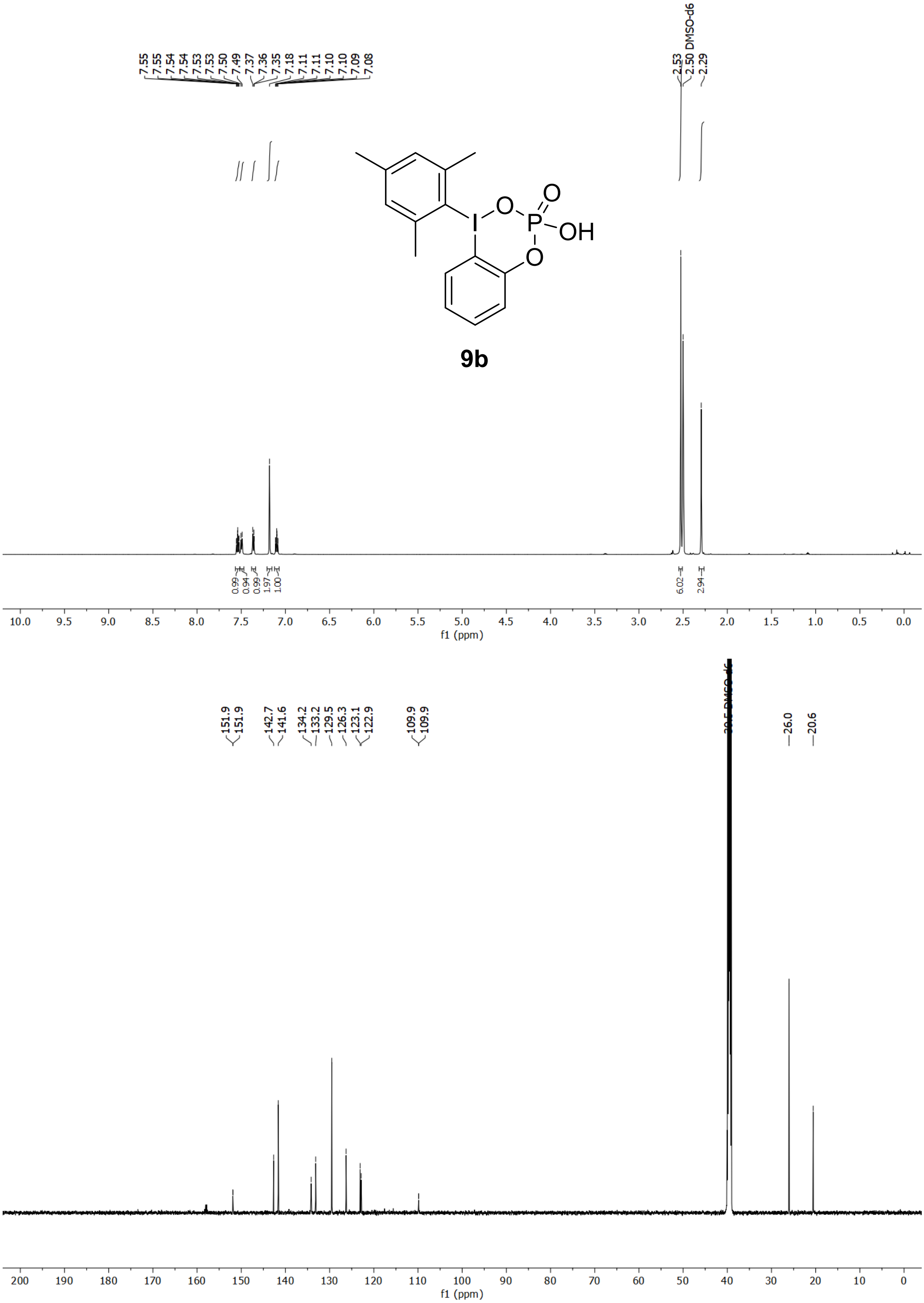


Figure 23: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9b** in DMSO-*d6*+TFA.

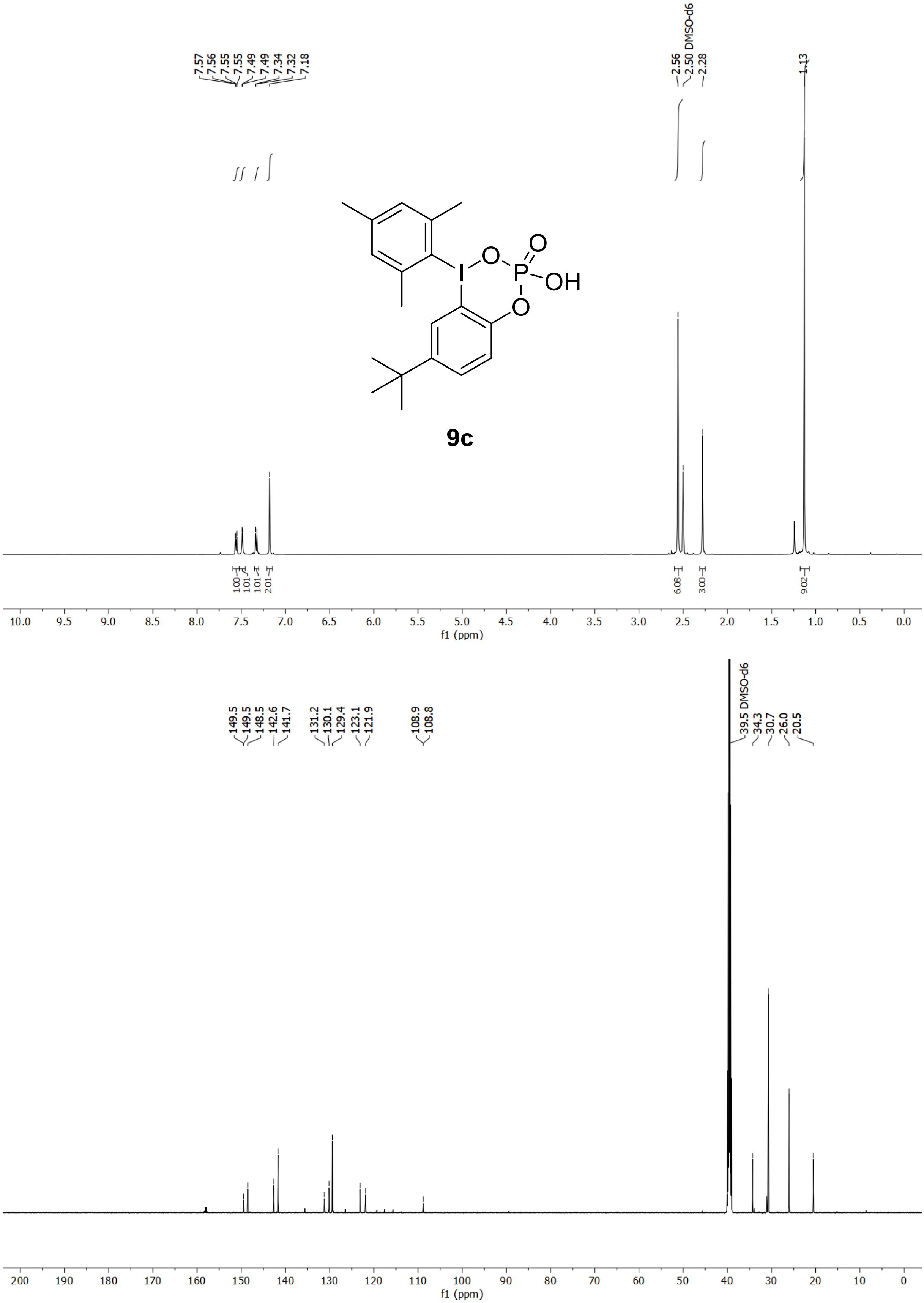


Figure 24: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9c** in DMSO-*d6*+TFA.

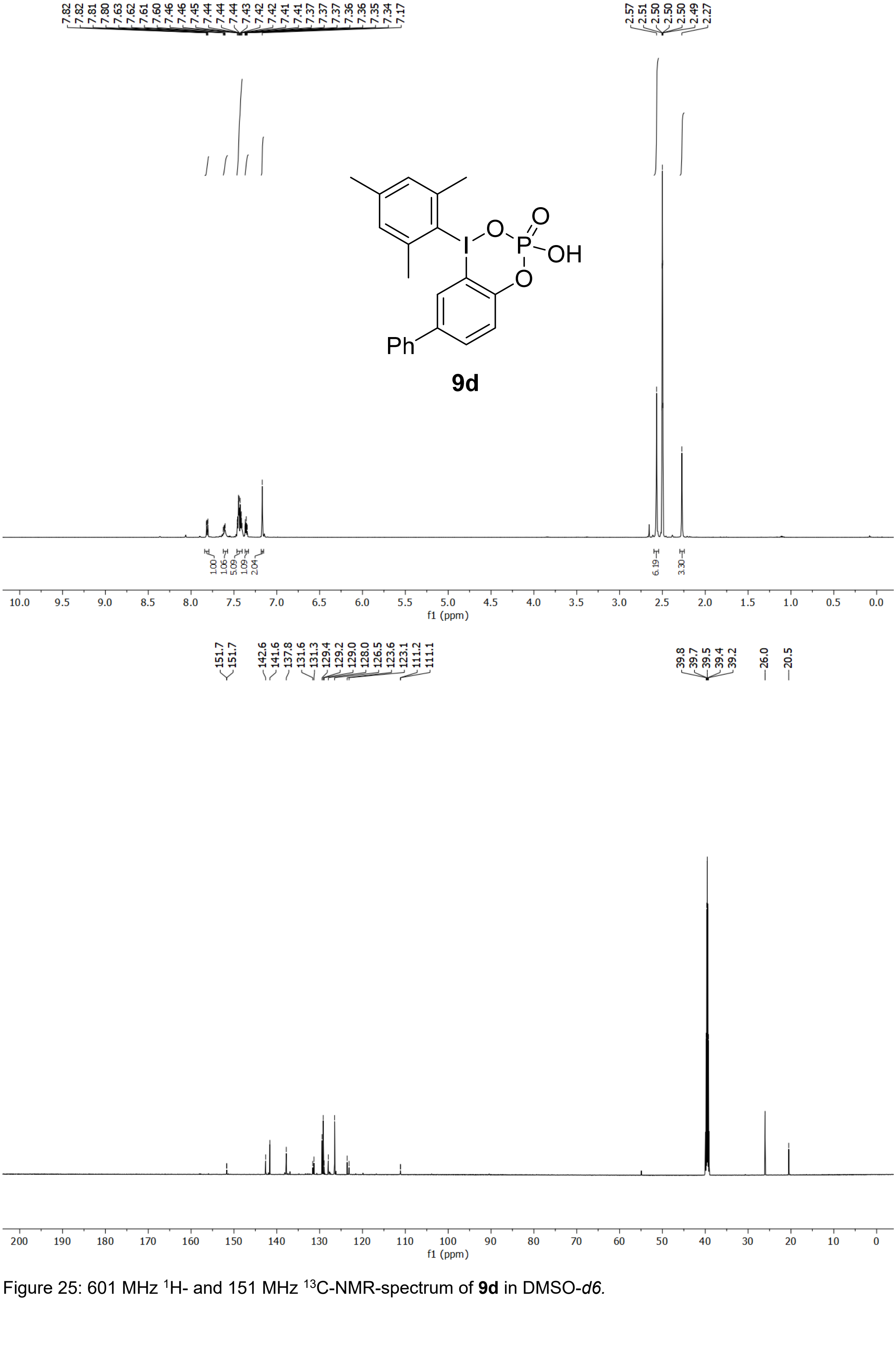


Figure 25: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9d** in DMSO-*d6.*

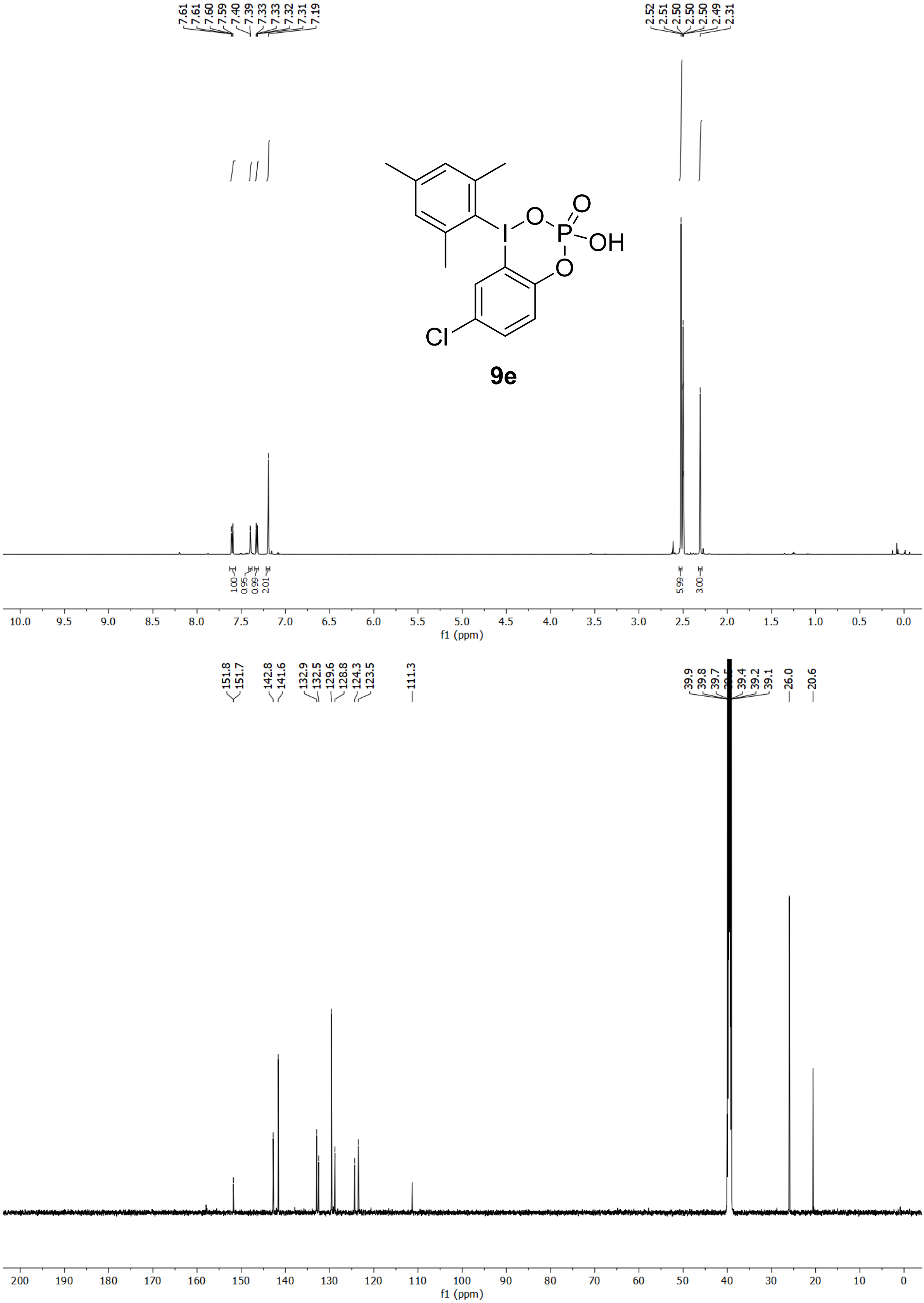


Figure 26: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9e** in DMSO-*d6.*

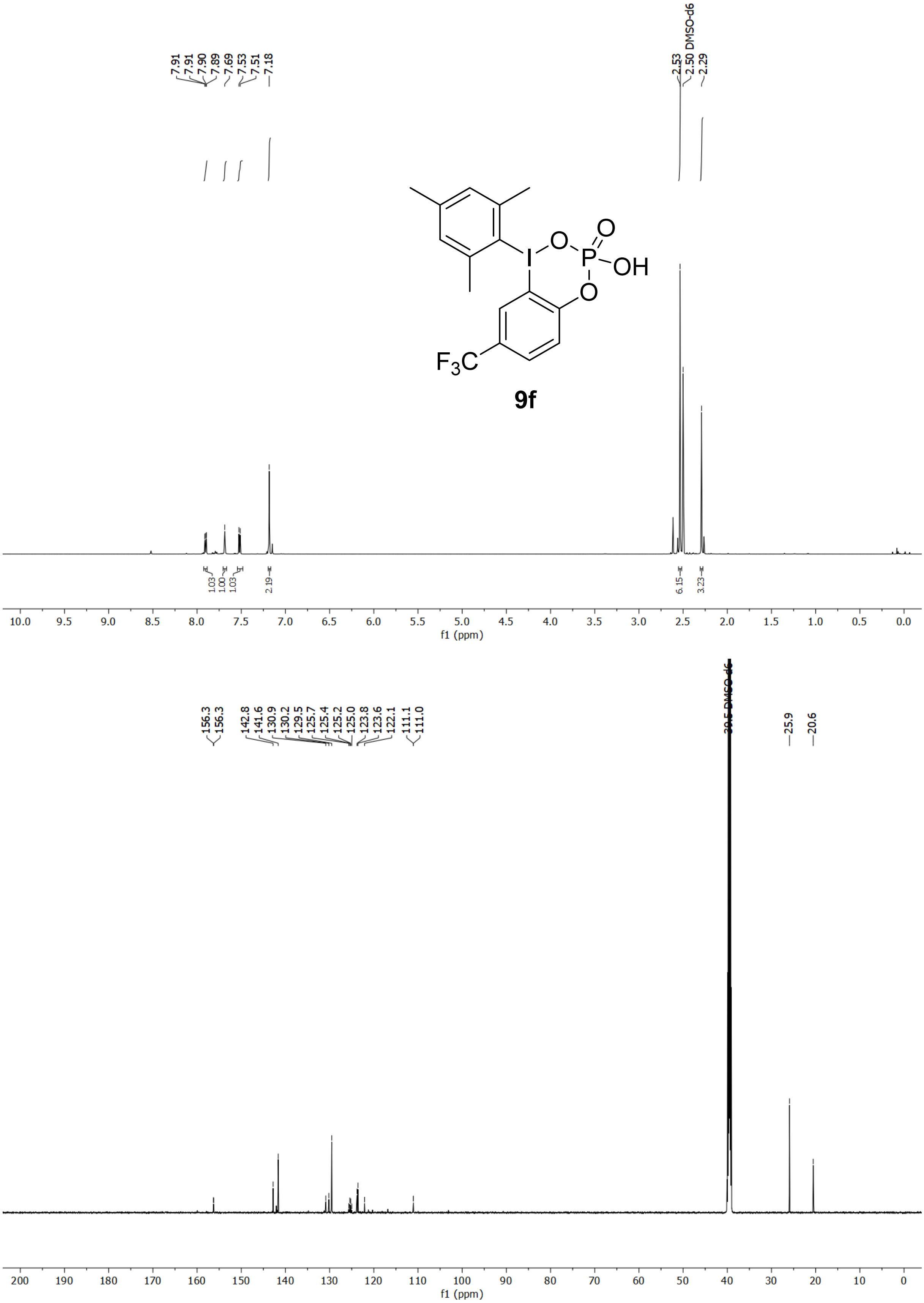


Figure 27: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9f** in DMSO-*d6*.

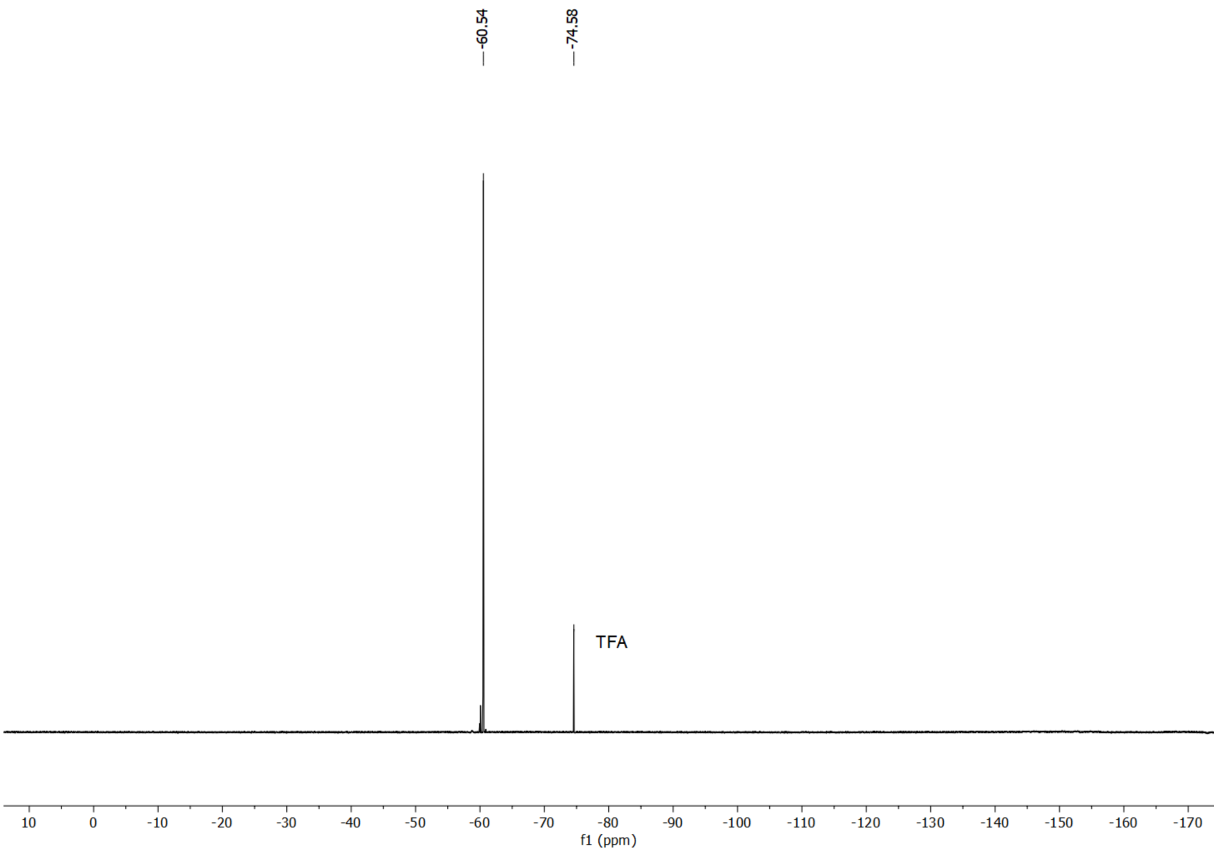


Figure 28: 565 MHz ^{19}F-NMR-spectrum of 9f in DMSO-*d6*+TFA.

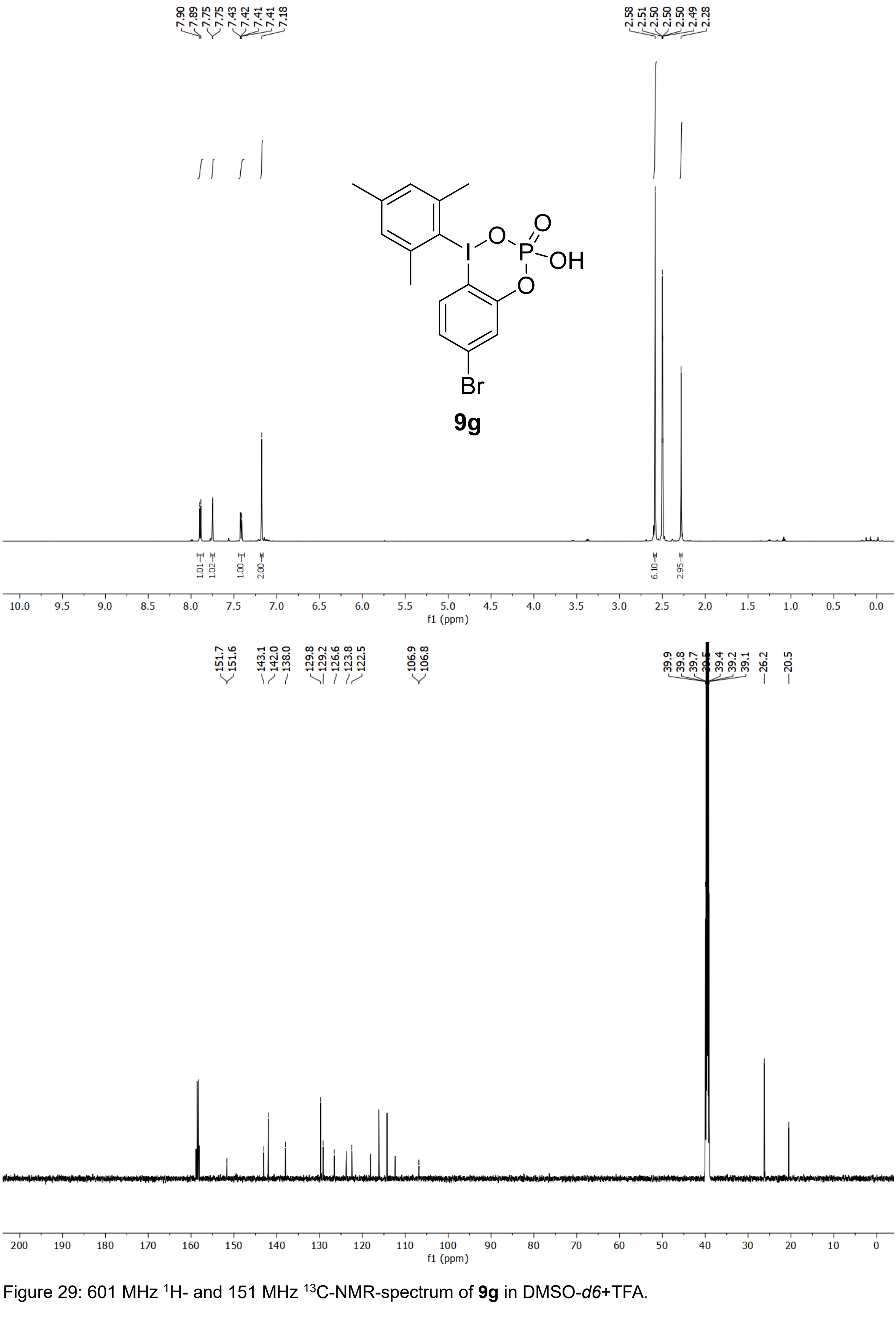


Figure 29: 601 MHz [1]H- and 151 MHz [13]C-NMR-spectrum of **9g** in DMSO-*d6*+TFA.

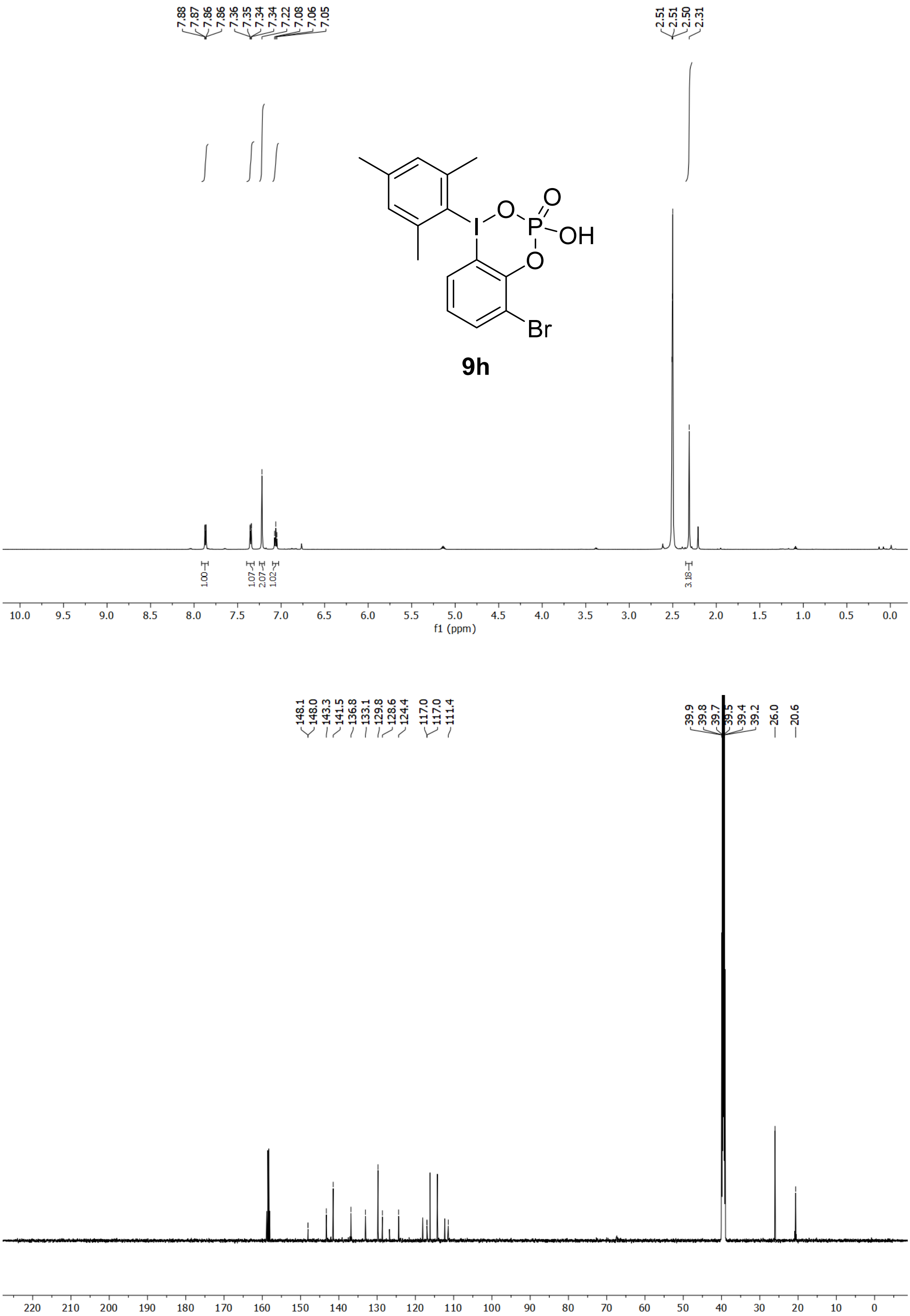


Figure 30: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9h** in DMSO-*d6*+TFA.

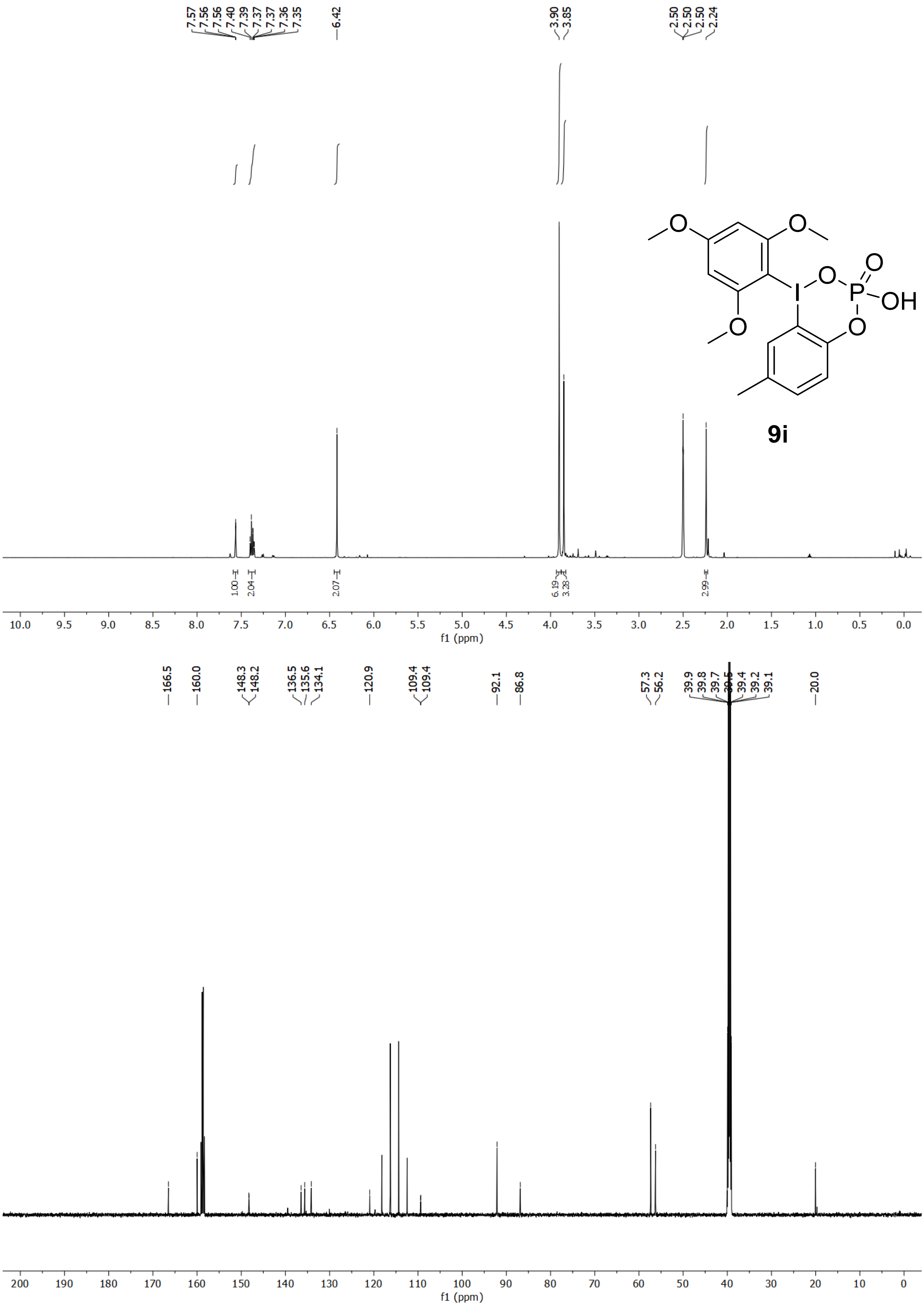


Figure 31: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9i** in DMSO-*d6*+TFA.

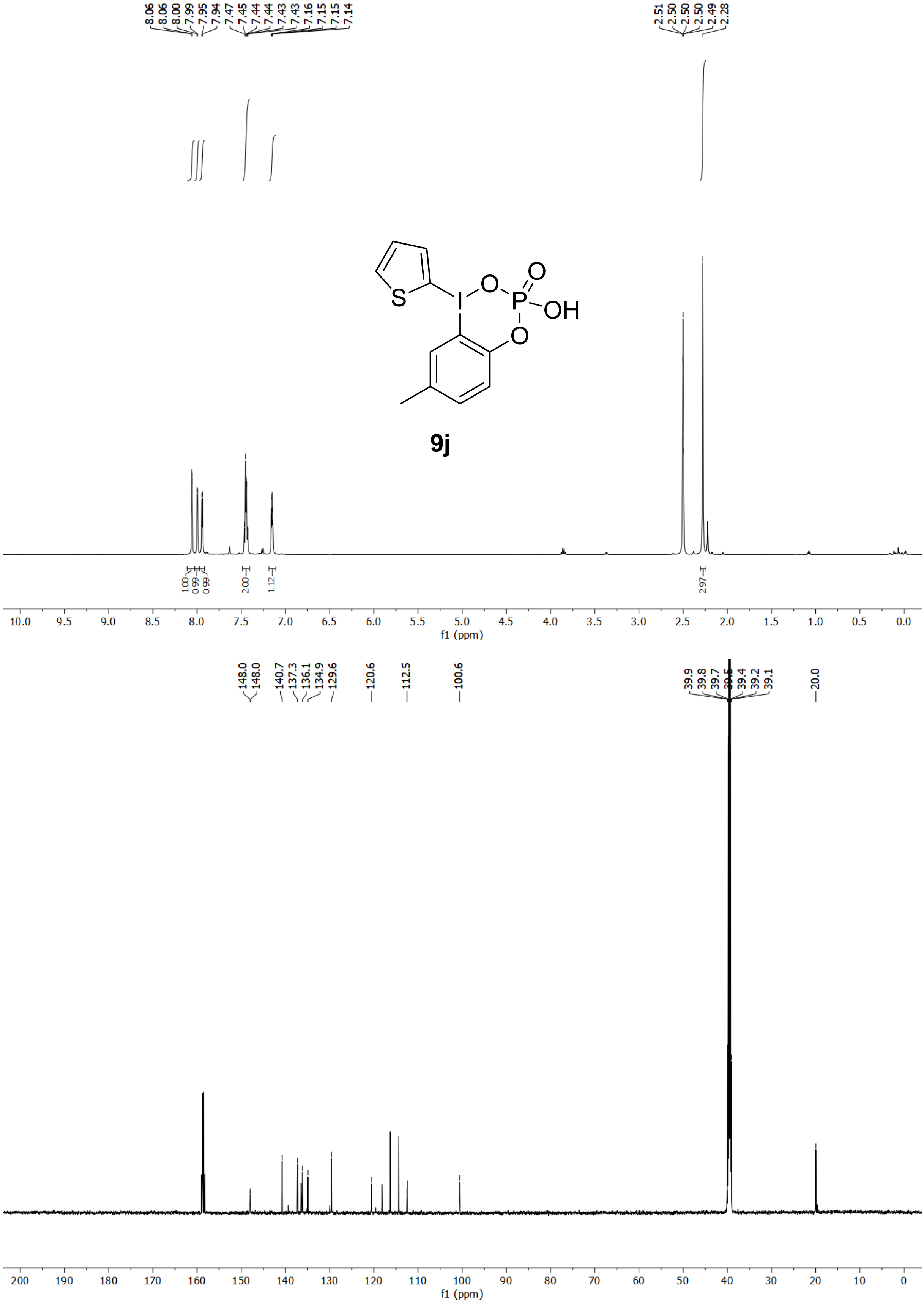


Figure 32: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9j** in DMSO-*d6*+TFA.

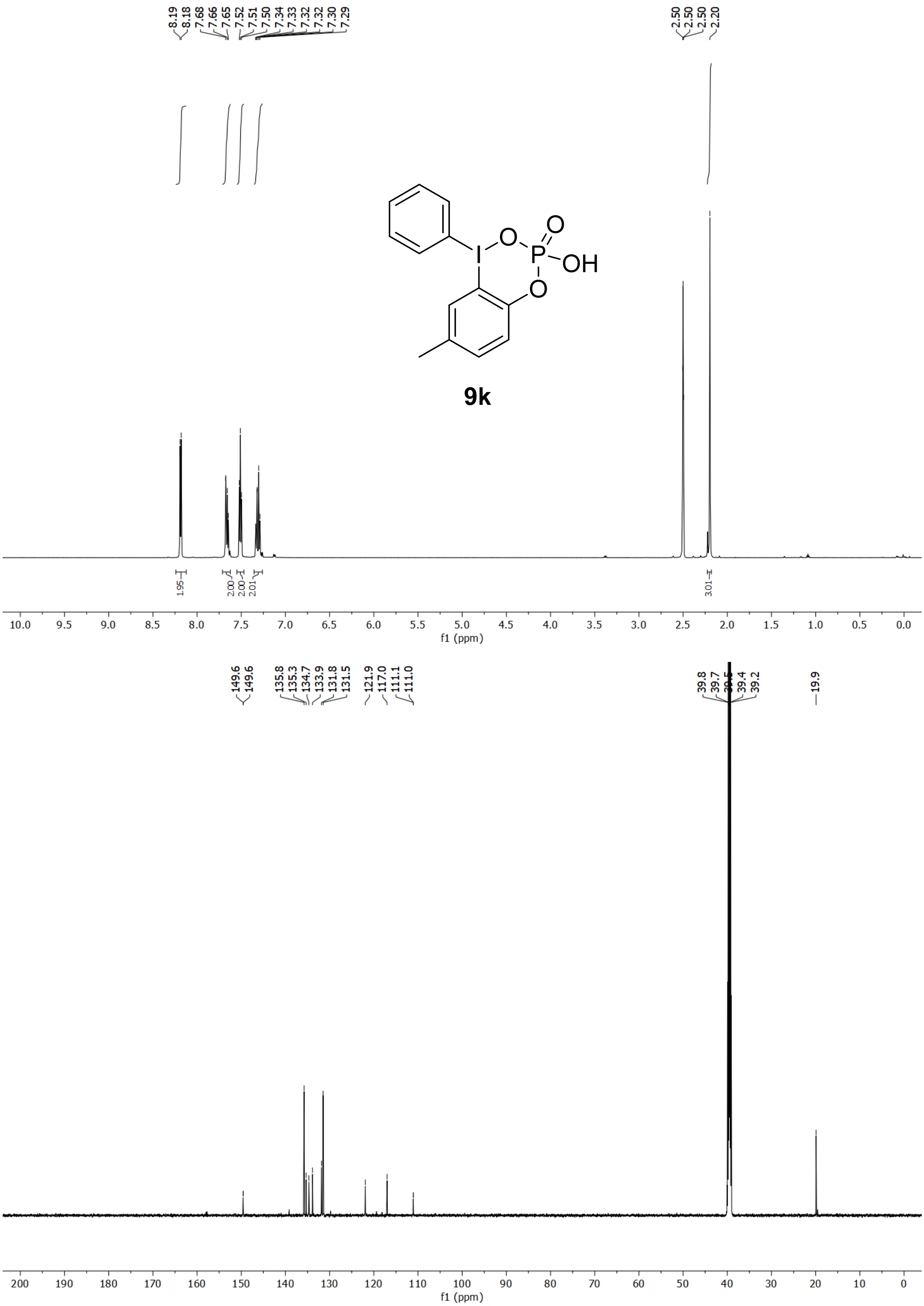


Figure 33: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9k** in DMSO-*d6*.

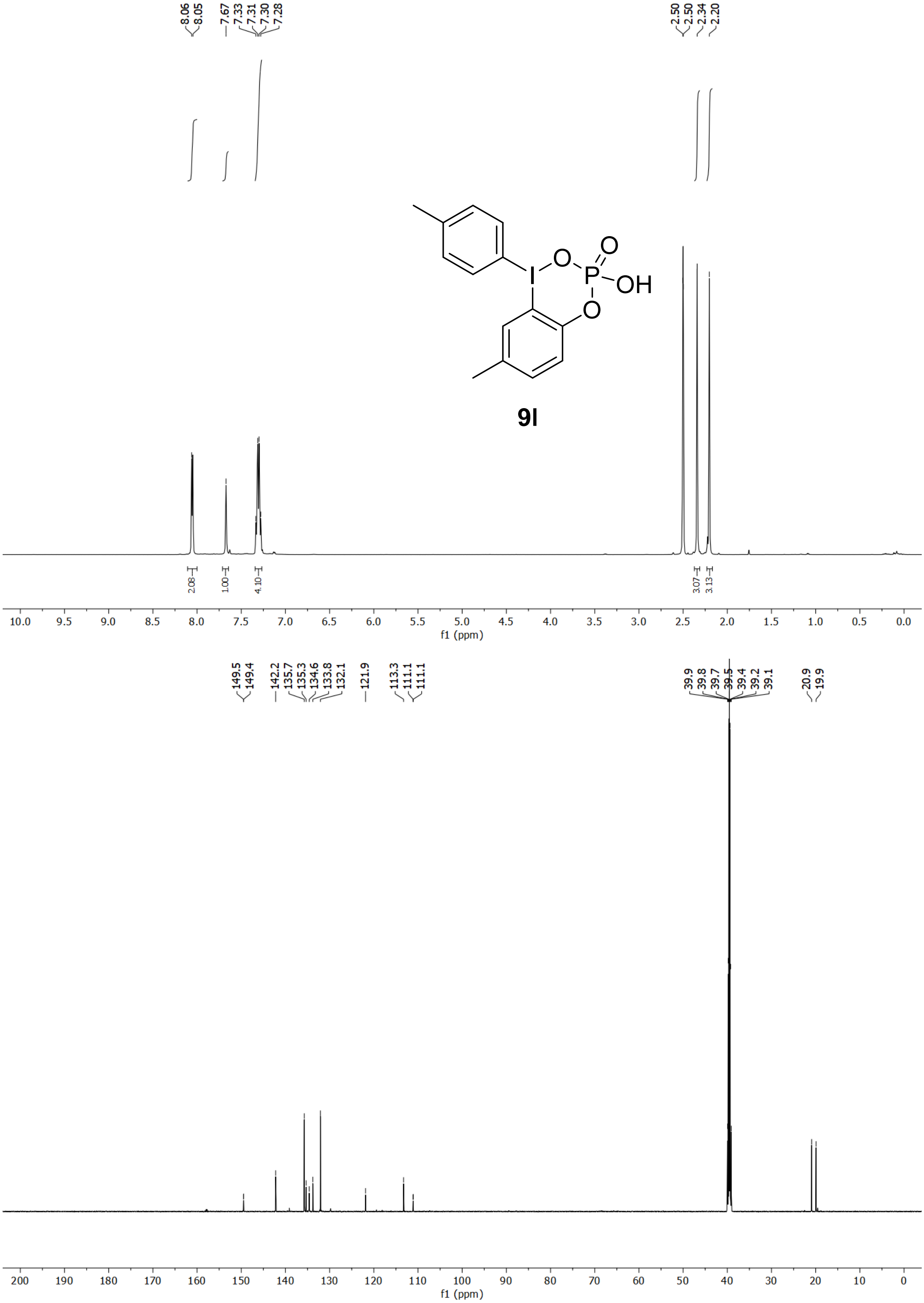
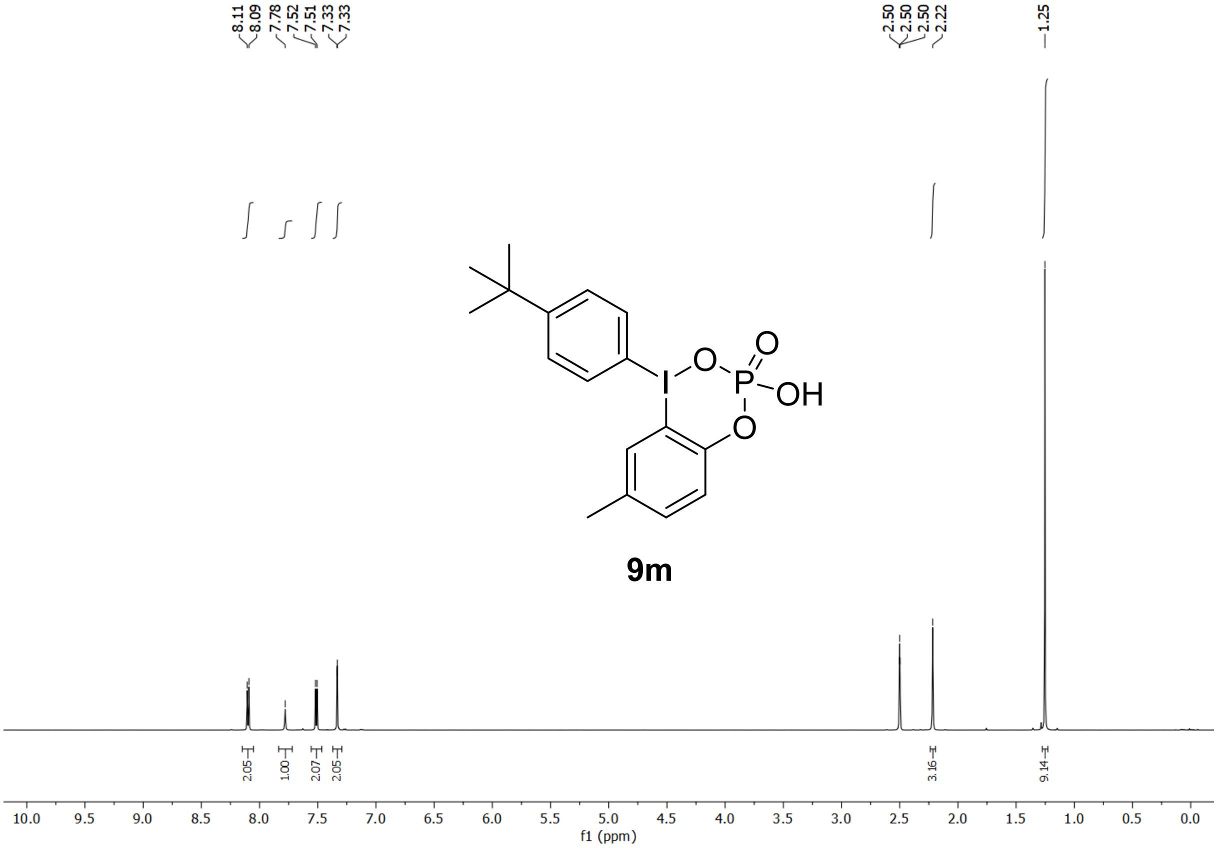


Figure 34: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9l** in DMSO-*d6*.



9m

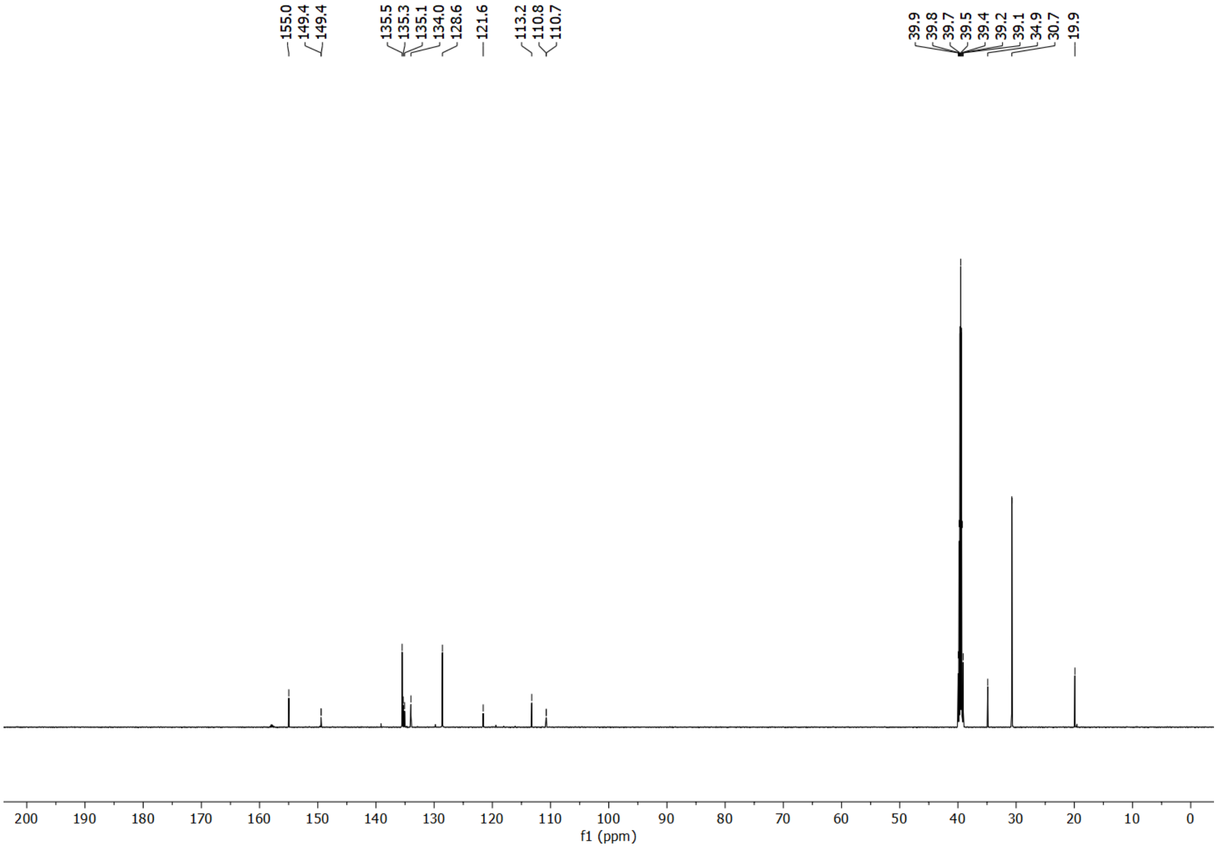


Figure 35: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9m** in DMSO-*d6*.

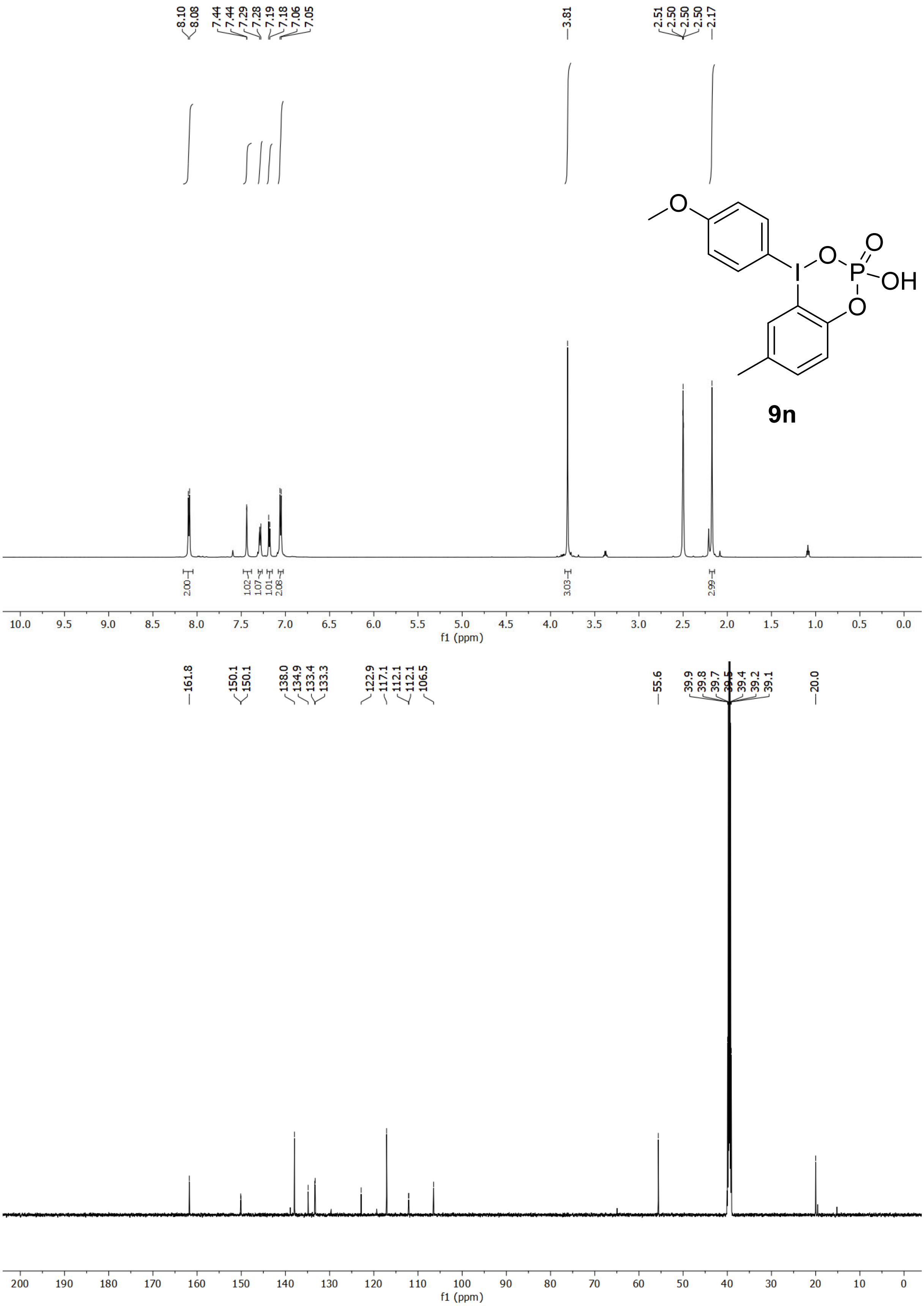


Figure 36: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9n** in DMSO-*d6*.

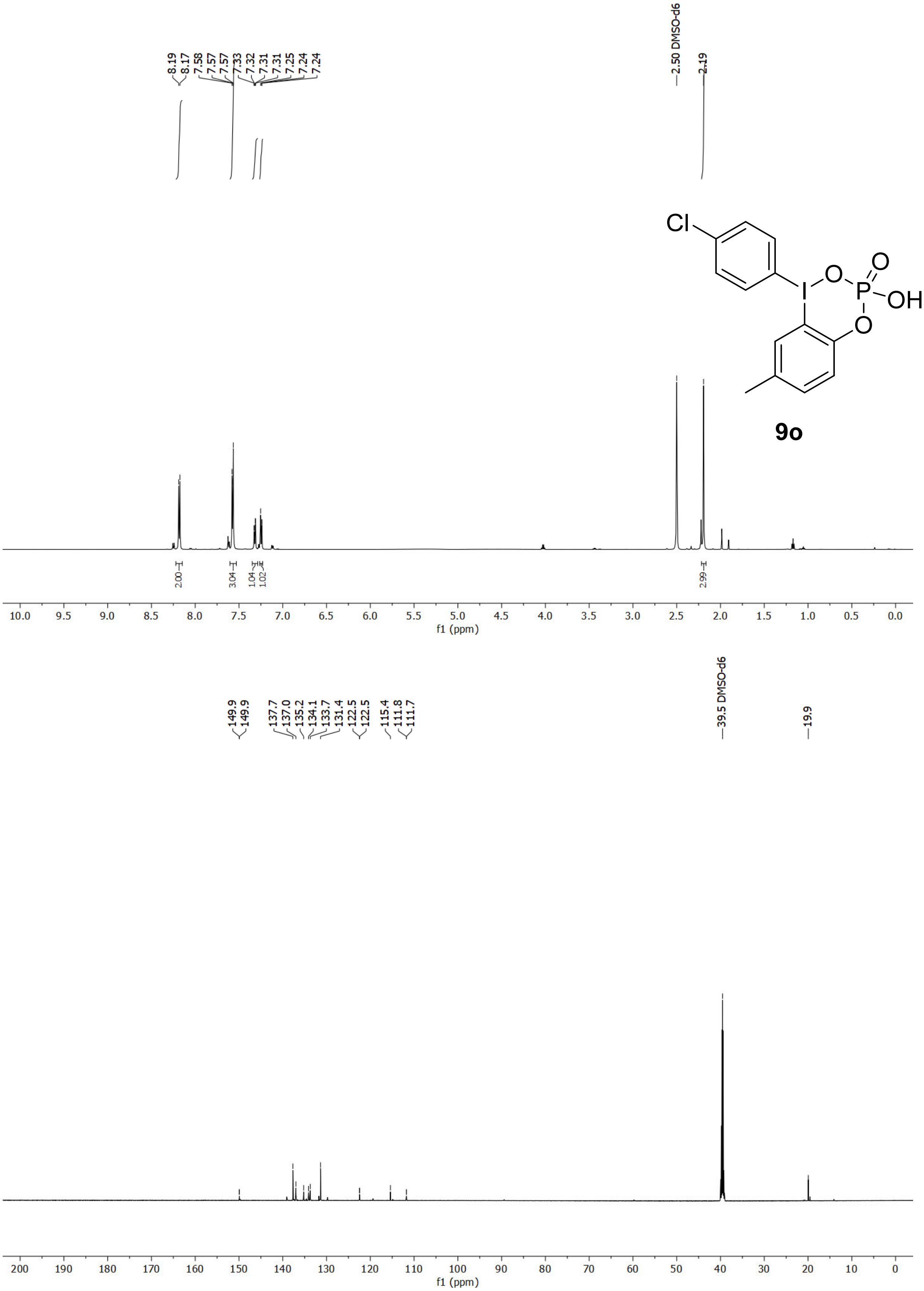


Figure 37: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9o** in DMSO-*d6*.

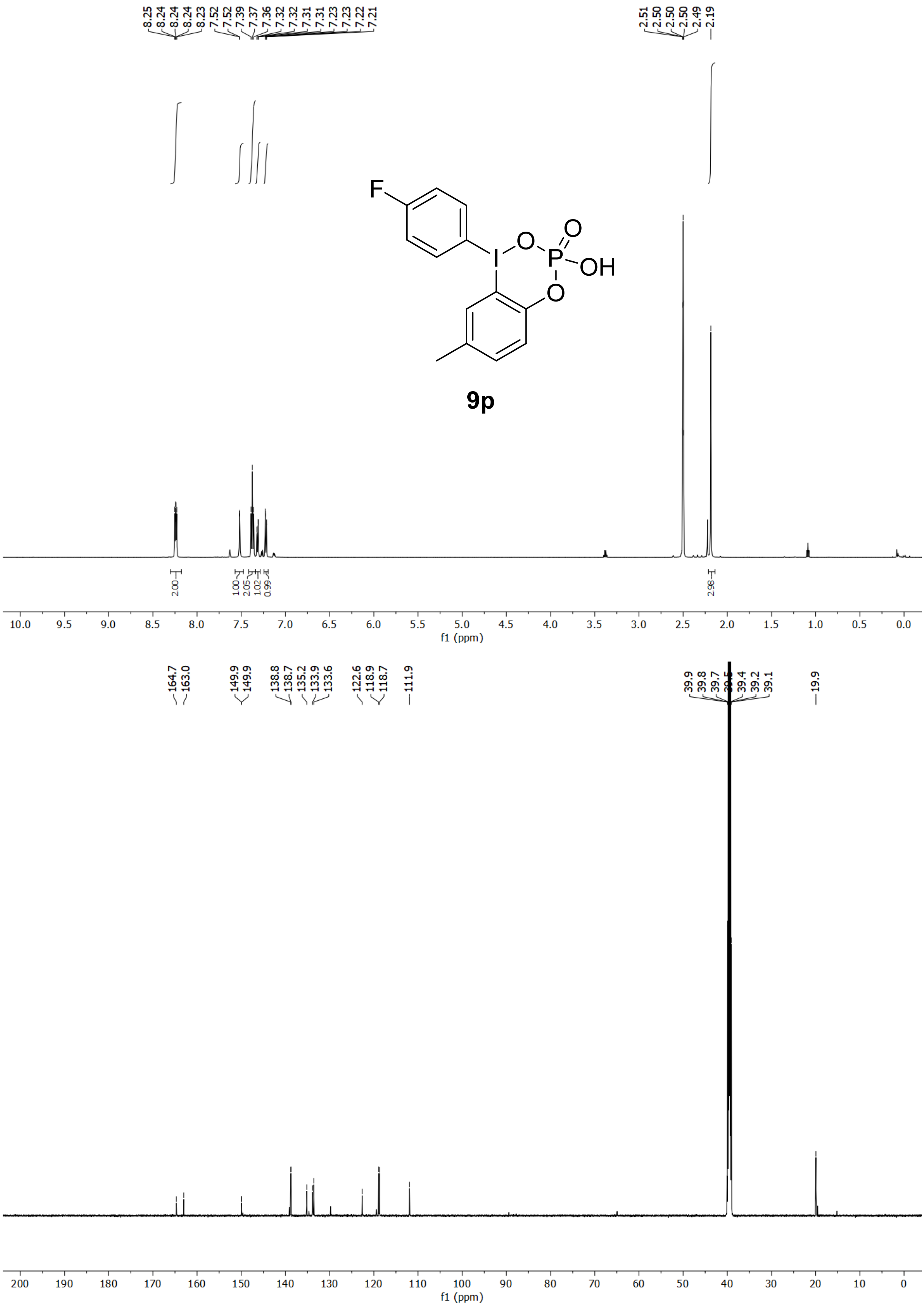


Figure 38: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9p** in DMSO-*d6*+TFA.

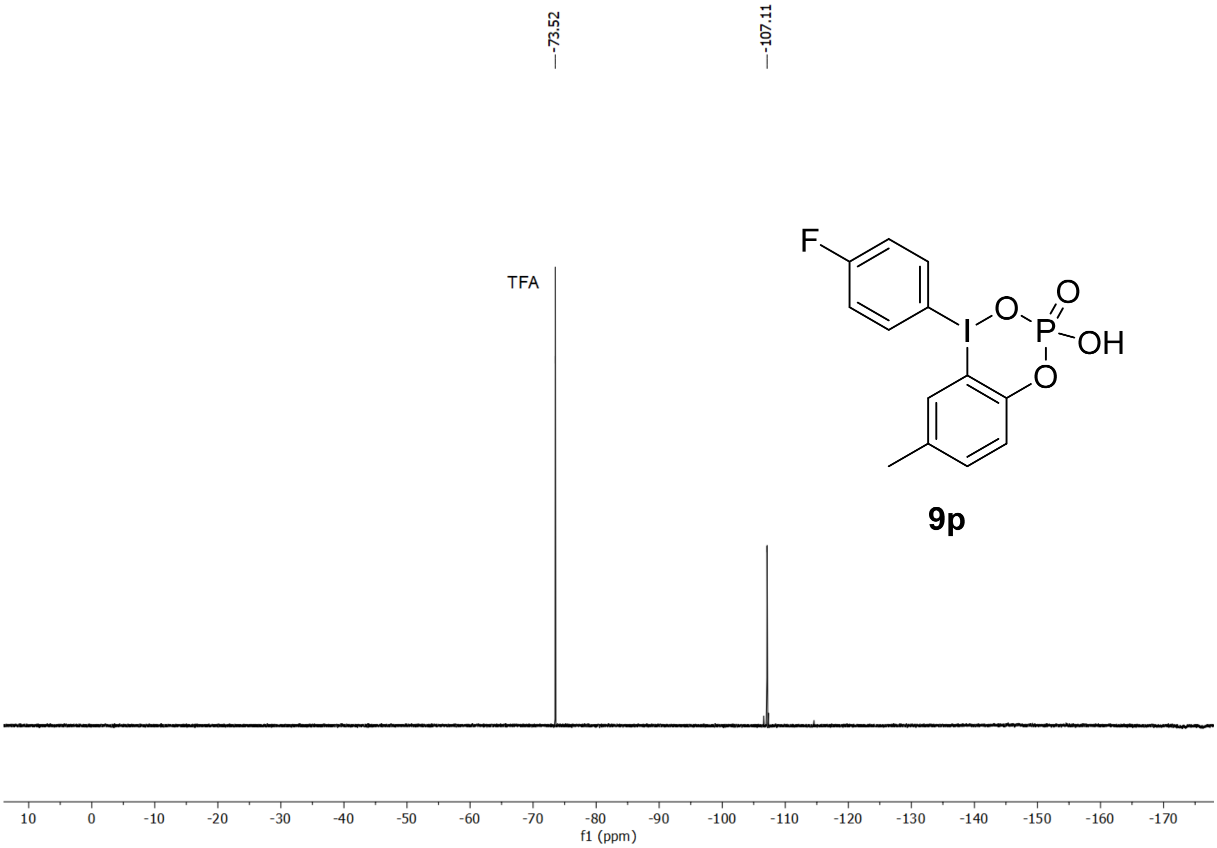


Figure 39: 565 MHz ^{19}F-NMR-spectrum of **9p** in DMSO-*d6*.

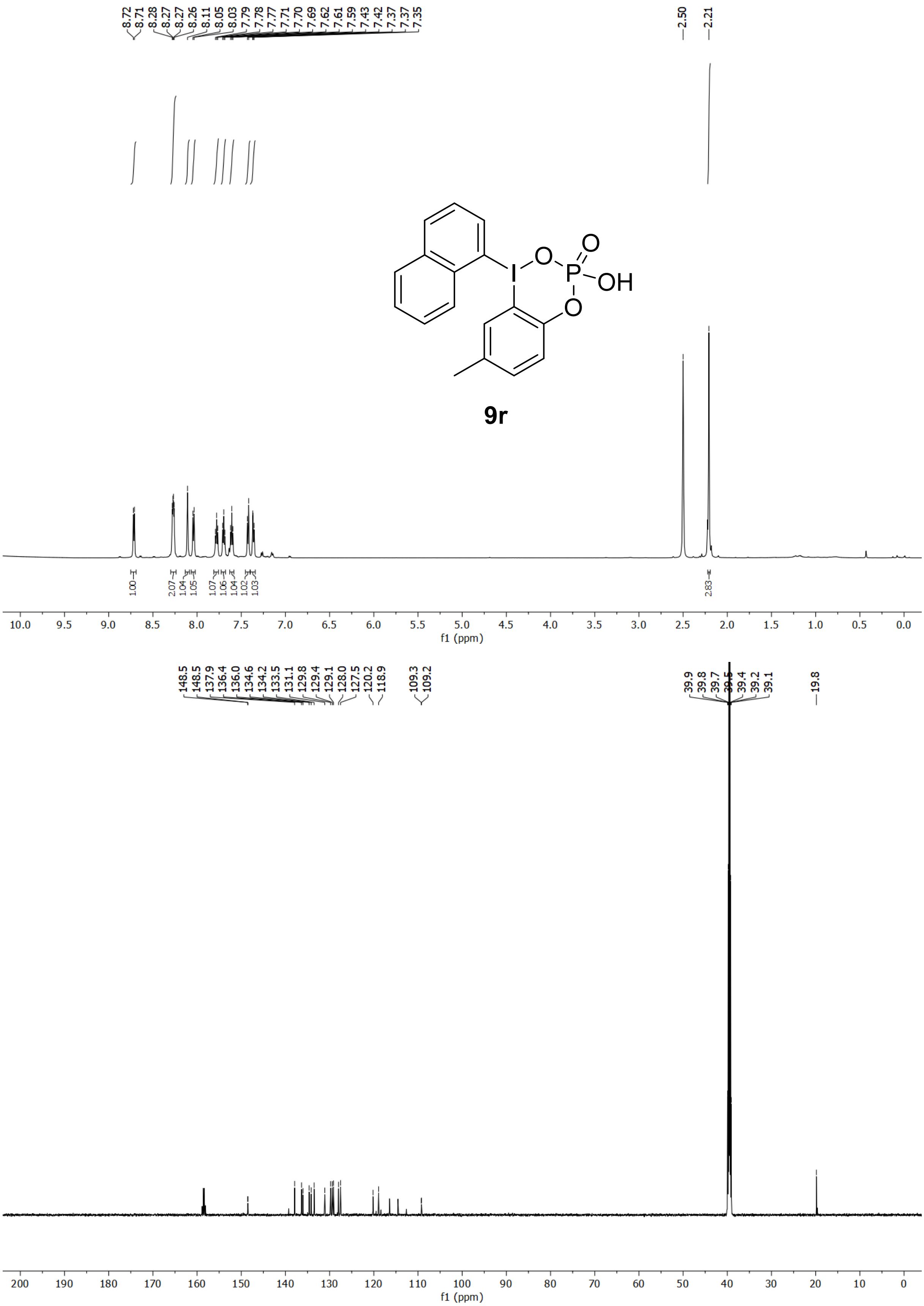


Figure 40: 600 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **9r** in DMSO-*d6*+TFA.

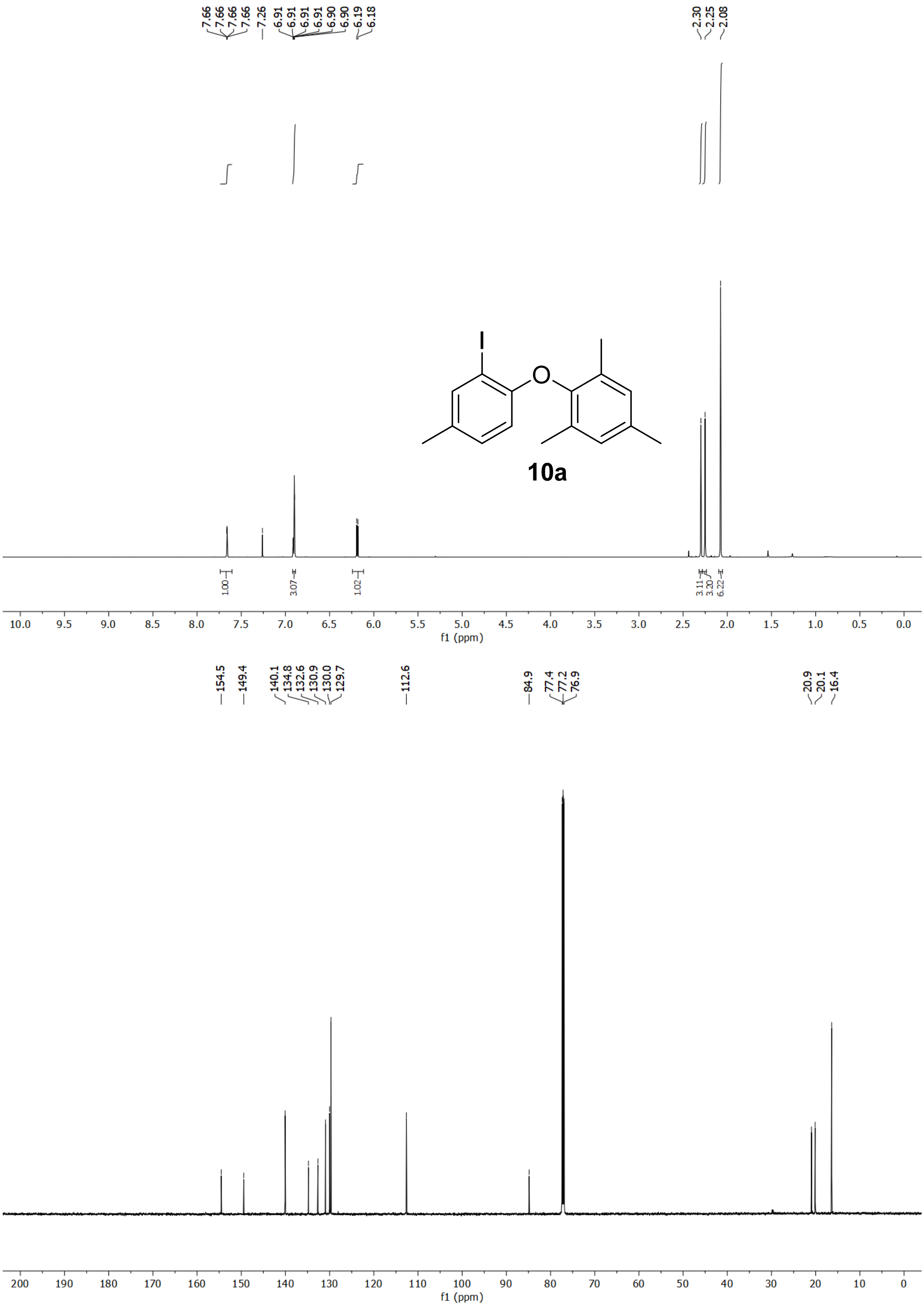
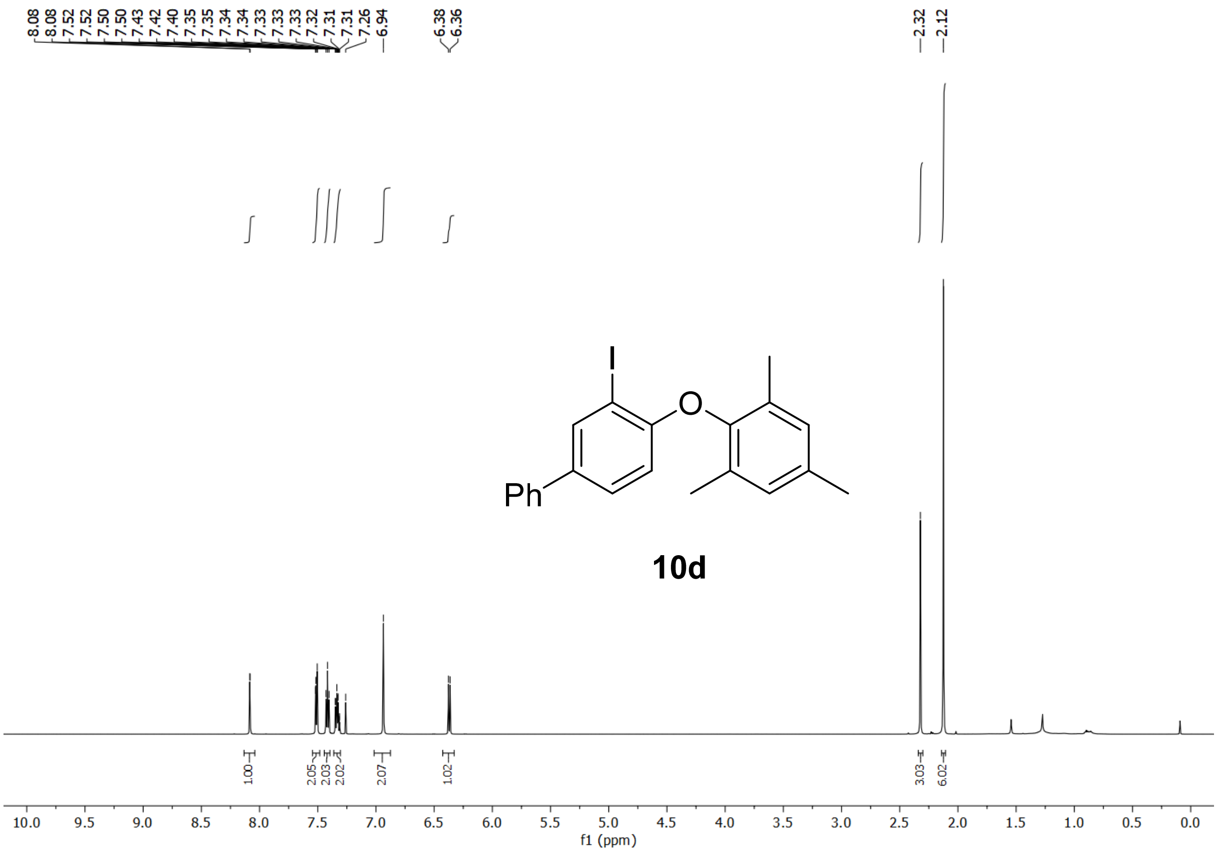


Figure 41: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10a** in $CDCl_3$.

Figure 42: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10c** in $CDCl_3$.



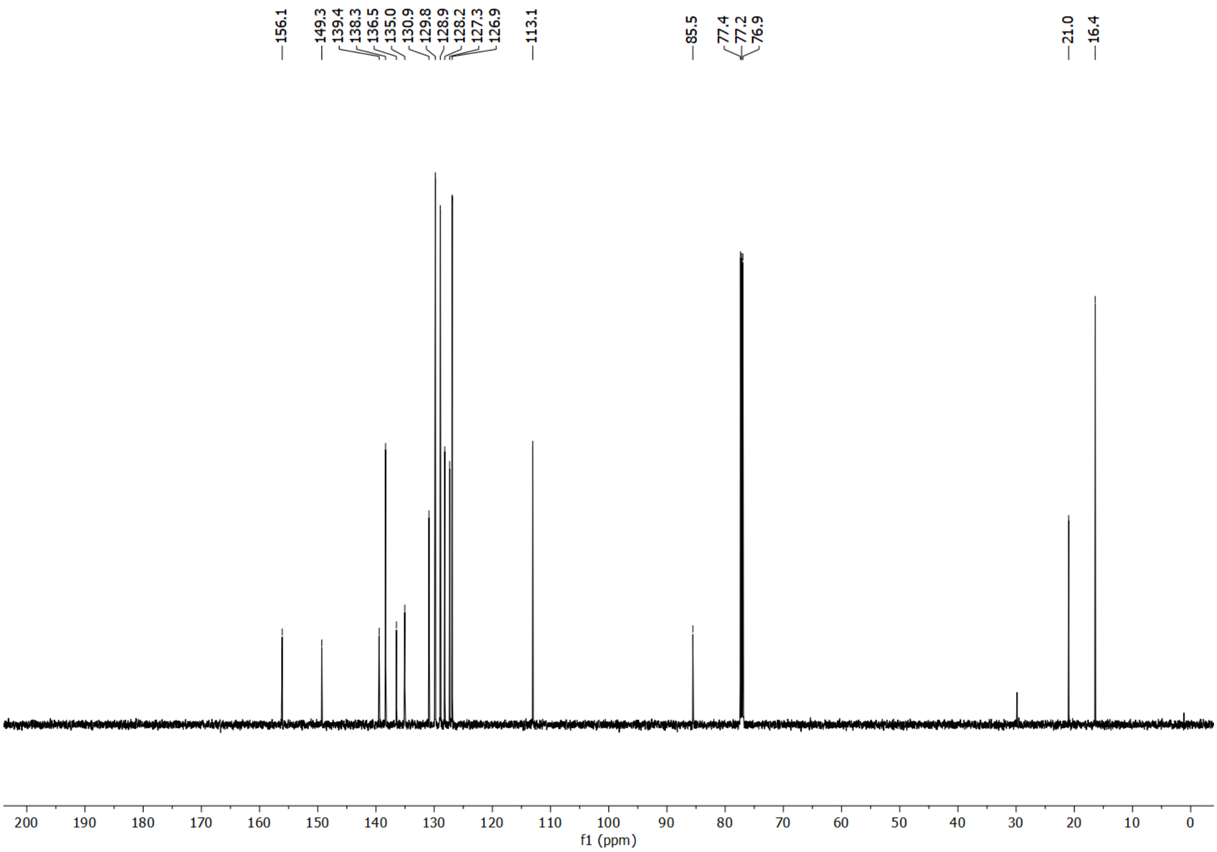


Figure 43: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10d** in $CDCl_3$.

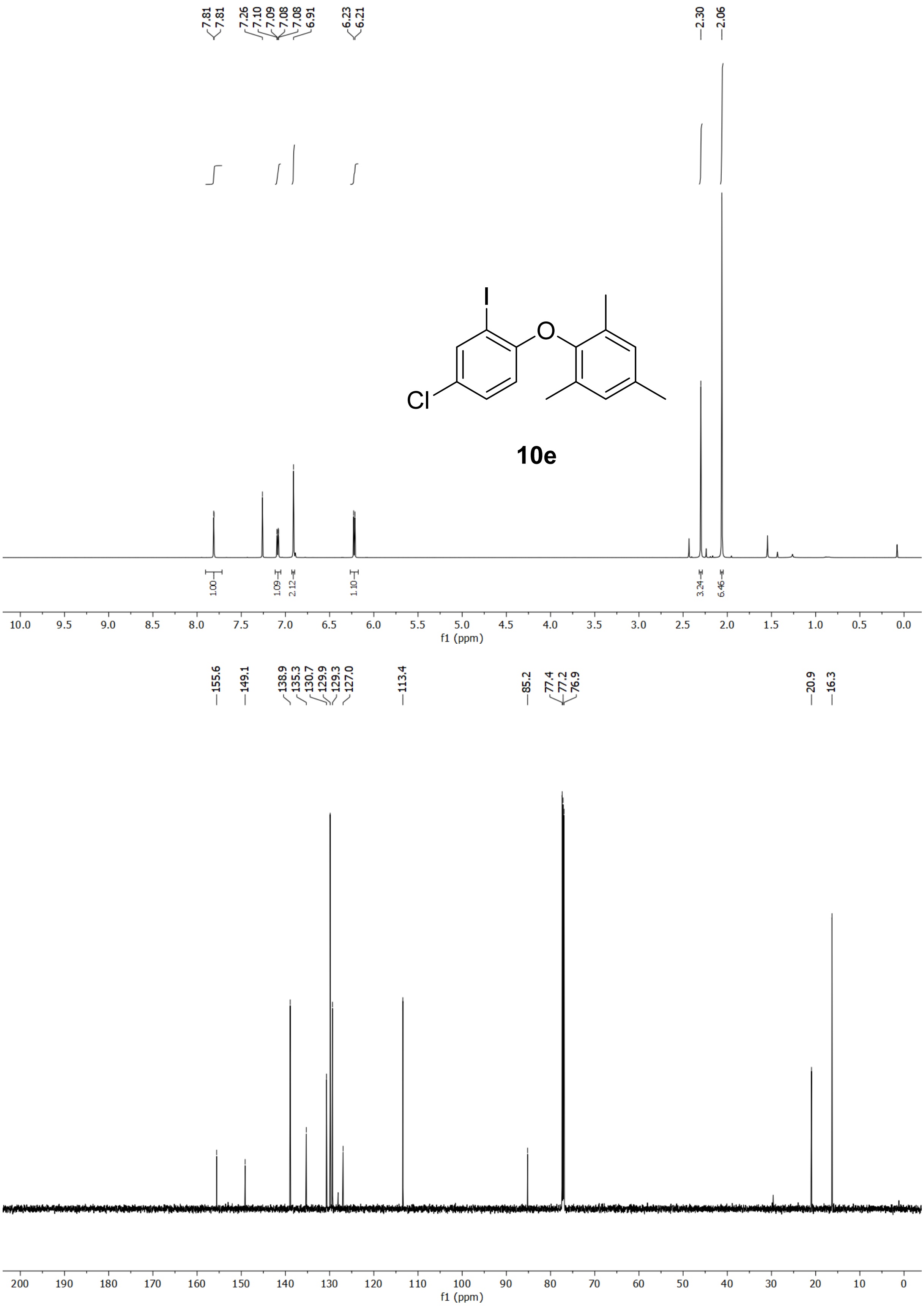


Figure 44: 601 MHz [1]H- and 151 MHz [13]C-NMR-spectrum of **10e** in $CDCl_3$.

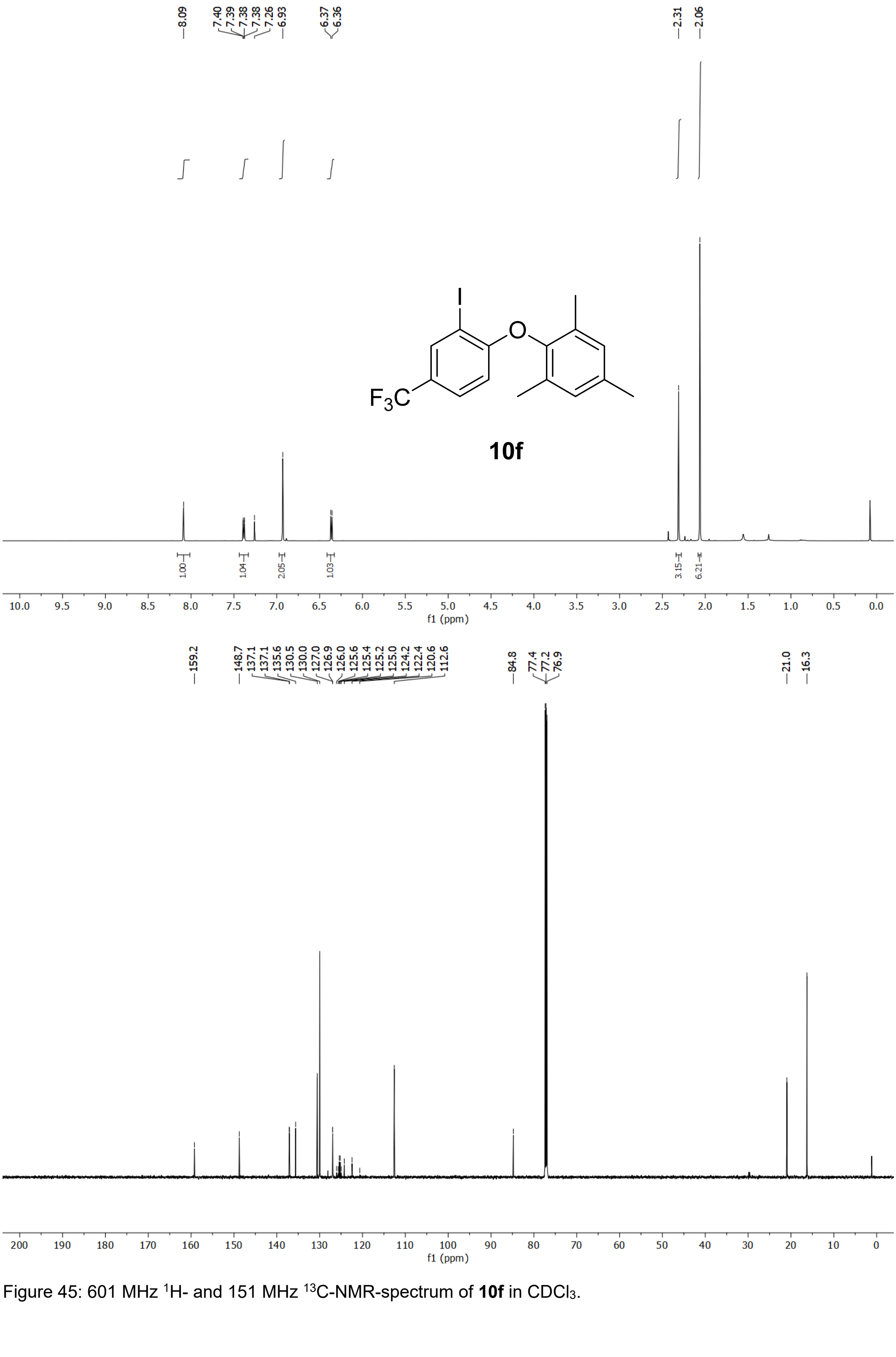
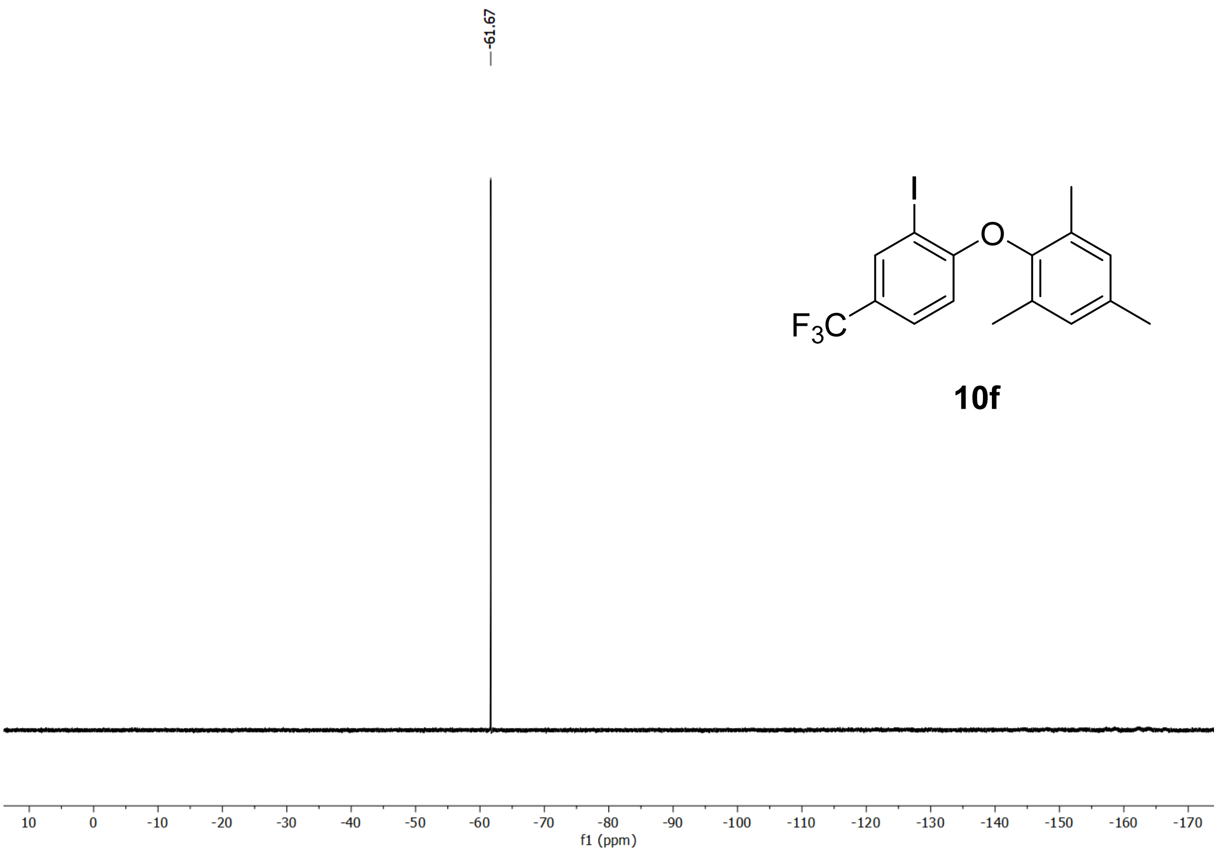
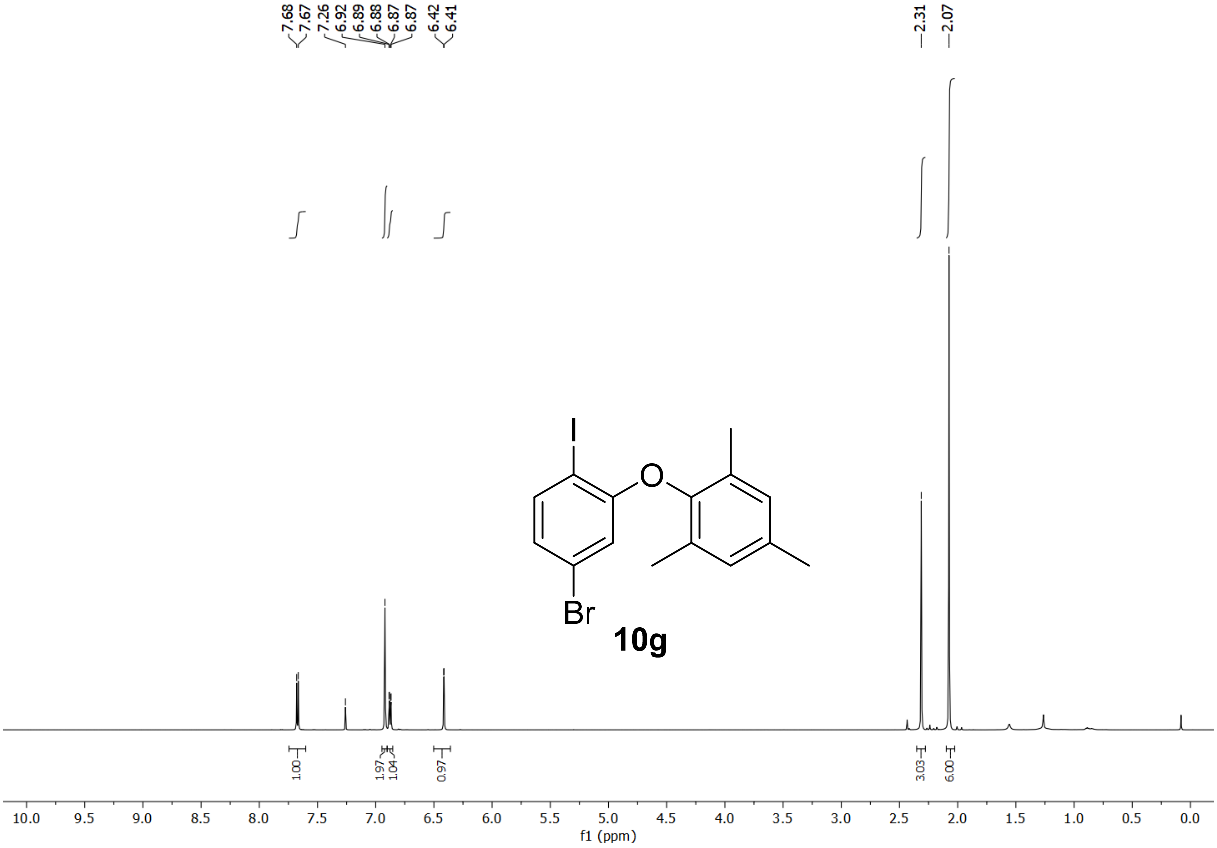


Figure 45: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10f** in $CDCl_3$.



10f

Figure 46: 565 MHz [19]F-NMR-spectrum of **10f** in $CDCl_3$.



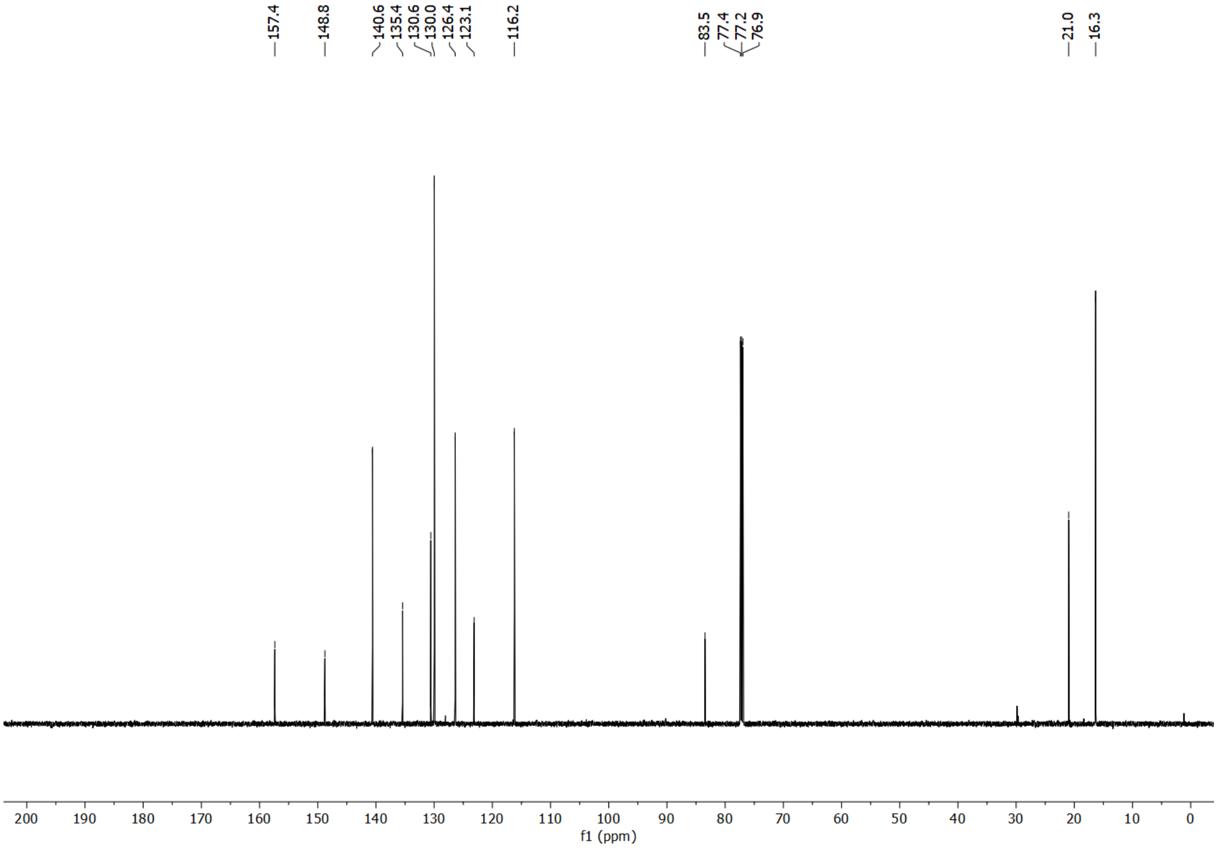


Figure 47: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10g** in $CDCl_3$.

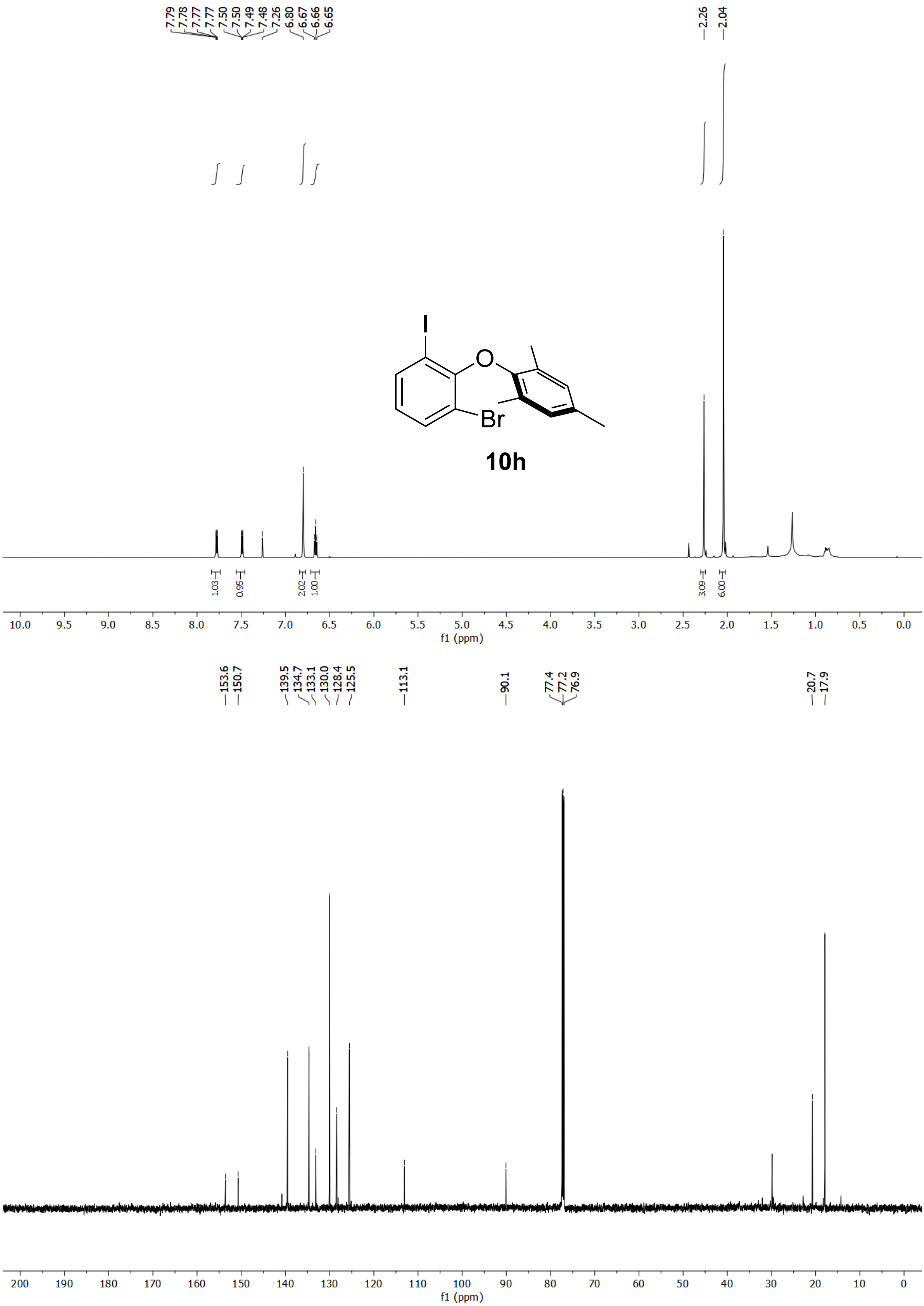
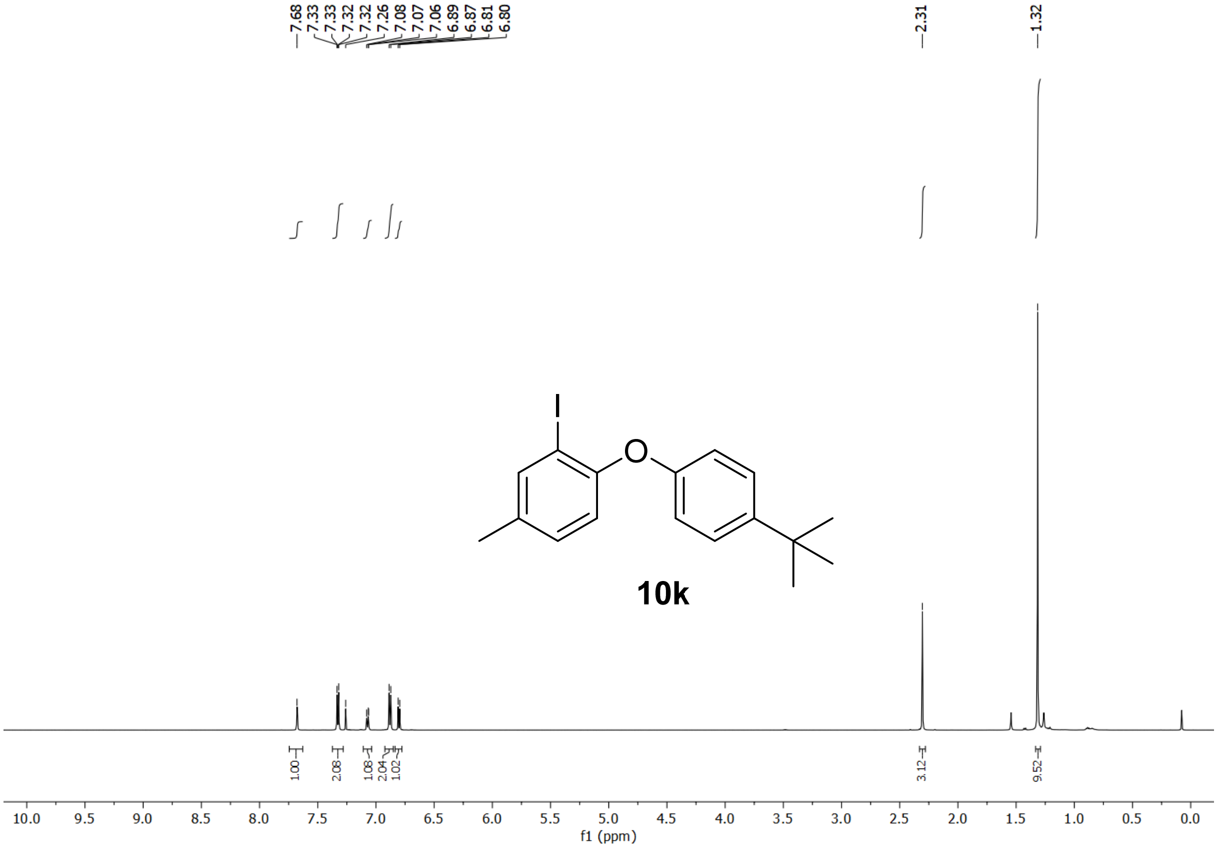


Figure 48: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10h** in $CDCl_3$.



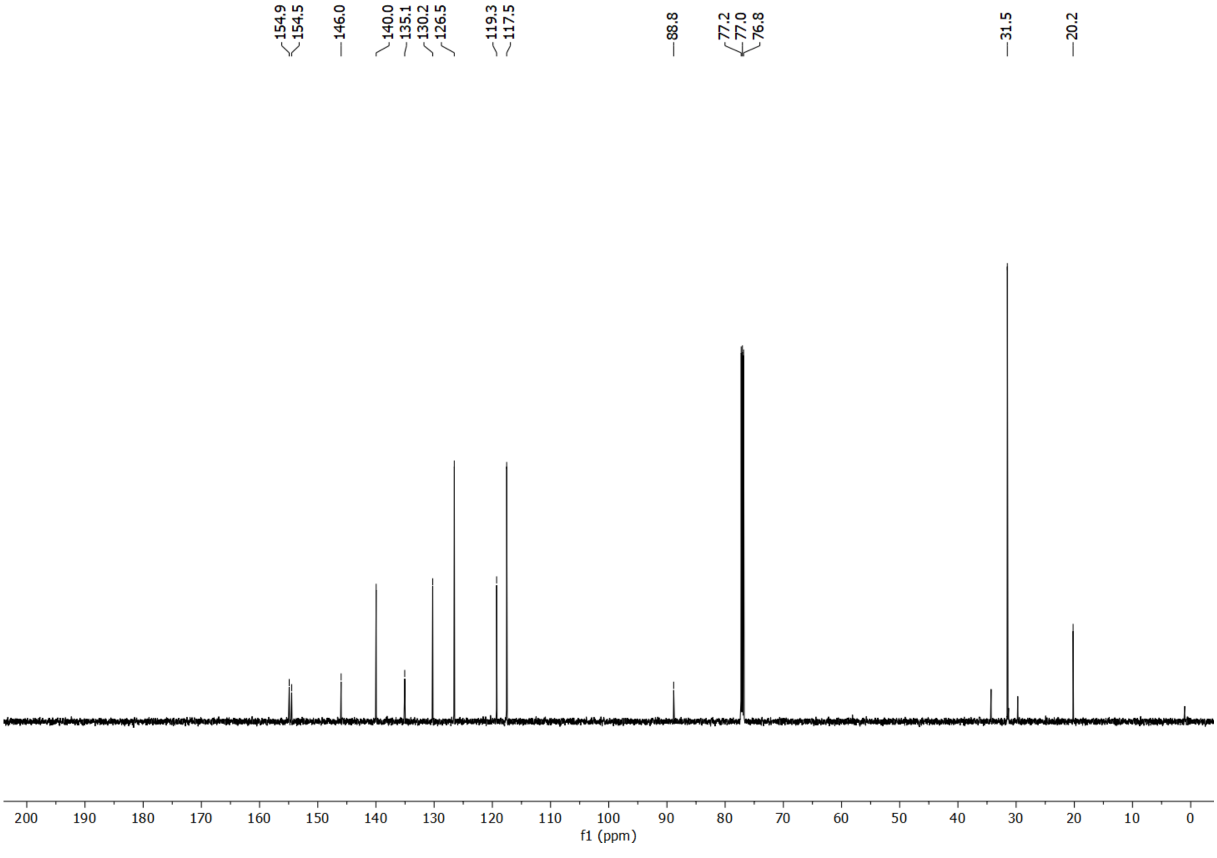


Figure 49: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10k** in $CDCl_3$.

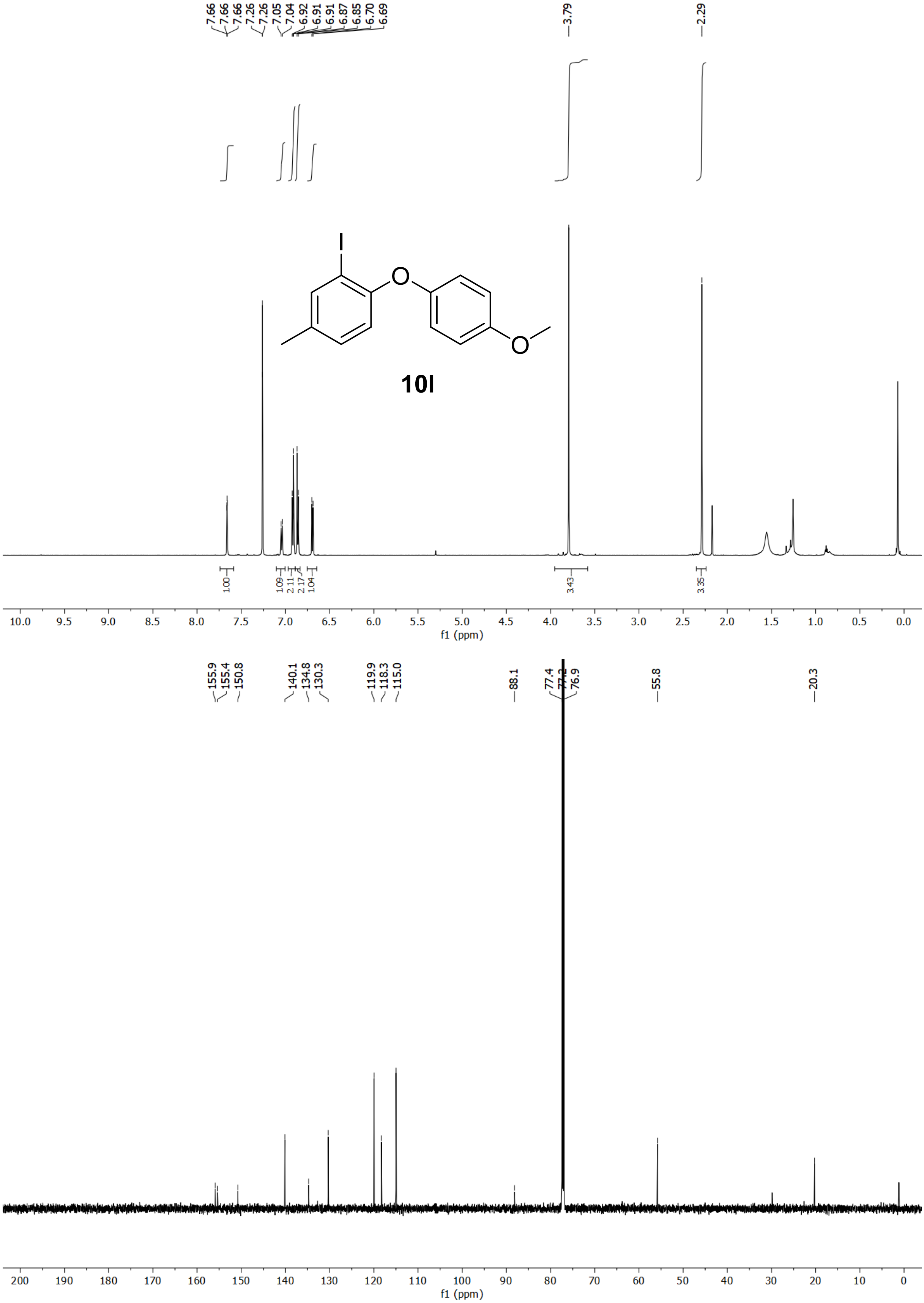
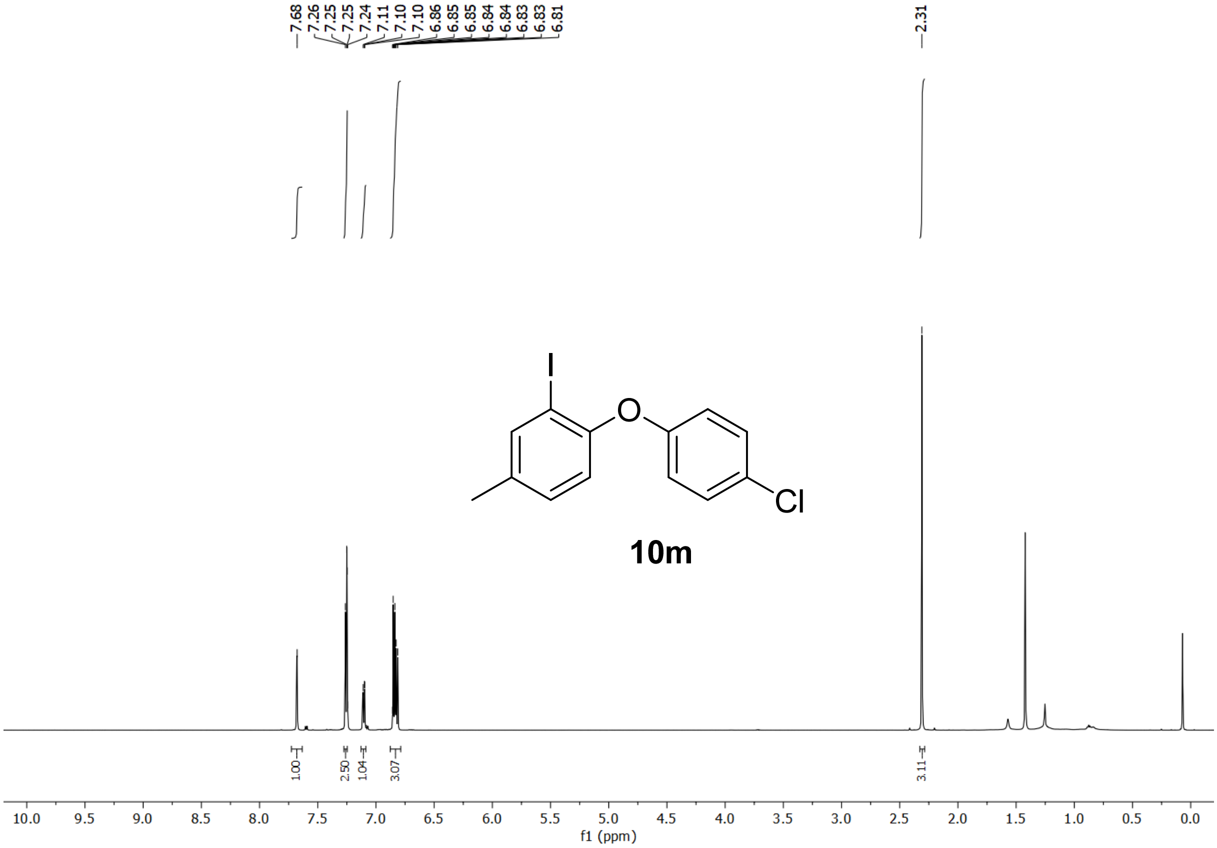


Figure 50: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10l** in $CDCl_3$.



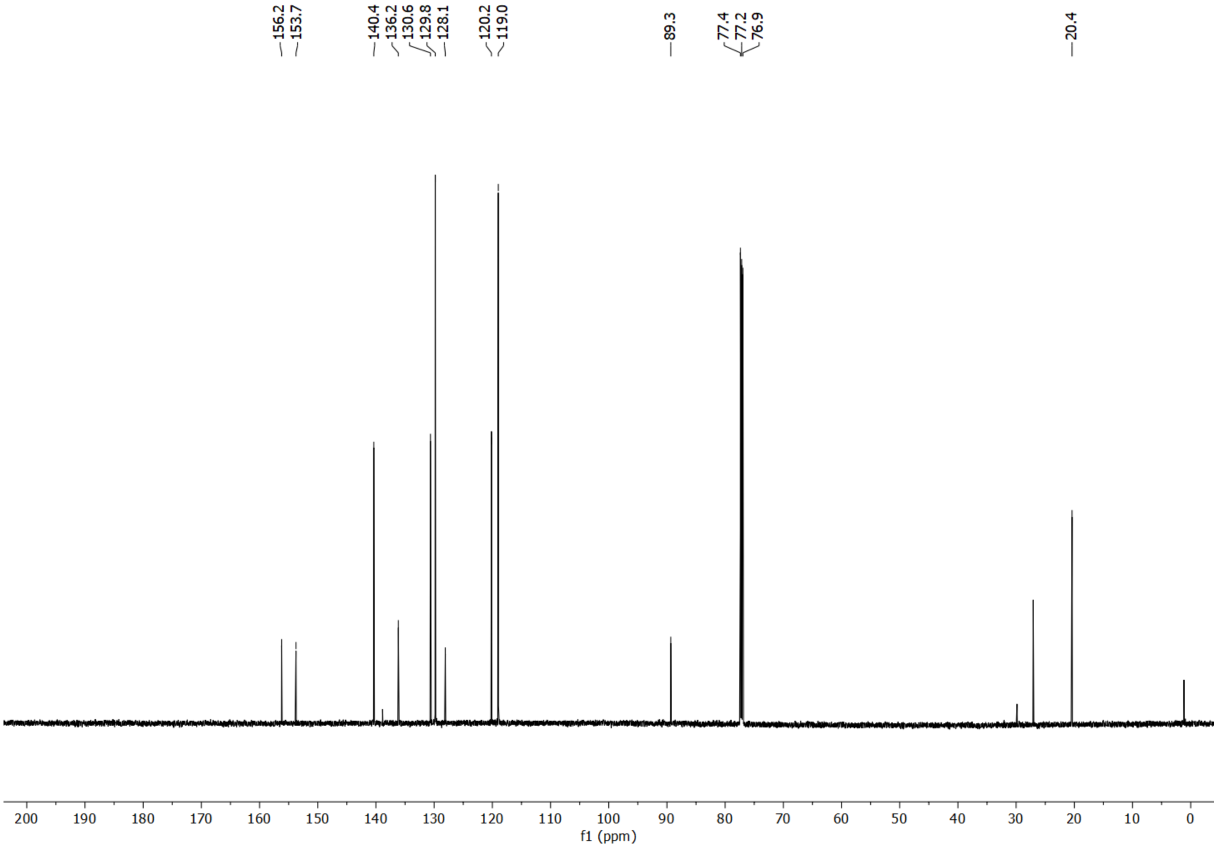


Figure 51: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10m** in $CDCl_3$.

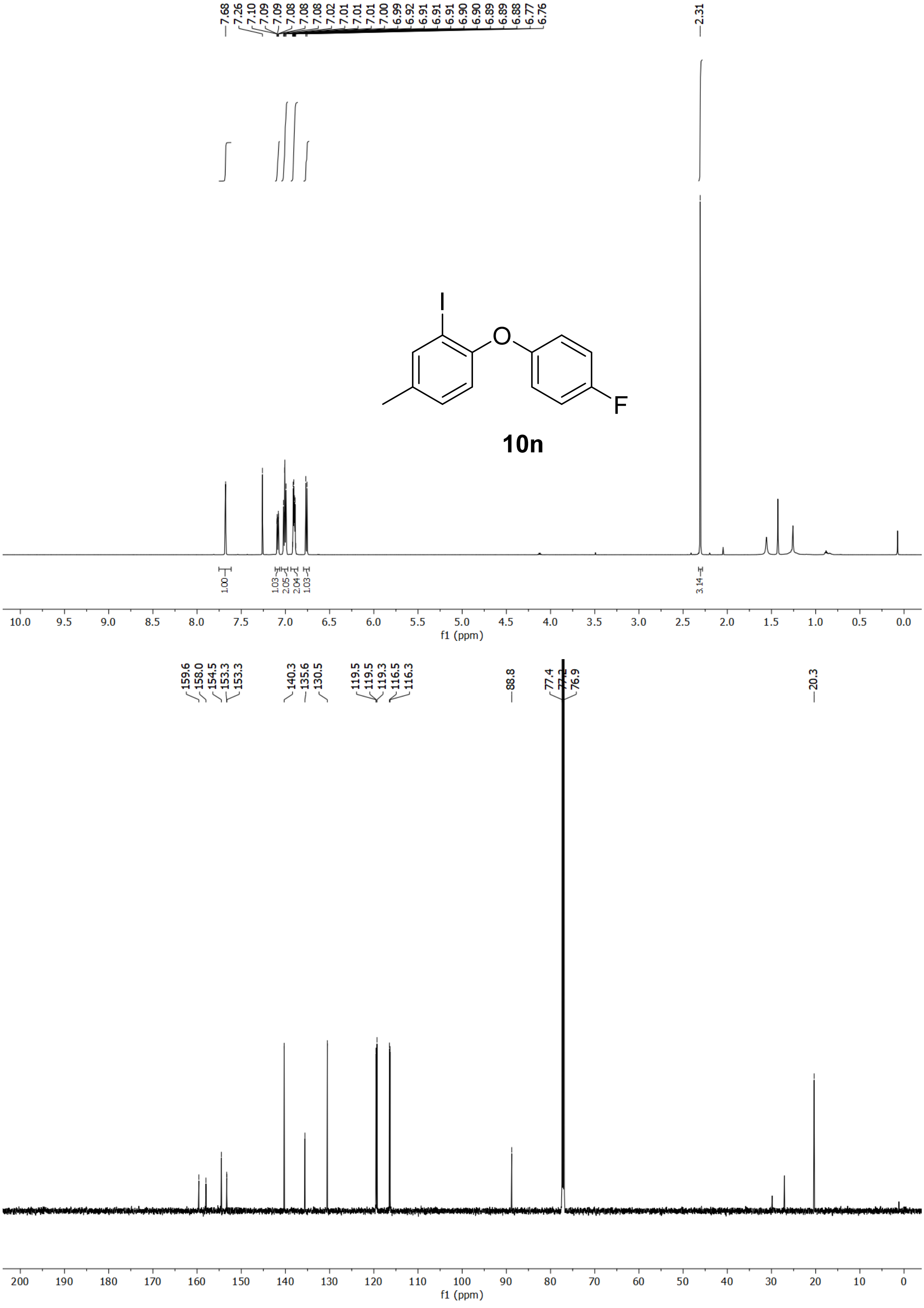


Figure 52: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10n** in $CDCl_3$.

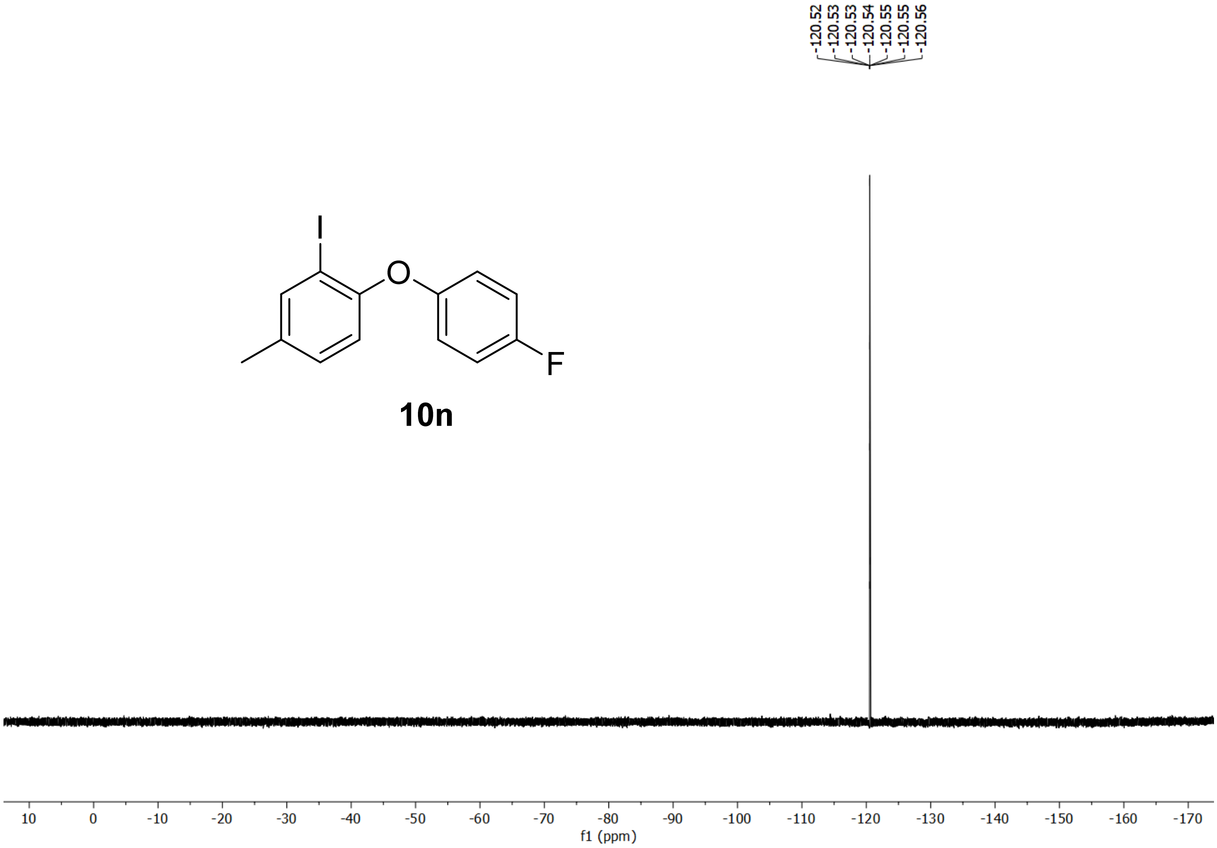


Figure 53: 565 MHz ^{19}F-NMR-spectrum of **10n** in $CDCl_3$.

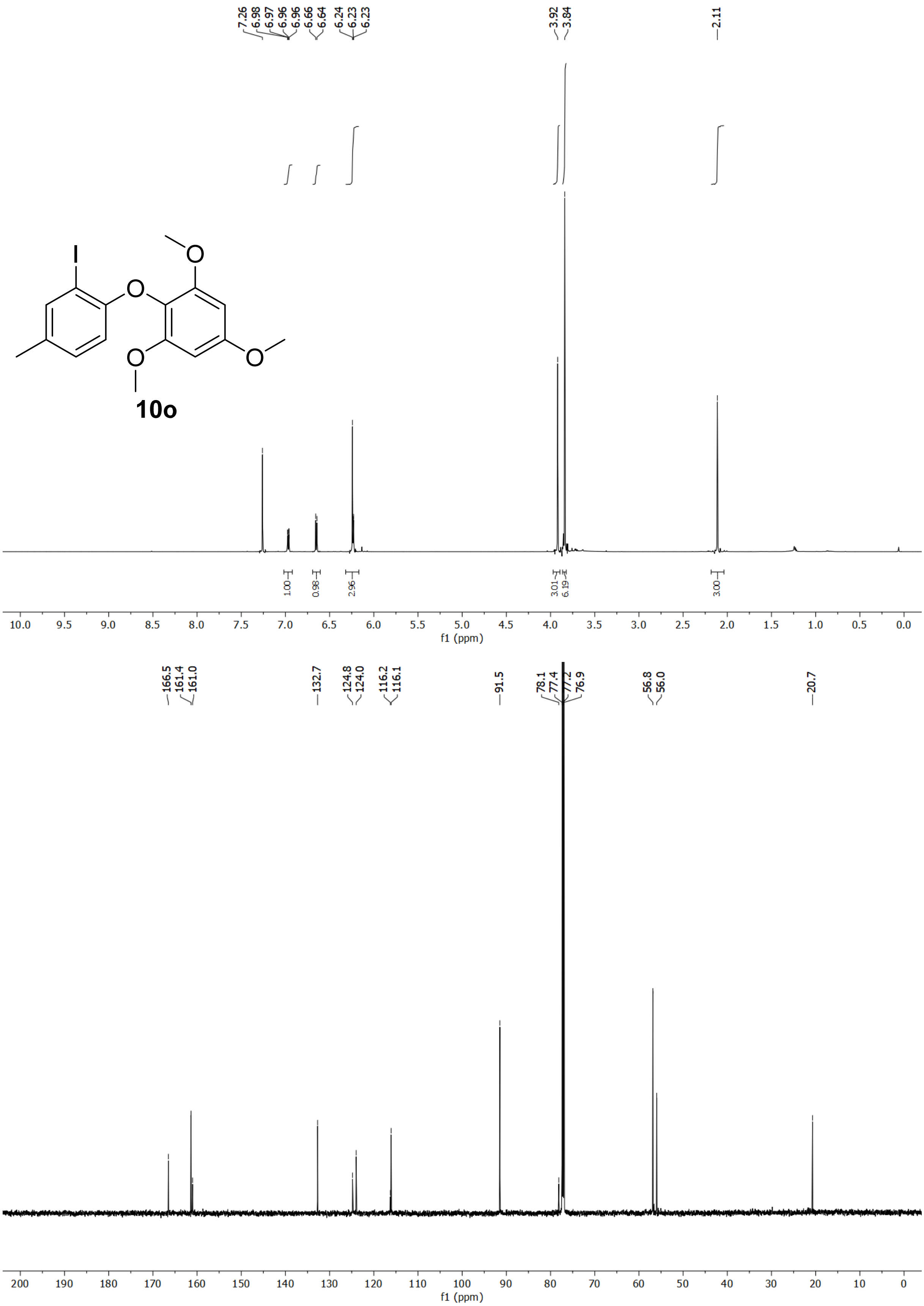


Figure 54: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10o** in $CDCl_3$.

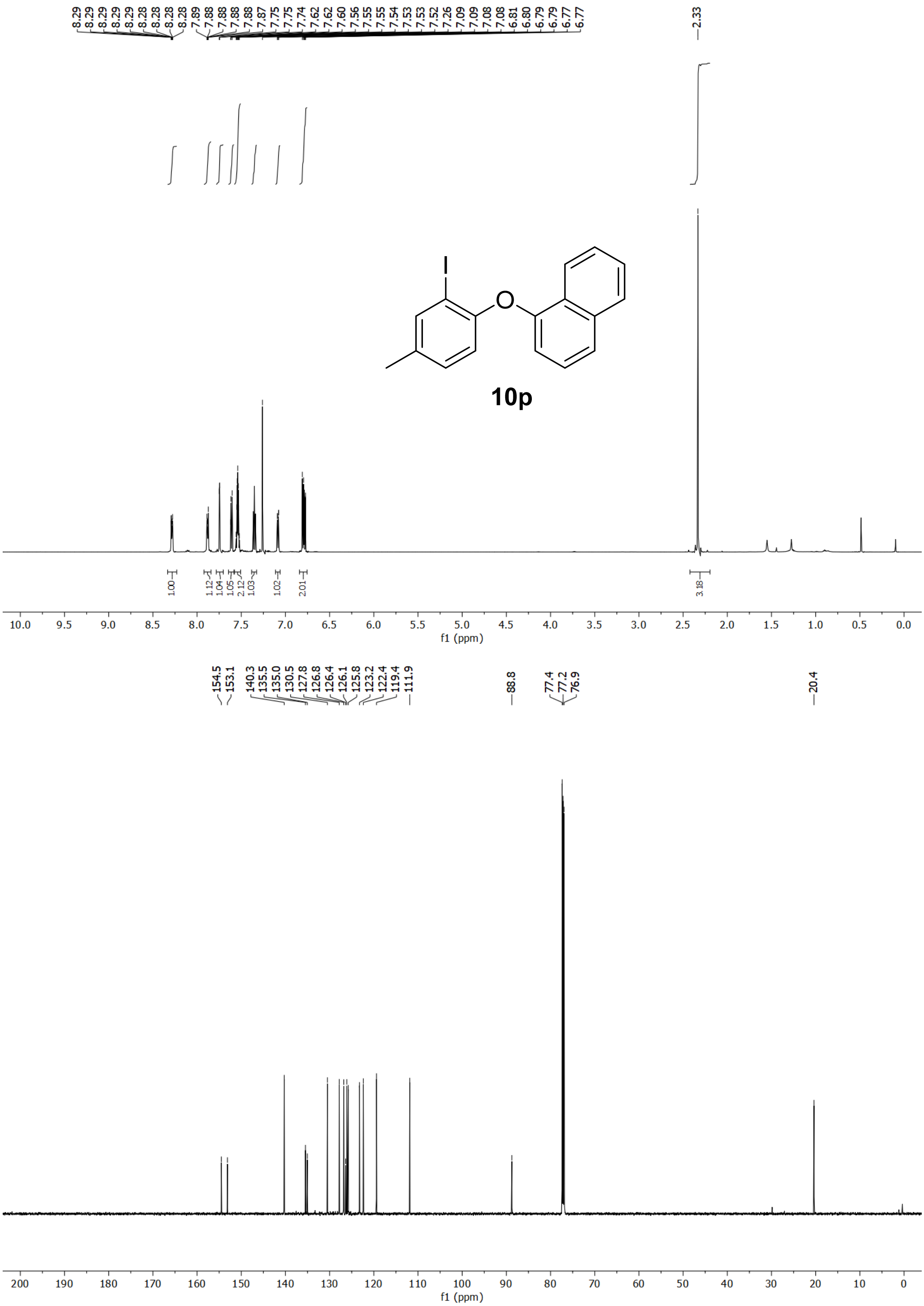


Figure 55: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10p** in $CDCl_3$.

Figure 56: 601 MHz ^{1}H- and 151 MHz ^{13}C-NMR-spectrum of **10q** in $CDCl_3$.

7. Crystallographic Data

Crystallographic Data for the obtained single crystal structures for **7a** and **9a**.

7.1 Crystallographic Data from Compound 8a

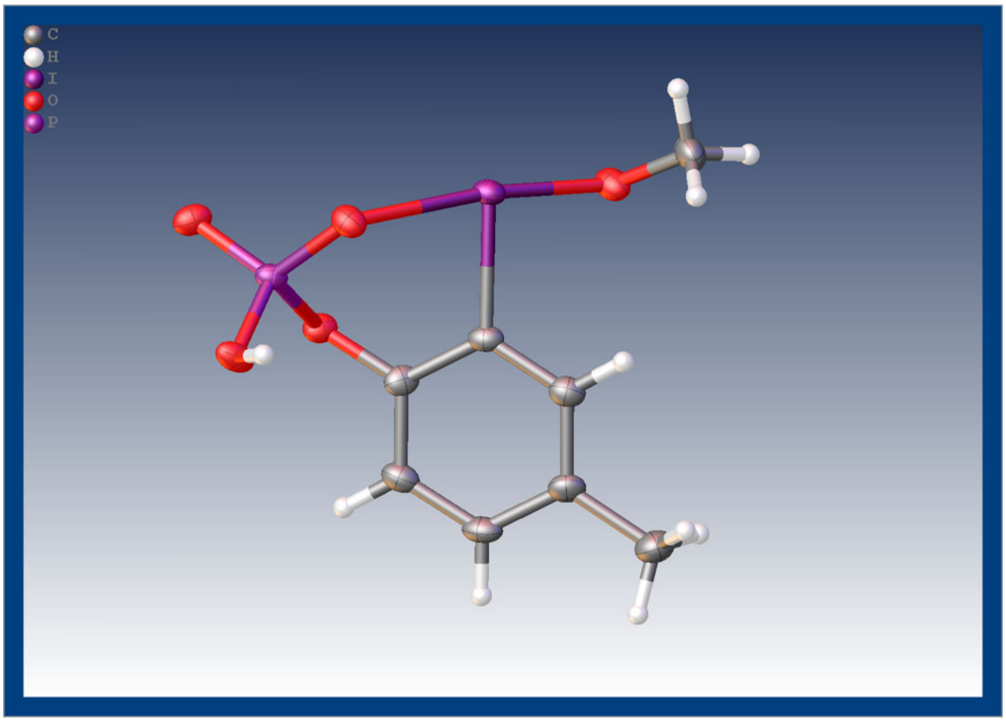


Figure 57: . Crystal data and structure refinement for **8a**.

Table 2: Crystal data and structure refinement for **8a**.

Empirical formula	$C_8H_{10}IO_5P$
Formula weight	344.03
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	22.585(3)
b/Å	4.4660(6)
c/Å	22.660(3)
α/°	90
β/°	99.875(4)
γ/°	90
Volume/Å^3	2251.8(5)
Z	8
ρ_{calc}g/cm^3	2.030
μ/mm^{-1}	2.985
F(000)	1328.0
Crystal size/mm^3	0.12 × 0.113 × 0.064
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.706 to 52.042

Index ranges	-27 ≤ h ≤ 27, -5 ≤ k ≤ 5, -27 ≤ l ≤ 27
Reflections collected	26909
Independent reflections	2218 [R_{int} = 0.0927, R_{sigma} = 0.0361]
Data/restraints/parameters	2218/0/139
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0271, wR_2 = 0.0622
Final R indexes [all data]	R_1 = 0.0348, wR_2 = 0.0653
Largest diff. peak/hole / e Å^{-3}	1.01/-0.45

Table 3: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **8a**.

Atom	x	*y*	*z*	U(eq)
I1	6670.0(2)	5333.2(5)	5187.8(2)	18.06(10)
P1	7938.8(4)	5740(2)	6164.2(4)	17.1(2)
O2	7643.1(12)	4337(6)	5578.6(12)	21.3(6)
O3	8342.5(13)	8323(6)	6115.0(12)	22.7(6)
O5	5793.4(12)	6098(7)	4949.1(12)	25.2(6)
O4	8252.0(13)	3314(6)	6591.9(12)	22.2(6)
O1	7405.4(12)	7073(6)	6480.0(11)	19.8(6)
C1	6534.9(17)	4140(8)	6048.1(17)	18.9(8)
C6	6926.4(18)	5217(8)	6543.2(18)	19.6(8)
C5	6823.7(19)	4509(9)	7114.9(18)	22.7(8)
C7	5501.7(19)	4120(10)	4480.9(19)	29.0(9)
C2	6056.1(18)	2310(9)	6116.5(18)	22.8(9)
C3	5948.2(19)	1597(9)	6684.9(18)	23.6(9)
C4	6338.0(18)	2749(9)	7180.7(18)	24.0(9)
C8	5424(2)	-336(10)	6768(2)	31.1(10)

Table 4: Anisotropic Displacement Parameters (Å^2×10^3) for **8a**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	22.33(15)	18.86(14)	13.55(14)	0.96(10)	4.65(9)	3.59(10)
P1	23.3(5)	14.3(4)	14.1(5)	0.0(4)	4.1(4)	1.6(4)
O2	22.2(14)	22.6(14)	19.6(14)	-3.7(11)	4.3(11)	6.1(11)
O3	30.6(16)	14.6(13)	25.2(15)	-1.3(11)	10.8(12)	0.8(11)
O5	24.1(15)	32.5(16)	19.3(14)	-0.5(12)	4.9(12)	5.6(12)
O4	35.8(17)	12.1(12)	17.1(14)	-0.9(11)	0.1(12)	2.8(11)
O1	26.8(15)	16.2(13)	17.6(13)	-3.5(11)	7.7(11)	-0.1(11)
C1	24(2)	19.2(18)	15.1(18)	3.1(15)	7.9(16)	7.1(15)
C6	25(2)	13.1(17)	22(2)	-4.0(15)	7.9(16)	0.7(15)
C5	28(2)	21.5(19)	18(2)	1.3(16)	3.0(16)	6.5(17)
C7	20(2)	42(3)	23(2)	2.1(19)	-2.0(17)	-1.6(18)
C2	28(2)	20.4(19)	21(2)	-0.8(16)	6.0(17)	3.2(16)
C3	30(2)	18.1(19)	23(2)	4.9(16)	7.2(18)	3.0(16)
C4	30(2)	27(2)	16(2)	4.3(16)	9.2(18)	9.2(17)
C8	32(2)	35(2)	28(2)	4.0(19)	10.7(19)	-2.4(19)

Table 5: Bond Lengths for **8a**.

Atom	Atom	Length/Å
I1	O2	2.268(3)
I1	O5	1.990(3)
I1	C1	2.093(4)
P1	O2	1.515(3)
P1	O3	1.486(3)
P1	O4	1.542(3)
P1	O1	1.617(3)
O5	C7	1.449(5)
O1	C6	1.390(5)
C1	C6	1.390(6)
C1	C2	1.385(5)
C6	C5	1.391(6)
C5	C4	1.378(6)
C2	C3	1.388(5)
C3	C4	1.401(6)
C3	C8	1.503(6)

Table 6: Bond Angles for **8a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5	I1	O2	172.66(10)	C6	C1	I1	119.3(3)
O5	I1	C1	89.99(13)	C2	C1	I1	119.7(3)
C1	I1	O2	82.69(13)	C2	C1	C6	121.0(3)
O2	P1	O4	110.20(15)	O1	C6	C5	119.2(4)
O2	P1	O1	106.87(15)	C1	C6	O1	121.5(3)
O3	P1	O2	116.06(16)	C1	C6	C5	119.2(4)
O3	P1	O4	111.80(17)	C4	C5	C6	119.6(4)
O3	P1	O1	105.11(15)	C1	C2	C3	120.3(4)
O4	P1	O1	106.07(15)	C2	C3	C4	118.3(4)
P1	O2	I1	120.84(14)	C2	C3	C8	121.0(4)
C7	O5	I1	113.6(2)	C4	C3	C8	120.7(4)
C6	O1	P1	118.6(2)	C5	C4	C3	121.7(4)

Table 7: Torsion Angles for **8a**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
I1	C1	C6	O1	0.1(5)	O1	C6	C5	C4	177.9(3)
I1	C1	C6	C5	177.7(3)	C1	C6	C5	C4	0.2(6)
I1	C1	C2	C3	-177.5(3)	C1	C2	C3	C4	-0.6(6)
P1	O1	C6	C1	-65.1(4)	C1	C2	C3	C8	178.8(4)
P1	O1	C6	C5	117.3(3)	C6	C1	C2	C3	2.1(6)
O2	P1	O1	C6	51..0(3)	C6	C5	C4	C3	1.2(6)
O3	P1	O2	I1	-101.90(19)	C2	C1	C6	O1	-179.5(3)
O3	P1	O1	C6	174.8(3)	C2	C1	C6	C5	-1.8(6)
O4	P1	O2	I1	129.76(17)	C2	C3	C4	C5	-1.0(6)
O4	P1	O1	C6	-66.6(3)	C8	C3	C4	C5	179.5(4)
O1	P1	O2	I1	14..9(2)					

Table 8: Hydrogen Atom Coordinates (Å×10[4]) and Isotropic Displacement Parameters (Å[2]×10[3]) for **8a**.

Atom	*x*	*y*	*z*	U(eq)
H4	8224.11	1651.65	6415.71	33
H5	7086.57	5234.13	7457.63	27
H7A	5666..04	4470.55	4113.78	43
H7B	5068..54	4517.84	4404.66	43
H7C	5573..2	2034.43	4607.74	43
H2	5800.65	1539.73	5773.22	27
H4A	6265..67	2305.42	7572.22	29
H8A	5050..94	810.51	6664.79	47
H8B	5472	-985.25	7186.83	47
H8C	5408..21	-2095.16	6507.35	47

7.2 Crystallographic Data from Compound 9a

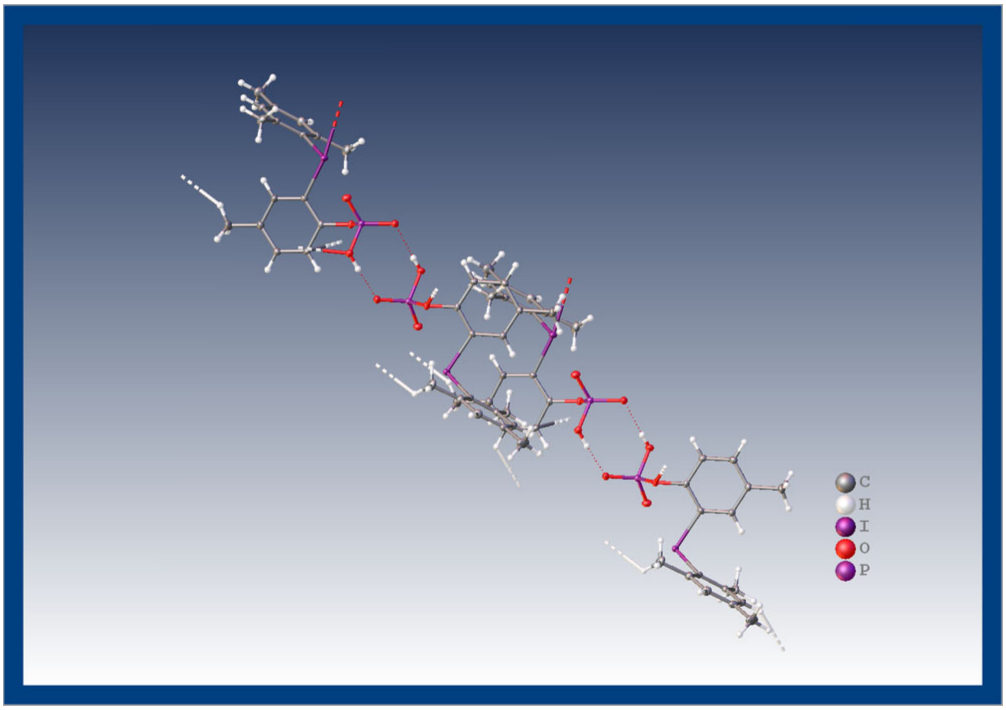


Figure 58: Crystal data and structure refinement for **9a**.

Table 9: Crystal data and structure refinement for **9a**.

Empirical formula	$C_{16}H_{18}IO_4P$
Formula weight	432.17
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	10.5418(5)
b/Å	12.7822(5)

c/Å	13.0647(6)
α/°	97.395(2)
β/°	95.008(2)
γ/°	107.951(2)
Volume/Å^3	1645.70(13)
Z	4
ρ_{calc}g/cm^3	1.744
μ/mm^{-1}	2.058
F(000)	856.0
Crystal size/mm^3	0.242 × 0.172 × 0.107
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.396 to 56.648
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -17 ≤ l ≤ 17
Reflections collected	48708
Independent reflections	8194 [R_{int} = 0.0374, R_{sigma} = 0.0246]
Data/restraints/parameters	8194/0/413
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0198, wR_2 = 0.0477
Final R indexes [all data]	R_1 = 0.0215, wR_2 = 0.0486
Largest diff. peak/hole / e Å^{-3}	1.81/-0.79

Table 10: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **9a**.

Atom	*x*	*y*	*z*	U(eq)
I1	3770.3(2)	407.0(2)	10812.8(2)	10.96(3)
I2	6101.8(2)	4448.1(2)	13808.2(2)	11.19(3)
P2	4605.6(5)	2978.3(4)	15808.3(4)	11.40(9)
P1	4905.9(5)	1908.3(4)	8643.3(4)	11.55(9)
O7	4065.8(13)	3217.9(11)	14805.8(10)	16.0(3)
O6	4024.2(13)	1706.0(10)	15850.4(11)	14.3(3)
O4	5720.8(13)	1648.7(11)	9510.3(11)	16.5(3)
O5	6228.3(12)	3212.9(10)	15796.4(10)	11.9(2)
O8	4557.8(13)	3689.9(11)	16804.9(10)	15.2(3)
O2	5453.1(14)	3186.1(11)	8580.2(11)	14.3(3)
O1	3403.2(12)	1731.6(10)	8986.5(10)	11.9(2)
O3	4627.9(14)	1189.6(11)	7600.8(10)	17.2(3)
C7	2242.4(17)	-268.9(14)	11710.3(13)	10.7(3)
C1	3269.4(17)	1887.1(14)	10830.0(14)	11.5(3)
C6	2978.5(18)	2416.4(15)	11736.8(14)	13.2(3)
C23	7803.8(17)	5160.5(14)	13081.9(14)	11.3(3)
C21	7646.8(19)	1653.2(15)	13338.3(15)	16.1(4)
C5	2691.2(17)	3405.4(15)	11735.4(14)	12.8(3)
C12	2540.3(18)	-1.4(14)	12791.8(14)	12.2(3)
C22	7276.4(19)	2588.2(15)	13228.5(14)	14.6(3)
C4	2723.7(18)	3853.1(15)	10813.8(15)	14.8(3)
C17	6761.9(17)	3085.7(14)	14032.9(14)	11.4(3)
C28	7694.4(18)	4932.4(14)	11996.3(14)	12.8(3)
C19	6974.6(18)	1727.3(15)	15067.7(14)	13.6(3)
C20	7465.6(19)	1218.5(15)	14261.3(15)	15.9(4)
C11	1460.8(19)	-347.3(16)	13350.0(14)	15.4(3)
C27	8865.9(19)	5360.4(15)	11556.1(15)	15.2(3)
C3	2991.0(18)	3312.9(15)	9909.8(14)	13.5(3)
C8	966.1(18)	-892.5(15)	11182.7(14)	14.1(3)

Atom	*x*	*y*	*z*	U(eq)
C18	6633.5(17)	2675.7(14)	14963.9(14)	11.2(3)
C14	675(2)	-1219.0(19)	10014.1(16)	23.5(4)
C24	9004.0(18)	5786.3(15)	13723.1(14)	13.8(3)
C2	3255.5(17)	2315.1(14)	9908.6(13)	10.7(3)
C13	2350(2)	3978.1(17)	12708.1(15)	19.1(4)
C29	8221(3)	1121.2(18)	12479.1(17)	27.2(5)
C32	6395.3(19)	4272.2(17)	11306.1(15)	19.3(4)
C10	167.7(19)	-964.3(16)	12872.8(16)	16.8(4)
C9	-52.6(18)	-1235.4(16)	11790.3(16)	17.3(4)
C16	3929.9(19)	602.5(16)	13362.0(15)	16.4(4)
C26	10085.5(18)	5990.9(15)	12154.6(15)	14.9(3)
C30	9095(2)	6048.7(18)	14892.1(16)	22.2(4)
C25	10130.4(18)	6190.2(16)	13232.2(15)	16.5(4)
C31	11332(2)	6459.3(18)	11663.7(18)	23.2(4)
C15	-972(2)	-1347.0(19)	13496.9(19)	27.0(5)

Table 11: Anisotropic Displacement Parameters (Å^2×10^3) for **9a**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	12.06(5)	10.22(5)	12.68(6)	4.19(4)	5.51(4)	4.63(4)
I2	11.88(5)	10.20(5)	13.20(6)	4.74(4)	4.45(4)	4.15(4)
P2	12.5(2)	10.9(2)	11.9(2)	3.53(16)	4.52(16)	3.96(16)
P1	13.6(2)	11.0(2)	11.5(2)	3.30(16)	4.42(16)	4.80(16)
O7	15.5(6)	18.1(6)	16.3(7)	6.7(5)	2.8(5)	6.2(5)
O6	17.9(6)	11.4(6)	13.0(6)	3.1(5)	4.4(5)	2.8(5)
O4	17.0(6)	16.7(6)	17.9(7)	6.2(5)	2.7(5)	7.0(5)
O5	12.7(6)	12.8(6)	10.0(6)	0.7(5)	2.6(5)	4.0(5)
O8	21.0(7)	13.8(6)	13.9(6)	3.8(5)	6.8(5)	8.3(5)
O2	16.8(6)	11.3(6)	15.3(7)	4.9(5)	4.9(5)	3.4(5)
O1	11.7(6)	12.6(6)	10.3(6)	0.1(5)	2.1(5)	2.9(5)
O3	26.8(7)	13.2(6)	13.9(6)	2.7(5)	7.9(5)	8.0(5)
C7	11.2(7)	10.5(7)	11.4(8)	3.7(6)	4.9(6)	3.2(6)
C1	11.0(7)	9.1(7)	14.2(8)	1.8(6)	2.3(6)	3.0(6)
C6	13.9(8)	13.7(8)	12.1(8)	2.3(6)	2.6(6)	4.5(6)
C23	11.3(8)	10.0(7)	13.3(8)	4.9(6)	4.2(6)	2.6(6)
C21	19.7(9)	13.2(8)	15.8(9)	0.9(7)	4.9(7)	5.6(7)
C5	12.9(8)	13.4(8)	11.8(8)	0.8(6)	1.1(6)	4.5(6)
C12	14.7(8)	12.0(8)	11.3(8)	1.9(6)	1.0(6)	6.5(6)
C22	19.5(9)	12.7(8)	12.5(8)	3.2(6)	5.3(7)	5.2(7)
C4	16.9(8)	12.8(8)	15.4(9)	2.4(7)	0.7(7)	6.1(7)
C17	12.6(8)	8.5(7)	13.5(8)	2.7(6)	2.3(6)	3.4(6)
C28	13.6(8)	11.9(8)	13.0(8)	3.8(6)	1.4(6)	3.5(6)
C19	15.8(8)	13.9(8)	10.7(8)	3.3(6)	0.8(6)	4.3(7)
C20	19.8(9)	13.2(8)	16.4(9)	2.9(7)	1.8(7)	7.7(7)
C11	20.9(9)	19.9(9)	10.7(8)	6.1(7)	5.3(7)	11.8(7)
C27	17.3(8)	16.6(8)	12.9(8)	5.0(7)	3.0(7)	6.0(7)
C3	14.0(8)	14.0(8)	13.3(8)	4.3(6)	1.0(6)	4.9(7)
C8	13.1(8)	16.0(8)	12.9(8)	2.9(7)	0.6(7)	4.2(7)
C18	9.1(7)	11.7(8)	11.3(8)	-0.1(6)	1.6(6)	1.8(6)
C14	20.0(9)	30.6(11)	13.4(9)	0.0(8)	-1.6(7)	1.3(8)
C24	14.8(8)	11.9(8)	14.4(9)	1.5(6)	1.9(7)	4.2(7)
C2	9.2(7)	11.6(8)	10.1(8)	0.0(6)	2.1(6)	2.2(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C13	25.4(10)	20.0(9)	15.1(9)	0.4(7)	5.1(7)	12.5(8)
C29	44.4(13)	21.2(10)	24.1(11)	5.2(8)	17.9(10)	17.9(10)
C32	17.0(9)	22.3(9)	14.0(9)	4.8(7)	-1.7(7)	-0.1(7)
C10	16.0(8)	19.5(9)	20.9(10)	10.1(7)	9.4(7)	9.7(7)
C9	10.9(8)	18.6(9)	21.0(10)	4.6(7)	1.9(7)	2.3(7)
C16	16.8(9)	17.6(9)	13.0(8)	-0.6(7)	-2.4(7)	5.3(7)
C26	12.6(8)	15.2(8)	19.8(9)	7.1(7)	5.9(7)	5.9(7)
C30	22.1(10)	24.4(10)	14.6(9)	-1.0(7)	0.2(7)	2.1(8)
C25	10.6(8)	16.4(8)	19.8(9)	1.6(7)	0.0(7)	1.5(7)
C31	16.8(9)	24.4(10)	31.6(12)	8.9(8)	11.5(8)	7.4(8)
C15	23.7(10)	32.3(11)	34.1(12)	17.2(9)	19.7(9)	13.1(9)

Table 12: Bond Lengths for **9a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C7	2.1091(17)	C21	C29	1.505(3)
I1	C1	2.1133(17)	C5	C4	1.397(3)
I2	C23	2.1121(17)	C5	C13	1.511(2)
I2	C17	2.1086(17)	C12	C11	1.393(2)
P2	O7	1.4878(14)	C12	C16	1.504(2)
P2	O6	1.5614(13)	C22	C17	1.394(2)
P2	O5	1.6450(13)	C4	C3	1.385(3)
P2	O8	1.5033(13)	C17	C18	1.386(2)
P1	O4	1.4946(14)	C28	C27	1.394(2)
P1	O2	1.5715(13)	C28	C32	1.509(2)
P1	O1	1.6404(13)	C19	C20	1.388(3)
P1	O3	1.4923(14)	C19	C18	1.385(2)
O5	C18	1.381(2)	C11	C10	1.390(3)
O1	C2	1.380(2)	C27	C26	1.392(3)
C7	C12	1.394(2)	C3	C2	1.387(2)
C7	C8	1.399(2)	C8	C14	1.508(3)
C1	C6	1.393(2)	C8	C9	1.387(3)
C1	C2	1.386(2)	C24	C30	1.509(3)
C6	C5	1.388(2)	C24	C25	1.389(3)
C23	C28	1.398(2)	C10	C9	1.393(3)
C23	C24	1.400(2)	C10	C15	1.503(3)
C21	C22	1.387(3)	C26	C25	1.392(3)
C21	C20	1.395(3)	C26	C31	1.503(3)

Table 13: Bond Angles for **9a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	I1	C1	92.37(7)	C11	C12	C16	119.90(16)
C17	I2	C23	91.07(7)	C21	C22	C17	120.34(17)
O7	P2	O6	109.94(8)	C3	C4	C5	121.37(17)
O7	P2	O5	107.21(7)	C22	C17	I2	119.39(13)
O7	P2	O8	118.66(8)	C18	C17	I2	119.46(13)
O6	P2	O5	104.37(7)	C18	C17	C22	121.11(16)
O8	P2	O6	112.39(8)	C23	C28	C32	123.47(16)
O8	P2	O5	102.89(7)	C27	C28	C23	116.50(16)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	P1	O2	110.06(8)	C27	C28	C32	120.03(16)
O4	P1	O1	106.71(7)	C18	C19	C20	120.32(17)
O2	P1	O1	103.75(7)	C19	C20	C21	121.22(17)
O3	P1	O4	118.66(8)	C10	C11	C12	122.72(17)
O3	P1	O2	112.66(8)	C26	C27	C28	122.42(17)
O3	P1	O1	103.50(7)	C4	C3	C2	120.19(17)
C18	O5	P2	118.04(11)	C7	C8	C14	123.29(16)
C2	O1	P1	120.13(11)	C9	C8	C7	116.73(17)
C12	C7	I1	118.01(12)	C9	C8	C14	119.96(17)
C12	C7	C8	123.98(16)	O5	C18	C17	121.65(16)
C8	C7	I1	117.85(13)	O5	C18	C19	119.63(16)
C6	C1	I1	121.14(13)	C19	C18	C17	118.67(16)
C2	C1	I1	117.44(12)	C23	C24	C30	122.84(17)
C2	C1	C6	121.42(16)	C25	C24	C23	116.86(17)
C5	C6	C1	120.02(17)	C25	C24	C30	120.28(17)
C28	C23	I2	118.53(13)	O1	C2	C1	121.33(15)
C28	C23	C24	123.57(16)	O1	C2	C3	119.87(16)
C24	C23	I2	117.80(13)	C1	C2	C3	118.63(16)
C22	C21	C20	118.26(17)	C11	C10	C9	118.28(17)
C22	C21	C29	120.63(18)	C11	C10	C15	121.56(19)
C20	C21	C29	121.11(17)	C9	C10	C15	120.16(18)
C6	C5	C4	118.31(16)	C8	C9	C10	122.15(17)
C6	C5	C13	120.59(17)	C27	C26	C25	118.39(17)
C4	C5	C13	121.10(16)	C27	C26	C31	121.59(18)
C7	C12	C16	124.03(16)	C25	C26	C31	120.02(17)
C11	C12	C7	116.06(16)	C24	C25	C26	122.26(17)

Table 14: Torsion Angles for **9a**.

Atom	Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Atom	Angle/°
I1	C7	C12	C11	172.19(13)	C5	C4	C3	C2	-1.1(3)
I1	C7	C12	C16	-9.0(2)	C12	C7	C8	C14	-177.11(18)
I1	C7	C8	C14	7..6(2)	C12	C7	C8	C9	1.4(3)
I1	C7	C8	C9	-173.88(13)	C12	C11	C10	C9	-0.6(3)
I1	C1	C6	C5	178.09(13)	C12	C11	C10	C15	178.69(18)
I1	C1	C2	O1	7.6(2)	C22	C21	C20	C19	-2.3(3)
I1	C1	C2	C3	-177.07(13)	C22	C17	C18	O5	174.69(16)
I2	C23	C28	C27	-175.96(13)	C22	C17	C18	C19	-2.7(3)
I2	C23	C28	C32	4.7(2)	C4	C3	C2	O1	174.28(16)
I2	C23	C24	C30	-5.3(2)	C4	C3	C2	C1	-1.1(3)
I2	C23	C24	C25	176.21(13)	C28	C23	C24	C30	178.41(18)
I2	C17	C18	O5	-7.6(2)	C28	C23	C24	C25	-0.1(3)
I2	C17	C18	C19	175.03(13)	C28	C27	C26	C25	0.5(3)
P2	O5	C18	C17	82.82(18)	C28	C27	C26	C31	-179.06(17)
P2	O5	C18	C19	-99.82(17)	C20	C21	C22	C17	1.2(3)
P1	O1	C2	C1	-90.46(18)	C20	C19	C18	O5	-175.88(16)
P1	O1	C2	C3	94..25(17)	C20	C19	C18	C17	1.6(3)
O7	P2	O5	C18	-54.00(14)	C11	C10	C9	C8	-1.2(3)
O6	P2	O5	C18	62.61(14)	C27	C26	C25	C24	-0.3(3)
O4	P1	O1	C2	56..81(14)	C8	C7	C12	C11	-3.1(3)
O8	P2	O5	C18	-179.87(12)	C8	C7	C12	C16	175.73(17)
O2	P1	O1	C2	-59.44(14)	C18	C19	C20	C21	1.0(3)

Atom	Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Atom	Angle/°
O3	P1	O1	C2	-177.25(13)	C14	C8	C9	C10	179.41(18)
C7	C12	C11	C10	2.7(3)	C24	C23	C28	C27	0.3(3)
C7	C8	C9	C10	0..9(3)	C24	C23	C28	C32	-179.06(17)
C1	C6	C5	C4	-1..0(3)	C2	C1	C6	C5	-1.2(3)
C1	C6	C5	C13	178.93(17)	C13	C5	C4	C3	-177.79(17)
C6	C1	C2	O1	-173.07(15)	C29	C21	C22	C17	-179.14(19)
C6	C1	C2	C3	2.3(3)	C29	C21	C20	C19	178.01(19)
C6	C5	C4	C3	2.1(3)	C32	C28	C27	C26	178.87(17)
C23	C28	C27	C26	-0.5(3)	C16	C12	C11	C10	-176.19(17)
C23	C24	C25	C26	0.1(3)	C30	C24	C25	C26	-178.48(18)
C21	C22	C17	I2	-176.42(14)	C31	C26	C25	C24	179.31(18)
C21	C22	C17	C18	1.3(3)	C15	C10	C9	C8	179.44(18)

Table 15: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **9a**.

Atom	x	y	z	U(eq)
H6	2976.68	2100.3	12356.36	16
H22	7373..84	2891.12	12601.86	18
H4	2559.15	4542.36	10806.72	18
H19	6872..02	1423.79	15693.72	16
H20	7682..26	562.18	14339.39	19
H11	1614..86	-153.43	14087.49	18
H27	8830..49	5216.35	10820.68	18
H3	2992.98	3626.8	9288.99	16
H14A	858..22	-545.99	9691.29	35
H14B	-271.7	-1674.44	9815.88	35
H14C	1250.41	-1648.69	9775.74	35
H13A	1390.67	3898.55	12618.44	29
H13B	2884.11	4771	12832.76	29
H13C	2555.11	3636.07	13304.08	29
H29A	8188.52	1492.04	11870.4	41
H29B	7691.58	329.44	12288.91	41
H29C	9156.71	1195.8	12718.32	41
H32A	6057.68	3527.06	11493.86	29
H32B	6556.31	4205.74	10576.71	29
H32C	5728.33	4654.97	11399.55	29
H9	-929.22	-1669.35	11457.5	21
H16A	4533.68	181	13173.82	25
H16B	3898.54	674.44	14114.56	25
H16C	4263.24	1345.67	13169.38	25
H30A	8462.24	6444.18	15070.61	33
H30B	10012.9	6518.89	15184.12	33
H30C	8870.67	5353.37	15180.84	33
H25	10960.1	6617.29	13645.95	20
H31A	12020.45	6142.48	11900.41	35
H31B	11671.94	7271.76	11866.51	35
H31C	11116.84	6269	10903.93	35
H15A	-622.24	-1173.63	14240.32	41
H15B	-1410.04	-2153.5	13296.63	41
H15C	-1628.27	-963.23	13360.43	41
H6A	4240(30)	1520(20)	16420(20)	43(9)
H2	5150(30)	3300(30)	8070(30)	56(11)