Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

A Novel and Efficient Method for the Olefination of Carbonyl Compounds with Grignard Reagents in the Presence of Diethyl Phosphite

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General: Tetrahydrofuran was distilled from sodium and benzophenone immediately prior to use. All reactions were carried out under a nitrogen atmosphere. Metallic magnesium and all other 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). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts in ^{1}H 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 (δ = 77.50 ppm). High-resolution mass spectra were obtained with a GCT-TOF instrument.

Materials:The other chemicals were purchased from Aldrich, Alfa or Acros chemical company and used thus, without further purification. Petroleum ether (PE) used refers to the 30-60℃ boiling point fraction of petroleum.

General procedure for the systhesis of olefins: A solution of Grignard reagents in THF (0.5 M, 2.2 mL, 1.1 mmol) was added to a solution of carbonyl compounds (0.5 mmol) in dry THF (6 mL) under a nitrogen atmosphere at room temperature. The mixture was stirred for about 30 min. Then the diethyl phosphite (0.6 mmol) was added (the reaction was monitored by TLC). The reaction mixture was stirred for 3-5 h and then was quenched with water. 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 as eluent).

Buta-1,3-diene-1,1-diyldibenzene (entry 1)[1] The title compound was obtained according to the general procedure. Colourless oil; Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.38-7.17 (m, 10H), 6.71 (d, *J* = 11.1 Hz, 1H), 6.44 (td, *J* = 10.5 Hz, *J* = 16.9 Hz, 1H), 5.38 (d, *J* = 16.9 Hz, 1H), 5.11 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ: 143.59, 142.53, 140.09, 135.41, 130.87, 128.97, 128.64, 128.63, 128.04, 127.96, 127.84, 119.08. HRMS (EI$^+$) calcd for $C_{16}H_{14}$ (M^+): 206.1096; found: 206.1096.

4,4'-(buta-1,3-diene-1,1-diyl)bis(chlorobenzene) (entry 2)[1]The title compound was obtained according to the general procedure. Colourless oil; Yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$): δ: 7.37-7.11 (m, 8H), 6.67 (d, *J* = 11.0 Hz, 1H), 6.38 (td, *J* = 10.5 Hz, *J* = 16.8 Hz, 1H), 5.42 (dd, *J* = 0.9 Hz, *J* = 16.8 Hz, 1H), 5.18 (dd, *J* = 0.9 Hz, *J* = 10.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 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 $C_{16}H_{12}{}^{35}Cl_2$ (M^+): 274.0316; found: 274.0316; HRMS(EI$^+$) calcd for $C_{16}H_{12}{}^{37}Cl_2$ (M^+): 276.0287; found: 276.0280.

4,4'-(buta-1,3-diene-1,1-diyl)bis(methoxybenzene) (entry 3) [1] The title compound was obtained according to the general procedure. Colourless oil; Yield: 95%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.24-7.12 (m, 4H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 11.0 Hz, 1H), 6.46 (td, *J* = 10.4 Hz, *J* = 16.7 Hz, 1H), 5.34 (dd, *J* = 1.7 Hz, *J* = 16.7 Hz, 1H), 5.07 (dd, *J* = 1.8 Hz, *J* = 10.0 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.63, 159.32, 142.84, 135.72, 135.55, 132.57, 132.08, 129.32, 127.17, 117.77, 113.98, 113.92, 55.75, 55.73. HRMS (EI$^+$) calcd for $C_{18}H_{18}O_2$ (M^+): 266.1307; found: 266.1306.

(E)-1-(buta-1,3-dienyl)-4-methoxybenzene (entry 4) [1] The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.67 (dd, *J* = 10.6 Hz, *J* = 15.3 Hz, 1H), 6.54-6.37 (m, 2H), 5.28 (d, *J* = 16.7 Hz, 1H), 5.11 (d, *J* = 9.3 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.74, 137.84, 132.87, 130.39, 128.42, 128.12, 116.94, 114.53, 55.77. HRMS (EI$^+$): calcd. for $C_{11}H_{12}O$ (M^+): 160.0888, found: 160.0888.

((E)-5-buta-1,3-dienyl)-benzo[1,3]dioxole (entry 5) The title compound was obtained according to the general procedure. Colourless oil; Yield: 87%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.62 (dd, *J* = 10.2 Hz, *J* = 15.4 Hz, 1H),

6.52-6.40 (m, 2H), 5.94 (s, 2H), 5.28 (d, *J* = 16.5 Hz, 1H), 5.12 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.52, 147.75, 137.60, 132.97, 132.09, 128.46, 121.83, 117.35, 108.81, 105.93, 101.54. IR (KBr) 3078, 2961, 2920, 1671, 1491, 1257, 1034, 930, 800, 669 cm^{-1} . HRMS (EI$^+$): calcd for $C_{11}H_{10}O_2$ (M^+) : 174.0681, found: 174.0680.

(E)-2-(buta-1,3-dienyl)furan (entry 6) The title compound was obtained according to the general procedure. Colourless oil; Yield: 70%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (s, 1H), 6.70 (dd, *J* = 10.8 Hz, *J* = 15.6 Hz, 1H), 6.50-6.26(m, 4H), 5.32 (d, *J* = 16.8 Hz, 1H), 5.15 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.41, 142.66, 137.17, 128.67, 120.90, 118.27, 112.05, 109.04. IR (KBr) 3078, 1647, 1516, 1460, 1383, 1115, 670, 523, 469 cm^{-1}. HRMS (EI$^+$): calcd for C_8H_8O (M^+) : 120.0575, found: 120.0576.

1-(penta-2,4-dien-2-yl)benzene (entry 7a) [2] The title compound was obtained according to the general procedure. Colourless solid; Yield: 47% . ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.21 (m, 5H), 6.76 (td, *J* = 10.5 Hz, *J* = 16.7 Hz, 1H), 6.46 (d, *J* = 11.0 Hz, 1H), 5.32 (d, *J* = 16.7 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.17, 143.43, 137.19, 134.02, 128.18, 127.64, 126.16, 118.09, 16.49. HRMS (EI$^+$): calcd. for $C_{11}H_{12}$ (M^+): 144.0939, found : 144.0939.

1-(penta-1,4-dien-2-yl)benzene (entry 7b). [3] The title compound was obtained according to the general procedure. Colourless solid; Yield: 35% . ^{1}H NMR (300 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.77, 141.39, 136.66, 128.74, 127.92, 126.46, 116.95, 113.63, 39.97. HRMS (EI$^+$): calcd. for $C_{11}H_{12}$ (M^+): 144.0939, found: 144.0939.

1-methyl-4-(1-phenylvinyl)benzene (entry 8) [4] The title compound was obtained according to the general procedure. Colourless oil; Yield: 91%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.29 (m, 5 H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.41 (d, *J* = 8.3 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.35, 142.15, 139.07, 137.98, 129.68, 129.33, 128.76, 128.62, 128.11, 114.13, 21.66. HRMS (EI$^+$): calcd. for $C_{15}H_{14}$ (M^+) : 194.1096, found: 194.1096.

1-chloro-4-(1-p-tolylvinyl)benzene (entry 9) [5] The title compound was obtained according to the general procedure. Colourless oil; Yield: 86%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.23 (m, 4H), 7.16 (dd, *J* = 8.1 Hz, *J* = 20.0 Hz, 4H), 5.42 (s, 1H), 5.38 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.29, 140.61, 138.60, 138.24, 133.97, 130.05, 129.44, 128.77, 128.55, 114.50, 21.65. HRMS (EI$^+$): calcd. for $C_{15}H_{13}{}^{35}Cl$ (M^+) : 228.0706, found: 228.0706 ; calcd. for $C_{15}H_{13}{}^{37}Cl$ (M^+) : 230.0676, found: 230.0657.

4,4'-(ethene-1,1-diyl)bis(methylbenzene) (entry 10) [6] The title compound was obtained according to the general procedure. Colourless oil; Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, *J* = 7.9 Hz, 4H), 7.13 (d, *J* = 7.8 Hz, 4H), 5.37 (s, 2H), 2.36 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.20, 139.27, 137.90, 129.29, 128.65, 113.48, 21.66. HRMS (EI$^+$): calcd. for $C_{16}H_{16}$ (M^+) :208.1252, found: 208.1252.

2-(1-p-tolylvinyl)naphthalene (entry 11) [7] The title compound was obtained according to the general procedure. Colourless oil; Yield: 81%; ^{11}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.76(m, 4H), 7.49-7.41 (m, 3H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.52 (d, *J* = 2.5 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ 150.33, 139.54, 139.07, 138.07, 133.74, 133.40, 129.40, 128.73, 128.63, 128.09, 128.05, 127.72, 126.96, 126.58, 126.43, 114.68, 21.68. HRMS (EI$^+$): calcd. for $C_{19}H_{16}$ (M^+): 244.1252, found: 244.1252.

2-(1-p-tolylvinyl)thiophene (entry 12) [8] The title compound was obtained according to the general procedure. Colourless oil; Yield: 89%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.26 (dd, *J* = 1.1 Hz, *J* = 5.0 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.01 (dd, *J* = 3.6 Hz, *J* = 5.0 Hz, 1H), 6.96 (dd, *J* = 1.0 Hz, *J* = 3.5 Hz, 1H), 5.58 (s, 1H), 5.26 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.43, 143.65, 138.62, 138.36, 129.33, 128.66, 127.70, 126.82, 125.41, 113.59, 21.69. HRMS (EI$^+$): calcd. for $C_{13}H_{12}S$ (M^+) :200.0660, found: 200.0660.

2-(1-p-tolylvinyl)furan (entry 13) The title compound was obtained according to the general procedure. Colourless oil; Yield: 61%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.37 (dd, *J* = 1.8 Hz, *J* = 3.2 Hz, 1H), 6.37 (dd, *J* = 1.8 Hz, *J* = 3.2 Hz, 1H), 5.70 (s, 1H), 5.20 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.67, 142.79, 139.57, 138.29, 137.15, 129.38, 128.63, 112.03, 111.69, 109.50, 21.68. IR (KBr) 3048 ,2926, 1728, 1684, 1511, 1459, 1178, 1110, 815, 745, 518 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{13}H_{12}O$ (M^+) :184.0888, found: 184.0887.

2-(1-phenylvinyl)thiophene (entry 14) [4] The title compound was obtained according to the general procedure. Colourless oil; Yield: 92%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.42 (m, 2H), 7.37-7.34 (m, 3H), 7.22 (dd, *J* = 0.9 Hz, *J* = 5.0 Hz, 1H), 6.96 (dd, *J* = 3.6 Hz, *J* = 5.0 Hz, 1H), 6.91-6.90 (m, 1H), 5.58 (s, 1H), 5.24 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.24, 143.83, 141.50, 128.78, 128.65, 128.53, 127.74, 126.94, 125.50, 114.10. HRMS (EI$^+$): calcd. for $C_{12}H_{10}S$ (M^+) :186.0503, found: 186.0503.

2-(1-(4-bromophenyl)vinyl)thiophene (entry 15) The title compound was obtained according to the general procedure. Colourless oil; Yield: 94%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 4.9 Hz, 1H), 6.98-6.95 (m, 1H), 6.87 (d, *J* = 3.4 Hz, 1H), 5.57 (s, 1H), 5.22 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.61, 142.78, 140.40, 131.82, 130.41, 127.82, 127.00, 125.79, 122.60, 114.49. IR (KBr) 3082, 1591, 1485, 1392, 1228, 1073, 1009, 830, 702, 556, 463 cm^{-1} . HRMS (EI$^+$): calcd. for $C_{12}H_9{}^{79}BrS$ (M^+) : 263.9608, found: 263.9606; calcd. for $C_{12}H_9{}^{81}BrS$ (M^+): 265.9588, found: 265.9576.

2-(1-p-tolylvinyl)thiophene (entry 16) [8] The title compound was obtained according to the general procedure. Colourless oil; Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.26 (dd, *J* = 1.1 Hz, *J* = 5.0 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.02-6.95 (m, 2H), 5.58 (s,

1H), 5.26 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.43, 143.65, 138.62, 138.36, 129.33, 128.66, 127.70, 126.82, 125.41, 113.59, 21.69. HRMS (EI^+): calcd. for $C_{13}H_{12}S$ (M^+) :200.0660, found: 200.0660.

2-(3H-inden-1-yl)thiophene (entry 17) The title compound was obtained according to the general procedure. Colourless oil; Yield: 87%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.40-7.20 (m, 4H), 7.11 (dd, *J* = 3.6 Hz, *J* = 5.0 Hz, 1H), 6.68 (t, *J* = 2.1 Hz, 1H), 3.49 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.01, 143.52, 138.47, 138.31, 131.36, 127.93, 126.78, 125.63, 124.94, 124.78, 124.54, 120.91, 38.62. IR (KBr) 3069, 2924, 1642, 1462, 1294, 1113, 1045, 837, 700 cm^{-1} . HRMS (EI^+): calcd. for $C_{13}H_{10}S$ (M^+) : 198.0503, found: 198.0503.

2-cyclopentenylthiophene (entry18) [9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 91%; 1H NMR (300 MHz, CDCl3): δ 7.12 (d, J = 4.9 Hz, 1H), 6.96-6.90 (m, 2H), 6.02-6.01 (m, 1H), 2.73-2.67 (m, 2H), 2.53-2,47 (m, 2H), 2.05-1.95 (m, 2H). 13C NMR (75 MHz, CDCl3): δ 141.74, 137.12, 127.63, 126.23, 124.10, 123.77, 34.71, 33.74, 23.88. HRMS (EI+): calcd. for C9H10S (M+) :150.0503 found: 150.0503.

2-cyclohexenylthiophene (entry 19) [10] The title compound was obtained according to the general procedure. Colourless oil; Yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07 (d, J = 3.7 Hz, 1H), 6.97-6.94 (m, 2H), 6.19 (t, *J* = 3.8 Hz, 1H), 2.41-2.39 (m, 2H), 2.20-2.16 (m, 2H), 1.80-1.72 (m, 2H), 1.67-1.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.54, 131.60, 127.55, 124.49, 123.04, 121.44, 28.02, 26.08, 23.21, 22.60. HRMS (EI^+): calcd. for $C_{10}H_{12}S$ (M^+) :164.0660, found: 164.0660

1,1-diphenylbut-1-ene (entry 20) [11] The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%;^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.17 (m, 10H), 6.07 (t, *J* = 7.5 Hz, 1H), 2.17-2.07 (m, 2H), (t, *J* = 7.5 Hz, 3H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 132.23, 130.38, 128.58, 127.69, 127.30, 127.23, 23.69, 15.01. HRMS (EI^+): calcd. for $C_{16}H_{16}$ (M^+) : 208.1252, found: 208.1260.

(E)-1-(but-1-enyl)-4-methoxybenzene (entry 21) [12] The title compound was obtained according to the general procedure. Colourless oil; Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.12 (td, *J* = 6.4 Hz, *J* = 15.7 Hz, 1H), 3.79 (s, 3H), 2.20 (p, *J* = 6.4 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 159.03, 131.23, 130.99, 128.55, 127.42, 114.35, 55.74, 26.51, 14.28. HRMS (EI^+): calcd. for $C_{11}H_{14}O$ (M^+): 162.1045, found: 162.1047.

((E)-5-but-1-enyl)-benzo[1,3]dioxole (entry 22) [13] The title compound was obtained according to the general procedure. Colourless oil; Yield: 84% ; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90 (s, 1H), 6.80-6.72 (m, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.09 (td, *J* = 6.4 Hz, *J* = 15.8 Hz, 1H), 5.93 (s, 2H), 2.25-2.15 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.36, 146.96, 132.93, 131.41, 128.76, 120.65, 108.68, 105.82, 101.37, 26.43, 14.15. HRMS (EI^+): calcd. for $C_{11}H_{12}O_2$ (M^+) : 176.0837, found : 176.0836.

2-Ethylidene-adamantane (entry 23) [14] The title compound was obtained according to the general procedure. Colourless oil; Yield: 43% ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (q, *J* = 6.7 Hz, 1H), 2.84 (s, 1H), 2.32 (s, 1H), 1.94-1.67 (m, 12H), 1.55 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.50, 110.27, 40.95, 40.26, 39.17, 37.79, 32.03, 29.12, 12.54. HRMS (EI^+): calcd. for $C_{12}H_{18}$ (M^+) :162.1409 found: 162.1408.

1-methoxy-4-(1-(4-methoxyphenyl)-2-phenylvinyl)benzene (entry 24) [15] The title compound was obtained according to the general procedure. Colourless solid; Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.8 Hz, 2H), 7.16-7.03 (m, 7H), 6.84 (dd, *J* = 2.4 Hz, *J* = 9.0 Hz, 5H), 3.82 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.77, 139.50, 136.51, 132.07, 131.40, 129.87, 129.33, 128.47, 128.00, 127.87, 127.15, 114.41, 113.99, 113.75, 55.69, 48.64. HRMS (EI^+): calcd. for $C_{22}H_{20}O_2$ (M^+) : 316.1463, found : 316.1462.

(E)-3,4-methylenedioxystilbene (entry 25) [16] The title compound was obtained according to the general procedure. Colourless solid; Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26-7.21 (m, 1H), 7.07-7.05 (m, 1H), 6.98 (d, *J* = 14.4Hz, 2H), 6.93-6.90 (m, 1H), 6.80 (d, *J* = 8.0Hz, 1H), 5.97(s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.60, 147.77, 137.83, 132.31, 129.14, 128.78, 127.84, 127.44, 126.77, 121.96, 108.88, 105.98, 101.60. HRMS (EI^+): calcd. for $C_{15}H_{12}O_2$ (M^+) : 224.0837, found: 224.0837.

(1E,3E)-1,4-diphenylbuta-1,3-diene (entry 26) [17] The title compound was obtained according to the general procedure. Colourless solid; Yield: 81%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.3 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 4H), 7.26-7.21 (m, 2H), 6.96 (dd, 1H, *J* = 2.8 Hz, J = 12.0 Hz, 1H), 6.67 (dd, *J* = 2.7 Hz, *J* = 12.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.79, 133.28, 129.70, 129.14, 128.05, 126.85. HRMS (EI^+): calcd. for $C_{16}H_{14}$ (M^+) : 206.1096, found : 206.1099.

1,2,3-triphenylprop-1-ene (entry 27) [18] The title compound was obtained according to the general procedure. Colourless solid; Yield: 70%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.1 Hz, 2H), 7.36-7.15 (m, 13H), 7.12 (s, 1H; trans), 6.43(s, 1H; cis), 4.13 (s, 2H; trans), 3.77(s, 2H; cis). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.83, 140.12, 139.43, 138.16, 130.79, 129.72, 129.50, 129.04, 128.98, 128.84, 128.30, 127.76, 127.45, 126.94, 126.41, 47.40(cis), 36.53(trans). HRMS (EI^+): calcd. for $C_{21}H_{18}$ (M^+) : 270.1409, found: 270.1407.

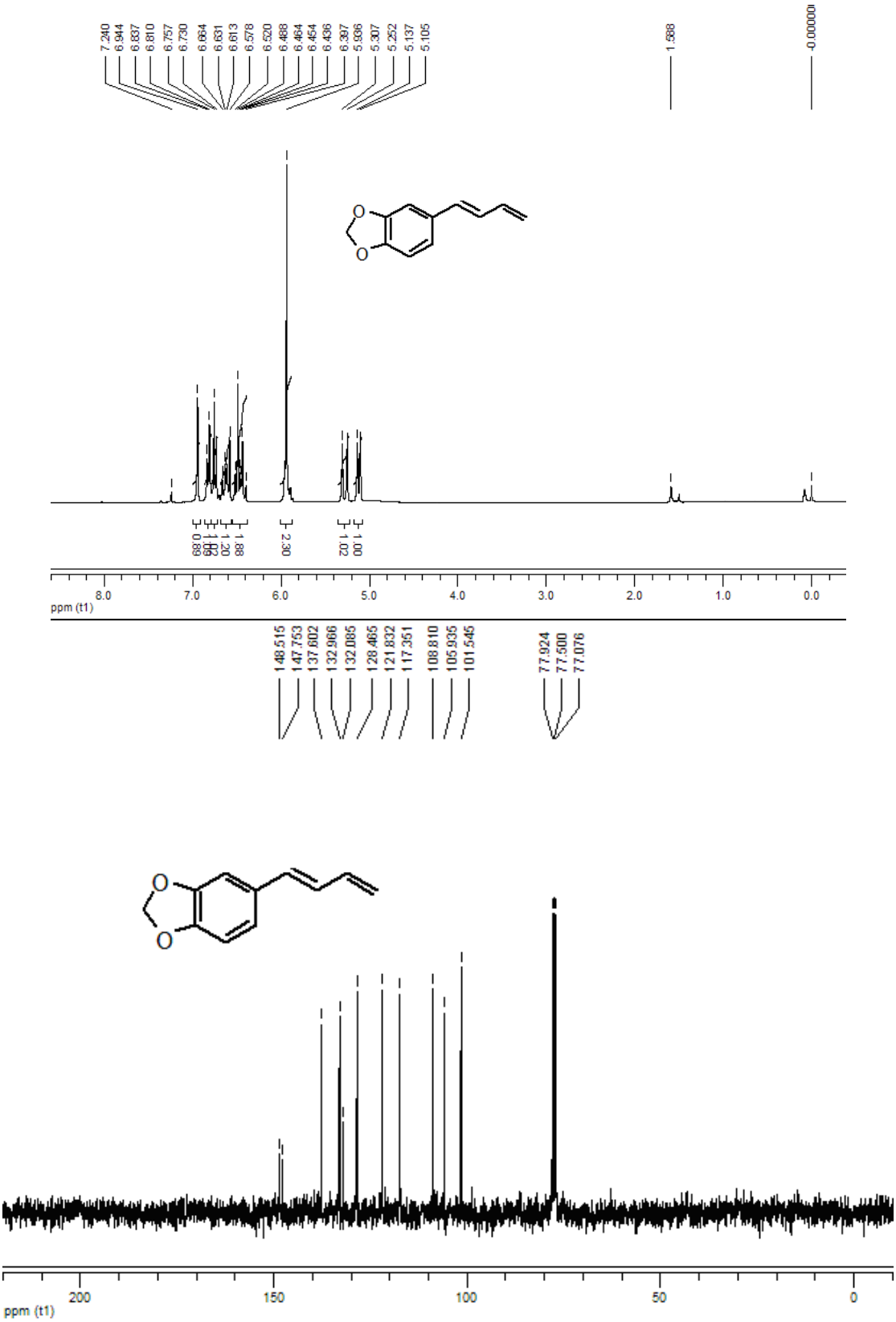
2,4-diphenylbut-1-en-3-yne (entry 28) [19] The title compound was obtained according to the general procedure. Colourless oil; Yield: 72%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 3.8 Hz, 2H), 7.44-7.22 (m, 6H), 5.98 (s, 1H), 5.76 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.72, 132.97, 132.14, 131.07, 129.68, 128.89, 128.83, 126.57, 123.56, 121.16, 91.26, 89.03. HRMS (EI^+): calcd. for $C_{16}H_{12}$(M^+) : 204.0939, found: 204.0940.

1-methyl-4-(4-phenylbut-1-en-3-yn-2-yl)benzene (entry 29) The title compound was obtained according to the general procedure. Colourless oil; Yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.52 (dd, *J* = 2.8 Hz, *J* = 6.6 Hz, 2H), 7.33 (dd, *J* = 1.8 Hz, *J* = 4.9 Hz, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.93 (s, 1H), 5.70 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.74, 134.95, 132.97, 132.14, 130.89, 129.58,

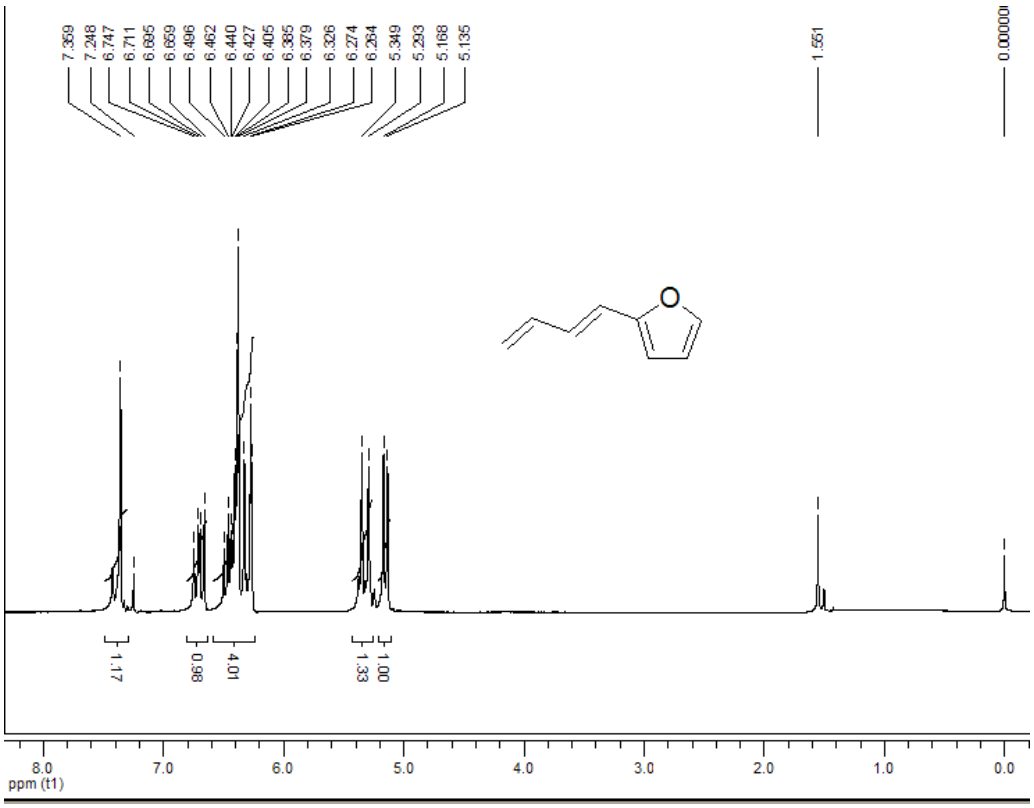
128.82, 126.47, 123.65, 120.28, 91.05, 89.22, 21.66. IR (KBr). 3057, 2974, 2861, 2199, 1603, 1512, 1448, 1277, 1176, 1025, 911, 818, 757, 693, 528cm^{-1}. HRMS (EI^{+}): calcd. for $C_{17}H_{14}$ (M^{+}) : 218.1096, found: 218.1100.

^{1}H and ^{13}C NMR spectrums

entry 5



entry 6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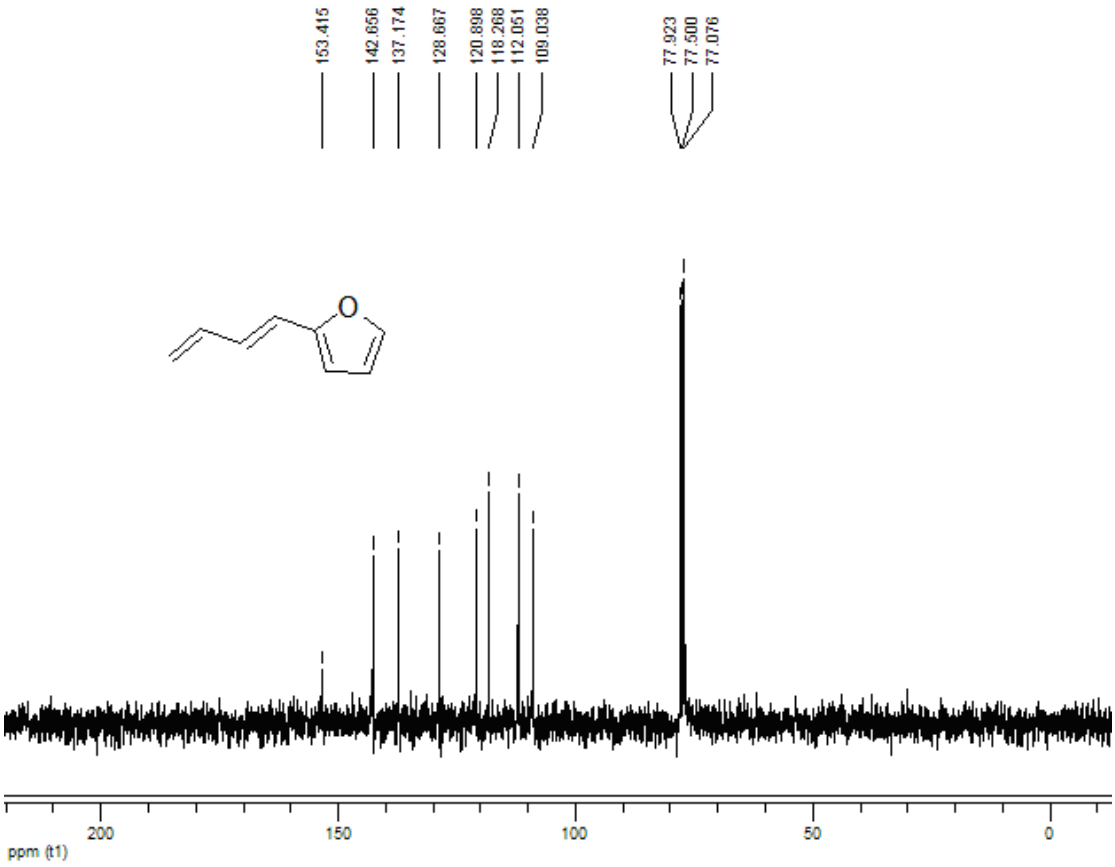
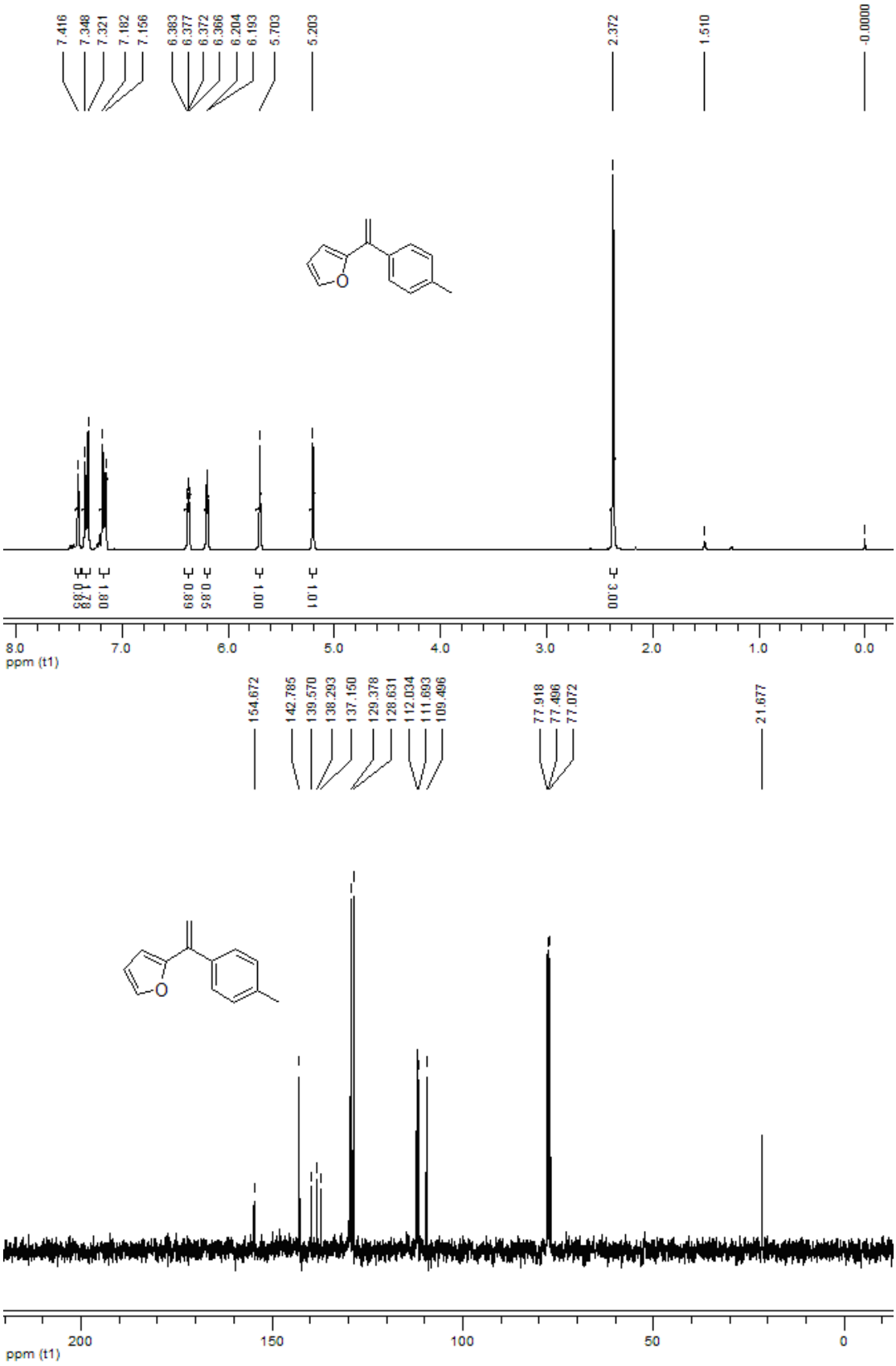
6.747
6.711
6.695
6.659
6.496
6.462
6.440
6.427
6.405
6.385
6.379
6.326
6.274
6.254
5.349
5.293
5.168
5.135
1.551
0.00000
O
1.17
0.98
4.01
1.33
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


153.415
142.656
137.174
128.667
120.898
118.268
112.051
109.038
77.923
77.500
77.076
O
200
150
100
50
0
ppm (t1)

entry 13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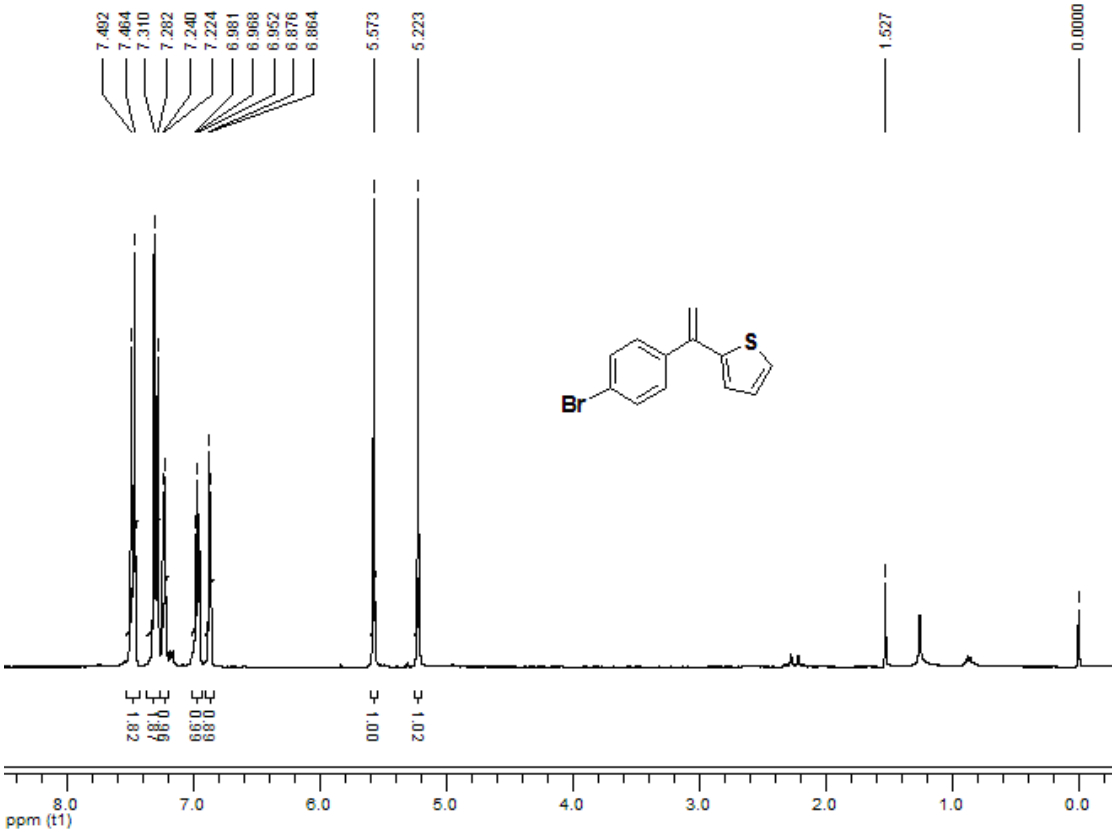
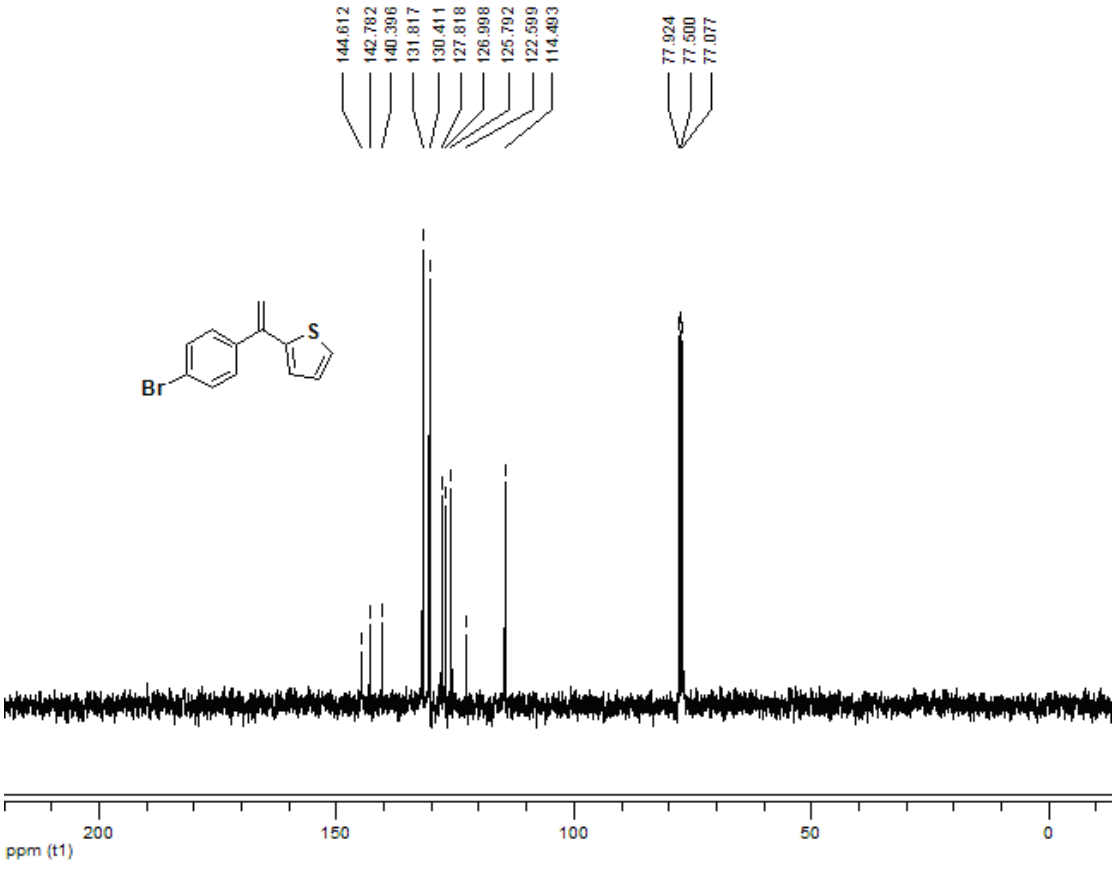
7.348
7.321
7.182
7.156
6.383
6.377
6.372
6.366
6.204
6.193
5.703
5.203
2.372
1.510
-0.0000
0.83
1.78
1.80
0.89
0.85
1.00
1.01
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
154.672
142.785
139.570
138.293
137.150
129.378
128.631
112.034
111.693
109.496
77.918
77.496
77.072
21.677
O
200
150
100
50
0
ppm (t1)

entry 15


7.492
7.464
7.310
7.282
7.240
7.224
6.981
6.968
6.952
6.876
6.864
5.573
5.223
1.527
0.0000
Br
S
1.82
1.87
0.99
0.89
1.00
1.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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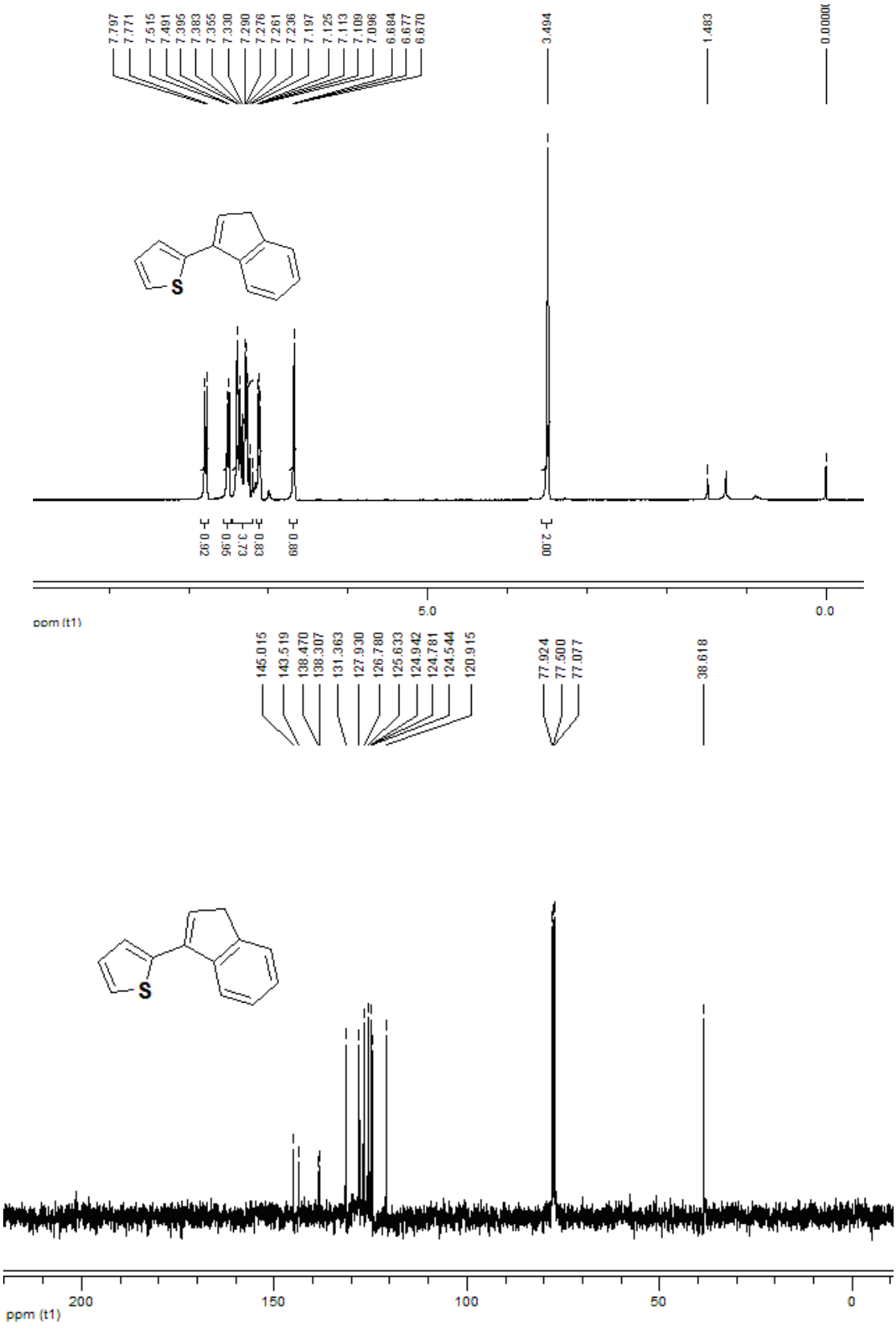
142.782
140.396
131.817
130.411
127.818
126.998
125.792
122.599
114.493
77.924
77.500
77.077
Br
S
200
150
100
50
0
ppm (t1)

entry 17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7.395
7.383
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7.330
7.290
7.276
7.261
7.236
7.197
7.125
7.113
7.109
7.096
6.684
6.677
6.670
3.494
1.483
0.0000
S
0.92
0.96
3.73
0.83
0.89
2.00
5.0
0.0
ppm (t1)
145.015
143.519
138.470
138.307
131.363
127.930
126.780
125.633
124.942
124.781
124.544
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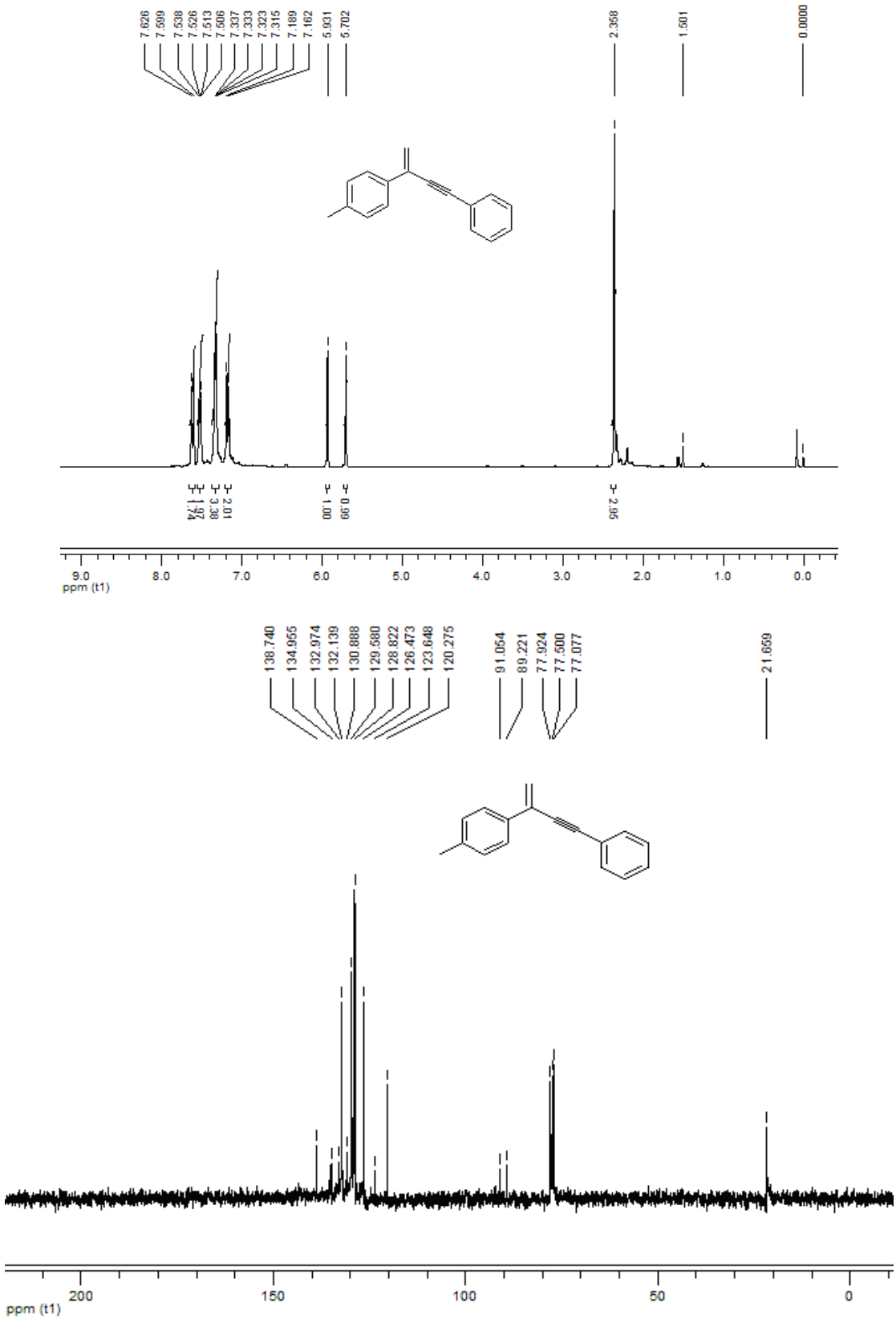
77.924
77.500
77.077
38.618
S
200
150
100
50
0
ppm (t1)

entry 29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7.526
7.513
7.506
7.337
7.333
7.323
7.315
7.189
7.162
5.931
5.702
2.358
1.501
0.0000
1.74
1.92
3.38
2.01
1.00
0.99
2.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
138.740
134.955
132.974
132.139
130.888
129.580
128.822
126.473
123.648
120.275
91.054
89.221
77.924
77.500
77.077
21.659
200
150
100
50
0
ppm (t1)

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