

Enantioselective Construction of Allylic Phosphine Oxides through Substitution of Morita-Baylis-Hillman Carbonates with Phosphine Oxides

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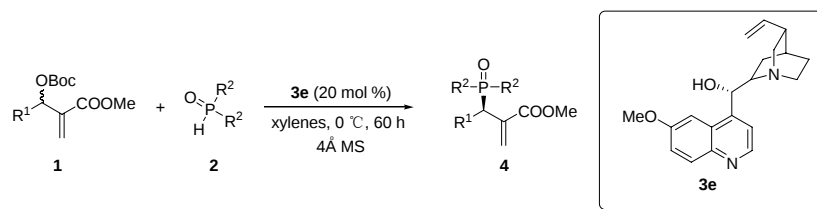
General Methods:

Unless stated otherwise, all reactions were carried out in flamedried glassware. All solvents were purified and dried according to standard methods prior to use. 4 Å molecular sieves were dried at 200 °C under vacuum for 12 h before usage. Morita-Baylis-Hillman carbonates **1** were prepared according to the literature.¹ Catalysts **3a-3e**, **3i** were purchased from Aldrich Chemical Company. Cinchona alkaloids catalysts **3f**,² **3g**,³ **3h**³ were prepared according to the literature. Phosphine oxides **2** were prepared according to the literature.⁴ ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian instrument (300, 75 and 121 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet or unresolved, coupling constant(s) in Hz, integration). Data for ¹³C and ³¹P NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm⁻¹. Optical rotations were reported as follows: [α]_D²⁵ (c: g/100 mL, in solvent). Highresolution mass spectra (HRMS) were obtained by the ESI ionization sources. The ee value determination was carried out using chiral HPLC with Daicel Chiracel OD-H, or AD column on Waters with a 996 UV-detector.

- [1] J. Feng, X. Lu, A. Kong, X. Han, *Tetrahedron*. **2007**, 63, 6035.
[2] F.-X. Chen, C. Shao, Q. Wang, P. Gong, D.-Y. Zhang, B.-Z. Zhang, R. Wang, *Tetrahedron Letters*, **48**, **2007**, 8456.
[3] B. Vakulya, S. Varga, A. Csampai, T. Soos, *Org. Lett.* **2005**, 7, 1967.
[4] Y. Uozumi, M. Kawatsura, T. Hayashi, *Org. Synth.* **2002**, 78, 1.

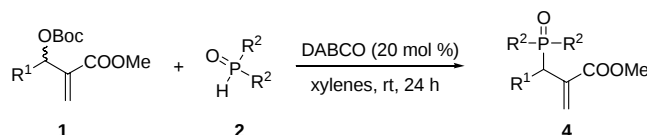
Experimental Procedures and Characterizations:

General Procedure A: Enantioselective Synthesis of **4**.



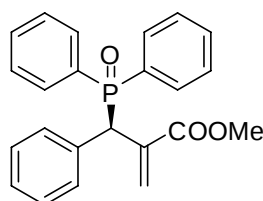
To a solution of Morita-Baylis-Hillman carbonates **1** (0.40 mmol) in the presence of 20 mol % catalyst **3e** and 4 Å MS (100 mg) in xylenes (4.0 mL) was added phosphine oxides **2** (0.20 mmol) and the resulting solution was stirred for 60 h at 0 °C. The reaction mixture was directly purified by silica gel chromatography without work-up and fractions were collected and concentrated in vacuo to provide the pure desired products.

General procedure B: Synthesis of Racemic Product **4**.



To a solution of Morita-Baylis-Hillman carbonates **1** (0.10 mmol) in the presence of 20 mol % DABCO in xylenes (1.0 mL) was added phosphine oxides **2** (0.10 mmol) and the resulting solution was stirred for 24 h at room temperature. The reaction mixture was directly purified by silica gel chromatography without work-up and fractions were collected and concentrated in vacuo to provide the pure desired products.

(*R*)-methyl 2-((diphenylphosphoryl)(phenyl)methyl)acrylate (**4a**)



4a was isolated by column chromatography using silica gel in 77% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.88 (t, *J* = 9.0 Hz, 2H), 7.49-7.16 (m, 13H), 6.82 (s, 1H), 6.43 (s, 1H), 5.06 (d, *J* = 8.4 Hz, 1H), 3.61 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.8 (*J* = 9.75 Hz), 136.5 (*J* = 2.25 Hz), 134.7 (*J* = 5.25 Hz), 132.9 (*J* = 6.75 Hz), 131.7 (*J* = 2.25 Hz), 131.5 (*J* = 3.0 Hz), 131.4 (*J* = 3.0 Hz), 131.2 (*J* = 9.0 Hz), 131.0 (*J* = 9.0 Hz), 130.4 (*J* = 6.0 Hz), 130.1 (*J* = 6.0 Hz), 128.6 (*J* = 11.25 Hz), 128.3 (*J* = 1.5 Hz), 128.1 (*J* = 12 Hz), 127.2 (*J* = 1.5 Hz), 52.3, 45.6 (*J* = 67.5 Hz);

³¹P NMR (121 MHz, CDCl₃): δ 31.6;

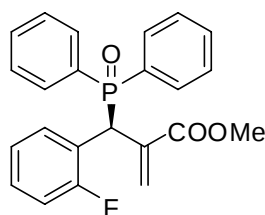
IR: 3058, 2226, 1718, 1438, 1241, 1187, 1125, 699 cm⁻¹;

HRMS (ESI): C₂₃H₂₁O₃P+H, Calc: 377.1301, Found: 377.1309;

[α]_D^{rt} = - 224 (c = 1.11, CHCl₃);

HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: *t*_{major} = 7.8, *t*_{minor} = 11.3, 95% ee.

(S)-methyl 2-((diphenylphosphoryl)(2-fluorophenyl)methyl)acrylate (4b)



4b was isolated by column chromatography using silica gel in 74% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.92-7.85 (m, 3H), 7.56-7.09 (m, 10H), 6.82-6.78 (m, 2H), 6.49 (d, *J* = 2.4 Hz, 1H), 5.53 (d, *J* = 8.7 Hz, 1H), 3.61 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.4 (*J* = 9.75 Hz), 160.0 (*J* = 6.75 Hz, *J* = 245.25 Hz), 135.8 (*J* = 2.25 Hz), 132.4, 131.8(*J* = 3.0 Hz), 131.6 (*J* = 3.0 Hz), 131.4 (*J* = 1.5 Hz, *J* = 4.5 Hz), 131.3 (*J* = 13.5 Hz), 131.2, 131.1, 130.8 (*J* = 9.0 Hz), 128.9 (*J* = 2.25 Hz, *J* = 8.25 Hz), 128.5 (*J* = 12.0 Hz), 128.0 (*J* = 11.25 Hz), 124.2 (*J* = 2.25 Hz, *J* = 3.75 Hz), 122.2 (*J* = 4.5 Hz, 14.25 Hz), 114.8 (*J* = 0.75 Hz, 22.5 Hz), 52.3, 36.5 (*J* = 2.25 Hz, *J* = 67.5 Hz);

³¹P NMR(121 MHz, CDCl₃): δ 31.3 (*J* = 2.78 Hz);

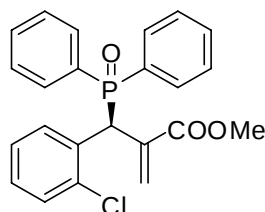
IR: 3059, 2951, 1719, 1489, 1438, 1233, 1190, 1125, 728, 700, 521 cm⁻¹;

HRMS (ESI): C₂₃H₂₀FO₃P+H, Calc: 395.1207, Found: 395.1212;

[α]_D^{rt} = - 138 (c = 1.10, CHCl₃);

HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: *t*_{major} = 14.8, *t*_{minor} = 27.1, 81% ee.

(S)-methyl 2-((2-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4c)



4c was isolated by column chromatography using silica gel in 83% yield.

¹H NMR (300 MHz, CDCl₃) : δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.91-7.85 (m, 2H), 7.56-7.09 (m, 11H), 6.69 (d, *J* = 2.4 Hz, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 5.72 (d, *J* = 9.0 Hz, 1H), 3.57 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.3 (*J* = 9.0 Hz), 135.8 (*J* = 3.0 Hz), 134.6 (*J* = 8.25 Hz), 133.1 (*J* = 3.75 Hz), 132.2 (*J* = 6.75 Hz), 131.8(*J* = 2.25 Hz), 131.7 (*J* = 5.25 Hz), 131.6 (*J* = 3.0 Hz), 131.5, 131.4 (*J* = 3.0 Hz), 131.0 (*J* = 9.0 Hz), 130.9 (*J* = 4.5 Hz), 129.2 (*J* = 0.75 Hz), 128.5 (*J* = 2.25 Hz), 128.4, 128.0 (*J* = 11.25 Hz), 126.9 (*J* = 1.5 Hz), 52.2, 41.1 (*J* = 66.75 Hz);

³¹P NMR(121 MHz, CDCl₃): δ 31.5;

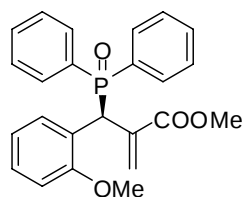
IR: 3059, 2950, 1721, 1473, 1438, 1237, 1193, 1122, 728, 697, 522 cm⁻¹;

HRMS (ESI): C₂₃H₂₀ClO₃P+H, Calc: 411.0911, Found: 411.0904;

[α]_D^{rt} = - 90 (c = 1.00, CHCl₃);

HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: *t*_{major} = 7.1, *t*_{minor} = 4.8, 76% ee.

(R)-methyl 2-((diphenylphosphoryl)(2-methoxyphenyl)methyl)acrylate (4d)



4d was isolated by column chromatography using silica gel in 61% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.93-7.86 (m, 2H), 7.79-7.76 (m, 1H), 7.54-7.11 (m, 9H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 6.57 (d, *J* = 8.1 Hz, 1H), 6.45 (d, *J* = 2.1 Hz, 1H), 5.77 (d, *J* = 8.7 Hz, 1H), 3.58 (s, 3H), 3.41 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.7 (*J* = 9.75 Hz), 156.4 (*J* = 5.25 Hz), 136.4 (*J* = 2.25 Hz), 133.1, 132.9, 131.8, 131.6 (*J* = 3.0 Hz), 131.4, 131.3, 131.1 (*J* = 3.75 Hz), 131.0 (*J* = 4.5 Hz), 130.9 (*J* = 2.25 Hz), 128.4 (*J* = 6.0 Hz, 7.5 Hz), 127.5 (*J* = 12.0 Hz), 122.9 (*J* = 5.25 Hz), 120.5 (*J* = 1.5 Hz), 110.1 (*J* = 1.5 Hz), 55.2, 52.1, 36.6 (*J* = 68.25 Hz);

³¹P NMR (121 MHz, CDCl₃): δ 32.1;

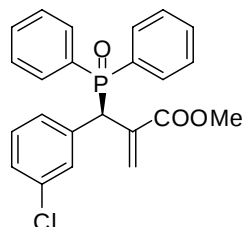
IR: 3057, 2950, 1720, 1491, 1438, 1247, 1185, 1126, 727, 699, 522 cm⁻¹;

HRMS (ESI): C₂₄H₂₃O₄P+H, Calc: 407.1407, Found: 407.1404;

[α]_D^{rt} = - 143 (*c* = 0.80, CHCl₃);

HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: *t*_{major} = 8.3, *t*_{minor} = 22.9, 90% ee.

(R)-methyl 2-((3-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4e)



4e was isolated by column chromatography using silica gel in 81% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.90-7.83 (m, 2H), 7.53-7.08 (m, 12H), 6.81 (d, *J* = 2.4 Hz), 6.45 (d, *J* = 2.1 Hz, 1H), 4.99 (d, *J* = 8.7 Hz, 1H), 3.64 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.6 (*J* = 9.75 Hz), 136.8 (*J* = 5.25 Hz), 135.9 (*J* = 2.25 Hz), 134.0 (*J* = 0.75 Hz), 132.5 (*J* = 8.25 Hz), 131.9 (*J* = 3.0 Hz), 131.7 (*J* = 3.0 Hz), 131.2 (*J* = 2.25 Hz), 131.0 (*J* = 6.75 Hz), 130.9 (*J* = 6.75 Hz), 130.8, 130.1 (*J* = 6.0 Hz), 129.4 (*J* = 1.5 Hz), 128.7 (*J* = 11.25 Hz), 128.3 (*J* = 12.0 Hz), 122.2 (*J* = 5.25 Hz), 127.5 (*J* = 2.25 Hz), 52.4, 45.4 (*J* = 66.75 Hz);

³¹P NMR (121 MHz, CDCl₃): δ 31.3;

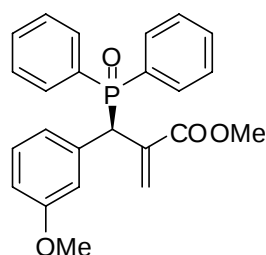
IR: 3056, 1717, 1591, 1438, 1238, 1185, 1130, 699, 517 cm⁻¹;

HRMS (ESI): C₂₃H₂₀ClO₃P+H, Calc: 411.0911, Found: 411.0909;

[α]_D^{rt} = - 241 (*c* = 0.97, CHCl₃);

HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 95/5, flow rate = 0.5 mL/min, retention time: *t*_{major} = 26.1, *t*_{minor} = 29.9, 89% ee.

(R)-methyl 2-((diphenylphosphoryl)(3-methoxyphenyl)methyl)acrylate (4f)



4f was isolated by column chromatography using silica gel in 82% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.90-7.83 (m, 2H), 7.54-6.69 (m, 13H), 6.43 (d, *J* = 2.1 Hz, 1H), 5.04 (d, *J* = 8.7 Hz, 1H), 3.67 (s, 3H), 3.62 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.7 (*J* = 9.75 Hz), 159.3 (*J* = 0.75 Hz), 136.3 (*J* = 2.25 Hz), 136.1 (*J* = 5.25 Hz), 132.8 (*J* = 6.75 Hz), 131.6 (*J* = 3.0 Hz, 20.25 Hz), 131.4 (*J* = 3.0 Hz), 131.2, 131.0 (*J* = 2.25 Hz), 130.9, 130.5 (*J* = 6.75 Hz), 129.1 (*J* = 1.5 Hz), 128.5 (*J* = 11.25 Hz), 128.1 (*J* = 11.25 Hz), 122.4 (*J* = 6 Hz), 115.2 (*J* = 6 Hz), 113.3 (*J* = 1.5 Hz), 55.1, 52.3, 45.5 (*J* = 67.5 Hz);

³¹P NMR(121 MHz, CDCl₃): δ 31.4;

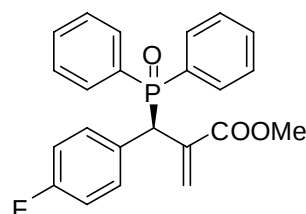
IR: 3057, 2952, 1716, 1599, 1438, 1234, 1191, 1123, 1047, 700, 519 cm⁻¹;

HRMS (ESI): C₂₄H₂₃O₄P+H, Calc:407.1407, Found:407.1400;

[α]_D^{rt} = - 208 (c = 0.96, CHCl₃);

HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: *t*_{major} = 10.4, *t*_{minor} = 12.1, 97% ee.

(R)-methyl 2-((diphenylphosphoryl)(4-fluorophenyl)methyl)acrylate (4g)



4g was isolated by column chromatography using silica gel in 55% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.90-7.84 (m, 2H), 7.55-7.25 (m, 10H), 6.86 (t, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 1.8 Hz, 1H), 6.42 (d, *J* = 1.8 Hz, 1H), 5.01 (d, *J* = 8.4 Hz, 1H), 3.64 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.6 (*J* = 9.75 Hz), 163.6 (*J* = 2.25 Hz), 160.4 (*J* = 2.25 Hz), 136.5 (*J* = 0.75 Hz), 132.6 (*J* = 15.0 Hz), 131.8 (*J* = 2.25 Hz), 131.7, 131.6 (*J* = 2.25 Hz), 131.5 (*J* = 1.5 Hz), 131.3 (*J* = 12.0 Hz), 131.0 (*J* = 9.0 Hz, *J* = 17.25 Hz), 130.4, 128.6 (*J* = 11.25 Hz), 128.2 (*J* = 12 Hz), 115.1 (*J* = 2.25 Hz, *J* = 21.75 Hz), 52.3, 44.8 (*J* = 67.5 Hz);

³¹P NMR(121 MHz, CDCl₃): δ 31.5 (*J* = 2.78 Hz);

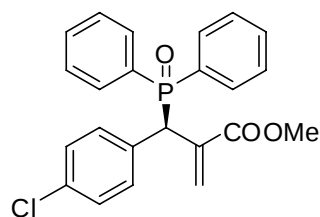
IR: 3058, 2953, 1717, 1507, 1438, 1238, 1189, 1124, 729, 700, 561 cm⁻¹;

HRMS (ESI): C₂₃H₂₀FO₃P+H, Calc: 395.1207, Found: 395.1209;

[α]_D^{rt} = - 183 (c = 0.80, CHCl₃);

HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: *t*_{major} = 8.8, *t*_{minor} = 9.4, 90% ee.

(R)-methyl 2-((4-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4h)



4h was isolated by column chromatography using silica gel in 84% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.86 (t, *J* = 7.8 Hz, 2H), 7.52-7.13 (m, 12H), 6.78 (d, *J* = 1.5 Hz, 1H), 6.43 (s, 1H), 5.00 (d, *J* = 8.4 Hz, 1H), 3.63 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.6 (*J* = 9.75 Hz), 136.2 (*J* = 1.5 Hz), 133.2, 132.5 (*J* = 9.0 Hz), 131.8 (*J* = 2.25 Hz), 131.6 (*J* = 2.25 Hz), 131.3 (*J* = 5.25 Hz), 131.2, 131.1, 131.0, 130.9 (*J* = 9.0 Hz), 130.5 (*J* = 6.75 Hz), 128.6 (*J* = 11.25 Hz), 128.4 (*J* = 1.5 Hz), 128.2 (*J* = 12 Hz), 52.4, 45.0 (*J* = 67.5 Hz);

³¹P NMR (121 MHz, CDCl₃): δ 31.3;

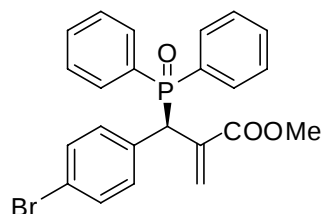
IR: 3057, 2952, 1720, 1489, 1438, 1240, 1189, 1126, 727, 697, 550 cm⁻¹;

HRMS (ESI): C₂₃H₂₀ClO₃P+H, Calc: 411.0911, Found: 411.0910;

[α]_D^{rt} = - 246 (c = 0.98, CHCl₃);

HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: *t*_{major} = 4.6, *t*_{minor} = 5.2, 92% ee.

(R)-methyl 2-((4-bromophenyl)(diphenylphosphoryl)methyl)acrylate (4i)



4i was isolated by column chromatography using silica gel in 85% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.86 (t, *J* = 7.8 Hz, 2H), 7.52-7.22 (m, 12H), 6.78 (s, 1H), 6.43 (s, 1H), 4.99 (d, *J* = 8.4 Hz, 1H), 3.63 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.6 (*J* = 9.0 Hz), 136.2 (*J* = 2.25 Hz), 133.8 (*J* = 5.25 Hz), 132.5 (*J* = 7.5 Hz), 131.8 (*J* = 2.25 Hz), 131.7, 131.6, 131.3 (*J* = 0.75 Hz), 131.1 (*J* = 3.75 Hz), 131.0 (*J* = 7.5 Hz), 130.9 (*J* = 9.0 Hz), 130.5 (*J* = 4.5 Hz), 128.6 (*J* = 11.25 Hz), 128.3 (*J* = 11.25 Hz), 121.4 (*J* = 2.25 Hz), 52.4 (*J* = 7.5 Hz), 45.0 (*J* = 66.75 Hz);

³¹P NMR (121 MHz, CDCl₃): δ 31.2;

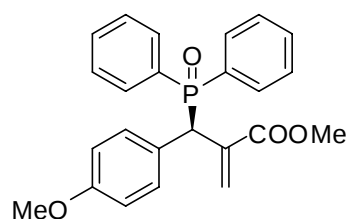
IR: 3057, 2951, 1716, 1485, 1438, 1238, 1189, 1122, 727, 702, 547 cm⁻¹;

HRMS (ESI): C₂₃H₂₀BrO₃P+H, Calc: 455.0406, Found: 455.0407;

[α]_D^{rt} = - 259 (c = 0.99, CHCl₃);

HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: *t*_{major} = 4.7, *t*_{minor} = 5.3, 92% ee.

(R)-methyl 2-((diphenylphosphoryl)(4-methoxyphenyl)methyl)acrylate (4j)



4j was isolated by column chromatography using silica gel in 87% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.90-7.83 (m, 2H), 7.51-7.24 (m, 10H), 6.76-6.70 (m, 3H), 6.40 (d, *J* = 2.1 Hz, 1H), 4.99 (d, *J* = 8.7 Hz, 1H), 3.72 (s, 3H), 3.62 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.8 (*J* = 9.75 Hz), 158.7 (*J* = 2.25 Hz), 136.7 (*J* = 1.5 Hz), 132.9 (*J* = 8.25 Hz), 131.6 (*J* = 2.25 Hz), 131.3 (*J* = 3.0 Hz), 131.1 (*J* = 5.25 Hz), 131.0 (*J* = 5.25 Hz), 131.0, 130.9, 130.0 (*J* = 6.75 Hz), 128.5 (*J* = 11.25 Hz), 128.1 (*J* = 12 Hz), 126.5 (*J* = 5.25 Hz), 113.7 (*J* = 1.5 Hz), 55.1, 52.3, 44.7 (*J* = 68.25 Hz);

³¹P NMR (121 MHz, CDCl₃): δ 31.7;

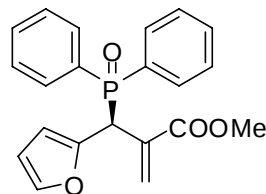
IR: 3057, 2953, 1717, 1510, 1438, 1253, 1183, 1124, 727, 700, 519 cm⁻¹;

HRMS (ESI): C₂₄H₂₃O₄P+H, Calc: 407.1407, Found: 407.1403;

[α]_D^{rt} = - 247 (*c* = 0.95, CHCl₃);

HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 0.5 mL/min, retention time: *t*_{major} = 10.3, *t*_{minor} = 11.4, 95% ee.

(S)-methyl 2-((diphenylphosphoryl)(furan-2-yl)methyl)acrylate (4k)



4k was isolated by column chromatography using silica gel in 98% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.81-7.65 (m, 4H), 7.52-7.35 (m, 6H), 7.24 (t, *J* = 0.9 Hz, 1H), 6.52 (m, 2H), 6.39 (t, *J* = 2.7 Hz, 1H), 6.22 (*J* = 1.8 Hz, 1H), 5.36 (d, *J* = 10.8 Hz, 1H), 3.56 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.4 (*J* = 6.0 Hz), 148.5 (*J* = 4.5 Hz), 142.1 (*J* = 2.25 Hz), 133.3 (*J* = 3.75 Hz), 132.2 (*J* = 18.75 Hz), 131.8, 131.8 (*J* = 3.0 Hz), 131.7, 131.6, 131.4 (*J* = 9.0 Hz), 131.1 (*J* = 9.0 Hz), 130.8 (*J* = 16.5 Hz), 128.3 (*J* = 12 Hz), 110.7 (*J* = 1.5 Hz), 109.8 (*J* = 4.5 Hz), 52.3, 39.9 (*J* = 66.0 Hz);

³¹P NMR (121 MHz, CDCl₃): δ 29.2;

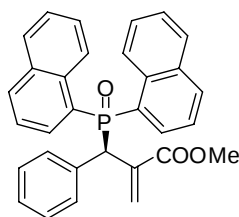
IR: 3057, 1717, 1438, 1271, 1199, 1120, 699, 526 cm⁻¹;

HRMS (ESI): C₂₁H₁₉O₄P+H, Calc: 367.1094, Found: 367.1088;

[α]_D^{rt} = + 3 (*c* = 1.04, CHCl₃);

HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: *t*_{major} = 13.4, *t*_{minor} = 16.6, 44% ee.

(R)-methyl 2-((dinaphthalen-1-ylphosphoryl)(phenyl)methyl)acrylate (4l)



4l was isolated by column chromatography using silica gel in 80% yield.

¹H NMR (300 MHz, CDCl₃): δ 8.72 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.04-6.95 (m, 18H), 6.56 (d, *J* = 1.8 Hz, 1H), 5.29 (d, *J* = 9 Hz, 1H), 3.58(s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.9 (*J* = 10.5 Hz), 137.0 (*J* = 2.25 Hz), 134.7(*J* = 5.25 Hz), 134.0 (*J* = 2.25 Hz, *J* = 8.25 Hz), 133.9, 133.2 (*J* = 9.0 Hz), 133.0 (*J* = 2.25 Hz), 132.7 (*J* = 3.0 Hz), 132.0 (*J* = 10.5 Hz), 131.4 (*J* = 9.75 Hz, *J* = 17.25Hz), 130.1 (*J* = 12.0 Hz), 129.8, 128.7, 128.5 (*J* = 0.75 Hz), 128.3, 128.0 (*J* = 1.5 Hz), 127.3, 127.1 (*J* = 5.25 Hz, *J* = 9.0 Hz), 126.8, 126.3, 126.2 (*J* = 3.75 Hz), 125.8, 124.1 (*J* = 11.25 Hz, *J* = 13.5 Hz), 52.3, 46.5 (*J* = 68.25 Hz);

³¹P NMR(121 MHz, CDCl₃): δ 38.4;

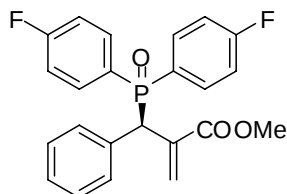
IR: 3059, 2230, 1714, 1505, 1438, 1241, 1174, 775, 732 cm⁻¹;

HRMS (ESI): C₃₁H₂₅O₃P+H, Calc: 477.1614, Found: 477.1606;

[α]_D^{rt} = - 16 (c = 1.34, CHCl₃);

HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: *t*_{major} = 25.4, *t*_{minor} = 42.7, 95% ee.

(R)-methyl 2-((bis(4-fluorophenyl)phosphoryl)(phenyl)methyl)acrylate (4m)



4m was isolated by column chromatography using silica gel in 63% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.91- 7.83 (m, 2H), 7.48-7.39 (m, 2H), 7.36-7.33 (dd, *J* = 2.1 Hz, *J* = 5.4 Hz, 2H), 7.22-7.15 (m, 5H), 6.99-6.92 (m, 2H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.44 (d, *J* = 2.1 Hz, 1H), 4.99 (d, *J* = 8.4 Hz, 1H), 3.64(s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.7 (*J* = 9.75 Hz), 165.0 (*J* = 3.75 Hz, *J* = 252 Hz), 164.7 (*J* = 3.75 Hz, *J* = 252.25 Hz), 136.1 (*J* = 9.75 Hz), 134.3(*J* = 5.25 Hz), 133.6 (*J* = 8.25 Hz, *J* = 9.75 Hz), 133.4 (*J* = 9.0 Hz, *J* = 10.5 Hz), 130.5 (*J* = 6.0 Hz), 130.0 (*J* = 6.0 Hz), 128.5 (*J* = 3.0 Hz, *J* = 19.5 Hz), 128.4 (*J* = 1.5 Hz), 127.4 (*J* = 2.25 Hz), 127.1 (*J* = 3.75 Hz, *J* = 15.75 Hz), 116.1 (*J* = 12.75 Hz, *J* = 21.0 Hz), 115.6 (*J* = 12.75 Hz, *J* = 21.0 Hz), 52.4, 45.7 (*J* = 68.25 Hz);

³¹P NMR(121 MHz, CDCl₃): δ 30.6;

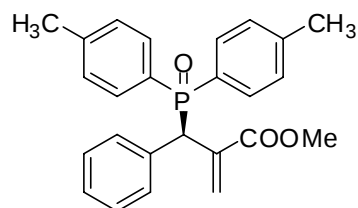
IR: 2229, 1716, 1592, 1498, 1237, 1190, 1118, 830, 542 cm⁻¹;

HRMS (ESI): C₂₃H₁₉F₂O₃P+H, Calc: 413.1113, Found: 413.1121;

[α]_D^{rt} = - 199 (c = 1.11, CHCl₃);

HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: *t*_{major} = 8.3, *t*_{minor} = 11.7, 90% ee.

(R)-methyl 2-((dip-tolylphosphoryl)(phenyl)methyl)acrylate (4n)



4n was isolated by column chromatography using silica gel in 81% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.74 (dd, *J* = 7.8 Hz, *J* = 10.5 Hz, 2H), 7.36-7.03 (m, 11H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.42 (d, *J* = 1.8 Hz, 1H), 4.99 (d, *J* = 8.7 Hz, 1H), 3.61 (s, 3H), 2.37 (s, 3H), 2.26 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.8 (*J* = 9.75 Hz), 141.9 (*J* = 3.0 Hz), 141.6 (*J* = 3.0 Hz), 136.6 (*J* = 2.25 Hz), 134.9 (*J* = 5.25 Hz), 131.1 (*J* = 9.0 Hz), 130.9 (*J* = 9.0 Hz), 130.2 (*J* = 6.75 Hz), 130.0 (*J* = 5.25 Hz), 129.8 (*J* = 9.0 Hz), 129.2 (*J* = 12.0 Hz), 128.8 (*J* = 12.0 Hz), 128.4 (*J* = 6.0 Hz), 128.2 (*J* = 0.75 Hz), 127.0 (*J* = 2.25 Hz), 52.2, 45.7 (*J* = 67.5 Hz), 21.5, 21.4;

³¹P NMR (121 MHz, CDCl₃): δ 31.9;

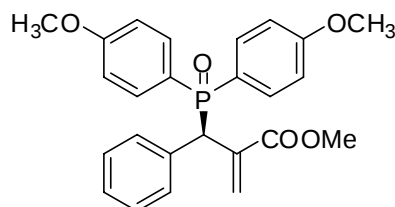
IR: 3027, 2223, 1716, 1440, 1239, 1185, 1118, 655 cm⁻¹;

HRMS (ESI): C₂₅H₂₅O₃P+H, Calc: 405.1614, Found: 405.1610;

[α]_D^{rt} = - 216 (c = 0.98, CHCl₃);

HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 12.3, t_{minor} = 9.3, 94% ee.

(R)-methyl 2-((bis(4-methoxyphenyl)phosphoryl)(phenyl)methyl)acrylate (4o)



4o was isolated by column chromatography using silica gel in 94% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.77 (dd, *J* = 8.7 Hz, *J* = 10.5 Hz, 2H), 7.37-7.30 (m, 4H), 7.22-7.17 (m, 3H), 6.97 (dd, *J* = 2.4 Hz, *J* = 9.0 Hz, 2H), 6.76 (dt, *J* = 2.4 Hz, *J* = 9.0 Hz, 3H), 6.42 (d, *J* = 2.1 Hz, 1H), 4.95 (d, *J* = 8.7 Hz, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 3.62 (s, 3H);

¹³C NMR (75 MHz, CDCl₃): δ 166.8 (*J* = 9.75 Hz), 162.2 (*J* = 3.0 Hz), 161.9 (*J* = 3.0 Hz), 136.6 (*J* = 2.25 Hz), 134.9 (*J* = 5.25 Hz), 132.9 (*J* = 9.75 Hz), 132.8 (*J* = 10.5 Hz), 130.2 (*J* = 6.0 Hz), 130.0 (*J* = 6.0 Hz), 128.2 (*J* = 1.5 Hz), 127.0 (*J* = 1.5 Hz), 124.2 (*J* = 30.0 Hz), 122.8 (*J* = 26.25 Hz), 114.1 (*J* = 12.75 Hz), 113.5 (*J* = 12.75 Hz), 55.2, 55.1, 52.2, 46.0 (*J* = 67.5 Hz);

³¹P NMR (121 MHz, CDCl₃): δ 32.1;

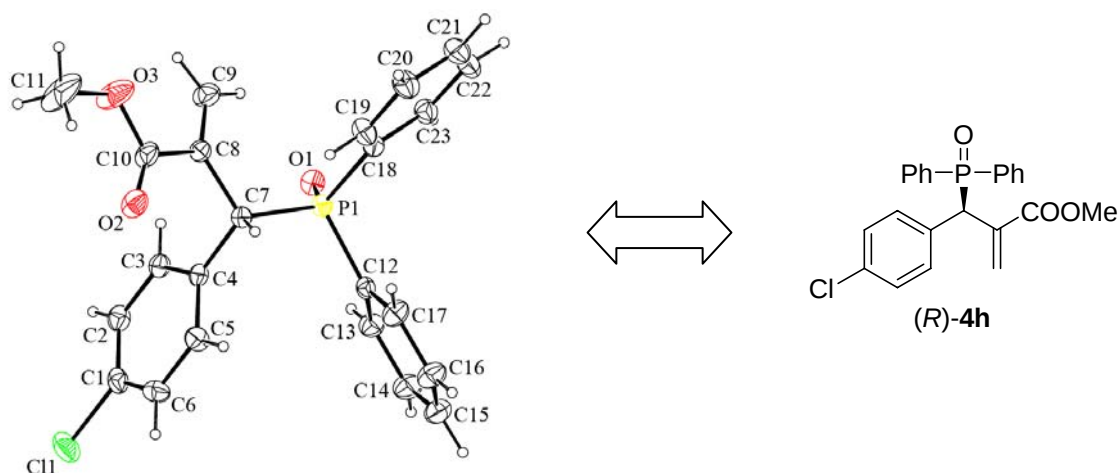
IR: 2953, 2222, 1716, 1597, 1501, 1256, 1179, 1119, 1028, 732, 549 cm⁻¹;

HRMS (ESI): C₂₅H₂₅O₅P+H, Calc: 437.1512, Found: 437.1519;

[α]_D^{rt} = - 227 (c = 0.96, CHCl₃);

HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 37.3, t_{minor} = 35.4, 94% ee.

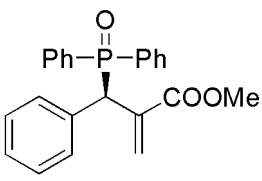
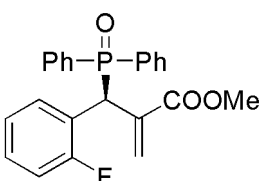
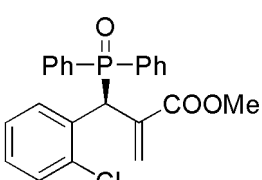
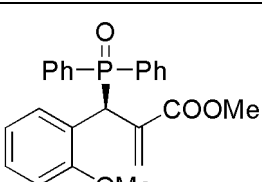
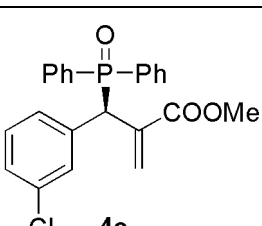
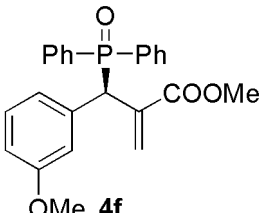
X-ray Structure of (R)-4h:

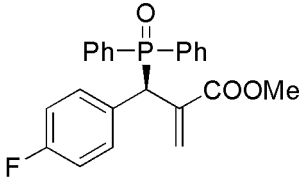
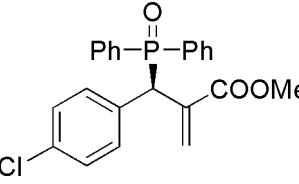
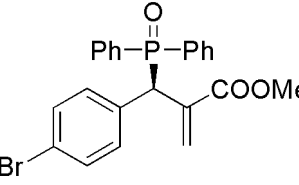
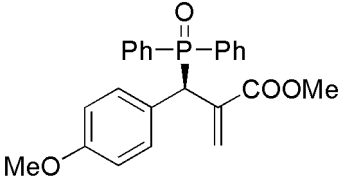
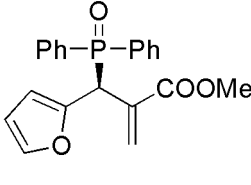
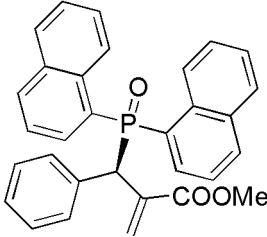
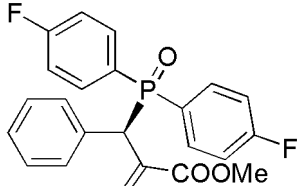


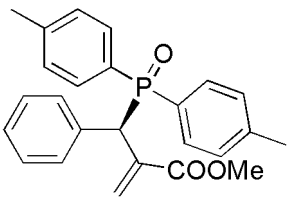
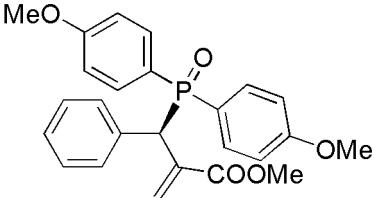
Datablock: p21

Bond precision:		C-C = 0.0050 Å	Wavelength=0.71073
Cell:	a=5.7884(6)	b=19.672(2)	c=9.4173(11)
	alpha=90	beta=103.446(6)	gamma=90
Temperature: 296 K			
	Calculated	Reported	
Volume	1043.0(2)	1043.0(2)	
Space group	P 21	P2(1)	
Hall group	P 2yb	?	
Moiety formula	C23 H20 Cl O3 P	?	
Sum formula	C23 H20 Cl O3 P	C23 H20 Cl O3 P	
Mr	410.81	410.81	
Dx,g cm-3	1.308	1.308	
Z	2	2	
Mu (mm-1)	0.280	0.280	
F000	428.0	428.0	
F000'	428.67		
h,k,lmax	7,24,11	7,24,11	
Nref	2227[4321]	4030	
Tmin,Tmax	0.899,0.930	0.901,0.931	
Tmin'	0.899		
Correction method= MULTI-SCAN			
Data completeness= 1.81/0.93		Theta(max)= 26.490	
R(reflections)= 0.0439(3264)		wR2(reflections)= 0.1017(4030)	
S = 1.042	Npar= 254		

HPLC Analytic Conditions:

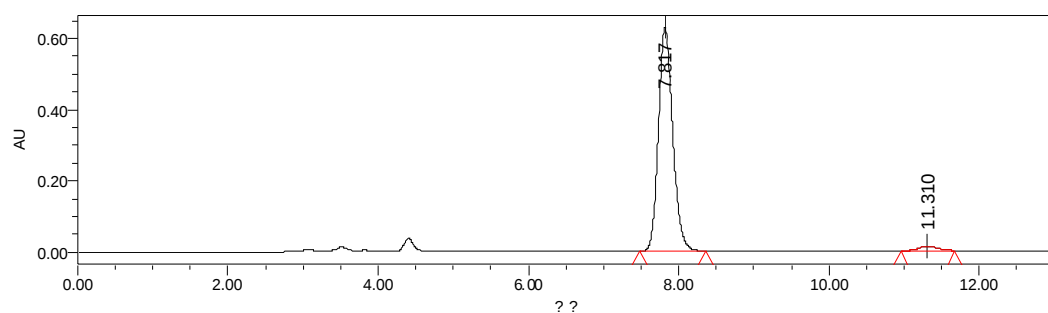
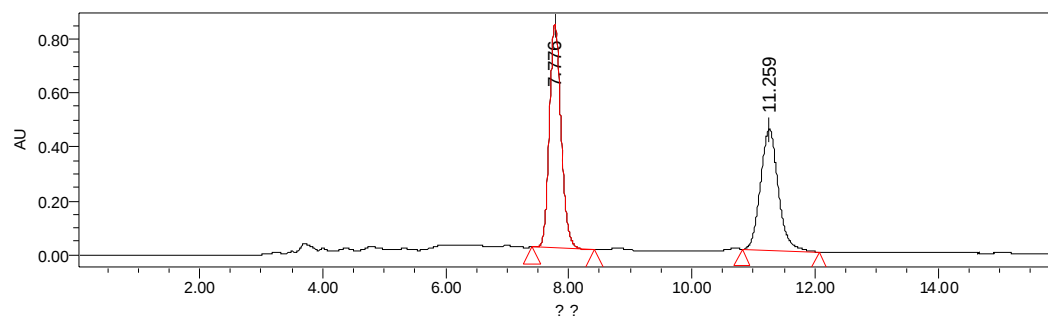
Entry	Product	Chiralcel column	Fluent phase Hexane/iPrOH	Flow rate	Retention time	ee (%)
1	 4a	AD	70:30	1.0	$t_{\text{major}} = 7.8$ $t_{\text{minor}} = 11.3$	95
2	 4b	AD	80:20	1.0	$t_{\text{major}} = 14.8$ $t_{\text{minor}} = 27.1$	81
3	 4c	OD-H	70:30	1.0	$t_{\text{major}} = 7.1$ $t_{\text{minor}} = 4.8$	76
4	 4d	AD	70:30	1.0	$t_{\text{major}} = 8.3$ $t_{\text{minor}} = 22.9$	90
5	 4e	OD-H	95:5	0.5	$t_{\text{major}} = 26.1$ $t_{\text{minor}} = 29.9$	89
6	 4f	AD	70:30	1.0	$t_{\text{major}} = 10.4$ $t_{\text{minor}} = 12.1$	97

7	 4g	OD-H	70:30	1.0	$t_{\text{major}} = 8.8$ $t_{\text{minor}} = 9.4$	90
8	 4h	OD-H	70:30	1.0	$t_{\text{major}} = 4.6$ $t_{\text{minor}} = 5.2$	92
9	 4i	OD-H	70:30	1.0	$t_{\text{major}} = 4.7$ $t_{\text{minor}} = 5.3$	92
10	 4j	OD-H	70:30	0.5	$t_{\text{major}} = 10.3$ $t_{\text{minor}} = 11.4$	95
11	 4k	AD	70:30	1.0	$t_{\text{major}} = 13.4$ $t_{\text{minor}} = 16.6$	44
12	 4l	AD	80:20	1.0	$t_{\text{major}} = 25.4$ $t_{\text{minor}} = 42.7$	95
13	 4m	AD	70:30	1.0	$t_{\text{major}} = 8.3$ $t_{\text{minor}} = 11.7$	90

14	 4n	AD	90:10	1.0	$t_{\text{major}} = 12.3$ $t_{\text{minor}} = 9.3$	94
15	 4o	AD	70:30	1.0	$t_{\text{major}} = 37.3$ $t_{\text{minor}} = 35.4$	94

(R)-methyl 2-((diphenylphosphoryl)(phenyl)methyl)acrylate (4a)

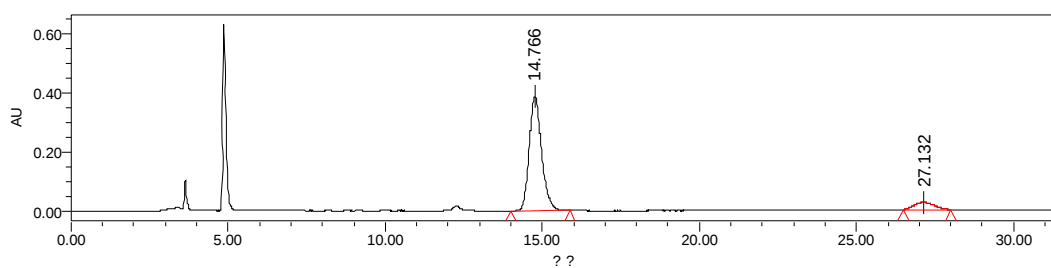
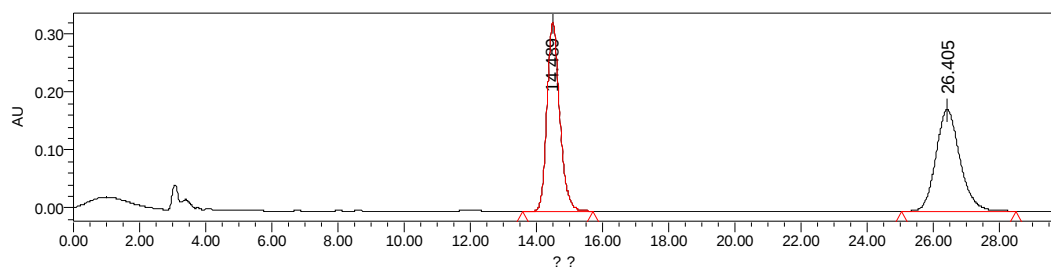
Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	名称	保留时间	面积	% 面积	高度	积分类型
1		7.817	8286292	97.36	629244	bb
2		11.310	224453	2.64	11889	bb

(S)-methyl 2-((diphenylphosphoryl)(2-fluorophenyl)methyl)acrylate (4b)

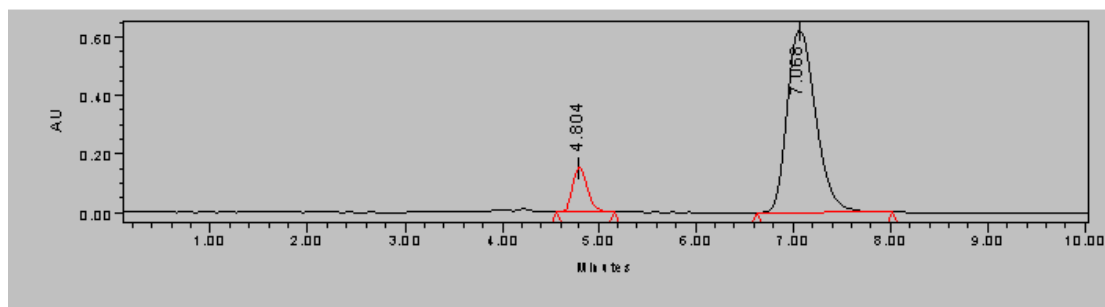
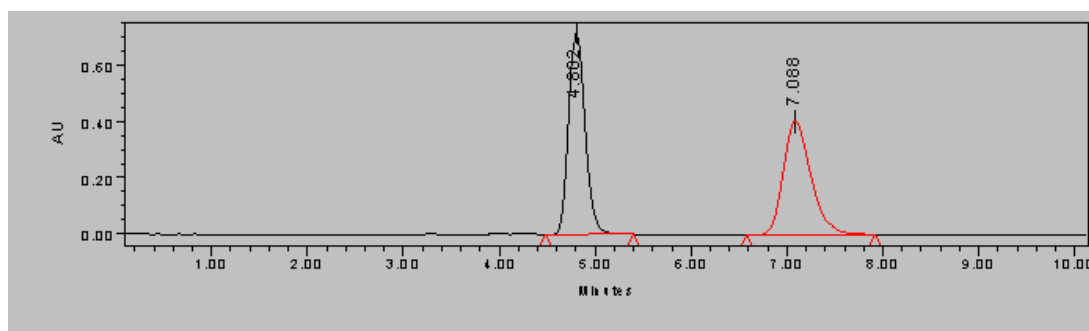
Chiralpak AD column, hexane/iPrOH (80:20), flow rate 1.0 mL/min.



	名称	保留时间	面积	% 面积	高度	积分类型
1		14.766	10565042	90.43	385282	bb
2		27.132	1118001	9.57	24777	bb

(S)-methyl 2-((2-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4c)

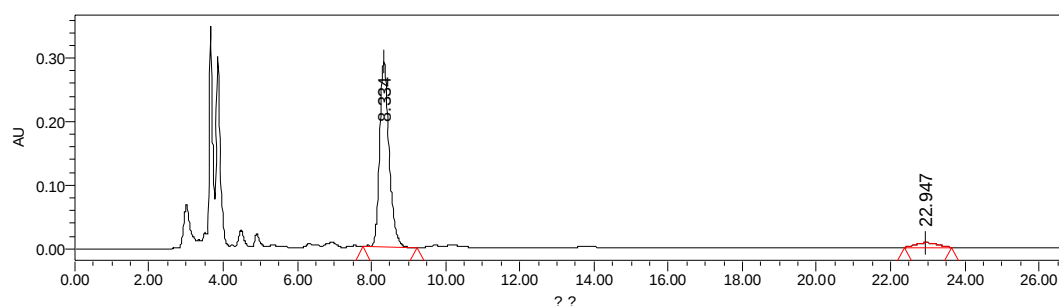
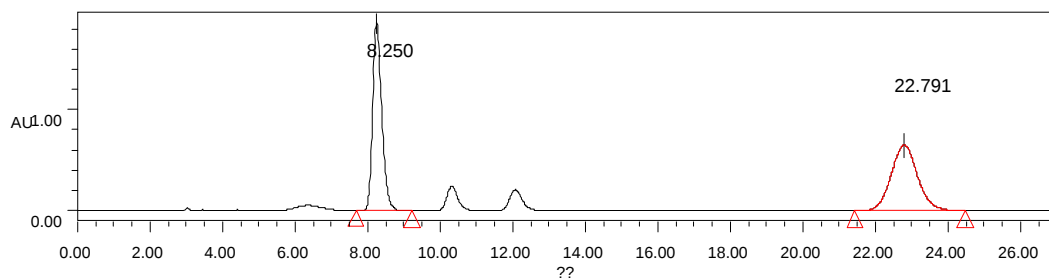
Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		4.804	1711865	11.96	153718	bb			Unknown	
2		7.068	12597053	88.04	623659	bb			Unknown	

(R)-methyl 2-((diphenylphosphoryl)(2-methoxyphenyl)methyl)acrylate (4d)

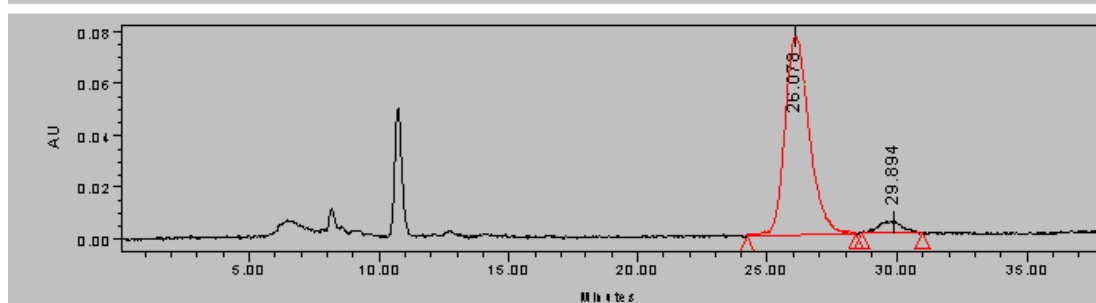
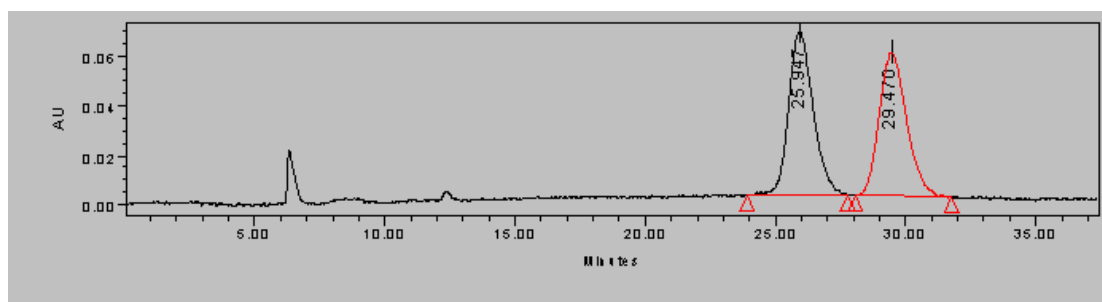
Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	名称	保留时间	面积	% 面积	高度	积分类型
1		8.334	5249128	94.95	291731	bb
2		22.947	279230	5.05	6879	bb

(R)-methyl 2-((3-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4e)

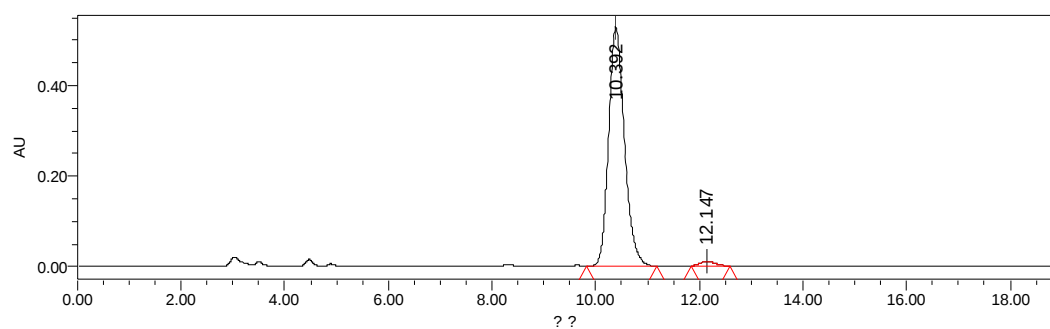
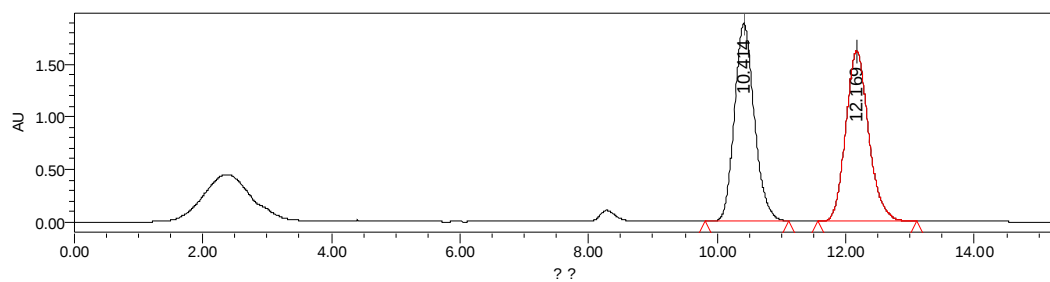
Chiralpak OD-H column, hexane/iPrOH (95:5), flow rate 0.5 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		26.078	4966129	94.57	76409	bb			Unknown	
2		29.894	285135	5.43	4519	bb			Unknown	

(R)-methyl 2-((diphenylphosphoryl)(3-methoxyphenyl)methyl)acrylate (4f)

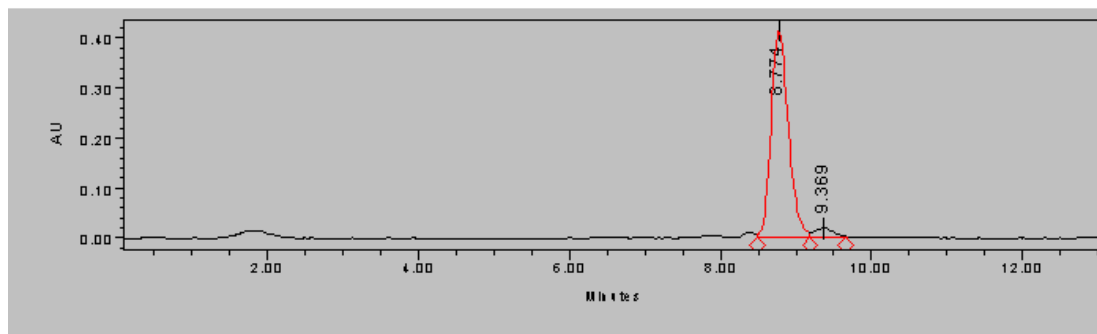
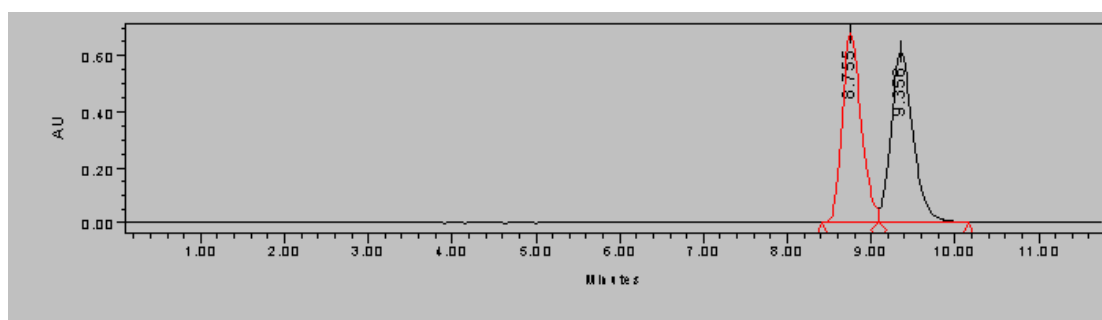
Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	名称	保留时间	面积	% 面积	高度	积分类型
1		10.392	11178740	98.49	527224	bb
2		12.147	171823	1.51	8590	bb

(R)-methyl 2-((diphenylphosphoryl)(4-fluorophenyl)methyl)acrylate (4g)

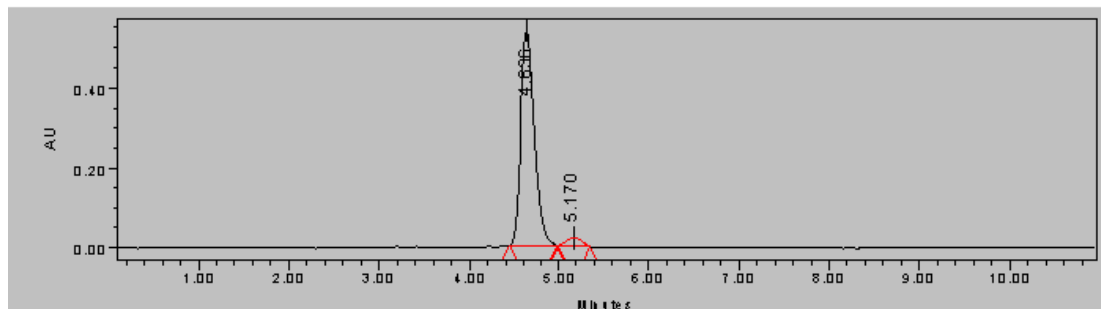
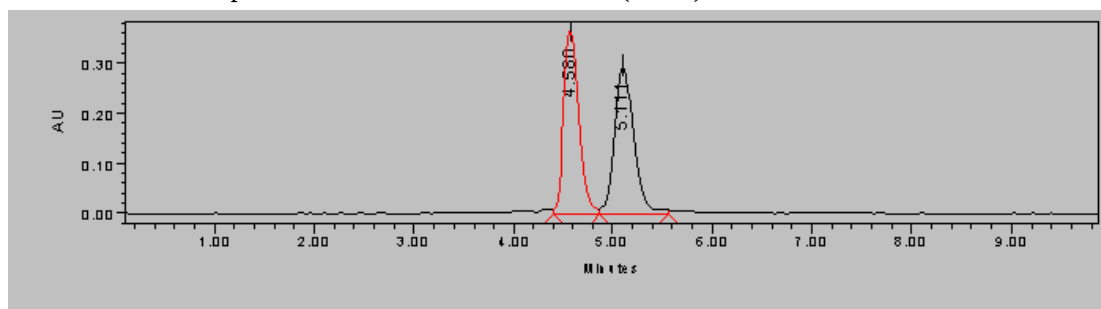
Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
2		9.369	350135	5.00	19340	VV			Unknown	
1		8.774	6652719	95.00	415314	VV			Unknown	

(R)-methyl 2-((4-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4h)

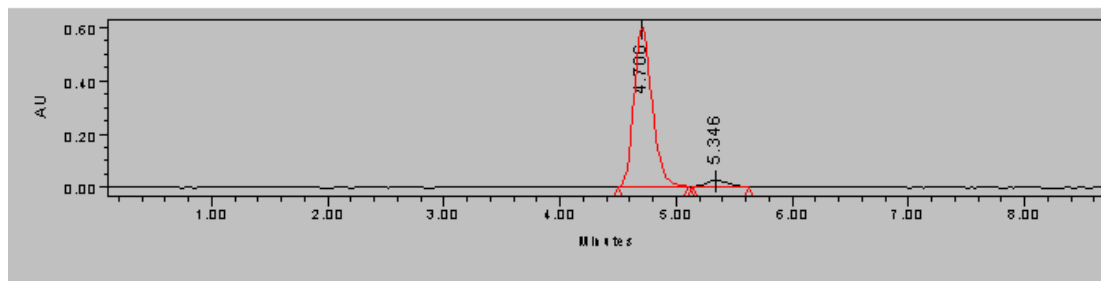
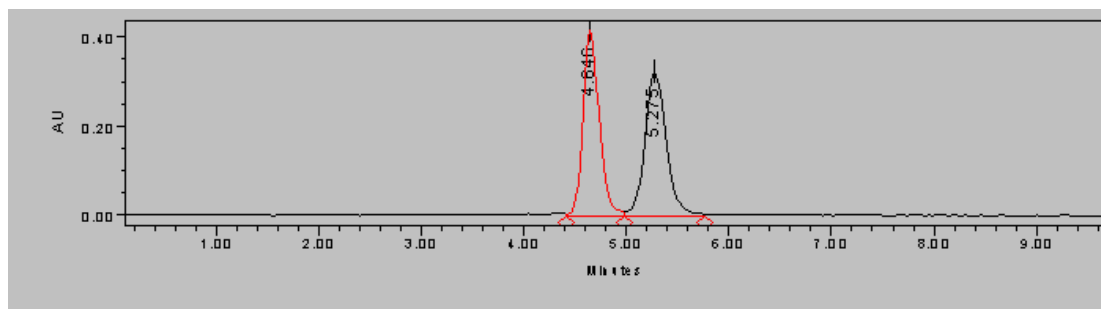
Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		4.636	5666253	96.19	538003	bb			Unknown	
2		5.170	224734	3.81	20494	bb			Unknown	

(R)-methyl 2-((4-bromophenyl)(diphenylphosphoryl)methyl)acrylate (4i)

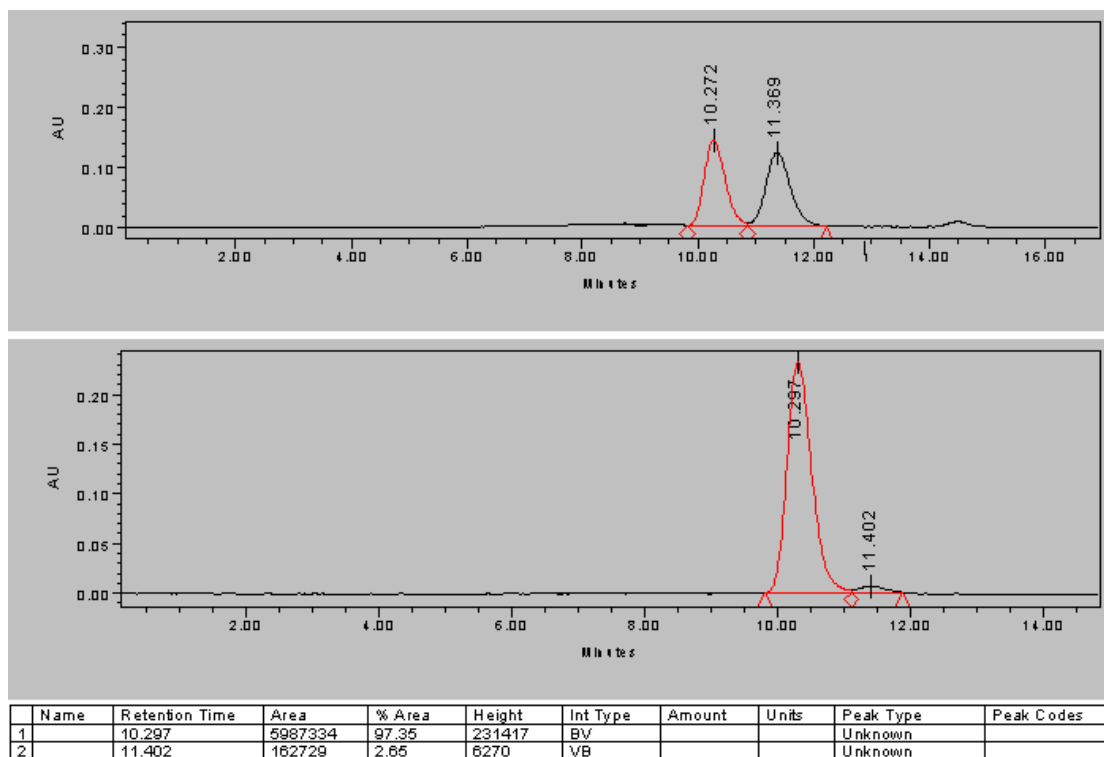
Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		4.706	6486342	95.89	595435	bb			Unknown	
2		5.346	277939	4.11	21974	bb			Unknown	

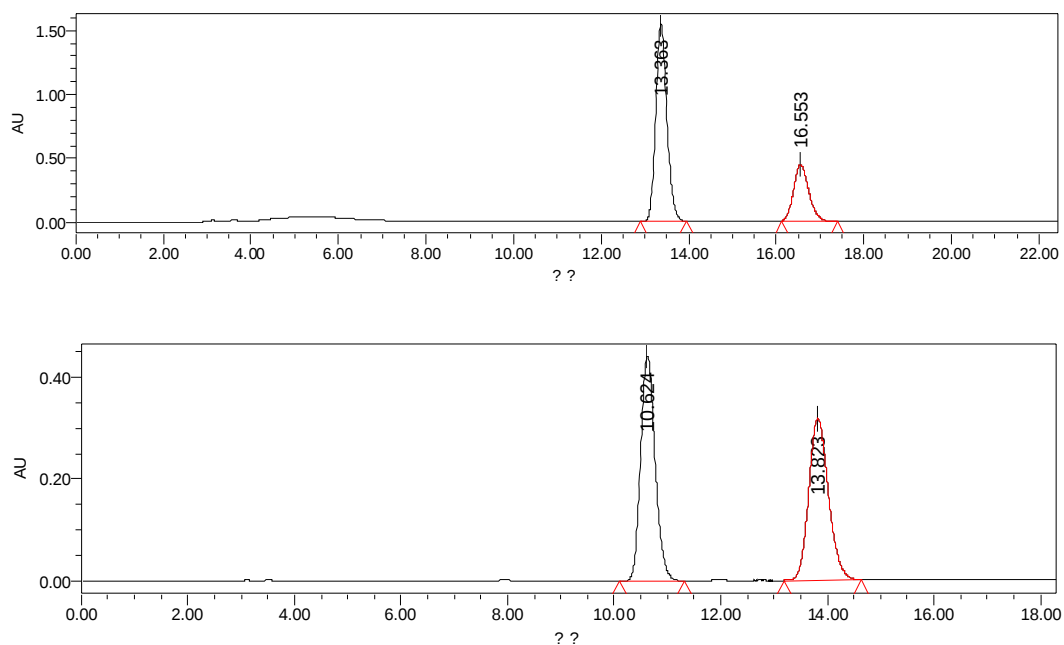
(R)-methyl 2-((diphenylphosphoryl)(4-methoxyphenyl)methyl)acrylate (4j)

Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 0.5 mL/min.



(S)-methyl 2-((diphenylphosphoryl)(furan-2-yl)methyl)acrylate (4k)

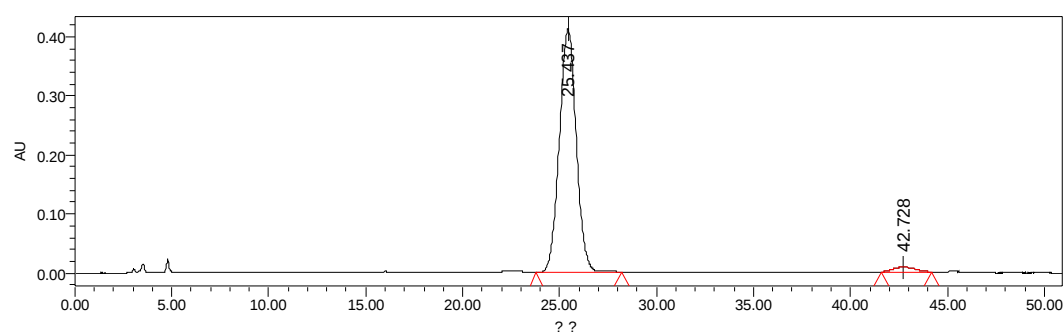
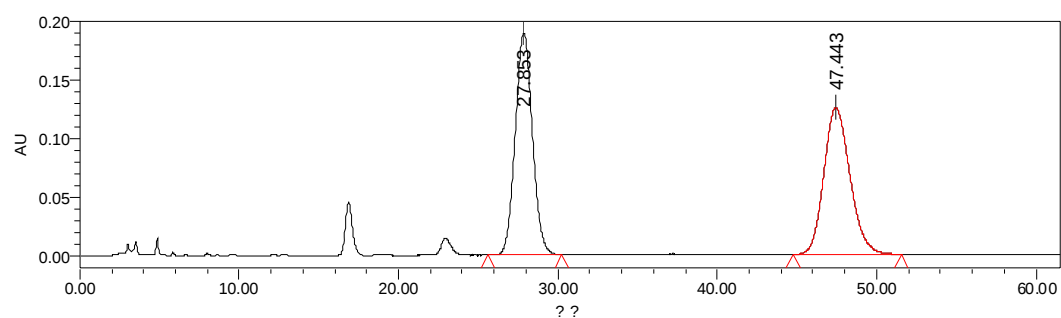
Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	名称	保留时间	面积	% 面积	高度	积分类型
1		13.363	27462035	71.99	1545070	bb
2		16.553	10683399	28.01	441817	bb

(R)-methyl 2-((dinaphthalen-1-ylphosphoryl)(phenyl)methyl)acrylate (4l)

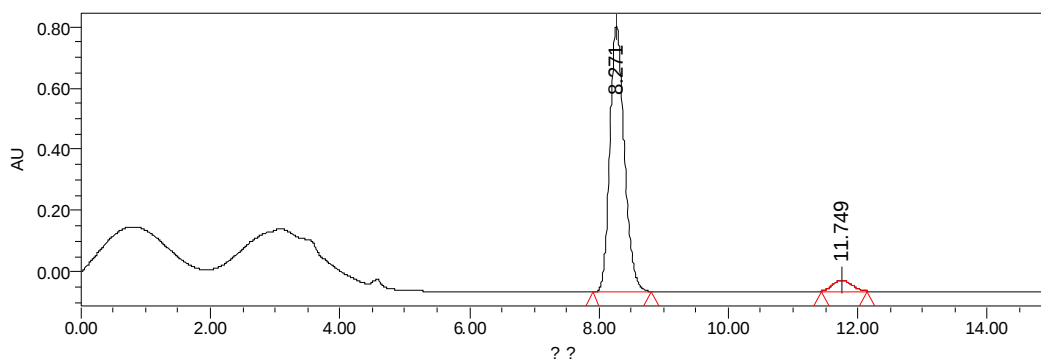
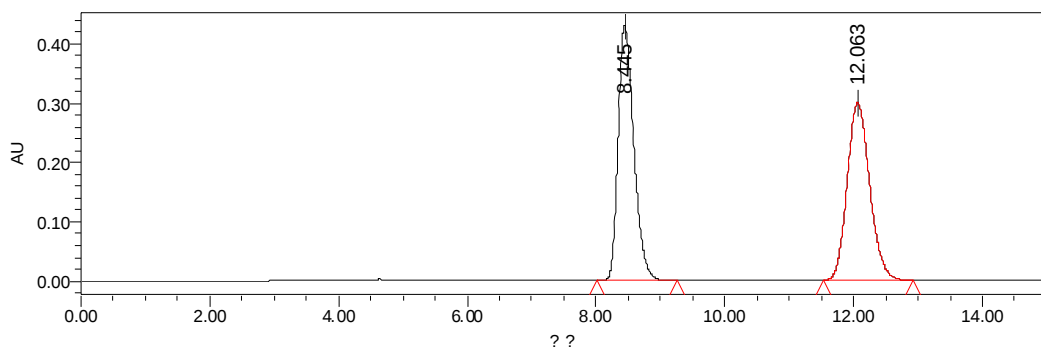
Chiralpak AD column, hexane/iPrOH (80:20), flow rate 1.0 mL/min.



	名称	保留时间	面积	% 面积	高度	积分类型
1		25.437	25019521	97.41	412177	bb
2		42.728	664290	2.59	8237	bb

(R)-methyl 2-((bis(4-fluorophenyl)phosphoryl)(phenyl)methyl)acrylate (4m)

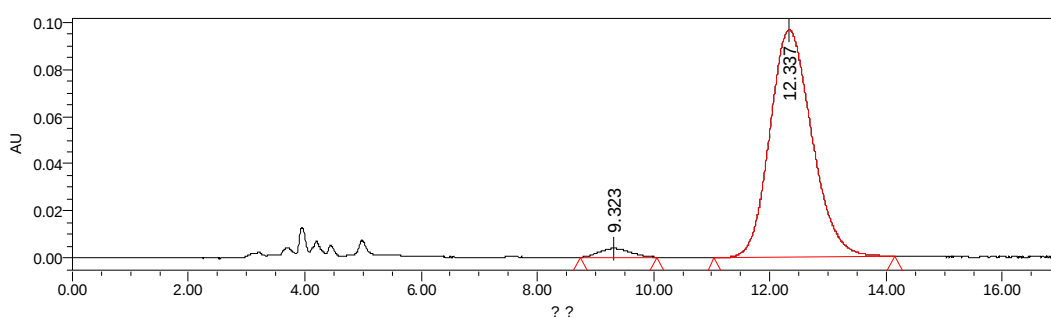
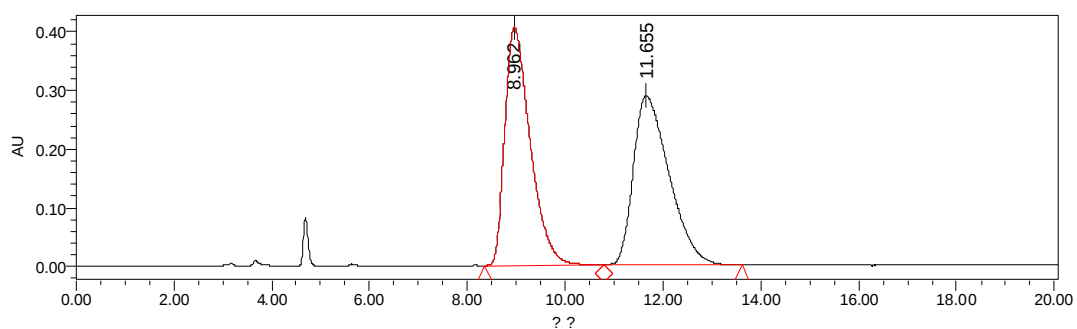
Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	名称	保留时间	面积	% 面积	高度	积分类型
1		8.271	13521215	94.87	865031	bb
2		11.749	731488	5.13	35602	bb

(R)-methyl 2-((dip-tolylphosphoryl)(phenyl)methyl)acrylate (4n)

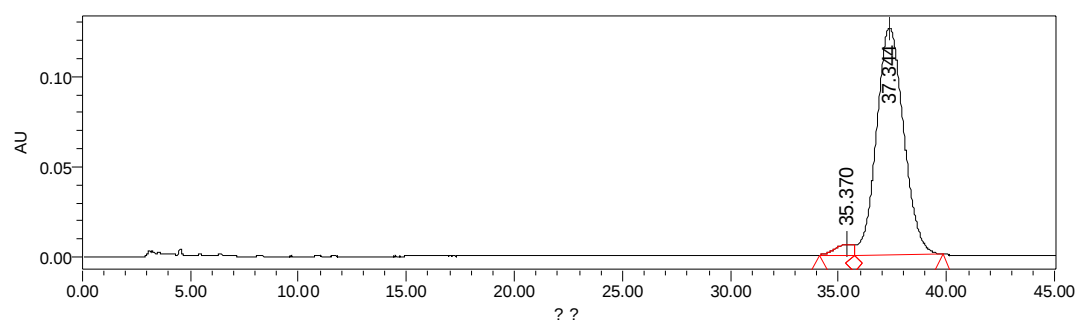
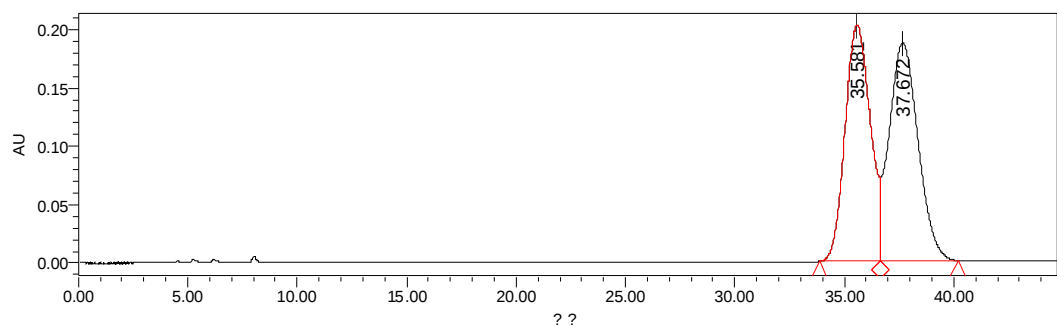
Chiralpak AD column, hexane/iPrOH (90:10), flow rate 1.0 mL/min.



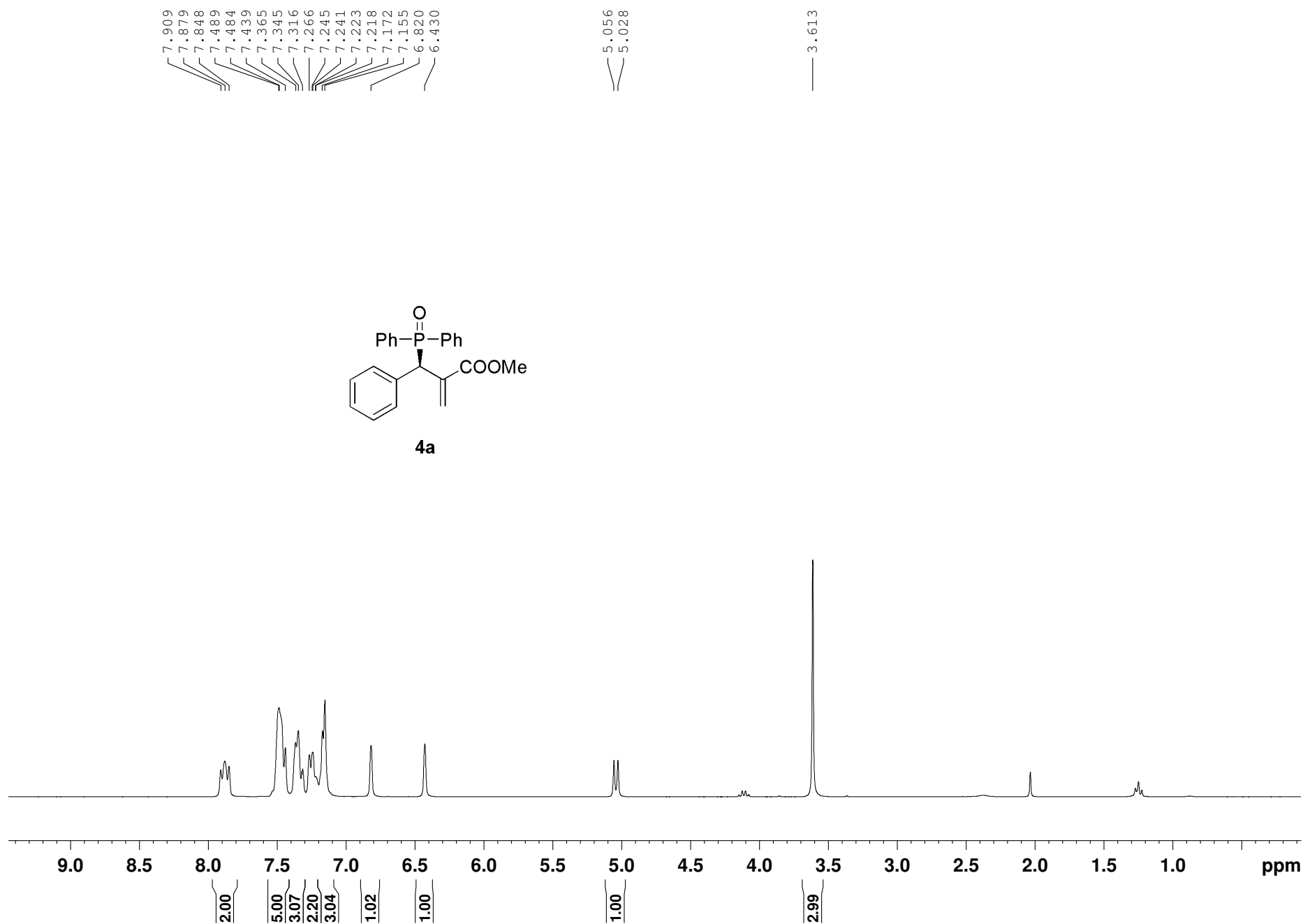
	名称	保留时间	面积	% 面积	高度	积分类型
1		9.323	137087	2.75	3687	bb
2		12.337	4839363	97.25	96427	bb

(R)-methyl 2-((bis(4-methoxyphenyl)phosphoryl)(phenyl)methyl)acrylate (4o)

Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.



	名称	保留时间	面积	% 面积	高度	积分类型
1		35.370	327304	2.89	5723	BV
2		37.344	10988257	97.11	125847	VB

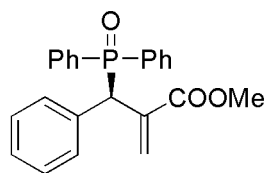


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127.11

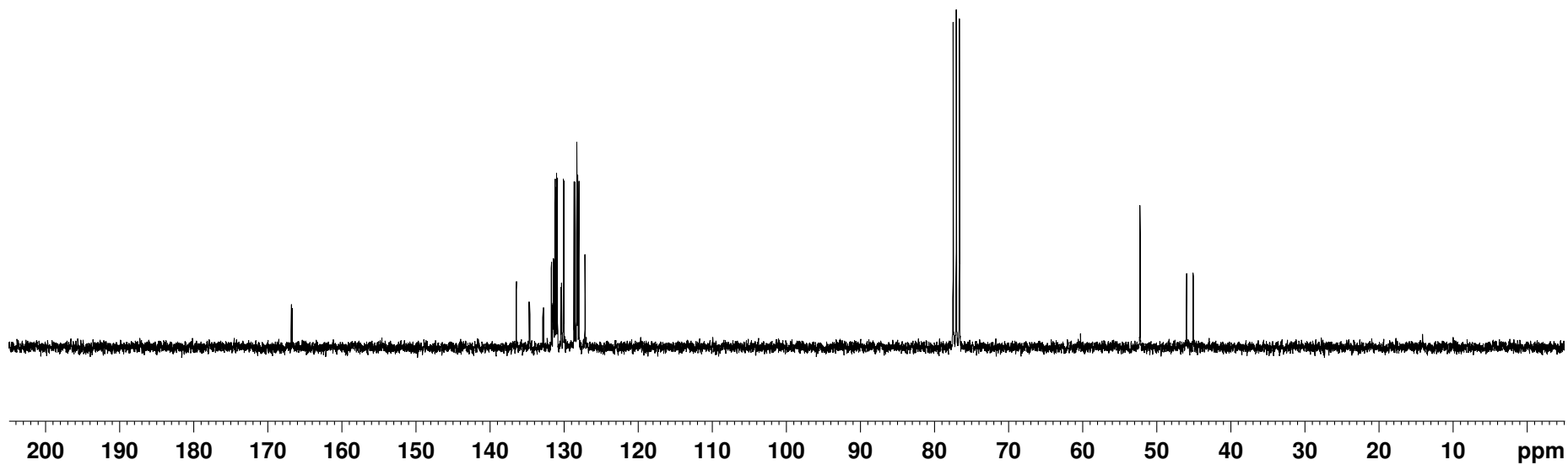
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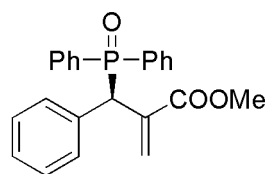
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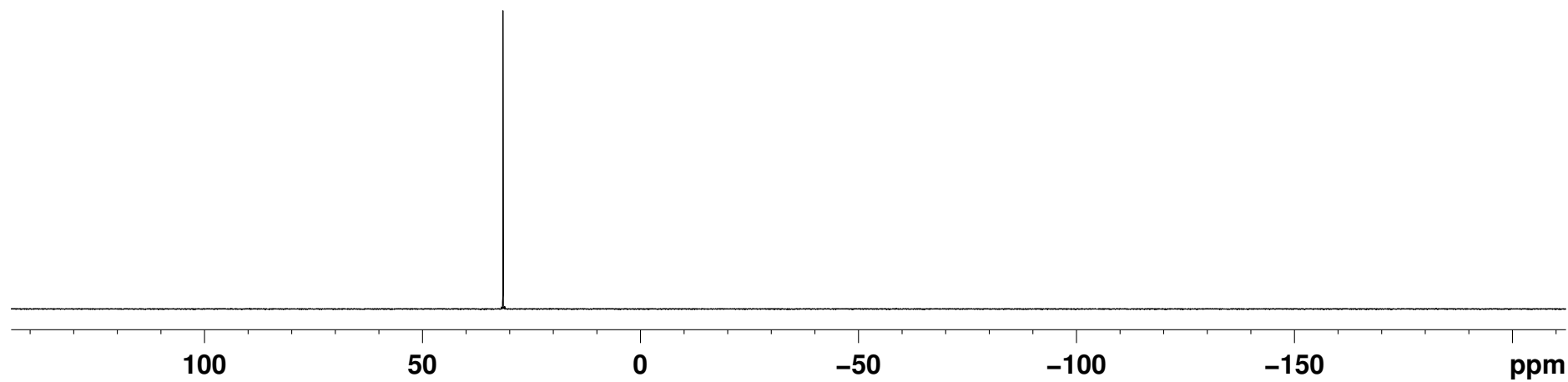
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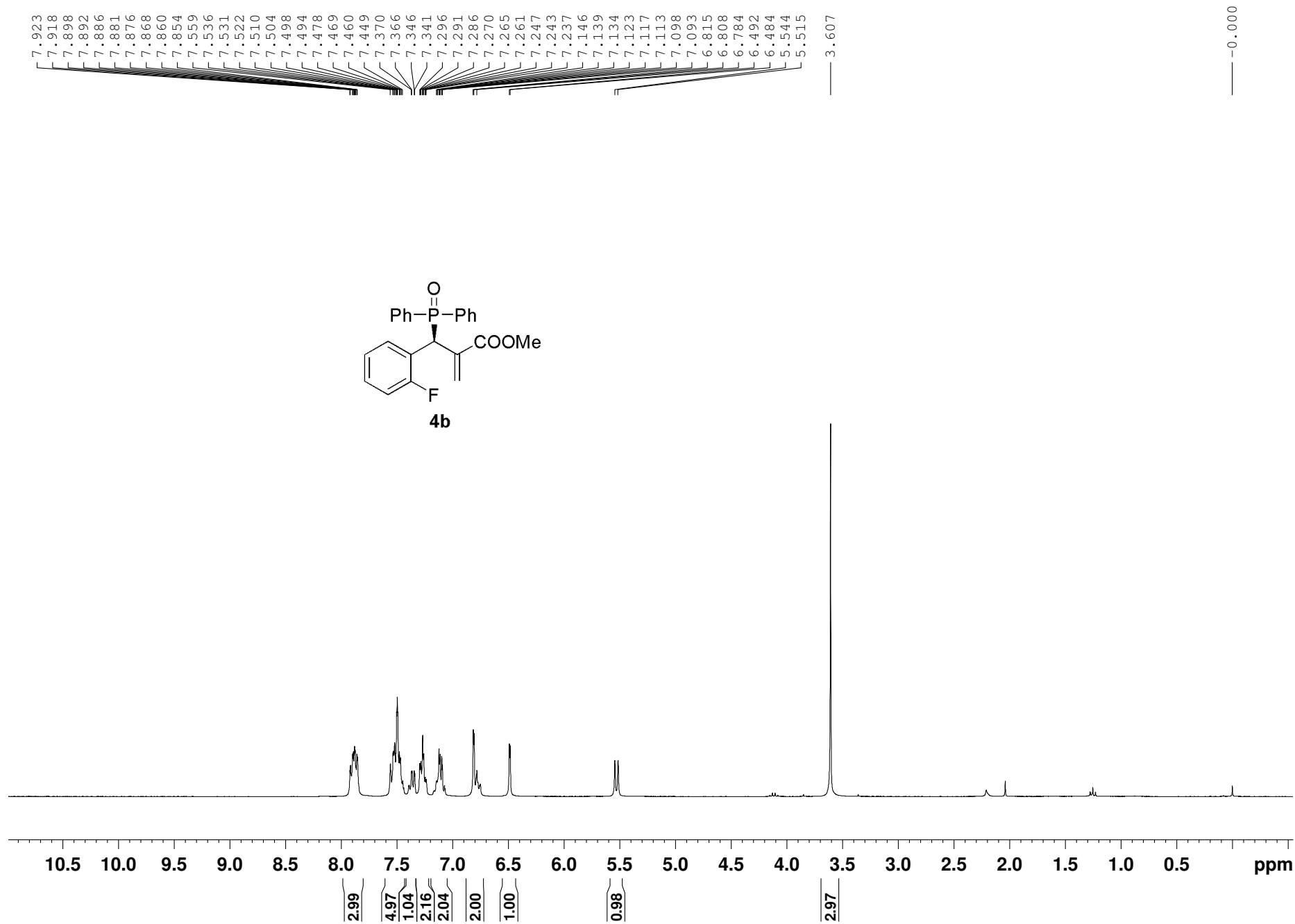


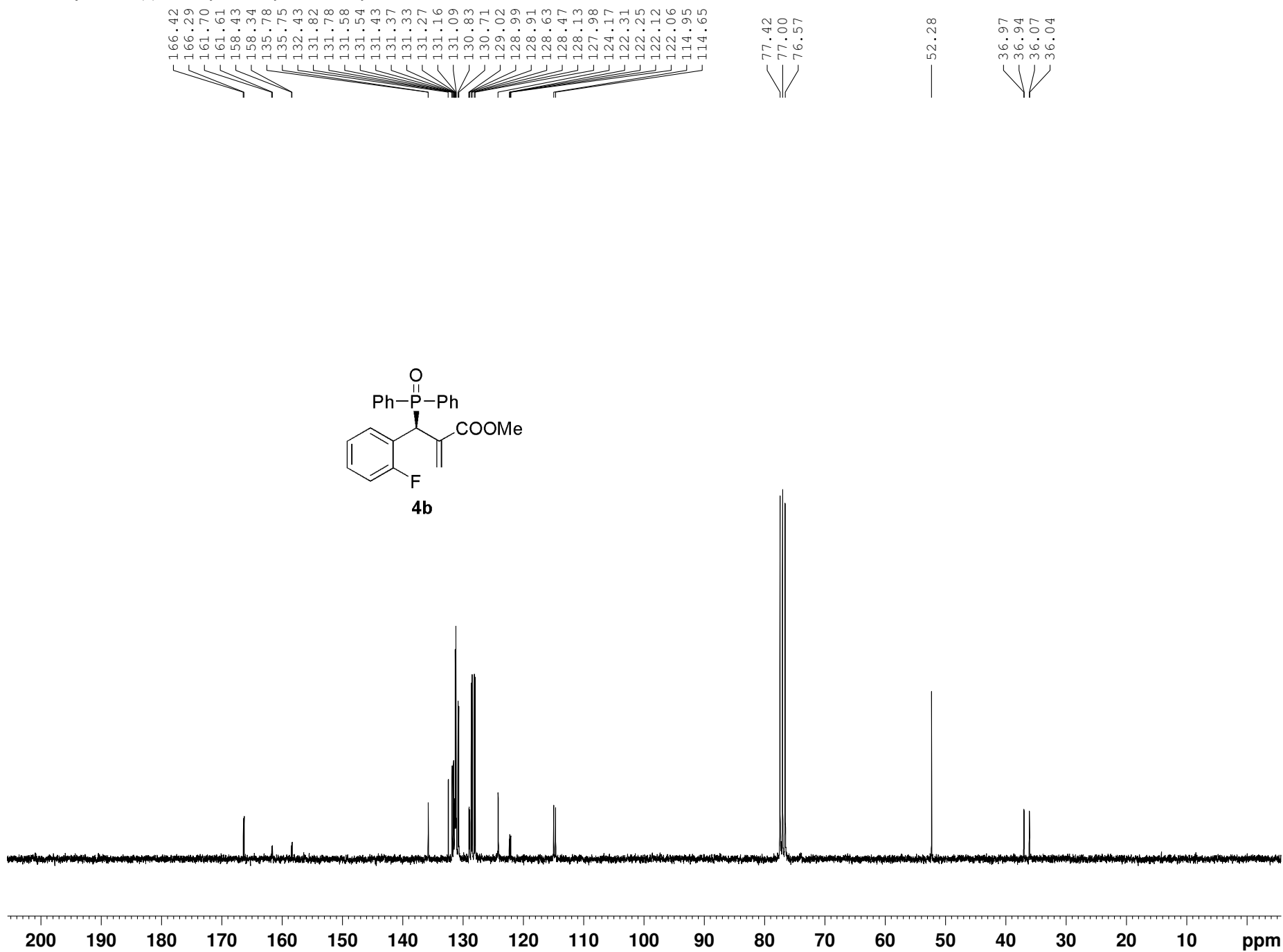


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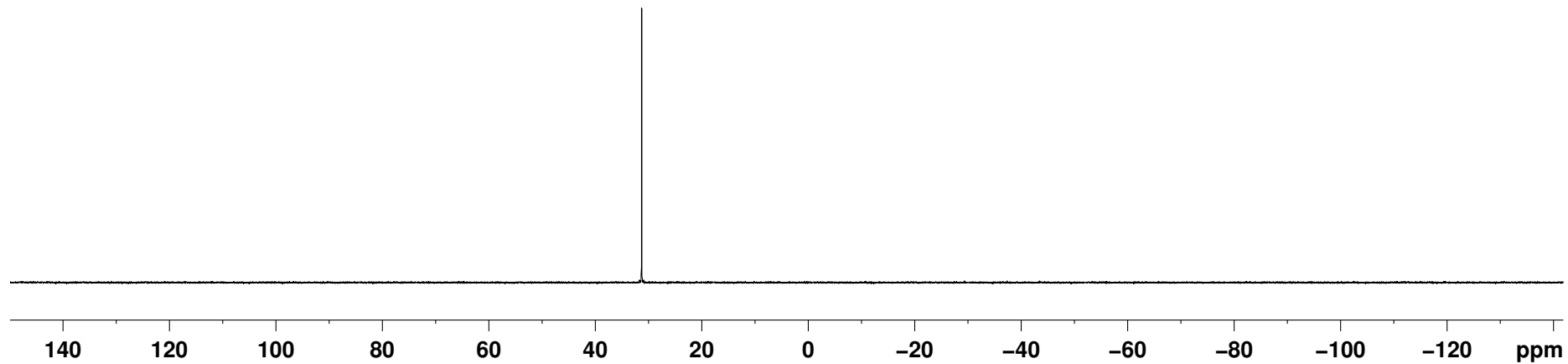
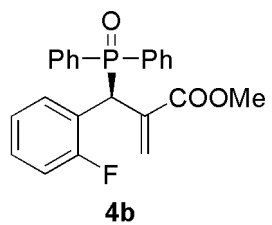
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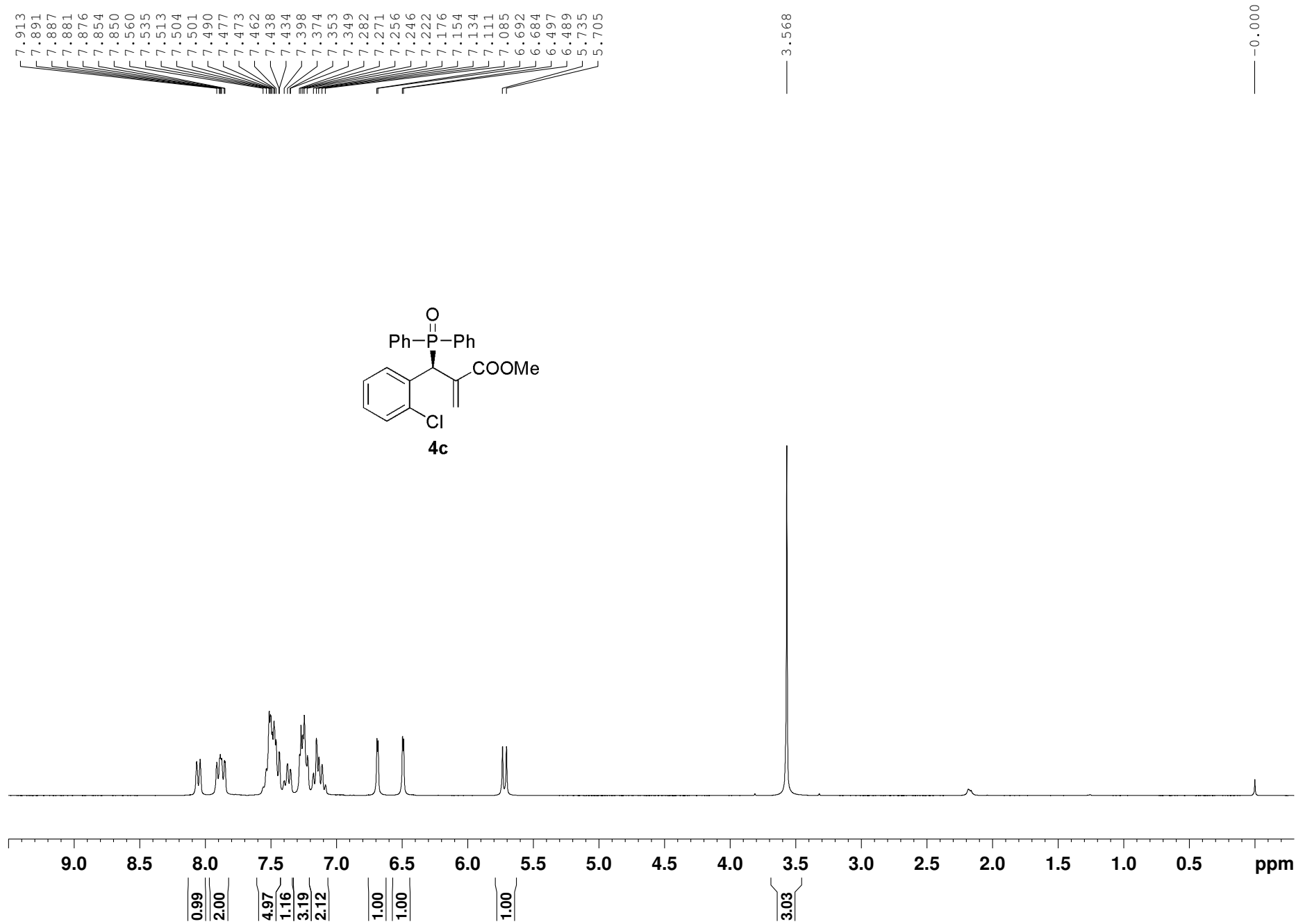






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31.297



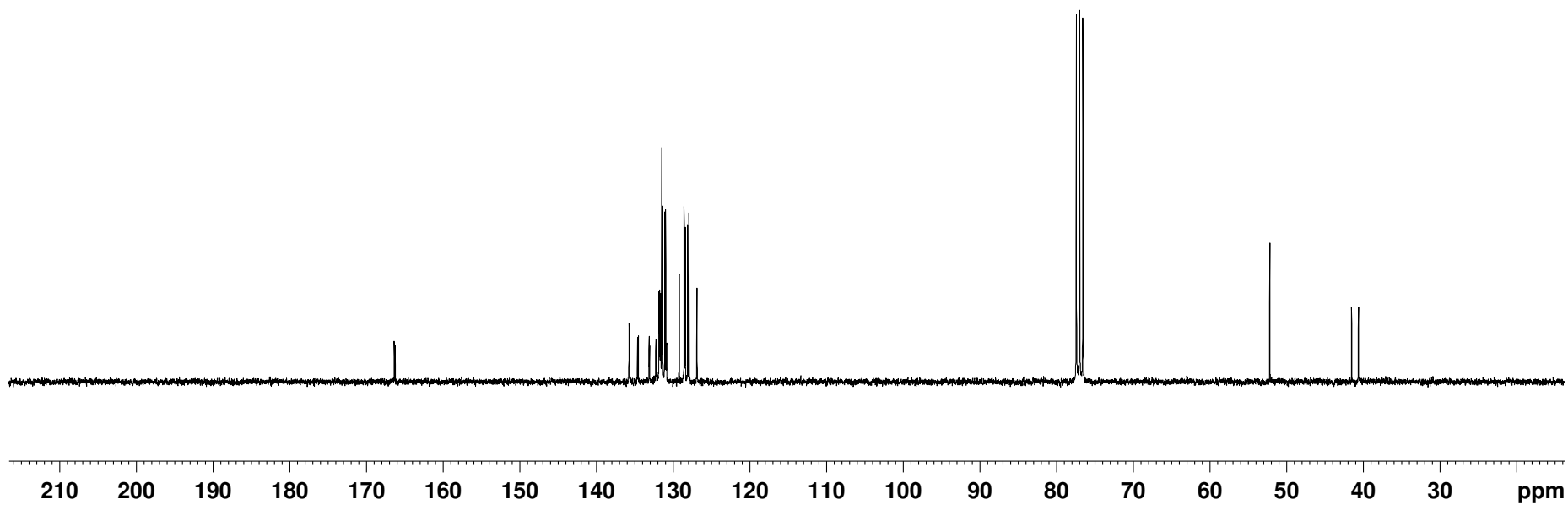
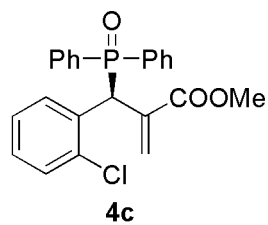


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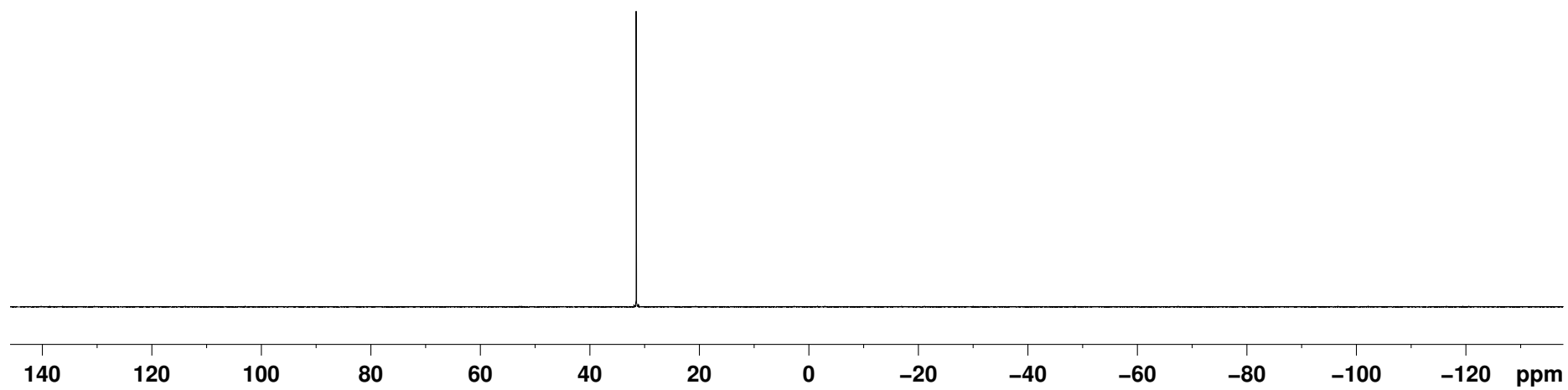
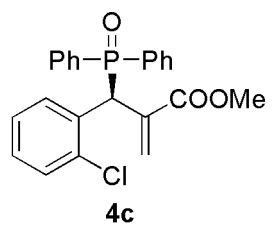
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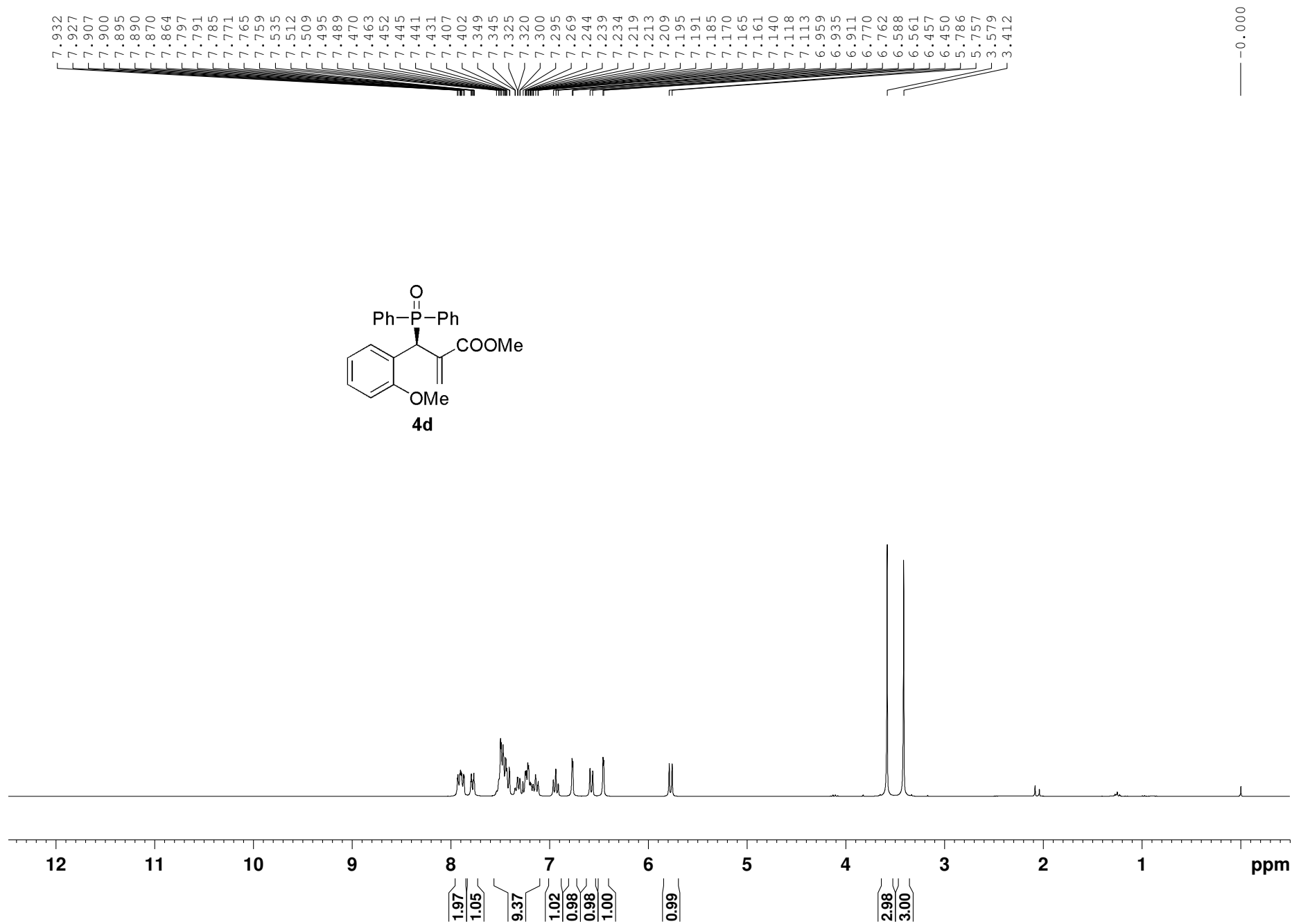
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— 31.543



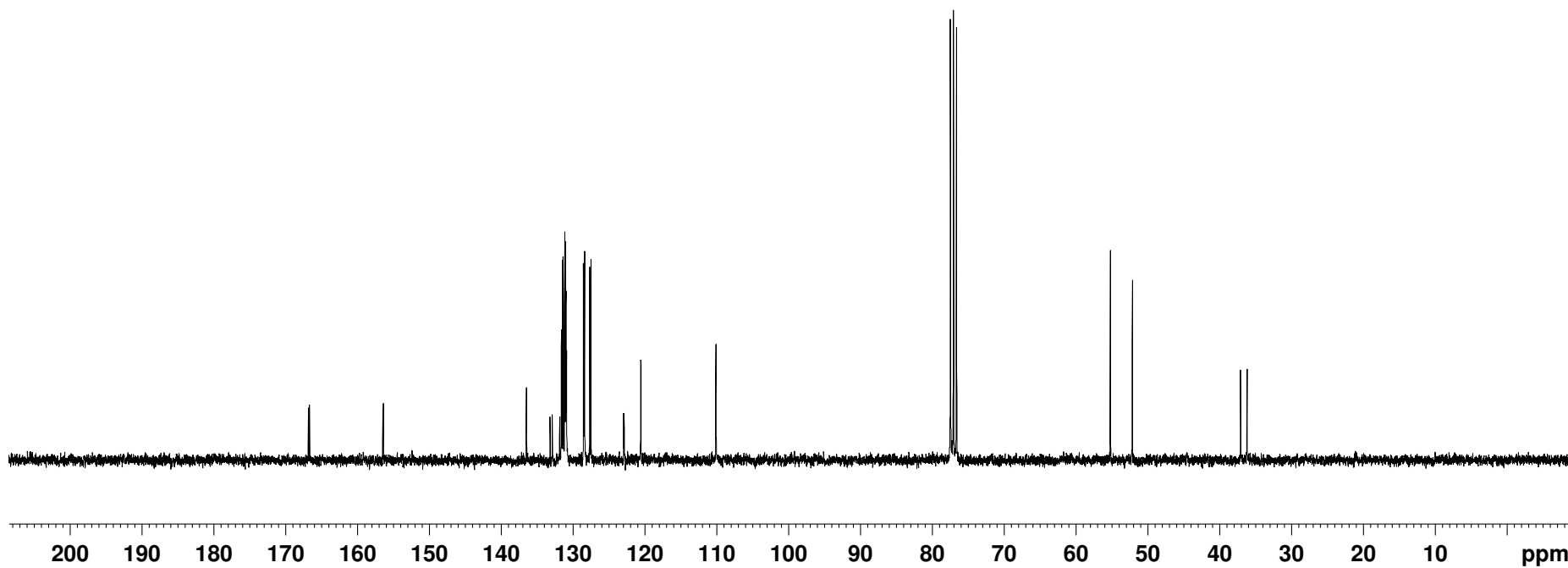
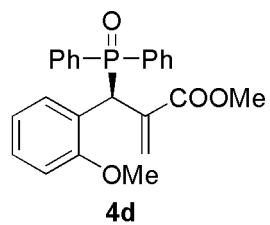


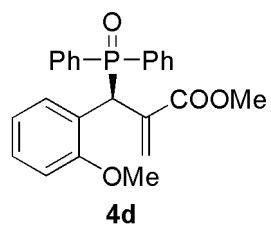
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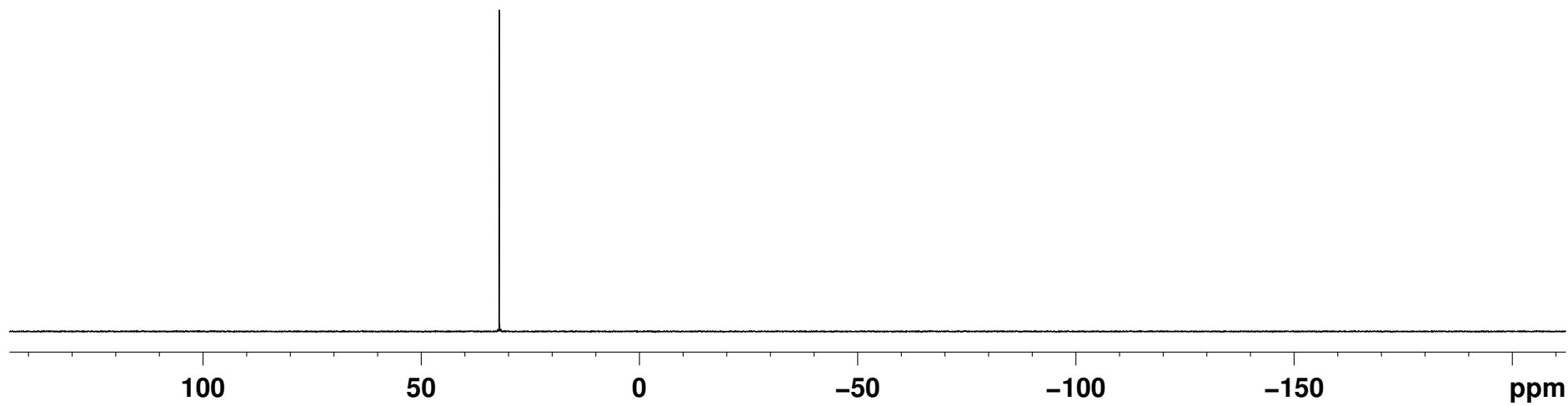
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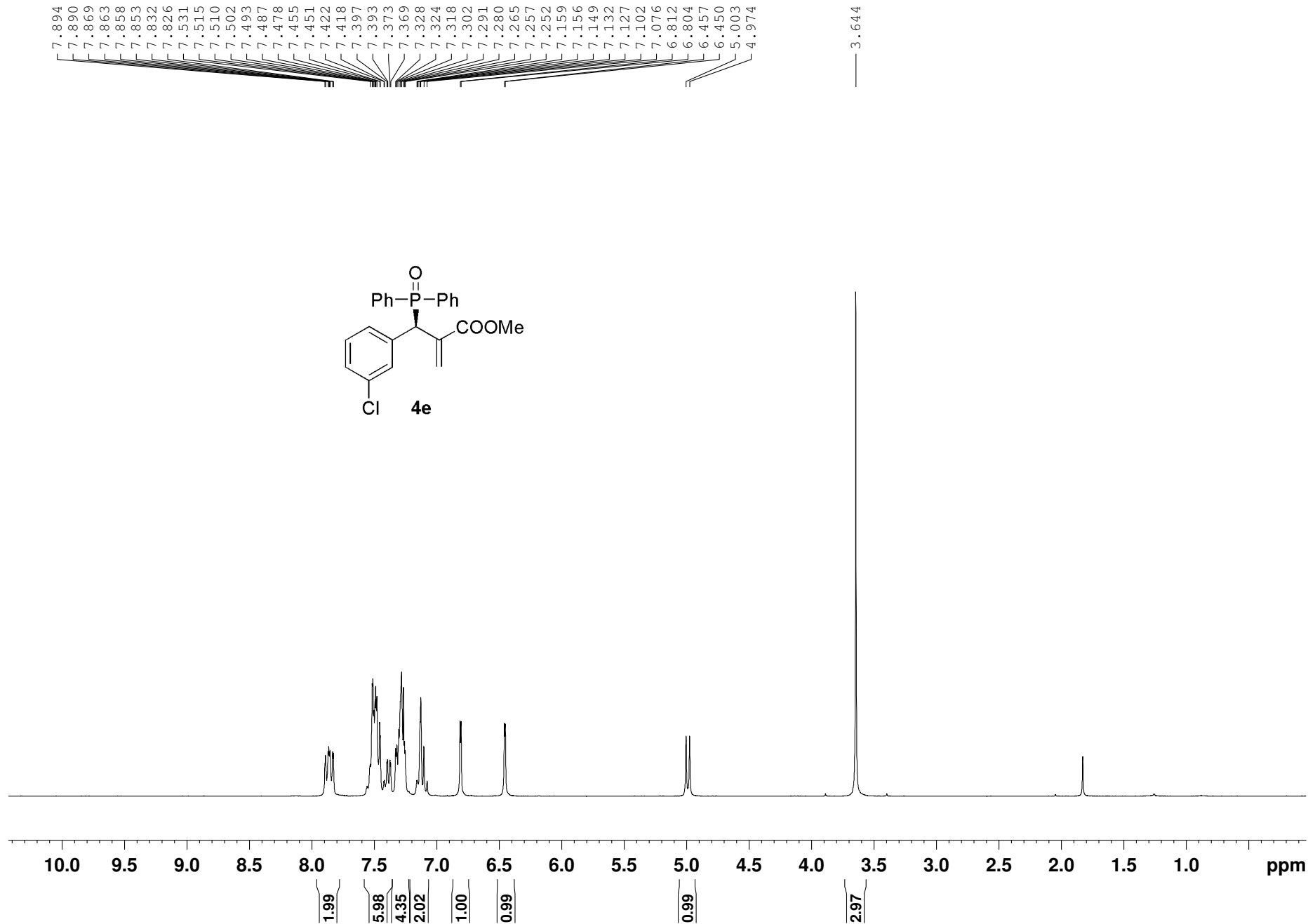
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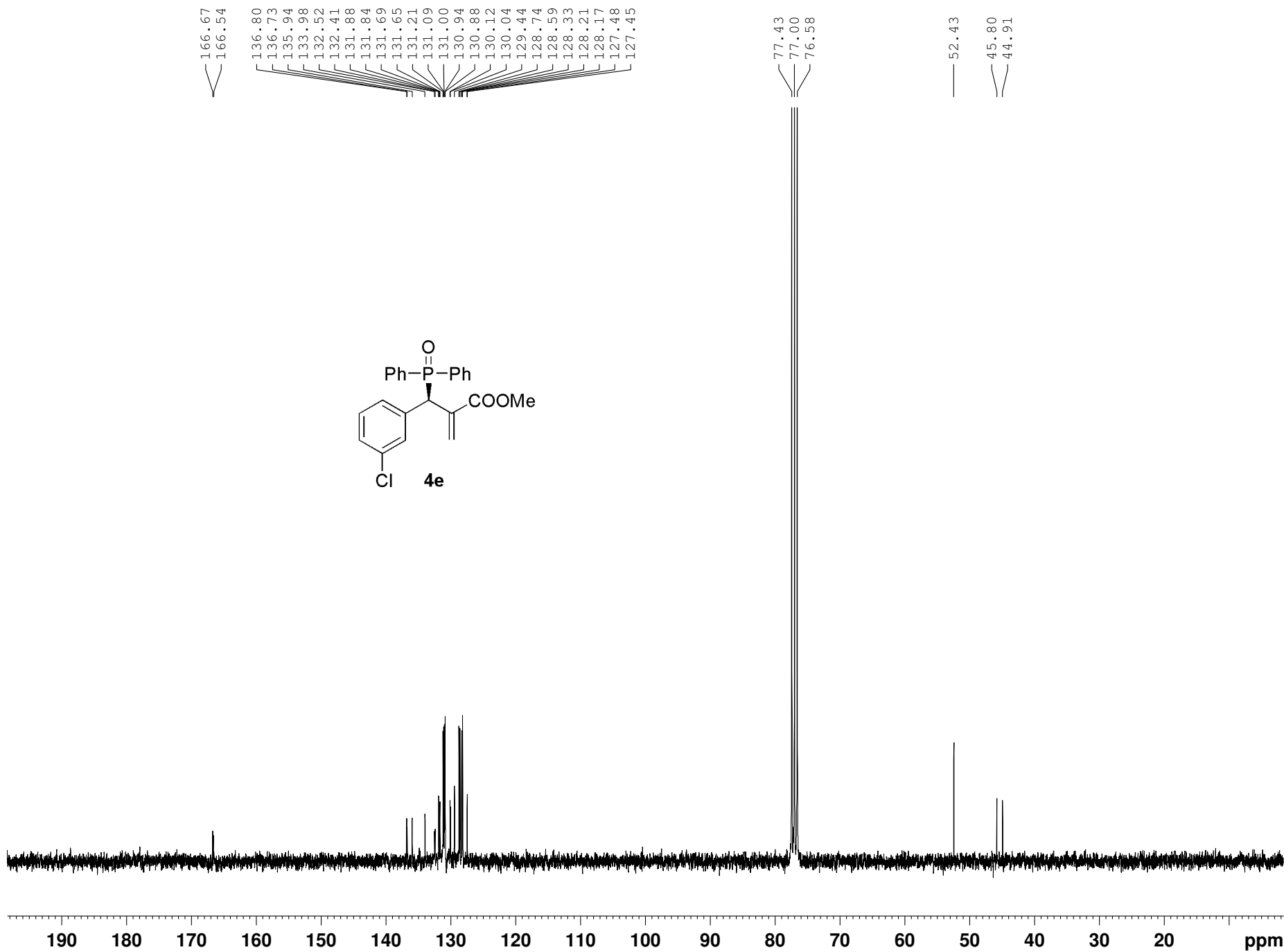


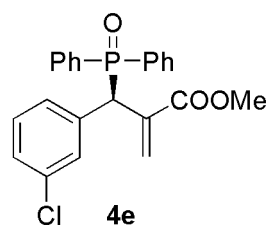


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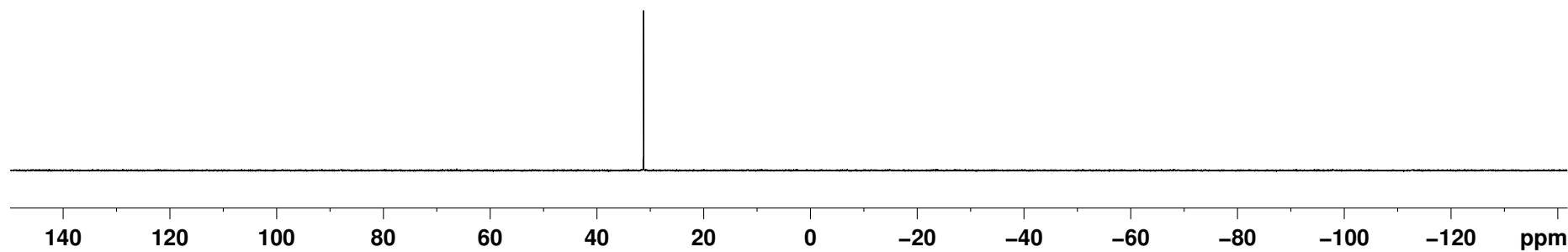


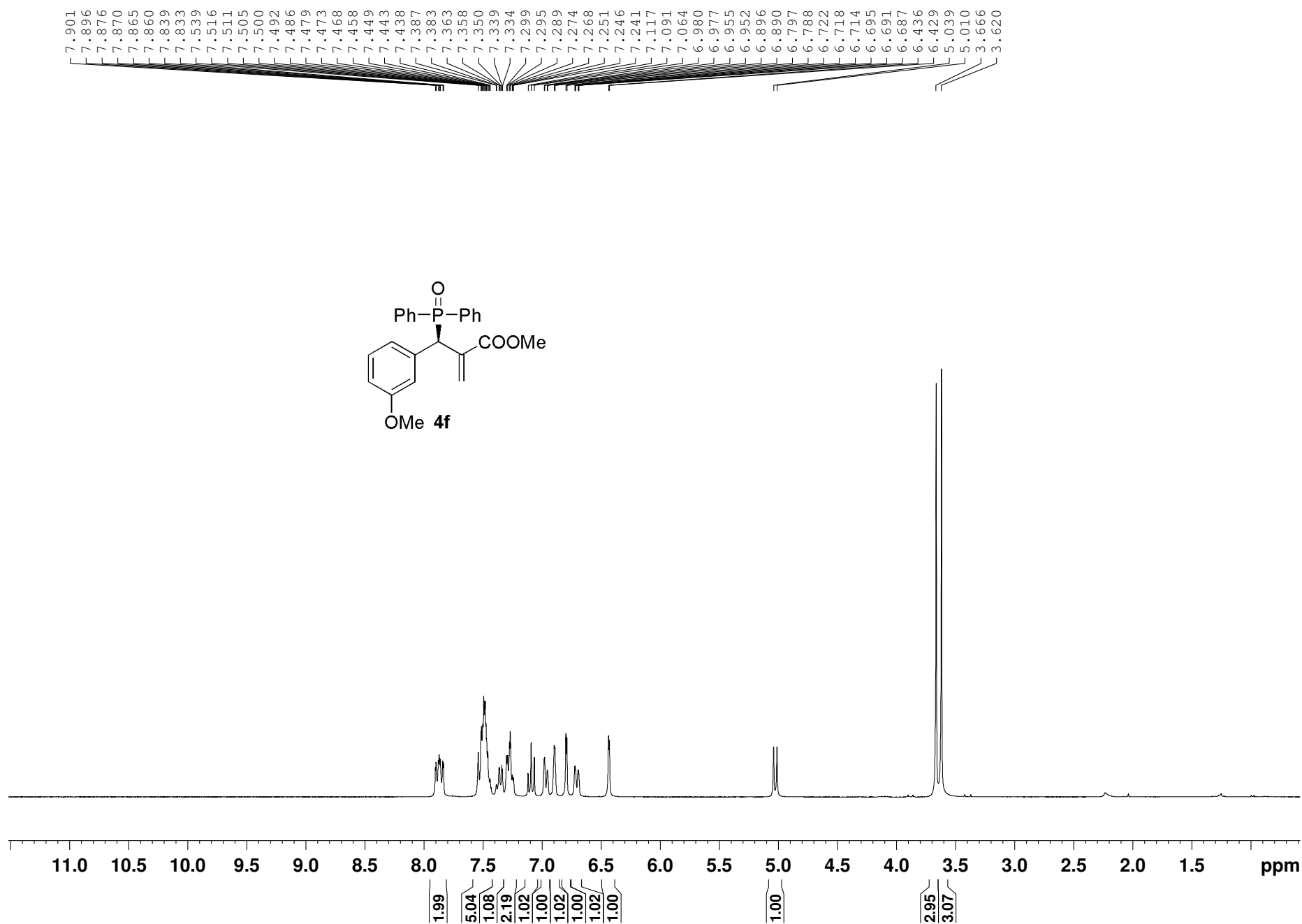






— 31.285



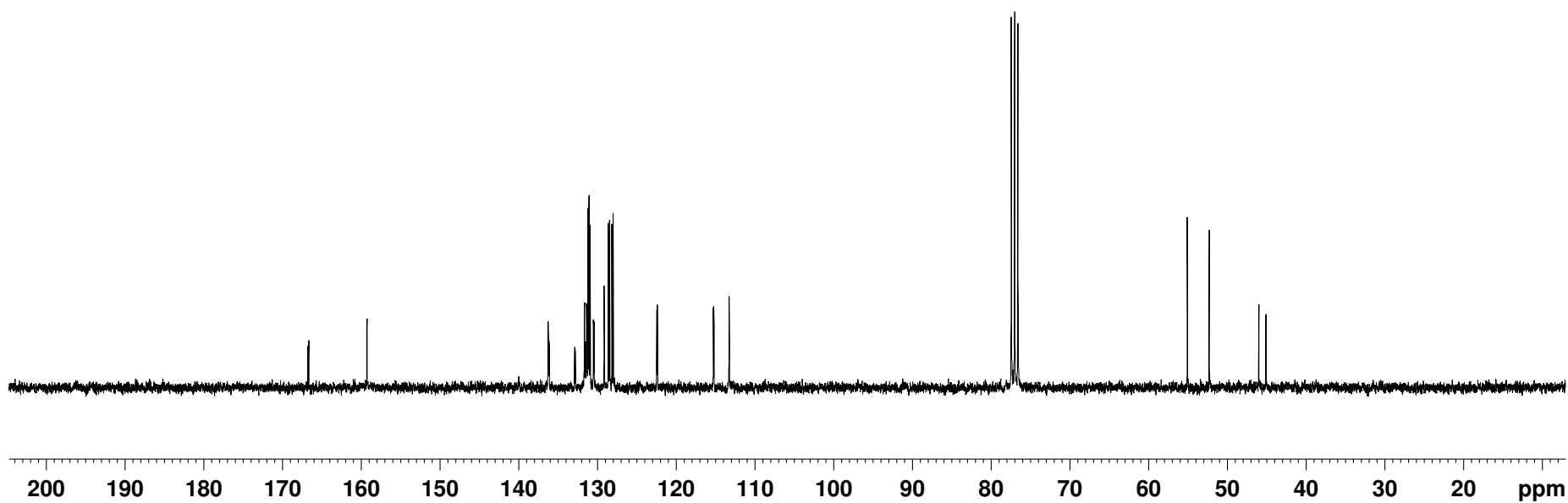
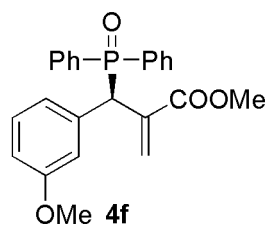


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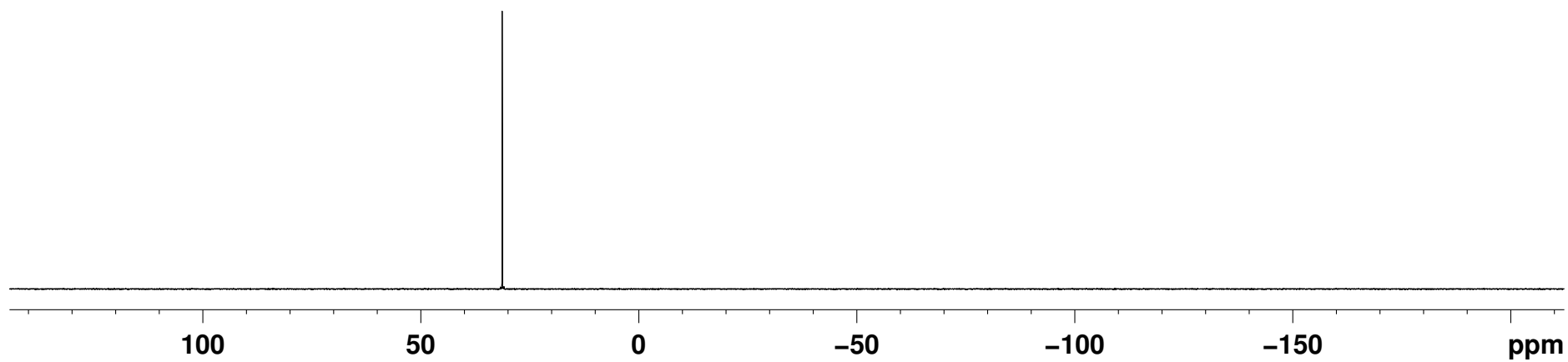
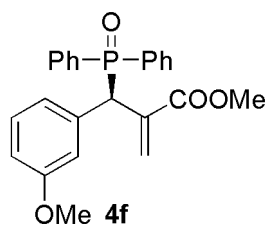
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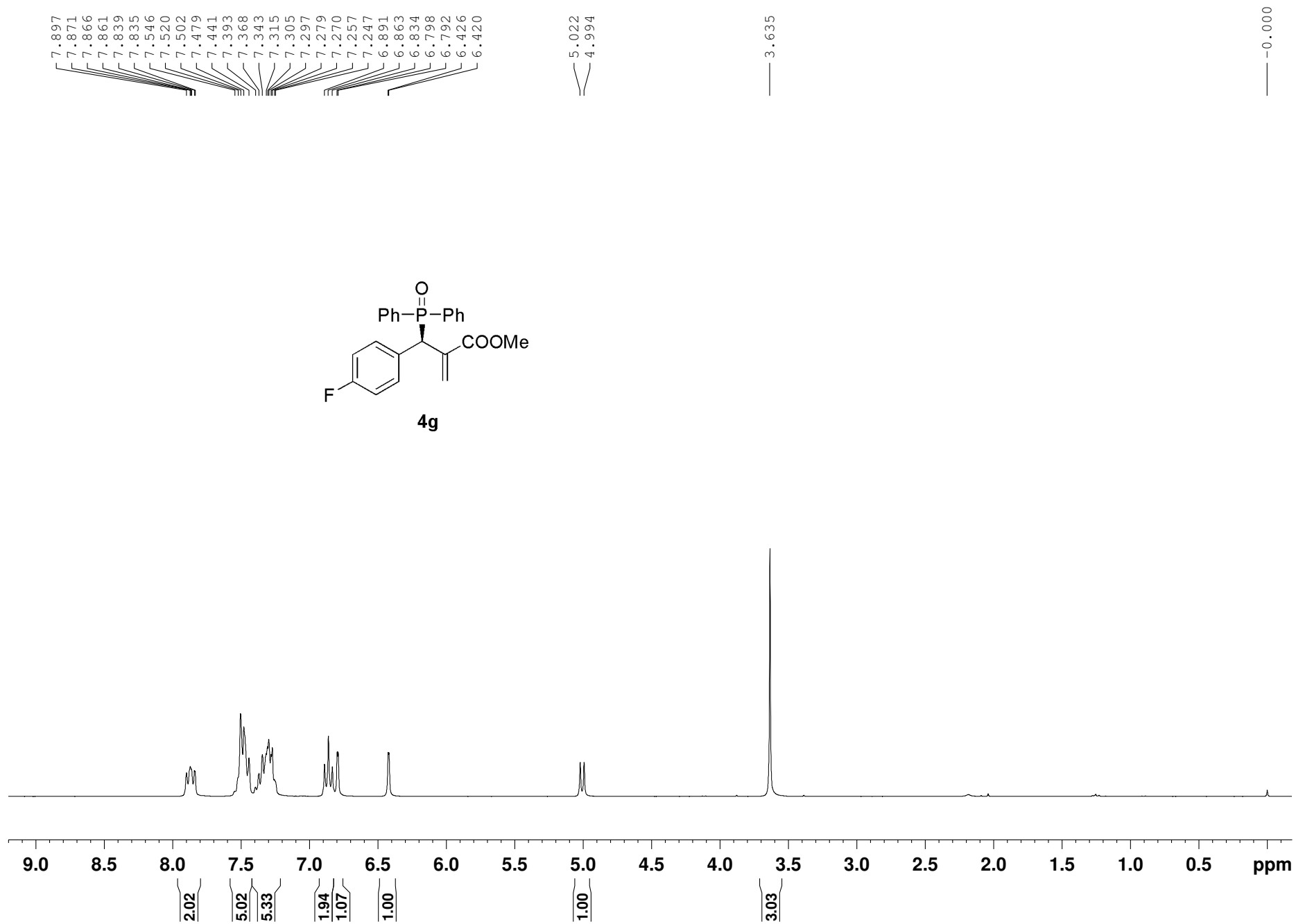
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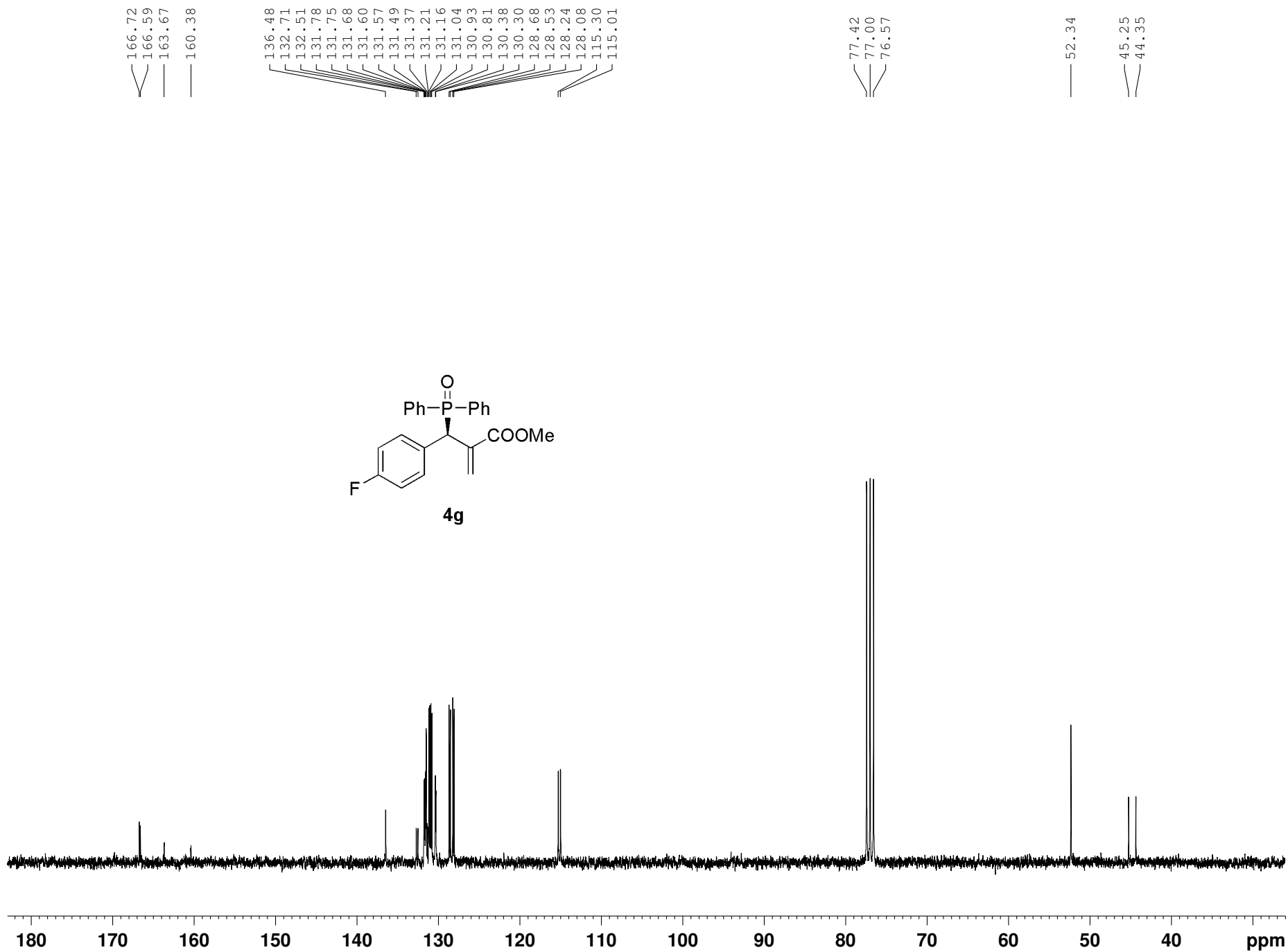
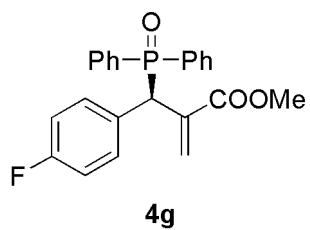
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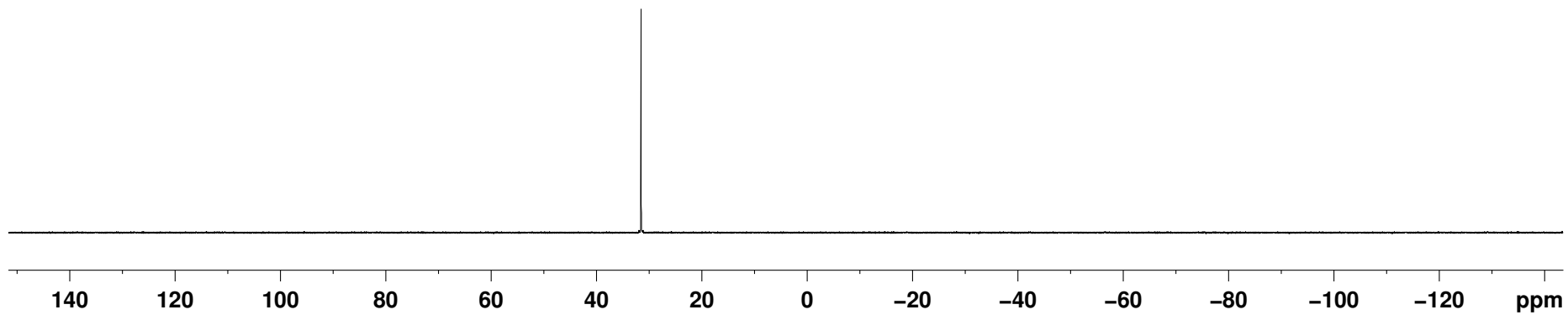
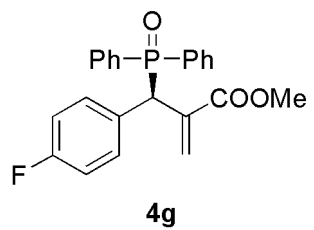
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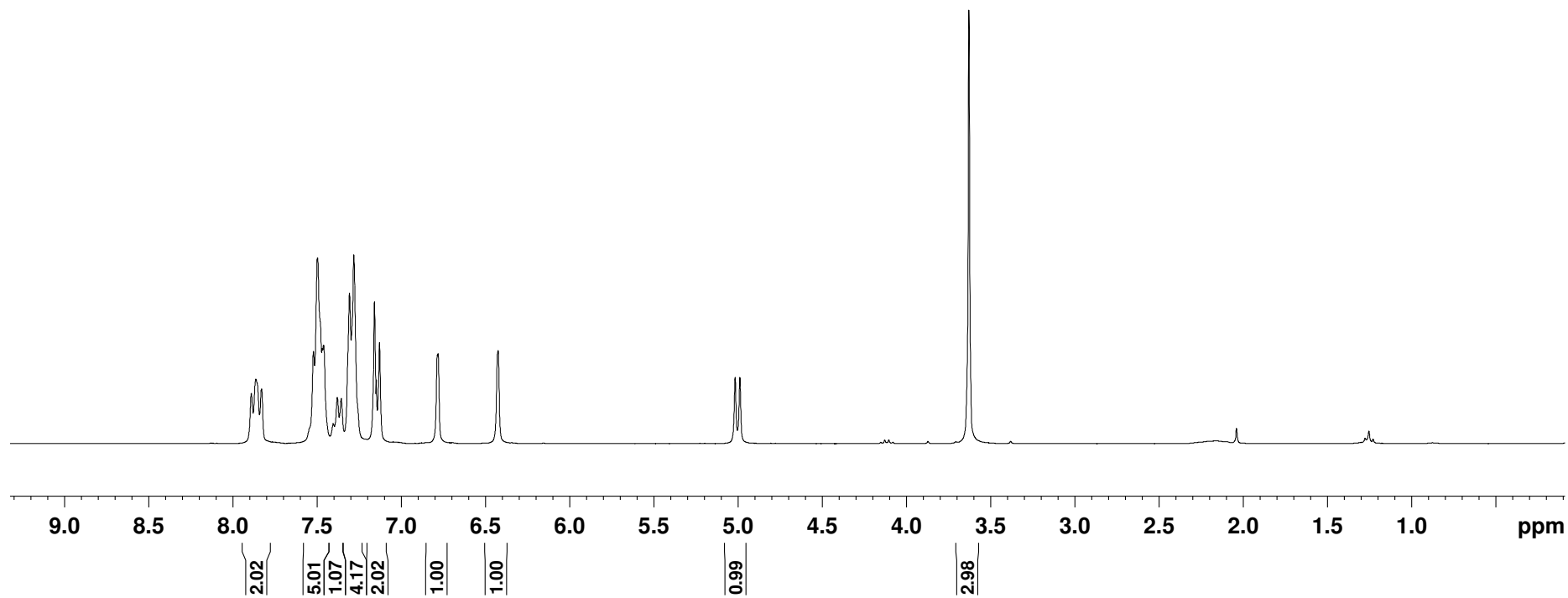
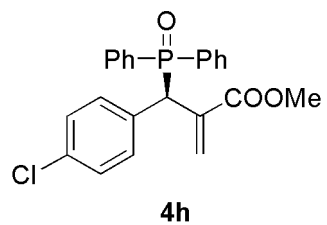
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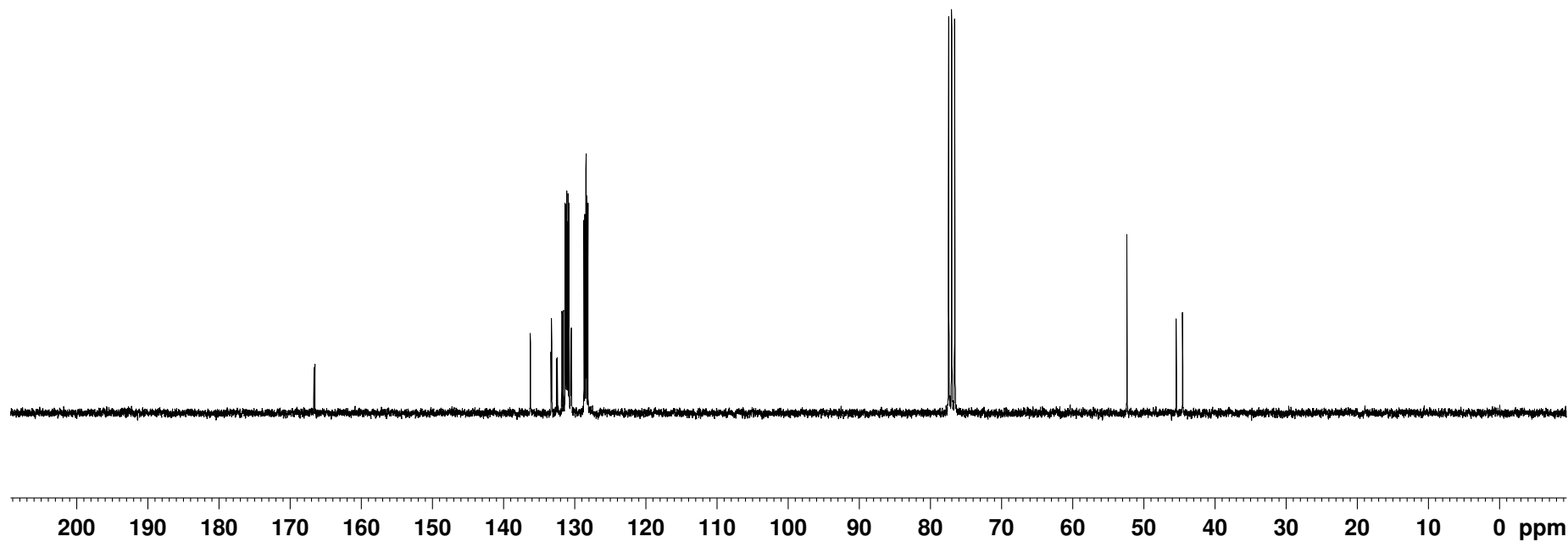
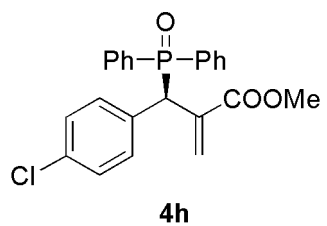
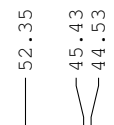
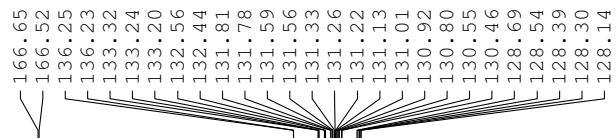


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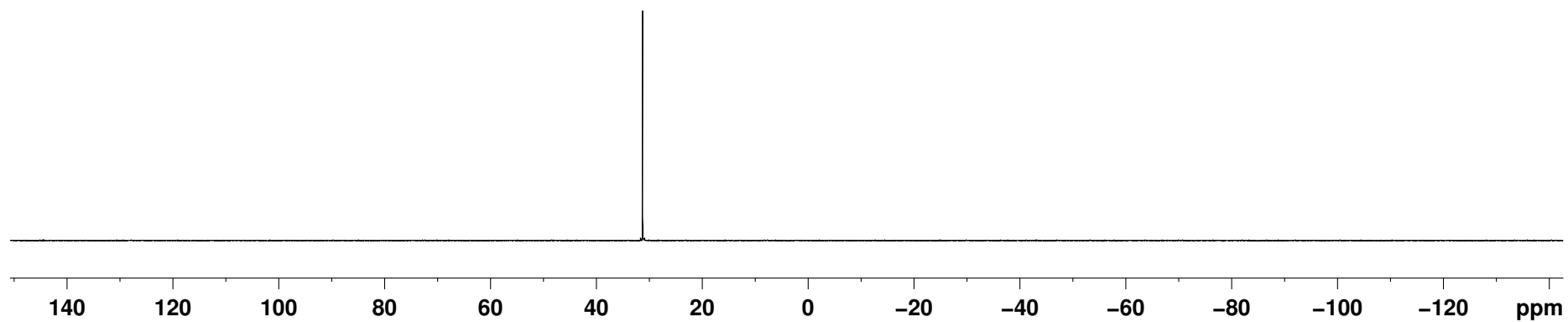
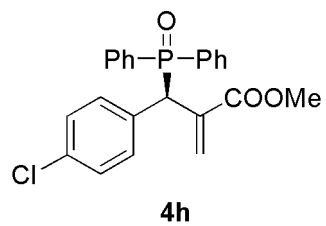
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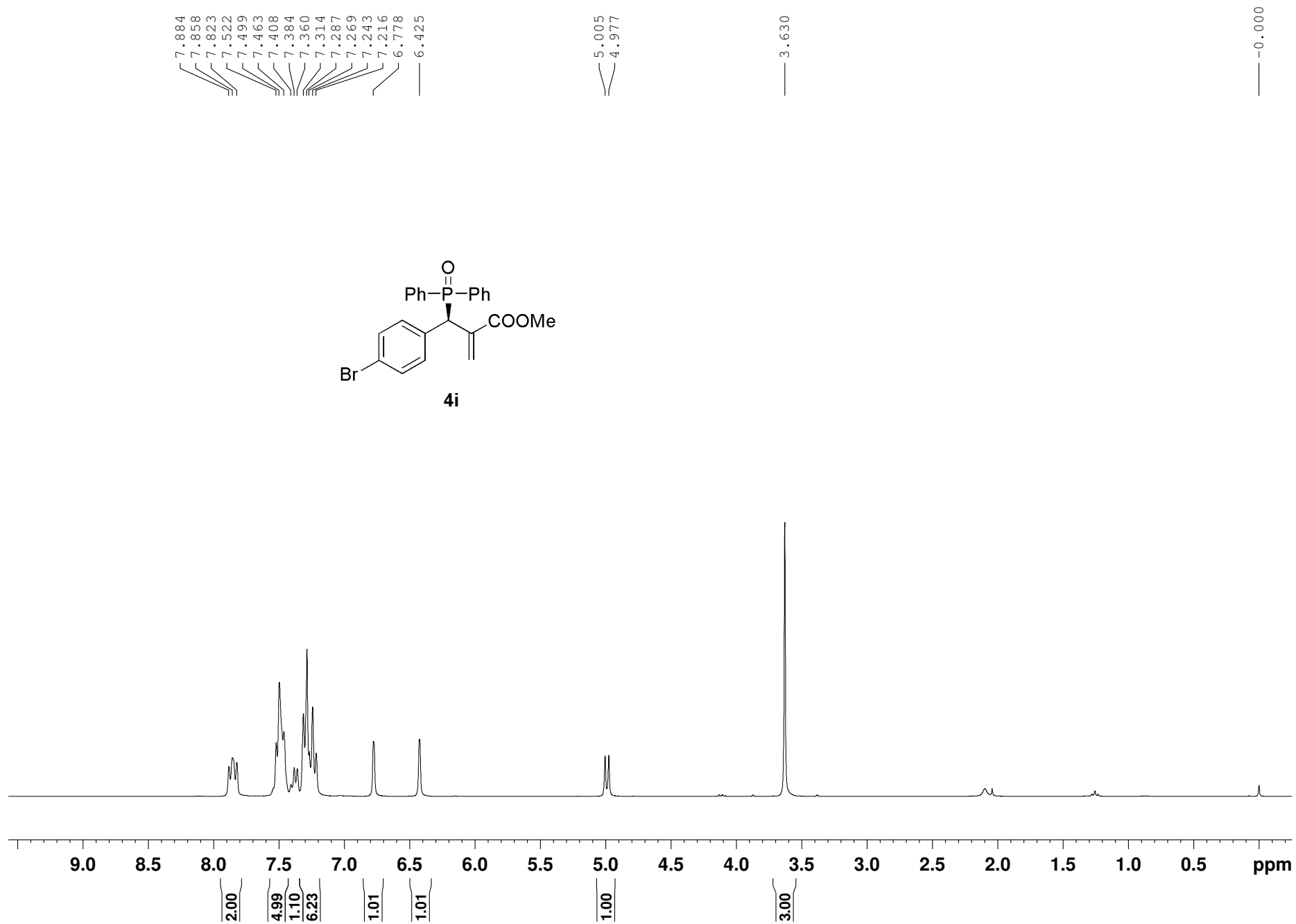
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— 31.276

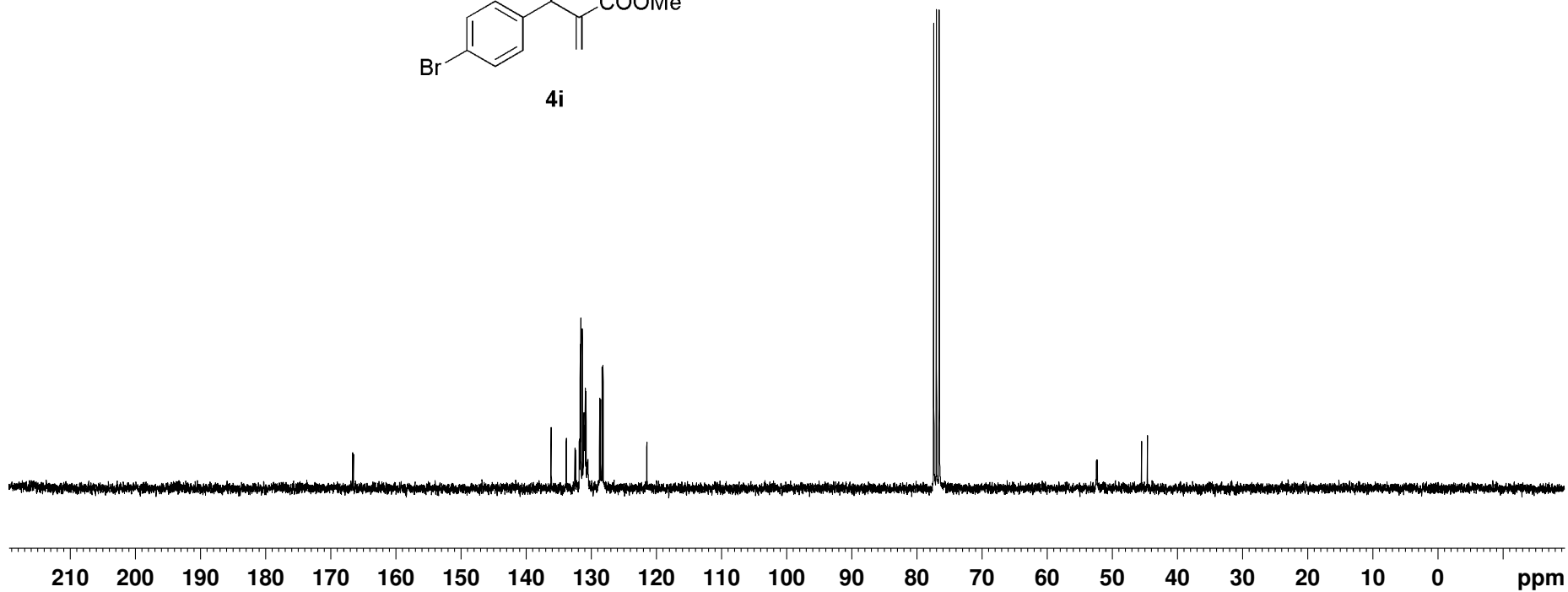
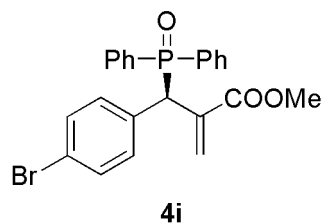


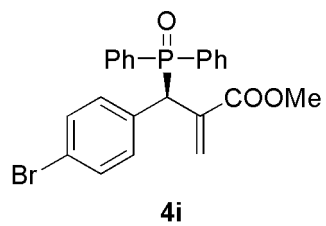


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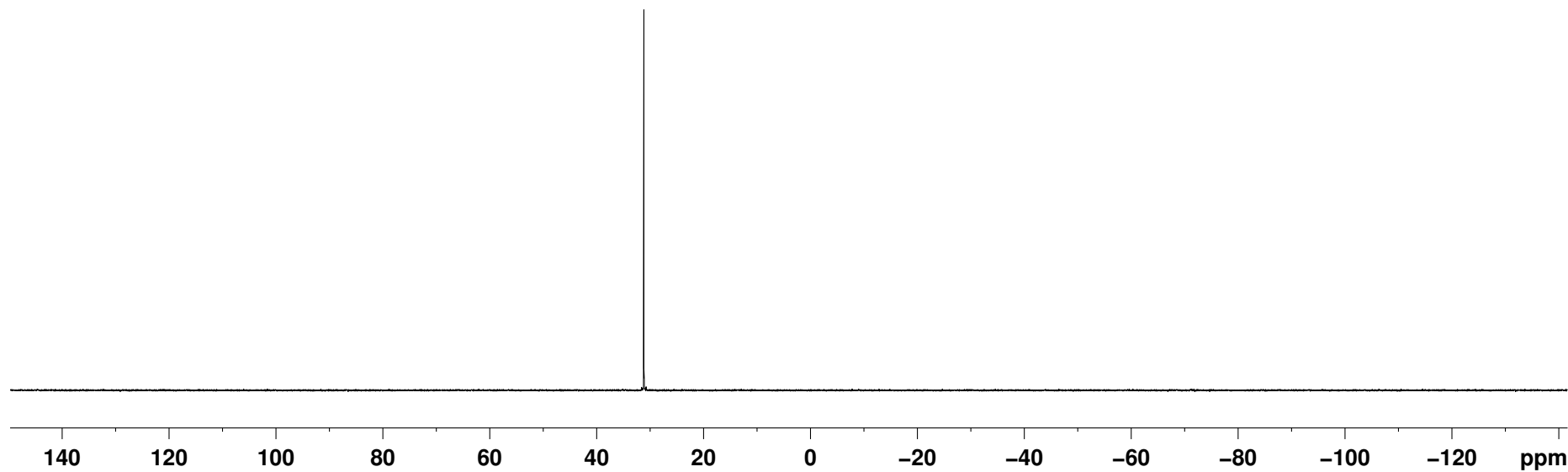
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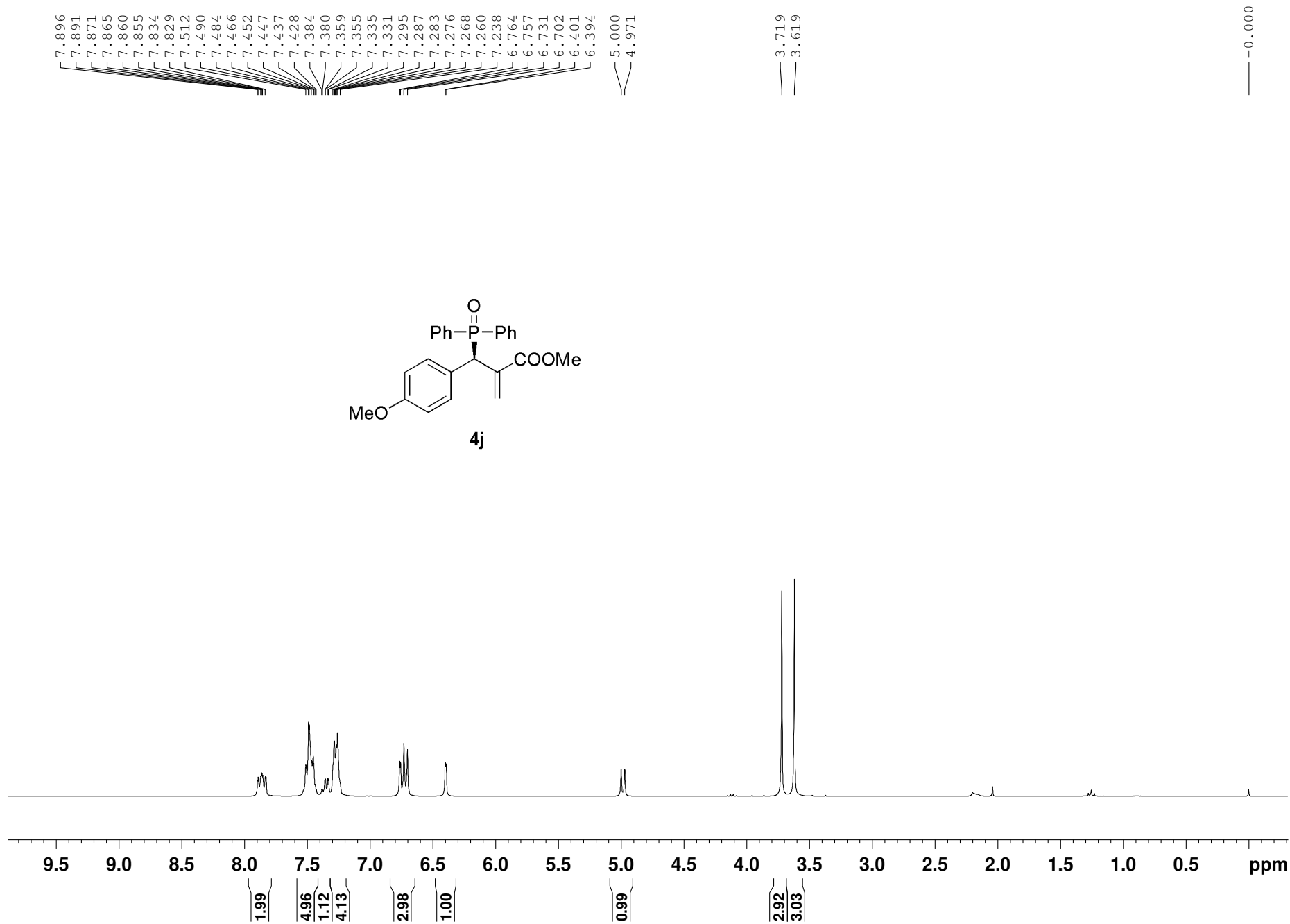
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— 31.174



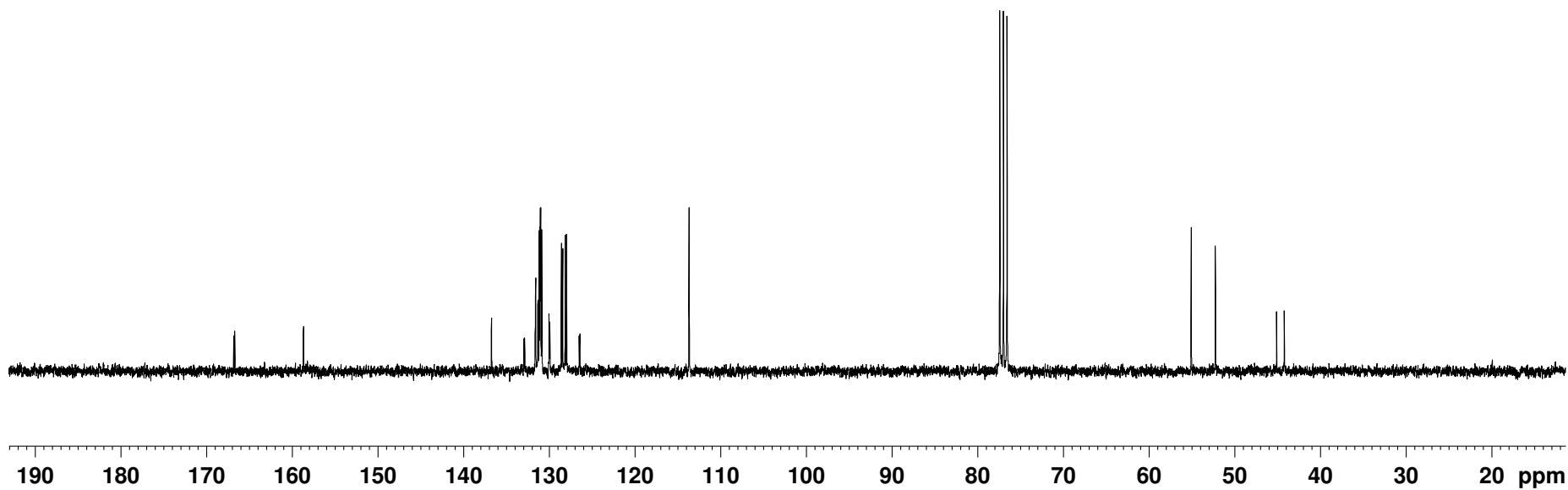
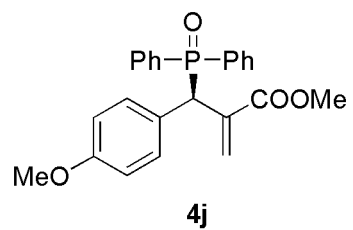


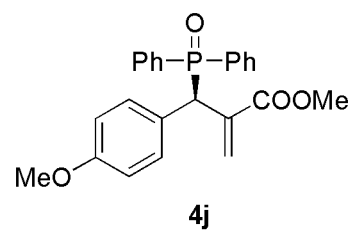
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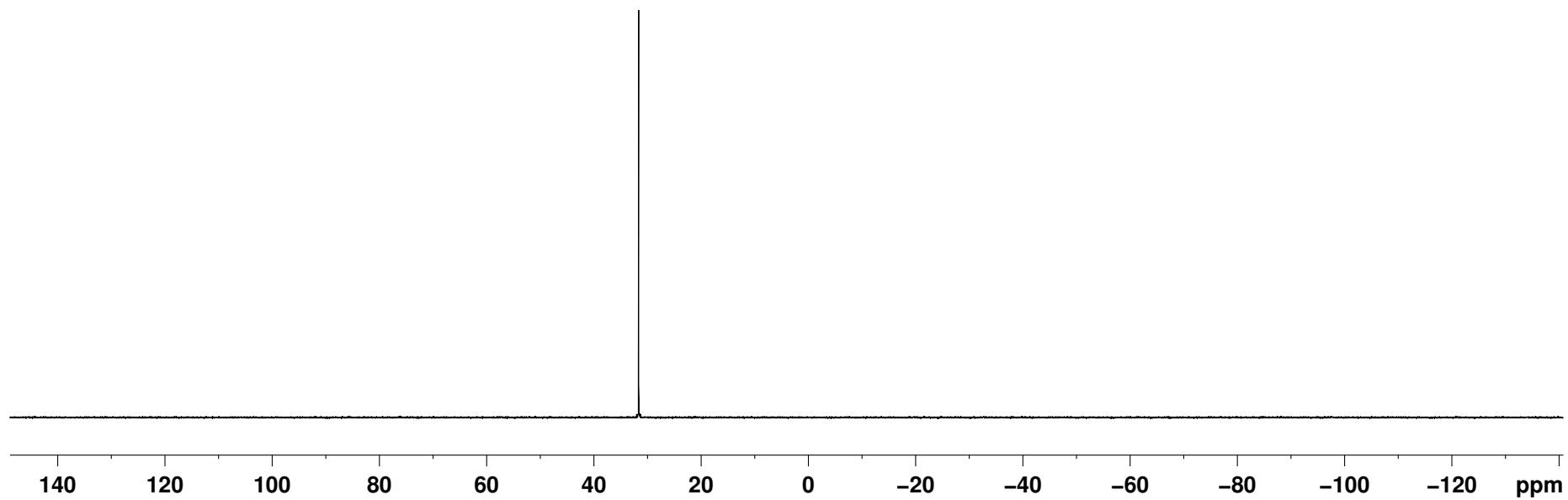
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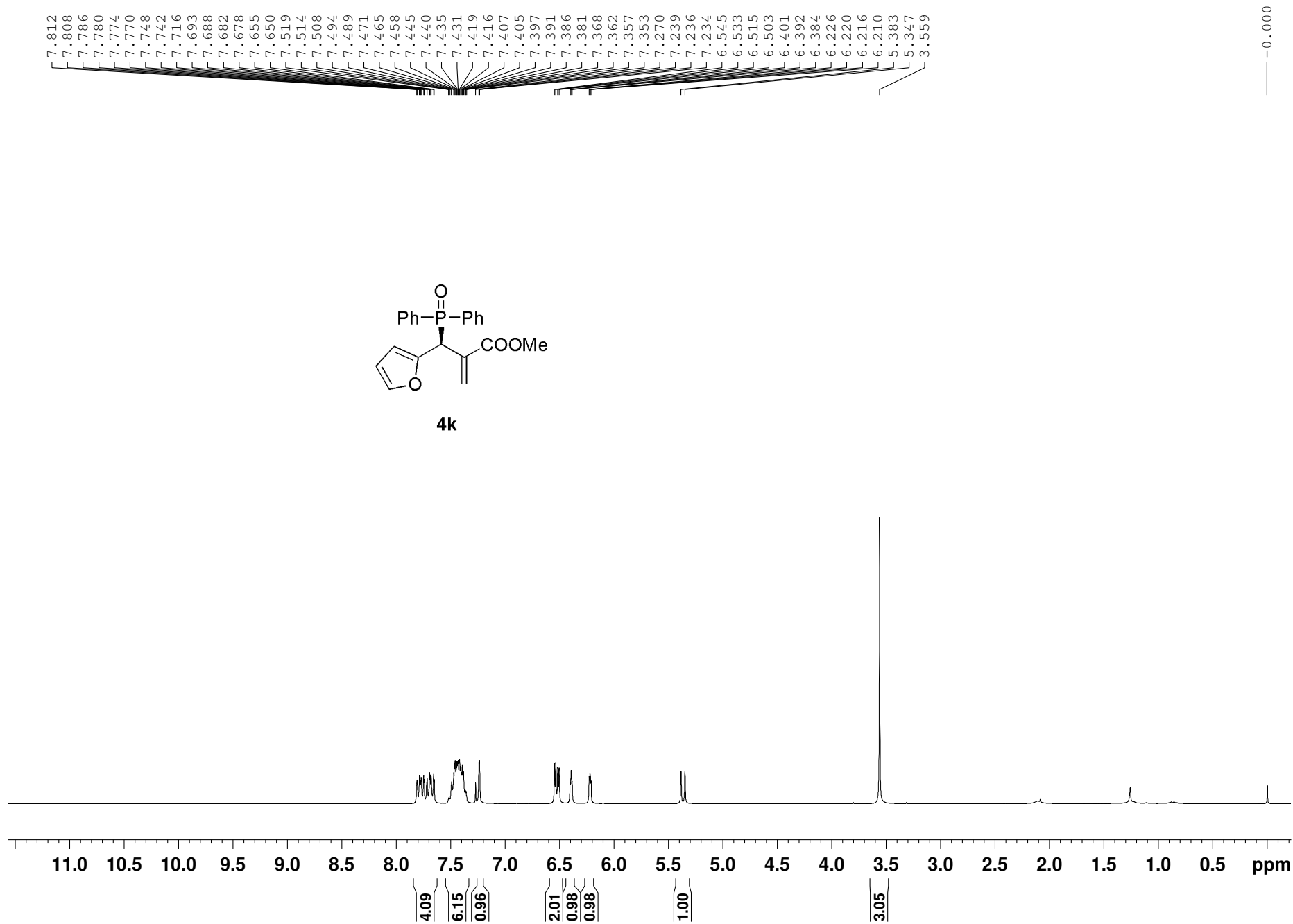
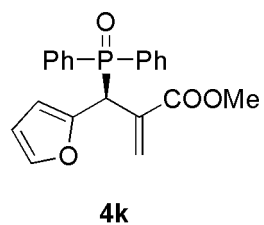
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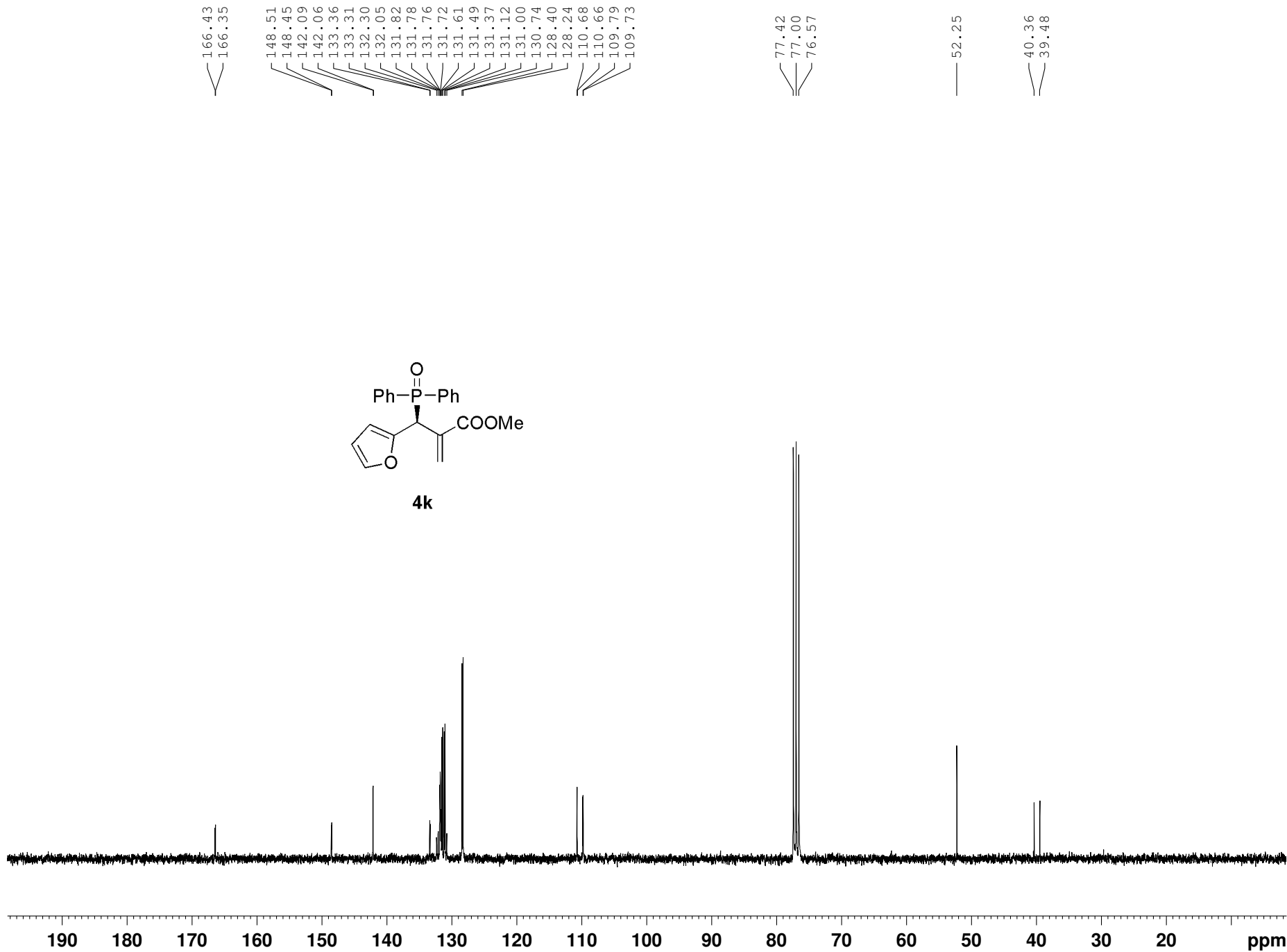
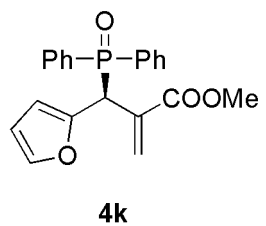




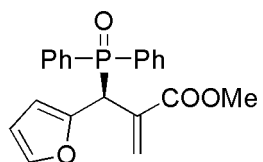
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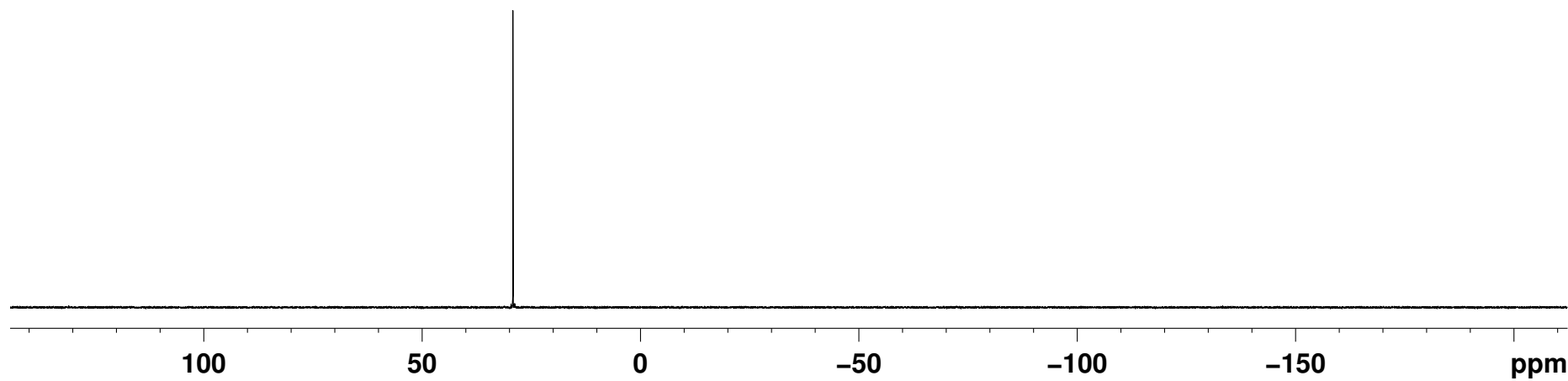


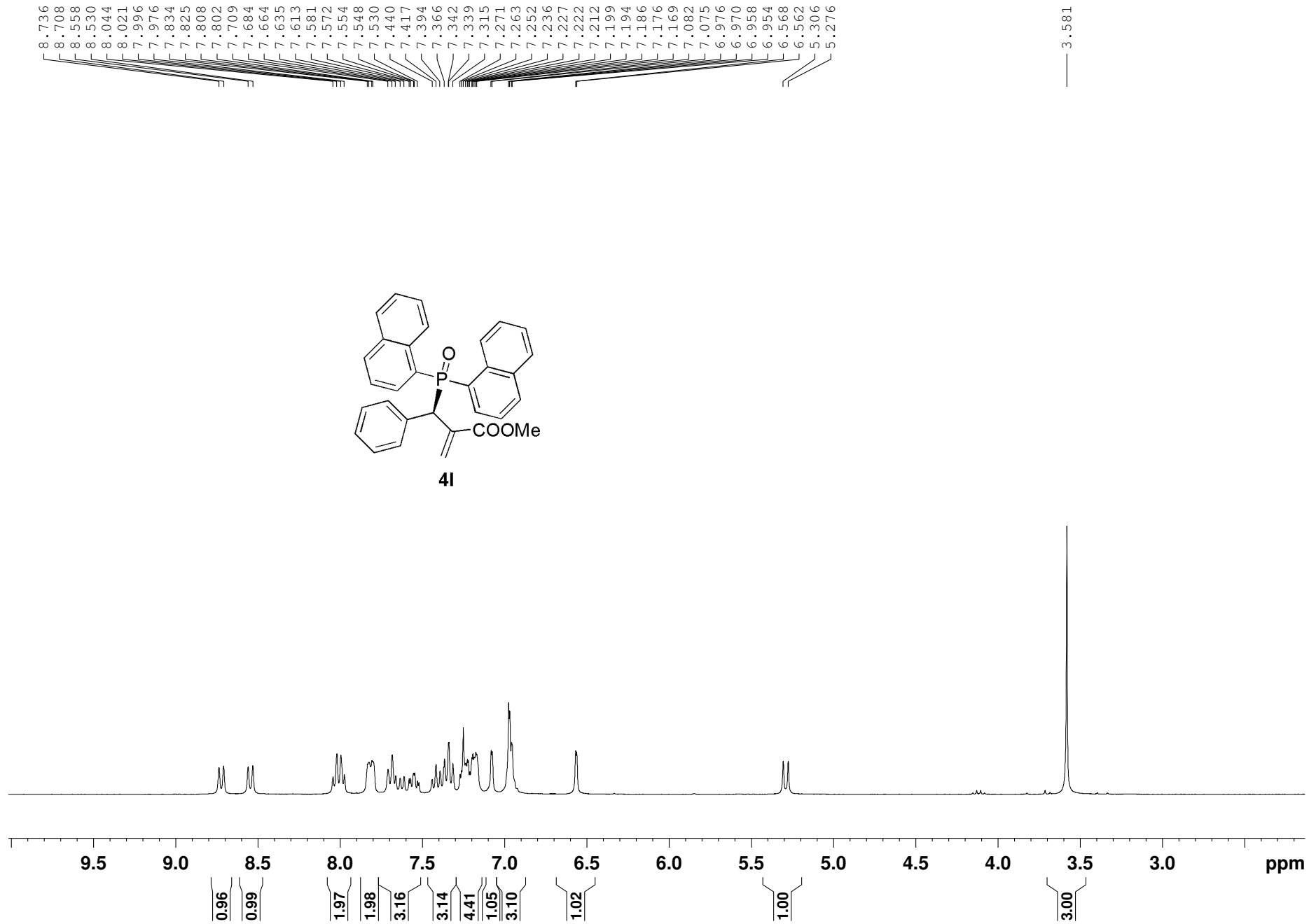


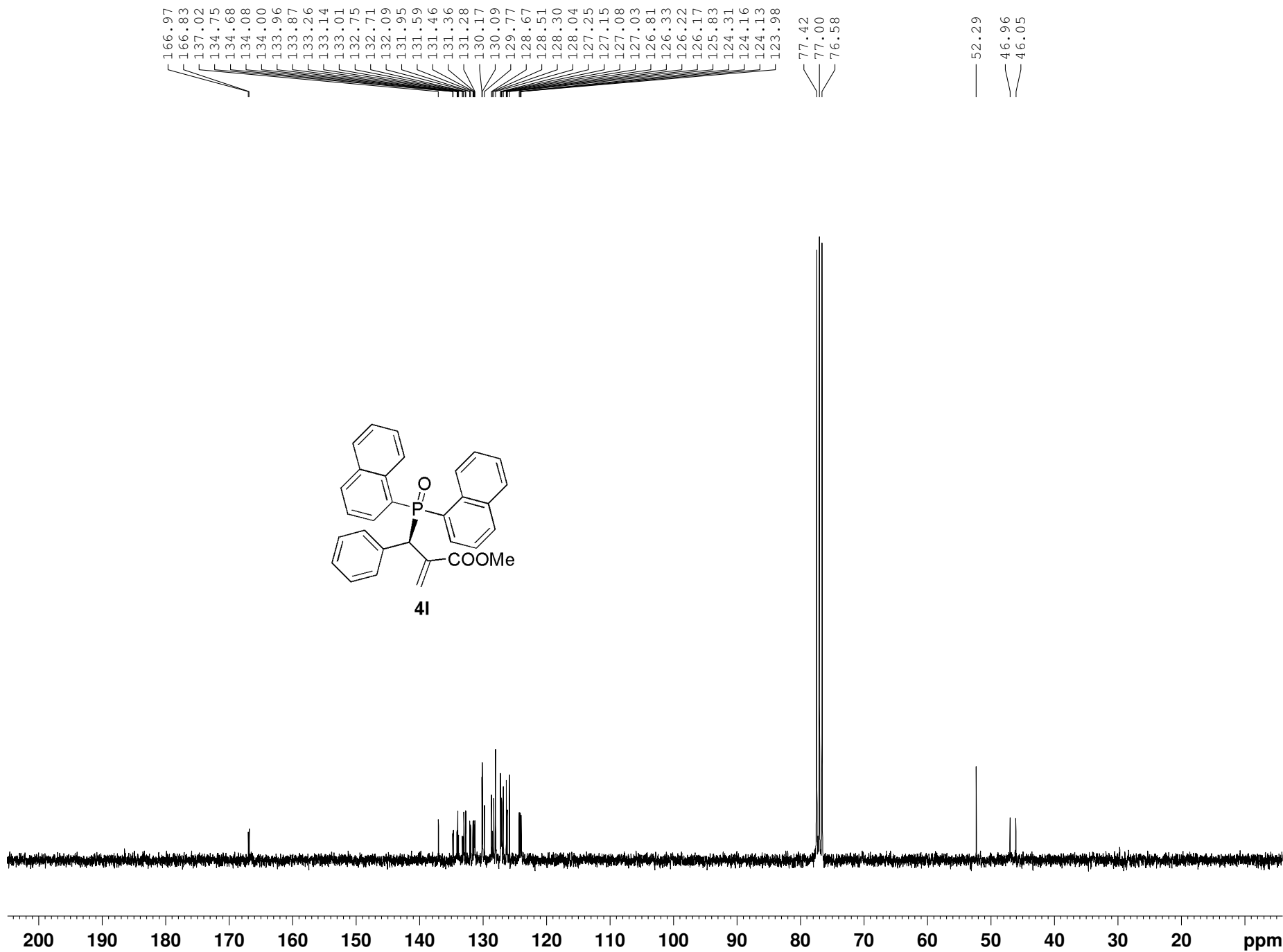
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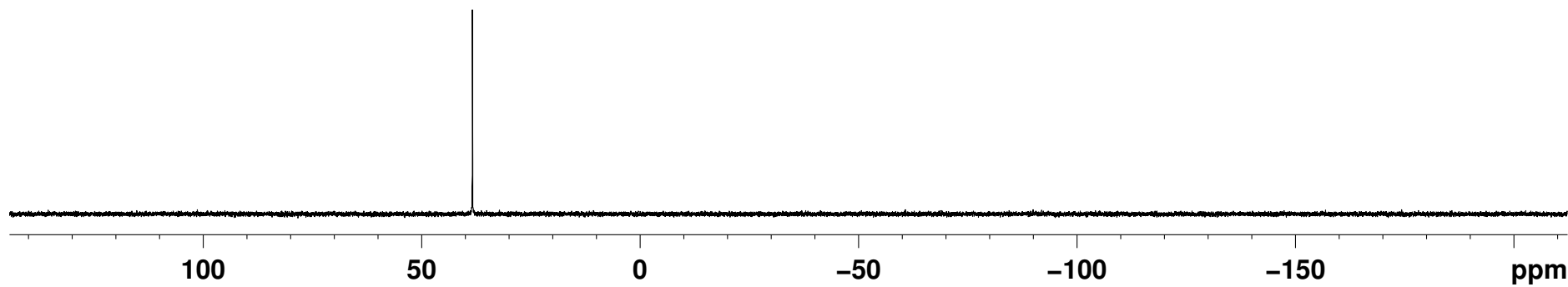
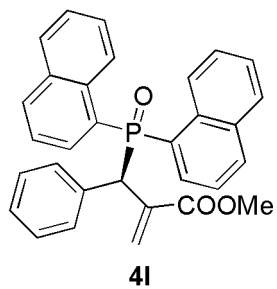
4k

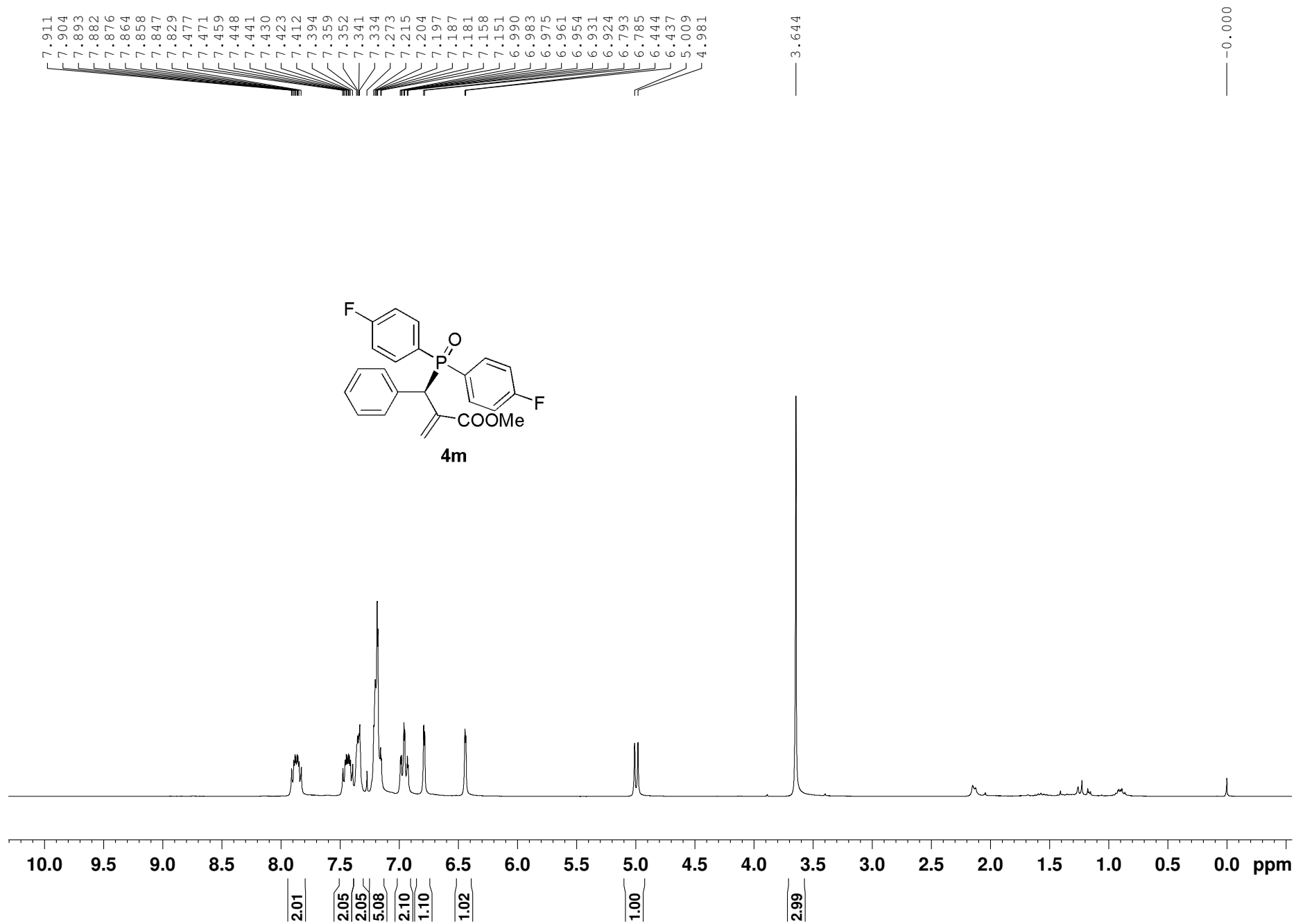


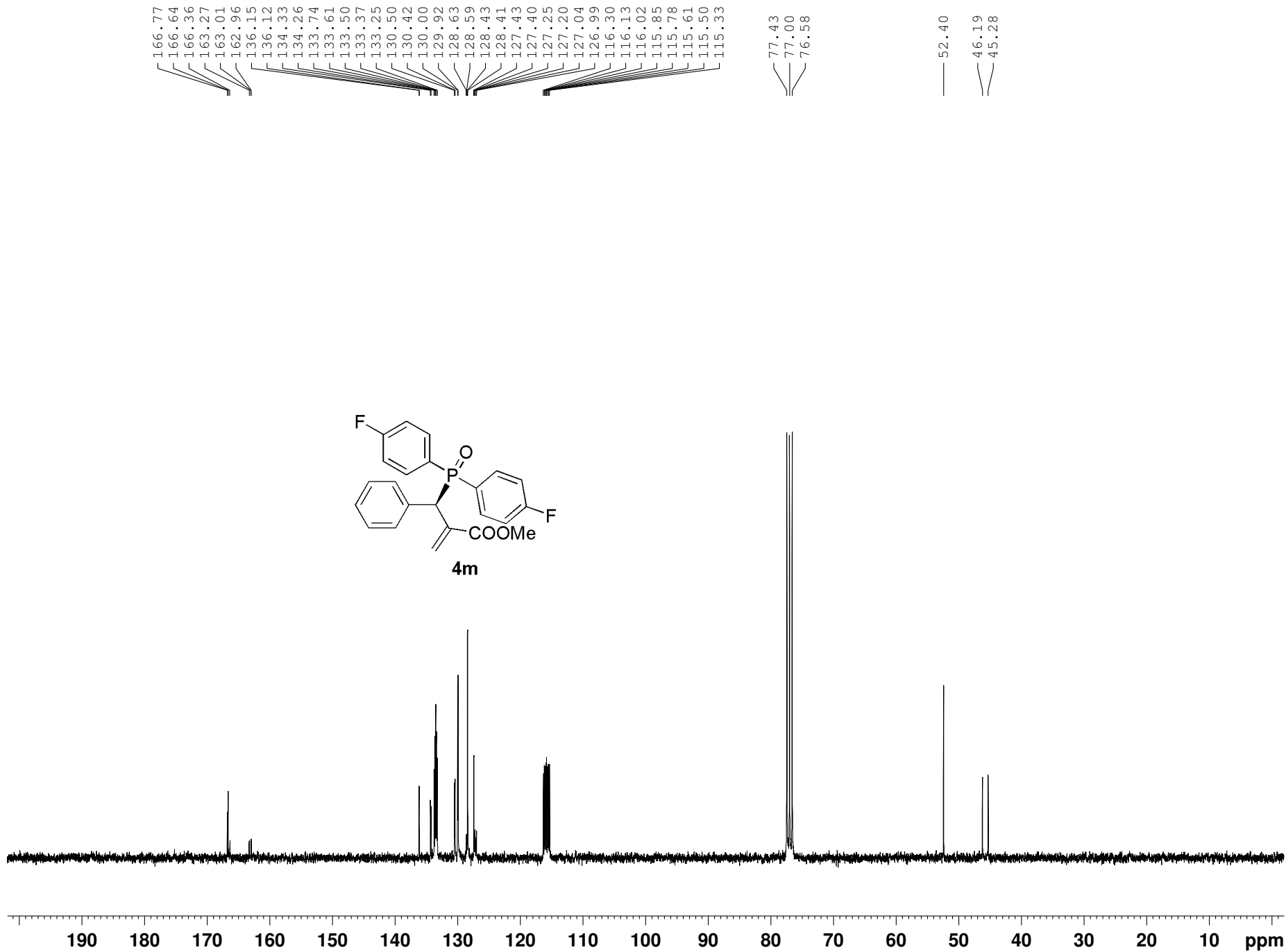


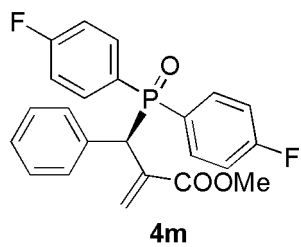


— 38.35

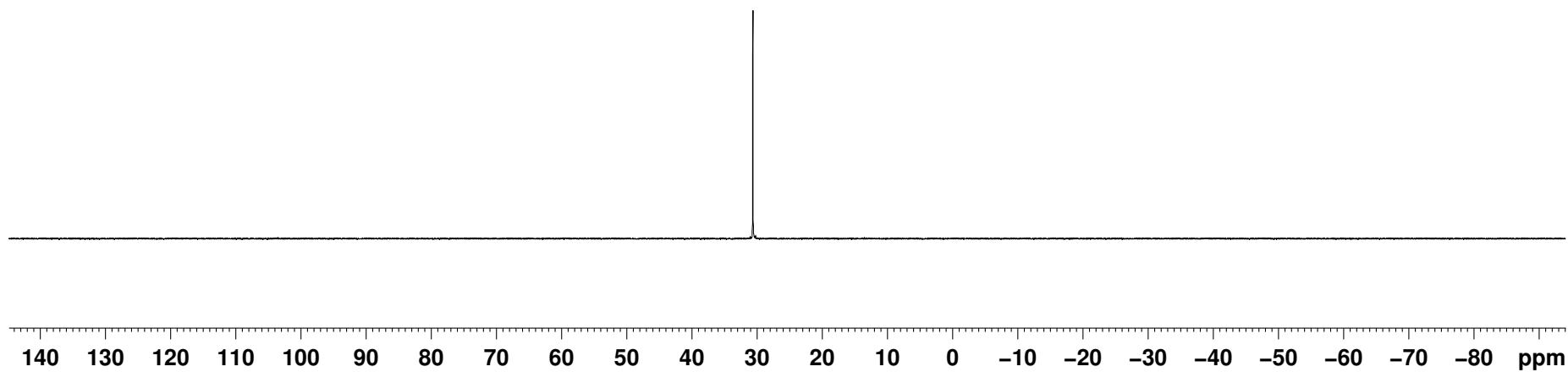


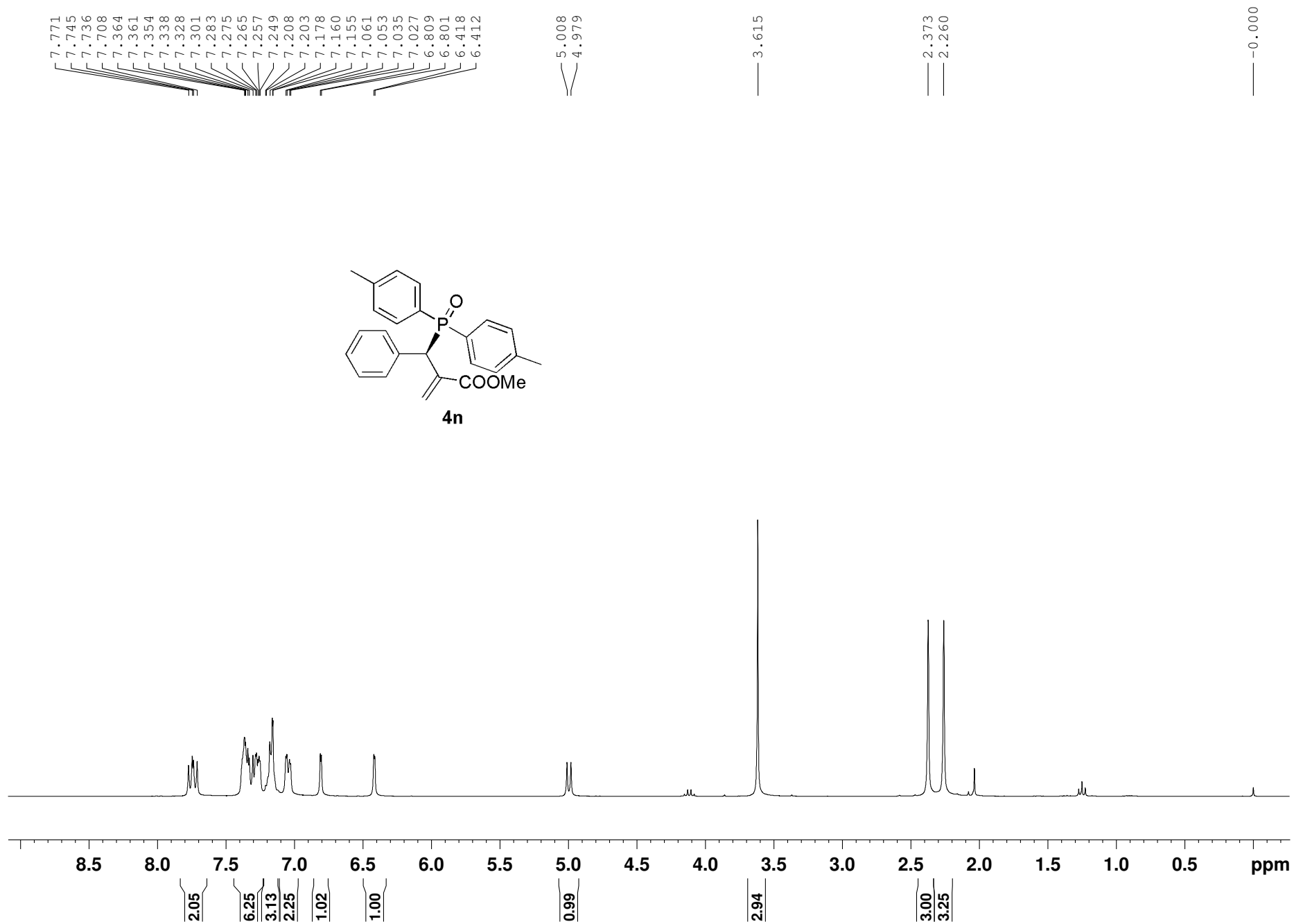






— 30.63





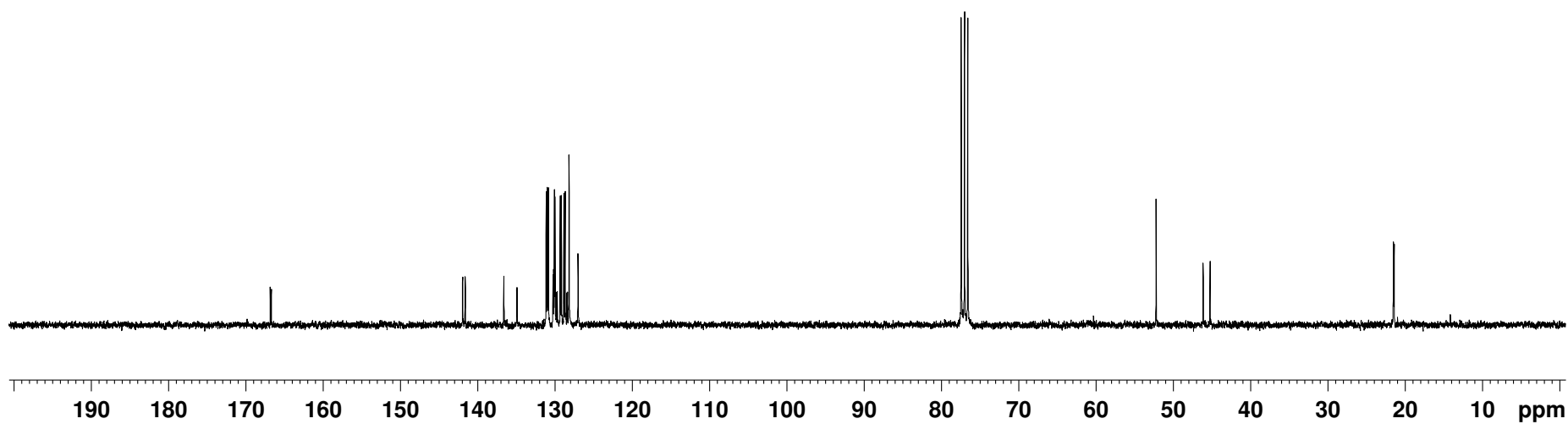
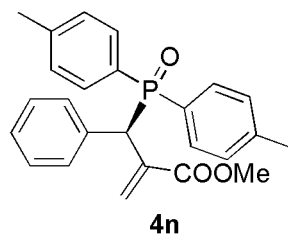
166.84
166.71
141.96
141.92
141.64
141.60
136.62
136.59
134.97
134.90
131.14
131.02
130.97
130.85
130.25
130.16
130.07
130.00
129.83
129.71
129.33
129.17
128.84
128.68
128.46
128.38
128.18
128.17
127.03
127.00

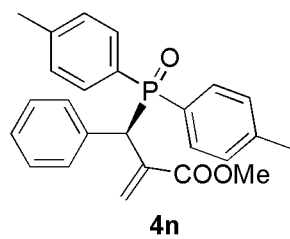
77.42
77.00
76.58

52.21

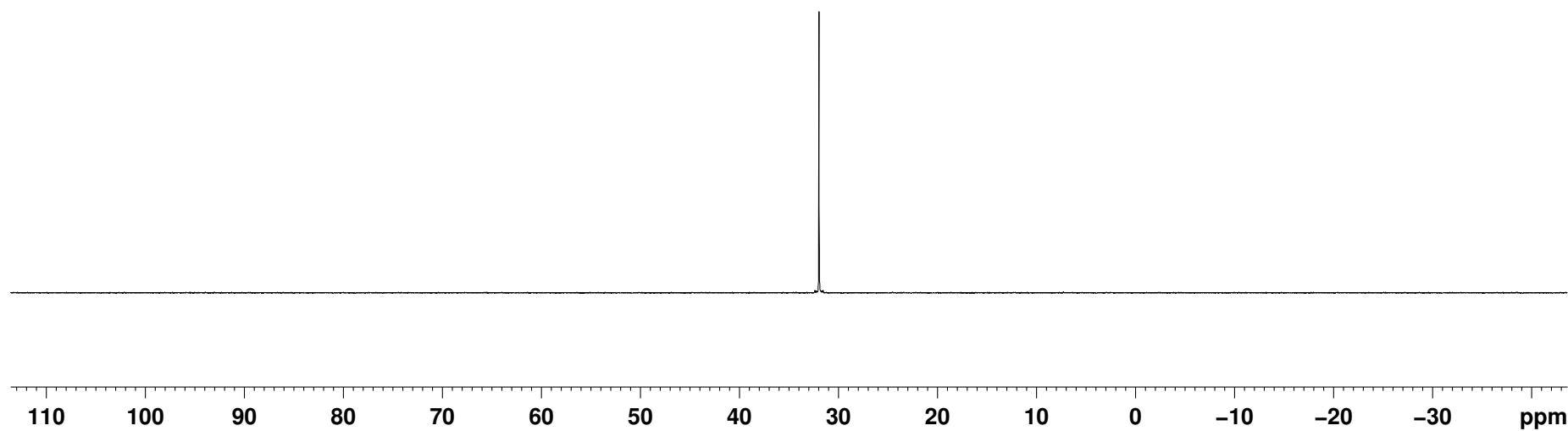
46.11
45.21

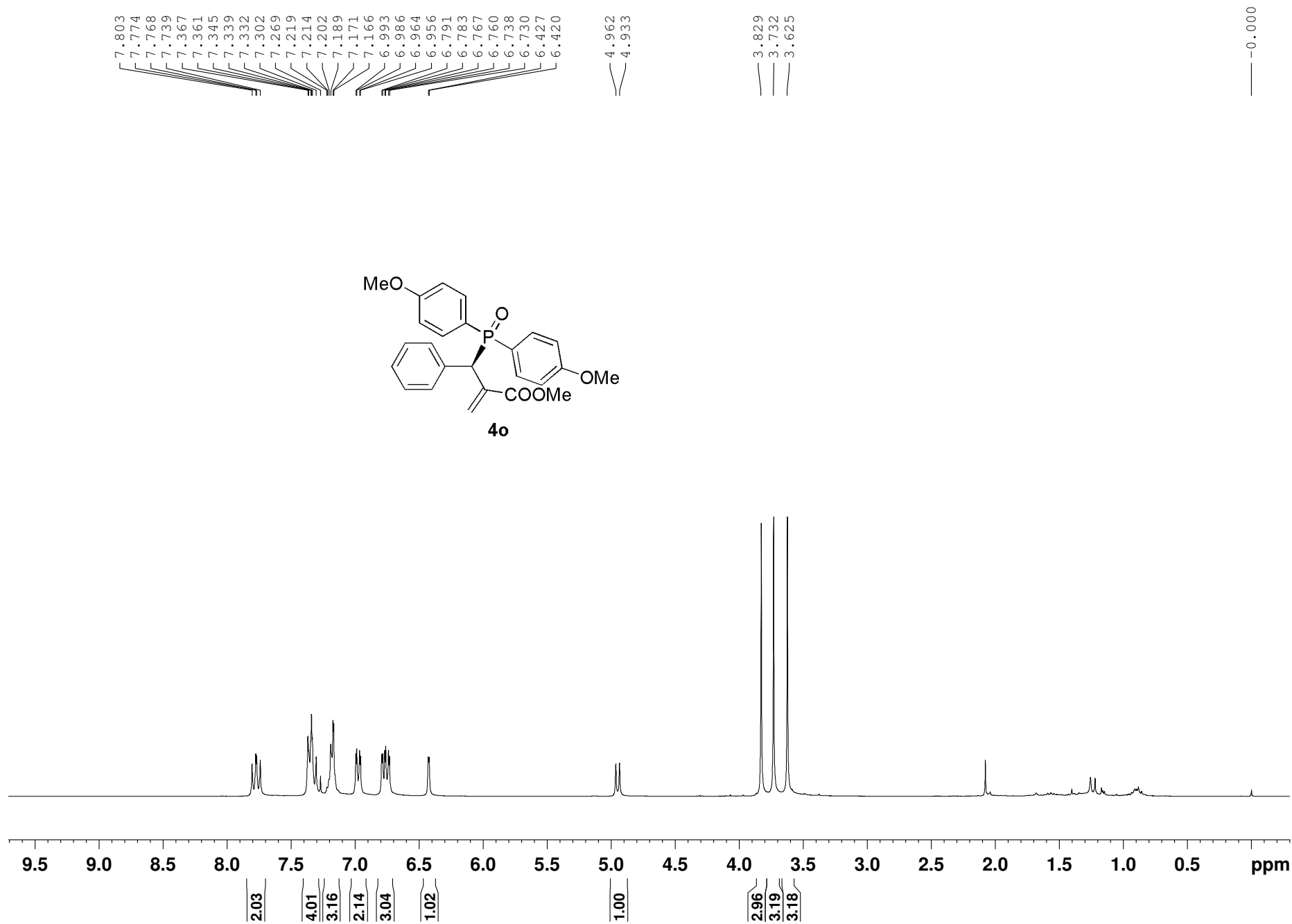
21.49
21.39

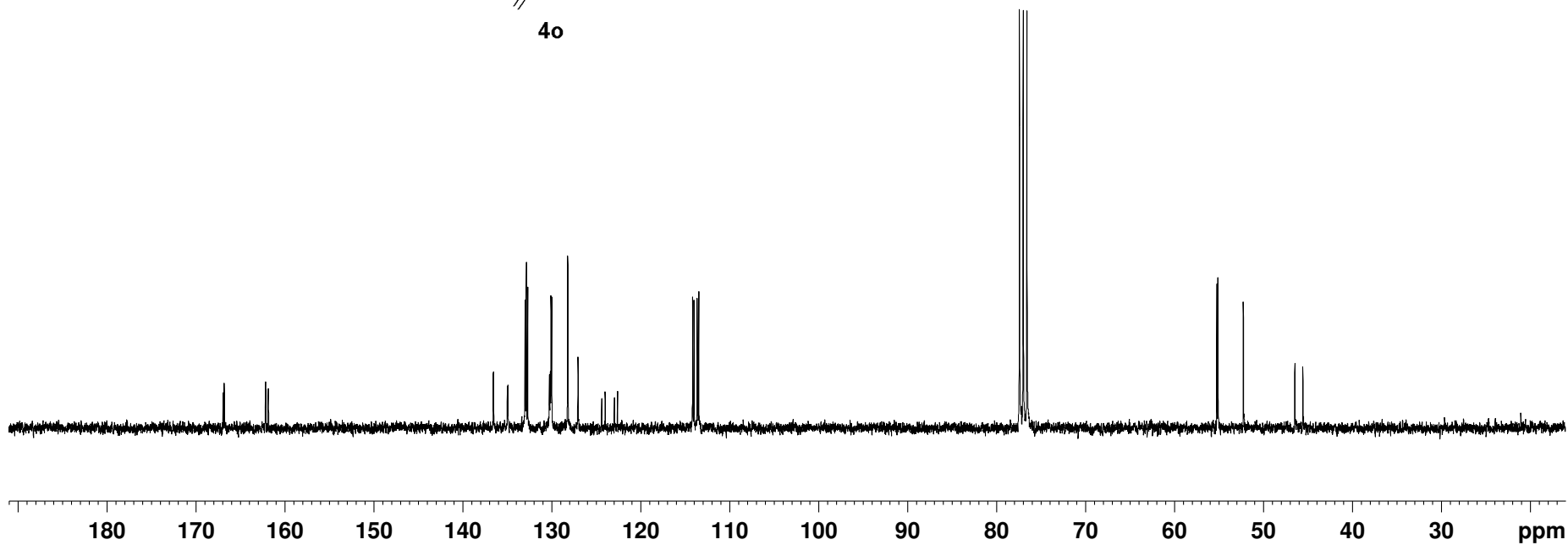
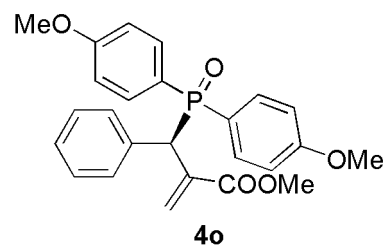
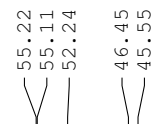
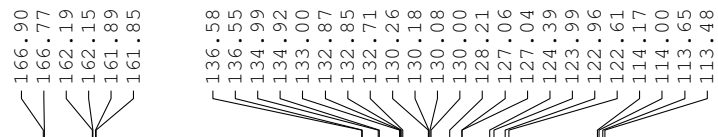




— 31.95







— 32.07

