Electronic Supplementary Material (ESI) for Green Chemistry.

Preparation of functional styrenes from biosourced carboxylic acid by copper catalyzed decarboxylation in PEG

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General information

All glassware was base-, acid-and water-washed and oven dried. The catalytic reactions were carried out under slight vacuum in a distillation apparatus consisting on a two-necked flask equipped with a condenser, a vacuum adapter and a receiving flask.

The qualitative and quantitative analysis of the reactants and the products was made by Gas Chromatography. Conversions and selectivities were determined by GC. Dodecane was used as external standard for GC-quantitative determinations.

All chemicals were purchased from Acros or Aldrich Chemicals in their highest purity. All solvents were used as supplied without further purification.

Metal trace analysis in PEG 6000 BioUltra (data provided by Aldrich Chemicals): aluminium (icp) <5 mg/kg, barium (icp) <5 mg/kg, bismuth (icp) <5 mg/kg, calcium (icp) <10 mg/kg, cadmium (icp) <5 mg/kg, cobalt (icp) <5 mg/kg, chromium (icp) <5 mg/kg, copper (icp) <5 mg/kg, iron (icp) <5 mg/kg, potassium (icp) <200 mg/kg, lithium (icp) <5 mg/kg, magnesium (icp) <5 mg/kg, manganese (icp) <5 mg/kg, molybdenum (icp) <5 mg/kg, sodium (icp) <200 mg/kg, nickel (icp) <5 mg/kg, lead (icp) <5 mg/kg, strontium (icp) <5 mg/kg, zinc (icp) < mg/kg, arsenic traces (mhs-aas) <0.100 mg/kg, total sulfur as SO_4 (icp) <50 mg/kg, chloride (cl) <50 mg/kg.

Metal trace analysis in $Cu(OH)_2$ (data provided by Aldrich Chemicals): Copper 64.8%, Sulfate ND, Chloride ND, Iron ND, Nickel ND, Cobalt ND, Chromium ND. ND: Not detected

Liquid NMR spectra were recorded on a BRUKER AC-250 or BRUKER DRX300 spectrometer. All chemical shifts were measured relative to residual ^1H NMR resonances in

the deuterated solvents: $CDCl_3$, δ 7.26 ppm for ^1H; D_2O, 4.79 ppm for ^1H. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants (in Hz), integration and assignments in that order. Thin layer chromatography was performed on Fluka Silica Gel 60 F_{254}. GC analyses were performed on a Shimadzu GC-2010 chromatograph equipped with a FID detector, a AOC-20i+ autosampler and a Phenomenex Zebron ZB-5HT column (cross-linked 5% Phenyl-Methylsiloxane, 30 m x 0.25 mm i. d. x 0.25 µm film thickness). Nitrogen is used as carrier gas. The mass spectra were obtained on a Shimadzu GC-MS-QP2010S equipped with a AOC-20i+ autosampler and a Sulpelco SLB-5MS column (95% methylpolysiloxane + 5% phenylpolysiloxane, 30m x 0.25mm x 0.25µm) with He as carrier gas was used. The experimental error was estimated to be $\Delta_{rel} = \pm 5\%$.

General procedures for the decarboxylation of carboxylic acids

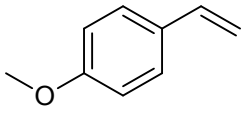
15 mmol of carboxylic acid, 0.75 mmol (73 mg) of $Cu(OH)_2$, 0.75 mmol (135 mg) 1,10-phenanthroline and 20 g PEG-6000 BioUltra are introduced in a two-necked flask. After adapting a condenser, a vacuum adapter and a receiving flask, the reaction mixture is degassed by a series of vacuum/argon under stirring. Then it is heated up to the effective reaction temperature (i.e. 130-230 °C) as attested by CO_2 release under slight vacuum (i.e. 0.5-1 mbar) until complete conversion. The pure decarboxylated compound is obtained directly in the receiving flask.

All compounds gave analytical data in agreement with reported literature; (**1**[11]; **2**[50]; **3**[51]; **4**[24] , **5**[24]; **7**[52]) or available data for commercially available compounds (**6**[CAS 100-42-5]; **8**[CAS 98-95-3]; **9**[CAS 2004-70-8]; **10**[CAS 64-04-0]; **11**[CAS 51-67-2]; **12**[78-81-9] **13**[CAS 541-23-1]; **14**[4104-45-4]; **15**[CAS 120-72-9]; **16**[CAS 271-89-6]; **17**[CAS 95-15-8]) from the National Institute of Advanced Industrial Science and Technology (AIST).

General procedure for recycling studies

The same distilling installation as for a classical run is used in these experiments. 30 mmol (5.8 g) of ferulic acid, 1.5 mmol (146 mg) of $Cu(OH)_2$, 1.6 mmol (288 mg) 1,10-phenanthroline and 50 g PEG-6000 BioUltra are introduced in the two-necked flask. After degassing the reaction mixture by a series of vacuum/argon under stirring, it is heated up to 140 °C under slight vacuum (i.e. 0.5-1 mbar) until quantitative conversion. After collecting the pure 4-vinylguiaicol from the receiving flask, a new charge of ferulic acid (30 mmol; 5.8 g) is added in the boiling flask and the decarboxylation procedure repeated, constituting thus a new run of the catalytic mixture (i.e; catalyst and solvent). The overall cycle is repeated twice.

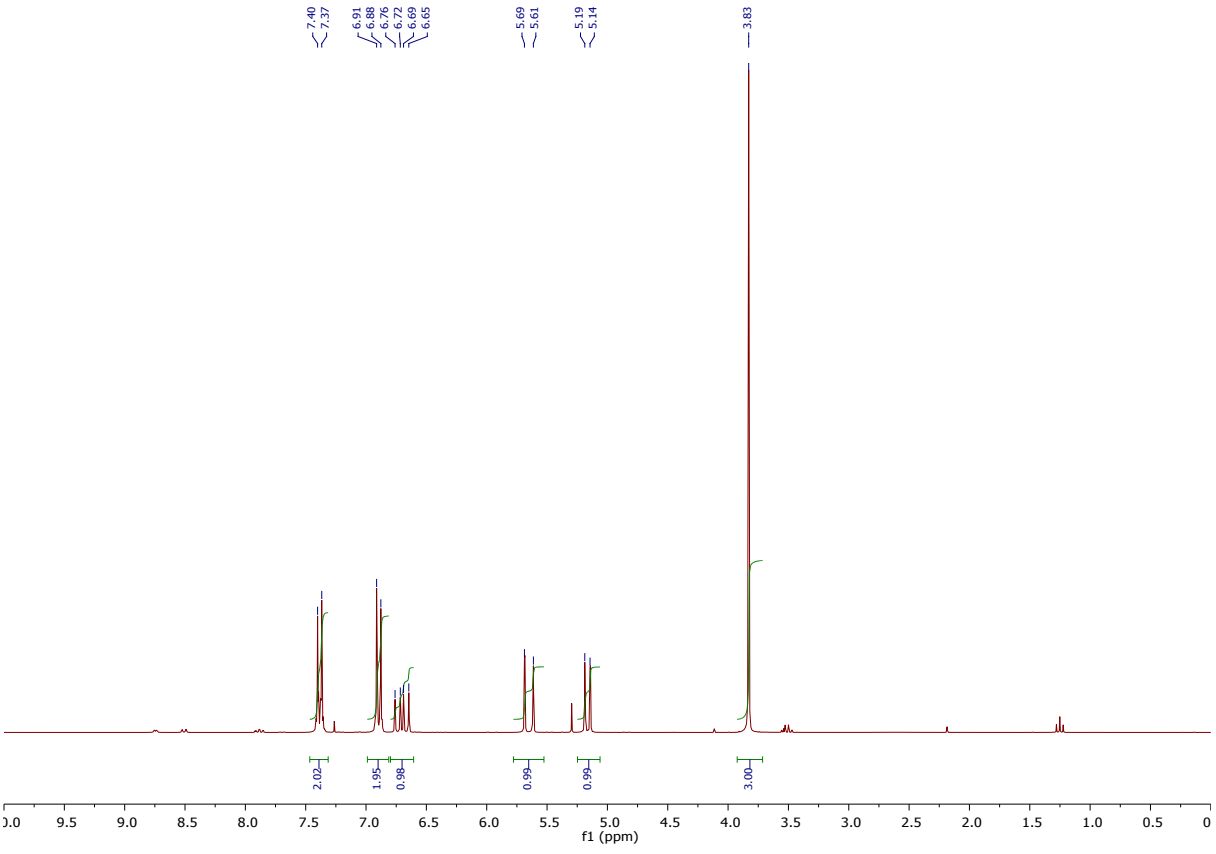
Characterization Data of the Products

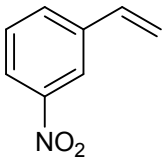


1-methoxy-4-vinylbenzene 1 as yellow liquid (CAS: 637-69-4)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.65 (d, *J* = 17.6 Hz, 1H), 5.16 (d, *J* = 9.9 Hz, 1H), 3.83 (s, 3H).

MS (EI): m/e (%) 135 (10), 134 (100), 119 (52), 91 (49), 89 (5), 77 (6), 65 (25), 63 (9), 51 (7).

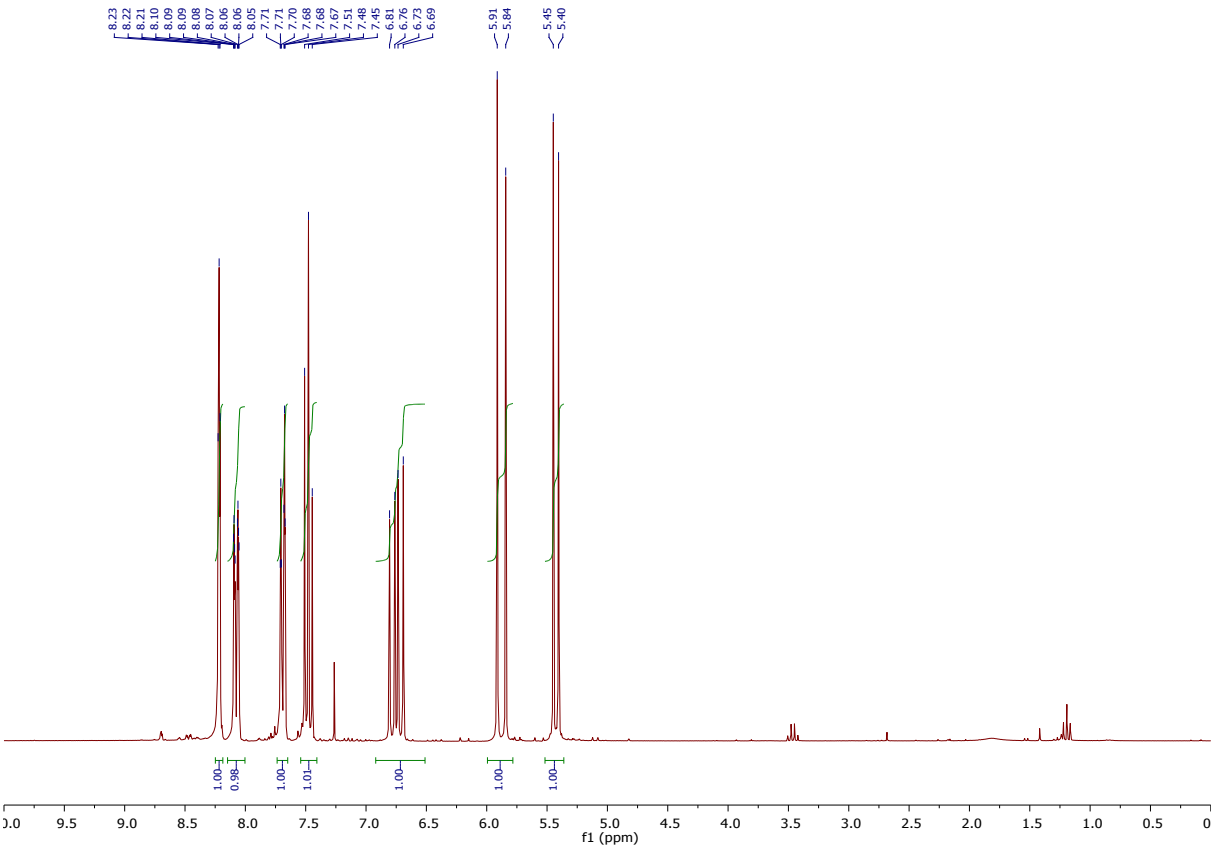


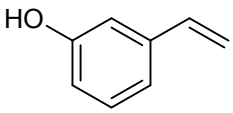


1-nitro-3-vinylbenzene 2 as yellow liquid (CAS: 586-39-0)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.22 (t, *J* = 2.0 Hz, 1H), 8.08 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 7.69 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.43 (d, *J* = 10.9 Hz, 1H).

MS (EI): m/e (%) 150 (10), 149 (100), 104 (9), 103 (98), 102 (25), 91 (20), 78 (6), 77 (98), 76 (12), 75 (8), 74 (8), 65 (8), 63 (11), 52 (5), 51 (35), 50 (17)

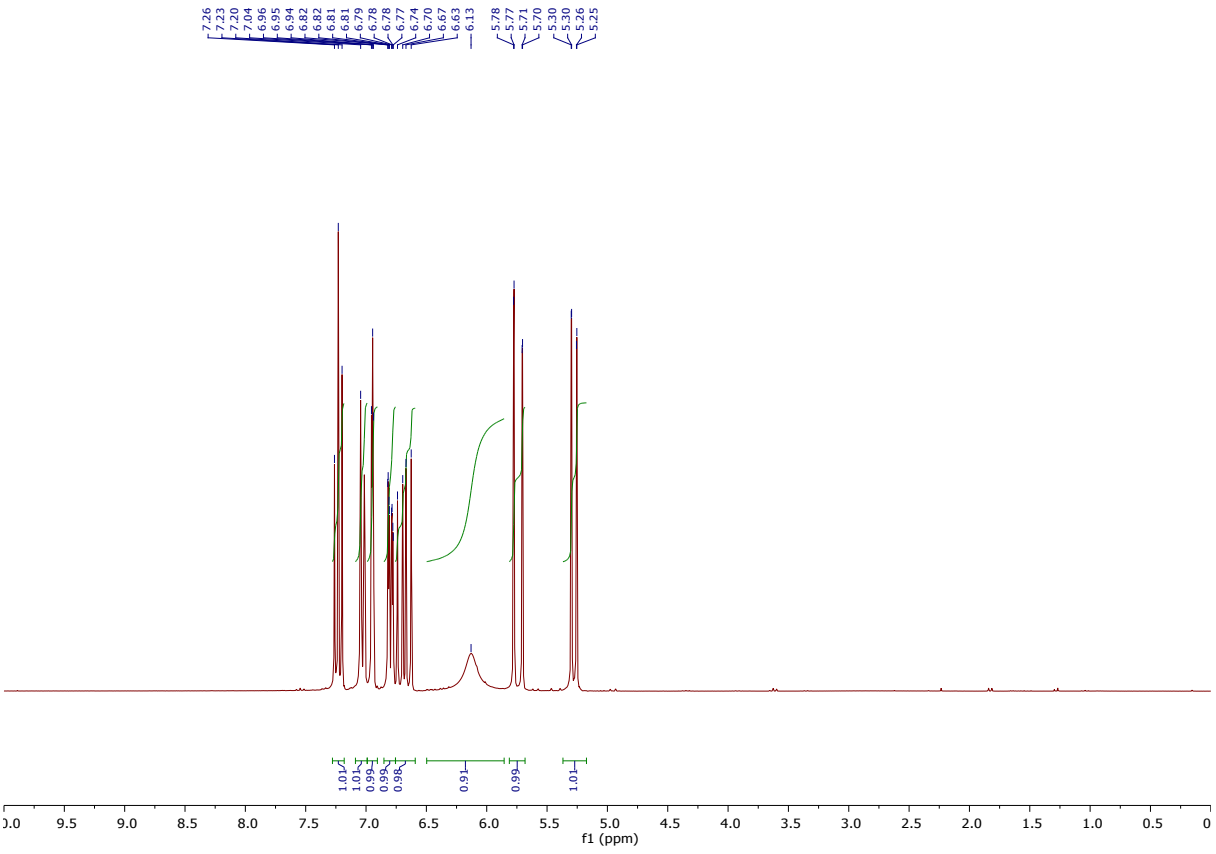


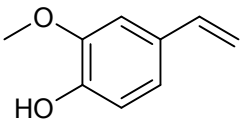


3-vinylphenol 3 as colorless liquid (CAS: 620-18-8)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.9 Hz, 1H), 7.03 (pseudo dt, *J* = 7.7 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.80 (ddd, *J* = 8.0, 2.5, 0.9 Hz, 1H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.13 (s, 1H), 5.74 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.28 (dd, *J* = 10.9, 0.8 Hz, 1H).

MS (EI): m/e (%) 121 (10), 120 (100), 119 (17), 94 (11), 92 (12), 91 (68), 89 (5), 66 (5), 65 (20), 63 (9), 51 (8).

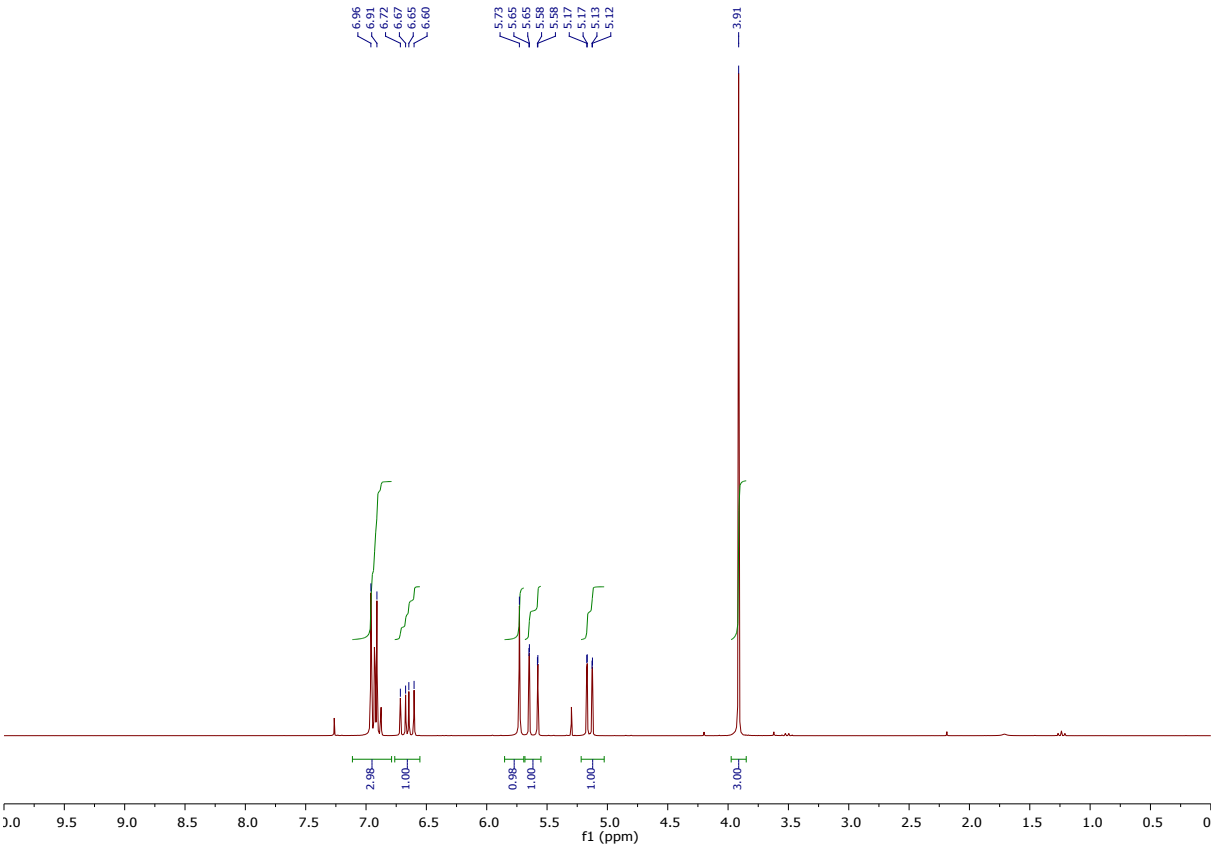


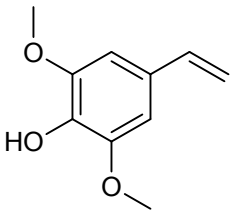


2-methoxy-4-vinylphenol 4 as colorless liquid (CAS: 7786-61-0)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.03 – 6.84 (m, 3H), 6.66 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.73 (s, 1H), 5.61 (dd, *J* = 17.5, 0.9 Hz, 1H), 5.15 (dd, *J* = 10.8, 0.9 Hz, 1H), 3.91 (s, 3H).

MS (EI): m/e (%) 151 (9), 150 (100), 136 (8), 135 (98), 107 (40), 91 (5), 89 (6), 79 (14), 78 (9), 77 (39), 65 (6), 63 (8), 55 (5), 53 (10), 52 (8), 51 (13), 50 (5).

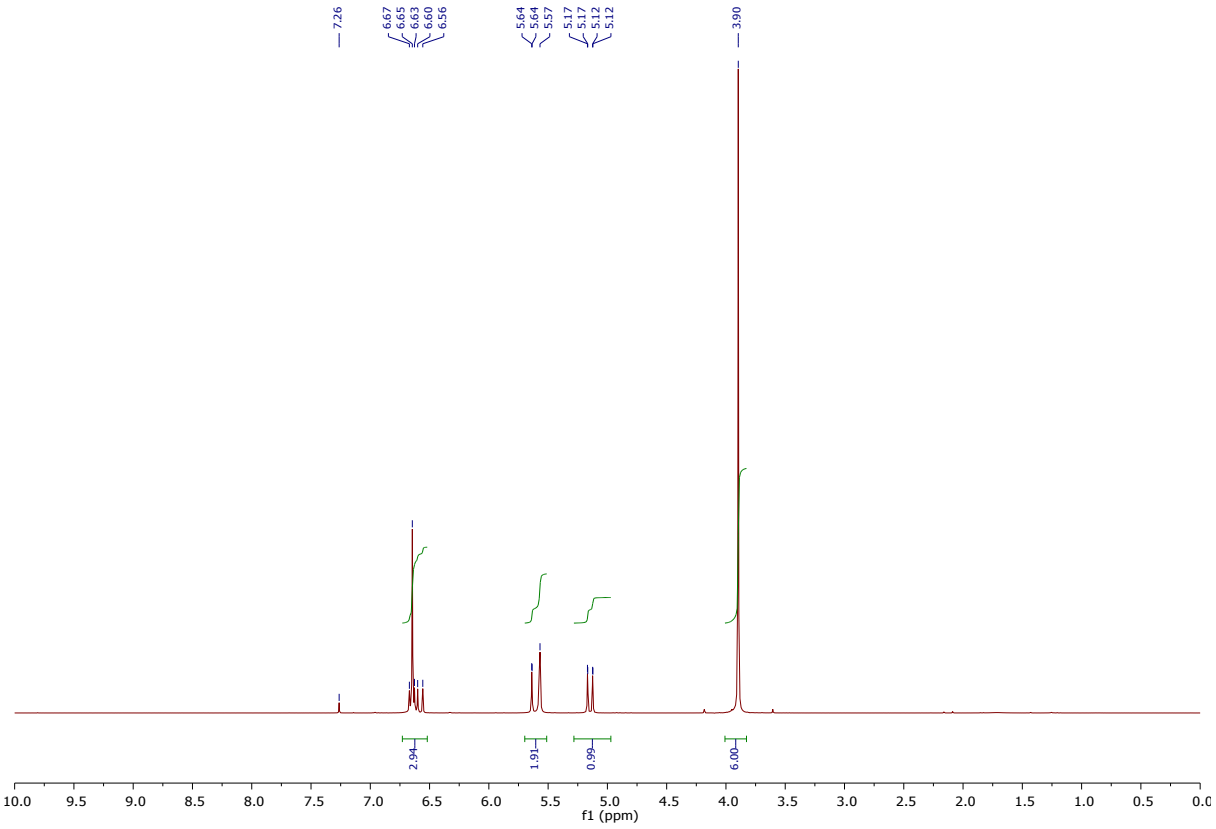


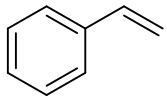


2,6-dimethoxy-4-vinylphenol 5 as colorless liquid (CAS: 51121-75-6)

^{1}H NMR (250 MHz, $CDCl_3$) δ 6.65 (s, 2H), 6.61 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.61 (dd, 1H), 5.57 (s, 1H), 5.15 (dd, *J* = 10.8, 0.5 Hz, 1H), 3.90 (s, 6H).

MS (EI): m/e (%) 181 (11), 180 (100), 166 (5), 165 (49), 137 (39), 122 (16), 119 (9), 105 (5), 94 (10), 91 (23), 79 (9), 78 (6), 77 (23), 66 (11), 65 (13), 63 (5), 55 (5), 53 (8), 51 (12).

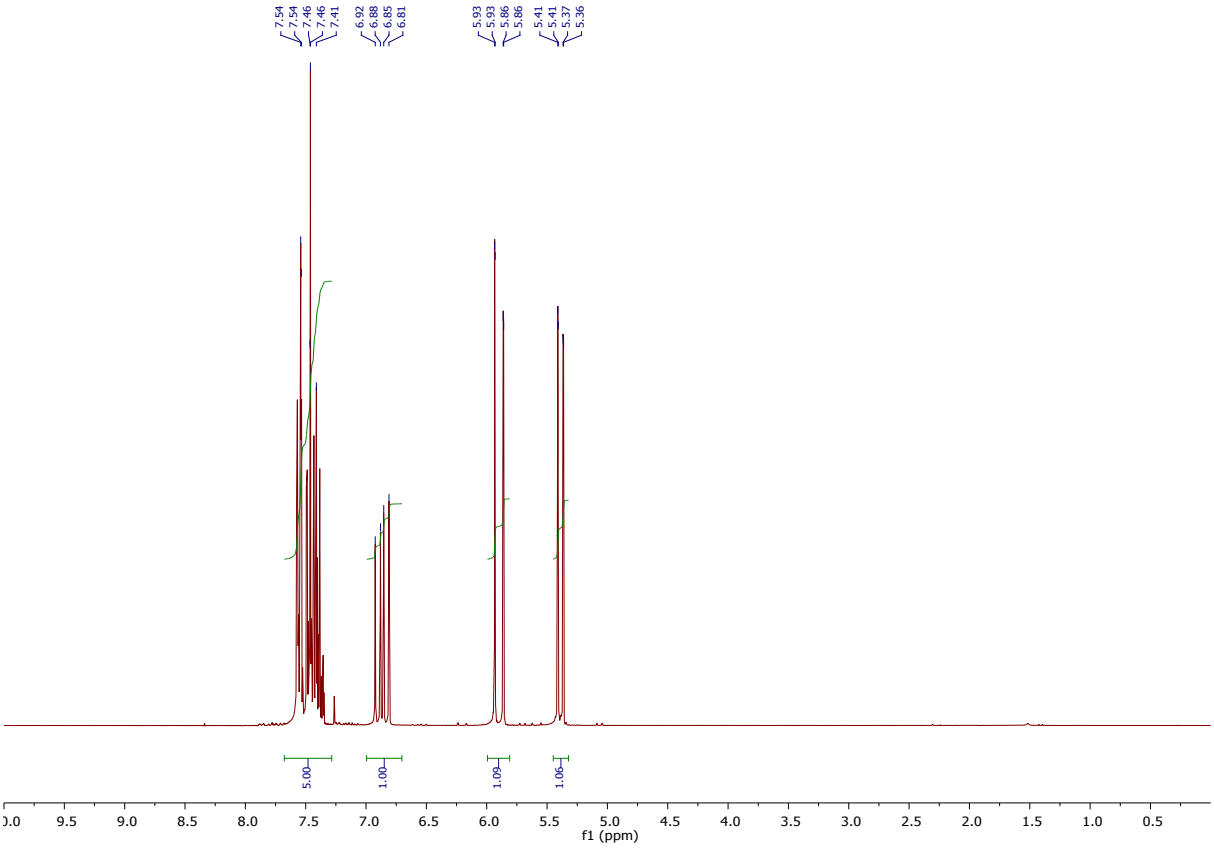


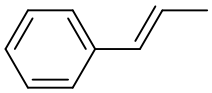


Styrene 6 as colorless liquid (CAS: 100-42-5)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.62 – 7.30 (m, 5H), 6.87 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.90 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.39 (dd, *J* = 10.9, 1.0 Hz, 1H).

MS (EI): m/e (%) 105 (9), 104 (100), 103 (46), 102 (8), 78 (42), 77 (20), 63 (6), 52 (8), 51 (23), 50 (9).

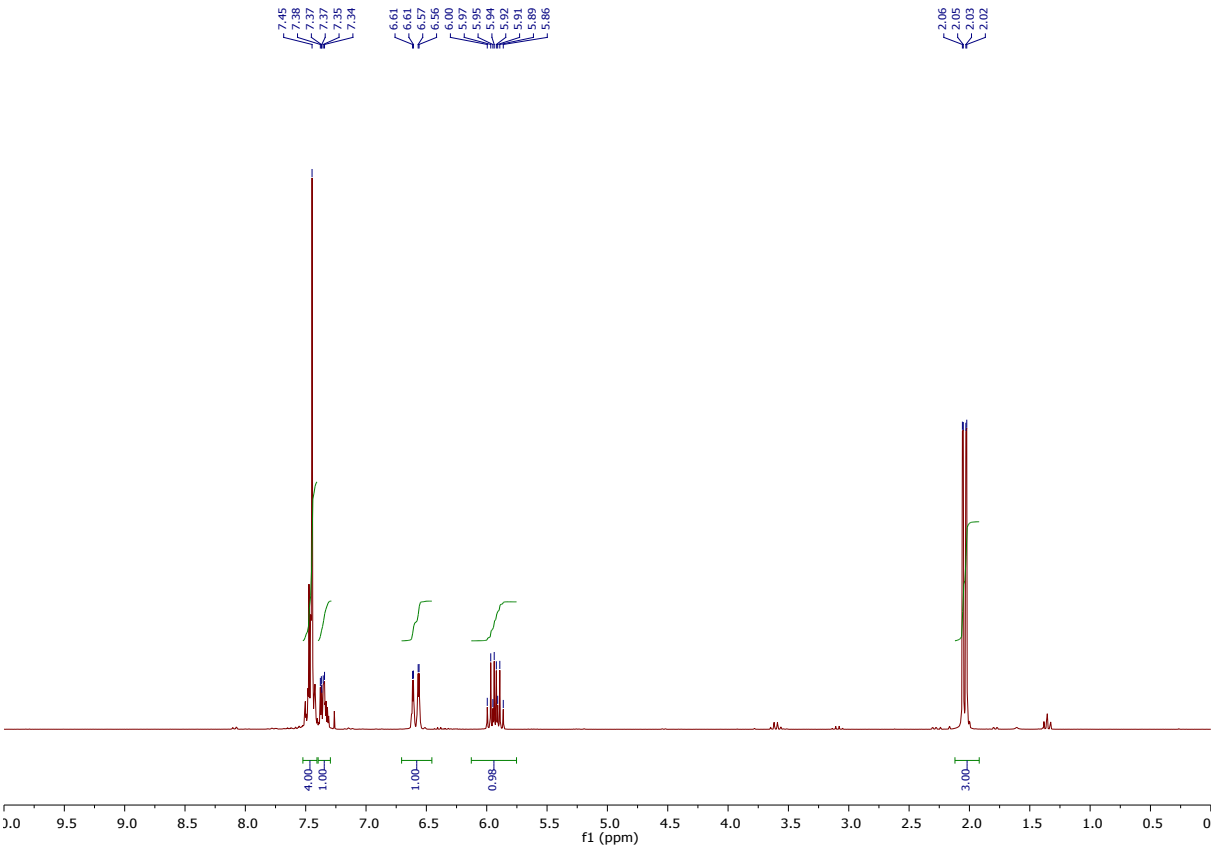


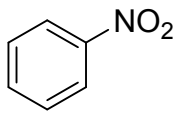


Propenylbenzene 7 as colorless liquid (CAS: 637-50-3)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 4H), 7.40 – 7.29 (m, 1H), 6.59 (dq, *J* = 11.6, 1.8 Hz, 1H), 5.93 (dq, *J* = 11.6, 7.2 Hz, 1H), 2.04 (dd, *J* = 7.2, 1.8 Hz, 3H).

MS (EI): m/e (%) 119 (7), 118 (77), 117 (100), 116 (9), 115 (45), 103 (9), 91 (32), 89 (8), 78 (7), 77 (9), 65 (10), 63 (9), 57 (9), 51 (13), 50 (6).

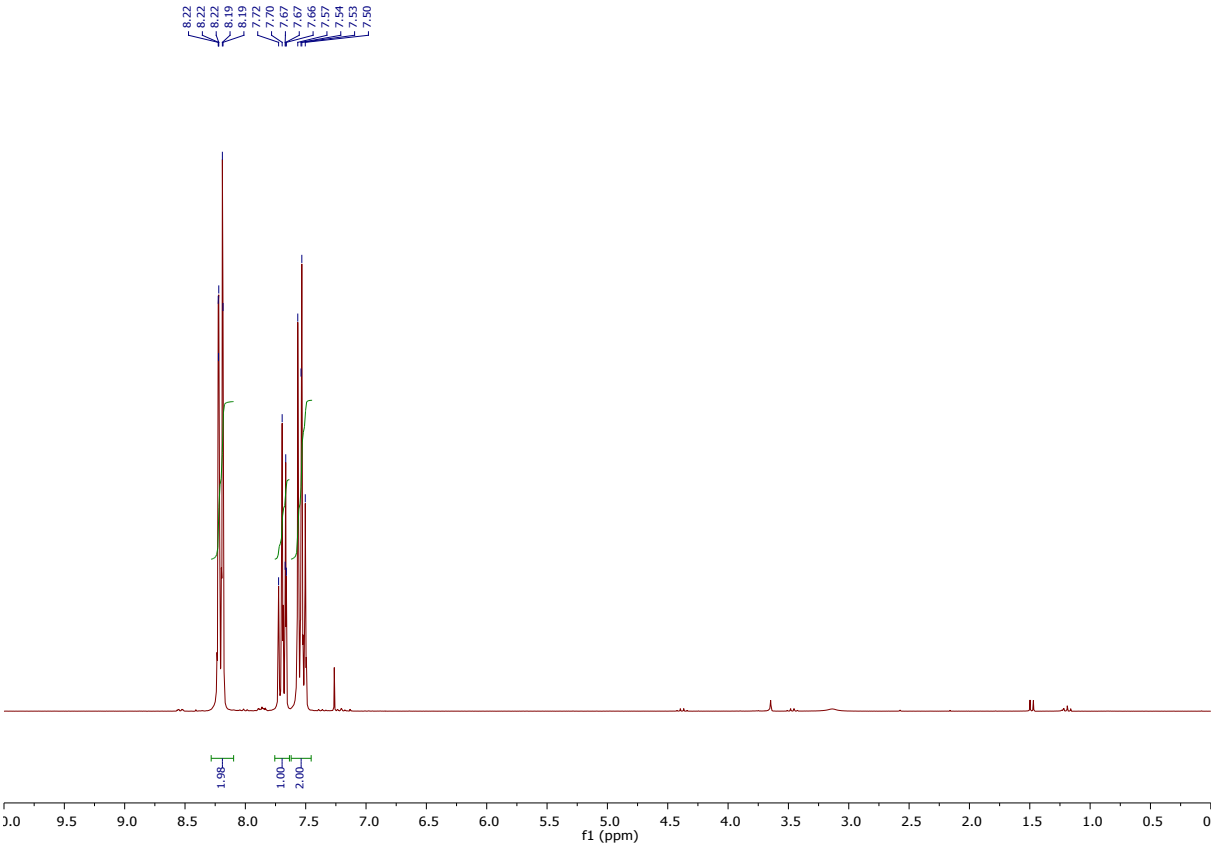


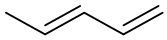


Nitrobenzene 8 as colorless liquid (CAS: 98-95-3)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.77 – 7.62 (m, 1H), 7.60 – 7.47 (m, 1H).

MS (EI): m/e (%) 123 (60), 93 (15), 78 (7), 77 (100), 74 (6), 65 (16), 51 (54), 50 (18).

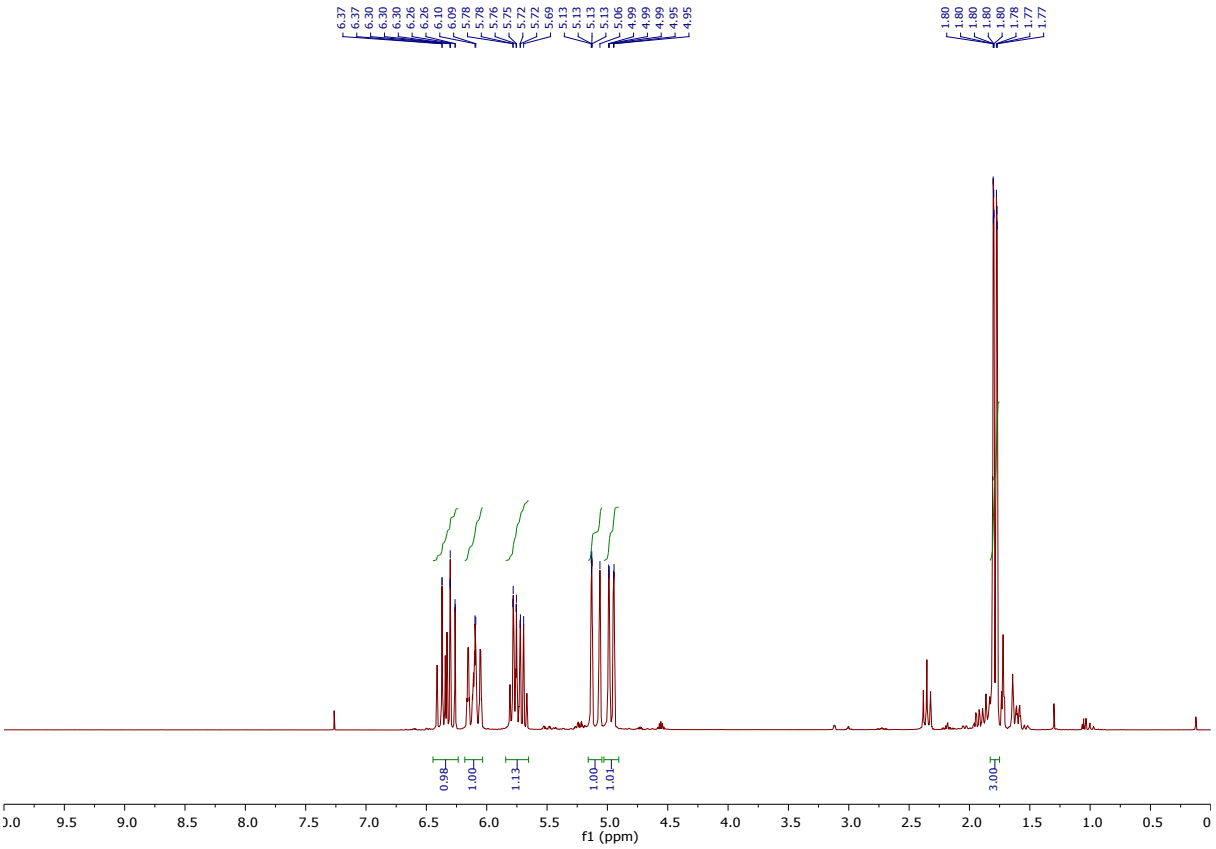


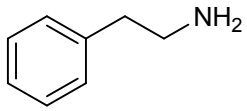


Penta-1,3-diene 9 as colorless liquid (CAS: 504-60-9)

^{1}H NMR (250 MHz, $CDCl_3$) δ 6.46 – 6.24 (m, 1H), 6.19 – 6.00 (m, 1H), 5.86 – 5.61 (m, 1H), 5.18 – 5.03 (m, 1H), 5.01 – 4.91 (m, 1H), 1.84 – 1.74 (m, 3H).

MS (EI): m/e (%) 27 (15), 38 (8), 39 (50), 40 (30), 41 (37), 42 (19), 50 (5), 51 (7), 53 (64), 63 (5), 65 (14), 66 (8), 67 (100), 68 (86).

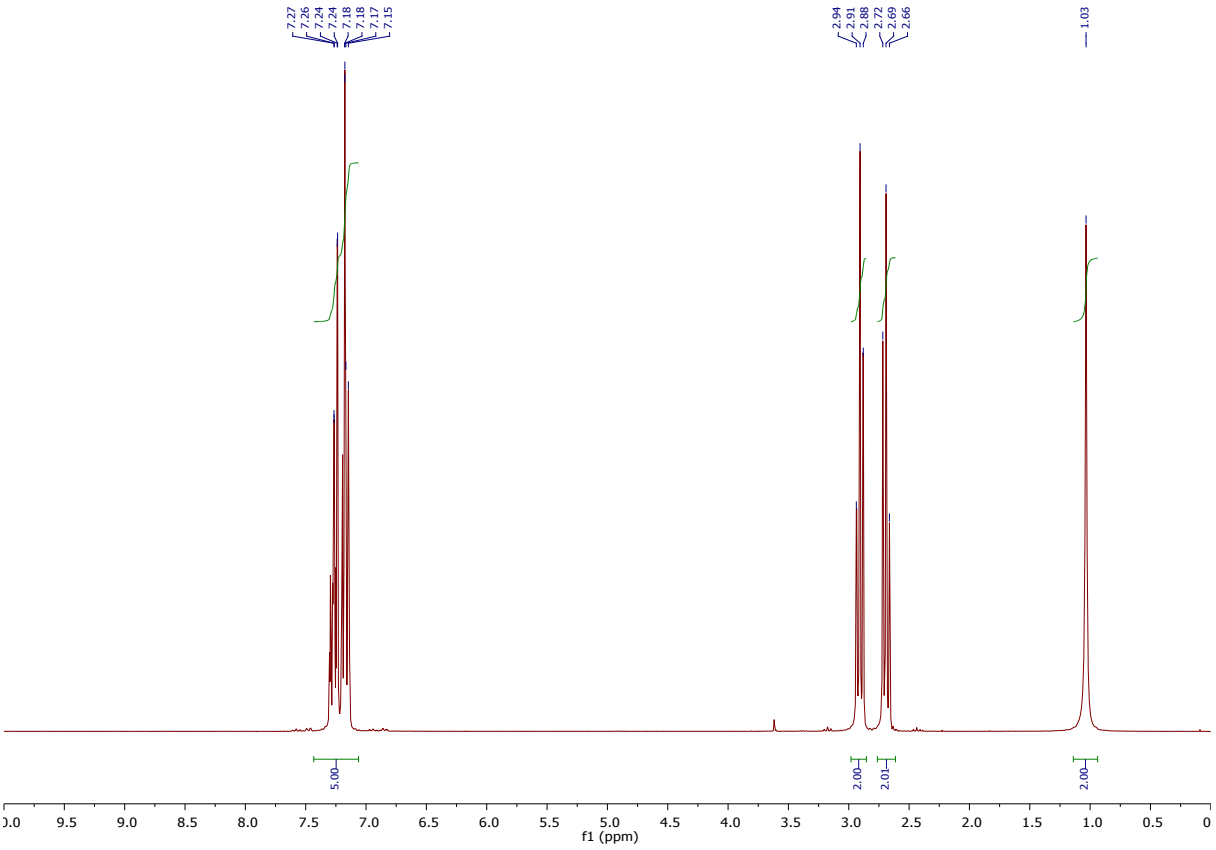


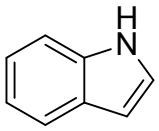


2-phenylethylamine <u>10</u> as colorless liquid (CAS: 64-04-0)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.41 – 7.09 (m, 5H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 6.9 Hz, 2H), 1.03 (s, 2H).

MS (EI): m/e (%) 121 (25), 118 (5), 103 (10), 92 (36), 91 (100), 90 (5), 89 (11), 78 (5), 77 (17), 65 (50), 63 (16), 62 (5), 52 (6), 51 (20), 50 (9), 42 (7), 41 (8).

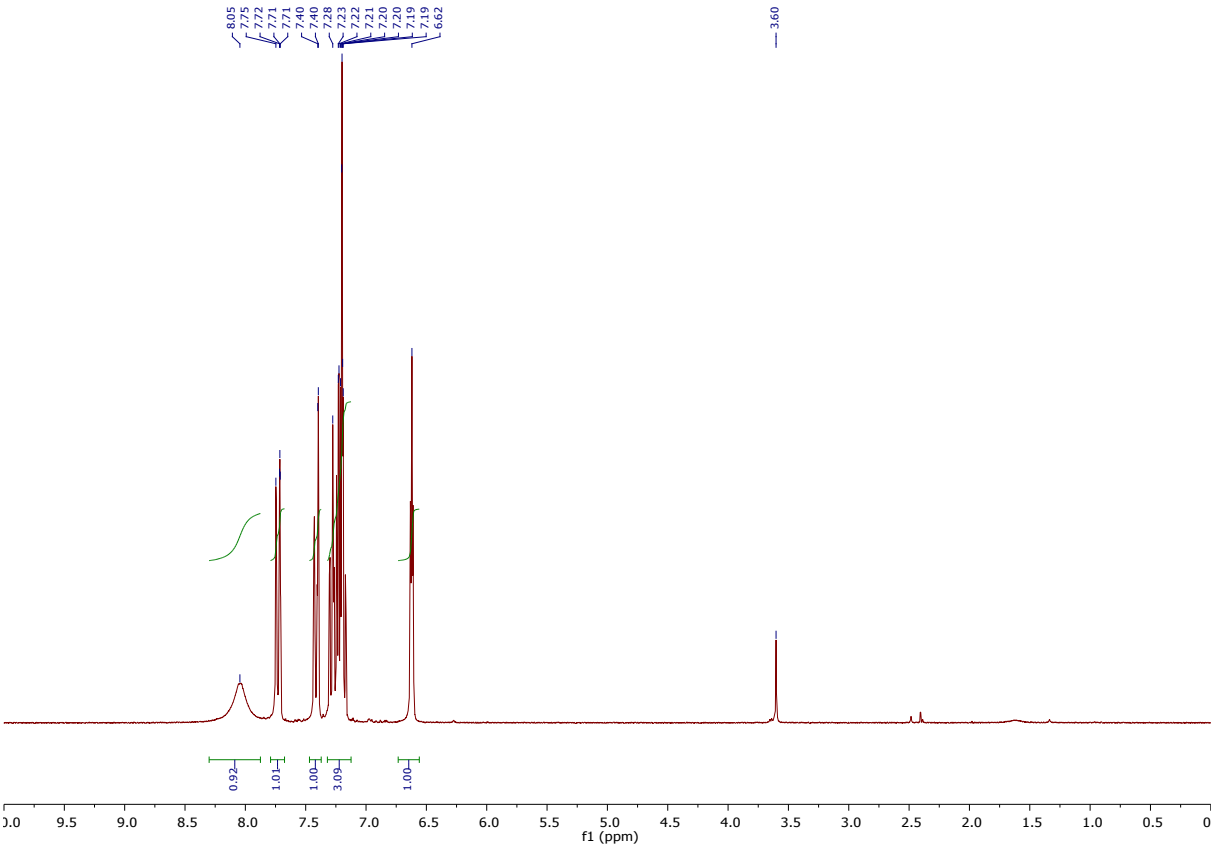


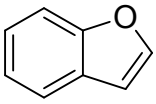


1H-indole <u>15</u> as white solid (CAS: 120-72-9)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.80 – 7.67 (m, 1H), 7.49 – 7.35 (m, 1H), 7.32 – 7.14 (m, 3H), 6.74 – 6.53 (m, 1H).

MS (EI): m/e (%) 118 (9), 117 (100), 116 (8), 90 (44), 89 (32), 63 (14), 62 (5), 58 (7), 39 (7).

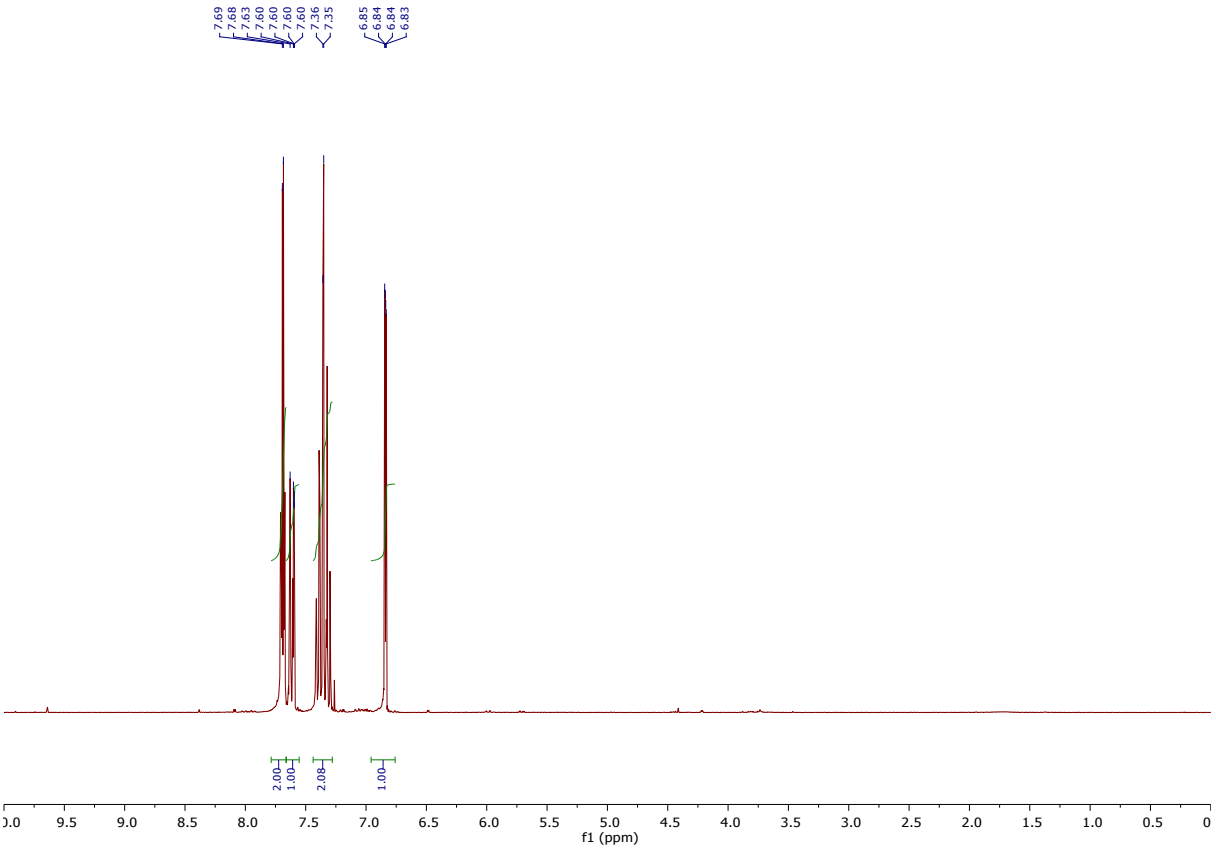


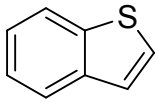


Benzo[*b*]furan <u>16</u> as yellow liquid (CAS: 271-89-6)

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 2H), 7.64 – 7.59 (m, 1H), 7.44 – 7.27 (m, 2H), 6.84 (dd, J = 2.2, 1.0 Hz, 1H).

MS (EI): m/e (%) 119 (10), 118 (100), 90 (44), 89 (47), 64 (6), 63 (23), 62 (9), 59 (5), 39 (9).

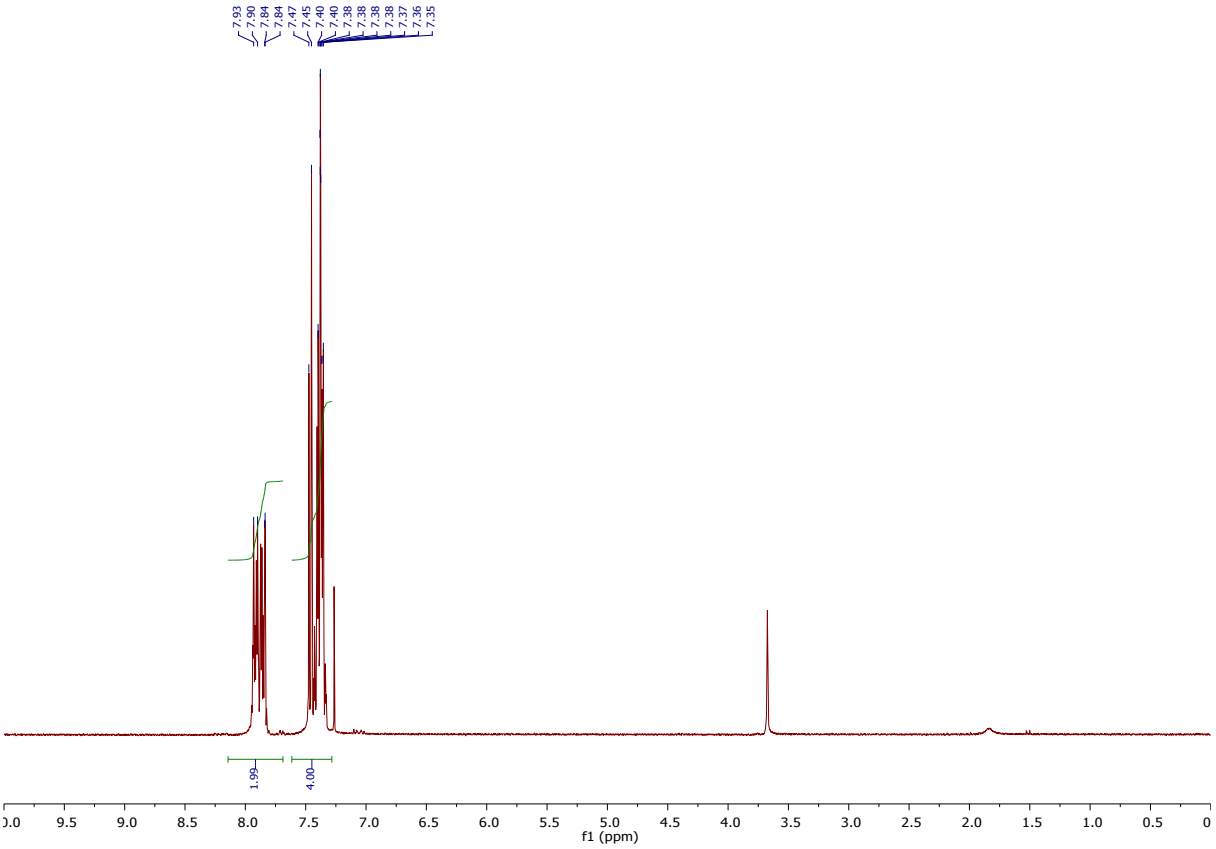


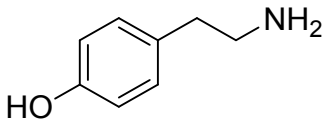


Benzothiophene 17 as beige solid (CAS: 95-15-8)

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.04 – 7.76 (m, 2H), 7.53 – 7.30 (m, 4H).

MS (EI): m/e (%) 136 (5), 135 (11), 134 (100), 108 (6), 90 (11), 89 (13), 68 (5), 67 (6), 63 (7).





4-(2-aminoethyl)phenol <u>11</u> as beige solid (CAS: 51-67-2)

^{1}H NMR (250 MHz, D_2O) δ 6.95 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 8.3 Hz, 2H), 4.68 (s, 3H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.64 (t, *J* = 7.0 Hz, 2H).

MS (EI): m/e (%) 137 (5), 109 (11), 108 (40), 107 (20), 77 (12), 31 (29), 30 (100).