

Supporting Information

A Novel Ketone Olefination via Organozinc Reagents in the Presence of Diphenyl Phosphite

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Experimental Section

General: THF was distilled from sodium benzophenone under nitrogen. All reactions were conducted under a nitrogen atmosphere. Metallic zinc and all solvents were purchased from commercial source, without further purification before use. The flash column chromatography was carried out on Merck silica gel (300–400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer as solutions in CDCl_3 . Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal ($\delta = 77.50$ ppm). High-resolution mass spectra were obtained with a GCT-TOF instrument.

Materials: All chemicals were purchased from Aldrich, Alfa or Acros chemical company and used thus, without further purification. Petroleum ether (PE) used refers to the 60–90 °C boiling point fraction of petroleum.

General procedure for the synthesis of organozinc reagent: Alkyl bromide (128 μL , 1.5 mmol) and zinc powder (0.1170 g, 1.8 mmol) in dry THF (3 mL) under a nitrogen atmosphere at room temperature. (for **4b** and **4c**, 5% I_2 was added to trigger the reaction.) The mixture was stirred for about 15 min, and zinc powder disappeared. The stirring was continued to 0.5 h. **2d** and **2e** were prepared according to Knochel's method.¹ The concentration of organozinc reagents was determined by titration with I_2 .²

General procedure for the olefination reaction: A solution of organozinc reagent in THF (1.5 mmol) was added to a solution of carbonyl compounds (0.5 mmol) in dry THF (3 mL) under a nitrogen atmosphere at room temperature. The mixture was stirred for about 30 min. Then diphenyl phosphite (0.6 mmol) was added (the reaction was monitored by TLC). The reaction mixture was stirred for 5h at 50 °C and then was quenched with dilute hydrochloric acid. The resulting mixture was extracted with diethyl ether (3×10 mL), and dried over anhydrous Na_2SO_4 . The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded olefins (300–400 mesh, petroleum ether and ethyl acetate as eluent).

1 Krasovskiy, A.; Malakhov, V.; Gavryushin, A.; Knochel, P. *Angew. Chem., Int. Ed.* 2006, **45**, 6040.
2 Ren, H.; Dunet, G.; Mayer, P.; Knochel, P. *J. Am. Chem. Soc.* 2007, **129**, 5376.

Characterization Data of Compounds

1,1-diphenylbuta-1,3-diene (3a)¹² The title compound was obtained according to the general procedure. Colourless oil; Yield: 87%; IR (KBr): 3080, 3056, 3026, 1666, 1619, 1598, 1493, 1445, 905, 765, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.38–7.16 (m, 10H), 6.71 (d, *J* = 11.0 Hz, 1H), 6.44 (td, *J* = 10.5 Hz, *J* = 16.9 Hz, 1H), 5.38 (d, *J* = 16.8 Hz, 1H), 5.11 (d, *J* = 10.1 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 143.64, 142.58, 140.14, 135.46, 130.93, 129.03, 128.71, 128.68, 128.10, 128.02, 127.90, 119.15. HRMS (EI⁺) calcd for C₁₆H₁₄ (M⁺): 206.1096; found: 206.1096.

1,1-bis(4-chlorophenyl)buta-1,3-diene (3b)¹² The title compound was obtained according to the general procedure. Colourless oil; Yield: 85%; IR (KBr): 3033, 1668, 1590, 1488, 1401, 908, 765, 730 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 11.0 Hz, 1H), 6.38 (td, *J* = 10.5 Hz, *J* = 16.9 Hz, 1H), 5.42 (d, *J* = 16.7 Hz, 1H), 5.18 (d, *J* = 10.0 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 141.06, 140.59, 137.99, 134.75, 134.02, 132.16, 129.74, 129.66, 129.22, 129.03, 128.91, 120.35. HRMS (EI⁺) calcd for C₁₆H₁₂³⁵Cl₂ (M⁺): 274.0316; found: 274.0316; HRMS(EI⁺) calcd for C₁₆H₁₂³⁷Cl₂ (M⁺): 276.0287; found: 276.0280.

1,1-bis(4-methoxyphenyl)buta-1,3-diene (3c)¹² The title compound was obtained according to the general procedure. Colourless oil; Yield: 92%; IR (KBr): 3035, 3002, 1659, 1605, 1505, 1463, 1287, 908, 831, 780 cm⁻¹; ¹H NMR (400 MHz CDCl₃): δ 7.21 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.4, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 11.0 Hz, 1H), 6.46 (td, *J* = 10.4 Hz, *J* = 16.7 Hz, 1H), 5.33 (d, *J* = 16.6 Hz, 1H), 5.07 (d, *J* = 9.9 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 159.51, 159.21, 142.72, 135.60, 135.42, 132.46, 131.95, 129.19, 127.04, 117.64, 113.87, 113.81, 55.59. HRMS (EI⁺) calcd for C₁₈H₁₈O₂ (M⁺): 266.1307; found: 266.1306.

9-allylidene-9H-fluorene (3d)¹⁸ The title compound was obtained according to the general procedure. Yellow oil; Yield: 71%; IR (KBr): 3061, 1659, 1609, 1476, 1448, 938, 917, 760, 730 cm⁻¹; ¹H NMR (300 MHz CDCl₃): δ 7.94 (d, *J* = 7.4 Hz, 1H), 7.73–7.67 (m, 3H), 7.60–7.47 (m, 1H), 7.37–7.22 (m, 4H), 7.15 (d, *J* = 11.7 Hz, 1H), 5.68 (d, *J* = 16.5 Hz, 1H), 5.56 (d, *J* = 9.9 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 141.28, 139.68, 139.45, 137.39, 135.65, 133.09, 128.35, 128.28, 127.42, 127.25, 127.20, 125.45, 123.84, 120.43, 120.17, 119.87. HRMS (EI⁺) calcd for C₁₆H₁₂ (M⁺): 204.0939; found: 204.0942.

Tricyclo[3.3.1.1^{3,7}]decane, 2-(2-propen-1-ylidene) (3e)¹⁹ The title compound was obtained according to the general procedure. Colourless oil; Yield: 85%; IR (KBr): 3042, 2908, 1674, 987, 968, 951, 890 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 6.63 (td, *J* = 10.6 Hz, *J* = 16.8 Hz, 1H), 5.78 (d, *J* = 11.0 Hz, 1H), 5.10 (d, *J* = 16.8 Hz, 1H), 4.93 (d, *J* = 9.1 Hz, 1H), 3.03 (s, 1H), 3.38 (s, 1H), 1.96–1.74 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz): δ 152.70, 132.63, 118.25, 114.14, 40.89, 40.03, 39.19, 37.40, 33.04, 28.75. HRMS (EI⁺) calcd for C₁₃H₁₈ (M⁺): 174.1409; found: 174.1410.

1,2-dichloro-4-(1-phenylbuta-1,3-dienyl)benzene (3f) The title compound was obtained according to the general procedure. Colourless oil;

Yield: 86%; Compound purity: 100% (confirmed by HPLC); IR (KBr): 3058, 1549, 1493, 1469, 1445, 945, 908, 765, 700 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.47–7.05(m, 8H), 6.70 (t, $J = 10.7$ Hz, 1H), 6.47–6.32 (m, 1H), 5.44 (d, $J = 16.8$ Hz, 1H), 5.20 (dd, $J = 5.4$ Hz, $J = 9.7$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 142.44, 141.34, 141.04, 140.79, 139.92, 138.74, 134.70, 134.32, 132.68, 132.38, 131.81, 131.55, 130.49, 130.30, 130.10, 129.99, 129.77, 129.44, 128.65, 128.15, 128.09, 127.72, 127.03, 120.33, 120.27. HRMS (EI^+) calcd for $\text{C}_{16}\text{H}_{12}^{35}\text{Cl}_2$ (M^+): 274.0316; found: 274.0316; HRMS (EI^+) calcd for $\text{C}_{16}\text{H}_{12}^{37}\text{Cl}_2$ (M^+): 276.0287; found: 276.0280.

1-methoxy-4-(1-phenylbuta-1,3-dienyl)benzene (3g)²⁰ The title compound was obtained according to the general procedure. Colourless oil; Yield: 72%; IR (KBr): 3055, 1604, 1510, 1462, 1442, 1290, 966, 904, 832 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.40–7.13(m, 7H), 6.93–6.80(m, 2H), 6.65 (dd, $J = 4.9$, $J = 10.9$ Hz, 1H), 6.47–6.34 (m, 1H), 5.36 (dd, $J = 9.0$ Hz, $J = 16.4$ Hz, 1H), 5.10 (t, $J = 11.9$ Hz, 1H), 3.84–3.79 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 159.47, 159.19, 143.09, 142.94, 142.75, 140.11, 135.36, 134.94, 131.90, 130.63, 129.96, 128.98, 128.51, 128.37, 127.95, 127.71, 127.57, 127.18, 121.02, 120.93, 118.47, 117.92, 113.85, 133.78, 55.52, 55.50. HRMS (EI^+) calcd for $\text{C}_{17}\text{H}_{16}\text{O}$ (M^+): 236.1201; found: 236.1201.

1-methyl-3-(1-phenylbuta-1,3-dienyl)benzene (3h)²¹ The title compound was obtained according to the general procedure. Colourless oil; Yield: 88%; IR (KBr): 3055, 3025, 1666, 1601, 1492, 1445, 904, 787, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.38–7.03(m, 9H), 6.70(d, $J = 10.9$ Hz, 1H), 6.49–6.39 (m, 1H), 5.38(d, $J = 16.8$ Hz, 1H), 5.12(d, $J = 9.9$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 143.72, 143.69, 142.58, 142.53, 140.17, 139.99, 138.19, 138.16, 135.52, 135.44, 131.38, 130.86, 128.87, 128.83, 128.78, 128.66, 128.62, 128.57, 128.53, 128.48, 128.02, 127.97, 127.90, 127.79, 125.32, 118.92, 118.89, 21.93, 21.90. HRMS (EI^+) calcd for $\text{C}_{17}\text{H}_{16}$ (M^+): 220.1252; found: 220.1253.

2-(1-phenylbuta-1,3-dienyl)thiophene (3i) The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; Compound purity: 100% (confirmed by HPLC); IR (KBr): 3048, 1609, 1596, 1490, 1444, 860, 840, 770, 700 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.41–7.28(m, 5H), 7.18(d, $J = 4.8$ Hz, 1H), 6.91–6.89 (m, 1H), 6.76–6.62(m, 2H), 6.30(td, $J = 10.5$ Hz, $J = 17.1$ Hz, 1H), 5.36(d, $J = 16.9$ Hz, 1H), 5.08(d, $J = 10.1$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 147.08, 139.04, 137.49, 137.74, 130.43, 128.67, 128.22, 127.94, 127.54, 126.75, 125.26, 118.87. HRMS (EI^+) calcd for $\text{C}_{14}\text{H}_{12}\text{S}$ (M^+): 212.0660, found: 212.0662.

2-(1-phenylbuta-1,3-dienyl)naphthalene (3j) The title compound was obtained according to the general procedure. White solid; Yield: 86%; Compound purity: 98% (confirmed by HPLC); IR (KBr): 3055, 1627, 1597, 1504, 1444, 899, 818, 763, 700 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.87–7.21(m, 12H), 6.83(dd, $J = 11.0$ Hz, $J = 17.4$ Hz, 1H), 6.55–6.43 (m, 1H), 5.43(d, $J = 16.8$ Hz, 1H), 5.14(t, $J = 8.8$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 143.37, 143.32, 142.28, 139.88, 139.68, 137.37, 135.27, 133.57, 133.46, 133.08, 132.95, 130.77, 129.71, 129.30, 129.19, 128.72, 128.51, 128.30, 127.97, 127.85, 127.77, 127.27, 126.42, 126.37, 126.25, 125.63, 119.13, 119.05. HRMS (EI^+) calcd for $\text{C}_{20}\text{H}_{16}$ (M^+): 256.1252, found: 256.1252.

1-(penta-2,4-dien-2-yl)benzene (3ka), 1-(penta-1,4-dien-2-yl)benzene (3kb)¹² The title compound was obtained according to the general procedure. Colourless solid; Yield: 82%; IR (KBr): 3081, 3057, 1599, 1494, 1445, 912, 863, 758, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.46–7.21 (m, 5H), 5.90 (tdd, *J* = 6.6 Hz, *J* = 10.1 Hz, *J* = 16.7 Hz, 1H), 5.39 (s, 1H), 5.14–5.05 (m, 3H), 3.25 (d, *J* = 6.5 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 146.77, 141.39, 136.66, 128.74, 127.92, 126.46, 116.95, 113.63, 39.97. HRMS (EI⁺): calcd. for C₁₁H₁₂ (M⁺): 144.0939; found: 144.0938.

(E)-1-bromo-4-(buta-1,3-dienyl)benzene (3l)²² The title compound was obtained according to the general procedure. Colourless oil; Yield: 31%; IR (KBr): 3051, 2962, 1638, 1501, 1407, 807, 680 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.42 (d, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 6.75 (dd, *J* = 10.7 Hz, *J* = 15.1 Hz, 1H), 6.54–6.41 (m, 2H), 5.34 (d, *J* = 17.0 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 134.30, 133.49, 129.14, 128.95, 127.72, 125.21, 118.76, 115.80. HRMS (EI⁺): calcd for C₁₁H₁₀O₂ (M⁺): 207.9888; found: 208.9612.

4-methyl-1,1-diphenylpenta-1,3-diene (3ab)²³ The title compound was obtained according to the general procedure. Colourless oil; Yield: 41%; IR (KBr): 3045, 2973, 1614, 1505, 1463, 908, 835 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.38–7.26 (m, 10H), 6.87 (d, *J* = 11.2 Hz, 1H), 5.92 (d, *J* = 10.5 Hz, 1H), 1.89 (s, 3H), 1.76 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 143.39, 140.49, 140.01, 137.95, 130.87, 130.43, 128.41, 127.72, 127.30, 127.19, 124.78, 123.49, 26.79, 18.92. HRMS (EI⁺) calcd for C₁₈H₁₈ (M⁺): 234.1409; found: 234.1412.

1,1-bis(4-chlorophenyl)buta-1,3-diene (3bb) The title compound was obtained according to the general procedure. Colourless oil; Yield: 33%; Compound purity: 99% (confirmed by HPLC); IR (KBr): 3032, 1593, 1492, 1440, 915, 863, 765, 697 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.17–7.11 (m, 4H), 6.83 (d, *J* = 11.4 Hz, 1H), 5.85 (d, *J* = 11.4 Hz, 1H), 1.88 (s, 3H), 1.77 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 141.36, 139.37, 138.38, 137.39, 133.34, 133.10, 132.09, 128.80, 128.71, 128.58, 125.51, 122.93, 26.76, 18.91. HRMS (EI⁺) calcd for C₁₈H₁₆³⁵Cl₂ (M⁺): 302.0629; found: 302.0630; HRMS (EI⁺) calcd for C₁₈H₁₆³⁷Cl₂ (M⁺): 304.0600; found: 304.0642.

1,1-diphenylbut-1-en-3-yne (3ac)²⁴ The title compound was obtained according to the general procedure. Colourless oil; Yield: 35%; IR (KBr): 3287, 3057, 3025, 1598, 1495, 1443, 849, 774, 763, 729, 697 cm⁻¹; ¹H NMR (300 MHz CDCl₃): δ 7.44–7.30 (m, 10H), 6.02 (s, 1H), 3.00 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 154.72, 141.35, 139.10, 130.17, 128.78, 128.56, 128.22, 106.25, 82.69, 81.76. HRMS (EI⁺) calcd for C₁₆H₁₂ (M⁺): 204.0939; found: 204.0938.

Ethyl 3,3-diphenylacrylate (5a)²⁵ The title compound was obtained according to the general procedure. Colourless oil; Yield: 89%; IR (KBr): 3057, 3026, 1723, 1617, 1575, 1492, 1445, 875, 771, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.36–7.21 (m, 10H), 6.36 (s, 1H), 4.04 (q, *J* = 6.9 Hz, 2H), 1.10 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 166.36, 156.74, 141.05, 139.25, 129.64, 129.37, 128.62, 128.54, 128.35, 128.12,

117.73, 60.30, 14.26. HRMS (EI⁺) calcd for C₁₇H₁₆O₂ (M⁺): 252.1150; found: 252.1152.

Ethyl 3,3-bis(4-chlorophenyl)acrylate (5b)²⁶ The title compound was obtained according to the general procedure. Colourless oil; Yield: 80%; IR (KBr): 3025, 1721, 1619, 1589, 1491, 1402, 880, 830, 768 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.34 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 165.85, 154.26, 139.08, 137.06, 136.00, 134.66, 130.79, 129.72, 128.96, 128.52, 118.38, 60.54, 14.26. HRMS (EI⁺) calcd for C₁₇H₁₄³⁵Cl₂O₂ (M⁺): 320.0371; found: 320.0371; HRMS (EI⁺) calcd for C₁₇H₁₄³⁷Cl₂O₂ (M⁺): 322.0341; found: 322.0350.

Ethyl 3,3-diphenylacrylate (5c)²⁷ The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; IR (KBr): 3039, 2969, 1688, 1592, 1495, 752, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.23 (s, 1H), 4.07 (q, *J* = 6.9 Hz, 2H), 3.82 (d, *J* = 8.2 Hz, 6H), 1.16 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 161.39, 155.65, 154.57, 151.38, 128.73, 126.17, 125.79, 124.94, 109.79, 108.61, 108.12, 54.82, 50.29, 50.17, 9.12. HRMS (EI⁺) calcd for C₁₉H₂₀O₄ (M⁺): 312.1362; found: 312.1408.

Ethyl 2-(9H-fluoren-9-ylidene)acetate (5d)²⁸ The title compound was obtained according to the general procedure. Yellow solid; Yield: 65%; IR (KBr): 3062, 2980, 1713, 1600, 1450, 869, 780, 730 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.89 (d, *J* = 7.8 Hz, 1H), 7.62 (dd, *J* = 7.5 Hz, *J* = 15.5 Hz, 3H), 7.42–7.22 (m, 4H), 6.74 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 166.52, 148.46, 142.71, 140.94, 139.05, 135.39, 131.07, 130.75, 129.41, 128.25, 127.66, 121.44, 119.97, 119.77, 114.14, 60.90, 14.58. HRMS (EI⁺) calcd for C₁₇H₁₄O₂ (M⁺): 250.0994; found: 250.0991.

Ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (5g)²⁹ The title compound was obtained according to the general procedure. Colourless oil; Yield: 68%; IR (KBr): 3058, 2980, 1720, 1604, 1511, 1462, 1251, 874, 833, 774, 699 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.37–7.15 (m, 7H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.31 (s, 1H; E isomer), 6.27 (s, 1H; Z isomer), 4.06 (dq, *J* = 7.0 Hz, *J* = 14.2 Hz, 2H), 3.82 (d, *J* = 9.9 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H; Z isomer), 1.10 (t, *J* = 7.1 Hz, 3H; E isomer). ¹³C NMR (CDCl₃, 100 MHz): δ 166.50, 161.00, 159.98, 156.82, 156.52, 141.78, 139.51, 133.34, 131.26, 131.18, 129.99, 129.57, 129.32, 128.80, 128.54, 128.23, 128.08, 117.12, 115.60, 114.00, 113.46, 60.24, 60.12, 55.56, 55.45, 14.40, 14.28. HRMS (EI⁺) calcd for C₁₈H₁₈O₃ (M⁺): 282.1256; found: 282.1256.

Ethyl 3-phenyl-3-m-tolylacrylate (5h)³⁰ The title compound was obtained according to the general procedure. Colourless oil; Yield: 88%; IR (KBr): 3048, 2979, 1720, 1603, 1511, 1493, 1444, 833, 774, 699 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.37–7.00 (m, 9H), 6.35 (s, 1H), 4.05 (dq, *J* = 2.3 Hz, *J* = 7.0 Hz, 2H), 2.35–2.32 (m, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 166.62, 157.19, 157.07, 141.37, 141.29, 139.56, 139.41, 138.45, 137.84, 130.66, 130.10, 129.78, 129.58, 129.31, 128.80, 128.75, 128.51, 128.29, 128.21, 126.75, 126.06, 117.85,

117.79, 60.46, 21.86, 14.47. HRMS (EI⁺) calcd for C₁₈H₁₈O₂ (M⁺): 266.1307; found: 266.1305.

(E)-ethyl 3-phenylbut-2-enoate (5ka)³¹ The title compound was obtained according to the general procedure. Colourless oil; Yield: 32%; IR (KBr): 3024, 1714, 1629, 1446, 1273, 873, 767, 694 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.49–7.26 (m, 5H), 6.13 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 167.21, 155.74, 142.46, 129.19, 128.71, 126.52, 117.40, 60.08, 18.18, 14.58. HRMS (EI⁺) calcd for C₁₂H₁₄O₂ (M⁺): 190.0994; found: 190.0993.

Ethyl 3-phenylbut-3-enoate (5kb)³¹ The title compound was obtained according to the general procedure. Colourless oil; Yield: 44%; IR (KBr): 3085, 1734, 1627, 1495, 1445, 906, 860, 776, 733, 701 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.44–7.25 (m, 5H), 5.54 (s, 1H), 5.23 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.51 (s, 2H), 1.18 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 171.77, 141.42, 140.26, 128.80, 128.19, 126.24, 116.60, 61.21, 41.77, 14.52. HRMS (EI⁺) calcd for C₁₂H₁₄O₂ (M⁺): 190.0994; found: 190.0995.

(E)-ethyl 3-(benzo[d][1,3]dioxol-5-yl)acrylate (5n)³² The title compound was obtained according to the general procedure. White solid; Yield: 67%; IR (KBr): 3062, 2980, 1709, 1604, 1503, 1447, 1250, 980, 931, 853, 810 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.59 (d, *J* = 15.9 Hz, 1H), 7.03–6.79 (m, 2H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.26 (d, *J* = 15.9 Hz, 1H), 6.00 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 167.39, 149.76, 148.54, 144.49, 129.11, 124.59, 116.42, 108.74, 106.69, 101.76, 60.61, 14.56. HRMS (EI⁺) calcd for C₁₂H₁₂O₄ (M⁺): 220.0736; found: 220.0740.

Ethyl 2,2-dimethyl-3-phenylbut-3-enoate (5kc)³³ The title compound was obtained according to the general procedure. Colourless oil; Yield: 73%; IR (KBr): 3083, 3056, 1731, 1626, 1493, 1444, 1255, 909, 776, 703 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.27–7.15 (m, 5H), 5.32 (s, 1H), 5.15 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.39 (s, 6H), 1.17 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 176.69, 153.44, 142.02, 128.18, 128.04, 127.27, 114.66, 60.78, 47.80, 26.14, 14.21. HRMS (EI⁺) calcd for C₁₄H₁₈O₂ (M⁺): 218.1307; found: 218.1315.

Ethyl 3-(4-chlorophenyl)-2,2-dimethylbut-3-enoate (5p) The title compound was obtained according to the general procedure. Colourless oil; Yield: 61%; Compound purity: 100% (confirmed by HPLC); IR (KBr): 3024, 2980, 1729, 1630, 1489, 1399, 1253, 908, 835 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.24 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 5.33 (s, 1H), 5.14 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.38 (s, 6H), 1.18 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 176.42, 152.30, 140.43, 133.21, 129.56, 128.19, 115.29, 61.07, 47.71, 26.03, 14.22. HRMS (EI⁺) calcd for C₁₄H₁₇³⁵ClO₂ (M⁺): 252.0917; found: 252.0916; HRMS (EI⁺) calcd for C₁₄H₁₇³⁷ClO₂ (M⁺): 254.0888; found: 254.0888.

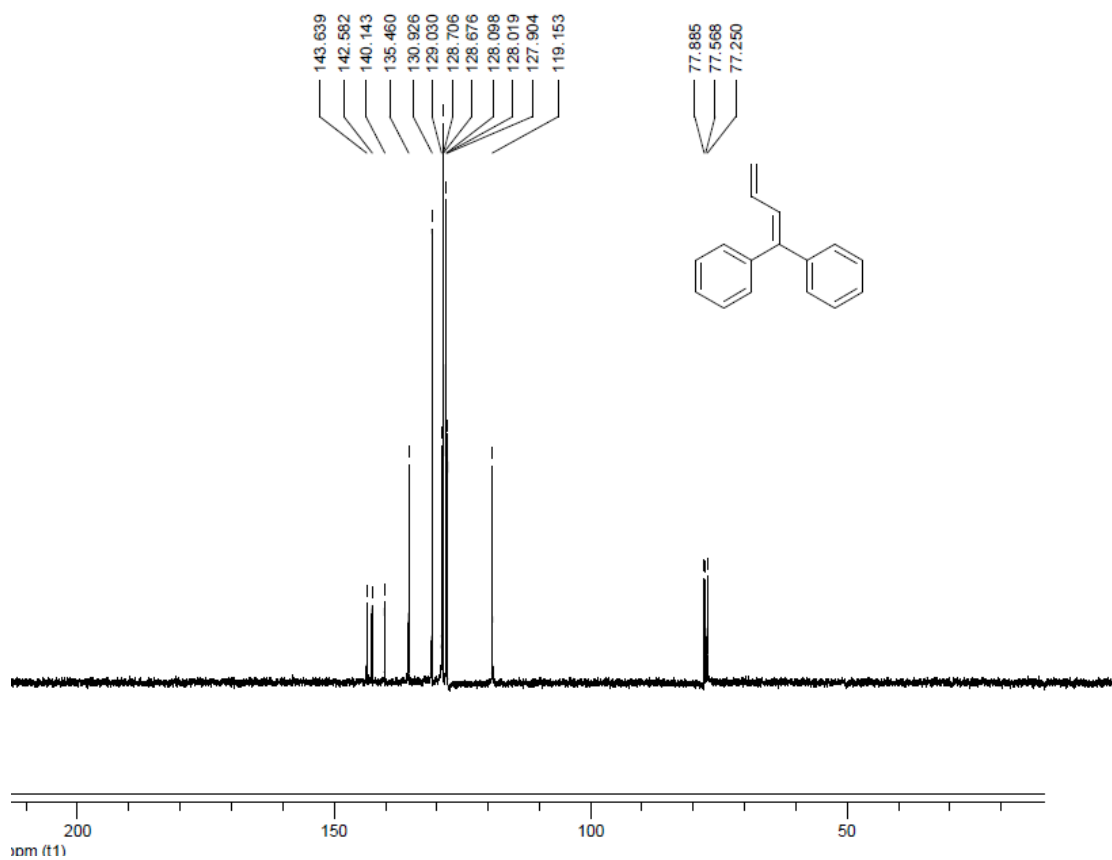
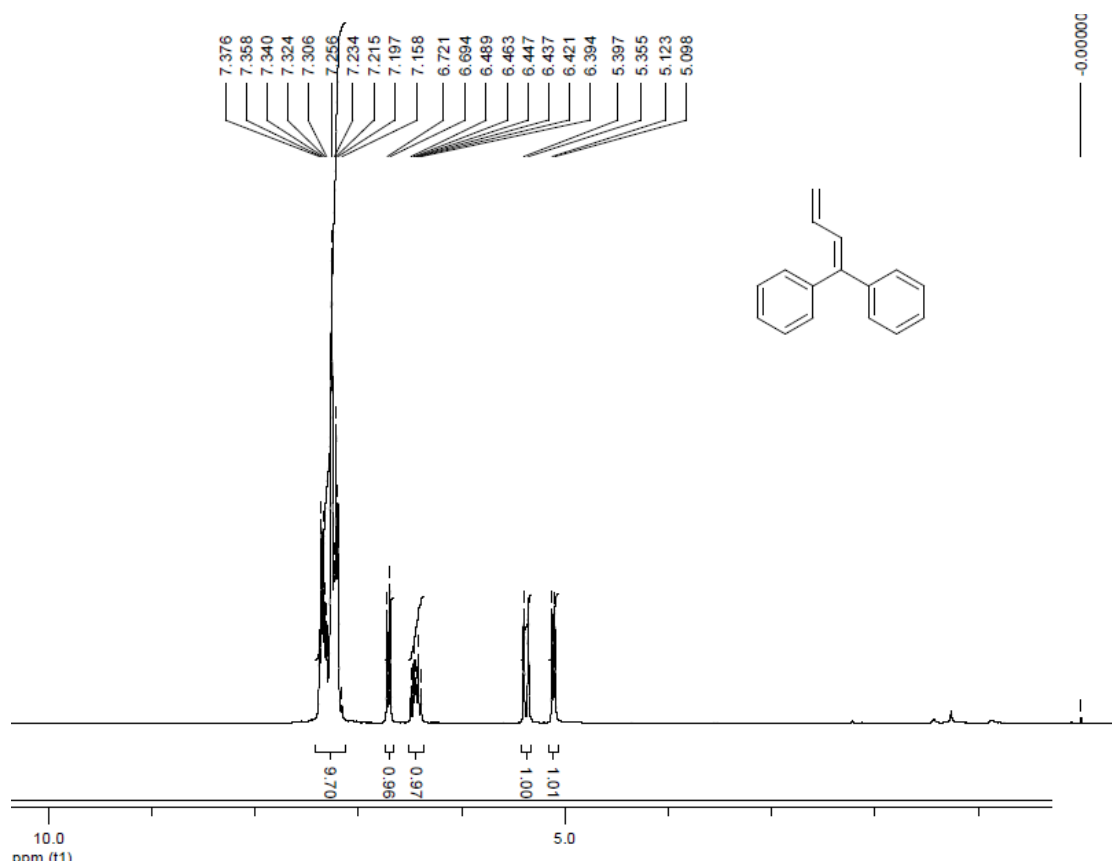
Ethyl 3-(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (5q) The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; Compound purity: 99% (confirmed by HPLC); IR (KBr): 3024, 1729, 1609, 1511, 1464, 1247, 909, 836 cm⁻¹; ¹H NMR (300 MHz,

CDCl₃): δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.27 (s, 1H), 5.12 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.38 (s, 6H), 1.18 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 176.79, 158.88, 152.88, 134.38, 129.22, 114.05, 113.39, 60.91, 55.37, 47.84, 26.12, 14.23. HRMS (EI⁺) calcd for C₁₆H₂₀O₃ (M⁺): 248.1412; found: 248.1414.

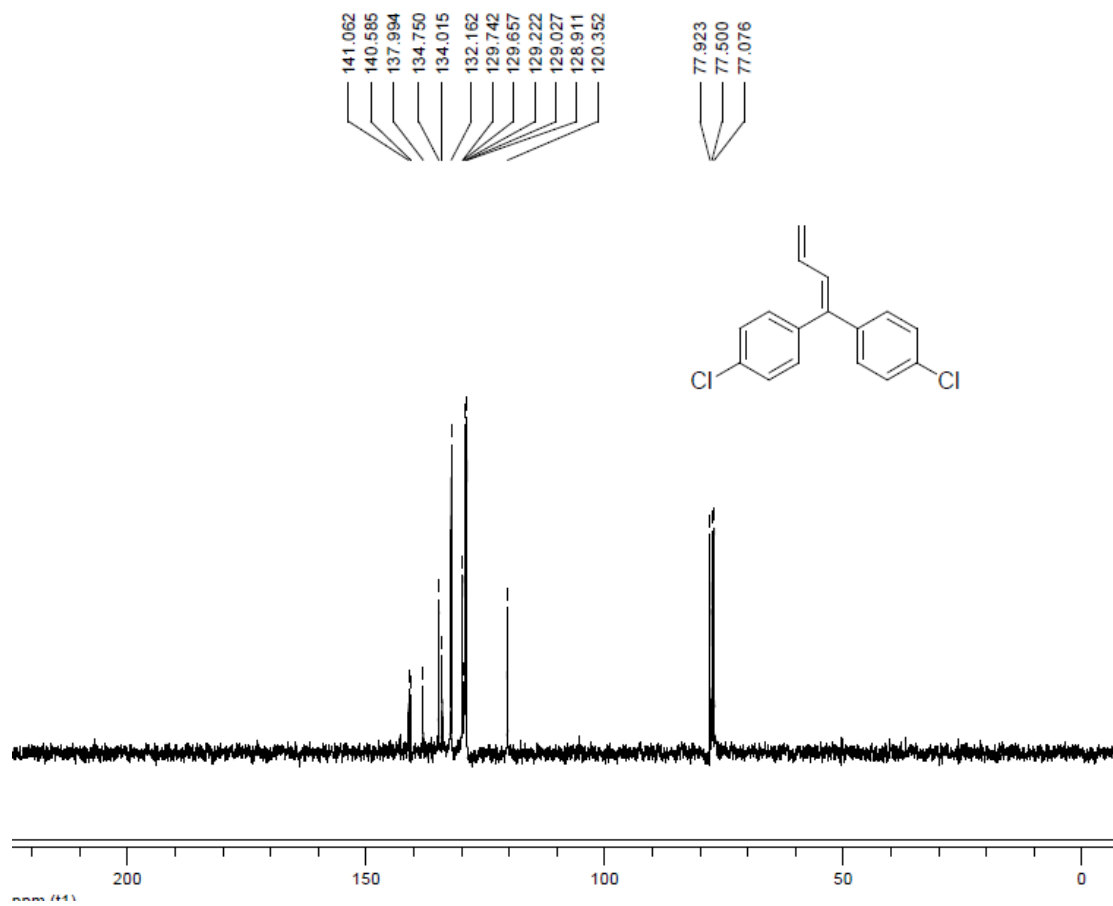
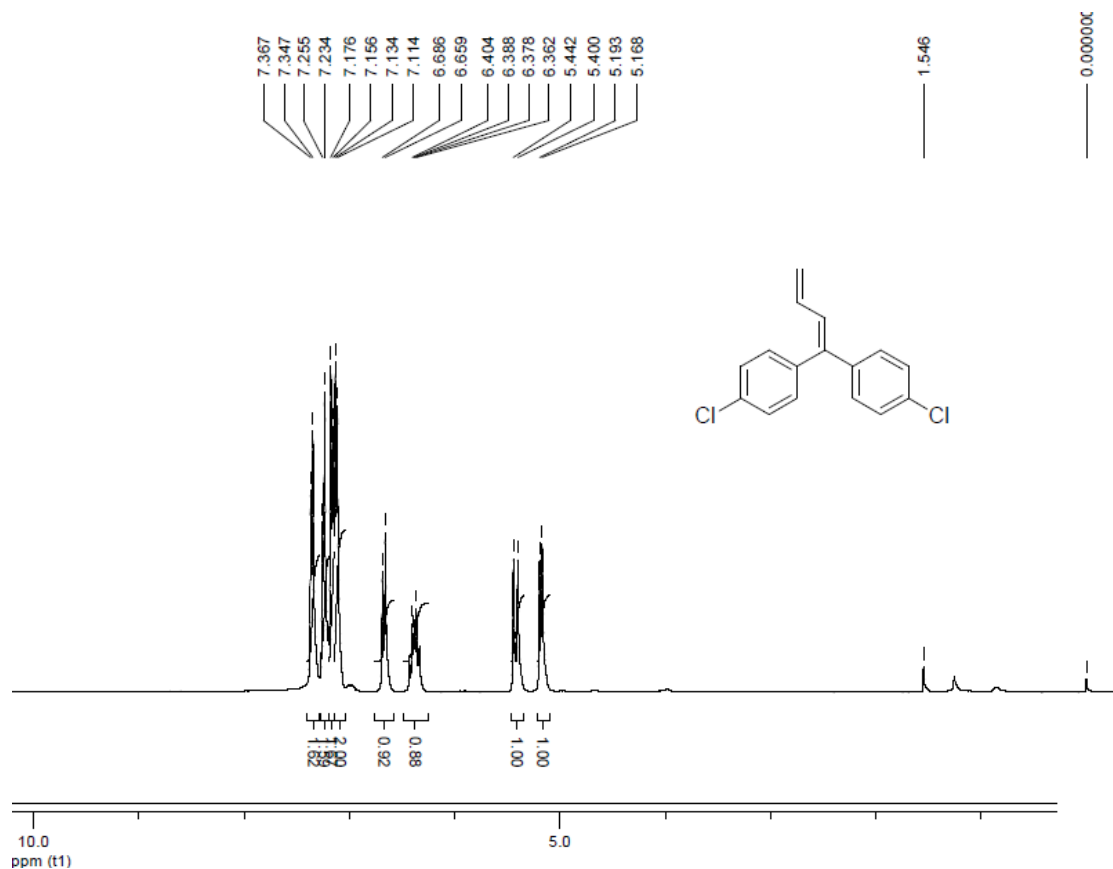
Ethyl 2-(3H-inden-1-yl)-2-methylpropanoate (5r) The title compound was obtained according to the general procedure. Colourless oil; Yield: 87%; Compound purity: 98% (confirmed by HPLC); IR (KBr): 3073, 2975, 1736, 1636, 1399, 907, 776, 699 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.45 (d, *J* = 7.1 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.25–7.15 (m, 2H), 6.36 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.35 (s, 2H), 1.59 (s, 6H), 1.13 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 177.08, 148.21, 145.24, 143.74, 127.98, 126.29, 124.86, 124.34, 120.88, 61.30, 43.87, 37.76, 25.76, 14.54. HRMS (EI⁺) calcd for C₁₅H₁₈O₂ (M⁺): 230.1307; found: 230.1308.

Ethyl 2-methyl-3-phenylbut-3-enoate (5kd)³⁴ The title compound was obtained according to the general procedure. Colourless oil; Yield: 45%; IR (KBr): 3073, 2977, 1733, 1628, 1503, 1446, 767, 701 cm⁻¹; ¹H NMR 300 MHz, CDCl₃): δ 7.40–7.25 (m, 5H), 5.39 (s, 1H), 5.23 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.67 (q, *J* = 7.1 Hz, 1H), 1.39 (d, *J* = 7.08 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 174.66, 148.29, 141.29, 128.51, 127.82, 126.70, 114.11, 60.87, 44.77, 17.22, 14.26. HRMS (EI⁺) calcd for C₁₃H₁₆O₂ (M⁺): 204.1150; found: 204.1151.

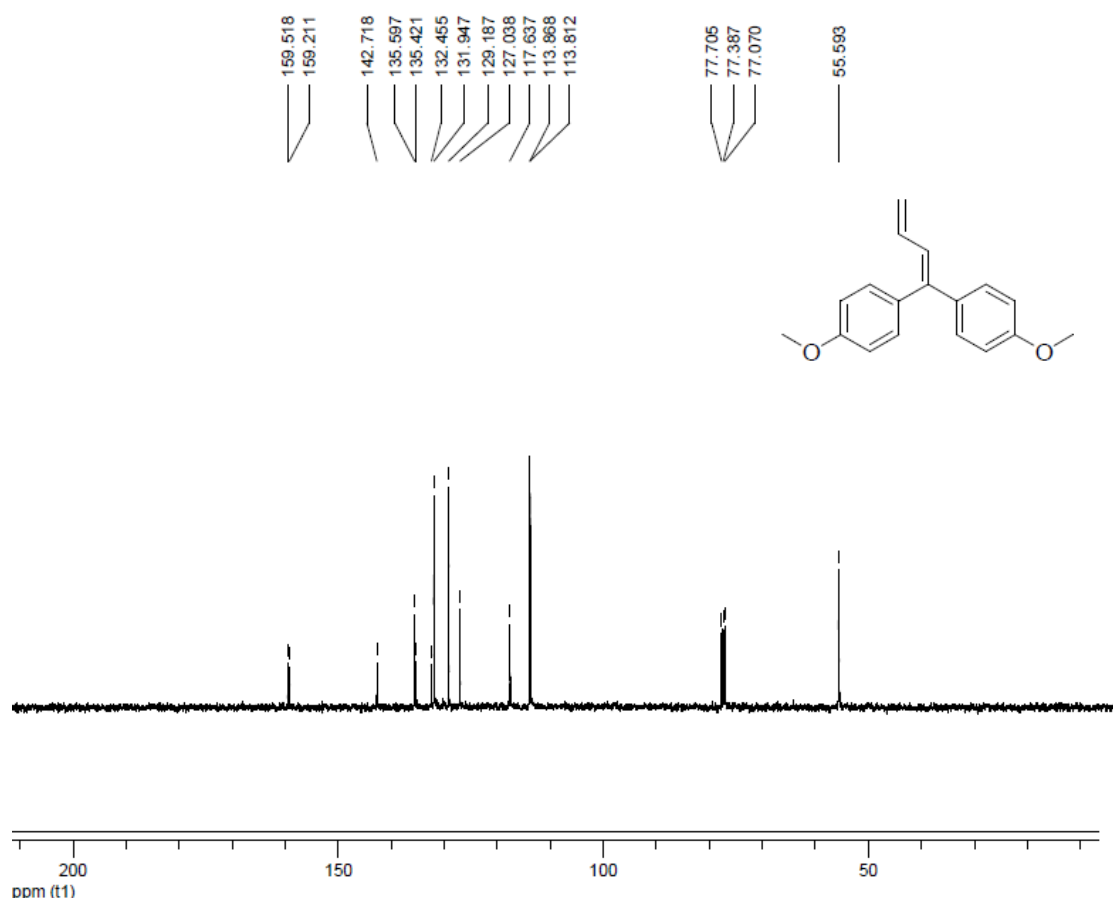
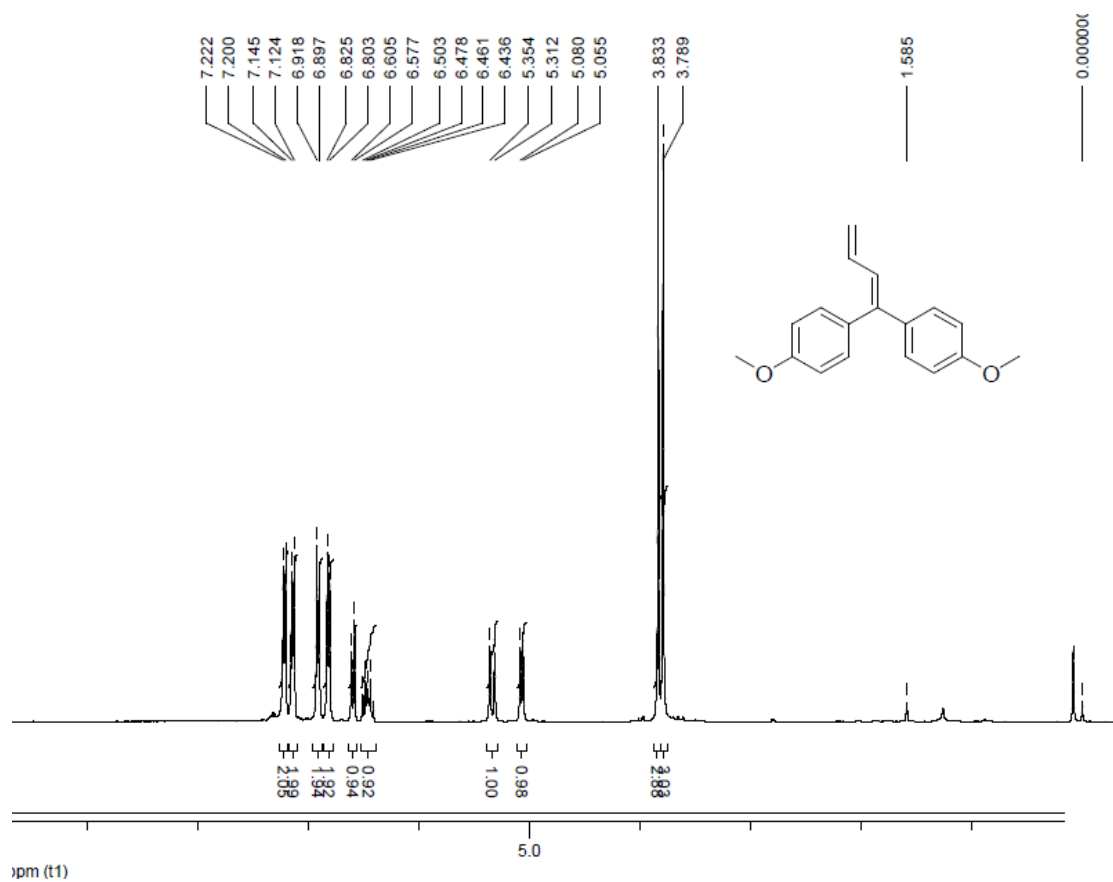
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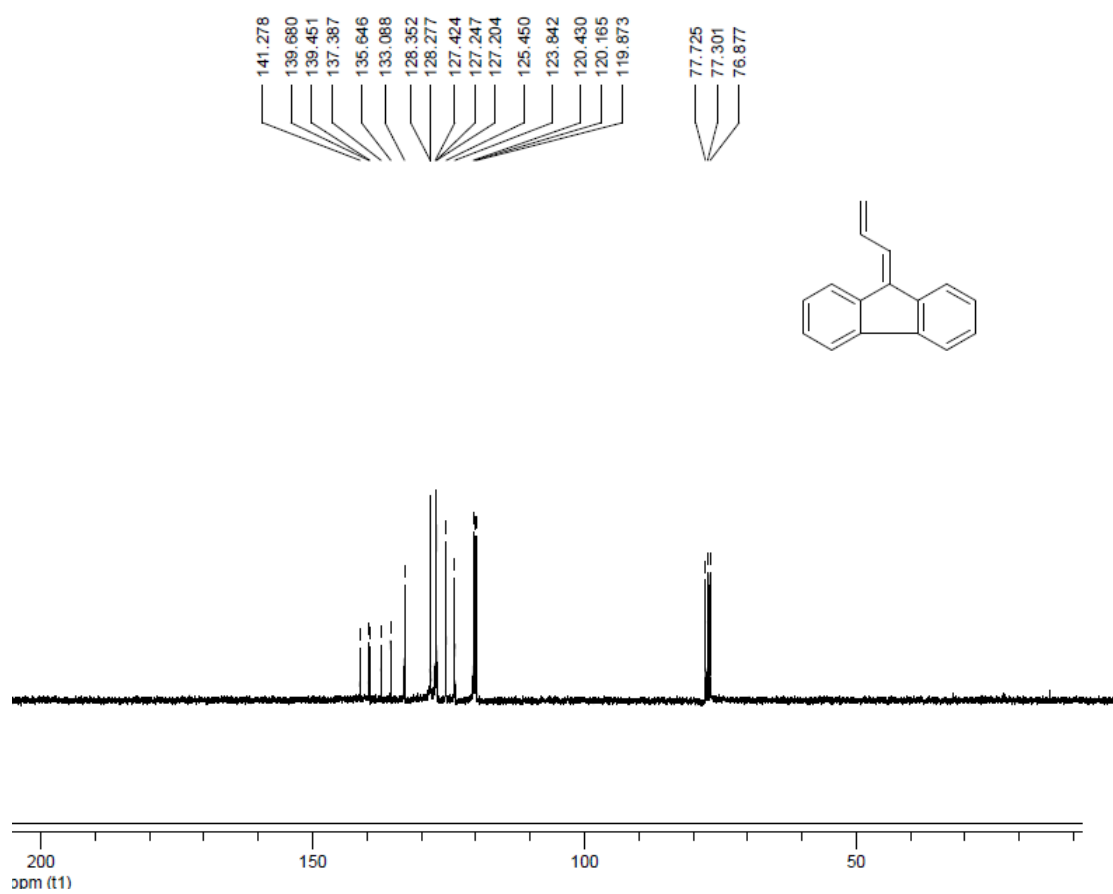
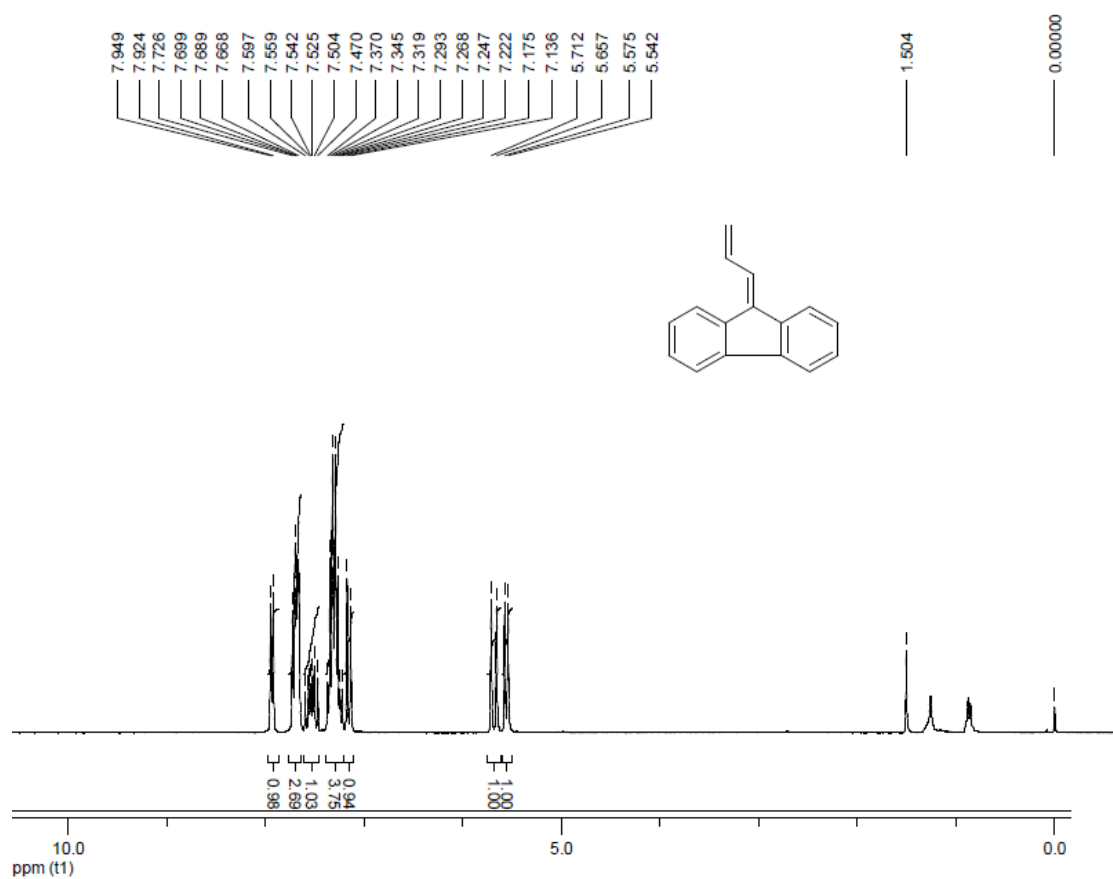
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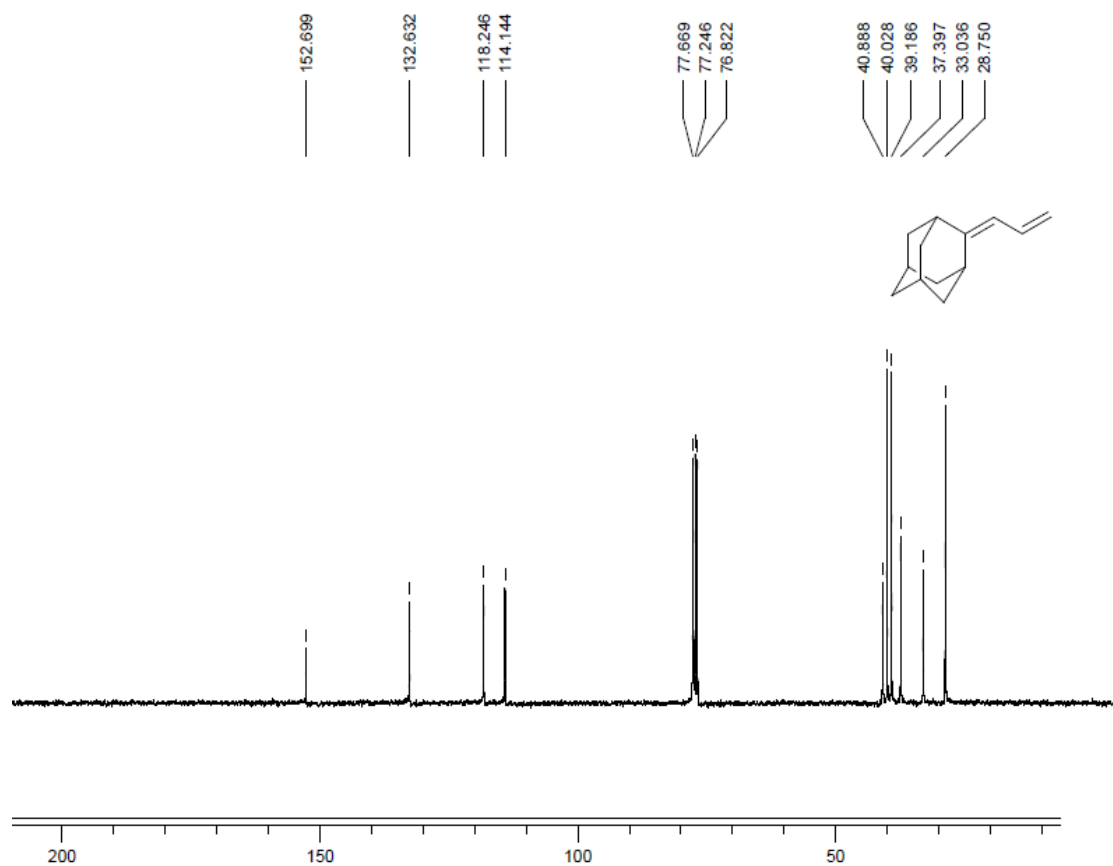
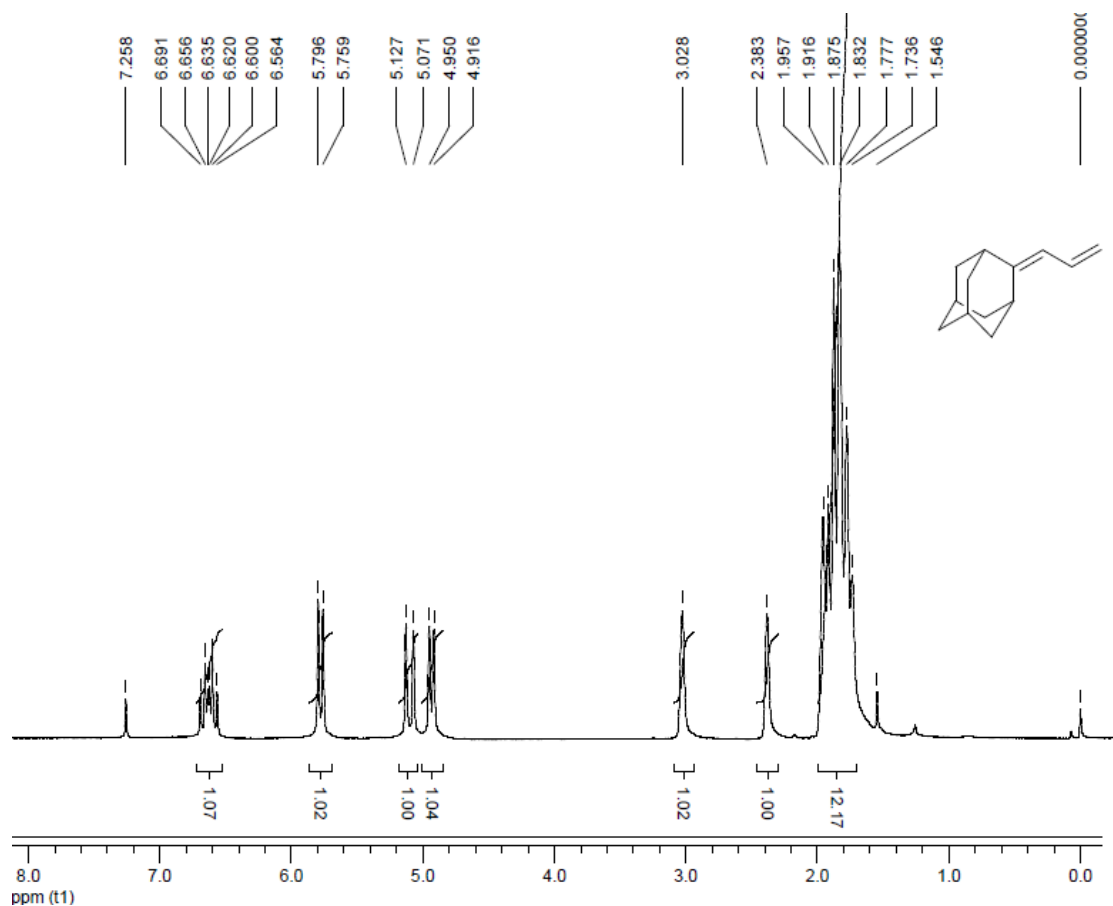
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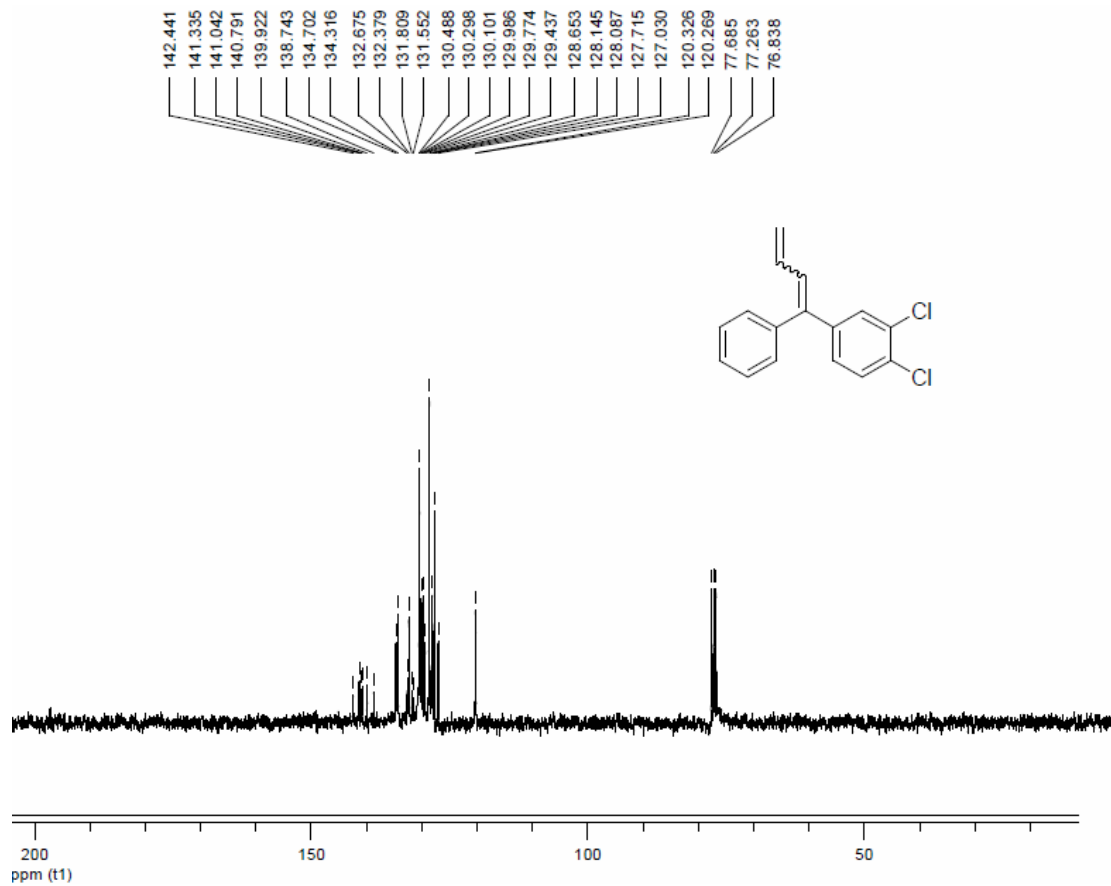
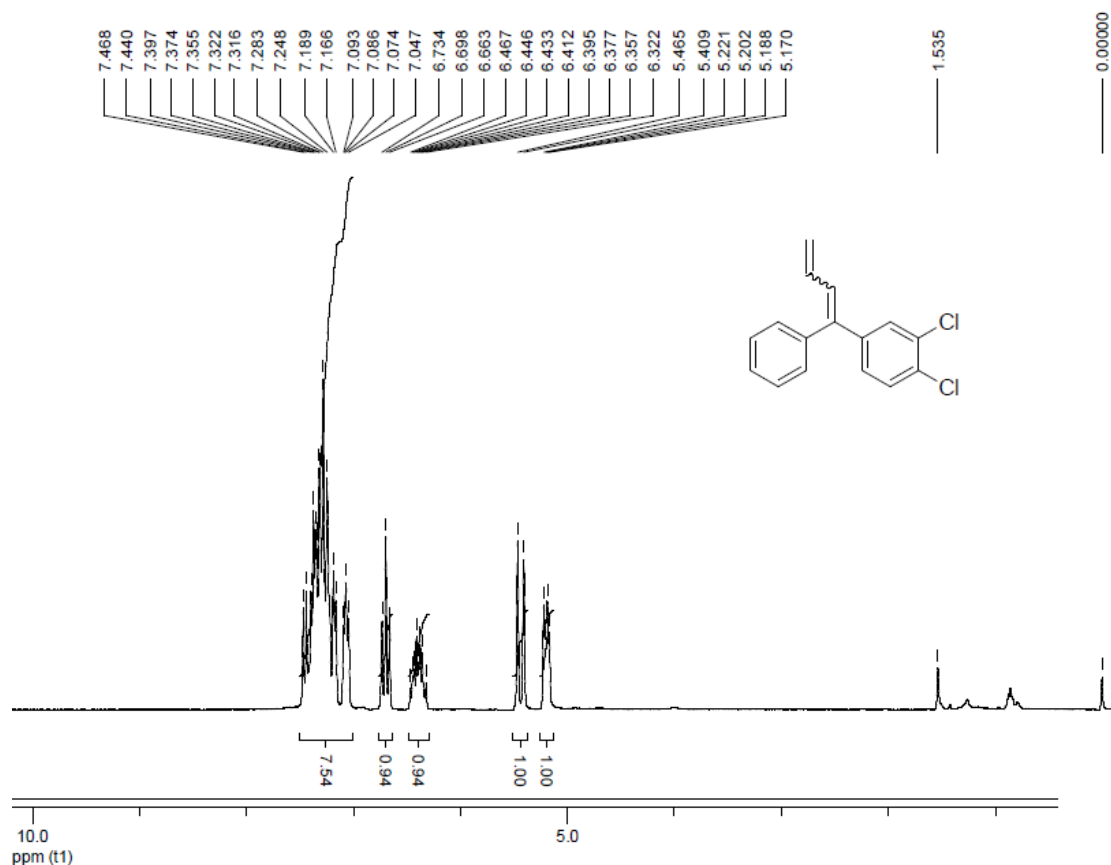
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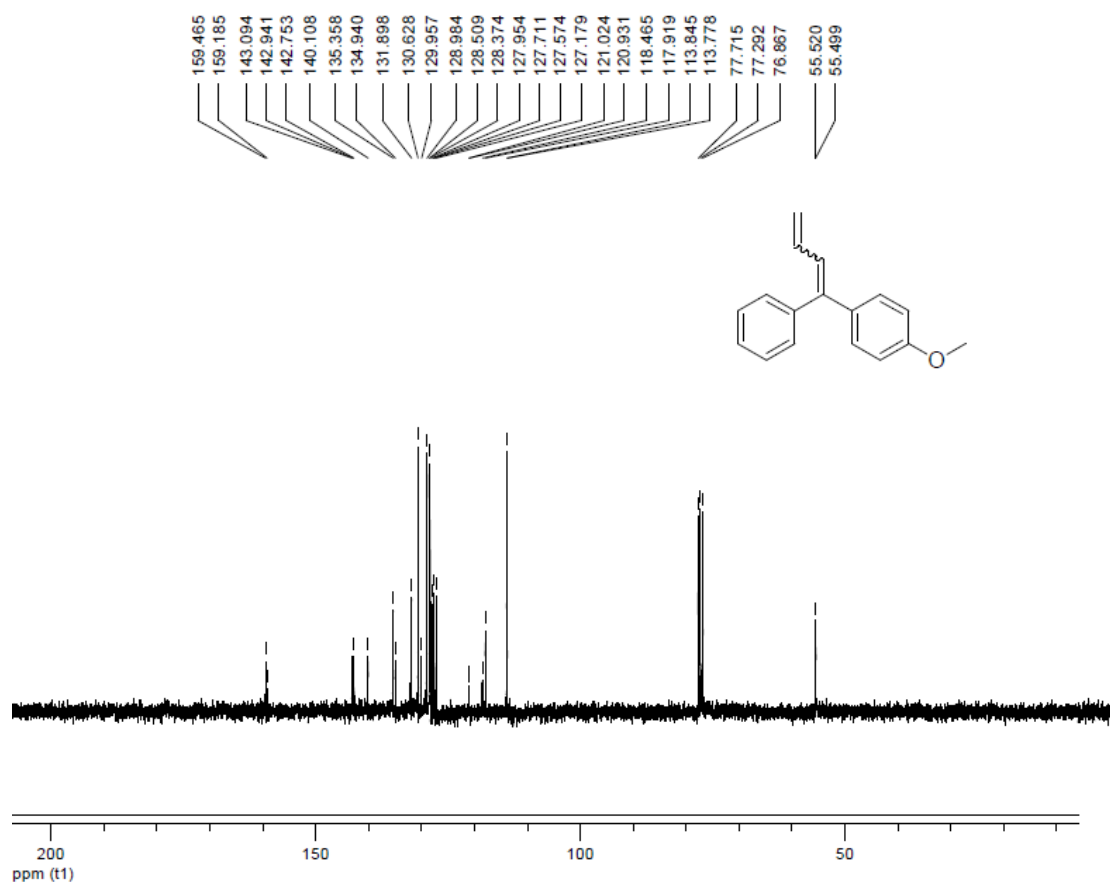
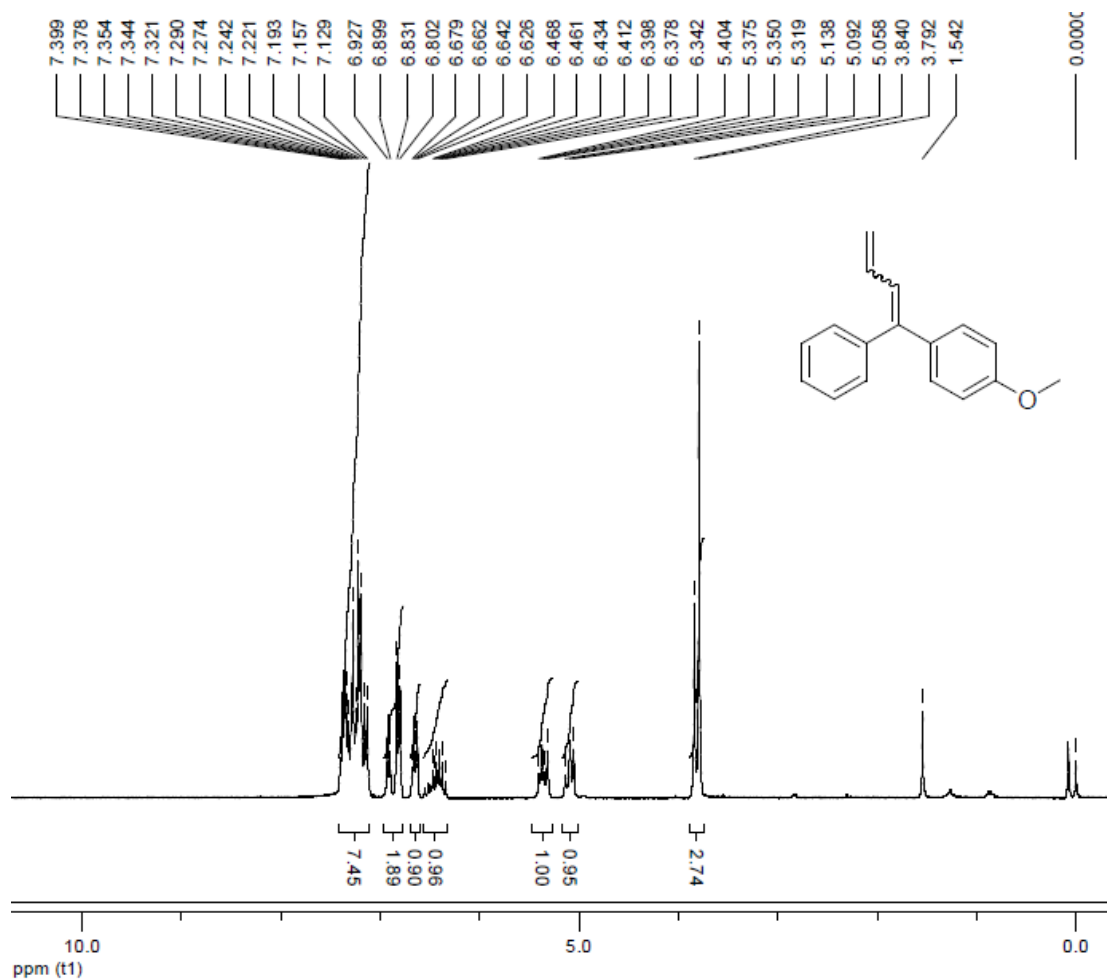
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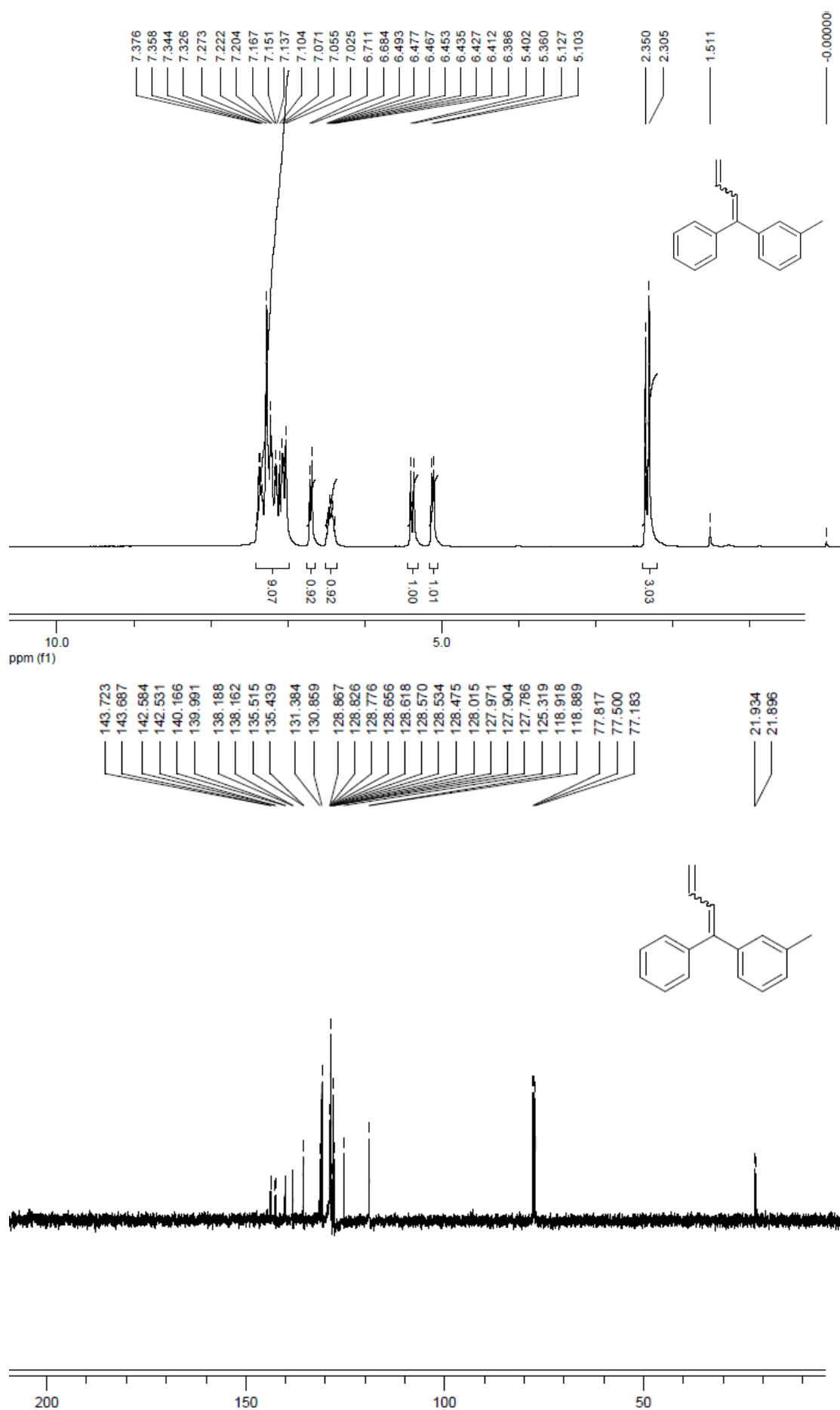
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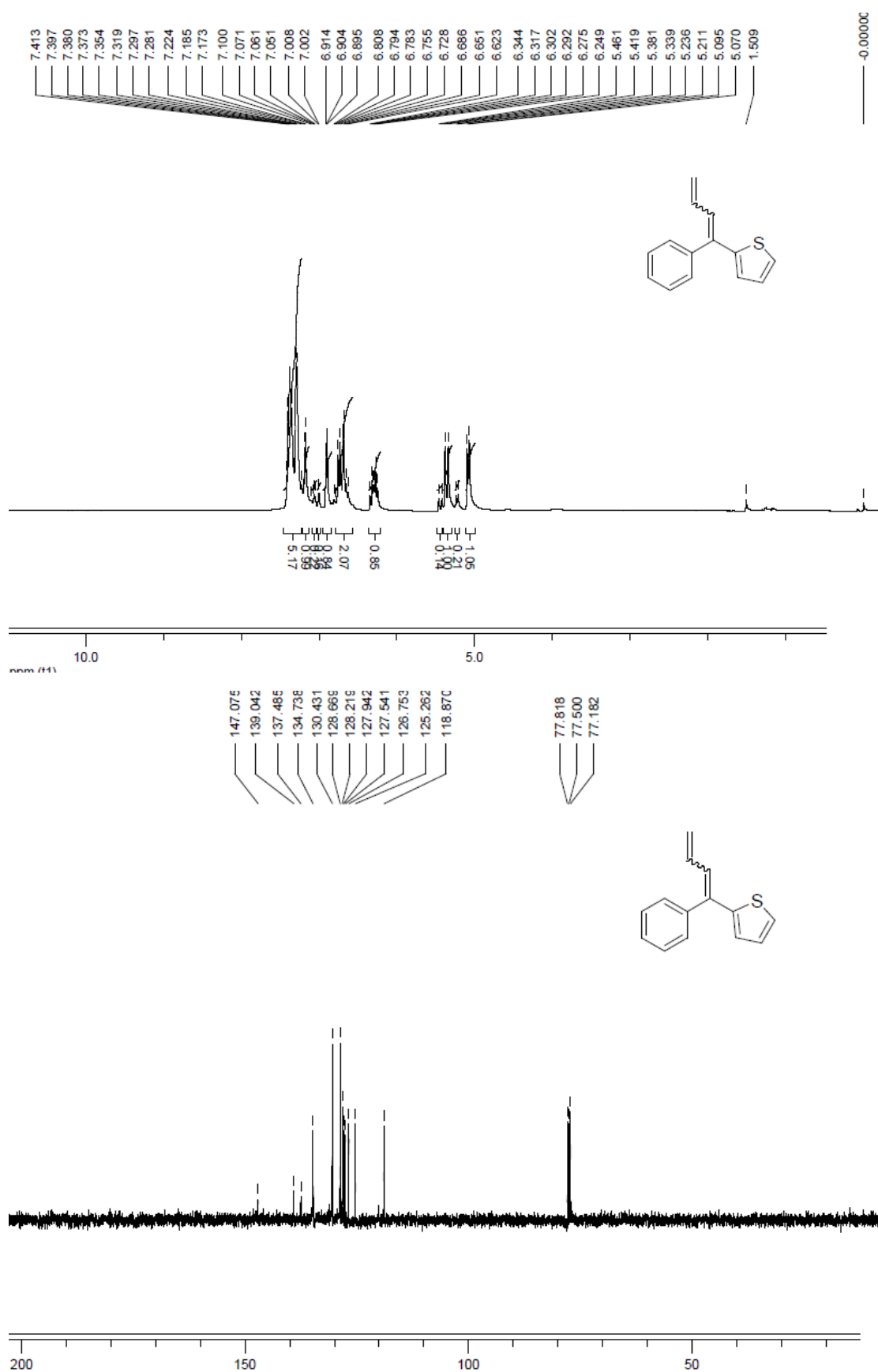
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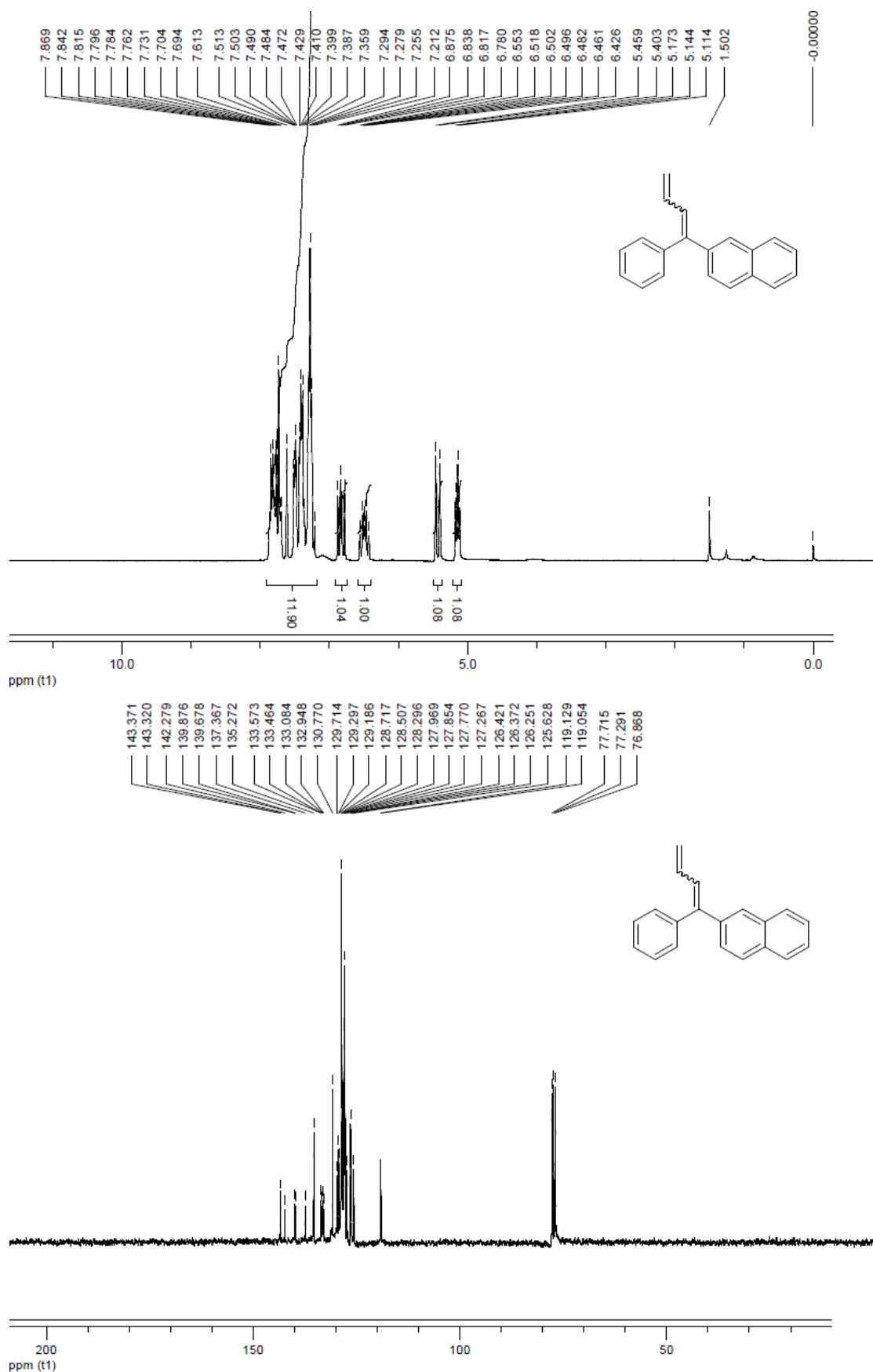
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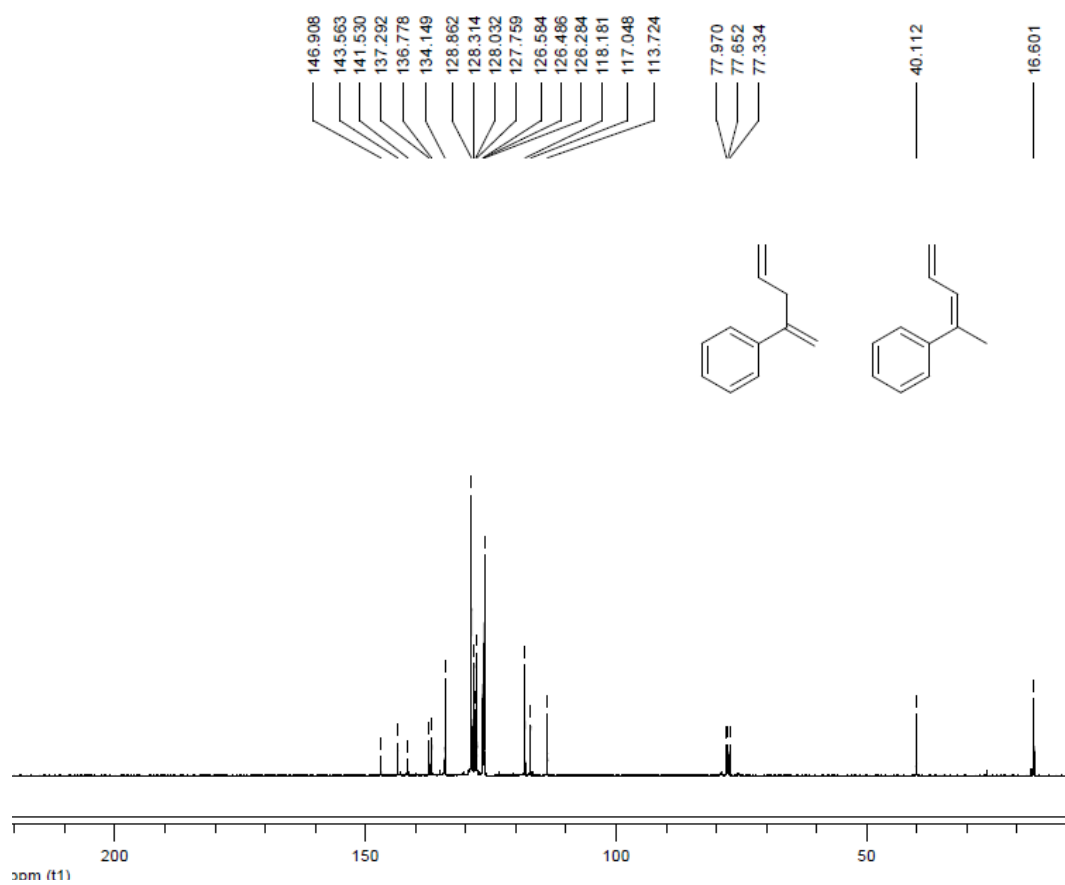
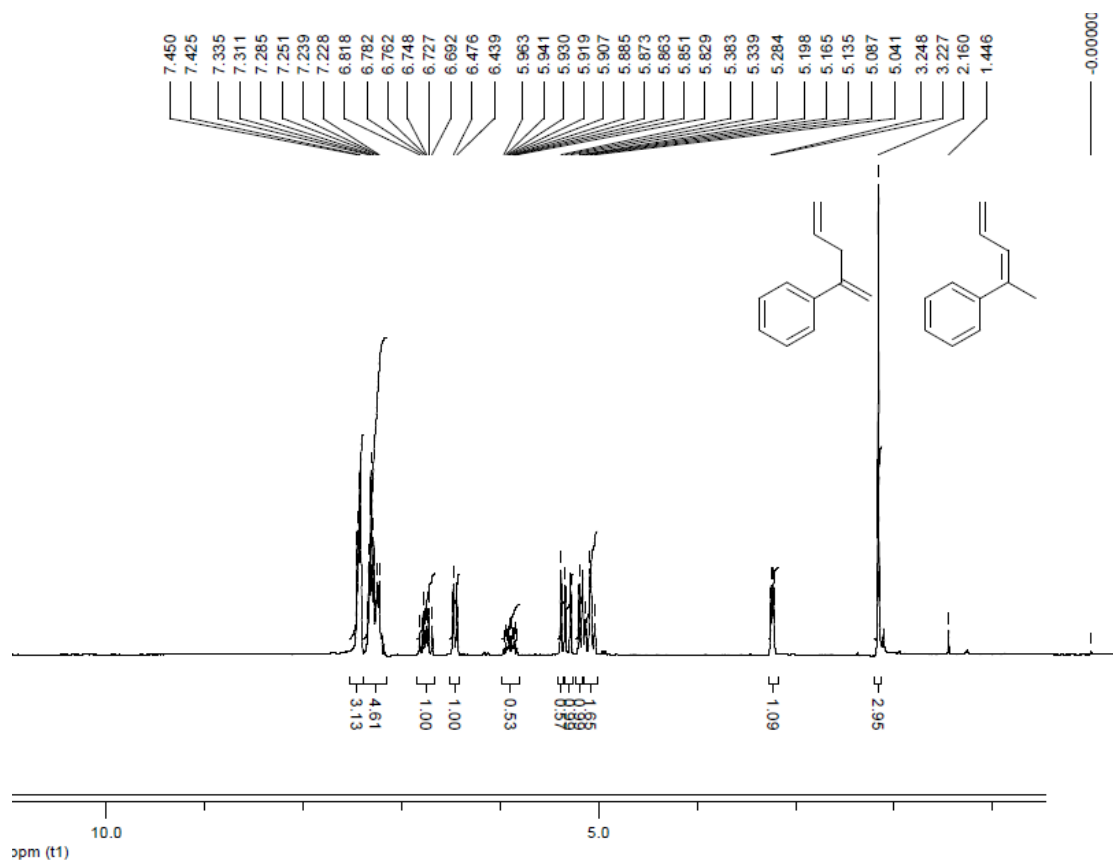
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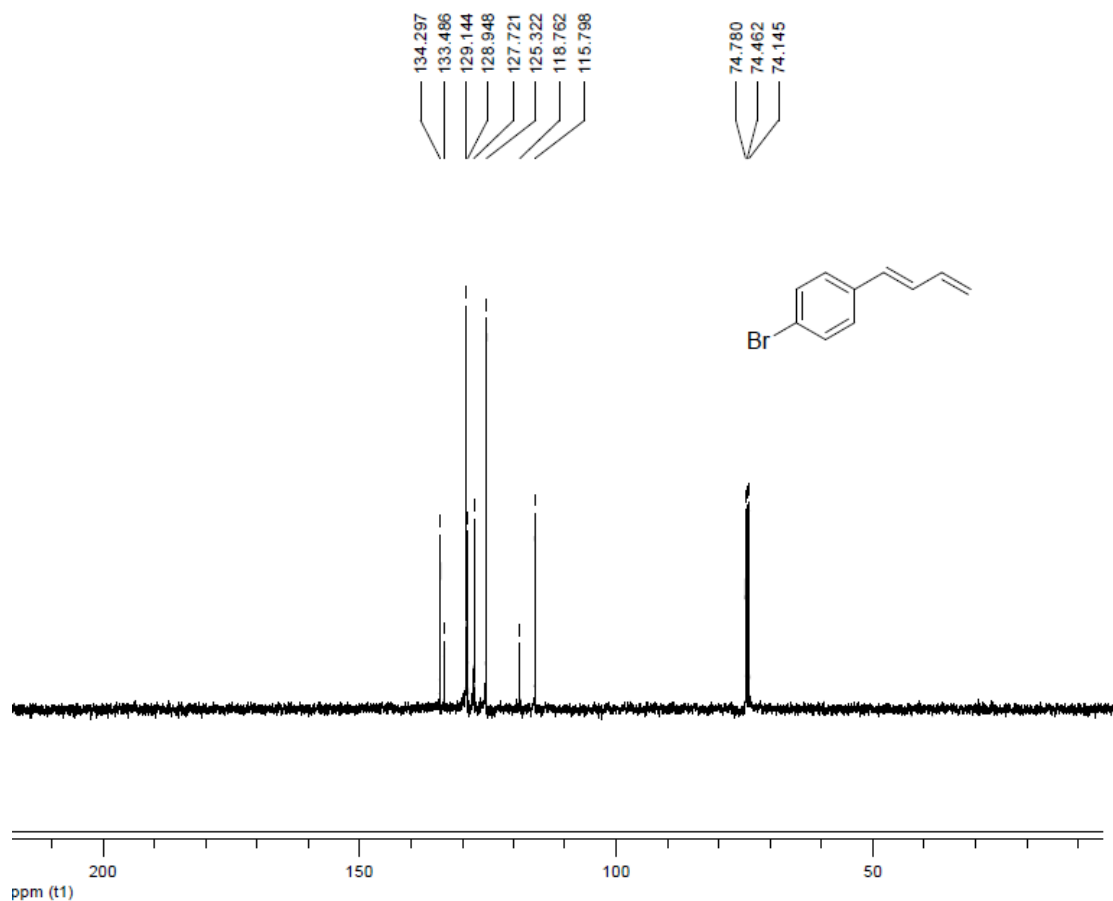
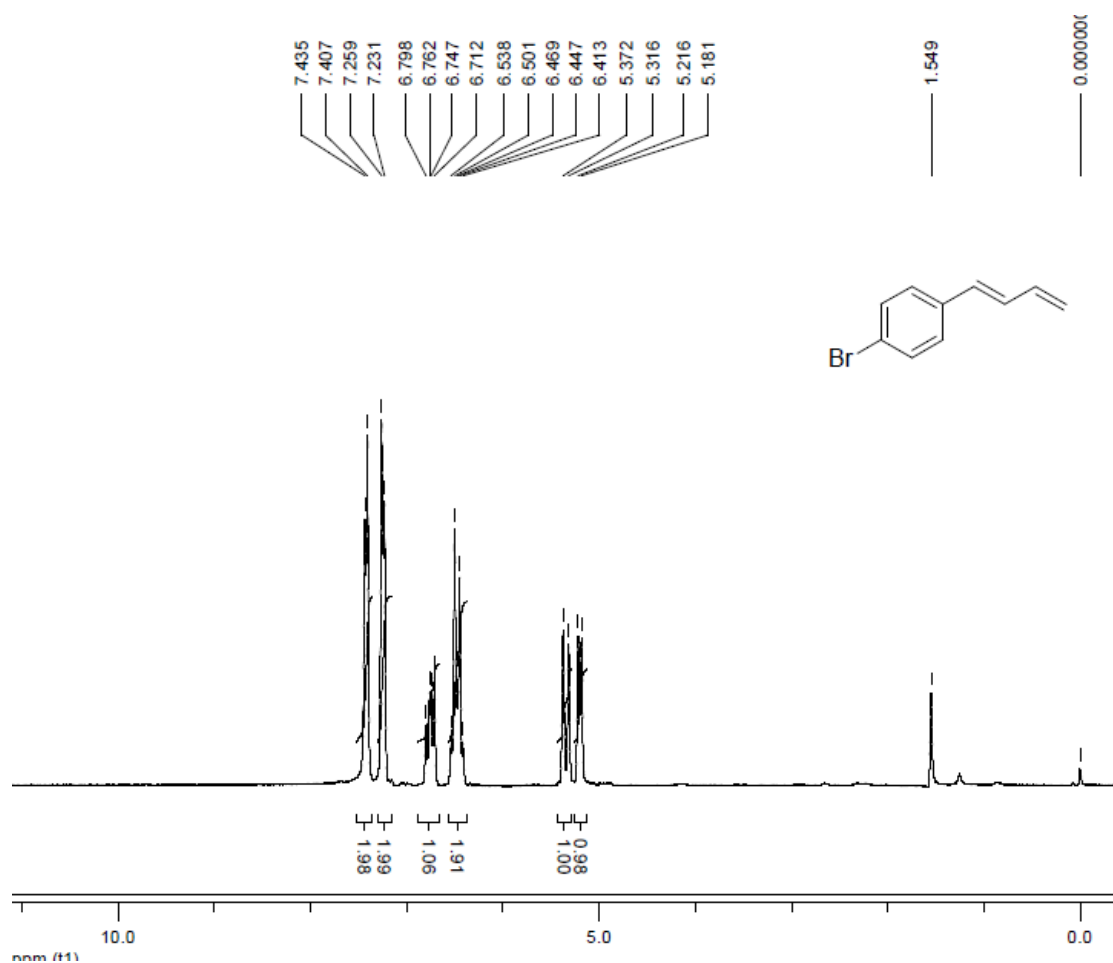
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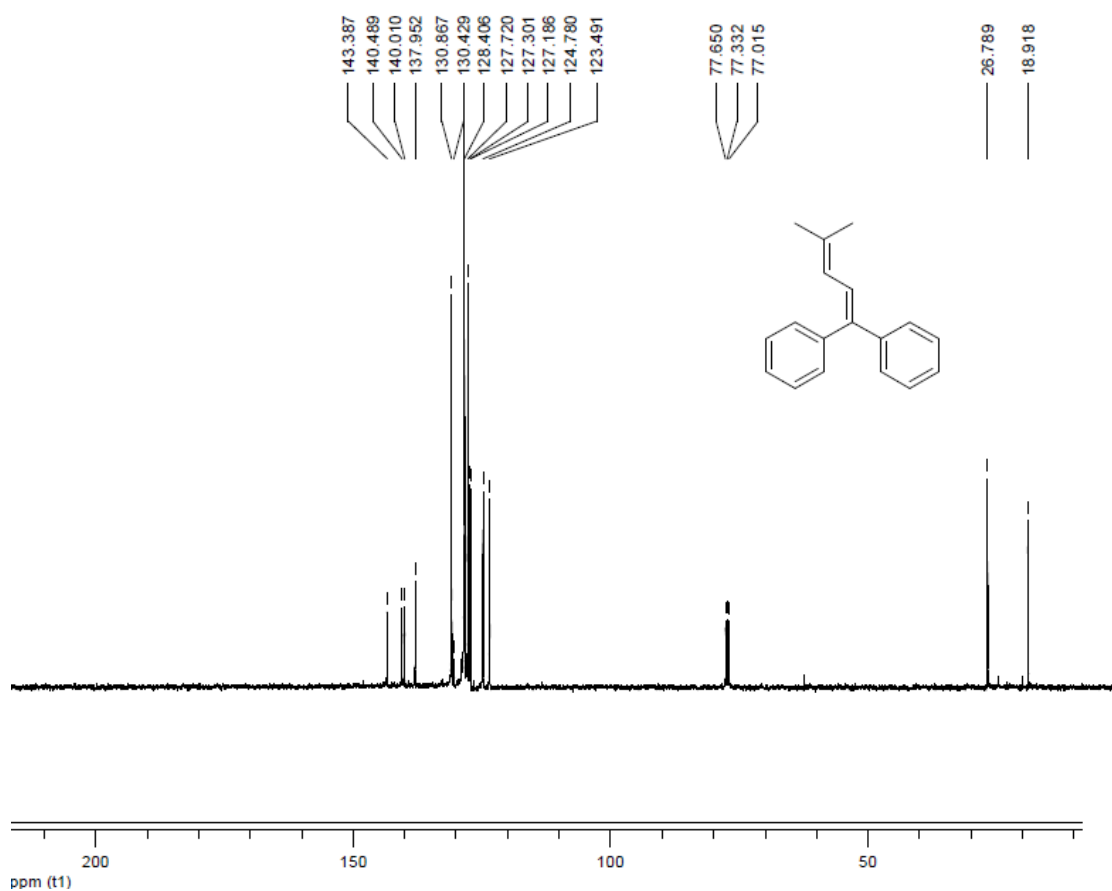
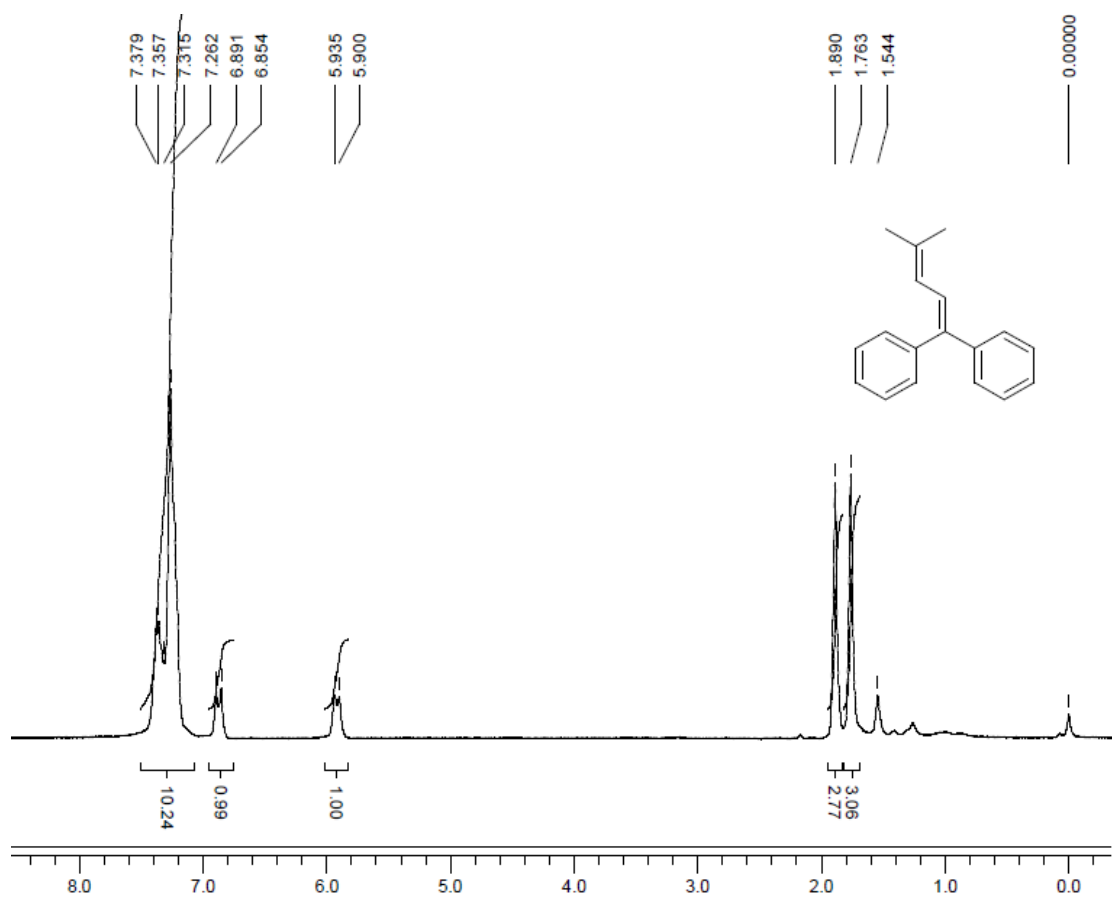
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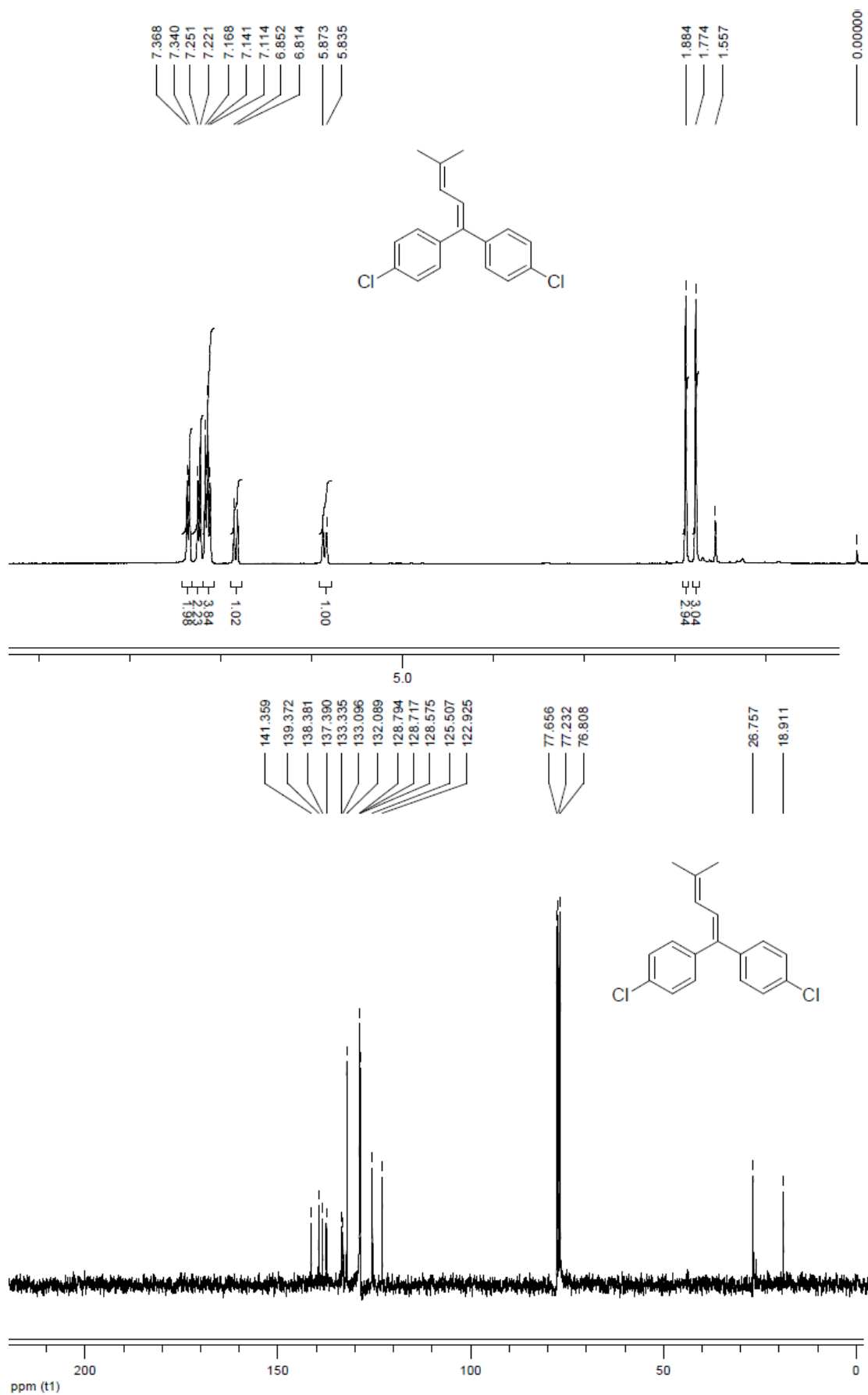
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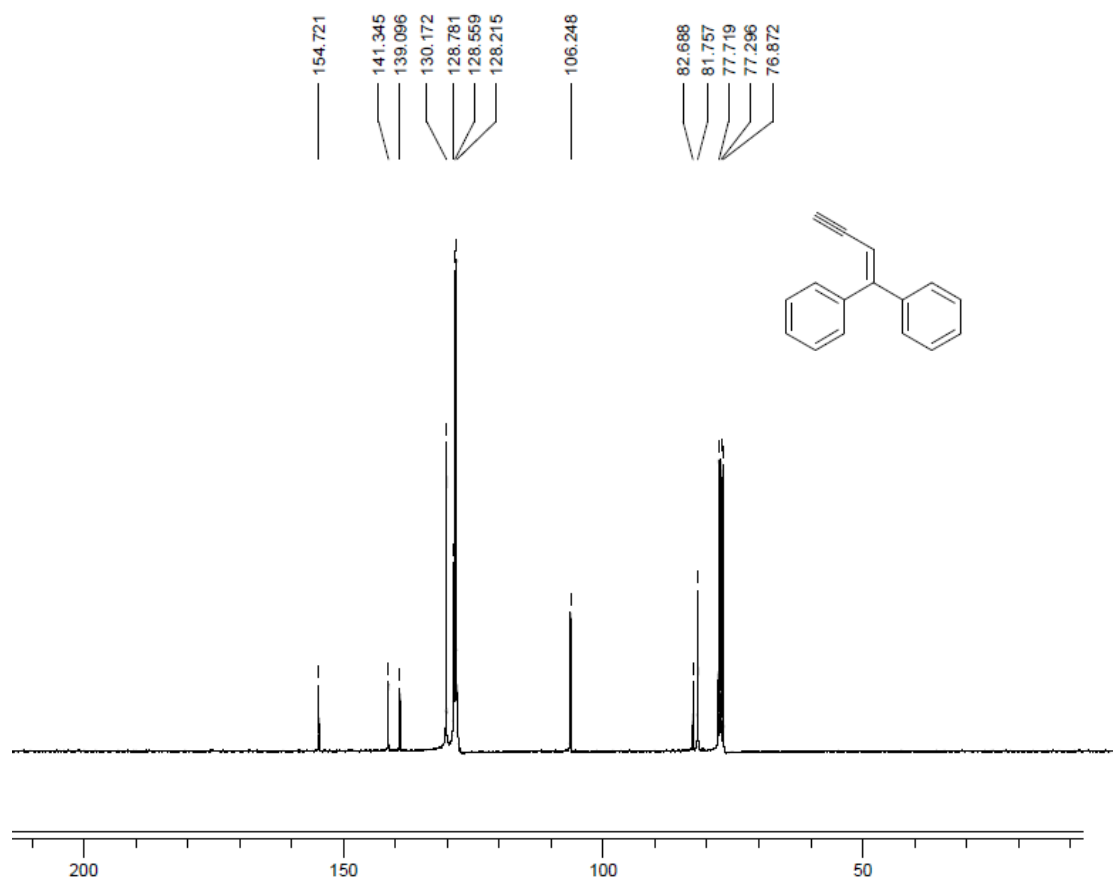
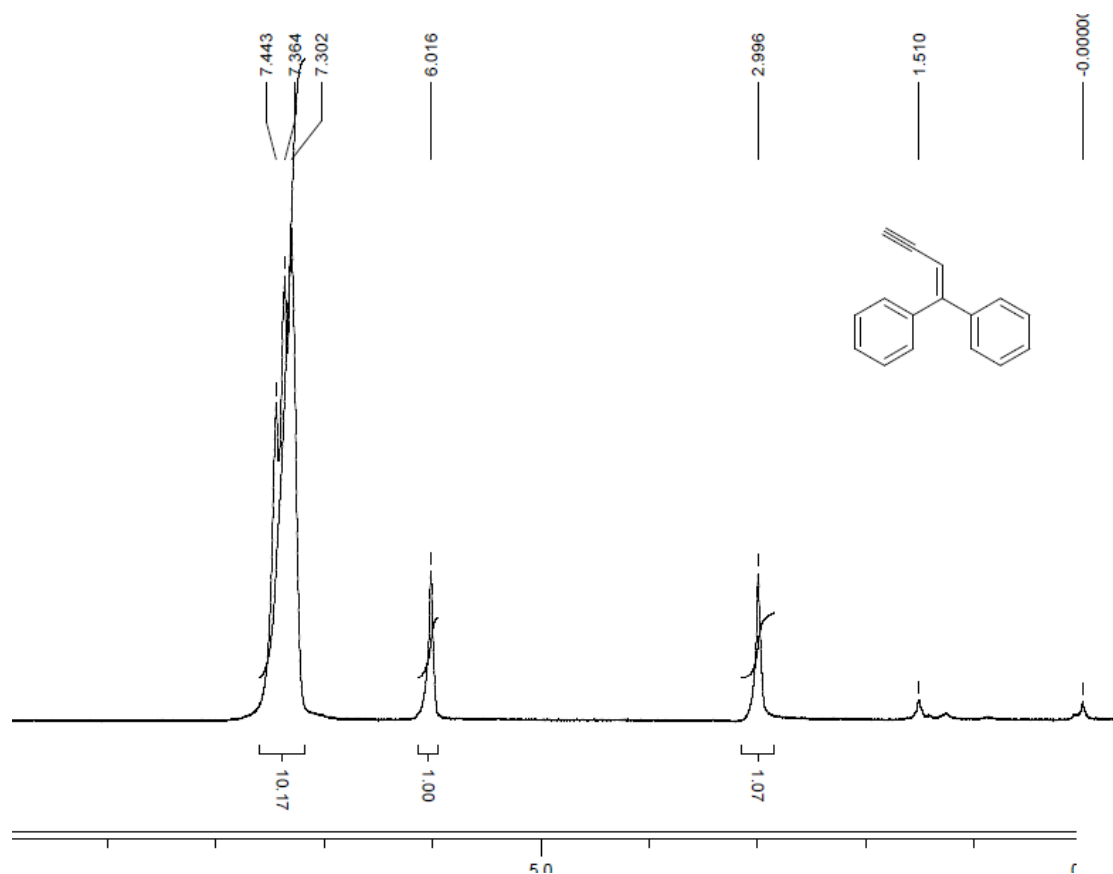
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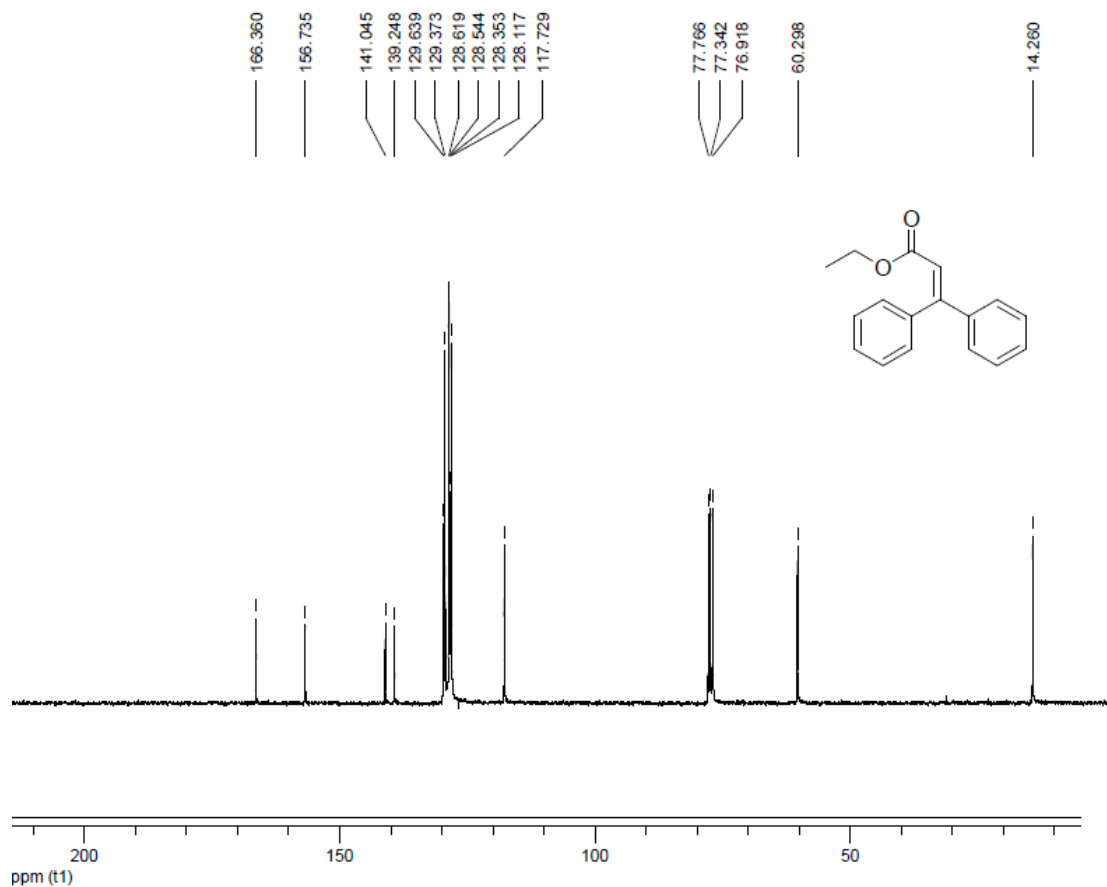
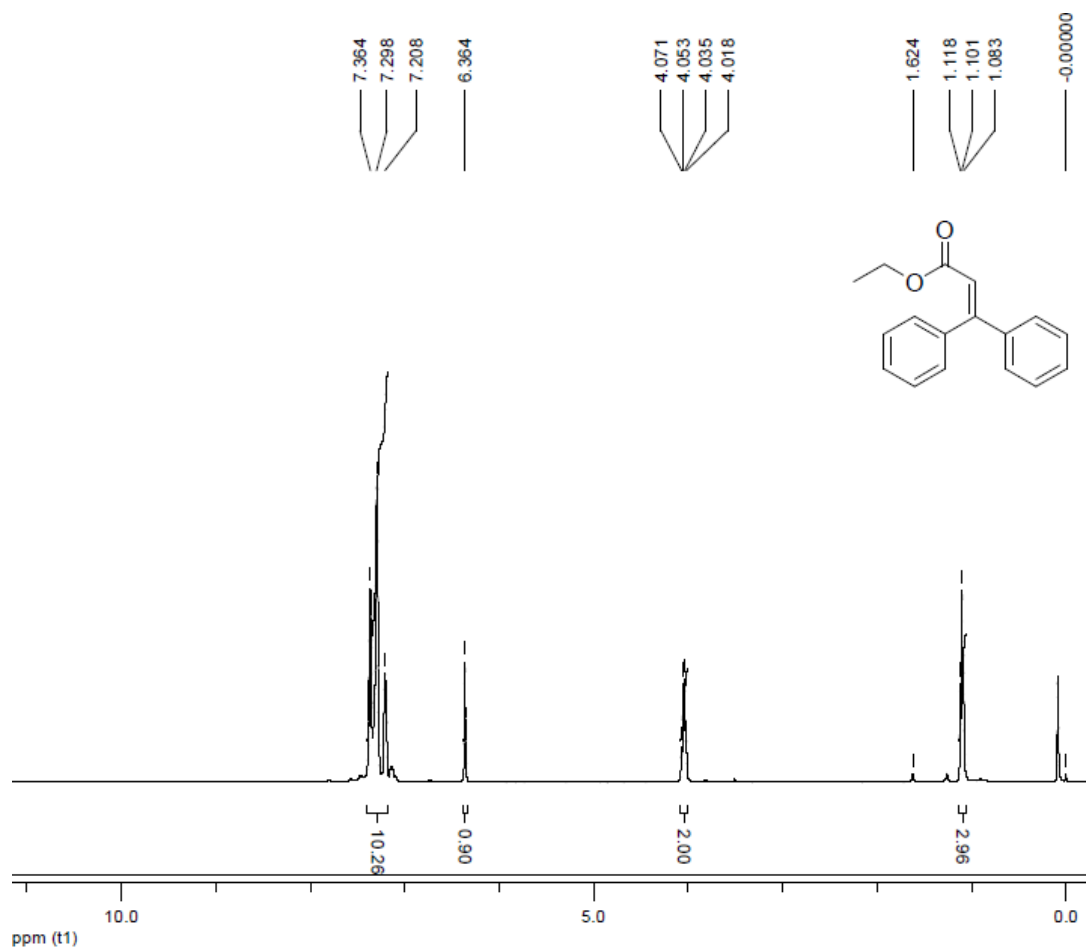
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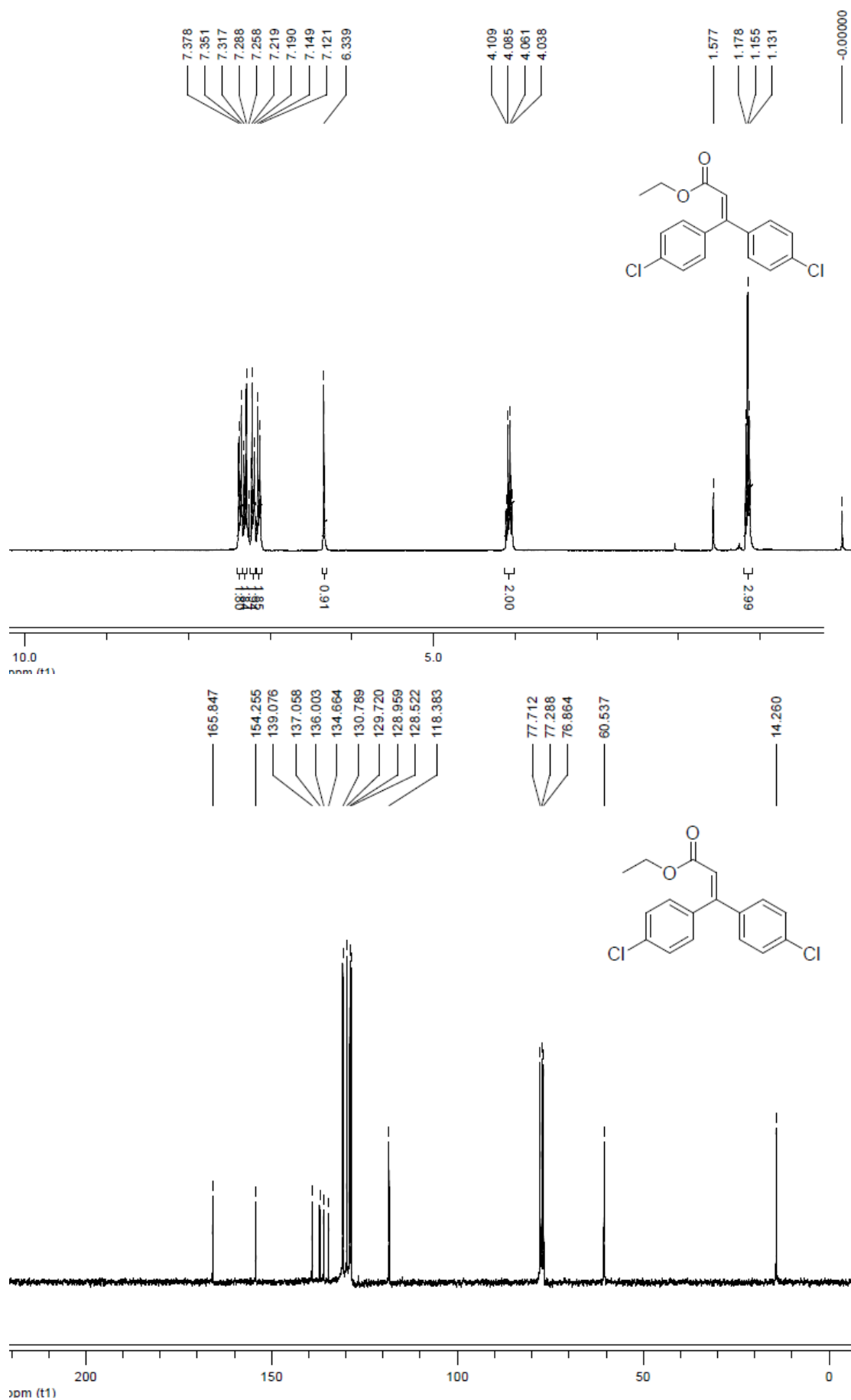
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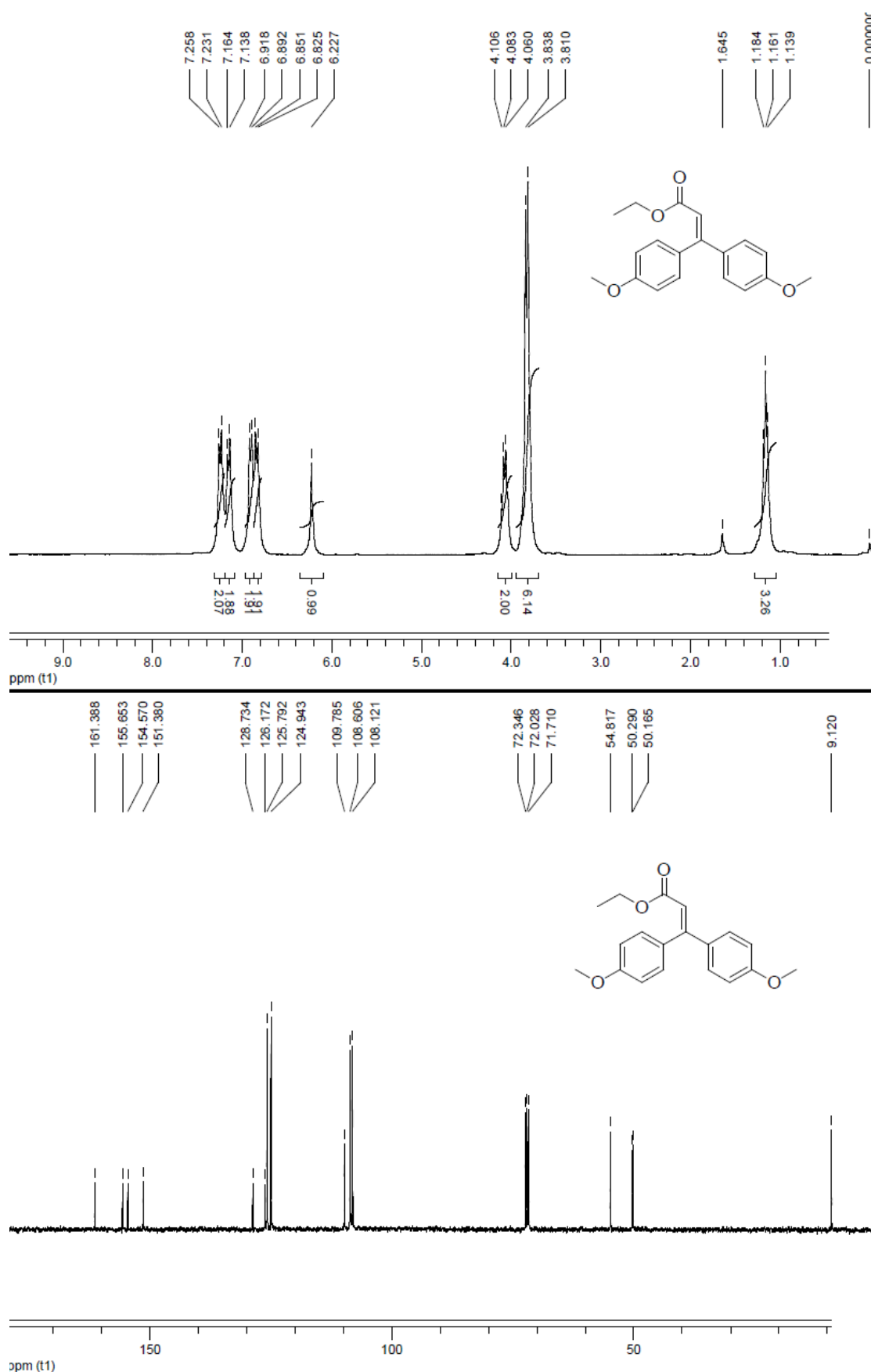
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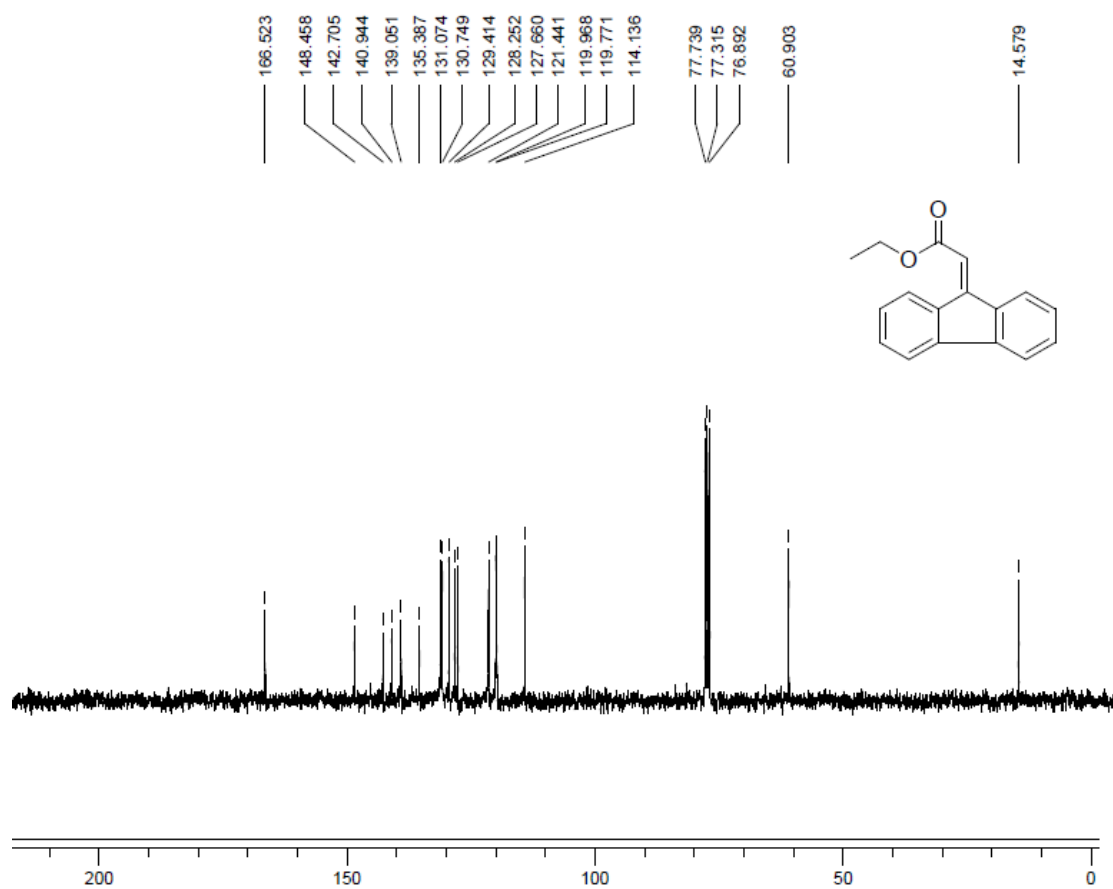
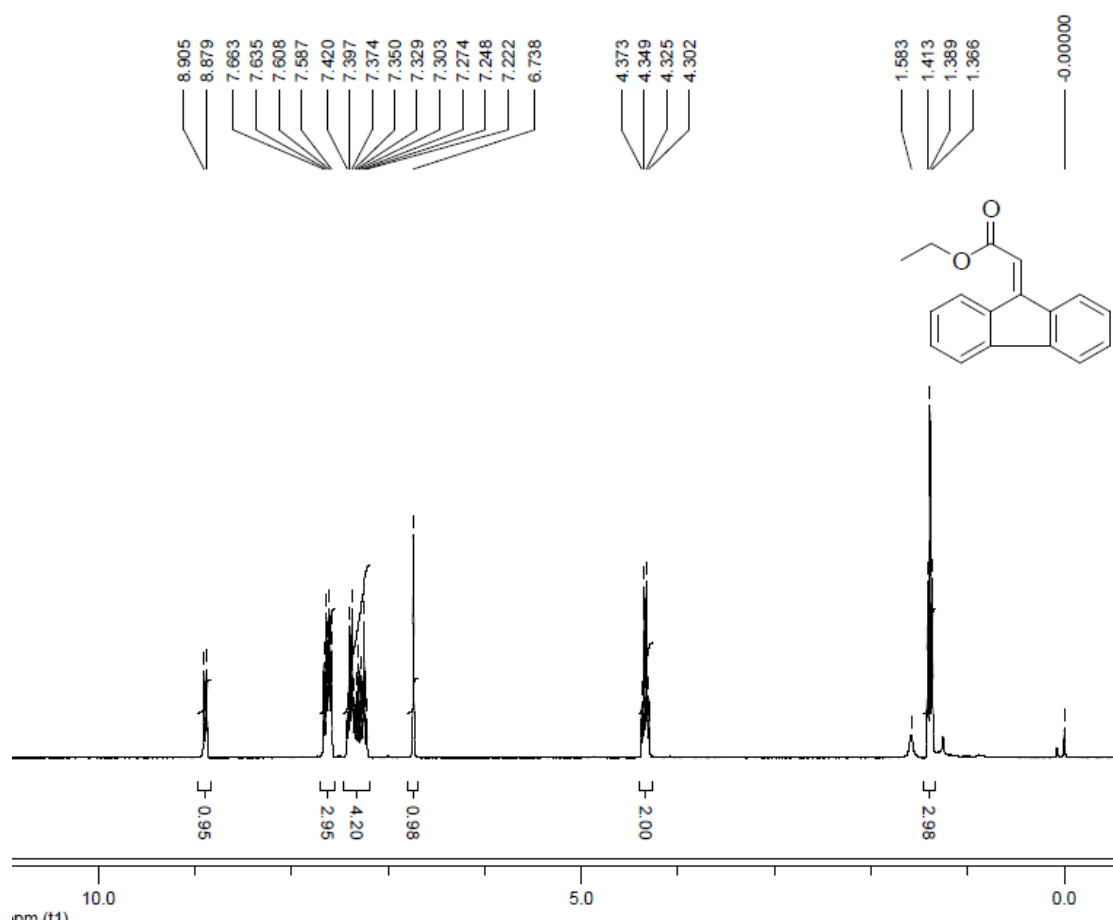
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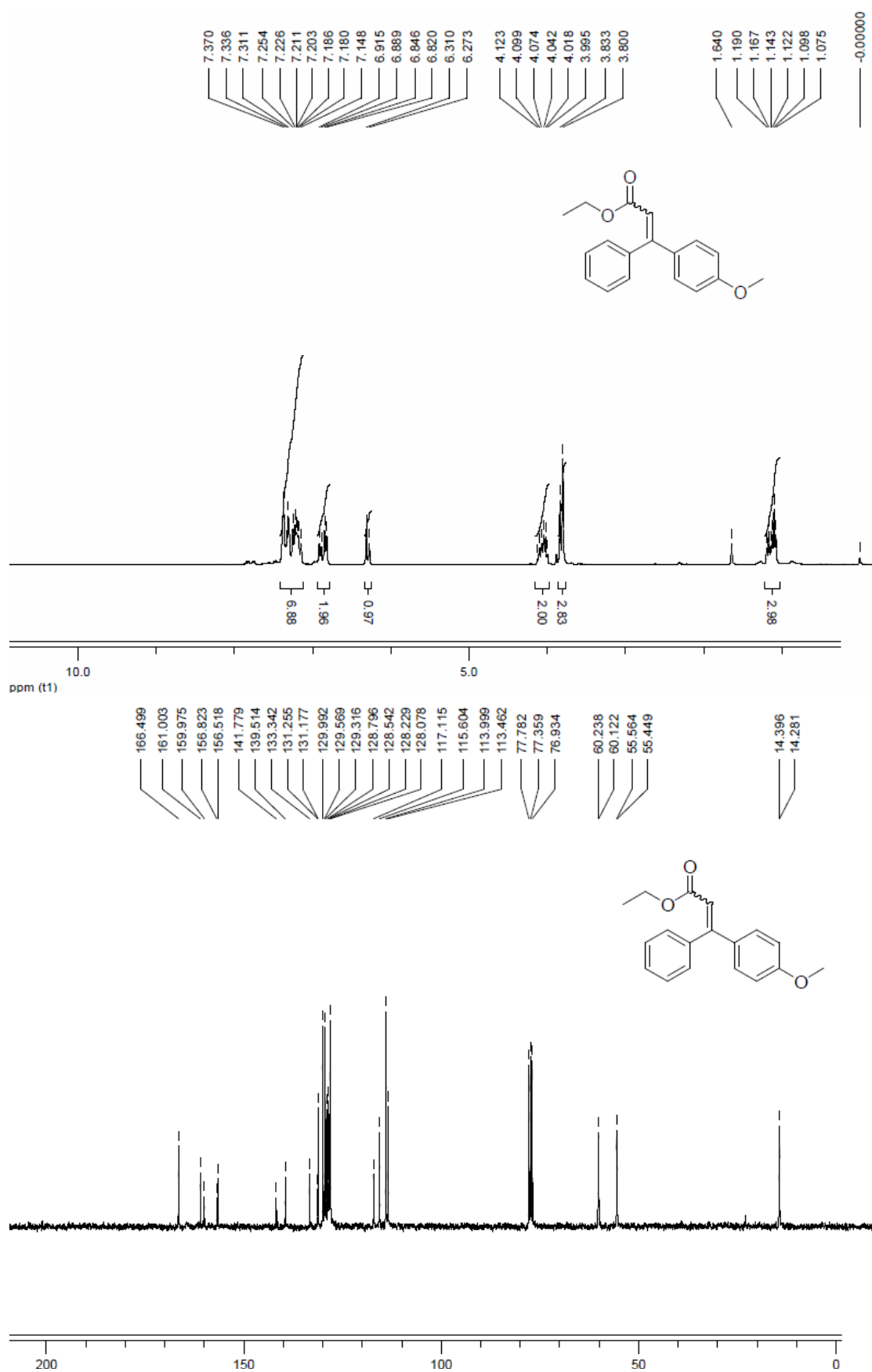
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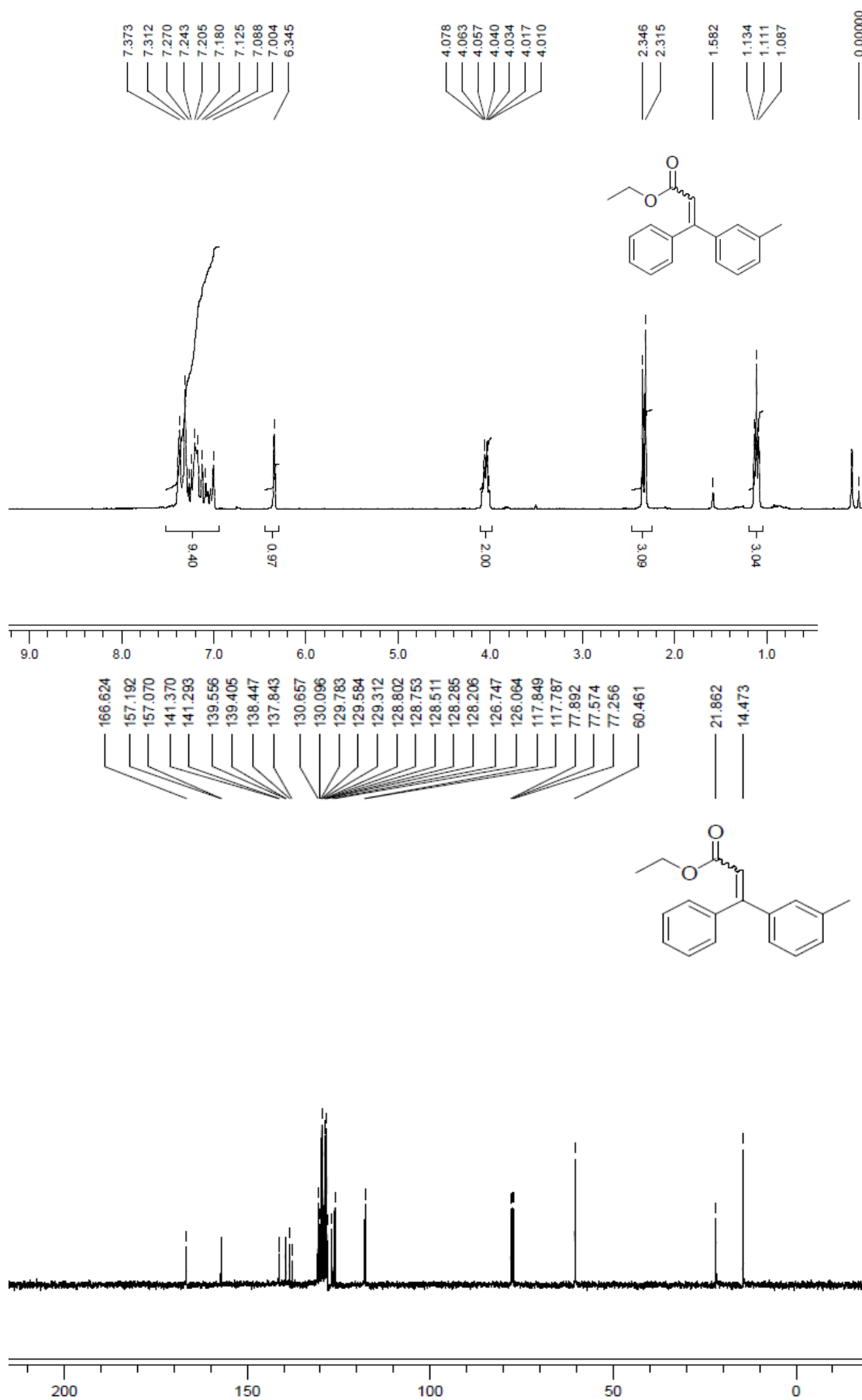
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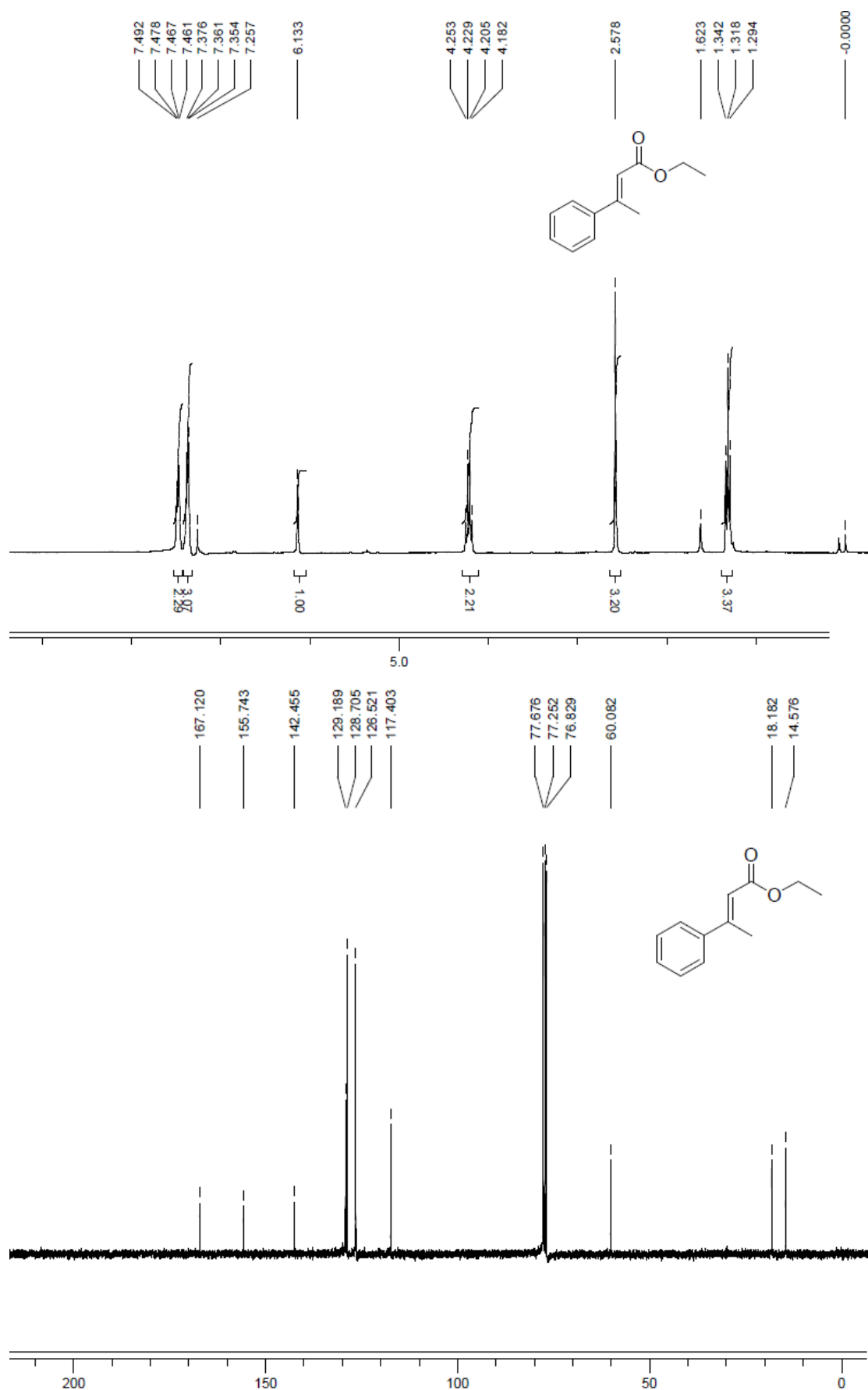
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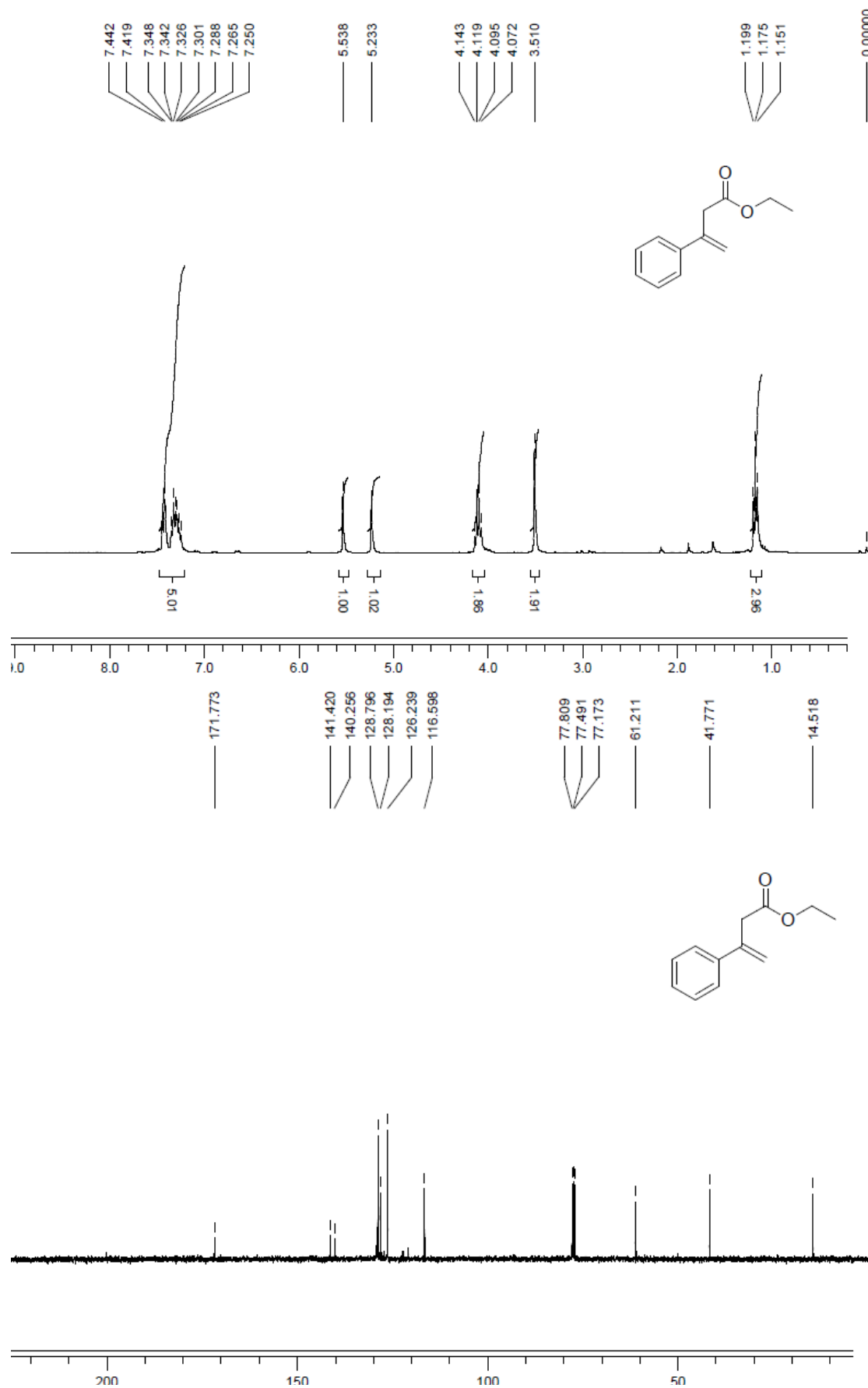
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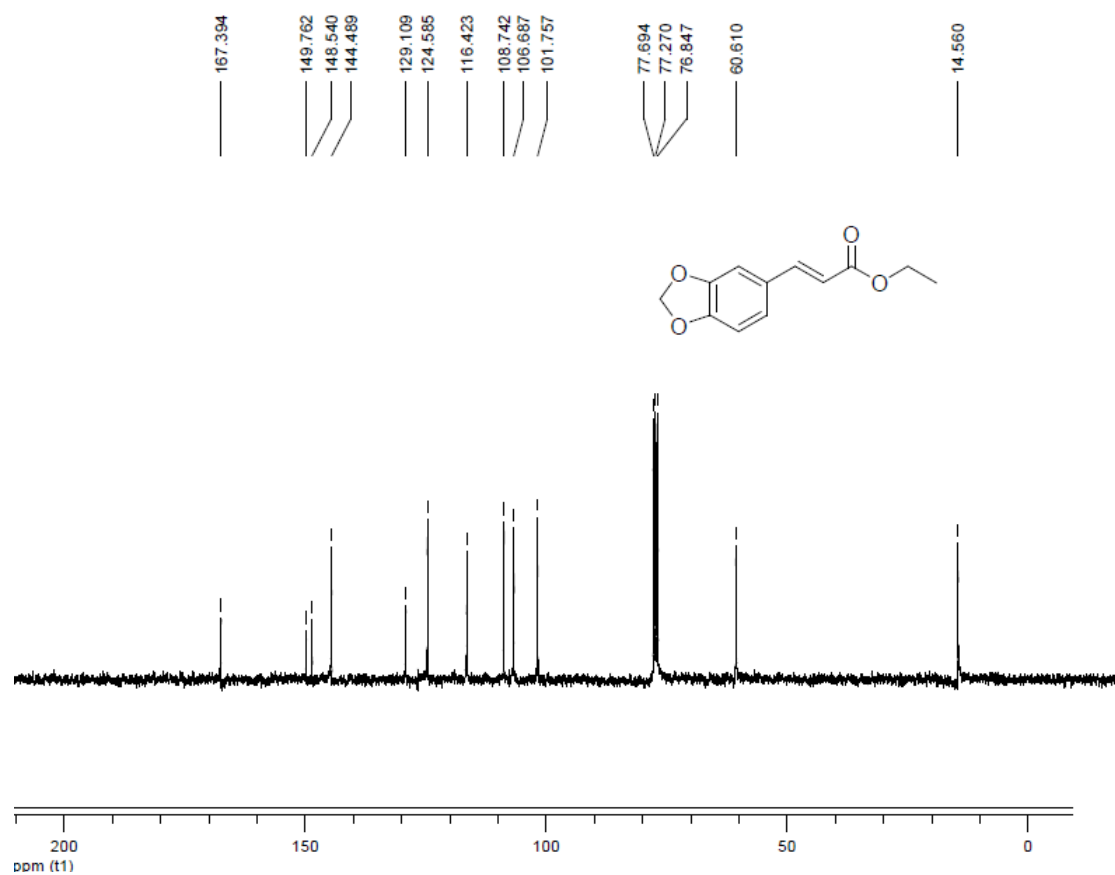
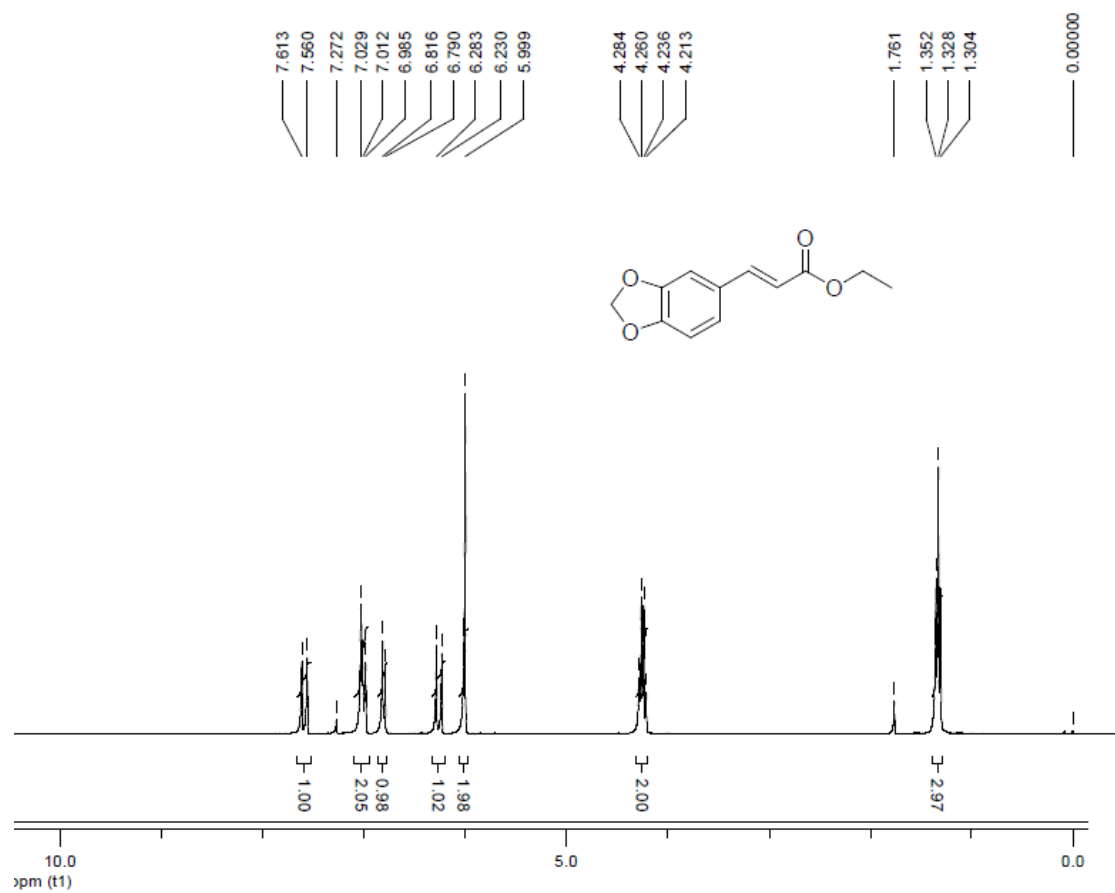
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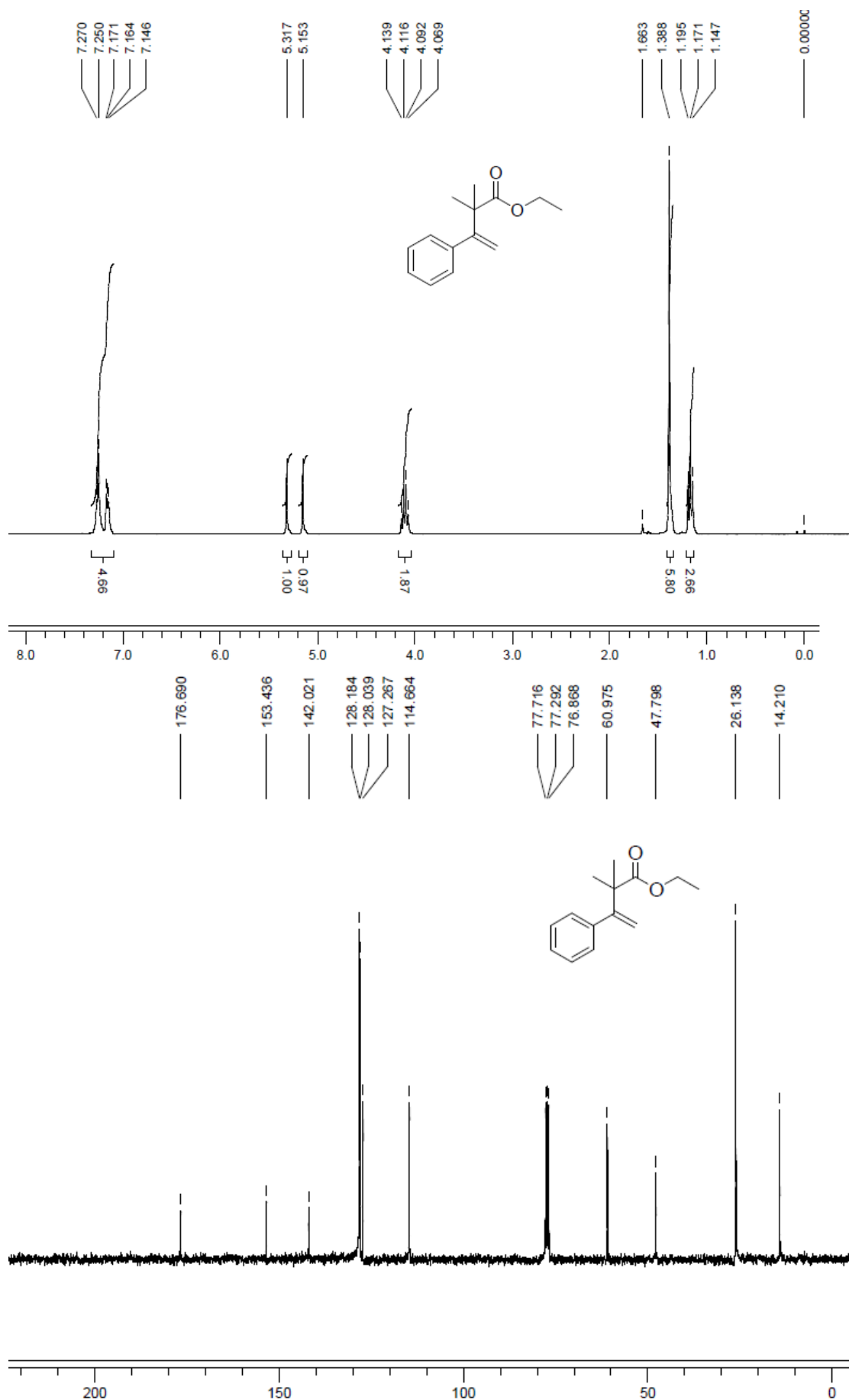
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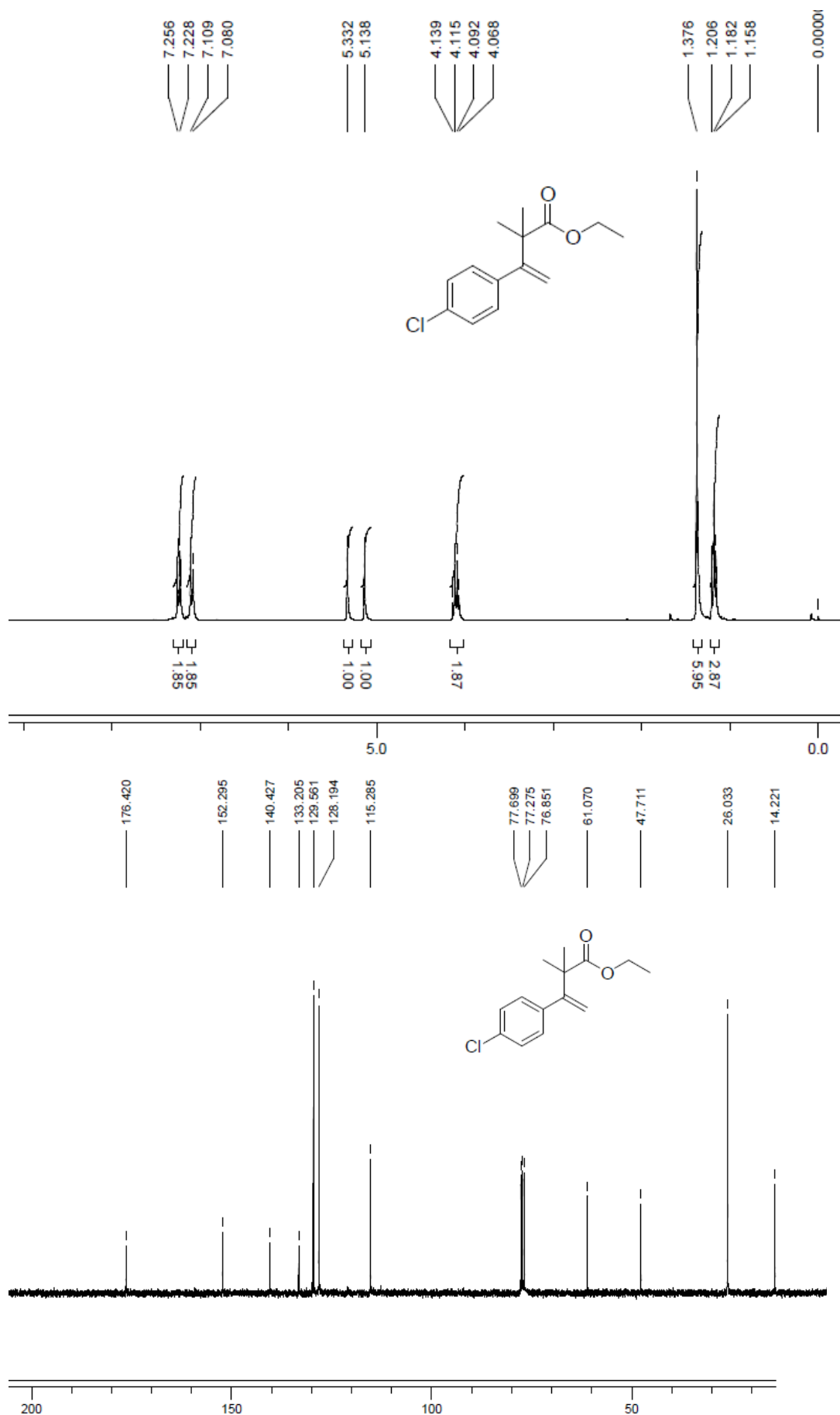
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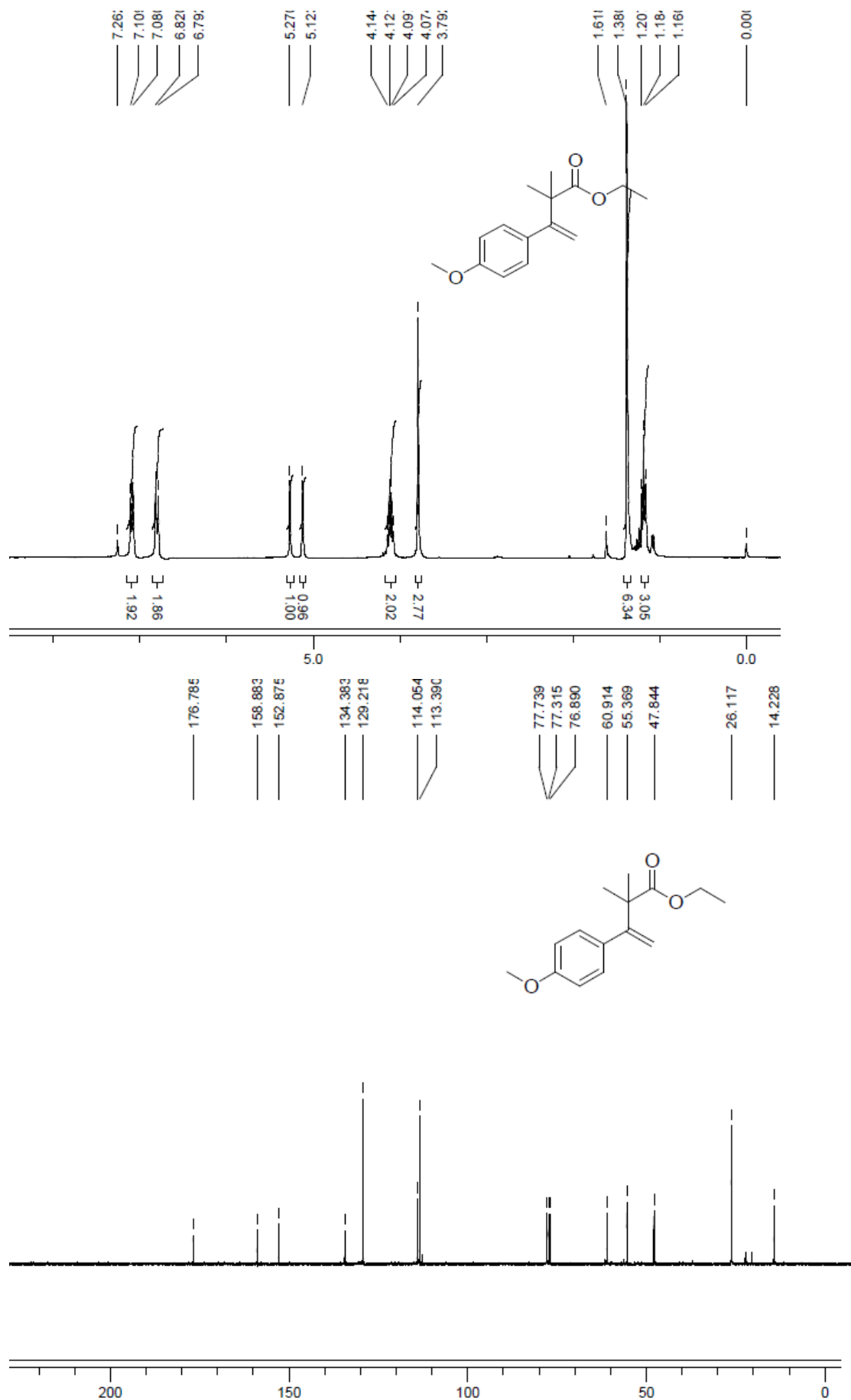
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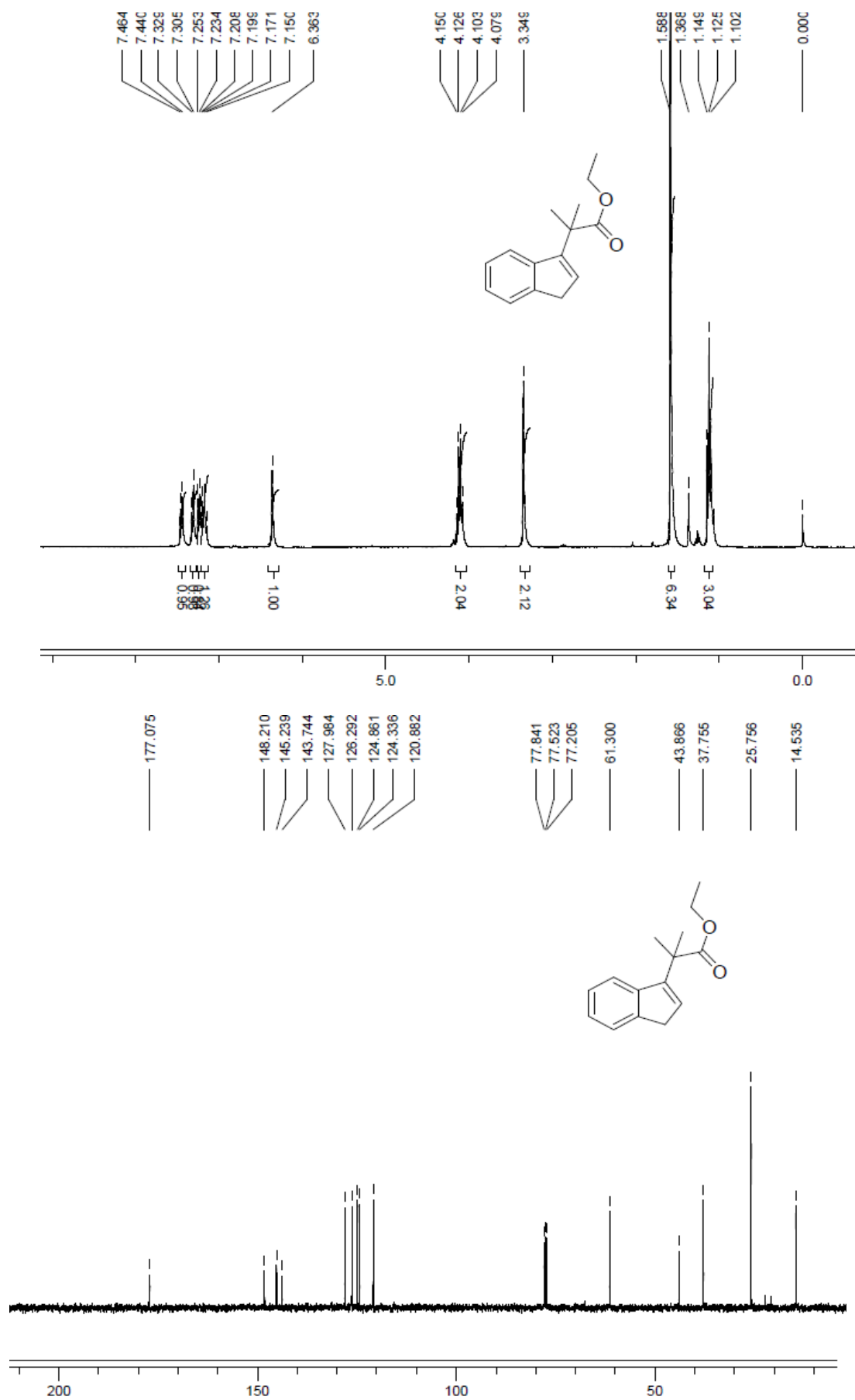
5p



5q



5r



5kd

