Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

FOR

Nucleophilic addition of phosphorus(III) derivatives to squaraines: colorimetric detection of transition metal-mediated or thermal reversion

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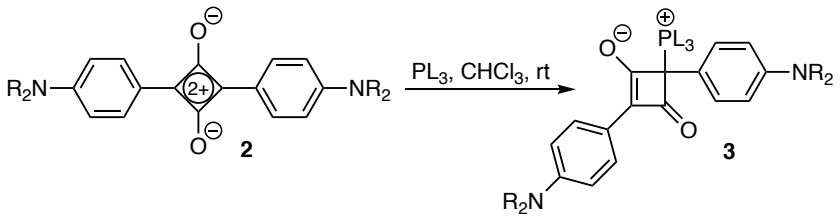
Contents

1. GENERAL

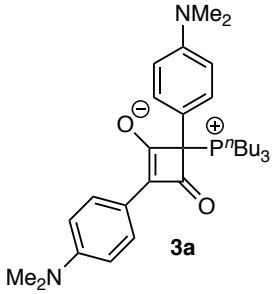
Solvents and reagents were ACS reagent grade and used without further purification unless noted below. Dichloromethane (CH_2Cl_2) was passed through a column of silica gel and stored under argon. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise specified. All phosphines were purchased commercially and used without purification. Squaraine dyes were prepared according to literature procedures.

^{1}H Nuclear magnetic resonance (NMR) spectra were obtained at either 300, 400, or 500 MHz, and ^{13}C NMR spectra at 100, 125, or 150 MHz. Chemical shifts are reported in parts per million (ppm, δ), and referenced to residual solvent. Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; comp, complex; app, apparent; and br, broad. Infrared (IR) spectra were obtained using a Thermo Electron Nicolet 380 FT-IR using a silicon (Si) crystal in an attenuated total reflectance (ATR) tower and reported as wavenumbers (cm^{-1}). High and Low resolution electrospray ionization (ESI) measurements were made with a Bruker MicroTOF II mass spectrometer. Absorption spectra were collected using an Evolution 201 UV-Vis Spectrometer with ThermoInsight software. Analytical thin layer chromatography (TLC) was performed using EMD 250 micron 60 F_{254} silica gel plates, visualized with UV light and stained with a *p*-anisaldehyde solution. Flash column chromatography was performed according to Still's procedure (Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923) using EMD 40-63 μm 60Å silica gel.

2. EXPERIMENTAL PROCEDURES

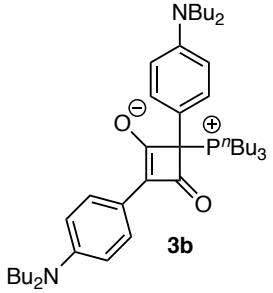


General procedure for the synthesis of Squaraine-Phosphine Derived Zwitterions. Squaraine dye **2** (0.10 mmol) was added to a 2-dram screw cap vial and the solid was suspended in $CHCl_3$ (1.0 mL). The corresponding phosphorus reagent (0.11 mmol) was added in one portion to provide a heterogeneous mixture that became homogeneous, changing color from blue/green to yellow, in <1 min. The resulting solution was then concentrated under reduced pressure, and the crude mixture was purified by vapor-vapor recrystallization ($CHCl_3$/pentane) to afford the title compound **3**.



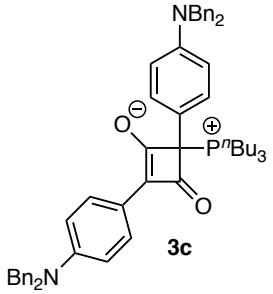
2,4-Bis(4-(dimethylamino)phenyl)-3-oxo-4-(tributylphosphonio)cyclobut-1-en-1-olate (3a). Formation of the squaraine-P(III) adduct was performed on 0.1 mmol scale. Purification by vapor-vapor recrystallization from $CHCl_3$/pentanes provided 50 mg (96%) of **3a** as pale yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.67 (comp, 4 H), 6.71-6.67 (comp, 4 H), 2.93 (s, 6 H), 2.89 (s, 6 H), 2.11-2.05 (m,

6 H), 1.62-1.57 (m, 6 H), 1.43-1.39 (m, 6 H), 0.91 (t, J = 7.3 Hz, 9 H); ^{13}C NMR (125 MHz) δ 176.2 (d, J = 6 Hz), 150.4, 147.9, 128.4 (d, J = 4.2 Hz), 125.7, 122.9, 122.1, 114.3 (d, J = 14.5 Hz), 112.9, 112.8 (d, J = 1.9 Hz), 66.1 (d, J = 31.7 Hz), 41.1, 40.7, 24.4 (d, J = 14.5 Hz), 24.0 (d, J = 4.6 Hz), 18.3 (d, J = 44 Hz), 13.6; IR (neat) 2959, 2364, 1735, 1586, 1518 cm^{-1}; HRMS (ESI MS) *m/z* 523.3427 g/mol [$C_{32}H_{48}N_2O_2P$(M+1) requires 523.3448 g/mol]; mp = 147 ˚C (decomp).



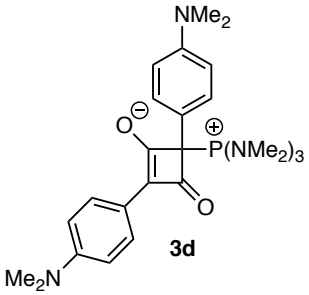
3b

2,4-Bis(4-(dibutylamino)phenyl)-3-oxo-4-(tributylphosphonio)cyclobut-1-en-1-olate (3b). Formation of the squaraine-P(III) adduct was performed on 0.1 mmol scale. Purification by vapor-vapor recrystallization from $CHCl_3$/pentanes provided 69 mg (100%) of **3b** as a pale, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.5 Hz, 2 H), 7.62 (dd, J = 8.9, 2.2 Hz, 2 H), 6.59 (d, J = 8.9 Hz, 2 H), 6.56 (d, J = 8.9 Hz, 2 H), 3.24-3.18 (m, 8 H), 2.09 (comp, 6 H), 1.63-1.57 (m, 6 H), 1.56-1.48 (comp, 8 H), 1.41 (qt, J = 7.4, 7.4 Hz, 6 H), 1.32 (tt, J = 15.3, 7.6 Hz, 8 H), 0.95-0.90 (m, 21 H); ^{13}C NMR (125 MHz) δ 176.2, 176.1, 147.9 (d, J = 1.7 Hz), 14.5, 128.5 (d, J = 3.9 Hz), 125.9, 121.5, 120.7, 114.5, 114.4, 112.2, 112.0, 51.1, 50.9, 29.7, 29.5, 24.5, 24.4, 24.0 (d, J = 4.9 Hz), 20.5 (d, J = 7.6 Hz), 18.5, 18.2, 14.2, (d, J = 3.7 Hz), 13.6; IR (neat) 2957, 1735, 1580, 1514 cm^{-1}; HRMS (ESI MS) *m/z* 691.5312 g/mol [$C_{44}H_{71}N_2O_2P$(M+1) requires 691.5326 g/mol]; mp = 145 ˚C (decomp).



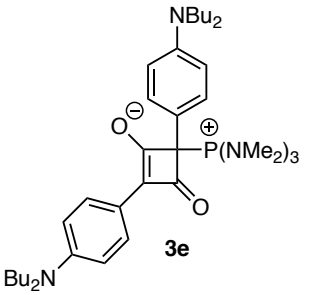
3c

2,4-Bis(4-(dibenzylamino)phenyl)-3-oxo-4-(tributylphosphonio)cyclobut-1-en-1-olate (3c). Formation of the squaraine-P(III) adduct was performed on 0.1 mmol scale. Purification by vapor-vapor recrystallization from $CHCl_3$/pentanes provided 82 mg (100%) of **3c** as a pale, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 2 H), 7.57 (dd, J = 8.9, 2.2 Hz, 2H), 7.31-7.20 (m, 20 H), 6.69 (d, J = 4.3 Hz, 2 H), 6.67 (d, J = 4.5 Hz, 2 H), 4.61 (s, 4 H), 4.56 (s, 4 H), 2.09-2.04 (comp, 6 H), 1.58-1.51 (m, 6 H), 1.40 (qt, J = 7.4, 7.4 Hz, 6 H), 0.90 (t, J = 5.9 Hz, 9 H); ^{13}C NMR (125 MHz) δ 176.1, 176.0, 149.1, 146.4, 139.2, 138.5, 128.9, 128.7, 128.55, 128.51, 127.30, 127.17, 126.9, 125.9, 122.8, 122.4, 114.2, 114.1, 112.89, 112.87, 54.3 (d, J = 14.8 Hz), 24.4 (d, J = 14.7 Hz), 24.0 (d, J = 4.6 Hz), 18.5, 18.2, 13.6; IR (neat) 3061, 2959, 2930, 2871, 2234, 1735, 1579, 1515, 1357, 1228, 954, 909, 817, 730 cm^{-1}; HRMS (ESI MS) *m/z* 827.4676 g/mol [$C_{56}H_{63}N_2O_2P$(M+1) requires 827.4700 g/mol]; mp = 155 ˚C (decomp).



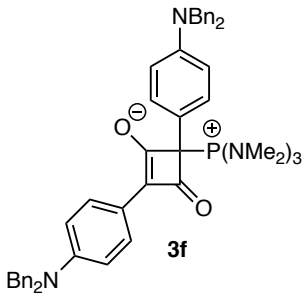
3d

2,4-Bis(4-(dimethylamino)phenyl)-3-oxo-4-(tris(dimethylamino)phosphonio) cyclobut-1-en-1-olate (3d). Formation of the squaraine-P(III) adduct was performed on 0.1 mmol scale. Purification by vapor-vapor recrystallization from $CHCl_3$/pentanes provided 44 mg (91%) of **3d** as pale, yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 6.72 (d, *J* = 8.5 Hz, 2 H), 6.67 (d, *J* = 8.5 Hz, 2 H), 2.91 (s, 6 H) 2.90 (s, 6 H), 2.80 (d, *J* = 9.3 Hz, 18 H); ^{13}C NMR (125 MHz) δ 174.9 (d, *J* = 6.4 Hz), 149.6, 148.0, 128.5, 128.4, 125.8, 123.6, 123.1, 118.2 (d, *J* = 14.6 Hz), 112.9 (d, *J* = 10.3 Hz), 65.7 (d, *J* = 9.8 Hz), 41.1, 40.7, 38.5 (d, *J* = 4.4 Hz); IR (neat) 2987, 2938, 1740, 1582, 1517 cm^{-1}; HRMS (ESI MS) *m/z* 484.2817 g/mol [$C_{26}H_{39}N_5O_2P$(M+1) requires 484.2836 g/mol]; mp = 158 ˚C (decomp).



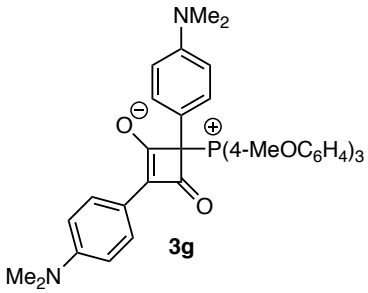
3e

2,4-Bis(4-(dibutylamino)phenyl)-3-oxo-4-(tris(dimethylamino)phosphonio)cyclobut-1-en-1-olate (3e). Formation of the squaraine-P(III) adduct was performed on 0.1 mmol scale. Purification by vapor-vapor recrystallization from $CHCl_3$/pentanes provided 65 mg (100%) of **3e** as a pale, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2 H), 7.33 (dd, *J* = 9.0, 0.9 Hz, 2 H), 6.61 (d, *J* = 9.0 Hz, 2 H), 6.55 (d, *J* = 8.5 Hz, 2 H), 3.25-3.19 (m, 8 H), 2.83 (d, *J* = 9.4 Hz, 18 H), 1.59-1.49 (m, 8 H), 1.37-1.28 (m, 8 H), 0.94 (t, *J* = 7.4 Hz, 6 H), 0.93 (t, *J* = 7.4 Hz, 6 H); ^{13}C NMR (125 MHz) δ 175.0, 174.9, 147.1, 145.3, 128.6 (d, *J* = 8.0 Hz), 126.0, 122.0 (d, *J* = 3.5 Hz), 121.6, 118.7, 118.6, 112.0, 111.9, 51.1, 50.9, 38.6, 38.5, 29.8, 29.6, 20.6, 20.5, 14.3, 14.2; IR (neat) 2930, 1741, 1592, 1514 cm^{-1}; HRMS (ESI MS) *m/z* 652.4713 g/mol [$C_{38}H_{62}N_5O_2P$(M+1) requires 652.4714 g/mol]; mp = 136 ˚C (decomp).



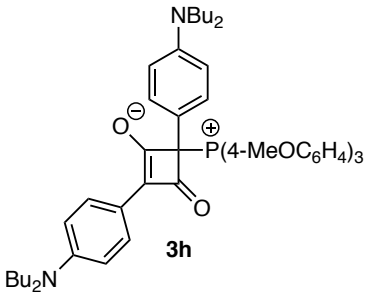
3f

2,4-bis(4-(dibenzylamino)phenyl)-3-oxo-4-(tris(dimethylamino)phosphonio) cyclobut-1-en-1-olate (3f). Formation of the squaraine-P(III) adduct was performed on 0.16 mmol scale. Purification by vapor-vapor recrystallization from $CHCl_3$/pentanes provided 103 mg (82%) of **3f** as pale yellow crystals. ^{1}H NMR (400 MHz) δ 7.72 (d, *J* = 8.2 Hz, 2 H), 7.25 (m, 22 H), 6.74 (d, *J* = 9.0 Hz, 2 H), 6.67 (d, *J* = 8.4 Hz, 2 H), 4.59 (d, *J* = 2.6 Hz, 8 H), 2.81 (d, *J* = 9.3 Hz, 18 H). ^{13}C NMR (100 MHz) δ 174.9 (d, *J* = 6.4 Hz), 148.2, 146.6, 139.3, 138.8, 128.8, 128.7, 128.7, 128.6, 127.2, 127.1, 127.0, 127.0, 126.0 (d, *J* = 1.4 Hz), 123.8 (d, *J* = 4.2 Hz), 123.1, 112.9, 112.8, 76.8, 54.4 (d, *J* = 3.5 Hz), 38.6, 38.5. IR (neat) 3003, 2361, 1740, 1591 cm^{-1}. MS (ESI) *m/z* 787.4003 [$C_{50}H_{54}N_5O_2P$ (M+1) requires 787.4010], mp = 153 ˚C (decomp).



3g

2,4-Bis(4-(dimethylamino)phenyl)-3-oxo-4-(tris(4-methoxyphenyl) phosphonio)cyclobut-1-en-1-olate (3g). Formation of the squaraine-P(III) adduct was performed on 0.1 mmol scale. Purification by vapor-vapor recrystallization from $CHCl_3$/pentanes provided 36 mg (51%) of **3g** a pale, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.69 (comp, 6 H), 7.62 (d, *J* = 8.3 Hz, 2 H), 7.42 (d, *J* = 7.4 Hz, 2 H), 6.96 (d, *J* = 7.0 Hz, 6 H), 6.63 (d, *J* = 8.1 Hz, 2 H), 6.50 (d, *J* = 8.5 Hz, 2 H), 3.83 (s, 9 H), 2.86 (s, 6 H), 2.85 (s, 6 H); ^{13}C NMR (125 MHz) δ 176.1 (d, *J* = 5.1 Hz), 163.7 (d, *J* = 3.2 Hz), 150.0, 137.3 (d, *J* = 11.2 Hz), 135.1 (d, *J* = 20.5 Hz), 130.3 (d, *J* = 4.6 Hz), 125.8, 122.4, 115.0 (d, *J* = 13.1 Hz), 114.3 (d, *J* = 7.3 Hz), 112.9, 112.2, 111.5, 110.8, 68.1 (d, *J* = 4.4 Hz), 55.7, 41.2, 40.6; IR (neat) 2957, 2234, 1736, 1584, 1517 cm^{-1}; HRMS (ESI MS) *m/z* 673.2796 g/mol [$C_{41}H_{42}N_2O_2P$(M+1) requires 673.2826 g/mol]; mp = 151 ˚C (decomp).



3h

Variable temperature monitoring in the synthesis of 2,4-bis(4-(dibutylamino)phenyl)-3-oxo-4-(tris(4-methoxyphenyl)phosphonio)cyclobut-1-en-1-olate (3h). Squaraine **2b** (4.4 mg, 7.0 μmol) and tris(4-methoxyphenyl)phosphine (2.7 mg, 7.7 μmol) were added sequentially to an NMR tube and then dissolved in $CDCl_3$ (0.7 mL). Variable temperature ^{1}H NMR was used to monitor reaction progress (50 ˚C to –40 ˚C), which revealed complete conversion of **2b** to **3h** at –40 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$, –40 ˚C) δ 7.70 (t, *J* = 9.5 Hz, 6 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.37 (dd, *J* = 8.9, 2.0 Hz, 2 H), 7.00 (d, *J* = 6.9 Hz, 6 H), 6.50 (d, *J* = 9.0 Hz, 2 H) 6.39 (d, *J* = 9.0 Hz, 2 H), 3.88 (s, 9 H), 3.17 (comp, 8 H), 1.48 (comp, 8 H), 1.28 (comp, 8 H), 0.91 (comp, 12 H); ^{13}C NMR (125 MHz) δ 176.1 (d, *J* = 5.6 Hz), 163.0 (d, *J* = 2.6 Hz), 146.6, 144.5, 136.8 (d, *J* = 10.4 Hz), 130.0 (4.1 Hz), 125.5, 120.4, 119.6, 116.5 (d, *J* = 16 Hz), 114.5 (d, *J* = 13.1 Hz), 110.6, 110.4, 109.7, 69.9 (d, *J* = 29.9 Hz), 55.5, 50.5, 50.4, 29.0, 28.8, 20.3, 20.2, 14.2, 14.1.

Titrations of squaraine-phosphine complex 3b with transition metal complexes. A $3x10^{-3}$ M solution of P^{n}Bu$_3$ (12 mmol) in DMSO (4 mL) was added slowly to a $3x10^{-3}$ M solution of **1c** (12 mmol) in DMSO (4 mL) at room temperature and stirred for 15 min resulting in a $1.5x10^{-3}$ M stock solution of zwitterion **3b**. Separately, $1.5x10^{-2}$ M solutions of $Pd(OAc)_2$, $[Ir(cod)Cl]_2$, $Rh(PPh_3)_3Cl$, and $Au(PPh_3)Cl$ were prepared by dissolving 0.03 mmol of the corresponding transition metal complex in 2 mL of DMSO.

A 1 mL aliquot of the stock solution containing **3b** was placed in a glass cuvet, and the absorbance measured. A 10 uL aliquot (0.1 eq) of the requisite transition metal complex in DMSO was added to the cuvet, placed on a shaking plate, and mixed for five minutes to ensure equilibration. The absorbance was measured again, and the process was repeated until a total of 1.5 equivalents of the metal had been added to the zwitterion solution.

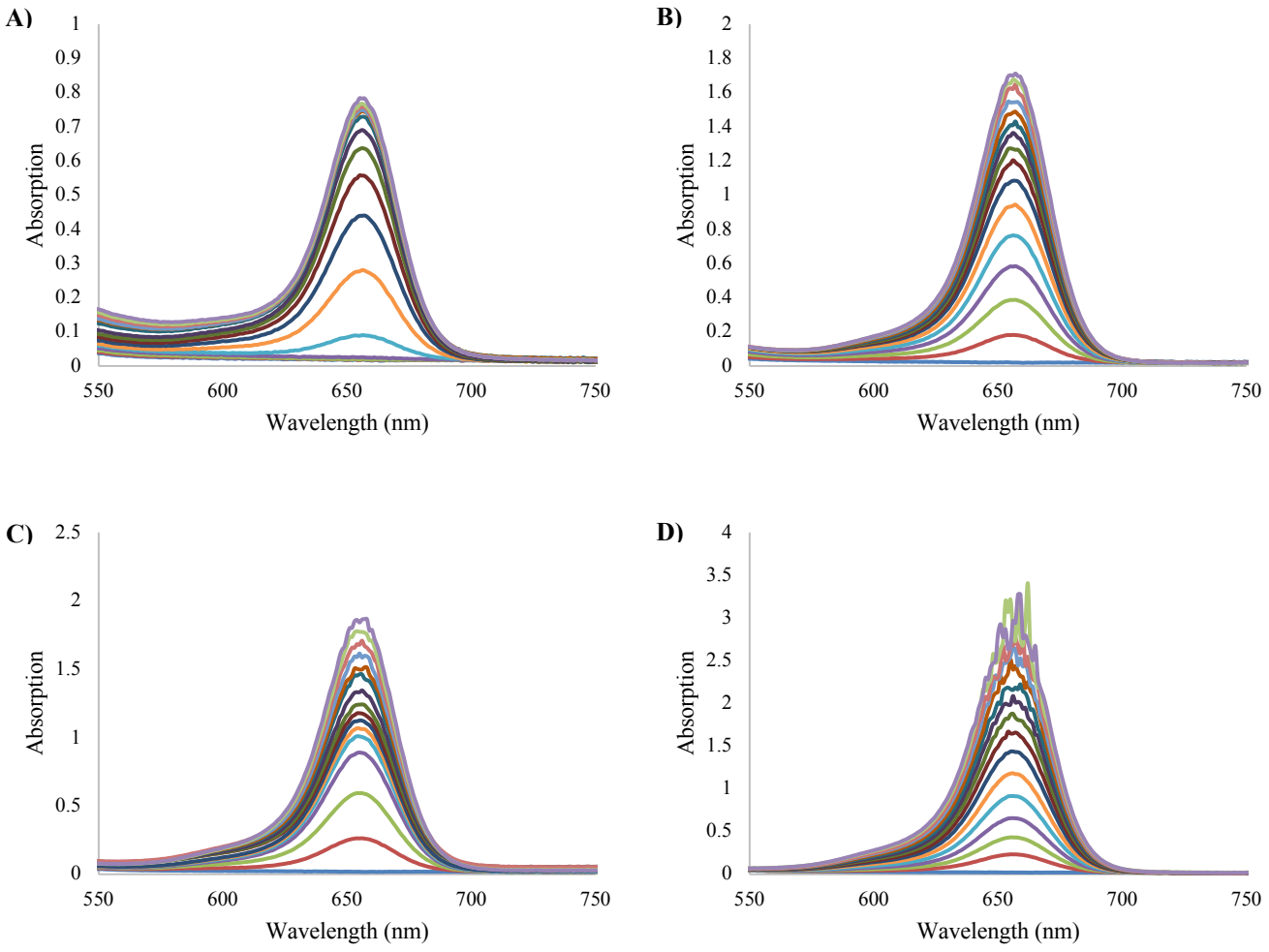


Figure S1. UV-Vis absorption spectra of titrations performed on a 1.5 x 10^{-3} M solution of **3b** in DMSO with **A)** $Rh(PPh_3)_3Cl$, **B)** $Pd(OAc)_2$, **C)** $[Ir(cod)Cl]_2$, and **D)** $Au(PPh_3)Cl$. Absorbance of regenerated squaraine **2b** measured at 656 nm.

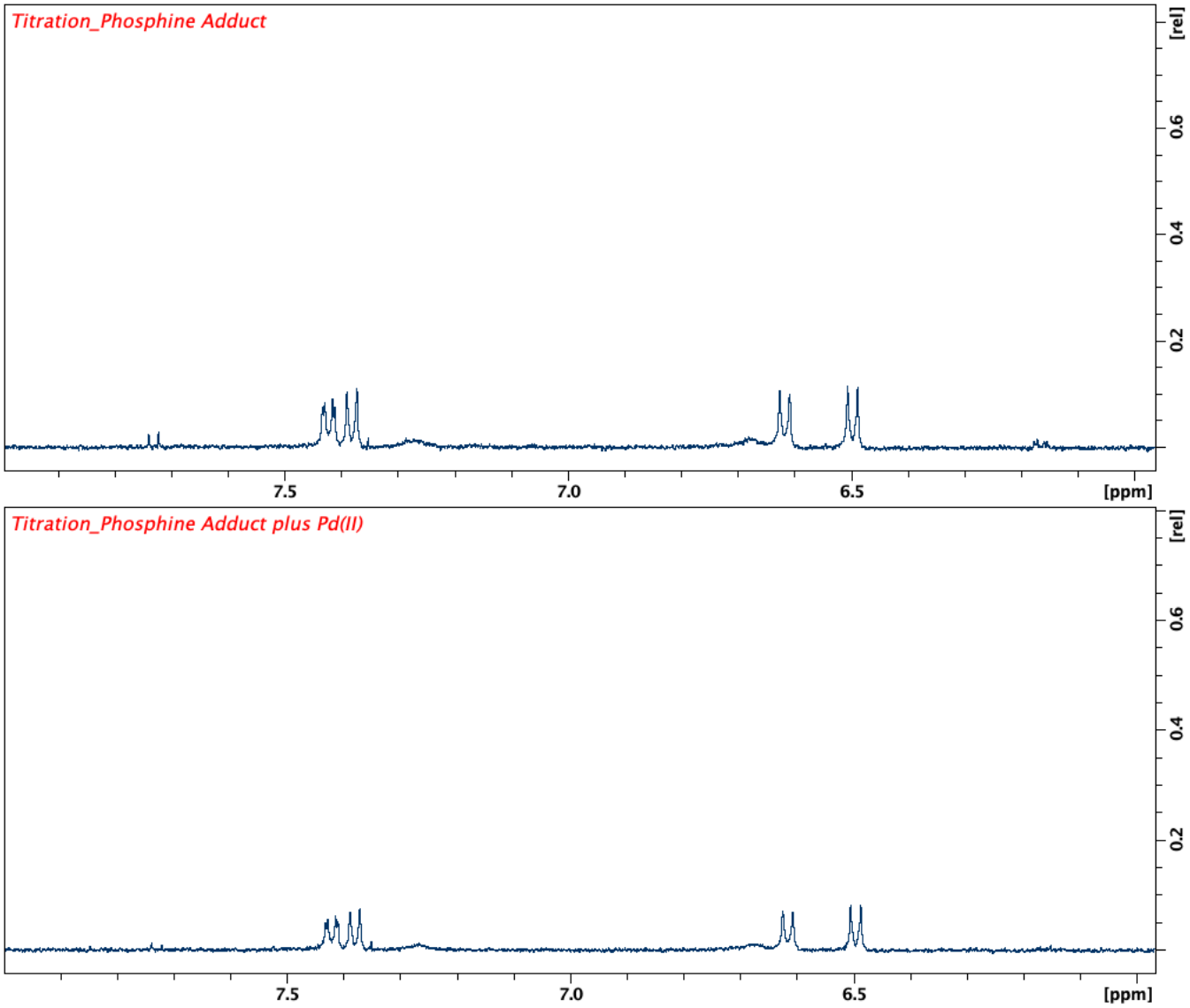
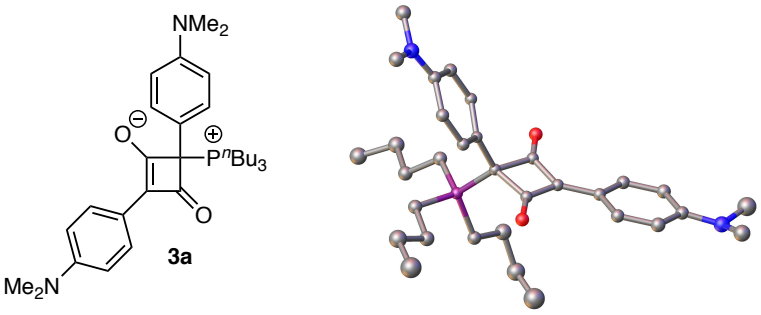


Figure S2. ^{1}H NMR spectra of a 1.5 x 10^{-3} M solution of **3b** in DMSO before (top) and after (bottom) addition of 1.5 molar equivalents of $Pd(OAc)_2$.

3. CRYSTAL SUMMARY FOR COMPOUND 3A



Crystal data for $C_{34}H_{49}Cl_6N_2O_2P$; M_r = 761.42; Monoclinic; space group $P2_1/n$; a = 12.7361(9) Å; b = 17.3444(12) Å; c = 17.9512(12) Å; α = 90°; β = 99.4550(10)°; γ = 90°; V = 3911.5(5) Å^3; Z = 4; T = 120(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 0.512 mm^{-1}; d_{calc} = 1.293g.cm^{-3}; 79630 reflections collected; 8013 unique (R_{int} = 0.0305); giving R_1 = 0.0381, wR_2 = 0.0971 for 6751 data with [I>2σ(I)] and R_1 = 0.0471, wR_2 = 0.1037 for all 8013 data. Residual electron density (e$^-$.Å^{-3}) max/min: 0.660/-0.720.

An arbitrary sphere of data were collected on a colorless block-like crystal, having approximate dimensions of 0.316 × 0.152 × 0.100 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by intrinsic phasing methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

TABLE 1: CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **3a**.

Identification code	al6nme	
Empirical formula	$C_{34}H_{49}Cl_6N_2O_2P$	
Formula weight	761.42	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.7361(9) Å	α = 90°
	b = 17.3444(12) Å	β = 99.4550(10)°
	c = 17.9512(12) Å	γ = 90°
Volume	3911.5(5) Å^3	
Z	4	
Density (calculated)	1.293 g.cm^{-3}	
Absorption coefficient (μ)	0.512 mm^{-1}	
F(000)	1600	
Crystal color, habit	colorless, block	
Crystal size	0.316 × 0.152 × 0.100 mm^3	
θ range for data collection	1.643 to 26.476°	
Index ranges	-15 ≤ h ≤ 15, -21 ≤ k ≤ 21, -22 ≤ l ≤ 22	

Reflections collected	79630
Independent reflections	8013 [R_{int} = 0.0305]
Completeness to θ = 25.242°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.9276 and 0.8075
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8013 / 0 / 413
Goodness-of-fit on F^2	1.050
Final R indices [I>2σ(I)]	R_1 = 0.0381, wR_2 = 0.0971
R indices (all data)	R_1 = 0.0471, wR_2 = 0.1037
Extinction coefficient	n/a
Largest diff. peak and hole	0.660 and -0.720 $e^{-}.Å^{-3}$

TABLE 2: ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2$) FOR **3a**.

	x	y	z	U(eq)
P(1)	0.22018(3)	0.42804(2)	0.69645(2)	0.020(1)
O(1)	0.18410(9)	0.32367(7)	0.53220(7)	0.025(1)
O(2)	0.46332(9)	0.32110(7)	0.72334(7)	0.024(1)
N(1)	0.39802(13)	-0.05524(9)	0.57857(9)	0.032(1)
N(2)	0.47928(12)	0.65466(9)	0.51208(9)	0.031(1)
C(1)	0.31113(12)	0.38832(9)	0.63756(9)	0.020(1)
C(2)	0.38543(12)	0.32048(9)	0.67214(9)	0.020(1)
C(3)	0.33087(12)	0.26553(9)	0.62208(9)	0.021(1)
C(4)	0.25869(12)	0.32115(9)	0.58523(9)	0.020(1)
C(5)	0.34748(13)	0.18367(9)	0.61013(9)	0.021(1)
C(6)	0.44058(13)	0.14663(10)	0.64468(9)	0.023(1)
C(7)	0.45848(13)	0.06937(10)	0.63267(10)	0.025(1)
C(8)	0.38273(14)	0.02414(10)	0.58637(10)	0.025(1)
C(9)	0.28989(14)	0.06133(10)	0.55125(10)	0.026(1)
C(10)	0.27315(13)	0.13905(10)	0.56282(10)	0.024(1)
C(11)	0.50687(16)	-0.08444(11)	0.59259(12)	0.036(1)
C(12)	0.32580(18)	-0.09639(12)	0.52115(13)	0.043(1)
C(13)	0.36088(12)	0.45405(9)	0.60061(9)	0.019(1)
C(14)	0.45760(13)	0.48654(10)	0.63417(9)	0.022(1)
C(15)	0.49883(13)	0.55116(10)	0.60392(9)	0.023(1)
C(16)	0.44380(13)	0.58707(10)	0.53879(10)	0.023(1)
C(17)	0.34956(13)	0.55143(10)	0.50274(9)	0.022(1)
C(18)	0.30946(12)	0.48690(9)	0.53352(9)	0.021(1)
C(19)	0.57681(14)	0.68946(10)	0.54937(10)	0.027(1)
C(20)	0.42016(14)	0.69077(11)	0.44584(11)	0.029(1)
C(21)	0.28582(13)	0.50176(10)	0.75753(10)	0.025(1)
C(22)	0.37815(14)	0.47002(11)	0.81549(10)	0.028(1)
C(23)	0.45634(16)	0.53266(12)	0.84642(13)	0.041(1)
C(24)	0.55212(19)	0.49979(15)	0.89833(16)	0.059(1)
C(25)	0.10767(13)	0.46912(11)	0.63516(10)	0.026(1)

C(26)	0.02791(13)	0.51056(11)	0.67599(10)	0.027(1)
C(27)	-0.07122(14)	0.53541(12)	0.62235(11)	0.032(1)
C(28)	-0.14456(16)	0.58562(13)	0.66034(12)	0.039(1)
C(29)	0.17601(13)	0.35537(10)	0.75525(10)	0.025(1)
C(30)	0.09566(15)	0.29677(12)	0.71528(11)	0.034(1)
C(31)	0.06416(17)	0.23843(12)	0.77100(13)	0.041(1)
C(32)	0.1586(2)	0.19785(14)	0.81579(16)	0.057(1)
C(33)	0.46415(15)	0.23034(11)	0.97055(12)	0.034(1)
Cl(1)	0.45058(5)	0.30992(4)	1.02874(4)	0.060(1)
Cl(2)	0.36946(4)	0.15921(3)	0.98276(3)	0.044(1)
Cl(3)	0.45101(4)	0.25868(3)	0.87564(3)	0.045(1)
C(34)	0.70530(17)	0.32080(14)	0.76435(14)	0.048(1)
Cl(4)	0.73544(4)	0.31794(4)	0.86288(4)	0.054(1)
Cl(5)	0.75980(6)	0.24079(5)	0.72433(4)	0.076(1)
Cl(6)	0.75122(7)	0.40697(5)	0.72979(5)	0.094(1)
H(6)	0.4927	0.1753	0.6772	0.028
H(7)	0.5232	0.0464	0.6562	0.030
H(9)	0.2375	0.0327	0.5189	0.031
H(10)	0.2096	0.1626	0.5380	0.029
H(11A)	0.5385	-0.0745	0.6452	0.055
H(11B)	0.5489	-0.0584	0.5590	0.055
H(11C)	0.5064	-0.1401	0.5830	0.055
H(12A)	0.2525	-0.0893	0.5299	0.065
H(12B)	0.3435	-0.1514	0.5236	0.065
H(12C)	0.3327	-0.0762	0.4712	0.065
H(14A)	0.4959	0.4638	0.6786	0.026
H(15A)	0.5653	0.5715	0.6275	0.028
H(17A)	0.3131	0.5720	0.4566	0.027
H(18A)	0.2453	0.4644	0.5084	0.025
H(19A)	0.5711	0.7002	0.6022	0.041
H(19B)	0.5892	0.7377	0.5238	0.041
H(19C)	0.6363	0.6541	0.5475	0.041
H(20A)	0.3468	0.6998	0.4536	0.044
H(20B)	0.4200	0.6570	0.4021	0.044
H(20C)	0.4535	0.7401	0.4368	0.044
H(21A)	0.3136	0.5416	0.7264	0.031
H(21B)	0.2333	0.5267	0.7847	0.031
H(22A)	0.3491	0.4458	0.8577	0.034
H(22B)	0.4160	0.4297	0.7913	0.034
H(23A)	0.4201	0.5706	0.8746	0.049
H(23B)	0.4807	0.5599	0.8039	0.049
H(24A)	0.6027	0.5413	0.9151	0.089
H(24B)	0.5867	0.4609	0.8711	0.089
H(24C)	0.5288	0.4760	0.9424	0.089
H(25A)	0.1343	0.5061	0.6006	0.031
H(25B)	0.0701	0.4274	0.6039	0.031
H(26A)	0.0071	0.4758	0.7148	0.033
H(26B)	0.0623	0.5566	0.7020	0.033
H(27A)	-0.0497	0.5643	0.5797	0.038

H(27B)	-0.1106	0.4890	0.6014	0.038
H(28A)	-0.2074	0.5995	0.6236	0.058
H(28B)	-0.1068	0.6326	0.6797	0.058
H(28C)	-0.1668	0.5572	0.7023	0.058
H(29A)	0.2392	0.3268	0.7807	0.030
H(29B)	0.1436	0.3813	0.7950	0.030
H(30A)	0.0314	0.3243	0.6901	0.040
H(30B)	0.1273	0.2694	0.6760	0.040
H(31A)	0.0243	0.2652	0.8063	0.049
H(31B)	0.0161	0.1996	0.7430	0.049
H(32A)	0.1339	0.1547	0.8436	0.085
H(32B)	0.1987	0.2341	0.8516	0.085
H(32C)	0.2048	0.1784	0.7814	0.085
H(33)	0.5369	0.2080	0.9861	0.041
H(34)	0.6262	0.3189	0.7495	0.058

TABLE 3: ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2$) FOR **3a**.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	0.0181(2)	0.0224(2)	0.0204(2)	0.0000(2)	0.0026(2)	0.0009(2)
O(1)	0.0205(6)	0.0273(6)	0.0248(6)	0.0002(5)	-0.0019(5)	-0.0009(5)
O(2)	0.0199(5)	0.0272(6)	0.0229(6)	0.0004(5)	-0.0014(5)	0.0020(5)
N(1)	0.0330(8)	0.0223(8)	0.0408(9)	-0.0031(7)	0.0048(7)	0.0030(6)
N(2)	0.0296(8)	0.0281(8)	0.0341(8)	0.0087(7)	0.0005(6)	-0.0067(6)
C(1)	0.0166(7)	0.0214(8)	0.0201(8)	-0.0001(6)	0.0011(6)	0.0011(6)
C(2)	0.0182(7)	0.0214(8)	0.0206(8)	0.0025(6)	0.0046(6)	0.0014(6)
C(3)	0.0198(7)	0.0228(8)	0.0205(8)	0.0018(6)	0.0031(6)	-0.0001(6)
C(4)	0.0186(7)	0.0223(8)	0.0200(8)	-0.0004(6)	0.0053(6)	-0.0027(6)
C(5)	0.0215(8)	0.0222(8)	0.0195(8)	0.0025(6)	0.0038(6)	0.0000(6)
C(6)	0.0229(8)	0.0239(8)	0.0219(8)	0.0018(7)	0.0008(6)	-0.0022(6)
C(7)	0.0230(8)	0.0256(9)	0.0261(9)	0.0051(7)	0.0024(7)	0.0031(7)
C(8)	0.0266(8)	0.0224(8)	0.0264(9)	0.0026(7)	0.0074(7)	0.0008(7)
C(9)	0.0244(8)	0.0247(9)	0.0282(9)	-0.0027(7)	0.0015(7)	-0.0026(7)
C(10)	0.0221(8)	0.0253(9)	0.0251(8)	0.0008(7)	0.0015(6)	0.0016(7)
C(11)	0.0366(10)	0.0283(10)	0.0453(12)	0.0030(8)	0.0102(9)	0.0095(8)
C(12)	0.0473(12)	0.0270(10)	0.0538(13)	-0.0112(9)	0.0021(10)	0.0010(9)
C(13)	0.0180(7)	0.0197(8)	0.0211(8)	-0.0015(6)	0.0045(6)	0.0018(6)
C(14)	0.0202(7)	0.0232(8)	0.0214(8)	0.0003(6)	0.0031(6)	0.0026(6)
C(15)	0.0191(7)	0.0248(8)	0.0252(8)	-0.0016(7)	0.0032(6)	-0.0014(6)
C(16)	0.0216(8)	0.0228(8)	0.0259(8)	0.0009(7)	0.0068(7)	0.0009(6)
C(17)	0.0214(8)	0.0247(8)	0.0210(8)	0.0016(6)	0.0032(6)	0.0029(6)
C(18)	0.0179(7)	0.0225(8)	0.0224(8)	-0.0030(6)	0.0029(6)	0.0007(6)
C(19)	0.0286(9)	0.0246(9)	0.0293(9)	-0.0020(7)	0.0079(7)	-0.0047(7)
C(20)	0.0286(9)	0.0276(9)	0.0325(10)	0.0077(7)	0.0075(7)	0.0008(7)
C(21)	0.0251(8)	0.0245(8)	0.0270(9)	-0.0039(7)	0.0049(7)	0.0001(7)
C(22)	0.0271(9)	0.0291(9)	0.0275(9)	-0.0062(7)	-0.0001(7)	0.0004(7)
C(23)	0.0297(10)	0.0362(11)	0.0528(13)	-0.0180(10)	-0.0046(9)	0.0014(8)
C(24)	0.0413(13)	0.0530(15)	0.0726(17)	-0.0232(13)	-0.0212(12)	0.0060(11)

C(25)	0.0226(8)	0.0315(9)	0.0230(8)	0.0008(7)	0.0023(7)	0.0059(7)
C(26)	0.0232(8)	0.0331(9)	0.0251(9)	-0.0007(7)	0.0029(7)	0.0056(7)
C(27)	0.0261(9)	0.0374(10)	0.0302(9)	0.0000(8)	0.0005(7)	0.0088(8)
C(28)	0.0287(9)	0.0453(12)	0.0404(11)	-0.0001(9)	0.0017(8)	0.0143(8)
C(29)	0.0232(8)	0.0269(9)	0.0245(8)	0.0017(7)	0.0057(7)	-0.0022(7)
C(30)	0.0291(9)	0.0372(10)	0.0352(10)	-0.0016(8)	0.0059(8)	-0.0114(8)
C(31)	0.0423(11)	0.0368(11)	0.0469(12)	-0.0048(9)	0.0193(10)	-0.0169(9)
C(32)	0.0644(16)	0.0359(12)	0.0712(17)	0.0195(12)	0.0145(13)	-0.0137(11)
C(33)	0.0265(9)	0.0289(10)	0.0459(11)	0.0058(8)	-0.0012(8)	0.0017(7)
Cl(1)	0.0574(4)	0.0430(3)	0.0737(4)	-0.0172(3)	-0.0063(3)	0.0062(3)
Cl(2)	0.0422(3)	0.0370(3)	0.0541(3)	0.0089(2)	0.0113(2)	-0.0062(2)
Cl(3)	0.0313(2)	0.0524(3)	0.0507(3)	0.0193(2)	0.0032(2)	-0.0015(2)
C(34)	0.0269(10)	0.0581(14)	0.0557(14)	0.0185(11)	-0.0066(9)	-0.0048(9)
Cl(4)	0.0357(3)	0.0698(4)	0.0539(3)	0.0141(3)	-0.0021(2)	0.0050(3)
Cl(5)	0.0602(4)	0.1001(6)	0.0679(5)	0.0089(4)	0.0107(3)	0.0270(4)
Cl(6)	0.0880(6)	0.0933(6)	0.0838(5)	0.0474(5)	-0.0352(4)	-0.0511(5)

TABLE 4: BOND LENGTHS [Å] FOR **3a.**

atom-atom	distance	atom-atom	distance
P(1)-C(29)	1.7928(17)	P(1)-C(21)	1.7985(17)
P(1)-C(25) 1	.8038(17)	P(1)-C(1)	1.8266(16) O(1)-C(4)
1.230(2) O(2)-C(2)		1.237(2)	
N(1)-C(8)	1.401(2)	N(1)-C(12)	1.451(3)
N(1)-C(11)	1.459(2)	N(2)-C(16)	1.371(2)
N(2)-C(20)	1.442(2)	N(2)-C(19)	1.443(2)
C(1)-C(13)	1.510(2)	C(1)-C(2)	1.572(2)
C(1)-C(4)	1.575(2)	C(2)-C(3)	1.412(2)
C(3)-C(4)	1.419(2)	C(3)-C(5)	1.456(2)
C(5)-C(10)	1.397(2)	C(5)-C(6)	1.401(2)
C(6)-C(7)	1.382(2)	C(6)-H(6)	0.9500
C(7)-C(8)	1.405(2)	C(7)-H(7)	0.9500
C(8)-C(9)	1.402(2)	C(9)-C(10)	1.386(2)
C(9)-H(9)	0.9500	C(10)-H(10)	0.9500
C(11)-H(11A)	0.9800	C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-C(18)	1.394(2) C(13)-C(14)	1.398(2) C(14)-C(15)	1.386(2)
C(14)-H(14A)	0.9500		
C(15)-C(16)	1.406(2) C(15)-H(15A)	0.9500	
C(16)-C(17)	1.409(2) C(17)-C(18)	1.383(2) C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500		
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800	C(20)-H(20C)	0.9800
C(21)-C(22)	1.538(2) C(21)-H(21A)	0.9900	
C(21)-H(21B)	0.9900	C(22)-C(23)	1.516(3) C(22)-H(22A)
0.9900 C(22)-H(22B)	0.9900		

C(23)-C(24)	1.519(3)	C(23)-H(23A)	0.9900		
C(23)-H(23B)	0.9900	C(24)-H(24A)	0.9800		
C(24)-H(24B)	0.9800	C(24)-H(24C)	0.9800		
C(25)-C(26)	1.526(2)	C(25)-H(25A)	0.9900		
C(25)-H(25B)	0.9900	C(26)-C(27)	1.519(2)	C(26)-H(26A)	
0.9900	C(26)-H(26B)	0.9900			
C(27)-C(28)	1.518(3)	C(27)-H(27A)	0.9900		
C(27)-H(27B)	0.9900	C(28)-H(28A)	0.9800		
C(28)-H(28B)	0.9800	C(28)-H(28C)	0.9800		
C(29)-C(30)	1.534(2)	C(29)-H(29A)	0.9900		
C(29)-H(29B)	0.9900	C(30)-C(31)	1.522(3)	C(30)-H(30A)	
0.9900	C(30)-H(30B)	0.9900			
C(31)-C(32)	1.507(3)	C(31)-H(31A)	0.9900		
C(31)-H(31B)	0.9900	C(32)-H(32A)	0.9800		
C(32)-H(32B)	0.9800	C(32)-H(32C)	0.9800		
C(33)-Cl(3)	1.755(2)	C(33)-Cl(1)	1.756(2)	C(33)-Cl(2)	
1.764(2)	C(33)-H(33)	1.0000			
C(34)-Cl(4)	1.748(3)	C(34)-Cl(6)	1.755(2)	C(34)-Cl(5)	
1.757(3)	C(34)-H(34)	1.0000			

TABLE 5: BOND ANGLES [˚] FOR **3a.**

atom-atom-atom	angle	atom-atom-atom	angle
C(29)-P(1)-C(21)	107.48(8)	C(29)-P(1)-C(25)	110.01(8)
C(21)-P(1)-C(25)	109.52(8)	C(29)-P(1)-C(1)	111.45(8)
C(21)-P(1)-C(1)	110.21(8)	C(25)-P(1)-C(1)	108.16(8)
C(8)-N(1)-C(12)	118.17(16)	C(8)-N(1)-C(11)	117.90(15)
C(12)-N(1)-C(11)	115.17(16)	C(16)-N(2)-C(20)	120.16(15)
C(16)-N(2)-C(19)	120.23(15)	C(20)-N(2)-C(19)	119.60(15)
C(13)-C(1)-C(2)	118.02(13)	C(13)-C(1)-C(4)	117.66(13)
C(2)-C(1)-C(4)	81.42(11)	C(13)-C(1)-P(1)	108.74(11)
C(2)-C(1)-P(1)	116.83(11)	C(4)-C(1)-P(1)	112.16(10)
O(2)-C(2)-C(3)	136.85(15)	O(2)-C(2)-C(1)	130.11(15)
C(3)-C(2)-C(1)	93.01(13)	C(2)-C(3)-C(4)	92.93(13)
C(2)-C(3)-C(5)	133.13(15)	C(4)-C(3)-C(5)	133.84(15)
O(1)-C(4)-C(3)	138.04(16)	O(1)-C(4)-C(1)	129.30(15)
C(3)-C(4)-C(1)	92.64(13)	C(10)-C(5)-C(6)	117.05(15)
C(10)-C(5)-C(3)	121.95(15)	C(6)-C(5)-C(3)	120.98(15)
C(7)-C(6)-C(5)	121.67(16)	C(7)-C(6)-H(6)	119.2
C(5)-C(6)-H(6)	119.2	C(6)-C(7)-C(8)	121.25(15)
C(6)-C(7)-H(7)	119.4	C(8)-C(7)-H(7)	119.4
N(1)-C(8)-C(9)	121.87(16)	N(1)-C(8)-C(7)	120.98(16)
C(9)-C(8)-C(7)	117.09(16)	C(10)-C(9)-C(8)	121.28(16)
C(10)-C(9)-H(9)	119.4	C(8)-C(9)-H(9)	119.4
C(9)-C(10)-C(5)	121.63(16)	C(9)-C(10)-H(10)	119.2
C(5)-C(10)-H(10)	119.2	N(1)-C(11)-H(11A)	109.5
N(1)-C(11)-H(11B)	109.5	H(11A)-C(11)-H(11B)	109.5

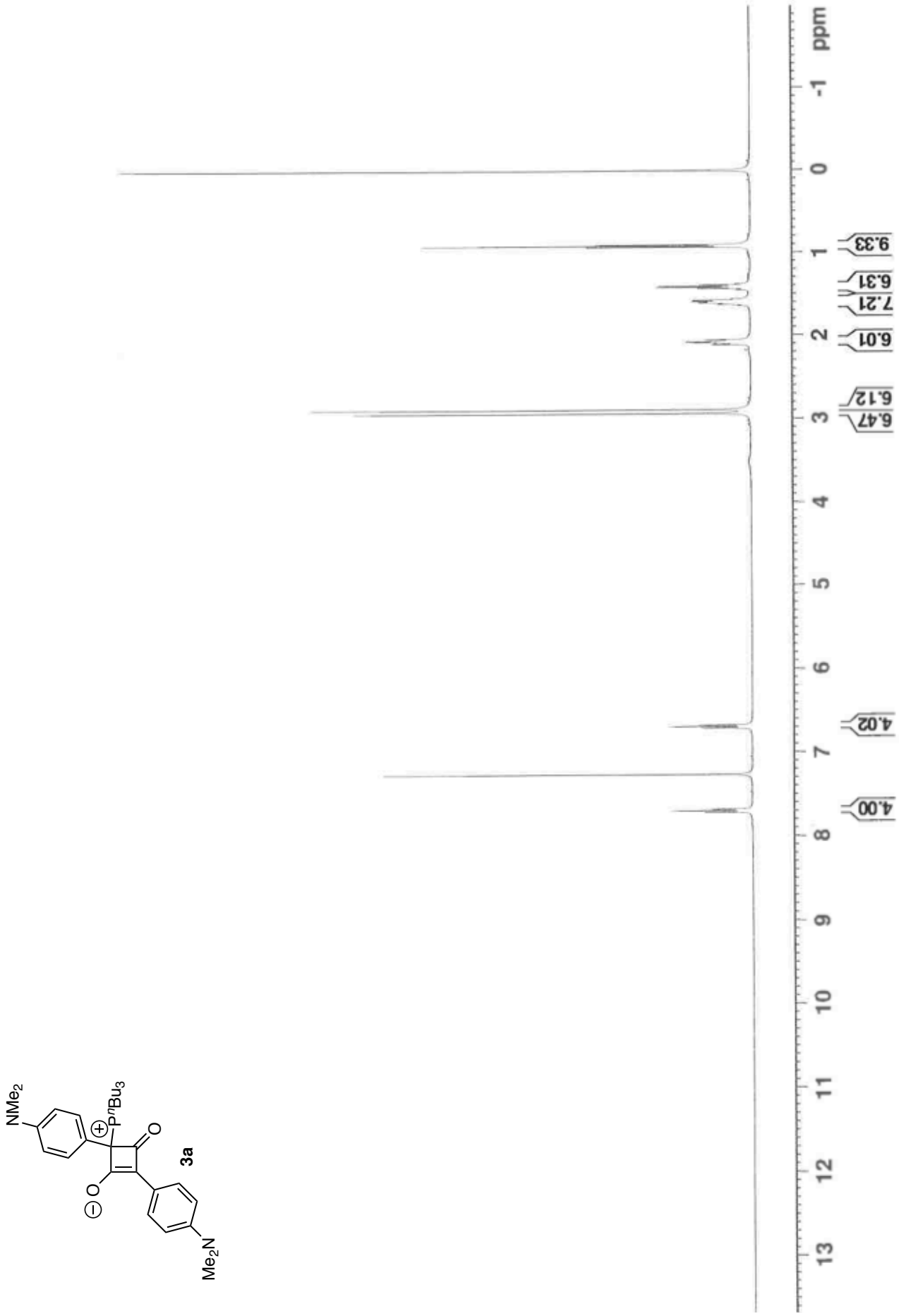
N(1)-C(11)-H(11C)	109.5	H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5	N(1)-C(12)-H(12A)	109.5
N(1)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
N(1)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(18)-C(13)-C(14)	117.59(15)
C(18)-C(13)-C(1)	121.09(14)	C(14)-C(13)-C(1)	121.26(14)
C(15)-C(14)-C(13)	121.40(15)	C(15)-C(14)-H(14A)	119.3
C(13)-C(14)-H(14A)	119.3	C(14)-C(15)-C(16)	120.99(15)
C(14)-C(15)-H(15A)	119.5	C(16)-C(15)-H(15A)	119.5
N(2)-C(16)-C(15)	121.45(15)	N(2)-C(16)-C(17)	121.27(15)
C(15)-C(16)-C(17)	117.27(15)	C(18)-C(17)-C(16)	120.93(15)
C(18)-C(17)-H(17A)	119.5	C(16)-C(17)-H(17A)	119.5
C(17)-C(18)-C(13)	121.60(15)	C(17)-C(18)-H(18A)	119.2
C(13)-C(18)-H(18A)	119.2	N(2)-C(19)-H(19A)	109.5
N(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
N(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	N(2)-C(20)-H(20A)	109.5
N(2)-C(20)-H(20B)	109.5	H(20A)-C(20)-H(20B)	109.5
N(2)-C(20)-H(20C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5	C(22)-C(21)-P(1)	112.64(12)
C(22)-C(21)-H(21A)	109.1	P(1)-C(21)-H(21A)	109.1
C(22)-C(21)-H(21B)	109.1	P(1)-C(21)-H(21B)	109.1
H(21A)-C(21)-H(21B)	107.8	C(23)-C(22)-C(21)	111.98(16)
C(23)-C(22)-H(22A)	109.2	C(21)-C(22)-H(22A)	109.2
C(23)-C(22)-H(22B)	109.2	C(21)-C(22)-H(22B)	109.2
H(22A)-C(22)-H(22B)	107.9	C(22)-C(23)-C(24)	111.63(18)
C(22)-C(23)-H(23A)	109.3	C(24)-C(23)-H(23A)	109.3
C(22)-C(23)-H(23B)	109.3	C(24)-C(23)-H(23B)	109.3
H(23A)-C(23)-H(23B)	108.0	C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5	C(26)-C(25)-P(1)	114.69(12)
C(26)-C(25)-H(25A)	108.6	P(1)-C(25)-H(25A)	108.6
C(26)-C(25)-H(25B)	108.6	P(1)-C(25)-H(25B)	108.6
H(25A)-C(25)-H(25B)	107.6	C(27)-C(26)-C(25)	112.25(14)
C(27)-C(26)-H(26A)	109.2	C(25)-C(26)-H(26A)	109.2
C(27)-C(26)-H(26B)	109.2	C(25)-C(26)-H(26B)	109.2
H(26A)-C(26)-H(26B)	107.9	C(28)-C(27)-C(26)	112.75(15)
C(28)-C(27)-H(27A)	109.0	C(26)-C(27)-H(27A)	109.0
C(28)-C(27)-H(27B)	109.0	C(26)-C(27)-H(27B)	109.0
H(27A)-C(27)-H(27B)	107.8	C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5	H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5	H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5	C(30)-C(29)-P(1)	116.12(13)
C(30)-C(29)-H(29A)	108.3	P(1)-C(29)-H(29A)	108.3
C(30)-C(29)-H(29B)	108.3	P(1)-C(29)-H(29B)	108.3
H(29A)-C(29)-H(29B)	107.4	C(31)-C(30)-C(29)	111.14(16)
C(31)-C(30)-H(30A)	109.4	C(29)-C(30)-H(30A)	109.4
C(31)-C(30)-H(30B)	109.4	C(29)-C(30)-H(30B)	109.4

H(30A)-C(30)-H(30B)	108.0	C(32)-C(31)-C(30)	112.79(17)
C(32)-C(31)-H(31A)	109.0	C(30)-C(31)-H(31A)	109.0
C(32)-C(31)-H(31B)	109.0	C(30)-C(31)-H(31B)	109.0
H(31A)-C(31)-H(31B)	107.8	C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5	H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5	H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5	Cl(3)-C(33)-Cl(1)	110.75(11)
Cl(3)-C(33)-Cl(2)	111.01(11)	Cl(1)-C(33)-Cl(2)	109.85(11)
Cl(3)-C(33)-H(33)	108.4	Cl(1)-C(33)-H(33)	108.4
Cl(2)-C(33)-H(33)	108.4	Cl(4)-C(34)-Cl(6)	110.57(14)
Cl(4)-C(34)-Cl(5)	110.82(12)	Cl(6)-C(34)-Cl(5)	110.55(14)
Cl(4)-C(34)-H(34)	108.3	Cl(6)-C(34)-H(34)	108.3
Cl(5)-C(34)-H(34)	108.3		

TABLE 6: TORSION ANGLES [°] FOR **3a**.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(29)-P(1)-C(1)-C(13)	-169.62(11)	C(21)-P(1)-C(1)-C(13)	-50.38(13)
C(25)-P(1)-C(1)-C(13)	69.33(12)	C(29)-P(1)-C(1)-C(2)	-32.95(14)
C(21)-P(1)-C(1)-C(2)	86.30(13)	C(25)-P(1)-C(1)-C(2)	-154.00(12)
C(29)-P(1)-C(1)-C(4)	58.51(13)	C(21)-P(1)-C(1)-C(4)	177.76(11)
C(25)-P(1)-C(1)-C(4)	-62.54(13)	C(13)-C(1)-C(2)-O(2)	61.1(2)
C(4)-C(1)-C(2)-O(2)	177.96(17)	P(1)-C(1)-C(2)-O(2)	-71.5(2)
C(13)-C(1)-C(2)-C(3)	-117.26(15)	C(4)-C(1)-C(2)-C(3)	-0.42(12)
P(1)-C(1)-C(2)-C(3)	110.13(12)	O(2)-C(2)-C(3)-C(4)	-177.7(2)
C(1)-C(2)-C(3)-C(4)	0.47(13)	O(2)-C(2)-C(3)-C(5)	-1.1(3)
C(1)-C(2)-C(3)-C(5)	177.05(18)	C(2)-C(3)-C(4)-O(1)	177.7(2)
C(5)-C(3)-C(4)-O(1)	1.2(3)	C(2)-C(3)-C(4)-C(1)	-0.47(13)
C(5)-C(3)-C(4)-C(1)	-177.00(18)	C(13)-C(1)-C(4)-O(1)	-60.8(2)
C(2)-C(1)-C(4)-O(1)	-178.04(17)	P(1)-C(1)-C(4)-O(1)	66.4(2)
C(13)-C(1)-C(4)-C(3)	117.63(14)	C(2)-C(1)-C(4)-C(3)	0.42(11)
P(1)-C(1)-C(4)-C(3)	-115.14(12)	C(2)-C(3)-C(5)-C(10)	171.47(17)
C(4)-C(3)-C(5)-C(10)	-13.3(3)	C(2)-C(3)-C(5)-C(6)	-9.9(3)
C(4)-C(3)-C(5)-C(6)	165.33(17)	C(10)-C(5)-C(6)-C(7)	0.0(2)
C(3)-C(5)-C(6)-C(7)	-178.66(16)	C(5)-C(6)-C(7)-C(8)	-1.4(3)
C(12)-N(1)-C(8)-C(9)	12.3(3)	C(11)-N(1)-C(8)-C(9)	158.35(17)
C(12)-N(1)-C(8)-C(7)	-170.44(17)	C(11)-N(1)-C(8)-C(7)	-24.4(3)
C(6)-C(7)-C(8)-N(1)	-175.54(16)	C(6)-C(7)-C(8)-C(9)	1.8(2)
N(1)-C(8)-C(9)-C(10)	176.35(17)	C(7)-C(8)-C(9)-C(10)	-1.0(3)
C(8)-C(9)-C(10)-C(5)	-0.3(3)	C(6)-C(5)-C(10)-C(9)	0.8(2)
C(3)-C(5)-C(10)-C(9)	179.48(16)	C(2)-C(1)-C(13)-C(18)	139.04(15)
C(4)-C(1)-C(13)-C(18)	44.0(2)	P(1)-C(1)-C(13)-C(18)	-84.87(16)
C(2)-C(1)-C(13)-C(14)	-44.0(2)	C(4)-C(1)-C(13)-C(14)	-139.04(15)
P(1)-C(1)-C(13)-C(14)	92.10(15)	C(18)-C(13)-C(14)-C(15)	2.9(2)
C(1)-C(13)-C(14)-C(15)	-174.22(15)	C(13)-C(14)-C(15)-C(16)	0.9(2)
C(20)-N(2)-C(16)-C(15)	-178.99(16)	C(19)-N(2)-C(16)-C(15)	2.0(3)
C(20)-N(2)-C(16)-C(17)	-0.1(3)	C(19)-N(2)-C(16)-C(17)	-179.13(16)

C(14)-C(15)-C(16)-N(2)	174.42(16)	C(14)-C(15)-C(16)-C(17)	-4.5(2)
N(2)-C(16)-C(17)-C(18)	-174.50(16)	C(15)-C(16)-C(17)-C(18)	4.5(2)
C(16)-C(17)-C(18)-C(13)	-0.7(2)	C(14)-C(13)-C(18)-C(17)	-2.9(2)
C(1)-C(13)-C(18)-C(17)	174.13(15)	C(29)-P(1)-C(21)-C(22)	56.45(14)
C(25)-P(1)-C(21)-C(22)	175.94(12)	C(1)-P(1)-C(21)-C(22)	-65.18(14)
P(1)-C(21)-C(22)-C(23)	159.22(14)	C(21)-C(22)-C(23)-C(24)	-175.02(19)
C(29)-P(1)-C(25)-C(26)	62.64(15)	C(21)-P(1)-C(25)-C(26)	-55.29(16)
C(1)-P(1)-C(25)-C(26)	-175.42(13)	P(1)-C(25)-C(26)-C(27)	-173.10(13)
C(25)-C(26)-C(27)-C(28)	-172.53(17)	C(21)-P(1)-C(29)-C(30)	166.10(13)
C(25)-P(1)-C(29)-C(30)	46.92(16)	C(1)-P(1)-C(29)-C(30)	-73.04(15)
P(1)-C(29)-C(30)-C(31)	-179.83(14)	C(29)-C(30)-C(31)-C(32)	-55.0(2)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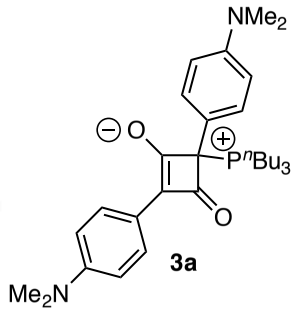
1
2
3
4
5
6
7
8
9
10
11
12
13
9.33
6.31
7.21
6.01
6.12
6.47
4.02
4.00

NMe2
P nBu3
O
O
O
Me2N

3a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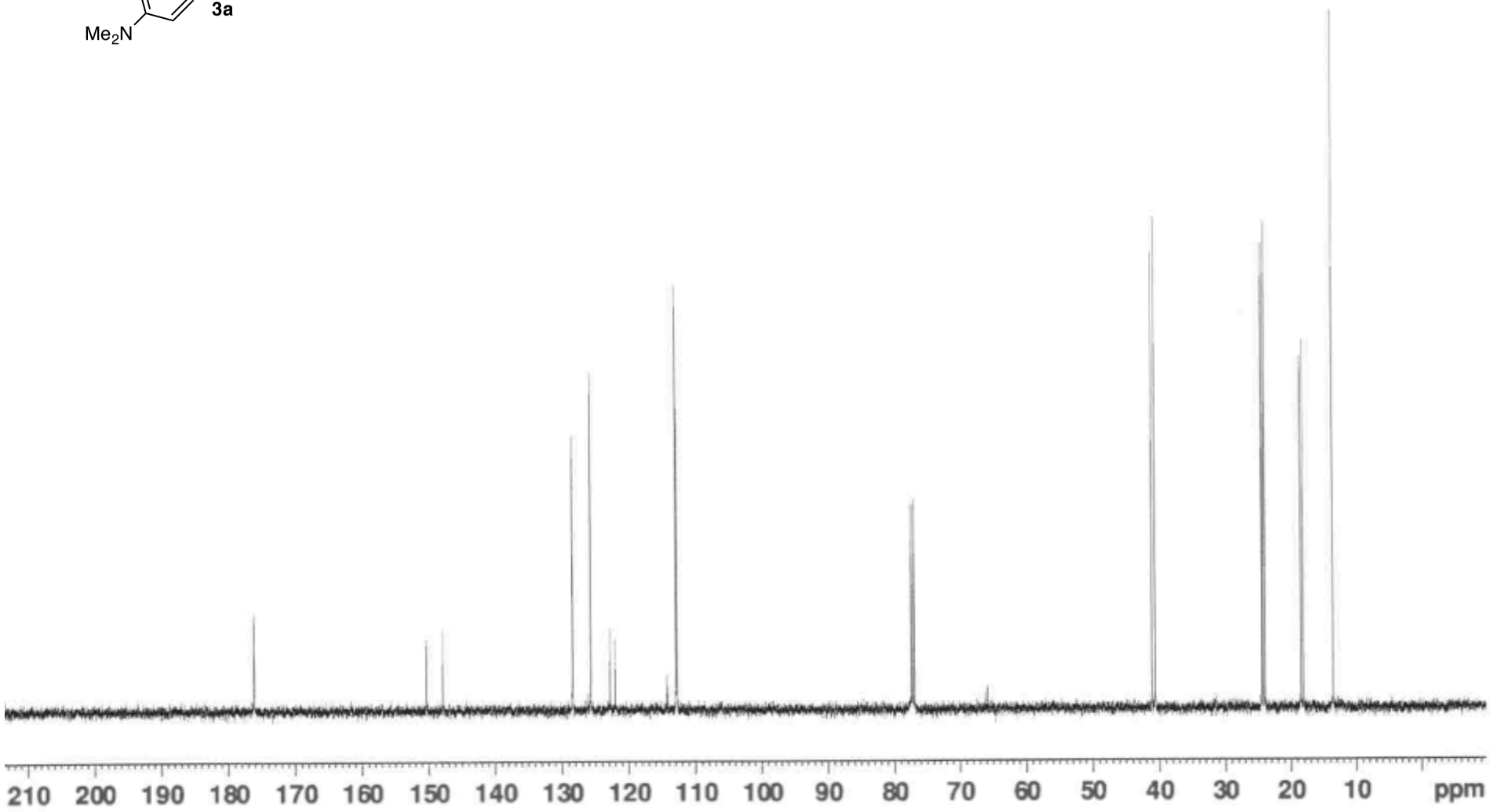
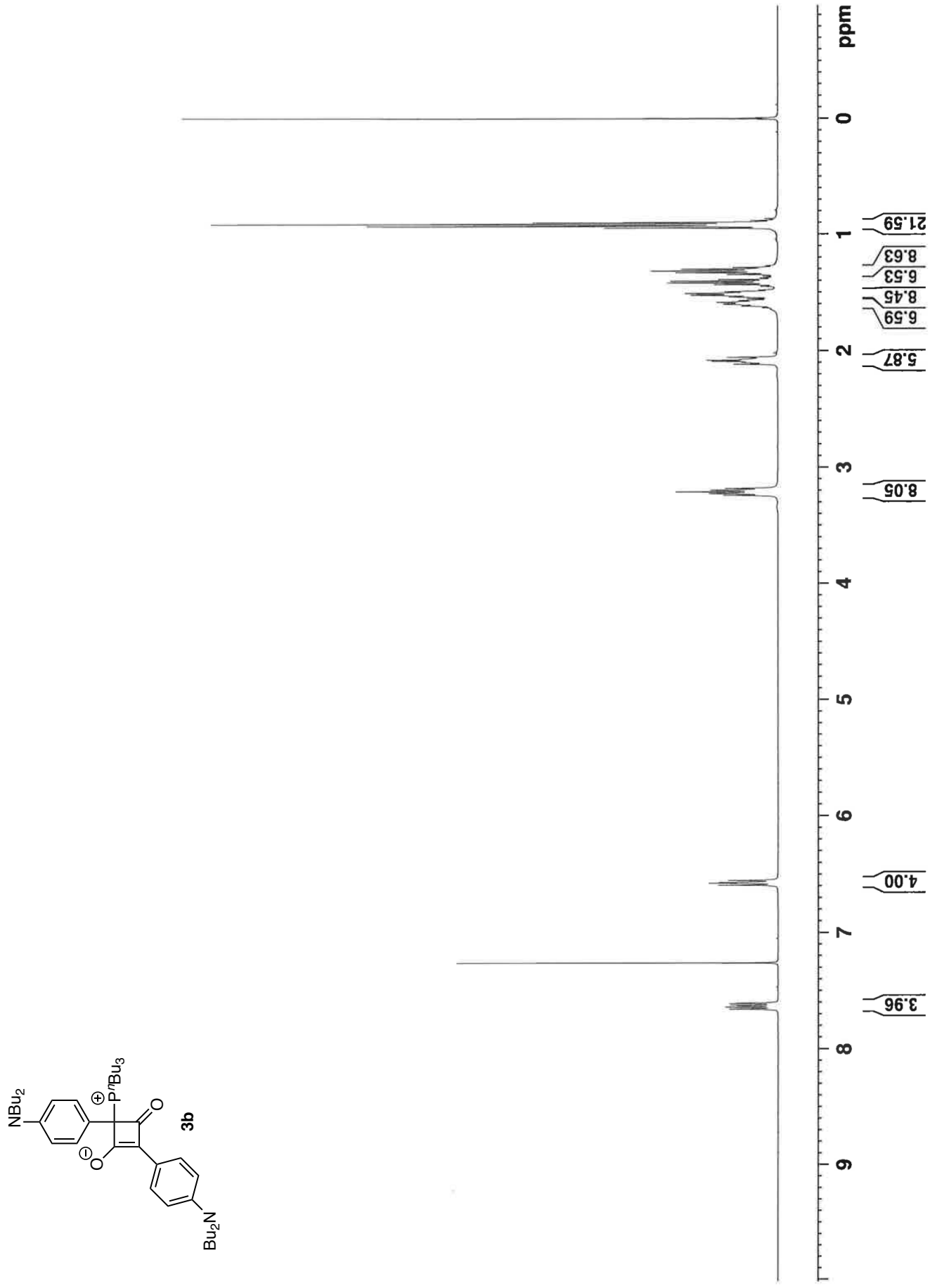
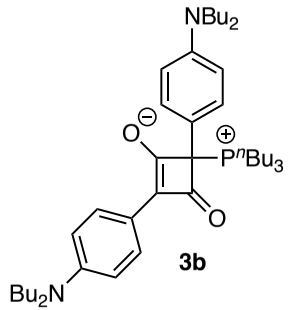
O
P^nBu3
O
Me2N

3a

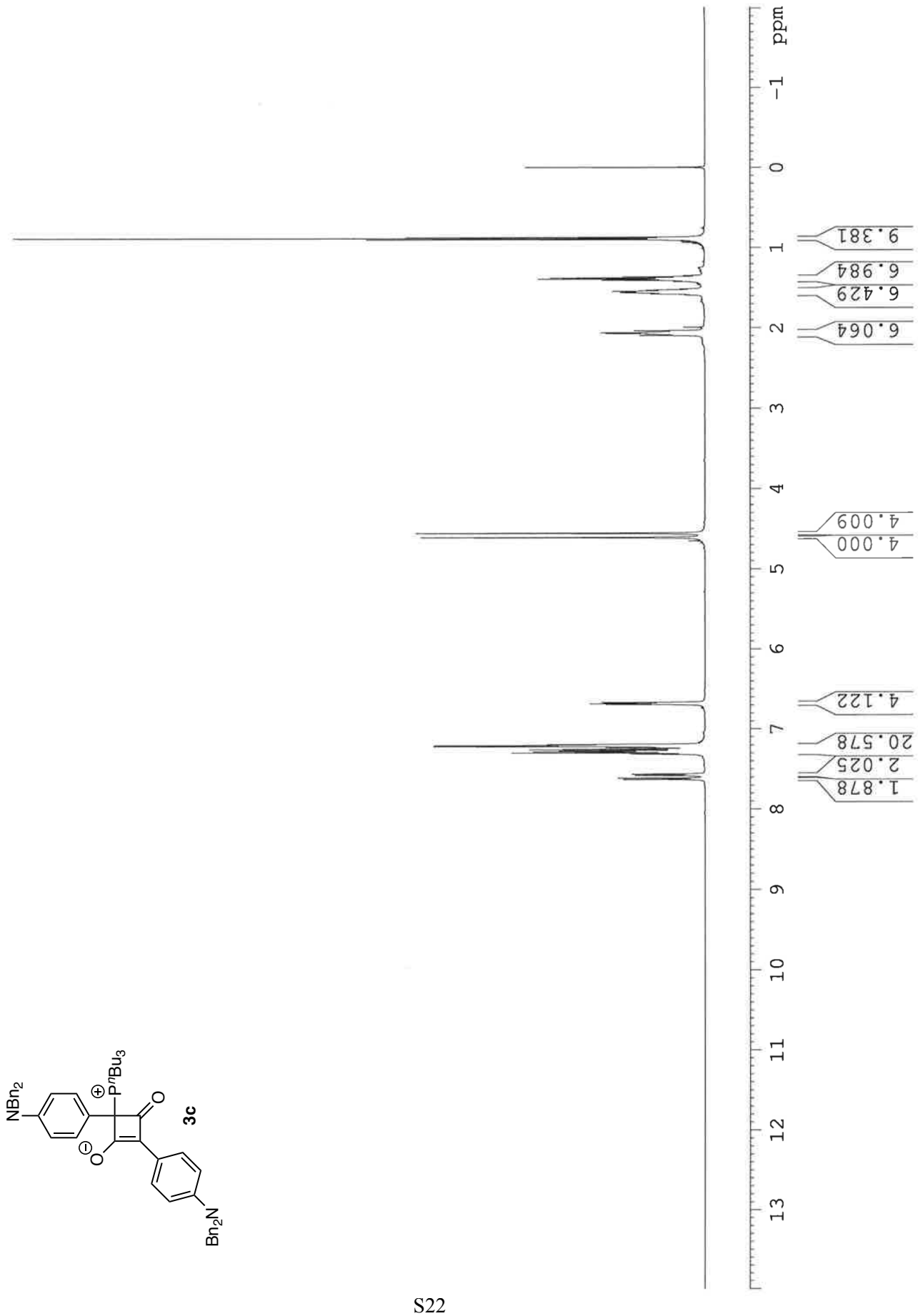

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


NBu2
P+nBu3
O
O-
3b
Bu2N
ppm
0
1
2
3
4
5
6
7
8
9
21.59
8.63
6.53
8.45
6.59
5.87
8.05
4.00
3.96


NBu2
O
P^{n}Bu3
O
Bu2N

3b

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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12
11
10
9
8
7
6
5
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3
2
1
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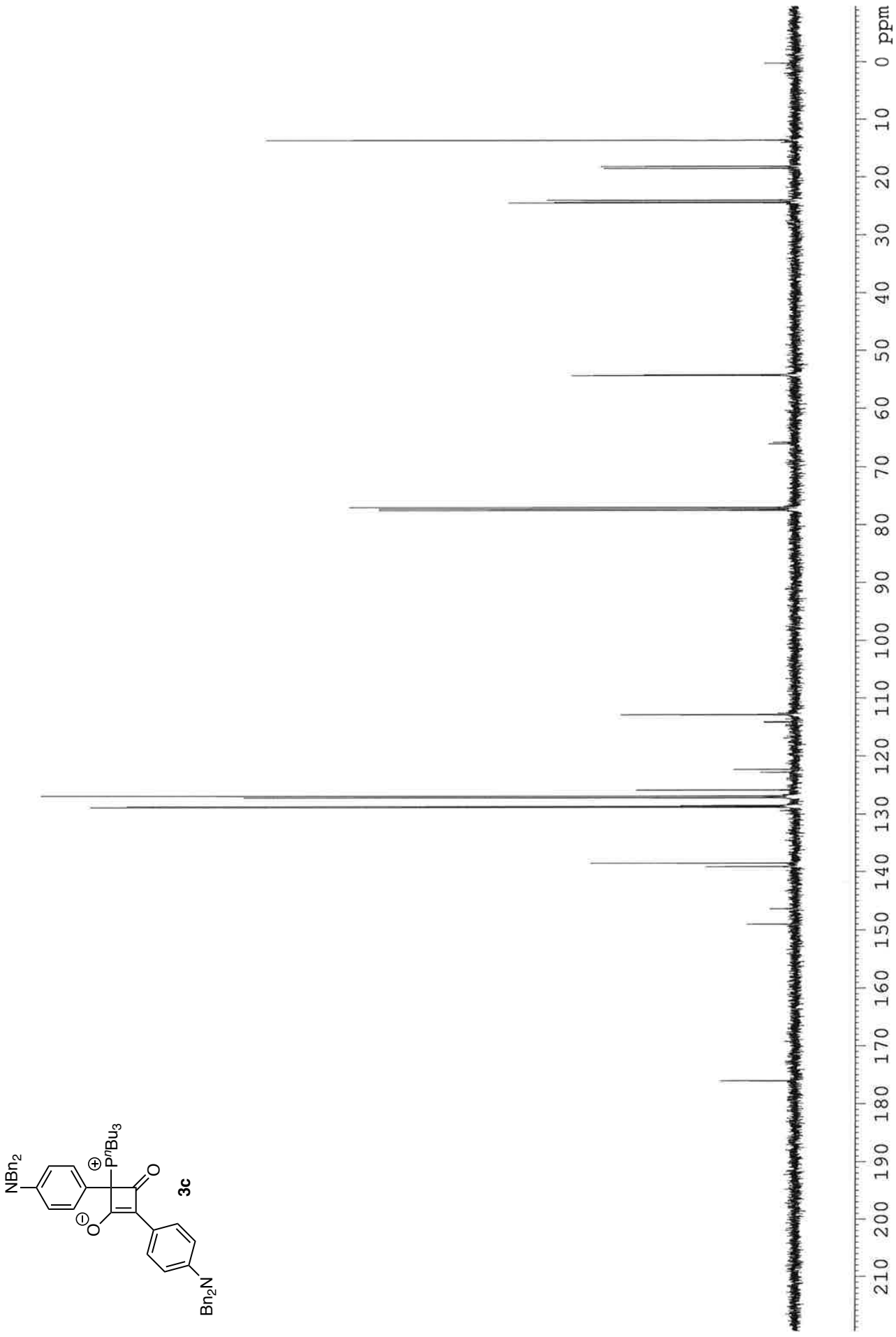
−1
9.381
6.984
6.429
6.064
4.009
4.000
4.122
20.578
2.025
1.878

NBn2
P''Bu3
O
O
Bn2N

3c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P^nBu3
O
O
Bn2N
3c
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20
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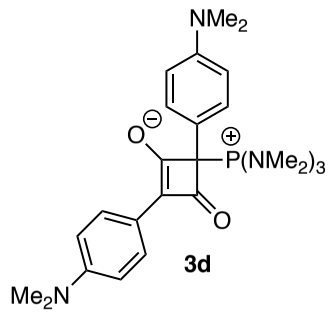
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


NMe2
O
P(NMe2)3
O
Me2N

3d

13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
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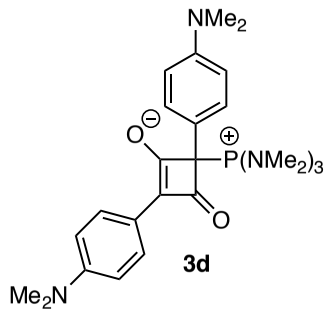
1.957
2.020
2.085
12.000
17.806


NMe2
O
P(NMe2)3
O
Me2N

3d

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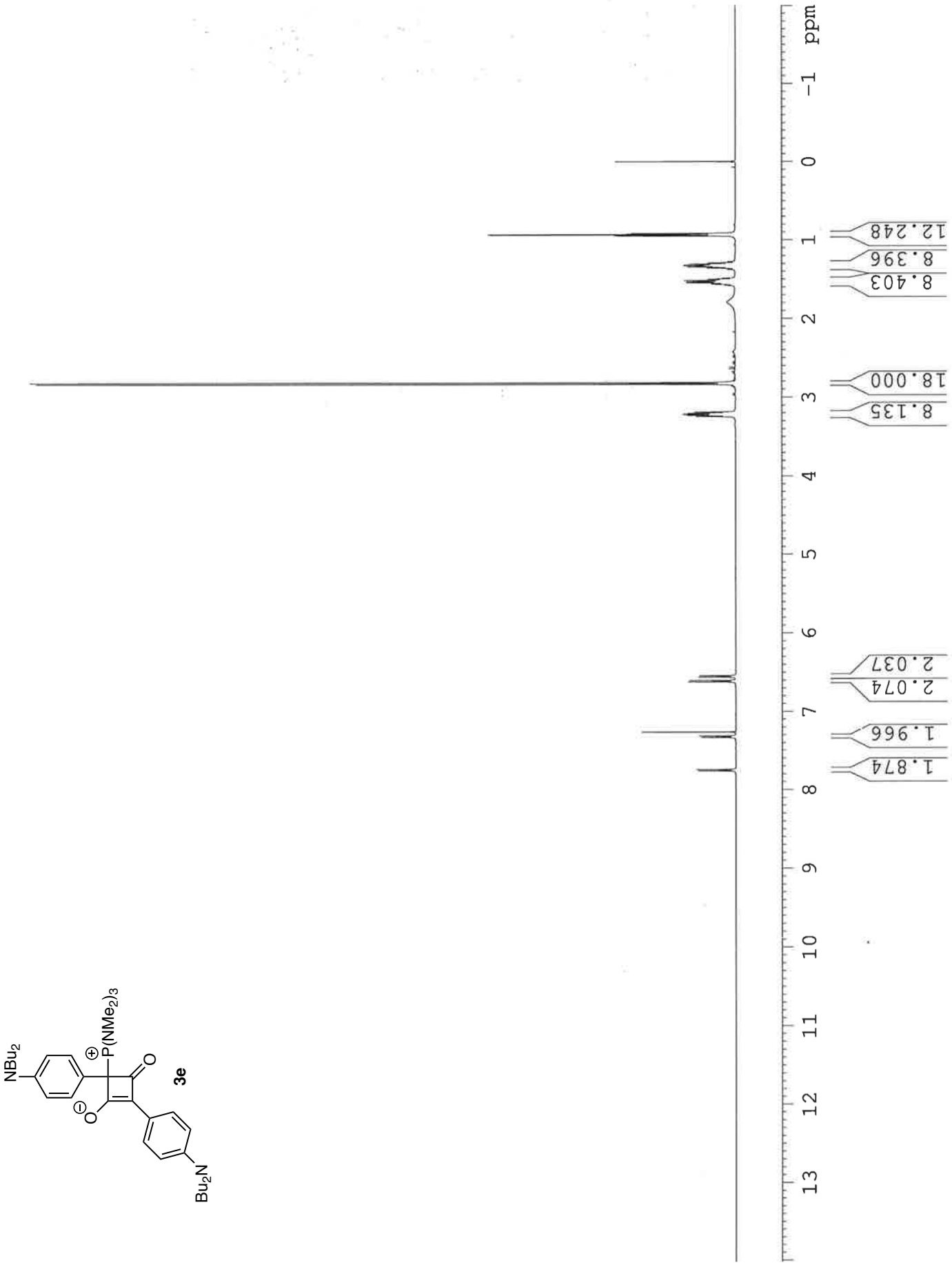
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12
11
10
9
8
7
6
5
4
3
2
1
0
−1
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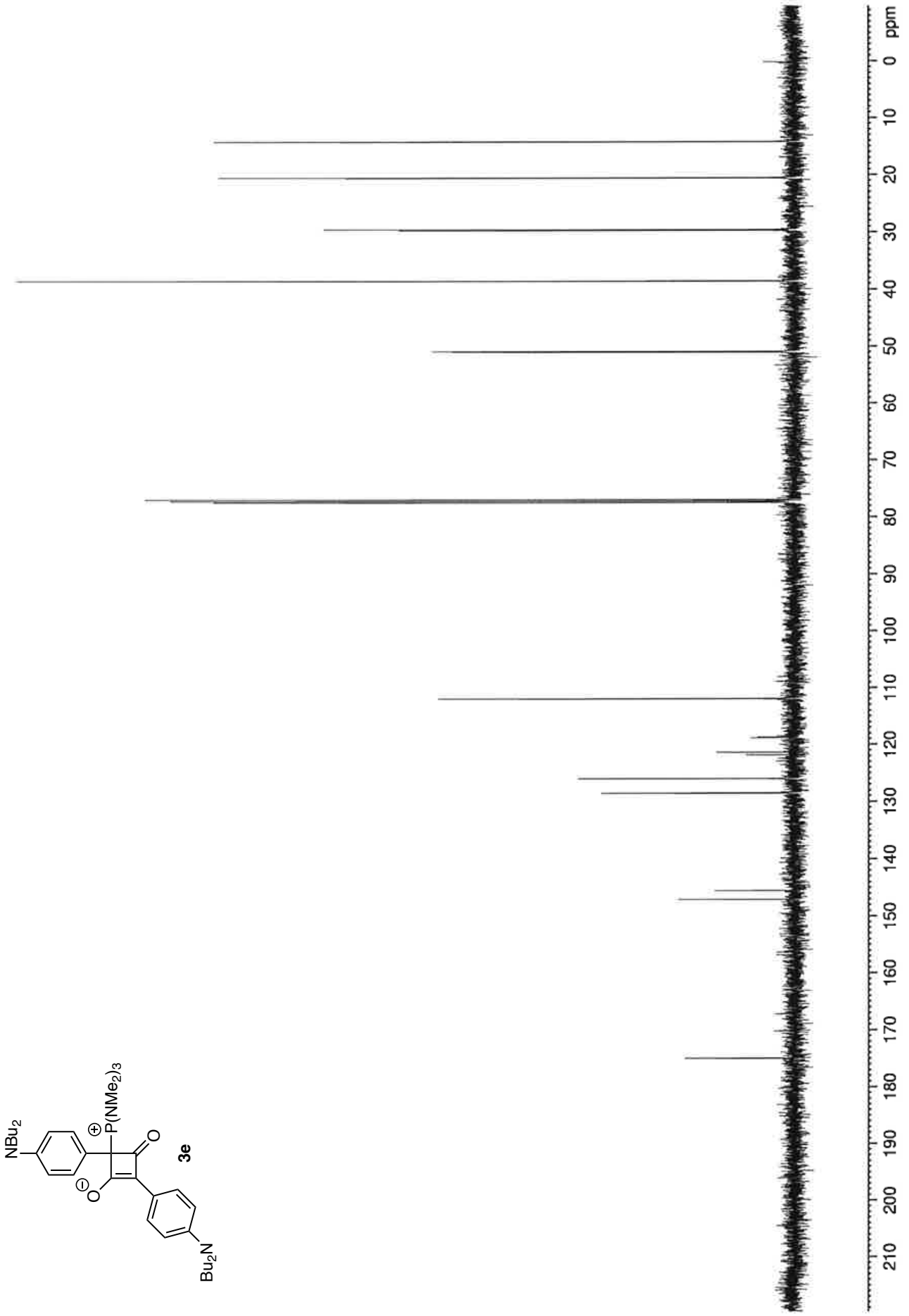
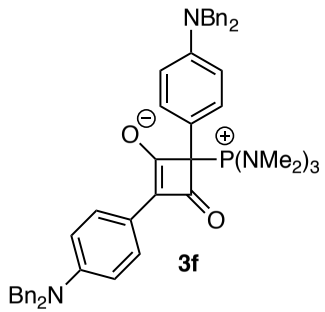
1.966
2.074
2.037
8.135
18.000
8.403
8.396
12.248

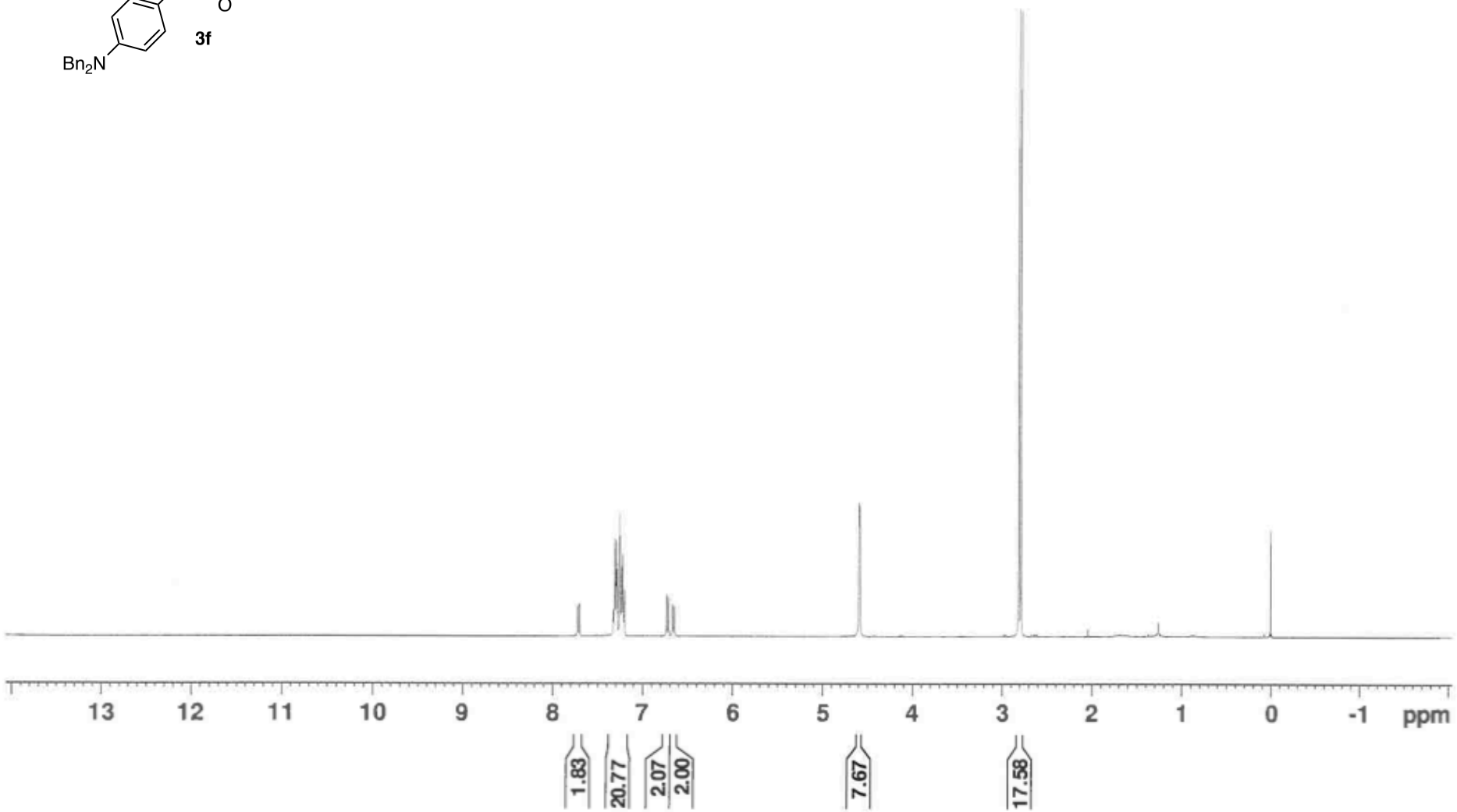
NBu2
P(NMe2)3
O
O
Bu2N

3e


NBu2
P(NMe2)3
O
O
Bu2N
3e
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
ppm


NBn2
O
P(NMe2)3
O
Bn2N

3f


13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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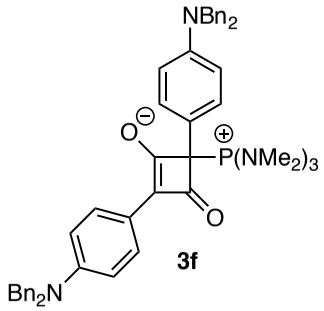
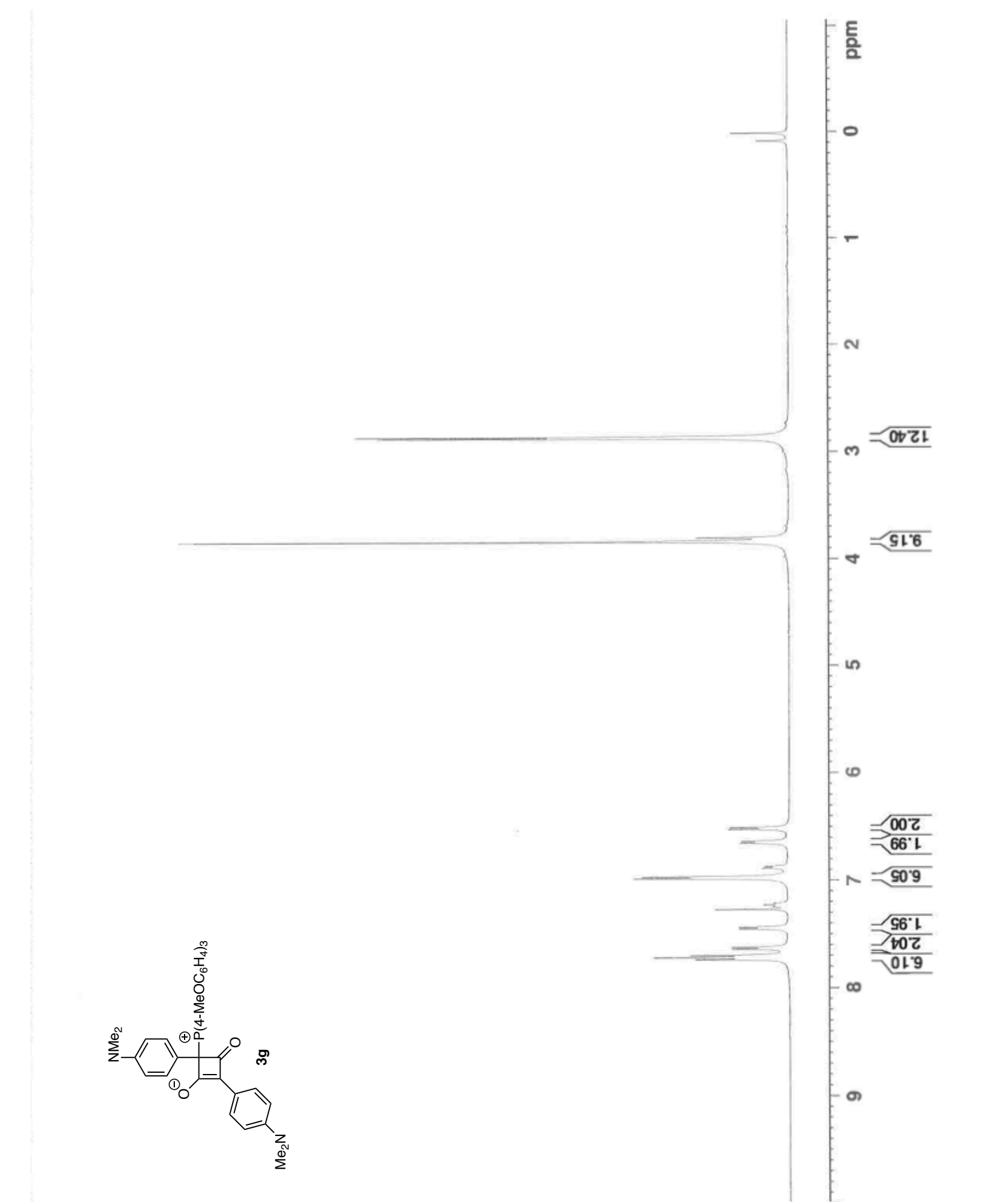
20.77
2.07
2.00
7.67
17.58


NBn2
O
P(NMe2)3
O
Bn2N

3f

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


NMe2
P(4-MeOC6H4)3
O
O
Me2N
3g
ppm
0
1
2
3
4
5
6
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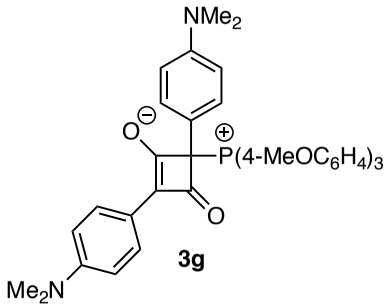
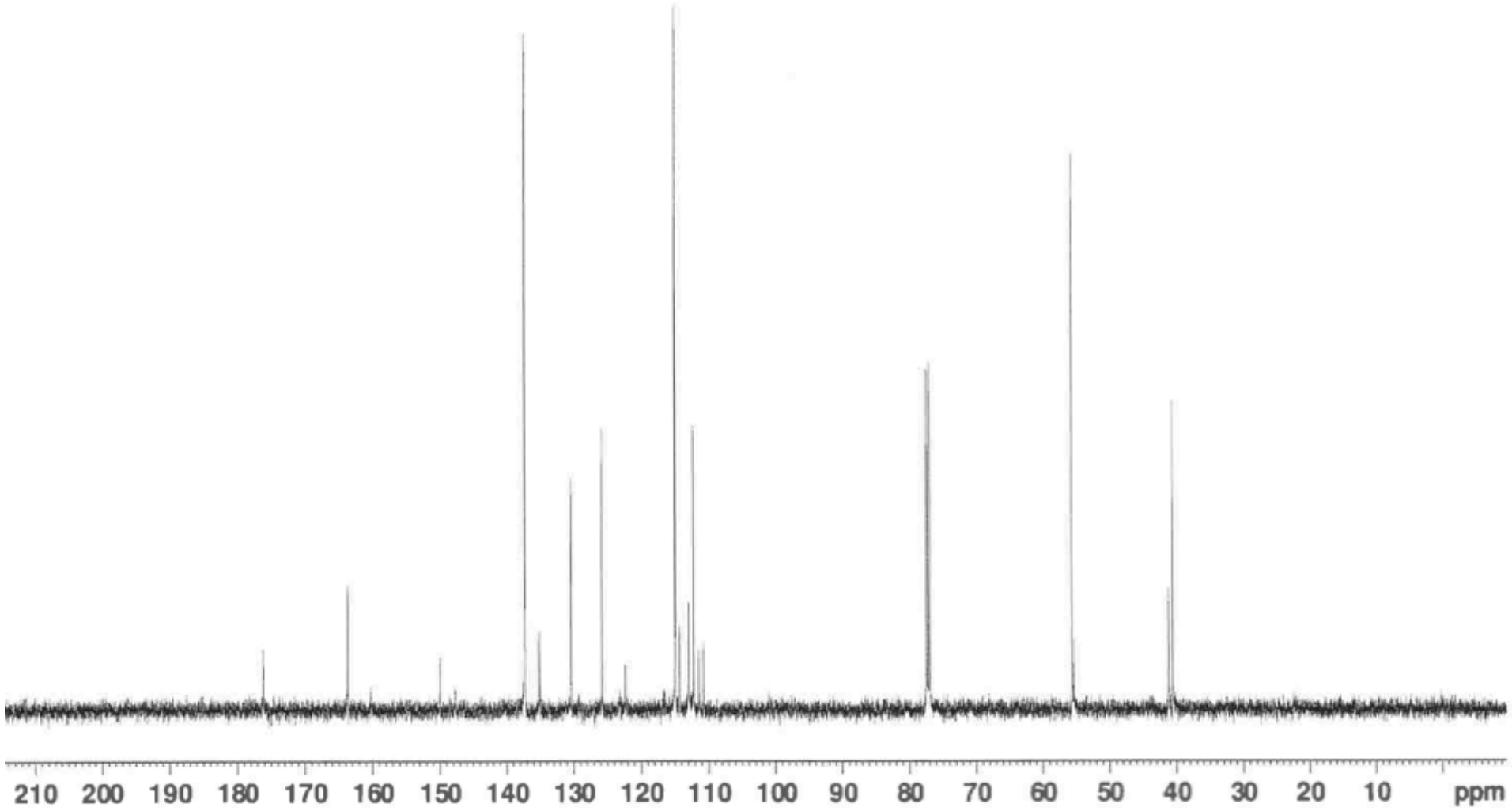
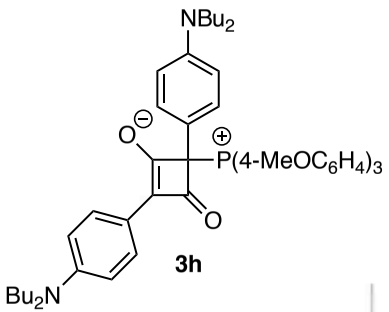
6.10
2.04
1.95
6.05
1.99
2.00


NMe2
O
P(4-MeOC6H4)3
O
Me2N

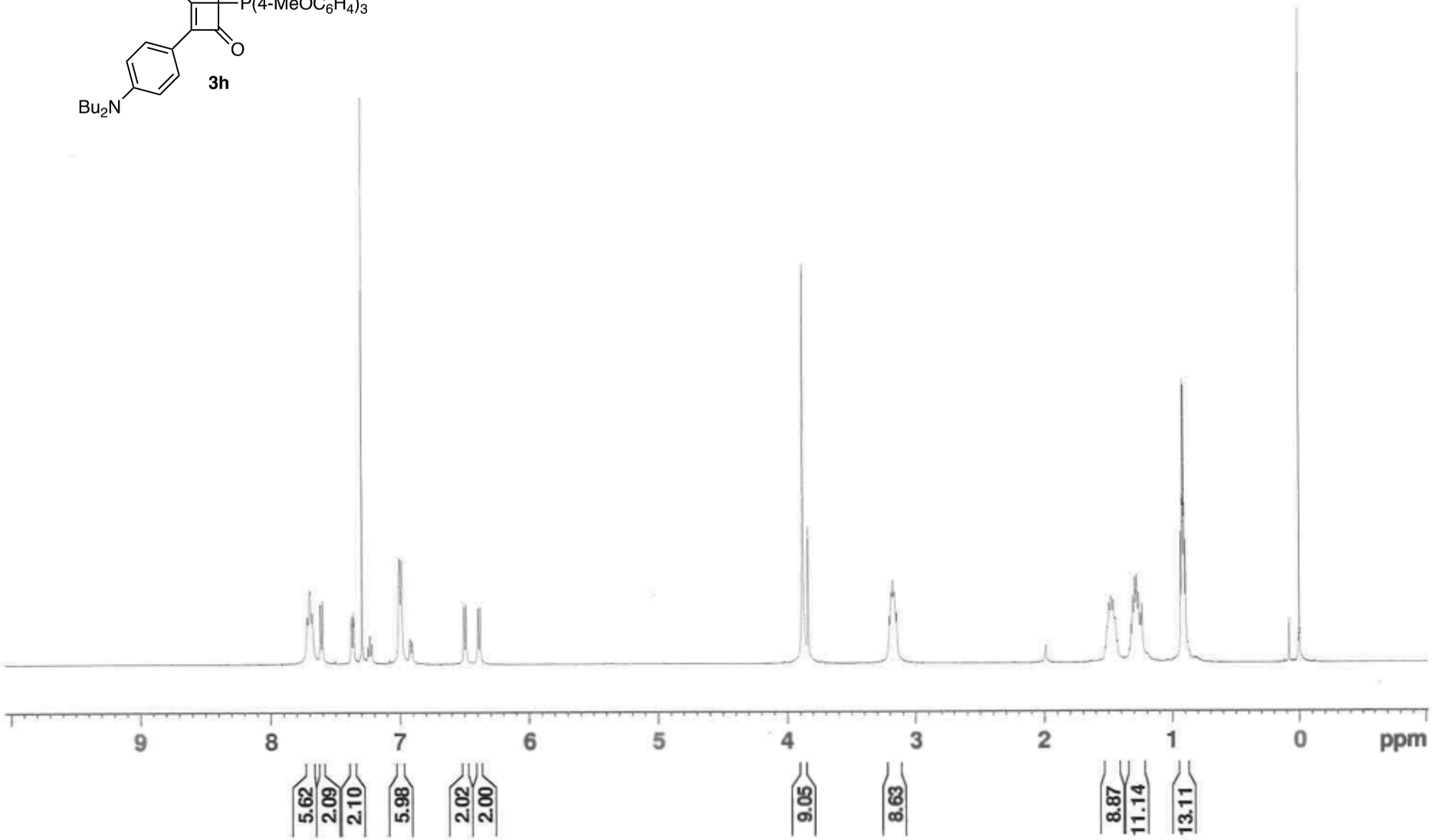
3g


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

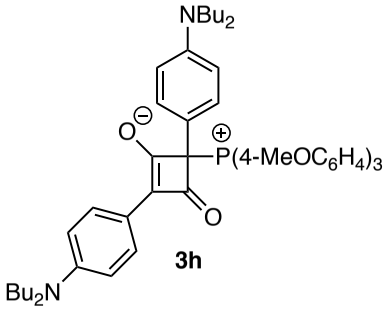
*Spectrum obtained at –40 ˚C



3h



*Spectrum obtained at –40 ˚C



3h