SUPPORTING INFORMATION

Tetraarylphosphonium Salts as Soluble Supports for Oxidative Catalysts and Reagents

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EXPERIMENTAL PROCEDURE AND CHARACTERIZATION DATA FOR NEW COMPOUNDS

General: All non-aqueous reactions were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.[1] All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas.

Anhydrous solvents were obtained by filtration through drying columns (DCM, DMF, THF, CH_3CN, methanol).

Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel. Visualization of the developed chromatogram was performed by UV absorbance, iodine, or aqueous potassium permanganate.

Flash column chromatography was performed using 230-400 mesh silica of the indicated solvent system according to standard technique.[2]

Melting points are uncorrected.

Infrared spectra are reported in reciprocal centimeters (cm^{-1}).

Nuclear magnetic resonance spectra were recorded either 300 or 400 MHz spectrometers. Chemical shifts for ^1H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sx = sextet, sep = septet, o = octet, n = nonet, m = multiplet and br = broad), coupling constant in Hz, integration, and assignment. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (77.23 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, HMQC and DEPT experiments.

Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary. Et_3N, pyridine, *i*-Pr_2NEt and $BF_3{\cdot}Et_2O$ were freshly distillated over calcium hydride prior use. Oxalyl chloride was freshly distillated prior use. *m*-CPBA was purified by washing with phosphate buffer of pH 7.5 and recrystillized prior used.

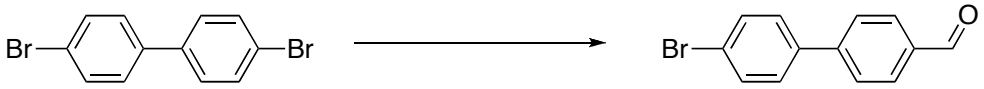
1. Shriver, D. F.; Drezdzon, M. A. The manipulation of air-sensitive compounds; 2nd Edition ed.; Wiley: New York, 1986.
2. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

TAP-SUPPORTED DMSO 14 SYNTHESIS AND APPLICATIONS

Synthesis of 4'-(carboxybiphenyl-4-yl)triphenylphosphonium perchlorate (12)[3]

The title compound was prepared in three steps from 4,4'-dibromobiphenyl.

4'-bromo-1,1'-biphenyl-4-carbaldehyde (S1).[4]



S1

A 3-L, three-neck, round-bottomed flask equipped with a 500 mL addition-funnel, thermocouple, and a mechanical stirrer was charged with 4,4'-dibromobiphenyl (100.0 g, 320.5 mmol) under an argon flow. THF (1.6 L, 0.2 M) was added and the solution was cooled to −25 °C while stirring. The addition-funnel was charged with *n*-Bu_3MgLi (313.5 mL, 128.5 mmol 0.4 equiv), which was added to the reaction flask over 30 min to keep the internal reaction temperature below −10 °C. The resulting yellow solution was stirred for 2 h at −20 °C and DMF (124 mL, 27.3 mol, 1.1 equiv) was then added over 30 min. The reaction was stirred 1h and allowed to warm to 0 °C, followed by the slow addition of 300 mL of saturated NH_4Cl solution. The layers were separated and the aqueous layer was extracted with DCM (2 x 500 mL). The combined organic layers were washed with water (3 x 400 mL), brine (400 mL), dried over $MgSO_4$, and concentrated under reduced pressure to afford a mixture of dibromobiphenyl/monoaldehyde/bialdehyde.

n-Bu_3MgLi was prepared as following: to a solution of *n*-BuMgCl (71.5 mL, 1.79 M in THF, 128.5 mmol, 0.40 equiv) in THF (160 mL, 0.8 M) was added at room temperature *n*-BuLi (82 mL, 3.06 M in hexane, 250.0 mmol, 0.78 equiv) over 30 min. The mixture was stirred for 5 min and directly used in the reaction.

The crude mixture of dibromobiphenyl/monoaldehyde/bialdehyde (74.61 g) was charged in a 1-L, three-neck, round-bottomed flask and dissolved in THF (286 mL, 1 M). An aqueous solution of $NaHSO_3$ (59.78 g, 572 mmol, 2 M) was then added. The formation of the bisulfite adduct[5] was immediately (precipitation of a white solid). The reaction mixture was heated at reflux for 1 h and then cooled down to room temperature. The white solid was filtered and washed with THF (2 x 200 mL). The white solid was transferred in a 2-L, three-neck, round-bottomed flask and DCM (1L) was added. An aqueous NaOH solution (300 mL, 1 M) was added to the suspension and the biphasic system was heated to reflux under vigorous stirring until the solid was dissolved in the organic layer (2-3 h). The biphasic solution was diluted with DCM (500 mL) and the layers were separated. The organic layer was washed with a saturated NH_4Cl solution (300 mL), water (300 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to afford a mixture of monoaldehyde and bialdehyde (96:4, by ^1H NMR). The crude aldehyde **S1** (62.7 g) was used in the next step without further purification. ^1H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.94-7.95 (m, 2H), 7.73-7.71 (m, 2H), 7.62-7.59 (m, 2H), 7.51-7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 146.1, 138.8, 135.6, 132.4, 130.6, 129.1, 127.7, 123.2.

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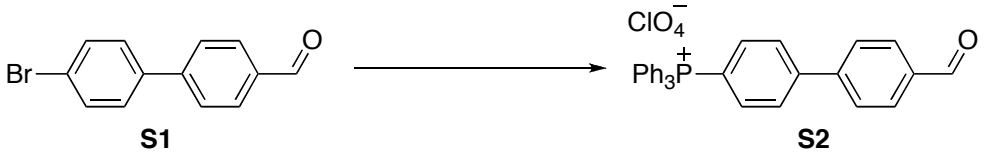
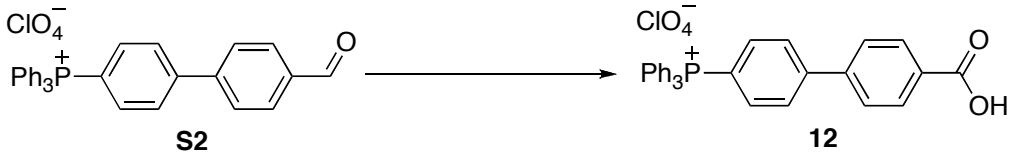
3. Stazi, F.; Marcoux, D.; Poupon, J. C.; Latassa, D.; Charette, A. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 5011.
4. Dolman, S. J.; Gosselin, F.; O'Shea, P. D.; Davies, I. W. *Tetrahedron* **2006**, *62*, 5092.
5. Ragan, J. A.; am Ende, D. J.; Brenek, S. J.; Eisenbeis, S. A.; Singer, R. A.; Tickner, D. L.; Teixeira, J. J.; Vanderplas, B. C.; Weston, N. *Org. Process Res. Dev.* **2003**, *7*, 155.

4'-(formyl-1,1'-biphenyl-4-yl)triphenylphosphonium perchlorate (S2).[3]



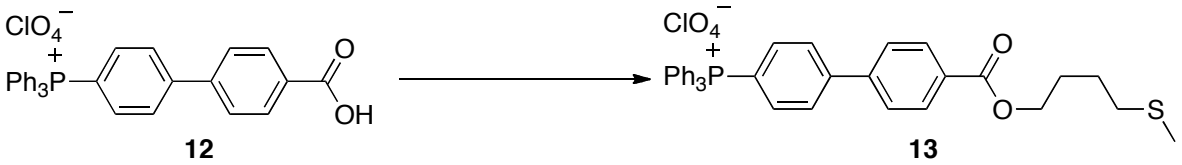
The crude aldehyde **S1** (62.7 g, 96 % pure, 230.4 mmol, 1.0 equiv), $NiBr_2$ (1.5 g, 6.91 mmol, 0.03 equiv), triphenylphosphine (63.5 g, 567.0 mmol, 1.5 equiv) and ethylene glycol (77 mL, 3 M) were charged in a 500-mL, three-neck, round-bottomed flask equipped with a condenser and a thermocouple. The mixture was heated to 180 °C with a heating mantle for 3 h. The starting materials dissolve with heating with the solution becoming green as the reaction proceeds. The reaction was cooled down to room temperature and diluted with DCM (1.2 L). The organic layer was washed with an aqueous solution of $LiClO_4 \cdot 3H_2O$ (13.6 g, 84 mmol, 1.05 equiv, 200 mL H_2O), with H_2O (4 x 200 mL) and transferred in a 3-L, three-neck, round-bottomed flask equipped with a mechanical stirrer. The mixture was cooled to 0 °C and aqueous HCl (300 mL, 6M) was added. The mixture was vigorously stirred until the aldehyde deprotection is complete (followed by LCMS-ES, typically 4 h). The aqueous layer was separated and the organic layer was neutralised with saturated $NaHCO_3$ (2 x 150 mL), washed with water (150 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Addition of Et_2O (300 mL, over 15 min) to the resultant oil with vigorous stirring gave a solid that was collected by filtration and further washed with Et_2O. The aldehyde **S2** was obtained as a white solid (125.1 g, 72% over two steps) mp: > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.15-8.10 (m, 2H), 7.92-7.89 (m, 2H), 7.91-7.84 (m, 4H), 7.75-7.72 (m, 9H), 7.61-7.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 146.6, 143.8, 136.3, 135.8 (d, J = 2.1 Hz), 135.1 (d, J = 10.6 Hz), 134.3 (d, J = 10.3 Hz), 130.8 (d, J = 12.9 Hz), 130.5, 129.5 (d, J = 13.1 Hz), 128.3, 117.2 (d, J = 89.1 Hz), 116.7 (d, J = 90.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.2; IR (solid) 3047, 1692, 1595, 1436, 1387, 1106 cm^{-1}; LRMS (ESI, Pos) Calcd for $C_{31}H_{24}O_1P_1$ $[M]^+$: 443.2, found 443.0.

4'-(carboxybiphenyl-4-yl)triphenylphosphonium perchlorate (12)[3]



Aldehyde **S2** (10.0 g, 19.1 mmol, 1.0 equiv.) was dissolved in acetone (120 ml, 0.16 M) and cooled to –10 °C. A 2.66 M solution of Jones' reagent (14.4 mL, 38.2 mmol, 2 equiv.) was slowly added and the reaction mixture was stirred 10 min at –10 °C and 1 h at room temperature. The temperature was then lowered to –10 °C and *i*-PrOH (2-3 mL) was added until the reddish solution became and remained green. The mixture was diluted with DCM (300 mL) and dried by addition of $MgSO_4$. The mixture was filtered through a pack of silica gel and washed with DCM/MeOH (9:1, 500 mL) and the solvent was removed under reduced pressure. Addition of Et_2O (100 mL, over 5 min) to the resultant oil with vigorous stirring gave a solid that was collected by filtration. The acid **12** (10.16g, 95 %) was obtained as a white solid. mp.: > 250 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): d 9.81 (s, 1H), 8.20 (d, J = 8.5 Hz, 2H), 8.10-7.89 (m, 2H), 7.88-7.84 (m, 3H), 7.82-7.59 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD 10/1): d 168.1, 147.1 (d, J = 3.0 Hz,), 142.4, 135.8, 135.1 (d, J = 10.7 Hz), 134.3 (d, J = 10.3 Hz), 131.1, 130.9 (d, J = 12.9 Hz), 130.8, 129.2 (d, J = 13.3 Hz), 127.4, 117.4 (d, J = 89.6 Hz), 116.3 (d, J = 91.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): d 23.3. IR (solid) 3065 (br), 1686, 1596, 1437, 1089, 996, 723, 688, 621 cm^{-1}. LRMS (ES, Pos)) Calcd for $C_{31}H_{24}O_2P_1$ $[M]^+$: 459.15, found: 459.2.

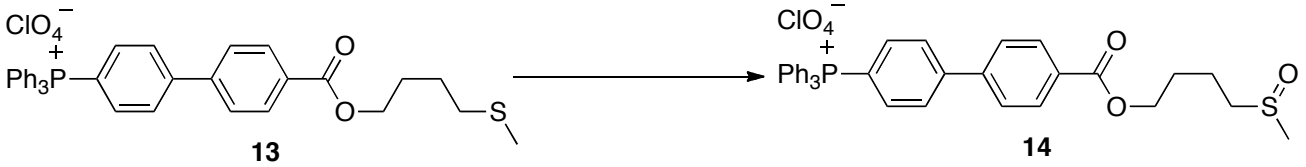
(4'-{[4-(Methylthio)butoxy]carbonyl}-1,1'-biphenyl-4-yl)(triphenyl)phosphonium perchlorate (13)



12 **13**

To a solution of acid **12** (9.0 g, 16.1 mmol, 1.0 equiv) in DCM (80 mL, 0.2 M) at 0 °C was added $(COCl)_2$ (1.69 mL, 19.32 mmol, 1.2 equiv) followed by DMF (5-6 drops). The solution was stirred for 2 h and the excess of $(COCl)_2$ was evaporated under reduced pressure. The resultant foam was dissolved in DCM (80 mL, 0.2 M) and pyridine (3.26 mL, 40.25 mmol, 2.5 equiv) was added followed by a solution of 4-methyl(thio)butanol (2.35 mL, 19.32 mmol, 1.2 equiv) in THF (33 mL, 0.6 M). The mixture was heated to reflux for 16 h and cooled to rt. The solution was diluted with DCM (200 mL) and washed with aqueous 10% (w/w) HCl (3 x 20 mL), once with saturated aqueous $NaHCO_3$ (20 mL) and once with water (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was dissolved with DCM (5 mL) and was precipitated upon Et_2O addition (50 mL, over 5 min). The ether layer was decanted and the above isolation protocol was repeated twice to afford pure TAP-supported sulfide **13** as a yellowish solid (9.6 g, 90%). mp: 72-75 °C; NMR ^{1}H (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.99 (dd, *J* = 2.1 Hz, 8.0 Hz, 2H), 7.86 (t, *J* = 7.2 Hz, 3H), 7.78-7.71 (m, 10H), 7.67-7.62 (m, 6H), 4.33 (t, *J* = 6.2 Hz, 2H), 2.55 (t, J = 7.0 Hz, 2H), 2.07 (s, 3H), 1.91-184 (m, 2H), 1.78-1.72 (m, 2H); NMR ^{13}C (100 MHz, $CDCl_3$): δ 166.1, 147.0 (d, *J* = 3.0 Hz), 142.7, 135.8 (d, *J* = 2.9 Hz), 135.2 (d, *J* = 10.7 Hz), 134.5 (d, *J* = 10.4 Hz), 130.9 (d, *J* = 12.9 Hz), 130.8, 130.4, 129.4 (d, *J* = 13.3 Hz), 127.7, 117.5 (d, *J* = 89.7 Hz), 116.7 (d, *J* = 90.8 Hz), 64.8, 33.8, 27.8, 25.6, 15.5; NMR ^{31}P (162 MHz, $CDCl_3$): δ 23.3; IR (solid): 2915, 2160, 1709, 1437, 1273, 1080, 996, 724, 688 cm^{-1}; HRMS (API-ES, Pos) Calcd. for $C_{36}H_{34}O_2PS$ $[M]^+$: 561.2009, found: 561.2012.

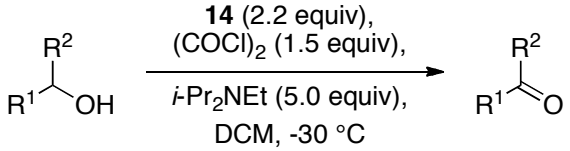
(4'-{[4-(Methylsulfinyl)butoxy]carbonyl}-1,1'-biphenyl-4-yl)(triphenyl)phosphonium perchlorate (14).



13 **14**

To a solution of sulfide **13** (5.0 g, 7.56 mmol, 1.0 equiv) in a mixture of DCM/MeOH (2:1, 27 mL, 0.3 M) at 0 °C was added H_2O_2 (35% (w/w) aq solution) (3.0 mL, 37.0 mmol, 5.0 equiv). The solution was vigorously stirred at rt for 3 h and diluted with DCM (100 mL). The organic layer was washed with brine (15 mL), water (15 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was dissolved with DCM (3 mL) and was precipitated upon Et_2O addition (30 mL, over 3 min). The ether layer was decanted and the above isolation protocol was repeated twice to afford pure TAP-supported sulfoxide **14** as a yellowish solid (5.15 g, 99%). mp: 75-80 °C; NMR ^{1}H (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.99 (dd, *J* = 3.1 Hz, 8.4 Hz, 2H), 7.86 (m, 3H), 7.79-7.70 (m, 10H), 7.67-7.62 (m, 6H), 4.35 (m, 2H), 2.79 (m, 2H), 2.58 (s, 3H), 1.91-184 (m, 2H), 1.97-1.95 (m, 4H); NMR ^{13}C (100 MHz, $CDCl_3$): δ 166.1, 147.0 (d, *J* = 3.1 Hz), 142.7, 135.9 (d, *J* = 3.0 Hz), 135.2 (d, *J* = 10.7 Hz), 134.5 (d, *J* = 10.4 Hz), 130.9 (d, *J* = 12.9 Hz), 130.7 130.6, 129.5 (d, *J* = 13.3 Hz), 127.7, 117.6 (d, *J* = 89.6 Hz), 116.7 (d, *J* = 90.9 Hz), 64.5, 54.0, 38.8, 27.9, 19.7; NMR ^{31}P (162 MHz, $CDCl_3$): δ 23.3; IR (solid) 2915, 2160, 1709, 1437, 1273, 1082, 996, 724, 688 cm^{-1}; HRMS (API-ES, Pos) cal. For $C_{36}H_{34}O_2PS$ $[M]^+$: Calcd. for 577.1961, found: 577.1960.

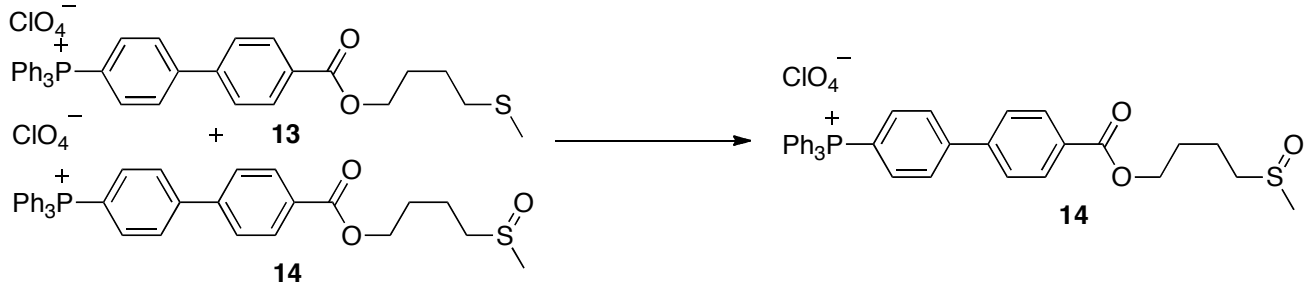
General procedure for the Swern oxidation using TAP-supported DMSO 14



To a solution of oxalyl chloride (131 μL, 1.5 mmol, 1.5 equiv) in DCM (1.5 mL, 1 M) at –40 °C was slowly added a solution of TAP-DMSO **14** (1.49 g, 2.2 mmol, 2.2 equiv) in DCM (6.0 mL, 0.37 M). After 10 min, a solution of alcohol (1.0 mmol, 1.0 equiv) in DCM (2.5 mL, 0.4 M) was added and the solution was stirred at –30 °C for 1-2 h. DIPEA (871 μL, 5.0 mmol, 5.0 equiv) was then added and the solution was stirred –30 °C for 10 min and at rt for 30 min. The solution was diluted with DCM (40 mL), washed with aq 10% (w/w) HCl (2 x 5 mL), water (5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Celite (3.0 g) was added to the residue followed by slow addition of Et_2O (10 mL, over 1 min) to induce the complete precipitation of the TAP-supported mixture of sulfide **13** and sulfoxide **14**. The mixture was filtered on Celite and concentrated under reduced pressure to afford aldehydes. If needed, aldehydes were subsequently purified by flash chromatography.

The observed characterization data (NMR ^1H, ^{13}C) of oxidation products was consistent with commercially available compound.

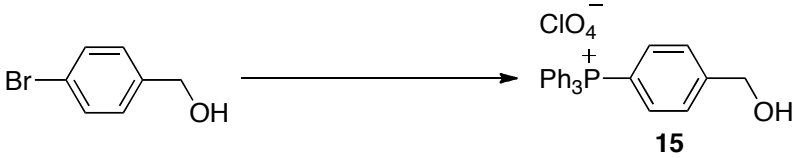
Recovery of TAP-supported DMSO 14



The recovered mixture of TAP-supported sulfide **13** and sulfoxide **14** (2.2 mmol, 1.0 equiv) was dissolved in a mixture of DCM/MeOH (2:1, 9 mL, 0.3 M). At 0 °C, was added H_2O_2 (35% (w/w) aq. sln) (686 μL, 5.5 mmol, 2.5 equiv). The solution was vigorously stirred at room temperature for 3 h and diluted with DCM (30 mL). The organic layer was washed with brine (15 mL), water (5 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was dissolved with DCM (1 mL) and was precipitated upon Et_2O addition (10 mL, over 1 min). The ether layer was decanted and the above isolation protocol was repeated twice to afford pure TAP-supported sulfoxide **5** as a yellowish solid (1.43 g, 96%).

TAP-SUPPORTED TEMPO 16 SYNTHESIS AND APPLICATIONS

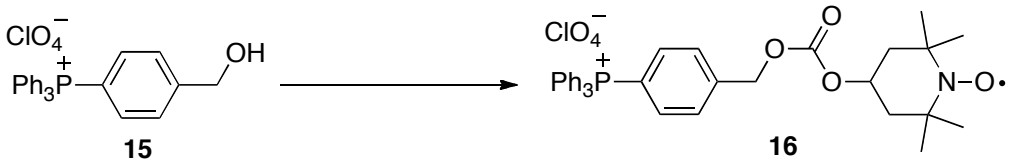
(4-(Hydroxymethyl)phenyl)triphenylphosphonium perchlorate (15)[6,7]



15

4-Bromobenzyl alcohol (50.0 g, 267 mmol, 1.0 equiv), $NiBr_2$ (1.75 g, 8.02 mmol, 0.03 equiv), triphenylphosphine (73.6 g, 281 mmol, 1.05 equiv) and ethylene glycol (89 mL, 3 M) were charged in a 500-mL, three-neck, round-bottomed flask equipped with a condenser and a thermocouple. The mixture was warmed to 180 °C with a heating mantle for 4 hours. The starting materials dissolve with heating and the solution becomes green as the reaction proceeds. The reaction was cooled to room temperature and diluted with DCM (1.5 L). The organic layer was washed with an aqueous solution of $LiClO_4 \cdot 3H_2O$ (45.0 g, 281 mmol, 1.05 equiv, 250 mL H_2O), with H_2O (4 x 250 mL), brine (250 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The phosphonium salt was completely precipitated by the addition of hexane (250 mL), to afford alcohol **15** as a white solid (122 g, 97 %). mp: 223-225 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.92-7.87 (m, 3H), 7.83-7.80 (m, 8H), 7.54-7.45 (m, 8H), 4.71 (s, 2H), 4.30 (s, 1H) ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.4 (d, *J* = 3.0 Hz, 1C), 136.4 (d, *J* = 3.0 Hz, 3C), 135.3 (d, *J* = 10.3, 6C), 135.0 (d, *J* = 10.8 Hz, 2C), 131.4 (d, *J* = 12.9 Hz, 6C), 129.4 (d, *J* = 13.3 Hz, 2C), 118.8 (d, *J* = 89.6, 3C), 115.0 (d, *J* = 91.6 Hz, 1C), 63.3 (s, 1C); ^{31}P NMR (122 MHz, CD_2Cl_2) δ 23.7; IR (film) 3251 (br), 3052, 1600, 1586, 1437, 1108, 1060, 954 cm-1; HRMS (ES+) Calcd for $C_{25}H_{22}O_1P_1$ [M]+: 369.1408, found 369.1403

4-({[4-(Triphenylphosphonio)benzyl]oxy}carbonyl)oxy]-2,2,6,6-tetramethylpiperidin-1-oxyl perchlorate. (16).



15 **16**

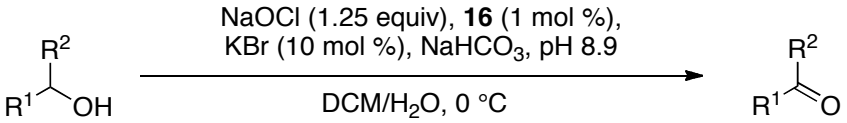
To a solution of triphosgene (356 mg, 1.2 mmol, 0.6 equiv) in DCM (4.0 mL) at –20 °C was added pyridine (970 μL, 12.0 mmol, 6.0 equiv) dropwise, followed by a solution of 4-hydroxy-TEMPO (690 mg, 4.0 mmol, 2.0 equiv) in DCM (4.0 mL). The mixture was stirred for 15 min and warmed to rt and stirred for 30 min. Alcohol **15** (936 mg, 2.0 mmol, 1.0 equiv) was added and the solution was stirred for 2 h. The solution was diluted with DCM and washed with water (2 x 10 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was dissolved with DCM (2 mL) and was precipitated upon Et_2O addition (10 mL, over 1 min). The ether layer was decanted and the above isolation protocol was repeated twice to afford pure TAP-supported TEMPO **16** as an orange solid (1.27 g, 95%). mp: 80-85 °C; NMR characterization was achieved by in situ reduction of the radical TAP-supported TEMPO **16** to the hydroxylamine derivative with phenylhydrazine.[26] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.87 (m, 3H), 7.79-7.74 (m, 8H), 7.68-7.60 (m, 8H), 5.31 (s, 2H), 4.95 (m, 1H), 3.90 (br, 1H), 2.08 (dd, *J* = 4.1 Hz, 12.8 Hz, 2H), 1.84 (t, *J* = 12.0 Hz, 2H), 1.34 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 144.0 (d, *J* = 3.0 Hz), 136.0 (d, *J* = 2.8 Hz), 135.0 (d, *J* = 10.7 Hz), 134.6 (d, *J* = 10.4 Hz), 131.0 (d, *J* = 12.9 Hz), 129.6

6. Marcoux, D.; Charette, A. B. *Adv. Synth. Catal.* **2008**, *350*, 2967.
7. Poupon, J. C.; Boezio, A. A.; Charette, A. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 1415.

(d, J = 13.3 Hz), 116.9 (d, J = 89.6 Hz), 117.0 (d, J = 90.4 Hz), 71.0, 68.0, 60.8, 42.9, 30.8, 21.0; ^{31}P RMN (162 MHz, CD_2Cl_2): δ 23.3. IR (solid): 2975, 2160, 1742, 1438, 1263, 1081, 689 cm^{-1}; HRMS (ES+) Calcd. for $C_{35}H_{38}N_1O_4P_1$ $[M]^+$: 567. 2529, found 567.2538.

General procedure for alcohol oxidation using TAP-supported TEMPO 16

Monoprotective diol 4-(benzyloxy)butanol and 4-(triisopropylsilyloxy)butanol were prepare from 1,4-butanediol according to literature precedents.[8,9]



To a solution of alcohol (1.00 mmol, 1.00 equiv) in DCM (2.5 mL, 0.4 M) at 0 °C was added TAP-supported TEMPO **16** (6.7 mg. 0.01 mmol, 0.01 equiv), an aqueous solution of NaOCl (3.57 mL, 1.25 mmol, 1.25 equiv) buffered at pH 8.9 with $NaHCO_3$ and an aqueous solution of KBr (11.9 mg, 0.10 mmol, 0.10 equiv, 0.2 M). The reaction mixture was vigorously stirred until TLC analysis indicated complete consumption of the starting material. The solution was diluted with DCM (10 mL), the layers were separated and the aqueous layer was extracted with DCM (3 mL). The combined organic layers were washed with water (2 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to a minimum volume. Celite (30 mg) was added to the residue followed by Et_2O (4 mL, over 1 min) to induce the complete precipitation of the TAP-supported TEMPO **16**. The mixture was filtered on Celite and concentrated under reduced pressure to afford pure aldehydes or ketones.

The observed characterization data (NMR ^{1}H, ^{13}C) of oxidation products was consistent with commercially available carbonyl compounds or with that previously reported in the literature for the case of 4-(benzyloxy)butanal[8] and 4-(triisopropylsilyloxy)butanal.[9]

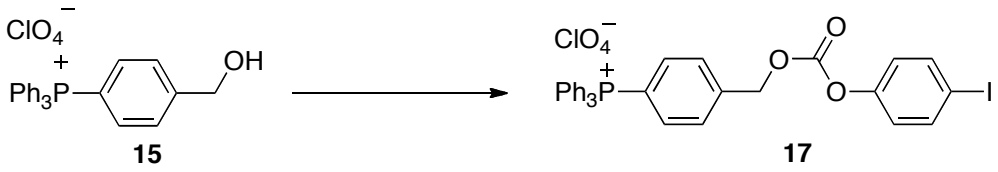
Oxidation of 3-Phenylpropanol: Recycling procedure

To a solution of 3-phenylpropanol (409 mg, 3.00 mmol, 1.00 equiv) in DCM (7.5 mL, 0.4 M) at 0 °C was added TAP-supported TEMPO **16** (20.0 mg, 0.01 mmol, 0.01 equiv), an aqueous solution of NaOCl (10.7 mL, 1.25 mmol, 1.25 equiv) buffered at pH 8.9 with $NaHCO_3$ and an aqueous solution of KBr (35.7 mg, 0.10 mmol, 0.10 equiv, 0.2 M). The reaction mixture was vigorously stirred for 15 min. The solution was diluted with DCM (30 mL), the layers were separated and the aqueous layer was extracted with DCM (10 mL). The combined organic layers were washed with water (6 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to a minimum volume. Celite (100 mg) was added to the residue followed by Et_2O (12 mL, over 1 min) to induce the complete precipitation of the TAP-supported TEMPO **16**. The mixture was filtered on Celite and concentrated under reduced pressure to afford pure 3-phenylpropanal as a colorless oil. TAP-supported TEMPO **16** was dissolved in DCM (7.5 mL) and directly used for subsequent run.

8. Moreau, B.; Ginisty, M.; Alberico, D.; Charette, A. B. *J. Org. Chem.* **2007**, *72*, 1235.
9. Delgado, M.; Martin, J. D. *J. Org. Chem.* **1999**, *64*, 4798.

TAP-SUPPORTED IODOBENZENE 17 SYNTHESIS AND APPLICATIONS

[4-({[(4-Iodophenoxy)carbonyl]oxy}methyl)phenyl](triphenyl)-phosphonium perchlorate (17).

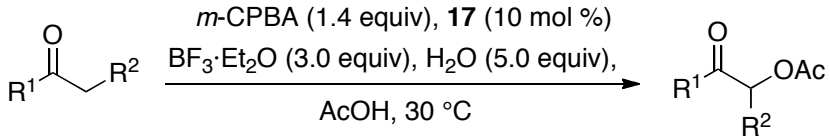


To a solution of triphosgene (1.27 g, 4.60 mmol, 0.43 equiv) in (75 mL) at –30 °C was added pyridine (2.25 mL, 27.8 mmol, 2.6 equiv) dropwise. The resulting mixture was warmed to rt and stirred for 30 min (it became a clear yellowish homogenous solution) and then cooled to –78 °C (heterogenous solution). A solution of alcohol **15** (5.0 g, 10.7 mmol, 1.0 equiv) in DCM (75 mL) at –78 °C was slowly added in a way to kept the internal reaction temperature below –70 °C. After 1 h, a solution of sodium 4-iodophenolate (5.18 g, 21.4 mmol, 2.0 equiv) in THF (30 mL) was added at –78 °C. The resulting yellow solution was left to warm to rt overnight.

Sodium 1,4-iodophenolate was prepared according to the following procedure: 1,4-iodophenol (4.40 g, 20.0 mmol, 1.0 equiv) was quickly added to a solution of sodium methanoate, prepare by adding metallic sodium (448 mg, 19.5 mmol, 0.98 equiv) to methanol (35 mL) at 0 °C. The solution was concentrated under reduced pressure to afford sodium 1,4-iodophenolate as a solid, and stock under argon.

The solution was diluted with DCM (300 mL), washed with brine (2 x 40 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (2 % isopropanol/DCM). Organic solvents were concentrated under reduced pressure until the total volume was reduced to about 10 mL. Addition of Et_2O (50 mL) with vigorous stirring, induce the complete precipitation of the phosphonium salt that was collected by filtration. TAP-supported iodobenzene **17** was obtained as a white solid (5.7 g, 75 %). R_f: 0.38 (2 % isopropanol/DCM); mp: 102-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.86 (m, 3H), 7.82-7.73 (m, 8H), 7.69-7.60 (m, 10H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 151.0, 143.3 (d, *J* = 3.1 Hz), 138.7, 136.0 (d, *J* = 3.1 Hz), 135.0 (d, *J* = 10.5 Hz), 134.6 (d, *J* = 11.0 Hz), 131.0 (d, *J* = 13.0 Hz), 129.8 (d, *J* = 13.3 Hz), 123.3, 117.8 (d, *J* = 90.4 Hz), 117.5 (d, *J* = 89.9 Hz), 90.5, 68.9; IR (film) 3520, 3062, 2968, 1761, 1578, 1437, 1236,1208, 1080 cm^{-1}; ^{31}P NMR (162 MHZ, $CDCl_3$): δ 23.3; HRMS (API-ES, Pos) Calcd. for $C_{32}H_{25}I_1O_3P_1$ $[M]^+$: 615.0583 found: 615.0581.

General procedure for α-acetoxylation of ketone

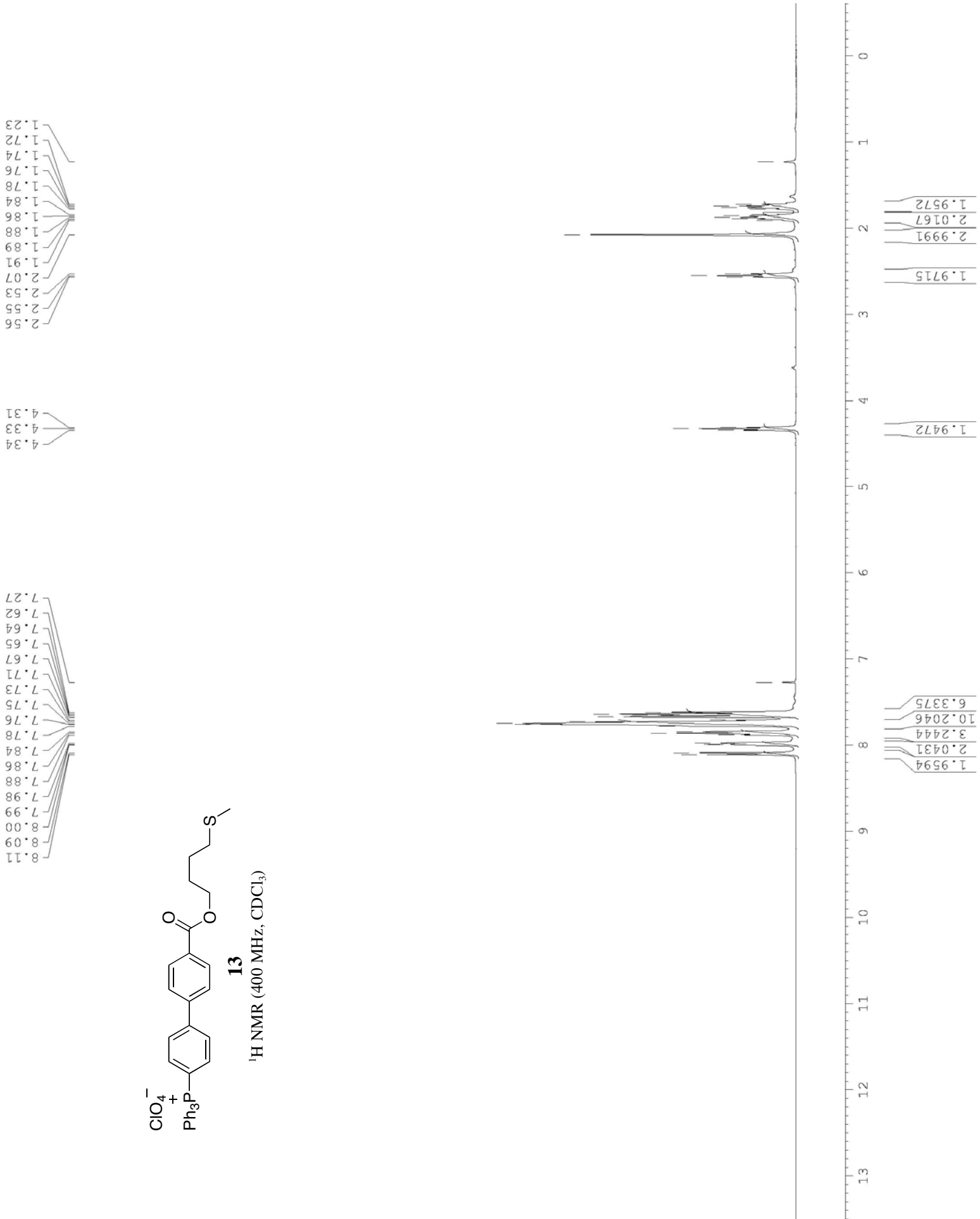


To a solution of *m*-CPBA (98% purity, 246 mg, 1.4 mmol, 1.0 equiv) in acetic acid (4 mL, 0.25 equiv) was added iodobenzene **17** (71 mg, 0.1 mmol, 0.1 equiv), ketone (1.0 mmol. 1.0 equiv), $BF_3{\cdot}Et_2O$ (370 μL, 3.0 mmol. 3.0 equiv) and water (90 μL, 5.0 mmol, 5.0 equiv.) at rt and the mixture was stirred at 25-30 °C for 24-48 h. Celite (350 mg) was added followed by Et_2O (40 mL, over 2 min), under vigorous stirring, to induce the complete precipitation of the TAP salt. The precipitate was filtered on Celite and the ether layer was neutralize with aq 10% (w/w) sodium carbonate solution, washed with pH 8.5 phosphate buffer, dried over Na_2SO_4 and concentrated under reduced pressure. The crude oil was purified by flash chromatography (10% EtOAc/hexane) to afford the pure 2-acetoxyketones.

The observed characterization data (NMR ^{1}H, ^{13}C) of 2-acetoxyacetophenone[10], 2-acetoxy-p-fluoroacetophenone[11] and 3-acetoxy-4-heptanone[11] was consistent with that previously reported in the literature.

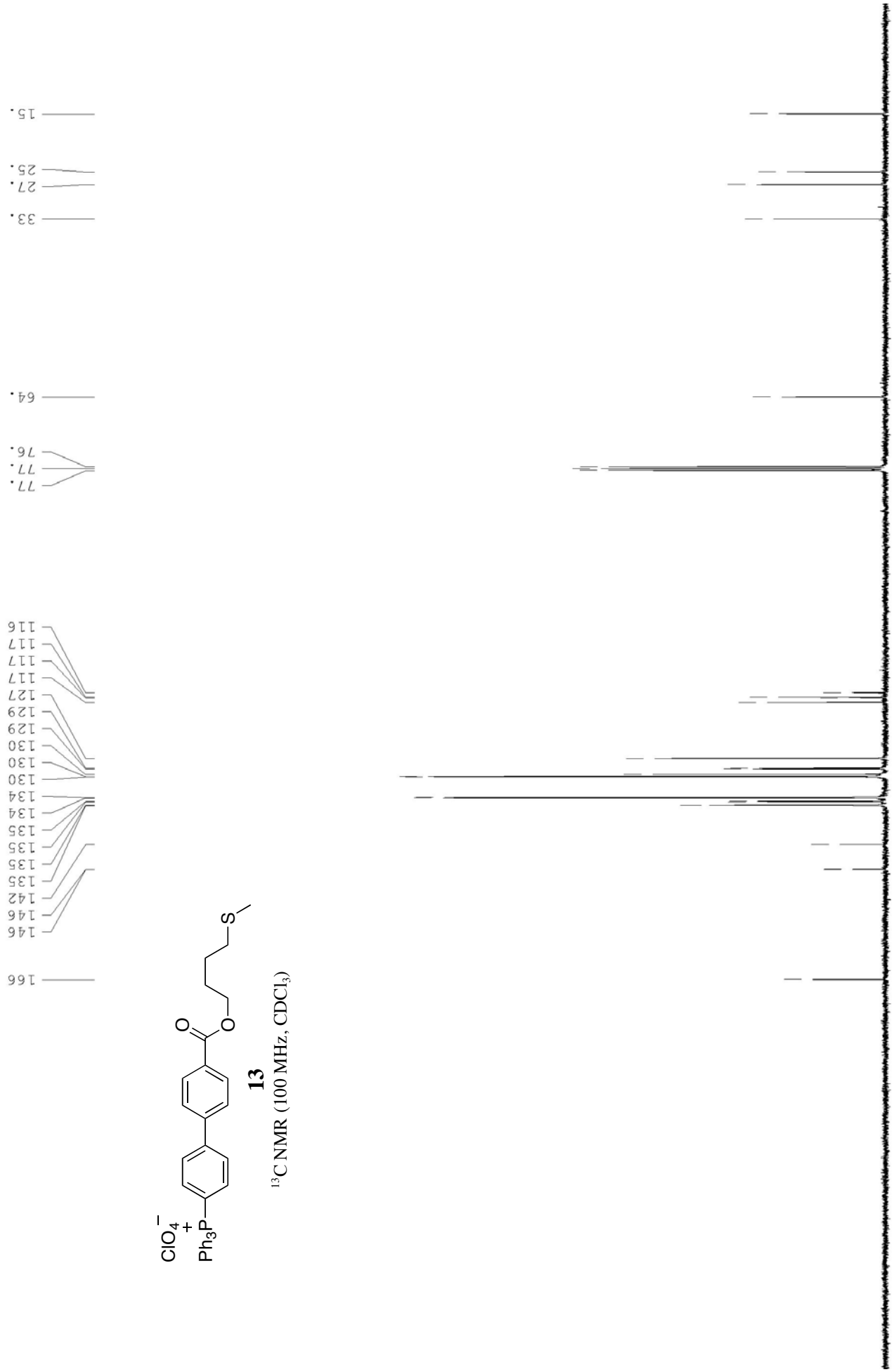
10. Sheng, J.; Li, X.; Tang, M.; Gao, B.; Huang, G. *Synthesis* **2007**, *2007*, 1165.
11. Ochiai, M.; Takeuchi, Y.; Katayama, T.; Sueda, T.; Miyamoto, K. *J. Am. Chem. Soc.* **2005**, *127*, 12244.

^{1}H AND ^{13}C SPECTRA OF SUPPORTED DERIVATIVES 14, 16-17



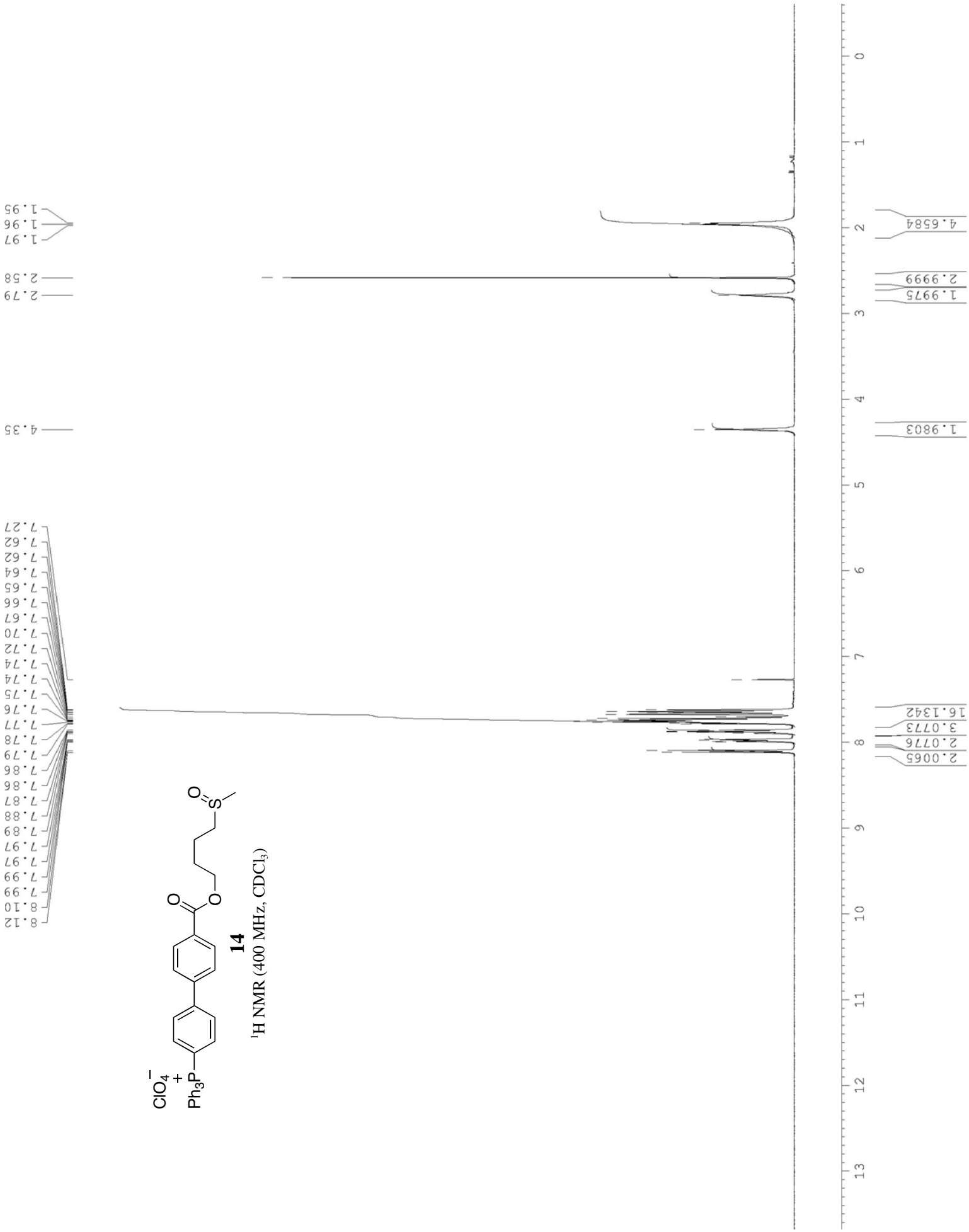
13

^{1}H NMR (400 MHz, $CDCl_3$)



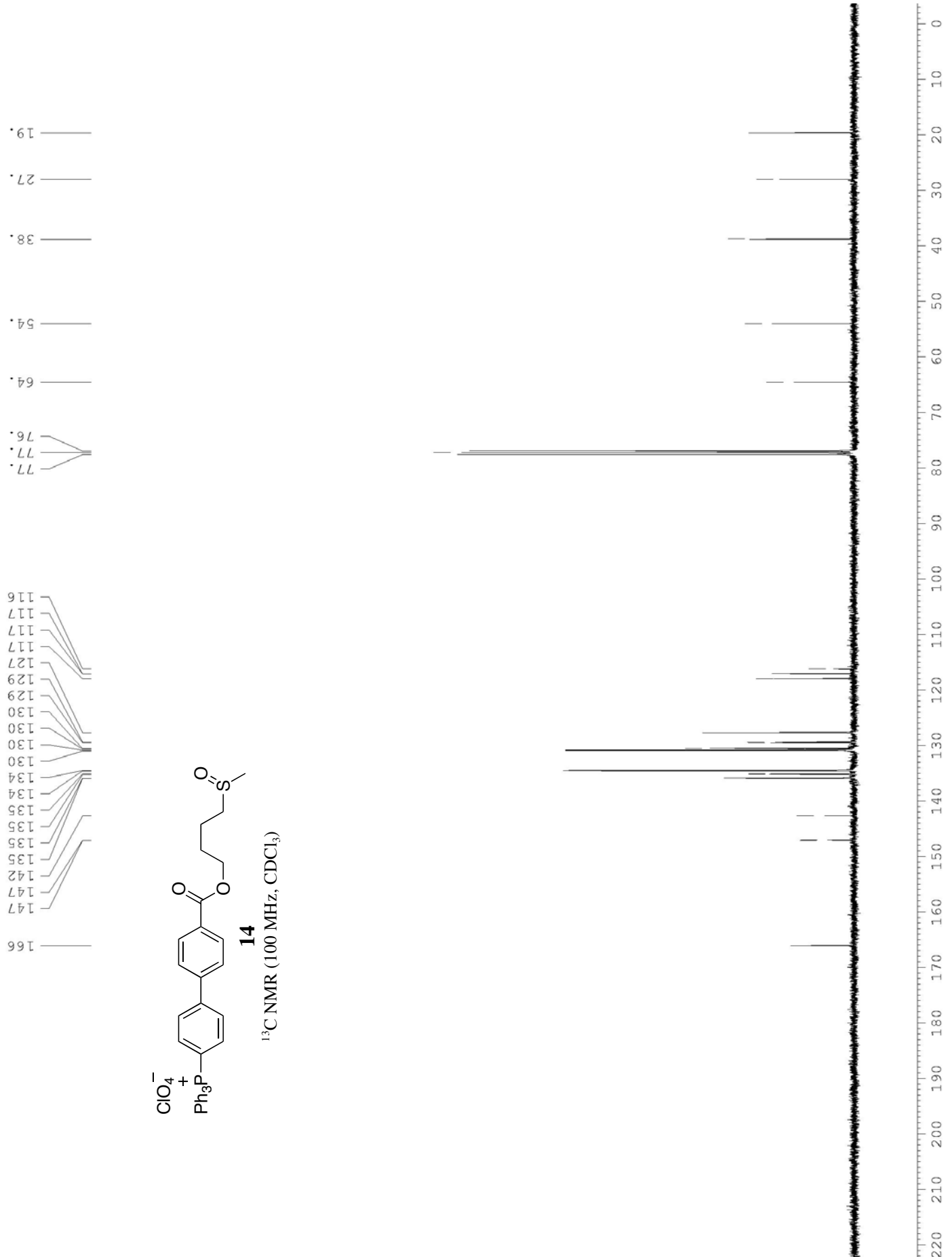
13

^{13}C NMR (100 MHz, $CDCl_3$)



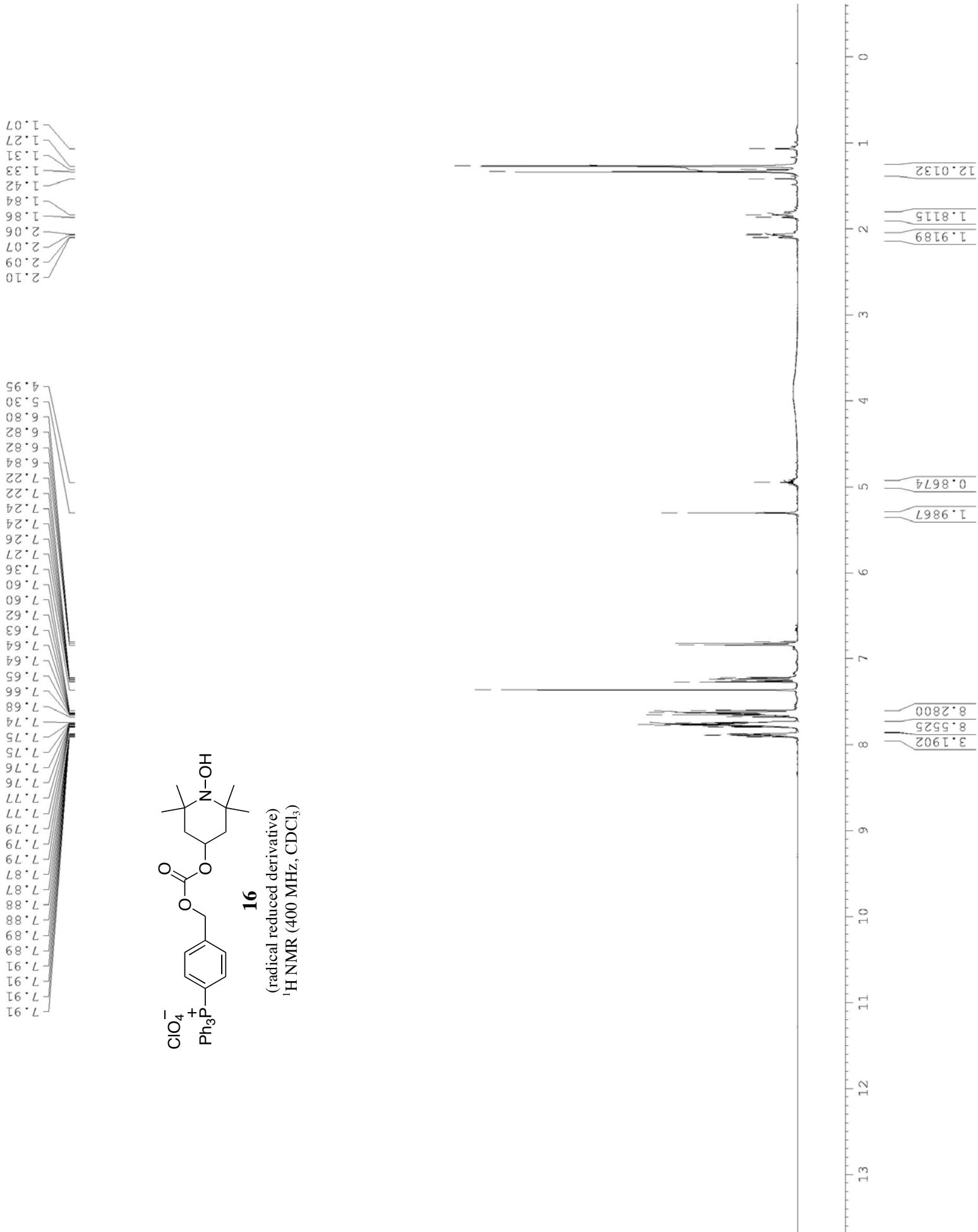
14

^{1}H NMR (400 MHz, $CDCl_3$)



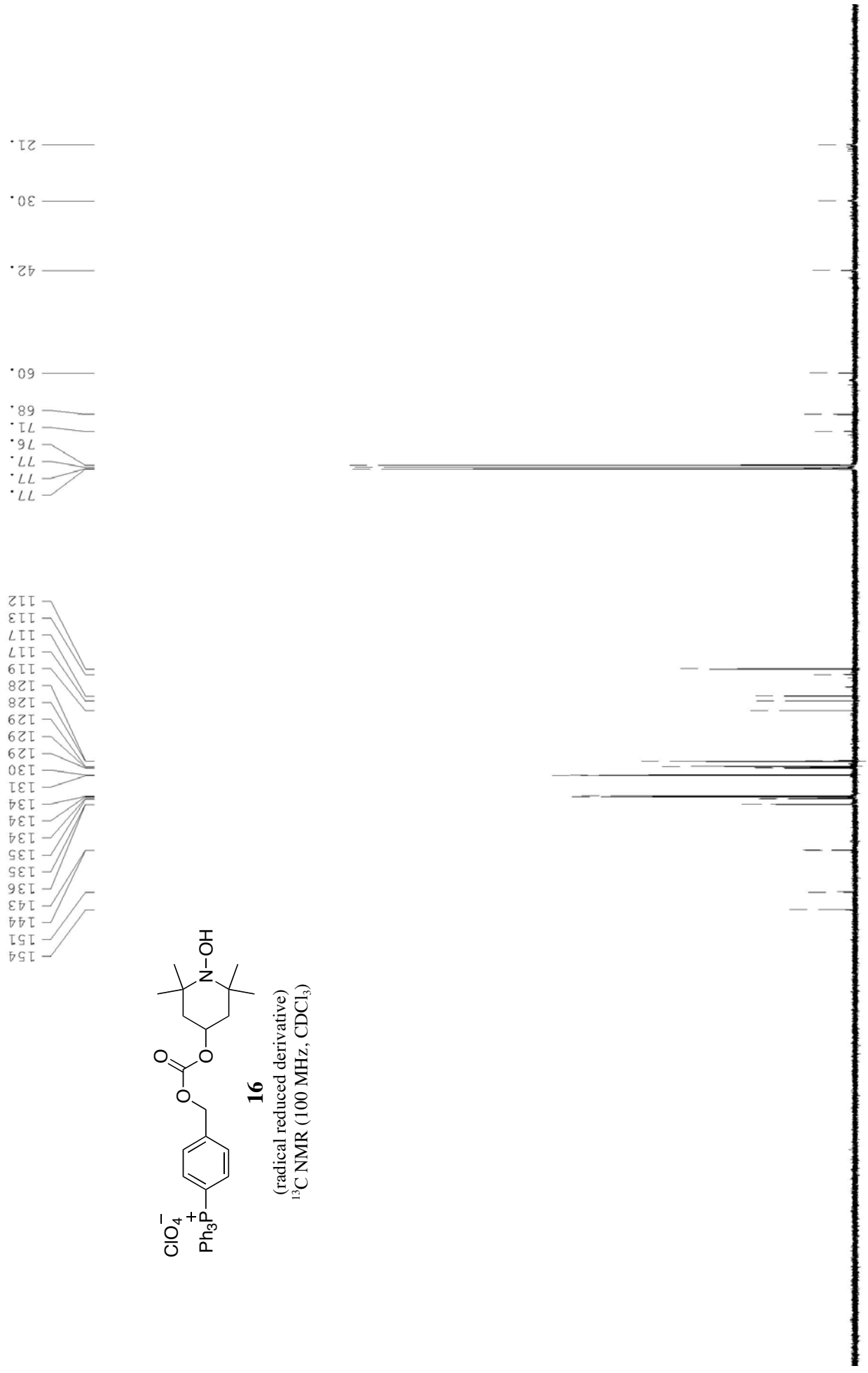
14

^{13}C NMR (100 MHz, $CDCl_3$)



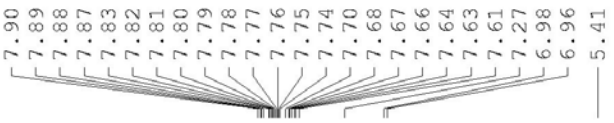
16

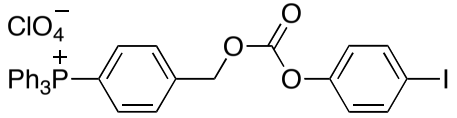
(radical reduced derivative)
^{1}H NMR (400 MHz, $CDCl_3$)



16

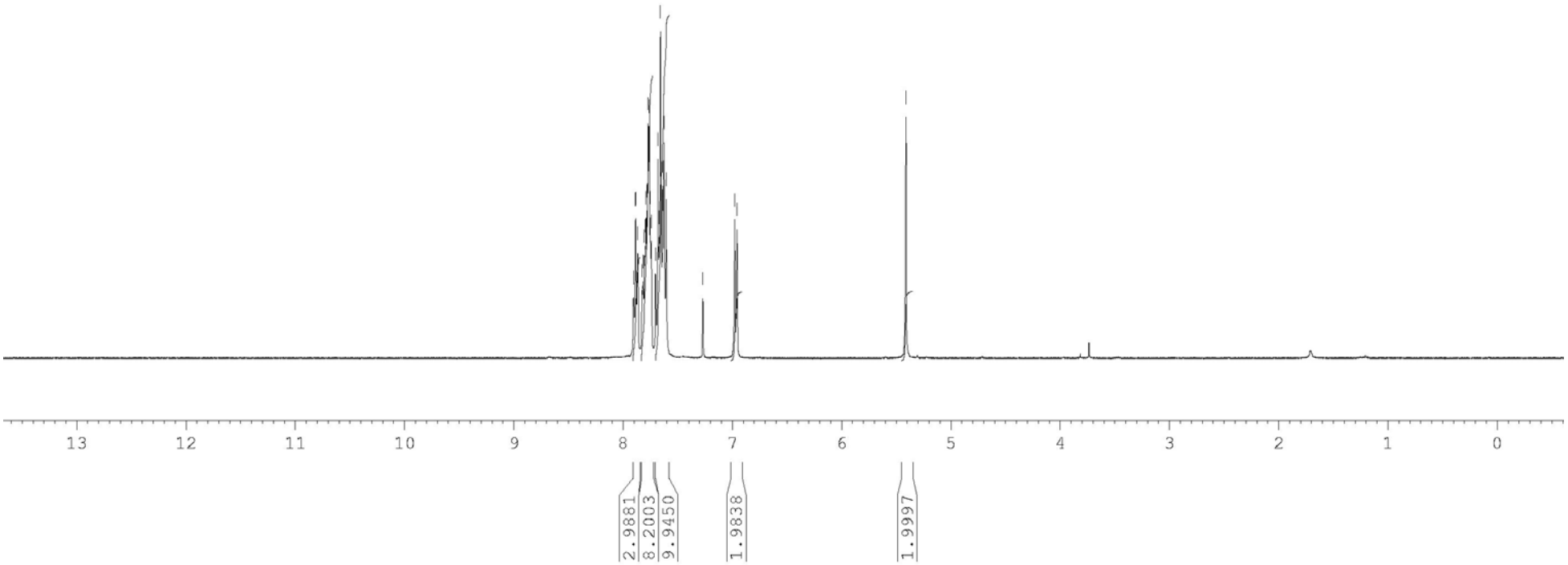
(radical reduced derivative)
^{13}C NMR (100 MHz, $CDCl_3$)

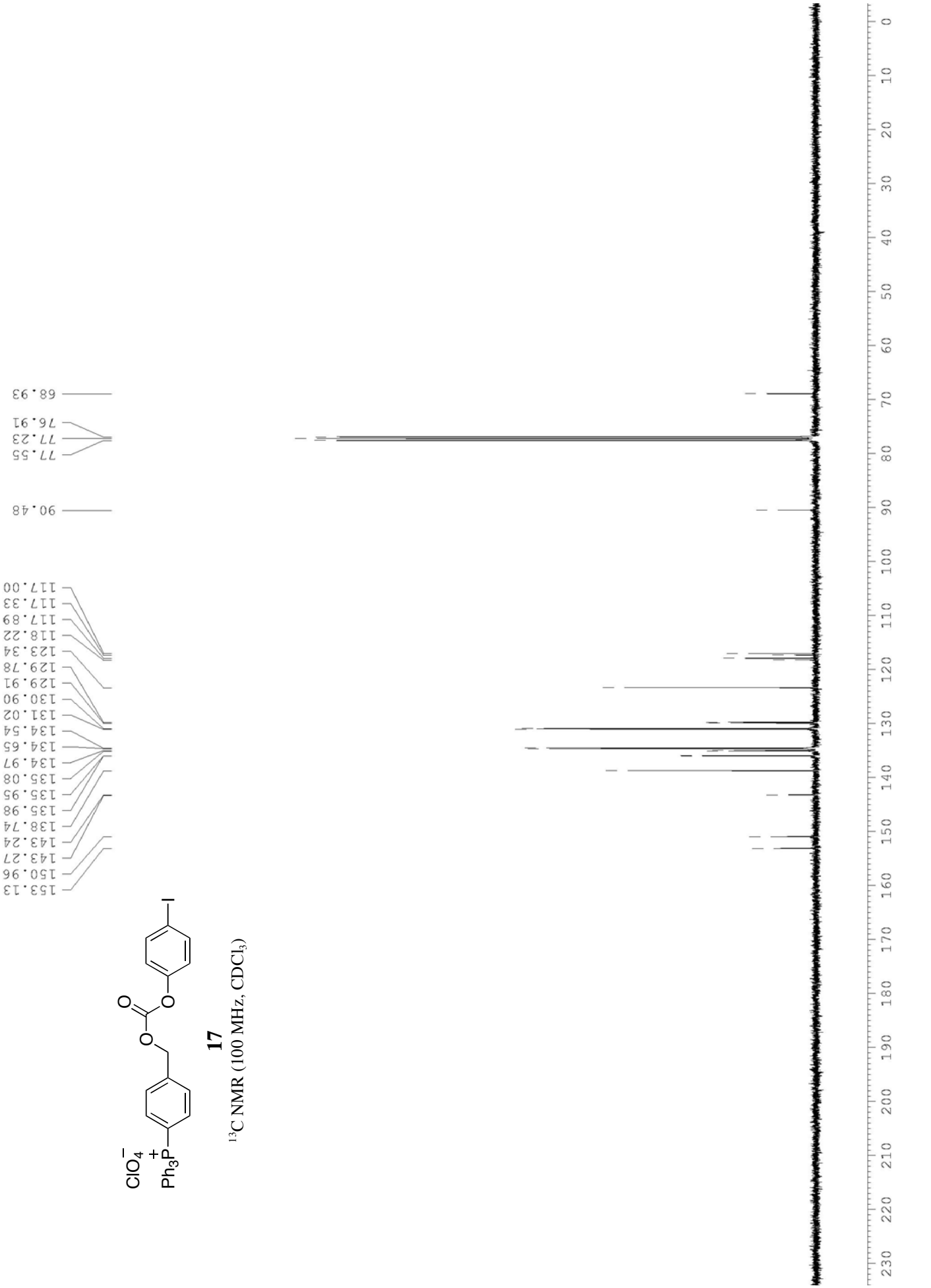




17

^{1}H NMR (400 MHz, $CDCl_3$)

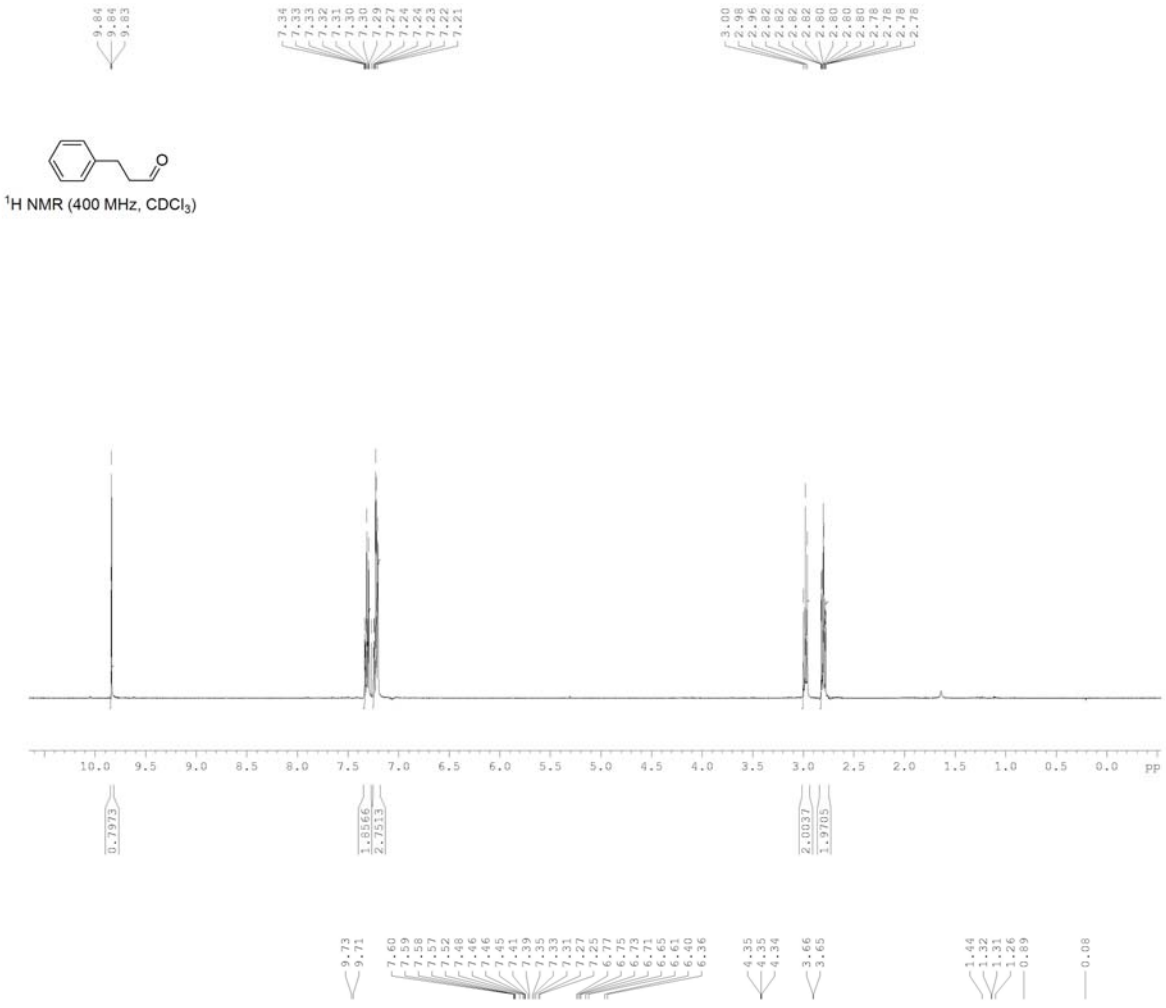




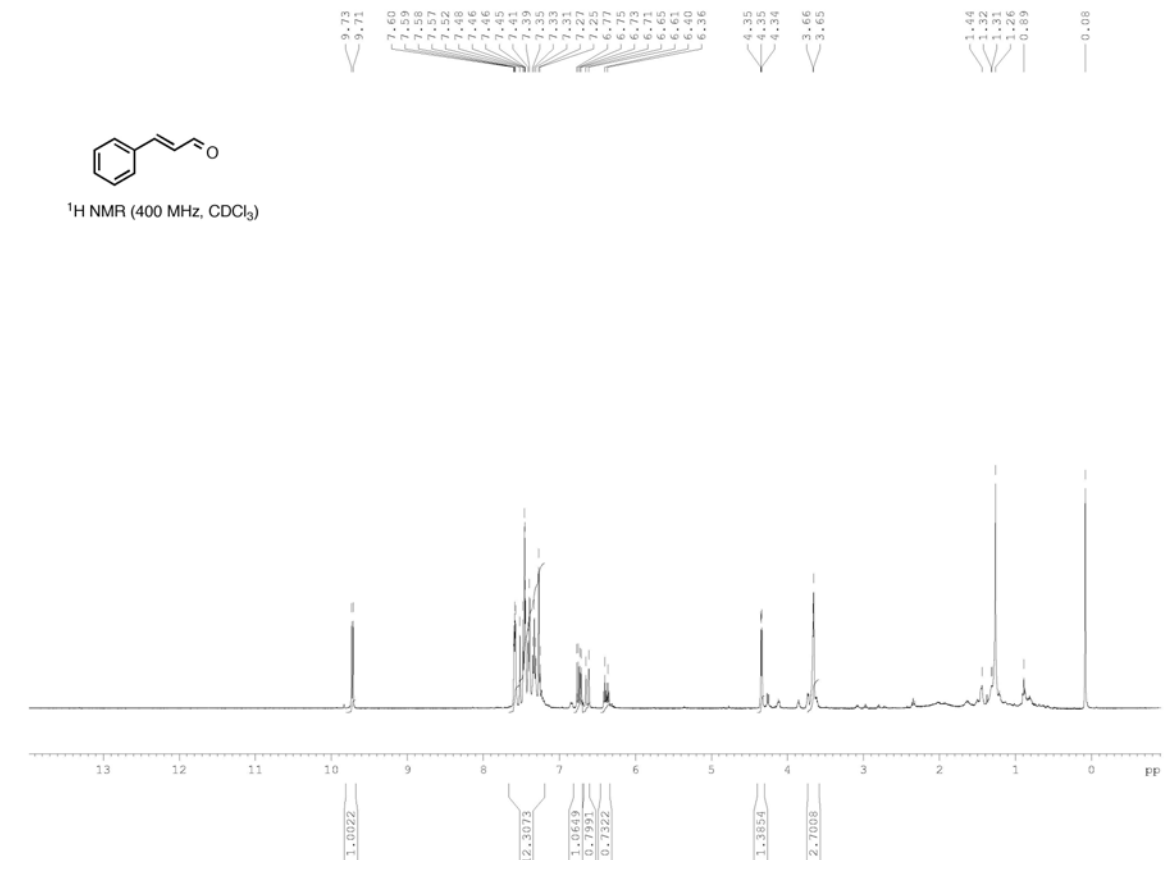
17

^{13}C NMR (100 MHz, $CDCl_3$)

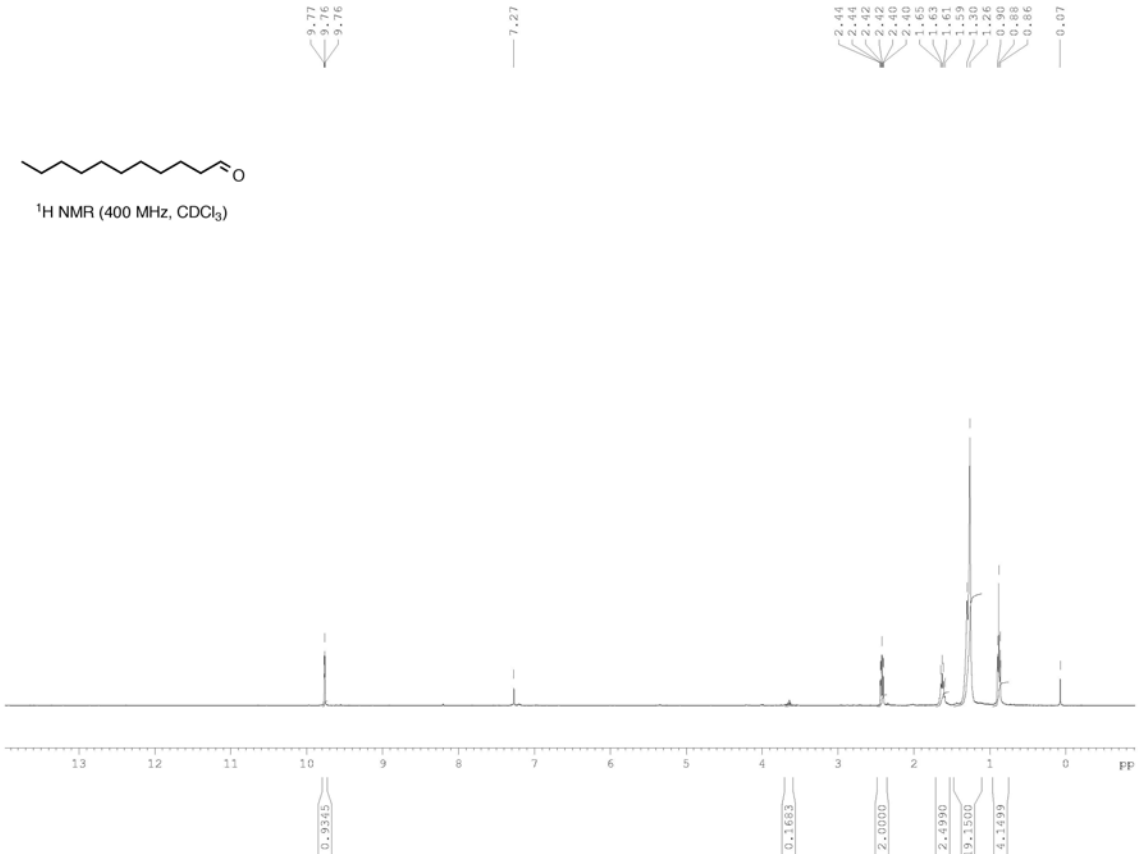
TYPICAL ^{1}H CRUDE NMR SPECTRA OXIDATION PRODUCTS



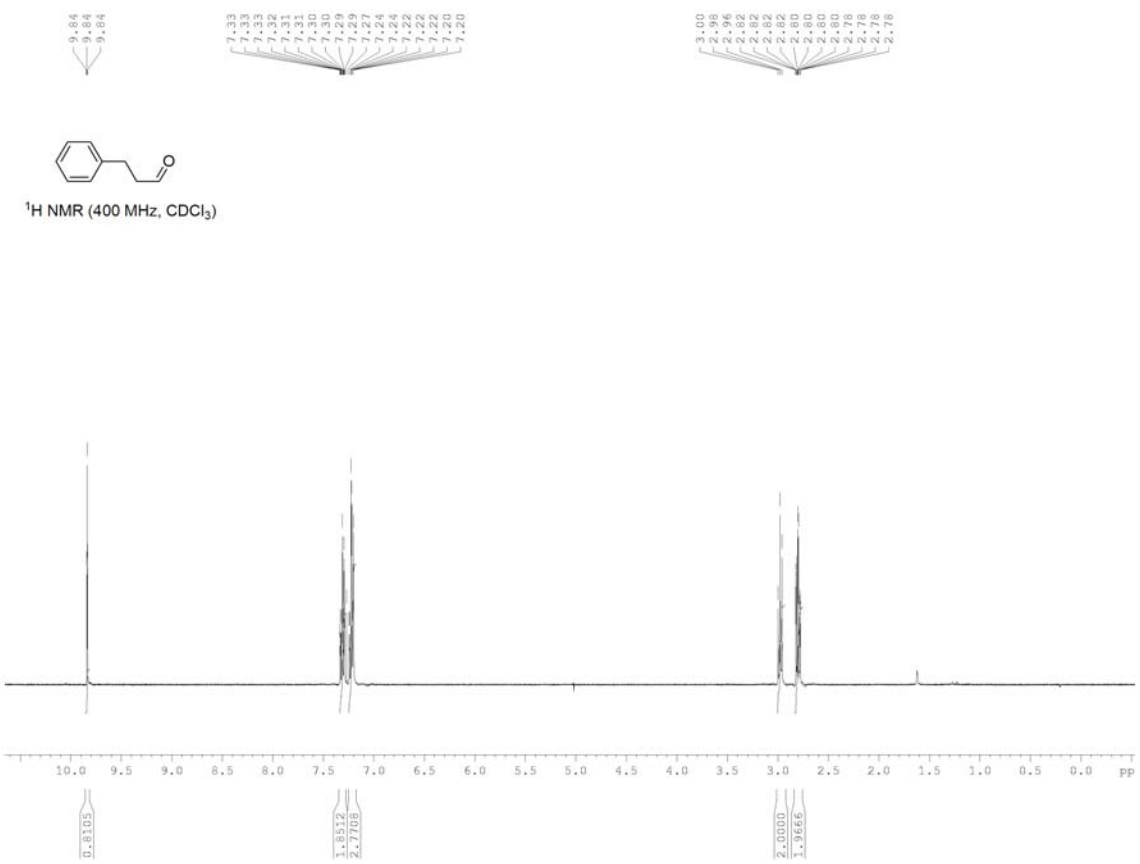
^{1}H NMR (400 MHz, $CDCl_3$)



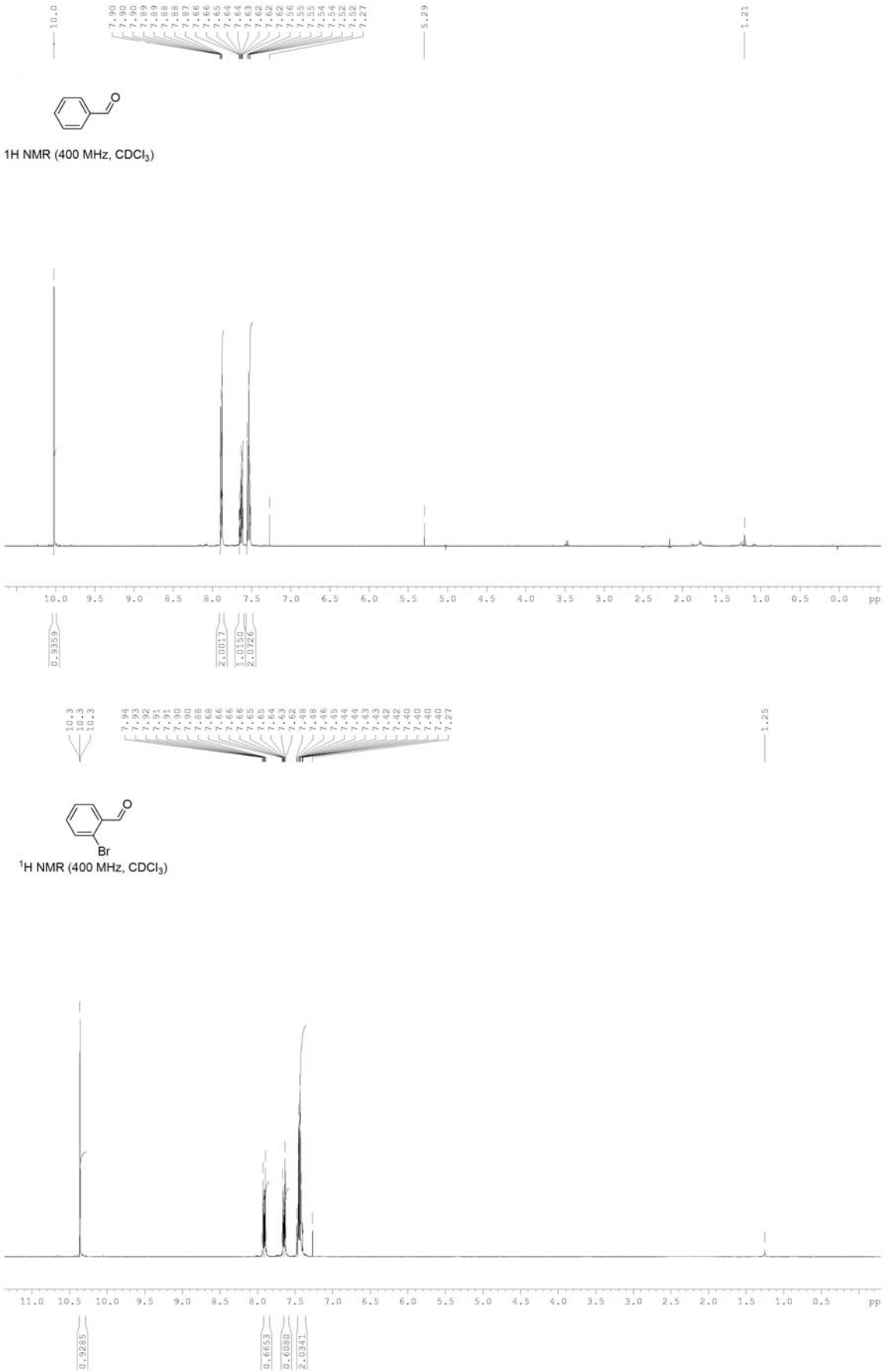
^{1}H NMR (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

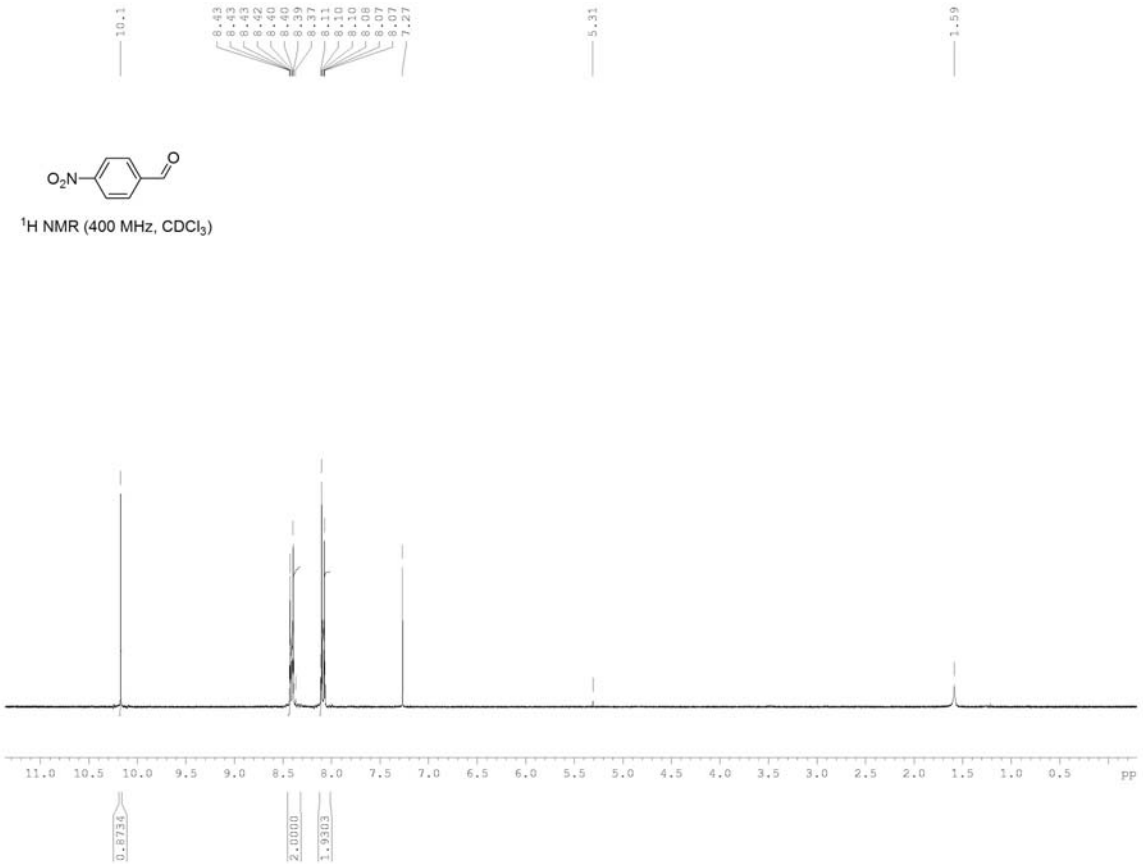


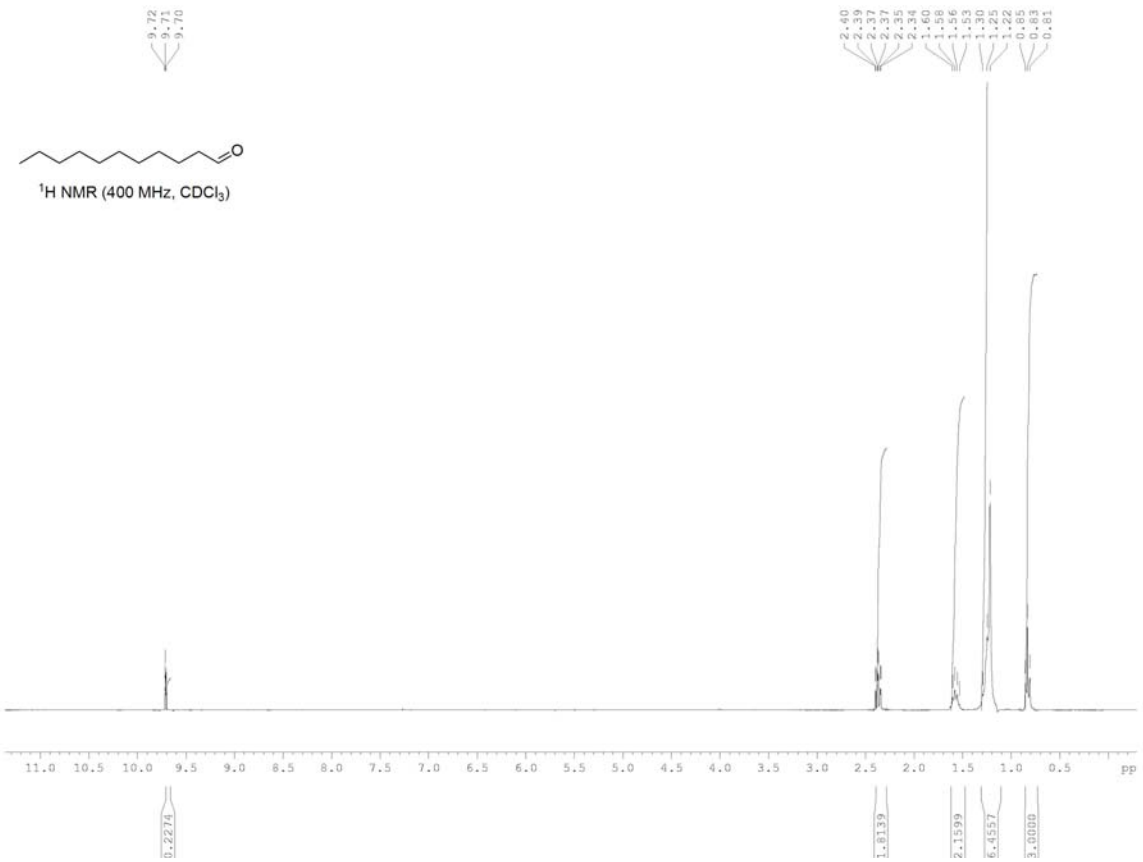
^{1}H NMR (400 MHz, $CDCl_3$)



1H NMR (400 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$)


10.1
8.43
8.43
8.43
8.42
8.40
8.40
8.39
8.37
8.11
8.10
8.08
8.07
8.07
7.27
5.31
1.59
O2N
O
1H NMR (400 MHz, CDCl3)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 pp
0.8734
2.0000
1.9303


9.72
9.71
9.70
2.40
2.39
2.37
2.37
2.35
2.34
1.60
1.58
1.56
1.53
1.30
1.25
1.22
0.85
0.83
0.81
O
1H NMR (400 MHz, CDCl3)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 pp
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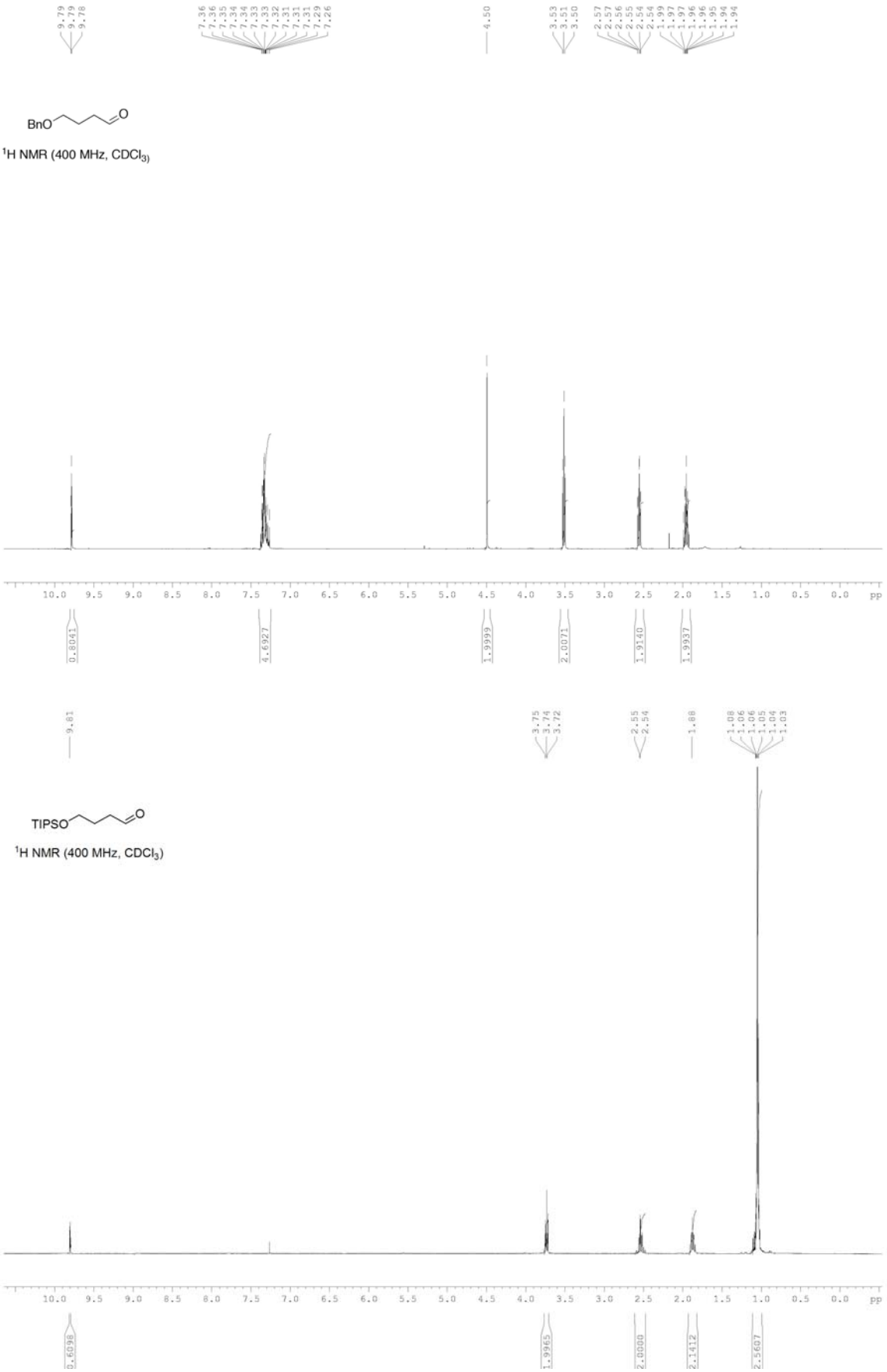
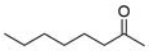
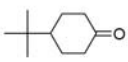
1.8139
2.1599
6.4557
3.0000

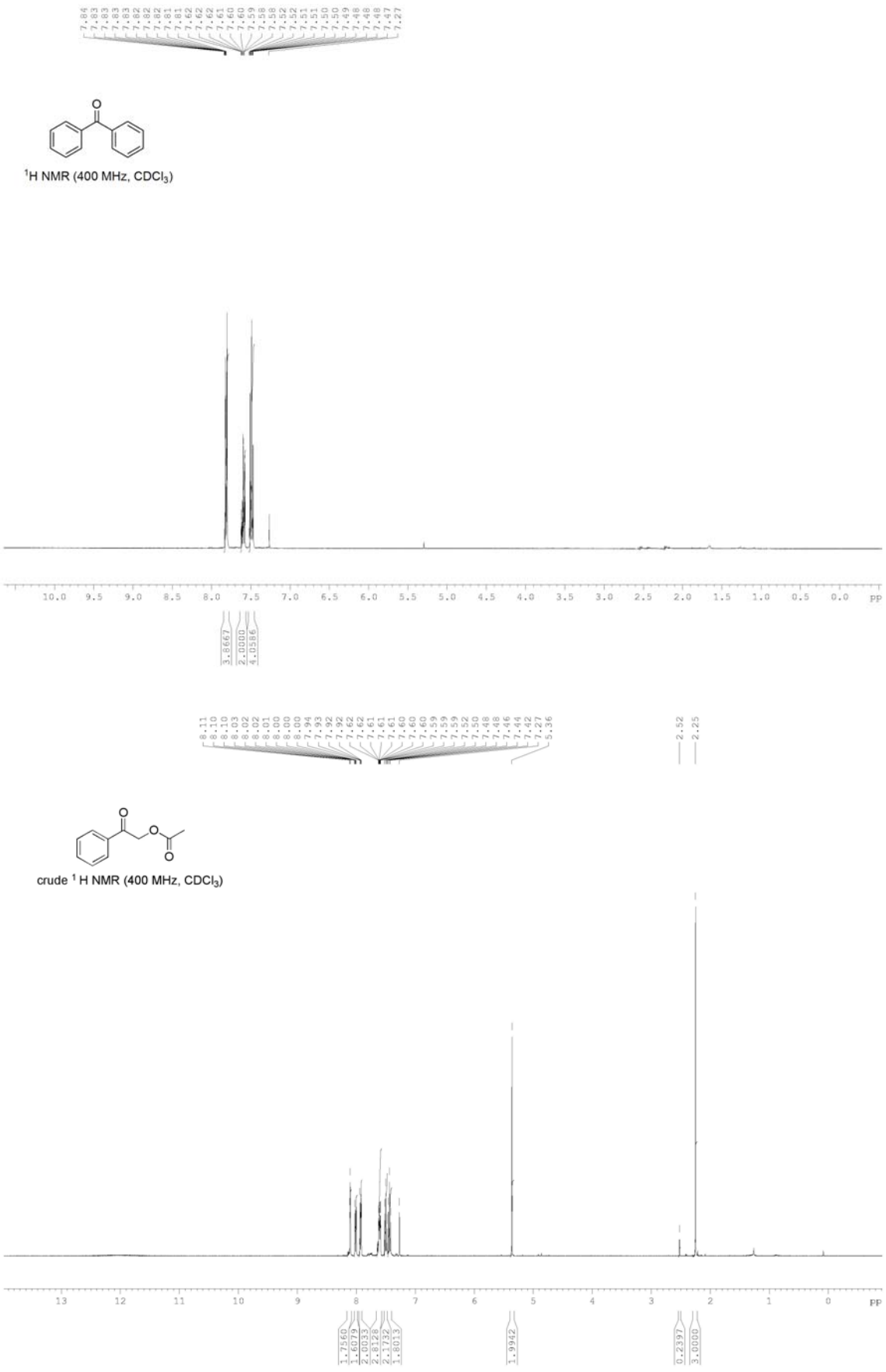

9.79
9.79
9.78
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.31
7.29
7.26
4.50
3.53
3.51
3.50
2.57
2.57
2.56
2.55
2.54
2.54
1.99
1.97
1.97
1.96
1.96
1.95
1.94
1.94
BnO
O
^{1}H NMR (400 MHz, $CDCl_3$)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 pp
0.8041
4.6927
1.9999
2.0071
1.9140
1.9937
9.61
3.75
3.74
3.72
2.55
2.54
1.88
1.08
1.06
1.06
1.05
1.04
1.03
TIPSO
O
^{1}H NMR (400 MHz, $CDCl_3$)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 pp
0.6098
1.9965
2.0000
2.1412
2.5607

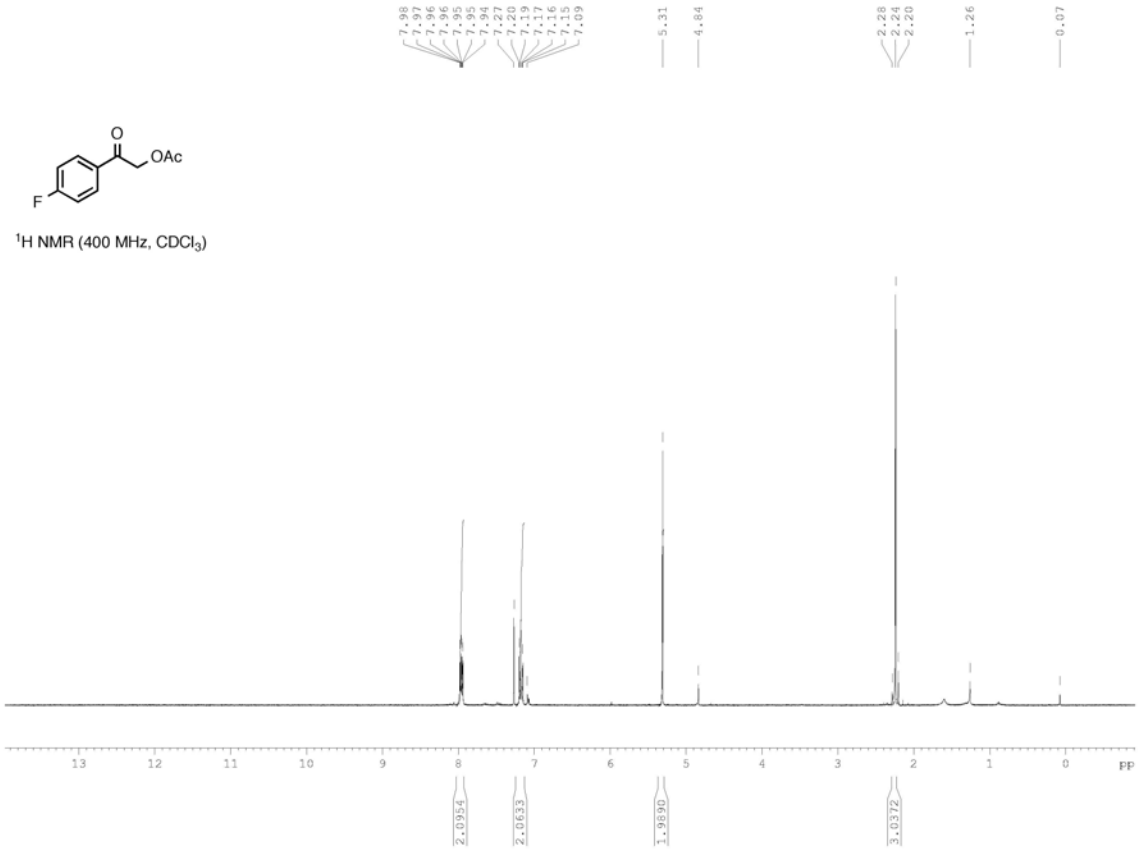


^{1}H NMR (400 MHz, $CDCl_3$)

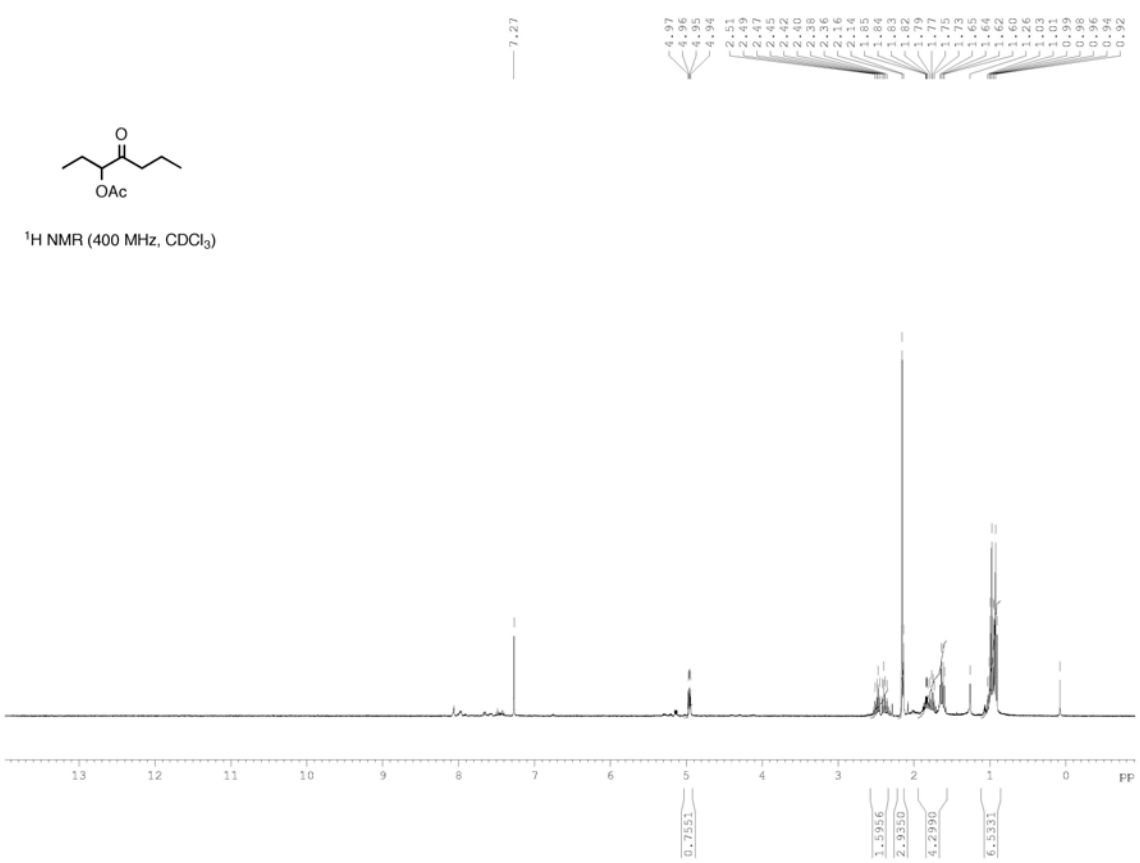


^{13}C NMR (100 MHz, $CDCl_3$)


7.84 7.83 7.83 7.83 7.83 7.82 7.82 7.82 7.81 7.81 7.62 7.62 7.62 7.61 7.60 7.60 7.59 7.58 7.52 7.51 7.50 7.49 7.48 7.48 7.47 7.27
O
^{1}H NMR (400 MHz, $CDCl_3$)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.8667 2.0000 4.0586
8.11 8.10 8.10 8.03 8.02 8.02 8.01 8.00 8.00 7.94 7.93 7.92 7.92 7.62 7.62 7.61 7.61 7.61 7.60 7.60 7.60 7.59 7.59 7.59 7.52 7.50 7.48 7.48 7.46 7.44 7.42 7.27 5.36
2.52 2.25
O O O
crude ^{1} H NMR (400 MHz, $CDCl_3$)
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.7560 1.6079 2.0035 2.8128 2.1732 1.8013 1.9942 0.2397 3.0000



^{1}H NMR (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)