

Supporting Information

Copper-catalyzed oxidative phosphonation of 3,4-Dihydro-1,4-benzoxazin-2-ones

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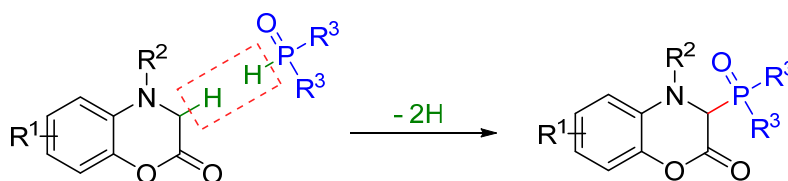


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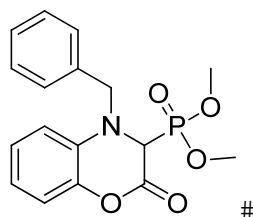
General Information.

The starting materials, reagents and solvents, purchased from commercial suppliers, were used without further purification. Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Flash chromatography was carried out using silica gel 200–300. ¹H NMR (600 MHz) and ¹³C NMR (150 MHz) spectra were measured with CDCl₃ as solvent. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. High resolution mass spectra (HR-MS) were recorded under electrospray ionization (ESI) conditions.

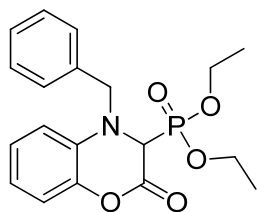
General procedure for Copper(II)-catalyzed oxidative phosphonation of 3,4-Dihydro-1,4-benzoxazin-2-ones.

3,4-Dihydro-1,4-benzoxazin-2-one (**1**, 0.2 mmol), MeCN (2 mL), phosphonate (**2**, 0.4 mmol), Cu(OTf)₂ (10 mol %) and PBQ (0.2 mmol) were placed into a 10 mL reaction tube with a magnetic stirring bar. The resulting reaction mixture was stirred at 70°C. The reaction was completed within 1-6 hours as monitored by TLC, whereupon the reaction mixture was concentrated under reduced pressure (0.2 atm, 50°C), and the residue was purified by column chromatography to afford the desired compounds **3** (acetone/petroleum ether = 1:15 to 1:10).

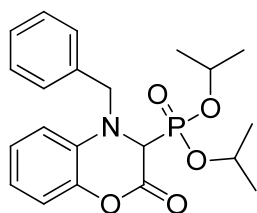
Characterization data for all compounds



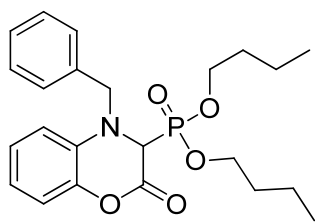
dimethyl(4-benzyl-2-oxo-3,4-dihydro-2H-benzoxazin-3-yl)phosphonate(3aa) The desired pure product was obtained in 69% yield (48 mg) as a white solid, mp 123-124 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.37 – 7.30 (m, 5H), 7.09 (dd, *J* = 12.3, 4.5 Hz, 2H), 6.95 – 6.88 (m, 2H), 4.74 (d, *J* = 14.0 Hz, 1H), 4.48 (dd, *J* = 14.0, 4.2 Hz, 1H), 4.41 (d, *J* = 15.7 Hz, 1H), 3.68 (d, *J* = 11.1 Hz, 3H), 3.29 (d, *J* = 11.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 161.9, 161.9, 142.2, 135.0, 133.1, 129.0, 128.5, 128.2, 125.5, 120.6, 116.5, 114.2, 114.2, 57.9, 57.0, 53.3, 53.3, 53.1, 53.0, 52.5. ³¹P NMR (162 MHz, CDCl₃) δ 19.3. HRMS (ESI) exact mass calcd for C₁₇H₁₈NNaO₅P [M+Na] m/z 370.0820, found 370.0815.



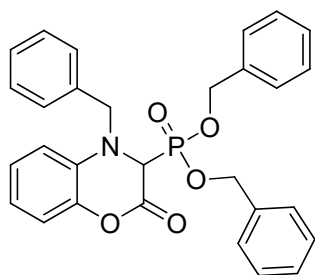
diethyl (4-benzyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3ab) The desired pure product was obtained in 66% yield (50 mg) as a yellow liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.38 – 7.28 (m, 5H), 7.08 – 7.02 (m, 2H), 6.92 – 6.86 (m, 2H), 4.75 (d, J = 14.0 Hz, 1H), 4.51 (dd, J = 14.0, 4.0 Hz, 1H), 4.37 (d, J = 15.6 Hz, 1H), 4.11 – 3.99 (m, 2H), 3.86 – 3.79 (m, 1H), 3.58 – 3.51 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.0, 161.9, 142.3, 135.2, 133.2, 128.9, 128.5, 128.1, 125.4, 120.3, 116.4, 114.0, 63.4, 63.3, 62.8, 62.8, 58.3, 57.4, 52.5, 16.2, 16.2, 16.0, 16.0. ^{31}P NMR (162 MHz, CDCl_3) δ 16.4. HRMS (ESI) exact mass calcd for $\text{C}_{19}\text{H}_{22}\text{NNaO}_5\text{P}$ [$\text{M}+\text{Na}$] m/z 398.1133, found 398.1137.



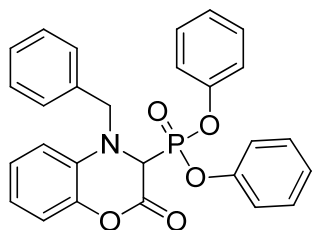
Diisopropyl (4-benzyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate(3ac) The desired pure product was obtained in 63% yield (51 mg) as a colourless liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.37 – 7.28 (m, 5H), 7.05 – 7.00 (m, 2H), 6.88 – 6.83 (m, 2H), 4.75 (d, J = 14.1 Hz, 1H), 4.65 – 4.60 (m, 1H), 4.54 (dd, J = 14.1, 3.9 Hz, 1H), 4.45 – 4.39 (m, 1H), 4.28 (d, J = 15.4 Hz, 1H), 1.29 (d, J = 6.2 Hz, 3H), 1.24 (d, J = 6.2 Hz, 3H), 1.13 (d, J = 6.2 Hz, 3H), 0.82 (d, J = 6.2 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.9, 161.9, 142.3, 135.4, 133.2, 128.9, 128.5, 128.0, 125.2, 120.0, 116.3, 113.9, 113.9, 72.5, 72.5, 72.2, 72.1, 58.9, 58.0, 52.4, 24.0, 24.0, 23.8, 23.8, 23.6, 23.6, 23.2, 23.2. ^{31}P NMR (162 MHz, CDCl_3) δ 14.3. HRMS (ESI) exact mass calcd for $\text{C}_{21}\text{H}_{26}\text{NNaO}_5\text{P}$ [$\text{M}+\text{Na}$] m/z 426.1446, found 426.1440.



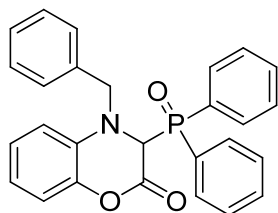
dibutyl (4-benzyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate(3ad) The desired pure product was obtained in 59% yield (50.5 mg) as a yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.31 (m, 5H), 7.10 – 7.03 (m, 2H), 6.93 – 6.86 (m, 2H), 4.76 (d, $J = 14.0$ Hz, 1H), 4.53 (dd, $J = 14.1$, 4.0 Hz, 1H), 4.38 (d, $J = 15.7$ Hz, 1H), 4.07 – 3.94 (m, 2H), 3.82 – 3.73 (m, 1H), 3.53 – 3.43 (m, 1H), 1.62 – 1.56 (m, 2H), 1.38 – 1.26 (m, 4H), 1.17 – 1.08 (m, 2H), 0.90 (t, $J = 7.4$ Hz, 3H), 0.80 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.9, 161.9, 142.2, 135.2, 133.2, 128.9, 128.5, 128.1, 125.4, 120.2, 116.4, 114.0, 67.1, 67.0, 66.4, 66.3, 58.1, 57.3, 52.4, 32.3, 32.3, 32.1, 32.1, 18.5, 18.4, 13.5, 13.4. ^{31}P NMR (162 MHz, CDCl_3) δ 16.6. HRMS (ESI) exact mass calcd for $\text{C}_{23}\text{H}_{30}\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]$ m/z 454.1759, found 454.1757.



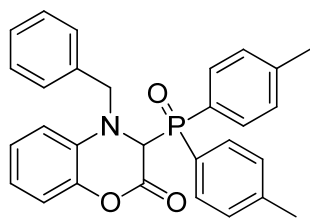
dibenzyl(4-benzyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate(3ae) The desired pure product was obtained in 60% yield (60 mg) as a colourless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.29 (m, 8H), 7.28 – 7.22 (m, 5H), 7.09 – 7.00 (m, 3H), 6.97 (dd, $J = 8.0$, 1.4 Hz, 1H), 6.93 – 6.82 (m, 2H), 4.94 – 4.84 (m, 2H), 4.76 – 4.67 (m, 2H), 4.49 – 4.42 (m, 2H), 4.36 (dd, $J = 11.5$, 9.9 Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.7, 142.2, 135.1, 133.0, 128.9, 128.6, 128.6, 128.5, 128.4, 128.4, 128.1, 128.1, 128.0, 127.9, 125.5, 120.5, 116.5, 114.1, 68.6, 68.5, 68.0, 68.0, 58.7, 57.8, 52.6. ^{31}P NMR (162 MHz, CDCl_3) δ 17.4. HRMS (ESI) exact mass calcd for $\text{C}_{29}\text{H}_{26}\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]$ m/z 522.1446, found 522.1447.



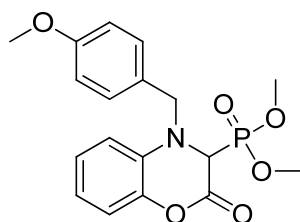
diphenyl(4-benzyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate(3af) The desired pure product was obtained in 64% yield (60 mg) as a colouless liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.31 – 7.25 (m, 7H), 7.21 – 7.18 (m, 1H), 7.18 – 7.13 (m, 4H), 7.12 – 7.09 (m, 1H), 7.09 – 7.03 (m, 2H), 6.98 – 6.90 (m, 2H), 6.60 (dd, $J = 7.6, 1.0$ Hz, 2H), 4.77 (d, $J = 13.7$ Hz, 1H), 4.67 (d, $J = 14.3$ Hz, 1H), 4.54 (dd, $J = 13.7, 5.1$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.2, 161.2, 149.6, 149.5, 149.3, 149.2, 142.3, 134.6, 132.9, 129.9, 129.6, 128.9, 128.7, 128.2, 125.8, 125.6, 125.4, 120.8, 120.7, 120.7, 120.0, 120.0, 116.7, 114.3, 114.3, 57.6, 56.7, 52.4. ^{31}P NMR (162 MHz, CDCl_3) δ 9.3. HRMS (ESI) exact mass calcd for $\text{C}_{27}\text{H}_{22}\text{NNaO}_5\text{P}$ [$\text{M}+\text{Na}$] m/z 494.1133, found 494.1136.



4-benzyl-3-(diphenylphosphoryl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one(3ag) The desired pure product was obtained in 73% yield (64 mg) as a white solid, mp 178-179 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.88 (m, 2H), 7.61 – 7.56 (m, 1H), 7.53 – 7.48 (m, 2H), 7.40 – 7.35 (m, 1H), 7.31 – 7.23 (m, 9H), 7.07 – 7.02 (m, 1H), 6.98 (dd, $J = 8.1, 1.3$ Hz, 1H), 6.72 – 6.67 (m, 1H), 6.45 (dd, $J = 8.0, 1.4$ Hz, 1H), 5.01 (d, $J = 9.2$ Hz, 1H), 4.92 (d, $J = 14.2$ Hz, 1H), 4.75 (dd, $J = 14.2, 3.0$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 163.9, 163.8, 142.0, 135.4, 133.1, 132.6, 132.5, 132.1, 132.1, 131.6, 131.5, 131.2, 131.1, 130.3, 129.7, 128.9, 128.8, 128.8, 128.6, 128.2, 128.1, 128.0, 125.5, 120.4, 116.1, 114.5, 62.3, 62.0, 53.6. ^{31}P NMR (162 MHz, CDCl_3) δ 30.0. HRMS (ESI) exact mass calcd for $\text{C}_{27}\text{H}_{22}\text{NNaO}_3\text{P}$ [$\text{M}+\text{Na}$] m/z 462.1235, found 462.1233.

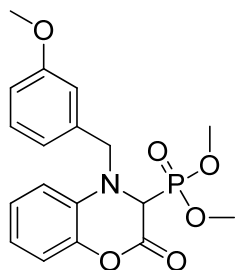


4-benzyl-3-(di-p-tolylphosphoryl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3ah) The desired pure product was obtained in 70% yield (66 mg) as a yellow liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.74 (dd, $J = 11.4, 8.1$ Hz, 2H), 7.30 (dd, $J = 8.1, 2.5$ Hz, 2H), 7.26 – 7.24 (m, 5H), 7.18 (dd, $J = 11.7, 8.1$ Hz, 2H), 7.02 (dd, $J = 7.9, 2.8$ Hz, 2H), 6.94 (d, $J = 7.9$ Hz, 1H), 6.88 – 6.78 (m, 1H), 6.71 – 6.67 (m, 1H), 6.46 (dd, $J = 8.0, 1.2$ Hz, 1H), 4.97 (d, $J = 9.2$ Hz, 1H), 4.89 (d, $J = 14.3$ Hz, 1H), 4.71 (dd, $J = 14.3, 2.7$ Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 163.9, 163.8, 143.1, 142.7, 141.9, 135.6, 133.2, 131.7, 131.6, 131.2, 131.1, 129.6, 129.5, 129.0, 128.9, 128.8, 128.5, 127.9, 125.4, 120.0, 116.0, 114.4, 62.4, 62.1, 53.5, 21.7, 21.5. ^{31}P NMR (162 MHz, CDCl_3) δ 30.7. HRMS (ESI) exact mass calcd for $\text{C}_{29}\text{H}_{26}\text{NNaO}_3\text{P}$ [$\text{M}+\text{Na}$] m/z 490.1548, found 490.1555.



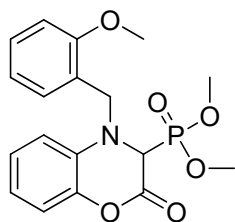
dimethyl(4-(4-methoxybenzyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate(3ba)

The desired pure product was obtained in 66% yield (50 mg) as a yellow liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.28 (d, $J = 8.6$ Hz, 2H), 7.11 – 7.06 (m, 2H), 6.96 (d, $J = 7.9$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 8.6$ Hz, 2H), 4.65 (d, $J = 13.4$ Hz, 1H), 4.42 (d, $J = 8.7$ Hz, 1H), 4.38 (d, $J = 15.8$ Hz, 1H), 3.80 (s, 3H), 3.68 (d, $J = 11.0$ Hz, 3H), 3.27 (d, $J = 11.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.0, 162.0, 159.5, 142.2, 133.3, 130.1, 126.7, 125.5, 120.5, 116.4, 114.4, 114.1, 114.1, 57.2, 56.3, 55.3, 53.3, 53.3, 53.0, 53.0, 51.8. ^{31}P NMR (162 MHz, CDCl_3) δ 19.4. HRMS (ESI) exact mass calcd for $\text{C}_{18}\text{H}_{20}\text{NNaO}_6\text{P}$ [$\text{M}+\text{Na}$] m/z 400.0926, found 400.0925.



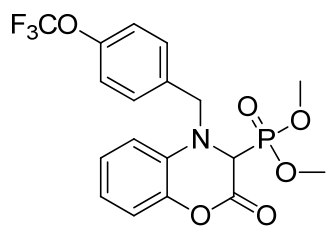
dimethyl(4-(3-methoxybenzyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate(3ca)

The desired pure product was obtained in 57% yield (43 mg) as a yellow liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.25 (dd, $J = 9.0, 6.8$ Hz, 1H), 7.10 – 7.06 (m, 2H), 6.95 – 6.88 (m, 4H), 6.84 (dd, $J = 8.2, 2.4$ Hz, 1H), 4.70 (d, $J = 14.0$ Hz, 1H), 4.47 – 4.39 (m, 2H), 3.77 (s, 3H), 3.68 (d, $J = 11.1$ Hz, 3H), 3.28 (d, $J = 11.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.9, 161.8, 160.1, 142.2, 136.6, 136.6, 133.1, 130.0, 125.6, 120.7, 120.6, 116.5, 114.2, 114.2, 113.9, 113.7, 57.9, 57.0, 55.2, 53.4, 53.3, 53.1, 53.0, 52.5. ^{31}P NMR (162 MHz, CDCl_3) δ 19.2. HRMS (ESI) exact mass calcd for $\text{C}_{18}\text{H}_{20}\text{NNaO}_6\text{P}$ [$\text{M}+\text{Na}$] m/z 400.0926, found 400.0928.

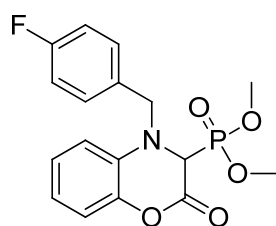


dimethyl(4-(2-methoxybenzyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate(3da)

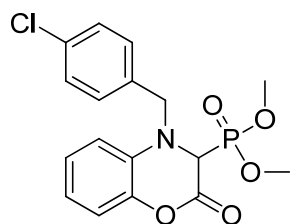
The desired pure product was obtained in 64% yield (48 mg) as a yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.24 (m, 2H), 7.07 – 7.00 (m, 2H), 6.96 (d, $J = 7.5$ Hz, 1H), 6.90 – 6.81 (m, 3H), 4.78 (d, $J = 15.0$ Hz, 1H), 4.68 (d, $J = 16.6$ Hz, 1H), 4.42 (dd, $J = 15.0, 2.4$ Hz, 1H), 3.80 (s, 3H), 3.74 (d, $J = 11.0$ Hz, 3H), 3.37 (d, $J = 10.9$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.7, 161.6, 157.9, 142.1, 132.3, 130.2, 129.4, 125.3, 123.5, 120.4, 119.9, 116.5, 114.7, 110.6, 59.5, 58.6, 55.3, 53.4, 53.4, 53.3, 53.3, 49.5. ^{31}P NMR (162 MHz, CDCl_3) δ 19.5. HRMS (ESI) exact mass calcd for $\text{C}_{18}\text{H}_{20}\text{NNaO}_6\text{P}$ [$\text{M}+\text{Na}$] m/z 400.0926, found 400.0927.



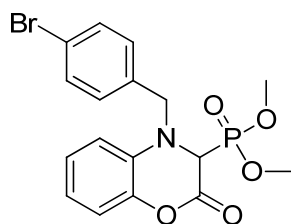
dimethyl(2-oxo-4-(4-(trifluoromethoxy)benzyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3ea) The desired pure product was obtained in 60% yield (52 mg) as a yellow liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.39 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.3$ Hz, 2H), 7.10 – 7.06 (m, 2H), 6.95 – 6.87 (m, 2H), 4.74 (d, $J = 14.3$ Hz, 1H), 4.49 (dd, $J = 14.3, 3.8$ Hz, 1H), 4.39 (d, $J = 15.6$ Hz, 1H), 3.70 (d, $J = 11.1$ Hz, 3H), 3.26 (d, $J = 11.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 163.4, 161.8, 161.8, 161.7, 142.3, 132.9, 130.7, 130.3, 130.2, 125.6, 120.8, 116.5, 116.0, 115.8, 114.1, 57.8, 56.9, 53.4, 53.3, 53.1, 53.0, 51.8. ^{31}P NMR (162 MHz, CDCl_3) δ 14.7. HRMS (ESI) exact mass calcd for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{NNaO}_6\text{P}$ $[\text{M}+\text{Na}]$ m/z 454.0643, found 454.0638.



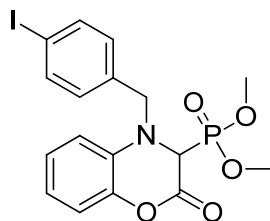
dimethyl(4-(4-fluorobenzyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3fa) The desired pure product was obtained in 64% yield (47 mg) as a colourless liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.34 (dd, $J = 8.4, 5.4$ Hz, 2H), 7.10 – 7.02 (m, 4H), 6.93 – 6.89 (m, 2H), 4.70 (d, $J = 13.9$ Hz, 1H), 4.46 (dd, $J = 13.9, 4.1$ Hz, 1H), 4.37 (d, $J = 15.7$ Hz, 1H), 3.69 (d, $J = 11.1$ Hz, 3H), 3.26 (d, $J = 11.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.7, 161.7, 149.0, 142.2, 133.8, 133.8, 132.7, 129.8, 125.6, 121.4, 120.9, 116.6, 114.1, 114.1, 58.3, 57.4, 53.4, 53.3, 53.1, 53.1, 51.8. ^{31}P NMR (162 MHz, CDCl_3) δ 14.4. HRMS (ESI) exact mass calcd for $\text{C}_{17}\text{H}_{17}\text{FNNaO}_5\text{P}$ $[\text{M}+\text{Na}]$ m/z 388.0726, found 388.0729.



dimethyl (4-(4-chlorobenzyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3ga) The desired pure product was obtained in 65% yield (50 mg) as a colourless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.34 – 7.28 (m, 4H), 7.10 – 7.06 (m, 2H), 6.93 – 6.87 (m, 2H), 4.70 (d, *J* = 14.2 Hz, 1H), 4.46 (dd, *J* = 14.2, 3.9 Hz, 1H), 4.38 (d, *J* = 15.6 Hz, 1H), 3.70 (d, *J* = 11.1 Hz, 3H), 3.26 (d, *J* = 11.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 161.8, 161.7, 142.2, 134.0, 133.6, 132.8, 129.8, 129.2, 125.6, 120.8, 116.6, 114.2, 114.1, 58.1, 57.3, 53.4, 53.4, 53.1, 53.1, 52.0. ³¹P NMR (162 MHz, CDCl₃) δ 19.0. HRMS (ESI) exact mass calcd for C₁₇H₁₇ClNNaO₅P [M+Na] m/z 404.0431, found 404.0428.

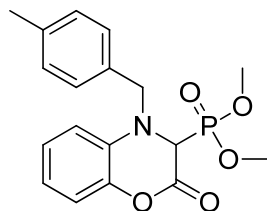


dimethyl(4-(4-bromobenzyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3ha) The desired pure product was obtained in 61% yield (52 mg) as a white solid, mp 125-126 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.09 – 7.05 (m, 2H), 6.94 – 6.85 (m, 2H), 4.68 (d, *J* = 14.3 Hz, 1H), 4.44 (dd, *J* = 14.3, 3.8 Hz, 1H), 4.38 (d, *J* = 15.6 Hz, 1H), 3.69 (d, *J* = 11.1 Hz, 3H), 3.26 (d, *J* = 11.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 161.7, 161.7, 142.2, 134.2, 132.8, 132.1, 130.1, 125.6, 122.1, 120.8, 116.6, 114.2, 114.1, 58.2, 57.3, 53.4, 53.4, 53.1, 53.1, 52.0. ³¹P NMR (162 MHz, CDCl₃) δ 14.3. HRMS (ESI) exact mass calcd for C₁₇H₁₇BrNNaO₅P [M+Na] m/z 447.9925, found 447.9933.

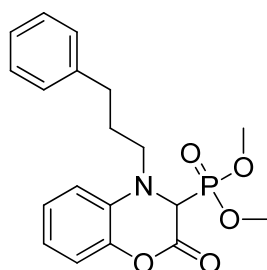


dimethyl (4-(4-iodobenzyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3ia) The desired pure product was obtained in 58% yield (55 mg) as a yellow liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.11 – 7.06 (m, 4H), 6.92 – 6.86 (m, 2H), 4.68 (d, *J* = 14.3 Hz, 1H), 4.43 (dd, *J* = 14.3, 3.8 Hz, 1H), 4.38 (d, *J* = 15.6 Hz, 1H), 3.70 (d, *J* = 11.1 Hz, 3H), 3.26 (d, *J* = 11.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 161.7, 142.2, 138.1, 134.9, 132.8, 130.3, 125.6, 120.8, 116.6, 114.1,

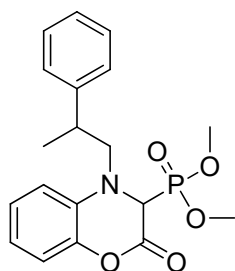
93.7, 58.3, 57.4, 53.4, 53.4, 53.1, 53.1, 52.1. ^{31}P NMR (162 MHz, CDCl_3) δ 13.8. HRMS (ESI) exact mass calcd for $\text{C}_{17}\text{H}_{17}\text{INNaO}_5\text{P}$ $[\text{M}+\text{Na}]$ m/z 495.9787, found 495.9793.



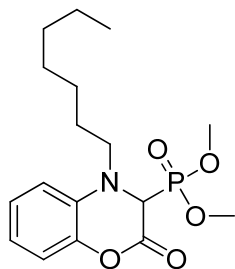
dimethyl (4-(4-methylbenzyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3ja) The desired pure product was obtained in 70% yield (50.5 mg) as a yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 7.9$ Hz, 2H), 7.18 (d, $J = 7.7$ Hz, 2H), 7.14 – 7.08 (m, 2H), 6.99 – 6.90 (m, 2H), 4.71 (d, $J = 13.7$ Hz, 1H), 4.49 – 4.40 (m, 2H), 3.71 (d, $J = 11.1$ Hz, 3H), 3.30 (d, $J = 11.1$ Hz, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.0, 161.9, 142.2, 138.0, 133.2, 131.8, 129.6, 129.5, 128.6, 125.5, 120.5, 116.4, 114.2, 114.1, 57.5, 56.7, 53.3, 53.3, 53.1, 53.0, 52.2, 21.1. ^{31}P NMR (162 MHz, CDCl_3) δ 19.4. HRMS (ESI) exact mass calcd for $\text{C}_{18}\text{H}_{20}\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]$ m/z 384.0977, found 384.0971.



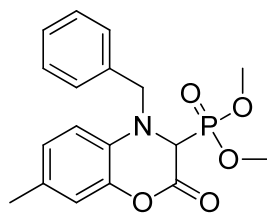
dimethyl(2-oxo-4-(3-phenylpropyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3ka) The desired pure product was obtained in 56% yield (42 mg) as a yellow liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.29 – 7.26 (m, 2H), 7.19 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.14 (d, $J = 7.0$ Hz, 2H), 7.08 – 7.05 (m, 1H), 7.04 (dd, $J = 8.0, 1.4$ Hz, 1H), 6.87 – 6.80 (m, 2H), 4.46 (d, $J = 16.2$ Hz, 1H), 3.70 (d, $J = 11.1$ Hz, 3H), 3.64 – 3.60 (m, 1H), 3.28 (d, $J = 11.0$ Hz, 3H), 3.20 – 3.17 (m, 1H), 2.70 – 2.67 (m, 1H), 2.65 – 2.62 (m, 1H), 2.03 – 1.99 (m, 1H), 1.97 – 1.93 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.6, 142.1, 140.8, 132.3, 128.5, 128.3, 126.1, 125.5, 120.1, 116.6, 113.9, 60.0, 59.1, 53.3, 53.3, 53.2, 53.1, 48.8, 32.8, 28.1, 28.1. ^{31}P NMR (162 MHz, CDCl_3) δ 19.1. HRMS (ESI) exact mass calcd for $\text{C}_{19}\text{H}_{22}\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]$ m/z 398.1133, found 398.1131.



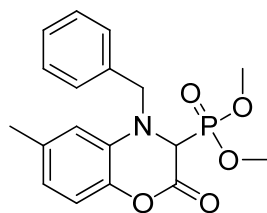
dimethyl (2-oxo-4-(2-phenylpropyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3la) The desired pure product was obtained in 53% yield (40 mg) as a colourless liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.30 – 7.26 (m, 4H), 7.23 – 7.18 (m, 4H), 7.11 – 7.07 (m, 4H), 7.01 (d, $J = 7.9$ Hz, 2H), 6.90 – 6.82 (m, 4H), 4.50 (d, $J = 16.4$ Hz, 1H), 3.91 – 3.85 (m, 3H), 3.71 (d, $J = 11.0$ Hz, 3H), 3.66 (d, $J = 11.0$ Hz, 3H), 3.31 – 3.27 (m, 6H), 3.26 – 3.22 (m, 1H), 3.17 – 3.14 (m, 1H), 3.11 – 3.05 (m, 2H), 1.30 (d, $J = 7.1$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.4, 161.3, 160.5, 160.5, 143.6, 143.3, 141.9, 141.5, 132.0, 131.3, 128.8, 128.7, 127.0, 126.9, 126.8, 126.8, 125.5, 125.5, 120.0, 119.6, 116.8, 116.7, 113.7, 113.3, 60.9, 60.6, 60.0, 59.7, 57.3, 56.6, 53.4, 53.4, 53.3, 53.3, 53.2, 37.5, 37.5, 37.2, 37.2, 19.3, 17.9. ^{31}P NMR (162 MHz, CDCl_3) δ 19.01, 18.64. HRMS (ESI) exact mass calcd for $\text{C}_{19}\text{H}_{22}\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]$ m/z 398.1133, found 398.1134.



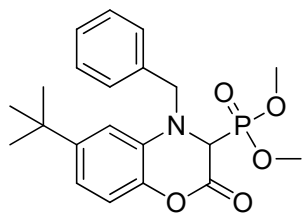
dimethyl (4-heptyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3ma) The desired pure product was obtained in 56% yield (40 mg) as a colourless liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.09 (dd, $J = 11.3, 4.2$ Hz, 1H), 7.03 (d, $J = 7.9$ Hz, 1H), 6.89 – 6.83 (m, 2H), 4.55 (d, $J = 16.4$ Hz, 1H), 3.73 (d, $J = 11.0$ Hz, 3H), 3.60 – 3.55 (m, 1H), 3.31 (d, $J = 11.0$ Hz, 3H), 3.22 – 3.17 (m, 1H), 1.64 – 1.57 (m, 3H), 1.32 – 1.25 (m, 7H), 0.86 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.6, 142.1, 132.6, 125.5, 119.9, 116.6, 113.8, 59.7, 58.8, 53.3, 53.3, 53.2, 53.1, 49.7, 31.7, 29.0, 26.8, 26.8, 22.5, 14.0. ^{31}P NMR (162 MHz, CDCl_3) δ 19.2. HRMS (ESI) exact mass calcd for $\text{C}_{17}\text{H}_{26}\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]$ m/z 378.1446, found 378.1452.



dimethyl (4-benzyl-7-methyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3na) The desired pure product was obtained in 65% yield (47 mg) as a yellow liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.34 (d, $J = 4.4$ Hz, 4H), 7.32 – 7.28 (m, 1H), 6.90 – 6.86 (m, 2H), 6.81 (d, $J = 8.0$ Hz, 1H), 4.69 (d, $J = 14.0$ Hz, 1H), 4.44 (dd, $J = 14.0, 4.2$ Hz, 1H), 4.38 (d, $J = 15.9$ Hz, 1H), 3.68 (d, $J = 11.1$ Hz, 3H), 3.31 (d, $J = 11.0$ Hz, 3H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.0, 162.0, 142.2, 135.3, 130.6, 130.6, 128.9, 128.5, 128.1, 125.9, 117.0, 114.2, 58.2, 57.3, 53.3, 53.2, 53.1, 53.0, 52.9, 20.5. ^{31}P NMR (162 MHz, CDCl_3) δ 19.5. HRMS (ESI) exact mass calcd for $\text{C}_{18}\text{H}_{20}\text{NNaO}_5\text{P}$ [$\text{M}+\text{Na}$] m/z 384.0977, found 384.0971.

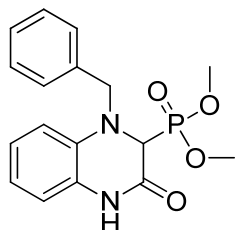


dimethyl (4-benzyl-6-methyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate(3oa) The desired pure product was obtained in 69% yield (50 mg) as a white solid, mp 163-164 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.35 (d, $J = 4.4$ Hz, 4H), 7.33 – 7.30 (m, 1H), 6.95 (d, $J = 8.1$ Hz, 1H), 6.76 (s, 1H), 6.70 (d, $J = 8.2$ Hz, 1H), 4.72 (d, $J = 13.8$ Hz, 1H), 4.46 (dd, $J = 13.8, 4.6$ Hz, 1H), 4.36 (d, $J = 15.7$ Hz, 1H), 3.68 (d, $J = 11.1$ Hz, 3H), 3.30 (d, $J = 11.0$ Hz, 3H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.9, 140.2, 135.3, 135.1, 132.8, 128.9, 128.6, 128.2, 121.0, 116.2, 114.7, 57.6, 56.8, 53.3, 53.2, 53.1, 53.0, 52.4, 21.3. ^{31}P NMR (162 MHz, CDCl_3) δ 19.6. HRMS (ESI) exact mass calcd for $\text{C}_{18}\text{H}_{20}\text{NNaO}_5\text{P}$ [$\text{M}+\text{Na}$] m/z 384.0977, found 384.0975.

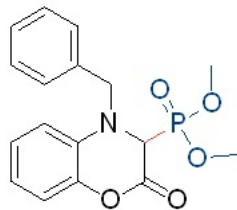


dimethyl(4-benzyl-6-(tert-butyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)phosphonate (3pa)

The desired pure product was obtained in 62% yield (50 mg) as a yellow liquid. ^1H NMR (600 MHz, CDCl_3) δ 7.38 – 7.33 (m, 4H), 7.31 – 7.29 (m, 1H), 6.98 (d, $J = 8.3$ Hz, 1H), 6.92 – 6.89 (m, 2H), 4.76 (d, $J = 13.9$ Hz, 1H), 4.48 (dd, $J = 13.9, 4.1$ Hz, 1H), 4.42 (d, $J = 15.8$ Hz, 1H), 3.67 (d, $J = 11.1$ Hz, 3H), 3.24 (d, $J = 11.0$ Hz, 3H), 1.24 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.0, 148.8, 140.2, 135.3, 132.3, 128.9, 128.8, 128.5, 128.1, 126.9, 117.4, 115.8, 111.6, 58.2, 57.4, 53.3, 53.2, 52.9, 52.9, 52.8, 34.7, 31.3. ^{31}P NMR (162 MHz, CDCl_3) δ 19.5. HRMS (ESI) exact mass calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_5\text{P}$ [$\text{M}+\text{Na}$] m/z 426.1446, found 426.1450.



dimethyl (1-benzyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)phosphonate (3qa) The desired pure product was obtained in 72% yield (50 mg) as a white solid, mp 222-223 °C. ^1H NMR (600 MHz, CDCl_3) δ 9.32 (s, 1H), 7.36 – 7.31 (m, 4H), 7.28 – 7.25 (m, 1H), 6.98 – 6.95 (m, 1H), 6.85 – 6.82 (m, 2H), 6.80 (d, $J = 7.4$ Hz, 1H), 4.77 (d, $J = 13.4$ Hz, 1H), 4.50 (dd, $J = 14.2, 4.0$ Hz, 1H), 4.31 (d, $J = 14.5$ Hz, 1H), 3.67 (d, $J = 11.0$ Hz, 3H), 3.34 (d, $J = 10.9$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 164.0, 135.8, 134.1, 128.8, 128.4, 127.9, 126.7, 124.4, 119.9, 115.6, 113.7, 60.1, 59.2, 53.0, 53.0, 52.9, 52.9. ^{31}P NMR (162 MHz, CDCl_3) δ 22.0. HRMS (ESI) exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_4\text{P}$ [$\text{M}+\text{Na}$] m/z 369.0980, found 369.0975.



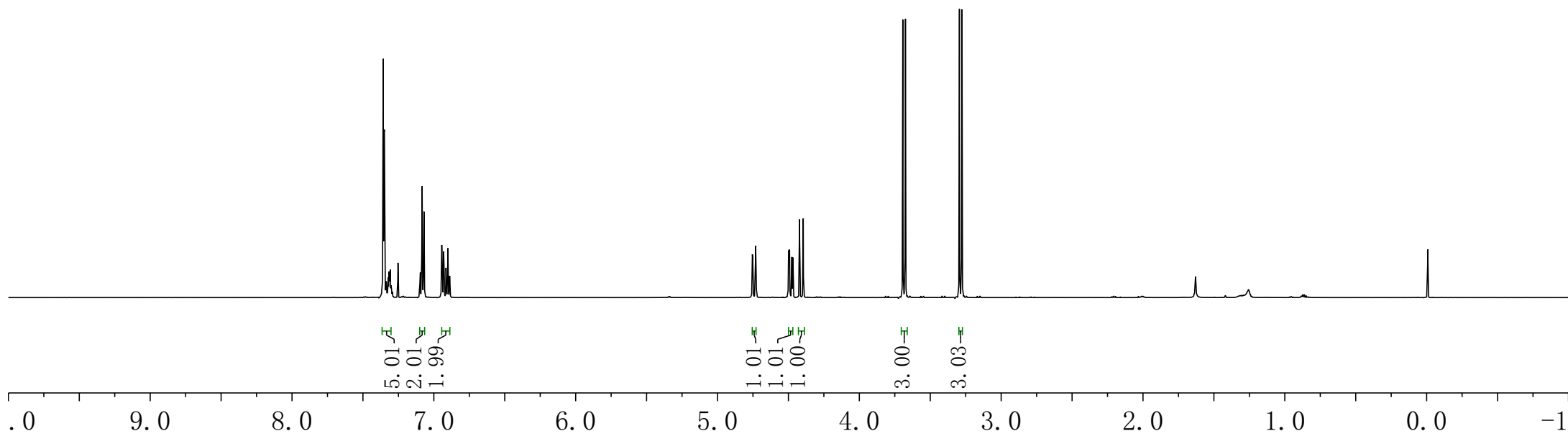
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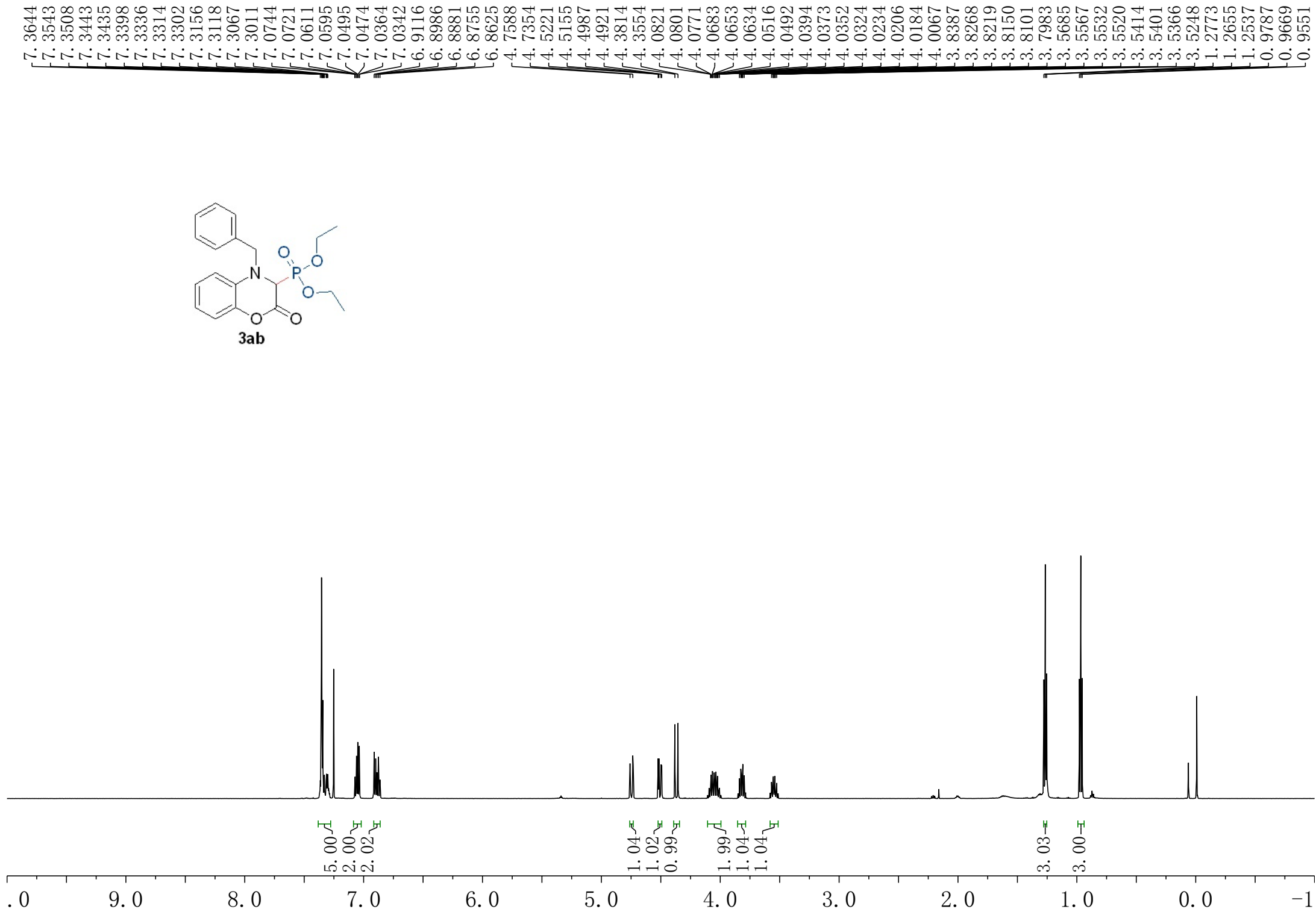
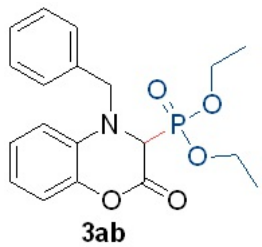
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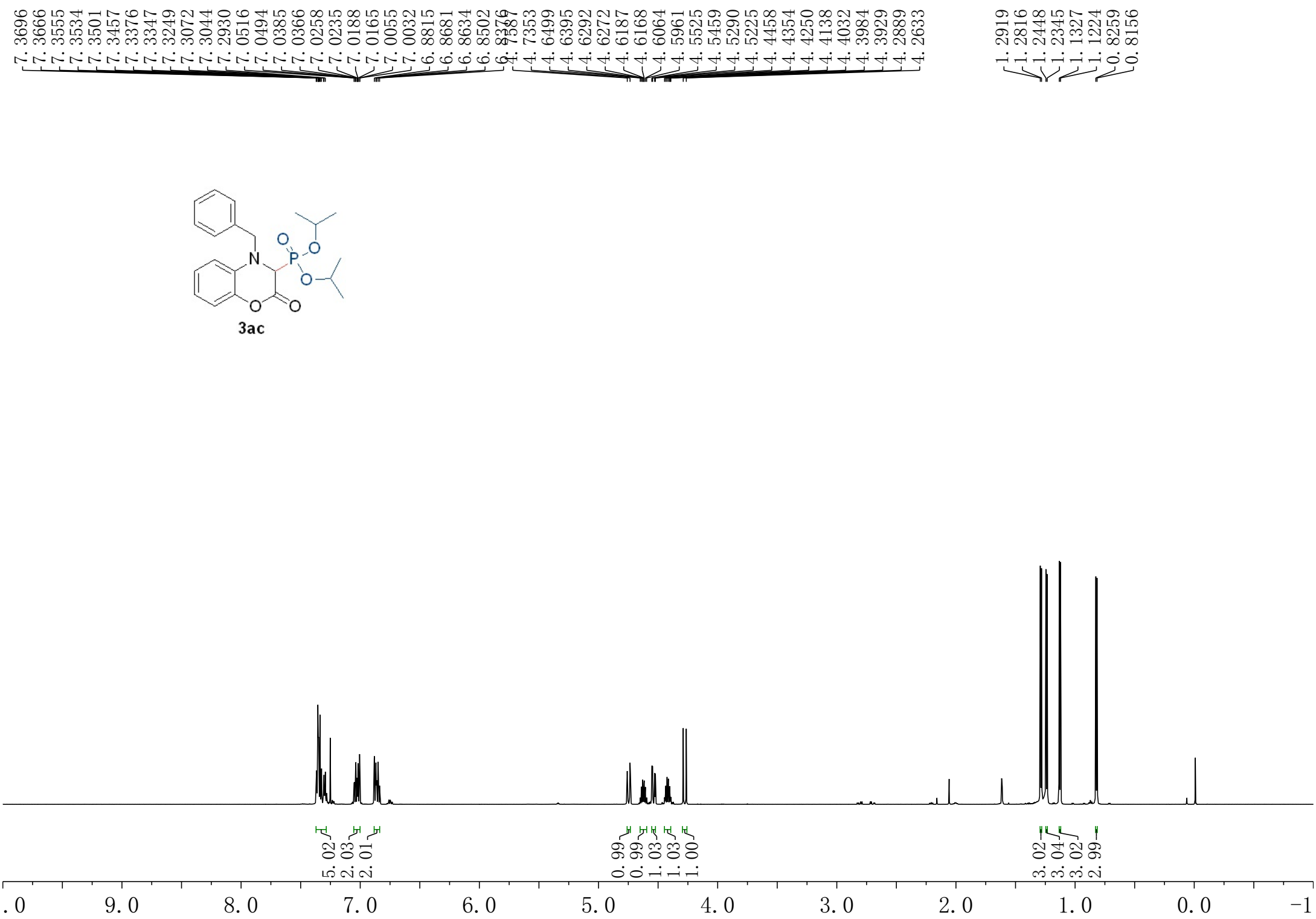
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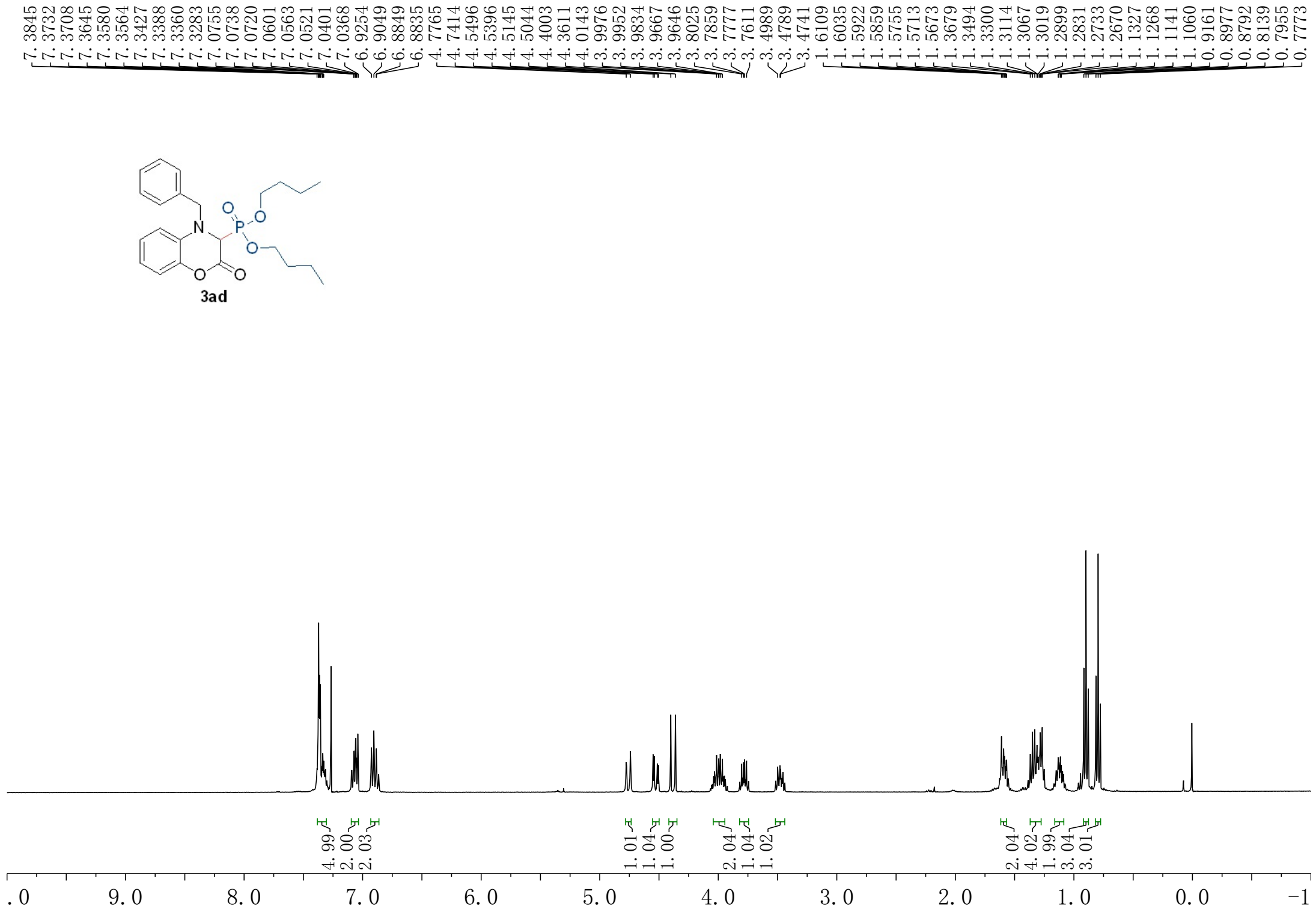
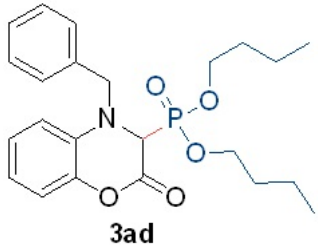
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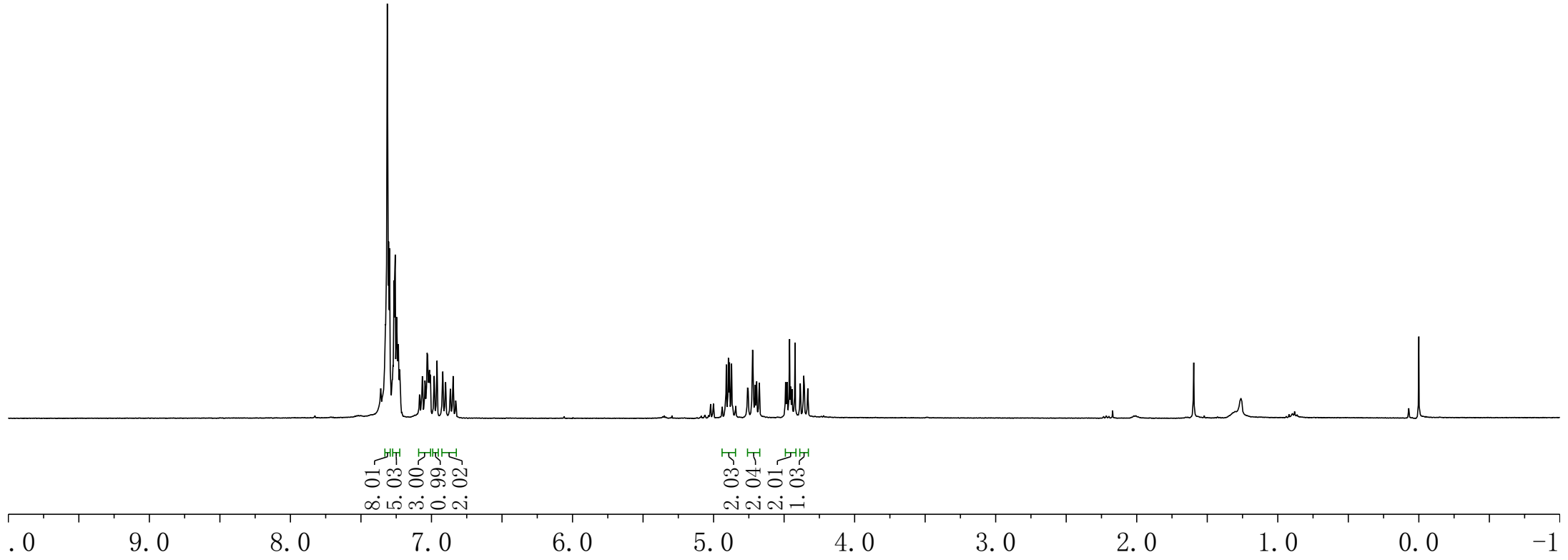
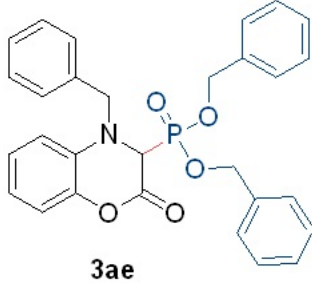


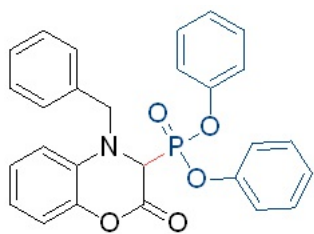




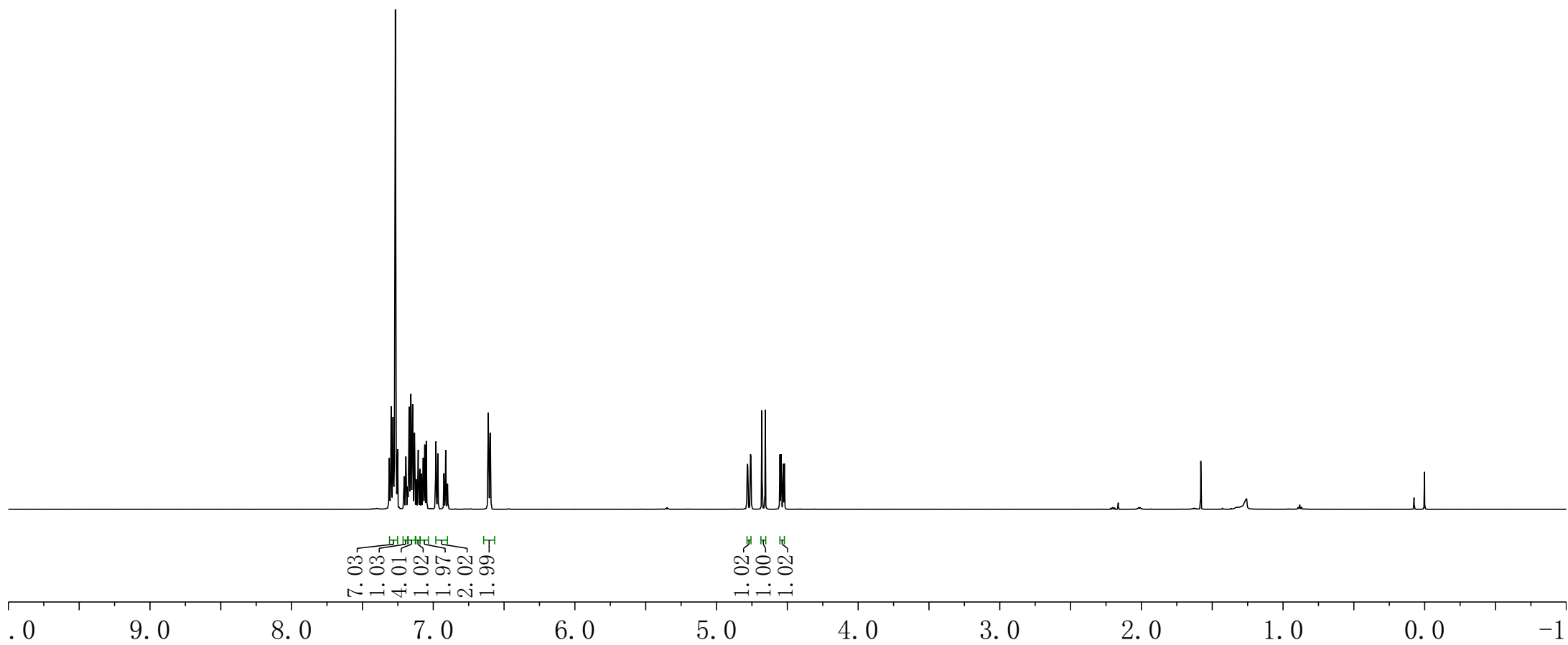


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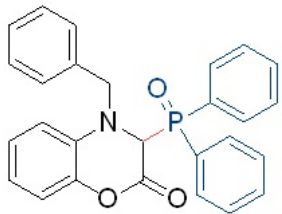




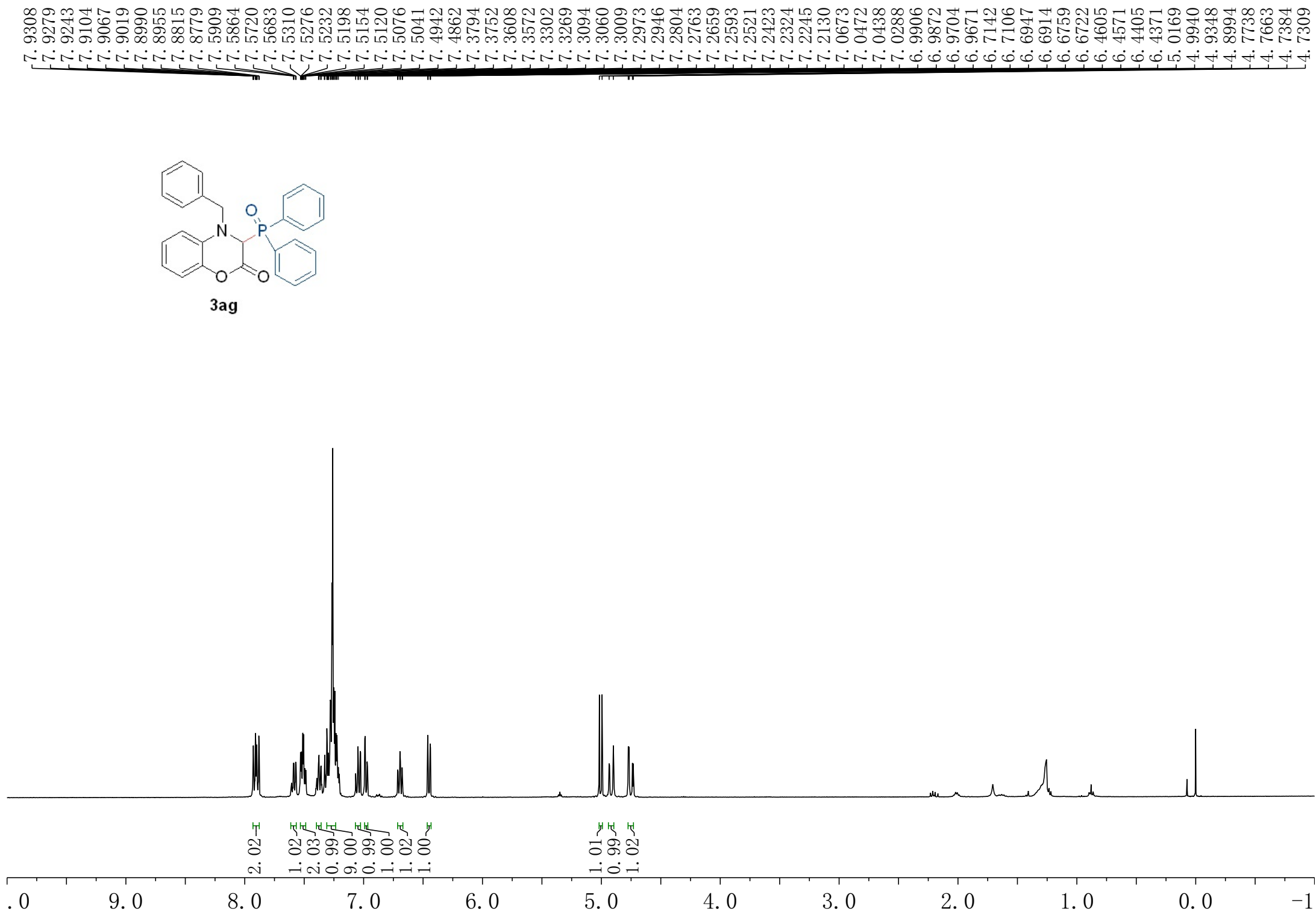
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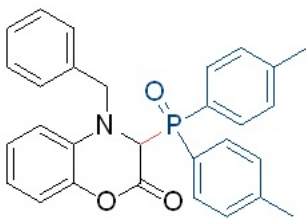
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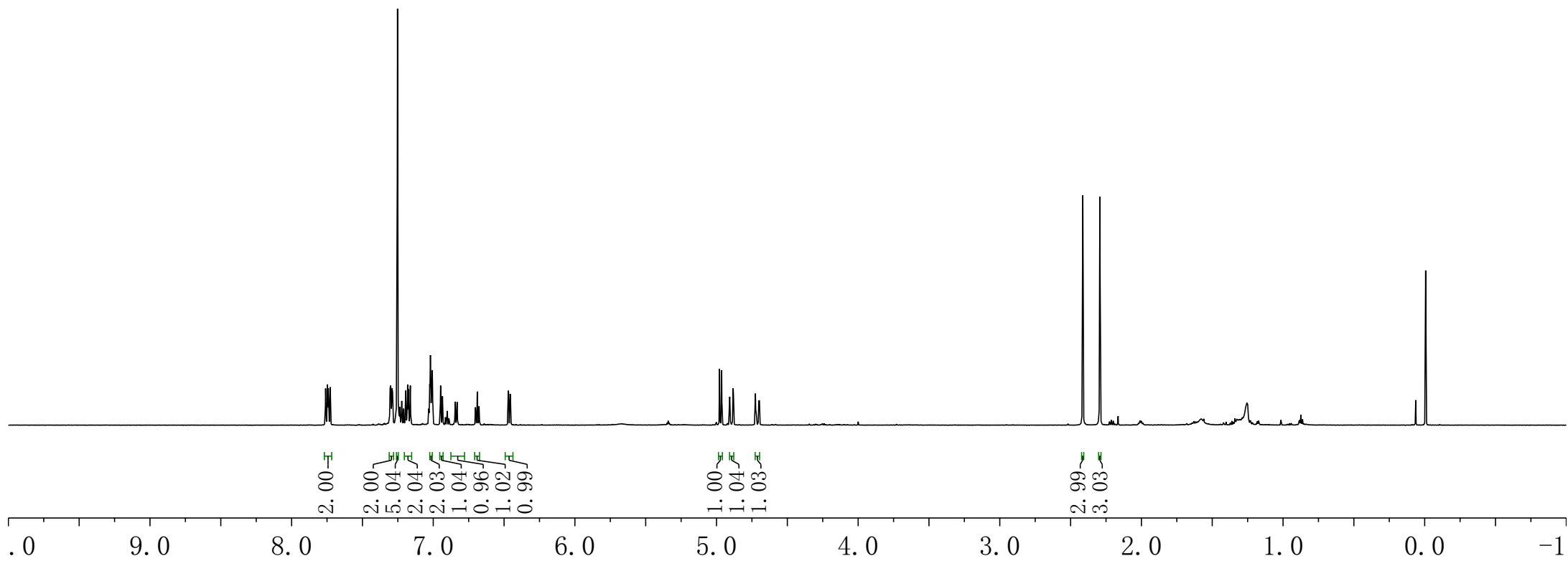
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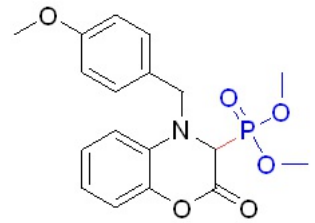


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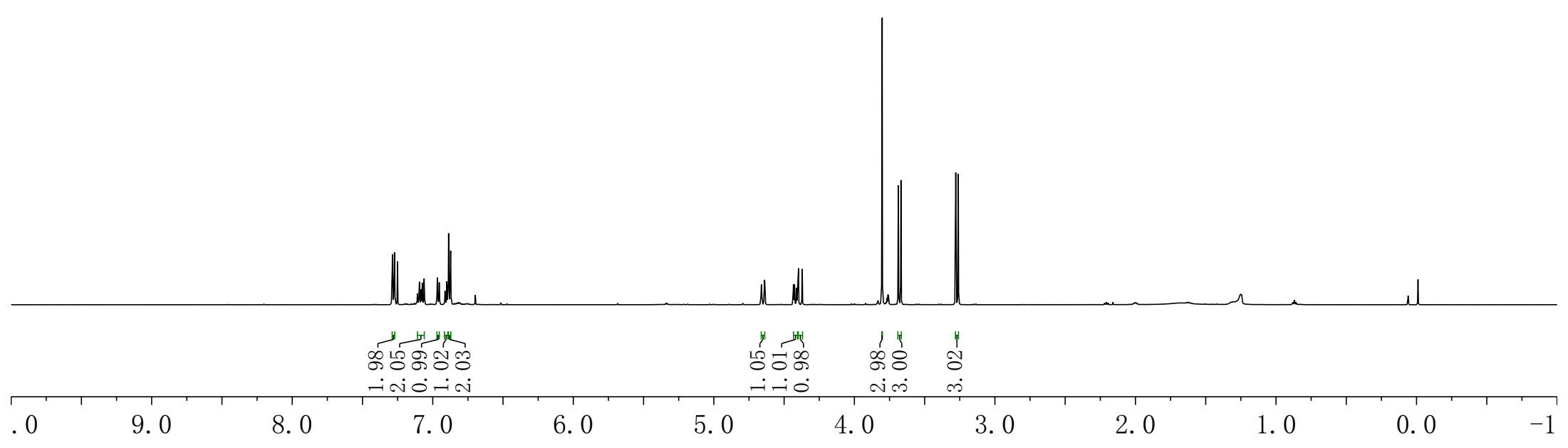


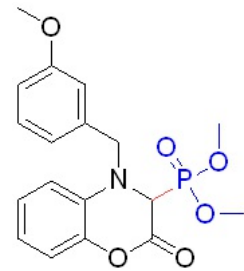
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3ba

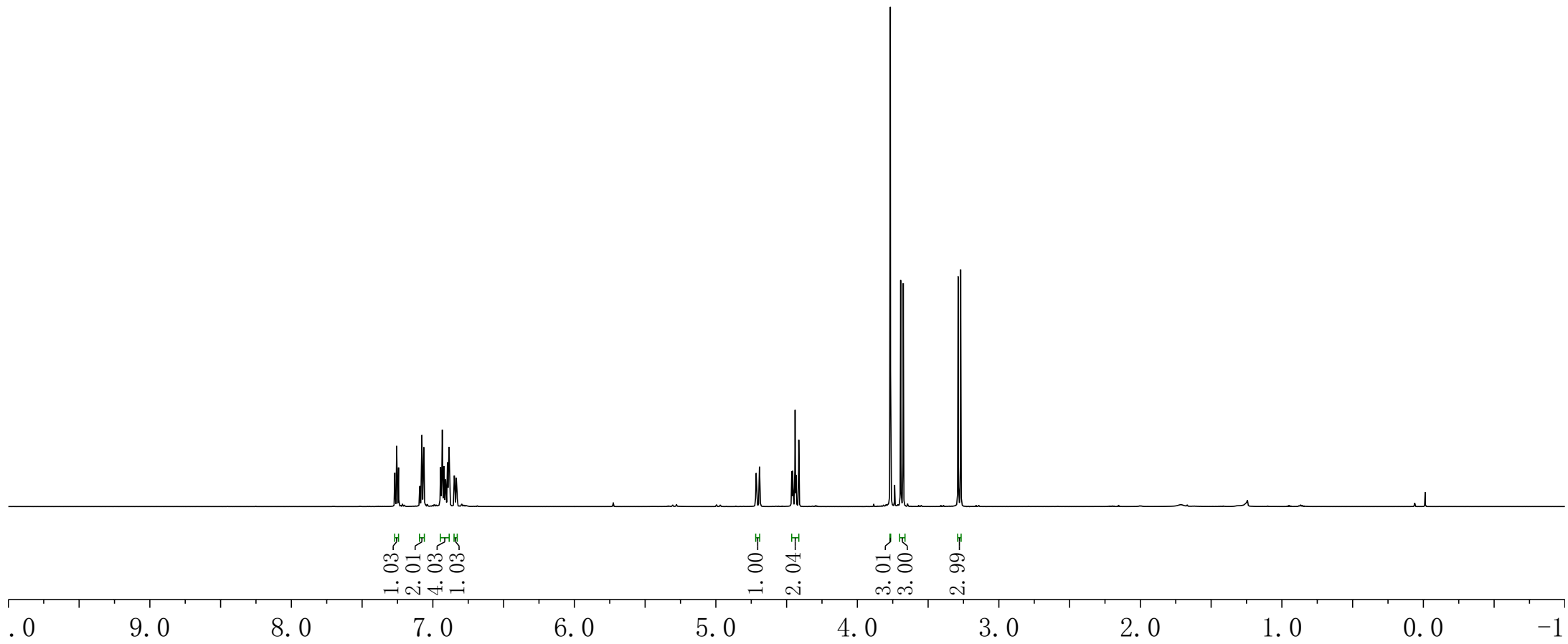




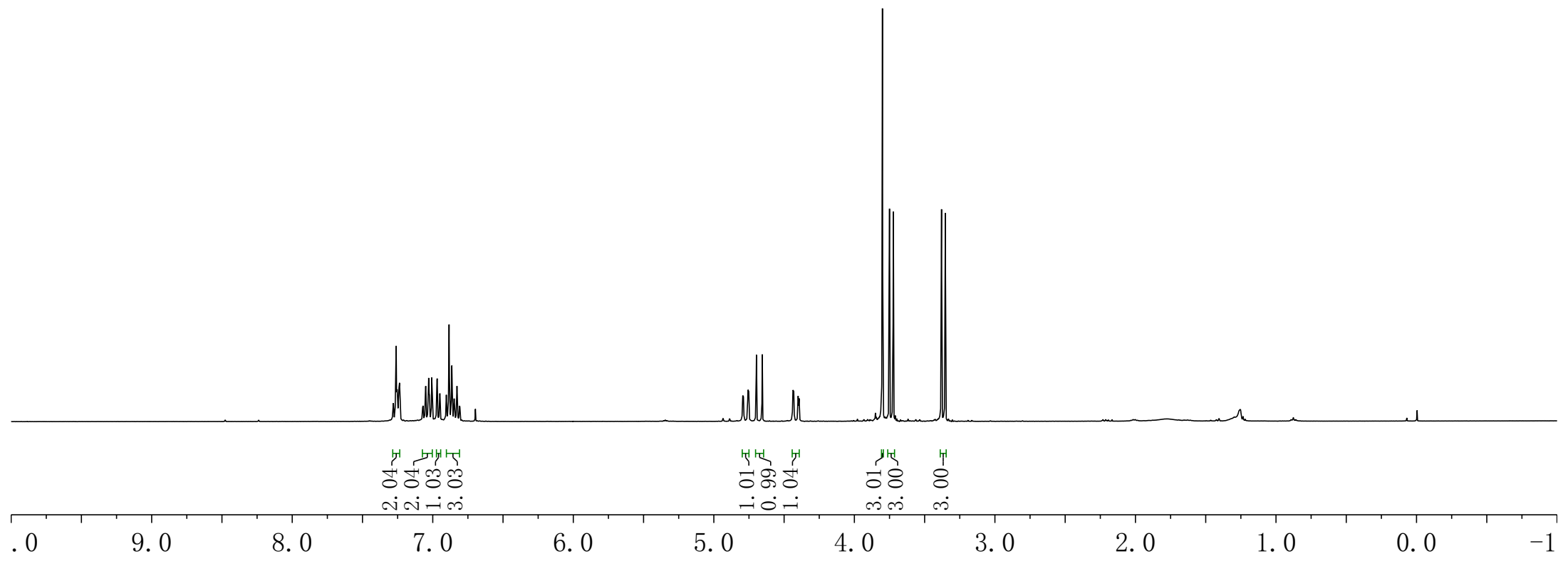
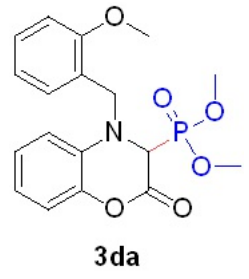
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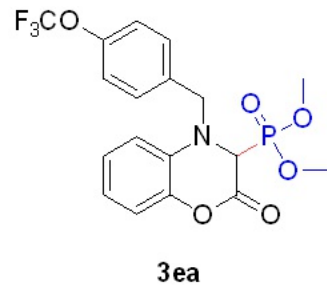
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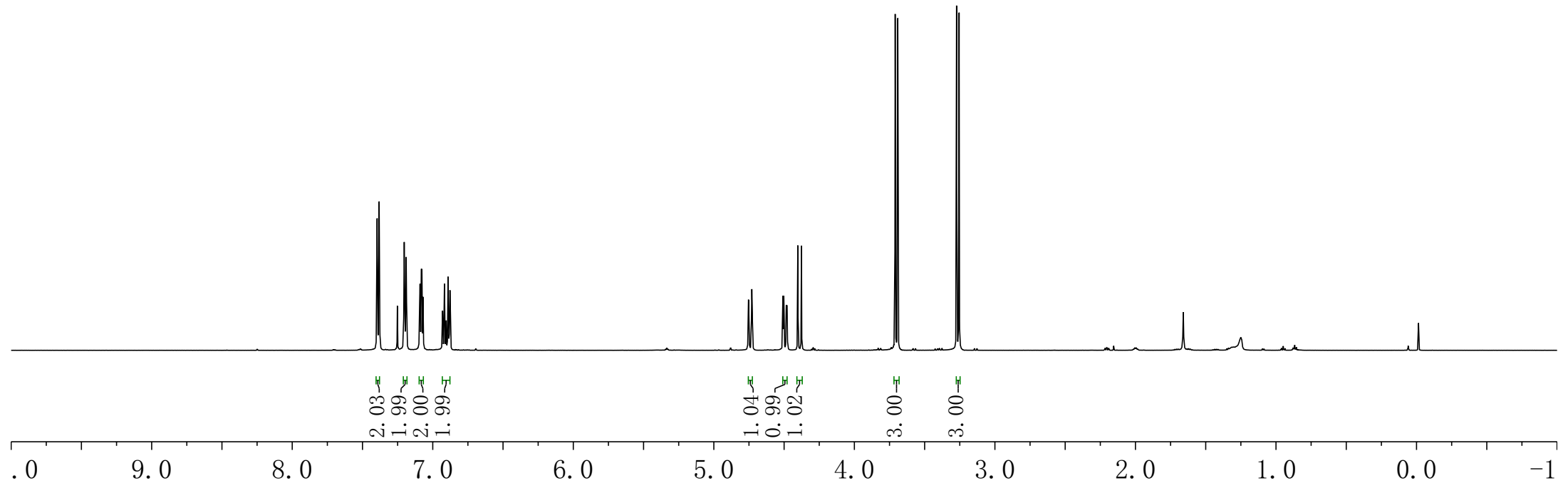
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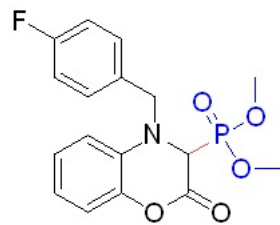
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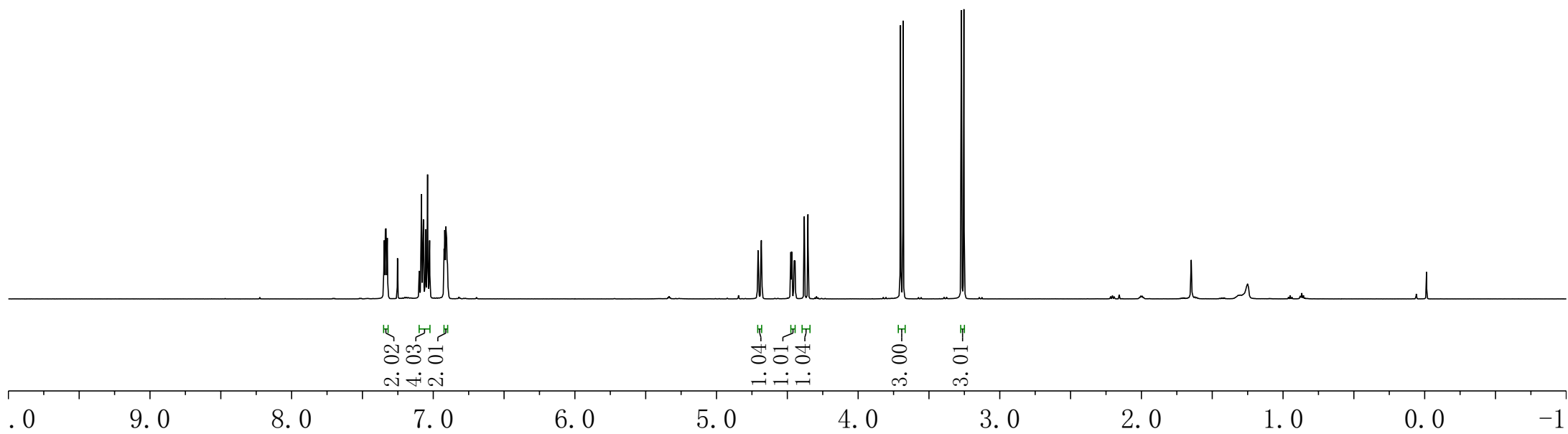


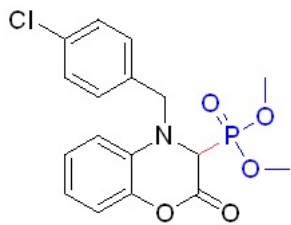
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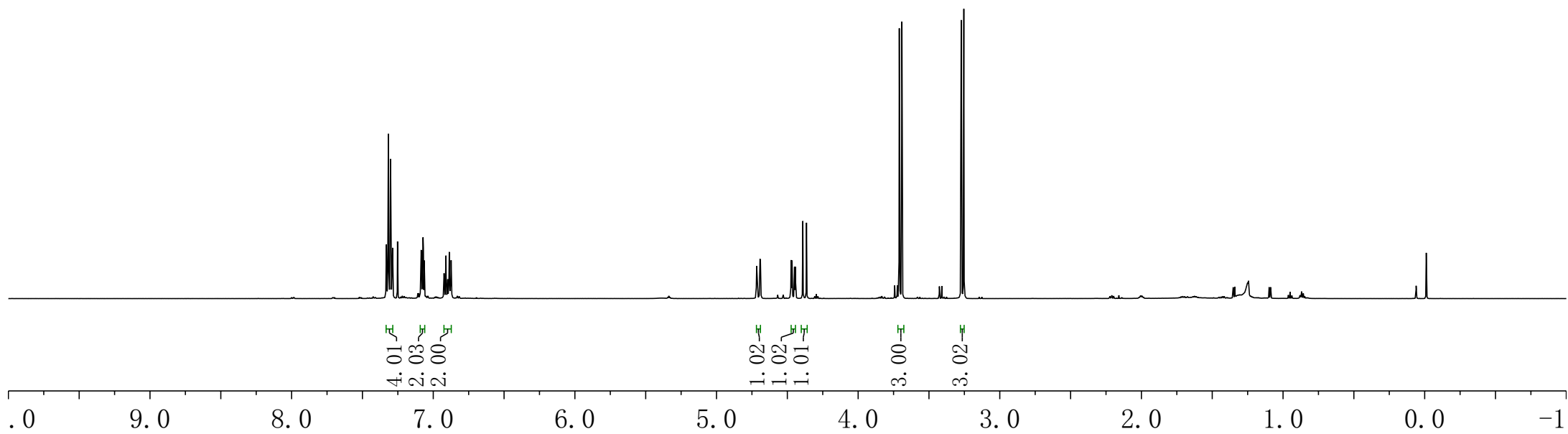
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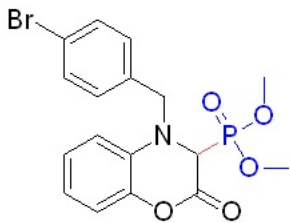




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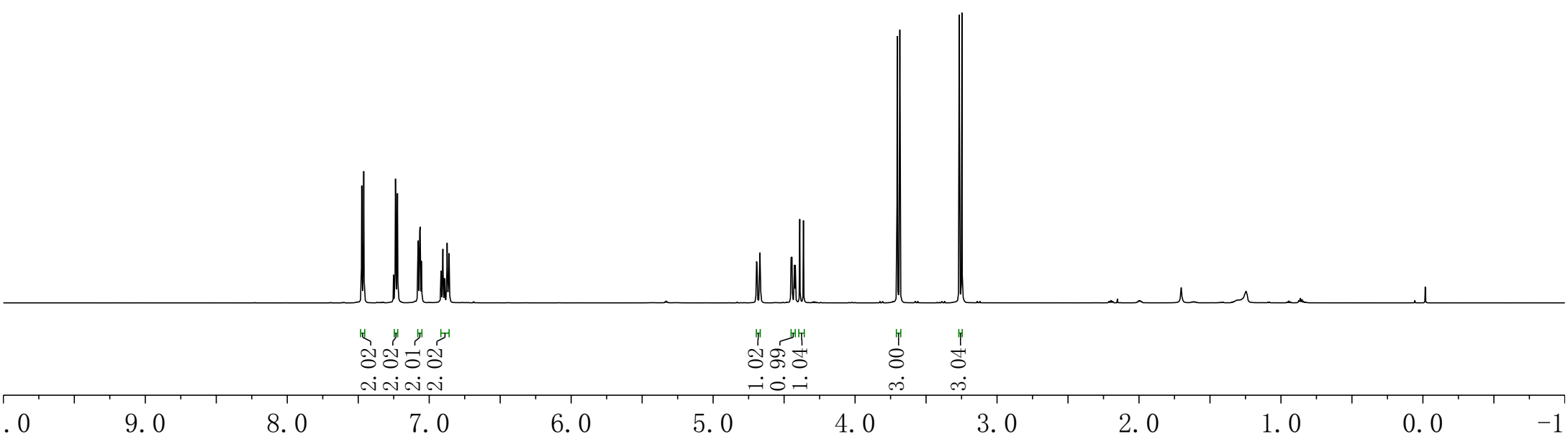


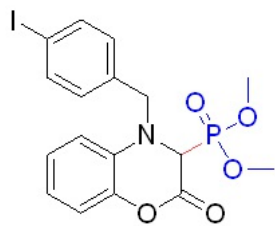


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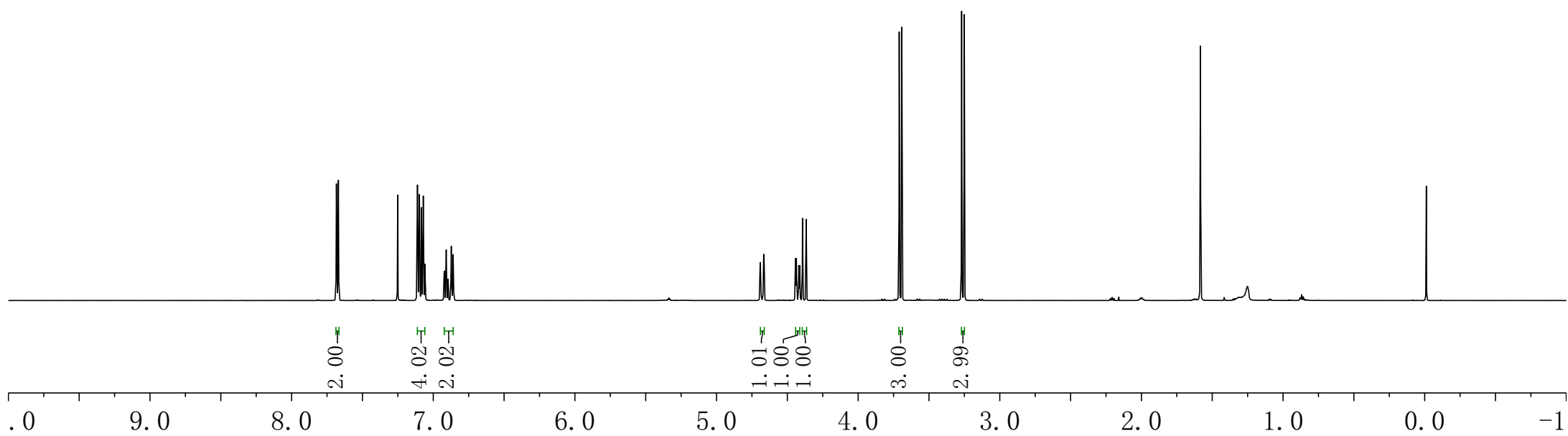


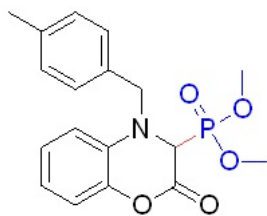


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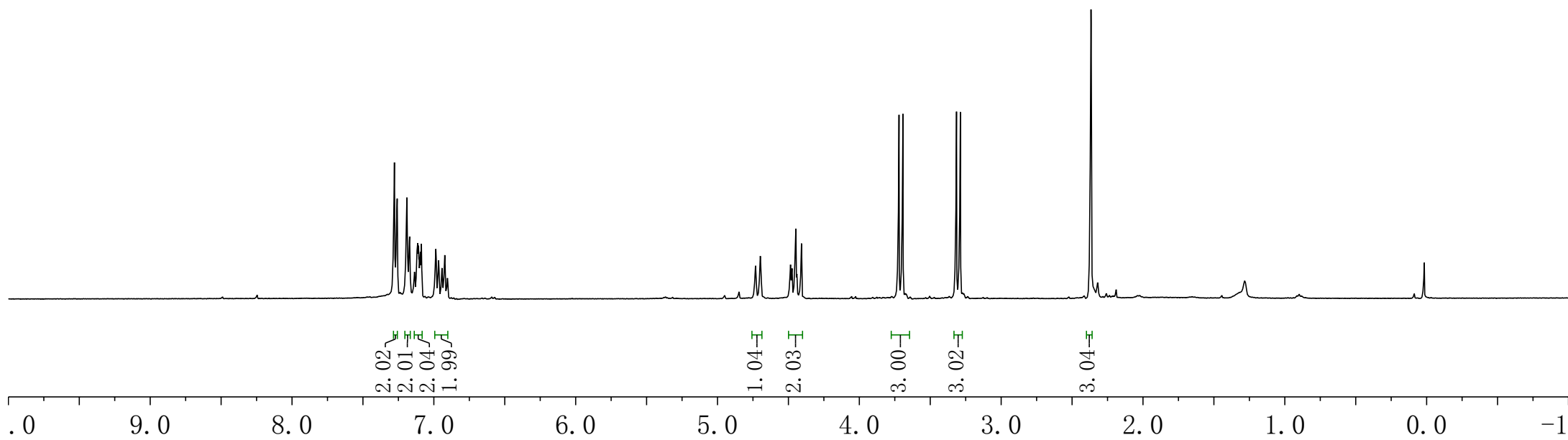
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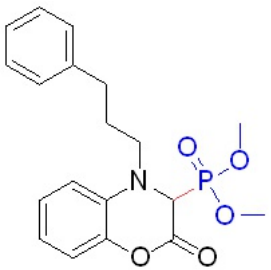
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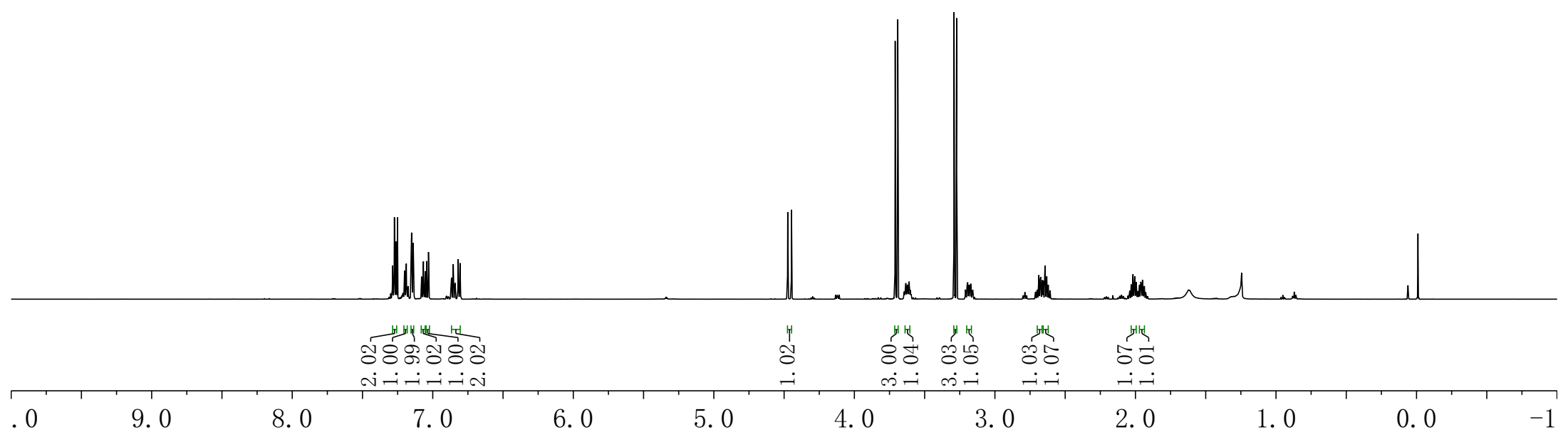


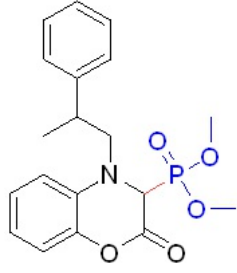
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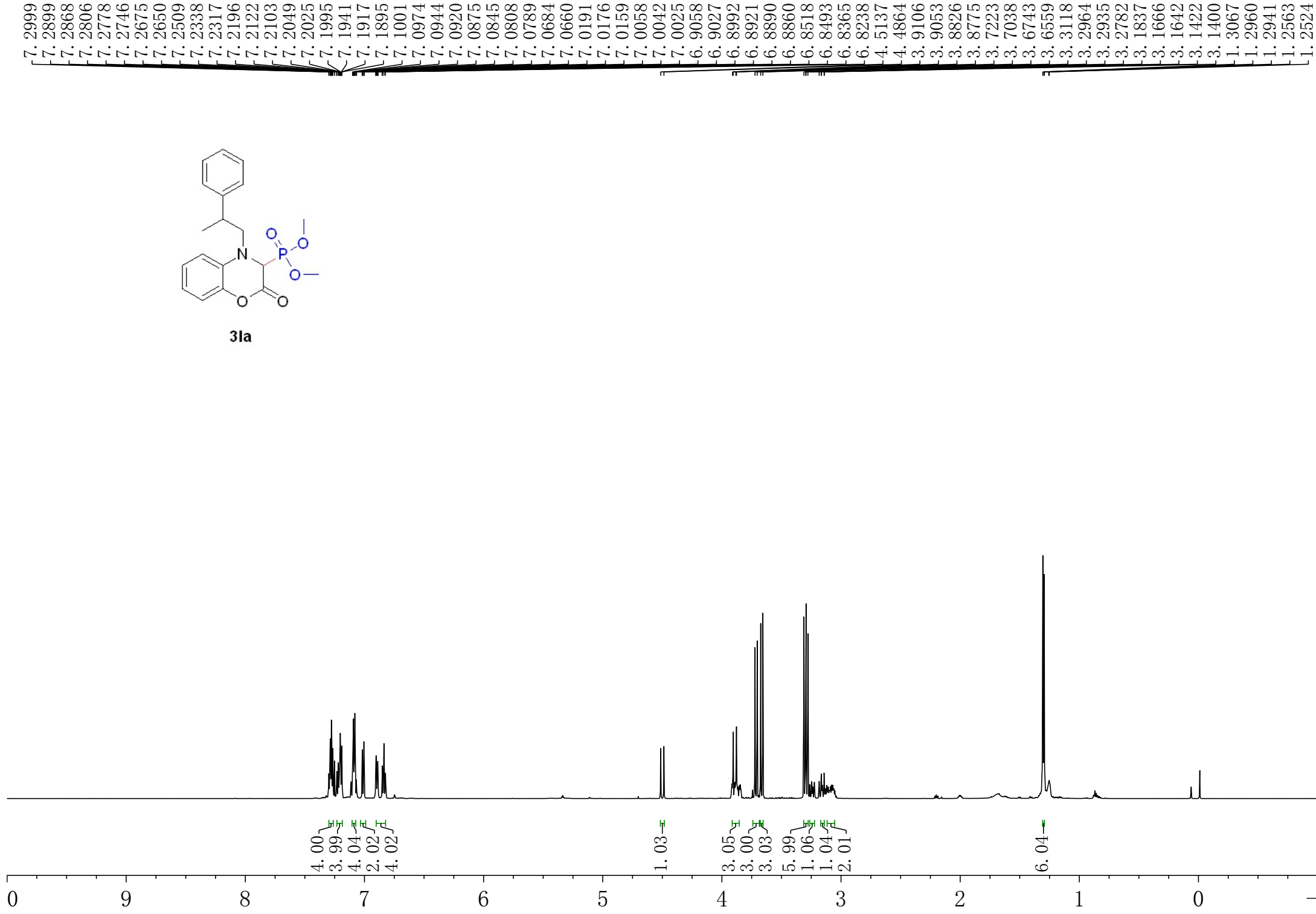


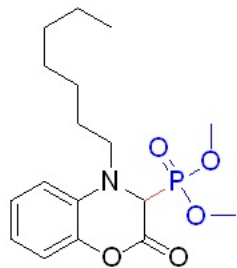
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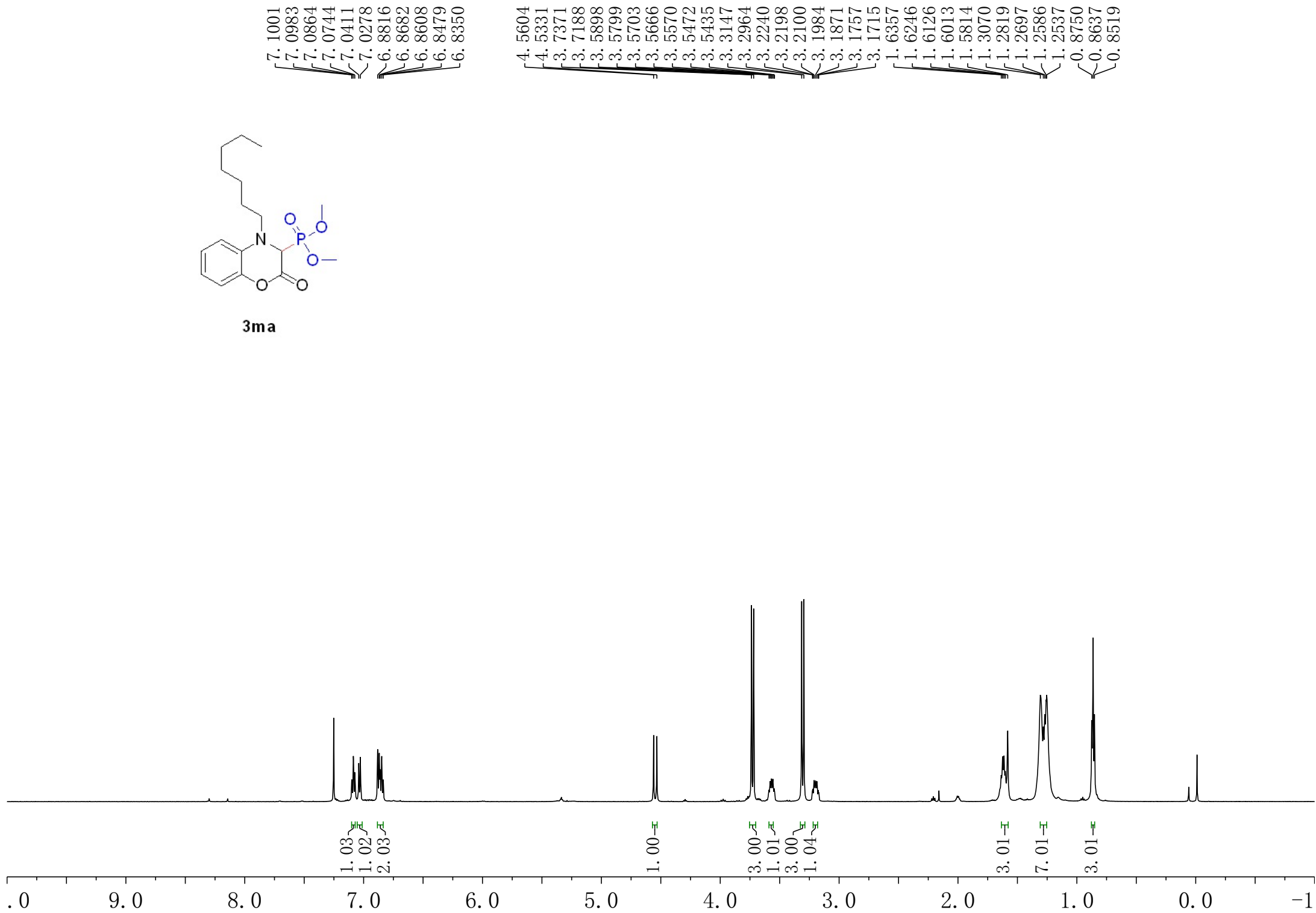


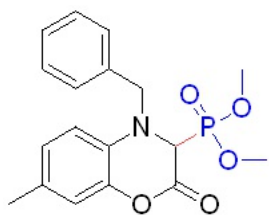
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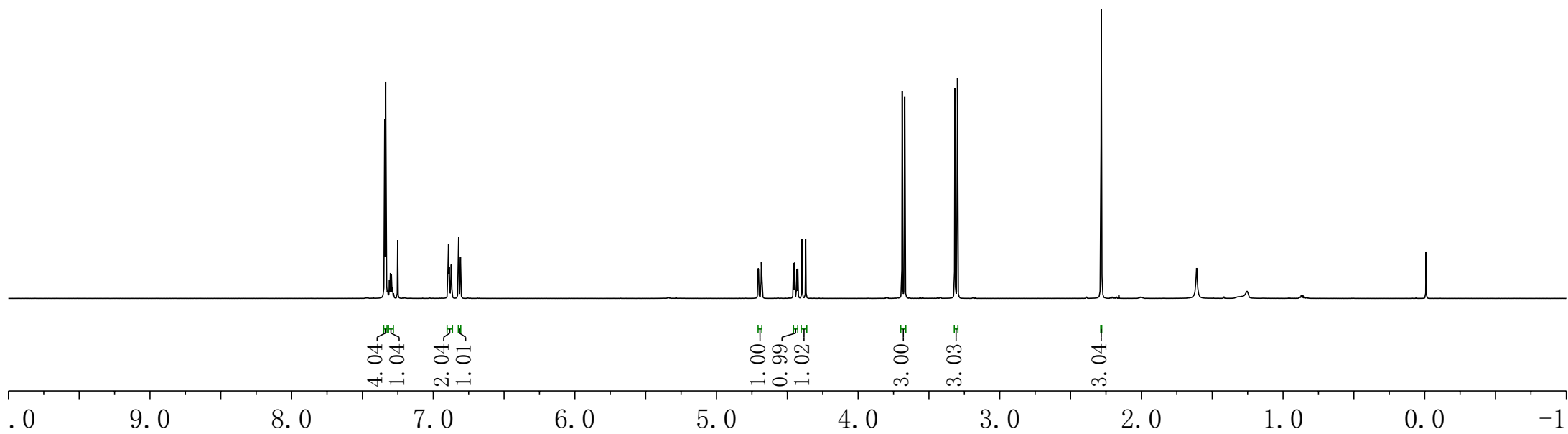


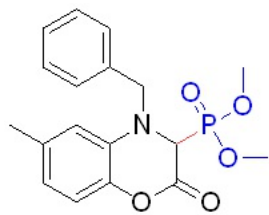
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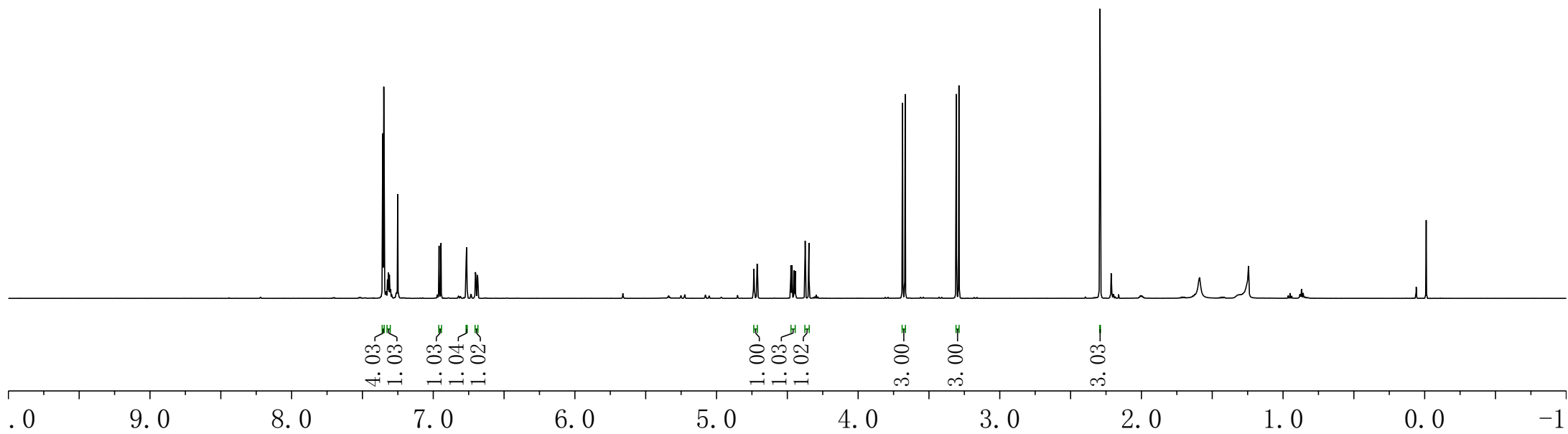


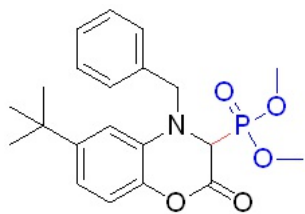
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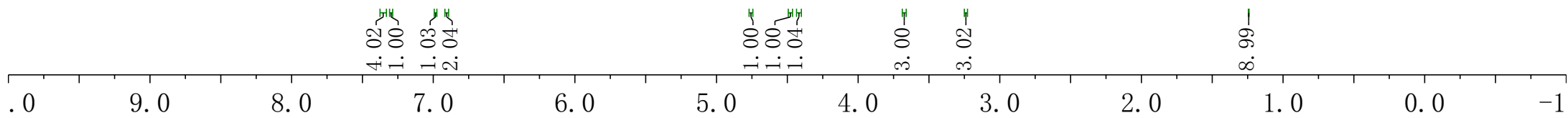
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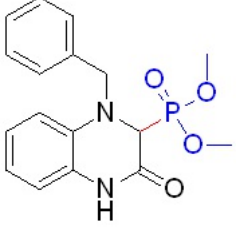
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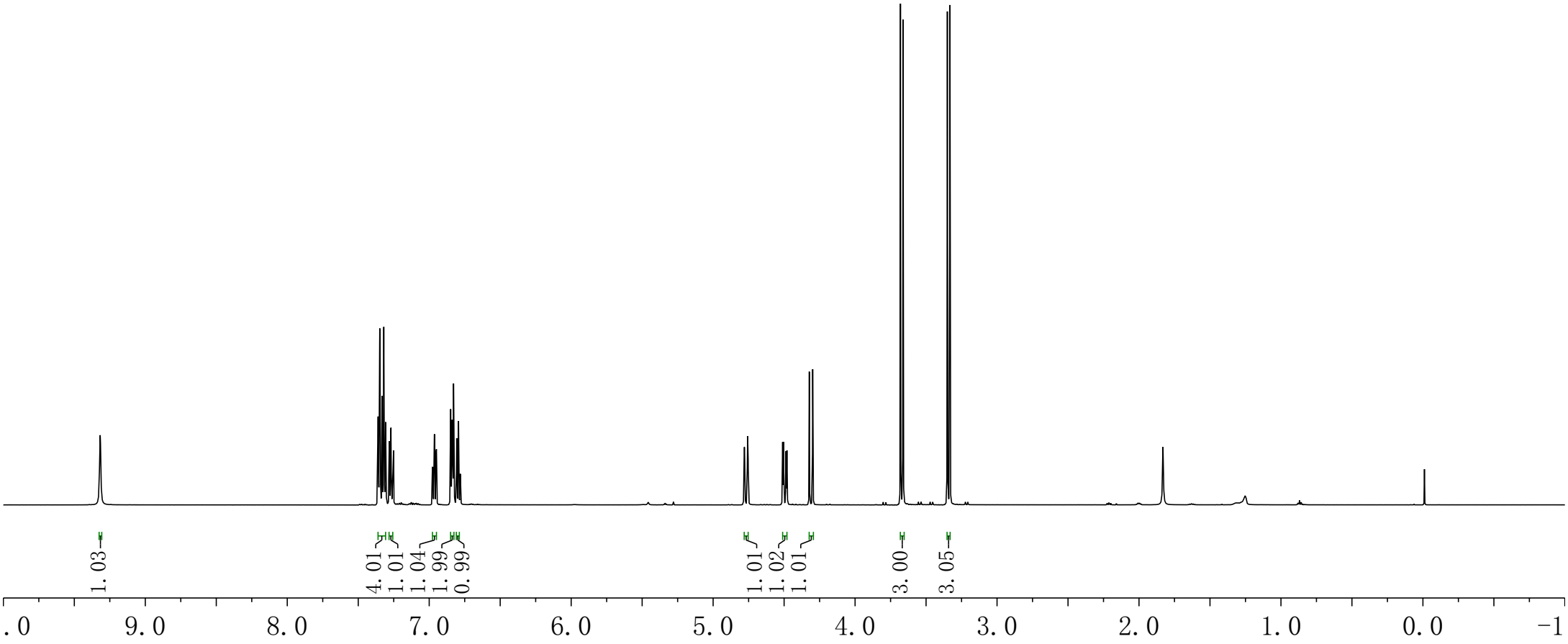
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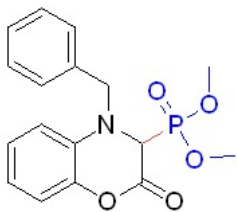
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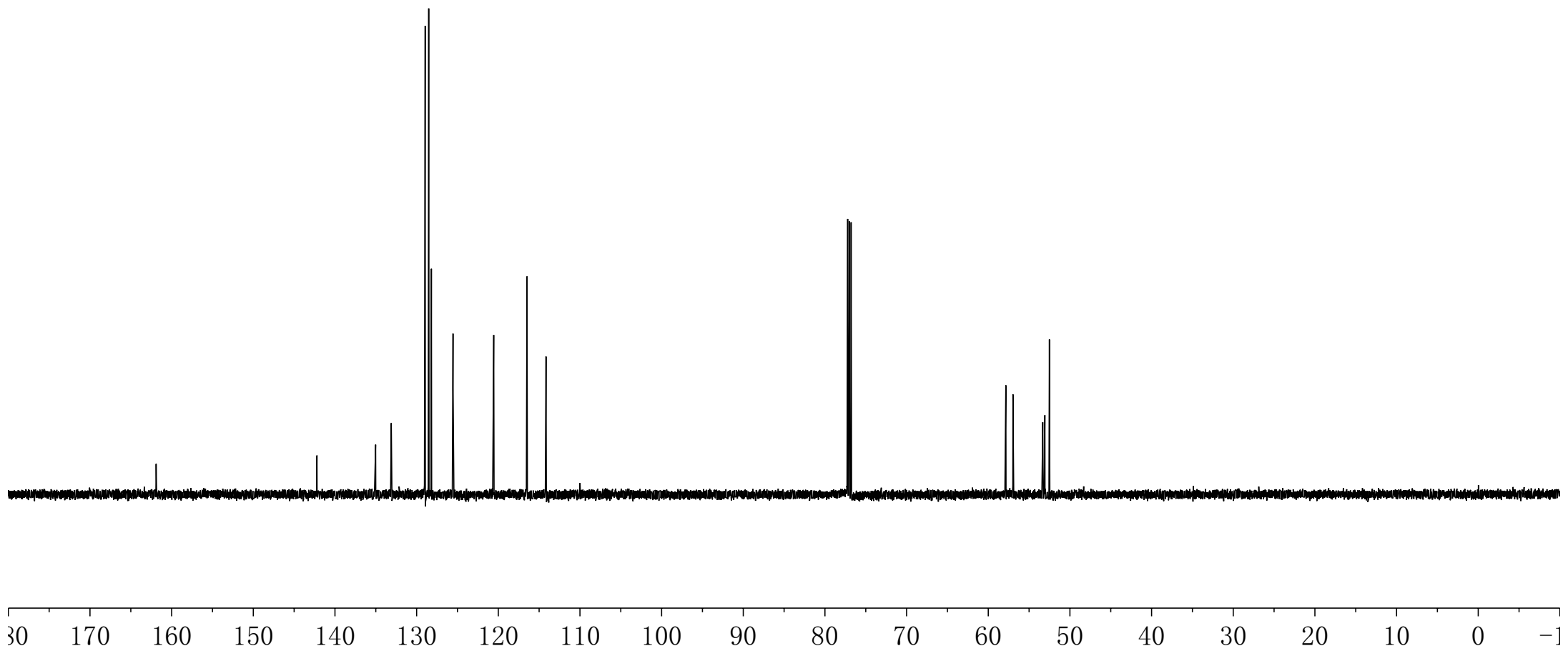
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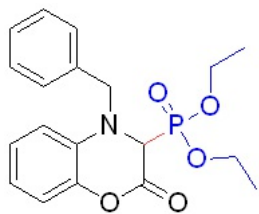
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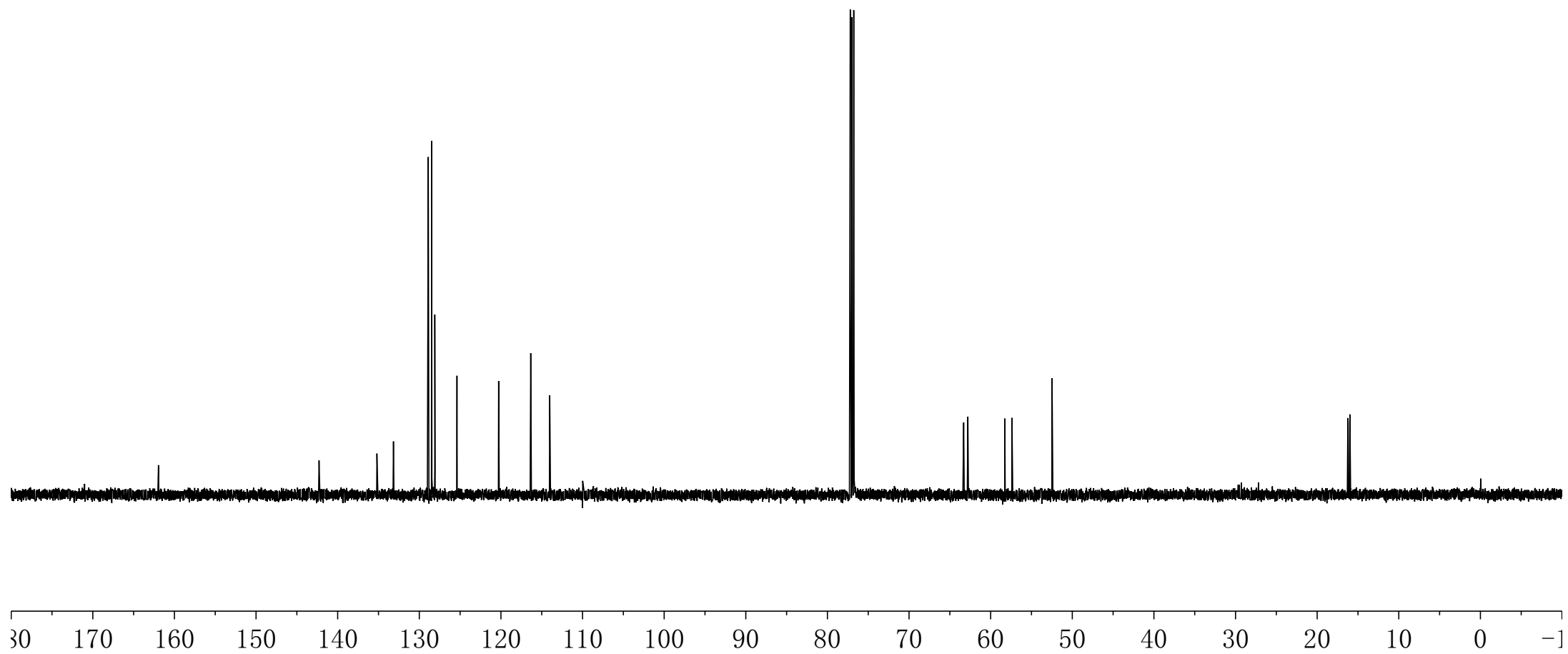
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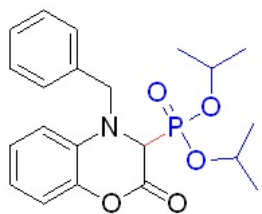
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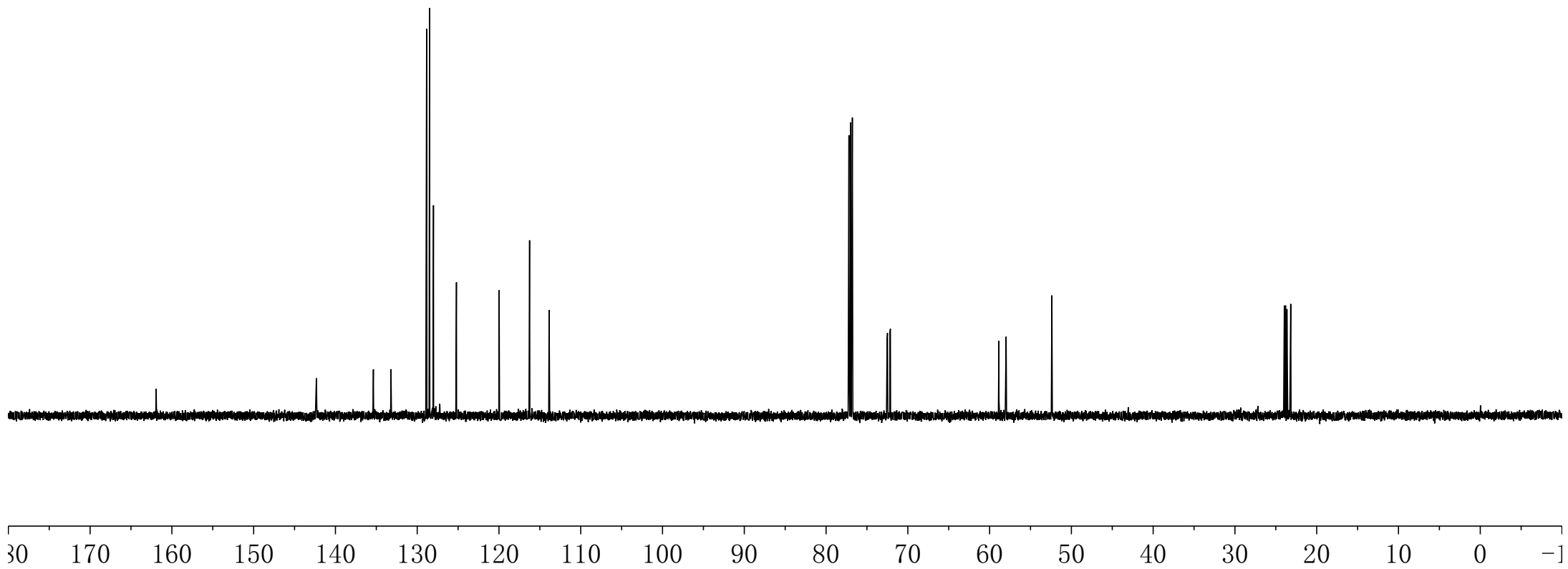
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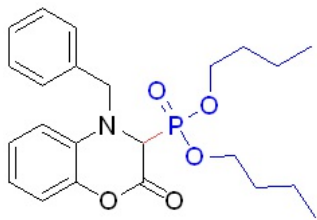
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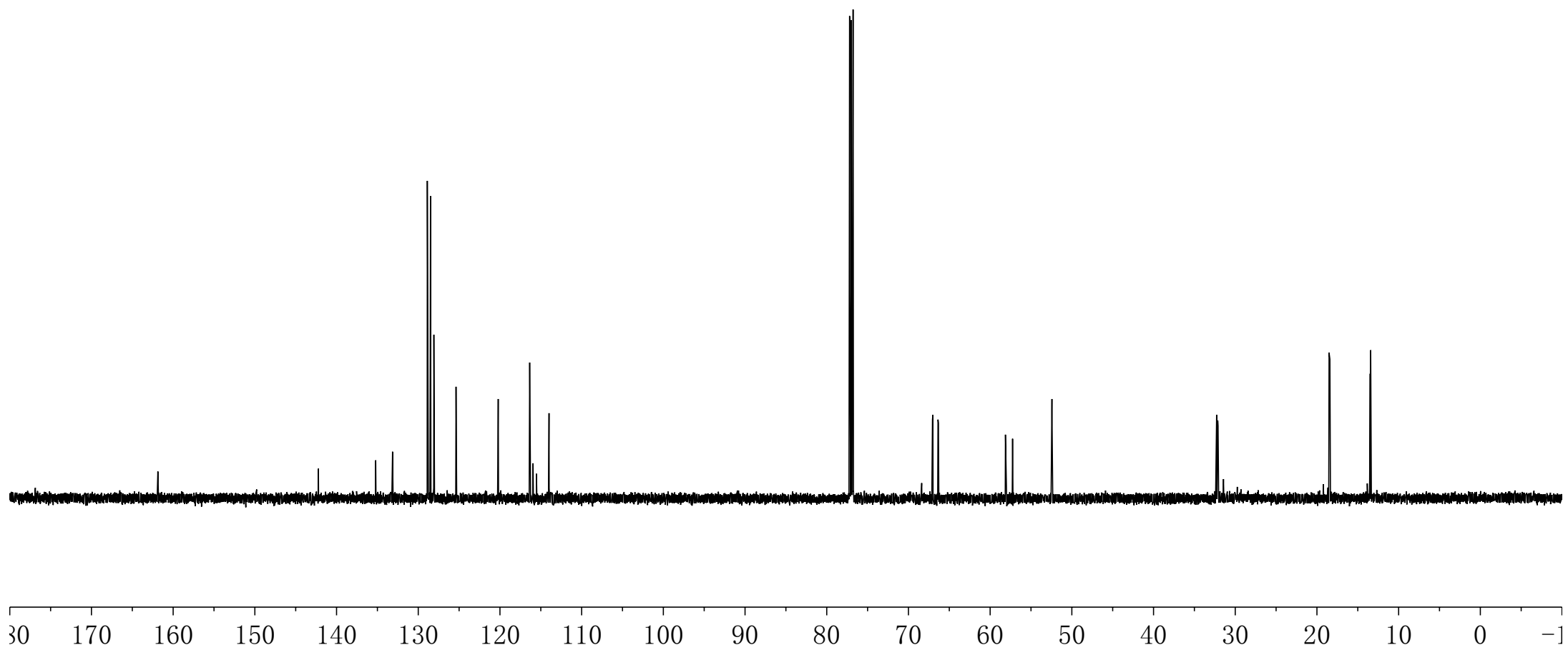
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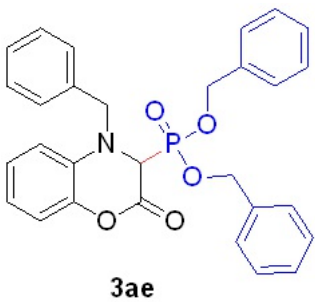
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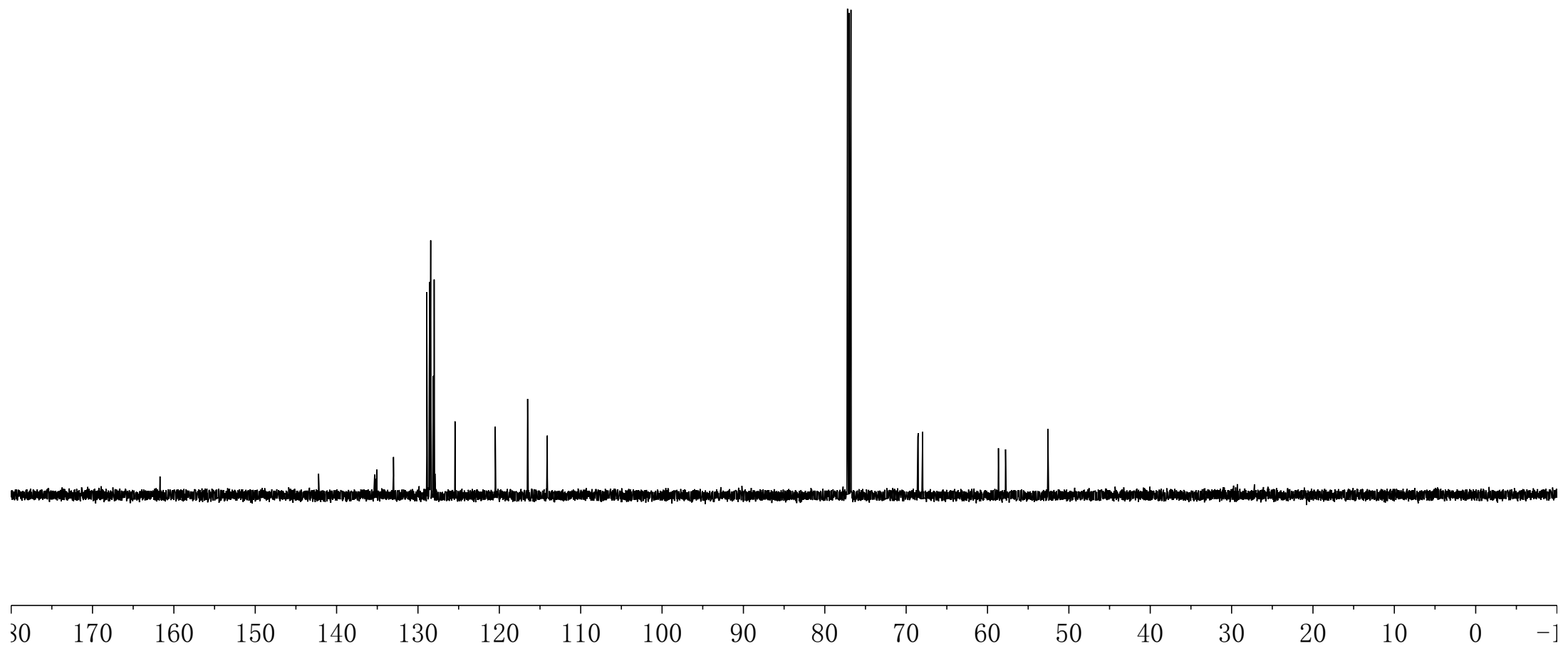
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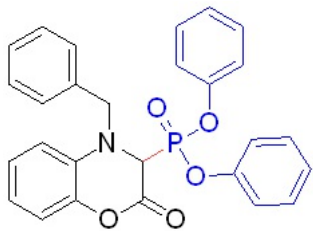
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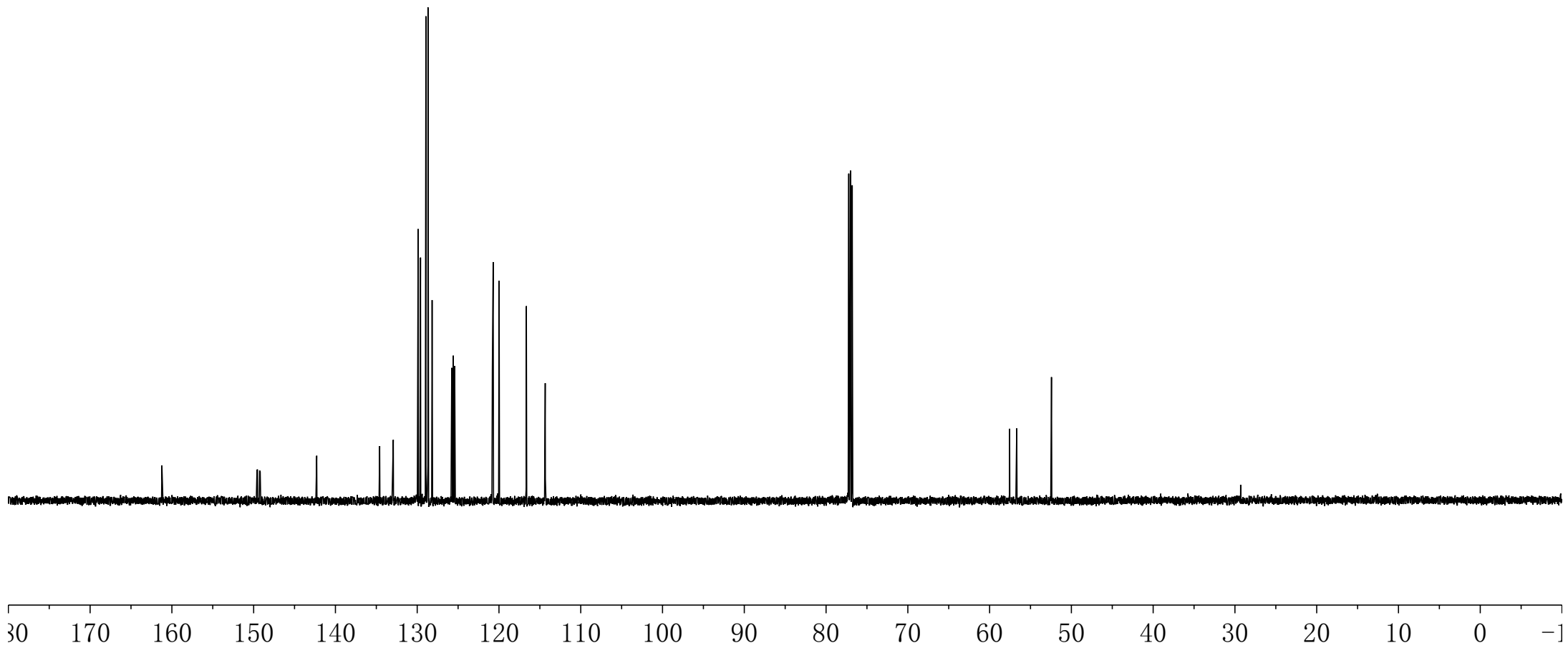


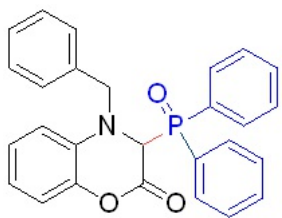
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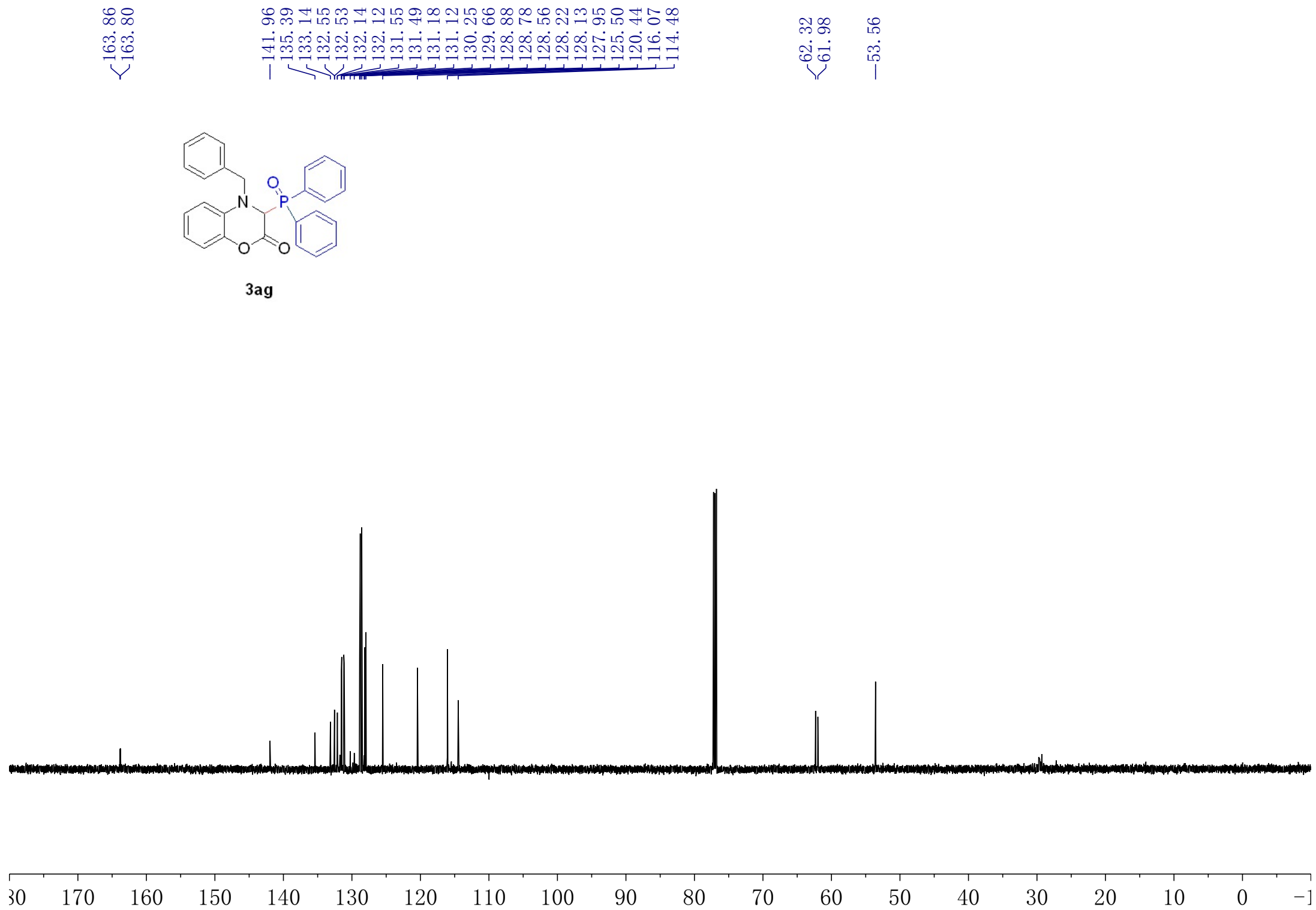


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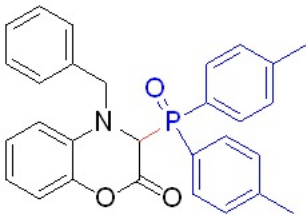
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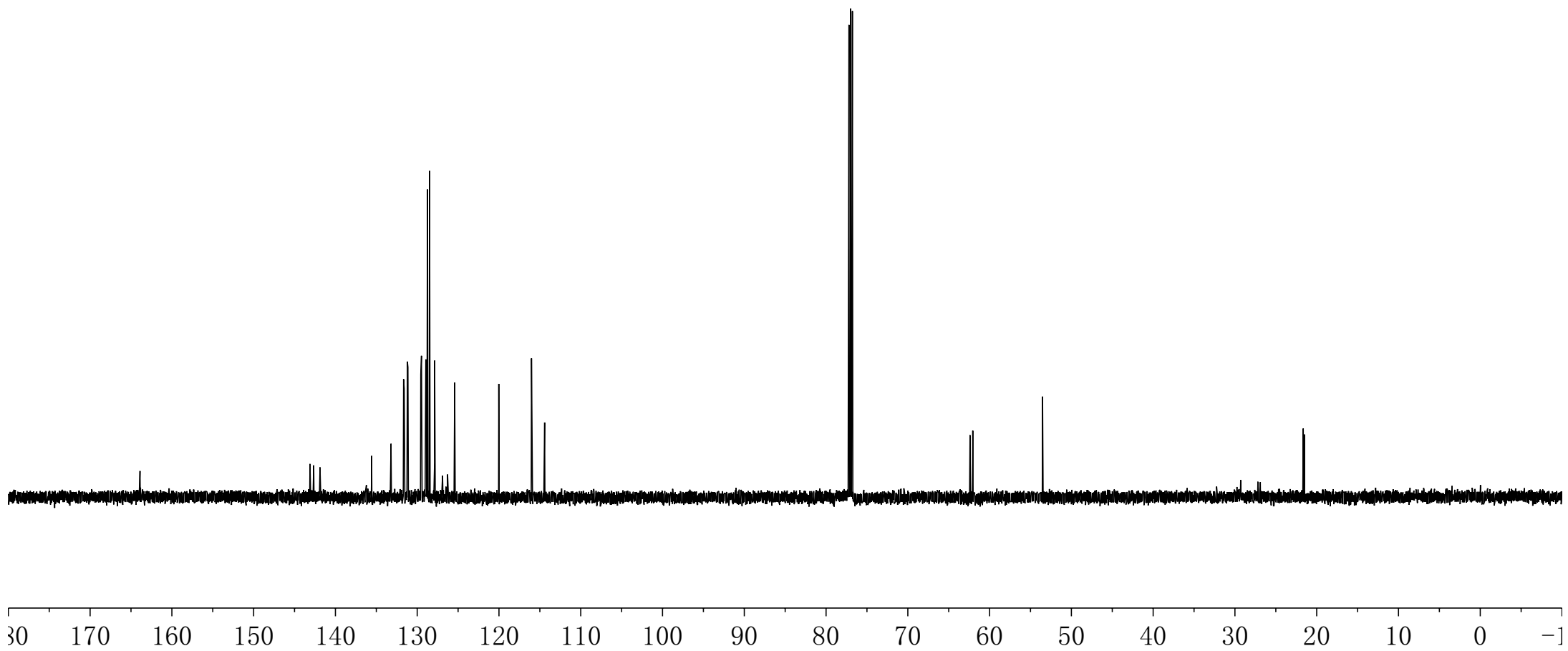
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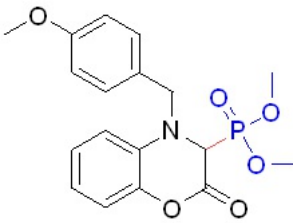


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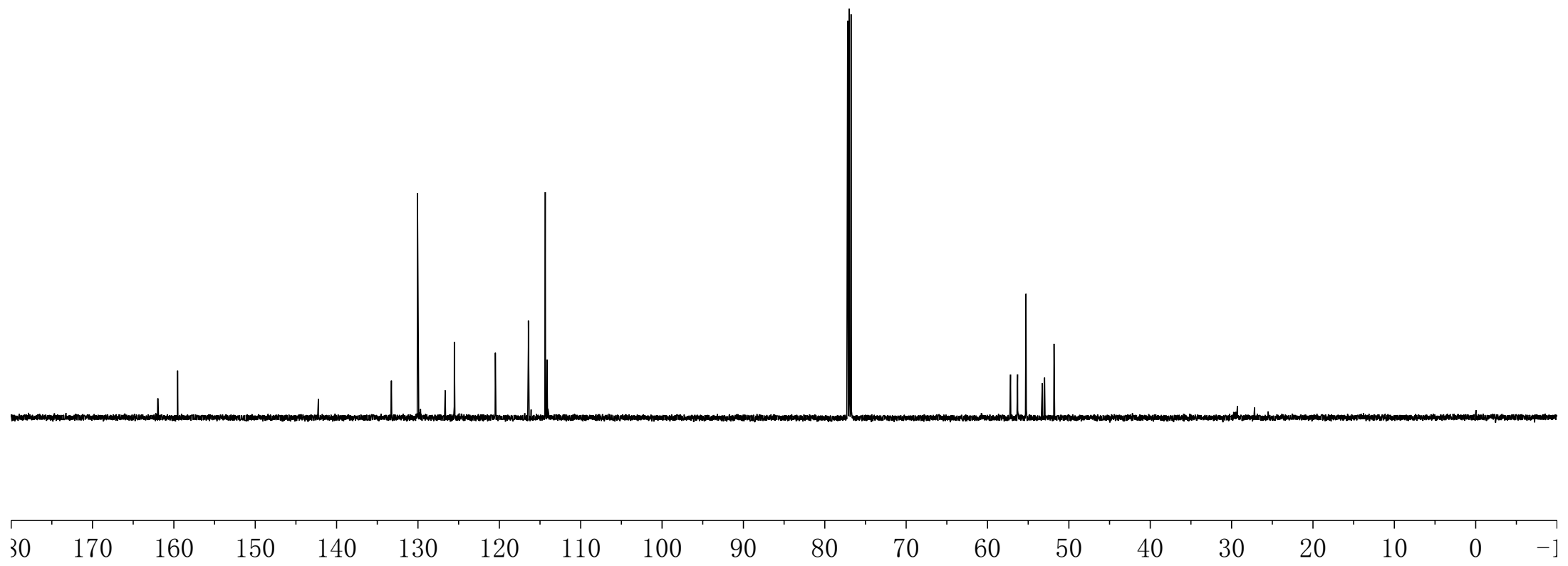
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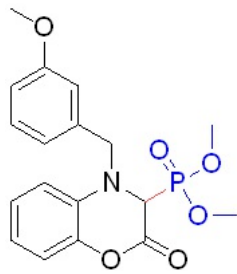
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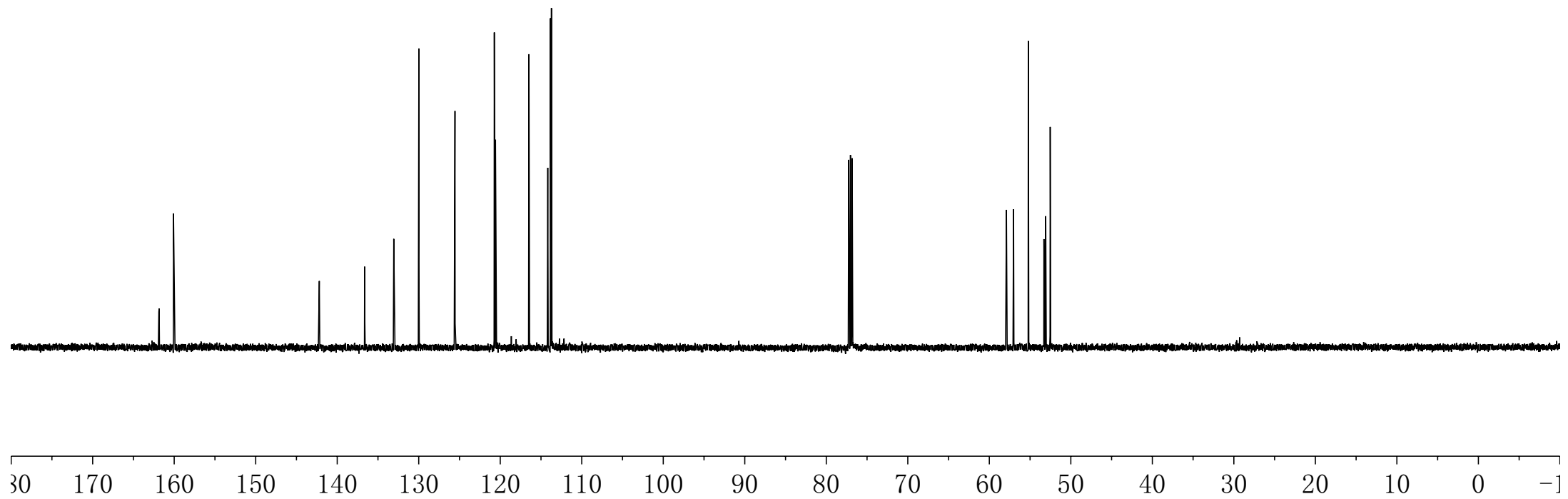
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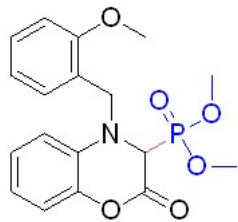


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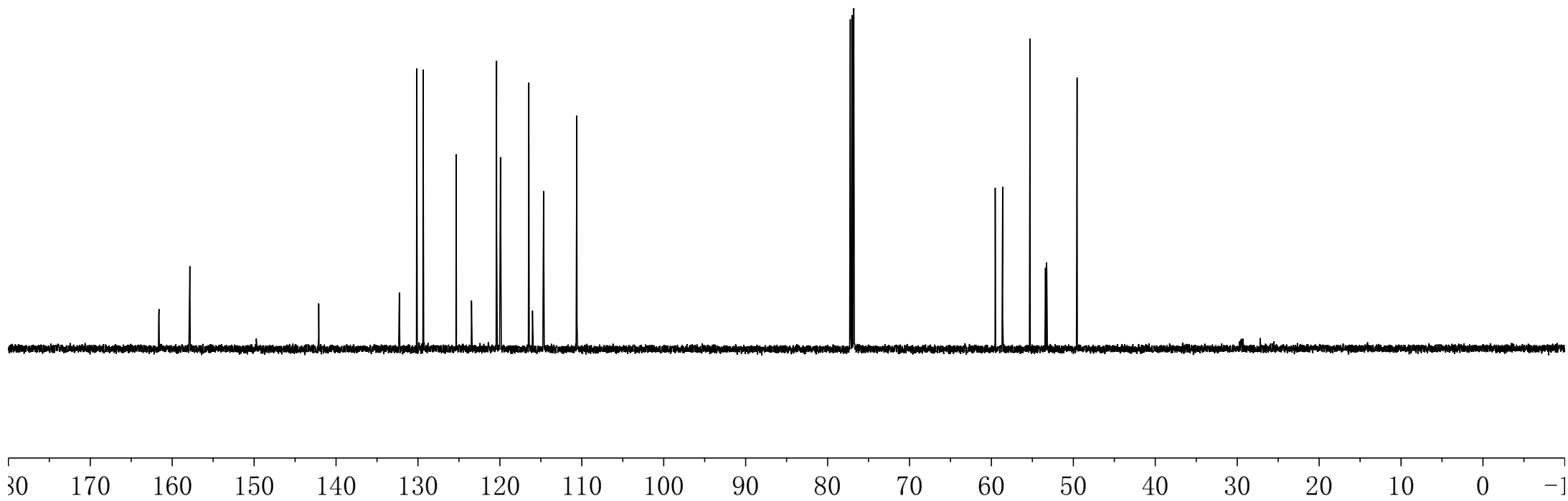
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3da

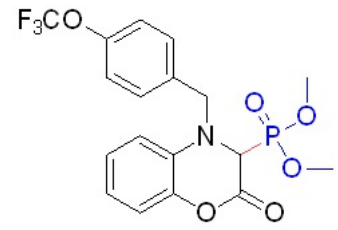


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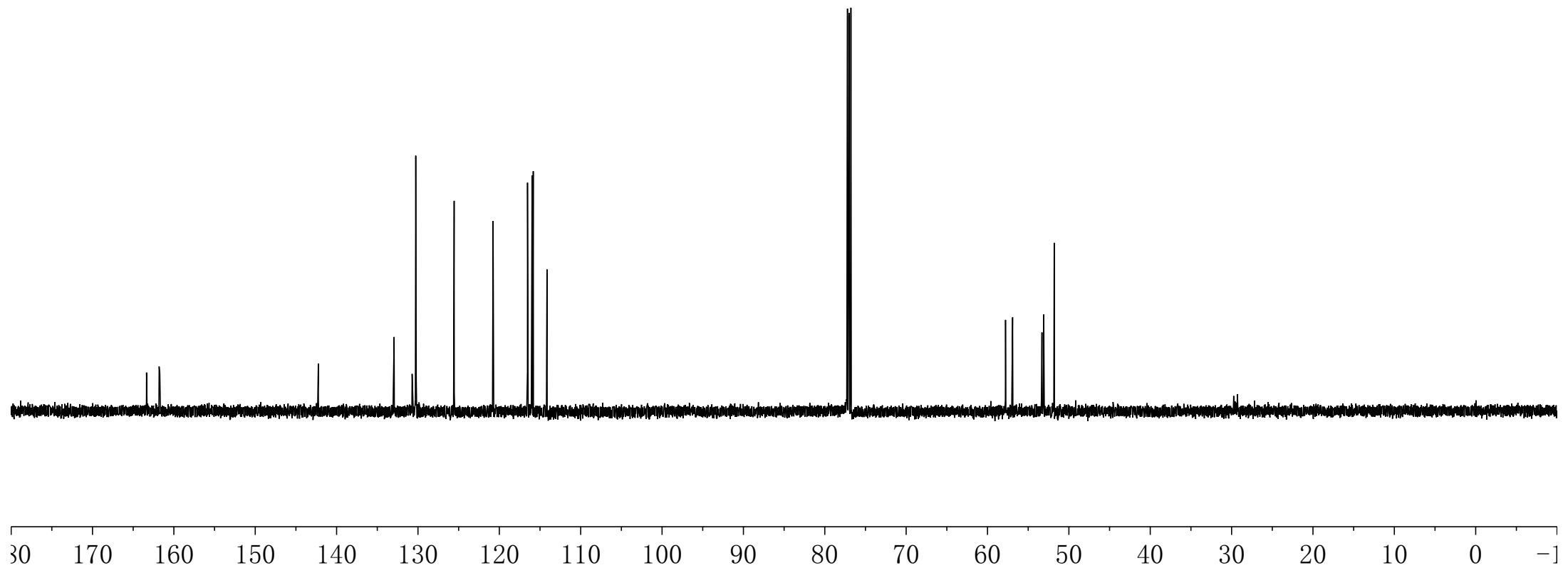
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57.79
56.91
53.36
53.31
53.09
53.04
51.81



3ea



161.74
161.71

148.98

142.22

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133.83

132.74

129.77

125.59

121.36

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58.25

57.38

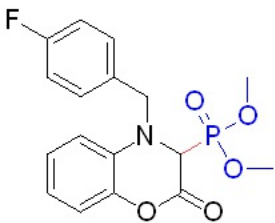
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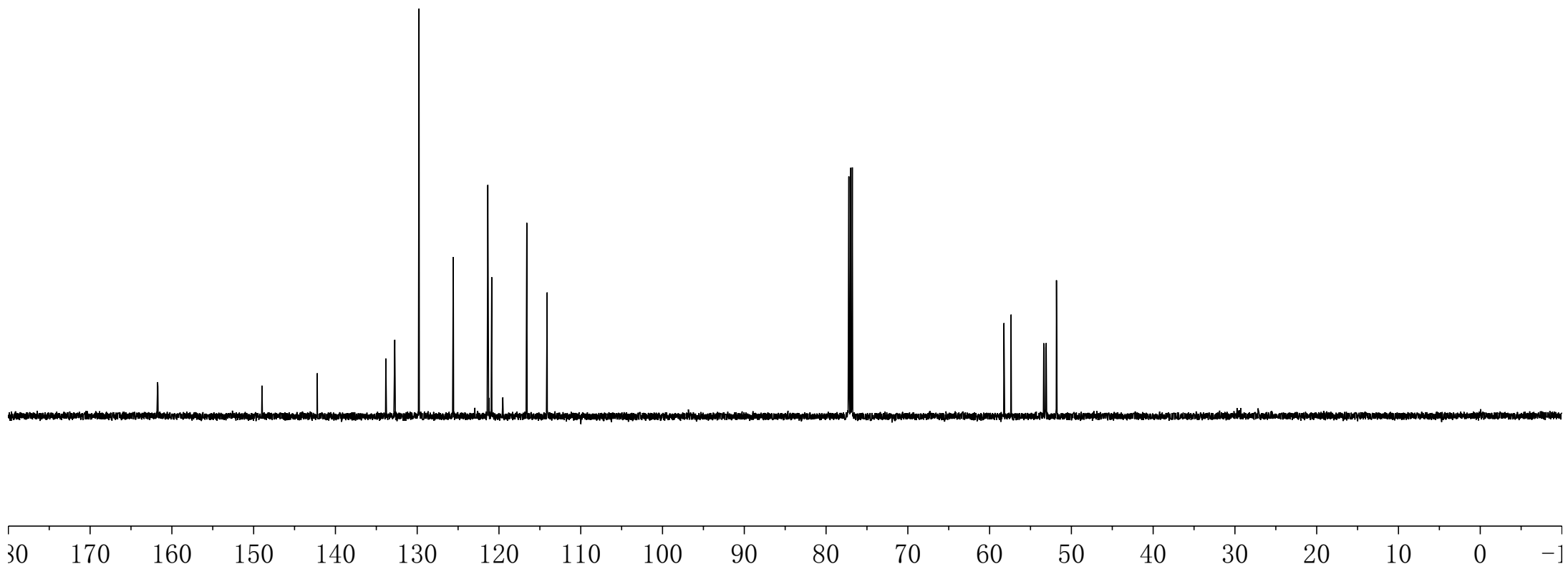
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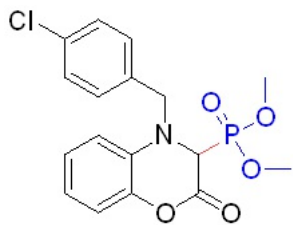


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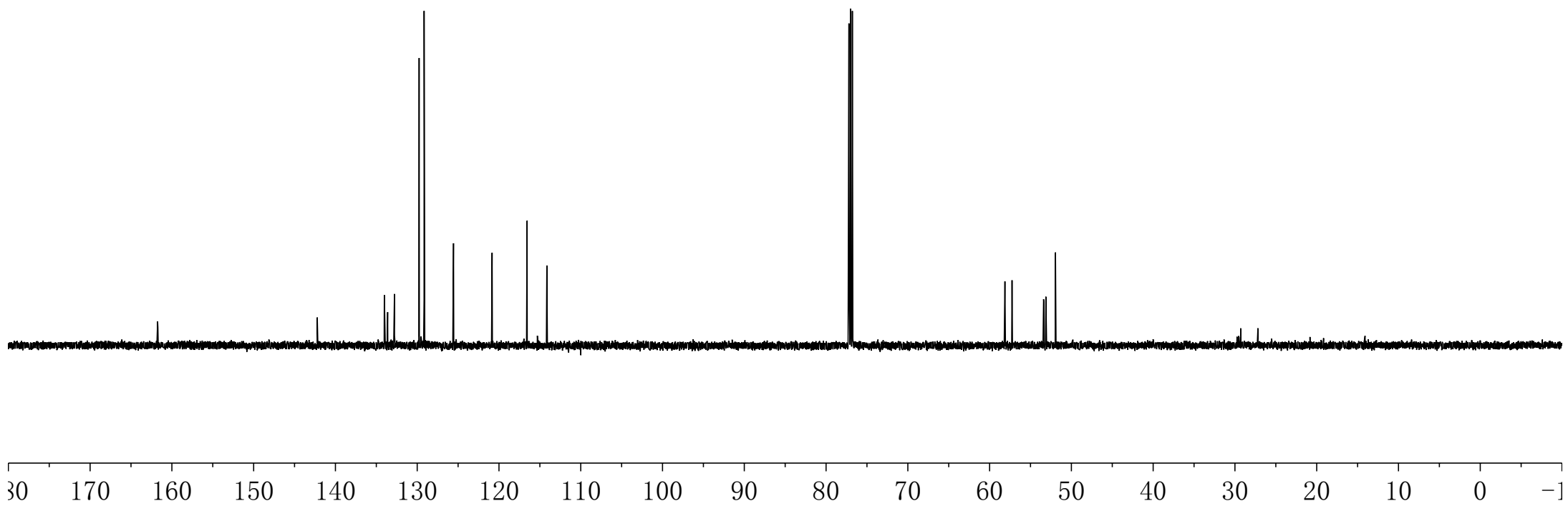
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53.08
51.95



3ga

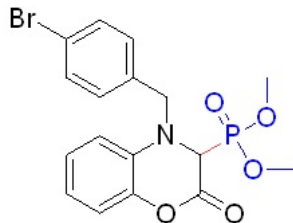


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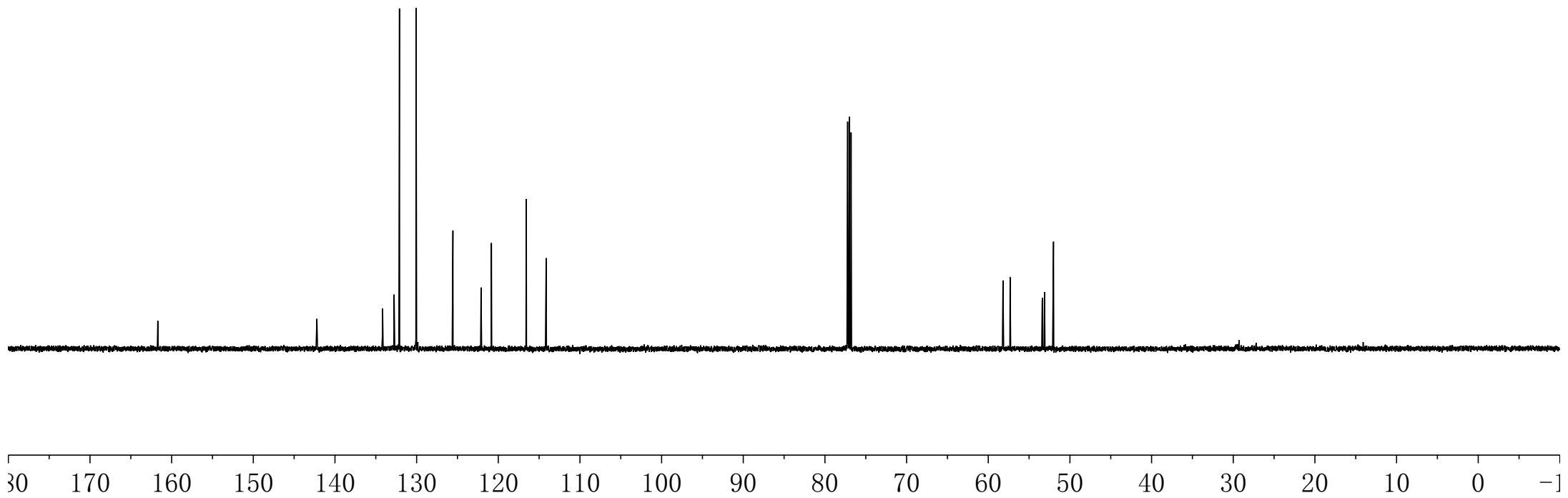
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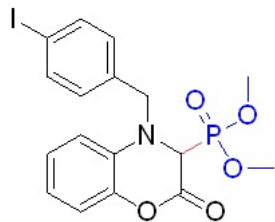
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3ha





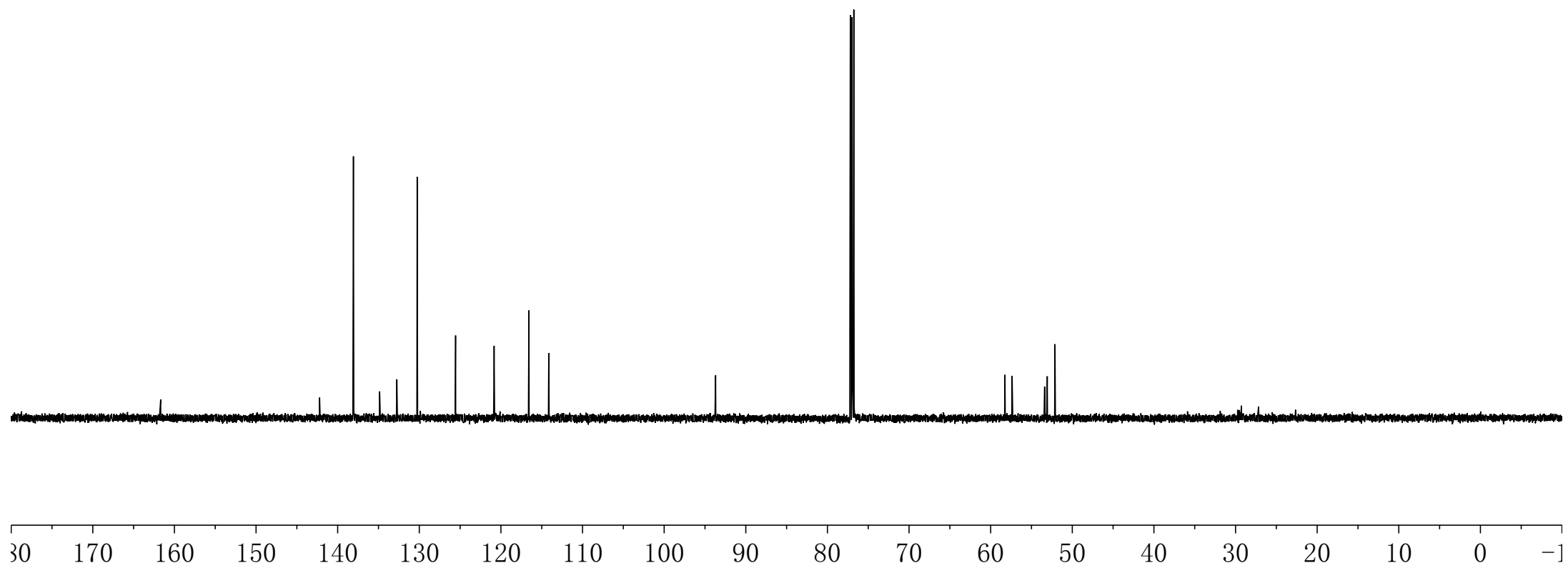
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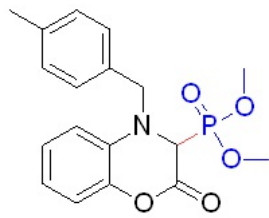


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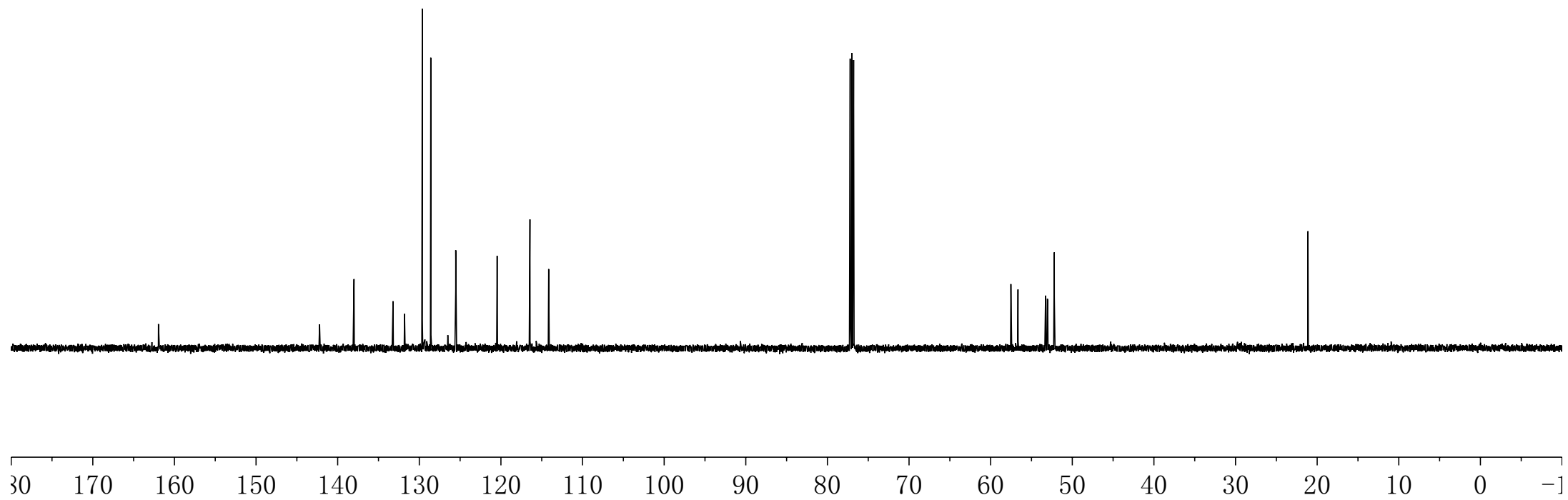
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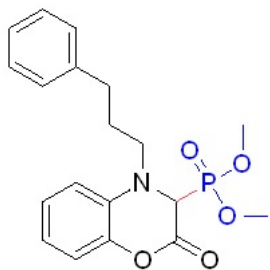
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21.13



3ja





3ka

—161.59

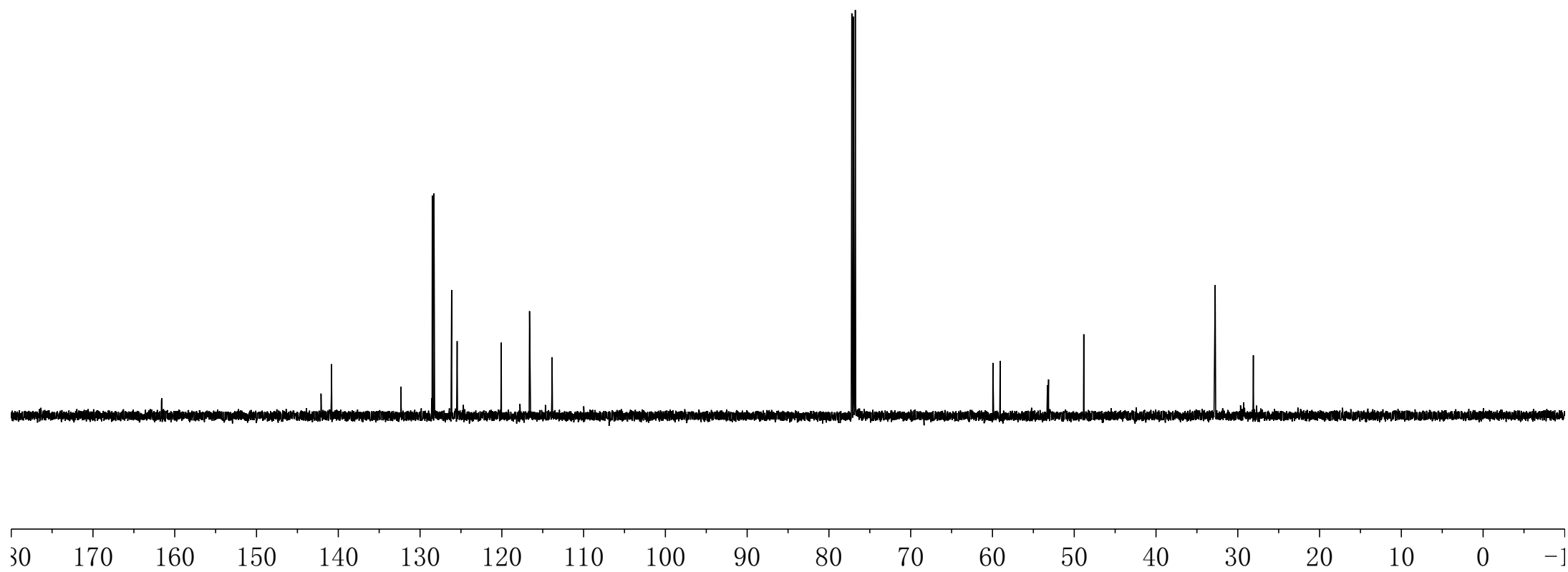
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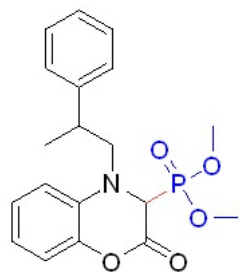
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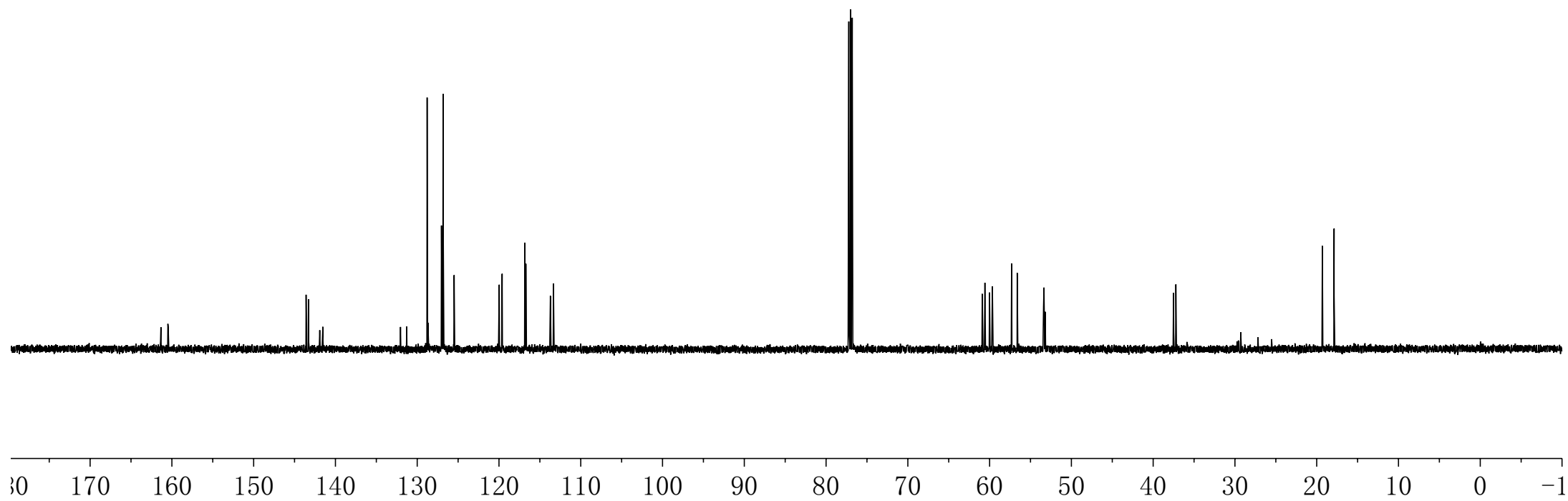
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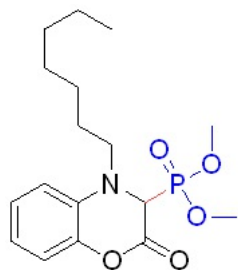
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37.49
37.22
37.20

19.31
17.87



3la





3ma

—161.64

—142.05

—132.58

—125.46

~119.90

~116.57

~113.84

~59.70

~58.82

~53.33

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~53.19

~53.14

~49.68

~31.69

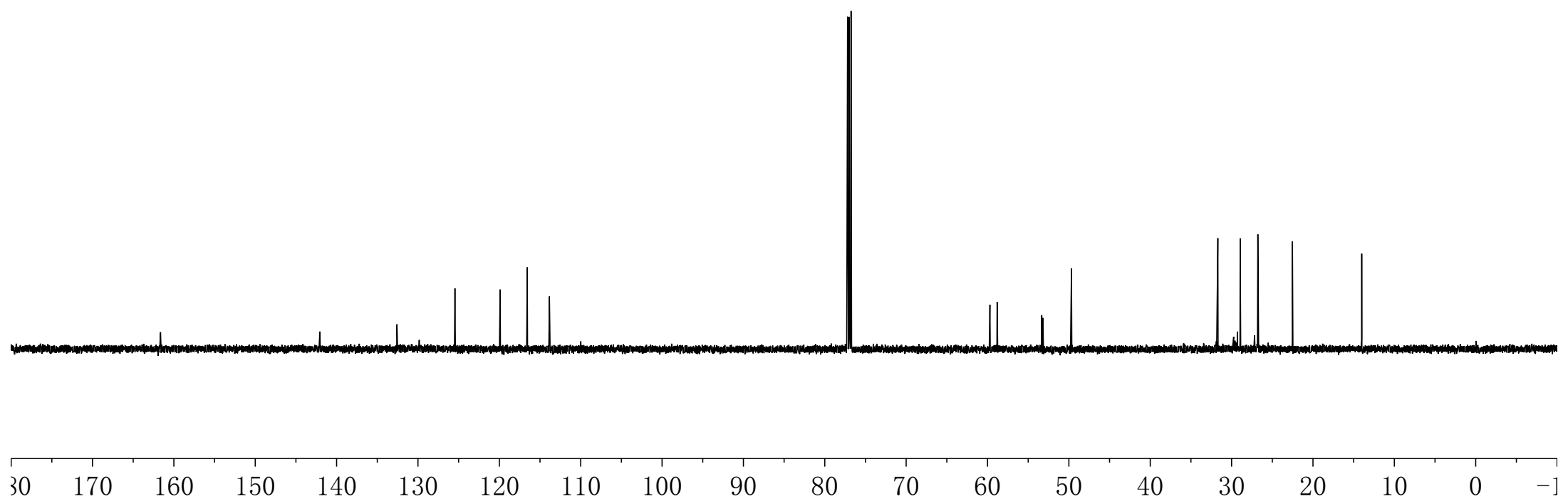
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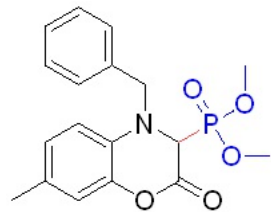
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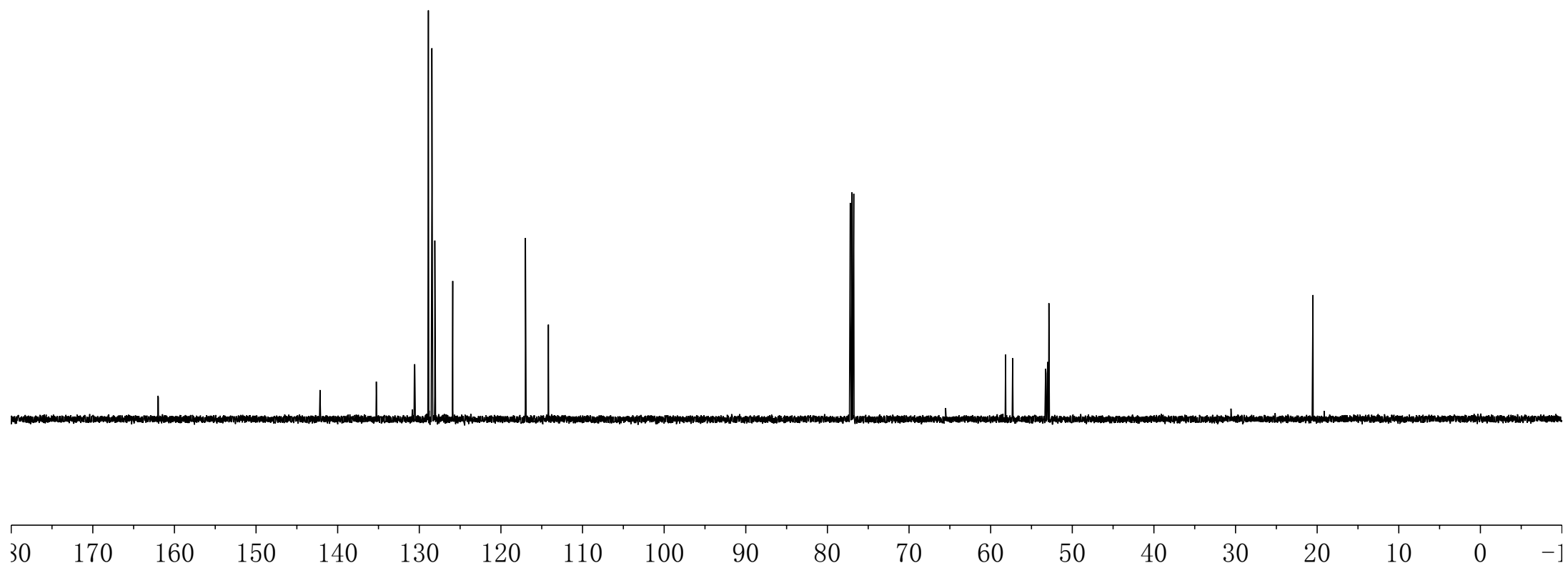
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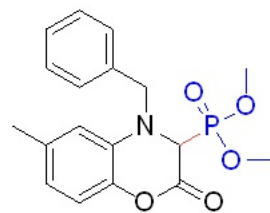
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30a

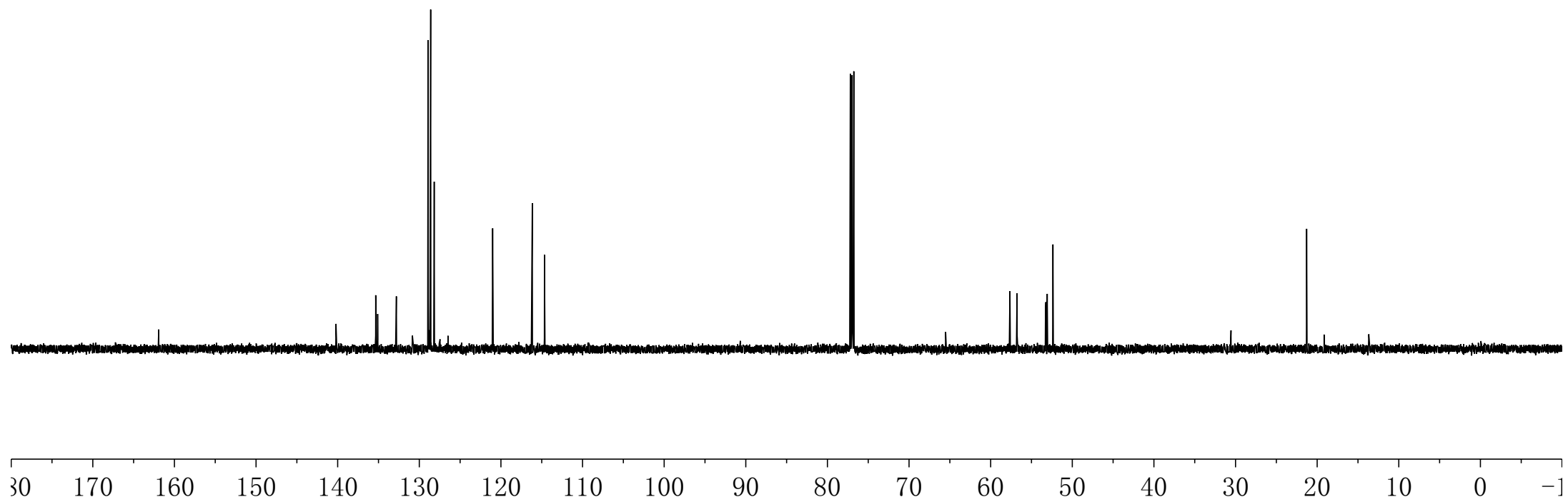
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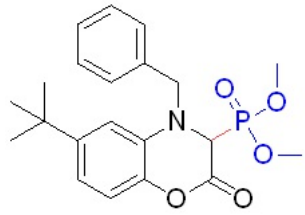


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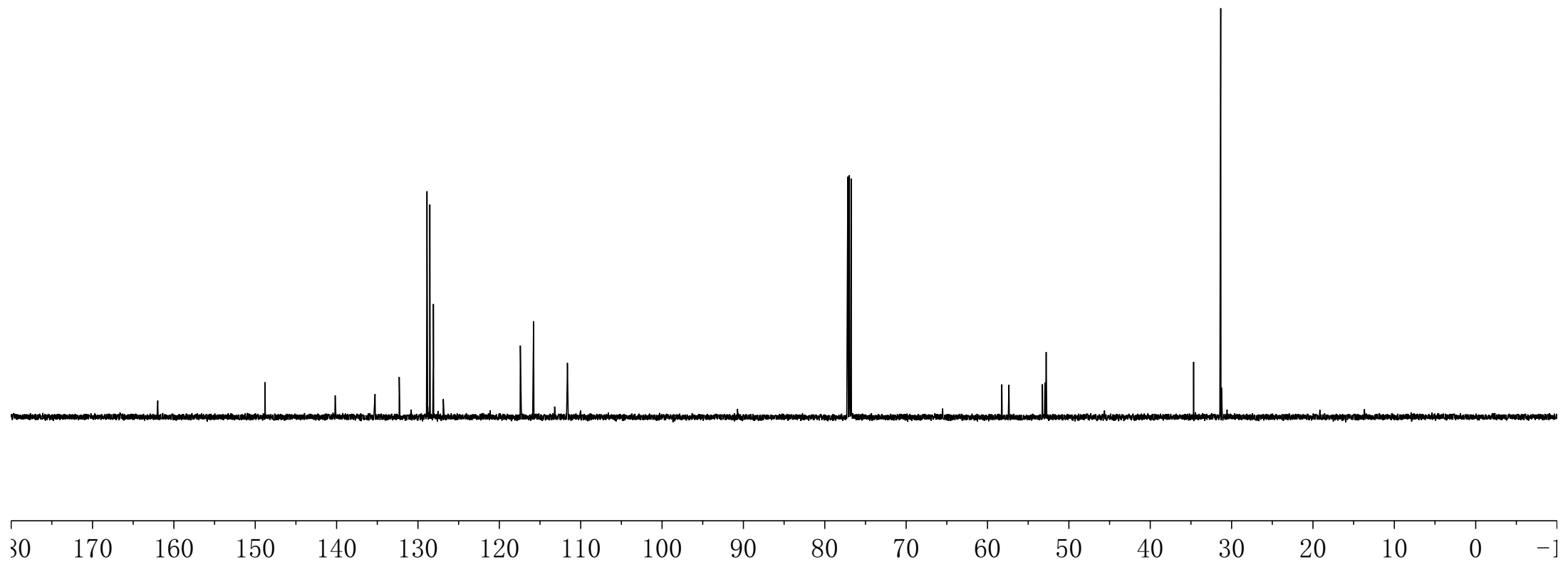
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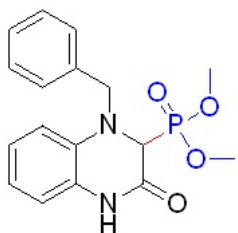
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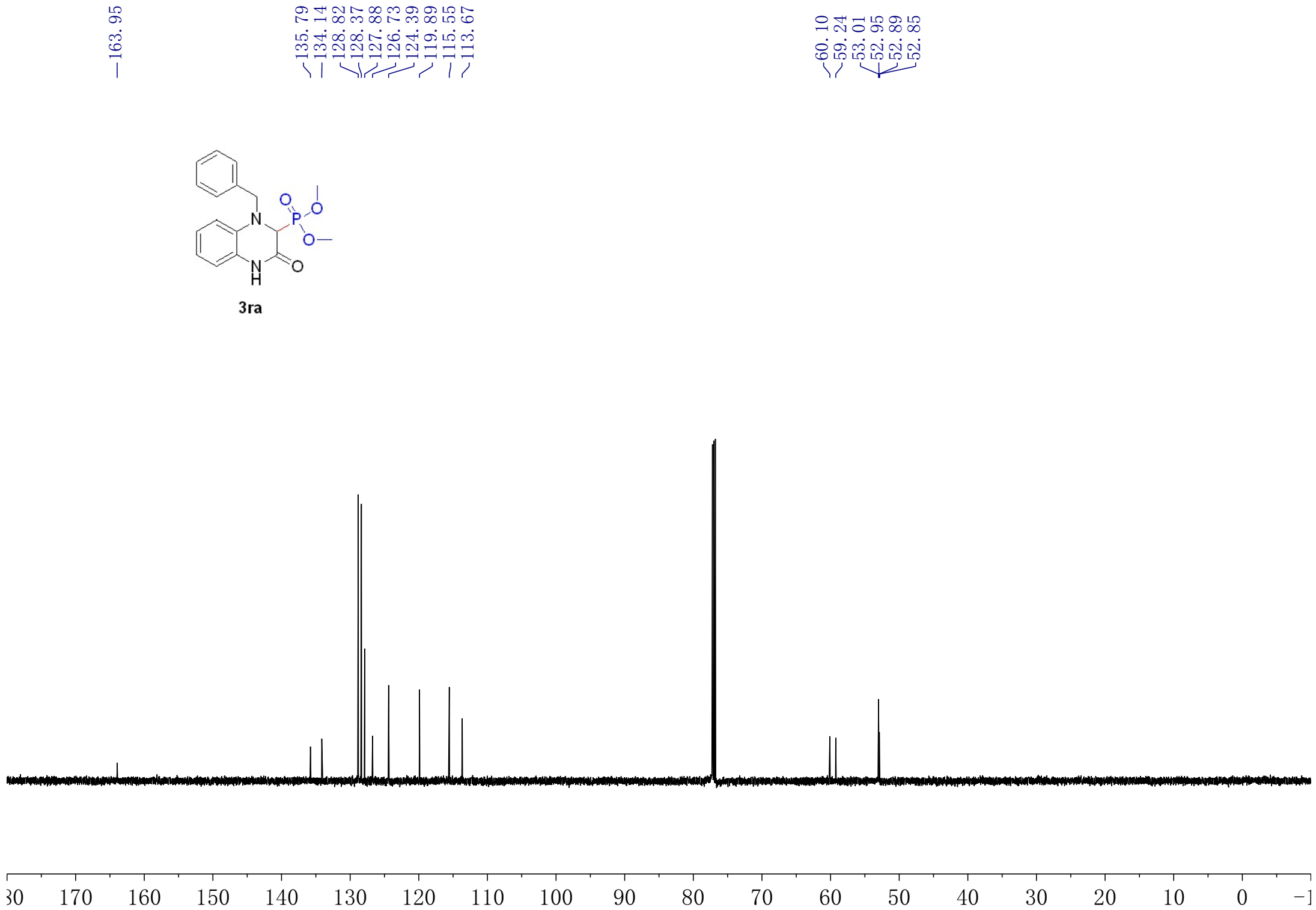


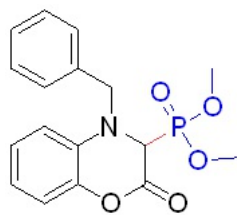
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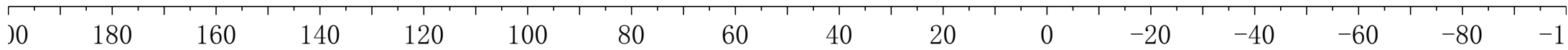
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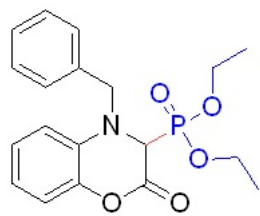




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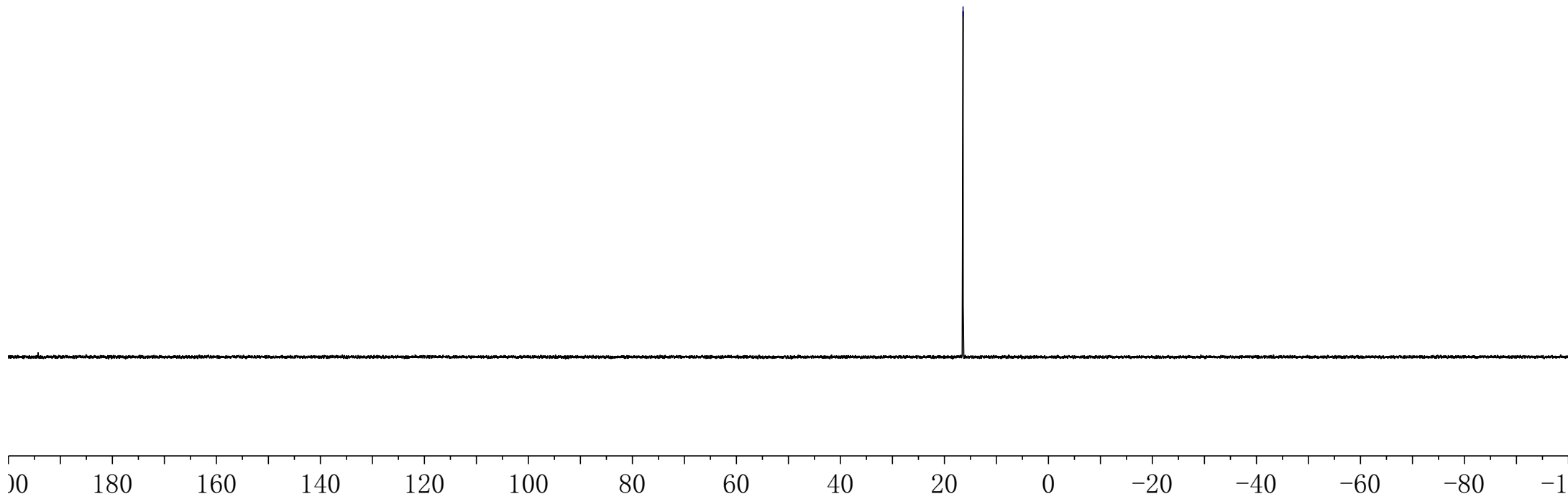
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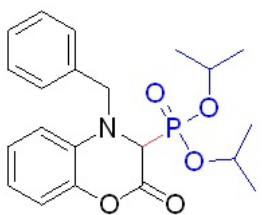




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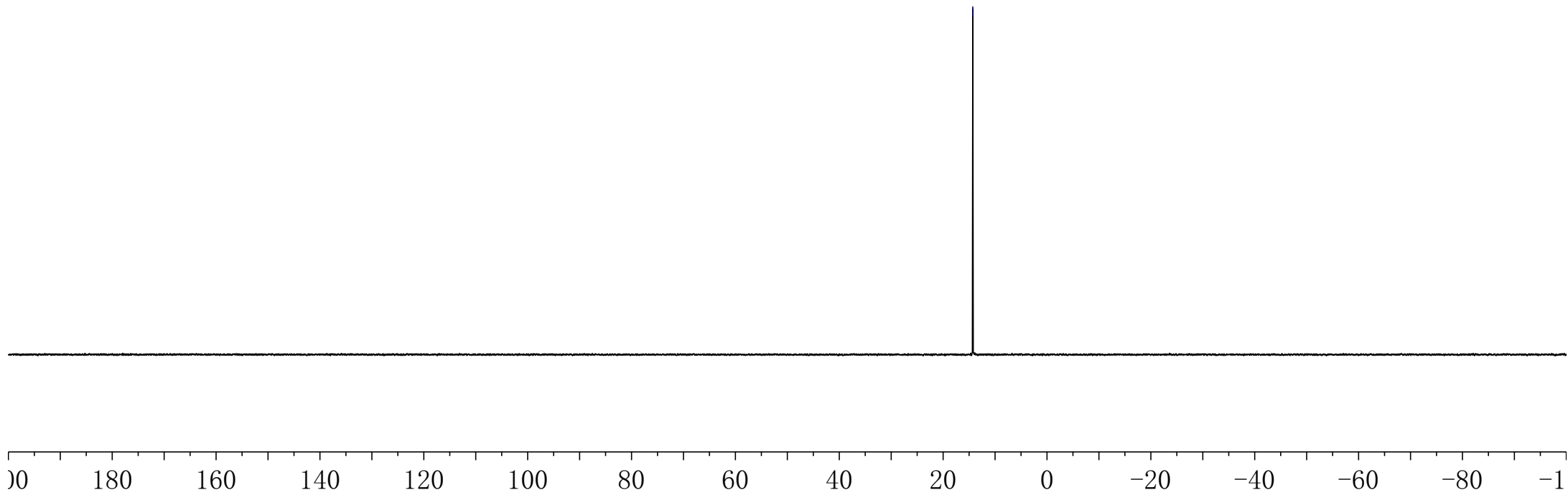
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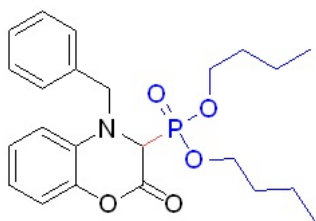




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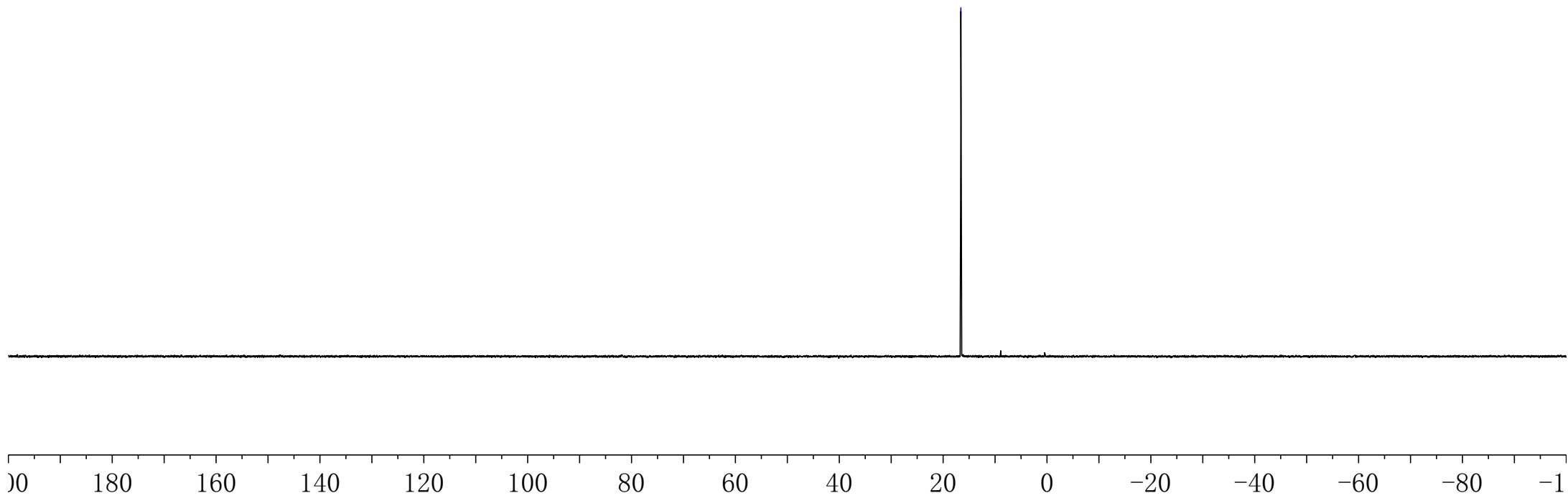
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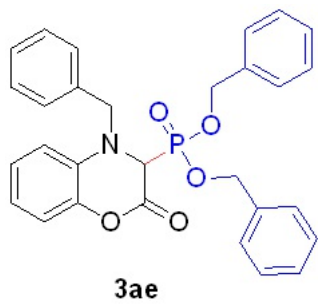




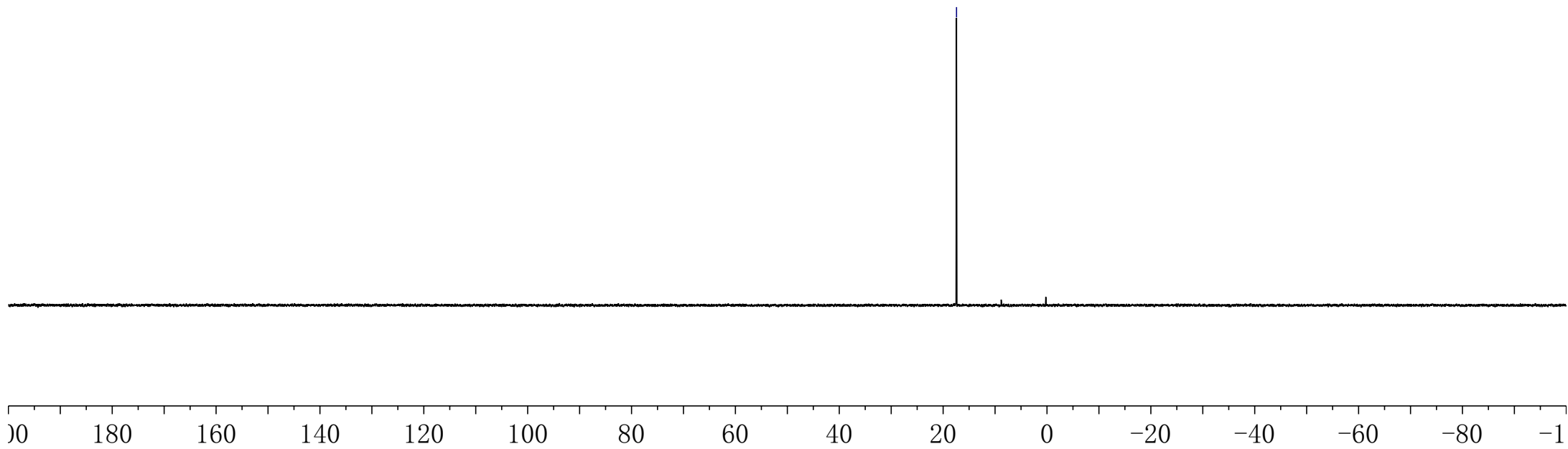
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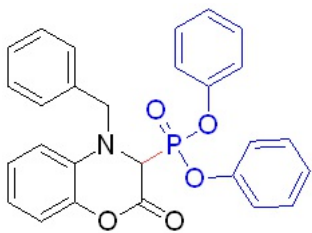
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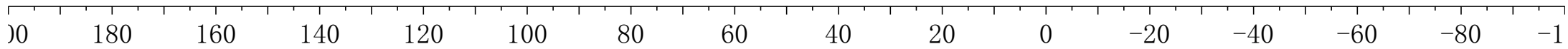
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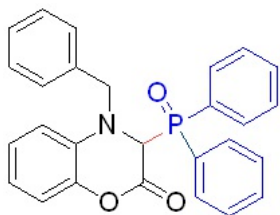




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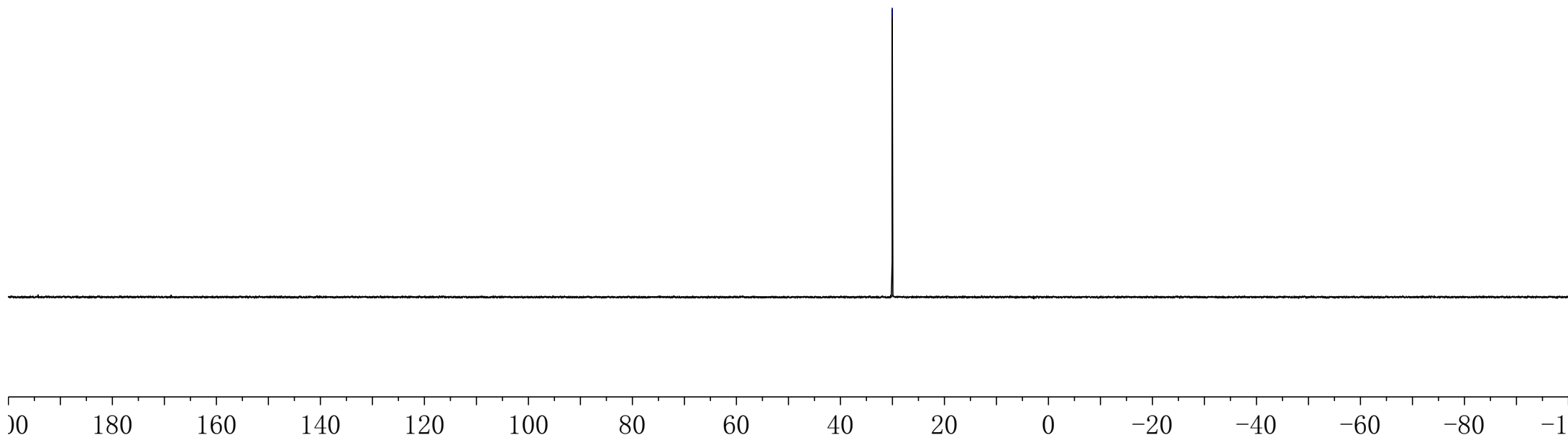
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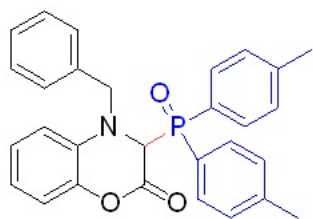




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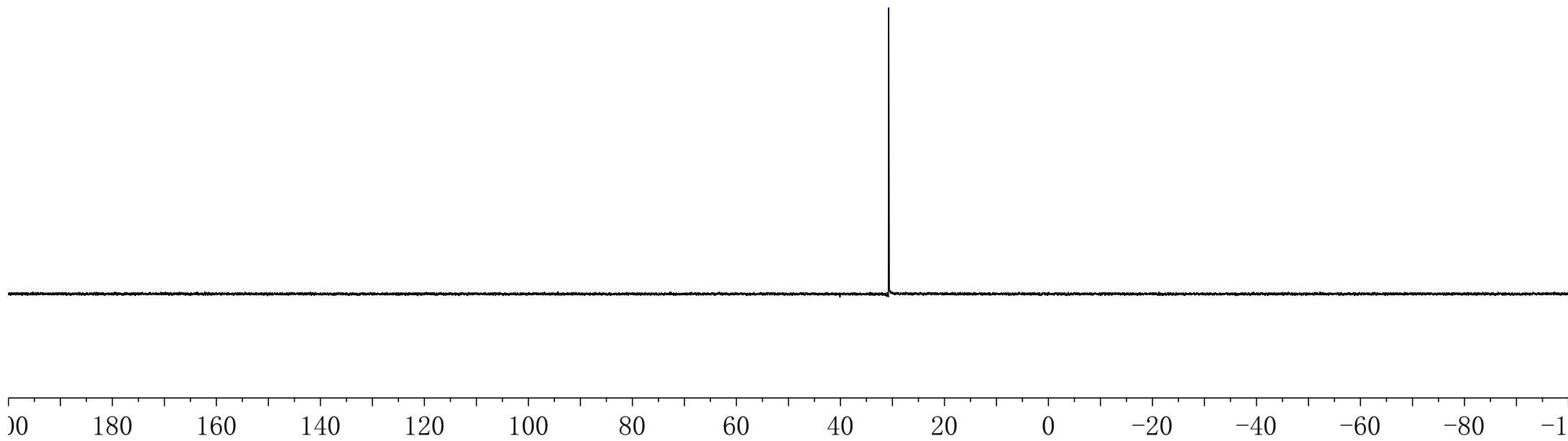
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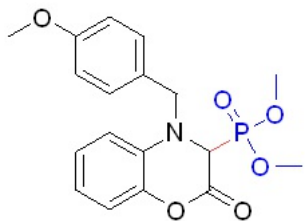




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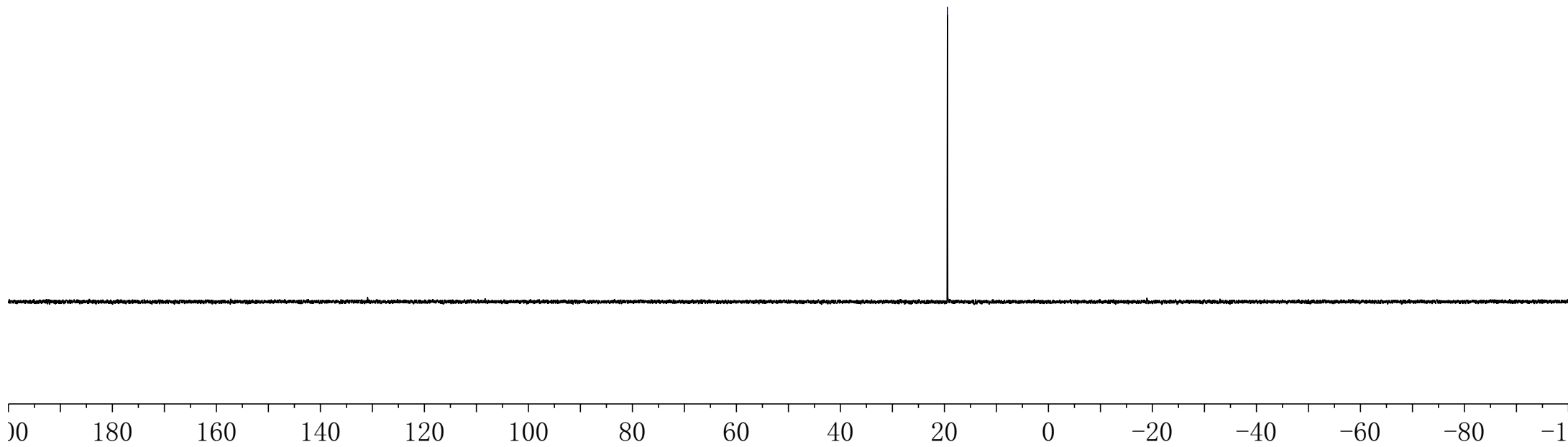
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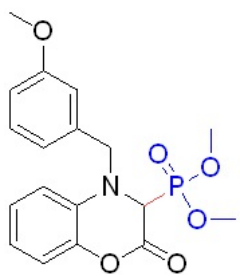




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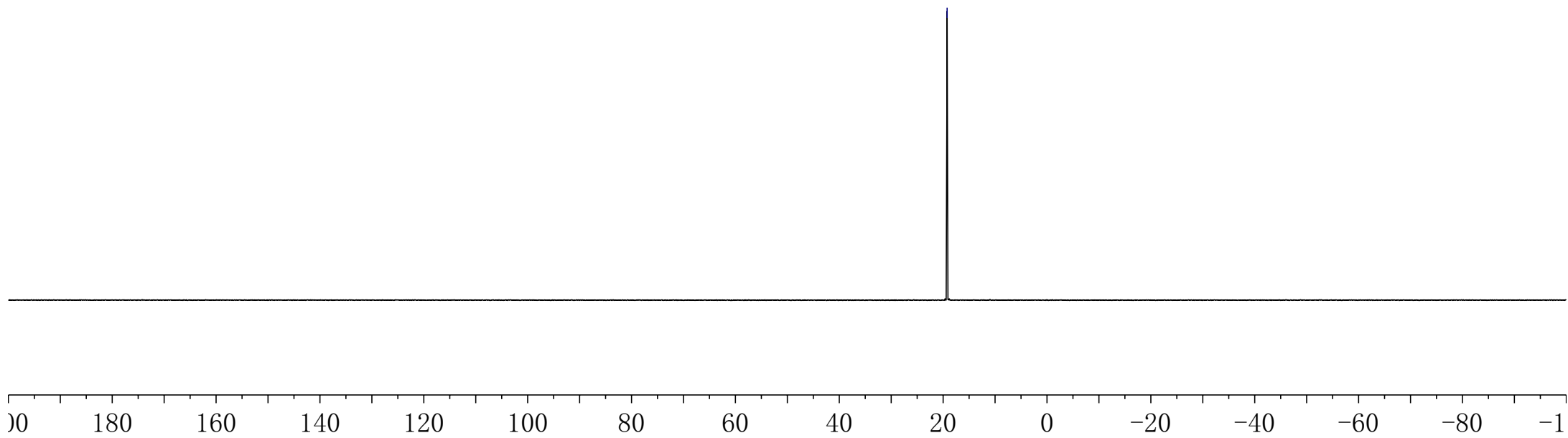
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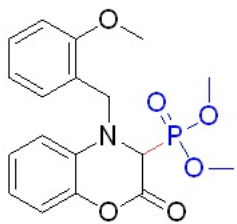




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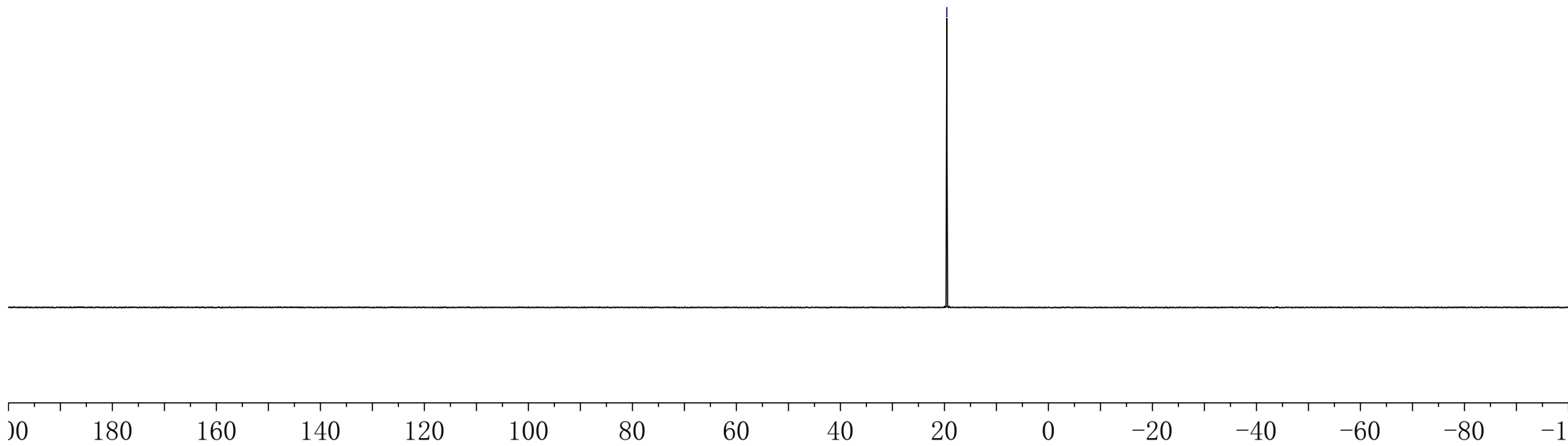
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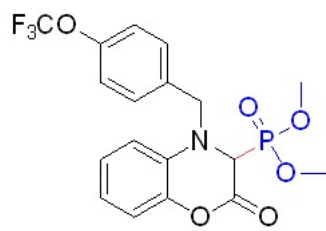




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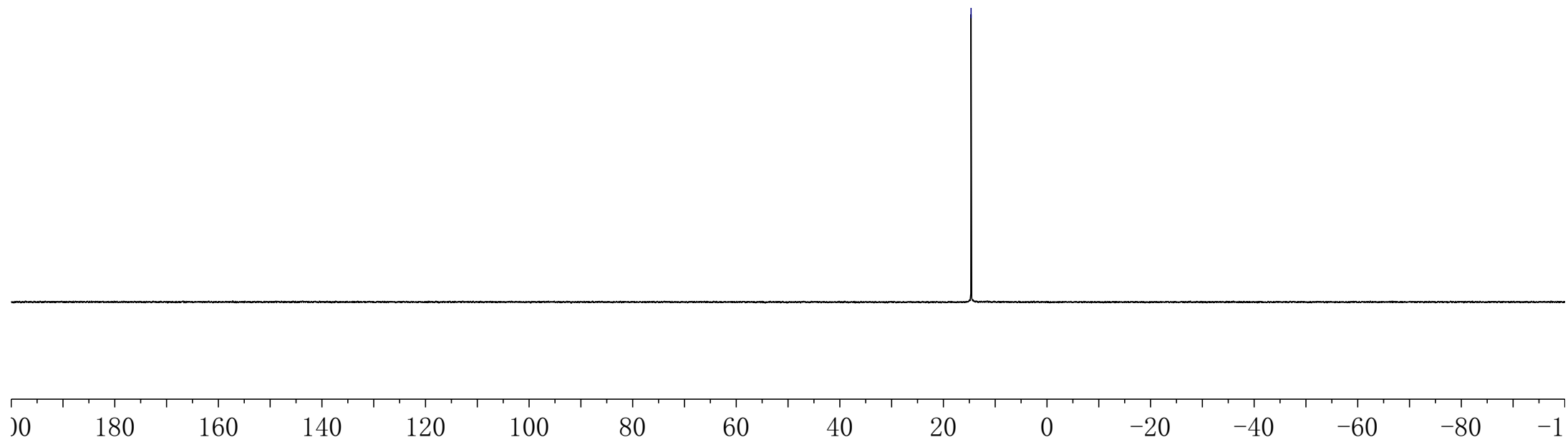
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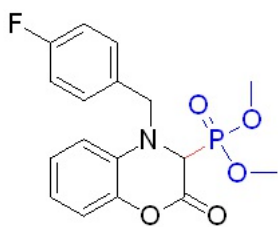




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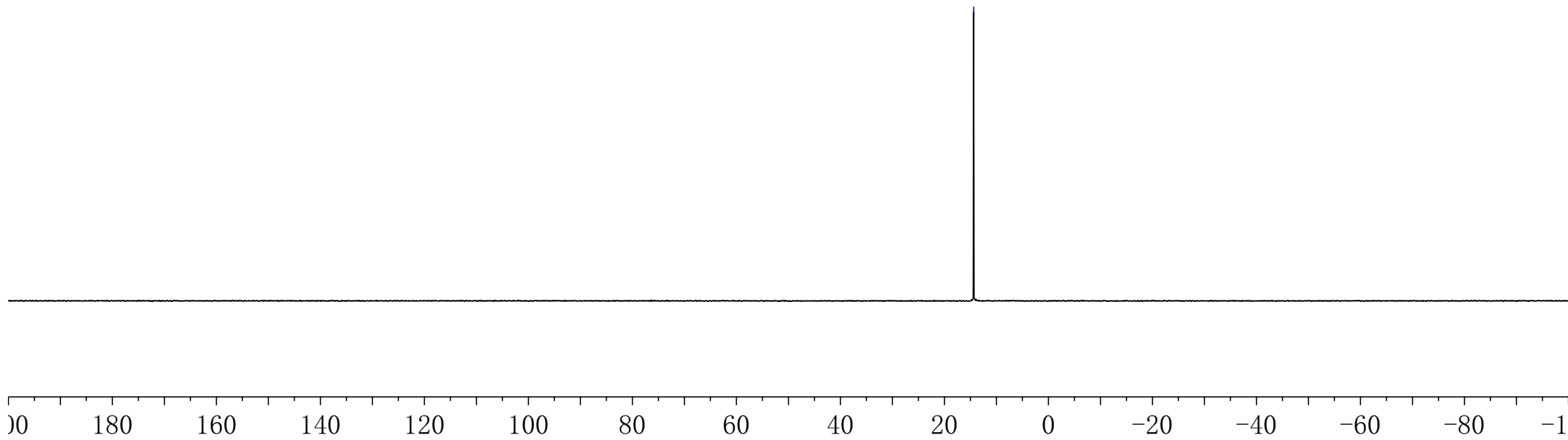
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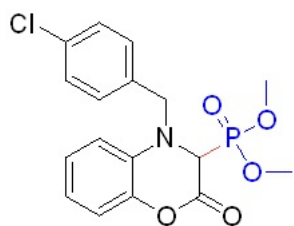




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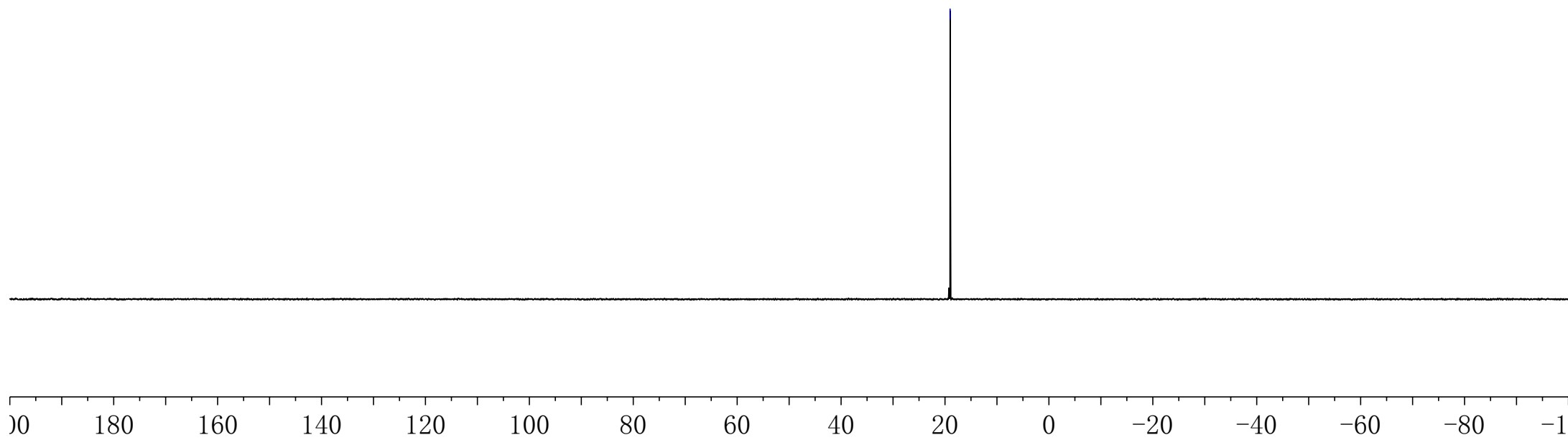
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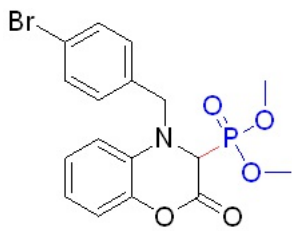




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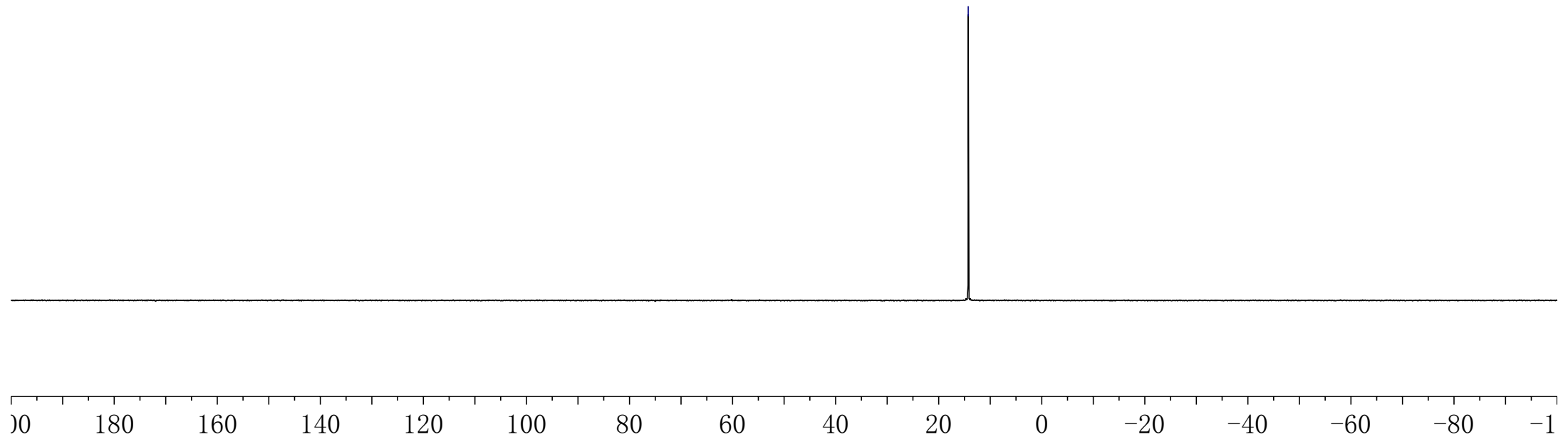
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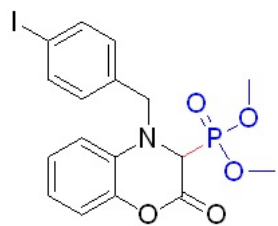




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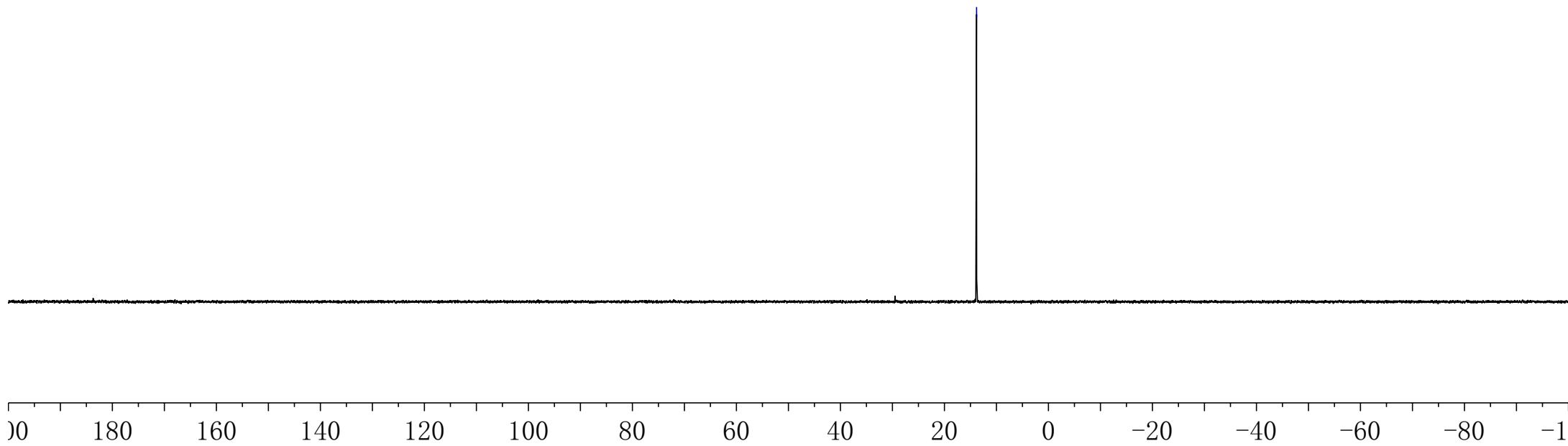
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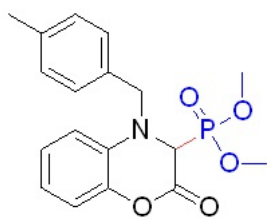




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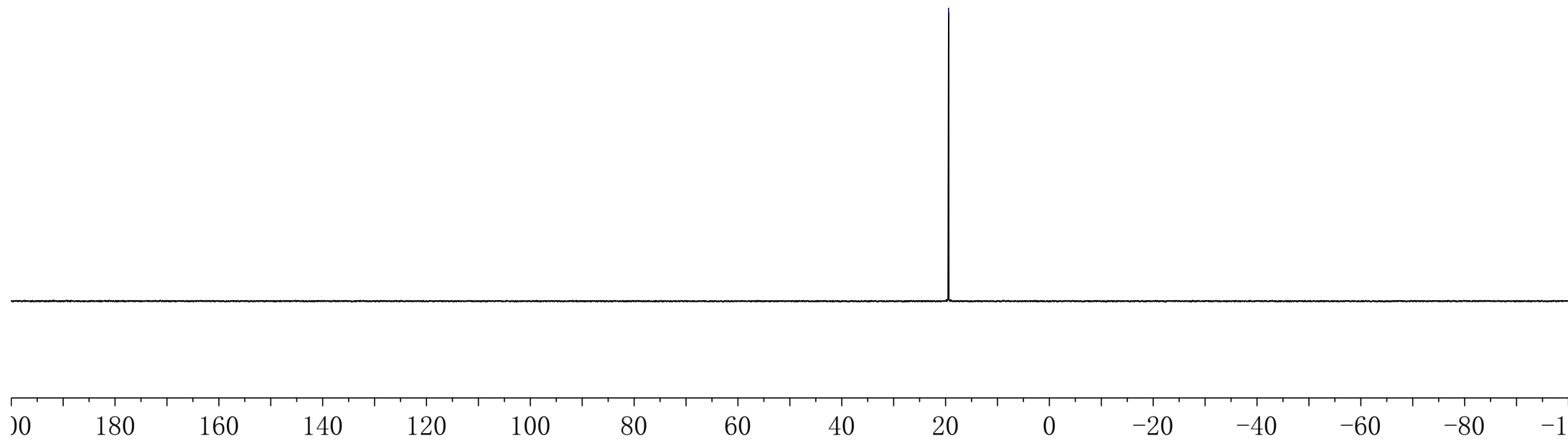
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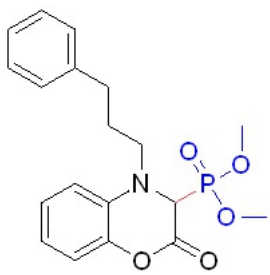




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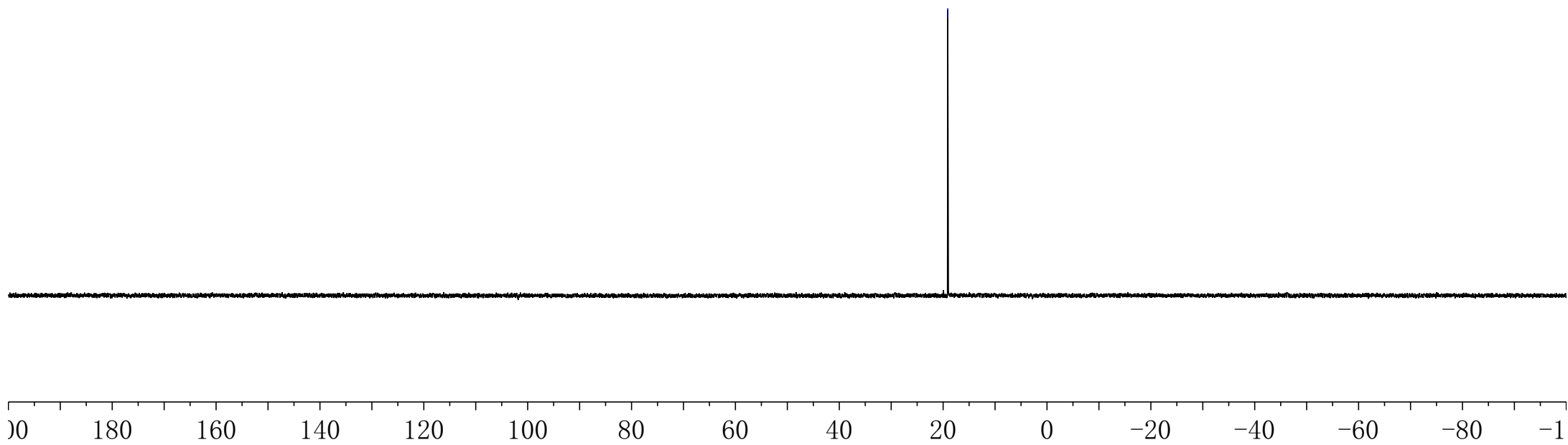
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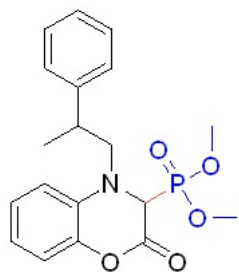




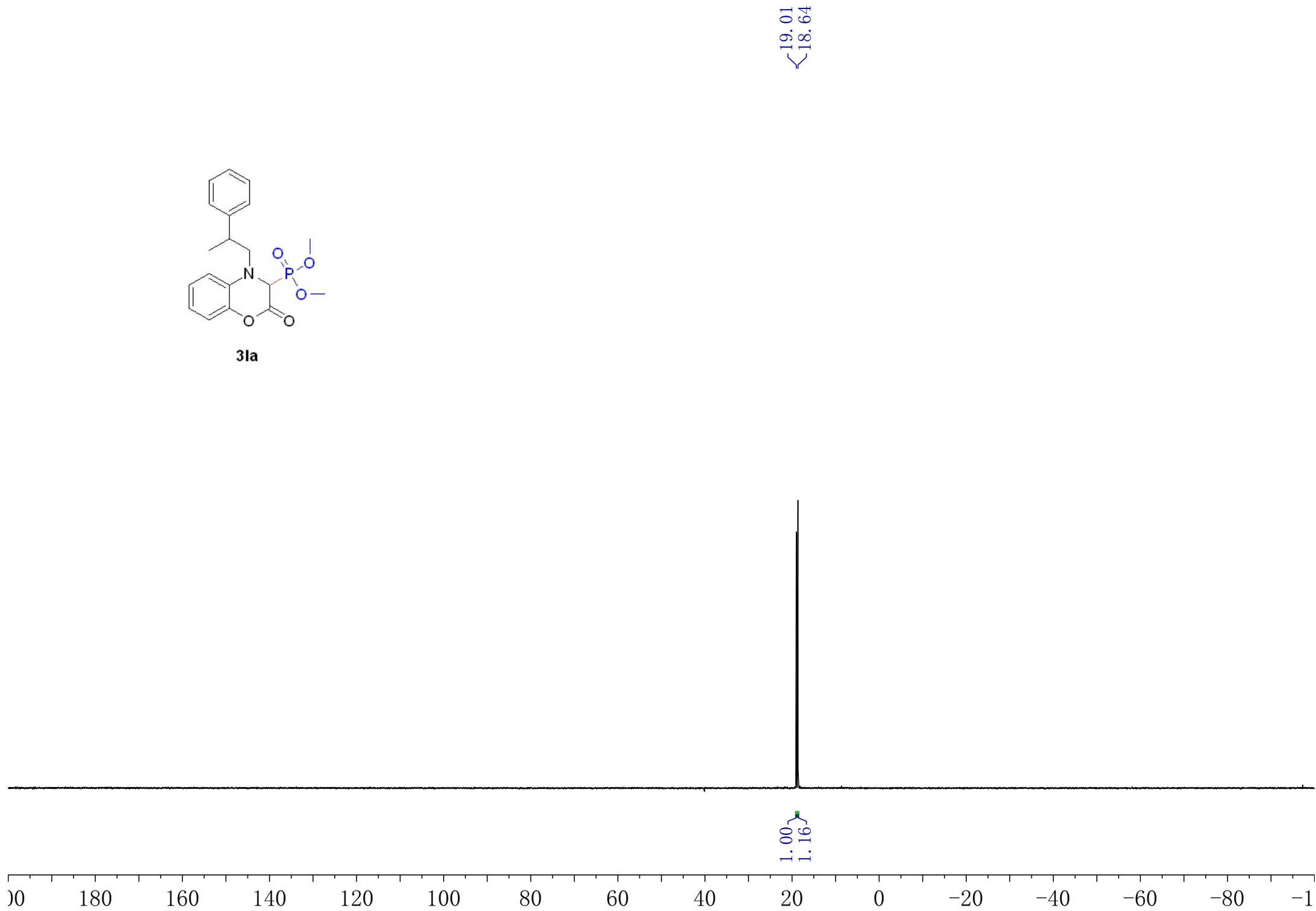
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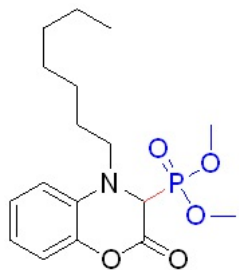
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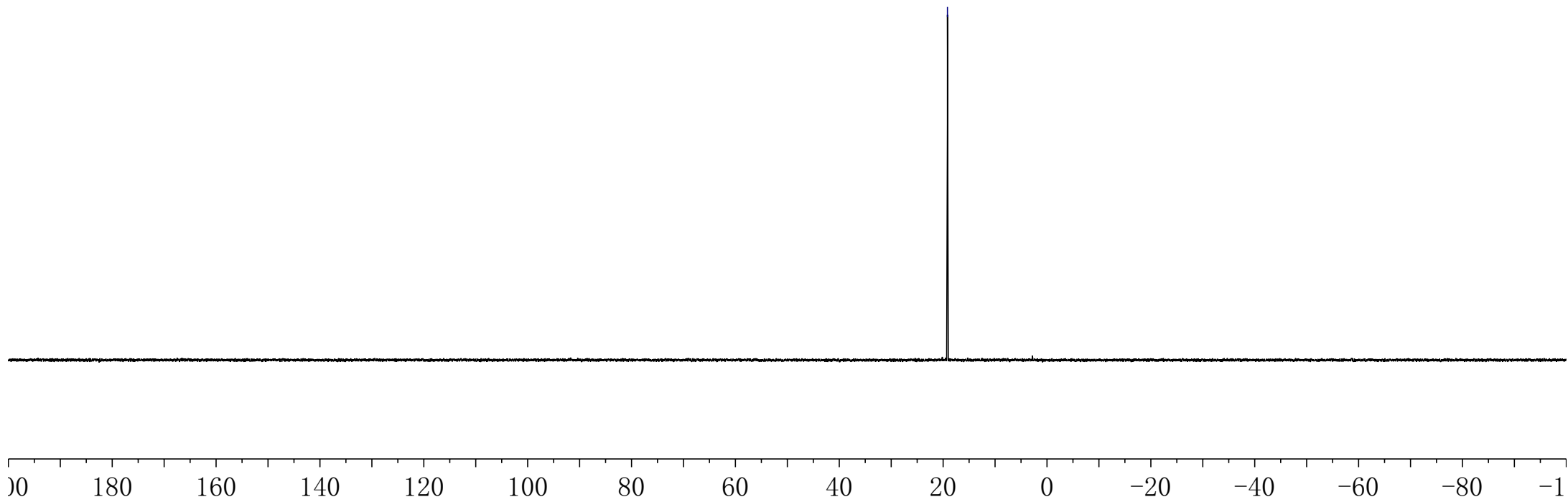
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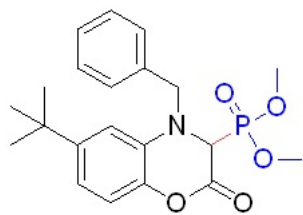




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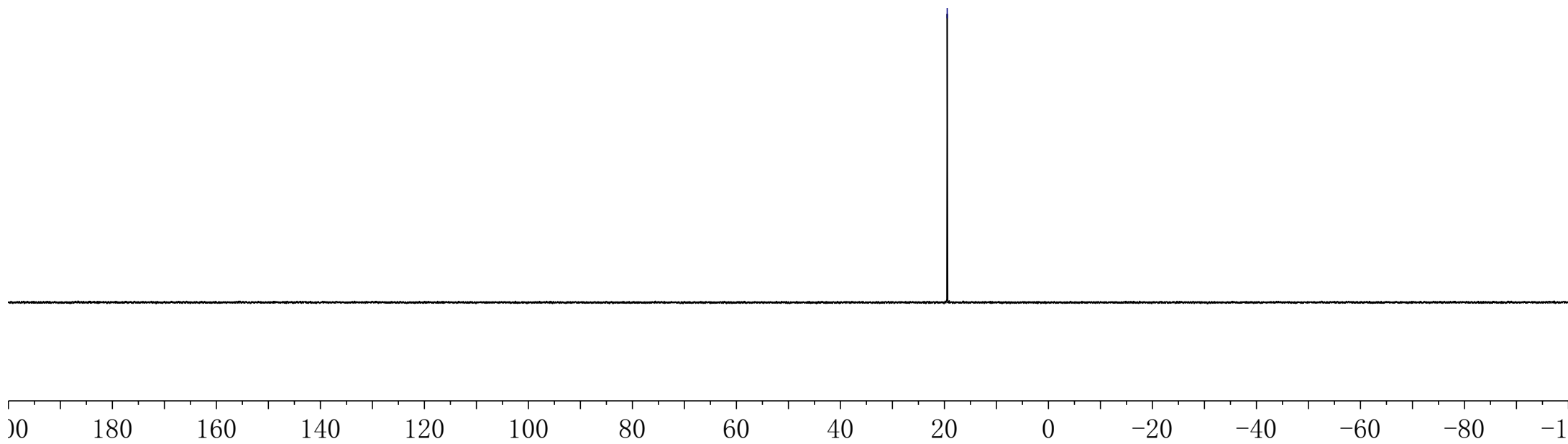
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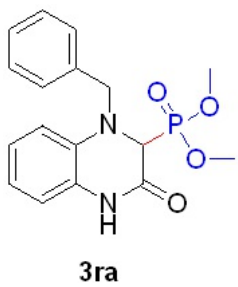




3pa

—19.47





-21.98

