

Supporting Information

for

Insertion of Benzyne into the P=N Bond of *P*- Alkenyl(alkynyl)- λ^5 -phosphazenes

Mateo Alajarin,* Carmen Lopez-Leonardo,* Rosalia Raja, Raul Angel Orenes

*Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia,
Campus de Espinardo, 30100 Murcia, Spain, and Servicio de Apoyo a la Investigación
(SAI), Universidad de Murcia, Campus de Espinardo, 30100 Murcia, Spain*

E-mail: alajarin@um.es, melill@um.es

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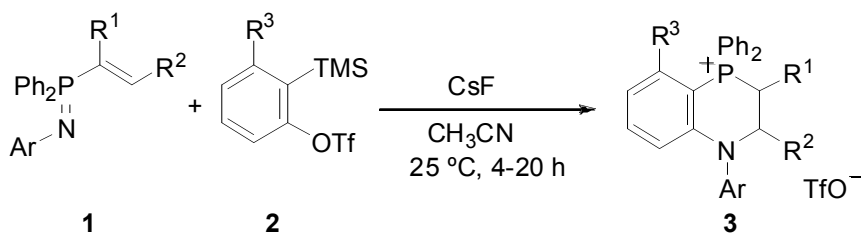
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General Information:

All the experiments were carried out under inert atmosphere. HPLC grade solvents (Scharlab) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System. Flash column chromatography was performed with the indicated solvents using silica gel 60 (60 Å CC, 35-70 µm; SDS) as stationary phase, and TLC was performed on precoated silica gel on aluminum cards (0.25 mm thick, with fluorescent indicator 254 nm, Fluka) and observed under UV light. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. Infrared spectra were recorded on a Bruker Vector 22 apparatus. ^1H - and ^{13}C -NMR spectra were recorded at 298 K on Bruker Avance 300 and 400 MHz instruments using TMS as internal reference for ^1H and ^{13}C NMR, 85% phosphoric acid as external reference for ^{31}P NMR and trifluorotoluene as external reference for ^{19}F NMR. Signals in the ^1H and ^{13}C NMR spectra of the synthesized compounds were assigned with the aid of ^1H $\{^{31}\text{P}\}$, DEPT and two-dimensional NMR experiments (HMQC). Abbreviations of coupling patterns are as follows: s, singlet; d, doublet; t, triplet; q = quadruplet; m, multiplet; br s, broad singlet. Mass spectra were recorded with Agilent VL (ESI) mass spectrometer.

Materials: Unless otherwise stated, all reagents were purchased from Aldrich Chemicals and used without further purification. The iminophosphoranes **1** and **4** are readily prepared by the stoichiometric reaction of aryl azides and the corresponding phosphane under the standard conditions of the Staudinger imination reaction.¹ 3-Methoxy-2-trimethylsilylphenyl trifluoromethanesulfonate,² and *P,P*-diphenyl-*P*-phenylethynylphosphane sulphide **5**³ were prepared according standard procedures.

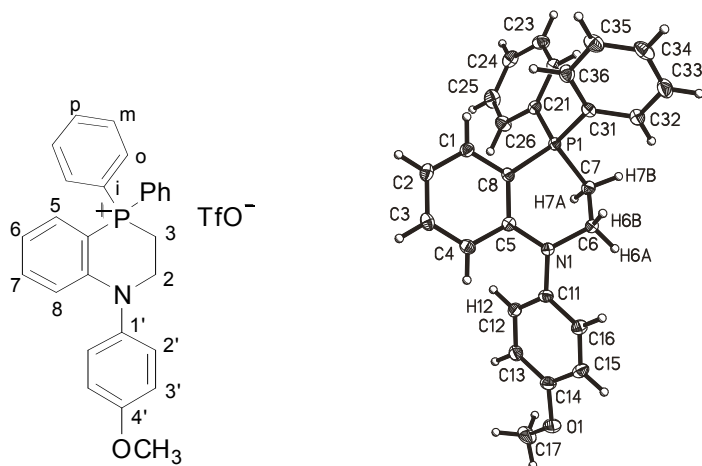
General Procedure for the Synthesis of 3:



To a suspension of the corresponding λ^5 -phosphazene **1** (0.3 mmol) and CsF (0.09 g, 0.6 mmol) in acetonitrile (3 mL) was added a solution of aryne precursor **2** (0.36 mmol) in acetonitrile (7 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 4 h (for the *P*-vinyl unsubstituted λ^5 -phosphazenes and benzyne) or 20 h (for the *P*-alkenyl substituted λ^5 -phosphazenes or 3-methoxybenzyne). Then the reaction was filtered through a Celite plug. The solvent was evaporated to dryness under reduced pressure, and the crude product was purified by flash column chromatography on silica gel deactivated with 5% Et₃N in *n*-hexane, using chloroform/methanol (9:1) as eluent.

Characterization of 3:

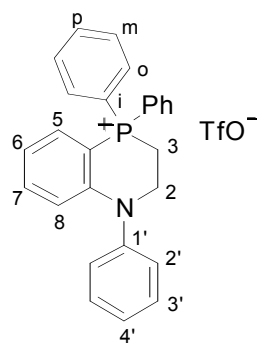
1-(4-Methoxyphenyl)-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3a).



White solid (0.15 g, 90%) that was recrystallized from CH₂Cl₂/Et₂O (colorless prisms); m.p. 186-188 °C; IR (Nujol): 3080, 1598, 1483, 1441, 1263, 1158, 1112, 1031, 911, 730 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 3.46-3.55 (m, 2 H, H3), 3.83 (s, 3 H, OCH₃), 3.94-4.03 (m, 2 H, H2), 6.59 (br t, ³J_{7,8} = ⁴J_{8,P} = 8.0 Hz, 1 H, H8), 6.83 (ddt, ³J_{5,6} = ³J_{6,7} = 8.0 Hz, ⁴J_{6,P} = 2.1 Hz, ⁴J_{6,8} = 0.9 Hz, 1 H, H6), 6.96 (d, ³J_{2',3'} = 8.2 Hz, 2 H, H2'), 7.12 (ddd, ³J_{5,P} = 14.0 Hz, ³J_{5,6} = 8.0 Hz, ⁴J_{5,7} = 1.5 Hz, 1 H, H5), 7.16 (d, ³J_{2',3'} = 8.2 Hz, 2 H, H3'),

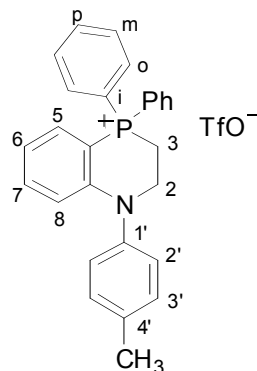
7.33 (dt, $^3J_{6,7}=^3J_{7,8}=8.0$ Hz, $^4J_{5,7}=1.5$ Hz, 1 H, H7), 7.68-7.81 (m, 10 H, PPh₂) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl₃): δ 18.83 (d, $^1J_{3,\text{P}}=53.7$ Hz, C3), 46.76 (d, $^2J_{2,\text{P}}=7.3$ Hz, C2), 55.64 (OCH₃), 94.48 (d, $^1J_{4\text{a},\text{P}}=90.0$ Hz, C4a), 115.83 (C3'), 117.50 (d, $^3J_{8,\text{P}}=7.1$ Hz, C8), 118.73 (d, $^3J_{6,\text{P}}=11.7$ Hz, C6), 119.28 (d, $^1J_{\text{i},\text{P}}=88.9$ Hz, C_i), 120.83 (q, $^1J_{\text{CF}}=320.7$ Hz, CF₃SO₃), 128.60 (C2'), 130.59 (d, $^3J_{\text{m},\text{P}}=13.1$ Hz, C_m), 133.54 (d, $^2J_{\text{o},\text{P}}=10.7$ Hz, C_o), 133.76 (d, $^2J_{5,\text{P}}=7.0$ Hz, C5), 135.25 (d, $^4J_{\text{p},\text{P}}=2.9$ Hz, C_p), 136.00 (d, $^4J_{7,\text{P}}=1.8$ Hz, C7), 137.73 (C1'), 153.05 (d, $^2J_{8\text{a},\text{P}}=3.8$ Hz, C8a), 158.98 (C4') ppm; ^{31}P NMR (162 MHz, CDCl₃): δ 8.63 ppm; ^{19}F NMR (282 MHz, CDCl₃): δ -78.25 ppm; HRMS (ESI) calcd for C₂₇H₂₅NOP ([M-OTf]⁺): 410.1668, found: 410.1673.

1,4,4-Triphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3b).



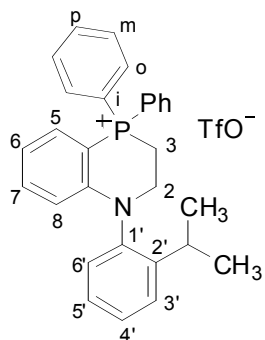
White solid (0.13 g, 80%) that was recrystallized from CH₂Cl₂/Et₂O (colorless prisms); m.p. 159-161 °C; IR (Nujol): 3067, 1589, 1483, 1440, 1336, 1262, 1148, 1111, 1031, 907, 694 cm⁻¹; ^1H NMR (400 MHz, CDCl₃): δ 3.58-3.64 (m, 2 H, H3), 4.03-4.12 (m, 2 H, H2), 6.68 (br t, $^3J_{7,8}=^4J_{8,\text{P}}=7.9$ Hz, 1 H, H8), 6.87 (dddd, $^3J_{5,6}=7.9$ Hz, $^3J_{6,7}=7.0$ Hz, $^4J_{6,\text{P}}=2.1$ Hz, $^4J_{6,8}=0.9$ Hz, 1 H, H6), 7.16 (ddd, $^3J_{5,\text{P}}=13.9$ Hz, $^3J_{5,6}=7.9$ Hz, $^4J_{5,7}=1.5$ Hz, 1 H, H5), 7.24 (d, $^3J_{2,3}=7.5$ Hz, 2 H, H2'), 7.32-7.38 (m, 2 H, H7 and H4'), 7.47 (t, $^3J_{2,3'}=^3J_{3,4'}=7.5$ Hz, 2 H, H3'), 7.69-7.74 (m, 4 H, H_m), 7.79-7.84 (m, 6 H, H_o and H_p) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl₃): δ 19.07 (d, $^1J_{3,\text{P}}=53.5$ Hz, C3), 46.72 (d, $^2J_{2,\text{P}}=7.2$ Hz, C2), 95.38 (d, $^1J_{4\text{a},\text{P}}=89.6$ Hz, C4a), 117.91 (d, $^3J_{8,\text{P}}=7.1$ Hz, C8), 119.10 (d, $^3J_{6,\text{P}}=11.7$ Hz, C6), 119.27 (d, $^1J_{\text{i},\text{P}}=88.6$ Hz, C_i), 120.85 (q, $^1J_{\text{CF}}=320.6$ Hz, CF₃SO₃), 127.11 (C2'), 127.81 (C4'), 130.61 (d, $^3J_{\text{m},\text{P}}=13.1$ Hz, C_m), 130.71 (C3'), 133.62 (d, $^2J_{\text{o},\text{P}}=10.7$ Hz, C_o), 133.83 (d, $^2J_{5,\text{P}}=6.9$ Hz, C5), 135.26 (d, $^4J_{\text{p},\text{P}}=2.8$ Hz, C_p), 135.96 (C7), 145.04 (C1'), 152.71 (d, $^2J_{8\text{a},\text{P}}=3.7$ Hz, C8a) ppm; ^{31}P NMR (162 MHz, CDCl₃): δ 8.52 ppm; HRMS (ESI) calcd for C₂₆H₂₃NP ([M-OTf]⁺): 380.1563; found: 380.1565.

1-(4-Methylphenyl)-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3c).



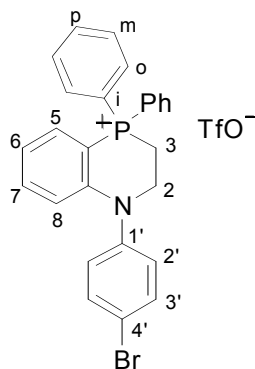
White solid (0.14 g, 85%) that was recrystallized from CH₂Cl₂/Et₂O (colorless prisms); m.p. 191-193 °C; IR (Nujol): 3070, 1596, 1483, 1441, 1262, 1151, 1031, 757, 669 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 2.37 (s, 3 H, CH₃), 3.49-3.55 (m, 2 H, H₃), 3.96-4.05 (m, 2 H, H₂), 6.64 (br t, ³J_{7,8} = ⁴J_{8,P} = 7.6 Hz, 1 H, H₈), 6.85 (ddt, ³J_{5,6} = ³J_{6,7} = 7.9 Hz, ⁴J_{6,P} = 2.1 Hz, ⁴J_{6,8} = 0.9 Hz, 1 H, H₆), 7.11 (d, ³J_{2',3'} = 8.2 Hz, 2 H, H_{2'}), 7.14 (ddd, ³J_{5,P} = 14.1 Hz, ³J_{5,6} = 7.9 Hz, ⁴J_{5,7} = 1.5 Hz, 1 H, H₅), 7.25 (d, ³J_{2',3'} = 8.2 Hz, 2 H, H_{3'}), 7.33 (dddd, ³J_{6,7} = 7.9 Hz, ³J_{7,8} = 7.6 Hz, ⁴J_{5,7} = 1.5 Hz, ⁵J_{7,P} = 0.9 Hz, 1 H, H₇), 7.67-7.72 (m, 4 H, H_m), 7.75-7.81 (m, 6 H, H_o and H_p) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 18.97 (d, ¹J_{3,P} = 53.7 Hz, C₃), 21.15 (CH₃), 46.66 (d, ²J_{2,P} = 7.4 Hz, C₂), 94.88 (d, ¹J_{4a,P} = 89.8 Hz, C_{4a}), 117.75 (d, ³J_{8,P} = 7.2 Hz, C₈), 118.93 (d, ³J_{6,P} = 12.0 Hz, C₆), 119.28 (d, ¹J_{i,P} = 88.5 Hz, C_i), 120.85 (q, ¹J_{CF} = 320.6 Hz, CF₃SO₃), 126.94 (C_{2'}), 130.60 (d, ³J_{m,P} = 12.9 Hz, C_m), 131.27 (C_{3'}), 133.56 (d, ²J_{o,P} = 10.7 Hz, C_o), 133.78 (d, ²J_{5,P} = 7.0 Hz, C₅), 135.25 (d, ⁴J_{p,P} = 2.9 Hz, C_p), 135.96 (C₇), 137.84 (C_{4'}), 142.43 (C_{1'}), 152.84 (d, ²J_{8a,P} = 3.9 Hz, C_{8a}) ppm; ³¹P NMR (162 MHz, CDCl₃): δ 8.51 ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ -78.27 ppm; HRMS (ESI) calcd for C₂₇H₂₅NP ([M-OTf]⁺): 394.1719; found: 394.1724.

1-(2-Isopropylphenyl)-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3d).



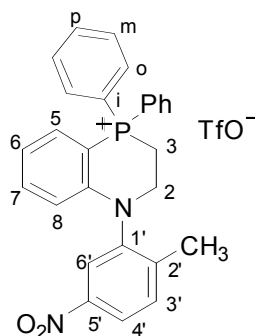
White solid (0.16 g, 95%) that was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (colorless prisms); m.p. 176-178 °C; IR (Nujol): 3020, 1597, 1484, 1440, 1266, 1161, 1030, 756, 637 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.12 (d, $^3J = 6.8$ Hz, 6 H, 2 CH_3), 2.86 (sept, $^3J = 6.8$ Hz, 1 H, 2 CH), 3.37-3.49 (m, 1 H, H3), 3.62-3.72 (m, 1 H, H3), 3.78-4.00 (m, 2 H, H2), 6.32 (t, $^3J_{7,8} = ^4J_{8,P} = 7.9$ Hz, 1 H, H8), 6.83 (t, $^3J_{5,6} = ^3J_{6,7} = 7.9$ Hz, 1 H, H6), 7.09 (d, $^3J_{5',6'} = 7.1$ Hz, 1 H, H6'), 7.13 (dd, $^3J_{5,P} = 14.1$ Hz, $^3J_{5,6} = 7.9$ Hz, 1 H, H5), 7.28 (d, $^3J_{3',4'} = 7.1$ Hz, 1 H, H3'), 7.32 (t, $^3J_{6,7} = ^3J_{7,8} = 7.9$ Hz, 1 H, H7), 7.38 (t, $^3J_{3',4'} = ^3J_{4',5'} = 7.1$ Hz, 1 H, H4'), 7.41 (t, $^3J_{4',5'} = ^3J_{5',6'} = 7.1$ Hz, 1 H, H5'), 7.68-7.77 (m, 6 H, H_m and 2 H_o), 7.80-7.85 (m, 4 H, 2 H_o + H_p) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 18.51 (d, $^1J_{3,P} = 53.8$ Hz, C3), 23.54 (CH_3), 24.26 (CH_3), 28.10 (CH), 46.33 (d, $^2J_{2,P} = 7.4$ Hz, C2), 94.11 (d, $^1J_{4a,P} = 90.2$ Hz, C4a), 117.11 (d, $^3J_{8,P} = 7.1$ Hz, C8), 118.66 (d, $^3J_{6,P} = 11.8$ Hz, C6), 118.83 (d, $^1J_{i,P} = 89.0$ Hz, C_i), 119.04 (d, $^1J_{i,P} = 88.9$ Hz, C_i), 120.81 (q, $^1J_{\text{CF}} = 320.7$ Hz, CF_3SO_3), 127.83 (C5'), 128.25 (C6'), 128.39 (C3'), 129.23 (C4'), 130.58 (d, $^3J_{m,P} = 13.1$ Hz, C_m), 130.64 (d, $^3J_{m,P} = 12.9$ Hz, C_m), 133.48 (d, $^2J_{o,P} = 9.9$ Hz, C_o), 133.58 (d, $^2J_{o,P} = 10.3$ Hz, C_o), 134.74 (d, $^2J_{5,P} = 7.1$ Hz, C5), 135.32 (d, $^4J_{p,P} = 2.6$ Hz, 2 C_p), 136.20 (C7), 141.90 (C2'), 146.69 (C1'), 152.71 (d, $^2J_{8a,P} = 4.0$ Hz, C8a) ppm; ^{31}P NMR (162 MHz, CDCl_3): δ 8.52 ppm; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{29}\text{NP}$ ($[\text{M-OTf}]^+$): 422.2032; found: 422.2045.

1-(4-Bromophenyl)-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3e).



White solid (0.14 g, 75%) that was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (colorless prisms); m.p. 196-198 °C; IR (Nujol): 3018, 1599, 1485, 1440, 1275, 1162, 1112, 1030, 756, 689, 668 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.51-3.57 (m, 2 H, H3), 3.99-4.08 (m, 2 H, H2), 6.67 (t, $^3J_{7,8}=^4J_{8,P}=7.8$ Hz, 1 H, H8), 6.90 (t, $^3J_{5,6}=^3J_{6,7}=7.8$ Hz, 1 H, H6), 7.15 (dd, $^3J_{5,P}=14.0$ Hz, $^3J_{5,6}=7.8$ Hz, 1 H, H5), 7.16 (d, $^3J_{2',3'}=8.5$ Hz, 2 H, H2'), 7.33 (t, $^3J_{6,7}=^3J_{7,8}=7.8$ Hz, 1 H, H7), 7.56 (d, $^3J_{2',3'}=8.5$ Hz, 2 H, H3'), 7.68-7.72 (m, 4 H, H_m), 7.75-7.82 (m, 6 H, H_o and H_p) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 19.05 (d, $^1J_{3,P}=53.7$ Hz, C3), 46.60 (d, $^2J_{2,P}=7.3$ Hz, C2), 95.98 (d, $^1J_{4a,P}=89.8$ Hz, C4a), 117.82 (d, $^3J_{8,P}=7.2$ Hz, C8), 119.01 (d, $^1J_{i,P}=88.6$ Hz, C_i), 119.70 (d, $^3J_{6,P}=11.6$ Hz, C6), 120.83 (q, $^1J_{\text{CF}}=320.7$ Hz, CF_3SO_3), 121.10 (C4'), 128.86 (C2'), 130.65 (d, $^3J_{m,P}=13.2$ Hz, C_m), 133.55 (d, $^2J_{o,P}=10.7$ Hz, C_o), 133.80 (C3'), 133.95 (d, $^2J_{5,P}=7.0$ Hz, C5), 135.36 (d, $^4J_{p,P}=3.1$ Hz, C_p), 136.15 (d, $^4J_{7,P}=1.3$ Hz, C7), 144.10 (C1'), 152.18 (d, $^2J_{8a,P}=3.6$ Hz, C8a) ppm; ^{31}P NMR (162 MHz, CDCl_3): δ 8.49 ppm; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{22}\text{BrNP}$ ($[\text{M}-\text{OTf}]^+$): 458.0668; found: 458.0672.

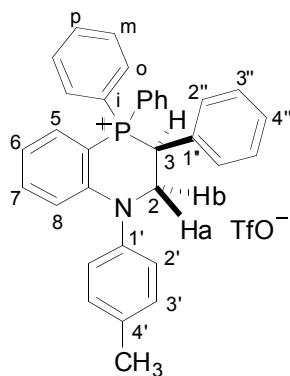
1-(2-Methyl-5-nitrophenyl)-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorin-3-ium triflate (3f).



Yellow solid (0.12 g, 70% that was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (yellow prisms); m.p. 98-100 °C; IR (Nujol): 3014, 1596, 1483, 1440, 1350, 1271, 1156, 1114, 1030,

741, 690, 665 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.31 (s, 3 H, CH_3), 3.62-3.67 (m, 2 H, H3), 3.96-4.05 (m, 2 H, H2), 6.28 (br t, $^3J_{7,8} = ^4J_{8,P} = 7.9$ Hz, 1 H, H8), 6.94 (ddt, $^3J_{5,6} = ^3J_{6,7} = 7.9$ Hz, $^4J_{6,P} = 2.0$ Hz, $^4J_{6,8} = 1.4$ Hz, 1 H, H6), 7.21 (ddd, $^3J_{5,P} = 14.2$ Hz, $^3J_{5,6} = 7.9$ Hz, $^4J_{5,7} = 1.5$ Hz, 1 H, H5), 7.40 (br t, $^3J_{6,7} = ^3J_{7,8} = 7.9$ Hz, 1 H, H7), 7.55 (d, $^3J_{3',4'} = 8.5$ Hz, 1 H, H3'), 7.67-7.88 (m, 10 H, PPh_2), 8.02 (d, $^4J_{4',6'} = 2.3$ Hz, 1 H, H6'), 8.14 (dd, $^3J_{3',4'} = 8.5$ Hz, $^4J_{4',6'} = 2.3$ Hz, 1 H, H4'); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 18.31 (CH_3), 18.81 (d, $^1J_{3,P} = 53.8$ Hz, C3), 45.77 (d, $^2J_{2,P} = 7.4$ Hz, C2), 95.69 (d, $^1J_{4a,P} = 89.6$ Hz, C4a), 116.47 (d, $^3J_{8,P} = 7.1$ Hz, C8), 118.51 (d, $^1J_{i,P} = 87.6$ Hz, C_i), 118.71 (d, $^1J_{i,P} = 89.8$ Hz, C_i), 119.83 (d, $^3J_{6,P} = 11.6$ Hz, C6), 120.74 (q, $^1J_{\text{CF}} = 320.7$ Hz, CF_3SO_3), 123.32 (C4'), 123.66 (C6'), 130.75 (d, $^3J_{m,P} = 13.1$ Hz, 2 C_m), 133.11 (C3'), 133.55 (d, $^2J_{o,P} = 10.8$ Hz, 2 C_o), 134.32 (d, $^2J_{5,P} = 6.9$ Hz, C5), 135.54 (d, $^4J_{p,P} = 3.0$ Hz, 2 C_p), 136.76 (C7), 143.84 (C2'), 145.06 (C1'), 147.73 (C5'), 151.14 (d, $^2J_{8a,P} = 3.6$ Hz, C8a) ppm; ^{31}P NMR (121 MHz, CDCl_3): δ 9.11 ppm; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_2\text{P}$ ($[\text{M-OTf}]^+$): 439.1570; found: 439.1590.

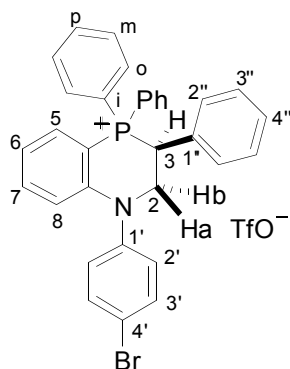
1-(4-Methylphenyl)-3,4,4-triphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3g).



White solid (0.14 g, 76%) that was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (colorless prisms); m.p. 112-114 $^\circ\text{C}$; IR (Nujol): 3011, 1593, 1485, 1438, 1266, 1156, 1111, 1029, 997, 829, 751, 694 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.36 (s, 3 H, CH_3), 4.18 (ddd, $^3J_{2b,P} = 24.6$ Hz, $^2J_{2a,2b} = 14.2$ Hz, $^3J_{2b,3} = 3.0$ Hz, 1 H, H2b), 4.28 (ddd, $^3J_{2a,P} = 20.0$ Hz, $^2J_{2a,2b} = 14.2$ Hz, $^3J_{2a,3} = 9.8$ Hz, 1 H, H2a), 5.27 (ddd, $^2J_{3,P} = 12.4$ Hz, $^3J_{2a,3} = 9.8$ Hz, $^3J_{2b,3} = 3.0$ Hz, 1 H, H3), 6.73 (t, $^3J_{7,8} = ^4J_{8,P} = 8.0$ Hz, 1 H, H8), 6.85 (t, $^3J_{5,6} = ^3J_{6,7} = 8.0$ Hz, 1 H, H6), 6.98-7.30 (m, 12 H, H5, H2', H3', H2'', H3'', H4'' and 2 H_o), 7.38 (t, $^3J_{6,7} = ^3J_{7,8} = 8.0$ Hz, 1 H, H7), 7.46-7.52 (m, 2 H, H_m), 7.73-7.84 (m, 4 H, 2 H_m and 2 H_p), 8.05 (dd, $^3J_{o,P} = 12.9$ Hz, $^3J_{o,p} = 8.1$ Hz, 2 H, 2 H_o) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ

21.16 (CH₃), 34.47 (d, $^1J_{3,P}$ = 46.9 Hz, C3), 51.96 (d, $^2J_{2,P}$ = 4.8 Hz, C2), 94.80 (d, $^1J_{4a,P}$ = 86.4 Hz, C4a), 115.98 (d, $^1J_{i,P}$ = 86.7 Hz, C_i), 117.45 (d, $^3J_{8,P}$ = 7.3 Hz, C8), 118.53 (d, $^1J_{i,P}$ = 87.2 Hz, C_i), 119.35 (d, $^3J_{6,P}$ = 11.4 Hz, C6), 120.95 (q, $^1J_{CF}$ = 320.7 Hz, CF₃SO₃), 127.24 (C2'), 129.05 (d, $^3J_{2'',P}$ = 4.9 Hz, C2''), 129.19 (C4''), 129.25 (d, $^4J_{3'',P}$ = 2.8 Hz, C3''), 129.59 (d, $^3J_{m,P}$ = 12.6 Hz, C_m), 130.29 (d, $^2J_{1'',P}$ = 6.4 Hz, C1''), 130.90 (d, $^3J_{m,P}$ = 12.9 Hz, C_m), 131.32 (C3'), 134.01 (d, $^2J_{o,P}$ = 10.2 Hz, C_o), 134.17 (d, $^2J_{5,P}$ = 6.6 Hz, C5), 135.40 (d, $^4J_{p,P}$ = 3.0 Hz, 2 C_p), 135.41 (d, $^2J_{o,P}$ = 9.5 Hz, C_o), 136.10 (d, $^4J_{7,P}$ = 1.3 Hz, C7), 137.99 (C4'), 142.24 (C1'), 152.74 (d, $^2J_{8a,P}$ = 4.2 Hz, C8a) ppm; ^{31}P NMR (162 MHz, CDCl₃): δ 14.16 ppm; HRMS (ESI) calcd for C₃₃H₂₉NP ([M-OTf]⁺): 470.2032; found: 470.2047.

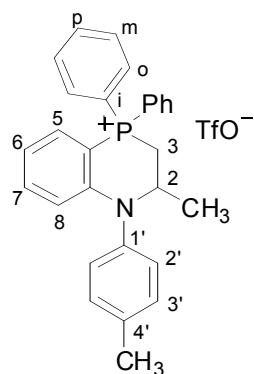
1-(4-Bromophenyl)-3,4,4-triphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3h).



White solid (0.12 g, 59%) that was recrystallized from CH₂Cl₂/Et₂O (colorless prisms); m.p. 118-120 °C; IR (Nujol): 3017, 1599, 1486, 1441, 1267, 1161, 1110, 1030, 756, 699, 667 cm⁻¹; ^1H NMR (400 MHz, CDCl₃): δ 4.16 (ddd, $^3J_{2b,P}$ = 26.7 Hz, $^2J_{2a,2b}$ = 14.1 Hz, $^3J_{2b,3}$ = 3.1 Hz, 1 H, H2b), 4.32 (ddd, $^3J_{2a,P}$ = 18.2 Hz, $^2J_{2a,2b}$ = 14.1 Hz, $^3J_{2a,3}$ = 11.0 Hz, 1 H, H2a), 5.48 (dt, $^2J_{3,P}$ = $^3J_{2a,3}$ = 11.0 Hz, $^3J_{2b,3}$ = 3.1 Hz, 1 H, H3), 6.71 (t, $^3J_{7,8}$ = $^4J_{8,P}$ = 7.9 Hz, 1 H, H8), 6.86 (t, $^3J_{5,6}$ = $^3J_{6,7}$ = 7.9 Hz, 1 H, H6), 6.93 (d, $^3J_{2'',3''}$ = 7.6 Hz, 2 H, H2''), 7.01-7.16 (m, 5 H, H5, H3'' and 2 H_o), 7.23 (t, $^3J_{3'',4''}$ = 7.6 Hz, 1 H, H4''), 7.35 (d, $^3J_{2',3'}$ = 8.6 Hz, 2 H, H2'), 7.38 (t, $^3J_{6,7}$ = $^3J_{7,8}$ = 7.9 Hz, 1 H, H7), 7.48-7.57 (m, 2 H, 2 H_m), 7.56 (d, $^3J_{2',3'}$ = 8.6 Hz, 2 H, H3'), 7.74-7.80 (m, 4 H, 2 H_m and 2 H_p), 8.08 (dd, $^3J_{o,P}$ = 12.9 Hz, $^3J_{o,m}$ = 7.2 Hz, 2 H, 2 H_o) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl₃): δ 34.41 (d, $^1J_{3,P}$ = 46.7 Hz, C3), 51.72 (d, $^2J_{2,P}$ = 4.7 Hz, C2), 96.00 (d, $^1J_{4a,P}$ = 86.0 Hz, C4a), 115.73 (d, $^1J_{i,P}$ = 86.2 Hz, C_i), 117.36 (d, $^3J_{8,P}$ = 7.4 Hz, C8), 118.20 (d, $^1J_{i,P}$ = 87.5 Hz, C_i), 119.88 (d, $^3J_{6,P}$ = 11.4 Hz, C6), 120.92 (q, $^1J_{CF}$ = 320.8 Hz, CF₃SO₃), 121.28

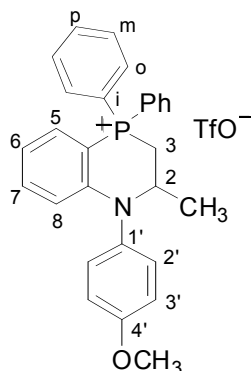
(C4'), 128.97 (d, $^3J_{2'',P}= 4.9$ Hz, C2''), 129.18 (C4''), 129.19 (d, $^4J_{3'',P}= 2.2$ Hz, C3''), 129.40 (C2'), 129.59 (d, $^3J_{m,P}= 12.6$ Hz, C_m), 130.05 (d, $^2J_{1'',P}= 6.8$ Hz, C1''), 130.83 (d, $^3J_{m,P}= 12.9$ Hz, C_m), 133.77 (C3'), 134.16 (d, $^2J_{o,P}= 10.5$ Hz, C_o), 134.26 (d, $^2J_{5,P}= 7.3$ Hz, C5), 135.40 (d, $^4J_{p,P}= 3.0$ Hz, C_p), 135.46 (d, $^4J_{p,P}= 2.4$ Hz, C_p), 135.52 (d, $^2J_{o,P}= 9.6$ Hz, C_o), 136.13 (d, $^4J_{7,P}= 1.6$ Hz, C7), 143.90 (C1'), 152.09 (d, $^2J_{8a,P}= 4.1$ Hz, C8a) ppm; ^{31}P NMR (162 MHz, CDCl₃): δ 14.85 ppm; HRMS (ESI) calcd for C₃₂H₂₆BrNP ([M-OTf]⁺): 534.0981; found: 534.0995.

2-Methyl-1-(4-methylphenyl)-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3i).



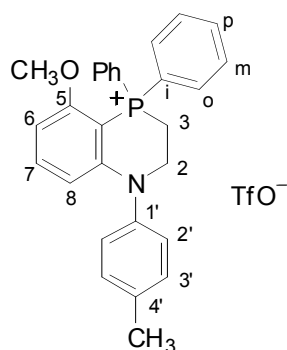
White solid (0.14 g, 81%) that was recrystallized from CH₂Cl₂/Et₂O (colorless prisms); m.p. 141-143 °C; IR (Nujol): 3019, 1598, 1475, 1441, 1273, 1163, 1111, 1030, 756, 668 cm⁻¹; ^1H NMR (400 MHz, CDCl₃): δ 1.14 (d, $^3J= 7.7$ Hz, 3 H, CH₃), 2.36 (s, 3 H, CH₃), 3.42-3.63 (m, 2 H, H3), 4.10-4.23 (m, 1 H, H2), 6.47 (t, $^3J_{7,8}= ^4J_{8,P}= 8.0$ Hz, 1 H, H8), 6.82 (t, $^3J_{5,6}= ^3J_{6,7}= 8.0$ Hz, 1 H, H6), 7.04 (d, $^3J_{2',3'}= 8.1$ Hz, 2 H, H2'), 7.13 (dd, $^3J_{5,P}= 14.0$ Hz, $^3J_{5,6}= 8.0$ Hz, 1 H, H5), 7.25 (d, $^3J_{2',3'}= 8.1$ Hz, 2 H, H3'), 7.29 (t, $^3J_{6,7}= ^3J_{7,8}= 8.0$ Hz, 1 H, H7), 7.66-7.85 (m, 10 H, PPh₂) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl₃): δ 21.11 (d, $^3J_{C,P}= 8.6$ Hz, CH₃), 21.17 (CH₃), 25.55 (d, $^1J_{3,P}= 52.4$ Hz, C3), 52.08 (d, $^2J_{2,P}= 6.1$ Hz, C2), 94.01 (d, $^1J_{4a,P}= 89.7$ Hz, C4a), 118.59 (d, $^3J_{8,P}= 7.8$ Hz, C8), 118.69 (d, $^3J_{6,P}= 11.5$ Hz, C6), 119.23 (d, $^1J_{i,P}= 88.8$ Hz, C_i), 120.16 (d, $^1J_{i,P}= 89.1$ Hz, C_i), 120.74 (q, $^1J_{\text{CF}}= 320.7$ Hz, CF₃SO₃), 128.77 (C2'), 130.54 (d, $^3J_{m,P}= 13.0$ Hz, 2 C_m), 131.20 (C3'), 133.30 (d, $^2J_{o,P}= 10.8$ Hz, 2 C_o), 133.78 (d, $^2J_{5,P}= 6.8$ Hz, C5), 135.04 (d, $^4J_{p,P}= 3.1$ Hz, C_p), 135.11 (d, $^4J_{p,P}= 3.0$ Hz, C_p), 135.98 (C7), 138.22 (C4'), 140.40 (C1'), 152.62 (d, $^2J_{8a,P}= 4.2$ Hz, C8a) ppm; ^{31}P NMR (121 MHz, CDCl₃): δ 5.00 ppm; HRMS (ESI) calcd for C₂₈H₂₇NP ([M-OTf]⁺): 408.1876; found: 408.1882.

2-Methyl-1-(4-methoxyphenyl)-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3j).



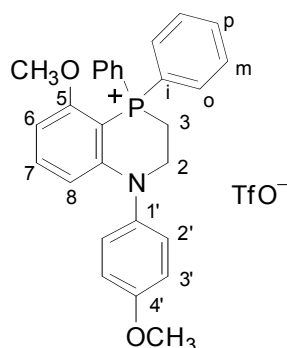
White solid (0.16 g, 94% that was recrystallized from CH₂Cl₂/Et₂O (colorless prisms); m.p. 89-91 °C; IR (Nujol): 3012, 1598, 1475, 1441, 1262, 1156, 1110, 1030, 912, 832, 747, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.14 (d, ³J = 6.6 Hz, 3 H, CH₃), 3.43-3.64 (m, 2 H, H3), 3.83 (s, 3 H, OCH₃), 4.09-4.18 (m, 1 H, H2), 6.47 (br t, ³J_{7,8} = ⁴J_{8,P} = 8.1 Hz, 1 H, H8), 6.83 (ddt, ³J_{5,6} = ³J_{6,7} = 8.1 Hz, ⁴J_{6,P} = 2.0 Hz, ⁴J_{6,8} = 0.8 Hz, 1 H, H6), 6.97 (d, ³J_{2,3} = 8.6 Hz, 2 H, H2'), 7.12 (d, ³J_{2,3} = 8.6 Hz, 2 H, H3'), 7.14 (ddd, ³J_{5,P} = 14.2 Hz, ³J_{5,6} = 8.1 Hz, ⁴J_{5,7} = 1.4 Hz, 1 H, H5), 7.31 (br t, ³J_{6,7} = ³J_{7,8} = 8.1 Hz, 1 H, H7), 7.66-7.84 (m, 10 H, PPh₂) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 21.08 (d, ³J_{C,P} = 10.7 Hz, CH₃), 25.26 (d, ¹J_{3,P} = 52.4 Hz, C3), 51.85 (d, ²J_{2,P} = 6.1 Hz, C2), 55.47 (OCH₃), 93.50 (d, ¹J_{4a,P} = 90.2 Hz, C4a), 115.53 (C3'), 118.18 (d, ³J_{8,P} = 7.7 Hz, C8), 118.52 (d, ³J_{6,P} = 11.8 Hz, C6), 119.05 (d, ¹J_{i,P} = 88.0 Hz, C_i), 119.90 (d, ¹J_{i,P} = 88.9 Hz, C_i), 120.74 (q, ¹J_{CF} = 320.9 Hz, CF₃SO₃), 130.28 (C2'), 130.39 (d, ³J_{m,P} = 13.0 Hz, C_m), 130.45 (d, ³J_{m,P} = 13.1 Hz, C_m), 133.12 (d, ²J_{o,P} = 10.7 Hz, 2 C_o), 133.65 (d, ²J_{5,P} = 6.9 Hz, C5), 134.95 (d, ⁴J_{p,P} = 3.1 Hz, C_p), 134.98 (d, ⁴J_{p,P} = 2.1 Hz, C_p), 135.33 (C1'), 135.91 (d, ⁴J_{7,P} = 1.2 Hz C7), 152.71 (d, ²J_{8a,P} = 4.3 Hz, C8a), 159.00 (C4') ppm; ³¹P NMR (162 MHz, CDCl₃): δ 4.75 ppm; HRMS (ESI) calcd for C₂₈H₂₇NOP ([M-OTf]⁺): 424.1825; found: 424.1829.

5-Methoxy-1-(4-methylphenyl)-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3k).



White solid (0.11 g, 66% that was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (colorless prisms); m.p. 214-216 °C; IR (Nujol): 3058, 1598, 1476, 1440, 1265, 1188, 1114, 1031, 863, 782 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.36 (s, 3 H, CH_3), 3.20-3.25 (m, 2 H, H3), 3.41 (s, 3 H, OCH_3), 3.84-3.93 (m, 2 H, H2), 6.27 (dd, $^3J_{7,8} = 8.4$ Hz, $^4J_{8,p} = 6.3$ Hz, 1 H, H8), 6.30 (dd, $^3J_{6,7} = 8.4$ Hz, $^4J_{6,p} = 3.9$ Hz, 1 H, H6), 7.13 (d, $^3J_{2',3'} = 8.3$ Hz, 2 H, H2'), 7.24 (d, $^3J_{2',3'} = 8.3$ Hz, 2 H, H3'), 7.30 (t, $^3J_{6,7} = ^3J_{7,8} = 8.4$ Hz, 1 H, H7), 7.63-7.68 (m, 4 H, H_m), 7.72-7.80 (m, 6 H, H_o and H_p) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 21.10 (CH_3), 21.29 (d, $^1J_{3,p} = 55.7$ Hz, C3), 46.34 (d, $^2J_{2,p} = 7.0$ Hz, C2), 55.92 (OCH_3), 85.35 (d, $^1J_{4a,p} = 93.4$ Hz, C4a), 100.40 (d, $^3J_{6,p} = 5.2$ Hz, C6), 110.53 (d, $^3J_{8,p} = 7.2$ Hz, C8), 119.90 (d, $^1J_{i,p} = 92.1$ Hz, C_i), 120.88 (q, $^1J_{\text{CF}} = 320.8$ Hz, CF_3SO_3), 126.91 ($\text{C2}'$), 130.00 (d, $^3J_{m,p} = 13.4$ Hz, C_m), 131.07 ($\text{C3}'$), 133.07 (d, $^2J_{o,p} = 11.1$ Hz, C_o), 134.51 (d, $^4J_{p,p} = 3.1$ Hz, C_p), 137.52 (C7), 137.68 ($\text{C4}'$), 142.46 ($\text{C1}'$), 153.98 (d, $^2J_{8a,p} = 2.1$ Hz, C8a) 162.36 (C5) ppm; ^{31}P NMR (162 MHz, CDCl_3): δ 6.57 ppm; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{27}\text{NOP}$ ($[\text{M-OTf}]^+$): 424.1825; found: 424.1840.

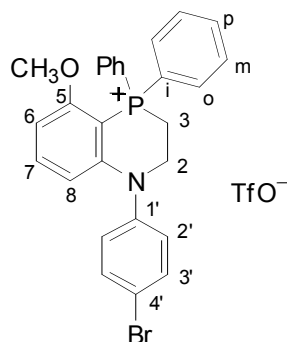
5-Methoxy-1-(4-methoxyphenyl)-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3l).



White solid (0.1 g, 57%) that was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (colorless prisms); m.p. 229-231 °C; IR (Nujol): 3070, 1558, 1475, 1440, 1153, 1112, 1031, 833, 740, 704 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.22-3.27 (m, 2 H, H3), 3.40 (s, 3 H, OCH_3), 3.81

(s, 3 H, OCH₃), 3.82-3.91 (m, 2 H, H₂), 6.22 (dd, ³J_{7,8} = 8.4 Hz, ⁴J_{8,P} = 6.5 Hz, 1 H, H₈), 6.27 (dd, ³J_{6,7} = 8.4 Hz, ⁴J_{6,P} = 4.2 Hz, 1 H, H₆), 6.96 (d, ³J_{2',3'} = 8.8 Hz, 2 H, H_{2'}), 7.18 (d, ³J_{2',3'} = 8.8 Hz, 2 H, H_{3'}), 7.30 (t, ³J_{6,7} = ³J_{7,8} = 8.4 Hz, 1 H, H₇), 7.63-7.68 (m, 4 H, H_m), 7.73-7.80 (m, 6 H, H_o and H_p) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 21.21 (d, ¹J_{3,P} = 55.6 Hz, C3), 46.44 (d, ²J_{2,P} = 7.1 Hz, C2), 55.63 (OCH₃), 55.90 (OCH₃), 85.08 (d, ¹J_{4a,P} = 93.6 Hz, C4a), 100.13 (d, ³J_{6,P} = 5.6 Hz, C6), 110.36 (d, ³J_{8,P} = 7.2 Hz, C8), 115.65 (C3'), 119.85 (d, ¹J_{i,P} = 92.2 Hz, C_i), 120.87 (q, ¹J_{CF} = 320.8 Hz, CF₃SO₃), 128.56 (C2'), 130.00 (d, ³J_{m,P} = 13.4 Hz, C_m), 133.11 (d, ²J_{o,P} = 11.2 Hz, C_o), 134.51 (d, ⁴J_{p,P} = 3.1 Hz, C_p), 137.52 (C7), 137.78 (C1'), 154.27 (d, ²J_{8a,P} = 2.1 Hz, C8a), 158.90 (C4'), 162.36 (C5) ppm; ³¹P NMR (162 MHz, CDCl₃): δ 6.65 ppm; HRMS (ESI) calcd for C₂₈H₂₇NO₂P ([M-OTf]⁺): 440.1774; found: 440.1792.

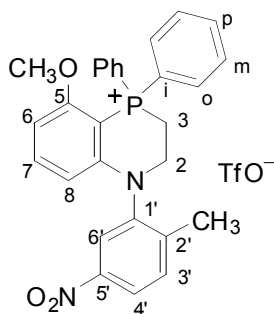
1-(4-Bromophenyl)-5-methoxy-4,4-diphenyl-1,2,3,4-tetrahydrobenzazaphosphorinium triflate (3m).



White solid (0.15 g, 76%) that was recrystallized from CH₂Cl₂/Et₂O (colorless prisms); m.p. 234-236 °C; IR (Nujol): 3080, 1599, 1472, 1440, 1259, 1224, 1111, 1055, 908, 782, 731, 687 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 3.24-3.29 (m, 2 H, H₃), 3.42 (s, 3 H, OCH₃), 3.87-3.96 (m, 2 H, H₂), 6.28 (dd, ³J_{7,8} = 8.4 Hz, ⁴J_{8,P} = 6.4 Hz, 1 H, H₈), 6.34 (dd, ³J_{6,7} = 8.4 Hz, ⁴J_{6,P} = 4.2 Hz, 1 H, H₆), 7.20 (d, ³J_{2',3'} = 8.5 Hz, 2 H, H_{2'}), 7.34 (t, ³J_{6,7} = ³J_{7,8} = 8.4 Hz, 1 H, H₇), 7.56 (d, ³J_{2',3'} = 8.5 Hz, 2 H, H_{3'}), 7.63-7.68 (m, 4 H, H_m), 7.71-7.80 (m, 6 H, H_o + H_p) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 21.25 (d, ¹J_{3,P} = 55.6 Hz, C3), 46.30 (d, ²J_{2,P} = 7.0 Hz, C2), 55.98 (OCH₃), 86.13 (d, ¹J_{4a,P} = 93.2 Hz, C4a), 101.07 (d, ³J_{6,P} = 5.6 Hz, C6), 110.51 (d, ³J_{8,P} = 7.3 Hz, C8), 119.66 (d, ¹J_{i,P} = 92.1 Hz, C_i), 120.84 (q, ¹J_{CF} = 320.8 Hz, CF₃SO₃), 121.09 (C4'), 128.99 (C2'), 130.05 (d, ³J_{m,P} = 13.5 Hz, C_m), 133.15 (d, ²J_{o,P} = 11.2 Hz, C_o), 133.63 (C3'), 134.62 (d, ⁴J_{p,P} = 3.0 Hz, C_p), 137.73 (C7), 144.08 (C1'), 153.35 (d, ²J_{8a,P} = 1.8 Hz, C8a), 162.44 (C5) ppm;

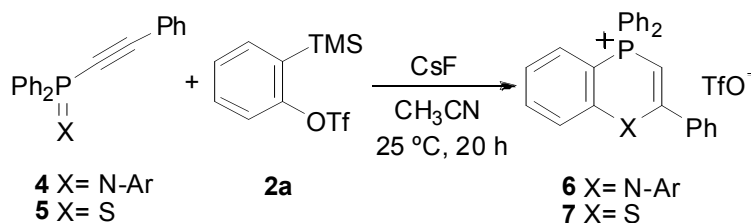
^{31}P NMR (162 MHz, CDCl_3): δ 6.61 ppm; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{24}\text{BrNOP}$ ($[\text{M-OTf}]^+$): 488.0773; found: 488.0787.

1-(2-Methyl-5-nitrophenyl)-5-methoxy-4,4-diphenyl-1,2,3,4-tetrahydrobenzaza-phosphorinium triflate (3n).



Yellow solid (0.11 g, 57%) that was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (yellow prisms); m.p. 102-104 $^\circ\text{C}$; IR (Nujol): 3067, 1597, 1477, 1440, 1350, 1264, 1159, 1107, 1031, 911, 808, 780, 689 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.37 (s, 3 H, CH_3), 3.34-3.42 (m, 2 H, H_3), 3.45 (s, 3 H, OCH_3), 3.83-3.95 (m, 2 H, H_2), 5.92 (dd, $^3J_{7,8} = 8.4$ Hz, $^4J_{8,\text{P}} = 6.2$ Hz, 1 H, H_8), 6.39 (dd, $^3J_{6,7} = 8.4$ Hz, $^4J_{6,\text{P}} = 4.1$ Hz, 1 H, H_6), 7.37 (t, $^3J_{6,7} = 8.4$ Hz, 1 H, H_7), 7.54 (d, $^3J_{3',4'} = 8.5$ Hz, 1 H, $\text{H}_{3'}$), 7.63-7.83 (m, 10 H, PPh_2), 8.03 (d, $^4J_{4',6'} = 2.3$ Hz, 1 H, $\text{H}_{6'}$), 8.13 (dd, $^3J_{3',4'} = 8.5$ Hz, $^4J_{4',6'} = 2.3$ Hz, 1 H, $\text{H}_{4'}$) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 18.47 (CH_3), 21.42 (d, $^1J_{3,\text{P}} = 55.6$ Hz, C_3), 45.55 (d, $^2J_{2,\text{P}} = 7.0$ Hz, C_2), 56.08 (OCH_3), 86.08 (d, $^1J_{4a,\text{P}} = 92.7$ Hz, C_{4a}), 101.49 (d, $^3J_{6,\text{P}} = 5.5$ Hz, C_6), 109.37 (d, $^3J_{8,\text{P}} = 7.3$ Hz, C_8), 119.31 (d, $^1J_{i,\text{P}} = 92.3$ Hz, C_i), 119.52 (d, $^1J_{i,\text{P}} = 92.4$ Hz, C_i), 120.77 (q, $^1J_{\text{CF}} = 320.7$ Hz, CF_3SO_3), 123.19 ($\text{C}_{4'}$), 123.47 ($\text{C}_{6'}$), 130.08 (d, $^3J_{m,\text{P}} = 13.3$ Hz, C_m), 130.21 (d, $^3J_{m,\text{P}} = 13.3$ Hz, C_m), 132.97 ($\text{C}_{3'}$), 133.02 (d, $^2J_{o,\text{P}} = 10.9$ Hz, C_o), 133.20 (d, $^2J_{o,\text{P}} = 11.2$ Hz, C_o), 134.70 (d, $^4J_{p,\text{P}} = 3.0$ Hz, C_p), 134.82 (d, $^4J_{p,\text{P}} = 3.1$ Hz, C_p), 138.35 (C_7), 143.99 ($\text{C}_{2'}$), 144.96 ($\text{C}_{1'}$), 147.61 ($\text{C}_{5'}$), 152.51 (d, $^2J_{8a,\text{P}} = 1.9$ Hz, C_{8a}), 162.73 (C_5) ppm; ^{31}P NMR (162 MHz, CDCl_3): δ 6.46 ppm; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_3\text{P}$ ($[\text{M-OTf}]^+$): 469.1676; found: 469.1680

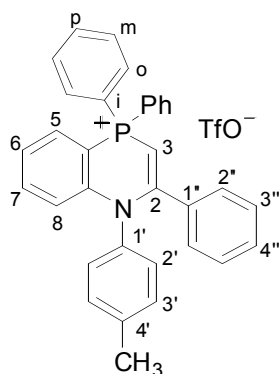
General Procedure for the Synthesis of 6 and 7:



To a suspension of the corresponding iminophosphorane **4** or sulfide **5** (0.3 mmol) and CsF (0.09 g, 0.6 mmol) in acetonitrile (3 mL) was added a solution of 2-(trimethylsilyl)phenyl triflate **2a** (0.11 g, 0.36 mmol) in acetonitrile (7 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 20 h. Then the reaction was filtered through a Celite plug. The solvent was evaporated to dryness under reduced pressure, and the crude product was purified by flash column chromatography on silica gel deactivated with 5% Et₃N in *n*-hexane, using chloroform/methanol (9:1) as eluent.

Characterization of **6** and **7**:

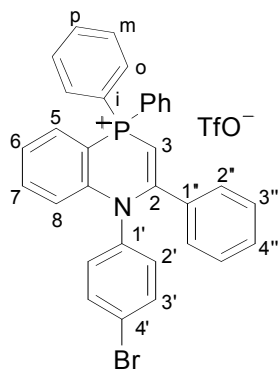
1-(4-Methylphenyl)-2,4,4-triphenyl-1,4-dihydrobenzazaphosphorinium triflate (6a).



White solid (0.13 g, 69%) that was recrystallized from CHCl₃/*n*-pentane (colorless prisms); m.p. 120-122 °C; IR (Nujol): 3060, 1574, 1442, 1264, 1153, 1109, 1031, 912, 731 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 2.27 (s, 3 H, CH₃), 5.25 (d, ²J_{3,P} = 11.2 Hz, 1 H, H3), 6.89 (dd, ³J_{7,8} = 7.7 Hz, ⁴J_{8,P} = 6.9 Hz, 1 H, H8), 7.03 (d, ³J_{2',3'} = 8.2 Hz, 2 H, H2'), 7.12 (d, ³J_{2',3'} = 8.2 Hz, 2 H, H3'), 7.18-7.24 (m, 5 H, H2'', H3'' and H4''), 7.45 (t, ³J_{5,6} = ³J_{6,7} = 7.7 Hz, 1 H, H6), 7.58 (t, ³J_{6,7} = ³J_{7,8} = 7.7 Hz, 1 H, H7), 7.72-7.80 (m, 11 H, H5 and PPh₂) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 21.15 (CH₃), 72.90 (d, ¹J_{3,P} = 91.3 Hz, C3), 99.50 (d, ¹J_{4a,P} = 90.4 Hz, C4a), 120.31 (d, ³J_{8,P} = 6.6 Hz, C8), 121.01 (q, ¹J_{CF} = 321.1 Hz, CF₃SO₃), 124.00 (d, ¹J_{i,P} = 95.1 Hz, C_i), 125.93 (d, ³J_{6,P} = 11.7 Hz, C6), 128.21 (C2'' or C3''), 128.56 (C2'' or C3''), 129.28 (C4''), 129.94 (C2'), 130.44 (d, ³J_{m,P} = 13.4 Hz, C_m), 130.73 (C3'), 132.58 (d, ²J_{5,P} = 6.8 Hz, C5), 132.94 (d, ²J_{o,P} = 11.5 Hz, C_o), 134.77 (d, ⁴J_{p,P} = 2.9 Hz, C_p), 135.26 (d, ⁴J_{7,P} = 1.2 Hz, C7), 136.48 (C4'), 137.21 (d, ²J_{2,P} = 12.0 Hz, C2), 139.63 (C1'), 145.04 (d, ²J_{8a,P} = 3.6 Hz, C8a), 161.31 (C1'') ppm; ³¹P

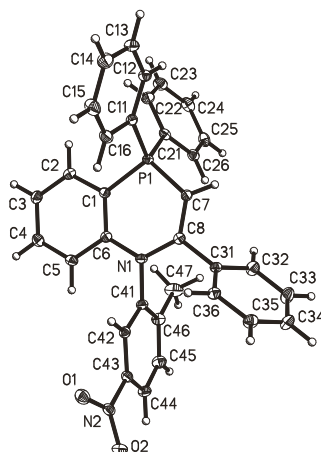
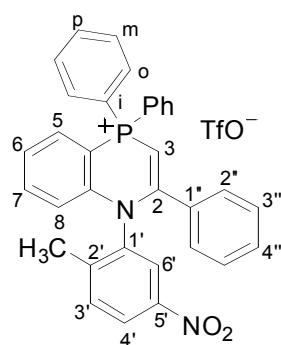
NMR (162 MHz, CDCl₃): δ -6.88 ppm; HRMS (ESI) calcd for C₃₃H₂₇NP ([M-OTf]⁺): 468.1876, found: 468.1889.

1-(4-Bromophenyl)-2,4,4-triphenyl-1,4-dihydrobenzazaphosphorinium triflate (6b).



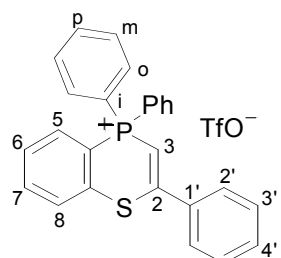
White solid (0.13 g, 65%) that was recrystallized from CH₂Cl₂/Et₂O (colorless prisms); m.p. 129-131 °C; IR (Nujol): 3062, 1587, 1493, 1443, 1263, 1110, 1031, 911, 731 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 5.29 (d, ²J_{3,P}= 11.1 Hz, 1 H, H3), 6.84 (br t, ³J_{7,8}= ⁴J_{8,P}= 7.8 Hz, 1 H, H8), 7.15 (d, ³J_{2',3'}= 8.2 Hz, 2 H, H2'), 7.22-7.27 (m, 5 H, H2'', H3'' and H4''), 7.43-7.48 (m, 3 H, H6 and H3'), 7.60 (br t, ³J_{6,7}= ³J_{7,8}= 7.8 Hz, 1 H, H7), 7.73-7.82 (m, 11 H, H5 and PPh₂) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 73.70 (d, ¹J_{3,P}= 91.1 Hz, C3), 99.69 (d, ¹J_{4a,P}= 90.5 Hz, C4a), 120.08 (d, ³J_{8,P}= 6.5 Hz, C8), 120.87 (q, ¹J_{CF}= 321.2 Hz, CF₃SO₃), 123.54 (C4'), 123.83 (d, ¹J_{i,P}= 95.3 Hz, C_i), 126.01 (d, ³J_{6,P}= 11.7 Hz, C6), 128.42 (C2'' or C3''), 128.69 (C2'' or C3''), 129.51 (C4''), 130.46 (d, ³J_{m,P}= 13.4 Hz, C_m), 132.24 (C2'), 132.75 (d, ²J_{5,P}= 6.8 Hz, C5), 133.11 (d, ²J_{o,P}= 11.6 Hz, C_o), 133.37 (C3'), 134.79 (d, ⁴J_{p,P}= 2.8 Hz, C_p), 135.39 (C7), 136.92 (d, ²J_{2,P}= 12.0 Hz, C2), 138.29 (C1'), 144.69 (d, ²J_{8a,P}= 3.4 Hz, C8a), 160.88 (C1'') ppm; ³¹P NMR (162 MHz, CDCl₃): δ -6.90 ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ -78.09 ppm; HRMS (ESI) calcd for C₃₂H₂₄BrNP ([M-OTf]⁺): 532.0824; found: 532.0828.

1-(2-Methyl-5-nitrophenyl)-2,4,4-triphenyl-1,4-dihydrobenzazaphosphorinium triflate (6c).



Yellow solid (0.12 g, 59%) that was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (yellow prisms); m.p. 135-137 °C; IR (Nujol): 3014, 1585, 1493, 1442, 1272, 1155, 1110, 1030, 755 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.15 (s, 3 H, CH_3), 5.51 (d, $^2J_{3,\text{P}} = 10.9$ Hz, 1 H, H3), 6.71 (dd, $^3J_{7,8} = 7.9$ Hz, $^4J_{8,\text{P}} = 6.8$ Hz, 1 H, H8), 7.22-7.30 (m, 5 H, H2'', H3'' and H4''), 7.43 (d, $^3J_{3',4'} = 8.3$ Hz, 1 H, H3'), 7.55 (t, $^3J_{6,7} = ^3J_{7,8} = 7.9$ Hz, 1 H, H6), 7.68 (t, $^3J_{6,7} = ^3J_{7,8} = 7.9$ Hz, 1 H, H7), 7.72-7.85 (m, 10 H, PPh_2), 7.86 (ddd, $^3J_{5,\text{P}} = 14.0$ Hz, $^3J_{5,6} = 7.9$ Hz, $^4J_{5,7} = 1.3$ Hz, 1 H, H5), 8.08 (d, $^3J_{3',4'} = 8.3$ Hz, 1 H, H4'), 8.11 (s, 1 H, H6') ppm; ^{13}C { ^1H } NMR (75 MHz, CDCl_3): δ 18.06 (CH_3), 75.12 (d, $^1J_{3,\text{P}} = 90.1$ Hz, C3), 99.97 (d, $^1J_{4a,\text{P}} = 90.3$ Hz, C4a), 118.84 (d, $^3J_{8,\text{P}} = 6.6$ Hz, C8), 120.92 (q, $^1J_{\text{CF}} = 320.4$ Hz, CF_3SO_3), 122.81 (d, $^1J_{i,\text{P}} = 95.9$ Hz, C_i), 123.63 (d, $^1J_{i,\text{P}} = 95.0$ Hz, C_i), 124.61 (C4'), 126.46 (C6'), 126.72 (d, $^3J_{6,\text{P}} = 11.5$ Hz, C6), 127.88 (C2'' or C3''), 128.63 (C2'' or C3''), 130.11 (C4''), 130.49 (d, $^3J_{m,\text{P}} = 13.7$ Hz, C_m), 130.71 (d, $^3J_{m,\text{P}} = 13.6$ Hz, C_m), 132.69 (d, $^2J_{o,\text{P}} = 11.7$ Hz, C_o), 133.28 (C3'), 133.33 (d, $^2J_{5,\text{P}} = 6.4$ Hz, C5), 133.35 (d, $^2J_{o,\text{P}} = 11.2$ Hz, C_o), 135.00 (d, $^4J_{p,\text{P}} = 2.9$ Hz, C_p), 135.08 (d, $^4J_{p,\text{P}} = 3.0$ Hz, C_p), 135.95 (d, $^2J_{2,\text{P}} = 11.9$ Hz, C2), 136.18 (C7), 138.43 (C2'), 143.33 (d, $^2J_{8a,\text{P}} = 3.4$ Hz, C8a), 144.97 (C1'), 146.59 (C5'), 160.25 (C1'') ppm; ^{31}P NMR (121 MHz, CDCl_3): δ -6.63 ppm; ^{19}F NMR (282 MHz, CDCl_3): δ -78.09 ppm; HRMS (ESI) calcd for $\text{C}_{33}\text{H}_{26}\text{N}_2\text{O}_2\text{P}$ ($[\text{M-OTf}]^+$): 513.1726; found: 513.1728.

2,4,4-Triphenyl-1,4-dihydro-1,4-benzothiaphosphorinane triflate (7).



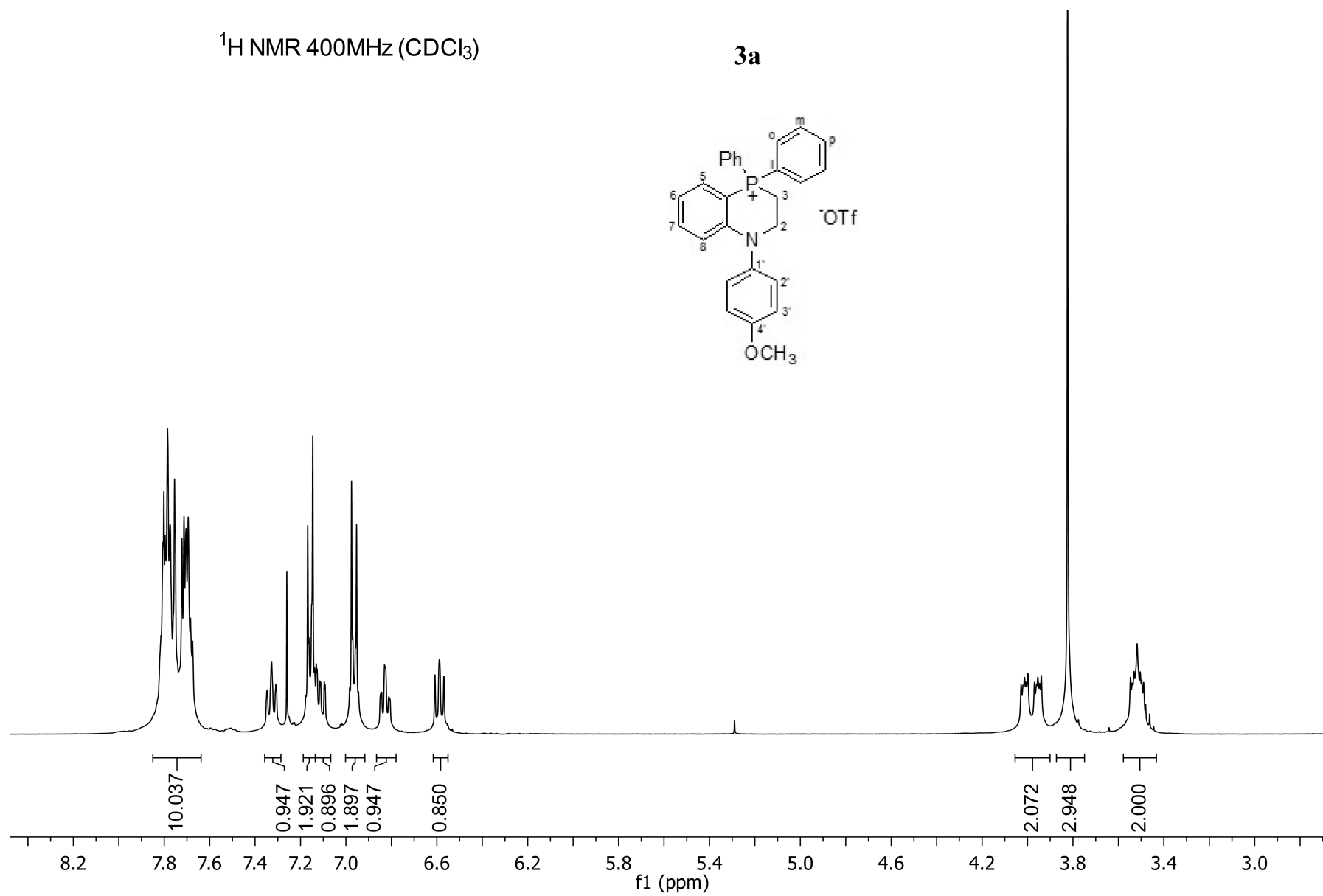
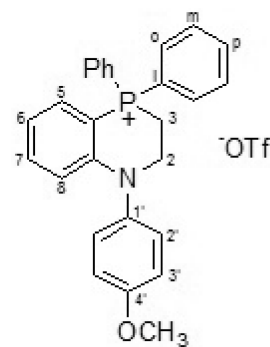
White solid (0.09 g, 82%) that was recrystallized from CH₂Cl₂/Et₂O (colorless prisms); m.p. 89-91 °C; IR (Nujol): 3060, 1581, 1440, 1264, 1156, 1114, 1031, 911, 689 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.05 (d, ²J_{3,p}= 15.5 Hz, 1 H, H₃), 7.49-7.65 (m, 4 H, H₅, H_{3'} and H_{4'}), 7.66-7.75 (m, 9 H, H₆, H_o and H_m), 7.76-7.80 (m, 2 H, H_p), 7.81-7.86 (m, 2 H, H₇ and H₈), 7.92 (dd, ³J_{2',3'}= 8.1 Hz, ⁴J_{2',4'}= 1.3 Hz, 2 H, H_{2'}) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 94.57 (d, ¹J_{3,p}= 95.3 Hz, C₃), 111.74 (d, ¹J_{4a,p}= 94.8 Hz, C_{4a}), 118.81 (d, ¹J_{i,p}= 95.0 Hz, C_i), 120.93 (q, ¹J_{CF}= 321.2 Hz, CF₃SO₃), 128.27 (C_{3'}), 128.58 (d, ³J_{8,p}= 7.3 Hz, C₈), 129.57 (C_{2'}), 130.12 (d, ³J_{6,p}= 11.6 Hz, C₆), 130.60 (d, ³J_{m,p}= 13.7 Hz, C_m), 132.78 (C_{4'}), 133.45 (d, ²J_{5,p}= 9.7 Hz, C₅), 133.61 (d, ²J_{o,p}= 11.6 Hz, C_o), 134.57 (d, ⁴J_{7,p}= 2.0 Hz, C₇), 135.45 (d, ⁴J_{p,p}= 2.9 Hz, C_p), 135.88 (d, ²J_{2,p}= 13.7 Hz, C₂), 138.51 (d, ²J_{8a,p}= 6.7 Hz, C_{8a}), 163.30 (C_{1'}) ppm; ³¹P NMR (162 MHz, CDCl₃): δ 1.50 ppm; HRMS (ESI) calcd for C₂₆H₂₀PS ([M-OTf]⁺): 395.1018; found: 395.1023.

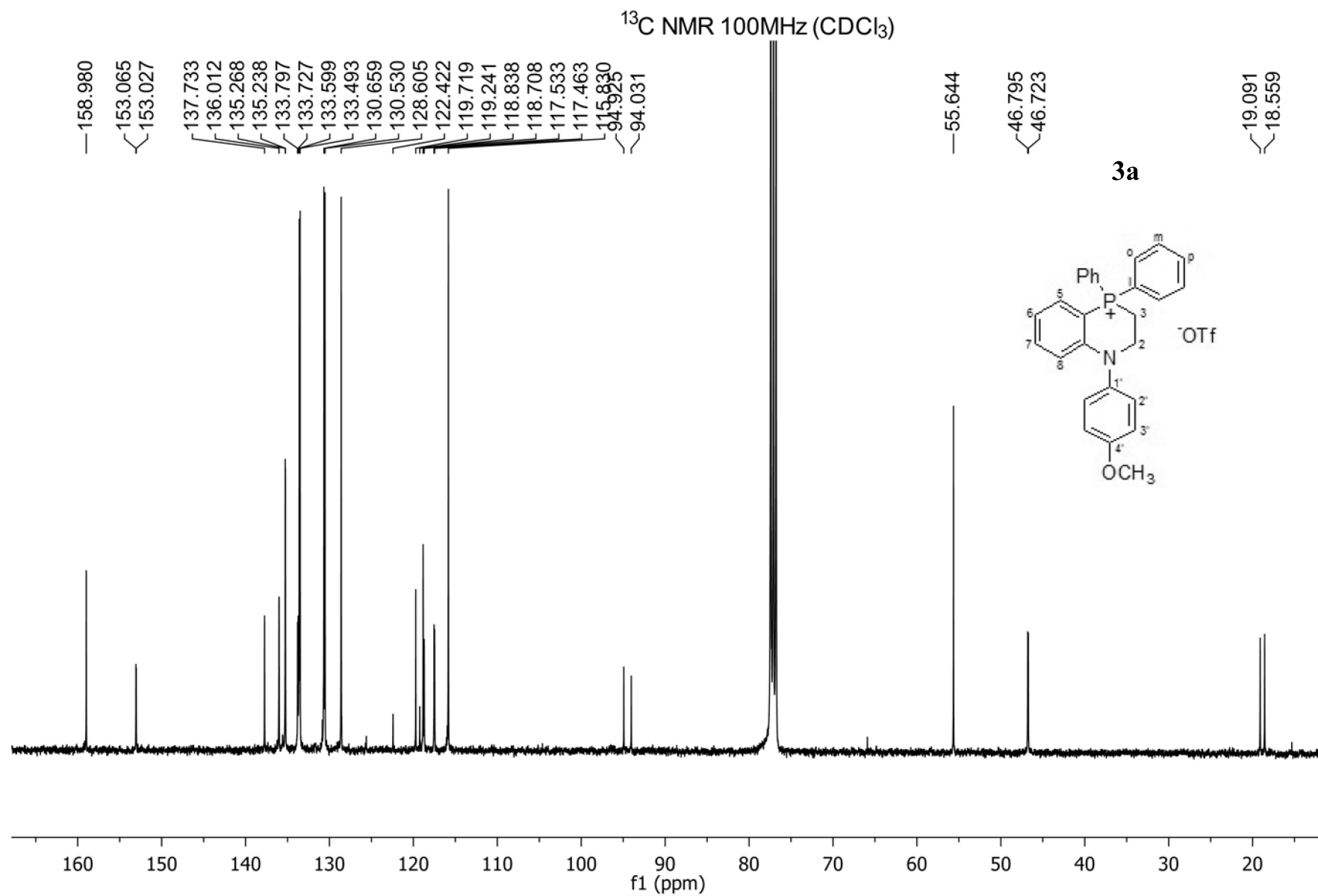
References

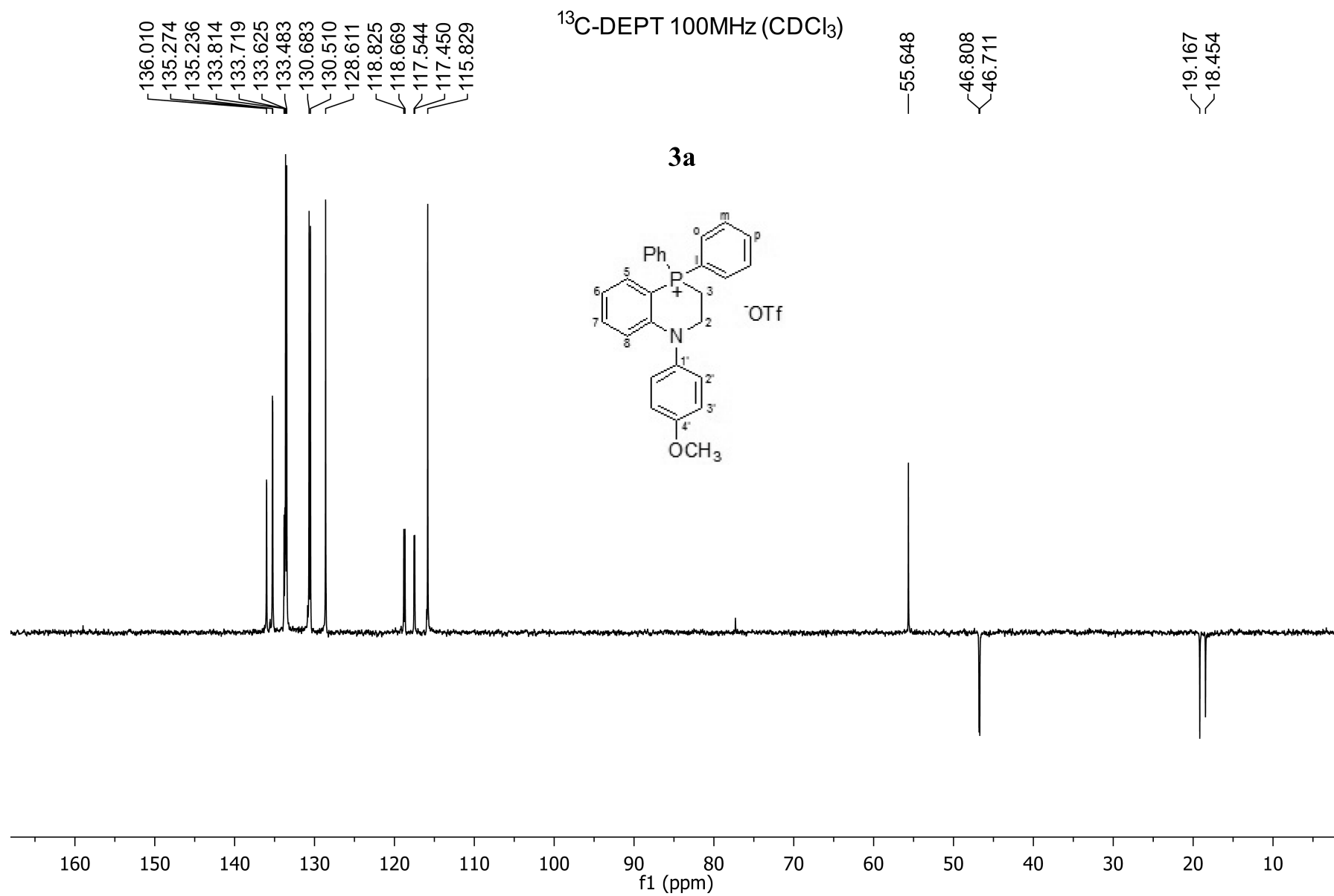
- (1) (a) Alajarin, M.; López-Leonardo, C.; Llamas-Lorente, P.; Bautista, D. *Dalton Trans.* **2003**, 426-434. (b) Alajarin, M.; Lopez-Leonardo, C.; Llamas-Lorente, P.; Raja, R. *Tetrahedron Letters* **2007**, 48, 6987-6991.
- (2) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, 121, 5827-5828.
- (3) Issleib, K.; Harzfeld, G. *Chem. Ber.* **1962**, 95, 268-272.

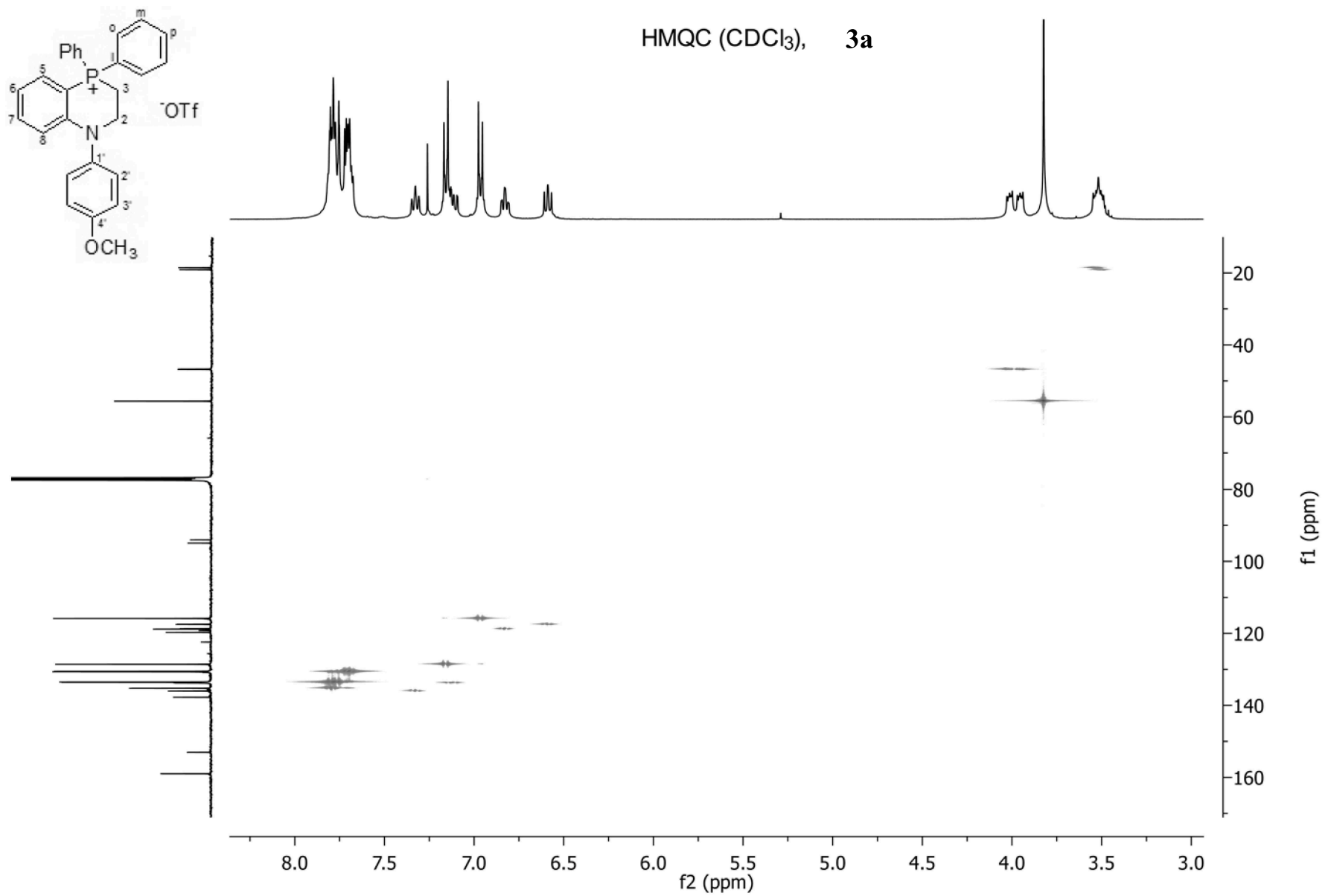
^1H NMR 400MHz (CDCl_3)

3a



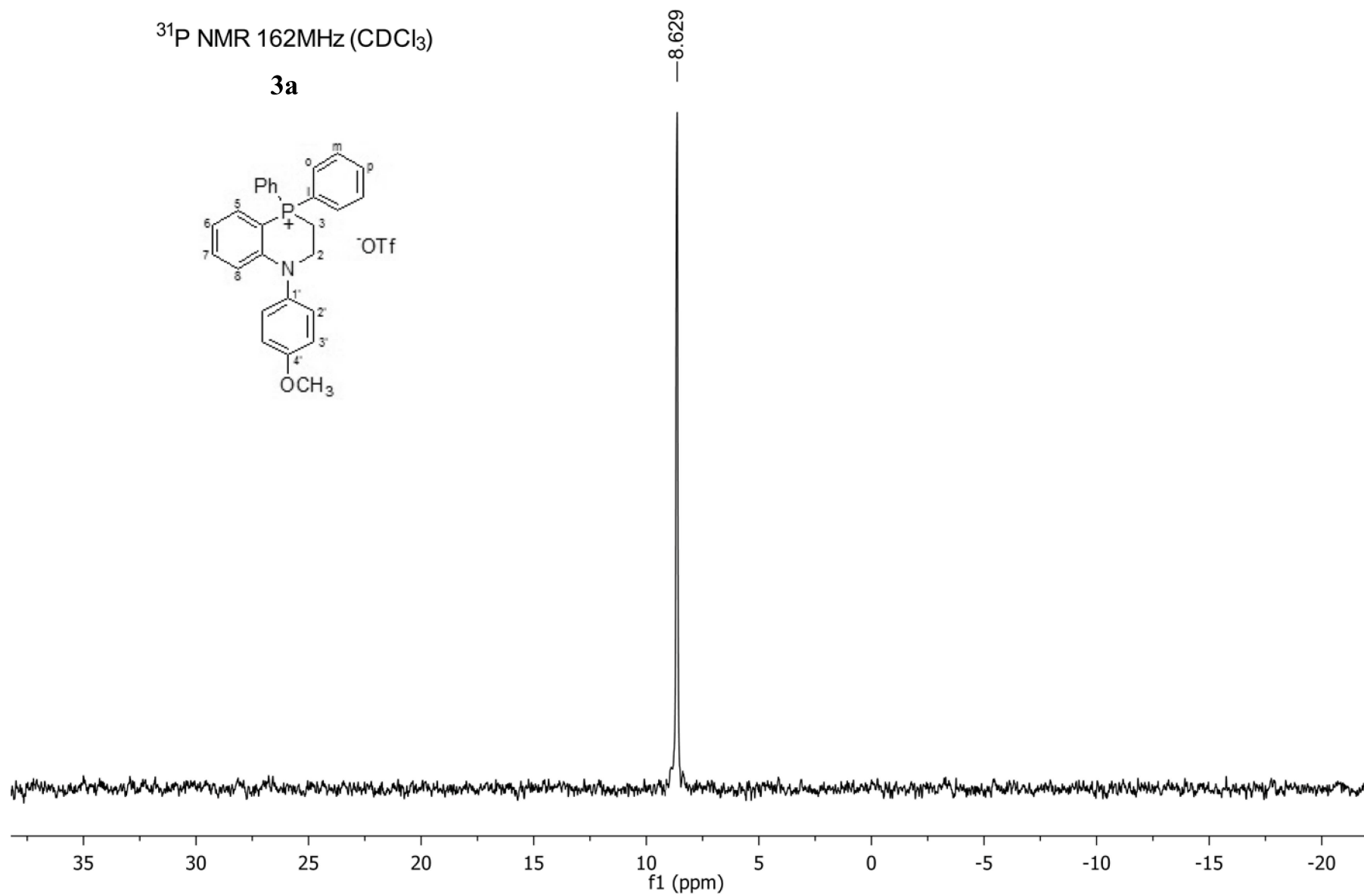
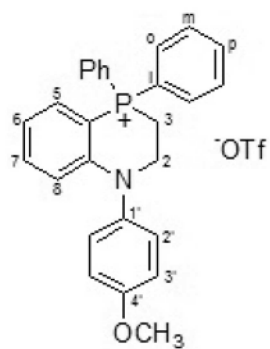






^{31}P NMR 162MHz (CDCl_3)

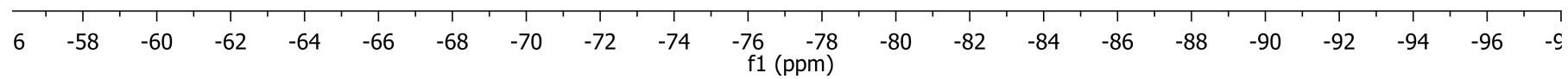
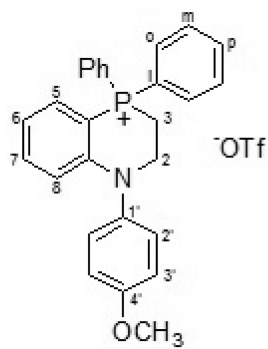
3a



^{19}F NMR 282MHz (CDCl_3)

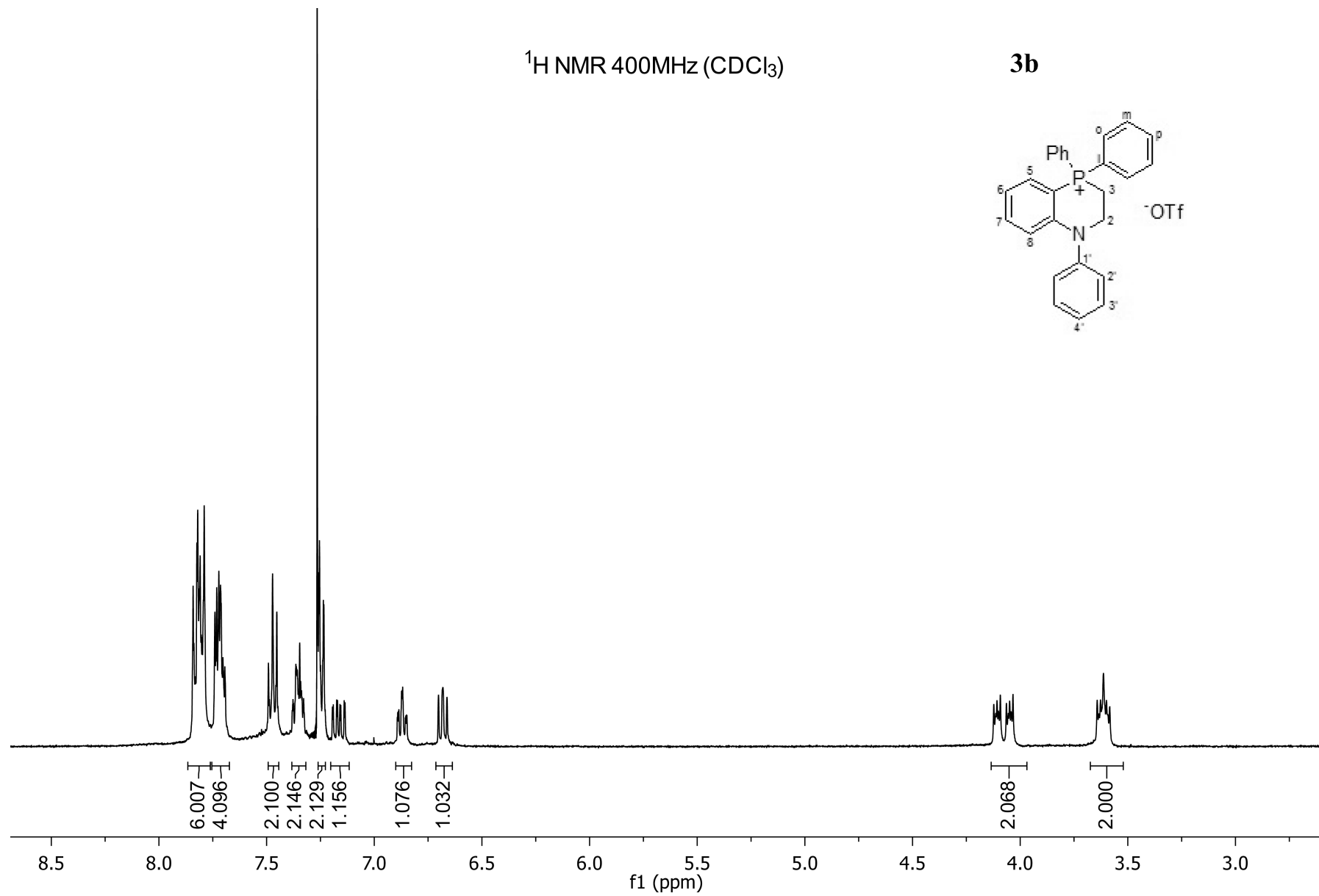
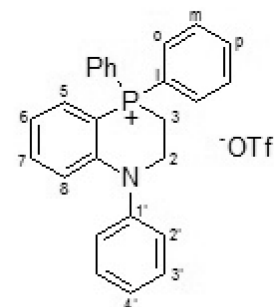
—78.247

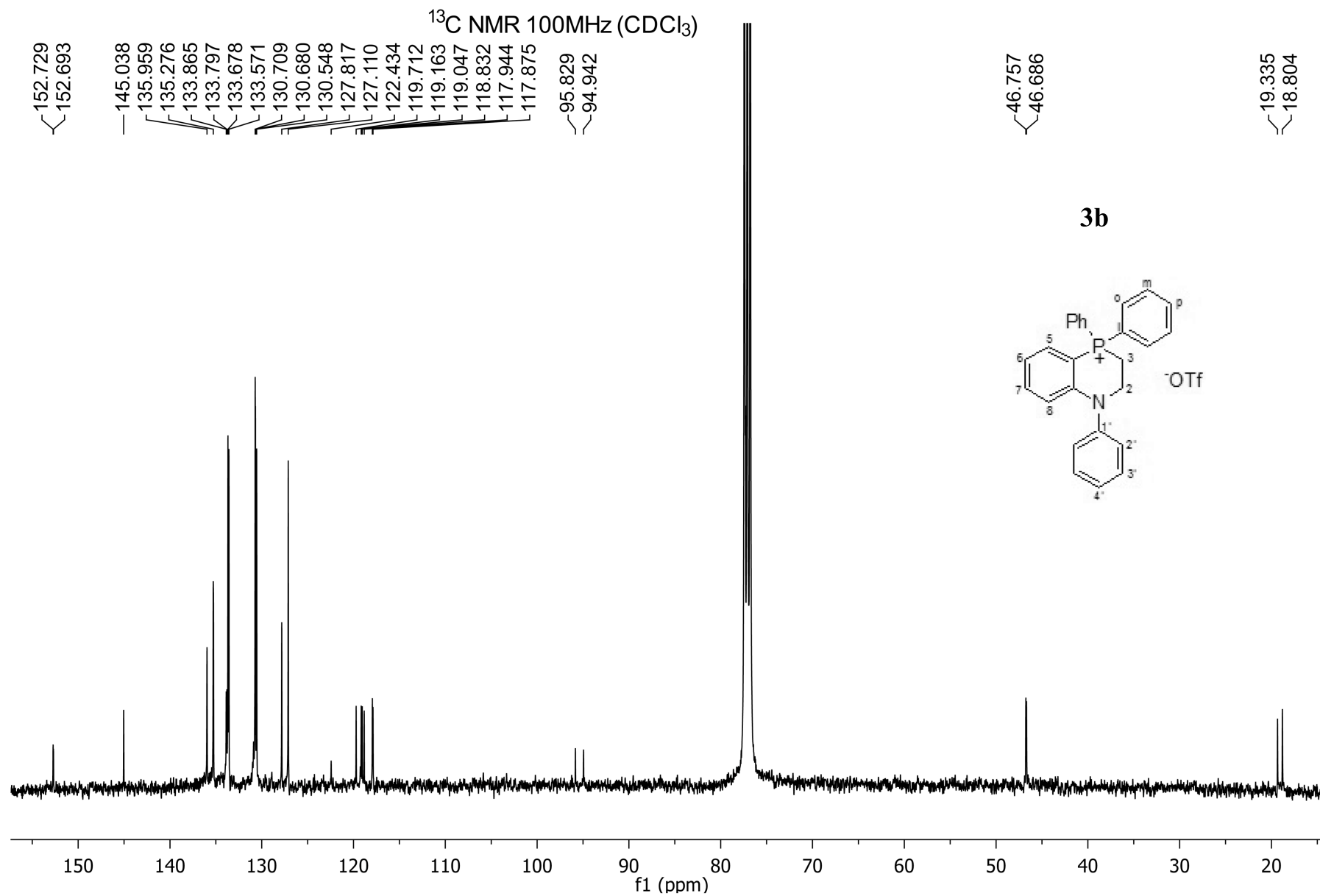
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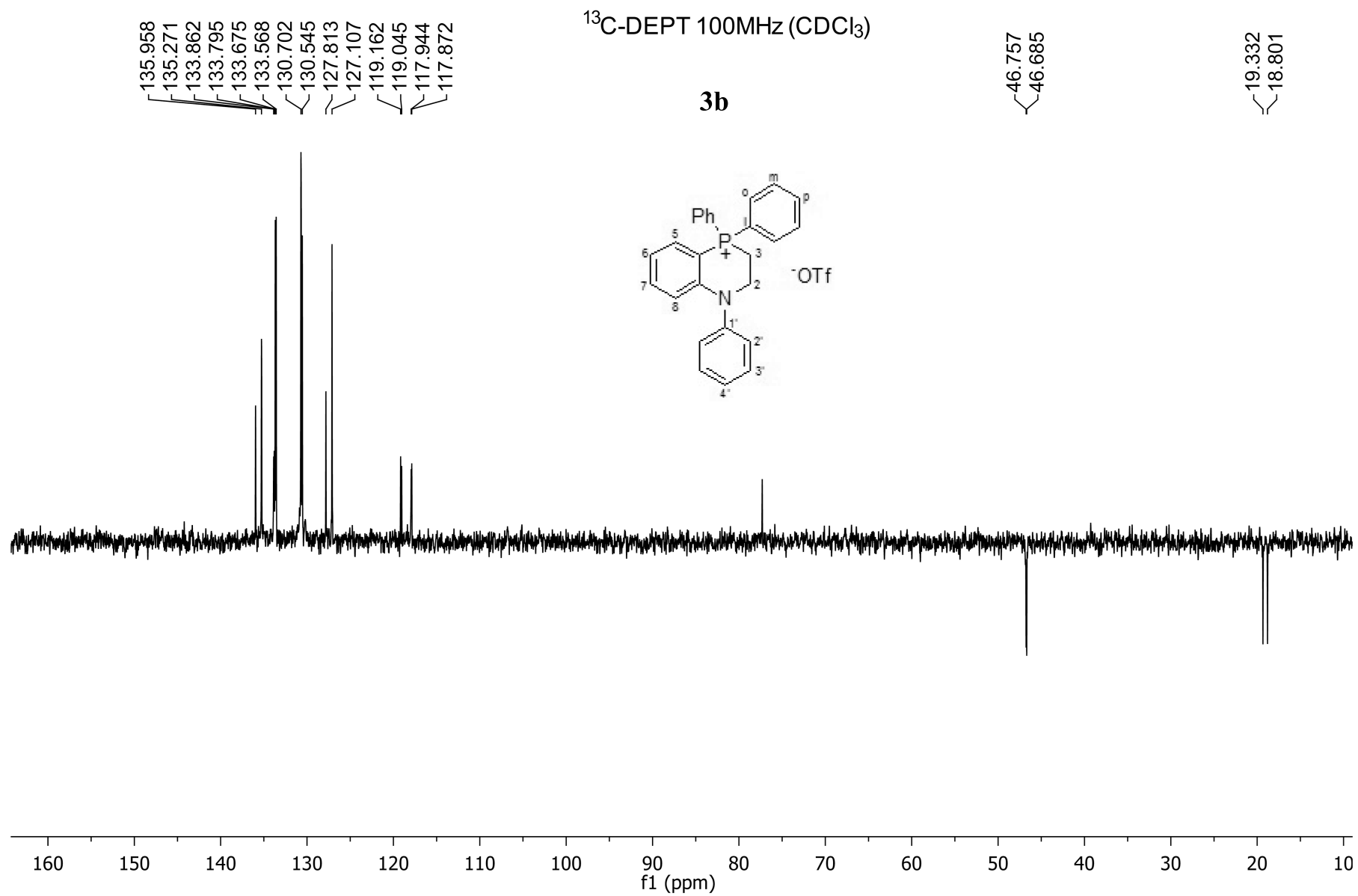


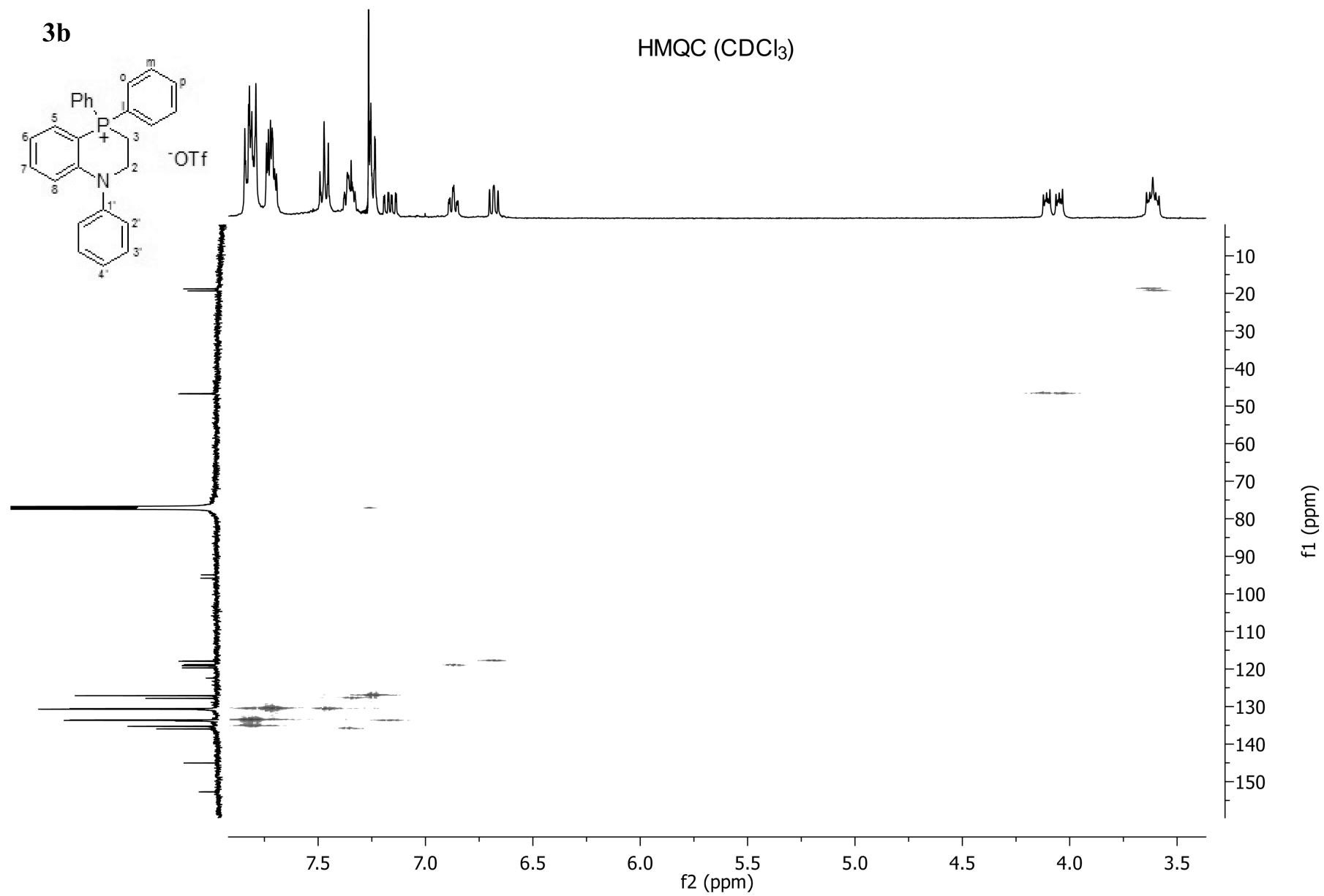
^1H NMR 400MHz (CDCl_3)

3b





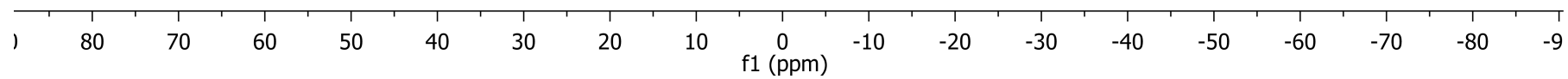
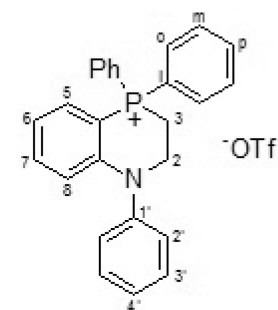




^{31}P NMR 162 MHz (CDCl_3)

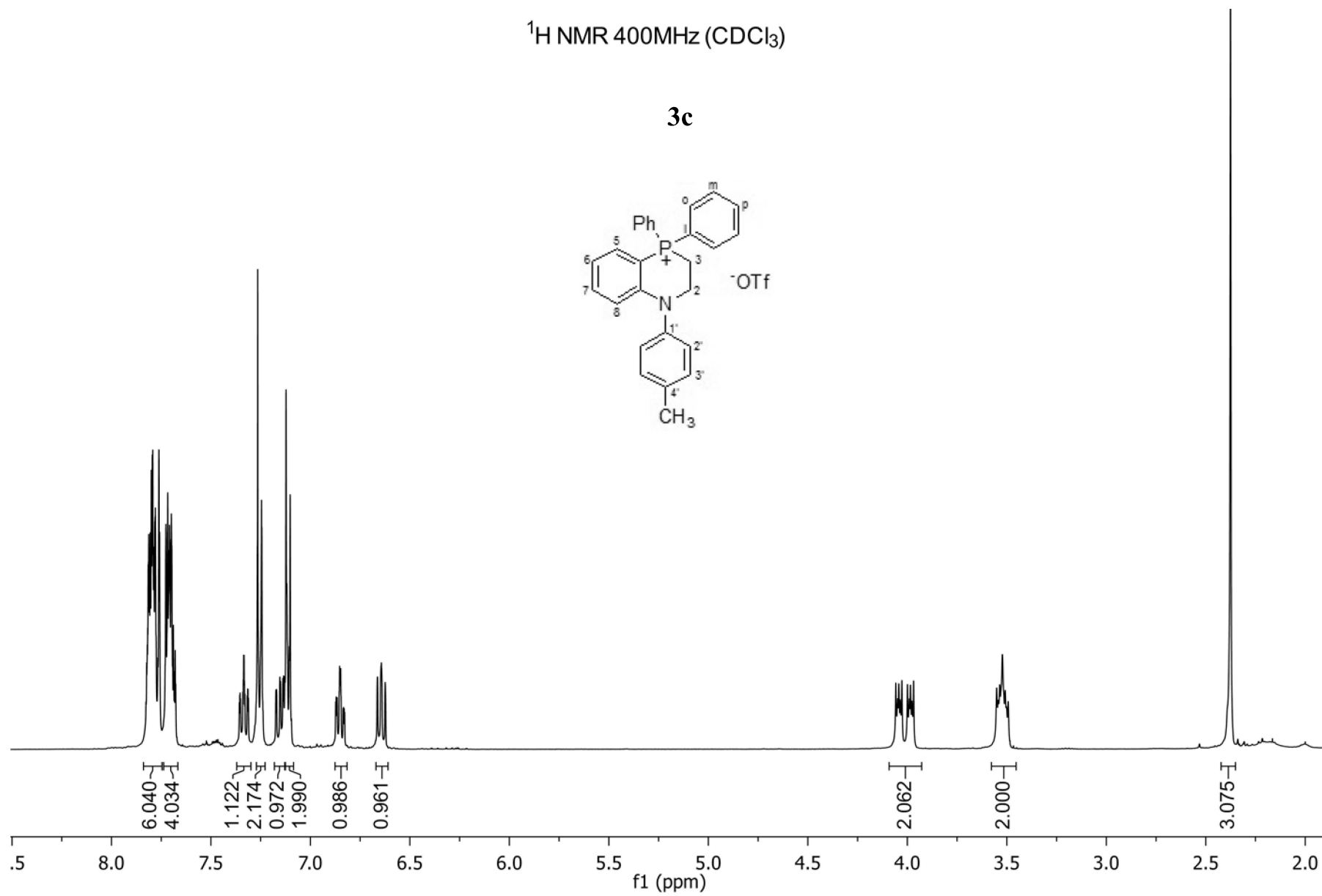
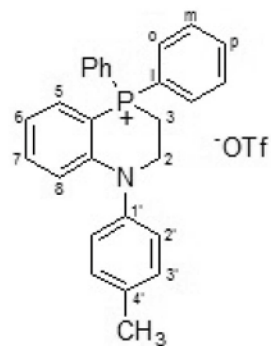
—8.521

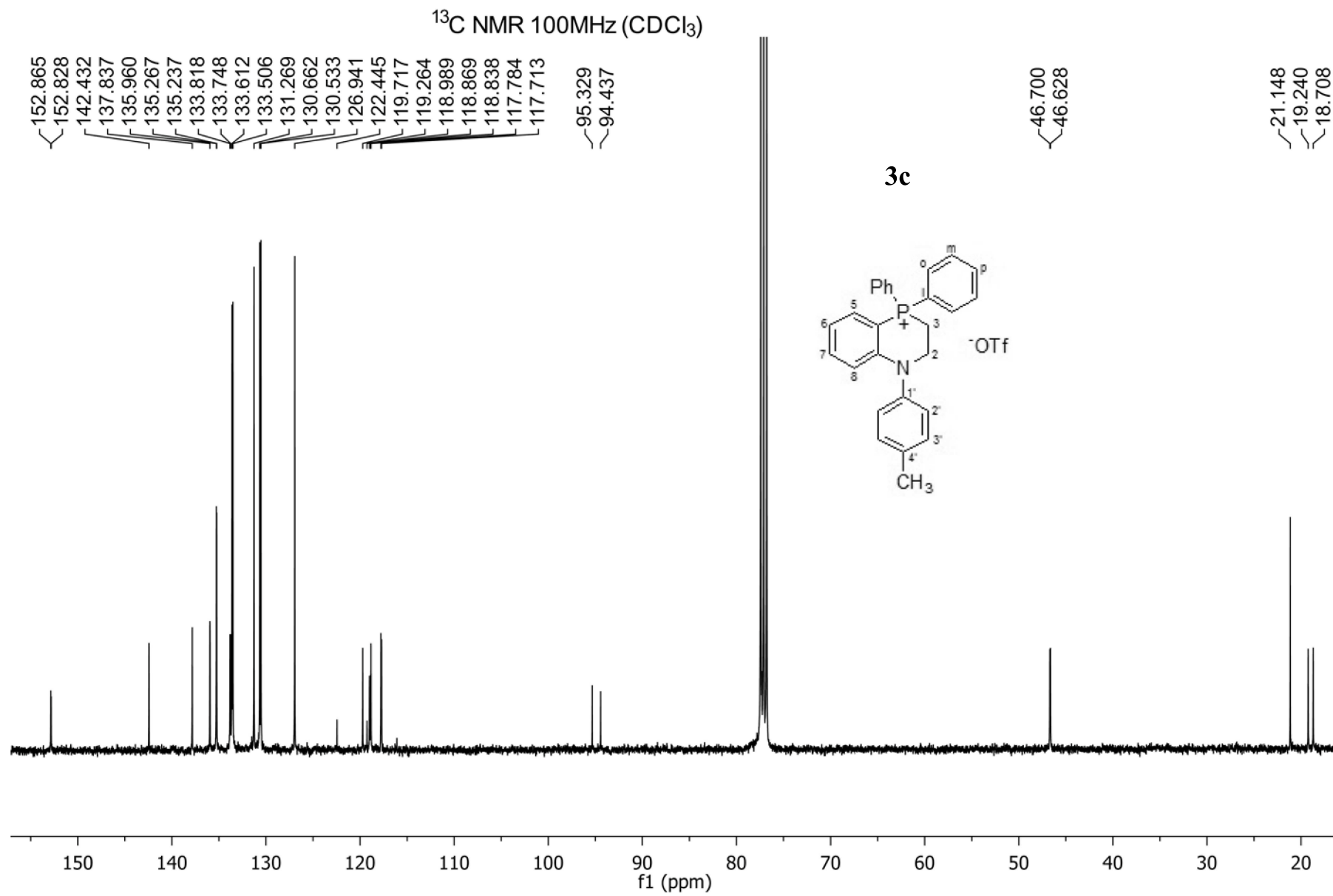
3b

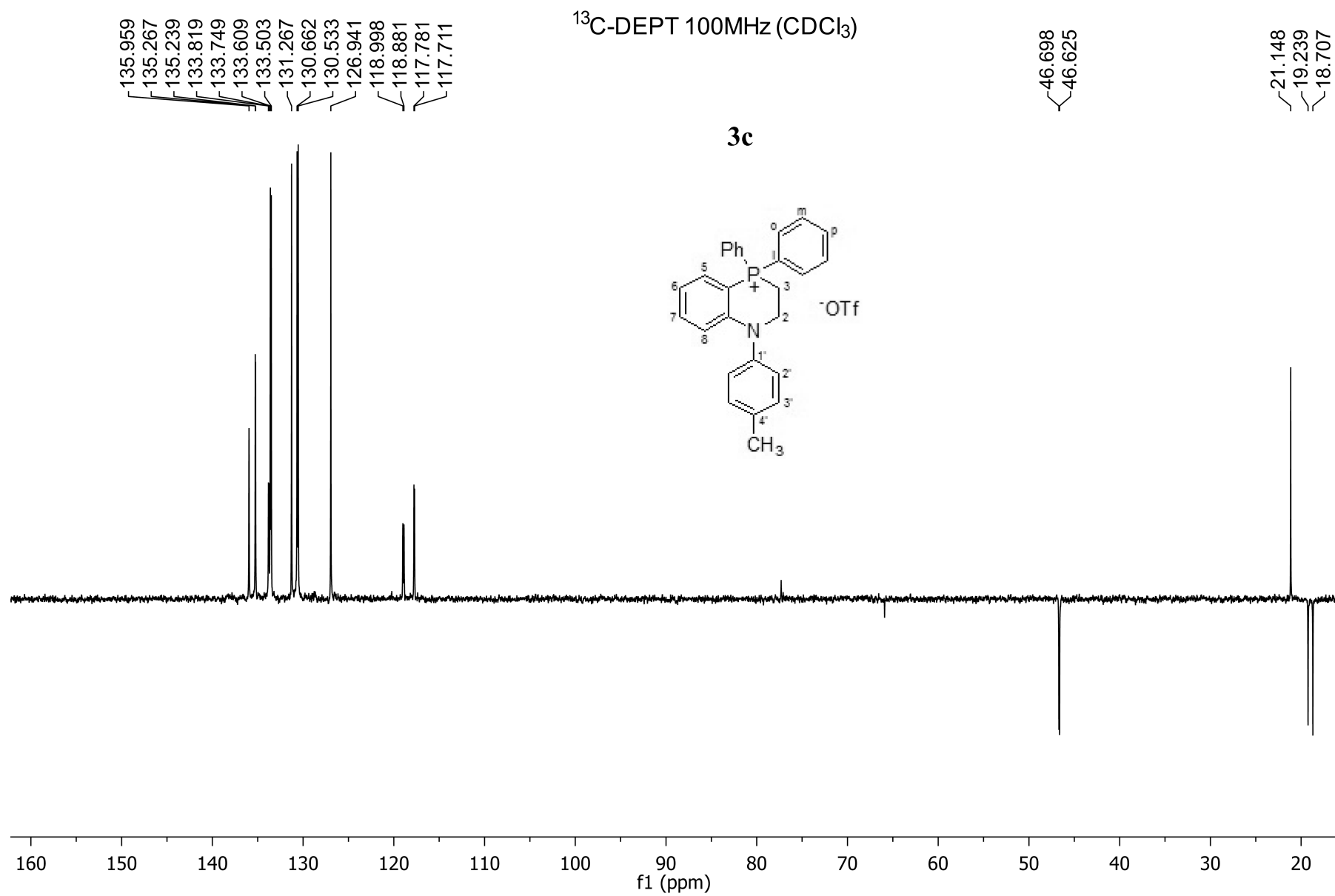


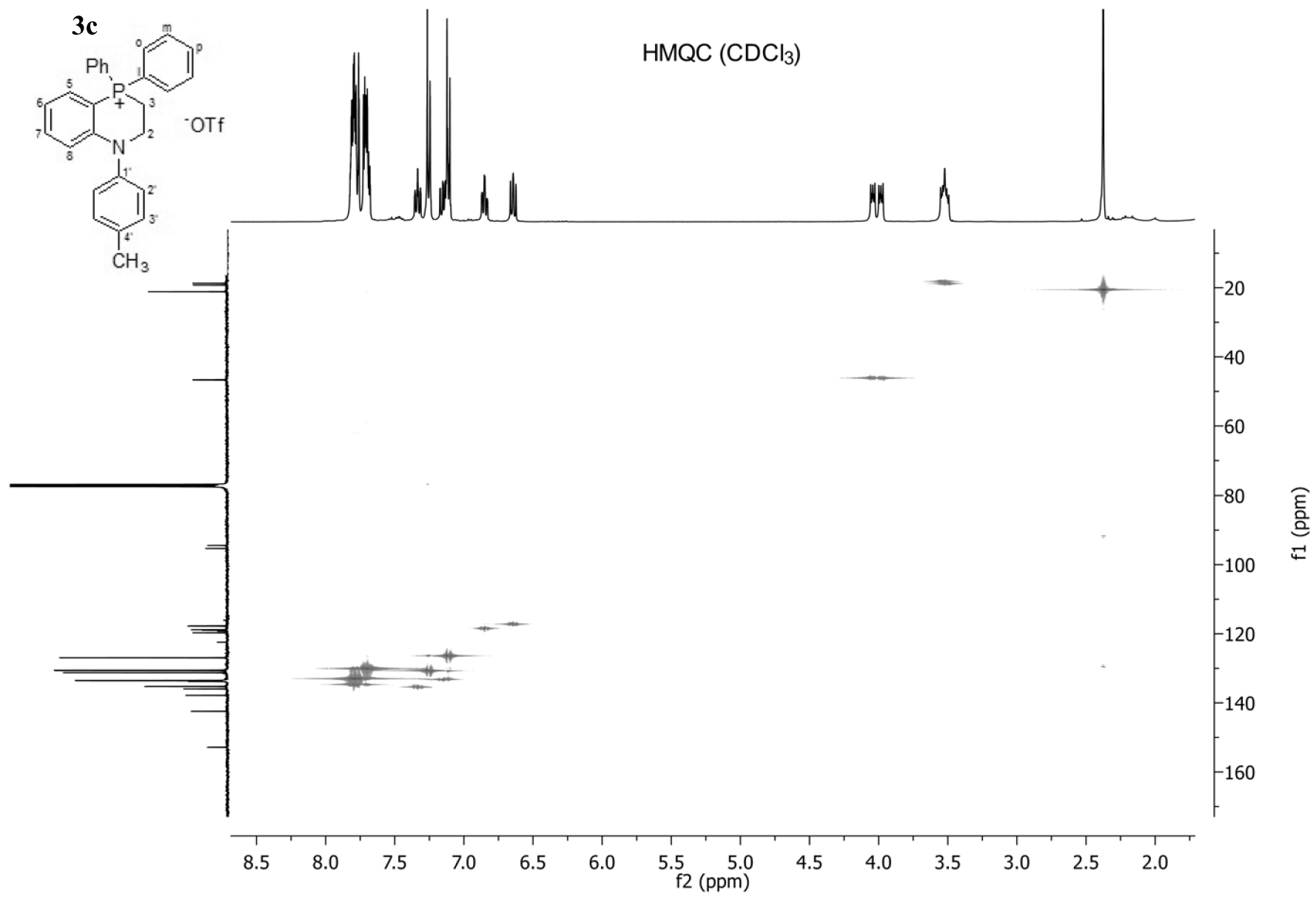
^1H NMR 400MHz (CDCl_3)

3c





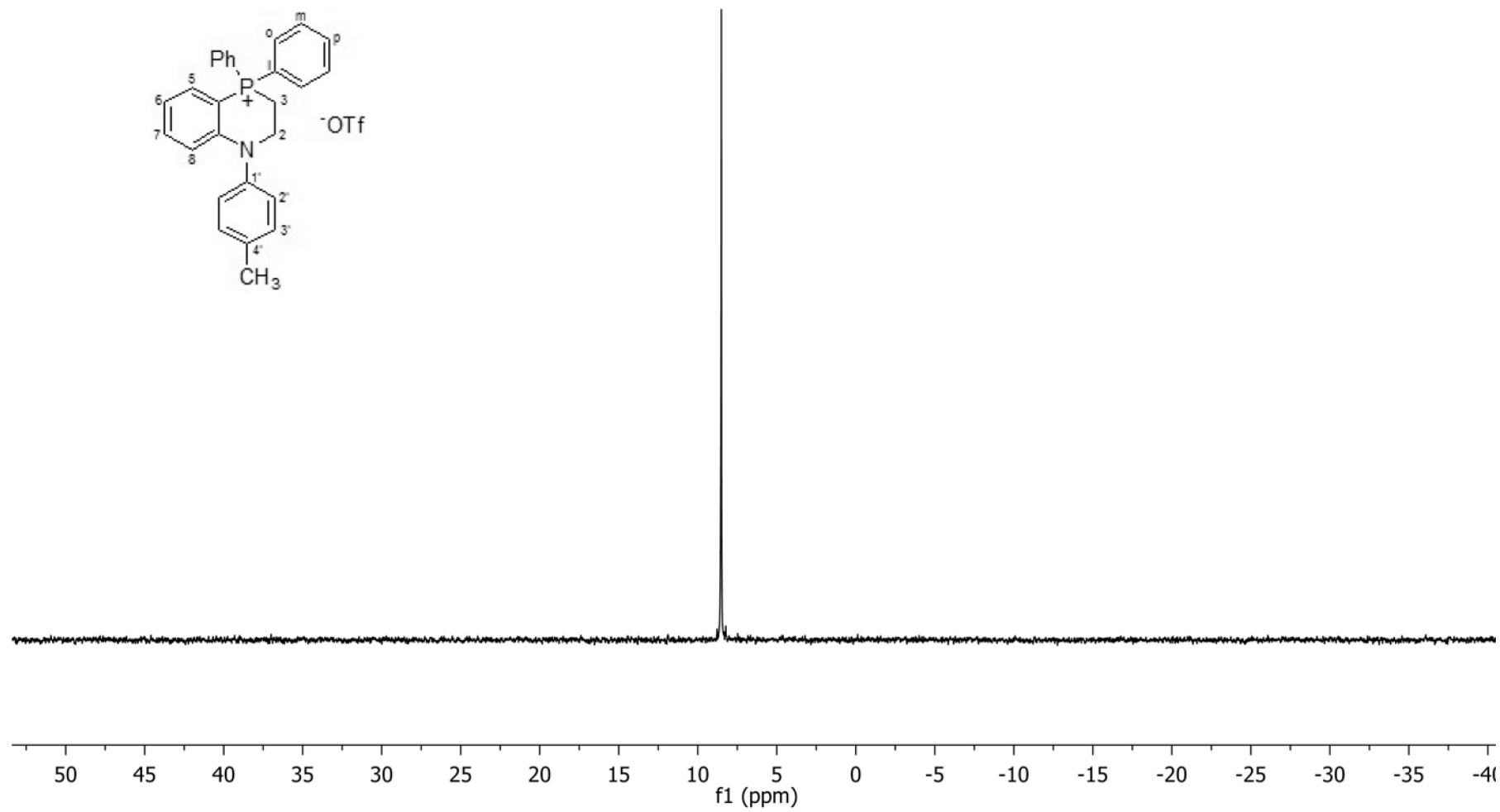
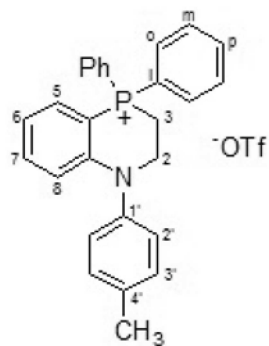




^{31}P NMR 162MHz (CDCl_3)

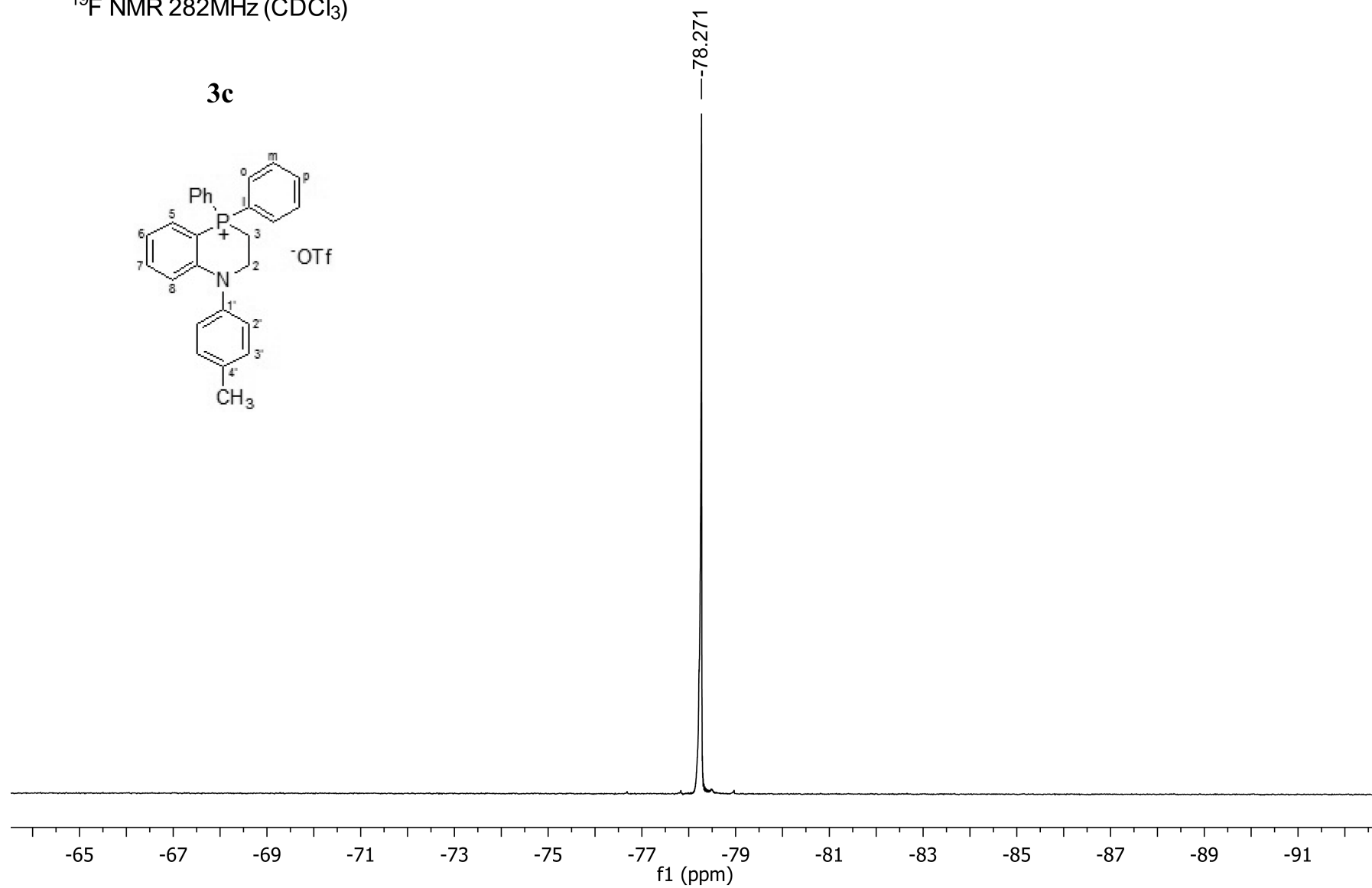
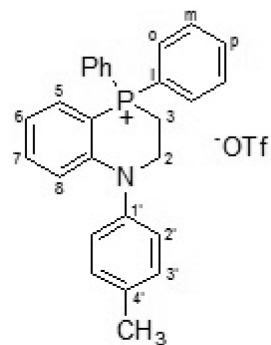
—8.507

3c



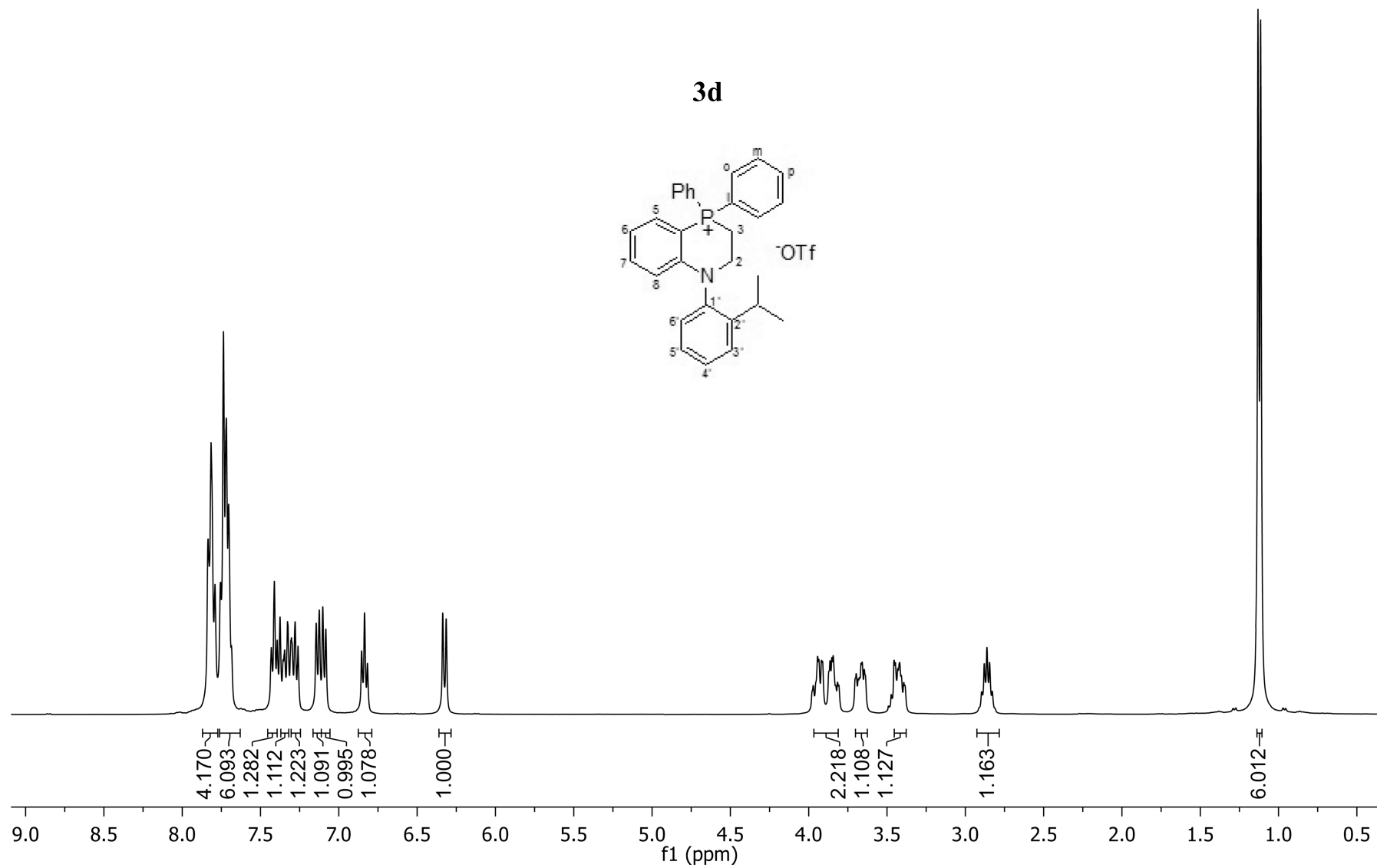
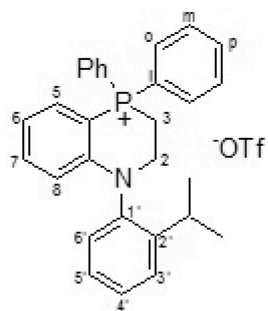
^{19}F NMR 282MHz (CDCl_3)

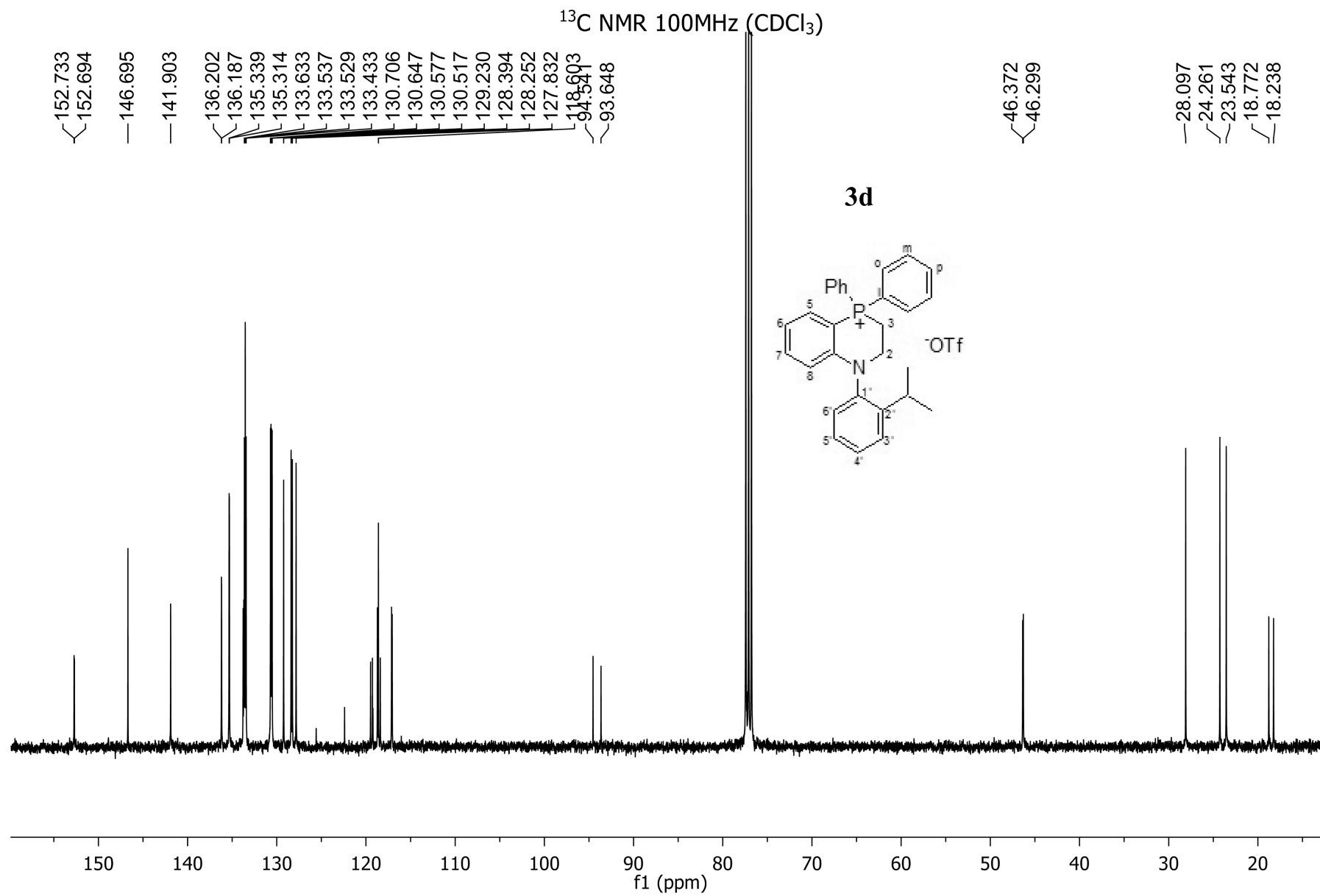
3c

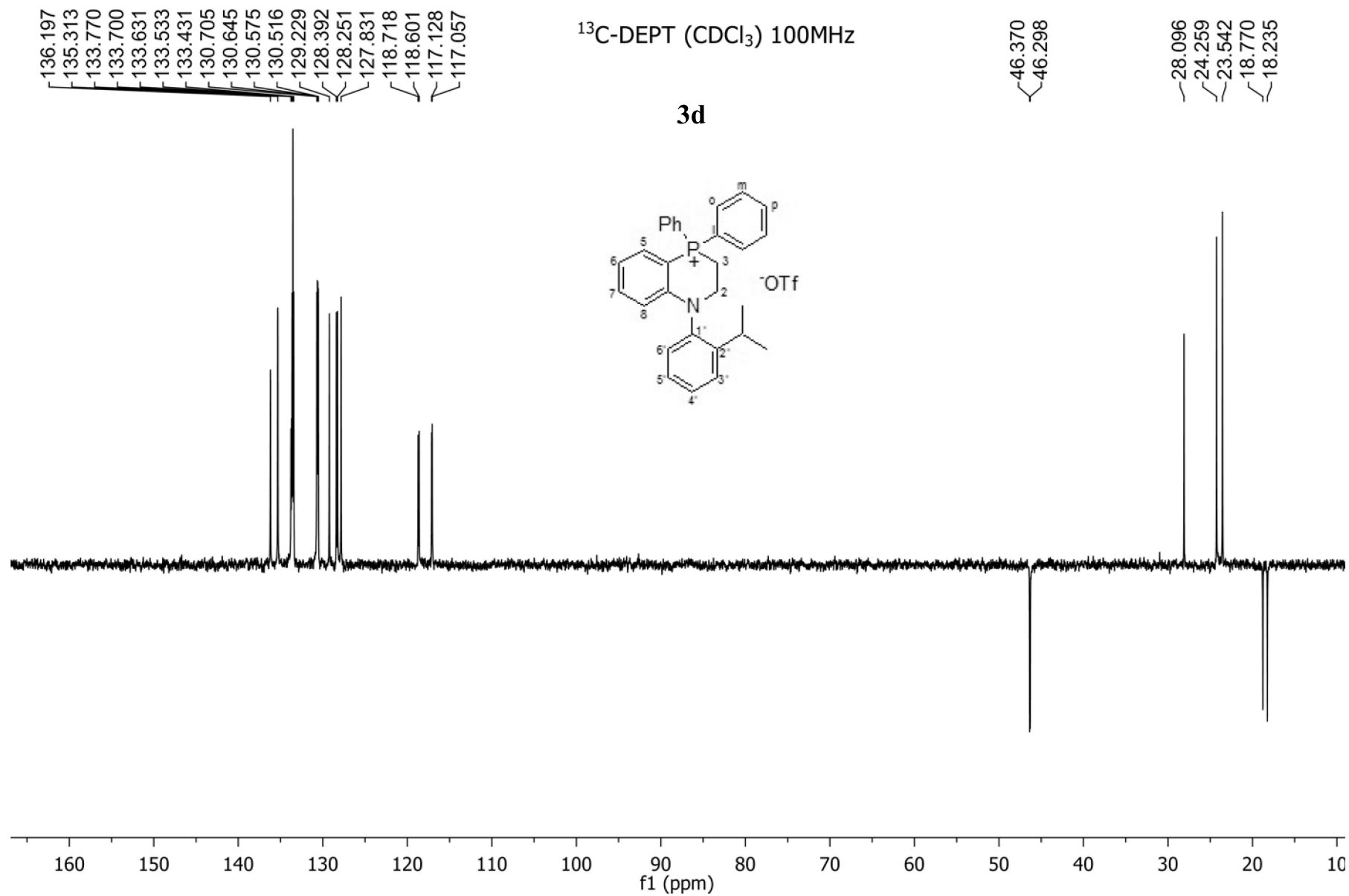


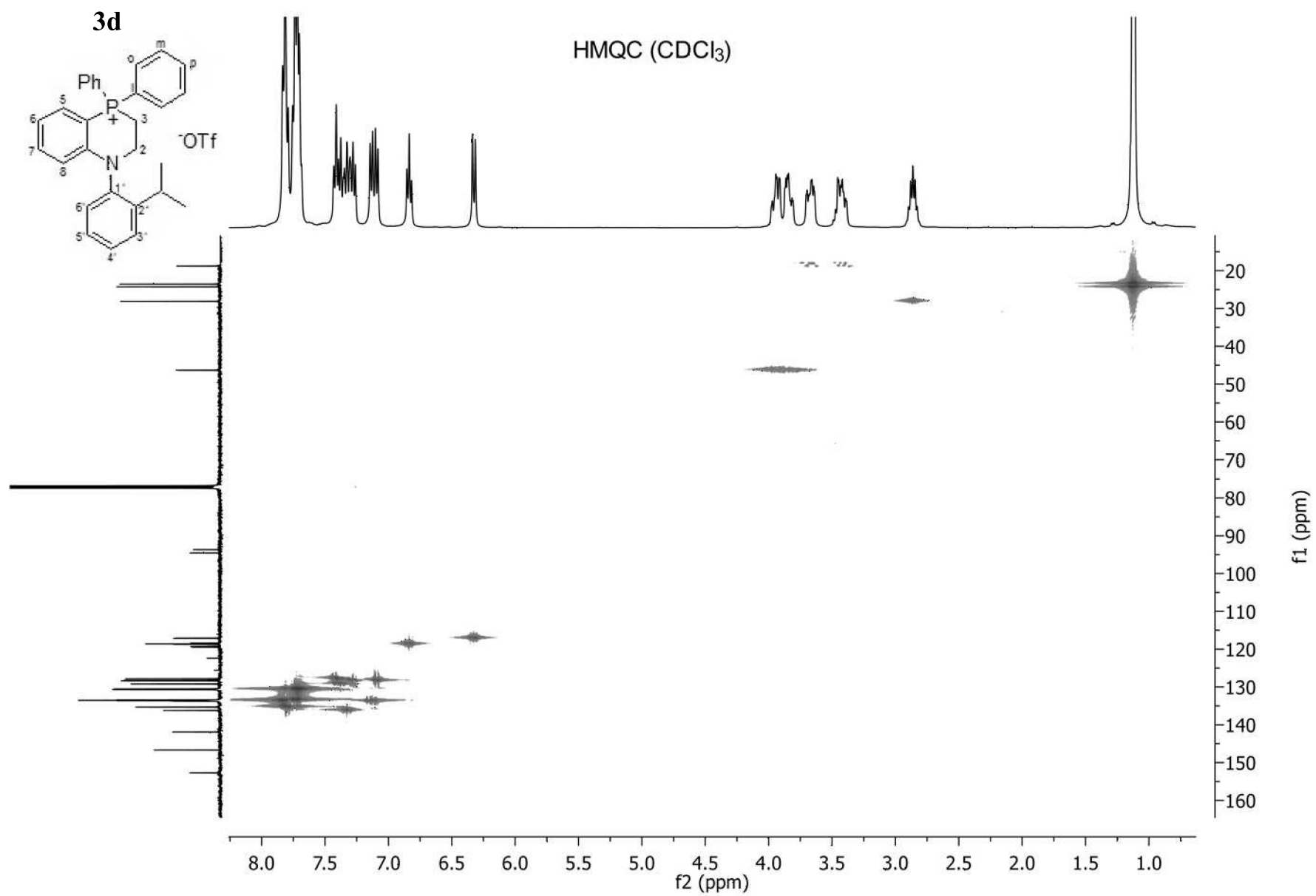
^1H NMR 400MHz (CDCl_3)

3d





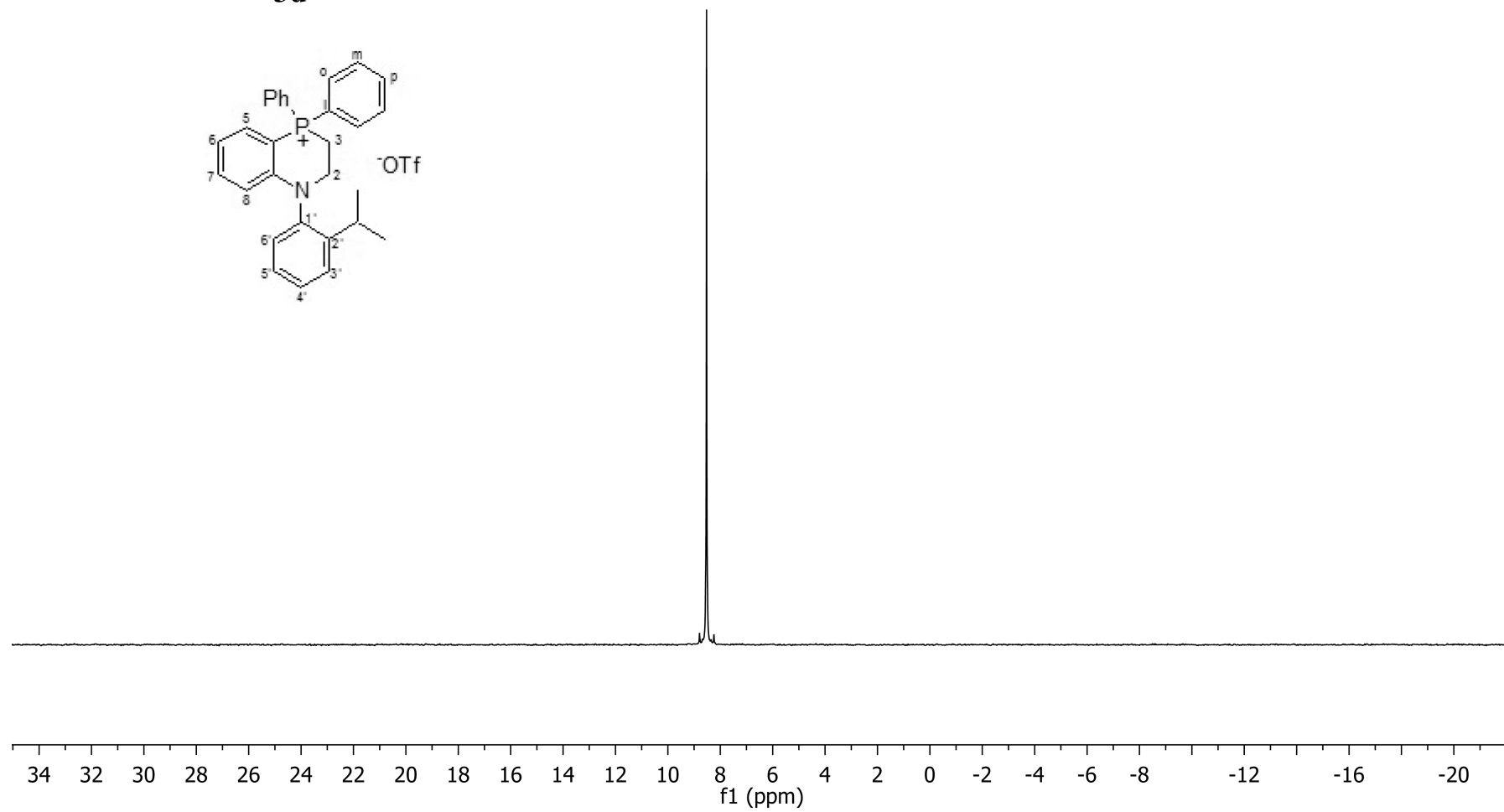
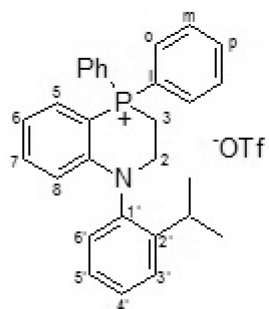




^{31}P NMR 162MHz (CDCl_3)

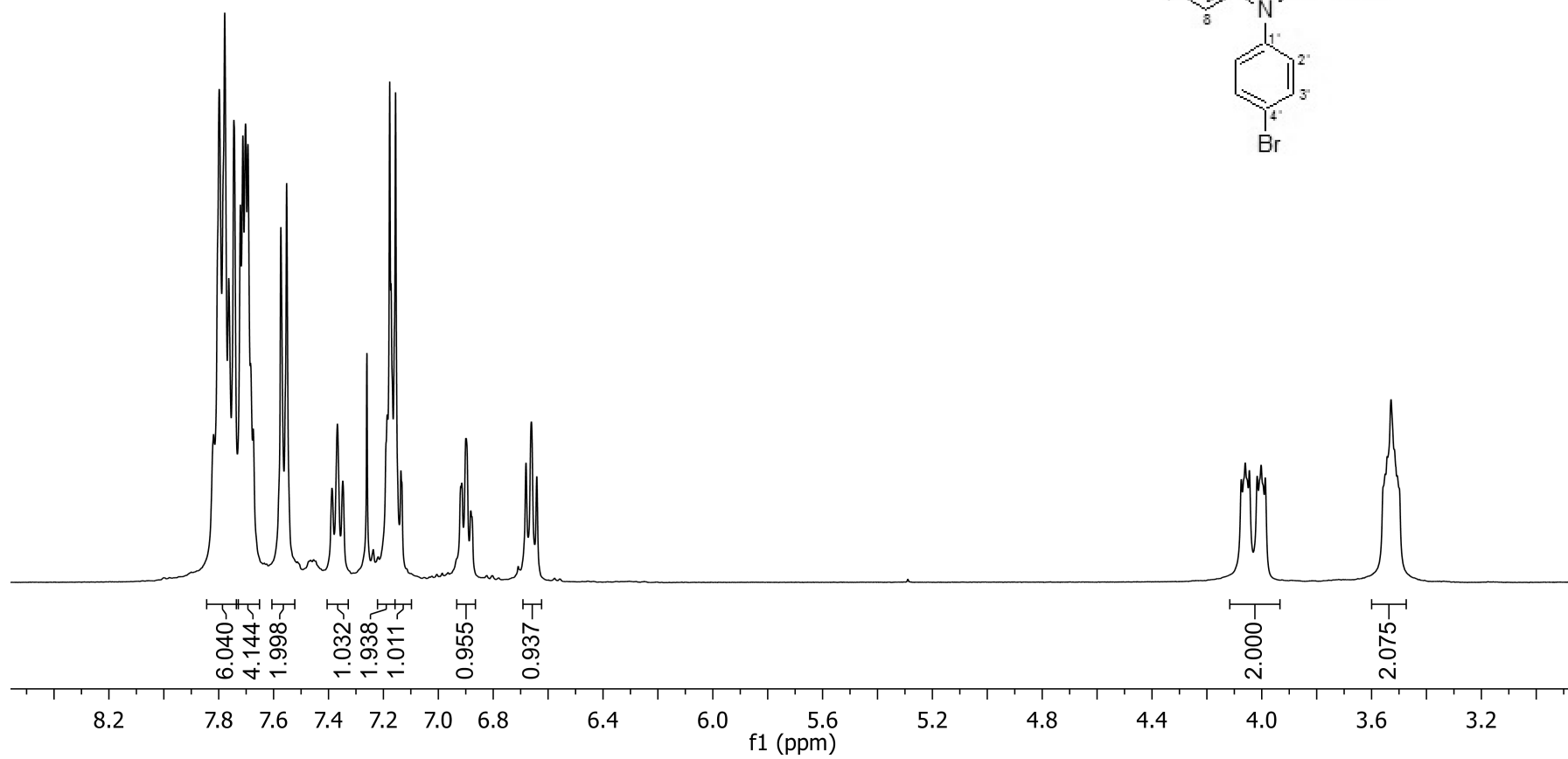
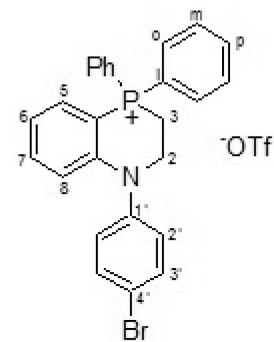
8.524

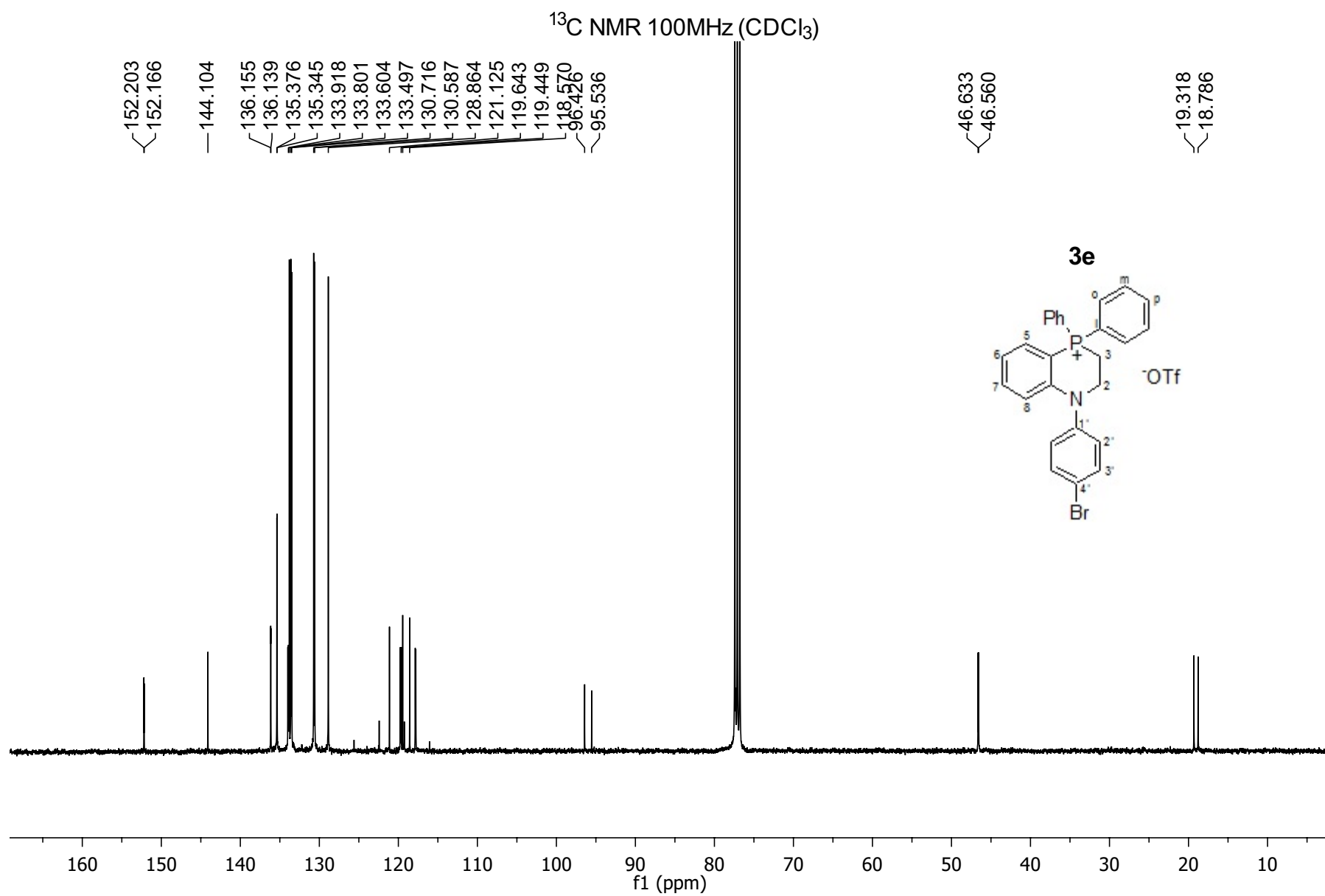
3d

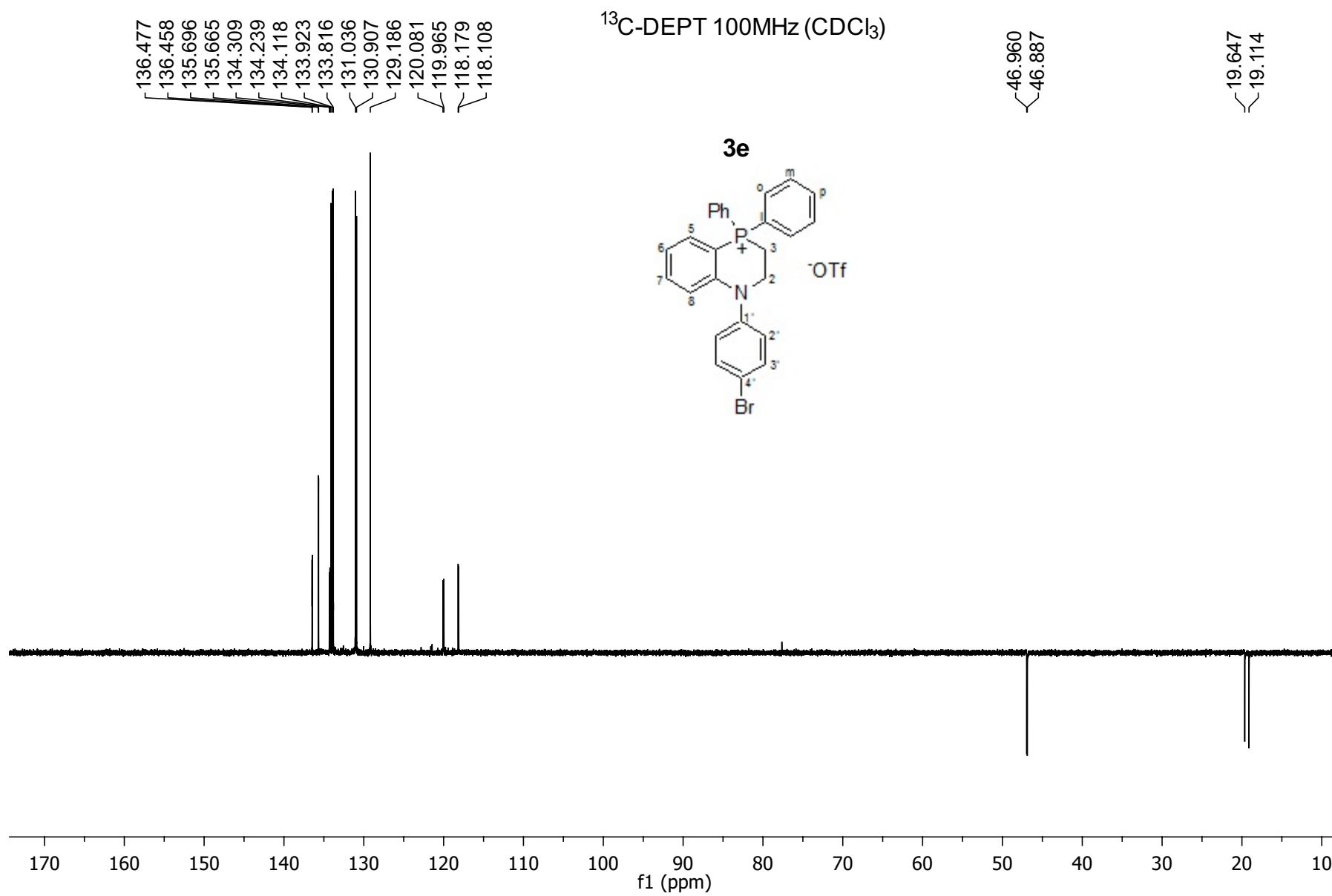


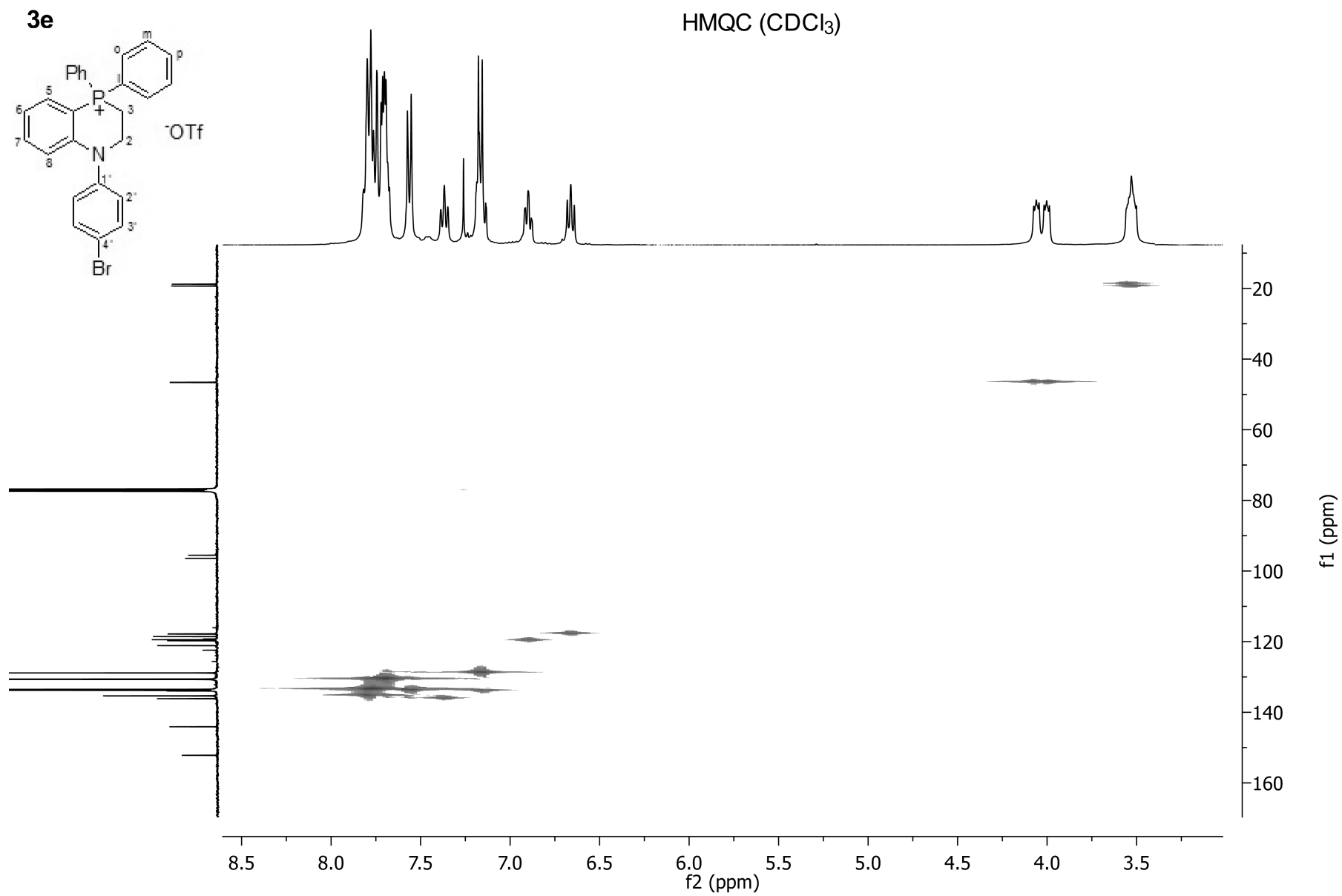
^1H NMR 400MHz (CDCl_3)

3e



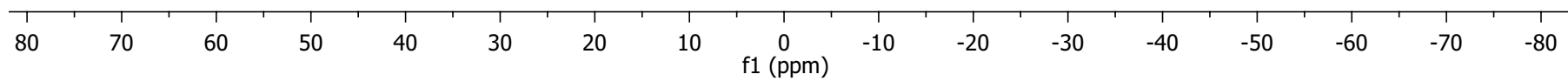
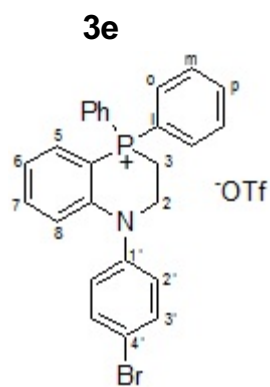






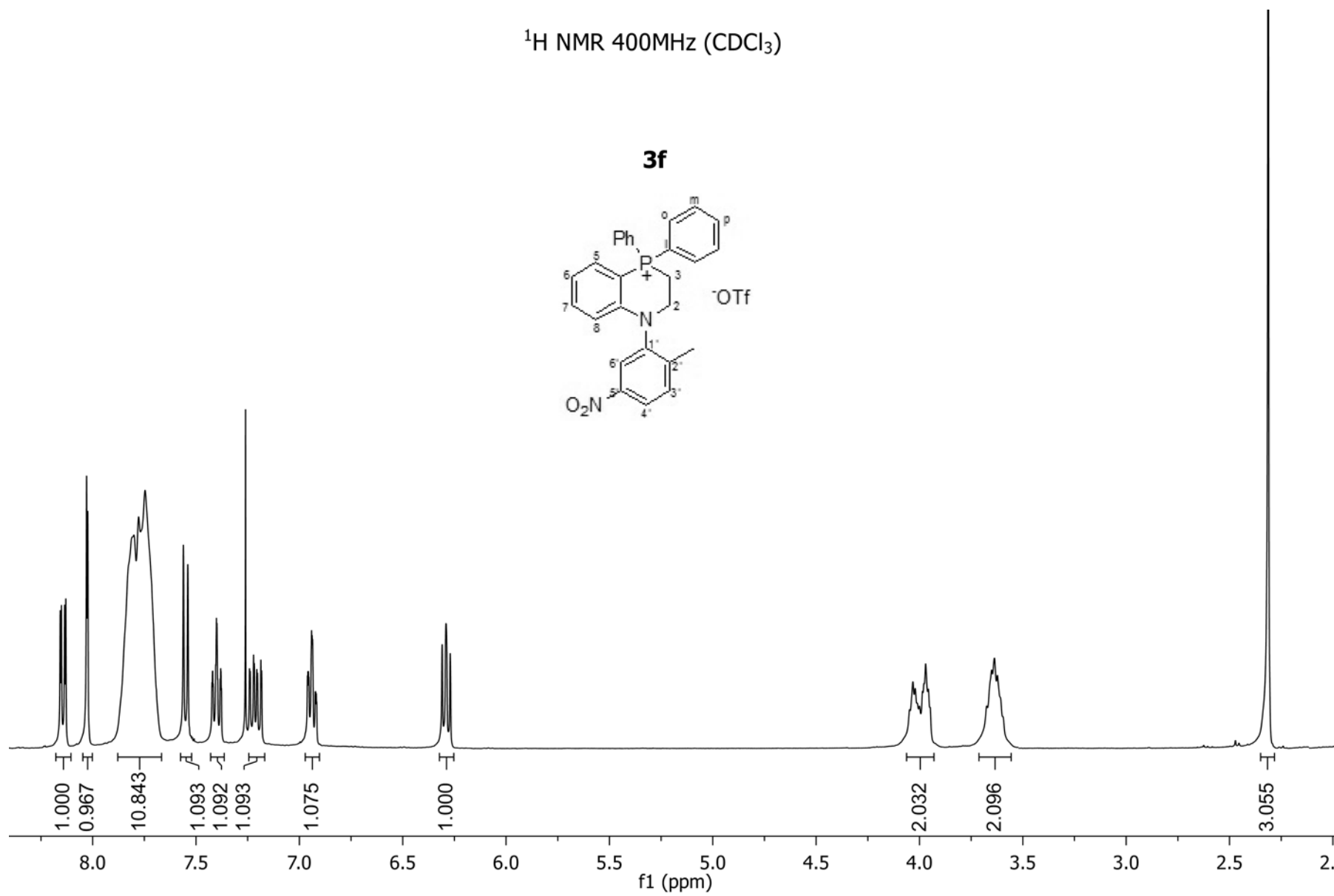
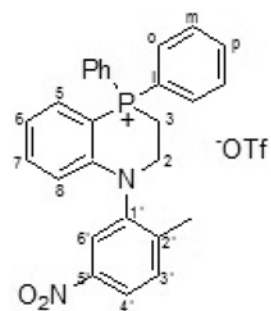
^{31}P NMR 162MHz (CDCl_3)

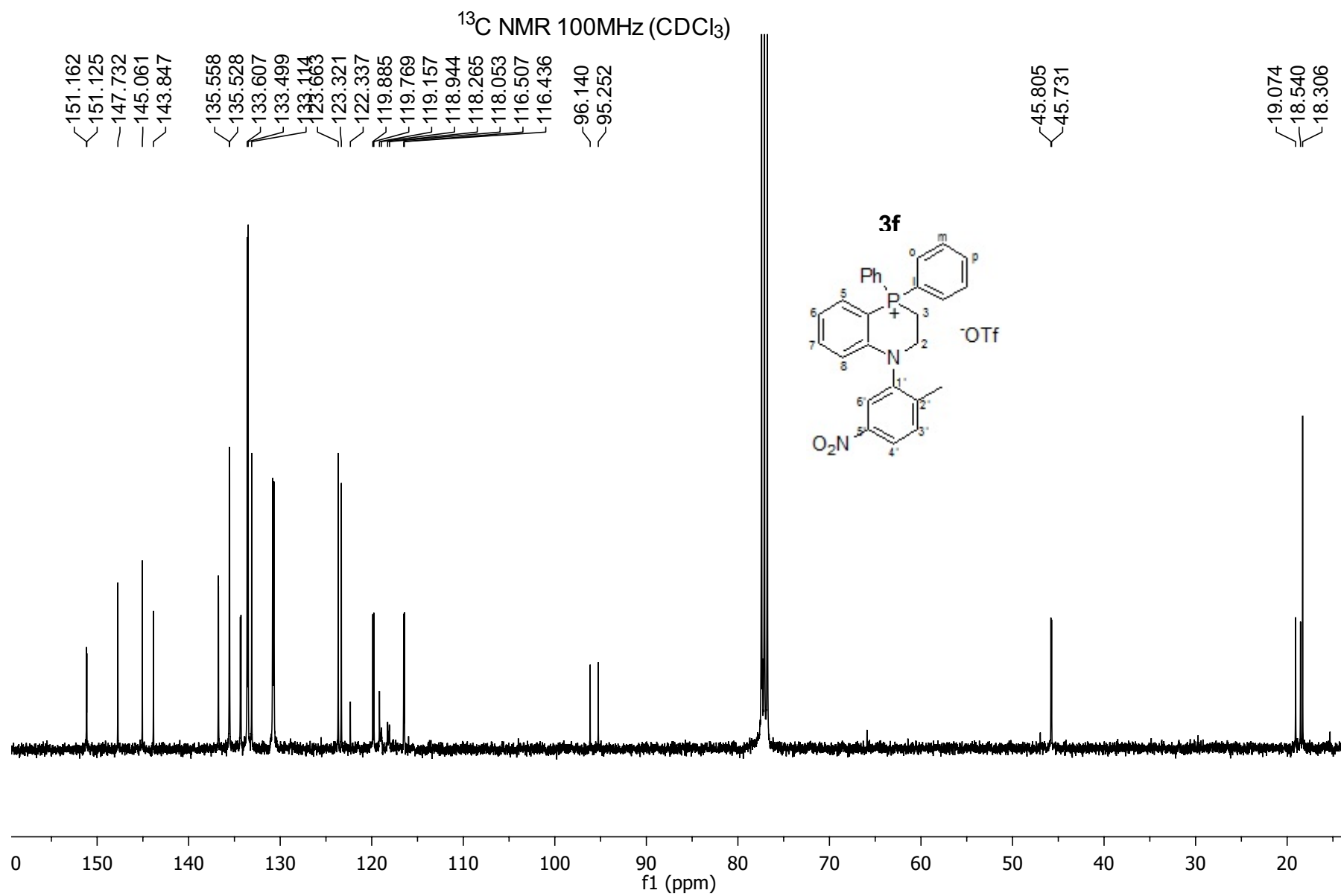
8.492

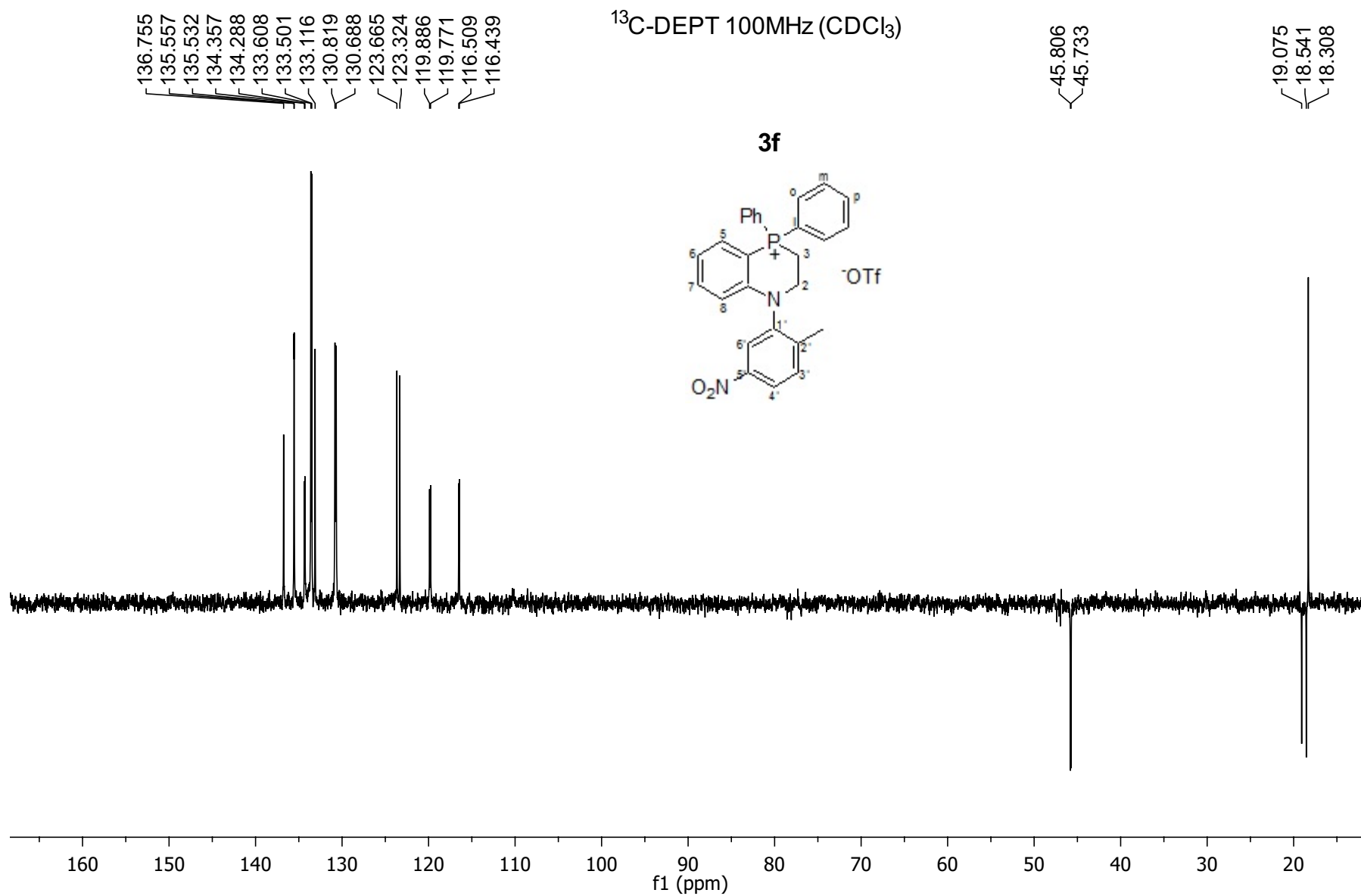


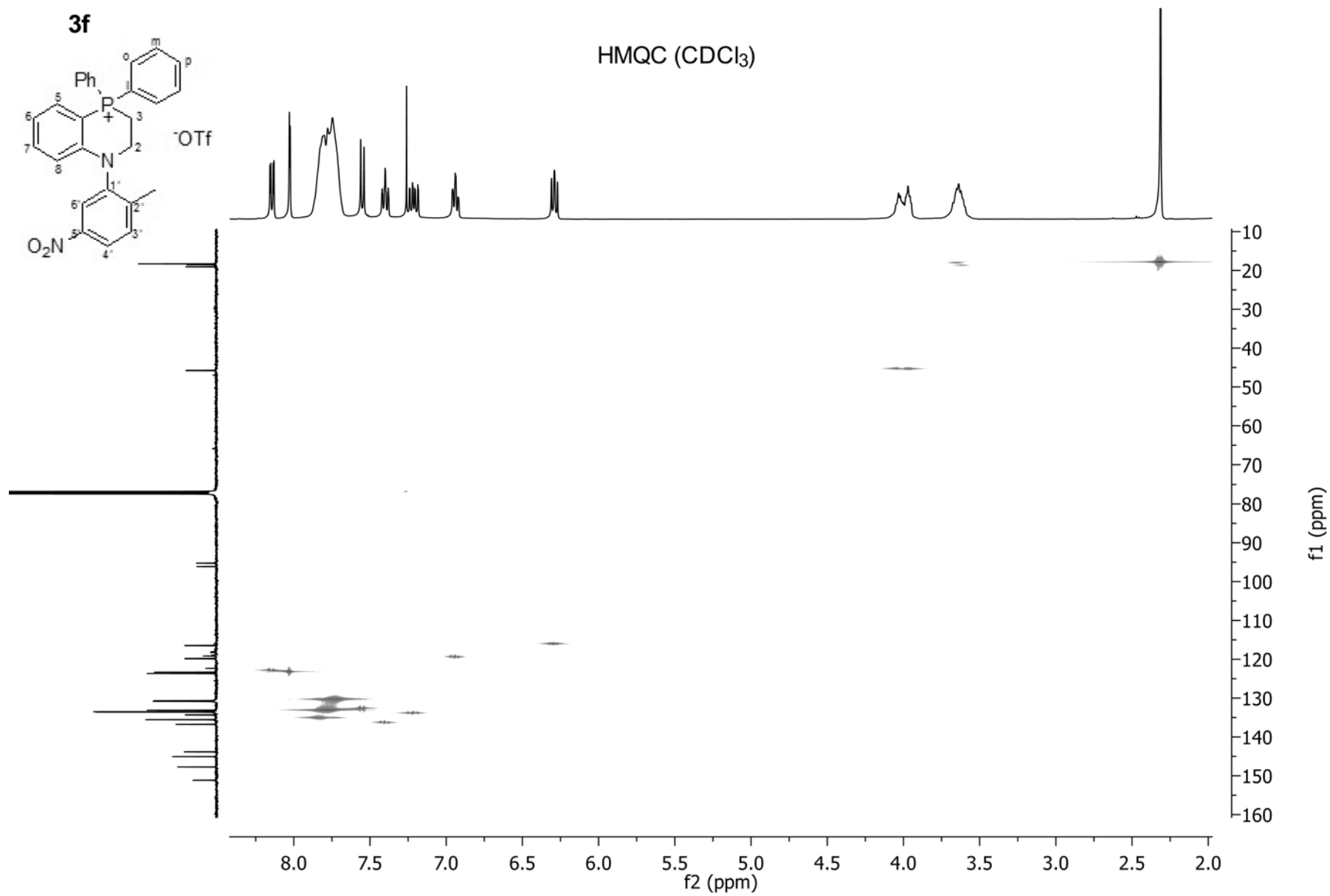
^1H NMR 400MHz (CDCl_3)

3f



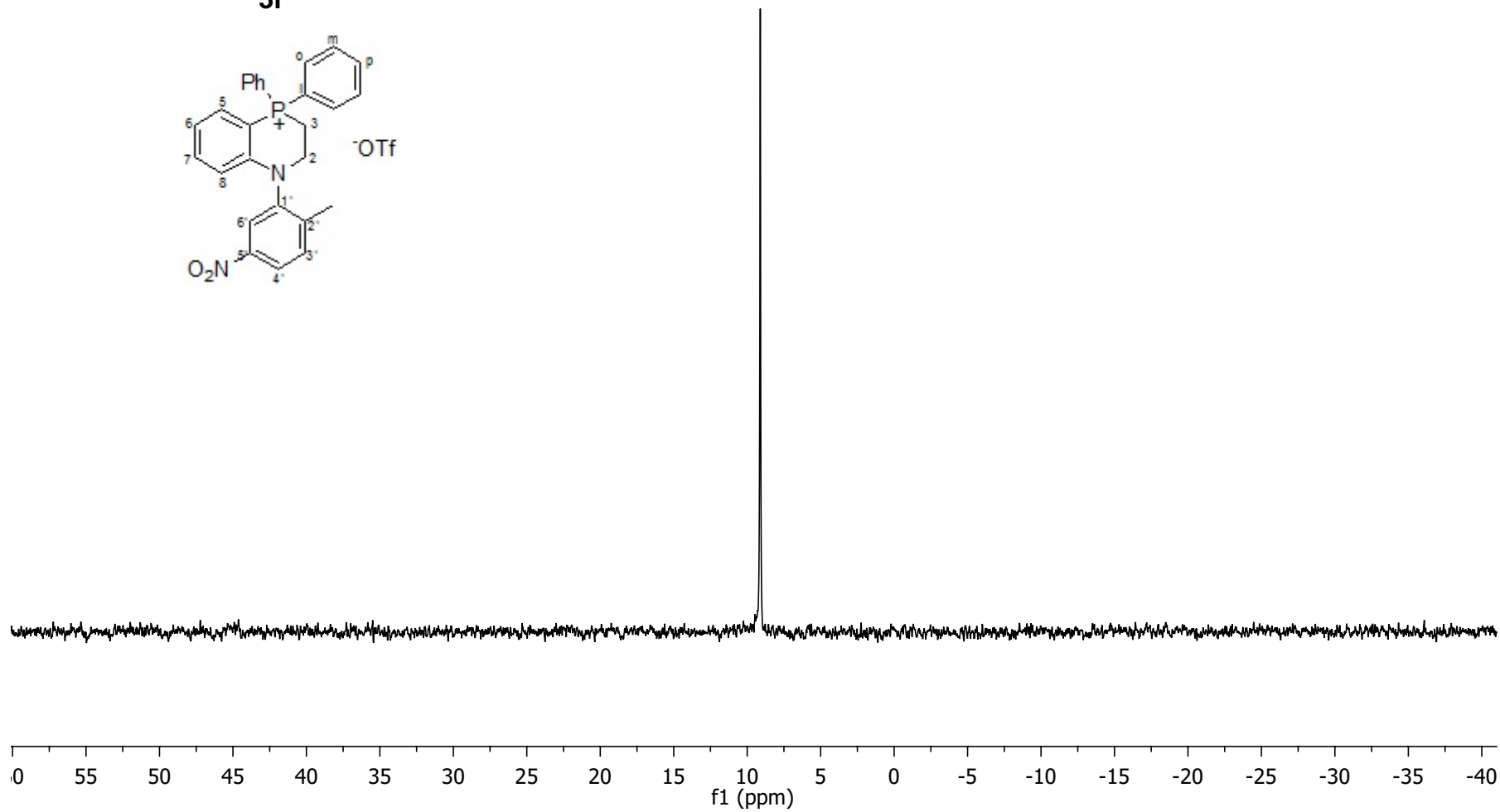
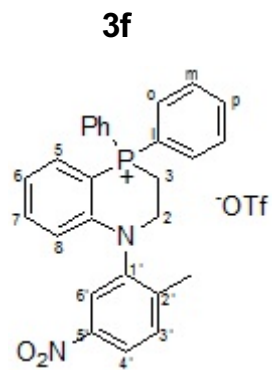






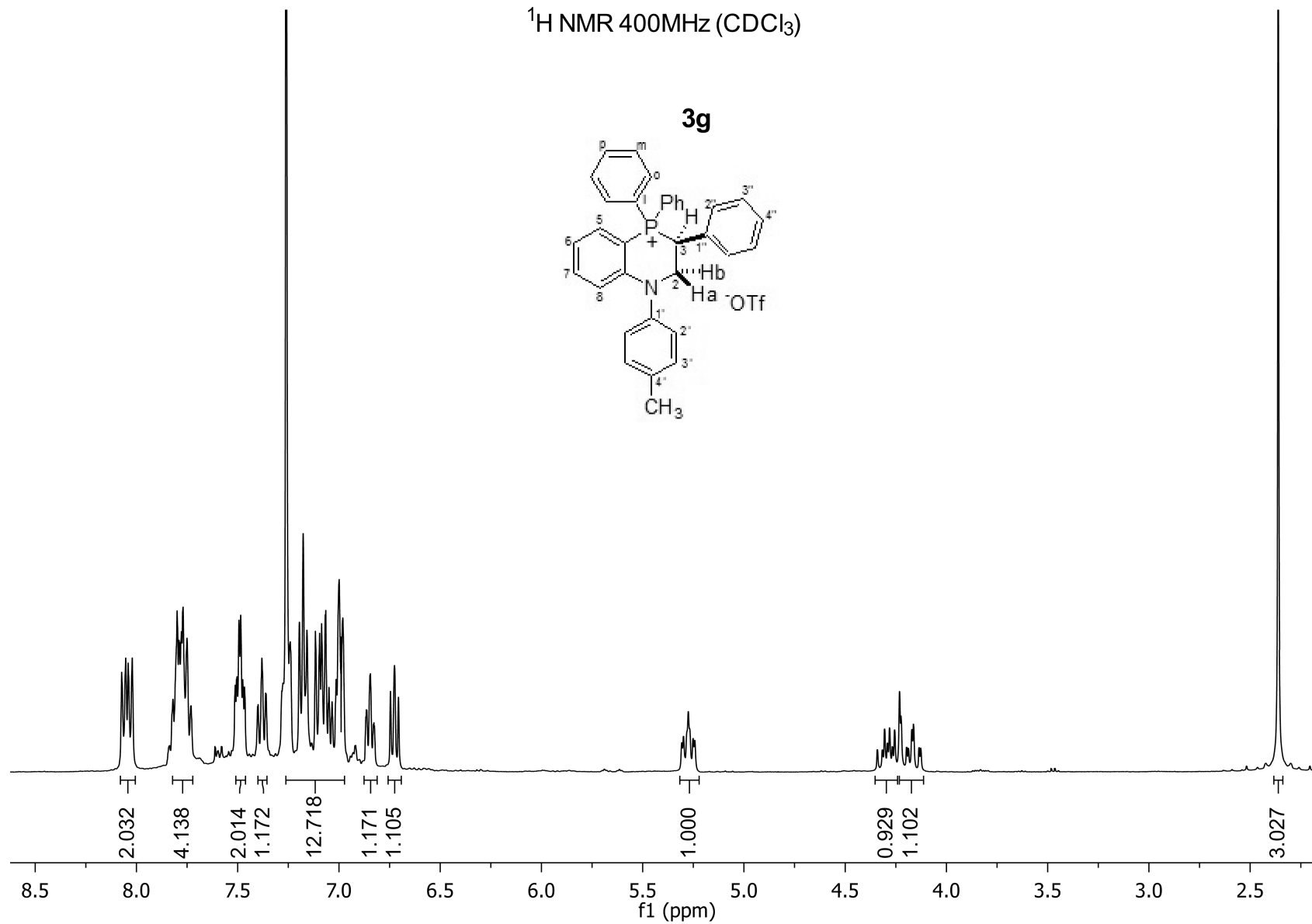
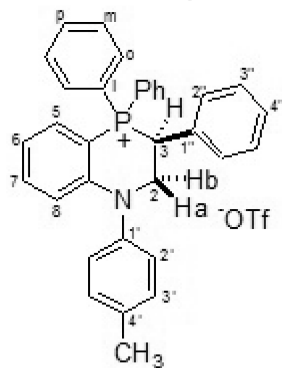
^{31}P NMR 121MHz (CDCl_3)

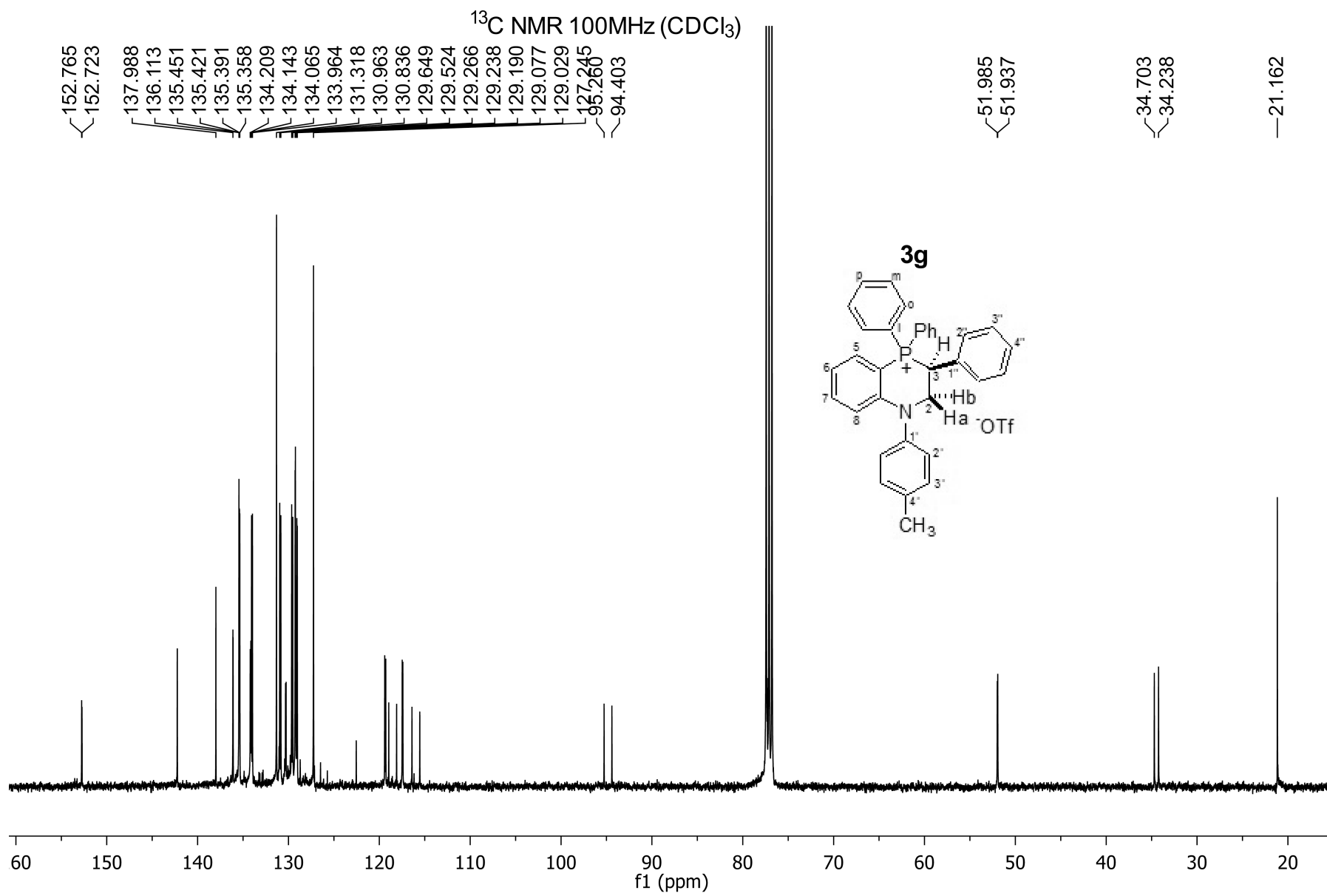
9.106

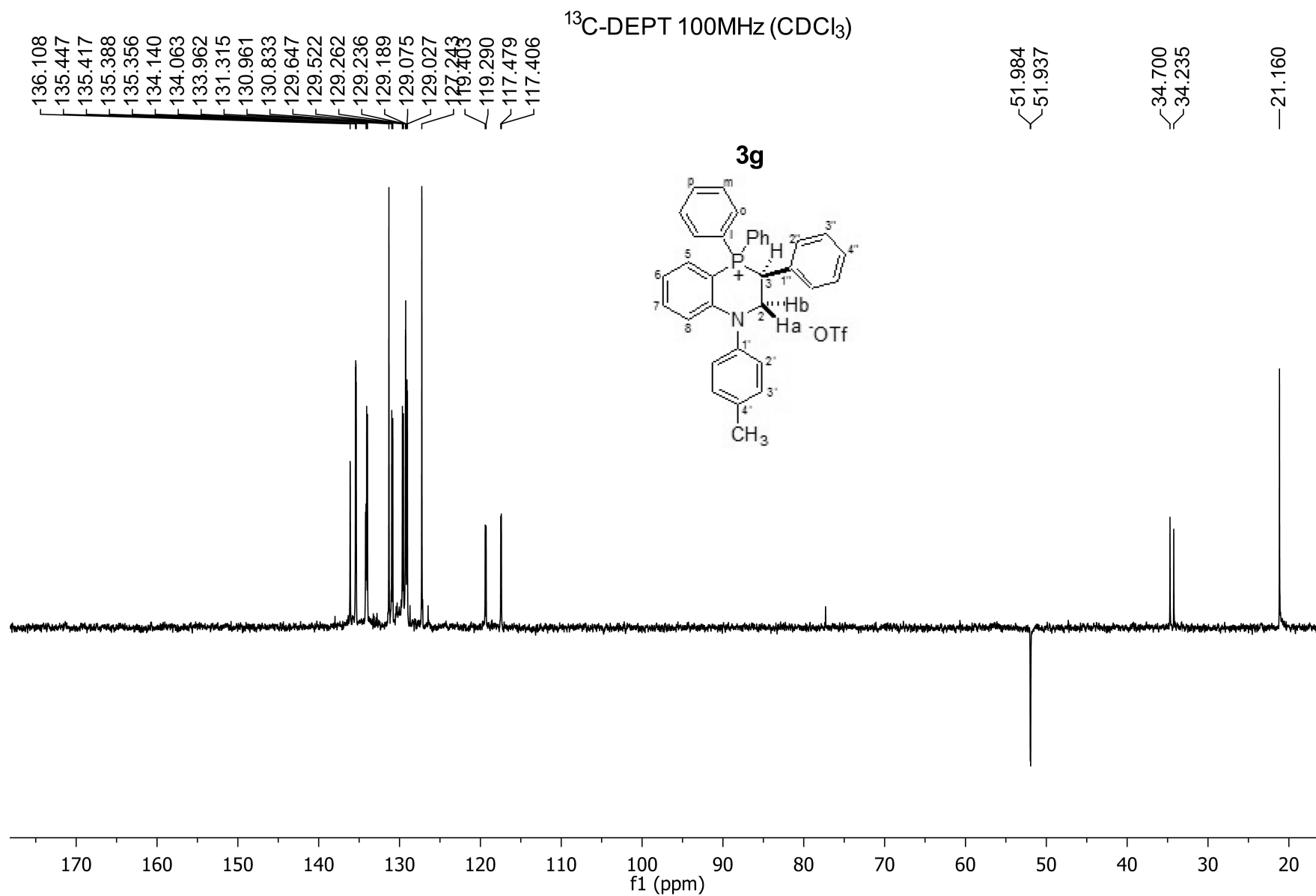


^1H NMR 400MHz (CDCl_3)

3g



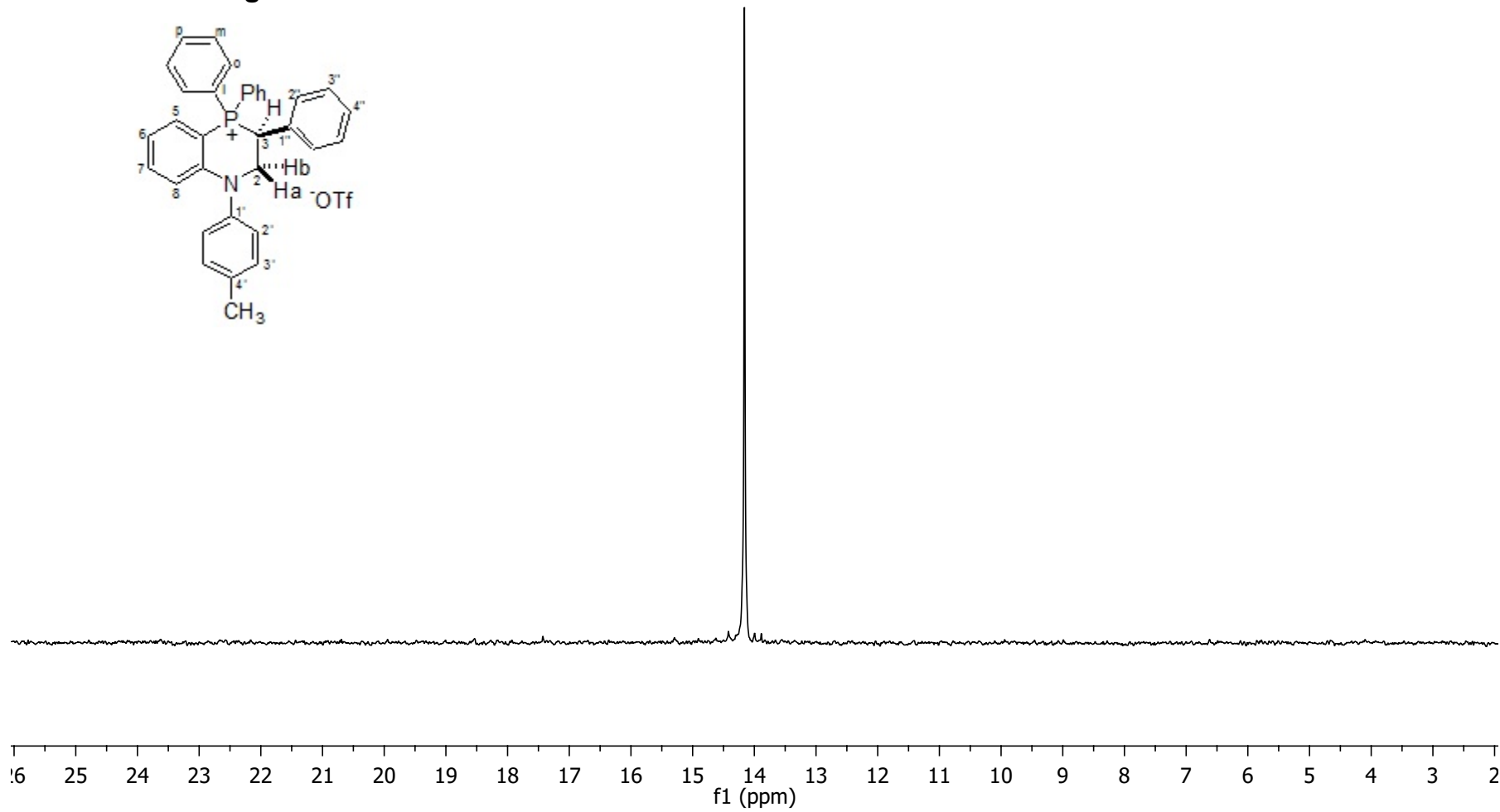
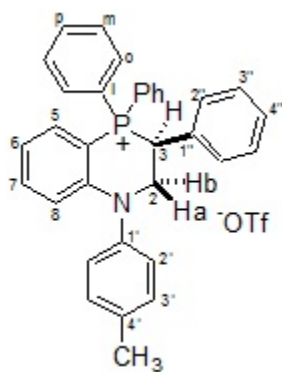




^{31}P NMR 162MHz (CDCl_3)

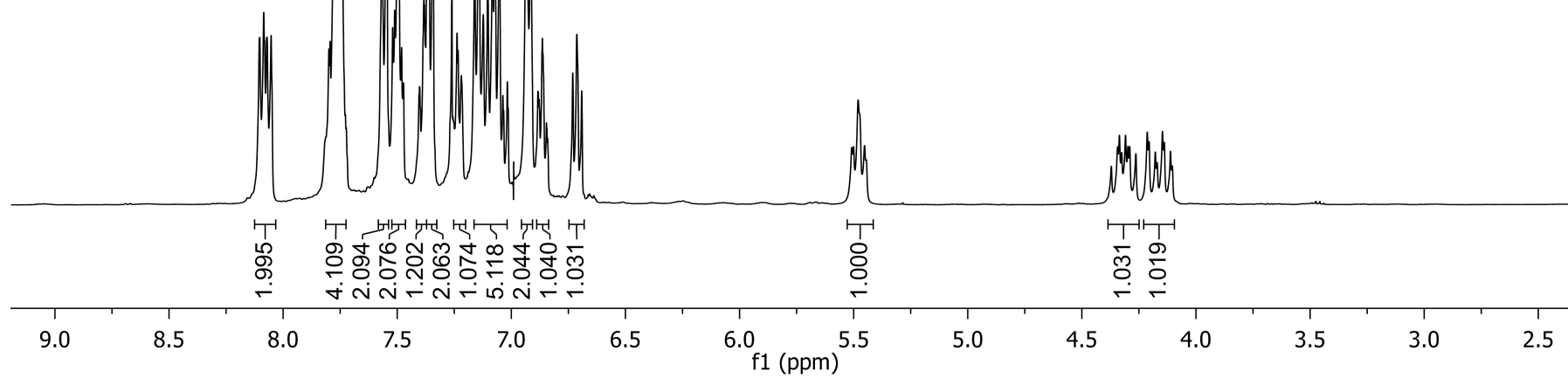
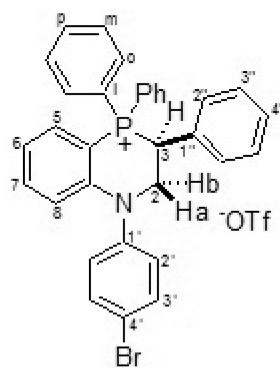
—14.161

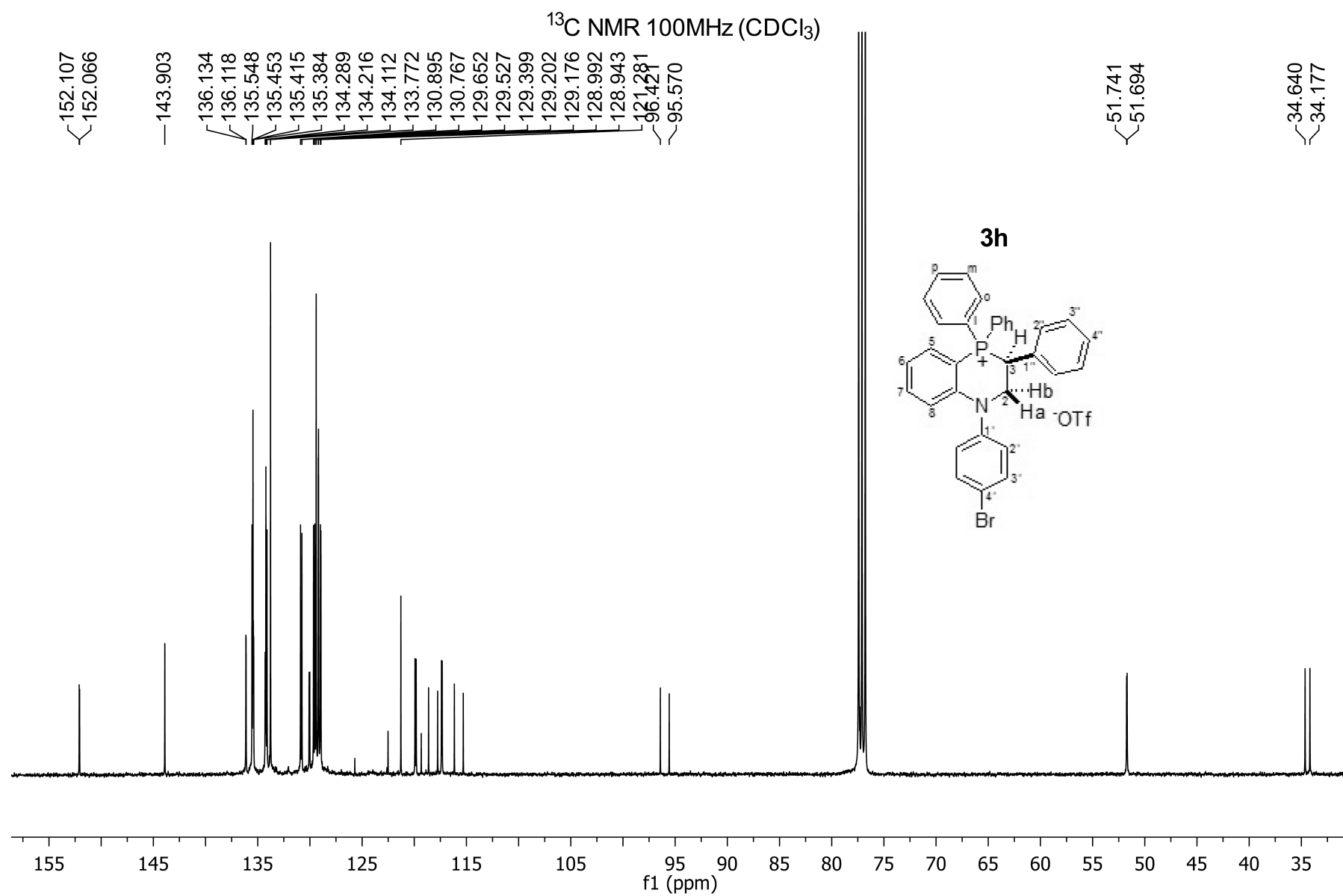
3g

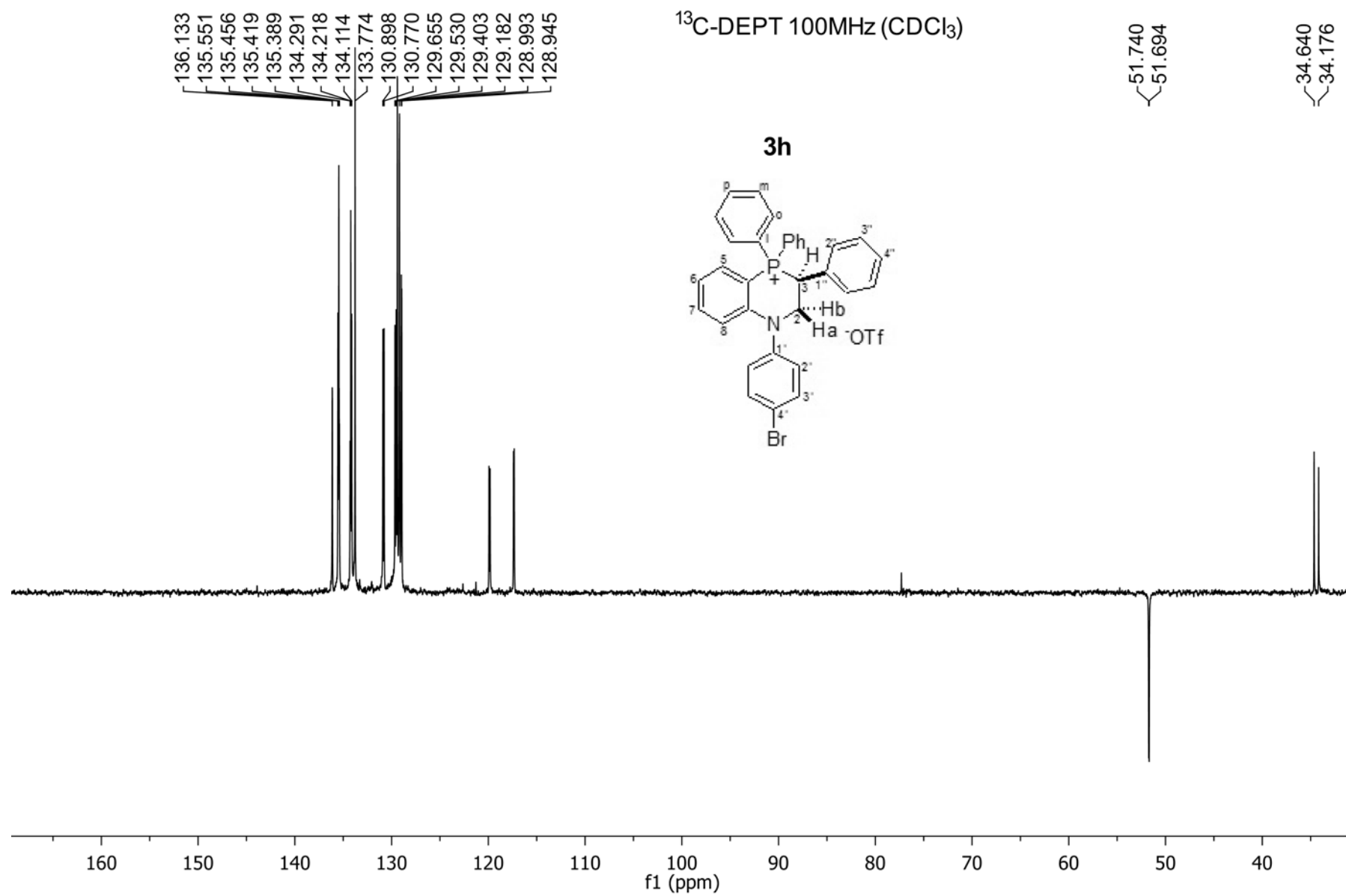


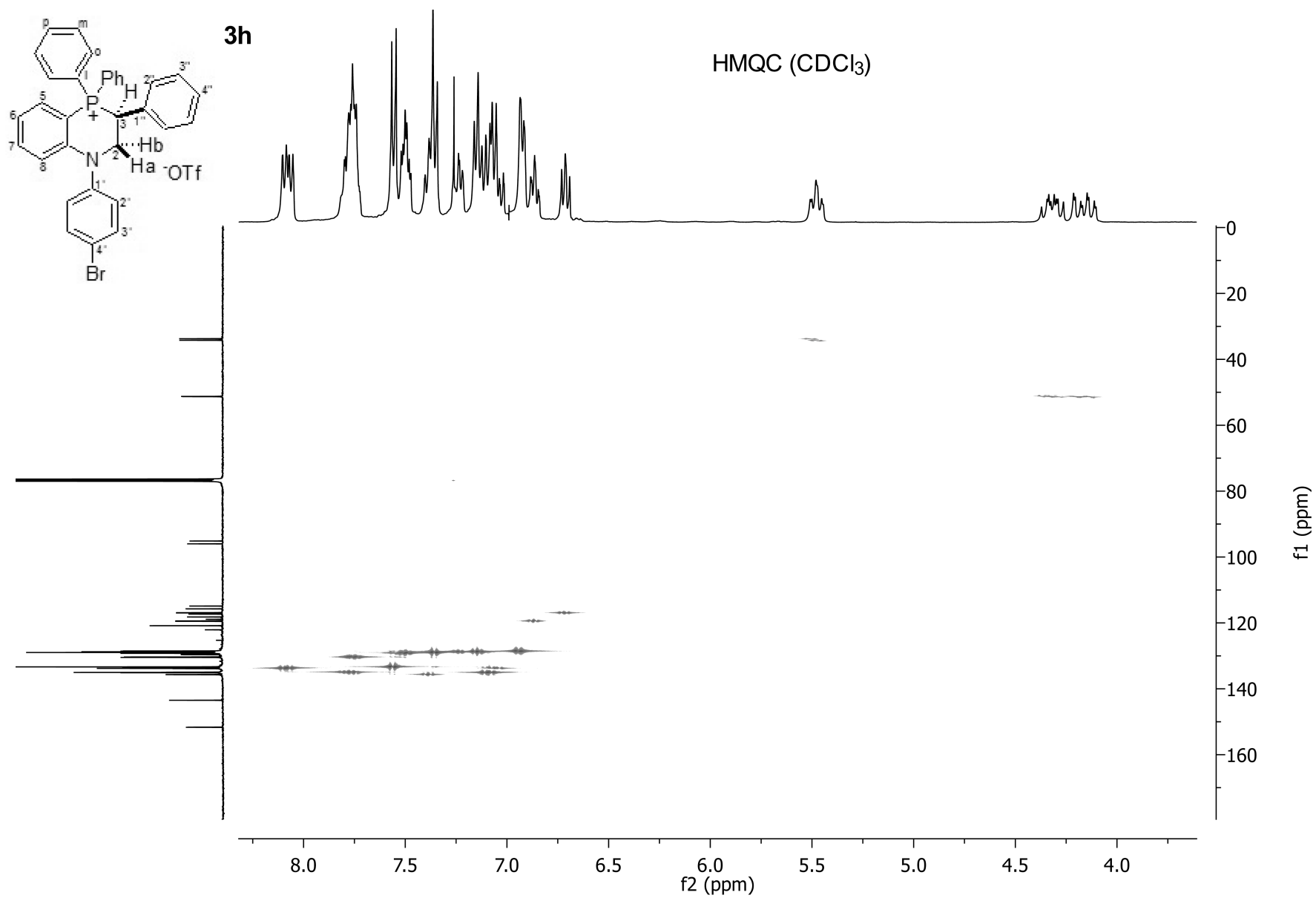
^1H NMR 400MHz (CDCl₃)

3h

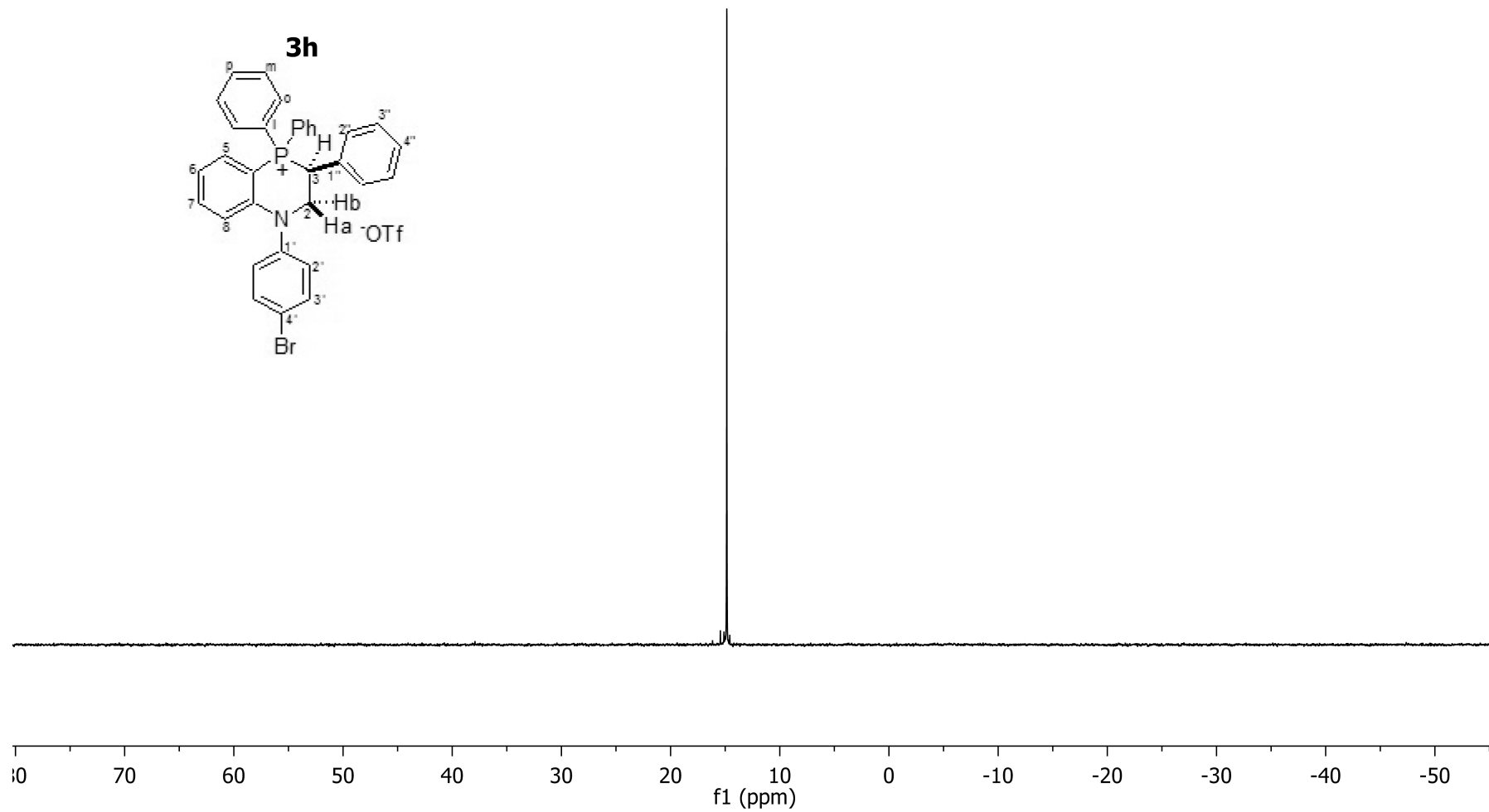
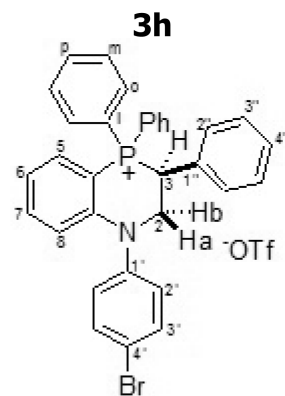




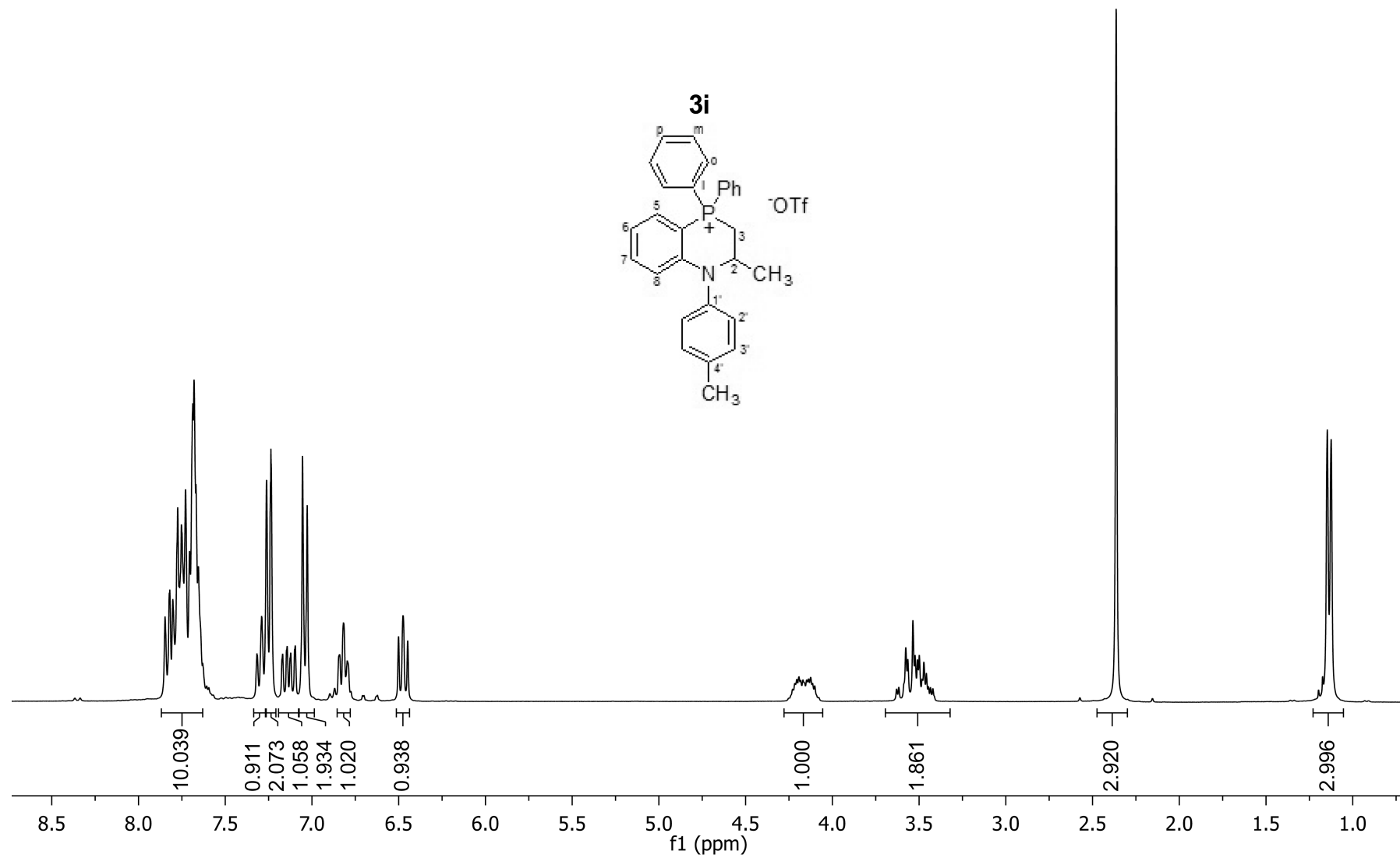


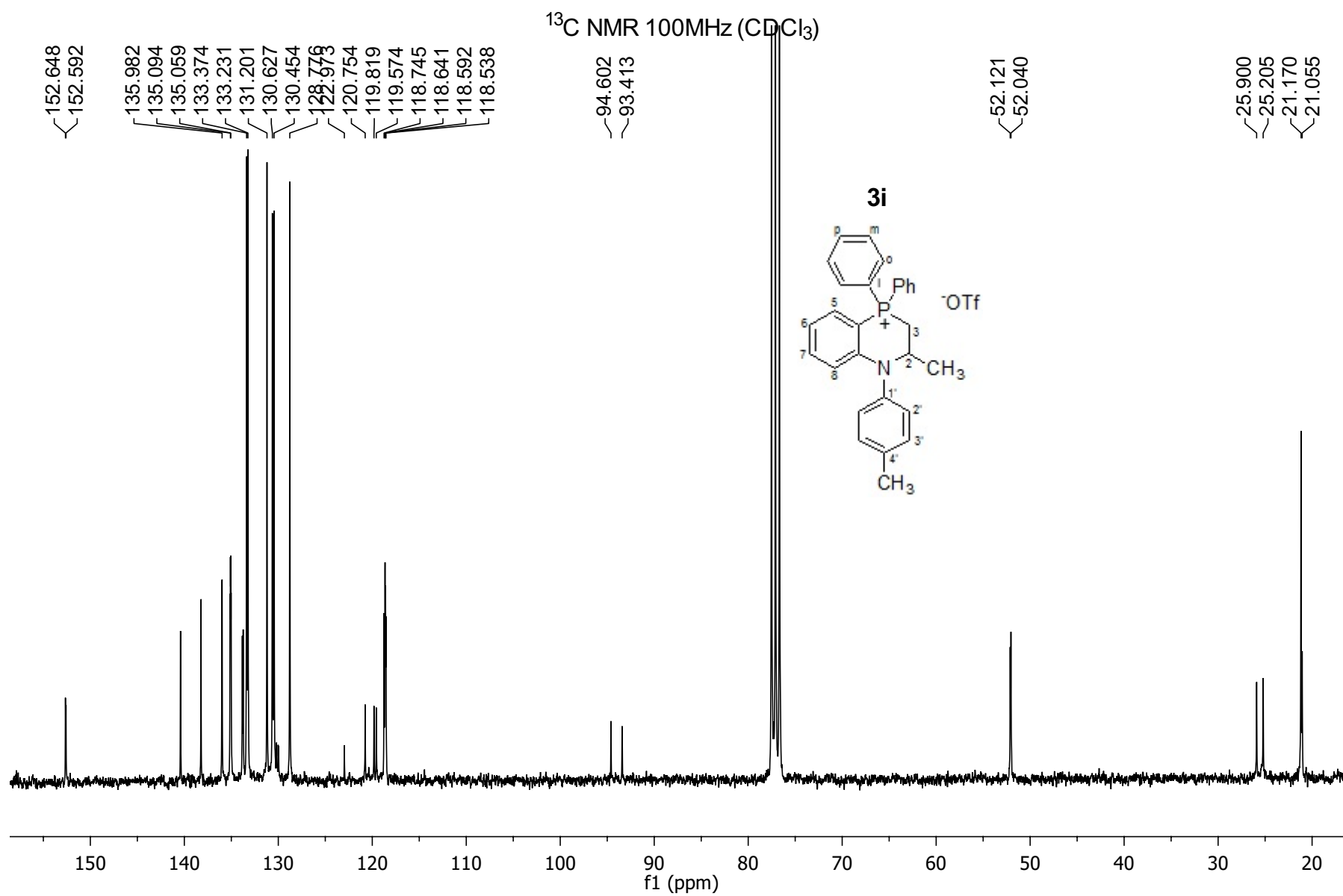


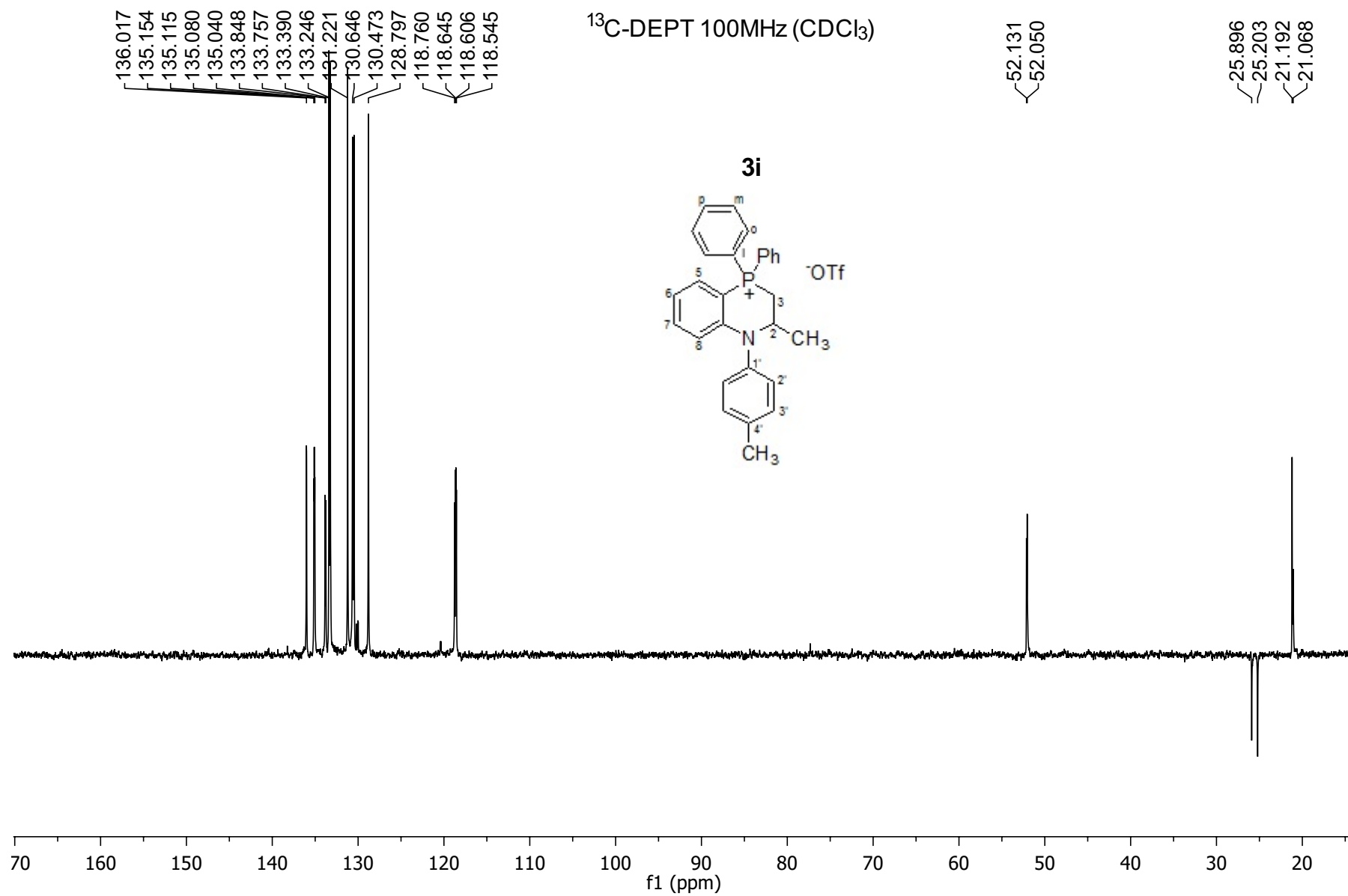
—14.851



^1H NMR 400MHz (CDCl_3)



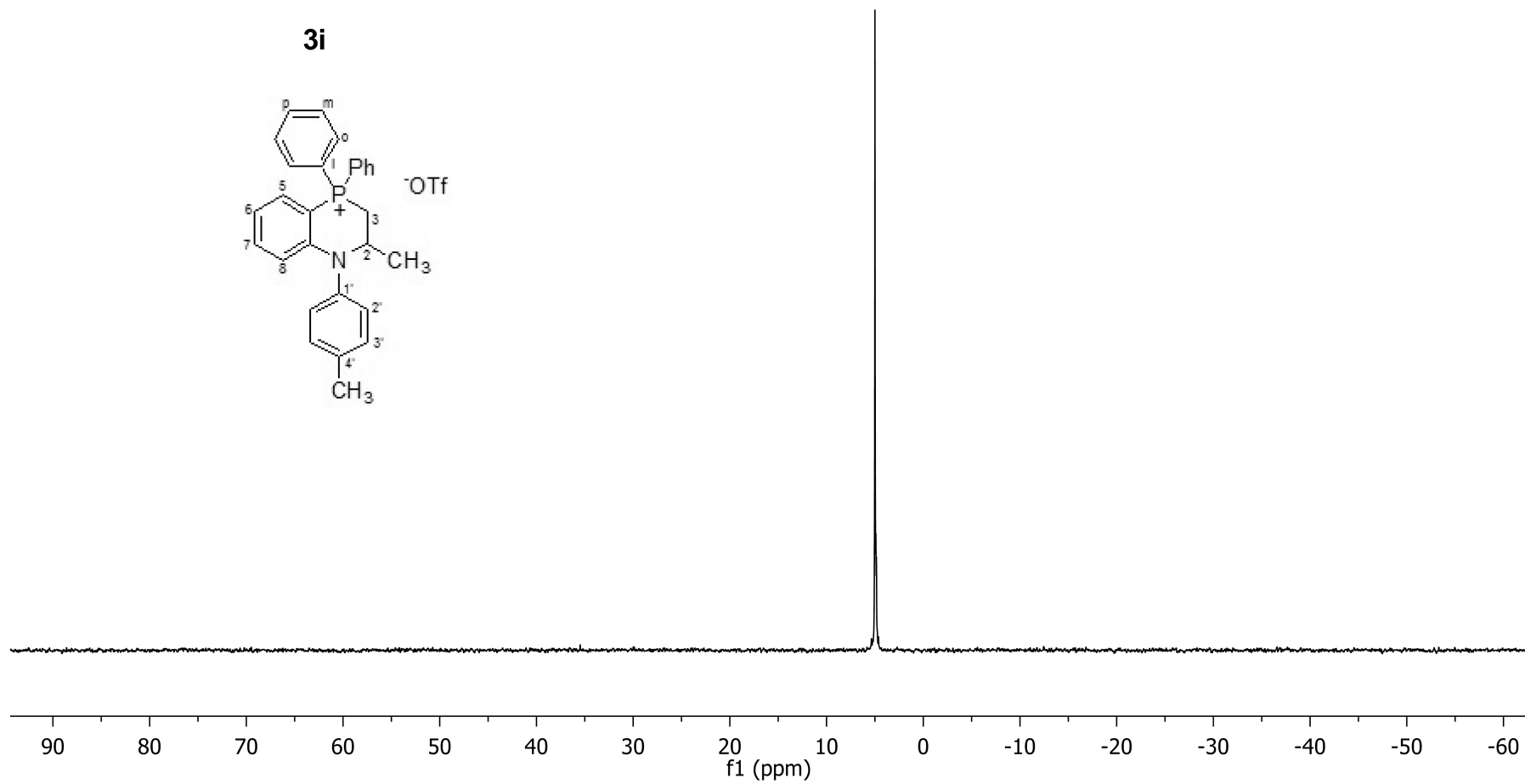
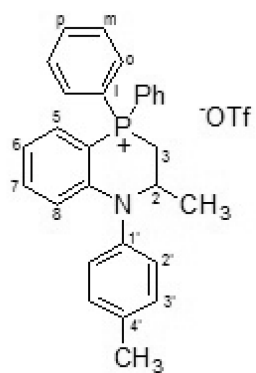


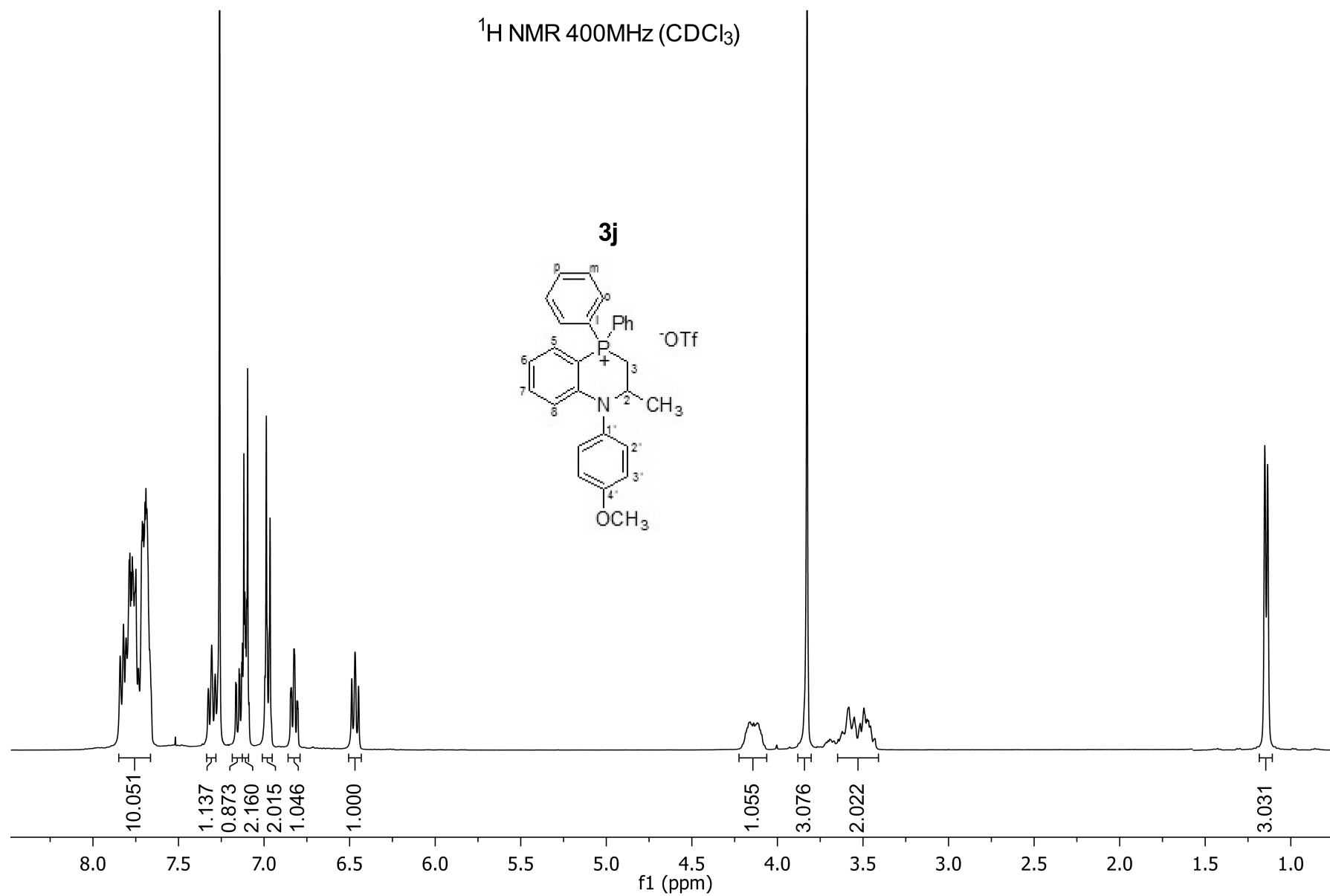


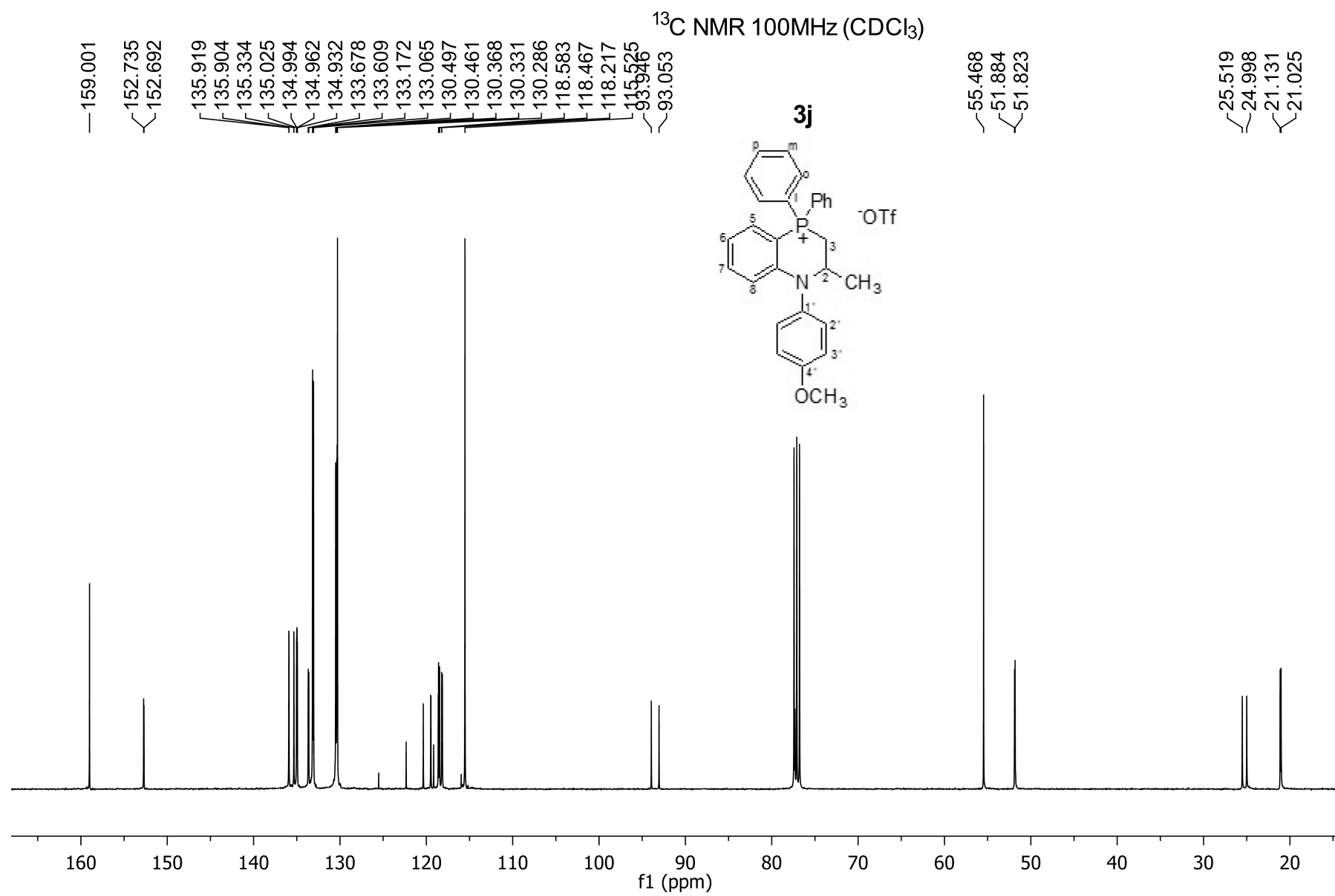
^{31}P NMR 121MHz (CDCl_3)

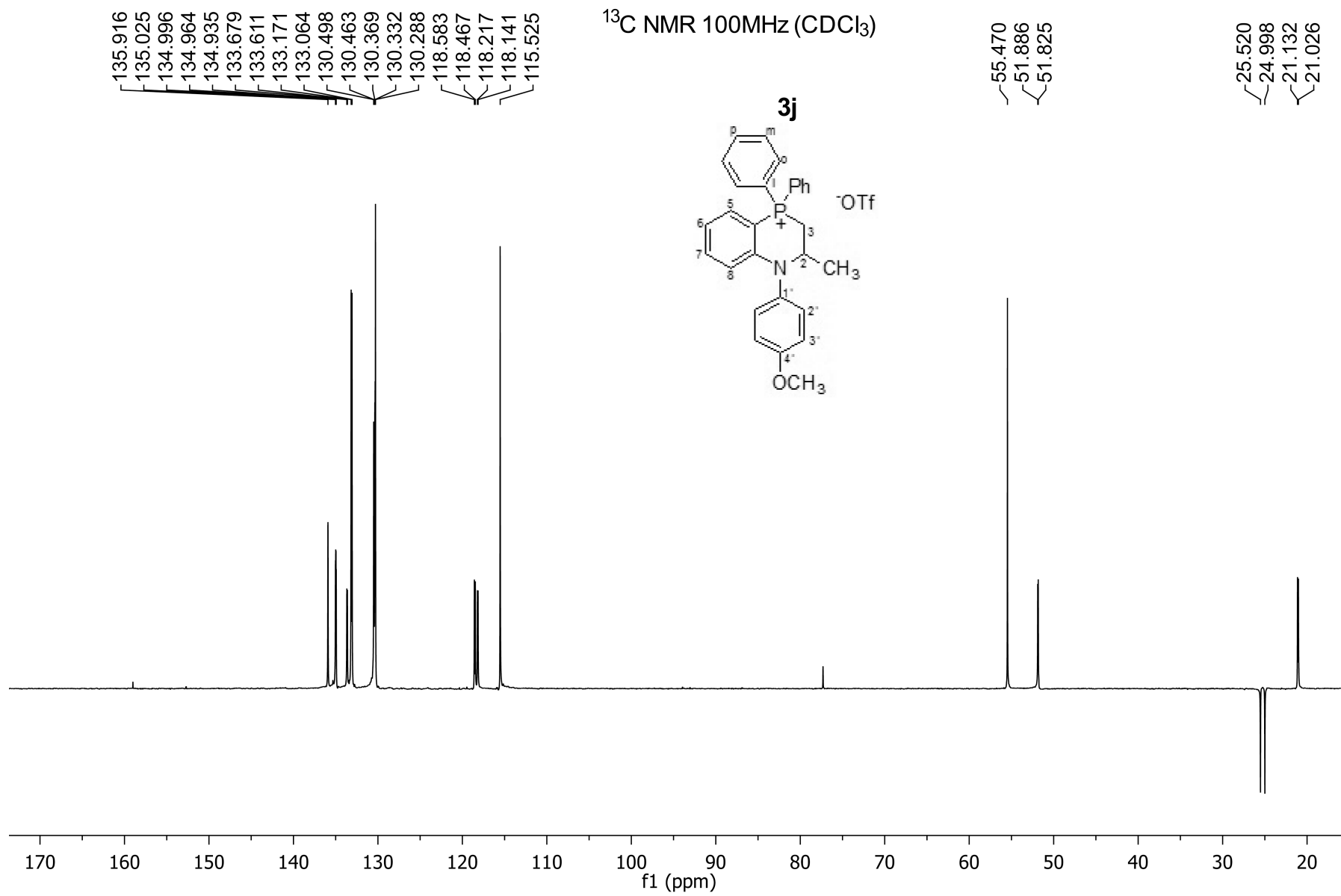
—4.996

3i

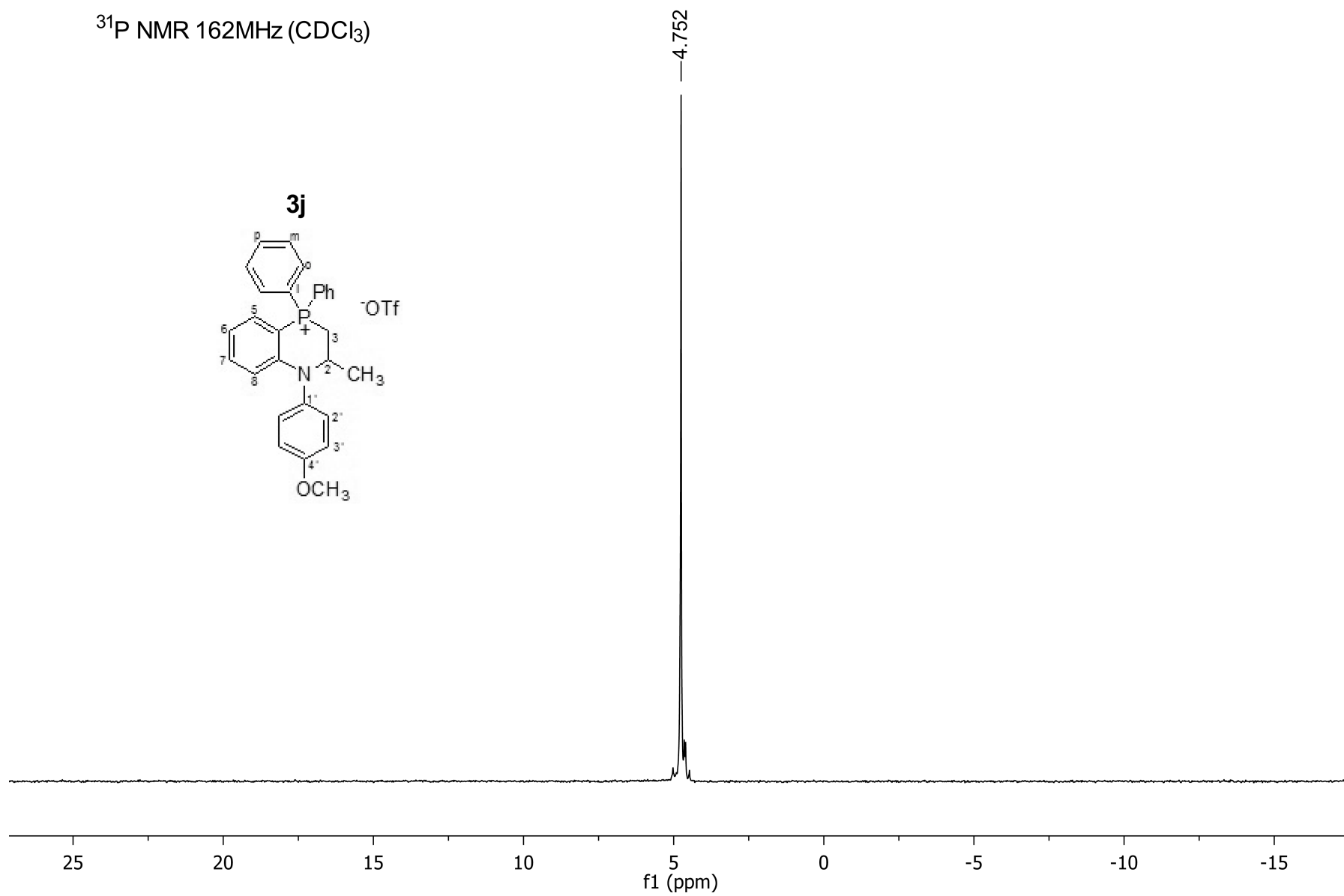
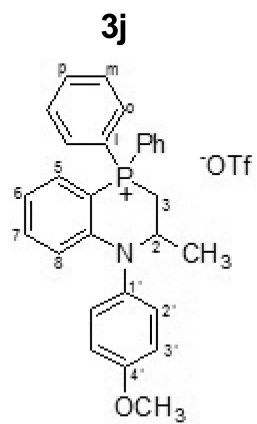




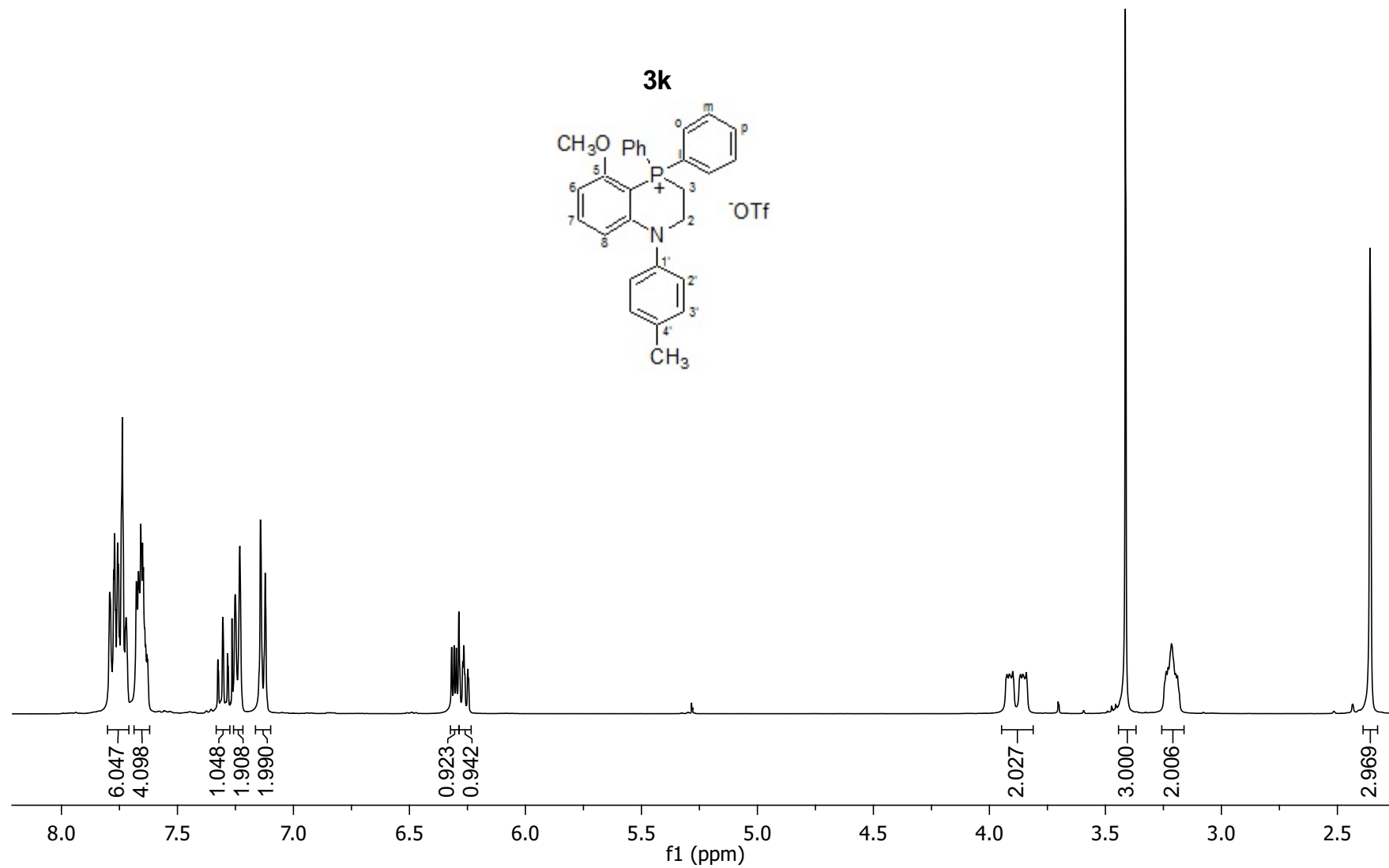
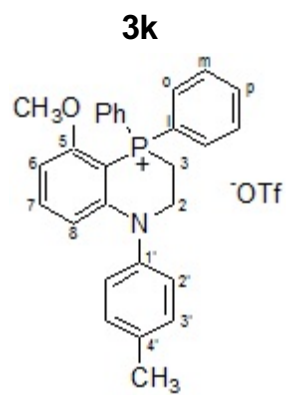


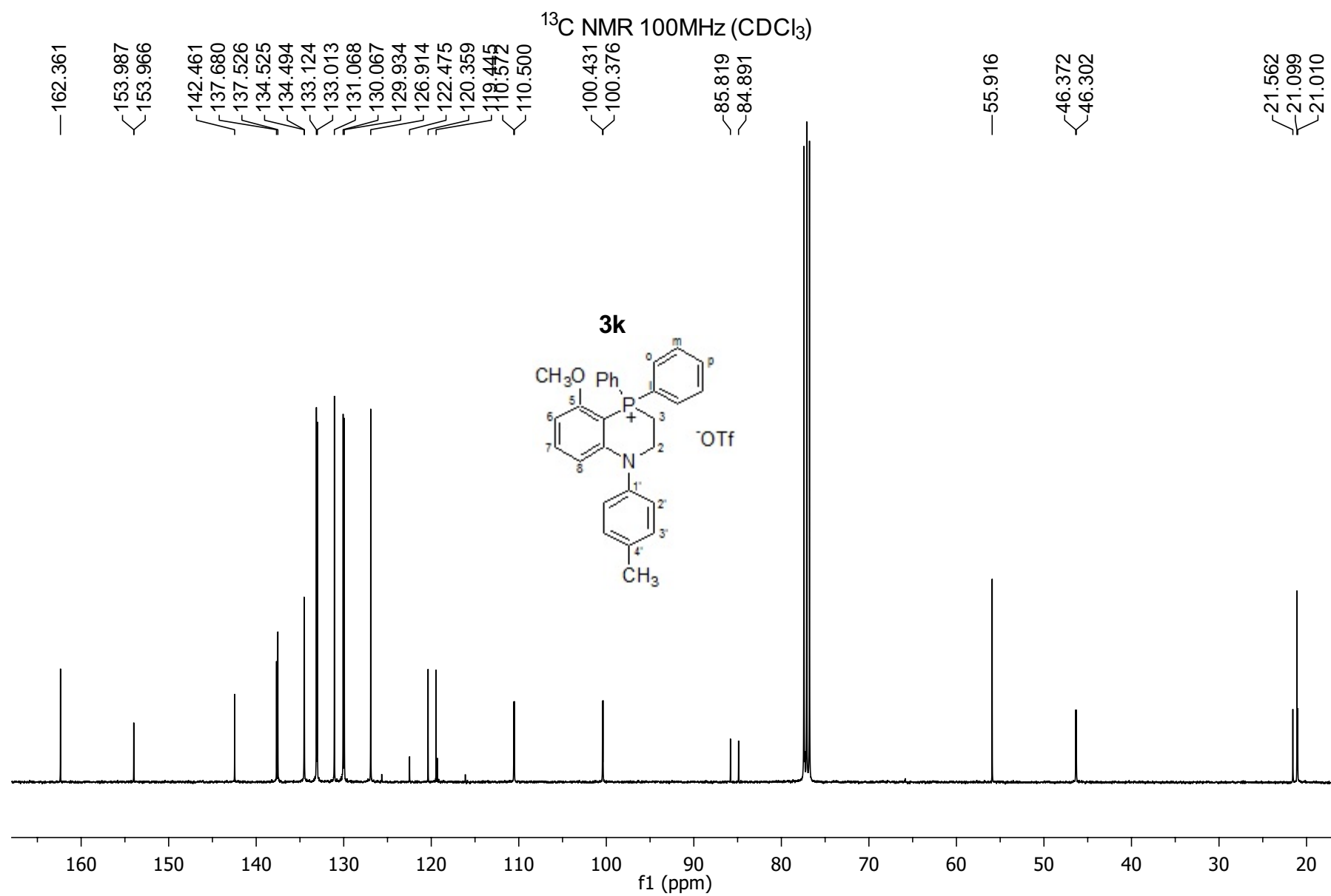


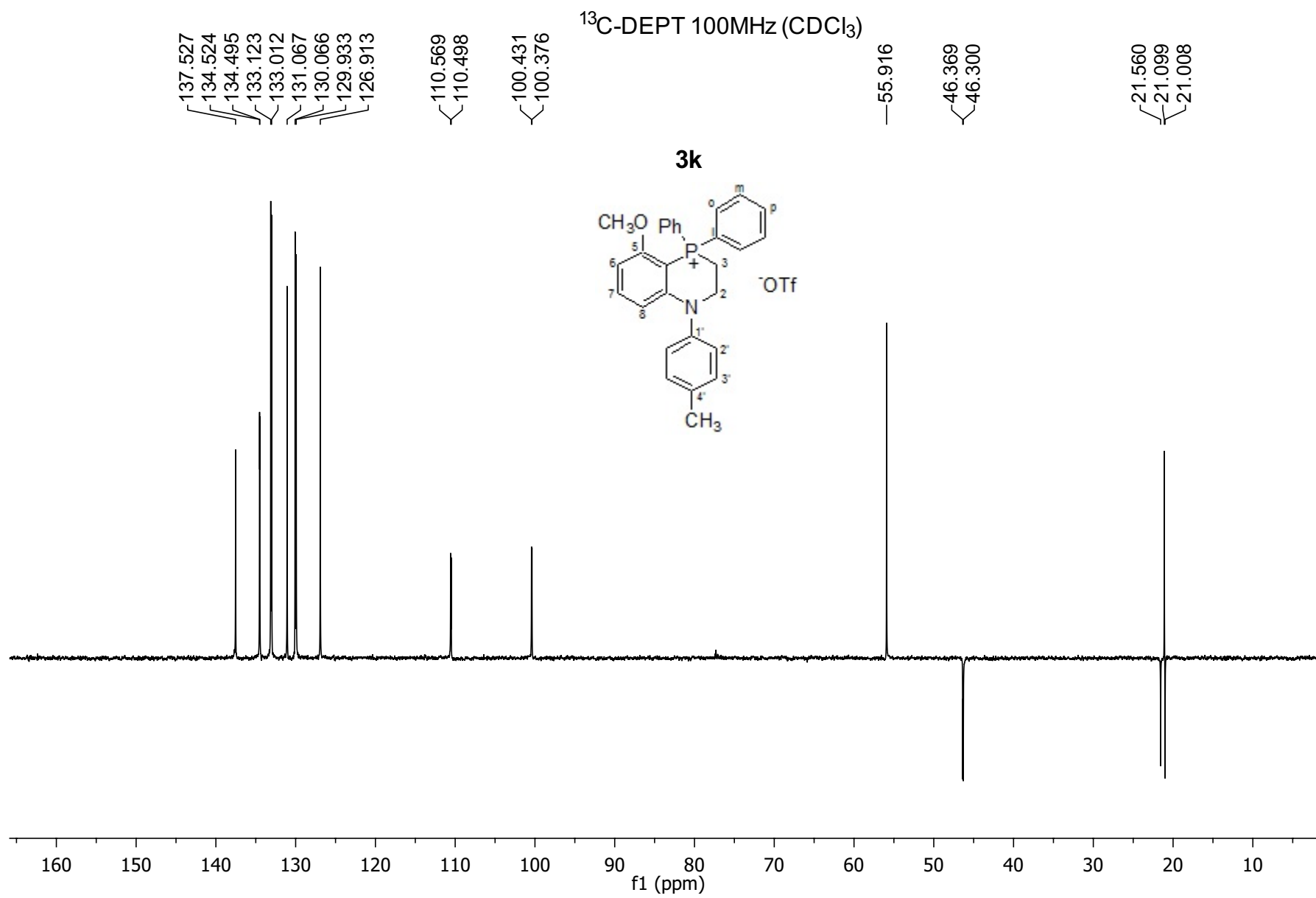
^{31}P NMR 162MHz (CDCl_3)

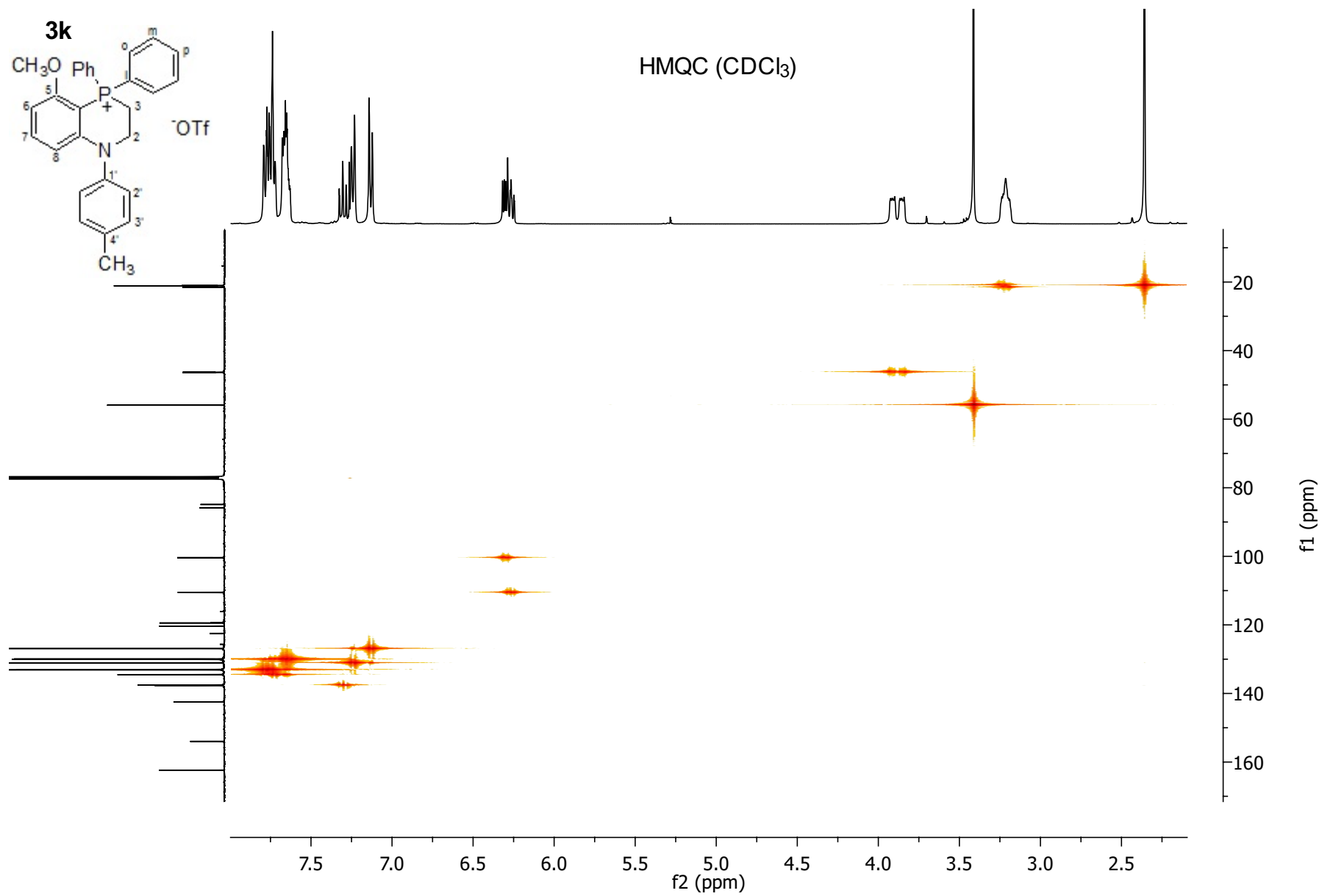


^1H NMR 400MHz (CDCl_3)





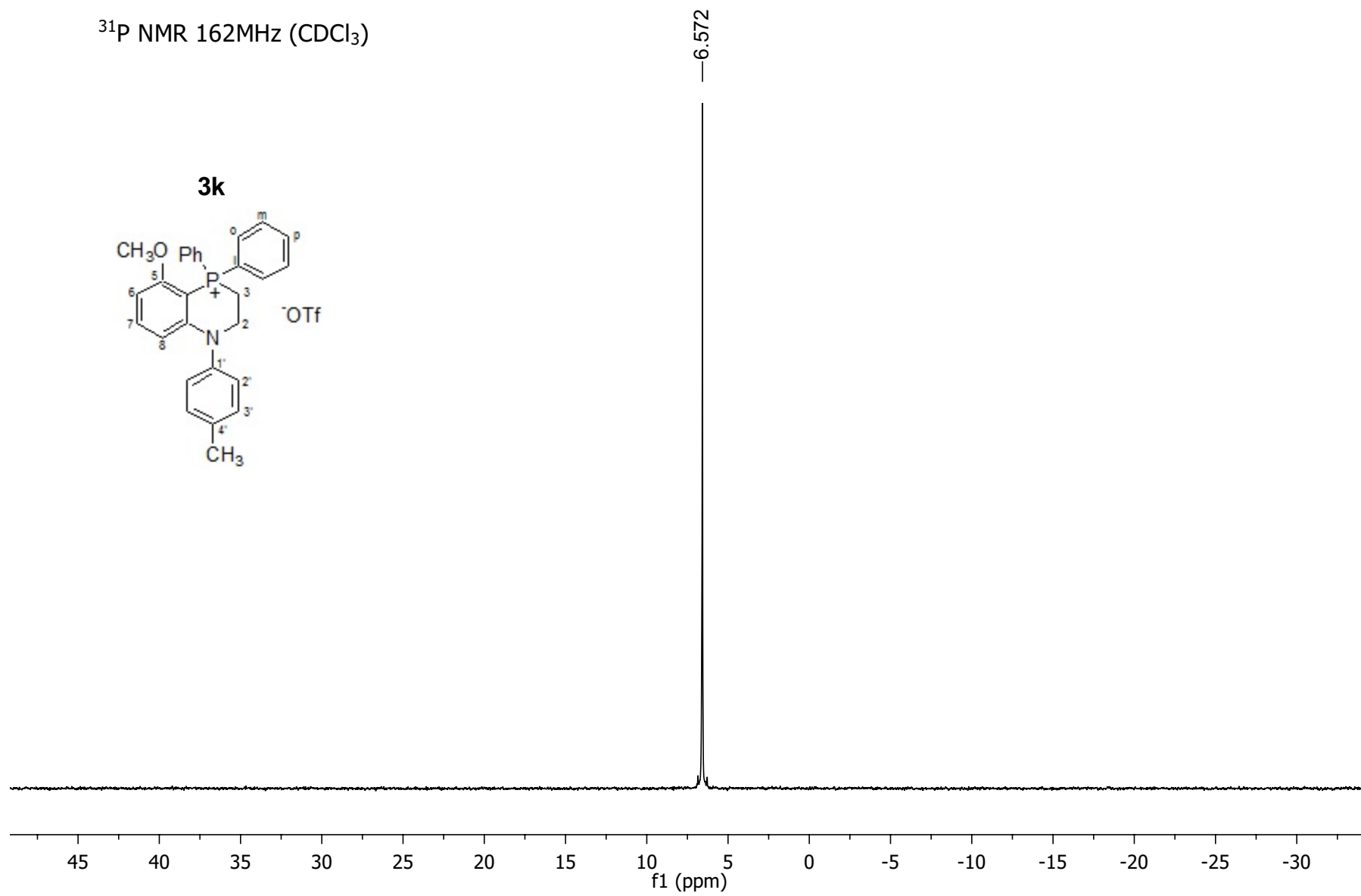
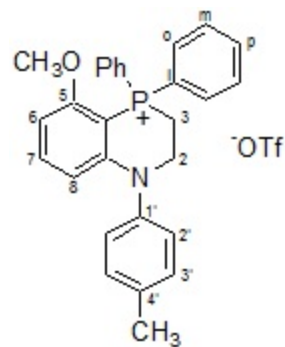


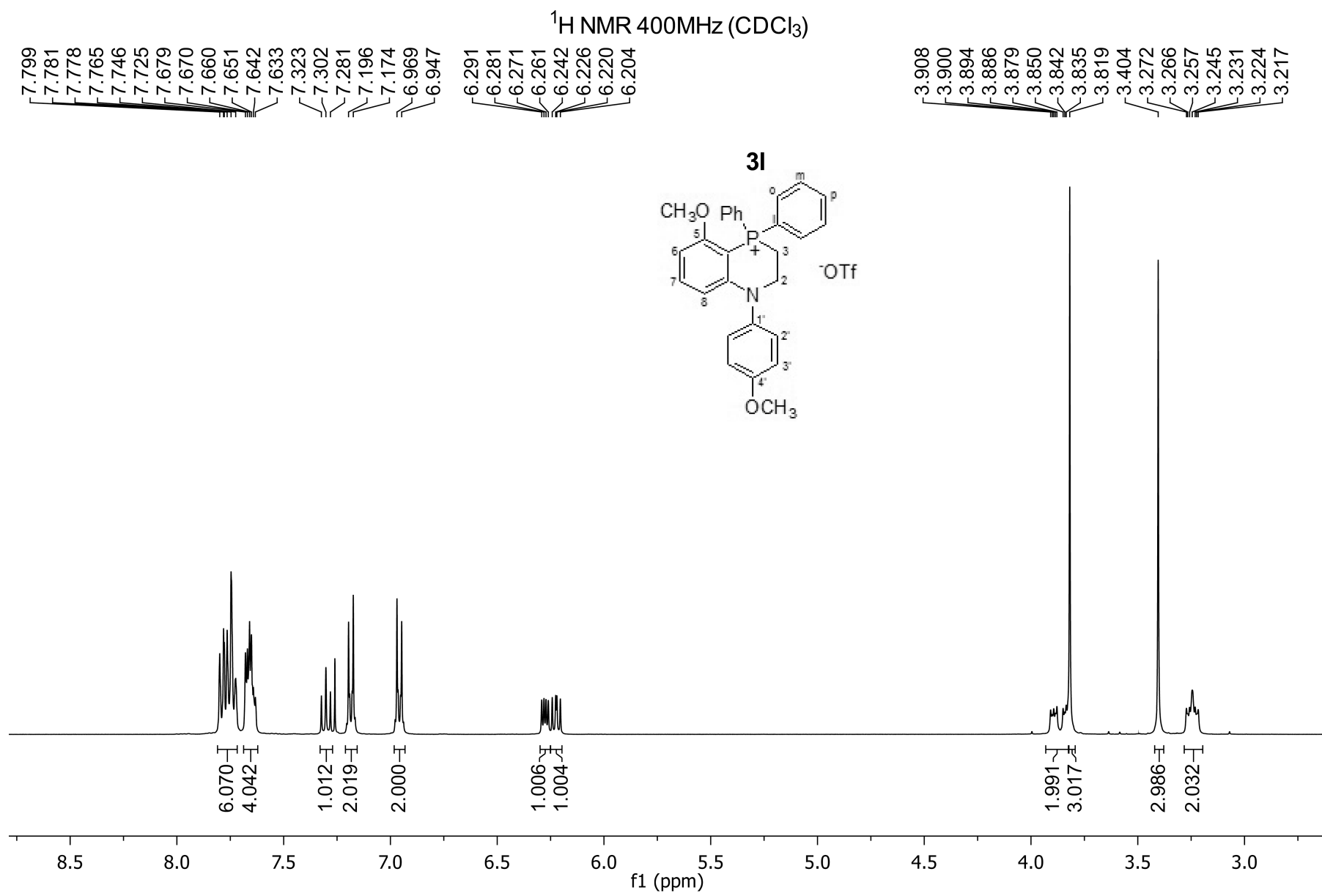


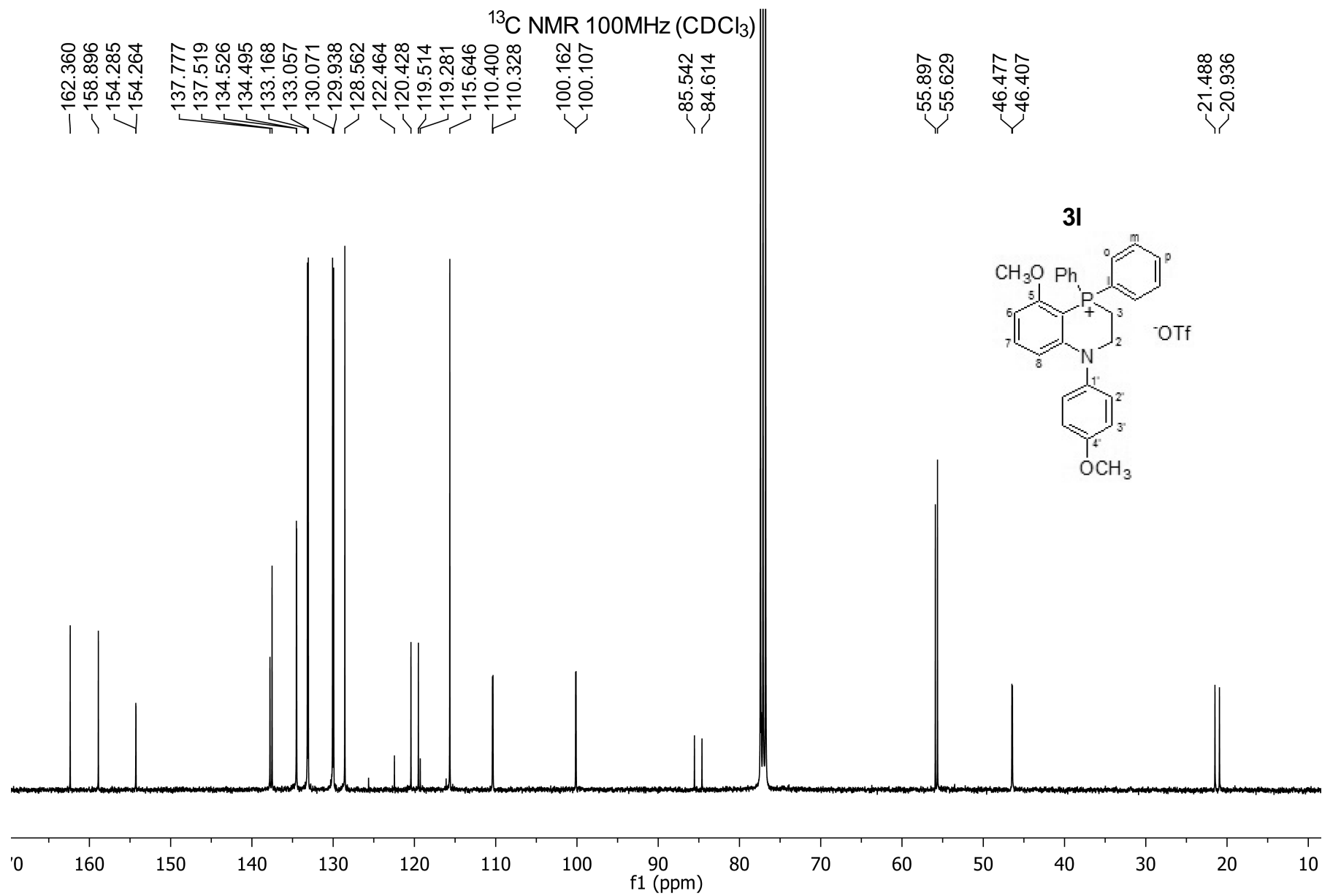
^{31}P NMR 162MHz (CDCl_3)

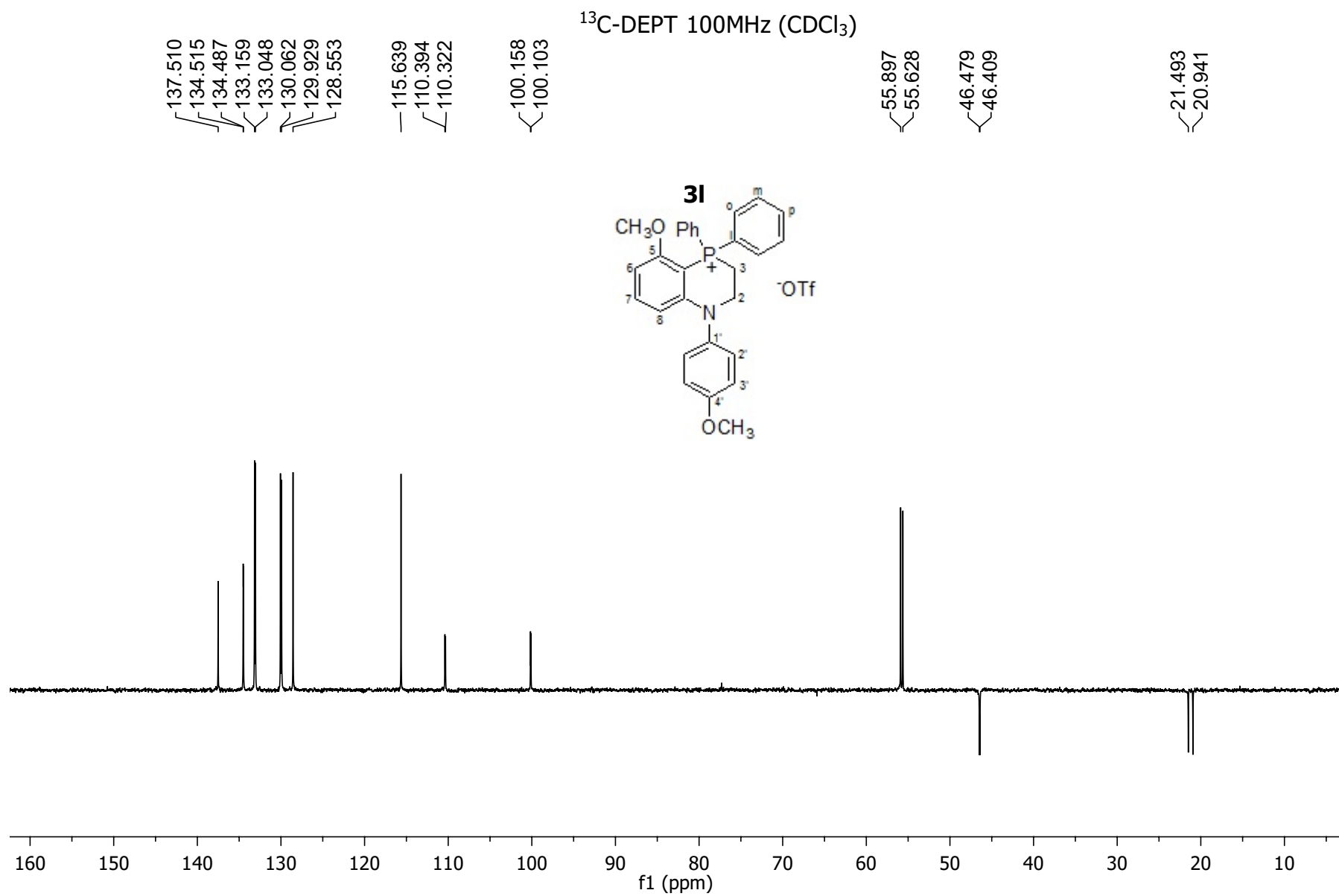
6.572

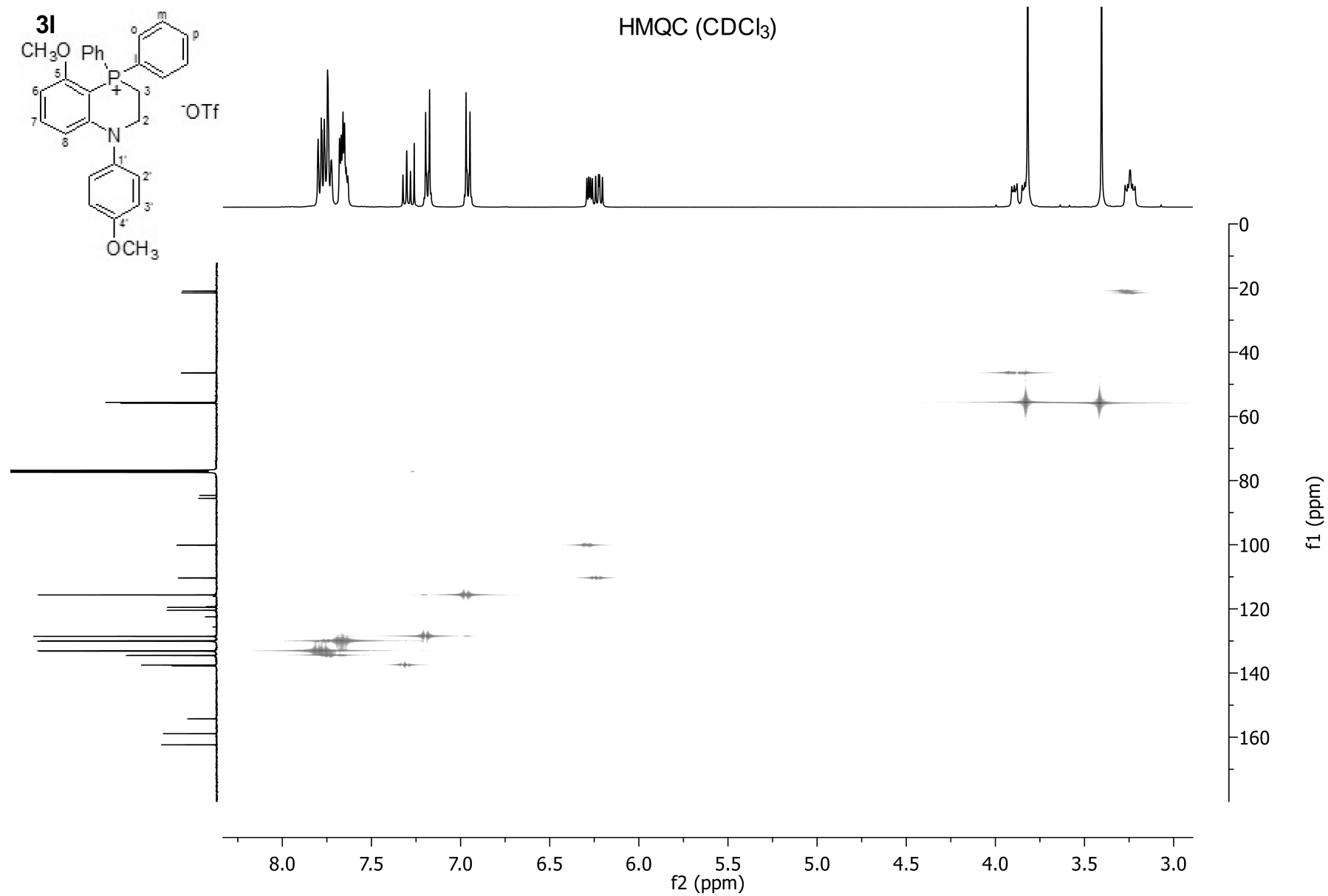
3k



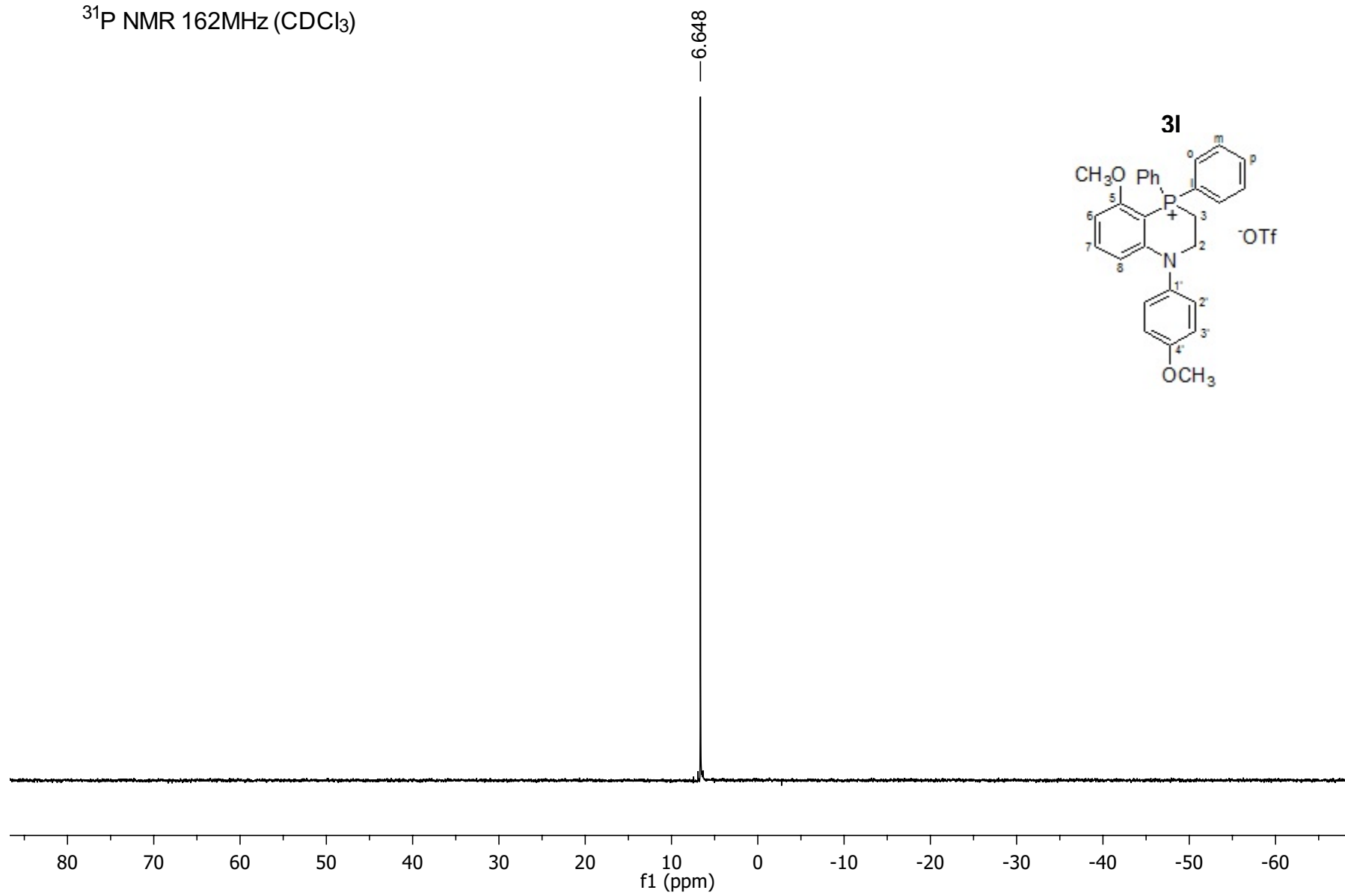


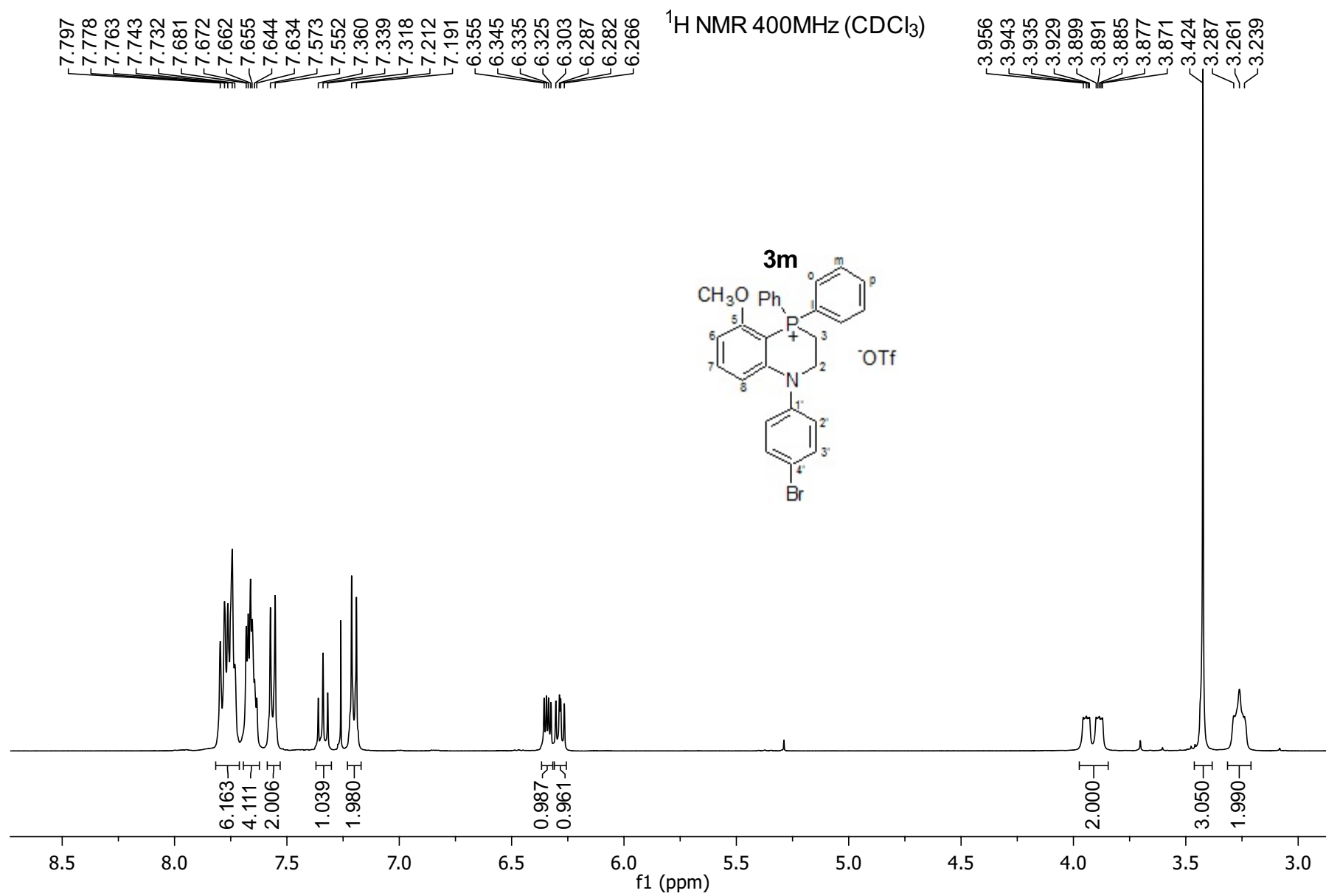


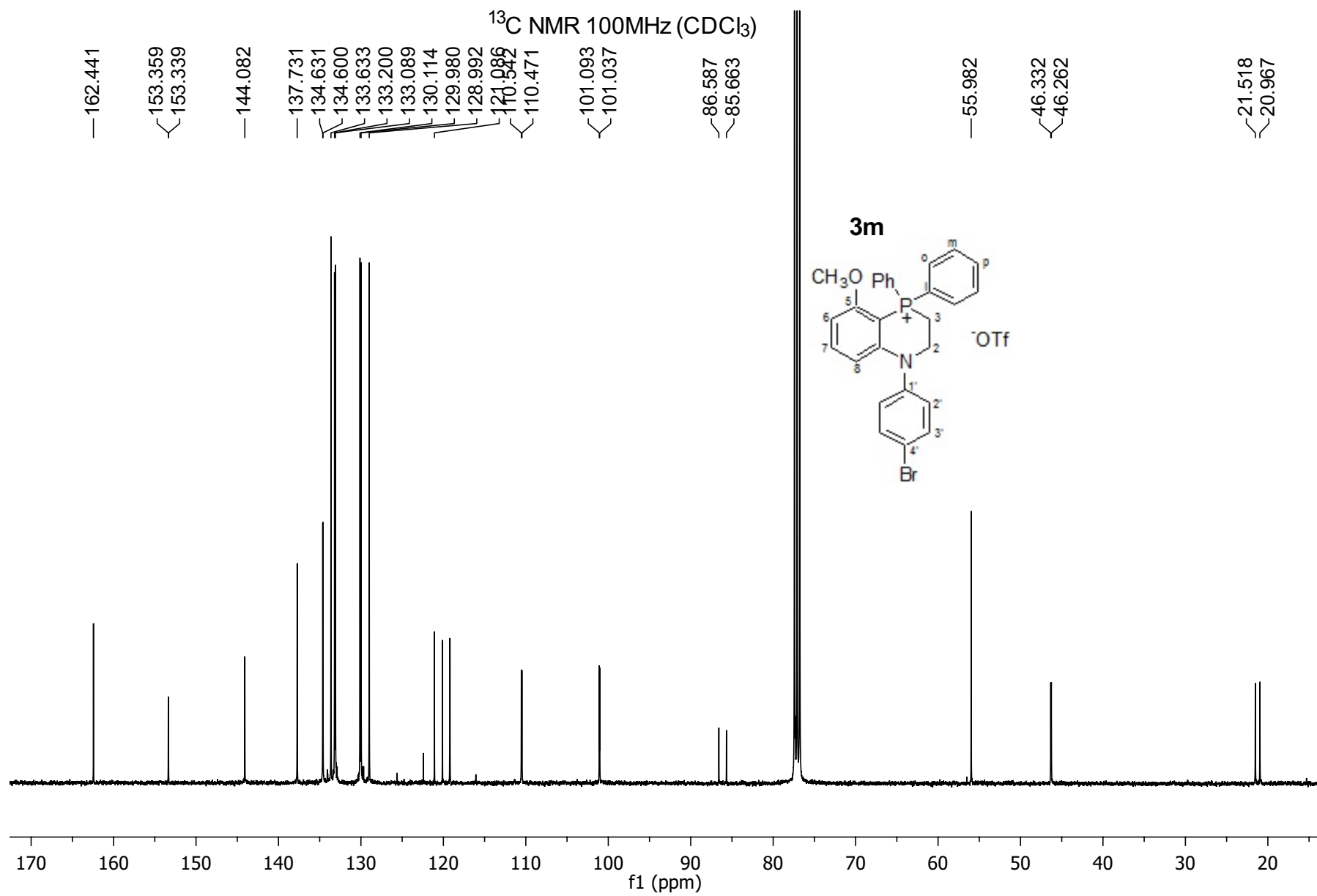


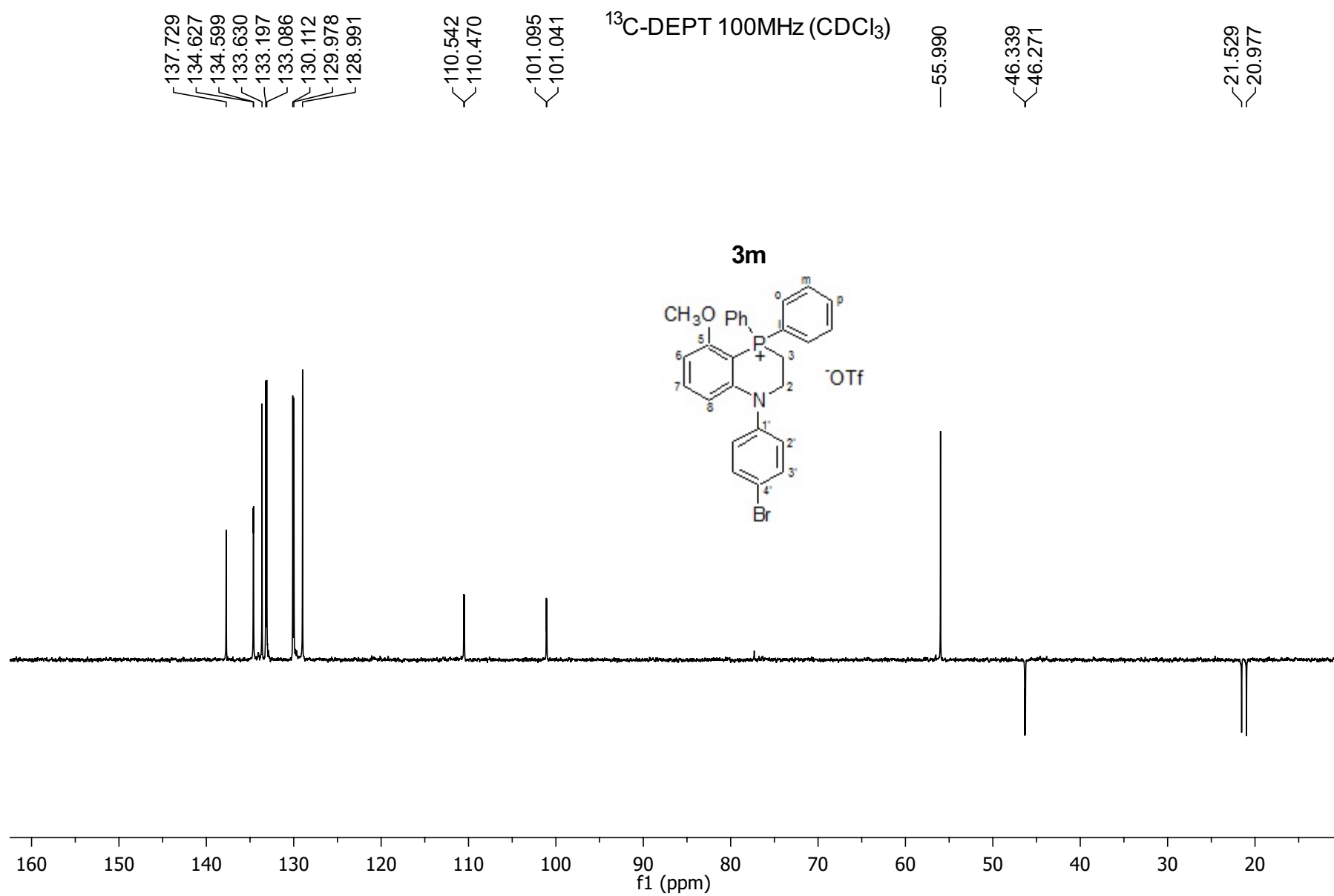


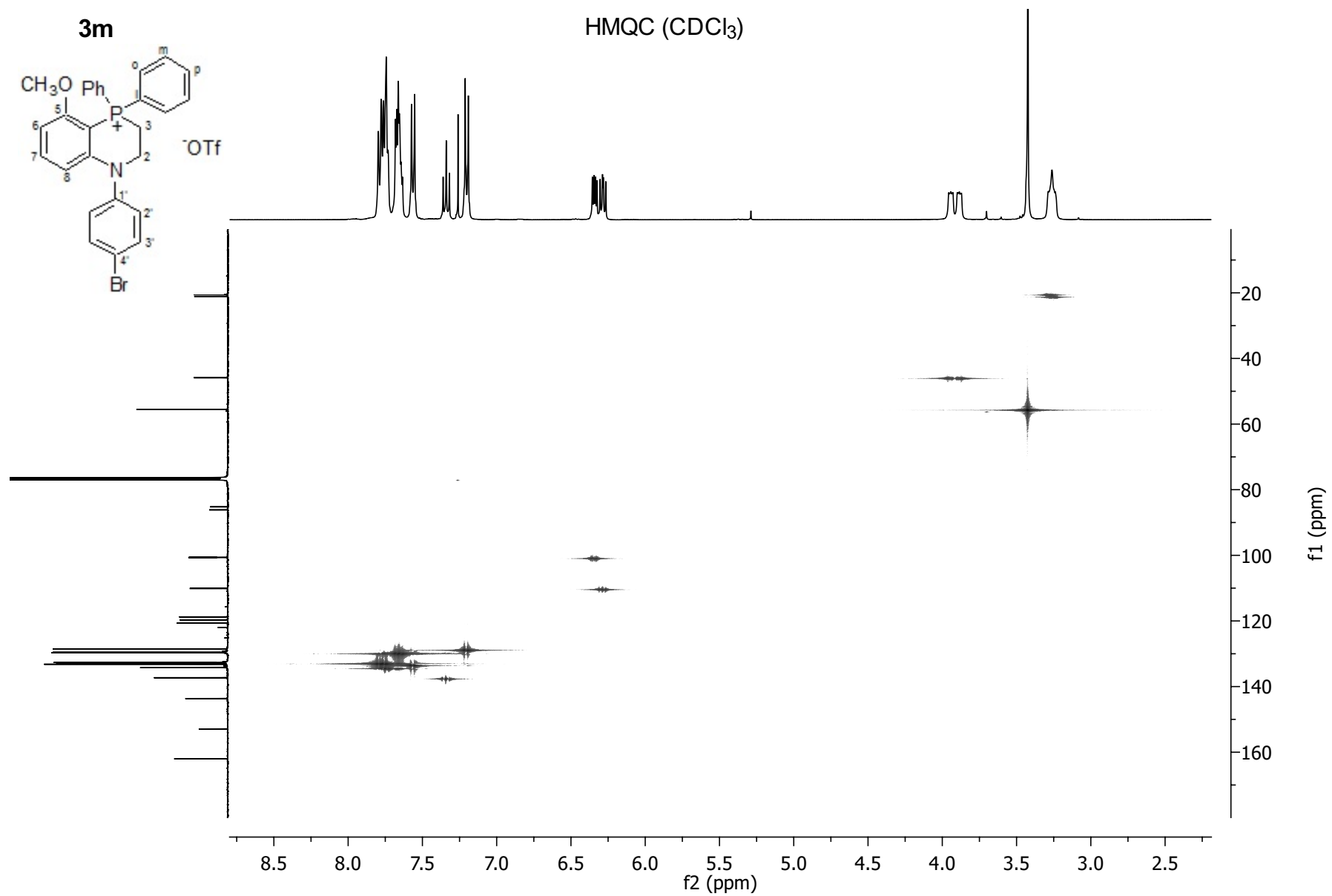
^{31}P NMR 162MHz (CDCl_3)



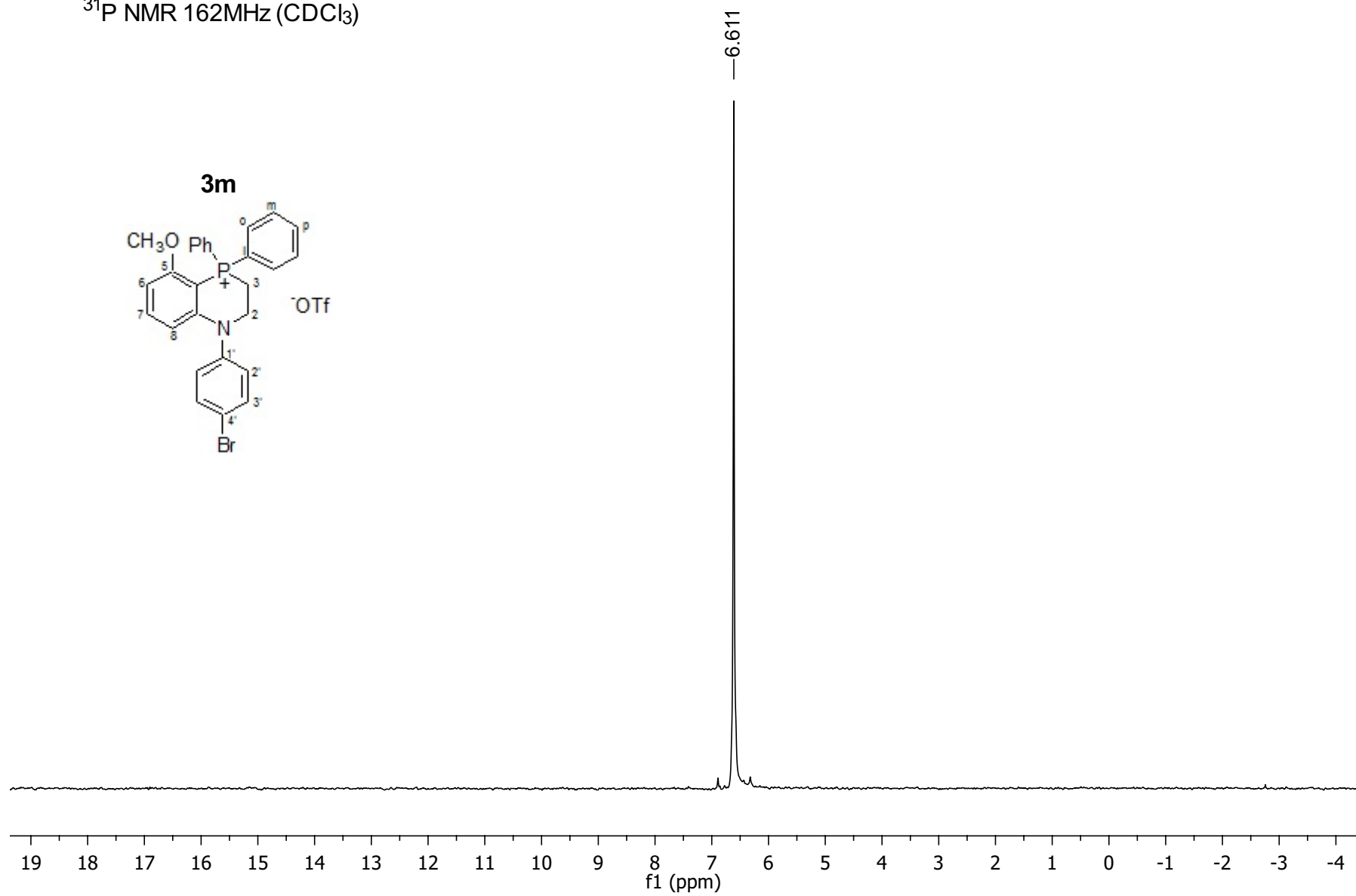


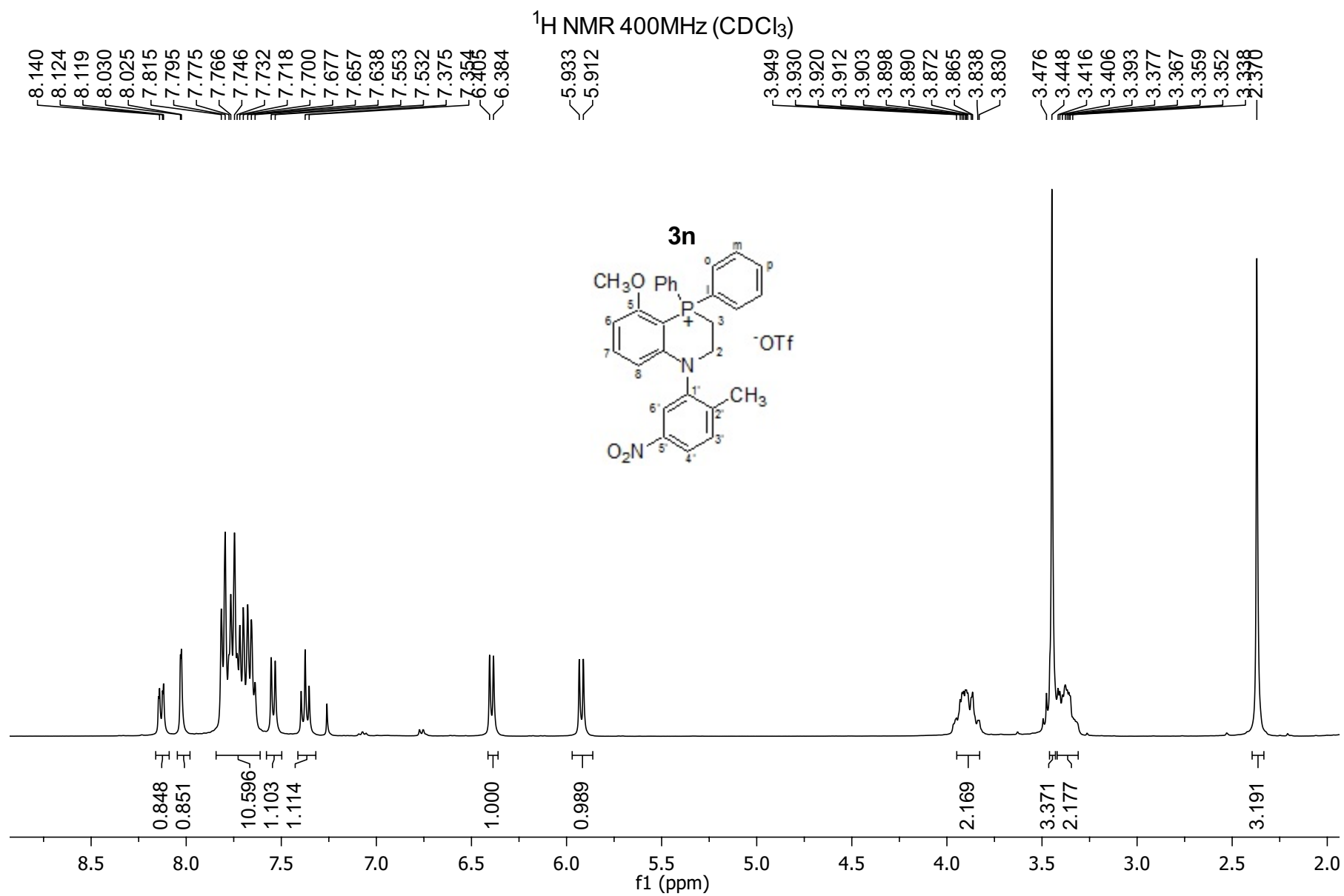


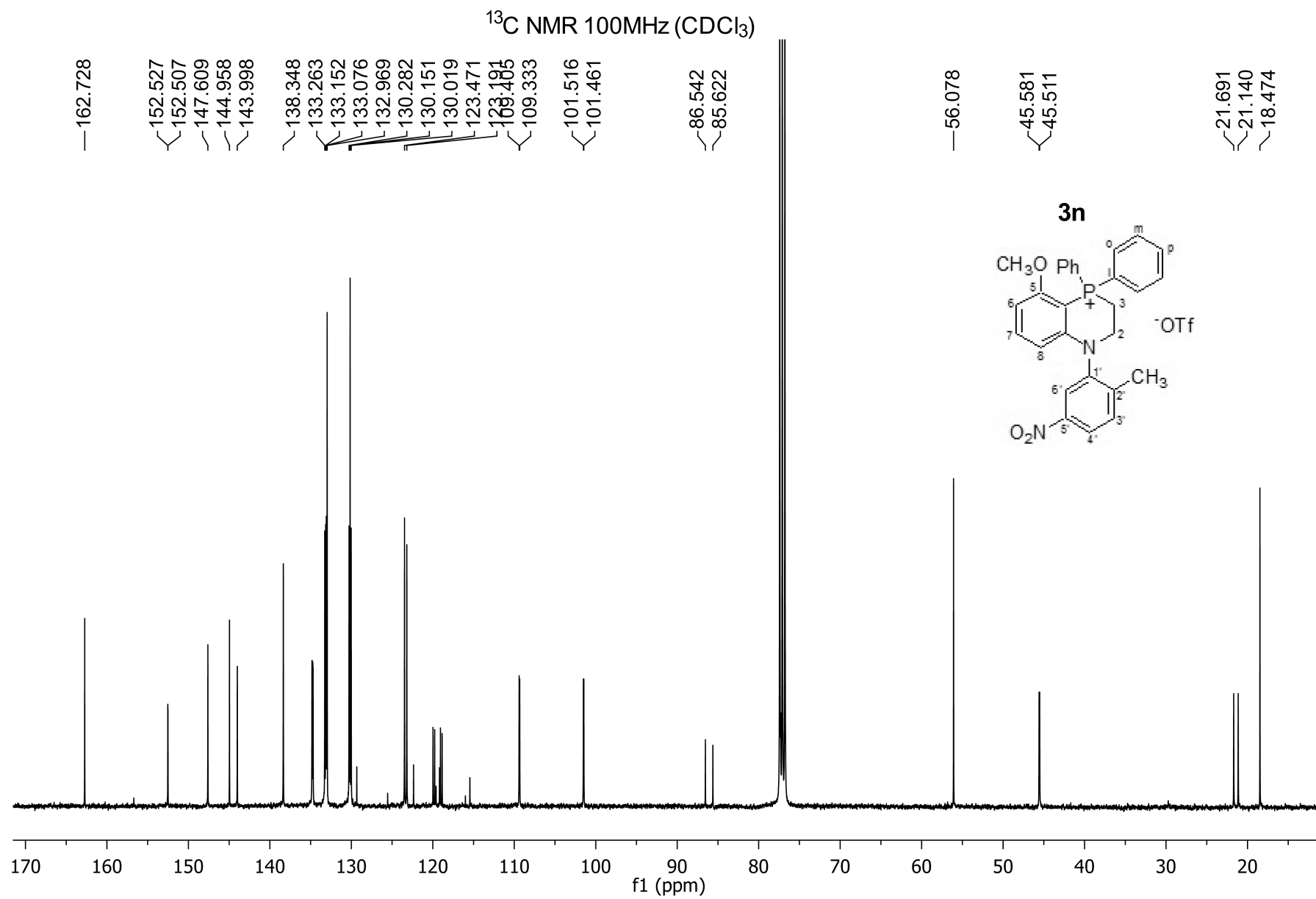


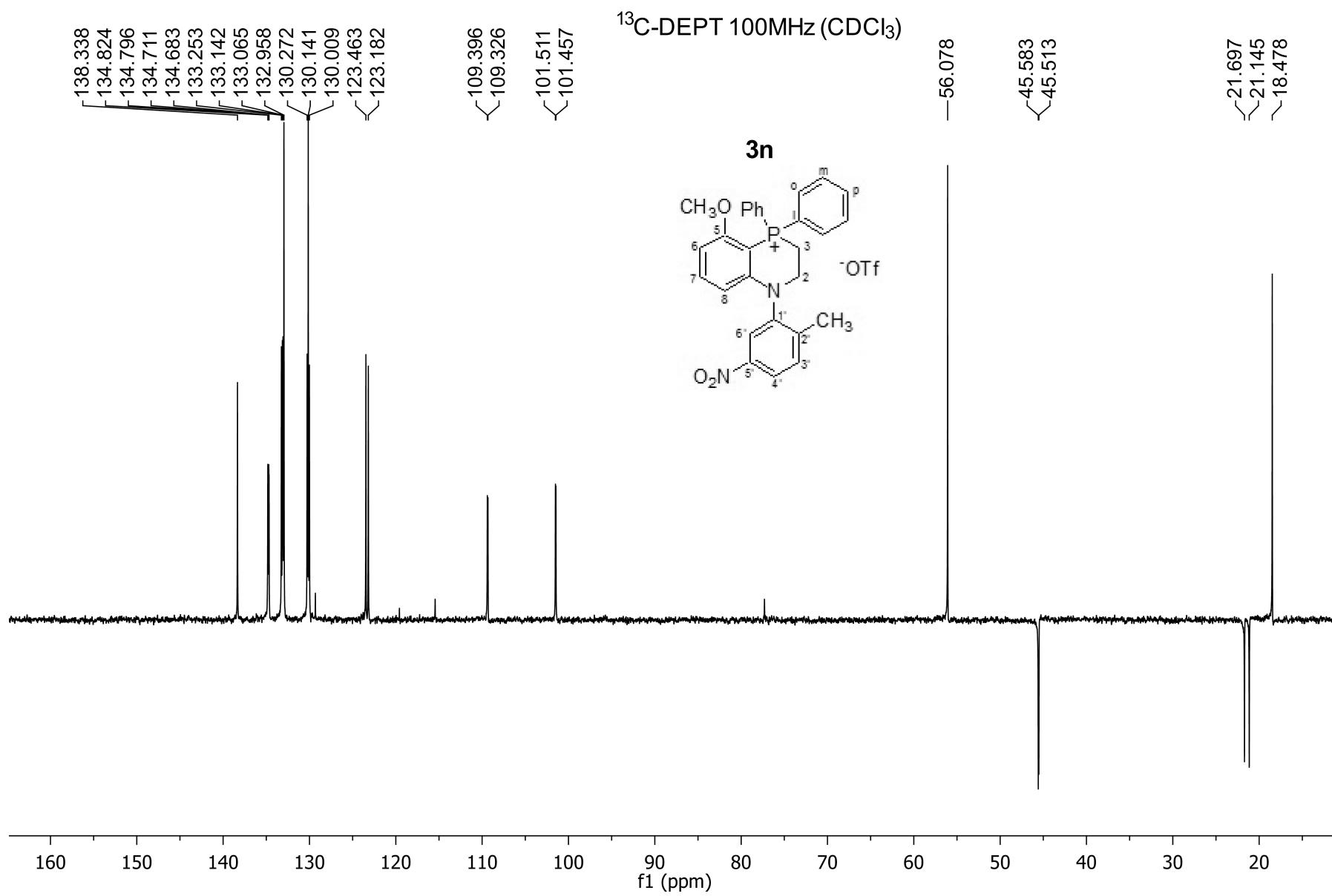


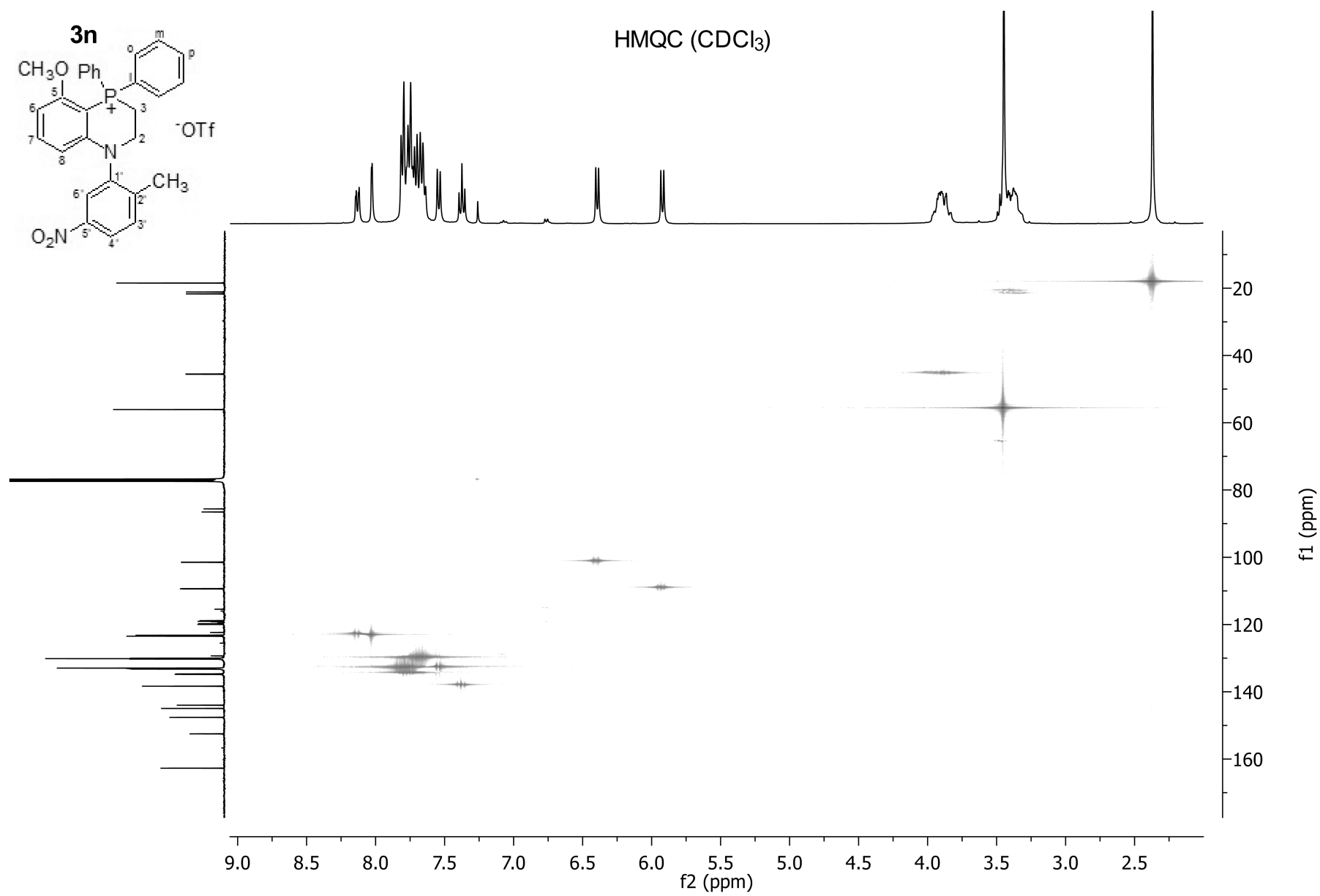
^{31}P NMR 162MHz (CDCl_3)







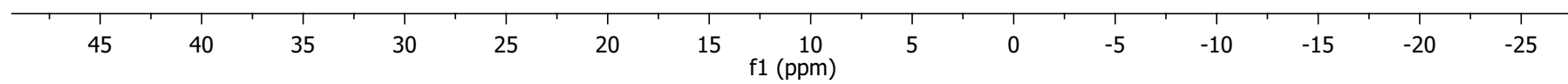
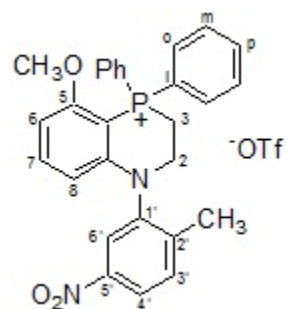


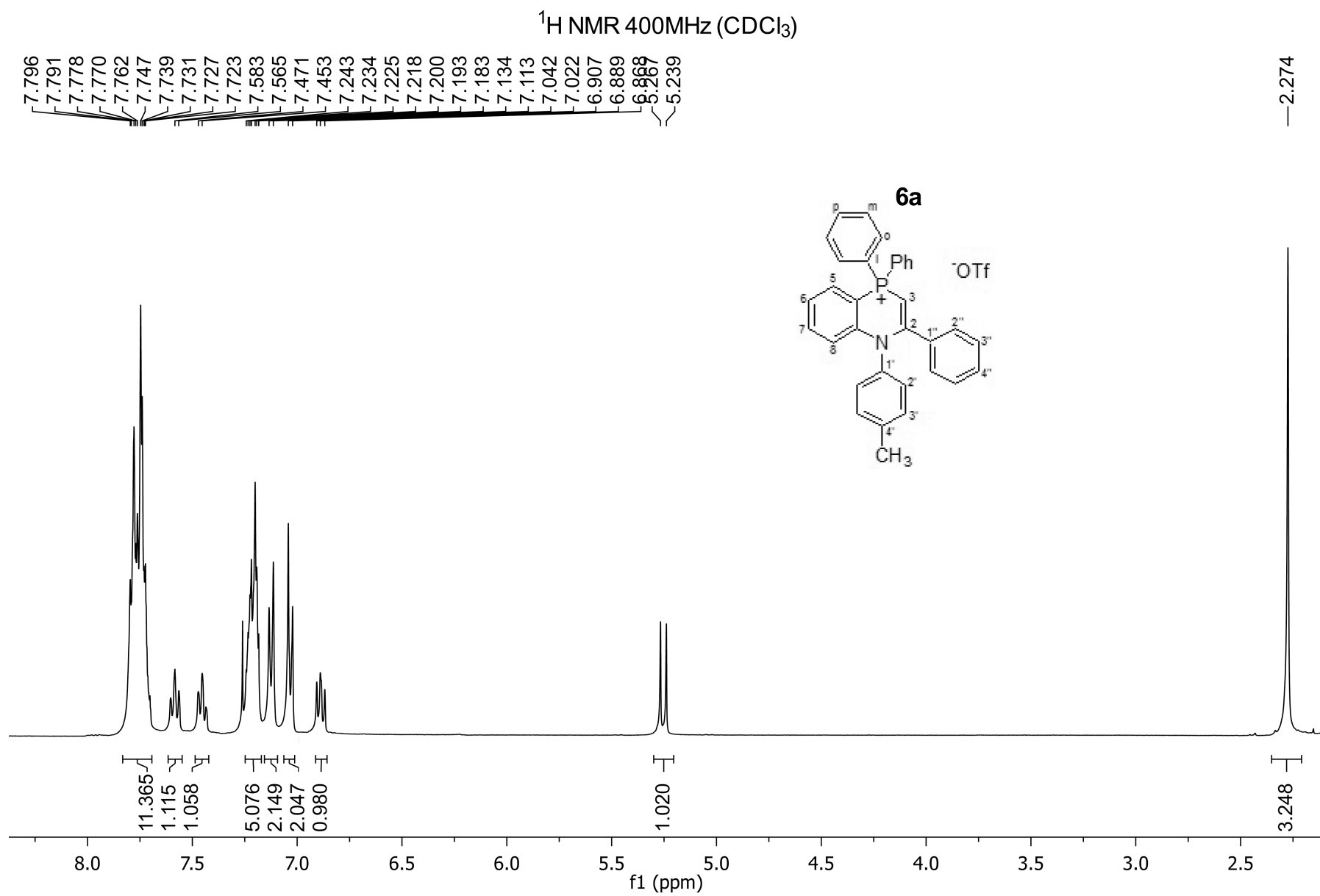


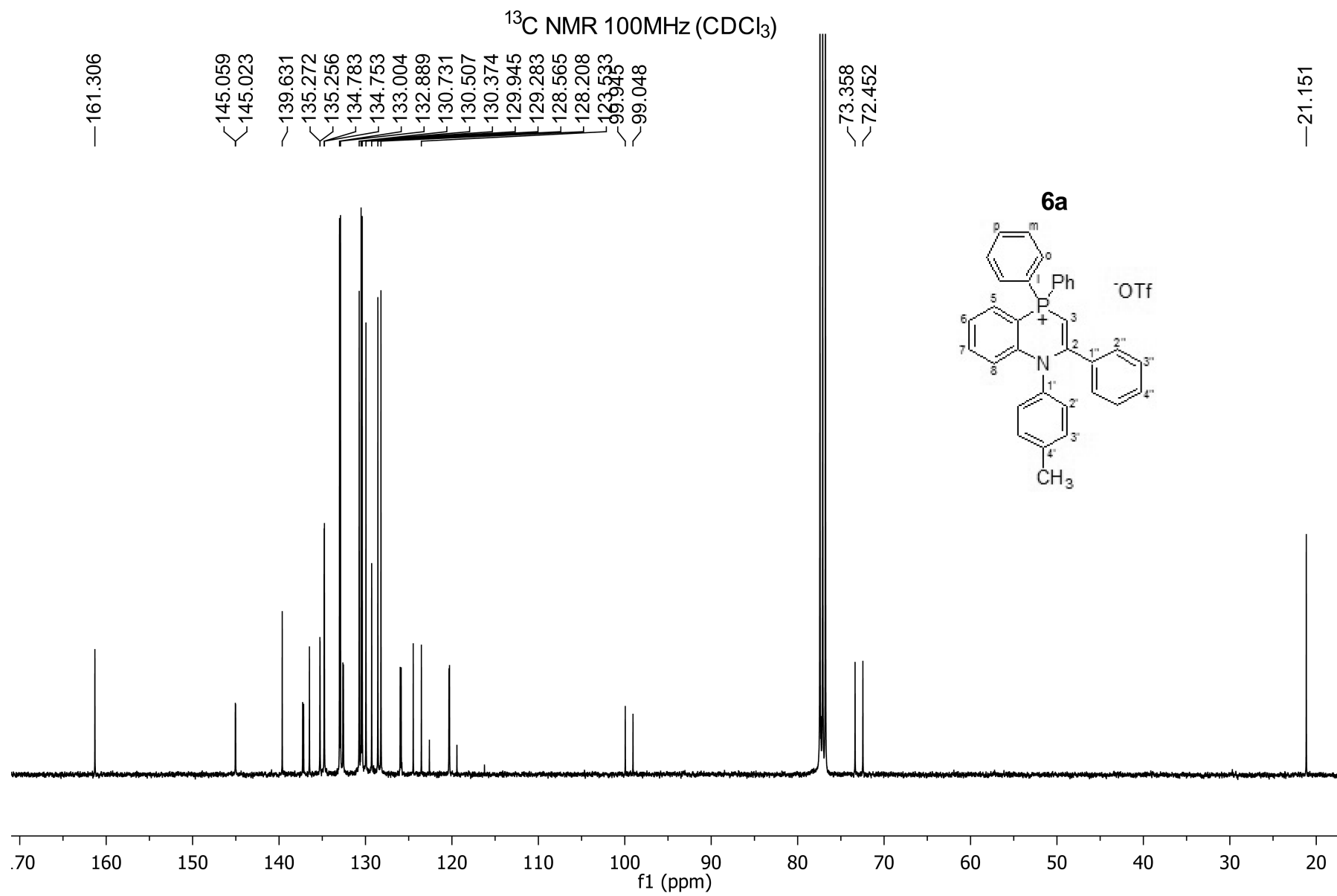
^{31}P NMR 162MHz (CDCl_3)

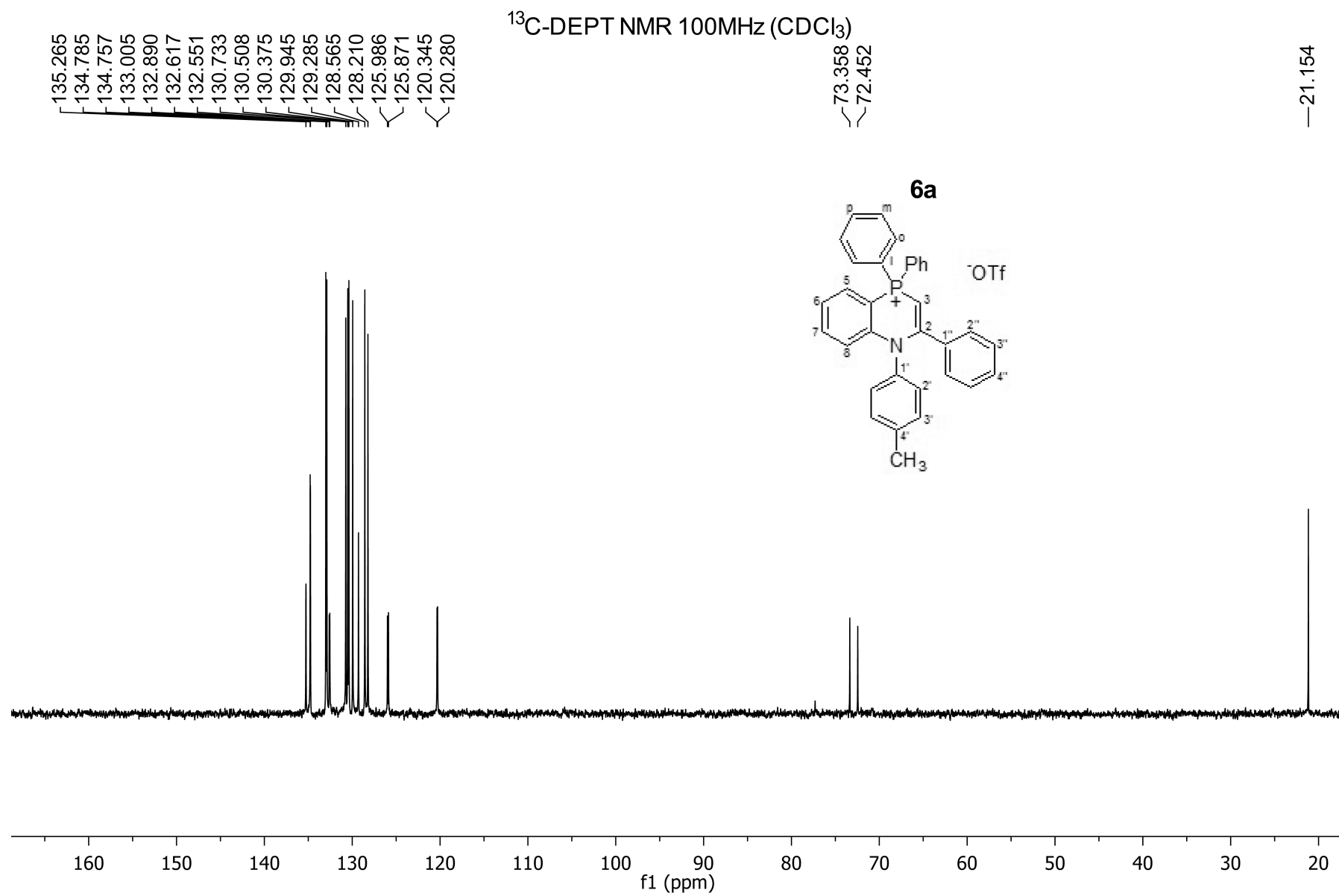
—6.457

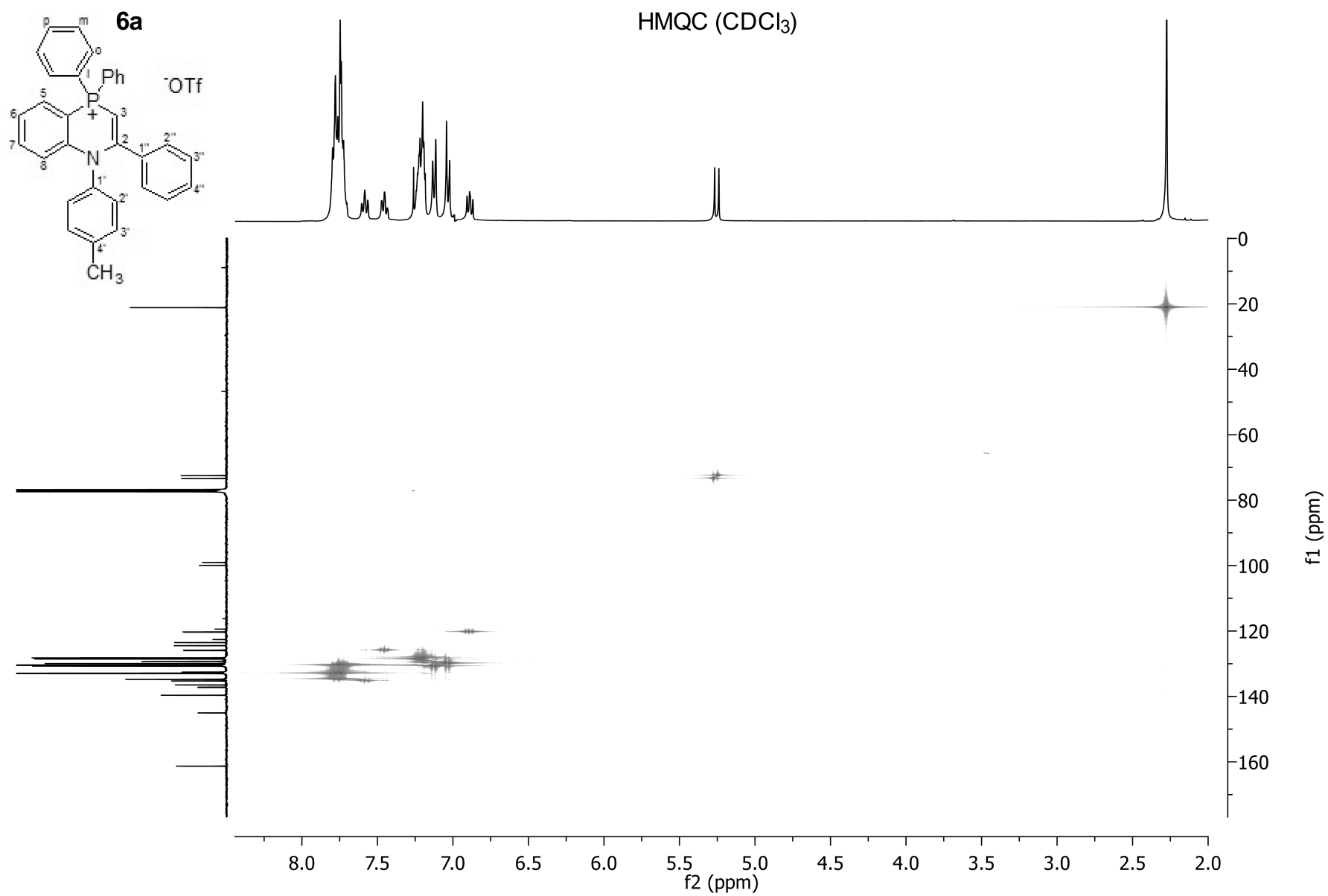
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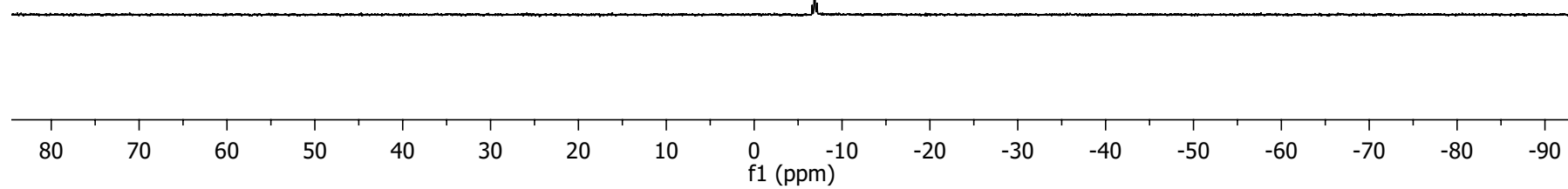
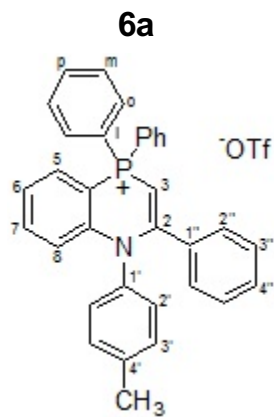




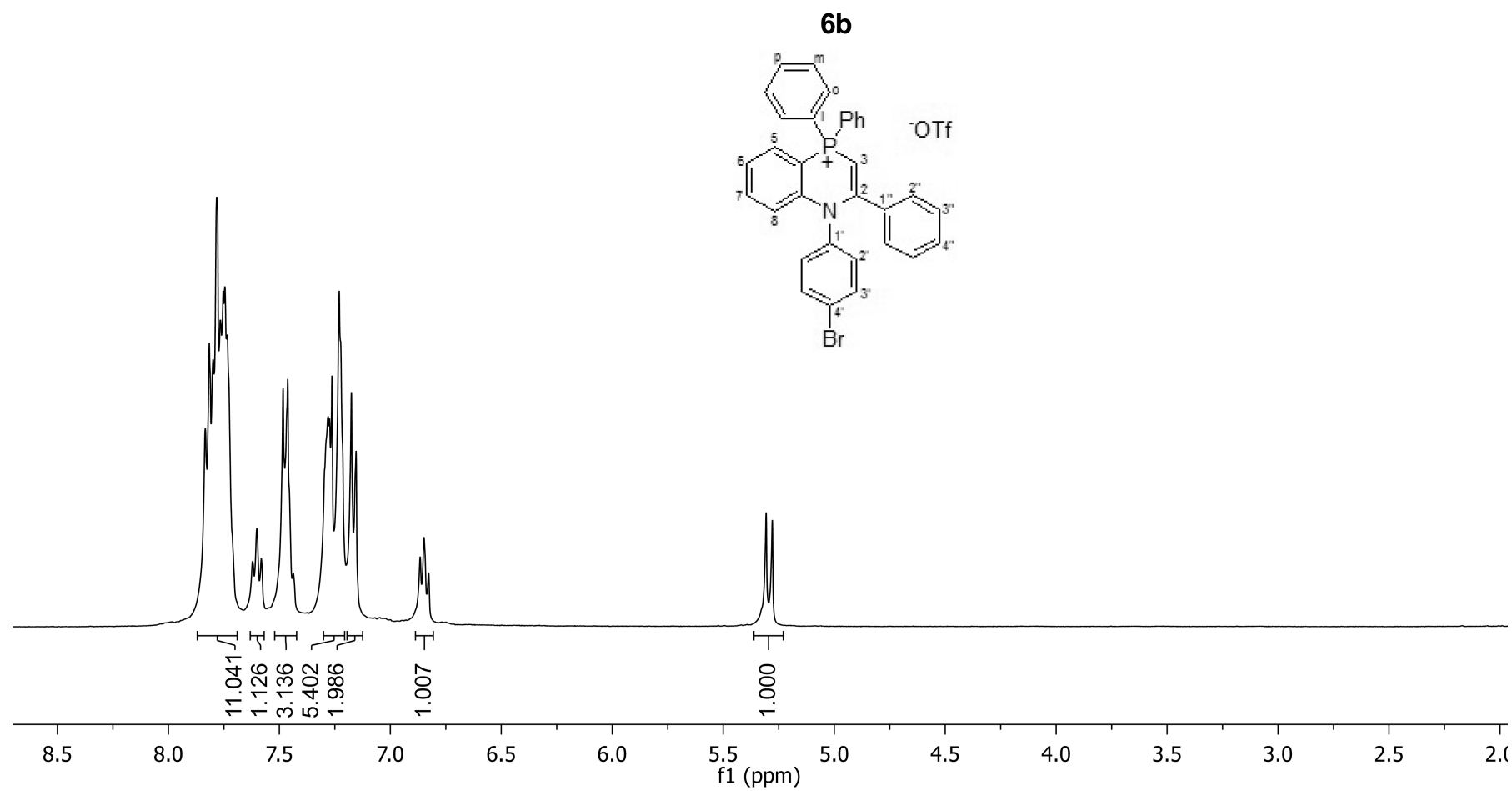


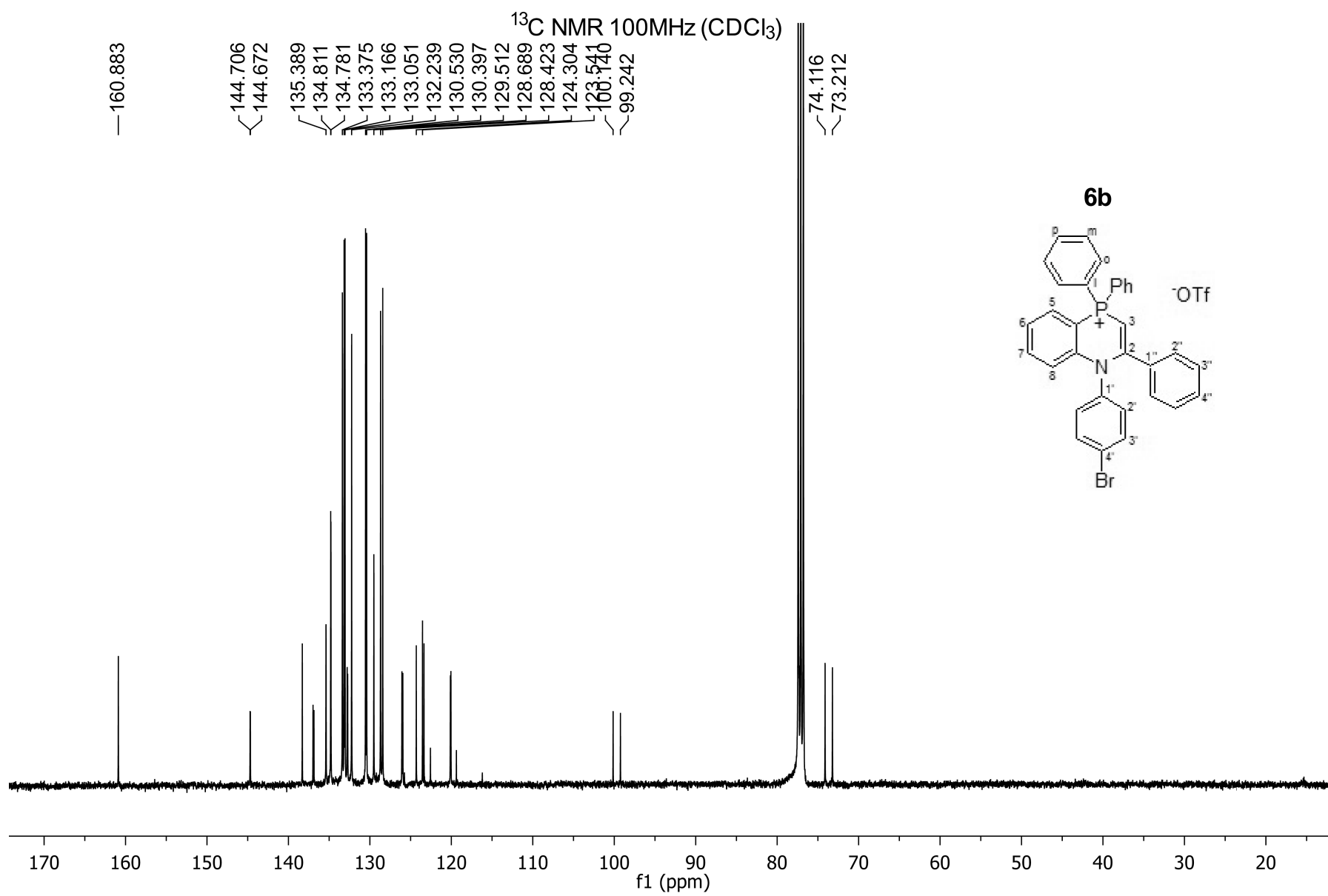
^{31}P NMR 162MHz (CDCl_3)

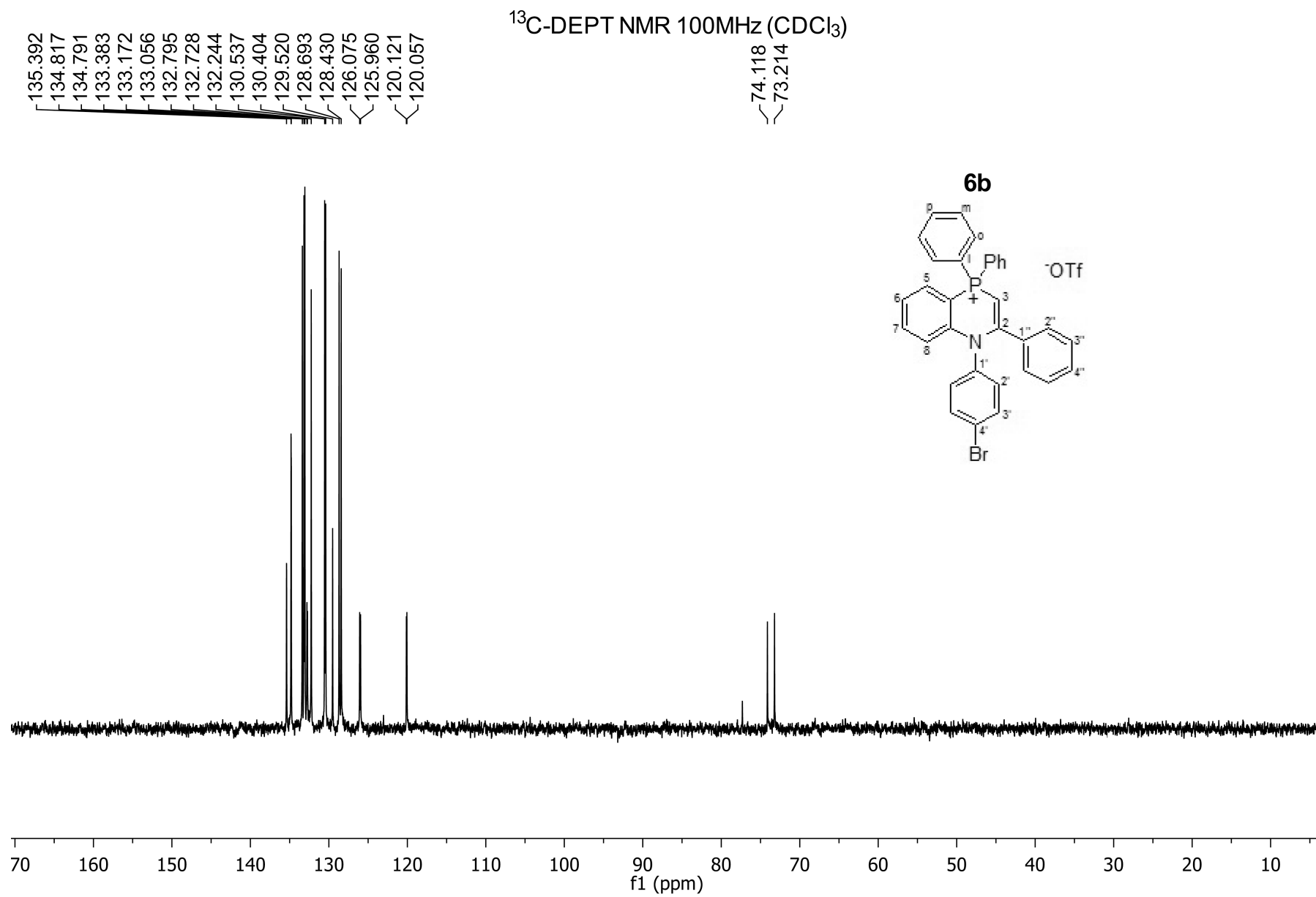
-6.878

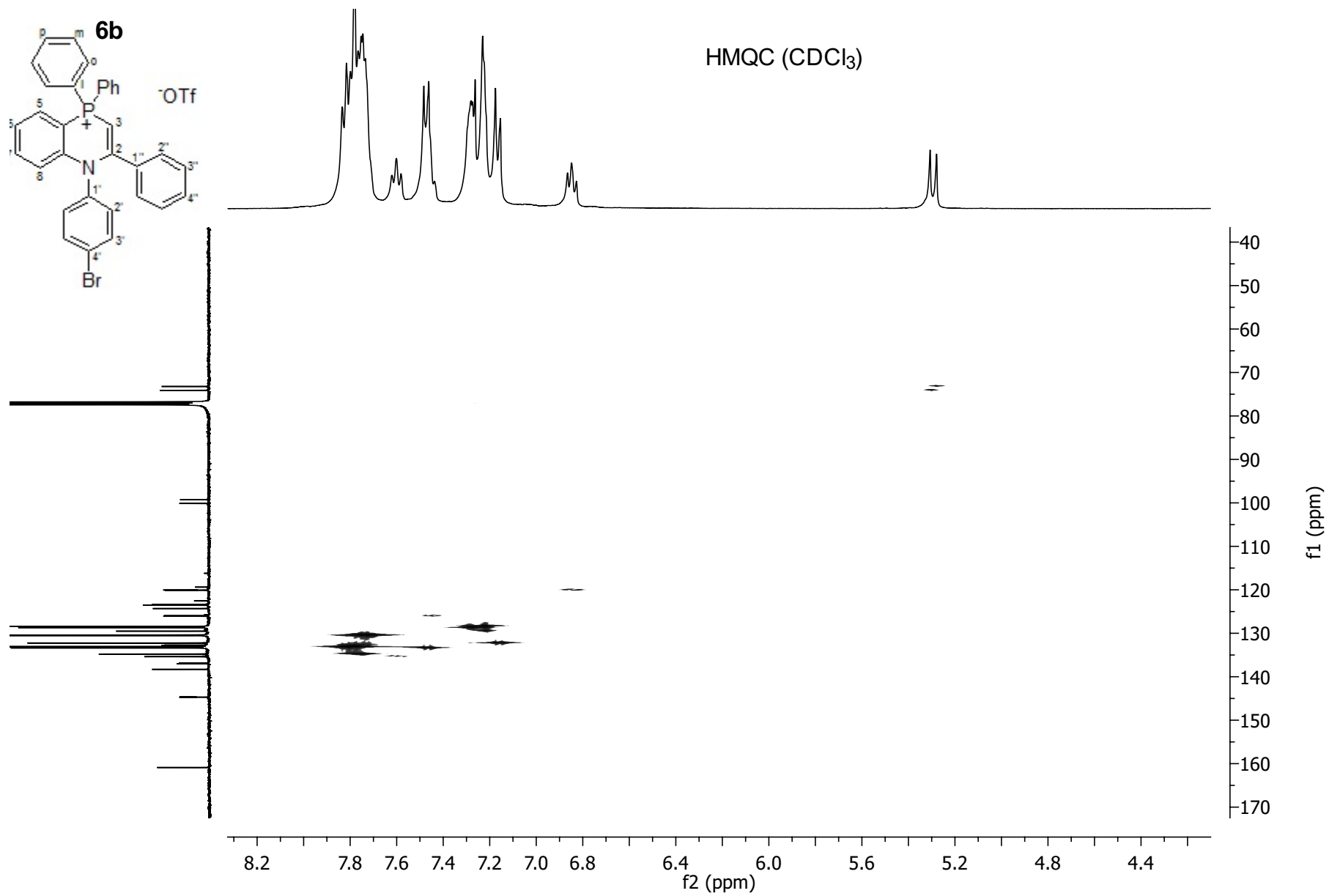


^1H NMR 400MHz (CDCl_3)



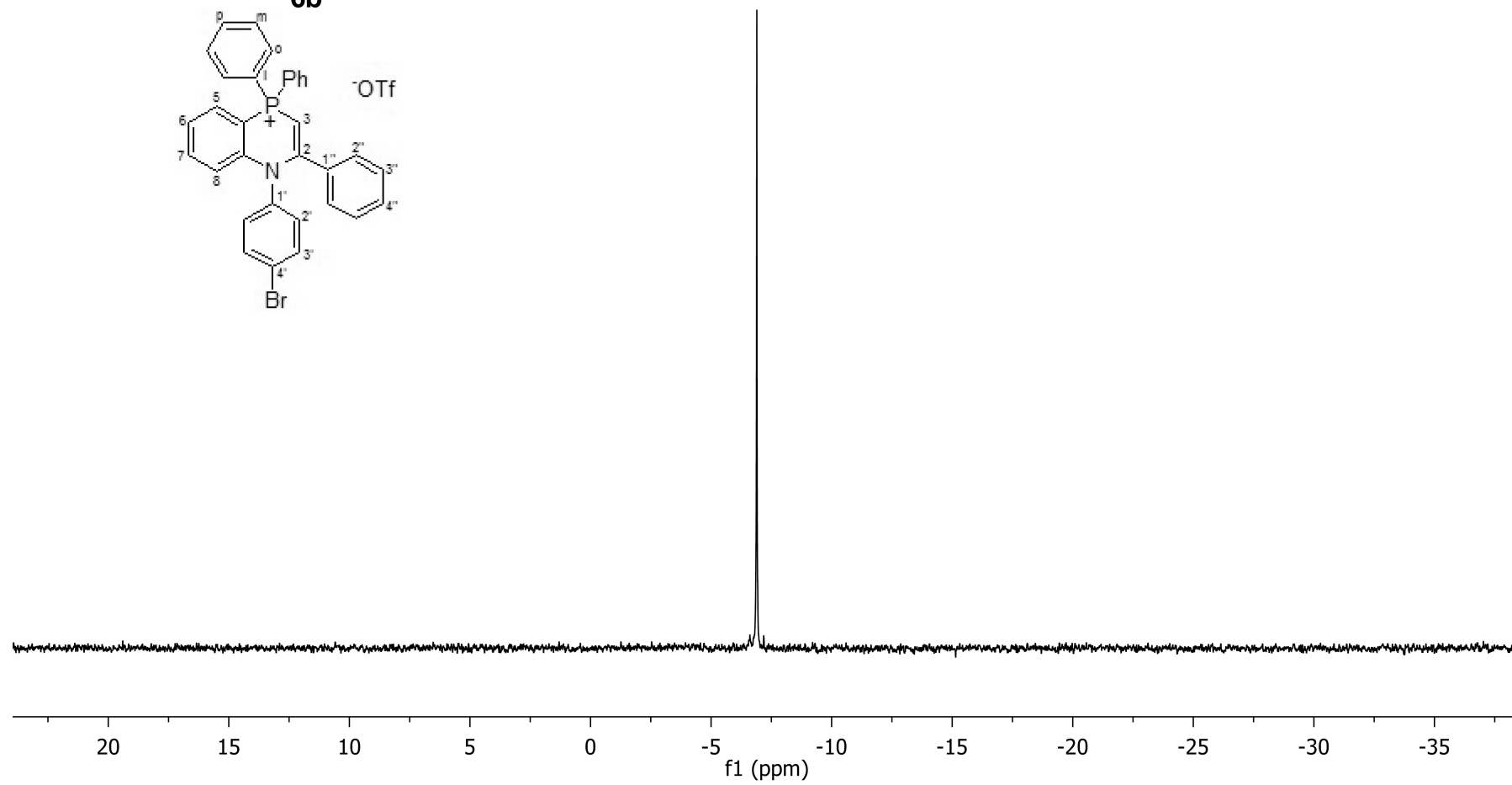
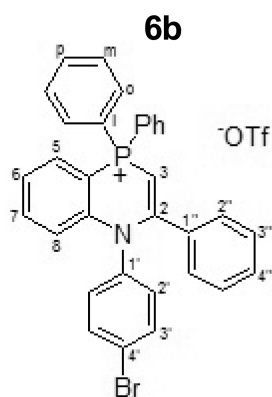






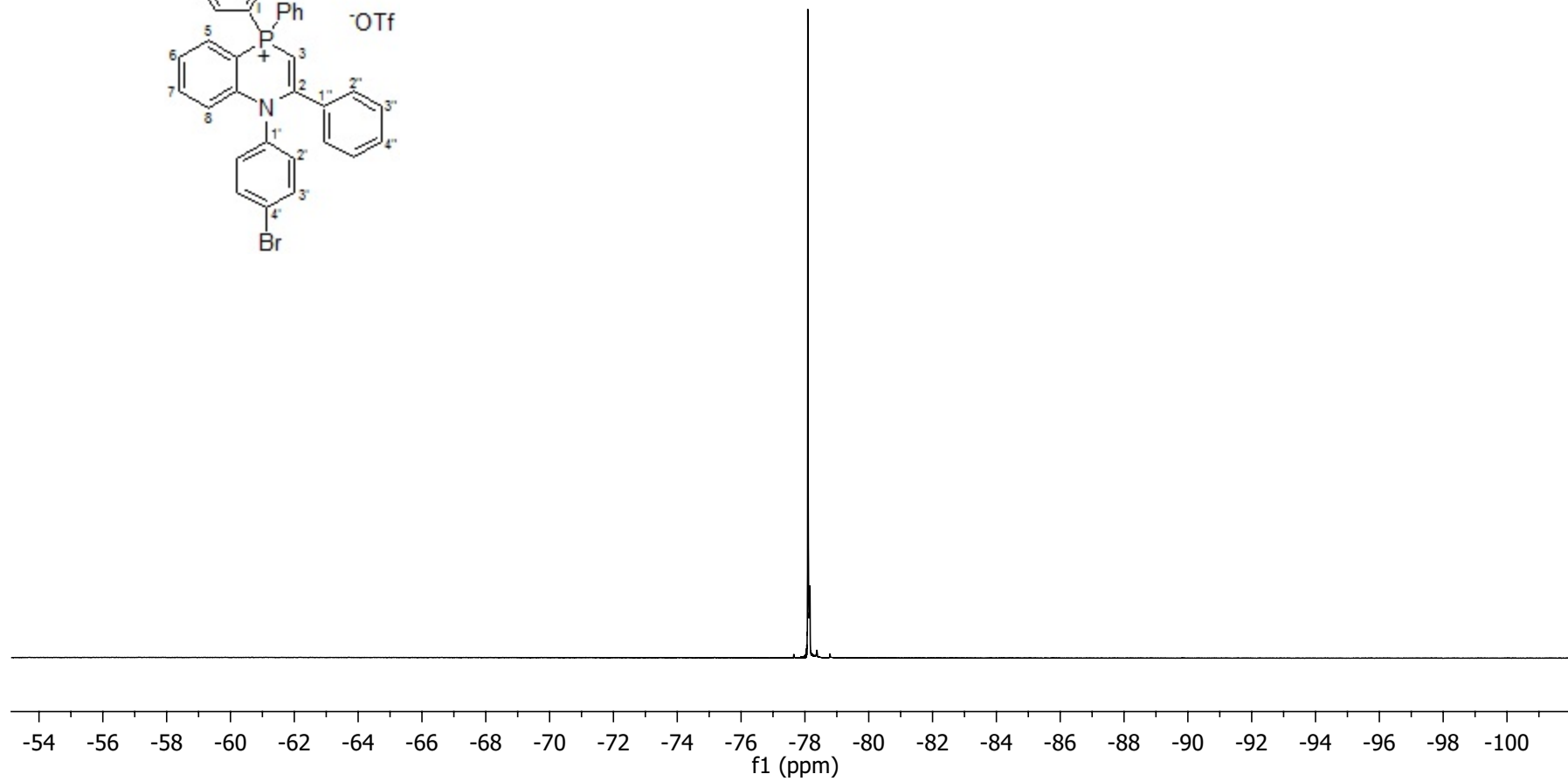
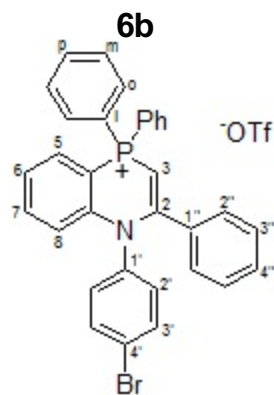
^{31}P NMR 162MHz (CDCl_3)

--6.897

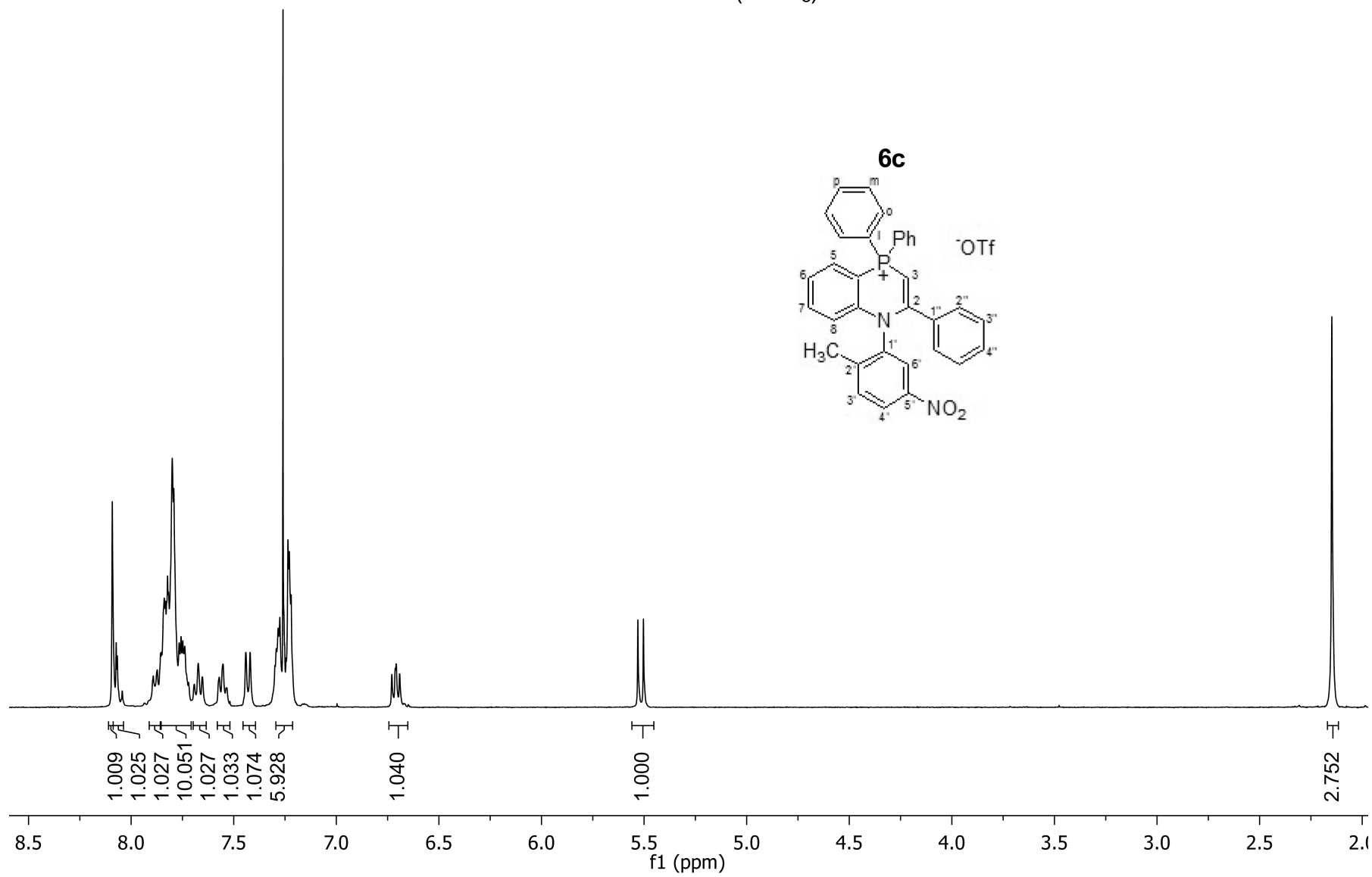


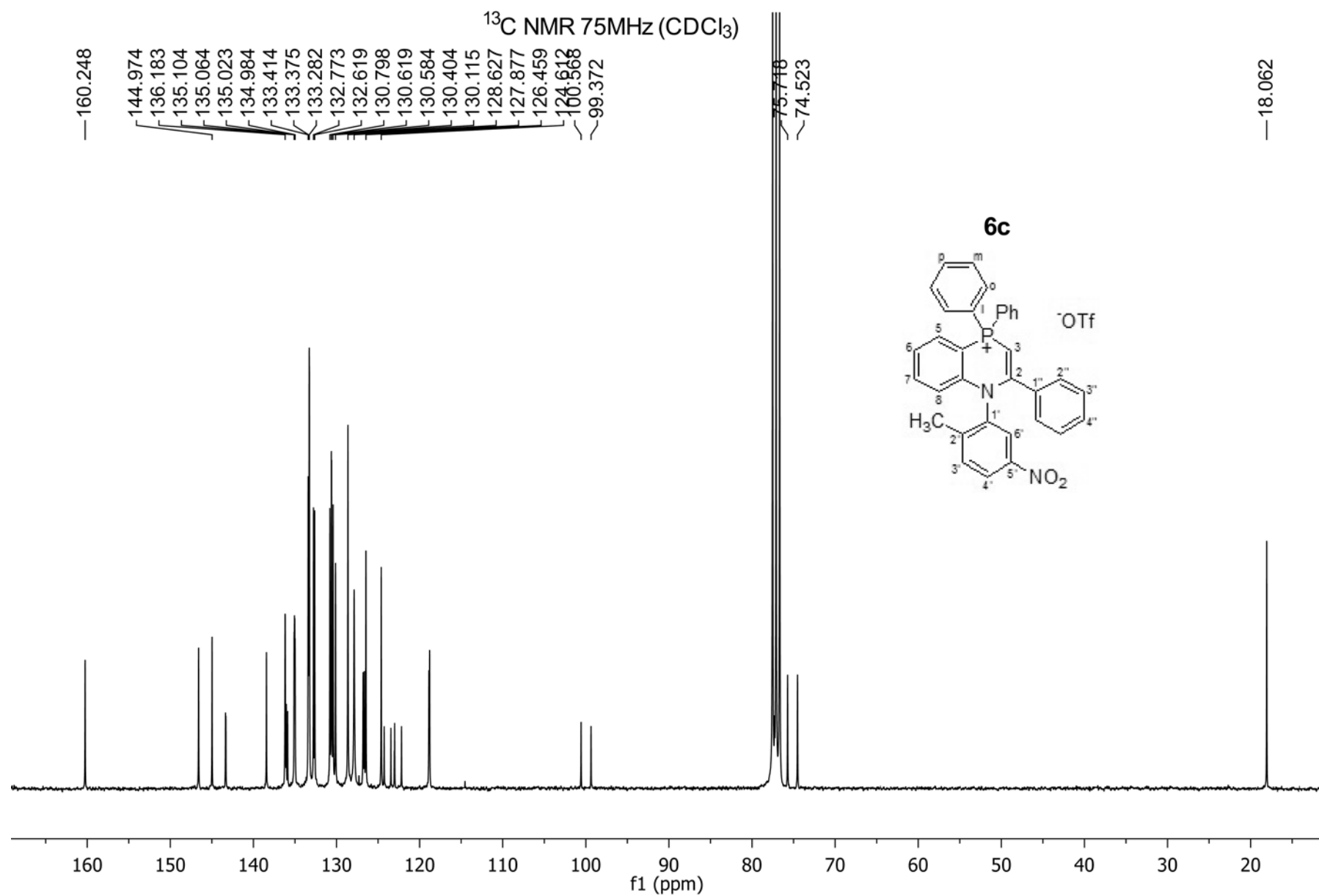
^{19}F NMR 282MHz (CDCl_3)

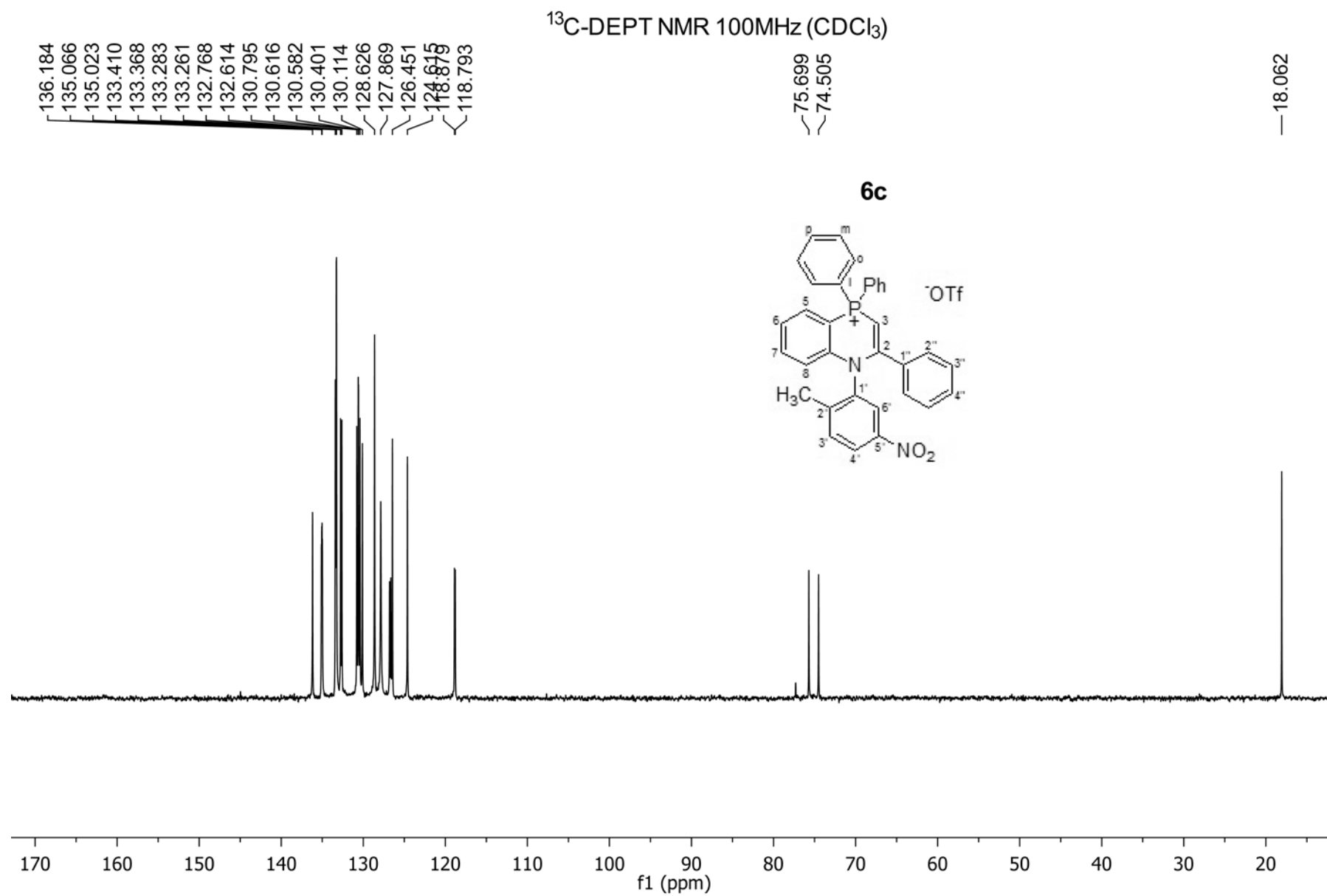
— -78.092

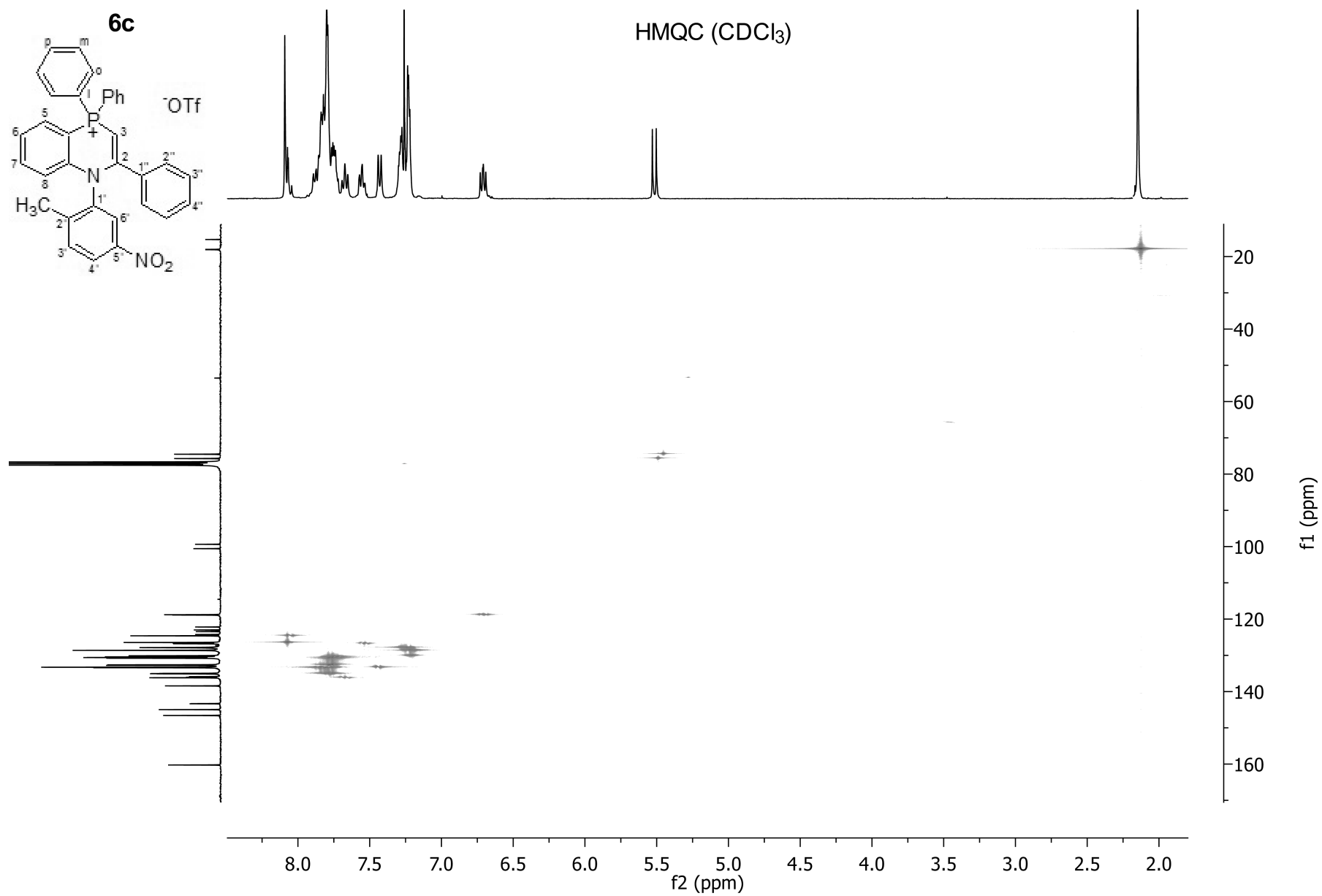


^1H NMR 400MHz (CDCl_3)



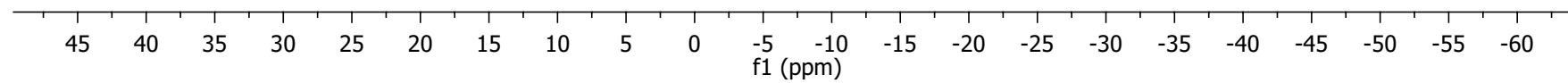
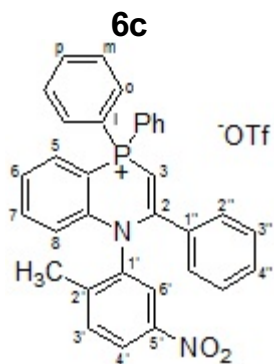






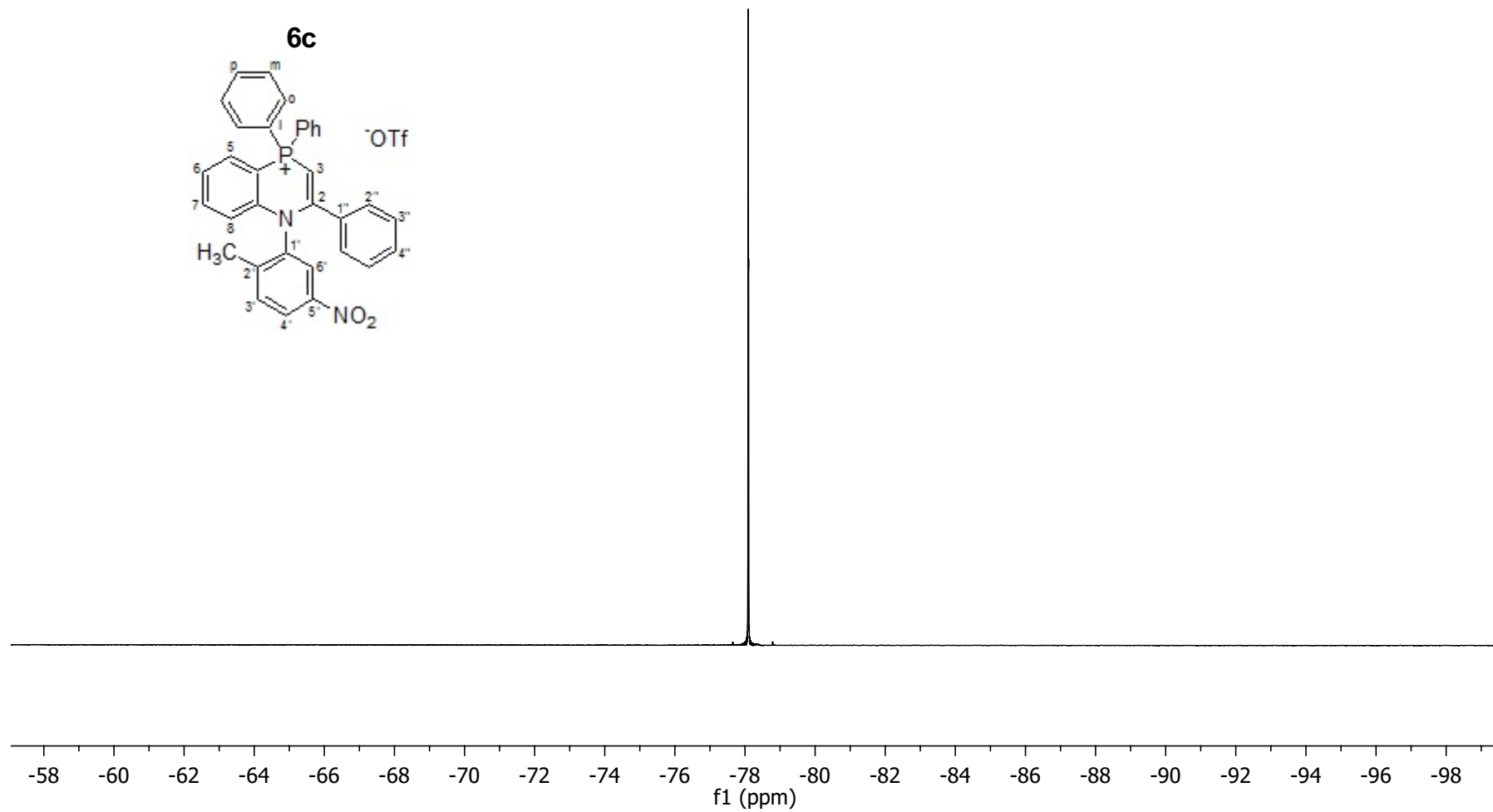
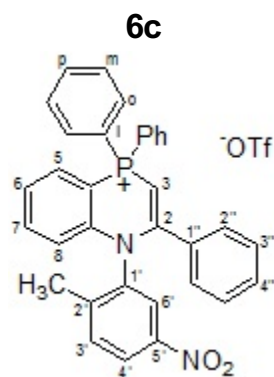
^{31}P NMR 121MHz (CDCl_3)

6.626

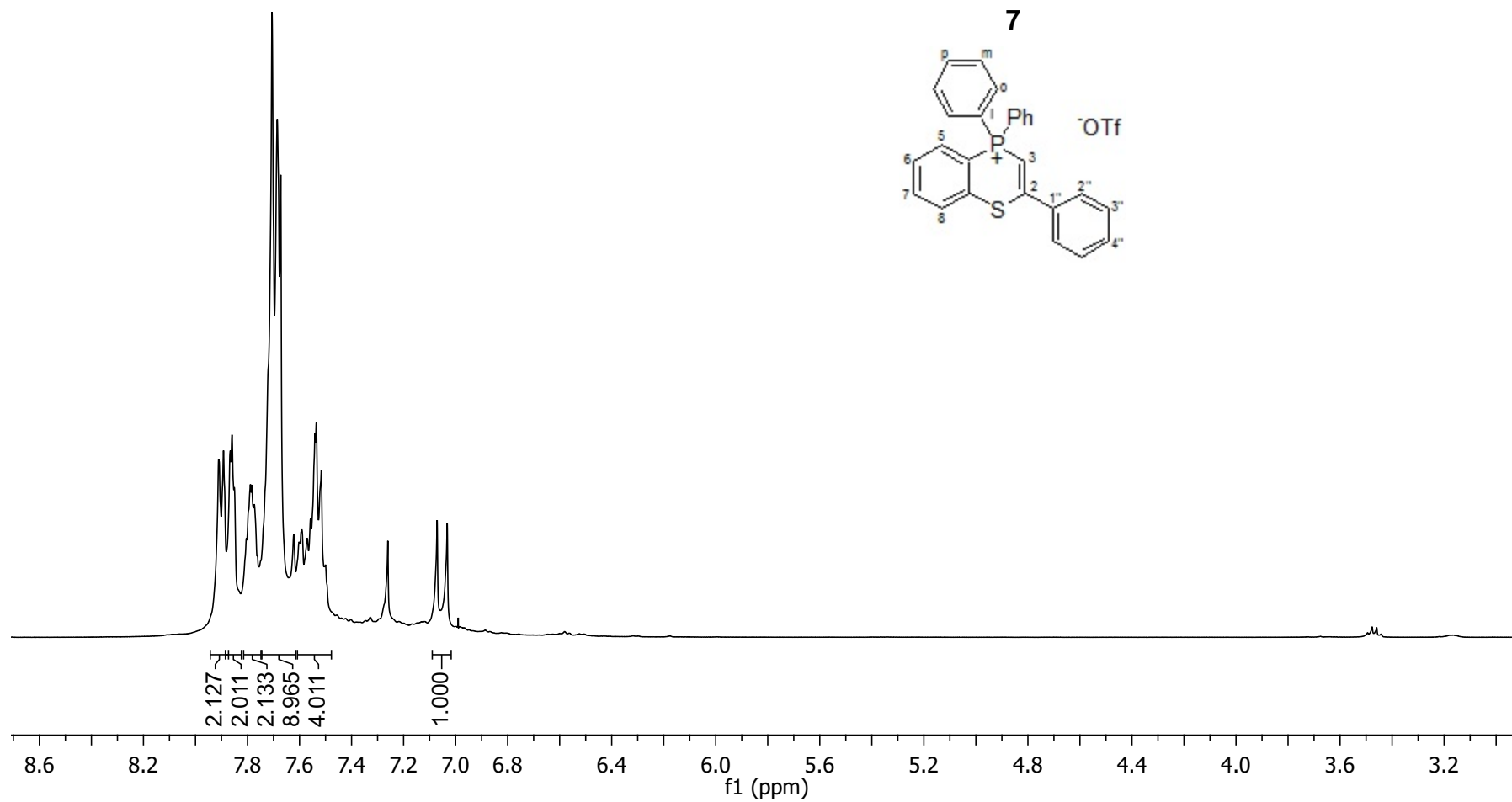


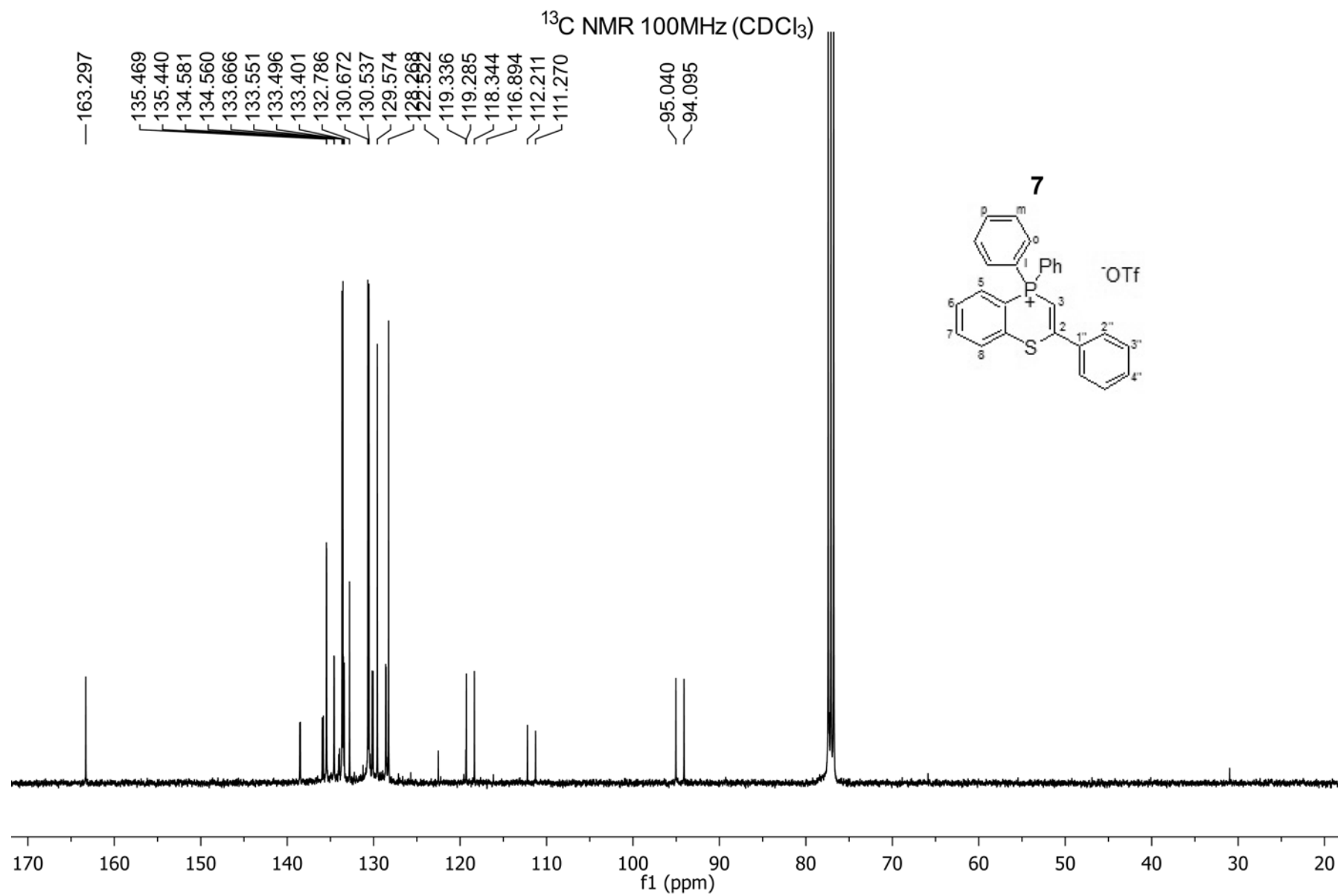
^{19}F NMR 282MHz (CDCl_3)

—-78.091



^1H NMR 400MHz (CDCl_3)

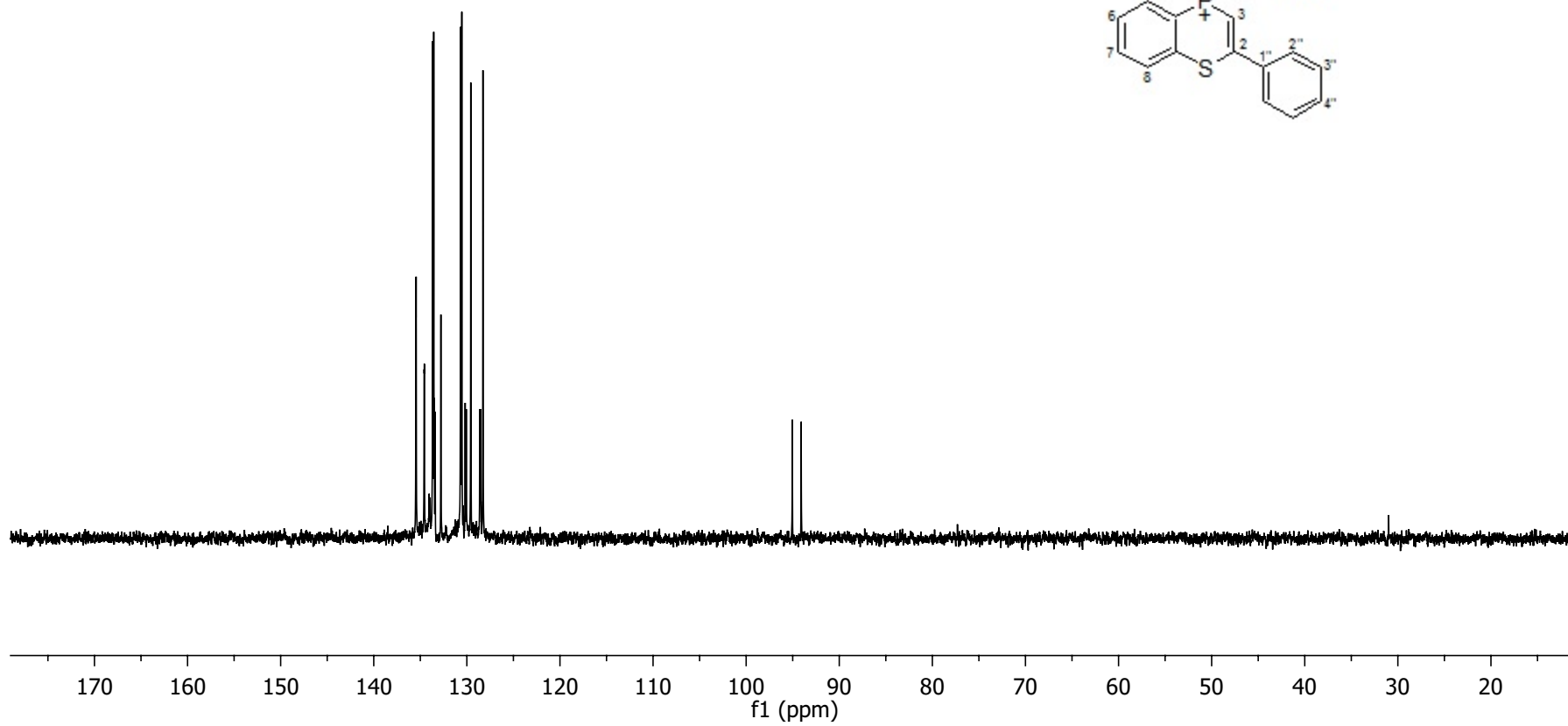
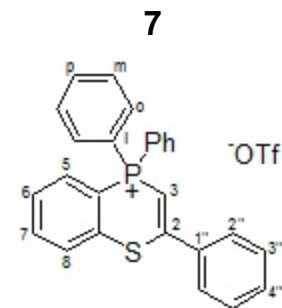




^{13}C -DEPT NMR 100MHz (CDCl_3)

135.472
135.444
134.566
133.669
133.555
133.500
133.404
132.790
130.676
130.541
130.179
130.064
129.578
128.617
128.545
128.272

95.039
94.093



^{31}P NMR 162MHz (CDCl_3)

—1.502

