

Nickel Mediated Asymmetric Allylic Alkylation between Nitroallylic Acetates and Acyl Imidazoles

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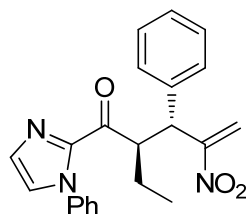
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General remarks

All reactions were performed under an argon atmosphere and solvents were dried according to established procedures. ^1H NMR (300 M), and ^{13}C NMR (75 M) spectra were obtained in CDCl_3 . The chemical shifts are reported in ppm relative to internal standard TMS (^1H NMR), to residual signals of the solvents (CHCl_3 , 7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR). The enantiomeric excess was determined by HPLC analysis.

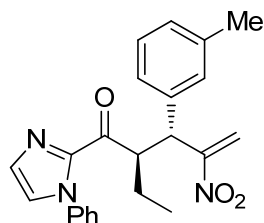
General procedure for the nickel catalyzed asymmetric allylic alkylation reaction

To a weighted together mixture of **L1**/**Ni(OAc) $_2$** (10 mol%), Al_2O_3 (12 eq, 360 mg), ketone **1** (0.3 mmol) and nitroallylic acetate **2** (1.2 eq, 0.36 mmol) was added THF (1.0 ml), Then the mixture was stirred at 10 °C for identified time. Then the reaction mixture was purified by silica gel column chromatography (PE : EA = 10:1 to PE : EA = 4:1) to afford product **3**.



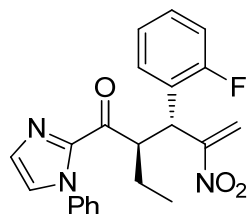
3a.

Reaction for 31 h, Yellow liquid; 75.6 mg; Yield 67.6%; d. r. > 20:1; 97.4% ee determined by HPLC on a Chiralpak IA-H column (*n*-hexane/ *i*-PrOH = 97/3, flow rate = 1.0 mL/min, t_{major} = 18.5 min, t_{minor} = 21.9 min); $[\alpha]_{\text{D}}^{25}$ = -23.000 (c = 0.9797, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.52 (s, 1H), 7.40 – 7.30 (m, 2H), 7.29 – 7.23 (m, 4H), 7.21 – 7.13 (m, 3H), 7.04 (d, J = 1.0 Hz, 1H), 6.68 – 6.59 (m, 3H), 5.95 (d, J = 2.4 Hz, 1H), 4.75 – 4.56 (m, 2H), 1.92 – 1.78 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 192.1, 159.7, 143.7, 138.0, 137.8, 129.5, 129.0, 128.7, 128.5, 128.2, 127.2, 127.1, 125.3, 117.4, 50.4, 47.4, 24.6, 11.4 ppm; HRMS (ESI): $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd: 398.1485, found: 398.1475.



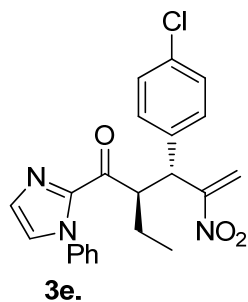
3b.

Reaction for 35 h, Yellow liquid; 75.15 mg; Yield 64.4%; d. r. > 20:1; 96% ee determined by HPLC on a Chiralpak IA-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, t_{minor} = 13.0 min, t_{major} = 15.1 min); $[\alpha]_{\text{D}}^{\text{rt}}$ = -31.674 (c = 0.9673, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.39 – 7.22 (m, 4H), 7.12 – 6.99 (m, 4H), 6.95 (d, J = 4.1 Hz, 1H), 6.71 – 6.56 (m, 3H), 5.95 (d, J = 2.1 Hz, 1H), 4.75 – 4.62 (m, 1H), 4.61 – 4.48 (m, 1H), 2.22 (s, 3H), 1.93 – 1.73 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.2, 159.7, 143.8, 137.8, 137.7, 130.1, 129.5, 128.6, 128.4, 128.0, 127.9, 127.0, 125.9, 125.3, 117.3, 50.4, 47.4, 24.5, 21.1, 11.5 ppm; **IR** (neat): 3346, 3112, 2926, 2549, 2413, 2198, 1949, 1878, 1794, 1679, 1405, 766, 604, 521, 447 cm^{-1} ; **HRMS** (ESI): $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd: 412.1632, found: 412.1645.

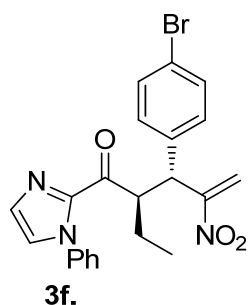


3d.

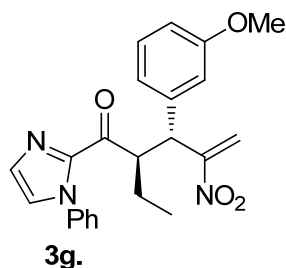
Reaction for 35 h, Faint yellow liquid; 61.31 mg; Yield 52.0%; d. r. = 25:1; 93% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 97/3, flow rate = 1.0 mL/min, t_{minor} = 39.7 min, t_{major} = 43.1 min); $[\alpha]_{\text{D}}^{\text{rt}}$ = -0.957 (c = 1.0214, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.48 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 7.15 (td, J = 7.4, 1.5 Hz, 1H), 7.08 (s, 1H), 7.02 – 6.88 (m, 2H), 6.77 (s, 1H), 6.75 (s, 1H), 6.69 (d, J = 2.0 Hz, 1H), 6.00 (s, 1H), 4.96 – 4.79 (m, 2H), 1.91 – 1.78 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.9, 160.9 (d, $J_{\text{C-F}}$ = 249.0 Hz), 157.8, 143.4, 137.9, 130.7 (d, $J_{\text{C-F}}$ = 3.5 Hz), 129.7, 129.1 (d, $J_{\text{C-F}}$ = 8.4 Hz), 128.8, 128.6, 127.3, 125.4, 123.9 (d, $J_{\text{C-F}}$ = 3.6 Hz), 119.6 (d, $J_{\text{C-F}}$ = 2.4 Hz), 115.6 (d, $J_{\text{C-F}}$ = 22.3 Hz), 48.9, 41.4, 24.6, 11.2 ppm; **IR** (neat): 3345, 3112, 3021, 2963, 2551, 2408, 1948, 1879, 1794, 1682, 1406, 759, 609, 520 cm^{-1} ; **HRMS** (ESI): $\text{C}_{22}\text{H}_{20}\text{FN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd: 394.1561, found: 394.1577.



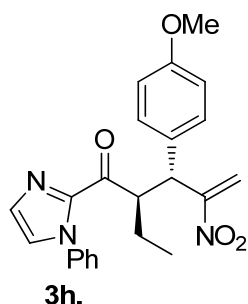
Reaction for 20 h, Faint yellow liquid; 68.34 mg; Yield 55.7%; d. r. > 20:1; 94% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 95/5, flow rate = 1.0 mL/min, $t_{\text{major}} = 12.9$ min, $t_{\text{minor}} = 14.2$ min); $[\alpha]_{\text{D}}^{25} = -25.352$ ($c = 0.9991$, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.47 – 7.32 (m, 3H), 7.28 – 7.23 (m, 1H), 7.22 – 7.11 (m, 4H), 7.08 (s, 1H), 6.78 (s, 1H), 6.76 (s, 1H), 6.67 (d, $J = 2.4$ Hz, 1H), 5.96 (d, $J = 2.2$ Hz, 1H), 4.73 – 4.62 (m, 1H), 4.61 – 4.52 (m, 1H), 1.89 – 1.76 (m, 2H), 0.91 (t, $J = 7.5$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.9, 159.3, 143.7, 137.9, 136.7, 133.2, 130.5, 129.8, 128.9, 128.8, 128.4, 127.5, 125.5, 117.9, 50.4, 46.7, 24.7, 11.4 ppm; IR (neat): 3343, 3112, 3020, 2965, 2549, 2404, 2197, 1949, 1873, 1681, 1403, 754, 625, 521, 479 cm^{-1} ; HRMS (ESI): $\text{C}_{22}\text{H}_{20}\text{ClN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd: 410.1266, found: 410.1281.



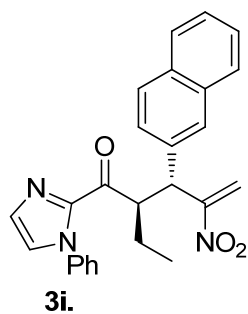
Reaction for 34 h, Faint yellow liquid; 82.49 mg; Yield 60.7%; d. r. = 20:1; 93% ee determined by HPLC on a Chiralpak IA-H column (*n*-hexane/ *i*-PrOH = 95/5, flow rate = 1.0 mL/min, $t_{\text{major}} = 13.3$ min, $t_{\text{minor}} = 15.6$ min); dr = 20:1 determined by NMR; $[\alpha]_{\text{D}}^{25} = -24.211$ ($c = 0.9860$, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.37 – 7.25 (m, 3H), 7.22 – 7.17 (m, 2H), 7.14 (s, 1H), 7.08 – 7.01 (m, 2H), 6.98 (s, 1H), 6.68 (d, $J = 6.6$ Hz, 2H), 6.55 (d, $J = 1.9$ Hz, 1H), 5.85 (d, $J = 1.9$ Hz, 1H), 4.64 – 4.52 (m, 1H), 4.51 – 4.42 (m, 1H), 1.74 (dd, $J = 14.4, 7.2$ Hz, 2H), 0.81 (t, $J = 7.5$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.6, 159.0, 143.5, 137.7, 137.1, 131.2, 130.7, 129.6, 128.7, 128.6, 127.3, 125.4, 121.2, 117.8, 50.2, 46.6, 24.5, 11.2 ppm; IR (neat): 3345, 3112, 2966, 2929, 2552, 2406, 1947, 1901, 1681, 1404, 1011, 759, 527, 404 cm^{-1} ; HRMS (ESI): $\text{C}_{22}\text{H}_{20}\text{BrN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd: 454.0761, found: 454.0755.



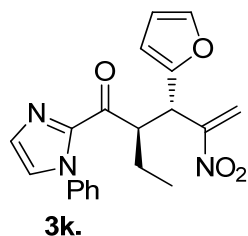
Reaction for 40 h, Faint yellow liquid; 68.65 mg; Yield 56.5%; d. r. = 25:1; 96.3% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, t_{minor} = 16.1 min, t_{major} = 17.7 min); $[\alpha]_{\text{D}}^{25}$ = 9.794 (c = 1.0034, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.47 – 7.36 (m, 1H), 7.36 – 7.30 (m, 2H), 7.28 – 7.25 (m, 1H), 7.25 – 7.13 (m, 2H), 7.05 (s, 1H), 6.86 – 6.79 (m, 2H), 6.71 – 6.66 (m, 2H), 6.63 (d, J = 2.4 Hz, 1H), 5.95 (d, J = 2.4 Hz, 1H), 4.75 – 4.65 (m, 1H), 4.58 (d, J = 11.8 Hz, 1H), 3.67 (s, 3H), 1.89 – 1.77 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.2, 159.7, 159.5, 144.0, 139.6, 137.9, 129.6, 129.8, 128.8, 128.6, 127.2, 125.5, 121.2, 117.7, 114.2, 113.71, 55.2, 50.5, 47.6, 24.7, 11.6 ppm; **IR** (neat): 3344, 3056, 2965, 2550, 2199, 1947, 1878, 1682, 1404, 737, 521 cm^{-1} ; **HRMS** (ESI): $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_4$ $[\text{M}+\text{Na}]^+$ calcd: 428.1581, found: 428.1587.



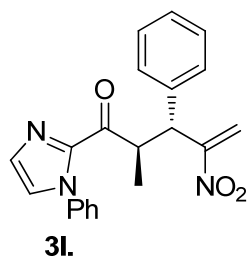
Reaction for 36 h, Faint yellow liquid; 74.97 mg; Yield 61.7%; d. r. = 25:1; 95% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, t_{major} = 18.8 min, t_{minor} = 23.4 min); $[\alpha]_{\text{D}}^{25}$ = -18.584 (c = 0.9962, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.48 – 7.22 (m, 5H), 7.17 (d, J = 8.6 Hz, 2H), 7.05 (s, 1H), 6.71 (d, J = 8.4 Hz, 3H), 6.60 (d, J = 2.2 Hz, 1H), 5.91 (d, J = 2.0 Hz, 1H), 4.73 – 4.50 (m, 2H), 3.70 (s, 3H), 1.91 – 1.76 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.3, 159.9, 158.6, 143.8, 137.9, 130.1, 129.9, 129.6, 128.7, 128.5, 127.1, 125.4, 117.0, 113.6, 55.1, 50.5, 46.7, 24.6, 11.4 ppm; **IR** (neat): 3344, 3111, 2965, 2876, 2551, 2197, 1952, 1886, 1685, 1404, 736, 695, 550 cm^{-1} ; **HRMS** (ESI): $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_4$ $[\text{M}+\text{Na}]^+$ calcd: 428.1581, found: 428.1589.



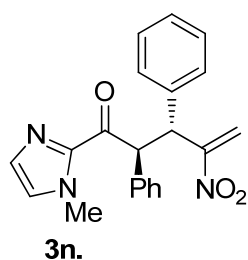
Reaction for 32 h, Faint yellow liquid; 83.39 mg; Yield 65.4%; d. r. = 14.3:1; 95% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 97/3, flow rate = 1.0 mL/min, t_{major} = 27.9 min, t_{minor} = 32.6 min); dr = 50:3 determined by NMR; $[\alpha]_{\text{D}}^{\text{rt}}$ = -17.122 (c = 1.0118, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.83 – 7.66 (m, 3H), 7.63 (d, J =8.6, 1H), 7.47 – 7.39 (m, 2H), 7.39 – 7.32 (m, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 7.05 (t, J =7.8, 2H), 6.91 (d, J =0.6, 1H), 6.68 (d, J =2.4, 1H), 6.35 (d, J =7.5, 2H), 6.04 (d, J =2.3, 1H), 4.87 – 4.71 (m, 2H), 1.97 – 1.77 (m, 2H), 0.95 (t, J =7.5, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.1, 159.4, 143.8, 137.6, 135.2, 133.0, 132.3, 129.5, 128.6, 128.5, 128.4, 127.8, 127.8, 127.3, 127.1, 126.2, 126.1, 126.0, 125.2, 117.6, 50.5, 47.5, 24.6, 11.5 ppm; IR (neat): 3345, 3115, 2926, 2372, 1871, 1681, 1404, 1093, 761, 692, 531 cm^{-1} ; HRMS (ESI): $\text{C}_{26}\text{H}_{23}\text{N}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd: 448.1632, found: 448.1639.



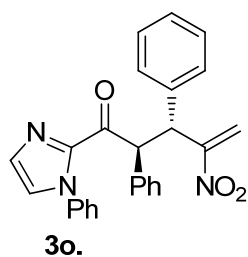
Reaction for 36 h, Yellow liquid; 91.0 mg; Yield 65%; d. r. = 5.6:1; >99% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, t_{major} = 15.0 min, t_{minor} = 18.8 min); dr = 28:5 determined by NMR; $[\alpha]_{\text{D}}^{\text{rt}}$ = 17.000 (c = 0.9973, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.47 – 7.40 (m, 3H), 7.31 (d, J =0.9, 1H), 7.23 (s, 1H), 7.17 (d, J =0.9, 1H), 7.12 – 7.06 (m, 2H), 6.70 – 6.64 (m, 1H), 6.22 – 6.16 (m, 2H), 5.90 (d, J =2.2, 1H), 4.88 – 4.78 (m, 1H), 4.73 – 4.62 (m, 1H), 1.82 – 1.68 (m, 2H), 0.86 (t, J =7.5, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.8, 156.7, 151.5, 143.2, 142.0, 138.1, 129.9, 128.9, 128.7, 127.4, 125.6, 120.4, 110.3, 108.0, 49.8, 41.0, 23.7, 11.2 ppm; IR (neat): 3347, 3117, 2967, 2877, 2371, 1948, 1878, 1793, 1682, 1405, 757, 667, 522 cm^{-1} ; HRMS (ESI): $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_4$ $[\text{M}+\text{Na}]^+$ calcd: 388.1268, found: 388.1276.



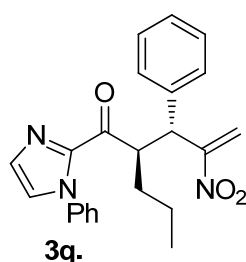
Reaction for 34 h, Faint yellow liquid; 70.72 mg; Yield 65.3%; d. r. = 50:1; 91% ee determined by HPLC on a Chiralpak IA-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, t_{major} = 19.9 min, t_{minor} = 24.2 min); $[\alpha]_{\text{D}}^{25}$ = 20.329 (c = 0.9962, CHCl₃); **¹H NMR** (300 MHz, CDCl₃): δ 7.39 – 7.12 (m, 9H), 7.07 (s, 1H), 6.72 (d, J = 7.0 Hz, 2H), 6.63 (d, J = 2.3 Hz, 1H), 5.91 (d, J = 2.2 Hz, 1H), 4.90 – 4.68 (m, 1H), 4.67 – 4.57 (m, 1H), 1.34 (d, J = 6.7 Hz, 3H) ppm; **¹³C NMR** (75 MHz, CDCl₃): δ 192.0, 159.5, 142.5, 138.3, 137.7, 129.6, 128.8, 128.7, 128.5, 128.3, 127.2, 125.2, 117.8, 48.1, 44.2, 16.7 ppm; **IR** (neat): 3354, 3113, 3022, 2404, 1952, 1871, 1733, 1686, 1404, 1216, 756, 524 cm⁻¹; **HRMS** (ESI): C₂₁H₁₉N₃O₃ [M+H]⁺ calcd: 362.1499, found: 362.1514.



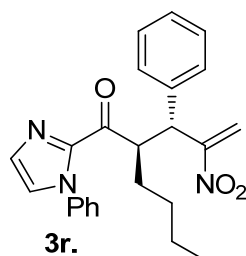
Reaction for 31 h, Faint yellow liquid; 72.89 mg; Yield 67.3%; d. r.= 25:1; 67% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, t_{major} = 15.4 min, t_{minor} = 22.5 min); $[\alpha]_{\text{D}}^{25}$ = -22.348 (c = 0.9962, CHCl₃); **¹H NMR** (300 MHz, CDCl₃): δ 7.50 (dd, J = 28.0, 7.2 Hz, 4H), 7.36 – 7.06 (m, 7H), 6.88 (s, 1H), 6.39 (d, J = 2.3 Hz, 1H), 6.07 (d, J = 12.5 Hz, 1H), 5.71 (d, J = 2.2 Hz, 1H), 5.40 (d, J = 12.5 Hz, 1H), 3.73 (s, 3H) ppm; **¹³C NMR** (75 MHz, CDCl₃): δ 189.0, 159.0, 142.4, 137.9, 136.2, 129.4, 129.1, 129.0, 128.7, 128.6, 127.7, 127.7, 127.4, 119.3, 55.3, 47.0, 36.0 ppm; **IR** (neat): 3339, 3030, 2926, 2199, 1955, 1880, 1734, 1674, 1403, 1075, 757, 700, 603 cm⁻¹; **HRMS** (ESI): C₂₁H₁₉N₃O₃ [M+H]⁺ calcd: 362.1499, found: 362.1515.



Reaction for 36 h, White solid, m.p. 160 – 162 °C; 125.68 mg; Yield 99%; d. r. > 20:1; 92.7% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, $t_{\text{major}} = 18.1$ min, $t_{\text{minor}} = 25.3$ min); $[\alpha]_{\text{D}}^{\text{rt}} = 20.098$ ($c = 0.9915$ CHCl₃); **¹H NMR** (300 MHz, CDCl₃): δ 7.54 (d, $J=7.3$, 2H), 7.44 (d, $J=7.3$, 2H), 7.36 – 7.24 (m, 5H), 7.23 – 7.11 (m, 5H), 6.97 (s, 1H), 6.67 (d, $J=7.4$, 2H), 6.34 (d, $J=2.1$, 1H), 6.09 (d, $J=12.4$, 1H), 5.71 (d, $J=1.9$, 1H), 5.29 (d, $J=12.4$, 1H) ppm; **¹³C NMR** (75 MHz, CDCl₃): δ 187.6, 158.6, 142.4, 137.7, 137.6, 135.8, 129.8, 129.0, 128.8, 128.8, 128.7, 128.5, 128.4, 127.7, 127.4, 127.4, 125.1, 119.0, 55.4, 47.1 ppm; **IR** (neat): 3354, 3030, 2928, 2854, 1952, 1880, 1803, 1685, 759, 531 cm⁻¹; **HRMS** (ESI): C₂₆H₂₁N₃O₃ [M+H]⁺ calcd: 424.1656, found: 424.1675.

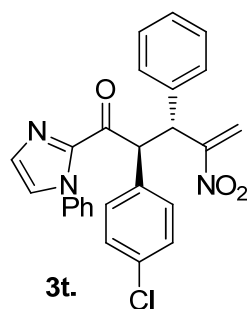


Reaction for 34 h, Faint yellow liquid; 59.52 mg; Yield 51%; d. r. > 20:1; 92% ee determined by HPLC on a Chiralpak IA-H column (*n*-hexane/ *i*-PrOH = 95/5, flow rate = 1.0 mL/min, $t_{\text{major}} = 11.9$ min, $t_{\text{minor}} = 13.5$ min); $[\alpha]_{\text{D}}^{\text{rt}} = -23.858$ ($c = 0.9962$, CHCl₃); **¹H NMR** (300 MHz, CDCl₃): δ 7.40 – 7.22 (m, 6H), 7.21 – 7.10 (m, 3H), 7.02 (d, $J = 0.7$ Hz, 1H), 6.67 – 6.58 (m, 3H), 5.96 (d, $J = 2.3$ Hz, 1H), 4.83 – 4.65 (m, 1H), 4.58 (d, $J = 11.7$ Hz, 1H), 1.92 – 1.75 (m, 1H), 1.75 – 1.61 (m, 1H), 1.47 – 1.28 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H) ppm; **¹³C NMR** (75 MHz, CDCl₃): δ 192.5, 159.8, 143.8, 137.9, 129.6, 129.2, 128.8, 128.5, 128.2, 127.3, 127.1, 125.4, 117.4, 49.2, 48.0, 34.0, 20.5, 14.2 ppm; **IR** (neat): 3344, 2960, 2733, 2198, 1952, 1880, 1682, 1036, 738, 610, 524, 450 cm⁻¹; **HRMS** (ESI): C₂₃H₂₃N₃O₃ [M+Na]⁺ calcd: 412.1632, found: 412.1643.

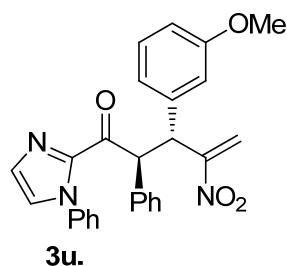


Reaction for 36 h, Faint yellow liquid; 80.16 mg; Yield 66.3%; d. r.= 24:1; 95% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 95/5, flow rate = 1.0 mL/min, $t_{\text{minor}} = 16.5$ min, $t_{\text{major}} = 18.2$ min); dr = 24:1 determined by NMR; $[\alpha]_{\text{D}}^{\text{rt}} = 6.360$ ($c = 1.0192$, CHCl₃); **¹H NMR** (300 MHz, CDCl₃):

δ 7.40 – 7.20 (m, 6H), 7.20 – 7.11 (m, 2H), 7.01 (s, 1H), 6.69 – 6.56 (m, 3H), 5.95 (d, J = 2.1 Hz, 1H), 4.81 – 4.65 (m, 1H), 4.58 (d, J = 11.7 Hz, 1H), 1.93 – 1.78 (m, 1H), 1.77 – 1.64 (m, 1H), 1.38 – 1.19 (m, 4H), 0.82 (t, J = 6.7 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, CDCl_3): δ 192.3, 159.8, 143.8, 137.8, 129.5, 129.1, 128.7, 128.4, 128.1, 127.2, 127.0, 125.3, 117.3, 49.2, 48.0, 31.4, 29.2, 22.7, 13.7 ppm; **IR** (neat): 3345, 3112, 2928, 2551, 1953, 1878, 1680, 1552, 1038, 760, 667, 526 cm^{-1} ; **HRMS** (ESI): $\text{C}_{24}\text{H}_{25}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd: 404.1969, found: 404.1985.



Reaction for 13 h, White solid, m.p. 138 – 140 $^{\circ}\text{C}$; 128.19 mg; Yield 93.5%; d. r. > 20:1; 93.9% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 98/2, flow rate = 1.0 mL/min, $t_{\text{minor}} = 27.5$ min, $t_{\text{major}} = 30.5$ min); $[\alpha]_{\text{D}}^{25} = 53.928$ ($c = 1.9286$, CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 7.49 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 7.3 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.26 – 7.15 (m, 5H), 7.04 (s, 1H), 6.72 (d, J = 7.3 Hz, 2H), 6.39 (d, J = 1.9 Hz, 1H), 6.08 (d, J = 12.4 Hz, 1H), 5.70 (d, J = 1.7 Hz, 1H), 5.23 (d, J = 12.3 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, CDCl_3): δ 187.3, 158.4, 142.2, 137.52, 137.4, 134.4, 133.7, 130.3, 130.0, 129.1, 128.8, 128.8, 128.7, 128.5, 127.6, 127.6, 125.2, 119.2, 54.6, 47.2 ppm;; **HRMS** (ESI): $\text{C}_{26}\text{H}_{20}\text{ClN}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd: 480.1085, found: 480.1099.

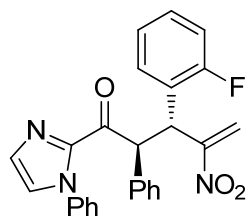


Reaction for 12 h, White solid, m.p. 81 – 83 $^{\circ}\text{C}$; 133.05 mg; Yield 97.9%; d. r. > 20:1; 93.7% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, $t_{\text{major}} = 22.3$ min, $t_{\text{minor}} = 41.1$ min); $[\alpha]_{\text{D}}^{25} = -57.036$ ($c = 1.1133$, CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 7.54 (d, J = 7.2 Hz, 2H), 7.36 – 7.24 (m, 5H), 7.23 – 7.11 (m, 3H), 7.04 – 6.97 (m, 3H), 6.71 (d, J = 7.0 Hz, 3H), 6.36 (d, J = 2.4 Hz, 1H), 6.08 (d, J = 12.4 Hz, 1H), 5.71 (d, J = 2.3 Hz, 1H), 5.27 (d, J = 12.4 Hz, 1H), 3.70 (s, 3H) ppm; **^{13}C NMR** (75 MHz, CDCl_3): δ 187.7, 159.4, 158.5, 142.4, 139.2, 137.6, 135.7, 129.8,

129.4, 129.0, 128.8, 128.7, 128.5, 127.7, 127.4, 125.1, 120.8, 119.2, 114.3, 113.4, 55.3, 55.0, 47.1 ppm;

IR (neat): 3364, 3064, 2928, 2201, 1879, 1693, 1402, 1152, 756, 694, 528 cm^{-1} ; **HRMS** (ESI):

$\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_4$ $[\text{M}+\text{Na}]^+$ calcd: 476.1581, found: 476.1591.



3v.

Reaction for 16 h, White solid, m.p. 138 – 140 $^{\circ}\text{C}$; 114.44 mg; Yield 86.5%; d. r. = 25:1; 84% ee

determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min,

$t_{\text{major}} = 19.6$ min, $t_{\text{minor}} = 24.6$ min); $[\alpha]_{\text{D}}^{\text{rt}} = -112.064$ ($c = 1.0166$, CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ

7.62 (td, $J = 7.6, 1.6$ Hz, 1H), 7.54 – 7.48 (m, 2H), 7.38 – 7.12 (m, 8H), 7.07 – 7.00 (m, 2H), 6.99 – 6.90

(m, 1H), 6.81 – 6.73 (m, 2H), 6.37 (d, $J = 2.1$ Hz, 1H), 6.30 (d, $J = 12.4$ Hz, 1H), 5.73 (s, 1H), 5.40 (d, $J =$

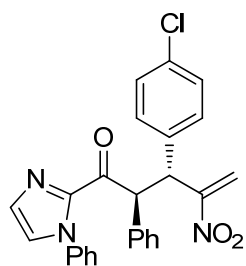
12.4 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, CDCl_3): δ 187.5, 161.0 (d, $J_{\text{C-F}} = 248.6$ Hz), 156.8, 142.3, 137.6,

135.4, 130.2 (d, $J_{\text{C-F}} = 3.5$ Hz), 130.0, 129.3, 129.2, 128.9, 128.8, 128.6, 127.9, 127.4, 125.0, 124.9 (d,

$J_{\text{C-F}} = 13.0$ Hz), 124.1 (d, $J_{\text{C-F}} = 3.5$ Hz), 121.0 (d, $J_{\text{C-F}} = 2.0$ Hz), 115.7 (d, $J_{\text{C-F}} = 22.1$ Hz), 54.1, 41.8 ppm; **IR**

(neat): 3354, 3064, 2925, 2406, 1952, 1884, 1795, 1685, 1230, 759, 602, 525 cm^{-1} ; **HRMS** (ESI):

$\text{C}_{26}\text{H}_{20}\text{FN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd: 464.1381, found: 464.1389.



3w.

Reaction for 9 h, Yellow solid, m.p. 80 – 82 $^{\circ}\text{C}$; 132.44 mg; Yield 96.6%; d. r. > 20:1; 93% ee

determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 80/20, flow rate = 1.0 mL/min,

$t_{\text{major}} = 10.7$ min, $t_{\text{minor}} = 12.0$ min); $[\alpha]_{\text{D}}^{\text{rt}} = -20.374$ ($c = 0.9816$, CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ

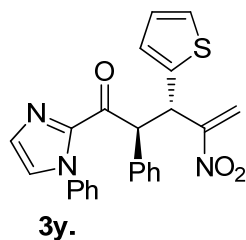
7.51 (d, $J = 7.2$ Hz, 2H), 7.42 – 7.16 (m, 11H), 7.04 (s, 1H), 6.77 (d, $J = 6.9$ Hz, 2H), 6.38 (d, $J = 2.4$ Hz,

1H), 6.04 (d, $J = 12.4$ Hz, 1H), 5.71 (d, $J = 2.3$ Hz, 1H), 5.25 (d, $J = 12.4$ Hz, 1H) ppm; **^{13}C NMR** (75 MHz,

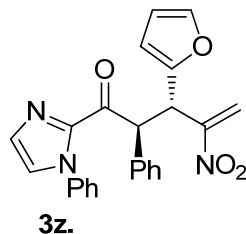
CDCl_3): δ 187.3, 158.2, 142.3, 137.5, 136.3, 135.5, 133.2, 130.2, 129.9, 129.0, 128.9, 128.8, 128.7,

128.6, 127.8, 127.6, 125.1, 119.5, 55.4, 46.4 ppm; **IR** (neat): 3353, 3063, 3029, 2929, 2405, 1951, 1897,

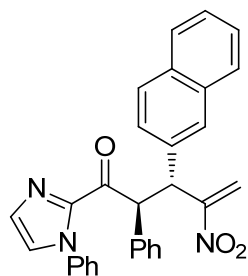
1735, 1685, 1400, 759, 532, 486 cm^{-1} ; **HRMS** (ESI): $\text{C}_{26}\text{H}_{20}\text{ClN}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd: 480.1085, found: 480.1091.



Reaction for 12 h, White solid, m.p. 151 – 153 $^{\circ}\text{C}$; 105.54 mg; Yield 82%; d. r. > 20:1; 96.06% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 80/20, flow rate = 1.0 mL/min, $t_{\text{major}} = 18.4$ min, $t_{\text{minor}} = 25.9$ min); $[\alpha]_{\text{D}}^{25} = 122.857$ ($c = 1.9866$, CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 7.50 – 7.44 (m, 2H), 7.42 – 7.19 (m, 7H), 7.15 (d, $J = 5.1$ Hz, 1H), 7.11 – 7.06 (m, 2H), 6.94 – 6.83 (m, 3H), 6.35 (d, $J = 2.2$ Hz, 1H), 6.10 (d, $J = 12.1$ Hz, 1H), 5.68 (d, $J = 2.3$ Hz, 1H), 5.55 (d, $J = 12.1$ Hz, 1H) ppm; **^{13}C NMR** (75 MHz, CDCl_3): δ 187.5, 158.2, 142.5, 141.3, 137.8, 135.5, 130.2, 129.2, 129.0, 129.0, 128.8, 128.0, 127.6, 126.9, 126.8, 125.4, 125.1, 120.1, 57.0, 42.9 ppm; **HRMS** (ESI): $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ calcd: 430.1220, found: 430.1224.

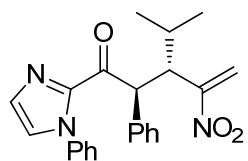


Reaction for 12 h, White solid, m.p. 136 – 138 $^{\circ}\text{C}$; 109.78 mg; Yield 88.6%; d. r. > 20:1; 97% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 80/20, flow rate = 1.0 mL/min, $t_{\text{major}} = 16.8$ min, $t_{\text{minor}} = 25.2$ min); $[\alpha]_{\text{D}}^{25} = 139$ ($c = 3.0147$, CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 7.44 – 7.34 (m, 5H), 7.30 – 7.19 (m, 5H), 7.12 (s, 1H), 7.01 (d, $J = 1.4$ Hz, 1H), 6.98 (d, $J = 2.0$ Hz, 1H), 6.38 (d, $J = 1.3$ Hz, 1H), 6.30 (d, $J = 3.2$ Hz, 1H), 6.26 – 6.22 (m, 1H), 6.05 (d, $J = 12.1$ Hz, 1H), 5.69 (d, $J = 2.1$ Hz, 1H), 5.36 (d, $J = 12.1$ Hz, 1H) ppm; **^{13}C NMR** (75 MHz, CDCl_3): δ 187.6, 156.1, 151.4, 142.2, 142.2, 137.9, 134.9, 130.2, 129.4, 129.0, 128.8, 128.0, 127.6, 125.4, 121.2, 110.5, 107.9, 54.9, 41.6 ppm; **IR** (neat): 3354, 3021, 2853, 2401, 1950, 1878, 1802, 1686, 1402, 756, 534, 478 cm^{-1} ; **HRMS** (ESI): $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_4$ $[\text{M}+\text{Na}]^+$ calcd: 436.1268, found: 436.1276.



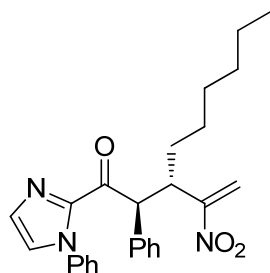
3aa.

Reaction for 12 h, White solid, m.p. 156 – 158 °C; 134.66 mg; Yield 94.9%; d. r. > 20:1; 93% ee determined by HPLC on a Chiralpak IC-H column (*n*-hexane/ *i*-PrOH = 80/20, flow rate = 1.0 mL/min, $t_{\text{major}} = 12.7$ min, $t_{\text{minor}} = 15.2$ min); $[\alpha]_{\text{D}}^{\text{rt}} = -76.071$ ($c = 4.0053$, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.93 (s, 1H), 7.82 – 7.70 (m, 3H), 7.62 – 7.51 (m, 3H), 7.50 – 7.40 (m, 2H), 7.36 – 7.13 (m, 7H), 6.96 (d, $J = 0.9$ Hz, 1H), 6.60 – 6.49 (m, 2H), 6.44 (d, $J = 2.4$ Hz, 1H), 6.17 (d, $J = 12.4$ Hz, 1H), 5.81 (d, $J = 2.3$ Hz, 1H), 5.47 (d, $J = 12.4$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 187.6, 158.4, 142.3, 137.4, 135.7, 135.0, 133.0, 132.4, 129.8, 129.0, 128.9, 128.6, 128.4, 128.3, 128.2, 127.8, 127.7, 127.4, 127.4, 126.2, 126.1, 126.0, 125.0, 119.3, 55.5, 47.2 ppm; IR (neat): 3353, 2959, 1953, 1880, 1720, 1685, 1401, 760, 697 cm^{-1} ; HRMS (ESI): $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd: 496.1632, found: 496.1640.



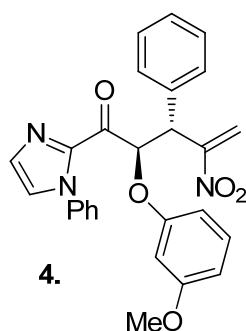
3ab.

Reaction for 30 h, White solid, m.p. 140 – 142 °C; 99.74 mg; Yield 82.9%; d. r. > 20:1; 86.78% ee determined by HPLC on a Chiralpak IA-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, $t_{\text{minor}} = 11.3$ min, $t_{\text{major}} = 12.1$ min); $[\alpha]_{\text{D}}^{\text{rt}} = 97.364$ ($c = 2.0233$, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.44 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 7.26 (s, 2H), 7.23 – 7.20 (m, 1H), 7.19 – 7.11 (m, 2H), 7.07 – 7.01 (m, 2H), 6.37 (s, 1H), 5.56 (d, $J = 11.6$ Hz, 1H), 5.43 (d, $J = 1.7$ Hz, 1H), 4.22 (s, 1H), 2.06 (dq, $J = 13.1$, 6.6 Hz, 1H), 0.94 (d, $J = 6.8$ Hz, 3H), 0.86 (d, $J = 6.8$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 188.7, 157.4, 142.4, 137.9, 136.3, 129.9, 129.6, 129.0, 128.8, 128.6, 127.5, 127.4, 125.4, 120.5, 77.2, 55.0, 30.3, 21.3 ppm; HRMS (ESI): $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd: 412.1632, found: 412.1622.



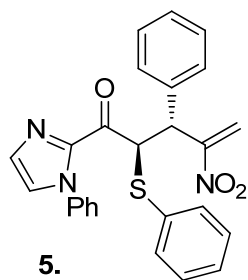
3ac.

Reaction for 12 h, Faint yellow liquid; 116.11 mg; Yield 89.8%; d. r. = 24:1; 96.88% ee determined by HPLC on a Chiralpak IA-H column (*n*-hexane/ *i*-PrOH = 90/10, flow rate = 1.0 mL/min, $t_{\text{major}} = 11.7$ min, $t_{\text{minor}} = 14.0$ min); dr = 49:2 determined by NMR; $[\alpha]_{\text{D}}^{\text{rt}} = 65.455$ ($c = 2.0166$, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.44 (d, $J = 1.7$ Hz, 1H), 7.43 – 7.40 (m, 1H), 7.31 – 7.16 (m, 5H), 7.14 (s, 1H), 7.12 – 7.07 (m, 2H), 6.24 (s, 1H), 5.53 (d, $J = 11.2$ Hz, 1H), 5.38 (d, $J = 1.6$ Hz, 1H), 3.87 (td, $J = 10.7, 3.8$ Hz, 1H), 1.77 – 1.51 (m, 2H), 1.25 – 1.05 (m, 10H), 0.82 (t, $J = 6.7$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 188.9, 158.6, 142.7, 138.0, 136.0, 129.9, 129.3, 129.0, 128.8, 128.7, 127.5, 127.4, 125.4, 120.1, 57.1, 43.3, 32.6, 31.5, 28.9, 27.3, 22.4, 14.0 ppm; **HRMS** (ESI): $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd: 454.2101, found: 454.2093.



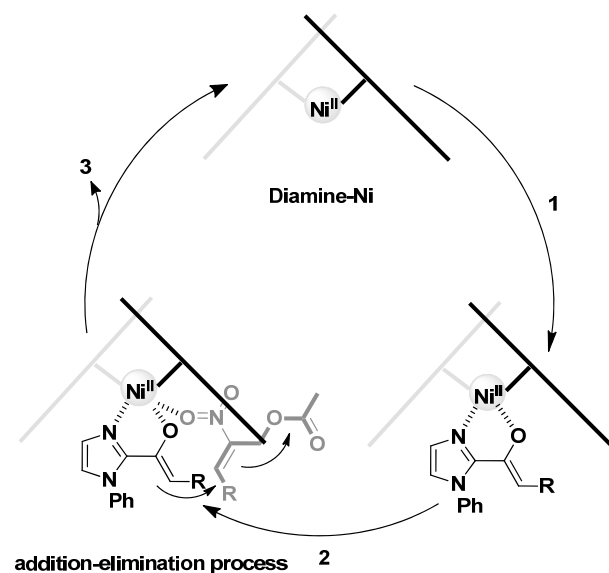
4.

Reaction for 31 h, White solid, m.p. 138 – 140 °C; 63.74 mg; Yield 45.3%; d. r. > 20:1; 93.9% ee determined by HPLC on a Chiralpak IA-H column (*n*-hexane/ *i*-PrOH = 80/20, flow rate = 1.0 mL/min, $t_{\text{minor}} = 35.6$ min, $t_{\text{major}} = 51.2$ min); $[\alpha]_{\text{D}}^{\text{rt}} = -23.369$ ($c = 0.9962$, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.31 (m, 4H), 7.17 (m, 5H), 6.97 (m, 4H), 6.67 (d, $J = 2.4$ Hz, 1H), 6.44 (m, 4H), 6.07 (d, $J = 1.8$ Hz, 1H), 5.19 (d, $J = 6.9$ Hz, 1H), 3.62 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 186.0, 160.7, 158.5, 156.3, 141.6, 137.3, 135.4, 130.3, 130.0, 129.1, 128.9, 128.9, 128.6, 127.9, 127.6, 125.6, 120.3, 107.9, 107.2, 101.5, 78.7, 55.2, 48.3 ppm; **IR** (neat): 3351, 3062, 3023, 2837, 2549, 2200, 1951, 1879, 1685, 1400, 760, 615, 529, 402 cm^{-1} ; **HRMS** (ESI): $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_5$ $[\text{M}+\text{Na}]^+$ calcd: 492.1530, found: 492.1541.

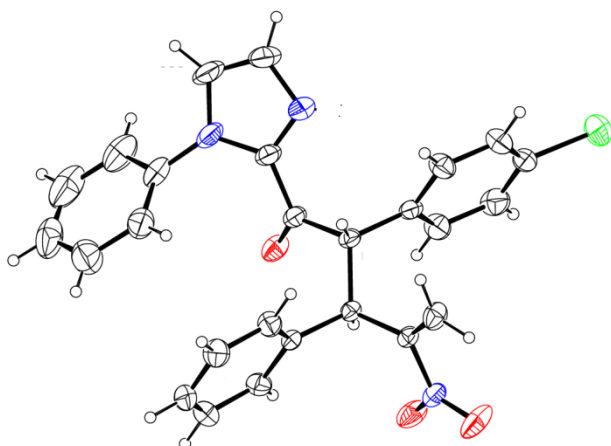


Reaction for 13 h, Faint yellow liquid; 99.90 mg; Yield 73.2%; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.45 – 7.40 (m, 2H), 7.36 (d, J = 7.6 Hz, 2H), 7.33 – 7.24 (m, 7H), 7.21 – 7.11 (m, 4H), 6.97 (d, J = 6.8 Hz, 2H), 6.68 (d, J = 2.4 Hz, 1H), 5.90 (d, J = 2.4 Hz, 1H), 5.77 (d, J = 12.3 Hz, 1H), 4.84 (d, J = 12.3 Hz, 1H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 183.7, 158.1, 142.0, 137.6, 137.2, 133.9, 131.9, 129.7, 129.0, 128.9, 128.7, 128.7, 128.7, 128.5, 127.6, 127.4, 125.3, 119.7, 53.9, 46.1 ppm; **HRMS** (ESI): $\text{C}_{26}\text{H}_{22}\text{N}_3\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ calcd: 456.1376, found: 456.1381.

Proposed mechanism cycle of the reaction



X-Ray crystallographic analysis of 3t



CCDC 1563146

Bond precision:

$$C-C = 0.0062 \text{ A}$$

Wavelength=0.71073

Cell:

$$a=5.9123(2)$$
$$b=16.6068(8)$$
$$c=23.6020(8)$$

alpha=90

beta=90

gamma=90

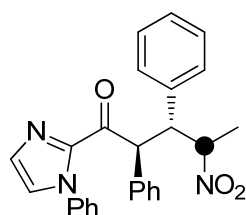
Temperature: 291 K

	Calculated	Reported
Volume	2317.35(16)	2317.35(16)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C26 H21 Cl N3 O3	C26 H21 Cl N3 O3
Sum formula	C26 H21 Cl N3 O3	C26 H21 Cl N3 O3
Mr	458.91	458.91
Dx,g cm-3	1.315	1.315
Z	4	4
Mu (mm-1)	0.198	0.198
F000	956.0	956.0
F000'	956.98	
h,k,lmax	7,20,29	7,20,29
Nref	4572[2649]	4048

Tmin,Tmax 0.965,0.973 0.943,1.000
 Tmin' 0.955
 Correction method= # Reported T Limits: Tmin=0.943 Tmax=1.000 AbsCorr =
 MULTI-SCAN
 Data completeness= 1.53/0.89 Theta(max)= 26.020
 R(reflections)= 0.0577(2930) wR2(reflections)= 0.1287(4048)
 S = 1.054 Npar= 298

Transformation of alkylation product

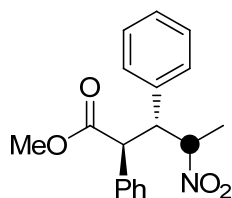
Synthesis of **3o** on 1.0 mmol scale. To a weighted together mixture of **L1**/**Ni(OAc)₂**(10 mol%), Al₂O₃ (12 eq, 1.22 g), ketone **1o** (1.0 mmol) and nitroallylic acetate **2a** (1.2 eq, 3.6 mmol) was added THF (3.0 ml), Then the mixture was stirred at 10 °C for 42h. Then the reaction mixture was purified by silica gel column chromatography (PE : EA = 10:1 to PE : EA = 4:1) to afford product **3o**, 393.4 mg, Yield 93%, dr > 20:1, ee = 90%.



6.

To a stirred solution of 4-nitro-2,3-diphenyl-1-(1-phenyl-1H-imidazol-2-yl)pent-4-en-1-one (199 mg, 0.47 mmol) in MeOH (4.0 mL) was added NaBH₄ (26.6mg, 0.7 mmol) portion wise at 0 °C. The reaction was stirred for 30 min at rt and quenched with sat. NH₄Cl (3.0 mL) and water (3.0 mL). The organic layer was extracted with CH₂Cl₂ (3 x 15 mL) and the combined organic layers was washed with brine, dried

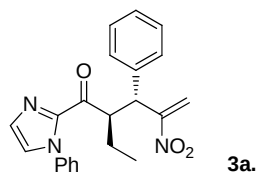
over anhydrous MgSO_4 , filtered and the solvent was removed under reduced pressure. The obtained crude product was purified by flash column chromatography on silica gel (PE:EA = 20:1) to afford **6** (144.3 mg, 72%) as a yellow solid. d. r. = 1.4:1; ^1H NMR (300 MHz, CDCl_3): δ 7.72 (d, J = 7.3 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.31 (dd, J = 7.1, 4.1 Hz, 2H), 7.27 – 7.19 (m, 8H), 6.99 (s, 1H), 6.53 (d, J = 7.5 Hz, 2H), 6.19 (d, J = 12.4 Hz, 1H), 4.58 (qd, J = 6.7, 2.8 Hz, 1H), 3.84 (dd, J = 12.4, 2.7 Hz, 1H), 1.29 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 189.0, 142.8, 137.8, 136.2, 135.9, 130.0, 129.8, 129.3, 129.0, 128.8, 128.4, 128.4, 127.9, 127.9, 127.1, 125.0, 82.4, 54.0, 53.0, 17.3 ppm.



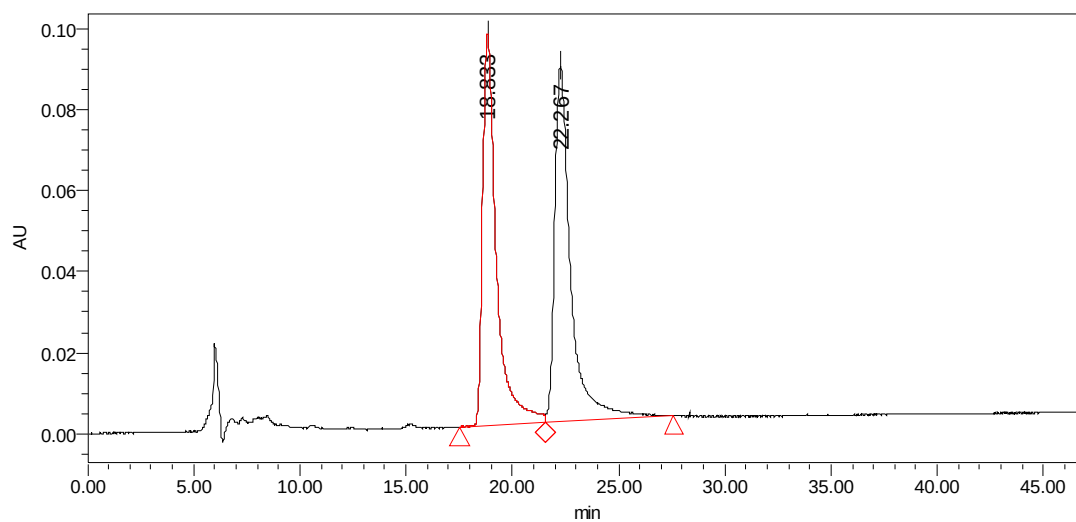
7.

6 (0.34 mmol, 144.3 mg, 1.00 equiv), 4Å molecular sieves (170 mg), and acetonitrile (2.0 ml) were combined in an oven dried airtight flask. The suspension was stirred vigorously under a positive pressure of nitrogen for 2 hours. Then methyl trifluoromethanesulfonate (0.578 mmol, 68 μl , 1.70 equiv.) was added. After 2 h another 0.6 equiv methyl trifluoromethanesulfonate was added and the reaction stirred an additional 30 minutes. Then the reaction was cooled to 0 °C. Then MeOH (138 μl , 3.40 mmol, 10.0 equiv) and DBU (104 μl , 0.68 mmol, 2.0 equiv) was added stepwise. The reaction was then stirred for 30 min before quenched by 1 M HCl (10 ml) and extracted with EA (3 x 15 ml) and the combined organic dried over anhydrous MgSO_4 and the solvent was removed in vacuo. The product was purified by flash chromatography (PE: EA= 20:1) to give **7** in 76% yield (80.88 mg). Faint yellow liquid; Yield 76%; d. r. = 6.6:1; $[\alpha]_D^{25} = 23.390$ (c = 0.9833, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.62 (d, J = 7.2 Hz, 2H), 7.47 – 7.36 (m, 3H), 7.32 (d, J = 6.5 Hz, 3H), 7.23 – 7.16 (m, 2H), 4.57 (d, J = 12.2 Hz, 1H), 4.54 – 4.45 (m, 1H), 3.65 (dd, J = 12.1, 2.3 Hz, 1H), 3.36 (s, 3H), 1.30 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 172.5, 136.0, 135.2, 129.1, 129.0, 128.7, 128.6, 128.4, 128.3, 81.6, 53.6, 53.4, 52.0, 17.3 ppm; HRMS (ESI): $\text{C}_{18}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{Na}]^+$ calcd: 336.1206, found: 336.1202.

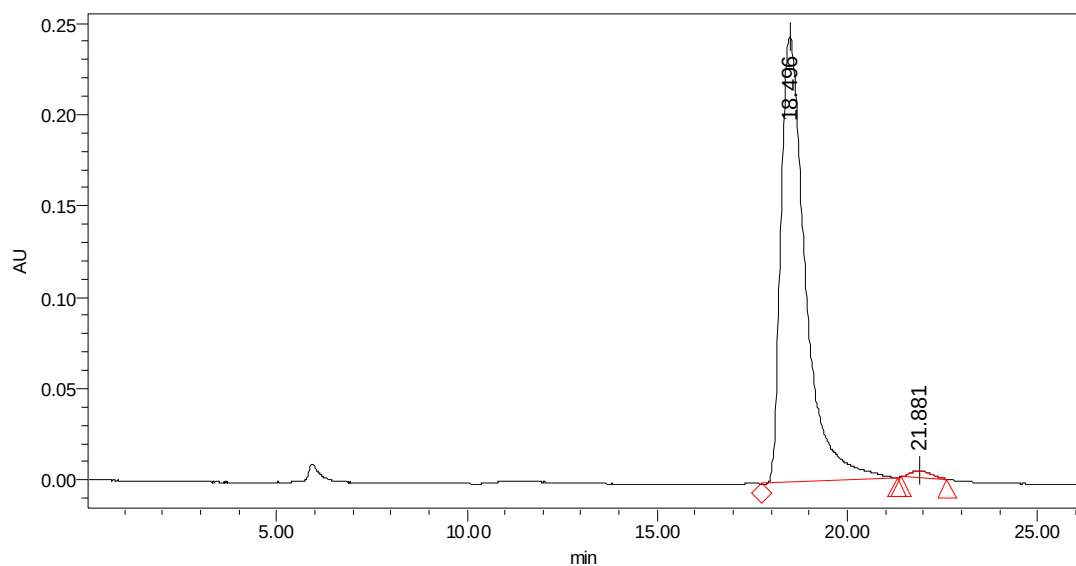
HPLC Results



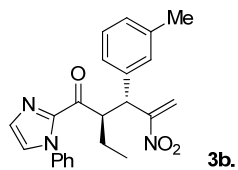
HPLC using an IA-H (*n*-Hexane/*i*-PrOH=97/3, flow rate 1.0 mL/min)



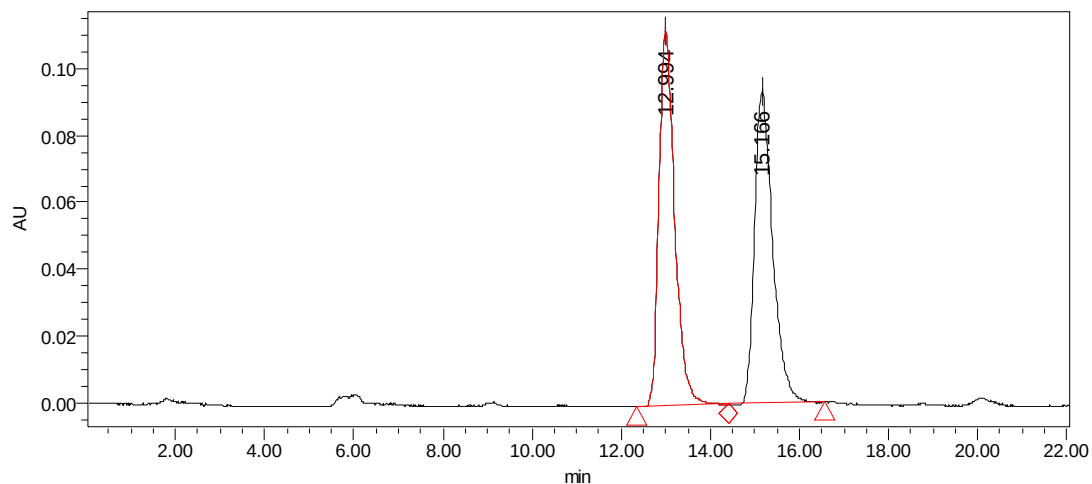
	Retention Time	Area	% Area	Height
1	18.833	4405359	48.80	96708
2	22.267	4622803	51.20	88024



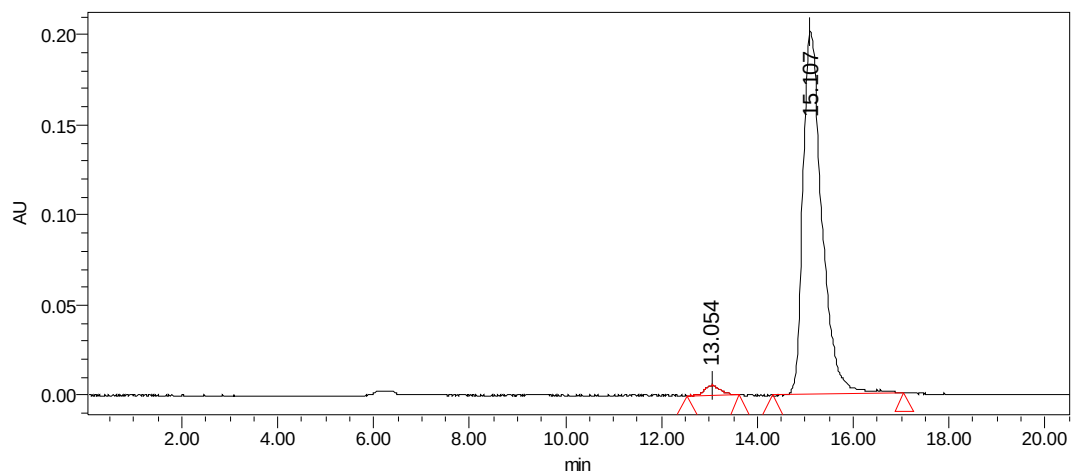
	Retention Time	Area	% Area	Height
1	18.496	10977659	98.69	243871
2	21.881	145480	1.31	3795



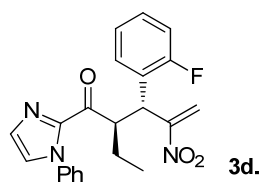
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



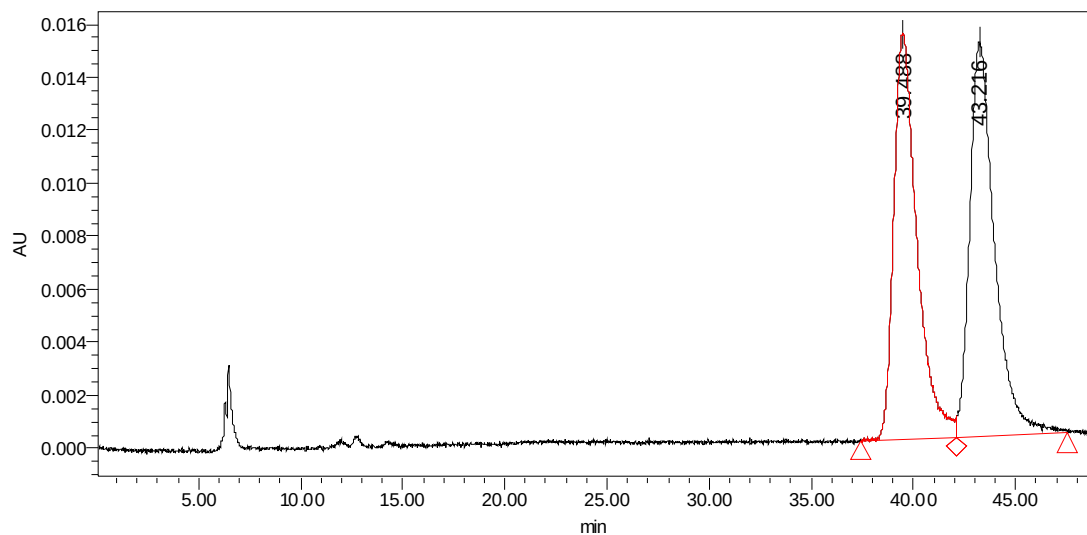
	Retention Time	Area	% Area	Height
1	12.994	2759666	51.22	112223
2	15.166	2628246	48.78	93294



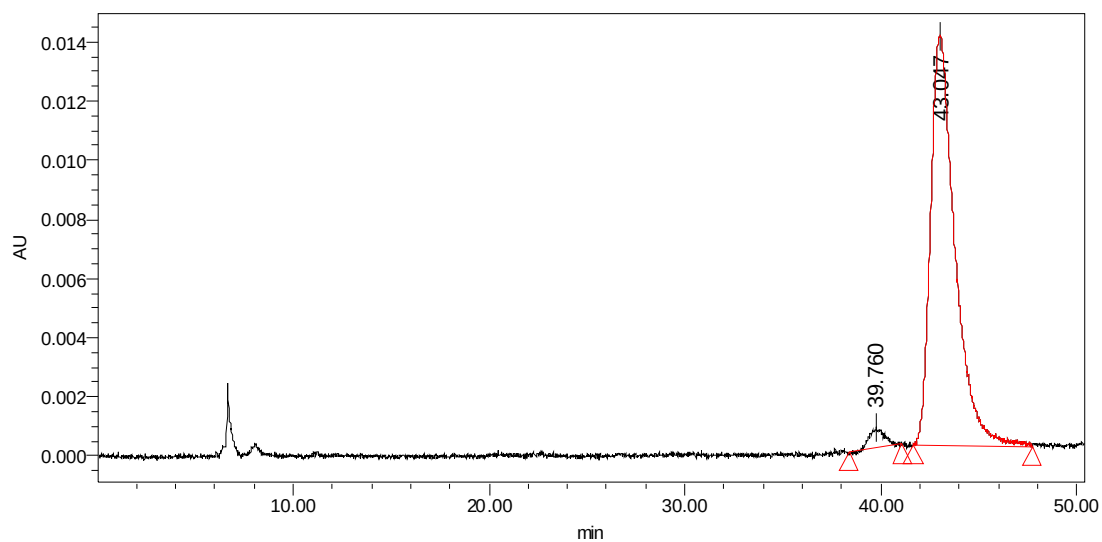
	Retention Time	Area	% Area	Height
1	13.054	124021	2.17	5540
2	15.107	5583206	97.83	202225



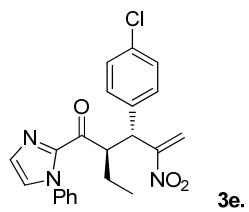
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=97/3, flow rate 1.0 mL/min)



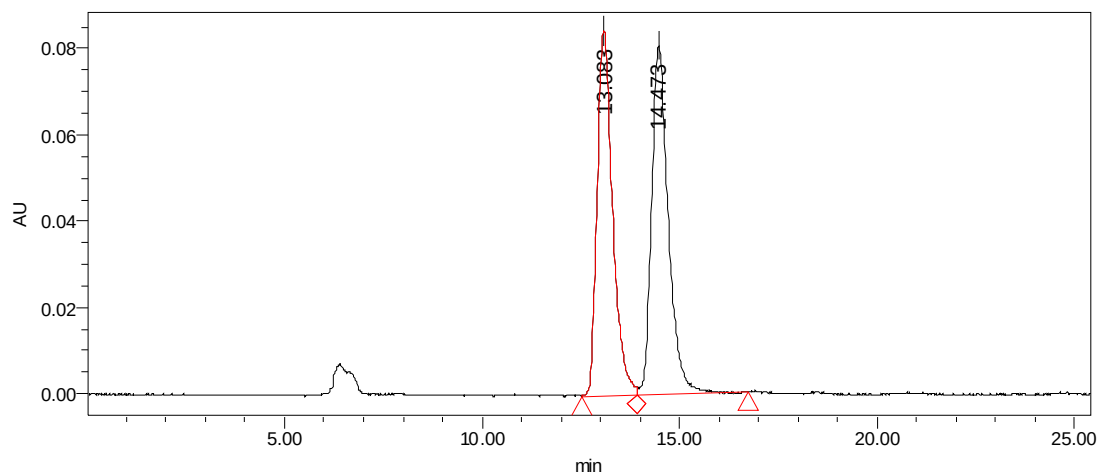
	Retention Time	Area	% Area	Height
1	39.488	1207242	48.97	15268
2	43.216	1258036	51.03	14865



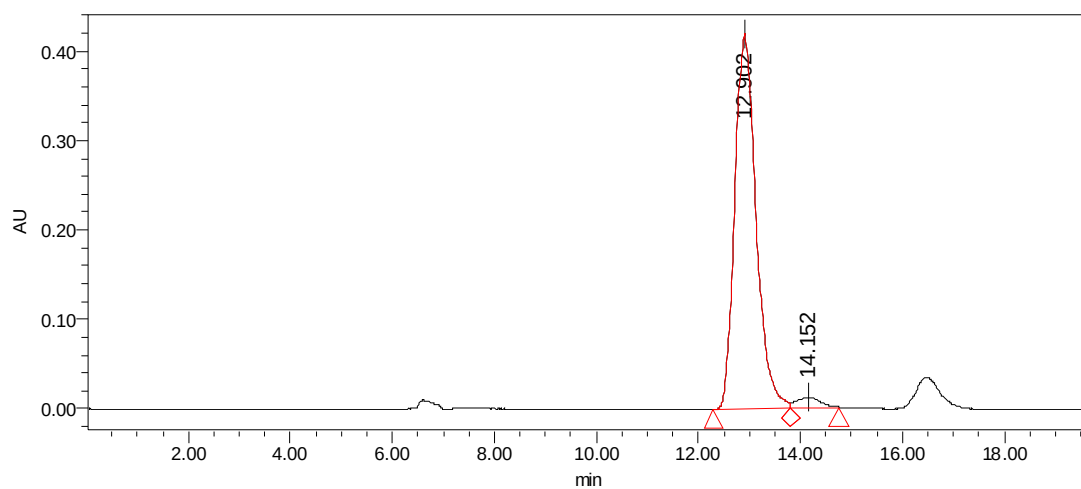
	Retention Time	Area	% Area	Height
1	39.760	36936	2.99	621
2	43.047	1200237	97.01	13867



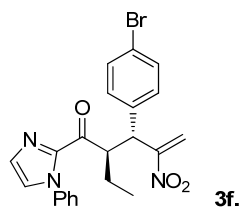
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=95/5, flow rate 1.0 mL/min)



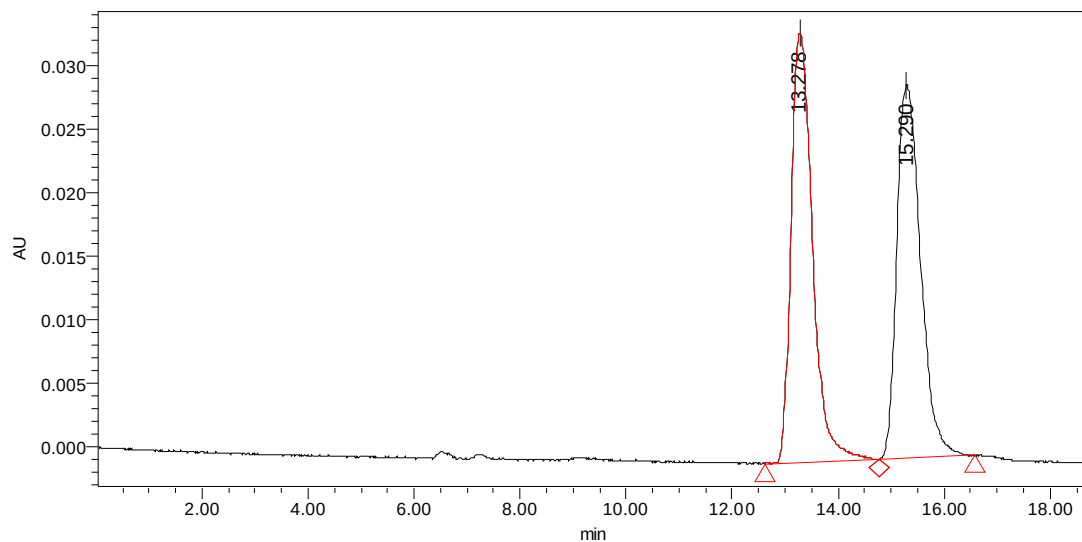
	Retention Time	Area	% Area	Height
1	13.083	2295320	49.11	84443
2	14.473	2378095	50.89	80803



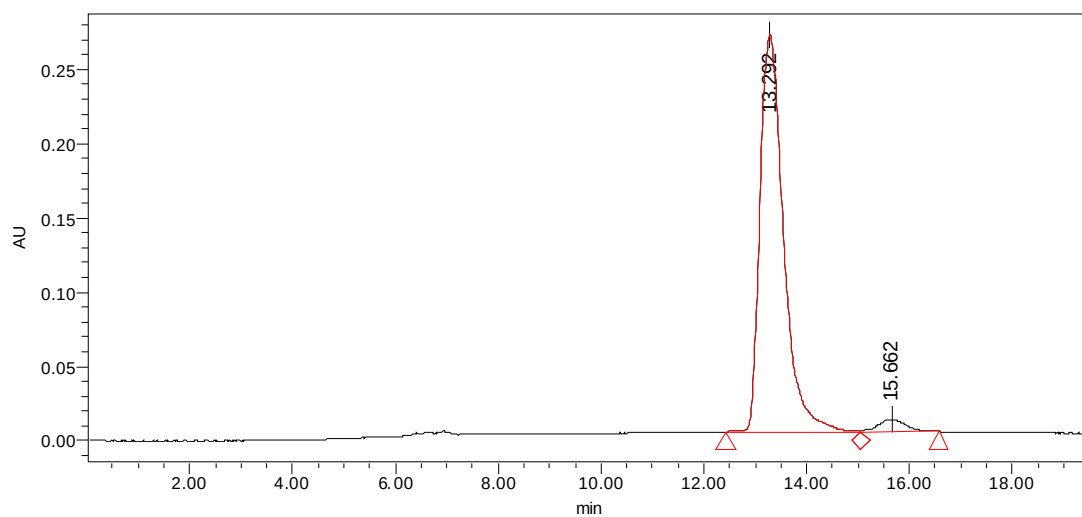
	Retention Time	Area	% Area	Height
1	12.902	11950163	96.96	420231
2	14.152	374595	3.04	11614



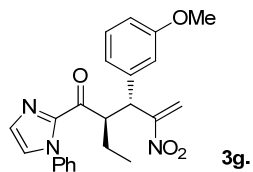
HPLC using an IA-H (*n*-Hexane/*i*-PrOH=95/5, flow rate 1.0 mL/min)



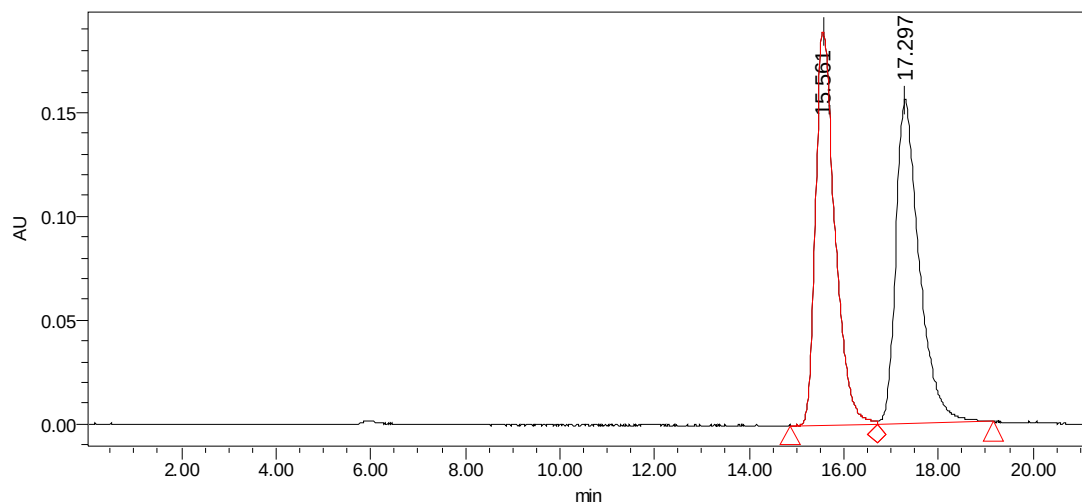
	Retention Time	Area	% Area	Height
1	13.278	942972	50.86	33799
2	15.290	911157	49.14	29358



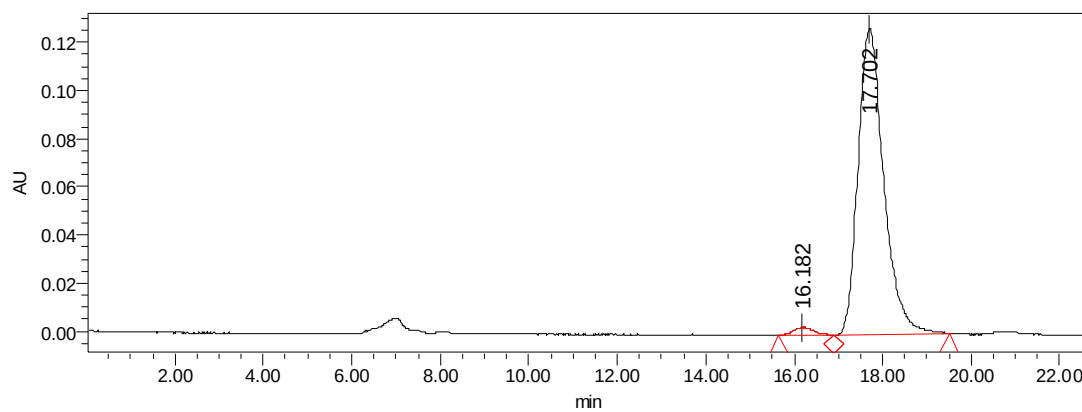
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1	13.292	8511310	96.52	267741
2	15.662	307202	3.48	8207



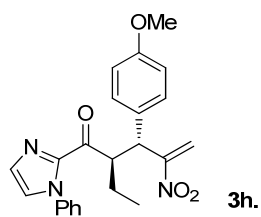
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



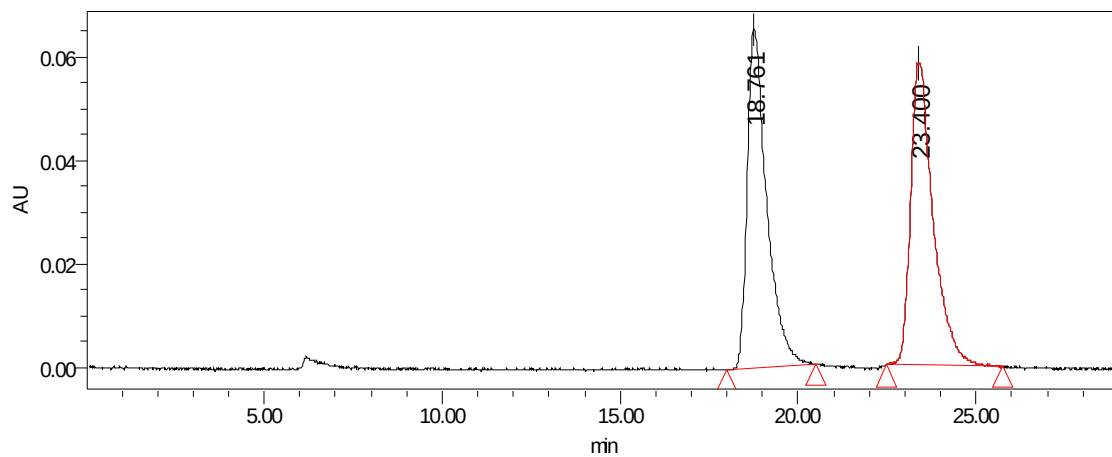
	Retention Time	Area	% Area	Height
1	15.561	5415345	50.15	189405
2	17.297	5382537	49.85	155898



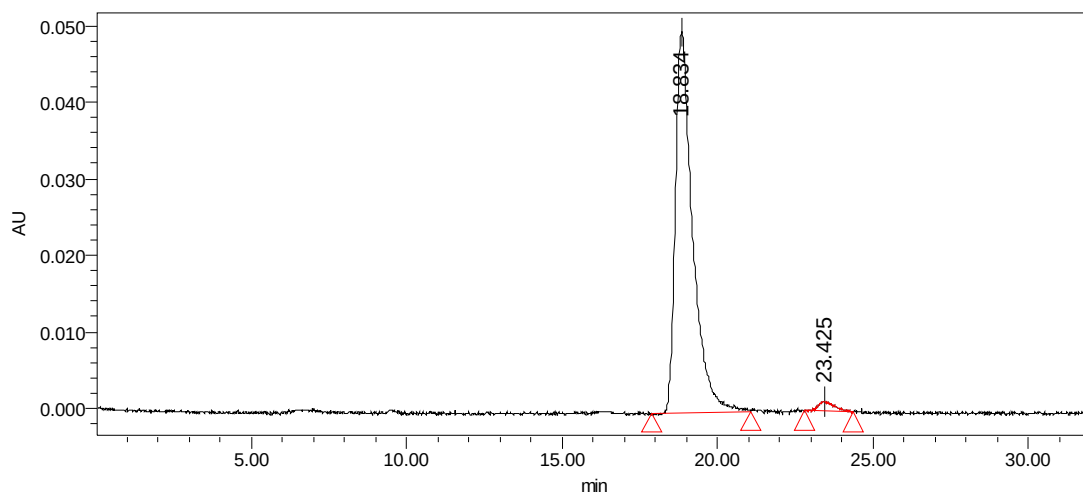
	Retention Time	Area	% Area	Height
1	16.182	96784	1.87	3083
2	17.702	5090453	98.13	126906



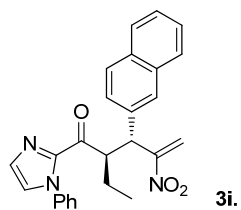
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



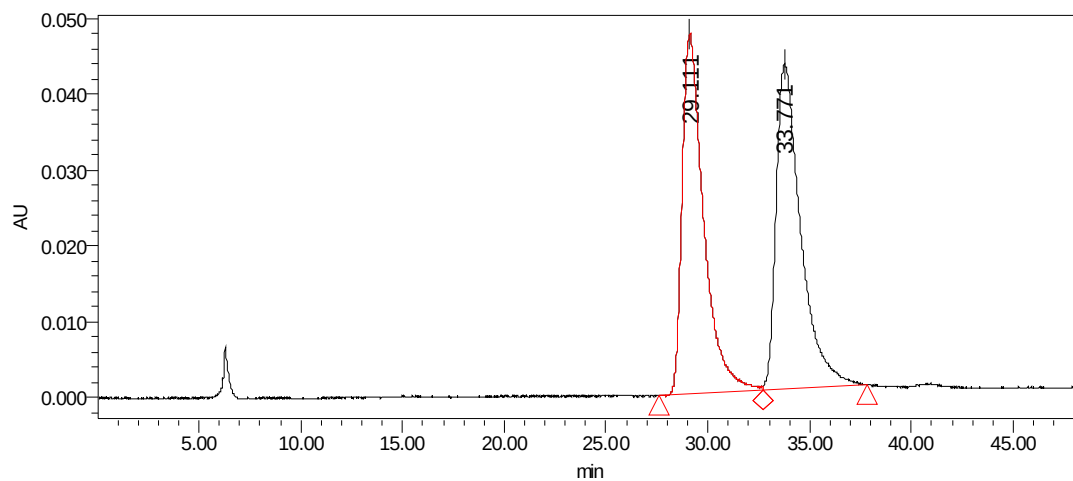
	Retention Time	Area	% Area	Height
1	18.761	2504799	49.47	65720
2	23.400	2558918	50.53	58364



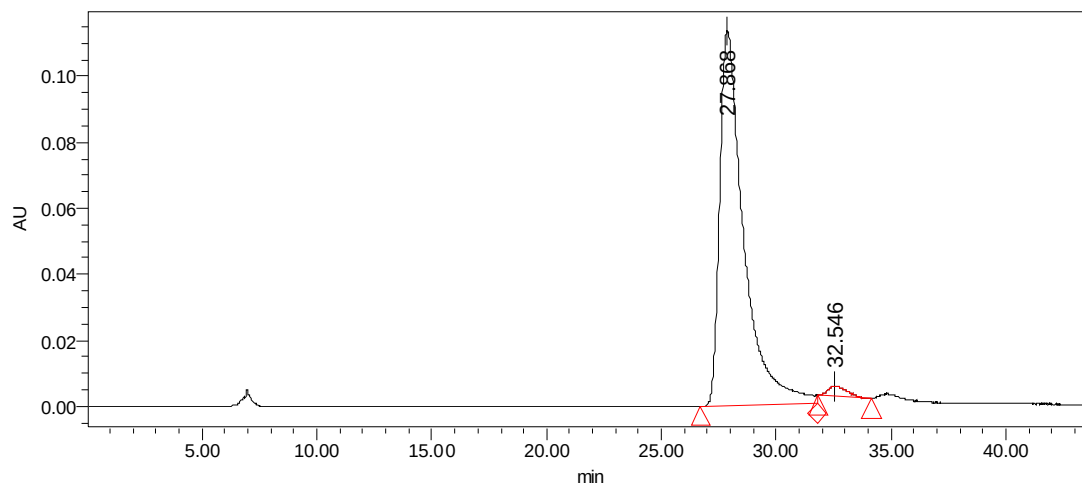
	Retention Time	Area	% Area	Height
1	18.834	1925357	97.52	49698
2	23.425	49038	2.48	1286



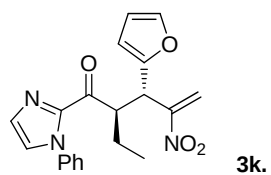
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=97/3, flow rate 1.0 mL/min)



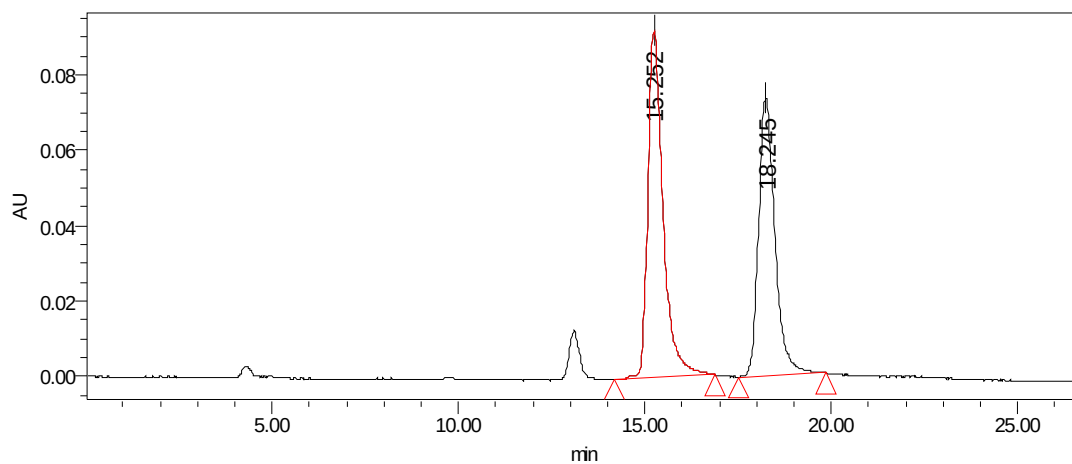
	Retention Time	Area	% Area	Height
1	29.111	3488985	49.25	47486
2	33.771	3595602	50.75	42796



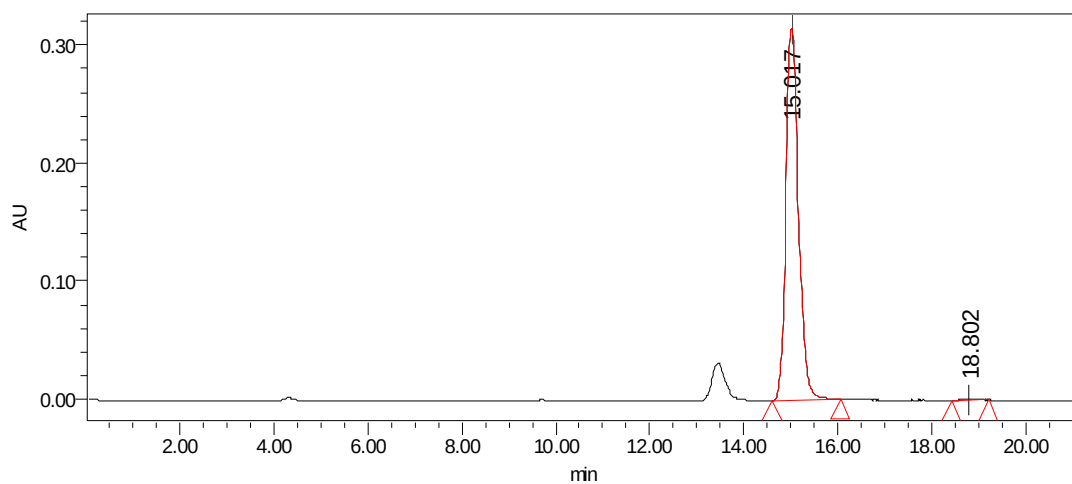
	Retention Time	Area	% Area	Height
1	27.868	8301254	97.92	113679
2	32.546	175927	2.08	3039



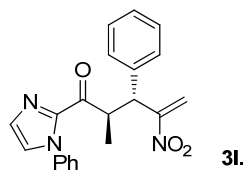
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



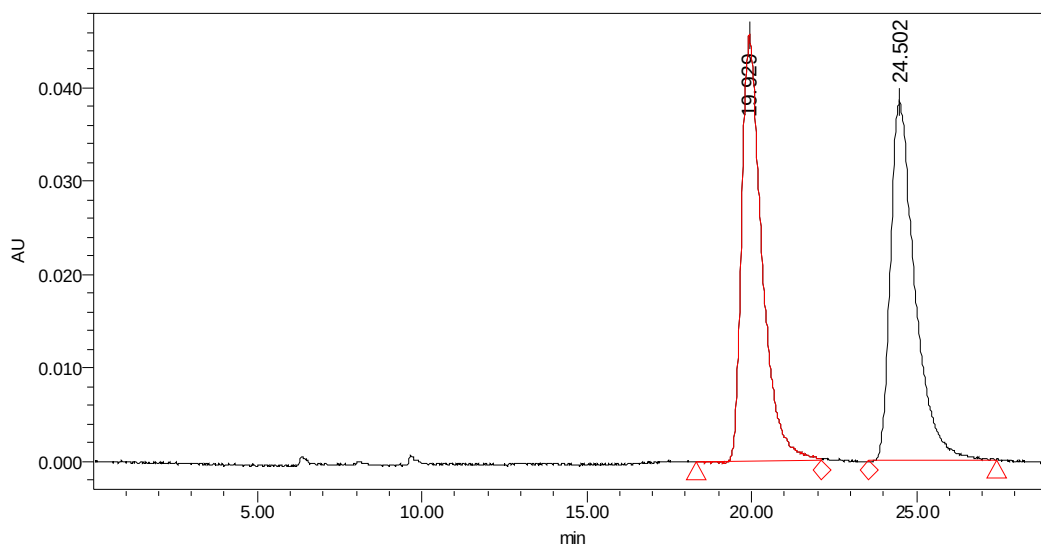
	Retention Time	Area	% Area	Height
1	15.252	2613502	53.69	92216
2	18.245	2254224	46.31	73631



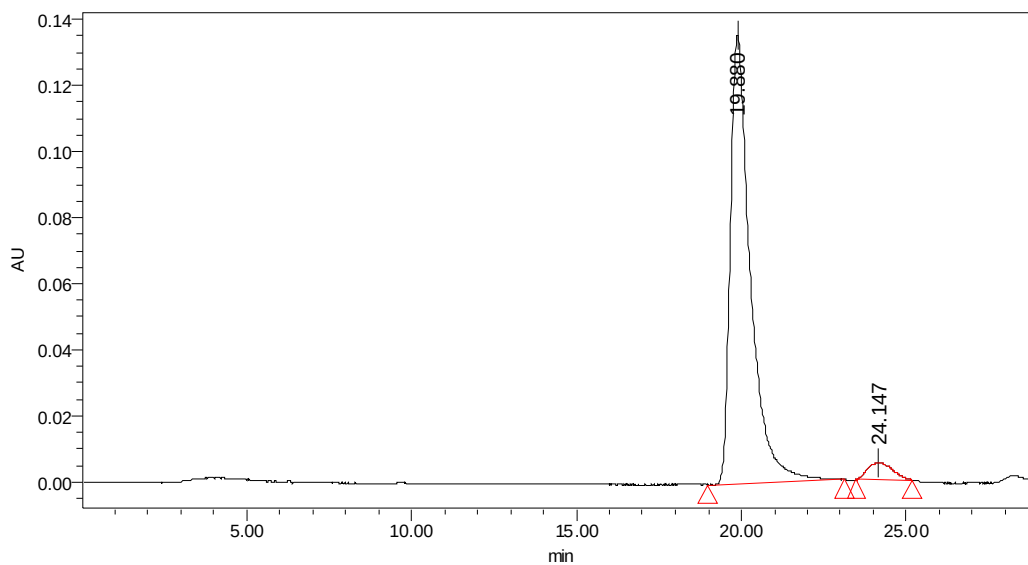
	Retention Time	Area	% Area	Height
1	15.017	5836373	99.82	314473
2	18.802	10442	0.18	527



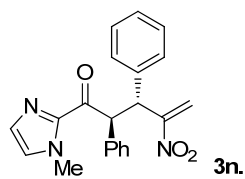
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



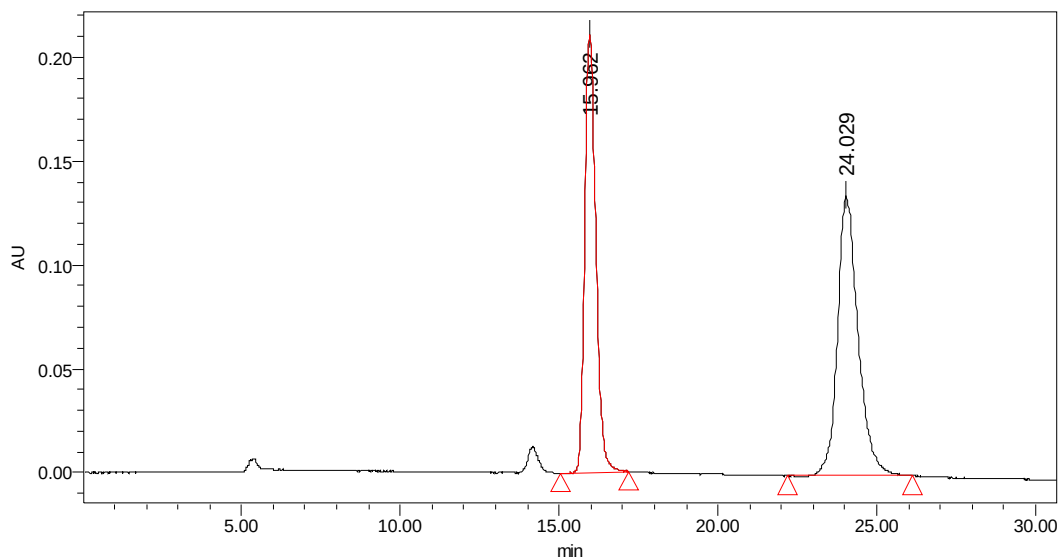
	Retention Time	Area	% Area	Height
1	19.929	1955966	49.73	45740
2	24.502	1977437	50.27	38410



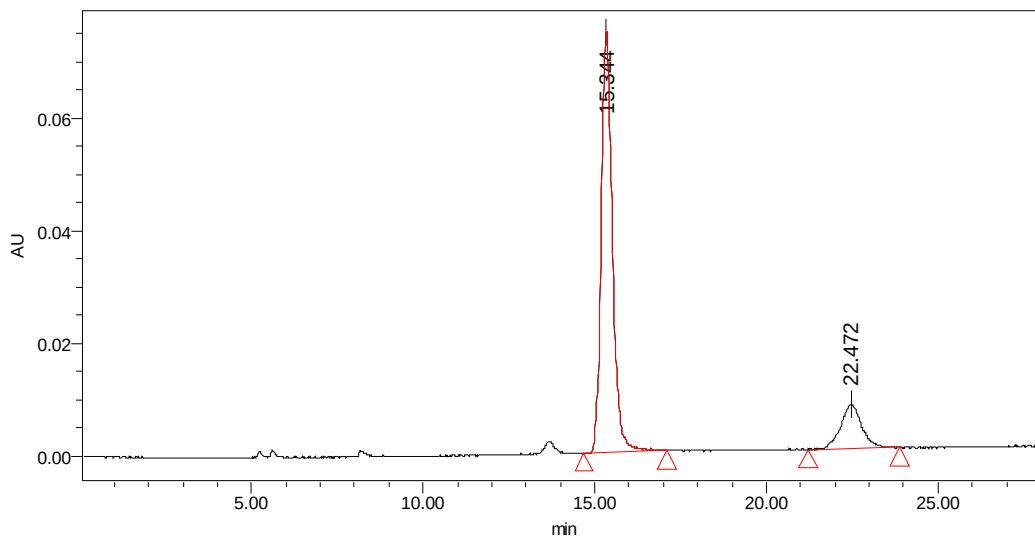
	Retention Time	Area	% Area	Height
1	19.880	5731756	95.52	135665
2	24.147	268836	4.48	5135



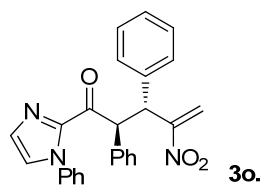
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



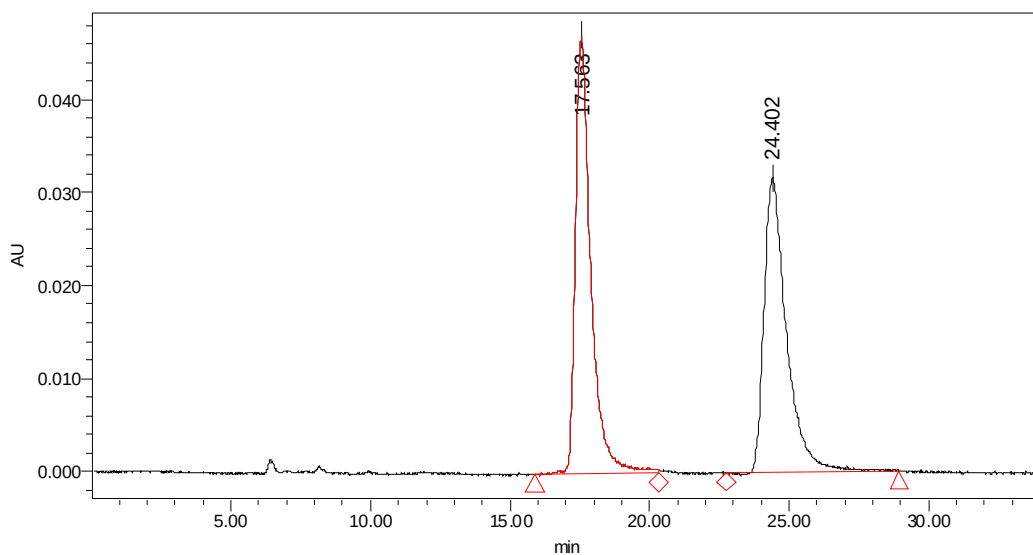
	Retention Time	Area	% Area	Height
1	15.962	5210187	46.03	211302
2	24.029	6109805	53.97	135400



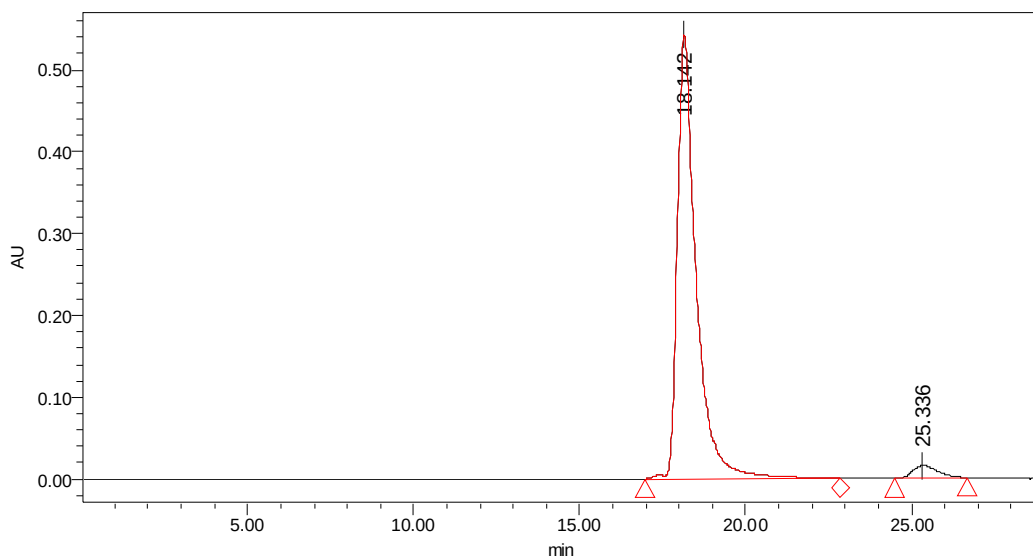
	Retention Time	Area	% Area	Height
1	15.344	1699416	83.47	74717
2	22.472	336530	16.53	7858



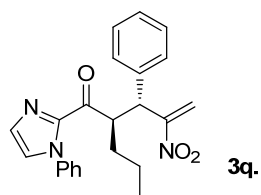
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



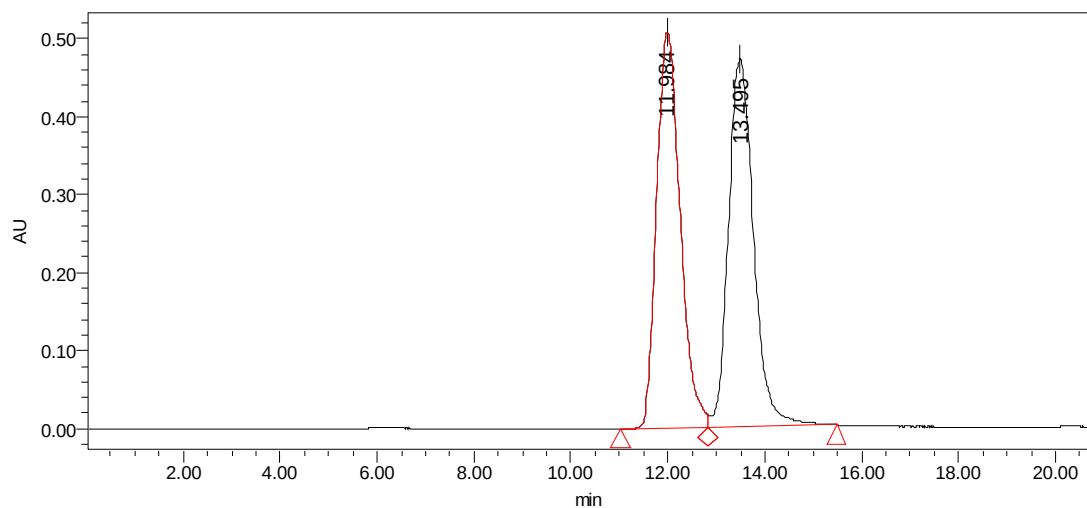
	Retention Time	Area	% Area	Height
1	17.563	1816452	50.70	47306
2	24.402	1766374	49.30	31583



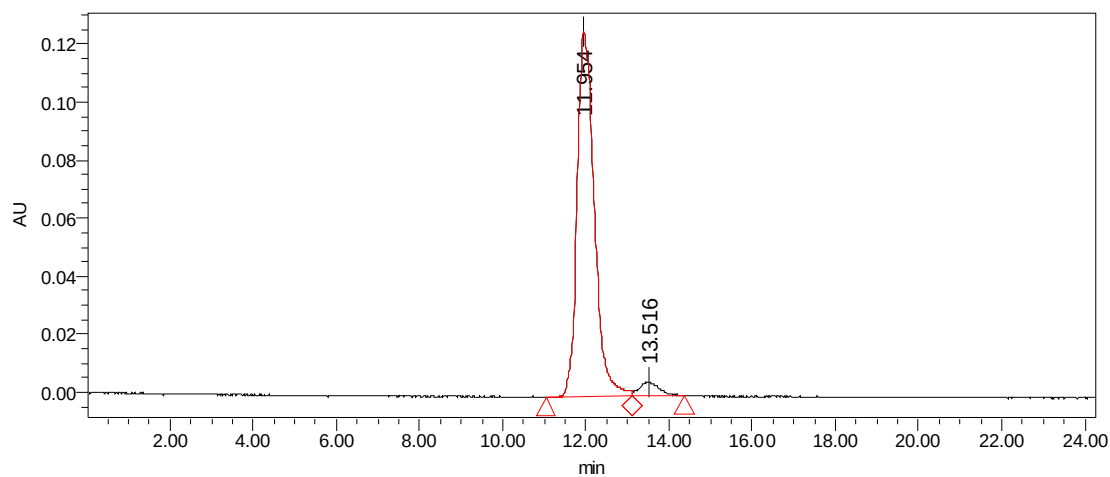
	Retention Time	Area	% Area	Height
1	18.142	21539923	96.34	542905
2	25.336	818178	3.66	15663



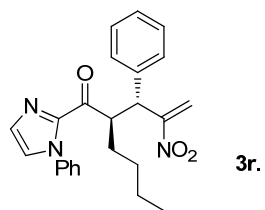
HPLC using an IA-H (*n*-Hexane/*i*-PrOH=95/5, flow rate 1.0 mL/min)



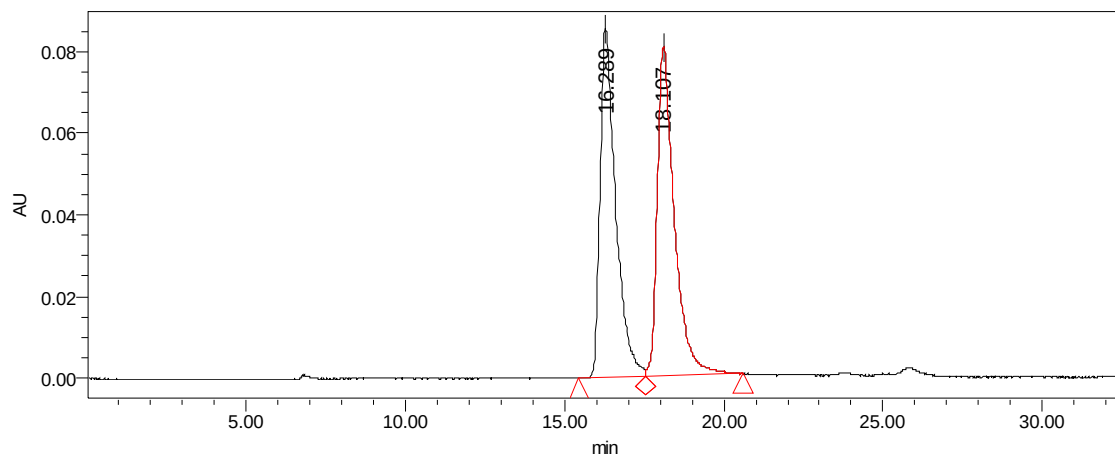
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1	11.984	17161316	50.18	507130
2	13.495	17035745	49.82	471620



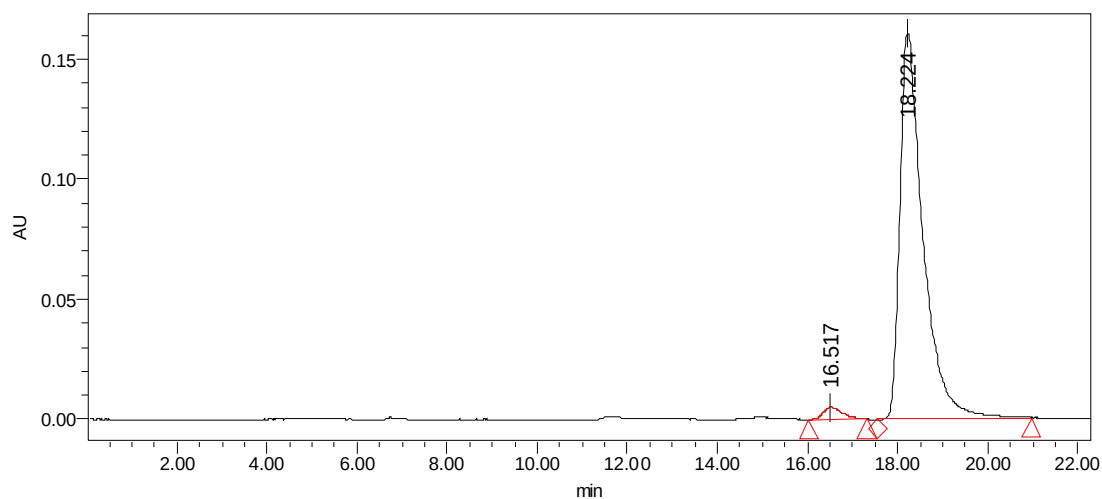
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1	11.954	3618931	96.01	125635
2	13.516	150343	3.99	4616



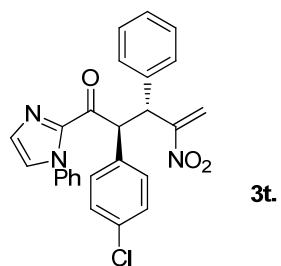
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=95/5, flow rate 1.0 mL/min)



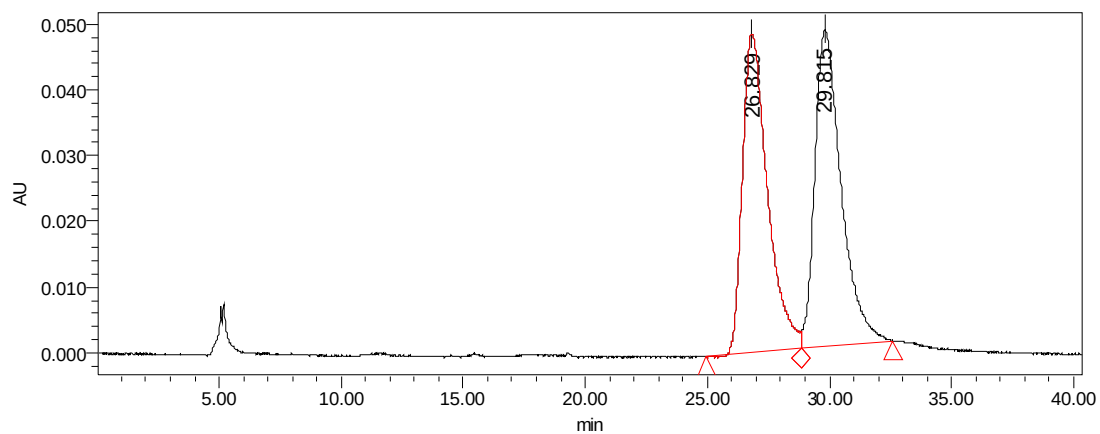
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1	16.289	2911217	49.19	85267
2	18.107	3006942	50.81	80429



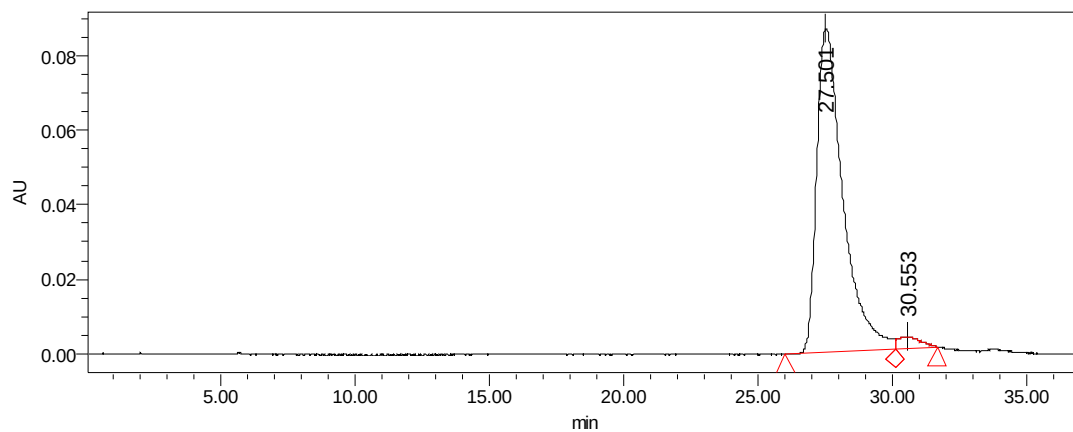
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1	16.517	149746	2.55	5047
2	18.224	5728913	97.45	160499



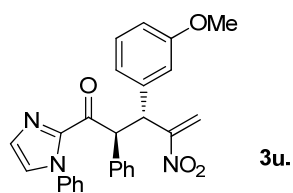
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=98/2, flow rate 1.0 mL/min)



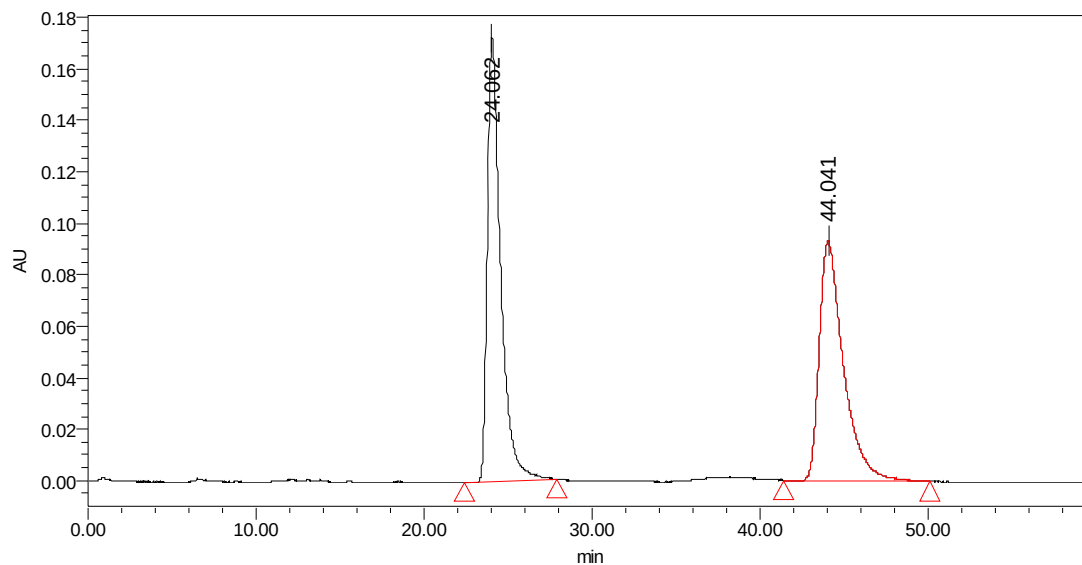
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1	26.829	3486741	49.13	48523
2	29.815	3610809	50.87	48280



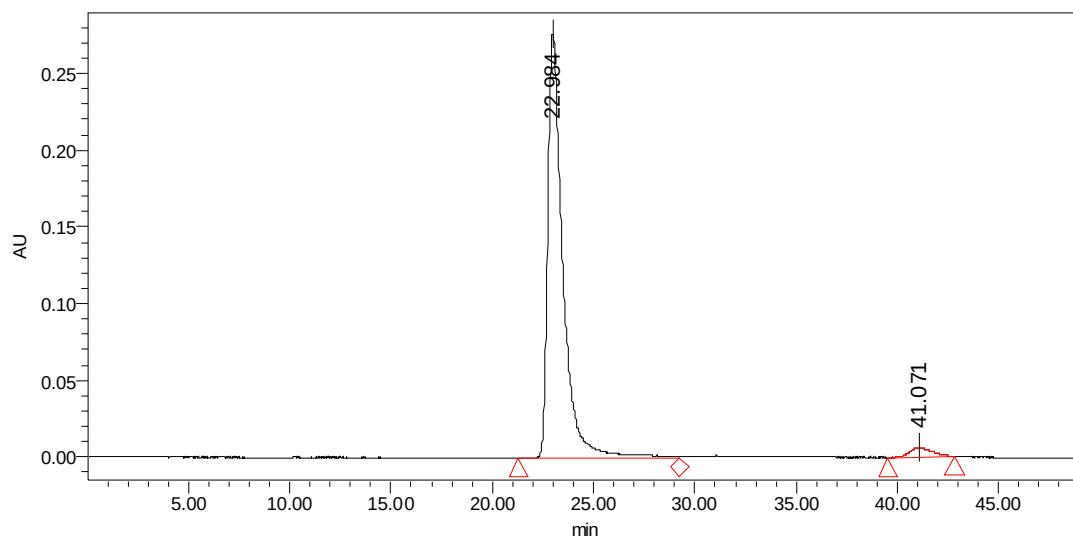
	Retention Time	Area	% Area	Height
1	27.501	5914374	96.96	86911
2	30.553	185721	3.04	3118



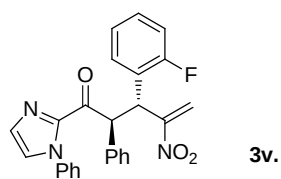
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



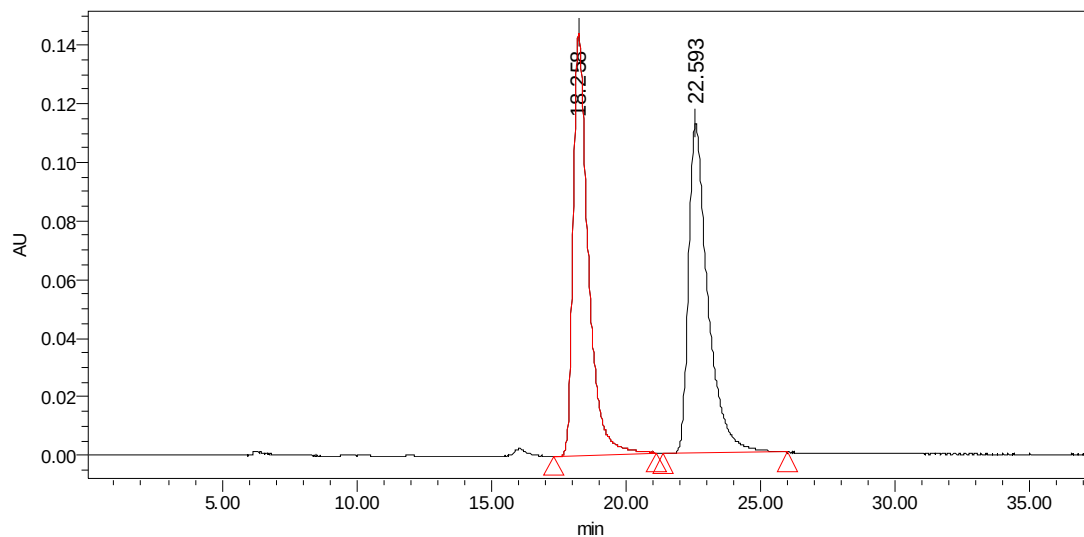
	Retention Time	Area	% Area	Height
1	24.062	9545421	50.58	172279
2	44.041	9327584	49.42	93191



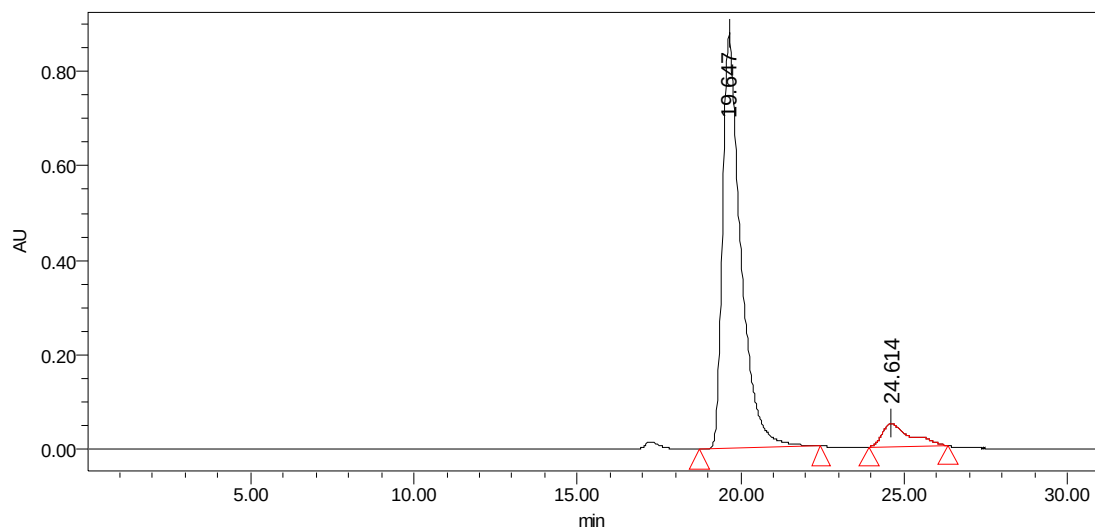
	Retention Time	Area	% Area	Height
1	22.984	14266820	96.88	276078
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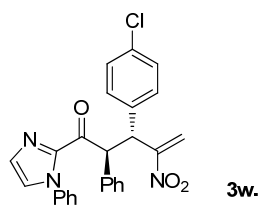
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



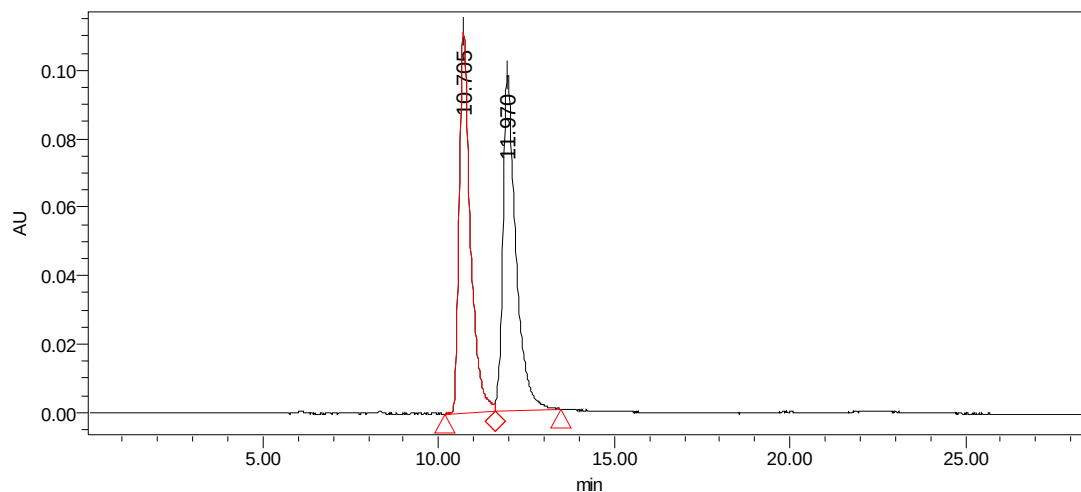
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1	18.258	5627312	49.99	144266
2	22.593	5630082	50.01	112461



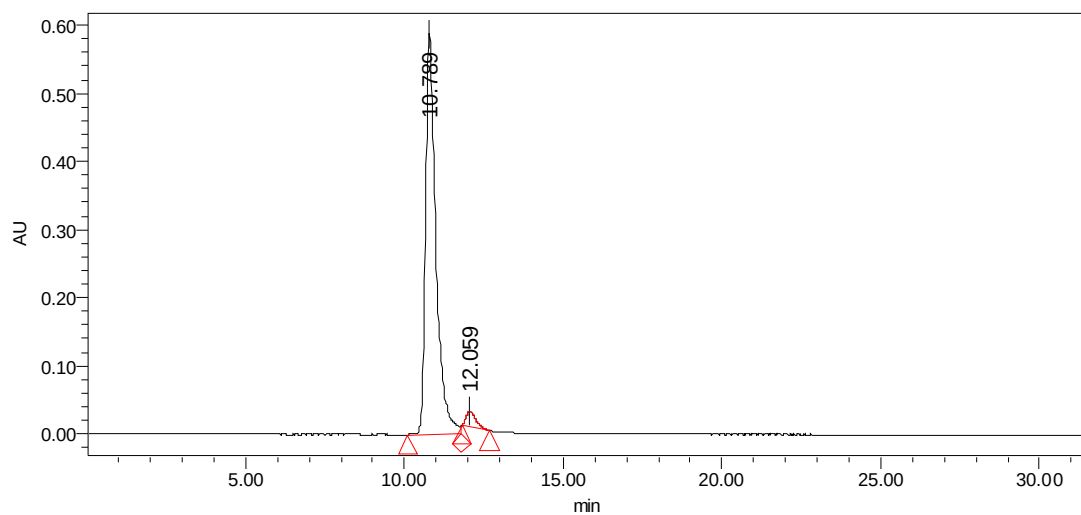
	Retention Time	Area	% Area	Height
1	19.647	34433211	92.07	880134
2	24.614	2966715	7.93	48927



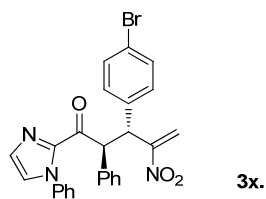
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=80/20, flow rate 1.0 mL/min)



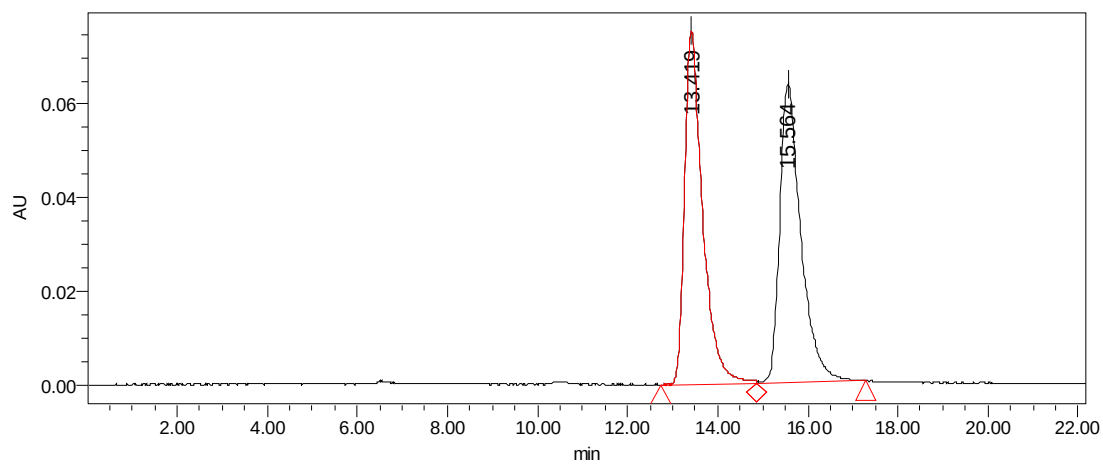
	Retention Time	Area	% Area	Height
1	10.705	2484744	49.38	111767
2	11.970	2547086	50.62	98269



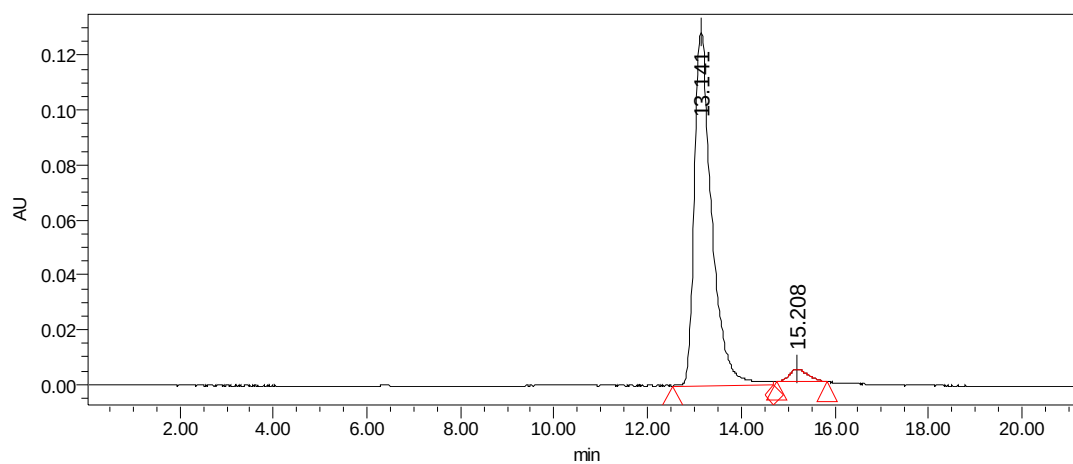
	Retention Time	Area	% Area	Height
1	10.789	13396770	96.47	589040
2	12.059	490617	3.53	22693



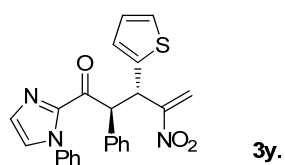
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



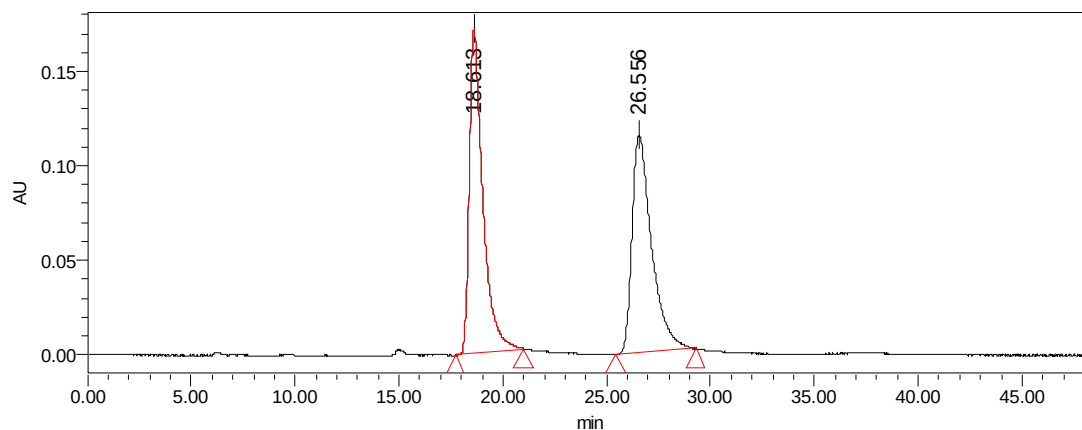
	Retention Time	Area	% Area	Height
1	13.419	2082035	50.19	75441
2	15.564	2066170	49.81	63732



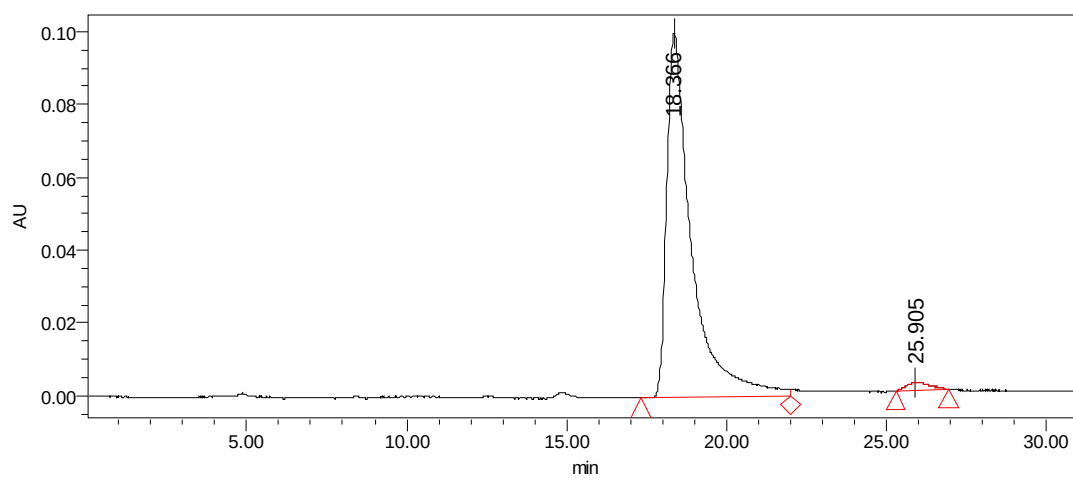
	Retention Time	Area	% Area	Height
1	13.141	3355754	96.47	128982
2	15.208	122716	3.53	4538



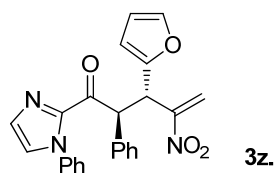
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=80/20, flow rate 1.0 mL/min)



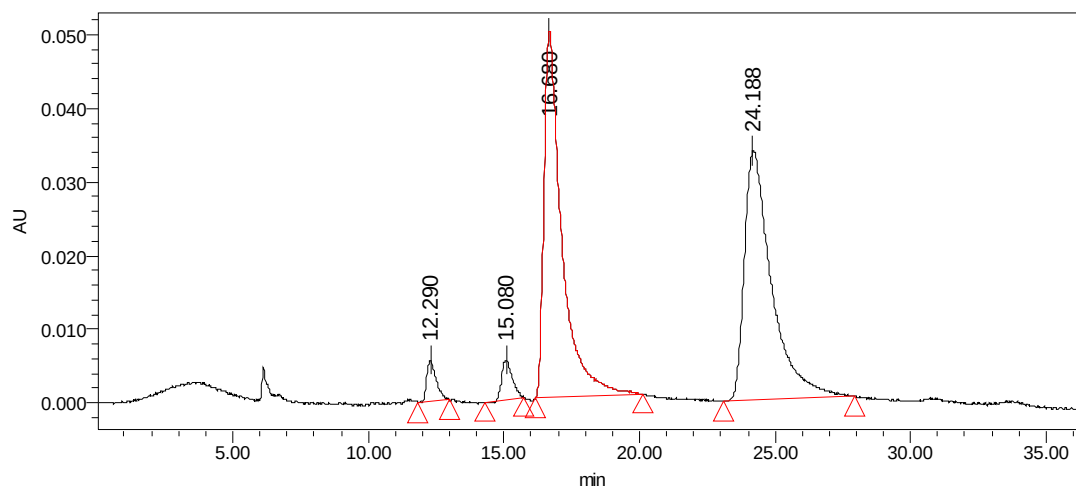
	Retention Time	Area	% Area	Height
1	18.613	7830731	50.82	171933
2	26.556	7577586	49.18	115147



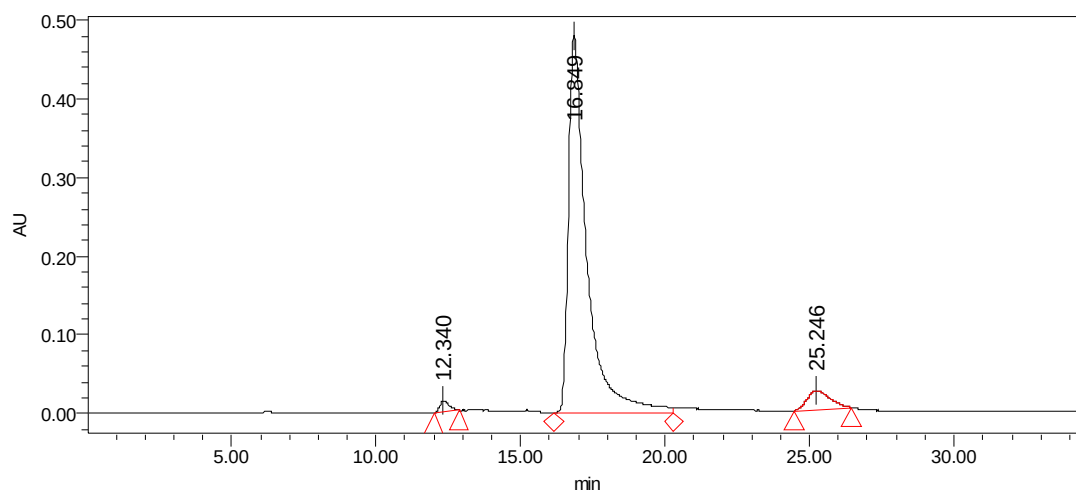
	Retention Time	Area	% Area	Height
1	18.366	5413612	98.08	100137
2	25.905	106179	1.92	2120



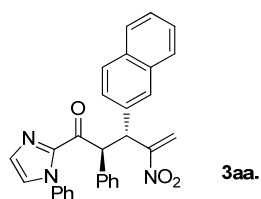
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=80/20, flow rate 1.0 mL/min)



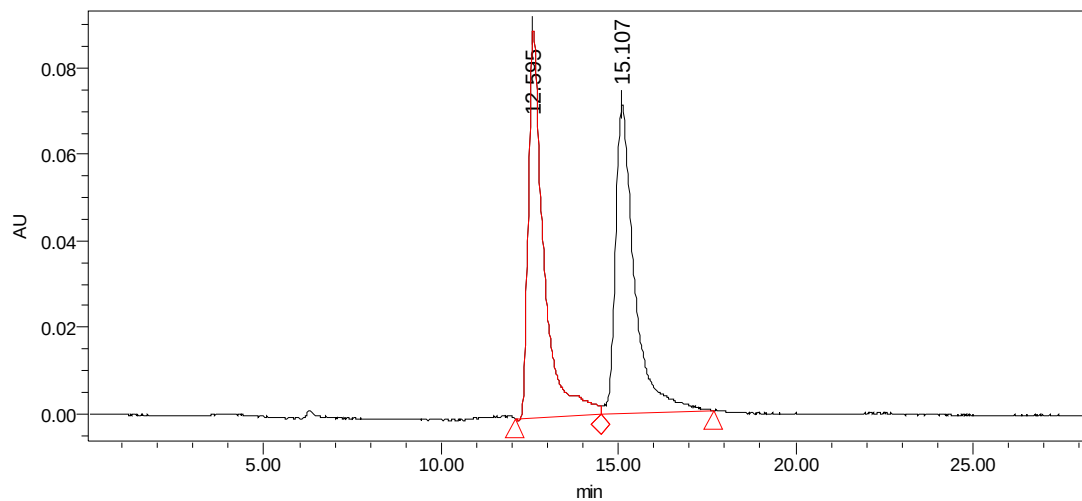
	Retention Time	Area	% Area	Height
1	12.290	135947	2.74	5621
2	15.080	146665	2.96	5350
3	16.680	2292819	46.23	49674
4	24.188	2384352	48.07	33890



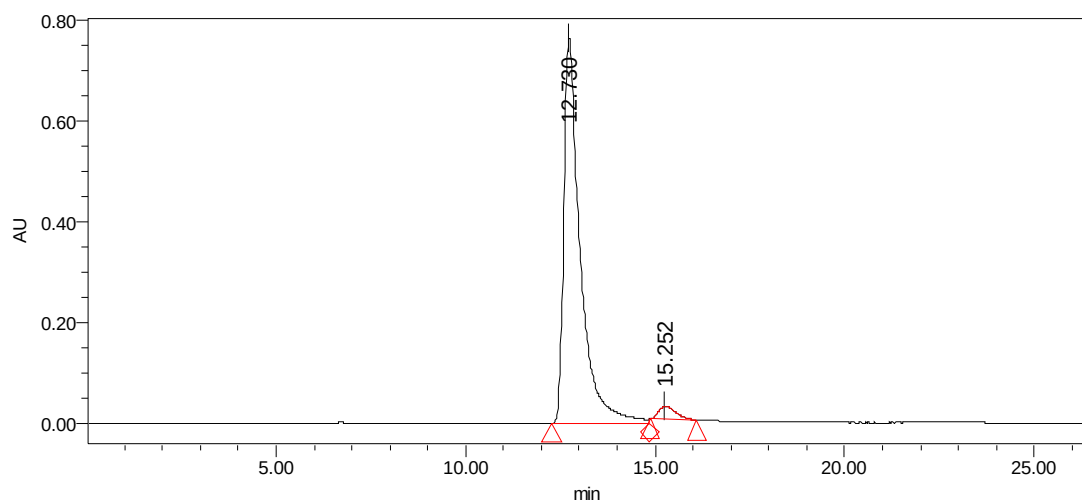
	Retention Time	Area	% Area	Height
1	12.340	320023	1.41	13929
2	16.849	21148585	92.86	479661
3	25.246	1305946	5.73	23757



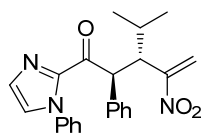
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=80/20, flow rate 1.0 mL/min)



	Retention Time	Area	% Area	Height
1	12.595	2764394	50.69	89665
2	15.107	2688914	49.31	71783

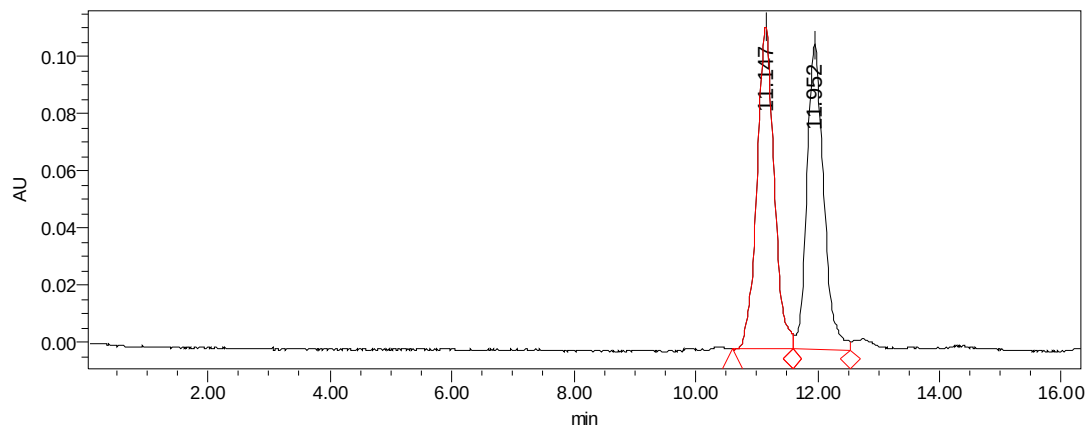


	Retention Time	Area	% Area	Height
1	12.730	22960590	96.48	764232
2	15.252	838792	3.52	26963

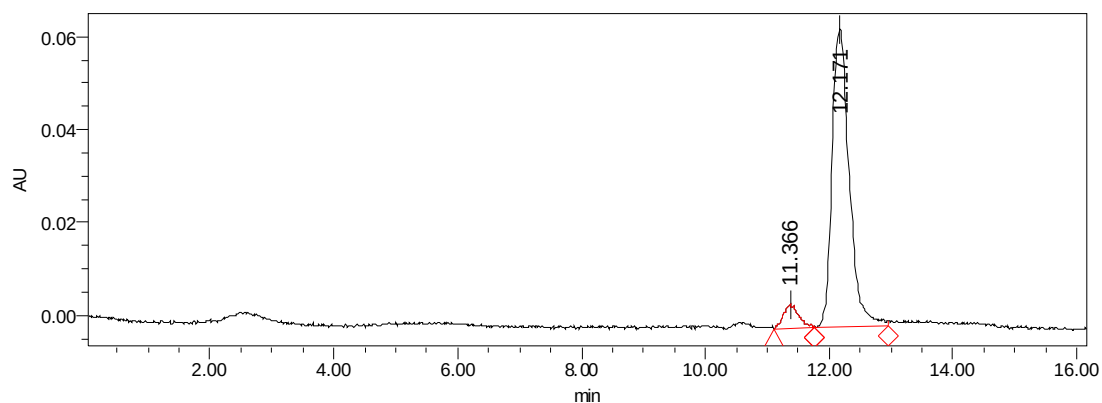


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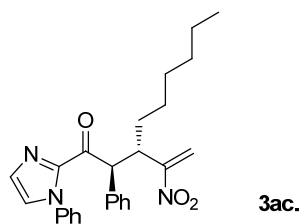
HPLC using an IA-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



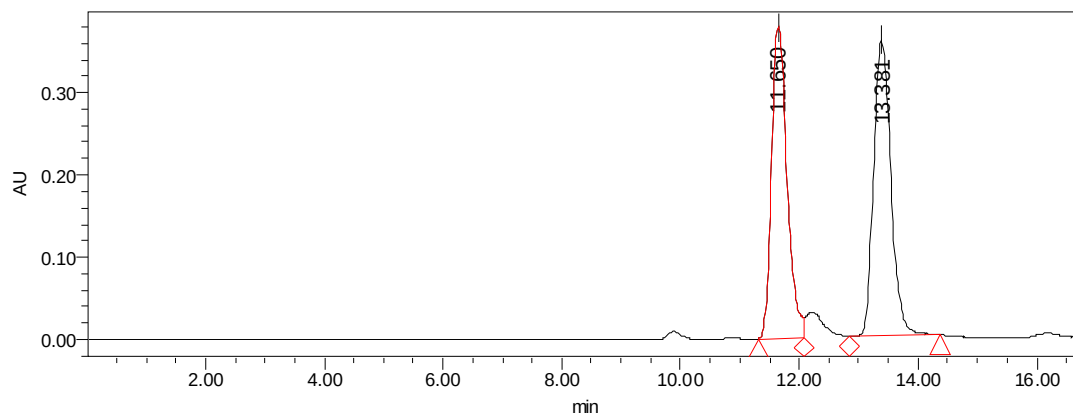
	Retention Time	Area	% Area	Height
1	11.147	2233736	51.97	112760
2	11.952	2064444	48.03	106342



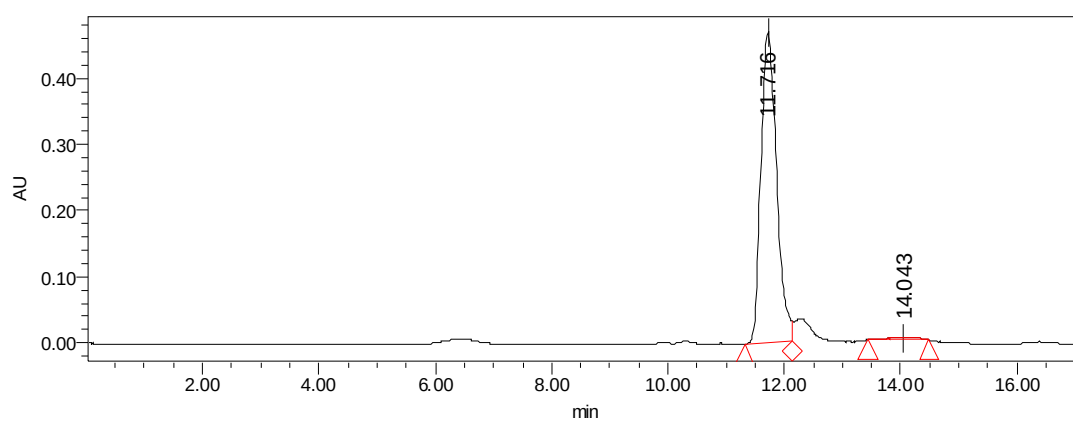
	Retention Time	Area	% Area	Height
1	11.366	87995	6.61	4888
2	12.171	1242609	93.39	64322



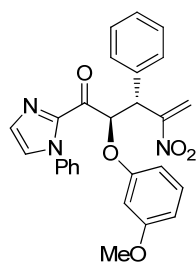
HPLC using an IA-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



	Retention Time	Area	% Area	Height
1	11.650	6811611	48.33	378035
2	13.381	7281137	51.67	360194

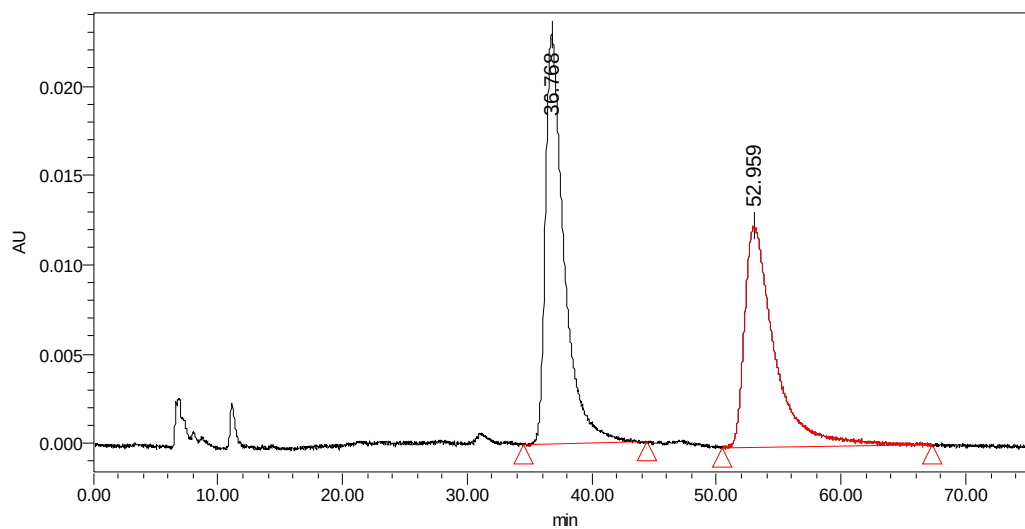


	Retention Time	Area	% Area	Height
1	11.716	8874918	98.44	470087
2	14.043	140319	1.56	3416

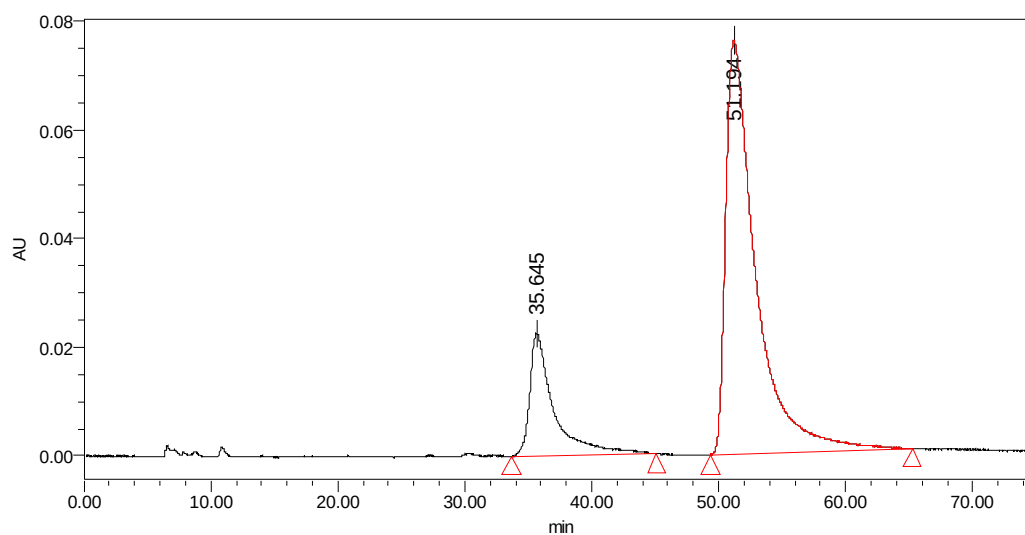


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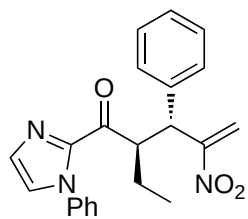
HPLC using an IC-H (*n*-Hexane/*i*-PrOH=90/10, flow rate 1.0 mL/min)



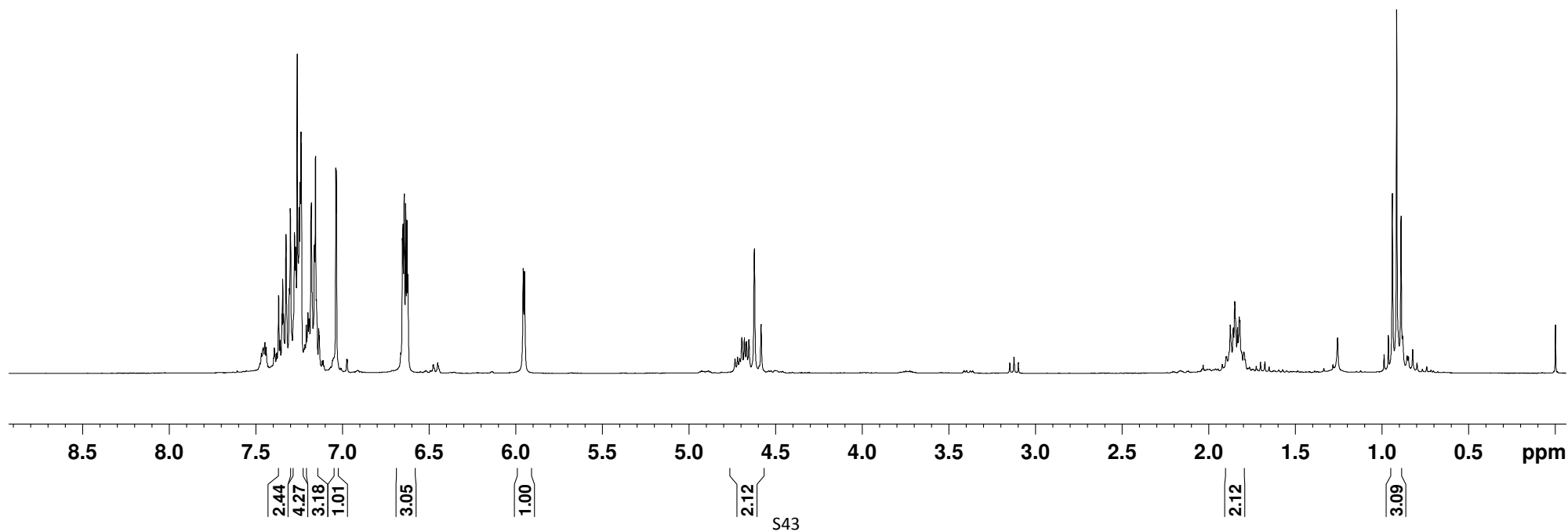
	Retention Time	Area	% Area	Height
1	36.768	2427496	53.65	22967
2	52.959	2097337	46.35	12343

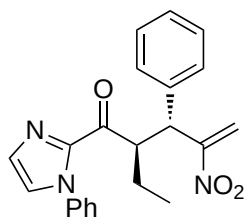


	Retention Time	Area	% Area	Height
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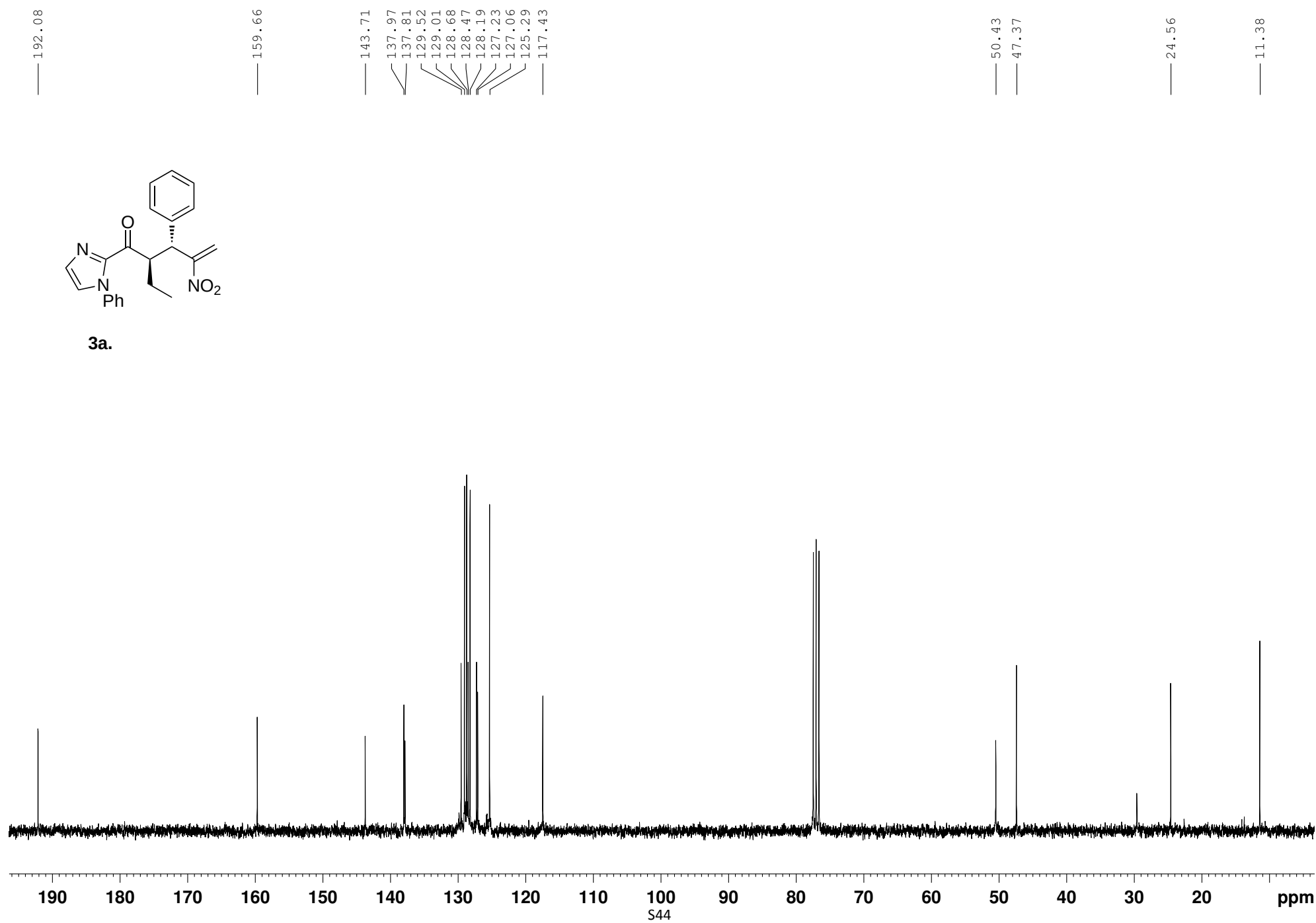


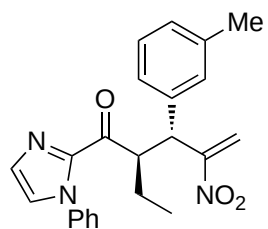
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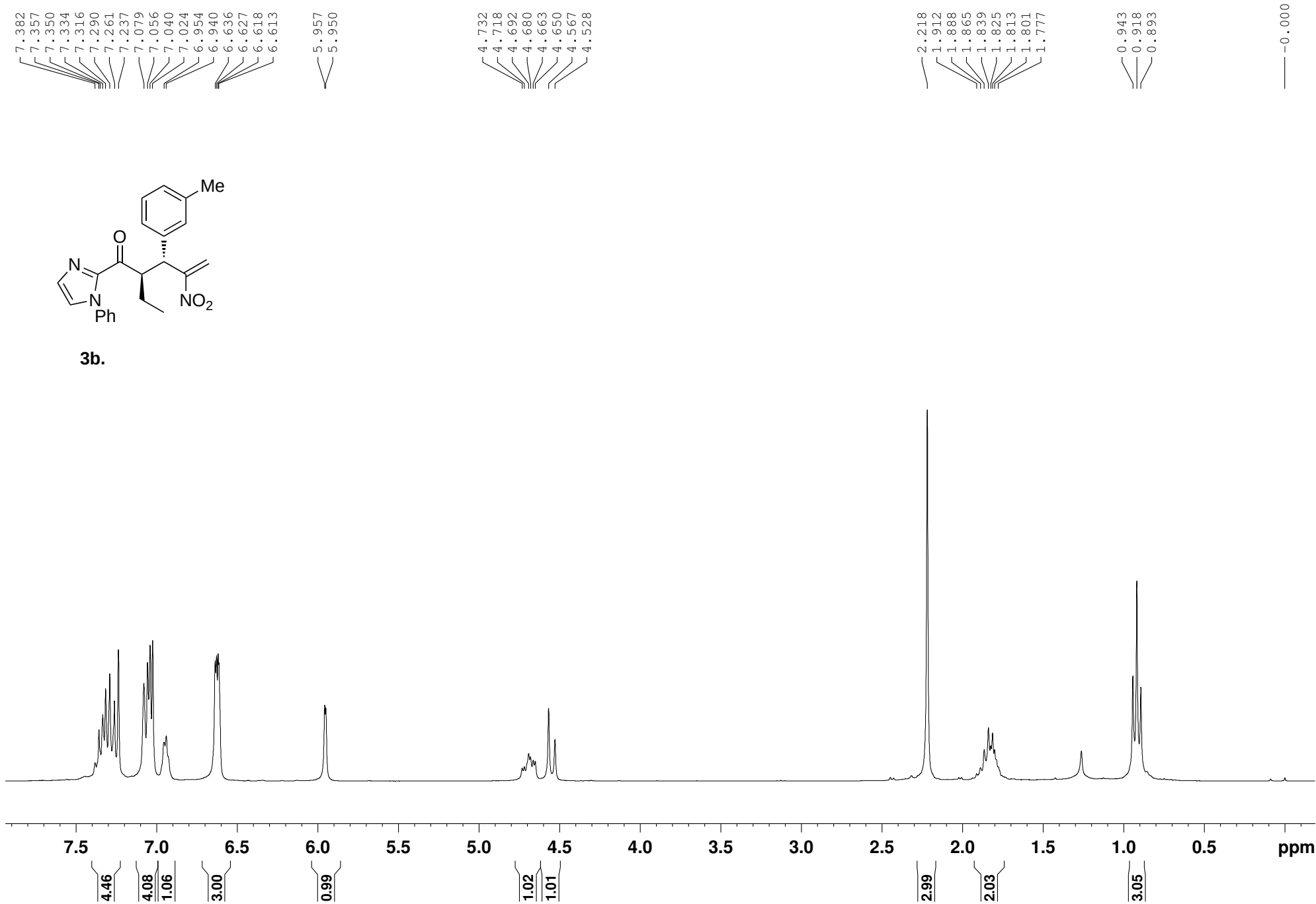


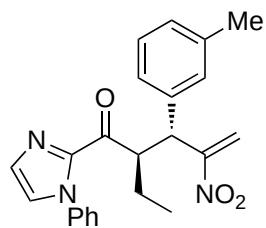
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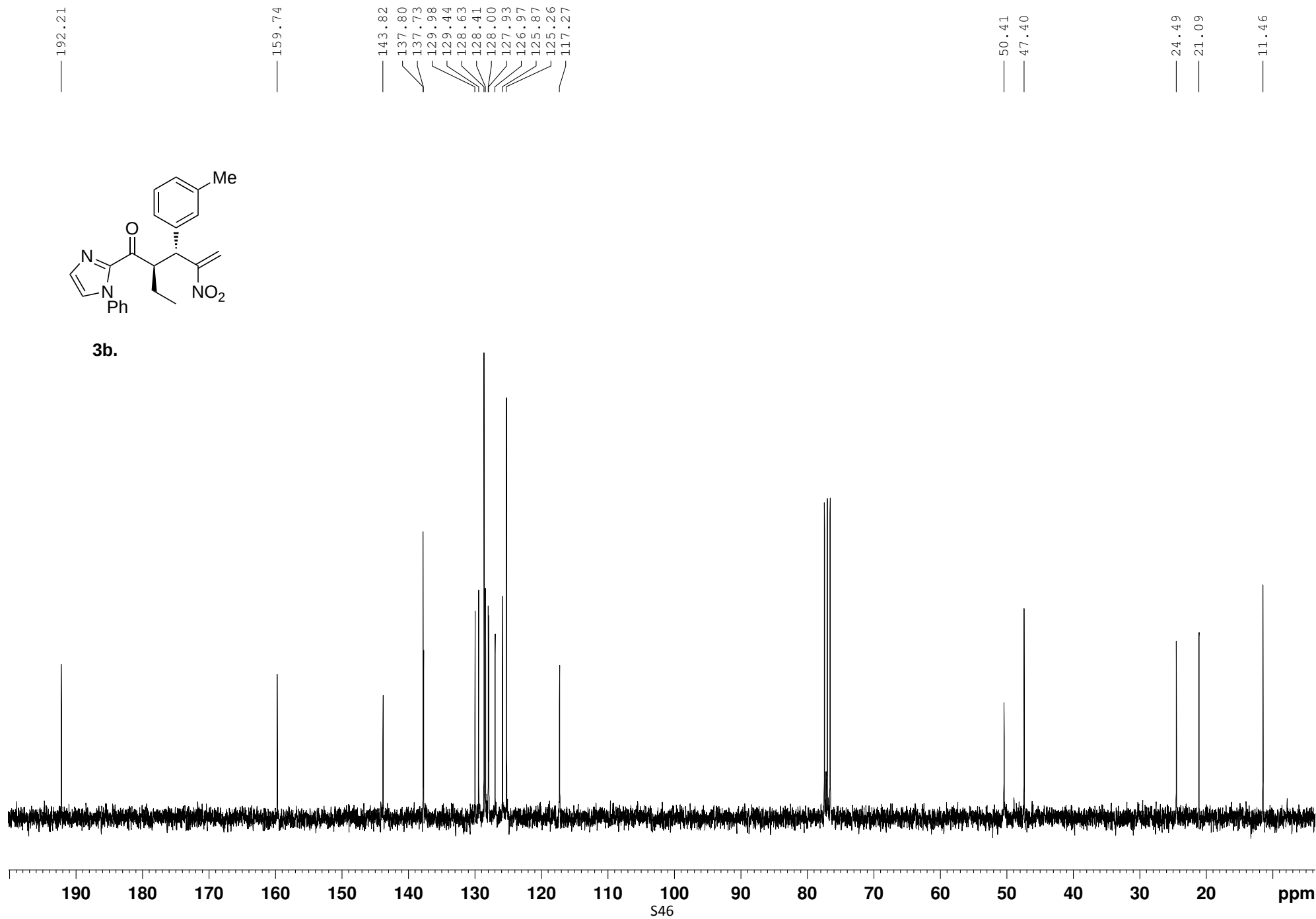


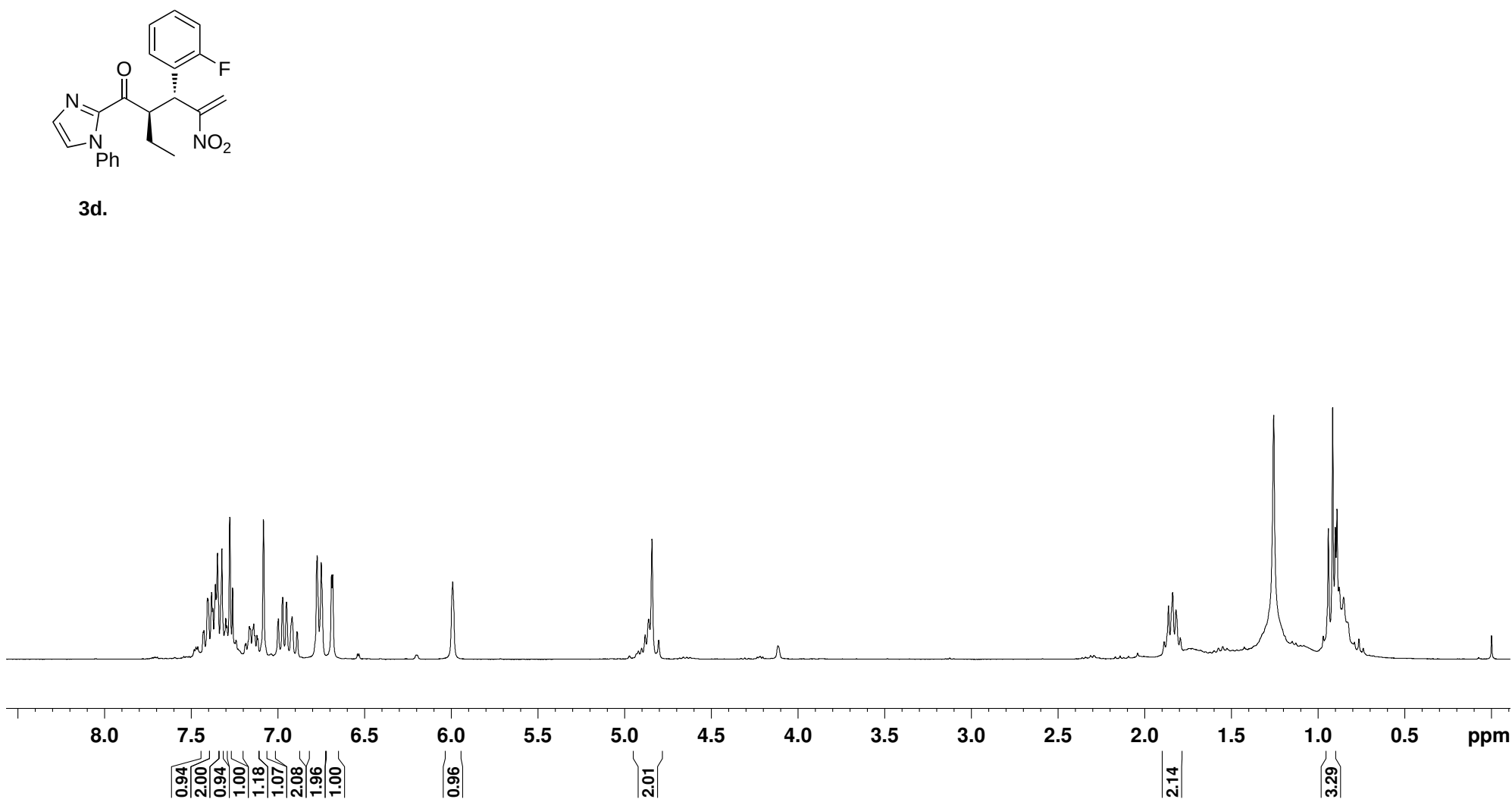
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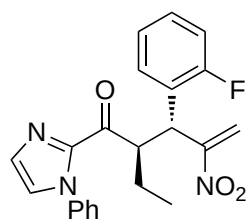




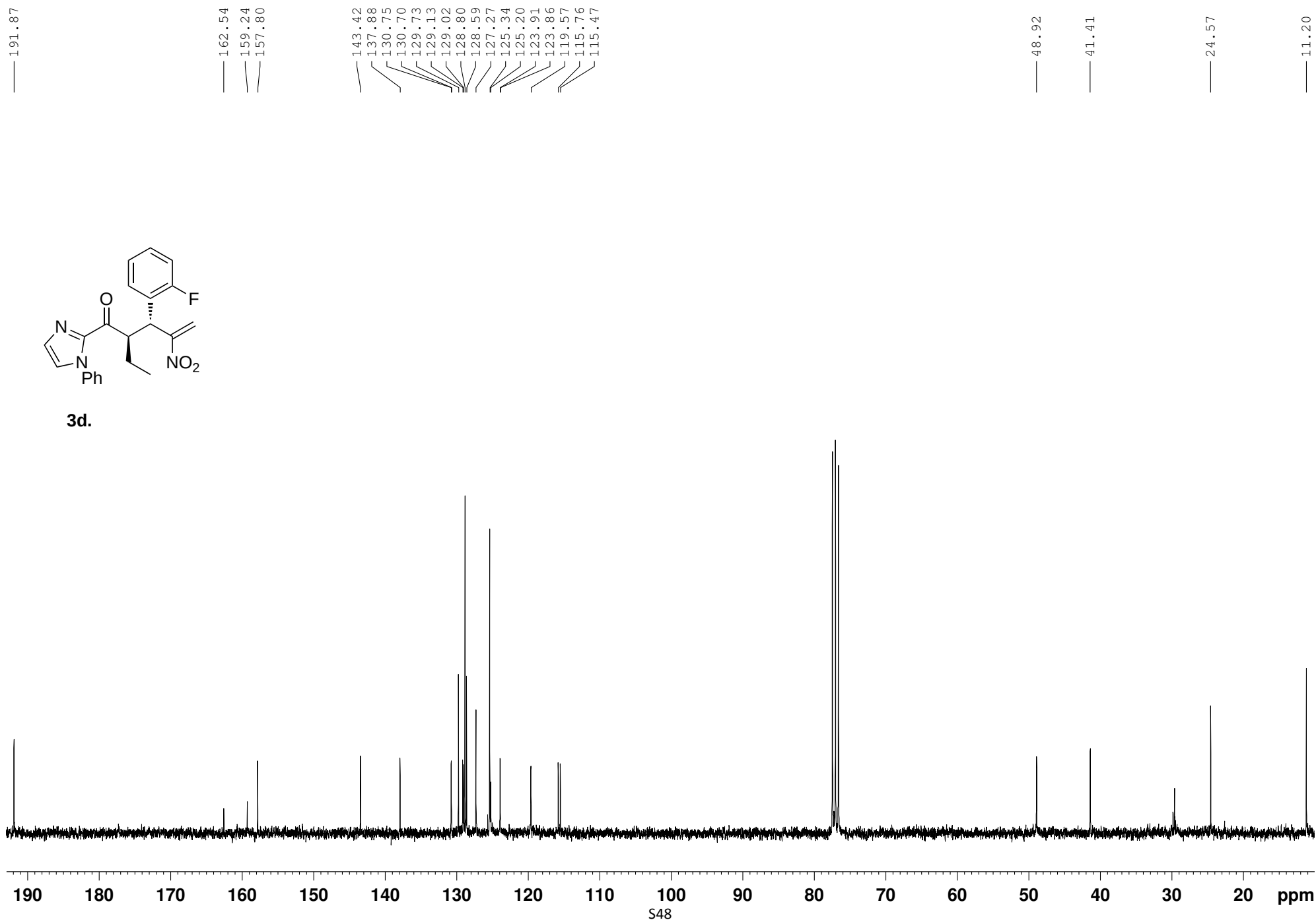
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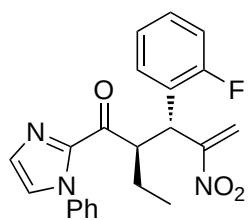




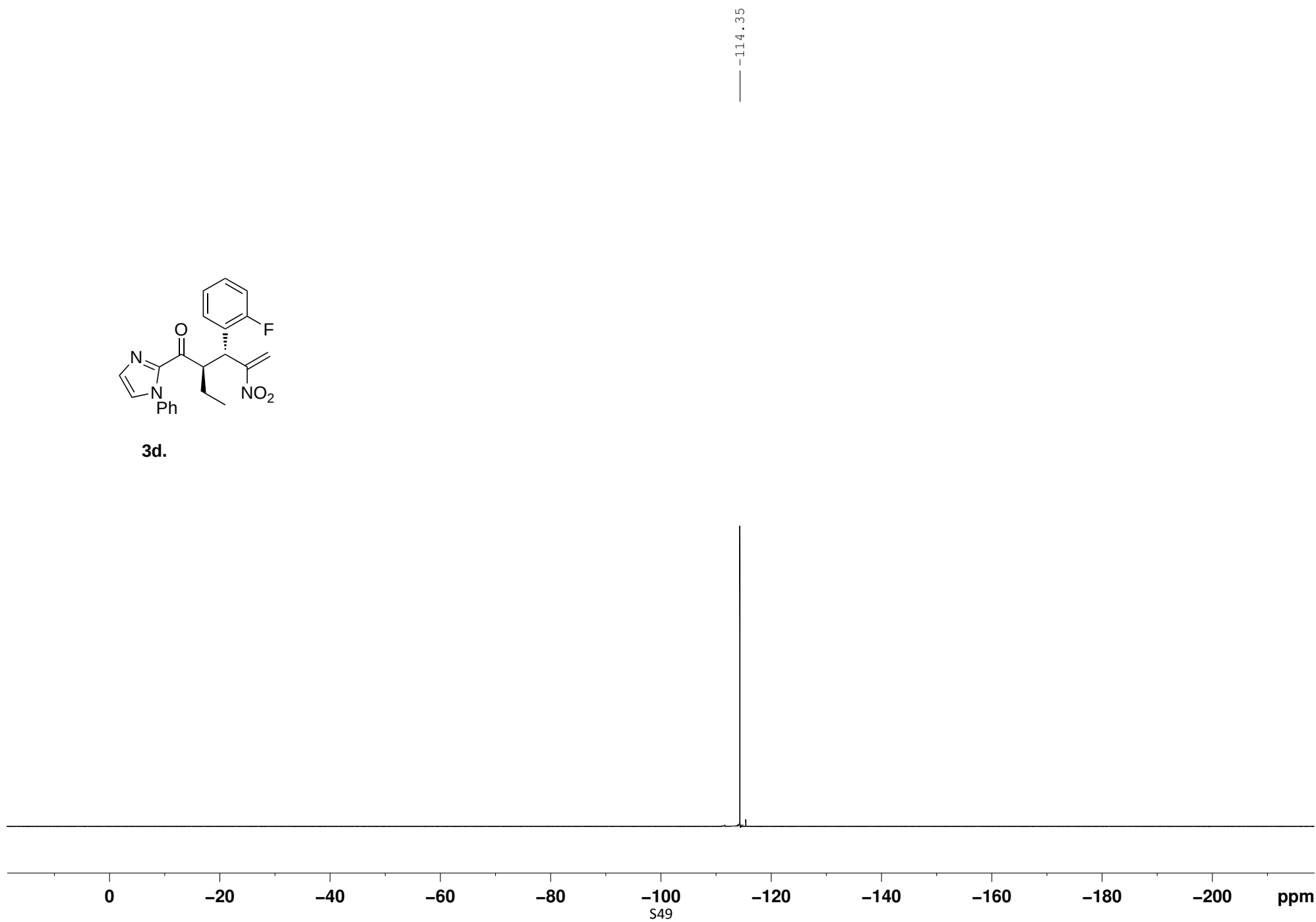


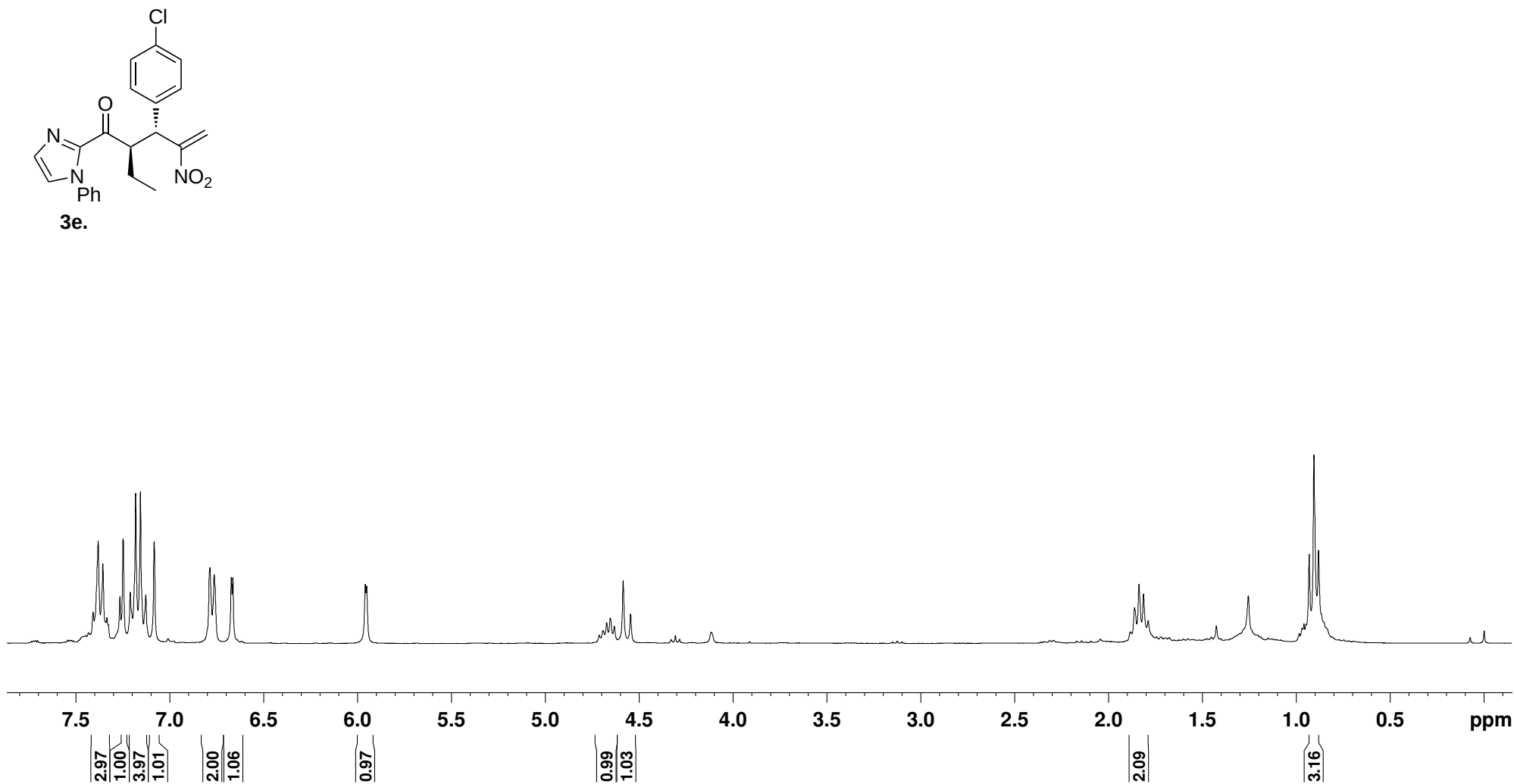
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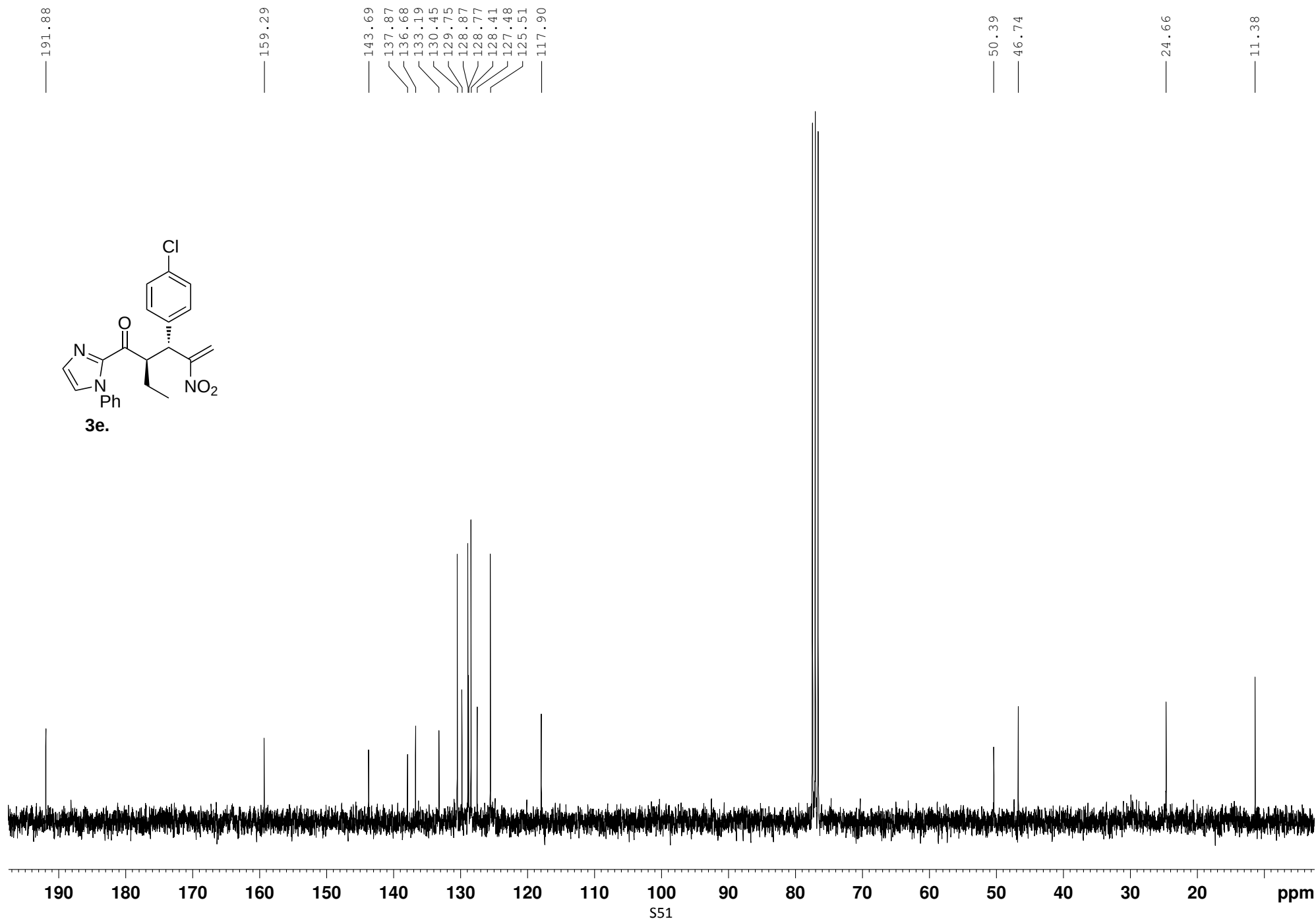
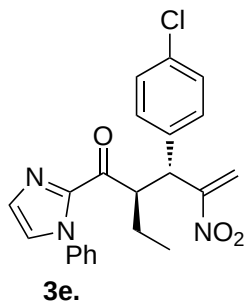




3d.







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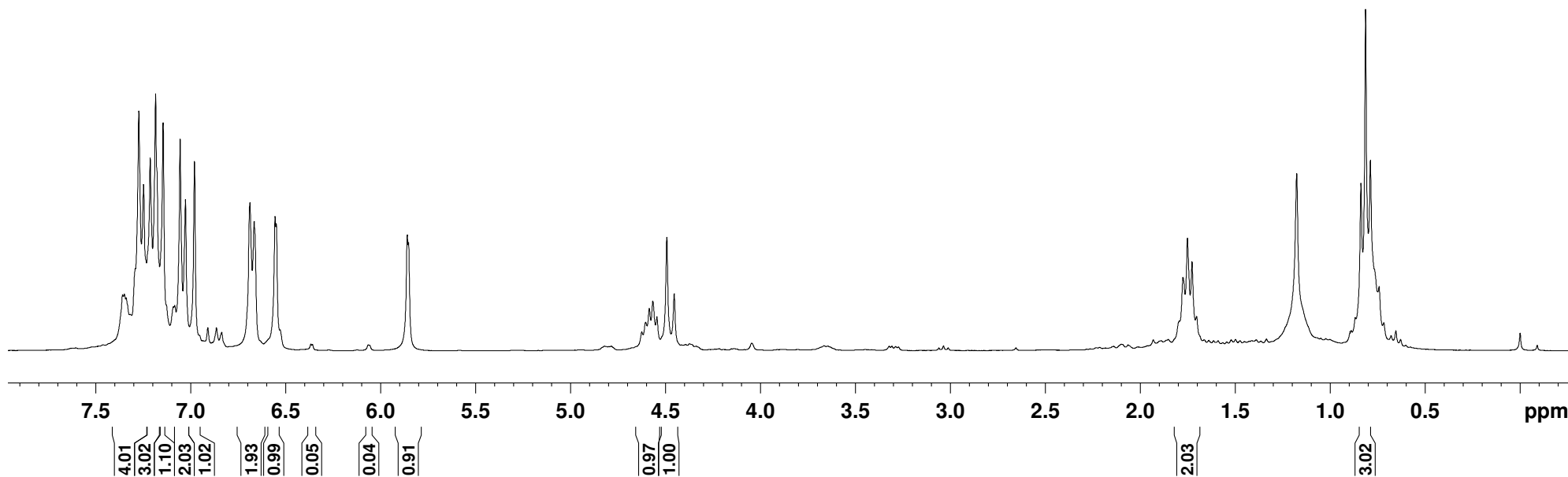
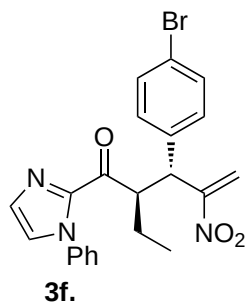
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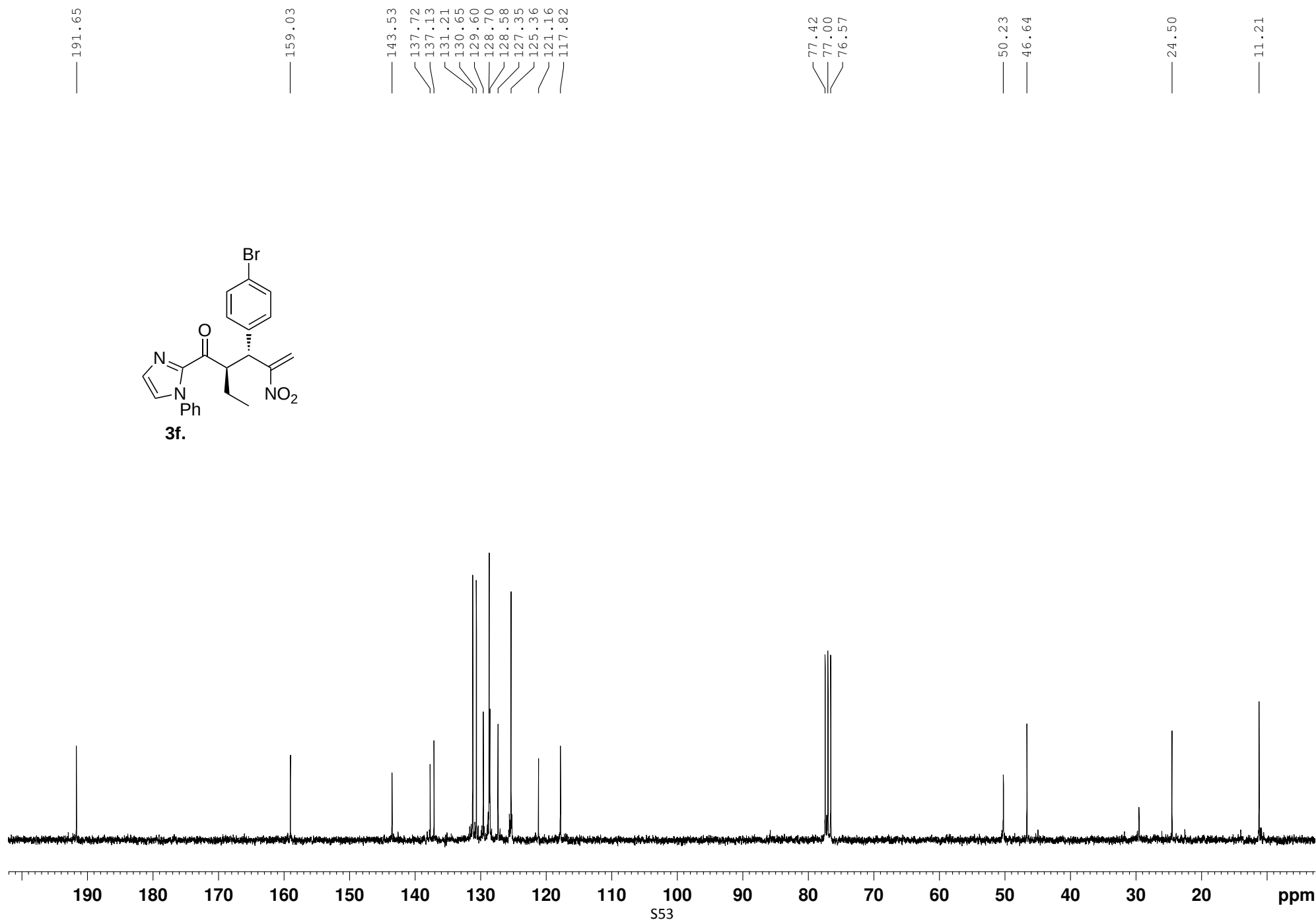
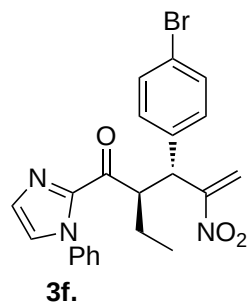
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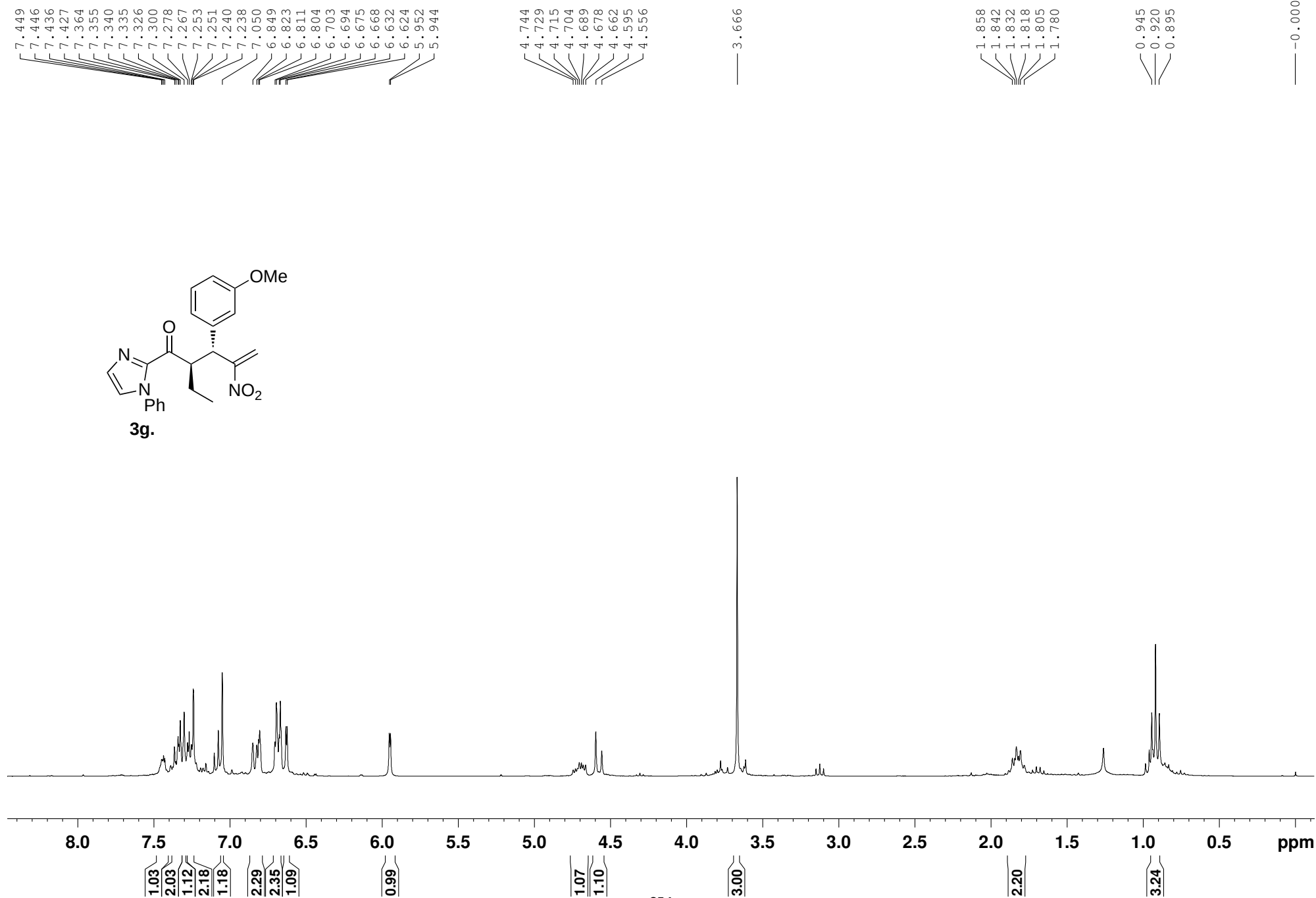
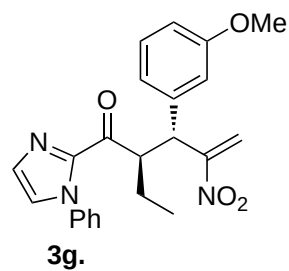
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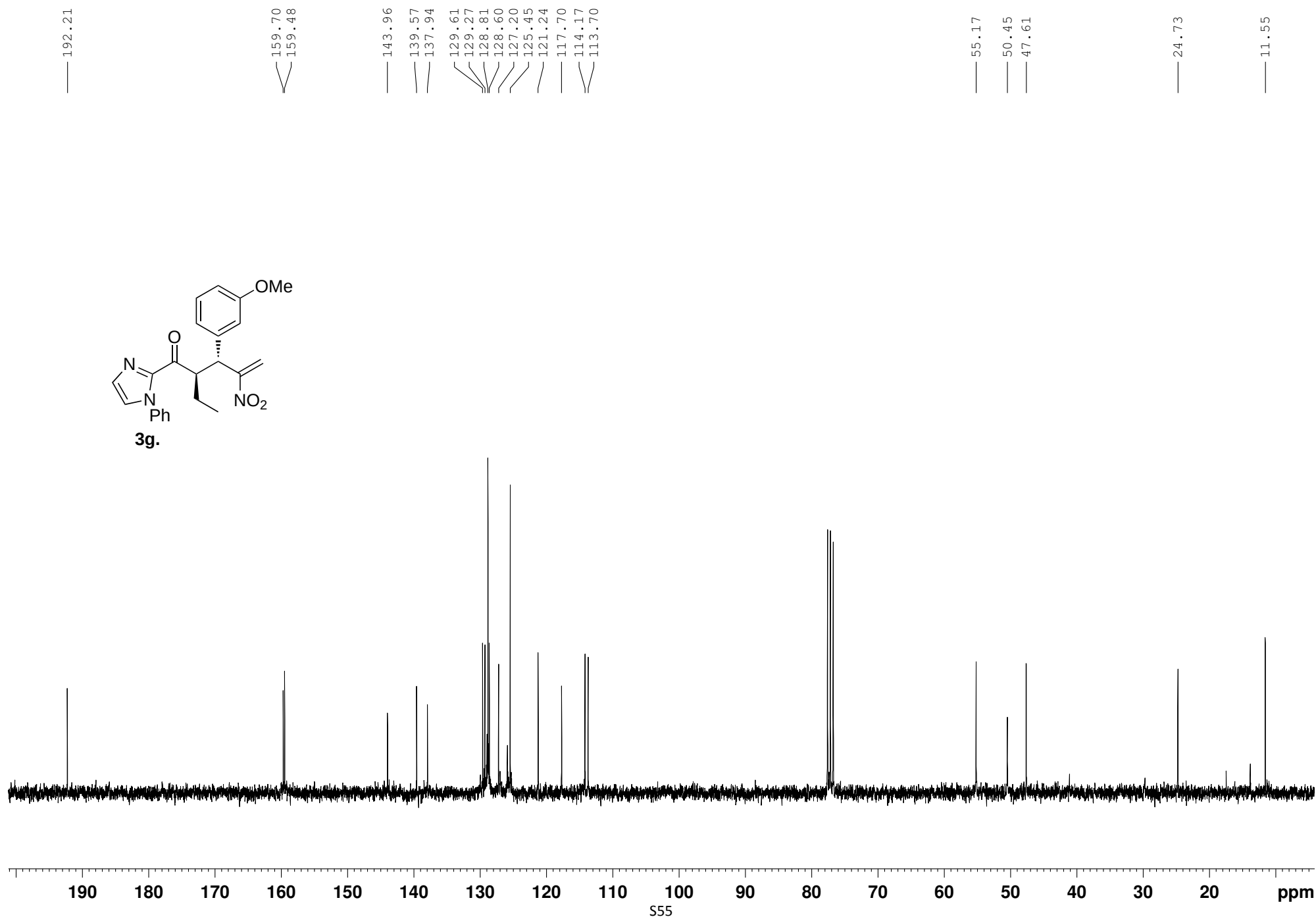
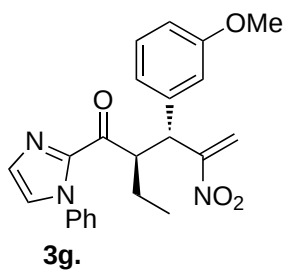
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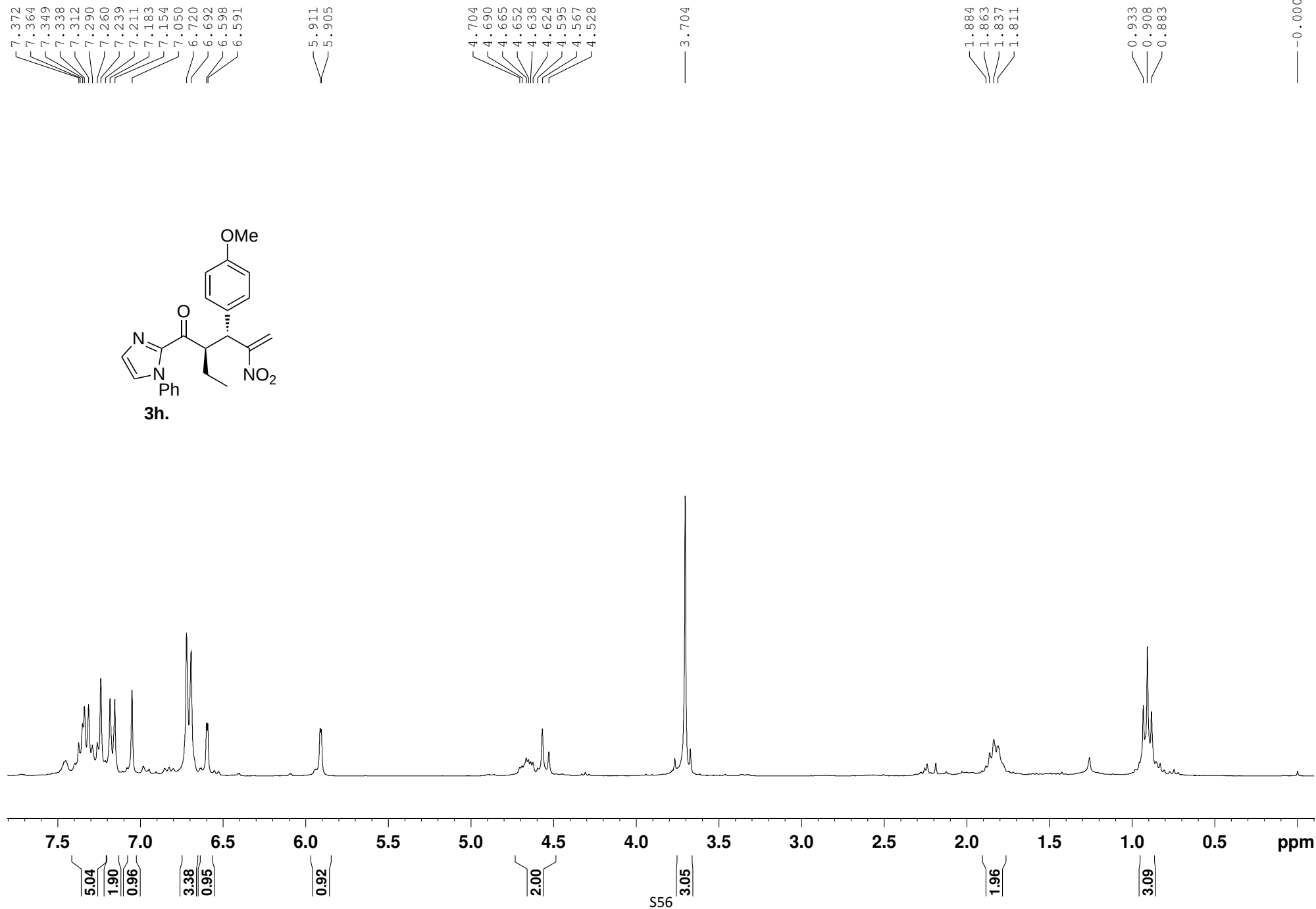
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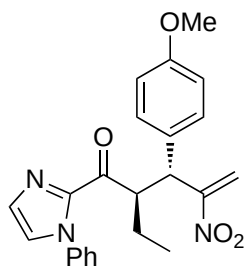




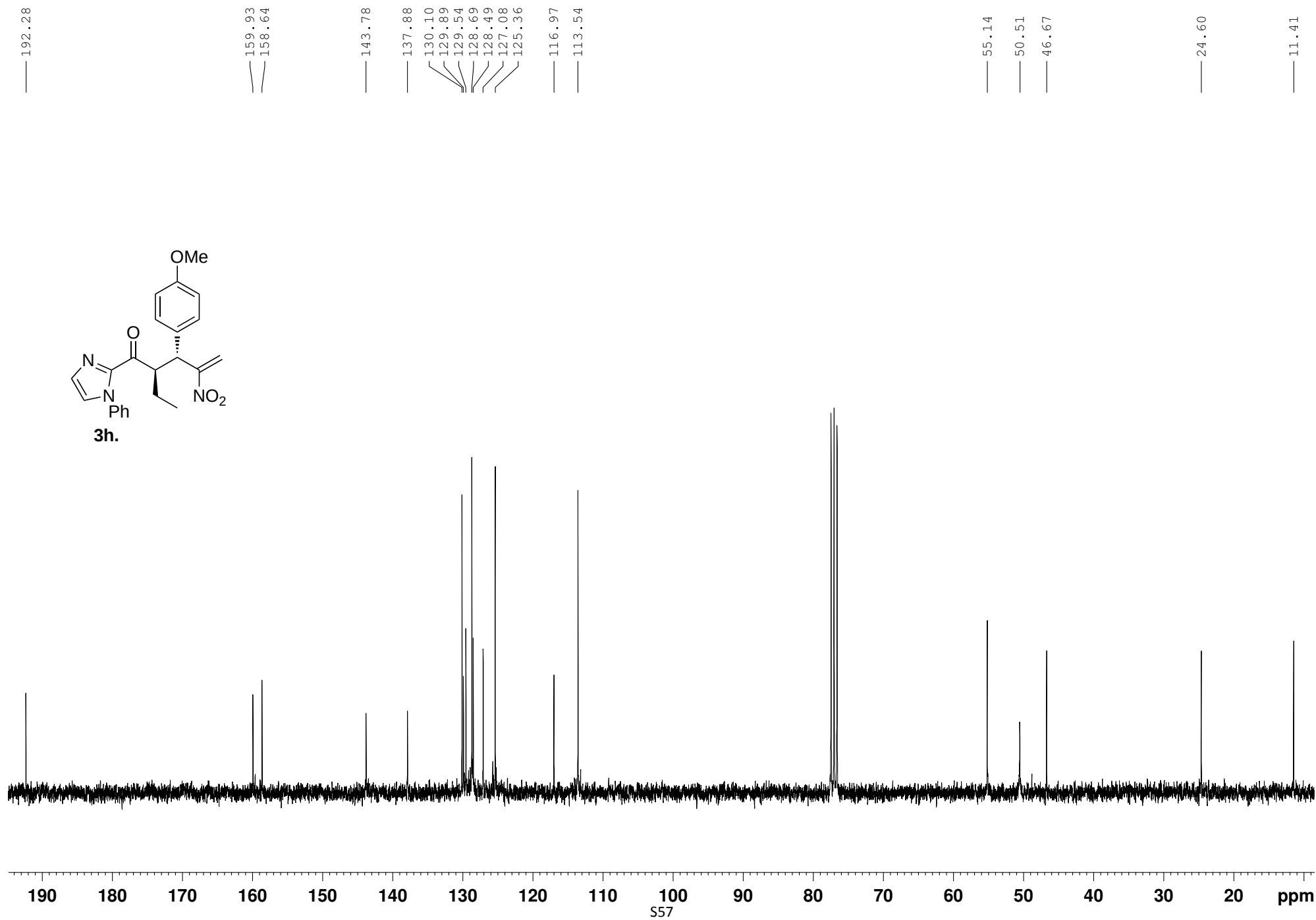


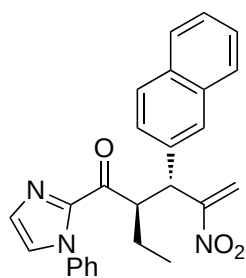




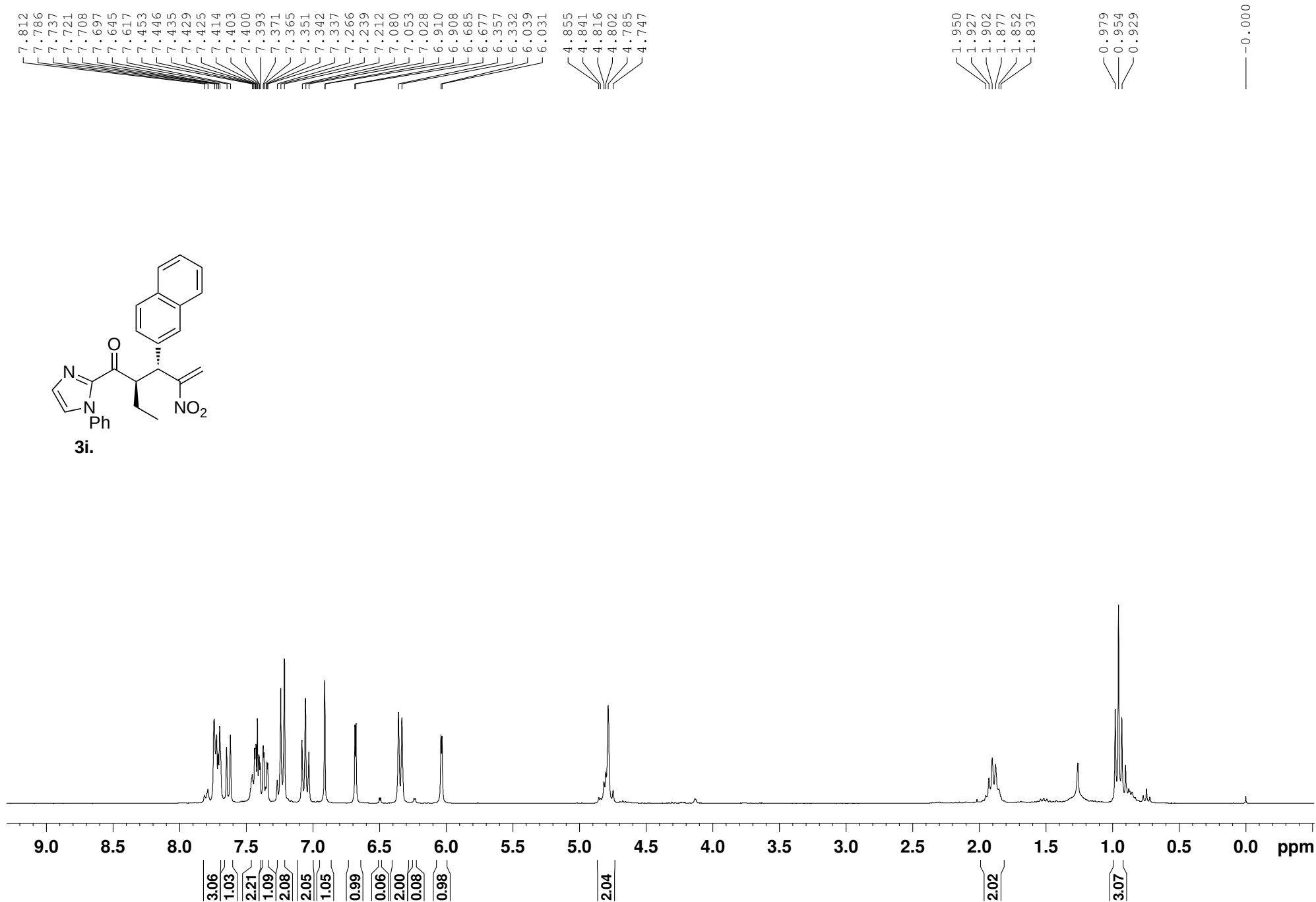


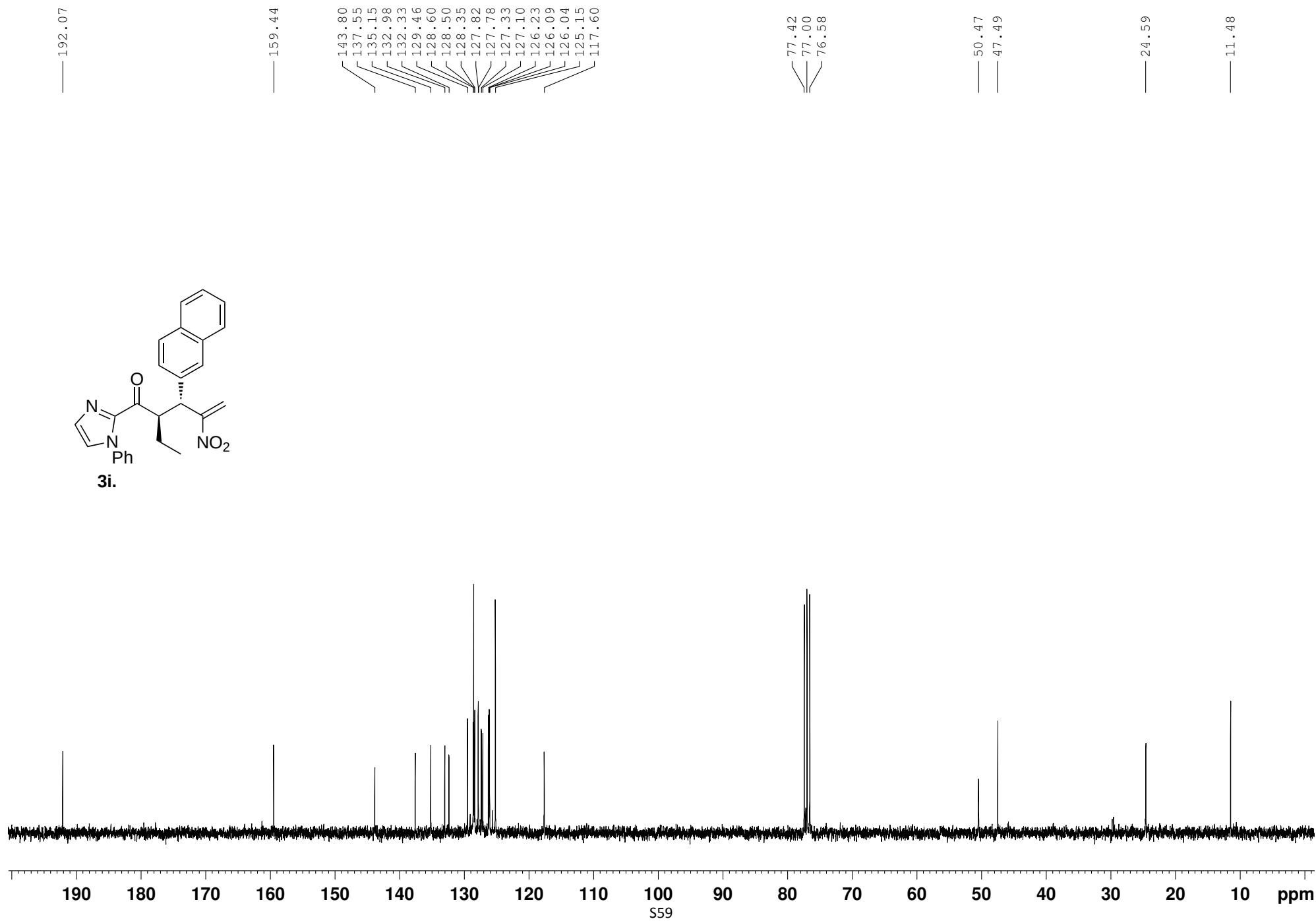
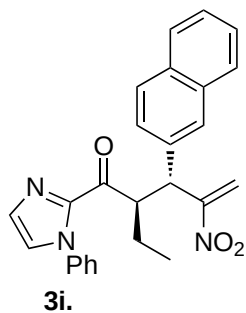
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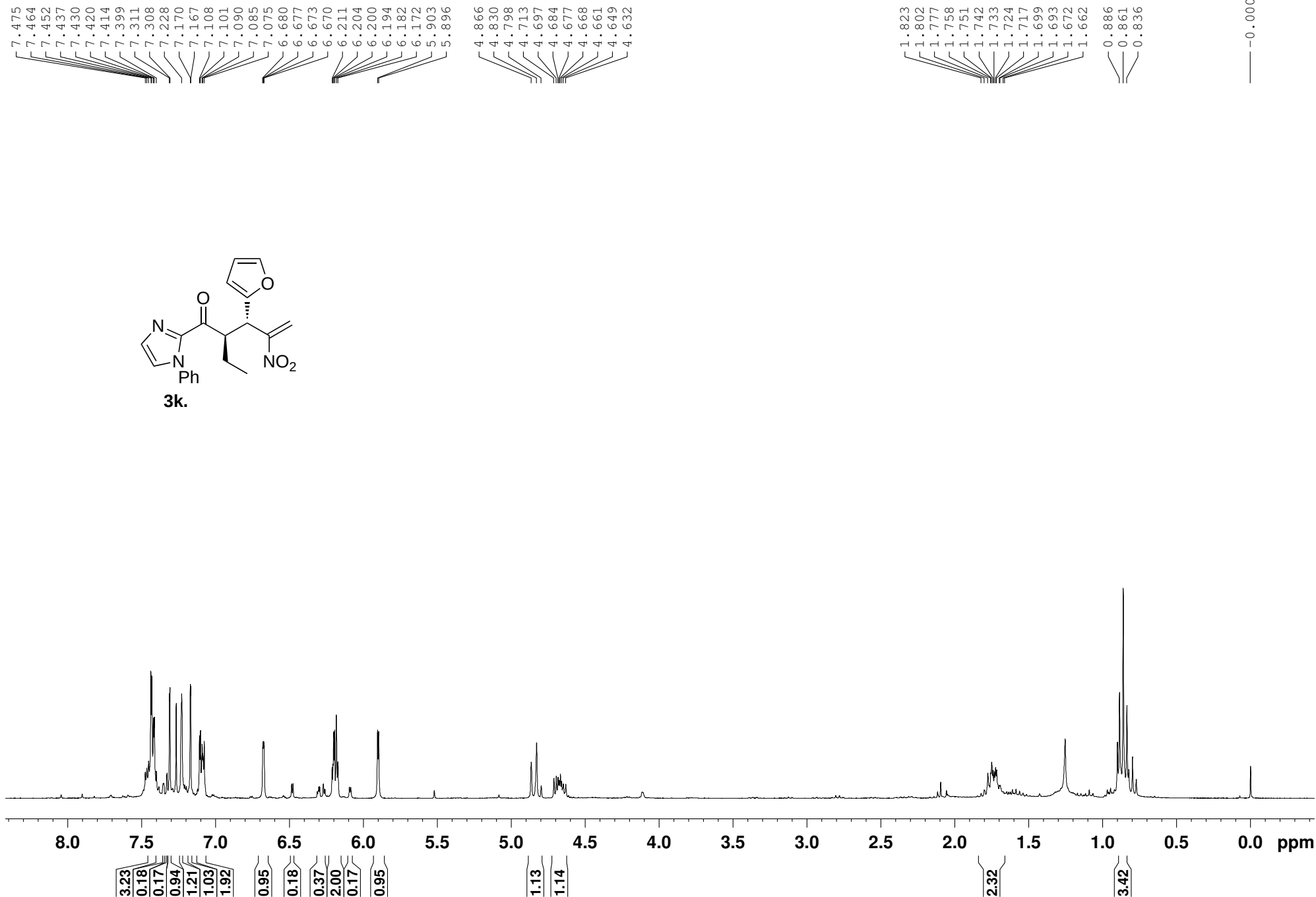


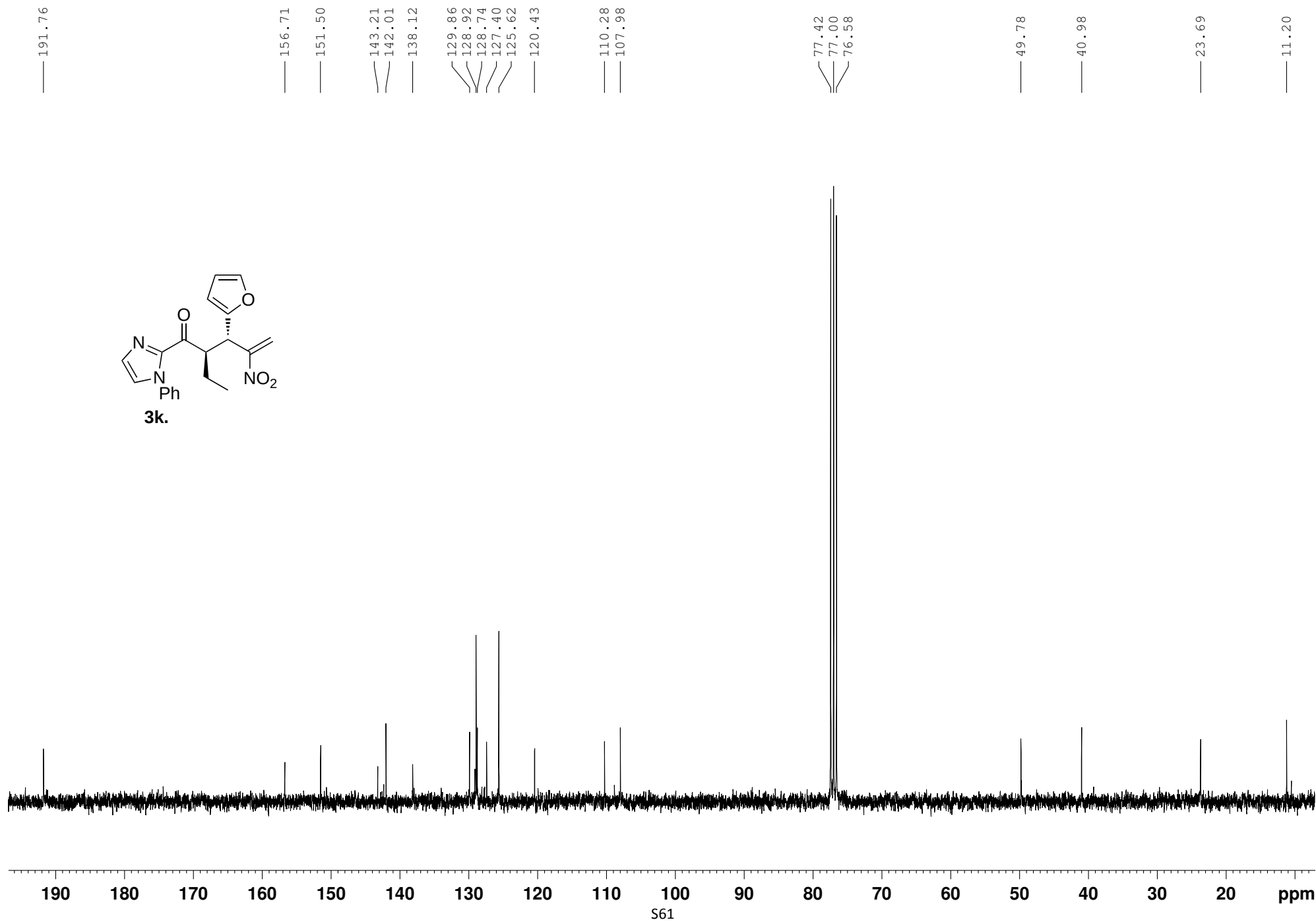
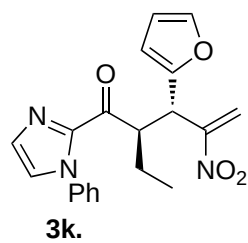


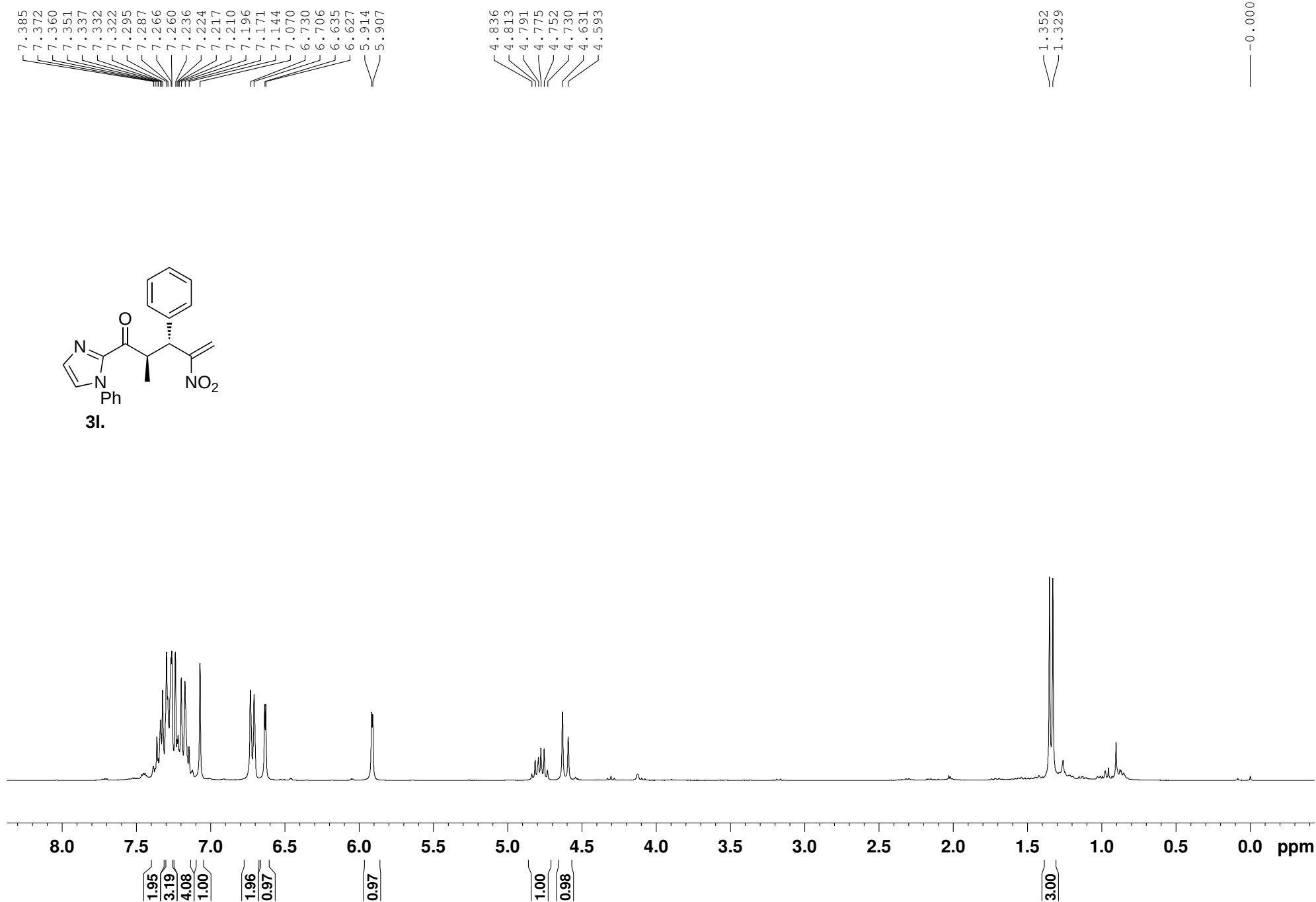
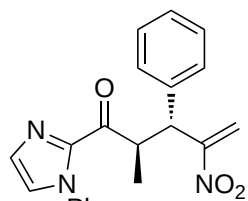
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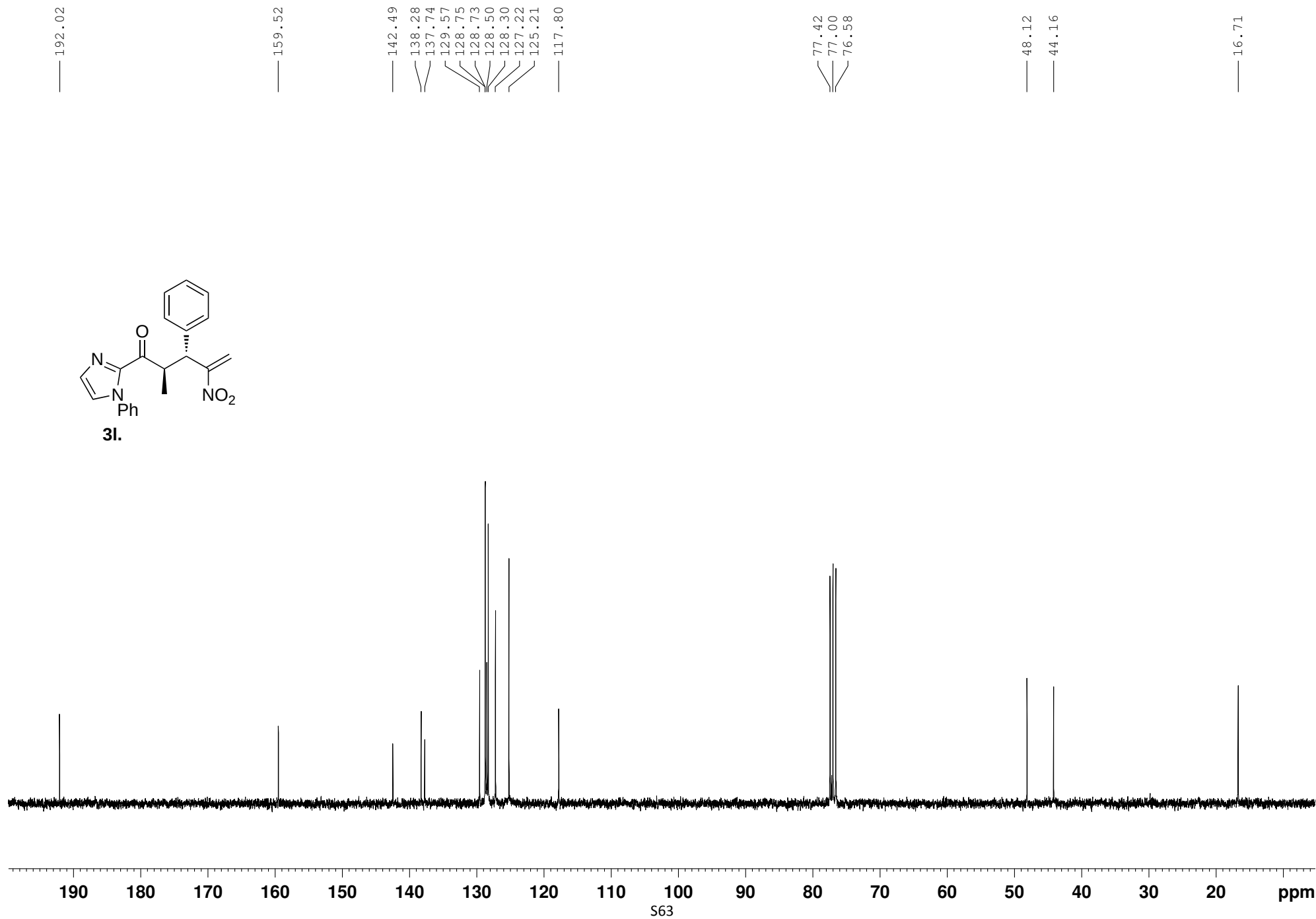
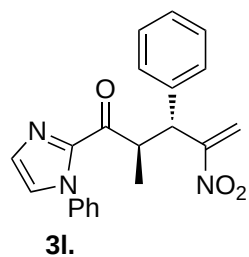


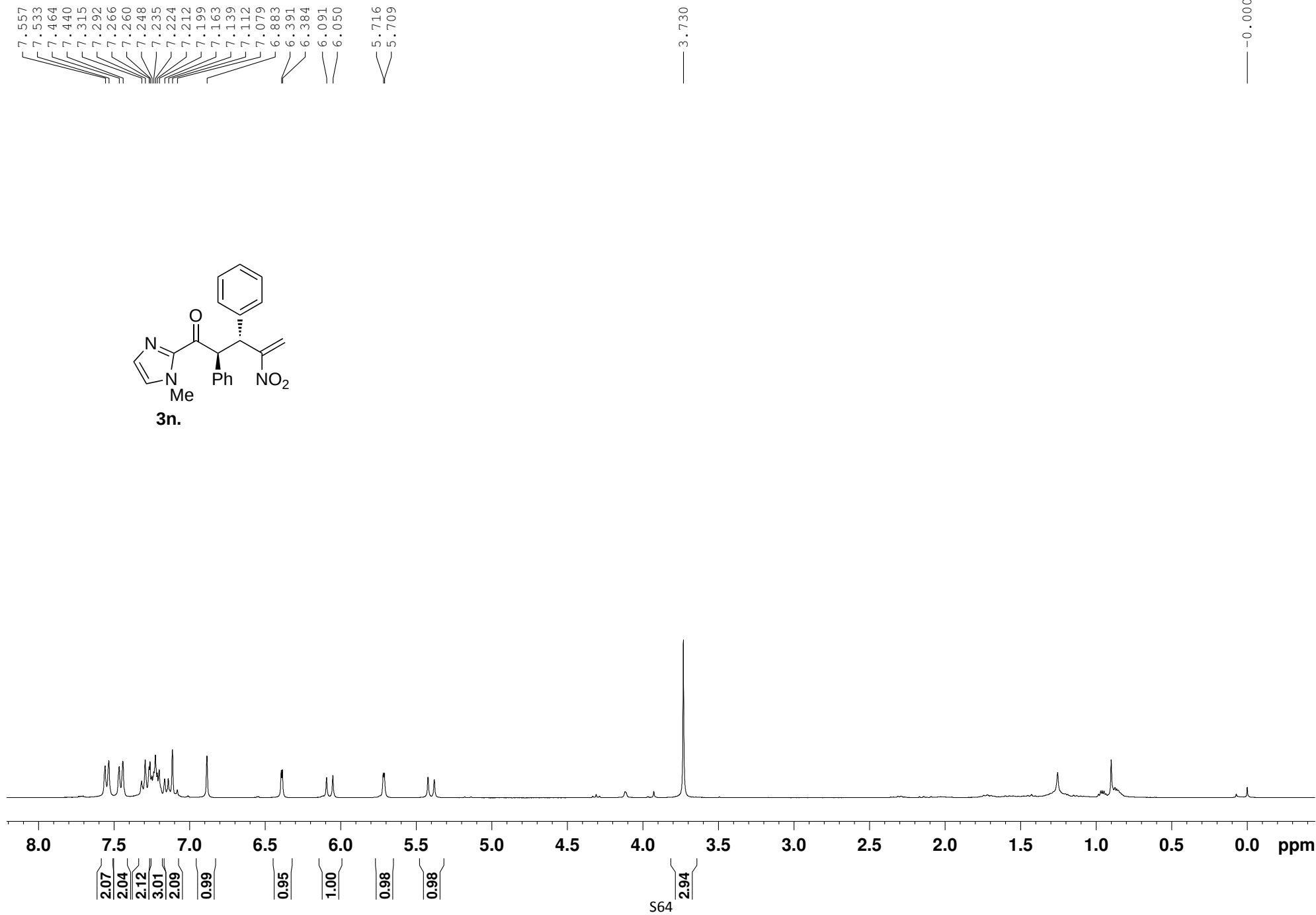


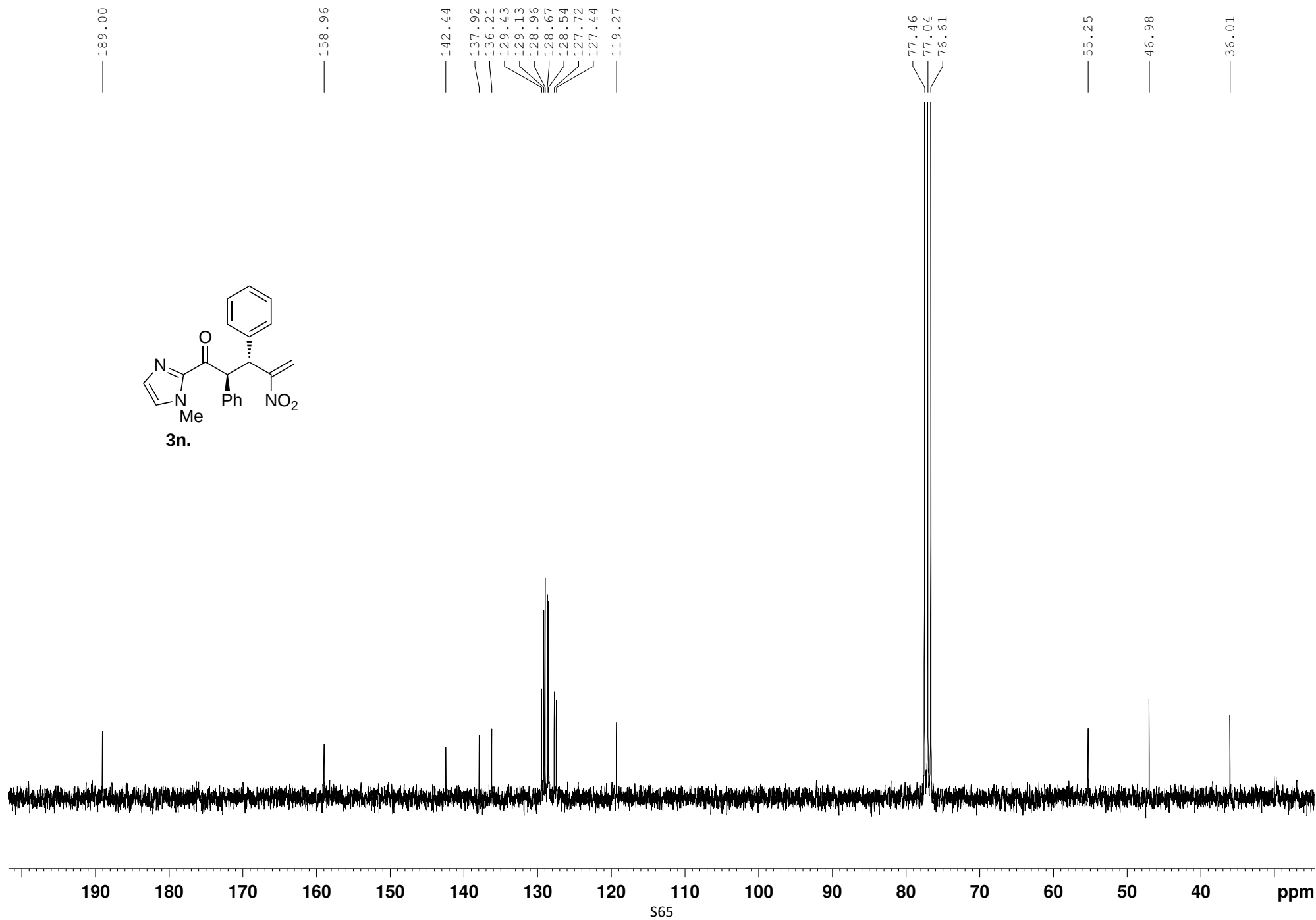
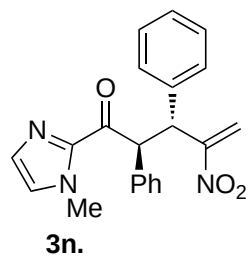


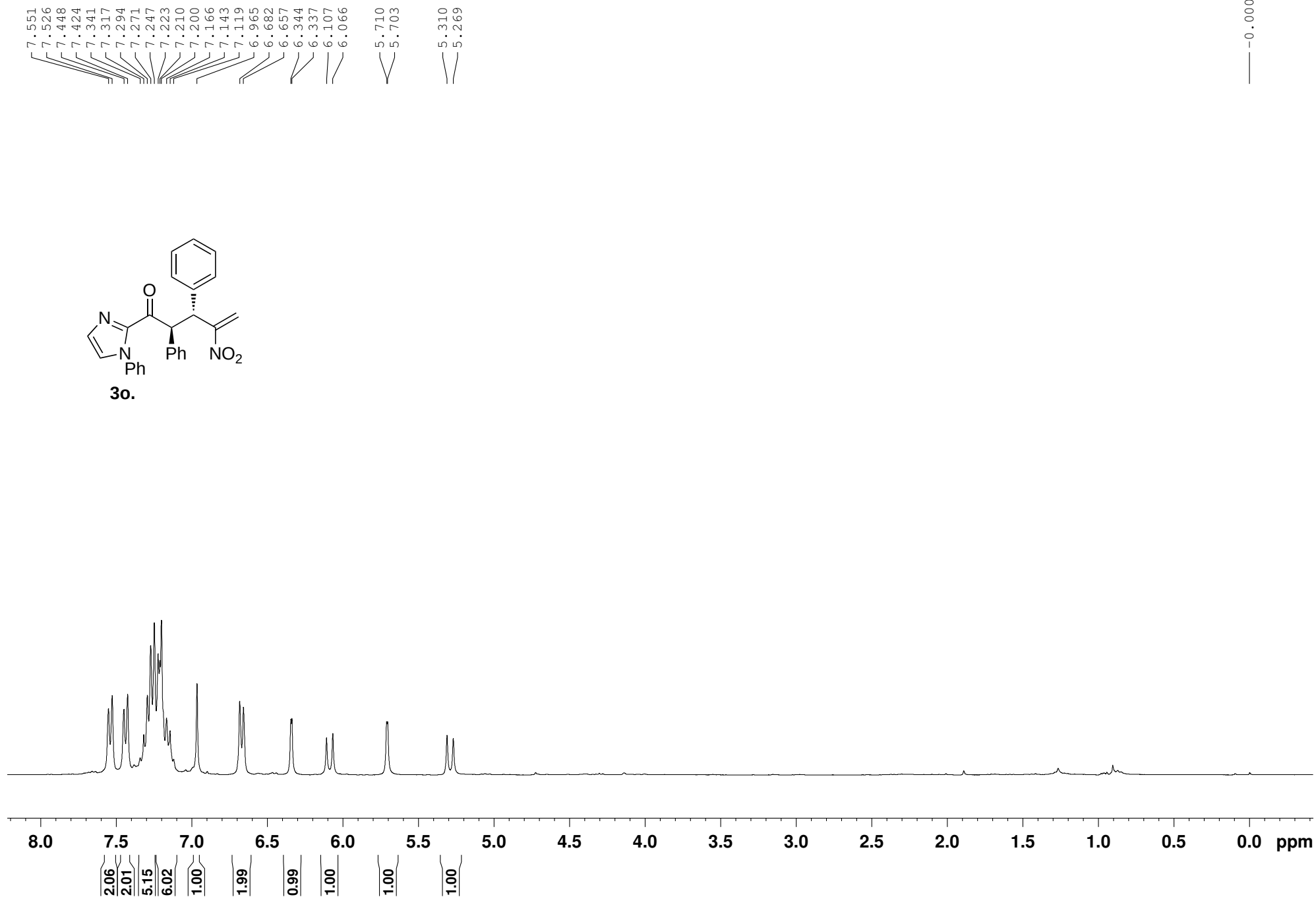
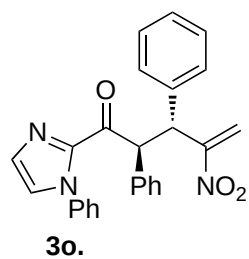


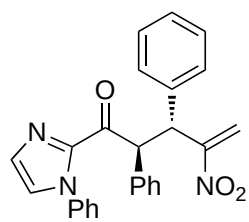




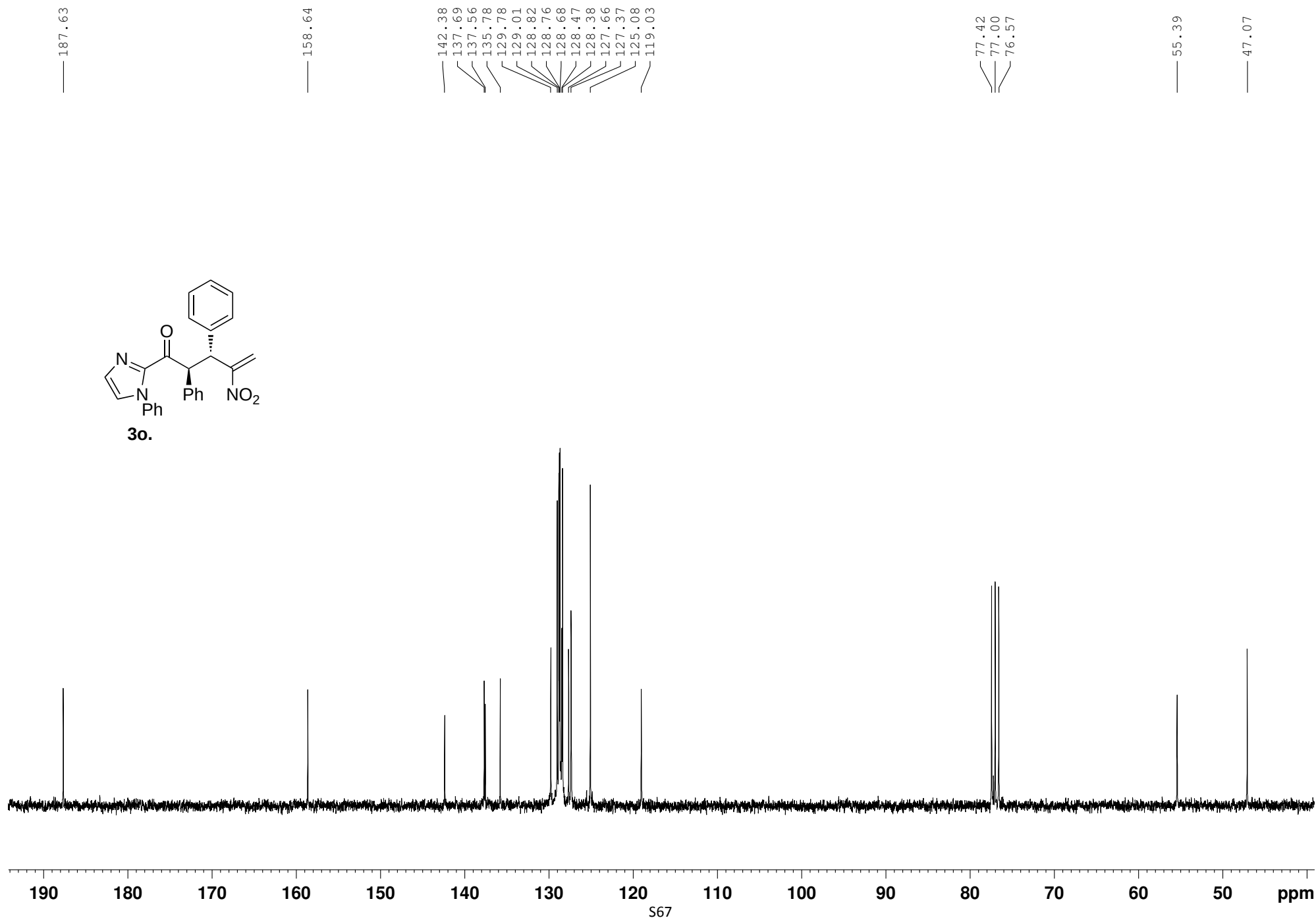








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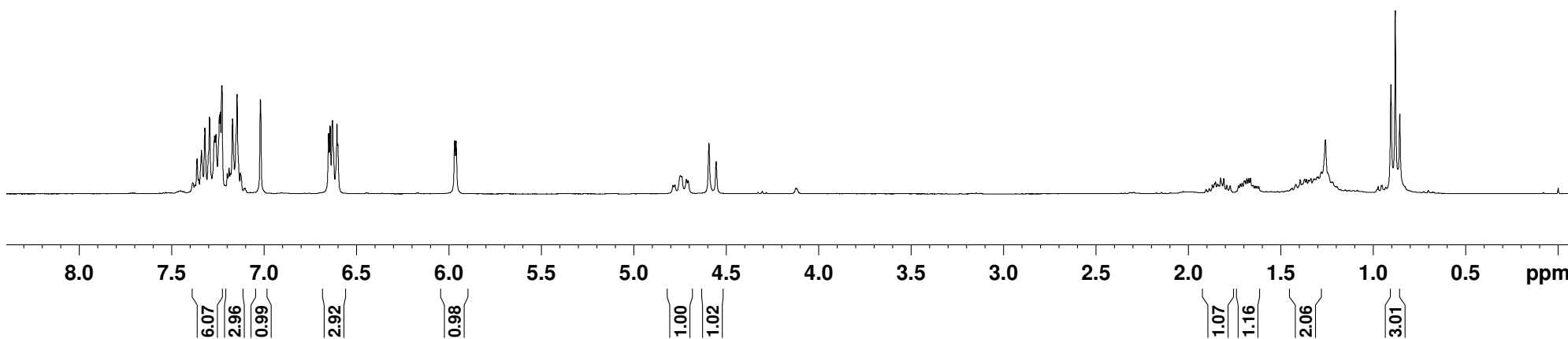
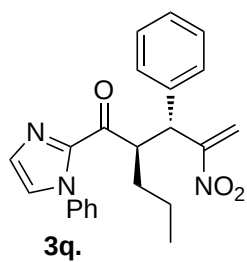


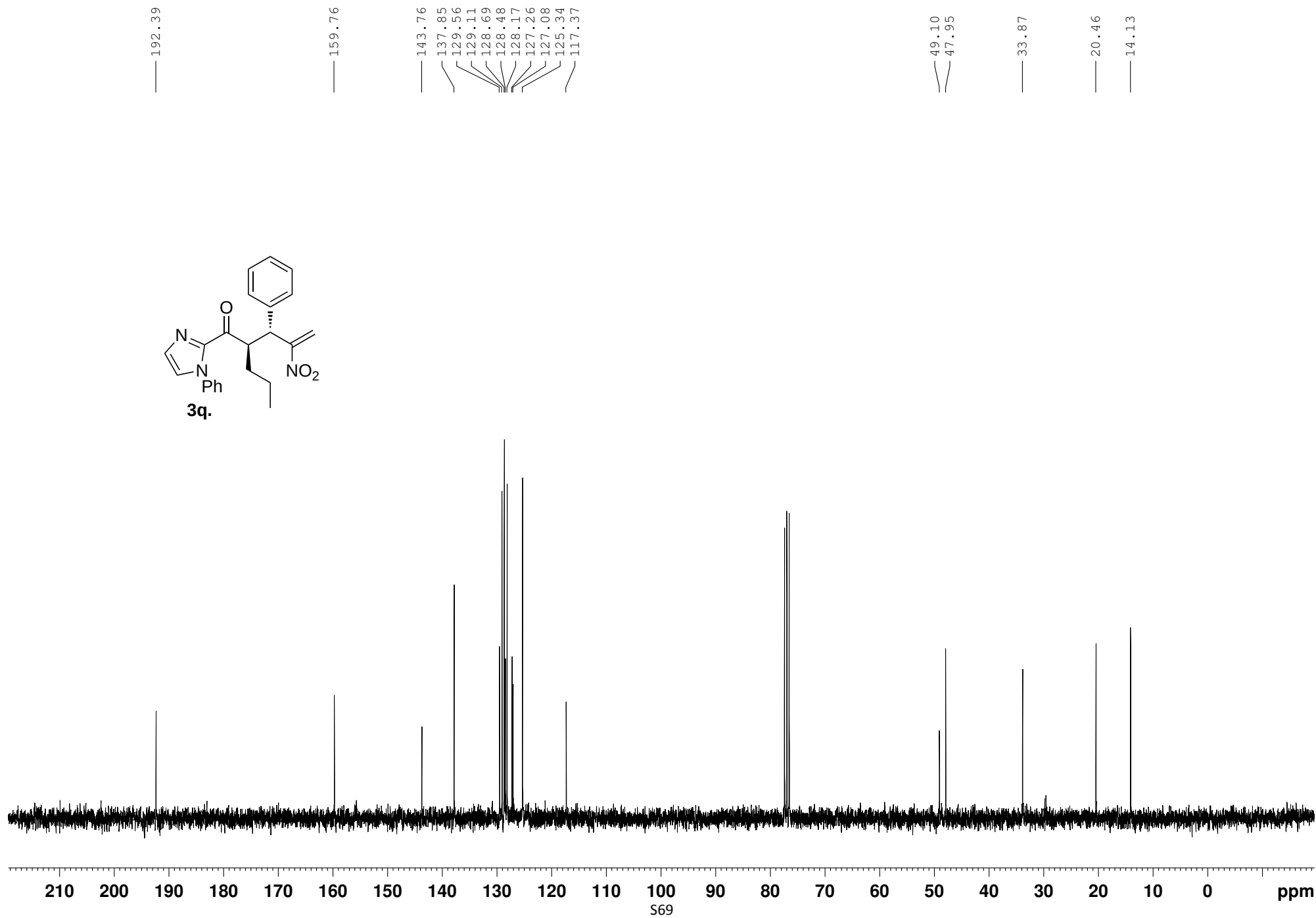
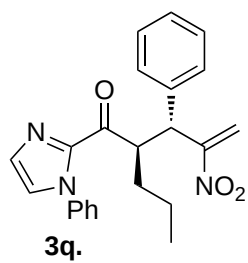
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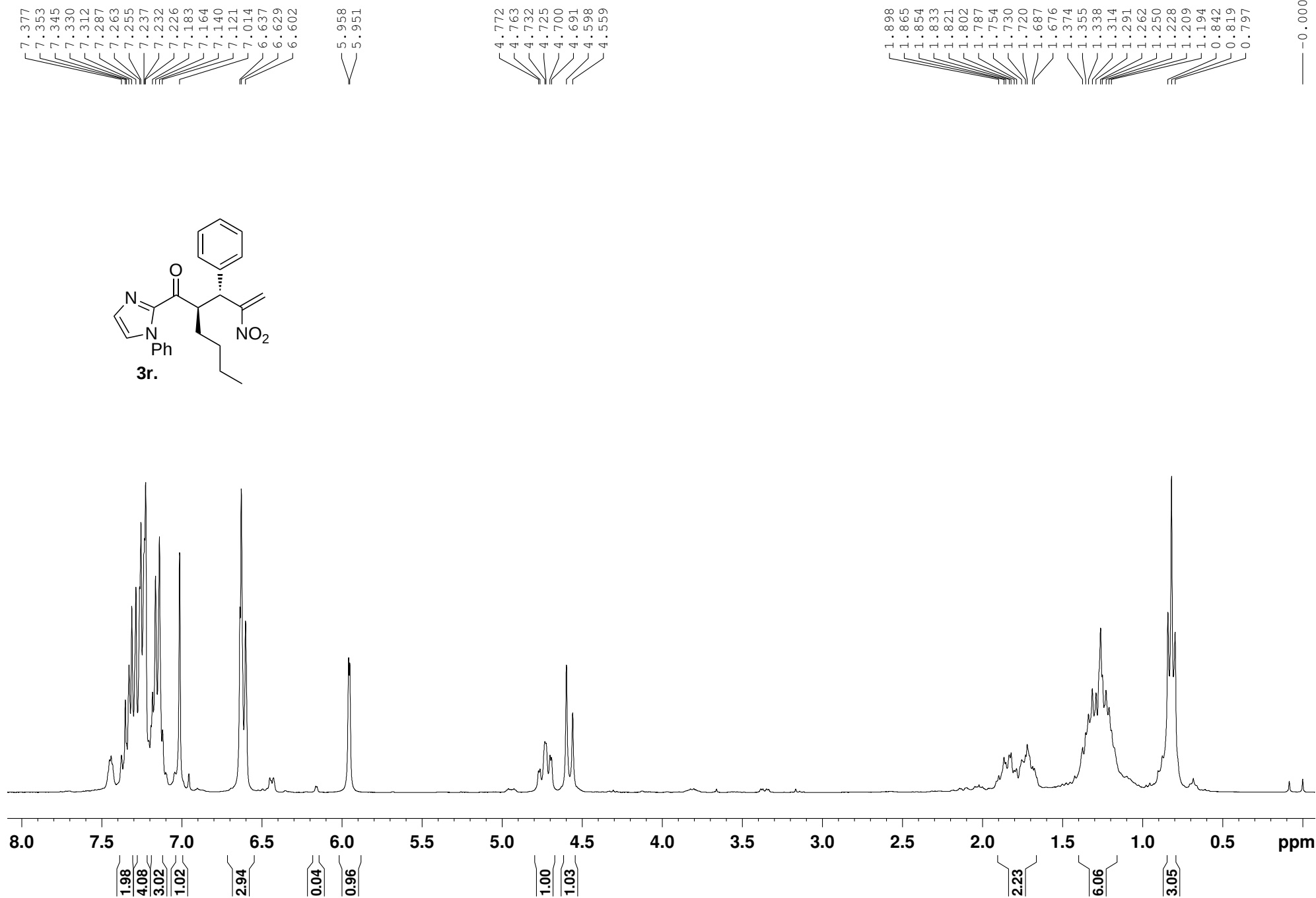
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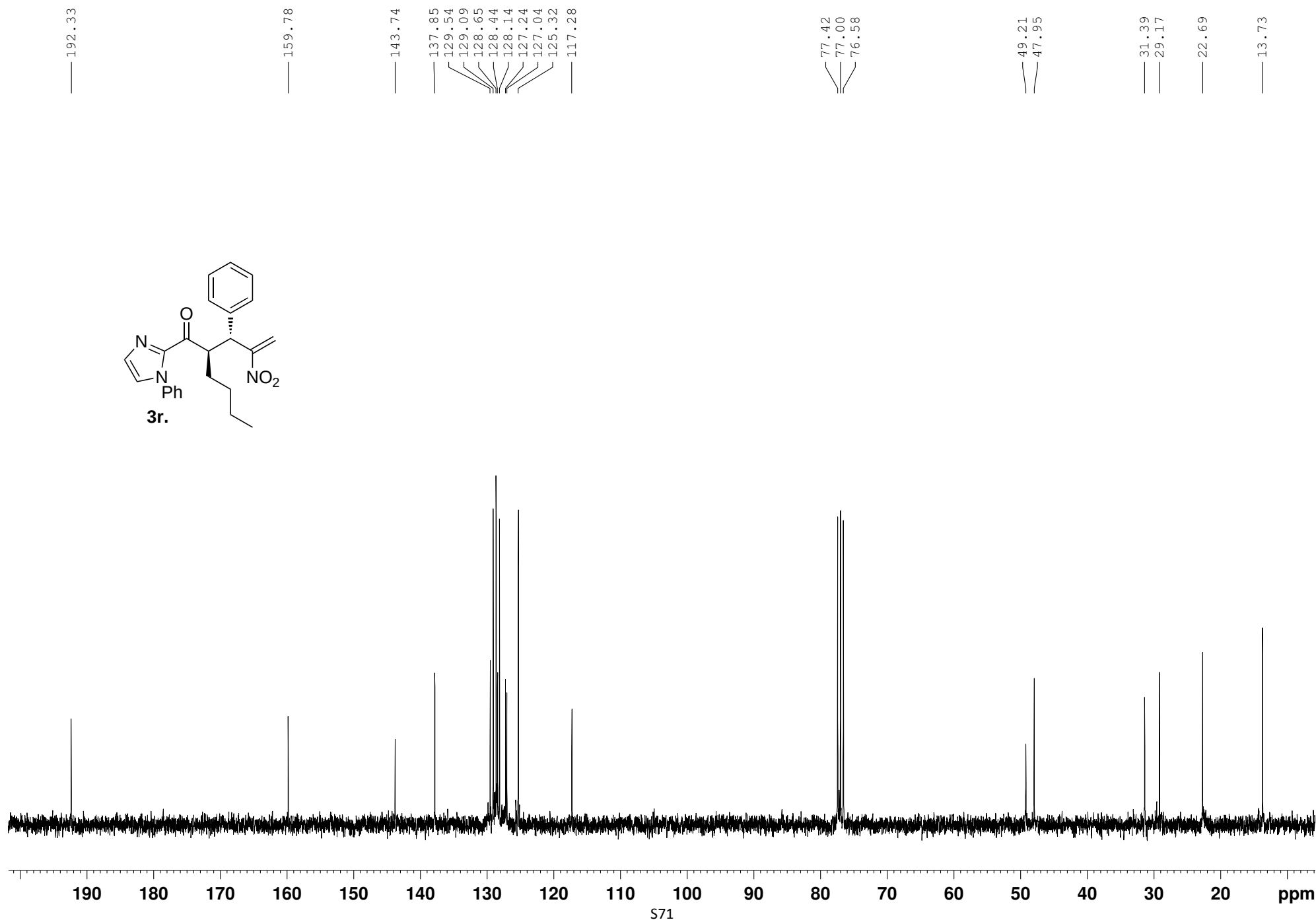
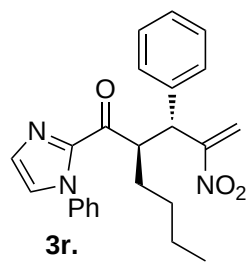
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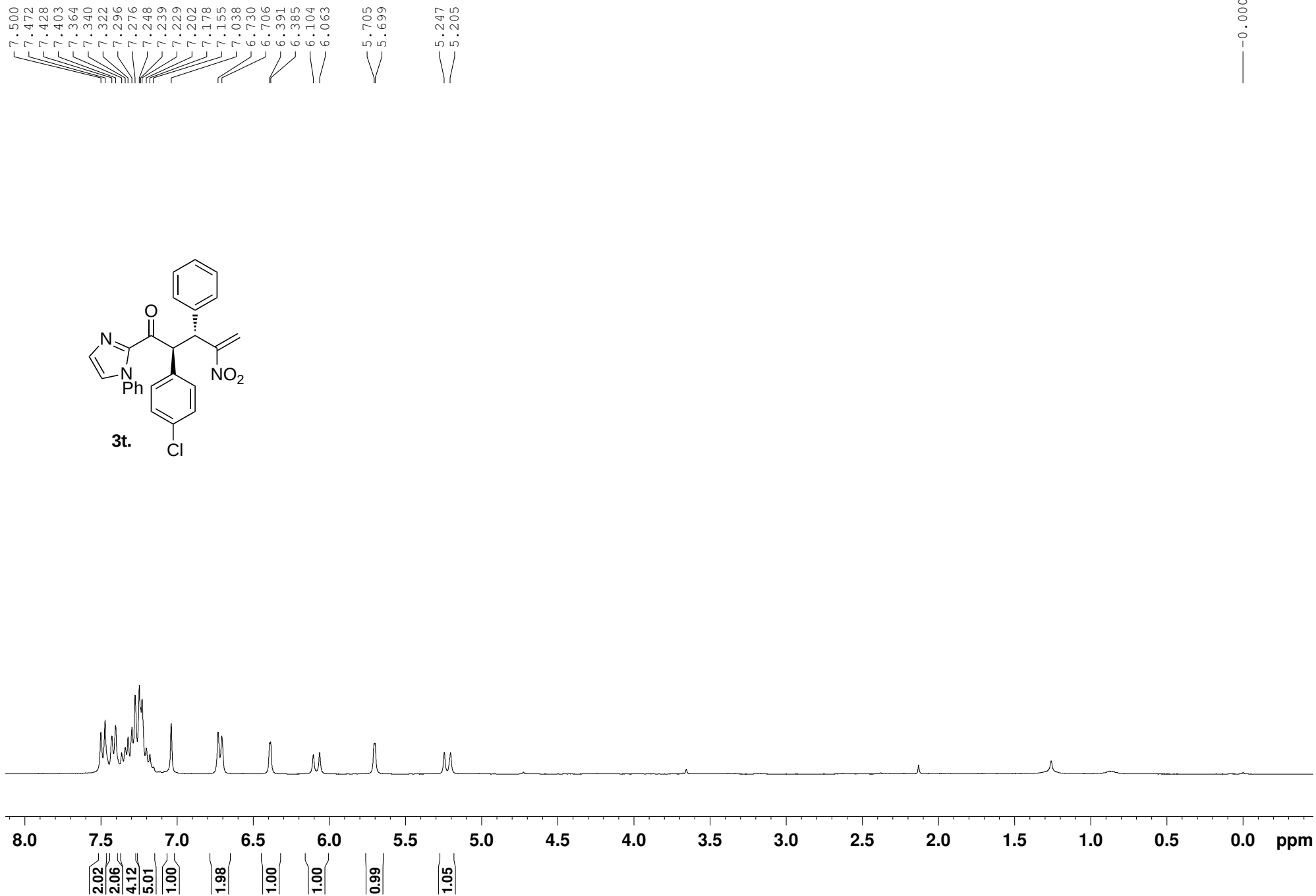
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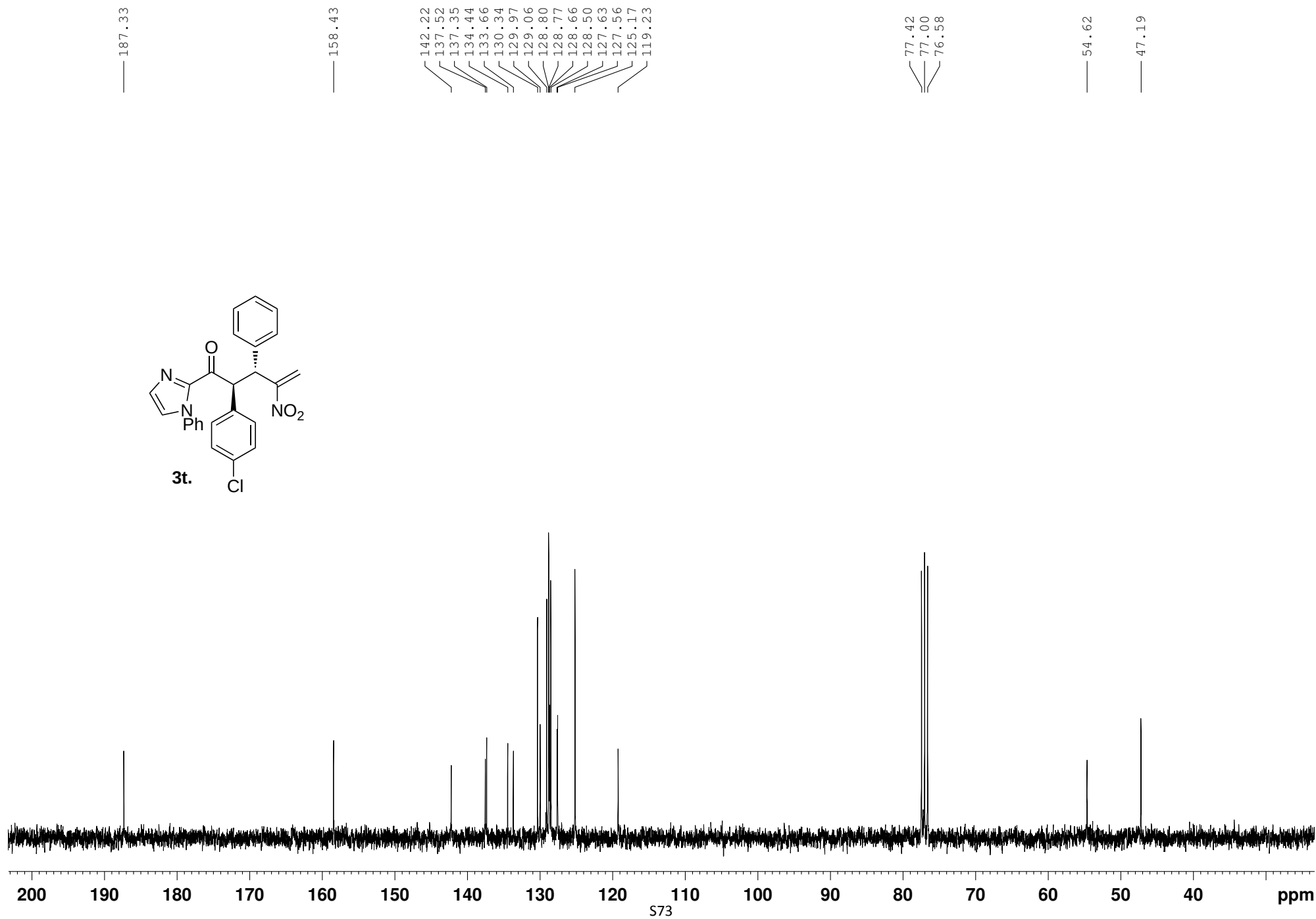
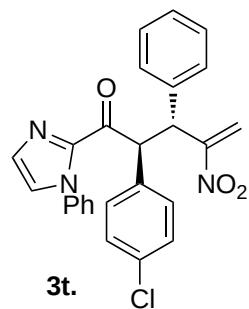


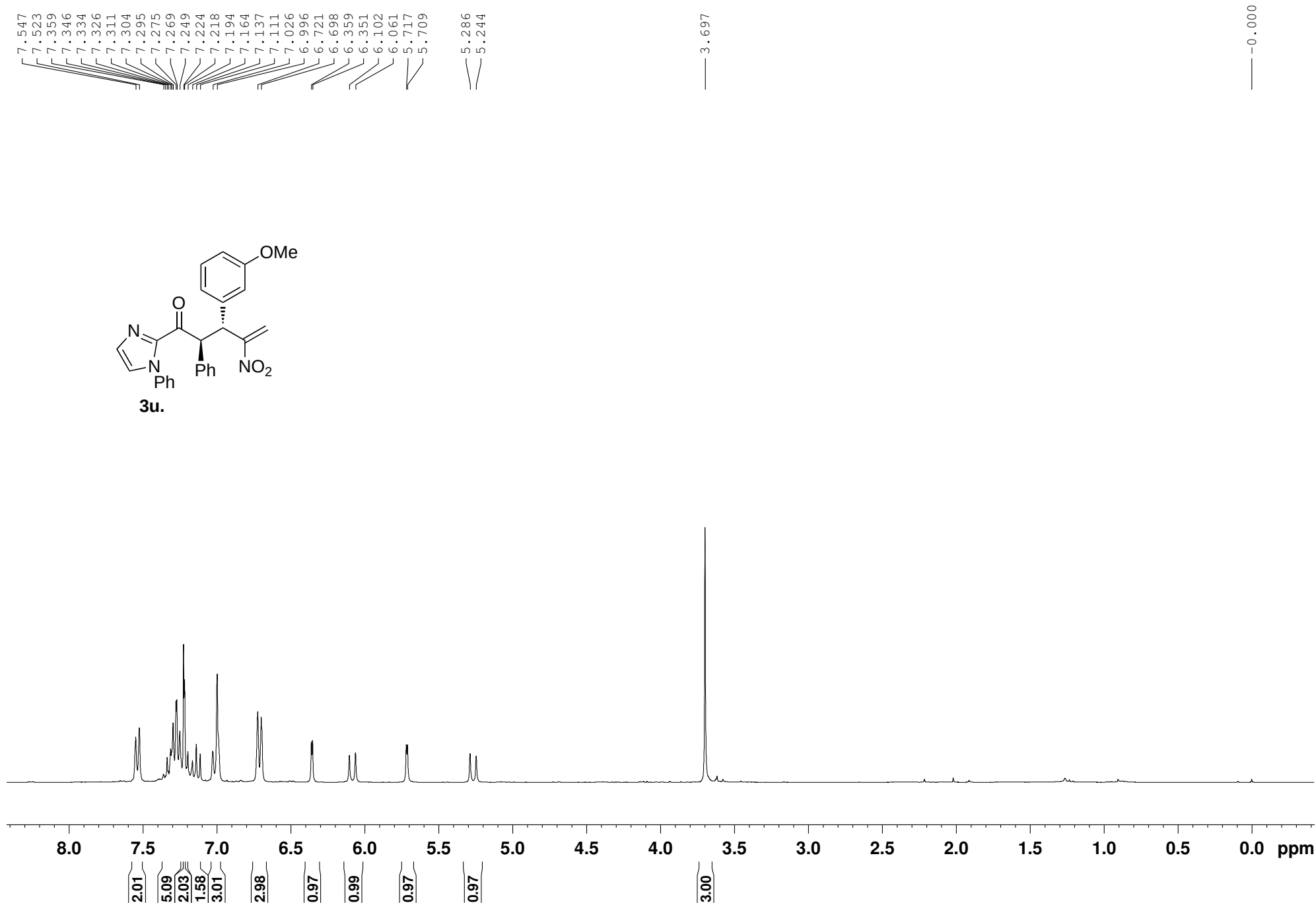
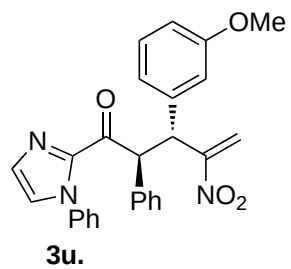


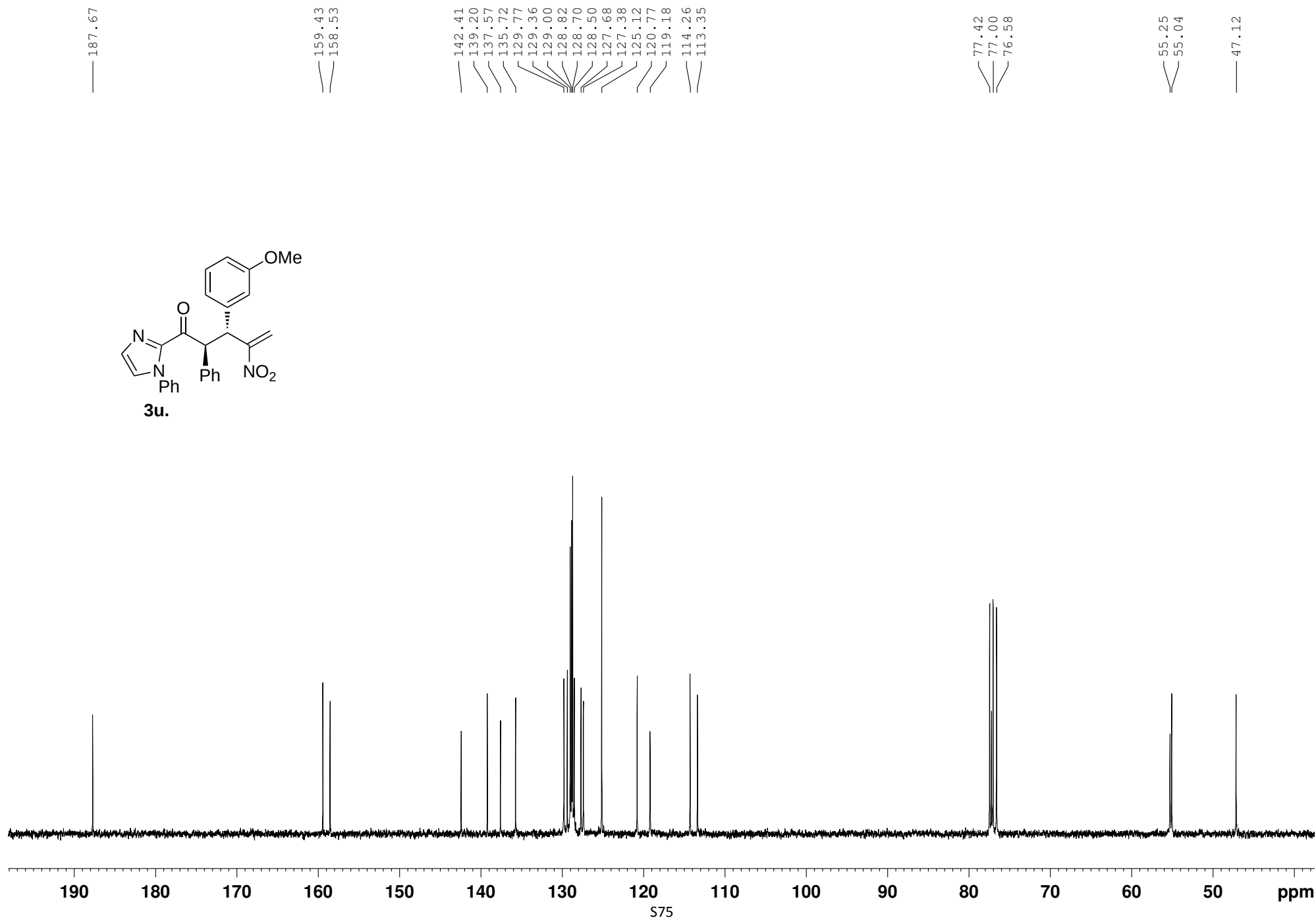
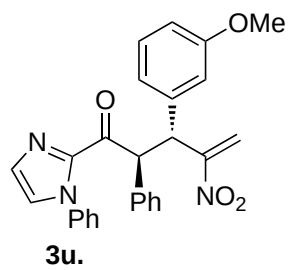


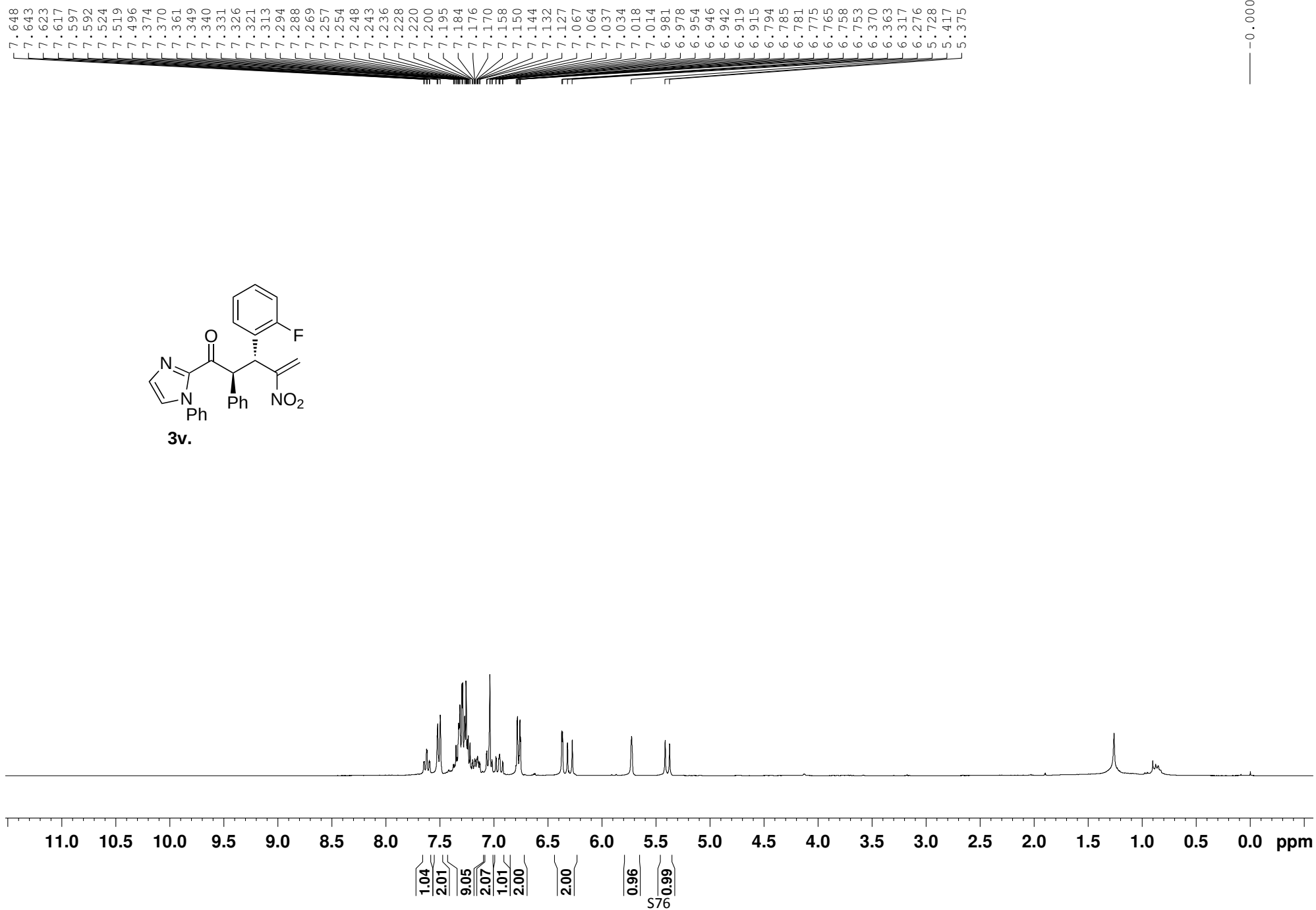
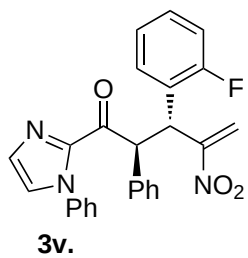


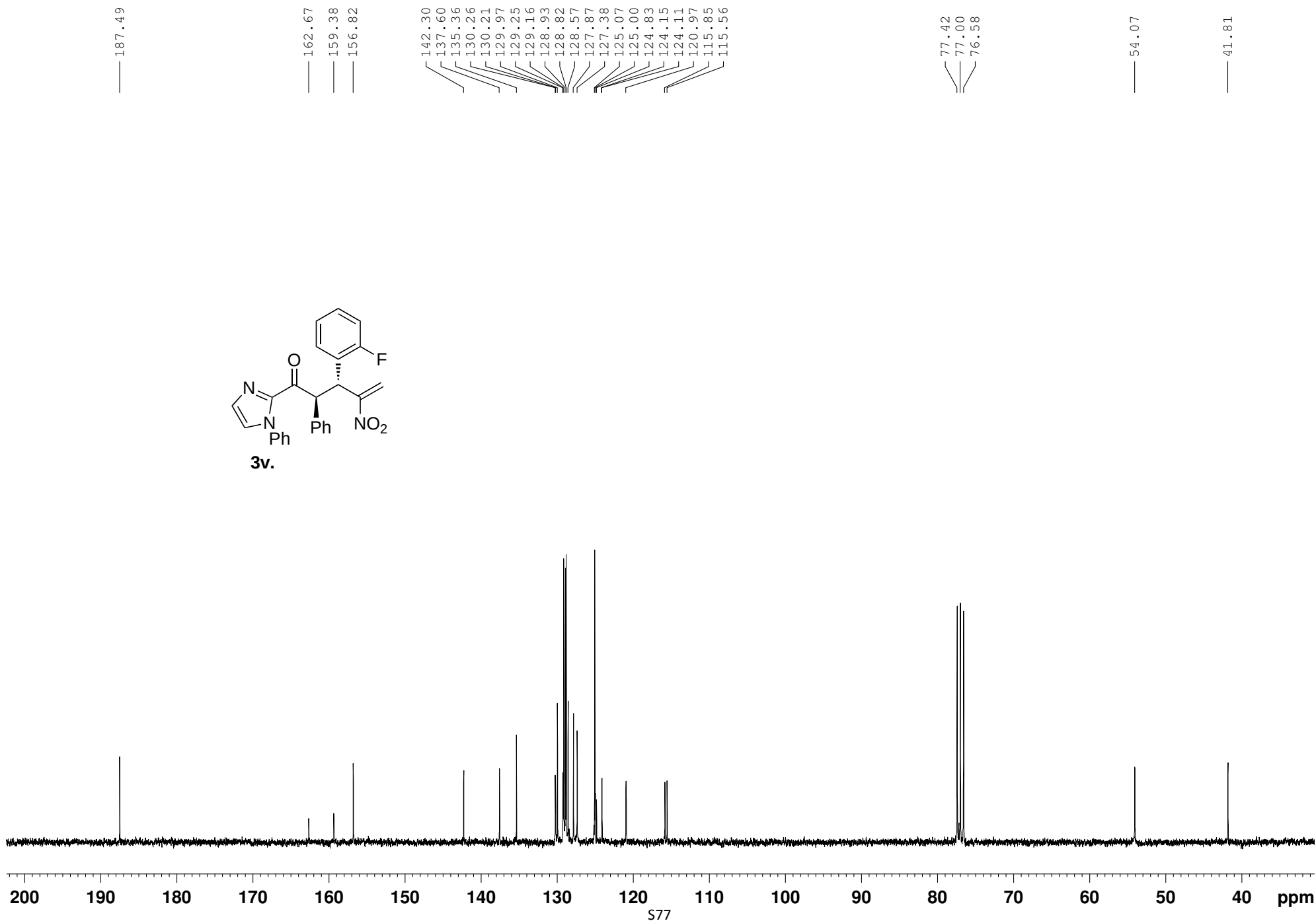
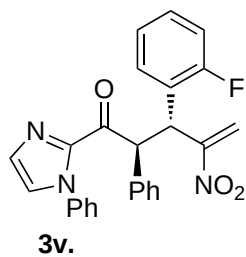


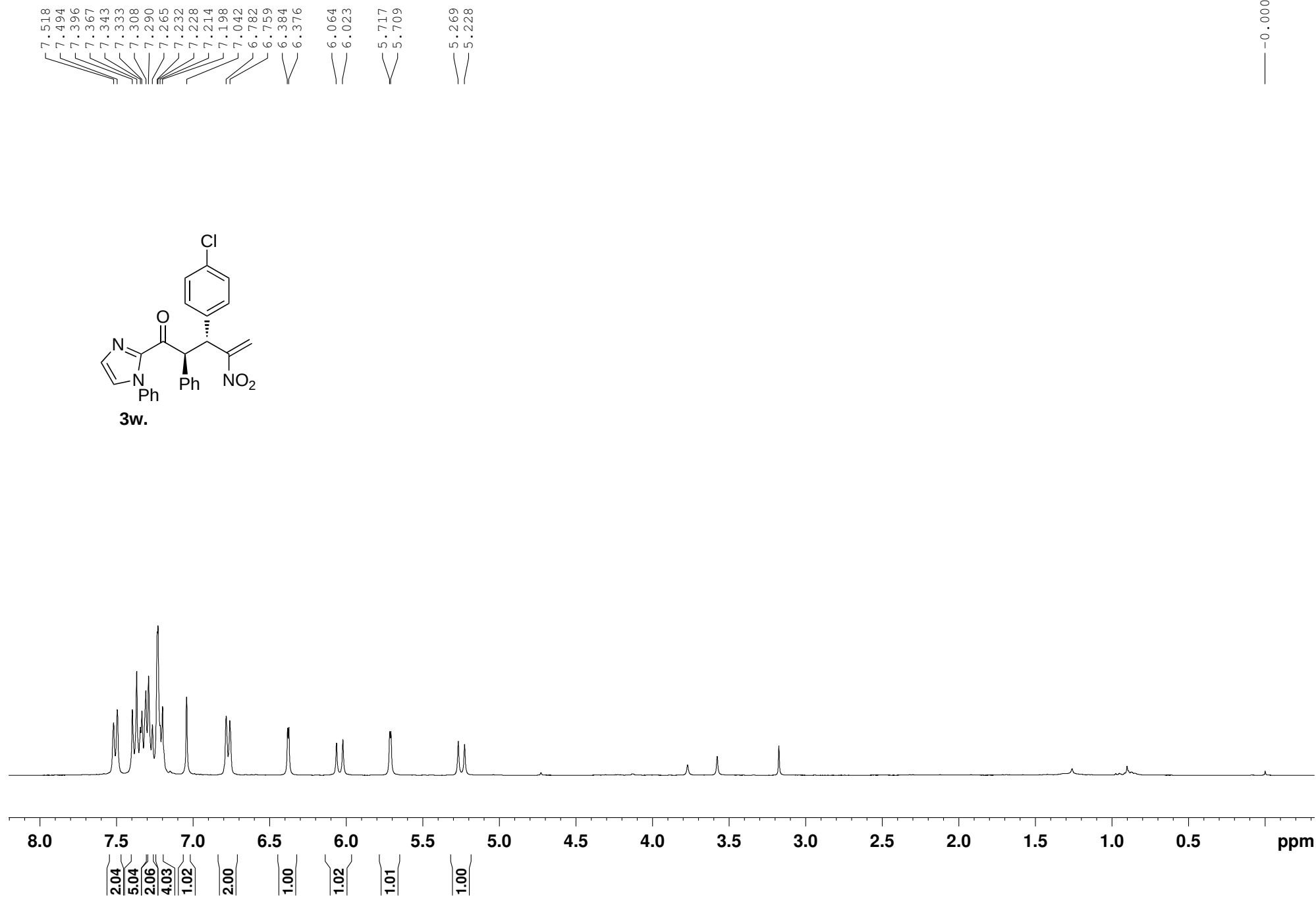


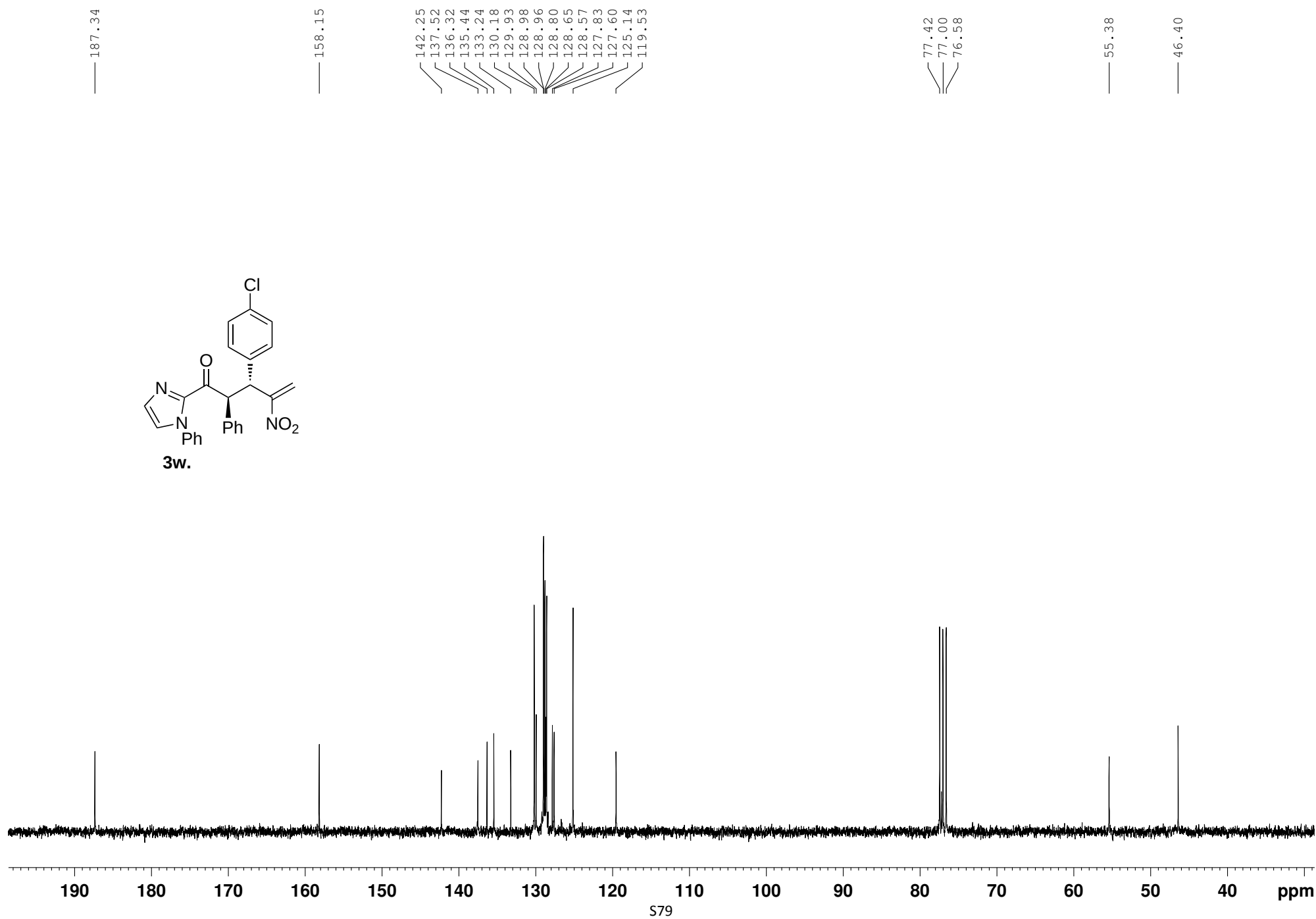
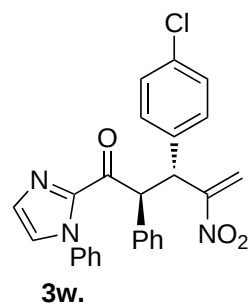


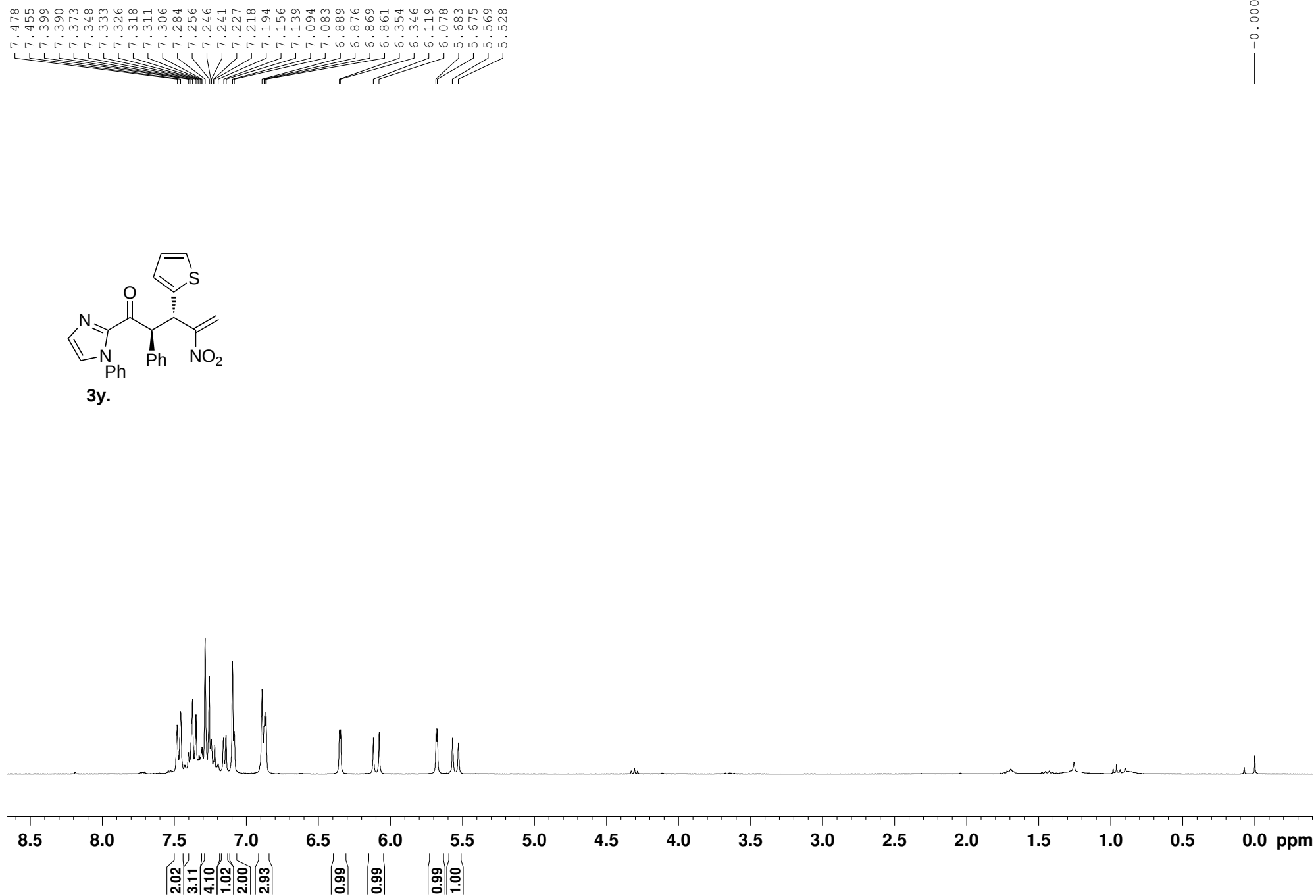
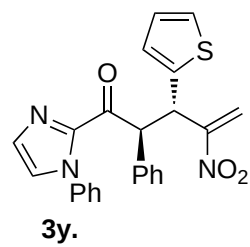


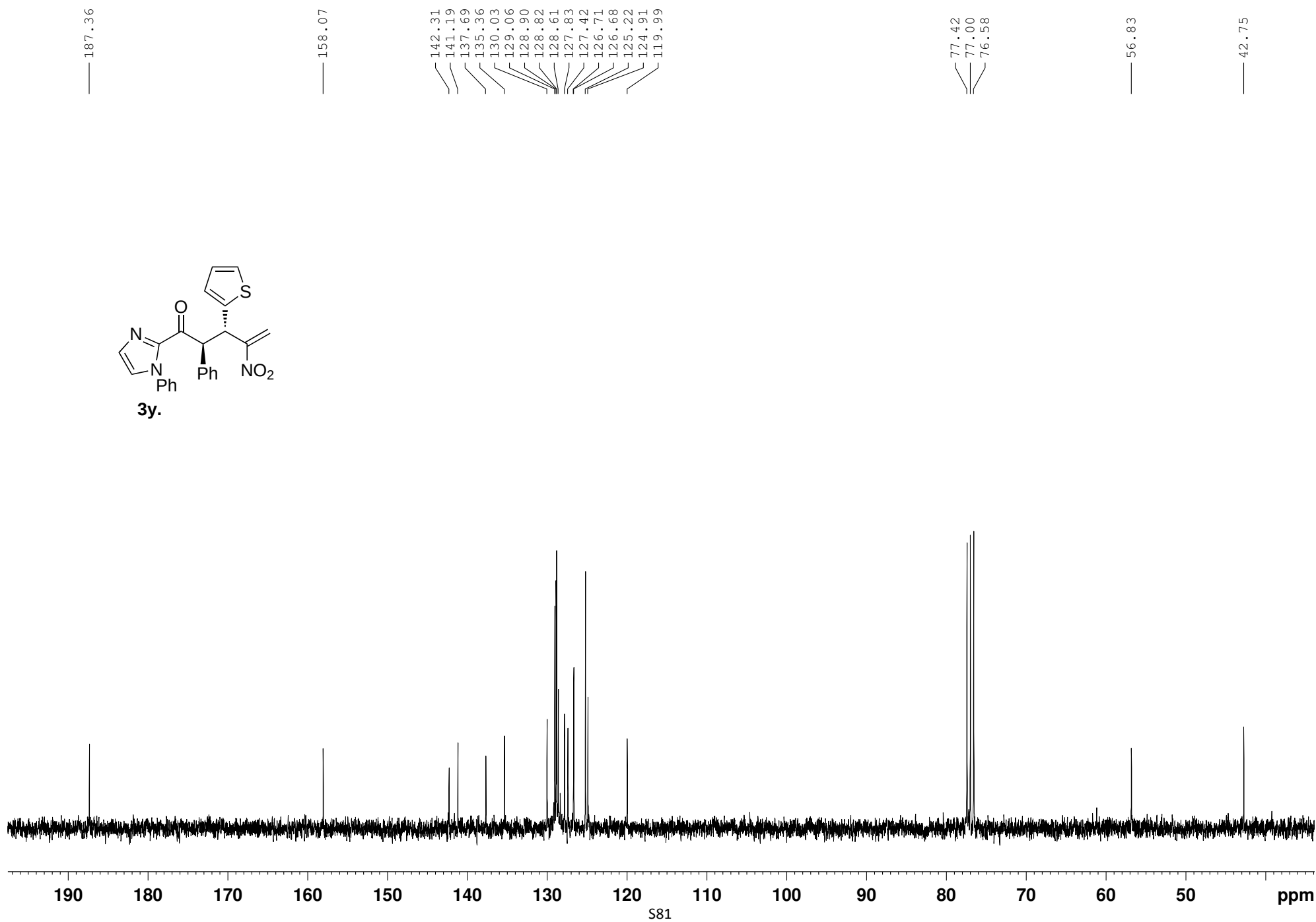
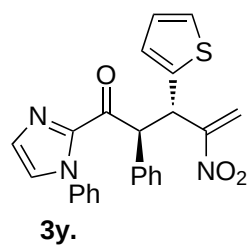


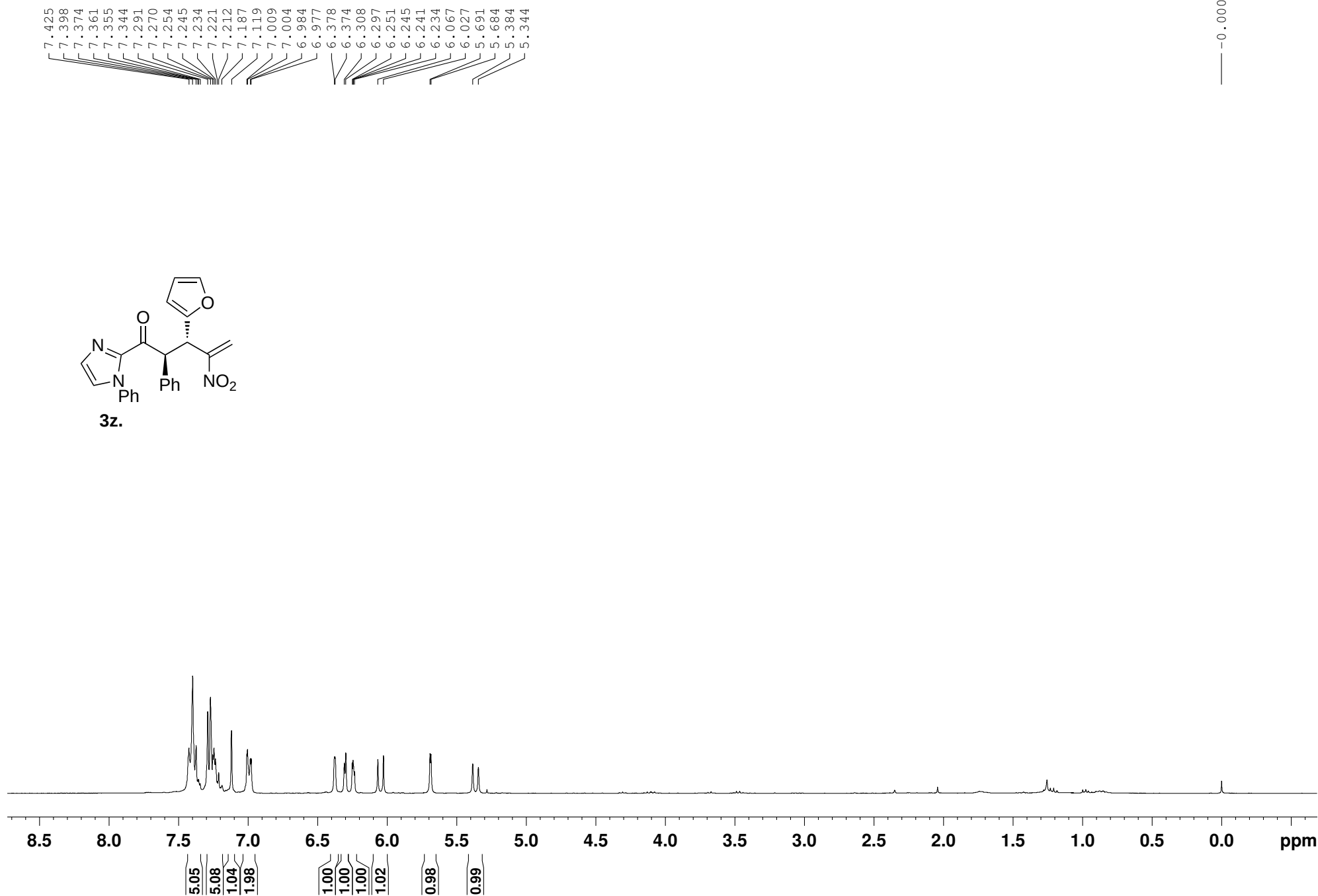


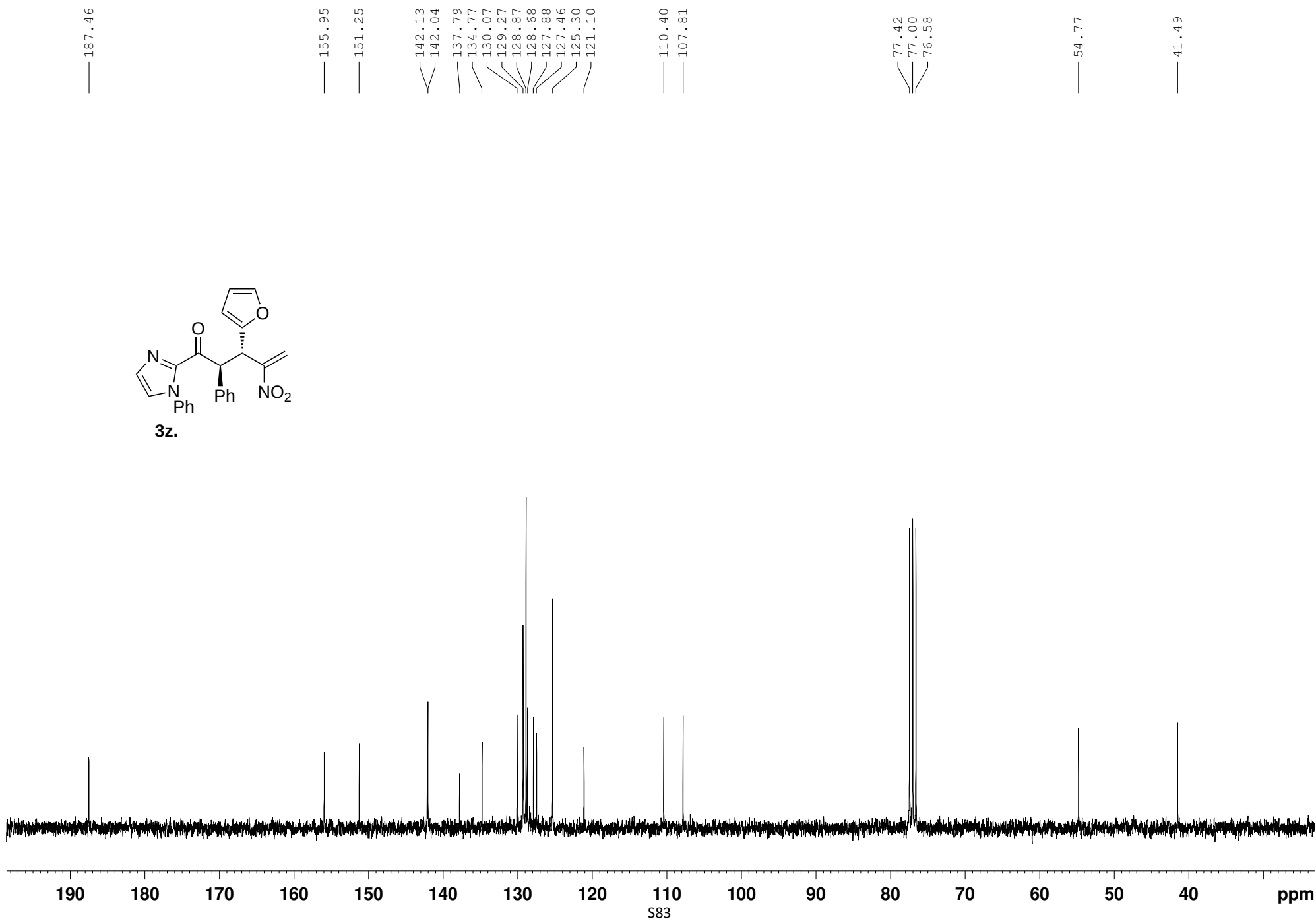
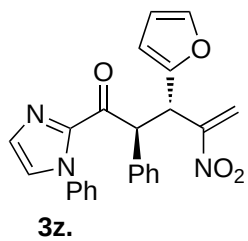


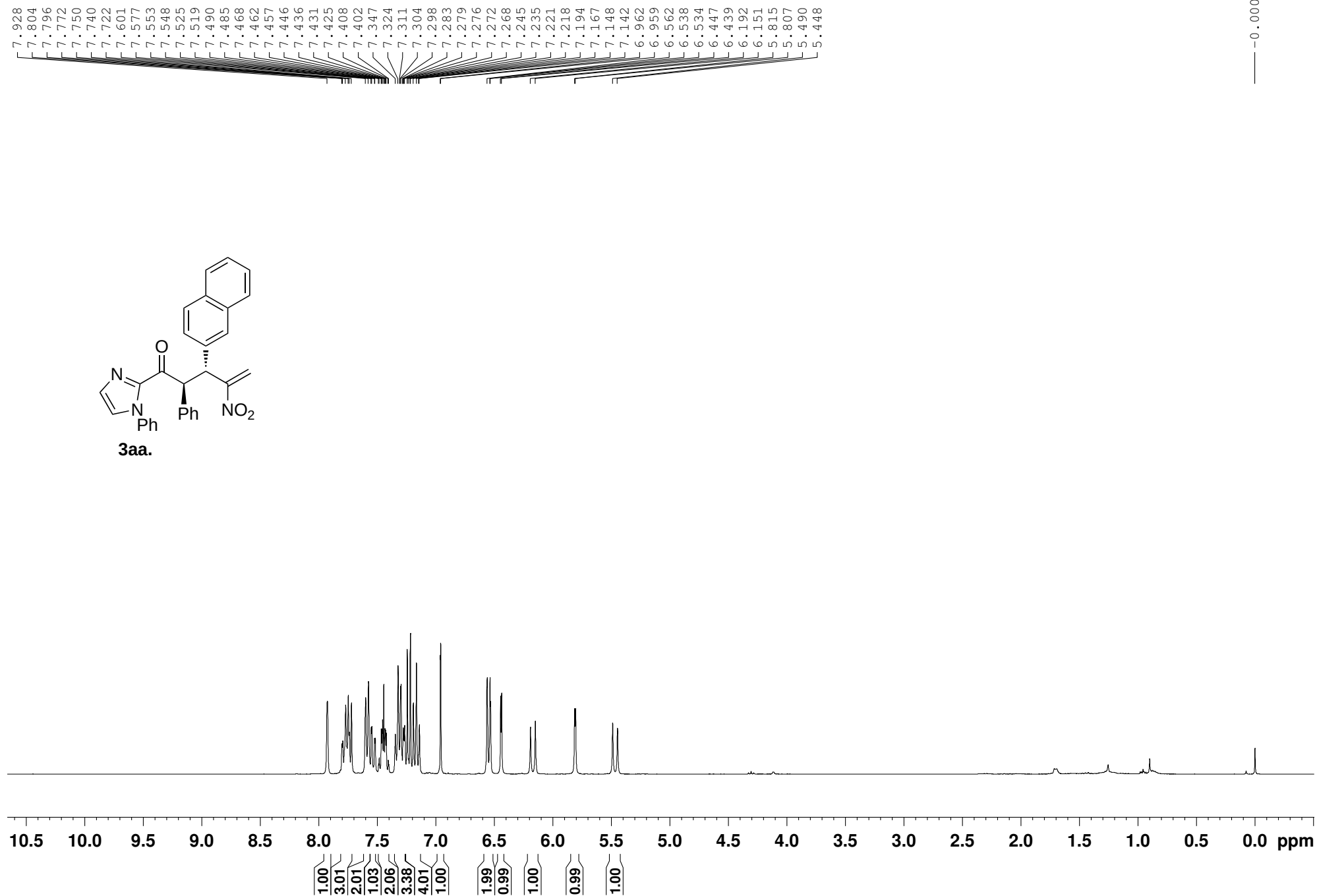
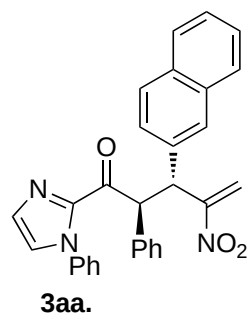


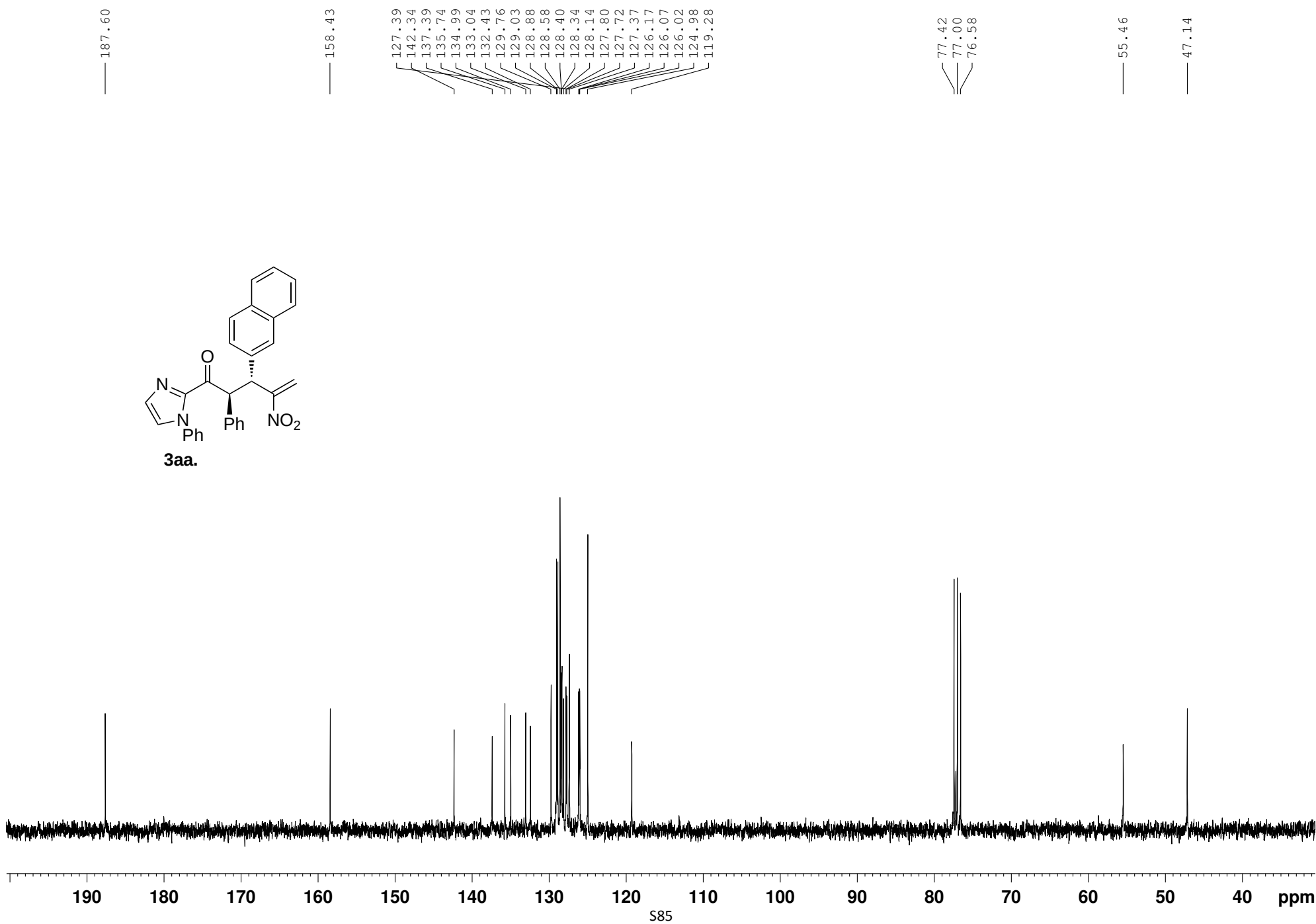
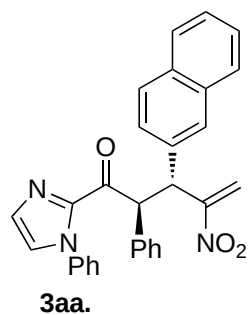


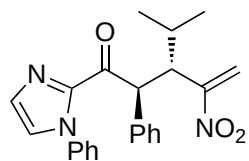




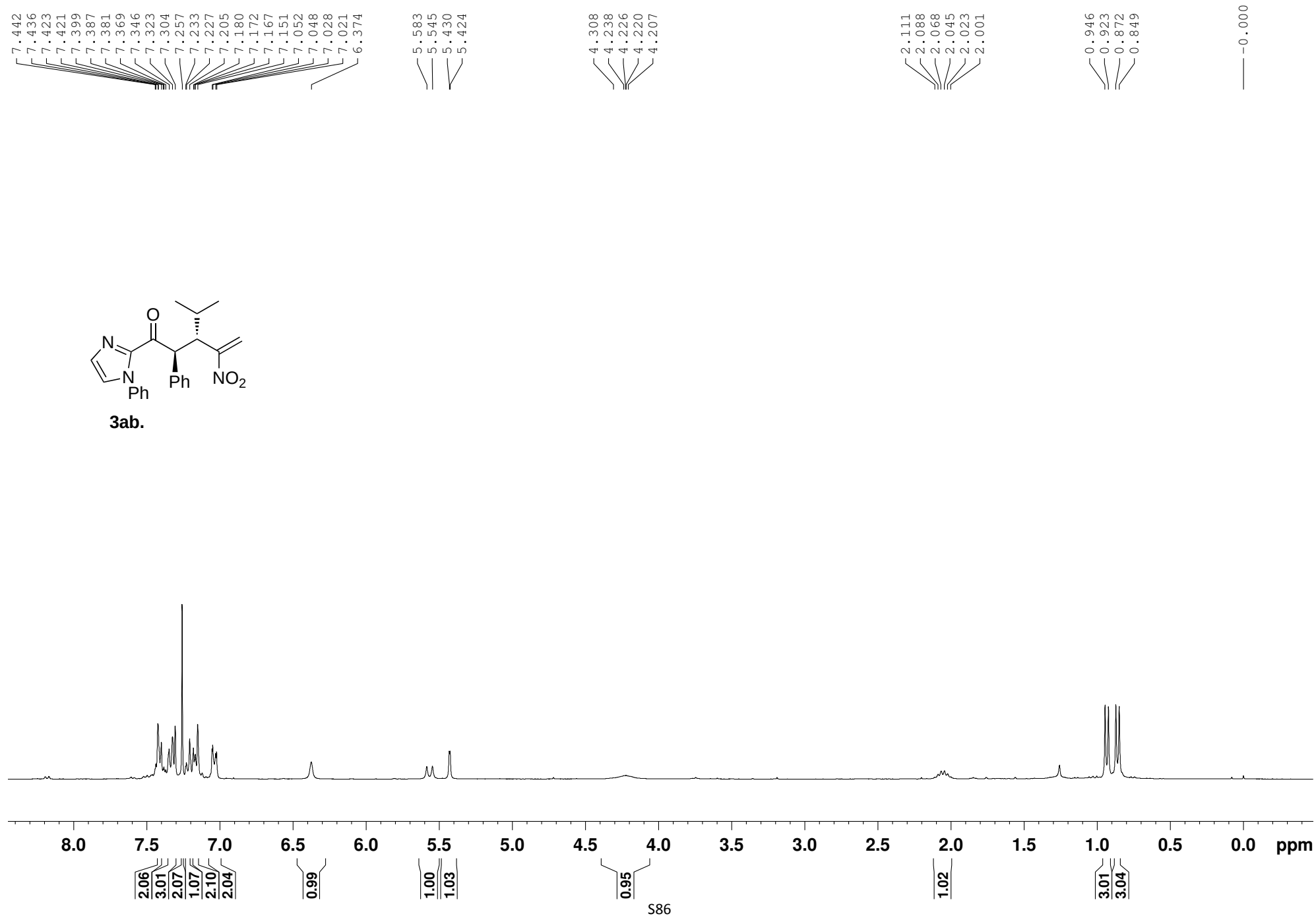


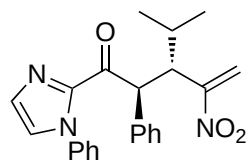




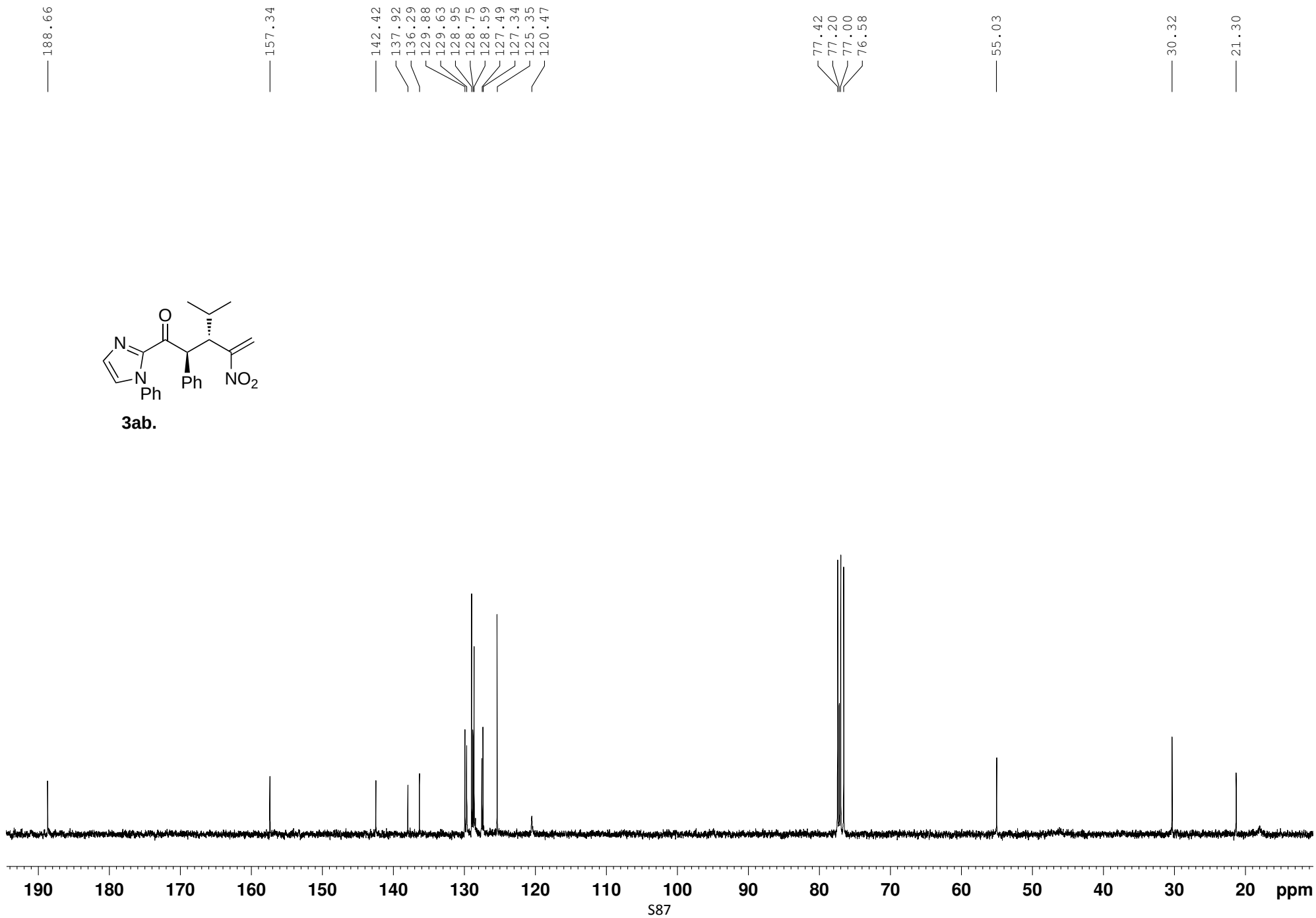


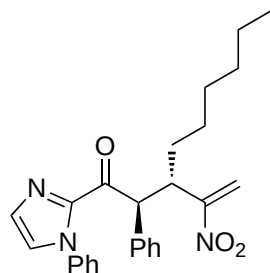
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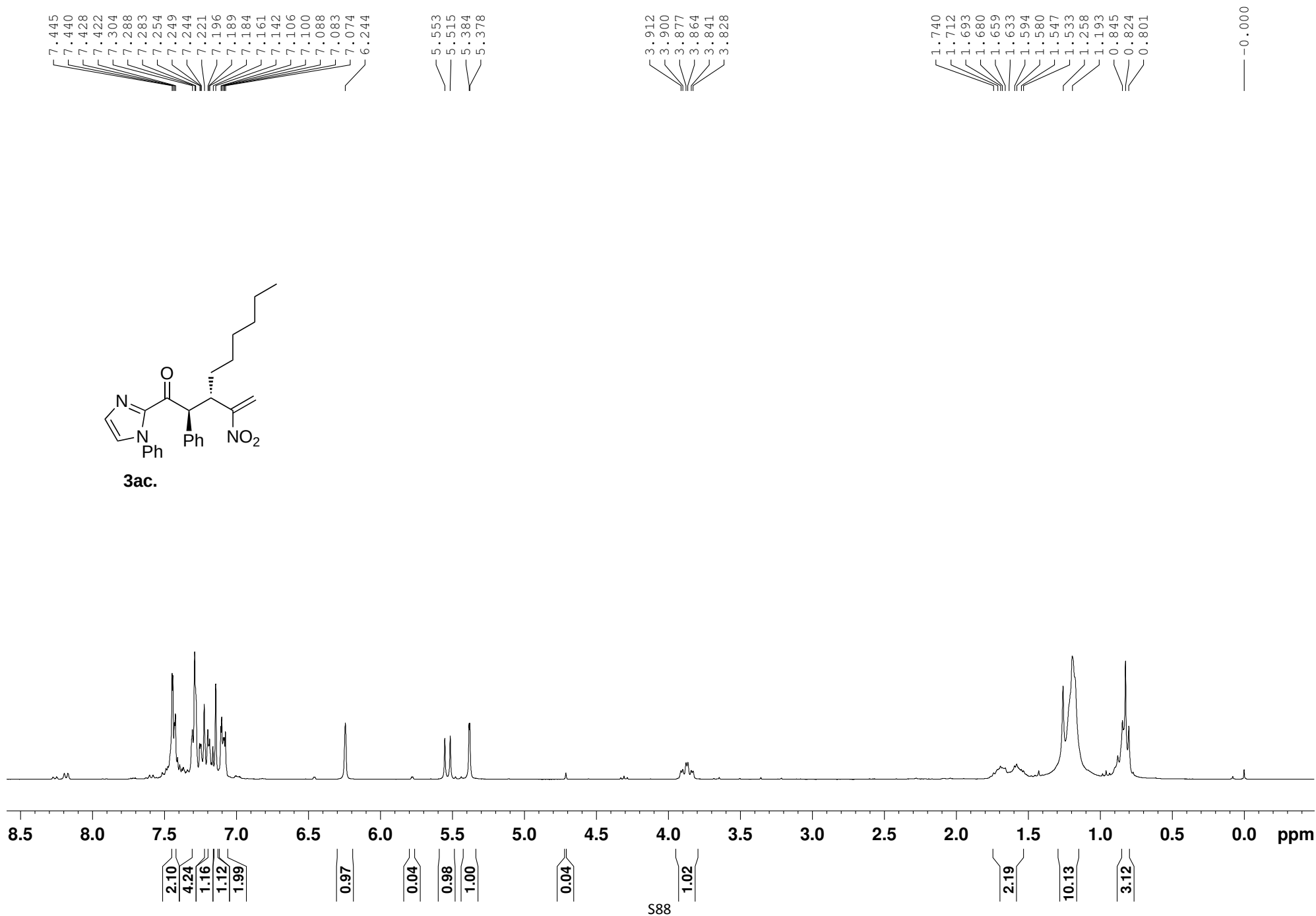


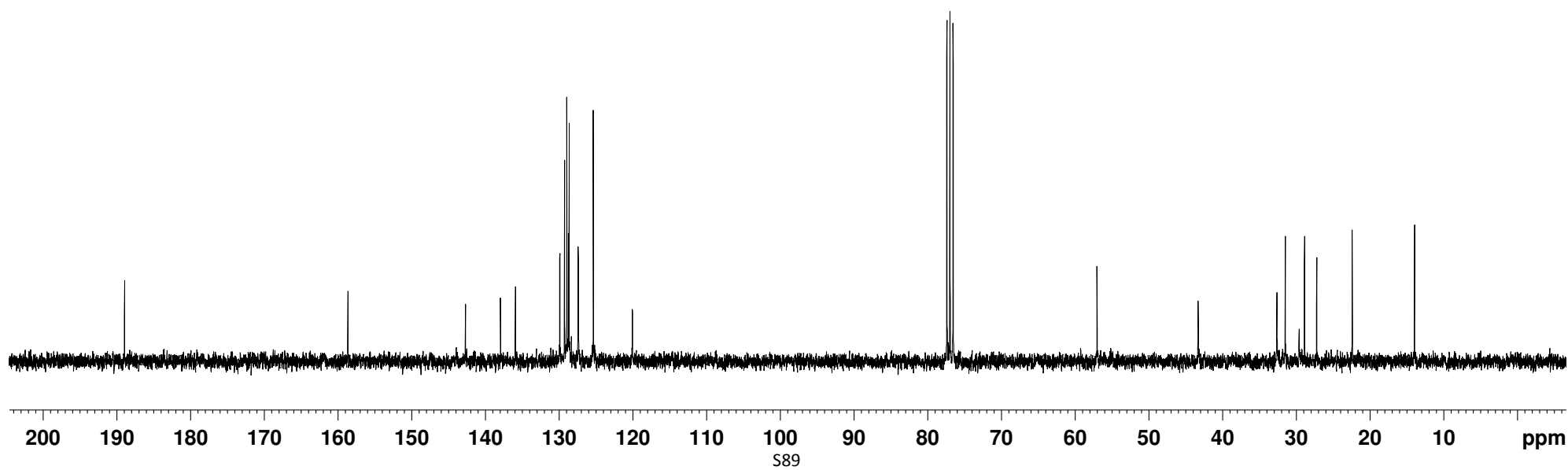
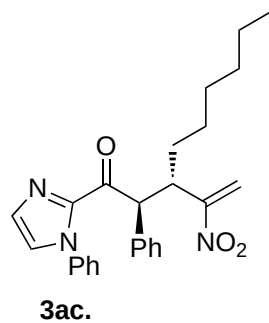
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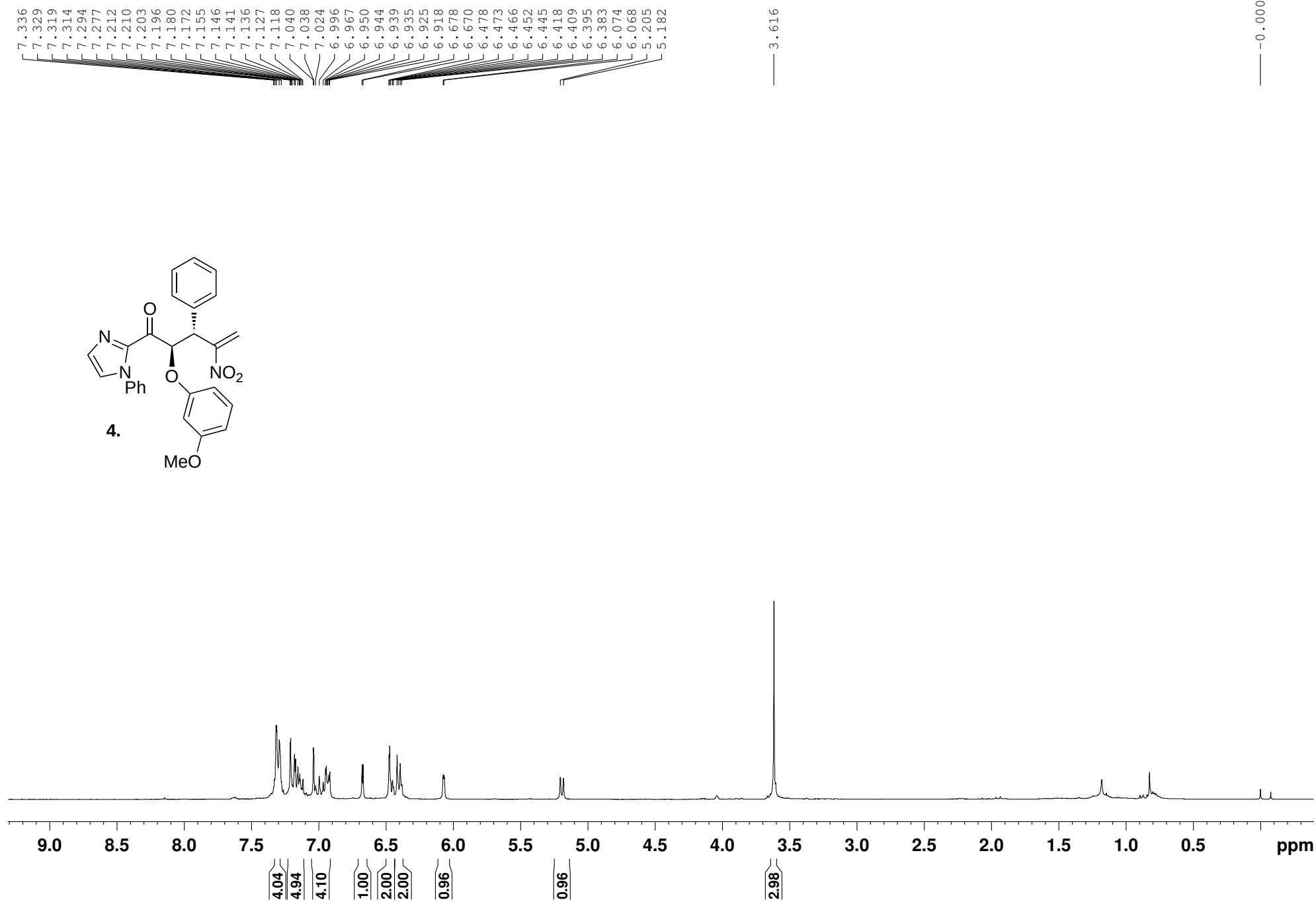


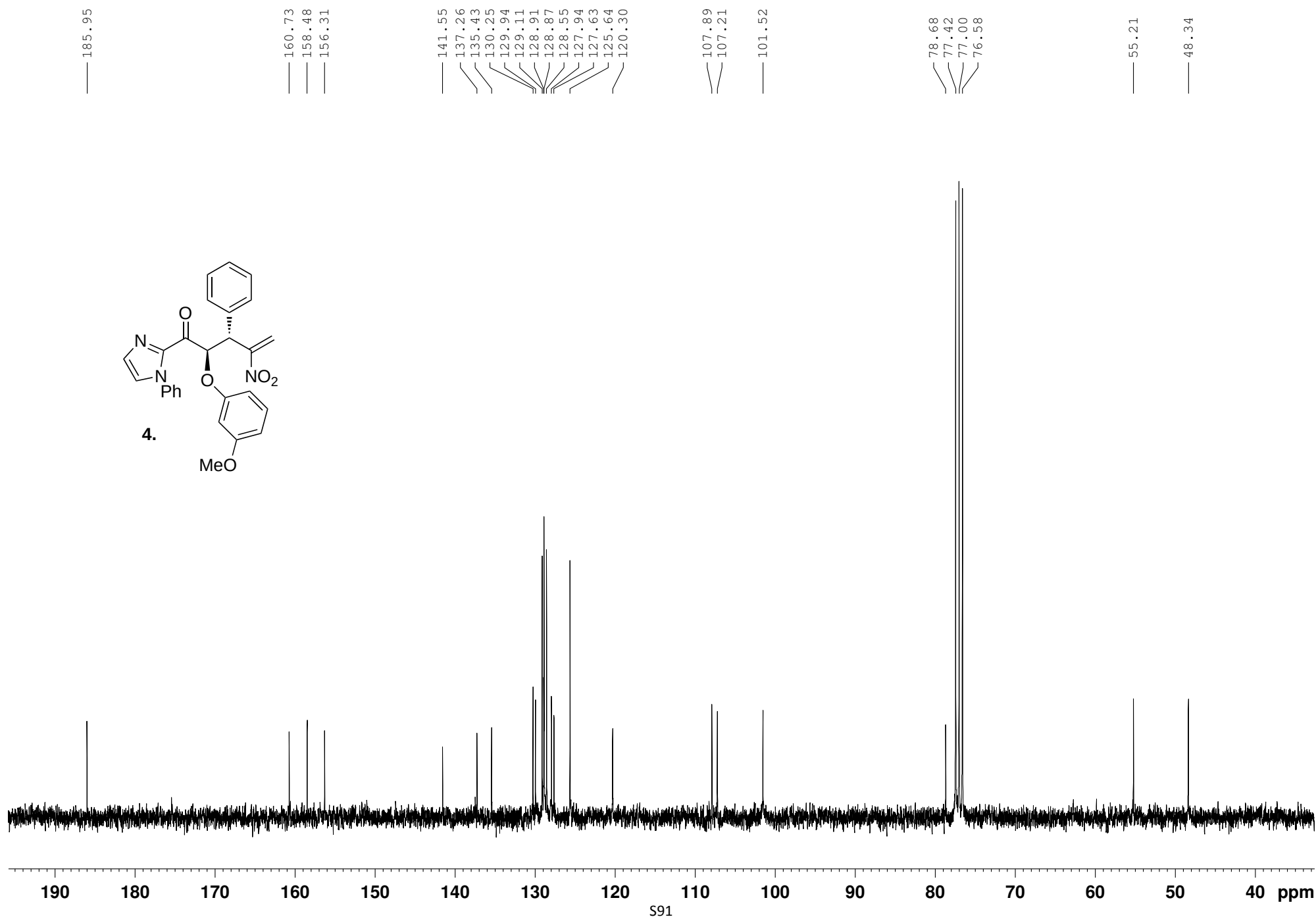
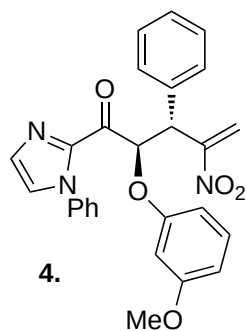


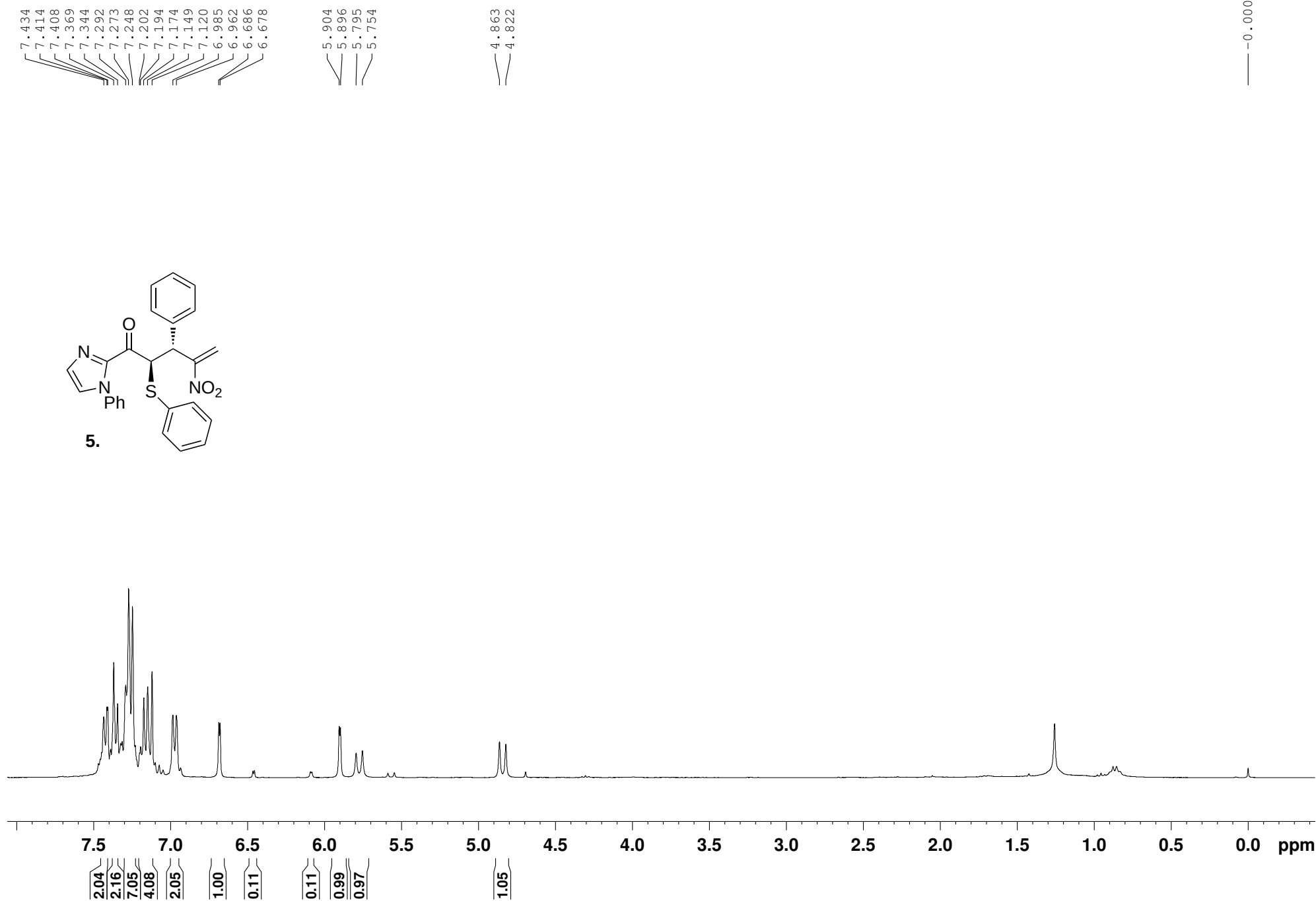
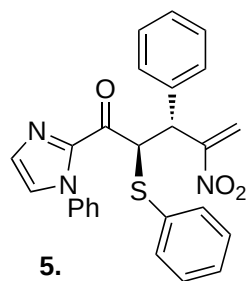
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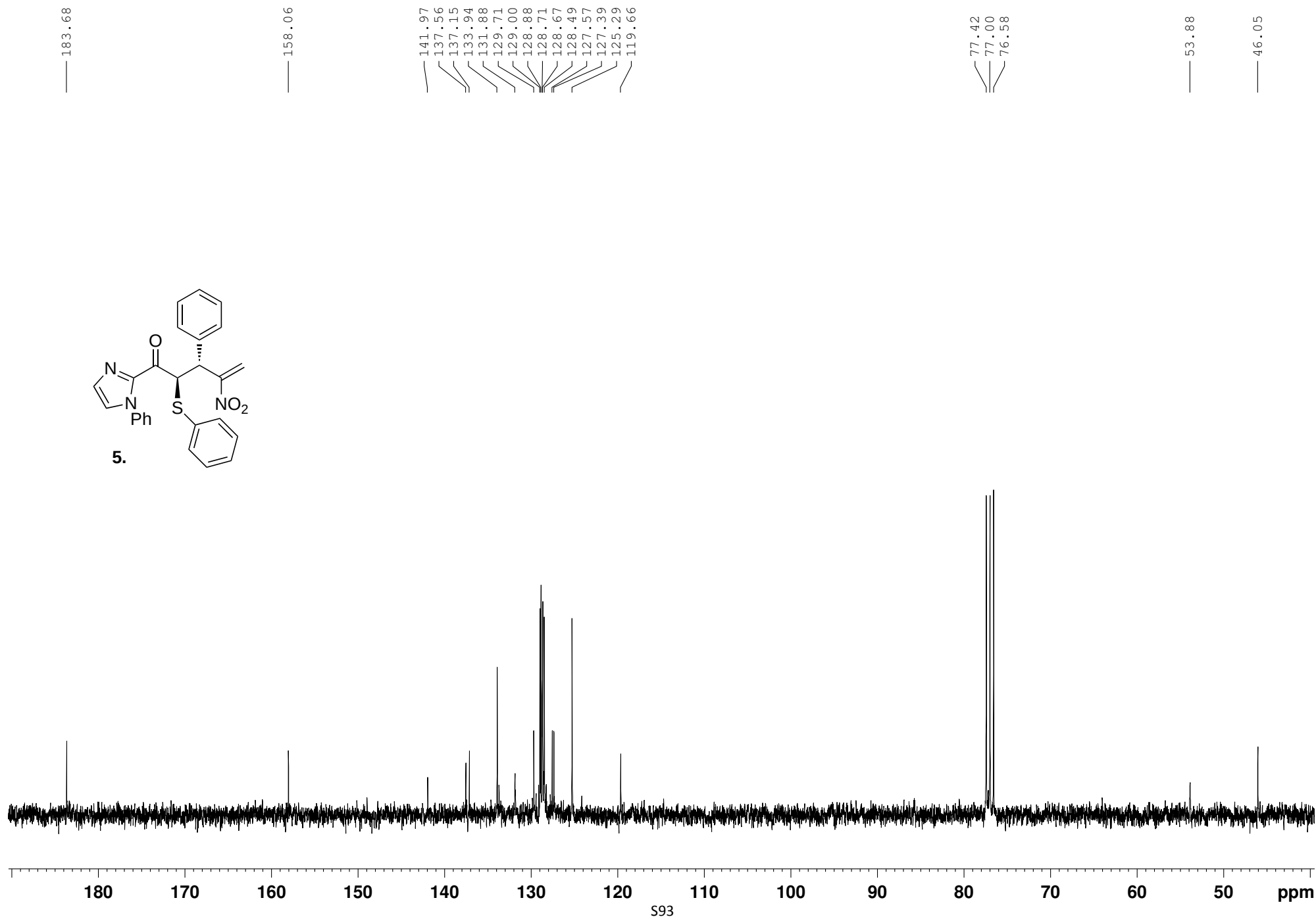
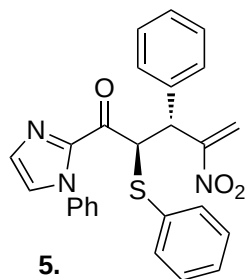


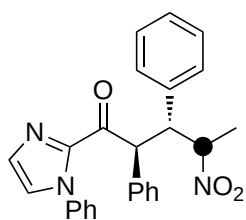




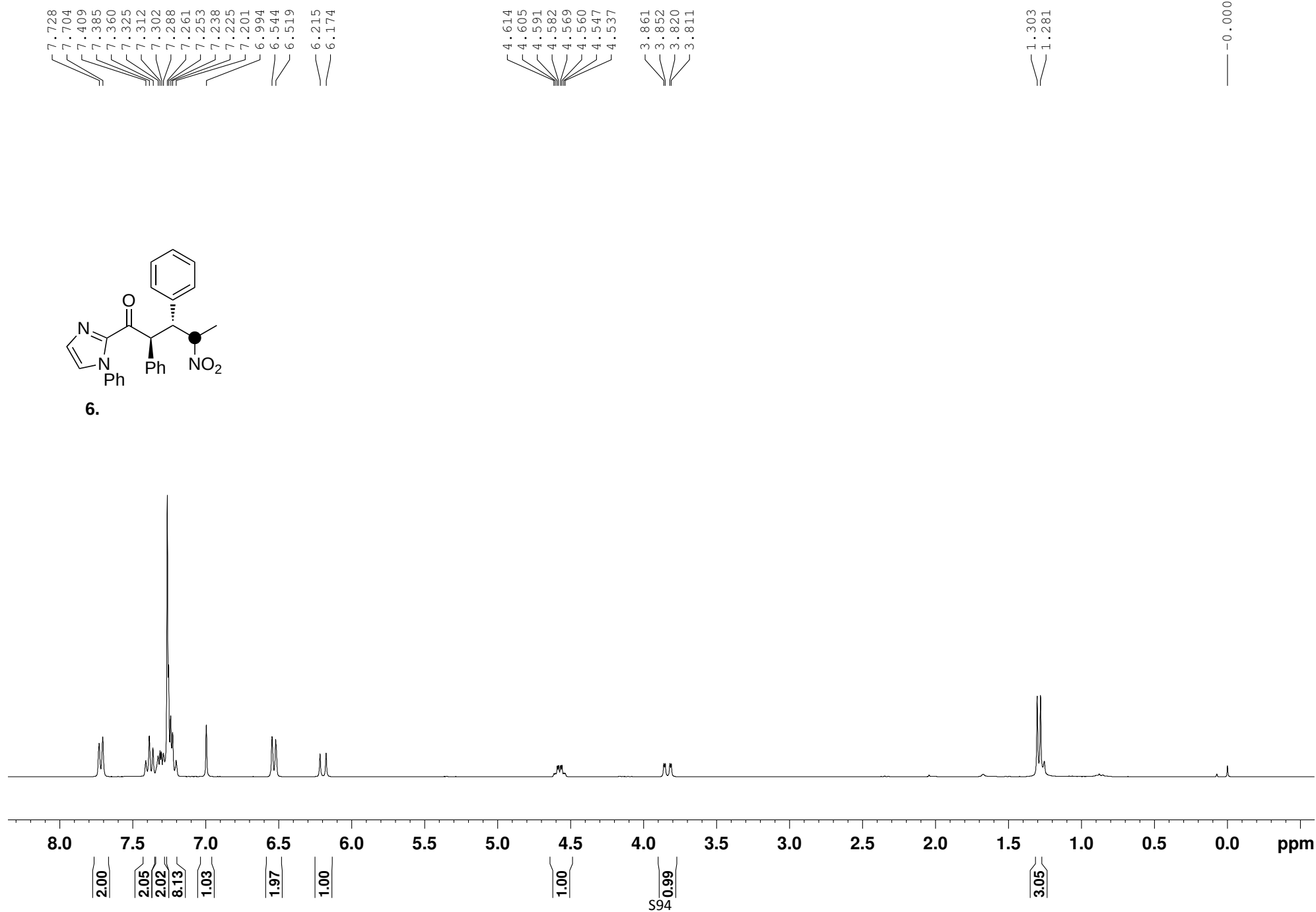


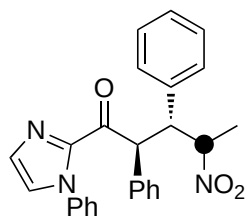




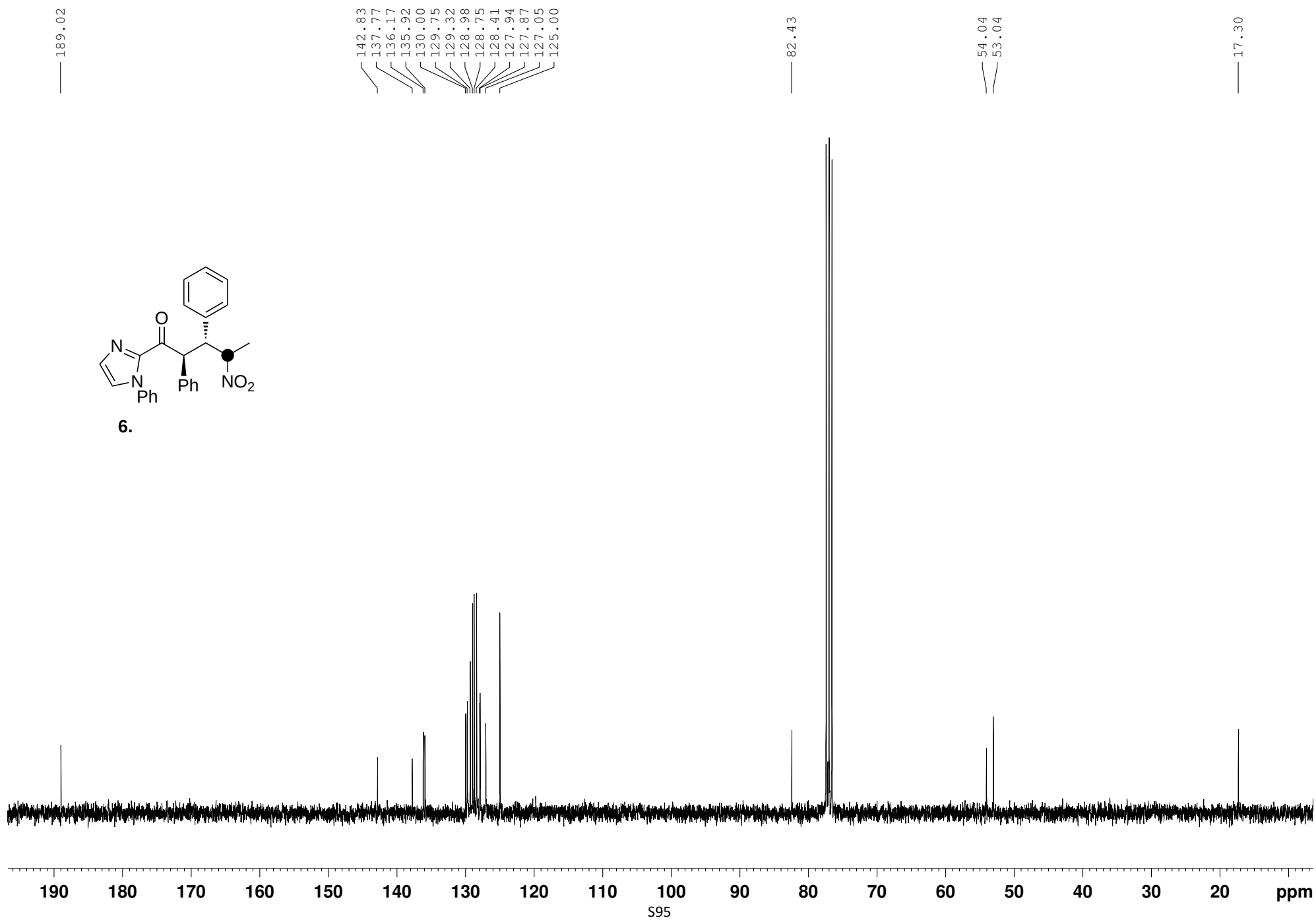


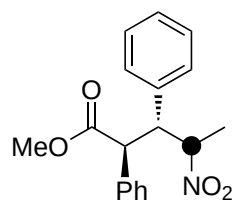
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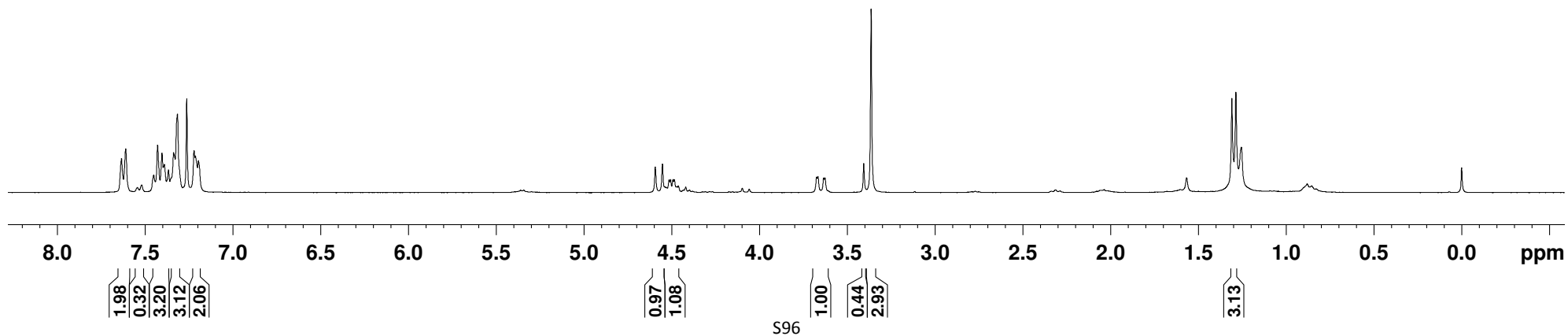


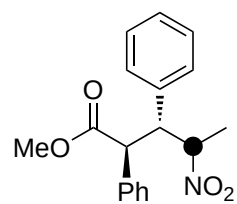
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