

Domino reactions for the synthesis of various α -substituted nitro alkenes

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(E)-2-Nitro-3-(4-nitrophenyl)prop-2-en-1-ol (E-2c)

Isolated yield 60%. Yellow oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 75:25). $\nu_{\max}$ cm^{-1} 3459, 1639, 1549. ^1H NMR (CDCl_3 , 300 MHz): δ 8.32-8.26 (m, 2H), 8.18 (s, 1H), 7.79-7.72 (m, 2H), 4.65 (s, 2H), 3.16 (br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 161.2, 144.9, 134.7, 131.0 (2C), 125.2, 124.2 (2C), 56.4. HRMS: m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_9\text{H}_8\text{N}_2\text{NaO}_5$ 224.0433, found 224.0438.

Ethyl (E/Z)-3-(4-fluorophenyl)-2-nitroacrylate (E/Z-3b) (Method A, E/Z = 50:50)

Isolated yield 76%. Yellow oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 9:1). $\nu_{\max}$ cm^{-1} 3015, 1732, 1649, 1538. ^1H NMR (CDCl_3 , 300 MHz): δ 8.04 (s, 1H, E isomer), 7.56-7.51 (m, 2H, isomer I), 7.49 (s, 1H, Z isomer), 7.46-7.41 (m, 2H, isomer II), 7.17-7.07 (m, 4H), 4.44 (q, $J = 7.1$ Hz, 2H, isomer I), 4.37 (q, $J = 7.1$ Hz, 2H, isomer II), 1.36 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 166.6 (isomer I), 166.4 (isomer II), 163.2 (isomer I), 163.0 (isomer II), 135.2 (2C), 132.8 (isomer I), 132.7 (isomer I), 132.1 (isomer II), 132.0 (isomer II), 131.5 (2C), 125.2 (2C), 116.9 (isomer II), 116.8 (isomer I), 116.6 (isomer II), 116.5 (isomer I), 63.2 (isomer I), 63.1 (isomer II), 14.0 (isomer I), 13.7 (isomer II). HRMS: m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{11}\text{H}_{10}\text{FNNaO}_4$ 262.0492, found 262.0494.

Ethyl (E)-2-nitro-3-(4-nitrophenyl)acrylate (E-3c) (Method B)

Isolated yield 33%. Yellow oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 8:2). $\nu_{\max}$ cm^{-1} 3026, 1738, 1653, 1542. ^1H NMR (CDCl_3 , 300 MHz): δ 8.33-8.29 (m, 2H), 8.09 (s, 1H), 7.75-7.67 (m, 2H), 4.44 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 160.04, 136.0, 135.2, 133.5, 130.9 (2C), 129.7, 124.2 (2C), 63.6, 13.7. HRMS: m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{NaO}_6$ 289.0437, found 289.0433.

Ethyl (Z)-2-nitro-3-(4-nitrophenyl)acrylate (Z-3c) (Method B)

Isolated yield 49%. Yellow oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 8:2). ^1H NMR (CDCl_3 , 300 MHz): δ 8.23-8.17 (m, 2H), 7.60 (s, 1H), 7.57-7.52 (m, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 158.2, 139.9, 134.8, 133.6, 130.8, 130.0 (2C), 124.1 (2C), 63.5, 13.7. HRMS: m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{NaO}_6$ 289.0437, found 289.0440.

Ethyl (E)-3-(4-methoxyphenyl)-2-nitroacrylate (E-3d) (Method B)

Isolated yield 32%. Yellow oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 1:1). $\nu_{\max}$ cm^{-1} 2974, 1736, 1639, 1537. ^1H NMR (CDCl_3 , 300 MHz): δ 8.04 (s, 1H), 7.51-7.46 (m, 2H), 6.97-6.92 (m, 2H), 4.45 (q, $J = 7.1$ Hz, 2H), 3.87 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 163.2, 161.7, 139.8, 136.5, 132.9 (2C), 121.2, 114.8 (2C), 62.9, 55.5, 13.7. HRMS: m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{12}\text{H}_{13}\text{NNaO}_5$ 274.0691, found 274.0697.

Ethyl (Z)-3-(4-methoxyphenyl)-2-nitroacrylate (Z-3d)

Isolated yield 62%. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 1:1). ^1H NMR (CDCl_3 , 300 MHz): δ 7.46 (s, 1H), 7.41-7.36 (m, 2H), 6.94-6.89 (m, 2H), 4.36 (q, $J = 7.1$ Hz, 2H), 3.85 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 162.82, 159.5, 138.1, 132.5, 132.1 (2C), 121.3, 114.9 (2C), 62.7, 55.4, 14.0. HRMS: m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{12}\text{H}_{13}\text{NNaO}_5$ 274.0691, found 274.0694.

Ethyl (E)-3-(furan-2-yl)-2-nitroacrylate (E-3f) (Method B)

Isolated yield 36%. Yellow oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 4:6). $\nu_{\max}$ cm^{-1} 3015, 1737, 1645, 1520. ^1H NMR (CDCl_3 , 300 MHz): δ 7.85 (s, 1H), 7.64-7.63 (m, 1H), 7.05 (d, $J = 3.6$ Hz, 1H), 6.61 (dd, $J = 3.6$ Hz, 1.8 Hz, 1H), 4.47 (q, $J = 7.1$ Hz, 2H), 1.40 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 160.4, 148.3, 145.0, 122.7, 120.6, 119.2, 113.6, 62.6, 13.5. HRMS: m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_9\text{H}_9\text{NNaO}_5$ 234.0378, found 234.0372.

Ethyl (Z)-3-(furan-2-yl)-2-nitroacrylate (Z-3f) (Method B)

Isolated yield 56%. Yellow oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 4:6). ^1H NMR (CDCl_3 , 300 MHz): δ 7.61-7.60 (m, 1H), 7.35 (s, 1H), 6.92 (d, $J = 3.6$ Hz, 1H), 6.56 (dd, $J = 1.8$ Hz, 3.6 Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 1.34 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 159.1,

147.8, 145.1, 122.3, 120.6, 119.3, 113.0, 62.6, 13.7. HRMS: m/z $[M + Na]^+$ calcd. for $C_9H_9NNaO_5$ 234.0378, found 234.0382.

Ethyl (*E/Z*)-2-nitro-3-(thiophen-2-yl)acrylate (*E/Z*-3g) (Method A, *E/Z* = 40:60)

Isolated yield 83%. Brown oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 8:2). ν_{max} cm^{-1} 3021, 1731, 1632, 1537. 1H NMR ($CDCl_3$, 300 MHz): δ 8.24 (s, 1H, minor isomer), 7.79-7.75 (m, 1H, minor), 7.71 (s, 1H, major isomer), 7.69-7.66 (m, 1H, major), 7.57-7.55 (m, 1H, minor), 7.47-7.45 (m, 1H, major), 7.23-7.13 (m, 2H), 4.47 (q, J = 7.1 Hz, 2H, minor), 4.36 (q, J = 7.1 Hz, 2H, major), 1.41 (t, J = 7.1 Hz, 3H, minor), 1.35 (t, J = 7.1 Hz, 3H, major). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.6 (minor isomer), 159.2 (major isomer), 143.8 (minor), 143.7 (major), 138.0 (2C), 136.2 (major), 135.7 (minor), 135.2 (major), 134.9 (minor), 128.4 (minor), 128.3 (2C), 128.1 (major), 62.9 (minor), 62.7 (major), 13.8 (major), 13.5 (minor). HRMS: m/z $[M + Na]^+$ calcd. for $C_9H_9N Na O_4 S$ 250.0150, found 250.0155.

Ethyl (*E/Z*)-3-(furan-3-yl)-2-nitroacrylate (*E/Z*-3h) (Method A, *E/Z* = 30:70)

Isolated yield 97%. Brown oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 8:2). ν_{max} cm^{-1} 2985, 1730, 1648, 1534. 1H NMR ($CDCl_3$, 300 MHz): δ 7.96 (s, 1H, minor isomer), 7.95-7.93 (m, 1H, minor), 7.83-7.82 (m, 1H, major isomer), 7.52-7.50 (m, 1H, minor), 7.48-7.47 (m, 1H major), 7.46 (s, 1H major), 6.56-6.54 (m, 1H, minor), 6.47-6.455 (m, 1H, major), 4.45 (q, J = 7.1 Hz, 2H, minor), 4.35 (q, J = 7.1 Hz, 2H, major), 1.39 (t, J = 7.1 Hz, 3H, minor), 1.34 (t, J = 7.1 Hz, 3H major). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.1 (major isomer), 161.0 (minor isomer), 149.3 (2C), 148.0 (2C), 145.4 (major), 145.3 (minor), 127.9 (minor), 124.4 (major), 116.9 (minor), 116.8 (major), 108.8 (minor), 107.8 (major), 62.9 (minor), 62.8 (major), 13.9 (major), 13.7 (minor). HRMS: m/z $[M + Na]^+$ calcd. for $C_9H_9N Na O_5$ 234.0378, found 234.0373.

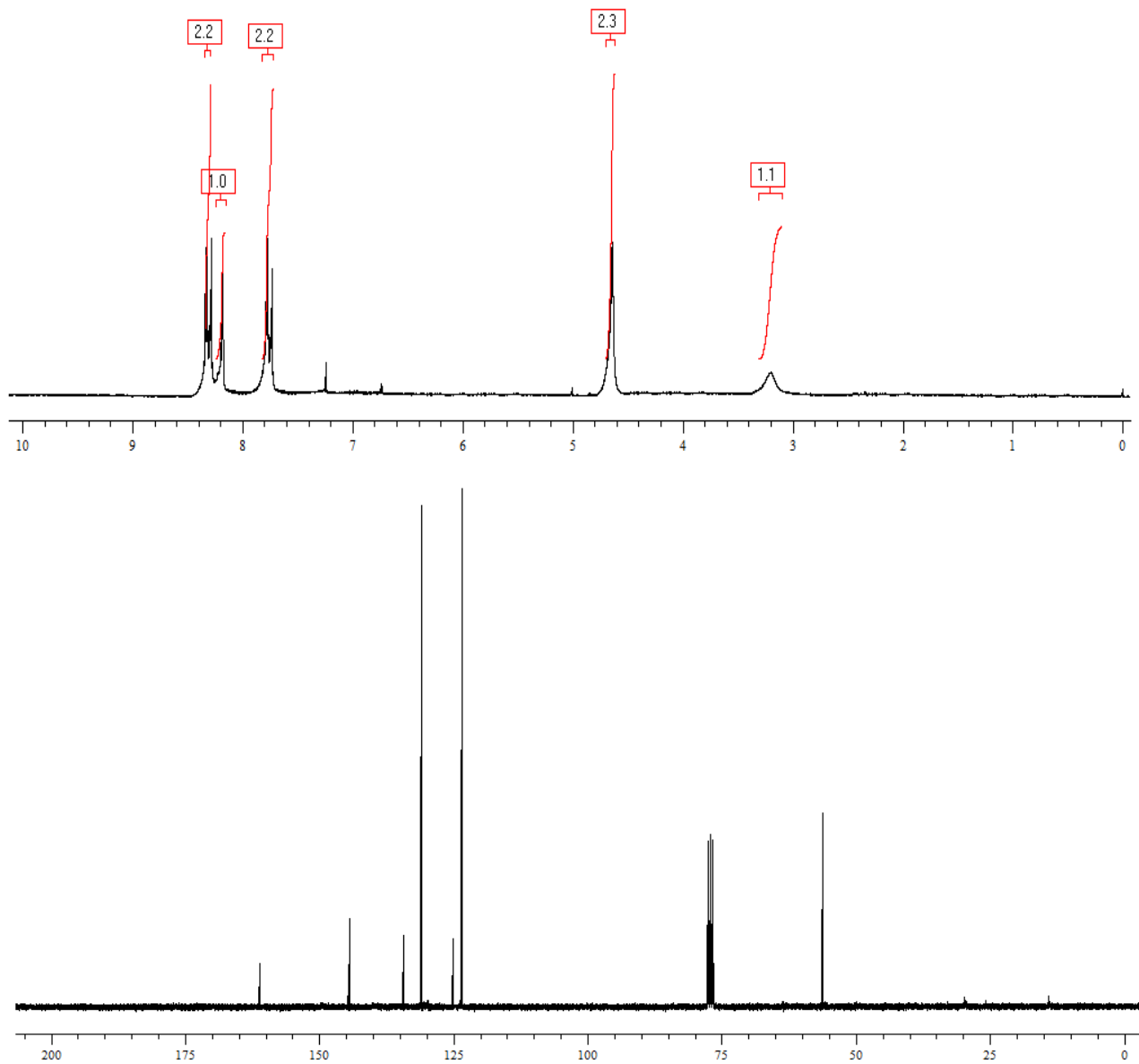
Ethyl (*E/Z*)-3-(naphthalen-1-yl)-2-nitroacrylate (*E/Z*-3i) (Method A, *E/Z* = 40:60)

Isolated yield 51%. Yellow oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 85:15). ν_{max} cm^{-1} 3018, 1730, 1646, 1540. 1H NMR ($CDCl_3$, 300 MHz): δ 8.81 (s, 1H, minor isomer), 8.31 (s, 1H, major isomer), 8.12-8.10 (m, 1H, minor), 8.09-8.07 (m, 1H, major), 7.97-7.87 (m, 4H), 7.73-7.53 (m, 4H), 7.51-7.41 (m, 4H), 4.44 (q, J = 7.1 Hz, 2H, major), 4.31 (q, J = 7.1 Hz, 2H, minor), 1.41 (t, J = 7.1 Hz, 3H, major), 1.19 (t, J = 7.1 Hz, 3H, minor). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.5 (minor isomer), 158.7 (major isomer), 143.6 (minor), 143.0 (major), 136.3 (2C), 134.9 (minor), 134.7 (major), 133.2 (minor), 133.1 (major), 131.6 (2C), 128.7 (2C), 127.3 (2C), 126.6 (2C), 126.3 (2C), 125.2 (major), 124.9 (minor), 124.6 (major), 124.5 (minor), 123.1 (minor), 123.0 (major), 62.9 (major), 62.7 (minor), 13.8 (major), 13.3 (minor). HRMS: m/z $[M + Na]^+$ calcd. for $C_{15}H_{13}N Na O_4$ 294.0742, found 294.0745.

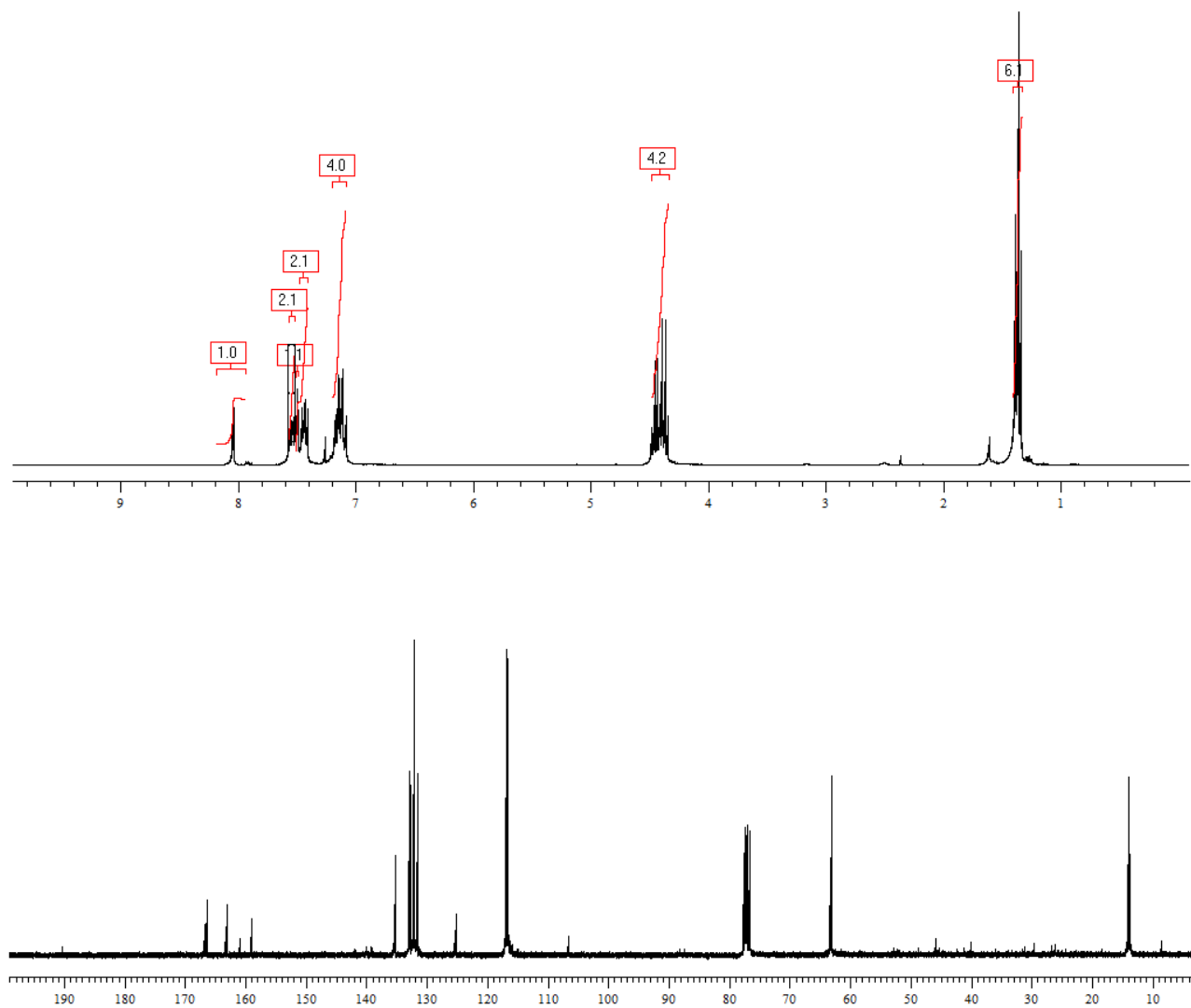
Ethyl (*E/Z*)-5-methyl-2-nitrohex-2-enoate (*E/Z*-3j) (Method B, *E/Z* = 30:70)

Isolated yield 95%. Yellow pail oil. Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 9:1). ν_{max} cm^{-1} 2965, 1731, 1662, 1542. 1H NMR ($CDCl_3$, 300 MHz): δ 7.25 (t, J = 8.3 Hz, 1H, minor isomer), 6.87 (t, J = 8.0 Hz, 1H, major isomer), 4.36 (q, J = 7.1 Hz, 2H, minor), 4.30 (q, J = 7.1 Hz, 2H, major), 2.30 (dd, J = 6.8 Hz, 8.3 Hz, 2H, minor), 2.15 (dd, J = 6.9 Hz, 8.0 Hz, 2H, major), 1.94-1.78 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H, minor), 1.31 (t, J = 7.1 Hz, 3H, major), 0.96 (d, J = 6.5 Hz, 6H, minor), 0.95 (d, J = 6.6 Hz, 6H, major). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.8 (minor isomer), 158.6 (major isomer), 142.2 (2C), 138.9 (2C), 62.7 (major), 62.5 (minor), 36.7 (major), 36.4 (minor), 28.2 (minor), 27.9 (major), 22.3 (2C, minor), 22.2 (2C, major), 13.9 (2C). HRMS: m/z $[M + Na]^+$ calcd. for $C_9H_{15}N Na O_4$ 224.0899, found 224.0896.

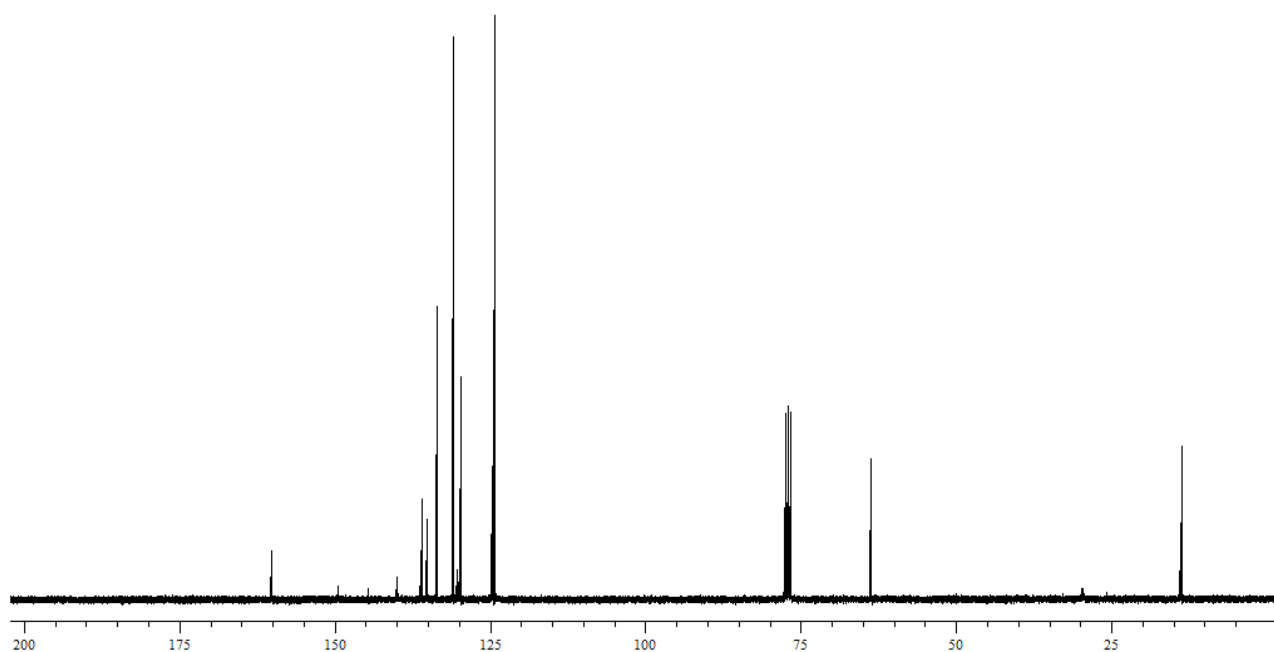
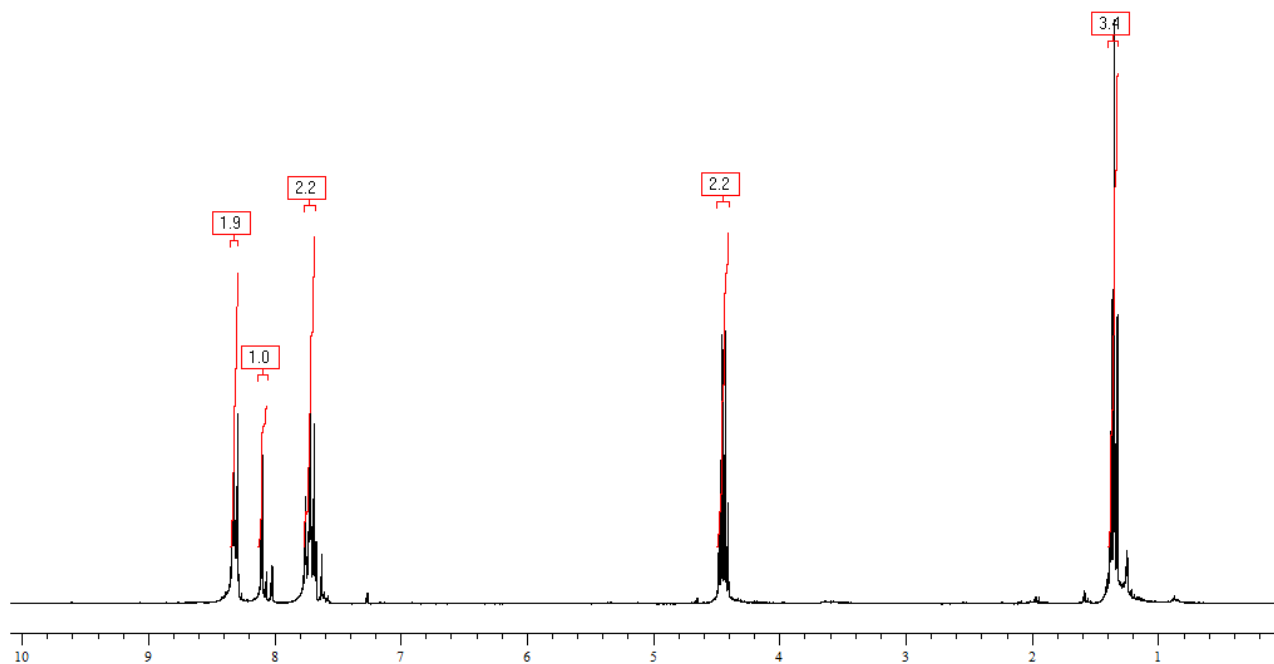
(E)-2c



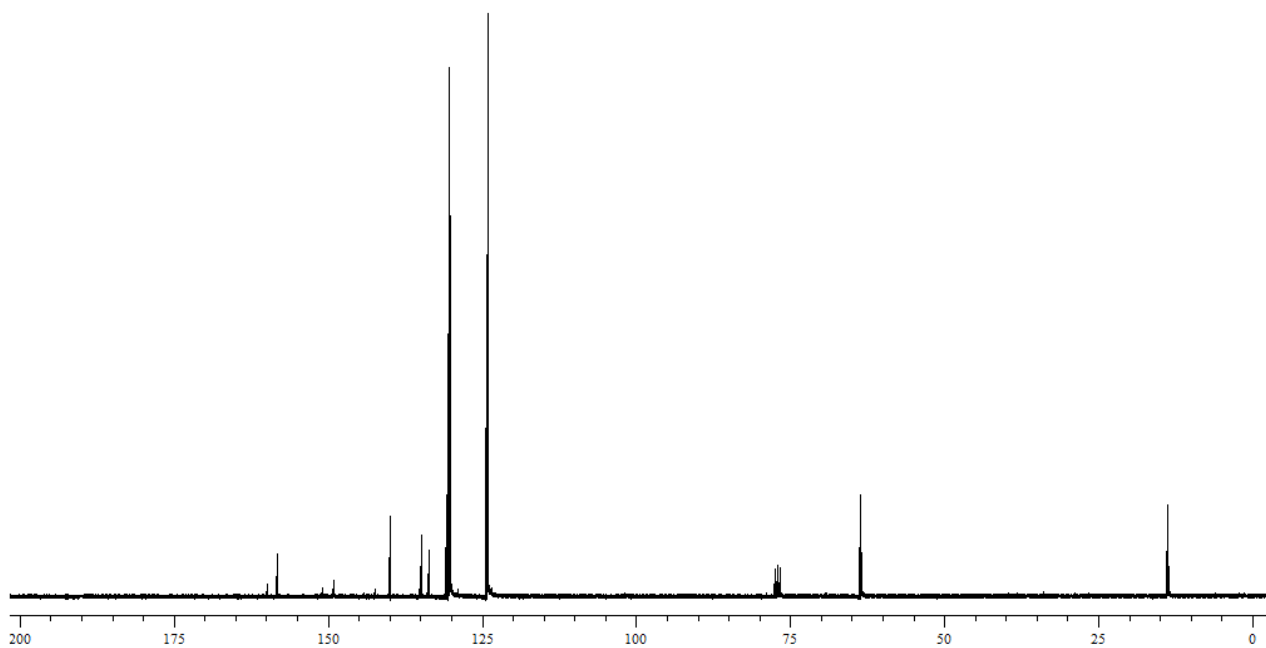
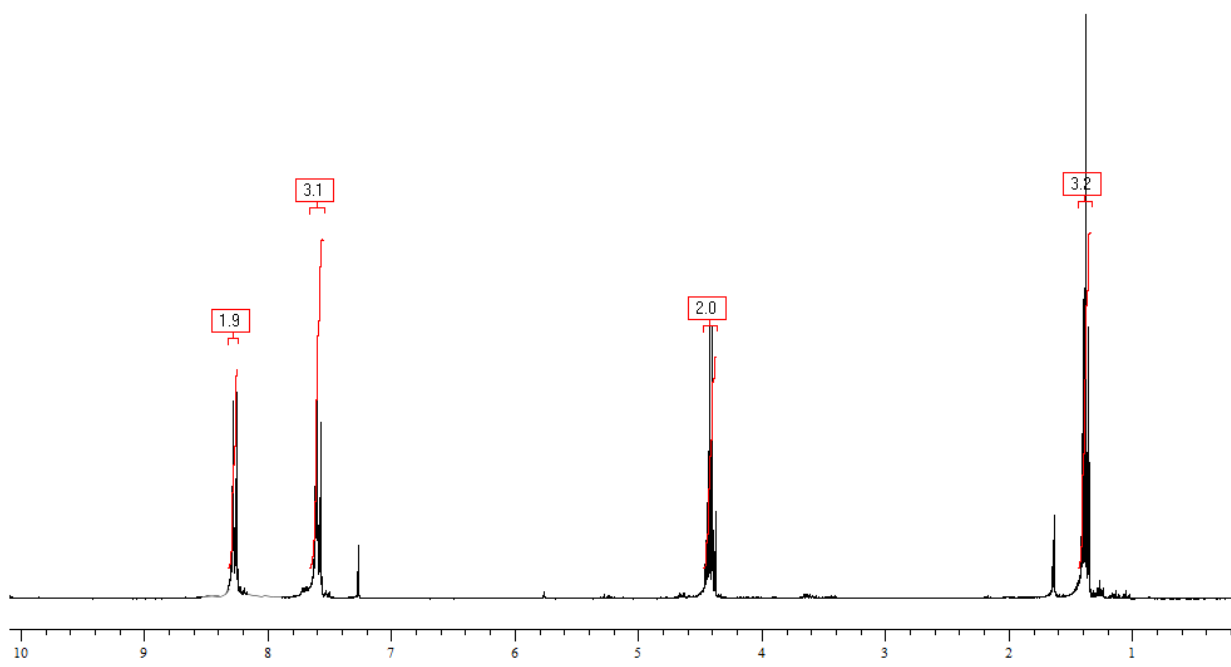
(E/Z)-3b



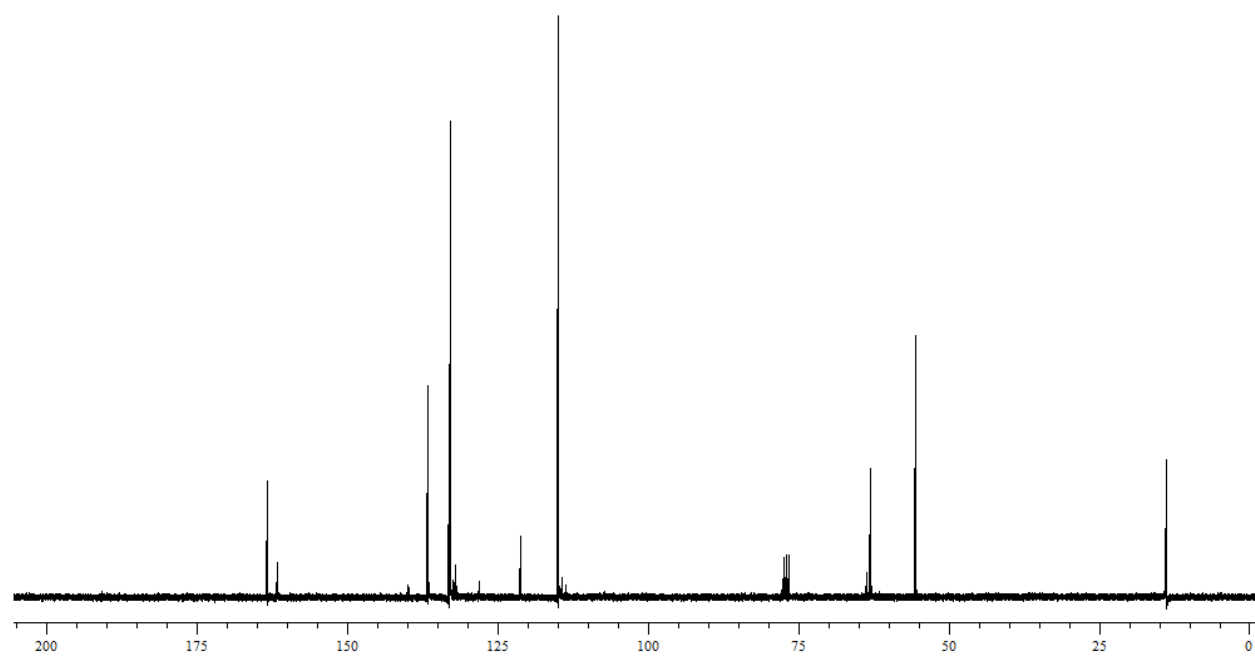
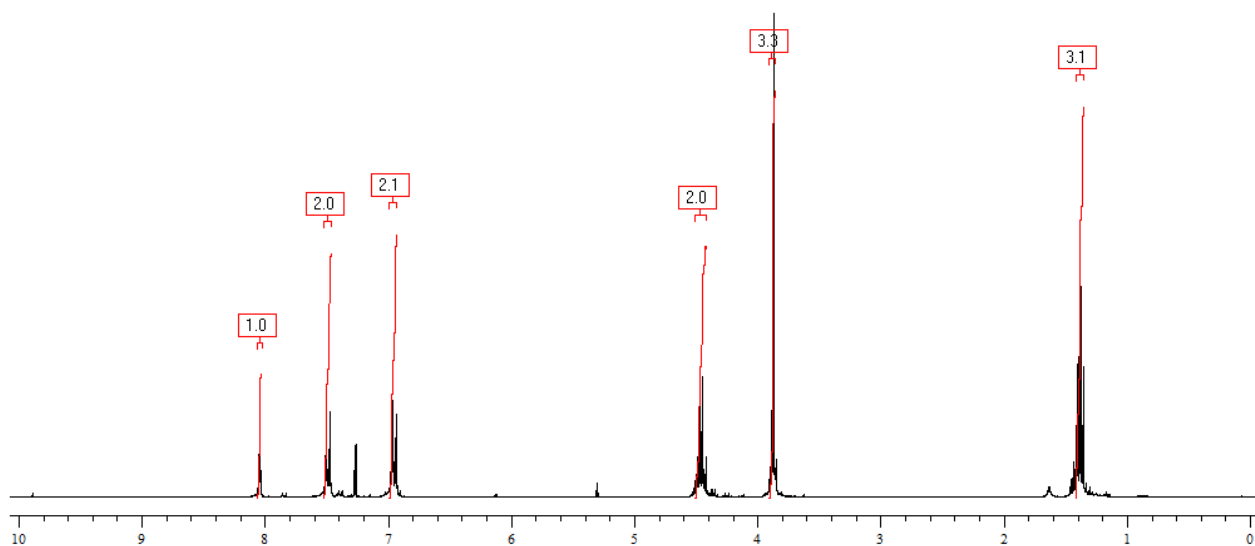
(E)-3c



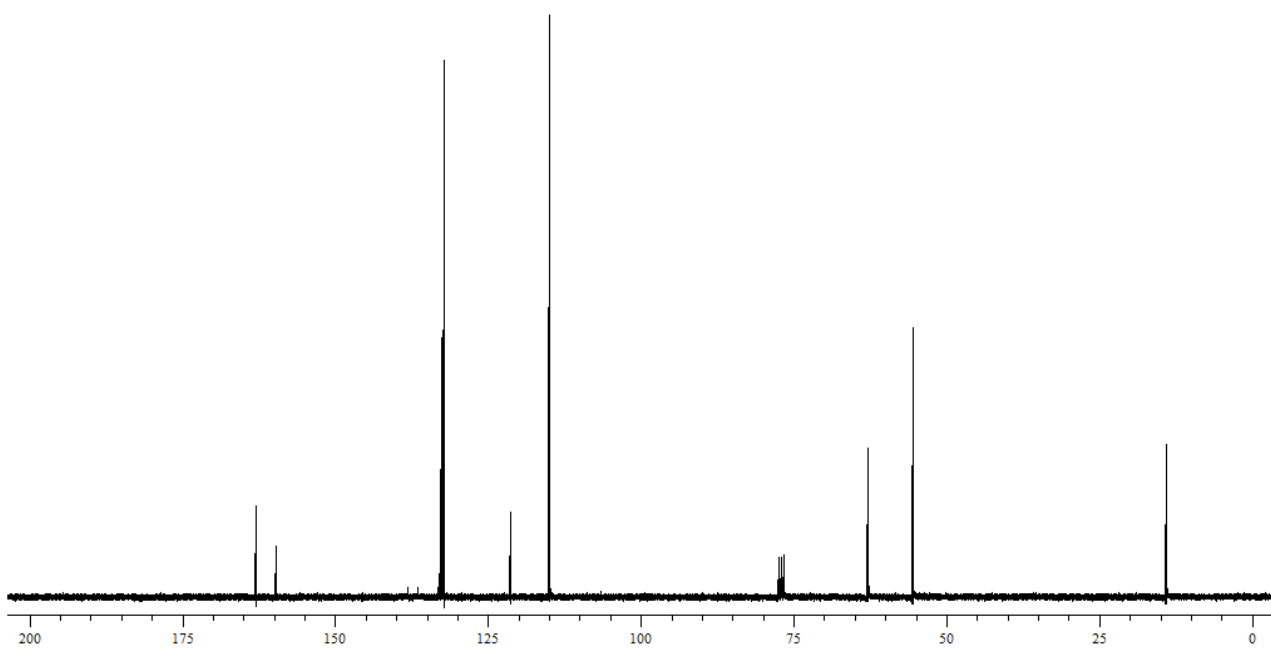
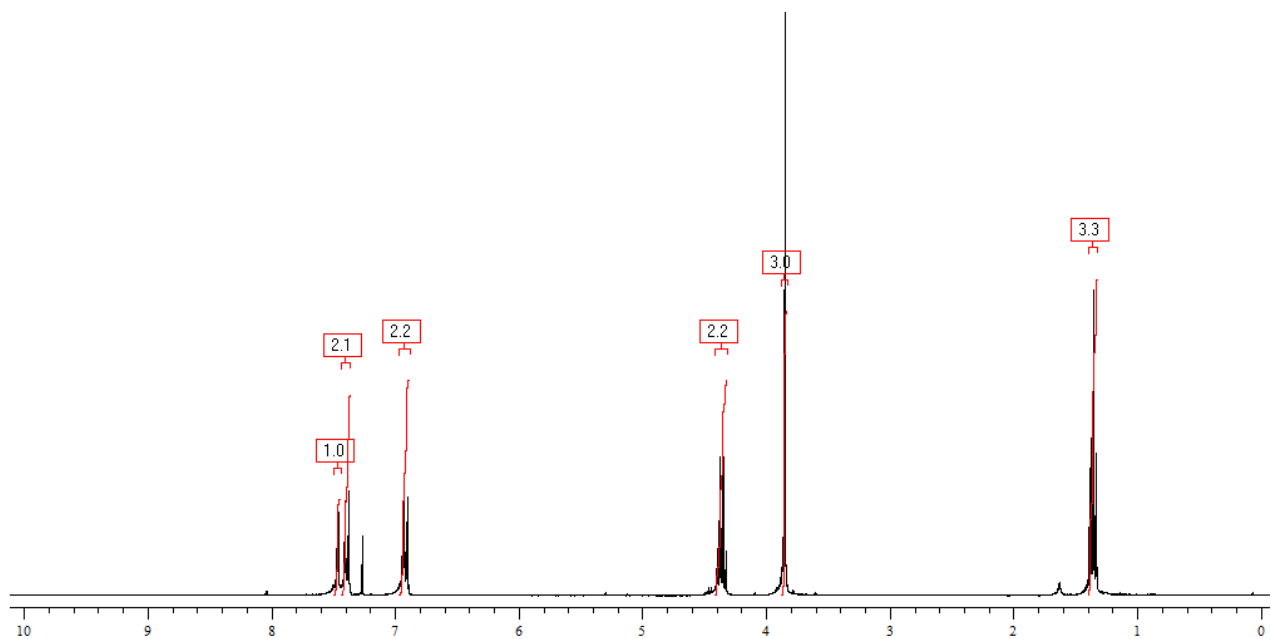
(Z)-3c



(*E*)-3d

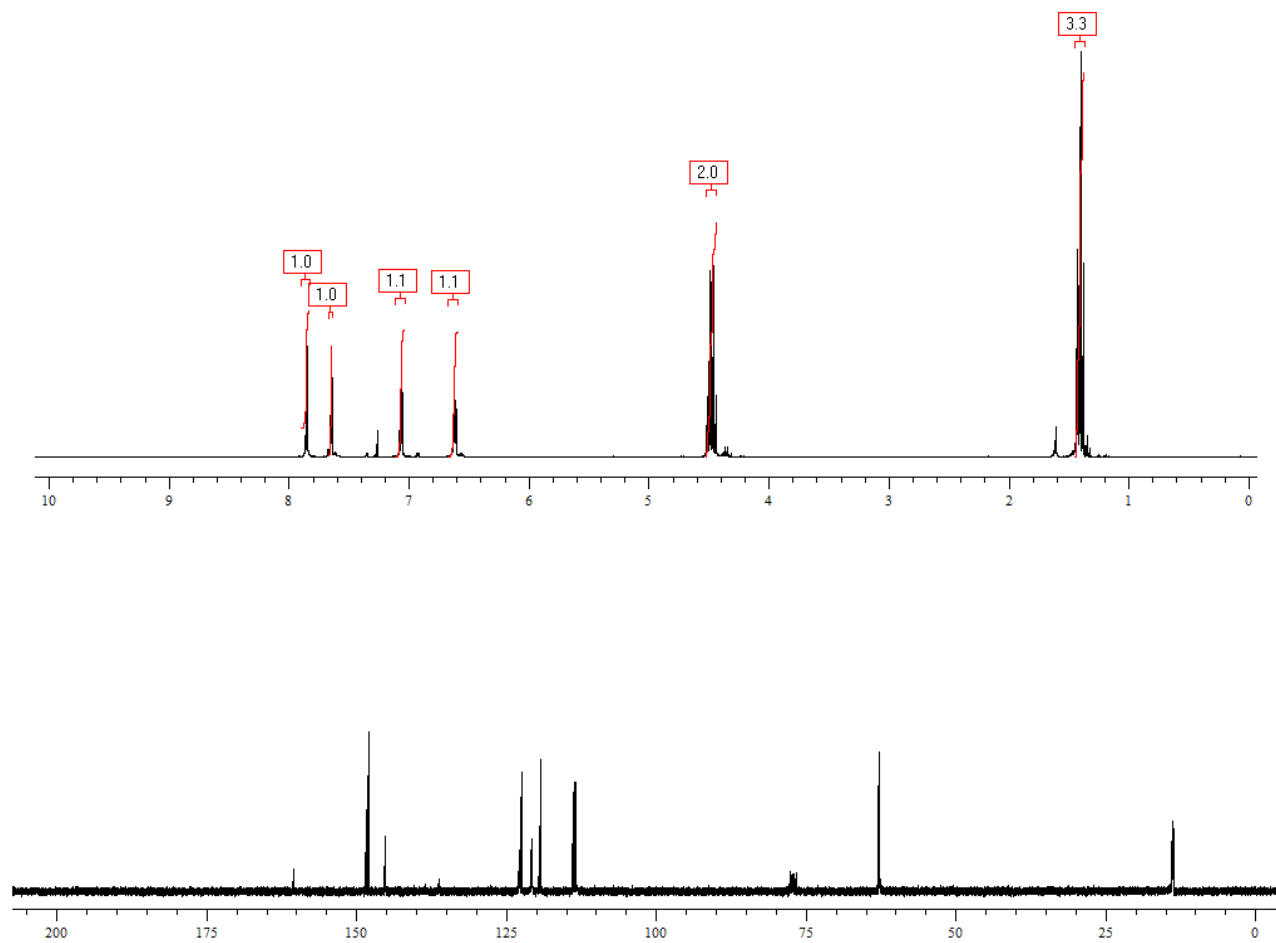


(Z)-3d



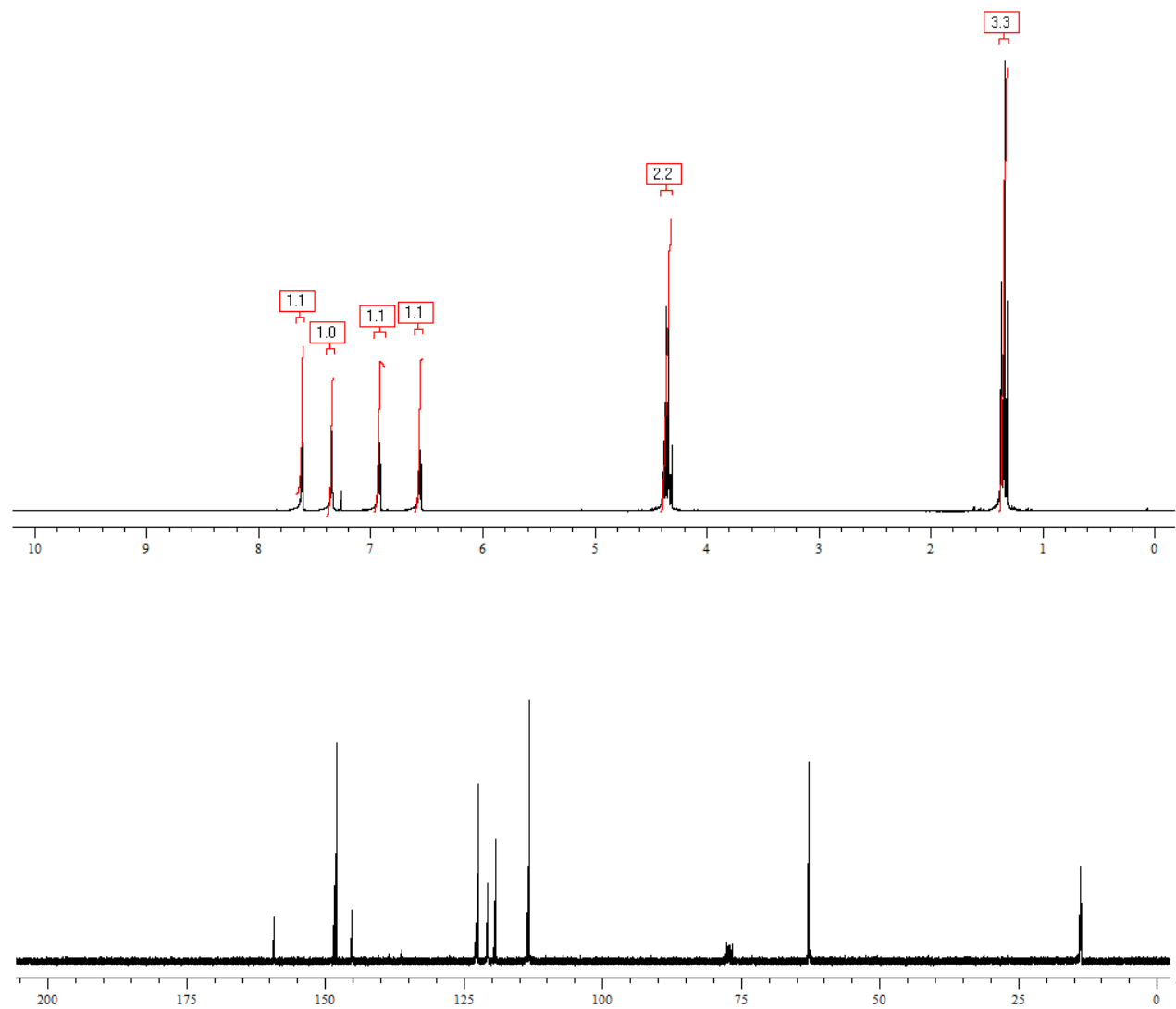
Supplementary Material (ESI) for Organic and Biomolecular Chemistry

(*E*)-3f

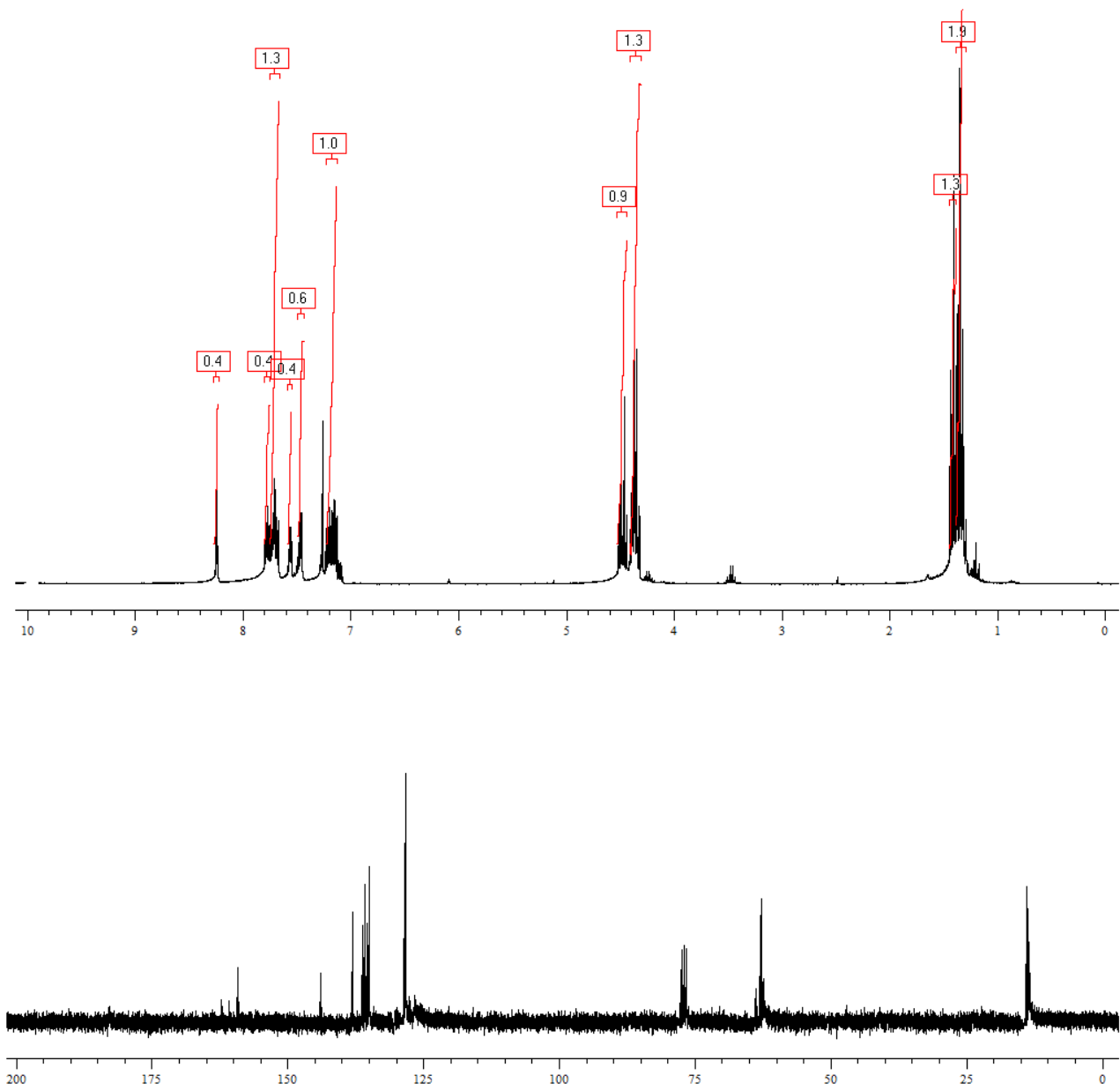


Supplementary Material (ESI) for Organic and Biomolecular Chemistry

(Z)-3f

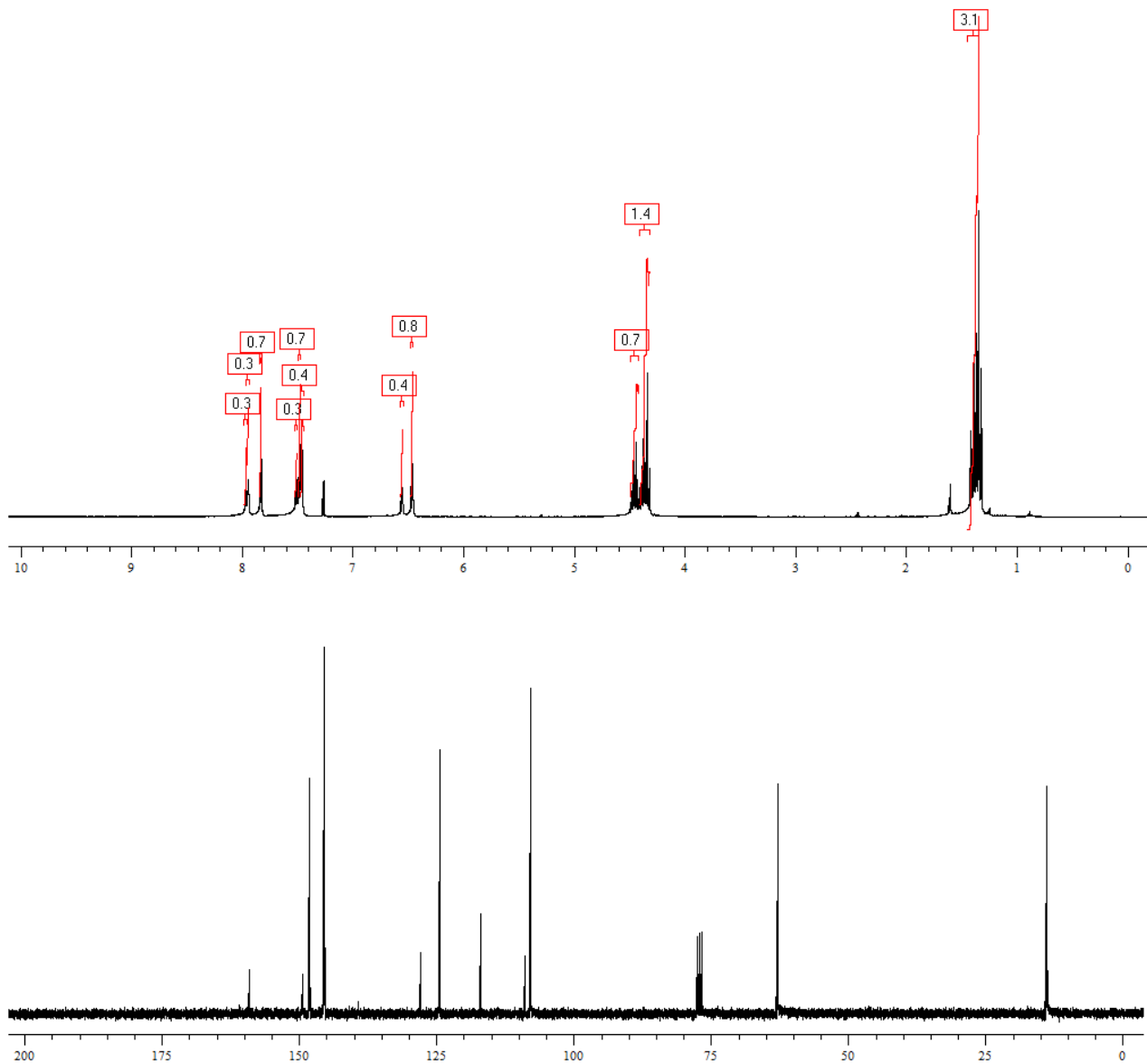


(E/Z)-3g

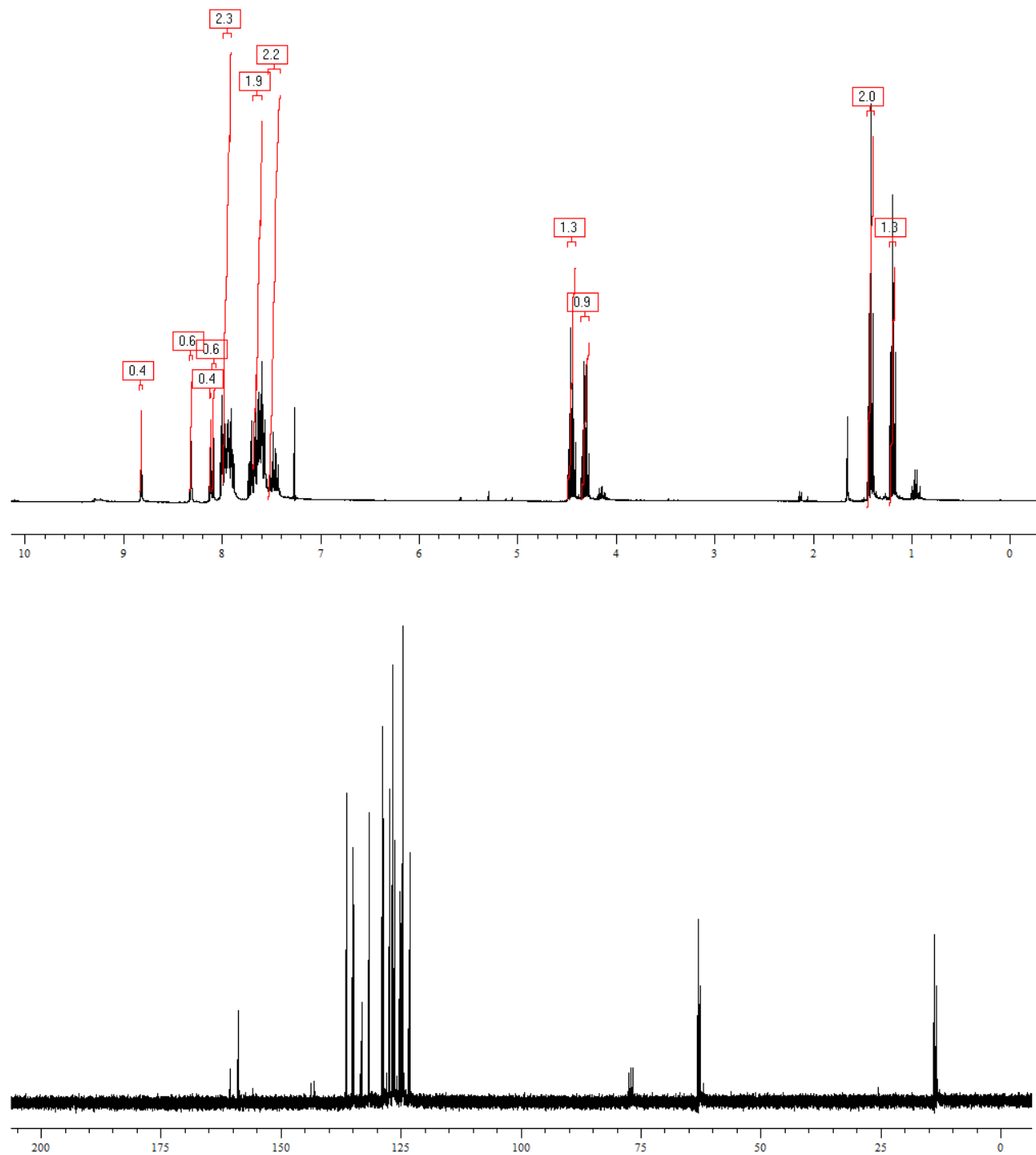


Supplementary Material (ESI) for Organic and Biomolecular Chemistry

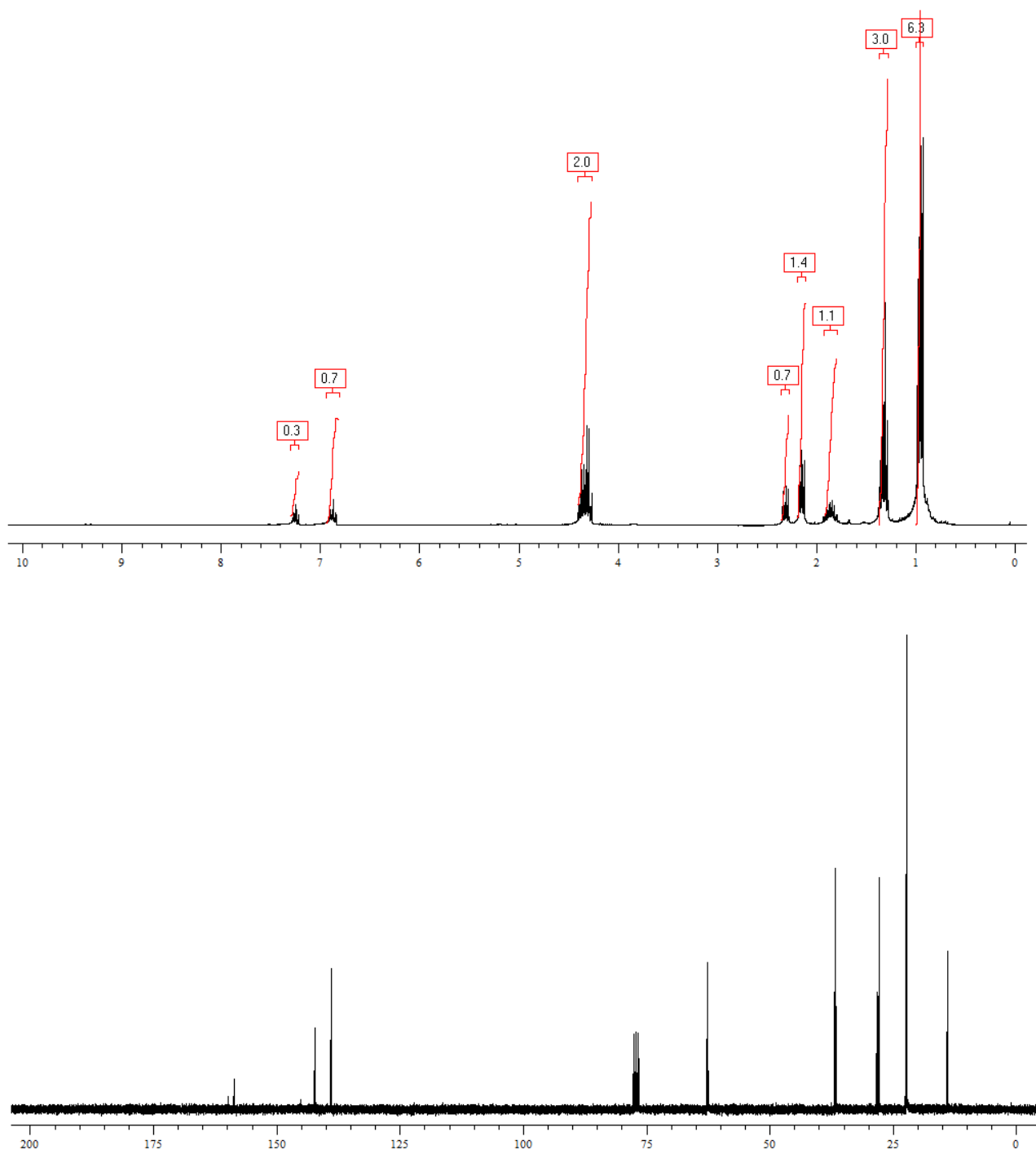
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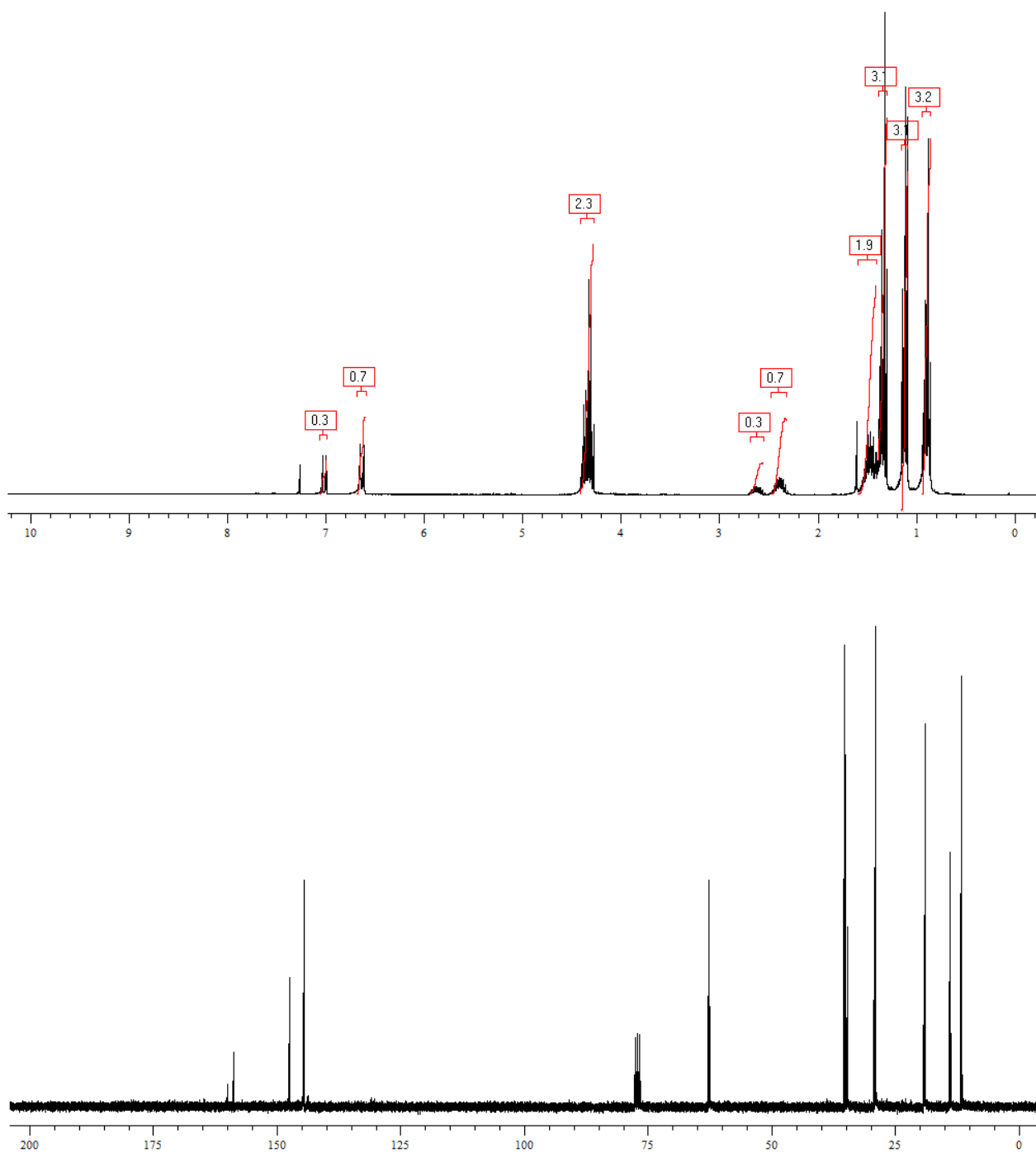
(E/Z)-3i



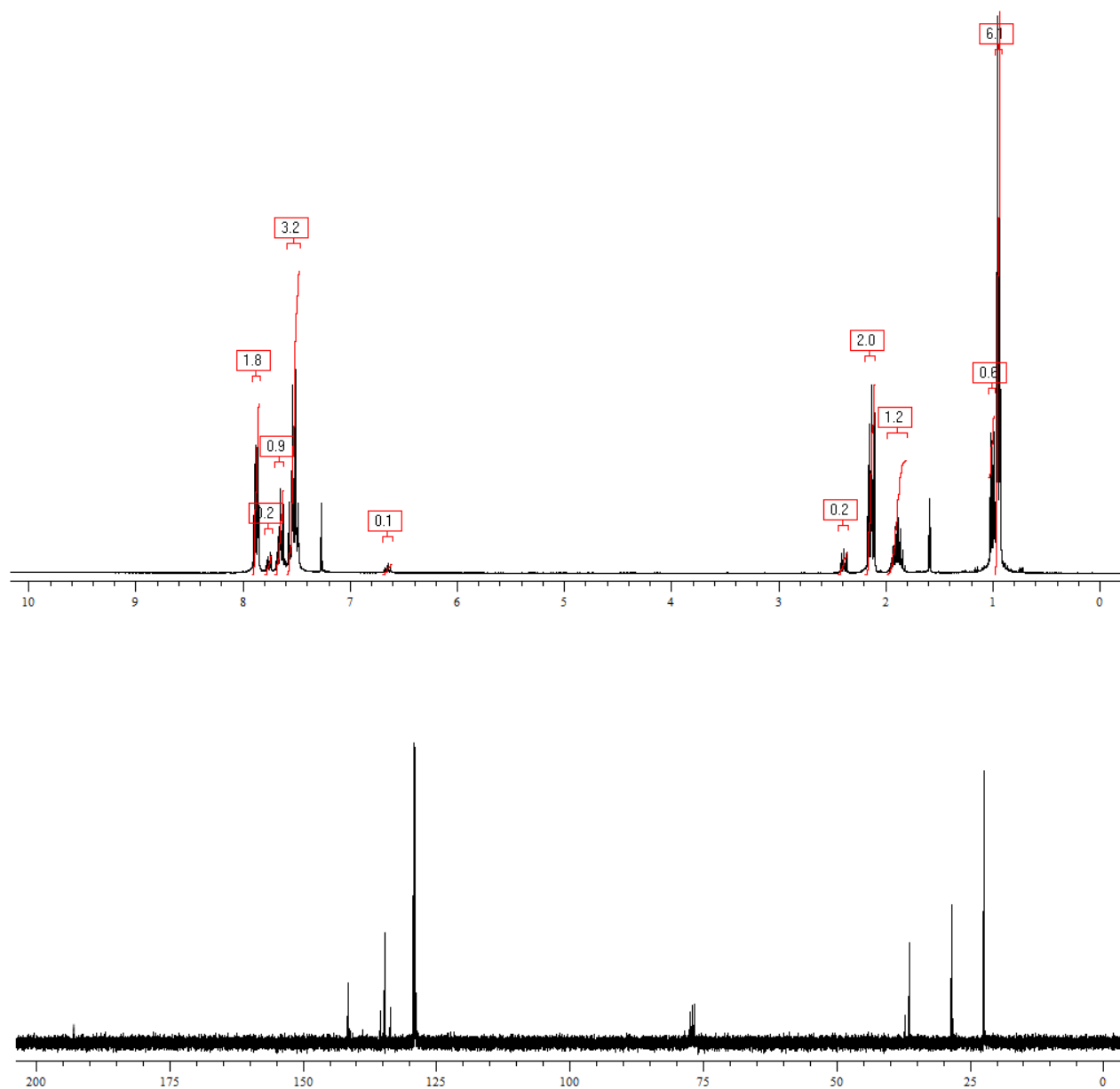
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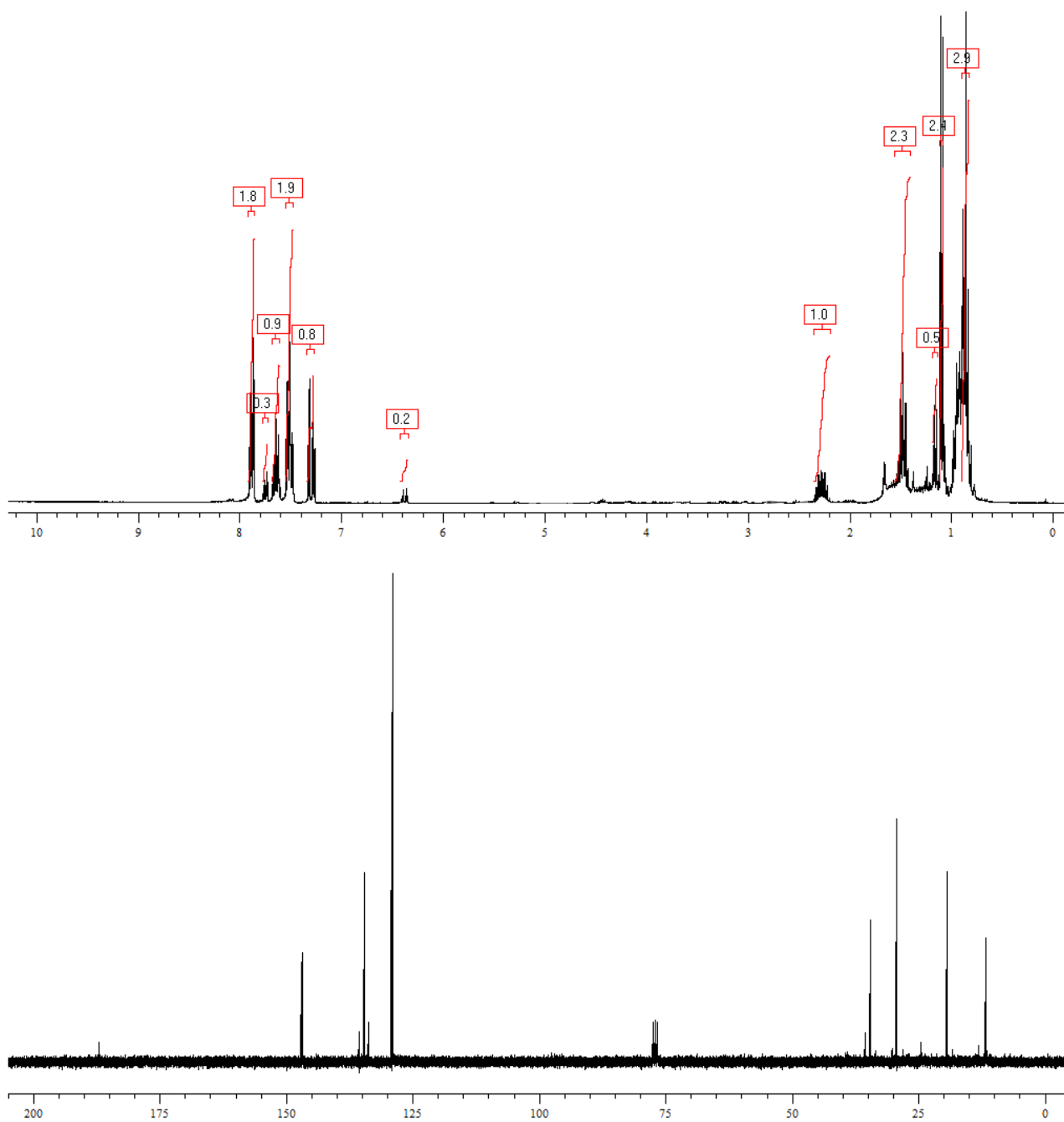
(*E/Z*)-3k



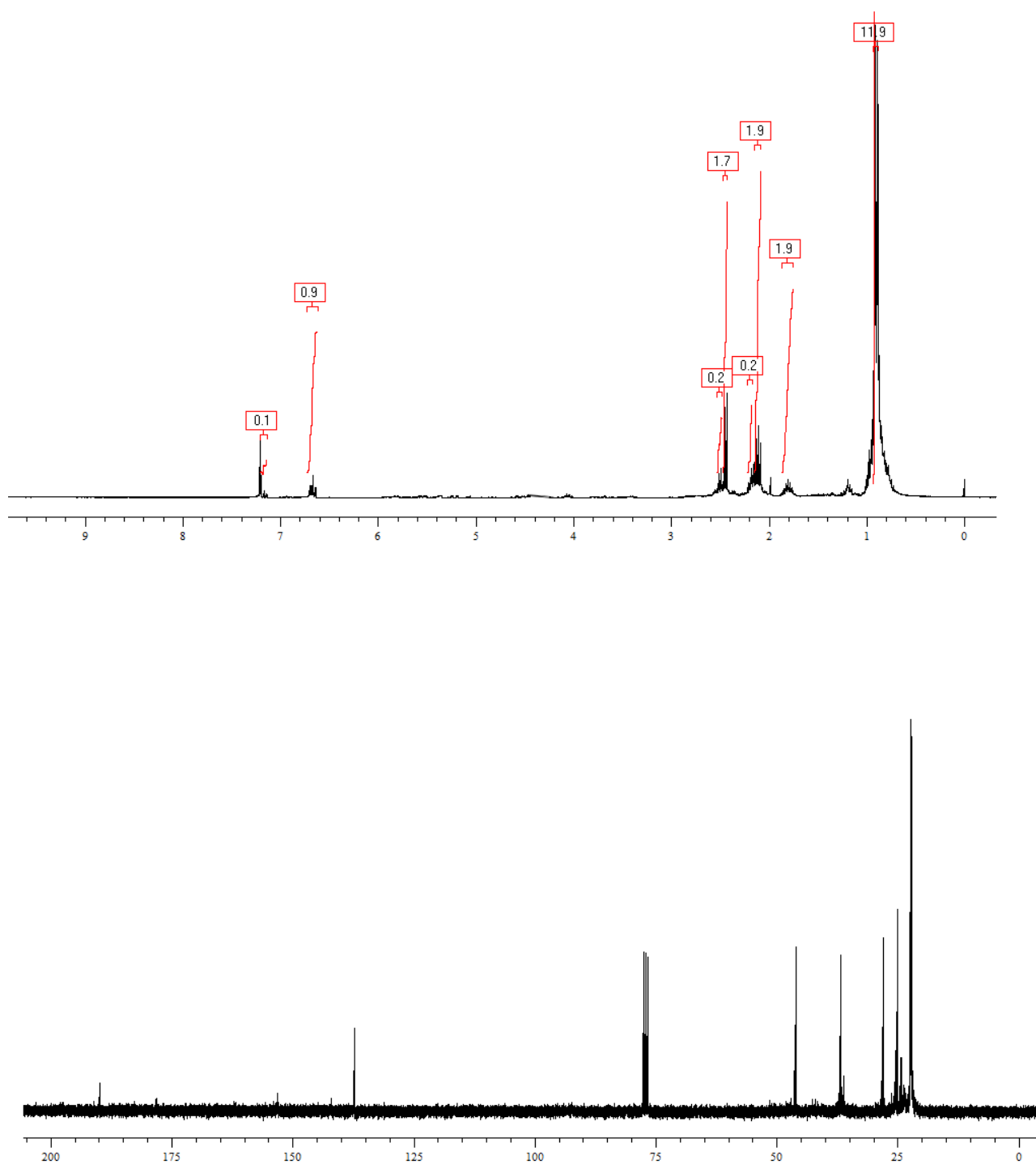
(E/Z)-6



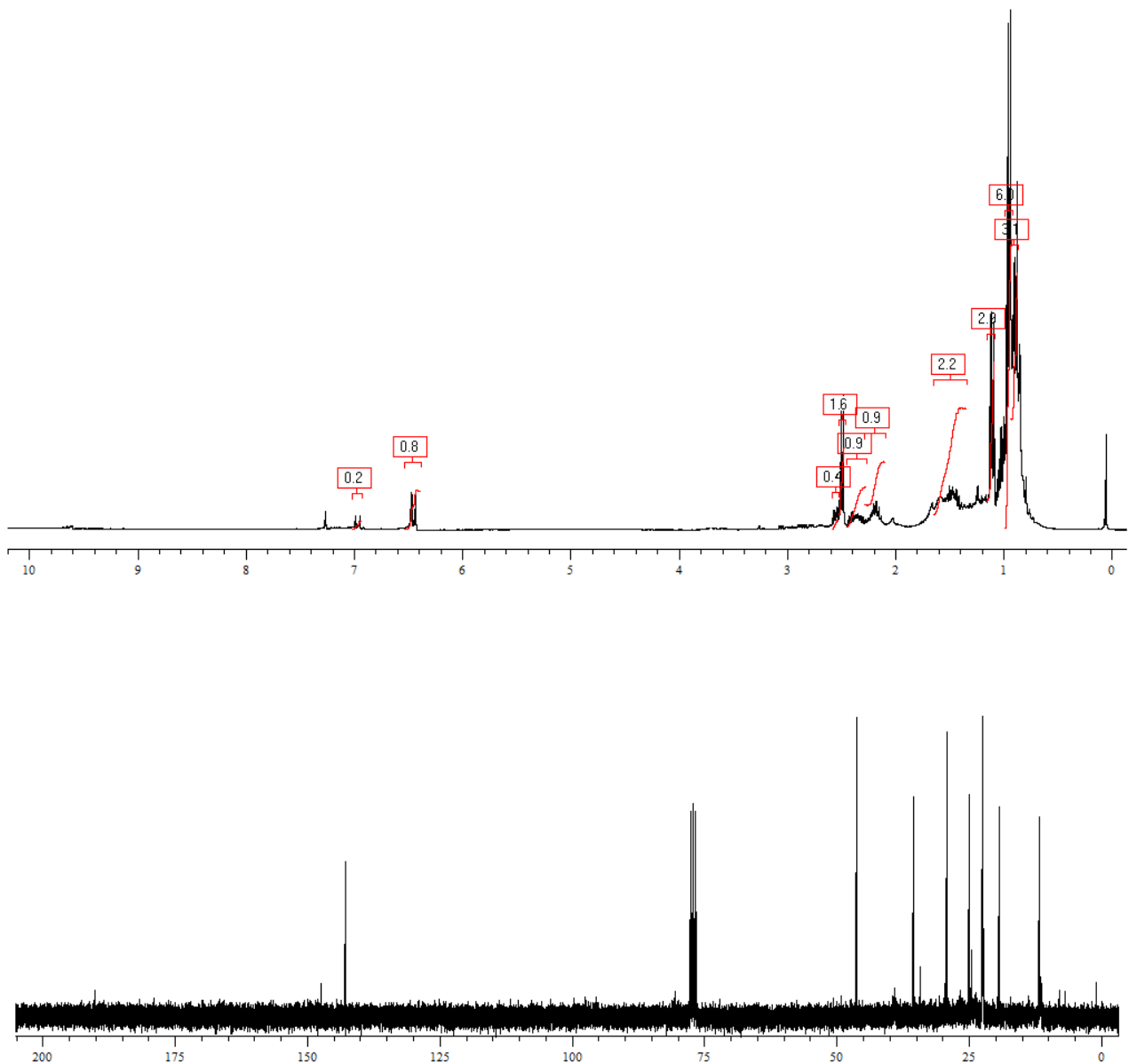
(E/Z)-7



(E/Z)-9



(E/Z)-10



(E/Z)-11

