Supplementary Information for

Iron-Catalyzed C(sp^3)-H Phosphorylation via Photoinduced LMCT

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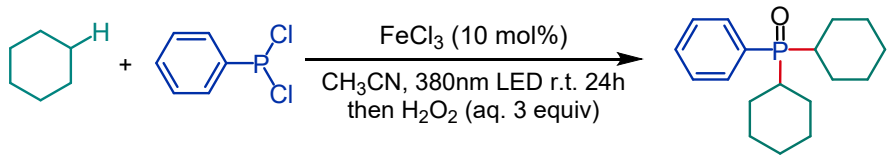
1. General Information

All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before using were dried by standard methods and stored under N_2 atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz or 500 MHz NMR spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. NMR data are reported as follows: chemical shift, multiplicity, coupling constants (Hz) and integration. Coupling constants (*J*) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker Micro TOF-QII mass instrument (ESI). All commercially available compounds were purchased from Adamas or Energy Chemical. Flash column chromatography was performed using 200-300 mesh silica gels.

2. Optimization of the Reaction Conditions

Table S1. Screening of temperature and solvents[a]



1a **2a** **3**

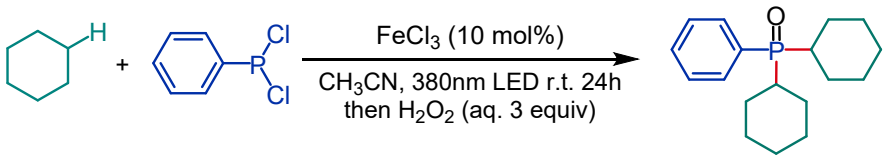
entry	Deviation from Standard Condition	yield (%)[b]
1	none	86
2	$CuCl_2$ instead of $FeCl_3$	< 5
3	$(Et_4N)_2CeCl_6$ instead of $FeCl_3$	< 5
4	$(PPh4)_2TiCl_6$ instead of $FeCl_3$	10
5	5 mol% $FeCl_3$	77
6	5 equiv of cyclohexane	82
7	12 hours	63
8	with 1 equiv of K_3PO_4	52
9	0 mol% $FeCl_3$	0
10	in the dark	0
11	440 nm LED	0
12	Irradiated 1 h, then in the dark	0

[a] **1a** (5 mmol), **2a** (0.5 mmol), $FeCl_3$ (10 mol %), CH_3CN (2.0 mL), room temperature, 380 nm LEDs, 24 h. [b] Isolated yields.

3. General procedure and spectral data of the products

3.1. General procedure for preparation of products

General Procedure A. Synthesis of phosphine oxide product **3**

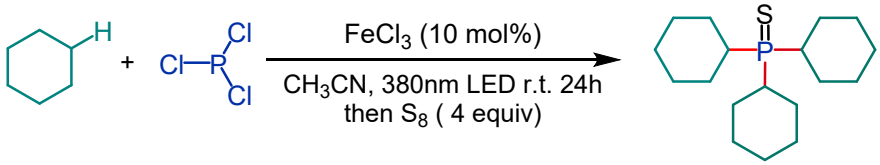


1a **2a** **3**

Phosphine oxide **3, 5-15 and 23-29** were synthesized according to the **General Procedure A**.

Cyclohexane **1a** (0.5mL, 5 mmol), dichlorophenylphosphine **2a** (89.5 mg, 0.5 mmol), $FeCl_3$ (8.1 mg, 10 mol %) and solvent (2.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at room temperature under 380 nm LED irradiation for 24 hours. After evaporation of the solvent under reduced pressure, the residue was dissolved in dichloromethane. The solution was quenched with H_2O_2(5 wt% aq., 1mL) and extracted with dichloromethane (2mL × 3), the combined organics were dried over sodium sulfate. The solvent was evaporated under reduced pressure to give the desired product **3** as white solid.

General Procedure B. Synthesis of phosphine Sulfide product **4**



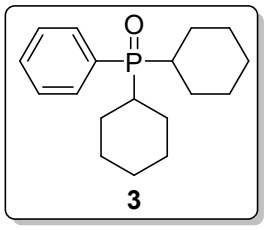
1a **2c** **4**

Phosphine sulfide **4, 16-22** were synthesized according to the **General Procedure B**.

Cyclohexane **1a** (0.5mL, 5 mmol), phosphorus trichloride **2c** (68.7 mg, 0.5 mmol), $FeCl_3$ (8.1 mg, 10 mol %) and solvent (2.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at room temperature under 380 nm LED irradiation for 24 hours. Then elemental sulfur (64mg, 4 equiv.) was added under N_2 atmosphere. The mixture was stirred at room temperature for 2 hours. The solvent was evaporated under reduced pressure to give the desired product **4** as white solid. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ dichloromethane = 10/1 to 1/1) to afford tricyclohexylphosphine sulfide **4** as white solid.

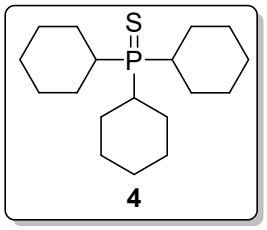
3.2. Products Characterization

Dicyclohexyl(phenyl)phosphine oxide (3)[1]



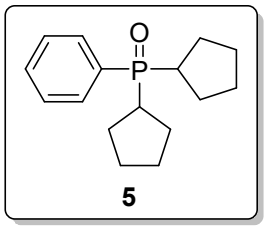
The title compound was prepared according to the **general procedure A** to give white solid, 120.7 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.52 (m, 2H), 7.49 – 7.35 (m, 3H), 2.11 – 1.88 (m, 4H), 1.81 – 1.48 (m, 8H), 1.32 – 0.78 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.4 (d, J = 7.7 Hz), 131.2 (d, J = 2.2 Hz), 129.7 (d, J = 85.4 Hz), 128.2 (d, J = 10.3 Hz), 35.0 (d, J = 67.2 Hz), 26.4 (d, J = 10.2 Hz), 26.2 (d, J = 9.7 Hz), 25.8, 25.4 (d, J = 2.2 Hz), 24.5 (d, J = 2.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.57; HRMS (ESI) calcd for $C_{18}H_{28}OP$ $[M+H]^+$: 291.1872, found: 291.1876.

Tricyclohexylphosphine sulfide (4)[2]



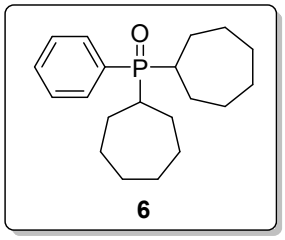
The title compound was prepared according to the **general procedure B** to give white solid, 68.6 mg, 44% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.06 – 1.96 (m, 6H), 1.95 – 1.82 (m, 9H), 1.77 – 1.70 (m, 3H), 1.53 – 1.37 (m, 6H), 1.34 – 1.19 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 37.0 (d, J = 44.4 Hz), 27.2 (d, J = 3.2 Hz), 27.0 (d, J = 12.3 Hz), 26.0 (d, J = 1.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 62.03. HRMS (ESI) calcd for $C_{18}H_{34}PS$ $[M+H]^+$: 313.2113, found: 313.2115.

Dicyclopentyl(phenyl)phosphine oxide (5)[3]



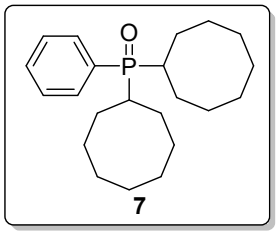
The title compound was prepared according to the **general procedure A** to give white solid, 112.7 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.54 (m, 2H), 7.48 – 7.31 (m, 3H), 2.46 – 2.15 (m, 2H), 2.07 – 1.71 (m, 5H), 1.71 – 1.24 (m, 11H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8 (d, J = 41.5 Hz), 131.3, 131.1 (d, J = 7.8 Hz), 128.4 (d, J = 10.5 Hz), 37.5 (d, J = 71.6 Hz), 26.7 (d, J = 8.9 Hz), 26.6 (d, J = 96.6 Hz), 26.0 (d, J = 9.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.27. HRMS (ESI) calcd for $C_{16}H_{24}OP$ $[M+H]^+$: 263.1559, found: 263.1557.

Dicycloheptyl(phenyl)phosphine oxide (6)



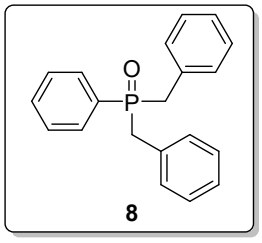
The title compound was prepared according to the **general procedure A** to give white solid, 144.7 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.53 (m, 2H), 7.48 – 7.33 (m, 3H), 2.54 – 1.80 (m, 6H), 1.80 – 1.10 (m, 20H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.4, 131.3, 130.4 (d, *J* = 86.7 Hz), 128.3 (d, *J* = 10.0 Hz), 35.8 (d, *J* = 63.8 Hz), 28.2, 27.9 (d, *J* = 13.3 Hz), 27.9 (d, *J* = 36.2 Hz), 26.7 (d, *J* = 122.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.74; HRMS (ESI) calcd for $C_{20}H_{32}OP$ $[M+H]^+$: 319.2185, found: 319.2203.

Dicyclooctyl(phenyl)phosphine oxide (7)



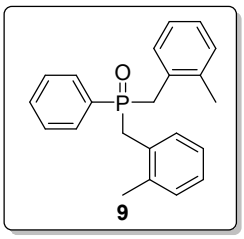
The title compound was prepared according to the **general procedure A** to give white solid, 145.3 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.53 (m, 2H), 7.49 – 7.27 (m, 3H), 2.31 – 1.79 (m, 5H), 1.78 – 0.99 (m, 25H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.5 (d, *J* = 7.5 Hz), 131.2 (d, *J* = 2.8 Hz), 129.6 (d, *J* = 173.4 Hz), 128.3 (d, *J* = 10.2 Hz), 33.5 (d, *J* = 63.9 Hz), 27.0, 26.8 (d, *J* = 12.0 Hz), 26.5, 26.0 (d, *J* = 23.2 Hz), 25.9 (d, *J* = 52.2 Hz), 25.7 (d, *J* = 1.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.51; HRMS (ESI) calcd for $C_{22}H_{36}OP$ $[M+H]^+$: 347.2498, found: 347.2495.

Dibenzyl(phenyl)phosphine oxide (8)[4]



The title compound was prepared according to the **general procedure A** to give white solid, 125 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.46 – 7.42 (m, 1H), 7.38 – 7.32 (m, 2H), 7.24 – 7.14 (m, 6H), 7.14 – 7.07 (m, 4H), 3.33 (d, *J* = 13.7 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7 (d, *J* = 2.8 Hz), 131.4 (d, *J* = 7.5 Hz), 131.0 (d, *J* = 8.4 Hz), 130.8 (d, *J* = 94.8 Hz), 130.0, 128.5 (d, *J* = 2.7 Hz), 128.2 (d, *J* = 11.5 Hz), 126.8 (d, *J* = 2.9 Hz), 37.3 (d, *J* = 63.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.14; HRMS (ESI) calcd for $C_{20}H_{20}OP$ $[M+H]^+$: 307.1246, found: 307.1243.

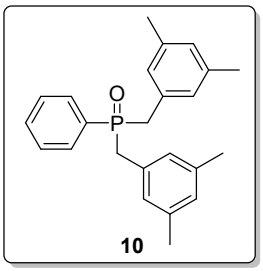
bis(2-Methylbenzyl)(phenyl)phosphine oxide (9)



The title compound was prepared according to the **general procedure A** to give white solid, 86.4 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.47 – 7.41 (m, 6H), 7.15 – 7.11 (m, 3H), 7.01 – 6.95 (m, 2H), 3.52 (t, *J* = 16.1 Hz,

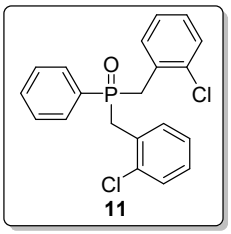
2H), 3.38 (td, J = 15.3, 4.3 Hz, 2H), 2.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9 (d, J = 5.5 Hz), 132.7 (d, J = 2.6 Hz), 30.7 (d, J = 2.9 Hz), 130.5 (d, J = 5.3 Hz), 130.1, 130.0, 128.9 (d, J = 7.2 Hz), 128.7 (d, J = 12.5 Hz), 127.5 (d, J = 3.6 Hz), 126.3 (d, J = 3.1 Hz), 36.1 (d, J = 61.5 Hz), 19.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.89; HRMS (ESI) calcd for $C_{22}H_{24}OP$ $[M+H]^+$: 335.1559, found: 335.1573.

bis(3,5-Dimethylbenzyl)(phenyl)phosphine oxide (10)



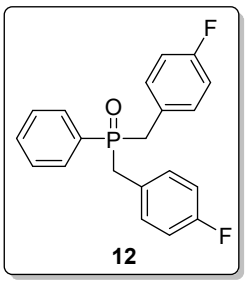
The title compound was prepared according to the **general procedure A** to give white solid, 124.9 mg, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 7.38 – 7.32 (m, 1H), 7.30 – 7.21 (m, 2H), 6.70 (s, 2H), 6.60 (s, 4H), 3.14 (d, J = 14.0 Hz, 4H), 2.09 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9 (d, J = 2.5 Hz), 131.7 (d, J = 2.6 Hz), 131.3 (d, J = 8.8 Hz), 131.2, 131.0, 128.5 (d, J = 2.9 Hz), 128.1 (d, J = 11.3 Hz), 127.9 (d, J = 5.1 Hz), 37.1 (d, J = 63.4 Hz), 21.2; ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.56; HRMS (ESI) calcd for $C_{24}H_{28}OP$ $[M+H]^+$: 363.1872, found: 363.1883.

bis(2-Chlorobenzyl)(phenyl)phosphine oxide (11)



The title compound was prepared according to the **general procedure A** to give white solid, 75.3 mg, 40% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.55 – 7.53 (m, 2H), 7.48 – 7.43 (m, 3H), 7.38 – 7.32 (m, 2H), 7.22 – 7.18 (m, 2H), 7.16 – 7.12 (m, 2H), 3.75 – 3.45 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1 (d, J = 6.3 Hz), 132.8 (d, J = 2.7 Hz), 132.0 (d, J = 5.3 Hz), 130.0 (d, J = 10.9 Hz), 129.8 (d, J = 3.0 Hz), 128.9 (d, J = 3.4 Hz), 128.8 (d, J = 12.6 Hz), 127.2 (d, J = 3.0 Hz), 36.6 (d, J = 62.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.56; HRMS (ESI) calcd for $C_{20}H_{18}Cl_2OP$ $[M+H]^+$: 375.0467, found: 375.0478.

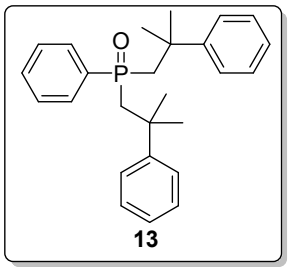
bis(4-Fluorobenzyl)(phenyl)phosphine oxide (12)



The title compound was prepared according to the **general procedure A** to give white solid, 101.1 mg, 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 3H), 7.36 – 7.28 (m, 2H),

7.04 – 6.94 (m, 4H), 6.87 – 6.76 (m, 4H), 3.22 (dd, *J* = 13.3, 5.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 3.3 Hz), 160.7 (d, *J* = 3.2 Hz), 132.0 (d, *J* = 2.8 Hz), 131.4 (dd, *J* = 8.1, 5.1 Hz), 130.9 (d, *J* = 8.8 Hz), 128.5 (d, *J* = 11.5 Hz), 126.9 (dd, *J* = 7.8, 3.3 Hz), 115.5 (dd, *J* = 21.4, 2.5 Hz), 36.5 (d, *J* = 63.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.87; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6 (d, *J* = 4.8 Hz); HRMS (ESI) calcd for $C_{20}H_{18}F_2OP$ $[M+H]^+$:343.1058, found: 343.1062

bis(2-Methyl-2-phenylpropyl)(phenyl)phosphine oxide (13)



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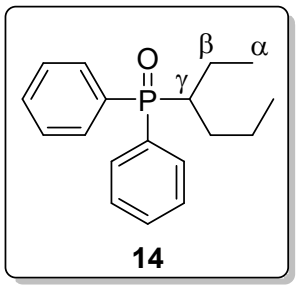
The title compound was prepared according to the **general procedure A** to give white solid, 104.6 mg, 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 5H), 7.43 – 7.40 (m, 5H), 7.35 – 7.31 (m, 3H), 7.24 – 7.20 (m, 2H), 2.40 (ddd, *J* = 17.3, 15.2, 6.8 Hz, 2H), 2.23 (dd, *J* = 15.2, 6.6 Hz, 2H), 1.72 (s, 6H), 1.51 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2 (d, *J* = 6.4 Hz), 132.2 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 97.0 Hz), 129.7 (d, *J* = 10.9 Hz), 128.8 (d, *J* = 12.4 Hz), 128.6, 126.6, 125.7, 46.3 (d, *J* = 67.5 Hz), 37.4 (d, *J* = 3.8 Hz), 32.0 (d, *J* = 9.4 Hz), 28.5 (d, *J* = 5.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.69; HRMS (ESI) calcd for $C_{26}H_{32}OP$ $[M+H]^+$: 391.2185, found: 391.2188.

Hexanyldiphenylphosphine oxide (14)



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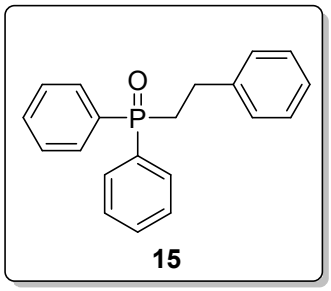
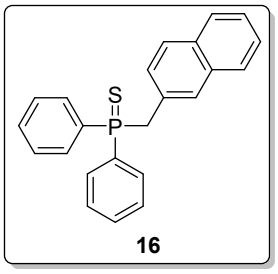
The title compound was prepared according to the **general procedure A** to give white solid, 132.7 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.54 (m, 4H), 7.50 – 7.10 (m, 6H), 2.47 – 0.34 (m, 13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2 (d, *J* = 15.6 Hz), 132.4 (d, *J* = 9.9 Hz), 132.2 (d, *J* = 11.7 Hz), 131.7, 131.5, 131.0 (d, *J* = 9.0 Hz), 130.9 – 130.6 (m), 128.6 (d, *J* = 6.6 Hz), 128.5 (d, *J* = 5.7 Hz), 128.0 (d, *J* = 12.5 Hz), 38.2 (d, *J* = 71.0 Hz), 31.8 (d, *J* = 72.1 Hz), 31.2, 30.6 (d, *J* = 14.7 Hz), 29.8 (d, *J* = 30.9 Hz), 29.4 (d, *J* = 28.2 Hz), 28.6 (d, *J* = 64.0 Hz), 22.3 (d, *J* = 3.7 Hz), 21.3, 21.1 (d, *J* = 9.8 Hz), 20.5, 14.1, 13.9 (d, *J* = 11.9 Hz), 12.5 (d, *J* = 9.3 Hz), 11.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.16, 37.55, 33.53; HRMS (ESI) calcd for $C_{18}H_{24}OP$ $[M+H]^+$: 287.1559, found: 287.1563.

Diphenyl(phenylethyl)phosphine oxide (15)[5]



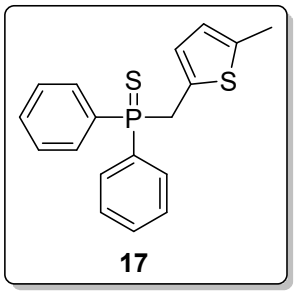
The title compound was prepared according to the **general procedure A** to give white solid, 99.1 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 4H), 7.60 – 7.44 (m, 6H), 7.31 – 7.22 (m, 2H), 7.23 – 7.10 (m, 3H), 3.02 – 2.84 (m, 2H), 2.65 – 2.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2 (d, *J* = 15.6 Hz), 132.6 (d, *J* = 98.8 Hz), 131.9 (d, *J* = 2.6 Hz), 130.8 (d, *J* = 9.3 Hz), 128.8 (d, *J* = 11.6 Hz), 128.6, 128.1, 126.4, 31.9 (d, *J* = 70.0 Hz), 27.5 (d, *J* = 2.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.89; HRMS (ESI) calcd for $C_{20}H_{20}OP$ $[M+H]^+$: 307.1246, found: 307.1257.

(Naphthalen-2-ylmethyl)diphenylphosphine sulfide (16)



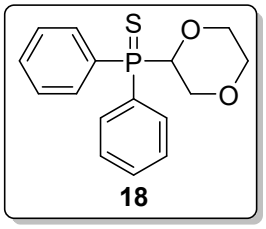
The title compound was prepared according to the **general procedure B** to give white solid, 53 mg, 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 4H), 7.74 – 7.70 (m, 1H), 7.63 – 7.58 (m, 2H), 7.49 – 7.44 (m, 2H), 7.44 – 7.34 (m, 7H), 7.13 – 7.06 (m, 1H), 3.95 (d, *J* = 13.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.1 (d, *J* = 3.3 Hz), 132.4 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 80.0 Hz), 131.7, 131.7, 131.7, 129.6 (d, *J* = 6.9 Hz), 128.6 (d, *J* = 12.1 Hz), 128.4 (d, *J* = 8.0 Hz), 127.8 (d, *J* = 1.7 Hz), 127.7 (d, *J* = 1.8 Hz), 127.5 (d, *J* = 2.7 Hz), 126.0, 125.8 (d, *J* = 1.8 Hz), 41.2 (d, *J* = 50.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 42.07; HRMS (ESI) calcd for $C_{23}H_{20}PS$ $[M+H]^+$: 359.1018, found: 359.1023.

((5-Methylthiophen-2-yl)methyl)diphenylphosphine sulfide (17)



The title compound was prepared according to the **general procedure B** to give white solid, 70.5 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 4H), 7.44 – 7.33 (m, 6H), 6.45 – 6.36 (m, 2H), 3.91 (d, *J* = 12.5 Hz, 2H), 2.25 (dd, *J* = 2.6, 1.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8 (d, *J* = 4.0 Hz), 131.9 (d, *J* = 80.2 Hz), 131.7 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 9.9 Hz), 129.2 (d, *J* = 8.6 Hz), 128.6 (d, *J* = 12.1 Hz), 128.2 (d, *J* = 7.6 Hz), 124.9 (d, *J* = 3.3 Hz), 36.4 (d, *J* = 53.7 Hz), 15.4 (d, *J* = 1.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.06; HRMS (ESI) calcd for $C_{18}H_{18}PS_2$ $[M+H]^+$: 329.0582, found: 329.0588.

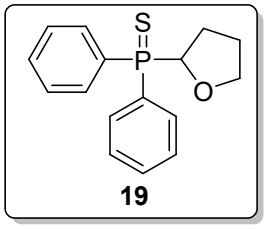
(1,4-Dioxan-2-yl)diphenylphosphine sulfide (18)



18

The title compound was prepared according to the **general procedure B** to give white solid, 108.4mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.85 – 7.72 (m, 2H), 7.48 – 7.29 (m, 6H), 4.53 (ddd, *J* = 10.8, 4.9, 2.7 Hz, 1H), 4.12 (dd, *J* = 11.7, 2.7 Hz, 1H), 3.75 (dd, *J* = 11.9, 2.8 Hz, 1H), 3.67 (td, *J* = 11.5, 2.7 Hz, 1H), 3.59 (dt, *J* = 11.8, 2.7 Hz, 1H), 3.52 – 3.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.8 (d, *J* = 10.2 Hz), 132.0 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 3.1 Hz), 131.5 (d, *J* = 10.1 Hz), 130.7, 129.1, 128.6 (d, *J* = 12.2 Hz), 128.3 (d, *J* = 12.4 Hz), 76.6 (d, *J* = 70.5 Hz), 68.1 (d, *J* = 8.1 Hz), 66.2, 66.0 (d, *J* = 8.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.09; HRMS (ESI) calcd for $C_{16}H_{18}O_2PS$ $[M+H]^+$:305.0760, found: 305.0764.

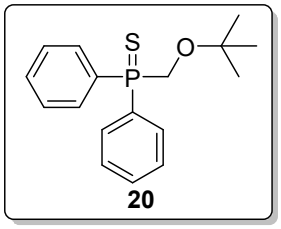
Diphenyl(tetrahydrofuran-2-yl)phosphine sulfide (19)



19

The title compound was prepared according to the **general procedure B** to give white solid, 60.5 mg, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.91 (m, 4H), 7.52 – 7.41 (m, 6H), 5.00 – 4.88 (m, 1H), 3.99 – 3.83 (m, 1H), 3.75 – 3.57 (m, 1H), 2.35 – 2.11 (m, 2H), 1.88 – 1.72 (m, 1H), 1.72 – 1.55 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.7 (d, *J* = 9.5 Hz), 132.2 (d, *J* = 79.2 Hz), 131.6 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 9.6 Hz), 131.4 (d, *J* = 2.9 Hz), 129.3 (d, *J* = 77.3 Hz), 128.5, 128.1 (d, *J* = 11.8 Hz), 79.2 (d, *J* = 70.3 Hz), 71.0 (d, *J* = 4.3 Hz), 27.5 (d, *J* = 2.4 Hz), 25.8 (d, *J* = 4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.33 HRMS (ESI) calcd for $C_{16}H_{18}OPS$ $[M+H]^+$: 289.0810, found: 289.0817.

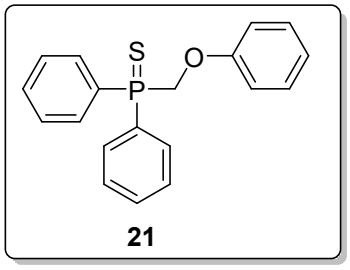
***(tert*-Butoxymethyl)diphenylphosphine sulfide (20)**



20

The title compound was prepared according to the **general procedure B** to give white solid, 52.9 mg, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 4H), 7.43 – 7.39 (m, 2H), 7.38 – 7.33 (m, 4H), 4.13 (d, *J* = 6.9 Hz, 2H), 0.99 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.2 (d, *J* = 10.1 Hz), 131.7 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 81.4 Hz), 128.2 (d, *J* = 12.2 Hz), 75.9 (d, *J* = 9.7 Hz), 65.7 (d, *J* = 73.0 Hz), 26.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.68; HRMS (ESI) calcd for $C_{17}H_{22}OPS$ $[M+H]^+$: 305.1123, found: 305.1126.

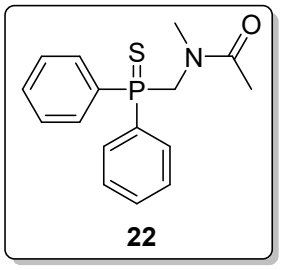
(Phenoxymethyl)diphenylphosphine sulfide (21)



21

The title compound was prepared according to the **general procedure B** to give white solid, 69.7 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 4H), 7.55 – 7.48 (m, 2H), 7.48 – 7.41 (m, 4H), 7.29 – 7.20 (m, 2H), 7.00 – 6.94 (m, 1H), 6.90 – 6.85 (m, 2H), 4.79 (d, *J* = 6.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3 (d, *J* = 11.0 Hz), 132.1 (d, *J* = 3.2 Hz), 132.1 (d, *J* = 10.3 Hz), 130.5 (d, *J* = 82.6 Hz), 129.7, 128.6 (d, *J* = 12.5 Hz), 122.1, 114.7, 70.0 (d, *J* = 70.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.13 HRMS (ESI) calcd for $C_{19}H_{17}OPSNa$ $[M+Na]^+$: 347.0630, found: 347.0625.

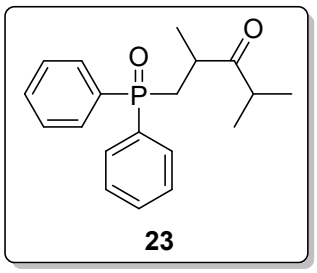
N-((Diphenylphosphorothioyl)methyl)-N-methylacetamide (22)



22

The title compound was prepared according to the **general procedure B** to give white solid, 60.4 mg, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.79 (m, 4H), 7.47 – 7.28 (m, 6H), 4.56 (d, *J* = 3.7 Hz, 2H), 3.08 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 131.9 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 10.4 Hz), 131.0 (d, *J* = 78.2 Hz), 128.6 (d, *J* = 12.2 Hz), 51.5 (d, *J* = 60.9 Hz), 38.3, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.99; HRMS (ESI) calcd for $C_{16}H_{19}NOPS$ $[M+H]^+$: 304.0919, found: 304.0929.

1-(Diphenylphosphoryl)-2,4-dimethylpentan-3-one (23)[6]

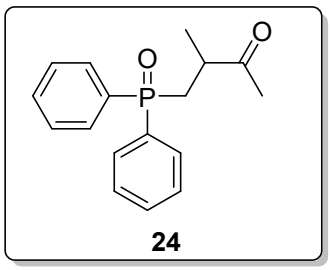


23

The title compound was prepared according to the **general procedure A** to give white solid, 94.2 mg, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 4H), 7.54 – 7.41 (m, 6H), 3.34 – 3.20 (m, 1H), 2.93 (ddd, *J* = 15.4, 9.2, 6.2 Hz, 1H), 2.66 (dq, *J* = 13.8, 6.9 Hz, 1H), 2.21 (ddd, *J* = 15.4, 12.3, 6.1 Hz, 1H), 1.19 (d, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.1 (d, *J* = 6.9 Hz), 133.7 (d, *J* = 98.8 Hz), 132.3 (d, *J* = 98.3 Hz), 131.8 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 2.7 Hz), 131.0 (d, *J* = 9.3 Hz), 130.5 (d, *J* = 9.3 Hz), 128.6, 128.6 (d, *J* = 24.0 Hz), 39.3, 37.9 (d, *J* = 2.6 Hz), 31.9 (d, *J* = 71.9 Hz), 19.5 (d, *J* = 7.7 Hz), 18.2 (d,

J = 32.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 30.79; HRMS (ESI) calcd for $C_{19}H_{24}O_2P$ $[M+H]^+$: 315.1508, found: 315.1505.

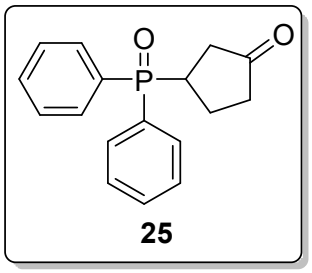
4-(Diphenylphosphoryl)-3-methylbutan-2-one (24)[6]



24

The title compound was prepared according to the **general procedure A** to give white solid, 72.4 mg, 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 4H), 7.54 – 7.44 (m, 6H), 3.11 – 3.01 (m, 1H), 2.96 (ddd, J = 15.5, 9.8, 5.8 Hz, 1H), 2.18 (ddd, J = 15.3, 11.7, 6.6 Hz, 1H), 2.05 (s, 3H), 1.22 (d, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.3 (d, J = 8.2 Hz), 133.4 (d, J = 98.9 Hz), 132.5 (d, J = 98.8 Hz), 131.8, 131.8 (d, J = 4.8 Hz), 130.9 (d, J = 9.3 Hz), 130.6 (d, J = 9.2 Hz), 128.7 (d, J = 8.3 Hz), 128.6 (d, J = 8.1 Hz), 40.6 (d, J = 2.4 Hz), 31.5 (d, J = 72.0 Hz), 28.1, 18.8 (d, J = 6.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.03; HRMS (ESI) calcd for $C_{17}H_{20}OPS$ $[M+H]^+$: 287.1195, found: 287.1192.

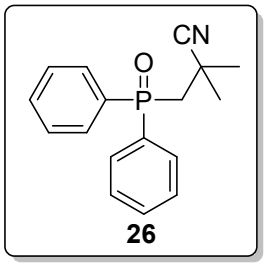
3-(Diphenylphosphoryl)cyclopentan-1-one (25)[7]



25

The title compound was prepared according to the **general procedure A** to give white solid, 80.9 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.68 (m, 4H), 7.54 – 7.41 (m, 6H), 3.10 – 2.98 (m, 1H), 2.62 – 2.49 (m, 1H), 2.44 – 2.34 (m, 1H), 2.32 – 2.12 (m, 3H), 2.07 – 1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.1 (d, J = 12.6 Hz), 132.1 (d, J = 2.9 Hz), 130.9 (d, J = 9.1 Hz), 130.7 (d, J = 9.0 Hz), 128.9 (d, J = 11.6 Hz), 38.0 (d, J = 6.3 Hz), 37.9 (d, J = 2.2 Hz), 35.2 (d, J = 77.3 Hz), 22.5 (d, J = 2.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.21; HRMS (ESI) calcd for $C_{17}H_{18}O_2P$ $[M+H]^+$: 285.1039, found: 285.1030.

3-(Diphenylphosphoryl)-2,2-dimethylpropanenitrile (26)

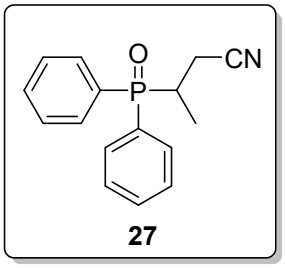


26

The title compound was prepared according to the **general procedure A** to give white solid, 107.0 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 4H), 7.44 – 7.35 (m, 6H), 2.56 (d, J = 10.6 Hz, 2H), 1.44 (s, 6H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 132.8 (d, *J* = 100.4 Hz), 132.2 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.5 Hz), 128.8 (d, *J* = 11.8 Hz), 123.9 (d, *J* = 9.0 Hz), 39.2 (d, *J* = 69.1 Hz), 30.5 (d, *J* = 4.0 Hz), 28.4 (d, *J* = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.21. HRMS (ESI) calcd for $C_{17}H_{19}NOP$ $[M+H]^+$: 284.1199, found: 284.1189.

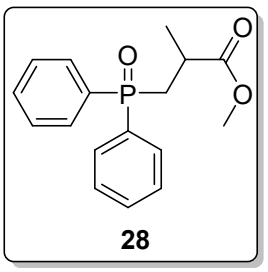
4-(Diphenylphosphoryl)butanenitrile (27)



27

The title compound was prepared according to the **general procedure A** to give white solid, 71.3 mg, 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.75 (m, 4H), 7.59 – 7.49 (m, 6H), 2.83 – 2.72 (m, 1H), 2.66 – 2.51 (m, 2H), 1.36 (dd, *J* = 15.5, 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.6 (d, *J* = 2.8 Hz), 132.5 (d, *J* = 2.6 Hz), 132.4 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 8.8 Hz), 130.8 (d, *J* = 8.9 Hz), 130.7 (d, *J* = 11.4 Hz), 129.2 (d, *J* = 11.5 Hz), 129.0 (d, *J* = 11.6 Hz), 118.0 (d, *J* = 19.2 Hz), 30.2 (d, *J* = 71.1 Hz), 18.6 (d, *J* = 1.7 Hz), 12.7 (d, *J* = 2.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.76.HRMS (ESI) calcd for $C_{16}H_{17}NOP$ $[M+H]^+$: 270.1042, found: 270.1049.

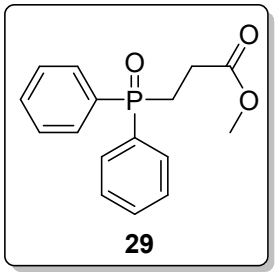
Methyl 3-(diphenylphosphoryl)-2-methylpropanoate (28)[8]



28

The title compound was prepared according to the **general procedure A** to give white solid, 96.6 mg, 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 4H), 7.45 – 7.38 (m, 6H), 3.41 (s, 3H), 2.94 – 2.75 (m, 2H), 2.29 – 2.19 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9 (d, *J* = 9.8 Hz), 131.9 (d, *J* = 2.4 Hz), 131.4 (d, *J* = 9.6 Hz), 131.0 (d, *J* = 9.4 Hz), 130.7 (d, *J* = 11.5 Hz), 130.6 (d, *J* = 9.5 Hz), 129.0 (d, *J* = 12.9 Hz), 128.8 (d, *J* = 9.9 Hz), 128.7 (d, *J* = 11.3 Hz), 52.0, 33.7 (d, *J* = 2.7 Hz), 33.0 (d, *J* = 71.8 Hz), 19.2 (d, *J* = 7.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 30.90; HRMS (ESI) calcd for $C_{17}H_{20}O_3P$ $[M+H]^+$:303.1145, found: 303.1157.

Methyl 3-(diphenylphosphoryl)propanoate (29)[6]



29

The title compound was prepared according to the **general procedure A** to give white solid, 80.6 mg, 56% yield, 2:1 r.r. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 4H), 7.48 – 7.34

(m, 6H), 4.79 (d, J = 5.1 Hz, 0.67H), 3.51 (s, 2H), 2.68 – 2.40 (m, 2.67H), 2.22 – 2.12 (m, 0.67H), 0.90 (t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 172.6 (d, J = 3.0 Hz), 132.7 (d, J = 2.9 Hz), 132.2 (d, J = 2.8 Hz), 132.1 (d, J = 2.7 Hz), 131.4 (d, J = 9.2 Hz), 131.4 (d, J = 9.7 Hz), 130.8 (d, J = 9.5 Hz), 128.9 (d, J = 4.1 Hz), 128.8 (d, J = 4.1 Hz), 61.0 (d, J = 44.3 Hz), 60.2 (d, J = 48.4 Hz), 52.1, 27.5, 26.8 (d, J = 77.0 Hz), 26.1, 24.8 (d, J = 73.4 Hz), 24.8 (d, J = 73.5 Hz), 9.2, 8.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.80, 27.42; HRMS (ESI) calcd for $C_{16}H_{18}O_3P$ $[M+H]^+$: 289.0988, found: 289.0991.

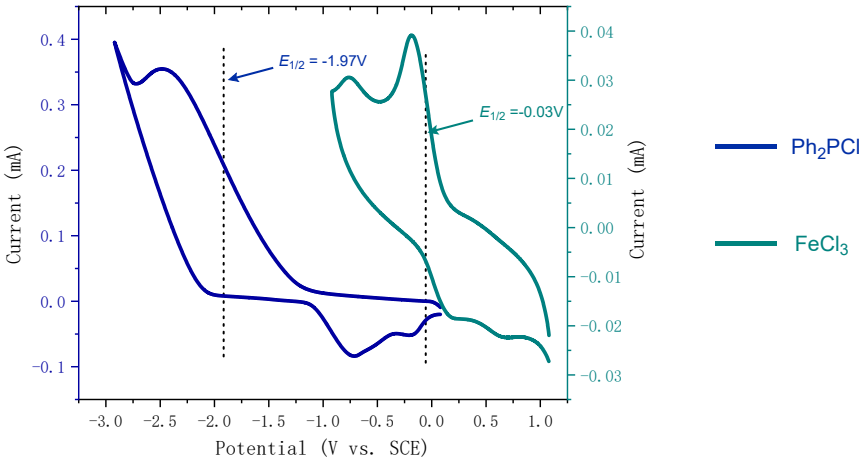
4. Mechanistic Studies

4.1. Cyclic voltammetry experiments

4.1.1. Methods

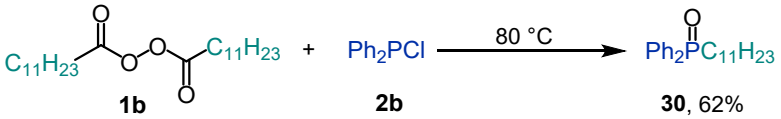
Cyclic voltammograms were conducted on a CHI660D electrochemical workstation using a 3-electrode cell configuration. Samples were prepared with 5-10 mM substrate in 15 mL of 0.1 M tetra-*n*-butylammonium hexafluorophosphate in CH_3CN. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, $Ag|Ag_2O$ (0.1 M tetra-n-butylammonium hexafluorophosphate in CH_3CN as electrolyte solution) reference electrode, and a scan rate of 50 mV/s. The glassy carbon electrode was polished between each scan. Ferrocene ($E_{1/2}$ = +0.46 V vs SCE)[25] was added at the end of the measurements as an internal standard to determine the precise potential scale. Potential values are given versus the saturated calomel electrode (SCE). Reversible waves were obtained in all cases; therefore, the potentials ($E_{p/2}$) were estimated at the average of the oxidation and reduction peaks.

4.1.2. Cyclic voltammograms



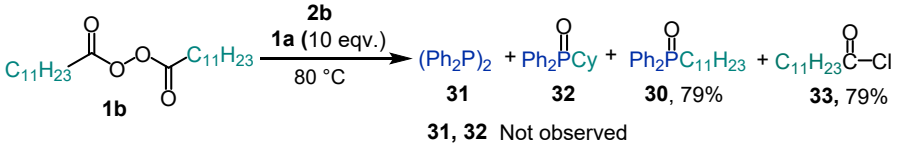
4.2. Direct free radical substitution experiments

In order to confirm the radical substitution of the alkyl radicals and chlorophosphines, we conducted a reaction of diphenylphosphorus chloride (**2b**) using dilauryl peroxide (**1b**) as the alkyl radical source. As a result, the target product **30** was isolated in 62% yield, indicating the plausible radical substitution Mechanism.

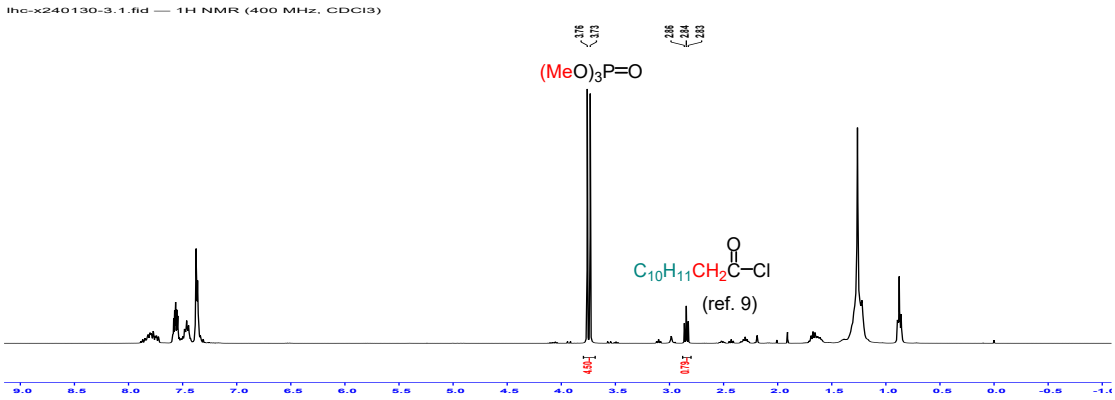


a: To a flame-dried Young-type tube was added dilauryl peroxide (**1b**) (199mg, 0.50 mmol, 1.0 equiv.). The tube was evacuated and refilled with N_2, then

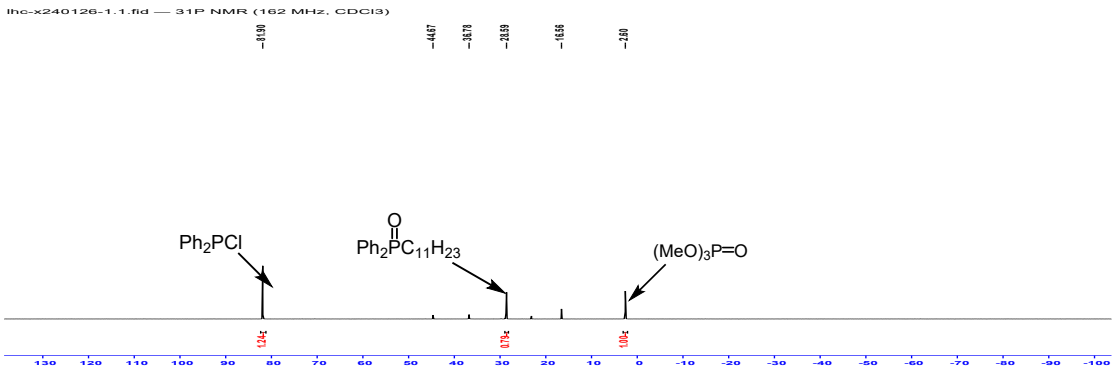
chlorodiphenylphosphine (**2b**) (110 mg, 0.50 mmol, 1.0 equiv.) and CH_3CN (5.0 mL) were added under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 1/1) to give the product **30** (110 mg, 62% yield) as white solid.



b: To a flame-dried Young-type tube was added dilauryl peroxide (**1b**) (80 mg, 0.2mmol). The tube was evacuated and refilled with N_2, then chlorodiphenylphosphine (**2b**) (110 mg, 0.50 mmol), cyclohexane (420 mg, 5 mmol), and CH_3CN (5.0 mL) were added under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours, then trimethyl phosphate (28 mg, 0.2 mmol) was added to this mixture. After evaporation of the solvent under reduced pressure, the residue was analyzed by ^1H NMR, ^{31}P NMR and GC-MS.

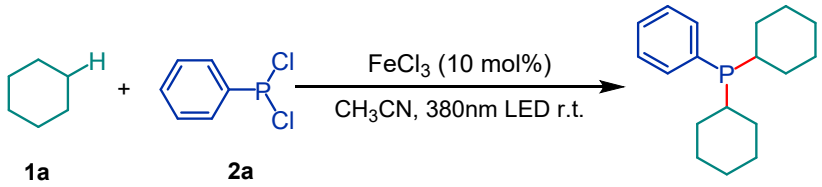


^1H NMR (400 Hz, $CDCl_3$)



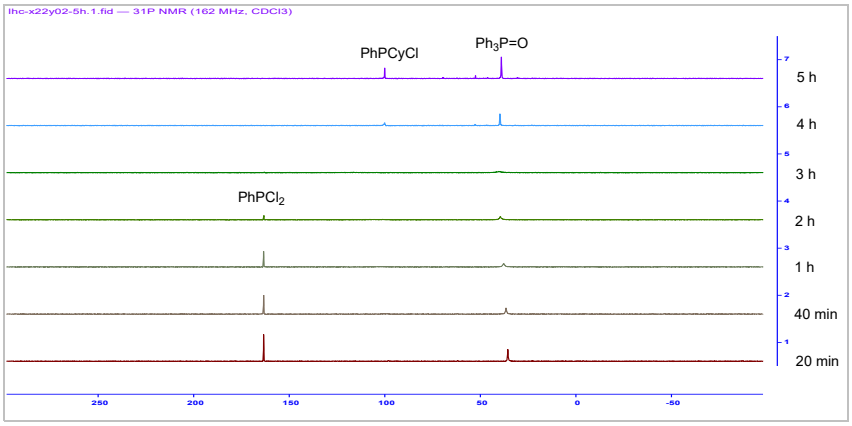
^{31}P NMR (162 Hz, $CDCl_3$)

4.2 ^{31}P MR Reaction Monitoring



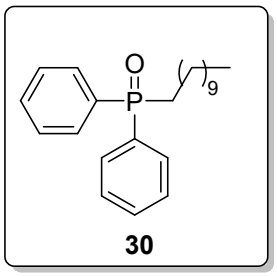
1a **2a**

Cyclohexane **1a** (0.5mL, 5 mmol), dichlorophenylphosphine **2a** (89.5 mg, 0.5 mmol), $FeCl_3$ (8.1 mg, 10 mol %), Ph_3PO (139 mg, 0.5 mmol) and CH_3CN (2.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at room temperature under 380 nm LED irradiation. After the reaction proceeded for 20 min, a small portion (0.2 mL) of the crude mixture of this reaction was taken out from the reactor. the crude mixture was dissolved in $CDCl_3$ and then analyzed by ^{31}P NMR, while the rest mixture was allowed to react for a certain time again. This procedure was repeated seven times.



^{31}P NMR Reaction Monitoring

diphenyl(undecyl)phosphine oxide (30)[10]



White solid, 110.2 mg, 62% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7 – 7.6 (m, 4H), 7.5 – 7.3 (m, 6H), 2.2 – 2.1 (m, 2H), 1.6 – 1.5 (m, 2H), 1.3 – 1.3 (m, 2H), 1.2 – 1.1 (m, 14H), 0.8 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.1 (d, J = 97.8 Hz), 131.6 (d, J = 2.6 Hz), 130.8 (d, J = 9.2 Hz), 128.6 (d, J = 11.6 Hz), 31.9, 31.0 (d, J = 14.7 Hz), 30.0, 29.7, 29.6, 29.4, 29.3 (d, J = 6.0 Hz), 29.1, 22.7, 21.4 (d, J = 3.9 Hz), 14.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ 32.80; HRMS (ESI) calcd for $C_{23}H_{34}OP$ $[M+H]^+$: 357.2342, found: 357.2361.

4.3 DFT Calculations

4.3.1 Computational methods

Density functional theory (DFT)[11] calculations were performed using Gaussian 16 C.01 software package[12] and the Gaussview[13] was used to generate input geometries and visualize output structures. Geometry optimizations and frequency calculations were performed using the M06 functional with a standard 6-31G* basis set. Calculations were carried out in the SMD solvation model (CH_3CN). Vibrational calculations were performed to confirm that no imaginary frequencies (equilibrium structures) or one imaginary frequency (transition structure) exist. IRC calculations were also performed to confirm the desired connection from the transition state. For more accurate electronic energies, single point calculations were performed using Gaussian 16 suite of programs employing M062X density functional and 6-311+G**

4.3.2. Computed energies

DFT Method: M06/6-31G*/SMD(CH_3CN)

[values are in Hartree]

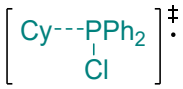
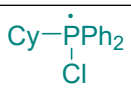
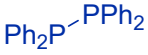
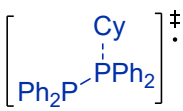
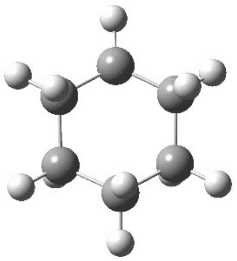
Species	Total Electronic Energy	Thermal Correction to Free Energy	Thermal Correction to Enthalpy	Gibbs Free Energy	Imaginary Frequency
Cy·	-235.013724	0.124832	0.161736	-234.888892	
Ph_2PCl	-1264.437966	0.142462	0.196779	-1264.295504	
	-1499.464582	0.290716	0.360538	-1499.173866	-84.78
	-1499.495867	0.291712	0.363375	-1499.204155	
	-1608.510372	0.311673	0.388859	-1608.198699	
	-1843.531871	0.460716	0.552510	-1843.071155	-235.02
$CyPPh_2$	-1039.334119	0.296538	0.360204	-1039.037581	
Ph_2P·	-804.216442	0.142554	0.192993	-804.073887	

Table S1 Computed energies of reaction intermediates and transition states.

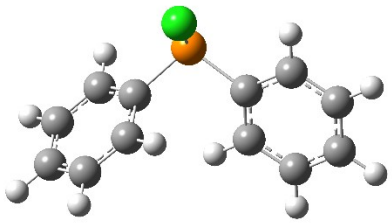
4.3.3. Optimized structures and Cartesian coordinates

Species	Optimized Structure

Cy·	

Cartesian Coordinates

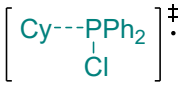
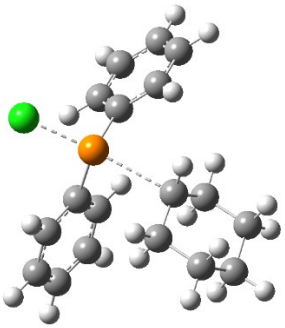
C	1.28021500	0.76907900	0.16150900
C	1.25547100	-0.70674600	-0.24763400
C	0.00000600	-1.39546300	0.27428300
C	-1.25546400	-0.70675600	-0.24763500
C	-1.28022200	0.76906900	0.16151000
C	-0.00000700	1.45277700	-0.17418700
H	0.00001000	-2.45818700	-0.00883500
H	1.27083200	-0.77731600	-1.34804100
H	2.15960900	-1.21532600	0.11731900
H	1.45102000	0.81162500	1.25861900
H	2.13688500	1.28606300	-0.29425700
H	-1.27082300	-0.77732500	-1.34804200
H	-2.15959900	-1.21534500	0.11731500
H	-2.13689700	1.28604600	-0.29425500
H	-1.45102700	0.81161100	1.25862000
H	-0.00001100	2.51851800	-0.40379800
H	0.00000500	-1.36212800	1.37827800

Species	Optimized Structure
Ph_2PCl	

Cartesian Coordinates

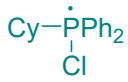
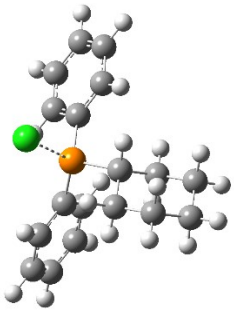
C	-2.46637100	-0.06353900	-1.19159700
C	-1.43519600	0.13531400	-0.26917500
C	-1.56473500	-0.36683100	1.03244000
C	-2.71122500	-1.05838400	1.39952800
C	-3.73335800	-1.26111600	0.47039200
C	-3.61155100	-0.76740000	-0.82379900
H	-2.37255500	0.33358700	-2.20306900
H	-0.76469800	-0.21440000	1.75757400
H	-2.81115700	-1.44423800	2.41276300
H	-4.62992600	-1.80596100	0.76209300
H	-4.40935000	-0.92334400	-1.54782600
P	0.02102100	1.06374000	-0.86845800
C	1.41043600	-0.00962200	-0.32789600
C	2.67043400	0.55351900	-0.08946200
C	1.27677100	-1.40276400	-0.32846900
C	3.76509200	-0.25935700	0.17991100
H	2.79665300	1.63642000	-0.10202300
C	2.37865100	-2.21422000	-0.06948900
H	0.30932900	-1.86240200	-0.52838800
C	3.62139900	-1.64560000	0.19135900

H	4.73582900	0.19188500	0.37926200
H	2.25992900	-3.29661700	-0.06540900
H	4.48008900	-2.28136400	0.40100700
Cl	0.14638000	2.58060800	0.63049600

Species	Optimized Structure
	

Cartesian Coordinates

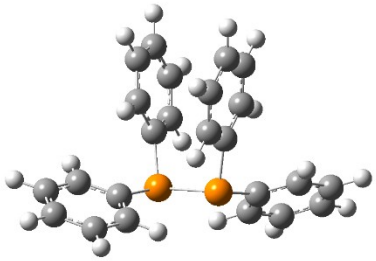
C	2.00469000	-1.88322400	0.53866200
C	1.86984000	-0.53996400	0.17015500
C	2.68831100	-0.02766000	-0.84502100
C	3.60145600	-0.85066100	-1.49337200
C	3.71434700	-2.19262200	-1.13136200
C	2.91867300	-2.70778300	-0.11274100
H	1.39136700	-2.28914500	1.34414500
H	2.61704400	1.02359800	-1.12405200
H	4.23160200	-0.44313700	-2.28242300
H	4.43122400	-2.83485300	-1.64065000
H	3.01195800	-3.75190200	0.18128100
C	-0.14442600	1.52154000	-0.11725700
C	-0.87003000	2.61985400	0.36426600
C	-0.23296600	1.19539100	-1.47427700
C	-1.65201200	3.38425200	-0.49341400
H	-0.82509200	2.87753600	1.42383900
C	-1.02655000	1.95585900	-2.33106200
H	0.31185100	0.33927900	-1.87036500
C	-1.73435300	3.05049000	-1.84436100
H	-2.20511300	4.23833600	-0.10573700
H	-1.08747300	1.68998300	-3.38535800
H	-2.35274100	3.64339800	-2.51645600
Cl	2.15278300	2.00604600	1.82293600
C	-1.32483600	-1.27938900	0.83986800
C	-2.51958900	-0.44319500	1.16052400
C	-1.37426500	-1.96464800	-0.48503700
H	-0.91813200	-1.86578900	1.67024400
C	-3.76818300	-1.34284500	1.13177000
H	-2.64409900	0.34311200	0.39512800
H	-2.41763800	0.05672800	2.13458000
C	-2.62504500	-2.86477500	-0.51929700
H	-1.46689200	-1.21707600	-1.29160400
H	-0.46806400	-2.55522700	-0.67897500
C	-3.88150300	-2.05883700	-0.20953900
H	-4.66588500	-0.74024100	1.33215100
H	-3.69443900	-2.08855000	1.94045400
H	-2.70324500	-3.35207100	-1.50196600
H	-2.51063400	-3.66661700	0.22865100
H	-4.76428200	-2.71447500	-0.21730700
H	-4.03573500	-1.31040500	-1.00571400
P	0.68704900	0.47226900	1.13928000

Species	Optimized Structure
	

Cartesian Coordinates

C	2.28248400	-1.56289200	-0.36830000
C	1.84830700	-0.26523900	-0.05815900
C	2.75333900	0.80278900	-0.15677600
C	4.05166400	0.57953500	-0.59796400
C	4.46849500	-0.70858400	-0.92818600
C	3.58325100	-1.77763100	-0.80802100
H	1.60384300	-2.41012900	-0.27109900
H	2.44091400	1.81214400	0.10984700
H	4.74304800	1.41635500	-0.68054400
H	5.48691800	-0.88025100	-1.27239000
H	3.90658700	-2.78665200	-1.05781600
C	-0.39938000	1.62643600	0.12149400
C	-1.22153800	2.32611200	1.01337100
C	-0.10623400	2.18097700	-1.13237800
C	-1.75358500	3.56005900	0.65250100
H	-1.44065000	1.90228200	1.99452500
C	-0.63660600	3.41740900	-1.48374900
H	0.53172900	1.64539000	-1.83499900
C	-1.45926900	4.10581600	-0.59387100
H	-2.39259500	4.09857400	1.34998500
H	-0.40880500	3.84384400	-2.45925500
H	-1.87064100	5.07419600	-0.87387200
Cl	0.42370800	-0.88567300	3.12546200
C	-0.94491300	-1.28582000	0.00952700
C	-2.31786200	-1.14066700	0.67050500
C	-1.06973800	-1.27401900	-1.51631200
H	-0.50424700	-2.24329600	0.33780200
C	-3.25253100	-2.25074200	0.20002900
H	-2.74818200	-0.16241000	0.39549700
H	-2.21477000	-1.15410700	1.76503700
C	-2.00739200	-2.38720200	-1.97719300
H	-1.47833700	-0.29946200	-1.83290100
H	-0.08356700	-1.37843400	-1.99119300
C	-3.37603700	-2.26472300	-1.31885700
H	-4.23940500	-2.12774700	0.66812000
H	-2.85755100	-3.22195500	0.54302600
H	-2.09929300	-2.36252100	-3.07238600
H	-1.56220900	-3.36258300	-1.71769300
H	-4.03195600	-3.08529300	-1.64280300
H	-3.85352300	-1.32711100	-1.65120400
P	0.21432800	-0.00160500	0.64636600

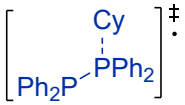
Species	Optimized Structure

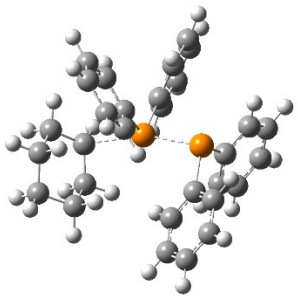
$Ph_2P^{-}PPh_2$	

Cartesian Coordinates

P	0.59529100	-1.15113600	0.95741900
P	-0.59543200	-1.15112700	-0.95735400
C	-0.50759800	0.60142500	-1.50123000
C	-1.33280700	1.62755700	-1.02527600
C	0.50845700	0.91831200	-2.41185700
C	-1.14756500	2.93754000	-1.45479900
H	-2.12363200	1.40420400	-0.30922200
C	0.70274900	2.23234800	-2.82964200
H	1.15546700	0.12792600	-2.79647600
C	-0.12739700	3.24399000	-2.35399100
H	-1.79714700	3.72584100	-1.07596100
H	1.49856900	2.46353900	-3.53621800
H	0.01809700	4.27115200	-2.68521800
C	-2.31481700	-1.32037400	-0.31428200
C	-2.63038200	-1.97630300	0.88134400
C	-3.36765300	-0.91578100	-1.14921100
C	-3.95740600	-2.19763400	1.24311500
H	-1.83583300	-2.32257400	1.54217400
C	-4.69167800	-1.13265700	-0.78405500
H	-3.15141100	-0.42208100	-2.09750100
C	-4.99251200	-1.77296400	0.41620700
H	-4.17935100	-2.70486300	2.18112100
H	-5.49250500	-0.80276400	-1.44442800
H	-6.02917200	-1.94367700	0.70218100
C	2.31468200	-1.32050100	0.31438300
C	3.36754200	-0.91563000	1.14913100
C	2.63019500	-1.97678000	-0.88107200
C	4.69155400	-1.13259400	0.78397200
H	3.15133900	-0.42161700	2.09726800
C	3.95720100	-2.19820700	-1.24283700
H	1.83561200	-2.32324000	-1.54176400
C	4.99234100	-1.77327200	-0.41610100
H	5.49240500	-0.80246500	1.44420000
H	4.17911000	-2.70572000	-2.18069800
H	6.02899000	-1.94406800	-0.70206400
C	0.50761400	0.60145600	1.50119800
C	1.33290400	1.62746200	1.02511200
C	-0.50833600	0.91853200	2.41187600
C	1.14784500	2.93750200	1.45454000
H	2.12366500	1.40396800	0.30903000
C	-0.70244700	2.23262300	2.82957200
H	-1.15538700	0.12825000	2.79664100
C	0.12777600	3.24414000	2.35377800
H	1.79751200	3.72568900	1.07561200
H	-1.49818800	2.46395800	3.53619000
H	-0.01759100	4.27134600	2.68492400

Species	Optimized Structure





Cartesian Coordinates

P	0.93960200	1.06077700	-1.25988500
P	-0.23413200	-0.49092800	0.08247000
C	1.04343100	-1.80504000	-0.12017000
C	1.34633000	-2.42223800	-1.34010100
C	1.84286100	-2.09351800	0.99308100
C	2.40477600	-3.32191400	-1.43612300
H	0.75358500	-2.19571800	-2.22687000
C	2.90572000	-2.98748800	0.89684300
H	1.64270800	-1.59938000	1.94591900
C	3.18497800	-3.60828000	-0.31804500
H	2.62431600	-3.79659800	-2.39160100
H	3.51767800	-3.19704000	1.77310700
H	4.01393200	-4.31026000	-0.39566800
C	-1.52865400	-0.92812500	-1.15243200
C	-2.30503900	0.10333900	-1.69910100
C	-1.87044500	-2.25150600	-1.45420500
C	-3.38627900	-0.17966200	-2.52807700
H	-2.07329700	1.14448700	-1.46494700
C	-2.95665000	-2.53516800	-2.27843700
H	-1.28737400	-3.07270300	-1.03669300
C	-3.71733600	-1.50132700	-2.81813000
H	-3.97445700	0.63659800	-2.94515800
H	-3.20745500	-3.57169500	-2.50027600
H	-4.56593400	-1.72476500	-3.46288200
C	0.12882700	2.63038900	-0.71348900
C	-0.01618700	3.62332000	-1.69170800
C	-0.39102800	2.87828700	0.56463900
C	-0.64256000	4.83256800	-1.39983100
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C	-1.02293900	4.08353300	0.85735400
H	-0.31659400	2.11617500	1.34022300
C	-1.14785400	5.06485300	-0.12353500
H	-0.74179700	5.59182200	-2.17441000
H	-1.42320800	4.25241100	1.85679300
H	-1.64420500	6.00680900	0.10537900
C	2.51253400	1.01939800	-0.30500700
C	2.68019000	1.49392600	1.00251300
C	3.59605400	0.38536800	-0.92970500
C	3.89338600	1.32975900	1.66608500
H	1.85971000	1.99809500	1.51277000
C	4.80607100	0.21435000	-0.26461900
H	3.48486100	0.01411100	-1.95005900
C	4.95674300	0.68482800	1.03807700
H	4.00655700	1.70452700	2.68272300
H	5.63380100	-0.28590200	-0.76580900
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C	-3.80391100	-1.23633000	1.56631900
C	-2.68049000	-2.24310000	1.80040400
C	-1.35186200	-1.60387000	2.07745000
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C	-3.83305800	-0.18154600	2.66632500
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H	-2.61380400	-2.95743600	0.96717700
H	-3.65425300	-0.73831700	0.59368500
H	-4.76775800	-1.76230900	1.50641200
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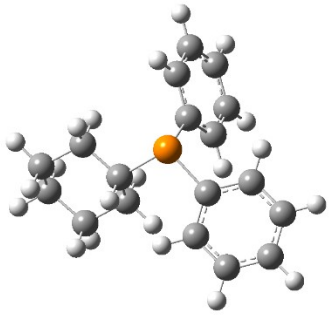
Species	Optimized Structure
$CyPPh_2$	

Cartesian Coordinates

C	-2.17898400	-1.72696800	-0.12415200
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C	-4.11671000	0.26152900	0.02334500
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C	-3.46399300	-2.03461000	0.31806500
H	-1.43797300	-2.52436200	-0.18291700
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H	-4.87098300	1.04579000	0.07509000
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C	1.12312100	2.41797600	-1.04942300
C	-0.12280000	1.87460300	0.93773600
C	1.58041700	3.58841400	-0.44820500
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C	0.32356400	3.04892200	1.53586100
H	-0.79054300	1.21235200	1.48919100
C	1.17815000	3.90681400	0.84539400
H	2.24350000	4.25652700	-0.99602700
H	0.00552900	3.29439300	2.54838000
H	1.52618900	4.82525100	1.31591600
C	0.95663800	-1.26573800	-0.51636000
C	2.35026200	-1.06048900	-1.11685200
C	1.03930700	-1.32887300	1.00673600
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H	2.73997700	-0.07941600	-0.79170800
H	2.29295800	-1.02841900	-2.21583500
C	1.99097500	-2.43520800	1.45490700
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H	0.04287100	-1.47830300	1.44805400
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H	2.96401000	-3.12399200	-1.06549300
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H	3.81224700	-1.30522000	1.25037000
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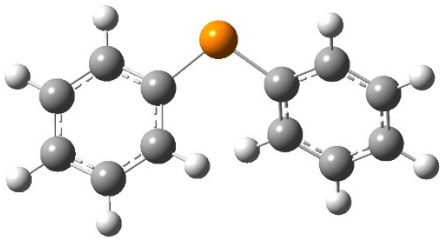
Species	Optimized Structure
Ph_2P ·	

Cartesian Coordinates

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C	-2.65280600	-1.52377900	0.66934200
C	-3.82821900	-0.99502800	0.13642600
C	-3.81863500	0.27667100	-0.43469400
H	-2.64023500	2.00636900	-0.92379000
H	-0.56592700	-1.21495200	1.05938000
H	-2.65975500	-2.50971500	1.13207000
H	-4.75180800	-1.57044000	0.17396200
H	-4.73437600	0.69796500	-0.84678200
P	0.00001200	1.58181200	0.00002800
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C	2.63977600	1.00989200	0.47872800
C	1.47082500	-0.79553800	-0.62137600
C	3.81866400	0.27668100	0.43458400
H	2.64025400	2.00637600	0.92372700
C	2.65277400	-1.52381800	-0.66931000
H	0.56586700	-1.21504100	-1.05919700
C	3.82821400	-0.99504100	-0.13649500
H	4.73444500	0.69797600	0.84658100
H	2.65966700	-2.50977400	-1.13199500
H	4.75182500	-1.57041700	-0.17406100

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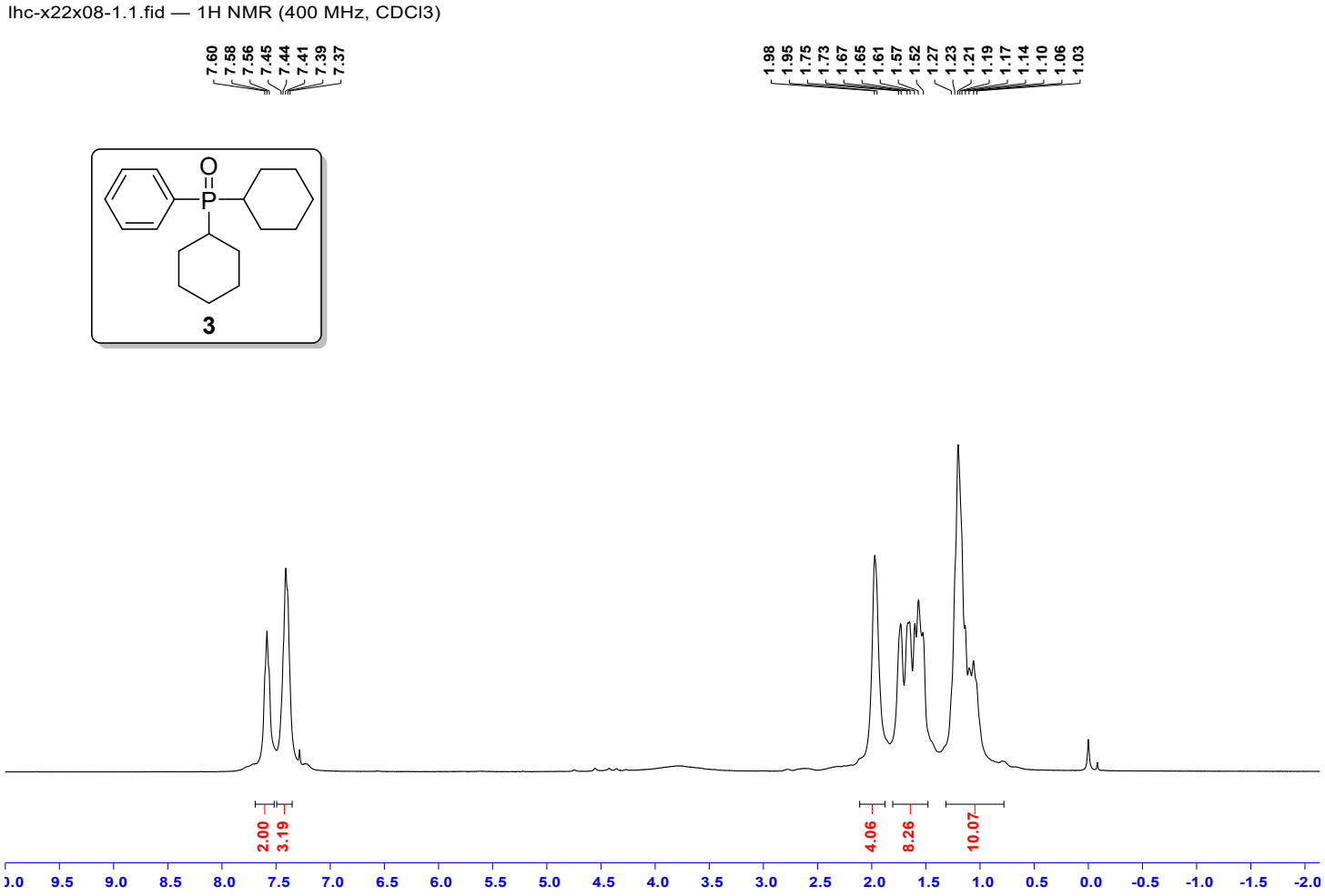
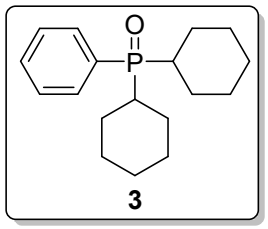
5. NMR Spectra of Products

^{1}H NMR (400 MHz, $CDCl_3$) spectra for 3



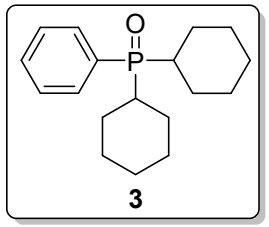
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 3

lhc-x22x08-1.2.fid — 1H NMR (400 MHz, CDCl3)



^{31}P NMR (162 MHz, $CDCl_3$) spectra for 3

lhc-x22x08-1.3.fid — 1H NMR (400 MHz, CDCl3)



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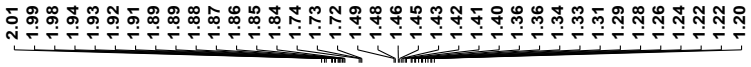
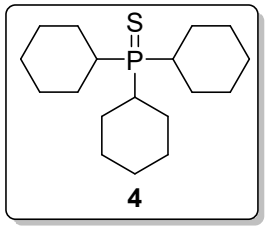
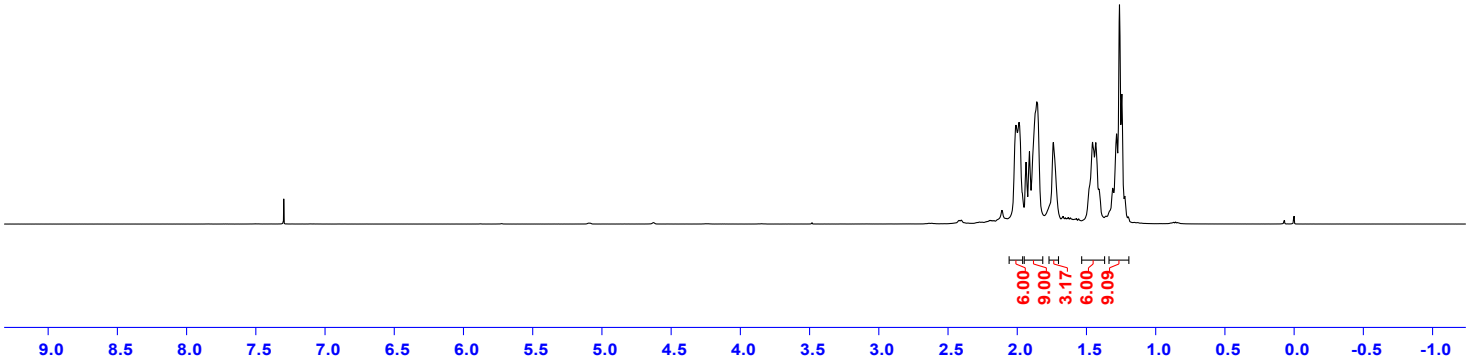
lhc-x230729-2.1.fid — 1H NMR (400 MHz, CDCl3)

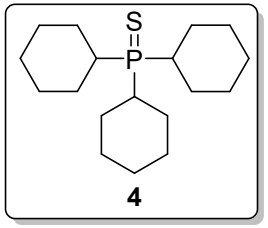






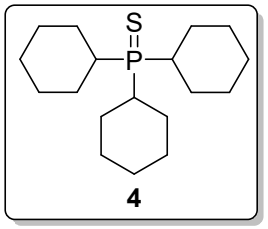
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 4

lhc-x230729-2.2.fid — 13C NMR (100 MHz, CDCl3)

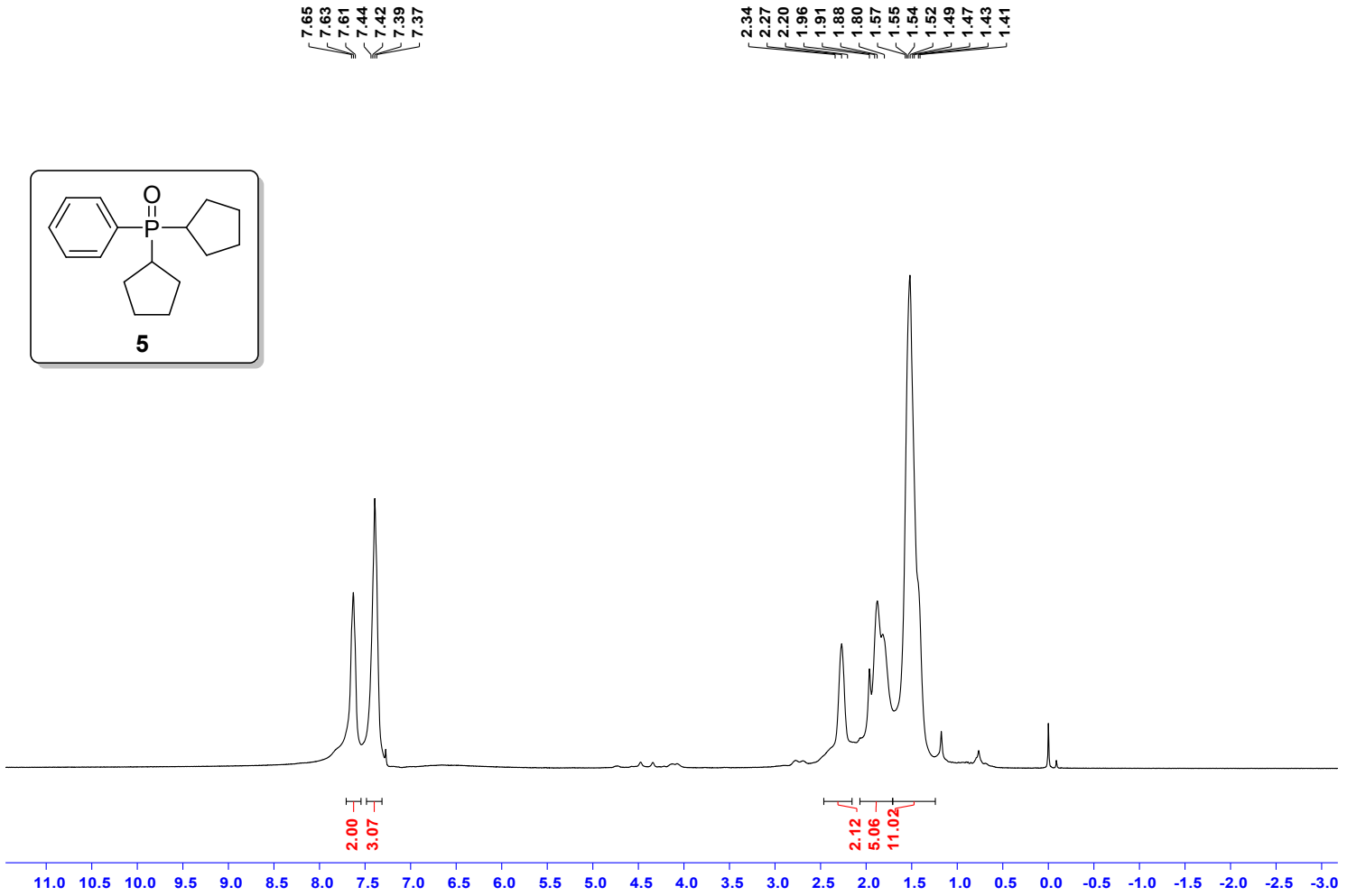


^{31}P NMR (202 MHz, $CDCl_3$) spectra for 4

lhc-x230729-2.3.fid — 1H NMR (400 MHz, CDCl3)

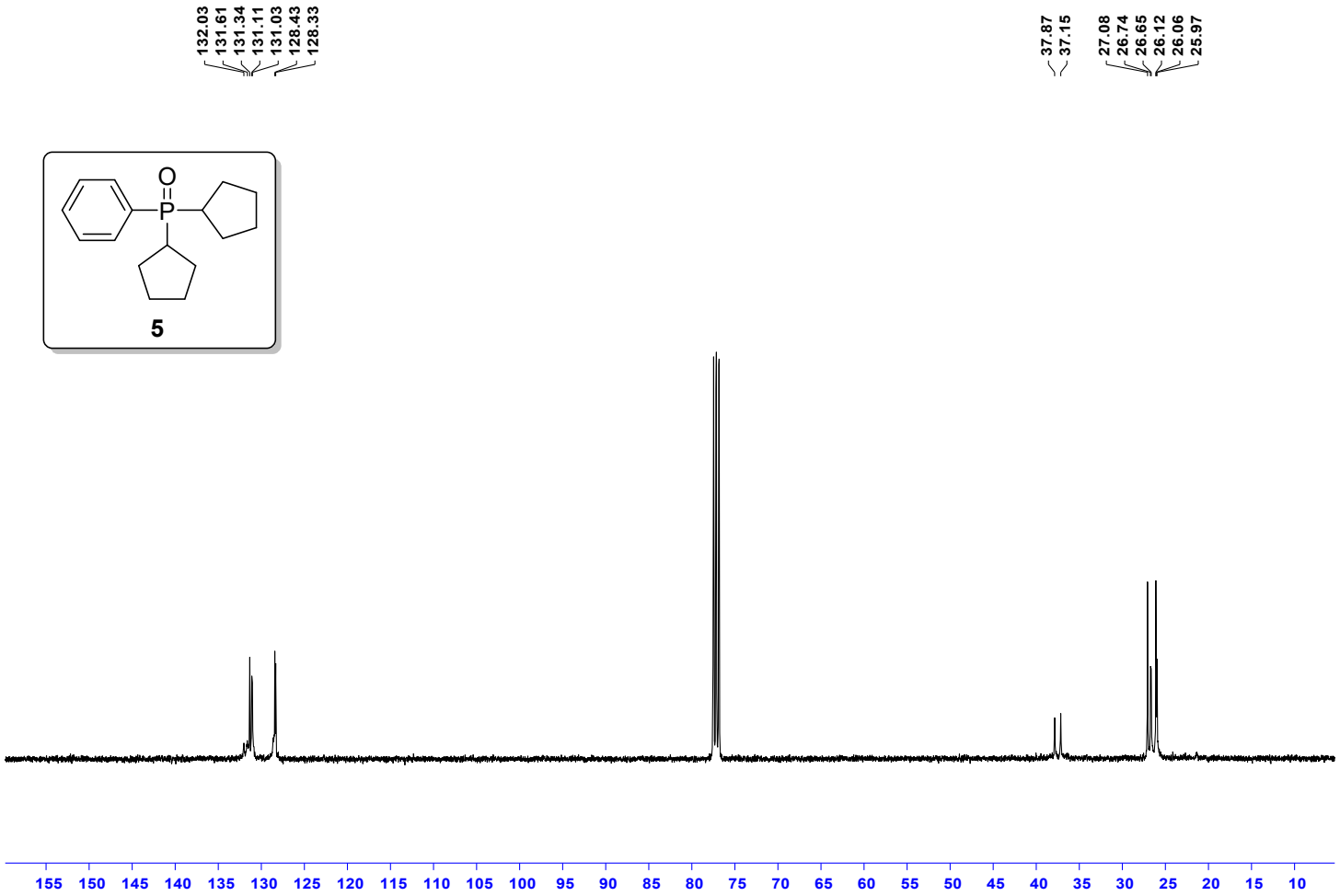


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 5



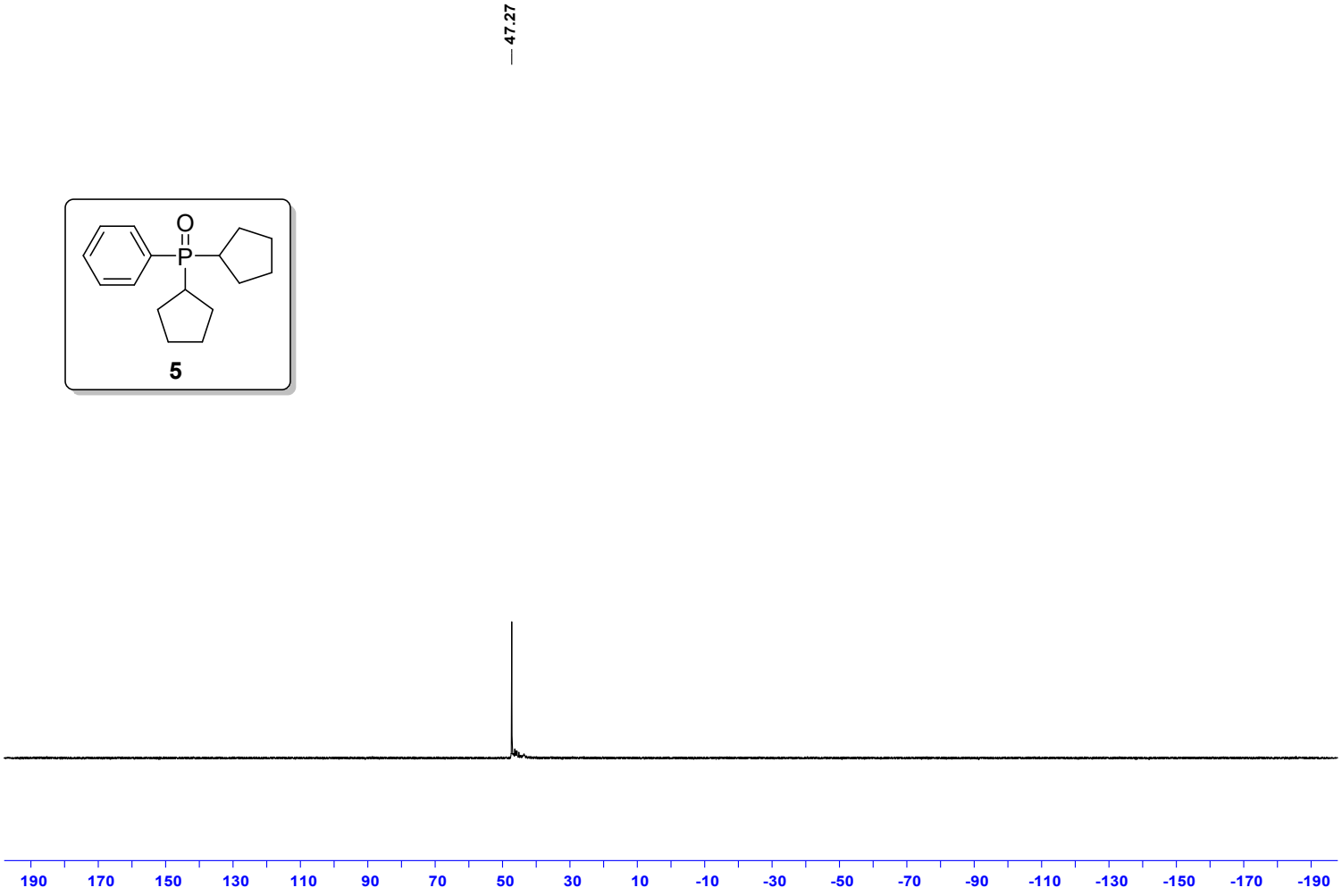
^{13}C NMR (101 MHz, CDCl3) spectra for 5

lhc-x22x24-4.11.fid — 1H NMR (400 MHz, CDCl3)



^{31}P NMR (162 MHz, $CDCl_3$) spectra for 5

lhc-x22x24-4-c5.2.fid — 1H NMR (400 MHz, CDCl3)



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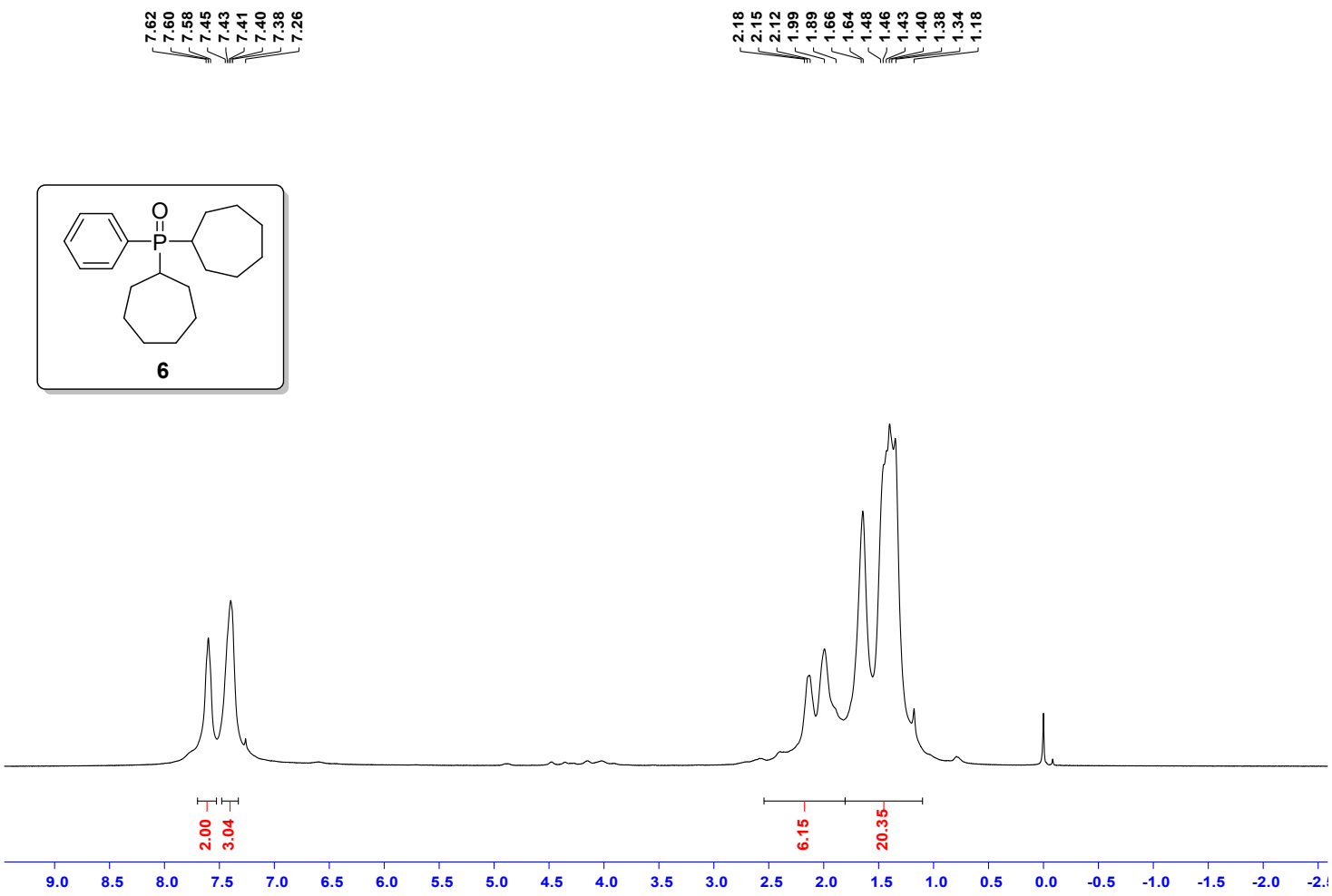
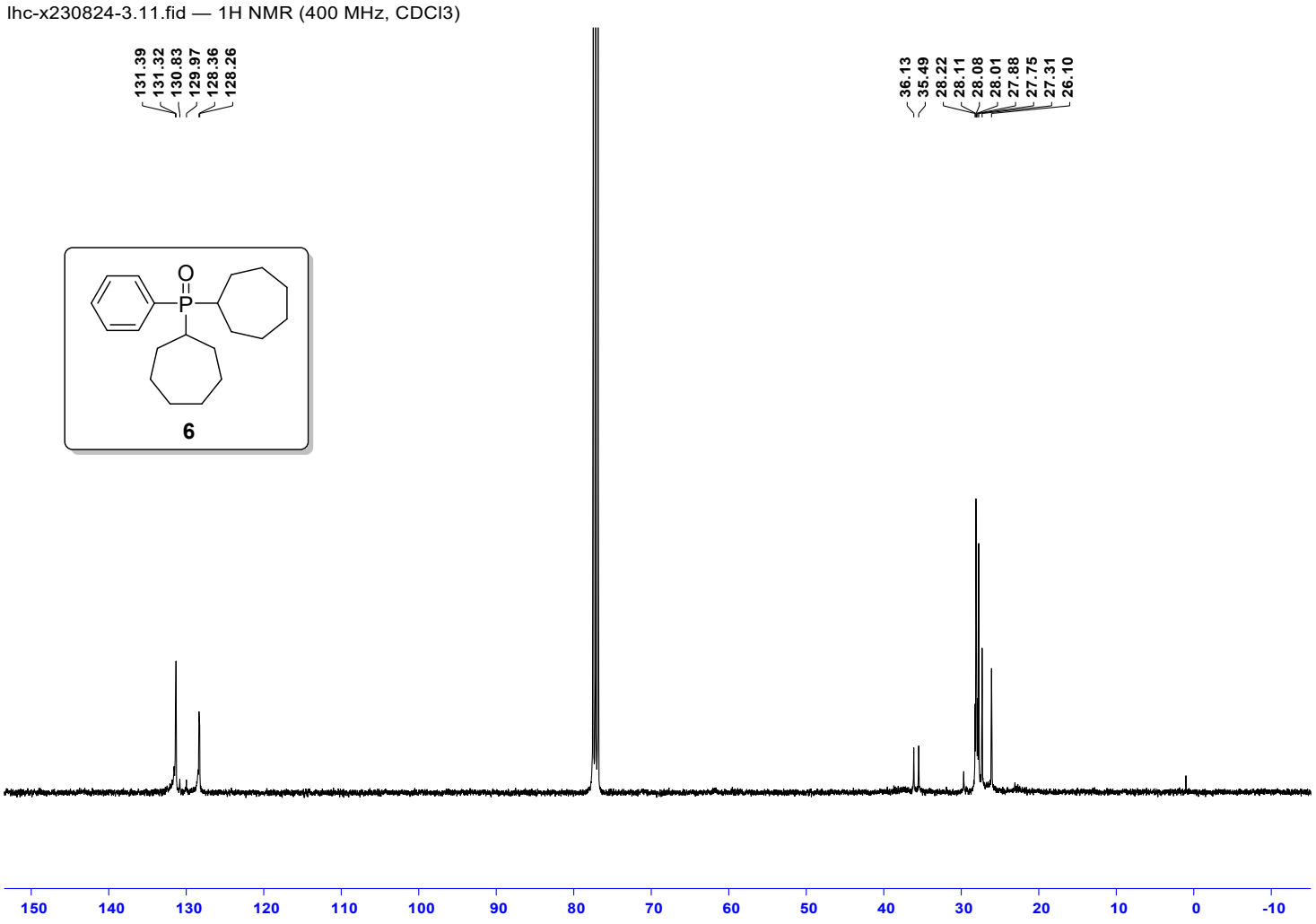


^{13}C NMR (101 MHz, CDCl3) spectra for 6



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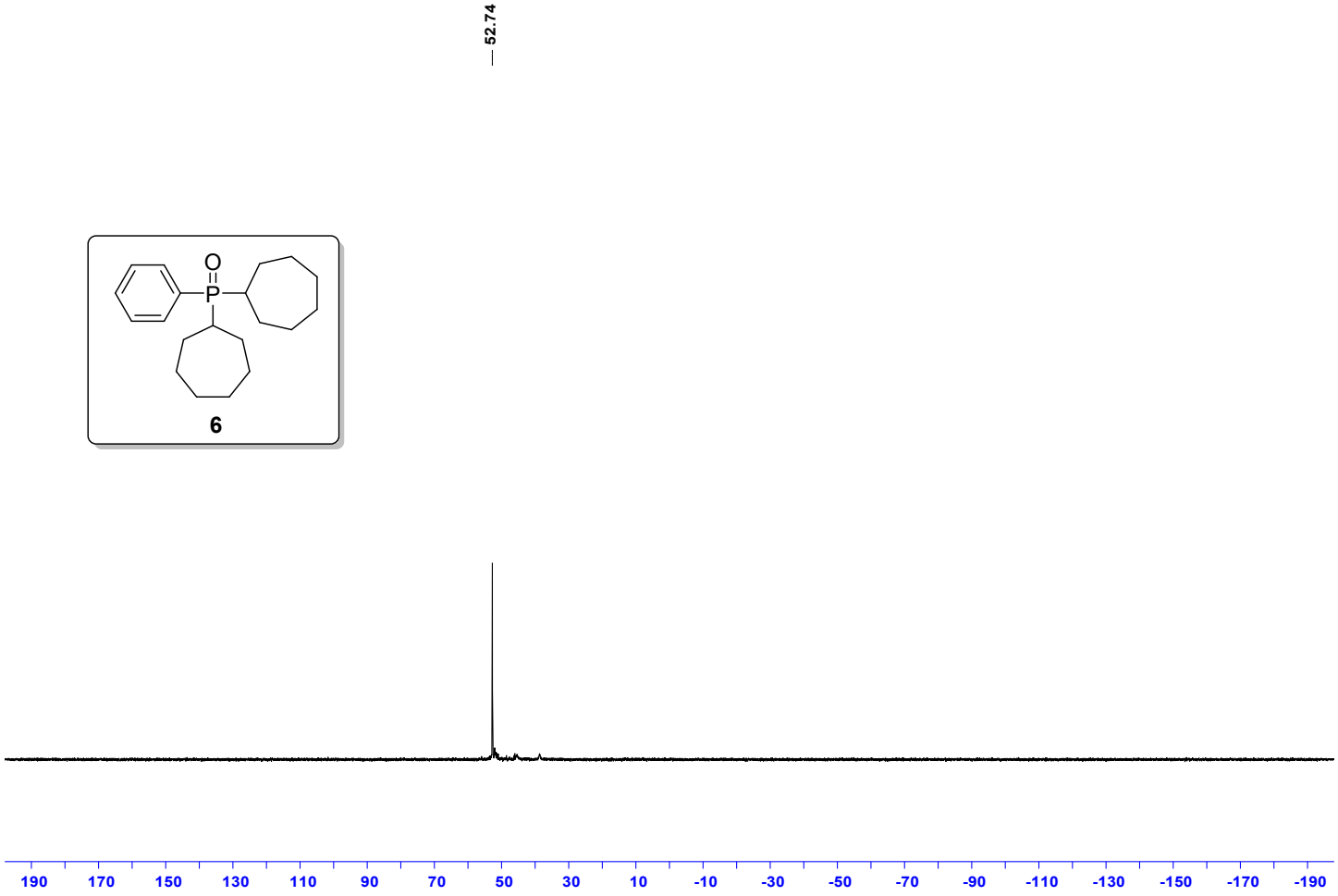
lhc-x22x24-3-c7.2.fid — 1H NMR (400 MHz, CDCl3)



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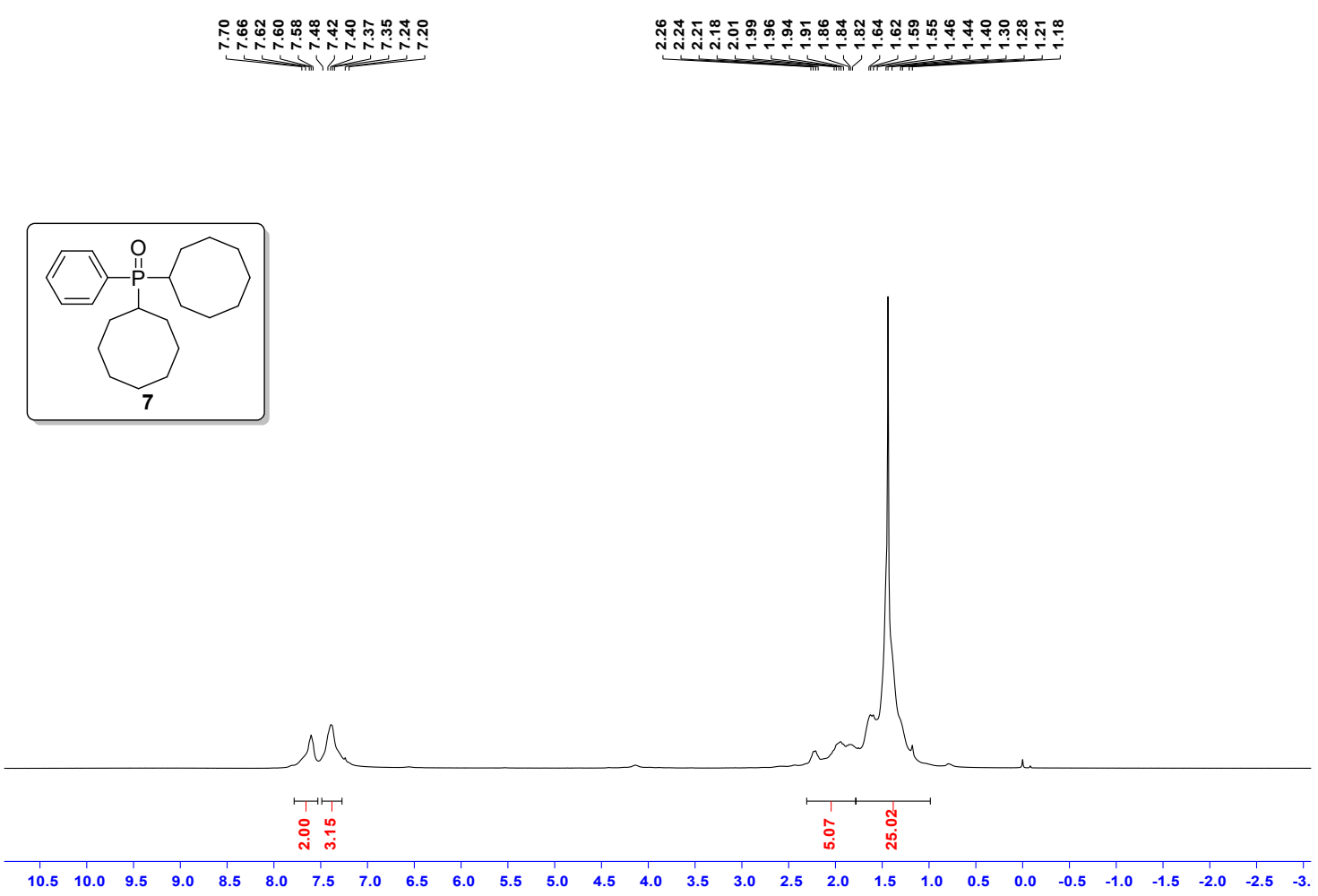
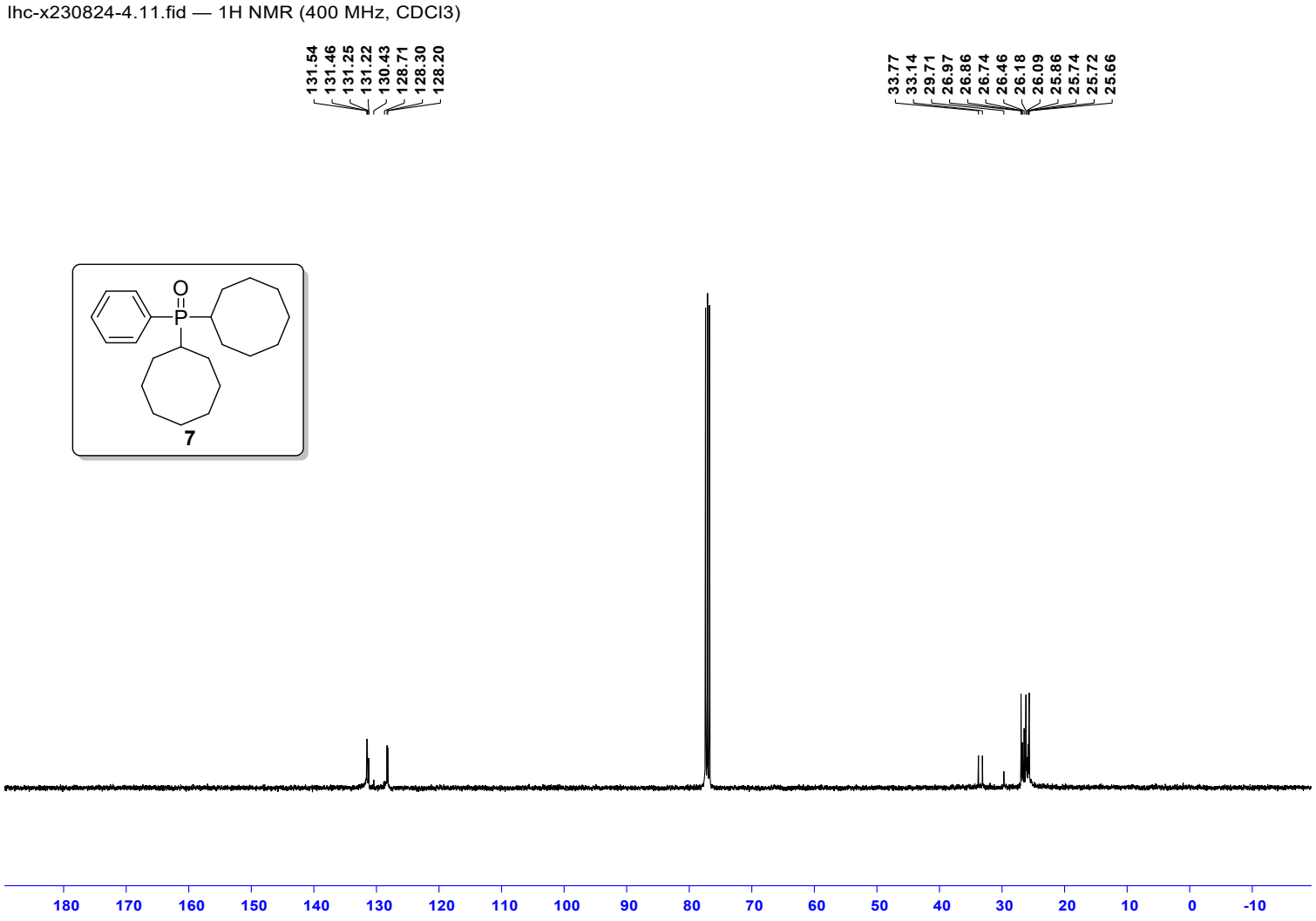


^{13}C NMR (101 MHz, $CDCl_3$) spectra for 7



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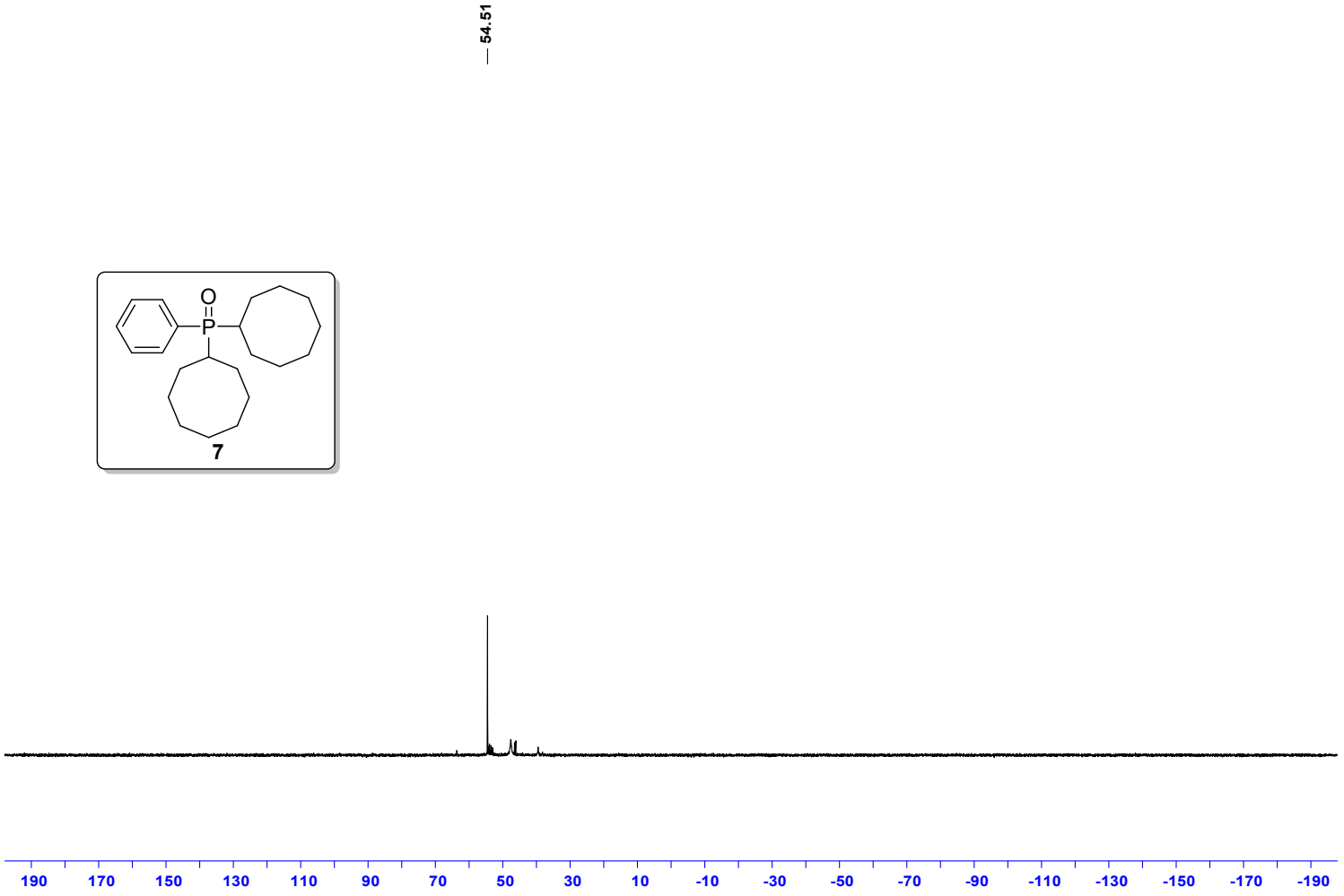
lhc-x22x24-5-c8.2.fid — 1H NMR (400 MHz, CDCl3)



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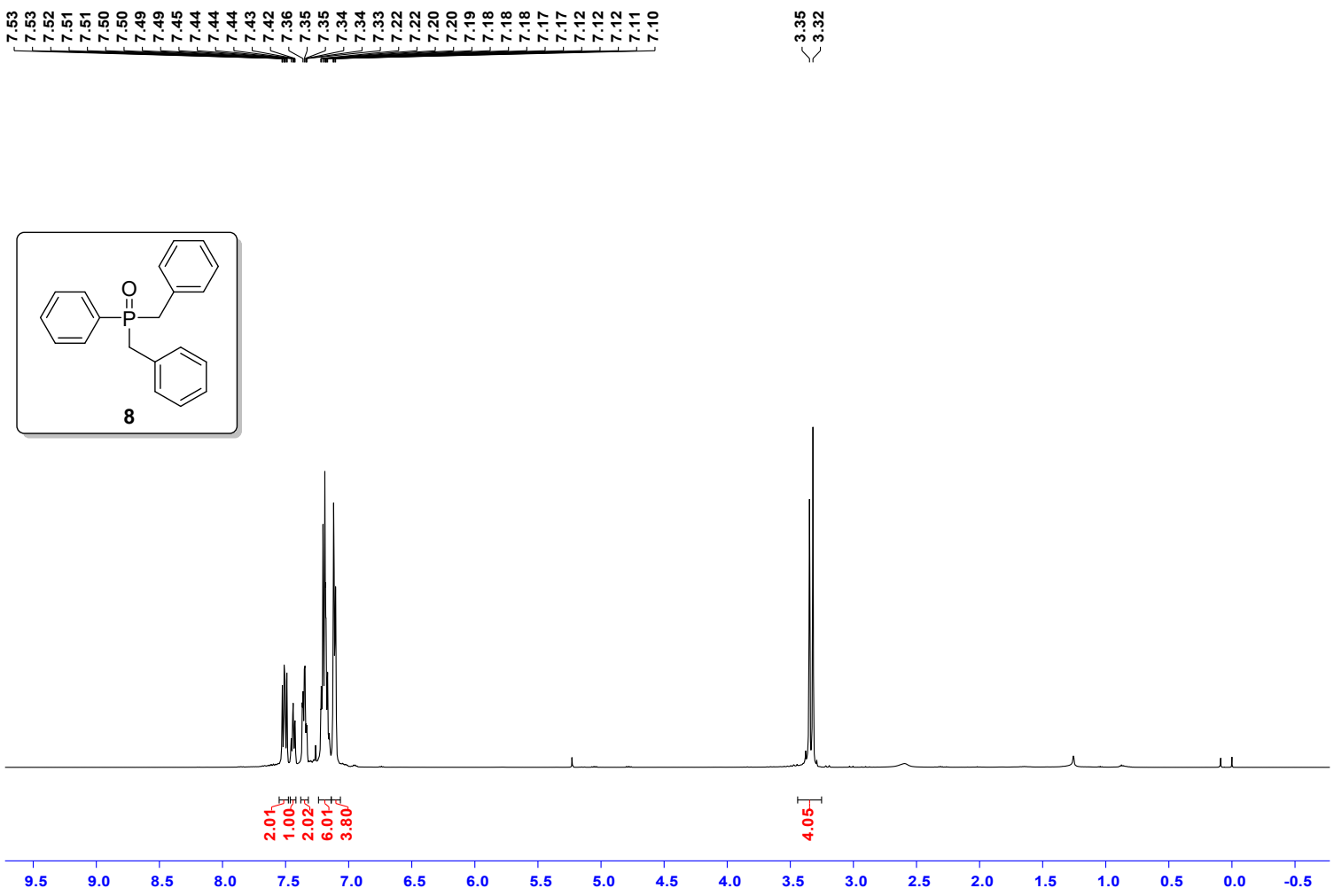

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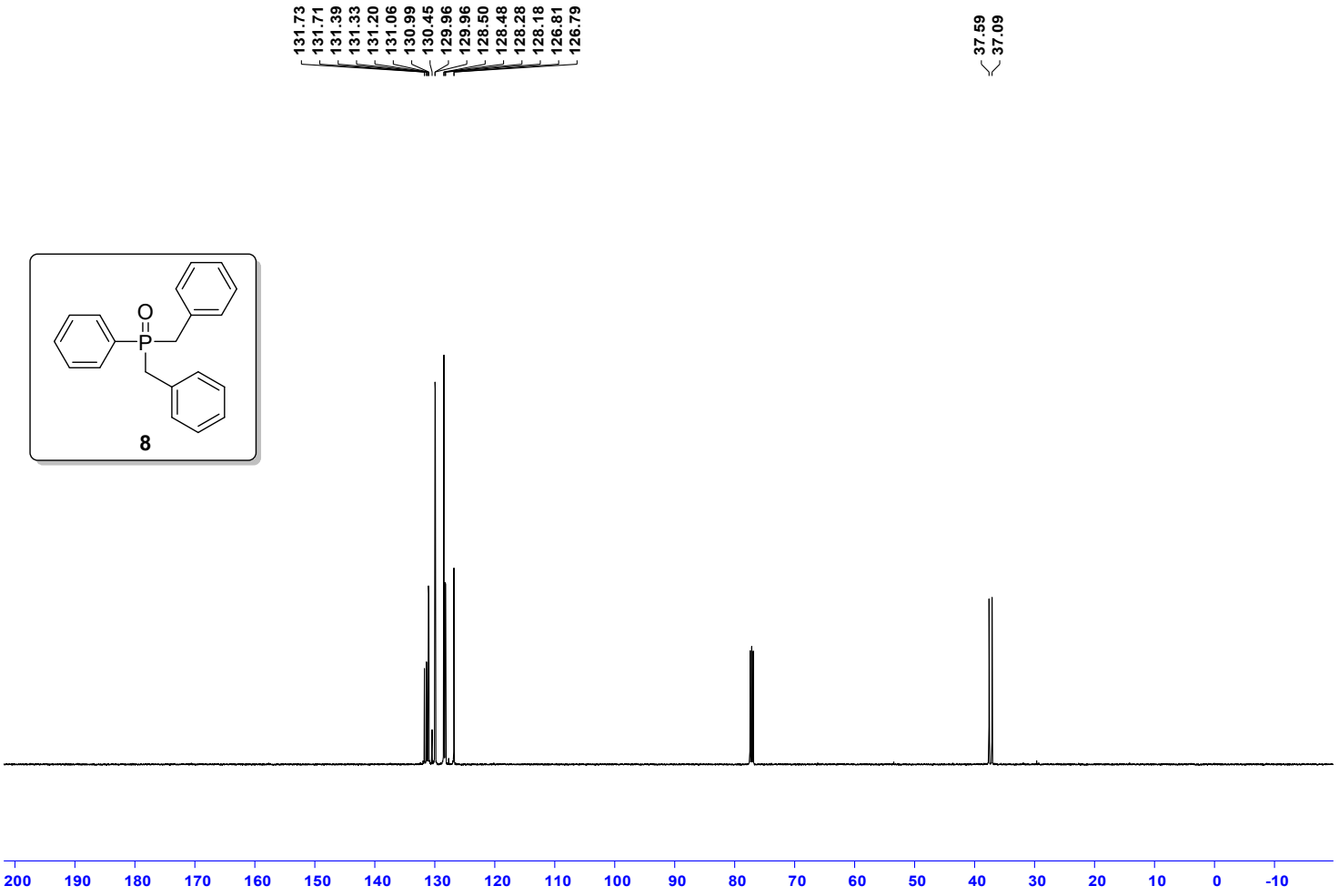

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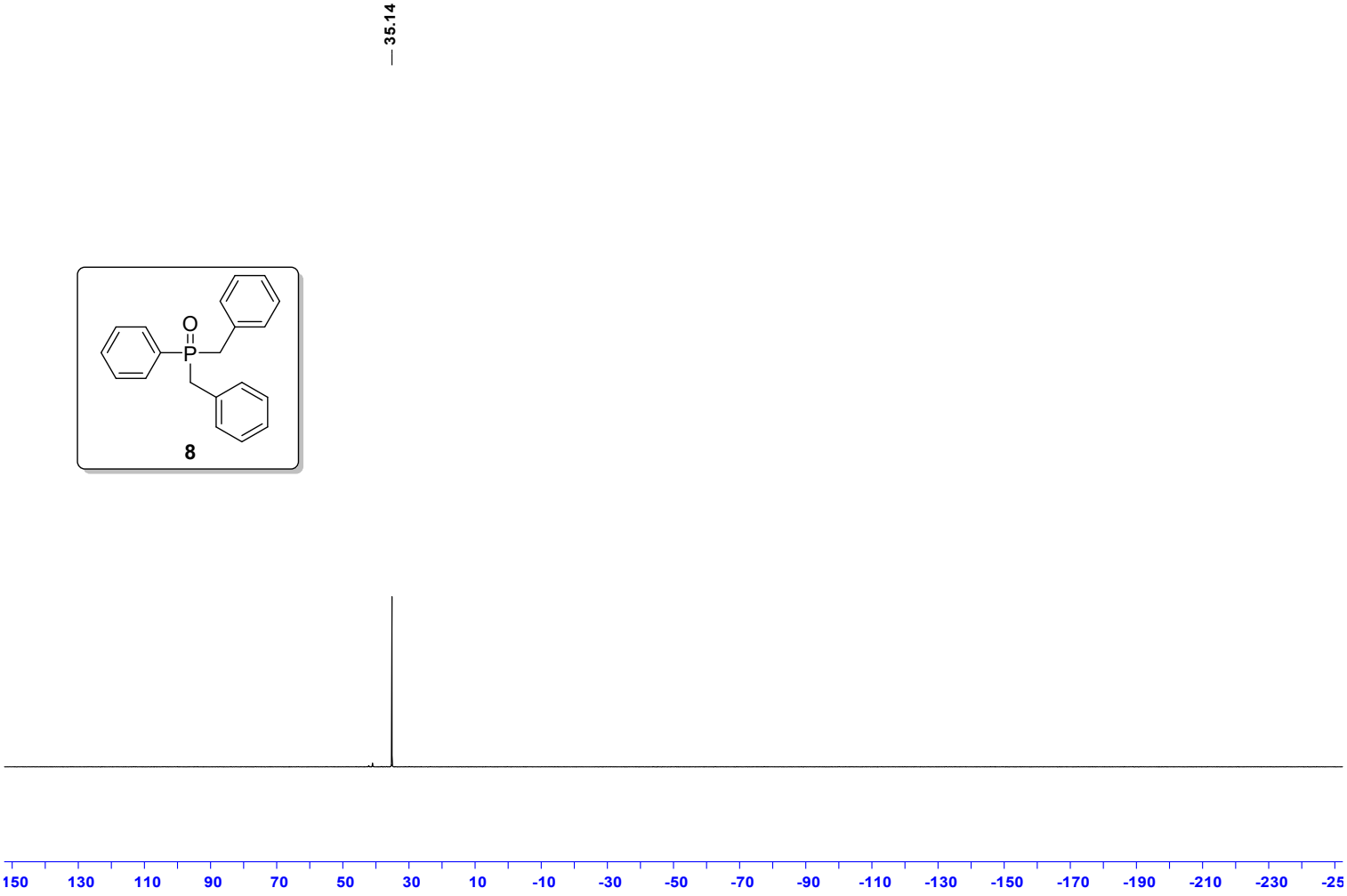
lhc-x230818-1.6.fid — 1H NMR (400 MHz, CDCl3)



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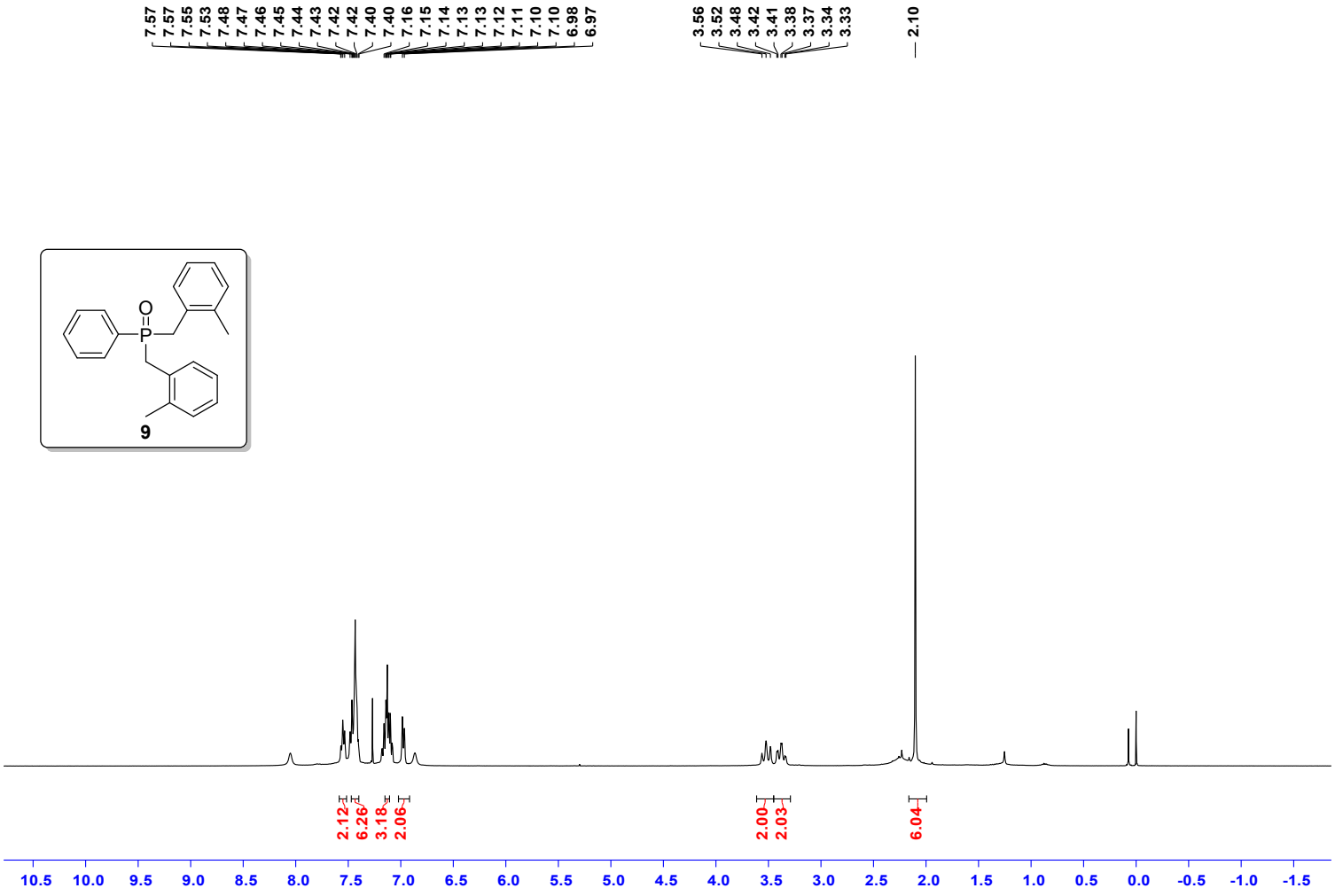

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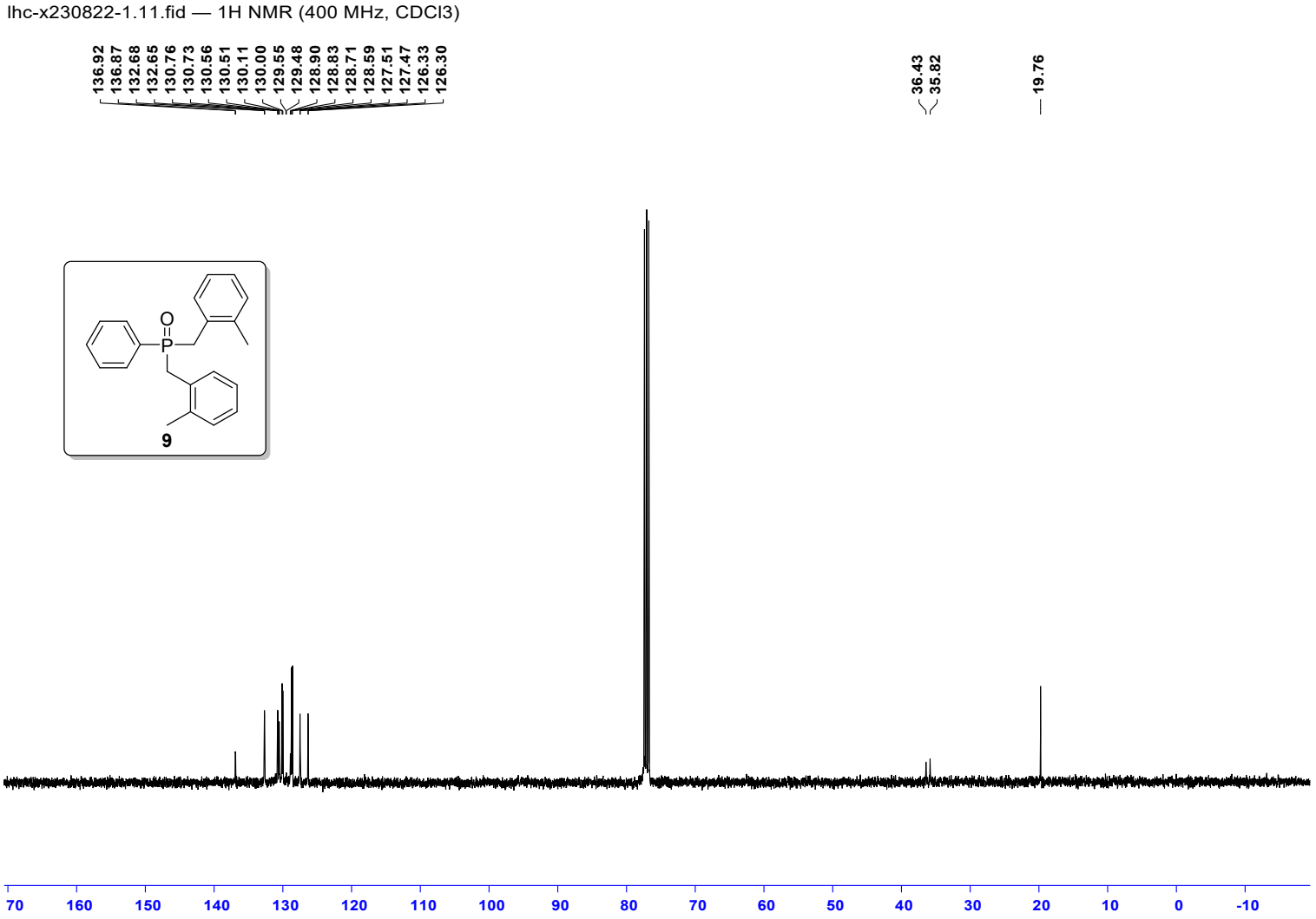

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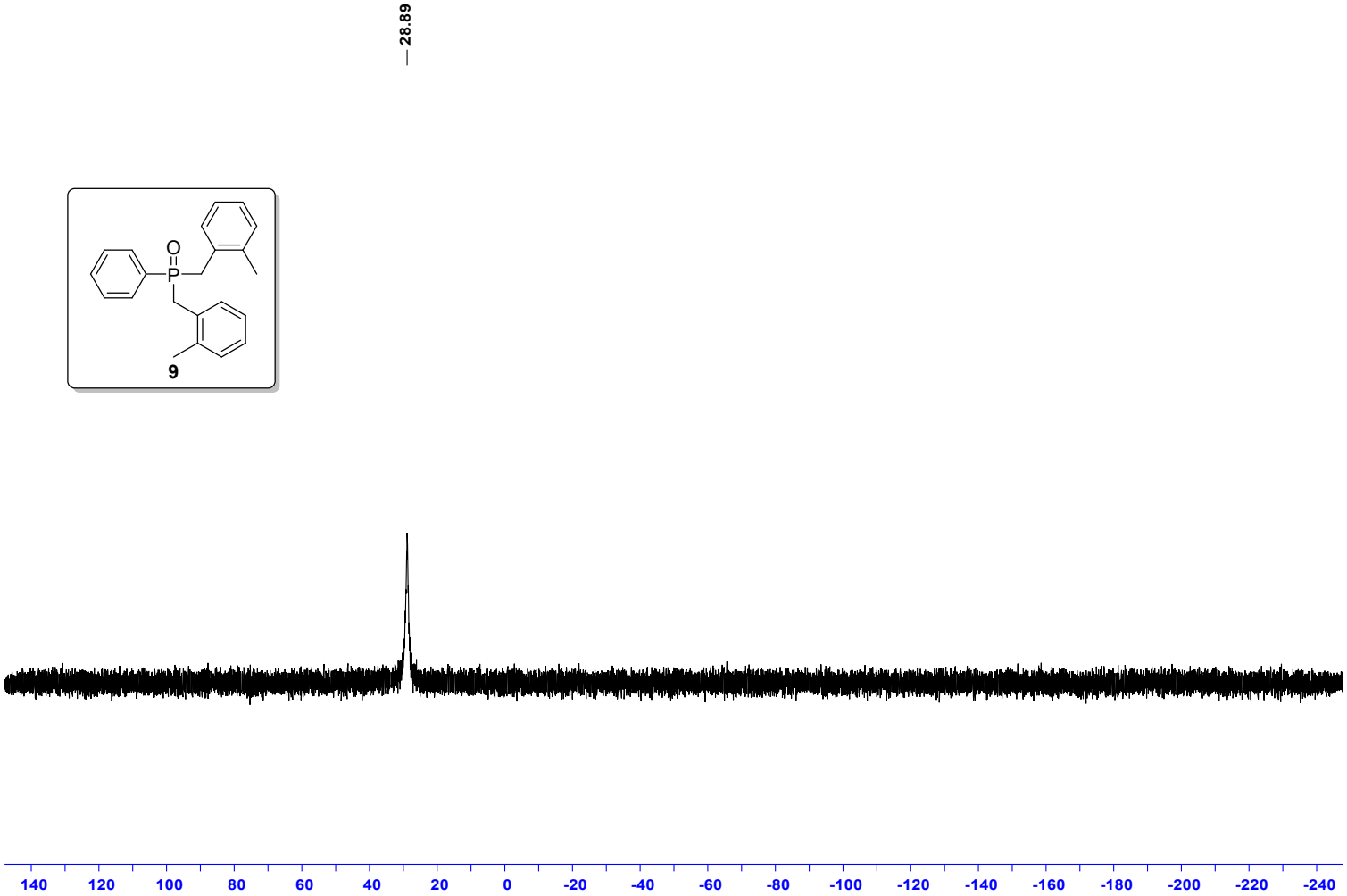
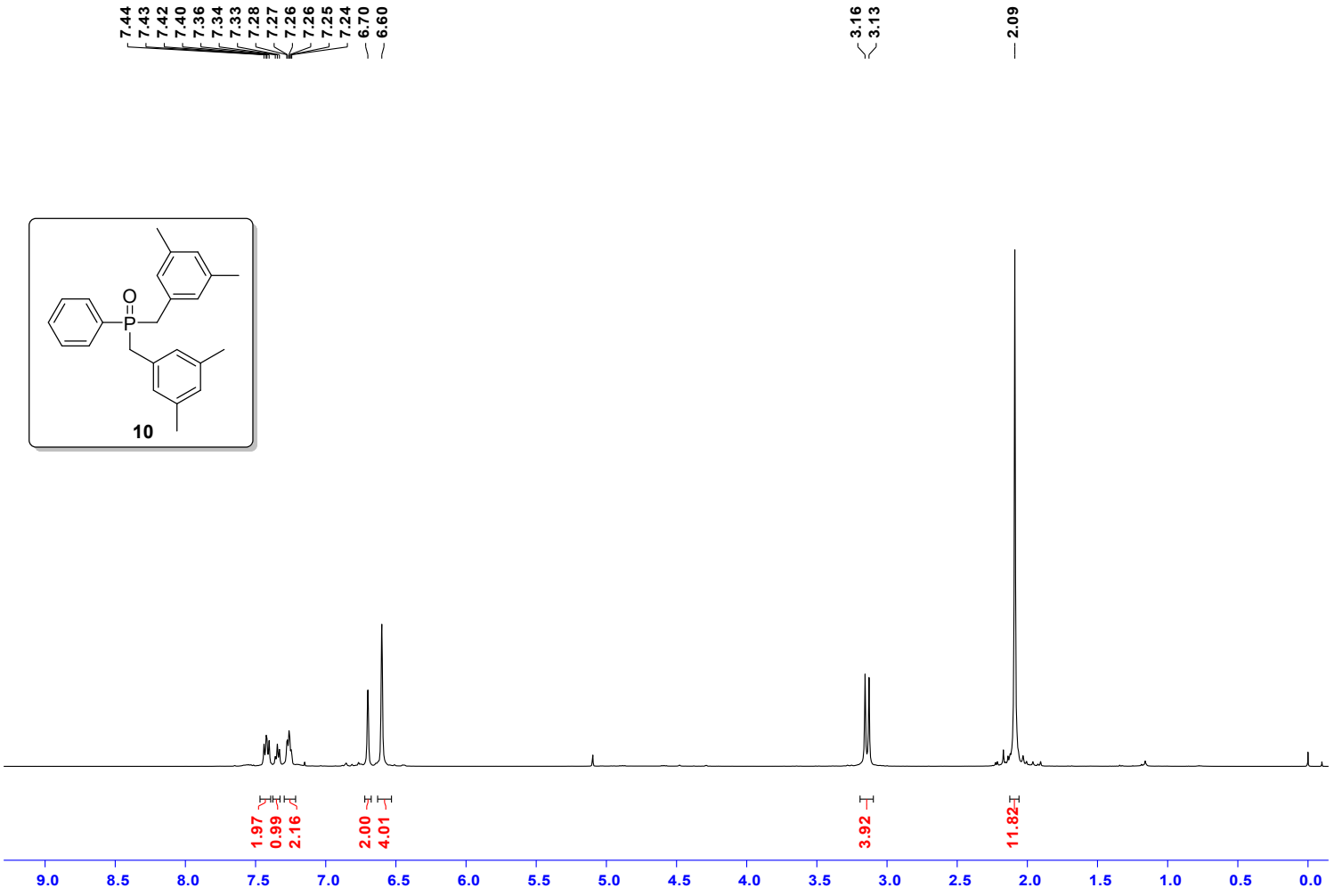
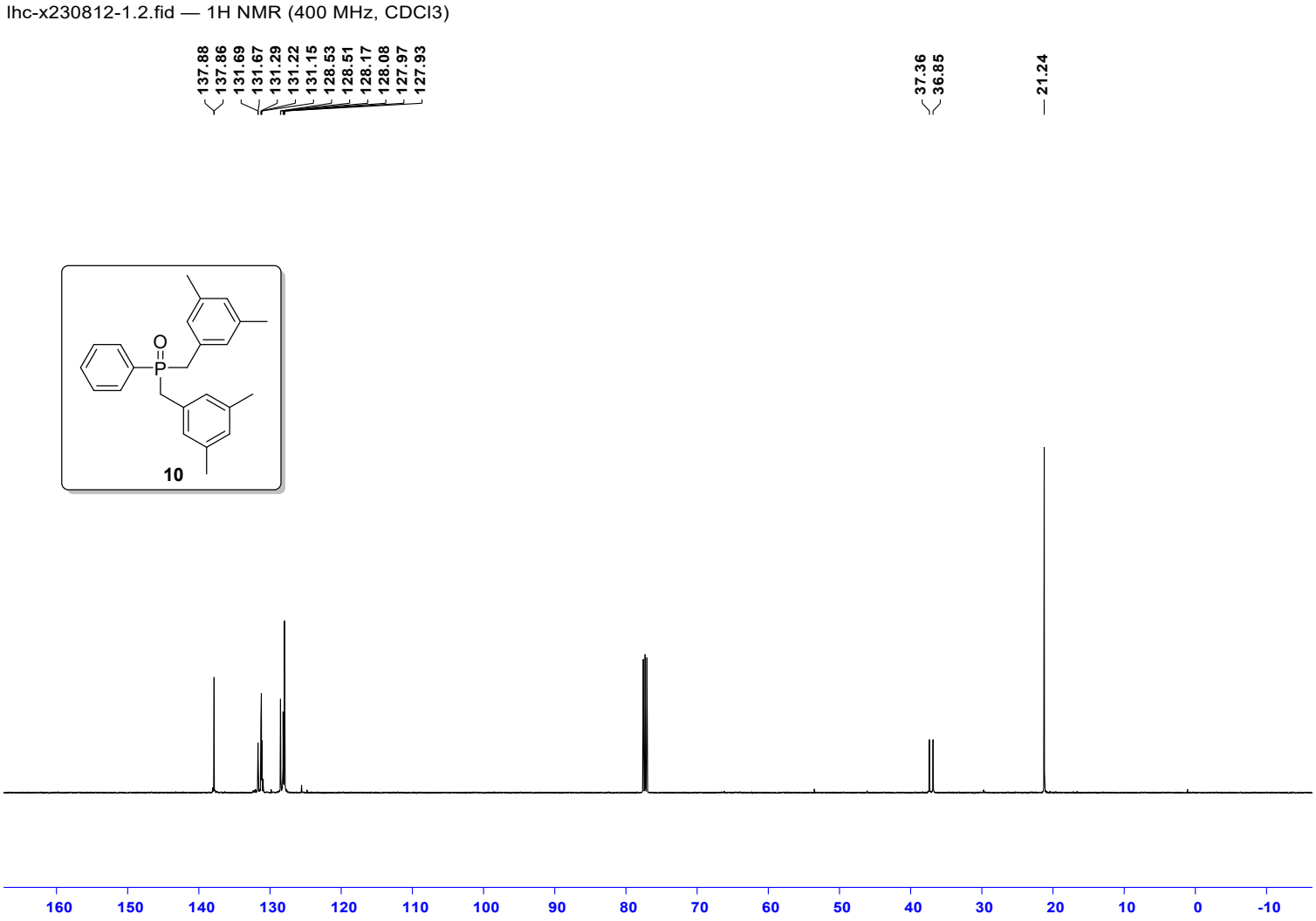


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 10

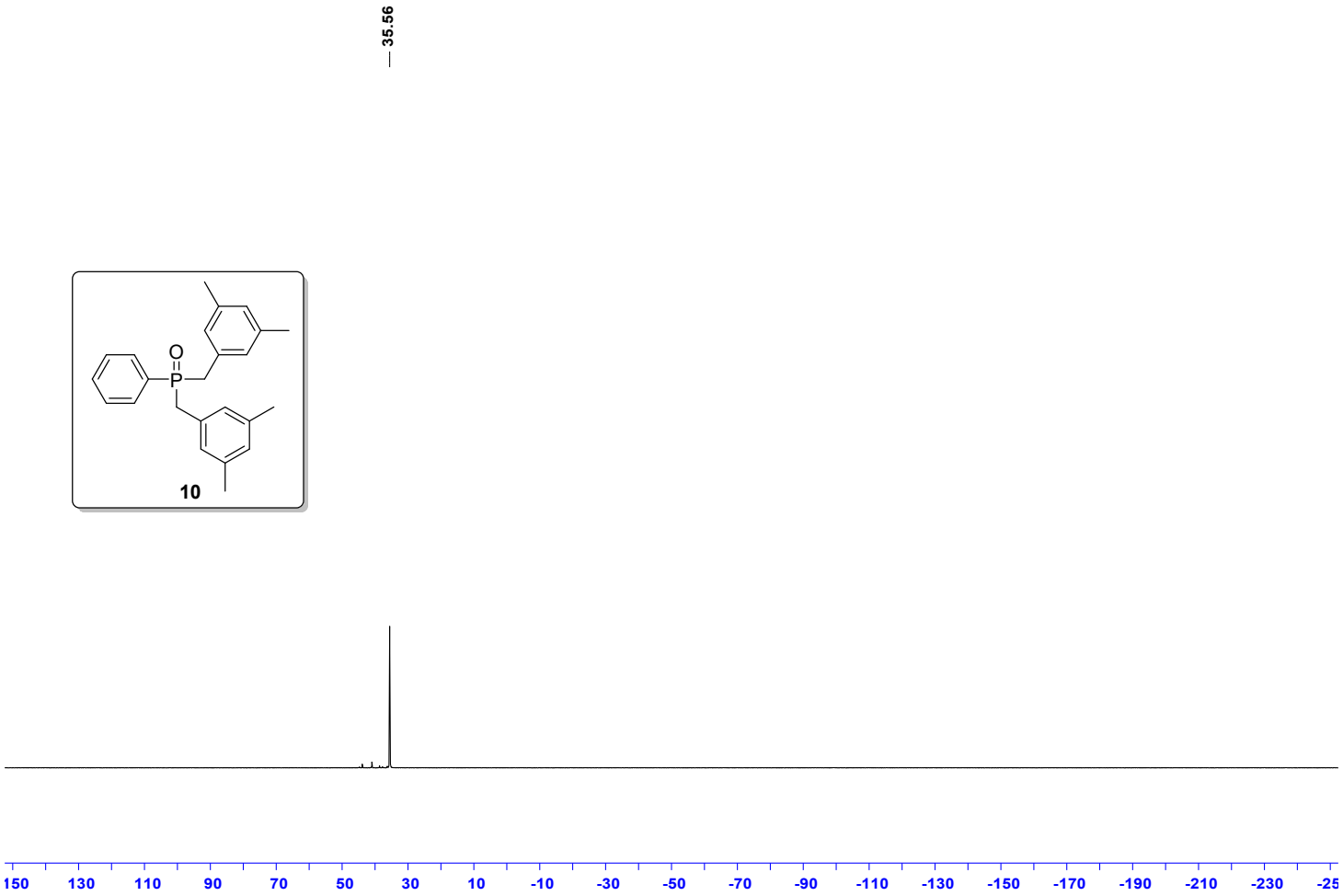


^{13}C NMR (126 MHz, CDCl3) spectra for 10



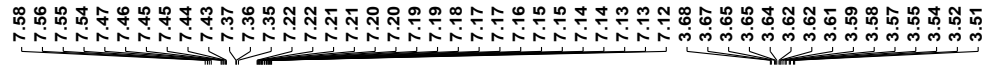
^{31}P NMR (202 MHz, $CDCl_3$) spectra for 10

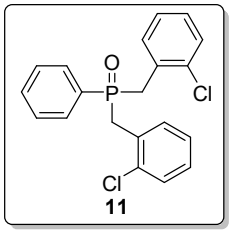
lhc-x230812-1.3.fid — 1H NMR (400 MHz, CDCl3)

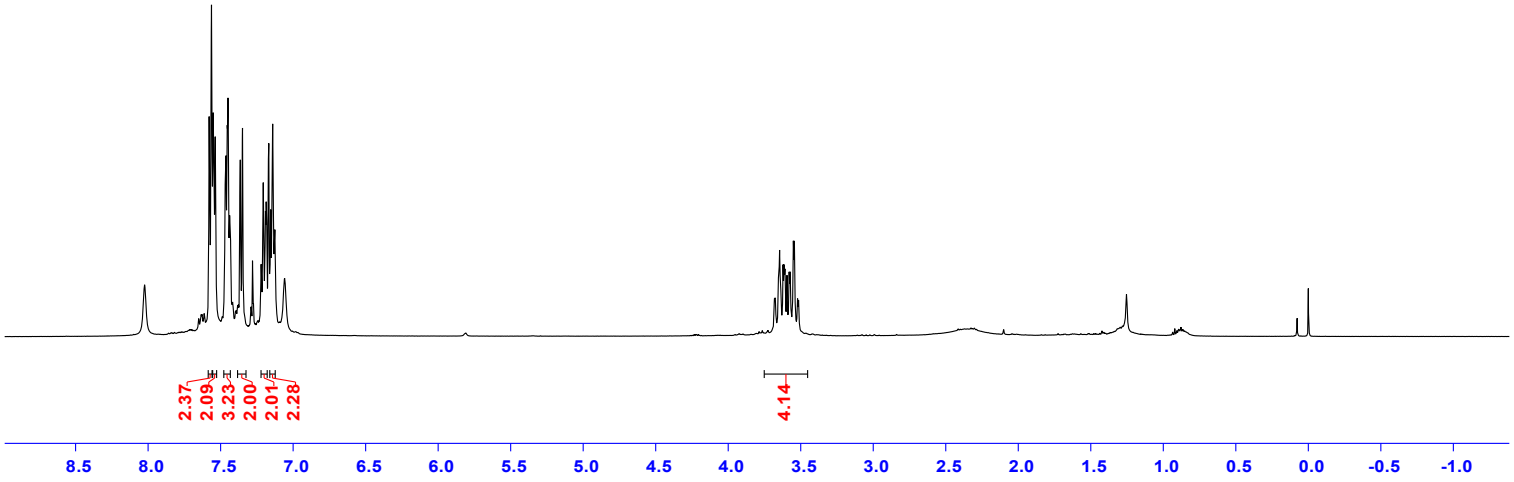


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 11

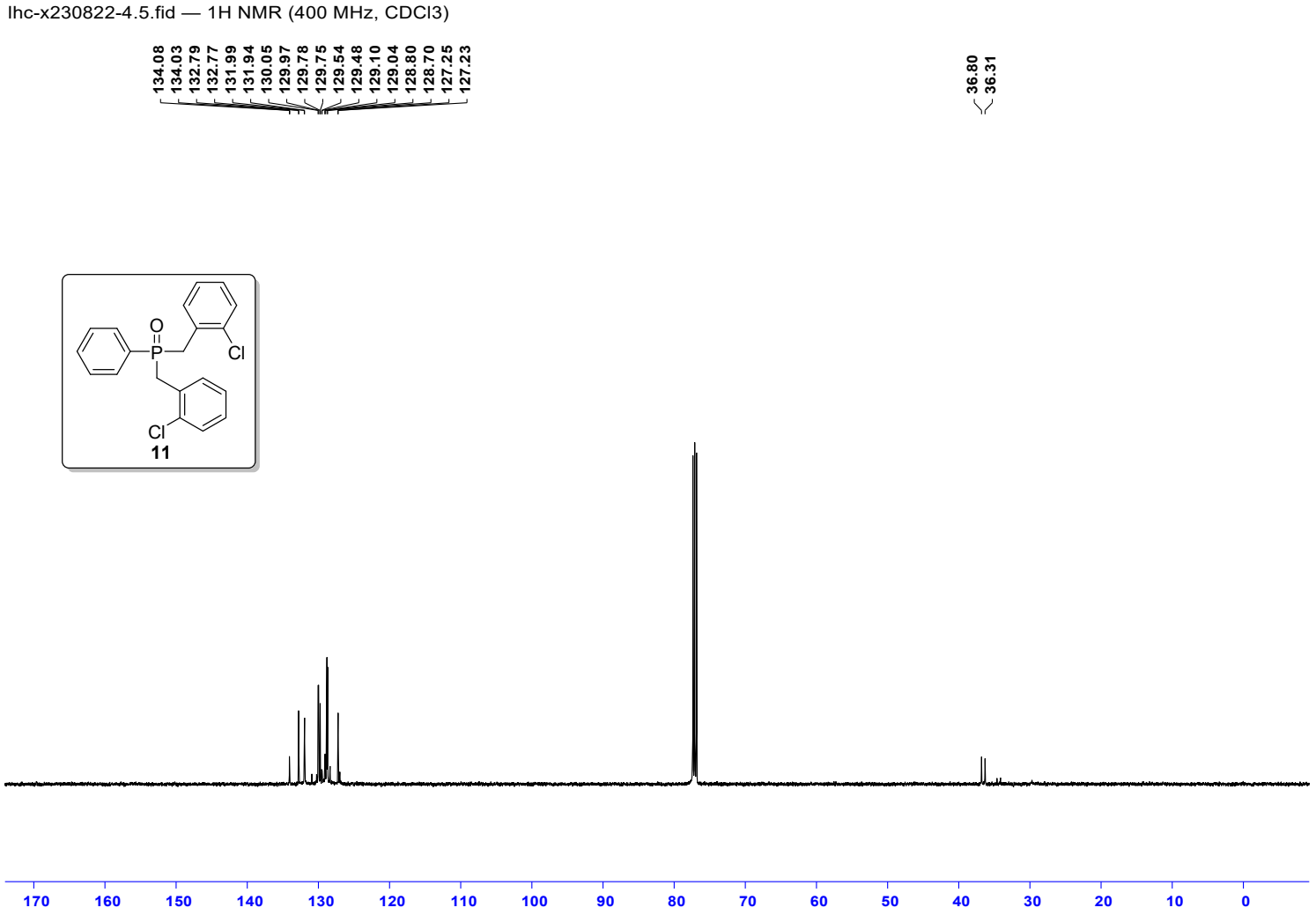
lhc-x230822-4.4.fid — 1H NMR (400 MHz, CDCl3)





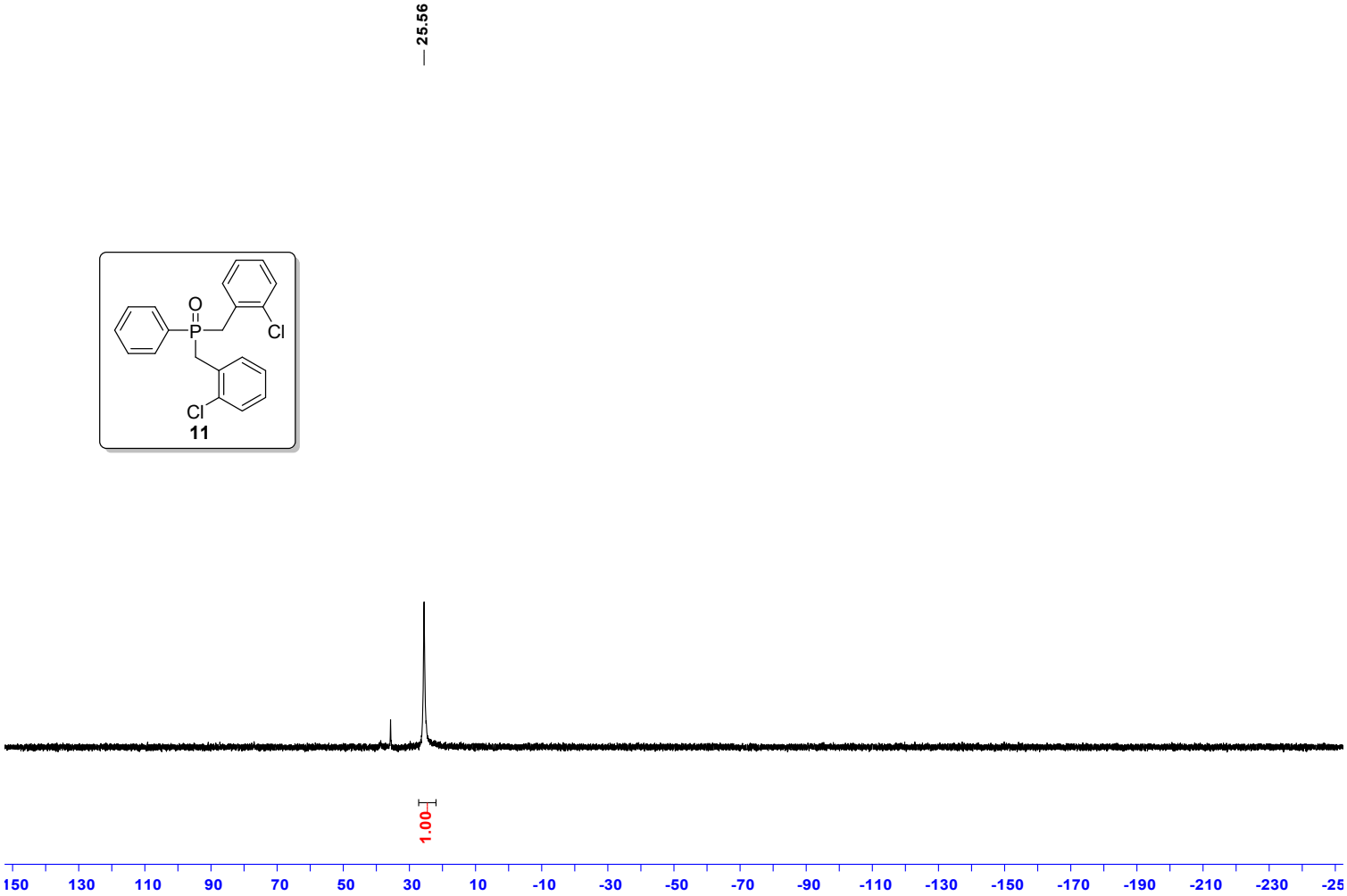


^{13}C NMR (126 MHz, CDCl3) spectra for 11

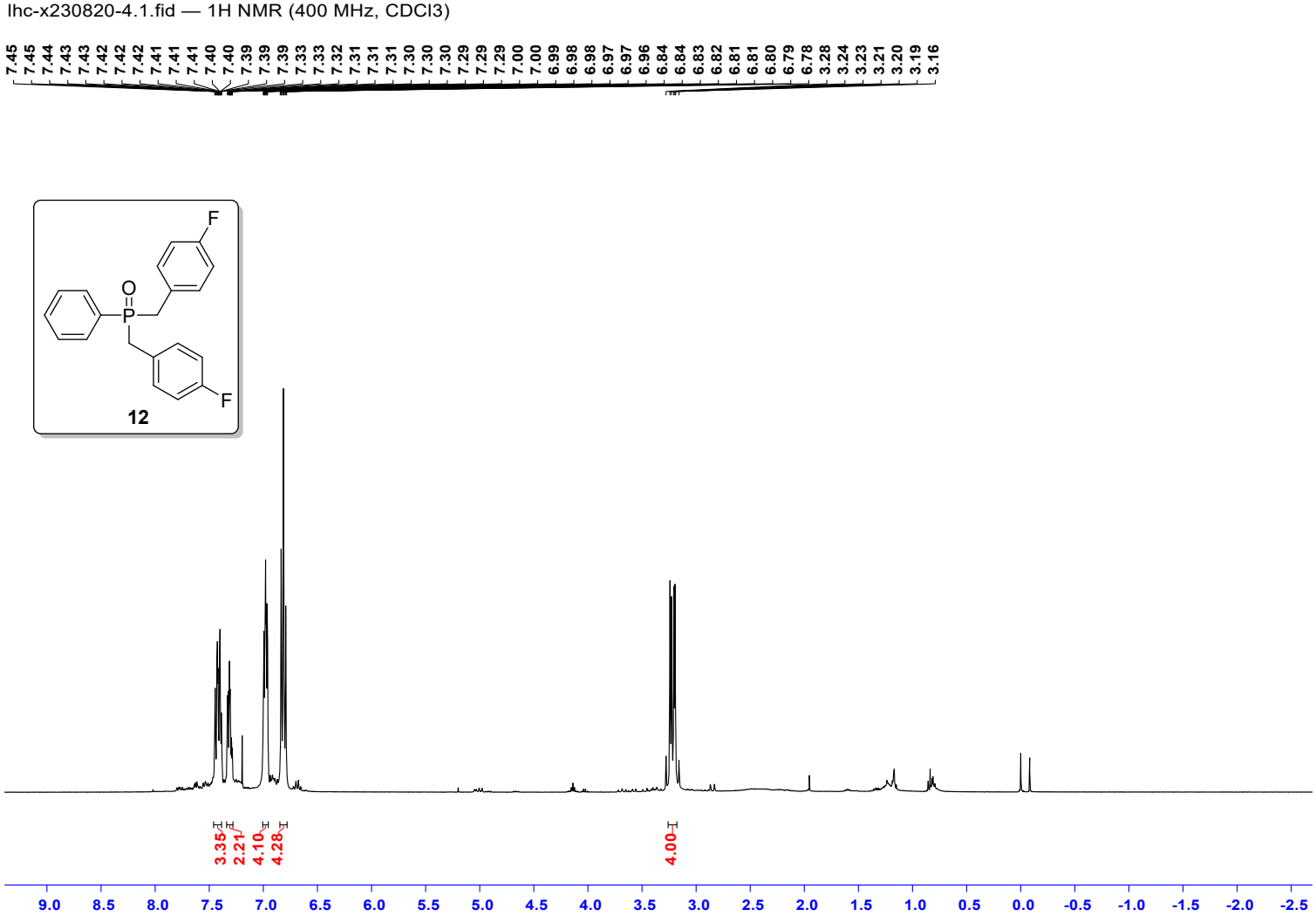


^{31}P NMR (202 MHz, $CDCl_3$) spectra for 11

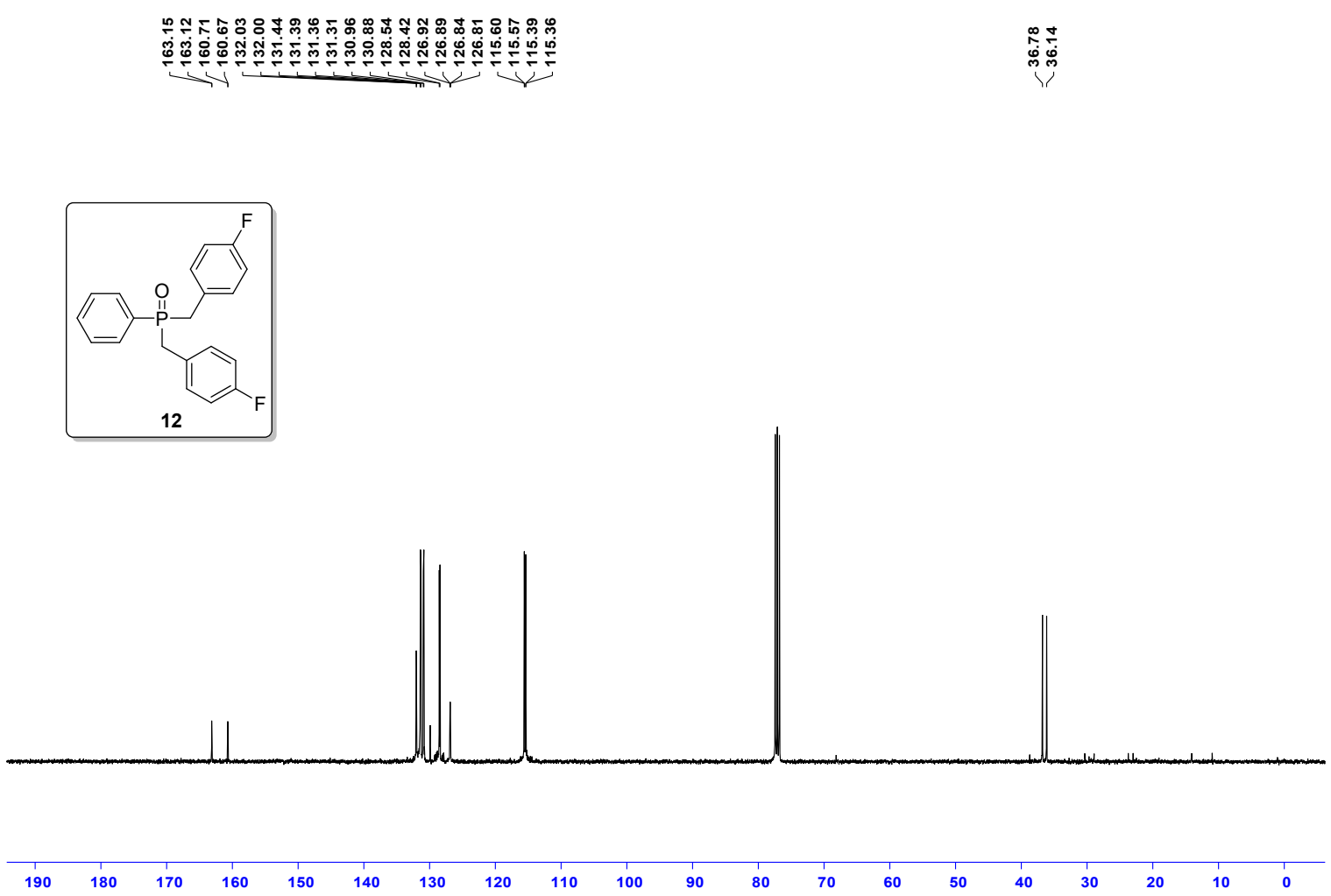
lhc-x230822-4.6.fid — 1H NMR (400 MHz, CDCl3)



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 12

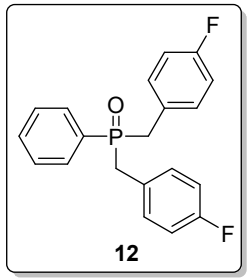


^{13}C NMR (101 MHz, CDCl3) spectra for 12



^{31}P NMR (162 MHz, $CDCl_3$) spectra for 12

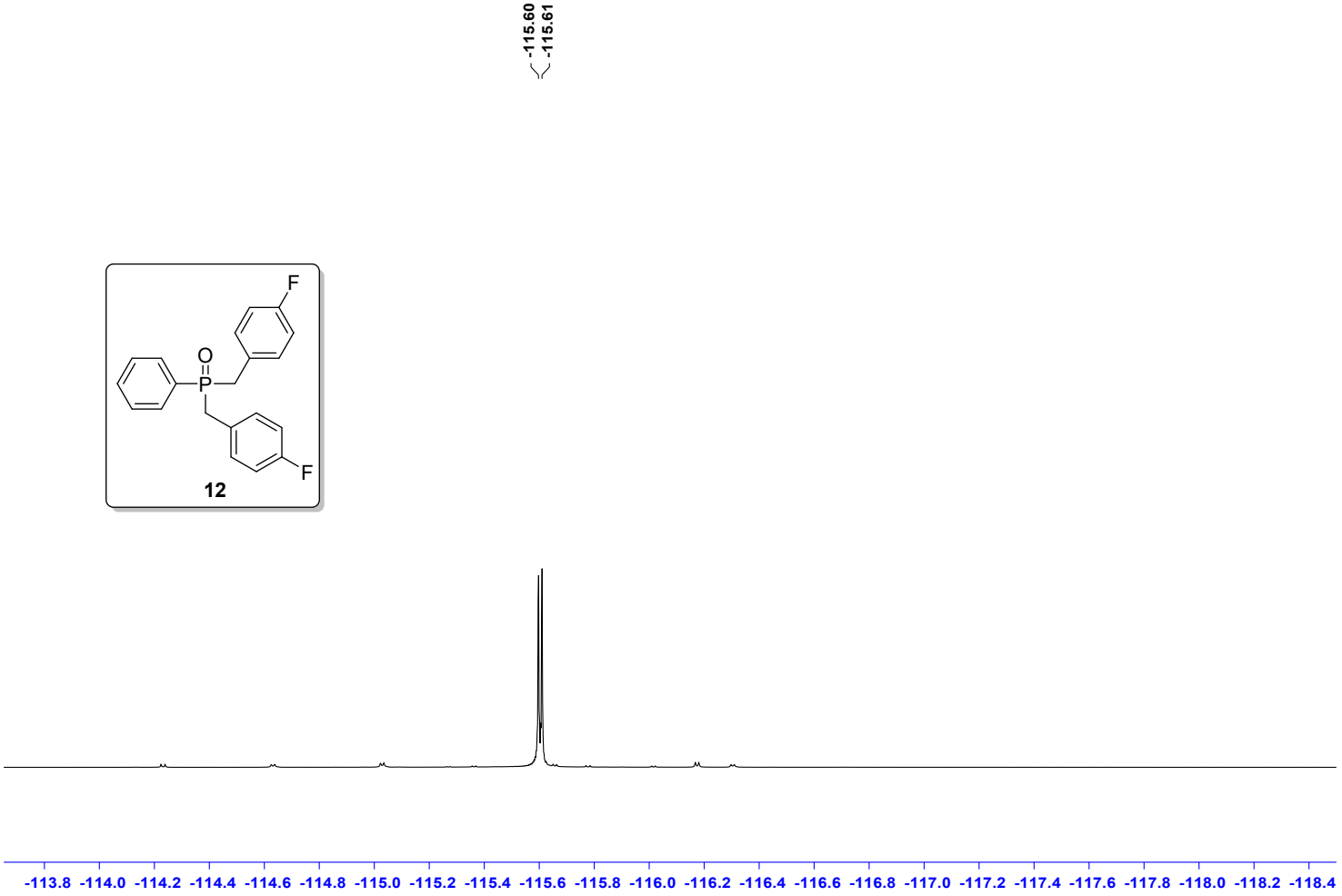
lhc-x230820-4.3.fid — 1H NMR (400 MHz, CDCl3)



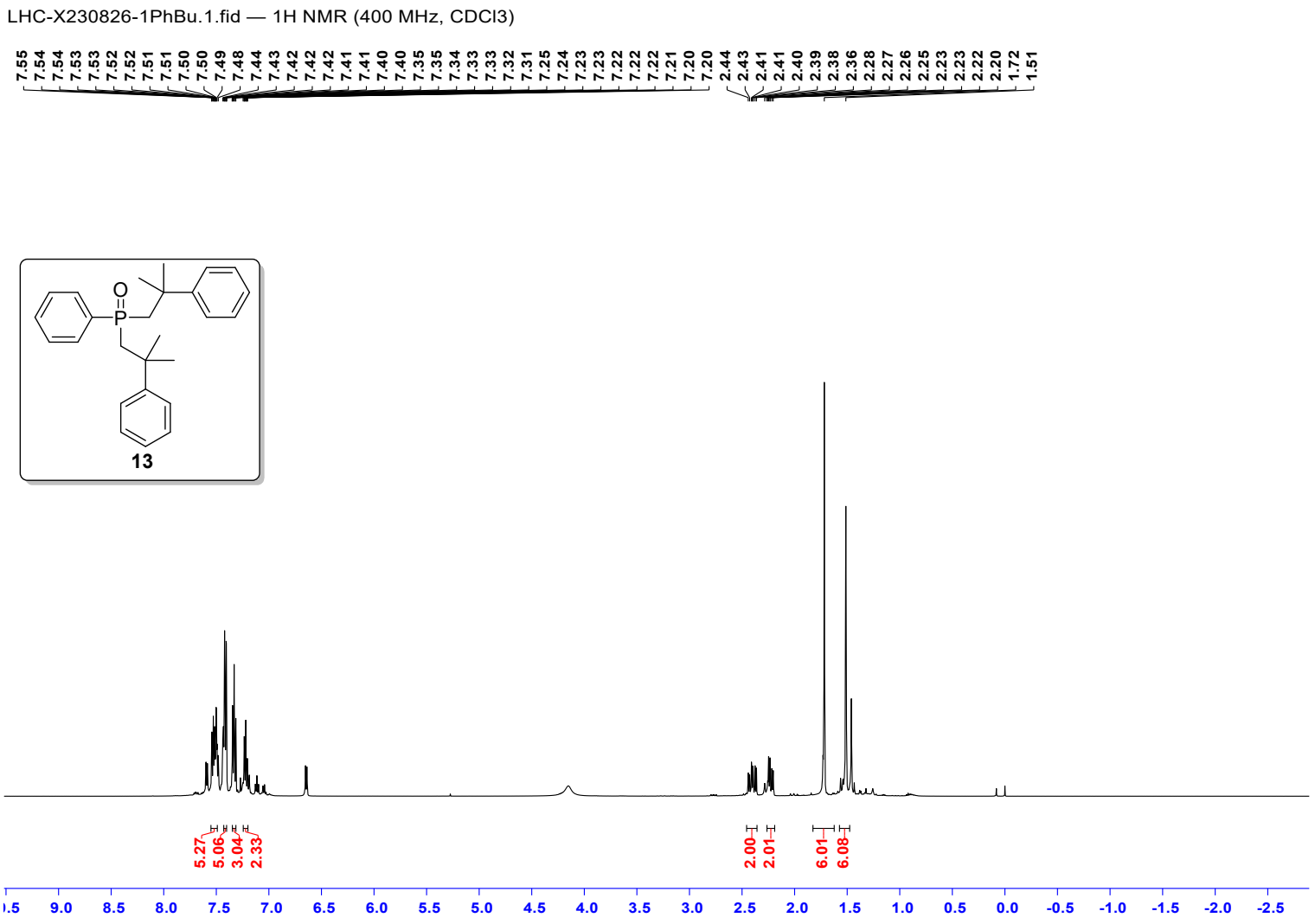
12

^{19}F NMR (376 MHz, $CDCl_3$) spectra for 12

lhc-x230820-4.4.fid — 1H NMR (400 MHz, CDCl3)

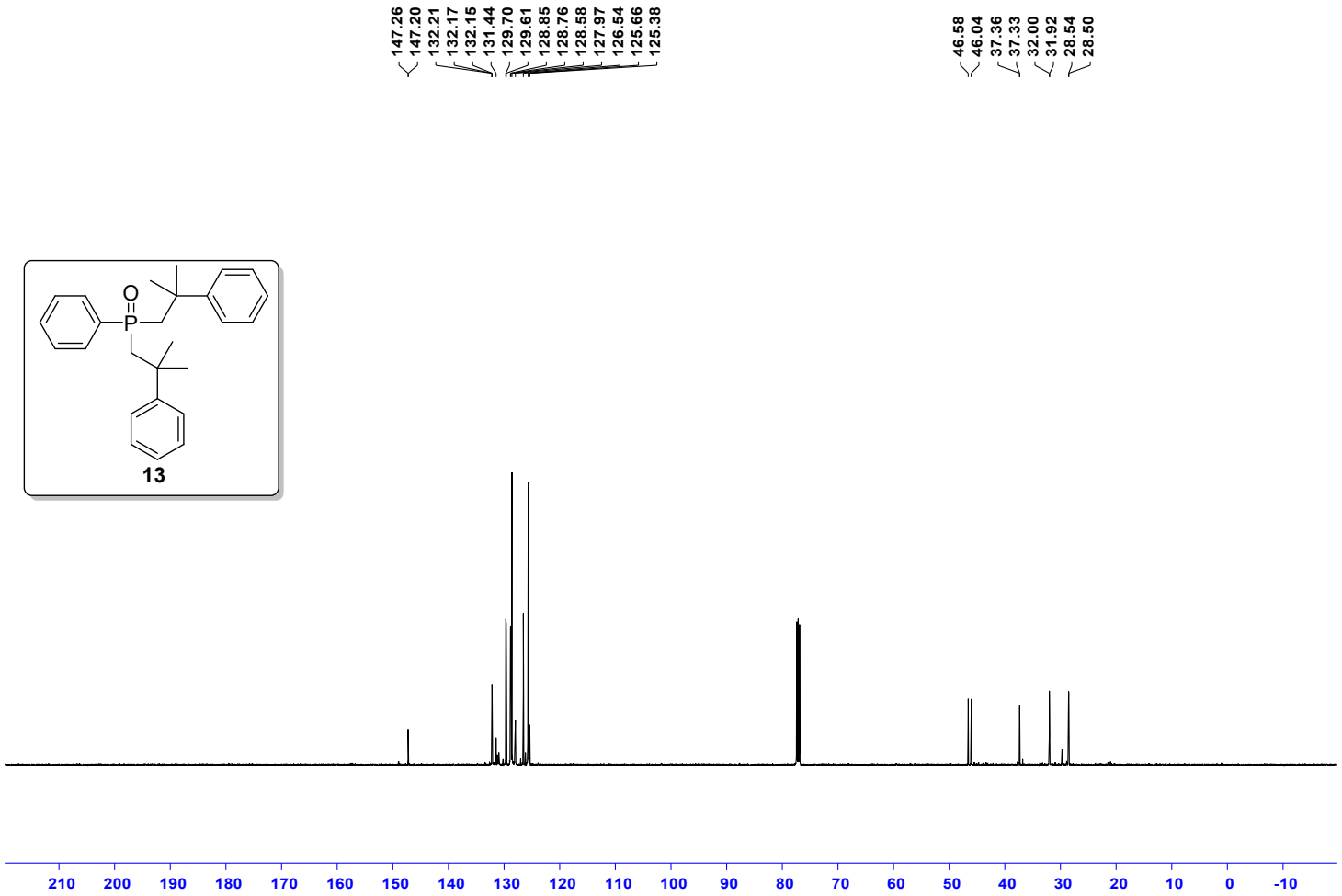


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 13



^{13}C NMR (126 MHz, $CDCl_3$) spectra for 13

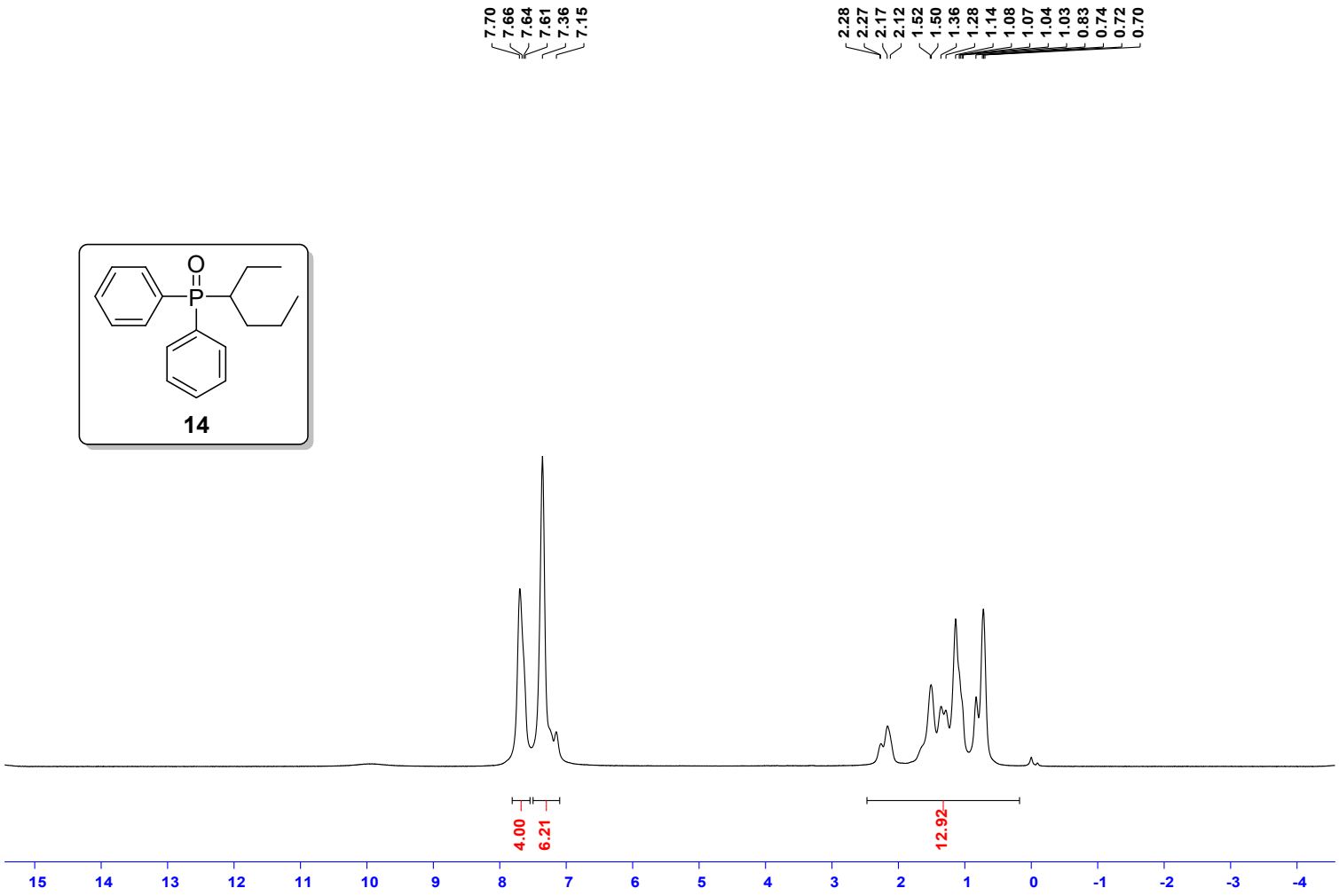
LHC-X230826-1PhBu.2.fid — 1H NMR (400 MHz, CDCl3)



^{31}P NMR (202 MHz, $CDCl_3$) spectra for 13

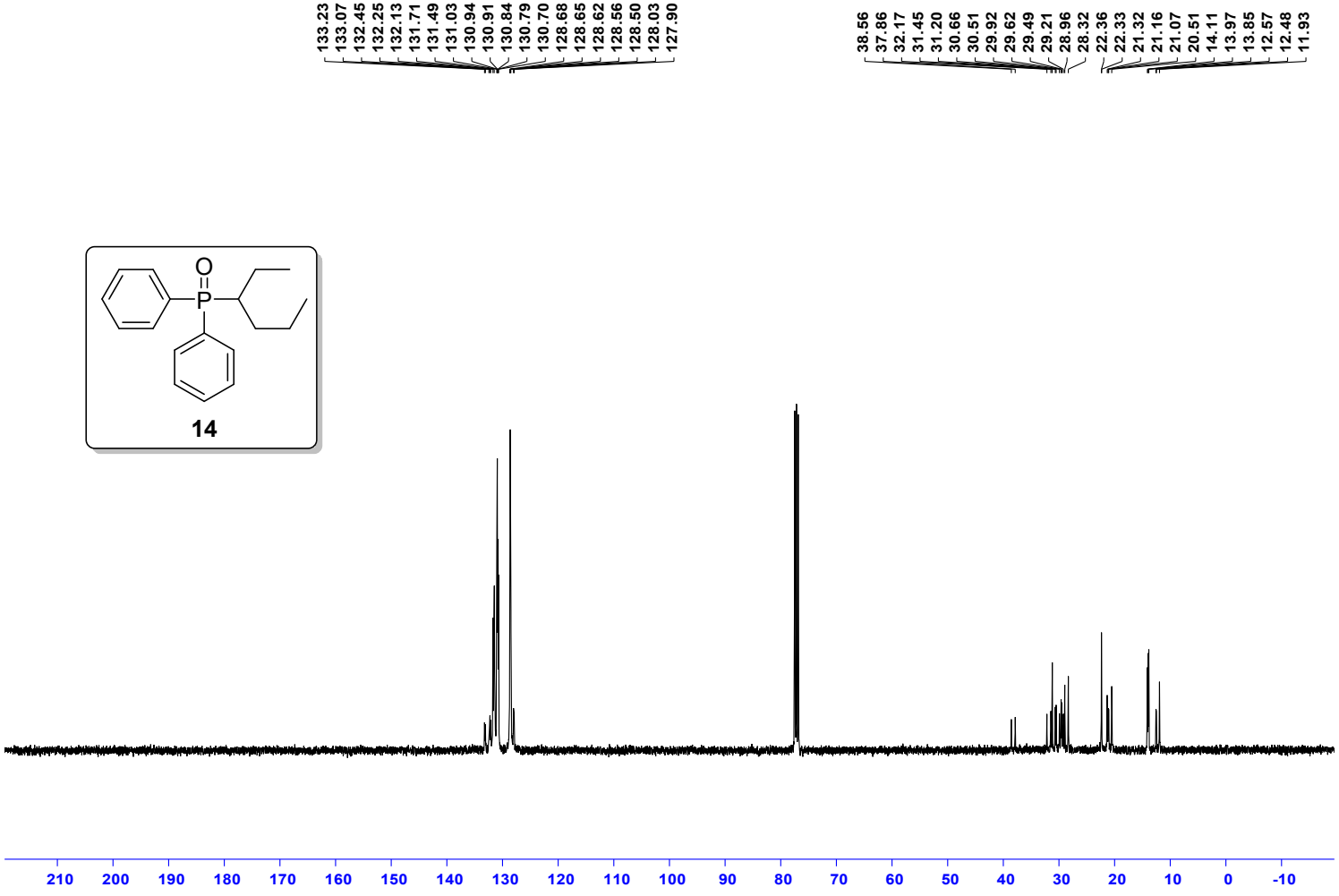
lhc-x230824-2.12.fid — 1H NMR (400 MHz, CDCl3)

^{1}H NMR (400 MHz, $CDCl_3$) spectra for 14



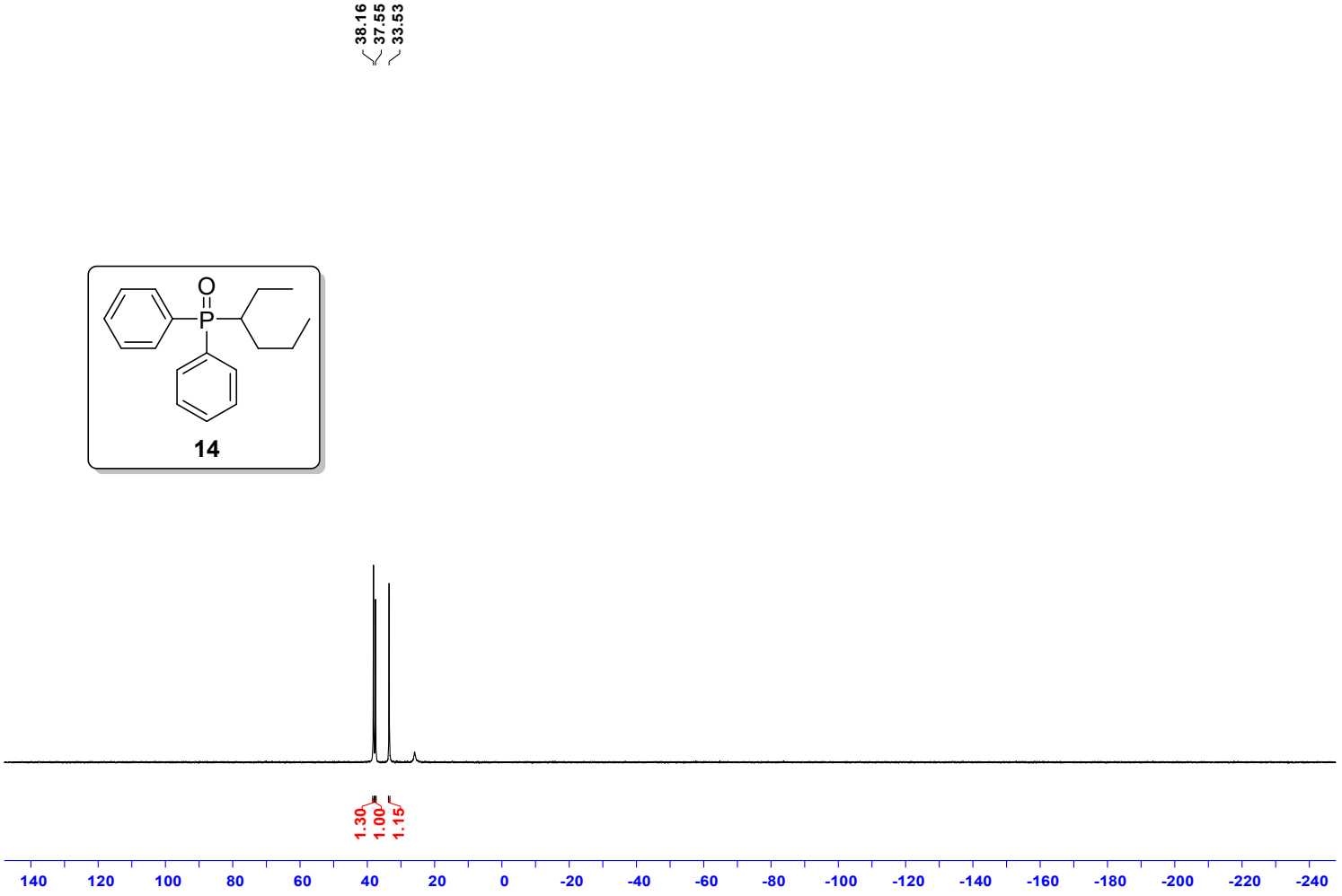
^{13}C NMR (101 MHz, CDCl3) spectra for 14

lhc-x22z11-1hexane.2.fid — 1H NMR (400 MHz, CDCl3)

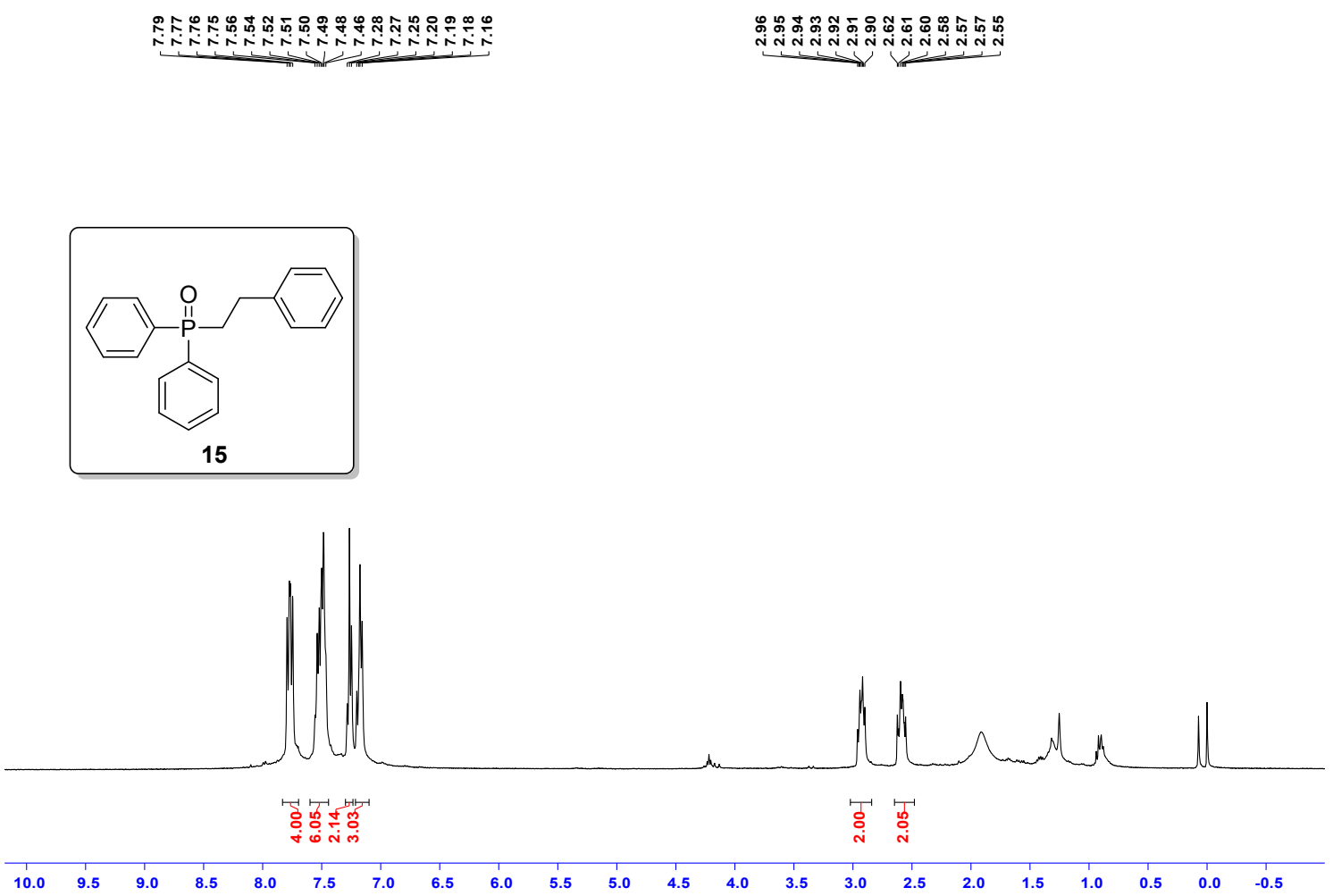


^{31}P NMR (162 MHz, $CDCl_3$) spectra for 14

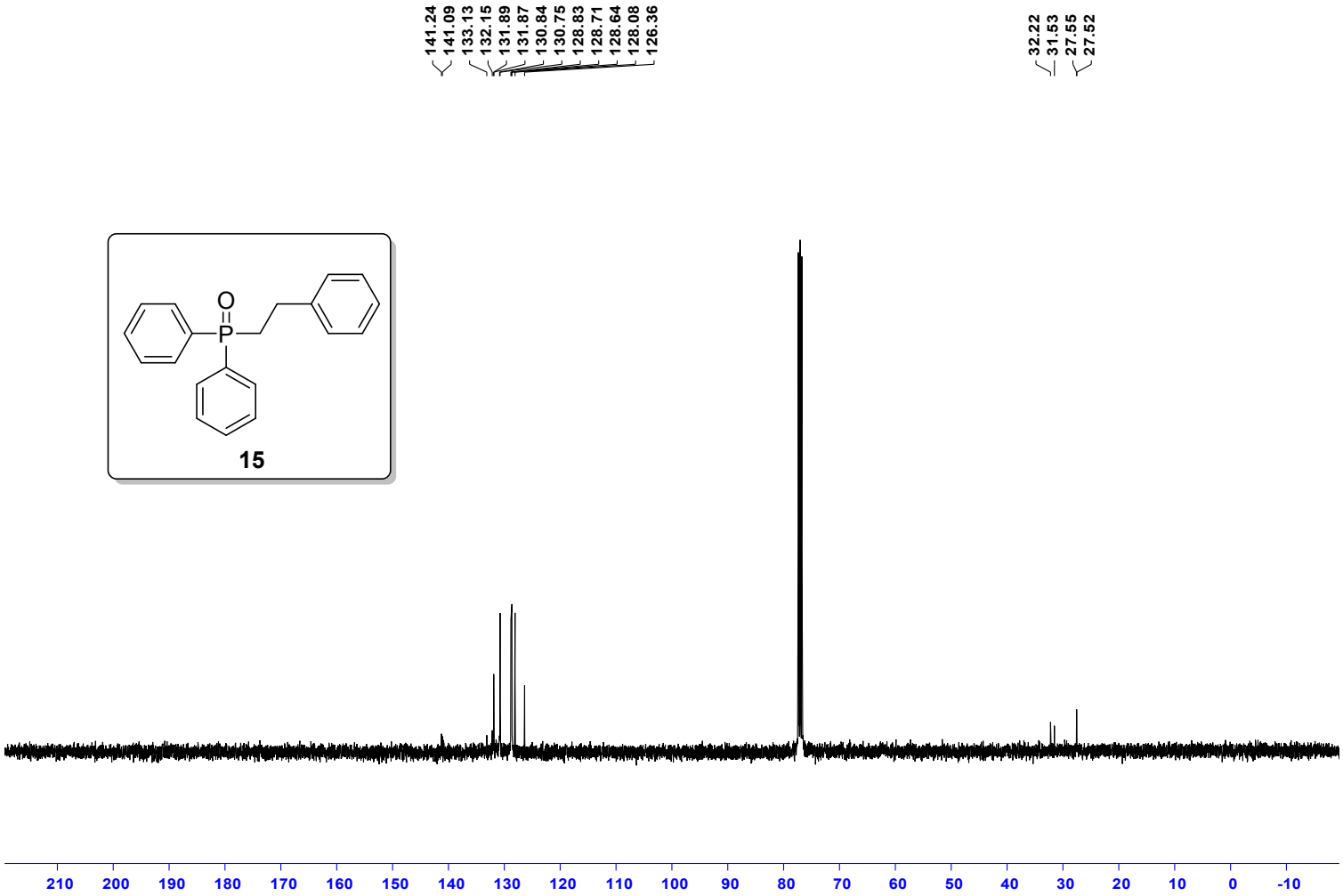
lhc-x22z11-1hexane.3.fid — 1H NMR (400 MHz, CDCl3)



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 15

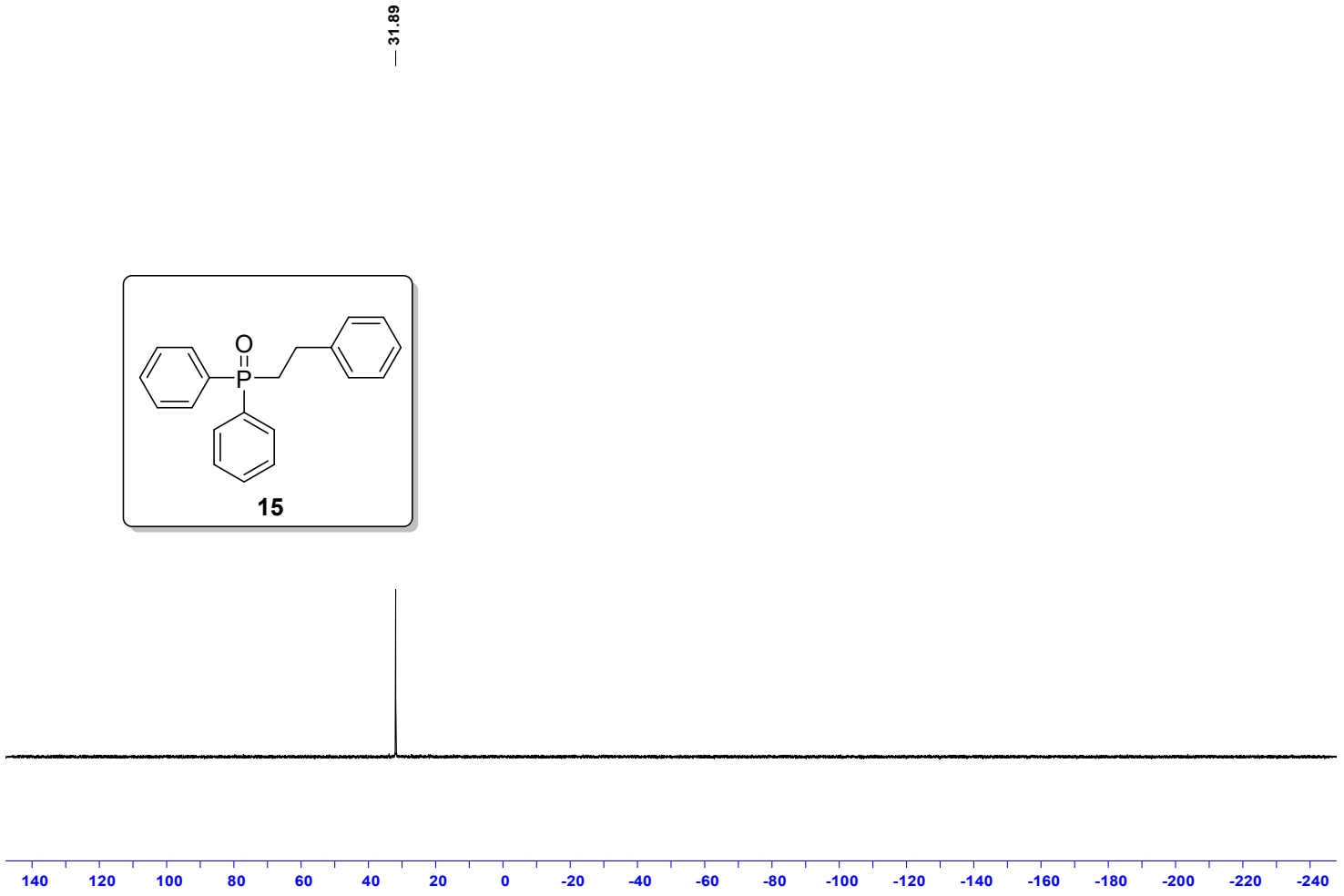


^{13}C NMR (101 MHz, CDCl3) spectra for 15

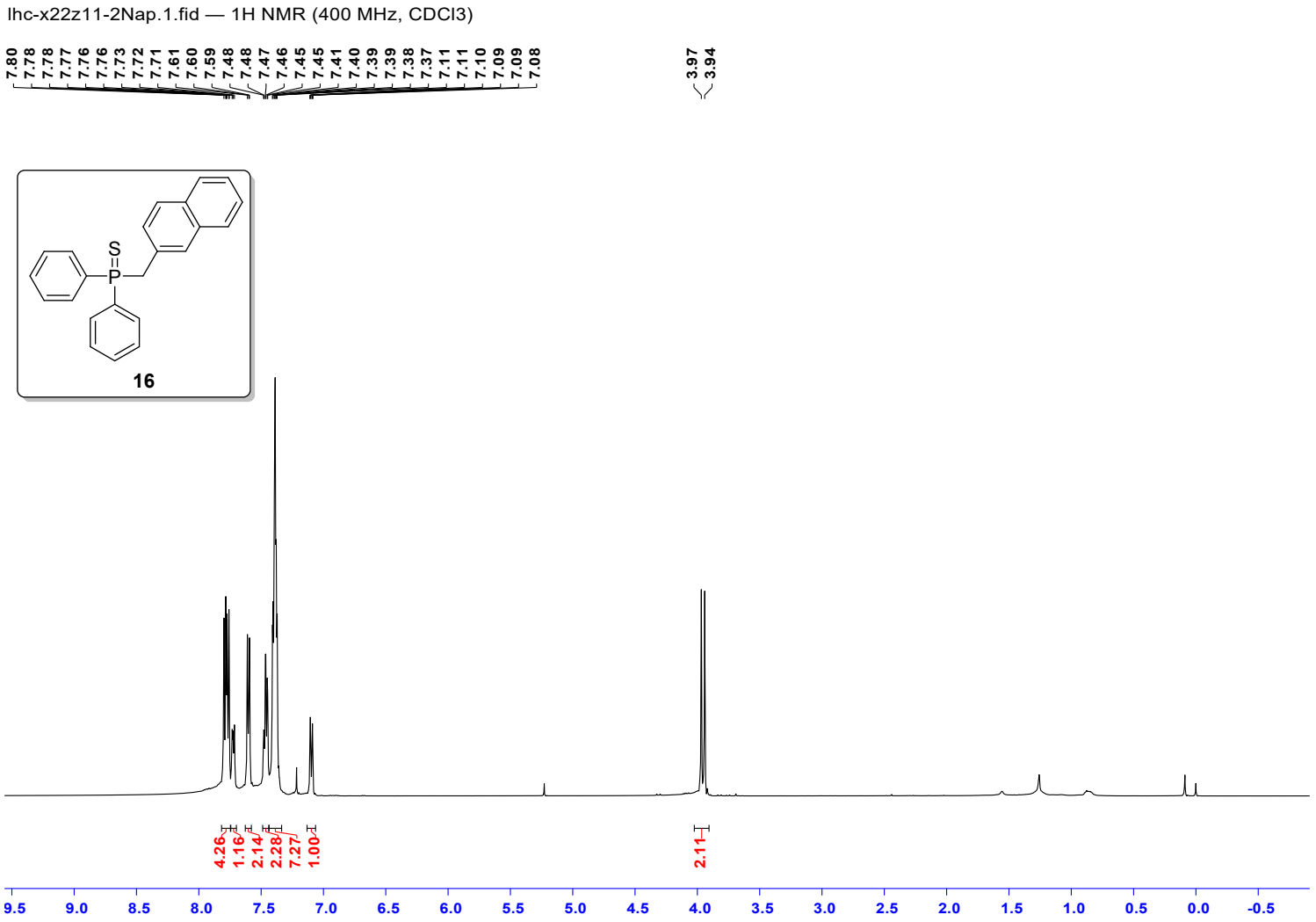


^{31}P NMR (162 MHz, $CDCl_3$) spectra for 15

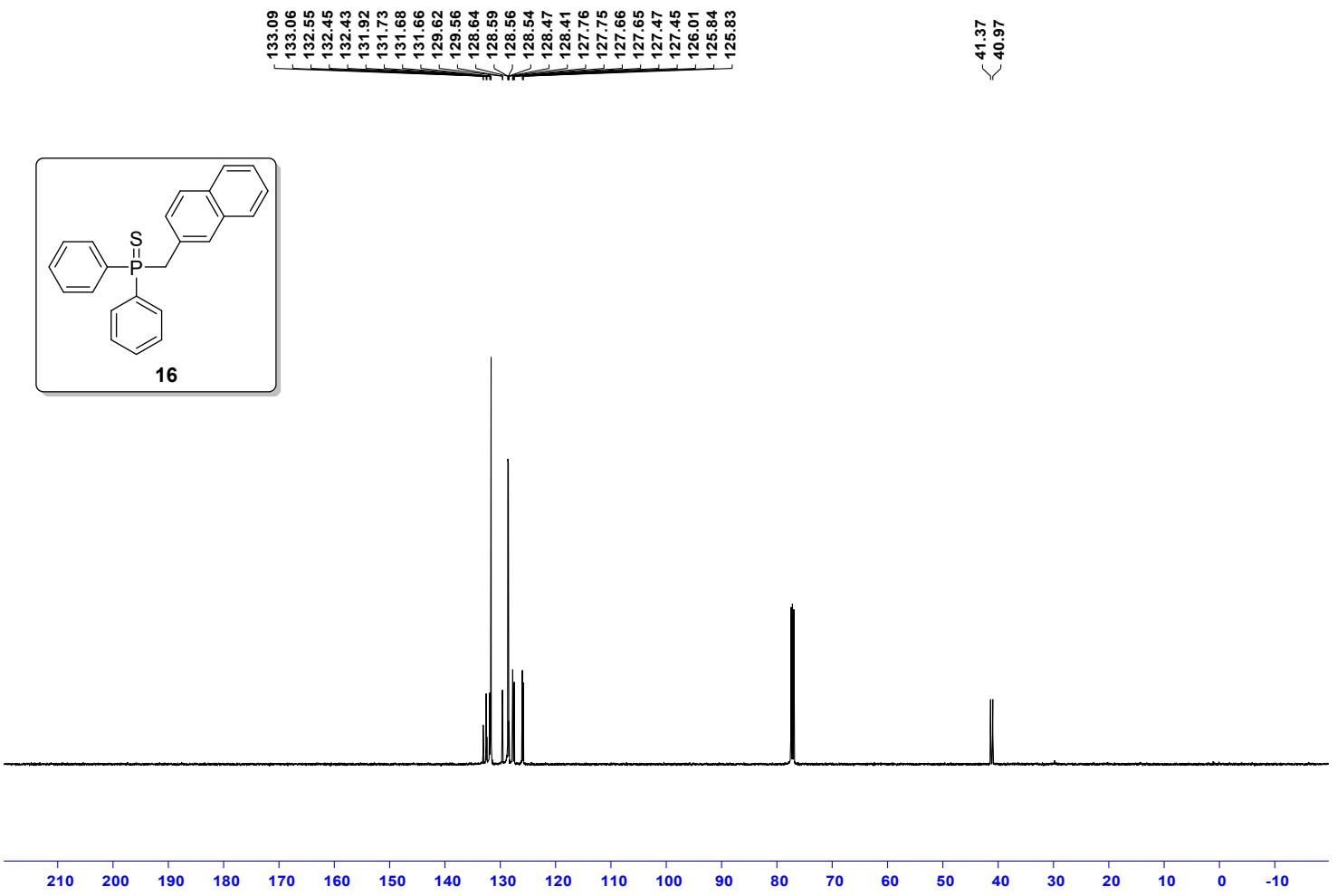
lhc-x230822-2.12.fid — 1H NMR (400 MHz, CDCl3)



^{1}H NMR (500 MHz, $CDCl_3$) spectra for 16

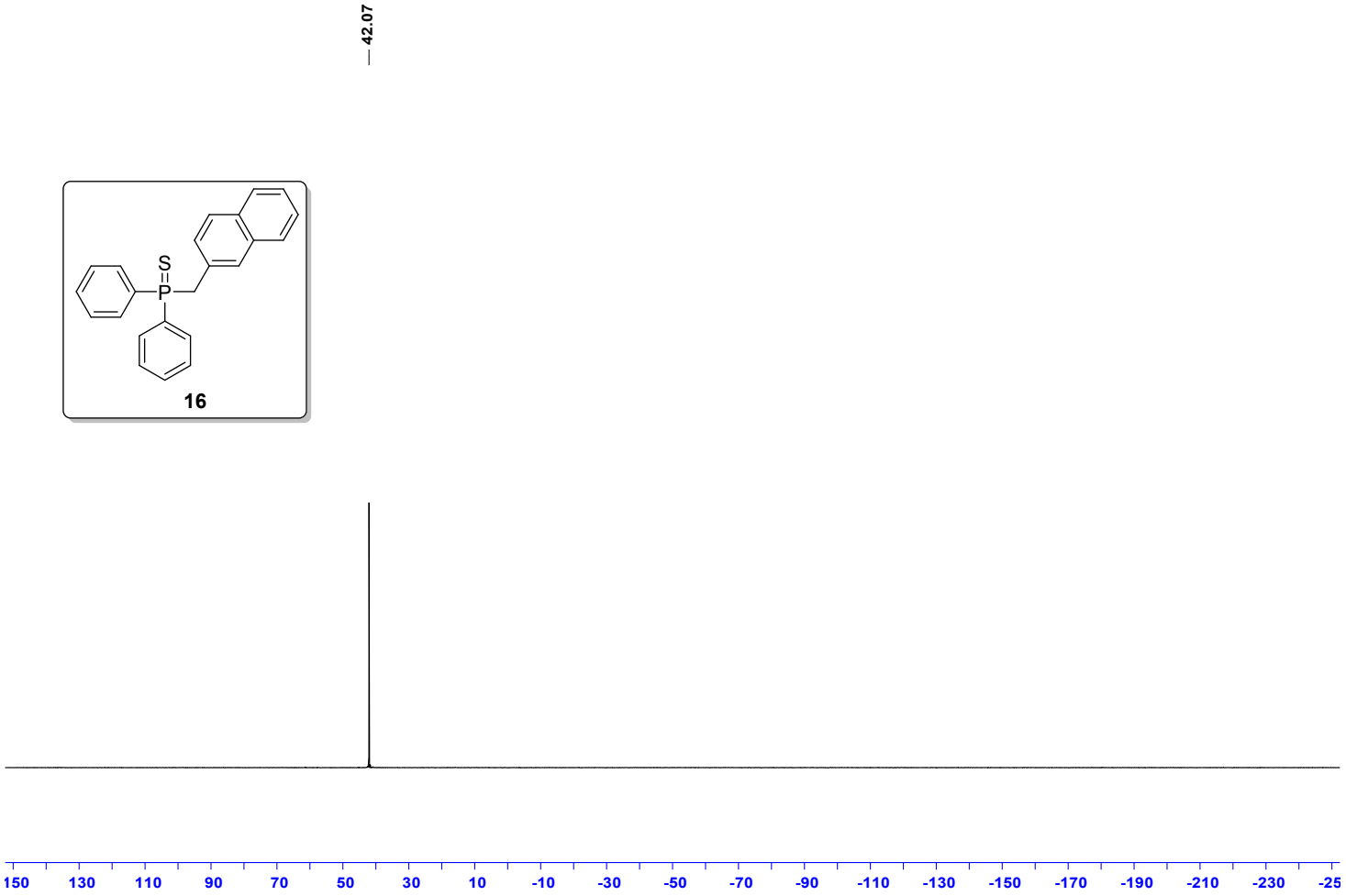


^{13}C NMR (126 MHz, CDCl3) spectra for 16



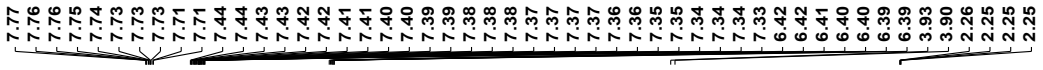
^{2031}P NMR (202 MHz, $CDCl_3$) spectra for 16

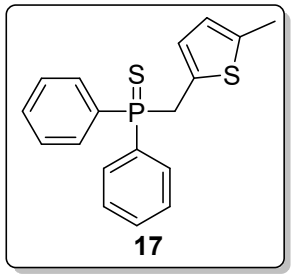
lhc-x22z11-2Nap.3.fid — 1H NMR (400 MHz, CDCl3)

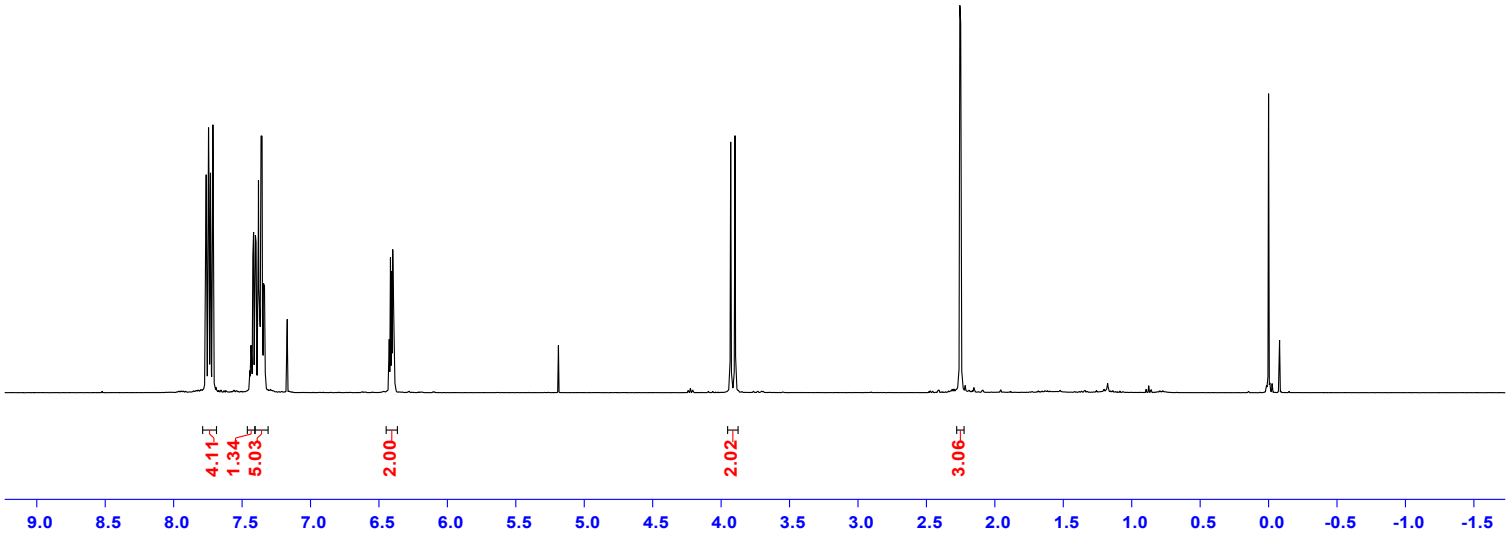


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 17

lhc-x22z04-8saifen.1.fid — 1H NMR (400 MHz, CDCl3)

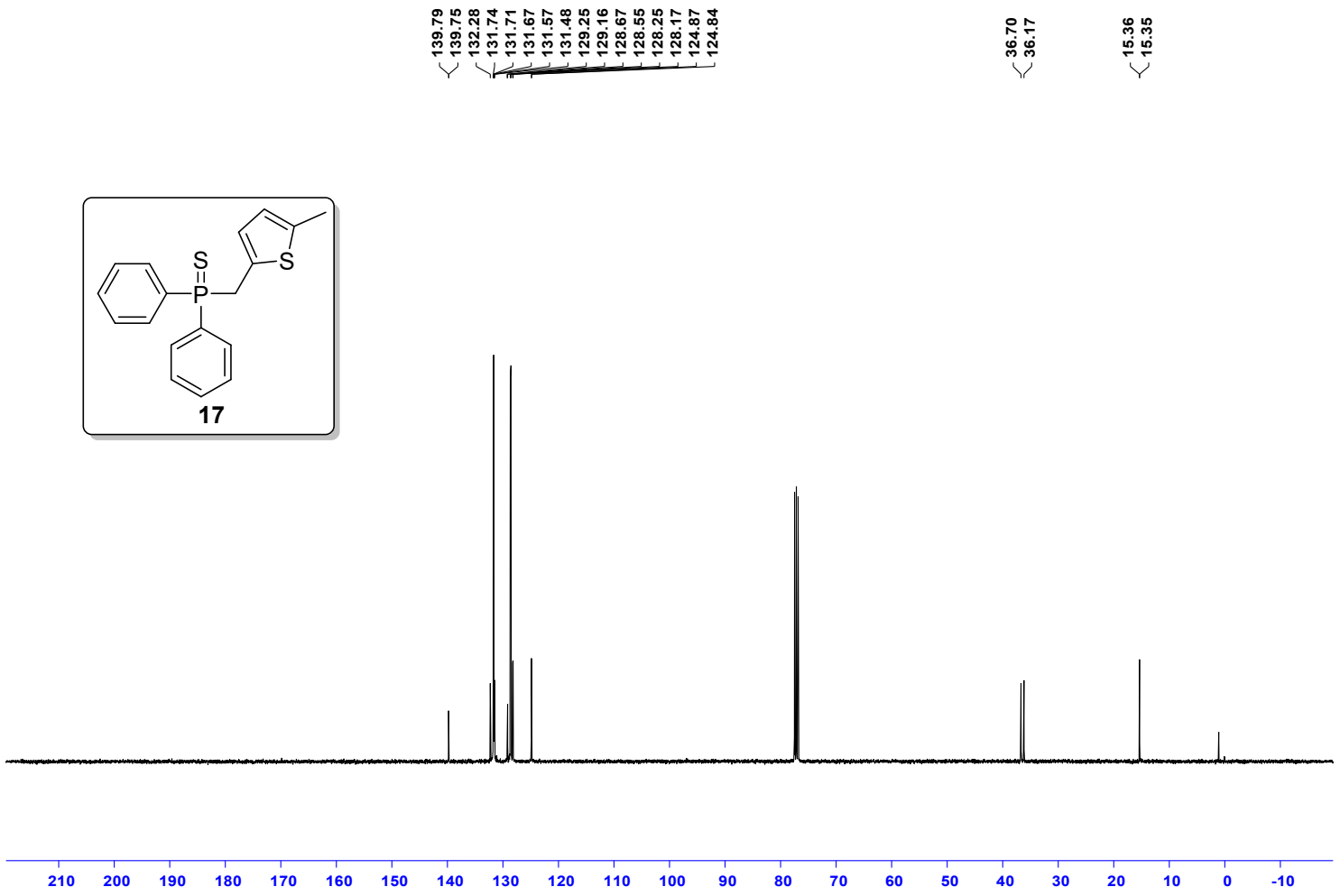






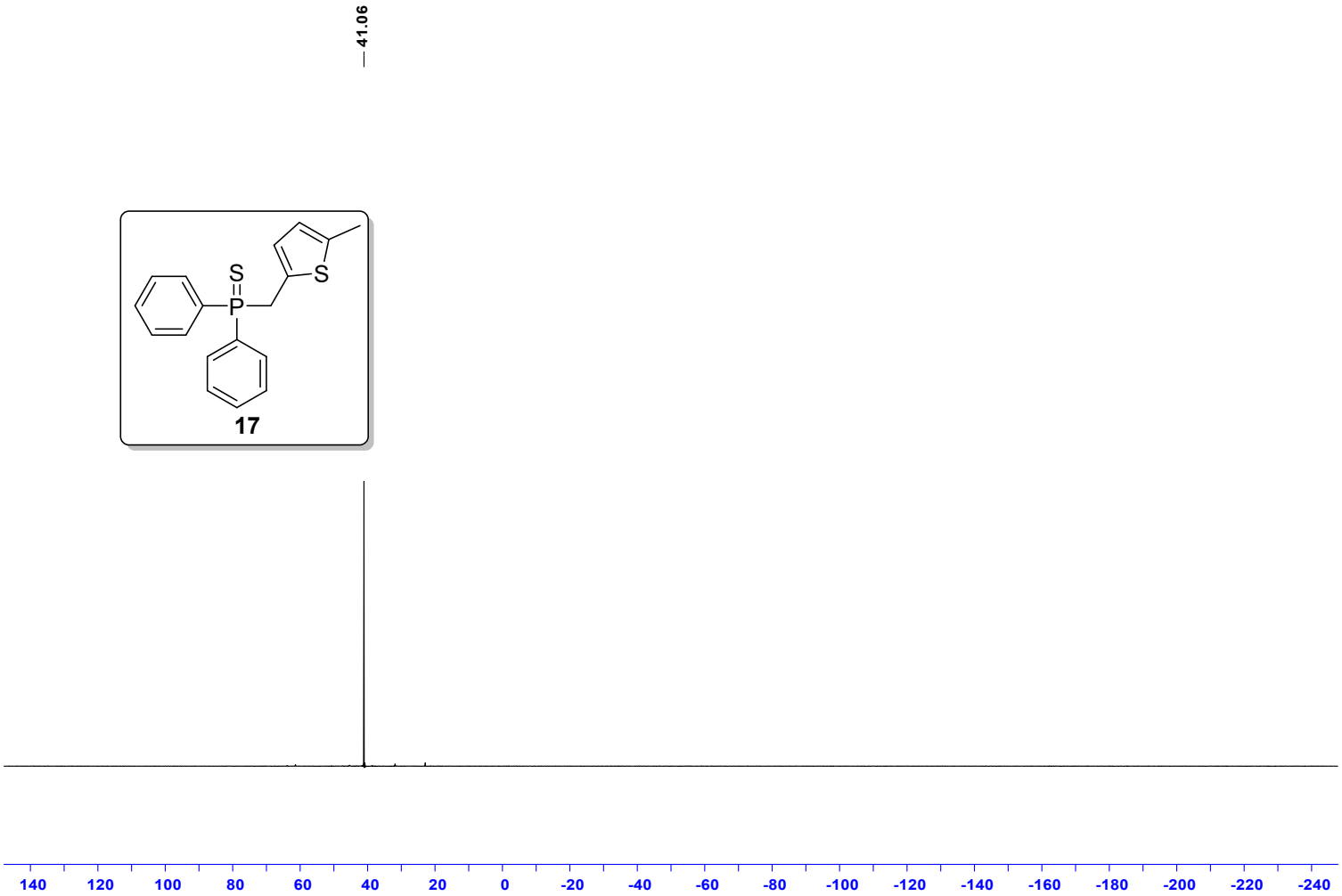
^{13}C NMR (101 MHz, CDCl3) spectra for 17

lhc-x22z04-8saifen.2.fid — 1H NMR (400 MHz, CDCl3)



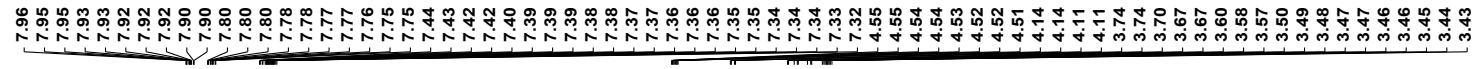
^{31}P NMR (162 MHz, $CDCl_3$) spectra for 17

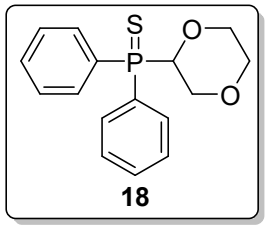
lhc-x22z04-8saifen.3.fid — 1H NMR (400 MHz, CDCl3)



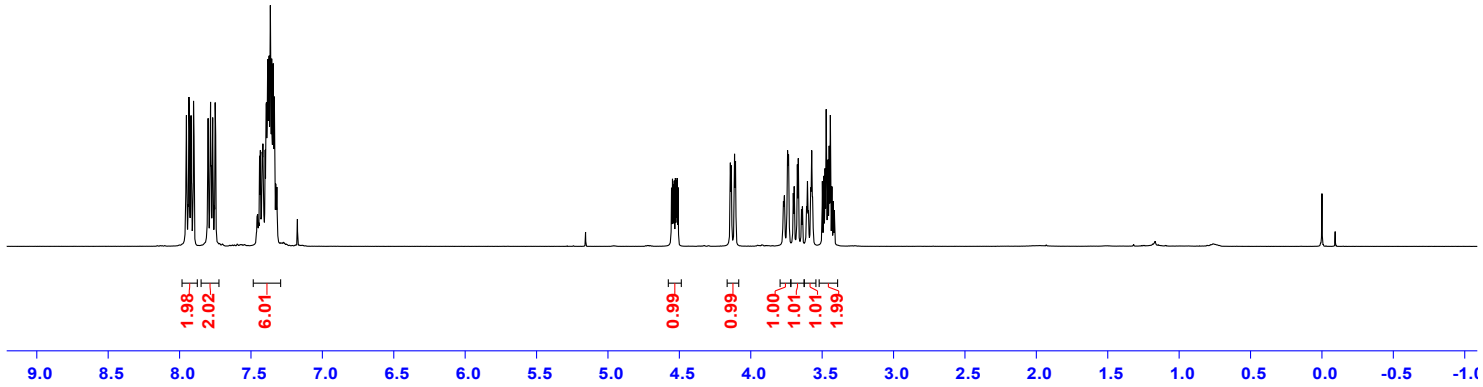
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 18

lhc-x22z04-4dioxane.1.fid — 1H NMR (400 MHz, CDCl3)



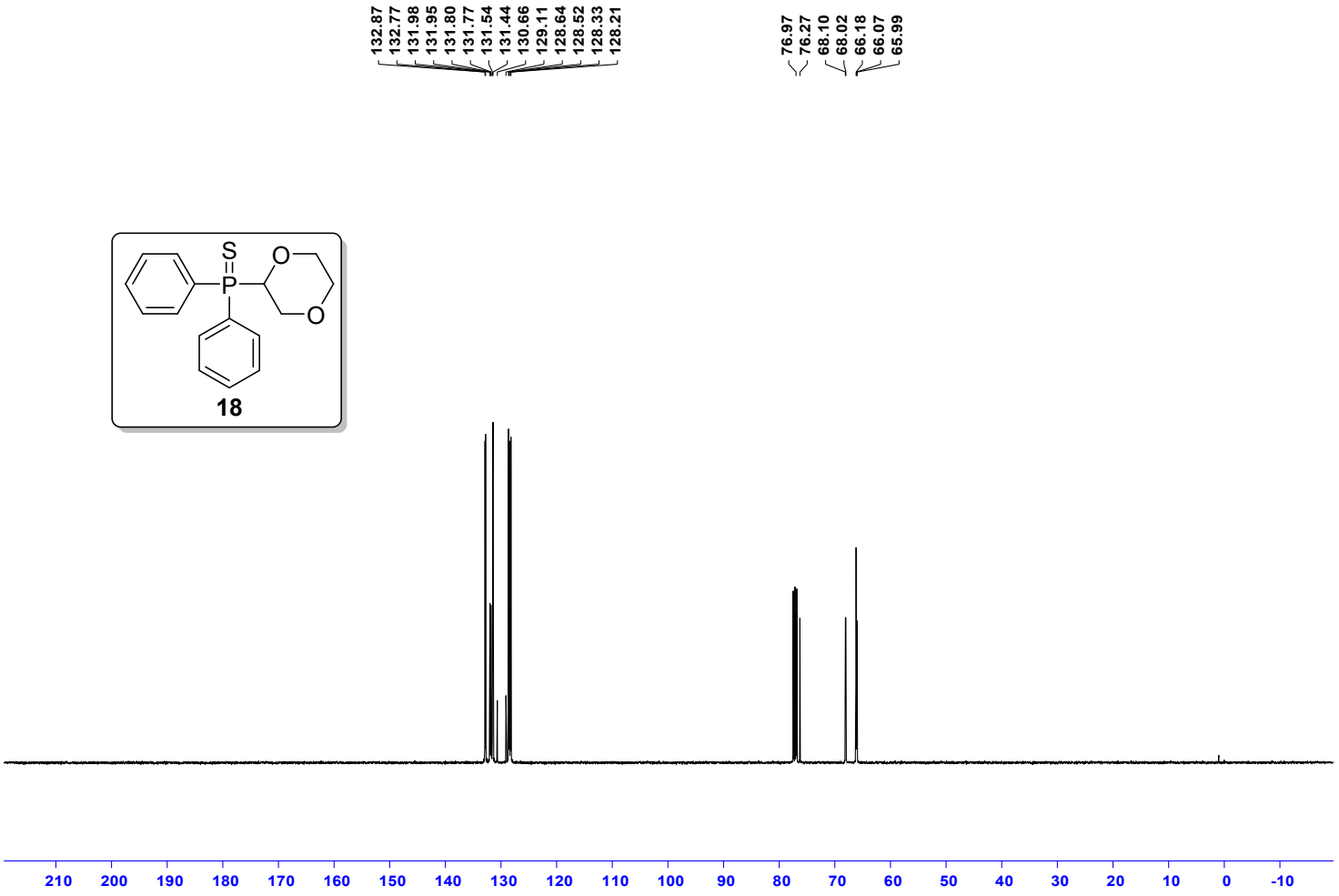


18



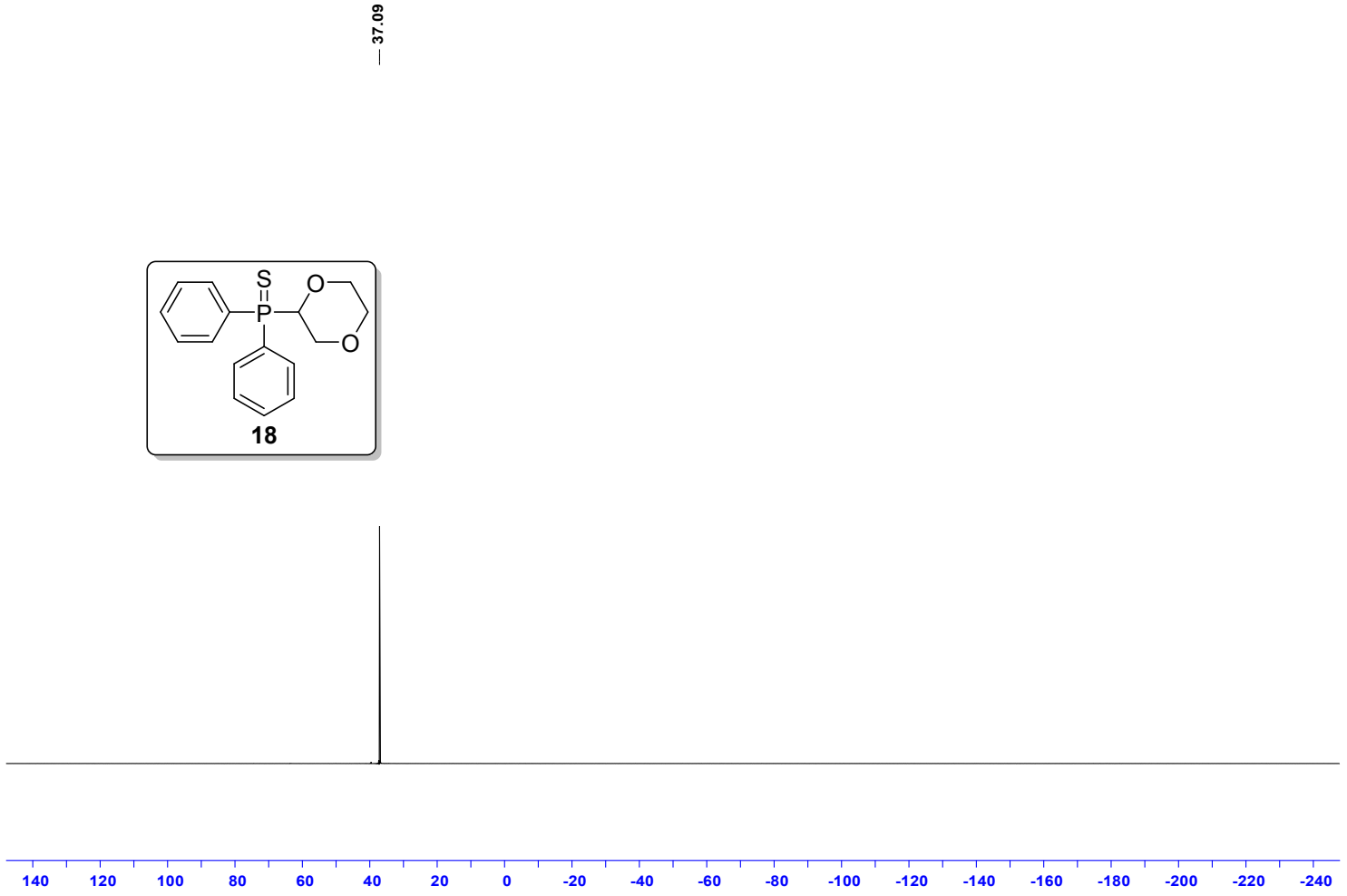
^{13}C NMR (101 MHz, CDCl3) spectra for 18

lhc-x22z04-4dioxane.2.fid — 1H NMR (400 MHz, CDCl3)



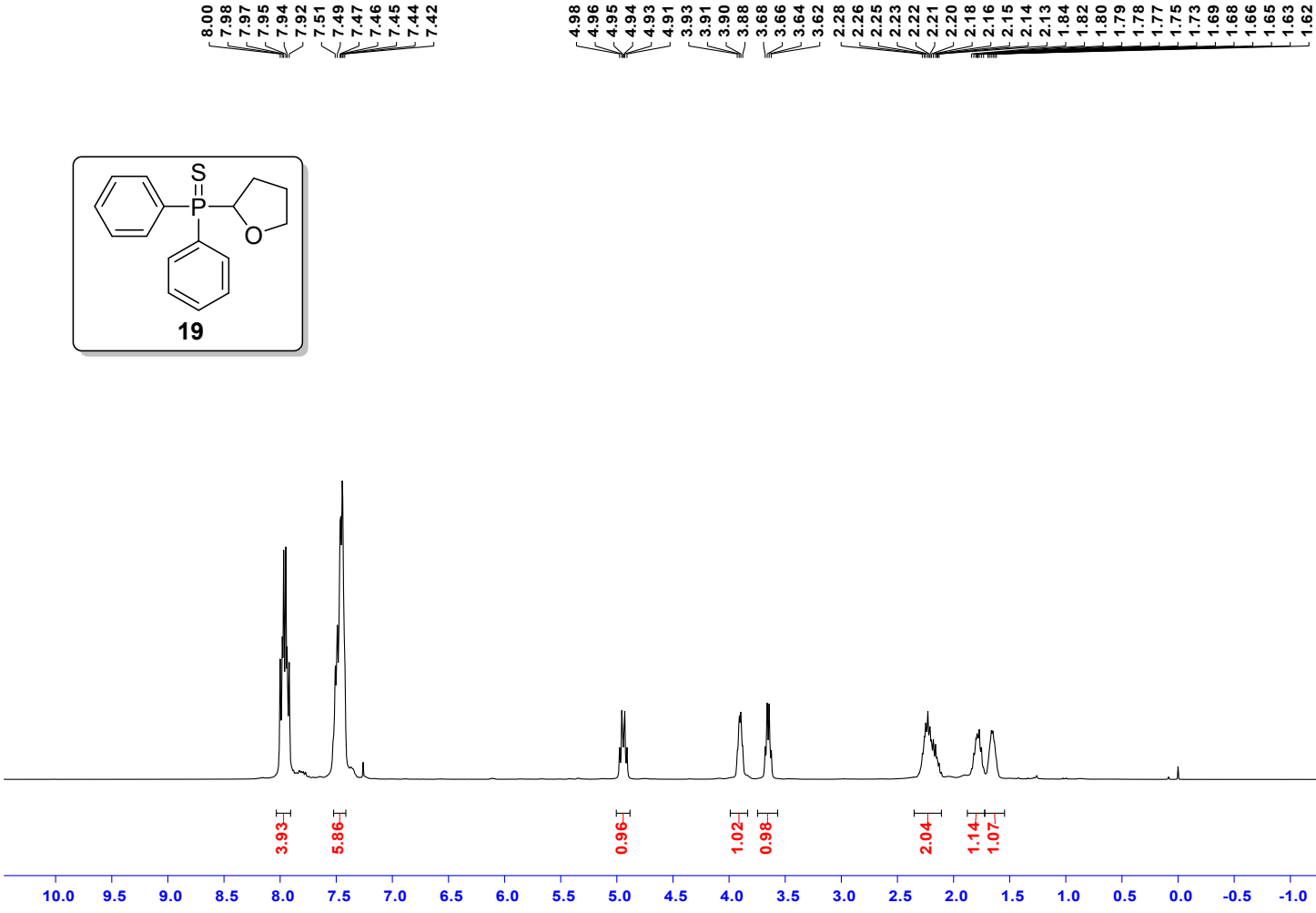
^{31}P NMR (162 MHz, $CDCl_3$) spectra for 18

lhc-x22z04-4dioxane.3.fid — 1H NMR (400 MHz, CDCl3)

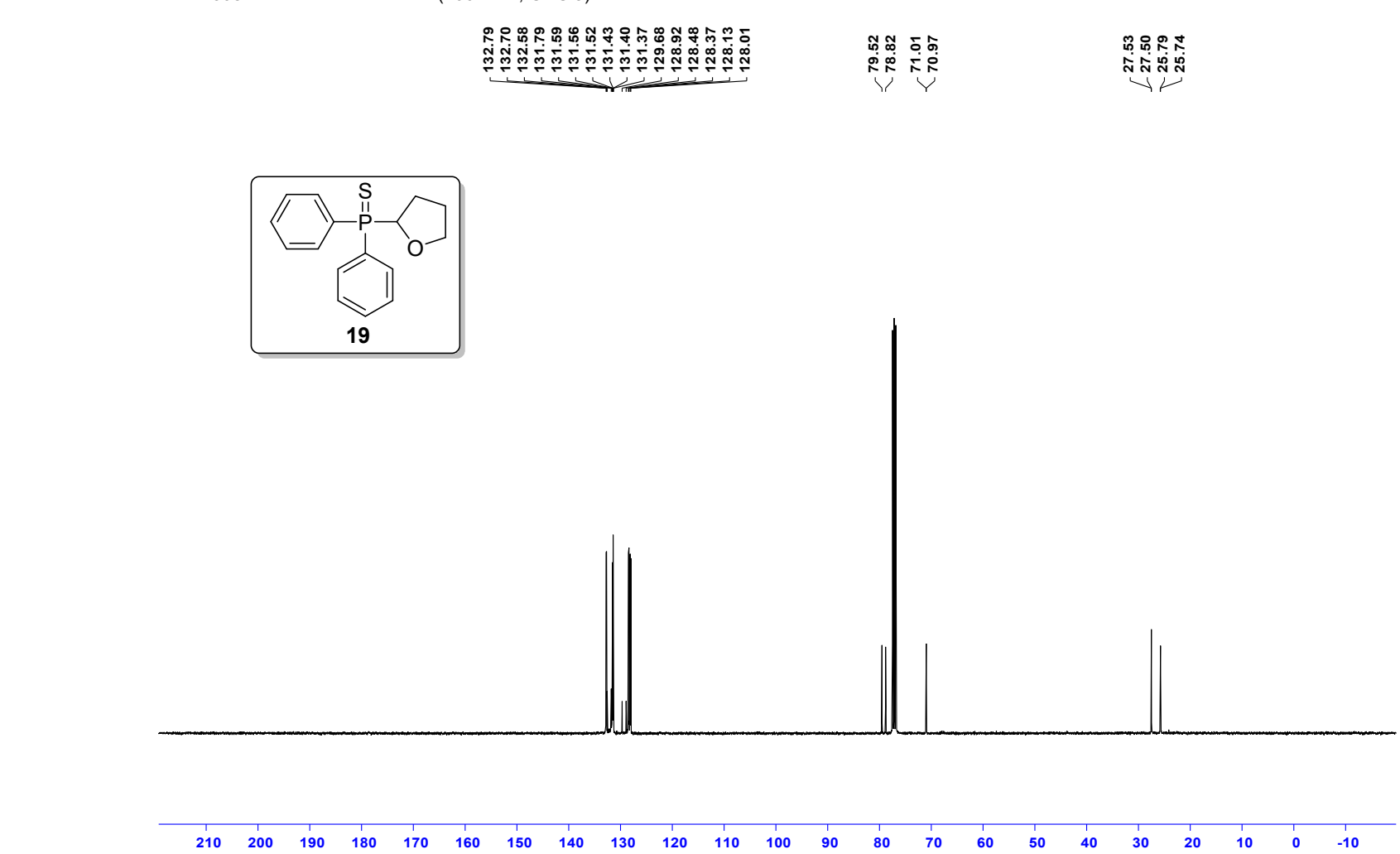


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 19

lhc-x230824-1.10.fid — 1H NMR (400 MHz, CDCl3)

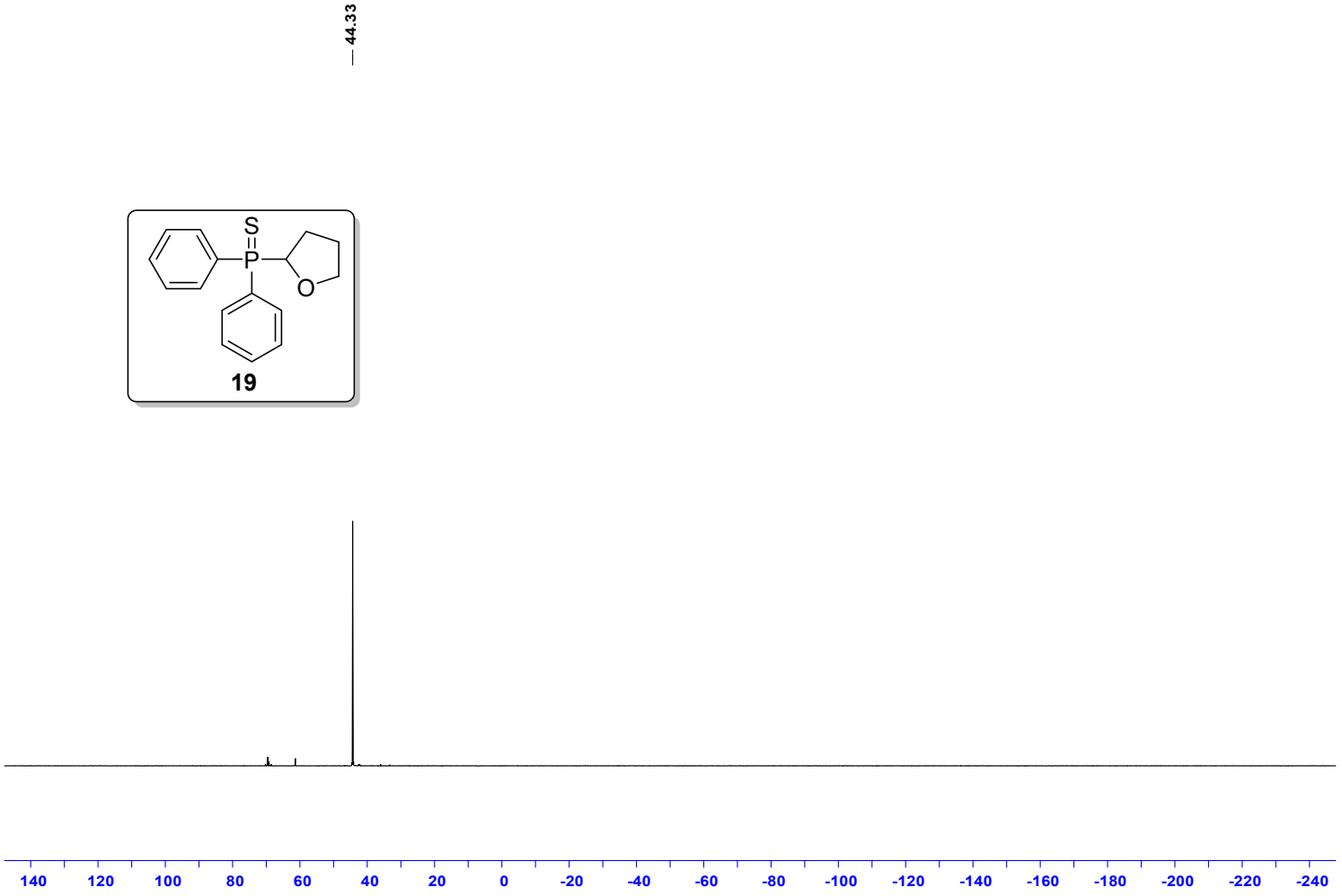


^{13}C NMR (101 MHz, CDCl3) spectra for 19

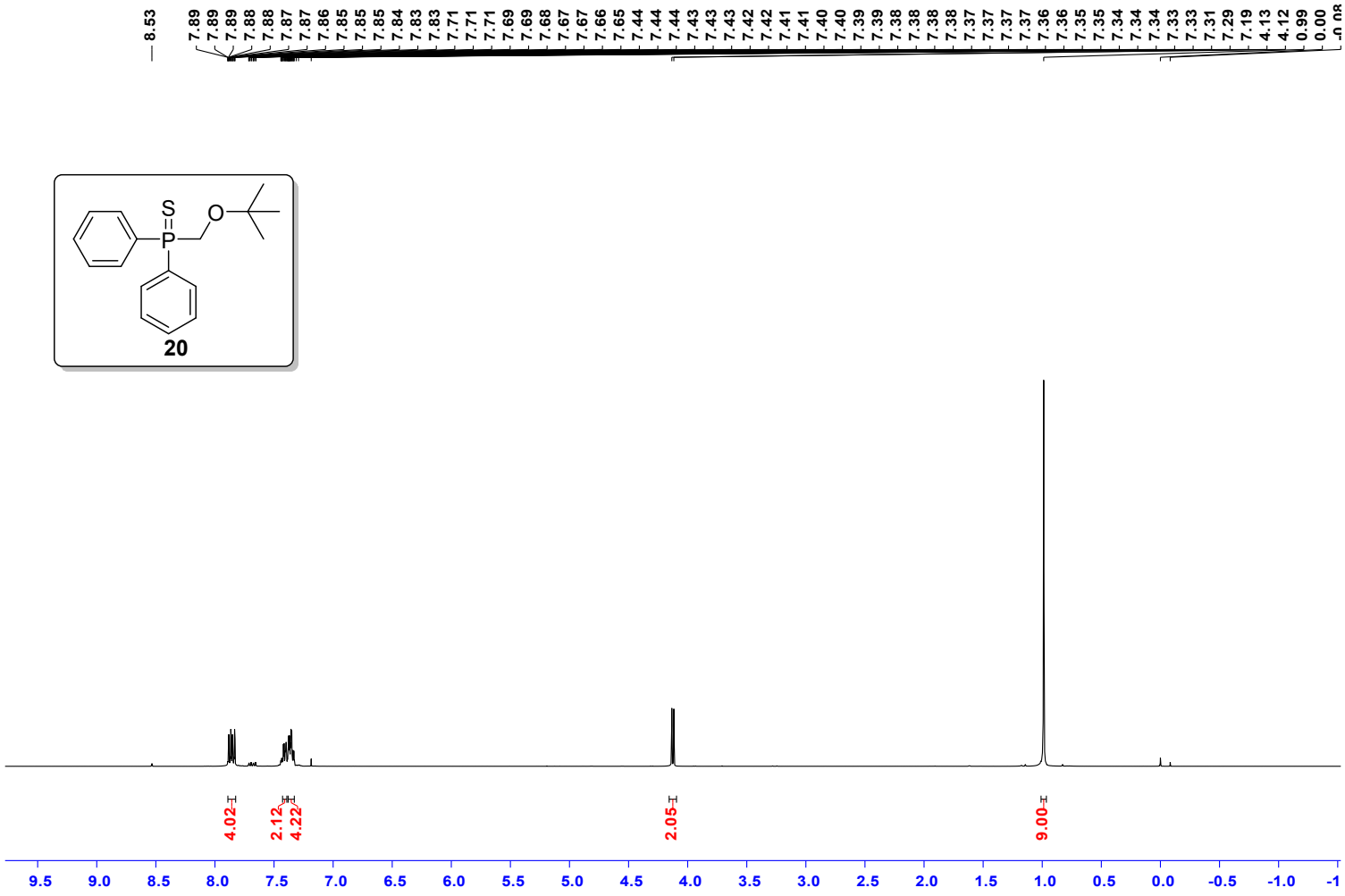


^{31}P NMR (162 MHz, $CDCl_3$) spectra for 19

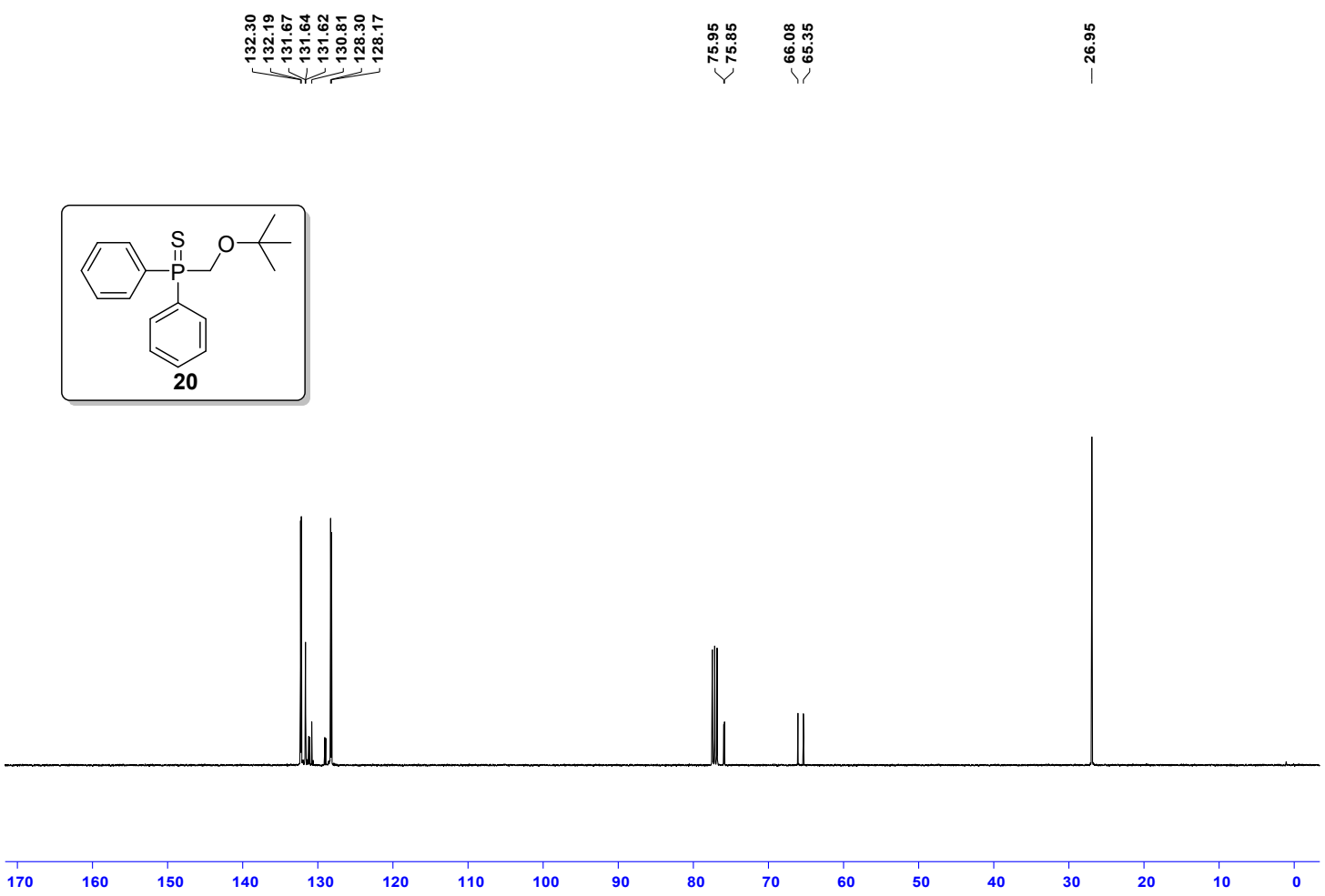
lhc-x230824-1.12.fid — 1H NMR (400 MHz, CDCl3)



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 20

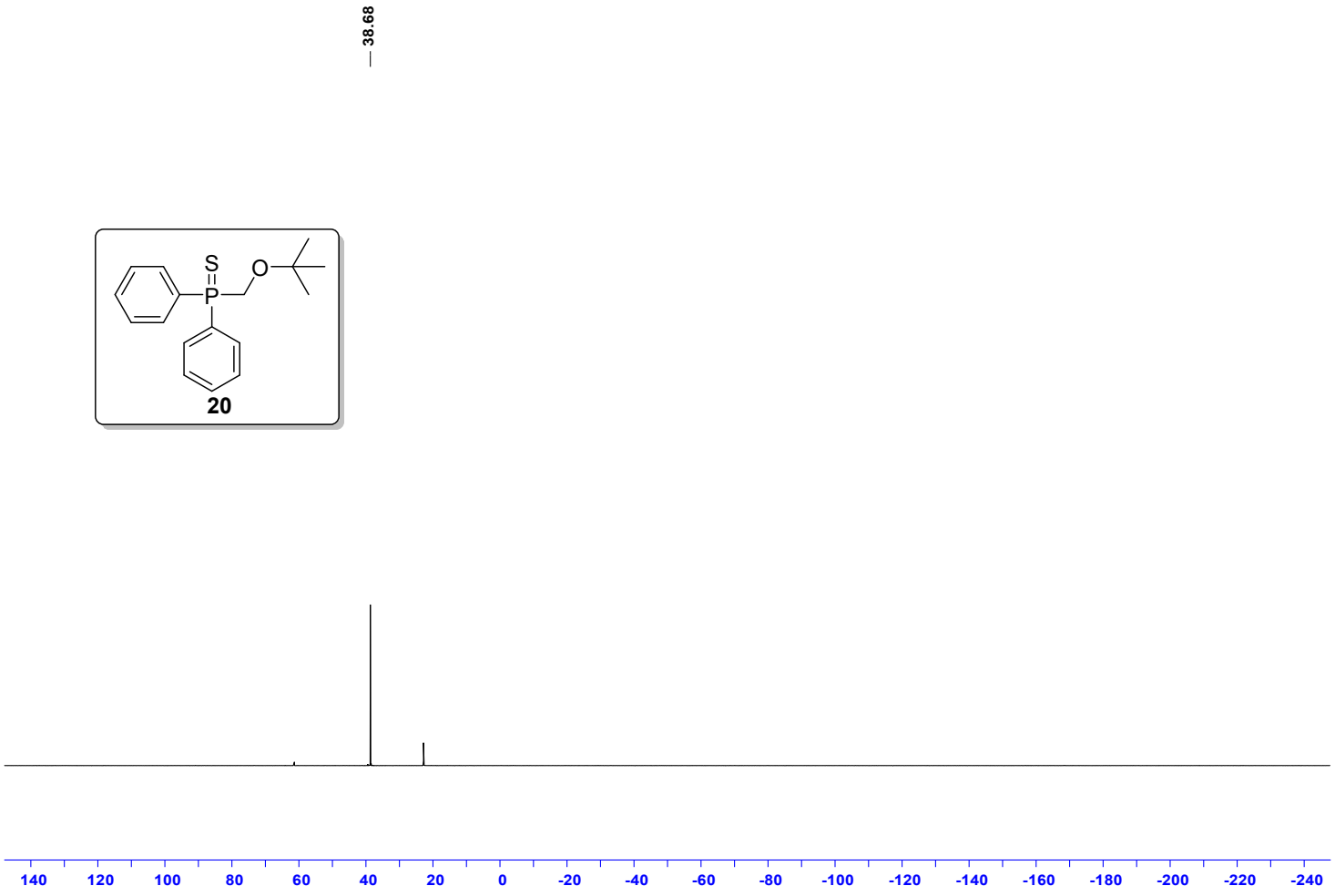


^{13}C NMR (101 MHz, CDCl3) spectra for 20

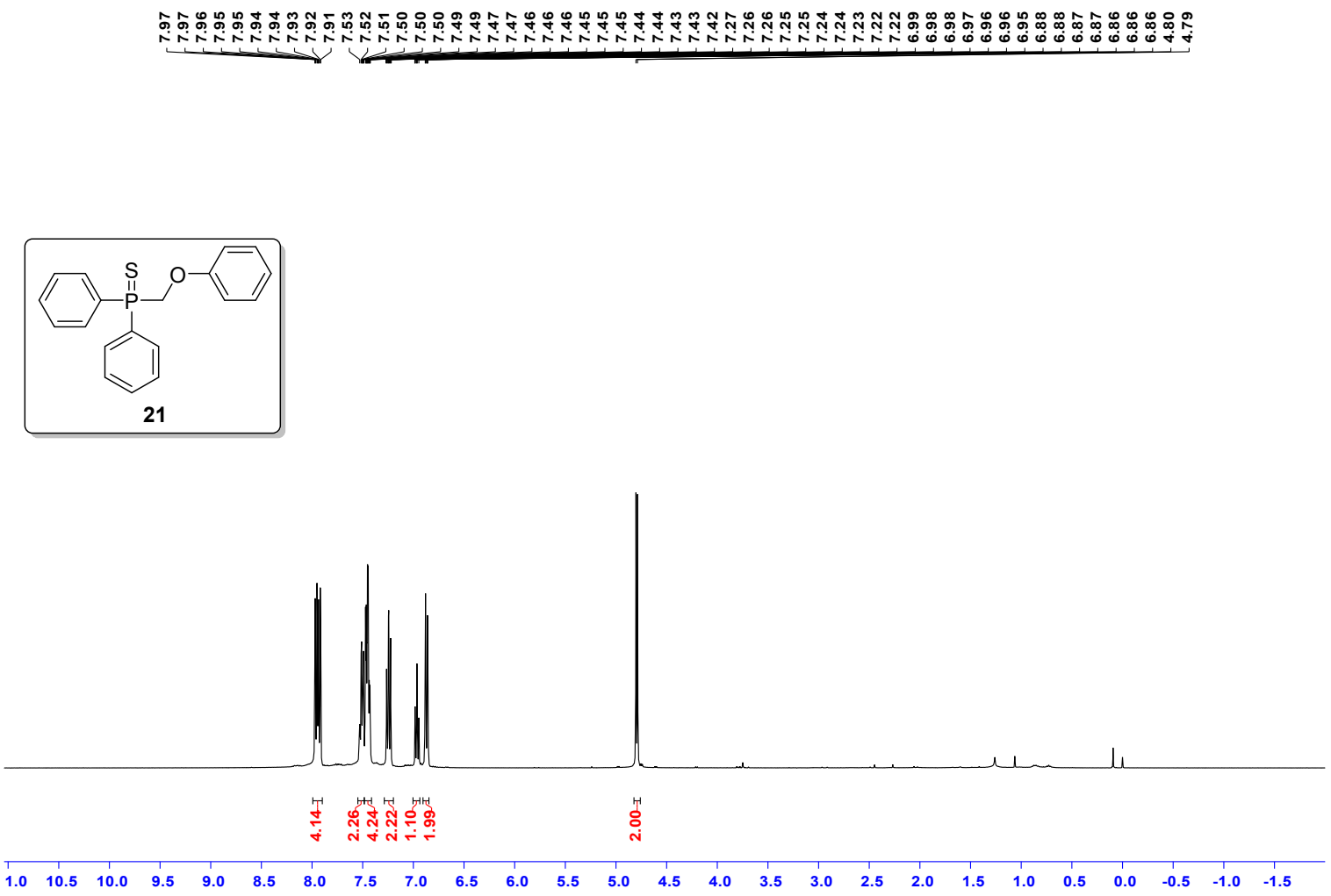


^{31}P NMR (162 MHz, $CDCl_3$) spectra for 20

lhc-x22z04-3tBuOMe.3.fid — 1H NMR (400 MHz, CDCl3)

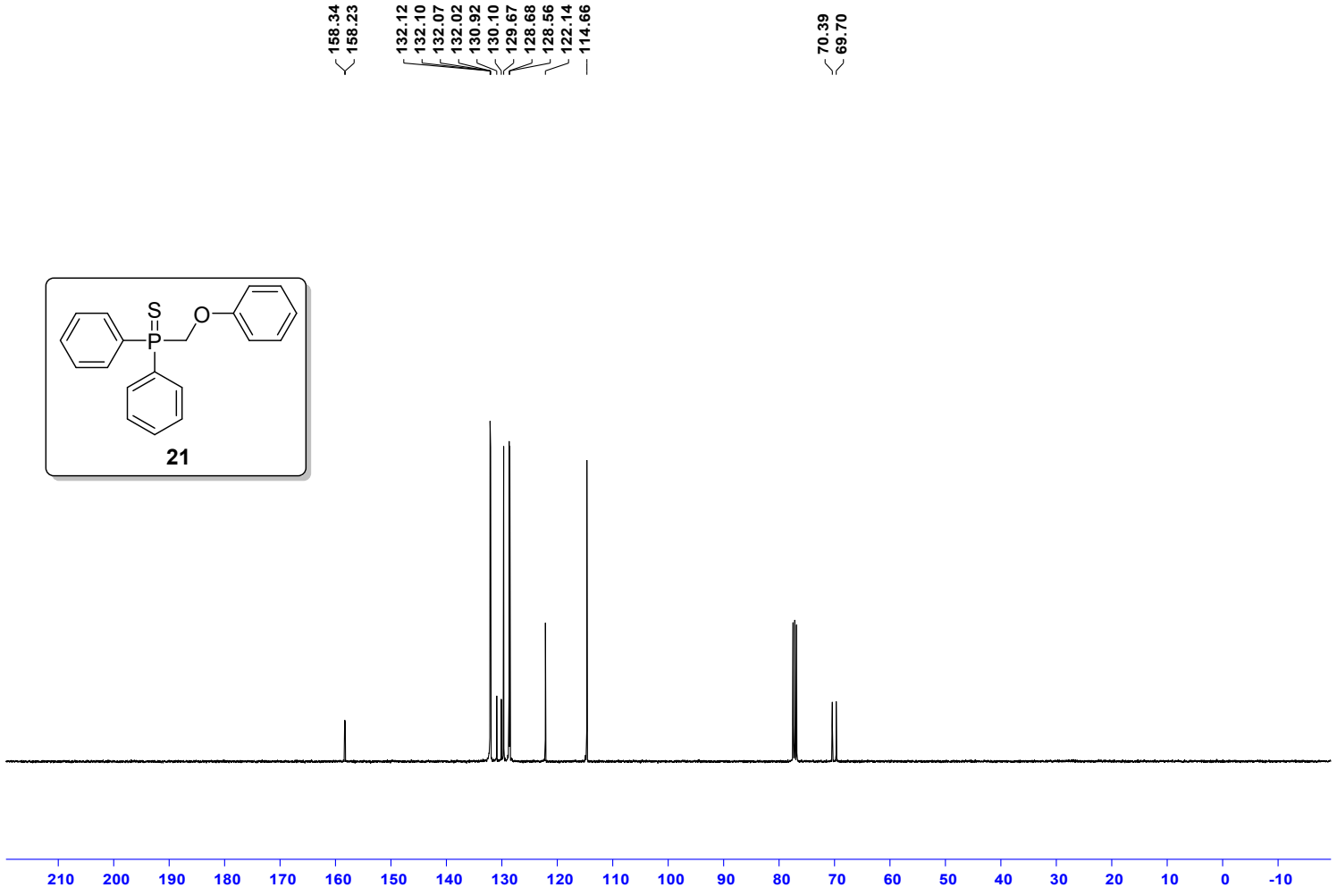


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 21



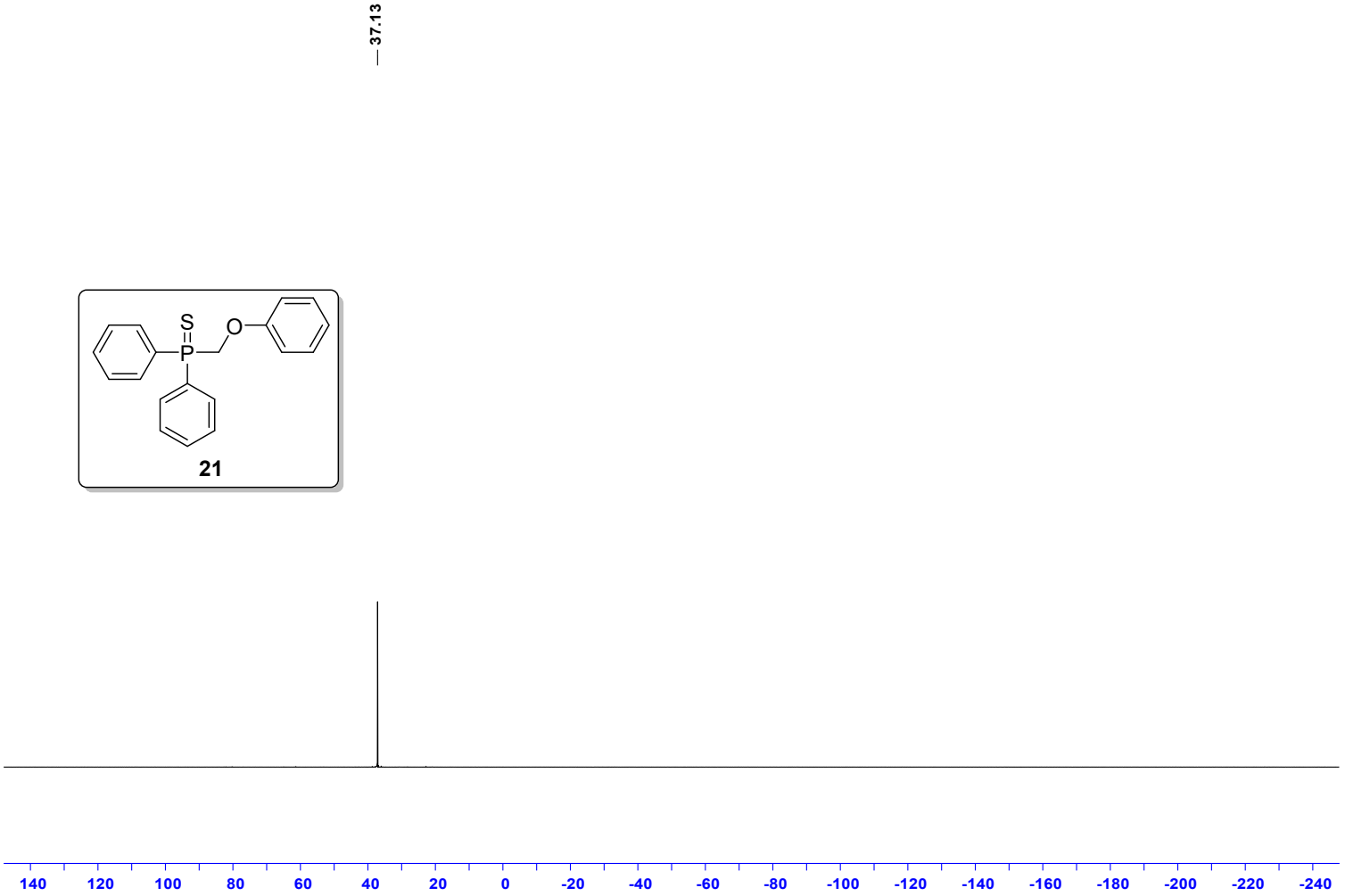
^{13}C NMR (101 MHz, CDCl3) spectra for 21

lhc-x22z17-1PhOMe.2.fid — 1H NMR (400 MHz, CDCl3)

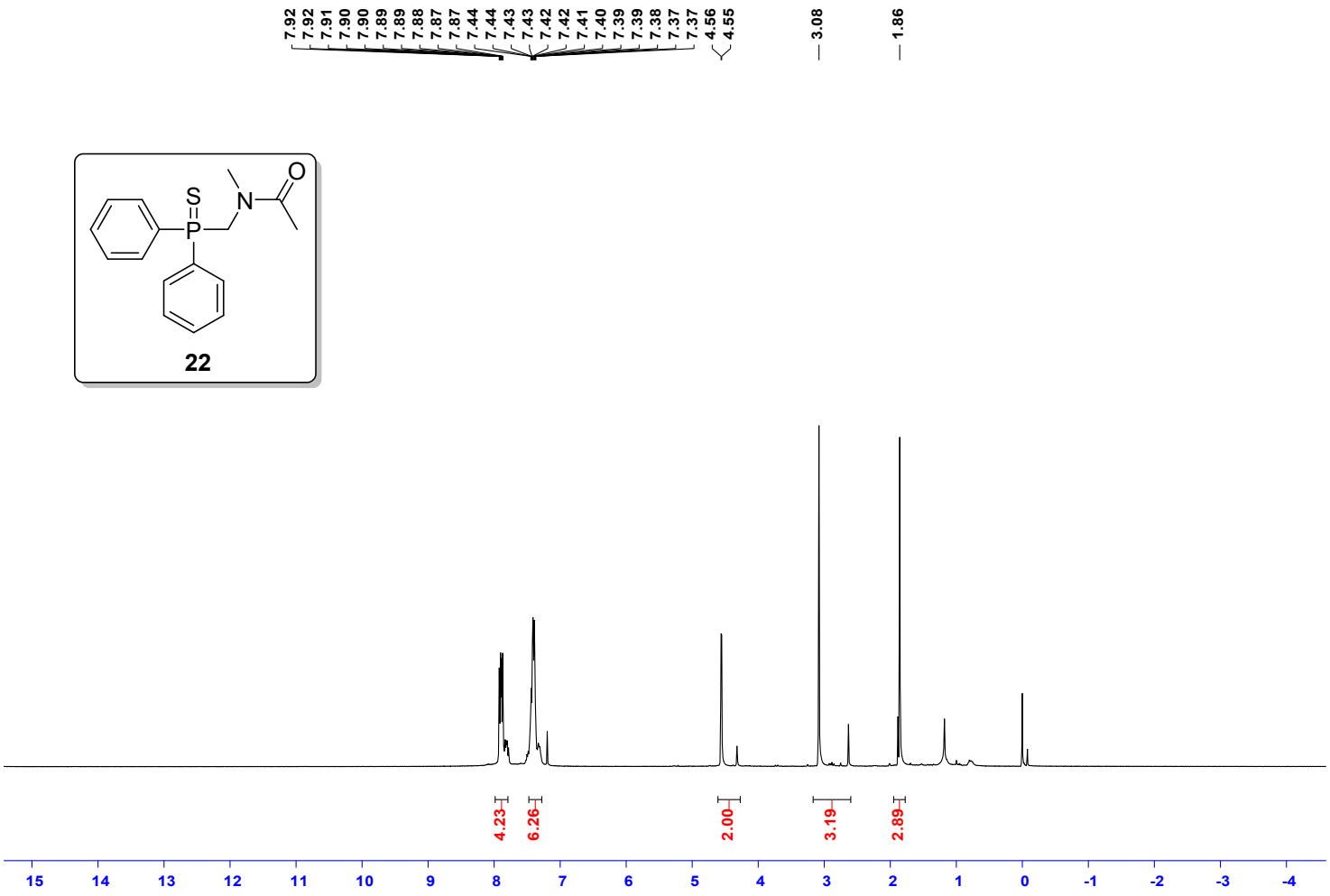


^{31}P NMR (162 MHz, $CDCl_3$) spectra for 21

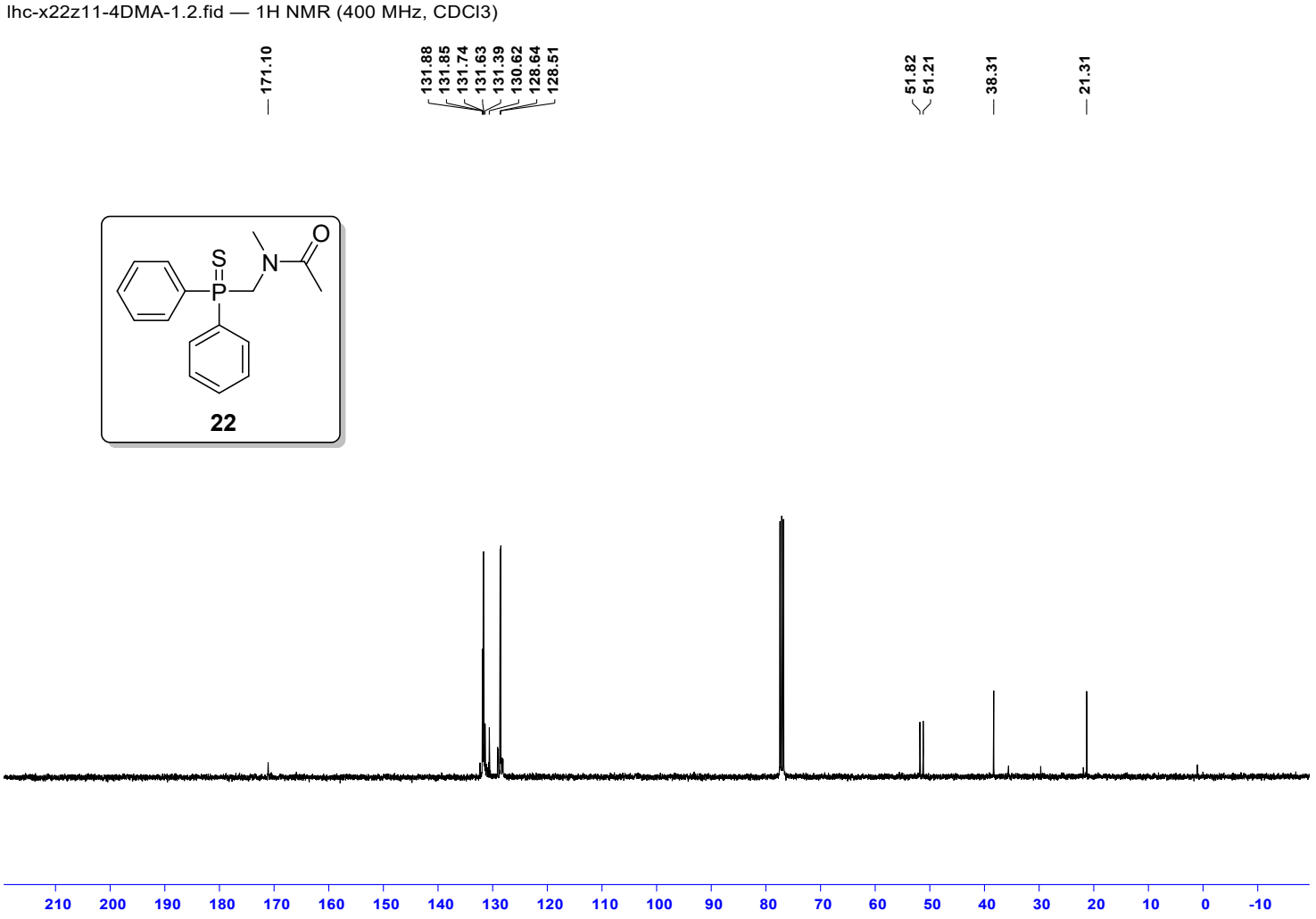
lhc-x22z17-1PhOMe.3.fid — 1H NMR (400 MHz, CDCl3)



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 22

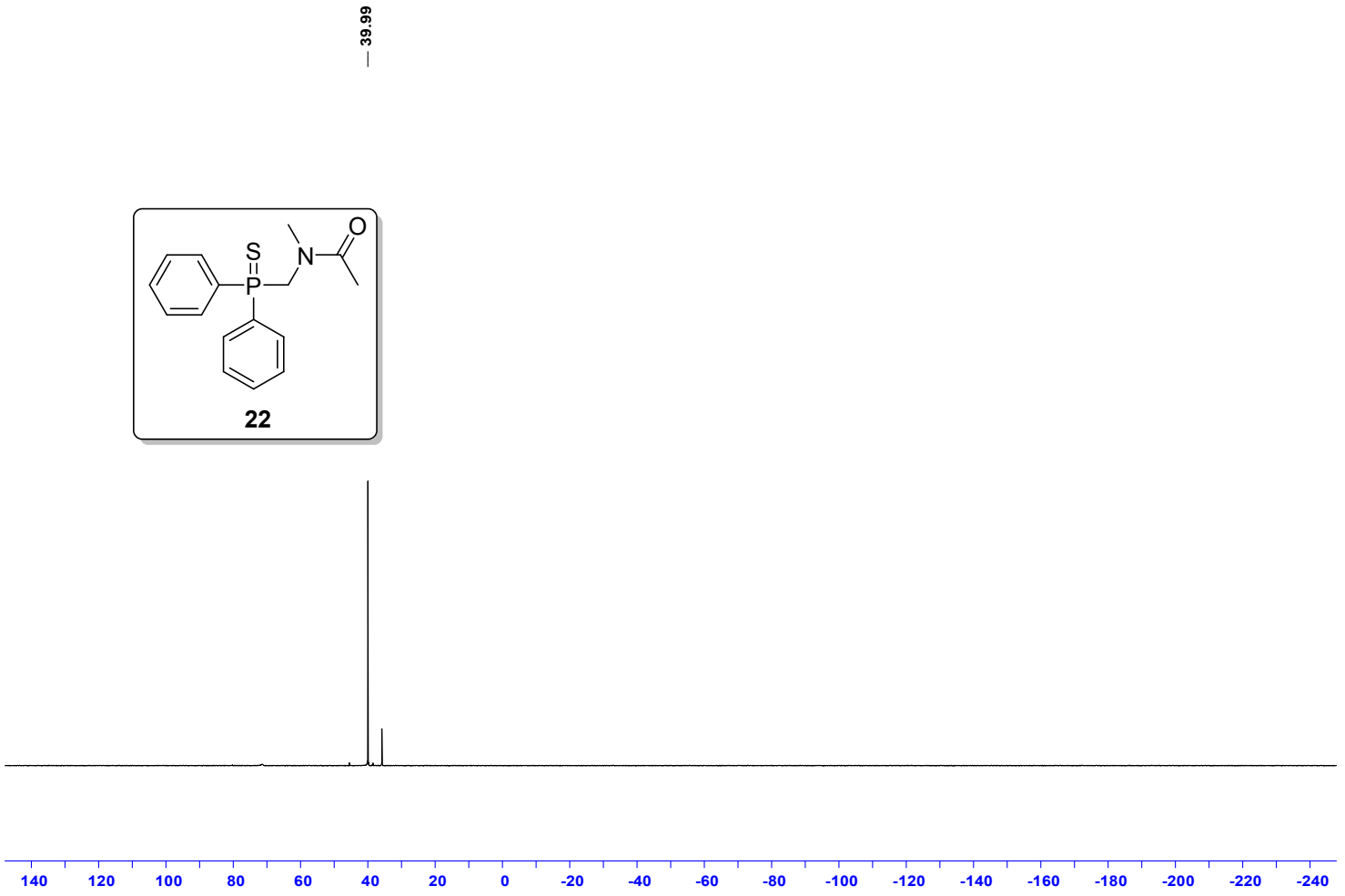


^{13}C NMR (101 MHz, CDCl3) spectra for 22



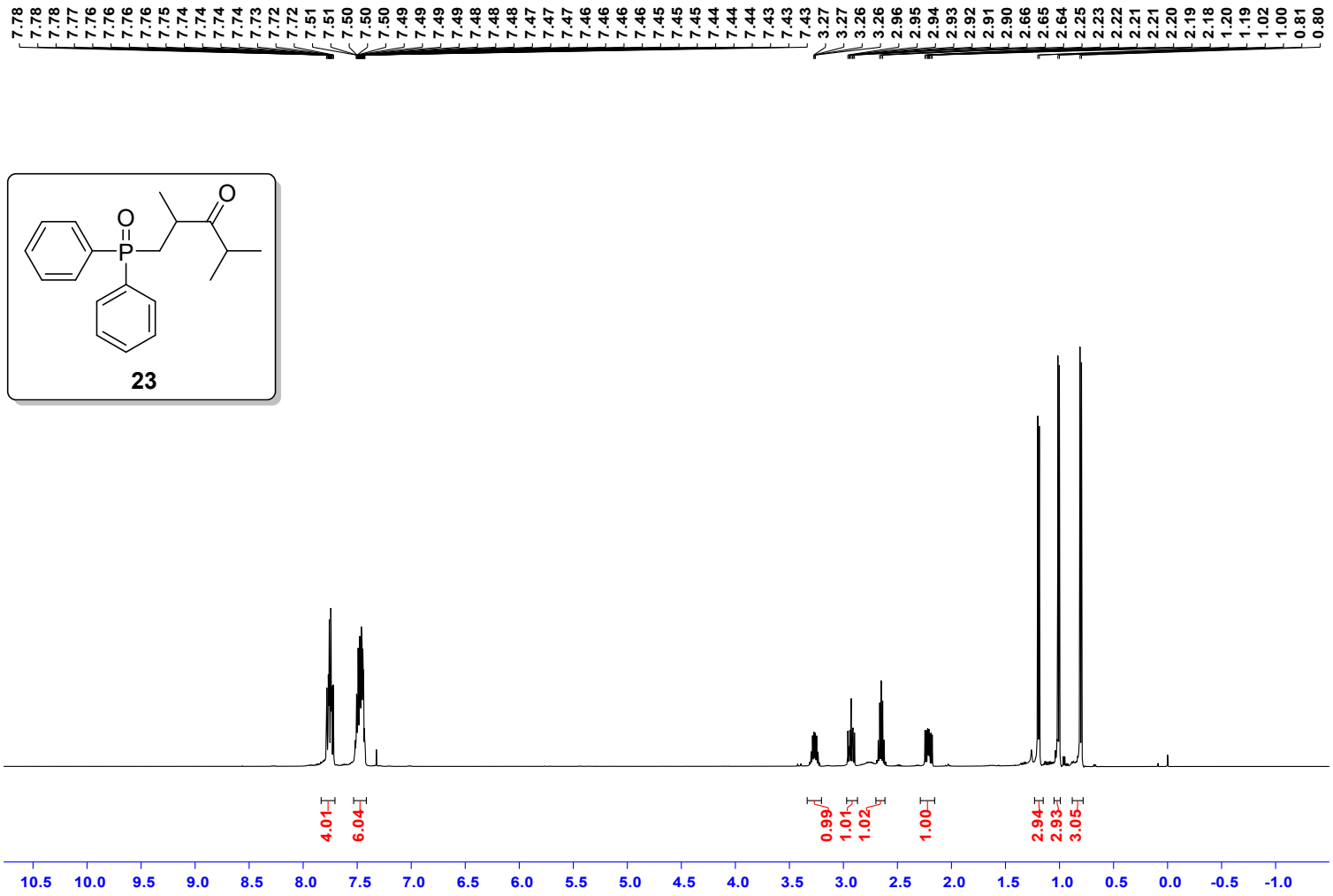
^{31}P NMR (162 MHz, $CDCl_3$) spectra for 22

lhc-x22z11-4DMA-1.3.fid — 1H NMR (400 MHz, CDCl3)

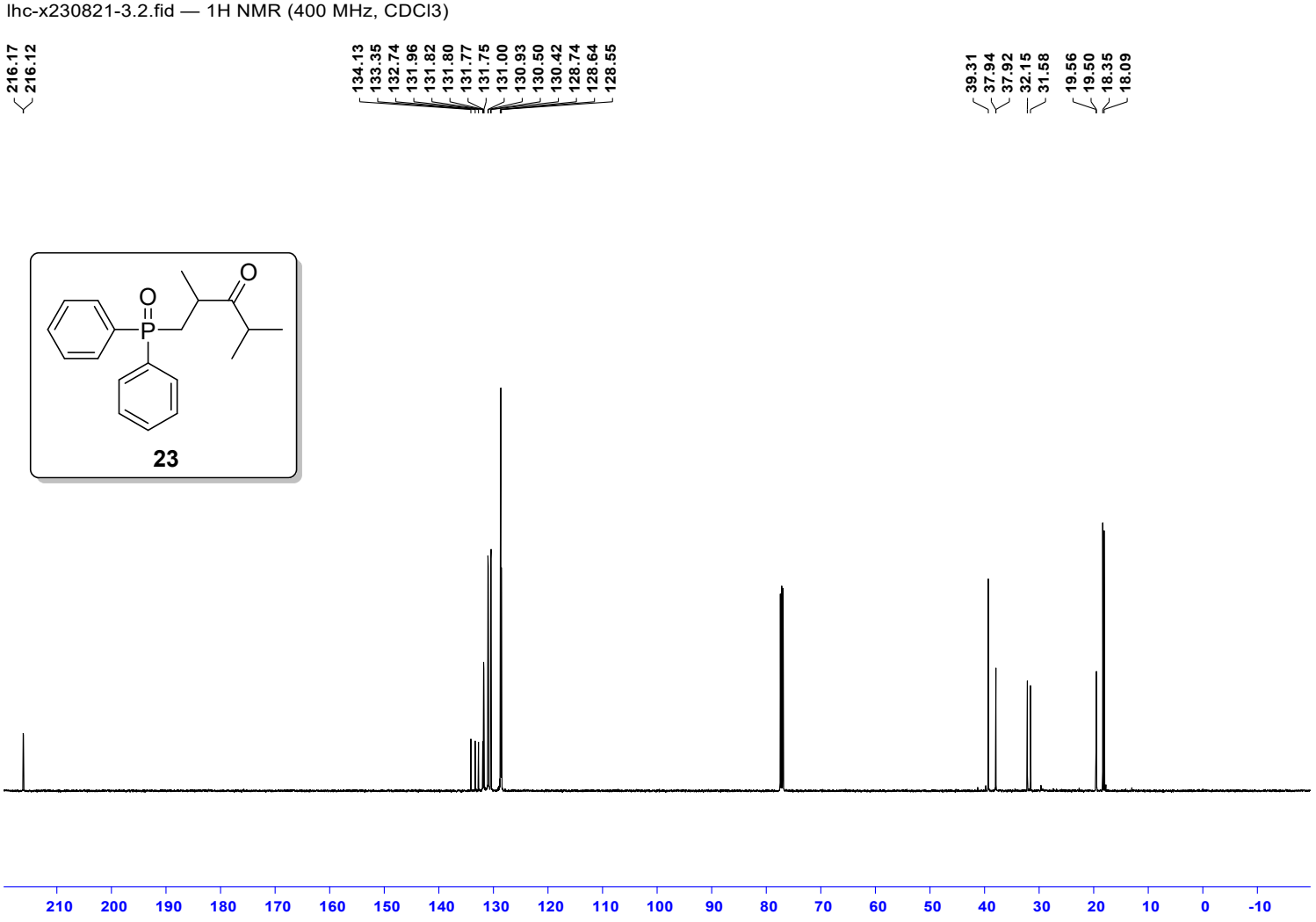


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 23

lhc-x230821-3.1.fid — 1H NMR (400 MHz, CDCl3)

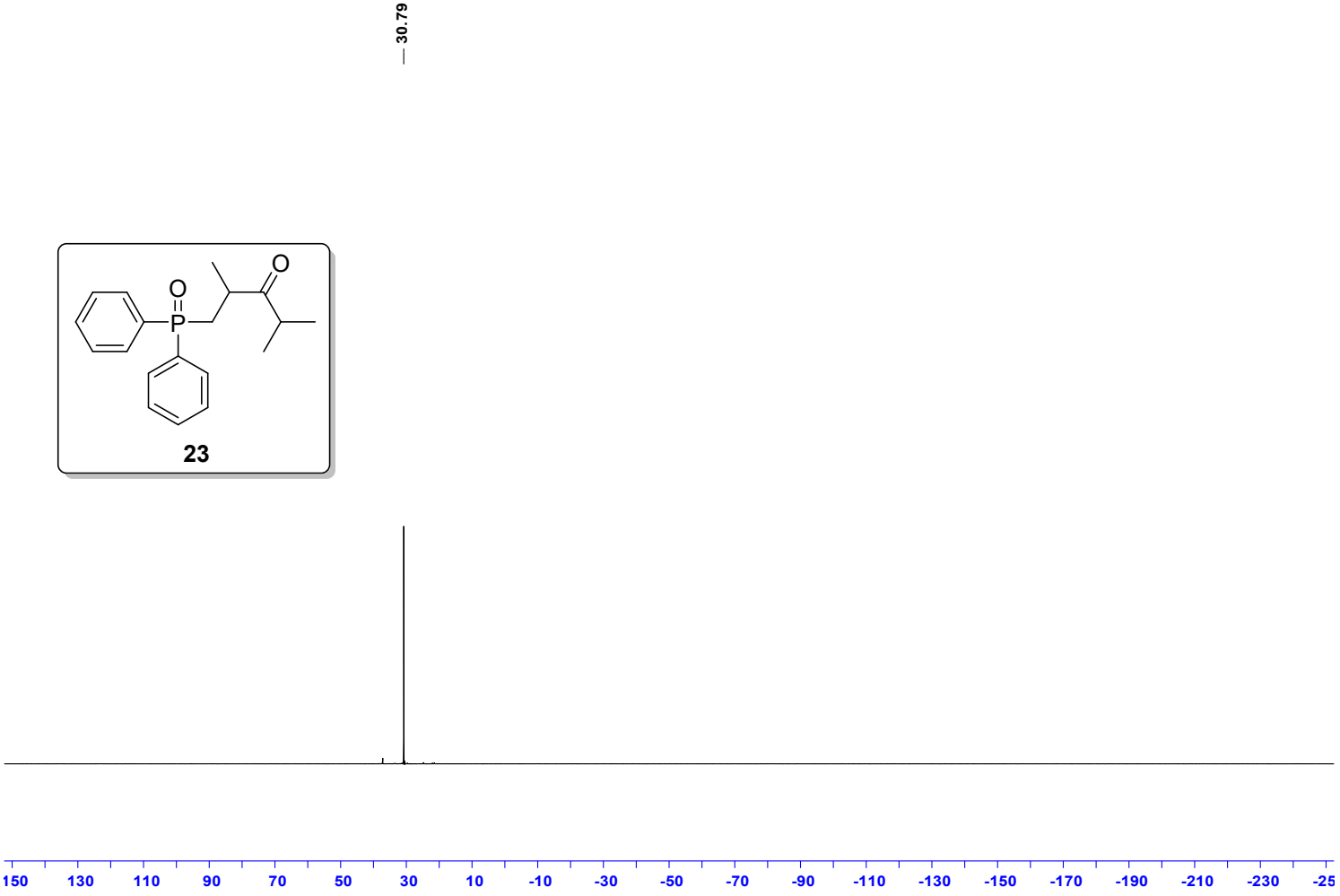


^{13}C NMR (126 MHz, CDCl3) spectra for 23

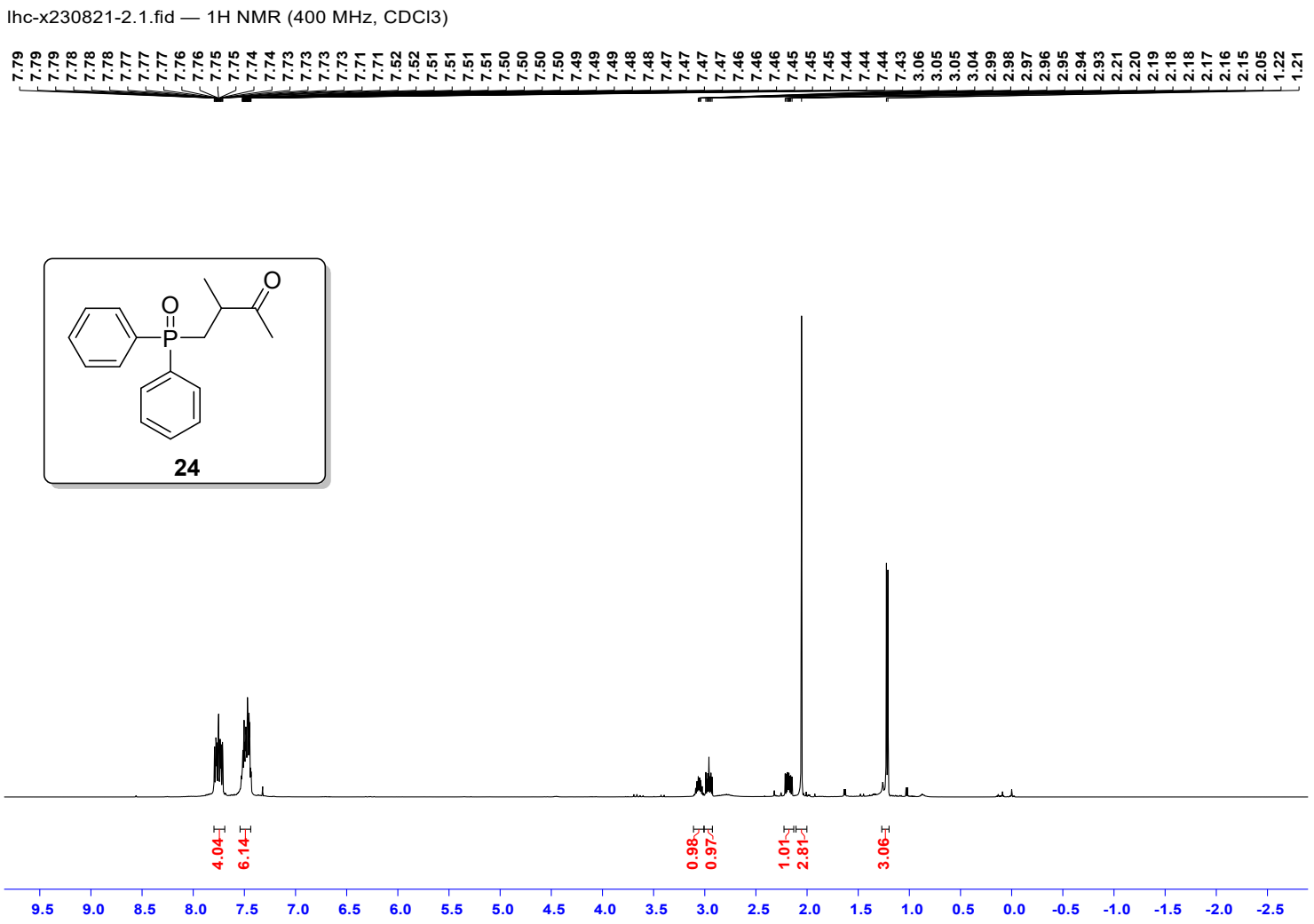


^{31}P NMR (202 MHz, $CDCl_3$) spectra for 23

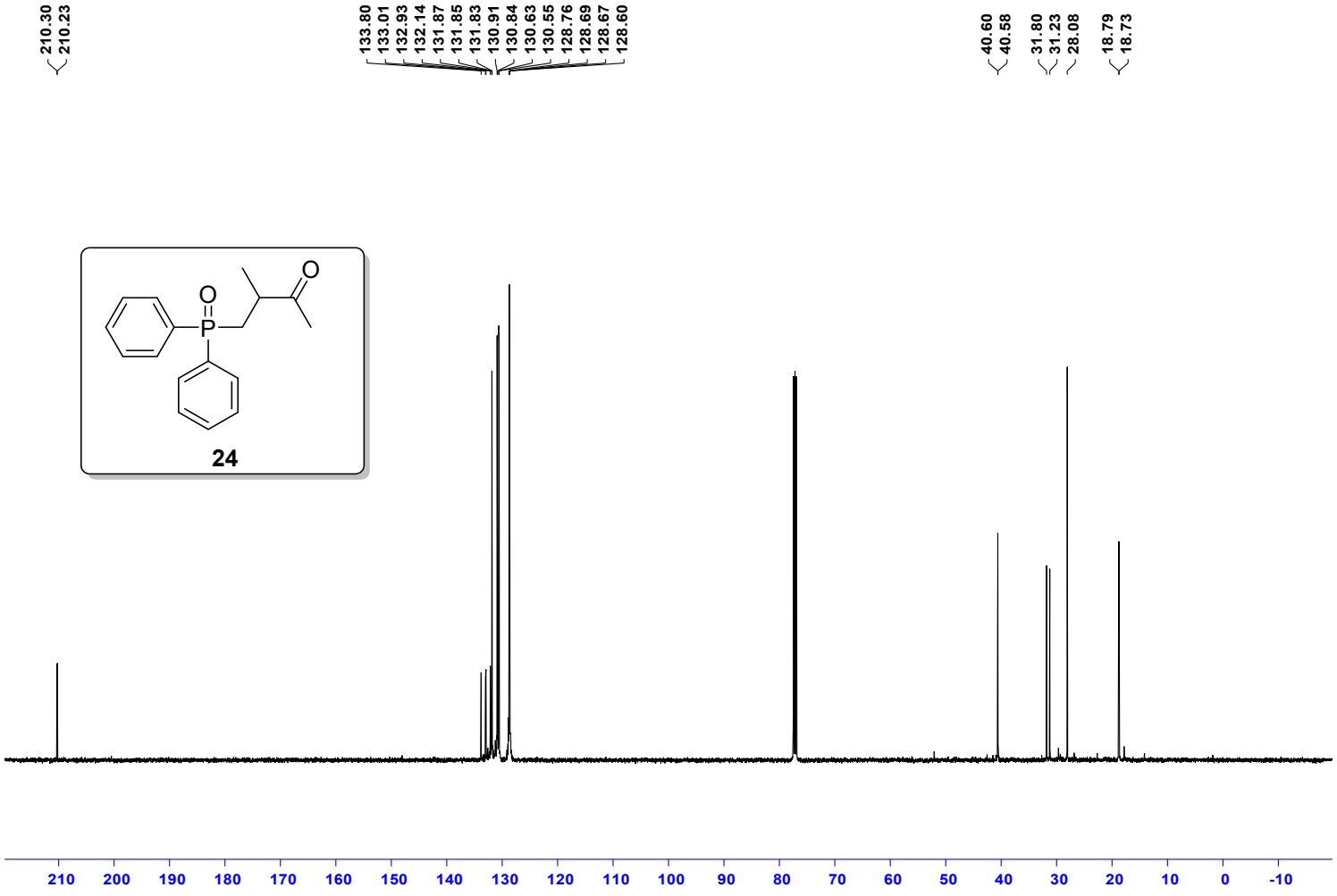
lhc-x230821-3.3.fid — 1H NMR (400 MHz, CDCl3)



^{1}H NMR (500 MHz, $CDCl_3$) spectra for 24

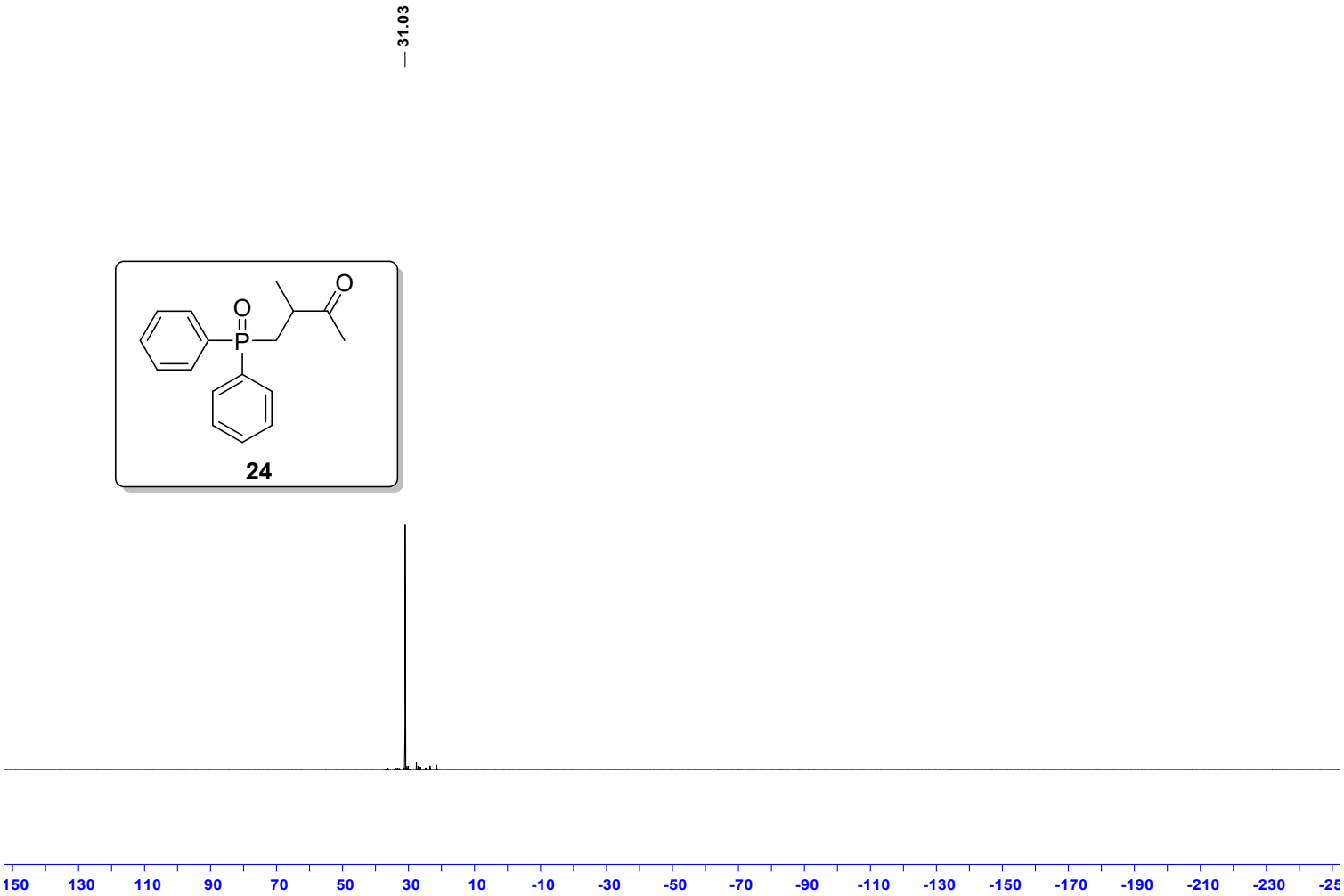


^{13}C NMR (126 MHz, CDCl3) spectra for 24

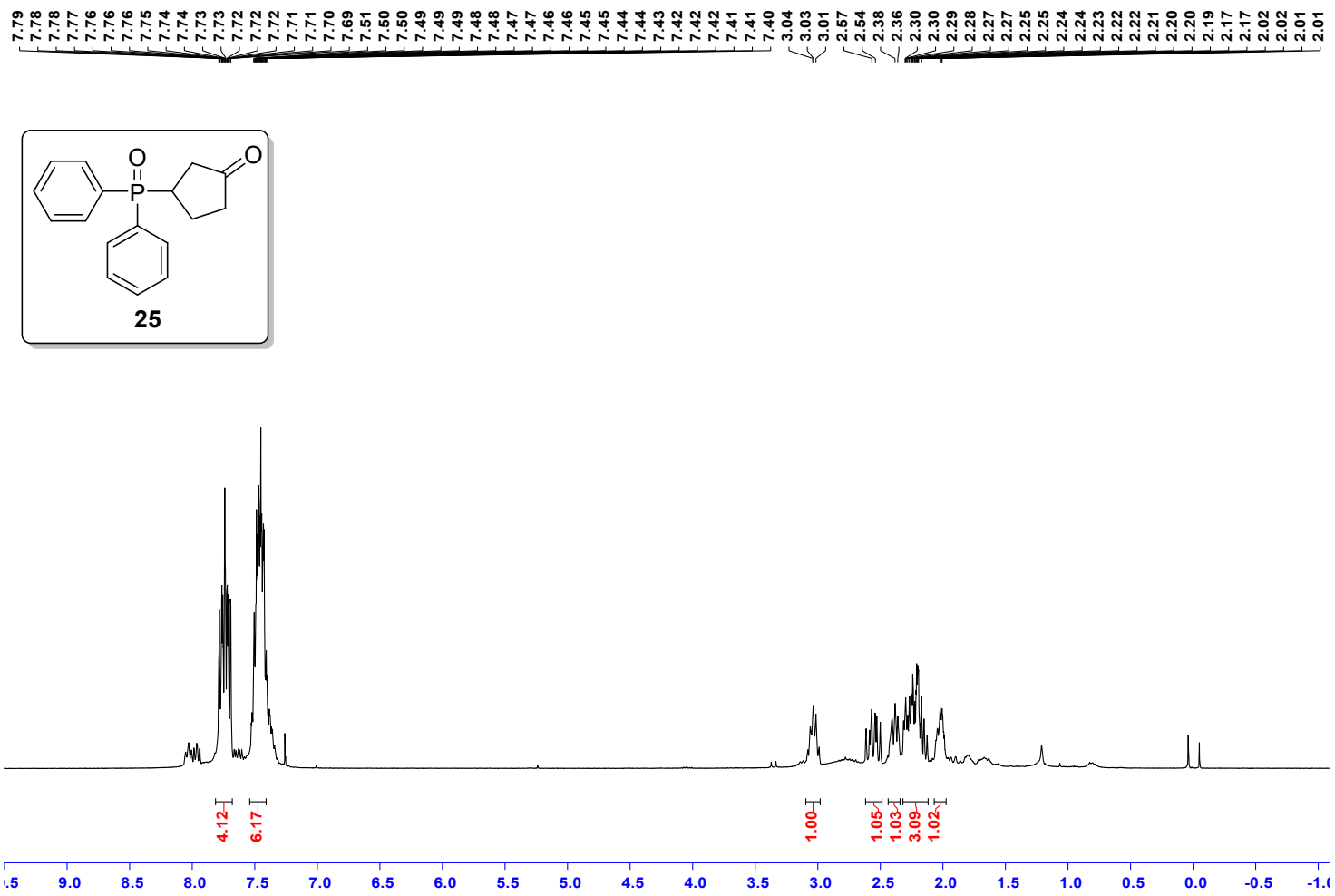


^{31}P NMR (202 MHz, $CDCl_3$) spectra for 24

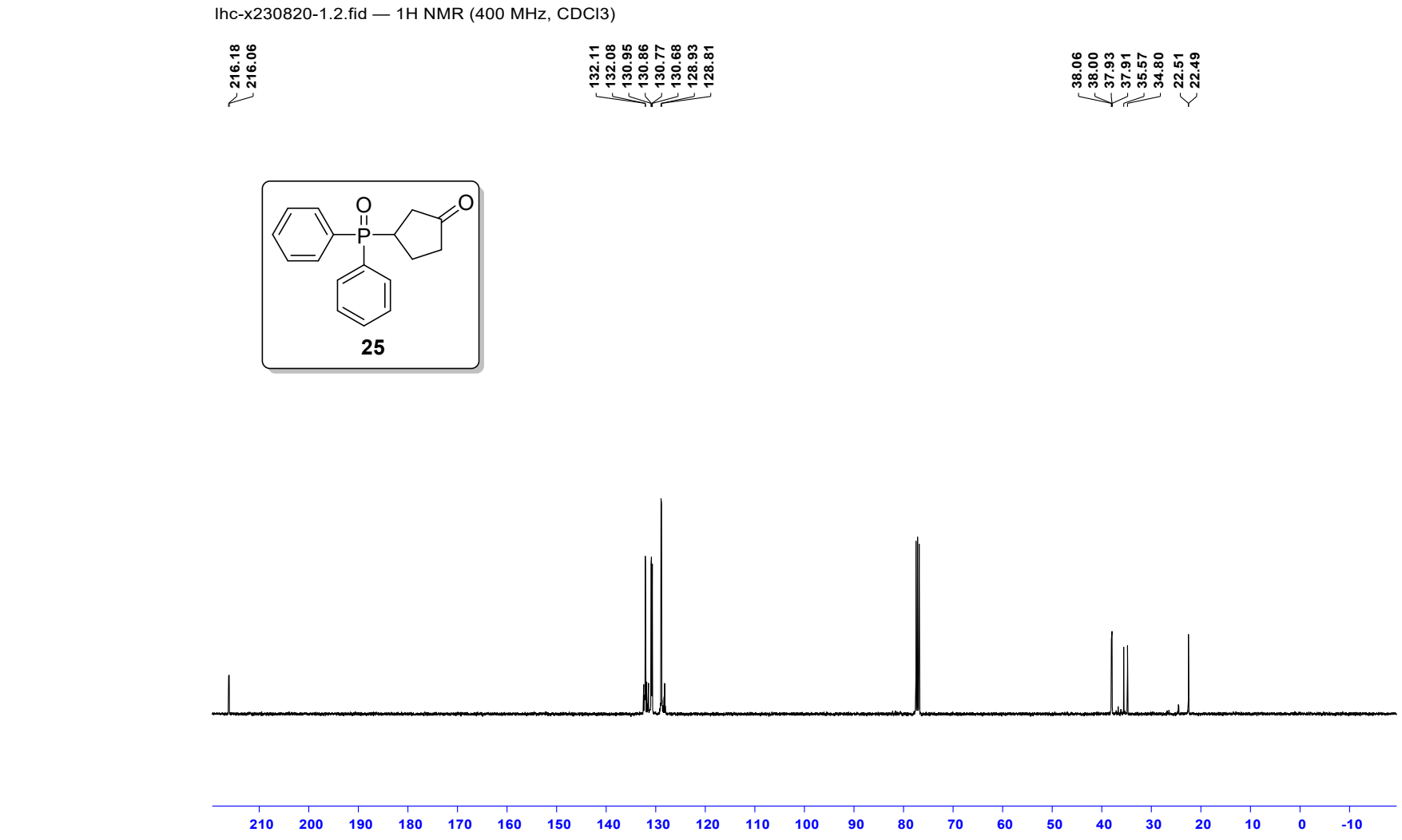
lhc-x230821-2.3.fid — 1H NMR (400 MHz, CDCl3)



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 25

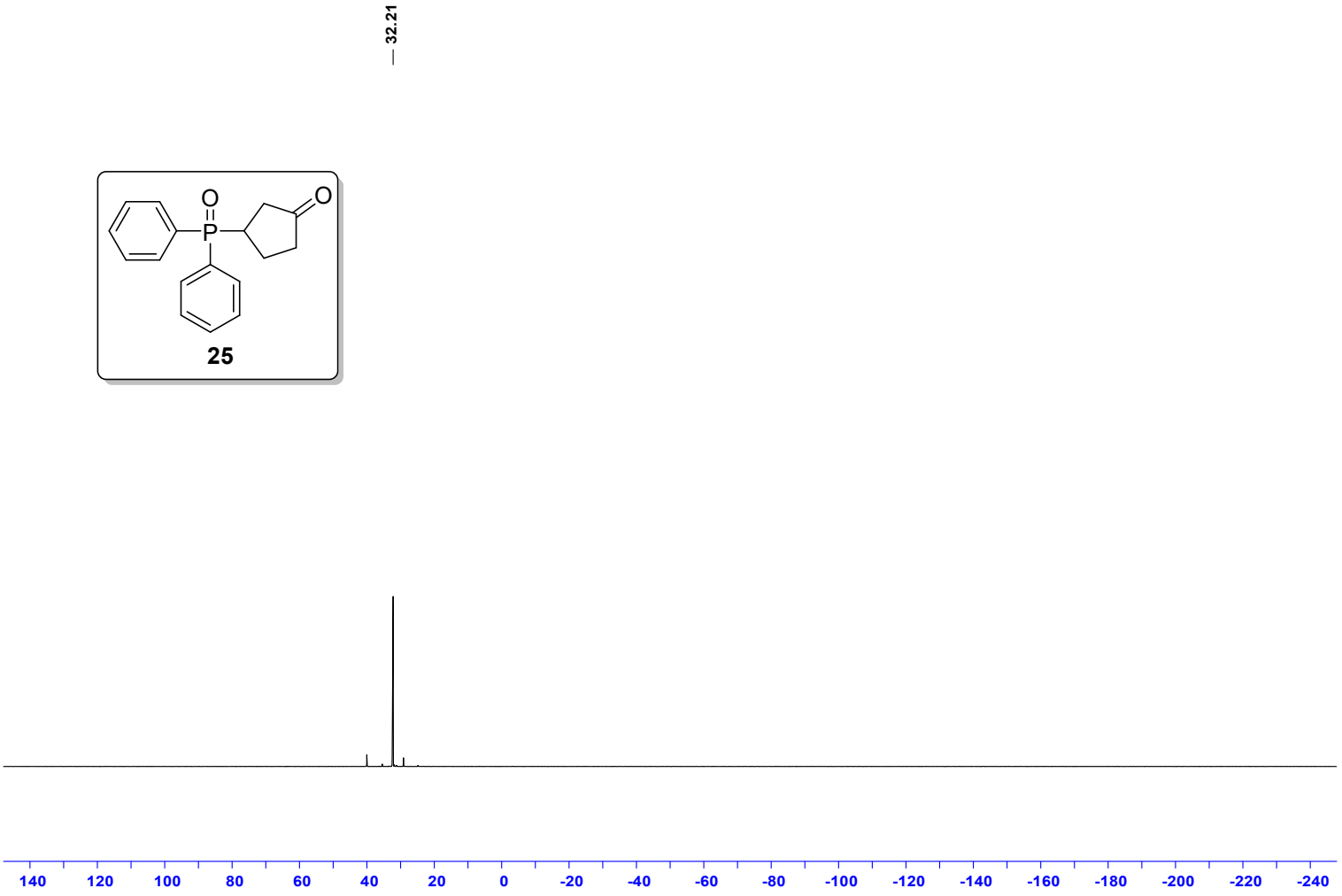


^{13}C NMR (101 MHz, CDCl3) spectra for 25

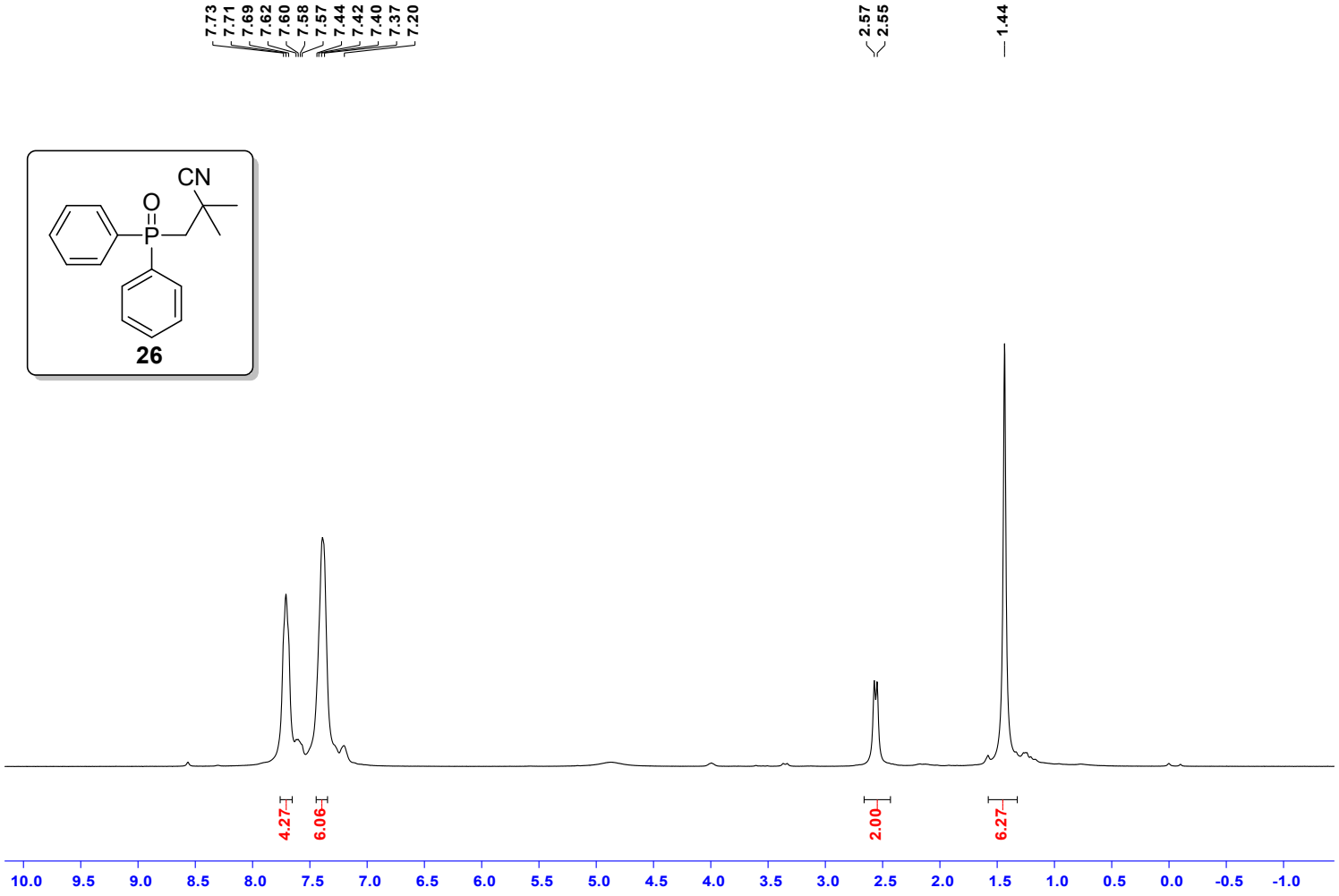


^{31}P NMR (162 MHz, $CDCl_3$) spectra for 25

lhc-x230820-1.3.fid — 1H NMR (400 MHz, CDCl3)

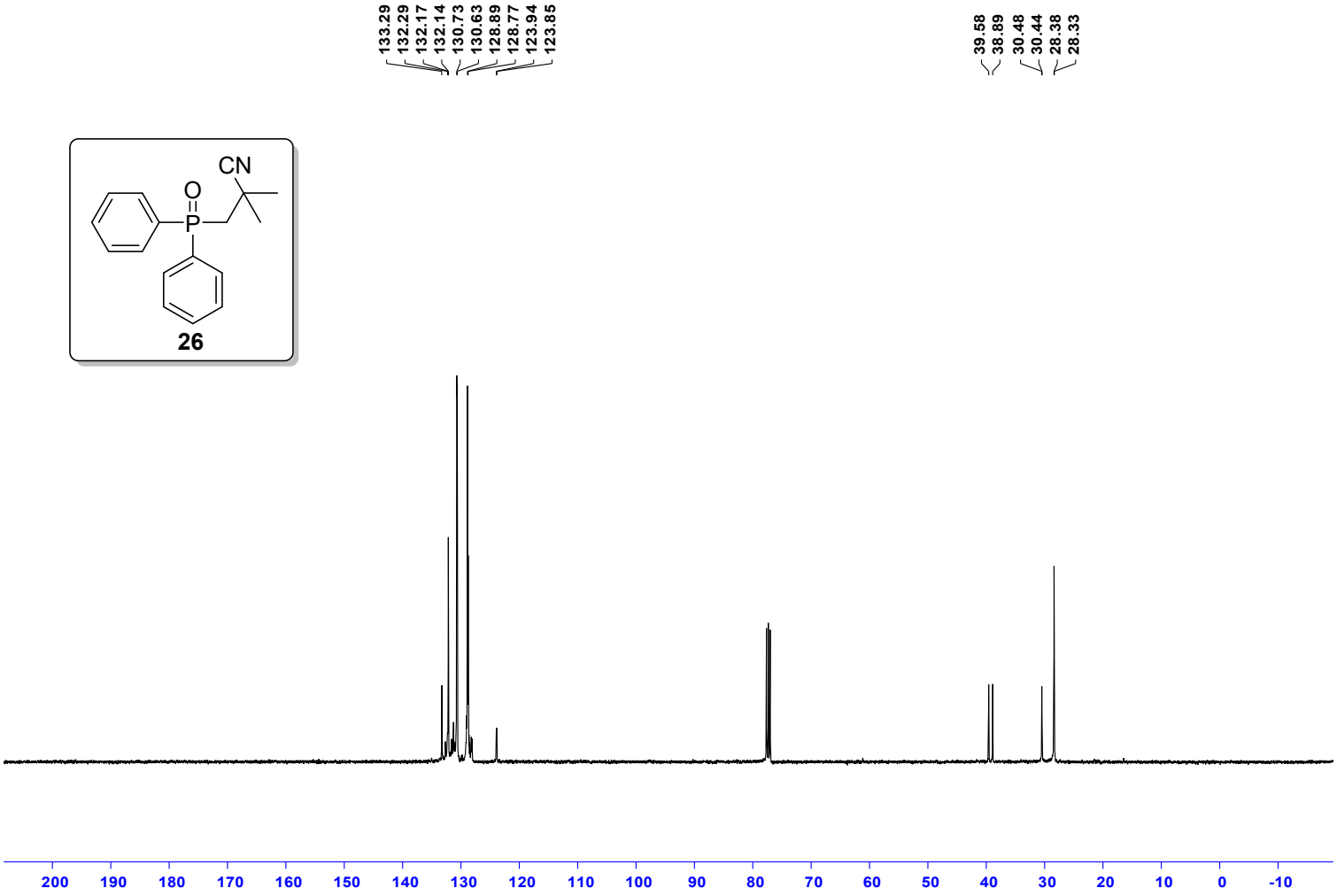


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 26



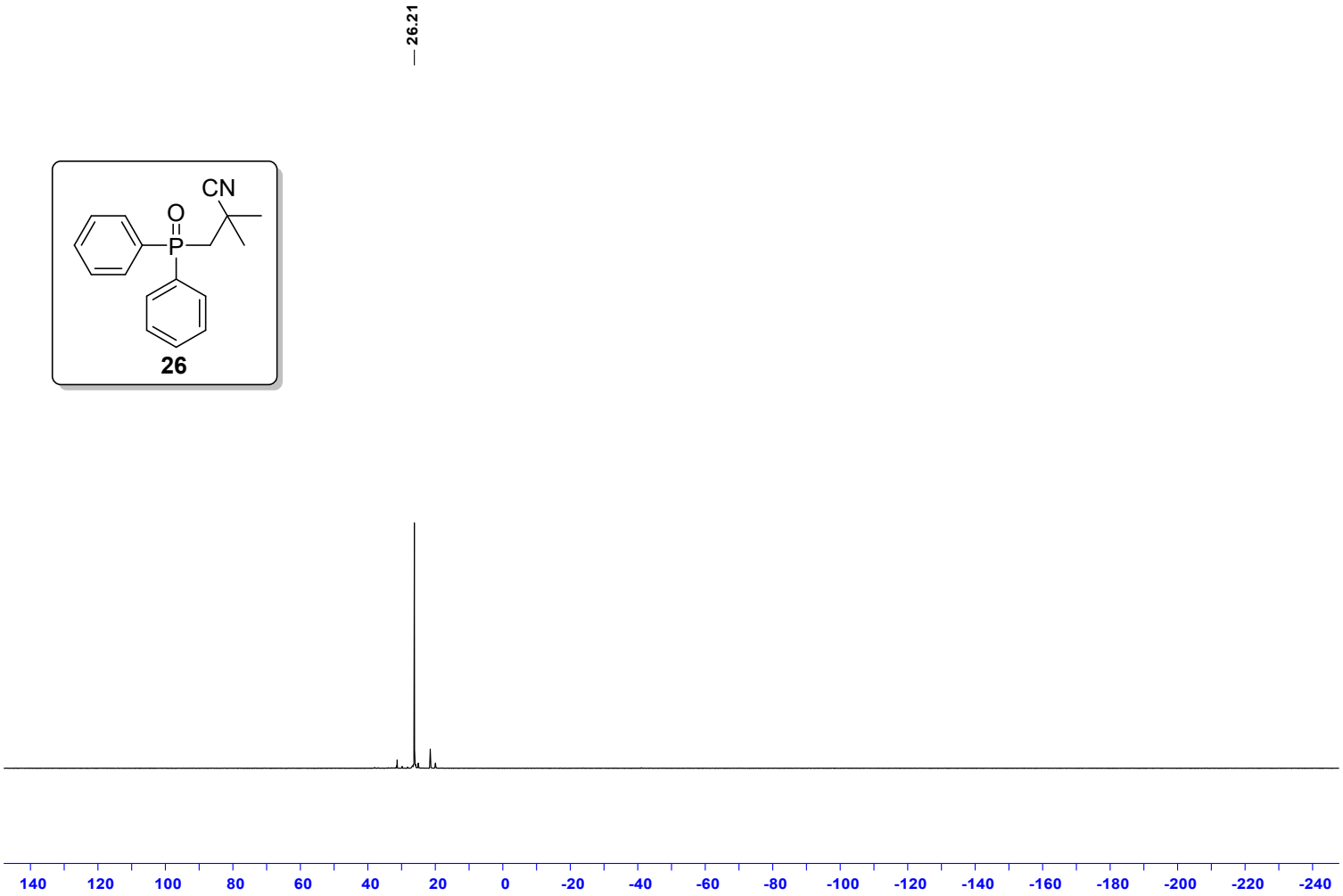
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 26

lhc-x230406-3.11.fid — 1H NMR (400 MHz, CDCl3)

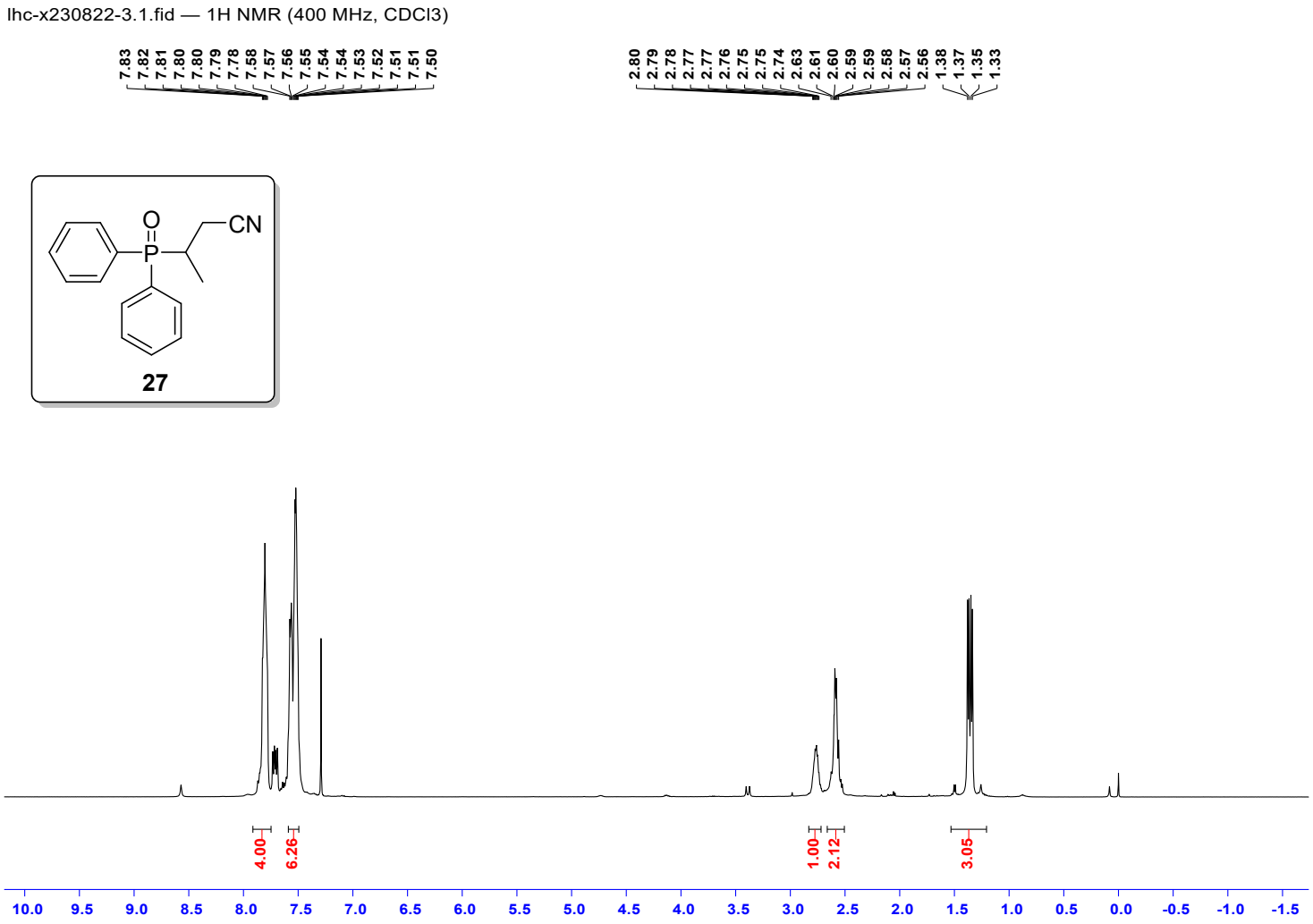


^{31}P NMR (162 MHz, $CDCl_3$) spectra for 26

lhc-x230406-3.2.fid — 1H NMR (400 MHz, CDCl3)

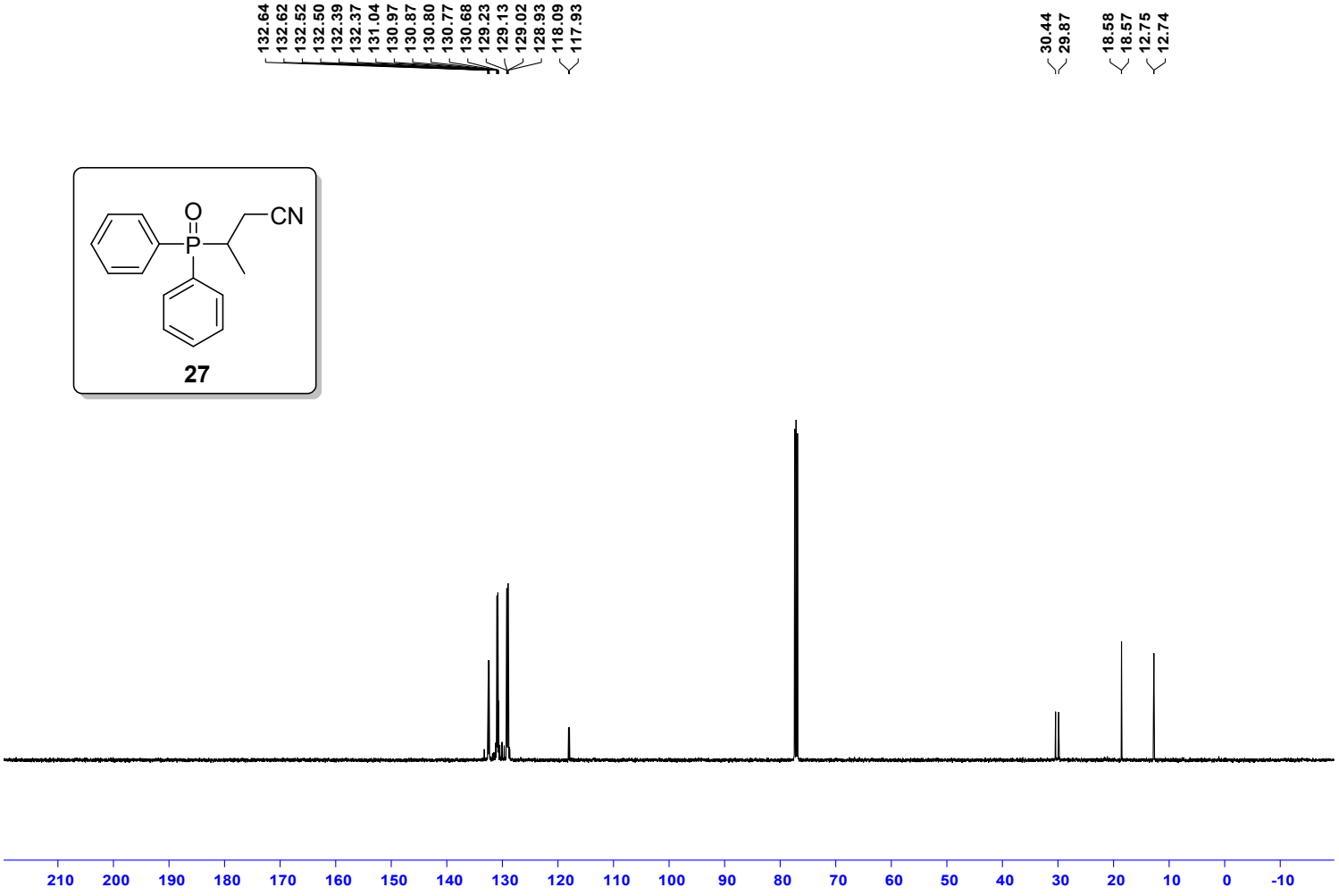


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 27



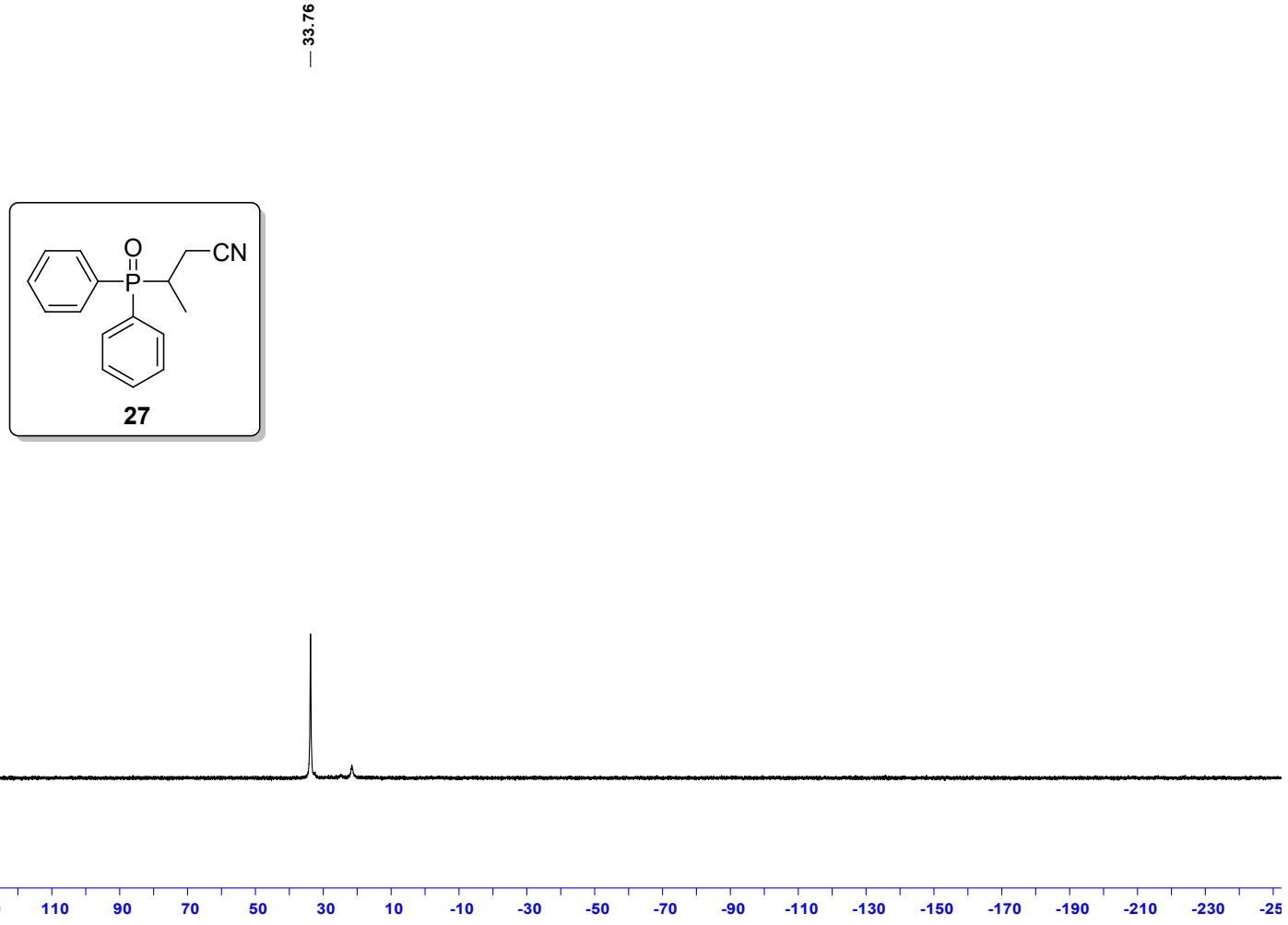
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 27

lhc-x230822-3.2.fid — 1H NMR (400 MHz, CDCl3)

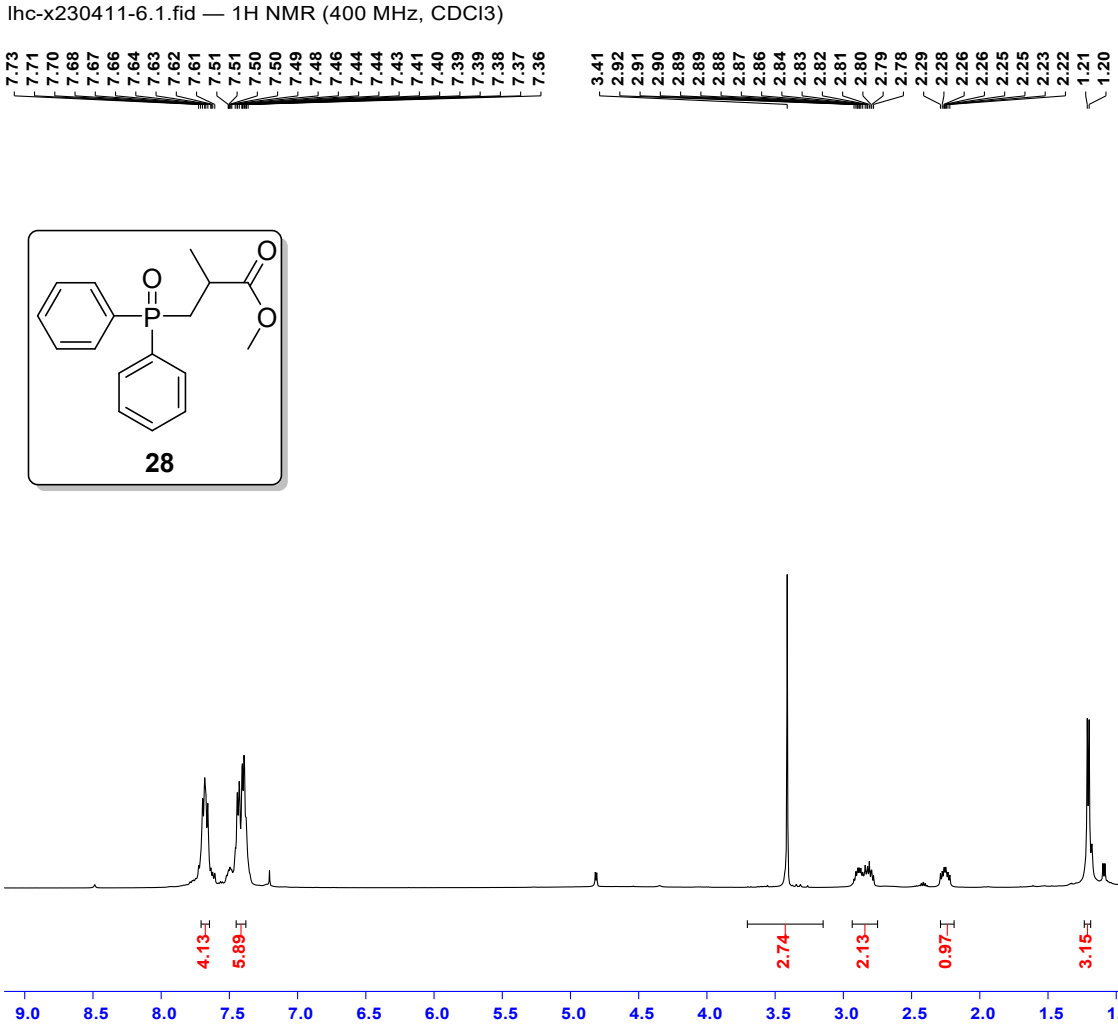


^{31}P NMR (202 MHz, $CDCl_3$) spectra for 27

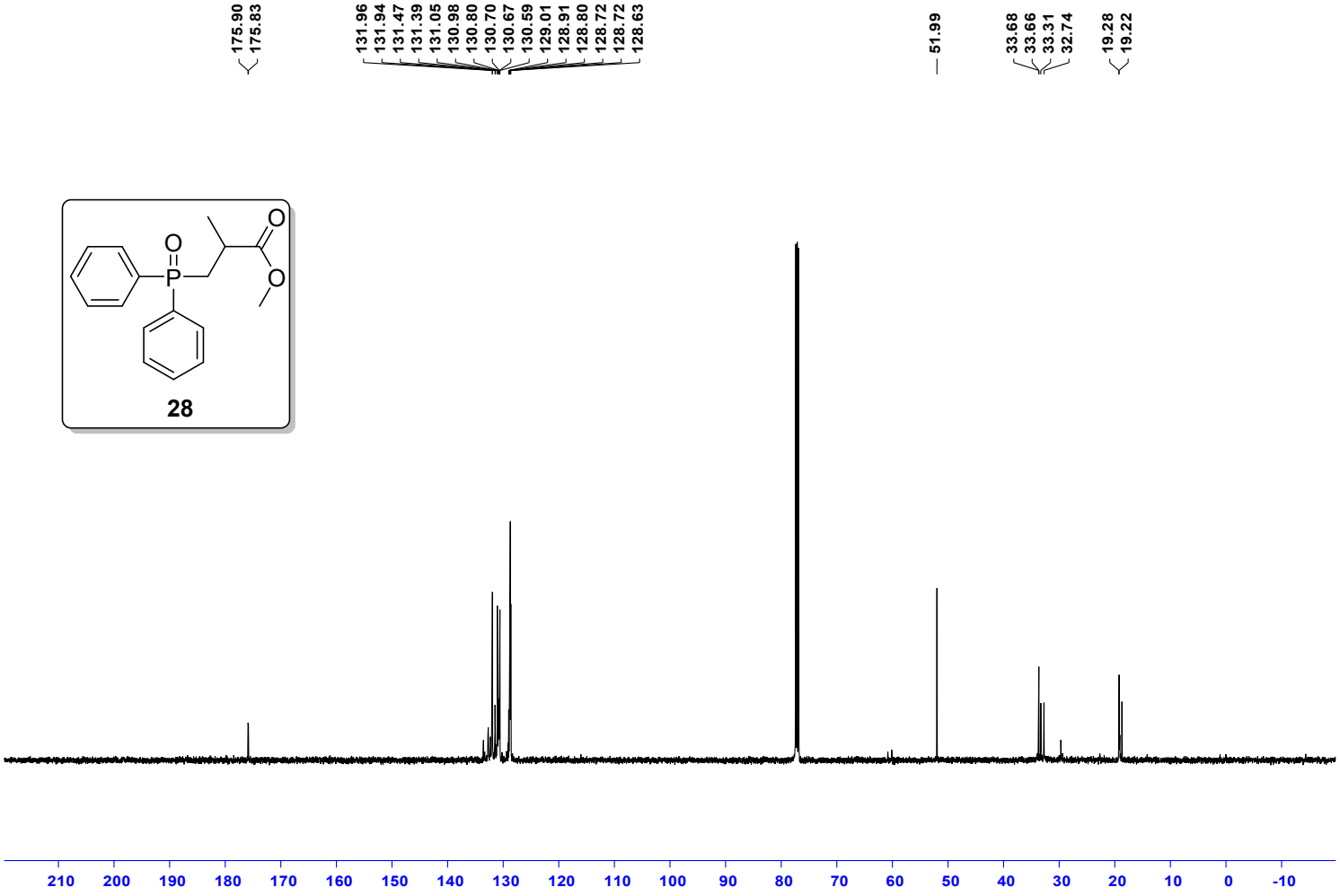
lhc-x230822-3.3.fid — 1H NMR (400 MHz, CDCl3)



^{1}H NMR (500 MHz, $CDCl_3$) spectra for 28

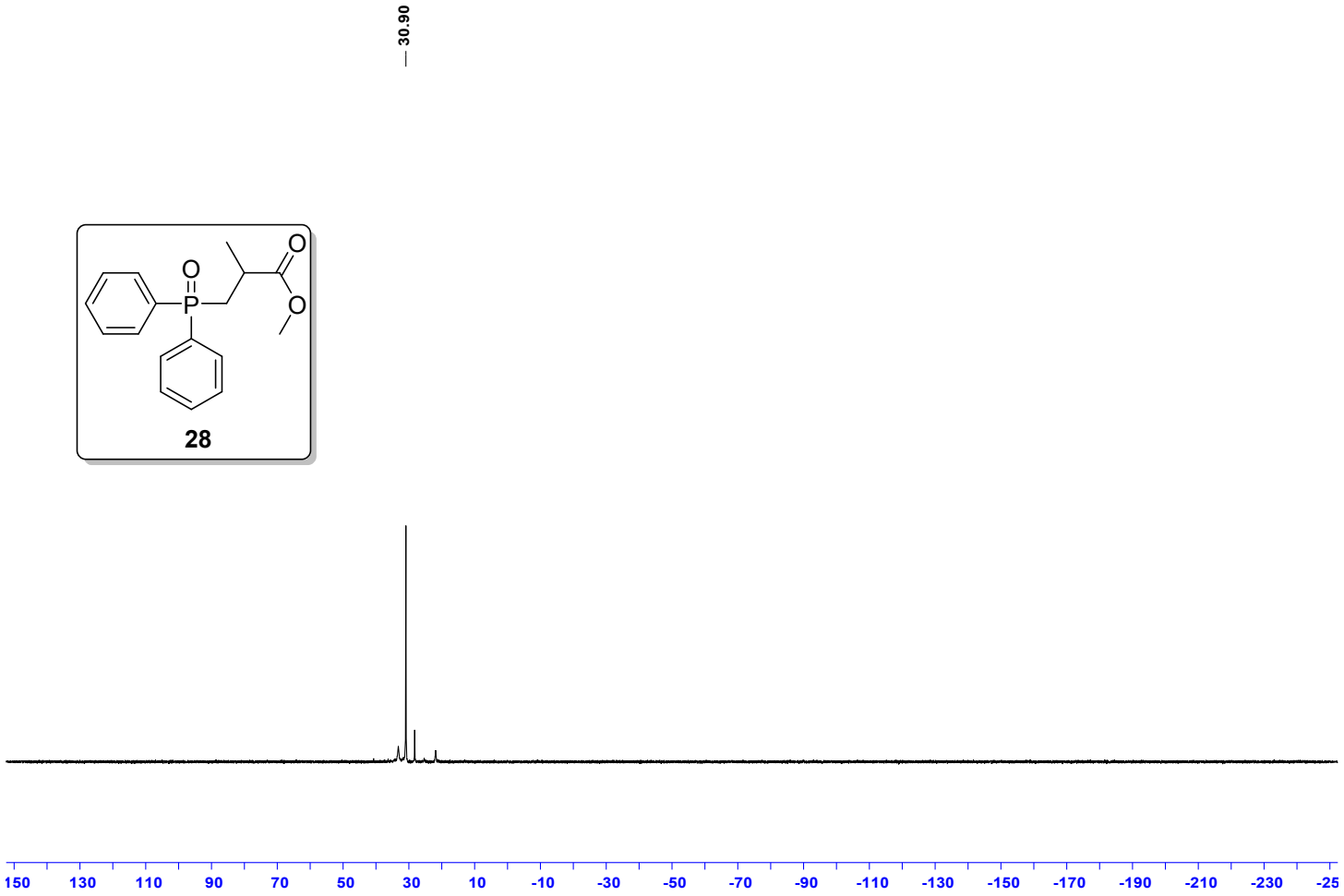


^{13}C NMR (126 MHz, $CDCl_3$) spectra for 28

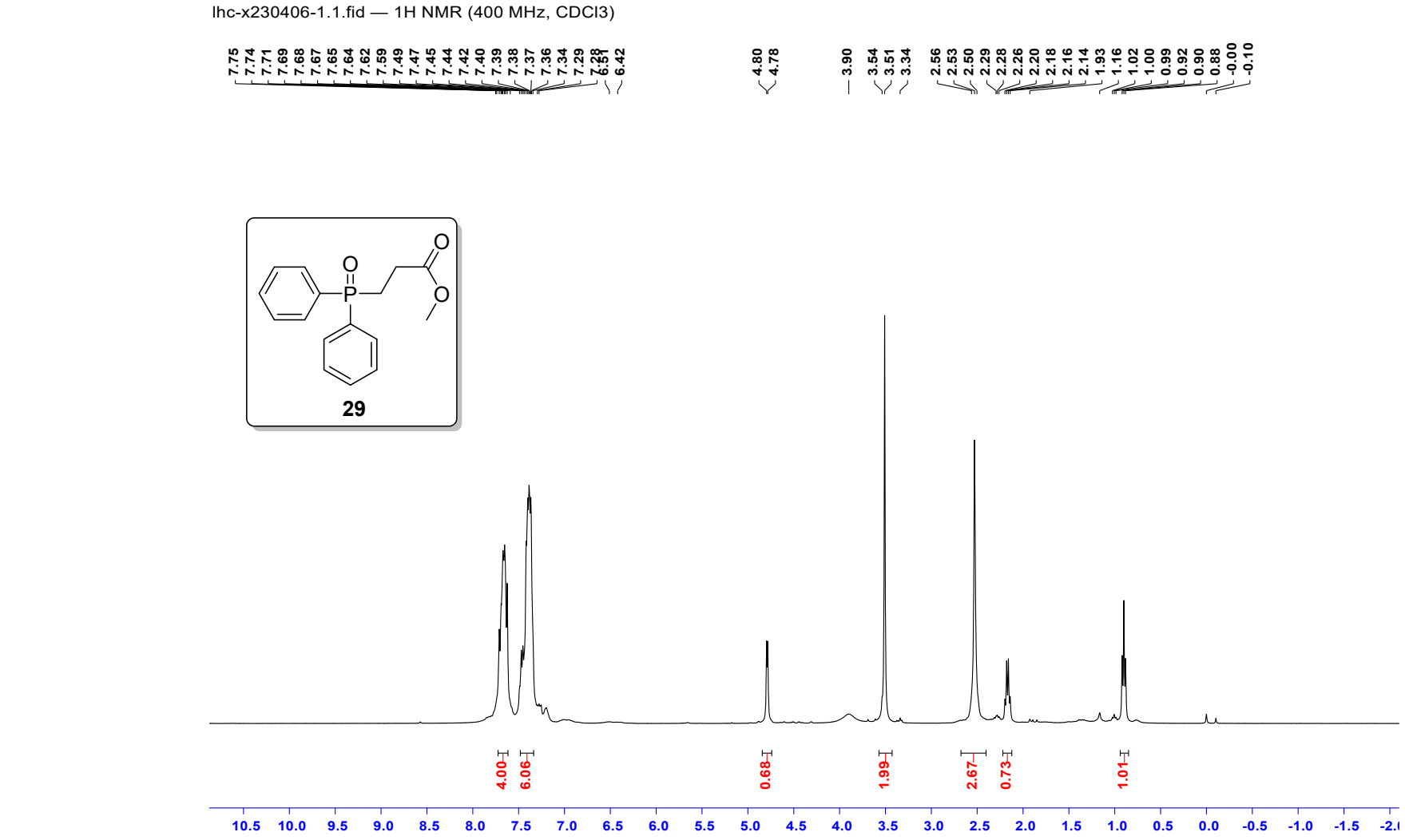


^{31}P NMR (202 MHz, $CDCl_3$) spectra for 28

lhc-x230411-6.3.fid — 1H NMR (400 MHz, CDCl3)

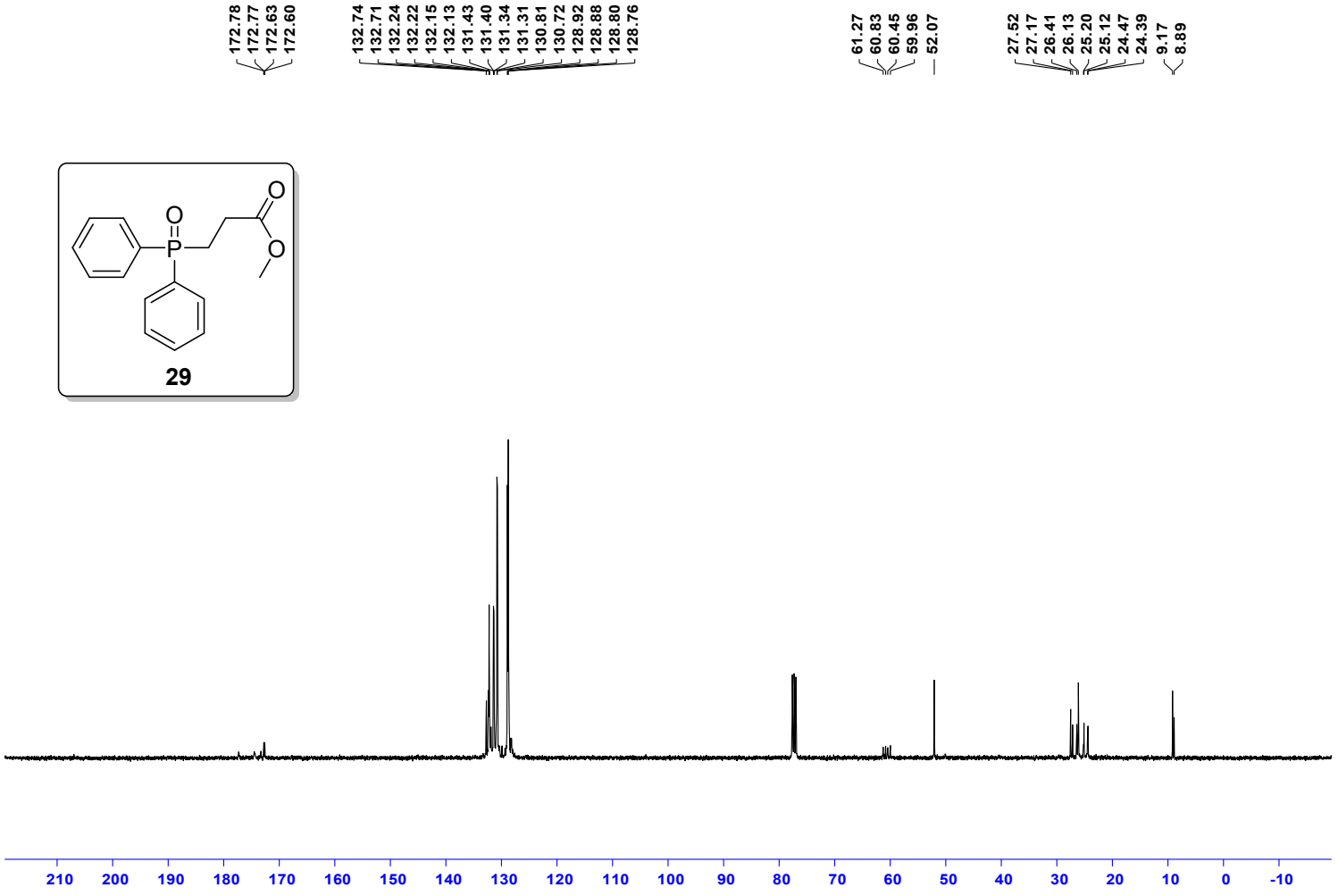


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 29



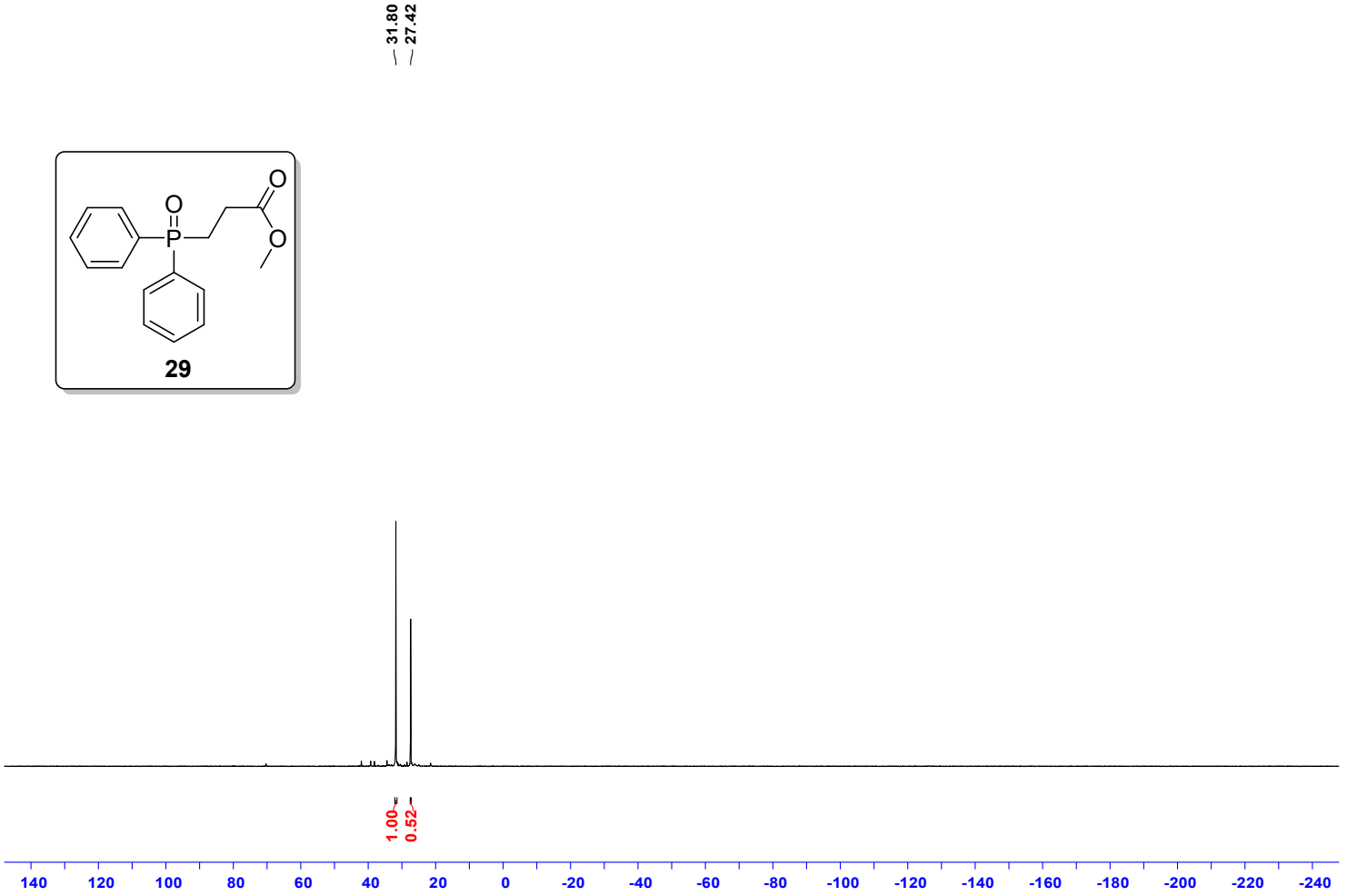
^{13}C NMR (101 MHz, $CDCl_3$) spectra for 29

lhc-x230406-1.10.fid — 1H NMR (400 MHz, CDCl3)



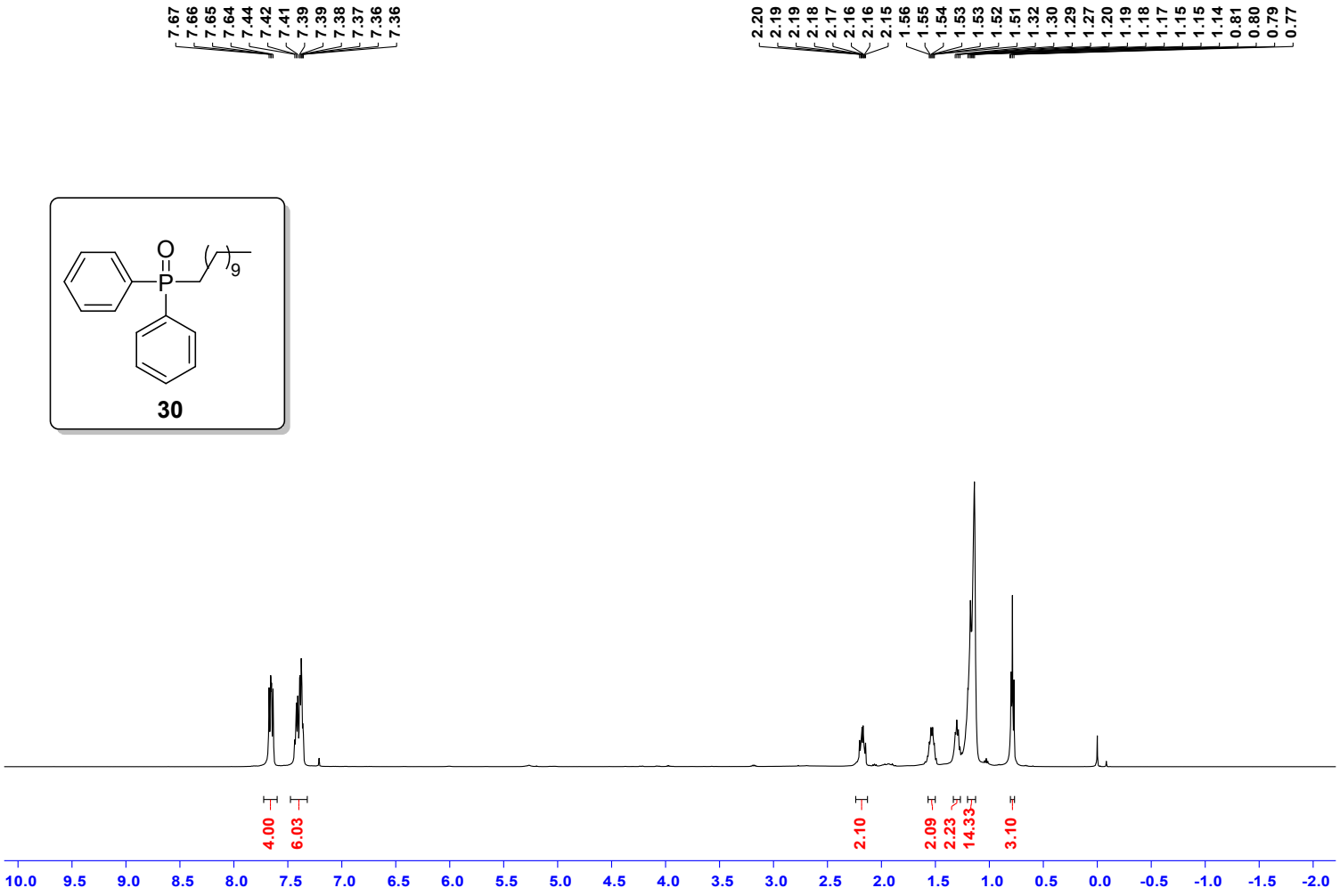
^{31}P NMR (162 MHz, $CDCl_3$) spectra for 29

lhc-x230406-1.2.fid — 1H NMR (400 MHz, CDCl3)

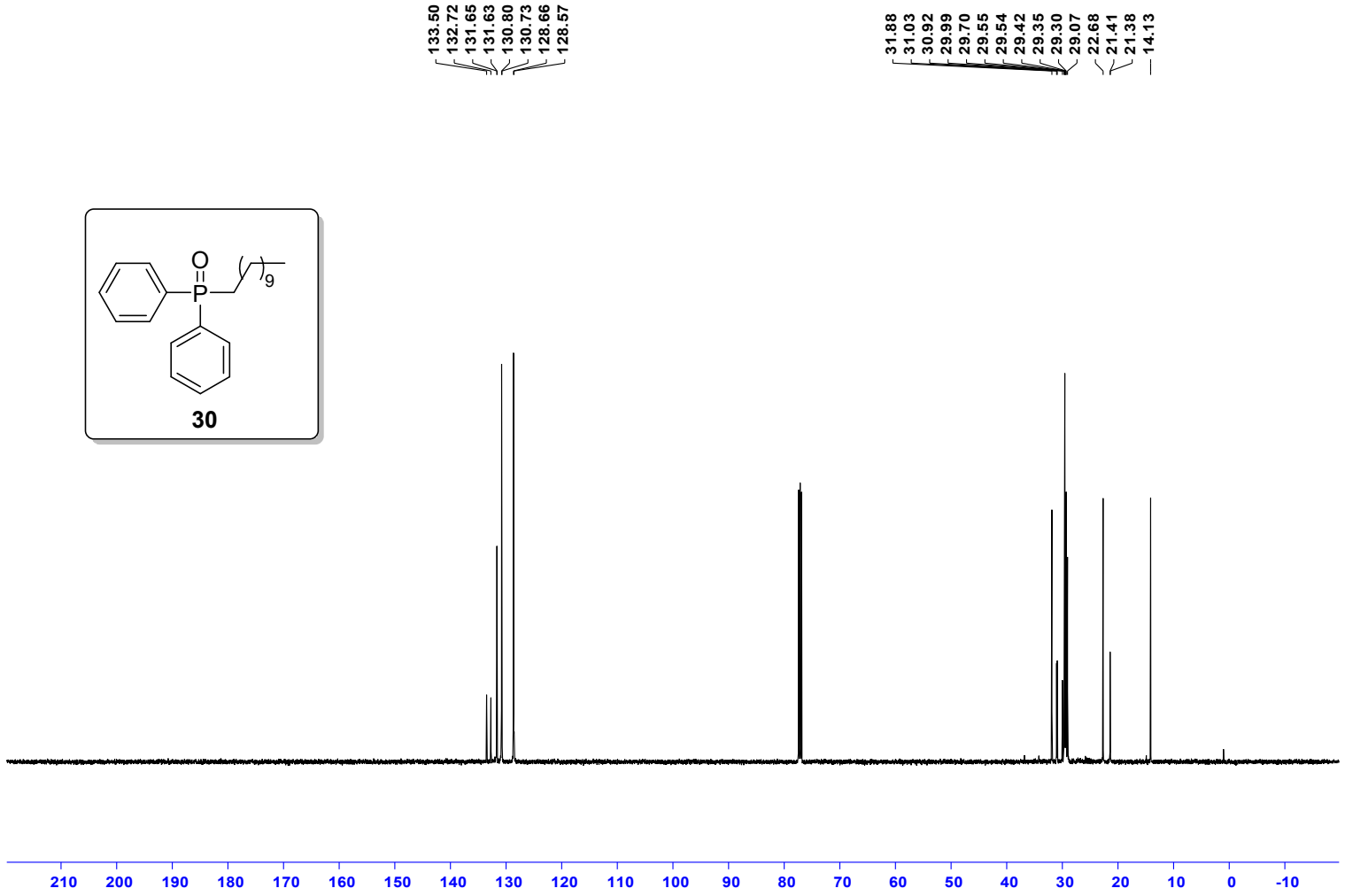


^{1}H NMR (400 MHz, $CDCl_3$) spectra for 30

lhc-x230812-2.1.fid — 1H NMR (400 MHz, CDCl3)



^{13}C NMR (101 MHz, $CDCl_3$) spectra for 30



^{31}P NMR (162 MHz, $CDCl_3$) spectra for 30

lhc-x230812-2.3.fid — 1H NMR (400 MHz, CDCl3)