Electronic Supplementary Material (ESI) for ChemComm.

Formation of α-Chalcogenyl Acrylamides through Unprecedented Chalcogen-Mediated Metal-Free Oxyfunctionalization of Ynamides with DMSO as Oxidant

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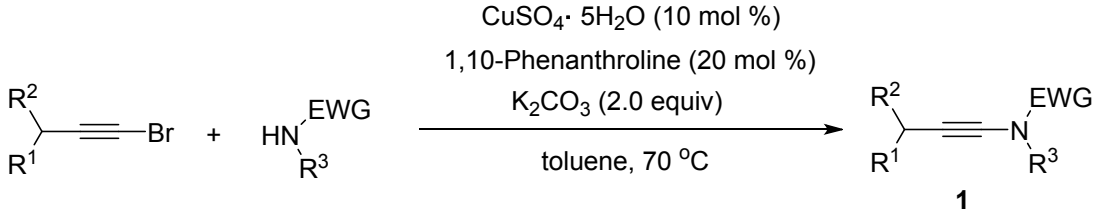
General Method

All reactions were performed in reaction tubes under nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR were recorded at respectively 400 MHz and 100 MHz spectrometer using $CDCl_3$ as solvent. The following abbreviations are used to describe peak patterns where appropriate: br =broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants are reported in Hertz (Hz). Chemical shifts are reported in ppm relative to the internal standard tetramethylsilane (δ = 0 ppm) for ^{1}H NMR and deuteriochloroform (δ = 77.00 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on an ESI-TOF (time-of- flight) mass spectrometer. Melting points were measured with micro melting point apparatus.

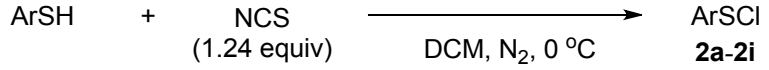
General experimental procedure and characterization data

1. General procedure for the preparation of ynamides 1; Typical Procedure I



Ynamides **1** were synthesized and characterized according to the method reported by Hsung.[1] To a mixture of *tert*-butyloxycarbamates (8.0 mmol), K_2CO_3 (16 mmol), $CuSO_4{\cdot}5H_2O$ (0.8 mmol), and 1,10-phenanthroline (1.6 mmol) in a reaction vial was added a solution of bromoalkyne[2] (8.8 mmol) in toluene (15 mL). The reaction mixture was capped and heated in an oil bath at 70 °C for 18 h while being monitored with TLC analysis. Upon completion, the reaction mixture was cooled to room temperature and diluted with EtOAc and filtered through Celite, and the filtrate was concentrated in vacuum. The crude products were purified by silica gel flash chromatography on a silica gel column with petroleum ether (PE) and ethyl acetate (EA) as eluent to afford directing products.

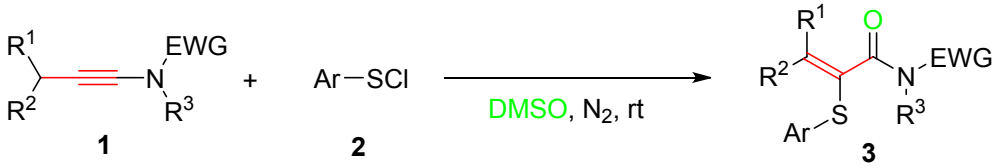
2. General procedure for the preparation of arenesulfenyl chlorides; Typical Procedure II



Arenesulfenyl chlorides were synthesized according to previously reported methodology.[3]

Under an atmosphere of N_2, *N*-chlorosuccinimide (1.66 g, 12.4 mmol) was placed in a 100-mL reaction flask and dissolved in dichloromethane (50 mL). Arenethiol (1.02 mL, 10.0 mmol) was added slowly at 0 ºC and the reaction mixture was stirred at 0 ºC for 15 min. After the volatiles were removed, hexane (15 mL) was added to the residue. The resulting white precipitate of succinimide was filtrated. Evaporation followed by distillation gave the desire arenesulfenyl chlorides.

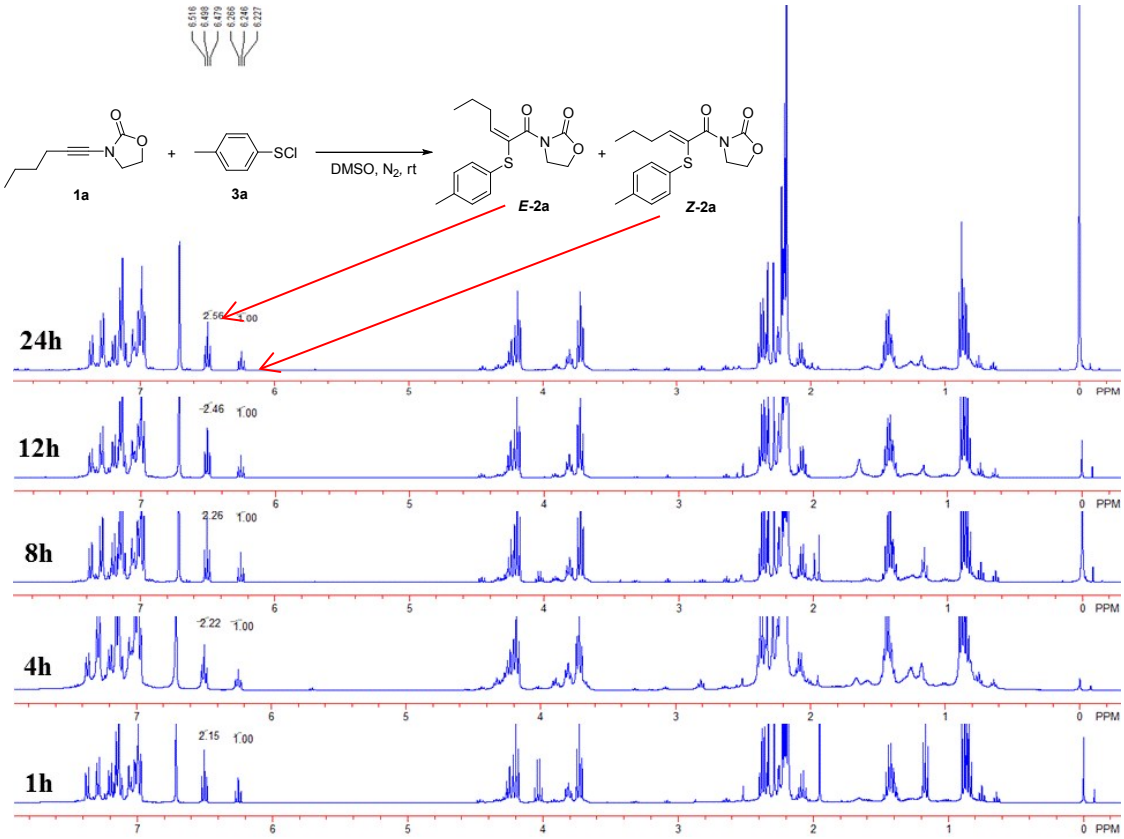
3. General procedure for the preparation of α-chalcogenyl acrylamides; Typical Procedure III



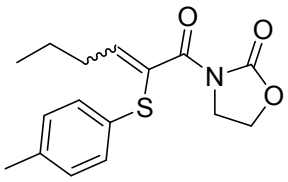
In a 10 mL flame-dried Schlenk tube were placed ynamides **1** (0.3 mmol), ArSCl **2** (2.0 equiv) and DMSO (2.0 mL) under nitrogen condition. The reaction mixture had been stirred at rt for 1 hour while was monitored with TLC analysis. The reaction mixture was quenched by adding EtOAc and water. The combined organic layers were washed by brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the desired product **3**.

3.1. ^{1}H NMR monitoring on the reaction of ynamides 1a at different time.

Figure 1. ^{1}H NMR monitoring on the reaction of ynamides **1a** at different time.

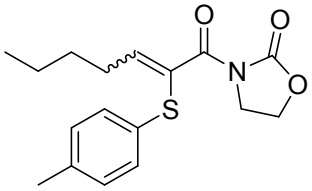


3.2. Characterization data for New compounds.

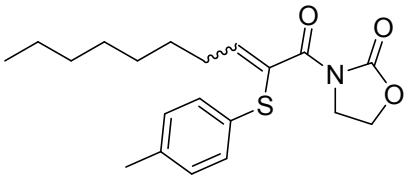


3-(2-(*p*-tolylthio)hex-2-enoyl)oxazolidin-2-one (3a): 72.3 mg, 79% total yield; **(*E*)-isomer**: 49.4 mg, 54% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 6.34 (t, *J* = 8.0 Hz, 1 H), 4.35 (t, *J* = 8.0 Hz, 2 H), 3.91 (t, *J* = 8.0 Hz, 2 H), 2.30 (s, 3 H), 2.17 (q, *J* = 7.6 Hz, 2 H), 1.55-1.44 (m, 2 H), 0.93 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 151.9, 144.7, 137.0, 130.8, 130.1, 129.7, 126.5, 62.0, 42.3, 32.9, 22.0,21.0, 13.7; **MS** (ESI):m/z (%) = 328.2 (100) $[M + Na]^+$. **IR** *ν* (KBr, cm^{-1}) 2961, 2922, 1784, 1680, 1384, 1358, 1286, 1218, 1111, 1038, 806, 756, 717; **HRMS** (ESI^+): m/z calcd. for $C_{16}H_{19}NO_3S$ ($[M+H]^+$) 306.1164, Found: 306.1172. **(*Z*)-isomer**: 22.9 mg, 25% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.59 (t, *J* = 7.2 Hz, 1 H), 4.30 (t, *J* = 8.0 Hz, 2 H), 3.83 (t, *J* = 7.6 Hz, 2 H), 2.45 (q, *J* = 7.6 Hz, 2 H), 2.29 (s, 3 H), 1.58-1.46 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 152.4, 146.6, 136.6, 131.0, 129.8, 129.5, 129.0, 62.2, 43.0, 31.8, 21.6, 21.0, 13.8; **MS** (ESI):m/z (%) = 328.2

(100) [M + Na]$^+$. **IR** ν (KBr, cm^{-1}) 2960, 2924, 2871, 1783, 1676, 1523, 1443, 1384, 1343, 1186, 1117, 1007, 807, 754; **HRMS** (ESI$^+$): m/z calcd. for $C_{16}H_{19}NO_3S$ ([M+H]$^+$) 306.1164, Found: 306.1161.

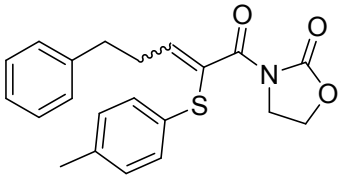


3-(2-(*p*-tolylthio)hept-2-enoyl)oxazolidin-2-one (3b): 69.8 mg, 73% total yield; **(*E*)-isomer**: 48.0 mg, 50 % yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 6.34 (t, *J* = 7.6 Hz, 1 H), 4.35 (t, *J* = 8.0 Hz, 2 H), 3.90 (t, *J* = 8.4 Hz, 2 H), 2.30 (s, 3 H), 2.19 (q, *J* = 7.2 Hz, 2 H), 1.49-1.40 (m, 2 H), 1.39-1.29 (m, 2 H), 0.89 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 151.9, 144.9, 136.9, 130.8, 130.1, 129.7, 126.3, 62.0, 42.3, 30.8, 30.7, 22.2, 21.0, 13.8; **MS** (ESI):m/z (%) = 342.2 (100) [M + Na]$^+$. **IR** ν (KBr, cm^{-1}) 2964, 2929, 2860, 1782, 1686, 1495, 1392, 1346, 1280, 1197, 1116, 1038, 880, 755; **HRMS** (ESI$^+$): m/z calcd. for $C_{17}H_{21}NO_3S$ ([M+Na]$^+$) 342.1140, Found: 342.1152. **(*Z*)-isomer**: 21.8 mg, 23 % yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.58 (t, *J* = 7.6 Hz, 1 H), 4.30 (t, *J* = 7.6 Hz, 2 H), 3.82 (t, *J* = 8.0 Hz, 2 H), 2.48 (q, *J* = 7.2 Hz, 2 H), 2.29 (s, 3 H), 1.51-1.42 (m, 2 H), 1.41-1.34 (m, 2 H), 0.90 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 152.4, 146.8, 136.5, 131.0, 129.7, 129.4, 128.8, 62.1, 43.0, 30.3, 29.6, 22.3, 20.9, 13.8; **MS** (ESI):m/z (%) = 342.2 (100) [M + Na]$^+$. **IR** ν (KBr, cm^{-1}) 2957, 2924, 2871, 1785, 1681, 1492, 1383, 1359, 1312, 1218, 1119, 1038, 807, 757; **HRMS** (ESI$^+$): m/z calcd. for $C_{17}H_{21}NO_3S$ ([M+Na]$^+$) 342.1140, Found: 342.1166.

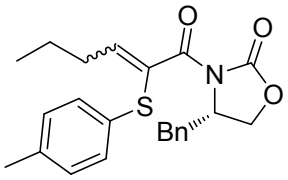


3-(2-(*p*-tolylthio)dec-2-enoyl)oxazolidin-2-one (3c): 69.2 mg, 64% total yield; **(*E*)-isomer**: 46.2 mg, 43 % yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 6.34 (t, *J* = 7.6 Hz, 1 H), 4.35 (t, *J* = 8.0 Hz, 2 H), 3.91 (t, *J* = 8.0 Hz, 2 H), 2.30 (s, 3 H), 2.18 (q, *J* = 7.6 Hz, 2 H), 1.50-1.41 (m, 2 H), 1.35-1.20 (m, 8 H), 0.88 (t, *J* = 6.4 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 151.8, 144.9, 137.0, 130.9, 130.2, 129.7, 126.3, 62.0, 42.3, 31.7, 31.0, 29.1, 29.0, 28.7, 22.6, 21.0, 14.0; **MS** (ESI):m/z (%) = 384.3 (100) [M + Na]$^+$. **IR** ν (KBr, cm^{-1}) 2961, 2930, 2873, 1784, 1681, 1492, 1386, 1364, 1302, 1205, 1068, 807, 768; **HRMS** (ESI$^+$): m/z calcd. for $C_{20}H_{27}NO_3S$

([M+H]$^+$) 362.1790, Found: 362.1782. **(*Z*)-isomer**: 23.0 mg, 21 % yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2 H), 7.07 (d, *J* = 7.6 Hz, 2 H), 6.59 (t, *J* = 7.2 Hz, 1 H), 4.31 (t, *J* = 7.6 Hz, 2 H), 3.83 (t, *J* = 8.0 Hz, 2 H), 2.47 (q, *J* = 7.2 Hz, 2 H), 2.29 (s, 3 H), 1.60-1.42 (m, 2 H), 1.38-1.20 (m, 8 H), 0.87 (t, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 152.4, 147.1, 136.5, 131.1, 129.8, 129.4, 128.8, 62.1, 43.0, 31.7, 29.9, 29.2, 29.0, 28.2, 22.6, 21.0, 14.1; **MS** (ESI):m/z (%) = 384.3 (100) [M + Na]$^+$. **IR** *ν* (KBr, cm^{-1}) 2961, 2922, 2871, 1783, 1676, 1532, 1455, 1382, 1364, 1288, 1076, 856, 807, 766; **HRMS** (ESI$^+$): m/z calcd. for $C_{20}H_{27}NO_3S$ ([M+H]$^+$) 362.1790, Found: 362.1785.

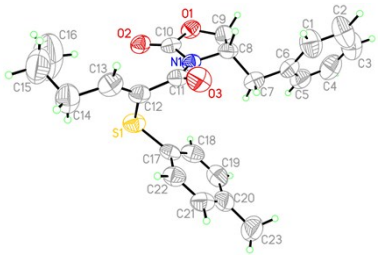


3-(5-phenyl-2-(*p*-tolylthio)pent-2-enoyl)oxazolidin-2-one (3d): 71.5 mg, 65% total yield; **(*E*)-isomer**: 48.2 mg, 44% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.16 (m, 7 H), 6.08 (d, *J* = 8.0 Hz, 2 H), 6.31 (t, *J* = 8.0 Hz, 1 H), 4.31 (t, *J* = 8.0 Hz, 2 H), 3.85 (t, *J* = 7.6 Hz, 2 H), 2.78 (q, *J* = 7.6 Hz, 2 H), 2.50 (q, *J* = 8.0 Hz, 2 H), 2.30 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 151.8, 142.7, 140.6, 137.2, 130.4, 130.3, 129.7, 128.4, 128.3, 127.4, 126.1, 62.0, 42.3, 34.7, 32.5, 21.0; **MS** (ESI):m/z (%) = 390.2 (100) [M + Na]$^+$. **IR** *ν* (KBr, cm^{-1}) 2961, 2923, 2873, 1778, 1682, 1543, 1443, 1376, 1352, 1254, 1068, 854, 754; **HRMS** (ESI$^+$): m/z calcd. for $C_{21}H_{21}NO_3S$ ([M+Na]$^+$) 390.1140, Found: 390.1158. **(*Z*)-isomer**: 23.3 mg, 21% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.4 Hz, 2 H), 7.22-7.16 (m, 5 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.60-6.52 (m, 1 H), 4.29 (t, *J* = 8.0 Hz, 2 H), 3.80 (t, *J* = 7.6 Hz, 1 H), 2.80-2.77 (br, 4 H), 2.29 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 152.4, 144.7, 140.8, 136.8, 130.7, 129.8, 129.7, 128.4, 126.1, 62.2, 42.9, 34.2, 31.4, 21.0; **MS** (ESI):m/z (%) = 390.2 (100) [M + Na]$^+$. **IR** *ν* (KBr, cm^{-1}) 2963, 2921, 2872, 1780, 1677, 1523, 1455, 1368, 1342, 1233, 1118, 854, 756; **HRMS** (ESI$^+$): m/z calcd. for $C_{21}H_{21}NO_3S$ ([M+Na]$^+$) 390.1140, Found: 390.1153.

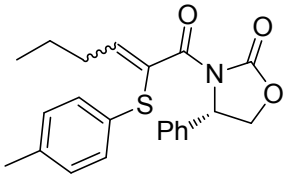


(*S*)-4-benzyl-3-(2-(*p*-tolylthio)hex-2-enoyl)oxazolidin-2-one (3e): 92.5 mg, 78% total yield; **(*E*)-isomer**: 59.1 mg, 50 % yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5 H), 7.15 (d, *J* = 6.8 Hz, 2 H), 7.10 (d, *J* = 7.2 Hz, 2 H), 6.37 (t, *J* = 8.0 Hz, 1 H), 4.53 (br,

1 H), 4.12-4.06 (m, 2 H), 3.16 (br, 1 H), 2.54 (br, 1 H), 2.29 (s, 3 H), 2.24-2.17 (m, 2 H), 1.58-1.47 (m, 2 H), 0.96 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 151.8, 144.5, 137.1, 135.1, 130.7, 130.3, 129.7, 129.3, 128.9, 127.3, 126.9, 66.2, 55.1, 37.6, 32.9, 22.0, 21.0, 13.8; **MS** (ESI):m/z (%) = 396.3 (100) $[M + H]^+$. **IR** ν (KBr, cm^{-1}) 2961, 2934, 2862, 1788, 1674, 1438, 1352, 1311, 1268, 1204, 1007, 856, 754, 701; **HRMS** (ESI^+): m/z calcd. for $C_{23}H_{25}NO_3S$ ($[M+Na]^+$) 418.1453, Found: 418.1461. **(*Z*)-isomer**: 33.4 mg, 28 % yield; white solid; mp 121-122 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 5 H), 7.12-7.06 (m, 4 H), 6.59 (d, J = 7.6 Hz, 2 H), 4.50-4.42 (m, 1 H), 4.09-4.00 (m, 2 H), 3.12 (dd, J_1 = 3.6 Hz, J_2 = 13.6 Hz, 1 H), 2.51-2.39 (m, 3 H), 2.28 (s, 3 H), 1.58-1.49 (m, 2 H), 0.98 (t, J = 7.6 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 152.4, 146.3, 136.7, 135.1, 130.9, 129.8, 129.7, 129.6, 129.3, 128.9, 127.2, 66.4, 55.5, 37.3, 31.9, 21.6, 21.0, 13.8; **MS** (ESI):m/z (%) = 396.3 (100) $[M + H]^+$. **IR** ν (KBr, cm^{-1}) 2957, 2932, 2854, 1790, 1678, 1493, 1454, 1352, 1297, 1279, 1218, 1089, 813, 753, 700; **HRMS** (ESI^+): m/z calcd. for $C_{23}H_{25}NO_3S$ ($[M+Na]^+$) 418.1453, Found: 418.1475. **Anal. calcd** for $C_{23}H_{25}NO_3S$: C 69.84, H 6.37, N 3.54. Found: C 69.92, H 6.55, N 3.66.

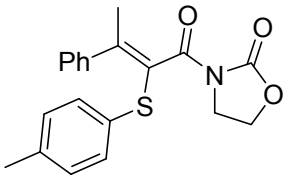


Crystal data for ***Z*-3e**: $C_{23}H_{25}NO_3S$; M = 395.50; Monoclinic'; space group $P2_1$; final R indices [I>2σ(I)]: R_1=0.0429, wR_2 =0.1192, R indices(all data): R_1=0.0489, wR_2=0.1234, a = 13.5980(8) Å, b = 5.7831(3) Å, c = 14.8716(8) Å; α =90 °, β = 111.469(2) °, γ = 90 °; V = 1088.34(10) Å^3; T = 296K; Z = 2; reflection measured/independent: 7583/3727 (R_{int} = 0.026), number of observations [I>2σ(I)]: 3350, parameters: 255. CCDC-1432338 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

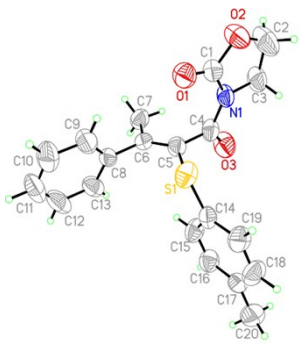


(*S*)-4-phenyl-3-(2-(p-tolylthio)hex-2-enoyl)oxazolidin-2-one (3f): 81.3 mg, 71% total yield; **(*E*)-isomer**: 45.8 mg, 40% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.12 (m, 7 H), 7.00 (d, J = 7.6 Hz, 2 H), 6.38 (t, J = 8.0 Hz, 1 H), 5.34 (q, J = 4.0 Hz, 1 H), 4.62 (t, J = 8.8 Hz, 1 H), 4.20 (dd, J = 8.4 Hz, 1 H), 2.27 (s, 3 H), 2.15-2.00 (m, 2 H), 1.50-1.39 (m, 2 H), 0.88 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 152.1, 146.4, 138.1, 136.5, 130.9,

129.6, 129.5, 128.9, 128.5, 126.5, 125.9, 69.9, 57.5, 32.7, 21.9, 21.0, 13.7; **MS** (ESI):m/z (%) = 382.3 (100) $[M + H]^+$. **IR** ν (KBr, cm^{-1}) 2960, 2928, 2861, 1788, 1687, 1492, 1382, 1320, 1197, 1100, 1044, 807, 713, 699; **HRMS** (ESI^+): m/z calcd. for $C_{22}H_{23}NO_3S$ ($[M+Na]^+$) 404.1296, Found: 404.1321. **(*Z*)-isomer**: 35.5 mg, 31% yield; white solid; mp 93-94 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.17 (m, 3 H), 7.15-7.09 (m, 4 H), 7.00 (d, J = 8.0 Hz, 2 H), 6.67 (t, J = 7.2 Hz, 1 H), 5.30 (dd, J_1 = 6.4 Hz, J_2 = 8.8 Hz, 1 H), 4.59 (t, J = 8.8 Hz, 1 H), 4.16 (dd, J_1 = 6.4 Hz, J_2 = 8.8 Hz, 1 H), 2.46 (q, J = 7.2 Hz, 2 H), 2.29 (s, 3 H), 1.55-1.44 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 152.8, 148.7, 137.6, 136.2, 131.2, 129.8, 129.4, 128.9, 126.0, 69.9, 58.2, 32.0, 21.6, 21.0, 13.8; **MS** (ESI):m/z (%) = 382.3 (100) $[M + H]^+$. **IR** ν (KBr, cm^{-1}) 2960, 2932, 2871, 1790, 1686, 1511, 1459, 1378, 1321, 1115, 1034, 854, 723; **HRMS** (ESI^+): m/z calcd. for $C_{22}H_{23}NO_3S$ ($[M+Na]^+$) 404.1296, Found: 404.1323. **Anal. calcd** for $C_{22}H_{23}NO_3S$: C 69.26, H 6.08, N 3.67. Found: C 69.26, H 6.13, N 3.76.

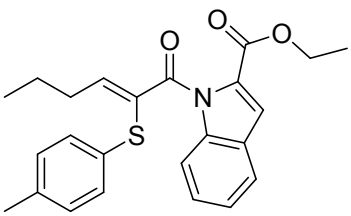


(*Z*)-3-(3-phenyl-2-(*p*-tolylthio)but-2-enoyl)oxazolidin-2-one (*Z*-3g): 68.7 mg, 65% yield; white solid; mp 114-115 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.29 (m, 5 H), 7.23 (d, J = 8.4 Hz, 2 H), 7.06 (d, J = 8.0 Hz, 2 H), 4.29 (t, J = 7.6 Hz, 2 H), 3.82 (b, 2 H), 2.29 (s, 3 H), 2.16 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 151.8, 145.2, 140.5, 137.4, 131.6, 130.0, 129.5, 128.1, 127.9, 127.6, 123.8, 61.9, 42.3, 23.5, 21.1; **MS** (ESI):m/z (%) = 354.2 (100) $[M + H]^+$. **IR** ν (KBr, cm^{-1}) 2961, 2922, 2871, 1775, 1682, 1533, 1448, 1367, 1320, 1117, 1034, 1006, 856, 754; **HRMS** (ESI^+): m/z calcd. for $C_{20}H_{19}NO_3S$ ($[M+Na]^+$) 376.0983, Found: 376.0997. **Anal. calcd** for $C_{20}H_{19}NO_3S$: C 67.97, H 5.42, N 3.96. Found: C 68.02, H 5.51, N 4.04.

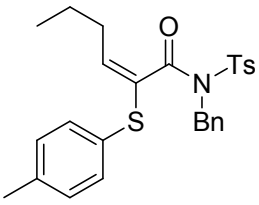


Crystal data for ***Z*-3g**: $C_{20}H_{19}NO_3S$, M = 353.42, Triclinic, space group *P*-1, final R indices [$I>2\sigma(I)$]: R_1 = 0.0417, wR_2 = 0.1127, R indices (all data): R_1 = 0.0572, wR_2 = 0.1248, a = 7.326(5) Å, b = 10.134(7) Å, c = 12.489(8) Å, α = 80.774(11)°, β = 82.540(12)°, γ =

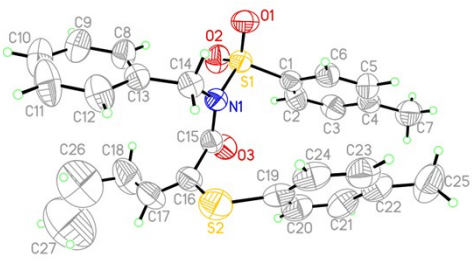
77.770(11)°, V = 890.0(10) Å^3, T = 296 K, Z = 2, reflection measured/independent: 4938/3122 (R_{int} = 0.021), number of observations [I>2σ(I)]: 2417, parameters: 228. CCDC-1422307 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



(*Z*)-ethyl 1-(2-(*p*-tolylthio)hex-2-enoyl)-1*H*-indole-2-carboxylate (*E*-3h): 78.2 mg, 64% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, J = 8.0 Hz, 2 H), 7.21 (s, 1 H), 7.19-7.13 (m, 1 H), 7.12-7.06 (m, 1 H), 7.02 (t, J = 7.6 Hz, 1 H), 6.87 (d, J = 8.0 Hz, 2 H), 6.63 (d, J = 8.0 Hz, 2 H), 4.28 (q, J = 7.2 Hz, 2 H), 2.49 (q, J = 7.2 Hz, 2 H), 1.99 (s, 3 H), 1.62-1.51 (m, 2 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.01 (t, J = 7.6 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 161.1, 149.6, 138.0, 136.9, 133.7, 130.3, 129.7, 129.2, 129.1, 126.9, 126.5, 122.8, 121.6, 115.2, 113.9, 61.2, 32.7, 21.8, 20.7, 14.3, 14.0; **MS** (ESI):m/z (%) = 408.3 (100) $[M + H]^+$. **IR** ν (KBr, cm^{-1}) 2959, 2930, 1719, 1688, 1540, 1444, 1397, 1378, 1298, 1203, 1147, 805, 747; **HRMS** (ESI$^+$): m/z calcd. for $C_{24}H_{25}NO_3S$ ($[M+Na]^+$) 430.1453, Found: 430.1489.

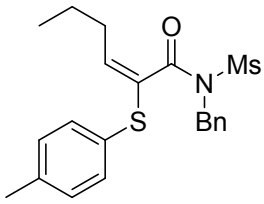


(E)-*N*-benzyl-2-(*p*-tolylthio)-*N*-tosylhex-2-enamide (*E*-3i): 94.3 mg, 66% yield; white solid; mp 96-97 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2 H), 7.34-7.24 (m, 5 H), 7.13 (d, J = 8.0 Hz, 2 H), 7.07 (d, J = 8.0 Hz, 2 H), 6.94 (d, J = 7.6 Hz, 2 H), 6.01 (t, J = 8.0 Hz, 1 H), 5.16 (s, 2 H), 2.39 (s, 3 H), 2.28 (s, 3 H), 1.70 (q, J = 7.6 Hz, 2 H), 1.19-1.09 (m, 2 H), 0.75 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 145.2, 144.3, 137.3, 136.8, 135.7, 130.6, 129.7, 129.2, 129.0, 128.7, 128.4, 127.5, 127.4, 127.1, 50.2, 32.4, 21.7, 21.6, 21.1, 13.5; **MS** (ESI):m/z (%) = 502.2 (100) $[M + Na]^+$. **IR** ν (KBr, cm^{-1}) 2956, 2927, 2849, 1680, 1596, 1494, 1455, 1343, 1164, 811, 750, 708; **HRMS** (ESI$^+$): m/z calcd. for $C_{27}H_{29}NO_3S_2$ ($[M+Na]^+$) 502.1487, Found: 502.1514. **Anal. calcd** for $C_{27}H_{29}NO_3S_2$: C 67.61, H 6.09, N 2.92. Found: C 67.53, H 6.11, N 2.87.

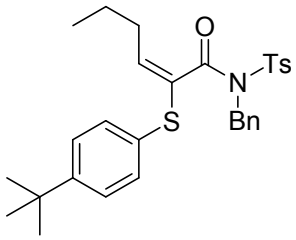


Crystal data for ***E*-3i**: $C_{27}H_{29}NO_3S_2$; M = 479.63; Monoclinic; space group $P2_1/c$; final R indices

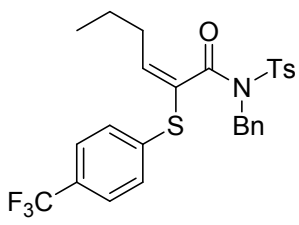
[I>2σ(I)]: R_1=0.0596, wR_2 =0.1564, R indices(all data): R_1=0.0837, wR_2=0.1731, a = 12.8698(16) Å, b = 13.2620(15) Å, c = 15.0271(18) Å; β = 92.583(4) °; V = 2562.2(5) Å^3; T = 296 K; Z = 4; reflection measured/independent: 17942/4495 (R_{int} = 0.049), number of observations [I>2σ(I)]: 3272, parameters: 295. CCDC-1432339 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



(*E*)-*N*-benzyl-*N*-(methylsulfonyl)-2-(*p*-tolylthio)hex-2-enamide (*E*-3j): 70.1 mg, 58% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.20 (m, 7 H), 7.13 (d, J = 8.4 Hz, 2 H), 6.10 (t, J = 7.6 Hz, 1 H), 5.11 (s, 2 H), 2.87 (s, 3 H), 2.32 (s, 3 H), 1.87 (q, J = 7.2 Hz, 2 H), 1.31-1.20 (m, 2 H), 0.83 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 144.0, 138.1, 136.4, 131.4, 129.9, 128.6, 127.7, 127.6, 127.4, 49.4, 41.8, 32.6, 21.8, 21.1, 13.6; **MS** (ESI):m/z (%) = 426.2 (100) $[M + Na]^+$. **IR** ν (KBr, cm^{-1}) 2964, 2926, 2867, 1683, 1602, 1488, 1400, 1353, 1164, 856, 756, 711; **HRMS** (ESI^+): m/z calcd. for $C_{21}H_{25}NO_3S_2$ ($[M+Na]^+$) 426.1174, Found: 426.1234.

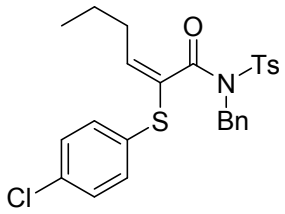


(*E*)-*N*-benzyl-2-((4-(*tert*-butyl)phenyl)thio)-*N*-tosylhex-2-enamide (*E*-3ib): 106.3 mg, 68% yield; white solid; mp 71-72 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2 H), 7.32-7.23 (m, 5 H), 7.21-7.16 (m, 4 H), 7.14-7.09 (m, 2 H), 6.06 (t, J = 7.6 Hz, 1 H), 5.09 (s, 2 H), 2.40 (s, 3 H), 1.73 (q, J = 7.6 Hz, 2 H), 1.27 (s, 9 H), 1.24-1.12 (m, 2 H), 0.76 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 150.4, 145.9, 144.4, 136.6, 135.9, 130.1, 129.8, 129.2, 128.6, 128.4, 127.6, 127.5, 126.8, 126.0, 50.3, 34.5, 32.5, 31.2, 21.7, 21.6, 13.6; **MS** (ESI):m/z (%) = 544.2 (100) $[M + Na]^+$. **IR** ν (KBr, cm^{-1}) 2960, 2869, 1673, 1497, 1455, 1361, 1341, 1169, 1117, 822, 756, 704; **HRMS** (ESI^+): m/z calcd. for $C_{30}H_{35}NO_3S_2$ ($[M+Na]^+$) 544.1956, Found: 544.1991. **Anal. calcd** for $C_{30}H_{35}NO_3S_2$: C 69.06, H 6.76, N 2.68. Found: C 69.14, H 6.74, N 2.74.

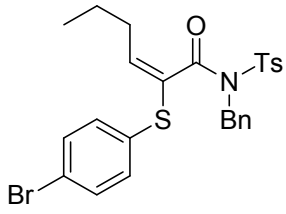


(*E*)-*N*-benzyl-*N*-tosyl-2-((4-(trifluoromethyl)phenyl)thio)hex-2-enamide (*E*-3ic): 84.9 mg, 53% yield; white solid; mp 142-143 °C

(*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.32-7.19 (m, 7 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 6.27 (t, *J* = 8.0 Hz, H), 5.10 (s, 2 H), 2.35 (s, 3 H), 1.80 (q, *J* = 7.6 Hz, 2 H), 1.28-1.17 (m, 2 H), 0.80 (q, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 150.7, 144.8, 139.6, 136.5, 135.4, 129.2, 128.5, 128.4, 127.8, 127.7, 127.5, 125.5 (q, J = 3.6 Hz), 124.3, 122.6, 50.0, 32.7, 21.6, 21.4, 13.6; **MS** (ESI):m/z (%) = 556.2 (100) $[M + Na]^+$. **IR** ν (KBr, cm^{-1}) 2956, 2921, 1682, 1602, 1498, 1454, 1330, 1184, 1104, 829, 809, 784, 701; **HRMS** (ESI^+): m/z calcd. for $C_{27}H_{26}F_3NO_3S_2$ ($[M+Na]^+$) 556.1204, Found: 556.1235; **Anal. calcd** for $C_{27}H_{26}F_3NO_3S_2$: C 60.77, H 4.91, N 2.62. Found: C 60.82, H 4.88, N 2.79.

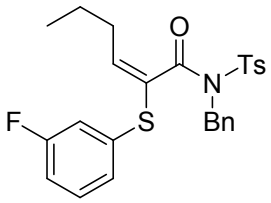


(*E*)-*N*-benzyl-2-((4-chlorophenyl)thio)-*N*-tosylhex-2-enamide (*E*-3id): 82.2 mg, 55% yield; white solid; mp 128-129 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2 H), 7.34-7.23 (m, 5 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 7.05 (s, 4 H), 6.12 (t, *J* = 8.0 Hz, 1 H), 5.16 (s, 2 H), 2.41 (s, 3 H), 1.73 (q, *J* = 7.6 Hz, 2 H), 1.21-1.11 (m, 2 H), 0.76 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 147.7, 144.8, 136.7, 135.5, 132.9, 131.9, 130.6, 129.1, 128.9, 128.6, 128.5, 127.6, 127.5, 125.8, 50.0, 32.6, 21.7, 13.6; **MS** (ESI):m/z (%) = 500.3 (100) $[M + H]^+$. **IR** ν (KBr, cm^{-1}) 2960, 2871, 1683, 1474, 1360, 1169, 1089, 1009, 811, 756, 705; **HRMS** (ESI^+): m/z calcd. for $C_{26}H_{26}ClNO_3S_2$ ($[M+Na]^+$) 522.0940, Found: 522.0972. **Anal. calcd** for $C_{26}H_{26}ClNO_3S_2$: C 62.45, H 5.24, N 2.80. Found: C 62.44, H 5.23, N 2.91.

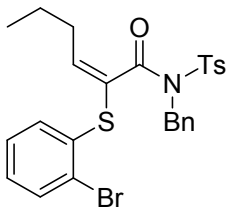


(*E*)-*N*-benzyl-2-((4-bromophenyl)thio)-*N*-tosylhex-2-enamide (*E*-3ie): 99.4 mg, 61% yield; white solid; mp 127-128 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2 H), 7.33-7.25 (m, 5 H), 7.22-7.17 (m, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.01-6.96 (m, 2 H), 6.13 (t, *J* = 7.6 Hz, 1 H), 5.16 (s, 2 H), 2.43 (s, 3 H), 1.73 (q, *J* = 7.6 Hz, 2 H), 1.21-1.11 (m, 2 H), 0.76 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 148.0, 144.8, 136.7, 135.5, 132.7, 131.8, 130.8, 129.1, 128.6, 128.5, 127.6, 127.5, 125.6, 120.9, 50.0, 32.6, 21.8, 21.6, 13.6; **MS** (ESI):m/z (%) = 544.2 (100) $[M + H]^+$. **IR** ν (KBr, cm^{-1}) 2959, 2929, 2869, 1683, 1471, 1359, 1169, 1085, 1005, 811, 756, 704; **HRMS** (ESI^+): m/z calcd. for

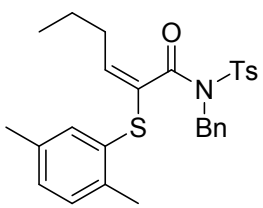
$C_{26}H_{26}BrNO_3S_2$ ([M+Na]$^+$) 566.0435, Found: 566.0464. **Anal. calcd** for $C_{26}H_{26}BrNO_3S_2$: C 57.35, H 4.81, N 2.57. Found: C 57.29, H 4.68, N 2.63.



(*E*)-*N*-benzyl-2-((3-fluorophenyl)thio)-*N*-tosylhex-2-enamide (*E*-3if): 86.4 mg, 57% yield; white solid; mp 73-74 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2 H), 7.33-7.22 (m, 5 H), 7.15-7.04 (m, 3 H), 6.92 (d, *J* = 8.0 Hz, 1 H), 6.85-6.74 (m, 2 H), 6.19 (t, *J* = 7.6 Hz, H), 5.13 (s, 2 H), 2.37 (s, 3 H), 1.76 (q, *J* = 8.0 Hz, 2 H), 1.24-1.14 (m, 2 H), 0.78 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 162.5 (d, *J* = 247.5 Hz), 149.1, 144.6, 136.7, 136.2 (d, *J* = 7.7 Hz), 135.4, 129.9 (d, *J* = 8.5 Hz), 129.1, 128.6, 128.5, 127.6, 127.5, 125.1, 124.4 (d, *J* = 2.9 Hz), 115.7 (d, *J* = 23.1 Hz), 113.5 (d, *J* = 21.1 Hz), 50.0, 32.6, 21.6, 21.5, 13.6; **MS** (ESI):m/z (%) = 484.2 (100) [M + H]$^+$. **IR** ν (KBr, cm^{-1}) 2961, 2930, 1677, 1598, 1577, 1473, 1454, 1342, 1174, 1117, 943, 875, 766; **HRMS** (ESI$^+$): m/z calcd. for $C_{26}H_{26}FNO_3S_2$ ([M+Na]$^+$) 506.1236, Found: 506.1263. **Anal. calcd** for $C_{26}H_{26}FNO_3S_2$: C 64.57, H 5.42, N 2.90. Found: C 64.33, H 5.51, N 3.02.

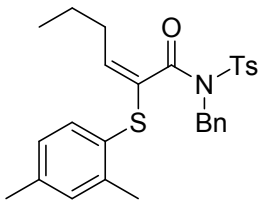


(*E*)-*N*-benzyl-2-((2-bromophenyl)thio)-*N*-tosylhex-2-enamide (*E*-3ig): 102.4 mg, 63% yield; white solid; mp 123-124 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 7.6 Hz, 1 H), 7.33-7.22 (m, 5 H), 7.15 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 7.00 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1 H), 6.92 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1 H), 6.26 (t, *J* = 7.6 Hz, H), 5.16 (s, 2 H), 2.33 (s, 3 H), 1.80 (q, *J* = 7.6 Hz, 2 H), 1.27-1.16 (m, 2 H), 0.79 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 151.0, 144.4, 136.7, 135.6, 135.3, 132.5, 129.6, 129.1, 128.5, 127.6, 127.5, 127.4, 127.1, 124.5, 121.6, 50.0, 32.7 21.6, 13.6; **MS** (ESI):m/z (%) = 544.2 (100) [M + H]$^+$. **IR** ν (KBr, cm^{-1}) 2961, 2930, 2871, 1679, 1448, 1351, 1186, 1169, 1115, 1089, 1018, 943, 757; **HRMS** (ESI$^+$): m/z calcd. for $C_{26}H_{26}BrNO_3S_2$ ([M+Na]$^+$) 566.0435, Found: 566.0449. **Anal. calcd** for $C_{26}H_{26}BrNO_3S_2$: C 57.35, H 4.81, N 2.57. Found: C 57.47, H 4.80, N 2.69.



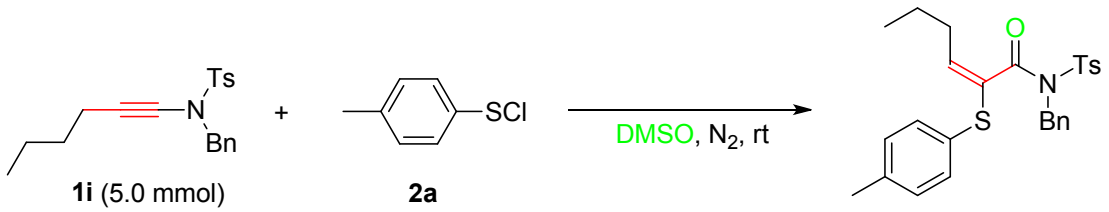
(*E*)-*N*-benzyl-2-((2,5-dimethylphenyl)thio)-*N*-tosylhex-2-enamide (*E*-

3ih): 105.3 mg, 71% yield; white solid; mp 67-68 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2 H), 7.35-7.22 (m, 5 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 7.00-6.94 (m, 2 H), 6.88-6.84 (m, 1 H), 5.90 (t, *J* = 7.6 Hz, 1 H), 5.21 (s, 2 H), 2.36 (s, 3 H), 2.25 (s, 3 H), 2.14 (s, 3 H), 1.74 (q, *J* = 7.6 Hz, 2 H), 1.21-1.10 (m, 2 H), 0.76 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 144.5, 144.3, 136.8, 136.0, 135.6, 135.2, 131.7, 131.2, 130.1, 129.0, 128.5, 128.4, 128.2, 127.5, 126.3, 50.2, 32.4, 21.8, 21.6, 20.7, 19.8, 13.5; **MS** (ESI):m/z (%) = 494.3 (100) $[M + H]^+$. **IR** *ν* (KBr, cm^{-1}) 2960, 2926, 2871, 1683, 1596, 1489, 1454, 1344, 1195, 1184, 1165, 1115, 1088, 943, 802, 755; **HRMS** (ESI^+): m/z calcd. for $C_{28}H_{31}NO_3S_2$ ($[M+Na]^+$) 516.1643, Found: 516.1679. **Anal. calcd** for $C_{28}H_{31}NO_3S_2$: C 68.12, H 6.33, N 2.84. Found: C 68.08, H 6.44, N 2.91.



(*E*)-*N*-benzyl-2-((2,4-dimethylphenyl)thio)-*N*-tosylhex-2-enamide (*E*-3ii): 110.2 mg, 74% yield; white solid; mp 81-82 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2 H), 7.35-7.22 (m, 5 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 7.6 Hz, 1 H), 6.91 (s, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.81 (t, *J* = 7.6 Hz, 1 H), 5.19 (s, 2 H), 2.39 (s, 3 H), 2.26 (s, 3 H), 2.25 (s, 3 H), 1.69 (q, *J* = 7.2 Hz, 2 H), 1.19-1.08 (m, 2 H), 0.74 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 144.4, 142.7, 139.4, 137.9, 136.8, 135.8, 132.4, 131.2, 129.0, 128.7, 128.4, 127.6, 127.5, 127.4, 127.3, 126.9, 50.4, 32.4, 21.8, 21.6, 21.0, 20.3, 13.5; **MS** (ESI):m/z (%) = 494.2 (100) $[M + H]^+$. **IR** *ν* (KBr, cm^{-1}) 2952, 2925, 2866, 1675, 1597, 1456, 1440, 1354, 1312, 1184, 1165, 1077, 828, 750, 703; **HRMS** (ESI^+): m/z calcd. for $C_{28}H_{31}NO_3S_2$ ($[M+Na]^+$) 516.1643, Found: 516.1675. **Anal. calcd** for $C_{28}H_{31}NO_3S_2$: C 68.12, H 6.33, N 2.84. Found: C 68.34, H 6.48, N 2.71.

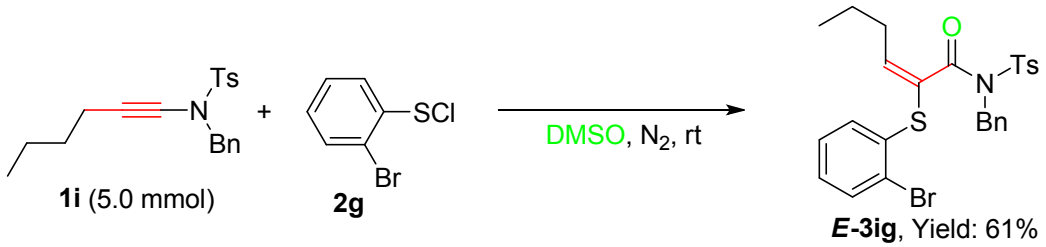
3.3. Large-scale experiments



1i (5.0 mmol) **2a** ***E*-3i**, Yield: 63%

The reaction of ynamide **1i** (5.0 mmol), **2a** (2.0 equiv) and DMSO (25 mL) was carried out at rt under N_2 atmosphere for 2 h, and the progress of the reaction was monitored by TLC analysis. The

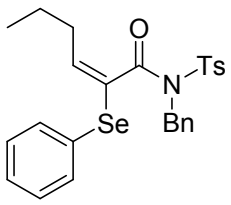
reaction mixture was quenched by adding EtOAc (30 mL) and water (30 mL). The water phase was extracted twice with EtOAc (20 mL), and the combined organic layers were washed by brine, dried over Na_2SO_4. Filtration and concentration gave the crude product, which was purified by chromatography on silica gel (PE/EtOAc, 10:1) to afford ***E*-3i** (1.50 g, 63% yield) as a white solid.



1i (5.0 mmol) **2g** ***E*-3ig**, Yield: 61%

The reaction of ynamide **1i** (5.0 mmol), **2g** (2.0 equiv) and DMSO (25 mL) was carried out at rt under N_2 atmosphere for 2 h, and the progress of the reaction was monitored by TLC analysis. The reaction mixture was quenched by adding EtOAc (30 mL) and water (30 mL). The water phase was extracted twice with EtOAc (20 mL), and the combined organic layers were washed by brine, dried over Na_2SO_4. Filtration and concentration gave the crude product, which was purified by chromatography on silica gel (PE/EtOAc, 10:1) to afford ***E*-3ig** (1.66 g, 61% yield) as a white solid.

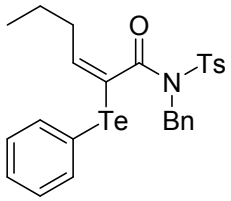
3.4. Synthesis of α-selanyl acrylamides



In a 10 mL flame-dried Schlenk tube were placed ynamide **1i** (0.3 mmol), PhSeCl (2.0 equiv) and DMSO (2.0 mL) under nitrogen condition. The reaction mixture had been stirred at rt for 1 hour while was monitored with TLC analysis. The reaction mixture was quenched by adding EtOAc and water. The combined organic layers were washed by brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the desired product **(*E*)-*N*-benzyl-2-(phenylselanyl)-*N*-tosylhex-2-enamide (*E*-4ia)**: 86.2 mg, 56% yield; white solid; mp 68-69 °C (*n*-hexane/ethylacetate); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2 H), 7.36-7.22 (m, 7 H), 7.19-7.10 (m, 5 H), 6.14 (t, *J* = 7.6 Hz, 1 H), 5.06 (s, 2 H), 2.37 (s, 3 H), 1.68 (q, *J* = 7.6 Hz, 2 H), 1.22-1.11 (m, 2 H), 0.73 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 147.2, 144.5, 136.6, 135.7, 132.0, 129.9, 129.2, 129.0, 128.5, 128.4, 127.6, 127.5, 127.2, 121.4, 50.2, 33.3, 21.6, 21.5, 13.5; **MS** (ESI):m/z (%) = 514.2 (100) $[M + H]^+$.

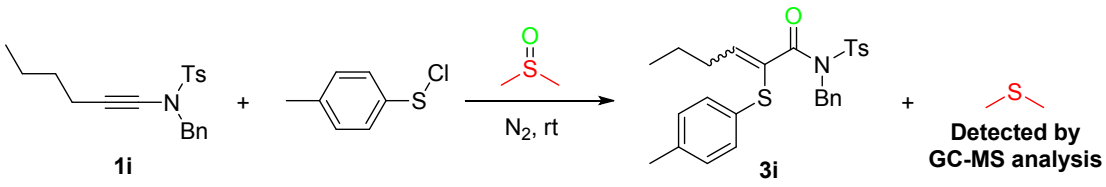
IR ν (KBr, cm^{-1}) 2964, 2935, 1689, 1346, 1182, 1163, 1120, 856, 740; **HRMS** (ESI^+): m/z calcd. for $C_{26}H_{27}NO_3SSe$ ($[M+Na]^+$) 536.0775, Found: 536.0805. **Anal. calcd** for $C_{26}H_{27}NO_3SSe$: C 60.93, H 5.31, N 2.73. Found: C 60.97, H 5.53, N 2.87.

3.5. Synthesis of α-tellanyl acrylamides.



1) Preparation of the phenyltellury l bromide solution: Bromine (101.6 mg, 0.6 mmol) was added to a flask containing diphenyl ditelluride (245.5 mg, 0.6 mmol) in 1,2-dichloroethane (1.0 mL) at 0 °C. The reaction mixture was stirred for 15 min at this temperature. 2) In a 10 mL flame-dried Schlenk tube were placed ynamide **1i** (0.3 mmol), PhTeBr (2.0 equiv, in DCE) and DMSO (2.0 mL) under nitrogen condition. The reaction mixture had been stirred at rt for 1 hour while was monitored with TLC analysis. The reaction mixture was quenched by adding EtOAc and water. The combined organic layers were washed by brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the desired product **(*E*)-*N*-benzyl-2-(phenyltellanyl)-*N*-tosylhex-2-enamide (*E*-5ia)**: 69.4 mg, 41% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.60 (m, 2 H), 7.56 (d, J = 8.4 Hz, 2 H), 7.30-7.18 (m, 8 H), 7.13 (t, J = 7.6 Hz, 2 H), 5.91 (t, J = 6.8 Hz, 1 H), 4.89 (s, 2 H), 2.41 (s, 3 H), 2.15 (q, J = 7.2 Hz, 2 H), 1.2 6-1.13 (m, 2 H), 0.77 (t, J = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 147.7, 144.5, 138.3, 136.5, 136.3, 129.4, 129.3, 128.5, 128.4, 128.1, 127.7, 113.9, 113.8, 50.1, 38.0, 21.6, 21.3, 13.8; **MS** (ESI):m/z (%) = 564.2 (100) $[M + H]^+$. **IR** ν (KBr, cm^{-1}) 1690, 1666, 1594, 1535, 1495, 1444, 1281, 1169, 879, 745; **HRMS** (ESI^+): m/z calcd. for $C_{26}H_{27}NO_3STe$ ($[M+Na]^+$) 586.0672, Found: 586.0706.

4. Experiment for Mechanistic Study



In a 10 mL flame-dried Schlenk tube were placed ynamide **1i** (0.3 mmol), *p*-tolylsulfenylchloride **2a** (2.0 equiv) and DMSO (2.0 mL) under nitrogen condition. The reaction mixture was stirred at rt for 1 hour while being monitored with TLC analysis. The reaction mixture was detected by GC-MS analysis.

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Instrument: Agilent 5977 GCMS
Sample Name:
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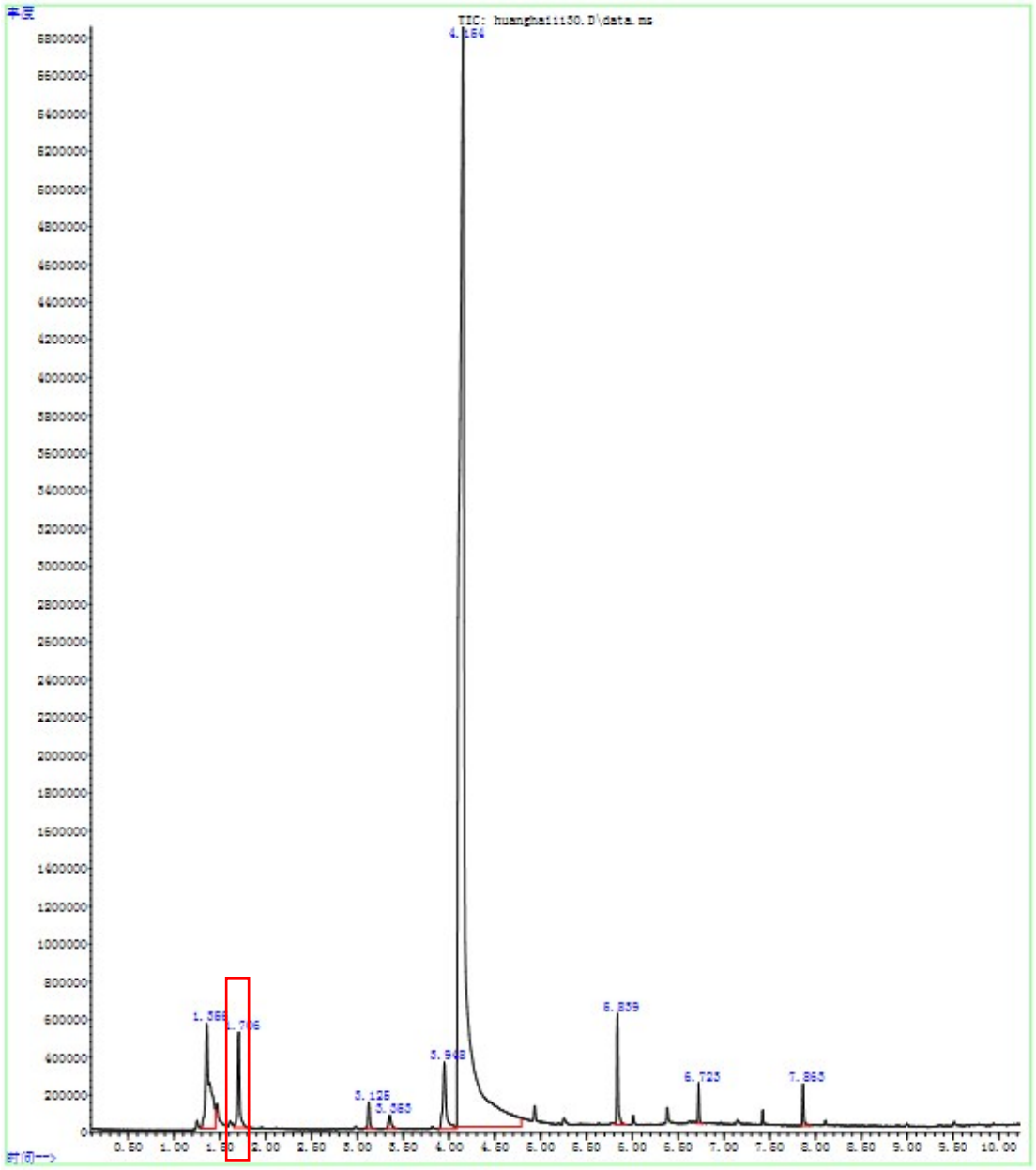
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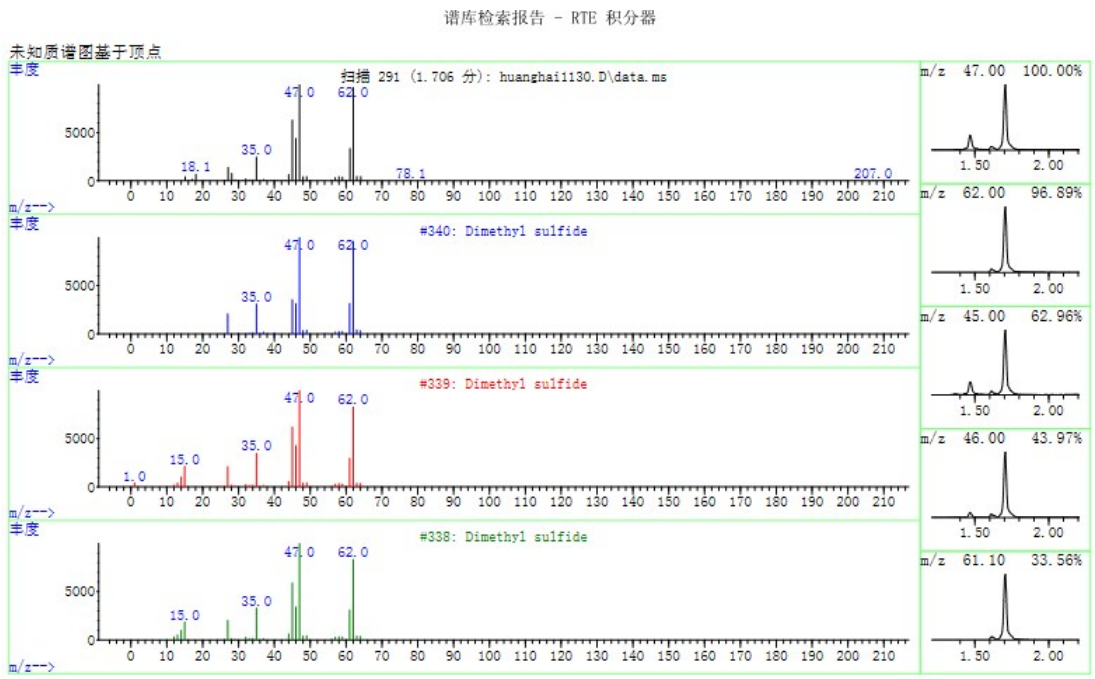

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峰编号: 2 1.706 分钟处 面积: 812772 面积 % 2.64

每个谱库中 3 个最匹配的记录。 Ref\# CAS\# 匹配度

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3 Dimethyl sulfide 338 000075-18-3 95

Signal Number: 2 1.706 Min **Area:** 812772 **Area** %: 2.64

Three best match records in date base	Ref\#	CAS\#	**Matching degree**
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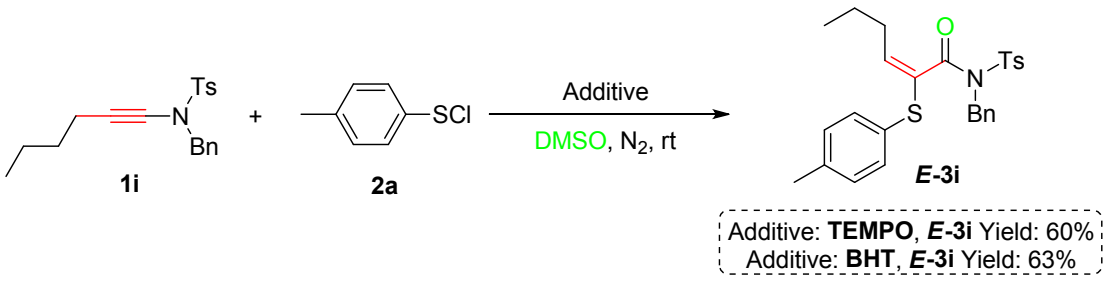


In a 10 mL flame-dried Schlenk tube were placed ynamide **1a** (0.3 mmol), *p*-tolylsulfenylchloride **2a** (2.0 equiv), Additive (2.0 equiv) and DMSO (2.0 mL) under nitrogen condition. The reaction mixture was stirred at rt for 1 hour while being monitored with TLC analysis. The reaction mixture was quenched by adding EtOAc and water. The combined organic layers were washed by brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give ***E*-3i**.

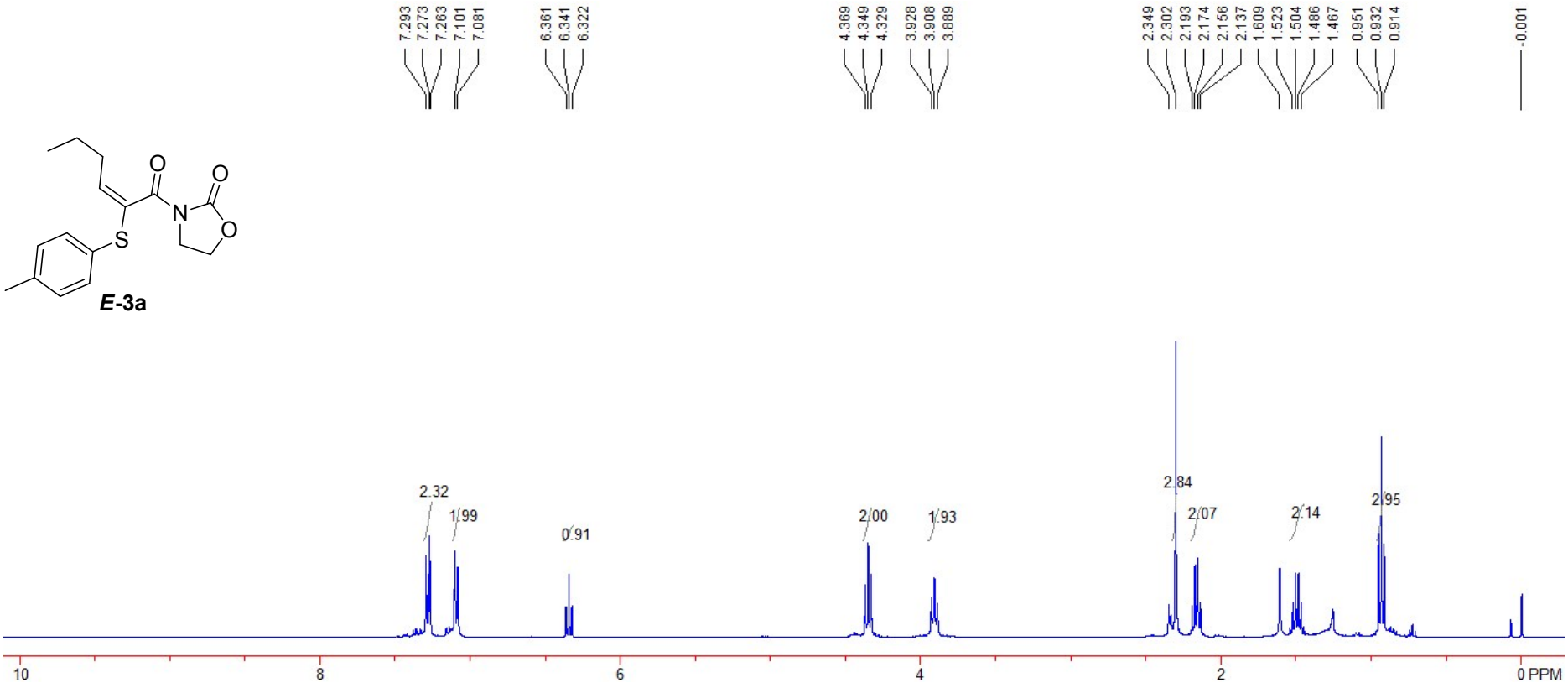
References

[1] Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz, E. L. Vera, *Org. Lett*. **2004**, *6*, 1151.

[2] H. Hofmeister, K. Annen, H. Laurent, R. Wiechert, *Angew. Chem*. **1984**, *96*, 720; *Angew. Chem., Int. Ed*. **1984**, *23*, 727.

[3] a) M. Iwasaki, T. Fujii, A. Yamamoto, K. Nakajima, Y. Nishihara, *Chem. Asian J.* **2014**, *9*, 58; b) M. Iwasaki, T. Fujii, K. Nakajima, Y. Nishihara, *Angew. Chem*. **2014**, *126*, 14100; *Angew. Chem. Int. Ed.* **2014**, *53*, 13880.

NMR Spectra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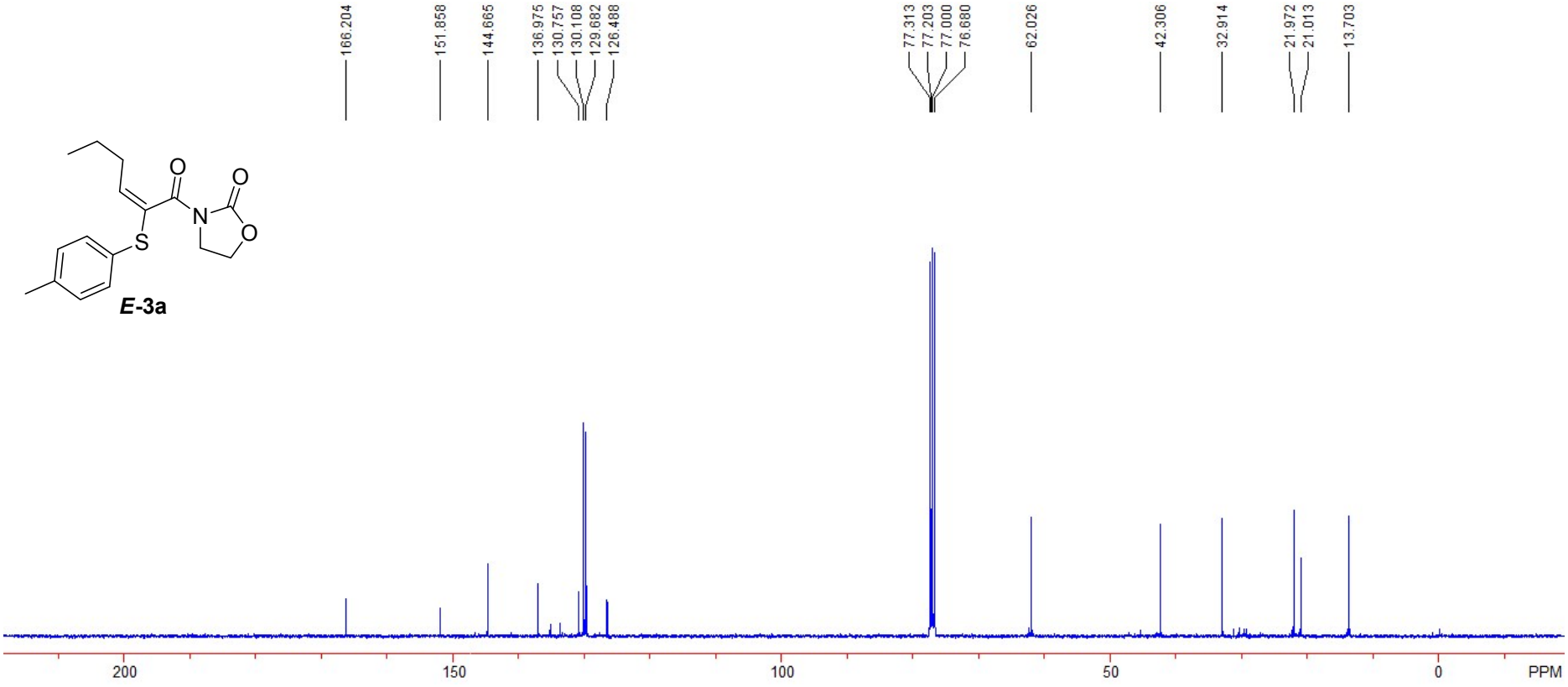
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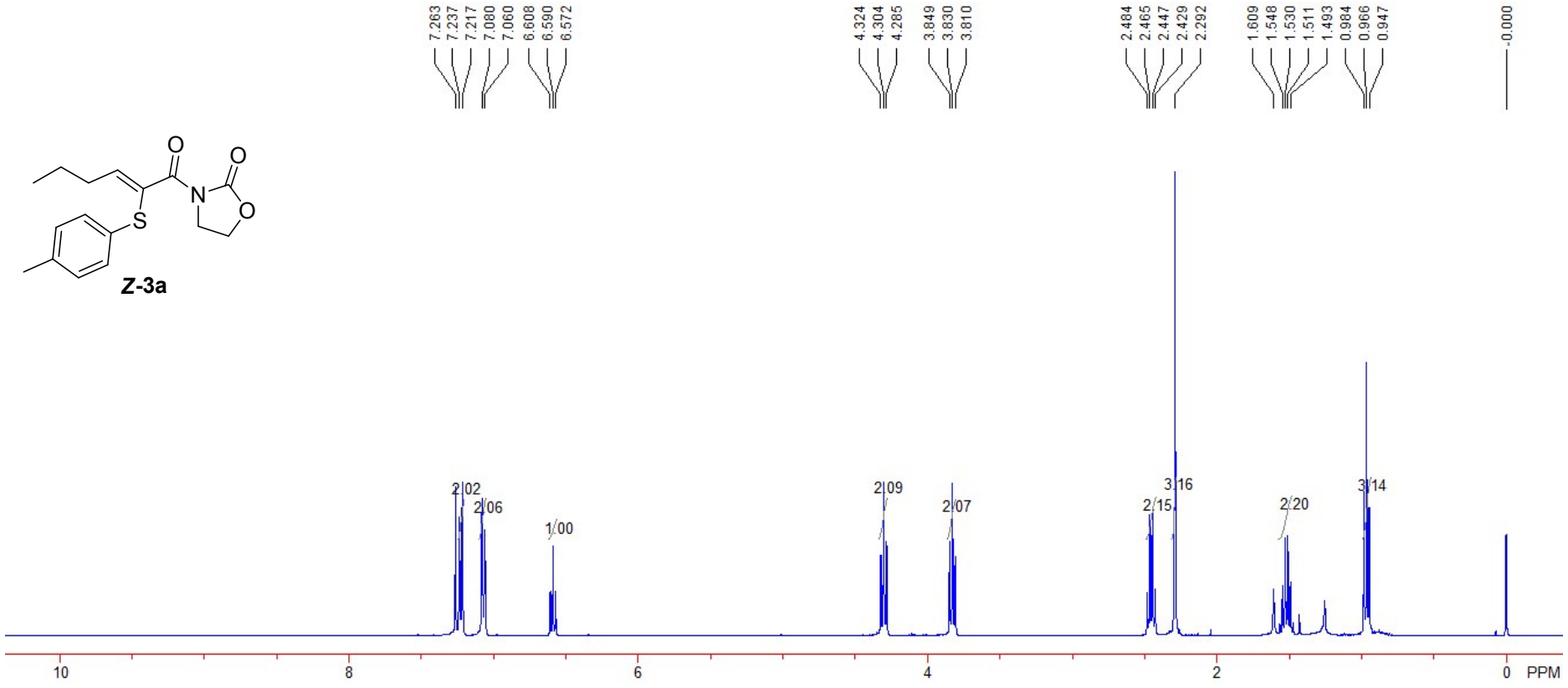
***E*-3a**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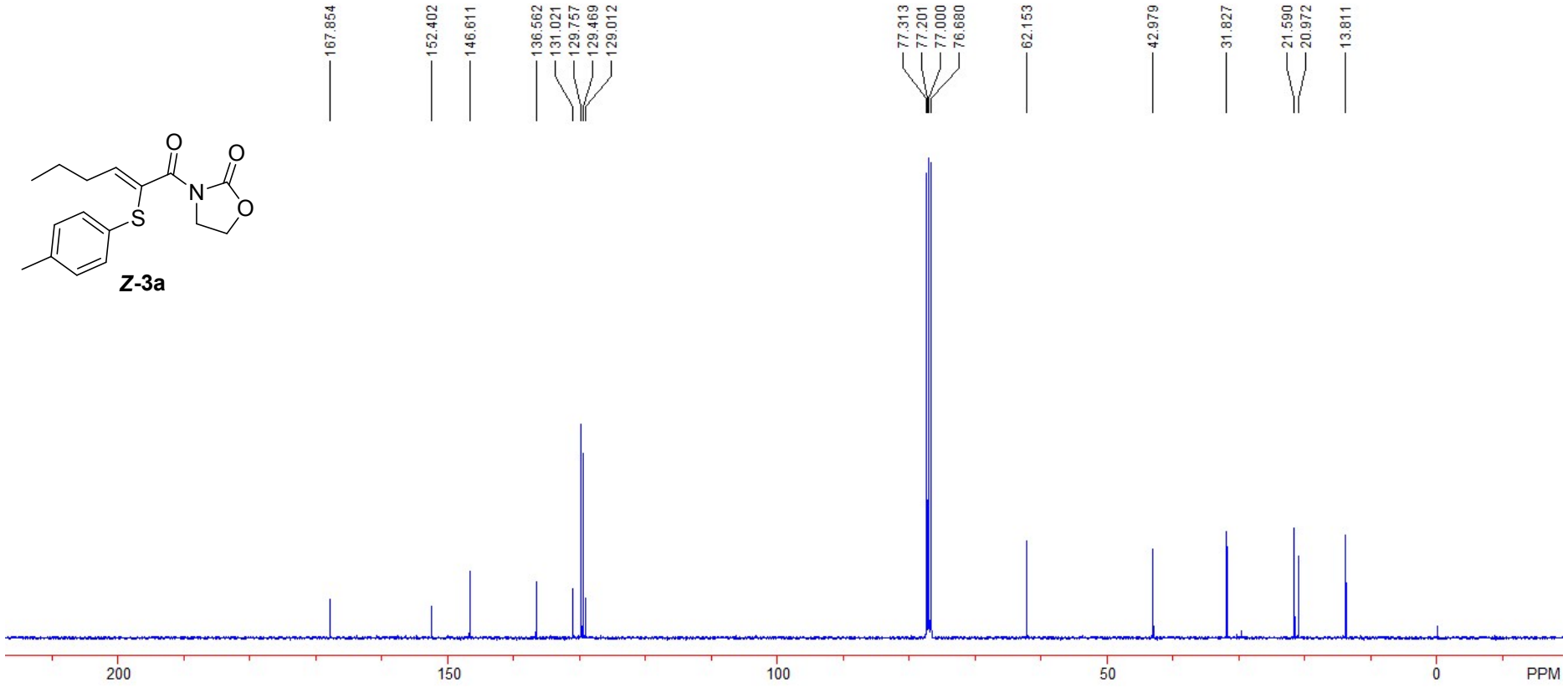
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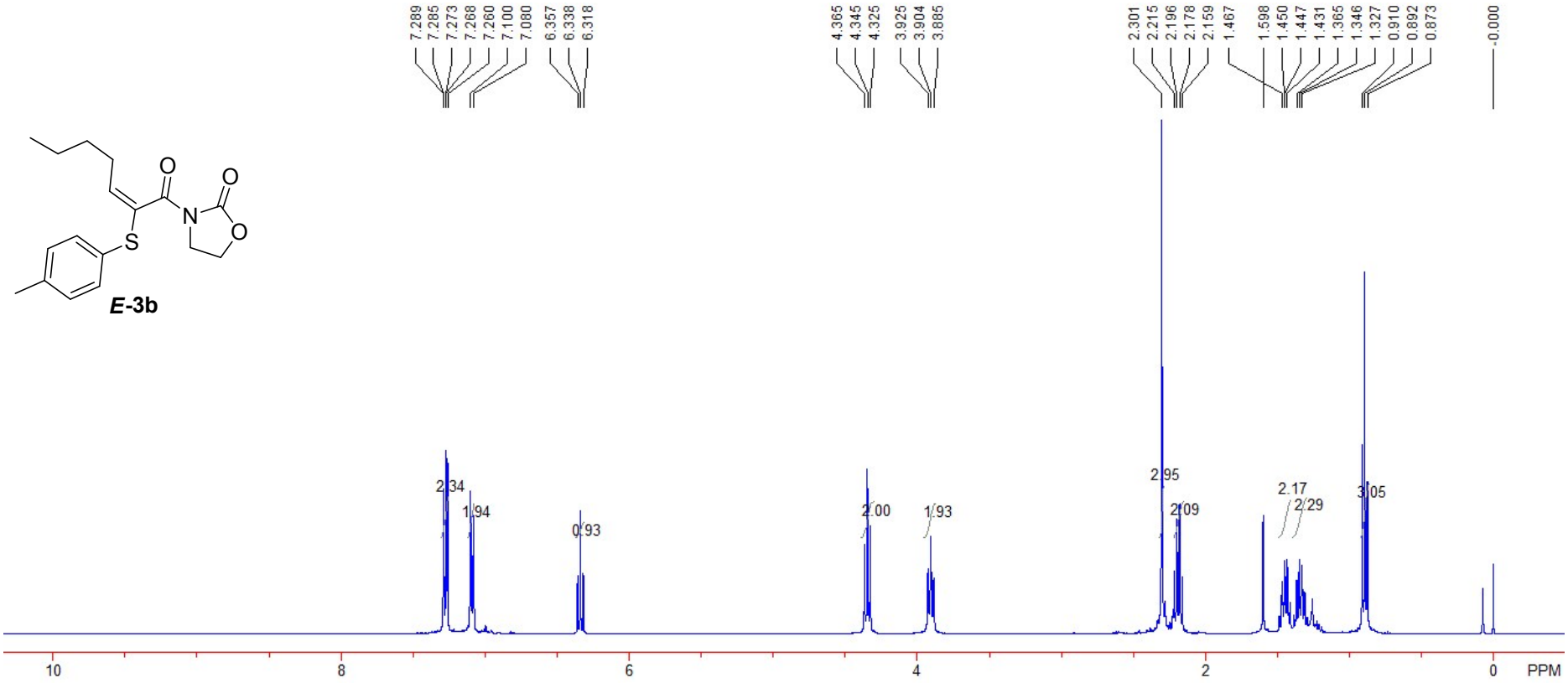
***Z*-3a**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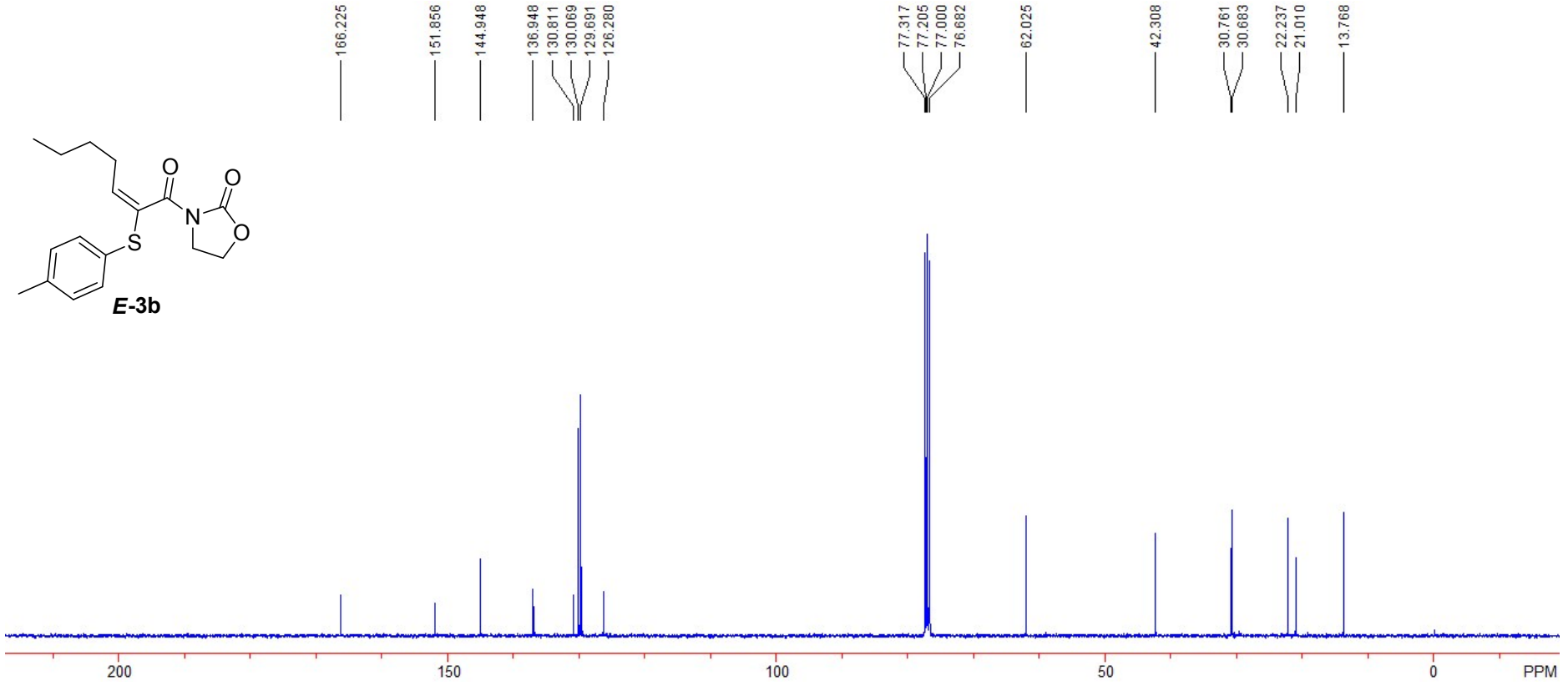
***E*-3b**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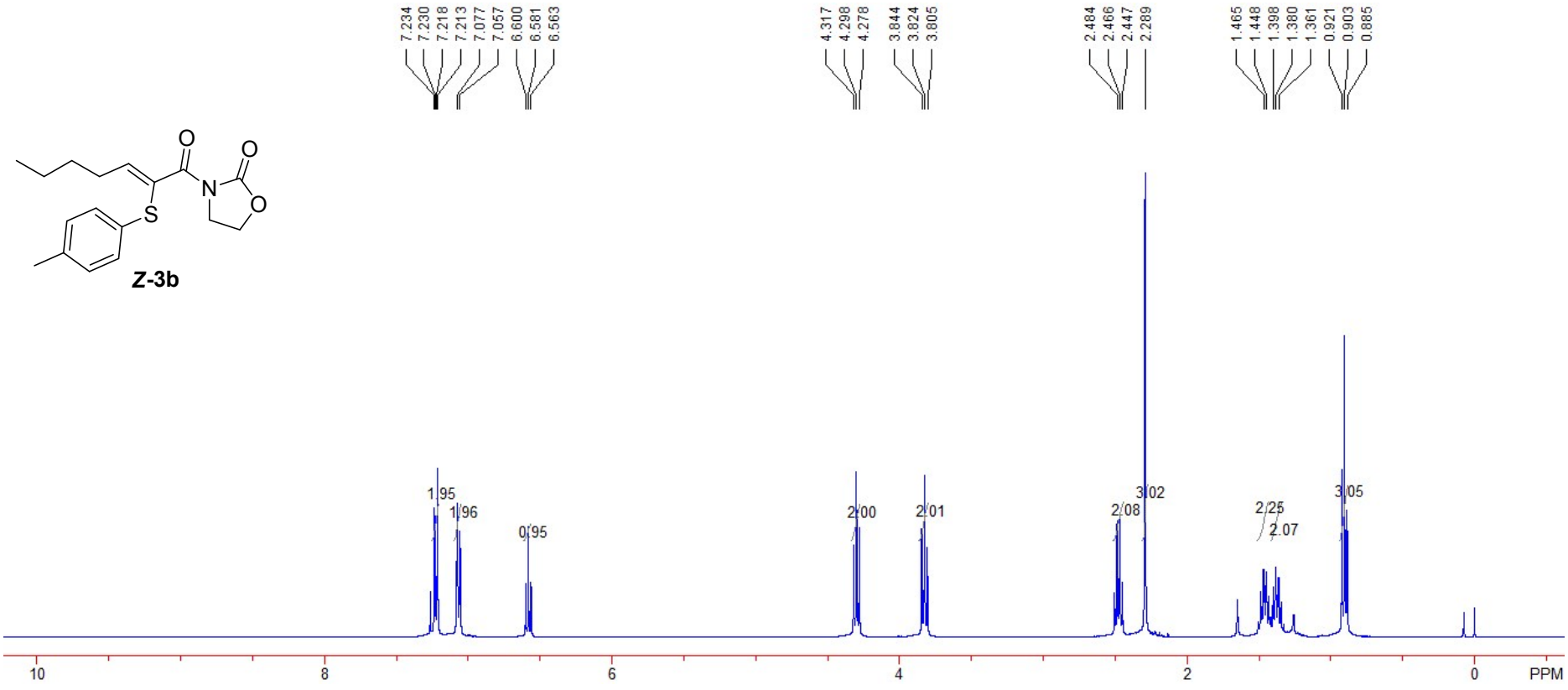
***E*-3b**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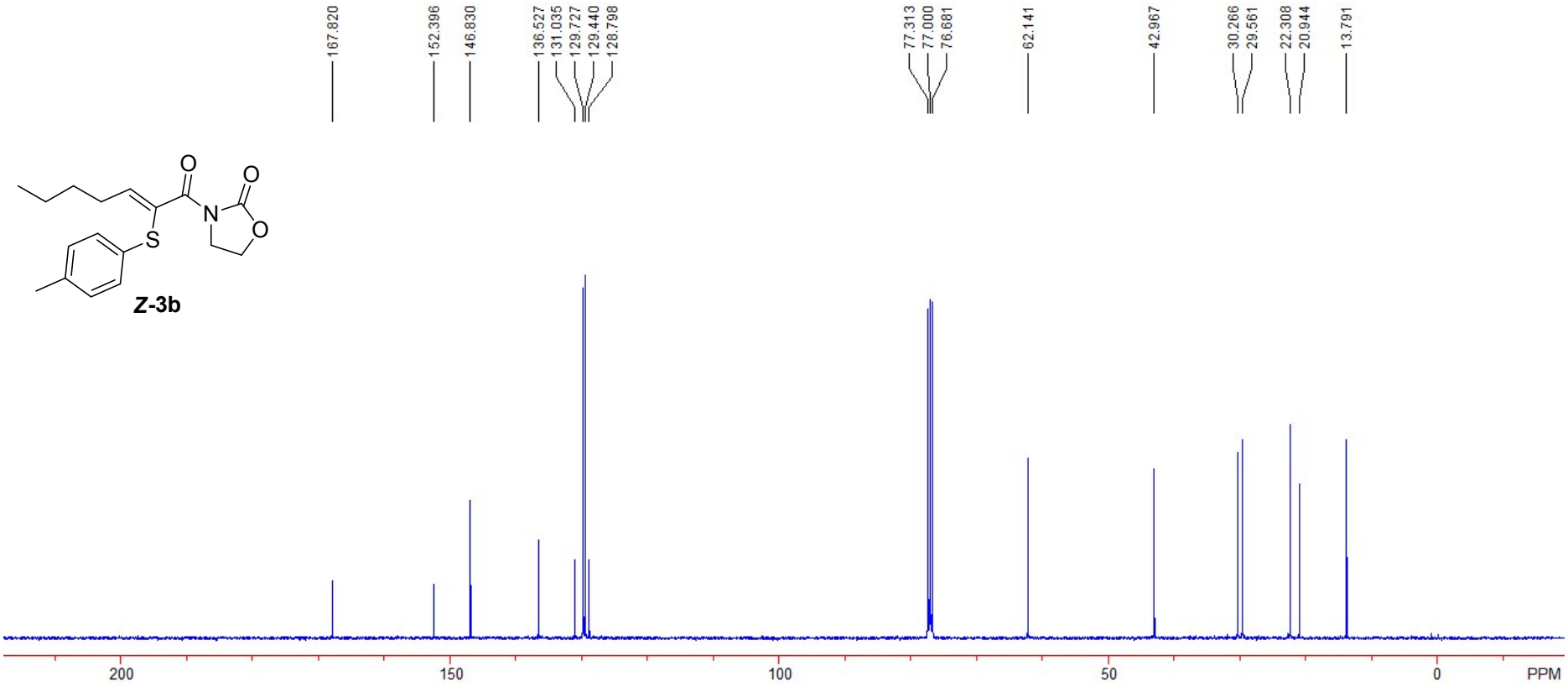
Z-3b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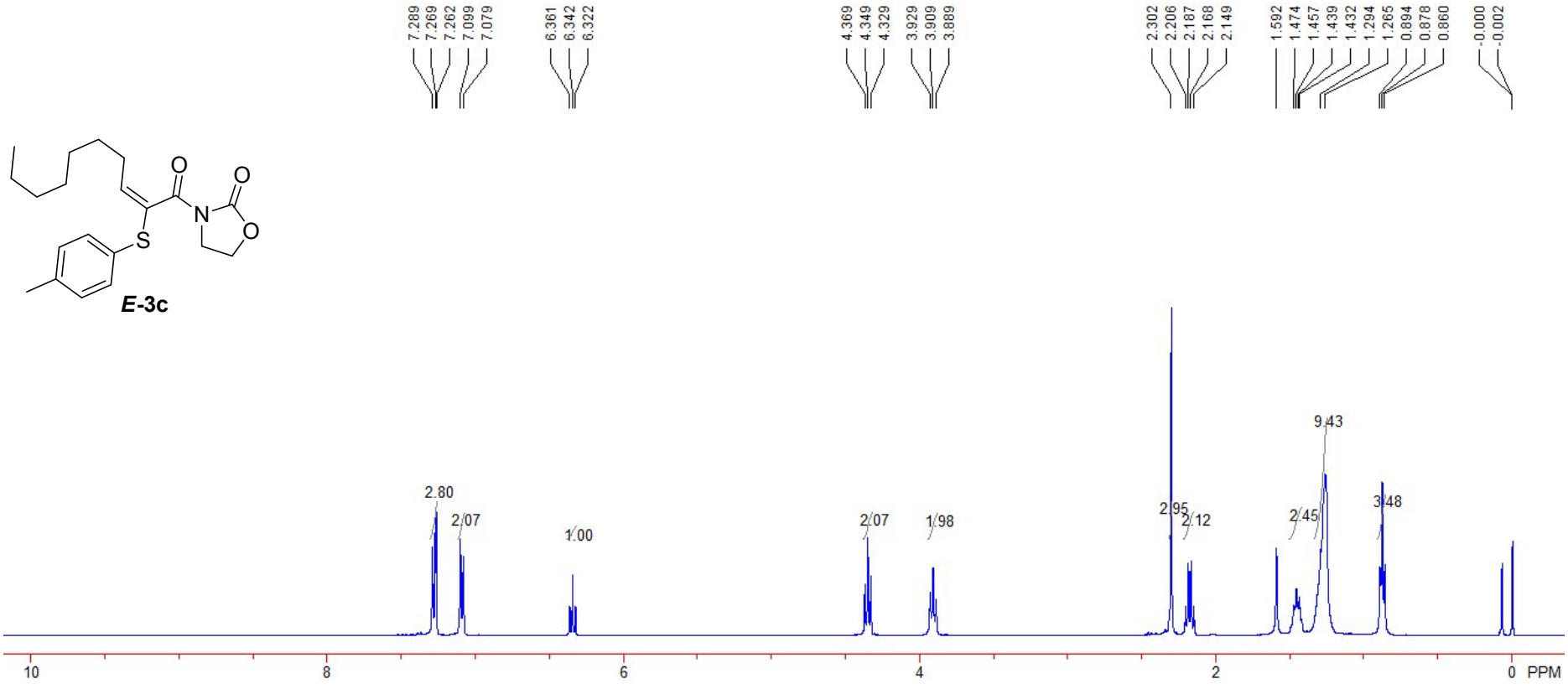
***Z*-3b**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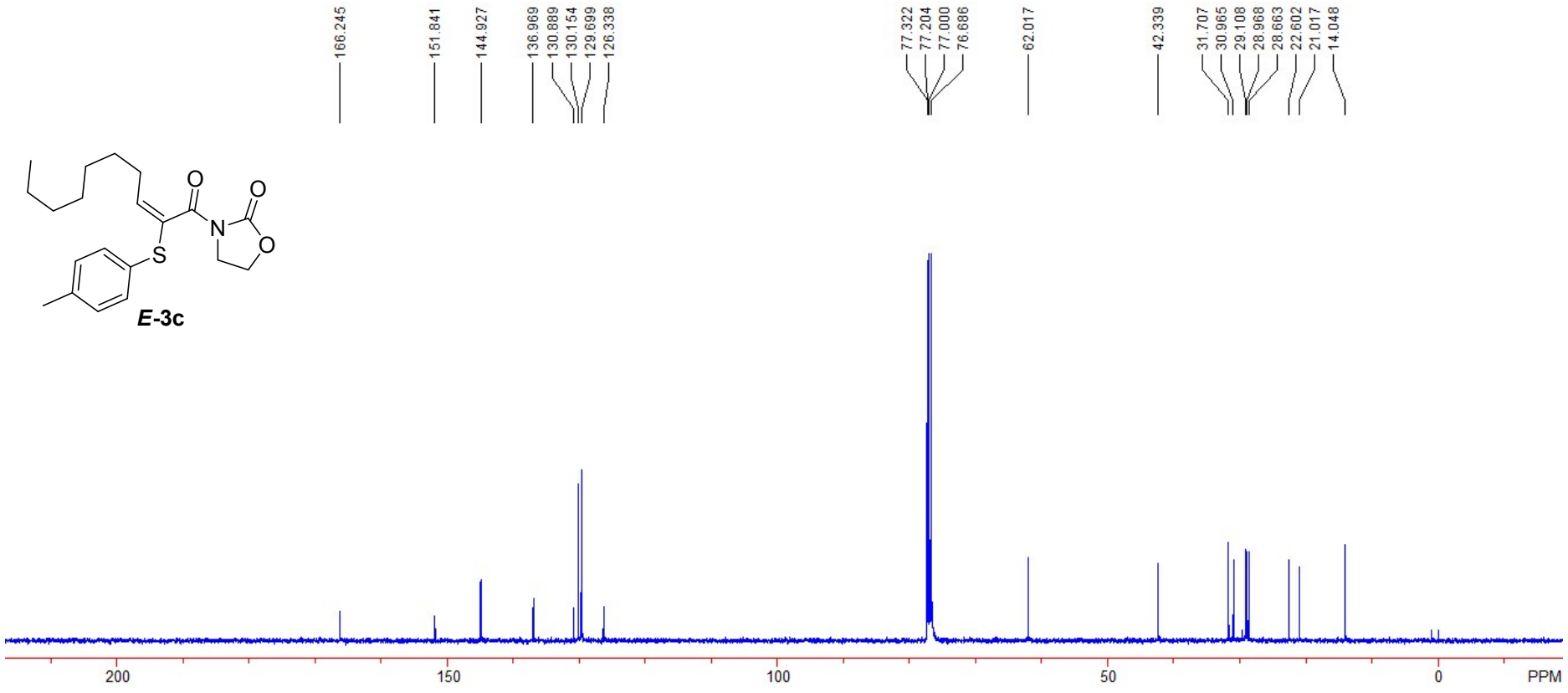
***E*-3c**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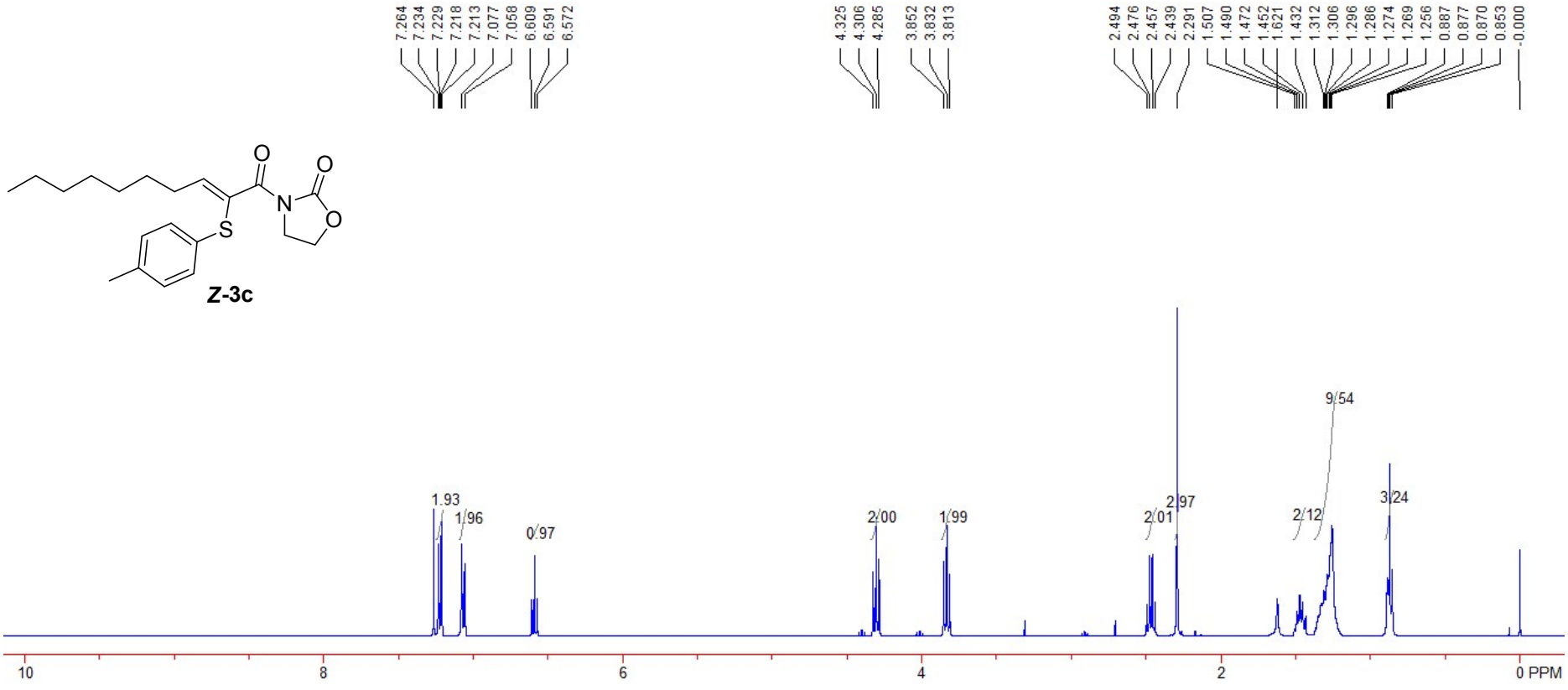
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7.077
7.058
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6.572
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4.306
4.285
3.852
3.832
3.813
2.494
2.476
2.457
2.439
2.291
1.507
1.490
1.472
1.452
1.621
1.432
1.312
1.306
1.296
1.286
1.274
1.269
1.256
0.887
0.877
0.870
0.853
-0.000
O
O
N
O
S
Z-3c
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1.96
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1.99
2.01
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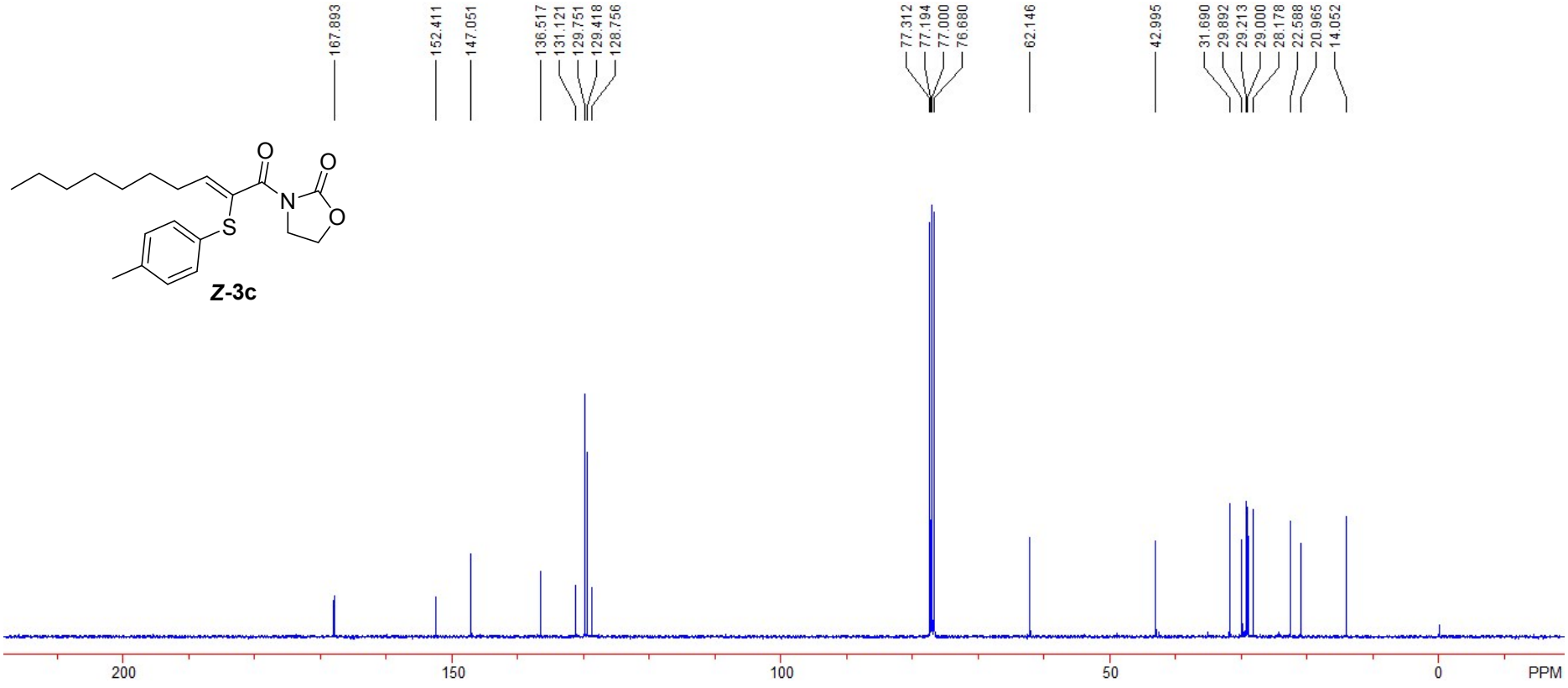
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128.756
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76.680
62.146
42.995
31.690
29.892
29.213
29.000
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14.052
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N
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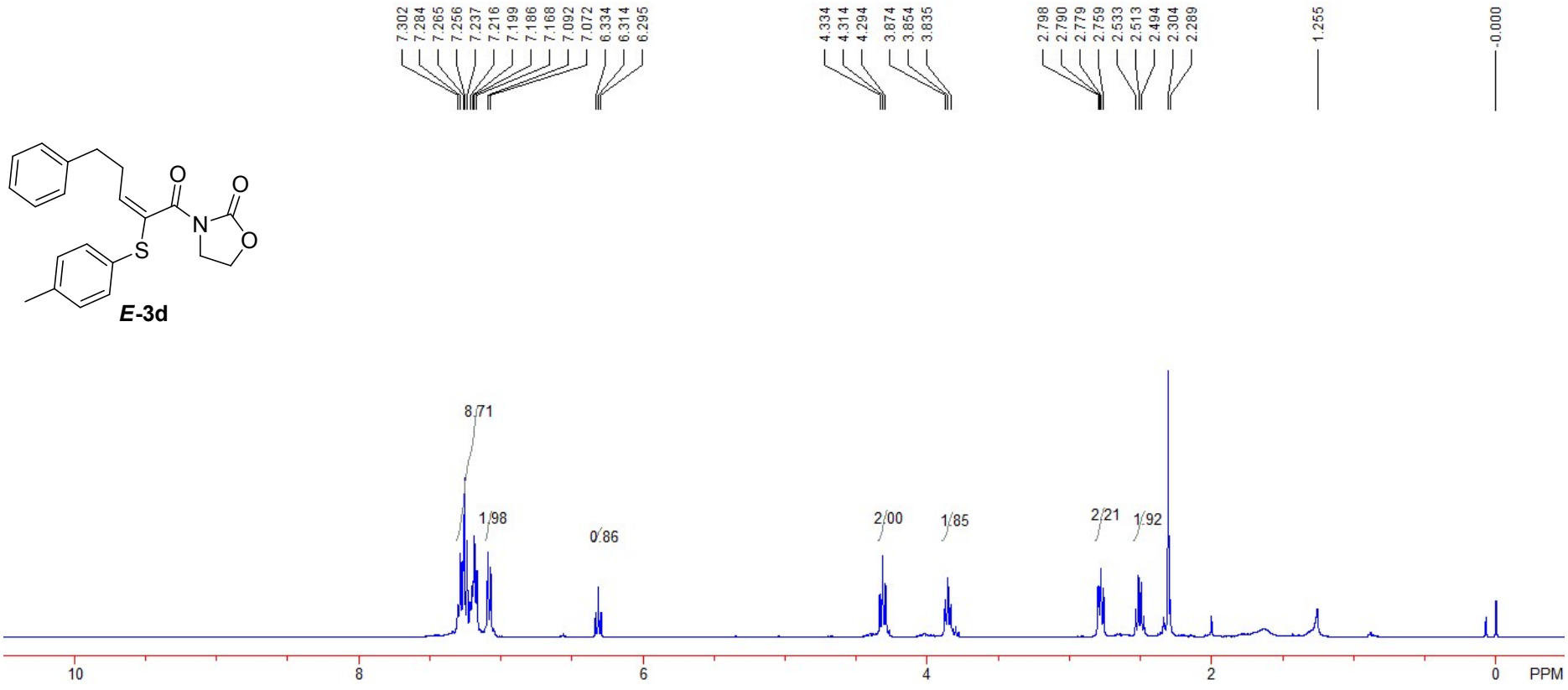
PPM

***Z*-3c**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7.199
7.186
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7.092
7.072
6.334
6.314
6.295
4.334
4.314
4.294
3.874
3.854
3.835
2.798
2.790
2.779
2.759
2.533
2.513
2.494
2.304
2.289
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O
N
O
S
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1.92
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PPM

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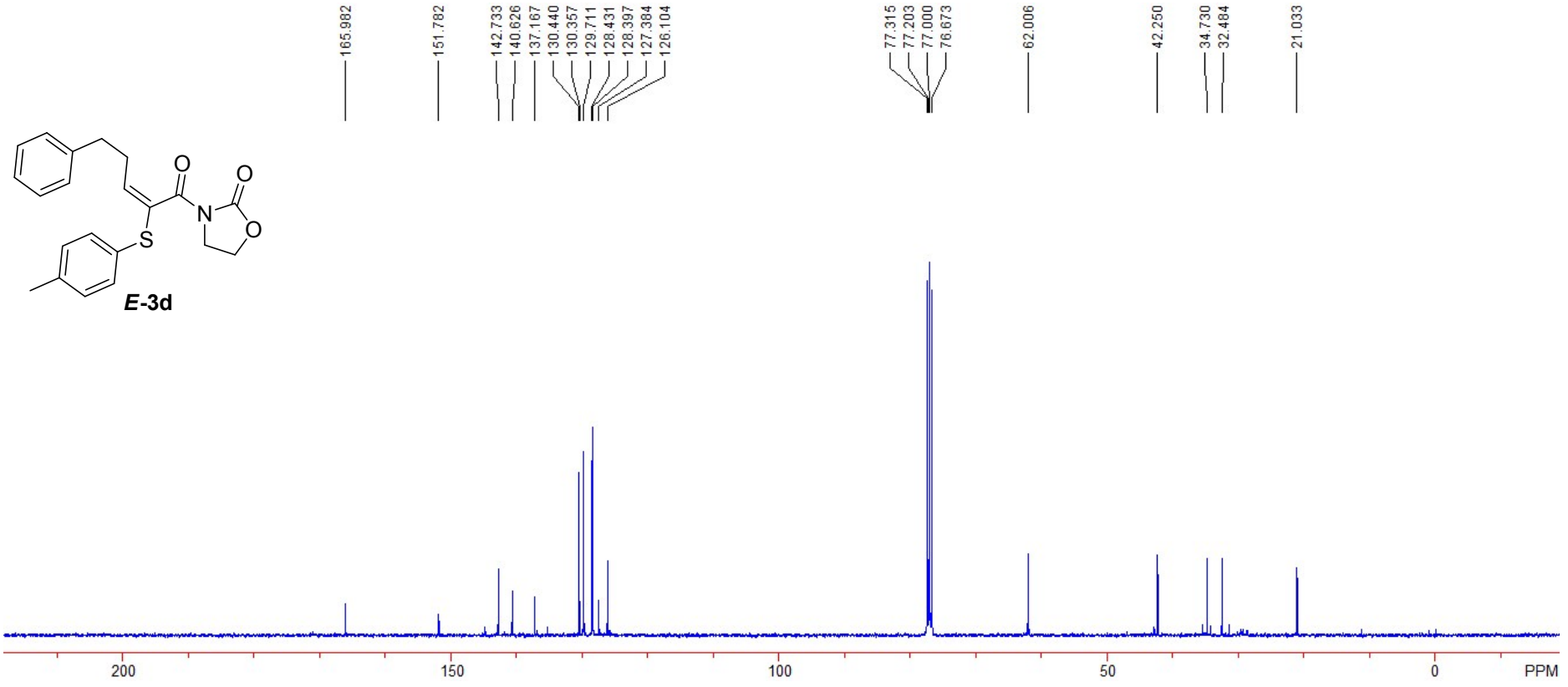
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126.104
77.315
77.203
77.000
76.673
62.006
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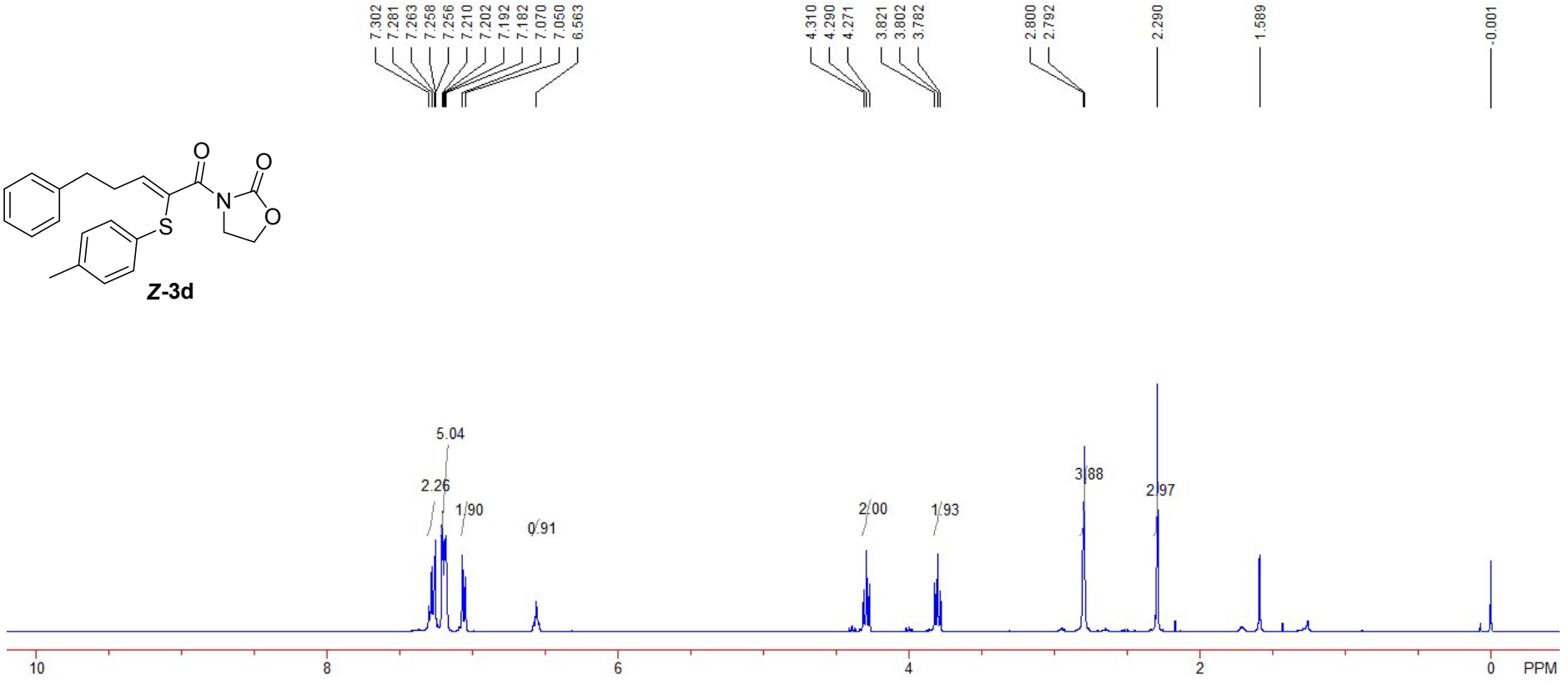
PPM

***E*-3d**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7.256
7.210
7.202
7.192
7.182
7.070
7.050
6.563
4.310
4.290
4.271
3.821
3.802
3.782
2.800
2.792
2.290
1.589
-0.001
O
O
N
O
S
5.04
2.26
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2.00
1.93
3.88
2.97
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6
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PPM

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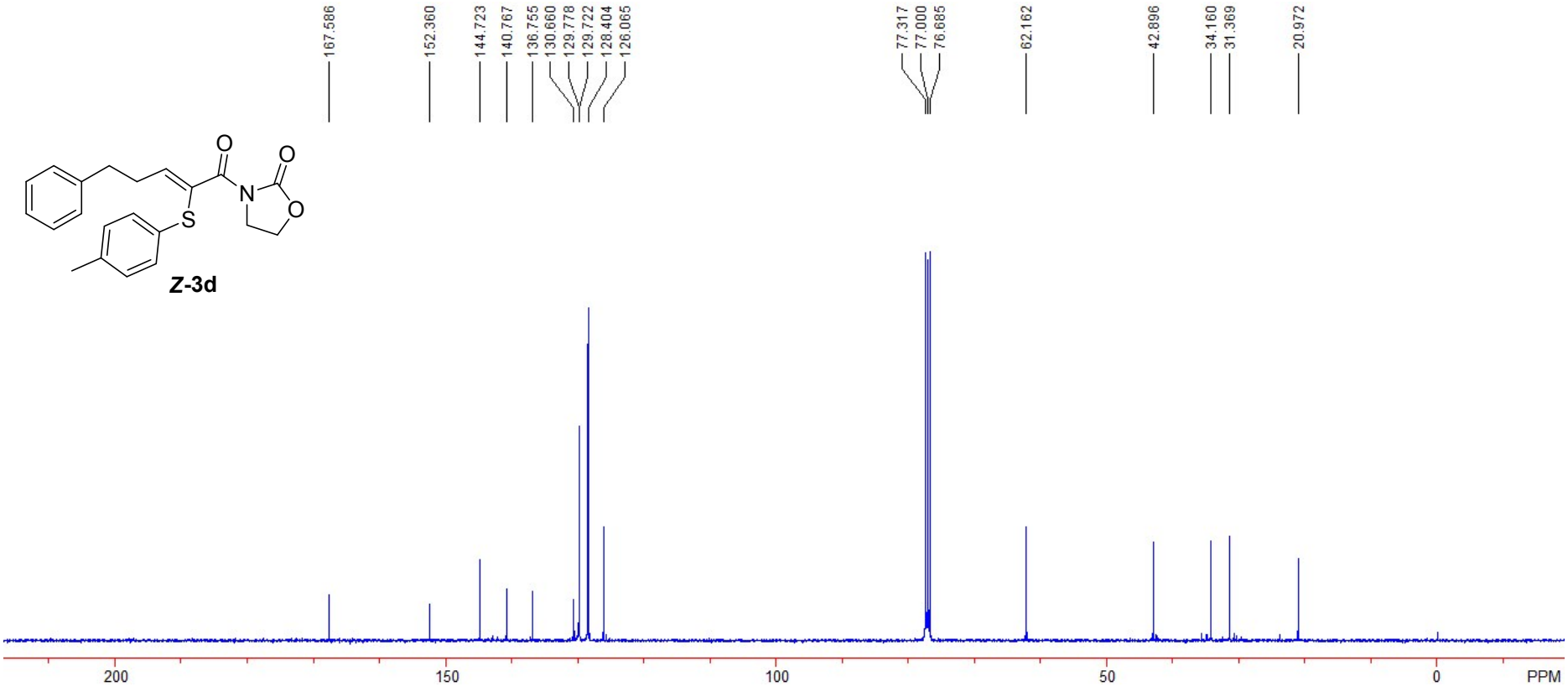
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126.065
77.317
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76.685
62.162
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20.972
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O
S
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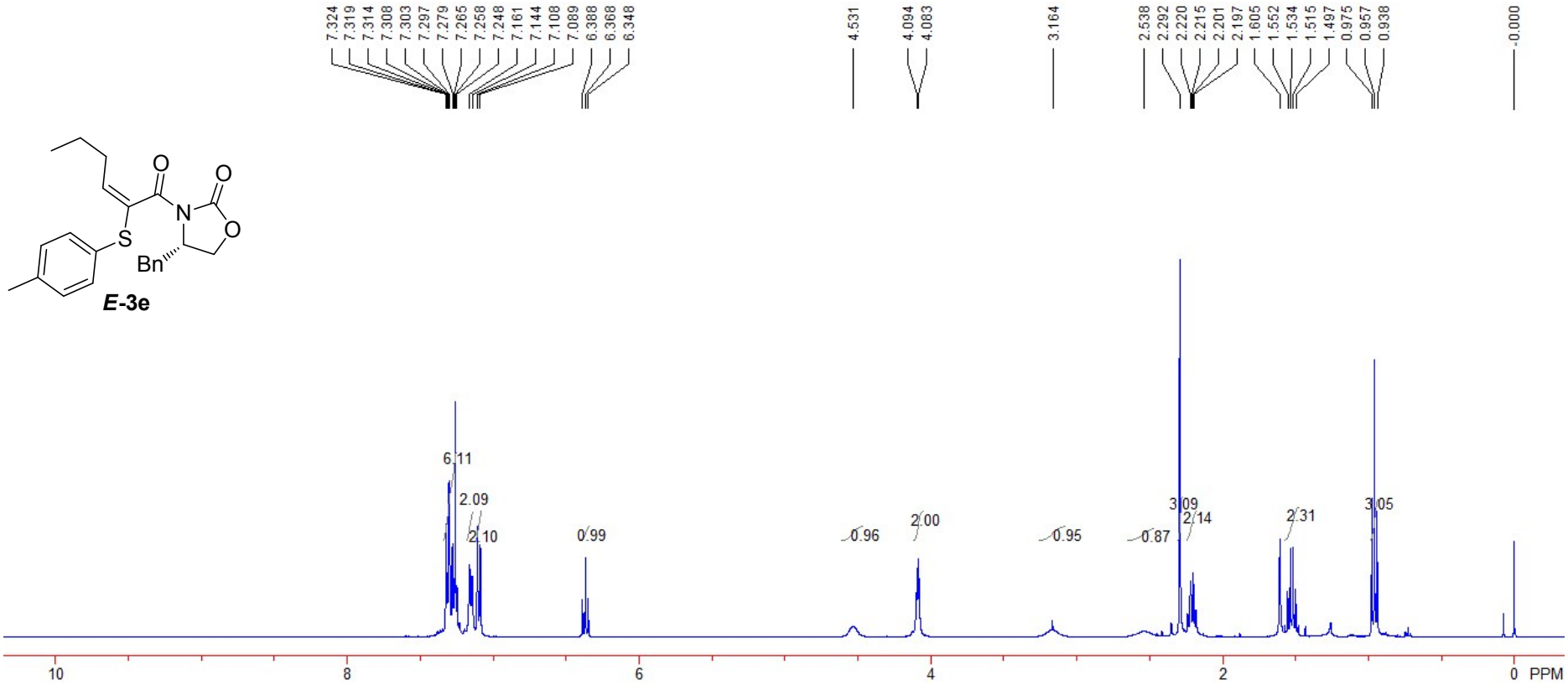
150
100
50
0
PPM

***Z*-3d**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7.279
7.265
7.258
7.248
7.161
7.144
7.108
7.089
6.388
6.368
6.348
4.531
4.094
4.083
3.164
2.538
2.292
2.220
2.215
2.201
2.197
1.605
1.552
1.534
1.515
1.497
0.975
0.957
0.938
-0.000
O
O
N
O
S
Bn
6.11
2.09
2.10
0.99
0.96
2.00
0.95
0.87
3.09
2.14
2.31
3.05
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8
6
4
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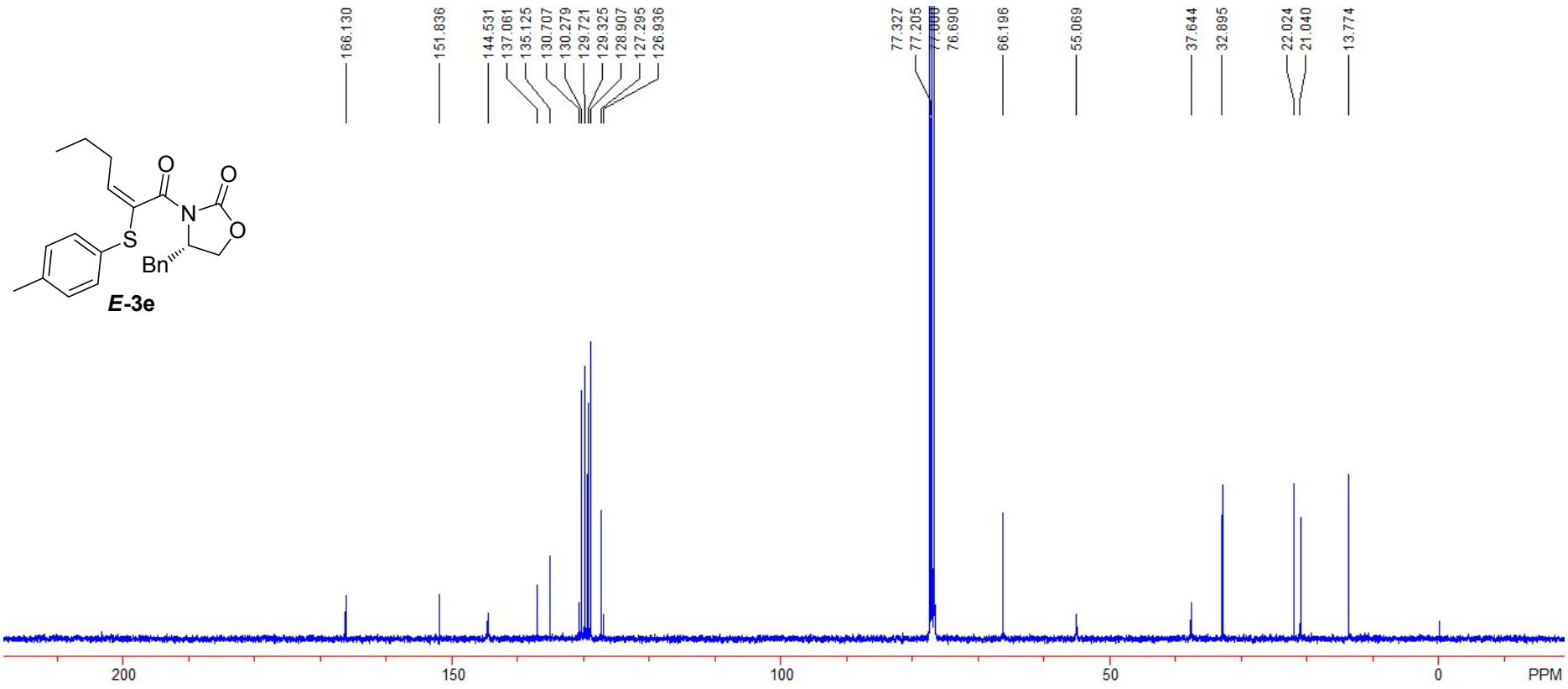
0 PPM

***E*-3e**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129.721
129.325
128.907
127.295
126.936
77.327
77.205
76.690
66.196
55.069
37.644
32.895
22.024
21.040
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O
O
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O
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Bn
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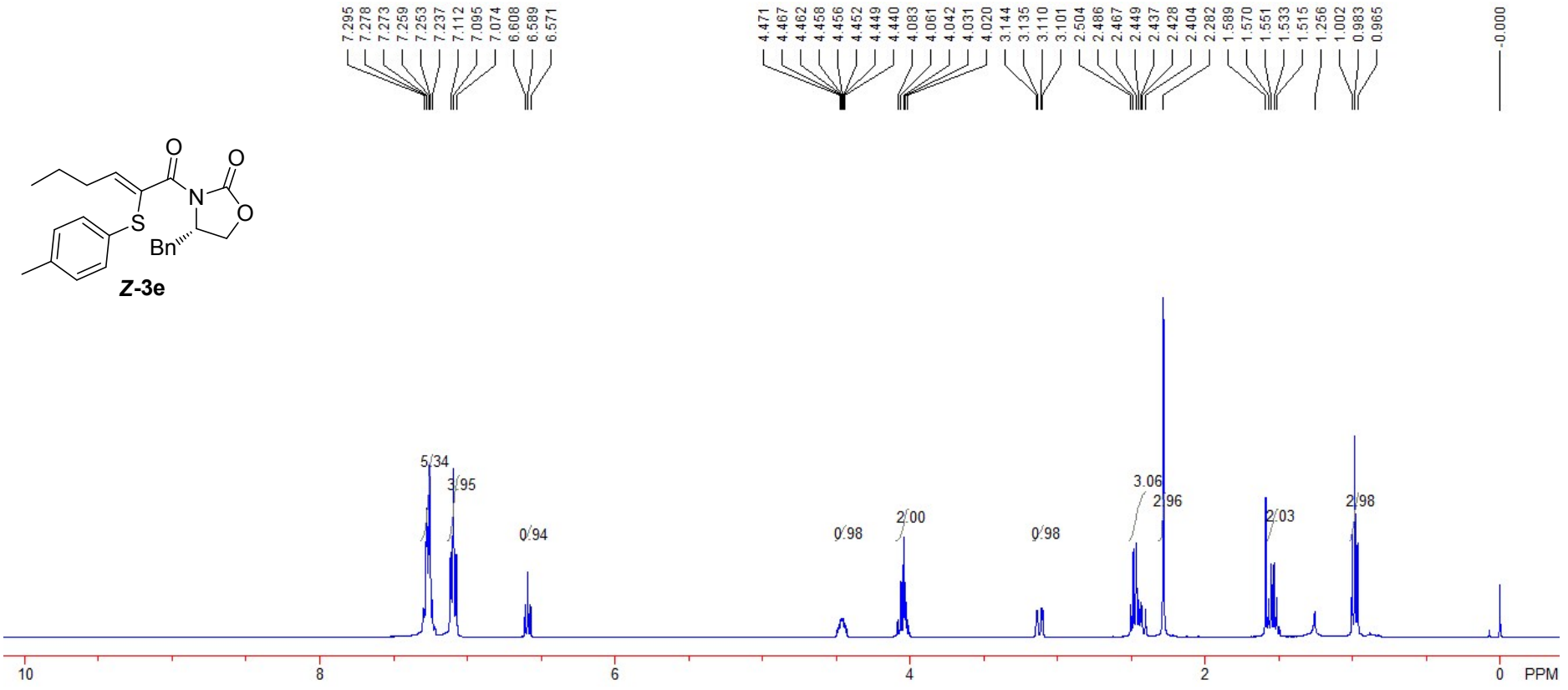
150
100
50
0
PPM

***E*-3e**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6.589
6.571
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4.467
4.462
4.458
4.456
4.452
4.449
4.440
4.083
4.061
4.042
4.031
4.020
3.144
3.135
3.110
3.101
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2.467
2.449
2.437
2.428
2.404
2.282
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1.570
1.551
1.533
1.515
1.256
1.002
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0.965
-0.000
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O
N
O
S
Bn
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3.95
0.94
0.98
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2.96
2.03
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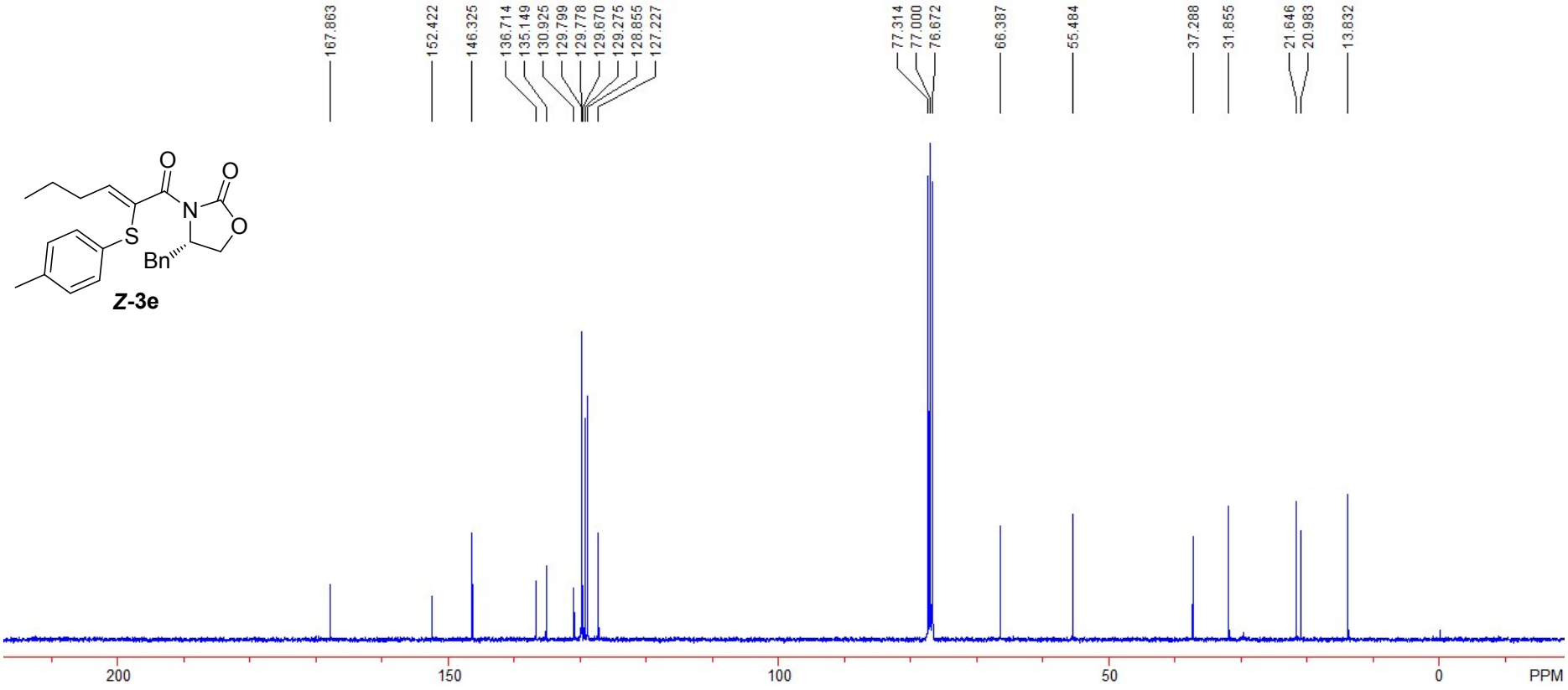
PPM

***Z*-3e**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77.314
77.000
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66.387
55.484
37.288
31.855
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O
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Bn
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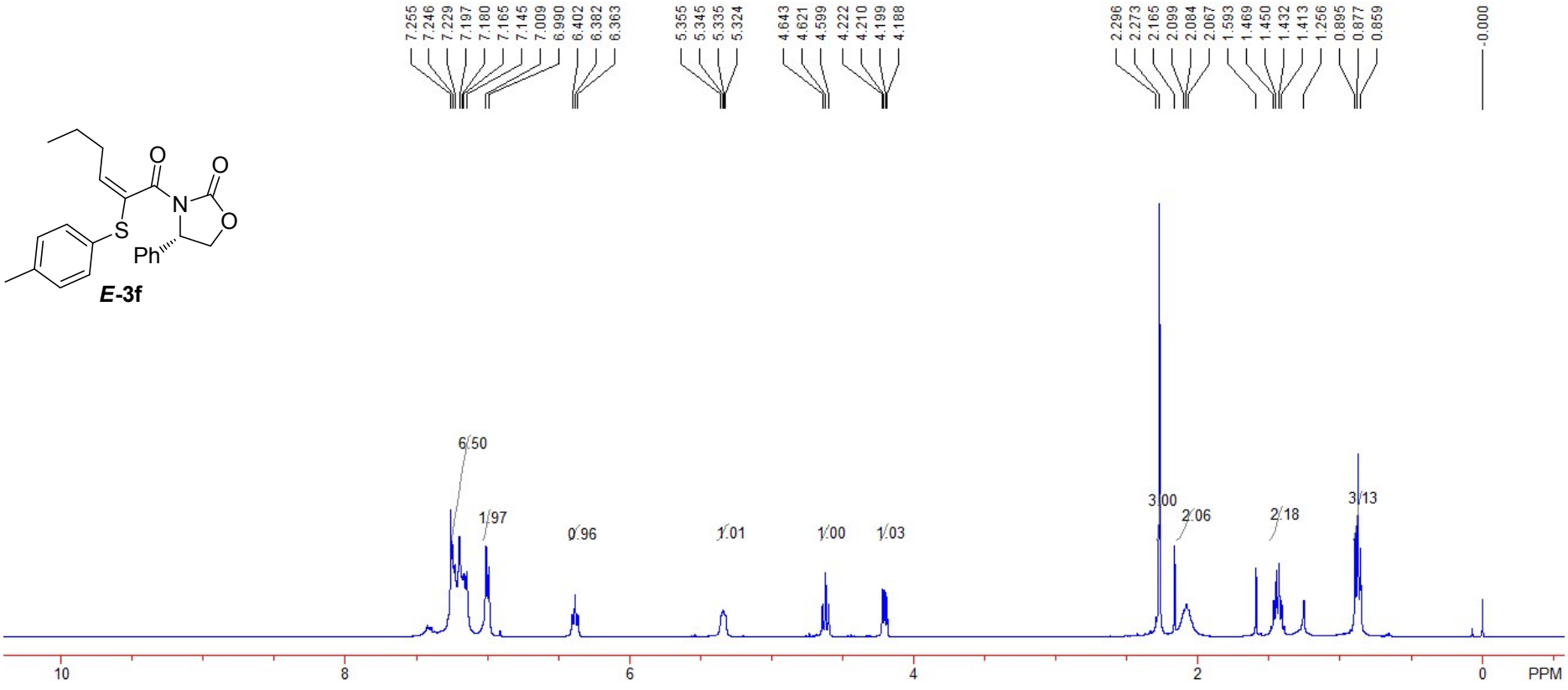
150
100
50
0
PPM

***Z*-3e**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5.335
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4.621
4.599
4.222
4.210
4.199
4.188
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2.273
2.165
2.099
2.084
2.067
1.593
1.469
1.450
1.432
1.413
1.256
0.895
0.877
0.859
-0.000
O
O
N
O
S
Ph
6.50
1.97
0.96
1.01
1.00
1.03
3.00
2.06
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3.13
10
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6
4
2
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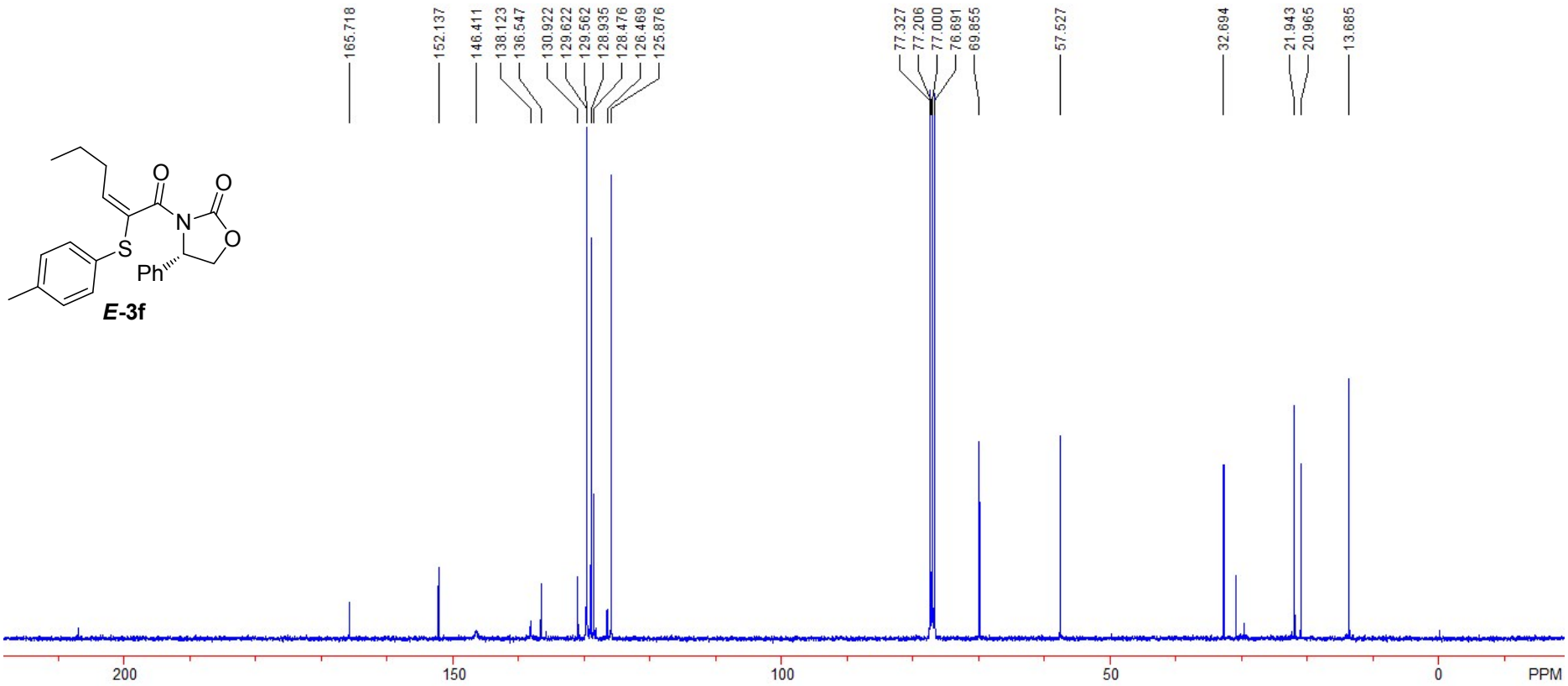
PPM

***E*-3f**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128.476
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77.327
77.206
77.000
76.691
69.855
57.527
32.694
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20.965
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O
O
N
O
S
Ph
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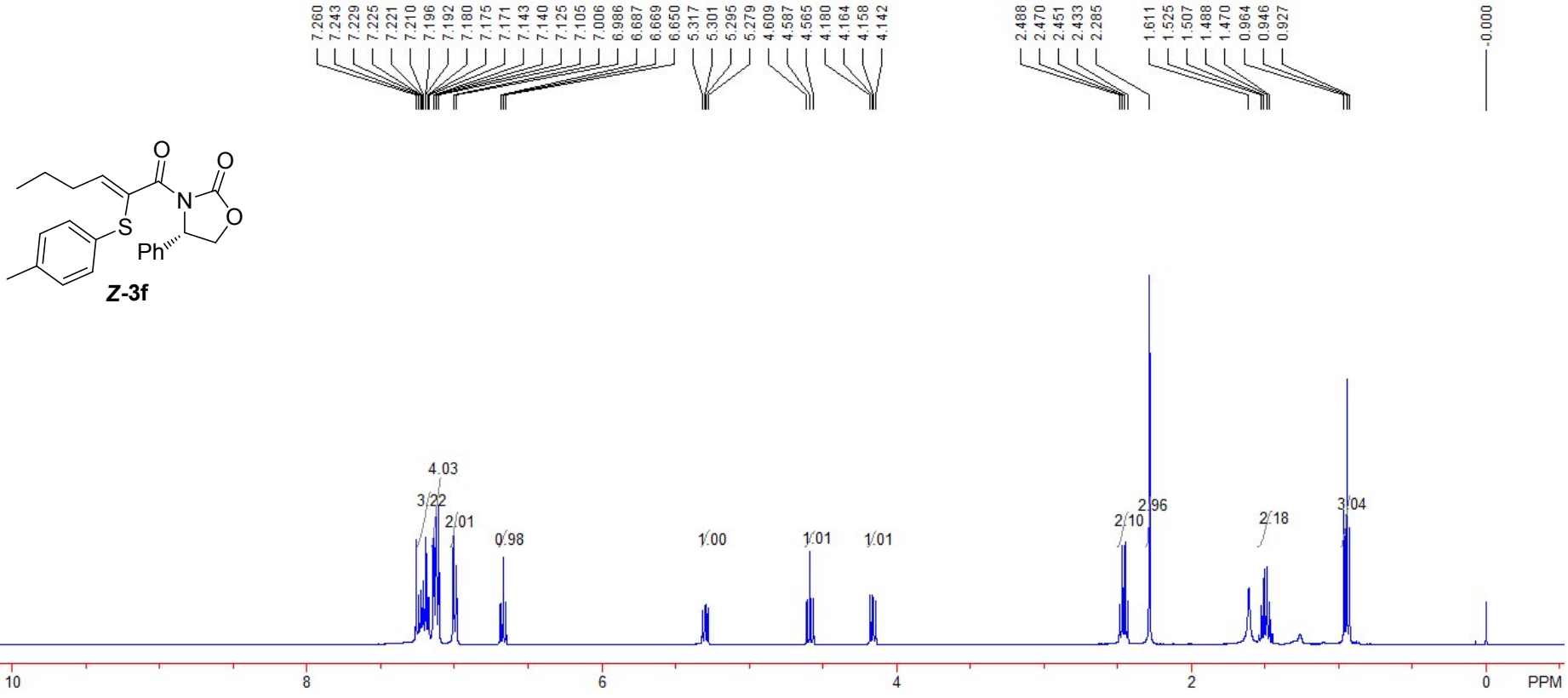
150
100
50
0
PPM

***E*-3f**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7.210
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7.192
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7.171
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7.140
7.125
7.105
7.006
6.986
6.687
6.669
6.650
5.317
5.301
5.295
5.279
4.609
4.587
4.565
4.180
4.164
4.158
4.142
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2.470
2.451
2.433
2.285
1.611
1.525
1.507
1.488
1.470
0.964
0.946
0.927
-0.000
O
O
N
O
S
Ph
Z-3f
4.03
3.22
2.01
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1.01
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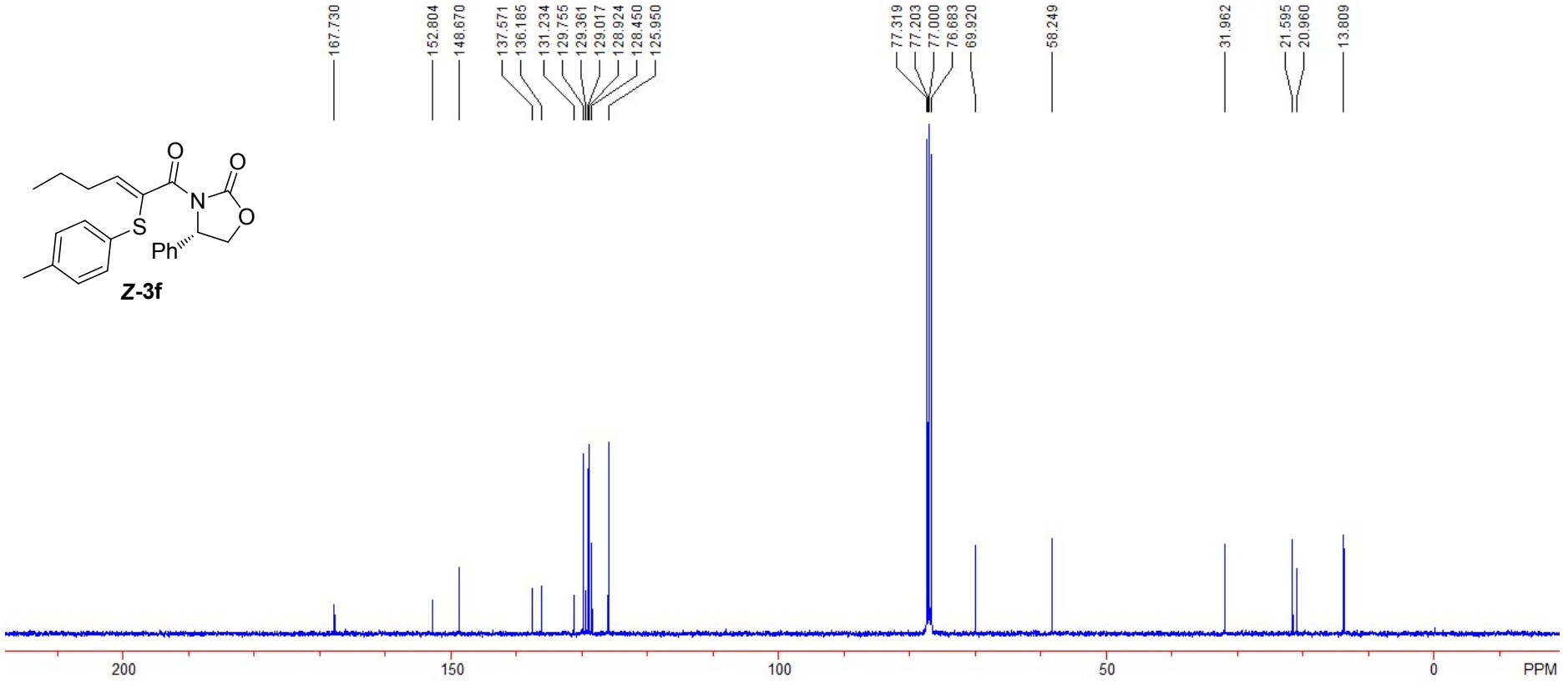
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128.450
125.950
77.319
77.203
77.000
76.683
69.920
58.249
31.962
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O
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O
S
Ph
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150
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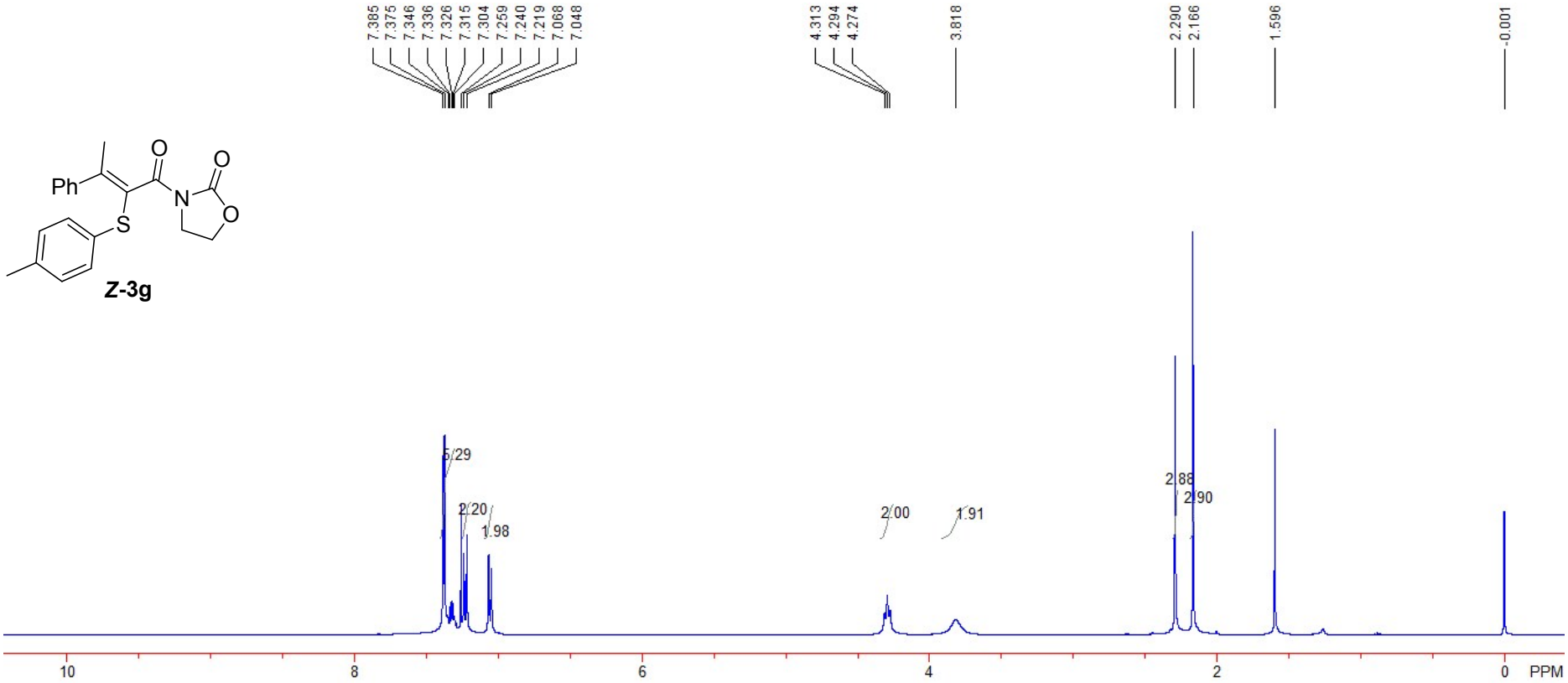
50
0
PPM

***Z*-3f**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7.068
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4.294
4.274
3.818
2.290
2.166
1.596
-0.001
Ph
O
O
N
O
S
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2.00
1.91
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2.90
10
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6
4
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PPM

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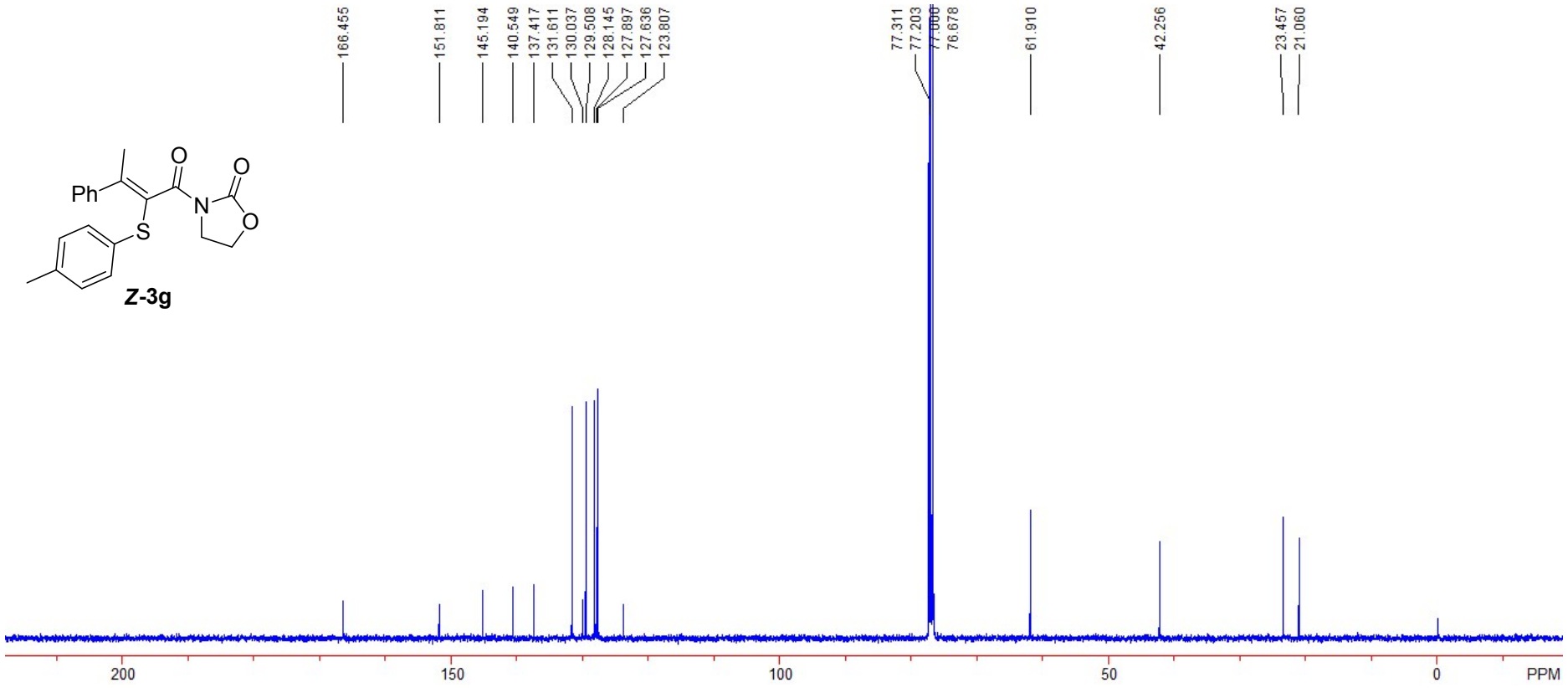
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127.897
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77.000
76.678
61.910
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Ph
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O
N
O
S
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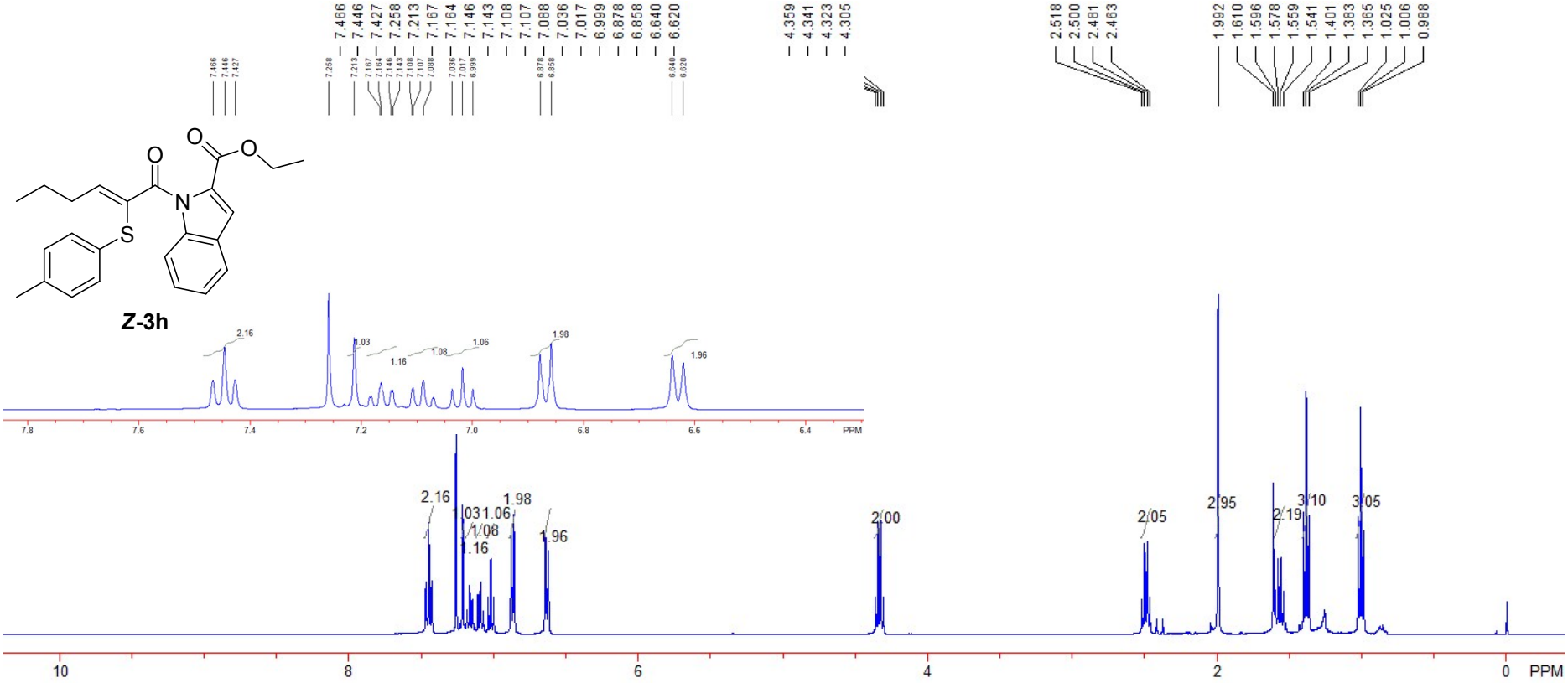
150
100
50
0
PPM

***Z*-3g**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7.143
7.108
7.107
7.088
7.036
7.017
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6.858
6.640
6.620
4.359
4.341
4.323
4.305
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2.500
2.481
2.463
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O
O
N
S
Z-3h
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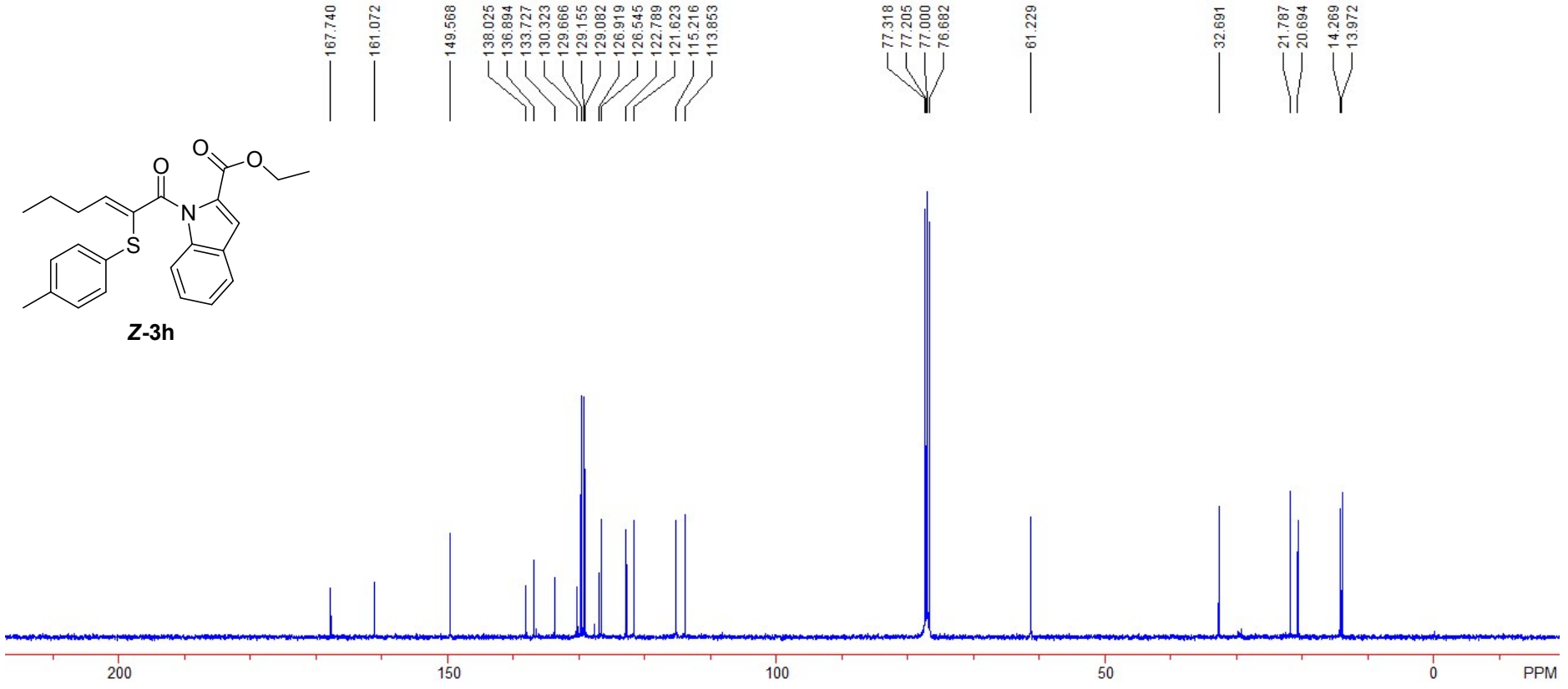
PPM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113.853
77.318
77.205
77.000
76.682
61.229
32.691
21.787
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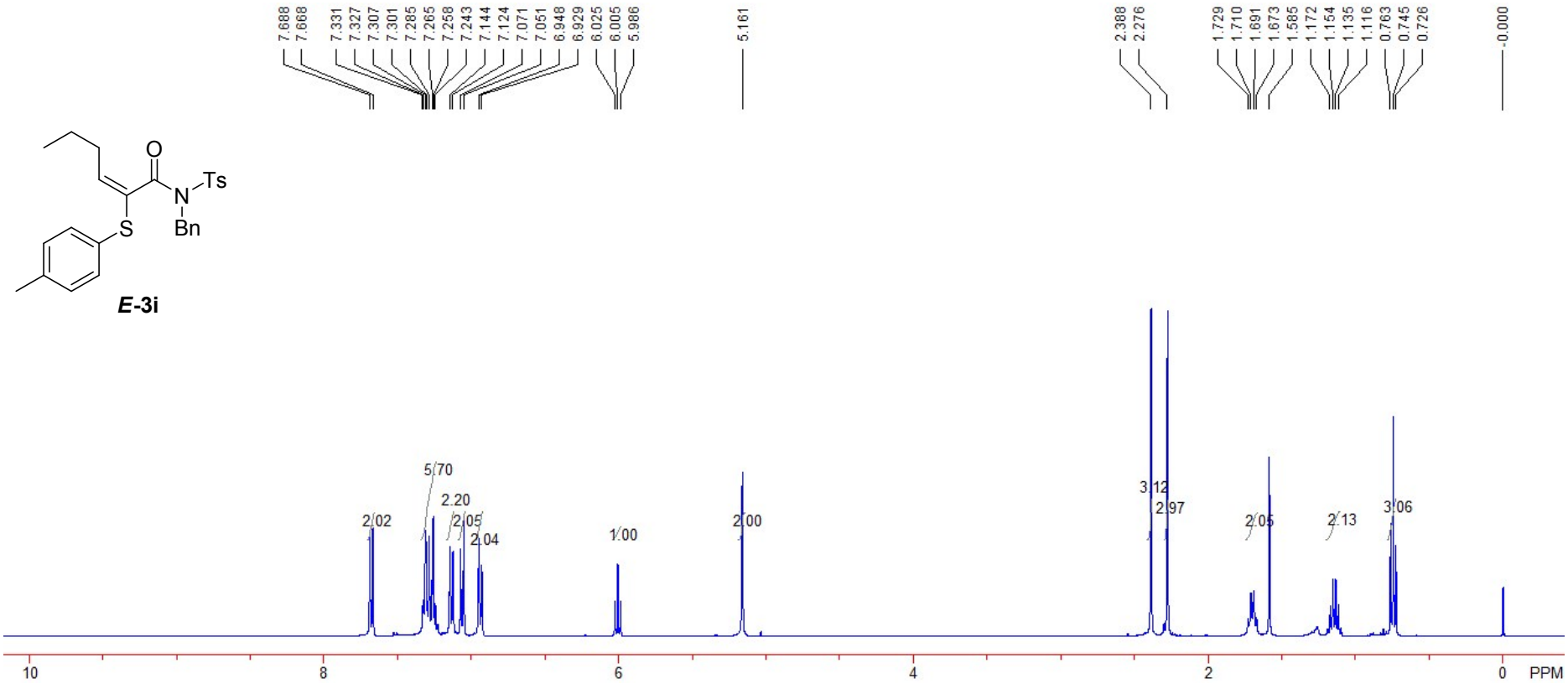
PPM

***Z*-3h**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6.005
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5.161
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1.710
1.691
1.673
1.585
1.172
1.154
1.135
1.116
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0.726
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N
Ts
Bn
S
E-3i
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2.20
2.05
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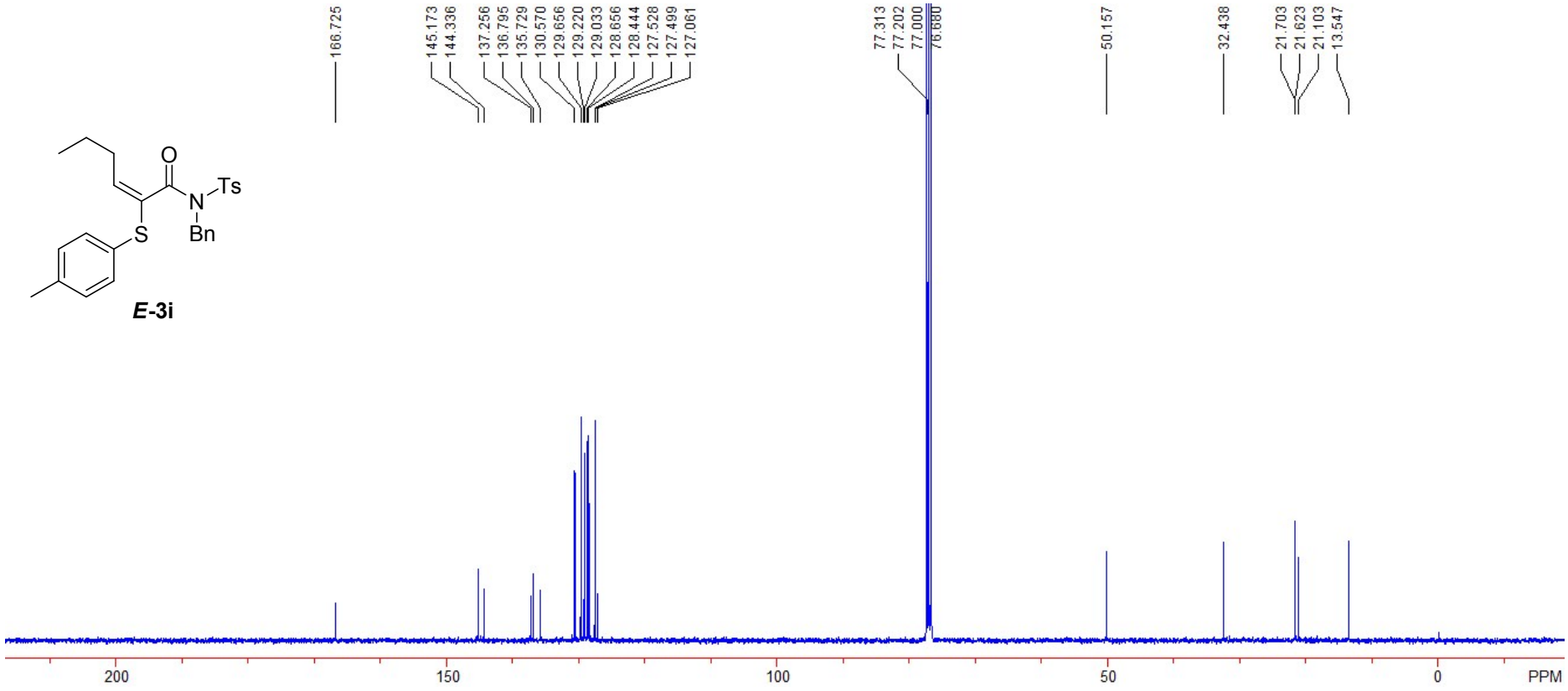
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127.528
127.499
127.061
77.313
77.202
77.000
76.680
50.157
32.438
21.703
21.623
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13.547
O
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Ts
Bn
S
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100
50
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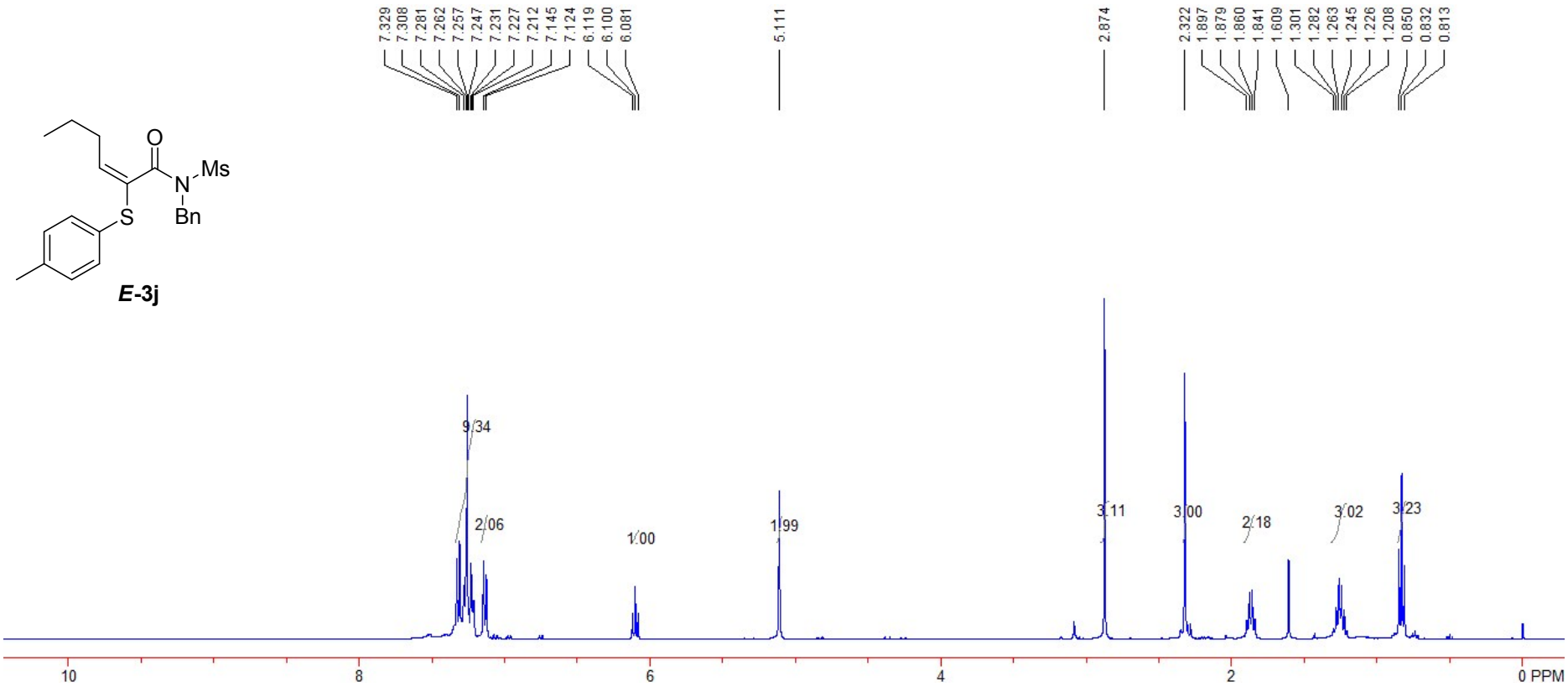
PPM

***E*-3i**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7.231
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7.145
7.124
6.119
6.100
6.081
5.111
2.874
2.322
1.897
1.879
1.860
1.841
1.609
1.301
1.282
1.263
1.245
1.226
1.208
0.850
0.832
0.813
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N
Ms
Bn
S
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2.06
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3.00
2.18
3.02
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8
6
4
2
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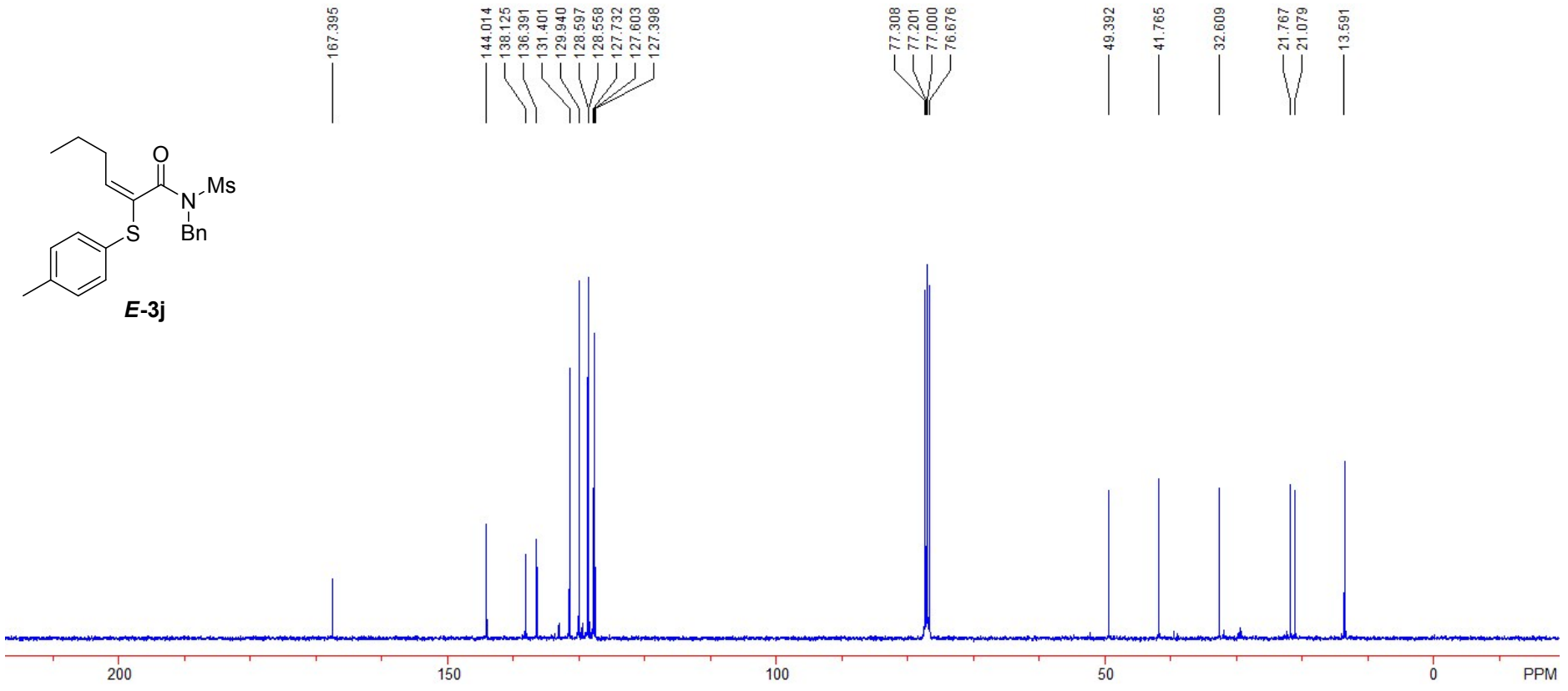
***E*-3j**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77.000
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41.765
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Bn
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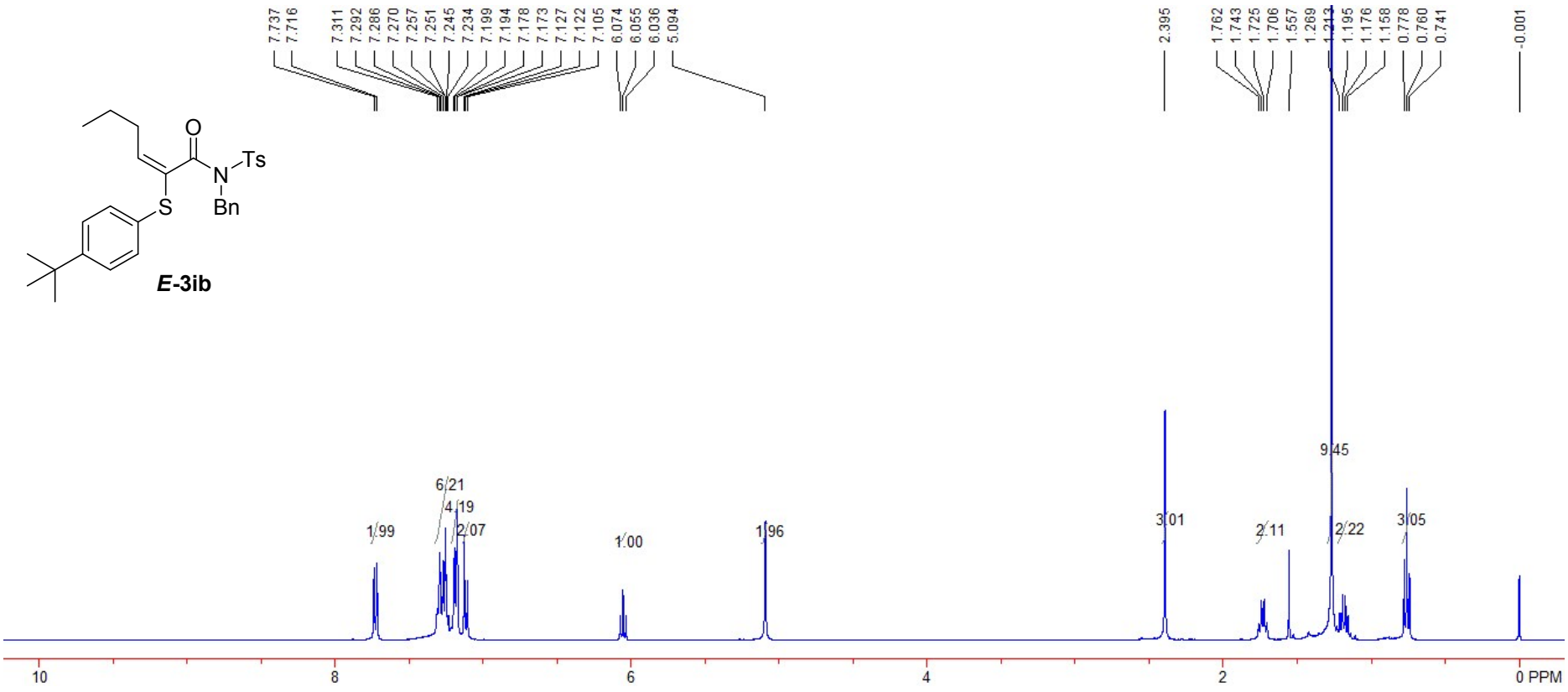
PPM

***E*-3j**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7.245
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7.178
7.173
7.127
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6.074
6.055
6.036
5.094
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1.269
1.213
1.195
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N
Ts
Bn
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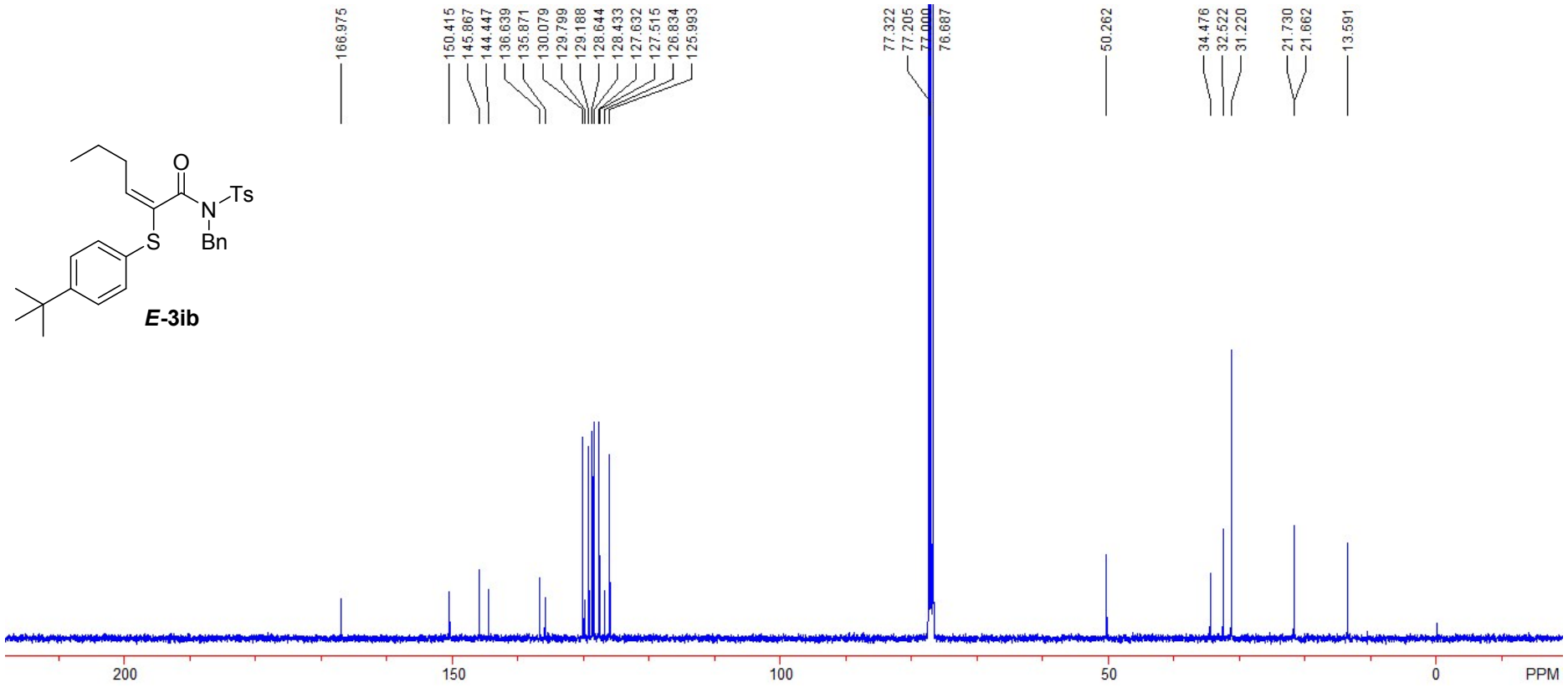
***E*-3ib**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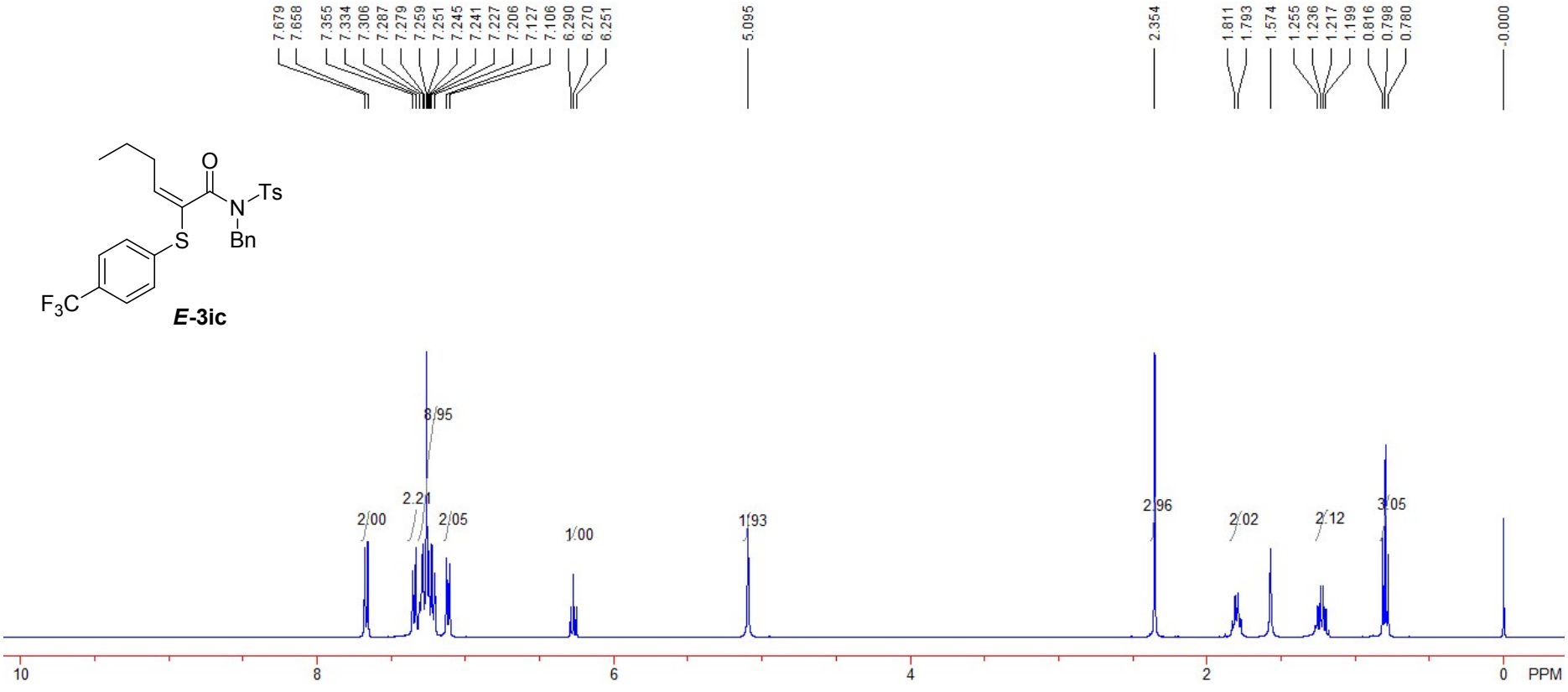
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6.251
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Ts
Bn
S
F3C
E-3ic
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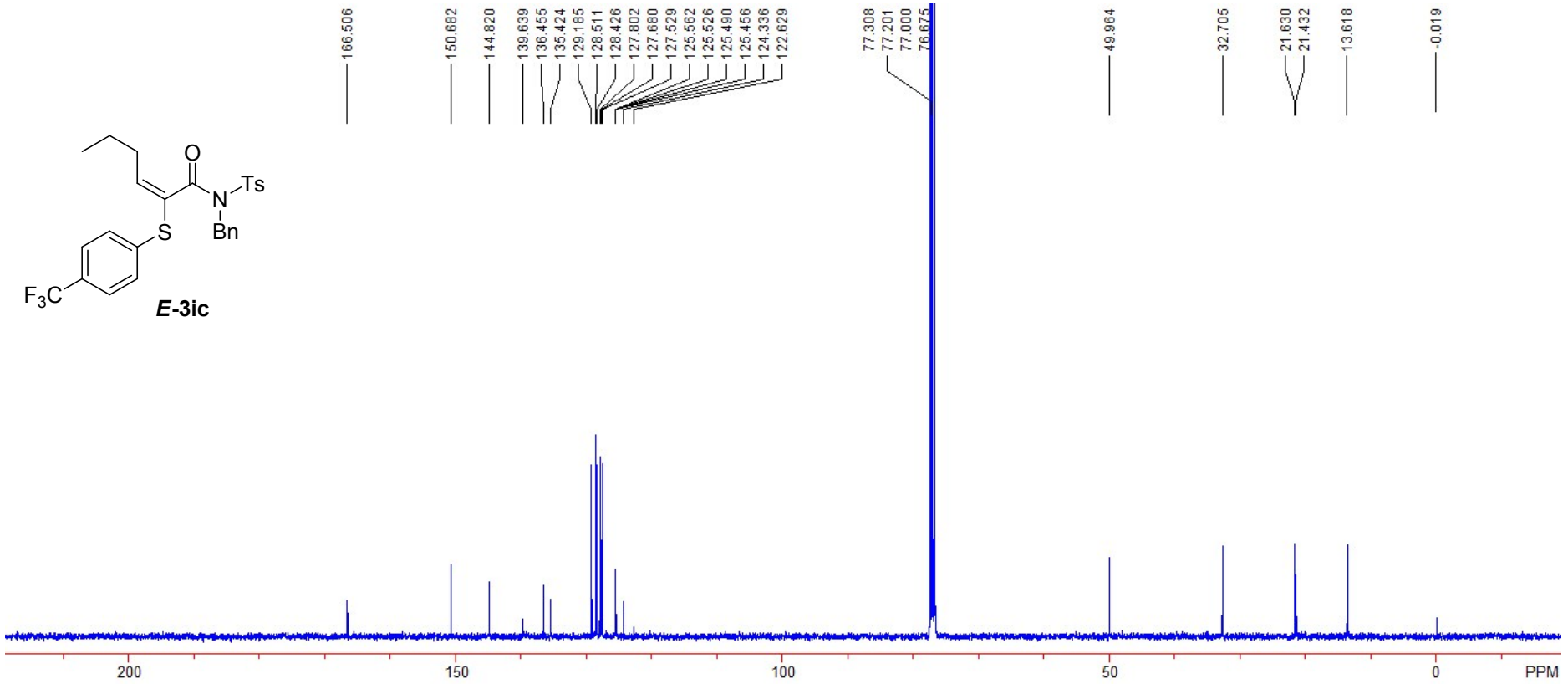
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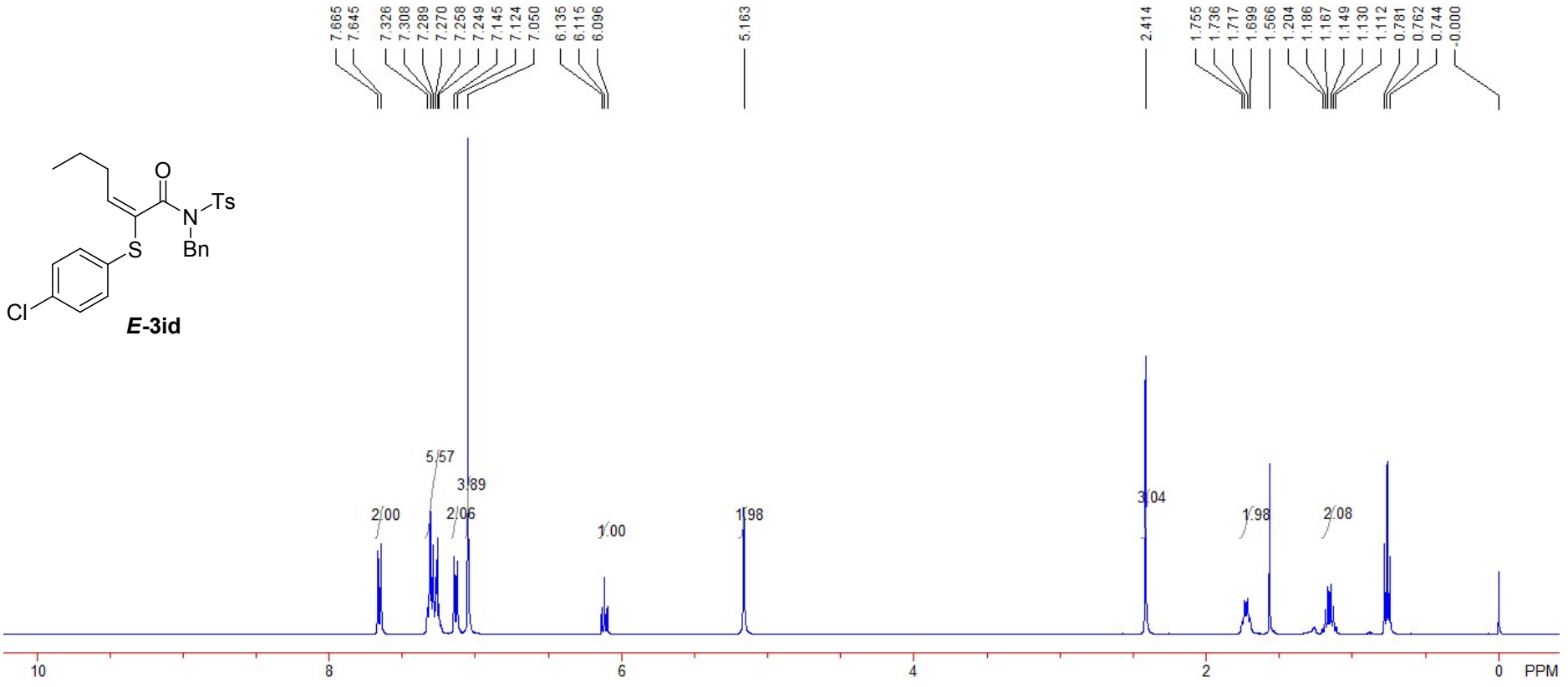
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Bn
S
Cl
E-3id
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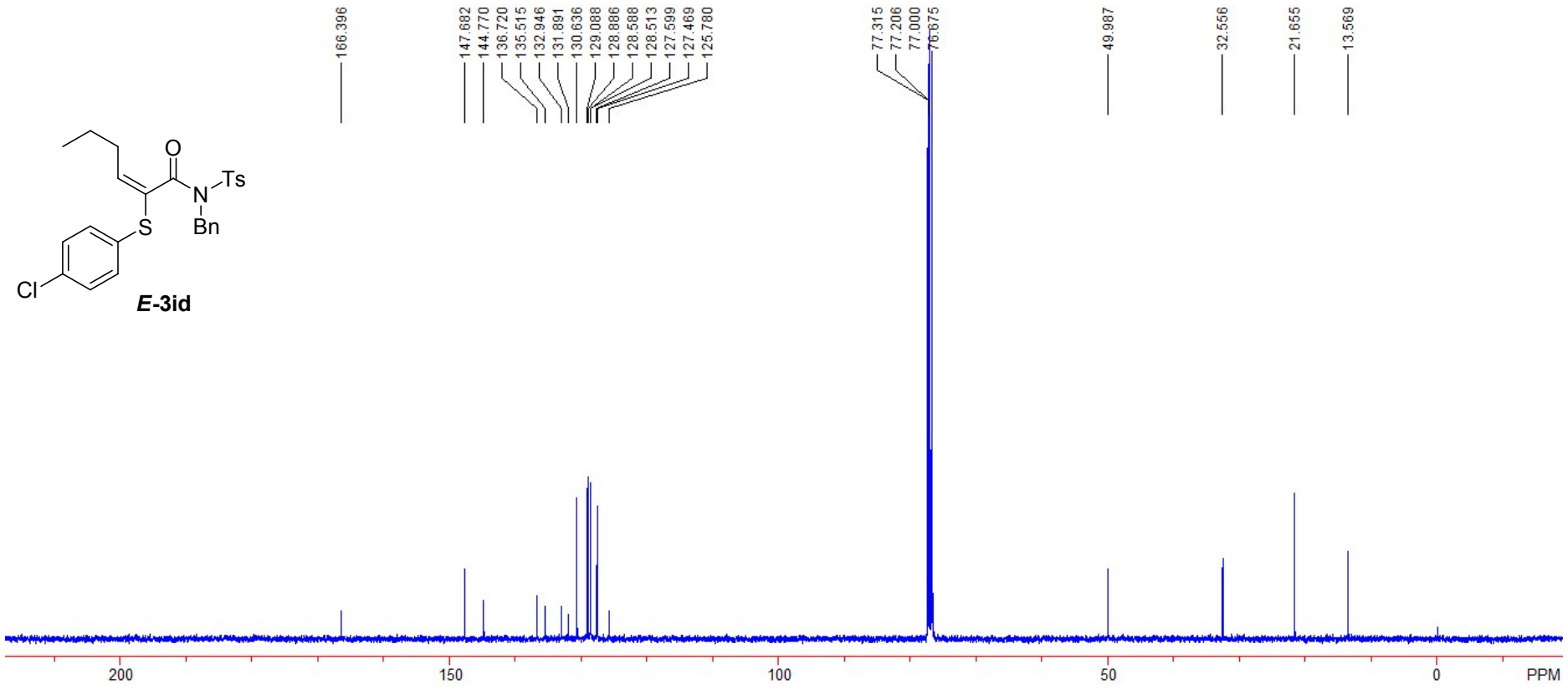
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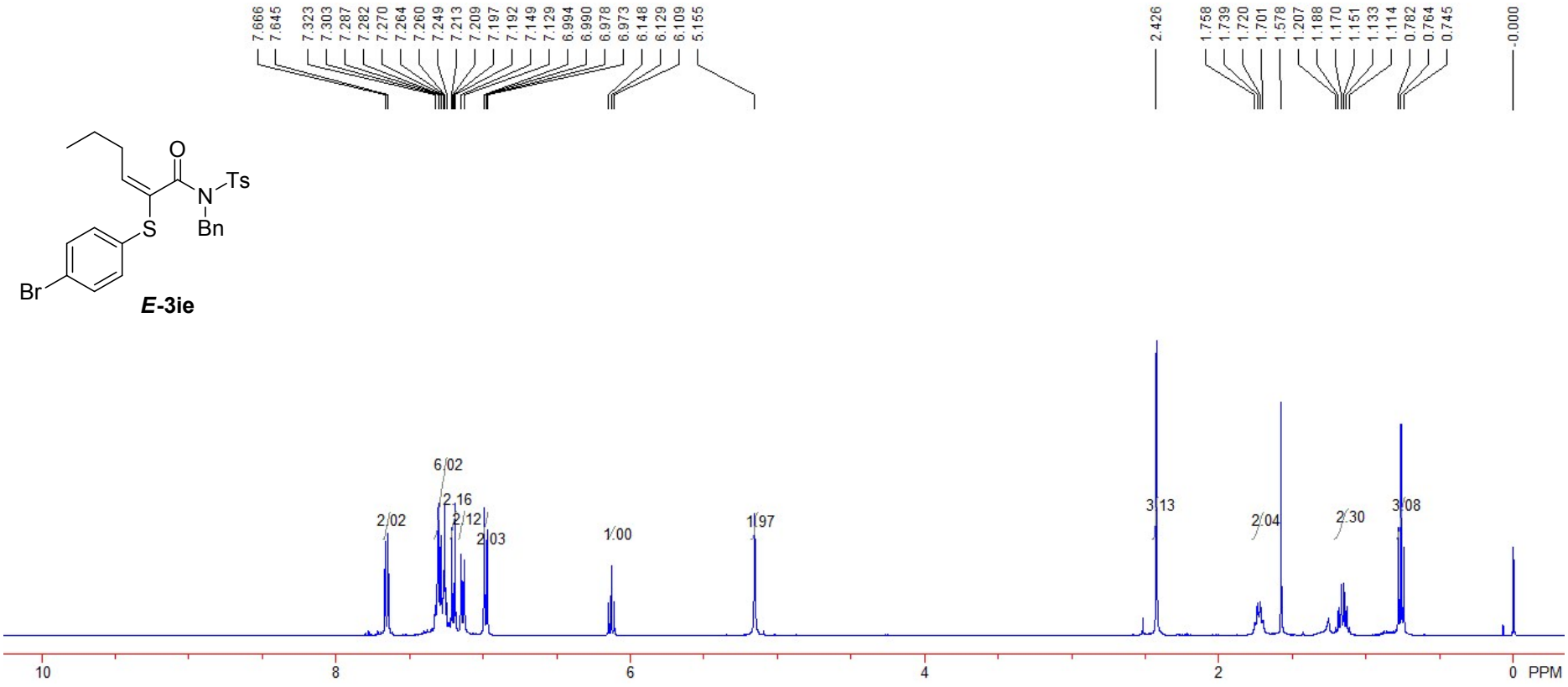
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Bn
S
Br
E-3ie
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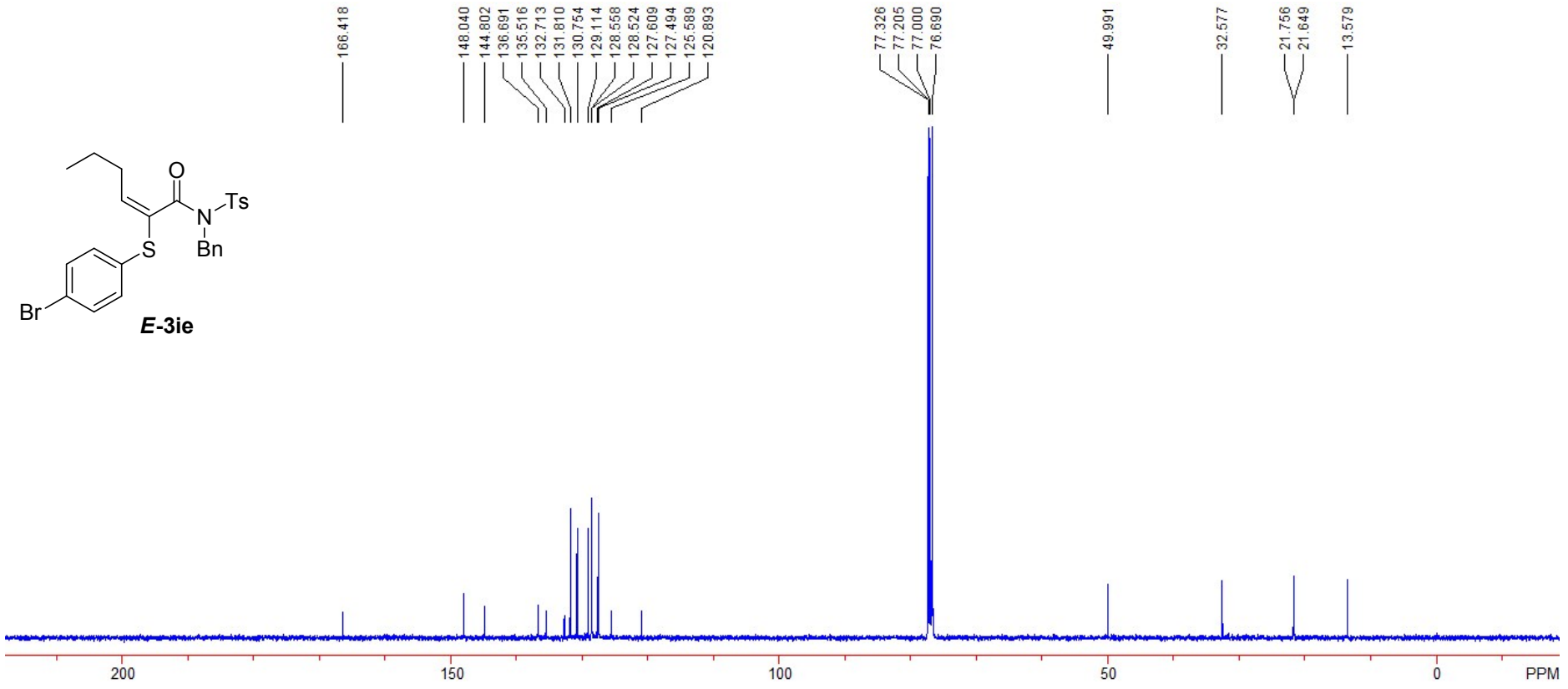
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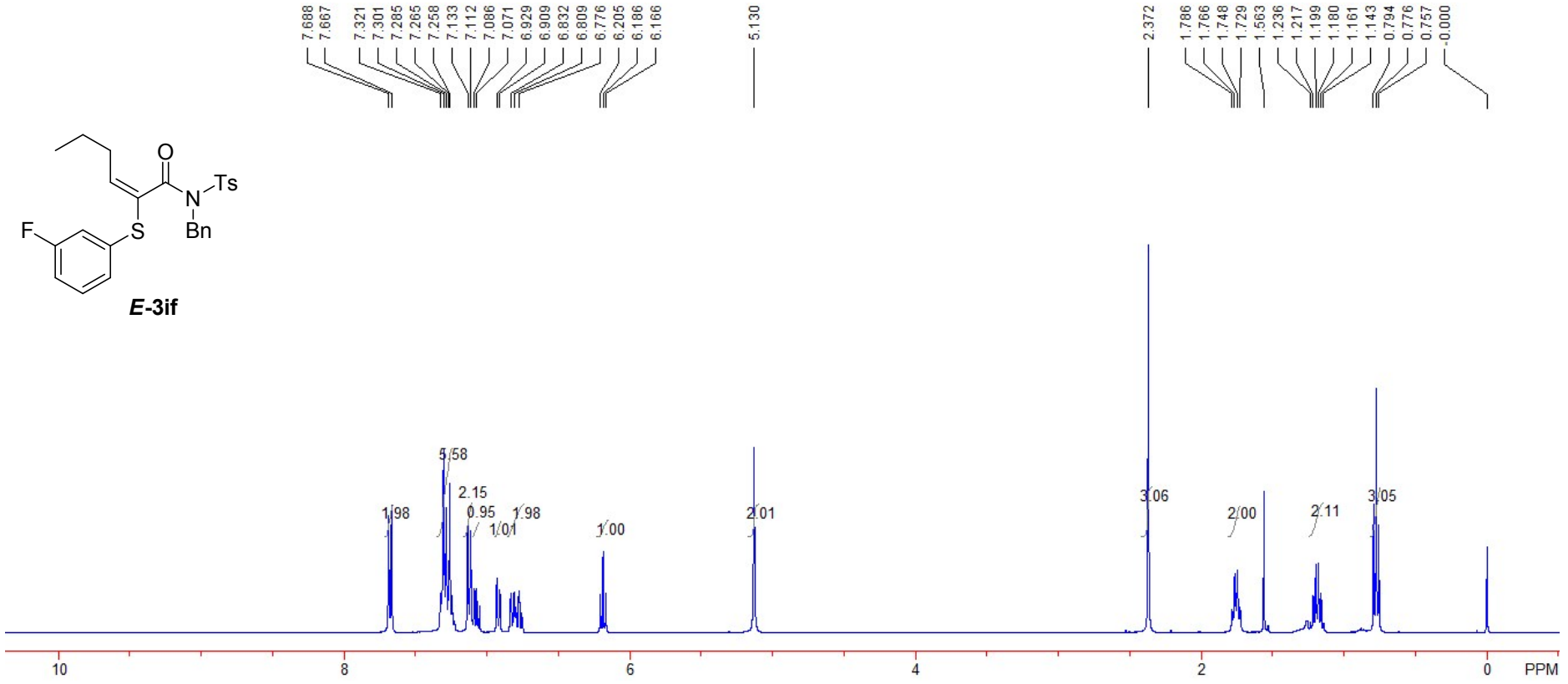
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6.809
6.776
6.205
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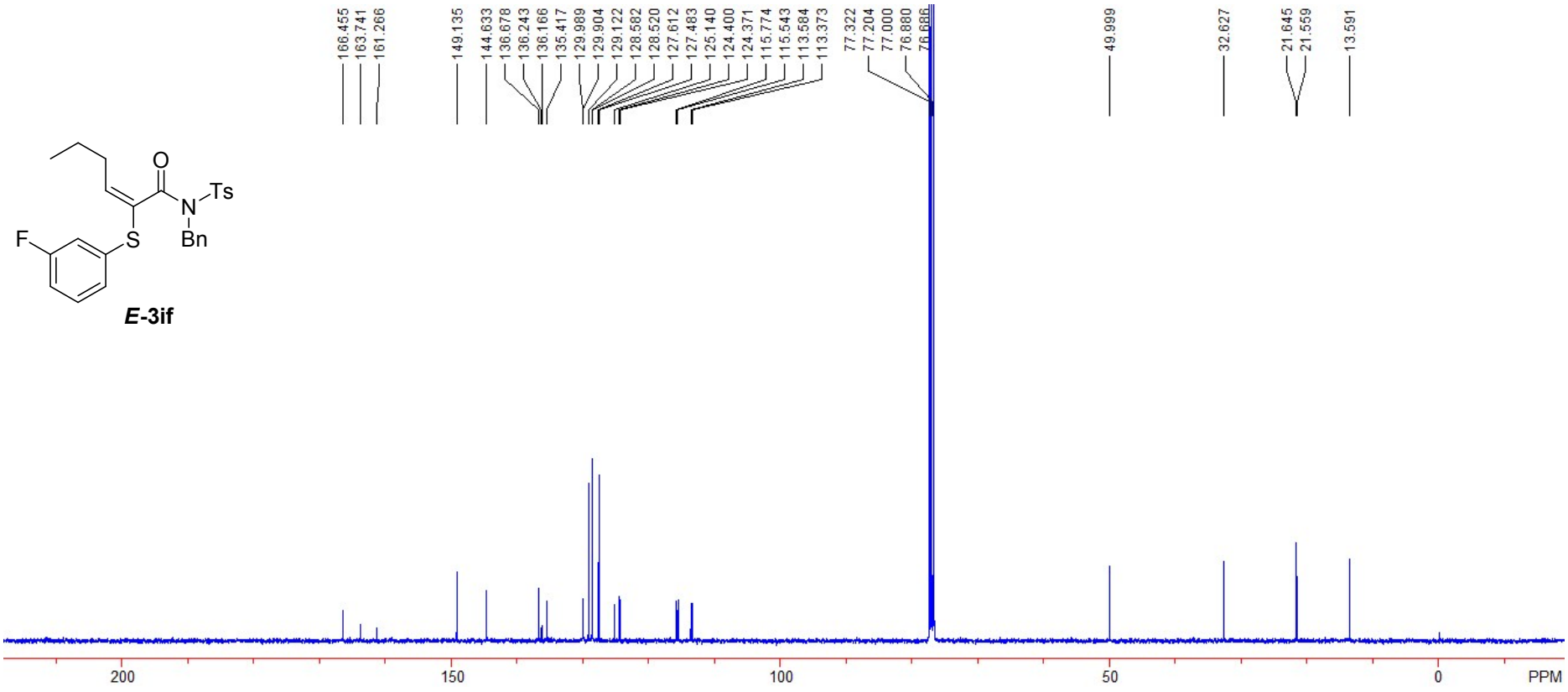
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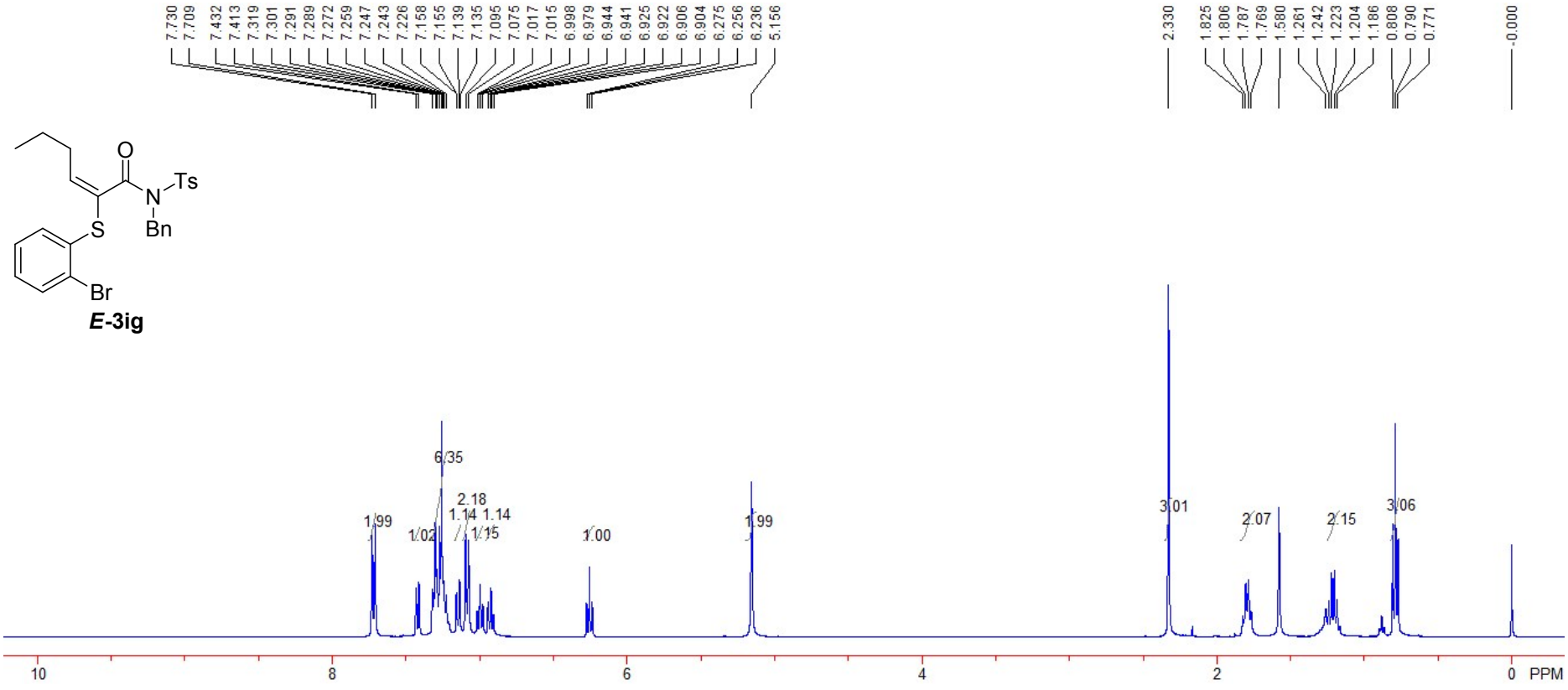
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1.186
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Bn
S
Br
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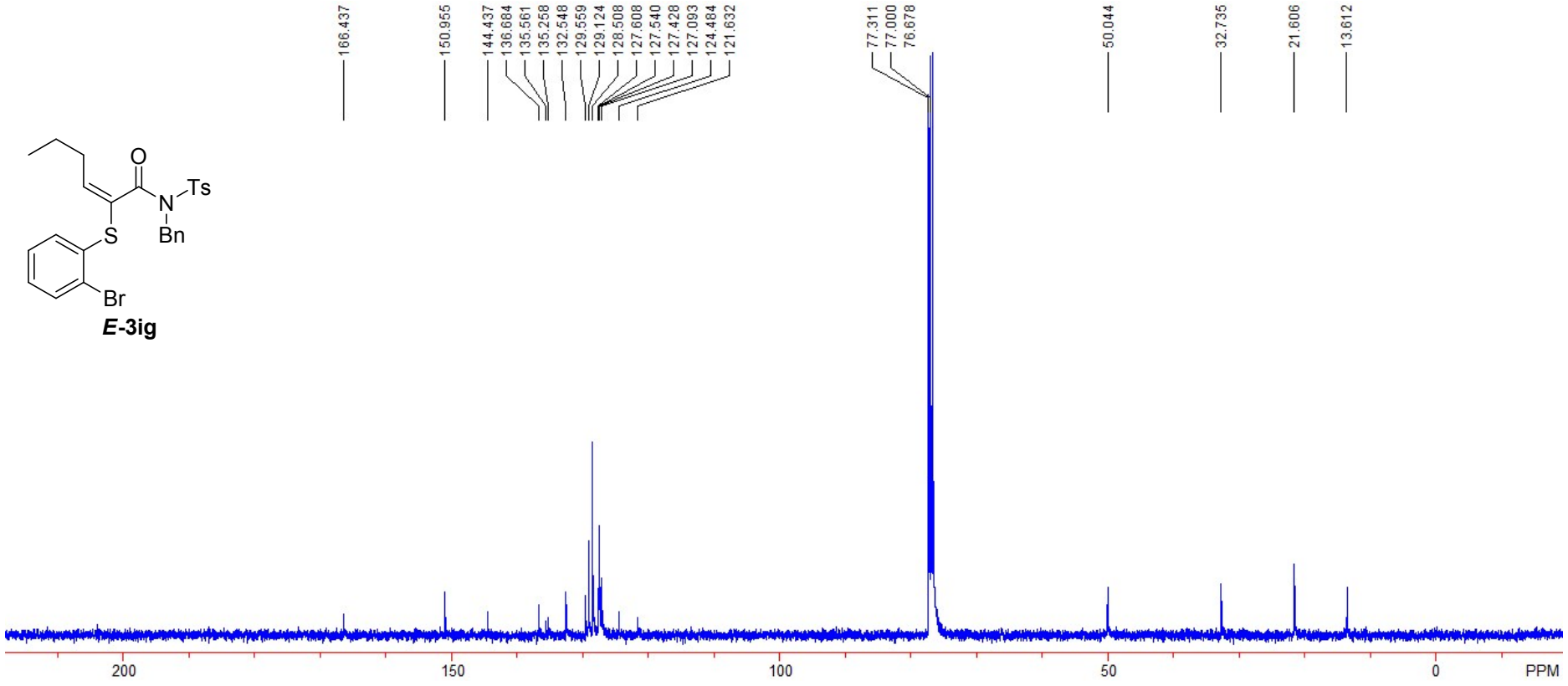
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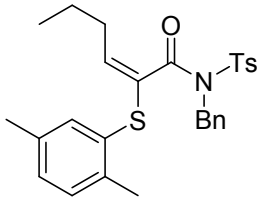
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***E*-3ih**

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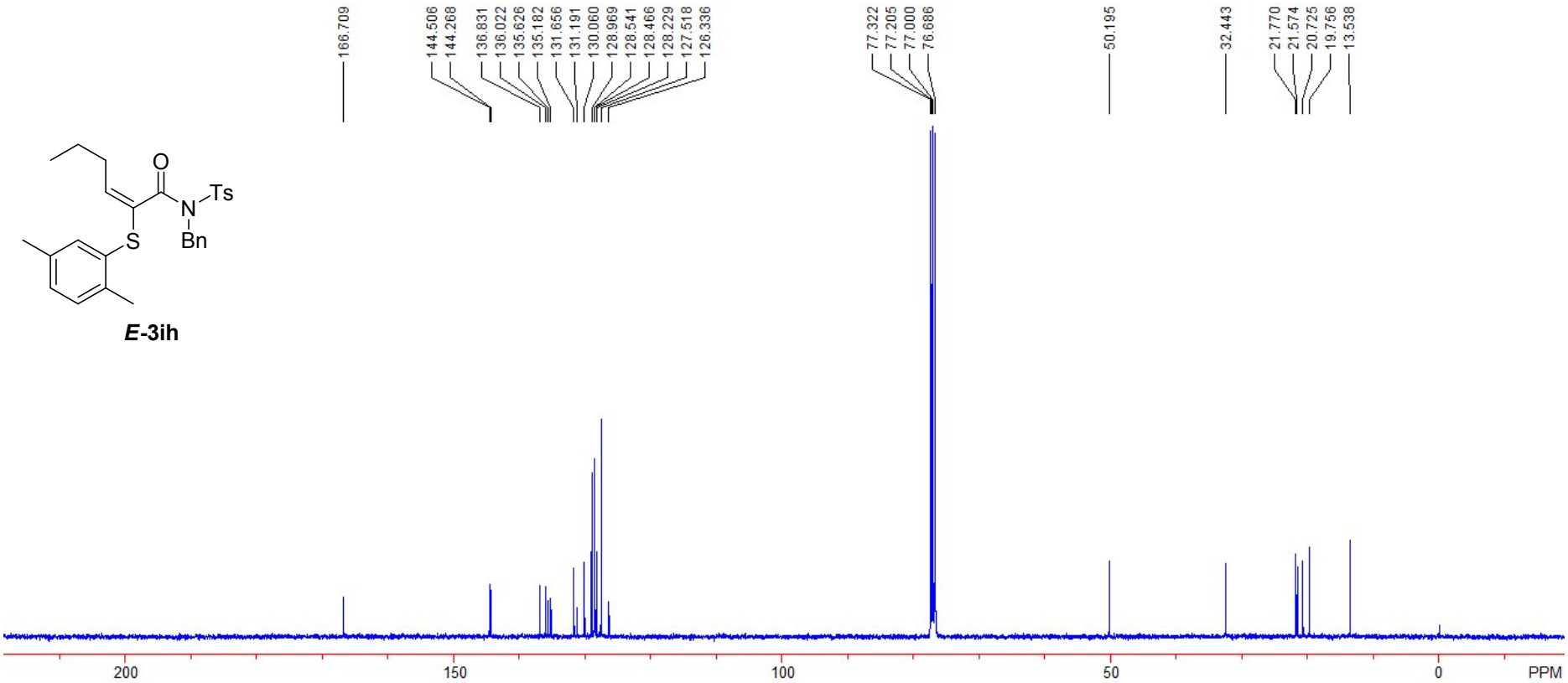
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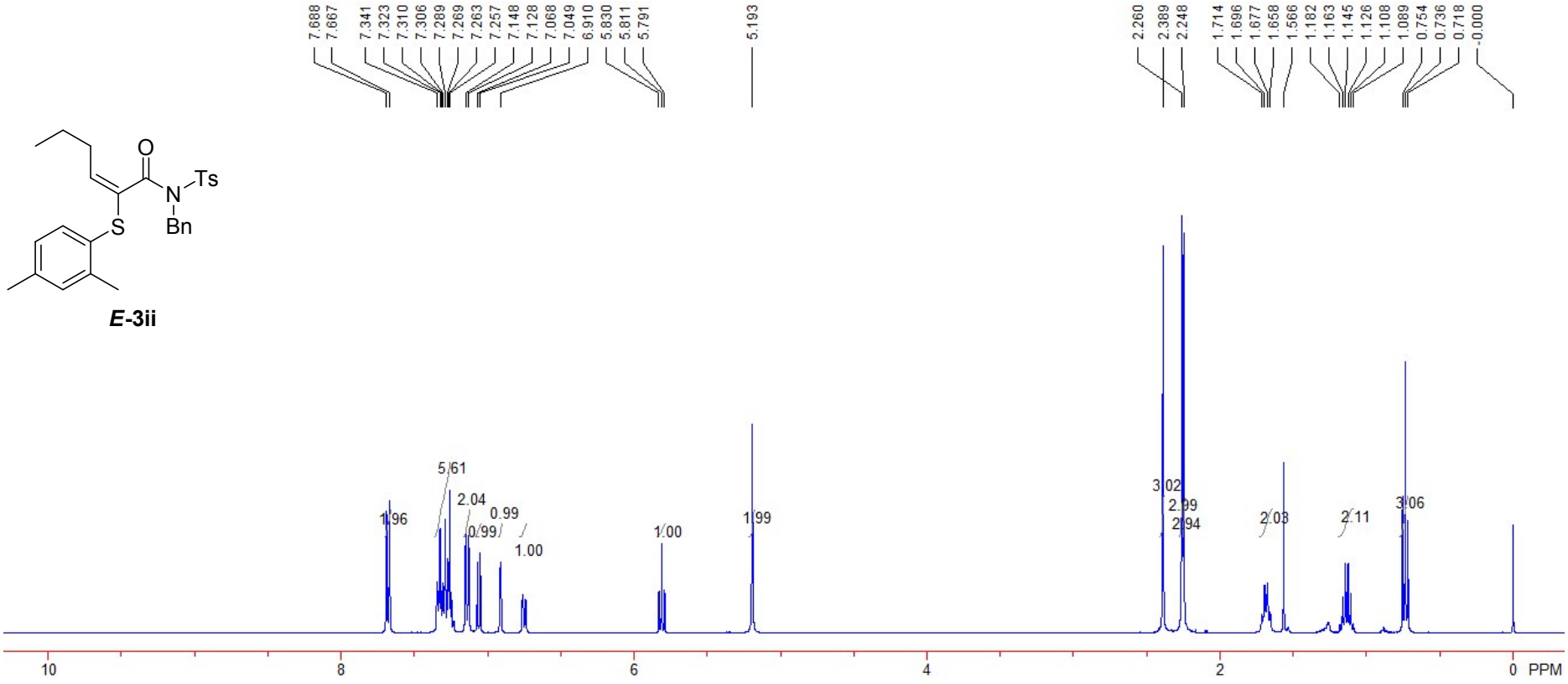
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Bn
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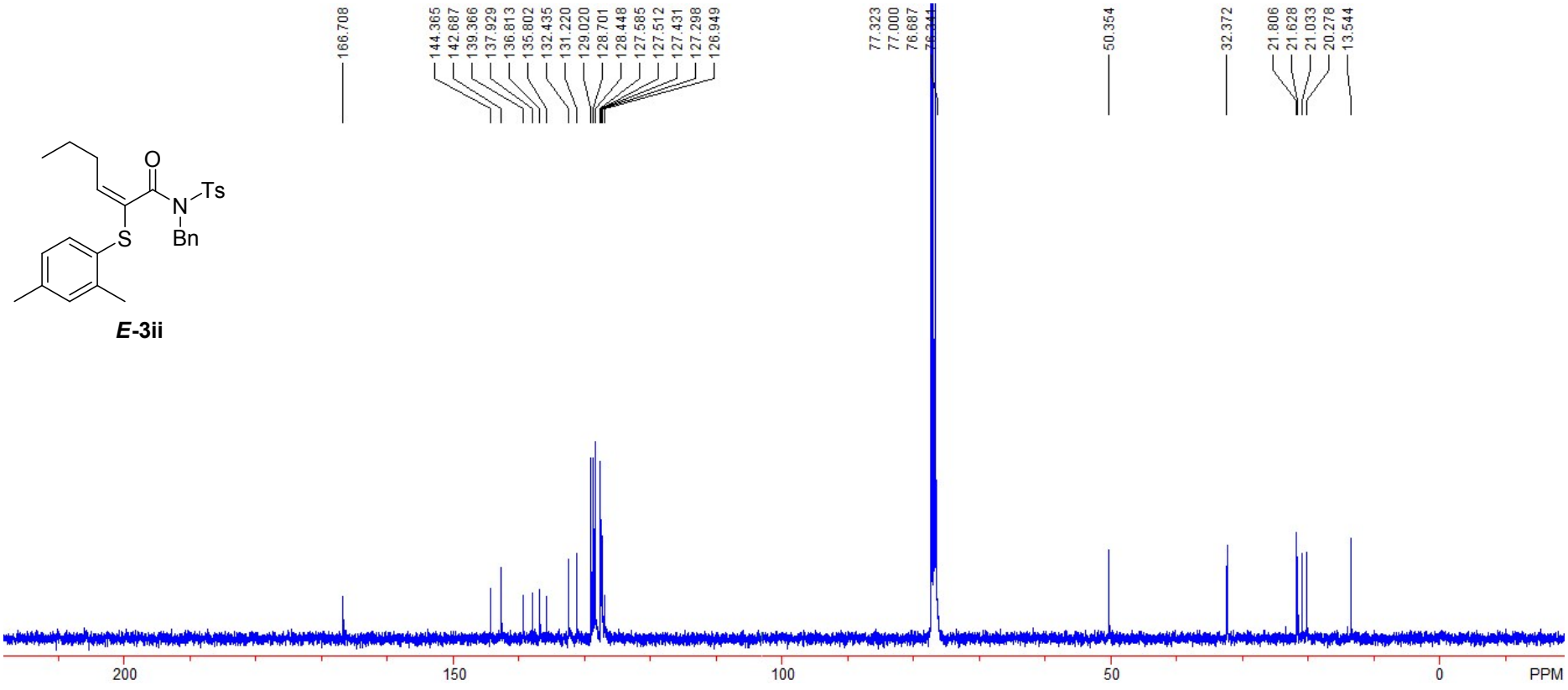
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76.687
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32.372
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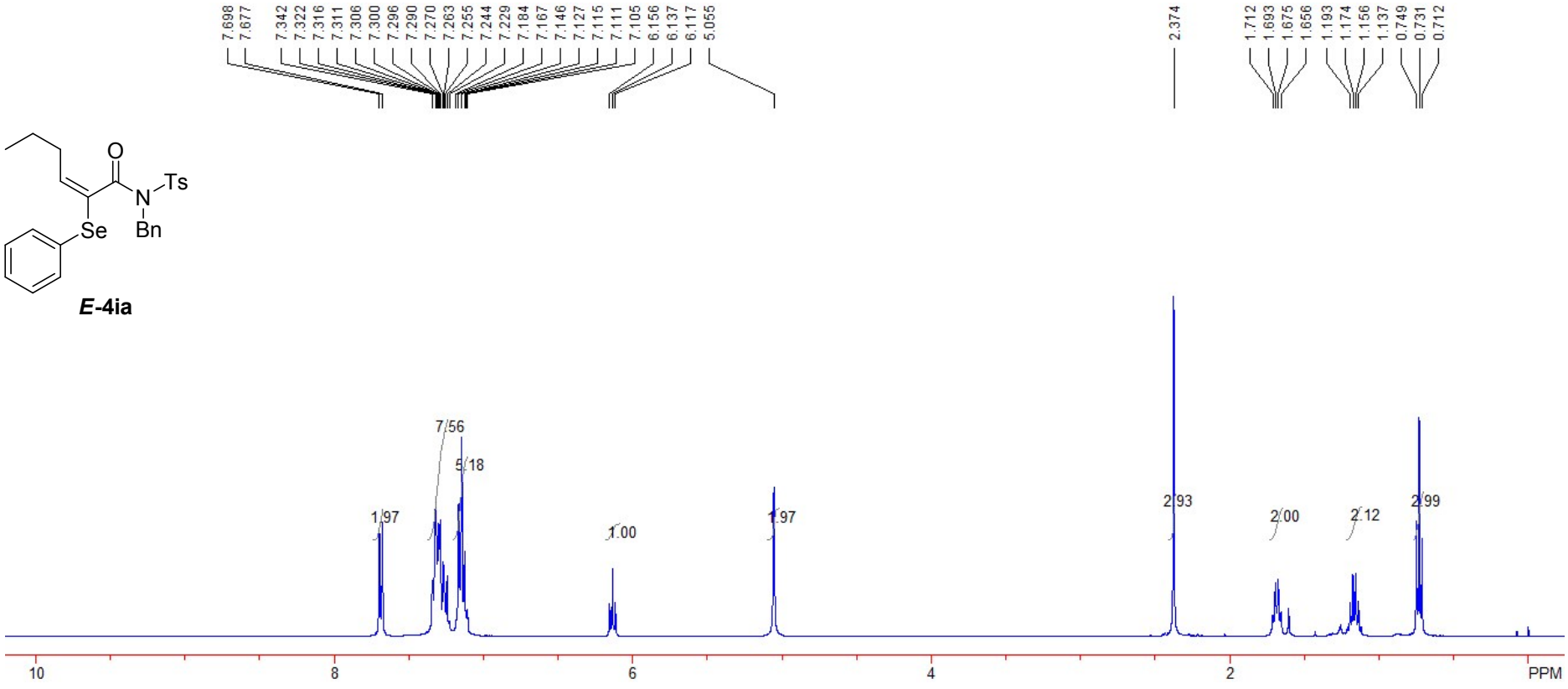
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6.117
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2.374
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Bn
Se
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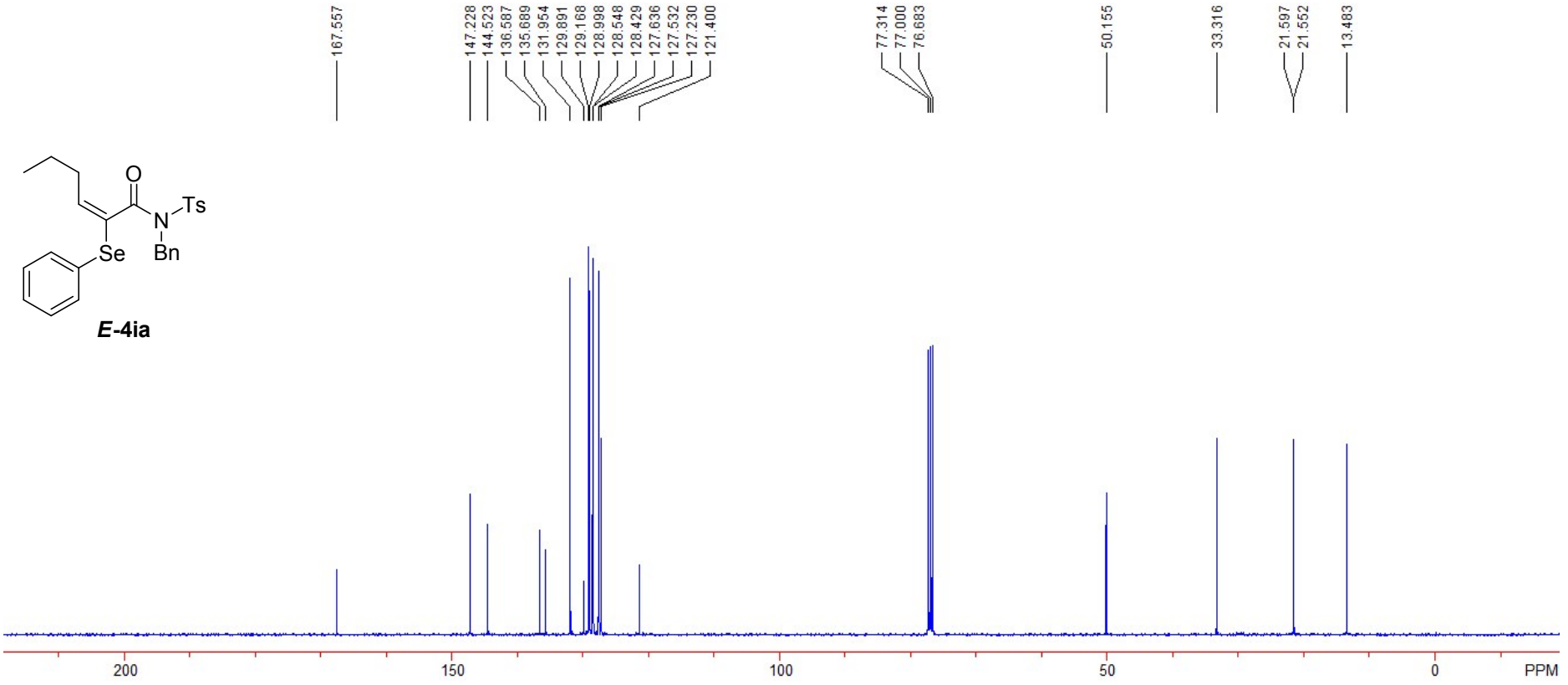
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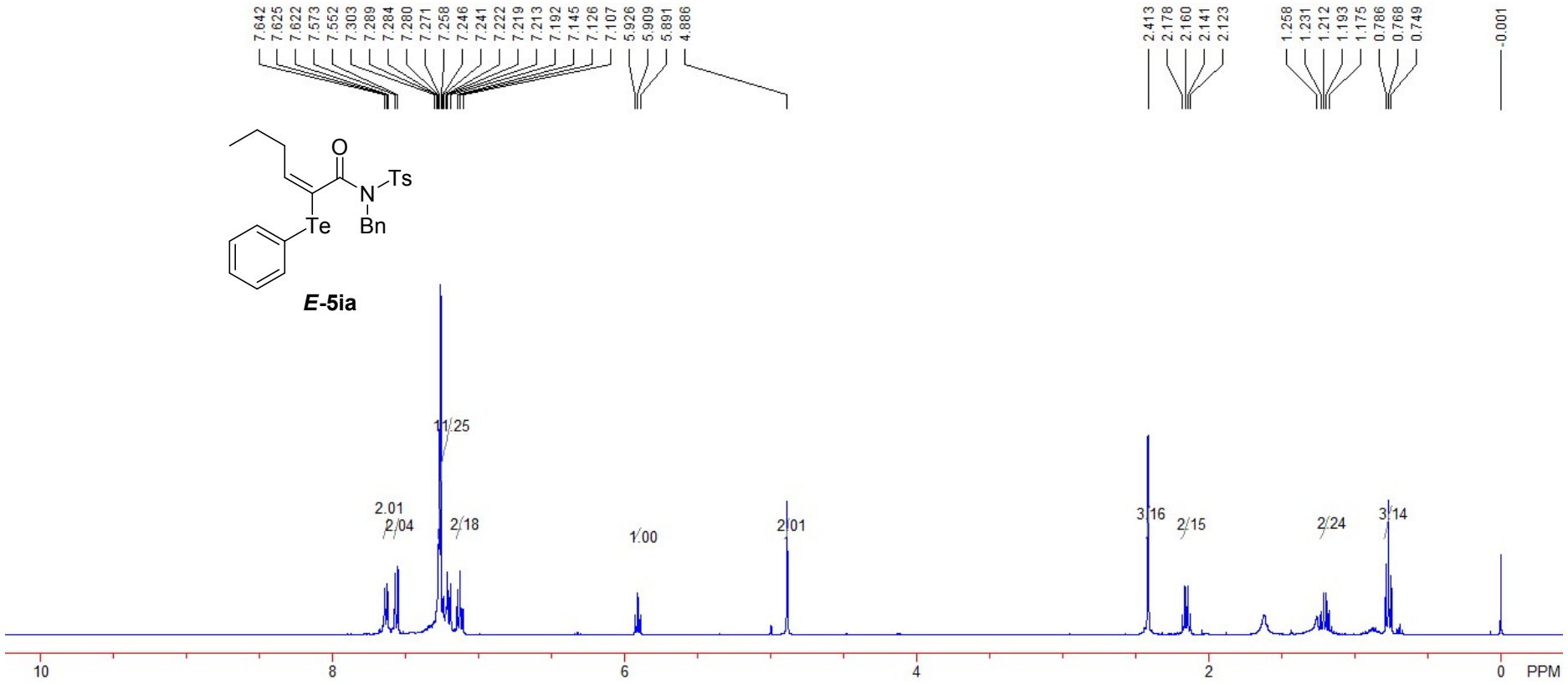
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Ts
N
Te
Bn
E-5ia
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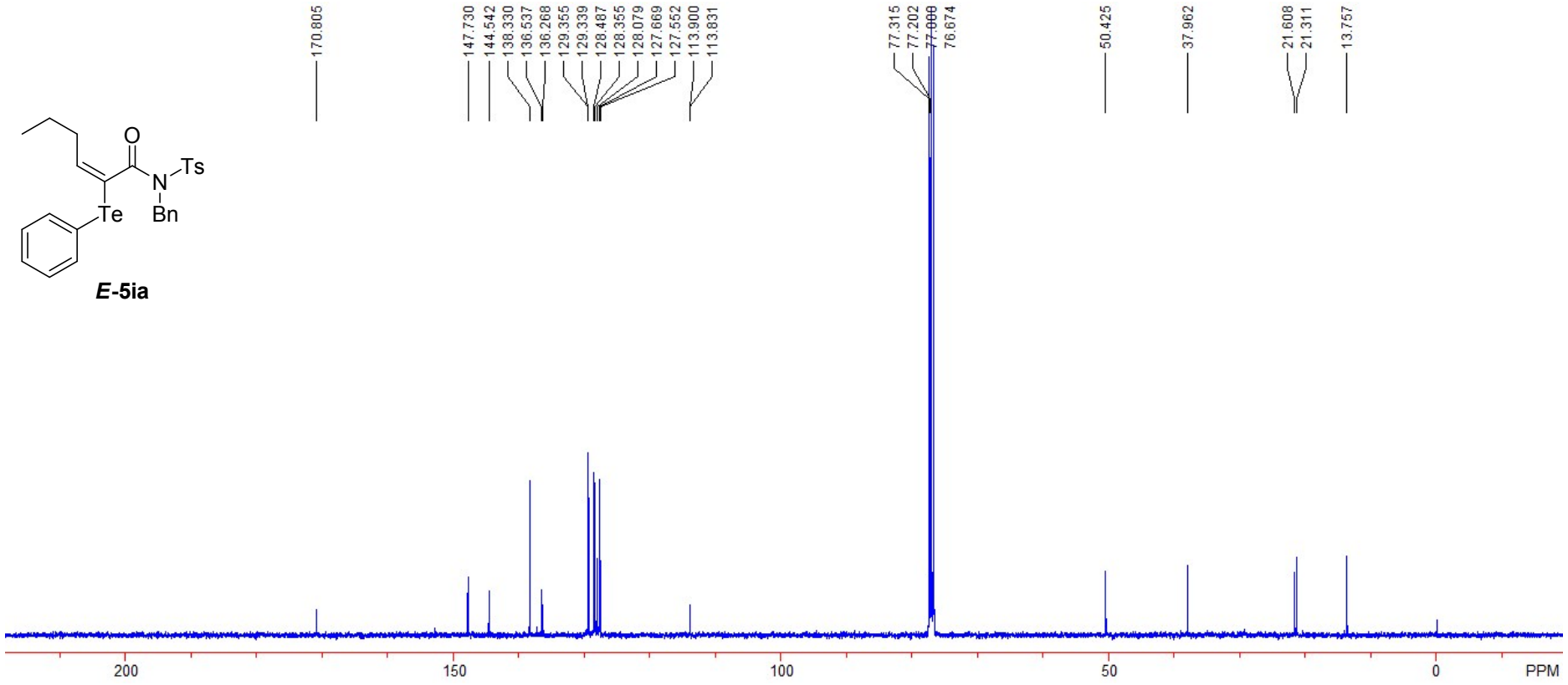
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200
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0
PPM

***E*-5ia**