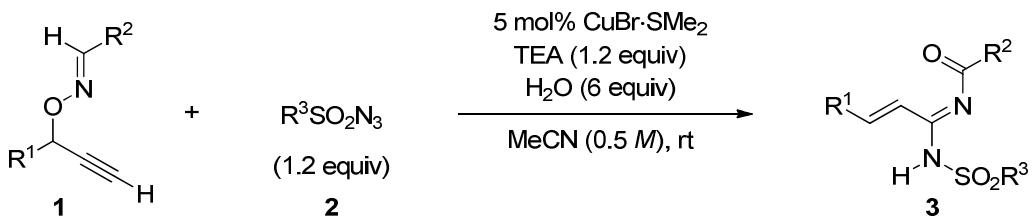


Copper-Catalyzed Cascade Transformation of *O*-Propargylic Oximes with Sulfonyl Azides to α,β -Unsaturated *N*-Acylamidines

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(Supporting Information)



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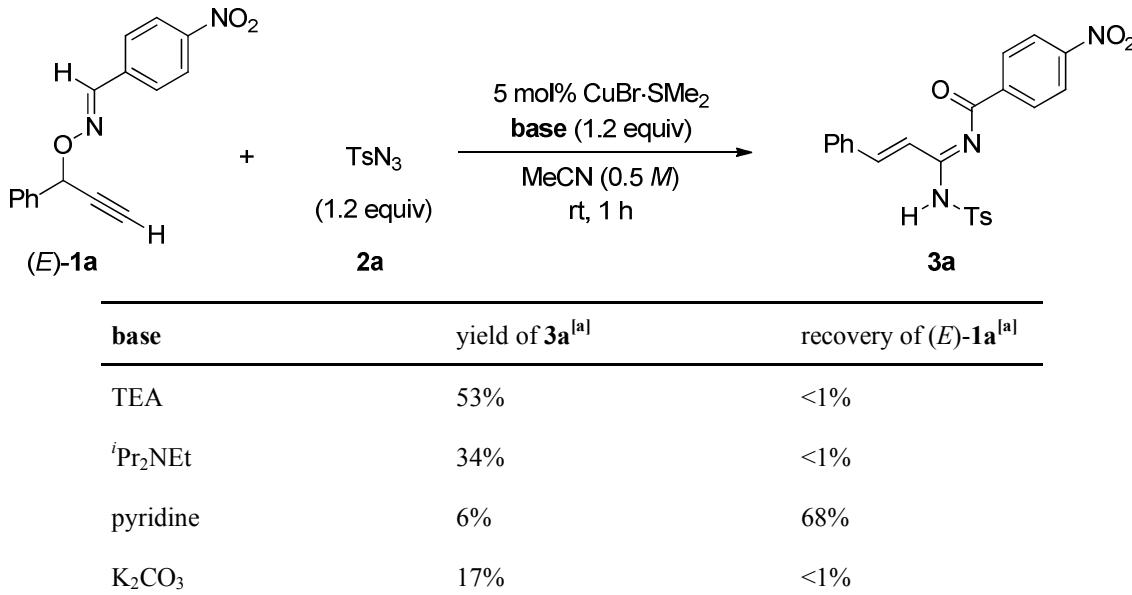
1. General information.

¹H and ¹³C NMR spectra were recorded on a JEOL JNM-ECS (400 MHz for ¹H and 100 MHz for ¹³C) spectrometer. Chemical shifts are reported in ppm relative to CHCl₃ (for ¹H, δ 7.26), and CDCl₃ (for ¹³C, δ 77.00). ¹H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, brs= broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets,) and coupling constants (Hz). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. High-resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T spectrometer at the Research and Analytical Center for Chemistry, Graduate School of Science, Tohoku University. Flash column chromatography was performed with Kanto Chemical silica gel 60 N (spherical, neutral, 40-50 μm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F₂₅₄). All reactions were carried out under argon atmosphere. Anhydrous DMSO, MeCN, THF, toluene, DCM (WAKO) were purchased and used as received.

Substrates **1** were synthesized in accordance with the literature method.^[1]

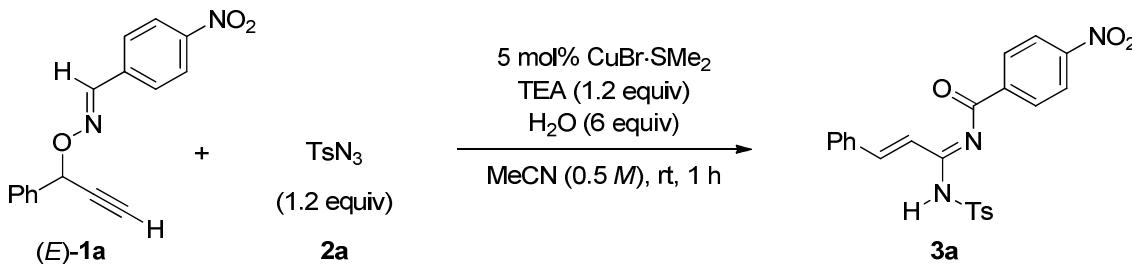
[1] I. Nakamura, T. Araki, D. Zhang, Y. Kudo, E. Kwon, M. Terada, *Org. Lett.*, **2011**, *13*, 3616-3619.

2. Optimization of bases.



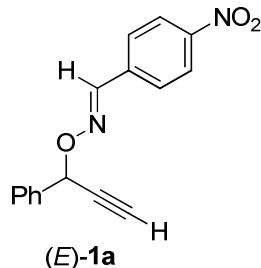
^[a] Yields were determined by ¹H NMR using CH₂Br₂ as an internal standard.

3. General procedure for the synthesis of 3a.



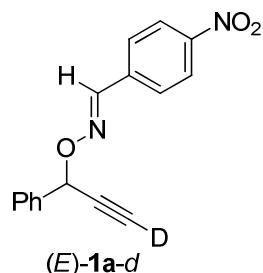
To a mixture of CuBr·SMe₂ (2.1 mg, 0.01 mmol), (E)-1a (56.1 mg, 0.2 mmol), **2a** (47.3 mg, 0.24 mmol), and water (0.022 mL, 1.2 mmol) in acetonitrile (0.4 mL) in a pressure vial was added triethylamine (0.034 mL, 0.24 mmol) at rt (20-25 °C). After stirring the mixture at rt for 1 h, the reaction mixture was filtered through a short pad of silica gel with EtOAc (50 mL). After removing the solvents *in vacuo*, the crude product was purified using flash column chromatography with hexane/EtOAc (6:1) as eluents to afford pure **3a** (white solid, 63.9 mg, 71%).

4. Analytical data of 1.



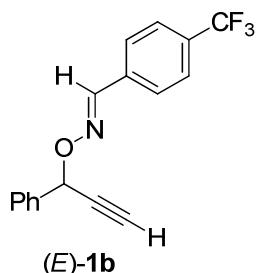
(*E*)-4-nitrobenzaldehyde *O*-(1-phenylprop-2-yn-1-yl) oxime

(E)-1a: ^1H NMR (400 MHz, CDCl_3) δ 2.76 (d, $J = 2.4$ Hz, 1H), 5.99 (d, $J = 2.4$ Hz, 1H), 7.37-7.45 (m, 3H), 7.60-7.62 (m, 2H), 7.75-7.77 (m, 2H), 8.19 (s, 1H), 8.22-8.24 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 76.11, 76.42, 80.87, 123.96, 127.89, 128.02, 128.64, 129.16, 136.41, 137.90, 147.75, 148.48. IR (ATR) 3283, 3278, 3066, 3036, 2123, 1597, 1588, 1516, 1341, 1012, 959, 940 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 303.0746, found 303.0740.



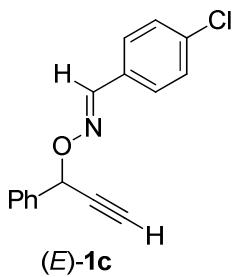
(D content : >99%)

(E)-1a-d: ^1H NMR (400 MHz, CDCl_3) δ 5.99 (s, 1H), 7.37-7.45 (m, 3H), 7.60-7.62 (m, 2H), 7.75-7.77 (m, 2H), 8.19 (s, 1H), 8.22-8.24 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 76.12, 123.96, 127.89, 128.02, 128.64, 129.15, 136.47, 137.93, 147.75, 148.52. IR (ATR) 3065, 2855, 2587, 1983, 1588, 1510, 1350, 953 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{DN}_2\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 304.0808, found 304.0803.



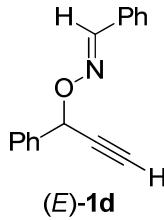
(*E*)-4-(trifluoromethyl)benzaldehyde *O*-(1-phenylprop-2-yn-1-yl) oxime

(E)-1b: ^1H NMR (400 MHz, CDCl_3) δ 2.74 (d, $J = 2.4$ Hz, 1H), 5.97 (d, $J = 2.4$ Hz, 1H), 7.36-7.44 (m, 3H), 7.60-7.62 (m, 4H), 7.69-7.71 (m, 2H), 8.16 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 75.78, 76.23, 123.8 ($q = 272.24$ Hz), 125.56 ($q = 3.82$ Hz), 127.43, 127.99, 128.59, 129.02, 131.60 ($q = 32.67$ Hz), 135.21, 136.66, 148.52. IR (ATR) 3309, 3065, 3036, 2906, 2123, 1321, 1166, 1123, 1107, 1065, 957, 936 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{NNaO}$ ($[\text{M} + \text{Na}]^+$) 326.0769, found 326.0763.



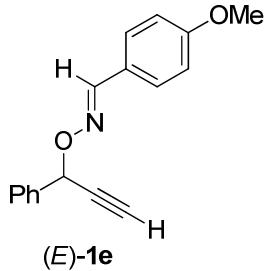
(*E*)-4-chlorobenzaldehyde *O*-(1-phenylprop-2-yn-1-yl) oxime

(*E*)-1c: ^1H NMR (400 MHz, CDCl_3) δ 2.72 (d, $J = 2.4$ Hz, 1H), 5.93 (d, $J = 2.4$ Hz, 1H), 7.32-7.43 (m, 5H), 7.51-7.53 (m, 2H), 7.59-7.61 (m, 2H), 8.09 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 75.54, 76.02, 81.31, 127.96, 128.46, 128.56, 128.94, 129.72, 130.33, 135.97, 136.84, 148.81. IR (ATR) 3294, 3062, 3033, 2904, 2121, 1595, 1491, 1454, 1402, 1272, 1089, 1013, 958, 934 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{12}\text{ClNNaO} ([\text{M} + \text{Na}]^+)$ 292.0505, found 292.0499.



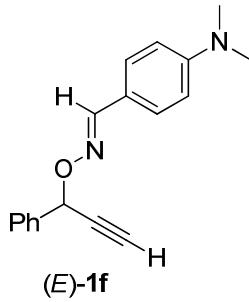
(*E*)-benzaldehyde *O*-(1-phenylprop-2-yn-1-yl) oxime

(*E*)-1d: ^1H NMR (400 MHz, CDCl_3) δ 2.71 (d, $J = 2.4$ Hz, 1H), 5.95 (d, $J = 2.4$ Hz, 1H), 7.34-7.43 (m, 6H), 7.57-7.62 (m, 4H), 8.14 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 75.37, 75.90, 81.43, 127.29, 127.95, 128.53, 128.64, 128.87, 130.08, 131.78, 136.96, 150.01. IR (ATR) 3289, 3064, 3030, 2994, 2900, 2121, 1494, 1454, 1447, 1271, 1022, 957, 950, 930 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{13}\text{NNaO} ([\text{M} + \text{Na}]^+)$ 258.0895, found 258.0889.



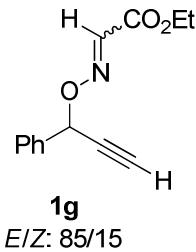
(*E*)-4-methoxybenzaldehyde *O*-(1-phenylprop-2-yn-1-yl) oxime

(*E*)-1e: ^1H NMR (400 MHz, CDCl_3) δ 2.70 (d, $J = 2.4$ Hz, 1H), 5.92 (d, $J = 2.4$ Hz, 1H), 6.86-6.90 (m, 2H), 7.33-7.43 (m, 3H), 7.51-7.60 (m, 2H), 7.61-7.62 (m, 2H), 8.09 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 55.29, 75.17, 75.73, 81.62, 114.10, 124.44, 127.92, 128.51, 128.78, 128.80, 137.14, 149.64, 161.12. IR (ATR) 3287, 3033, 2935, 2837, 2125, 1604, 1512, 1454, 1280, 11170, 1024, 957, 928 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{NNaO}_2 ([\text{M} + \text{Na}]^+)$ 288.1000, found 288.0994.



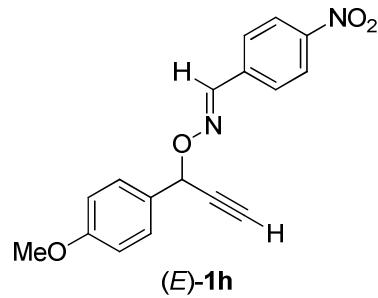
(*E*)-4-(dimethylamino)benzaldehyde *O*-(1-phenylprop-2-yn-1-yl) oxime

(E)-1f: ^1H NMR (400 MHz, CDCl_3) δ 2.69 (d, $J = 2.4$ Hz, 1H), 2.99 (s, 6H), 5.90 (d, $J = 2.4$ Hz, 1H), 6.65-6.68 (m, 2H), 7.33-7.42 (m, 3H), 7.45-7.48 (m, 2H), 7.60-7.63 (m, 2H), 8.07 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 40.19, 74.87, 75.54, 81.86, 111.73, 119.31, 127.92, 128.48, 128.60, 128.69, 137.33, 150.46, 151.56. IR (ATR) 3285, 2891, 2806, 2117, 1610, 1601, 1526, 1361, 1183, 926 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{NaO}$ ($[\text{M} + \text{Na}]^+$) 301.1317, found 301.1311.



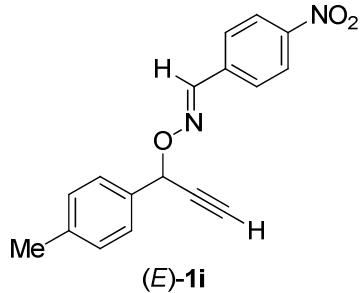
Ethyl 2-(((1-phenylprop-2-yn-1-yl)oxy)imino)acetate

1g (*E/Z* = 85/15): ^1H NMR (400 MHz, CDCl_3) δ 1.29 (t, $J = 7.6$ Hz, 0.69H), 1.33 (t, $J = 7.6$ Hz, 3H), 2.74 (d, $J = 2.4$ Hz, 0.17H), 2.77 (d, $J = 2.4$ Hz, 1H), 4.24 (q, $J = 7.6$ Hz, 0.43H), 4.31 (q, $J = 7.6$ Hz, 2H), 5.93 (d, $J = 2.4$ Hz, 0.17H), 6.04 (d, $J = 2.4$ Hz, 1H), 7.05 (s, 0.16H), 7.35-7.44 (m, 3.97H), 7.54-7.58 (m, 3.57H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.96, 14.06, 61.35, 61.75, 76.29, 76.53, 80.09, 80.46, 127.70, 127.99, 128.44, 128.48, 128.63, 128.90, 129.05, 129.29, 131.22, 135.74, 136.27, 138.84, 142.10, 158.62, 161.54. IR (ATR) 3285, 2985, 2123, 1739, 1721, 1602, 1456, 1321, 1299, 1265, 1195, 1038, 951 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{13}\text{NNaO}_3$ ($[\text{M} + \text{Na}]^+$) 254.0793, found 254.0788.



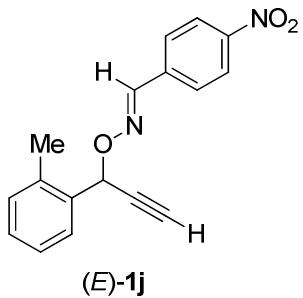
(*E*)-4-nitrobenzaldehyde *O*-(1-(4-methoxyphenyl)prop-2-yn-1-yl) oxime

(E)-1h: ^1H NMR (400 MHz, CDCl_3) δ 2.75 (d, $J = 2.4$ Hz, 1H), 3.83 (s, 3H) 5.93 (d, $J = 2.4$ Hz, 1H), 6.92-6.96 (m, 2H), 7.53-7.56 (m, 2H), 7.75-7.77 (m, 2H), 8.17 (s, 1H), 8.22-8.24 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 55.33, 75.78, 76.17, 81.12, 113.97, 123.97, 127.87, 128.57, 129.60, 138.02, 147.59, 148.46, 160.26. IR (ATR) 3283, 3004, 2956, 2935, 2907, 2836, 2117, 1611, 1586, 1511, 1341, 1247, 1174, 944 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{NaO}_4$ ($[\text{M} + \text{Na}]^+$) 333.0851, found 333.0846.



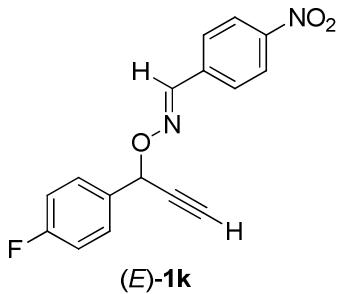
(E)-4-nitrobenzaldehyde *O*-(1-(*p*-tolyl)prop-2-yn-1-yl) oxime

(E)-1i: ^1H NMR (400 MHz, CDCl_3) δ 2.38 (s, 3H) 2.74 (d, $J = 2.4$ Hz, 1H), 5.95 (d, $J = 2.4$ Hz, 1H), 7.22-7.24 (m, 2H), 7.49-7.51 (m, 2H), 7.75-7.77 (m, 2H), 8.17 (s, 1H), 8.22-8.24 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.26, 75.80, 76.20, 81.06, 123.96, 127.88, 128.03, 129.34, 133.51, 137.99, 139.19, 147.64, 148.46. IR (ATR) 3295, 2921, 2121, 1597, 1588, 1516, 1341, 938 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 317.0902, found 317.0897.



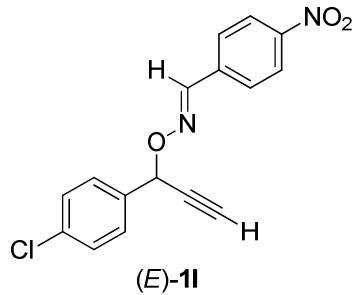
(E)-4-nitrobenzaldehyde *O*-(1-(*o*-tolyl)prop-2-yn-1-yl) oxime

(E)-1j: ^1H NMR (400 MHz, CDCl_3) δ 2.47 (s, 3H) 2.74 (d, $J = 2.4$ Hz, 1H), 6.16 (d, $J = 2.4$ Hz, 1H), 7.22-7.32 (m, 3H), 7.71-7.79 (m, 3H), 8.19 (s, 1H), 8.21-8.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 19.19, 73.98, 76.32, 80.90, 123.96, 126.20, 127.91, 128.27, 129.23, 130.74, 134.27, 136.75, 137.93, 147.67, 148.48. IR (ATR) 3294, 3081, 3027, 2924, 2117, 1597, 1588, 1516, 1341, 949 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 317.0902, found 317.0897.



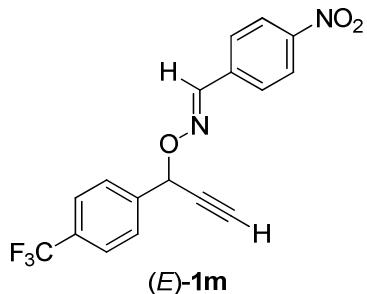
(E)-4-nitrobenzaldehyde *O*-(1-(4-fluorophenyl)prop-2-yn-1-yl) oxime

(E)-1k: ^1H NMR (400 MHz, CDCl_3) δ 2.77 (d, $J = 2.4$ Hz, 1H), 5.96 (d, $J = 2.4$ Hz, 1H), 7.08-7.13 (m, 2H), 7.57-7.61 (m, 2H), 7.74-7.78 (m, 2H), 8.18 (s, 1H), 8.22-8.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 75.31, 76.62, 80.64, 115.57 (d, $J = 22.17$ Hz), 123.98, 127.90, 129.99 (d, $J = 7.6$ Hz), 132.38 (d, $J = 2.8$ Hz), 137.78, 147.87, 148.52, 163.10 (d, $J = 248.31$ Hz). IR (ATR) 3293, 3076, 2127, 1602, 1589, 1519, 1516, 1509, 1342, 1224, 960, 943 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{FN}_2\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 321.0651, found 321.0646.



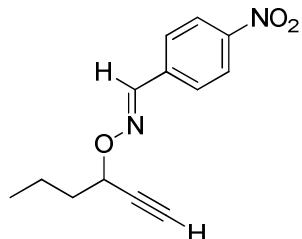
(*E*)-4-nitrobenzaldehyde *O*-(1-(4-chlorophenyl)prop-2-yn-1-yl) oxime

(E)-1l: ^1H NMR (400 MHz, CDCl_3) δ 2.77 (d, $J = 2.4$ Hz, 1H), 5.95 (d, $J = 2.4$ Hz, 1H), 7.38-7.41 (m, 2H), 7.53-7.56 (m, 2H), 7.75-7.77 (m, 2H), 8.18 (s, 1H), 8.22-8.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 75.29, 76.76, 80.41, 124.01, 127.94, 128.84, 129.43, 135.06, 135.12, 137.74, 148.00, 148.58. IR (ATR) 3291, 2127, 1597, 1588, 1519, 1490, 1090, 1016, 960, 939 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{ClN}_2\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 337.0356, found 337.0350.



(*E*)-4-nitrobenzaldehyde *O*-(1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl) oxime

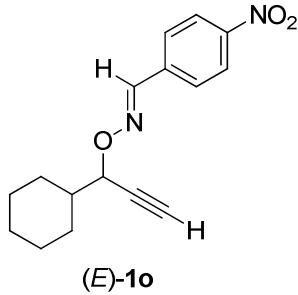
(E)-1m: ^1H NMR (400 MHz, CDCl_3) δ 2.79 (d, $J = 2.4$ Hz, 1H), 6.03 (d, $J = 2.4$ Hz, 1H), 7.67-7.77 (m, 6H), 8.21 (s, 1H), 8.23-8.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 75.22, 77.14, 80.08, 123.89 (q, $J = 272.24$ Hz), 124.03, 125.65 (q, $J = 3.82$ Hz), 127.99, 128.30, 131.19 (q, $J = 32.60$ Hz), 137.61, 140.44, 148.27, 148.64. IR (ATR) 3295, 3115, 3077, 2935, 2855, 2123, 1589, 1519, 1516, 1420, 1342, 1321, 1164, 1123, 1111, 1066, 964, 940 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{11}\text{F}_3\text{N}_2\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 371.0619, found 371.0614.



(E)-1n

(*E*)-4-nitrobenzaldehyde *O*-hex-1-yn-3-yl oxime

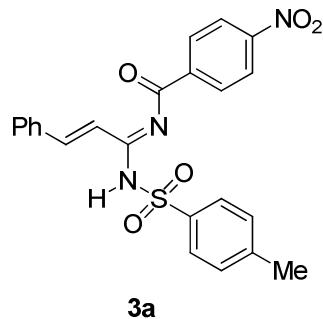
(E)-1n: ^1H NMR (400 MHz, CDCl_3) δ 0.99 (t, $J = 7.6$ Hz, 3H), 1.56 (sext, $J = 7.6$ Hz, 2H), 1.80-1.96 (m, 2H), 2.53 (d, $J = 2.4$ Hz, 1H), 4.93 (td, $J = 7.6, 2.4$ Hz, 1H), 7.76-7.80 (m, 2H), 8.17 (s, 1H), 8.22-8.26 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.73, 18.31, 36.35, 74.13, 74.17, 82.33, 123.97, 127.78, 138.15, 147.13, 148.40. IR (ATR) 3301, 2960, 2935, 2874, 2112, 1520, 1313, 994, 955 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 269.0902, found 269.0897.



(*E*)-4-nitrobenzaldehyde *O*-(1-cyclohexylprop-2-yn-1-yl) oxime

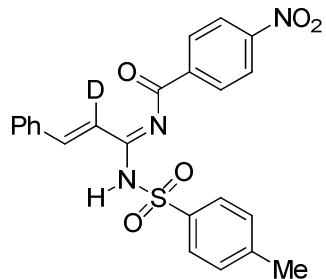
(E)-1o: ^1H NMR (400 MHz, CDCl_3) δ 1.17-1.33 (m, 5H), 1.69-1.93 (m, 6H), 2.54 (d, $J = 2.4$ Hz, 1H), 4.75 (dd, $J = 6.0, 2.4$ Hz, 1H), 7.76-7.79 (m, 2H), 8.17 (s, 1H), 8.22-8.26 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 25.70, 25.79, 26.23, 27.94, 28.69, 41.43, 74.99, 79.09, 81.21, 123.95, 127.75, 138.18, 146.99, 148.36. IR (ATR) 3294, 2926, 2852, 1519, 1341, 1312, 1011, 980, 955 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 309.1215, found 309.1210.

5. Analytical data of 3.



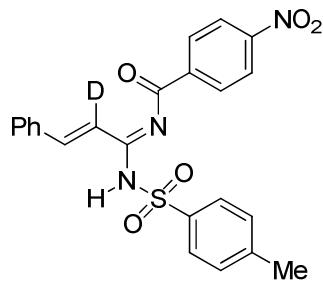
(*E*)-*N*-((*E*)-1-(4-methylphenylsulfonamido)-3-phenylallylidene)-4-nitrobenzamide

3a: (white solid, 63.9 mg, 71%) ^1H NMR (400 MHz, CDCl_3) δ 2.45 (s, 3H), 7.35-7.42 (m, 5H), 7.60-7.63 (m, 2H), 7.90-7.94 (m, 2H), 7.96 (d, $J = 16.4$ Hz, 1H), 7.99 (d, $J = 16.4$ Hz, 1H), 8.20-8.23 (m, 2H), 8.41-8.43 (m, 2H), 11.98 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.65, 118.59, 124.40, 126.81, 128.96, 129.01, 129.26, 129.76, 131.27, 134.37, 137.56, 137.62, 144.34, 147.38, 150.74, 158.68, 162.83. IR (ATR) 3246, 3061, 1718, 1630, 1582, 1528, 1346, 1297, 1243, 1145, 1072, 994, 850 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{NaO}_5\text{S}$ ($[\text{M} + \text{Na}]^+$) 472.0943, found 472.0938.



(D content = 83%)

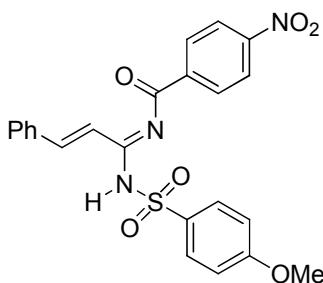
3a-d: (white solid, 66.6 mg, 74%) ^1H NMR (400 MHz, CDCl_3) δ 2.45 (s, 3H), 7.35-7.42 (m, 5H), 7.60-7.63 (m, 2H), 7.90-7.94 (m, 2H), 7.97-7.98 (m, 1.12H), 8.20-8.23 (m, 2H), 8.41-8.43 (m, 2H), 11.97 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.65, 118.65, 124.41, 126.83, 128.99, 129.03, 129.28, 129.79, 131.29, 134.36, 137.59, 137.64, 144.35, 147.32, 150.76, 158.65, 162.85. IR (ATR) 3253, 2931, 2856, 2127, 1712, 1606, 1571, 1522, 1446, 1337, 1279, 1142, 1066, 959 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{DN}_3\text{NaO}_5\text{S}$ ($[\text{M} + \text{Na}]^+$) 473.1006, found 473.1000.



3a-d

(D content = 96%)

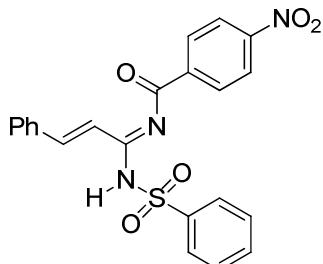
3a-d: (white solid, 64.8 mg, 72%) ^1H NMR (400 MHz, CDCl_3) δ 2.45 (s, 3H), 7.35-7.42 (m, 5H), 7.60-7.63 (m, 2H), 7.90-7.94 (m, 2H), 7.92-7.95 (m, 1.04H), 8.20-8.22 (m, 2H), 8.39-8.41 (m, 2H), 11.96 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.60, 124.35, 126.78, 128.94, 128.99, 129.23, 129.74, 131.23, 134.33, 137.58, 137.60, 144.31, 147.22, 150.72, 158.61, 162.81. IR (ATR) 3252, 3030, 1716, 1609, 1581, 1526, 1337, 1316, 1242, 1145, 1071, 958 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{DN}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 473.1006, found 473.1000.



3b

(*E*)-*N*-((*E*)-1-(4-methoxyphenylsulfonamido)-3-phenylallylidene)-4-nitrobenzamide

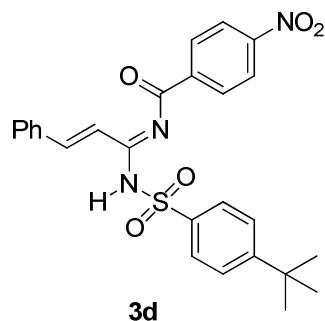
3b: (yellow solid, 70.0 mg, 72%) ^1H NMR (400 MHz, CDCl_3) δ 3.89 (s, 3H), 7.01-7.03 (m, 2H), 7.40-7.42 (m, 3H), 7.60-7.62 (m, 2H), 7.94-7.97 (m, 4H), 8.21-8.23 (m, 2H), 8.41-8.43 (m, 2H), 11.97 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 55.68, 114.33, 118.65, 124.37, 128.93, 129.00, 129.24, 131.20, 132.09, 134.38, 137.65, 147.10, 150.71, 158.27, 162.82, 163.45. IR (ATR) 3251, 3016, 2841, 1716, 1635, 1575, 1526, 1520, 1496, 1346, 1290, 1258, 1243, 1142, 1070, 992 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{NaO}_6\text{S} ([\text{M} + \text{Na}]^+)$ 488.0892, found 488.0887.



3c

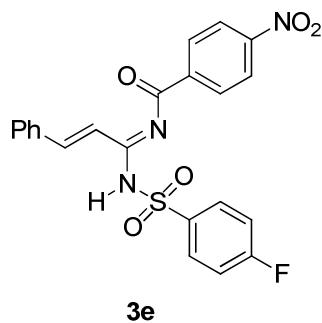
(*E*)-4-nitro-*N*-((*E*)-3-phenyl-1-(phenylsulfonamido)allylidene)benzamide

3c: (white solid, 61.8 mg, 71%) ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.43 (m, 3H), 7.56-7.67 (m, 5H), 7.96-8.05 (m, 4H), 8.21-8.23 (m, 2H), 8.41-8.43 (m, 2H), 11.96 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 118.50, 124.40, 126.74, 129.00, 129.03, 129.15, 129.26, 131.36, 133.32, 134.30, 137.55, 140.49, 147.64, 150.75, 159.03, 162.83. IR (ATR) 3261, 3086, 1717, 1628, 1576, 1526, 1446, 1346, 1232, 1145, 1071, 993, 849 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 458.0787, found 458.0781.



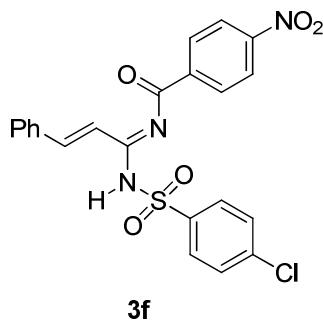
(*E*)-*N*-((*E*)-1-(4-(*tert*-butyl)phenylsulfonamido)-3-phenylallylidene)-4-nitrobenzamide

3d: (white solid, 64.8 mg, 66%) ^1H NMR (400 MHz, CDCl_3) δ 1.35 (s, 9H), 7.41-7.42 (m, 3H), 7.56-7.58 (m, 2H), 7.61-7.63 (m, 2H), 7.93-7.99 (m, 4H), 8.21-8.23 (m, 2H), 8.41-8.43 (m, 2H), 11.99 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 31.02, 35.24, 118.60, 124.37, 126.17, 126.61, 127.36, 128.95, 129.00, 129.24, 131.26, 134.35, 137.60, 147.36, 150.71, 157.24, 158.71, 162.81. IR (ATR) 3257, 2965, 2131, 1718, 1625, 1606, 1593, 1527, 1348, 1284, 1239, 1223 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 514.1413, found 514.1407.



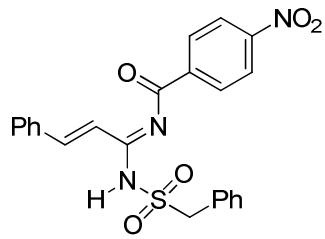
(*E*)-*N*-((*E*)-1-(4-fluorophenylsulfonamido)-3-phenylallylidene)-4-nitrobenzamide

3e: (white solid, 60.7 mg, 67%) ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.27 (m, 2H), 7.41-7.43 (m, 3H), 7.61-7.64 (m, 2H), 7.98-8.07 (m, 4H), 8.20-8.22 (m, 2H), 8.41-8.43 (m, 2H), 11.89 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 116.42 (d, $J = 22.02$ Hz), 118.41, 124.40, 129.03 (d, $J = 2.92$ Hz), 129.23, 129.55, 129.64, 131.43, 134.23, 136.62 (d, $J = 2.81$ Hz), 137.48, 147.76, 150.76, 159.02, 162.79, 165.43 (d, $J = 255.95$ Hz). IR (ATR) 3261, 3111, 1720, 1629, 1580, 1528, 1494, 1347, 1286, 1231, 1145, 1071 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{FN}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 476.0692, found 476.0687.



(*E*)-*N*-((*E*)-1-(4-chlorophenylsulfonamido)-3-phenylallylidene)-4-nitrobenzamide

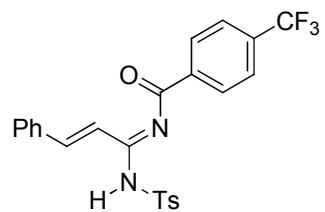
3f: (white solid, 57.2 mg, 61%) ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.45 (m, 3H), 7.53-7.56 (m, 2H), 7.61-7.64 (m, 2H), 7.95-8.04 (m, 4H), 8.20-8.22 (m, 2H), 8.42-8.44 (m, 2H), 11.87 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 118.35, 124.42, 128.25, 129.06, 129.25, 129.45, 131.49, 134.21, 137.45, 139.00, 139.89, 147.99, 150.78, 159.21, 162.79. IR (ATR) 3261, 3106, 3026, 1718, 1628, 1579, 1526, 1447, 1344, 1292, 1230, 1145, 1070, 995, 849 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{ClN}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 492.0397, found 492.0391.



3g

(*E*)-4-nitro-*N*-((*E*)-3-phenyl-1-(phenylmethylsulfonamido)allylidene)benzamide

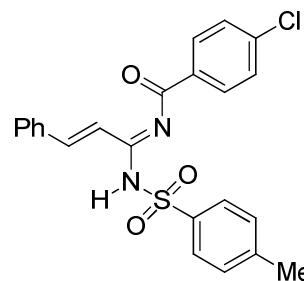
3g: (white solid, 18.0 mg, 20%) ^1H NMR (400 MHz, CDCl_3) δ 4.50 (s, 2H), 7.26-7.29 (m, 4H), 7.42-7.47 (m, 5H), 7.65-7.67 (m, 2H), 7.85-7.93 (m, 3H), 8.10 (d, $J = 15.6$ Hz, 1H), 8.33-8.35 (m, 2H), 11.36 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 60.61, 118.04, 124.19, 128.42, 128.80, 129.12, 129.15, 131.04, 131.53, 134.31, 137.31, 147.71, 150.64, 160.93, 162.38. IR (ATR) 3251, 2925, 2852, 1719, 1630, 1583, 1526, 1448, 1347, 1297, 1088, 996, 848 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{NaO}_5\text{S}$ ($[\text{M} + \text{Na}]^+$) 472.0943, found 472.0938.



3h

(*E*)-*N*-((*E*)-1-(4-methylphenylsulfonamido)-3-phenylallylidene)-4-(trifluoromethyl)benzamide

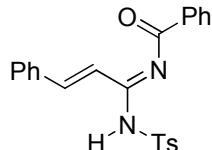
3h: (white solid, 56.7 mg, 60%) ^1H NMR (400 MHz, CDCl_3) δ 2.44 (s, 3H), 7.34-7.41 (m, 5H), 7.60-7.62 (m, 2H), 7.83-7.85 (m, 2H), 7.90-8.03 (m, 4H), 8.15-8.17 (m, 2H), 11.93 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.61, 118.81, 123.32 (q, $J = 273.14$ Hz), 126.31 (q, $J = 2.81$ Hz), 126.77, 128.48, 128.92, 128.96, 129.72, 131.14, 134.42, 135.11 (q, $J = 32.57$ Hz), 135.50, 137.71, 144.20, 147.06, 158.88, 163.51. IR (ATR) 3246, 3021, 2123, 1717, 1630, 1575, 1447, 1356, 1325, 1315, 1297, 1281, 1228, 1208, 1119, 1066, 992, 857 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{F}_3\text{N}_2\text{NaO}_3\text{S}$ ($[\text{M} + \text{Na}]^+$) 495.0966, found 495.0961.



3i

(*E*)-4-chloro-*N*-((*E*)-1-(4-methylphenylsulfonamido)-3-phenylallylidene)benzamide

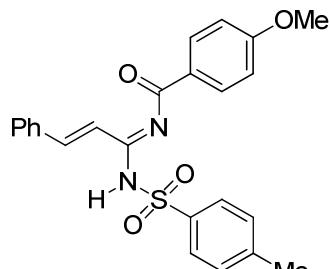
3i: (white solid, 50.8 mg, 58%) ^1H NMR (400 MHz, CDCl_3) δ 2.43 (s, 3H), 7.33-7.39 (m, 5H), 7.52-7.54 (m, 2H), 7.58-7.60 (m, 2H), 7.89-8.02 (m, 6H), 11.82 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.58, 118.99, 126.71, 128.85, 128.91, 129.41, 129.56, 129.67, 130.61, 134.47, 137.85, 140.38, 144.06, 146.74, 159.07, 162.67. IR (ATR) 3256, 3059, 3027, 2126, 1713, 1629, 1580, 1446, 1356, 1283, 1242, 1144, 1070, 992 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{ClN}_2\text{NaO}_3\text{S}$ ($[\text{M} + \text{Na}]^+$) 461.0703, found 461.0697.



3j

(*E*)-*N*-((*E*)-1-(4-methylphenylsulfonamido)-3-phenylallylidene)benzamide

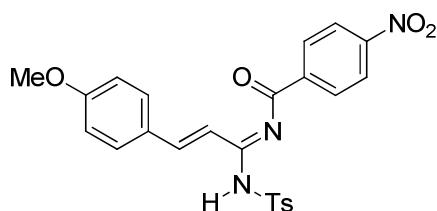
3j: (white solid, 48.5 mg, 60%) ^1H NMR (400 MHz, CDCl_3) δ 2.44 (s, 3H), 7.33-7.40 (m, 5H), 7.56-7.67 (m, 5H), 7.90-8.06 (m, 6H), 11.85 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.58, 119.19, 126.71, 128.01, 128.84, 128.89, 129.25, 129.65, 130.92, 132.18, 133.80, 134.53, 137.94, 143.97, 146.55, 159.26, 164.71. IR (ATR) 3261, 3061, 3036, 2916, 1714, 1635, 1579, 1448, 1356, 1283, 1236, 1145, 1067, 992 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}$ ($[\text{M} + \text{Na}]^+$) 427.1092, found 427.1087.



3k

(*E*)-4-methoxy-*N*-((*E*)-1-(4-methylphenylsulfonamido)-3-phenylallylidene)benzamide

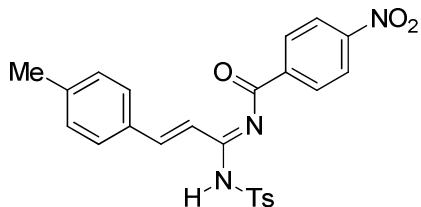
3k: (white solid, 20.0 mg, 23%) ^1H NMR (400 MHz, CDCl_3) δ 2.43 (s, 3H), 3.91 (s, 3H), 7.03-7.05 (m, 2H), 7.32-7.39 (m, 5H), 7.59-7.61 (m, 2H), 7.89-7.94 (m, 3H), 8.01-8.05 (m, 3H), 11.77 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.59, 55.61, 114.52, 119.37, 124.37, 126.69, 128.83, 128.88, 129.64, 130.31, 130.84, 134.65, 138.13, 143.89, 146.31, 159.48, 164.09, 164.11. IR (ATR) 3298, 3258, 3025, 2930, 2840, 1706, 1628, 1600, 1515, 1357, 1281, 1210, 1174, 1068, 989 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}_4\text{S}$ ($[\text{M} + \text{Na}]^+$) 457.1198, found 457.1192.



3l

(*E*)-*N*-((*E*)-3-(4-methoxyphenyl)-1-(4-methylphenylsulfonamido)allylidene)-4-nitrobenzamide

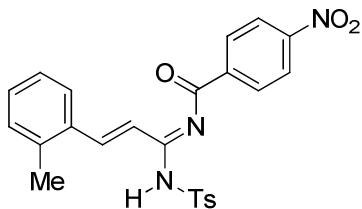
3l: (yellow solid, 53.7 mg, 53%) ^1H NMR (400 MHz, CDCl_3) δ 2.44 (s, 3H), 3.86 (s, 3H), 7.34-7.36 (m, 2H), 7.57-7.59 (m, 2H), 7.86-7.91 (m, 3H), 7.99 (d, $J = 15.2$ Hz), 8.20-8.23 (m, 2H), 8.40-8.42 (m, 2H), 11.98 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.62, 55.45, 114.51, 115.70, 124.35, 126.69, 127.20, 129.21, 129.71, 131.03, 137.78, 137.86, 144.11, 147.77, 150.67, 158.97, 162.40, 162.85. IR (ATR) 3256, 2926, 2836, 1718, 1624, 1604, 1579, 1569, 1559, 1540, 1511, 1422, 1345, 1244, 1171, 1145, 1071 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{NaO}_6\text{S}$ ($[\text{M} + \text{Na}]^+$) 502.1049, found 502.1043.



3m

(*E*)-*N*-((*E*)-1-(4-methylphenylsulfonamido)-3-(*p*-tolyl)allylidene)-4-nitrobenzamide

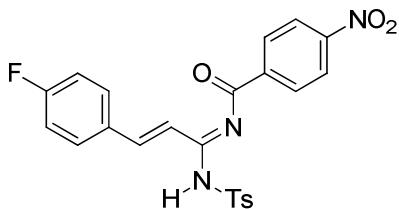
3m: (yellow solid, 64.8 mg, 70%) ^1H NMR (400 MHz, CDCl_3) δ 2.39 (s, 3H), 2.45 (s, 3H), 7.20-7.22 (m, 2H), 7.34-7.36 (m, 2H), 7.50-7.52 (m, 2H), 7.89-7.96 (m, 4H), 8.20-8.22 (m, 2H), 8.40-8.42 (m, 2H), 11.97 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.61, 117.33, 124.35, 126.75, 129.05, 129.22, 129.73, 129.76, 131.67, 137.68, 142.12, 144.22, 147.73, 150.68, 158.85, 162.83. IR (ATR) 3251, 2911, 2871, 1716, 1628, 1576, 1526, 1344, 1282, 1243, 1181, 1145, 1071 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 486.1100, found 486.1094.



3n

(*E*)-*N*-((*E*)-1-(4-methylphenylsulfonamido)-3-(*o*-tolyl)allylidene)-4-nitrobenzamide

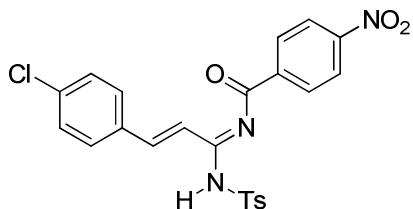
3n: (white solid, 58.4 mg, 63%) ^1H NMR (400 MHz, CDCl_3) δ 2.45 (s, 6H), 7.20-7.23 (m, 2H), 7.30-7.37 (m, 3H), 7.66-7.69 (m, 1H), 7.86-7.92 (m, 3H), 8.20-8.26 (m, 3H), 8.41-8.43 (m, 2H), 11.96 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 19.90, 21.63, 119.59, 124.37, 126.49, 126.74, 127.38, 129.25, 129.73, 130.98, 133.28, 137.64, 138.59, 144.27, 144.83, 150.71, 158.76, 162.81. IR (ATR) 3246, 3031, 1718, 1624, 1579, 1525, 1458, 1343, 1285, 1235, 1144, 1070, 994, 849 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 486.1100, found 486.1094.



3o

(*E*)-*N*-((*E*)-3-(4-fluorophenyl)-1-(4-methylphenylsulfonamido)allylidene)-4-nitrobenzamide

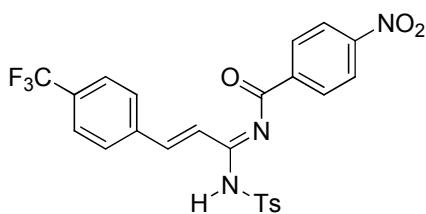
3o: (white solid, 67.3 mg, 72%) ^1H NMR (400 MHz, CDCl_3) δ 2.45 (s, 3H), 7.08-7.12 (m, 2H), 7.35-7.37 (m, 2H), 7.59-7.63 (m, 2H), 7.89-7.92 (m, 4H), 8.20-8.22 (m, 2H), 8.41-8.43 (m, 2H), 11.98 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.62, 116.26 (d, $J = 22.02$ Hz), 118.31 (d, $J = 2.81$ Hz), 124.39, 126.80, 129.24, 129.77, 130.67 (d, $J = 2.92$ Hz), 130.90, 130.99, 137.50, 137.55, 144.38, 145.90, 150.74, 158.51, 164.29 (d, $J = 286.62$ Hz). IR (ATR) 3251, 3106, 1719, 1635, 1582, 1528, 1506, 1344, 1282, 1222, 1144, 1071, 994 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{FN}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 490.0849, found 490.0843.



3p

(*E*)-*N*-((*E*)-3-(4-chlorophenyl)-1-(4-methylphenylsulfonamido)allylidene)-4-nitrobenzamide

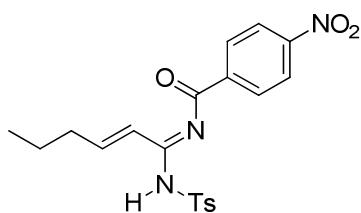
3p: (white solid, 72.5 mg, 75%) ^1H NMR (400 MHz, CDCl_3) δ 2.45 (s, 3H), 7.35-7.39 (m, 4H), 7.52-7.55 (m, 2H), 7.87-7.97 (m, 4H), 8.20-8.22 (m, 2H), 8.41-8.43 (m, 2H), 11.97 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.65, 119.16, 124.42, 126.84, 129.26, 129.33, 129.79, 130.03, 132.84, 137.24, 137.41, 137.50, 144.45, 145.60, 150.78, 158.37, 162.87. IR (ATR) 3265, 1718, 1630, 1583, 1528, 1520, 1407, 1344, 1285, 1244, 1145, 1072, 992 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{ClN}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 506.0553, found 506.0548.



3q

(*E*)-*N*-((*E*)-1-(4-methylphenylsulfonamido)-3-(4-(trifluoromethyl)phenyl)allylidene)-4-nitrobenzamide

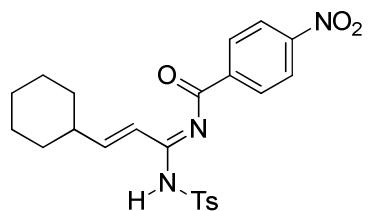
3q: (yellow solid, 64.1 mg, 62%) ^1H NMR (400 MHz, CDCl_3) δ 2.46 (s, 3H), 7.37-7.39 (m, 2H), 7.65-7.72 (m, 4H), 7.89-7.93 (m, 3H), 8.03 (d, $J = 15.6$ Hz, 1H), 8.21-8.23 (m, 2H), 8.42-8.44 (m, 2H), 11.98 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.63, 121.32, 123.66 (d, $J = 272.24$ Hz), 124.40, 125.89 (d, $J = 3.82$ Hz), 126.89, 128.86, 129.25, 129.81, 130.48, 132.27 (d, $J = 32.57$ Hz), 137.17, 137.34, 137.61, 144.52, 144.59, 150.78, 158.01, 162.86. IR (ATR) 3259, 1720, 1633, 1584, 1528, 1344, 1320, 1242, 1145, 1124, 1065 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{N}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 540.0817, found 540.0812.



3r

(*E*)-*N*-((*E*)-1-(4-methylphenylsulfonamido)hex-2-en-1-ylidene)-4-nitrobenzamide

3r: (white solid, 28.2 mg, 34%) ^1H NMR (400 MHz, CDCl_3) δ 0.96 (t, $J = 7.2$ Hz, 3H) 1.53 (sext, $J = 7.2$ Hz, 2H), 2.26-2.31 (m, 2H), 2.45 (s, 3H), 7.26-7.27 (m, 2H), 7.33-7.35 (m, 2H), 7.85-7.87 (m, 2H), 8.17-8.19 (m, 2H), 8.39-8.41 (m, 2H), 11.83 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.68, 21.14, 21.54, 35.05, 121.89, 124.24, 126.69, 129.16, 129.62, 137.45, 137.55, 144.17, 150.59, 152.92, 158.53, 162.57. IR (ATR) 3251, 2962, 2931, 2866, 1717, 1640, 1586, 1526, 1342, 1283, 1241, 1145, 1071, 983, 849 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 438.1100, found 438.1094.

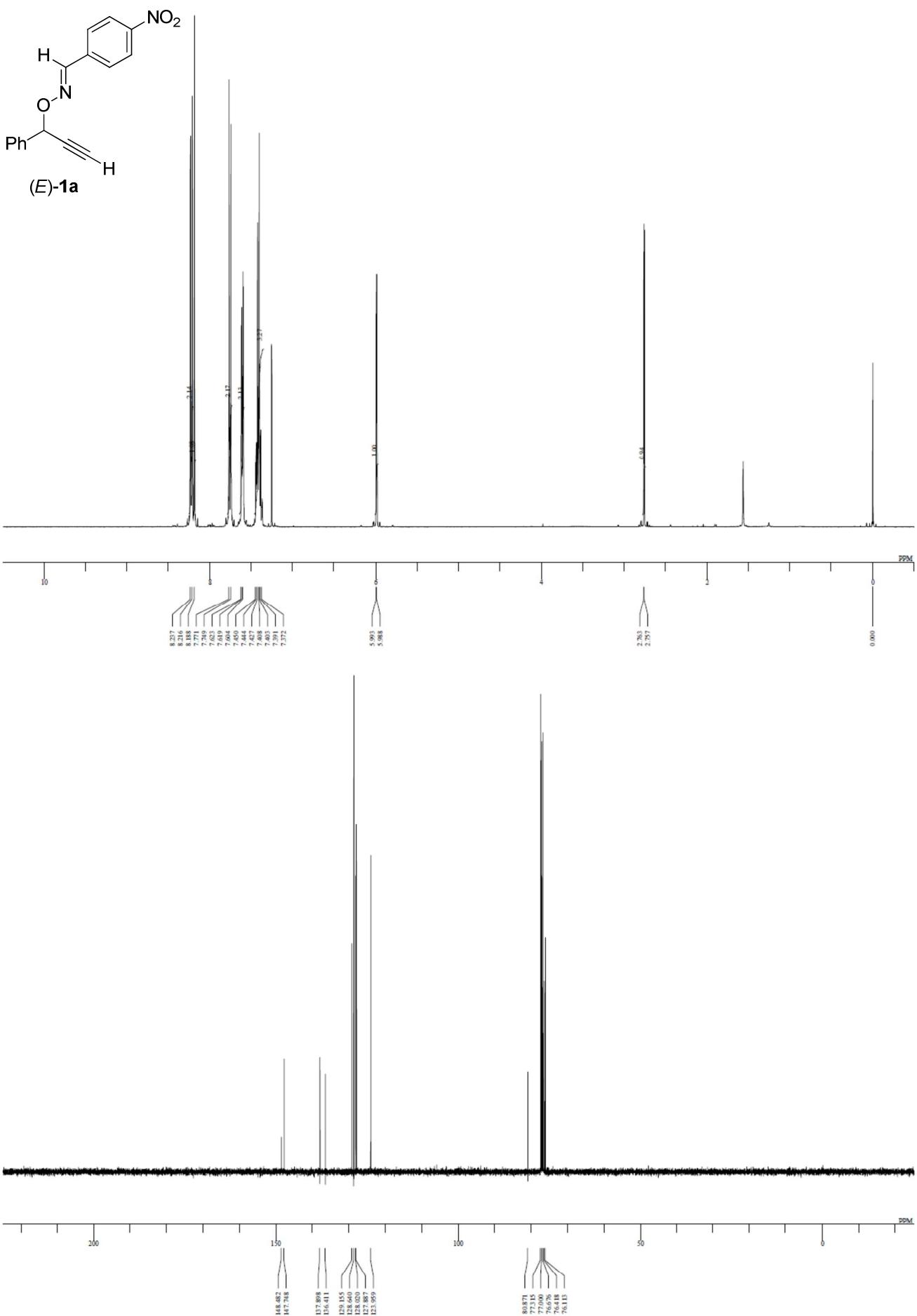


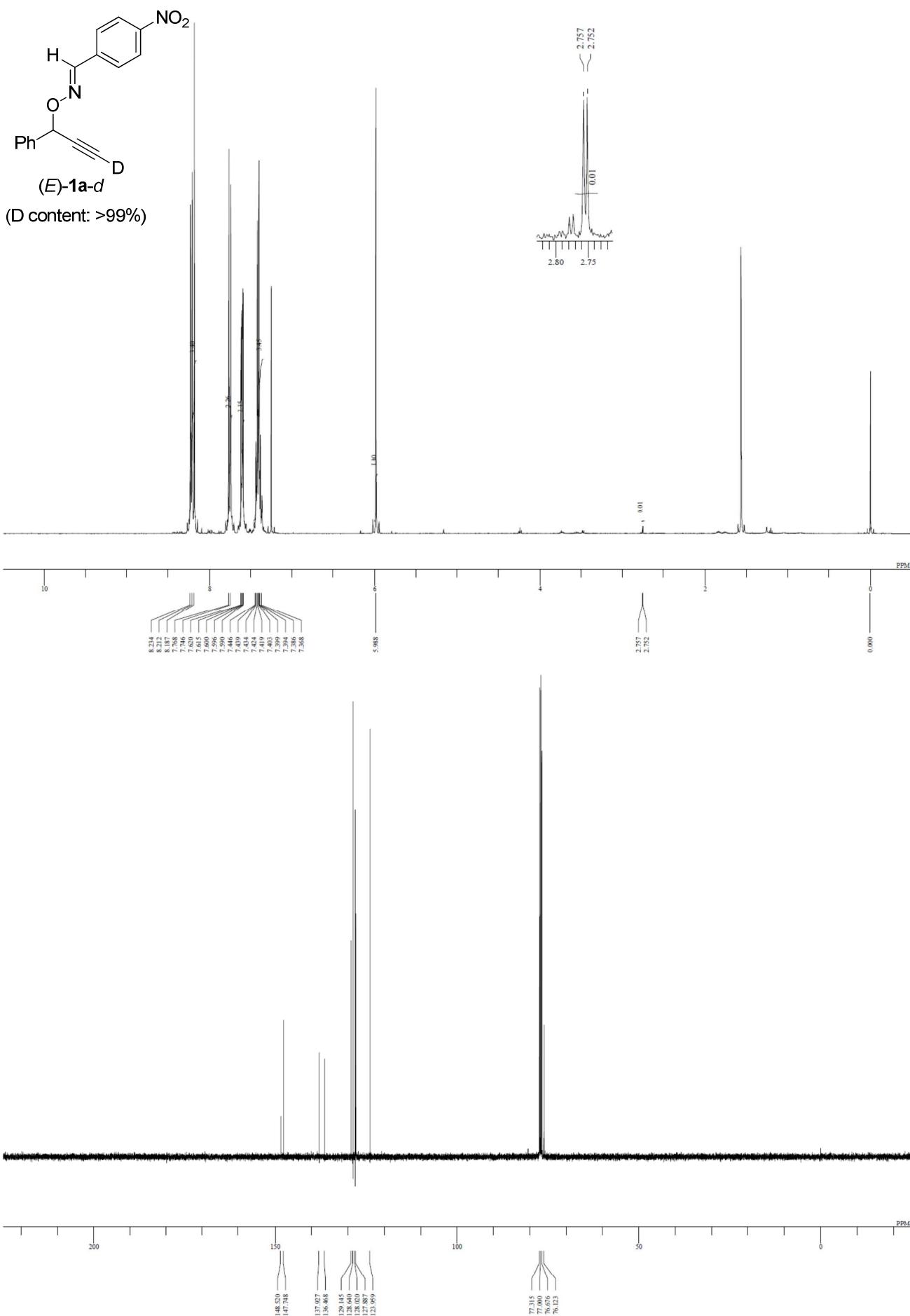
3s

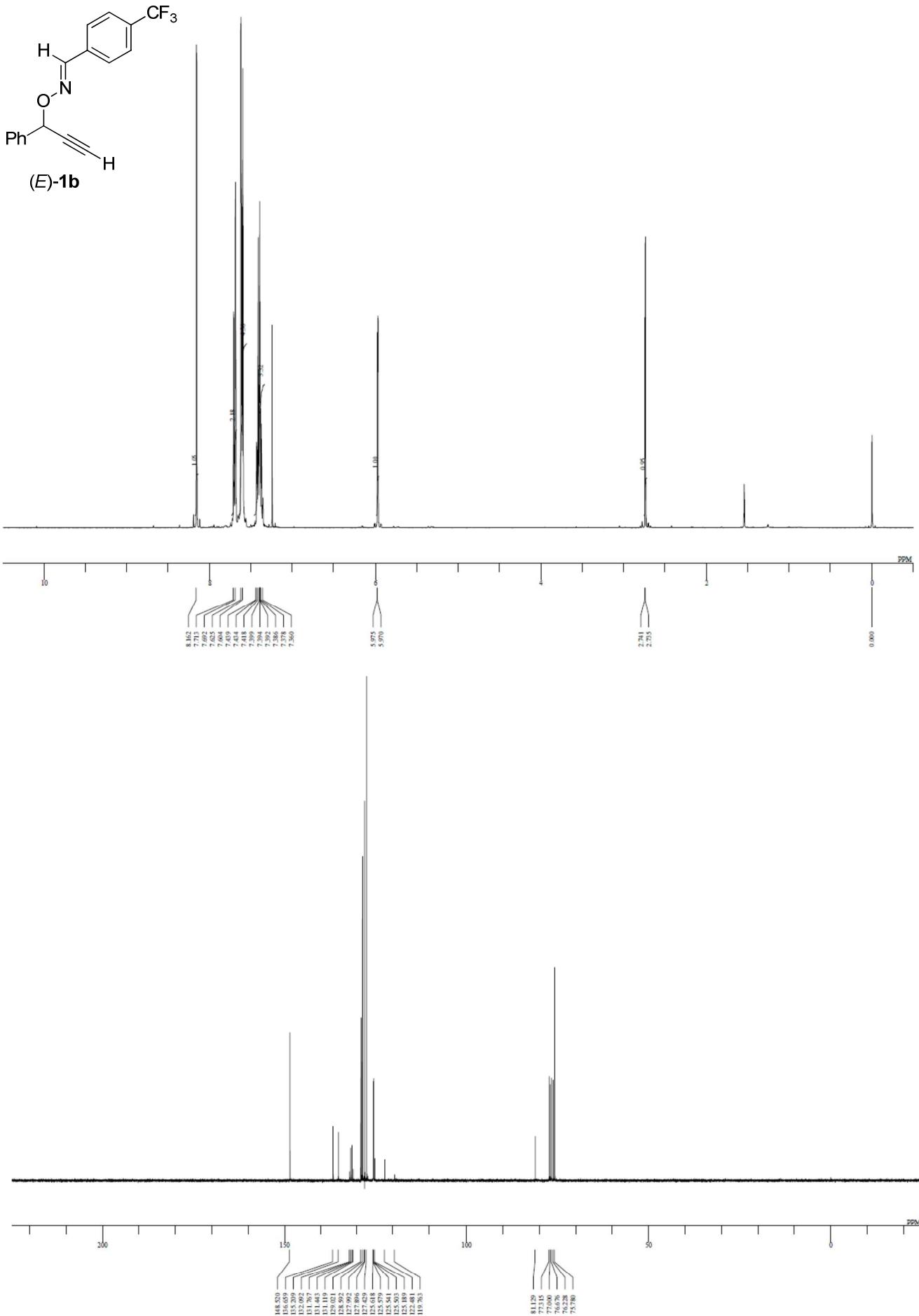
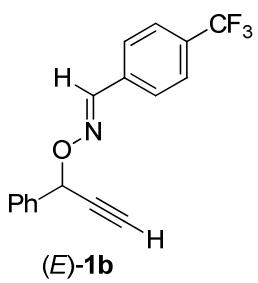
(*E*)-*N*-((*E*)-3-cyclohexyl-1-(4-methylphenylsulfonamido)allylidene)-4-nitrobenzamide

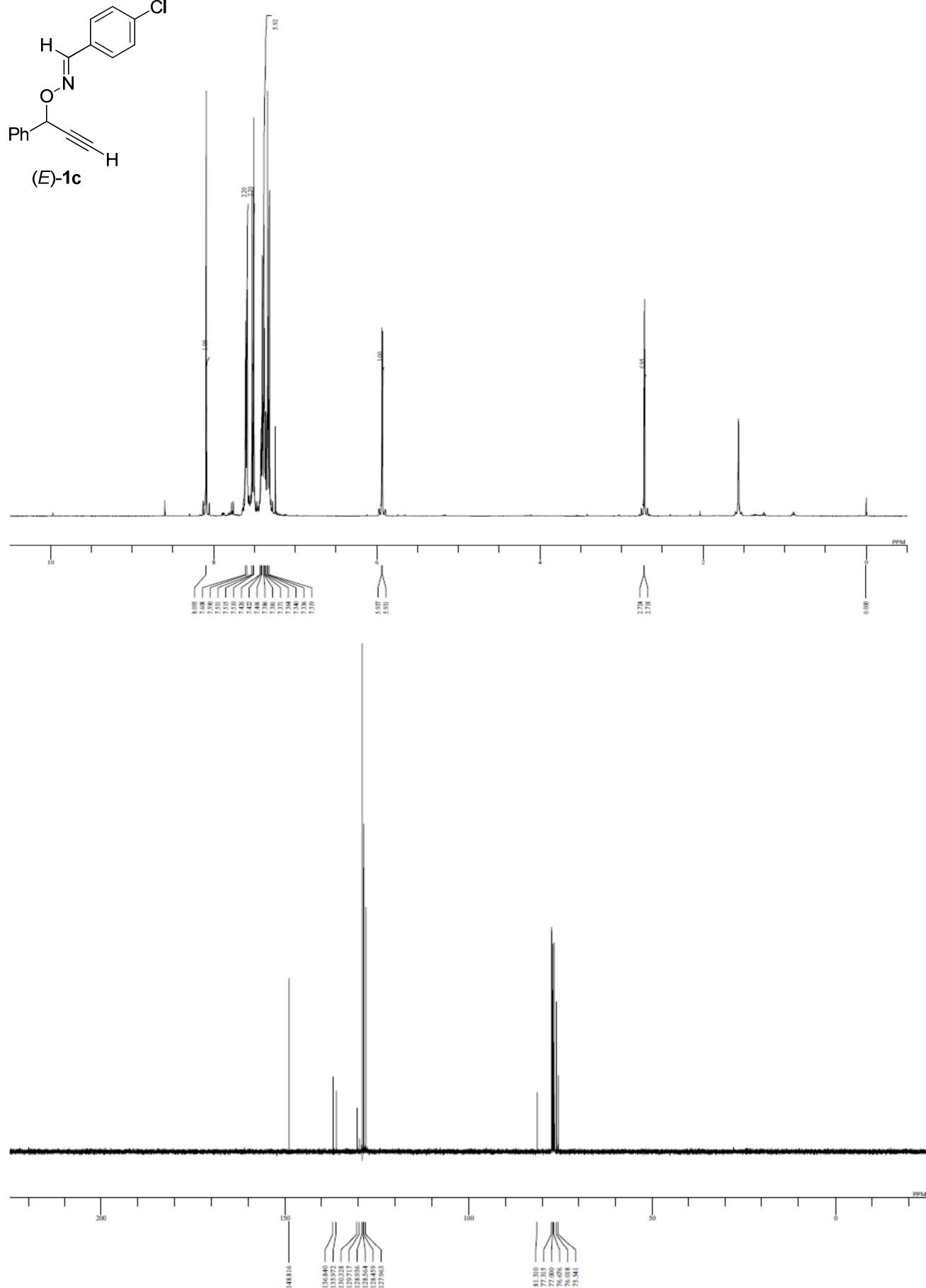
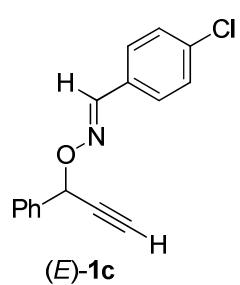
3s: (white solid, 48.2 mg, 53%) ^1H NMR (400 MHz, CDCl_3) δ 1.16-1.32 (m, 5H), 1.67-1.82 (m, 5H), 2.20-2.29 (m, 1H), 2.45 (s, 3H), 7.20-7.25(m, 2H), 7.33-7.35 (m, 2H), 7.85-7.87 (m, 2H), 8.16-8.19 (m, 2H), 8.39-8.41 (m, 2H), 11.84 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.63, 25.65, 25.82, 31.57, 41.41, 119.70, 124.34, 126.78, 129.22, 129.69, 137.54, 137.66, 144.22, 150.68, 157.95, 159.05, 162.66. IR (ATR) 3251, 2926, 2852, 1718, 1638, 1588, 1526, 1342, 1283, 1243, 1144, 1071, 985, 850 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{25}\text{N}_3\text{NaO}_5\text{S} ([\text{M} + \text{Na}]^+)$ 478.1413, found 478.1407.

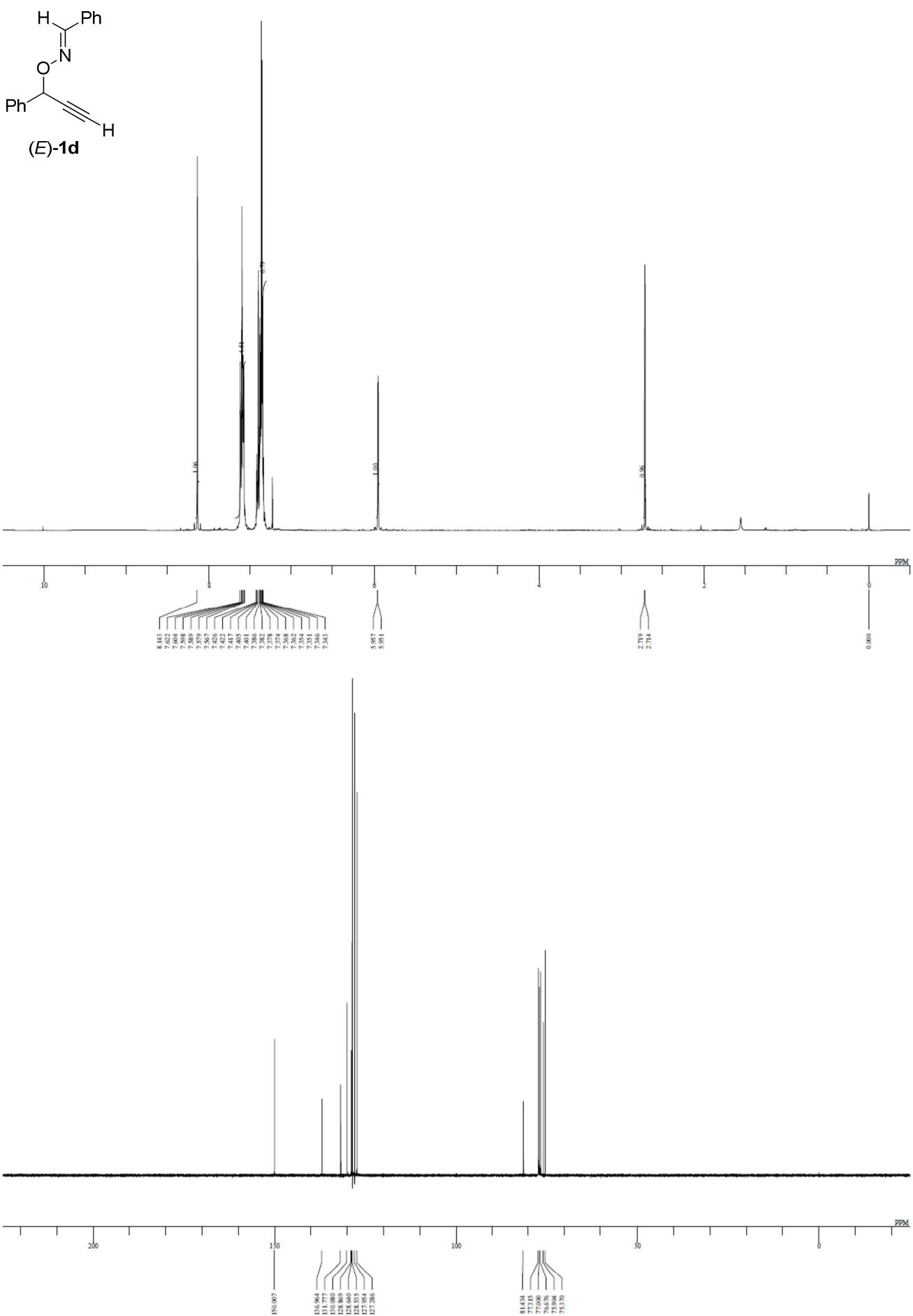
6. ^1H and ^{13}C NMR charts of 1 and 3.

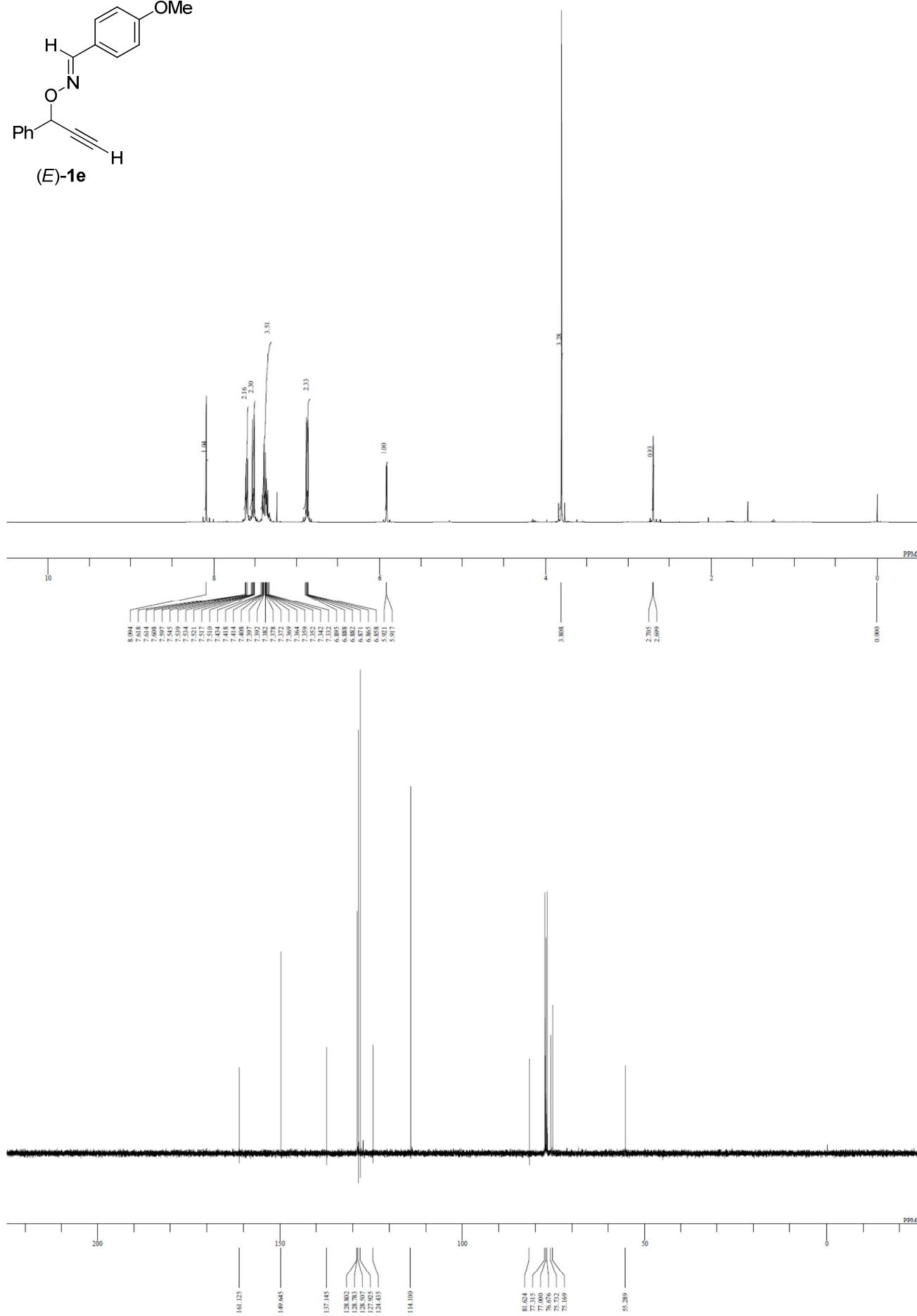
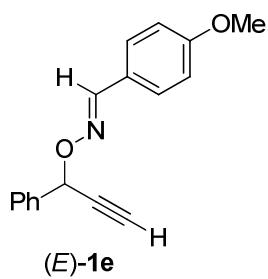


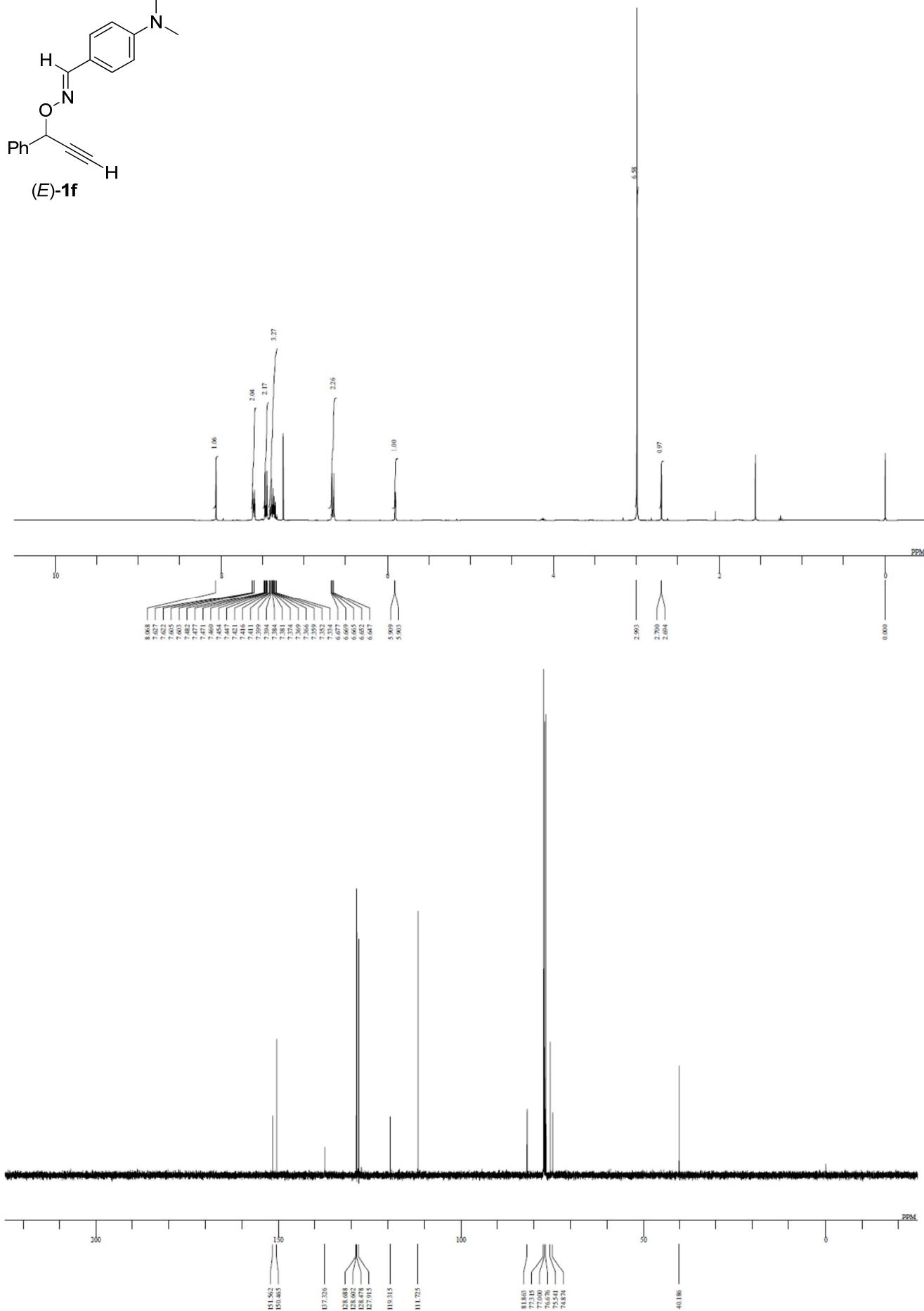
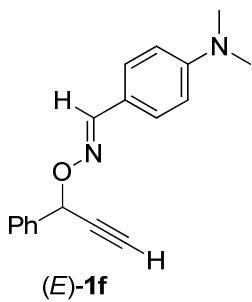


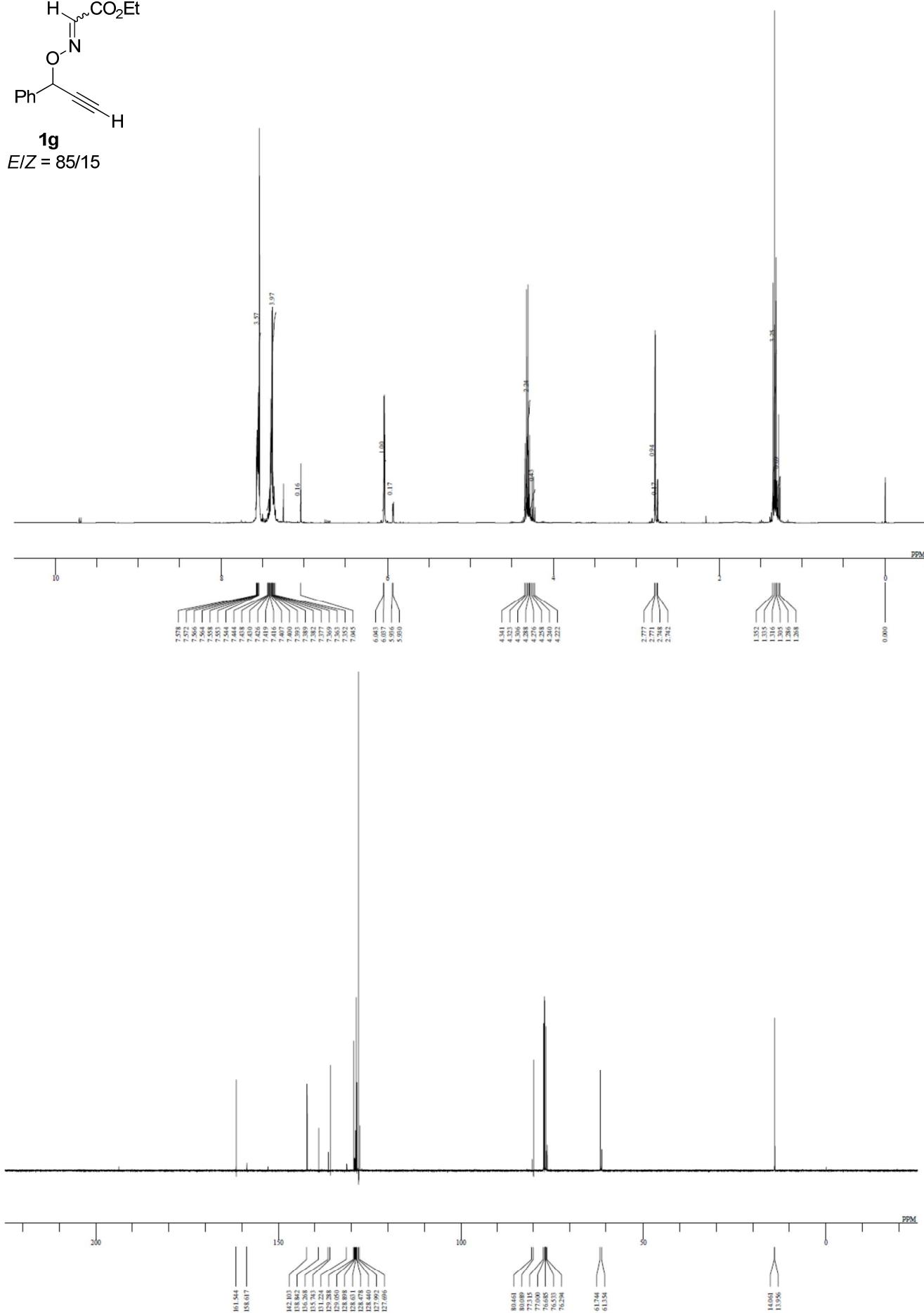
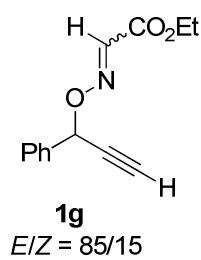


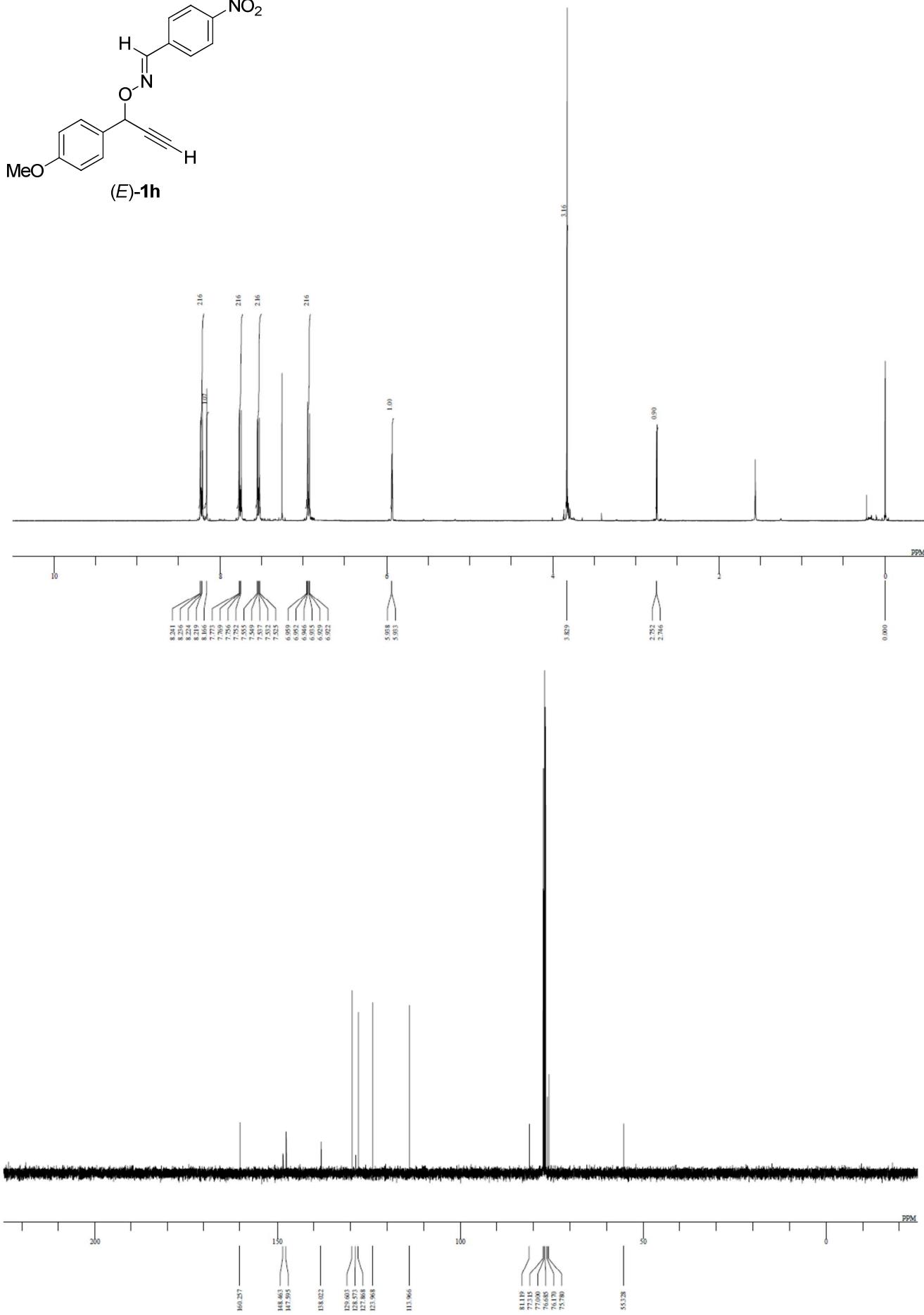
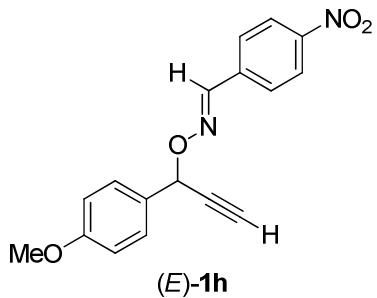


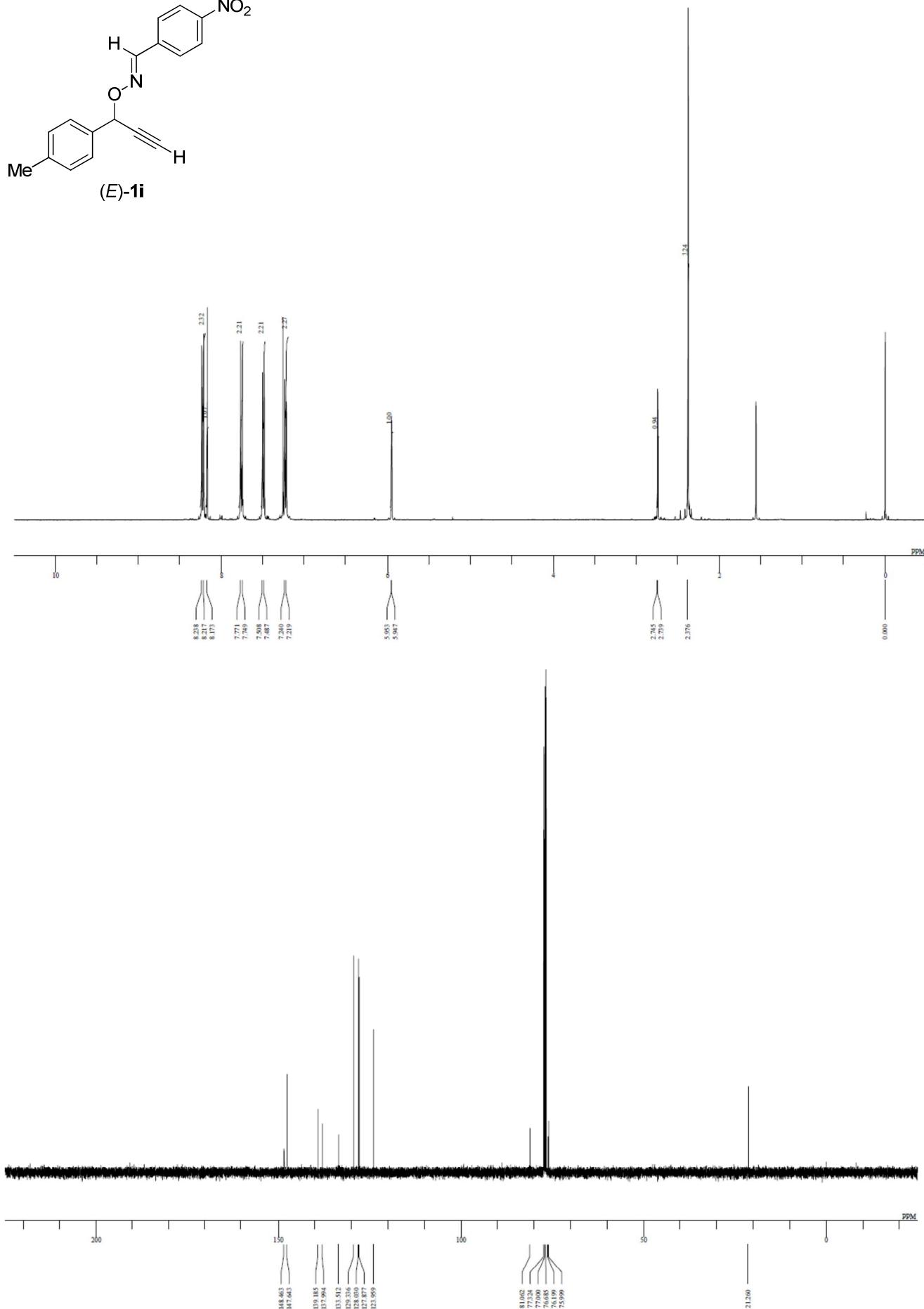
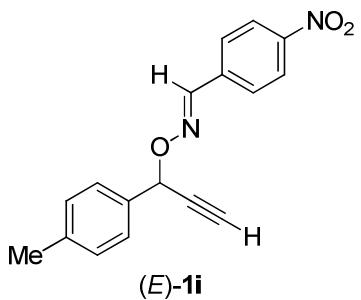


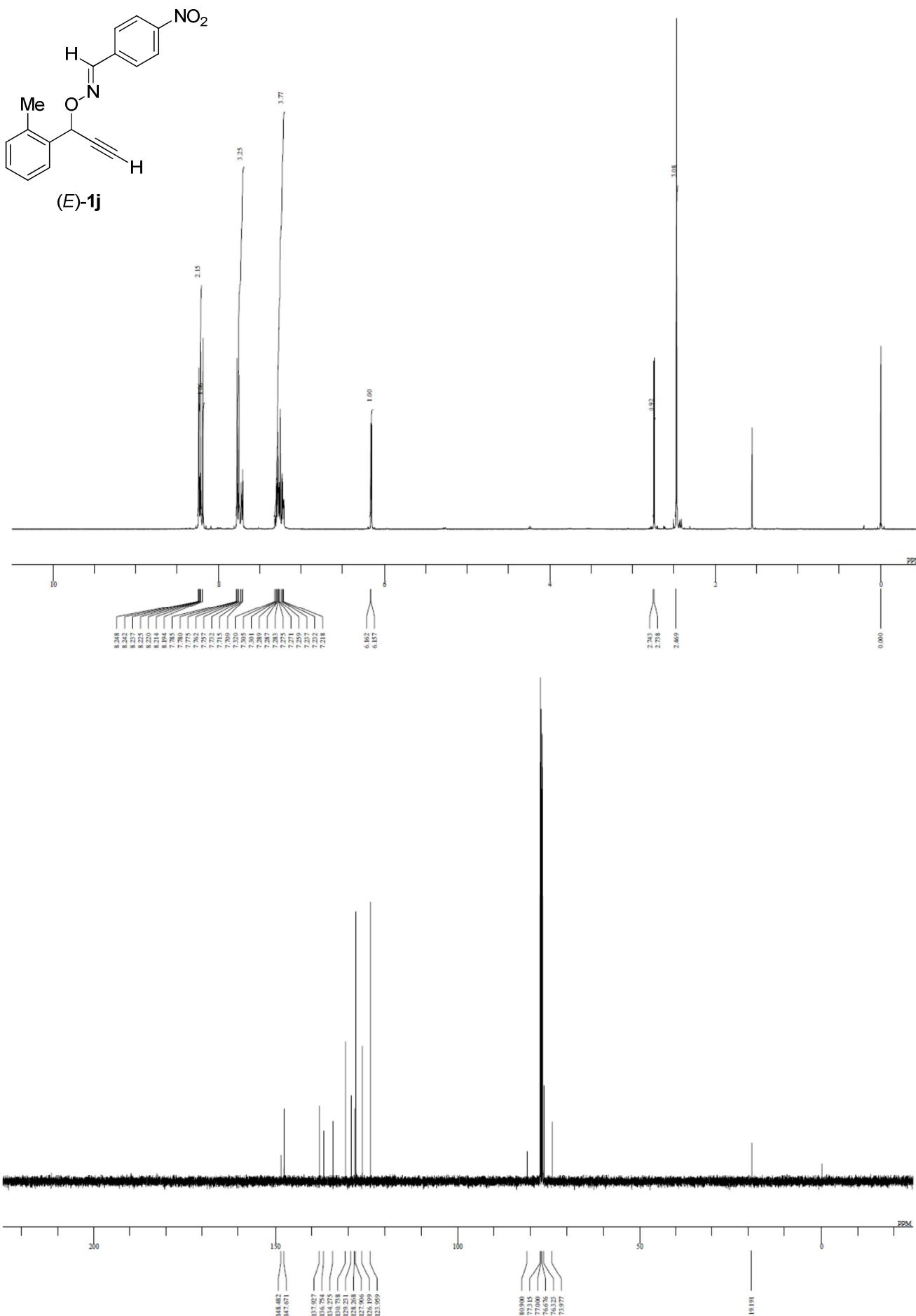


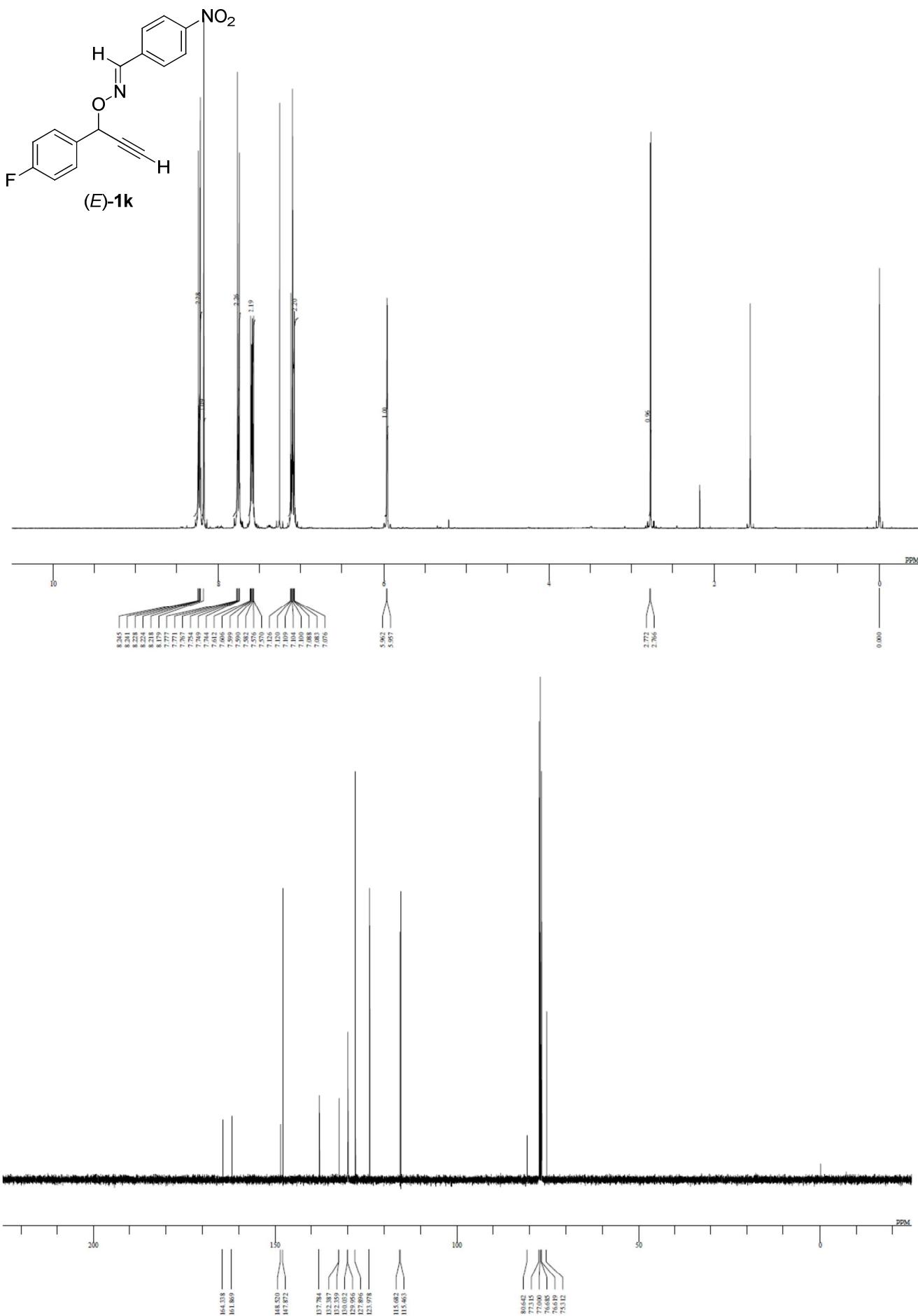


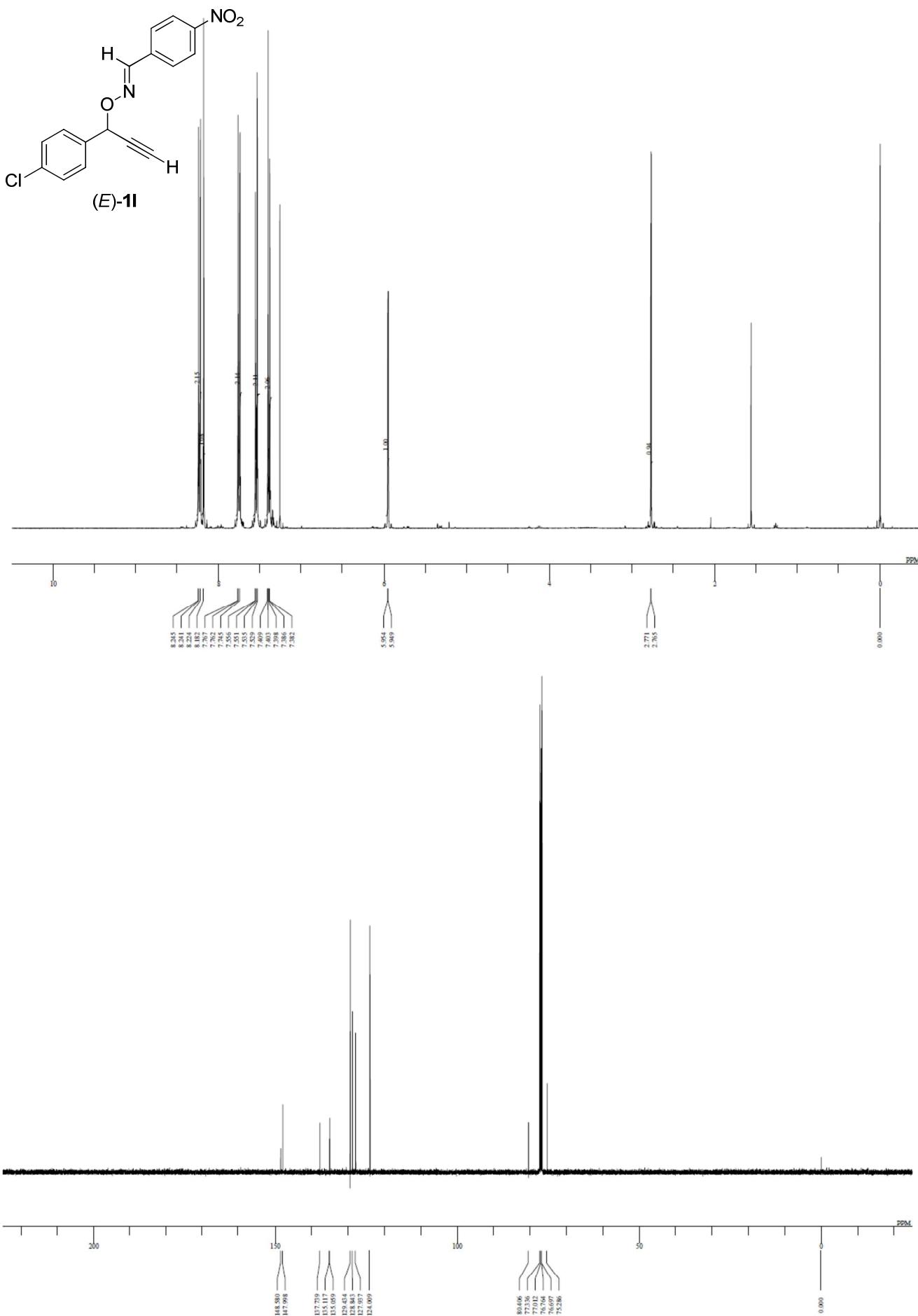


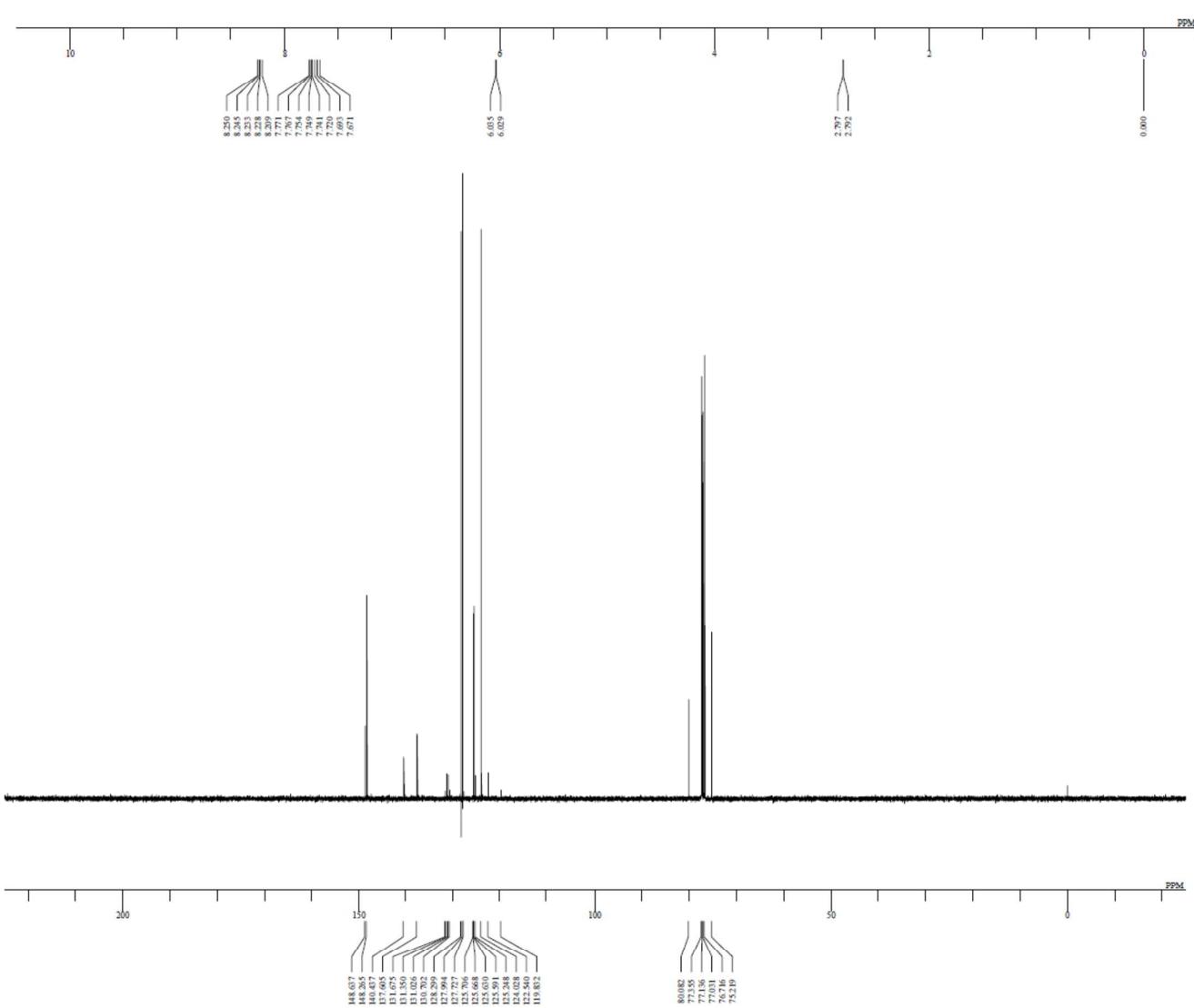
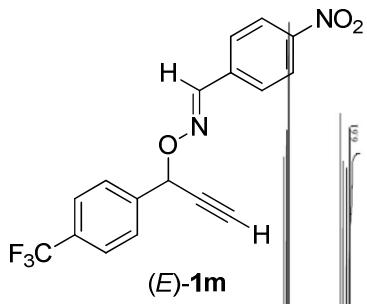


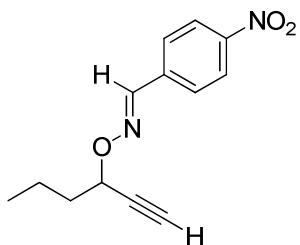




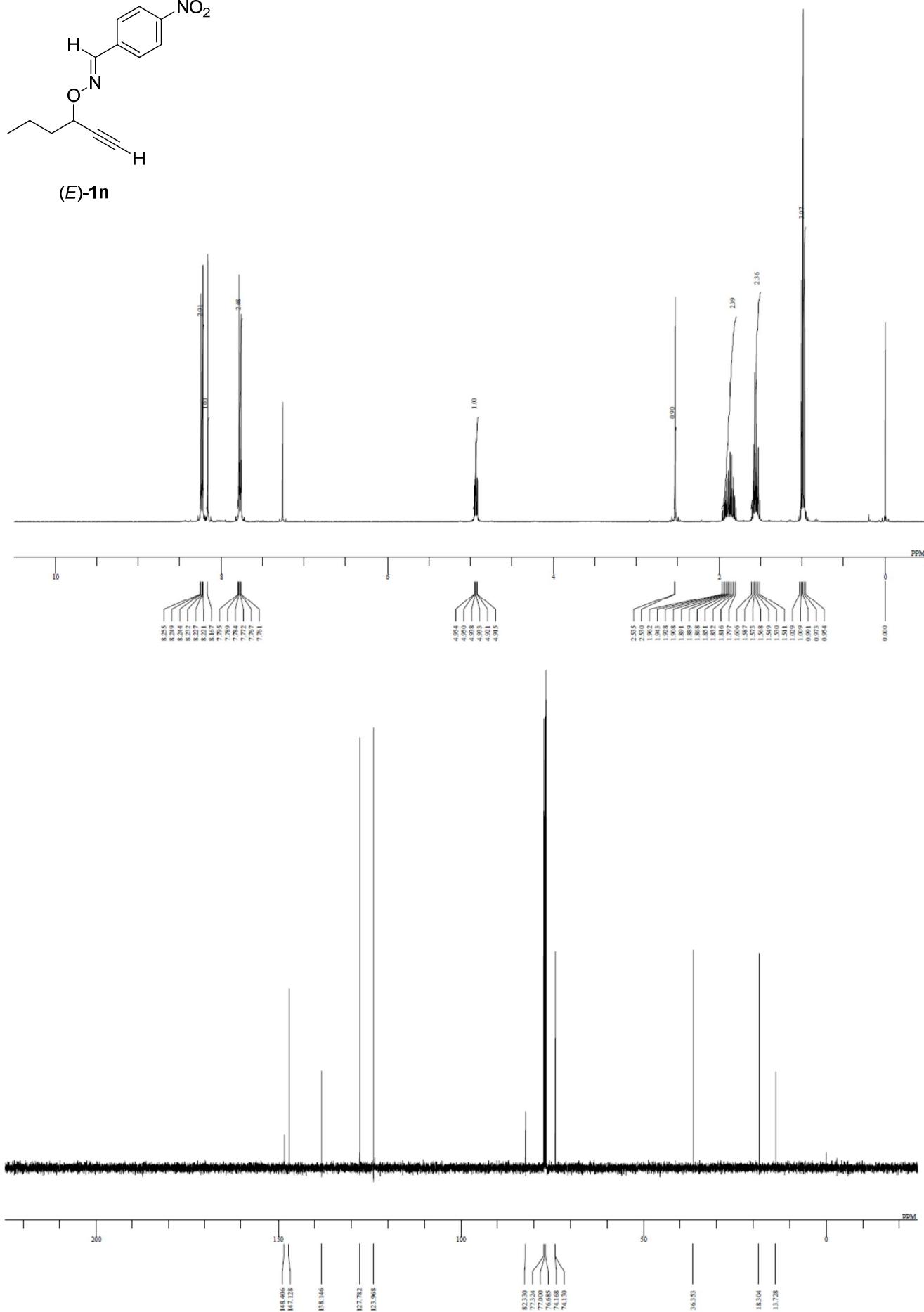


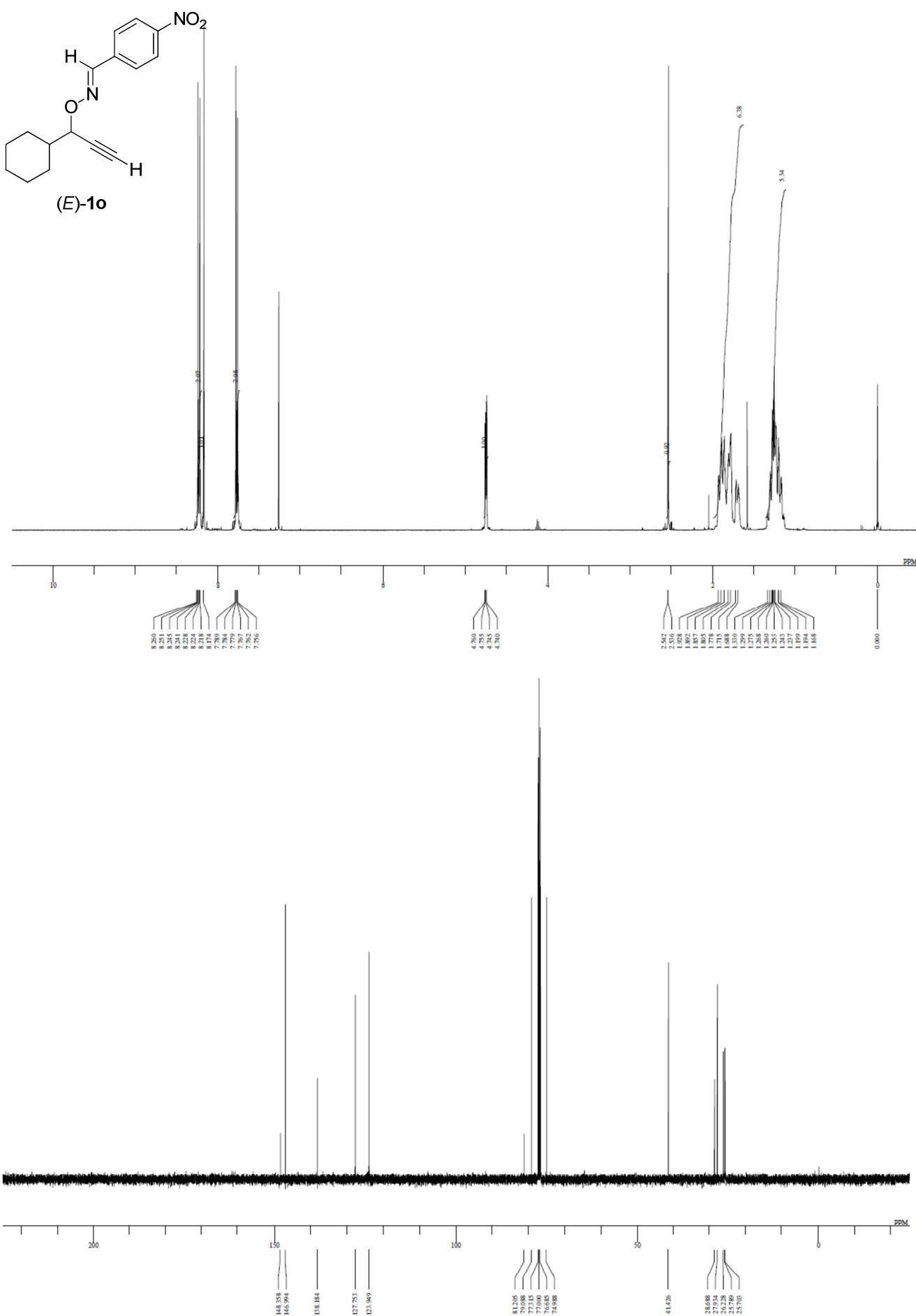


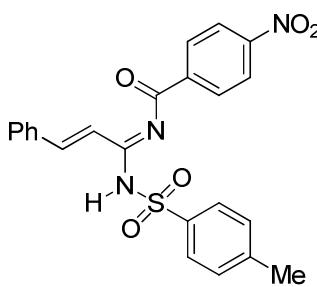




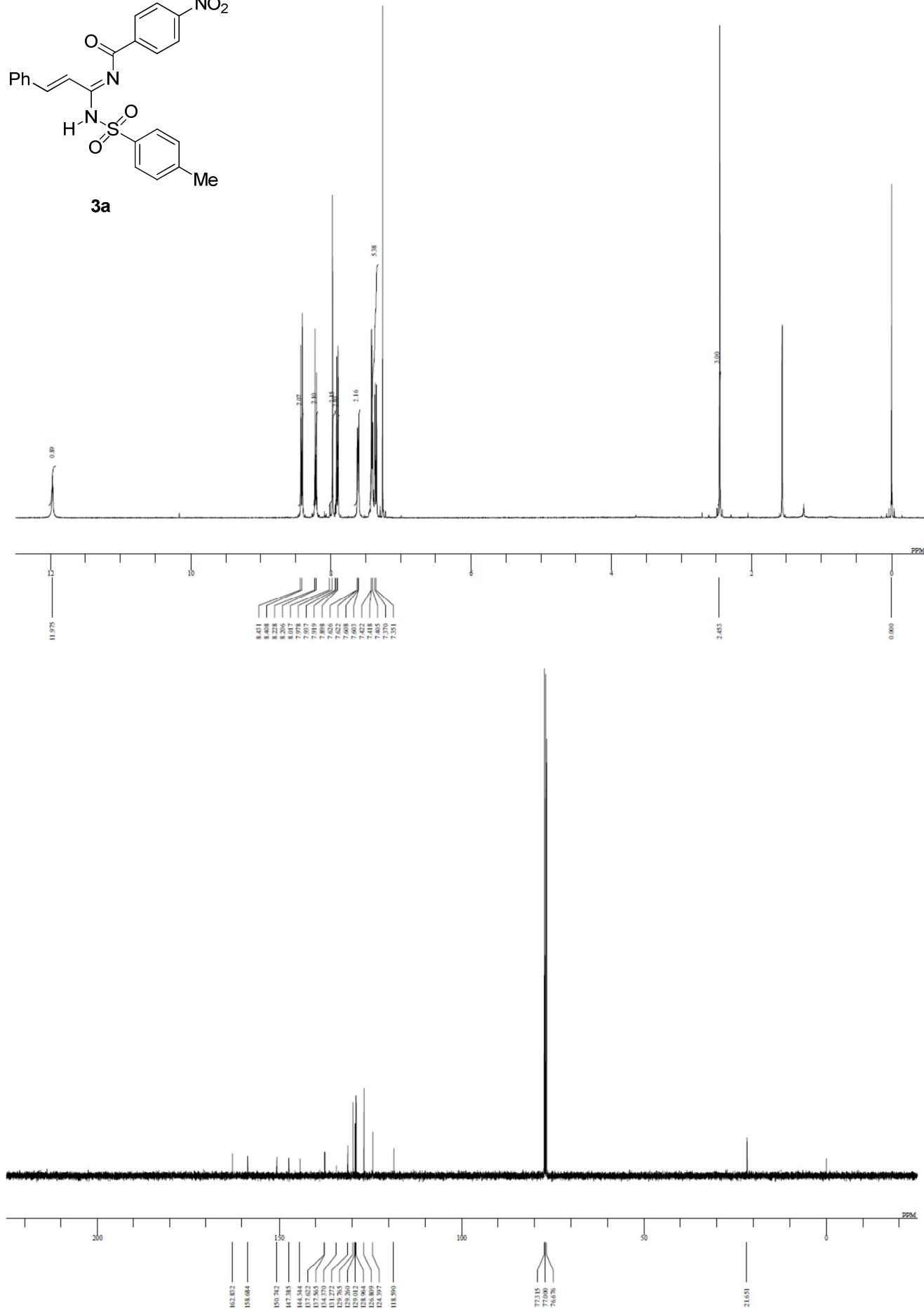
(*E*)-1n

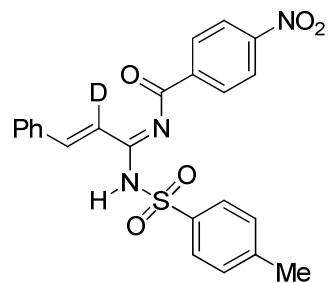




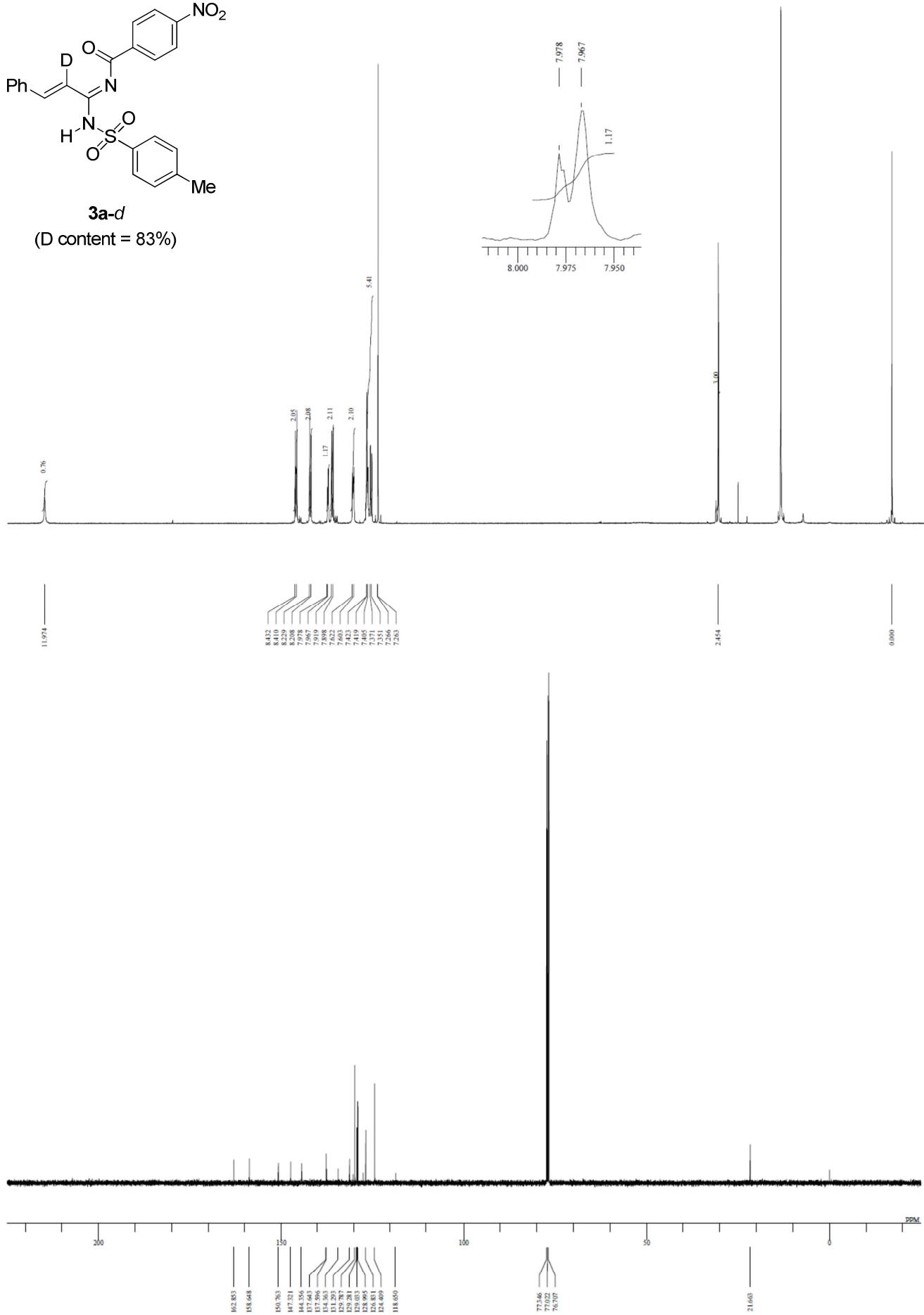


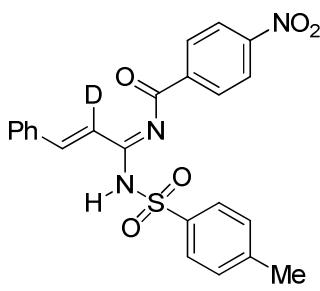
3a





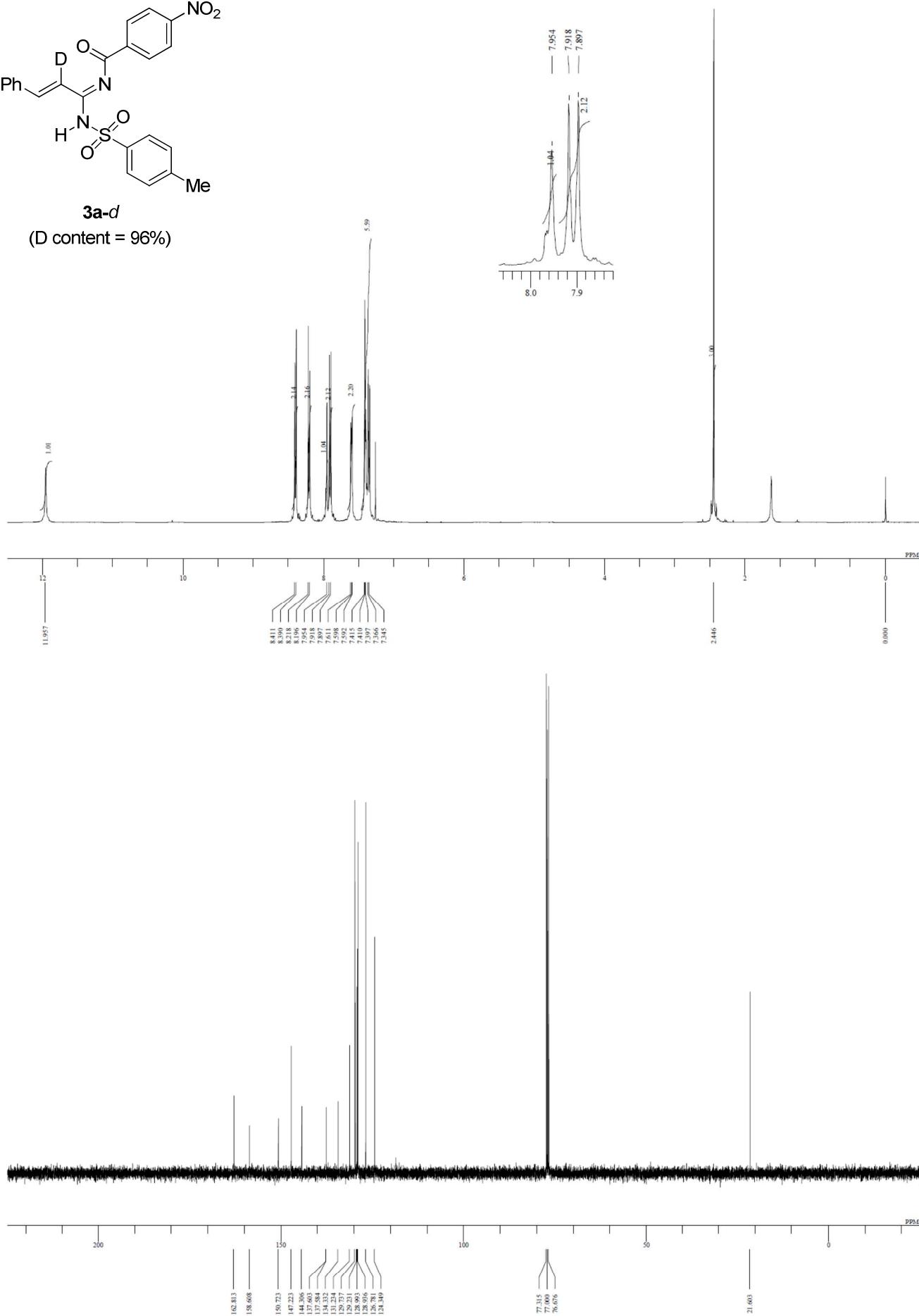
3a-d
(D content = 83%)

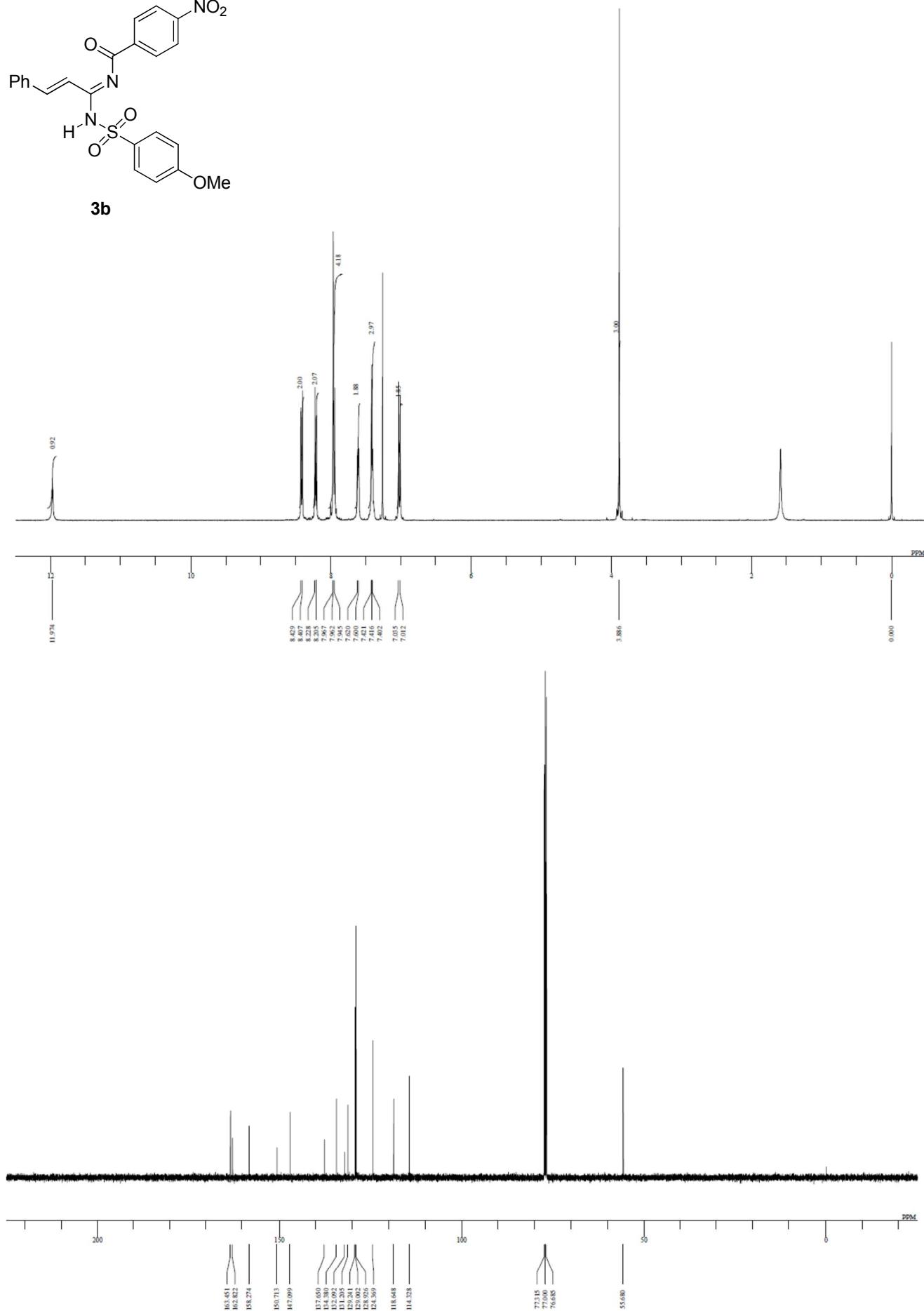
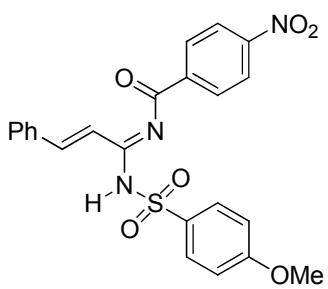


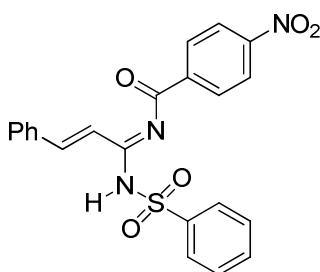


3a-d

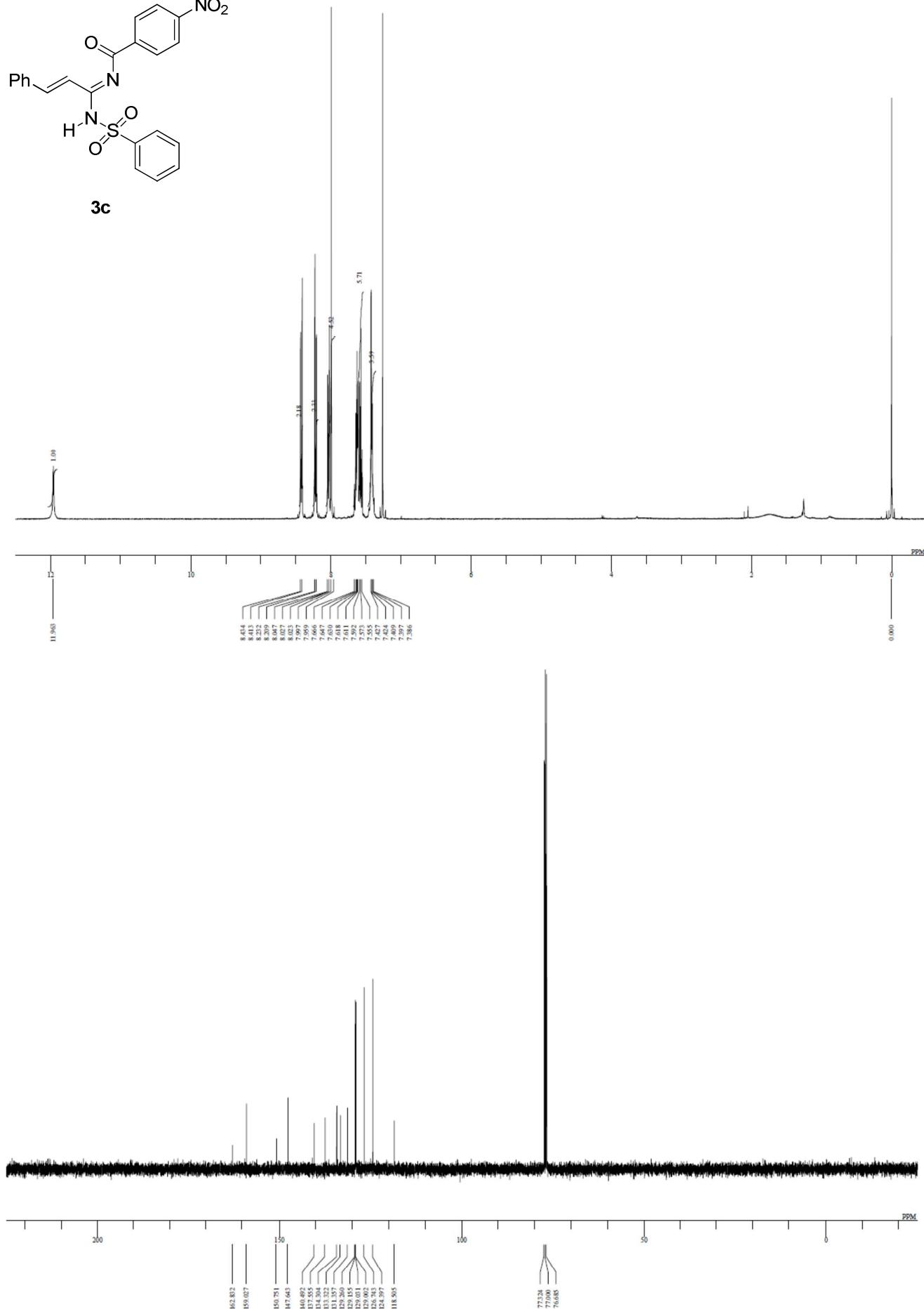
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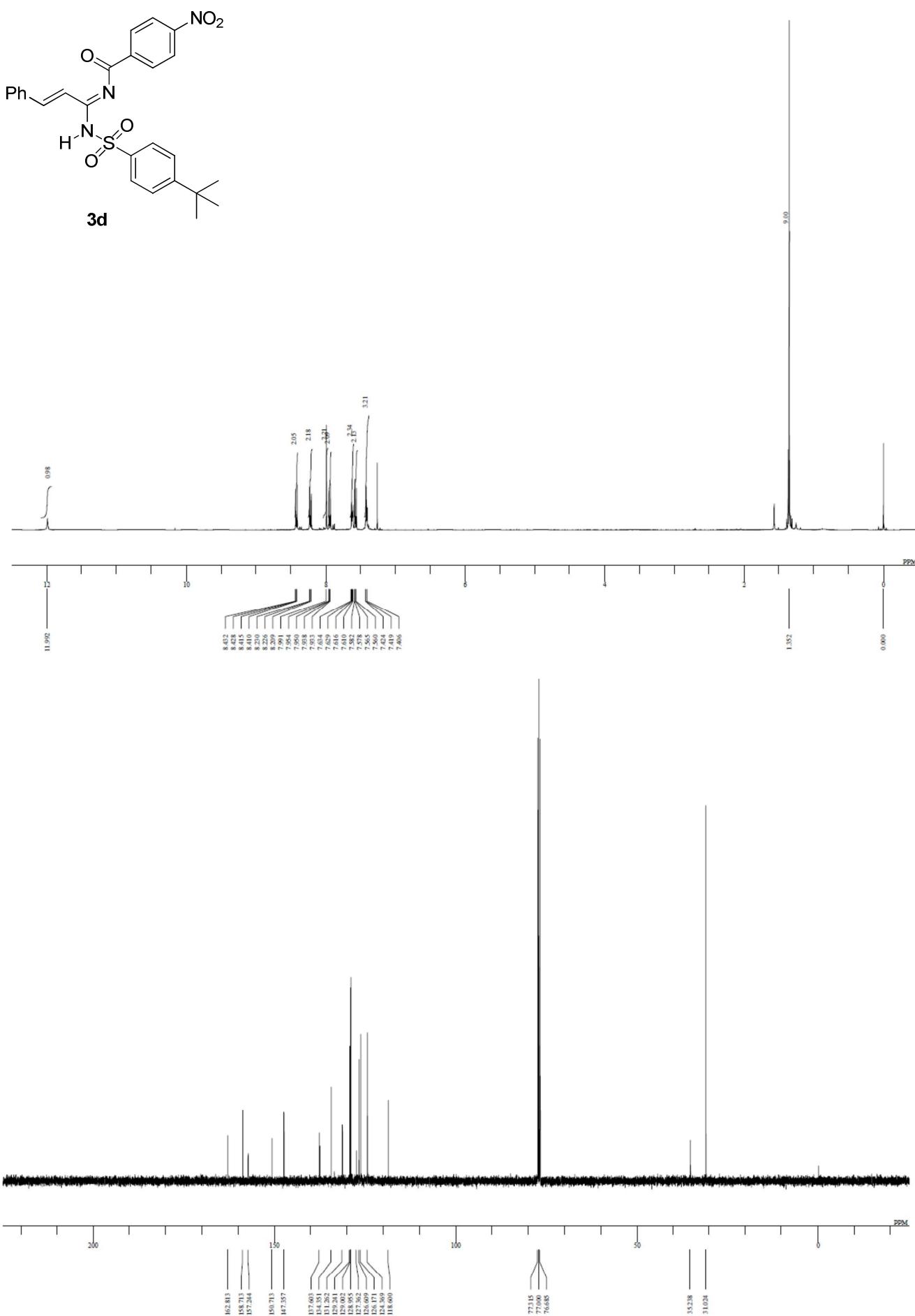


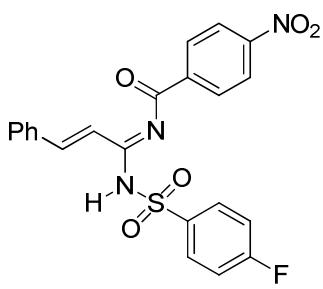




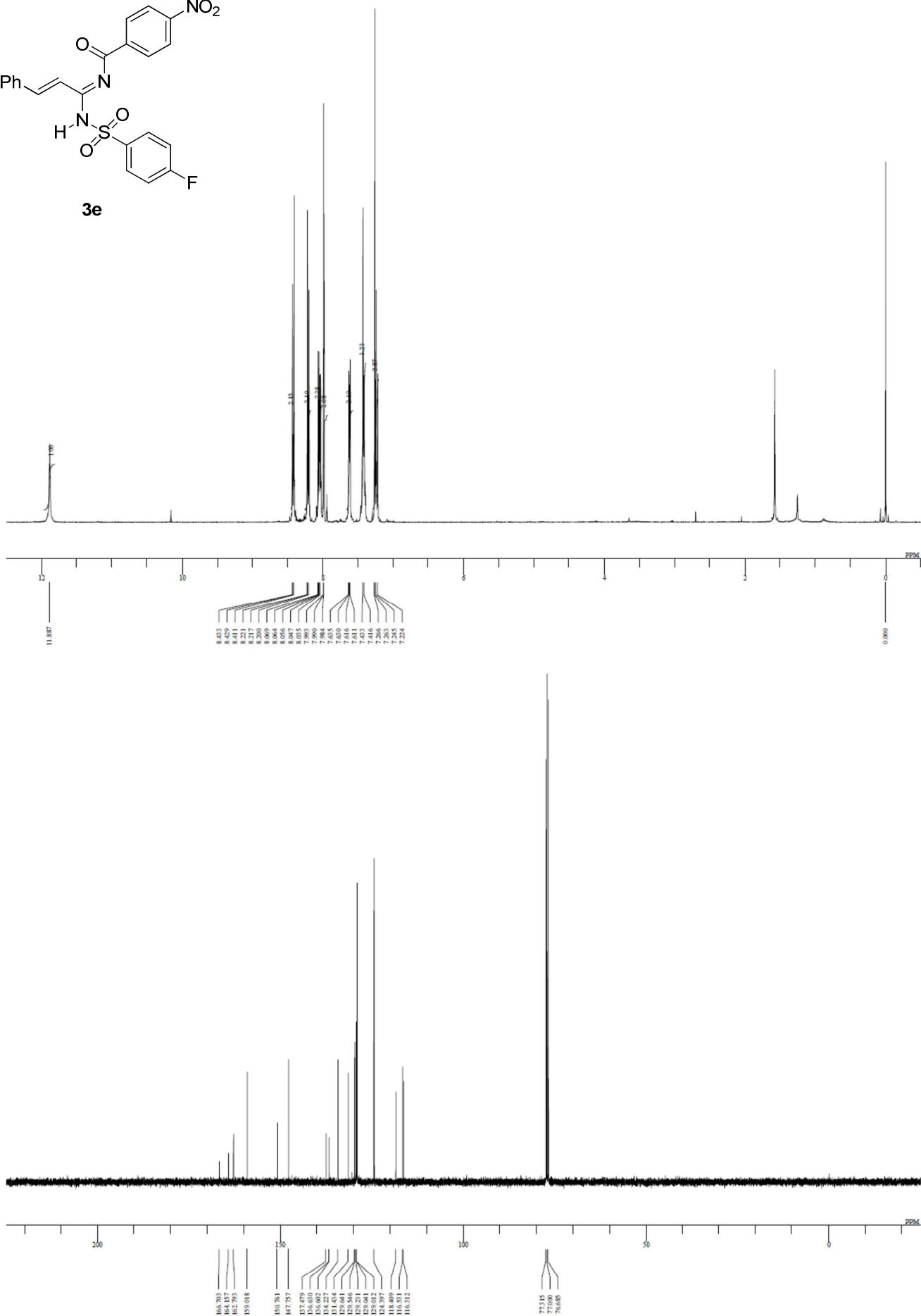
3c

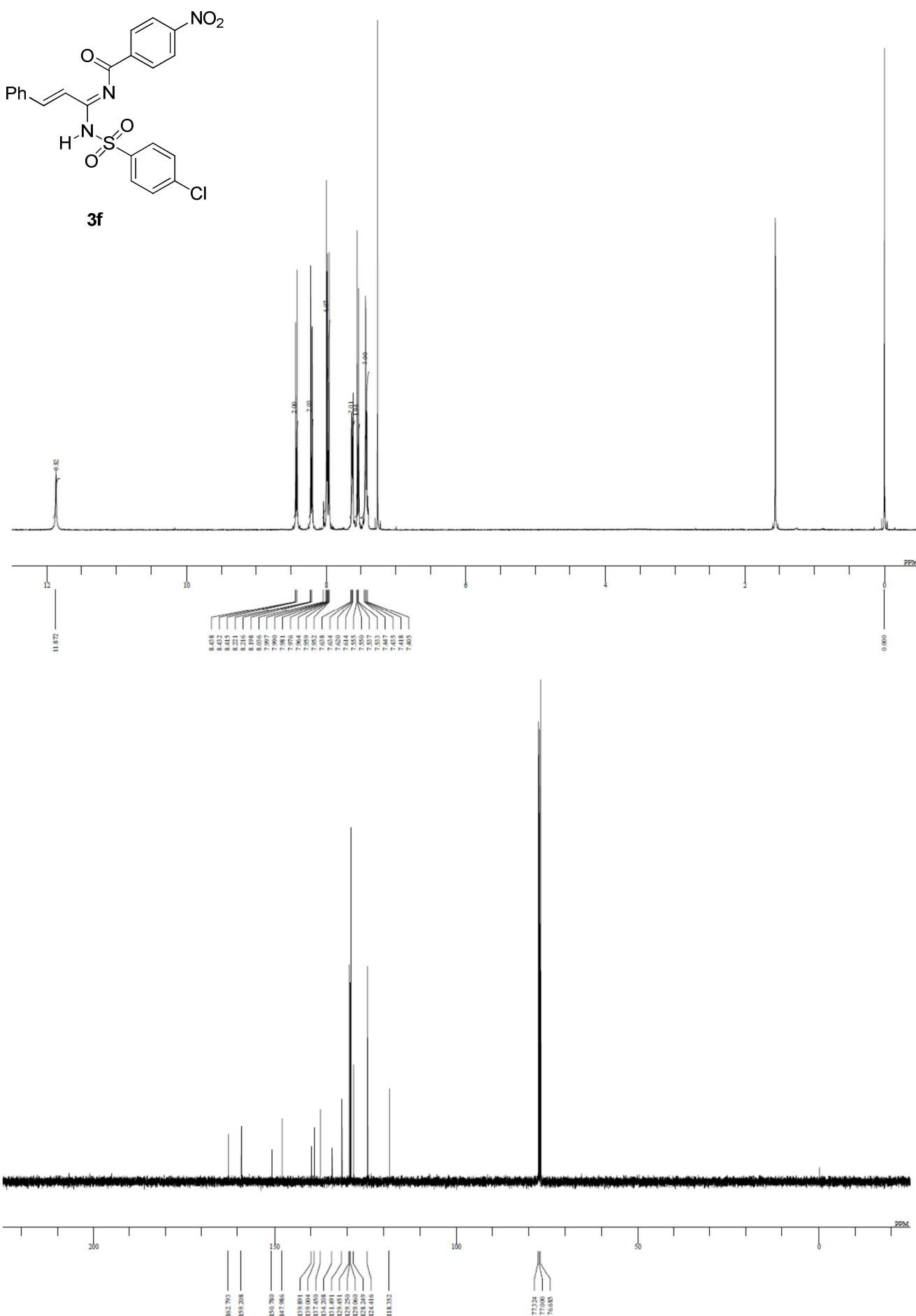


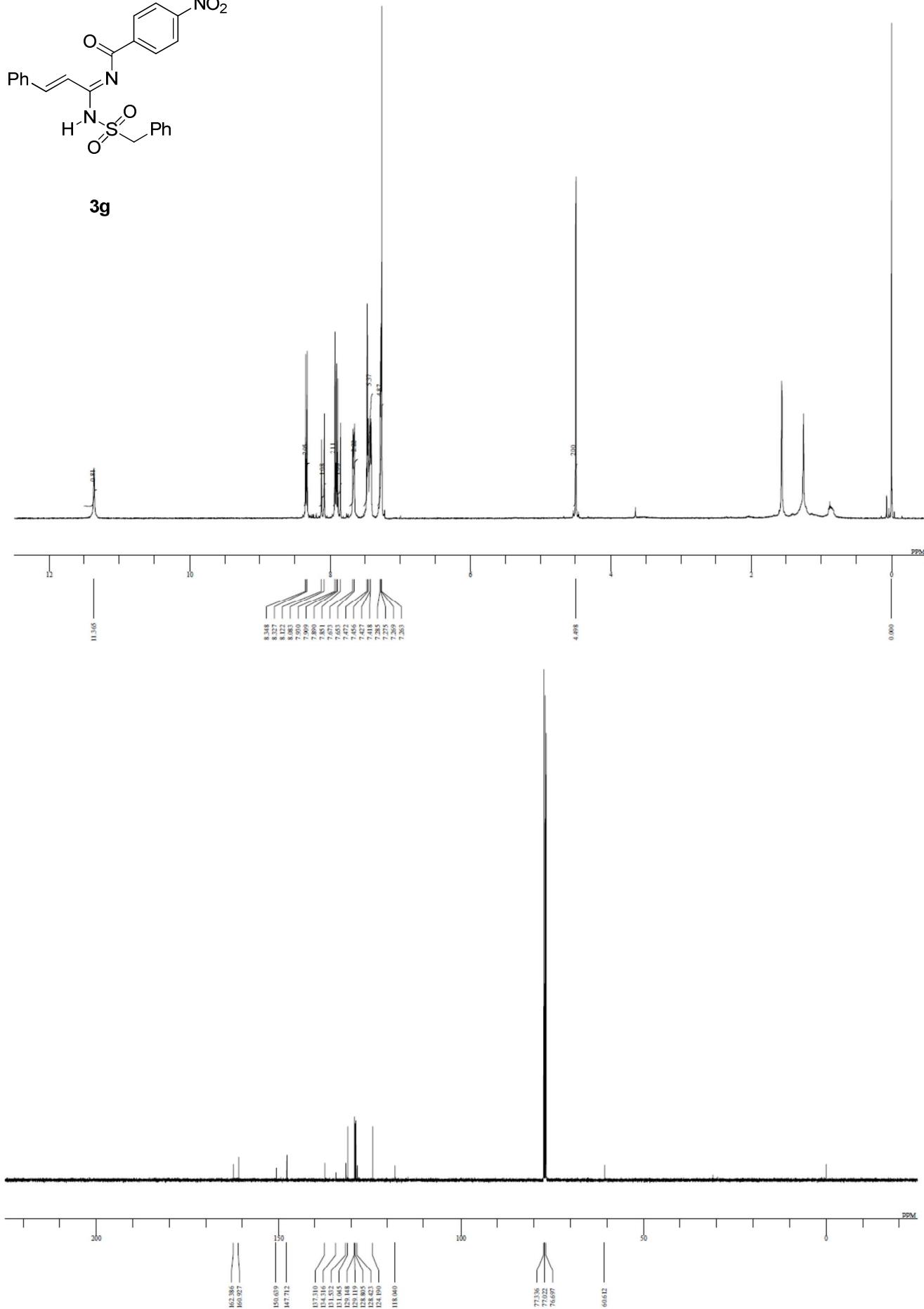
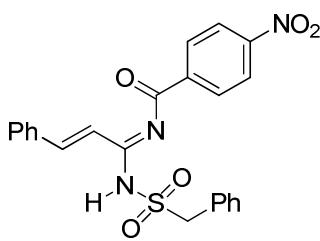


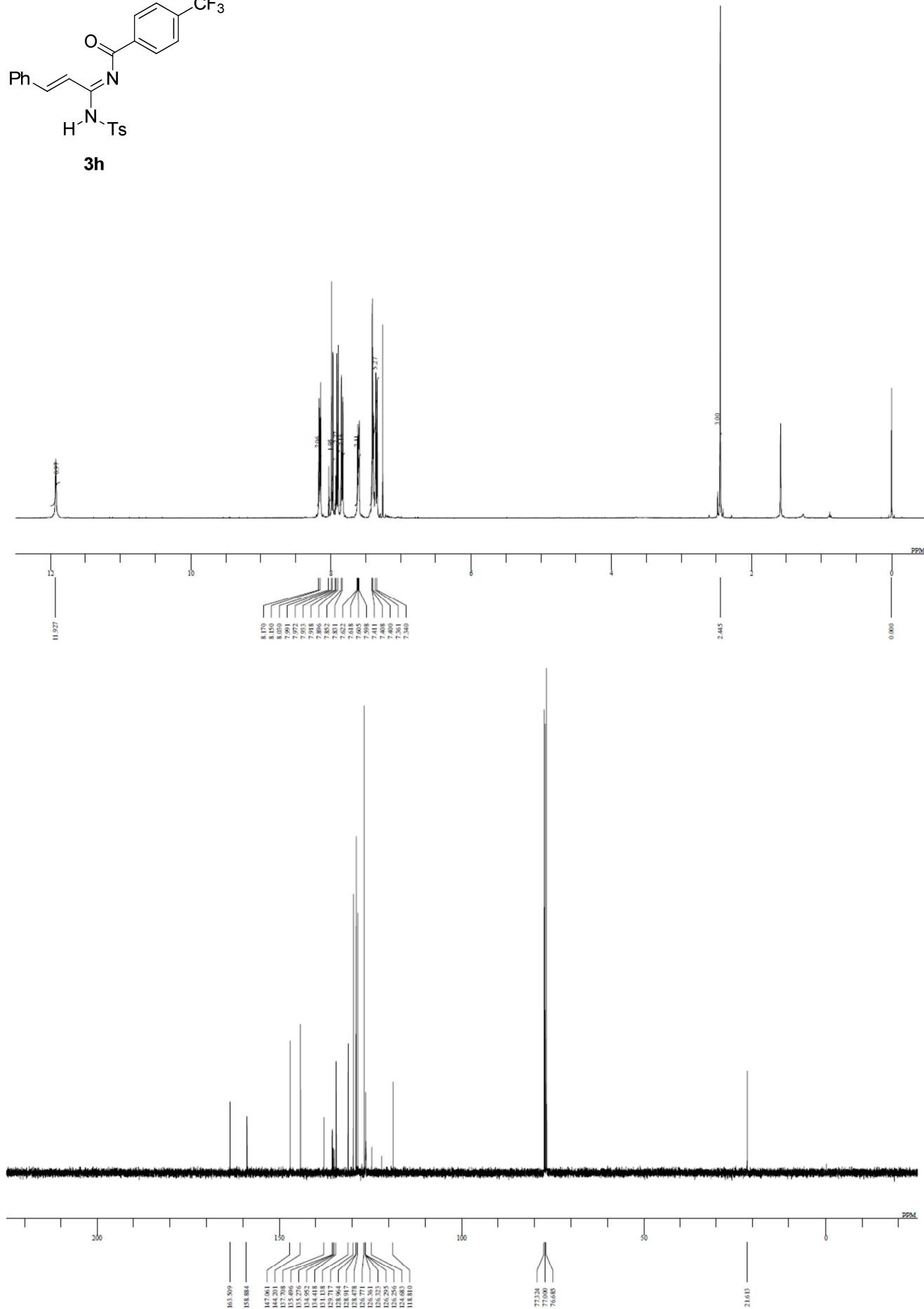
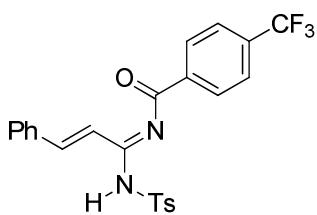


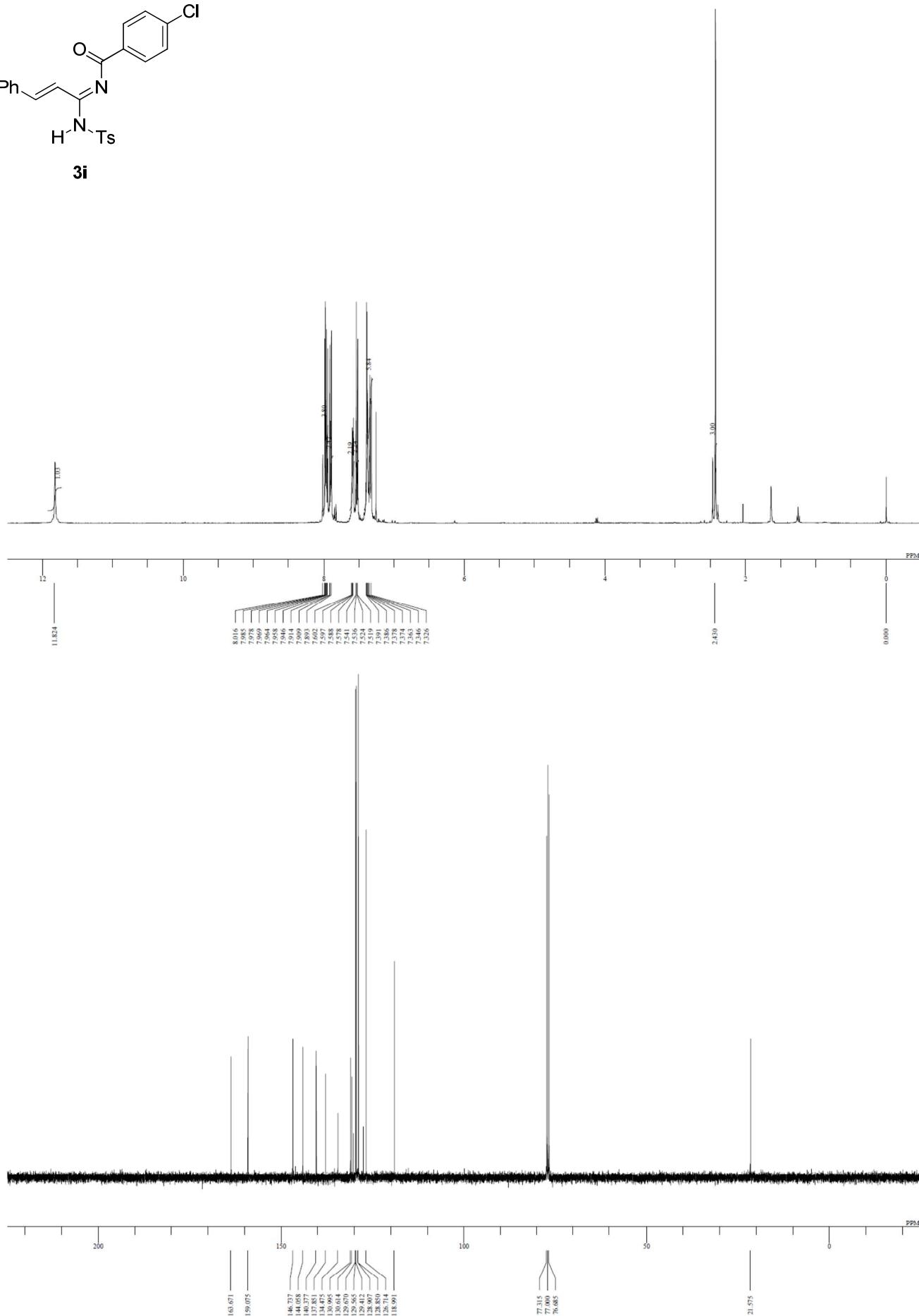
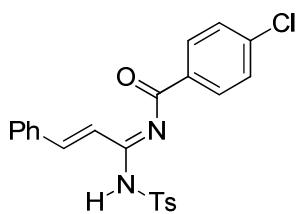
3e

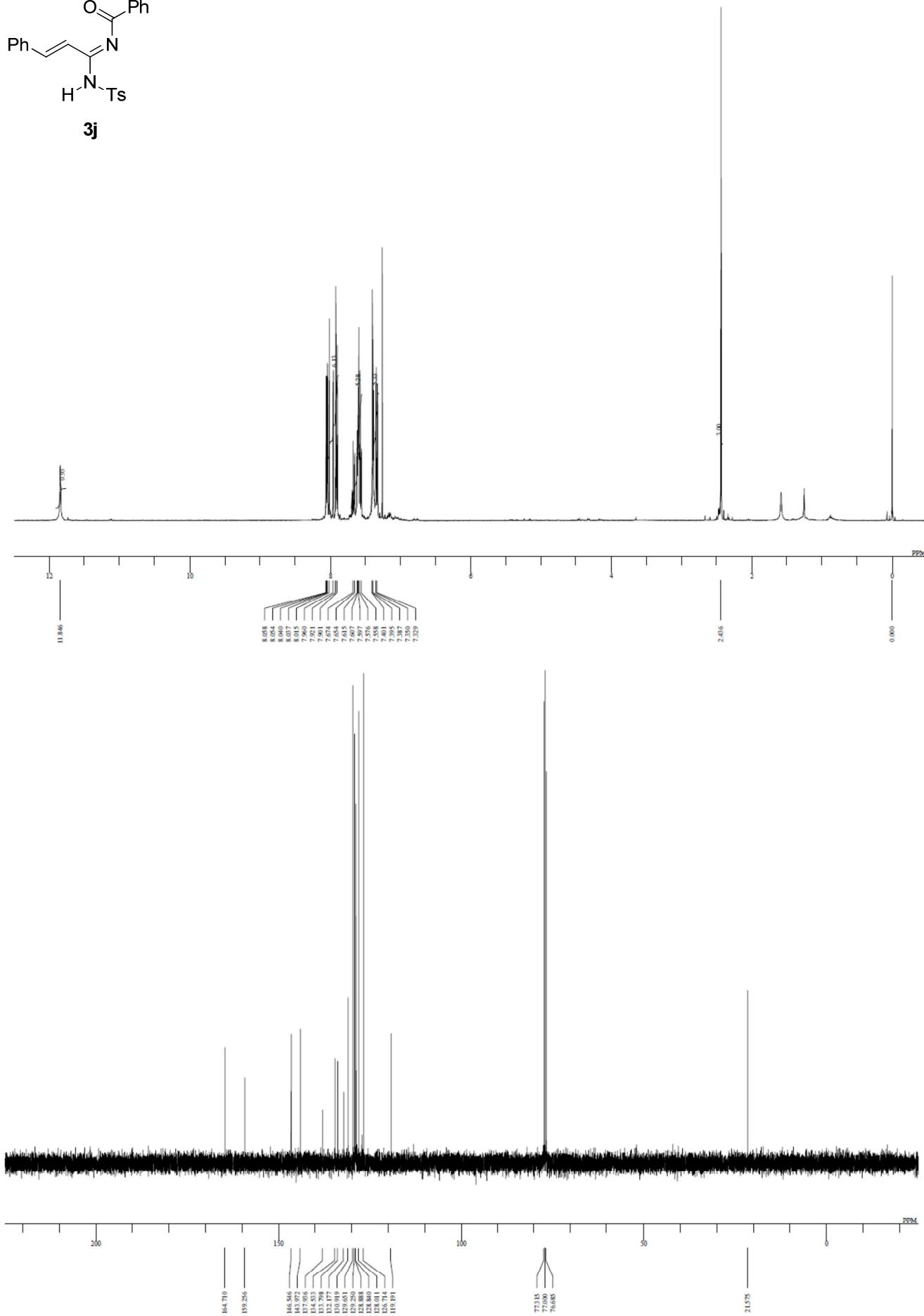
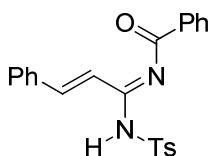


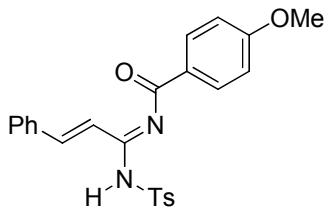












3k

