Electronic Supplementary Information

Efficient Methods for Enol Phosphate Synthesis Using Carbon-centred Magnesium Bases

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Contents

I. General Synthetic Methods

All reagents were obtained from commercial suppliers (Aldrich, Lancaster, Alfa-Aesar, or Acros) and used without further purification, unless otherwise stated. Purification was carried out according to standard laboratory methods.[1]

- Tetrahydrofuran and 1,4-dioxane were dried by heating to reflux over sodium wire, using benzophenone ketyl as an indicator, and then distilled under nitrogen.
- DMPU and diphenylphosphoryl chloride were distilled over CaH_2 under high vacuum and were stored over 4 Å molecular sieves under argon.
- Organometallic reagents were standardised using salicylaldehyde phenylhydrazone.[2]
- 4-*tert*-Butylcyclohexanone, 4-phenylcyclohexanone, 4-methyl-4-phenylcyclohexanone,[3]4'-bromoacetophenone, 4'-methoxyacetophenone, 4-acetylbenzonitrile, mesitylethanone, and 4'-nitroacetophenone were purified by recrystallization from hexane and were dried by storing under vacuum (0.005 mbar) for 16 h.
- 4-Methylcyclohexanone, 4-((*tert*-butyldimethylsilyl)oxy)cyclohexanone,[4] 4-(dimethylamino)cyclohexanone,[5] acetophenone, and 2-methylcyclohexanone were dried by distillation over $CaCl_2$ and were stored under argon over 4 Å molecular sieves.

Thin layer chromatography was carried out using Camlab silica plates, coated with fluorescent indicator UV_{254}, and analysed using a Mineralight UVGL-25 lamp.

Flash column chromatography was carried out using Prolabo silica gel (230-400 mesh).

IR spectra were recorded on a SHIMADZU IRAFFINITY-1 spectrophotometer.

^1H, ^{13}C, and ^{31}P spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz, 100 MHz, and 162 MHz, respectively. Chemical shifts are reported in ppm. Coupling constants are reported in Hz and refer to $^3J_{H\text{-}H}$ interactions, unless otherwise specified.

II. Experimental procedures

1. Experimental procedure: Scheme 2

1A. Synthesis of dimesitylmagnesium 1

A Schlenk flask was flame-dried under vacuum (0.005 mbar) and filled with argon. The flask was then evacuated and refilled with argon, this cycle repeated one further time, then the flask was allowed to cool to room temperature before addition of magnesium turnings (1.9 g, 80 mmol). THF (80 mL) was added followed by a dropwise addition of MesBr (15.9 g, 12.24 mL, 80 mmol). A cold finger was quickly swapped with a suba seal and the Schlenk flask was heated slowly to 40 °C over 1 h. After 5 min, a reflux of the THF was observed due to the Grignard reaction initiating. After 30 min, the end of the reflux was observed and the mixture was stirred at 40 °C for a further 90 min before being allowed to cool to room temperature. The solution of MesMgBr was standardised with salicylalhdehyde phenylhydrazone.[2] 1,4-Dioxane (1.05 eq., 105 mmol, 9.25 g, 8.95 mL) was then added dropwise to the mixture with stirring. The reaction mixture (now a yellow solution with a fine white precipitate) was then left to settle for 72 h. After this time, the precipitate had settled to a thick white layer at the bottom of the Schlenk tube, allowing removal of the yellow Mes_2Mg solution *via* cannula, to a previously flame-dried pear-shaped flask. Care was taken to avoid withdrawing any of the precipitate. The Mes_2Mg solution was standardised before use, using salicylaldehyde phenylhydrazone as the indicator.[2] The molarity of the Mes_2Mg solution was typically 0.5 M (100 % conversion of MesMgBr to Mes_2Mg, yield typically ~ 90 mL, ~ 90%).

1B. Synthesis of bis(*tert*-butyl)magnesium 2

To a solution of *t*-BuMgBr (1 M solution in THF, 100 mL, 100 mmol) charged to a flame-dried Schlenk tube under argon at rt was slowly added 1,4-dioxane (1.05 eq., 105 mmol, 9.25 g, 8.95 mL) over 5 min. The mixture was stirred vigorously for 3 h before discontinuation of the stirring. The mixture (now a dark solution with a fine white precipitate) was then left to settle for 72 h. After this time, the precipitate had settled to a thick white layer at the bottom of the Schlenk tube, allowing removal of the yellow *t*-Bu_2Mg solution *via* cannula to a previously flame-dried pear-shaped flask. Care was taken to avoid withdrawing any of the precipitate. The *t*-Bu_2Mg solution was standardised before use using salicylaldehyde phenylhydrazone as indicator.[2] The molarity of the $^tBu_2Mg$ solution was typically 0.5 M (100 % conversion of *t*-BuMgBr to *t*-Bu_2Mg, yield typically ~ 90 mL, ~ 90%).

2. Experimental procedure: Table 1

2A. Typical reaction procedure with LiCl as additive

A Schlenk flask was charged with LiCl (2 eq., 2 mmol, 85 mg) and flame-dried under high vacuum (0.005 mbar), taking care not to melt the LiCl, and then filled with argon. The flask was then evacuated and refilled with argon, this cycle repeated one further time, then the flask was allowed to cool to room temperature. A solution of carbon-centred base (0.5 M solution in THF, 0.5 eq., 0.5 mmol, 1 mL) and THF (9 mL) were added to the flask, cooled to 0 °C and stirred for an additional 5 min before addition of diphenylphosphoryl chloride (1 mmol, 0.21 mL). The mixture was then stirred for 5 min before addition of the ketone **3** (1 mmol, 154 mg) as a solution in THF (2 mL) over 1 h *via* syringe pump, followed by stirring at 0 °C for the stated time. The reaction was quenched with a saturated solution of $NaHCO_3$ (10 mL) and allowed to warm to room temperature. The aqueous phase was extracted with Et_2O (50, 25, 25 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil, which was purified by flash column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** as a colourless oil.

2B. Typical reaction procedure with DMPU as additive

A solution of base (0.5 M solution in THF, 0.5 eq., 0.5 mmol, 1 mL) was added to THF (9 mL) in a flame-dried Schlenk flask under argon. The mixture was cooled to 0 °C and stirred for an additional 5 min before addition of diphenylphosphoryl chloride (1 mmol, 0.21 mL) and DMPU (2 mmol, 0.24 mL), and stirred for a further 5 min. The ketone **3** (1 mmol, 154 mg), as a solution in THF (2 mL), was added over 1 h *via* syringe pump followed by

stirring at 0 °C for the stated time. The reaction mixture was quenched with a saturated solution of $NaHCO_3$ (5 mL) and allowed to warm to room temperature. The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil, which was purified by flash column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** as a colourless oil.

For the entries in Table 1, each reaction was run twice under identical conditions, and the average yield is presented in the Table.

Following typical Procedure 2A or 2B, data are presented as: (a) Mg base, (b) reaction temperature, (c) additive, (d) amount of additive, (e) amount of $P(O)(OPh)_2Cl$, (f) ketone, (g) amount of ketone, (h) reaction time, (i) yield of run 1, and (j) yield of run 2.

Table 1, Entry 1: General Procedure 2A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) 0 °C, (c) LiCl, (d) 84 mg, 2 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 16 h, (i) 108 mg, 28 %, and (j) 112 mg, 29%.

Table 1, Entry 2: General Procedure 2A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) 0 °C, (c) LiCl, (d) 84 mg, 2 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 8 h, (i) 120 mg, 31 %, and (j) 119 mg, 31%.

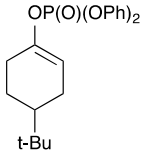
Table 1, Entry 3: General Procedure 2A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) 0 °C, (c) LiCl, (d) 84 mg, 2 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 100 mg, 26 %, and (j) 104 mg, 27%.

Table 1, Entry 4: General Procedure 2B: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) 0 °C, (c) DMPU, (d) 0.24 mL, 2 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 153 mg, 40 %, and (j) 150 mg, 39%.

Table 1, Entry 5: General Procedure 2A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) 0 °C, (c) LiCl, (d) 84 mg, 2 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 262 mg, 68 %, and (j) 263 mg, 68%.

Table 1, Entry 6: General Procedure 2B: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) 0 °C, (c) DMPU, (d) 0.24 mL, 2 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 290 mg, 75 %, and (j) 289 mg, 75%.

Diphenyl 4-(*tert*-butyl)cyclohex-1-en-1-yl phosphate 4:[6]



ν_{max}: 1690, 1191, 963 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 4H, ArH), 7.27-7.17 (m, 6H, ArH), 5.58-5.53 (m, 1H, C=CH), 2.36-2.18 (m, 2H, CH_2), 2.16-2.05 (m, 1H, CH_2), 1.94-1.80 (m, 2H, CH_2), 1.39-1.22 (m, 2H, CH_2), 0.89 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 148.1, 130.1, 125.7, 120.5, 112.2, 43.6, 32.4, 29.0, 27.6, 25.3, 24.8.

^{31}P NMR (162 Hz, $CDCl_3$): δ -17.46.

3. Experimental procedure: Scheme 3

3A. Specific procedure for the co-addition protocol

A solution of base **2** (0.5 M solution in THF, 0.5 eq., 0.5 mmol, 1 mL) was added to THF (9 mL) in a flame-dried Schlenk flask under argon. The mixture was cooled to 0 °C and stirred for an additional 5 minutes before addition of DMPU (2 mmol, 0.24 mL) and stirred for a further 5 min. The ketone **3** (1 mmol, 154 mg) and diphenylphosphoryl chloride (1 mmol, 0.21 mL) and THF (2 mL) were added to a previously flame-dried pear shaped flask under argon. This mixture was added to the Schlenk flask over 1 h *via* syringe pump, followed by stirring at 0 °C for 1 h. The reaction mixture was quenched with a saturated solution of $NaHCO_3$ (5 mL) and allowed to warm to room temperature. The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil, which was purified by flash column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** as a colourless oil (317 mg, 82% yield).

3B. Specific procedure for the reverse addition protocol

A Schlenk flask was flame-dried under vacuum (0.005 mbar), purged three times with argon, and allowed to cool to room temperature before addition of the ketone **3** (1 mmol, 154 mg), diphenylphosphoryl chloride (1 mmol, 0.21 mL), DMPU (2 mmol, 0.24 mL), and THF (11 mL). The mixture was cooled to 0 °C and stirred for 5 min before dropwise addition of base **2** (0.5 M solution in THF, 0. 5 eq., 0. 5 mmol, 1 mL) over 5 min. After 1 h the reaction was quenched with a saturated solution of $NaHCO_3$ (5 mL) and allowed to warm to room temperature. The aqueous phase was extracted with Et_2O (25, 10, 10 mL). Removal of the solvent *in vacuo* gave an oil, which was purified by flash column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** as a colourless oil (310 mg, 80% yield).

4. Experimental procedure: Table 2

4A. Typical reaction procedure at room temperature using the reverse addition protocol

A Schlenk flask was flame-dried under vacuum (0.005 mbar), purged three times with argon, and allowed to cool to room temperature before addition of the ketone **3** (1 mmol, 154 mg), diphenylphosphoryl chloride (1 mmol, 0.21 mL), DMPU (as stated in Table 2), and THF (11 mL). The mixture was stirred for 5 min before dropwise addition of base **2** (0.5 M solution in THF, 0.5 eq., 0.5 mmol, 1 mL) over 5 min. After 1 h the reaction was quenched with a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil, which was purified by flash column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product as a colourless oil.

Following typical Procedure 4A, data are presented as: (a) Mg base, (b) reaction temperature, (c) additive, (d) amount of additive, (e) amount of $P(O)(OPh)_2Cl$, (f) ketone, (g) amount of ketone, (h) reaction time, (i) yield of run 1, and (j) yield of run 2.

For the entries in Table 2, each reaction was run twice under identical conditions, and the average yield is presented in the Table.

Table 2, Entry 1: General Procedure 4A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) n/a, (d) n/a, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 324 mg, 84 %, and (j) 325 mg, 84%.

Table 2, Entry 2: General Procedure 4A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.06 mL, 0.5 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 332 mg, 86 %, and (j) 334 mg, 86%.

Table 2, Entry 3: General Procedure 4A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.12 mL, 1 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 336 mg, 87 %, and (j) 340 mg, 88%.

Table 2, Entry 4: General Procedure 4A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.18 mL, 1.5 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 348 mg, 90 %, and (j) 349 mg, 90%.

Table 2, Entry 5: General Procedure 4A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.24 mL, 2 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 352 mg, 91 %, and (j) 349 mg, 90%.

Table 2, Entry 6: General Procedure 4A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.36 mL, 3 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 359 mg, 93%, and (j) 371 mg, 96%.

Table 2, Entry 7: General Procedure 4A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 369 mg, 95 %, and (j) 368 mg, 95%.

Table 2, Entry 8: General Procedure 4A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.60 mL, 5 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 359 mg, 93 %, and (j) 355 mg, 92%.

5. Experimental procedure: Table 3

5A. Typical reaction procedure for the substrate scope using base 2

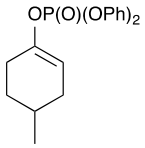
A Schlenk flask was flame-dried under vacuum (0.005 mbar), purged three times with argon, and allowed to cool to room temperature before addition of the ketone, diphenylphosphoryl chloride (1 mmol, 0.21 mL), DMPU (4 mmol, 0.48 mL) and THF (11 mL). The mixture was stirred for 5 min before dropwise addition of base **1** (0.5 M solution in THF, 0.5 eq., 0.5 mmol, 1 mL) over 5 min. After 1 h the reaction was quenched with a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil which was purified by column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product.

Following typical Procedure 5A, data are presented as: (a) Mg base, (b) reaction temperature, (c) additive, (d) amount of additive, (e) amount of $P(O)(OPh)_2Cl$, (f) ketone, (g) amount of ketone, (h) reaction time, (i) yield of run 1, (j) yield of run 2, and (k) appearance.

For the entries in Table 3, each reaction was run twice under identical conditions, and the average yield is presented in the Table.

Table 3, compound 5: General Procedure 5A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-methylcyclohexanone, (g) 112 mg, 1 mmol, (h) 1 h, (i) 316 mg, 92 %, (j) 323 mg, 94%, and (k) colourless oil.

Diphenyl 4-methylcyclohex-1-enyl phosphate 5:



ν_{max}: 1589, 1487, 1296, 1186, 1114, 945 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.33 (m, 4H, ArH), 7.26-7.18 (m, 6H, ArH), 5.58-5.50 (m, 1H, C=CH), 2.36-2.20 (m, 3H, CH_2), 1.80-1.62 (m, 3H, CH_2,CH), 1.43-1.31 (m, 1H, CH_2), 0.97 (d, J = 6.4 Hz, 3H, CH_3).

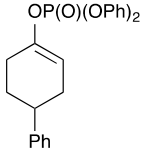
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 148.0, 130.1, 125.7, 120.4, 111.6, 32.2, 31.0, 27.9, 27.7, 21.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ –17.46.

HRMS (ESI) Calculated for $C_{19}H_{22}O_4P$ $[M+H]^+$: 345.1250; found: 345.1244.

Table 3, compound 6: General Procedure 5A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-phenylcyclohexanone, (g) 174 mg, 1 mmol, (h) 1 h, (i) 365 mg, 90 %, (j) 366 mg, 90%, and (k) white solid.

Diphenyl (1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl) phosphate 6:



ν_{max}: 1688, 1587, 1489, 1282, 1188, 1105, 939 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.34 (m, 4H, ArH), 7.32-7.25 (m, 6H, ArH), 7.24-7.19 (m, 5H, ArH), 5.70-5.65 (m, 1H, C=CH), 2.87-2.77 (m, 1H, CH), 2.54-2.21 (m, 4H, CH_2), 2.07-1.98 (m, 1H, CH_2), 1.97-1.85 (m, 1H, CH_2).

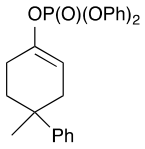
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 147.8, 145.5, 129.9, 128.6, 126.9, 126.4, 125.5, 120.2, 111.6, 39.2, 31.6, 29.7, 28.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ -17.40.

HRMS (ESI) Calculated for $C_{24}H_{24}O_4P$ $[M+H]^+$: 407.1407; found: 407.1408.

Table 3, compound 7: General Procedure 5A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-methyl-4-phenylcyclohexanone, (g) 188 mg, 1 mmol, (h) 1 h, (i) 378 mg, 90 %, (j) 374 mg, 89%, and (k) colourless oil.

Diphenyl 1-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl phosphate 7:



ν_{max}: 1687, 1589, 1487, 1294, 1186, 1114, 943 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.29 (m, 8H, ArH), 7.24-7.17 (m, 7H, ArH), 5,7-5.65 (m, 1H, C=CH), 2.67-2.56 (m, 1H, CH_2), 2.32-2.2 (m, 2H, CH_2), 2.11-1.97 (m, 2H, CH_2), 1.91-1.82 (m, 1H, CH_2), 1.31 (s, 3H, CH_3).

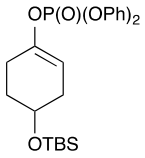
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 48.1, 147.6, 130.1, 128.6, 126.2, 125.9, 125.7, 120.4, 110.8, 36.5, 36.0, 35.2, 28.8, 25.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ – 17.64.

HRMS (ESI) Calculated for $C_{25}H_{26}O_4P$ $[M+H]^+$: 421.1563; found: 421.1554.

Table 3, compound 8: General Procedure 5A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-((*tert*-butyldimethylsilyl)oxy)cyclohexanone, (g) 228 mg, 1 mmol, (h) 1 h, (i) 359 mg, 78 %, (j) 368 mg, 80%, and (k) colourless oil.

Diphenyl 4-((*tert*-butyldimethylsilyl)oxy)cyclohex-1-enyl phosphate 8:



ν_{max}: 1589, 1489, 1296, 1251, 1188, 1101, 943 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 4H, ArH), 7.26-7.18 (m, 6H, ArH), 5.47-5.42 (m, 1H, C=CH), 3.96-3.87 (m, 1H, CH), 2.40-2.24 (m, 3H, CH_2), 2.14-2.03 (m, 1H, CH_2), 1.83-1.70 (m, 2H, CH_2), 0.88 (s, 9H, $C(CH_3)_3$), 0.06 (s, 6H, CH_3).

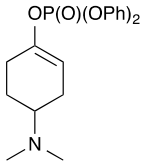
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 147.4, 130.1, 125.8, 120.5, 109.4, 66.5, 33.3, 31.5, 26.2, 26.0, 18.5, - 4.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ -17.62.

HRMS (ESI) Calculated for $C_{24}H_{34}O_5PSi$ $[M+H]^+$: 461.1908; found: 461.1896.

Table 3, compound 9: General Procedure 5A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-(dimethylamino)cyclohexanone, (g) 141 mg, 1 mmol, (h) 1 h, (i) 280 mg, 75%, (j) 272 mg, 73%, and (k) yellow oil.

Diphenyl 4-(dimethylamino)cyclohex-1-enyl phosphate 9:



ν_{max}: 1591, 1487, 1222, 1155, 1083, 887 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 4H ArH), 7.26-7.18 (m, 6H ArH), 5.54-5.49 (m, 1H C=CH), 2.61-2.46 (m, 2H, CH_2, CH), 2.33 (s, 6H, *N*-CH_3), 2.30-2.21 (m, 2H, CH_2), 2.17-2.06 (m, 1H, CH_2), 2.04-1.96 (m, 1H, CH_2), 1.65-1.53 (m, 1H, CH_2).

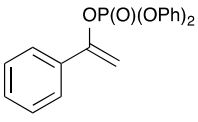
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 147.6, 130.2, 129.6, 125.8, 120.4, 59.7, 41.9, 27.8, 25.7, 25.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ – 17.53.

HRMS (ESI) Calculated for $C_{20}H_{25}NO_4P$ $[M+H]^+$: 374.1516; found: 374.1516.

Table 3, compound 10: General Procedure 5A: (a) *t*-Bu_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 ml, 4 mmol, (e) 0.21 ml, 1 mmol, (f) acetophenone, (g) 120 mg, 1 mmol, (h) 1 h, (i) 7 mg, 2 %, (j) 21 mg, 6%, and (k) yellow oil.

Diphenyl 1-phenylethen-1-yl phosphate 10:[7]



ν_{max}: 1683, 1589, 1487, 1184, 1010, 947 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.29 (m, 10H, ArH), 7.25-7.16 (m, 5H, ArH), 5.42-5.39 (m, 1H, C=CH), 5.36-5.34 (m, 1H, C=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 150.8, 130.2, 130.1, 129.6, 128.8, 125.9, 125.6, 120.5, 98.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ -17.77.

HRMS (ESI) Calculated for $C_{20}H_{17}NaO_4P$ $[M+Na]^+$: 375.0757; found: 375.0757.

6. Experimental procedure: Scheme 4

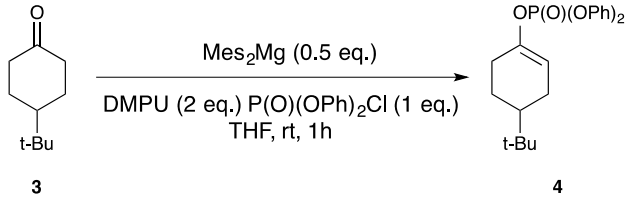
6A. Specific reaction procedure at room temperature

A solution of base **1** (0.5 M solution in THF, 0.5 eq., 0.5 mmol, 1 mL) was added to THF (9 mL) in a flame-dried Schlenk flask. Diphenylphosphoryl chloride (1 mmol, 0.21 mL) and DMPU (2 mmol, 0.24 mL) were added to the mixture and stirred for a further 5 min. The ketone **3** (1 mmol, 154 mg), as a solution in THF (2 mL), was added over 1 h *via* syringe pump followed by stirring at room temperature for the stated time. The mixture was quenched with a saturated solution of $NaHCO_3$ (5 mL) after the stated time. The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil, which was purified by flash column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** as a colourless oil.

Reaction time 1 h: 185 mg**,** 48% yield.

Reaction time 16 h: 185 mg**,** 48% yield.

7. Additional experiments: Determining the optimised quench protocol with Mes_2Mg 1



3 **4**

7A. Reverse addition:

A Schlenk flask was flame-dried under vacuum (0.005 mbar) and filled with argon. The flask was then evacuated and refilled with argon, this cycle repeated one further time, then the flask was allowed to cool to room temperature, before addition of the ketone **3** (1 mmol, 154 mg), diphenylphosphoryl chloride (1 mmol, 0.21 mL), DMPU (0.24 mL, 2 mmol), and THF (11 mL). The mixture was stirred for 5 min before dropwise addition of base **1** (0.5 M solution in THF, 0.25 eq., 0.25 mmol, 0.5 mL) over 5 min. After 1 h, the reaction was quenched with a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil which was purified by column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** as a colourless oil (120 mg, 31% yield).

7B. Co-addition:

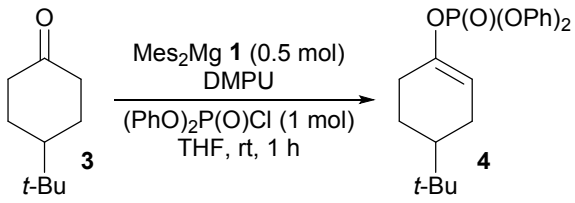
A solution of base **1** (0.5 M solution in THF, 0.5 eq., 0.5 mmol, 1 mL) was added to THF (9 mL) in a flame-dried Schlenk flask under argon, followed by the addition of DMPU (2 mmol, 0.24 mL). The ketone **3** (1 mmol, 154 mg), diphenylphosphoryl chloride (1 mmol, 0.21 mL) and THF (2 mL) were added to a flame-dried pear shaped flask under argon. This mixture was added into the Schlenk flask over 1 h *via* syringe pump, followed by stirring at rt for 1 h. The reaction mixture was quenched with a saturated solution of $NaHCO_3$ (5 mL) and allowed to warm to room temperature. The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil, which was purified by flash column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** a colourless oil (185 mg, 48% yield).

8. Additional experiments: Defining the optimised additive loading

8A. Typical reaction procedure

A solution of base **1** (0.5 M solution in THF, 0.5 eq., 0.5 mmol, 1 mL) was added to THF (9 mL) in a flame-dried Schlenk flask under argon. Diphenylphosphoryl chloride and DMPU were added to the mixture and stirred for a further 5 min. The ketone **3**, as a solution in THF (2 mL), was added over 1 h *via* syringe pump followed by stirring at room temperature for the stated time. The mixture was quenched with a saturated solution of $NaHCO_3$ (5 mL) after the stated time. The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil which was purified by column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** as a colourless oil.

Following typical Procedure 8A, data are presented as (a) Mg base, (b) reaction temperature, (c) additive, (d) amount of additive, (e) amount of $P(O)(OPh)_2Cl$, (f) ketone, (g) amount of ketone, (h) reaction time, and (i) yield.



Entry	DMPU (mmol)	Isolated Yield
1	1	36%
2	4	57%
3	6	45%
4	8	41%

Table S1 Varying the DMPU loading with the application of base **1**

Table S1, Entry 1: General Procedure 8A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.12 mL, 1 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, and (i) 139 mg, 36%.

Table S1, Entry 2: General Procedure 8A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, and (i) 220 mg, 57%.

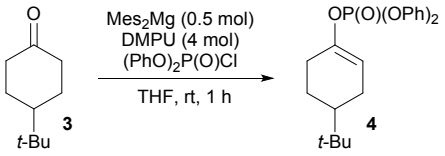
Table S1, Entry 3: General Procedure 8A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.72 mL, 6 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 174 mg, 45%.

Table S1, Entry 4: General Procedure 8A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.96 mL, 8 mmol, (e) 0.21 mL, 1 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, (i) 158 mg, 41%.

9. Experimental procedure: Scheme 5

A solution of base (0.5 M solution in THF, 0.75 eq., 0.75 mmol, 1.5 mL) was added to THF (9 mL) in a flame-dried Schlenk flask under argon. Diphenylphosphoryl chloride (1 mmol, 0.21 mL) and DMPU (4 mmol, 0.48 mL) were added to the mixture and stirred for a further 5 min. The ketone **3** (1 mmol, 154 mg) as a solution in THF (2 mL) was added over 1 h *via* syringe pump followed by stirring at room temperature for 1 h. The mixture was quenched with a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil which was purified by column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** as a colourless oil (348 mg**,** 90% yield).

10. Additional experiments: Increasing the electrophile loading with the use of base 1



Entry	Electrophile loading (mmol)	Isolated yield
1	1.5	74%
2	2	69%
3	4	69%

Table S2 Varying the electrophile loading with the use of base **1**

10A. Typical experimental procedure for the electrophile loading study

A solution of base **1** and THF (9 mL) were added to a flame-dried Schlenk flask under argon. Diphenylphosphoryl chloride and DMPU were added to the mixture and stirred for a further 5 min. The ketone **3** as a solution in THF (2 mL) was added over 1 h *via* syringe pump followed by stirring at room temperature for 1 h. The mixture was quenched with a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil which was purified by column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **4** as a colourless oil.

Following typical Procedure 10A, data are presented as: (a) Mg base, (b) reaction temperature, (c) additive, (d) amount of additive, (e) amount of $P(O)(OPh)_2Cl$, (f) ketone, (g) amount of ketone, (h) reaction time, and (i) yield.

Table S2, Entry 1: General Procedure 10A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.31 mL, 1.5 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, and (i) 286 mg, 74%.

Table S2, Entry 2: General Procedure 10A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.42 mL, 2 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, and (i) 266 mg, 69%.

Table S2, Entry 3: General Procedure 10A: (a) Mes_2Mg (0.5 mmol, 1 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.84 mL, 4 mmol, (f) 4-*tert*-butylcyclohexanone, (g) 154 mg, 1 mmol, (h) 1 h, and (i) 267 mg, 69%.

11. Experimental procedure: Table 4

11A. Typical procedure for the aryl methyl ketone substrate scope using base 1

A solution of base (0.5 M solution in THF, 0.75 eq., 0.75 mmol, 1.5 mL) was added to THF (9 mL) in a flame-dried Schlenk flask under argon. Diphenylphosphoryl chloride (1 mmol, 0.21 mL) and DMPU (4 mmol, 0.48 mL) were added to the mixture and stirred for a further 5 min. The ketone substrate was added as a solution in THF (2 mL) over 1 h *via* syringe pump followed by stirring at room temperature for 1 h. The mixture was quenched with a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil which was purified by column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product.

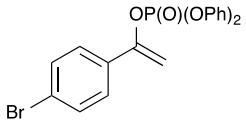
Following typical Procedure 11A, data are presented as: (a) Mg base, (b) reaction temperature, (c) additive, (d) amount of additive, (e) amount of $P(O)(OPh)_2Cl$, (f) ketone, (g) amount of ketone, (h) reaction time, (i) yield run 1, (j) yield run 2, and (k) appearance.

For the entries in Table 4, each reaction was run twice under identical conditions, and the average yield is presented in the Table.

Table 4, compound 10: General Procedure 11A: (a) Mes_2Mg (0.75 mmol, 1.5 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) acetophenone, (g) 120 mg, 1 mmol, (h) 1 h, (i) 271 mg, 77%, (j) 268 mg, 76%, and (k) colourless oil.

Table 4, compound 11: General Procedure 11A: (a) Mes_2Mg (0.75 mmol, 1.5 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-bromoacetophenone, (g) 199 mg, 1 mmol, (h) 1 h, (i) 322 mg, 75%, (j) 323 mg, 75%, and (k) colourless oil.

Diphenyl 1-(4-bromophenyl)ethen-1-yl phosphate 11:



ν_{max}: 1587, 1487, 1184, 1298, 1265, 1211, 1006, 954, 941 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42 (m, 2H, ArH), 7.38-7.33 (m, 6H, ArH), 7.26-7.16 (m, 6H, ArH), 5.41-5.36 (m, 2H, $C=CH_2$).

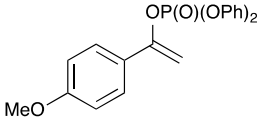
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 150.8, 131.9, 130.2, 130.6, 127.1, 126.6, 123.9, 120.5, 99.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ -17.80.

HRMS (ESI) Calculated for $C_{20}H_{17}BrO_4P$ $[M+H]^+$: 431.0042/433.0022; found: 431.0035/433.0012.

Table 4, compound 12: General Procedure 11A: (a) Mes_2Mg (0.75 mmol, 1.5 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-methoxyacetophenone, (g) 150 mg, 1 mmol, (h) 1 h, (i) 290 mg, 76%, (j) 294 mg, 77%, and (k) colourless oil.

Diphenyl 1-(4-methoxyphenyl)ethen-1-yl phosphate 12:[8]



ν_{max}: 1671, 1595, 1489, 1257, 1186, 918 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.40 (m, 2H, ArH), 7.38-7.32 (m, 4H, ArH), 7.28-7.17 (m, 6H, ArH), 6.87-6.81 (m, 2H, ArH), 5.28-5.21 (m, 2H, C=CH_2), 3.82 (s, 3H, CH_3).

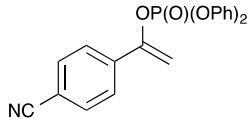
^{13}C NMR (100 MHz, $CDCl_3$): 160.8, 152.6, 150.9, 130.2, 127.1, 125.9, 120.6, 120.5, 114.1, 96.8, 55.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ -17.75.

HRMS (ESI) Calculated for $C_{21}H_{20}O_5P$ $[M+H]^+$: 383.1045; found: 383.1043.

Table 4, compound 13: General Procedure 11A: (a) Mes_2Mg (0.75 mmol, 1.5 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) 4-cyanoacetophenone, (g) 145 mg, 1 mmol, (h) 1 h, (i) 256 mg, 68%, (j) 257 mg, 68%, and (k) colourless oil.

Diphenyl 1-(4-cyanophenyl)ethen-1-yl phosphate 13:[8]



ν_{max}: 2227, 1589, 1487, 1300, 1182, 1093, 1008, 958 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.54 (m, 4H, ArH), 7.40-7.33 (m, 4H, ArH), 7.26-7.16 (m, 6H, ArH), 5.56-5.50 (m, 2H, C=CH_2).

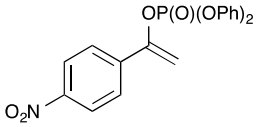
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 150.7, 138.12, 132.6, 130.30, 126.2, 126.1 120.43, 118.7 113.1, 101.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ -17.78.

HRMS (ESI) Calculated for $C_{21}H_{17}NO_4P$ $[M+H]^+$: 378.0898; found: 378.0888.

Table 4, compound 14: General Procedure 11A: (a) Mes_2Mg (0.75 mmol, 1.5 ml), (b) rt, (c) DMPU, (d) 0.48 ml, 4 mmol, (e) 0.21 ml, 1 mmol, (f) (4-nitrophenyl)ethanone, (g) 165 mg, 1 mmol, (h) 1 h, (i) 8 mg, 2%, (j) 15 mg, 4%, and (k) red oil.

Diphenyl 1-(4-nitrophenyl)ethen-1-yl phosphate 14:



ν_{max}: 1591, 1485, 1456, 1296, 1265, 1222, 1184, 1161, 1128, 1008, 948 cm^{-1}.

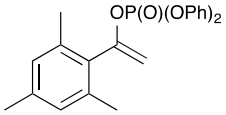
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 4H, ArH), 7.25-7.17 (m, 6H, ArH), 6.94-6.89 (m, 1H, C=CH_2), 6.87-6.83 (m, 2H, ArH), 6.82-6.77 (m, 2H, ArH), 5.32 (s, 1H, C=CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 150.9, 146.3, 135.4, 130.1, 129.9, 125.8, 120.8, 120.6, 115.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ -17.23.

Table 4, compound 15: General Procedure 11A: (a) Mes_2Mg (0.75 mmol, 1.5 mL), (b) rt, (c) DMPU, (d) 0.48 mL, 4 mmol, (e) 0.21 mL, 1 mmol, (f) mesitylethanone, (g) 162 mg, 1 mmol, (h) 1 h, (i) 296 mg, 75%, (j) 296 mg, 75%, and (k) yellow oil.

Diphenyl 1-mesitylethen-1-yl phosphate 15:



ν_{max}: 1589, 1487, 1296, 1213, 1186, 1161, 1008, 939 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.28 (m, 4H, ArH), 7.23-7.15 (m, 6H, ArH), 6.85 (s, 2H, ArH), 5.51-5.47 (m, 1H, C=CH_2), 4.81-4.78 (m, 1H, C=CH_2), 2.31 (s, 6H, CH_3), 2.29 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 150.8, 139.1, 137.5, 131.8, 130.0, 128.5, 125.7, 120.4, 103.9, 21.4, 20.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ -18.34.

HRMS (ESI) Calculated for $C_{23}H_{24}O_4P$ $[M+H]^+$: 395.1407; found: 395.1403.

12. Experimental procedure: Scheme 6

12A. Experimental procedure for the formation of enol phosphate 16 using base 1

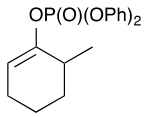
A solution of base **1** (0.5 M solution in THF, 0.75 eq., 0.75 mmol, 1.5 mL) was added to THF (9 mL) in a flame-dried Schlenk flask under argon. Diphenylphosphoryl chloride (1 mmol, 0.21 mL) and DMPU (4 mmol, 0.48 mL) were added to the mixture and stirred for a further 5 min. 2-Methylcyclohexanone (112 mg, 1 mmol) was added as a solution in THF (2 mL) over 1 h *via* syringe pump, followed by stirring at room temperature for 1 h. The reaction mixture was quenched with a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil, which was purified by flash column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product **16** (230 mg, 67% yield) as a colourless oil.

12B. Experimental procedure for the formation of enol phosphate 16 using base 2

A Schlenk flask was flame-dried under vacuum (0.005 mbar) and filled with argon. The flask was then evacuated and refilled with argon, this cycle repeated one further time, then the flask was allowed to cool to room temperature, before addition of 2-methylcyclohexanone (112 mg, 1 mmol), diphenylphosphoryl chloride (1 mmol, 0.21 mL), DMPU (4 mmol, 0.48 mL), and THF (11 mL). The mixture was stirred for 5 min before

dropwise addition of base **2** (0.5 M solution in THF, 0.5 eq., 0.5 mmol, 1 mL) over 5 min. After 1 h the reaction was quenched with a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was extracted with Et_2O (25, 10, 10 mL) and the extracts combined. Removal of the solvent *in vacuo* gave an oil, which was purified by flash column chromatography on silica gel using 0-30 % Et_2O in petroleum ether (40-60 °C) to give the desired product (175 mg, 51% yield) as a colourless oil.

Diphenyl 6-methylcyclohex-1-en-1-yl phosphate 17:[9]



ν_{max}: 1589, 1487, 1294, 1186, 1101, 950 cm^{-1}

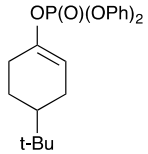
^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.33 (m, 5H, ArH), 7.26-7.33 (m, 5H, ArH), 5.63-5.59 (m, 1H, C=CH), 2.45-2.37 (m, 1H), 2.12-2.06 (m, 2H), 1.87-1.80 (m, 1H), 1.67-1.58 (m, 1H), 1.56-1.48 (m, 1H), 1.47-1.37 (m, 1H), 1.04 (d, J = 7.0 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 150.9, 130.1, 125.7, 120.5, 111.7, 32.4, 31.5, 24.5, 19.7, 18.4.

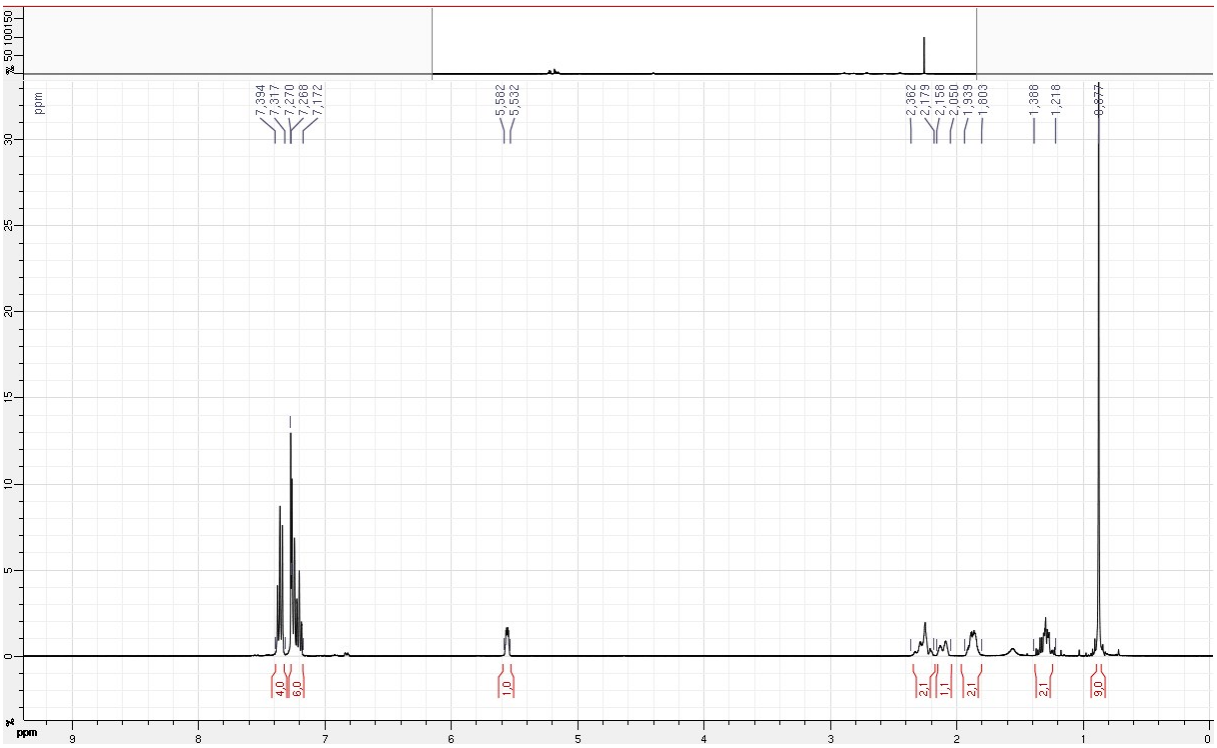
^{31}P NMR (162 MHz, $CDCl_3$): δ -17.52.

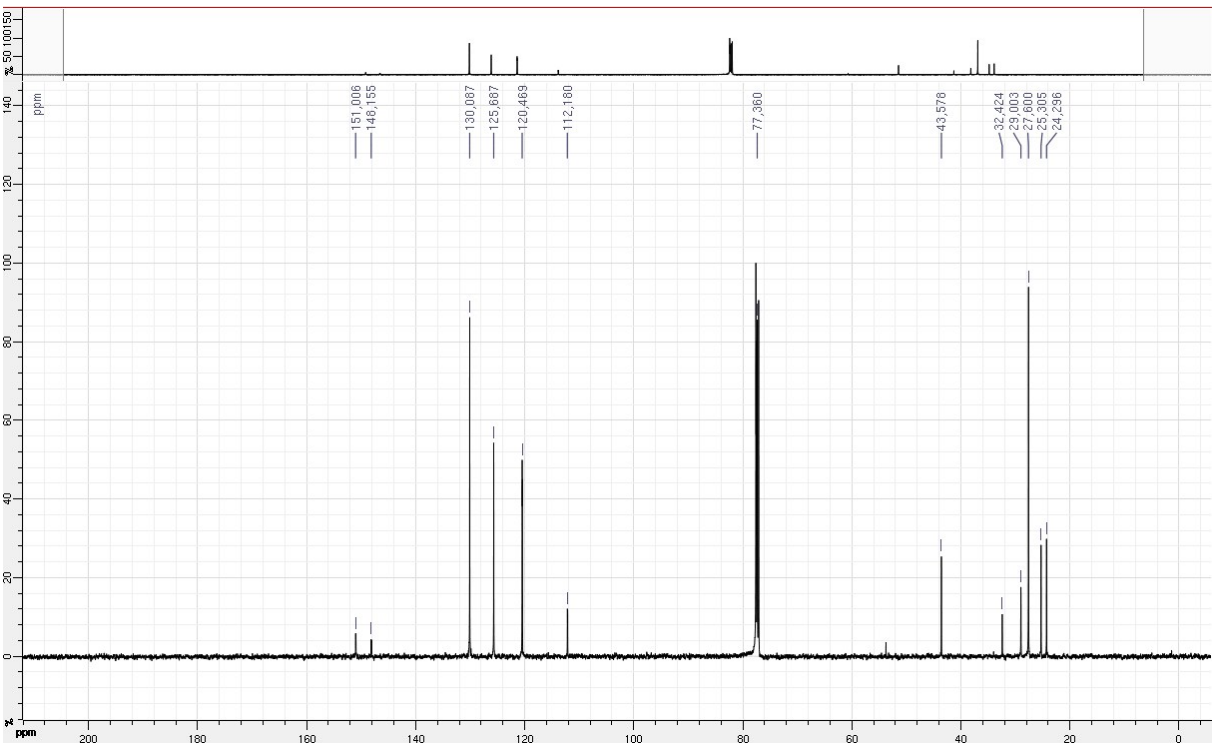
HRMS (ESI) Calculated for $C_{19}H_{22}O_4P$ $[M+H]^+$: 345.1250; found: 345.1246

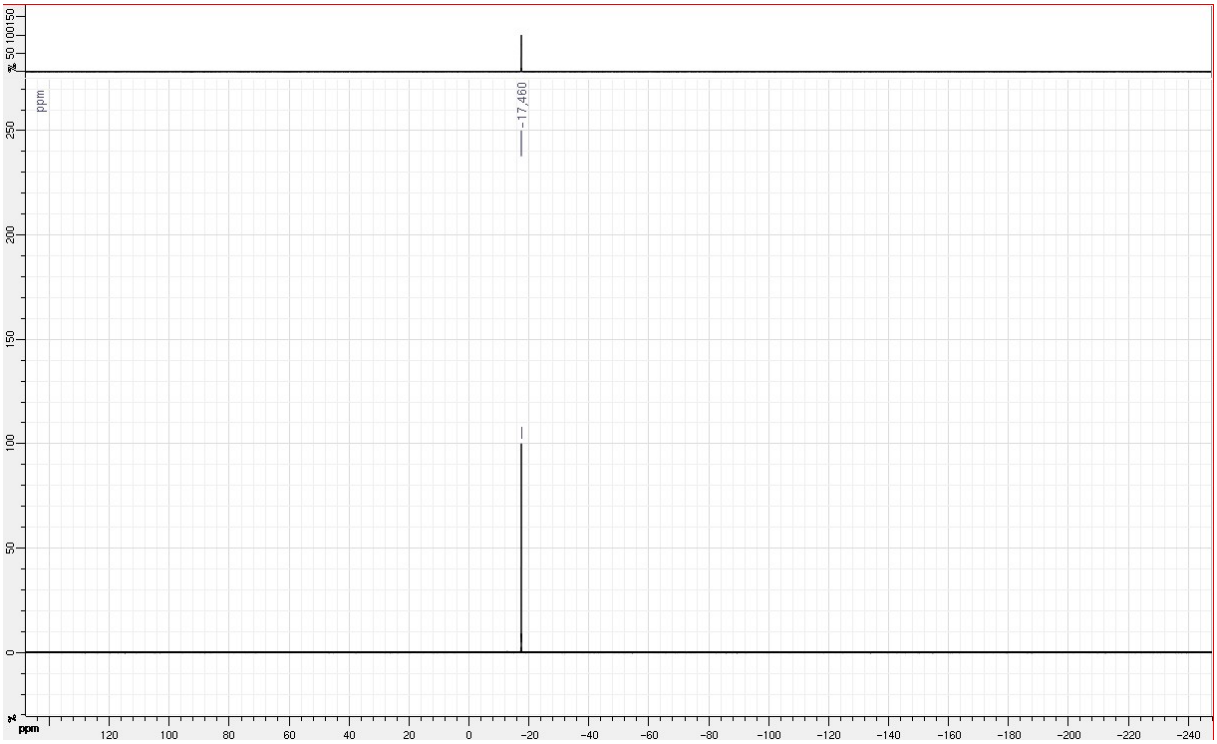
III. NMR spectra (^{1}H, ^{13}C, ^{31}P)



4



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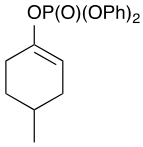
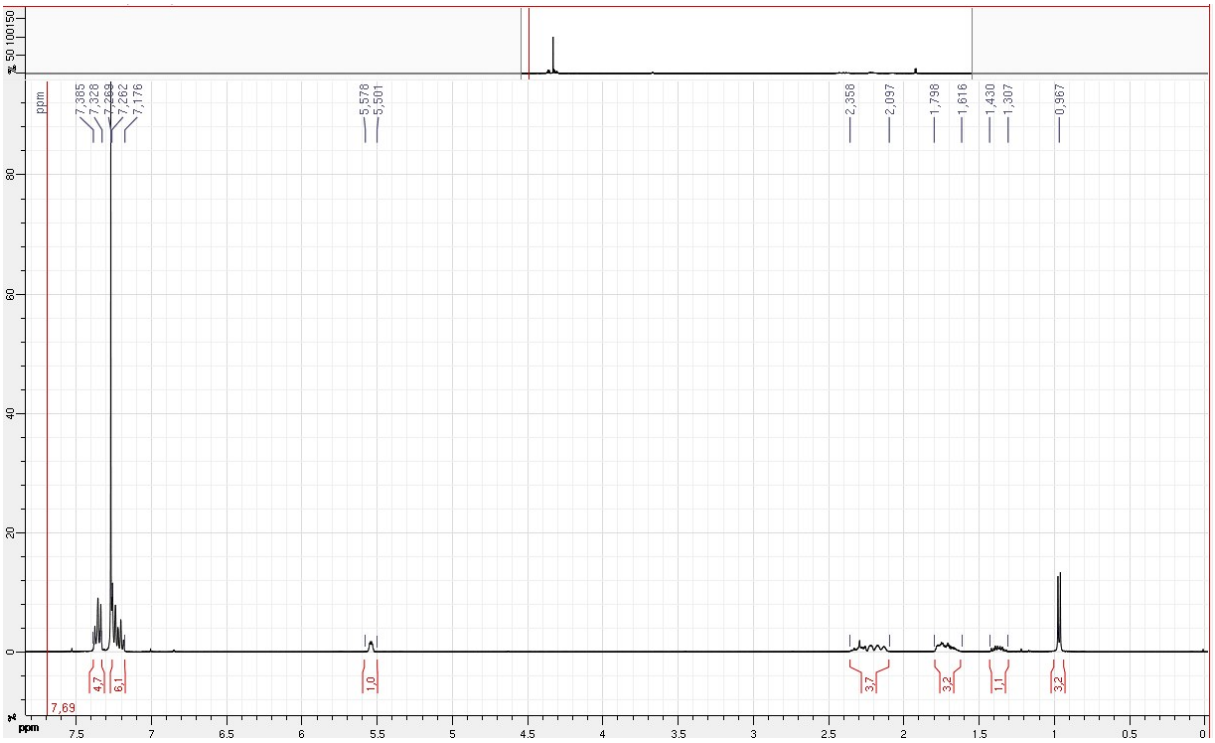

OP(O)(OPh)2

5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7,176
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1,798
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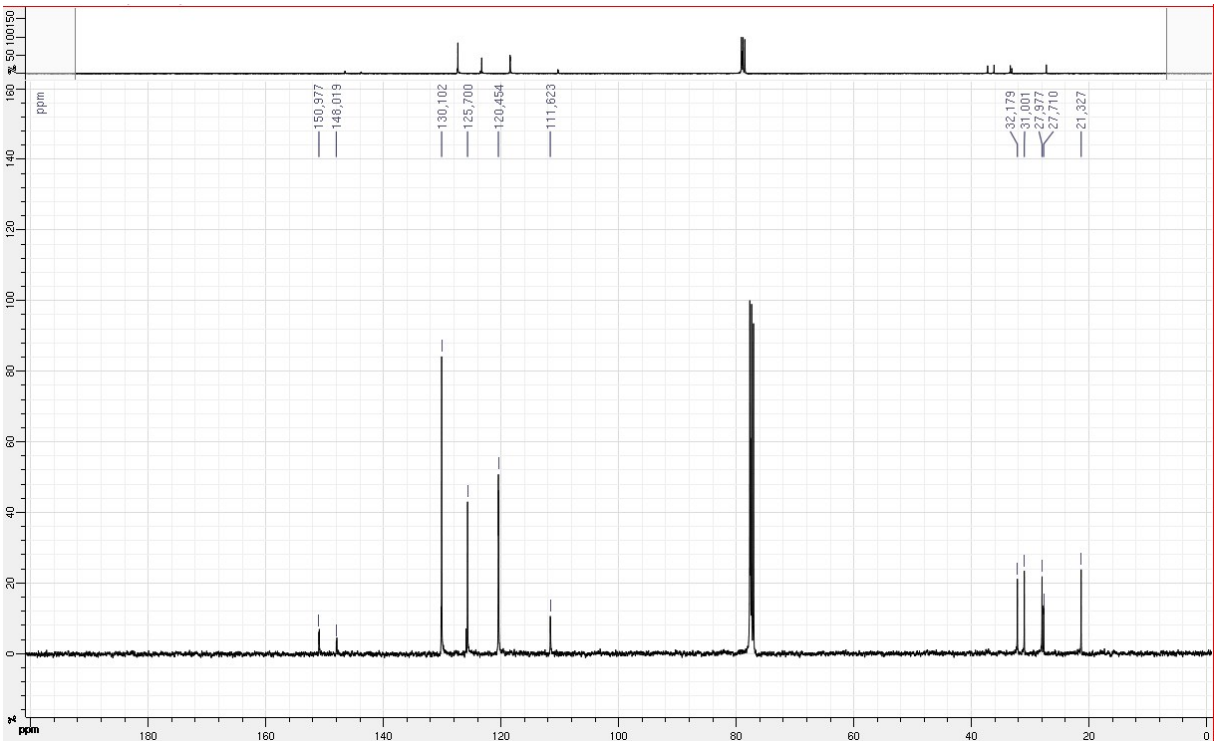
0,967
4,7
6,1
1,0
3,7
3,2
1,1
3,2
7,69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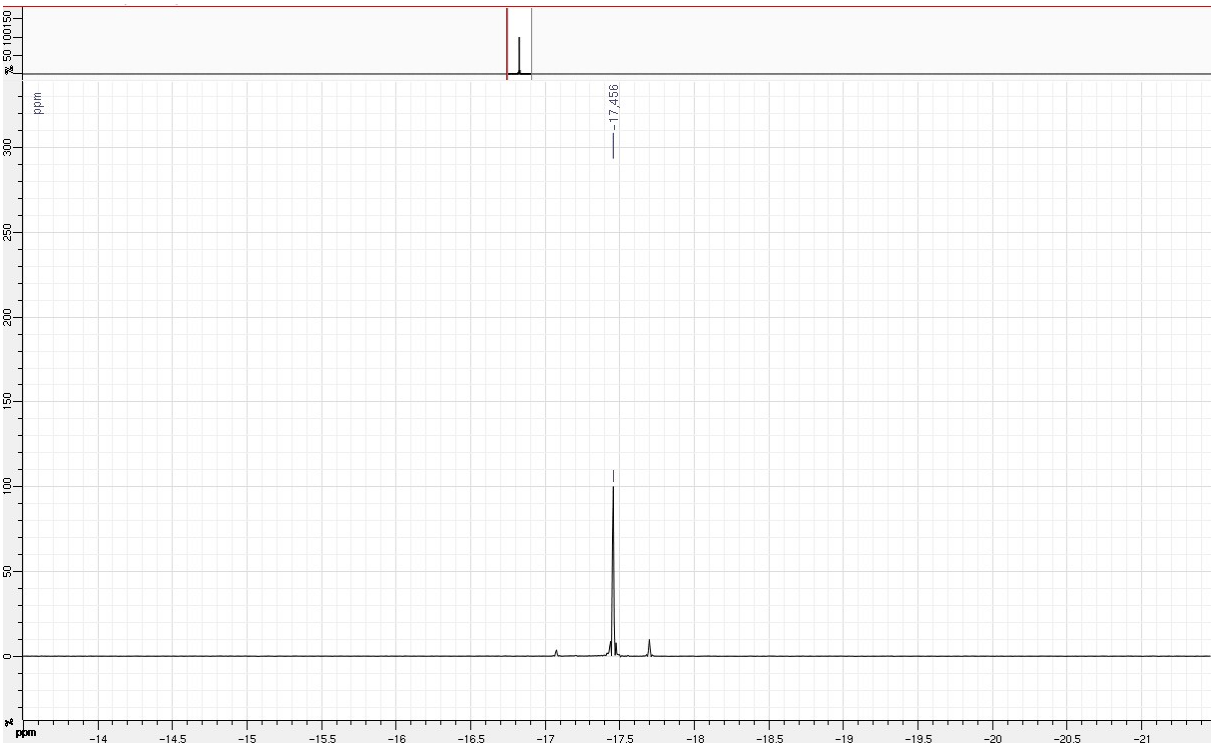
27,977
27,710
21,327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ppm
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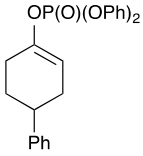
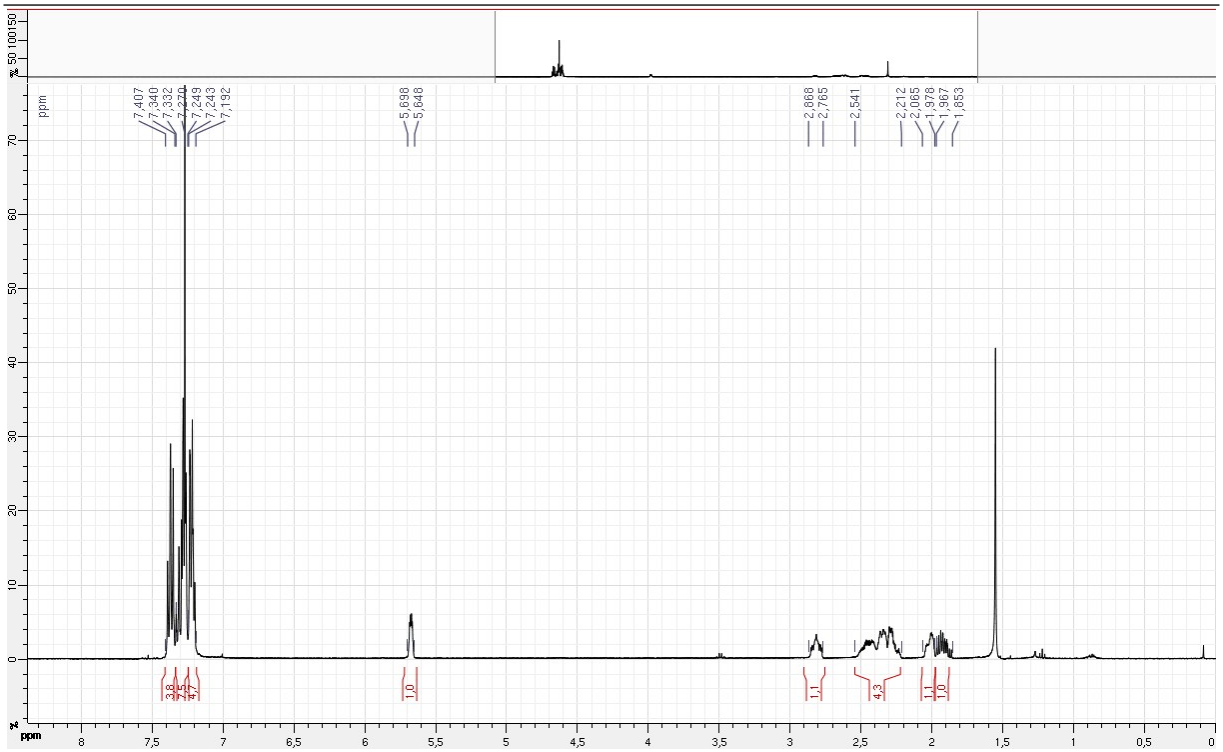
-19.5
-20
-20.5
-21


OP(O)(OPh)2
Ph

6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2,765
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2,212
2,065
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1,967
1,853
3,8
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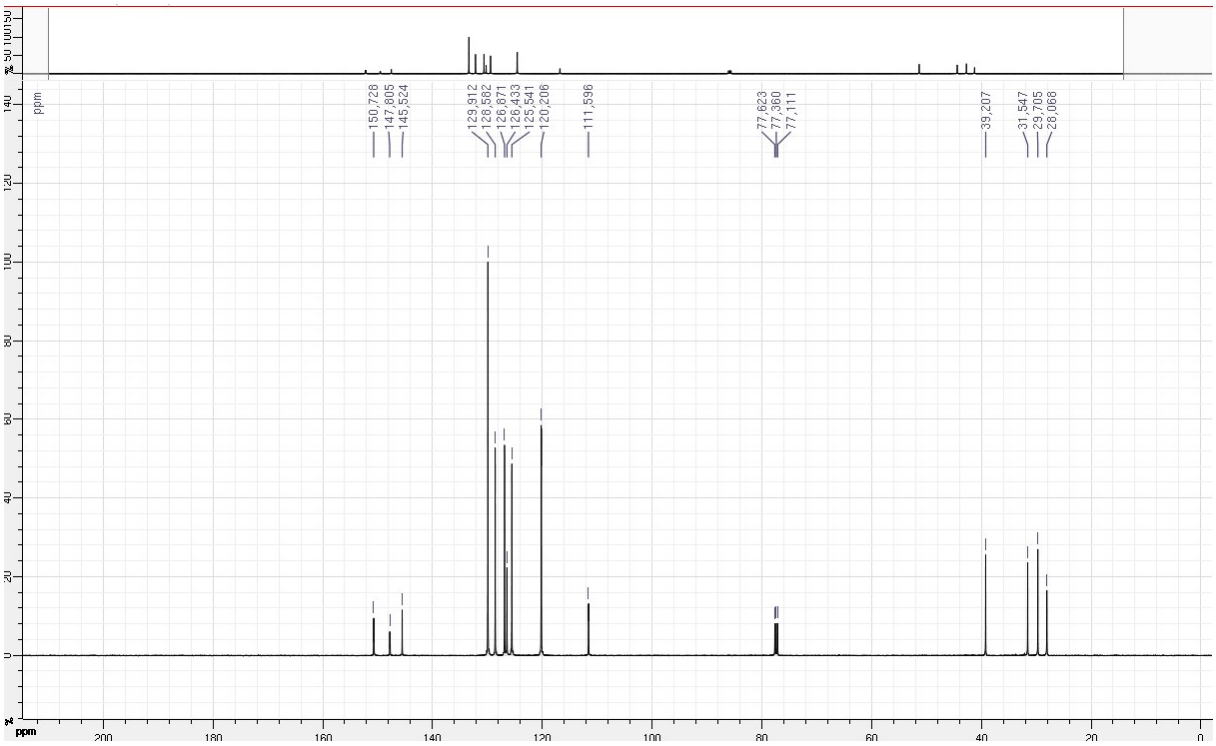
1,0
1,1
4,3
1,1
1,0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128,582
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120,206
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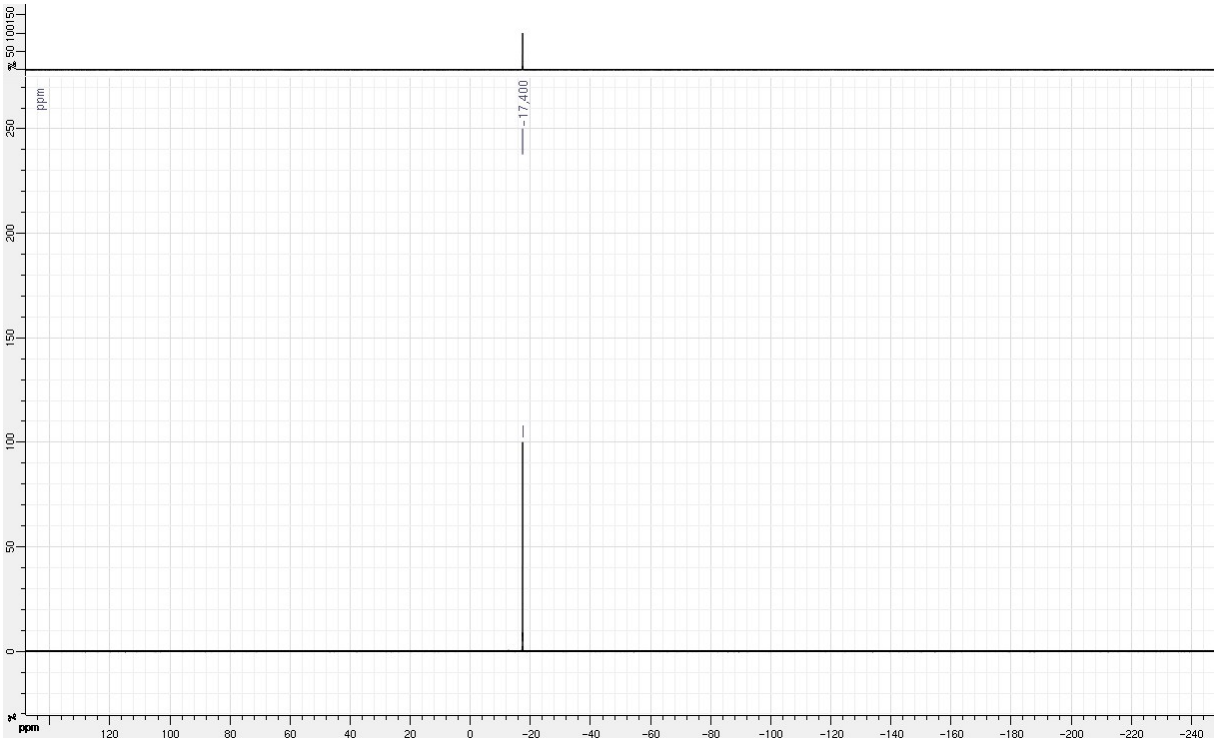
77,360
77,111
39,207
31,547
29,705
28,068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-100
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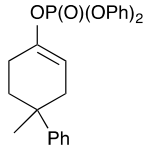
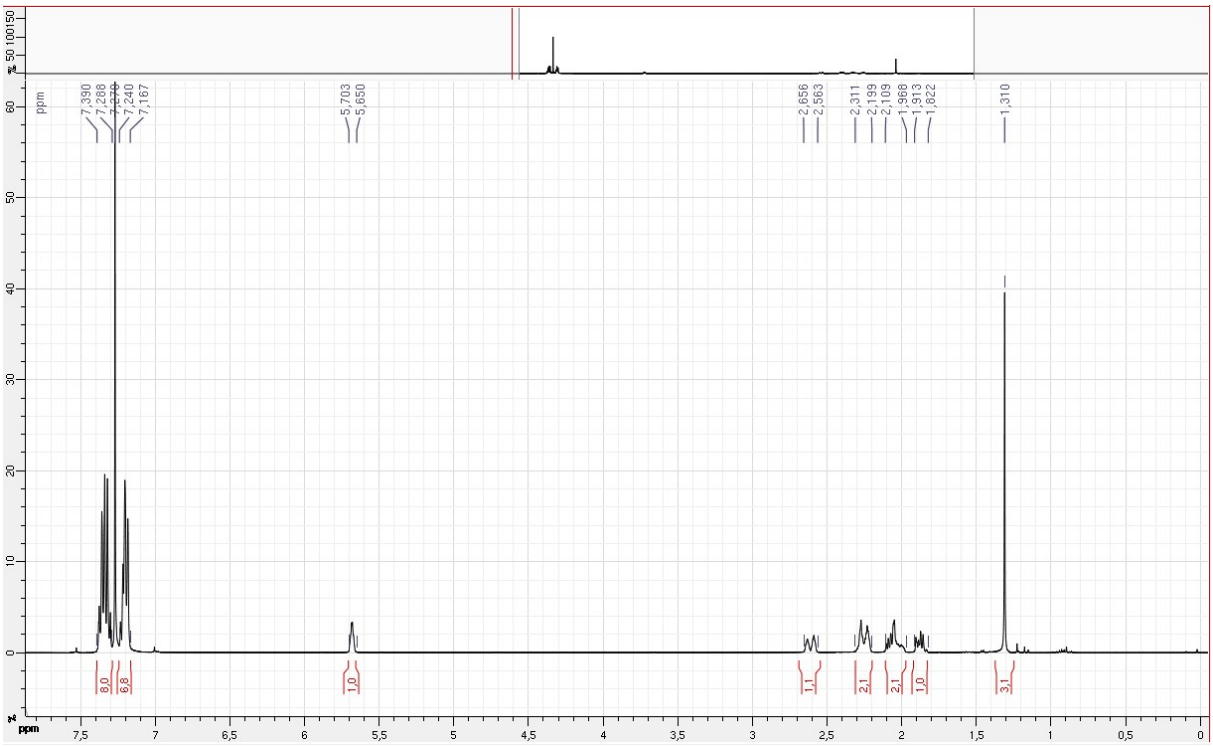
-200
-220
-240


OP(O)(OPh)2
Ph

7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2,311
2,199
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1,822
1,310
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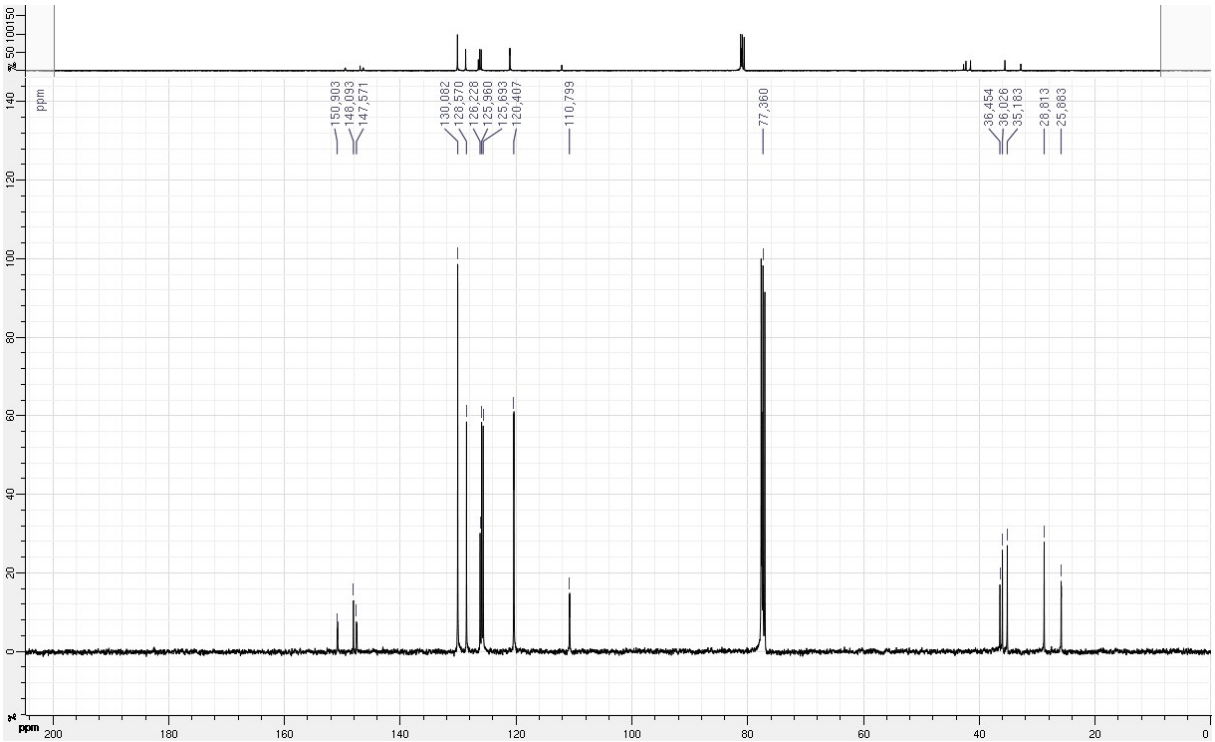
6,8
1,0
1,1
2,1
2,1
1,0
3,1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130,082
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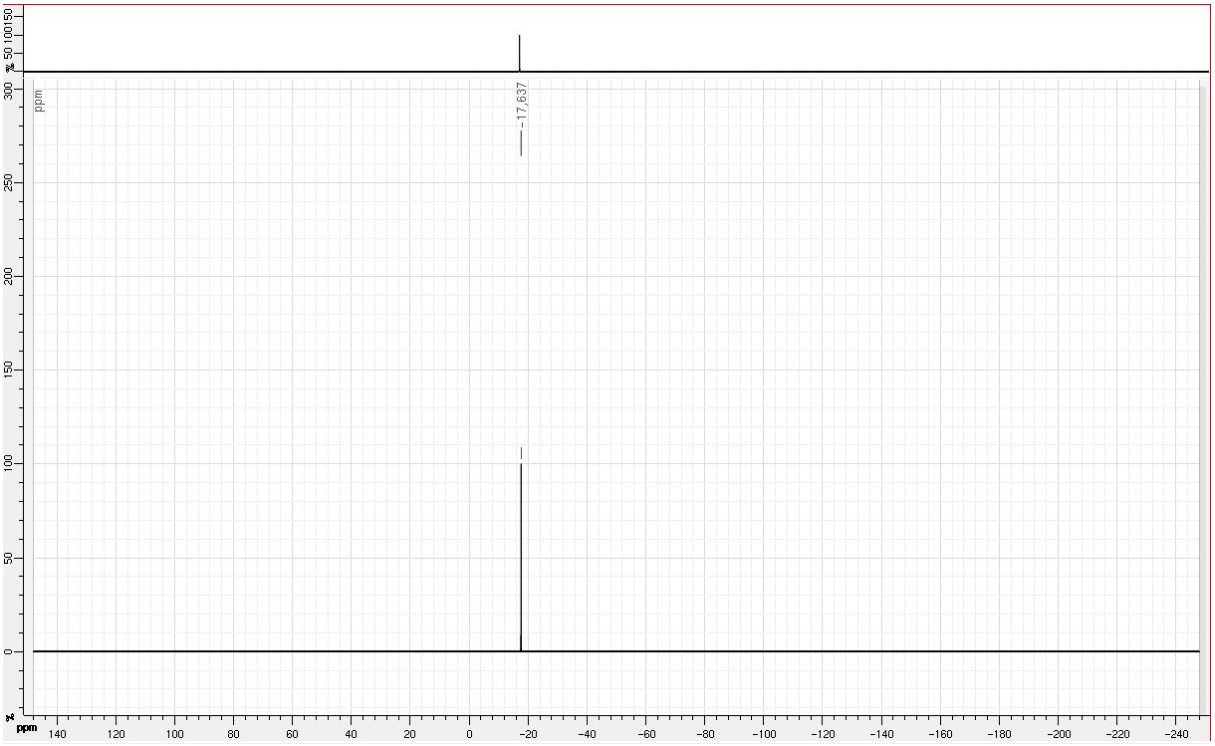
35,183
28,813
25,883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-220
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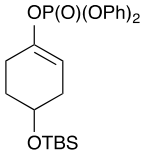
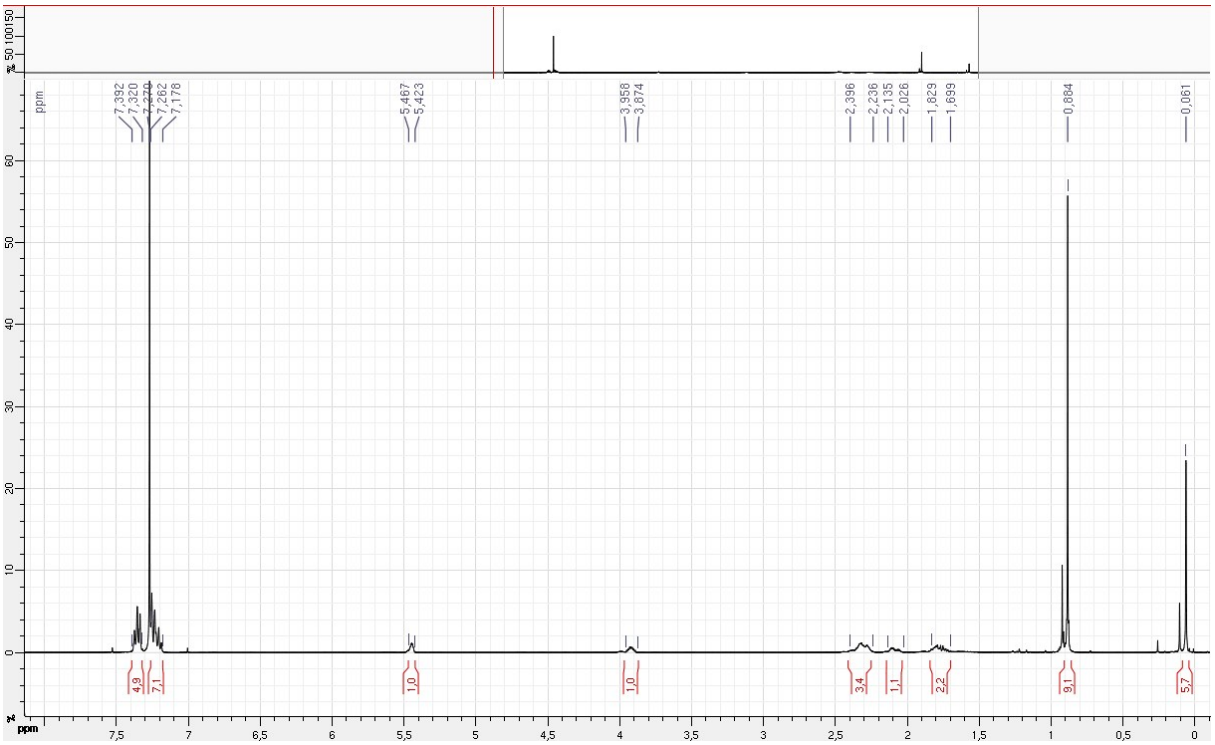

OP(O)(OPh)2
OTBS

8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5,423
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3,874
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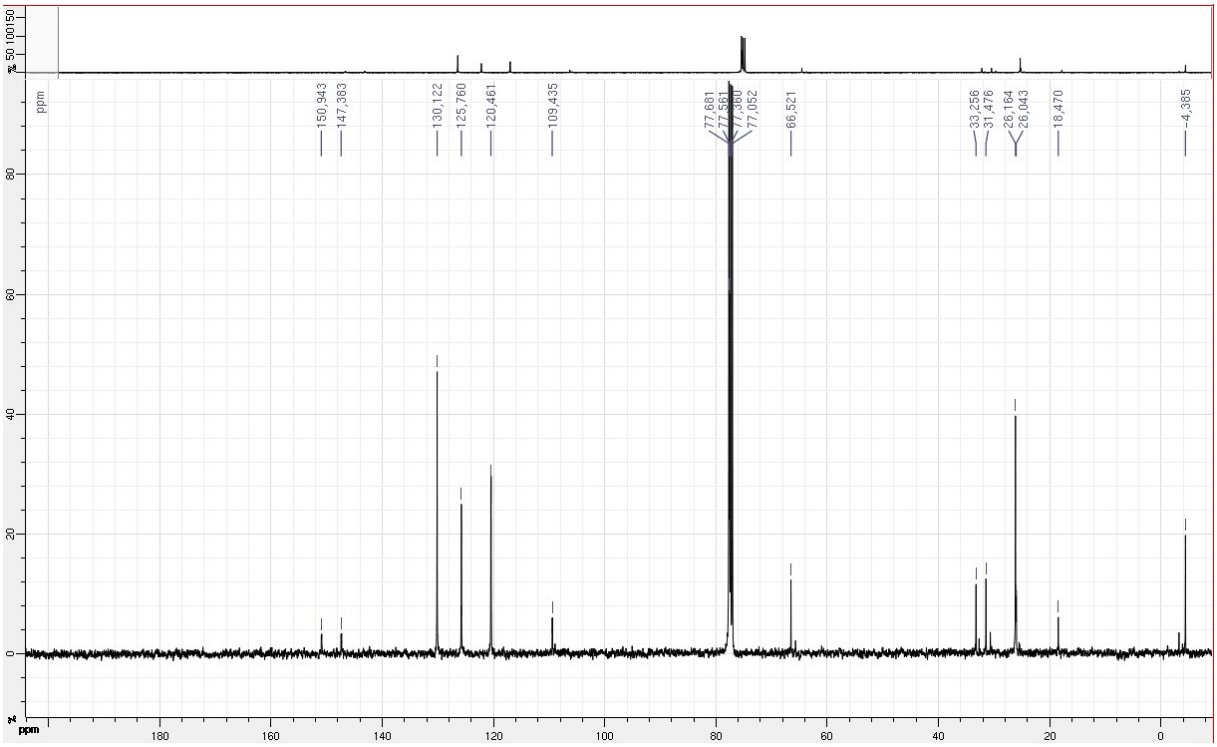
2,236
2,135
2,026
1,829
1,699
0,884
0,061
4,9
7,1
1,0
1,0
3,4
1,1
2,2
9,1
5,7
ppm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130,122
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120,461
109,435
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77,561
77,360
77,052
66,521
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26,164
26,043
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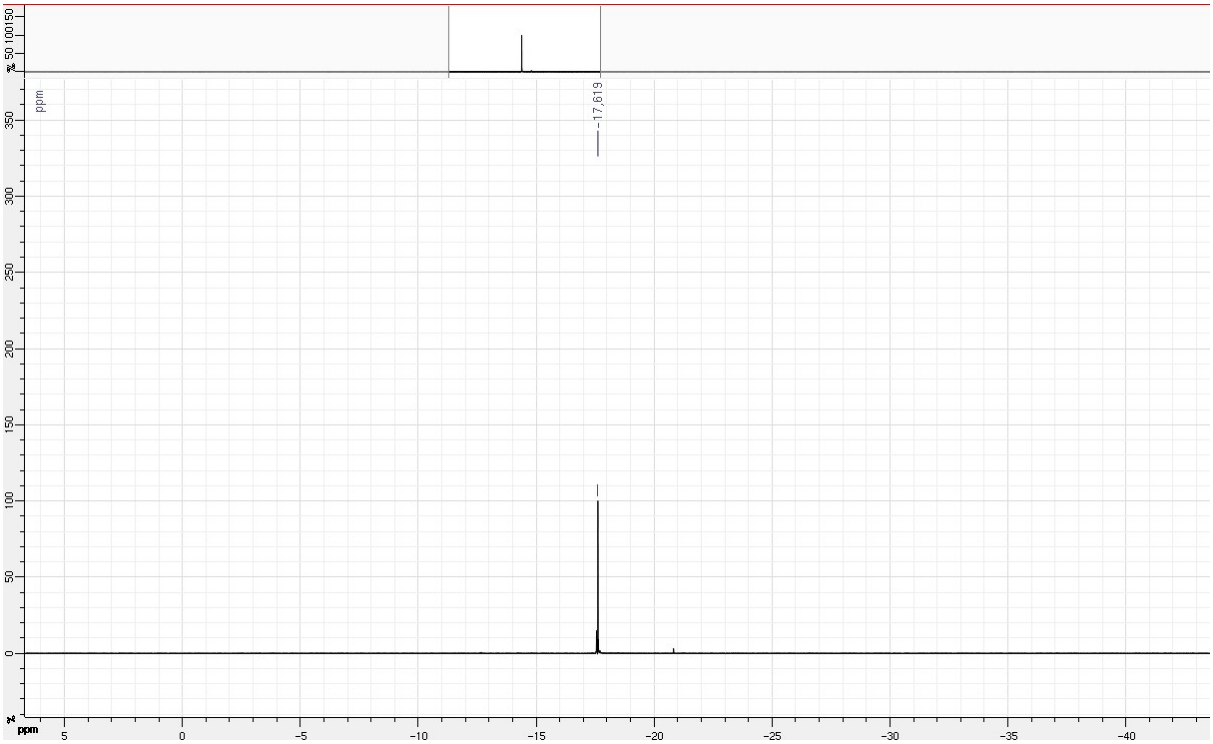
ppm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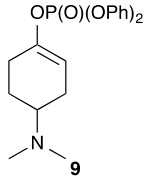
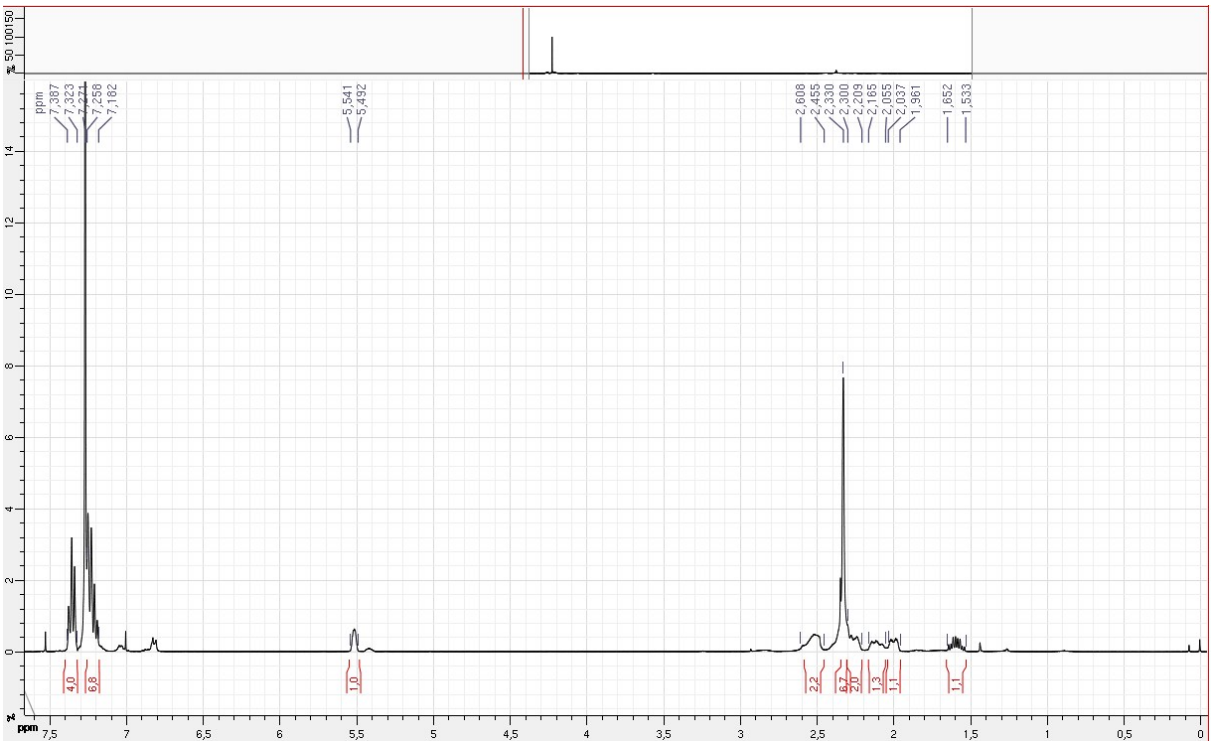

OP(O)(OPh)2
N
9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2,300
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2,165
2,055
2,037
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1,533
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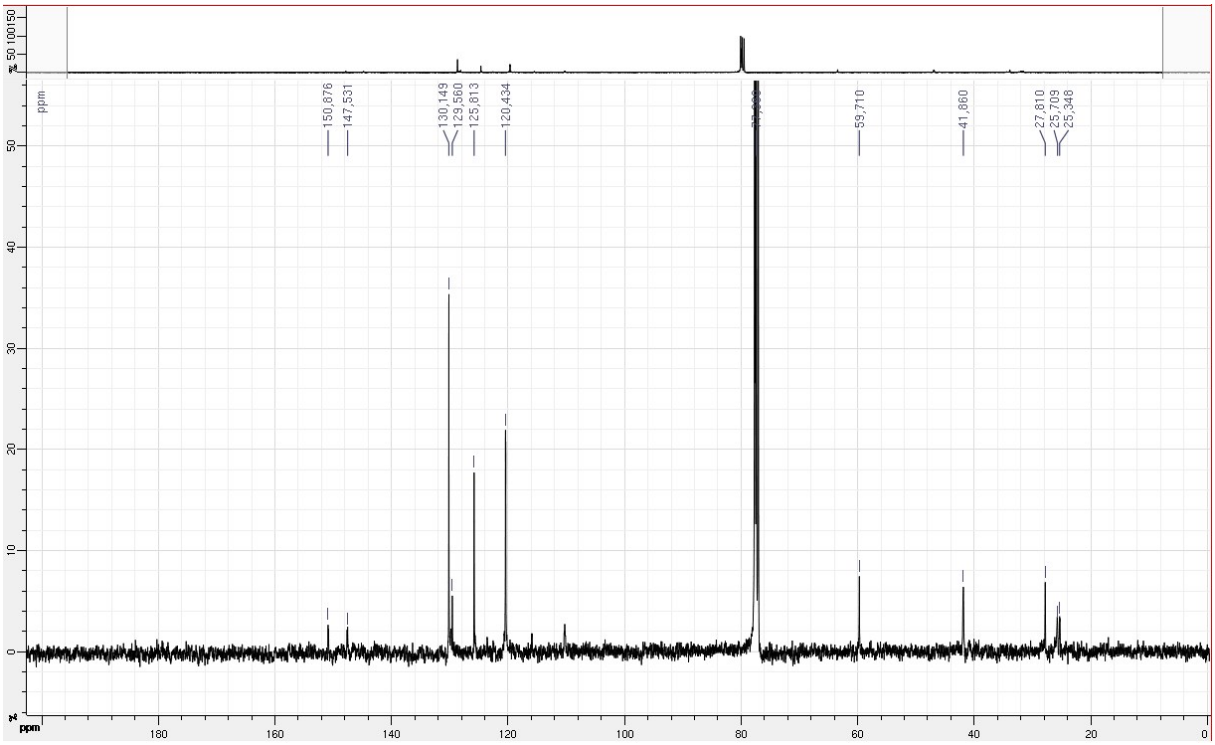
6,8
1,0
2,2
0,7
2,0
1,3
1,1
1,1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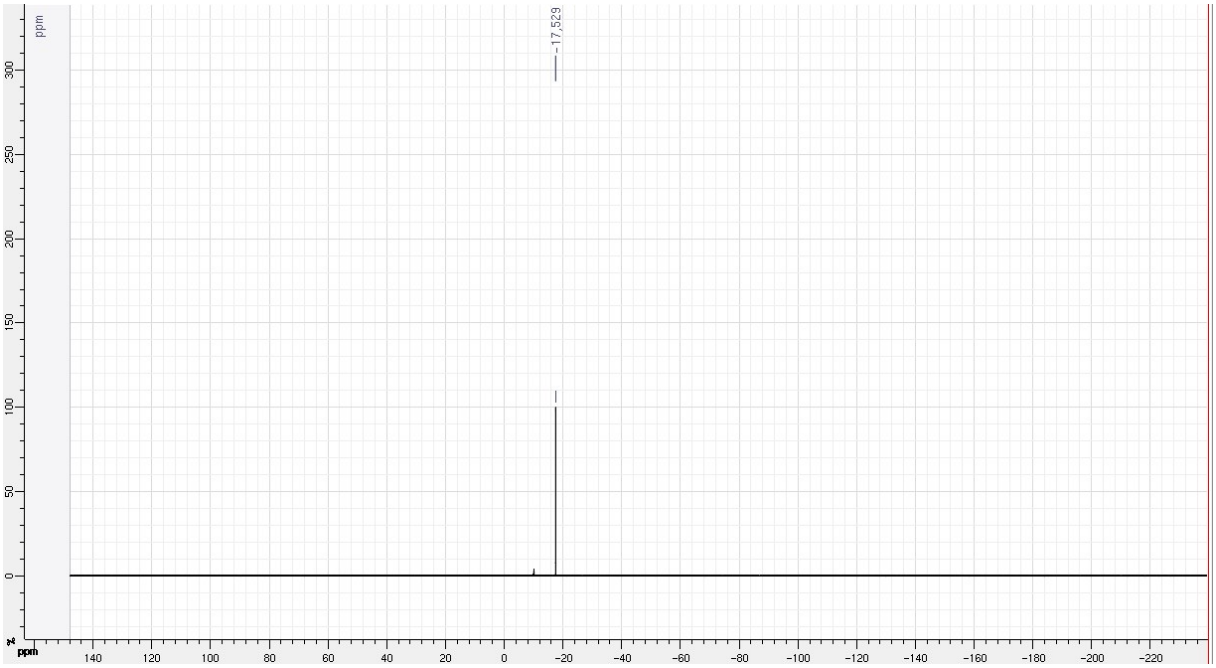
41,860
27,810
25,709
25,348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150
100
50
0
ppm
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120
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60
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-200
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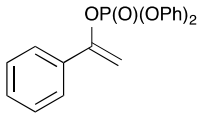
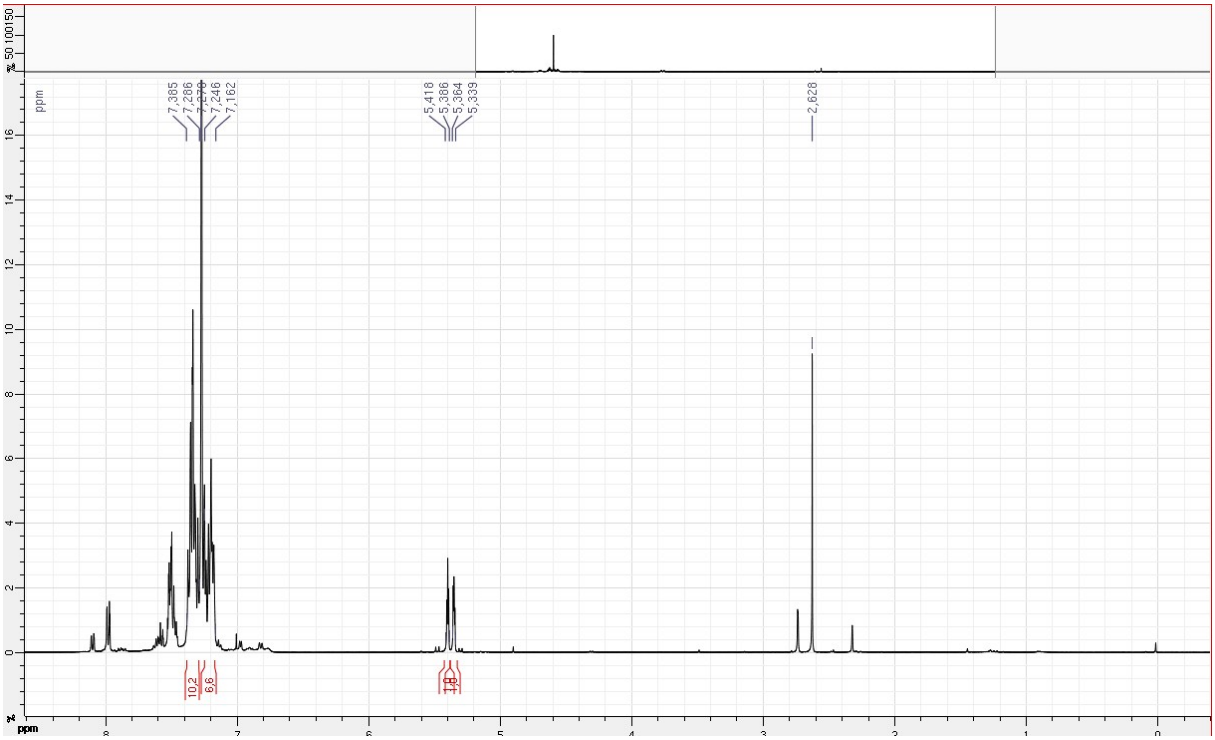

OP(O)(OPh)2

10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10,2
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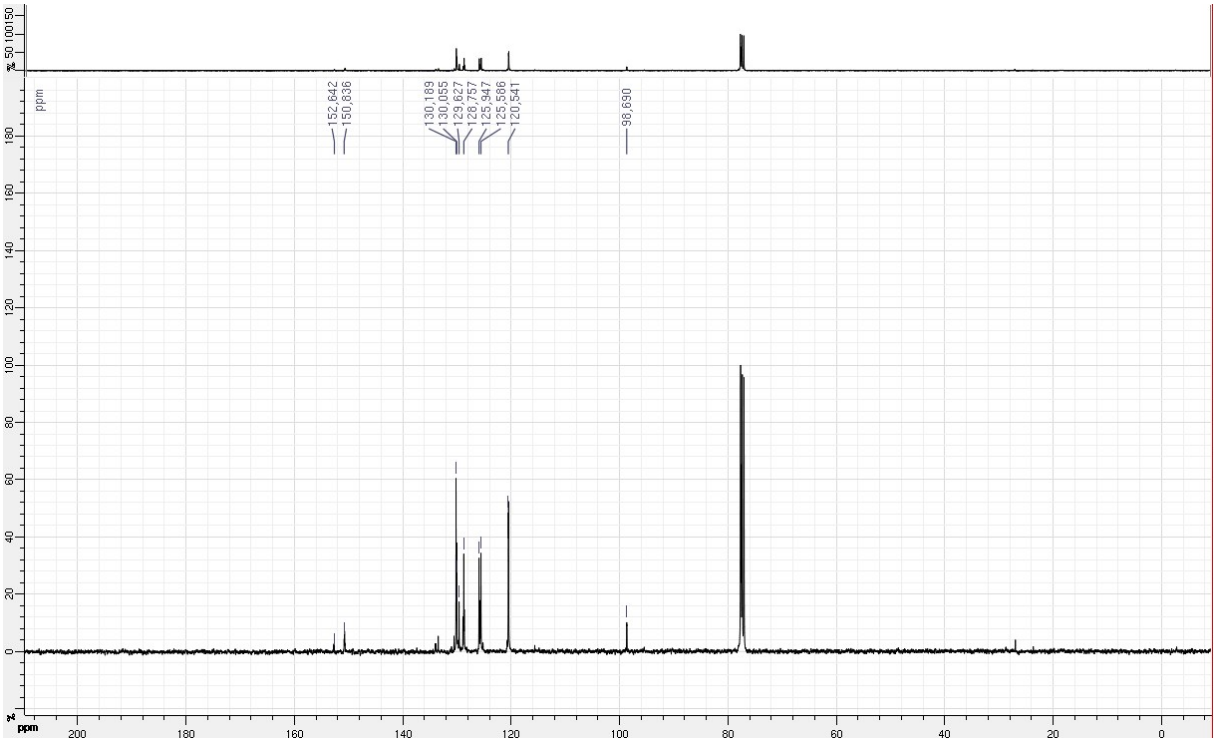
4,8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120,541
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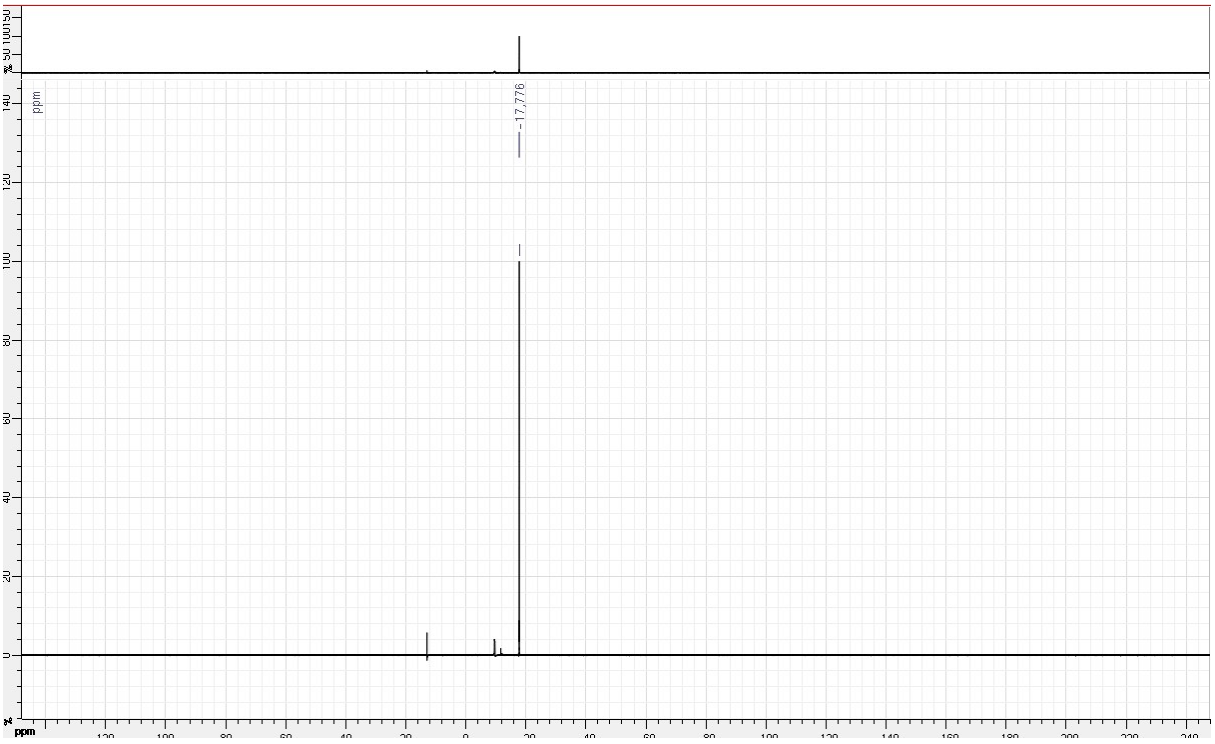
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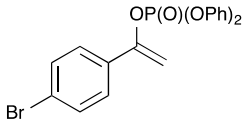
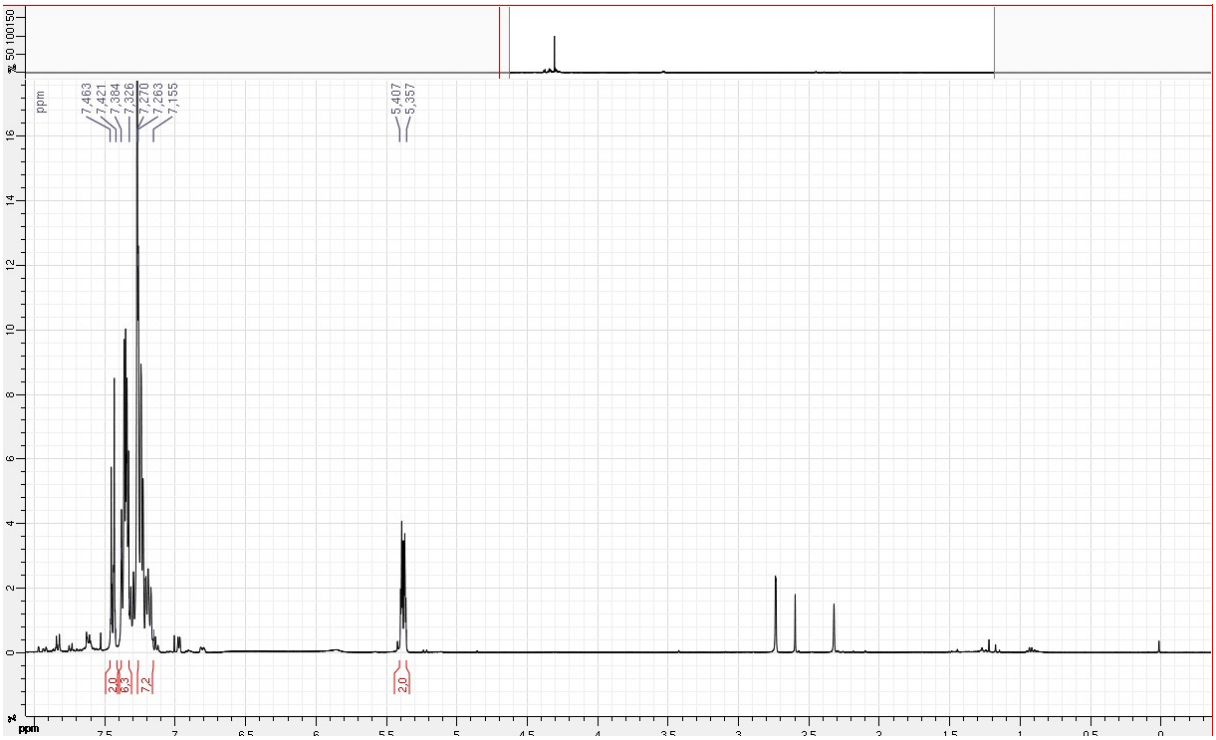

OP(O)(OPh)2
Br

11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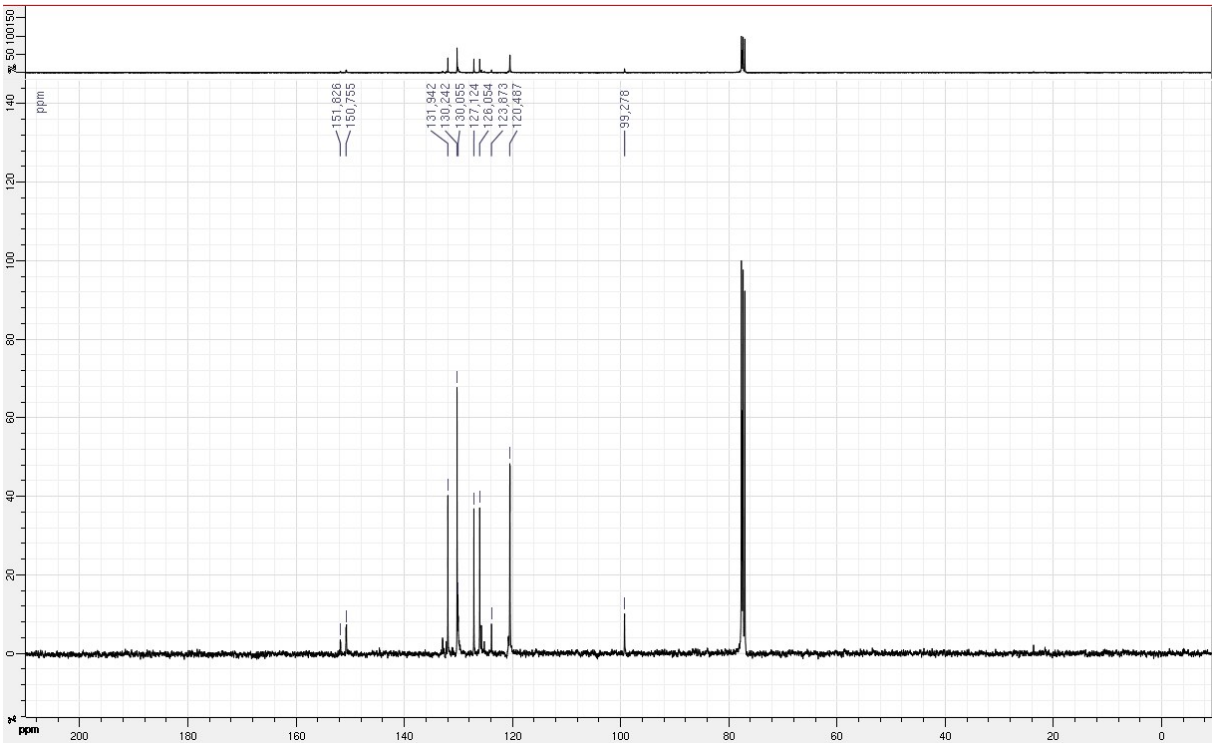
2,0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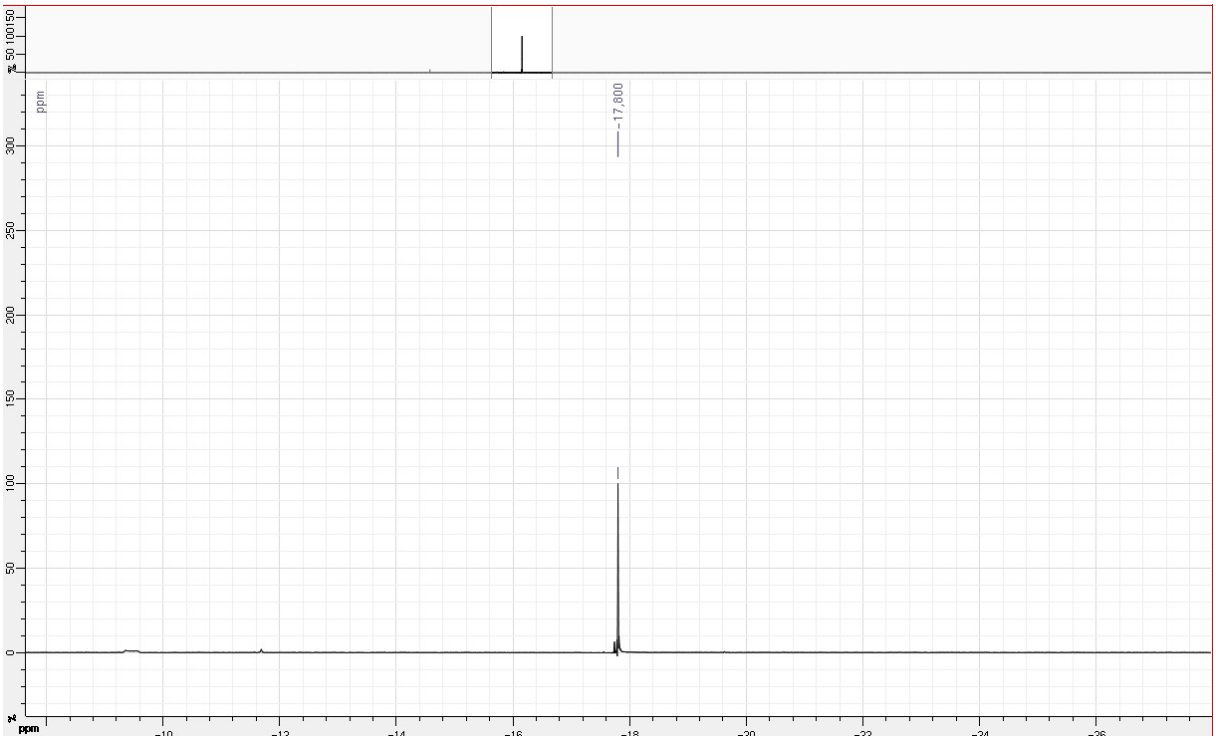
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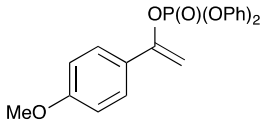
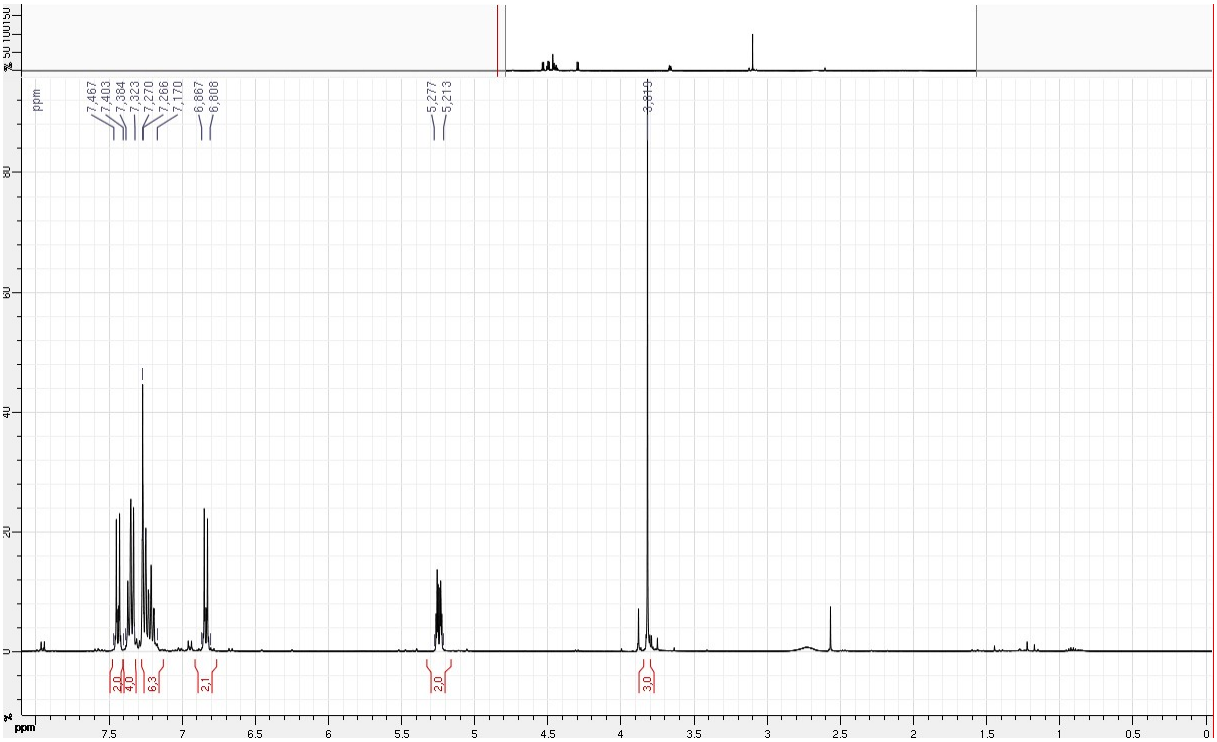

OP(O)(OPh)2
MeO

12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7,323
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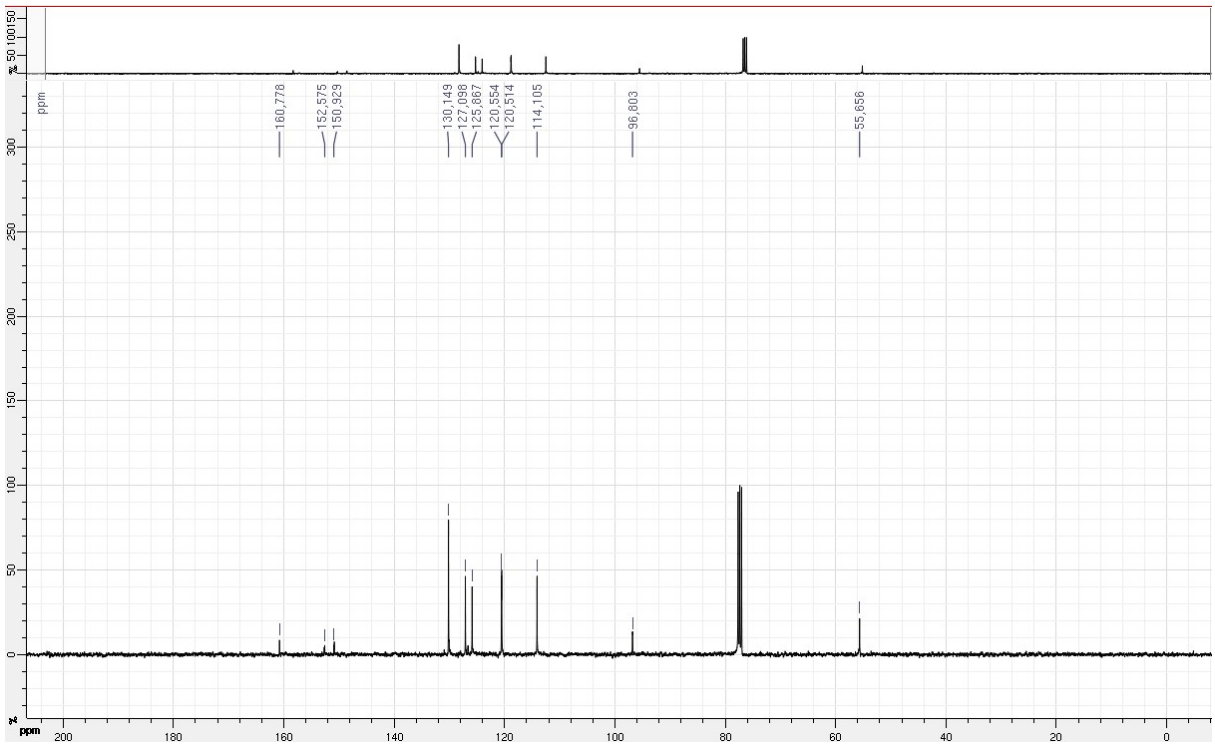
ppm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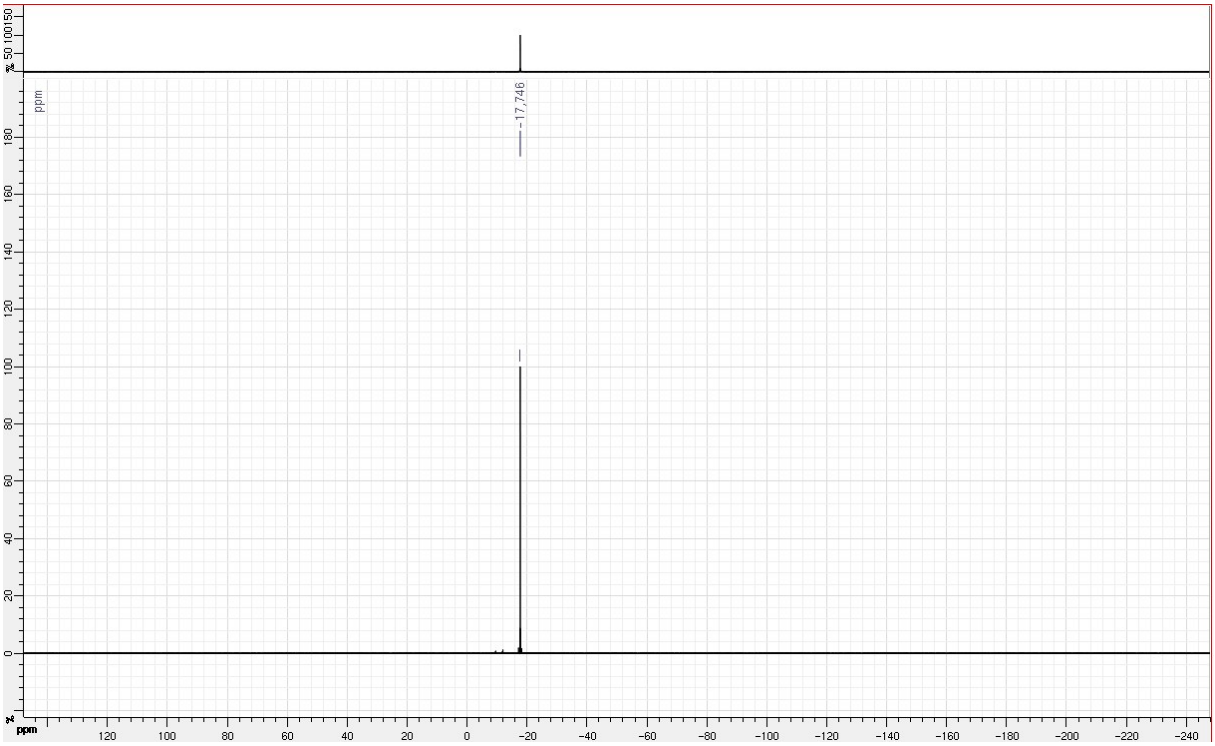
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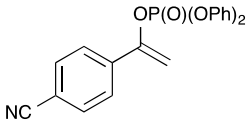
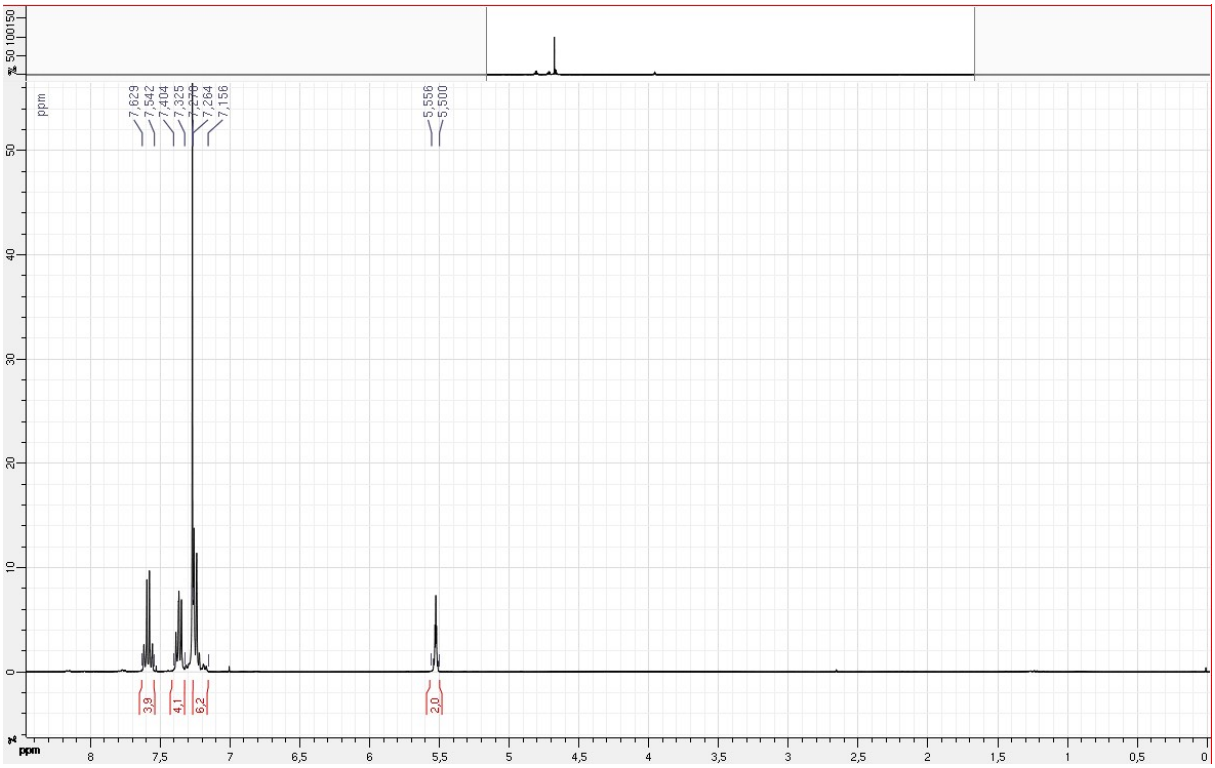
-180
-200
-220
-240


OP(O)(OPh)2
NC

13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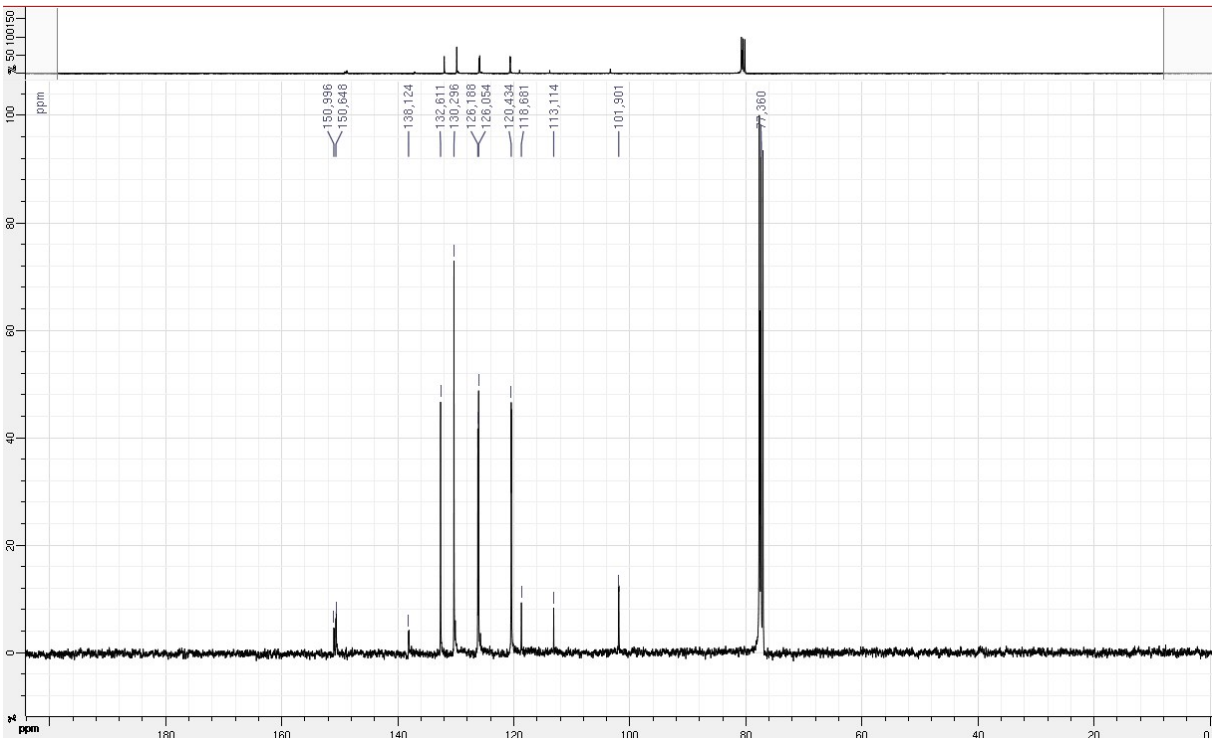
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126,188
126,054
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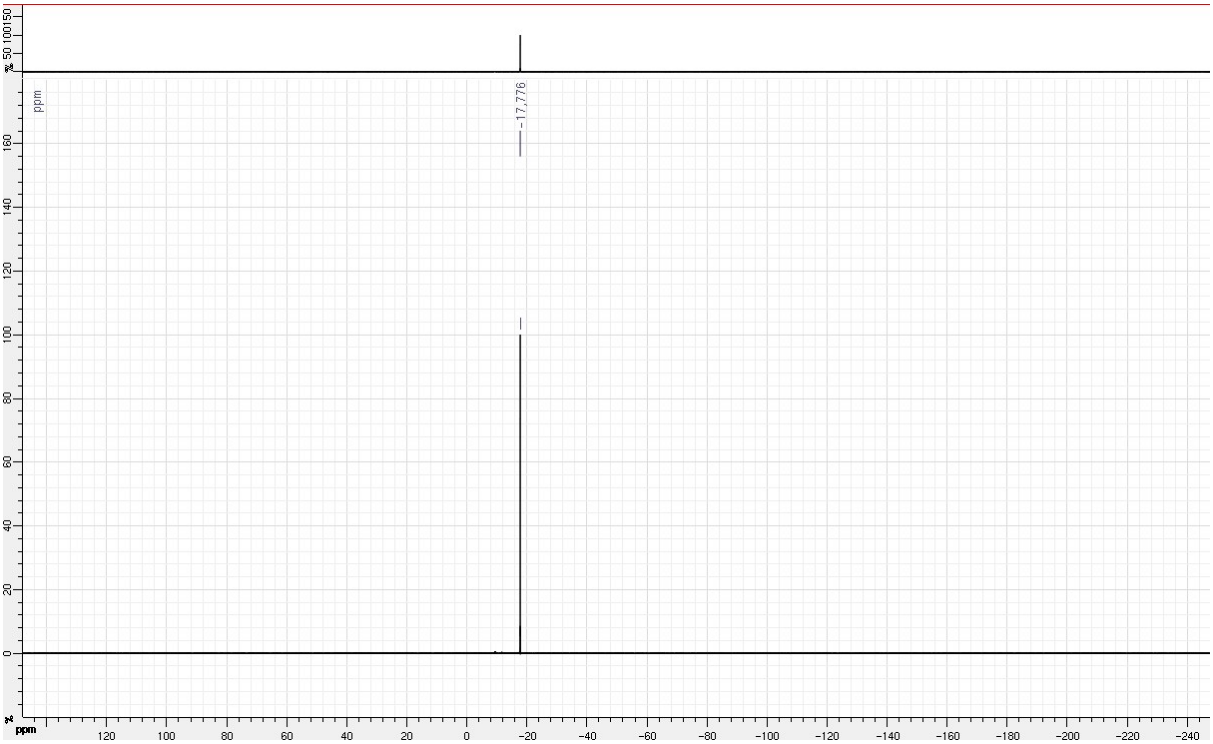
118,681
113,114
101,901
77,360
ppm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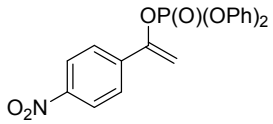
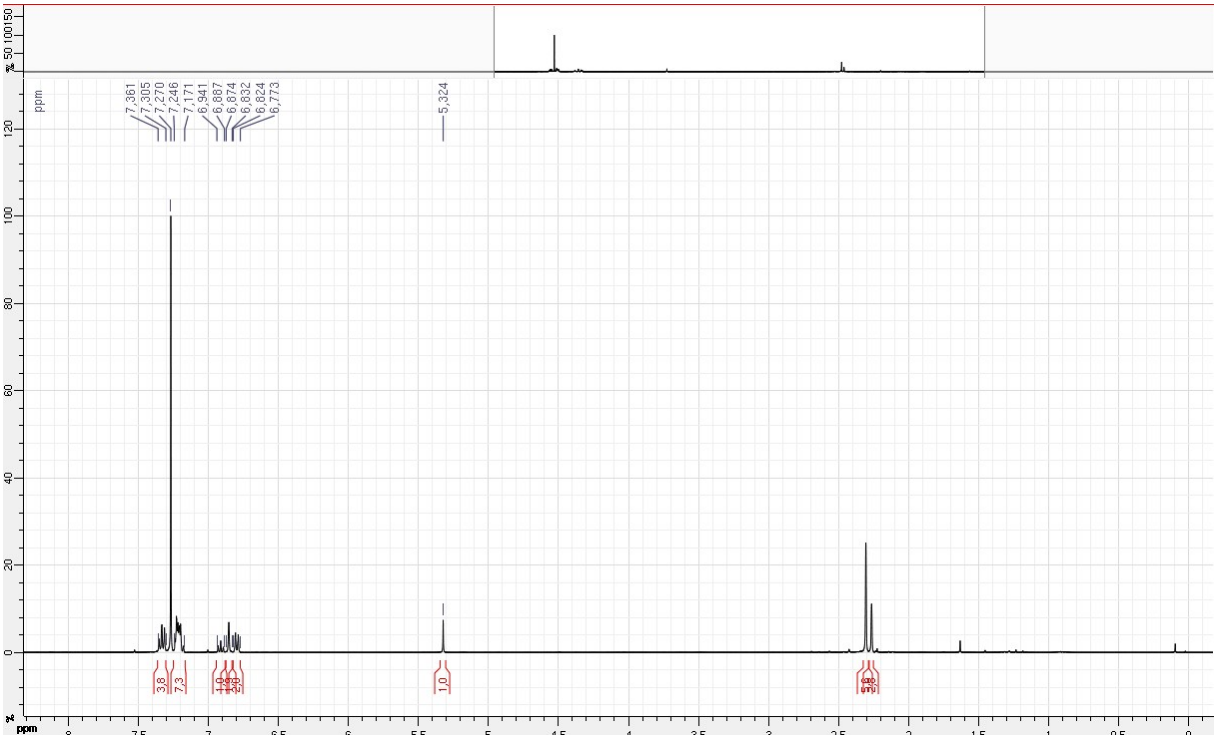
-240


OP(O)(OPh)2
O2N

14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6,773
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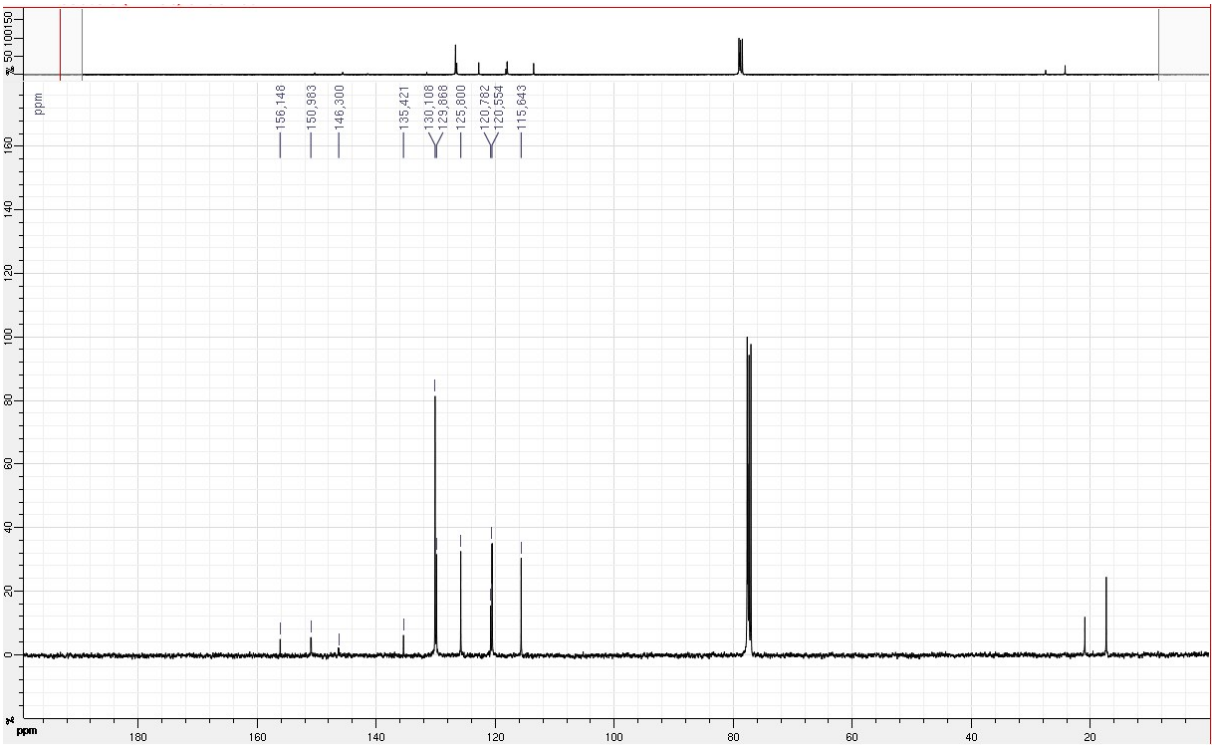
1,0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129,868
129,800
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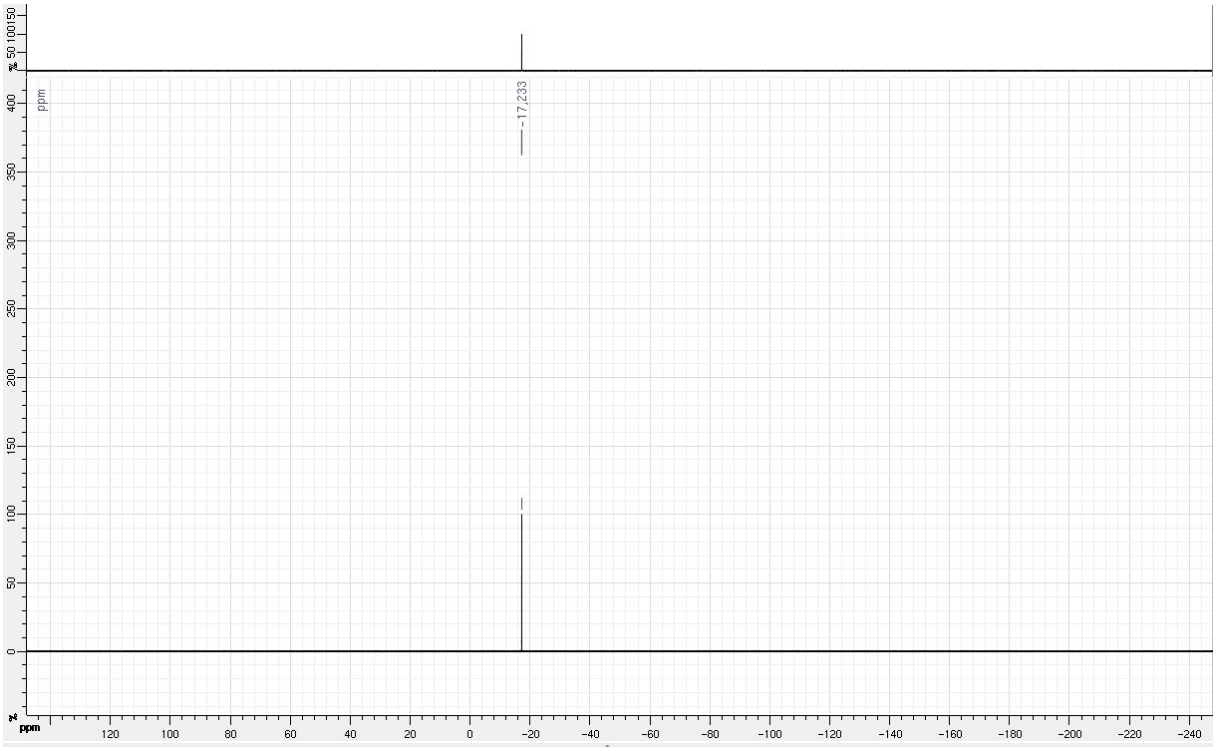
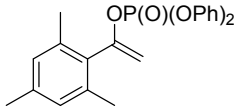
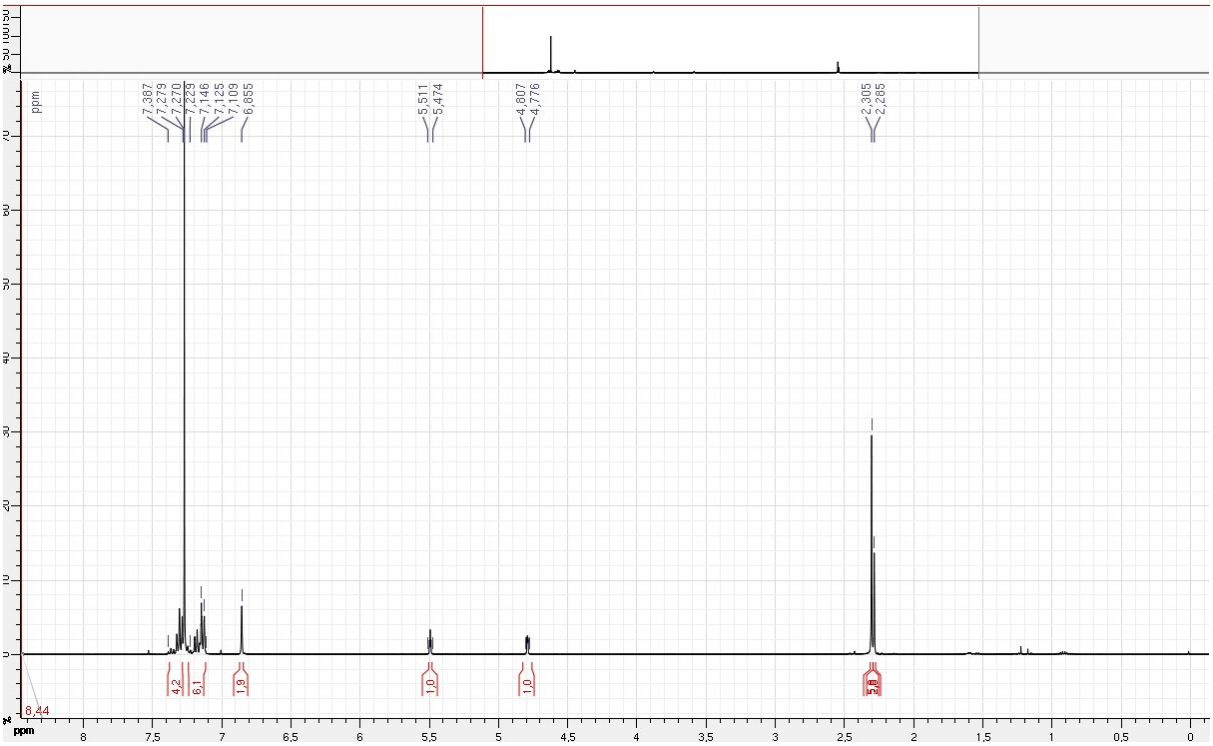
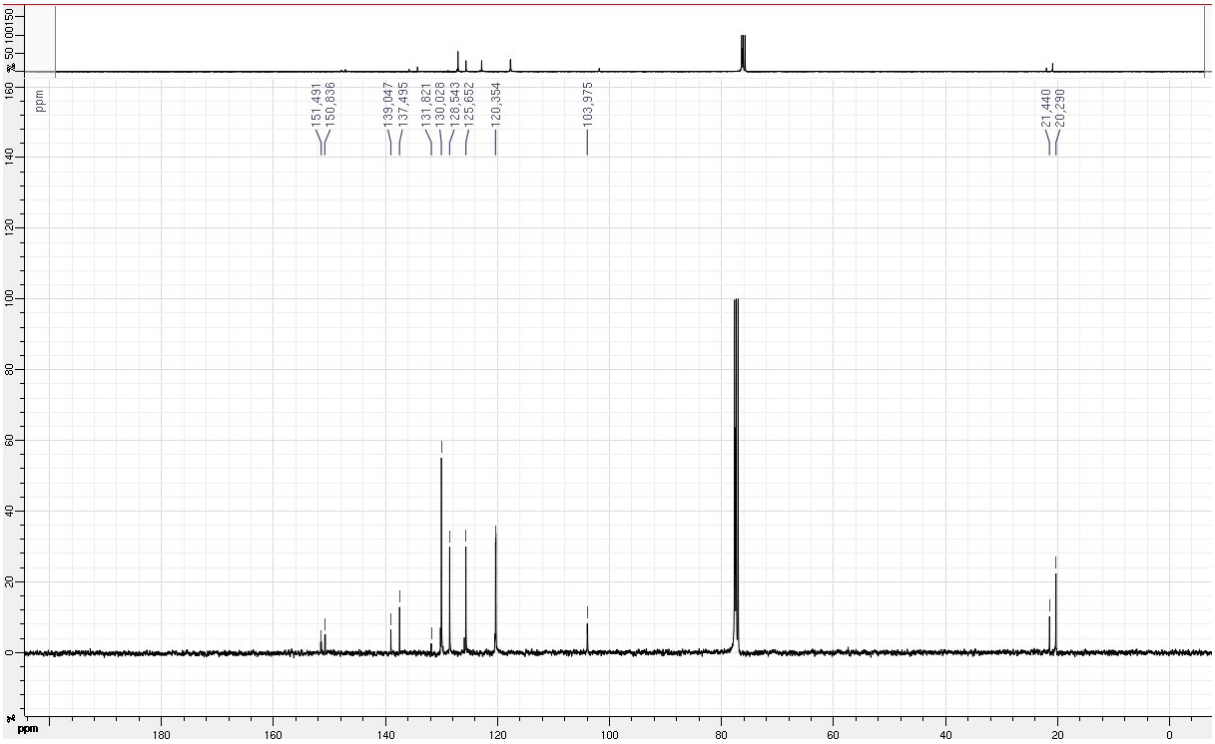
120,554
115,643

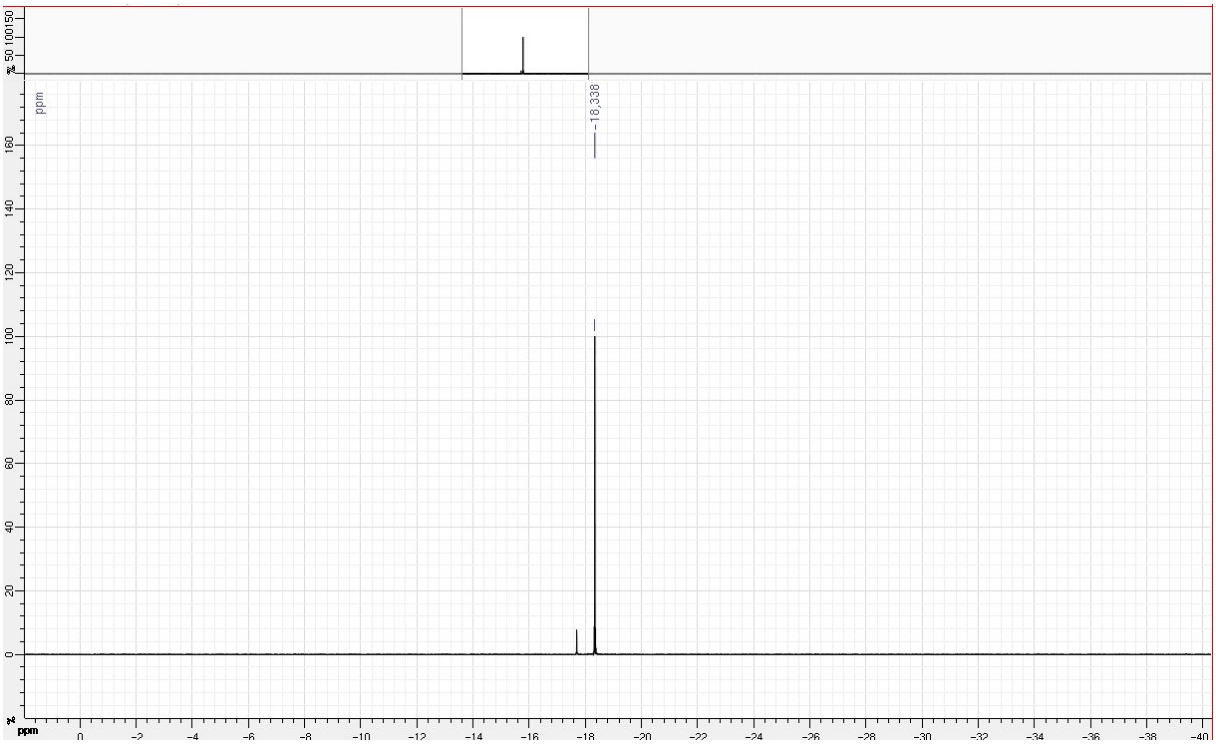

17.233
ppm
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240


OP(O)(OPh)2

15


ppm
7,387
7,279
7,270
7,229
7,146
7,125
7,109
6,855
5,511
5,474
4,807
4,776
2,305
2,285
4,2
6,1
1,9
1,0
1,0
5,0
8,44


ppm
151,491
150,836
139,047
137,495
131,821
130,028
128,543
125,652
120,354
103,975
21,440
20,290


ppm
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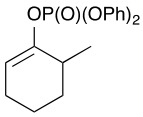
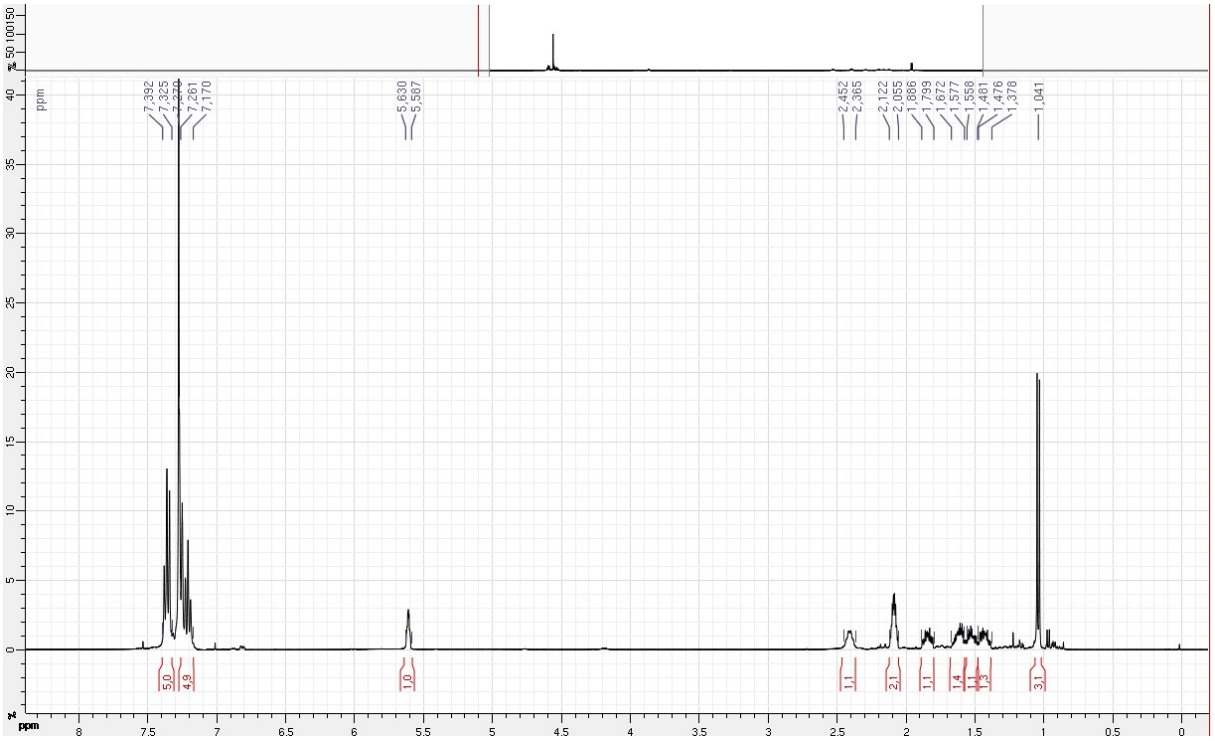
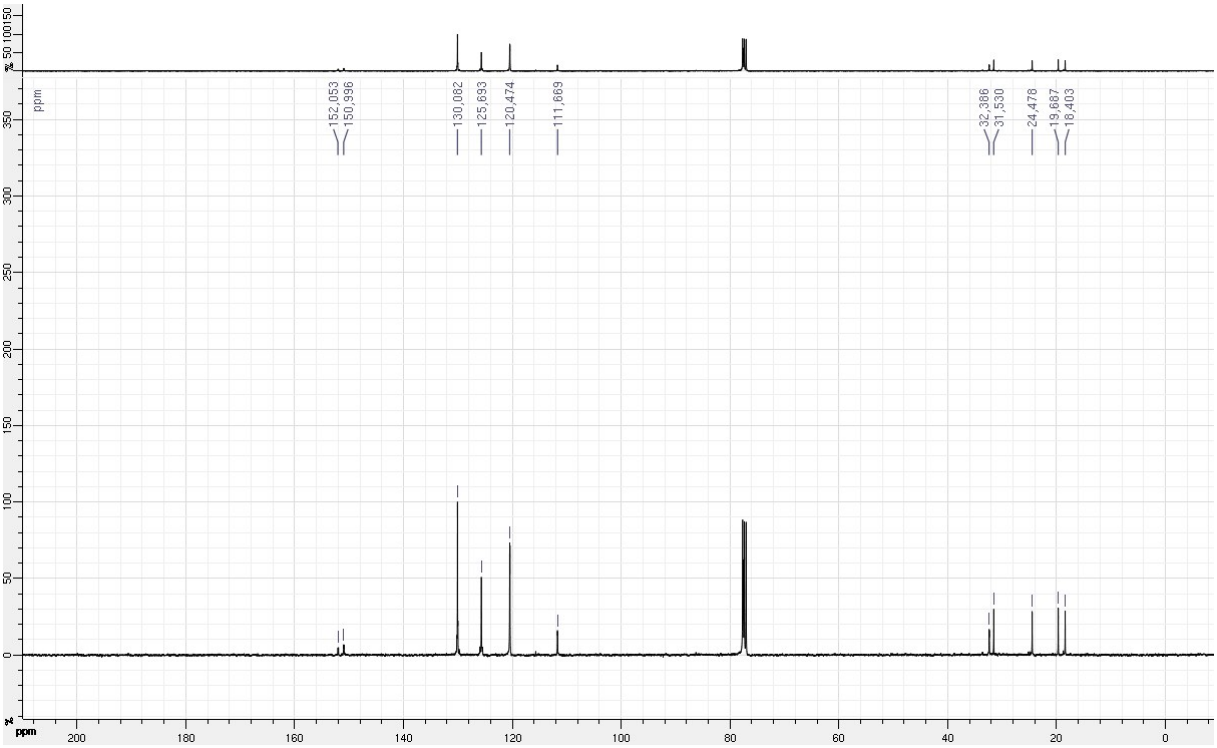
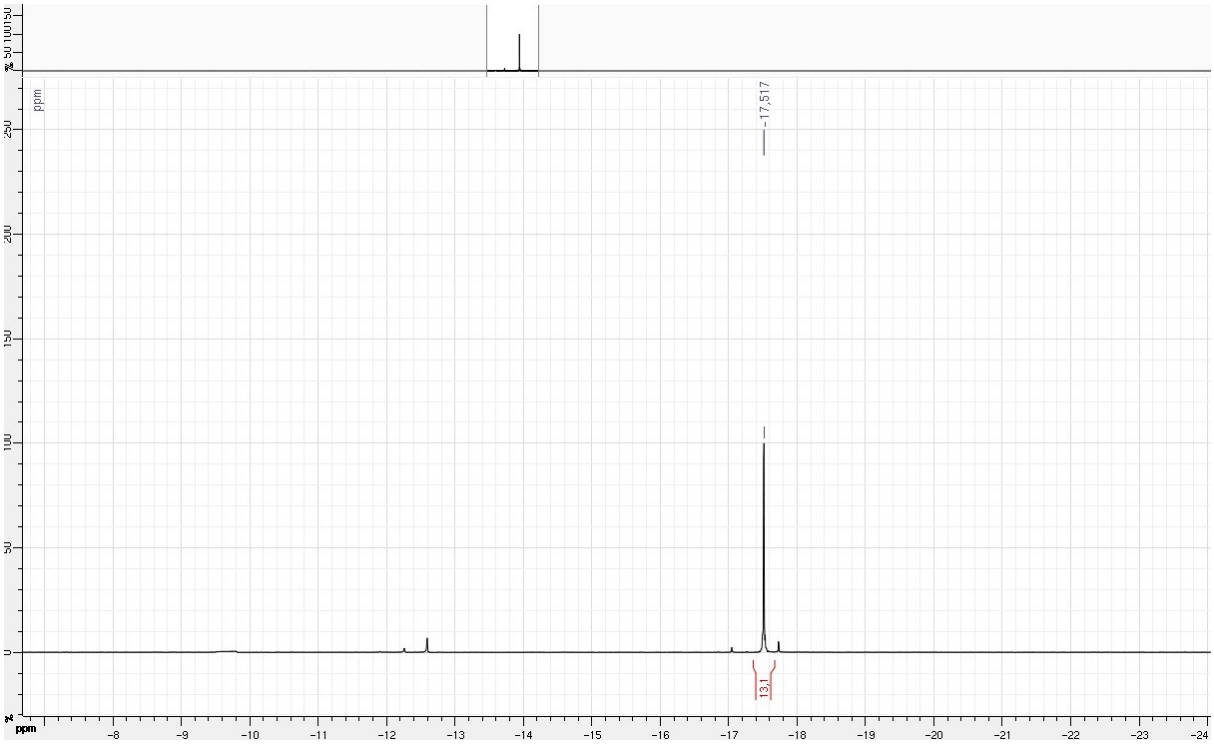
ppm


OP(O)(OPh)2

17


7,392
7,325
7,279
7,261
7,170
5,630
5,587
2,452
2,365
2,122
2,055
1,886
1,793
1,672
1,577
1,558
1,481
1,476
1,378
1,041
5,0
4,9
1,0
1,1
2,1
1,1
1,4
1,1
1,3
3,1
ppm


152,053
150,996
130,082
125,693
120,474
111,669
32,386
31,530
24,478
19,687
18,403
ppm


ppm
-17,517
13,1
ppm
-8
-9
-10
-11
-12
-13
-14
-15
-16
-17
-18
-19
-20
-21
-22
-23
-24

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