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Supporting information

Organocatalytic Hetero-[4+2] Cycloaddition Reactions of 2-(1-Alkynyl)-2-alkene-1-ones: Metal-free Access to Highly Substituted 4*H*-pyrans

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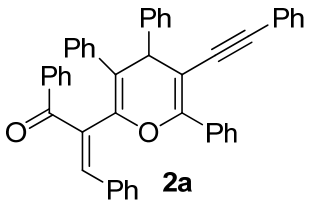
General information

NMR spectra were recorded on a NMR spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C with complete proton decoupling. Petroleum ether refers to the fraction of Petroleum ether having a boiling point between 60 – 90 ^{o}C. The starting materials 2-(1-alkynyl)-alken-1-ones **1** were prepared according to known procedures.[1] Unless otherwise stated, all reagents were obtained from commercial sources and used as received.

Typical Procedure for the synthesis of pyrans 2 from 1:

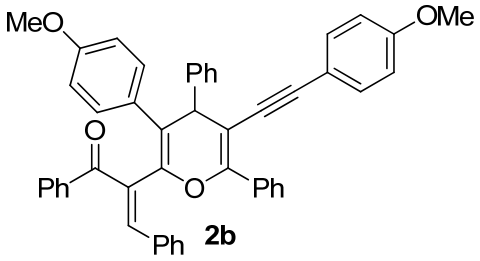
1. (*E*)-1,3-diphenyl-2-(3,4,6-triphenyl-5-(2-phenylethynyl)-4*H*-pyran-2-yl)prop-2-en-1-one(2a).



2a

A mixture of **1a** (154 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 11 h till the enyne **1a** was consumed by TLC analysis, 3 mL of H_2O was added to quench the reaction and the mixture was extracted by ether. The combined organic layer was dried over $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography on silica gel (hexanes: acetate = 10:1) to give a **2a** in 91% yield. Rf = 0.6 (hexanes: acetate = 5:1). Straw yellow solid, m.p.:103 ~104 ^{o}C . ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 ~ 7.63 (m, 4 H), 7.54 ~ 7.21 (m, 22 H) , 7.16 ~ 7.04 (m, 3 H), 6.88 ~ 6.85 (m, 2 H), 4.42 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 195.5, 152.5, 144.4, 143.3, 142.7, 138.0, 137.0, 134.8, 134.7, 133.4, 131.9, 131.0, 123.0, 129.9, 129.1, 129.0, 128.8, 128.7, 128.4, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.6, 127.5, 126.9, 123.7, 117.9, 98.1, 93.2, 88.6, 49.2 ppm. IR (neat): ν (cm^{-1}) 3058, 1646, 1594, 1490, 1444, 1255, 1177, 1112, 1010. HRMS calcd for $C_{46}H_{32}O_2$: 616.2402, found: 616.2416. MS (70 eV): m/z (%): 616 (M^+, 9.50), 105 (100).

2. (*E*)-2-(3-(4-methoxyphenyl)-5-(2-(4-methoxyphenyl)ethynyl)-4,6-diphenyl-4*H*-pyran-2-yl)-1,3-diphenylprop-2-en-1-one (2b).

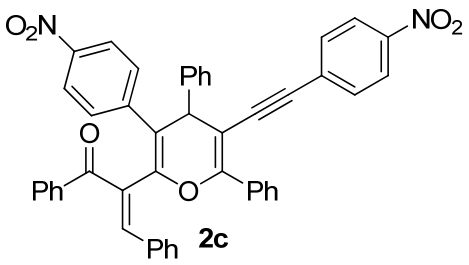


2b

Conditions A: A mixture of **1b** (169 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 62 h to afford **2b**, purified by column chromatography on silica gel to give yellow solid, yield: 60%. Rf = 0.4 (hexanes: acetate = 5:1), m.p.: 181 ~ 182 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 6.9 Hz, 2 H), 7.58 (d, *J* = 6.9 Hz, 2 H), 7.51 ~ 7.45 (m, 3 H), 7.40 ~ 7.17 (m, 16 H), 7.78 ~ 7.74 (m, 4 H), 6.58 (d, *J* = 11.7 Hz, 2 H), 4.33 (s, 1 H), 3.74 (s, 3 H), 3.66 (s, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 195.5, 159.2, 138.9, 151.7, 143.7, 143.5, 142.5, 138.0, 134.9, 134.9, 133.4, 132.4, 131.8, 130.2, 129.9, 129.8, 129.3, 129.0, 128.9, 128.7, 128.6, 128.3, 128.0, 127.8, 127.5, 126.8, 117.5, 115.9, 113.9, 113.3, 98.2, 93.1, 87.2, 55.2, 55.0, 49.4 ppm. IR (neat): *v* (cm^{-1}) 3030, 2836, 1658, 1603, 1508, 1243, 1172, 1076, 1021. HRMS calcd for $C_{48}H_{36}O_4$: 676.2614, found: 676.2625. MS (70 eV): m/z (%): 676 (M^+, 13.11), 105 (100).

Conditions B: A mixture of **1b** (169 mg, 0.5 mmol) and *n*-Bu_3P (20.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 25 ^{o}C for 22 h to afford **2b**, purified by column chromatography on silica gel to give yellow solid; yield: 76%. The ^{1}H NMR and ^{13}CNMR data is same as the above.

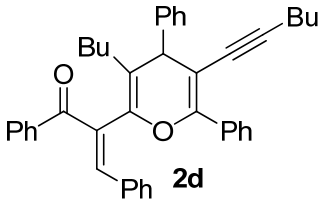
3. (*E*)-2-(3-(4-nitrophenyl)-5-(2-(4-nitrophenyl)ethynyl)-4,6-diphenyl-4*H*-pyran-2-yl)-1,3-diphenylprop-2-en-1-one (2c).



2c

A mixture of **1c** (176.5 mg, 0.5 mmol) and DBU (15.2 mg, 0.1 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 4 h to afford **2c**, purified by column chromatography on silica gel to give straw yellow solid, yield: 91%. Rf = 0.4 (hexanes: acetate = 5:1), m.p.: 195 ~ 196 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.1 Hz, 2 H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2 H), 7.40 (d, *J* = 2 Hz, 2 H), 7.58 ~ 7.53 (m, 2 H), 7.46 ~ 7.29 (m, 16 H), 7.14 (s, 1 H), 6.97 (d, *J* = 8.4 Hz, 2 H), 4.44 (s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 195.3, 154.3, 146.8, 146.1, 144.0, 143.9, 142.2, 137.4, 134.1, 133.3, 132.7, 132.5, 131.5, 130.7, 130.4, 130.3, 129.9, 129.5, 129.4,129.2, 129.0, 128.9, 128.8, 128.5, 128.4, 128.0, 127.9, 127.6, 123.5, 123.07, 116.2, 97.4, 94.0, 91.7, 48.3 ppm. IR (neat): *v* (cm^{-1}) 2925, 2196, 1646, 1587, 1514, 1340, 1184, 1108. HRMS calcd for $C_{46}H_{30}N_2O_6$: 706.2104, found: 706.2083. MS (70 eV): m/z (%): 706 (M^+, 13.67), 105 (100).

4. (*E*)-2-(3-butyl-5-(hex-1-ynyl)-4,6-diphenyl-4*H*-pyran-2-yl)-1,3-diphenylprop-2-en-1-one (2d).

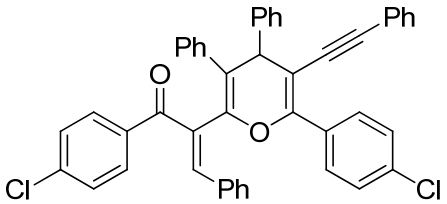


2d

A mixture of **1d** (144 mg, 0.5 mmol) and *n*-Bu_3P (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at rt for 22 h to afford **2d**, purified by column chromatography on silica gel to give yellow solid, yield: 50%. Rf = 0.7 (hexanes: acetate = 5:1),m.p.: 78 ~ 79 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.2 Hz,3 H), 7.69 ~ 7.66 (m, 2 H), 7.61 ~ 7.57 (m, 3 H), 7.50 ~ 7.44 (m, 3 H), 7.39 ~ 7.35 (m, 3 H), 7.29 ~ 7.15 (m, 8 H), 4.10 (s, 1 H), 2.26 (t, *J* = 6.9 Hz, 2 H), 1.95 ~ 1.85 (m, 1 H), 1.62 ~ 1.37 (m, 6 H), 1.35 ~ 1.11 (m, 2 H), 0.88 (t, *J* = 7.2 Hz, 3

H), 0.76 (t, *J* = 6.6 Hz, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 196.0, 151.1, 143.9, 143.3, 140.1, 138.4, 134.6, 134.1, 133.8, 132.0, 130.1, 129.9, 129.0, 128.6, 128.5, 128.5, 128.3, 128.1, 127.7, 127.4, 126.54, 115.7, 97.8, 94.1, 79.1, 46.3, 30.6, 29.2, 28.5, 22.5, 21.8, 19.3, 13.7, 13.5 ppm. IR (neat): *v* (cm^{-1}) 2956, 2931, 2871, 1646, 1598, 1448, 1252, 1217, 1179, 1114. HRMS calcd for $C_{42}H_{40}O_2$: 576.3028, found: 576.3028. MS (70 eV): m/z (%): 576 (M^+, 2.80), 105 (100).

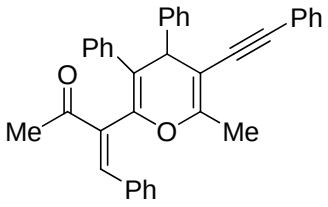
5. (*E*)-1-(4-chlorophenyl)-2-(6-(4-chlorophenyl)-3,4-diphenyl-5-(2-phenylethynyl)-4*H*-pyran-2-yl)-3-phenylprop-2-en-1-one (2e).



2e

A mixture of **1e** (171.5 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 15 h to afford **2e**, purified by column chromatography on silica gel to give orange solid, yield: 94%. Rf = 0.7 (hexanes: acetate = 5:1),m.p.: 187 ~188 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 ~ 7.71 (m, 2 H), 7.52 ~ 7.49 (m, 2 H), 7.44 ~ 7.40 (m, 5 H), 7.37 ~ 7.35 (m, 3 H), 7.33 ~ 7.26 (m, 10 H), 7.22 ~7.01 (m, 5 H), 6.88 ~ 6.85 (m, 2 H), 4.41 (s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 194.14, 151.28, 144.17, 143.04, 142.58, 138.30, 136.69, 136.14, 134.85, 134.60, 134.34, 131.63, 131.00, 130.41, 130.21, 129.79, 129.10, 128.97, 128.89, 128.57, 128.46, 128.34, 128.27, 128.07, 128.01, 127.80, 127.75, 127.15, 123.36, 118.33, 98.62, 93.83, 88.00, 49.21 ppm. IR (neat): *v* (cm^{-1}) 3027, 2205, 1651, 1588, 1489, 1398, 1255, 1176, 1089, 1010. HRMS calcd for $C_{46}H_{30}O_2Cl_2$: 684.1623, found: 684.1618. MS (70 eV): m/z (%): 684 (M^+, 6.36), 686 (M+2, 4.79), 686 (M+4, 1.18) 139 (100).

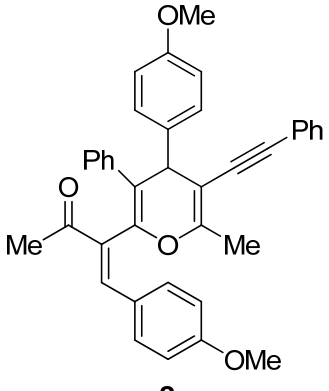
6. (*E*)-3-(6-methyl-3,4-diphenyl-5-(2-phenylethynyl)-4*H*-pyran-2-yl)-4-phenylbut-3-en-2-one (2f).



2f

A mixture of **1f** (123 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 38 h to afford **2f**, purified by column chromatography on silica gel to give orange solid, yield: 88%. Rf = 0.5 (hexanes: acetate = 5:1),m.p.: 59 ~ 60 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 ~ 7.55 (m, 2 H), 7.50 (s, 1 H), 7.45 ~ 7.23 (m, 13 H), 7.08 ~ 7.00 (m, 3 H), 4.39 (s, 1 H), 2.34 (s, 3 H), 2.24 (s, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 197.31, 153.51, 142.99, 142.89, 142.00, 137.25, 134.42, 133.99, 130.98, 130.04, 129.96, 128.50, 128.45, 128.19, 128.06, 127.91, 127.78, 127.64, 127.06, 126.79, 123.61, 117.01, 97.94, 92.98, 87.14, 47.62, 26.92, 17.94 ppm. IR (neat): ν (cm^{-1}) 3058, 2203, 1671, 1596, 1491, 1219, 1162, 1111. HRMS calcd for $C_{36}H_{28}O_2$: 492.2089, found: 492.2099, MS (70 eV): m/z (%): 492 (M^+, 54.29), 43 (100).

7. (*E*)-4-(4-methoxyphenyl)-3-(4-(4-methoxyphenyl)-6-methyl-3-phenyl-5-(2-phenylethynyl)-4*H*-pyran-2-yl)but-3-en-2-one (2g).



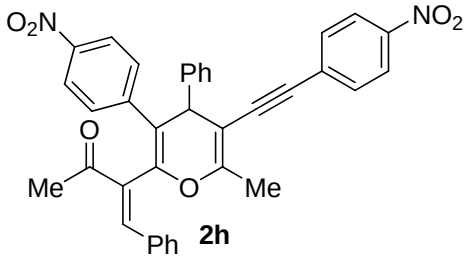
2g

Condition A: A mixture of **1g** (136 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 60 h to afford **2g**, purified by column chromatography on silica gel to give orange solid, yield: 45%. Rf = 0.4 (hexanes: acetate = 5:1), m.p.: 55 ~ 56 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.4 Hz, 2 H), 7.46 (s, 1 H), 7.37 ~ 7.26 (m, 7 H), 7.07 ~ 7.00 (m, 3 H), 6.95 (d, J =

8.4 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.77 (d, *J* = 8.4 Hz, 2 H), 4.35 (s, 1 H), 3.88 (s, 3 H), 3.78 (s, 3 H), 2.28 (s, 3 H), 2.23 (s, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 197.2, 161.2, 158.4, 153.5, 142.7, 142.1, 137.5, 135.5, 132.3, 131.6, 131.0, 129.4, 128.1, 128.1, 127.8, 127.6, 127.02, 126.9, 123.7, 117.0, 114.1, 113.6, 98.1, 92.8, 87.3, 55.3, 55.0, 46.7, 26.84, 18.0 ppm. IR (neat): *v* (cm^{-1}) 2930, 2837, 2203, 1666, 1600, 1509, 1254, 1174, 1029. HRMS calcd for $C_{38}H_{32}O_4$: 552.2301, found: 552.2291. MS (70 eV): m/z (%): 522 (M^+, 49.28), 105 (100).

Condition B: A mixture of **1** (136 mg, 0.5 mmol) and *n*-Bu_3P (20.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 25 ^{o}C for 22 h to afford **2g**, purified by column chromatography on silica gel to give yellow solid; yield: 82%. The ^{1}H NMR and ^{13}CNMR data is same as the above.

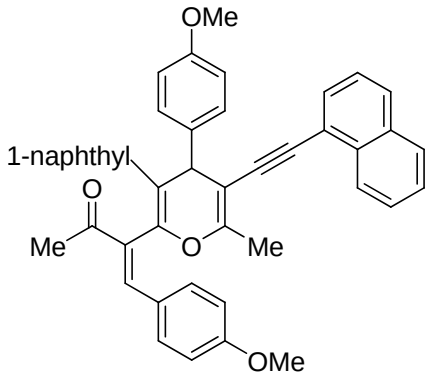
8. (*E*)-3-(6-methyl-3-(4-nitrophenyl)-5-(2-(4-nitrophenyl)ethynyl)-4-phenyl-4*H*-pyran-2-yl)-4-phenylbut-3-en-2-one (2h).



2h

A mixture of **1h** (145.5 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 1 h to afford **2h**, purified by column chromatography on silica gel to give brown solid, yield: 80%. Rf = 0.3 (hexanes: acetate = 5:1), m.p.: 99 ~ 100 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.7 Hz, 2 H), 7.78 (d, *J* = 8.7 Hz, 2 H), 7.44 ~ 7.20 (m, 13 H), 6.68 (d, *J* = 8.7 Hz, 2 H), 4.29 (s, 1 H), 2.39 (s, 3 H), 2.27 (s, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 196.9, 155.1, 146.7, 146.6, 144.5, 144.3, 142.7, 142.0, 134.0, 133.8, 131.5, 130.5, 130.4, 129.7, 129.0, 128.8, 128.5, 128.4, 127.4, 123.5, 123.0, 115.4, 97.4, 92.7, 92.1, 47.0, 26.6, 18.3 ppm. IR (neat): *v* (cm^{-1}) 3064, 2923, 2849, 2199, 1671, 1590, 1514, 1341, 1222, 1107. HRMS calcd for $C_{36}H_{26}N_2O_6$: 582.1791, found: 582.1808. MS (70 eV): m/z (%): 582 (M^+, 9.60), 43 (100).

9. (*E*)-4-(4-methoxyphenyl)-3-(4-(4-methoxyphenyl)-6-methyl-3-(naphthalen-1-yl)-5-(2-(naphthalen-1-yl)ethynyl)-4*H*-pyran-2-yl)but-3-en-2-one (2i).

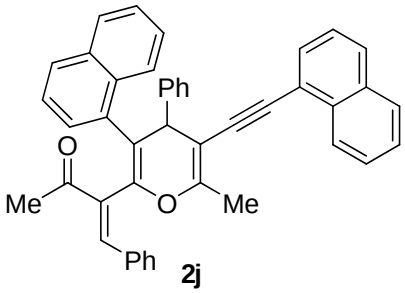


2i

Condition A: A mixture of **1i** (163 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 60 h to afford **2i**, purified by column chromatography on silica gel to give brown solid, yield: 51%. Rf = 0.3 (hexanes: acetate = 5:1), m.p.: 100 ~ 101 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (s, 1 H), 7.82 ~ 772 (m, 4 H), 7.58 ~ 7.52 (m, 2 H), 7.45 ~ 7.26 (m, 8 H), 7.14 ~ 7.10 (m, 2 H), 6.92 ~ 6.79 (m, 5 H), 6.13 (s, 1 H), 4.52 (s, 1 H), 3.89 (s, 3 H), 3.77 (s, 3 H), 2.52 (s, 3 H), 2.23 (s, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 197.1, 161.3, 158.5, 143.1, 142.4, 135.1, 133.6, 133.5, 133.1, 133.1, 132.0, 131.9, 130.4, 129.7, 129.7, 129.4, 128.3, 128.1, 128.1, 128.1, 127.8, 127.4, 127.2, 127.2, 126.4, 126.2, 125.6, 125.3, 125.2, 125.1, 124.8, 121.4, 115.6, 114.1, 113.4, 97.7, 92.6, 91.2, 55.4, 55.1, 26.6, 18.6 ppm. IR (neat): ν (cm^{-1}) 3044, 2919, 2849, 2192, 1664, 1603, 1509, 1258, 1177, 1154, 1118, 1031. HRMS calcd for $C_{46}H_{36}O_4$: 652.2614, found: 652.2625. MS (70 eV): m/z (%): 652 (M^+, 54.39), 239 (100).

Condition B. A mixture of **1i** (169 mg, 0.5 mmol) and *n*-Bu_3P (20.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 25 ^{o}C for 22 h to afford **2i**, purified by column chromatography on silica gel to give yellow solid; yield: 60%. The ^{1}H NMR and ^{13}CNMR data is same as the above.

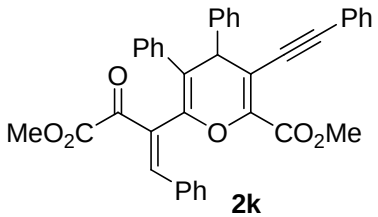
10. (*E*)-3-(6-methyl-3-(naphthalen-1-yl)-5-(2-(naphthalen-1-yl)ethynyl)-4-phenyl-4*H*-pyran-2-yl)-4-phenylbut-3-en-2-one (2j).



2j

A mixture of **1j** (148 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 60 h to afford **2j**, purified by column chromatography on silica gel to give brown solid, yield: 75%. Rf = 0.5 (hexanes: acetate = 5:1),m.p.: 121 ~ 122 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.1 Hz, 3 H), 7.76 ~ 7.64 (m, 4 H), 7.52 ~ 7.48 (m, 2 H), 7.42 ~ 7.15 (m, 16 H), 7.08 ~ 7.00 (m, 1 H), 6.85 ~ 6.80 (m, 1 H), 5.97 (d, *J* = 7.2 Hz, 1 H), 4.54 (s, 1 H), 2.50 (s, 3 H), 2.20 (s, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 197.0, 154.1, 143.4, 142.6, 142.2, 130.3, 129.9, 129.3, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 127.5, 126.8, 126.4, 126.1 126.1, 125.7, 125.3, 125.1, 125.0, 124.6, 121.2, 115.5, 97.5, 92.3, 91.3, 47.6, 26.6, 18.5 ppm. IR (neat): *v* (cm^{-1}) 3676, 2988, 2921, 2185, 1665, 1647, 1381, 1217, 1188, 1165, 1075. HRMS calcd for $C_{44}H_{32}O_2$: 592.2402, found: 592.2416. MS (70 eV): m/z (%): 592(M^+, 69.39), 252 (100).

11. (*E*)-methyl 6-(4-methoxy-3,4-dioxo-1-phenylbut-1-en-2-yl)-4,5-diphenyl-3-(2-phenylethynyl)-4*H*-pyran-2-carboxylate (2k).

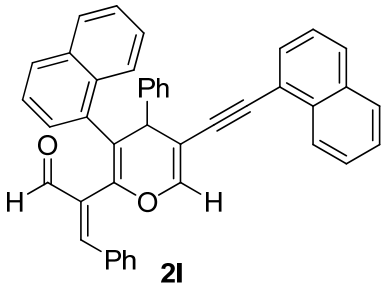


2k

A mixture of **1k** (145 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 3 h to afford **2k**, purified by column chromatography on silica gel to give straw yellow solid, yield: 80%. Rf = 0.2 (hexanes: acetate = 5:1), m.p.: 147 ~148 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.52 (d, *J* = 6.6 Hz, 4 H), 7.45 ~ 735 (m, 10 H), 7.15 ~ 7.03 (m, 4 H), 6.83 (d, *J* = 7.2 Hz, 4

H), 4.44 (s, 1 H), 3.78 (s, 3 H), 3.72 (s, 3 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 184.8, 163.4, 160.8, 149.4, 143.0, 141.4, 140.8, 136.1, 133.8, 131.5, 130.9, 130.2, 129.7, 129.3, 128.9, 128.6, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.5, 122.9, 117.5, 110.4, 98.7, 85.9, 52.6, 52.1, 49.8 ppm. IR (neat): ν (cm^{-1}) 3056, 2954, 2204, 1736, 1677, 1603, 1491, 1439, 1282, 1239, 1200, 1181, 1139, 1051. HRMS calcd for $C_{38}H_{26}O_6$: 580.1886, found: 580.1862. MS (70 eV): m/z (%): 580 (M^+, 43.64), 202 (100).

12. (*E*)-2-(3-(naphthalen-1-yl)-5-(2-(naphthalen-1-yl)ethynyl)-4-phenyl-4*H*-pyran-2-yl)-3-phenylacrylaldehyde (2l).



2l

A mixture of **1l** (141 mg, 0.5 mmol) and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 0 ^{o}C for 60 h to afford **2l**, purified by column chromatography on silica gel to give yellow solid; yield: 50%. Rf = 0.5 (hexanes: acetate = 5:1), m.p.:164 ~ 165 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.25 (s, 1 H), 8.06 (d, J = 7.2 Hz, 3 H), 7.79 ~ 7.73 (m, 4 H), 7.63 ~ 7.25 (m, 16 H), 7.15 ~ 7.08 (m, 2 H), 6.93 ~ 6.84 (m, 1 H), 6.10 (d, J = 6.9 Hz , 1 H), 4.59 (s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 191.4, 152.1, 145.1, 142.3, 139.9, 135.1, 133.8, 133.4, 133.1, 133.0, 131.0, 130.4, 130.3, 130.1, 129.6, 128.9, 128.7, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 127.1, 126.5, 126.2, 126.1, 125.9, 125.54, 125.3, 125.1, 124.5, 120.8, 116.4, 102.3, 91.1, 89.1, 46.7 ppm. IR (neat): ν (cm^{-1}) 3058, 2853, 1694, 1607, 1454, 1397, 1174, 1116, 1018. HRMS calcd for $C_{42}H_{28}O_2$: 564.2089, found: 564.2079. MS (70 eV): m/z (%): 564 (M^+, 80.42), 252 (100).

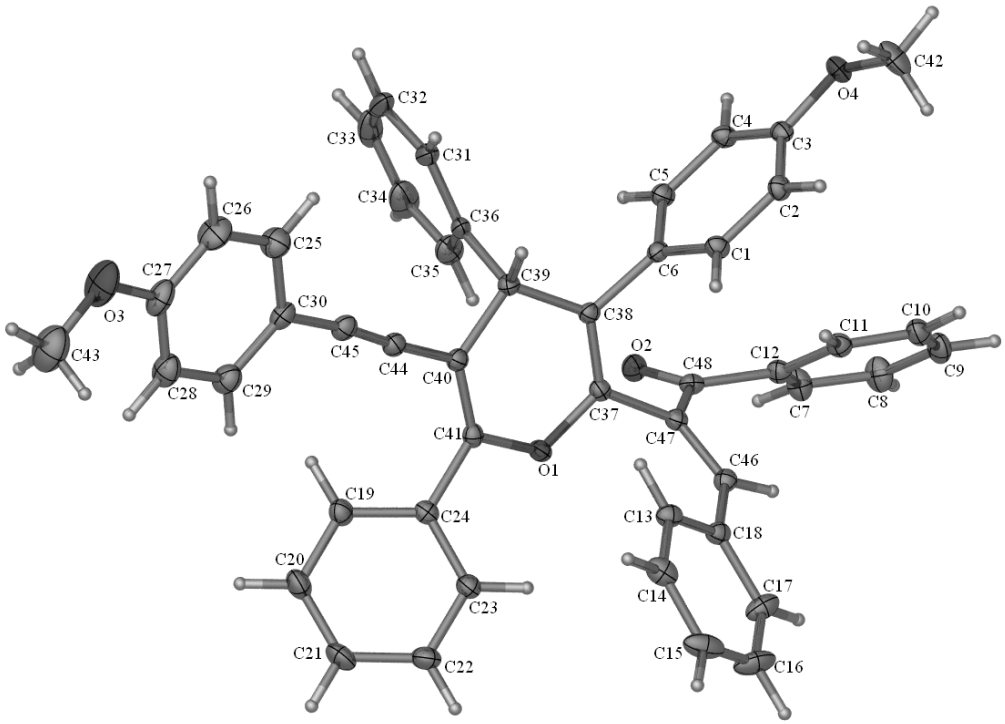
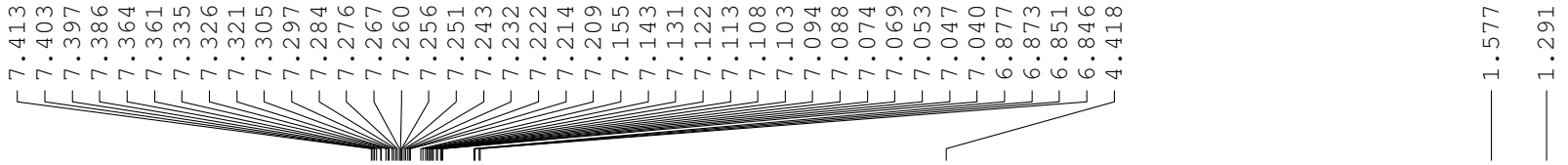


Figure 1. ORTEP representation of compound **2b**.

CCDC 738752 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge form The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Reference:

1. a)T. Yao, X. Zhang, R. C. Larock, *J. Am. Chem. Soc*. **2004**, *126*, 11164; b) T. Yao, X. Zhang, R. C. Larock, *J. Org. Chem*. **2005**, *70*,7679.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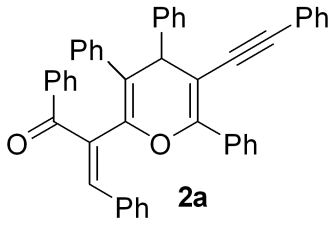
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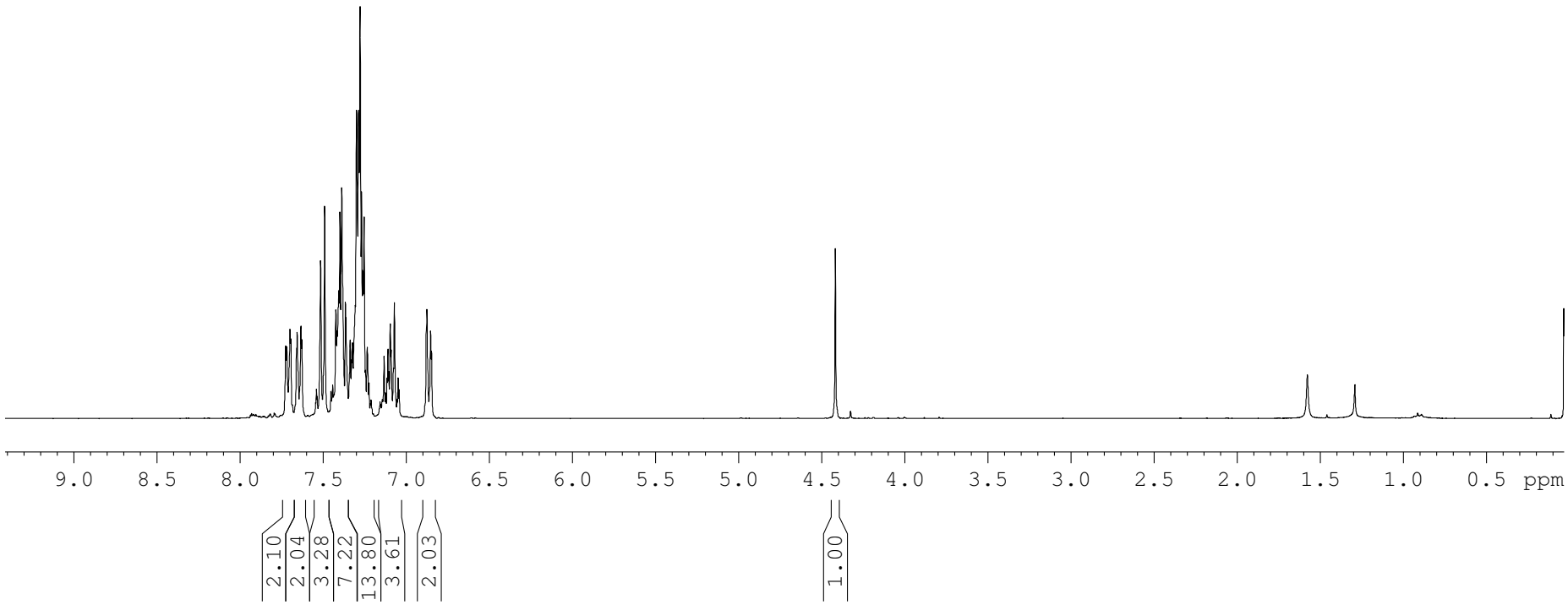
Ph

2a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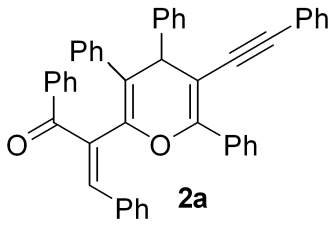

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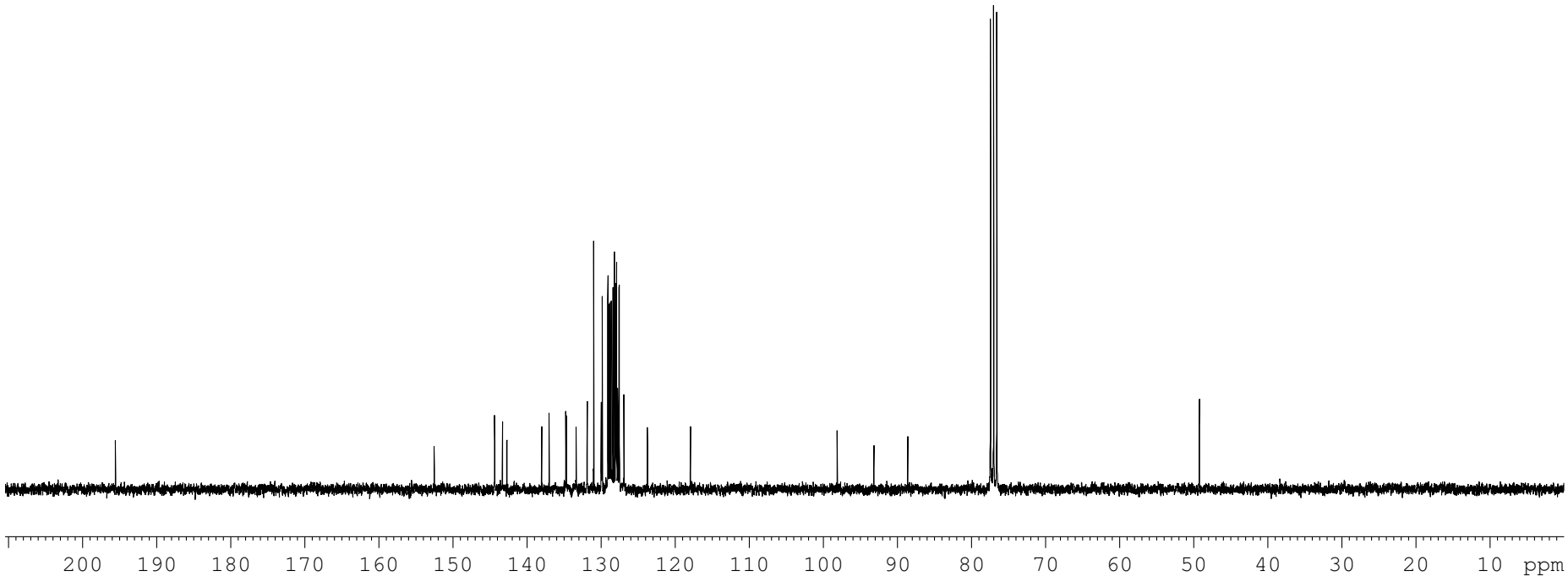

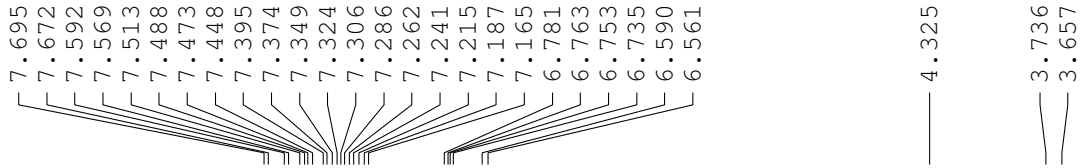
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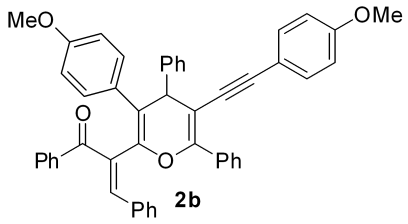
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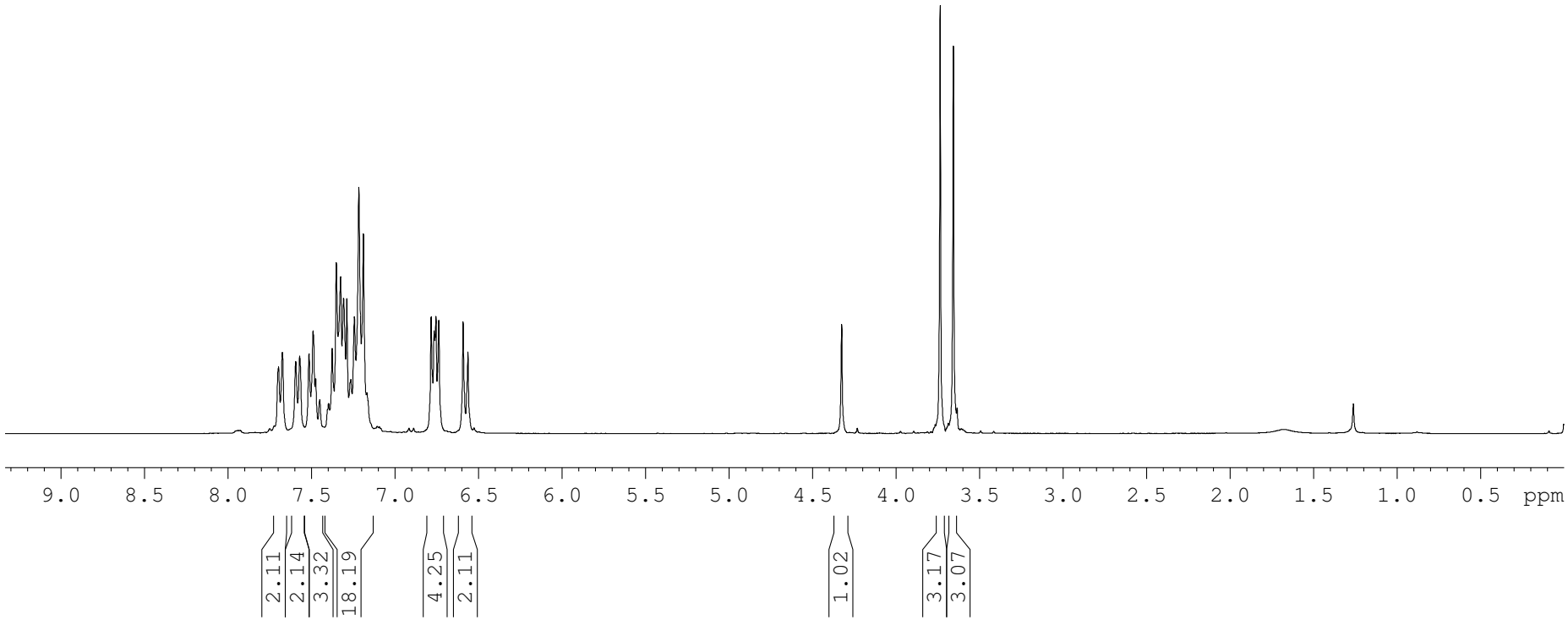
Ph

2b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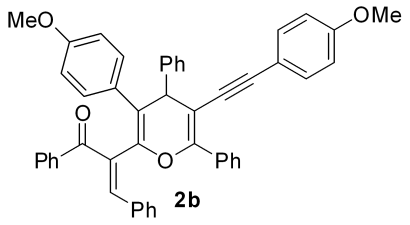

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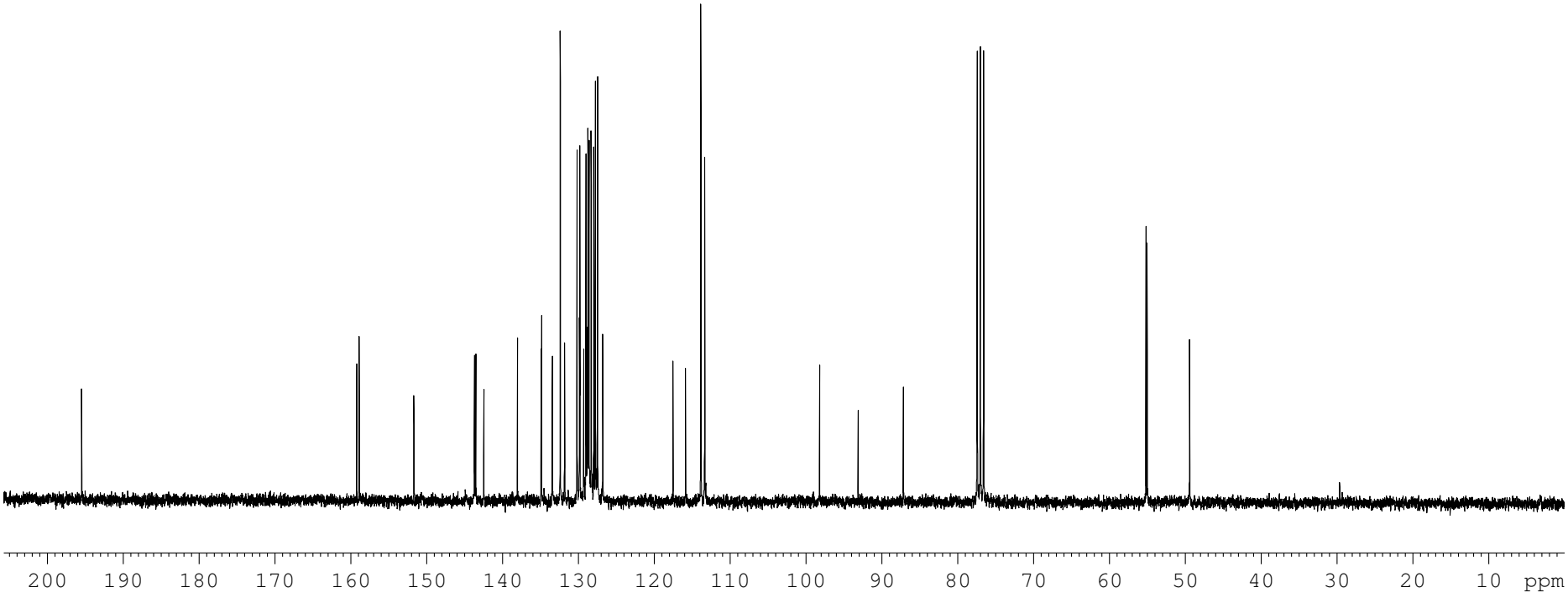

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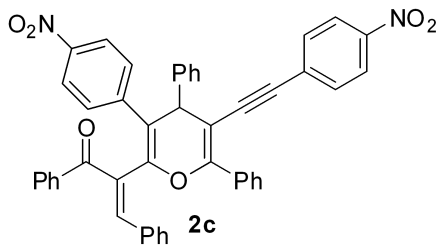

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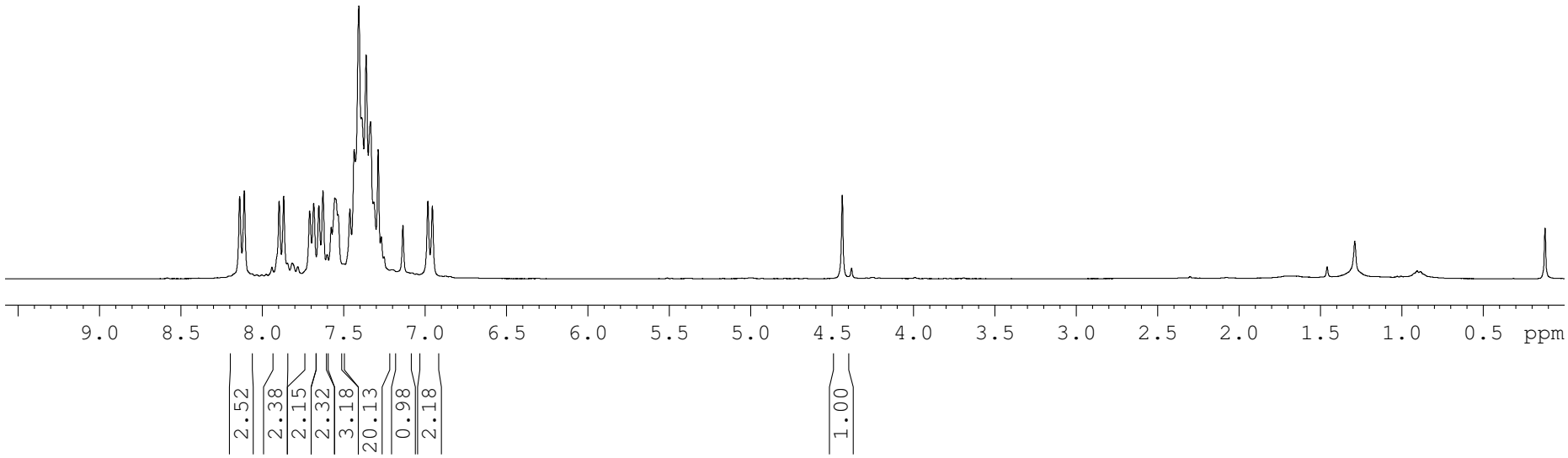

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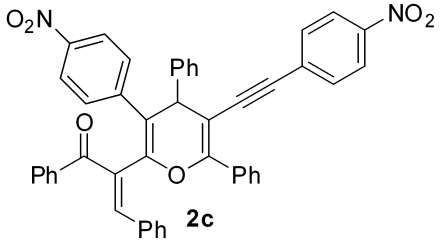

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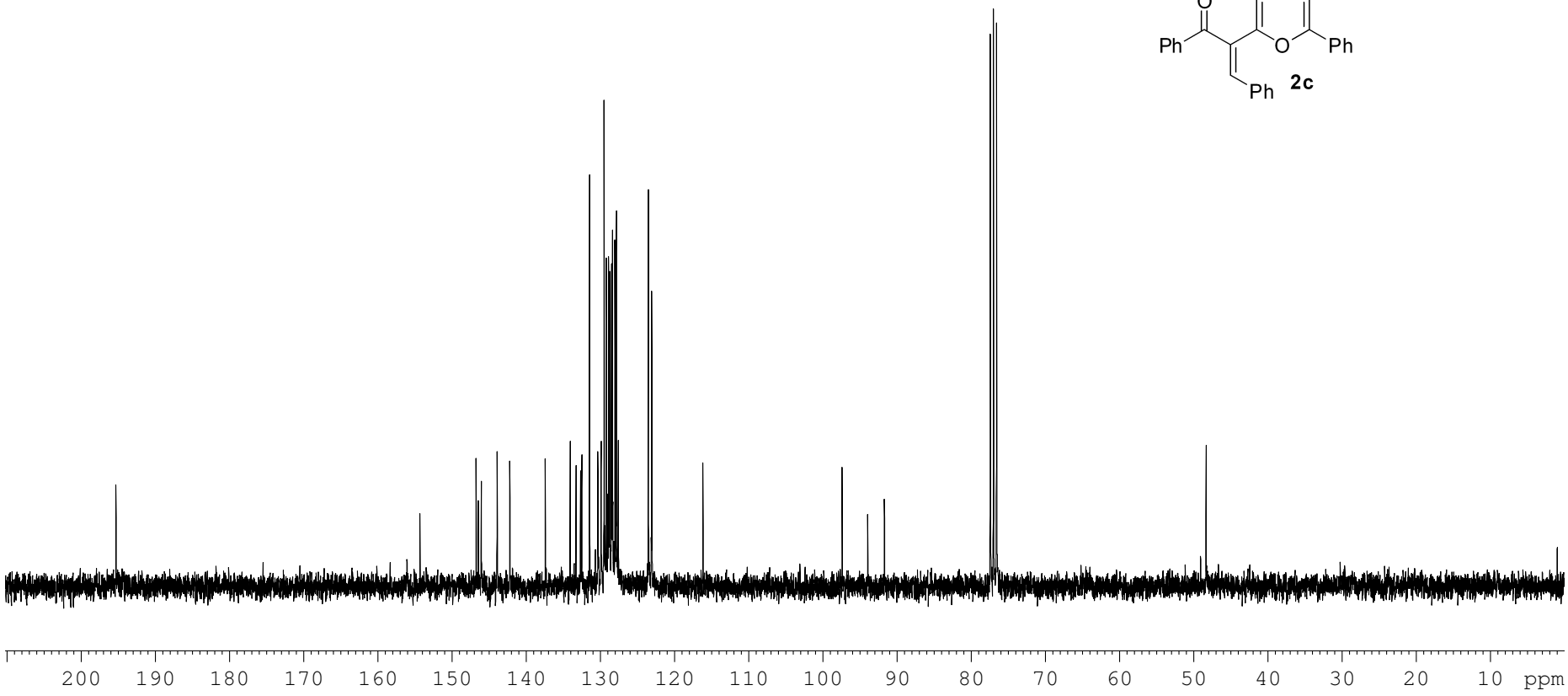

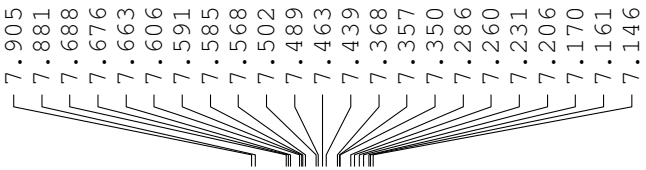
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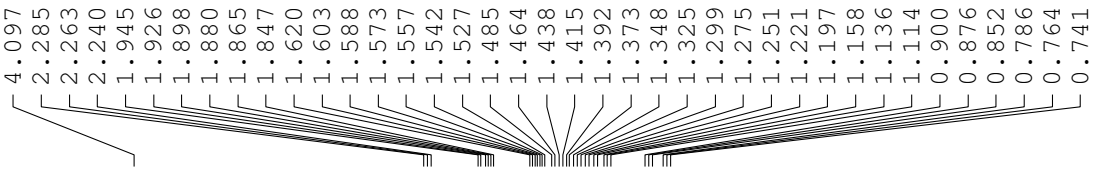
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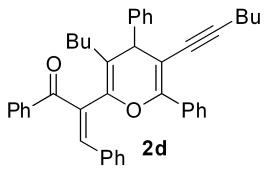
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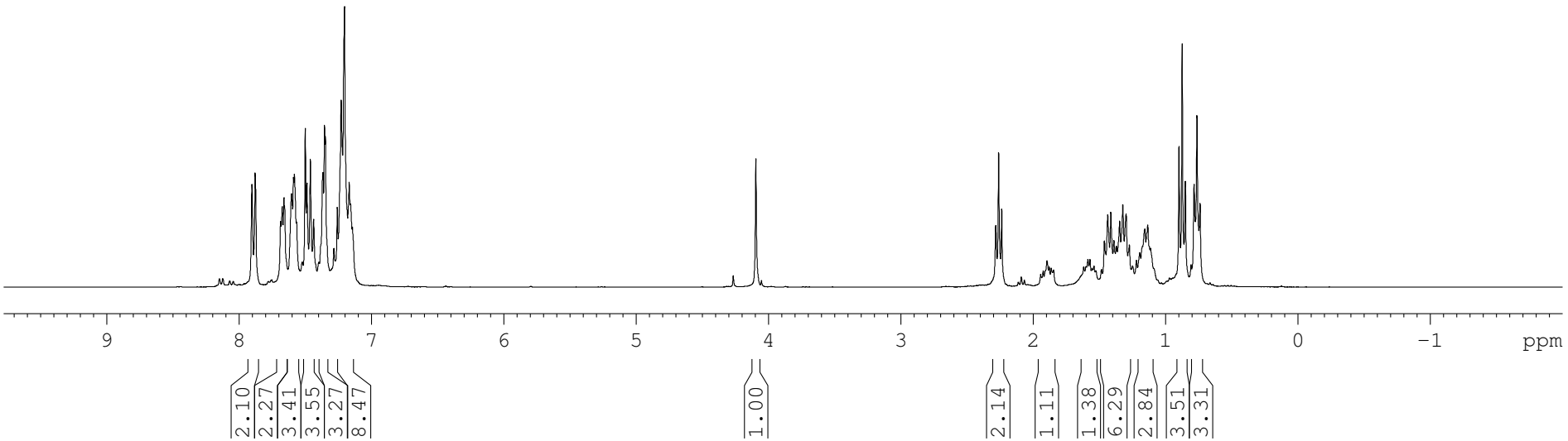
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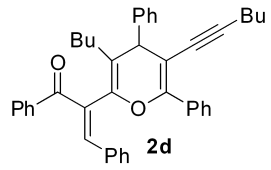

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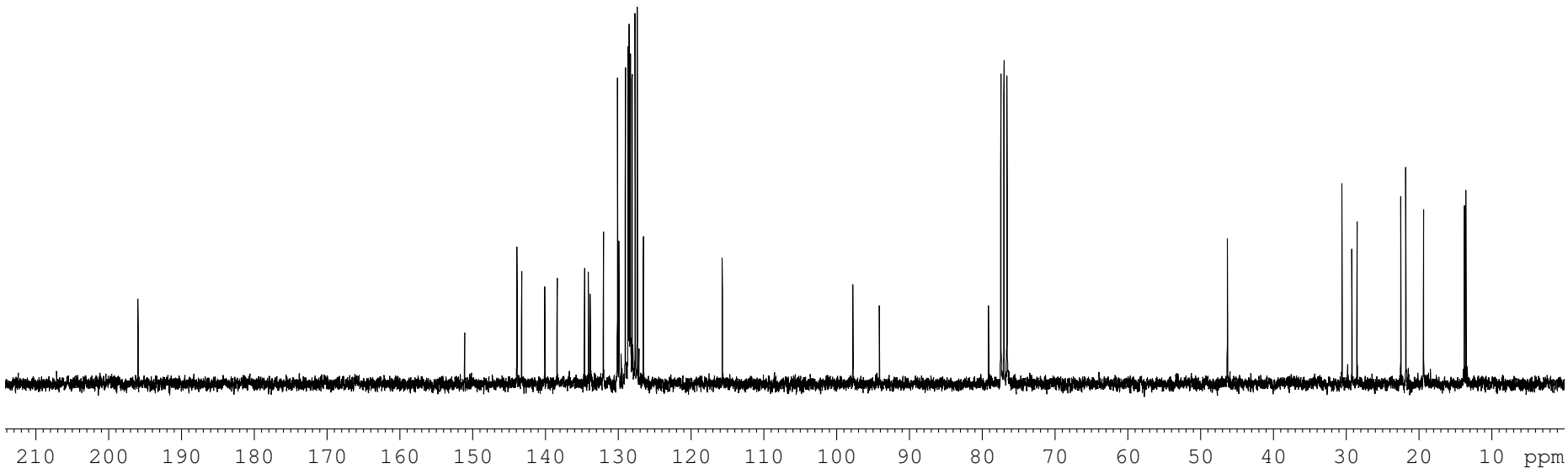

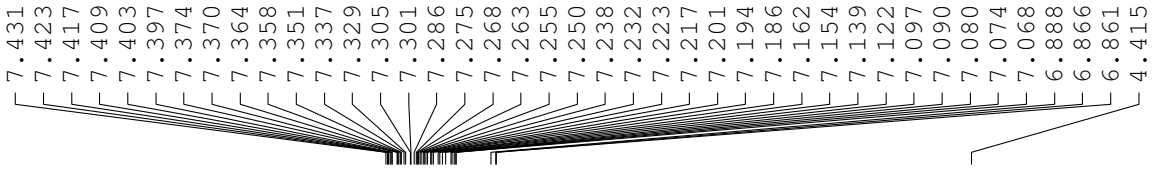
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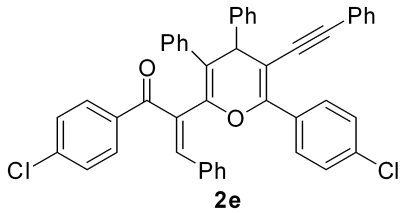
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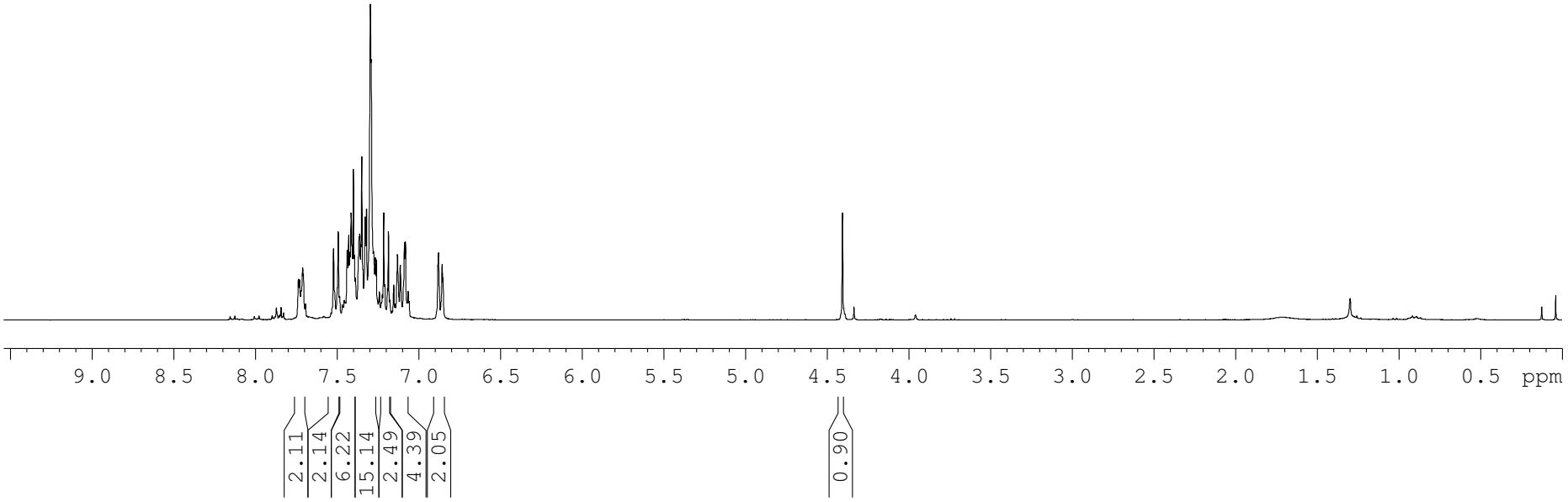
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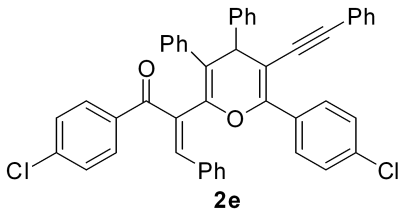

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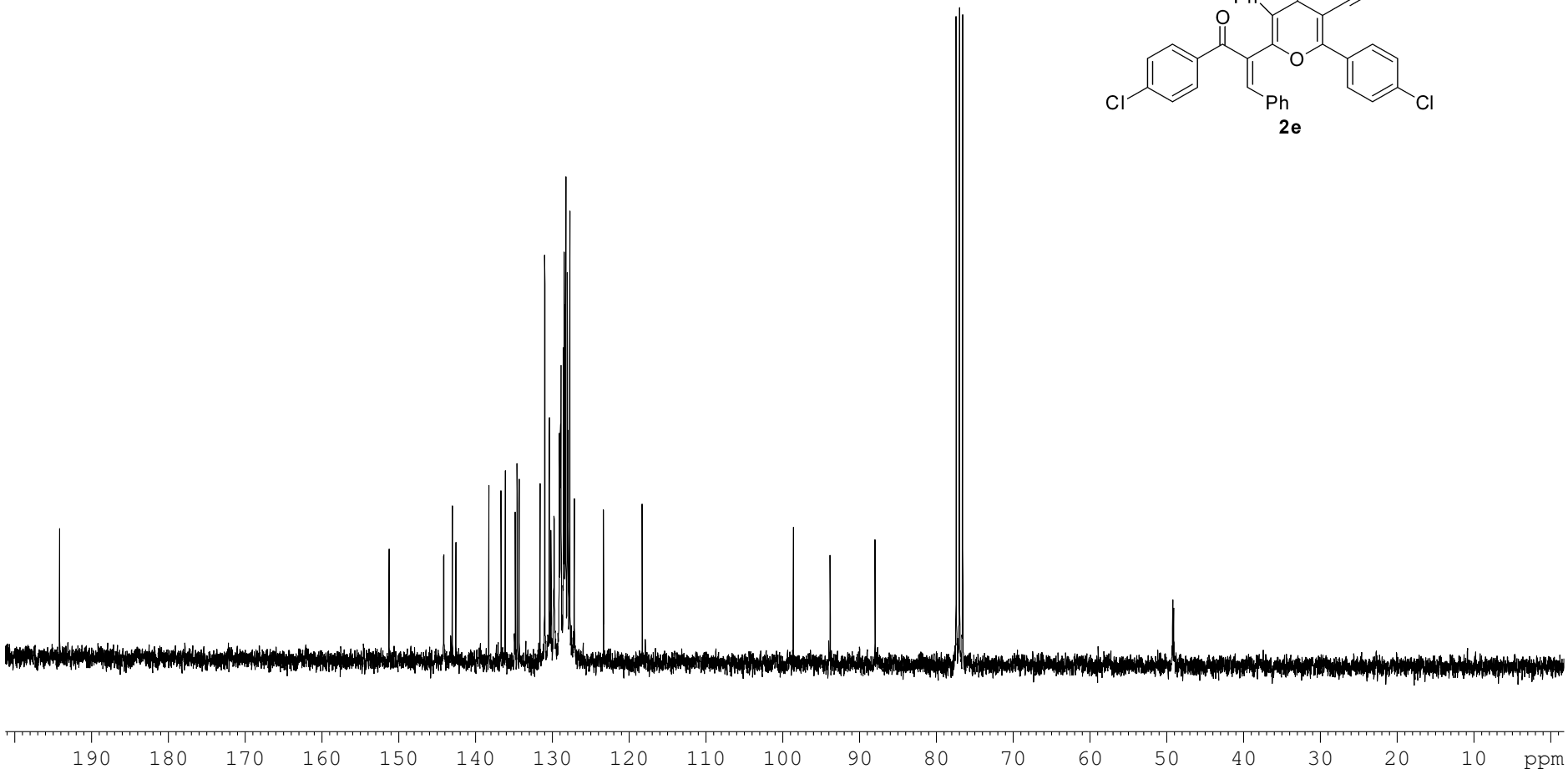

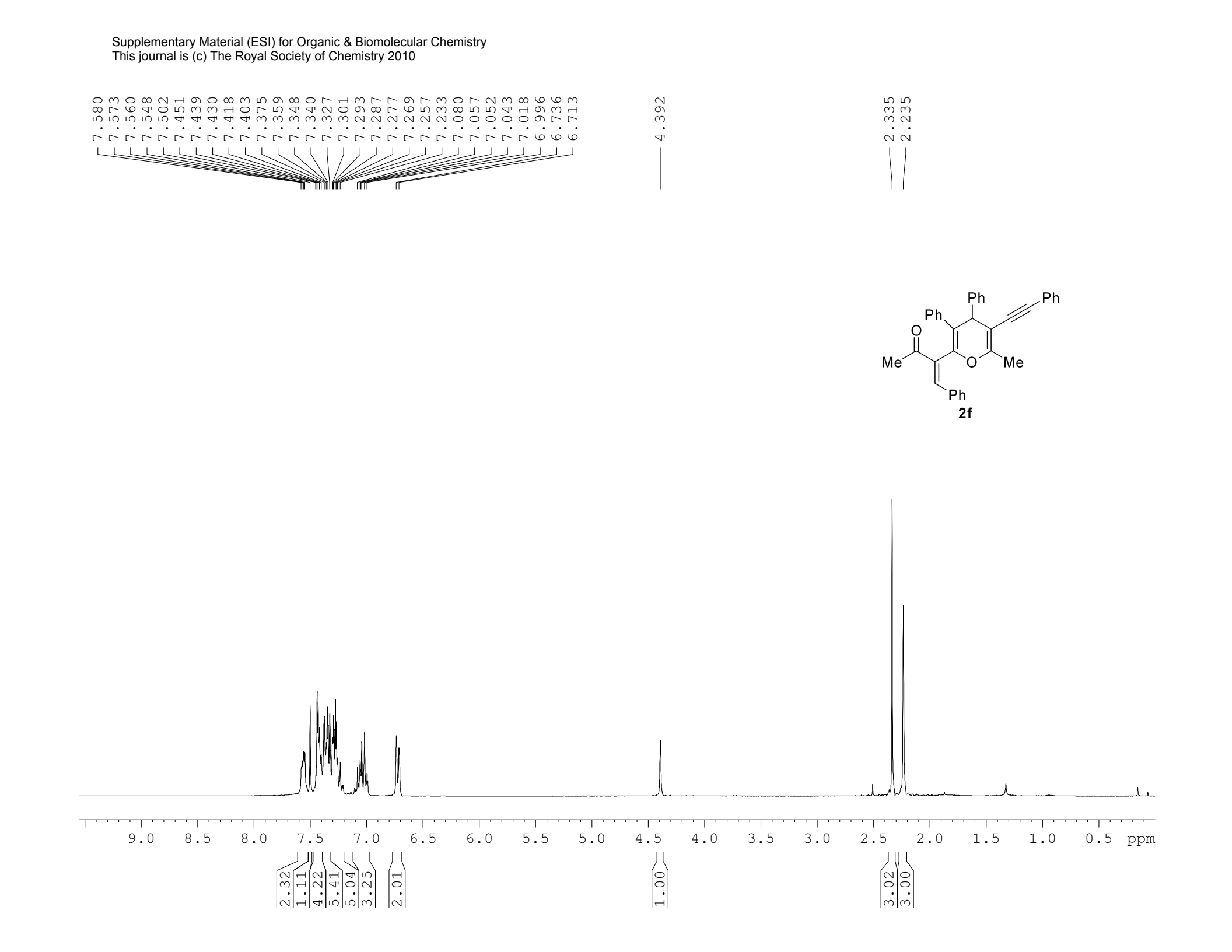
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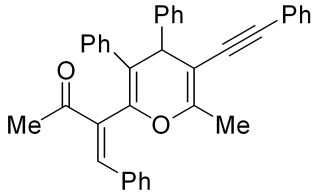

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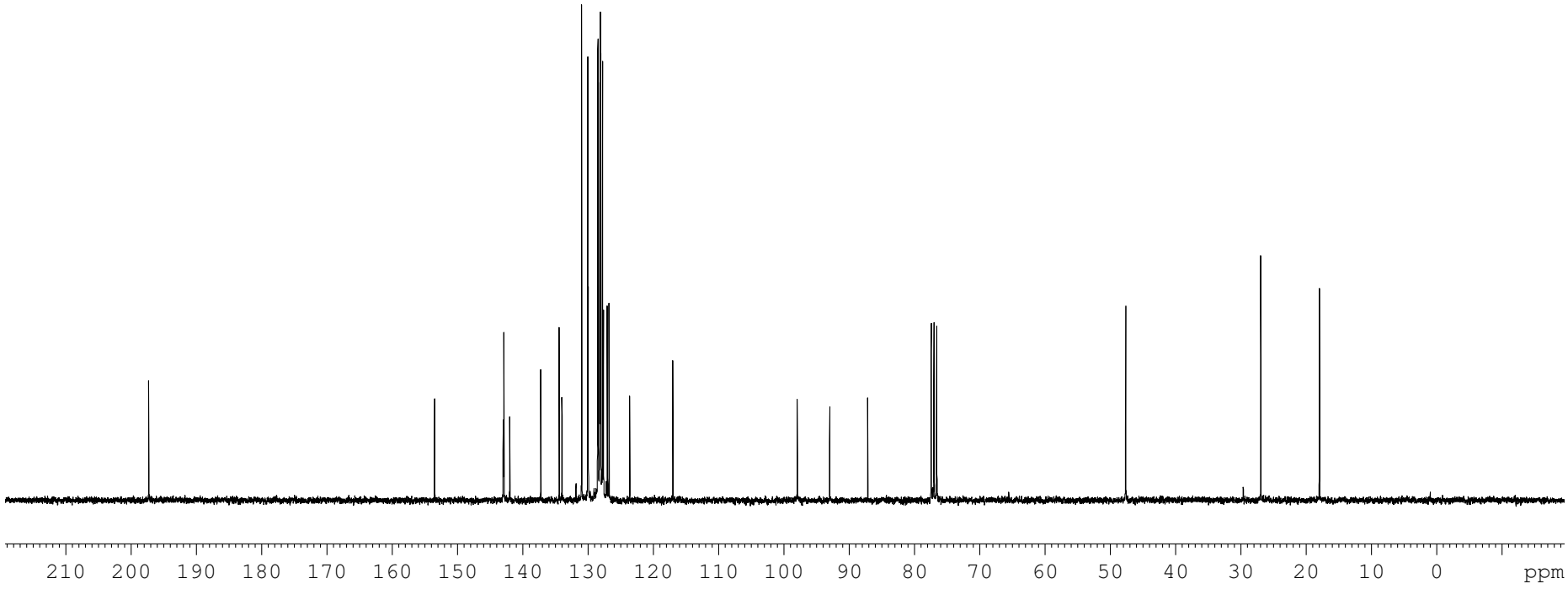

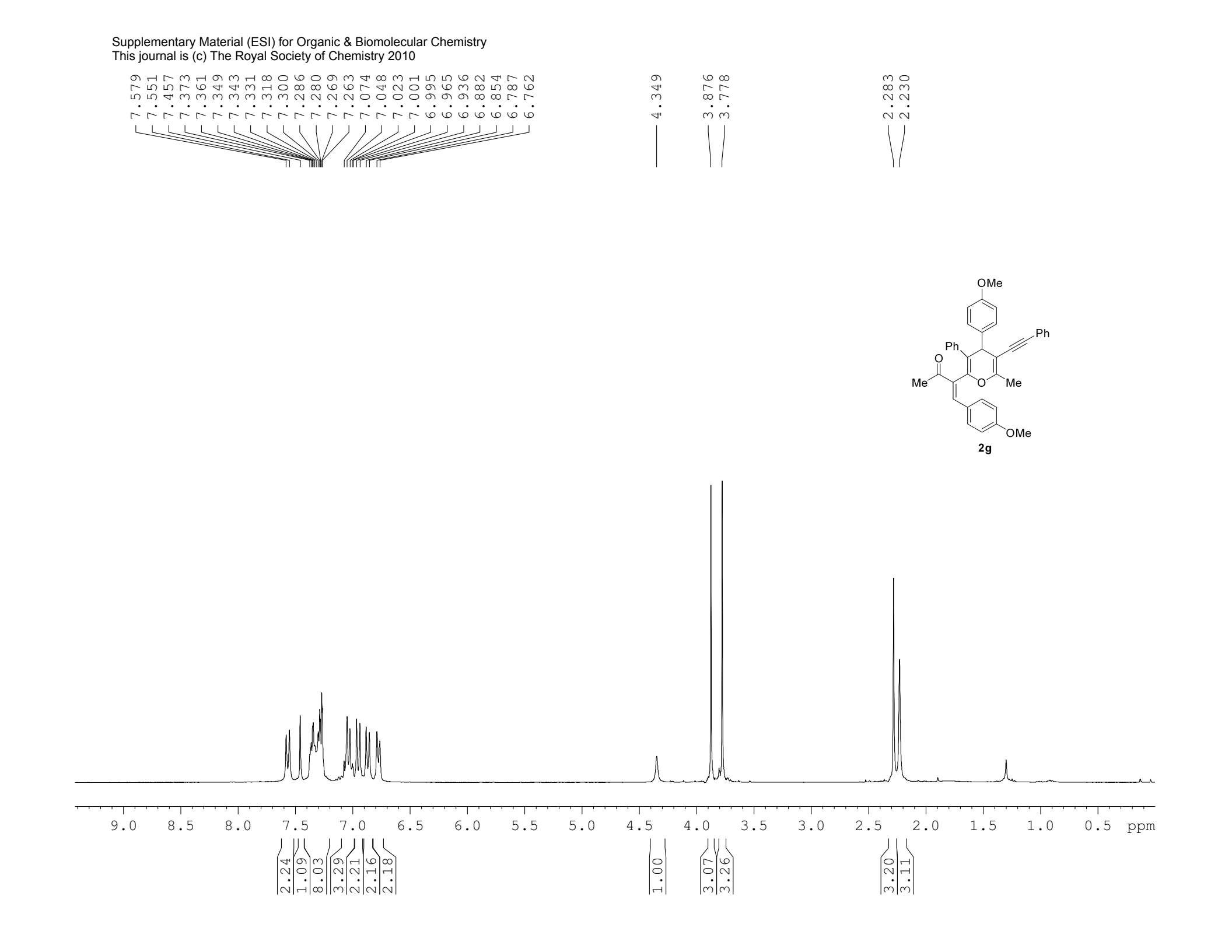
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Ph
O
Me
O
Me
OMe
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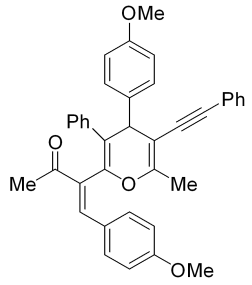

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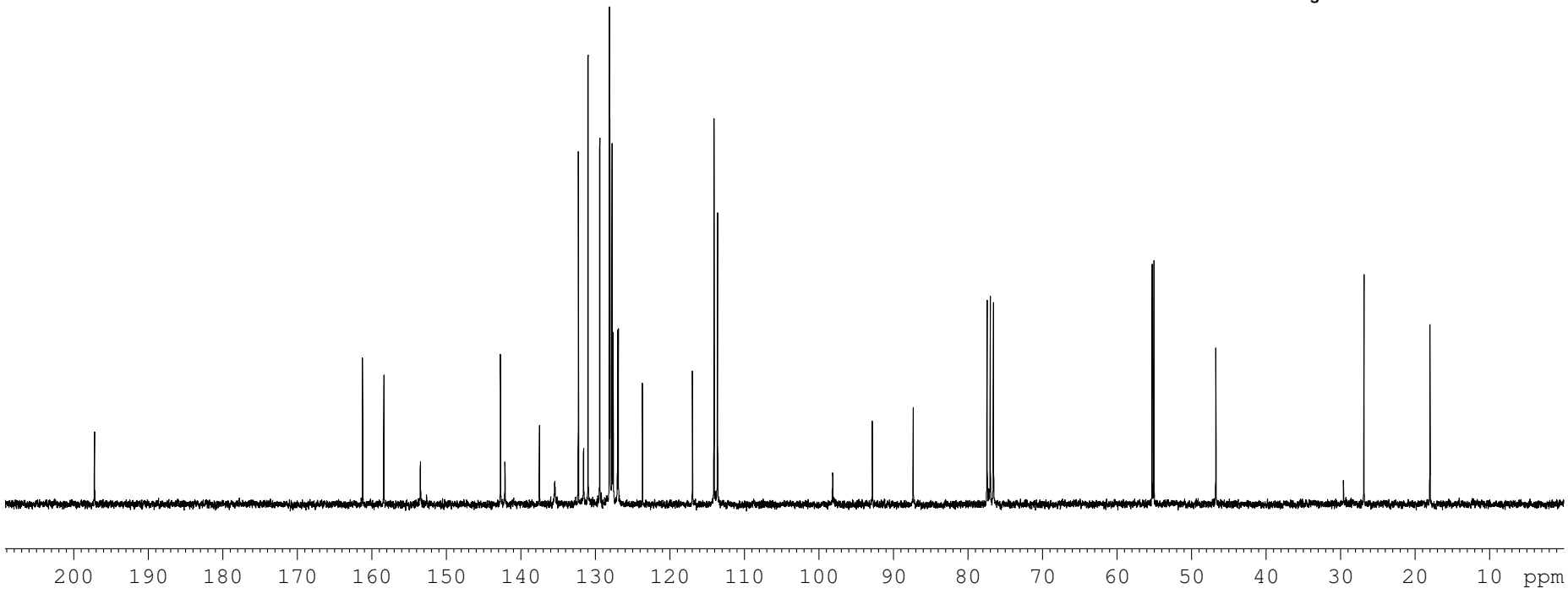

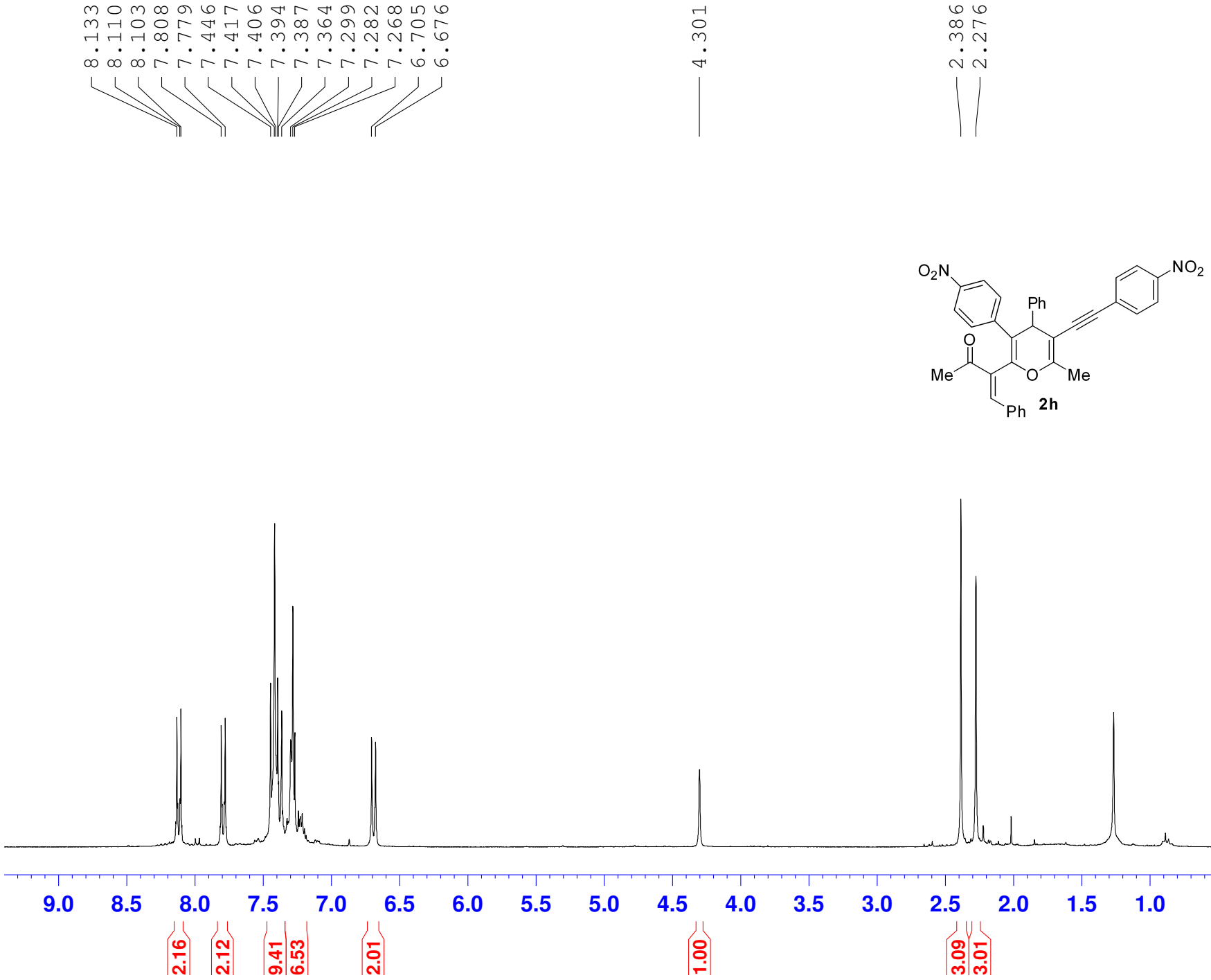
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O2N
NO2
Ph
O
Me
O
Me
Ph
2h
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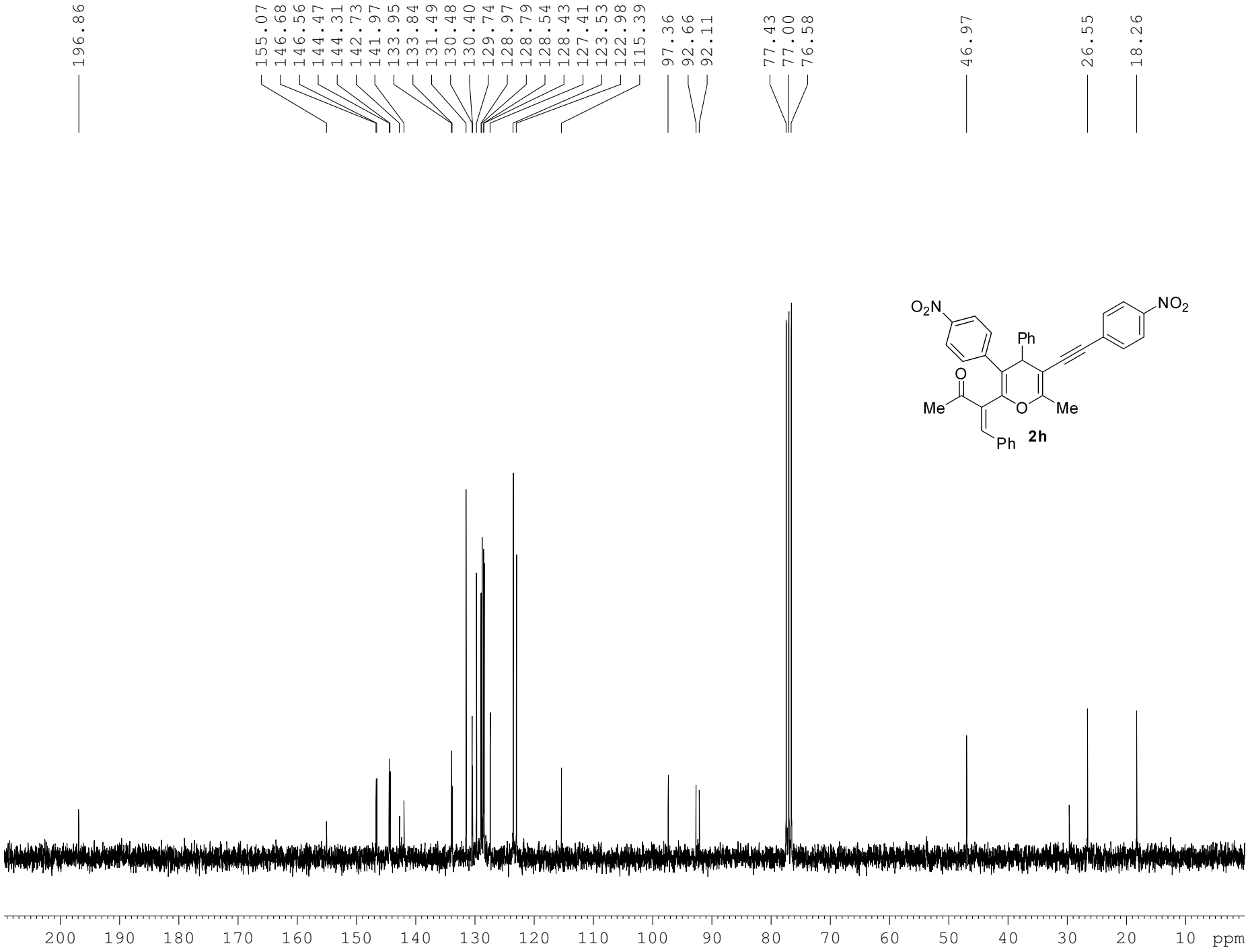

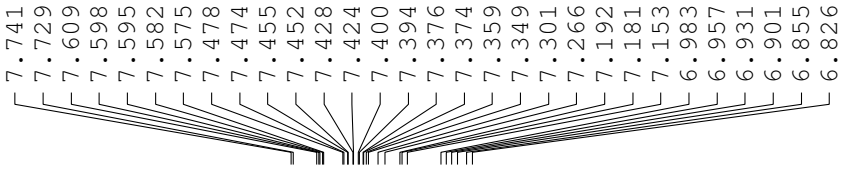
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6.826

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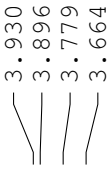
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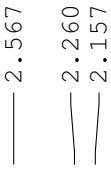
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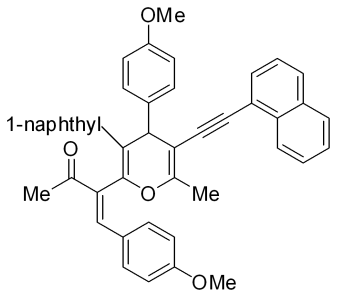
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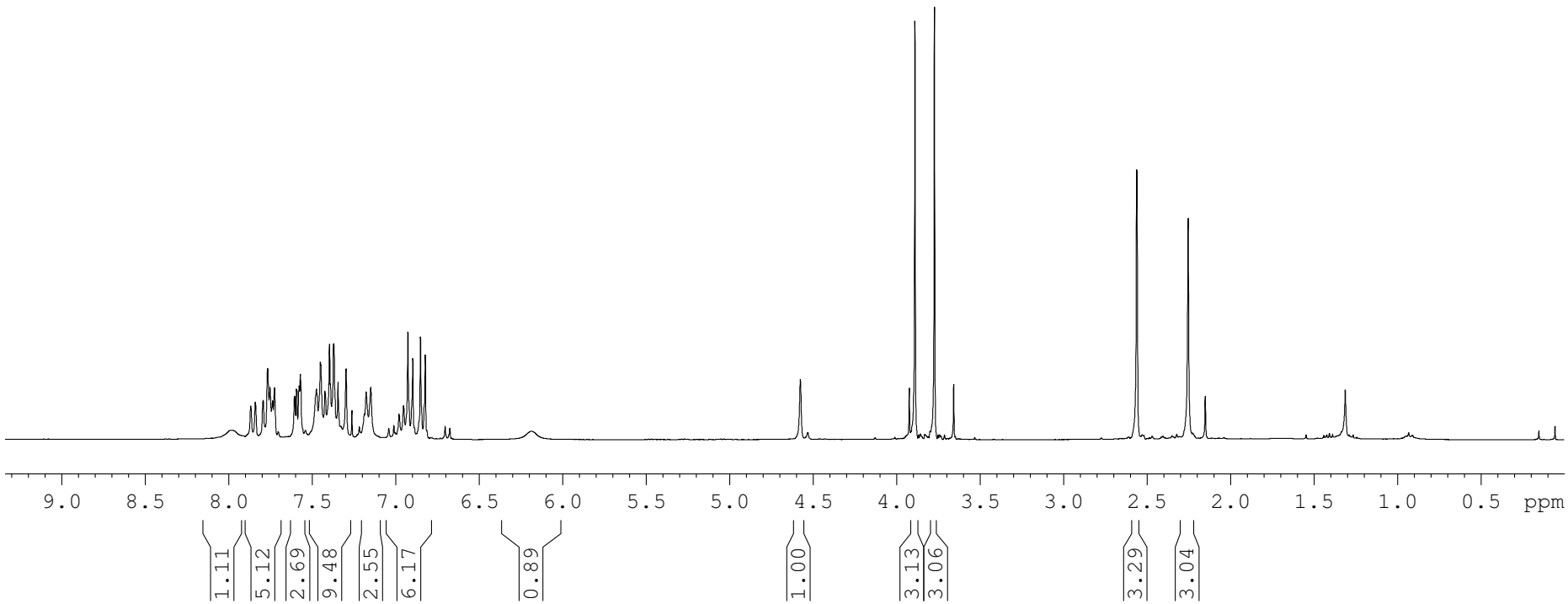
O
Me
OMe

2i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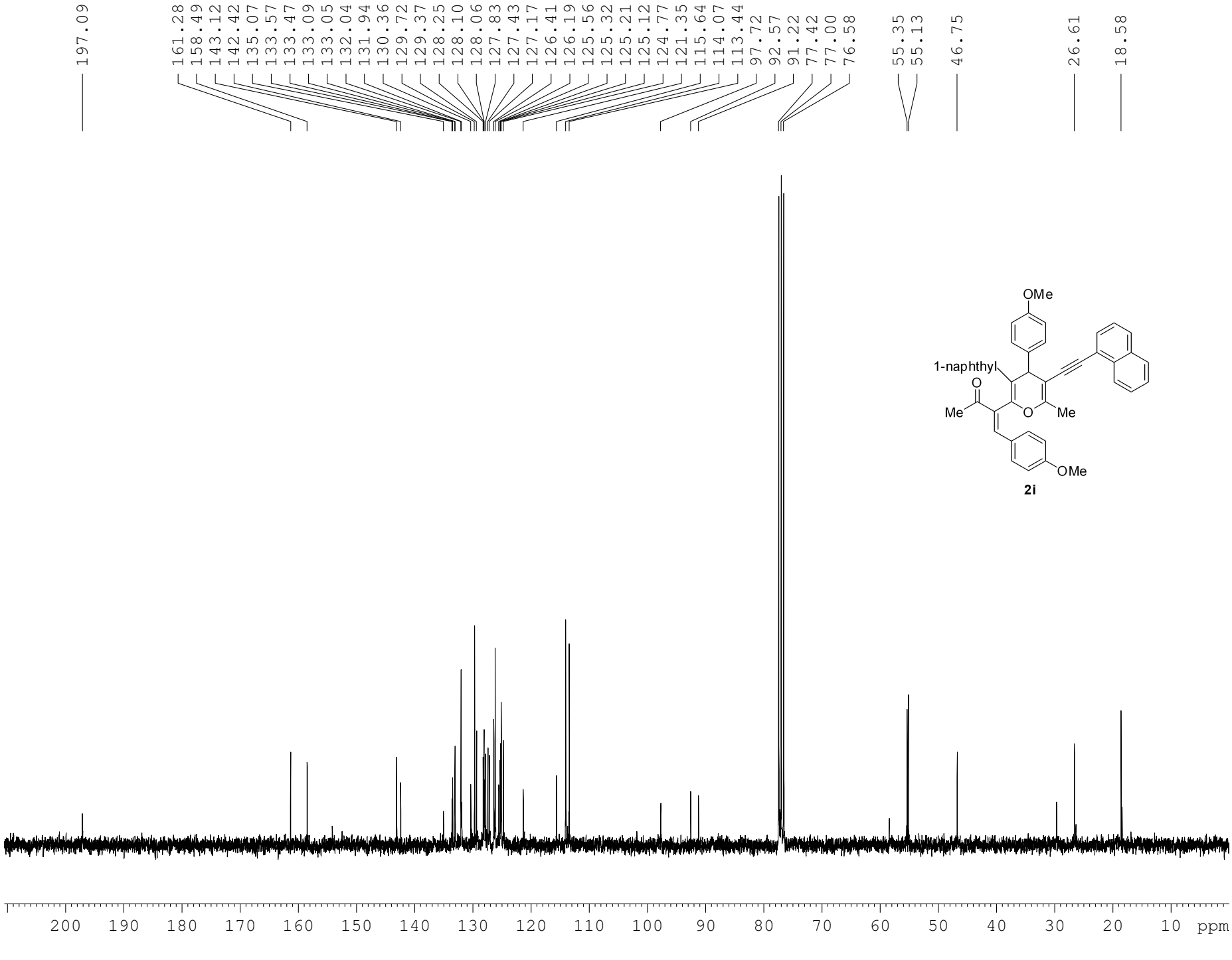
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125.12
124.77
121.35
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113.44
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91.22
77.42
77.00
76.58
55.35
55.13
46.75
26.61
18.58
OMe
1-naphthyl
O
Me
O
Me
OMe
2i
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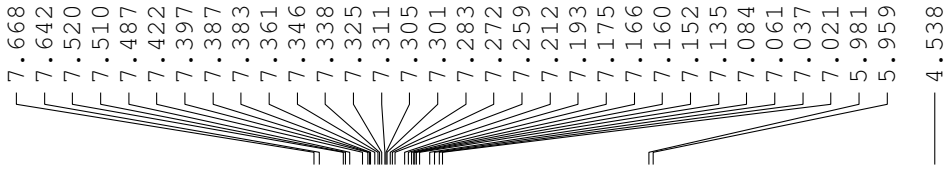
10
ppm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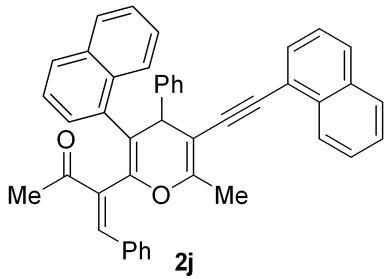
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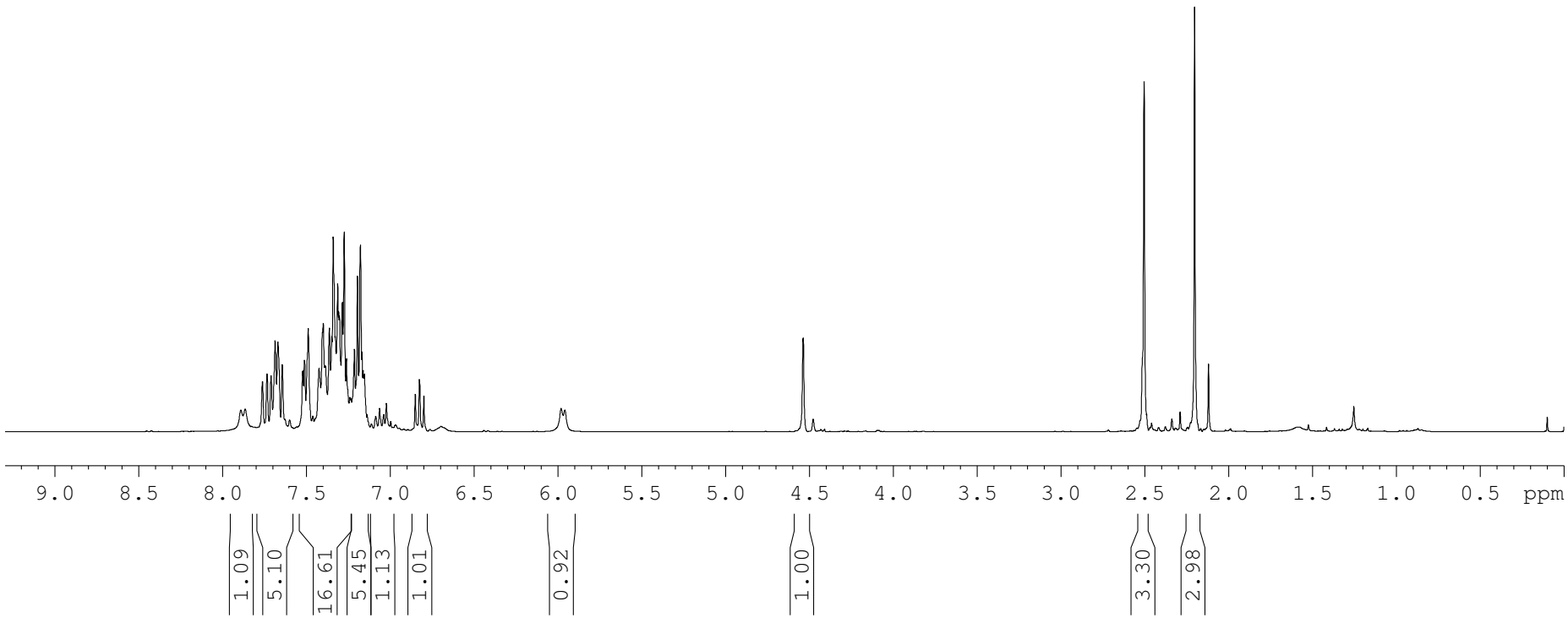
2j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1.01
0.92
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2.98

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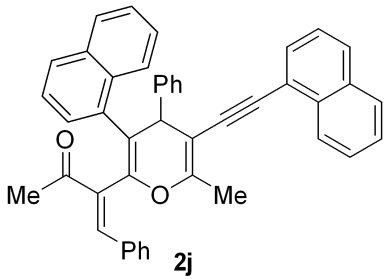

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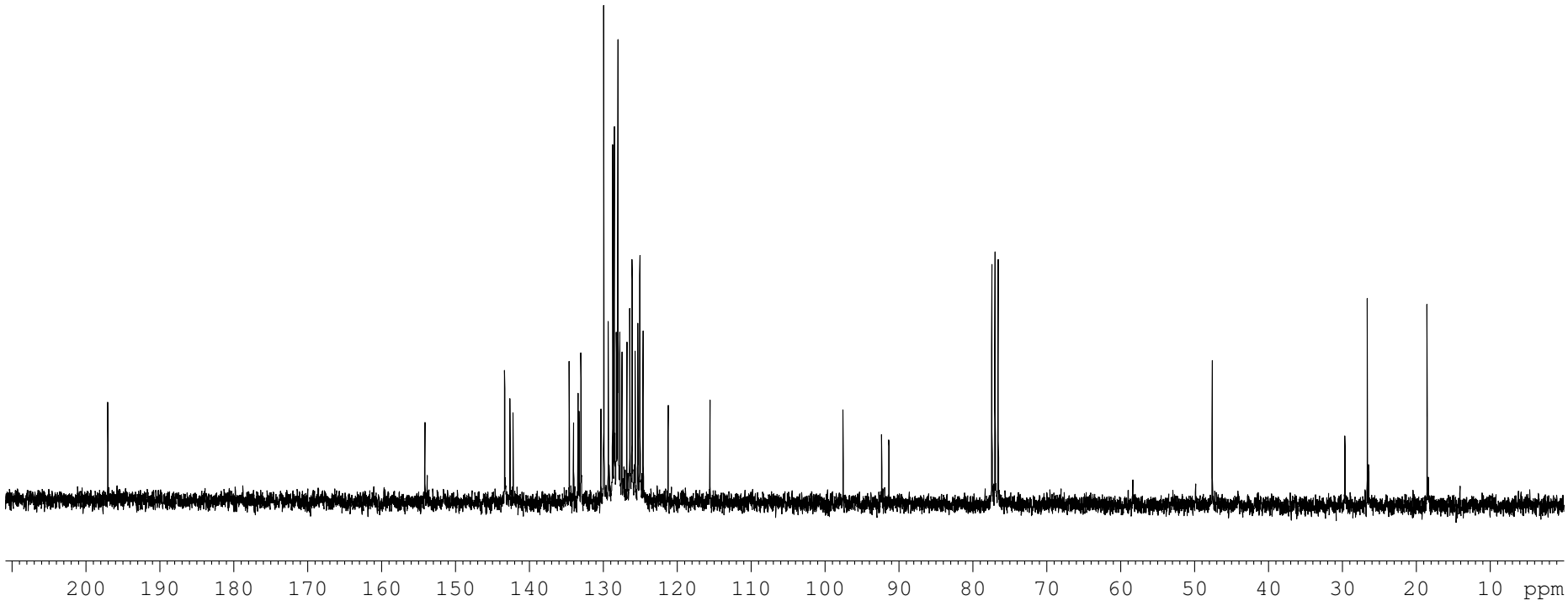

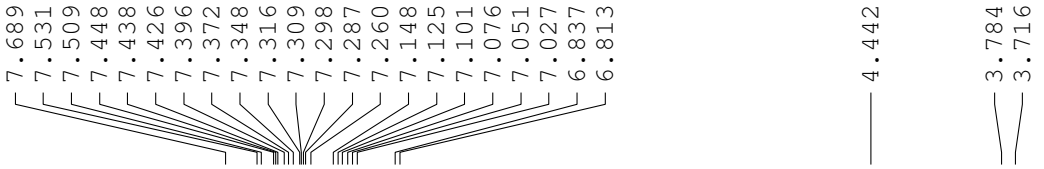
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7.051
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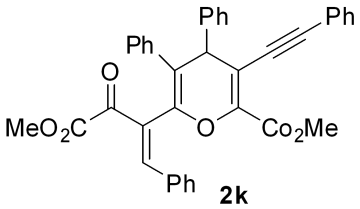
3.716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Ph
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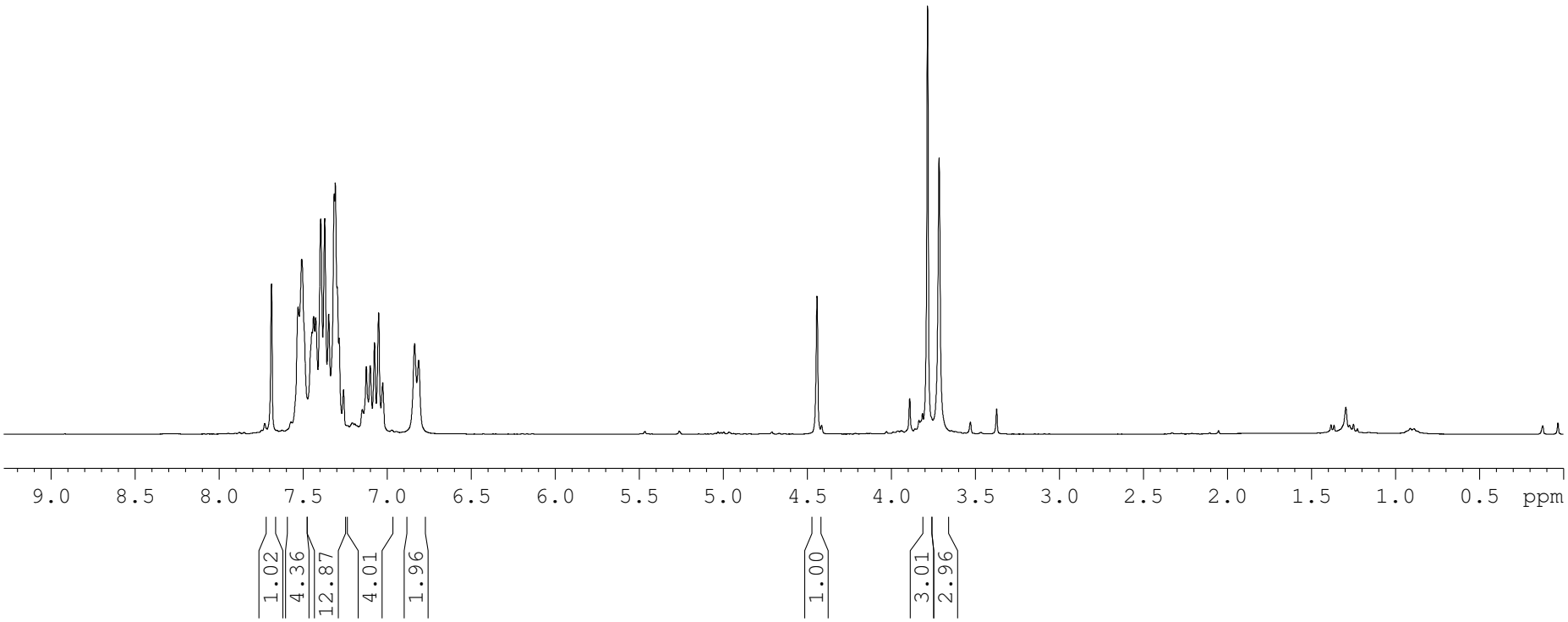
O
Co2Me
Ph

2k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1.00
3.01
2.96

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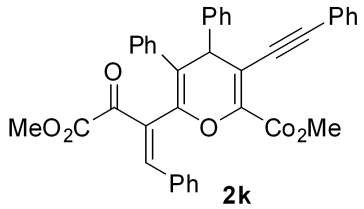

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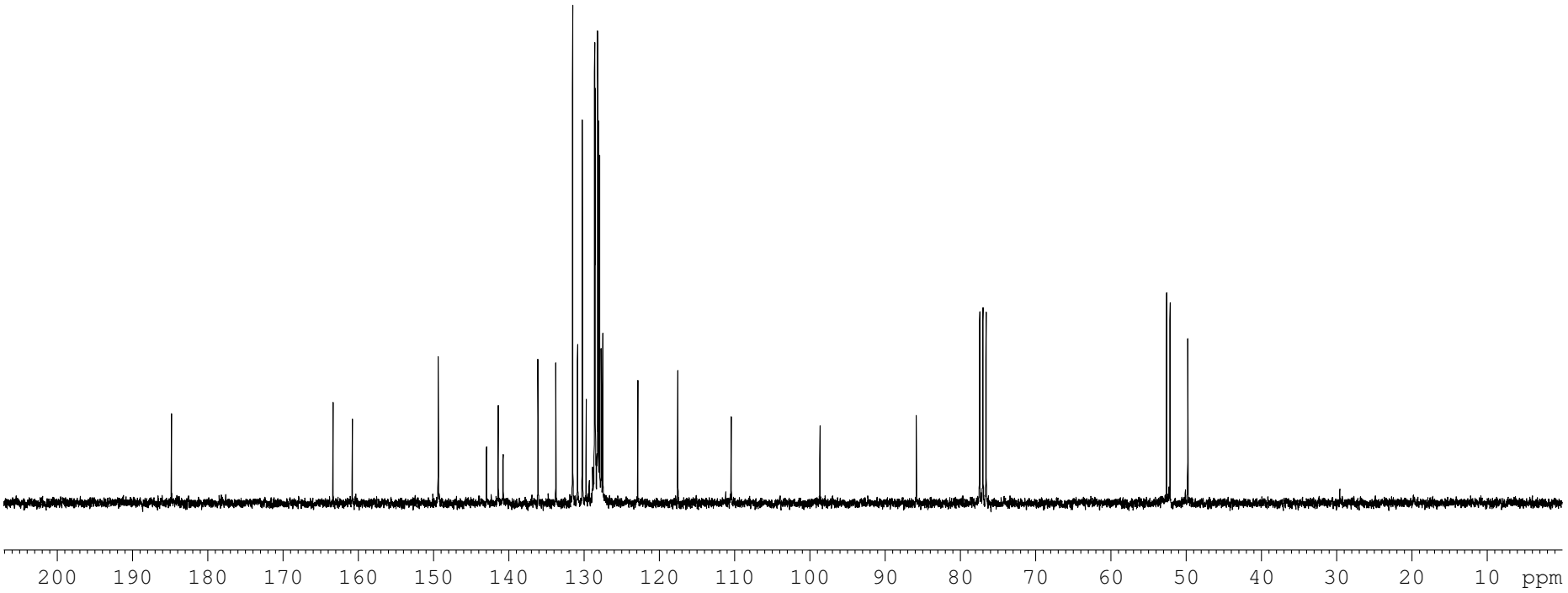

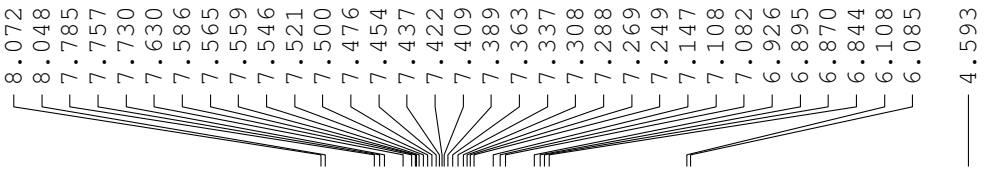
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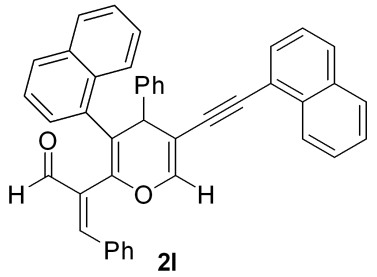
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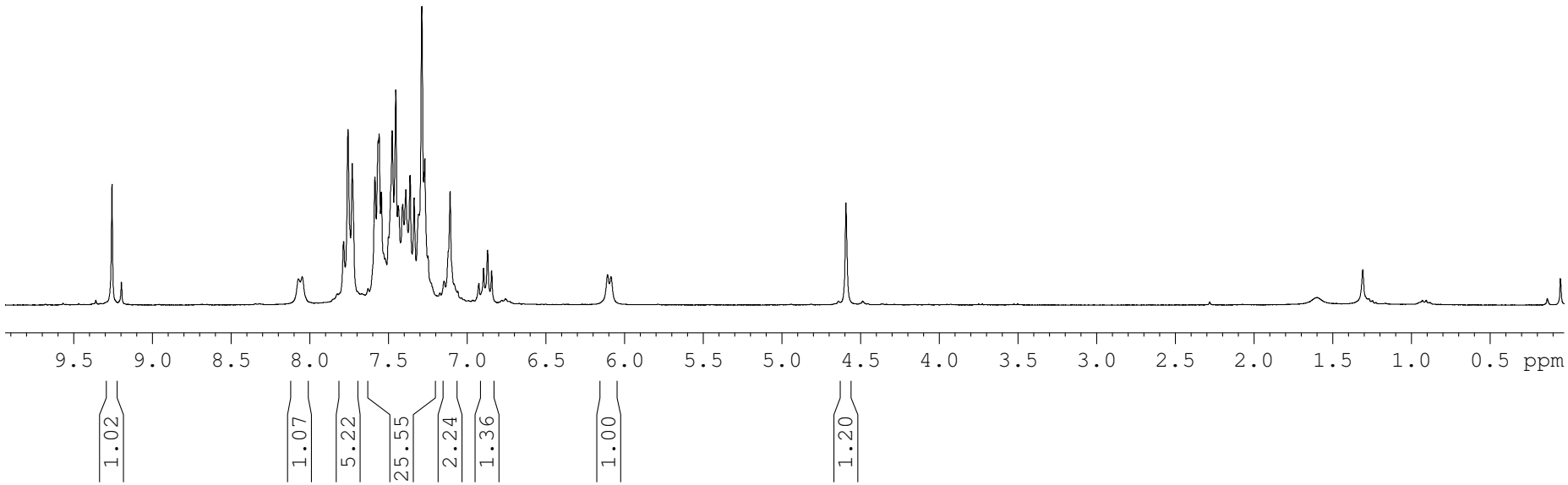
O
H
Ph

2l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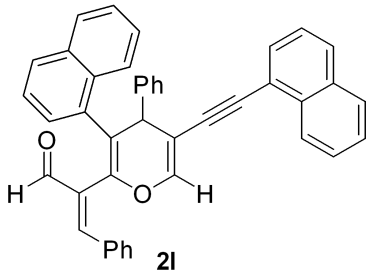

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