SUPPORTING INFORMATION

FOR

A Phosphine-Mediated Dearomative Skeletal Rearrangement of Dianiline Squaraine Dyes

Emily P. Bacher, Kevin J. Koh, Antonio J. Lepore, Allen G. Oliver, Olaf Wiest,* and Brandon L. Ashfeld*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States.

bashfeld@nd.edu, owiest@nd.edu

CONTENTS

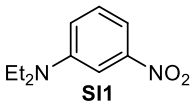
I. GENERAL

Solvents and reagents were ACS reagent grade and used without further purification unless noted below. Dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2) and diethyl ether (Et_2O) were passed through a column of molecular sieves and stored under argon. All reactions were carried out in flame-dried glassware under a nitrogen atmosphere unless otherwise specified. 3-(Diethylamino)phenol, 3-nitroaniline, squaric acid, P^{n}Bu$_3$, and *N*-(3-(diethylamino)phenyl)acetamide were purchased and used without further purification. 3-(Diphenylamino)phenol,[1] 3-(dibenzylamino)phenol,[2] 3-morpholinophenol,[3] 3-(pyrrolidin-1-yl)phenol,[3] *N*,*N*-diallyl-3-nitroaniline,[4] *N*,*N*-dibenzyl-3-nitroaniline,[5] *N*1,*N*1-diethylbenzene-1,3-diamine,[6] *N*1,*N*1-dibenzylbenzene-1,3-diamine,[5] and semisquaraines[7] were prepared according to literature procedures, and spectral data matched reported values.

^{1}H Nuclear magnetic resonance (NMR) spectra were obtained at 400, 500, or 600 MHz, and ^{13}C NMR spectra at 100 or 125 MHz. Chemical shifts are reported in parts per million (ppm, δ), and referenced to residual solvent or tetramethylsilane (TMS). 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; hom, higher order multiplet; 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. Analytical thin layer chromatography (TLC) was performed using EMD 250 micron 60 F_{254} silica gel plates and visualized with UV. 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.

An arbitrary sphere of data was collected on a Bruker (PHOTON-II/APEX-II) diffractometer using a combination of ω- and φ-scans of 0.5°.[8] Data were corrected for absorption and polarization effects and analyzed for space group determination.[9] The structure was solved by dual-space methods and expanded routinely.[10] The model was refined by full-matrix least-squares analysis of F^2 against all reflections.[11] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded (U_{iso}(H) = 1.5U_{eq}(C) for methyl, 1.2U_{eq}(C) for all others).

II. EXPERIMENTAL PROCEDURES



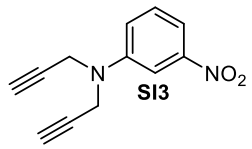
SI1

***N*,*N*-Diethyl-3-nitroaniline.** Li_2CO_3 (4.43 g, 60.0 mmol) was added to a solution of 3-nitroaniline (2.07 g, 15.0 mmol) in DMF (75 mL) at rt. Ethyl iodide (5.85 g, 37.5 mmol, 3.01 mL) was added dropwise, and the resulting mixture warmed to 90 ˚C and stirred for 20 h. The reaction was allowed to cool to rt by removal of the oil bath, then diluted with H_2O (150 mL), and extracted with EtOAc (3 x 50 mL). The combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (4:1) to give 5.82 g (50%) of the title compound as a yellow oil: ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.43 (m, 2 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 6.90 (dd, *J* = 2.0, 8.0 Hz, 1 H), 3.40 (q, *J* = 7.1 Hz, 4 H), 1.19 (t, *J* = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz) δ 149.9, 148.5, 129.9, 117.3, 109.9, 105.7, 44.8, 12.5; IR (neat) 2974, 2934, 2898, 2869, 1620, 1526, 1346, 1268, 1199, 76 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{10}H_{15}N_2O_2$ 195.1128; Found 195.1145.

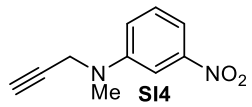
SI2

***N*-Allyl-*N*-methyl-3-nitroaniline.** Allyl bromide (0.32 mL, 3.6 mmol) was added to a mixture of *N*-methyl-3-nitroaniline (346 mg, 1.80 mmol) and K_2CO_3 (373 mg, 2.70 mmol) in MeCN (10 mL) at rt. The mixture was then heated to reflux, stirred for 20 h, then allowed to cool to rt by removal of the oil bath. The resulting solution was diluted with H_2O (20 mL), extracted with EtOAc (3 x 10 mL), and the combined organic fractions dried ($MgSO_4$) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (3:1) to give 251 mg (73%) of the title compound as an orange oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2 H), 7.31 (t, *J* = 8.2 Hz, 1 H), 6.95 (dd, *J* = 7.9, 2.6 Hz, 1 H), 5.83 (ddt, *J* = 17.2, 10.4, 4.9 Hz, 1 H), 5.19 (dq, *J* = 10.4, 1.6 Hz, 1H), 5.15 (dq, *J* = 17.2, 1.7 Hz, 1 H), 3.99 (dt, *J* = 4.8, 1.7 Hz, 2 H), 3.04 (s, 3 H); ^{13}C NMR (125 MHz) δ 150.0, 149.6, 132.5, 129.8, 117.9, 116.9, 110.9, 106.4, 55.2, 38.5; IR (neat) 2968, 2915, 2831, 1617, 1521, 1341, 1249, 1211, 1001, 918, 845, 779, 732, 670, 559 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{10}H_{13}N_2O_2$,193.0972; Found 193.0969.



SI3

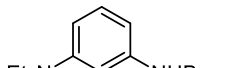
3-Nitro-*N*,*N*-di(prop-2-yn-1-yl)aniline. Propargyl bromide (1.72 g, 14.5 mmol, 1.10 mL) was added to a mixture of 3-nitroaniline (500 mg, 3.62 mmol) and Na_2CO_3 (1.53 g, 14.5 mmol) in MeCN (8 mL) at rt. The mixture was then heated to reflux, stirred for 12 h, then allowed to cool to rt by removal of the oil bath. The resulting solution was diluted with H_2O (20 mL), extracted with EtOAc (3 x 10 mL), and the combined organic fractions dried ($MgSO_4$) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (2:1) to give 350 mg (45%) of the title compound as a yellow solid: ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (t, *J* = 2.3 Hz, 1 H), 7.68 (ddd, *J* = 8.1, 2.1, 0.7 Hz, 1 H), 7.41 (t, *J* = 8.2 Hz, 1 H), 7.21 (ddd, *J* = 8.3, 2.6, 0.6 Hz, 1 H), 4.18 (d, *J* = 2.4 Hz, 4 H), 2.31 (t, *J* = 2.4 Hz, 2 H); ^{13}C NMR (125 MHz) δ 149.4, 148.3, 130.1, 120.8, 114.0, 109.4, 78.4, 73.7, 40.7; IR (neat) 3309, 2924, 2844, 1632, 1527, 1347, 1241, 1200, 735 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{12}H_{12}N_2O_2$ 215.0815; Found 215.0810; mp = 42-44 ˚C.



SI4

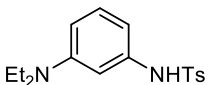
***N*-Methyl-3-nitro-*N*-(prop-2-yn-1-yl)aniline.** Propargyl bromide (430 mg, 3.6 mmol, 0.28 mL) was added to a mixture of *N*-allyl-*N*-methyl-3-nitroaniline (274 mg, 1.80 mmol) and K_2CO_3 (373 mg, 2.70 mmol) in MeCN (10 mL) at rt. The mixture was then heated to reflux, stirred for 20

h, then allowed to cool to rt by removal of the oil bath. The resulting solution was diluted with H_2O (20 mL), extracted with EtOAc (3 x 10 mL), and the combined organic fractions dried ($MgSO_4$) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (5:1) to give 342 mg (>99%) of the title compound as an orange solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2 H), 7.37 (td, *J* = 8.3, 0.5 Hz, 1 H), 7.11-7.08 (m, 1 H), 4.11 (d, *J* = 2.4 Hz, 2 H), 3.06 (s, 3 H), 2.22 (t, *J* = 2.4 Hz, 1 H); ^{13}C NMR (125 MHz) δ 149.7, 149.5, 129.9, 119.4, 112.7, 108.2, 78.4, 72.9, 42.4, 38.9; IR (neat) 3290, 3095, 2953, 2924, 2855, 1619, 1572, 1523, 1344, 1206, 1119, 1005, 940, 911, 875, 735 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{10}H_{11}N_2O_2$ 191.0815; Found 191.0814; mp = 47-48 ˚C.



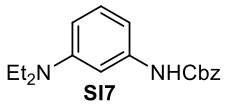
SI5

***tert*-Butyl (3-(diethylamino)phenyl)carbamate.** 4-DMAP (30 mg, 0.24 mmol) and Boc_2O (520 mg, 2.4 mmol) were added sequentially to a solution of *N*,*N*-diethylbenzene-1,3-diamine (390 mg, 2.37 mmol) in THF (12 mL) at rt. The mixture was then warmed to 45 ˚C, stirred for 96 h, and then allowed to cool to rt by removal of the oil bath. The resulting solution was concentrated under reduced pressure, diluted with EtOAc (15 mL), and washed with saturated aqueous $NaHCO_3$ (20 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL) and the combined organic fractions were washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (2:1) to afford 150 mg (24%) of the title compound as an orange solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 8.2, 1 H), 6.76 (br s, 1 H), 6.56 (d, *J* = 7.6 Hz, 1 H), 6.39 (ddd, *J* = 8.4, 2.5, 0.5 Hz, 1 H), 3.32 (q, *J* = 7.1 Hz, 4 H), 1.50 (s, 9 H), 1.14 (t, *J* = 7.1 Hz, 6 H); ^{13}C NMR (100 MHz) δ 152.7, 148.5, 139.5, 129.6, 106.9, 105.9, 102.0, 80.1, 44.3, 28.4, 12.6; IR (neat) 3384, 2879, 2940, 2875, 1805, 1753, 1729, 1610, 1371, 1210, 1112, 1058, 842 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{15}H_{25}N_2O_2$ 265.1911; Found 265.1890; mp = 105-106 ˚C.



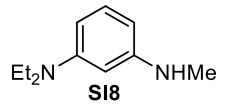
SI6

***N*-(3-(Diethylamino)phenyl)-4-methylbenzenesulfonamide.** TsCl (512 mg, 2.68 mmol) and K_2CO_3 (674 mg, 4.88 mmol) were added sequentially to a solution of *N*,*N*-diethylbenzene-1,3-diamine (400 mg, 2.44 mmol) in EtOH (6 mL) at rt. The mixture was then warmed to 50 ˚C, stirred for 3.5 hours, and then allowed to cool to rt by removal of the oil bath. The resulting solution was concentrated under reduced pressure, diluted with DCM (15 mL), and washed with water (15 mL). The aqueous layer was extracted with DCM (2 x 10 mL), and the combined organic fractions were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (3:1) to afford 518 mg (67%) of the title compound as a pink solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2 H), 7.20 (dd, *J* = 8.6, 0.6 Hz, 2 H), 6.98 (dt, *J* = 7.9, 1.1 Hz, 1 H), 6.67 (s, 1 H), 6.37 (m, 2 H), 6.22 (m, 1 H), 3.23 (q, *J* = 7.1 Hz, 4 H), 2.34 (s, 3 H), 1.05 (q, *J* = 7.0 Hz, 6 H); ^{13}C NMR (100 MHz) δ 148.5, 143.6, 137.6, 136.4, 129.8, 129.5, 127.3, 108.7, 108.3, 104.7, 44.3, 21.5; IR (neat) 3245, 2975, 2920, 1703, 1653, 1604, 1576, 1558, 1508, 1162, 1092, 1025 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{17}H_{23}N_2O_2S$ 319.1503; Found 319.1514; mp = 81-83 ˚C.



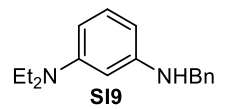
SI7

Benzyl (3-(diethylamino)phenyl)carbamate. $NaHCO_3$ (281 mg, 3.35 mmol) and benzyl chloroformate (0.480 mL, 3.35 mmol) were added sequentially to a solution of *N*,*N*-diethylbenzene-1,3-diamine (500 mg, 3.05 mmol) in THF (7 mL) at rt. The mixture was then cooled to 0 ˚C with a water/ice bath, stirred for 4 h, and then allowed to warm to rt by removal of the ice bath. The reaction was diluted with water (10 mL) and extracted with EtOAc (3 x 15 mL). The combined organic fractions were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under reduced pressure to afford 909 mg (>99%) of the title compound as a pink oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.33 (m, 5 H), 7.10 (t, *J* = 8.2 Hz, 1 H), 6.88 (br s, 1 H), 6.57 (br s, 1 H), 6.52 (d, *J* = 7.8 Hz, 1 H), 6.39 (dd, *J* = 7.9, 2.0 Hz, 1 H), 5.19 (s, 2 H), 3.33 (q, *J* = 7.0 Hz, 4 H), 1.15 (t, *J* = 7.1 Hz, 6 H); ^{13}C NMR (100 MHz) δ 148.5, 147.4, 140.0, 136.2, 131.3, 129.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 126.3, 107.2, 44.4, 37.1, 12.6; IR (neat) 3060, 2964, 2930, 1725, 1606, 1541, 1497, 1216, 1061 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{18}H_{23}N_2O_2$ 299.1754; Found 299.1743.



SI8

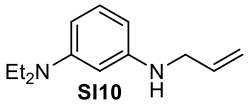
***N*^{1},*N*^{1}-Diethyl-*N*^{3}-methylbenzene-1,3-diamine.** NaOMe (385 mg, 7.12 mmol) and paraformaldehyde (143 mg, 4.75 mmol) were added sequentially to a solution of *N*^{1},*N*^{1}-diethylbenzene-1,3-diamine (290 mg, 2.37 mmol) in MeOH (12 mL) at rt. The mixture was then warmed to 40 ˚C, stirred for 4 h, and then allowed to cool to rt by removal of the oil bath. $NaBH_4$(179 mg, 4.75 mmol) was then added portion wise. The mixture was then heated to reflux, stirred for 12 h, and then allowed to cool to rt by removal of the oil bath. The reaction was diluted with water (20 mL) and extracted with EtOAc (3 x 15 mL). The combined organic fractions were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (2:1) to afford 250 mg (49%) of the title compound as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (t, *J* = 8.1 Hz, 1 H), 6.11 (ddd, *J* = 8.25, 2.4, 0.7 Hz, 1 H), 5.98 (ddd, *J* = 8.65, 2.15, 0.7 Hz, 1 H), 5.94 (t, *J* = 2.3 Hz, 1 H), 3.58 (br s, 1 H), 3.31 (q, *J* = 7.1 Hz, 4 H), 2.82 (s, 3 H), 1.15 (t, *J* = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz) δ 150.9, 149.2, 130.1, 102.4, 100.9, 96.5, 44.6, 31.2 13.0; IR (neat) 3403, 2968, 2930, 2870, 2806, 1607, 1580, 1513, 1498, 1237, 1145, 772 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{11}H_{20}N_2$ 179.1543; Found 179.1541.



SI9

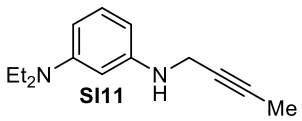
***N*1-Benzyl-*N*3,*N*3-diethylbenzene-1,3-diamine.** *N*-benzyl-*N*-(3-(diethylamino)phenyl)acetamide (710 mg, 2.4 mmol) was dissolved in 6M HCl (10 mL). The mixture was then warmed to 95 ˚C, stirred for 16 h, and then allowed to cool to room temperature by removal of the oil bath. The pH of the reaction was then adjusted to 9 with saturated aqueous $NaHCO_3$. The reaction was extracted with DCM (3 x 15 mL). The combined organic fractions were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under reduced

pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (2:1) to afford 415 mg (68%) of the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 2 H), 7.30 (t, *J* = 7.2 Hz, 2 H), 7.22 (tt, *J* = 7.2, 1.4 Hz, 1 H), 6.98 (t, *J* = 8.1 Hz, 1 H), 6.08 (dd, *J* = 8.3, 1.9 Hz, 1 H), 5.97 (ddd, *J* = 7.9, 2.1, 0.6 Hz, 1 H), 5.90 (t, *J* = 2.2 Hz, 1 H), 4.28 (s, 2 H), 3.91 (br s, 1 H), 3.24 (q, *J* = 7.0 Hz, 4 H), 1.07 (t, *J* = 7.0 Hz, 6 H); ^{13}C NMR (100 MHz) δ 149.4, 148.8, 139.9, 129.9, 128.5, 127.5, 127.0, 102.2, 101.0, 96.5, 48.5, 44.3 12.7; IR (neat) 3389, 3085, 3062, 3026, 2970, 2817, 2735, 2695, 1698, 1596, 1455, 1310, 1202, 1166 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{17}H_{23}N_2$ 255.1856; Found 255.1824.



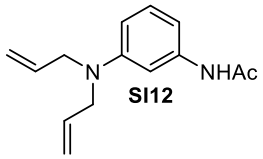
SI10

***N*1-Allyl-*N*3,*N*3-diethylbenzene-1,3-diamine.** Allyl bromide (0.360 mL, 4.14 mmol) and K_2CO_3 (858 mg, 6.21 mmol) were added sequentially to a solution of *N*1,*N*1-diethylbenzene-1,3-diamine (680 mg, 4.14 mmol) in DMF (11 mL) at rt. The mixture was then warmed to 70 ˚C, stirred for 16 h, and then allowed to cool to rt by removal of the oil bath. The reaction was diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic fractions were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (4:1) to afford 216 mg (26%) of the title compound as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (t, *J* = 8.1 Hz, 1 H), 6.11 (dd, *J* = 8.3, 2.4 Hz, 1 H), 6.02-5.94 (m, 3 H), 5.29 (dq, *J* = 10.3, 1.4 Hz, 1 H), 3.77 (dt, *J* = 5.5, 1.5 Hz, 2 H), 3.68 (br s, 1 H), 3.31 (q, *J* = 7.1 Hz, 4 H), 1.15 (t, *J* = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz) δ 149.7, 149.2, 136.5, 130.2, 116.2, 102.7, 101.6, 97.1, 47.2, 44.7, 13.1; IR (neat) 3404, 3079, 2970, 2927, 2870, 1606, 1579, 1514, 1448, 1374, 1234, 1150, 1094, 1026, 918 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{13}H_{21}N_2$ 205.1699; Found 205.1680.



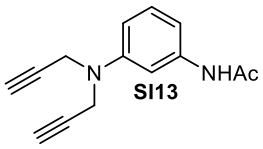
SI11

***N*^{1}-(But-2-yn-1-yl)-*N*3,*N*3-diethylbenzene-1,3-diamine.** 1-Bromobut-2-yne (0.360 mL, 4.14 mmol) and K_2CO_3 (858 mg, 6.21 mmol) were added sequentially to a solution of *N*1,*N*1-diethylbenzene-1,3-diamine (680 mg, 4.14 mmol) in DMF (11 mL) at rt. The reaction was stirred at rt for 16 h. The reaction was diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic fractions were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under reduced pressure. The crude mixture was purified by flash chromatography eluting with hexanes/EtOAc (4:1) to afford 295 mg (33%) of the title compound as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (t, *J* = 8.4 Hz, 1 H), 6.17 (ddd, *J* = 8.4, 2.3, 0.5 Hz, 1 H), 6.04-6.02 (m, 2 H), 3.87 (q, *J* = 2.3 Hz, 2 H), 3.33 (q, *J* = 7.1, 4 H), 1.81 (t, *J* = 2.3 Hz, 3 H), 1.17 (t, *J* = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz) δ 149.1, 148.8, 130.1, 103.1, 101.6, 97.4, 79.1, 76.7, 44.6, 34.4, 12.9, 3.8; IR (neat) 3399, 2969, 2925, 1608, 1580, 1513, 1374, 1233, 1177, 1151, 1095, 1077, 1025, 911 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{14}H_{21}N_2$ 217.1699; Found 217.1673.



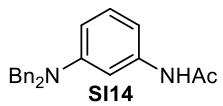
SI12

***N*-(3-(Diallylamino)phenyl)acetamide.** *N*,*N*-diallyl-3-nitroaniline (473 mg, 2.17 mmol) was dissolved in a 5:1 mixture of EtOAc/AcOH (24 mL), stirring vigorously. Iron powder (606 mg, 10.85 mmol) was then added. The reaction was then warmed to 110 ˚C, stirred for 16 h, and then allowed to cool to rt by removal of the oil bath. The resulting solution was concentrated under reduced pressure, diluted with DCM (20 mL), and washed with saturated aqueous $NaHCO_3$ (20 mL). The organic fraction was then filtered through celite. The filtrate was washed with saturated aqueous NaCl (20 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography eluting with EtOAc/hexanes (2:1) to afford 471 mg (94%) of the title compound as a yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (br s, 1 H), 7.01 (t, *J* = 8.2 Hz, 1 H), 6.49 (m, 1 H), 6.65 (dd, *J* = 7.9, 1.2 Hz, 1 H), 6.36 (dd, *J* = 8.3, 2.2 Hz, 1 H), 5.78-5.71 (m, 2 H), 5.10-5.05 (m, 4 H), 3.81 (d, *J* = 4.8 Hz, 4 H), 2.04 (s, 3 H); ^{13}C NMR (125 MHz) δ 168.7, 149.5, 139.2, 134.0, 129.6, 116.3, 108.6, 108.2, 104.1, 53.0, 24.9; IR (neat) 3275, 3089, 3005, 2971, 1669, 1629, 1589, 1545, 1499, 1214, 744, 667 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{14}H_{19}N_2O$ 231.1492; Found 231.1498; mp = 60-61 ˚C.



SI13

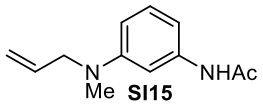
***N*-(3-(Di(prop-2-yn-1-yl)amino)phenyl)acetamide.** 3-Nitro-*N*,*N*-di(prop-2-yn-1-yl)aniline (500 mg, 2.34 mmol) was dissolved in a 5:1 mixture of EtOAc/AcOH (30 mL), stirring vigorously. Iron powder (652 mg, 11.68 mmol) was then added. The reaction was then warmed to 110 ˚C, stirred for 16 h, and then allowed to cool to rt by removal of the oil bath. The resulting solution was concentrated under reduced pressure, diluted with DCM (20 mL), and washed with saturated aqueous $NaHCO_3$ (20 mL). The organic fraction was then filtered through celite. The filtrate was washed with saturated aqueous NaCl (20 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography eluting with EtOAc/hexanes (2:1) to afford 216 mg (41%) of the title compound as an orange solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.20 (m, 2 H), 7.11 (br s, 1 H), 6.95 (d, *J* = 7.8 Hz, 1 H), 6.71 (dd, *J* = 8.2, 2.0 Hz, 1 H), 4.12 (d, *J* = 2.4 Hz, 4 H), 2.26 (t, *J* = 2.2 Hz, 2 H), 2.17 (s, 3 H); ^{13}C NMR (100 MHz) δ 168.1, 148.4, 138.8, 129.6, 111.6, 111.1, 107.0, 79.1, 72.7, 40.4, 24.8; IR (neat) 3289, 3154, 3087, 1664, 1608, 1551, 1496, 1440, 1370, 1314, 1252, 1178, 954, 919, 772 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{14}H_{15}N_2O$ 227.1179; Found 227.1162; mp = 117-119 ˚C.



SI14

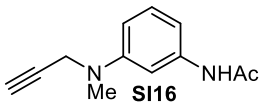
***N*-(3-(Dibenzylamino)phenyl)acetamide.** *N*,*N*-dibenzyl-3-nitroaniline (421 mg, 1.32 mmol) was dissolved in a 5:1 mixture of EtOAc/AcOH (12 mL), stirring vigorously. Iron powder (370 mg, 6.62 mmol) was then added. The reaction was then warmed to 110 ˚C, stirred for 16 h, and then allowed to cool to rt by removal of the oil bath. The resulting solution was concentrated under

reduced pressure, diluted with DCM (20 mL), and washed with saturated aqueous $NaHCO_3$ (20 mL). The organic fraction was then filtered through celite. The filtrate was washed with saturated aqueous NaCl (20 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography eluting with EtOAc/hexanes (2:1) to afford 245 mg (56%) of the title compound as a light brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 4 H), 7.26-7.23 (m, 6 H), 7.09 (t, *J* = 10.5 Hz, 1 H), 6.98 (br s, 1 H), 6.88-6.87 (m, 2 H), 6.48 (d, *J* = 10.3 Hz, 1 H), 4.64 (s, 4 H), 2.09 (s, 3 H); ^{13}C NMR (100 MHz) δ 168.1, 149.8, 138.9, 138.3, 129.8, 128.7, 126.9, 126.7, 108.7, 108.6, 103.7, 54.1, 24.7; IR (neat) 3301, 3086, 3061, 3027, 2924, 2857, 1662, 1608, 1583, 1550, 1494, 1450, 1362, 1253, 1199, 1176, 963, 730 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{22}H_{23}N_2O$ 331.1805; Found 331.1797; mp = 144-146 ˚C.



SI15

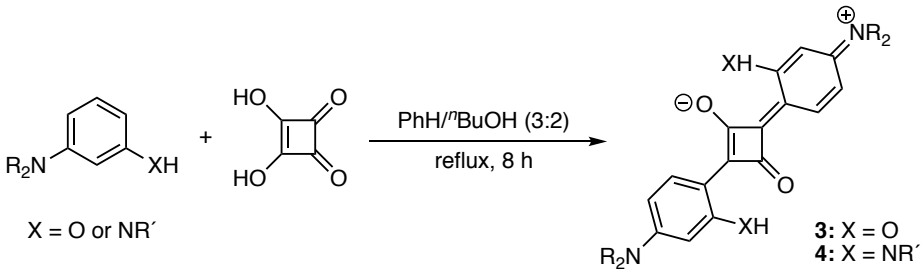
***N*-(3-(Allyl(methyl)amino)phenyl)acetamide.** *N*-allyl-*N*-methyl-3-nitroaniline (220 mg, 1.14 mmol) was dissolved in a 5:1 mixture of EtOAc/AcOH (18 mL), stirring vigorously. Iron powder (320 mg, 5.72 mmol) was then added. The reaction was then warmed to 110 ˚C, stirred for 16 h, and then allowed to cool to rt by removal of the oil bath. The resulting solution was concentrated under reduced pressure, diluted with DCM (20 mL), and washed with saturated aqueous $NaHCO_3$ (20 mL). The organic fraction was then filtered through celite. The filtrate was washed with saturated aqueous NaCl (20 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography eluting with hexanes/EtOAc (1:1) to afford 132 mg (59%) of the title compound as a light brown solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (br s, 1 H), 7.13 (t, *J* = 8.2 Hz, 1 H), 7.05 (t, *J* = 1.9 Hz, 1 H), 6.71 (dd, *J* = 7.8, 1.1 Hz, 1 H), 6.46 (dd, *J* = 8.3, 2.2 Hz, 1 H), 5.82 (ddt, *J* = 17.1, 10.4, 5.0 Hz, 1 H), 5.17-5.13 (m, 2 H), 3.90 (d, *J* = 5.0 Hz, 2 H), 2.93 (s, 3 H), 2.15 (s, 3 H); ^{13}C NMR (100 MHz) δ 168.3, 150.1, 138.9, 133.5, 129.4, 116.2, 108.5, 107.9, 104.0, 55.2, 38.1, 24.7; IR (neat) 3302, 3139, 3083, 2981, 2925, 1661, 1608, 1582, 1551, 1496, 1424, 1369, 1314, 1254, 1023 990, 920, 838 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{12}H_{17}N_2O$ 205.1335; Found 205.1359; mp = 69-70 ˚C.



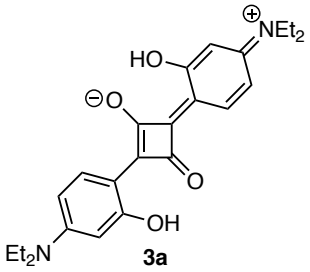
SI16

***N*-(3-(Methyl(prop-2-yn-1-yl)amino)phenyl)acetamide.** 3-nitro-*N*,*N*-di(prop-2-yn-1-yl)aniline (500 mg, 2.34 mmol) was dissolved in a 5:1 mixture of EtOAc/AcOH (30 mL), stirring vigorously. Iron powder (652 mg, 11.68 mmol) was then added. The reaction was then warmed to 110 ˚C, stirred for 16 h, and then allowed to cool to rt by removal of the oil bath. The resulting solution was concentrated under reduced pressure, diluted with DCM (20 mL), and washed with saturated aqueous $NaHCO_3$ (20 mL). The organic fraction was then filtered through celite. The filtrate was washed with saturated aqueous NaCl (20 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude mixture was then purified by flash chromatography eluting with hexanes/EtOAc (1:1) to afford 216 mg (41%) of the title comound as an orange solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.20 (m, 2 H), 7.11 (br s, 1 H), 6.95 (d, *J* = 7.8 Hz, 1 H), 6.71 (dd, *J* = 8.2, 2.0 Hz, 1 H), 4.12 (d, *J* = 2.4 Hz, 4 H), 2.26 (t, *J* = 2.2 Hz, 2 H), 2.17 (s, 3 H); ^{13}C NMR (100

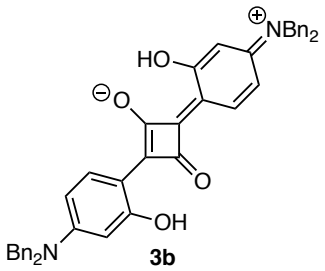
MHz) δ 168.1, 148.4, 138.8, 129.6, 111.6, 111.1, 107.0, 79.1, 72.7, 40.4, 24.8; IR (neat) 3289, 3154, 3087, 1664, 1608, 1551, 1496, 1440, 1370, 1314, 1252, 1178, 954, 919, 772 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{14}H_{15}N_2O$ 227.1179; Found 227.1162; mp = 117-119 ˚C.



General procedure for the synthesis of dianiline squaraine dyes (3/4). A flame dried round bottom flask was charged with squaric acid (1 mmol) and the indicated 1,3-disubstituted benzene derivative (2 mmol) then constituted in a 3:2 mixture of PhH/^{n}BuOH (9 mL). The round bottom flask mixture was then equipped with a Dean Stark trap, heated to reflux, stirred for 8 h with the azeotropic removal of H_2O, and then allowed to cool to rt by removal of the oil bath. The resulting mixture was then concentrated under reduced pressure, the residue reconstituted in MeOH (10 mL) in a sealed round bottomed flask, and placed in a –20 ˚C freezer for 14 h. The heterogenous mixture removed from the freezer and the solid immediately collected by vacuum filtration rinsing with MeOH (2 x 5 mL) cooled by an ice bath. The filtrate was dried under vacuum to afford the desired *ortho*-substituted dianiline squaraine dye **3** or **4**.

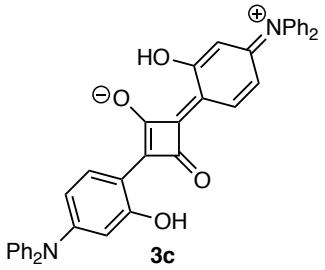


(*E*)-2-(4-(Diethylamino)-2-hydroxyphenyl)-4-(4-(diethyliminio)-2-hydroxycyclohexa-2,5- dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (3a). The condensation of 3-(diethylamino)phenol and squaric acid was performed on a 2 mmol scale to afford 496 mg (61%) of **3a** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.05 (s, 1 H), 8.17 (br s, 2 H), 8.08 (d, *J* = 9.3 Hz, 1 H), 6.68 (d, *J* = 9.3 Hz, 2 H), 6.35 (dd, *J* = 9.3, 2.4 Hz, 1 H), 6.11 (d, *J* = 2.4 Hz, 1 H), 3.48 (q, *J* = 7.2 Hz, 4 H), 3.40 (t, *J* = 7.7 Hz, 4 H), 1.64-1.60 (m, 4 H), 1.39 (qt, *J* = 7.5, 7.5 Hz, 4 H), 1.26 (t, *J* = 7.2 Hz, 6 H), 0.98 (t, *J* = 7.4 Hz, 6 H); ^{13}C NMR (125 MHz) δ 183.2, 164.7, 156.3, 133.2, 132.8, 110.0, 98.6, 45.6, 13.2; IR (neat) 2961, 2926, 2857, 1590, 1392, 1340, 1278, 1248, 1173, 1139 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{28}H_{37}N_2O_4$ 449.2799; Found 449.2796; mp = 198-200 ˚C.



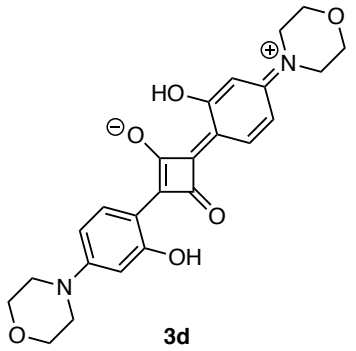
3b

(*E*)-2-(4-(Dibenzylamino)-2-hydroxyphenyl)-4-(4-(dibenzyliminio)-2-hydroxycyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (3b). The condensation of 3-(dibenzylamino)phenol and squaric acid was performed on a 2 mmol scale to afford 809 mg (62%) of **3b** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.14 (s, 1 H), 7.88 (d, *J* = 9.2 Hz, 2 H), 7.37 (t, *J* = 7.0 Hz, 8 H), 7.31-7.29 (m, 4 H), 7.18 (d, *J* = 7.1 Hz, 8 H), 6.47 (dd, *J* = 9.2, 2.5 Hz, 2 H), 6.28 (d, *J* = 2.5 Hz, 2 H), 4.73 (s, 8 H); ^{13}C NMR (100 MHz) δ 182.8, 174.4, 165.1, 158.2, 135.8, 132.9, 129.1, 127.8, 126.4, 111.0, 108.2, 99.5, 54.0; IR (neat) 3070, 3028, 2931, 1735, 1601, 1381, 1344, 1214, 1168 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{44}H_{37}N_2O_4$ 679.2567; Found 679.2594; mp >240 ˚C.



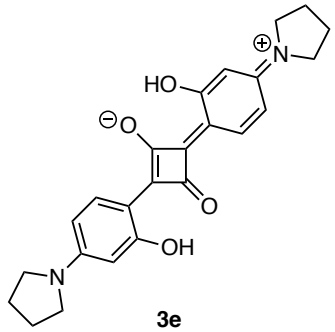
3c

(*E*)-2-(4-(Diphenylamino)-2-hydroxyphenyl)-4-(4-(diphenyliminio)-2-hydroxycyclohexa-2,5-dien-1- ylidene)-3-oxocyclobut-1-en-1-olate (3c). The condensation of 3-(diphenylamino)phenol and squaric acid was performed on a 0.44 mmol scale to afford 197 mg (75%) of **3c** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.13 (s, 2 H), 7.84 (d, *J* = 9.1 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 8 H), 7.27 (t, *J* = 7.5 Hz, 4 H), 7.21 (d, *J* = 7.35 Hz, 8 H), 6.45 (dd, *J* = 9.1, 2.3 Hz, 2 H), 6.30 (d, *J* = 2.3 Hz, 2 H); ^{13}C NMR (125 MHz) δ 183.0, 175.6, 165.2, 158.0, 144.7, 132.2, 130.1, 127.5, 127.0, 113.2, 113.1, 105.3; IR (neat) 3062, 2929, 1594, 1493, 1461, 1439, 1378, 1336, 1294, 1218, 1184, 1106, 1024, 697 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{40}H_{30}N_2O_4$ 601.2122; Found 601.2126; mp >240 ˚C.



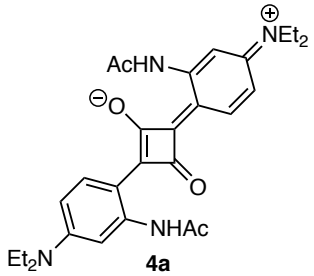
3d

(*E*)-4-(2-Hydroxy-4-(morpholino-4-ium)cyclohexa-2,5-dien-1-ylidene)-2-(2-hydroxy-4-morpholinophenyl)-3-oxocyclobut-1-en-1-olate (3d). The condensation of 3-morpholinophenol and squaric acid was performed on a 0.84 mmol scale to afford 308 mg (84%) of **3d** as a blue solid that was insoluble in a wide array of solvents, preventing further spectroscopic analysis. The isolated solid was therefore carried forward without further analysis: IR (neat) 2986, 2953, 2921, 2855, 1624, 1601, 1427, 1399, 1326, 1175, 1109, 1039, 887, 812, 778, 748 cm^{-1}; mp >240 ˚C.



3e

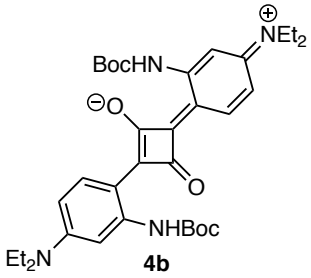
(*E*)-4-(2-Hydroxy-4-(pyrrolidin-1-ium-1-ylidene)cyclohexa-2,5-dien-1-ylidene)-2-(2-hydroxy-4-(pyrrolidin-1-yl)phenyl)-3-oxocyclobut-1-en-1-olate (3e). The condensation of 3-(pyrrolidin-1-yl)phenol and squaric acid was performed on a 0.92 mmol scale to afford 314 mg (85%) of **3e** as a teal solid that was insoluble in a wide array of solvents, preventing further spectroscopic analysis. The isolated solid was therefore carried forward without further analysis: IR (neat) 2956, 2918, 2847, 1607, 1532, 1369, 1351, 1316, 1246, 1202, 1153, 1104, 884, 805, 776, 736 cm^{-1}; mp >240 ˚C.



4a

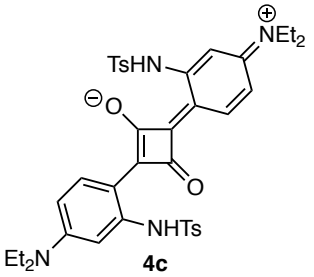
(*E*)-2-(2-Acetamido-4-(diethylamino)phenyl)-4-(2-acetamido-4-(diethyliminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4a). The condensation of *N*-(3-(diethylamino)phenyl)acetamide and squaric acid was performed on a 1.09 mmol scale to afford 480 mg (90%) of **4a** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.11

(s, 2 H), 8.44 (d, *J* = 9.3 Hz, 2 H), 8.26 (d, *J* = 2.6 Hz, 2 H), 9.46 (dd, *J* = 9.4, 2.5 Hz, 2 H), 3.53 (q, *J* = 7.1 Hz, 8 H), 2.36 (s, 6 H), 1.29 (t, *J* = 7.2 Hz, 12 H); ^{13}C NMR (125 MHz) δ 183.1, 171.0, 155.2, 144.2, 134.2, 133.5, 112.5, 108.7, 102.6, 45.8, 25.4, 13.1; IR (neat) 2981, 2930, 1700, 1617, 1580, 1487, 1399, 1342, 1301, 1248, 1209, 1174, 1154, 1074, 1007, 964 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{28}H_{35}N_4O_4$ 491.2652; Found 491.2632; mp >240 ˚C.



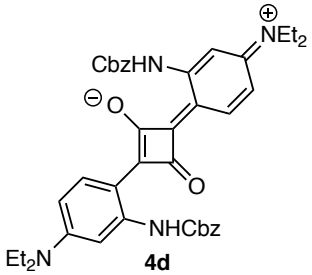
4b

(*E*)-2-(2-((*tert*-Butoxycarbonyl)amino)-4-(diethylamino)phenyl)-4-(2-((tert-butoxycarbonyl)amino)-4- (diethyliminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4b). The condensation of *tert*-butyl (3-(diethylamino)phenyl)carbamate and squaric acid was performed on a 0.43 mmol scale to afford 260 mg (>99%) of **4b** as a gold solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.57 (br s, 1 H), 11.06 (br s, 1 H), 8.53 (m, 2 H), 7.90 (m, 2 H), 6.38 (dd, *J* = 9.3, 2.4 Hz, 2 H), 3.50 (q, *J* = 7.1 Hz, 8 H), 1.57 (s, 18 H), 1.27 (t, *J* = 7.1 Hz, 12 H); ^{13}C NMR (100 MHz) δ 154.8, 153.6, 145.2, 134.0, 133.7, 112.1, 107.6, 100.1, 80.2, 77.2, 45.3, 28.4, 13.0; IR (neat) 2979, 2934, 2909, 1726, 1606, 1582, 1487, 1399, 1385, 1340, 1256, 1226, 1140, 1074, 907, 727 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{34}H_{47}N_4O_6$ 607.3490; Found 607.3472; mp = 220 ˚C (decomp.).



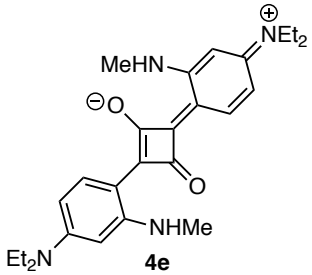
4c

(*E*)-2-(4-(Diethylamino)-2-((4-methylphenyl)sulfonamido)phenyl)-4-(4-(diethyliminio)-2-((4- methylphenyl)sulfonamido)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4c). The condensation of *N*-(3-(diethylamino)phenyl)-4-methylbenzenesulfonamide and squaric acid was performed on a 0.47 mmol scale to afford 273 mg (81%) of **4c** as a gold solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.54 (s, 2 H), 8.32 (d, *J* = 9.3 Hz, 2 H), 7.83 (d, *J* = 8.4 Hz, 4 H), 7.23 (d, *J* = 8.0 Hz, 4 H), 6.83 (d, *J* = 2.5 Hz, 2 H), 6.34 (dd, *J* = 9.3, 2.4 Hz, 2 H), 3.45 (q, *J* = 7.0 Hz, 8 H), 2.37 (s, 6 H), 1.22 (t, *J* = 7.1 Hz, 12 H); ^{13}C NMR (100 MHz) δ 182.3, 174.2 154.5, 143.9, 137.1, 134.1, 129.6, 127.3, 112.3, 108.5, 100.0, 83.4, 45.6, 21.6, 12.9; IR (neat) 3303, 2971, 2924, 2867, 2652, 1667, 1601, 1495, 1389, 1337, 1254, 1177, 1153, 1073, 971, 903, 816, 771 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{38}H_{43}N_2O_6S_2$ 715.2619; Found 715.2621; mp >240 ˚C.



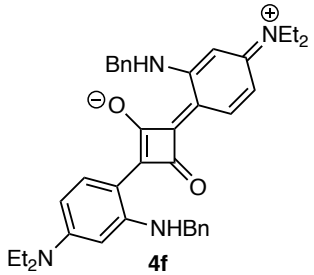
4d

(*E*)-2-(2-(((Benzyloxy)carbonyl)amino)-4-(diethylamino)phenyl)-4-(2-(((benzyloxy)carbonyl)amino)-4-(diethyliminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4d). The condensation of benzyl (3-(diethylamino)phenyl)carbamate and squaric acid was performed on a 1.00 mmol scale to afford 390 mg (59%) of **4d** as a gold solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.99 (s, 2 H), 8.46 (d, J = 9.3 Hz, 2 H), 7.88 (d, J = 2.1 Hz, 2 H), 7.47 (d, J = 7.8 Hz, 2 H), 7.39-7.29 (m, 8 H), 6.40 (dd, J = 9.3, 2.5 Hz, 2 H), 5.31 (s, 4 H), 3.51 (q, J = 7.1 Hz, 8 H), 1.27 (t, J = 7.1 Hz, 12 H); ^{13}C NMR (100 MHz) δ 182.6, 174.3, 154.8, 154.3, 144.5, 136.7, 133.7, 128.5, 128.3, 127.8, 127.7, 127.4, 112.1, 108.0, 100.6, 66.4, 45.5, 12.9; IR (neat) 2975, 2958, 2897, 1731, 1613, 1399, 1381, 1336, 1259, 1223, 1171, 1150, 1077 cm^{-1};; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{40}H_{43}N_4O_6$ 697.2997; Found 607.3013; mp = 235 ˚C.



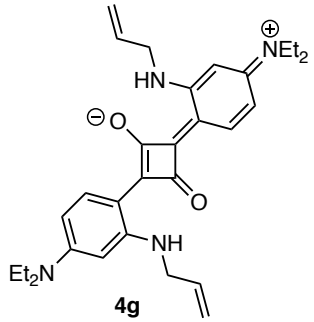
4e

(*E*)-2-(4-(Diethylamino)-2-(methylamino)phenyl)-4-(4-(diethyliminio)-2-(methylamino)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4e). The condensation of N^1,N^1-diethyl-N^3-methylbenzene-1,3-diamine and squaric acid was performed on a 0.67 mmol scale to afford 25 mg (9%) of **4e** as a copper solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (br s, 2 H), 8.28-8.20 (m, 2 H), 6.09 (dd, J = 9.3, 2.4 Hz, 2 H), 5.49 (d, J = 1.9 Hz, 2 H), 3.44 (q, J = 7.1 Hz, 8 H), 2.90 (d, J = 4.7 Hz, 6 H), 1.23 (t, J = 7.1 Hz, 12 H); ^{13}C NMR (125 MHz) δ 192.0, 154.6, 154.4, 129.7, 106.6, 104.5, 89.6, 89.2, 45.1, 29.9, 13.2; IR (neat) 2962, 2924, 1596, 1549, 1431, 1384, 1338, 1308, 1260, 1076, 1016, 916, 799, 725 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{26}H_{35}N_4O_2$ 435.2755; Found 435.2726; mp = >240 ˚C (decomp.).



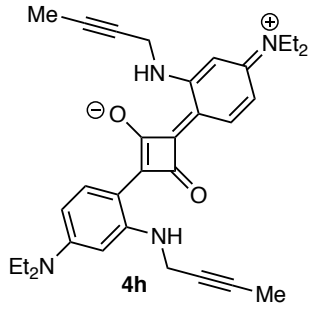
4f

(*E*)-2-(2-(Benzylamino)-4-(diethylamino)phenyl)-4-(2-(benzylamino)-4-(diethyliminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4f). The condensation of N^1-benzyl-N^3,N^3-diethylbenzene-1,3-diamine and squaric acid was performed on a 0.69 mmol scale to afford 196 mg (34%) of **4f** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76-9.53 (br m, 2 H), 8.35-8.24 (br m, 2 H), 7.41 (d, *J* = 7.3 Hz, 4 H), 7.32 (t, *J* = 7.5 Hz, 4 H), 7.22 (t, *J* = 7.4 Hz, 2 H), 6.06 (d, *J* = 8.6 Hz, 2 H), 5.41 (br s, 2 H), 4.51 (br s, 4 H), 3.26 (q, *J* = 7.1 Hz, 8 H), 1.02 (t, *J* = 7.1 Hz, 12 H); ^{13}C NMR (125 MHz) δ 185.4, 154.2, 153.5, 139.5, 135.6, 133.8, 133.0, 128.8, 127.1, 123.1, 104.7, 91.6, 47.5, 45.2, 13.0; IR (neat) 2982, 2933, 1596, 1560, 1395, 1340, 1226, 1171, 1149, 1074, 1004 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{38}H_{43}N_4O_2$ 586.3326; Found 587.3326; mp = >240 ˚C (decomp.).



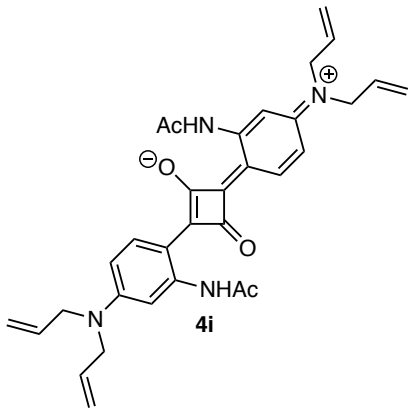
4g

(*E*)-2-(2-(Allylamino)-4-(diethylamino)phenyl)-4-(2-(allylamino)-4-(diethyliminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4g). The condensation of N^1-allyl-N^3,N^3-diethylbenzene-1,3-diamine and squaric acid was performed on a 0.52 mmol scale to afford 60 mg (12%) of **4g** as a purple solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (br m, 2 H), 8.28 (br m, 2 H), 6.08 (d, *J* = 9.0 Hz, 2 H), 5.98 (br m, 2 H), 5.54 (d, *J* = 1.7 Hz, 2 H), 5.35 (dd, *J* = 17.2, 1.5, 2 H), 5.21 (d, *J* = 10.1 Hz, 2 H), 3.90 (t, *J* = 0.2 Hz, 4 H), 3.40 (q, *J* = 7.1 Hz, 8 H), 1.21 (t, *J* = 7.1 Hz, 12 H); ^{13}C NMR (125 MHz) δ 183.6, 172.0, 154.3, 153.6, 135.14, 135.13, 116.7, 110.3, 104.6, 90.5, 46.2, 45.2, 13.3; IR (neat) 2980, 2364, 2244, 1602, 1563, 1497, 1388, 1342, 1307, 1251, 1224, 1173, 1151, 1078, 913 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{30}H_{39}N_4O_2$ 487.3068; Found 487.3069; mp = 206 - 208 ˚C.



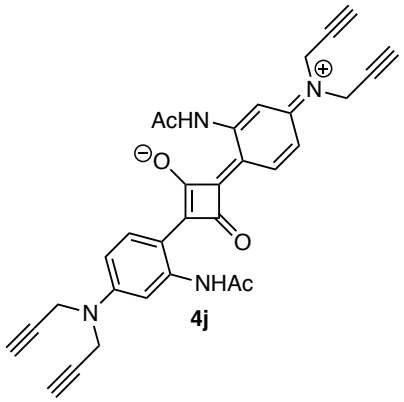
4h

(*E*)-2-(2-(But-2-yn-1-ylamino)-4-(diethylamino)phenyl)-4-(2-(but-2-yn-1-ylamino)-4-(diethyliminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4h). The condensation of N^1-(but-2-yn-1-yl)-N^3,N^3-diethylbenzene-1,3-diamine and squaric acid was performed on a 0.55 mmol scale to afford 56.8 mg (10%) of **4h** as a blue solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39-9.01 (br m, 2 H), 8.31-8.22 (m, 2 H), 6.13 (dd, J = 8.8, 2.3 Hz, 2 H), 5.76 (d, J = 2.3 Hz, 2 H), 3.99 (br s, 4 H), 3.46 (q, J = 7.1 Hz, 8 H), 1.80 (t, J = 2.3 Hz, 6 H), 1.25 (t, J = 7.1 Hz, 12 H); ^{13}C NMR (125 MHz) δ 183.5, 172.3, 154.4, 152.9, 133.2, 110.4, 104.5, 91.0, 79.0, 75.6, 45.4, 32.9, 13.3, 3.9; IR (neat) 2986, 2974, 2924, 2871, 2850, 1599, 1497, 1391, 1341, 1306, 1224, 1174, 1151, 1075, 999 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{32}H_{39}N_4O_2$ 511.3068; Found 511.3067; mp >240 ˚C (decomp.).



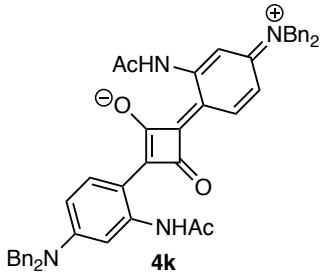
4i

(*E*)-2-(2-Acetamido-4-(diallylamino)phenyl)-4-(2-acetamido-4-(diallyliminio)cyclohexa-2,5-dien-1- ylidene)-3-oxocyclobut-1-en-1-olate (4i). The condensation of *N*-(3-(diallylamino)phenyl)acetamide and squaric acid was performed on a 0.65 mmol scale to afford 297 mg (85%) of **4i** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.10 (s, 2 H), 8.44 (d, J = 9.3, 2 H), 8.31 (d, J = 2.5 Hz, 2 H), 6.48-6.46 (m, 2 H), 5.87 (ddt, J = 17.1, 10.4, 5.0 Hz, 4 H), 5.27 (d, J = 10.3, 4 H), 5.22 (d, J = 17.1, 4 H), 4.09 (d, J = 4.9 Hz, 8 H), 2.35 (s, 6 H); ^{13}C NMR (100 MHz) δ 182.7, 175.7, 170.7, 156.4, 144.3, 133.3, 131.3, 117.9, 113.0, 109.2, 102.8, 53.3, 25.1; IR (neat) 3082, 3006, 2976, 2926, 2677, 1708, 1614, 1577, 1525, 1480, 1379, 1327, 1224, 1164, 1009, 925, 863, 777 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{32}H_{35}N_4O_4$ 539.2653; Found 539.2667; mp = 175-177 ˚C.



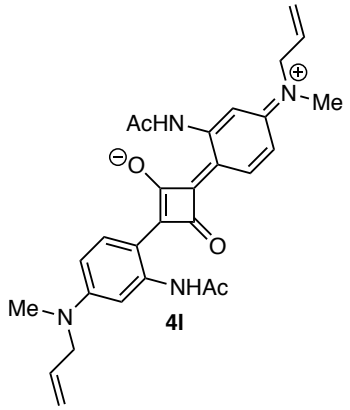
4j

(*E*)-2-(2-Acetamido-4-(di(prop-2-yn-1-yl)amino)phenyl)-4-(2-acetamido-4-(di(prop-2-yn-1- yl)iminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4j). The condensation of *N*-(3-(di(prop-2-yn-1-yl)amino)phenyl)acetamide and squaric acid was performed on a 0.78 mmol scale to afford 58 mg (14%) of **4j** as a green solid that was insoluble in a wide array of solvents, preventing further spectroscopic analysis. The isolated solid was therefore carried forward without further analysis: IR (neat) 3232, 2953, 2925, 2855, 1702, 1616, 1580, 1384, 1223, 1174, 873, 773, 668 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{32}H_{35}N_4O_4$ 539.2653; Found 5392667; mp >240 ˚C.



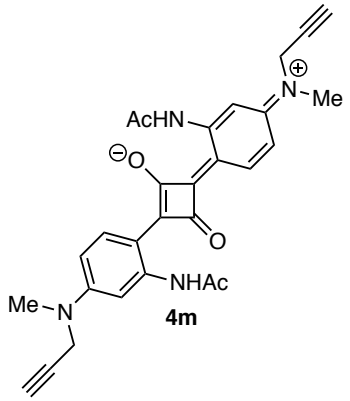
4k

(*E*)-2-(2-Acetamido-4-(dibenzylamino)phenyl)-4-(2-acetamido-4-(dibenzyliminio)cyclohexa-2,5- dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4k). The condensation of *N*-(3-(dibenzylamino)phenyl)acetamide and squaric acid was performed on a 0.37 mmol scale to afford 186 mg (68%) of **4k** as a green solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.05 (s, 2 H), 8.49 (d, *J* = 2.5 Hz, 2 H), 8.46-8.45 (m, 1 H), 8.40 (d, *J* = 9.3 Hz, 1 H), 7.37-7.28 (m, 12 H), 7.22 (d, *J* = 6.9 Hz, 8 H), 6.54 (dd, *J* = 9.3, 2.5 Hz, 2 H), 4.79 (s, 8 H), 4.29 (s, 6 H); ^{13}C NMR (100 MHz) δ 182.6, 176.2, 170.6, 156.9, 144.5, 135.9, 133.5, 129.0, 127.8, 126.8, 113.4, 109.6, 102.9, 54.3, 25.1; IR (neat) 3060, 3033, 3002, 2926, 2873, 2845, 1707, 1615, 1575, 1524, 1479, 1382, 1344, 1263, 1221, 892, 777 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{48}H_{43}N_4O_4$ 739.3261; Found 739.3261; mp >240 ˚C.



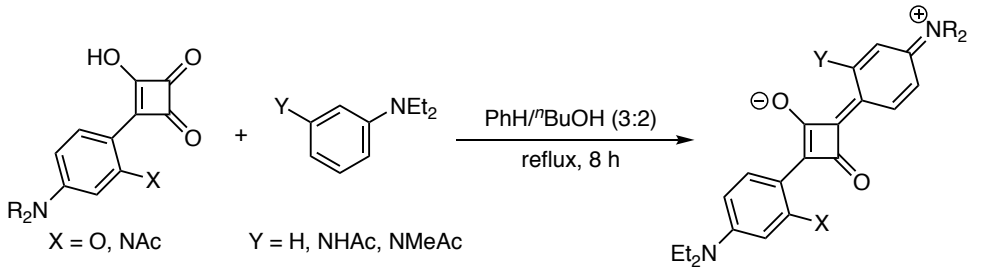
4l

(*E*)-2-(2-Acetamido-4-(allyl(methyl)amino)phenyl)-4-((*Z*)-2-acetamido-4-(allyl(methyl)iminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4l). The condensation of *N*-(3-(allyl(methyl)amino)phenyl)acetamide and squaric acid was performed on a 0.29 mmol scale to afford 121 mg (86%) of **4l** as a green solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.11 (s, 2 H), 8.44 (d, *J* = 9.2 Hz, 2 H), 8.27 (d, *J* = 2.6 Hz, 2 H), 6.47 (dd, *J* = 9.3, 2.5 Hz, 2 H), 5.84 (ddt, *J* = 17.1, 10.3, 5.0 Hz, 2 H), 5.26 (dd, *J* = 10.3, 1.0 Hz, 2 H), 5.18 (dd, *J* = 17.1, 1.0 Hz, 2 H), 4.10 (d, *J* = 5.0 Hz, 3 H), 3.18 (s, 6 H), 2.35 (s, 6 H); ^{13}C NMR (100 MHz) δ 182.7, 175.4, 170.7, 156.5, 144.2, 133.3, 131.1, 117.7, 112.8, 108.9, 102.5, 55.2, 38.8, 25.2; IR (neat) 2922, 2856, 2684, 1703, 1616, 1577, 1530, 1467, 1429, 1363, 1267, 1241, 1221, 1171, 1013, 917, 864, 817 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{28}H_{31}N_4O_4$ 487.2340; Found 487.2358; mp = 234-245 ˚C (decomp.).



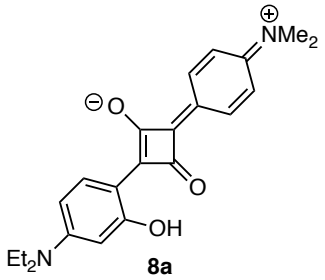
4m

(*E*)-2-(2-Acetamido-4-(methyl(prop-2-yn-1-yl)amino)phenyl)-4-((*Z*)-2-acetamido-4-(methyl(prop-2- yn-1-yl)iminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (4m). The condensation of *N*-(3-(methyl(prop-2-yn-1-yl)amino)phenyl)acetamide and squaric acid was performed on a 0.19 mmol scale to afford 43 mg (48%) of **4m** as a green solid that was insoluble in deuterated NMR solvent: HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{28}H_{27}N_4O_4$ 483.2027; Found 483.2018; IR (neat) 3309, 3086, 2962, 2878, 1665, 1609, 1583, 1551, 1497, 1370, 1251 cm^{-1}; mp >240 ˚C.



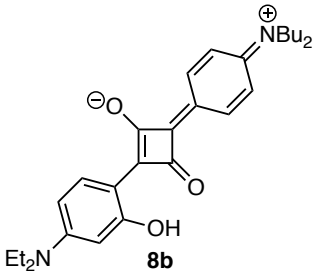
8: X = O, NAc; Y = H, NHAc, NMeAc

General procedure for the synthesis of unsymmetrical dianiline squaraine dyes. The indicated semisquaraine (1 mmol) and 1,3-disubstituted benzene derivative (1 mmol) were constituted in a 3:2 mixture of PhH/^{n}BuOH (10 mL). The round bottom flask mixture was then equipped with a Dean Stark trap, heated to reflux, stirred for 8 h with the azeotropic removal of H_2O, and then allowed to cool to rt by removal of the oil bath. The resulting mixture was then concentrated under reduced pressure, the residue reconstituted in MeOH (5 mL) in a sealed round bottomed flask, and placed in a –20 ˚C freezer for 14 h. The heterogenous mixture removed from the freezer and the solid immediately collected by vacuum filtration rinsing with MeOH (2 x 5 mL) cooled by an ice bath. The filtrate was dried under vacuum to afford the desired unsymmetrical squaraine dyes **8**.



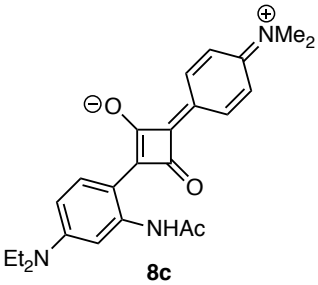
8a

2-(4-(Diethylamino)-2-hydroxyphenyl)-4-(4-(dimethyliminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (8a). The condensation of semisquaraine (R=Me, X=H) and aniline derivative (Y=OH) was performed on a 0.115 mmol scale to afford 12 mg (28%) of **8a** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.13 (s, 1 H), 8.20 (d, J = 8.5 Hz, 2 H), 8.09 (d, J = 9.3 Hz, 1 H), 6.74 (d, J = 9.2 Hz, 2 H), 6.37 (dd, J = 9.3, 2.5 Hz, 1 H), 6.12 (d, J = 2.5 Hz, 1 H) 3.50 (q, J = 7.2 Hz, 8 H), 3.15 (s, 6 H), 1.27 (t, J = 7.2 Hz, 12 H); ^{13}C NMR (125 MHz) δ 184.8, 184.3, 181.5, 174.4, 166.6, 157.7, 153.9, 133.9, 132.1, 119.4, 112.3, 111.8, 108.4, 98.4, 45.8, 40.5, 13.2; IR (neat) 2987, 1596, 1538, 1449, 1400, 1348, 1249, 1185, 10073, 911, 822, 775, 741 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{22}H_{25}N_2O_3$ 365.1860; Found 365.1856; mp >240 ˚C.



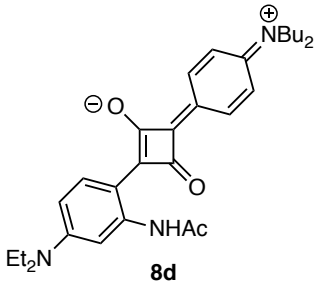
8b

4-(4-(Dibutyliminio)cyclohexa-2,5-dien-1-ylidene)-2-(4-(diethylamino)-2-hydroxyphenyl)-3-oxocyclobut-1-en-1-olate (8b). The condensation of semisquaraine (R=Bu, X=H) and aniline derivative (Y=OH) was performed on a 0.33 mmol scale to afford 65.8 mg (44%) of **8b** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.05 (s, 1 H), 8.17 (br , 2 H), 8.08 (d, *J* = 9.3 Hz, 1 H), 6.68 (d, *J* = 9.3 Hz, 2 H), 6.35 (dd, *J* = 9.3, 2.4 Hz, 1 H), 6.11 (d, *J* = 2.4 Hz, 1 H), 3.48 (q, *J* = 7.2 Hz, 4 H), 3.40 (t, *J* = 7.7 Hz, 4 H), 1.64-1.60 (m, 4 H), 1.39 (qt, *J* = 7.5, 7.5 Hz, 4 H), 1.26 (t, *J* = 7.2 Hz, 6 H), 0.98 (t, *J* = 7.4 Hz, 6 H); ^{13}C NMR (125 MHz) δ 184.8, 183.4, 181.6, 174.6, 166.3, 157.3, 152.5, 133.7, 132.4, 118.9, 112.3, 111.6, 108.1, 98.4, 51.3, 45.7, 29.8, 20.5, 14.1, 13.2; IR (neat) 2961, 2926, 2857, 1590, 1392, 1340, 1278, 1248, 1173, 1139 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{28}H_{37}N_2O_3$ 449.2799; Found 449.2796; mp = 198-200 ˚C.



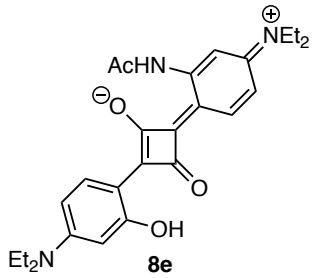
8c

2-(2-Acetamido-4-(diethylamino)phenyl)-4-(4-(dimethyliminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (8c). The condensation of semisquaraine (R=Me, X=H) and aniline derivative (Y=NHAc) was performed on a 0.115 mmol scale to afford 22 mg (47%) of **8c** as a blue solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.39 (s, 1 H), 8.60 (d, *J* = 9.4, 1 H), 8.28 (m, 3 H), 6.74 (d, *J* = 9.2 Hz, 2 H), 6.48 (dd, *J* = 9.4, 2.6 Hz, 1 H), 3.55 (q, *J* = 7.2 Hz, 4 H), 3.17 (s, 6 H), 1.30 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (125 MHz) δ 184.1, 183.7, 182.7, 177.5, 171.3, 156.3, 154.2, 145.3, 134.7, 132.2, 119.6, 113.6, 112.4, 109.1, 102.4, 46.0, 40.5, 25.4, 13.1; IR (neat) 2973, 2932, 2870, 1632, 1599, 1398, 1372, 1346, 1261, 1181, 910, 735 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{24}H_{28}N_2O_3$ 428.1945; Found 428.1926; mp = 214 ˚C.



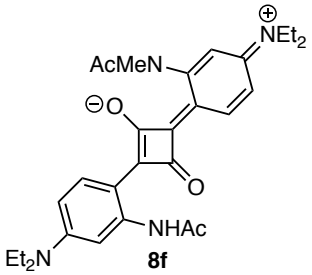
8d

2-(2-Acetamido-4-(diethylamino)phenyl)-4-(4-(dibutyliminio)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (8d). The condensation of semisquaraine (R=Bu, X=H) and aniline derivative (Y=NHAc) was performed on a 0.33 mmol scale to afford 95.2 mg (59%) of **8d** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.38 (s, 1 H), 8.58 (d, *J* = 9.3 Hz, 1 H), 8.27-8.24 (m, 3 H), 6.70 (d, *J* = 9.3 Hz, 2 H), 6.46 (dd, *J* = 9.4, 2.6 Hz, 1 H), 3.54 (q, *J* = 7.2 Hz. 4 H), 3.41 (t, *J* = 7.7 Hz, 4 H), 2.37 (s, 3 H), 1.66-1.60 (m, 4 H), 1.40 (qt, *J* = 7.6, 7.6 Hz, 4 H), 1.29 (t, *J* = 7.1 Hz, 6 H), 0.98 (t, *J* = 7.4 Hz, 6 H); ^{13}C NMR (125 MHz) δ 183.7, 183.2, 182.7, 177.7, 156.0, 152.9, 145.1, 134.5, 132.6, 119.1, 113.4, 112.4, 108.9, 102.4, 51.3, 45.9, 29.8, 25.4, 20.5, 14.1, 13.1; IR (neat) 2963, 2927, 2873, 1630, 1580, 1487, 1387, 1339, 1297, 1257, 1173, 1076 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{30}H_{40}N_3O_3$ 490.3064; Found 490.3074; mp = 177 ˚C (decomp.).



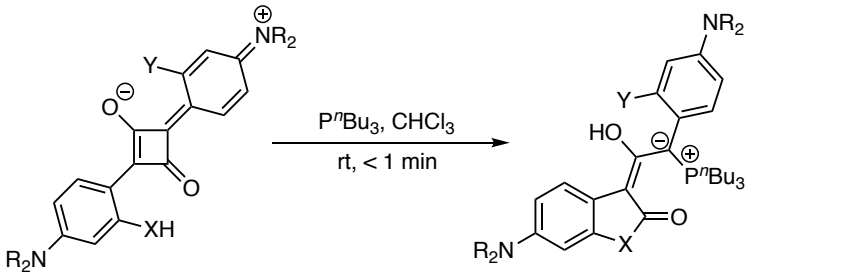
8e

(*E*)-4-(2-Acetamido-4-(diethyliminio)cyclohexa-2,5-dien-1-ylidene)-2-(4-(diethylamino)-2-hydroxyphenyl)-3-oxocyclobut-1-en-1-olate (8e). The condensation of semisquaraine (R=Et, OH) and aniline derivative (Y=NHAc) was performed on a 0.116 mmol scale to afford 39 mg (75%) of **8e** as a green solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.41 (br s, 1 H), 11.91 (br s., 1 H), 8.29 (d, *J* = 9.2 Hz, 1 H), 8.23 (d, *J* = 2.6 Hz, 1 H), 7.98 (d, *J* = 9.2 Hz, 1 H), 6.44 (dd, *J* = 9.2, 2.5 Hz, 1 H), 6.34 (dd, *J* = 9.3, 2.5 Hz, 1 H), 6.14 (d, *J* = 2.4 Hz, 1 H), 3.51 (q, *J* = 7.1 Hz, 4 H), 3.48 (q, *J* = 7.1 Hz, 4 H), 2.35 (s, 3 H), 1.28 (t, *J* = 7.1 Hz, 6 H), 1.26 (t, *J* = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz) δ 184.2, 182.1, 174.7, 171.8, 170.9, 165.0, 156.6, 154.8, 144.1, 133.6, 132.8, 112.0, 110.6, 108.6, 107.8, 102.5, 98.6, 45.8, 45.6, 25.4, 13.2, 13.1; IR (neat) 2976, 2921, 2856, 1610, 1397, 1340, 1246, 1175, 1073, 761 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{26}H_{33}N_3O_4$ 450.2387; Found 450.2368; mp = 231 ˚C.



8f

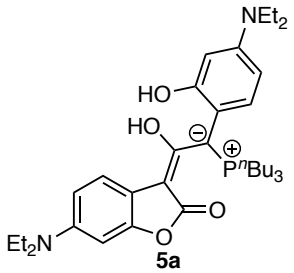
(*E*)-2-(2-Acetamido-4-(diethylamino)phenyl)-4-(4-(diethyliminio)-2-(*N*-methylacetamido)cyclohexa-2,5-dien-1-ylidene)-3-oxocyclobut-1-en-1-olate (8f). The condensation of semisquaraine (R=Et, NHAc) and aniline derivative (Y=NMeAc) was performed on a 0.67 mmol scale to afford 292 mg (87%) of **8f** as a copper solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.60 (br s, 1 H), 8.68 (d, *J* = 9.4 Hz, 1 H), 8.62 (d, *J* = 9.2 Hz, 1 H), 8.28 (d, *J* = 2.6 Hz, 1 H), 6.70 (dd, *J* = 9.2, 2.7 Hz, 1 H), 6.50 (d, *J* = 2.7 Hz, 1 H), 6.45 (dd, *J* = 9.5, 2.6 Hz, 1 H), 3.58-3.52 (m, 4 H), 3.51-3.45 (m, 4 H), 3.28 (s, 3 H), 3.25 (s, 3 H), 1.92 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 6 H), 1.25 (t, *J* = 7.1 Hz, 6 H); ^{13}C NMR (125 MHz) δ 185.6, 182.9, 180.6, 174.1, 171.5, 170.4, 157.3, 152.3, 146.7, 146.0, 135.3, 133.5, 117.7, 114.1, 112.7, 111.2, 109.5, 102.4, 46.2, 45.3, 38.4, 25.4, 22.7, 13.2, 12.9; IR (neat) 2965, 2922, 2854, 1640, 1588, 1395, 1342, 1251, 1167, 1063, 910, 761 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{29}H_{38}N_4O_4$ 505.2809; Found 505.2802; mp = 144-146 ˚C.



3: X = O; Y = OH
4: X = NR´; Y = NHR´
8: X = O, NAc; Y = H, NHAc, NMeAc

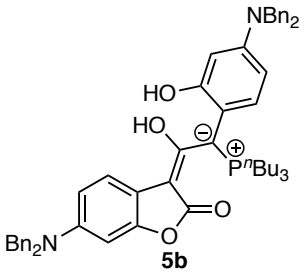
5: X = O; Y = OH
4: X = NR´; Y = NHR´
9: X = O, NAc; Y = H, NHAc, NMeAc

General procedure for the dearomatizative rearrangement of *ortho*-substituted dianiline squaraine dyes. P*n*Bu$_3$ (0.11 mmol) was added in one portion to a suspension of squaraine dye **3/4/8** (0.1 mmol) in $CHCl_3$ (1 mL) to provide a heterogeneous mixture that became homogeneous and underwent a color change from blue/green to yellow in <1 min. The resulting solution was then concentrated under reduced pressure, and the crude mixture was reconstituted in MeCN (2 mL). The solution was washed with pentanes (5 mL) and concentrated under reduced pressure to afford the title compound **5/6/9** without the need for further purification.



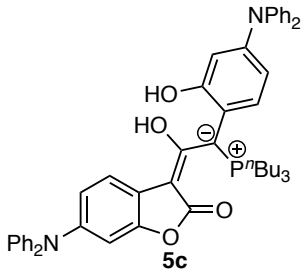
5a

(*E*)-1-(4-(Diethylamino)-2-hydroxyphenyl)-2-(6-(diethylamino)-2-oxobenzofuran-3(2H)-ylidene)-2-hydroxy-1-(tributyl-λ4-phosphanyl)ethan-1-ide (5a). The reaction of squaraine dye **3a** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 57 mg (94%) of **5a** as a blue oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1 H), 9.72 (s, 1 H), 7.57-7.49 (m, 2 H), 6.26-6.13 (m, 4 H), 3.31 (q, *J* = 6.6 Hz, 4 H), 3.29 (q, *J* = 6.8 Hz, 4 H), 2.11 (m, 6 H), 1.52 (m, 6 H), 1.42 (sx, *J* = 7.1 Hz, 6 H), 1.13 (t, *J* = 6.3 Hz, 6 H), 1.12 (t, *J* = 6.7 Hz, 6 H), 0.90 (t, *J* = 7.3 Hz, 9 H); ^{13}C NMR (125 MHz) δ 176.1, 176.0, 157.7 (d, *J* = 3.6 Hz), 155.5, 149.7, 148.3, 129.5 (d, *J* = 3.6 Hz), 127.6, 115.4, 115.3, 106.7, 106.2, 104.7, 103.9, 101.5, 99.8, 44.5, 24.4 (d, *J* = 14.7 Hz), 24.1 (d, *J* = 4.9 Hz), 18.8, 18.5, 13.6, 12.9, 12.8; IR (neat) 3087, 2965, 2931, 2872, 1724, 1622, 1569, 1515, 1463, 1396, 1375, 1355, 1269, 1217, 1093, 790 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{36}H_{56}N_2O_4P$ 611.3972; Found 611.3994.



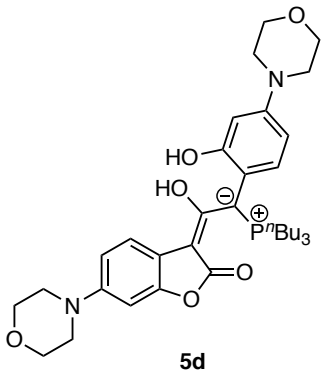
5b

(*E*)-6-(Dibenzylamino)-3-(2-(4-(dibenzylamino)-2-hydroxyphenyl)-1-hydroxy-2-(tributyl-λ5-phosphaneylidene)ethylidene)benzofuran-2(3*H*)-one (5b). The reaction of squaraine dye **3b** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 86 mg (>99%) of **5b** as a red oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.31 (s, 1 H), 9.70 (s, 1 H), 7.50 (d, *J* = 8.6 Hz, 1 H), 7.47 (dd, *J* = 8.7, 2.2 Hz, 1 H), 7.31-7.19 (m, 20 H), 6.32 (d, *J* = 2.6 Hz, 1 H), 6.28-6.22 (m, 3 H), 4.59 (s, 4 H), 4.57 (s, 4 H), 2.12-2.07 (comp., 6 H), 1.51-1.36 (m, 12 H), 0.88 (t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz) δ 175.8 (d, *J* = 5.8 Hz), 172.9, 157.4, 155.2, 151.3, 151.0, 149.8, 149.6, 146.6, 1389, 138.7, 138.2, 138.1, 129.2, 128.6, 128.5, 126.9, 126.8, 126.7, 126.6, 120.7, 118.0, 114.9, 114.8, 107.9, 107.7, 105.4, 104.8, 104.4, 102.7, 102.3, 100.4, 95.3, 64.9 (d, *J* = 31.9 Hz), 54.7, 53.8 (d, *J* = 10.1 Hz), 24.2 (d, *J* = 14.5 Hz), 23.8 (d, *J* = 4.9 Hz), 18.5 (d, *J* = 42 Hz), 13.3; IR (neat) 2955, 2923, 2857, 1602, 1441, 1385, 1345, 1218, 1162 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{56}H_{64}N_2O_4P$ 859.4598; Found 859.4571.



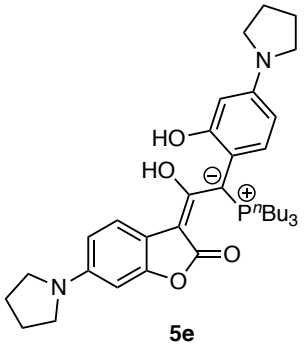
5c

(*E*)-6-(Diphenylamino)-3-(2-(4-(diphenylamino)-2-hydroxyphenyl)-1-hydroxy-2-(tributyl-λ5- phosphanylidene)ethylidene)benzofuran-2(3H)-one (5c). The reaction of squaraine dye **3c** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 77 mg (93%) of **5c** as a red oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1 H), 9.70 (d, *J* = 1.5 Hz, 1 H), 7.58 (d, *J* = 8.4 Hz, 1 H), 7.55 (dd, *J* = 8.9, 1.2 Hz, 1 H), 7.22 (t, *J* = 7.2 Hz, 4 H), 7.20 (t, *J* = 7.8 Hz, 4 H), 7.07 (t, *J* = 7.6 Hz, 8 H), 7.03 (t, *J* = 7.4 Hz, 2 H), 6.96 (t, *J* = 7.3 Hz, 2 H), 6.57 (m, 4 H), 2.17 (m, 6 H), 1.52 (m, 6 H), 1.44 (sx, *J* = 7.2 Hz, 6 H), 0.92 (t, *J* = 7.3 Hz, 9 H); ^{13}C NMR (125 MHz) δ 176.51, 176.47, 157.49, 157.46, 155.1, 150.2, 147.9, 147.8, 147.4, 129.6, 129.3, 125.3, 124.6, 123.8, 122.8, 115.5, 115.1, 114.8, 114.7, 113.1, 112.84, 112.78, 112.2, 24.4 (d, *J* = 14.7 Hz), 24.1 (d, *J* = 4.8 Hz), 18.9, 18.6, 13.6; IR (neat) 2959, 1722, 1567, 1402, 1335, 1272, 1218, 1094, 990, 904, 754, 697 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{52}H_{56}N_2O_4P$ 803.3972; Found 803.3966.



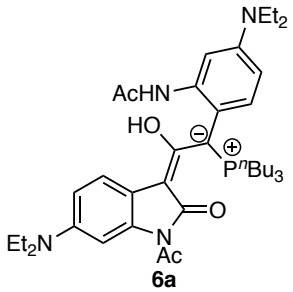
5d

(*E*)-3-(1-Hydroxy-2-(2-hydroxy-4-morpholinophenyl)-2-(tributyl-λ5-phosphaneylidene)ethylidene)-6- morpholinobenzofuran-2(3H)-one (5d). The reaction of squaraine dye **3d** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 43 mg (67%) of **5d** as a red oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1 H), 9.75 (s, 1 H), 7.60-7.58 (m, 2 H), 6.47-6.43 (m, 2 H), 6.38-6.36 (m, 2 H), 3.82 (q, *J* = 5.0 Hz, 8 H), 3.15-3.11 (m, 8 H), 2.14-2.08 (m, 6 H), 1.55-1.48 (m, 6 H), 1.41 (sx, *J* = 7.3 Hz, 6 H), 0.90 (t, *J* = 7.3 Hz, 9 H); ^{13}C NMR (100 MHz) δ 176.0 (d, *J* = 5.9 Hz), 157.4 (d, *J* = 3.7 Hz), 155.0 (d, *J* = 1.2 Hz), 153.0 (d, *J* = 2.4 Hz), 151.3, 133.8, 133.6, 129.2 (d, *J* = 3.7 Hz), 129.0, 128.7, 128.5, 128.4, 128.2, 127.1, 125.3, 114.7, 114.6, 110.2, 110.1, 107.8, 107.0, 105.2 (d, *J* = 2.3 Hz), 103.4, 66.9, 66.7, 65.2, 64.9, 50.5, 49.0, 48.5, 24.2, 24.1, 23.8 (d, *J* = 4.9 Hz), 18.6, 18.2, 13.3; IR (neat) 2959, 2871, 2816, 1810, 1697, 1621, 1547, 1495, 1449, 1379, 1255, 1210, 1120, 965, 750 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{36}H_{52}N_2O_6P$ 639.3558; Found 639.3544.



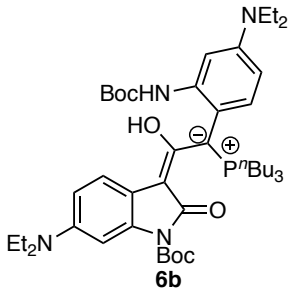
5e

(*E*)-3-(1-Hydroxy-2-(2-hydroxy-4-(pyrrolidin-1-yl)phenyl)-2-(tributyl-λ5-phosphaneylidene)ethylidene)-6-(pyrrolidin-1-yl)benzofuran-2(3*H*)-one (5e). The reaction of squaraine dye **3e** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 16 mg (25%) of **5e** as a red oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.42 (s, 1 H), 9.78 (s, 1 H), 7.57 (d, J = 8.6 Hz, 1 H), 7.54 (dd, J = 8.5, 2.2 Hz, 1 H), 6.15-6.05 (m, 4 H), 3.25 (m, 8 H), 2.12 (m, 6 H), 1.97 (m, 8 H), 1.53 (m, 6 H), 1.41 (m, 6 H), 0.91 (t, J = 7.3 Hz, 9 H); ^{13}C NMR (100 MHz) δ 175.8 (d, J = 5.6 Hz), 157.3 (d, J = 6.2 Hz), 155.2, 149.6, 148.2, 129.4, 127.4, 106.6, 106.2, 104.8, 103.7, 101.5, 99.5, 65.3, 65.0, 47.6, 28.2, 28.0, 26.9, 26.8, 25.4, 24.5, 24.6, 24.5, 24.3, 24.1, 23.9 (d, J = 4.8 Hz), 18.6, 18.2, 13.9, 13.4; IR (neat) 3365, 2957, 2931, 2871, 1676, 1619, 1464, 1379, 1228, 1146, 1093, 967, 903, 804, 773 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{36}H_{52}N_2O_4P$ 607.3659; Found 607.3647.



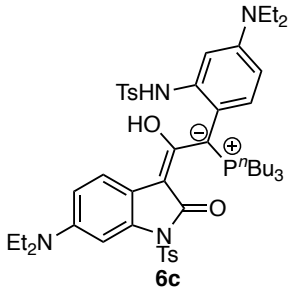
6a

(*E*)-*N*-(2-(2-(1-Acetyl-6-(diethylamino)-2-oxoindolin-3-ylidene)-2-hydroxy-1-(tributyl-λ5- phosphaneylidene)ethyl)-5-(diethylamino)phenyl)acetamide (6a). The reaction of squaraine dye **4a** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 69 mg (>99%) of **6a** as a purple oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.44 (br s, 1 H), 10.82 (br s, 1 H), 7.83 (m, 2 H), 7.75 (d, J = 8.8 Hz, 1 H), 7.61 (d, J = 2.7 Hz, 1 H), 6.36 (ddd, J = 20.5, 8.9, 2.7 Hz, 2 H), 3.33 (q, J = 7.0 Hz, 8 H), 2.25 (s, 3 H), 2.21 (s, 3 H), 2.08 (comp., 6 H), 1.50-1.43 (m, J = 6.9 Hz, 6 H), 1.42-1.35 (m, J = 7.2 Hz, 6 H), 1.14 (t, J = 7.0 Hz, 12 H), 0.89 (t, J = 7.2 Hz, 9 H); ^{13}C NMR (125 MHz) δ 176.52, 176.47, 169.2, 169.0, 148.4, 146.9, 138.7, 136.5, 129.9, 128.0, 115.4, 115.2, 110.1, 109.8, 107.8, 107.3, 106.3, 104.6; IR (neat) 2963, 2924, 2872, 1695, 1622, 1575, 1489, 1344, 1260, 1095 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{40}H_{61}N_4O_4P$ 693.4503; Found 693.4499.



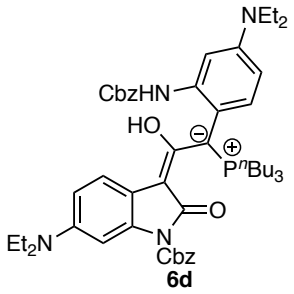
6b

***tert*-Butyl-(*E*)-3-(2-(2-((*tert*-butoxycarbonyl)amino)-4-(diethylamino)phenyl)-1-hydroxy-2-(tributyl-λ5- phosphaneylidene)ethylidene)-6-(diethylamino)-2-oxoindoline-1-carboxylate (6b).** The reaction of squaraine dye **4b** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 58 mg (72%) of **6b** as a purple oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.72 (s, 1 H), 9.94 (s, 1 H), 7.85 (dd, *J* = 8.8, 2.3 Hz, 1 H), 7.70 (d, *J* = 8.7 Hz, 1 H), 7.49 (br s, 1 H), 7.44 (d, *J* = 2.6 Hz, 1 H), 6.30 (m, 2 H), 3.34 (q, *J* = 6.8 Hz, 4 H), 3.32 (q, *J* = 7 Hz, 4 H), 2.10 (comp., 6 H), 1.54 (s, 9 H), 1.52 (s, 9 H), 1.49-1.42 (m, *J* = 7.9 Hz, 6 H), 1.41-1.34 (m, *J* = 7.1 Hz, 6 H), 1.14 (t, *J* = 7.0 Hz, 6 H). 1.13 (t, *J* = 7.0 Hz, 6 H), 0.88 (t, *J* = 7.3 Hz, 9 H); ^{13}C NMR (100 MHz) δ 176.1 (d, *J* = 5.8 Hz), 154.8 (d, *J* = 6.7 Hz), 148.2 (d, *J* = 2.6 Hz), 146.8, 139.3 (d, *J* = 3.5 Hz), 136.7, 129.7 (d, *J* = 4.4 Hz), 127.9, 114.5, 114.4, 110.2 (d, *J* = 10.8 Hz), 106.9, 106.5, 104.9, 103.3, 79.4, 78.5, 77.3, 65.4, 65.1, 44.2, 28.6, 24.3, 24.2, 23.9 (d, *J* = 5.1 Hz), 19.1, 18.7, 13.4, 12.7, 12.6; IR (neat) 2965, 2938, 2869, 1723, 1700, 1653, 1635, 1617, 1576, 1560, 1457, 1341, 1253, 1158 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{46}H_{75}N_4O_6P$ 809.5340; Found 809.5363.



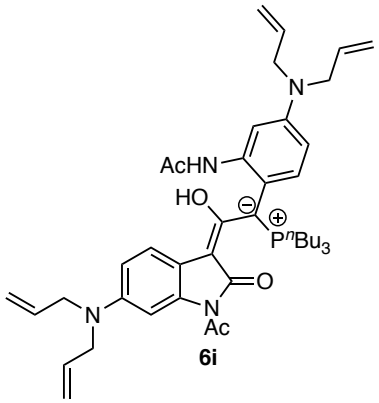
6c

(*E*)-*N*-(5-(Diethylamino)-2-(2-(6-(diethylamino)-2-oxo-1-tosylindolin-3-ylidene)-2-hydroxy-1-(tributyl- λ5-phosphaneylidene)ethyl)phenyl)-4-methylbenzenesulfonamide (6c). The reaction of squaraine dye **4c** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 88 mg (96%) of **6c** as a red oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.89 (s, 1 H), 10.27 (s, 1 H), 8.00 (d, *J* = 8.3 Hz, 2 H), 7.68 (dd, *J* = 8.8, 2.2 Hz, 1 H), 7.50 (d, *J* = 8.7 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 4 H), 6.84 (d, *J* = 2.6, 1 H), 6.51 (d, *J* = 8.0 Hz, 2 H), 6.37 (m, 2 H), 6.28 (dd, *J* = 8.8, 2.5 Hz, 1 H), 3.34-3.17 (m, 8 H), 2.38 (s, 3 H), 2.20 (comp., 6 H), 1.98 (s, 3 H), 1.52-1.39 (m, 12 H), 1.13 (t, *J* = 7.0 Hz, 6 H), 1.03 (t, *J* = 7.0 Hz, 6 H), 0.90 (t, *J* = 7.2 Hz, 9 H); ^{13}C NMR (100 MHz) δ 174.2, 174.0 (d, *J* = 5.9 Hz), 146.0 (d, *J* = 2.0 Hz), 144.8, 141.5, 140.2, 137.0, 136.8 (d, *J* = 3.4 Hz), 135.2, 132.7, 128.4 (d, *J* = 4.0 Hz), 128.0, 126.8, 125.6, 125.2, 124.9, 112.1, 112.0, 110.9, 107.4, 106.8, 105.4, 104.4, 99.4, 63.3, 63.0, 42.5 (d, *J* = 3.8 Hz), 22.4, 22.2, 22.1 (d, *J* = 5.1 Hz), 19.6, 19.3, 17.4, 16.9, 11.4, 10.7, 10.6; IR (neat) 3083, 2069, 2873, 2254, 1728, 1613, 1558, 1521, 1437, 1377, 1334, 1266, 1156, 1086, 908, 813, 725 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{50}H_{71}N_4O_6PS_2$ 917.4469; Found 917.4443.



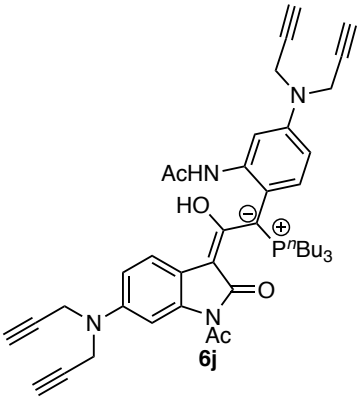
6d

Benzyl-(*E*)-3-(2-(2-(((benzyloxy)carbonyl)amino)-4-(diethylamino)phenyl)-1-hydroxy-2-(tributyl-λ5-phosphaneylidene)ethylidene)-6-(diethylamino)-2-oxoindoline-1-carboxylate (6d). The reaction of squaraine dye **4d** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 72 mg (82%) of **6d** as a teal oil: ^{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) 2964, 2928, 2880, 1726, 1609, 1560, 1497, 1453, 1375, 1344, 1312, 1215, 1051 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{52}H_{70}N_4O_6P$ 877.5027; Found 877.5017.



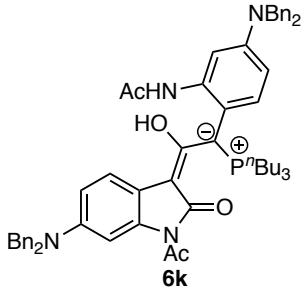
6i

(*E*)-*N*-(2-(2-(1-Acetyl-6-(diallylamino)-2-oxoindolin-3-ylidene)-2-hydroxy-1-(tributyl-λ5-phosphaneylidene)ethyl)-5-(diallylamino)phenyl)acetamide (6i). The reaction of squaraine dye **4i** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 58 mg (78%) of **6i** as a purple oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1 H), 10.81 (s, 1 H), 7.88 (d, *J* = 2.6 Hz, 1 H), 7.82 (dd, *J* = 8.8, 2.3 Hz, 1 H), 7.74 (d, *J* = 8.7 Hz, 1 H), 7.67 (d, *J* = 2.6 Hz, 1 H), 6.38 (ddd, *J* = 16.4, 8.8, 2.7 Hz, 2 H), 5.90-5.78 (m, 4 H), 5.19-5.11 (m, 8 H), 3.90 (s, 8 H), 2.24 (s, 3 H), 2.20 (s, 3 H), 2.12-2.05 (comp, 6 H), 1.50-1.35 (m, 12 H), 0.87 (t, *J* = 7.1 Hz, 9 H); ^{13}C NMR (100 MHz) δ 176.2 (d, *J* = 5.9 Hz), 168.9, 168.8, 149.1 (d, *J* = 2.2 Hz), 147.6, 138.4 (d, *J* = 3.7 Hz), 136.1, 134.1, 133.4, 129.5 (d, *J* = 4.2 Hz), 127.6, 116.3, 116.1, 115.0, 114.9, 110.7, 110.6, 108.3, 107.7, 106.6, 104.7, 65.7, 65.4, 52.7 (d, *J* = 11.4 Hz), 24.7 (d, *J* = 7.3 Hz), 24.3, 24.2, 23.9 (d, *J* = 5.2 Hz), 19.1, 18.6, 13.3; IR (neat) 3283, 3207, 2960, 2931, 2872, 1692, 1623, 1575, 1536, 1495, 1446, 1381, 1294, 1242, 1227, 1173, 1097, 920 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{44}H_{62}N_4O_4P$ 741.4503; Found 741.4504.



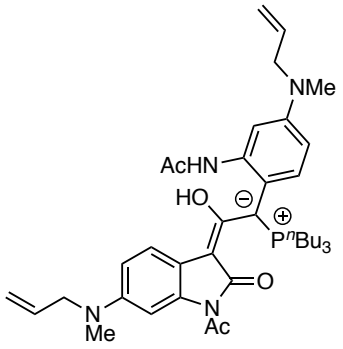
6j

(*E*)-*N*-(2-(2-(1-Acetyl-6-(di(prop-2-yn-1-yl)amino)-2-oxoindolin-3-ylidene)-2-hydroxy-1-(tributyl-λ5-phosphaneylidene)ethyl)-5-(di(prop-2-yn-1-yl)amino)phenyl)acetamide (6j). The reaction of squaraine dye **4j** and P^{n}Bu$_3$ was performed on a 0.06 mmol scale to afford 36 mg (94%) of **6j** as a purple oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.46 (s, 1 H), 10.83 (s, 1 H), 8.10 (d, *J* = 2.6 Hz, 1 H), 7.94 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.90 (d, *J* = 2.6 Hz, 1 H), 7.84 (d, *J* = 8.7 Hz, 1 H), 6.67 (dd, *J* = 8.8, 2.6 Hz, 1 H), 6.62 (dd, *J* = 8.7, 2.7 Hz, 1 H), 4.14-4.13 (m, 8 H), 2.27 (s, 3 H), 2.22 (s, 3 H), 2.12-2.06 (m, 6 H), 1.48-1.37 (m, 12 H), 0.89 (t, *J* = 7.2 Hz, 9 H); ^{13}C NMR (125 MHz) δ 176.6, 176.5, 169.3, 169.1, 148.4, 146.8, 138.8, 136.2, 129.9, 127.7, 114.8, 114.7, 114.0, 113.8, 111.1, 109.7, 108.4, 79.5, 79.0, 73.0, 72.7, 40.4, 40.2, 31.2, 24.9 (d, *J* = 8.3 Hz), 24.4 (d, *J* = 14.7 Hz), 24.1 (d, *J* = 5.1 Hz), 19.2, 18.9, 13.5; IR (neat) 3316, 3241, 2934, 2856, 1688, 1622, 1564, 1483, 1440, 1366, 1238, 1014, 908, 800, 727 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{44}H_{54}N_4O_4P$ 733.3877; Found 733.3868.



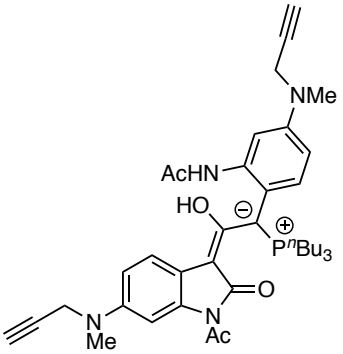
6k

(*E*)-*N*-(2-(2-(1-Acetyl-6-(dibenzylamino)-2-oxoindolin-3-ylidene)-2-hydroxy-1-(tributyl-λ5- phosphaneylidene)ethyl)-5-(dibenzylamino)phenyl)acetamide (6k). The reaction of squaraine dye **4k** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 76 mg (81%) of **6k** as a purple oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1 H), 10.76 (s, 1 H), 7.99 (d, *J* = 2.6 Hz, 1 H), 7.79-7.77 (m, 2 H), 7.69 (d, *J* = 8.7 Hz, 1 H), 7.32-7.18 (m, 20 H), 6.39 (ddd, *J* = 13.4, 8.9, 2.7 Hz, 2 H), 4.62-4.60 (m, 8 H), 2.18 (s, 3 H), 2.15 (s, 3 H), 2.10-2.03 (m, 6 H), 1.46-1.32 (m, 12 H), 0.86 (t, *J* = 7.1 Hz, 9 H); ^{13}C NMR (100 MHz) δ 174.4 (d, *J* = 5.9 Hz), 167.0, 166.8, 147.7 (d, *J* = 2.2 Hz), 146.2, 136.9, 136.6 (d, *J* = 3.6 Hz), 136.2, 134.3, 127.8 (d, *J* = 4.1 Hz), 126.7, 126.6, 125.8, 125.2, 125.1, 125.0, 124.9, 114.5, 113.0, 112.9, 109.4 (d, *J* = 2.3 Hz), 106.7, 106.2, 105.0, 103.2, 63.8, 63.5, 52.0 (d, *J* = 3.6 Hz), 22.8 (d, *J* = 7.4 Hz), 22.4, 22.3, 22.0 (d, *J* = 5.1 Hz), 17.2, 16.8, 11.4; IR (neat) 3272, 3209, 3028, 2960, 2931, 2872, 1691, 1625, 1562, 1494, 1450, 1362, 1294, 1241, 1221, 1166, 966, 750 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{60}H_{70}N_4O_4P$ 941.5129; Found 941.5162.



6l

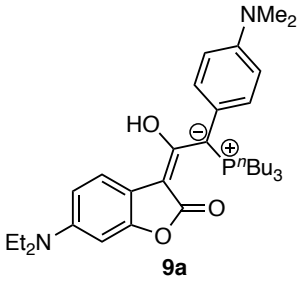
(*E*)-*N*-(2-(2-(1-Acetyl-6-(allyl(methyl)amino)-2-oxoindolin-3-ylidene)-2-hydroxy-1-(tributyl-λ5-phosphaneylidene)ethyl)-5-(allyl(methyl)amino)phenyl)acetamide (6l). The reaction of squaraine dye **4l** and P^{n}Bu$_3$ was performed on a 0.1 mmol scale to afford 69 mg (>99%) of **6l** as a purple oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.45 (s, 1 H), 10.84 (s, 1 H), 7.88 (d, *J* = 2.6 Hz, 1 H), 7.85 (dd, *J* = 8.9, 2.4 Hz, 1 H), 7.77 (d, *J* = 8.7 Hz, 1 H), 7.67 (d, *J* = 2.7 Hz, 1 H), 6.41 (ddd, *J* = 17.5, 8.9, 2.7 Hz, 2 H), 5.86-5.77 (m, 2 H), 3.92-3.90 (m, 4 H), 2.95 (s, 3 H), 2.93 (s, 3 H), 2.26 (s, 3 H), 2.22 (s, 3 H), 2.12-2.06 (m, 6 H), 1.49-1.35 (m, 12 H), 0.89 (t, *J* = 7.2 Hz, 9 H); ^{13}C NMR (125 MHz) δ 176.6, 176.5, 169.2, 169.0 150.1, 148.6, 138.6, 136.3, 134.0, 133.3, 129.8, 127.9, 116.6, 116.4, 115.2, 115.1, 111.0, 110.7, 108.5, 108.0, 106.7, 105.1, 55.4, 55.0, 38.1, 25.0 (d, *J* = 8.6 Hz), 24.5 (d, *J* = 14.5 Hz), 24.1 (d, *J* = 5.0 Hz), 19.2, 18.9, 14.1, 13.5; IR (neat) 3265, 2960, 2932, 2872, 1690, 1623, 1559, 1495, 1440, 1366, 1289, 1247, 1091, 992, 918, 802, 750 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{40}H_{58}N_4O_4P$ 689.4190; Found 689.4195.



6m

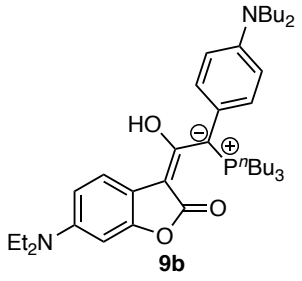
(*E*)-*N*-(2-(2-(1-Acetyl-6-(methyl(prop-2-yn-1-yl)amino)-2-oxoindolin-3-ylidene)-2-hydroxy-1-(tributyl-λ5-phosphaneylidene)ethyl)-5-(methyl(prop-2-yn-1-yl)amino)phenyl)acetamide (6m). The reaction of squaraine dye **4m** and P^{n}Bu$_3$ was performed on a 0.065 mmol scale to afford 44 mg (>99%) of **6m** as a red oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.46 (s, 1 H), 10.84 (s, 1 H), 7.99 (d, *J* = 2.5 Hz, 1 H), 7.91 (dd, *J* = 8.8, 2.3 Hz, 1 H), 7.82 (d, *J* = 9.0 Hz, 1 H), 7.80 (d, *J* = 2.5 Hz, 1 H), 6.57 (dd, *J* = 8.8, 2.6 Hz, 1 H), 6.52 (dd, *J* = 8.7, 2.6 Hz, 1 H), 4.05-4.04 (m, 4 H), 2.99 (s, 3 H), 2.97 (s, 3 H), 2.27 (s, 3 H), 2.26 (s, 3 H), 2.17-2.15 (m, 2 H), 2.12-2.07 (m, 6 H), 1.47-1.43 (m, 6 H), 1.41-1.37 (m, 6 H), 0.89 (t, *J* = 7.2 Hz, 9 H); ^{13}C NMR (100 MHz) δ 176.3 (d, *J* = 6.0 Hz), 169.0, 168.8, 149.5 (d, *J* = 2.4 Hz), 147.9, 138.5 (d, *J* = 3.7 Hz), 136.0, 129.6 (d, *J* = 4.2 Hz), 127.6, 114.8, 114.7, 112.4, 112.2, 109.7 (d, *J* = 1.9 Hz), 109.4, 108.2 (d, *J* = 2.1 Hz), 106.7, 79.5, 78.9, 72.1, 71.8, 65.8, 65.5, 42.4, 42.0, 38.4 (d, *J* = 10.7 Hz), 24.7 (d, *J* = 6.8 Hz), 24.3, 24.2, 23.9 (d, *J* = 5.1 Hz), 19.0, 18.6, 13.3; IR (neat) 3243, 2960, 2932,

2872, 1689, 1624, 1562, 1494, 1441, 1367, 1290, 1245, 1088, 1019, 999, 960, 804, 752 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{40}H_{54}N_4O_4P$ 685.3877; Found 685.3890.



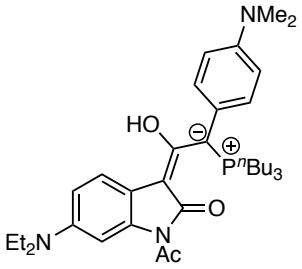
9a

(*E*)-6-(Diethylamino)-3-(2-(4-(dimethylamino)phenyl)-1-hydroxy-2-(tributyl-λ5-phosphaneylidene)ethylidene)benzofuran-2(3H)-one (9a). The reaction of squaraine dye **8a** and P^{n}Bu$_3$ was performed on a 0.032 mmol scale to afford 17 mg (91%) of **9a** as a purple oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (br s, 1 H), 7.63 (dd, *J* = 9.0, 2.2 Hz, 2 H), 7.57 (d, *J* = 8.6 Hz, 1 H), 6.70-6.67 (m, 2 H), 6.25-6.13 (m, 2 H), 3.32-3.36 (m, 4 H), 2.94 (s, 6 H), 2.11-2.05 (m, 6 H), 1.62-1.51 (m, 6 H), 1.47-1.38 (m, 6 H), 1.14-1.09 (m, 6 H), 0.94-0.88 (m, 9 H); ^{13}C NMR (100 MHz) δ 175.4, 175.3, 155.3, 150.3, 148.2, 147.6, 128.2, 127.1, 125.9, 121.0, 112.5, 103.7, 99.8, 44.3 (d, *J* = 2.9 Hz), 40.4, 24.1 (d, *J* = 14.6 Hz), 23.8 (d, *J* = 4.7 Hz), 18.3, 16.9, 13.4, 12.7; IR (neat) 2962, 2926, 2864, 1610, 1569, 1519, 1445, 1354, 1216, 1093, 770 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{34}H_{53}N_2O_3P$ 567.3710; Found 567.3728.



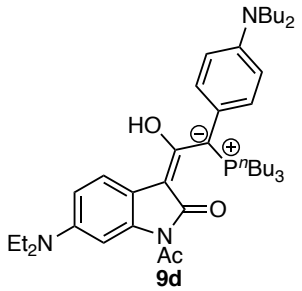
9b

(*E*)-3-(2-(4-(Dibutylamino)phenyl)-1-hydroxy-2-(tributyl-λ5-phosphaneylidene)ethylidene)-6-(diethylamino)benzofuran-2(3*H*)-one (9b). The reaction of squaraine dye **8b** and P^{n}Bu$_3$ was performed on a 0.10 mmol scale to afford 65 mg (99%) of **9b** as a red oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1 H), 7.61-7.56 (m, 3 H), 6.59 (d, *J* = 8.9 Hz, 2 H), 6.24-6.12 (m, 2 H), 3.32-3.20 (m, 8 H), 2.12-2.06 (comp., 6 H), 1.61-1.50 (m, 10 H), 1.46-1.38 (m, 6 H), 1.36-1.29 (m, 4 H), 1.14-1.09 (m, 6 H), 0.95-0.88 (m, 15 H); ^{13}C NMR (125 MHz) δ 175.8 (d, *J* = 6.0 Hz), 158.1, 155.4, 149.5, 148.2, 147.8, 146.1, 129.6, 128.6, 128.1, 127.3, 126.3, 124.8, 122.4, 120.0, 119.7, 114.6, 111.9, 109.9, 108.0, 106.9, 104.5, 103.9, 101.5, 100.0, 50.9, 44.5, 29.6, 24.4 (d, *J* = 14.7 Hz), 24.0 (d, *J* = 4.8 Hz), 20.5, 18.8, 18.5, 18.1, 14.2, 13.6, 12.9, 12.8; IR (neat) 2958, 2928, 1735, 1569, 1515, 1463, 1343, 1262, 1218, 1180, 1093 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{40}H_{64}N_2O_3P$ 651.4649; Found 651.4650.



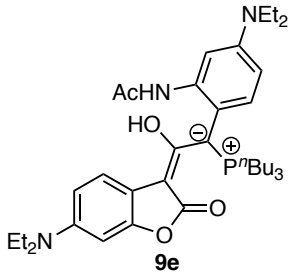
9c

(*E*)-1-Acetyl-6-(diethylamino)-3-(2-(4-(dimethylamino)phenyl)-1-hydroxy-2-(tributyl-λ5-phosphaneylidene)ethylidene)indolin-2-one (9c). The reaction of squaraine dye **8c** and P^{n}Bu$_3$ was performed on a 0.061 mmol scale to afford 34 mg (91%) of **9c** as a clear oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.02 (br s, 1 H), 7.88-7.82 (m, 1 H), 7.77 (d, *J* = 8.7 Hz, 1 H), 7.69-7.64 (m, 2 H), 6.70 (d, *J* = 8.8 Hz, 1 H). 6.34 (dd, *J* = 8.8, 2.7 Hz, 1 H), 3.31 (q, *J* = 7.0 Hz, 4 H), 2.94 (s, 6 H), 2.22 (s, 3 H), 2.11-2.07 (m, 6 H), 1.60-1.53 (m, 6 H), 1.46-1.36 (m, 6 H), 1.13 (t, *J* = 7.0 Hz, 6 H), 0.92 (t, *J* = 7.3 Hz, 9 H); ^{13}C NMR (100 MHz) δ 176.0, 175.9, 168.9, 150.3, 146.2, 136.0, 128.2, 127.5, 121.0, 112.5, 111.2, 107.3, 104.5, 44.4, 40.4, 24.8, 24.2 (d, *J* = 14.6 Hz), 23.8 (d, *J* = 4.9 Hz), 18.4, 18.0, 13.4, 12.7; IR (neat) 2962, 2931, 2872, 1725, 1688, 1630, 1564, 1508, 1443, 1355, 1263, 1094, 818 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{36}H_{56}N_3O_3P$ 608.3976; Found 608.3998.



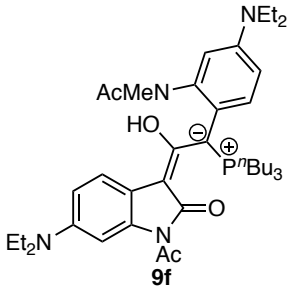
9d

(*E*)-1-Acetyl-3-(2-(4-(dibutylamino)phenyl)-1-hydroxy-2-(tributyl-λ5-phosphaneylidene)ethylidene)-6-(diethylamino)indolin-2-one (9d). The reaction of squaraine dye **8d** and P^{n}Bu$_3$ was performed on a 0.10 mmol scale to afford 65 mg (94%) of **9d** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.06 (s, 1 H), 7.83 (d, *J* = 2.6 Hz, 1 H), 7.77 (d, *J* = 8.7 Hz, 1 H), 7.60 (dd, *J* = 8.9, 2.1 Hz, 2 H), 6.60 (d, *J* = 8.9 Hz, 2 H), 6.33 (dd, *J* = 8.8, 2.6 Hz, 1 H), 3.32 (q, *J* = 7.1 Hz, 4 H), 3.24 (t, *J* = 7.7 HZ, 4 H), 2.22 (s. 3 H), 2.12-2.06 (comp., 6 H), 1.61-1.51 (m, 10 H), 1.46-1.38 (m, 6 H), 1.37-1.30 (m, 4 H), 1.13 (t, *J* = 6.9 Hz, 6 H), 0.96-0.90 (m, 15 H); ^{13}C NMR (125 MHz) δ 176.3 (d, *J* = 6.0 Hz), 169.1, 148.2, 146.4, 136.1, 128.6, 127.7, 129.7, 123.8, 111.9, 107.5, 104.7, 50.9, 44.7, 29.5, 25.0, 24.5, 24.4, 24.0 (d, *J* = 4.6 Hz), 20.5, 18.5, 18.2, 14.2, 13.6, 12.9; IR (neat) 2958, 2929, 2871, 1690, 1630, 1607, 1565, 1515, 1464, 1367, 1296, 1261, 1183, 1094 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{42}H_{67}N_3O_3P$ 692.4915; Found 692.4924.



9e

(*E*)-1-(2-Acetamido-4-(diethylamino)phenyl)-2-(6-(diethylamino)-2-oxobenzofuran-3(2*H*)-ylidene)-2-hydroxy-1-(tributyl-λ4-phosphaneyl)ethan-1-ide (9e). The reaction of squaraine dye **8e** and P^{n}Bu$_3$ was performed on a 0.061 mmol scale to afford 38 mg (94%) of **9e** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.69 (br s, 1 H). 10.55 (br s, 1 H). 7.81 (d, *J* = 2.7 Hz, 1 H), 7.73 (d, *J* = 8.8 Hz, 1 H), 7.55 (dd, *J* = 8.7, 2.3 Hz, 1 H), 6.34 (dd, *J* = 8.8, 2.7 Hz, 1 H), 6.25-6.21 (m, 2 H), 3.36-3.29 (m, 8 H), 2.22 (s, 3 H), 2.15-2.10 (comp., 6 H), 1.54-1.36 (m, 12 H), 1.16-1.13 (m, 12 H), 0.91 (t, *J* = 14.7 Hz, 9 H); ^{13}C NMR (125 MHz) δ 176.5, 176.4, 169.2, 147.8 (d, *J* = 2.8 Hz), 149.8, 146.9, 136.4, 129.6, 128.0, 114.6, 110.1, 107.3, 106.1, 104.6 (d, *J* = 17.6 Hz), 101.5, 44.6 (d, *J* = 13.4 Hz), 28.3 (d, *J* = 9.8 Hz), 27.1 (d, *J* = 9.1 Hz), 25.0, 24.5 (d, *J* = 11.5 Hz), 24.1 (d, *J* = 3.9 Hz), 18.9, 18.5, 13.6, 12.9, 12.8; IR (neat) 2958, 2932, 2871, 1619, 1564, 1517, 1465, 1256, 1231, 1158, 1128 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{38}H_{60}N_3O_4P$ 652.4238; Found 652.4234.



9f

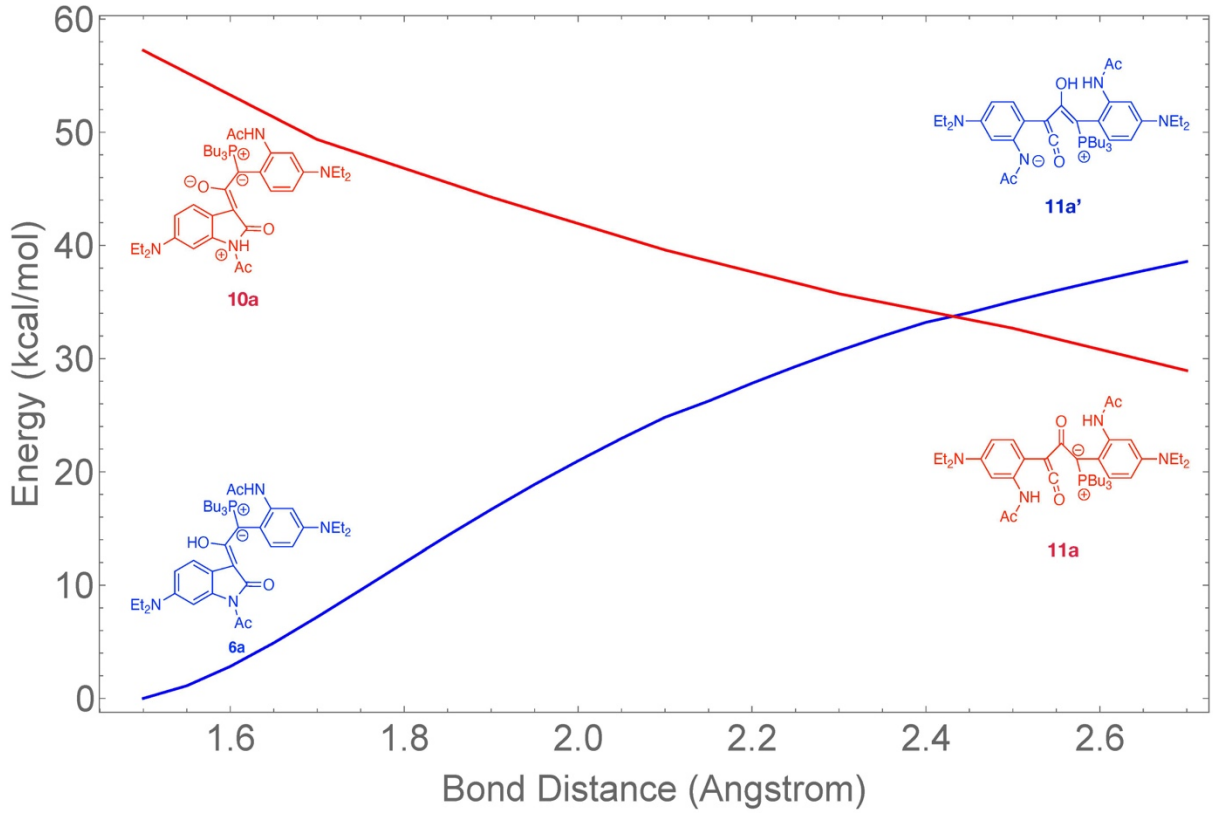
(*E*)-*N*-(2-(2-(1-Acetyl-6-(diethylamino)-2-oxoindolin-3-ylidene)-2-hydroxy-1-(tributyl-λ5-phosphaneylidene)ethyl)-5-(diethylamino)phenyl)-N-methylacetamide (9f). The reaction of squaraine dye **8f** and P^{n}Bu$_3$ was performed on a 0.10 mmol scale to afford 71 mg (>99%) of **9f** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.56 (br s, 1 H), 7.85 (dd, *J* = 8.9, 2.4 Hz, 1 H), 7.72 (br s, 1 H), 7.63 (d, *J* = 2.98 Hz, 1 H), 6.60 (dd, *J* = 8.8, 2.7 Hz, 1 H) 6.36-6.33 (m, 2 H), 3.36-3.28 (m, 8 H), 3.19-3.13 (m, 3 H), 2.25 (s, 3 H), 2.10 (br s, 3 H), 1.90-1.85 (m, 3 H), 1.44-1.36 (m, 12 H), 1.15 (t, *J* = 7.0 Hz, 6 H), 1.13 (t, *J* = 7.1 Hz, 6 H), 0.89 (t, *J* = 7.1 Hz, 9 H); ^{13}C NMR (125 MHz) δ 171.3, 169.4, 148.23, 148.22, 146.9, 141.8, 138.93, 138.90, 130.1, 130.0, 129.7, 111.6, 110.2, 107.7, 44.6, 44.5, 25.1, 24.5, 24.1, 9.1, 18.8, 13.6, 12.8, 12.7; IR (neat) 2964, 2931, 2871, 1654, 1609, 1584, 1522, 1375, 1354, 1253, 1076, 808 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{41}H_{65}N_4O_4P$ 707.4660; Found 707.4659.

Acid Promoted Reversion of 6a to Parent Squaraine 4a. Ylide **6a** (0.1 mmol) was dissolved in $CDCl_3$ (1 mL) and *p*-tolylsulfonic acid (0.1 mmol) was then added at room temperature. Immediately, the blue solid **4a** was observable. Thereafter, a 500 MHz ^{1}H NMR spectrum was acquired within 5 min following the addition of the *p*-tolylsulfonic acid addition to confirm regeneration of **4a**.

III. COMPUTATIONAL DETAILS

Computational Methods: DFT calculations for the mechanistic studies were performed using the B3LYP functional with D3 empirical dispersion correction and the 6-311+G* basis set using Gaussian 16.[12] All geometry optimizations were performed using a CPCM solvent model with parameters for chloroform unless noted otherwise. Initial guesses for the transition structure calculations were generated using the QST2 method in G16. Frequency calculations were performed at the transition structures to ensure that the structure have only a single imaginary frequency corresponding to the reaction coordinate.
DFT calculations for distance scan shown in Figure S1 below were performed with the B3LYP/6-311G+ method and a CPCM implicit solvent model with a dielectric constant of 4.8069 using Q-Chem.[13] The pKa estimation of the protonated ylide in water was performed using the pKa estimation in Jaguar.[14]

Figure S1



Computational Results (energies, imaginary frequencies of transition structures, cartisian coordinates)

PBu_3

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -814.756323 hartrees

P	0.39545300	-0.15374700	1.24611400
C	1.80474700	0.60771900	0.28143500
C	3.01741900	-0.31967000	0.13568000
H	2.09810400	1.51797300	0.81766500

H	1.45767500	0.92225600	-0.70889600
C	4.18274400	0.33743700	-0.61275400
H	2.72671300	-1.23469100	-0.39514900
H	3.35973000	-0.63987400	1.12764500
C	5.39315600	-0.58745200	-0.75926100
H	5.13204700	-1.49607000	-1.31175800
H	5.77556200	-0.89631500	0.21911500
H	6.21138900	-0.09757400	-1.29522600
H	4.47936300	1.25238200	-0.08489200
H	3.84071300	0.65672300	-1.60507000
C	-0.31181200	-1.28753800	-0.06261200
C	-1.68017400	-1.87420400	0.30087300
H	0.41106700	-2.09970500	-0.19584300
H	-0.36756600	-0.76139900	-1.02243600
C	-2.20578900	-2.85644800	-0.75203300
H	-2.41104400	-1.06616500	0.42758100
H	-1.62026200	-2.38286100	1.27146300
C	-3.57770400	-3.43310200	-0.39546600
H	-3.54448900	-3.97302300	0.55650000
H	-3.93201500	-4.13080000	-1.15991800
H	-4.32656900	-2.64023300	-0.29762800
H	-1.48315400	-3.67241400	-0.87640900
H	-2.26058300	-2.34840300	-1.72290300
C	-0.83833900	1.25544200	1.24375700
C	-1.29311600	1.84989500	-0.09363400
H	-0.38929600	2.03794700	1.86731700
H	-1.70931300	0.89973700	1.80583100
C	-2.30575800	2.98808600	0.08238400
H	-1.74486500	1.07027300	-0.71734800
H	-0.42967700	2.22647800	-0.65317700
C	-2.76974100	3.58131700	-1.24987200
H	-1.92621400	3.98965600	-1.81618200
H	-3.49125700	4.39008100	-1.10111500
H	-3.24843600	2.82098800	-1.87581100
H	-1.86022700	3.77632000	0.70188600
H	-3.17298900	2.61603400	0.64206700

4 a

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -1607.362567 hartrees

C	0.03807900	1.05984500	-0.06227400
C	-1.04179500	0.06450700	-0.11051900
C	1.05181500	-0.00264000	-0.11132100
C	-0.02841200	-0.99810900	-0.15910500
C	2.45410600	-0.12814500	-0.11760100
C	3.39210600	0.96467900	-0.06607400
C	3.00185500	-1.44220600	-0.17175200

C	4.34686500	-1.69125300	-0.18484100
C	5.27945100	-0.61049300	-0.15477900
C	4.75494000	0.70668200	-0.08057700
C	-2.44452100	0.19049100	-0.11007900
C	-3.38336600	-0.90291900	-0.15859700
C	-2.99148100	1.50305800	-0.04923600
C	-4.74427700	-0.64435300	-0.15564300
C	-5.26968700	0.67455900	-0.11467800
C	-4.33804800	1.75340900	-0.04557700
O	0.08158400	2.29608400	-0.00346900
O	-0.07173600	-2.23433000	-0.21760400
H	5.41198700	1.55408800	-0.02729600
H	4.67942200	-2.71836600	-0.21234000
H	2.30921900	-2.27444100	-0.19939700
H	-2.29886600	2.33436400	-0.00004900
H	-4.67066600	2.77884000	0.01466100
H	-5.40125700	-1.49337800	-0.17732600
N	6.62763000	-0.82091300	-0.19841900
N	2.89316200	2.27082600	0.00336300
N	-6.61618200	0.89722700	-0.14251700
N	-2.88407100	-2.21101300	-0.20148800
C	-3.57008500	-3.40253100	-0.22567300
C	-2.68103300	-4.62976900	-0.27305000
H	-2.92766000	-5.20272400	-1.16979200
H	-2.91167400	-5.25924300	0.58930000
H	-1.61510700	-4.40216500	-0.27579000
O	-4.79231000	-3.50711200	-0.21107900
C	7.53755700	0.33520400	-0.04261200
C	7.17169300	-2.17892500	-0.06997100
C	9.01876800	0.03856900	-0.24264300
H	9.22702500	-0.36583500	-1.23595700
H	9.42283800	-0.64488800	0.50675000
H	9.56439900	0.98067600	-0.15097200
H	7.38632300	0.77796900	0.94968200
H	7.24465400	1.09157200	-0.77390800
C	7.21897900	-2.67155200	1.37826100
H	7.85047600	-2.02310400	1.99102600
H	7.62918400	-3.68417600	1.42119500
H	6.22138700	-2.68760000	1.82328700
H	8.16909700	-2.18753000	-0.50205900
H	6.58693500	-2.85541900	-0.69307500
C	-7.11505900	2.27636200	0.05015100
C	-7.55952400	-0.22513200	-0.04640300
C	-7.75638200	-0.72424900	1.38697900
H	-8.15393200	0.06853500	2.02604300
H	-6.81394700	-1.06681700	1.81966000

H	-8.46163700	-1.55945700	1.40240500
H	-7.21652900	-1.03107100	-0.69507200
H	-8.50982500	0.09391200	-0.46676700
C	-8.61745300	2.46418700	-0.12356800
H	-8.95595400	2.17409200	-1.12087300
H	-8.83965500	3.52657100	0.00227200
H	-9.20393200	1.91928000	0.61858400
H	-6.61207800	2.91974200	-0.67515700
H	-6.81990000	2.62701500	1.04696800
C	3.57824800	3.46253600	0.05928800
H	1.87429500	2.37464700	0.00848500
C	2.68727500	4.68792000	0.11766800
H	2.91912300	5.32656600	-0.73768700
H	2.93105200	5.25188400	1.02075500
H	1.62167300	4.45887100	0.11471700
O	4.80014300	3.56799900	0.06344300
H	-1.86538300	-2.31481300	-0.21381800

10 a

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -2422.125119 hartrees

C	0.52350600	-0.65779900	1.05422200
C	1.51671300	-0.62795900	0.03654800
C	-0.59678000	-0.09608100	0.09409800
C	0.58822400	-0.16187000	-0.93493300
C	-1.83230900	-0.91809500	-0.21553700
C	-2.68766600	-1.44540200	0.77401900
C	-2.20032400	-1.14126400	-1.54906800
C	-3.35101100	-1.82511700	-1.90445800
C	-4.21572000	-2.35533000	-0.91873700
C	-3.84782900	-2.13685200	0.42545100
C	2.93478500	-0.97355600	0.06470300
C	3.87833400	-0.58070900	-0.91857200
C	3.43393500	-1.70551400	1.15239100
C	5.21938200	-0.93767500	-0.80255400
C	5.70953400	-1.68032000	0.29183200
C	4.77332300	-2.04462600	1.28404700
O	0.45411800	-0.97739900	2.24652000
O	0.60754800	0.13751800	-2.13686600
H	-4.45914900	-2.50123900	1.23268900
H	-3.56784900	-1.93537800	-2.95754100
H	-1.57333200	-0.74144200	-2.33596900
H	2.74242500	-2.00114000	1.93326000
H	5.07293100	-2.58824700	2.16859500
H	5.88294200	-0.60827000	-1.58237600
N	-5.35488900	-3.08307800	-1.24899400
N	-2.34577200	-1.29243100	2.14272300

N	7.05622000	-2.05000400	0.36428700
N	3.43209000	0.18126100	-2.02733300
C	4.13550900	1.07996600	-2.77702000
C	3.31776100	1.76758000	-3.85525800
H	3.70325100	1.46980900	-4.83362400
H	3.45966700	2.84592100	-3.76188800
H	2.25219600	1.53905800	-3.81010800
O	5.32611400	1.34577000	-2.62216300
C	-6.28938400	-3.41931400	-0.16154500
C	-5.90426600	-2.95545500	-2.60225100
C	-7.44817300	-4.32612600	-0.56317000
H	-7.09579900	-5.24746400	-1.03433700
H	-8.15725600	-3.84066200	-1.23691300
H	-7.99761200	-4.60383300	0.33973200
H	-6.68512900	-2.50186600	0.29919400
H	-5.72284200	-3.93773900	0.61501400
C	-6.61786000	-1.62450000	-2.85708400
H	-7.46550200	-1.49787300	-2.17791500
H	-6.99609100	-1.57905200	-3.88236500
H	-5.93957200	-0.78140100	-2.70712700
H	-6.58860300	-3.78489600	-2.77059100
H	-5.10198300	-3.10511400	-3.32564600
C	7.51006400	-2.69040500	1.60732800
C	8.04119200	-1.24266200	-0.36616400
C	8.28294700	0.14194700	0.24260200
H	8.65560500	0.06065700	1.26784500
H	7.36038400	0.72691900	0.26183700
H	9.02305600	0.69489300	-0.34296000
H	7.72634000	-1.15009500	-1.40579900
H	8.97363300	-1.80308900	-0.40655800
C	8.93640700	-3.23134300	1.56683900
H	9.09107600	-3.89155600	0.70916500
H	9.11390700	-3.81473700	2.47392300
H	9.69106500	-2.44260700	1.53718800
H	6.84450600	-3.53336900	1.80464400
H	7.40554000	-2.00218000	2.46103900
C	-3.19923100	-1.05341700	3.18268700
H	-1.34742600	-1.25743100	2.35577300
C	-2.51951700	-0.90587400	4.53043700
H	-2.84479900	-1.72332900	5.17855300
H	-2.85317800	0.02645400	4.99054200
H	-1.42996000	-0.91287600	4.47652600
O	-4.41751200	-0.94641400	3.06904400
P	-1.01864400	1.68402100	0.43935700
C	0.48850700	2.59412300	0.94327900
C	1.50136100	2.95421100	-0.15411500

H	0.96128800	1.99097300	1.72443300
H	0.12839500	3.50614800	1.42847100
C	2.65716600	3.78178500	0.42015900
H	1.00984000	3.52074000	-0.95192300
H	1.90256700	2.05015300	-0.61321600
C	3.70960600	4.13091800	-0.63343200
H	3.26545100	4.67833300	-1.47118600
H	4.18438900	3.23294000	-1.03650300
H	4.49874000	4.75822600	-0.20977000
H	3.12729100	3.22203100	1.23738500
H	2.25785300	4.70053100	0.86686300
C	-1.70815300	2.43717000	-1.08017000
C	-3.20674300	2.19239800	-1.32121100
H	-1.10650700	2.03873500	-1.90203900
H	-1.50154000	3.51042500	-1.02396500
C	-3.64928000	2.75803100	-2.67450800
H	-3.79598500	2.65927500	-0.52589300
H	-3.42993300	1.12390600	-1.28772800
C	-5.14608400	2.56511800	-2.92278000
H	-5.41523900	1.50497000	-2.90523900
H	-5.44379100	2.96736500	-3.89490800
H	-5.74331900	3.06982200	-2.15678400
H	-3.07514800	2.27127300	-3.47165000
H	-3.39946000	3.82483100	-2.72379100
C	-2.23244100	1.84278800	1.79402600
C	-2.65648800	3.28021700	2.13270500
H	-1.79042600	1.35873200	2.66680900
H	-3.09825600	1.24341700	1.50327200
C	-3.80412100	3.28873000	3.14958400
H	-2.97046000	3.81652500	1.23129600
H	-1.80813500	3.83609000	2.54379500
C	-4.23863500	4.70541800	3.52765700
H	-3.41290200	5.26826100	3.97435400
H	-5.05820900	4.68857800	4.25102500
H	-4.58208700	5.26201700	2.64982700
H	-3.49387200	2.74256600	4.04794200
H	-4.65514000	2.73575300	2.73604600
H	2.43868100	0.11542200	-2.25042700

TS 2 a

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -2422.089048 hartrees

Single imaginary frequency: -180.83 cm-1

C	0.57517000	-0.71385900	-0.50149600
C	1.45372800	0.01157800	0.39361500
C	-0.80949100	-0.61271200	0.02467400
C	0.77933200	0.10075200	1.56316700

C	-1.55511100	0.66328600	-0.24058100
C	-2.37664500	1.28151800	0.72583300
C	-1.47275400	1.30172000	-1.48641500
C	-2.16311400	2.46727200	-1.78214900
C	-3.00400200	3.06834100	-0.82180500
C	-3.07843400	2.45600100	0.44268000
C	2.84939600	0.48336300	0.23864700
C	3.90264700	-0.36806100	-0.15843500
C	3.18457000	1.80601400	0.54103800
C	5.21076500	0.09918200	-0.23367300
C	5.55290100	1.42433200	0.11499000
C	4.48943900	2.27882400	0.48690000
O	0.94089100	-1.42806100	-1.45692100
O	0.54025400	0.26011700	2.70117500
H	-3.67052700	2.88372900	1.23255300
H	-2.06899900	2.88423800	-2.77642200
H	-0.85642100	0.85138200	-2.25836700
H	2.39260100	2.49111100	0.82849200
H	4.66156300	3.31800500	0.72678700
H	5.96313700	-0.60037000	-0.55710700
N	-3.76117900	4.20967700	-1.13215400
N	-2.43320400	0.68168800	2.00365400
N	6.87828400	1.85792600	0.10106900
N	3.59319400	-1.70629000	-0.51103800
C	4.33466500	-2.82057000	-0.25116600
C	3.71758900	-4.11731000	-0.74205600
H	3.70572000	-4.83278600	0.08187000
H	4.35366900	-4.53306200	-1.52747500
H	2.70623400	-4.00247400	-1.13482900
O	5.41986300	-2.81489500	0.32583500
C	-4.69122400	4.69651700	-0.10464000
C	-3.11785000	5.24553500	-1.95532600
C	-5.68250500	5.74155400	-0.61045900
H	-6.19181500	5.39974000	-1.51566500
H	-5.21344200	6.70484200	-0.82218100
H	-6.43986900	5.91316400	0.15858600
H	-4.15264200	5.09811300	0.76820100
H	-5.25967900	3.83472900	0.25123000
C	-2.07981700	6.08054600	-1.19871300
H	-2.53246000	6.62172000	-0.36343800
H	-1.62158300	6.81717400	-1.86495500
H	-1.28628200	5.44377200	-0.79833200
H	-3.89730300	5.88911400	-2.36332600
H	-2.65498100	4.77458800	-2.82106600
C	7.12208200	3.29852700	0.27120100
C	7.86476200	1.09212800	-0.66788300

C	7.73799200	1.26290400	-2.18499600
H	7.87839700	2.30828300	-2.47441900
H	6.75292100	0.94634500	-2.53641300
H	8.49283800	0.66495500	-2.70379400
H	7.78901100	0.03991000	-0.39204600
H	8.85786900	1.39407200	-0.34004200
C	8.58993300	3.69270100	0.40476700
H	9.08519300	3.13610600	1.20478200
H	8.64193300	4.75496400	0.65656000
H	9.15597100	3.55086800	-0.51820900
H	6.61445600	3.61458100	1.18502000
H	6.66540100	3.86685800	-0.55399000
C	-3.36745500	0.81053900	2.99102200
H	-1.67141000	0.04269300	2.17991200
C	-3.07950900	0.00130500	4.24185200
H	-3.03790300	0.68172200	5.09488200
H	-2.14864600	-0.56673000	4.20202400
H	-3.91007200	-0.68686500	4.41481900
O	-4.37537100	1.50651000	2.90352200
P	-1.73676200	-2.11353800	-0.26729800
C	-0.72586800	-3.58249700	0.15383500
C	0.05907500	-3.48084800	1.46785800
H	-0.04445600	-3.73686700	-0.68534800
H	-1.41106400	-4.43538700	0.17534400
C	0.78174200	-4.79049900	1.79945300
H	-0.60725100	-3.21216800	2.29551100
H	0.79453600	-2.67610200	1.39137800
C	1.70003900	-4.65666400	3.01525500
H	1.14016100	-4.34895700	3.90424500
H	2.47789200	-3.90713500	2.83855200
H	2.19704000	-5.60281600	3.24651400
H	1.36896900	-5.10688500	0.93005900
H	0.04205200	-5.58146200	1.97226300
C	-3.27100400	-2.22431500	0.73450000
C	-4.46119900	-1.38602300	0.24470000
H	-3.00626500	-1.96781600	1.76183200
H	-3.54141200	-3.28508200	0.74322700
C	-5.66000500	-1.49238900	1.19224800
H	-4.76264600	-1.72089900	-0.75318200
H	-4.17817300	-0.33717900	0.14206800
C	-6.84238100	-0.64249700	0.72458000
H	-6.56494100	0.41437600	0.66897400
H	-7.69019000	-0.72812600	1.40981900
H	-7.18475000	-0.95043200	-0.26875300
H	-5.35761400	-1.17225900	2.19512100
H	-5.96418600	-2.54257500	1.28090000

C	-2.23491600	-2.30313700	-2.02308600
C	-2.98569900	-3.59527300	-2.37016400
H	-1.30258100	-2.22024300	-2.58774000
H	-2.83208300	-1.42032100	-2.27126400
C	-3.39553700	-3.63623300	-3.84676400
H	-3.88196400	-3.69723500	-1.74812600
H	-2.35588600	-4.46368800	-2.14797300
C	-4.13555000	-4.92323500	-4.21581100
H	-3.51237800	-5.80463400	-4.03357100
H	-4.41976000	-4.93091100	-5.27170200
H	-5.05024800	-5.03747500	-3.62518200
H	-2.50093300	-3.53010400	-4.47162700
H	-4.02804500	-2.76830500	-4.06813800
H	2.68541300	-1.83098900	-0.96014600

12 a

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -2422.108282 hartrees

C	-0.68604000	0.48675800	-0.11219600
C	-1.23250300	-0.90082300	0.09306500
C	0.70710100	0.70534400	-0.00394700
C	-0.54079800	-1.97305200	0.45313400
C	1.69486300	-0.35439600	0.32053100
C	2.26222200	-1.16972600	-0.69067900
C	2.17198600	-0.56015300	1.62125600
C	3.14691500	-1.49456300	1.92866100
C	3.71149100	-2.30489200	0.91541200
C	3.24243400	-2.11660700	-0.40218500
C	-2.69115800	-1.17080200	-0.10595500
C	-3.64912000	-0.75093700	0.84586200
C	-3.16071100	-1.81133200	-1.24910700
C	-5.00764700	-0.96426600	0.62989700
C	-5.47781300	-1.62043600	-0.53106500
C	-4.51413600	-2.03337000	-1.47831400
O	-1.51254600	1.39988100	-0.36525700
O	-0.06885600	-2.99245500	0.76122100
H	3.64815400	-2.67575300	-1.22518500
H	3.46256800	-1.58709800	2.95848500
H	1.75871500	0.04823800	2.41974000
H	-2.44117100	-2.13090900	-1.99660500
H	-4.80102100	-2.51559000	-2.40129900
H	-5.68911200	-0.61120300	1.38265400
N	4.68494700	-3.26096100	1.20261700
N	1.78402900	-0.95059700	-1.99705100
N	-6.83928800	-1.86406000	-0.70958200
N	-3.15631800	-0.12499100	2.00820900
C	-3.81786600	0.53118400	3.00827100

C	-2.91064000	1.17200400	4.04181700
H	-1.88492100	0.80107000	4.01712300
H	-3.32853700	1.00369000	5.03470000
H	-2.89102400	2.25108900	3.86853000
O	-5.03911400	0.63026100	3.08319100
C	5.27537900	-3.99111800	0.06918800
C	5.54923200	-3.04317200	2.36945400
C	6.17880700	-5.15623800	0.46189100
H	5.67550100	-5.83954100	1.15118900
H	7.11809800	-4.83453200	0.91667600
H	6.43269400	-5.71856600	-0.44012500
H	5.82863200	-3.30452800	-0.58968600
H	4.45261500	-4.39550200	-0.52332600
C	6.57932100	-1.92708700	2.16881100
H	7.24359900	-2.15130600	1.32952000
H	7.19603400	-1.80652600	3.06407100
H	6.08751400	-0.97334000	1.96200700
H	6.05108500	-3.98134300	2.59983300
H	4.92907500	-2.83668600	3.24128500
C	-7.26677500	-2.39575800	-2.01267800
C	-7.80659100	-1.04827700	0.03397300
C	-7.92551000	0.39046300	-0.47773500
H	-8.25144200	0.40973000	-1.52170500
H	-6.96655400	0.91013200	-0.41334400
H	-8.65556300	0.94956000	0.11455600
H	-7.54143600	-1.05650500	1.09135100
H	-8.77435900	-1.54421000	-0.01402000
C	-8.73607600	-2.79906800	-2.09360400
H	-9.00671400	-3.49606700	-1.29599800
H	-8.90536600	-3.30318700	-3.04847600
H	-9.41587700	-1.94545900	-2.05358600
H	-6.67063900	-3.28766100	-2.21697700
H	-7.04133600	-1.67689700	-2.81571700
C	2.19954900	-1.45869400	-3.19584400
H	1.04391600	-0.25796600	-2.01861200
C	1.44068000	-0.93582400	-4.40094000
H	0.99081500	-1.78194000	-4.92480800
H	2.15217000	-0.46873400	-5.08542000
H	0.65794100	-0.21542800	-4.15797800
O	3.11110800	-2.27106000	-3.32394300
P	1.20122000	2.38405500	-0.16541400
C	0.40925300	3.50544300	1.05259900
C	0.53993200	3.02508400	2.50198700
H	-0.64088400	3.57393800	0.76124400
H	0.85679700	4.49627900	0.92871600
C	-0.16446300	3.96377900	3.48686900

H	1.59762300	2.94230900	2.77904400
H	0.11818100	2.01828900	2.58919300
C	-0.00614400	3.51836900	4.94177500
H	1.04822200	3.49766300	5.23552200
H	-0.41064700	2.51388500	5.09719500
H	-0.52789000	4.19399500	5.62522200
H	-1.22829400	4.02238000	3.22778800
H	0.23259300	4.97915000	3.36845900
C	3.00558600	2.48317000	0.11080600
C	3.85805900	1.84645400	-1.00819400
H	3.18748000	1.97869400	1.06248400
H	3.26238500	3.53452400	0.26211600
C	5.09852500	1.13405300	-0.45998600
H	4.15087600	2.61935800	-1.72661700
H	3.27440900	1.11908500	-1.57671000
C	5.90526100	0.43481000	-1.55388500
H	5.29602000	-0.31794400	-2.06342800
H	6.77946500	-0.07443800	-1.13816800
H	6.26050900	1.14519300	-2.30762500
H	4.77364300	0.39323200	0.27802500
H	5.72984300	1.85363500	0.07576300
C	0.85833400	3.07882600	-1.82860000
C	1.22334200	4.55491600	-2.02806000
H	-0.20501200	2.90094000	-2.00410600
H	1.40875300	2.44833100	-2.53406300
C	0.98973700	5.01000000	-3.47319000
H	2.27425000	4.72506800	-1.76511500
H	0.62932800	5.18239800	-1.35521800
C	1.33714100	6.48398900	-3.68997800
H	0.72963000	7.13217600	-3.05029900
H	1.16518600	6.78642300	-4.72672500
H	2.38845800	6.68151200	-3.45675800
H	-0.05867200	4.83267600	-3.74078200
H	1.58735200	4.38564000	-4.14826700
H	-2.14722300	-0.09531400	2.04973500

6 a

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -2422.118879 hartrees

C	0.68314800	-1.19777500	0.01026800
C	1.72830800	-0.27735600	0.30224700
C	-0.66117700	-0.93209300	-0.07034100
C	1.64516800	0.73315300	1.29394300
C	-1.23343900	0.41255500	-0.34306600
C	-2.04913600	1.09318000	0.57444300
C	-1.12482200	0.96842400	-1.62735200
C	-1.86453500	2.07184800	-2.01966700

C	-2.77521400	2.68181400	-1.12822600
C	-2.81077900	2.19614200	0.18904700
C	3.07992800	-0.30188400	-0.21906100
C	3.82146400	0.71900000	0.42355400
C	3.70843700	-1.04959900	-1.21282400
C	5.13812400	0.98988300	0.08903500
C	5.78046600	0.20774100	-0.89619900
C	5.04868900	-0.80703000	-1.53330600
O	1.05519200	-2.50697700	-0.23119200
O	0.72654300	1.04465600	2.06693500
H	-3.42351200	2.67029000	0.93970500
H	-1.78519700	2.41449600	-3.04385800
H	-0.48941600	0.47137900	-2.35356200
H	3.16665200	-1.82252900	-1.74848800
H	5.51395100	-1.42750200	-2.28838800
H	5.65998600	1.80358400	0.56441200
N	-3.63633600	3.70093600	-1.56591400
N	-2.01354100	0.66981600	1.92701400
N	7.13047600	0.51137800	-1.22491800
N	2.95922400	1.37028200	1.34658900
C	3.33173800	2.43351600	2.16760400
H	1.93298000	-2.66700700	0.14129800
C	2.27790800	3.09245400	3.02531900
H	1.41700600	3.40629700	2.43517200
H	2.74268400	3.95138700	3.50762700
H	1.89817500	2.40089300	3.77779300
O	4.48897200	2.83283900	2.18288100
C	-4.71888400	4.09641400	-0.65763300
C	-3.05525700	4.77790600	-2.38277600
C	-5.81994200	4.90546400	-1.33860400
H	-6.17703500	4.40182200	-2.24100200
H	-5.49823800	5.91298800	-1.61132700
H	-6.66389700	5.00986600	-0.65204600
H	-4.33935900	4.65606100	0.21163500
H	-5.16049800	3.17698700	-0.26733200
C	-2.26980400	5.81449600	-1.57264500
H	-2.90905500	6.33337300	-0.85350300
H	-1.83568800	6.56782300	-2.23631500
H	-1.45530800	5.33867700	-1.01946800
H	-3.86091800	5.26067800	-2.93758800
H	-2.40726800	4.33523800	-3.13770300
C	7.64033500	-0.06369600	-2.47238600
C	8.07623400	0.48839700	-0.09382900
C	8.45105500	-0.91593000	0.39430300
H	8.97625100	-1.48855700	-0.37490300
H	7.55821200	-1.47767000	0.68330900

H	9.10855200	-0.85181400	1.26631500
H	7.63833200	1.05315100	0.72891000
H	8.97341100	1.03847800	-0.38439100
C	8.95980800	0.55549300	-2.92951500
H	8.89685000	1.64702000	-2.94446000
H	9.18994500	0.21333500	-3.94209900
H	9.80068700	0.27045900	-2.29297100
H	6.88509600	0.11902800	-3.24101800
H	7.76083500	-1.15793400	-2.40912900
C	-3.04921200	0.61774000	2.80332900
H	-1.05861500	0.51718600	2.25222400
C	-2.66367500	0.29586700	4.23366800
H	-3.33699700	-0.47050700	4.62045600
H	-2.80350100	1.19320500	4.84247500
H	-1.63210700	-0.04044100	4.34418700
O	-4.22472400	0.80219000	2.48255400
P	-1.79298300	-2.31786400	-0.14595700
C	-1.48597200	-3.52159100	1.20135900
C	-1.36123300	-2.87060600	2.58439400
H	-0.57410700	-4.06198100	0.94239000
H	-2.31135800	-4.23935400	1.18020900
C	-1.08062600	-3.90089000	3.68225800
H	-2.27992600	-2.32578200	2.82609700
H	-0.55840700	-2.12729500	2.56535900
C	-0.94221200	-3.25681700	5.06315600
H	-1.86014900	-2.73523800	5.35076100
H	-0.12897300	-2.52433800	5.07759800
H	-0.73001200	-4.00437400	5.83239700
H	-0.16297800	-4.44842000	3.43558000
H	-1.88615300	-4.64489300	3.69936300
C	-3.52803000	-1.76331800	0.03406900
C	-4.13757600	-1.00999800	-1.15972900
H	-3.57464600	-1.14746000	0.93178000
H	-4.10538100	-2.66740100	0.25204100
C	-5.47135100	-0.35415900	-0.78377300
H	-4.28310200	-1.69645000	-2.00138800
H	-3.45624800	-0.23314700	-1.50777000
C	-6.01914700	0.52542200	-1.90957600
H	-5.32410500	1.33854600	-2.14156400
H	-6.97596600	0.97702200	-1.63181000
H	-6.17849700	-0.04973400	-2.82791000
H	-5.31976300	0.25094100	0.11565000
H	-6.20207400	-1.12885700	-0.51961600
C	-1.67207200	-3.20667100	-1.74351200
C	-2.60543500	-4.41483200	-1.89678300
H	-0.62426400	-3.49687200	-1.84662000

H	-1.87117300	-2.45809000	-2.51682100
C	-2.47467600	-5.06095400	-3.28083600
H	-3.64714800	-4.11373900	-1.73988000
H	-2.37947300	-5.16266300	-1.12888800
C	-3.39236300	-6.27291100	-3.45151300
H	-3.16443500	-7.04935800	-2.71428000
H	-3.28481300	-6.71713500	-4.44484900
H	-4.44348700	-5.99481500	-3.32437200
H	-1.43204800	-5.35934000	-3.44222900
H	-2.70163400	-4.31290900	-4.04972100

4 e

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -1380.587488 hartrees

C	0.03528900	-0.99368300	-0.22145500
C	-1.04378400	0.00016200	-0.13942700
C	1.05117200	0.06646700	-0.13317100
C	-0.02861200	1.06005100	-0.05105600
C	2.45588300	0.03413400	-0.13604500
C	3.30541200	1.20293900	-0.03667900
C	3.10468200	-1.23031100	-0.23558300
C	4.46434500	-1.37741700	-0.24926700
C	5.31649300	-0.22808100	-0.16965600
C	4.70040000	1.03361200	-0.05046400
C	-2.44960300	0.03343500	-0.13855500
C	-3.30038900	-1.13565800	-0.23280100
C	-3.09648400	1.29598700	-0.02940900
C	-4.69290200	-0.96526800	-0.21856900
C	-5.31007700	0.29980000	-0.13067400
C	-4.45800600	1.44522700	-0.02018700
O	0.07946900	-2.22883100	-0.32323100
O	-0.07196700	2.29524600	0.05233700
H	5.31004100	1.91620300	0.04496500
H	4.87455000	-2.37385100	-0.31806600
H	2.47599500	-2.11041100	-0.30078000
H	-2.46746700	2.17433700	0.05413900
H	-4.86664500	2.43934500	0.07923300
H	-5.30382300	-1.85095400	-0.27115400
N	6.68462200	-0.35339300	-0.21797900
N	2.76610400	2.44194700	0.07588400
N	-6.67736400	0.43858600	-0.15590000
N	-2.76016800	-2.37722000	-0.32676400
C	-3.53917500	-3.59364900	-0.42524800
C	7.51037400	0.85098600	-0.01116100
C	7.31225700	-1.66873900	-0.04025400
C	9.00671100	0.66911800	-0.24051200
H	9.22375400	0.29761400	-1.24502000

H	9.47255700	0.00187300	0.48733300
H	9.48669000	1.64554000	-0.13908700
H	7.34269400	1.24216200	1.00186300
H	7.15895000	1.61695700	-0.70631000
C	7.35854700	-2.12435600	1.42020400
H	7.92935500	-1.42056100	2.03210800
H	7.83484300	-3.10563300	1.49935300
H	6.35265500	-2.19747000	1.84046600
H	8.31814300	-1.62305000	-0.45114100
H	6.78978300	-2.39894700	-0.65728700
C	-7.26485300	1.76627200	0.11849600
C	-7.53847000	-0.74338500	-0.04544900
C	-7.67357900	-1.26485000	1.38803400
H	-8.11999300	-0.50731200	2.03781300
H	-6.69997400	-1.53352800	1.80383700
H	-8.31313600	-2.15161200	1.41283000
H	-7.15683400	-1.52131600	-0.70742900
H	-8.51803200	-0.49091200	-0.44482600
C	-8.77175300	1.87056000	-0.08975200
H	-9.06373000	1.59891400	-1.10716700
H	-9.06433500	2.91118000	0.07023800
H	-9.34395200	1.26144200	0.61276000
H	-6.79040500	2.48754600	-0.54921000
H	-7.01879100	2.07179200	1.14406600
C	3.54393300	3.65959500	0.17317700
H	1.75141000	2.54180500	0.08391300
H	2.85573400	4.50128500	0.24084400
H	4.18188900	3.80904200	-0.70560800
H	4.18259100	3.66836900	1.06399900
H	-4.17668800	-3.74499100	0.45359900
H	-2.85217500	-4.43621900	-0.49486300
H	-4.17899900	-3.59993200	-1.31551600
H	-1.74589400	-2.47714300	-0.33665000

10e

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -2195.338418 hartrees

C	0.66689700	-0.52107400	1.03559900
C	1.59156200	-0.57534600	-0.04533100
C	-0.53451100	-0.11136200	0.10184200
C	0.58387800	-0.25406400	-0.99804900
C	-1.78090500	-0.96174600	-0.04274800
C	-2.54612500	-1.40823200	1.06893900
C	-2.26000000	-1.25504300	-1.32516600
C	-3.45643100	-1.91901600	-1.54876000
C	-4.25280500	-2.32132600	-0.45869100
C	-3.77321200	-2.06289700	0.83355300

C	3.02668400	-0.84868000	-0.06291100
C	3.89136500	-0.48868400	-1.14324600
C	3.61272900	-1.44923200	1.05593200
C	5.26068000	-0.77019400	-1.04169900
C	5.83576800	-1.36456300	0.09793500
C	4.97933800	-1.70196600	1.15930700
O	0.69813400	-0.67832700	2.26203600
O	0.50813200	-0.08636400	-2.22277900
H	-4.36331600	-2.35741200	1.68747600
H	-3.75789700	-2.13822100	-2.56548600
H	-1.67607100	-0.93313600	-2.17850600
H	2.97087800	-1.71022600	1.89026700
H	5.35637200	-2.14194600	2.07223600
H	5.89688800	-0.54066100	-1.88425100
N	-5.46962400	-2.99837800	-0.68485300
N	-2.12973000	-1.15388900	2.35879600
N	7.22245400	-1.63536000	0.12263900
N	3.38860400	0.16677600	-2.25477500
C	-6.10910100	-3.63499800	0.47150200
C	-6.39248900	-2.36904300	-1.64594900
C	-7.22030100	-4.61043600	0.08911700
H	-6.87435700	-5.32628500	-0.66141100
H	-8.10787700	-4.10723500	-0.30088700
H	-7.52887500	-5.17042100	0.97568400
H	-6.50766500	-2.89300800	1.18194800
H	-5.33254200	-4.18889800	1.00374100
C	-7.17406800	-1.18248600	-1.07019200
H	-7.84642800	-1.49085000	-0.26541300
H	-7.78161200	-0.71224200	-1.84871200
H	-6.49273300	-0.42689100	-0.66978900
H	-7.08002800	-3.13092000	-2.01728800
H	-5.81981700	-2.04166000	-2.51198200
C	7.71817500	-2.43273200	1.24984600
C	8.11647300	-0.55379100	-0.32274000
C	8.26098100	0.59288800	0.68417700
H	8.70086000	0.25156700	1.62516000
H	7.28680300	1.03639500	0.90780000
H	8.90760400	1.37728700	0.27974200
H	7.75018000	-0.16246500	-1.27048000
H	9.09288700	-0.98589700	-0.54614200
C	9.14388000	-2.94663600	1.05987900
H	9.25875800	-3.44354400	0.09254200
H	9.37015800	-3.67445200	1.84355300
H	9.89260100	-2.15430900	1.12950000
H	7.05494100	-3.29459500	1.34965400
H	7.65671800	-1.87973100	2.20110900

H	-1.13833000	-0.97884500	2.49195500
P	-0.98486000	1.68656000	0.30714200
C	0.54295600	2.66364900	0.57006800
C	1.38455100	2.97373200	-0.67771800
H	1.12938500	2.09903900	1.30142000
H	0.24077700	3.59243300	1.06125100
C	2.73966400	3.58015200	-0.29873100
H	0.83909900	3.66696400	-1.32708100
H	1.56252200	2.07152100	-1.26273500
C	3.59946800	3.88106600	-1.52750100
H	3.10717600	4.59938900	-2.19134100
H	3.78325900	2.96720500	-2.09864100
H	4.56797300	4.30189200	-1.24291600
H	3.27040100	2.87760800	0.35448700
H	2.58604600	4.49398200	0.28843400
C	-1.83229600	2.26036300	-1.21257000
C	-3.34147600	1.97138000	-1.27994400
H	-1.30185200	1.77229600	-2.03527300
H	-1.64289700	3.33390900	-1.30377400
C	-3.90313600	2.26815500	-2.67394200
H	-3.87169400	2.57733800	-0.53843100
H	-3.54273800	0.92768600	-1.03190700
C	-5.39769300	1.95926700	-2.77517100
H	-5.59336600	0.90181600	-2.57584100
H	-5.78549800	2.18789000	-3.77171800
H	-5.97515900	2.54375900	-2.05160400
H	-3.35468700	1.67308700	-3.41370400
H	-3.71913000	3.31918500	-2.92784300
C	-2.08334600	1.96326600	1.74049400
C	-2.49566200	3.42627200	1.96379900
H	-1.57146100	1.56034200	2.61641900
H	-2.95646700	1.32718400	1.57945300
C	-3.57400800	3.54082600	3.04756400
H	-2.87161100	3.87156500	1.03655000
H	-1.62588300	4.02101300	2.26019000
C	-3.98513100	4.98986000	3.31355400
H	-3.13277500	5.58855200	3.64997300
H	-4.75698900	5.04868900	4.08574900
H	-4.38368000	5.46070000	2.40917700
H	-3.20513900	3.08296400	3.97286000
H	-4.45059500	2.95607000	2.74477300
H	2.39726000	0.04844900	-2.43711300
C	-2.82869100	-1.66007600	3.52151900
H	-2.26866100	-1.37126300	4.41129000
H	-3.83220800	-1.22921500	3.60518800
H	-2.92926600	-2.75437900	3.52055400

C	4.19273500	0.40321200	-3.43593300
H	5.02815000	1.07723800	-3.22029500
H	4.60757000	-0.51788800	-3.87079700
H	3.56647100	0.88386600	-4.18843700

TS 2 e

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -2195.301514 hartrees

Single imaginary frequency: -175.79 cm-1

C	-0.58420200	-0.71642000	0.49621800
C	-1.48321900	-0.06539600	-0.44533800
C	0.79319400	-0.67806200	-0.07584200
C	-0.85304400	-0.01742000	-1.63729800
C	1.56629200	0.60240200	0.05479600
C	2.35515200	1.11186500	-1.00941300
C	1.55021600	1.33892400	1.24434900
C	2.26755800	2.51747900	1.41835500
C	3.06290900	3.01884400	0.37144100
C	3.07817000	2.30420700	-0.83850600
C	-2.89413700	0.34854900	-0.25431600
C	-3.95604200	-0.56717400	-0.48567600
C	-3.22267500	1.62955200	0.17737100
C	-5.27986500	-0.15280600	-0.29112900
C	-5.60544100	1.15255800	0.13822800
C	-4.53602600	2.04239600	0.38562100
O	-0.93497700	-1.31251900	1.52358900
O	-0.64753800	0.09714700	-2.78876800
H	3.64392100	2.68459500	-1.67550600
H	2.23803000	3.01642200	2.37931600
H	0.96398700	0.95818800	2.07584600
H	-2.41616500	2.33197200	0.36785300
H	-4.70607700	3.04642700	0.74512600
H	-6.06682400	-0.86711200	-0.47741400
N	3.84178000	4.18350600	0.56189400
N	2.43332500	0.39406100	-2.19576900
N	-6.94105700	1.54804800	0.28427700
N	-3.66378500	-1.86341900	-0.87258300
C	4.82821100	4.50207300	-0.47522400
C	3.15041900	5.34256200	1.15138900
C	5.84140400	5.56286900	-0.04983100
H	6.29004100	5.31431400	0.91592200
H	5.40312200	6.56073300	0.02262000
H	6.64176100	5.61457700	-0.79268100
H	4.34997800	4.81748100	-1.41679000
H	5.36980300	3.57939700	-0.69710800
C	2.22161600	6.07831300	0.17908300
H	2.77195700	6.50260500	-0.66504400

H	1.70985300	6.90014500	0.68847200
H	1.46213800	5.39973000	-0.21909500
H	3.90229600	6.02700600	1.54761700
H	2.57983100	5.00460700	2.01504000
C	-7.19042800	2.87759100	0.86075200
C	-7.95197000	0.51761000	0.54779600
C	-7.87844400	-0.07733200	1.95761700
H	-8.03100600	0.69441600	2.71755700
H	-6.90425000	-0.53882700	2.13663800
H	-8.64906600	-0.84168700	2.09453600
H	-7.86543100	-0.26871300	-0.20229900
H	-8.93423800	0.95531200	0.37720200
C	-8.64689100	3.33208800	0.81810900
H	-9.06111600	3.25764500	-0.19110900
H	-8.69380100	4.38101800	1.12189600
H	-9.29026500	2.77021800	1.49854900
H	-6.60509500	3.59867600	0.28709000
H	-6.82289300	2.92944800	1.89767300
H	1.63583600	-0.21169600	-2.32678700
P	1.69644400	-2.16689800	0.29404700
C	0.66189600	-3.61922700	-0.12132400
C	0.16806300	-3.64919700	-1.57380600
H	-0.18173100	-3.59099000	0.57265600
H	1.24315300	-4.51626400	0.11001800
C	-0.83964600	-4.77758000	-1.81553000
H	1.01717100	-3.76381800	-2.25738700
H	-0.29510600	-2.69094100	-1.82486400
C	-1.36994800	-4.79138900	-3.25047600
H	-0.55901600	-4.93646600	-3.97127500
H	-1.86452700	-3.84681200	-3.49912100
H	-2.09565300	-5.59551100	-3.40077800
H	-1.67518800	-4.66718300	-1.11322400
H	-0.37306100	-5.74203300	-1.58176000
C	3.25474000	-2.31175400	-0.65938300
C	4.41100900	-1.43493700	-0.15166900
H	3.01604800	-2.06043900	-1.69292600
H	3.53658100	-3.36954400	-0.64022800
C	5.54918000	-1.34467400	-1.17151100
H	4.79484900	-1.83810700	0.79177600
H	4.05677000	-0.42575100	0.06580400
C	6.68751600	-0.44223200	-0.69157300
H	6.32708600	0.57450400	-0.50418100
H	7.48953700	-0.38006500	-1.43264100
H	7.12491600	-0.81454600	0.24053500
H	5.14431800	-0.95711500	-2.11313800
H	5.93307700	-2.34953700	-1.38768800

C	2.15615300	-2.32349900	2.06679200
C	2.89854700	-3.60432600	2.46796200
H	1.21602100	-2.21656300	2.61303900
H	2.75472900	-1.43602700	2.29673700
C	3.31097500	-3.58623400	3.94448600
H	3.79320600	-3.74003300	1.84983000
H	2.26258900	-4.47748800	2.28546400
C	4.03878400	-4.86333300	4.36855500
H	3.40628800	-5.74548500	4.22607900
H	4.32554800	-4.82819600	5.42331600
H	4.95087300	-5.01286900	3.78160500
H	2.41877200	-3.44385300	4.56560600
H	3.95260500	-2.71593900	4.12743800
H	-2.71427100	-2.00107000	-1.18223300
C	2.94069500	0.99217700	-3.41616700
H	2.79050500	0.28931500	-4.23612000
H	2.44187800	1.93752200	-3.67383500
H	4.01469100	1.18462900	-3.33917300
C	-4.65327300	-2.75432300	-1.44631300
H	-5.39731900	-3.05297400	-0.70171000
H	-5.18450500	-2.30652800	-2.29751600
H	-4.15023000	-3.65812000	-1.79081300

12 e

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -2195.323595 hartrees

C	-0.51886600	0.72405300	-0.38996300
C	-1.27336700	-0.56555000	-0.34129600
C	0.88244800	0.72610200	-0.24968400
C	-0.71644400	-1.76219800	-0.18719900
C	1.71163900	-0.50397900	-0.24161400
C	2.18755300	-1.07789700	0.96720500
C	2.07769600	-1.13944100	-1.43612100
C	2.85609600	-2.28386900	-1.47780700
C	3.33095300	-2.85969500	-0.27742200
C	2.97867900	-2.23625700	0.93339500
C	-2.76955400	-0.64224300	-0.40565900
C	-3.61565800	0.01778300	0.53109300
C	-3.38024400	-1.45940500	-1.35490700
C	-4.99646200	-0.20404300	0.48128700
C	-5.60145800	-1.07012300	-0.45702500
C	-4.75437600	-1.68123600	-1.40389500
O	-1.19776300	1.79046000	-0.50170600
O	-0.39867600	-2.87817700	-0.06362100
H	3.28523700	-2.67423500	1.87077900
H	3.11458400	-2.70844000	-2.43884500
H	1.73258800	-0.70165300	-2.36838400

H	-2.75225200	-1.94945900	-2.09373000
H	-5.14090100	-2.31884600	-2.18534800
H	-5.61442900	0.31527100	1.19611400
N	4.14901700	-4.00116300	-0.30917800
N	1.85822900	-0.46879400	2.16741000
N	-6.98168000	-1.31144900	-0.43194600
N	-3.04764100	0.85439400	1.49332000
C	4.71532200	-4.46138500	0.96454800
C	3.78232100	-5.06181400	-1.26229300
C	5.81584600	-5.50892600	0.81195900
H	6.57770300	-5.18240800	0.09880800
H	5.43539200	-6.48013000	0.48848000
H	6.30115800	-5.65831200	1.77990800
H	3.93427500	-4.85106400	1.63660800
H	5.14560700	-3.58839900	1.46011400
C	2.55647400	-5.87570400	-0.83510100
H	2.73004500	-6.39669500	0.11051000
H	2.31518000	-6.62873300	-1.59098300
H	1.68553600	-5.22700200	-0.70940200
H	4.64505000	-5.71472700	-1.39595200
H	3.60628900	-4.61484300	-2.23891400
C	-7.54575400	-2.09067600	-1.54363600
C	-7.85866700	-0.30656800	0.17890200
C	-8.00778500	0.97487400	-0.64769300
H	-8.43738100	0.75996900	-1.63037400
H	-7.03892400	1.45625000	-0.80129900
H	-8.66619900	1.68646900	-0.14073000
H	-7.49264800	-0.07425200	1.17932200
H	-8.83426000	-0.76230200	0.34070900
C	-9.01163500	-2.48110000	-1.37523700
H	-9.18637000	-2.98107200	-0.41861600
H	-9.28006500	-3.18031700	-2.17133900
H	-9.69218500	-1.63026800	-1.45030000
H	-6.96784300	-3.01346600	-1.62381500
H	-7.41797300	-1.55736500	-2.49899200
H	1.05530600	0.13877300	2.07951400
P	1.61898900	2.31738200	-0.17356000
C	0.81614700	3.45766900	1.02775700
C	0.44770600	2.80285500	2.36141400
H	-0.07701400	3.84211400	0.53380000
H	1.50215500	4.29657500	1.18173500
C	-0.29134000	3.75948800	3.30131500
H	1.34866700	2.42780900	2.86068000
H	-0.19059300	1.93503800	2.16922000
C	-0.65494900	3.09764900	4.63210900
H	0.24186600	2.77344700	5.16986700

H	-1.28045000	2.21298000	4.47588500
H	-1.20429200	3.78218800	5.28443900
H	-1.20063400	4.11782600	2.80356700
H	0.32679600	4.64660800	3.48486200
C	3.36309500	2.14292200	0.36378300
C	4.34094100	1.62338600	-0.69996900
H	3.33831800	1.47074200	1.22568800
H	3.68581400	3.12137500	0.73223000
C	5.71372200	1.30161000	-0.10078200
H	4.45648400	2.36810700	-1.49565400
H	3.94168000	0.72195200	-1.17038000
C	6.69436200	0.76353500	-1.14437400
H	6.31455400	-0.15529100	-1.60238800
H	7.66740300	0.53577900	-0.69996100
H	6.85796100	1.49002000	-1.94702400
H	5.58707700	0.56287700	0.69972100
H	6.12802600	2.20045600	0.37257100
C	1.61795000	3.20815300	-1.77854000
C	2.23378200	4.61286000	-1.76745400
H	0.57084600	3.23503900	-2.09236300
H	2.14295600	2.55658600	-2.48397000
C	2.25739300	5.24083700	-3.16559700
H	3.25702300	4.57577400	-1.37517700
H	1.66820600	5.26354900	-1.09171400
C	2.86187400	6.64621300	-3.17055800
H	2.29286900	7.32420000	-2.52628900
H	2.87002100	7.07425900	-4.17690400
H	3.89448200	6.63429600	-2.80675500
H	1.23553300	5.27514500	-3.56169700
H	2.82554000	4.59110900	-3.84217500
H	-2.29016600	1.39257600	1.08248000
C	1.97784700	-1.15424100	3.44160100
H	1.46611200	-2.12634200	3.45443400
H	3.02732500	-1.31908600	3.70111300
H	1.54183400	-0.52298400	4.21642800
C	-3.89391700	1.66306400	2.35531400
H	-4.59363700	2.30797500	1.80282500
H	-4.47676000	1.03349200	3.03296300
H	-3.25354800	2.30092600	2.96572000

6 e

Free Energy(6-311+G(d),B3LYP-D3,CPCM,solvent=chloroform): -2195.348676 hartrees

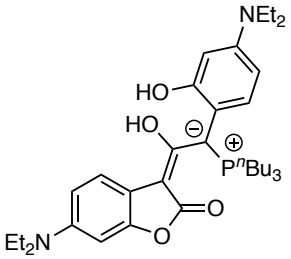
C	0.71020700	-1.01889200	0.06196800
C	1.72391400	-0.09354200	0.40469800
C	-0.65462300	-0.82953600	0.06244900
C	1.62511600	0.88266300	1.45989700

C	-1.32691300	0.49043500	-0.07699400
C	-2.13709600	1.04498400	0.94333300
C	-1.30841300	1.14237200	-1.31396300
C	-2.11314500	2.23817200	-1.59863700
C	-3.00024400	2.72963000	-0.62126900
C	-2.96605400	2.13914000	0.65308600
C	3.07793100	-0.04311800	-0.11253500
C	3.76012500	0.97617500	0.60871900
C	3.77656400	-0.68695000	-1.13347400
C	5.07025100	1.33585200	0.33969300
C	5.77793700	0.65346500	-0.67313800
C	5.11341000	-0.35143500	-1.39573000
O	1.12965000	-2.28270100	-0.33114000
O	0.69634900	1.15013100	2.24663300
H	-3.57712500	2.54816900	1.44331300
H	-2.10329200	2.65639600	-2.59779300
H	-0.68433900	0.72855400	-2.10073500
H	3.29812900	-1.45149300	-1.73824300
H	5.63277100	-0.89475500	-2.17510500
H	5.54086900	2.14926300	0.88047000
N	-3.91657800	3.75426600	-0.94245400
N	-2.11021600	0.44899300	2.20430800
N	7.12655700	1.03891100	-0.93574300
N	2.88385400	1.51731700	1.53536000
C	3.22079100	2.54177100	2.49589500
H	2.02208400	-2.43840700	0.00678800
C	-4.99329800	4.01193800	0.01816800
C	-3.37189400	4.94137700	-1.62103600
C	-6.13642200	4.84419100	-0.55873100
H	-6.48857000	4.42456800	-1.50509900
H	-5.85692300	5.88636600	-0.72857000
H	-6.97290700	4.84433300	0.14507800
H	-4.62165200	4.49430000	0.93657300
H	-5.39310600	3.04061200	0.31755300
C	-2.62012500	5.90112200	-0.69211400
H	-3.27562900	6.31664300	0.07795100
H	-2.20604000	6.73776400	-1.26247400
H	-1.79374100	5.38820900	-0.19226500
H	-4.19217700	5.46113800	-2.11914400
H	-2.70741900	4.61132700	-2.41814900
C	7.67488800	0.62740300	-2.23076200
C	8.04652800	0.88173700	0.20636300
C	8.43962600	-0.56689200	0.52091200
H	9.00328100	-1.02379000	-0.29693000
H	7.55177700	-1.17915100	0.70252300
H	9.06729300	-0.60425300	1.41630800

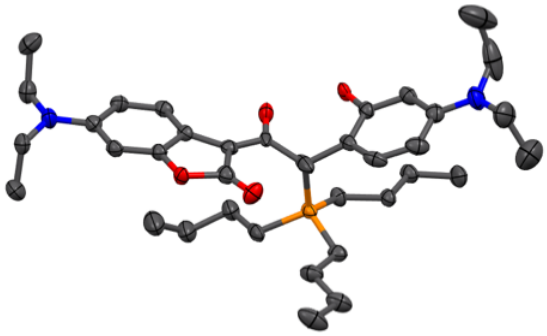
H	7.57448800	1.32623700	1.08307500
H	8.93982300	1.48031000	0.01470000
C	8.97311200	1.34733200	-2.59192000
H	8.86326100	2.43028800	-2.48712600
H	9.23409200	1.12983300	-3.63125800
H	9.81582000	1.02860900	-1.97374900
H	6.92060100	0.86380700	-2.98546400
H	7.84172900	-0.46088100	-2.29016500
C	-2.77242000	1.09154400	3.32665600
H	-1.15115700	0.19141000	2.42117000
P	-1.69278900	-2.27381600	-0.06802700
C	-1.23781800	-3.56790500	1.15062100
C	-0.97237300	-3.01153700	2.55512600
H	-0.35564900	-4.07989300	0.76270800
H	-2.05787300	-4.29239200	1.16568500
C	-0.65253100	-4.11851600	3.56360900
H	-1.83849000	-2.43798700	2.90280800
H	-0.13961100	-2.30297800	2.51102300
C	-0.36581000	-3.56566100	4.96122600
H	-1.22615000	-3.01230100	5.35127400
H	0.48721500	-2.87994400	4.94695200
H	-0.13706600	-4.36665000	5.66986100
H	0.21190600	-4.69293100	3.20854800
H	-1.49077700	-4.82457400	3.60946100
C	-3.44222300	-1.84688700	0.26672900
C	-4.17415300	-1.05125900	-0.82651700
H	-3.42514900	-1.29048400	1.20554900
H	-3.95464300	-2.79401200	0.46188200
C	-5.49481400	-0.46879900	-0.31143900
H	-4.36821700	-1.69490500	-1.69217400
H	-3.55142400	-0.22954200	-1.18226300
C	-6.17435600	0.43173400	-1.34485800
H	-5.53195000	1.27932100	-1.60257300
H	-7.11857600	0.83338200	-0.96562200
H	-6.39364000	-0.11462700	-2.26815800
H	-5.28989200	0.11328900	0.59436100
H	-6.16938700	-1.28144300	-0.01425300
C	-1.63818100	-3.03609200	-1.73557800
C	-2.51337300	-4.28286500	-1.91838300
H	-0.58634800	-3.25546600	-1.93128000
H	-1.93253700	-2.24619600	-2.43406300
C	-2.44914300	-4.82029600	-3.35260100
H	-3.55583000	-4.05551600	-1.66877600
H	-2.19367400	-5.06917600	-1.22560000
C	-3.31187200	-6.06776800	-3.55221600
H	-2.99128800	-6.88076700	-2.89288000

H	-3.25323400	-6.43293300	-4.58130800
H	-4.36429200	-5.86047500	-3.33317600
H	-1.40663000	-5.04569300	-3.60671900
H	-2.76956700	-4.03347300	-4.04590200
H	-2.55903000	0.51700200	4.22923100
H	-3.85699100	1.09672400	3.18622800
H	-2.44387600	2.12821200	3.49239200
H	4.04751600	2.22184000	3.13829900
H	2.34327100	2.72879300	3.11249600
H	3.50984400	3.47126700	1.99540700

IV. X-RAY CRYSTAL SUMMARY FOR 5A



5a



Atomic displacement ellipsoids are depicted at 50% probability. Crystals were grown through vapor/vapor diffusion with CH_2Cl_2/^{n}pentane.

TABLE S1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **3.24A**.

Identification code	al5nbuohsq	
Empirical formula	$C_{36}H_{55}N_2O_4P$	
Formula weight	610.79	
Temperature	120(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 22.3445(8) Å	α = 90°
	b = 10.6716(3) Å	β = 94.048(2)°
	c = 14.5597(5) Å	γ = 90°
Volume	3463.1(2) Å^3	
Z	4	
Density (calculated)	1.171 g.cm^{-3}	
Absorption coefficient (μ)	1.007 mm^{-1}	
F(000)	1328	
Crystal color, habit	colorless, tablet	
Crystal size	0.146 × 0.119 × 0.050 mm^3	
θ range for data collection	1.982 to 59.011°	
Index ranges	-24 ≤ h ≤ 24, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16	
Reflections collected	55252	
Independent reflections	4972 [R_{int} = 0.0516]	
Completeness to θ = 59.011°	99.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9610 and 0.7210	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4972 / 9 / 426	

Goodness-of-fit on F^2	1.087
Final R indices [I>2σ(I)]	$R_1 = 0.0766$, $wR_2 = 0.2003$
R indices (all data)	$R_1 = 0.0808$, $wR_2 = 0.2042$
Extinction coefficient	n/a
Largest diff. peak and hole	0.884 and -0.557 $e^{-}.Å^{-3}$

TABLE S2
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2$) FOR **3.24A**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
P(1)	0.75810(4)	0.13460(7)	0.41456(6)	0.029(1)
N(1)	0.92265(14)	0.7201(3)	0.7564(2)	0.043(1)
N(2)	0.57424(14)	-0.2649(3)	0.5813(2)	0.050(1)
C(1)	0.7266(2)	0.1562(3)	0.5274(3)	0.047(1)
O(1)	0.80809(17)	0.1429(3)	0.6326(2)	0.039(1)
O(2)	0.74347(13)	0.5546(3)	0.5984(2)	0.030(1)
O(3)	0.67516(15)	0.4174(4)	0.5295(2)	0.043(1)
O(4)	0.76609(12)	-0.0795(3)	0.6287(2)	0.029(1)
C(2)	0.7701(2)	0.2119(5)	0.5945(3)	0.039(1)
C(3)	0.7700(2)	0.3399(5)	0.6070(3)	0.030(1)
C(4)	0.7235(2)	0.4312(4)	0.5715(3)	0.037(1)
O(1A)	0.6903(5)	0.3435(12)	0.5493(8)	0.044(3)
O(2A)	0.8929(4)	0.2858(8)	0.7148(7)	0.038(3)
O(3A)	0.8443(6)	0.1040(10)	0.6434(8)	0.044(3)
O(4A)	0.6153(6)	0.1709(13)	0.4910(9)	0.062(4)
C(2A)	0.7308(5)	0.2896(11)	0.5645(9)	0.027(3)
C(3A)	0.7899(6)	0.2968(13)	0.6206(11)	0.034(5)
C(4A)	0.8443(9)	0.2140(14)	0.6615(17)	0.093(8)
C(5)	0.79760(15)	0.5414(3)	0.6444(2)	0.029(1)
C(6)	0.81624(14)	0.4163(3)	0.6553(2)	0.026(1)
C(7)	0.87210(15)	0.3970(3)	0.7009(2)	0.032(1)
C(8)	0.90731(15)	0.4954(3)	0.7340(2)	0.032(1)
C(9)	0.88811(16)	0.6212(3)	0.7219(2)	0.034(1)
C(10)	0.83150(15)	0.6423(3)	0.6754(2)	0.031(1)
C(11)	0.90712(19)	0.8484(3)	0.7316(3)	0.043(1)
C(12)	0.9225(2)	0.8840(4)	0.6353(3)	0.060(1)
C(13)	0.98000(17)	0.6980(4)	0.8069(3)	0.046(1)
C(14)	0.9736(2)	0.6625(4)	0.9066(3)	0.054(1)
C(15)	0.68882(16)	0.0450(3)	0.5505(2)	0.031(1)
C(16)	0.70949(15)	-0.0660(3)	0.5946(2)	0.030(1)
C(17)	0.67151(15)	-0.1664(3)	0.6045(2)	0.034(1)
C(18)	0.61157(16)	-0.1647(3)	0.5699(2)	0.038(1)

C(19)	0.59096(17)	-0.0549(4)	0.5249(3)	0.043(1)
C(20)	0.62875(17)	0.0454(3)	0.5174(2)	0.039(1)
C(21)	0.5942(2)	-0.3733(5)	0.6405(6)	0.096(2)

TABLE S2 (CONTINUED)

	x	y	z	U(eq)
C(22)	0.5878(3)	-0.3463(8)	0.7431(5)	0.120(3)
C(23)	0.5121(2)	-0.2649(5)	0.5483(4)	0.067(1)
C(24)	0.5010(3)	-0.3043(7)	0.4497(5)	0.111(2)
C(25)	0.69749(16)	0.1496(3)	0.3269(2)	0.035(1)
C(26)	0.67264(18)	0.2829(4)	0.3158(3)	0.043(1)
C(27)	0.61480(18)	0.2883(4)	0.2557(3)	0.051(1)
C(28)	0.5888(2)	0.4217(4)	0.2523(4)	0.064(1)
C(29)	0.81102(17)	0.2578(3)	0.3928(2)	0.036(1)
C(30)	0.87532(18)	0.2429(4)	0.4348(3)	0.047(1)
C(31)	0.9169(2)	0.3503(4)	0.4108(3)	0.061(1)
C(32)	0.9061(3)	0.4680(5)	0.4591(3)	0.076(2)
C(33)	0.79230(15)	-0.0177(3)	0.4059(2)	0.032(1)
C(34)	0.74885(15)	-0.1260(3)	0.3801(2)	0.030(1)
C(35)	0.77796(17)	-0.2523(3)	0.4010(3)	0.037(1)
C(36)	0.7368(2)	-0.3602(3)	0.3712(3)	0.049(1)
H(1)	0.6964	0.2244	0.5153	0.056
H(1A)	0.7634	0.1262	0.5639	0.056
H(4O)	0.7827	-0.0090	0.6330	0.044
H(4OA)	0.6371	0.2201	0.5236	0.094
H(5A)	0.7594	0.5571	0.6139	0.034
H(7)	0.8865	0.3137	0.7095	0.038
H(8)	0.9451	0.4785	0.7655	0.039
H(10)	0.8170	0.7253	0.6655	0.037
H(11A)	0.9285	0.9056	0.7762	0.051
H(11B)	0.8635	0.8603	0.7365	0.051
H(12A)	0.9092	0.9700	0.6219	0.090
H(12B)	0.9021	0.8267	0.5906	0.090
H(12C)	0.9660	0.8782	0.6310	0.090
H(13A)	1.0048	0.7747	0.8048	0.055
H(13B)	1.0012	0.6299	0.7764	0.055
H(14A)	1.0134	0.6483	0.9375	0.081
H(14B)	0.9497	0.5859	0.9092	0.081
H(14C)	0.9536	0.7306	0.9377	0.081
H(16A)	0.7502	-0.0718	0.6179	0.036
H(17)	0.6866	-0.2390	0.6360	0.040
H(19)	0.5507	-0.0501	0.4995	0.052
H(20)	0.6131	0.1191	0.4880	0.047
H(21A)	0.6367	-0.3924	0.6311	0.116
H(21B)	0.5699	-0.4479	0.6219	0.116
H(22A)	0.5979	-0.4218	0.7793	0.180

H(22B)	0.5463	-0.3217	0.7521	0.180
H(22C)	0.6150	-0.2781	0.7634	0.180

TABLE S2 (CONTINUED)

	x	y	z	U(eq)
H(23A)	0.4958	-0.1795	0.5554	0.081
H(23B)	0.4899	-0.3220	0.5873	0.081
H(24A)	0.4583	-0.3239	0.4371	0.166
H(24B)	0.5251	-0.3788	0.4383	0.166
H(24C)	0.5122	-0.2361	0.4093	0.166
H(25A)	0.7118	0.1219	0.2673	0.042
H(25B)	0.6645	0.0928	0.3420	0.042
H(26A)	0.6656	0.3171	0.3774	0.052
H(26B)	0.7029	0.3366	0.2886	0.052
H(27A)	0.5853	0.2301	0.2801	0.061
H(27B)	0.6223	0.2609	0.1926	0.061
H(28A)	0.5514	0.4226	0.2128	0.096
H(28B)	0.6177	0.4791	0.2272	0.096
H(28C)	0.5806	0.4483	0.3146	0.096
H(29A)	0.8126	0.2660	0.3253	0.043
H(29B)	0.7949	0.3375	0.4156	0.043
H(30A)	0.8919	0.1632	0.4130	0.057
H(30B)	0.8746	0.2377	0.5026	0.057
H(31A)	0.9589	0.3241	0.4258	0.073
H(31B)	0.9119	0.3655	0.3436	0.073
H(32A)	0.9347	0.5316	0.4412	0.114
H(32B)	0.9113	0.4543	0.5257	0.114
H(32C)	0.8651	0.4969	0.4426	0.114
H(33A)	0.8224	-0.0133	0.3592	0.038
H(33B)	0.8140	-0.0376	0.4657	0.038
H(34A)	0.7126	-0.1176	0.4151	0.036
H(34B)	0.7361	-0.1211	0.3137	0.036
H(35A)	0.8154	-0.2586	0.3687	0.045
H(35B)	0.7887	-0.2588	0.4679	0.045
H(36A)	0.7571	-0.4398	0.3860	0.073
H(36B)	0.7268	-0.3552	0.3047	0.073
H(36C)	0.7000	-0.3551	0.4038	0.073

TABLE S3
ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR **3.24A**.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	0.0409(5)	0.0187(5)	0.0272(5)	0.0003(3)	0.0069(4)	-0.0010(3)
N(1)	0.0479(18)	0.0320(17)	0.0476(18)	0.0040(14)	-0.0077(14)	-0.0133(14)
N(2)	0.0432(18)	0.045(2)	0.063(2)	0.0068(17)	0.0035(16)	-0.0161(15)
C(1)	0.083(3)	0.0246(19)	0.036(2)	-0.0030(16)	0.024(2)	-0.0114(18)
O(1)	0.041(2)	0.0304(18)	0.045(2)	-0.0049(15)	-0.0041(16)	-0.0112(17)
O(2)	0.0332(17)	0.0185(15)	0.0360(17)	0.0007(12)	-0.0048(13)	0.0022(12)
O(3)	0.0339(19)	0.050(2)	0.044(2)	-0.0086(17)	-0.0061(16)	0.0033(17)
O(4)	0.0296(16)	0.0170(15)	0.0414(18)	0.0059(13)	0.0008(13)	-0.0039(12)
C(2)	0.061(3)	0.038(3)	0.018(2)	-0.007(2)	0.012(2)	-0.033(3)
C(3)	0.034(3)	0.032(3)	0.025(2)	0.004(2)	0.007(2)	-0.002(2)
C(4)	0.049(3)	0.028(3)	0.034(2)	-0.001(2)	0.008(2)	0.000(2)
C(5)	0.0368(18)	0.0225(17)	0.0270(16)	-0.0004(13)	0.0029(14)	0.0016(14)
C(6)	0.0294(17)	0.0227(16)	0.0260(16)	-0.0004(13)	0.0059(13)	0.0018(13)
C(7)	0.0364(18)	0.0285(18)	0.0307(17)	0.0029(14)	0.0071(14)	0.0058(14)
C(8)	0.0327(18)	0.0332(19)	0.0307(17)	0.0024(15)	0.0013(14)	0.0014(15)
C(9)	0.040(2)	0.0312(19)	0.0308(18)	0.0011(15)	0.0041(15)	-0.0054(15)
C(10)	0.0417(19)	0.0208(17)	0.0305(17)	0.0013(14)	0.0039(14)	0.0019(14)
C(11)	0.055(2)	0.0292(19)	0.043(2)	-0.0043(16)	0.0007(17)	-0.0109(17)
C(12)	0.075(3)	0.057(3)	0.048(2)	0.011(2)	0.002(2)	-0.030(2)
C(13)	0.041(2)	0.041(2)	0.054(2)	-0.0052(19)	-0.0006(17)	-0.0095(17)
C(14)	0.060(3)	0.055(3)	0.044(2)	-0.012(2)	-0.0111(19)	0.008(2)
C(15)	0.050(2)	0.0185(16)	0.0255(16)	-0.0009(13)	0.0120(14)	0.0014(14)
C(16)	0.0364(19)	0.0236(17)	0.0299(17)	-0.0027(14)	0.0069(14)	-0.0013(14)
C(17)	0.0393(19)	0.0241(17)	0.0383(19)	0.0027(15)	0.0094(15)	0.0018(14)
C(18)	0.040(2)	0.038(2)	0.0360(19)	-0.0028(16)	0.0086(15)	-0.0041(16)
C(19)	0.038(2)	0.054(2)	0.038(2)	0.0091(18)	0.0086(16)	0.0078(18)
C(20)	0.049(2)	0.036(2)	0.0343(19)	0.0124(16)	0.0135(16)	0.0139(17)
C(21)	0.047(3)	0.049(3)	0.195(8)	-0.004(4)	0.020(4)	-0.015(2)
C(22)	0.074(4)	0.179(8)	0.106(5)	0.089(6)	-0.002(4)	-0.015(4)
C(23)	0.046(2)	0.082(4)	0.073(3)	0.007(3)	-0.006(2)	-0.020(2)
C(24)	0.131(6)	0.111(5)	0.086(4)	-0.009(4)	-0.026(4)	-0.036(5)
C(25)	0.045(2)	0.0331(19)	0.0287(18)	0.0022(15)	0.0068(15)	0.0019(15)
C(26)	0.058(2)	0.036(2)	0.0349(19)	0.0068(16)	0.0063(17)	0.0115(18)
C(27)	0.050(2)	0.054(3)	0.050(2)	0.018(2)	0.0103(18)	0.0095(19)
C(28)	0.056(3)	0.062(3)	0.076(3)	0.034(3)	0.022(2)	0.020(2)
C(29)	0.056(2)	0.0186(16)	0.0354(19)	-0.0008(14)	0.0125(16)	-0.0046(15)

TABLE S3 (CONTINUED)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

C(30)	0.056(2)	0.041(2)	0.046(2)	0.0016(18)	0.0050(18)	-0.0183(19)
C(31)	0.078(3)	0.059(3)	0.047(2)	0.000(2)	0.006(2)	-0.033(2)
C(32)	0.110(4)	0.063(3)	0.057(3)	-0.007(2)	0.019(3)	-0.037(3)
C(33)	0.0355(18)	0.0225(17)	0.0387(19)	-0.0005(14)	0.0052(14)	0.0007(14)
C(34)	0.0391(18)	0.0213(17)	0.0304(17)	-0.0031(13)	0.0067(14)	-0.0011(14)
C(35)	0.051(2)	0.0243(18)	0.0374(19)	0.0004(15)	0.0064(16)	0.0016(15)
C(36)	0.075(3)	0.0216(19)	0.050(2)	-0.0034(17)	0.000(2)	-0.0038(18)

TABLE S4
BOND LENGTHS [Å] FOR **3.24A**.

atom-atom	distance	atom-atom	distance	
P(1)-C(25)	1.802(4)	P(1)-C(33)	1.805(3)	P(1)-
C(29)	1.811(3)	P(1)-C(1)	1.846(4)	N(1)-
C(9)	1.381(5)	N(1)-C(13)	1.451(5)	N(1)-
C(11)	1.452(5)	N(2)-C(18)	1.374(5)	N(2)-
C(23)	1.436(5)	N(2)-C(21)	1.491(7)	C(1)-
C(2)	1.456(6)	C(1)-C(15)	1.508(5)	C(1)-
C(2A)	1.524(12)	C(1)-H(1)	1.0000	C(1)-
H(1A)	1.0000	O(1)-C(2)	1.226(6)	O(2)-
C(5)	1.348(4)	O(2)-C(4)	1.435(5)	O(3)-
C(4)	1.211(6)	O(4)-C(16)	1.333(4)	O(4)-
H(4O)	0.8400	C(2)-C(3)	1.379(7)	C(3)-
C(6)	1.458(5)	C(3)-C(4)	1.489(7)	O(1A)-
C(2A)	1.083(13)	O(2A)-C(7)	1.285(9)	O(2A)-
C(4A)	1.498(15)	O(3A)-C(4A)	1.203(15)	O(4A)-
C(20)	1.420(14)	O(4A)-H(4OA)	0.8400	C(2A)-
C(3A)	1.503(14)	C(3A)-C(6)	1.479(14)	C(3A)-
C(4A)	1.585(17)	C(5)-C(10)	1.375(5)	C(5)-
C(6)	1.404(5)	C(5)-H(5A)	0.9500	C(6)-
C(7)	1.387(5)	C(7)-C(8)	1.379(5)	C(7)-
H(7)	0.9500	C(8)-C(9)	1.417(5)	C(8)-
H(8)	0.9500	C(9)-C(10)	1.410(5)	C(10)-
H(10)	0.9500	C(11)-C(12)	1.515(6)	C(11)-
H(11A)	0.9900	C(11)-H(11B)	0.9900	C(12)-
H(12A)	0.9800	C(12)-H(12B)	0.9800	C(12)-
H(12C)	0.9800	C(13)-C(14)	1.517(6)	C(13)-
H(13A)	0.9900	C(13)-H(13B)	0.9900	C(14)-
H(14A)	0.9800	C(14)-H(14B)	0.9800	C(14)-
H(14C)	0.9800	C(15)-C(20)	1.394(5)	C(15)-
C(16)	1.409(5)	C(16)-C(17)	1.381(5)	C(16)-
H(16A)	0.9500	C(17)-C(18)	1.398(5)	C(17)-
H(17)	0.9500	C(18)-C(19)	1.404(5)	C(19)-

C(20)	1.373(6)	C(19)-H(19)	0.9500	C(20)-
H(20)	0.9500	C(21)-C(22)	1.538(10)	C(21)-
H(21A)	0.9900	C(21)-H(21B)	0.9900	C(22)-
H(22A)	0.9800	C(22)-H(22B)	0.9800	C(22)-
H(22C)	0.9800	C(23)-C(24)	1.500(8)	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)	1.532(5)	

TABLE S4 (CONTINUED)

atom-atom	distance	atom-atom	distance	
C(25)-H(25A)	0.9900	C(25)-H(25B)	0.9900	C(26)-
C(27)	1.510(6)	C(26)-H(26A)	0.9900	C(26)-
H(26B)	0.9900	C(27)-C(28)	1.537(6)	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)	1.530(6)	C(29)-
H(29A)	0.9900	C(29)-H(29B)	0.9900	C(30)-
C(31)	1.530(5)	C(30)-H(30A)	0.9900	C(30)-
H(30B)	0.9900	C(31)-C(32)	1.468(7)	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)-C(34)	1.538(4)	C(33)-
H(33A)	0.9900	C(33)-H(33B)	0.9900	C(34)-
C(35)	1.518(5)	C(34)-H(34A)	0.9900	C(34)-
H(34B)	0.9900	C(35)-C(36)	1.517(5)	C(35)-
H(35A)	0.9900	C(35)-H(35B)	0.9900	C(36)-
H(36A)	0.9800	C(36)-H(36B)	0.9800	C(36)-
H(36C)	0.9800			

Symmetry transformations used to generate equivalent atoms:

TABLE S5
BOND ANGLES [°] FOR **3.24A**.

atom-atom-atom	angle	atom-atom-atom	angle	
C(25)-P(1)-C(33)	109.36(16)	C(25)-P(1)-C(29)	106.20(17)	C(33)-
P(1)-C(29)	110.90(16)	C(25)-P(1)-C(1)	107.73(19)	C(33)-
P(1)-C(1)	111.37(17)	C(29)-P(1)-C(1)	111.09(17)	C(9)-
N(1)-C(13)	120.7(3)	C(9)-N(1)-C(11)	120.8(3)	C(13)-
N(1)-C(11)	117.8(3)	C(18)-N(2)-C(23)	122.7(4)	C(18)-
N(2)-C(21)	121.0(3)	C(23)-N(2)-C(21)	115.8(3)	C(2)-
C(1)-C(15)	121.9(3)	C(15)-C(1)-C(2A)	132.7(6)	C(2)-
C(1)-P(1)	111.7(3)	C(15)-C(1)-P(1)	110.8(2)	C(2A)-

C(1)-P(1)	114.5(5)	C(2)-C(1)-H(1)	103.3	C(15)-
C(1)-H(1)	103.3	P(1)-C(1)-H(1)	103.3	C(15)-
C(1)-H(1A)	94.7	C(2A)-C(1)-H(1A)	94.7	P(1)-
C(1)-H(1A)	94.7	C(5)-O(2)-C(4)	106.9(3)	C(16)-
O(4)-H(4O)	109.5	O(1)-C(2)-C(3)	122.9(4)	O(1)-
C(2)-C(1)	117.8(4)	C(3)-C(2)-C(1)	119.1(5)	C(2)-
C(3)-C(6)	127.5(5)	C(2)-C(3)-C(4)	127.6(4)	C(6)-
C(3)-C(4)	104.8(4)	O(3)-C(4)-O(2)	119.9(4)	O(3)-
C(4)-C(3)	132.1(4)	O(2)-C(4)-C(3)	108.0(4)	C(7)-
O(2A)-C(4A)	98.6(9)	C(20)-O(4A)-H(4OA)	109.5	O(1A)-
C(2A)-C(3A)	140.6(13)	O(1A)-C(2A)-C(1)	113.2(11)	C(3A)-
C(2A)-C(1)	105.7(9)	C(6)-C(3A)-C(2A)	122.9(11)	C(6)-
C(3A)-C(4A)	94.3(9)	C(2A)-C(3A)-C(4A)	142.8(12)	O(3A)-
C(4A)-O(2A)	126.9(16)	O(3A)-C(4A)-C(3A)	118.2(14)	O(2A)-
C(4A)-C(3A)	114.7(11)	O(2)-C(5)-C(10)	122.4(3)	O(2)-
C(5)-C(6)	113.8(3)	C(10)-C(5)-C(6)	123.8(3)	C(10)-
C(5)-H(5A)	118.1	C(6)-C(5)-H(5A)	118.1	C(7)-
C(6)-C(5)	116.4(3)	C(7)-C(6)-C(3)	137.0(3)	C(5)-
C(6)-C(3)	106.4(3)	C(7)-C(6)-C(3A)	111.0(6)	C(5)-
C(6)-C(3A)	132.4(6)	O(2A)-C(7)-C(8)	117.2(5)	O(2A)-
C(7)-C(6)	121.0(5)	C(8)-C(7)-C(6)	121.8(3)	C(8)-
C(7)-H(7)	119.1	C(6)-C(7)-H(7)	119.1	C(7)-
C(8)-C(9)	121.2(3)	C(7)-C(8)-H(8)	119.4	C(9)-
C(8)-H(8)	119.4	N(1)-C(9)-C(10)	120.8(3)	N(1)-
C(9)-C(8)	121.5(3)	C(10)-C(9)-C(8)	117.7(3)	C(5)-
C(10)-C(9)	119.1(3)	C(5)-C(10)-H(10)	120.4	C(9)-
C(10)-H(10)	120.4	N(1)-C(11)-C(12)	113.6(4)	N(1)-
C(11)-H(11A)	108.8	C(12)-C(11)-H(11A)	108.8	N(1)-
C(11)-H(11B)	108.8	C(12)-C(11)-H(11B)	108.8	
H(11A)-C(11)-H(11B)	107.7	C(11)-C(12)-H(12A)	109.5	C(11)-
C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5	

TABLE S5 (CONTINUED)

atom-atom-atom	angle	atom-atom-atom	angle	
C(11)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5	
H(12B)-C(12)-H(12C)	109.5	N(1)-C(13)-C(14)	112.7(3)	N(1)-
C(13)-H(13A)	109.0	C(14)-C(13)-H(13A)	109.0	N(1)-
C(13)-H(13B)	109.0	C(14)-C(13)-H(13B)	109.0	
H(13A)-C(13)-H(13B)	107.8	C(13)-C(14)-H(14A)	109.5	C(13)-
C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5	C(13)-
C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5	
H(14B)-C(14)-H(14C)	109.5	C(20)-C(15)-C(16)	115.9(3)	C(20)-
C(15)-C(1)	117.4(3)	C(16)-C(15)-C(1)	126.3(3)	O(4)-
C(16)-C(17)	116.8(3)	O(4)-C(16)-C(15)	122.2(3)	C(17)-
C(16)-C(15)	121.0(3)	C(17)-C(16)-H(16A)	119.5	C(15)-
C(16)-H(16A)	119.5	C(16)-C(17)-C(18)	122.2(3)	C(16)-

C(17)-H(17)	118.9	C(18)-C(17)-H(17)	118.9	N(2)-
C(18)-C(17)	121.4(3)	N(2)-C(18)-C(19)	121.6(3)	C(17)-
C(18)-C(19)	117.0(3)	C(20)-C(19)-C(18)	120.3(3)	C(20)-
C(19)-H(19)	119.8	C(18)-C(19)-H(19)	119.8	C(19)-
C(20)-C(15)	123.5(3)	C(19)-C(20)-O(4A)	129.7(6)	C(15)-
C(20)-O(4A)	106.1(6)	C(19)-C(20)-H(20)	118.2	C(15)-
C(20)-H(20)	118.2	N(2)-C(21)-C(22)	111.8(5)	N(2)-
C(21)-H(21A)	109.3	C(22)-C(21)-H(21A)	109.3	N(2)-
C(21)-H(21B)	109.3	C(22)-C(21)-H(21B)	109.3	
H(21A)-C(21)-H(21B)	107.9	C(21)-C(22)-H(22A)	109.5	C(21)-
C(22)-H(22B)	109.5	H(22A)-C(22)-H(22B)	109.5	C(21)-
C(22)-H(22C)	109.5	H(22A)-C(22)-H(22C)	109.5	
H(22B)-C(22)-H(22C)	109.5	N(2)-C(23)-C(24)	114.3(5)	N(2)-
C(23)-H(23A)	108.7	C(24)-C(23)-H(23A)	108.7	N(2)-
C(23)-H(23B)	108.7	C(24)-C(23)-H(23B)	108.7	
H(23A)-C(23)-H(23B)	107.6	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)	113.9(3)	C(26)-
C(25)-H(25A)	108.8	P(1)-C(25)-H(25A)	108.8	C(26)-
C(25)-H(25B)	108.8	P(1)-C(25)-H(25B)	108.8	
H(25A)-C(25)-H(25B)	107.7	C(27)-C(26)-C(25)	112.6(3)	C(27)-
C(26)-H(26A)	109.1	C(25)-C(26)-H(26A)	109.1	C(27)-
C(26)-H(26B)	109.1	C(25)-C(26)-H(26B)	109.1	
H(26A)-C(26)-H(26B)	107.8	C(26)-C(27)-C(28)	111.1(4)	C(26)-
C(27)-H(27A)	109.4	C(28)-C(27)-H(27A)	109.4	C(26)-
C(27)-H(27B)	109.4	C(28)-C(27)-H(27B)	109.4	
H(27A)-C(27)-H(27B)	108.0	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	

TABLE S5 (CONTINUED)

atom-atom-atom	angle	atom-atom-atom	angle	
H(28B)-C(28)-H(28C)	109.5	C(30)-C(29)-P(1)	117.5(2)	C(30)-
C(29)-H(29A)	107.9	P(1)-C(29)-H(29A)	107.9	C(30)-
C(29)-H(29B)	107.9	P(1)-C(29)-H(29B)	107.9	
H(29A)-C(29)-H(29B)	107.2	C(29)-C(30)-C(31)	113.5(3)	C(29)-
C(30)-H(30A)	108.9	C(31)-C(30)-H(30A)	108.9	C(29)-
C(30)-H(30B)	108.9	C(31)-C(30)-H(30B)	108.9	
H(30A)-C(30)-H(30B)	107.7	C(32)-C(31)-C(30)	114.1(4)	C(32)-
C(31)-H(31A)	108.7	C(30)-C(31)-H(31A)	108.7	C(32)-
C(31)-H(31B)	108.7	C(30)-C(31)-H(31B)	108.7	
H(31A)-C(31)-H(31B)	107.6	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	C(34)-C(33)-P(1)	115.5(2)	C(34)-

C(33)-H(33A)	108.4	P(1)-C(33)-H(33A)	108.4	C(34)-
C(33)-H(33B)	108.4	P(1)-C(33)-H(33B)	108.4	
H(33A)-C(33)-H(33B)	107.5	C(35)-C(34)-C(33)	111.4(3)	C(35)-
C(34)-H(34A)	109.4	C(33)-C(34)-H(34A)	109.4	C(35)-
C(34)-H(34B)	109.4	C(33)-C(34)-H(34B)	109.4	
H(34A)-C(34)-H(34B)	108.0	C(36)-C(35)-C(34)	112.0(3)	C(36)-
C(35)-H(35A)	109.2	C(34)-C(35)-H(35A)	109.2	C(36)-
C(35)-H(35B)	109.2	C(34)-C(35)-H(35B)	109.2	
H(35A)-C(35)-H(35B)	107.9	C(35)-C(36)-H(36A)	109.5	C(35)-
C(36)-H(36B)	109.5	H(36A)-C(36)-H(36B)	109.5	C(35)-
C(36)-H(36C)	109.5	H(36A)-C(36)-H(36C)	109.5	
H(36B)-C(36)-H(36C)	109.5			

Symmetry transformations used to generate equivalent atoms:

TABLE S6
TORSION ANGLES [°] FOR **3.24A**.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle	
C(25)-P(1)-C(1)-C(2)	-149.1(3)	C(33)-P(1)-C(1)-C(2)	90.9(3)	C(29)-P(1)-
C(1)-C(2)	-33.2(4)	C(25)-P(1)-C(1)-C(15)	71.4(3)	C(33)-P(1)-
C(1)-C(15)	-48.5(3)	C(29)-P(1)-C(1)-C(15)	-172.7(3)	C(25)-
P(1)-C(1)-C(2A)	-94.5(6)	C(33)-P(1)-C(1)-C(2A)	145.6(6)	C(29)-
P(1)-C(1)-C(2A)	21.5(6)	C(15)-C(1)-C(2)-O(1)	54.2(6)	P(1)-C(1)-
C(2)-O(1)	-80.2(4)	C(15)-C(1)-C(2)-C(3)	-131.1(4)	P(1)-
C(1)-C(2)-C(3)	94.6(4)	O(1)-C(2)-C(3)-C(6)	8.2(7)	C(1)-C(2)-
C(3)-C(6)	-166.3(4)	O(1)-C(2)-C(3)-C(4)	-174.0(4)	C(1)-
C(2)-C(3)-C(4)	11.5(7)	C(5)-O(2)-C(4)-O(3)	179.3(4)	C(5)-
O(2)-C(4)-C(3)	1.1(4)	C(2)-C(3)-C(4)-O(3)	4.4(8)	C(6)-C(3)-
C(4)-O(3)	-177.3(5)	C(2)-C(3)-C(4)-O(2)	-177.7(4)	C(6)-
C(3)-C(4)-O(2)	0.6(4)	C(15)-C(1)-C(2A)-O(1A)	-65.9(14)	P(1)-
C(1)-C(2A)-O(1A)	96.0(12)	C(15)-C(1)-C(2A)-C(3A)	108.0(10)	P(1)-
C(1)-C(2A)-C(3A)	-90.2(10)	O(1A)-C(2A)-C(3A)-C(6)	-20(3)	C(1)-C(2A)-
C(3A)-C(6)	168.9(11)	O(1A)-C(2A)-C(3A)-C(4A)	163(2)	C(1)-C(2A)-
C(3A)-C(4A)	-8(3)	C(7)-O(2A)-C(4A)-O(3A)	172(2)	C(7)-
O(2A)-C(4A)-C(3A)	-4(2)	C(6)-C(3A)-C(4A)-O(3A)	-175(2)	C(2A)-
C(3A)-C(4A)-O(3A)	3(4)	C(6)-C(3A)-C(4A)-O(2A)	2(2)	C(2A)-C(3A)-
C(4A)-O(2A)	179.5(19)	C(4)-O(2)-C(5)-C(10)	176.0(3)	C(4)-
O(2)-C(5)-C(6)	-2.5(4)	O(2)-C(5)-C(6)-C(7)	179.0(3)	C(10)-
C(5)-C(6)-C(7)	0.6(5)	O(2)-C(5)-C(6)-C(3)	2.8(4)	C(10)-C(5)-
C(6)-C(3)	-175.6(3)	C(10)-C(5)-C(6)-C(3A)	-173.6(9)	C(2)-
C(3)-C(6)-C(7)	1.4(7)	C(4)-C(3)-C(6)-C(7)	-176.9(4)	C(2)-
C(3)-C(6)-C(5)	176.3(4)	C(4)-C(3)-C(6)-C(5)	-1.9(4)	C(2A)-
C(3A)-C(6)-C(7)	-177.0(11)	C(4A)-C(3A)-C(6)-C(7)	1.4(14)	C(2A)-
C(3A)-C(6)-C(5)	-2.5(19)	C(4A)-C(3A)-C(6)-C(5)	175.8(11)	C(4A)-

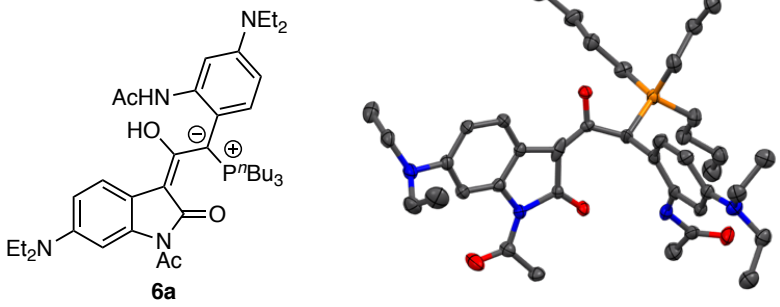
O(2A)-C(7)-C(8)	-175.1(11)	C(4A)-O(2A)-C(7)-C(6)	5.6(13) C(5)-C(6)-
C(7)-O(2A)	179.5(6)	C(3A)-C(6)-C(7)-O(2A)	-5.1(10) C(5)-C(6)-
C(7)-C(8)	0.2(5)	C(3)-C(6)-C(7)-C(8)	174.8(4) C(3A)-
C(6)-C(7)-C(8)	175.6(8)	O(2A)-C(7)-C(8)-C(9)	180.0(6) C(6)-C(7)-
C(8)-C(9)	-0.7(5)	C(13)-N(1)-C(9)-C(10)	178.0(3) C(11)-
N(1)-C(9)-C(10)	-11.3(5)	C(13)-N(1)-C(9)-C(8)	-0.3(5) C(11)-N(1)-
C(9)-C(8)	170.4(3)	C(7)-C(8)-C(9)-N(1)	178.8(3) C(7)-C(8)-
C(9)-C(10)	0.4(5)	O(2)-C(5)-C(10)-C(9)	-179.1(3) C(6)-
C(5)-C(10)-C(9)	-0.8(5)	N(1)-C(9)-C(10)-C(5)	-178.1(3) C(8)-
C(9)-C(10)-C(5)	0.3(5)	C(9)-N(1)-C(11)-C(12)	-75.8(5) C(13)-
N(1)-C(11)-C(12)	95.2(4)	C(9)-N(1)-C(13)-C(14)	-80.7(4) C(11)-
N(1)-C(13)-C(14)	108.3(4)	C(2)-C(1)-C(15)-C(20)	139.0(4) C(2A)-
C(1)-C(15)-C(20)	76.0(8)	P(1)-C(1)-C(15)-C(20)	-86.3(4)

TABLE S6 (CONTINUED)

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(2)-C(1)-C(15)-C(16)	-48.0(6)	C(2A)-C(1)-C(15)-C(16)	-110.9(8) P(1)-
C(1)-C(15)-C(16)	86.7(4)	C(20)-C(15)-C(16)-O(4)	179.3(3) C(1)-
C(15)-C(16)-O(4)	6.2(5)	C(20)-C(15)-C(16)-C(17)	-0.7(5) C(1)-C(15)-
C(16)-C(17)	-173.9(3)	O(4)-C(16)-C(17)-C(18)	-178.5(3) C(15)-
C(16)-C(17)-C(18)	1.6(5)	C(23)-N(2)-C(18)-C(17)	178.6(4) C(21)-
N(2)-C(18)-C(17)	7.2(6)	C(23)-N(2)-C(18)-C(19)	0.2(6) C(21)-N(2)-
C(18)-C(19)	-171.3(5)	C(16)-C(17)-C(18)-N(2)	-179.2(3) C(16)-
C(17)-C(18)-C(19)	-0.7(5)	N(2)-C(18)-C(19)-C(20)	177.7(4) C(17)-
C(18)-C(19)-C(20)	-0.8(5)	C(18)-C(19)-C(20)-C(15)	1.7(6) C(18)-C(19)-
C(20)-O(4A)	-167.0(8)	C(16)-C(15)-C(20)-C(19)	-0.9(5) C(1)-C(15)-
C(20)-C(19)	172.9(3)	C(16)-C(15)-C(20)-O(4A)	170.1(6) C(1)-
C(15)-C(20)-O(4A)	-16.2(7)	C(18)-N(2)-C(21)-C(22)	81.3(5) C(23)-
N(2)-C(21)-C(22)	-90.6(5)	C(18)-N(2)-C(23)-C(24)	85.6(6) C(21)-
N(2)-C(23)-C(24)	-102.6(6)	C(33)-P(1)-C(25)-C(26)	-169.3(3) C(29)-
P(1)-C(25)-C(26)	-49.5(3)	C(1)-P(1)-C(25)-C(26)	69.6(3) P(1)-C(25)-
C(26)-C(27)	-168.9(3)	C(25)-C(26)-C(27)-C(28)	175.6(3) C(25)-
P(1)-C(29)-C(30)	-160.3(3)	C(33)-P(1)-C(29)-C(30)	-41.5(3) C(1)-P(1)-
C(29)-C(30)	82.9(3)	P(1)-C(29)-C(30)-C(31)	178.7(3) C(29)-
C(30)-C(31)-C(32)	73.3(5)	C(25)-P(1)-C(33)-C(34)	-37.1(3) C(29)-
P(1)-C(33)-C(34)	-153.9(2)	C(1)-P(1)-C(33)-C(34)	81.8(3) P(1)-C(33)-
C(34)-C(35)	-163.7(2)	C(33)-C(34)-C(35)-C(36)	-177.0(3)

Symmetry transformations used to generate equivalent atoms:

V. X-RAY CRYSTAL SUMMARY FOR 6A



Atomic displacement ellipsoids are depicted at 50% probability. Crystals were grown through vapor/vapor diffusion with CH_2Cl_2/^{n}pentane.

TABLE S7
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **3.24F**.

Identification code	al5oxindole	
Empirical formula	$C_{41}H_{61.38}Cl_3N_4O_4P$	
Formula weight	811.64	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8123(17) Å	α = 65.269(3)°
	b = 13.5673(19) Å	β = 85.520(3)°
	c = 15.054(2) Å	γ = 79.850(3)°
Volume	2156.9(5) Å^3	
Z	2	
Density (calculated)	1.250 g.cm^{-3}	
Absorption coefficient (μ)	0.293 mm^{-1}	
F(000)	867	
Crystal color, habit	green, prism	
Crystal size	0.310 × 0.142 × 0.117 mm^3	
θ range for data collection	1.489 to 26.345°	
Index ranges	$-14 \le h \le 14$, $-16 \le k \le 16$, $-18 \le l \le 18$	
Reflections collected	52258	
Independent reflections	8772 [R_{int} = 0.0489]	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.7031	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8772 / 57 / 552	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2σ(I)]	R_1 = 0.0676, wR_2 = 0.1686	

R indices (all data)	$R_1 = 0.0922$, $wR_2 = 0.1856$
Extinction coefficient	n/a
Largest diff. peak and hole	0.874 and -0.687 $e^{-}.Å^{-3}$

TABLE S8
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2$) FOR **3.24F**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
P(1)	0.71779(6)	0.77346(6)	0.66216(5)	0.027(1)
O(3)	0.4050(2)	0.26829(18)	1.06433(19)	0.050(1)
O(4)	0.27806(19)	0.88341(17)	0.55625(16)	0.039(1)
N(1)	0.51233(19)	0.38489(18)	0.95015(16)	0.025(1)
N(2)	0.3962(2)	0.73534(18)	0.66055(17)	0.029(1)
N(3)	0.7505(2)	0.01936(19)	1.06737(18)	0.034(1)
N(4)	0.4309(2)	0.6746(2)	0.36345(18)	0.033(1)
O(1)	0.8102(5)	0.5351(3)	0.7396(3)	0.024(1)
O(2)	0.4607(4)	0.5706(3)	0.8474(3)	0.025(1)
C(2)	0.7067(5)	0.5512(4)	0.7651(4)	0.020(1)
C(4)	0.5359(4)	0.4887(3)	0.8722(3)	0.020(1)
O(1A)	0.8413(6)	0.5177(5)	0.7000(6)	0.029(2)
O(2A)	0.5076(6)	0.6091(5)	0.8331(4)	0.027(2)
C(2A)	0.7486(12)	0.5390(7)	0.7355(8)	0.021(2)
C(4A)	0.5983(6)	0.5817(5)	0.7954(5)	0.024(2)
C(1)	0.6419(3)	0.6567(2)	0.7020(2)	0.034(1)
C(3)	0.6626(3)	0.4769(2)	0.8332(2)	0.040(1)
C(5)	0.6148(2)	0.3105(2)	0.95725(19)	0.025(1)
C(6)	0.7002(2)	0.3626(2)	0.89352(19)	0.023(1)
C(7)	0.8054(2)	0.2994(2)	0.8916(2)	0.026(1)
C(8)	0.8243(2)	0.1865(2)	0.9491(2)	0.027(1)
C(9)	0.7383(2)	0.1350(2)	1.0098(2)	0.027(1)
C(10)	0.6328(2)	0.1979(2)	1.0155(2)	0.029(1)
C(11)	0.4117(2)	0.3597(2)	1.0015(2)	0.030(1)
C(12)	0.3097(2)	0.4496(2)	0.9741(2)	0.032(1)
C(13)	0.8668(3)	-0.0419(2)	1.0859(2)	0.035(1)
C(14)	0.9330(3)	-0.0129(3)	1.1515(2)	0.045(1)
C(15)	0.6710(3)	-0.0361(3)	1.0409(3)	0.046(1)
C(16)	0.6952(4)	-0.0415(3)	0.9423(3)	0.060(1)
C(17)	0.5815(2)	0.6587(2)	0.6151(2)	0.027(1)
C(18)	0.4651(2)	0.7015(2)	0.5936(2)	0.026(1)
C(19)	0.4150(2)	0.7055(2)	0.5111(2)	0.026(1)

C(20)	0.4787(2)	0.6667(2)	0.4466(2)	0.029(1)
C(21)	0.5941(3)	0.6185(2)	0.4713(2)	0.032(1)
C(22)	0.6422(3)	0.6159(2)	0.5528(2)	0.033(1)

TABLE S8 (CONTINUED)

	x	y	z	U(eq)
C(23)	0.3082(2)	0.8202(2)	0.6394(2)	0.030(1)
C(24)	0.2491(3)	0.8322(3)	0.7274(2)	0.042(1)
C(25)	0.3200(3)	0.7436(3)	0.3261(2)	0.038(1)
C(26)	0.2195(3)	0.6822(3)	0.3612(3)	0.046(1)
C(27)	0.4906(3)	0.6186(3)	0.3051(2)	0.037(1)
C(28)	0.5698(3)	0.6860(3)	0.2276(2)	0.042(1)
C(29)	0.8161(3)	0.7707(3)	0.5621(2)	0.037(1)
C(30)	0.8951(3)	0.8556(3)	0.5255(2)	0.035(1)
C(31)	0.9637(3)	0.8488(3)	0.4384(2)	0.044(1)
C(32)	1.0456(3)	0.9330(3)	0.3967(3)	0.048(1)
C(33)	0.7943(3)	0.7779(3)	0.7583(2)	0.032(1)
C(34)	0.9020(3)	0.6954(3)	0.7990(2)	0.035(1)
C(35)	0.9624(3)	0.7244(3)	0.8695(3)	0.043(1)
C(36)	1.0683(3)	0.6415(3)	0.9128(3)	0.056(1)
C(37)	0.6160(3)	0.8985(2)	0.6129(2)	0.035(1)
C(38)	0.5522(3)	0.9345(3)	0.6889(2)	0.039(1)
C(39)	0.4601(3)	1.0355(3)	0.6409(2)	0.040(1)
C(40)	0.4019(3)	1.0794(3)	0.7109(3)	0.052(1)
Cl(1)	1.16579(13)	0.54920(11)	0.67104(10)	0.088(1)
C(41)	1.0808(6)	0.4468(6)	0.7203(5)	0.066(2)
Cl(2)	1.1075(3)	0.3533(3)	0.6644(2)	0.124(1)
Cl(3)	1.11212(12)	0.36995(12)	0.84540(11)	0.059(1)
C(41A)	1.0563(15)	0.4633(13)	0.6569(16)	0.081(4)
Cl(2A)	1.1040(5)	0.3307(4)	0.7272(8)	0.160(4)
Cl(3A)	1.0241(5)	0.4981(4)	0.5502(4)	0.089(2)
H(1N)	0.5127	0.4539	0.9091	0.038
H(2)	0.4127	0.6967	0.7229	0.034
H(7)	0.8653	0.3333	0.8507	0.031
H(8)	0.8968	0.1444	0.9467	0.033
H(10)	0.5742	0.1643	1.0586	0.034
H(12A)	0.3301	0.5146	0.9781	0.047
H(12B)	0.2459	0.4247	1.0192	0.047
H(12C)	0.2863	0.4684	0.9072	0.047
H(13A)	0.9083	-0.0261	1.0229	0.042
H(13B)	0.8631	-0.1216	1.1171	0.042
H(14A)	0.9397	0.0654	1.1196	0.067
H(14B)	1.0099	-0.0570	1.1634	0.067
H(14C)	0.8920	-0.0281	1.2139	0.067
H(15A)	0.5917	0.0028	1.0406	0.055
H(15B)	0.6745	-0.1119	1.0920	0.055

H(16A)	0.6881	0.0331	0.8906	0.091
H(16B)	0.6397	-0.0809	0.9310	0.091

TABLE S8 (CONTINUED)

	x	y	z	U(eq)
H(16C)	0.7733	-0.0804	0.9418	0.091
H(19)	0.3360	0.7353	0.4984	0.032
H(21)	0.6390	0.5875	0.4314	0.038
H(22)	0.7204	0.5834	0.5671	0.040
H(24A)	0.2458	0.9077	0.7205	0.063
H(24B)	0.2922	0.7812	0.7865	0.063
H(24C)	0.1709	0.8154	0.7325	0.063
H(25A)	0.3222	0.7755	0.2538	0.045
H(25B)	0.3085	0.8051	0.3467	0.045
H(26A)	0.1484	0.7324	0.3333	0.069
H(26B)	0.2151	0.6526	0.4327	0.069
H(26C)	0.2297	0.6218	0.3404	0.069
H(27A)	0.4329	0.6001	0.2727	0.044
H(27B)	0.5365	0.5488	0.3491	0.044
H(28A)	0.5245	0.7536	0.1816	0.063
H(28B)	0.6087	0.6431	0.1922	0.063
H(28C)	0.6272	0.7048	0.2590	0.063
H(29A)	0.8638	0.6970	0.5843	0.044
H(29B)	0.7694	0.7801	0.5064	0.044
H(30A)	0.9481	0.8429	0.5783	0.042
H(30B)	0.8493	0.9299	0.5063	0.042
H(31A)	0.9099	0.8603	0.3865	0.052
H(31B)	1.0087	0.7742	0.4583	0.052
H(32A)	1.0870	0.9251	0.3405	0.072
H(32B)	1.1008	0.9206	0.4470	0.072
H(32C)	1.0015	1.0072	0.3758	0.072
H(33A)	0.8156	0.8522	0.7344	0.039
H(33B)	0.7400	0.7700	0.8135	0.039
H(34A)	0.9548	0.6953	0.7446	0.042
H(34B)	0.8814	0.6209	0.8339	0.042
H(35A)	0.9844	0.7983	0.8339	0.052
H(35B)	0.9086	0.7266	0.9227	0.052
H(36A)	1.1193	0.6358	0.8600	0.084
H(36B)	1.0458	0.5698	0.9534	0.084
H(36C)	1.1086	0.6652	0.9531	0.084
H(37A)	0.6573	0.9582	0.5680	0.042
H(37B)	0.5588	0.8887	0.5739	0.042
H(38A)	0.6077	0.9523	0.7239	0.046
H(38B)	0.5154	0.8734	0.7375	0.046
H(39A)	0.4964	1.0939	0.5884	0.047
H(39B)	0.4018	1.0154	0.6104	0.047

H(40A)	0.3447	1.1439	0.6761	0.078

TABLE S8 (CONTINUED)

	x	y	z	U(eq)
H(40B)	0.4590	1.1004	0.7407	0.078
H(40C)	0.3636	1.0228	0.7620	0.078
H(41)	0.9978	0.4808	0.7125	0.079
H(41A)	0.9838	0.4828	0.6891	0.097

TABLE S9
ANISOTROPIC DISPLACEMENT PARAMETERS ($Å^2$) FOR **3.24F**.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	0.0301(4)	0.0185(3)	0.0304(4)	-0.0059(3)	-0.0070(3)	-0.0036(3)
O(3)	0.0395(13)	0.0320(12)	0.0614(16)	-0.0055(11)	0.0198(11)	-0.0049(10)
O(4)	0.0382(12)	0.0315(11)	0.0355(12)	-0.0044(9)	-0.0081(9)	0.0061(9)
N(1)	0.0246(12)	0.0202(11)	0.0274(12)	-0.0056(9)	-0.0013(9)	-0.0035(9)
N(2)	0.0323(13)	0.0237(11)	0.0266(12)	-0.0072(10)	-0.0099(10)	-0.0015(10)
N(3)	0.0325(13)	0.0238(12)	0.0355(14)	-0.0041(10)	0.0023(11)	-0.0024(10)
N(4)	0.0331(13)	0.0358(14)	0.0336(13)	-0.0168(11)	-0.0037(11)	-0.0058(11)
O(1)	0.021(2)	0.0224(18)	0.026(2)	-0.0083(15)	0.003(2)	-0.0027(17)
O(2)	0.026(2)	0.0190(18)	0.0250(18)	-0.0053(14)	0.0026(14)	0.0003(15)
C(2)	0.019(3)	0.023(2)	0.023(3)	-0.014(2)	-0.003(2)	-0.0024(19)
C(4)	0.023(2)	0.018(2)	0.017(2)	-0.0067(16)	-0.0019(16)	-0.0029(15)
O(1A)	0.024(3)	0.027(3)	0.030(3)	-0.008(3)	-0.003(2)	0.000(2)
O(2A)	0.027(3)	0.022(3)	0.026(3)	-0.008(2)	-0.002(2)	0.003(2)
C(2A)	0.023(5)	0.014(4)	0.020(4)	-0.002(3)	-0.002(4)	-0.002(3)
C(4A)	0.029(3)	0.021(3)	0.021(3)	-0.008(3)	-0.006(2)	-0.003(2)
C(1)	0.0326(16)	0.0327(15)	0.0278(15)	0.0035(12)	-0.0114(12)	-0.0166(13)
C(3)	0.058(2)	0.0261(15)	0.0392(18)	-0.0199(14)	-0.0294(16)	0.0136(14)
C(5)	0.0226(13)	0.0304(14)	0.0224(13)	-0.0109(11)	-0.0018(10)	-0.0035(11)
C(6)	0.0239(13)	0.0256(13)	0.0200(13)	-0.0082(11)	-0.0039(10)	-0.0026(10)
C(7)	0.0231(13)	0.0251(14)	0.0263(14)	-0.0062(11)	-0.0003(11)	-0.0047(11)
C(8)	0.0222(13)	0.0244(13)	0.0284(14)	-0.0060(11)	-0.0016(11)	0.0015(11)
C(9)	0.0298(14)	0.0239(13)	0.0246(14)	-0.0065(11)	-0.0022(11)	-0.0040(11)
C(10)	0.0266(14)	0.0313(15)	0.0237(14)	-0.0067(12)	0.0015(11)	-0.0062(11)
C(11)	0.0296(15)	0.0284(15)	0.0325(15)	-0.0130(13)	0.0039(12)	-0.0061(12)
C(12)	0.0228(14)	0.0380(16)	0.0325(16)	-0.0144(13)	0.0027(12)	-0.0026(12)
C(13)	0.0377(17)	0.0233(14)	0.0337(16)	-0.0053(12)	0.0000(13)	0.0018(12)
C(14)	0.048(2)	0.0435(19)	0.0341(17)	-0.0122(15)	-0.0060(15)	0.0084(15)

C(15)	0.0444(19)	0.0314(17)	0.057(2)	-0.0091(15)	0.0019(16)	-0.0159(14)
C(16)	0.069(3)	0.049(2)	0.074(3)	-0.031(2)	-0.006(2)	-0.021(2)
C(17)	0.0302(14)	0.0169(12)	0.0287(14)	-0.0020(11)	-0.0082(11)	-0.0057(11)
C(18)	0.0302(14)	0.0149(12)	0.0289(14)	-0.0037(11)	-0.0066(11)	-0.0055(10)
C(19)	0.0256(14)	0.0209(13)	0.0304(15)	-0.0070(11)	-0.0081(11)	-0.0032(11)
C(20)	0.0318(15)	0.0212(13)	0.0325(15)	-0.0083(12)	-0.0063(12)	-0.0072(11)
C(21)	0.0317(15)	0.0260(14)	0.0393(17)	-0.0148(13)	-0.0023(13)	-0.0054(12)
C(22)	0.0265(15)	0.0221(14)	0.0458(18)	-0.0073(13)	-0.0113(13)	-0.0023(11)
C(23)	0.0245(14)	0.0258(14)	0.0360(16)	-0.0086(12)	-0.0058(12)	-0.0049(11)

TABLE S9 (CONTINUED)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(24)	0.0380(18)	0.0407(18)	0.0406(18)	-0.0133(15)	0.0014(14)	-0.0012(14)
C(25)	0.0398(17)	0.0401(17)	0.0345(17)	-0.0168(14)	-0.0094(14)	-0.0038(14)
C(26)	0.0428(19)	0.051(2)	0.048(2)	-0.0229(17)	-0.0069(16)	-0.0063(16)
C(27)	0.0427(18)	0.0350(16)	0.0411(18)	-0.0223(14)	-0.0022(14)	-0.0110(14)
C(28)	0.0464(19)	0.050(2)	0.0394(18)	-0.0262(16)	0.0032(15)	-0.0131(15)
C(29)	0.0482(19)	0.0318(16)	0.0284(15)	-0.0085(13)	-0.0023(13)	-0.0096(14)
C(30)	0.0345(16)	0.0338(16)	0.0372(17)	-0.0150(13)	-0.0008(13)	-0.0056(13)
C(31)	0.054(2)	0.0445(19)	0.0310(17)	-0.0133(15)	0.0036(15)	-0.0116(16)
C(32)	0.046(2)	0.048(2)	0.048(2)	-0.0167(17)	0.0008(16)	-0.0138(16)
C(33)	0.0306(15)	0.0376(16)	0.0345(16)	-0.0205(13)	-0.0001(12)	-0.0042(12)
C(34)	0.0353(16)	0.0357(16)	0.0312(16)	-0.0133(13)	-0.0025(13)	-0.0019(13)
C(35)	0.0348(17)	0.053(2)	0.0441(19)	-0.0204(16)	-0.0078(14)	-0.0069(15)
C(36)	0.050(2)	0.059(2)	0.055(2)	-0.0185(19)	-0.0172(18)	-0.0048(18)
C(37)	0.0422(17)	0.0258(14)	0.0310(16)	-0.0076(12)	-0.0058(13)	-0.0015(13)
C(38)	0.0410(18)	0.0373(17)	0.0317(16)	-0.0106(14)	-0.0036(14)	0.0013(14)
C(39)	0.0459(19)	0.0290(15)	0.0389(18)	-0.0088(13)	-0.0022(14)	-0.0067(14)
C(40)	0.058(2)	0.0377(19)	0.057(2)	-0.0187(17)	0.0030(18)	-0.0011(17)
Cl(1)	0.1060(10)	0.0784(8)	0.0699(8)	-0.0210(6)	0.0186(7)	-0.0254(7)
C(41)	0.060(4)	0.092(4)	0.067(4)	-0.050(3)	0.009(3)	-0.027(3)
Cl(2)	0.118(2)	0.187(3)	0.147(2)	-0.136(3)	0.0216(18)	-0.066(2)
Cl(3)	0.0481(8)	0.0631(9)	0.0673(9)	-0.0237(7)	0.0011(6)	-0.0232(6)
C(41A)	0.055(8)	0.048(7)	0.099(8)	0.004(6)	-0.005(7)	0.005(6)
Cl(2A)	0.054(3)	0.041(2)	0.270(10)	0.040(4)	0.001(5)	0.014(2)
Cl(3A)	0.100(4)	0.074(3)	0.089(3)	-0.026(2)	0.010(3)	-0.032(2)

TABLE S10
BOND LENGTHS [Å] FOR **3.24F**.

atom-atom	distance	atom-atom	distance	
P(1)-C(33)	1.793(3)	P(1)-C(37)	1.800(3)	P(1)-C(1)
1.815(3)	P(1)-C(29)	1.838(3)	O(3)-	

C(11)	1.217(4)	O(4)-C(23)	1.222(3)	N(1)-
C(11)	1.381(4)	N(1)-C(5)	1.413(3)	N(1)-
C(4)	1.464(4)	N(1)-H(1N)	0.8800	N(2)-
C(23)	1.353(4)	N(2)-C(18)	1.420(4)	N(2)-
H(2)	0.8800	N(3)-C(9)	1.427(3)	N(3)-
C(13)	1.456(4)	N(3)-C(15)	1.470(4)	N(4)-
C(20)	1.369(4)	N(4)-C(27)	1.455(4)	N(4)-
C(25)	1.467(4)	O(1)-C(2)	1.261(7)	O(2)-
C(4)	1.233(5)	C(2)-C(3)	1.255(7)	C(2)-
C(1)	1.459(6)	C(4)-C(3)	1.571(6)	O(1A)-
C(2A)	1.222(14)	O(2A)-C(4A)	1.245(9)	C(2A)-
C(3)	1.713(13)	C(2A)-C(1)	1.764(12)	C(2A)-
C(4A)	2.031(16)	C(4A)-C(3)	1.390(7)	C(4A)-
C(1)	1.467(7)	C(1)-C(17)	1.526(4)	C(3)-
C(6)	1.437(4)	C(5)-C(10)	1.393(4)	C(5)-
C(6)	1.403(4)	C(6)-C(7)	1.386(4)	C(7)-
C(8)	1.395(4)	C(7)-H(7)	0.9500	C(8)-
C(9)	1.388(4)	C(8)-H(8)	0.9500	C(9)-
C(10)	1.400(4)	C(10)-H(10)	0.9500	C(11)-
C(12)	1.500(4)	C(12)-H(12A)	0.9800	C(12)-
H(12B)	0.9800	C(12)-H(12C)	0.9800	C(13)-
C(14)	1.515(5)	C(13)-H(13A)	0.9900	C(13)-
H(13B)	0.9900	C(14)-H(14A)	0.9800	C(14)-
H(14B)	0.9800	C(14)-H(14C)	0.9800	C(15)-
C(16)	1.519(6)	C(15)-H(15A)	0.9900	C(15)-
H(15B)	0.9900	C(16)-H(16A)	0.9800	C(16)-
H(16B)	0.9800	C(16)-H(16C)	0.9800	C(17)-
C(22)	1.392(4)	C(17)-C(18)	1.402(4)	C(18)-
C(19)	1.392(4)	C(19)-C(20)	1.400(4)	C(19)-
H(19)	0.9500	C(20)-C(21)	1.409(4)	C(21)-
C(22)	1.376(4)	C(21)-H(21)	0.9500	C(22)-
H(22)	0.9500	C(23)-C(24)	1.504(4)	C(24)-
H(24A)	0.9800	C(24)-H(24B)	0.9800	C(24)-
H(24C)	0.9800	C(25)-C(26)	1.505(5)	C(25)-
H(25A)	0.9900	C(25)-H(25B)	0.9900	C(26)-
H(26A)	0.9800	C(26)-H(26B)	0.9800	C(26)-
H(26C)	0.9800	C(27)-C(28)	1.521(5)	

TABLE S10 (CONTINUED)

atom-atom	distance	atom-atom	distance	
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)	1.507(4)	C(29)-
H(29A)	0.9900	C(29)-H(29B)	0.9900	C(30)-
C(31)	1.514(4)	C(30)-H(30A)	0.9900	C(30)-
H(30B)	0.9900	C(31)-C(32)	1.525(5)	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)-C(34)	1.514(4)	C(33)-
H(33A)	0.9900	C(33)-H(33B)	0.9900	C(34)-
C(35)	1.535(4)	C(34)-H(34A)	0.9900	C(34)-
H(34B)	0.9900	C(35)-C(36)	1.508(5)	C(35)-
H(35A)	0.9900	C(35)-H(35B)	0.9900	C(36)-
H(36A)	0.9800	C(36)-H(36B)	0.9800	C(36)-
H(36C)	0.9800	C(37)-C(38)	1.523(4)	C(37)-
H(37A)	0.9900	C(37)-H(37B)	0.9900	C(38)-
C(39)	1.533(4)	C(38)-H(38A)	0.9900	C(38)-
H(38B)	0.9900	C(39)-C(40)	1.485(5)	C(39)-
H(39A)	0.9900	C(39)-H(39B)	0.9900	C(40)-
H(40A)	0.9800	C(40)-H(40B)	0.9800	C(40)-
H(40C)	0.9800	Cl(1)-C(41)	1.733(7)	Cl(1)-
C(41A)	1.96(2)	C(41)-Cl(3)	1.761(8)	C(41)-
Cl(2)	1.769(7)	C(41)-H(41)	1.0000	
C(41A)-Cl(3A)	1.53(2)	C(41A)-Cl(2A)	1.679(16)	
C(41A)-H(41A)	1.0000	Cl(3A)-Cl(3A)#1	1.632(10)	

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1

TABLE S11
BOND ANGLES [°] FOR **3.24F**.

atom-atom-atom	angle	atom-atom-atom	angle	
C(33)-P(1)-C(37)	107.66(14)	C(33)-P(1)-C(1)	113.61(14)	C(37)-
P(1)-C(1)	109.18(15)	C(33)-P(1)-C(29)	110.69(15)	C(37)-
P(1)-C(29)	107.07(14)	C(1)-P(1)-C(29)	108.43(15)	C(11)-
N(1)-C(5)	126.2(2)	C(11)-N(1)-C(4)	129.4(3)	C(5)-
N(1)-C(4)	104.2(2)	C(11)-N(1)-H(1N)	116.9	C(5)-
N(1)-H(1N)	116.9	C(23)-N(2)-C(18)	127.4(2)	C(23)-
N(2)-H(2)	116.3	C(18)-N(2)-H(2)	116.3	C(9)-
N(3)-C(13)	117.3(2)	C(9)-N(3)-C(15)	114.2(2)	C(13)-
N(3)-C(15)	112.9(2)	C(20)-N(4)-C(27)	121.4(3)	C(20)-
N(4)-C(25)	121.9(2)	C(27)-N(4)-C(25)	116.6(2)	C(3)-
C(2)-O(1)	121.4(5)	C(3)-C(2)-C(1)	123.9(5)	O(1)-
C(2)-C(1)	114.3(5)	O(2)-C(4)-N(1)	119.8(4)	O(2)-
C(4)-C(3)	129.1(4)	N(1)-C(4)-C(3)	111.1(3)	O(1A)-
C(2A)-C(3)	139.3(7)	O(1A)-C(2A)-C(1)	133.6(7)	C(3)-
C(2A)-C(1)	87.2(7)	O(1A)-C(2A)-C(4A)	176.6(8)	C(3)-
C(2A)-C(4A)	42.5(4)	C(1)-C(2A)-C(4A)	44.8(4)	O(2A)-
C(4A)-C(3)	123.9(6)	O(2A)-C(4A)-C(1)	121.9(6)	C(3)-
C(4A)-C(1)	114.1(5)	O(2A)-C(4A)-C(2A)	178.4(7)	C(3)-
C(4A)-C(2A)	56.4(4)	C(1)-C(4A)-C(2A)	57.9(4)	C(2)-

C(1)-C(17)	116.1(3)	C(4A)-C(1)-C(17)	111.6(3)	C(4A)-
C(1)-C(2A)	77.3(5)	C(17)-C(1)-C(2A)	104.5(4)	C(2)-
C(1)-P(1)	115.6(3)	C(4A)-C(1)-P(1)	135.9(3)	C(17)-
C(1)-P(1)	109.80(18)	C(2A)-C(1)-P(1)	106.2(4)	C(2)-
C(3)-C(6)	135.0(4)	C(4A)-C(3)-C(6)	162.3(4)	C(2)-
C(3)-C(4)	125.6(4)	C(6)-C(3)-C(4)	99.3(3)	C(4A)-
C(3)-C(2A)	81.0(5)	C(6)-C(3)-C(2A)	116.7(4)	C(10)-
C(5)-C(6)	121.7(2)	C(10)-C(5)-N(1)	126.7(2)	C(6)-
C(5)-N(1)	111.6(2)	C(7)-C(6)-C(5)	118.1(2)	C(7)-
C(6)-C(3)	128.0(3)	C(5)-C(6)-C(3)	113.7(3)	C(6)-
C(7)-C(8)	120.7(3)	C(6)-C(7)-H(7)	119.6	C(8)-
C(7)-H(7)	119.6	C(9)-C(8)-C(7)	120.8(2)	C(9)-
C(8)-H(8)	119.6	C(7)-C(8)-H(8)	119.6	C(8)-
C(9)-C(10)	119.4(2)	C(8)-C(9)-N(3)	123.5(2)	C(10)-
C(9)-N(3)	117.1(2)	C(5)-C(10)-C(9)	119.2(3)	C(5)-
C(10)-H(10)	120.4	C(9)-C(10)-H(10)	120.4	O(3)-
C(11)-N(1)	121.8(3)	O(3)-C(11)-C(12)	121.4(3)	N(1)-
C(11)-C(12)	116.8(2)	C(11)-C(12)-H(12A)	109.5	C(11)-
C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5	C(11)-
C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5	

TABLE S11 (CONTINUED)

atom-atom-atom	angle	atom-atom-atom	angle	
H(12B)-C(12)-H(12C)	109.5	N(3)-C(13)-C(14)	112.1(3)	N(3)-
C(13)-H(13A)	109.2	C(14)-C(13)-H(13A)	109.2	N(3)-
C(13)-H(13B)	109.2	C(14)-C(13)-H(13B)	109.2	
H(13A)-C(13)-H(13B)	107.9	C(13)-C(14)-H(14A)	109.5	C(13)-
C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5	C(13)-
C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5	
H(14B)-C(14)-H(14C)	109.5	N(3)-C(15)-C(16)	114.7(3)	N(3)-
C(15)-H(15A)	108.6	C(16)-C(15)-H(15A)	108.6	N(3)-
C(15)-H(15B)	108.6	C(16)-C(15)-H(15B)	108.6	
H(15A)-C(15)-H(15B)	107.6	C(15)-C(16)-H(16A)	109.5	C(15)-
C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5	C(15)-
C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5	
H(16B)-C(16)-H(16C)	109.5	C(22)-C(17)-C(18)	116.5(3)	C(22)-
C(17)-C(1)	120.0(3)	C(18)-C(17)-C(1)	123.4(3)	C(19)-
C(18)-C(17)	121.3(3)	C(19)-C(18)-N(2)	119.8(2)	C(17)-
C(18)-N(2)	118.8(2)	C(18)-C(19)-C(20)	121.4(3)	C(18)-
C(19)-H(19)	119.3	C(20)-C(19)-H(19)	119.3	N(4)-
C(20)-C(19)	121.6(3)	N(4)-C(20)-C(21)	121.4(3)	C(19)-
C(20)-C(21)	117.1(3)	C(22)-C(21)-C(20)	120.6(3)	C(22)-
C(21)-H(21)	119.7	C(20)-C(21)-H(21)	119.7	C(21)-
C(22)-C(17)	123.0(3)	C(21)-C(22)-H(22)	118.5	C(17)-
C(22)-H(22)	118.5	O(4)-C(23)-N(2)	123.8(3)	O(4)-
C(23)-C(24)	121.6(3)	N(2)-C(23)-C(24)	114.5(3)	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	N(4)-
C(25)-C(26)	113.4(3)	N(4)-C(25)-H(25A)	108.9	C(26)-
C(25)-H(25A)	108.9	N(4)-C(25)-H(25B)	108.9	C(26)-
C(25)-H(25B)	108.9	H(25A)-C(25)-H(25B)	107.7	C(25)-
C(26)-H(26A)	109.5	C(25)-C(26)-H(26B)	109.5	
H(26A)-C(26)-H(26B)	109.5	C(25)-C(26)-H(26C)	109.5	
H(26A)-C(26)-H(26C)	109.5	H(26B)-C(26)-H(26C)	109.5	N(4)-
C(27)-C(28)	113.5(3)	N(4)-C(27)-H(27A)	108.9	C(28)-
C(27)-H(27A)	108.9	N(4)-C(27)-H(27B)	108.9	C(28)-
C(27)-H(27B)	108.9	H(27A)-C(27)-H(27B)	107.7	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)	116.2(2)	C(30)-C(29)-H(29A)	108.2	P(1)-
C(29)-H(29A)	108.2	C(30)-C(29)-H(29B)	108.2	P(1)-
C(29)-H(29B)	108.2	H(29A)-C(29)-H(29B)	107.4	C(29)-
C(30)-C(31)	110.0(3)	C(29)-C(30)-H(30A)	109.7	

TABLE S11 (CONTINUED)

atom-atom-atom	angle	atom-atom-atom	angle	
C(31)-C(30)-H(30A)	109.7	C(29)-C(30)-H(30B)	109.7	C(31)-
C(30)-H(30B)	109.7	H(30A)-C(30)-H(30B)	108.2	C(30)-
C(31)-C(32)	113.2(3)	C(30)-C(31)-H(31A)	108.9	C(32)-
C(31)-H(31A)	108.9	C(30)-C(31)-H(31B)	108.9	C(32)-
C(31)-H(31B)	108.9	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	C(34)-
C(33)-P(1)	119.3(2)	C(34)-C(33)-H(33A)	107.5	P(1)-
C(33)-H(33A)	107.5	C(34)-C(33)-H(33B)	107.5	P(1)-
C(33)-H(33B)	107.5	H(33A)-C(33)-H(33B)	107.0	C(33)-
C(34)-C(35)	110.3(3)	C(33)-C(34)-H(34A)	109.6	C(35)-
C(34)-H(34A)	109.6	C(33)-C(34)-H(34B)	109.6	C(35)-
C(34)-H(34B)	109.6	H(34A)-C(34)-H(34B)	108.1	C(36)-
C(35)-C(34)	111.2(3)	C(36)-C(35)-H(35A)	109.4	C(34)-
C(35)-H(35A)	109.4	C(36)-C(35)-H(35B)	109.4	C(34)-
C(35)-H(35B)	109.4	H(35A)-C(35)-H(35B)	108.0	C(35)-
C(36)-H(36A)	109.5	C(35)-C(36)-H(36B)	109.5	
H(36A)-C(36)-H(36B)	109.5	C(35)-C(36)-H(36C)	109.5	
H(36A)-C(36)-H(36C)	109.5	H(36B)-C(36)-H(36C)	109.5	C(38)-
C(37)-P(1)	114.9(2)	C(38)-C(37)-H(37A)	108.5	P(1)-
C(37)-H(37A)	108.5	C(38)-C(37)-H(37B)	108.5	P(1)-
C(37)-H(37B)	108.5	H(37A)-C(37)-H(37B)	107.5	C(37)-
C(38)-C(39)	111.1(3)	C(37)-C(38)-H(38A)	109.4	C(39)-

C(38)-H(38A)	109.4	C(37)-C(38)-H(38B)	109.4	C(39)-
C(38)-H(38B)	109.4	H(38A)-C(38)-H(38B)	108.0	C(40)-
C(39)-C(38)	113.2(3)	C(40)-C(39)-H(39A)	108.9	C(38)-
C(39)-H(39A)	108.9	C(40)-C(39)-H(39B)	108.9	C(38)-
C(39)-H(39B)	108.9	H(39A)-C(39)-H(39B)	107.8	C(39)-
C(40)-H(40A)	109.5	C(39)-C(40)-H(40B)	109.5	
H(40A)-C(40)-H(40B)	109.5	C(39)-C(40)-H(40C)	109.5	
H(40A)-C(40)-H(40C)	109.5	H(40B)-C(40)-H(40C)	109.5	Cl(1)-
C(41)-Cl(3)	109.6(4)	Cl(1)-C(41)-Cl(2)	112.0(4)	Cl(3)-
C(41)-Cl(2)	106.7(4)	Cl(1)-C(41)-H(41)	109.5	Cl(3)-
C(41)-H(41)	109.5	Cl(2)-C(41)-H(41)	109.5	
Cl(3A)-C(41A)-Cl(2A)	119.8(16)	Cl(3A)-C(41A)-Cl(1)	112.8(10)	
Cl(2A)-C(41A)-Cl(1)	107.0(10)	Cl(3A)-C(41A)-H(41A)	105.4	
Cl(2A)-C(41A)-H(41A)	105.3	Cl(1)-C(41A)-H(41A)	105.3	
C(41A)-Cl(3A)-Cl(3A)#1	163.7(8)			

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1

TABLE S12
TORSION ANGLES [°] FOR **3.24F**.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle	
C(11)-N(1)-C(4)-O(2)	3.4(6)	C(5)-N(1)-C(4)-O(2)	178.9(4)	C(11)-
N(1)-C(4)-C(3)	-178.0(3)	C(5)-N(1)-C(4)-C(3)	-2.6(3)	C(3)-
C(2)-C(1)-C(17)	-83.7(6)	O(1)-C(2)-C(1)-C(17)	89.4(4)	C(3)-
C(2)-C(1)-P(1)	145.5(4)	O(1)-C(2)-C(1)-P(1)	-41.4(5)	O(2A)-
C(4A)-C(1)-C(17)	-81.2(7)	C(3)-C(4A)-C(1)-C(17)	94.7(5)	C(2A)-
C(4A)-C(1)-C(17)	100.7(5)	O(2A)-C(4A)-C(1)-C(2A)	178.1(8)	C(3)-
C(4A)-C(1)-C(2A)	-6.0(5)	O(2A)-C(4A)-C(1)-P(1)	77.9(8)	C(3)-
C(4A)-C(1)-P(1)	-106.2(5)	C(2A)-C(4A)-C(1)-P(1)	-100.2(5)	O(1A)-
C(2A)-C(1)-C(4A)	-175.8(12)	C(3)-C(2A)-C(1)-C(4A)	4.4(4)	O(1A)-
C(2A)-C(1)-C(17)	74.8(11)	C(3)-C(2A)-C(1)-C(17)	-105.0(4)	C(4A)-
C(2A)-C(1)-C(17)	-109.4(4)	O(1A)-C(2A)-C(1)-P(1)	-41.3(12)	C(3)-
C(2A)-C(1)-P(1)	139.0(3)	C(4A)-C(2A)-C(1)-P(1)	134.6(3)	C(33)-
P(1)-C(1)-C(2)	-45.2(4)	C(37)-P(1)-C(1)-C(2)	-165.4(3)	C(29)-
P(1)-C(1)-C(2)	78.3(4)	C(33)-P(1)-C(1)-C(4A)	21.7(5)	C(37)-
P(1)-C(1)-C(4A)	-98.4(5)	C(29)-P(1)-C(1)-C(4A)	145.3(5)	C(33)-
P(1)-C(1)-C(17)	-178.9(2)	C(37)-P(1)-C(1)-C(17)	60.9(3)	C(29)-
P(1)-C(1)-C(17)	-55.4(3)	C(33)-P(1)-C(1)-C(2A)	-66.5(4)	C(37)-
P(1)-C(1)-C(2A)	173.3(4)	C(29)-P(1)-C(1)-C(2A)	57.0(4)	O(1)-
C(2)-C(3)-C(6)	-5.2(8)	C(1)-C(2)-C(3)-C(6)	167.4(3)	O(1)-
C(2)-C(3)-C(4)	178.6(4)	C(1)-C(2)-C(3)-C(4)	-8.8(7)	O(2A)-
C(4A)-C(3)-C(6)	2.9(17)	C(1)-C(4A)-C(3)-C(6)	-173.0(9)	C(2A)-
C(4A)-C(3)-C(6)	-179.1(13)	O(2A)-C(4A)-C(3)-C(2A)	-178.1(8)	C(1)-

C(4A)-C(3)-C(2A)	6.1(6)	O(2)-C(4)-C(3)-C(2)	-3.3(7)	N(1)-
C(4)-C(3)-C(2)	178.3(4)	O(2)-C(4)-C(3)-C(6)	179.4(4)	N(1)-
C(4)-C(3)-C(6)	1.1(3)	O(1A)-C(2A)-C(3)-C(4A)	175.7(13)	C(1)-
C(2A)-C(3)-C(4A)	-4.6(4)	O(1A)-C(2A)-C(3)-C(6)	-4.7(14)	C(1)-
C(2A)-C(3)-C(6)	175.1(3)	C(4A)-C(2A)-C(3)-C(6)	179.7(4)	C(11)-
N(1)-C(5)-C(10)	1.4(4)	C(4)-N(1)-C(5)-C(10)	-174.2(3)	C(11)-
N(1)-C(5)-C(6)	178.8(3)	C(4)-N(1)-C(5)-C(6)	3.2(3)	C(10)-
C(5)-C(6)-C(7)	-1.7(4)	N(1)-C(5)-C(6)-C(7)	-179.3(2)	C(10)-
C(5)-C(6)-C(3)	174.8(3)	N(1)-C(5)-C(6)-C(3)	-2.8(3)	C(2)-
C(3)-C(6)-C(7)	0.2(6)	C(4A)-C(3)-C(6)-C(7)	-170.9(11)	C(4)-
C(3)-C(6)-C(7)	177.0(3)	C(2A)-C(3)-C(6)-C(7)	10.2(6)	C(2)-
C(3)-C(6)-C(5)	-175.9(4)	C(4A)-C(3)-C(6)-C(5)	13.1(13)	C(4)-
C(3)-C(6)-C(5)	1.0(3)	C(2A)-C(3)-C(6)-C(5)	-165.9(5)	C(5)-
C(6)-C(7)-C(8)	2.1(4)	C(3)-C(6)-C(7)-C(8)	-173.8(3)	C(6)-
C(7)-C(8)-C(9)	-0.3(4)	C(7)-C(8)-C(9)-C(10)	-2.1(4)	C(7)-
C(8)-C(9)-N(3)	177.4(3)	C(13)-N(3)-C(9)-C(8)	18.8(4)	C(15)-
N(3)-C(9)-C(8)	-116.7(3)	C(13)-N(3)-C(9)-C(10)	-161.7(3)	

TABLE S12 (CONTINUED)

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle	
C(15)-N(3)-C(9)-C(10)	62.8(4)	C(6)-C(5)-C(10)-C(9)	-0.6(4)	N(1)-
C(5)-C(10)-C(9)	176.6(3)	C(8)-C(9)-C(10)-C(5)	2.5(4)	N(3)-
C(9)-C(10)-C(5)	-177.0(3)	C(5)-N(1)-C(11)-O(3)	4.8(5)	C(4)-
N(1)-C(11)-O(3)	179.3(3)	C(5)-N(1)-C(11)-C(12)	-173.6(2)	C(4)-
N(1)-C(11)-C(12)	0.9(4)	C(9)-N(3)-C(13)-C(14)	67.9(3)	C(15)-
N(3)-C(13)-C(14)	-156.1(3)	C(9)-N(3)-C(15)-C(16)	69.4(4)	C(13)-
N(3)-C(15)-C(16)	-68.0(4)	C(2)-C(1)-C(17)-C(22)	-50.4(4)	C(4A)-
C(1)-C(17)-C(22)	-112.2(4)	C(2A)-C(1)-C(17)-C(22)	-30.4(5)	P(1)-
C(1)-C(17)-C(22)	83.1(3)	C(2)-C(1)-C(17)-C(18)	129.1(4)	C(4A)-
C(1)-C(17)-C(18)	67.3(4)	C(2A)-C(1)-C(17)-C(18)	149.1(5)	P(1)-
C(1)-C(17)-C(18)	-97.4(3)	C(22)-C(17)-C(18)-C(19)	-3.2(4)	C(1)-
C(17)-C(18)-C(19)	177.3(2)	C(22)-C(17)-C(18)-N(2)	173.3(2)	C(1)-
C(17)-C(18)-N(2)	-6.2(4)	C(23)-N(2)-C(18)-C(19)	-38.0(4)	C(23)-
N(2)-C(18)-C(17)	145.5(3)	C(17)-C(18)-C(19)-C(20)	0.3(4)	N(2)-
C(18)-C(19)-C(20)	-176.1(2)	C(27)-N(4)-C(20)-C(19)	-169.8(3)	C(25)-
N(4)-C(20)-C(19)	13.1(4)	C(27)-N(4)-C(20)-C(21)	9.9(4)	C(25)-
N(4)-C(20)-C(21)	-167.2(3)	C(18)-C(19)-C(20)-N(4)	-177.4(3)	C(18)-
C(19)-C(20)-C(21)	3.0(4)	N(4)-C(20)-C(21)-C(22)	176.9(3)	C(19)-
C(20)-C(21)-C(22)	-3.4(4)	C(20)-C(21)-C(22)-C(17)	0.5(4)	C(18)-
C(17)-C(22)-C(21)	2.8(4)	C(1)-C(17)-C(22)-C(21)	-177.7(3)	C(18)-
N(2)-C(23)-O(4)	-2.7(5)	C(18)-N(2)-C(23)-C(24)	177.7(3)	C(20)-
N(4)-C(25)-C(26)	-93.6(3)	C(27)-N(4)-C(25)-C(26)	89.2(3)	C(20)-
N(4)-C(27)-C(28)	-88.4(4)	C(25)-N(4)-C(27)-C(28)	88.9(3)	C(33)-
P(1)-C(29)-C(30)	-49.2(3)	C(37)-P(1)-C(29)-C(30)	67.9(3)	C(1)-
P(1)-C(29)-C(30)	-174.4(2)	P(1)-C(29)-C(30)-C(31)	-175.6(2)	C(29)-
C(30)-C(31)-C(32)	179.7(3)	C(37)-P(1)-C(33)-C(34)	-167.3(2)	C(1)-

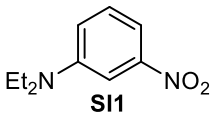
P(1)-C(33)-C(34)	71.7(3)	C(29)-P(1)-C(33)-C(34)	-50.6(3)	P(1)-
C(33)-C(34)-C(35)	171.9(2)	C(33)-C(34)-C(35)-C(36)	178.5(3)	C(33)-
P(1)-C(37)-C(38)	-42.3(3)	C(1)-P(1)-C(37)-C(38)	81.4(3)	C(29)-
P(1)-C(37)-C(38)	-161.4(2)	P(1)-C(37)-C(38)-C(39)	-174.9(2)	C(37)-
C(38)-C(39)-C(40)	-175.3(3)	Cl(2A)-C(41A)-Cl(3A)-Cl(3A)#1	38(4)	Cl(1)-
C(41A)-Cl(3A)-Cl(3A)#1	165(2)			

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1

VI. REFERENCES

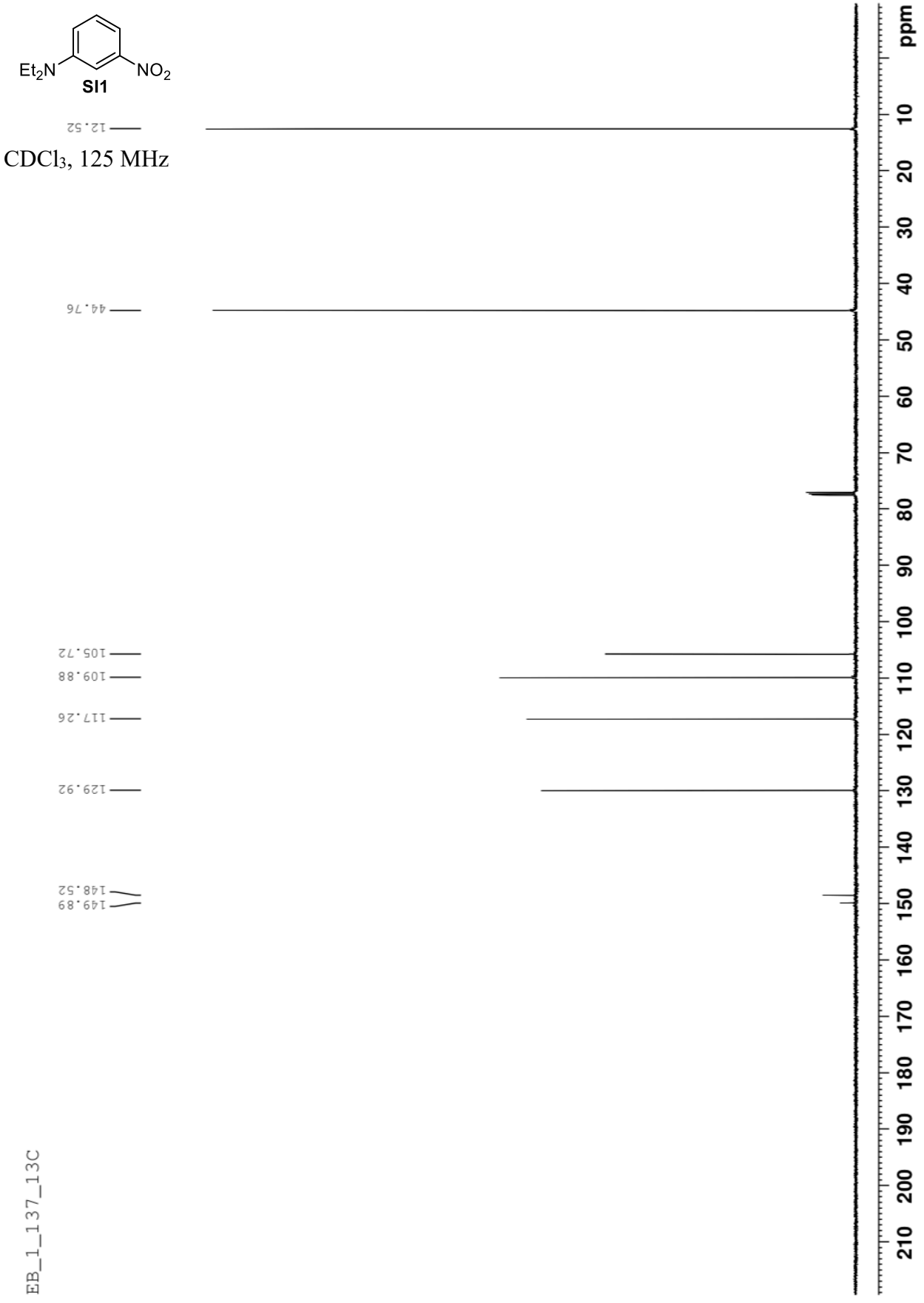
1. Chen, C.-T.; Chiang, C.-L.; Lin, Y.-C.; Chan, L.-H.; Huang; Tsai, Z.-W.; Chen, C.-T. *Org. Lett.* **2003**, *5*, 1261-1264.
2. Buta, A.; Maximyuk, O.; Kovalskyy, D.; Sukach, V.; Vovk, M.; Ievglevskyi, O.; Isaeva, E.; Isaev, D.; Savotchenko, A.; Krishtal, O. *J. Med. Chem.* **2015**, *58*, 4449-4461.
3. Lu, H.-H.; Liu, H.; Wu, W.; Wang, X.-F.; Lu, L.-Q.; Xiao, W.-J. *Chem. Eur. J.* **2009**, *15*, 2742-2746.
4. Lee, M.; Tremblay, M. S.; Jockusch, S.; Turro, N. J.; Sames, D. *Org. Lett.* **2011**, *13*, 2802-2805.
5. Tremblay, M. S.; Halim, M.; Sames, D. *J. Am. Chem. Soc.* **2007**, *129*, 7570-7577.
6. Lu, Y.; Mao, F.; Li, X.; Zheng, X.; Wang, M.; Xu, Q.; Zhu, J.; Li, J. *J. Med. Chem.* **2017**, *60*, 5099-5119.
7. (a) Wang, W.; Fu, A.; You, J.; Gao, G.; Lan, J.; Chen, L. *Tetrahedron* **2010**, *66*, 3695-3701. (b) Shafeekh, K. M.; Rahim, M. K. A.; Basheer, M. C.; Suresh, C. H.; Das, S. *Dyes Pigm.* **2013**, *96*, 714-721. (c) Luo, C.; Zhou, Q.; Jiang, G.; He, L.; Zhang, B.; Wang, X. *New J. Chem.* **2011**, *35*, 1128-1132.
8. *APEX-3*. Bruker AXS. Madison, Wisconsin, USA. **2016**.
9. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, & D. Stalke. *J. Appl. Cryst.* **2015** *48*, 3.
10. G. M. Sheldrick. *Acta Crystallogr.*, **2015**, *A71*, 3.
11. G. M. Sheldrick. *Acta Crystallogr.*, **2015**, *C71*, 3.
12. Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
13. Shao, Y., Gan, Z., Epifanovsky, E., Gilbert, A.T., Wormit, M., Kussmann, J., Lange, A.W., Behn, A., Deng, J., Feng, X.; Ghosh, D. *Mol. Phys.*, **2015,** *113*, 184–215
14. Schrödinger Release 2019-4: Jaguar pKa, Schrödinger, LLC, New York, NY, 2019.

VII. ^{1}H AND ^{13}C NMR SPECTRA



SI1

$CDCl_3$, 500 MHz


Et2N
NO2
SI1
CDCl3, 125 MHz
12.52
44.76
105.72
109.88
117.26
129.92
148.52
149.89
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
EB_1_137_13C

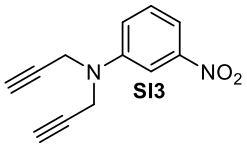
SI2

$CDCl_3$, 500 MHz

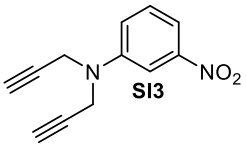
SI2

$CDCl_3$, 125 MHz

EB_2_188_13C

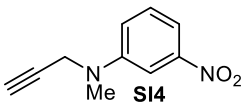


$CDCl_3$, 500 MHz



$CDCl_3$, 125 MHz

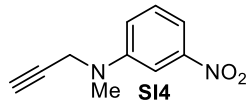
EB_8_101_13C



SI4

$CDCl_3$, 500 MHz

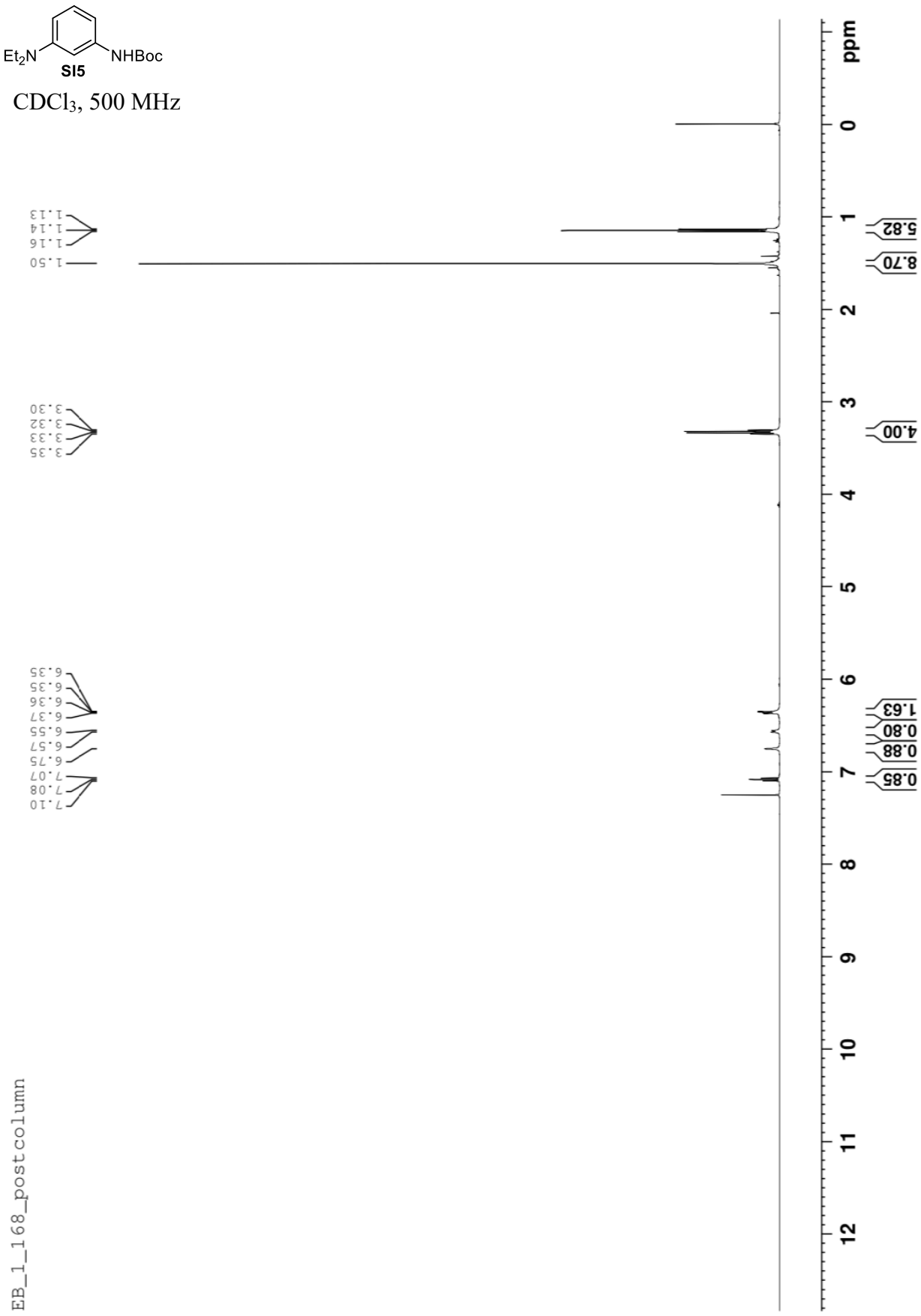
EB_2_189_highvac

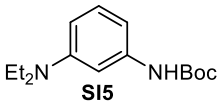


SI4

$CDCl_3$, 125 MHz

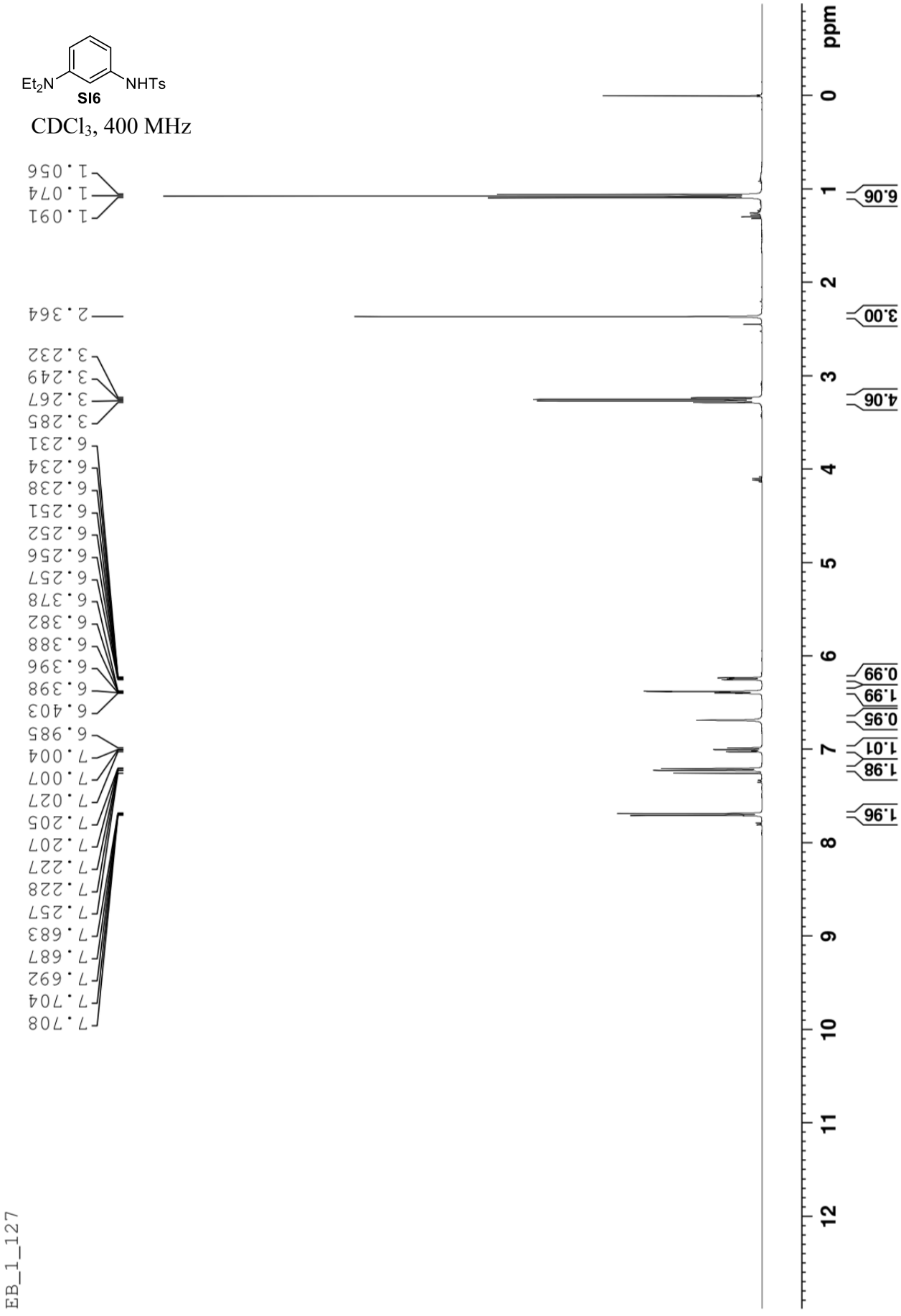
EB_2_189_13C

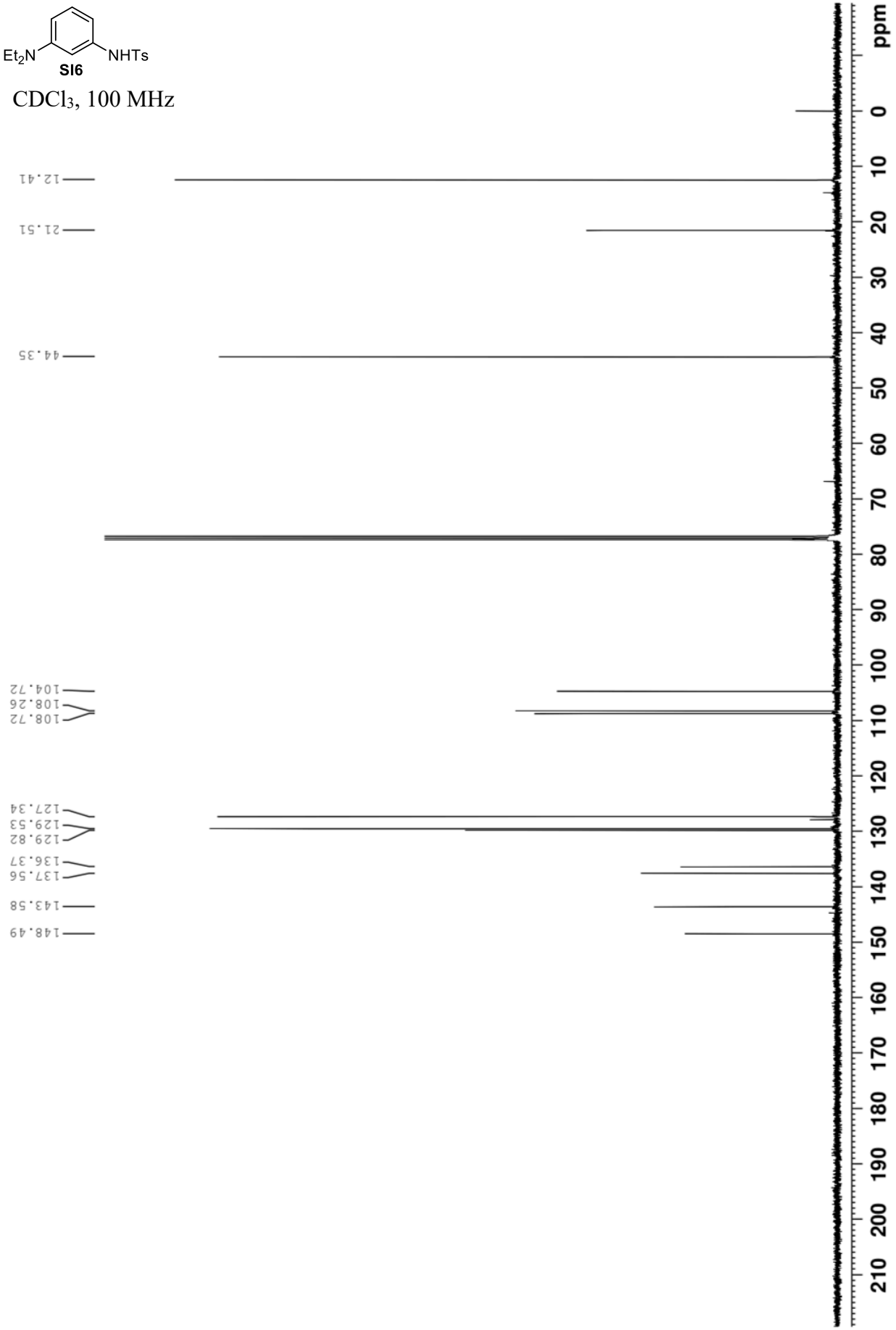

Et2N
NHBoc
SI5
CDCl3, 500 MHz
EB_1_168_postcolumn
ppm
0.85
0.88
0.80
1.63
4.00
8.70
5.82

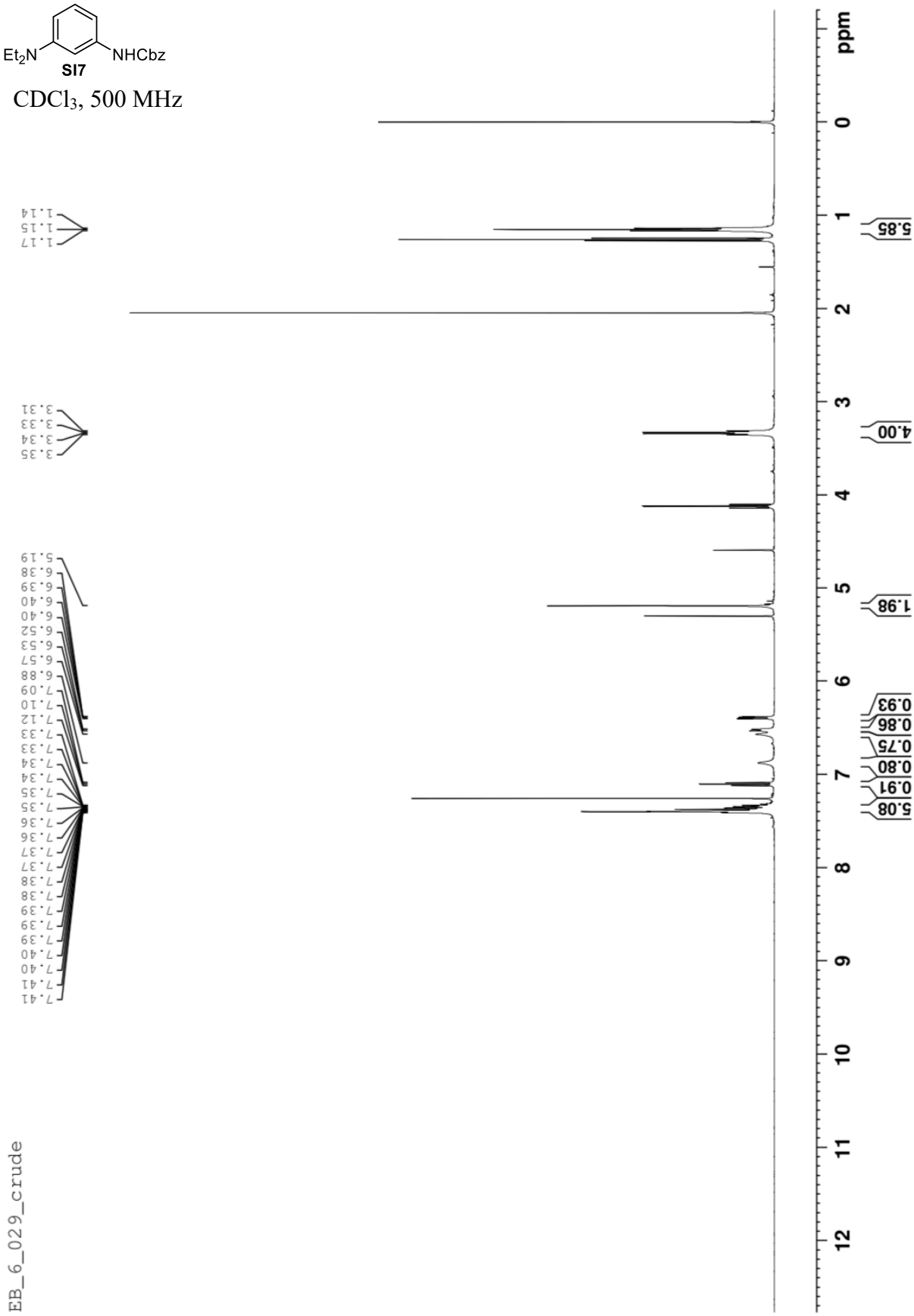


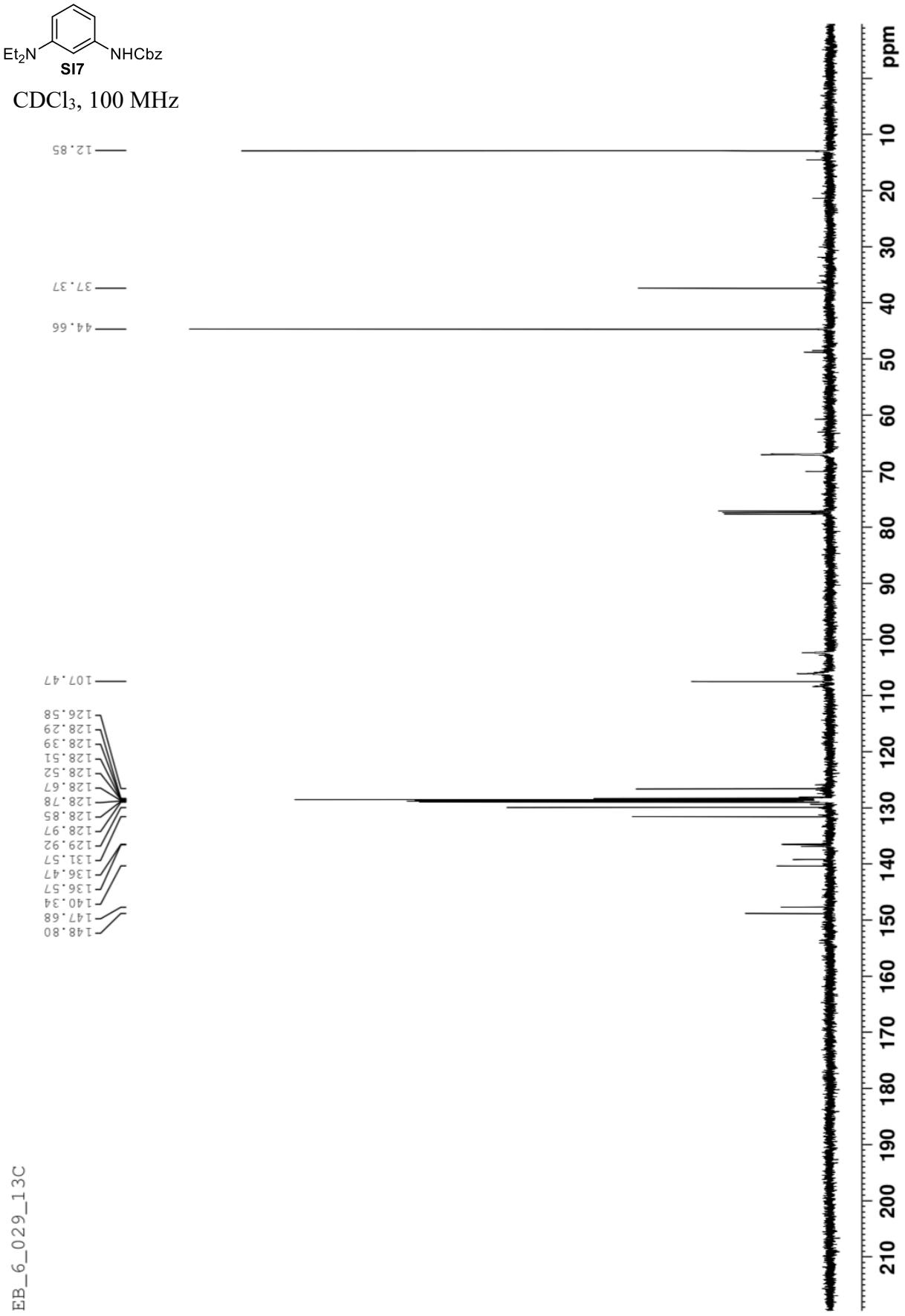
SI5

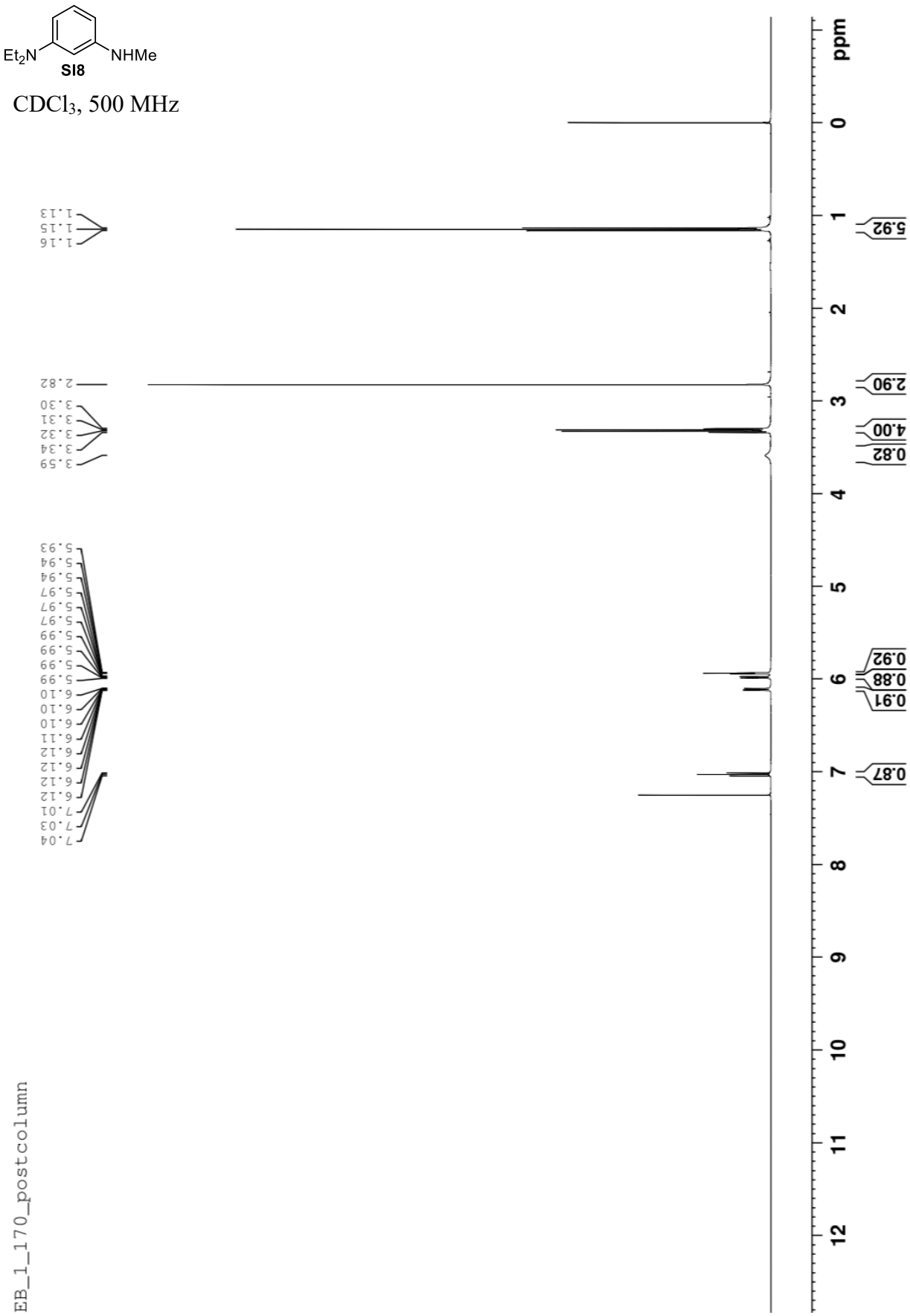
$CDCl_3$, 100 MHz

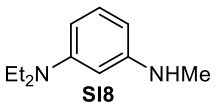

Et2N
NHTs
SI6
CDCl3, 400 MHz
1.056
1.074
1.091
2.364
3.232
3.249
3.267
3.285
6.231
6.234
6.238
6.251
6.252
6.256
6.257
6.378
6.382
6.388
6.396
6.398
6.403
6.985
7.004
7.007
7.027
7.205
7.207
7.227
7.228
7.257
7.683
7.687
7.692
7.704
7.708
6.06
3.00
4.06
0.99
1.99
0.95
1.01
1.98
1.96
ppm
EB_1_127


Et2N
NHTs
SI6
CDCl3, 100 MHz
12.41
21.51
44.35
104.72
108.26
108.72
127.34
129.53
129.82
136.37
137.56
143.58
148.49
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
EB_1_127_13C


Et2N
NHCbz
SI7
CDCl3, 500 MHz
EB_6_029_crude
ppm
5.85
4.00
1.98
0.93
0.86
0.75
0.80
0.91
5.08

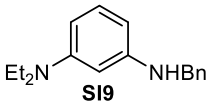

Et2N
NHCbz
SI7
CDCl3, 100 MHz
12.85
37.37
44.66
107.47
126.58
128.29
128.39
128.51
128.52
128.67
128.78
128.85
128.97
129.92
131.57
136.47
136.57
140.34
147.68
148.80
ppm
EB_6_029_13C


Et2N
NHMe
SI8
CDCl3, 500 MHz
EB_1_170_postcolumn
ppm
5.92
2.90
4.00
0.82
0.92
0.88
0.91
0.87



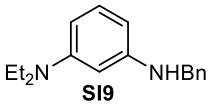
SI8

$CDCl_3$, 125 MHz



SI9

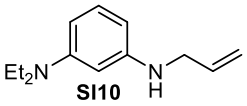
$CDCl_3$, 400 MHz



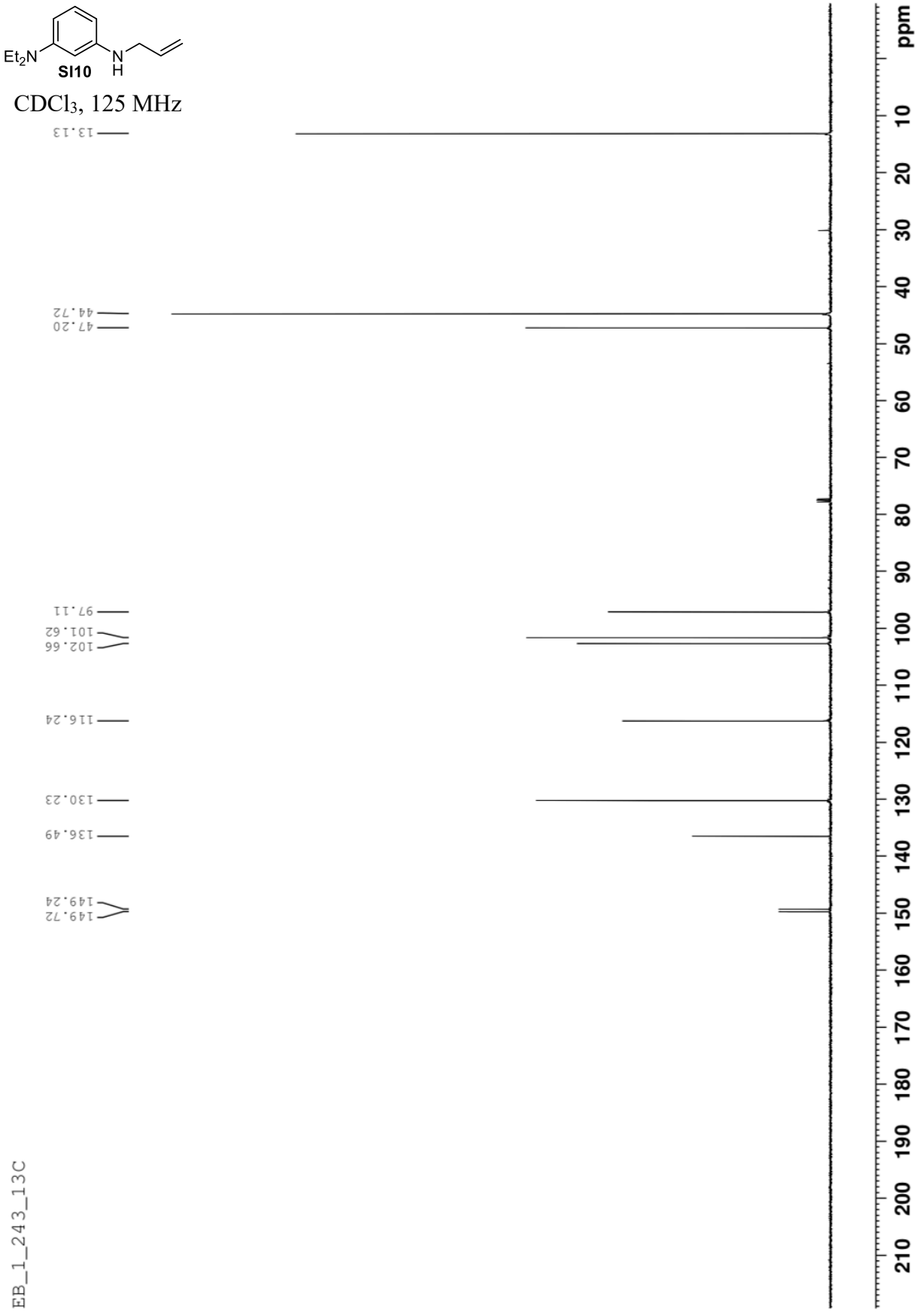
SI9

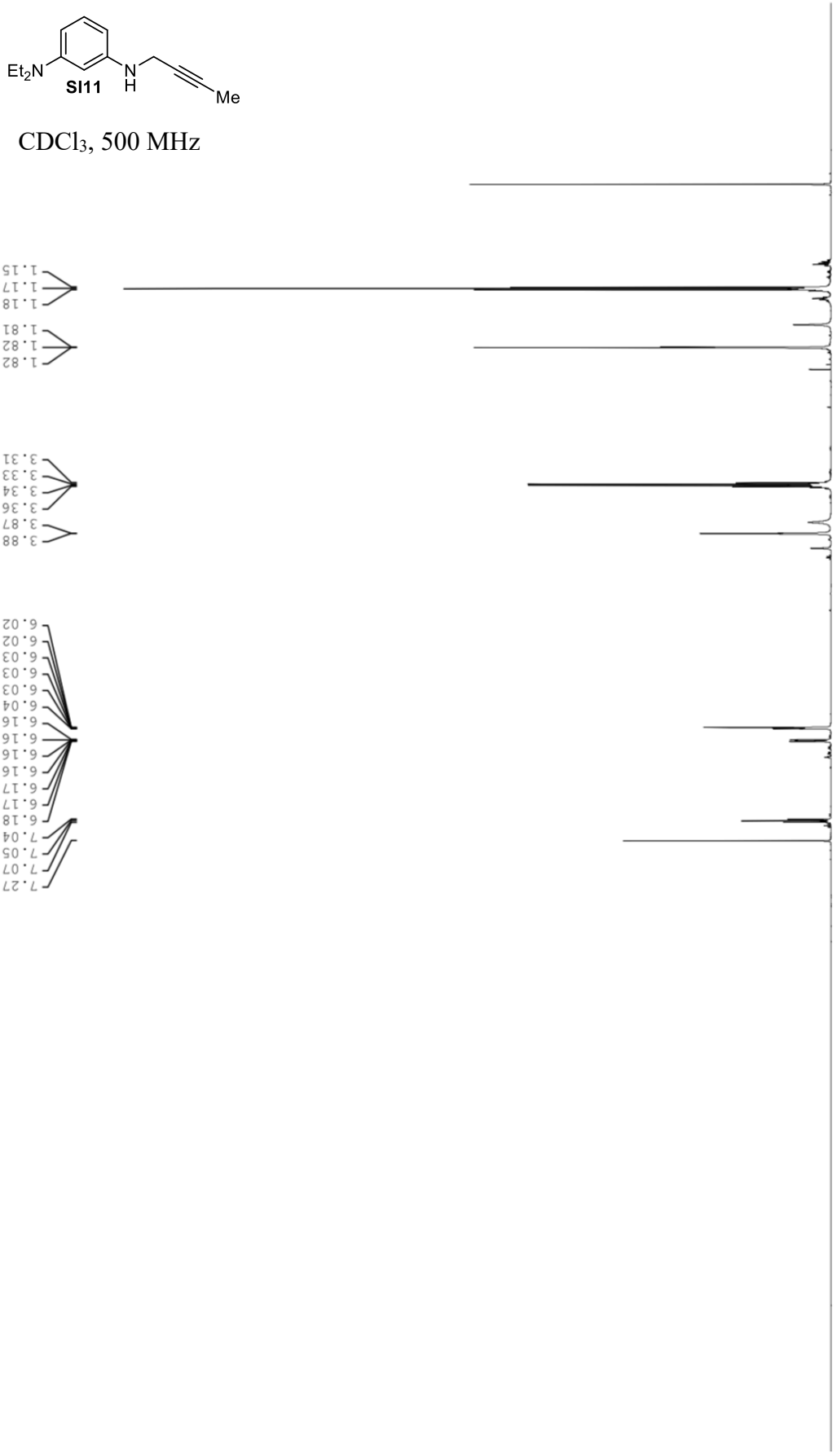
$CDCl_3$, 100 MHz

EB_2_027_13C

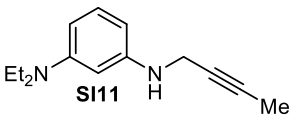


$CDCl_3$, 500 MHz


Et2N
N
H
SI10
CDCl3, 125 MHz
13.13
44.72
47.20
97.11
101.62
102.66
116.24
130.23
136.49
149.24
149.72
ppm
EB_1_243_13C

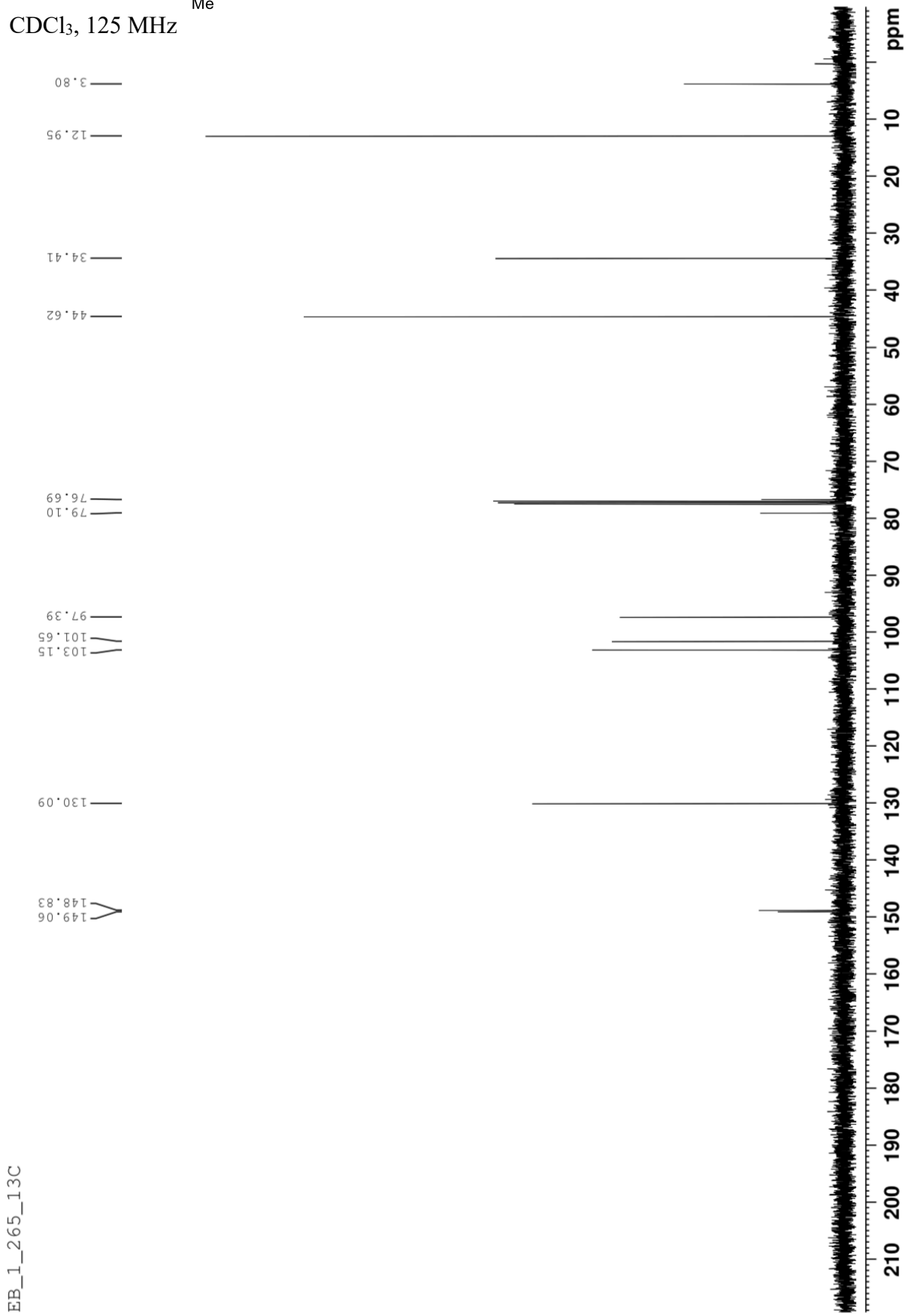


$CDCl_3$, 500 MHz

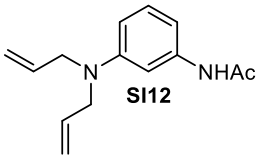


SI11

$CDCl_3$, 125 MHz



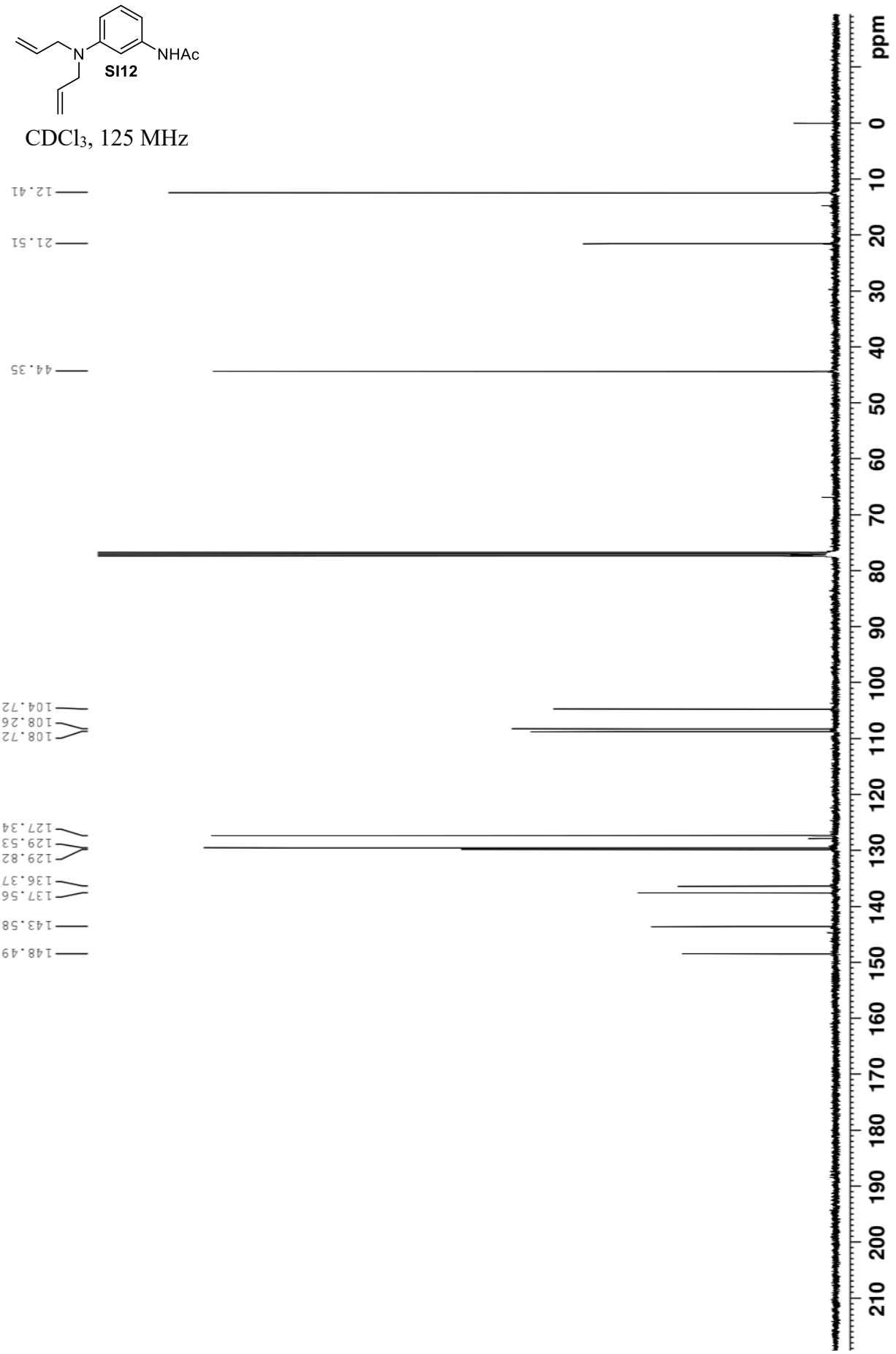
EB_1_265_13C

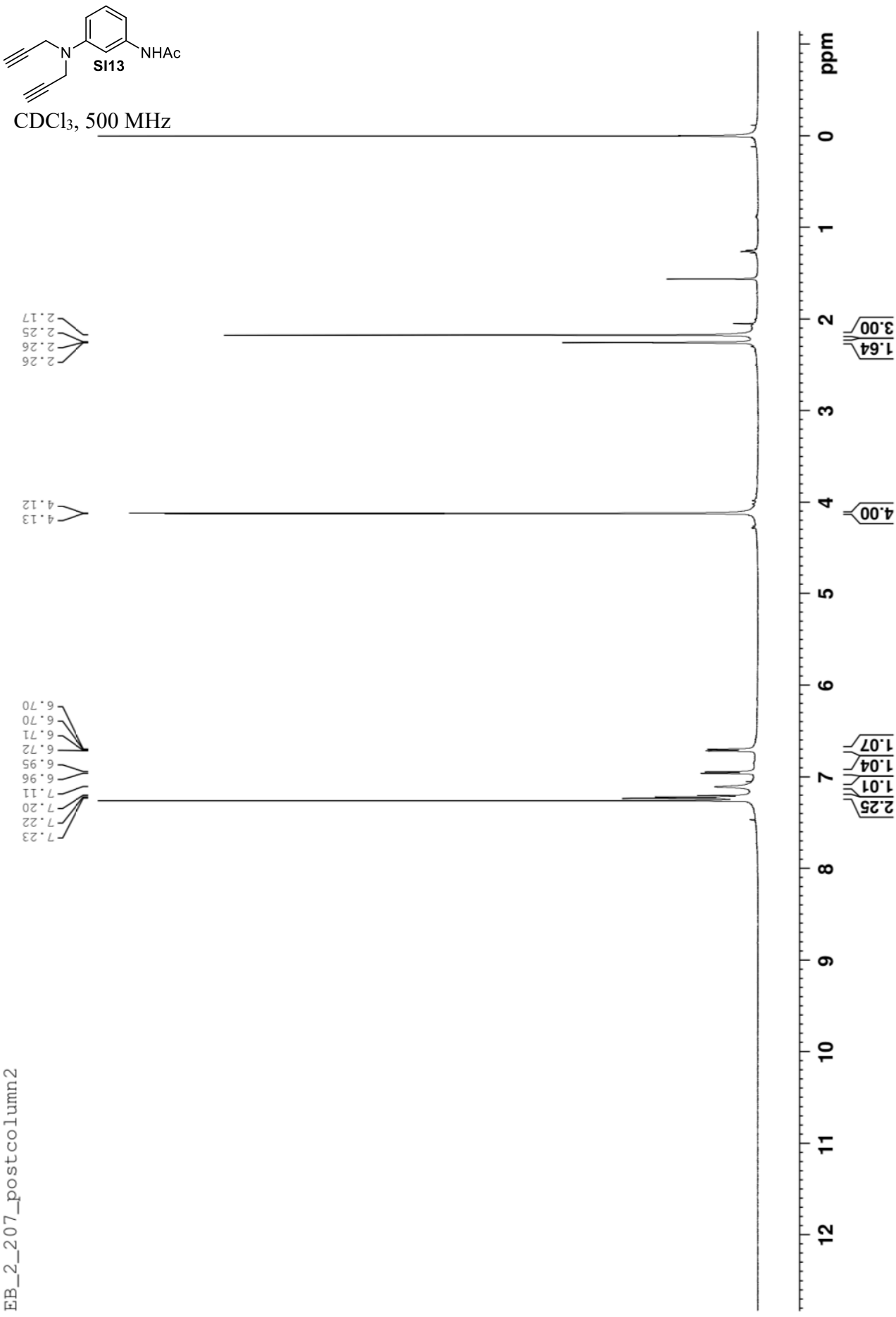


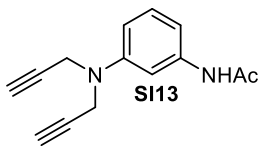
SI12

$CDCl_3$, 500 MHz

EB_2_192_highvac


NHAc
SI12
CDCl3, 125 MHz
12.41
21.51
44.35
104.72
108.26
108.72
127.34
129.53
129.82
136.37
137.56
143.58
148.49
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
EB_1_127_13C

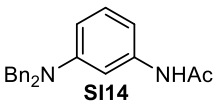

SI13
NHAc
CDCl3, 500 MHz
EB_2_207_postcolumn2
ppm
2.17
2.25
2.26
2.26
4.13
4.12
6.70
6.70
6.71
6.72
6.95
6.96
7.11
7.20
7.22
7.23
3.00
1.64
4.00
1.07
1.04
1.01
2.25



SI13

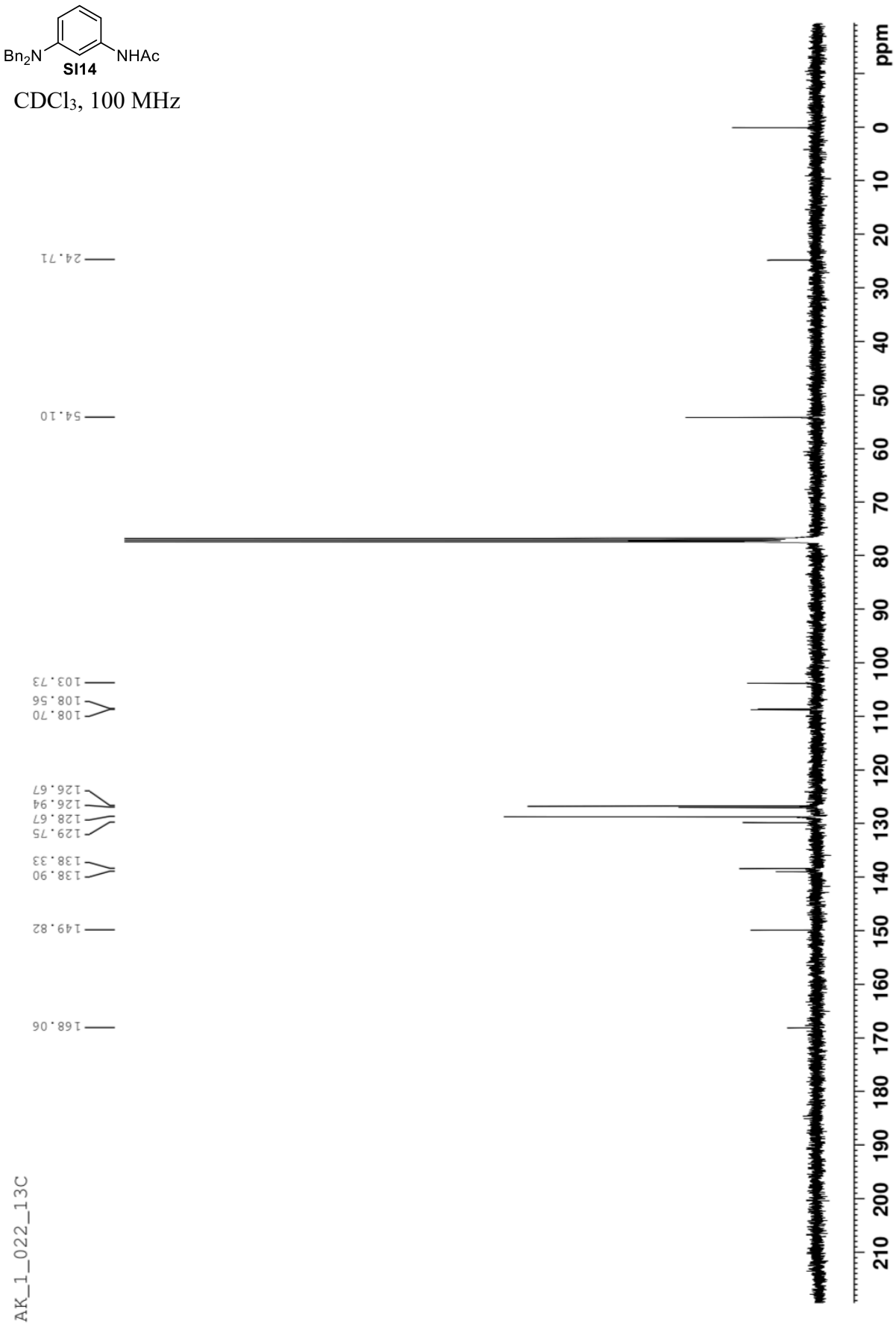
$CDCl_3$, 100 MHz

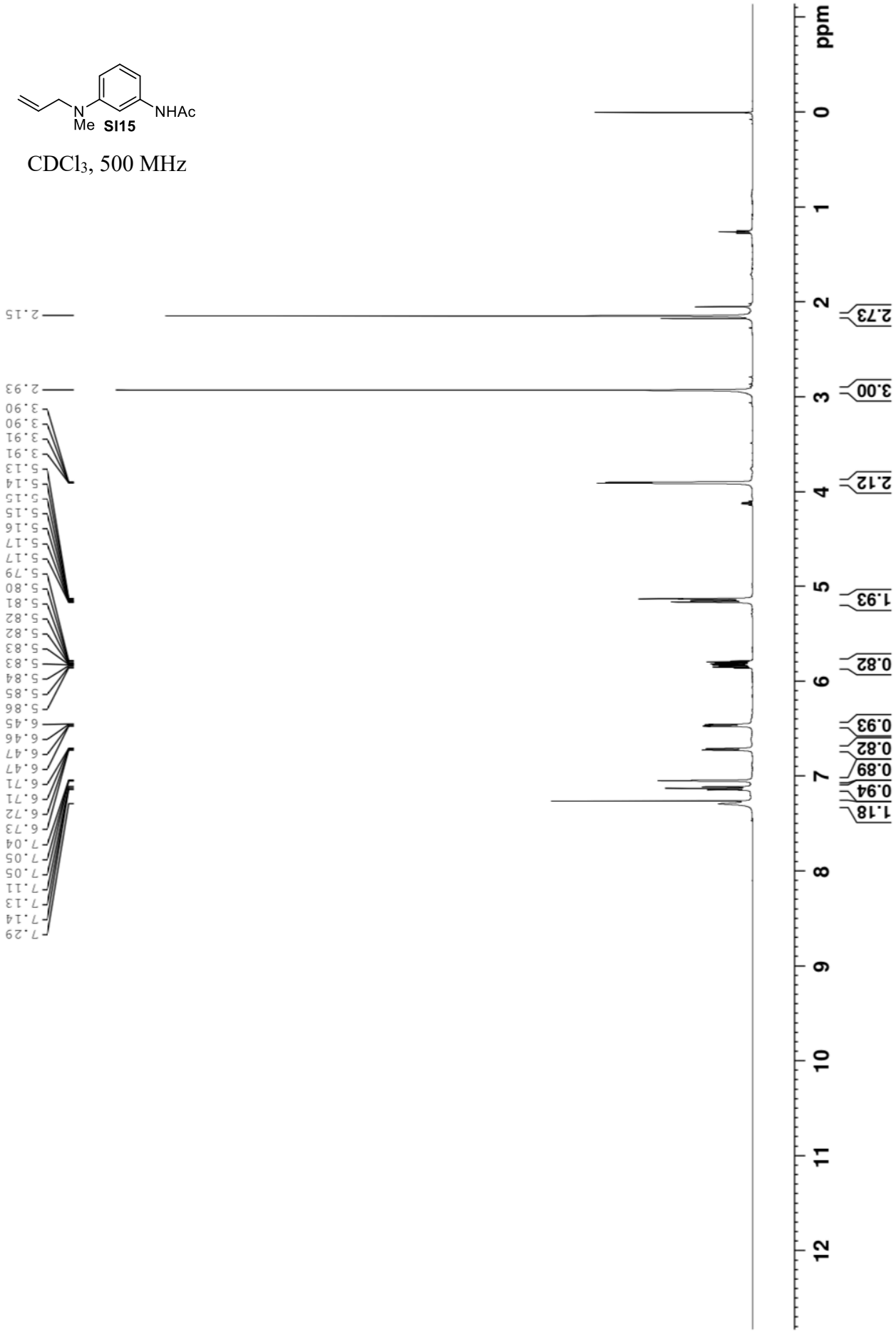
EB_2_207_13C

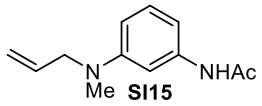


SI14

$CDCl_3$, 400 MHz

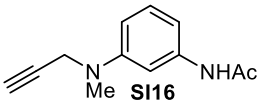

Bn2N
NHAc
SI14
CDCl3, 100 MHz
24.71
54.10
103.73
108.56
108.70
126.67
126.94
128.67
129.75
138.33
138.90
149.82
168.06
AK_1_022_13C
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


N
Me
SI15
NHAc
CDCl3, 500 MHz
2.15
2.93
3.90
3.90
3.91
3.91
5.13
5.14
5.15
5.15
5.16
5.17
5.17
5.79
5.80
5.81
5.82
5.82
5.83
5.83
5.84
5.85
5.86
6.45
6.46
6.47
6.47
6.71
6.71
6.72
6.73
7.04
7.05
7.05
7.11
7.13
7.14
7.29
2.73
3.00
2.12
1.93
0.82
0.93
0.82
0.89
0.94
1.18
ppm
EB_2_195_postcolumn



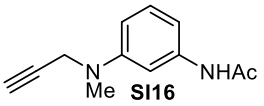
SI15

$CDCl_3$, 100 MHz



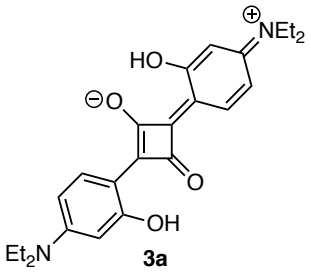
SI16

$CDCl_3$, 500 MHz



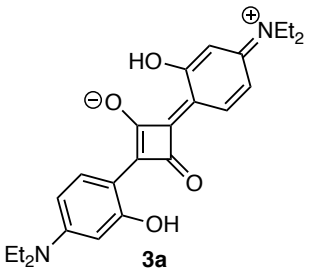
SI16

$CDCl_3$, 100 MHz



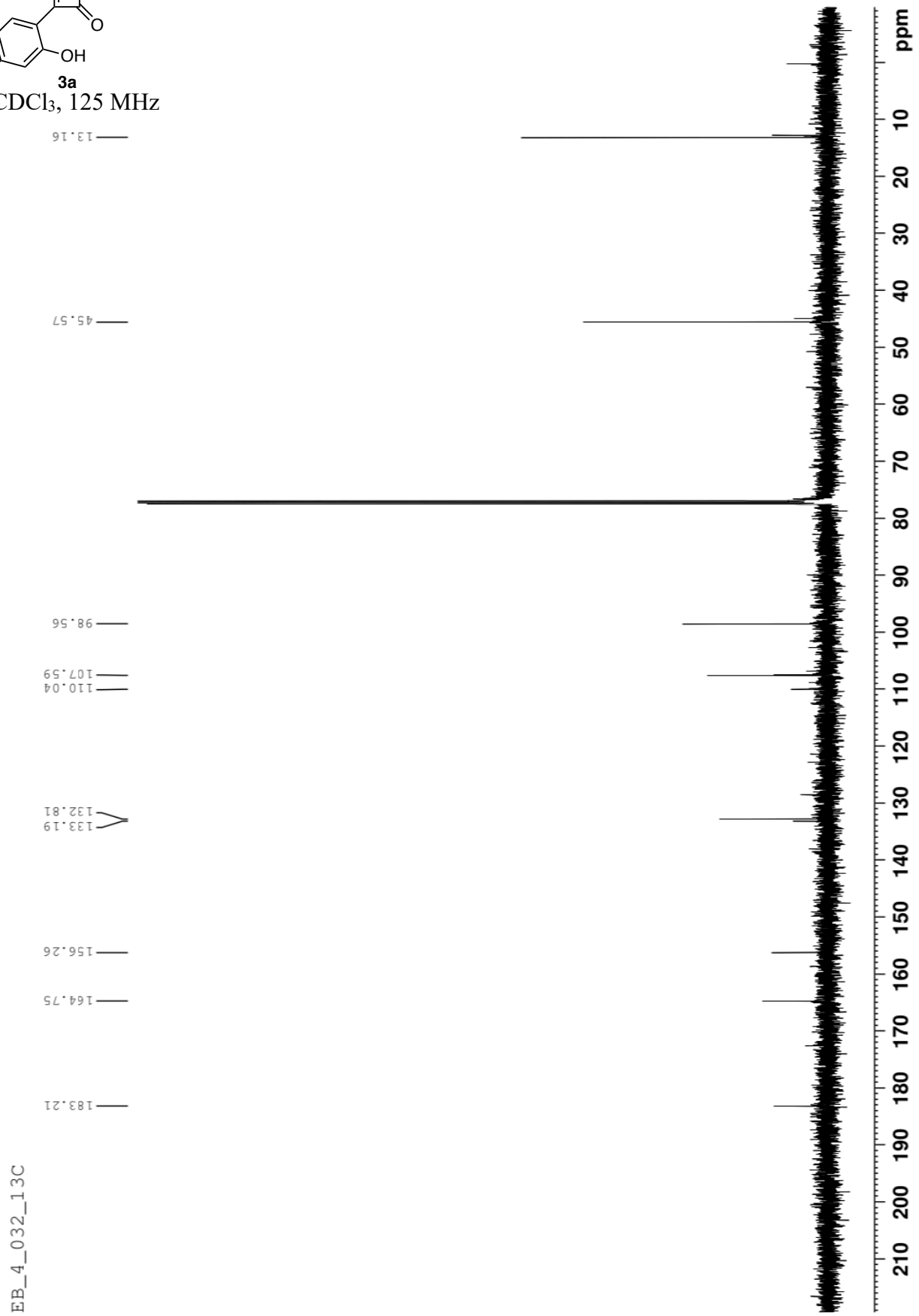
3a

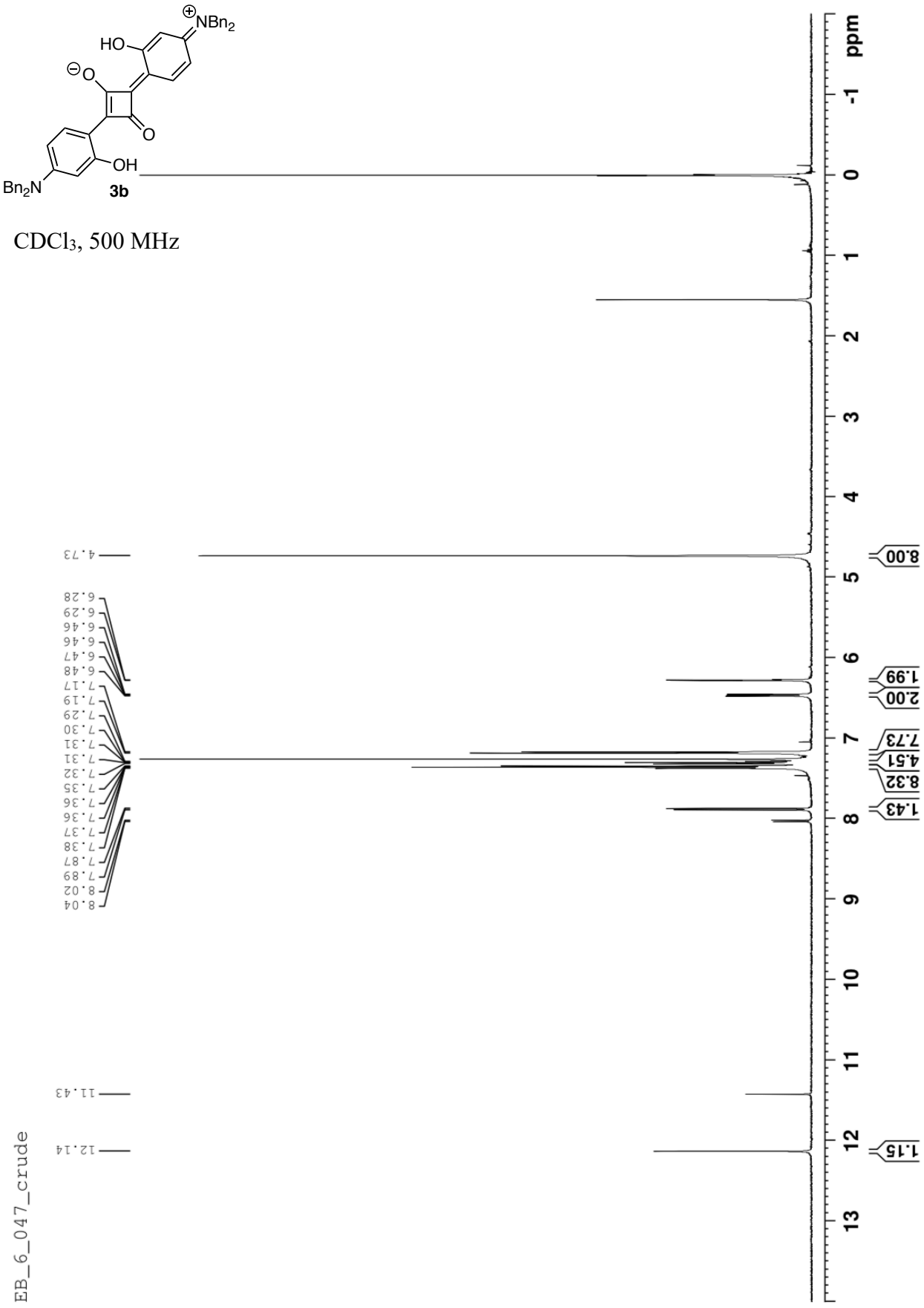
$CDCl_3$, 500 MHz

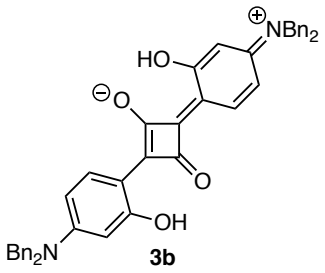


3a

$CDCl_3$, 125 MHz

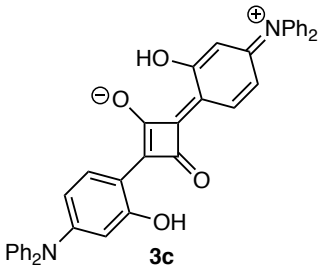



HO
O
O
NBn2
OH
Bn2N
3b
CDCl3, 500 MHz
EB_6_047_crude
ppm
8.00
1.99
2.00
7.73
4.51
8.32
1.43
1.15



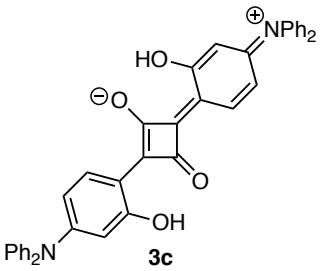
3b

$CDCl_3$, 100 MHz



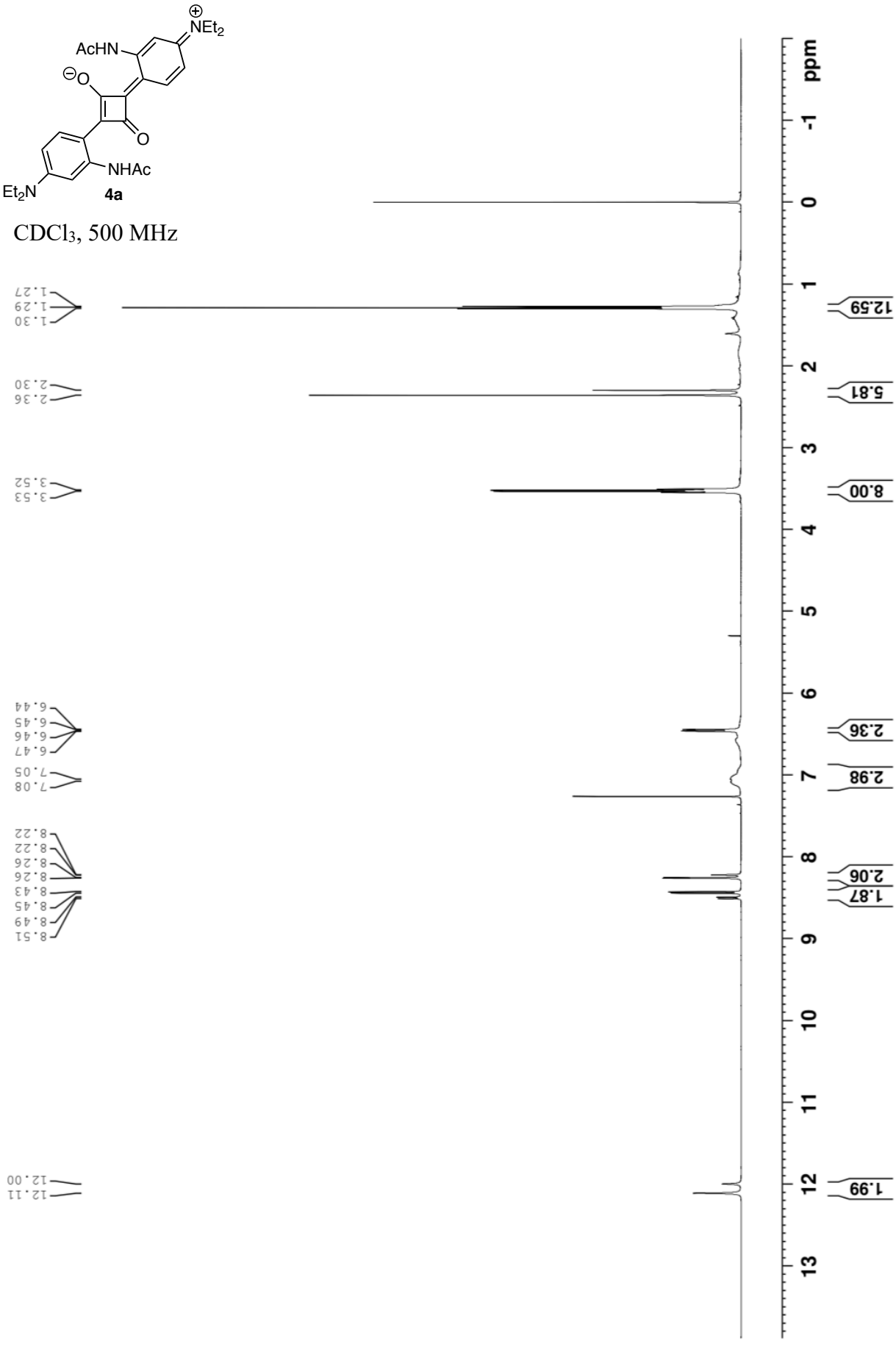
3c

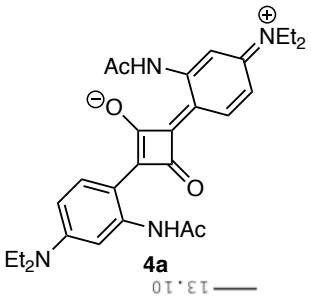
$CDCl_3$, 500 MHz



3c

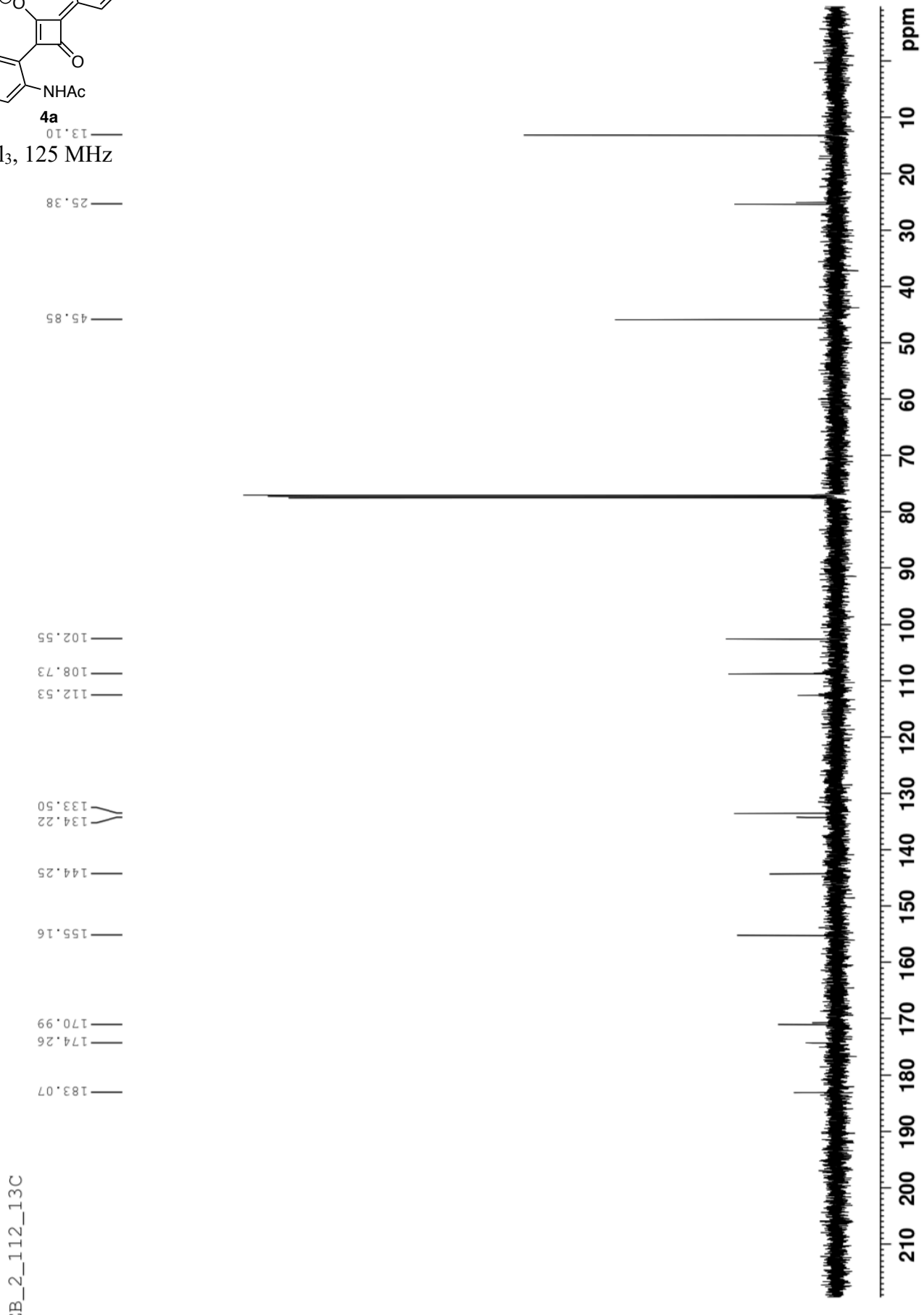
$CDCl_3$, 125 MHz


AcHN
NEt2
O
O
NHAc
Et2N
4a
CDCl3, 500 MHz
EB_2_112_1H?
ppm

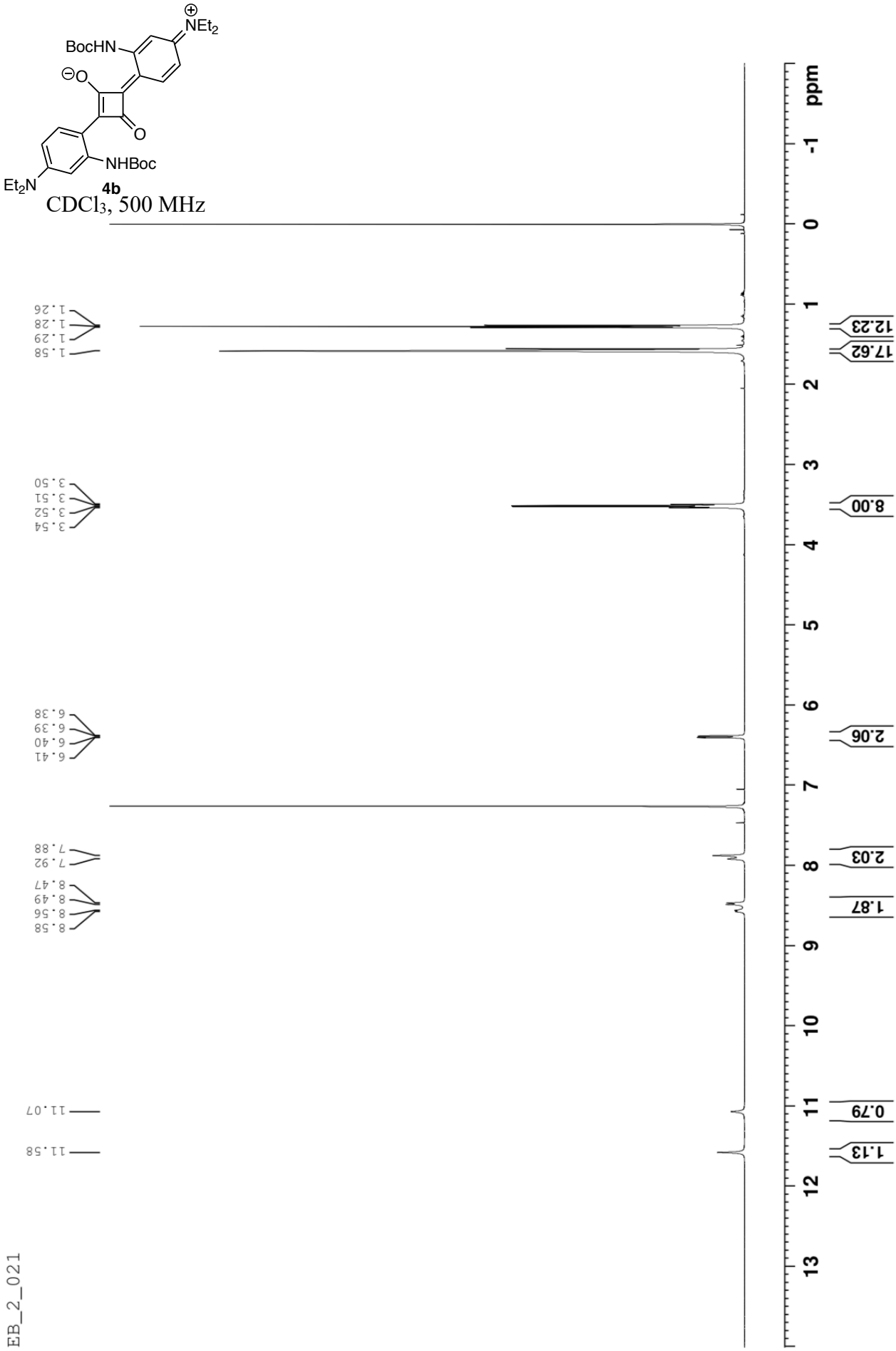


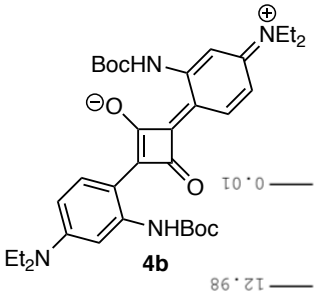
4a

$CDCl_3$, 125 MHz

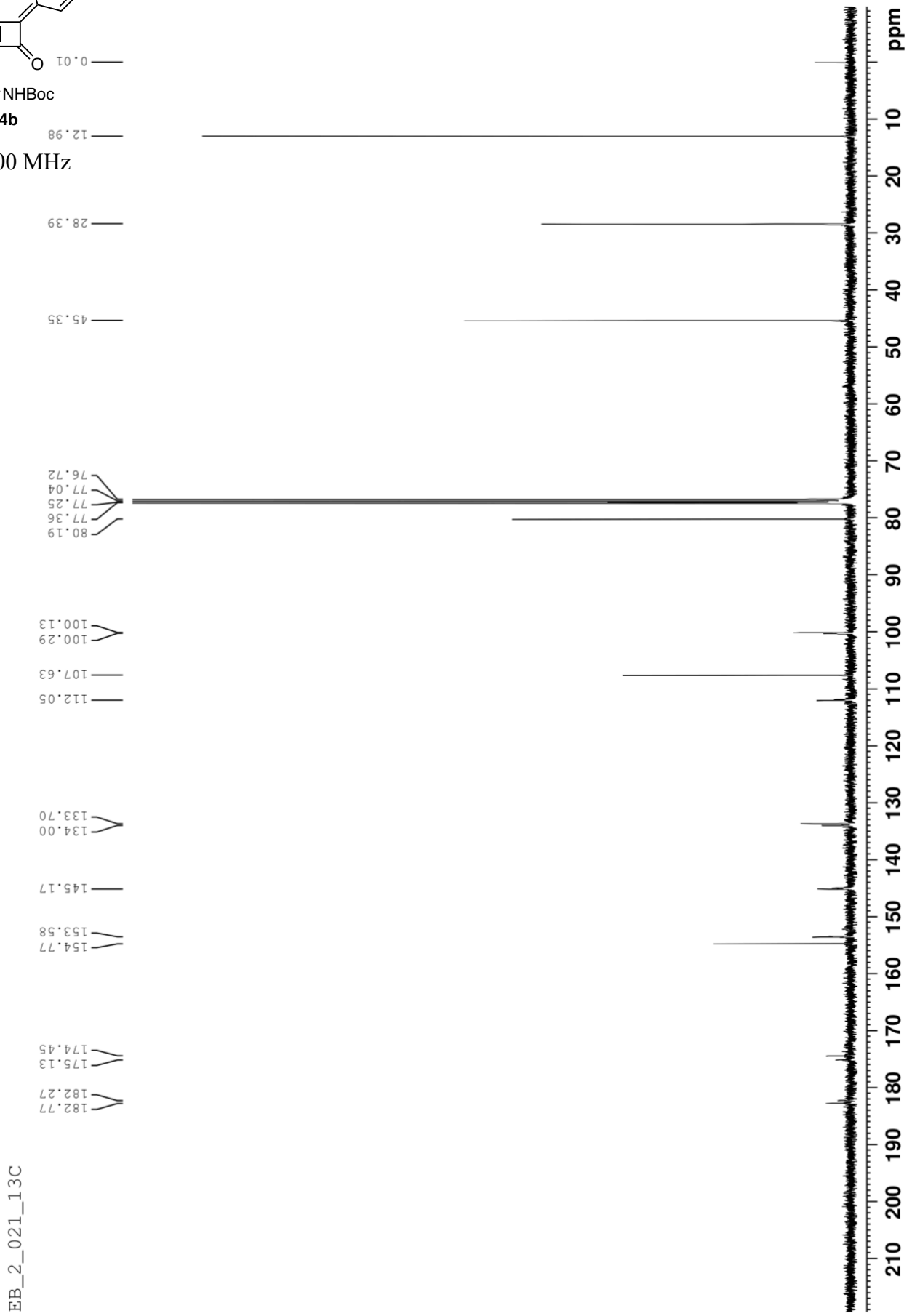


EB_2_112_13C

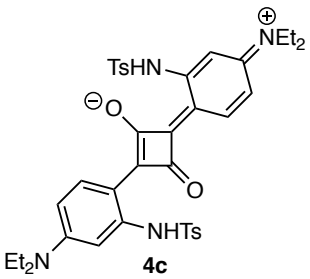

BocHN
NEt2
O
O
NHBoc
Et2N
4b
CDCl3, 500 MHz
ppm
12.23
17.62
8.00
2.06
2.03
1.87
0.79
1.13
EB_2_021



$CDCl_3$, 100 MHz

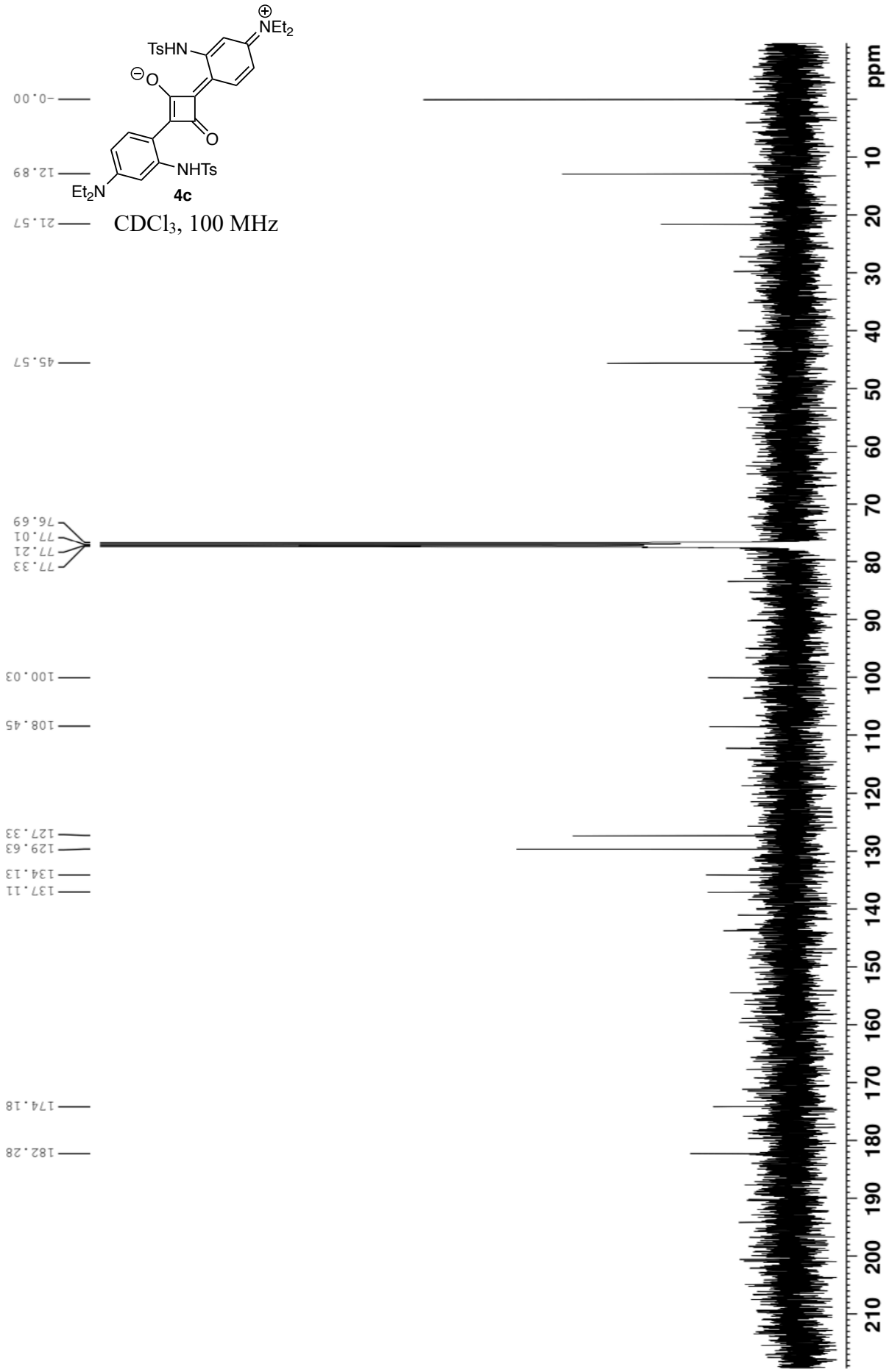


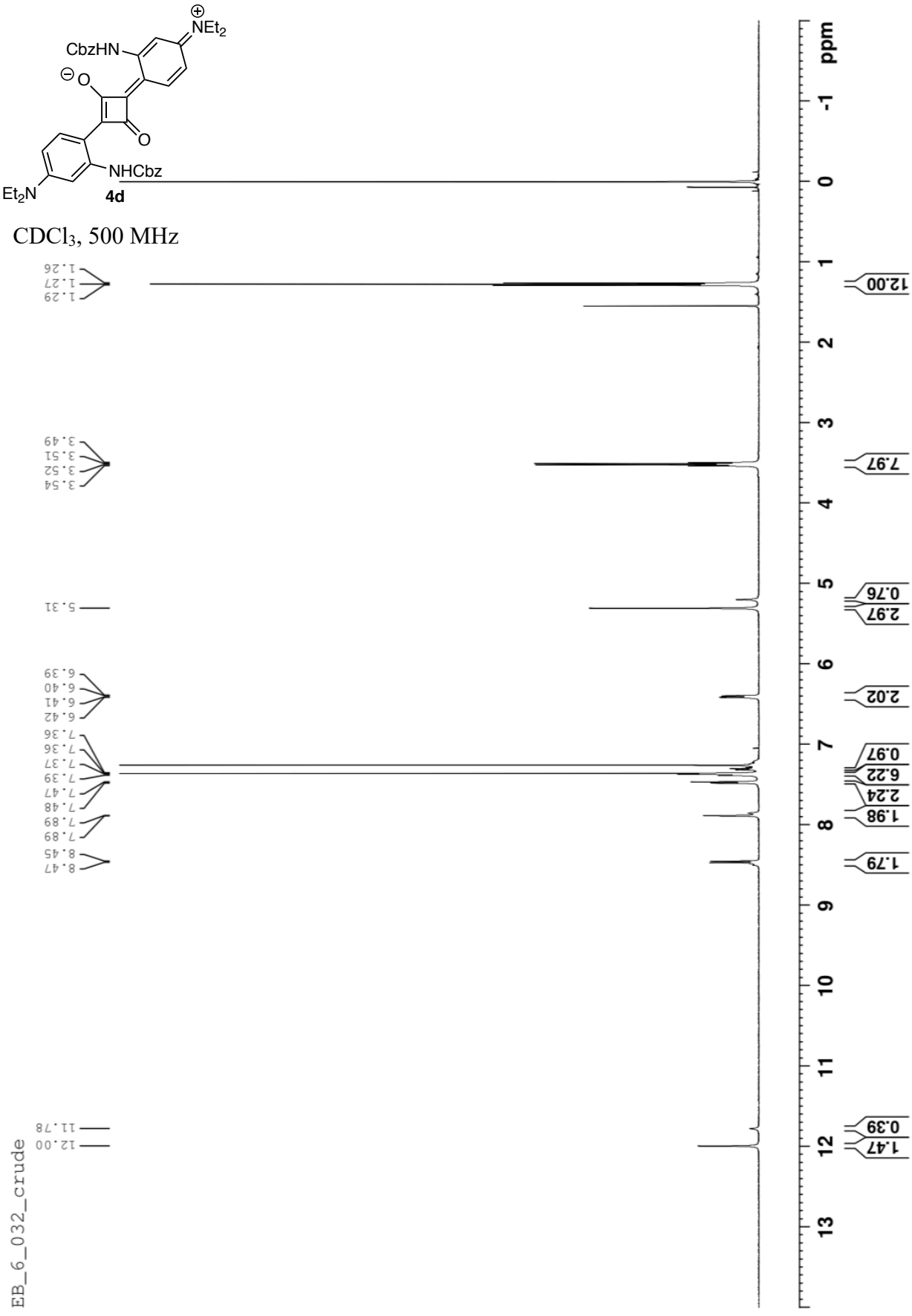
EB_2_021_13C

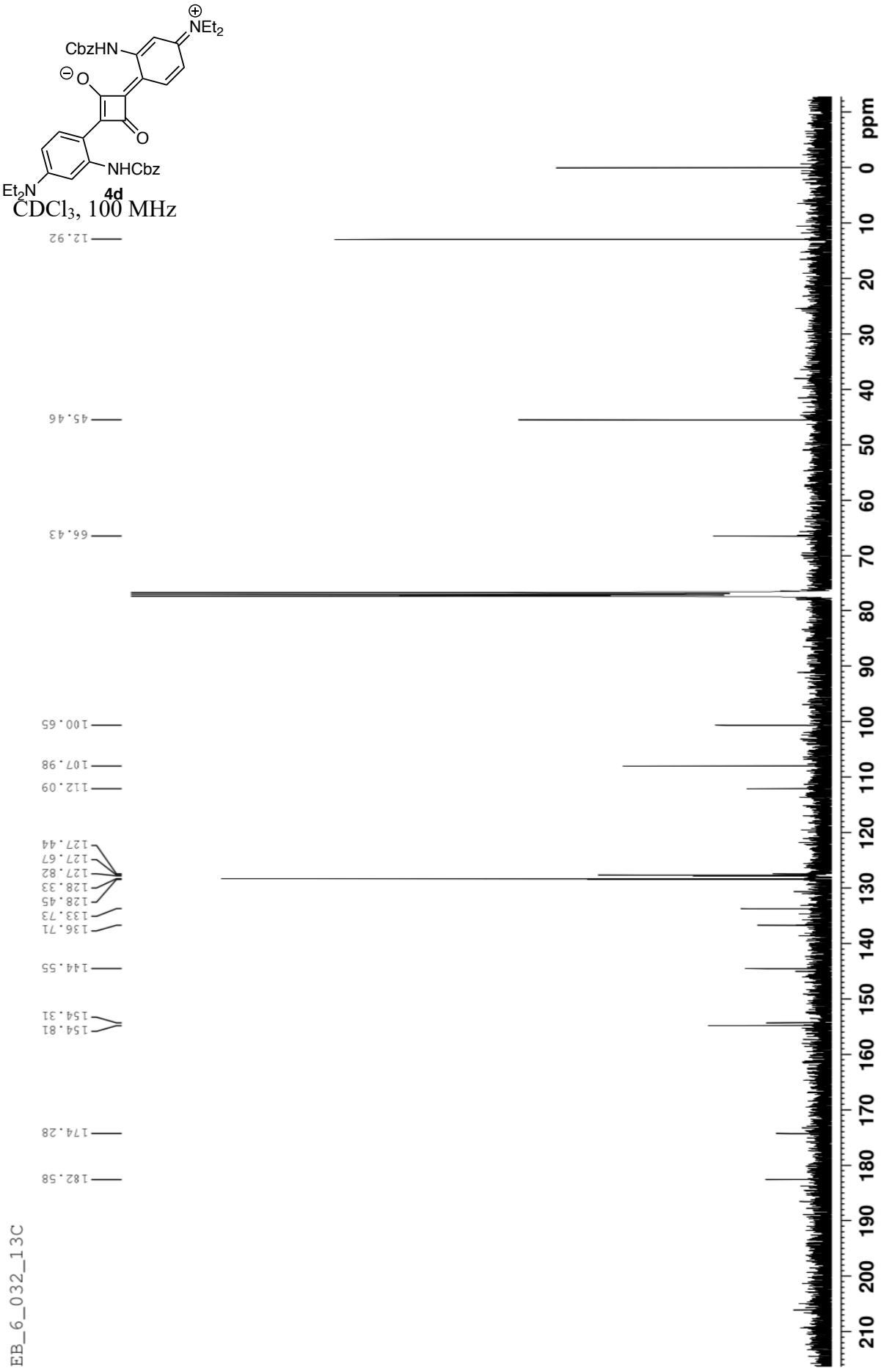


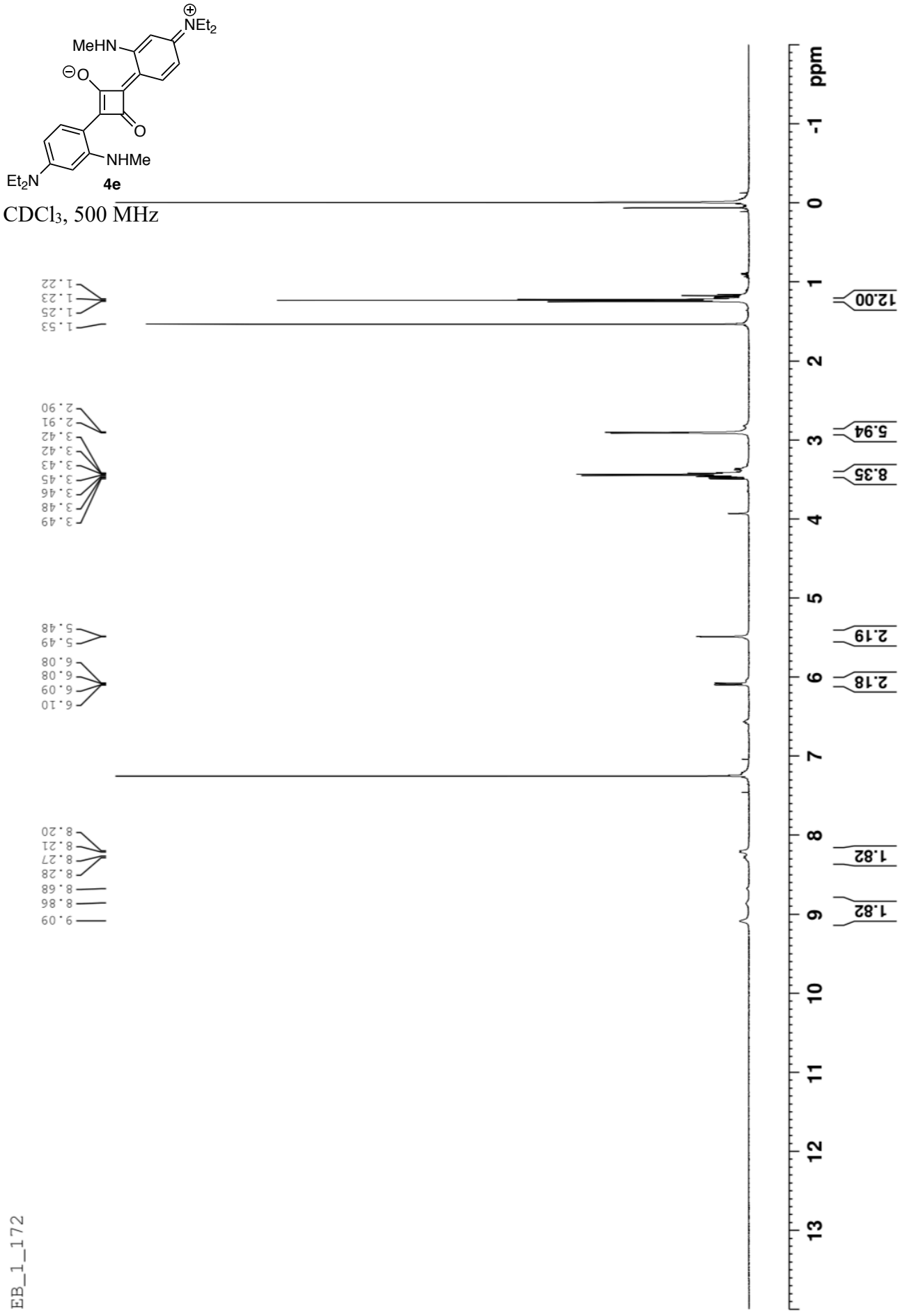
4c

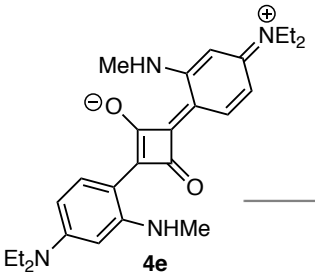
$CDCl_3$, 500 MHz


TsHN
NEt2
O
O
NHTs
Et2N
4c
CDCl3, 100 MHz
-0.00
12.89
21.57
45.57
76.69
77.01
77.21
77.33
100.03
108.45
127.33
129.63
134.13
137.11
174.18
182.28
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
EB_2_134_13C


CbzHN
NEt2
O
O
NHCbz
Et2N
4d
CDCl3, 500 MHz
EB_6_032_crude
ppm

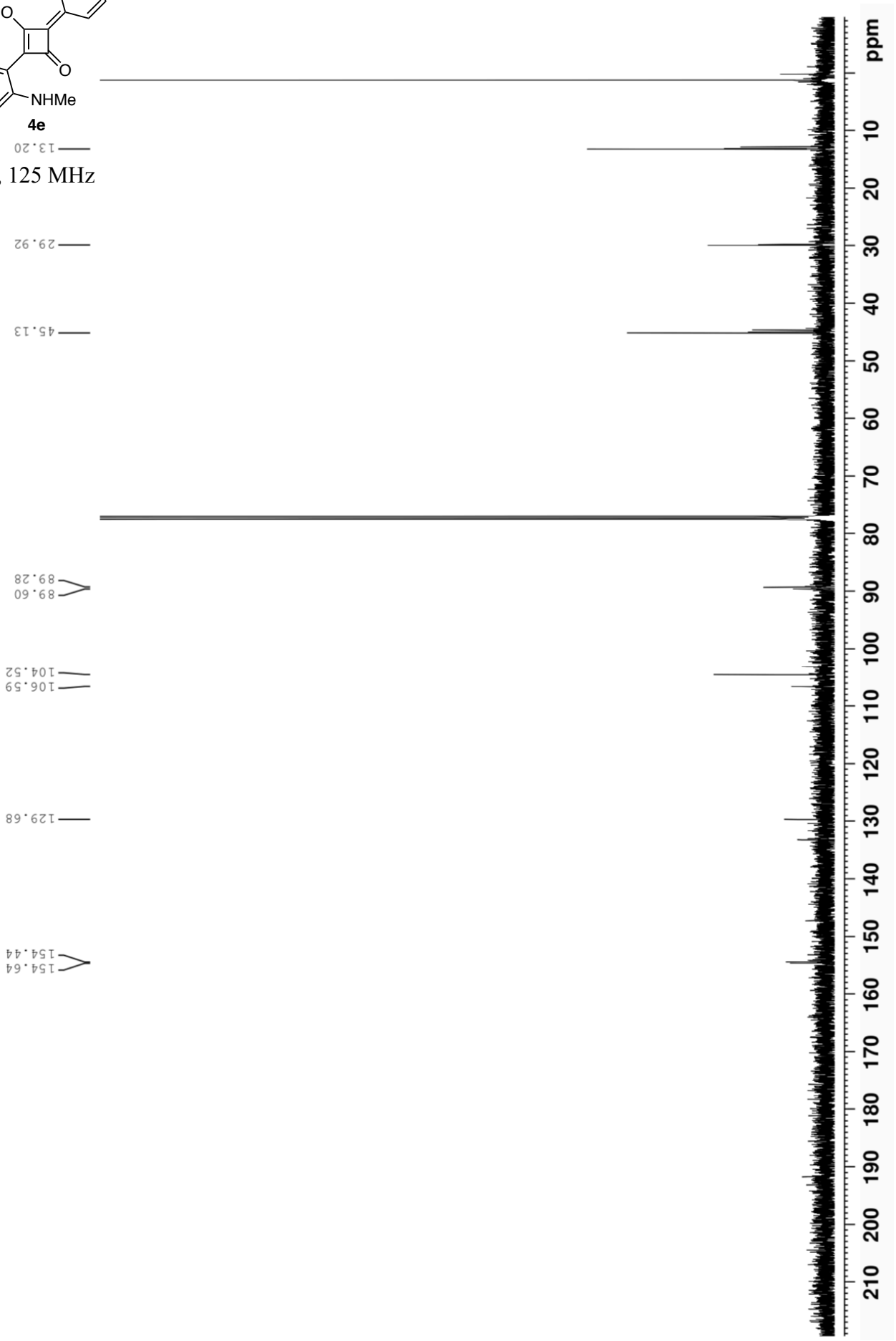

CbzHN
NEt2
O
O
NHCbz
Et2N
4d
CDCl3, 100 MHz
12.92
45.46
66.43
100.65
107.98
112.09
127.44
127.67
127.82
128.33
128.45
133.73
136.71
144.55
154.31
154.81
174.28
182.58
EB_6_032_13C
ppm


MeHN
NEt2
O
O
NHMe
Et2N
4e
CDCl3, 500 MHz
1.22
1.23
1.25
1.53
2.90
2.91
3.42
3.42
3.43
3.45
3.46
3.48
3.49
5.48
5.49
6.08
6.08
6.09
6.10
8.20
8.21
8.27
8.28
8.68
8.86
9.09
12.00
5.94
8.35
2.19
2.18
1.82
1.82
ppm
EB_1_172

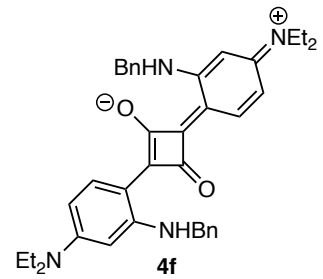


4e

$CDCl_3$, 125 MHz

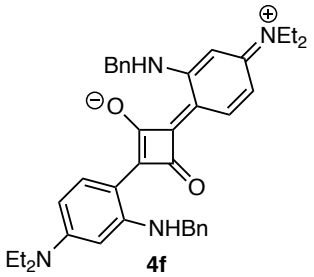


EB_1_172_13C



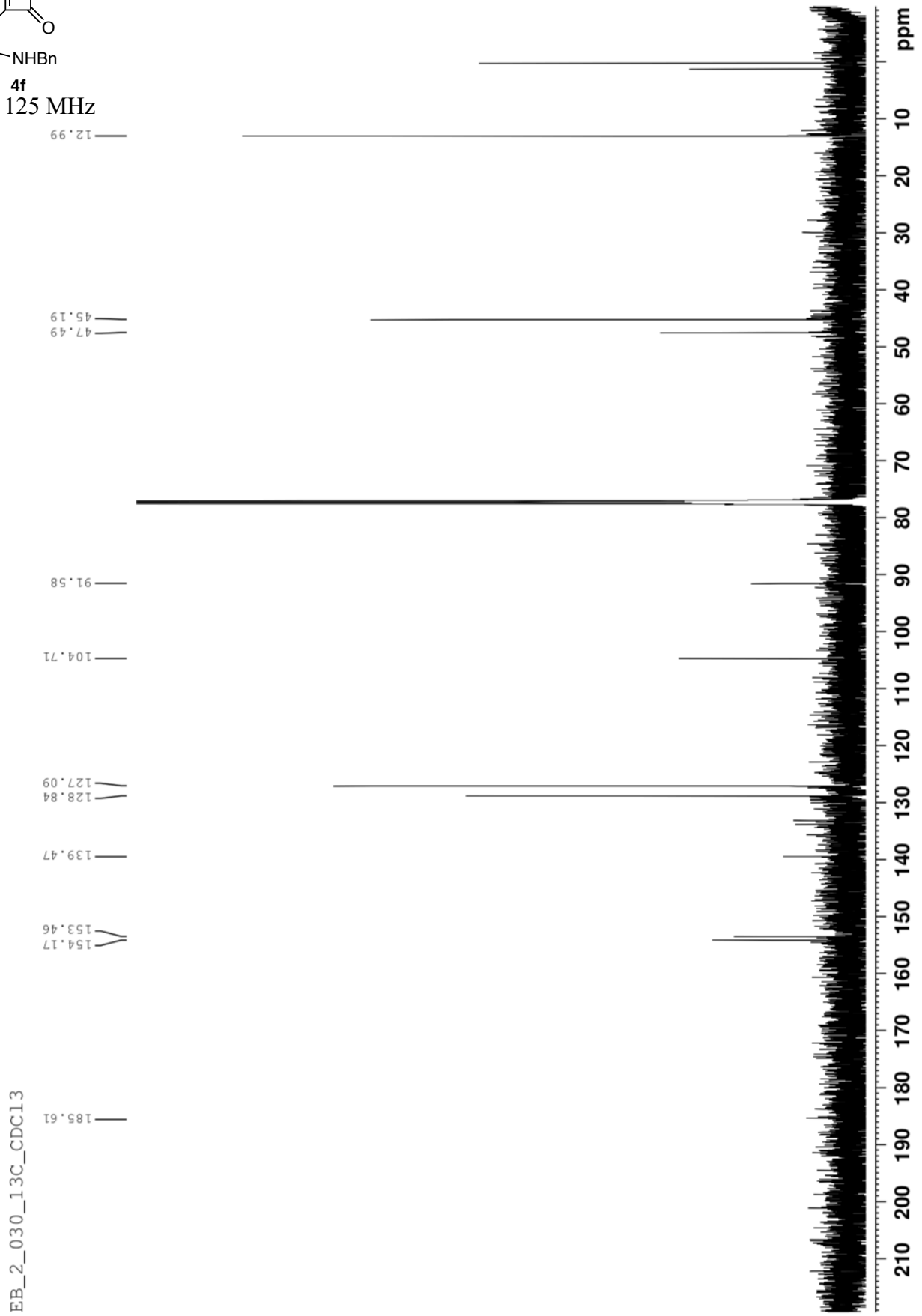
4f

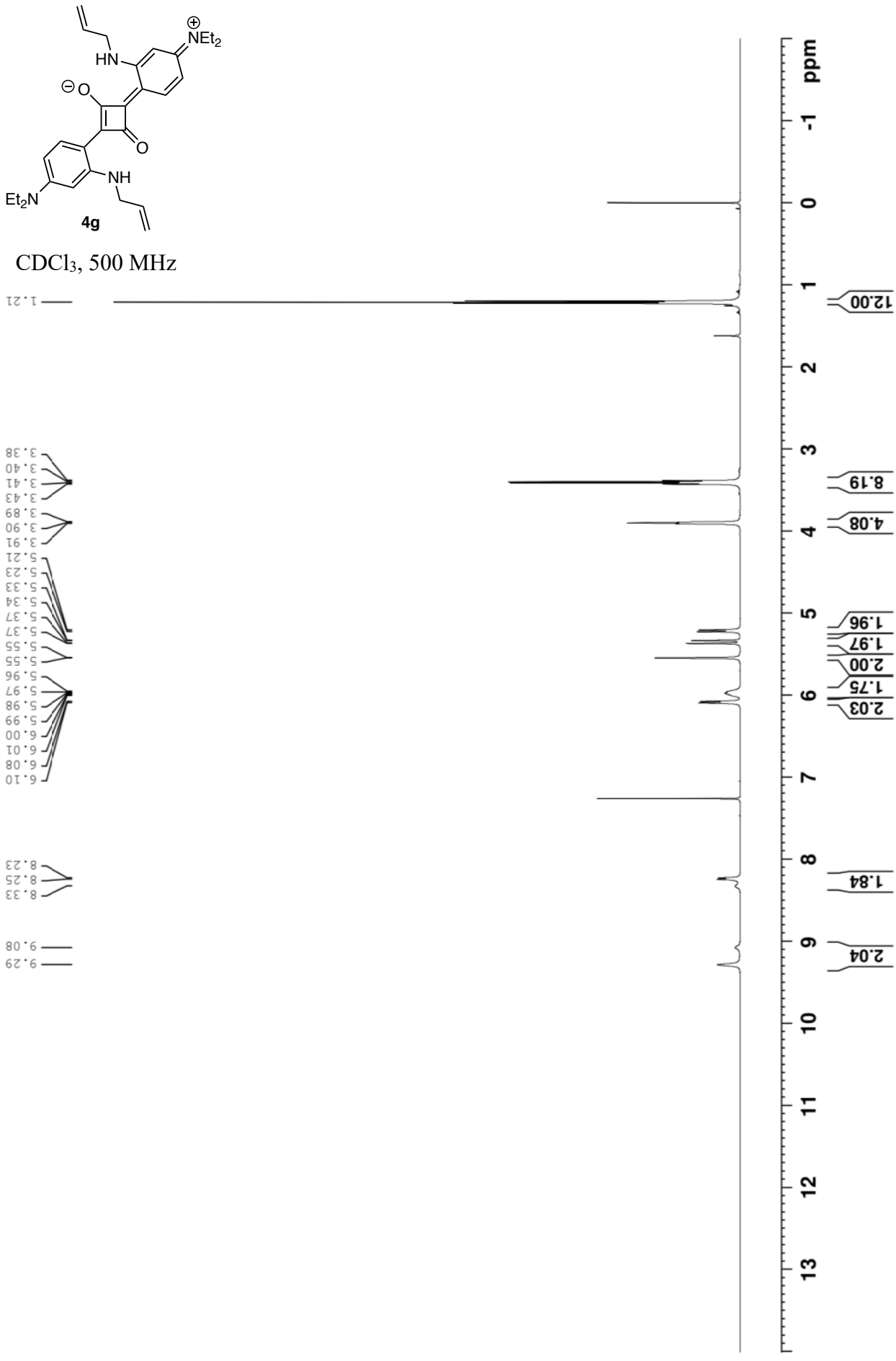
$CDCl_3$, 500 MHz

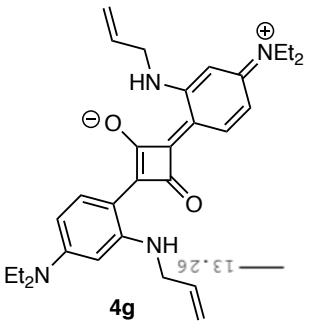


4f

$CDCl_3$, 125 MHz

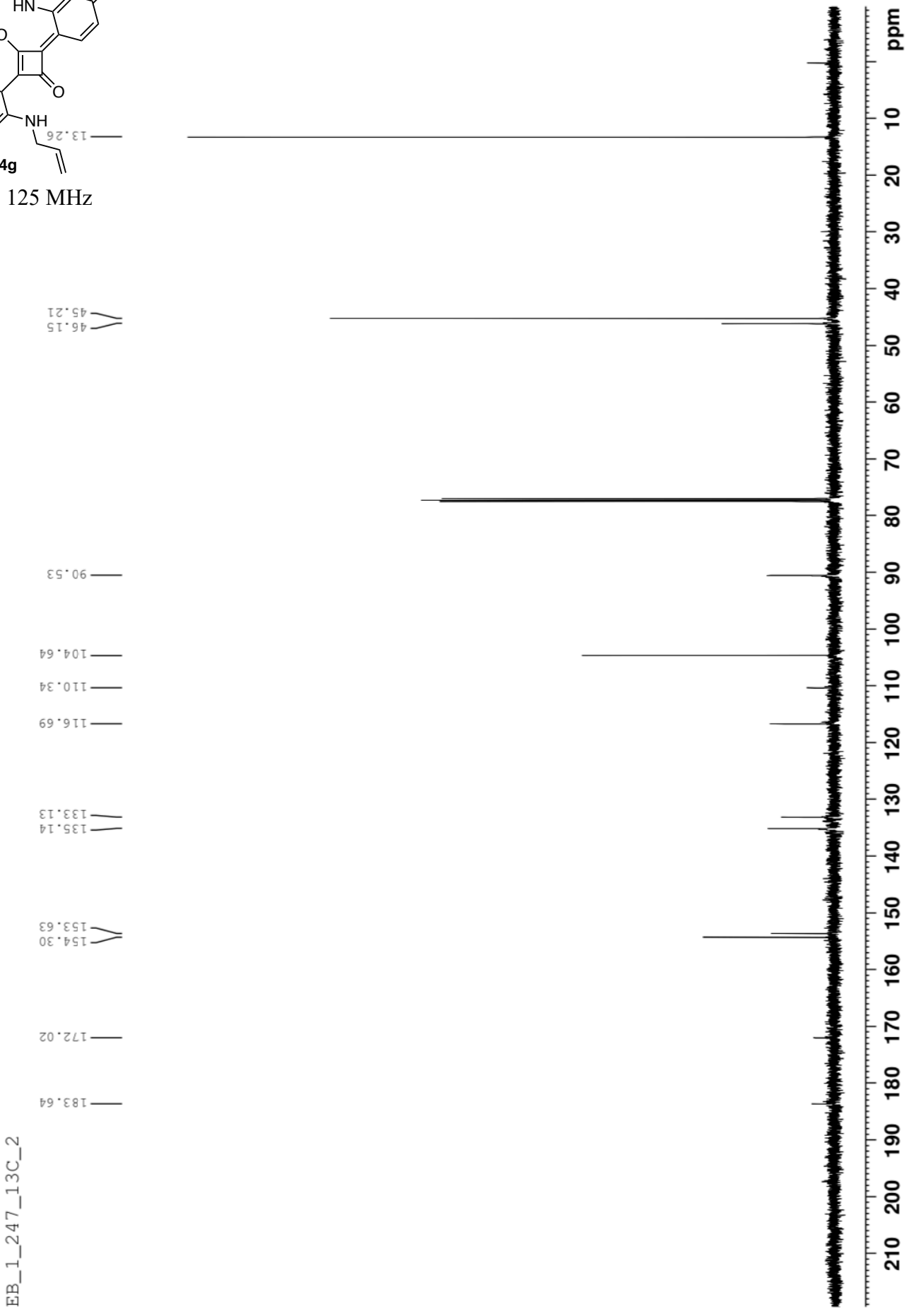


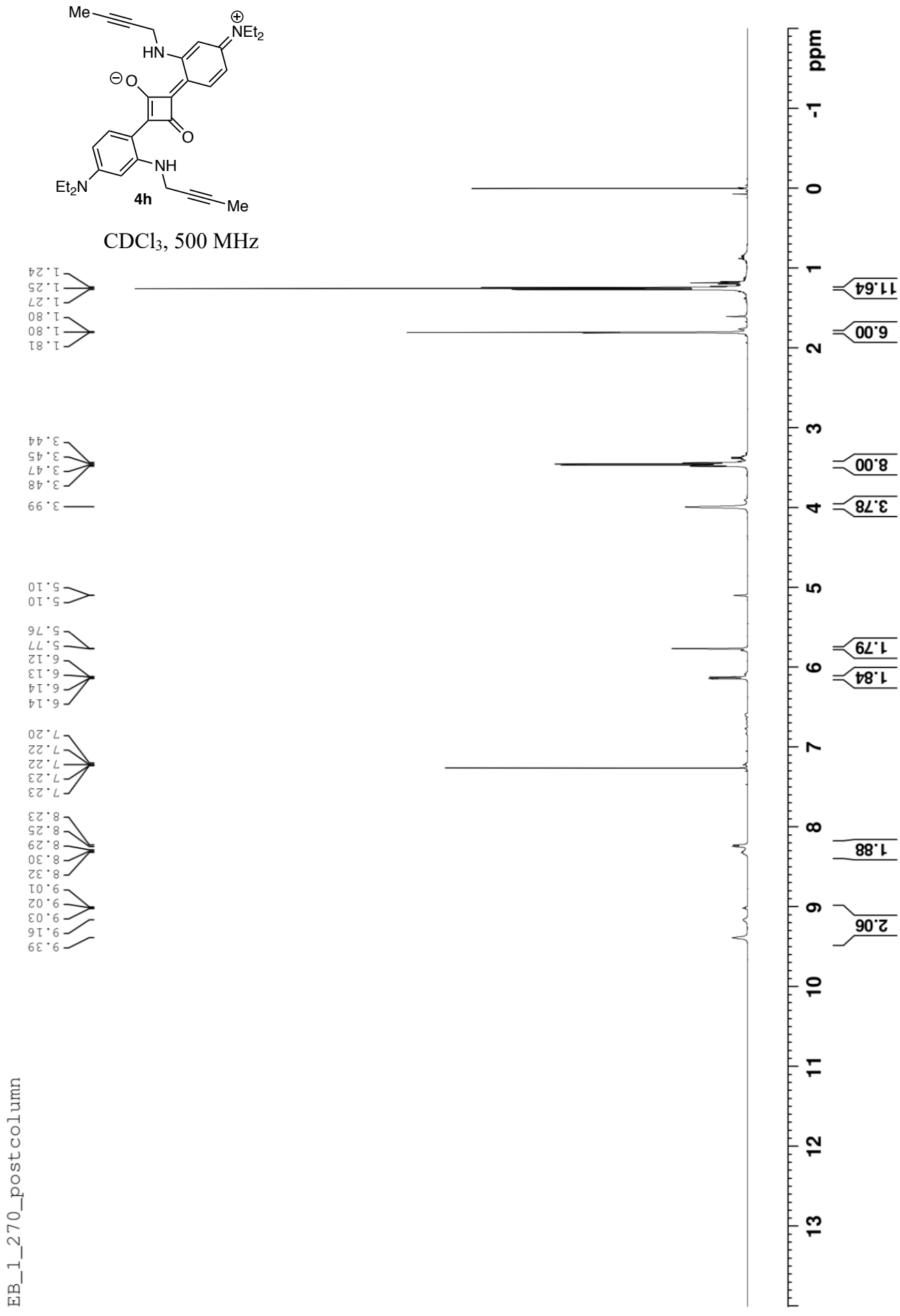

4g
CDCl3, 500 MHz
EB_1_247_vacoven
ppm
12.00
8.19
4.08
1.96
1.97
2.00
1.75
2.03
1.84
2.04

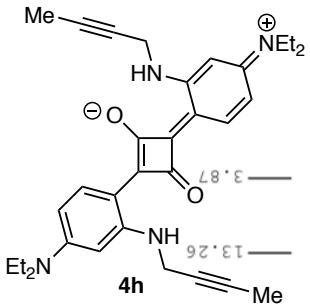


4g

$CDCl_3$, 125 MHz

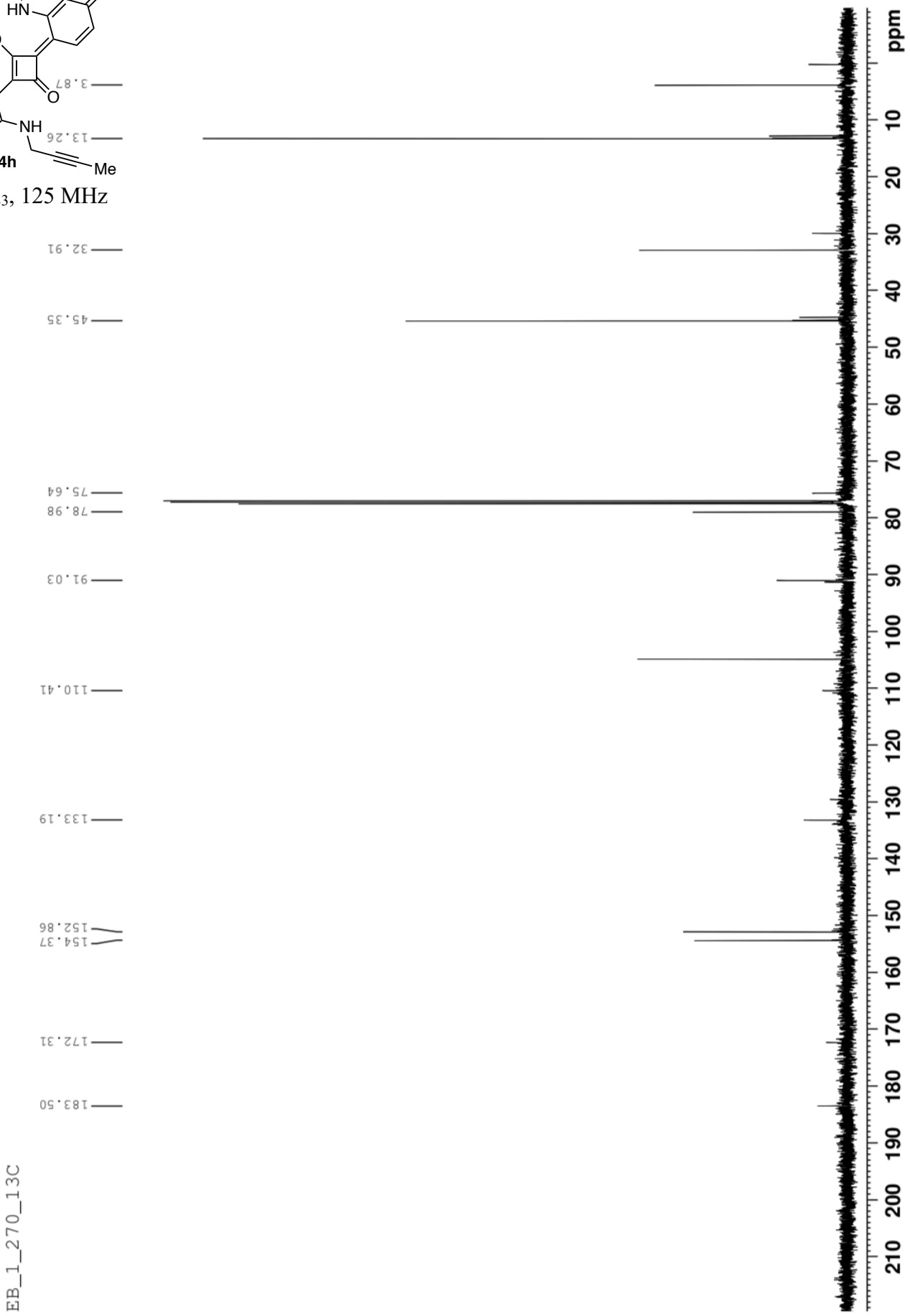


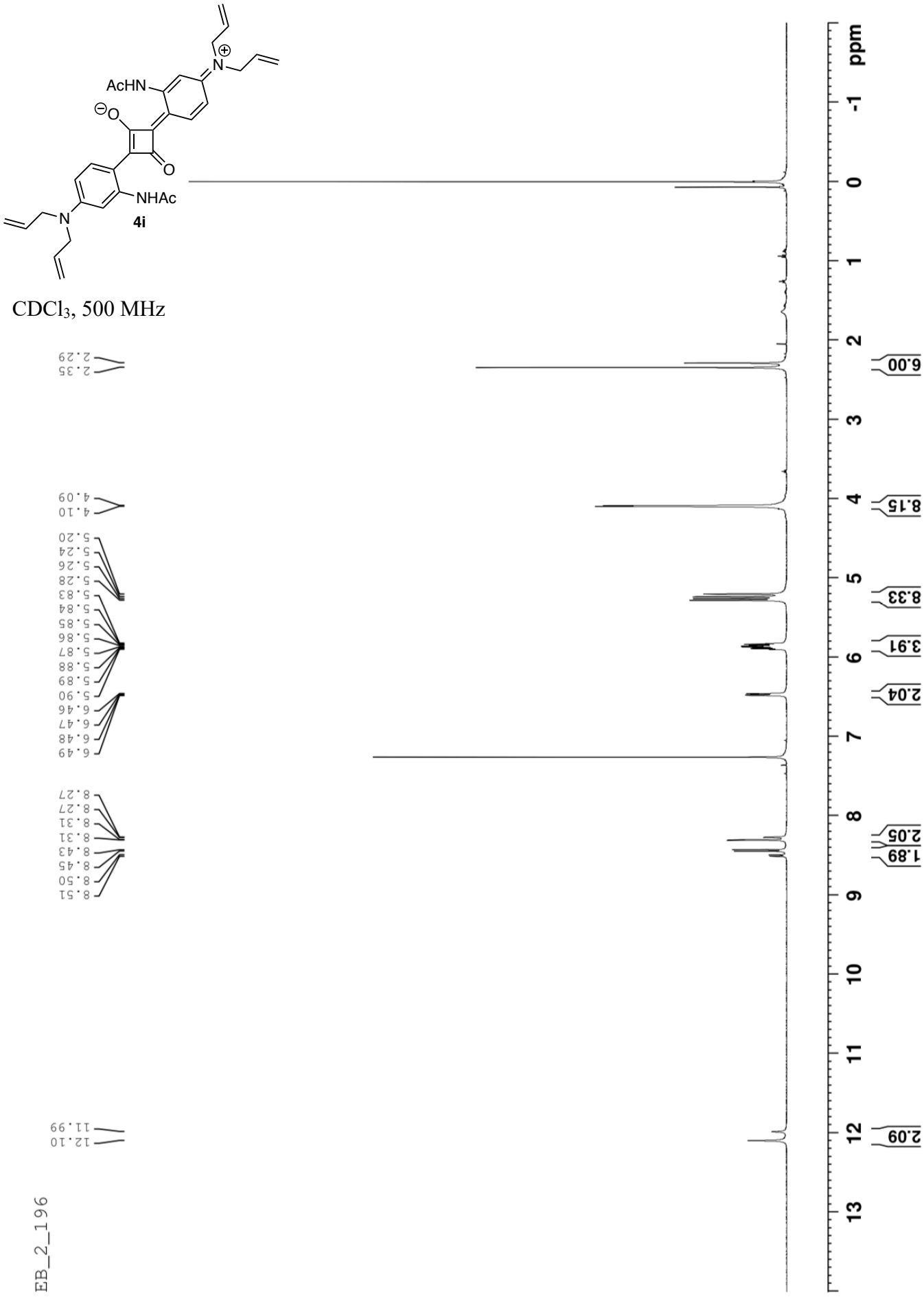

Me
HN
NEt2
O
O
NH
Et2N
Me
4h
CDCl3, 500 MHz
1.24
1.25
1.27
1.80
1.80
1.81
3.44
3.45
3.47
3.48
3.99
5.10
5.10
5.76
5.77
6.12
6.13
6.14
6.14
7.20
7.22
7.22
7.23
7.23
8.23
8.25
8.29
8.30
8.32
9.01
9.02
9.03
9.16
9.39
11.64
6.00
8.00
3.78
1.79
1.84
1.88
2.06
ppm
EB_1_270_postcolumn

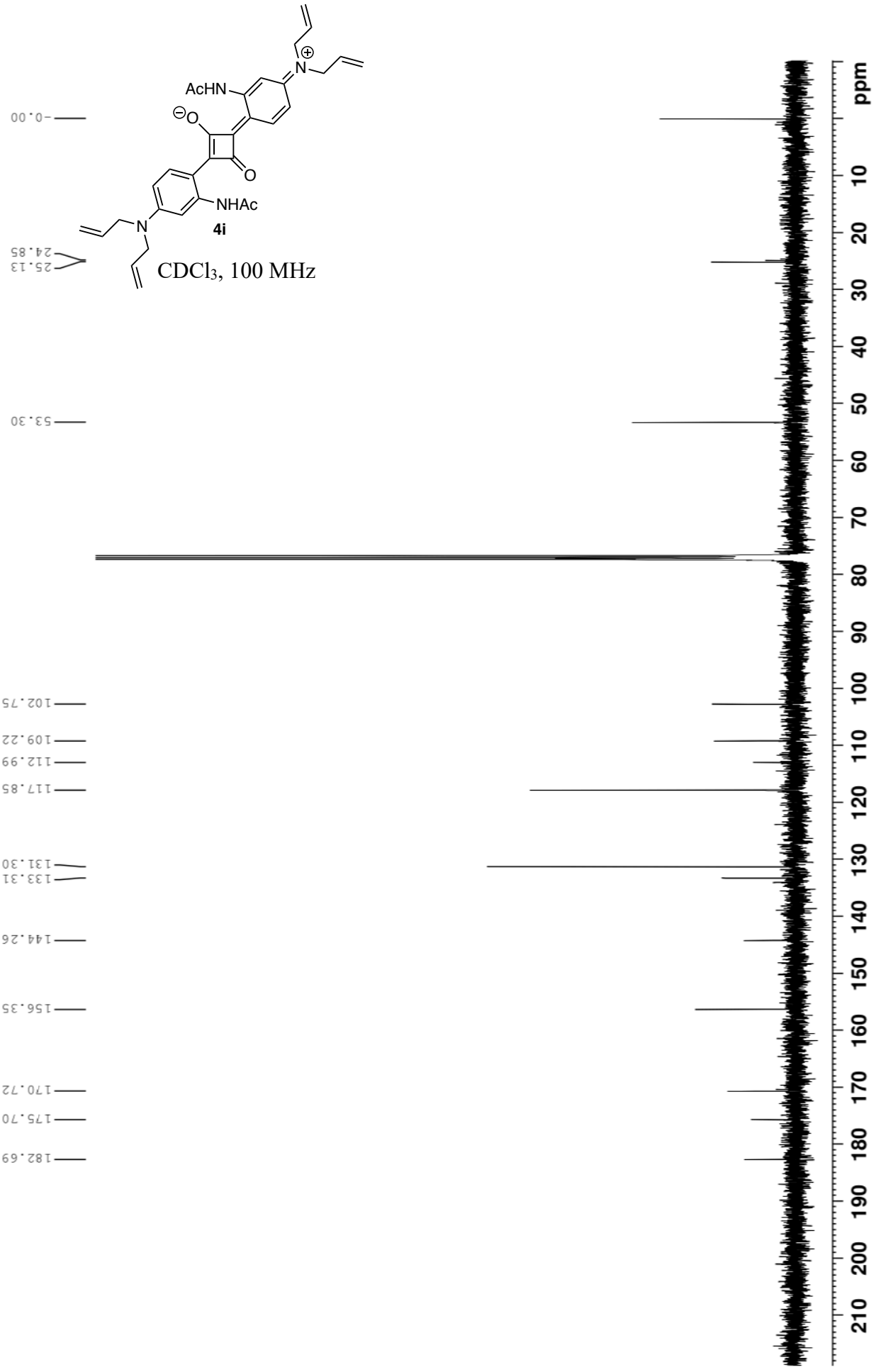


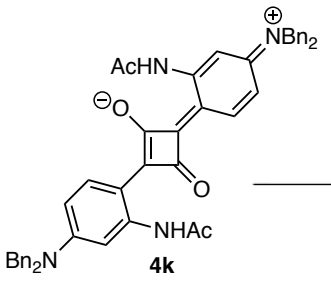
4h

$CDCl_3$, 125 MHz



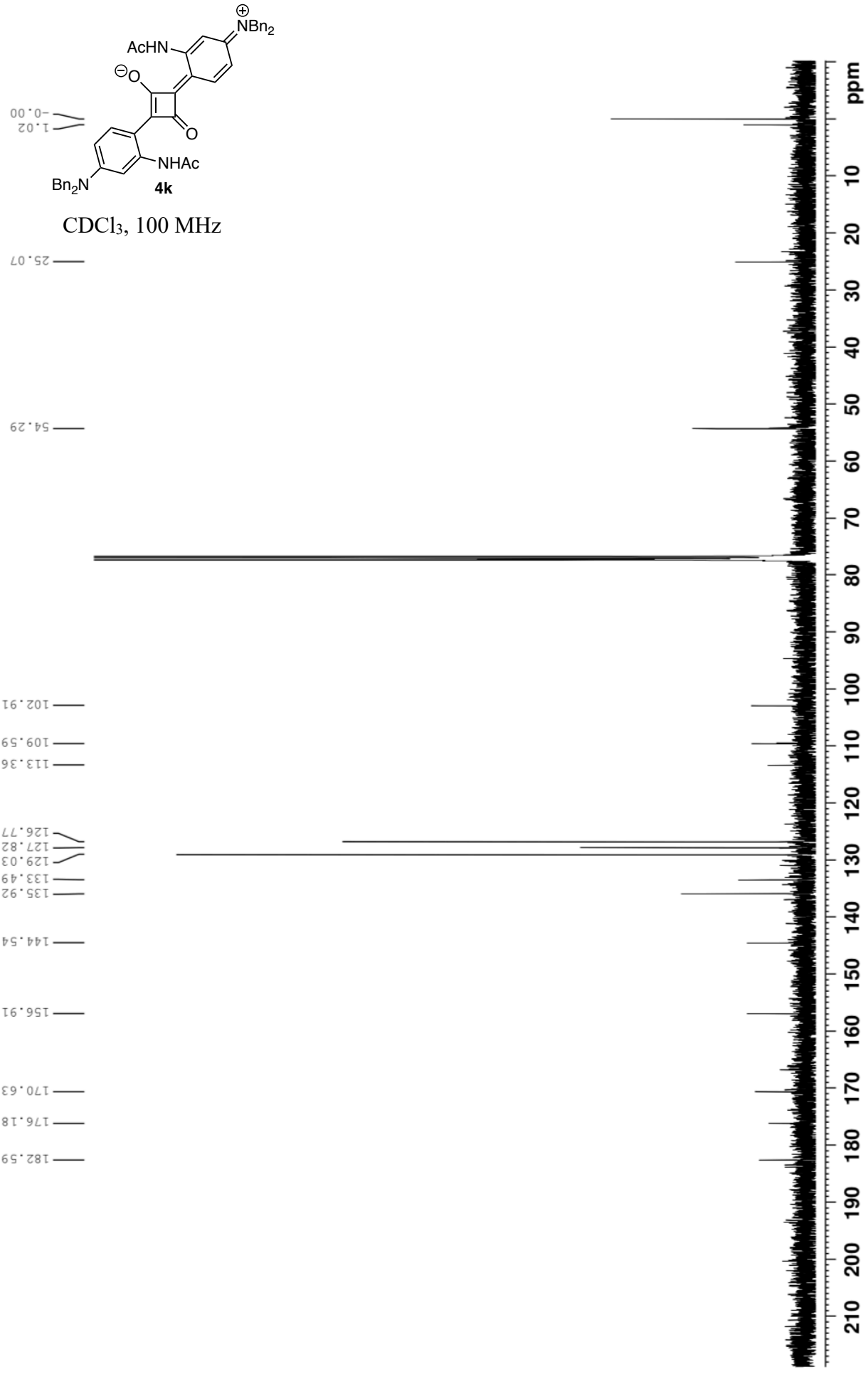

AcHN
NHAc
4i
CDCl3, 500 MHz
EB_2_196
ppm
6.00
8.15
8.33
3.91
2.04
2.05
1.89
2.09

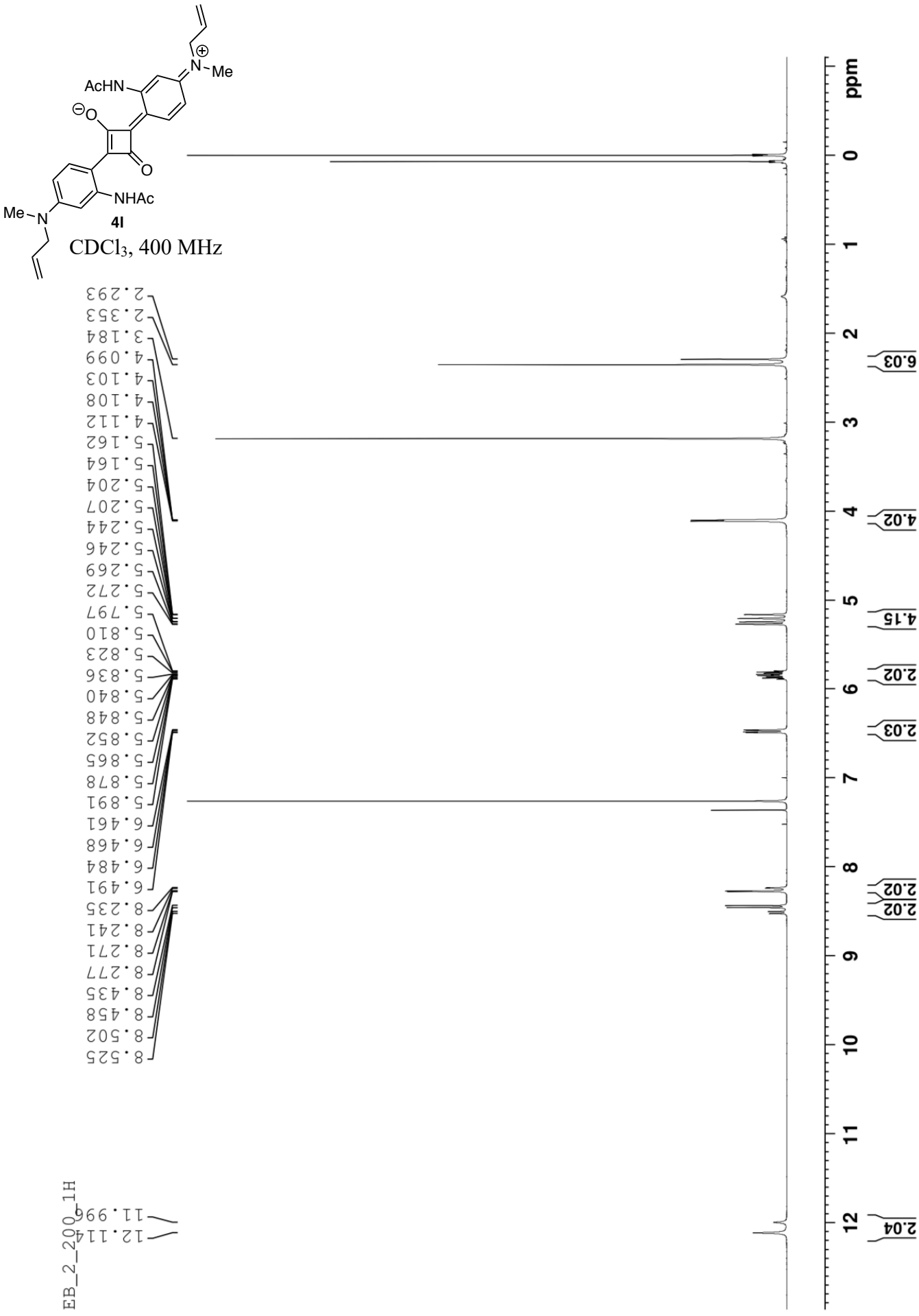

AcHN
NHAc
4i
CDCl3, 100 MHz
-0.00
24.85
25.13
53.30
102.75
109.22
112.99
117.85
131.30
133.31
144.26
156.35
170.72
175.70
182.69
ppm
EB_2_196_13C

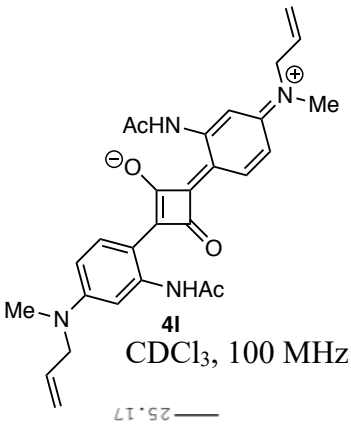


4k

$CDCl_3$, 400 MHz

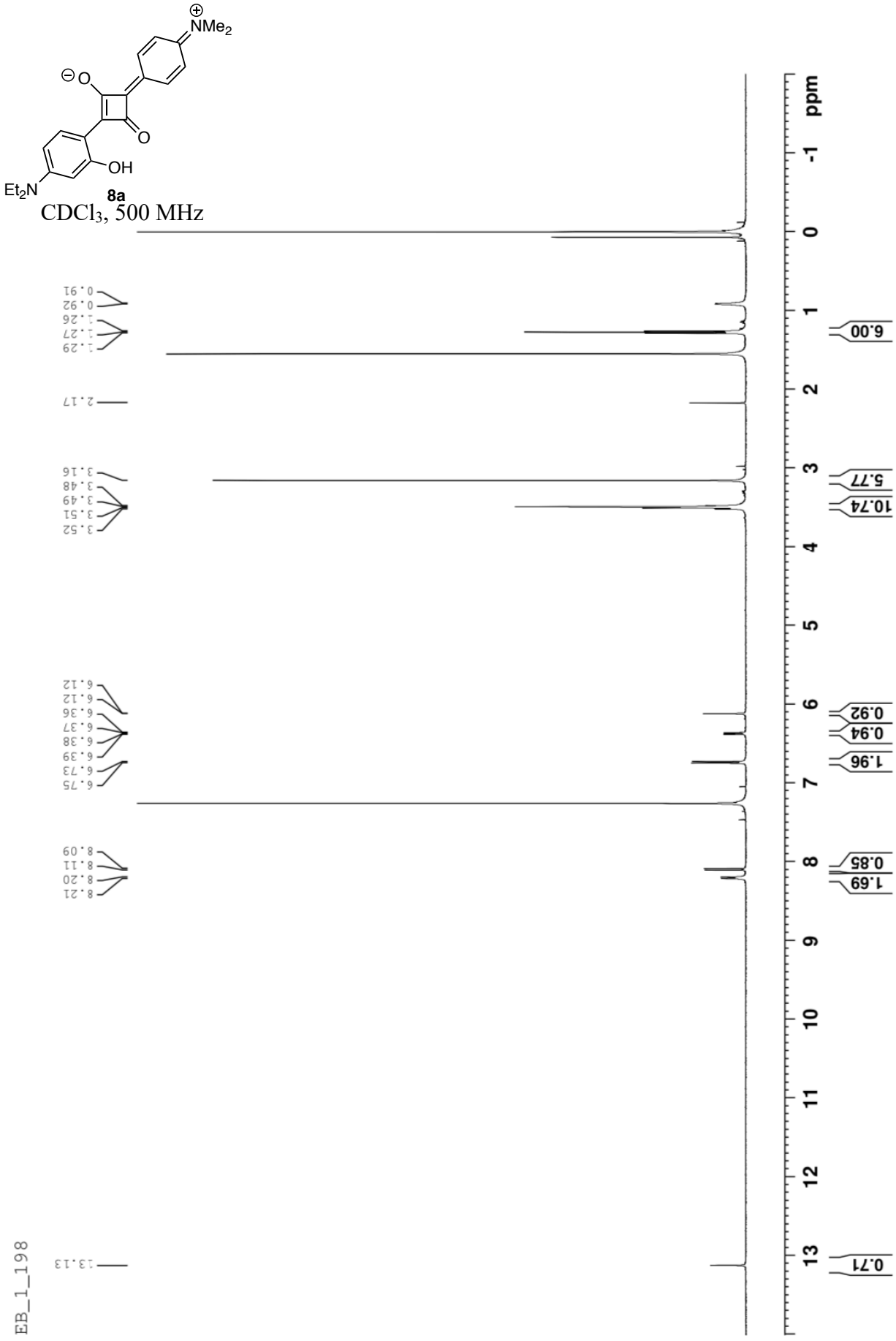

AcHN
NBn2
O
O
NHAc
Bn2N
4k
CDCl3, 100 MHz
AK_1_023_13C
ppm

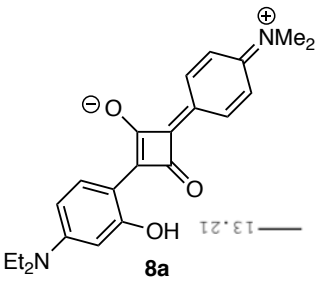

AcHN
N
Me
O
O
NHAc
Me
N
4l
CDCl3, 400 MHz
EB_2_200_1H
ppm
6.03
4.02
4.15
2.02
2.03
2.02
2.02
2.04



4l

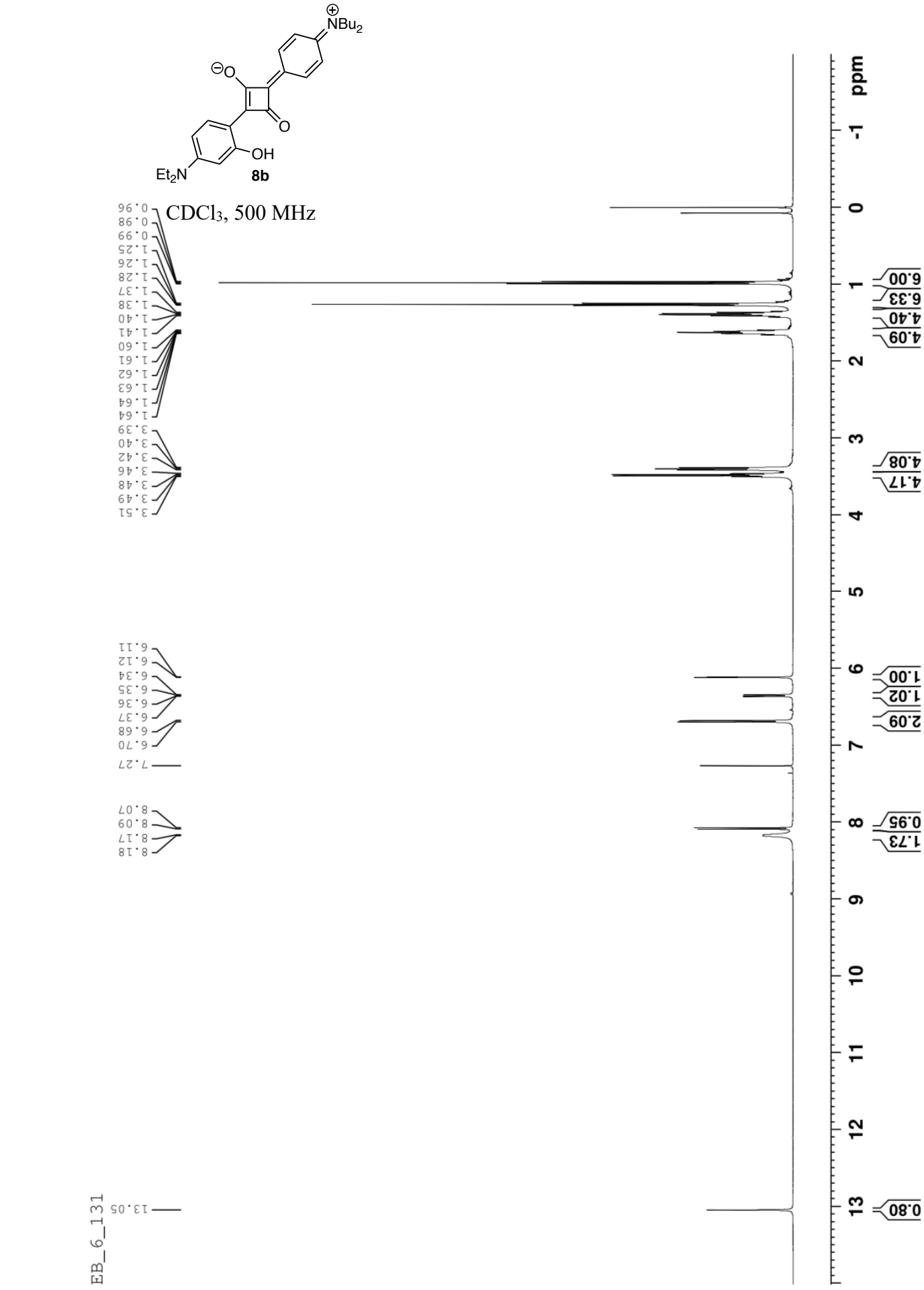
$CDCl_3$, 100 MHz

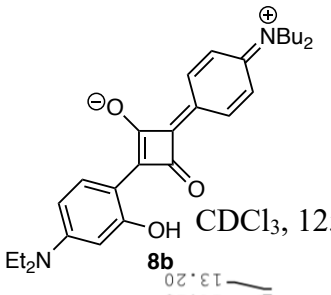

NMe2
O
O
OH
Et2N
8a
CDCl3, 500 MHz
EB_1_198
ppm
13.13
8.21
8.20
8.11
8.09
6.75
6.73
6.39
6.38
6.37
6.36
6.12
6.12
3.52
3.51
3.49
3.48
3.16
2.17
1.29
1.27
1.26
0.92
0.91
0.71
1.69
0.85
1.96
0.94
0.92
10.74
5.77
6.00



8a

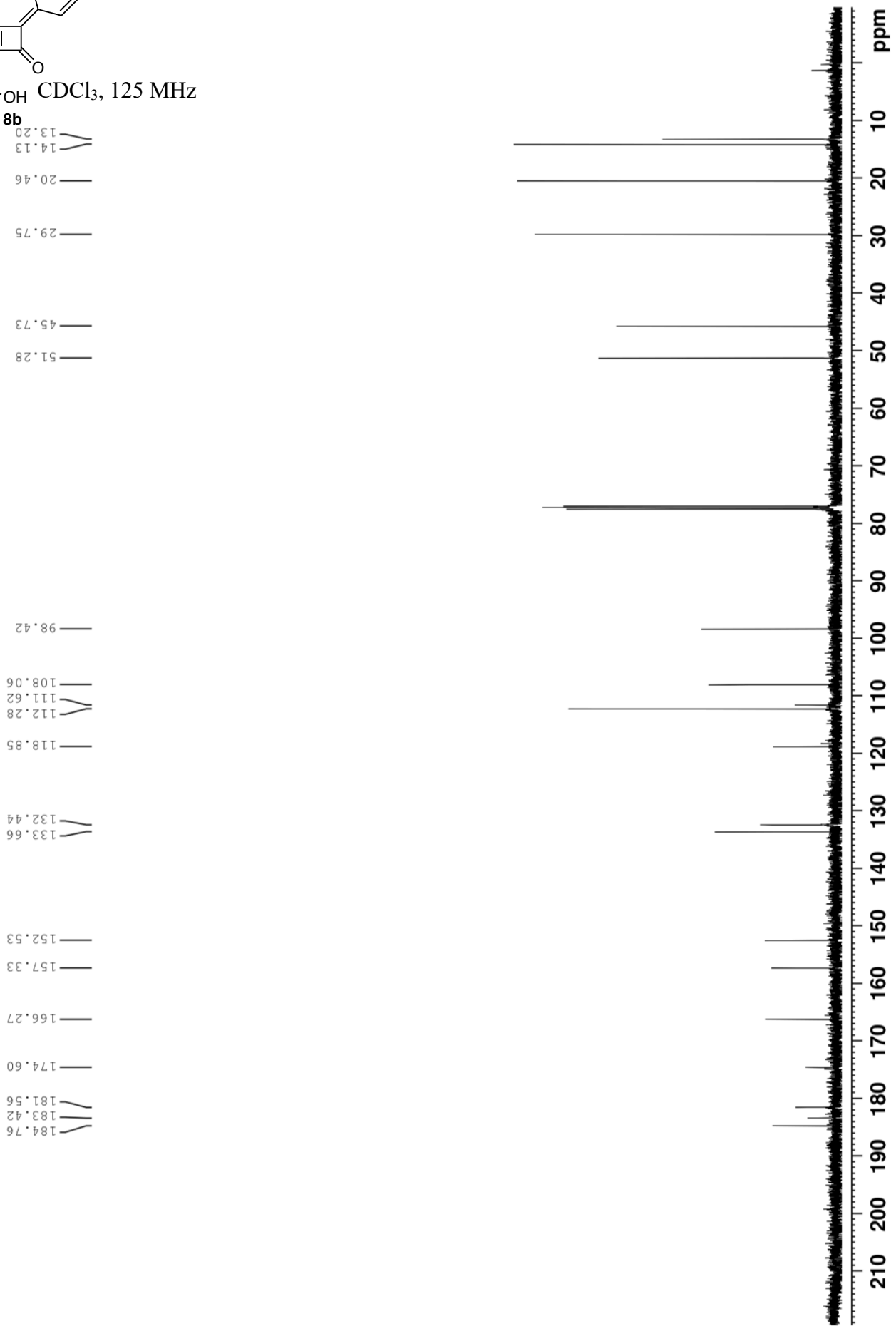
$CDCl_3$, 125 MHz


NBu2
O
O
OH
Et2N
8b
CDCl3, 500 MHz
EB_6_131
ppm

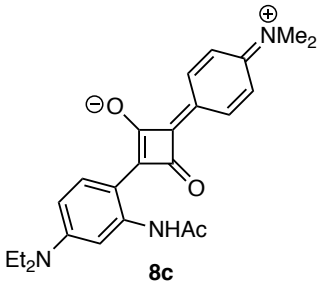


8b

$CDCl_3$, 125 MHz

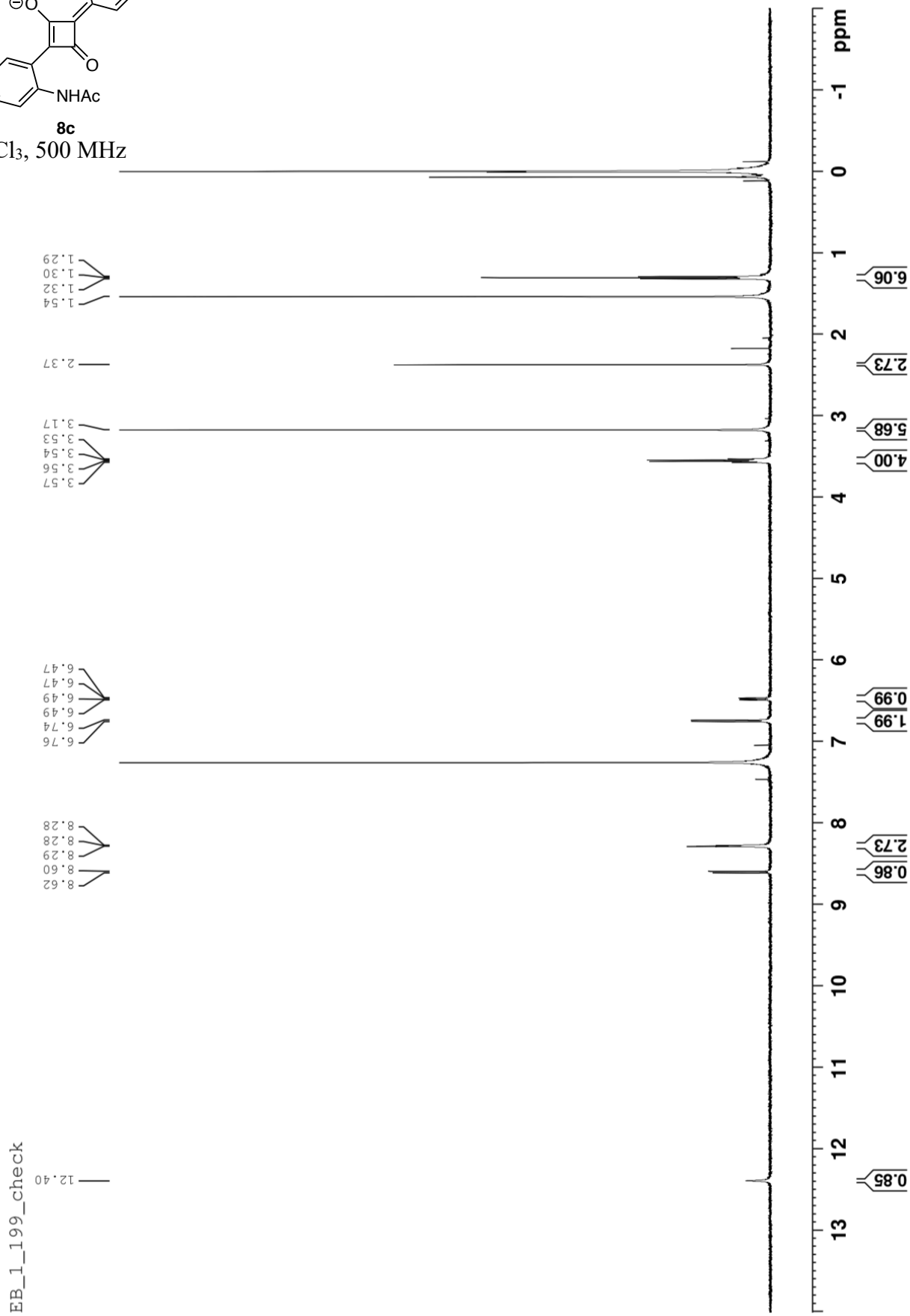


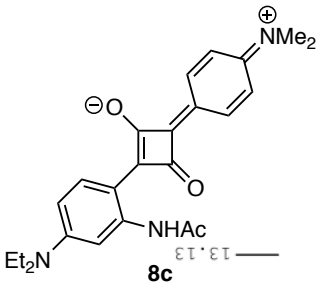
EB_6_131_13C



8c

$CDCl_3$, 500 MHz

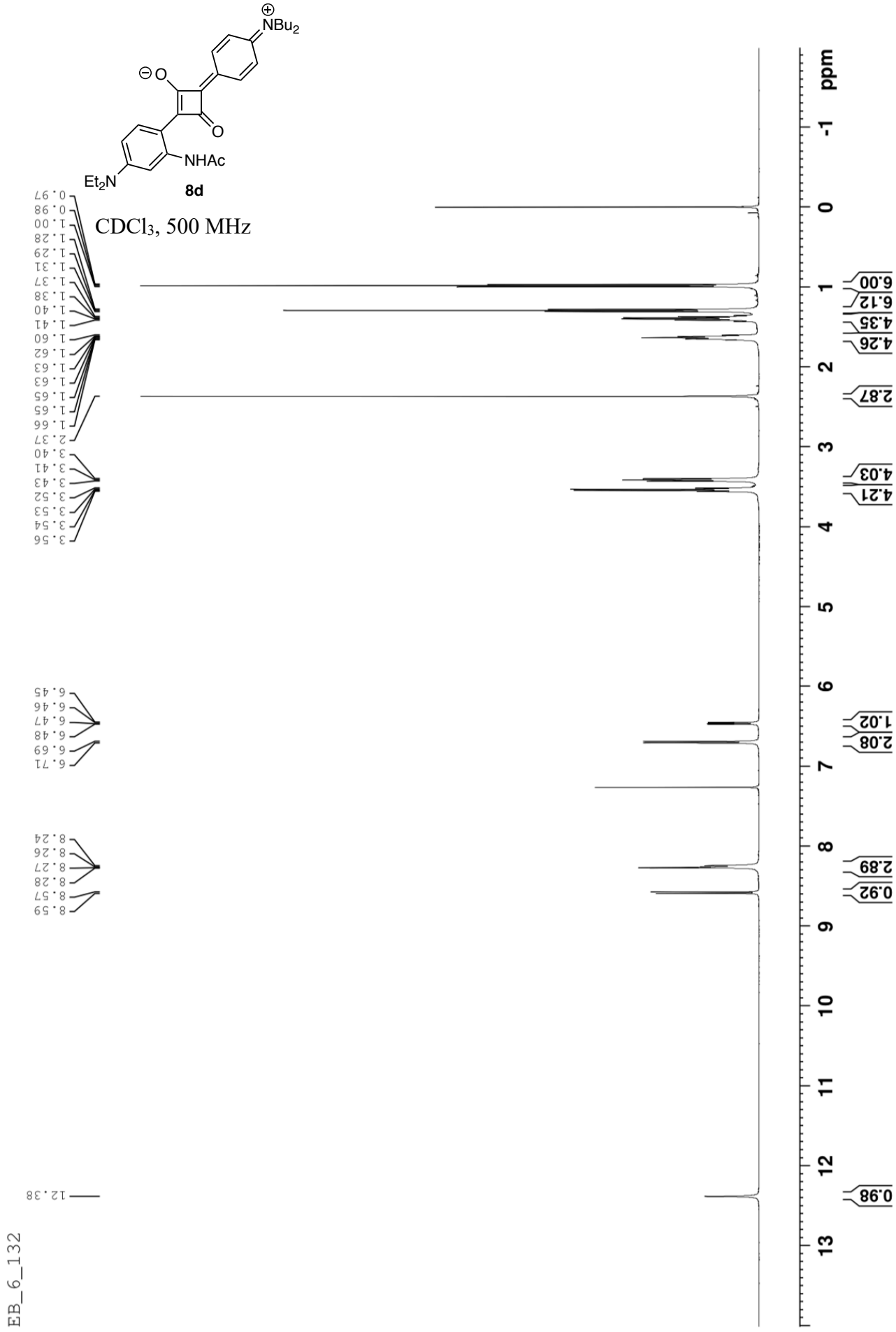


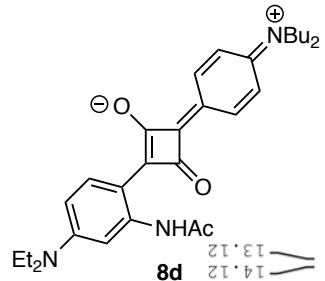


8c

$CDCl_3$, 125 MHz

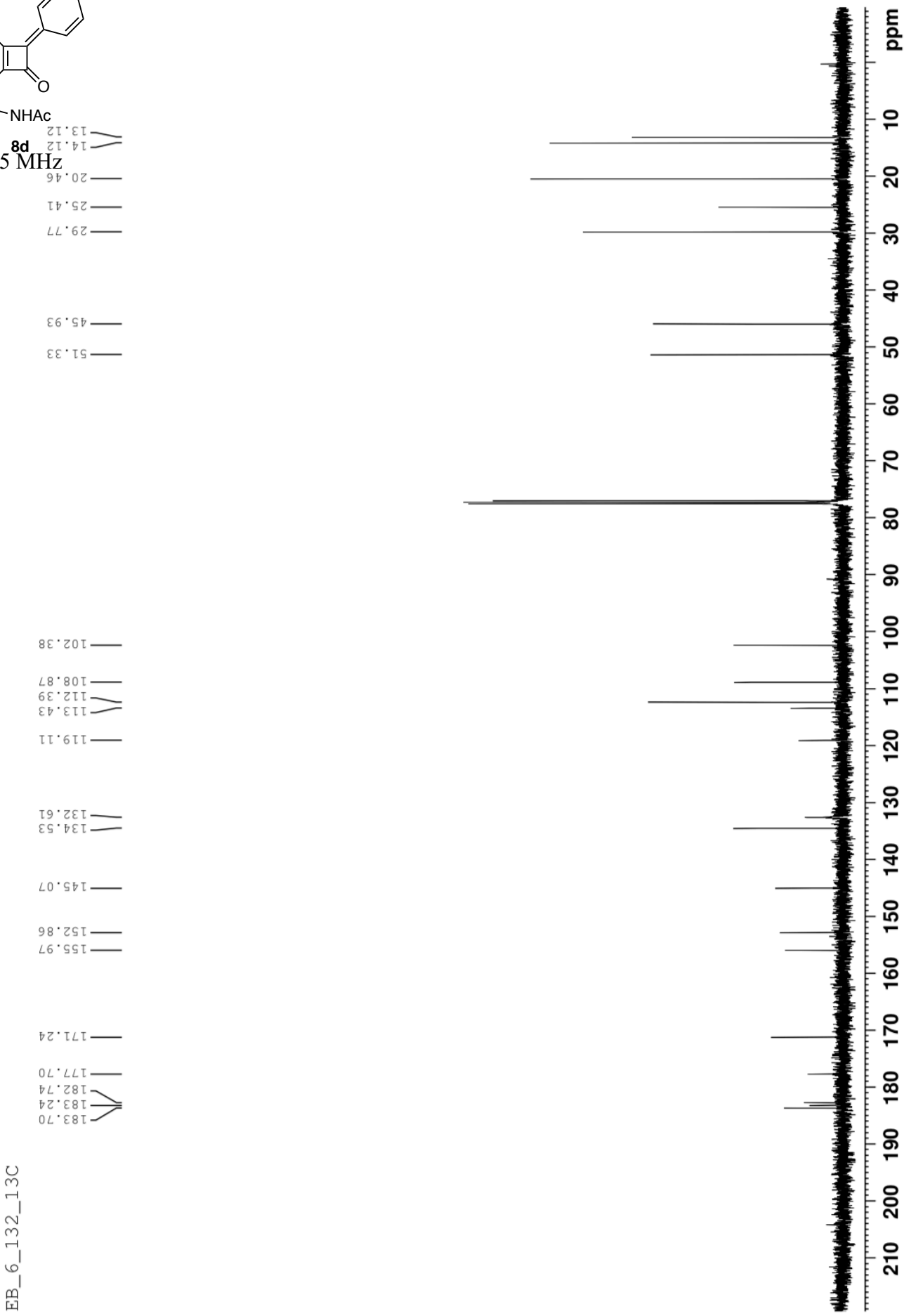
EB_6_165_13C


NBu2
O
O
NHAc
Et2N
8d
CDCl3, 500 MHz
EB_6_132
ppm

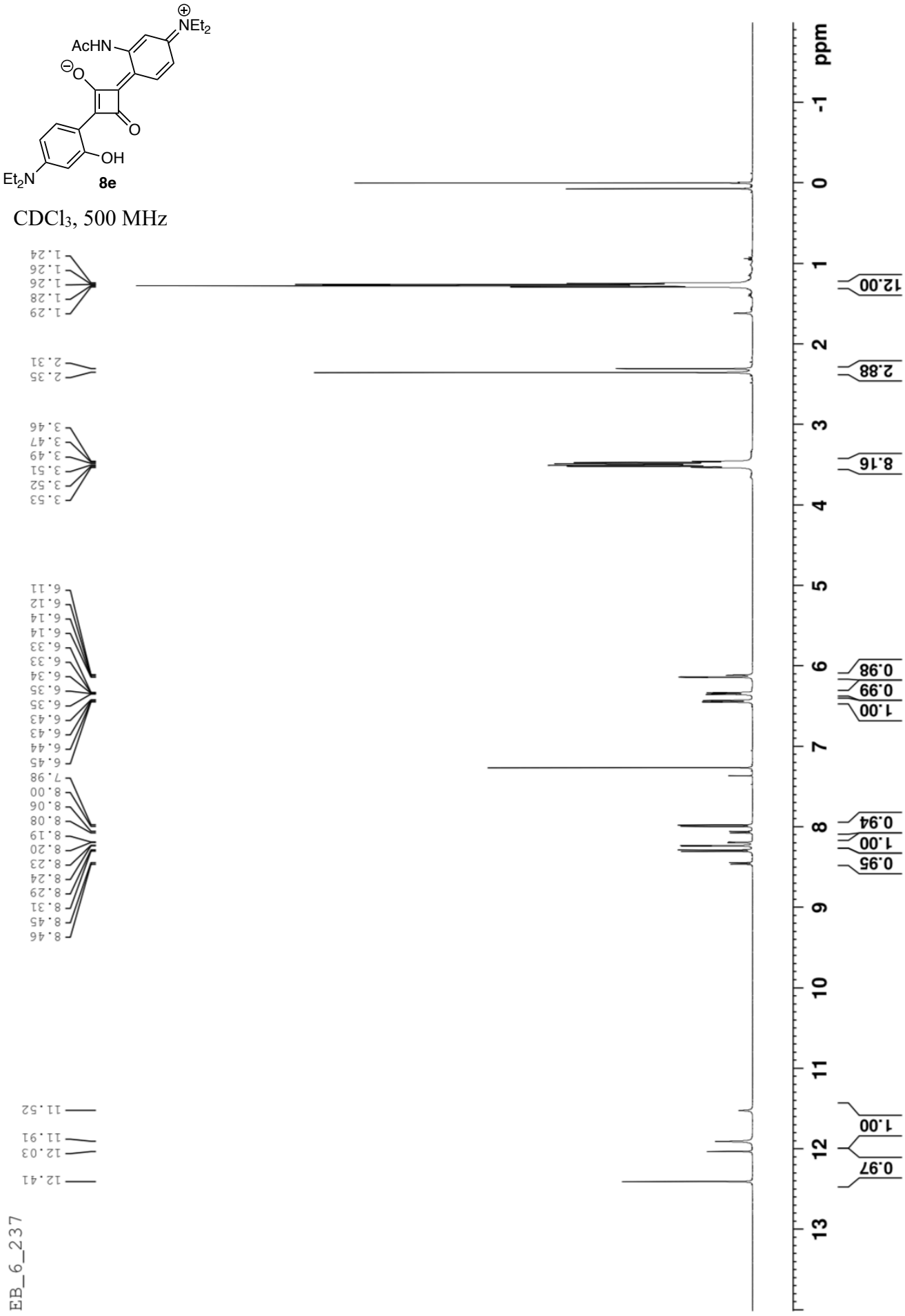


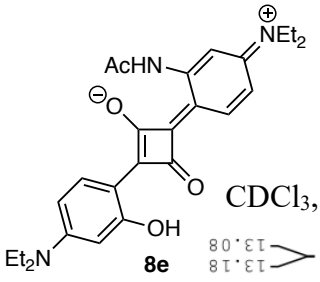
8d

$CDCl_3$, 125 MHz



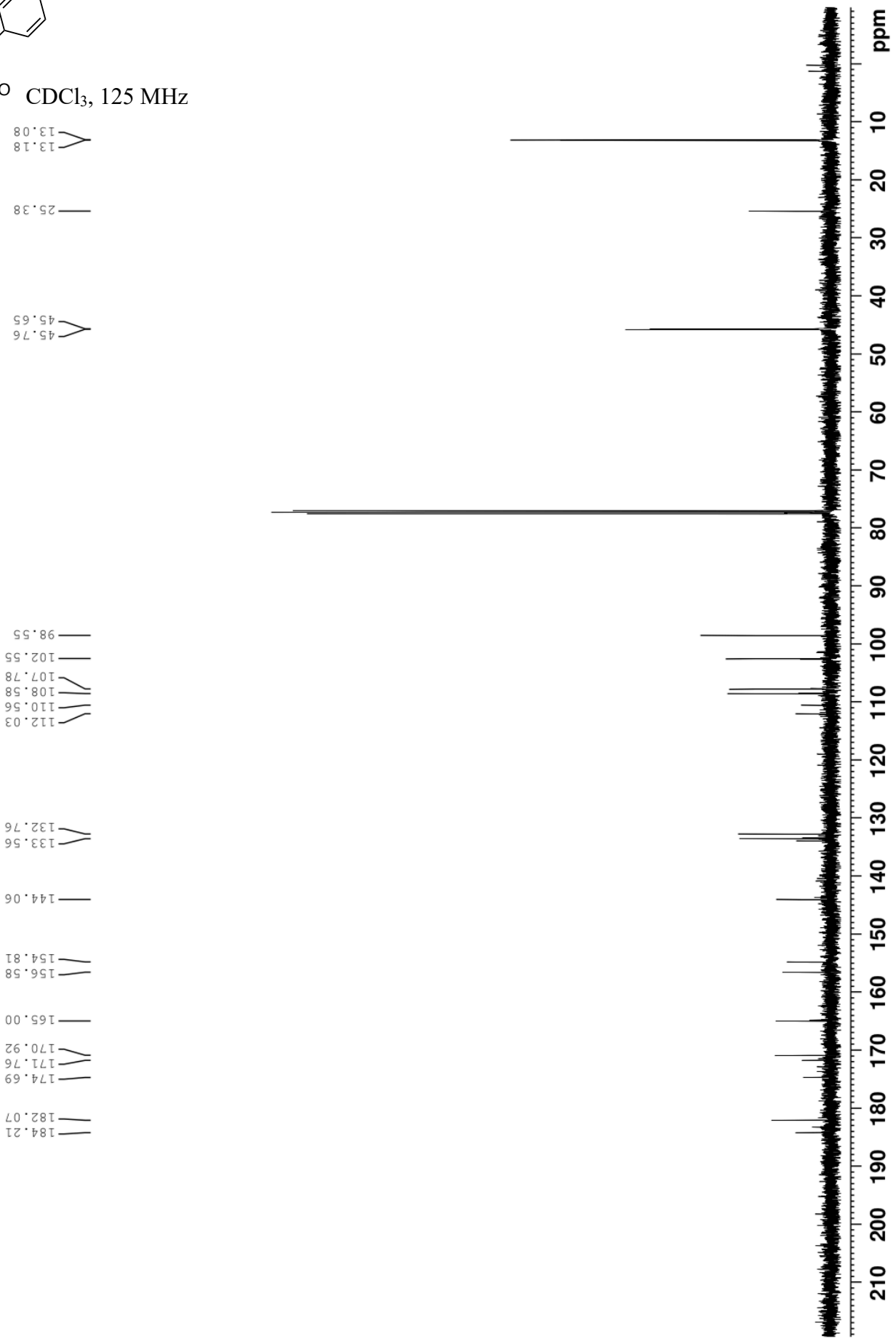
EB_6_132_13C


AcHN
NEt2
O
O
OH
Et2N
8e
CDCl3, 500 MHz
EB_6_237
ppm
12.00
2.88
8.16
0.98
0.99
1.00
0.94
1.00
0.95
1.00
0.97

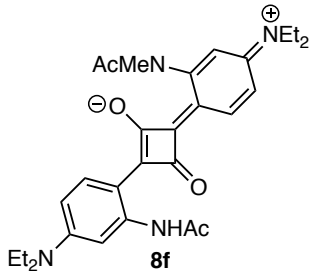


8e

$CDCl_3$, 125 MHz

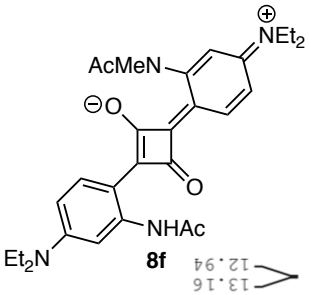


EB_6_237_13C

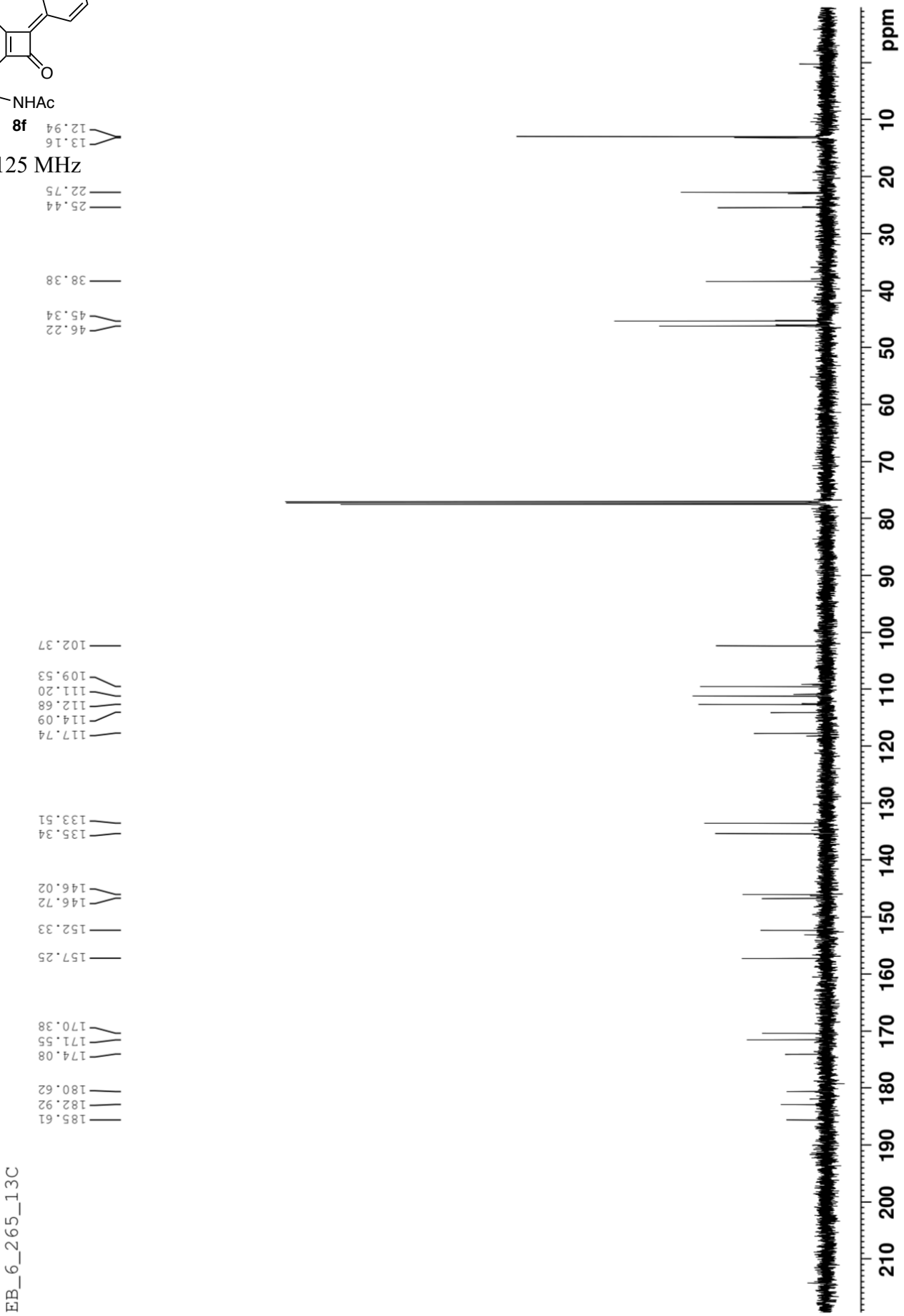


8f

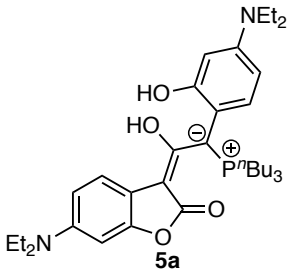
$CDCl_3$, 500 MHz



CDCl$_3$, 125 MHz



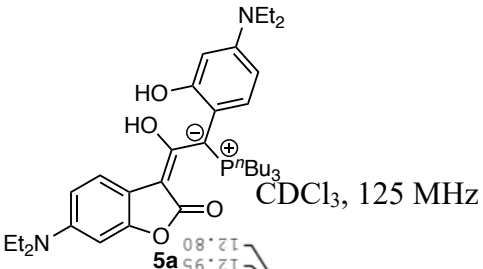
EB_6_265_13C



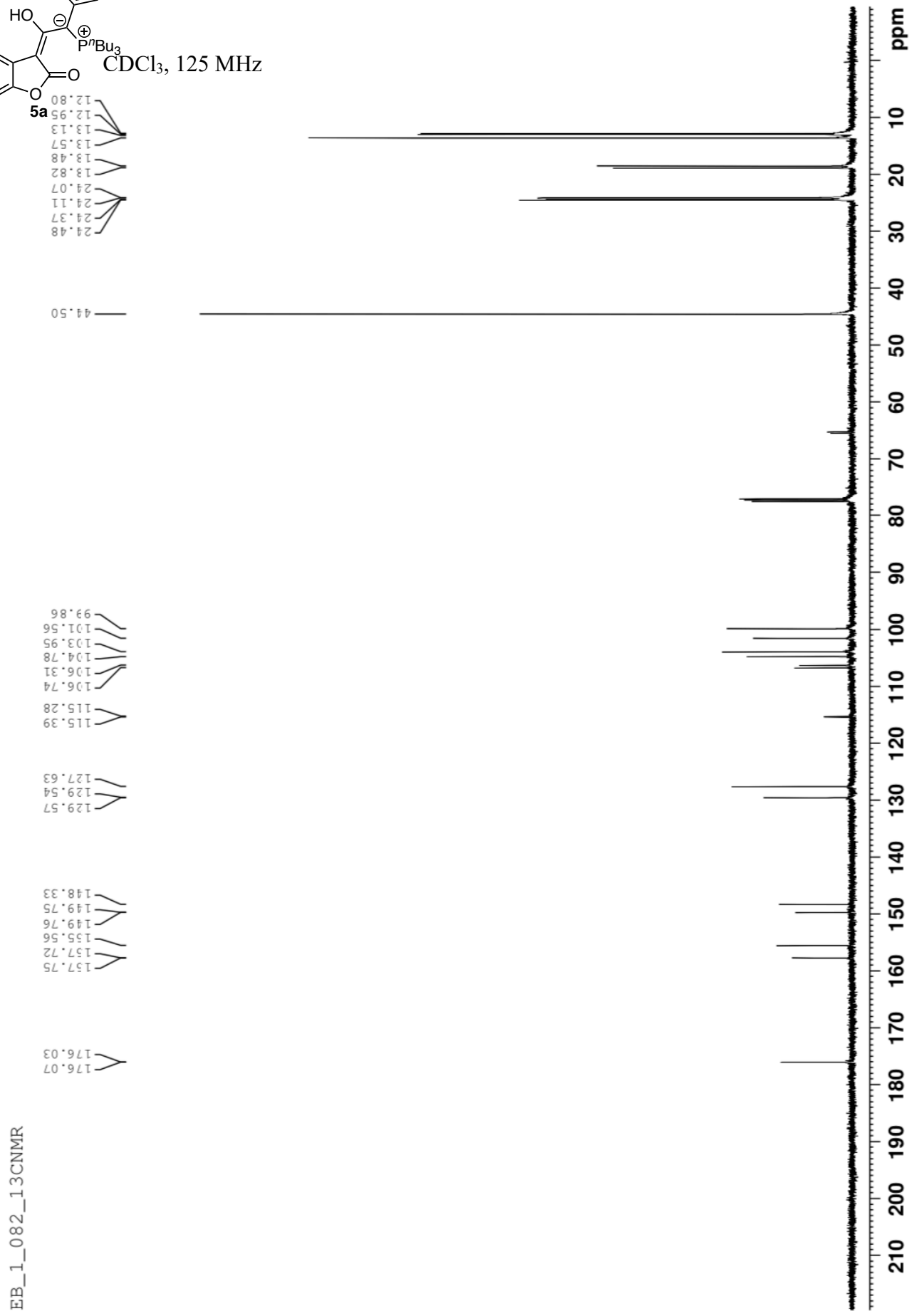
5a

$CDCl_3$, 500 MHz

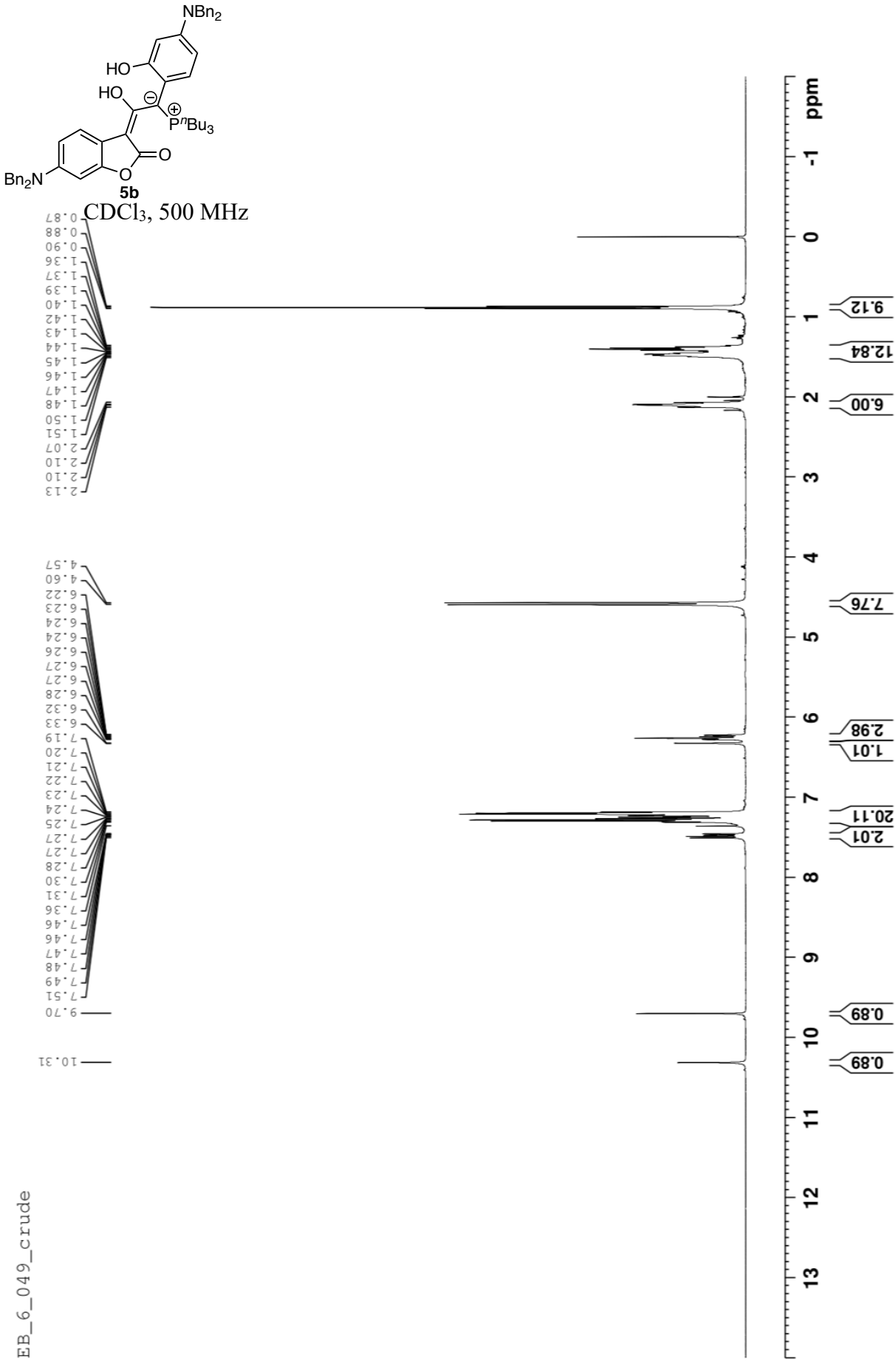
EB_1_082_1HNMR

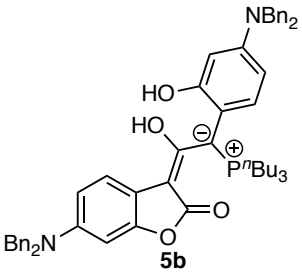


$CDCl_3$, 125 MHz



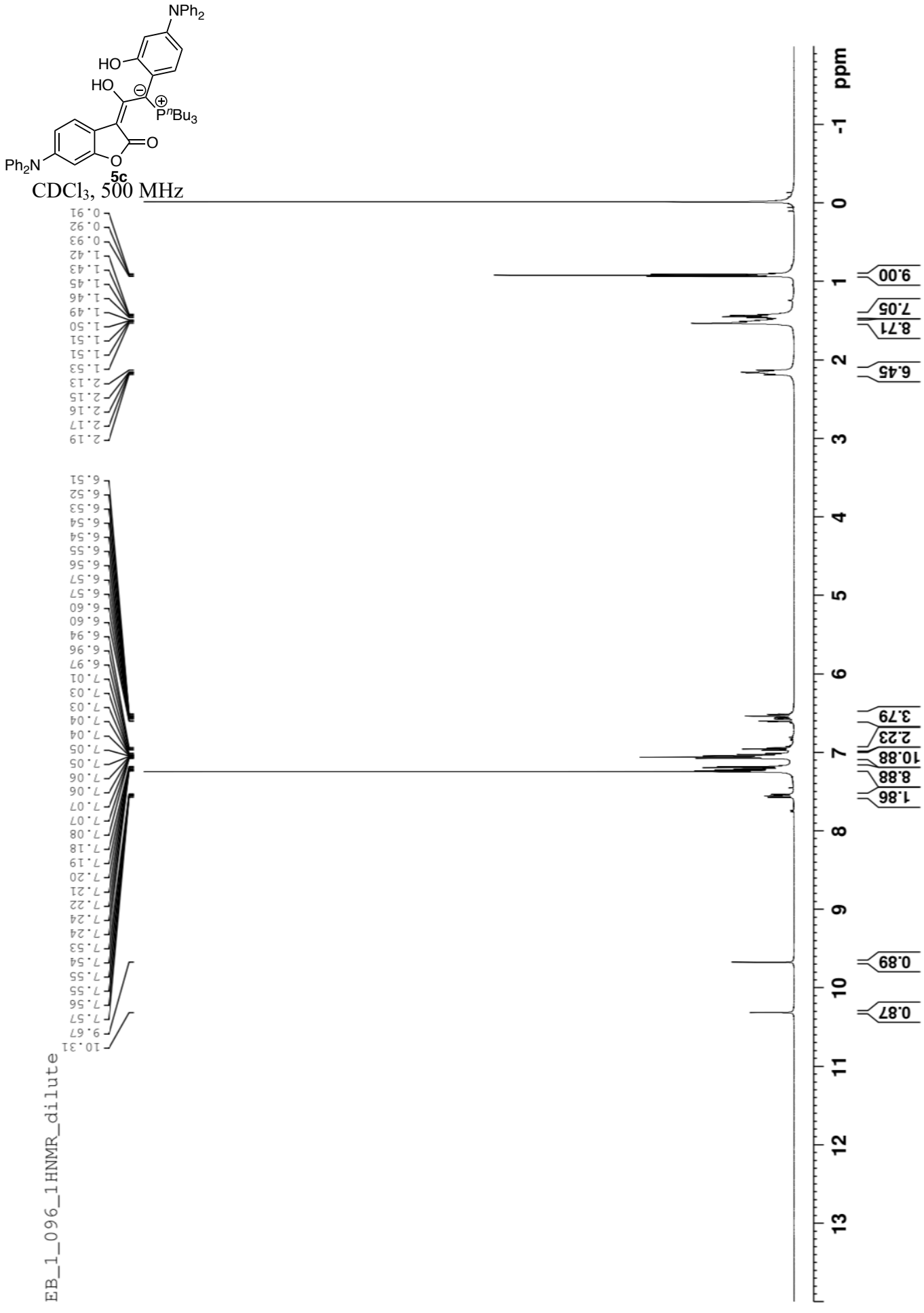
EB_1_082_13CNMR

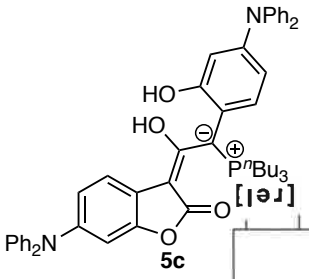

NBn2
HO
HO
P^nBu3
O
O
Bn2N
5b
CDCl3, 500 MHz
EB_6_049_crude
ppm
9.12
12.84
6.00
7.76
2.98
1.01
20.11
2.01
0.89
0.89



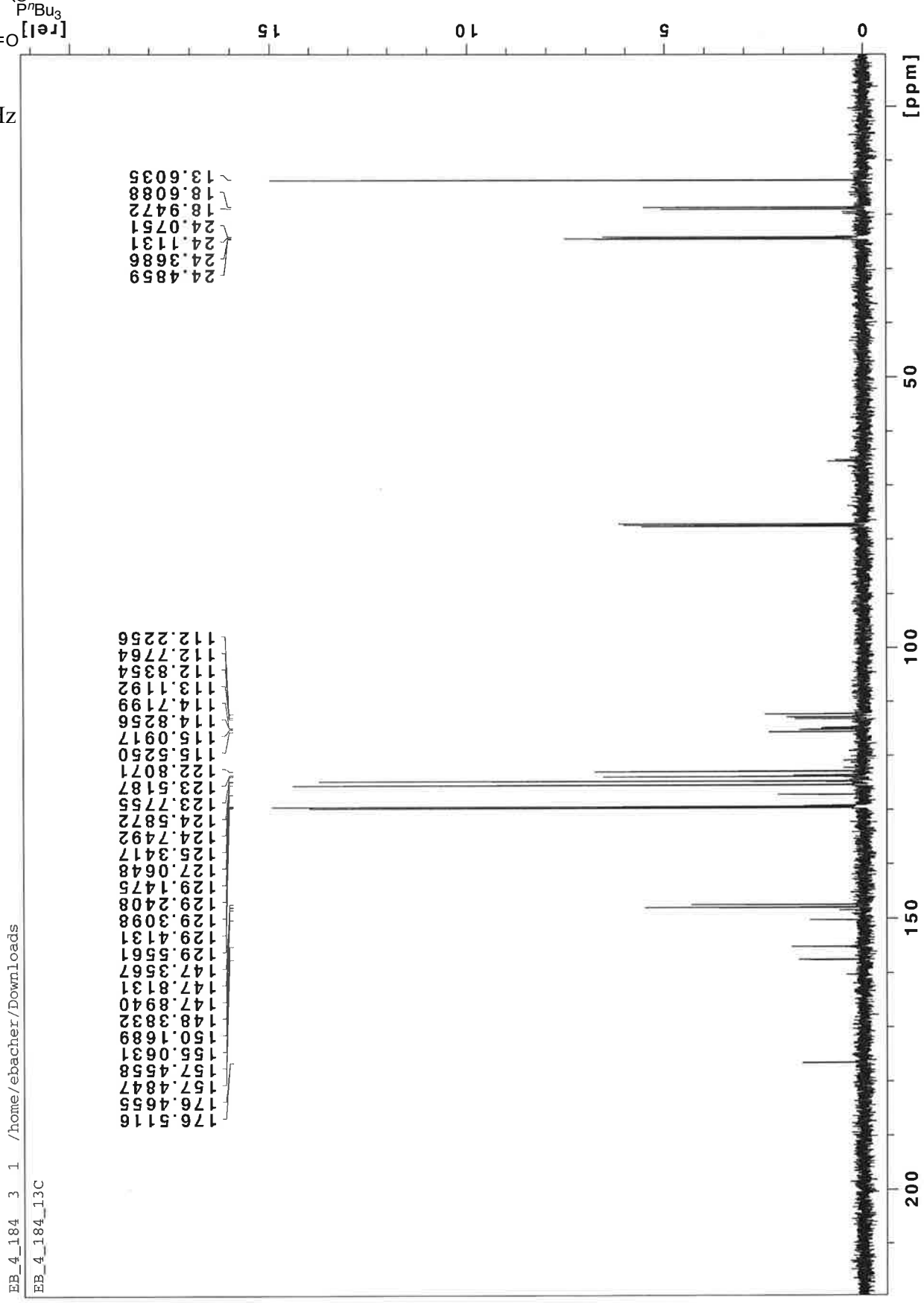
5b

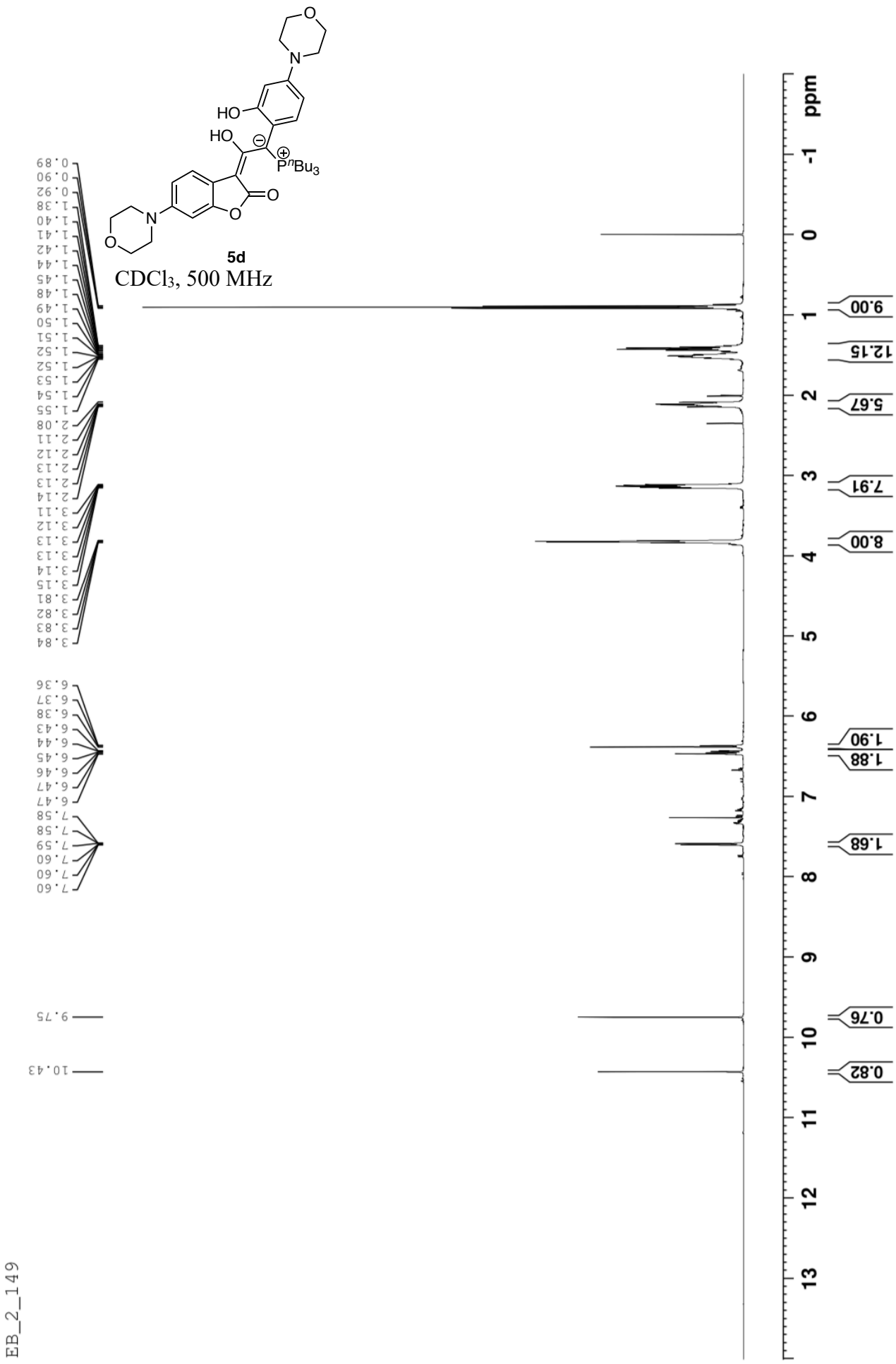
$CDCl_3$, 100 MHz

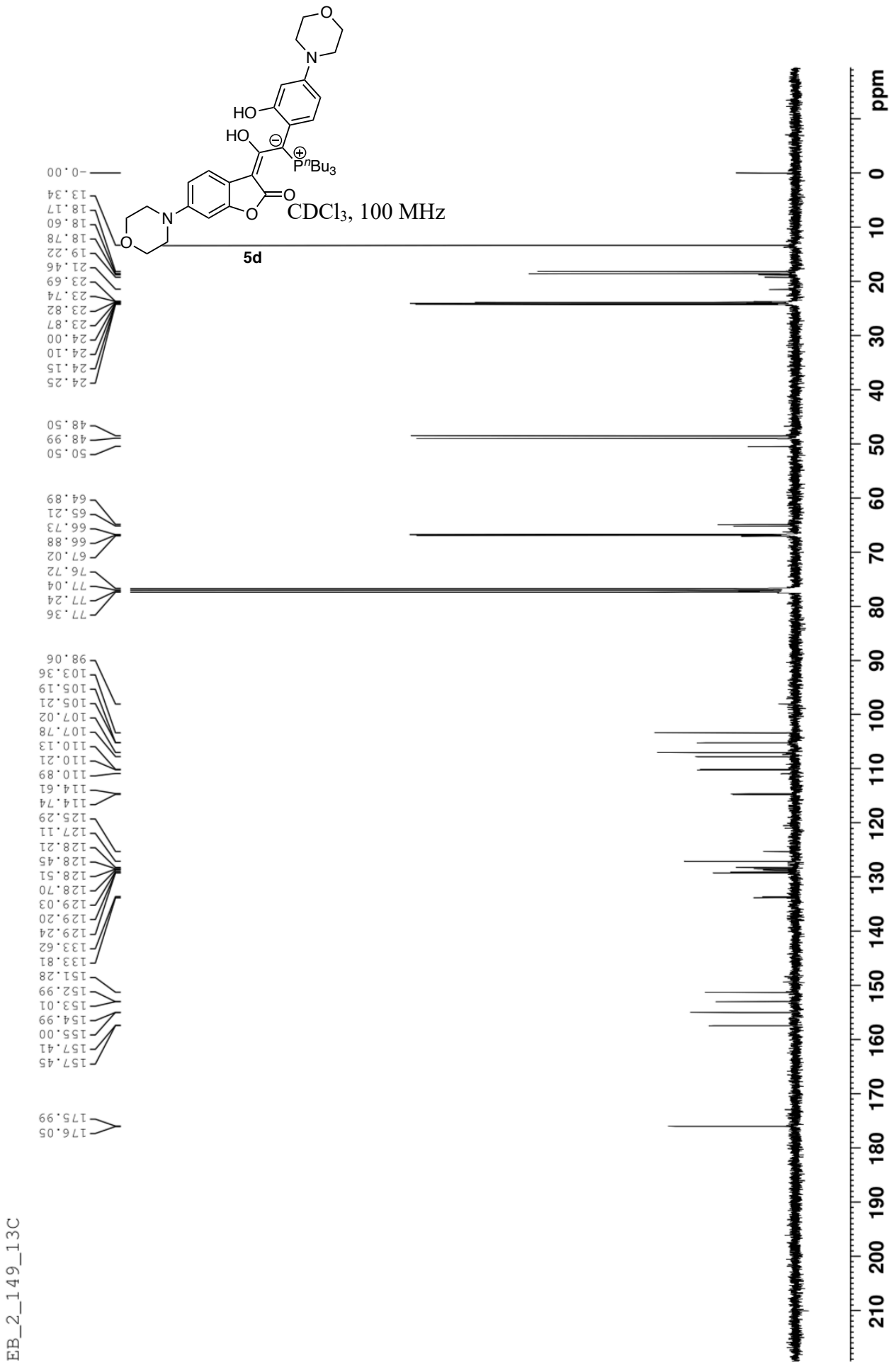

NPh2
HO
HO
P+nBu3
O
Ph2N
O
5c
CDCl3, 500 MHz
EB_1_096_1HNMR_dilute
ppm
9.00
7.05
8.71
6.45
3.79
2.23
10.88
8.88
1.86
0.89
0.87

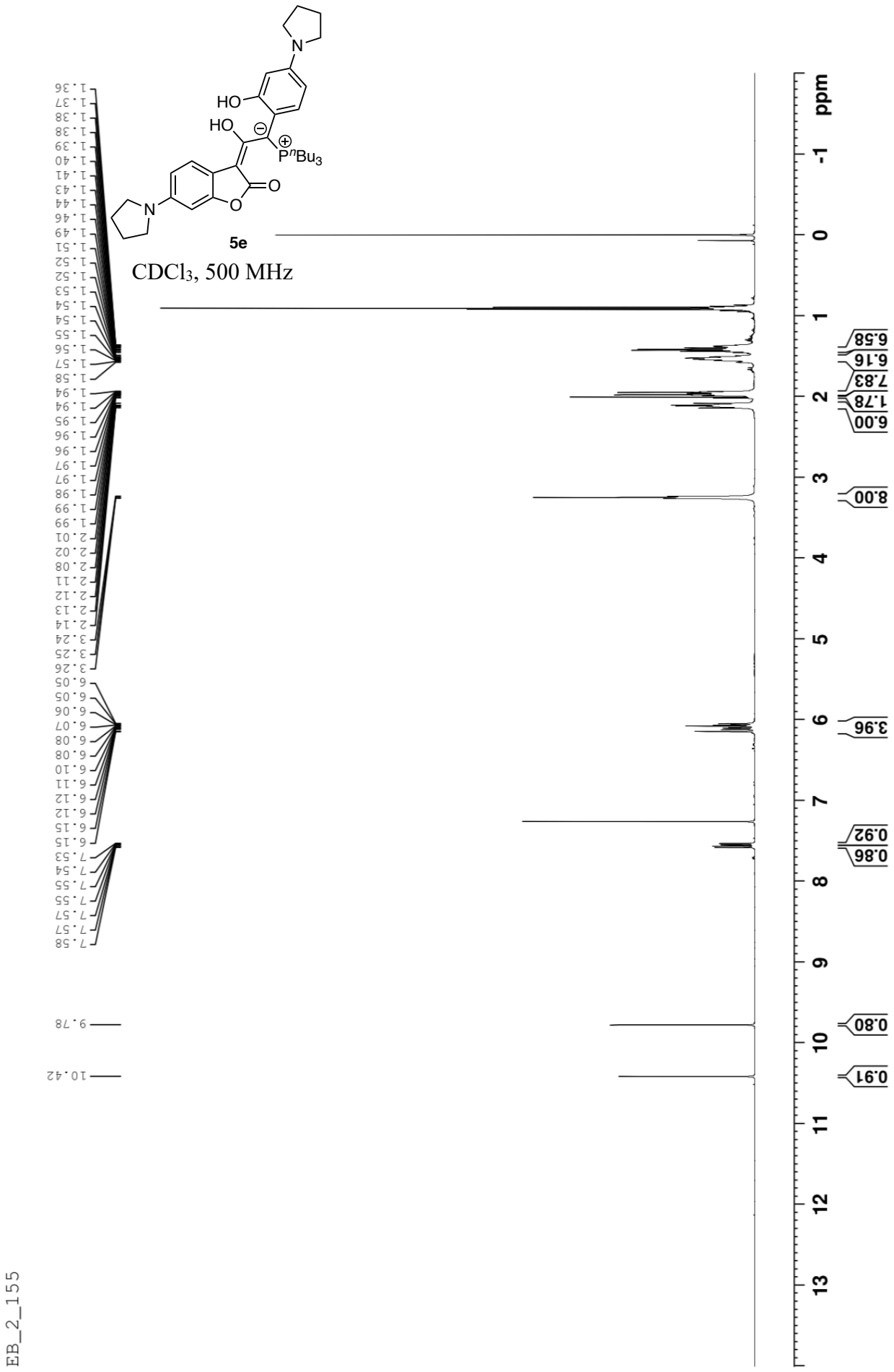


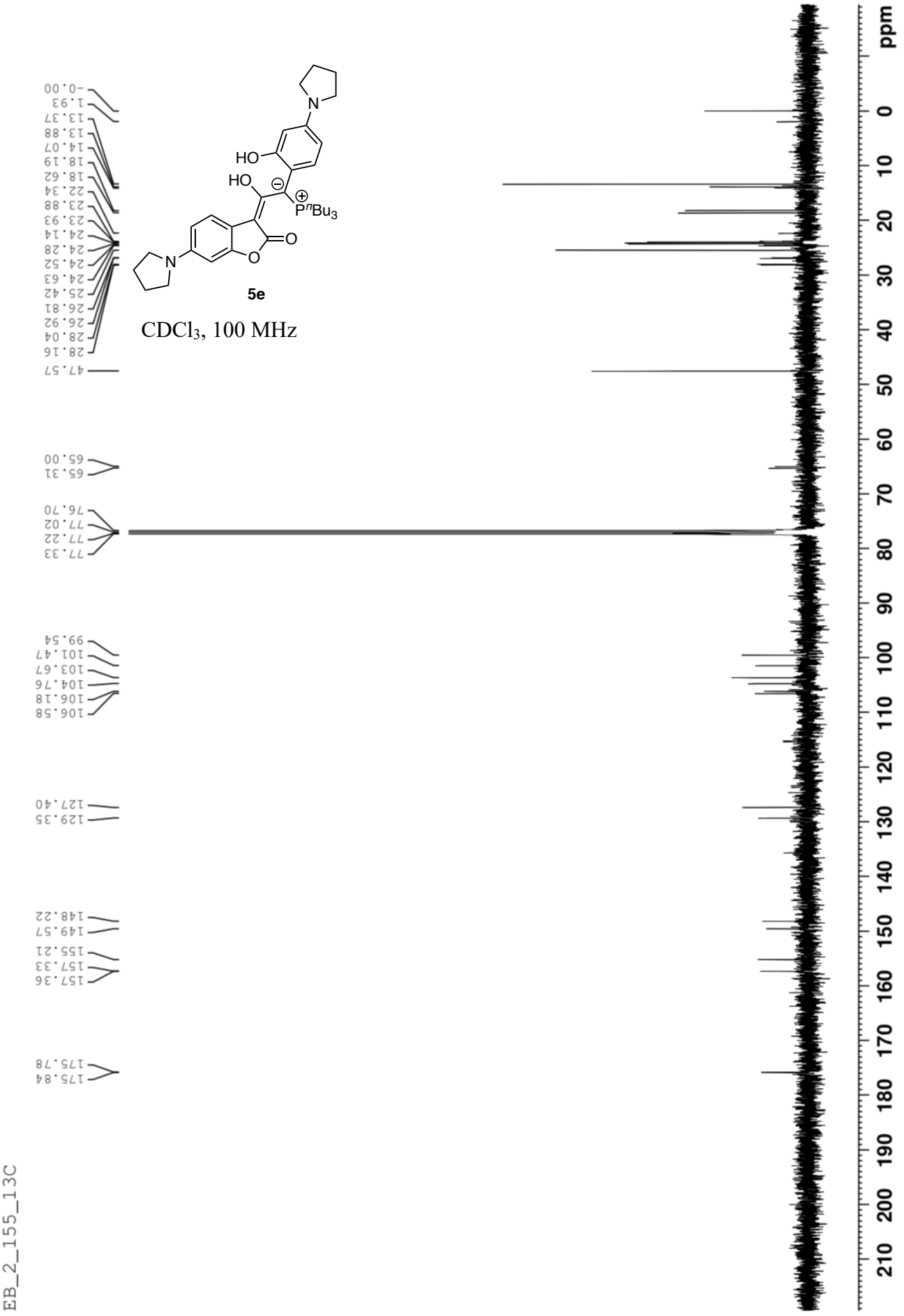
$CDCl_3$, 125 MHz

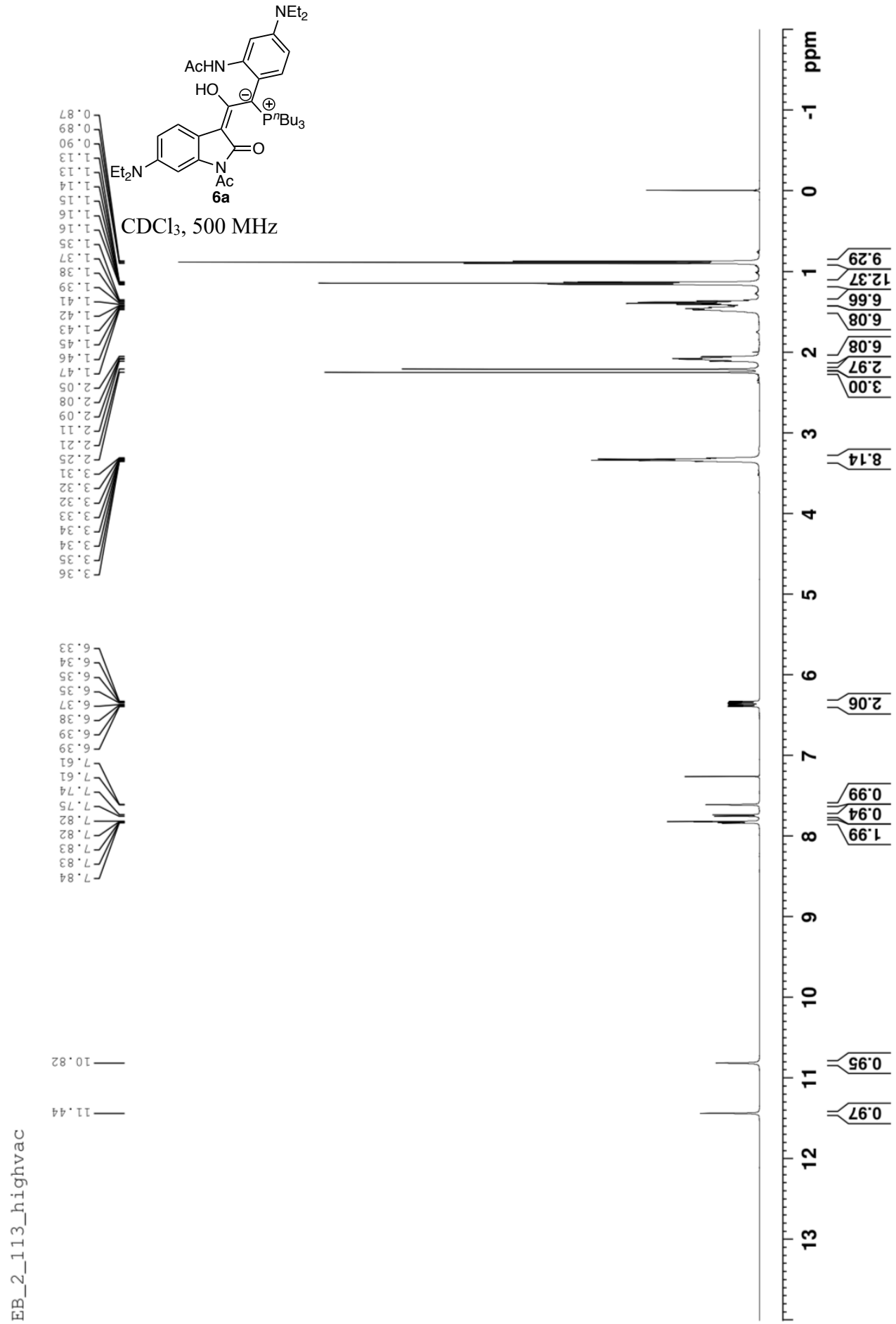


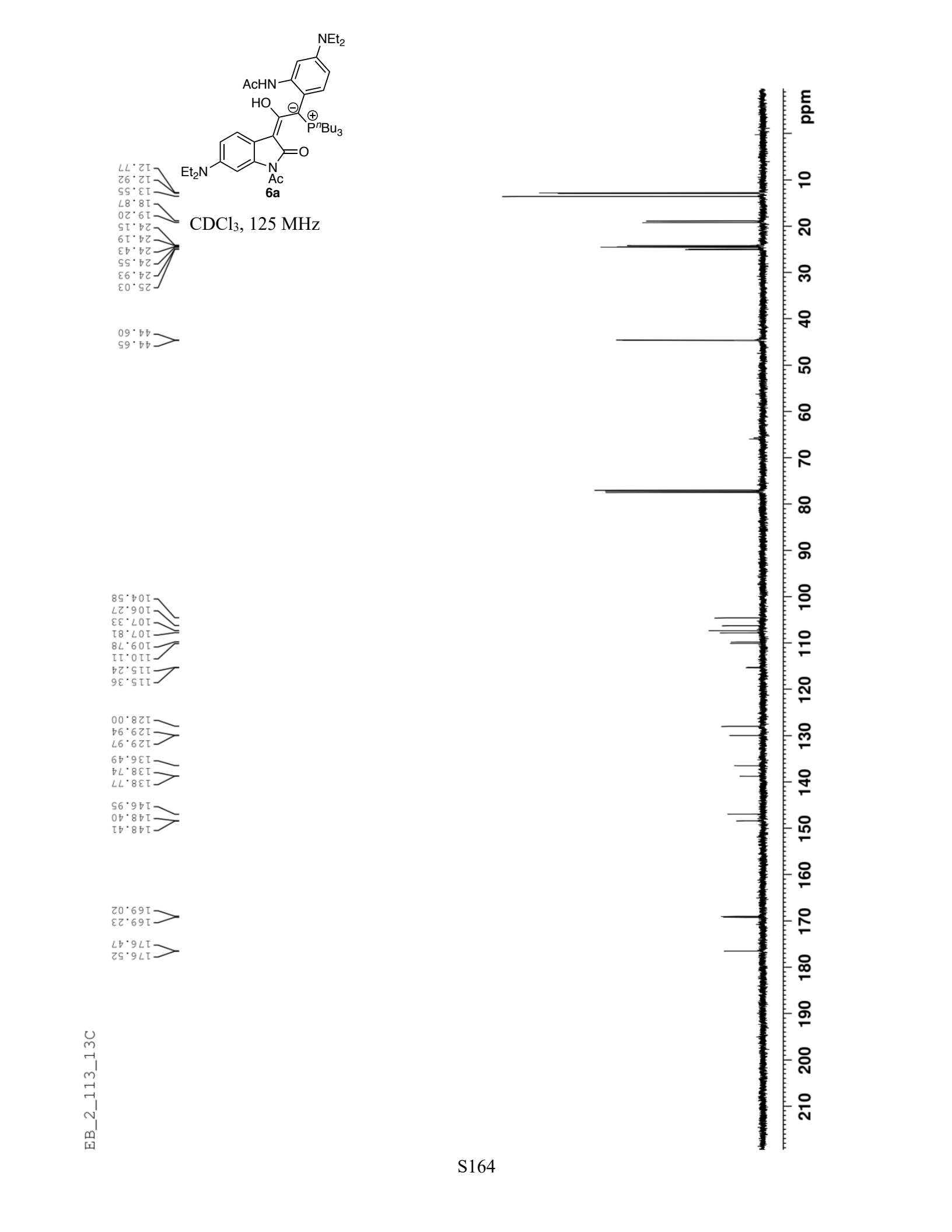

HO
HO
P^{n}Bu$_3$
O
N
O
O
N
O
5d
CDCl$_3$, 500 MHz
EB_2_149
ppm
9.00
12.15
5.67
7.91
8.00
1.90
1.88
1.68
0.76
0.82

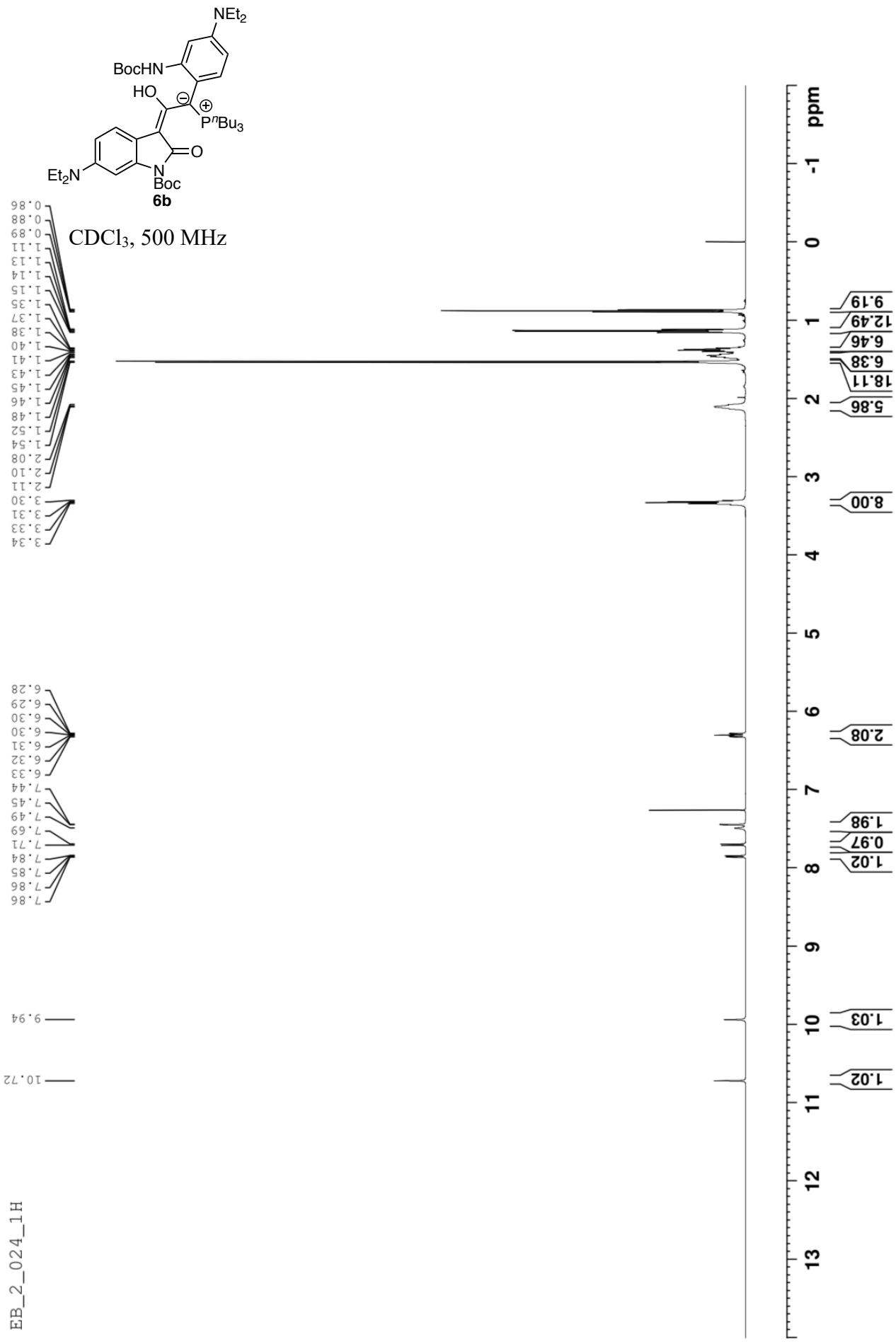

HO
HO
P^nBu_3
$CDCl_3$, 100 MHz
5d
ppm
EB_2_149_13C

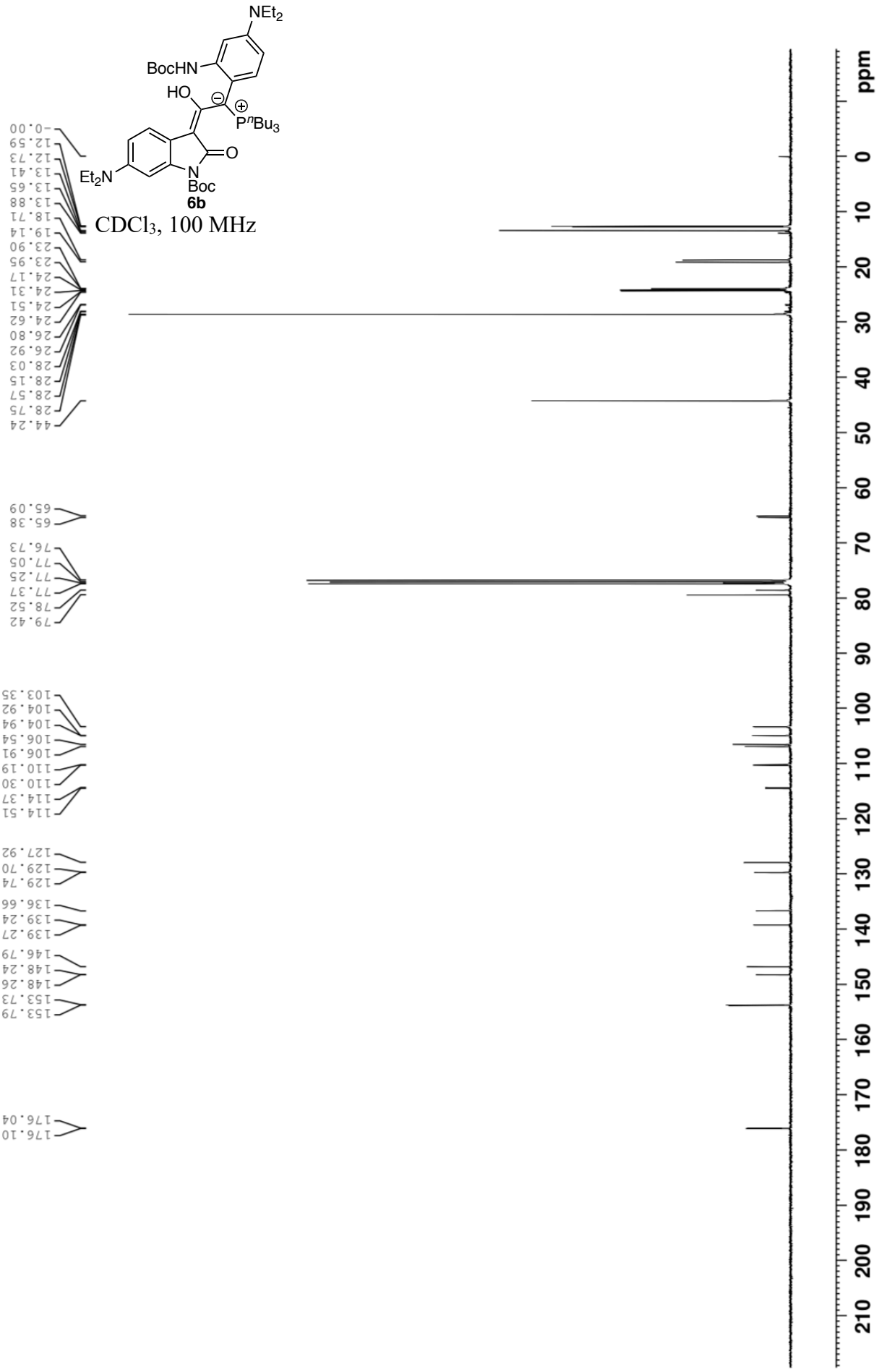

HO
HO
P^{n}Bu$_3$
O
O
N
N
5e
CDCl$_3$, 500 MHz
ppm
EB_2_155

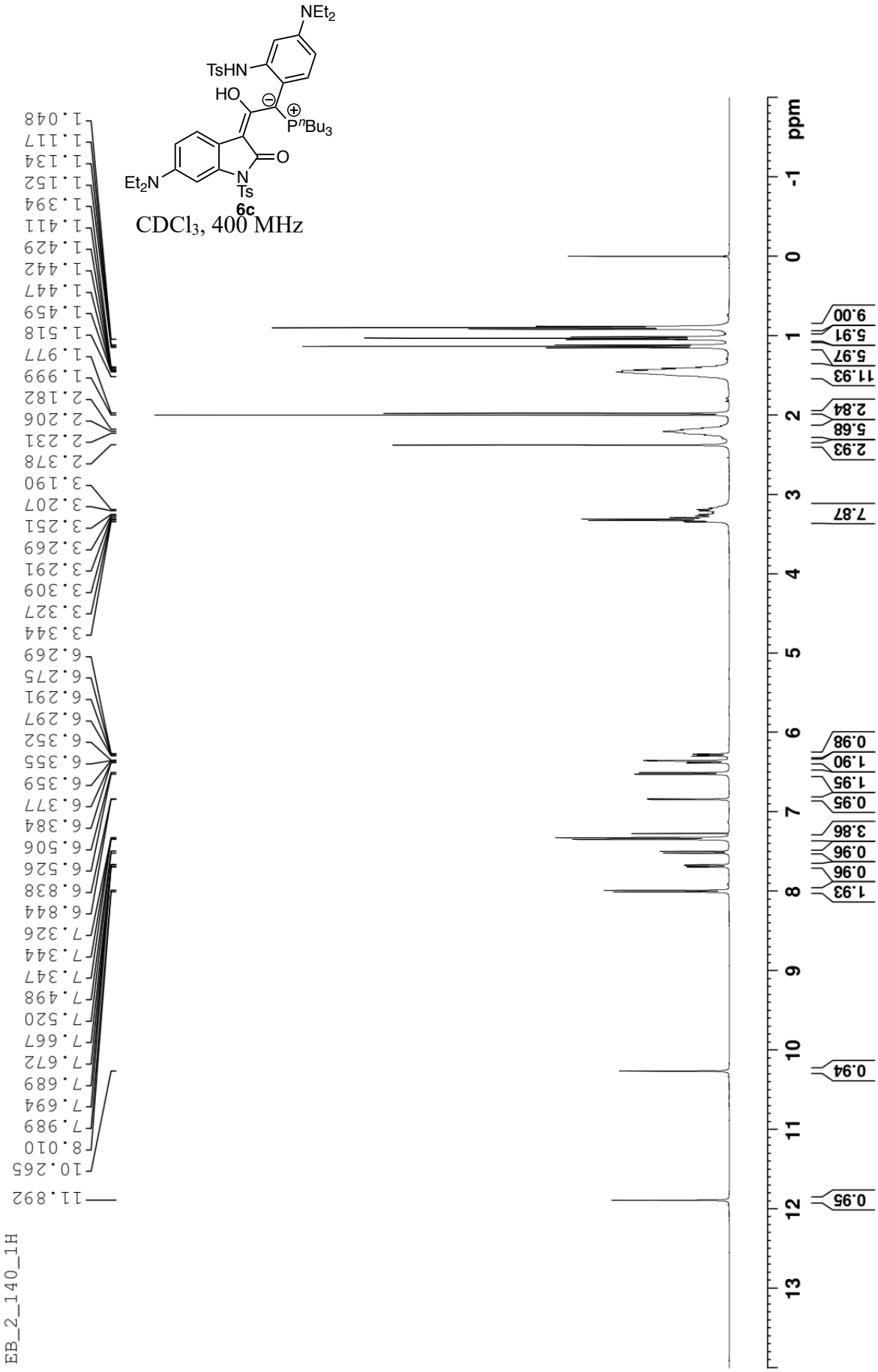

HO
HO
N
P^{n}Bu$_3$
O
O
N
5e
CDCl$_3$, 100 MHz
EB_2_155_13C
ppm

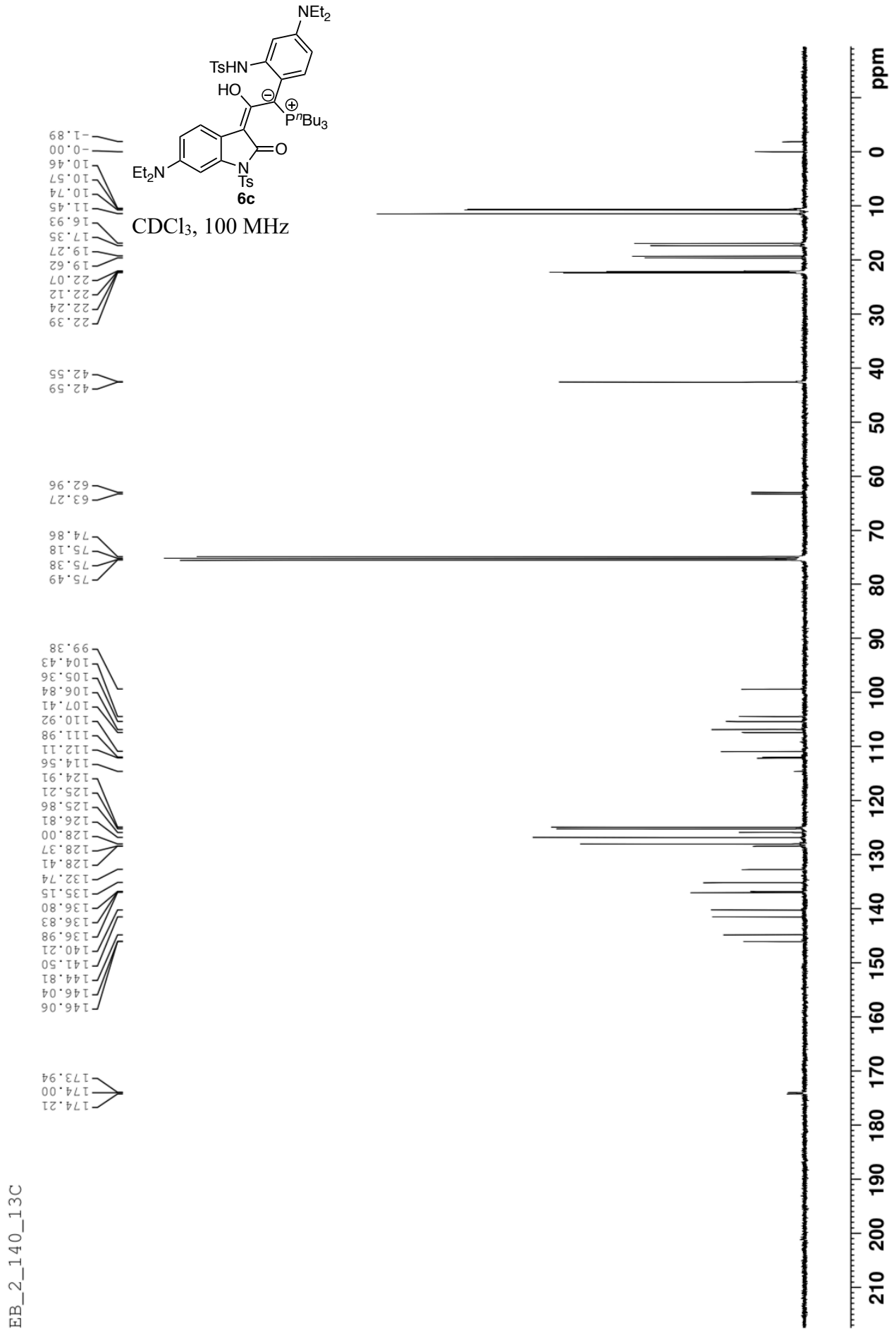

NEt2
AcHN
HO
P^nBu3
O
N
Ac
Et2N
6a
CDCl3, 500 MHz
EB_2_113_highvac
ppm

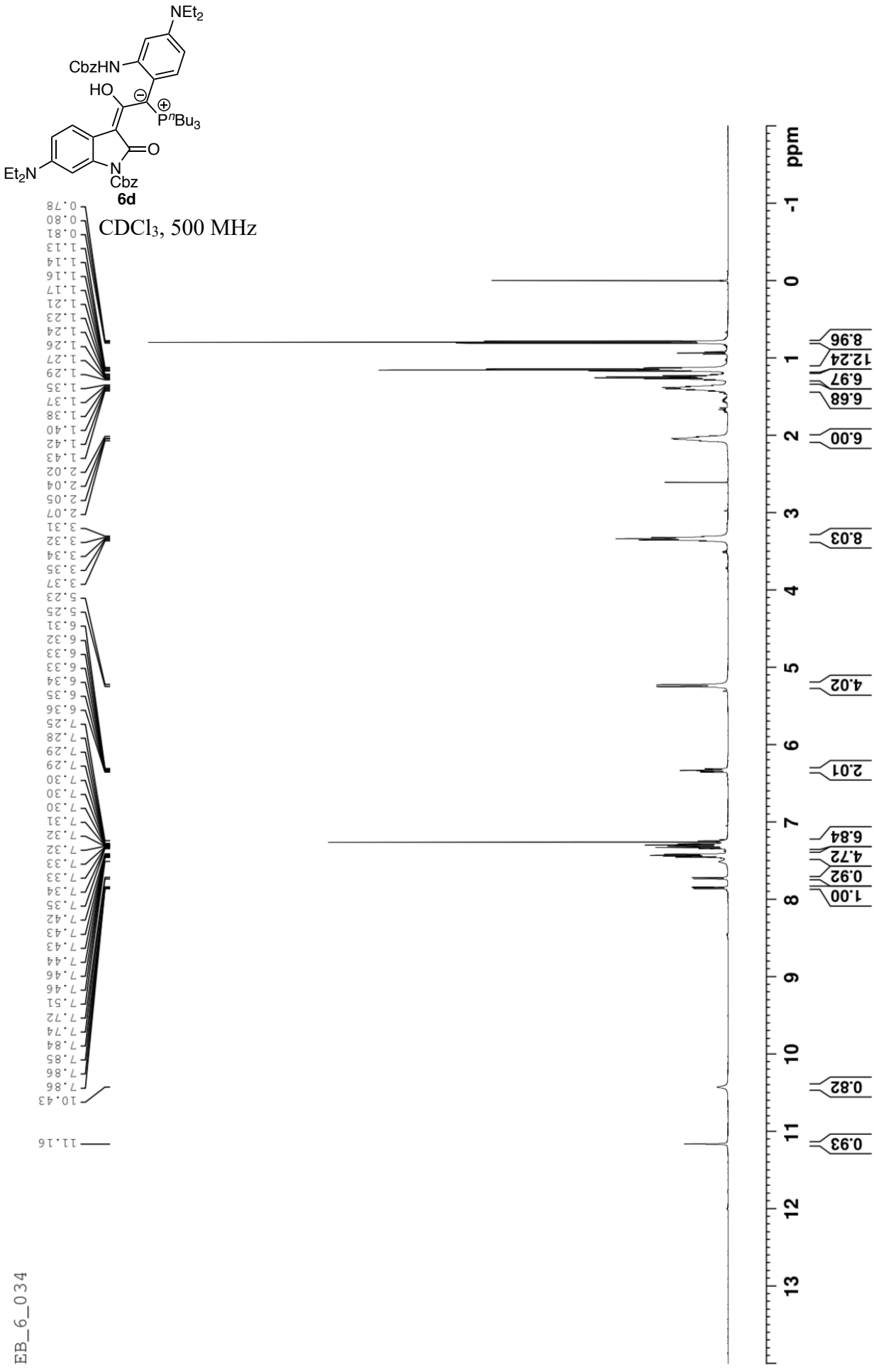

NEt2
AcHN
HO
P^nBu3
O
Et2N
N
Ac
6a
CDCl3, 125 MHz
12.77
12.92
13.55
18.87
19.20
24.15
24.19
24.43
24.55
24.93
25.03
44.60
44.65
104.58
106.27
107.33
107.81
109.78
110.11
115.24
115.36
128.00
129.94
129.97
136.49
138.74
138.77
146.95
148.40
148.41
169.02
169.23
176.47
176.52
ppm
EB_2_113_13C

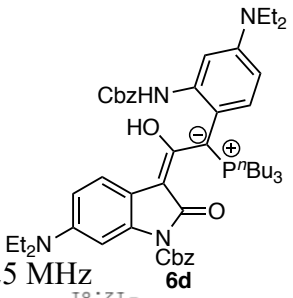

NEt2
BocHN
HO
P^{n}Bu3
O
Et2N
N
Boc
6b
CDCl3, 500 MHz
EB_2_024_1H
ppm


NEt2
BocHN
HO
P^nBu3
Et2N
O
N
Boc
6b
CDCl3, 100 MHz
EB_2_024_13C
ppm

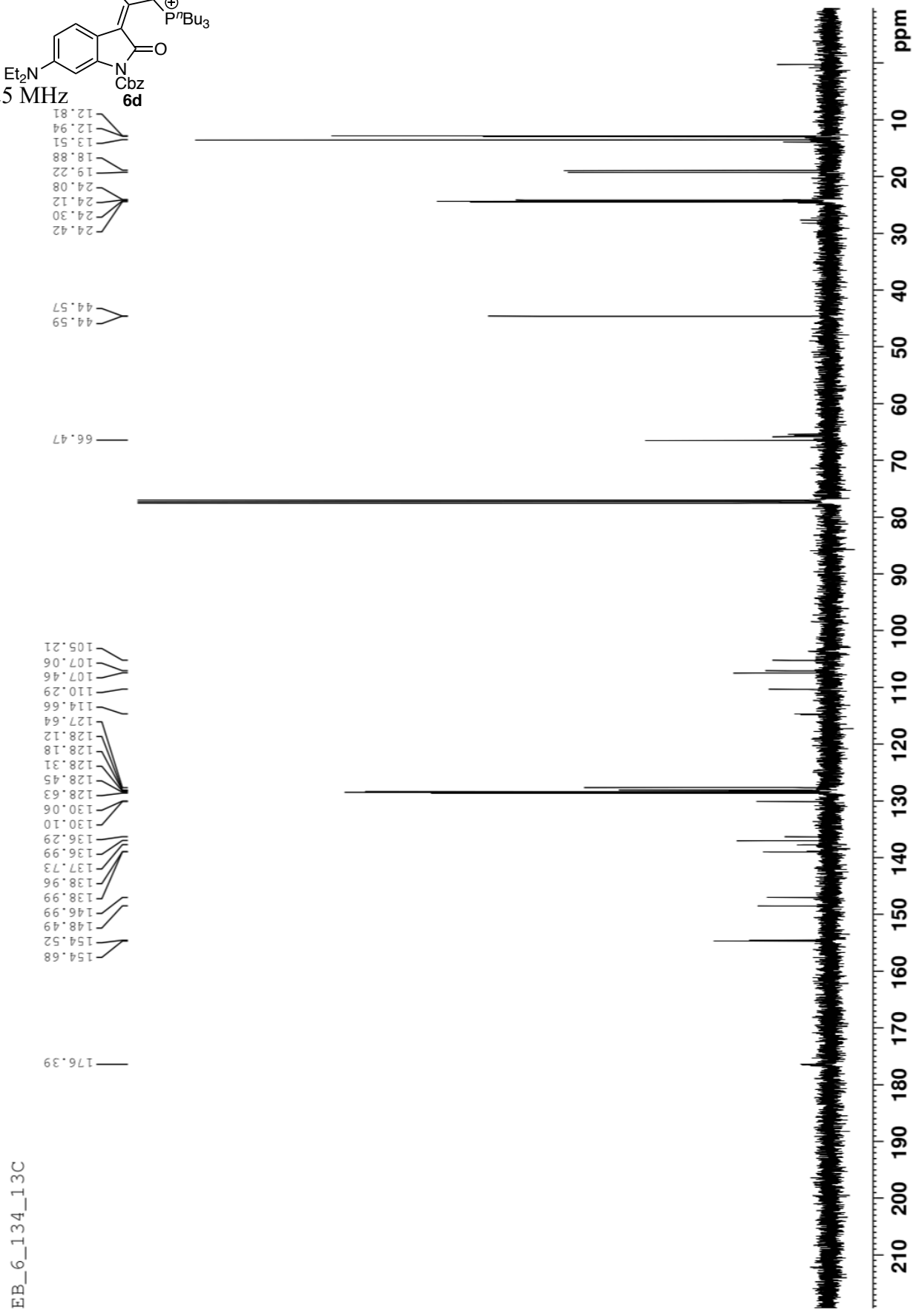

NEt2
TsHN
HO
P^{n}Bu3
O
Et2N
N
Ts
6c
CDCl3, 400 MHz
EB_2_140_1H
ppm

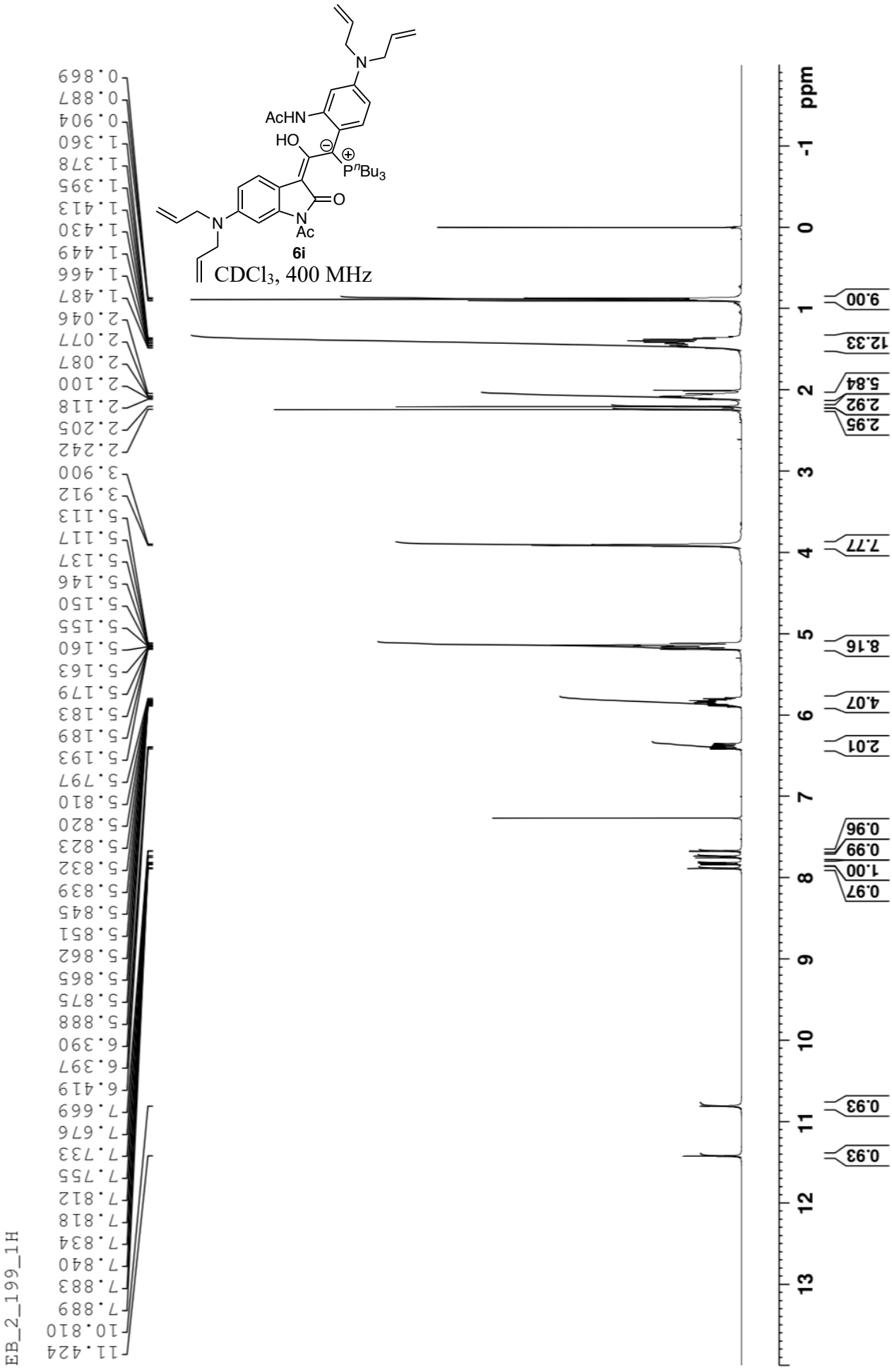

NEt2
TsHN
HO
P^{n}Bu3
O
Et2N
N
Ts
6c
CDCl3, 100 MHz
-1.89
-0.00
10.46
10.57
10.74
11.45
16.93
17.35
19.27
19.62
22.07
22.12
22.24
22.39
42.55
42.59
62.96
63.27
74.86
75.18
75.38
75.49
99.38
104.43
105.36
106.84
107.41
110.92
111.98
112.11
114.56
124.91
125.21
125.86
126.81
128.00
128.37
128.41
132.74
135.15
136.80
136.83
136.98
140.21
141.50
144.81
146.04
146.06
173.94
174.00
174.21
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
EB_2_140_13C

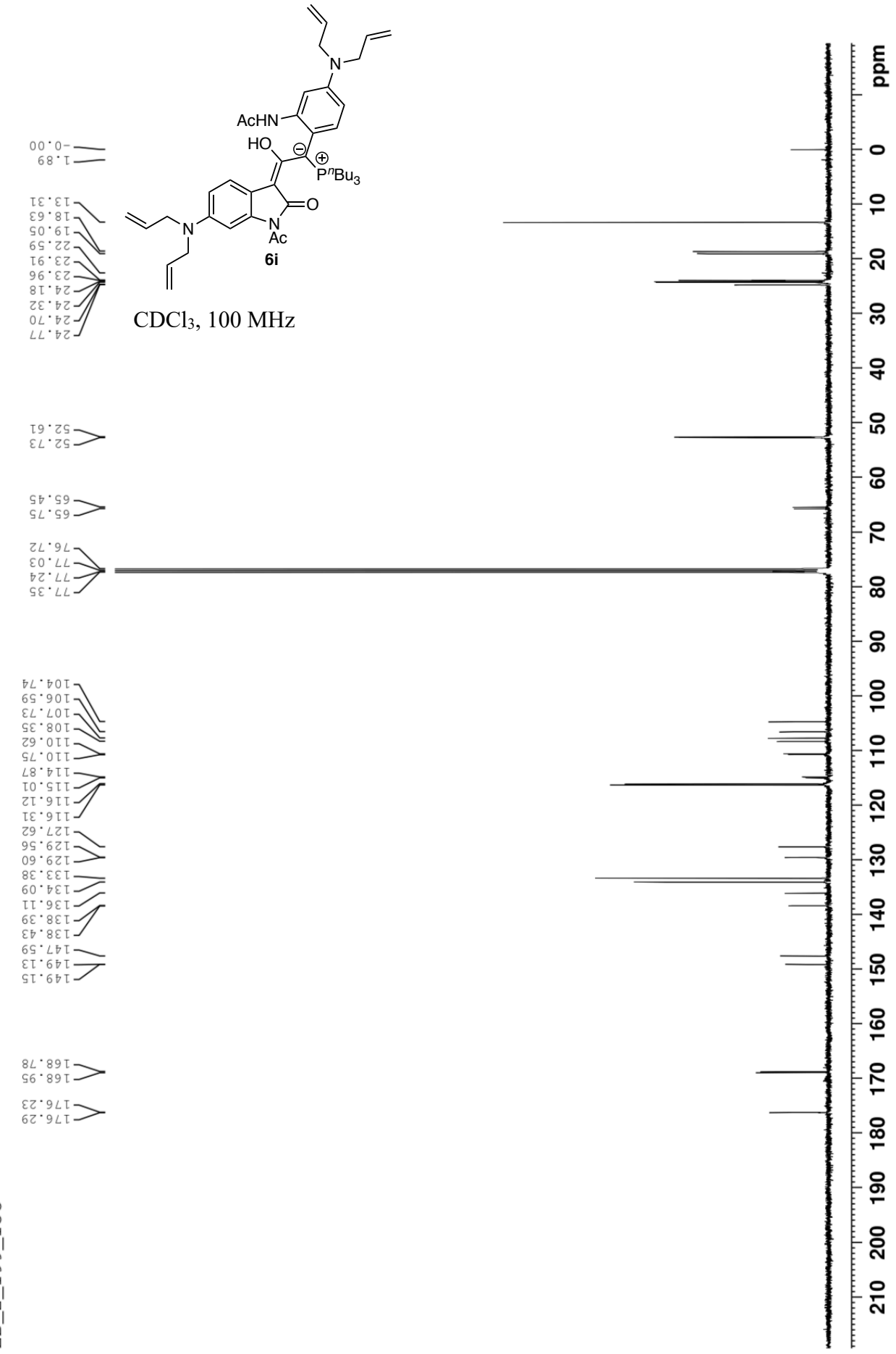

NEt2
CbzHN
HO
P^nBu3
O
N
Cbz
Et2N
6d
CDCl3, 500 MHz
ppm
8.96
12.24
6.97
6.68
6.00
8.03
4.02
2.01
6.84
4.72
0.92
1.00
0.82
0.93
EB_6_034

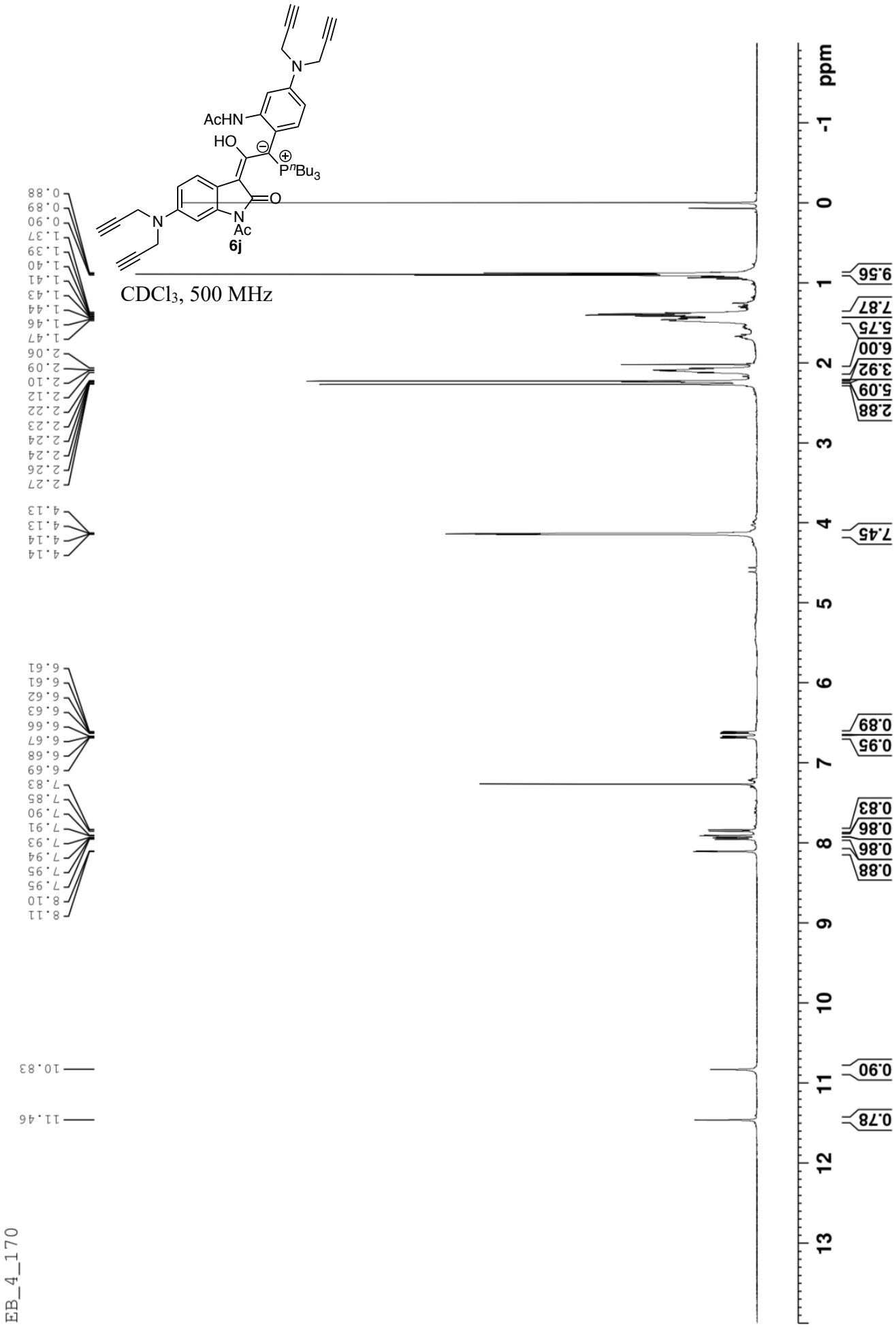


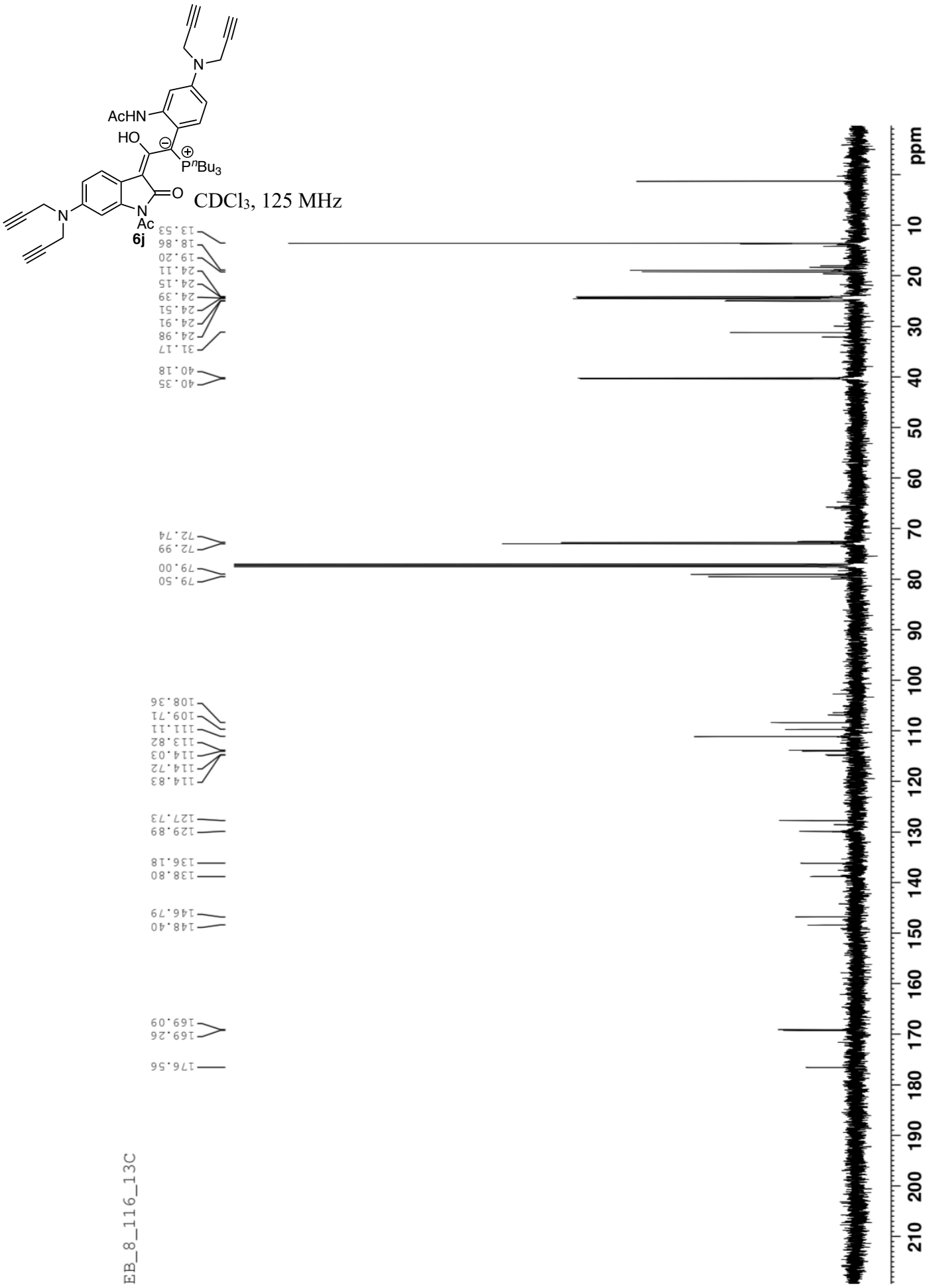
$CDCl_3$, 125 MHz

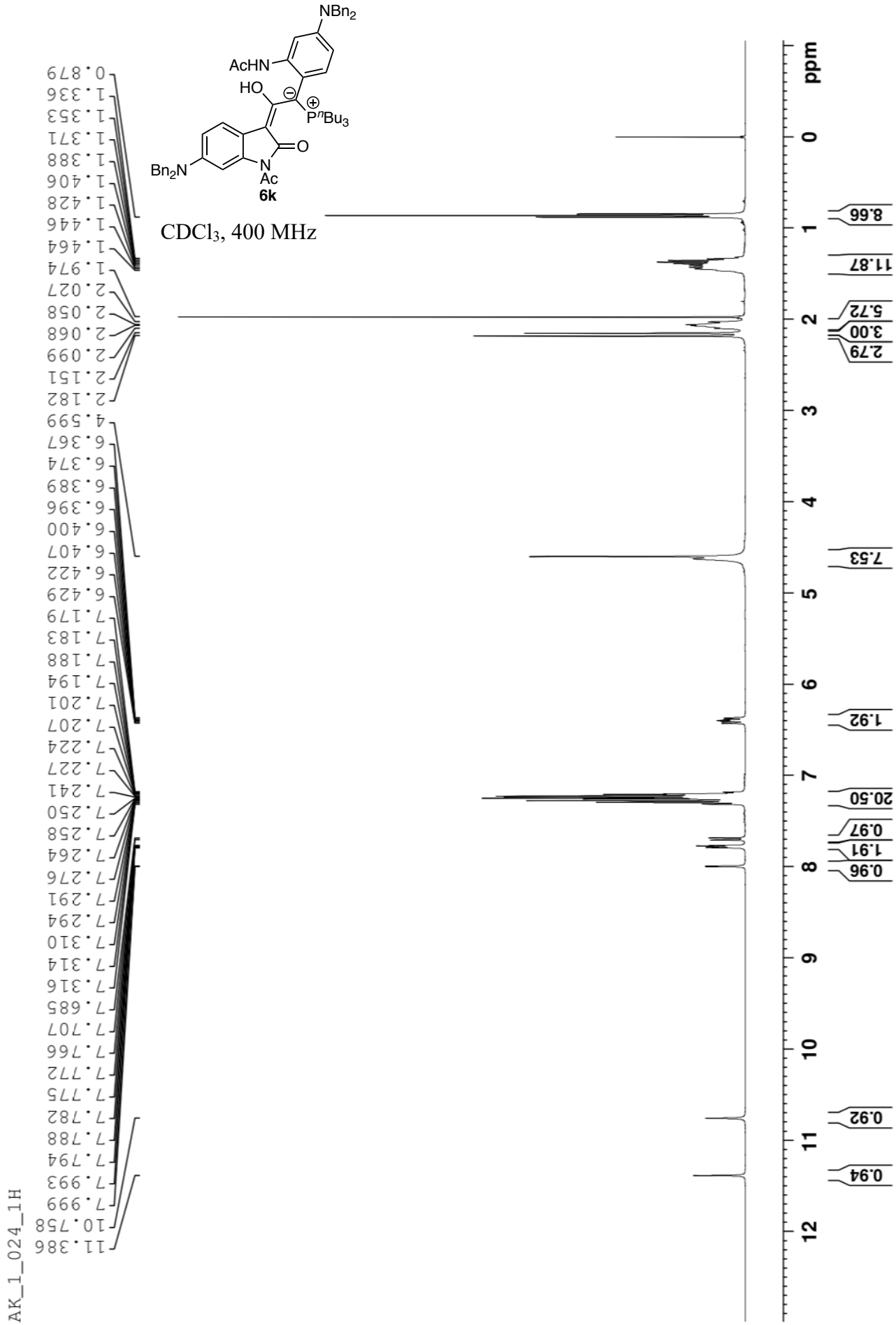


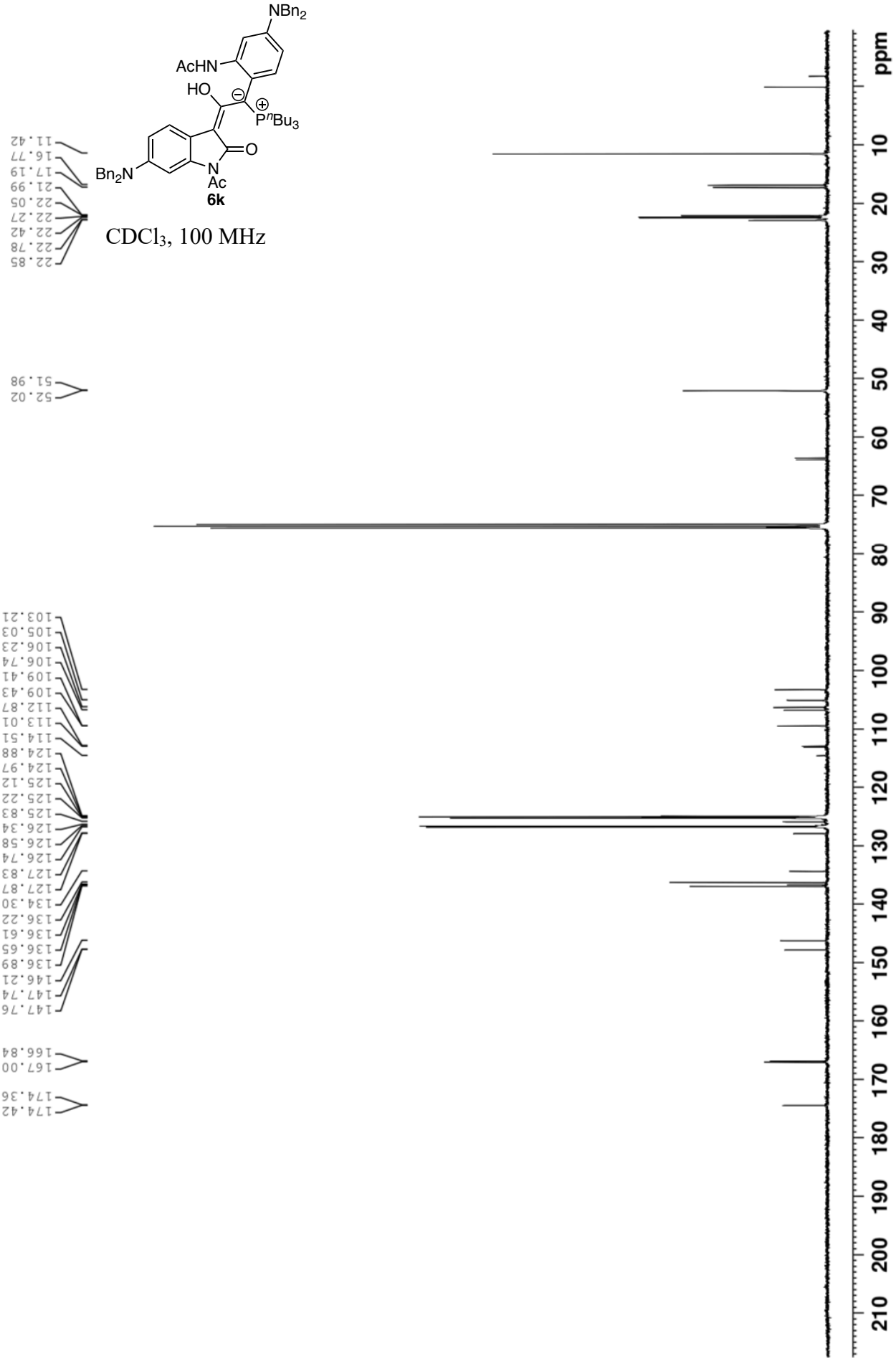

AcHN
HO
P^{n}Bu$_3$
O
N
Ac
6i
CDCl$_3$, 400 MHz
ppm
9.00
12.33
5.84
2.92
2.95
7.77
8.16
4.07
2.01
0.96
0.99
1.00
0.97
0.93
0.93
EB_2_199_1H

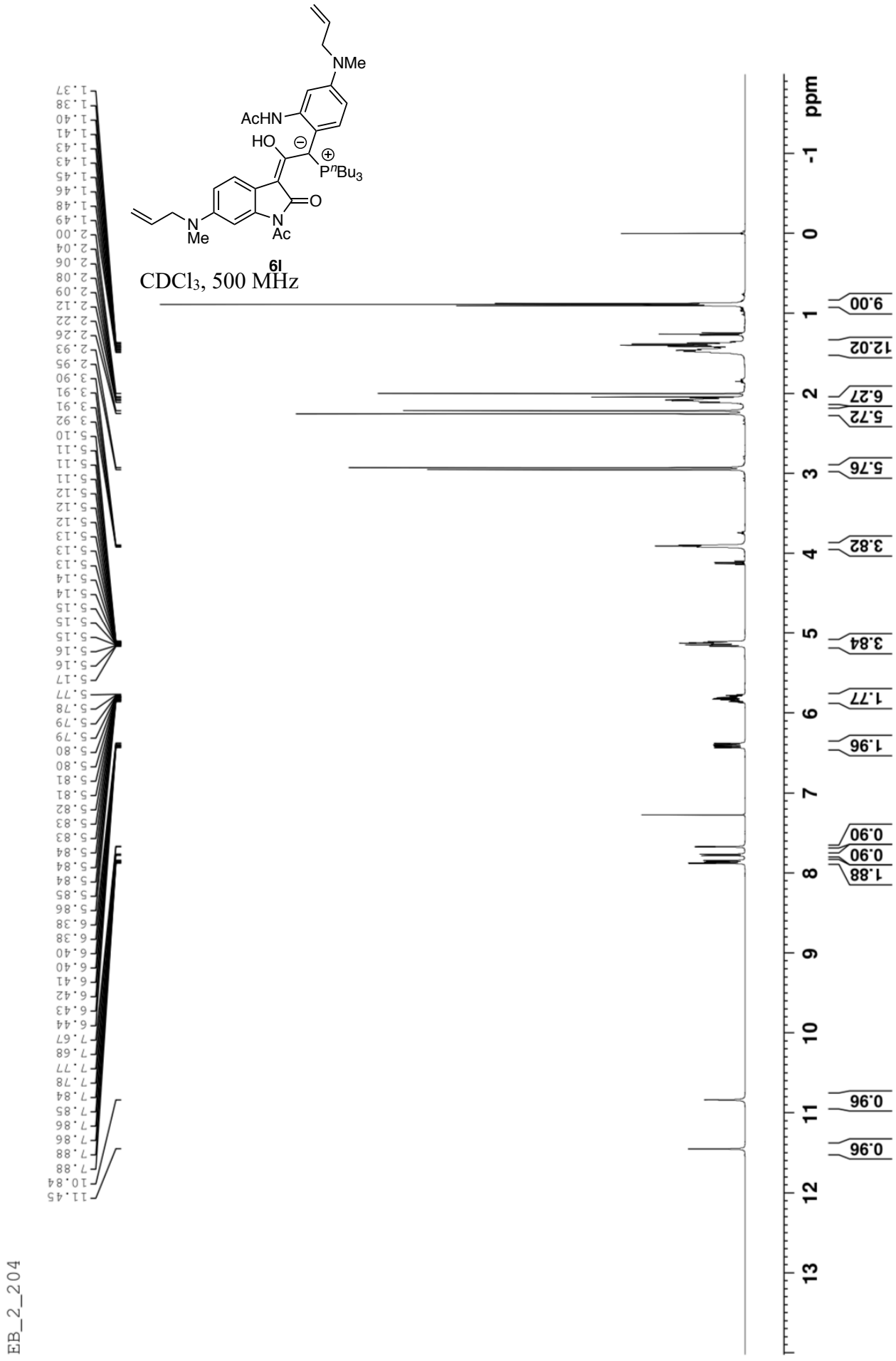

AcHN
HO
P^{n}Bu$_3$
O
N
Ac
6i
CDCl$_3$, 100 MHz
ppm
EB_2_199_13C

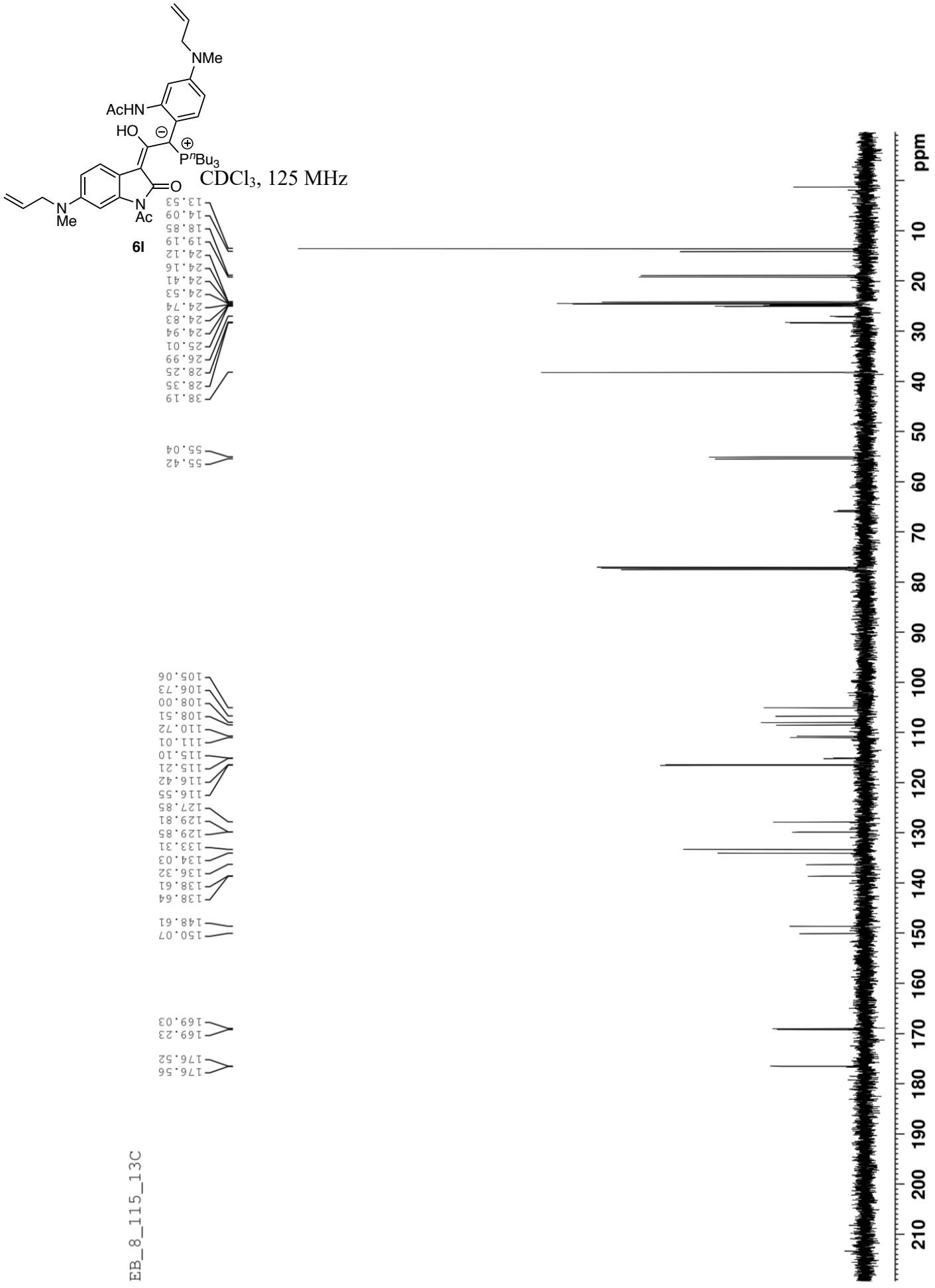

AcHN
HO
P^{n}Bu$_3$
N
O
N
Ac
6j
CDCl$_3$, 500 MHz
ppm
EB_4_170

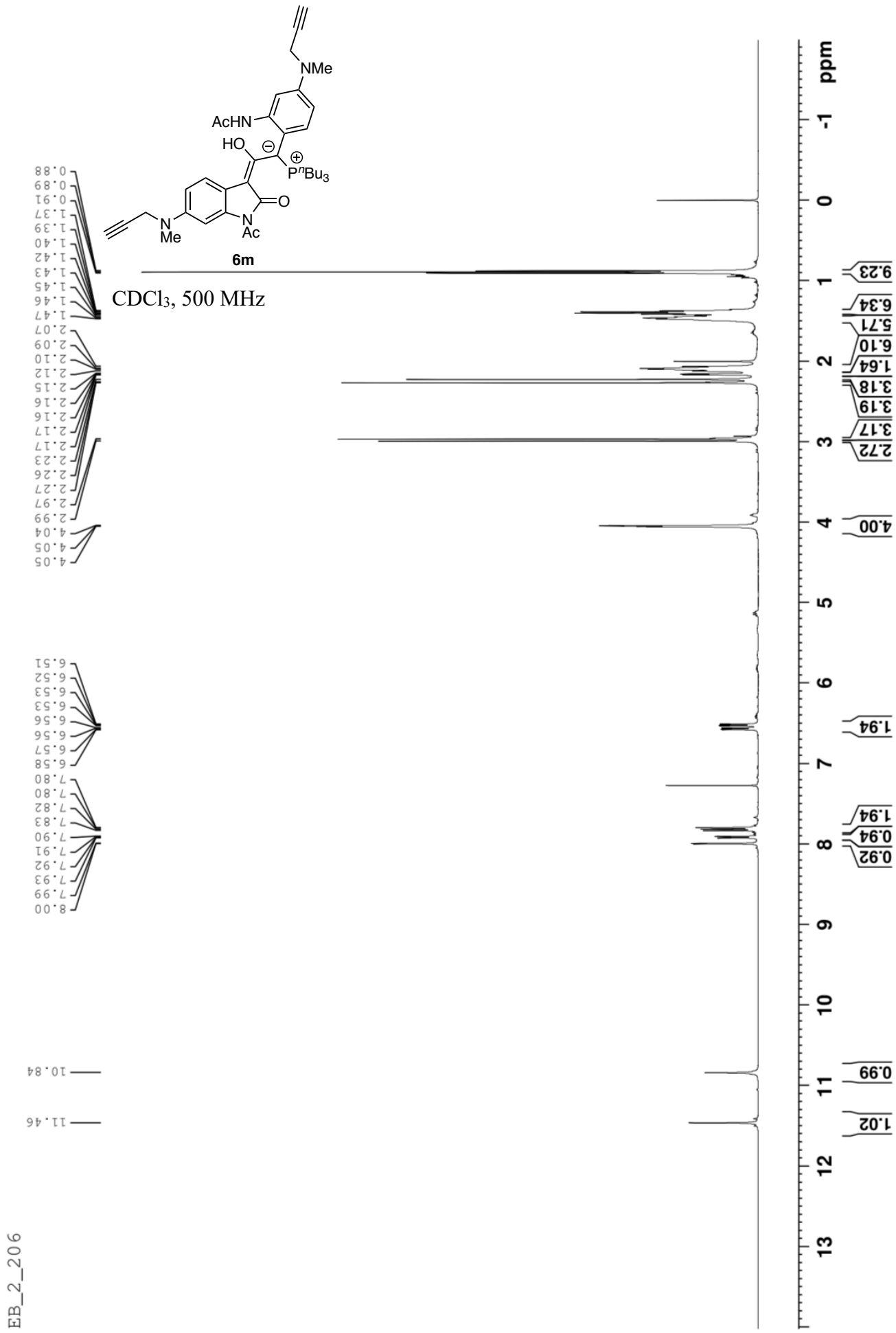

AcHN
HO
P^{n}Bu$_3$
O
N
Ac
6j
CDCl$_3$, 125 MHz
13.53
18.86
19.20
24.11
24.15
24.39
24.51
24.91
24.98
31.17
40.18
40.35
72.74
72.99
79.00
79.50
108.36
109.71
111.11
113.82
114.03
114.72
114.83
127.73
129.89
136.18
138.80
146.79
148.40
169.09
169.26
176.56
ppm
EB_8_116_13C

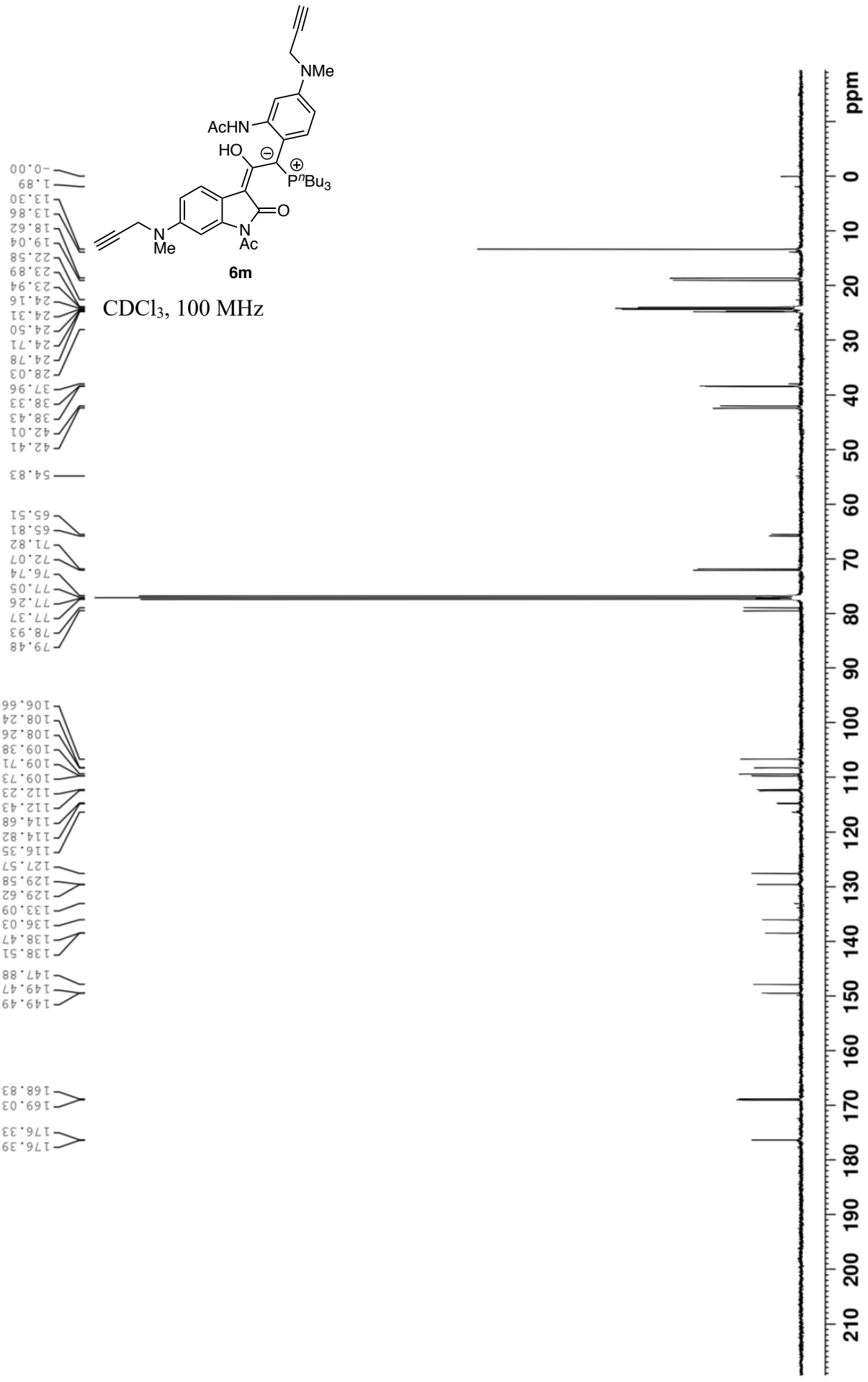

NBn2
AcHN
HO
P^{n}Bu3
O
N
Ac
Bn2N
6k
CDCl3, 400 MHz
AK_1_024_1H
ppm
8.66
11.87
5.72
3.00
2.79
7.53
1.92
20.50
0.97
1.91
0.96
0.92
0.94

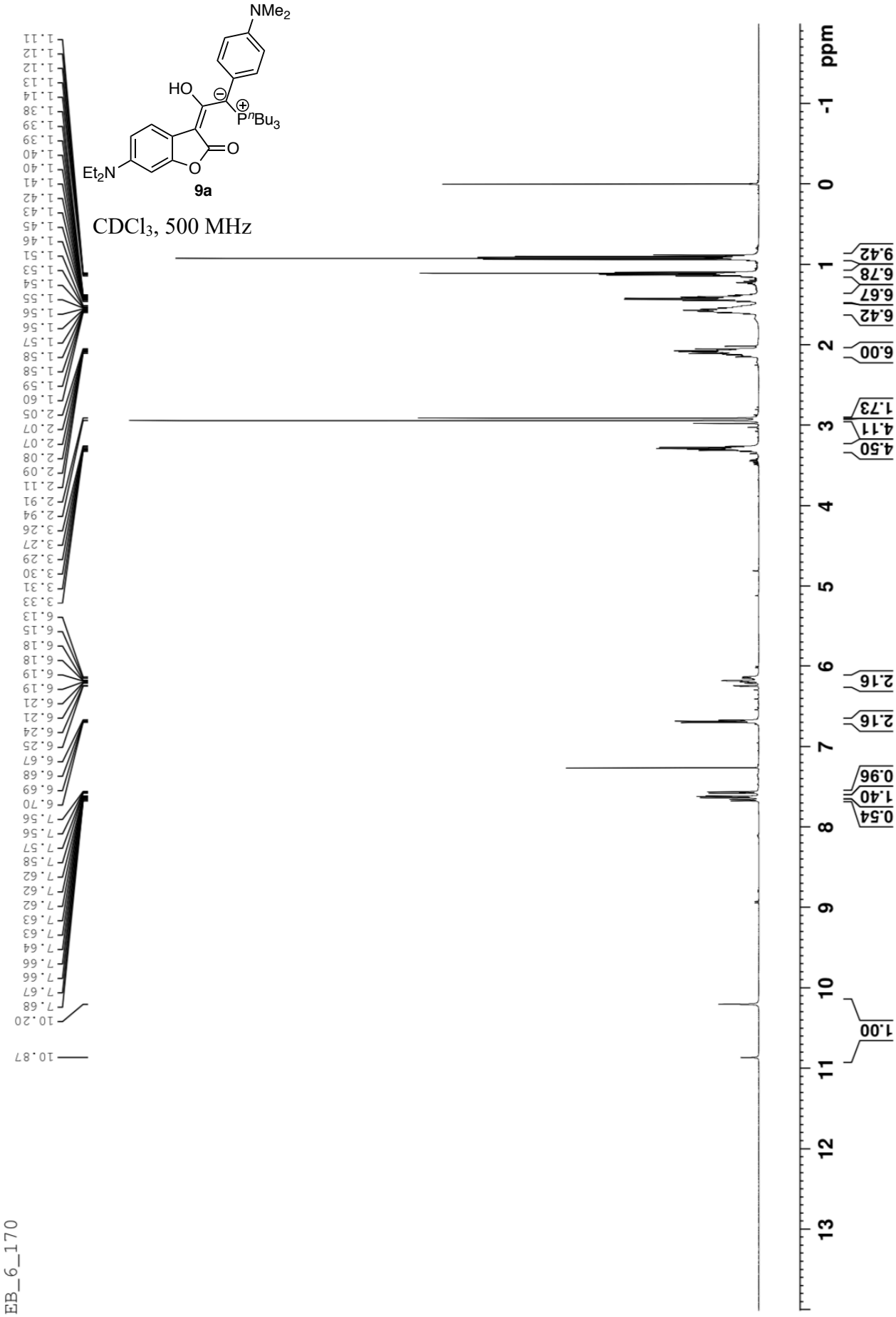

NBn2
AcHN
HO
P^nBu3
Bn2N
O
N
Ac
6k
CDCl3, 100 MHz
ppm
AK_1_024_13C

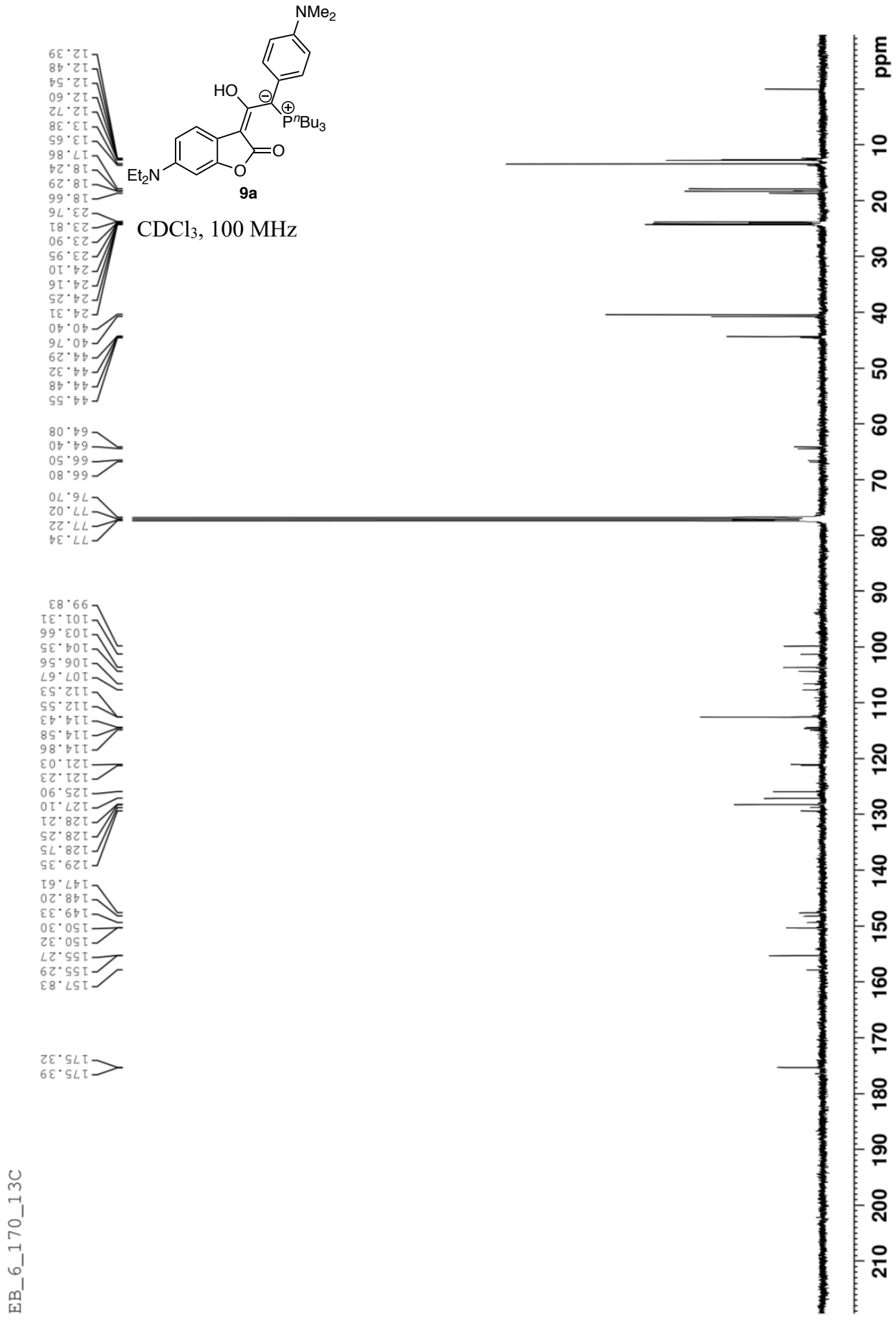

NMe
AcHN
HO
P^{n}Bu$_3$
O
N
Me
N
Ac
6l
CDCl$_3$, 500 MHz
ppm
9.00
12.02
6.27
5.72
5.76
3.82
3.84
1.77
1.96
0.90
0.90
1.88
0.96
0.96
EB_2_204

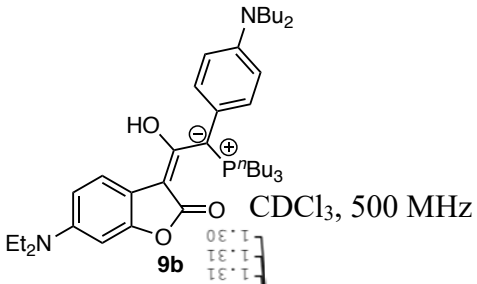

NMe
AcHN
HO
P^{n}Bu$_3$
O
N
Me
N
Ac
6l
CDCl$_3$, 125 MHz
13.53
14.09
18.85
19.19
24.12
24.16
24.41
24.53
24.74
24.83
24.94
25.01
26.99
28.25
28.35
38.19
55.04
55.42
105.06
106.73
108.00
108.51
110.72
111.01
115.10
115.21
116.42
116.55
127.85
129.81
129.85
133.31
134.03
136.32
138.61
138.64
148.61
150.07
169.03
169.23
176.52
176.56
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
EB_8_115_13C


NMe
AcHN
HO
P^{n}Bu$_3$
O
N
Ac
N
Me
6m
CDCl$_3$, 500 MHz
ppm
EB_2_206


NMe
AcHN
HO
P^{n}Bu$_3$
O
N
Me
N
Ac
6m
CDCl$_3$, 100 MHz
ppm
EB_2_206_13C

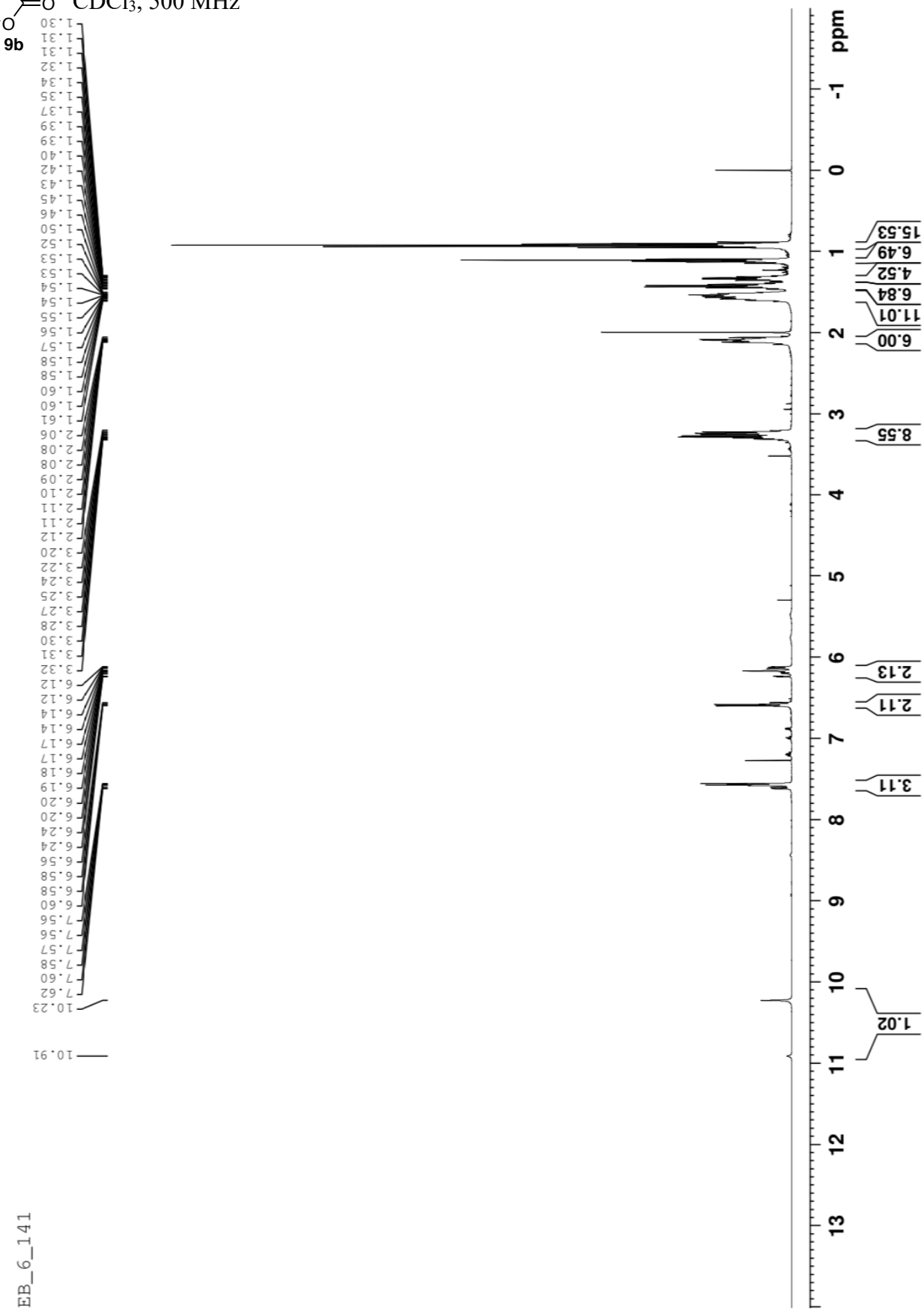

NMe2
HO
P^{n}Bu3
O
O
Et2N
9a
CDCl3, 500 MHz
ppm
EB_6_170

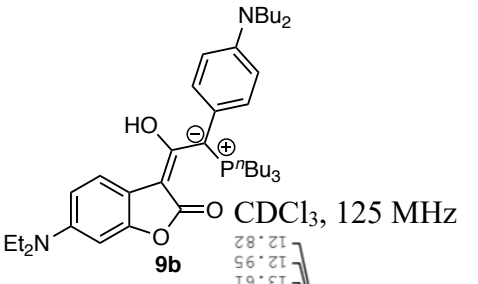

NMe2
HO
P^{n}Bu3
Et2N
O
O
9a
CDCl3, 100 MHz
ppm
EB_6_170_13C



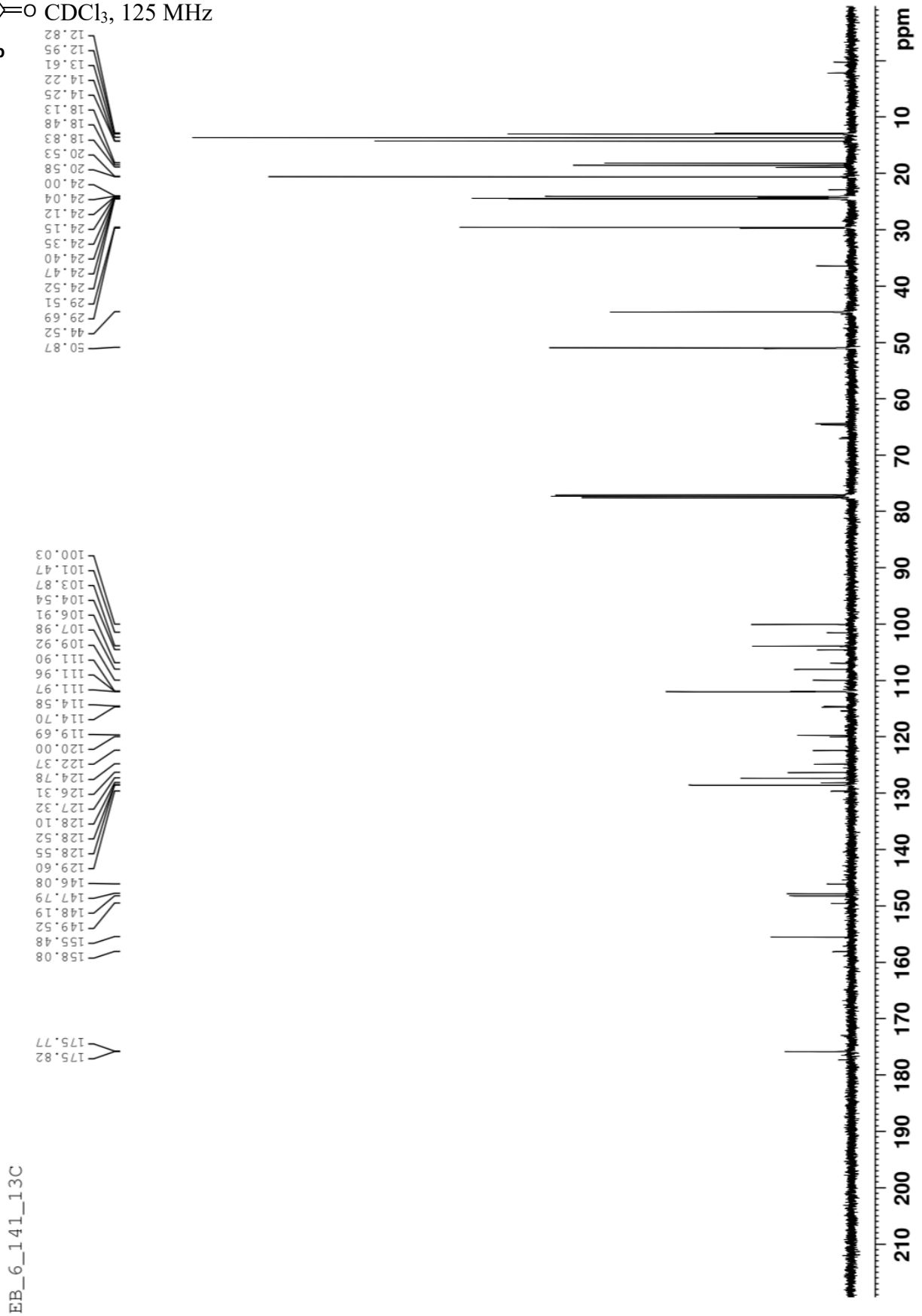
9b

$CDCl_3$, 500 MHz

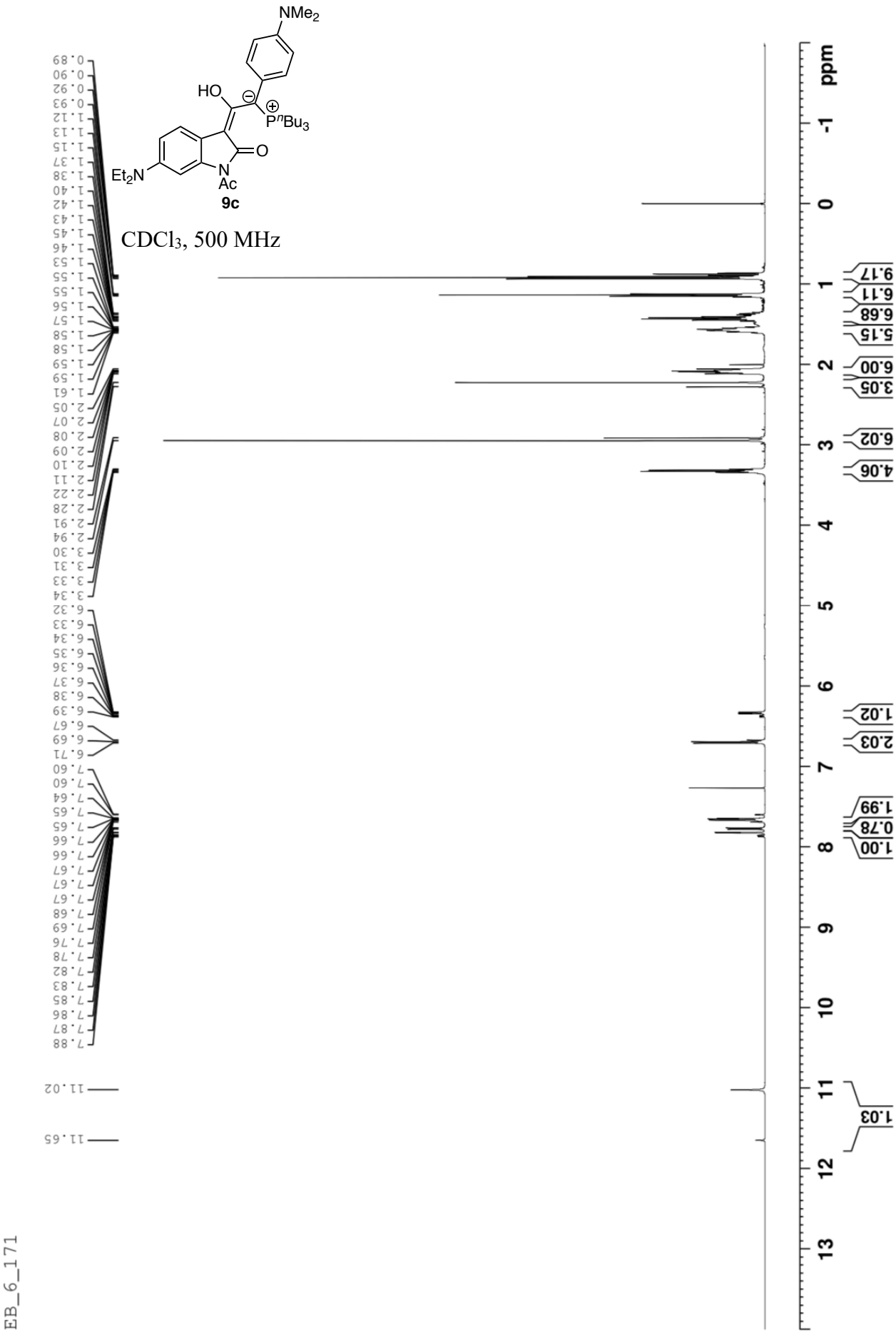


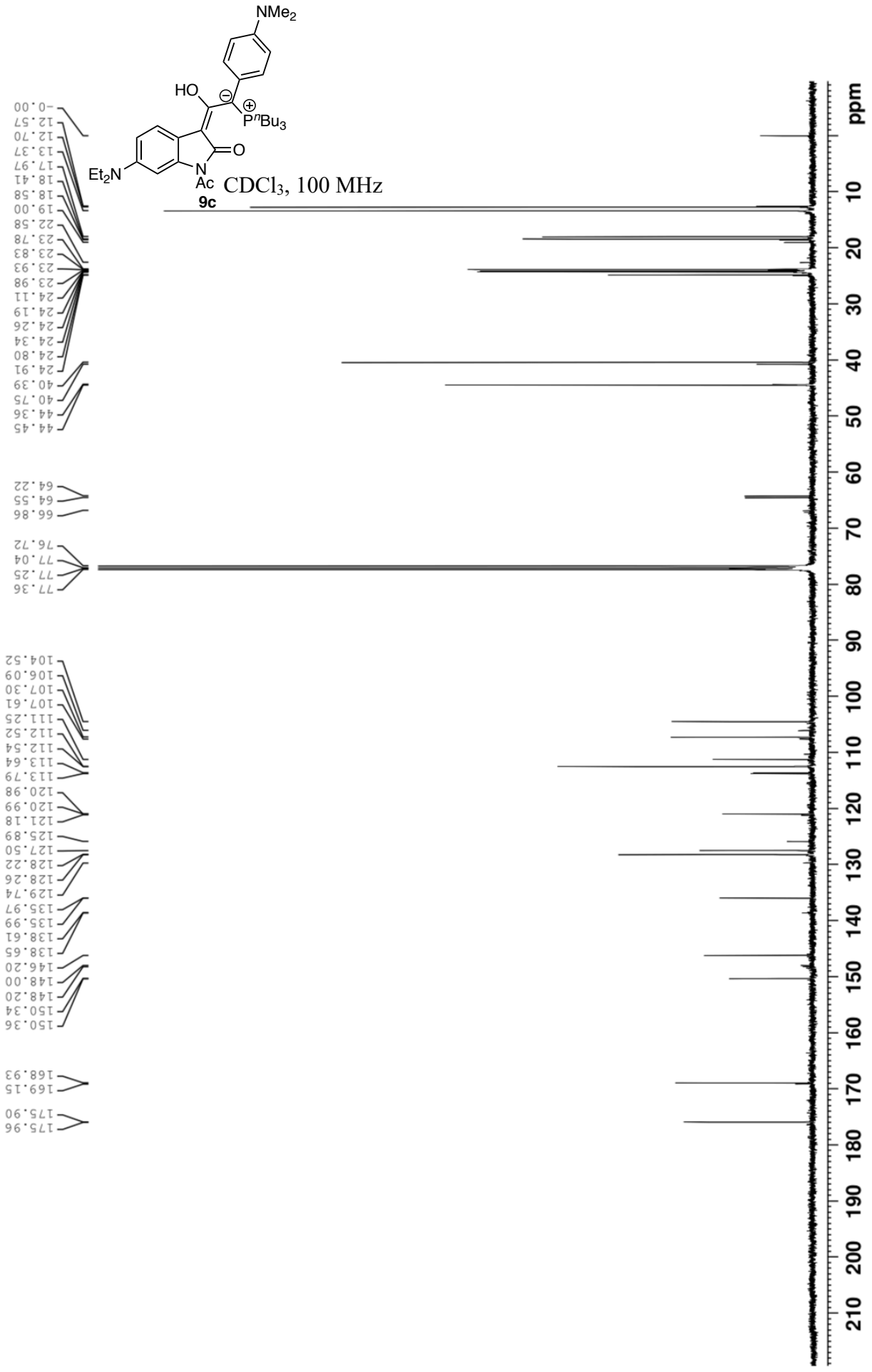


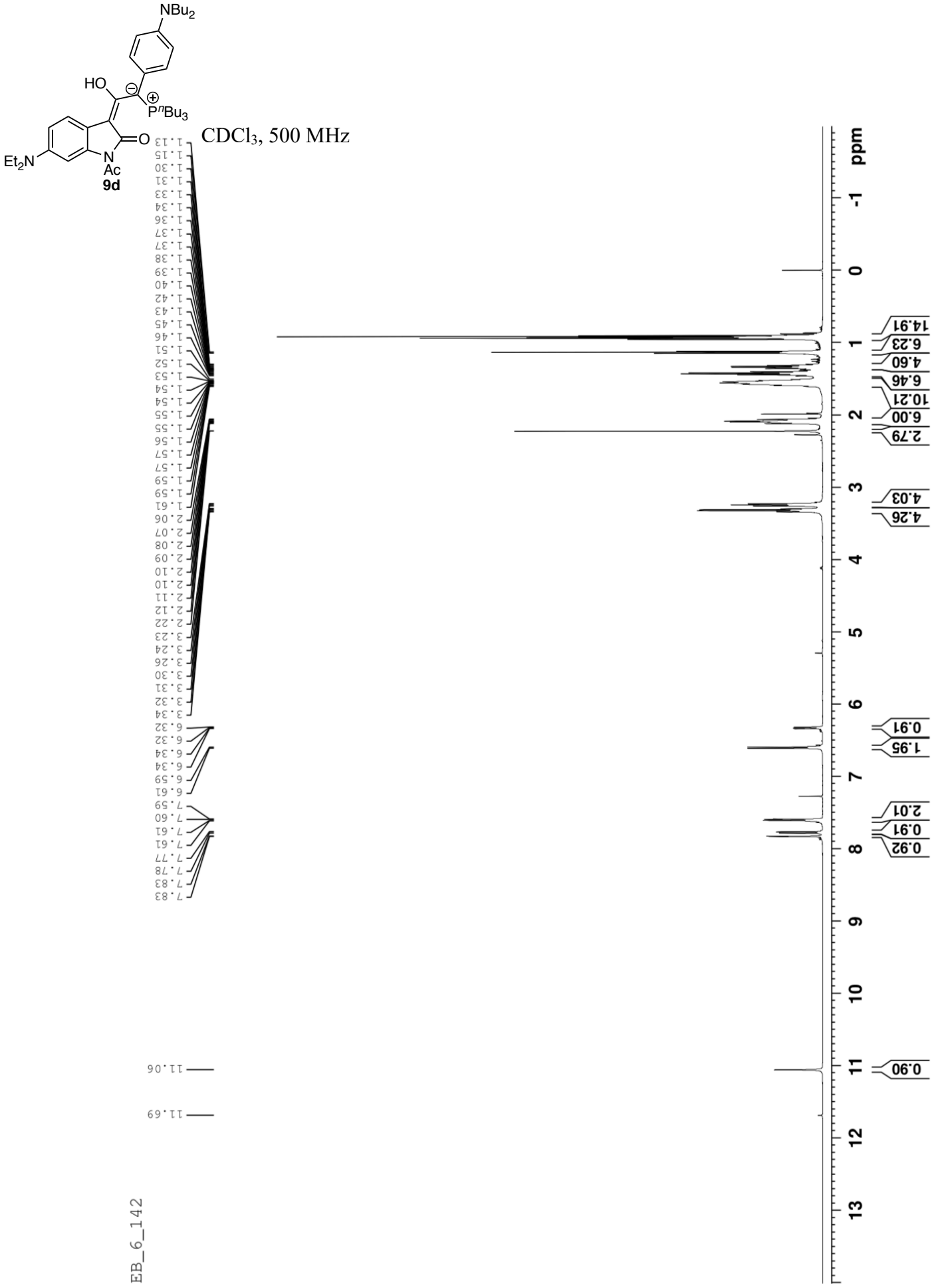
$CDCl_3$, 125 MHz

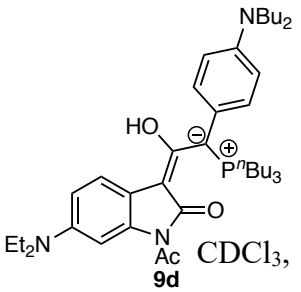


EB_6_141_13C


NMe2
HO
P^{n}Bu3
O
N
Ac
Et2N
9c
CDCl3, 500 MHz
ppm
EB_6_171

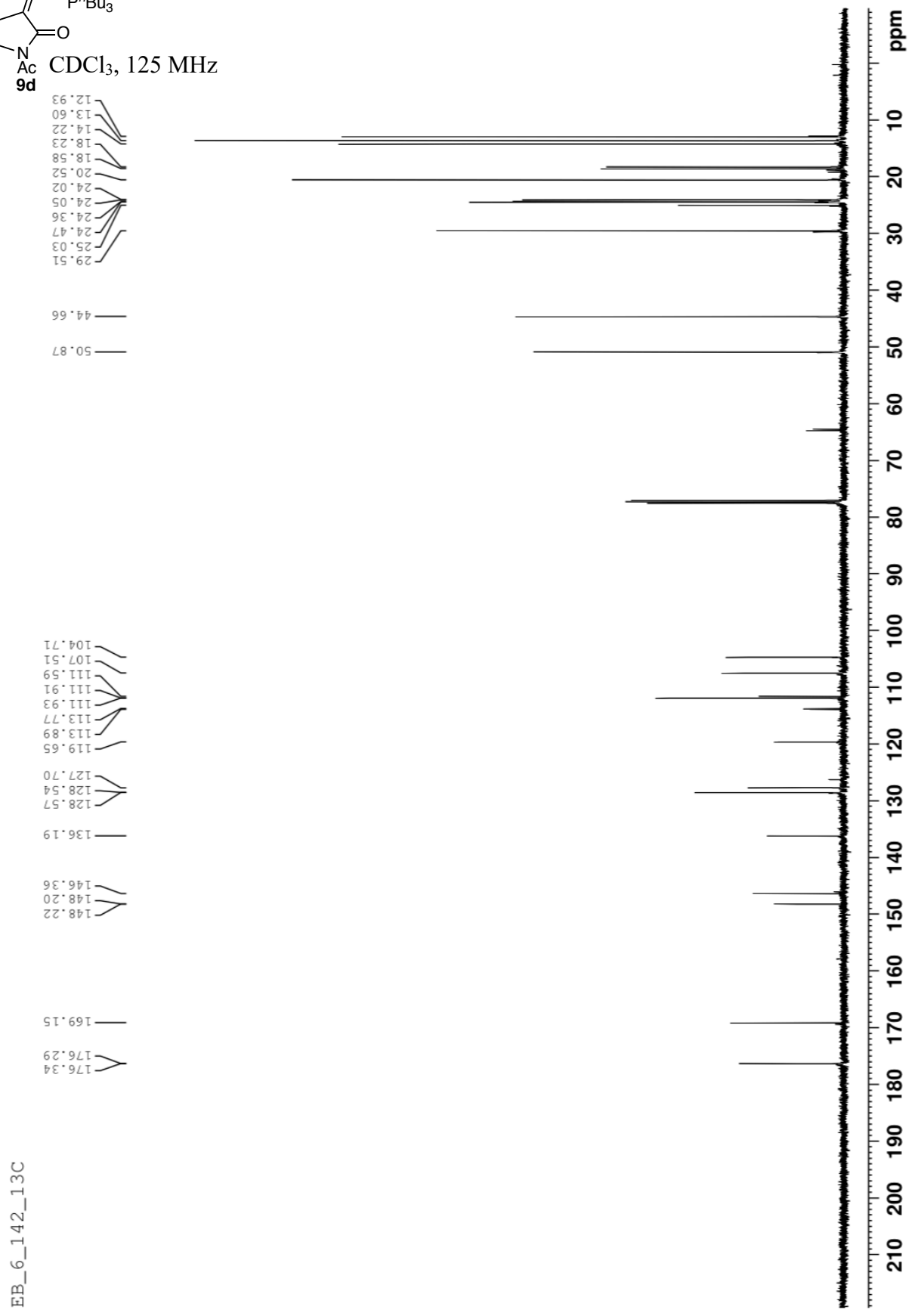

NMe2
HO
P^nBu3
O
Et2N
N
Ac
9c
CDCl3, 100 MHz
ppm
EB_6_171_13C


NBu2
HO
P+nBu3
O
Et2N
N
Ac
9d
CDCl3, 500 MHz
ppm
14.91
6.23
4.60
6.46
10.21
6.00
2.79
4.03
4.26
0.91
1.95
2.01
0.91
0.92
0.90
EB_6_142

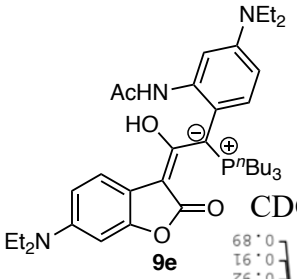


9d

$CDCl_3$, 125 MHz

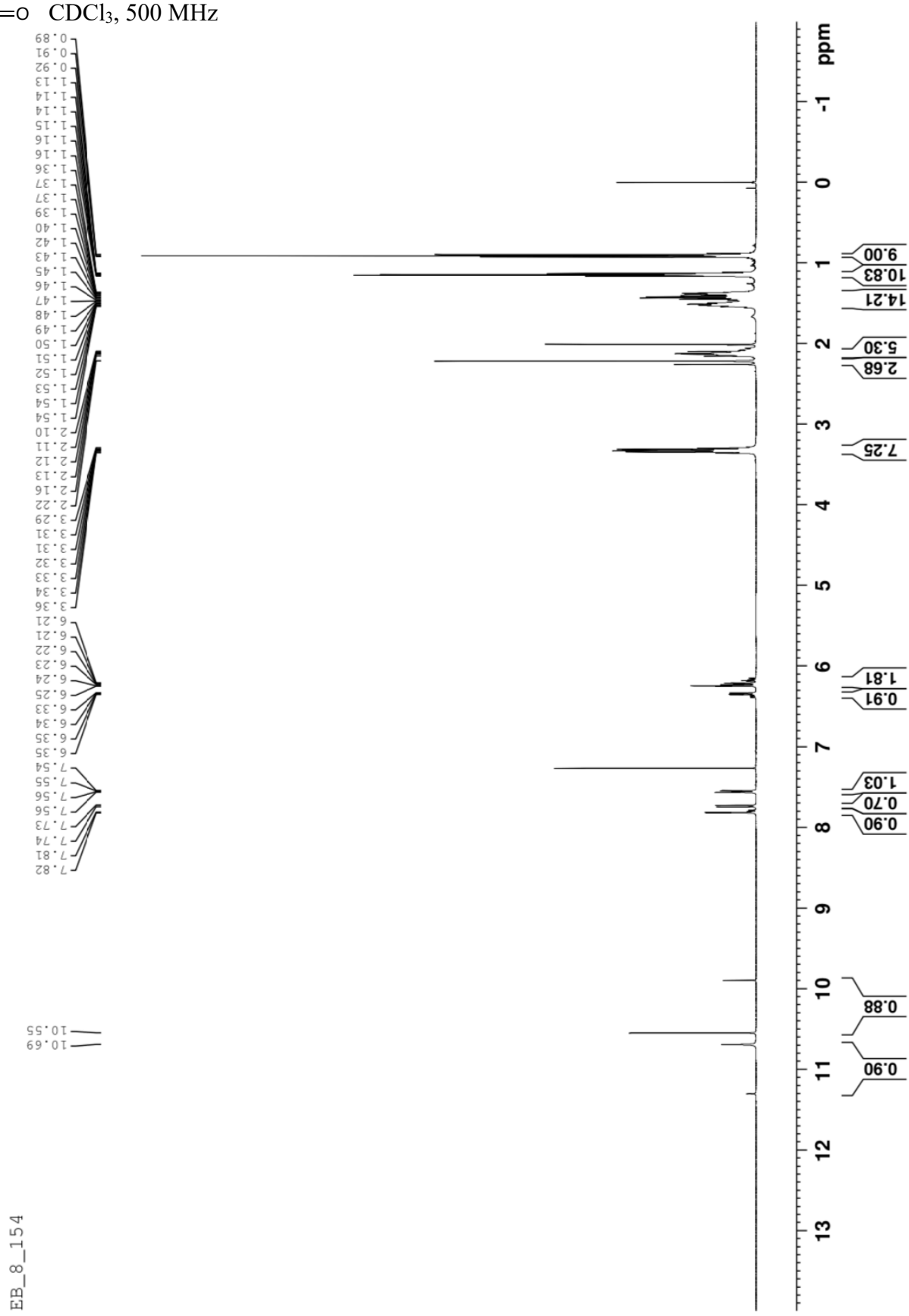


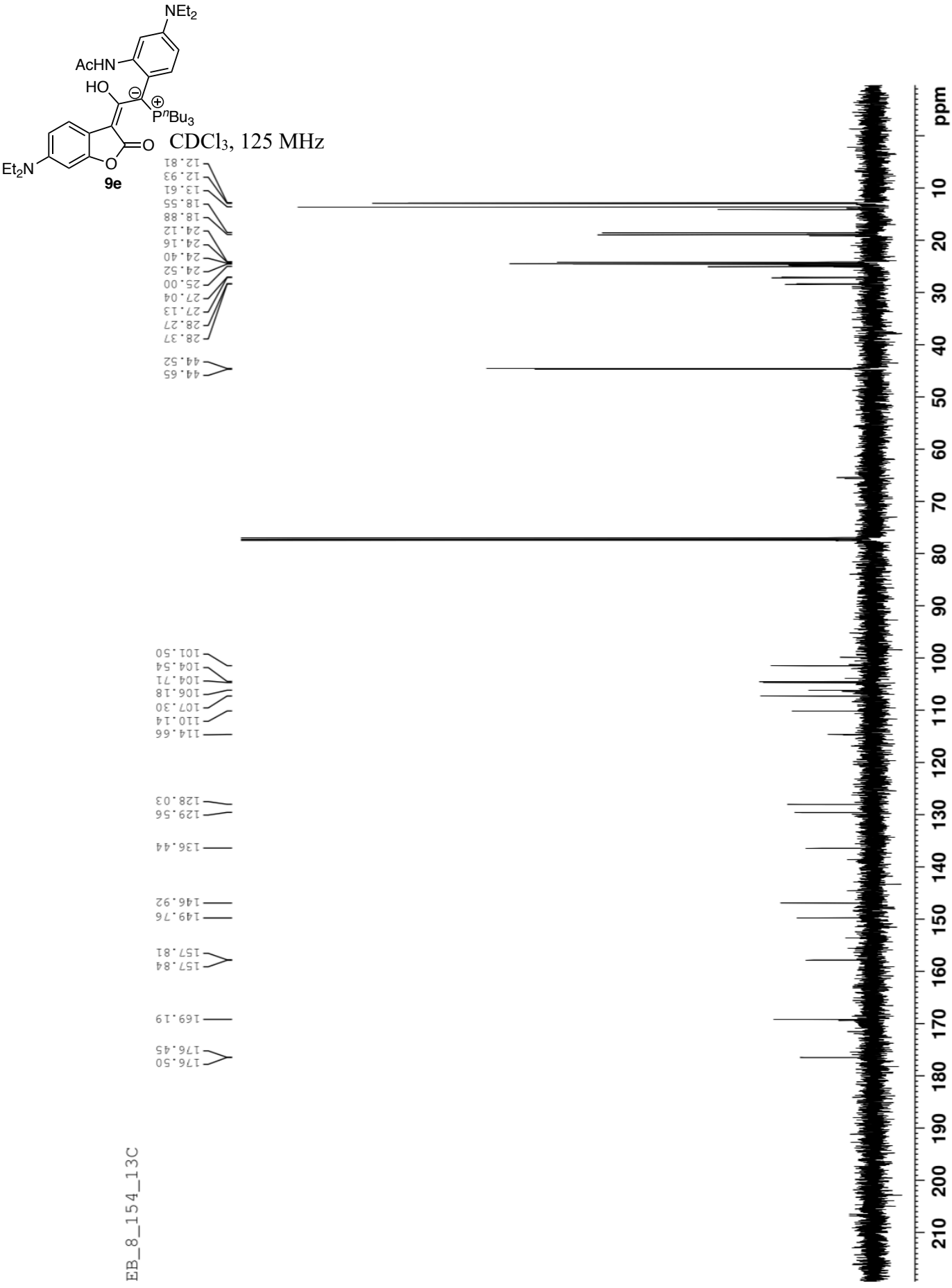
EB_6_142_13C

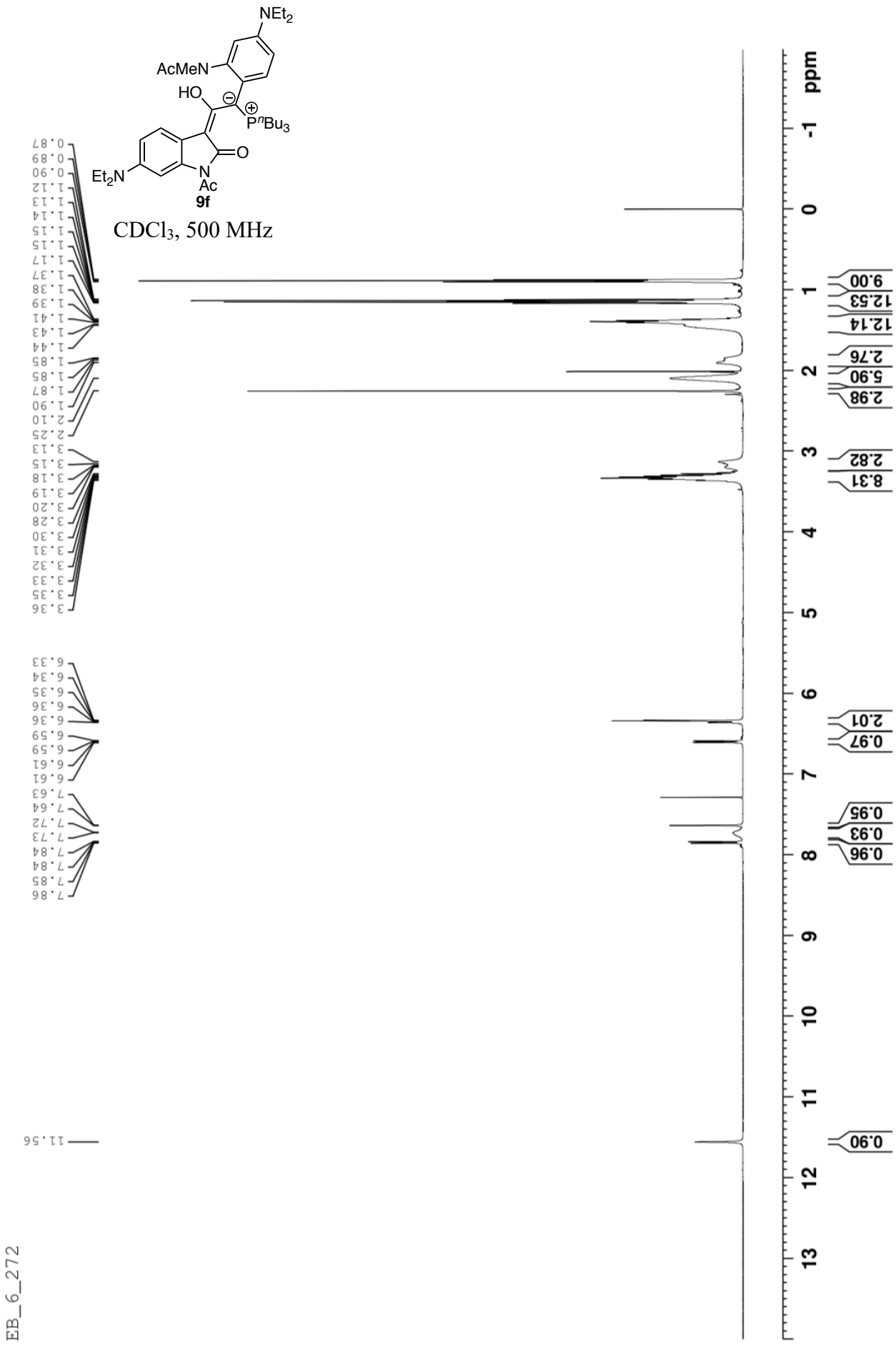


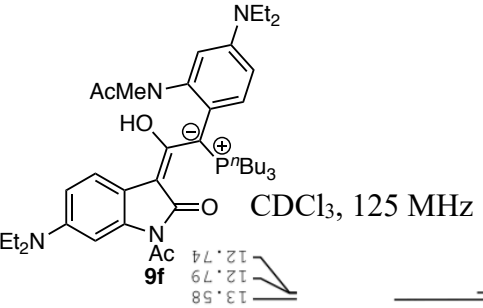
9e

$CDCl_3$, 500 MHz




NEt2
AcHN
HO
P^{n}Bu3
Et2N
O
9e
CDCl3, 125 MHz
12.81
12.93
13.61
18.55
18.88
24.12
24.16
24.40
24.52
25.00
27.04
27.13
28.27
28.37
44.52
44.65
101.50
104.54
104.71
106.18
107.30
110.14
114.66
128.03
129.56
136.44
146.92
149.76
157.81
157.84
169.19
176.45
176.50
EB_8_154_13C
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


NEt2
AcMeN
HO
P^nBu3
O
N
Ac
Et2N
9f
CDCl3, 500 MHz
ppm
EB_6_272



$CDCl_3$, 125 MHz

EB_6_272_13C