

The first one-pot metathesis-hydroformylation procedure: a straight synthesis of arylaldehydes from renewable 1-propenylbenzenes

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Supporting Information

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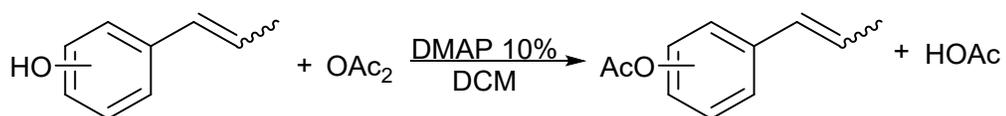
GENERAL CONSIDERATIONS

All manipulations of air- or water- sensitive compounds were carried out under dry argon using a glovebox (MBRAUN UNILAB PRO) or by standard Schlenk techniques. NMR (^1H , 400 MHz; ^{13}C , 100 MHz) spectra were recorded on a Bruker NanoBay spectrometer and referenced to residual solvent.

GC analysis were performed on samples diluted with untreated solvents (ethanol, THF or toluene) on Shimadzu GC2010 Plus instrument equipped with an auto-sampler, fitted with a nonpolar Rtx[®]-5MS column (30 m length, 250 μm internal diameter) and a flame ionization detector (FID). The conversion and selectivity were determined using undecane as internal standard. GC and column conditions: injection temperature, 310 $^{\circ}\text{C}$; inlet split ratio 50:1; detector temperature, 320 $^{\circ}\text{C}$; oven temperature, starting temperature 50 $^{\circ}\text{C}$; hold time, 5 min, 15 $^{\circ}\text{C}/\text{min}$ to 280 $^{\circ}\text{C}$, held for 5 min. Carrier gas: H_2 (UHP grade), makeup gas N_2 (UHP grade). The GC/MS analyses were performed using a Shimadzu GC2010/QP2010-GC/MS instrument, employing an electron impact detector at 70 eV. The GC/MS conditions were identical to that of the GC/FID setup, except for the carrier gas (He).

MATERIALS

Toluene (99.8%, anhydrous, Sigma-Aldrich) was purified in a MBRAUN solvent purifier system, then stored under argon in a glovebox over 4 Å molecular sieve for at least 24 h prior to use. The substrates *trans*-anethole (99%, Sigma-Aldrich), isoeugenol (98%, *cis-trans* mixture, Sigma-Aldrich) and methyl isoeugenol ($\geq 98\%$, FG, Sigma-Aldrich) were purified by treating with Magnesol® (5% m/m) and heated to 80 °C under vigorous stirring by 2 h, then distilled in a Kugelrohr distillation apparatus at 2 mmHg (50 °C anethole, 90 °C isoeugenol and methyl isoeugenol) collected under argon as a colorless liquid and stored in a glovebox over 4 Å molecular sieve for at least 24 h prior to use. Propenyl guaethol ($\geq 99\%$, FCC, FG, Sigma-Aldrich), isoeugenyl acetate and propenyl guaethyl acetate were submitted to three cycles of vacuum/argon and stored under argon in a glovebox. Undecane ($\geq 99\%$, Sigma-Aldrich) was degassed by bubbling argon and stored under argon in a glovebox over 4 Å molecular sieve for at least 24 h prior to use. Ruthenium metathesis catalyst M73SIPr (Umicore) and ethylene (Ultra-High Purity grade 3.0, 99.9%, Praxair) were used as received. $[\text{Rh}_2(\mu\text{-OMe})_2(\text{COD})_2]$ (COD = 1,5-cyclooctadiene), was prepared according to the literature procedure [1]. Tris(2,4-di-*tert*-butylphenyl)phosphite $[(2,4\text{-di-}^t\text{BuC}_6\text{H}_3\text{O})_3\text{P}$, 98%], and acetic anhydride (99.5%) were from Sigma-Aldrich and used as received.

SYNTHESIS OF ISOEUGENYL ACETATE (**1e**) AND PROPENYL GUAETHYL ACETATE (**1f**)

In an oven dried three neck round bottom flask, the phenol derivative (isoeugenol or propenyl guaethol, 10 mmol) was dissolved in 100 mL of dichloromethane (DCM) followed by the addition of Ac₂O (50 mmol). Then, 4-dimethylaminopyridine (DMAP-10 mol%) was added to the reaction mixture and stirred at room temperature. The reaction progress was monitored by thin layer chromatography (TLC). Once the reaction was completed, a saturated solution of NaHCO₃ was added and the evolution of CO₂ was observed. After quenching, the two resulting layers were separated, and the aqueous phase was extracted with DCM (x3). The organic layers were combined, dried over anhydrous MgSO₄ and concentrated under vacuum to give the products **1e** or **1f** in quantitative yield as white solids. The obtained products were recrystallized in hot acetone.

GENERAL PROCEDURE FOR ETHENOLYSIS OF 1-PROPENYLBENZENES

The ethenolysis experiments were carried out in a stainless steel homemade high-pressure reactor equipped with a pressure gauge and a magnetic stirrer. Initially the reactor was dried, sealed and kept under vacuum. In a glovebox, a Schlenk flask was loaded with 2.5 mmol of the corresponding 1-propenylbenzene, 1.25 mmol of undecane (internal standard), 9 mL of toluene (solvent) and 1 mL of a solution of the metathesis catalyst (1.25 $\mu\text{mol/mL}$ in toluene). The Schlenk flask was sealed and taken out of the glovebox. The reactor was loaded with the reaction solution using Schlenk techniques, then pressurized to 5 bar with ethylene and heated to 60 °C. After 2 h of magnetic stirring, the reactor was opened to air and a sample (0.2 mL) was taken, diluted with ethanol (1.0 mL) and analyzed by gas chromatography.

GENERAL PROCEDURE FOR THE ONE-POT ETHENOLYSIS-HYDROFORMYLATION OF 1-PROPENYLBENZENES

- One pot ethenolysis-hydroformylation of anethole (**1a**) with Ru catalyst

The experiments were carried out in a stainless steel homemade high-pressure reactor equipped with a pressure gauge and a magnetic stirrer. The reactor was dried, sealed and kept under vacuum. In a glovebox, a Schlenk flask was loaded with 2.5 mmol of the corresponding 1-propenylbenzene, 1.25 mmol of undecane (internal standard), 9 mL of toluene as solvent and 1 mL of a previously prepared solution of the metathesis catalyst (1.25 $\mu\text{mol/mL}$ in toluene). A second Schlenk flask was loaded with (2,4-di-^tBuC₆H₃O)₃P in toluene. Both Schlenk flasks were sealed and taken out of the glovebox. Using Schlenk techniques, the reactor was loaded with the solution from the first Schlenk flask and pressurized to 5 bar with ethylene and heated to 60 °C. After 2 h, the reactor was depressurized and the solution from the second Schlenk flask containing the phosphite ligand was transferred to the reactor. The reactor was then pressurized to 60 bar of CO/H₂ = 1/1 mixture and heated to 60 or 120 °C. After 24 h of magnetic stirring, the reactor was slowly depressurized in a fume hood, opened to air and a sample (0.2 mL) was taken, diluted with ethanol (1.0 mL) and analyzed by gas chromatography.

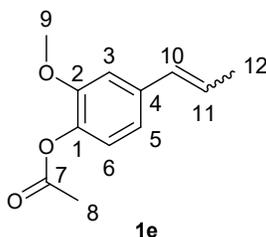
- One pot ethenolysis-hydroformylation of anethole (**1a**) with Ru and Rh catalysts

The experiments were carried out in a stainless steel homemade high-pressure reactor equipped with a pressure gauge and a magnetic stirrer. Initially, the reactor was dried, sealed and kept under vacuum. In a glovebox a Schlenk flask was loaded with 2.5 mmol of the corresponding 1-propenylbenzene, 1.25 mmol of undecane (internal standard), 9 mL of toluene as solvent and 1 mL of a solution of the metathesis catalyst (1.25 $\mu\text{mol/mL}$ in toluene). A second Schlenk flask was loaded with 303 μL of a Rh₂($\mu\text{-Cl}$)₂(cod)₂ solution in toluene, and, 606 μL of a solution of (2,4-di-^tBuC₆H₃O)₃P in toluene (20,65 $\mu\text{mol/mL}$; P:Rh = 10:1 at 0.05 mol% of Rh) and 3 mL of toluene. Both Schlenk flasks were sealed and taken out of the glovebox. Using Schlenk techniques

the reactor was loaded with the solution from the first Schlenk flask, pressurized to 5 bar with ethylene and heated to 60 °C. After 2 h, the reactor was depressurized and the solution from the second Schlenk flask containing the rhodium catalyst was transferred to the reactor. The reactor was then pressurized to 40 bar of CO/H₂ = 1/1 mixture and heated to 60 °C. After 4 – 24 h of magnetic stirring, the reactor was slowly depressurized in a fume hood, opened to air and a sample (0.2 mL) was taken, diluted with ethanol (1.0 mL) and analyzed by gas chromatography.

CHARACTERIZATION DATA

- Compound **1e**: isoeugenylacetate (2-methoxy-4-(prop-1-en-1-yl)phenyl acetate)



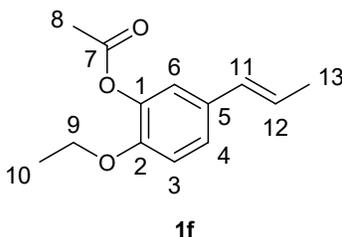
¹H-NMR (CDCl₃, 400 MHz) δ ppm: 6.93 (d, *J* = 8.1 Hz, 1H, C⁶H), 6.91 (d, *J* = 1.7 Hz, 1H, C³H), 6.87 (dd, *J* = 8.1 Hz, *J* = 1.8 Hz, 1H, C⁵H), 6.35 (dd, *J* = 15.7 Hz, *J* = 1.5 Hz, 1H, C¹⁰H), 6.17 (dq, *J* = 15.7 Hz, *J* = 6.6 Hz, 1H, C¹¹H), 3.82 (s, 3H, C⁹H₃), 2.29 (s, 3H, C⁸H₃), 1.86 (dd, *J* = 6.6 Hz, *J* = 1.6 Hz, 3H, C¹²H₃).

¹³C-NMR (100 MHz, CDCl₃) δ ppm: 169.35 (C⁷), 151.16 (C²), 138.76 (C¹), 137.26 (C⁴), 130.63 (C¹⁰), 126.27 (C¹¹), 122.85 (C⁶), 118.55 (C⁵), 109.80 (C³), 55.97 (C⁹), 20.86 (C⁸), 18.60 (C¹²).

Mass calculated for C₁₂H₁₄O₃ *m/z* = 206.24. MS (70 eV, EI): observed *m/z* (%): 206 (5) [M]⁺, 165 (11), 164 (100), 149 (25), 133 (11), 132 (7), 131 (15), 121 (9), 104 (8), 103 (9).

The ¹H-NMR, ¹³C-NMR signals assignments and MS data were confirmed by comparison to the literature values [2].

- Compound **1f**: propenylguatehylacetate
(2-ethoxy-5-(prop-1-en-1-yl)phenyl acetate)



$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ ppm: 7.08 (dd, $J = 8.4$ Hz, $J = 2.1$ Hz, 1H, C^4H), 7.00 (d, $J = 2.1$ Hz, 1H, C^6H), 6.85 (d, $J = 8.4$ Hz, 1H, C^3H), 6.28 (dd, $J = 15.7$ Hz, $J = 1.5$ Hz, 1H, C^{11}H), 6.06 (dq, $J = 15.7$ Hz, $J = 6.6$ Hz, 1H, C^{12}H), 4.01 (q, $J = 7.0$ Hz, 2H, C^9H_2), 2.88 (s, 3H, C^8H_3), 1.82 (dd, $J = 6.6$ Hz, $J = 1.6$ Hz, 3H, C^{13}H_3), 1.35 (t, $J = 7.0$ Hz, 3H, C^{10}H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 169.26 (C^7), 149.46 (C^2), 140.34 (C^1), 131.50 (C^5), 129.93 (C^{11}), 124.70 (C^4), 124.51 (C^{12}), 119.98 (C^6), 113.61 (C^3), 64.61 (C^9), 20.81 (C^8), 18.56 (C^{13}), 14.96 (C^{10}).

Mass calculated for $\text{C}_{13}\text{H}_{16}\text{O}_3$ $m/z = 220.27$. MS (70 eV, EI): observed m/z (%): 220 (23) $[\text{M}]^+$, 179 (13), 178 (100), 150 (62), 149 (52), 133 (13), 132 (13), 131 (15), 121 (7), 104 (13).

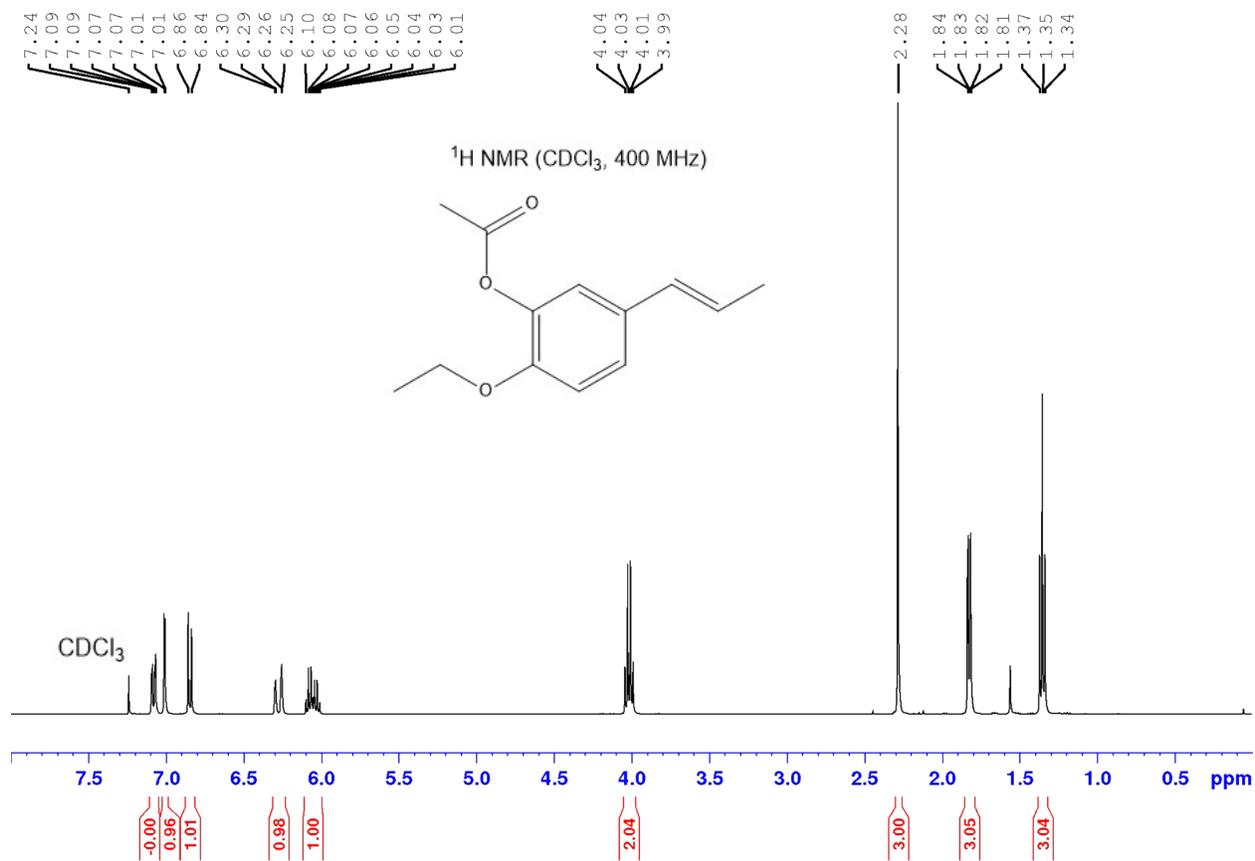


Figure S1. ¹H-NMR spectrum of **1f**.

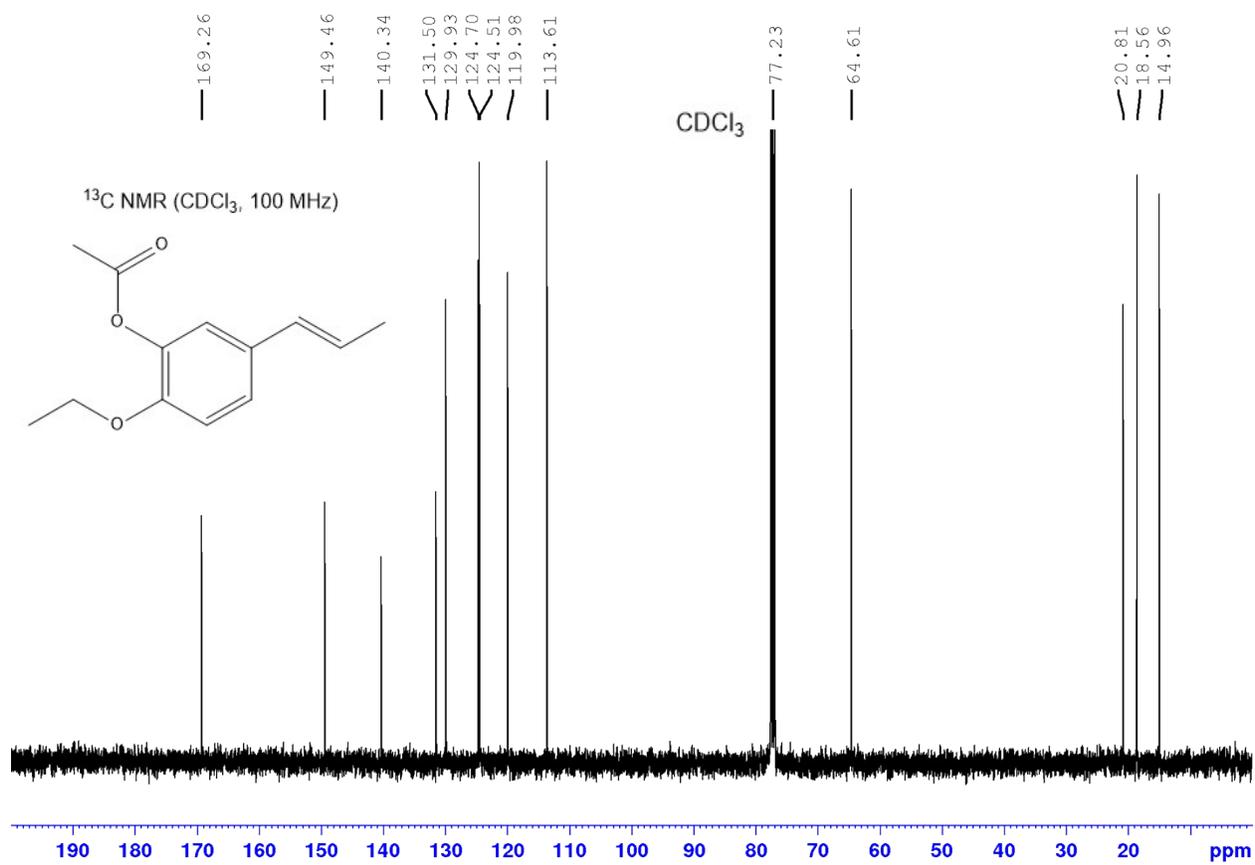
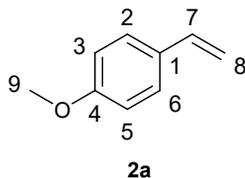


Figure S2. ¹H-NMR spectrum of 1f.

- Compound **2a**: 4-vinylanisole (1-ethenyl-4-methoxybenzene)



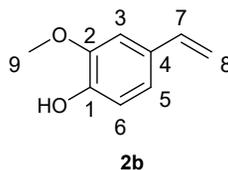
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ ppm: 7.35 (d, $J = 8.8$ Hz, 2H, C^2H , C^6H), 6.86 (d, $J = 8.8$ Hz, 2H, C^3H , C^5H), 6.66 (dd, $J = 10.8$ Hz, $J = 17.6$ Hz, 1H, C^7H), 5.61 (dd, $J = 0.8$ Hz, $J = 17.6$ Hz, 1H, $\text{C}^8\text{H}^{\text{a}}$), 5.12 (dd, $J = 0.8$ Hz, $J = 10.8$ Hz, 1H, $\text{C}^8\text{H}^{\text{b}}$), 3.80 (s, 3H, C^9H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 159.60 (C^4), 136.44 (C^7), 130.67 (C^1), 127.58 (C^2 , C^6), 114.13 (C^8), 111.75 (C^3 , C^5), 55.47 (C^9).

Mass calculated for $\text{C}_9\text{H}_{10}\text{O}$ $m/z = 134.18$. MS (70 eV, EI): observed m/z (%): 135 (10) $[\text{M}+1]^+$, 134, (100) $[\text{M}]^+$, 119 (59), 120 (5), 91 (45), 89 (5), 77 (6), 65 (21), 63 (7), 51 (5).

The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ signals assignments and MS data were confirmed by comparison to the literature values [3].

- Compound **2b**: 2-methoxy-4-vinyl-phenol (4-ethenyl-2-methoxyphenol)



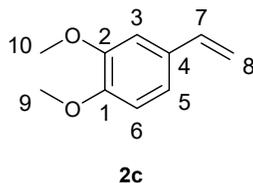
$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 6.97-6.81 (m, 3H, C^3H , C^5H , C^6H), 6.62 (dd, $J = 10.8$ Hz, $J = 17.6$ Hz, 1H, C^7H), 5.85 (s, 1H, OH), 5.57 (dd, $J = 0.6$ Hz, $J = 17.6$ Hz, 1H, C^8H^a), 5.11 (dd, $J = 0.6$ Hz, $J = 10.8$ Hz, 1H, C^8H^b), 3.82 (s, 3H, C^9H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 146.73 (C^2), 145.73 (C^1), 136.74 (C^7), 130.35 (C^4), 120.11 (C^5), 114.53 (C^6), 111.46 (C^8), 108.18 (C^3), 55.87 (C^9).

Mass calculated for $\text{C}_9\text{H}_{10}\text{O}_2$ $m/z = 150.18$. MS (70 eV, EI): observed m/z (%): 151 (10) $[\text{M}+1]^+$, 150, (100) $[\text{M}]^+$, 136 (8), 135 (59), 107 (37), 91 (11), 79 (13), 78 (8), 77 (32), 51 (7).

The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ signals assignments and MS data were confirmed by comparison to the literature values [4].

- Compound **2c**: 3,4-dimethoxystyrene (4-ethenyl-1,2-dimethoxybenzene)



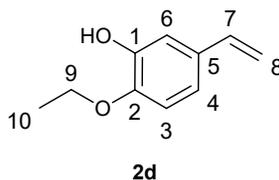
$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 6.95-6.71 (m, 3H, C^3H , C^5H , C^6H), 6.61 (dd, $J = 10.8$ Hz, $J = 17.6$ Hz, 1H, C^7H), 5.57 (d, $J = 17.6$ Hz, 1H, C^{8a}H), 5.10 (d, $J = 10.8$ Hz, 1H, C^{8b}H), 3.84 (s, 3H, C^9H_3 , 3H), 3.81 (s, 3H, C^{10}H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 149.0 (C^2), 148.91 (C^1), 136.44 (C^7), 130.61 (C^4), 119.37 (C^5), 111.65 (C^8), 110.94 (C^3), 108.43 (C^6), 55.75 (C^{10}), 55.66 (C^9).

M calculated for $\text{C}_{10}\text{H}_{12}\text{O}_2 = 164.20$ g/mol. MS (70 eV, EI): observed m/z (%): 165 (11) $[\text{M}+1]^+$, 165 (100) $[\text{M}]^+$, 149 (41), 121 (16), 103 (22), 93 (11), 91 (30), 78 (13), 77 (25), 65 (7).

The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ signals assignments and MS data were confirmed by comparison to the literature values [4].

- Compound **2d**: 5-ethenyl-2-ethoxyphenol



$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 7.06 (d, $J = 2.1$, 1H, C^6H), 6.85 (dd, $J = 2.1$ Hz, $J = 8.3$ Hz, 1H, C^4H), 6.77 (d, $J = 8.3$ Hz, 1H, C^3H), 6.61 (dd, $J = 10.8$ Hz, $J = 17.6$ Hz, 1H, C^7H), 5.71 (s, 1H, OH), 5.60 (dd, $J = 0.8$ Hz, $J = 17.6$ Hz, 1H, C^8H^a), 5.13 (dd, $J = 0.8$ Hz, $J = 10.8$ Hz, 1H, C^8H^b), 4.09 (q, $J = 7.0$, 2H, C^9H_2), 1.43 (t, $J = 7.0$, 3H, C^{10}H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 145.93 (C^2), 145.89 (C^1), 136.51 (C^7), 131.43 (C^5), 118.96 (C^4), 112.15 (C^8), 111.77 (C^6), 111.53 (C^3), 64.68 (C^9), 14.99 (C^{10}).

Mass calculated for $\text{C}_{11}\text{H}_{12}\text{O}_3 = 192.21$ g/mol. MS (70 eV, EI): observed m/z (%): 165 (10) $[\text{M}+1]^+$, 164 (62) $[\text{M}]^+$, 137 (9), 136 (100), 135 (27), 107 (15), 90 (6), 89 (10), 79 (7), 77 (14).

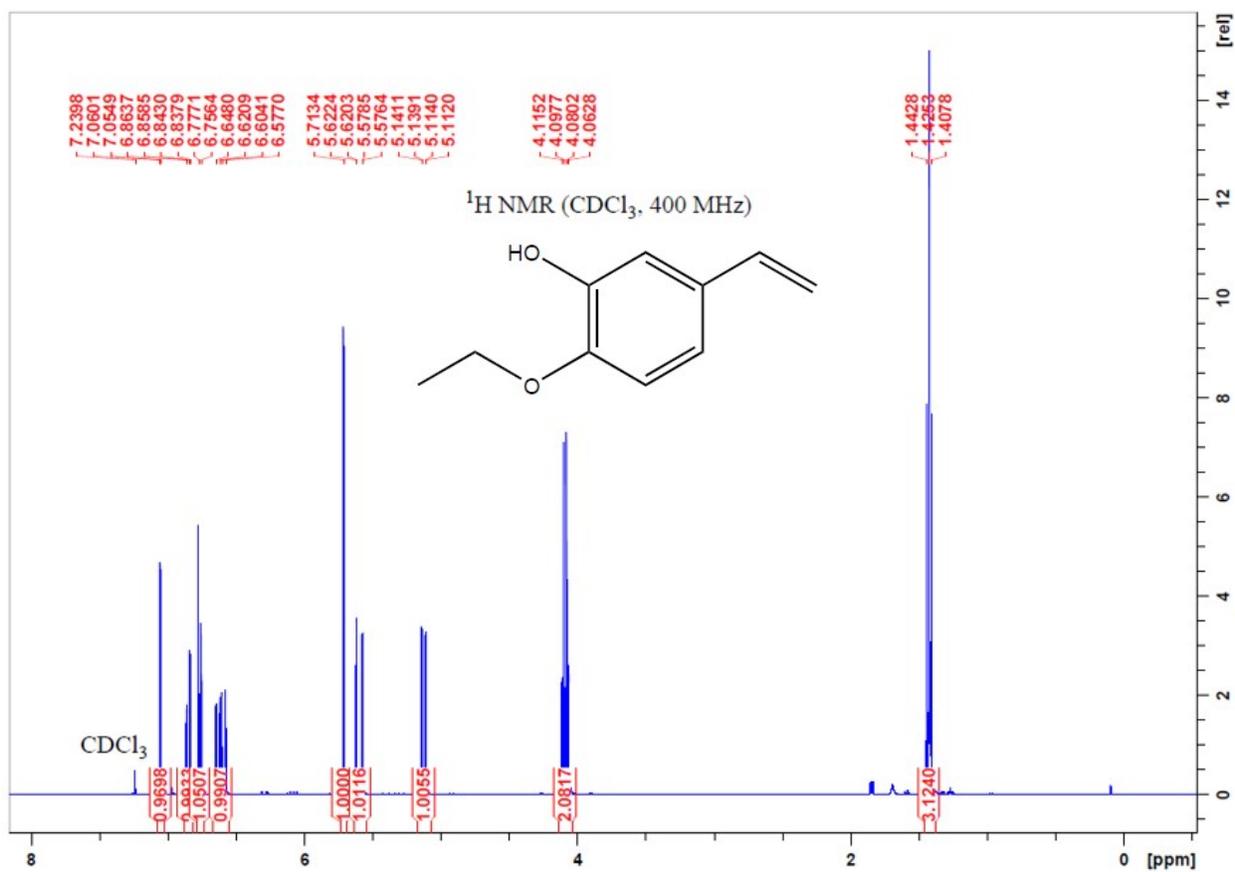


Figure S3. ¹H NMR spectrum of 2d.

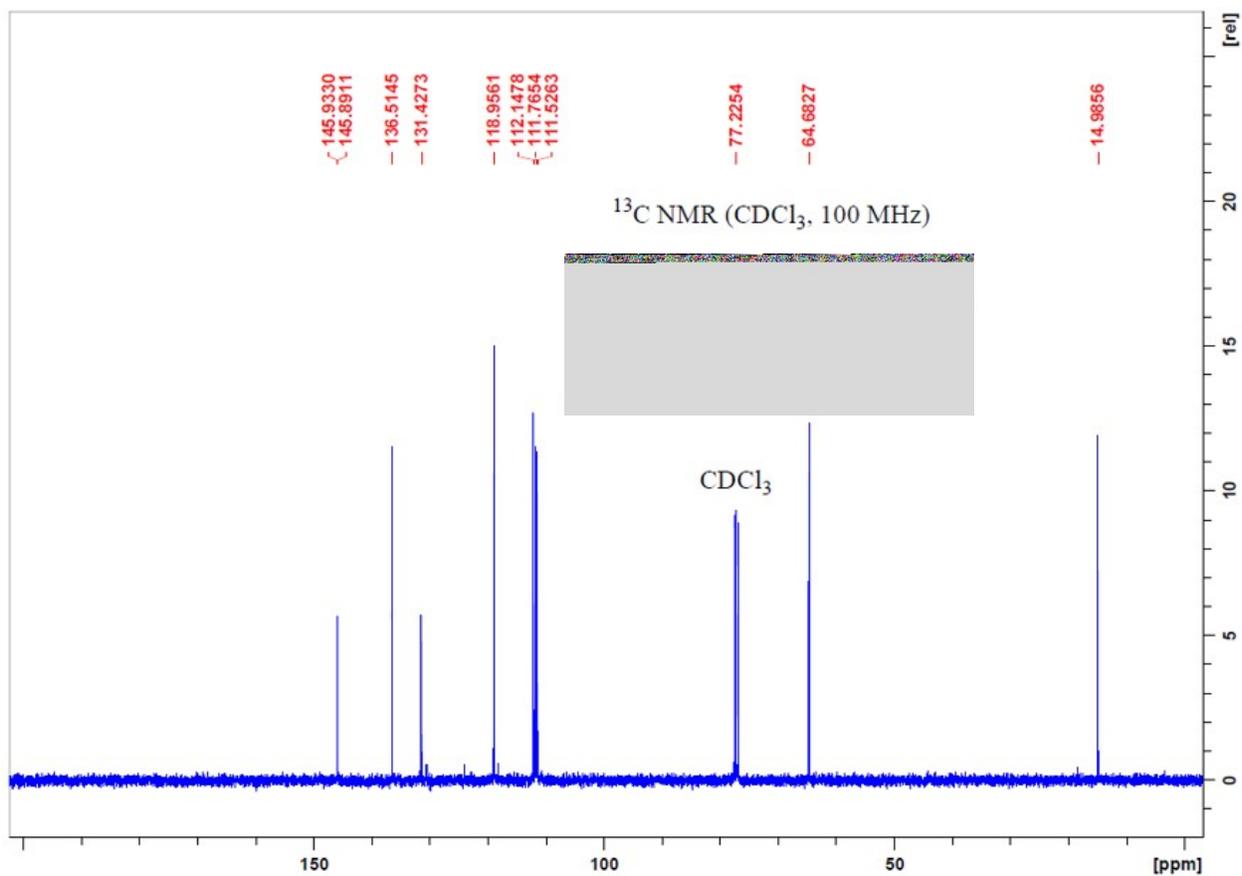
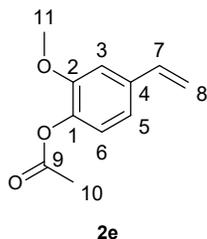


Figure S4. ^{13}C - NMR spectrum of **2d**.

- Compound **2e**: 4-ethenyl-2-methoxyphenyl acetate



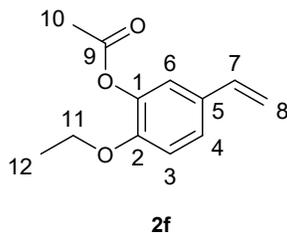
$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 7.01-6.96 (m, 3H, C^3H , C^5H , C^6H), 6.67 (dd, $J = 10.9$ Hz, $J = 17.6$ Hz, 1H, C^7H), 5.68 (d, $J = 17.6$ Hz, 1H, C^8H^a), 5.23 (d, $J = 10.9$ Hz, 1H, C^8H^b), 3.83 (s, 3H, C^{11}H_3), 2.30 (s, 3H, C^{10}H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 169.2 (C^9), 151.24 (C^2), 139.58 (C^1), 136.82 (C^4), 136.44 (C^7), 122.92 (C^6), 119.08 (C^5), 114.25 (C^8), 110.04 (C^3), 55.97 (C^{11}), 20.81 (C^{10}).

Mass calculated for $\text{C}_{11}\text{H}_{12}\text{O}_3 = 192.21$ g/mol. MS (70 eV, EI): observed m/z (%): 192 (4) $[\text{M}]^+$, 151 (10), 150 (100), 136 (5), 135 (54), 107 (19), 91 (5), 78 (6), 77 (12), 52 (5).

The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ signals assignments and MS data were confirmed by comparison to the literature values [5].

- Compound **2f**: 5-ethenyl-2-ethoxyphenyl acetate



$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 7.18 (dd, $J = 2.2$, $J = 8.5$, 1H, C^4H), 7.11 (d, $J = 2.2$ Hz, 1H, C^6H), 6.88 (d, $J = 8.5$ Hz, 1H, C^3H), 6.60 (dd, $J = 10.9$ Hz, $J = 17.6$ Hz, 1H, C^7H), 5.58 (dd, $J = 0.6$, $J = 17.6$, 1H, C^8H^a), 5.14 (dd, $J = 0.6$ Hz, $J = 10.9$ Hz, 1H, C^8H^b), 4.03 (q, $J = 7.0$ Hz, 2H, C^{11}H_2), 2.29 (s, 3H, C^{10}H_3), 1.43 (t, $J = 7.0$, 3H, C^{12}H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 169.15 (C^9), 150.24 (C^2), 140.30 (C^1), 135.75 (C^7), 130.98 (C^5), 125.12 (C^4), 120.26 (C^6), 113.40 (C^3), 112.65 (C^8), 64.53 (C^{11}), 20.72 (C^{10}), 14.83 (C^{12}).

Mass calculated for $\text{C}_{12}\text{H}_{14}\text{O}_3 = 206.24$ g/mol. MS (70 eV, EI): observed m/z (%): 206 (24) $[\text{M}]^+$, 165 (8), 164 (76), 137 (8), 136 (100), 135 (20), 107 (7), 89 (5), 77 (8), 43 (7).

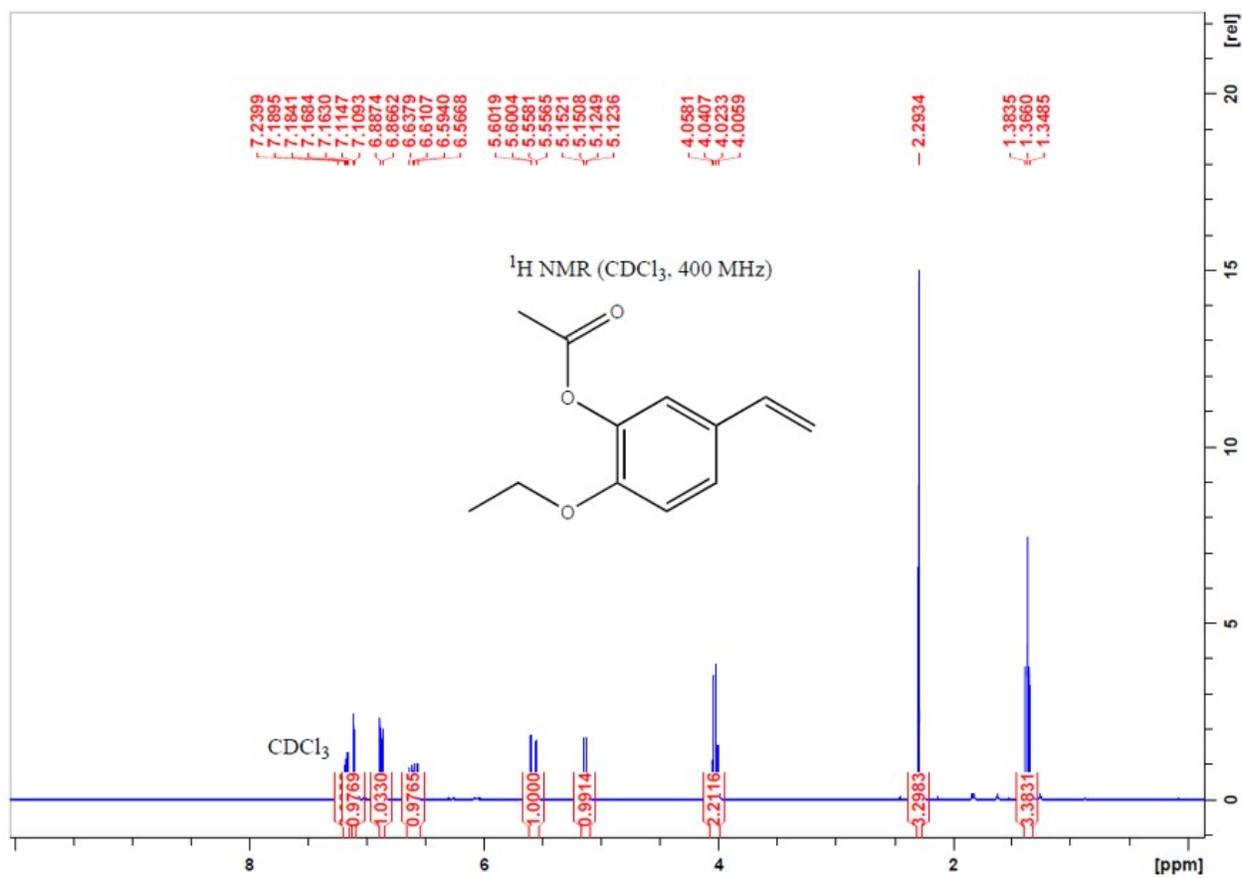


Figure S5. ¹H-NMR spectrum of **2f**.

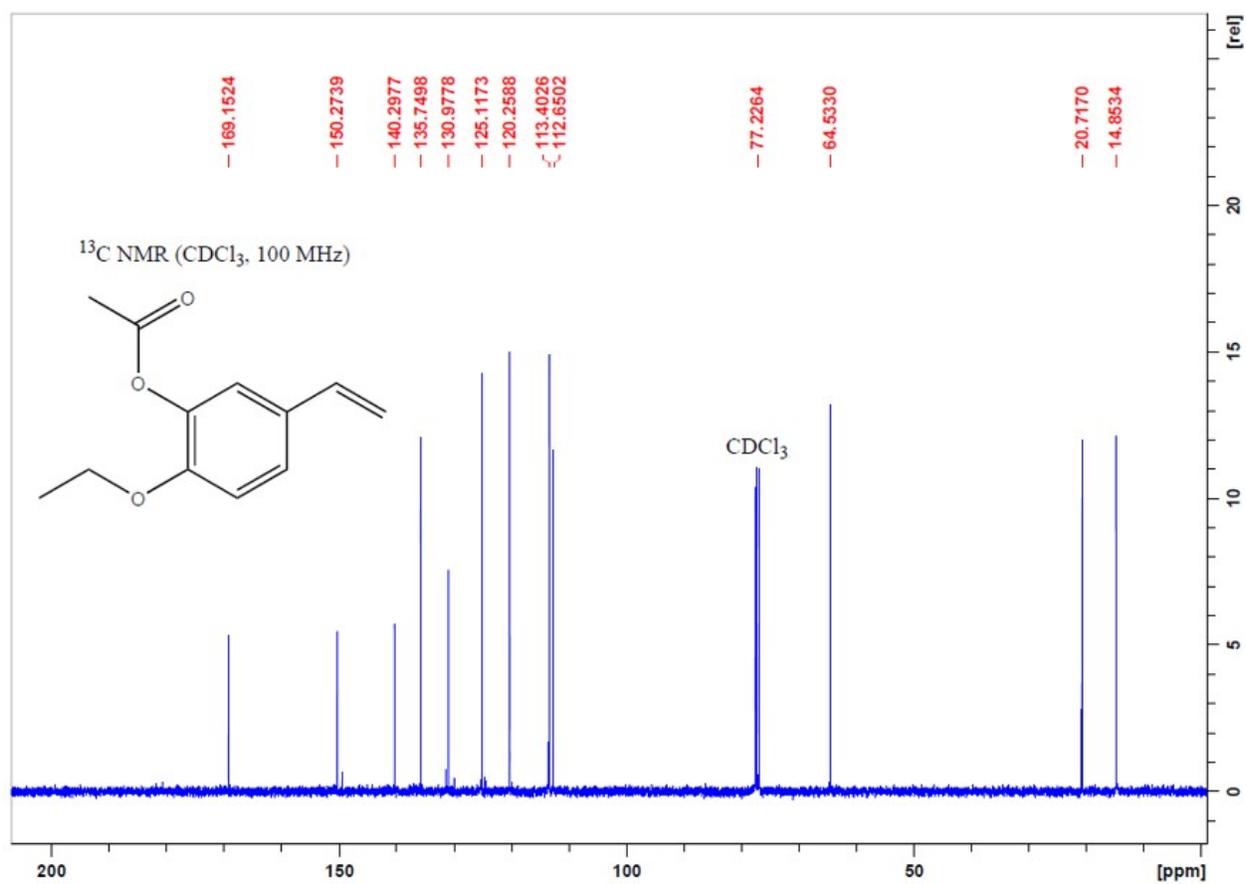
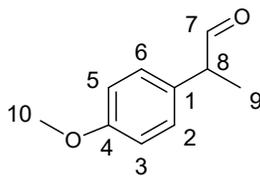


Figure S6. ¹³C-NMR spectrum of **2f**.

- Compound **3a** (iso): 2-(4-methoxyphenyl)propanal



3a (iso)

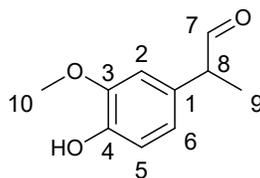
$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 9.62 (d, $J = 1.4$, 1H, C^7H), 7.10 (d, $J = 8.7$ Hz, 2H, C^2H , C^4H), 6.89 (d, $J = 8.7$ Hz, 2H, C^3H , C^5H), 3.78 (s, 3H, C^{10}H), 3.56 (bq, $J = 7.0$ Hz, 1H, C^8H), 1.39 (d, $J = 7.0$ Hz, 3H, C^9H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 201.29 (C^7), 159.17 (C^4), 129.72 (C^1), 129.49 (C^2 , C^6), 114.65 (C^3 , C^5), 55.42 (C^{10}), 52.27 (C^8), 14.79 (C^9).

Mass calculated for $\text{C}_{10}\text{H}_{12}\text{O}_2$ $m/z = 164.20$. MS (70 eV, EI): observed m/z (%): 164 (8) $[\text{M}]^+$, 136 (10), 135 (100), 120 (8), 105 (26), 103 (13), 91 (14), 79 (16), 77 (13), 65 (5).

The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ signals assignments and MS data were confirmed by comparison to the literature values [6]

- Compound **3b** (iso): 2-(4-hydroxy-3-methoxyphenyl)propanal



3b (iso)

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 9.62 (d, $J = 1.51$ Hz, 1H, C^7H), 6.0 (d, $J = 8.07$ Hz, 1H, C^5H), 6.71 (dd, $J = 1.97$ Hz, $J = 8.07$ Hz, 1H, C^6H), 6.64 (d, $J = 1.97$ Hz, 1H, C^2H), 5.59 (br s, 1H, OH), 3.87 (s, 3H, C^{10}H_3), 3.54 (dq, $J = 1.3$ Hz, $J = 7.0$ Hz, 1H, C^8H), 1.39 (d, $J = 7.0$ Hz, 3H, C^9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 201.32 (C^7), 147.17 (C^3), 145.33 (C^4), 129.53 (C^1), 121.45 (C^5), 115.08 (C^6), 110.75 (C^2), 56.15 (C^{10}), 52.83 (C^8), 14.83 (C^9).

Mass calculated for $\text{C}_{10}\text{H}_{12}\text{O}_3$ $m/z = 180.20$. MS (70 eV, EI): observed m/z (%): 180 (18) $[\text{M}]^+$, 152 (10), 151 (100), 136 (7), 119 (31), 107 (5), 91 (44), 79 (7), 77 (9), 65 (7).

MS analytical data were consistent with the literature [7].

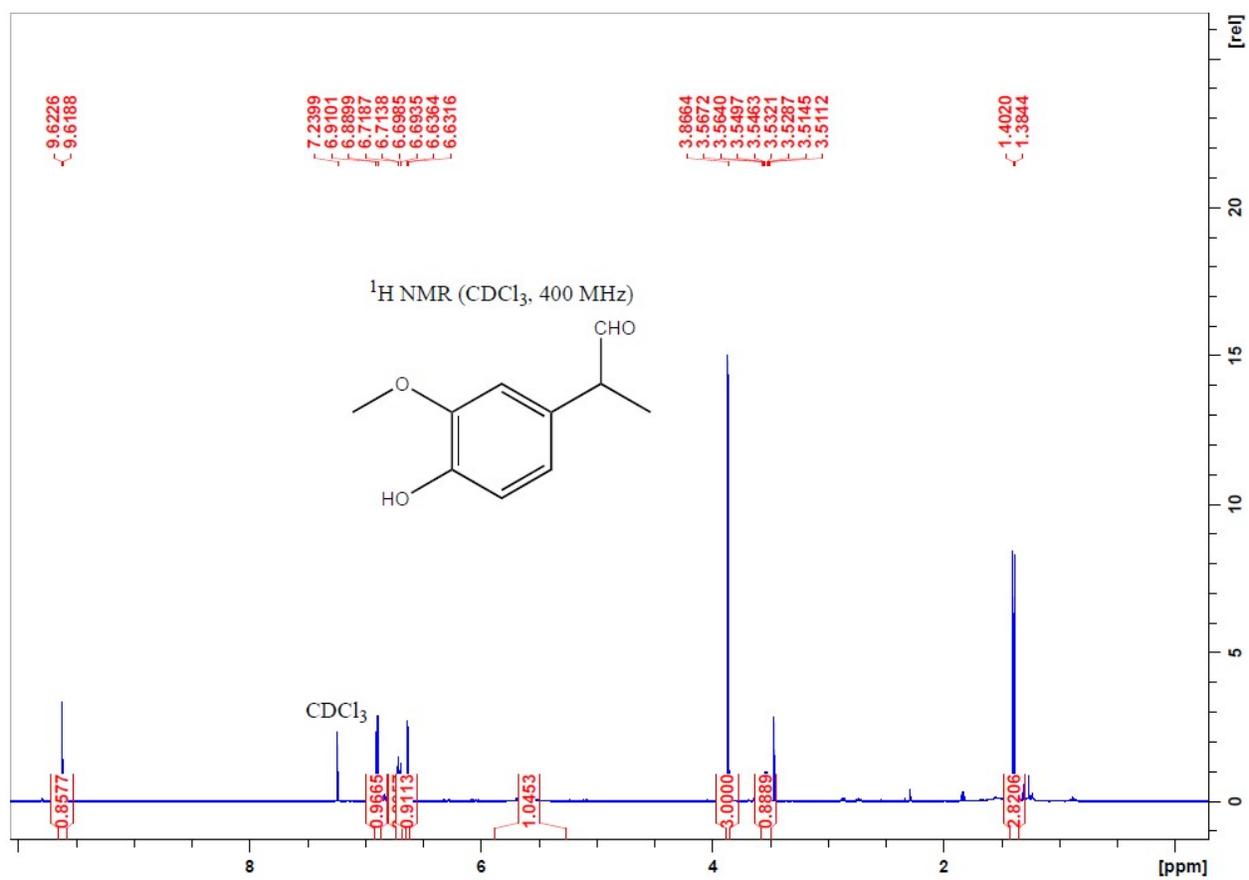


Figure S7. ¹H-NMR spectrum of 3b (*iso*).

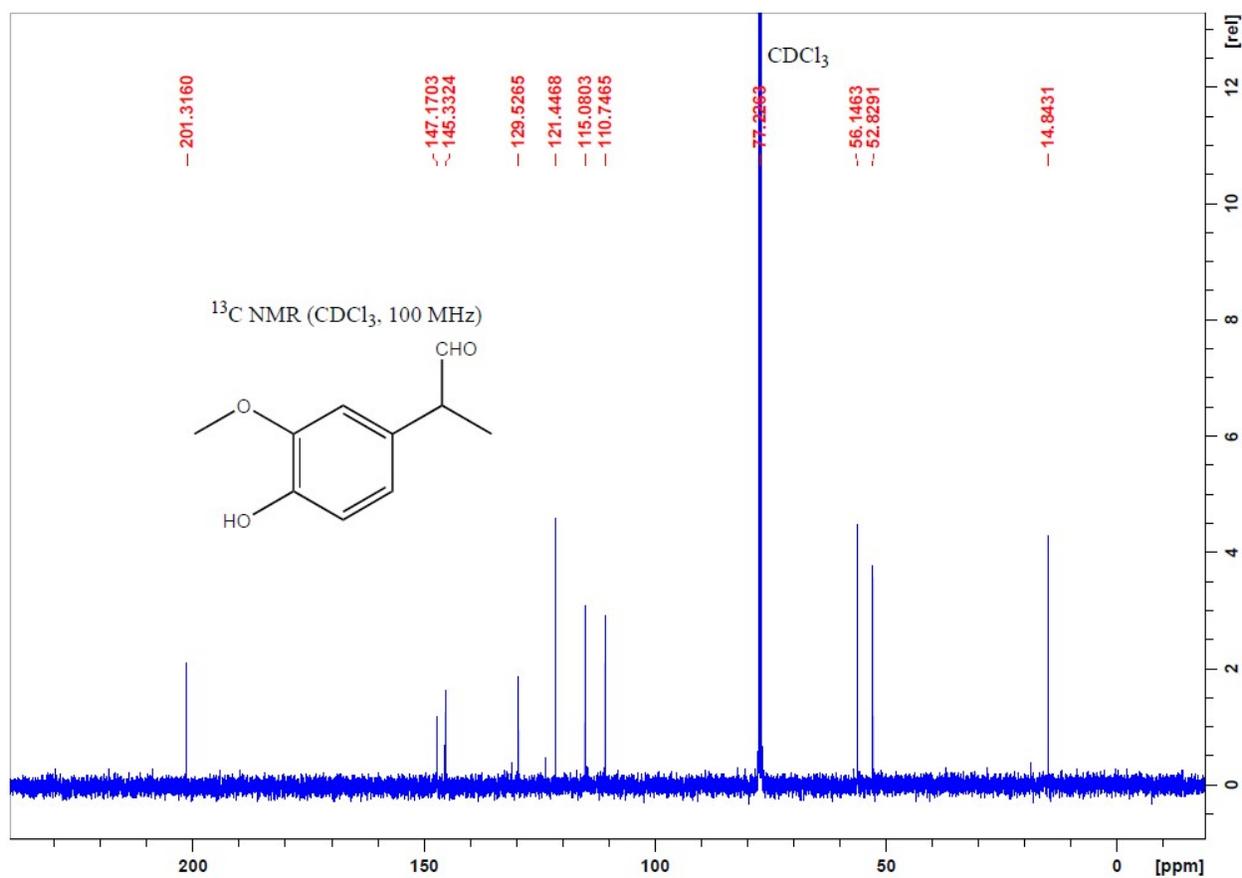
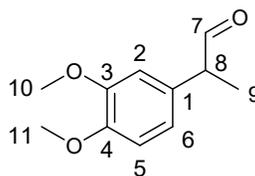


Figure S8. ¹³C-NMR spectrum of **3b** (*iso*).

- Compound **3c** (iso): 2-(3,4-dimethoxyphenyl)propanal



3c (iso)

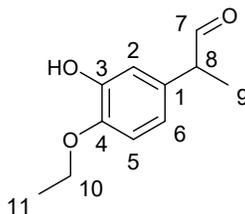
$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 9.60 (d, $J = 1,46$ Hz, 1H, C^7H), 6.83 (d, $J = 8.18$ Hz, 1H, C^5H), 6.71 (dd, $J = 2.01$ Hz, $J = 8.10$ Hz, 1H, C^6H), 6.64 (d, $J = 2.01$ Hz, 1H, C^2H), 3.88 (coupled signal, 6H, C^{10}H_3 , C^{11}H_3), 3.52 (dq, $J = 1.24$ Hz, $J = 7.1$ Hz, 1H, C^8H), 1.37 (d, $J = 7.08$ Hz, 3H, C^9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 201.07 (C^7), 149.51 (C^4), 148.58 (C^3), 130.11 (C^1), 120.56 (C^5), 11.74 (C^6), 111.42 (C^2), 56.00 (C^{10} , C^{11}), 55.99 (C^{10} , C^{11}), 52.61 (C^8), 14.67 (C^9).

Mass calculated for $\text{C}_{11}\text{H}_{14}\text{O}_3$ $m/z = 194.23$. MS (70 eV, EI): observed m/z (%): 194 (16), 166 (12), 165 (100), 150 (21), 135 (8), 134 (9), 105 (11), 91 (11), 79 (9), 77 (10).

The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ signals assignments and MS data were confirmed by comparison to the literature values [7].

- Compound **3d** (iso): 2-(4-ethoxy-3-hydroxyphenyl)propanal



3d (iso)

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 9.59 (d, $J = 1.45$ Hz, 1H, C^7H), 6.80 (d, $J = 8.2$ Hz, 1H, C^5H), 6.76 (d, $J = 2.1$, 1H, C^2H), 6.63 (dd, $J = 2.1$ Hz, $J = 8.2$, 1H, C^6H), 5.91 (br s, 1H, OH), 4.06 (q, $J = 7.0$, 2H, C^{10}H_2), 3.48 (br q, $J = 7.0$, 1H, C^8H), 1.40 (t, $J = 7.0$, 3H, C^{11}H_3), 1.35 (d, $J = 7.0$, 3H, C^9H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 201.30 (C^7), 146.35 (C^3), 145.41 (C^4), 130.68 (C^1), 119.89 (C^6), 114.55 (C^2), 112.16 (C^5), 64.67 (C^{10}), 52.37 (C^8), 14.92 (C^{11}), 14.57 (C^9).

Mass calculated for $\text{C}_{11}\text{H}_{14}\text{O}_3 = 194.23$. MS (70 eV, EI): observed m/z (%): 194 (36) $[\text{M}]^+$, 166 (11), 165 (98), 138 (9), 137 (100), 119 (23), 91 (38), 79 (8), 77 (8), 65 (8).

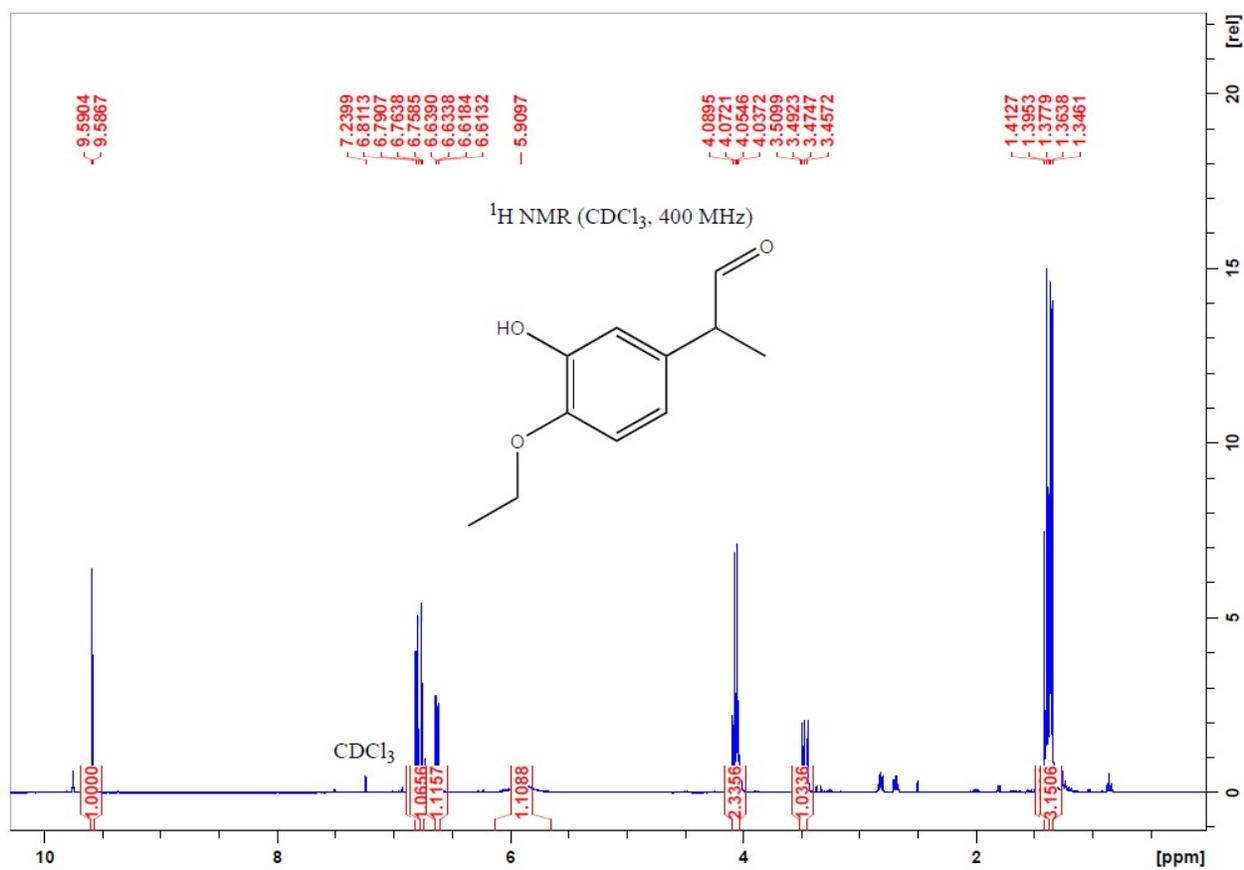


Figure S9. ¹H-NMR spectrum of 3d (*iso*).

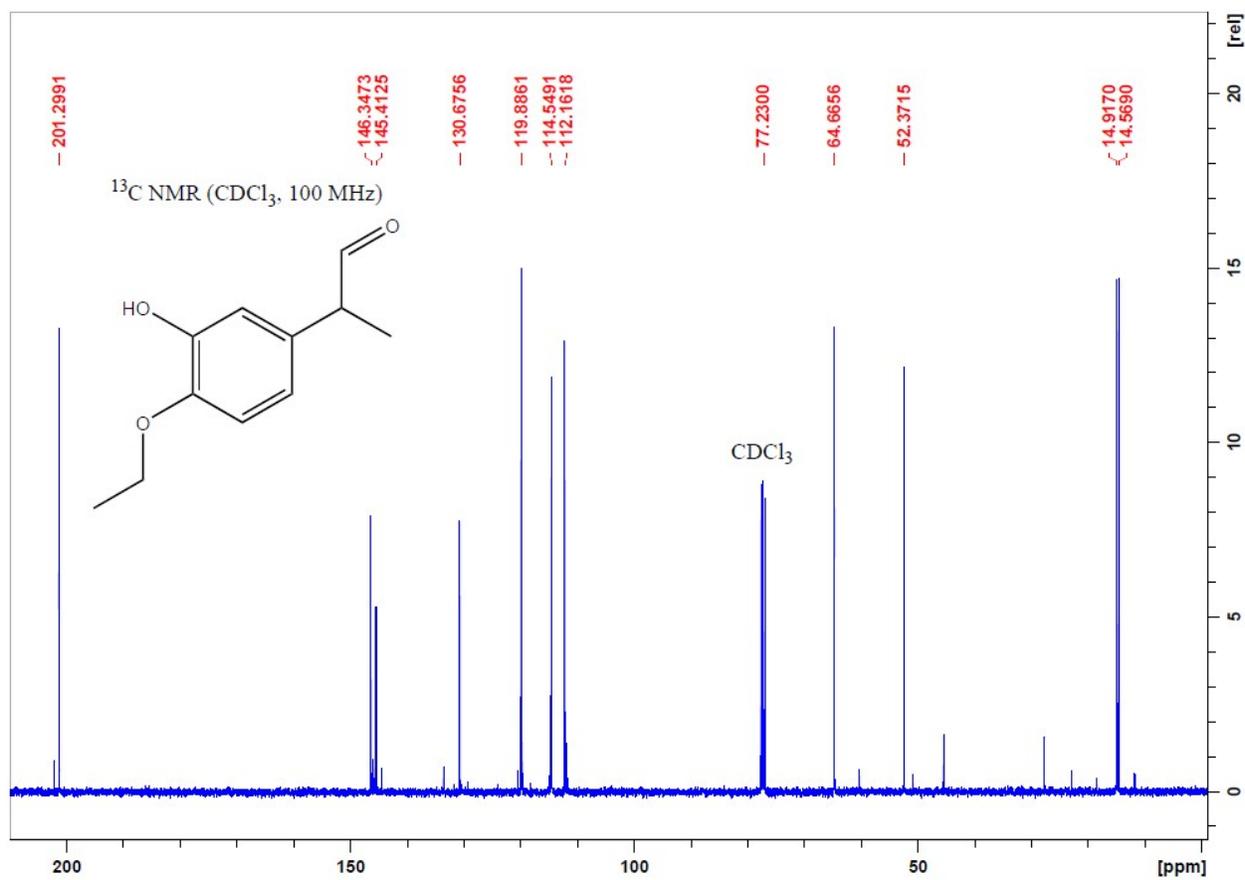
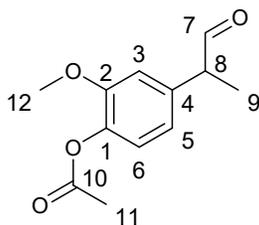


Figure S10. ¹³C-NMR spectrum of **3d** (*iso*).

- Compound **3e** (iso): 2-methoxy-4-(1-oxopropan-2-yl)phenyl acetate



3e (iso)

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 9.64 (d, $J = 1.13$ Hz, 1H, C^7H), 7.00 (d, $J = 8.0$ Hz, 1H, C^6H), 6.76 (m, 2H, C^3H , C^5H), 3.80 (s, 3H, C^{12}H_3), 3.59 (br q, $J = 7,1$, 1H, C^8H), 2.28 (s, 3H, C^{11}H_3), 1.41 (d, $J = 7.1$, 3H, C^9H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 200.86 (C^7), 169.19 (C^{10}), 151.64 (C^2), 139.30 (C^1), 136.66 (C^4), 123.43 (C^6), 120.65 (C^5), 112.47 (C^3), 56.06 (C^{12}), 52.98 (C^8), 20.80 (C^1), 14.77 (C^9).

Mass calculated for $\text{C}_{12}\text{H}_{14}\text{O}_4 = 222.24$. MS (70 eV, EI): observed m/z (%): 222 (3) $[\text{M}]^+$, 181 (3), 180 (28), 152 (10), 151 (100), 119 (10), 91 (13), 79 (3), 77 (4), 43 (6).

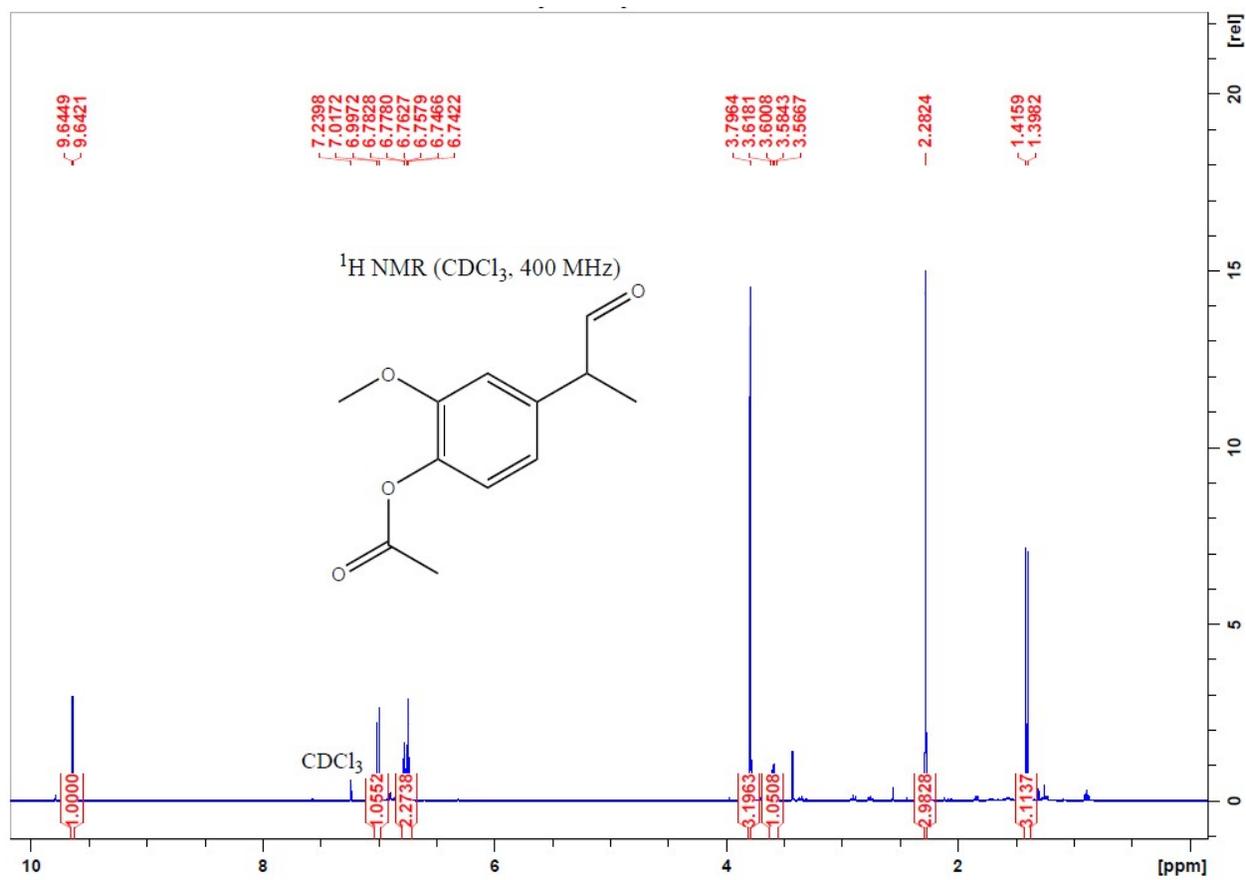


Figure S11. ¹H-NMR spectrum of **3e (iso)**.

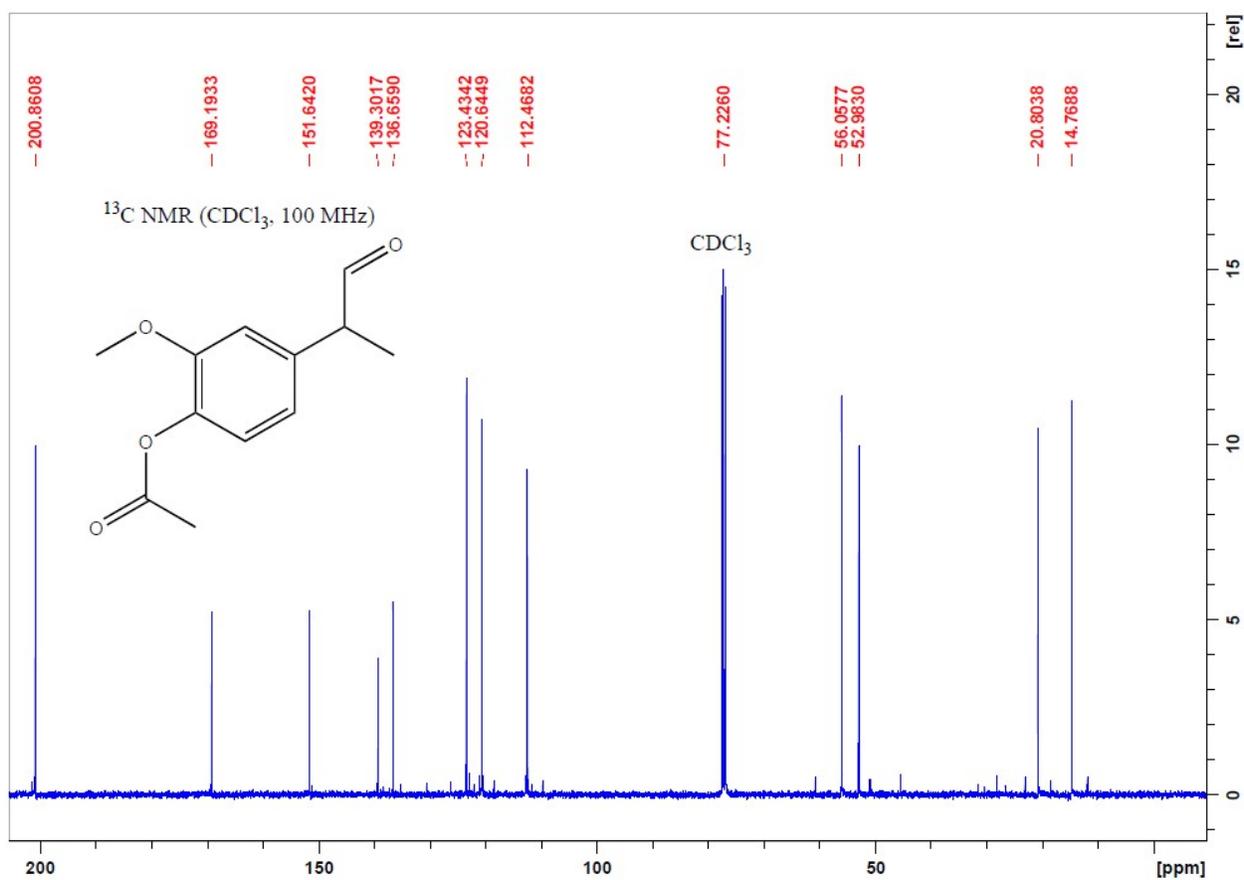
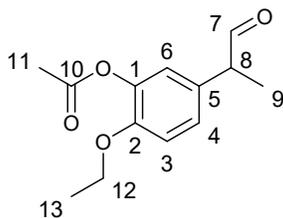


Figure S12. ¹³C-NMR spectrum of **3e** (*iso*).

- Compound **3f** (iso): 2-ethoxy-5-(1-oxopropan-2-yl)phenyl acetate



3f (iso)

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 9.59 (d, $J = 1.37$ Hz, 1H, C^7H), 6.98 (dd, $J = 2.1$, $J = 8.4$ Hz, 1H, C^4H), 6.91 (d, $J = 8.4$ Hz, 1H, C^3H), 6.86 (d, $J = 2.1$ Hz, 1H, C^6H), 4.00 (q, $J = 6.9$ Hz, 2H, C^{12}H_2), 3.52 (br q, $J = 7.1$ Hz, 1H, C^8H), 2.26 (s, 3H, C^{11}H_3), 1.36 (d, $J = 7.1$ Hz, 3H, C^9H_3), 1.34 (d, $J = 6.9$ Hz, 3H, C^{13}H_3).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 200.87 (C^7), 168.96 (C^{10}), 149.97 (C^2), 140.51 (C^1), 129.99 (C^5), 126.61 (C^4), 122.68 (C^6), 114.01 (C^3), 64.52 (C^{12}), 51.97 (C^8), 20.63 (C^{11}), 14.79 (C^9), 14.55 (C^{13}).

Mass calculated for $\text{C}_{13}\text{H}_{16}\text{O}_4 = 236.27$. MS (70 eV, EI): observed m/z (%): 236 (8) $[\text{M}]^+$, 207 (10), 194 (33), 166 (12), 165 (100), 137 (56), 119 (9), 91 (14), 79 (5), 43 (10).

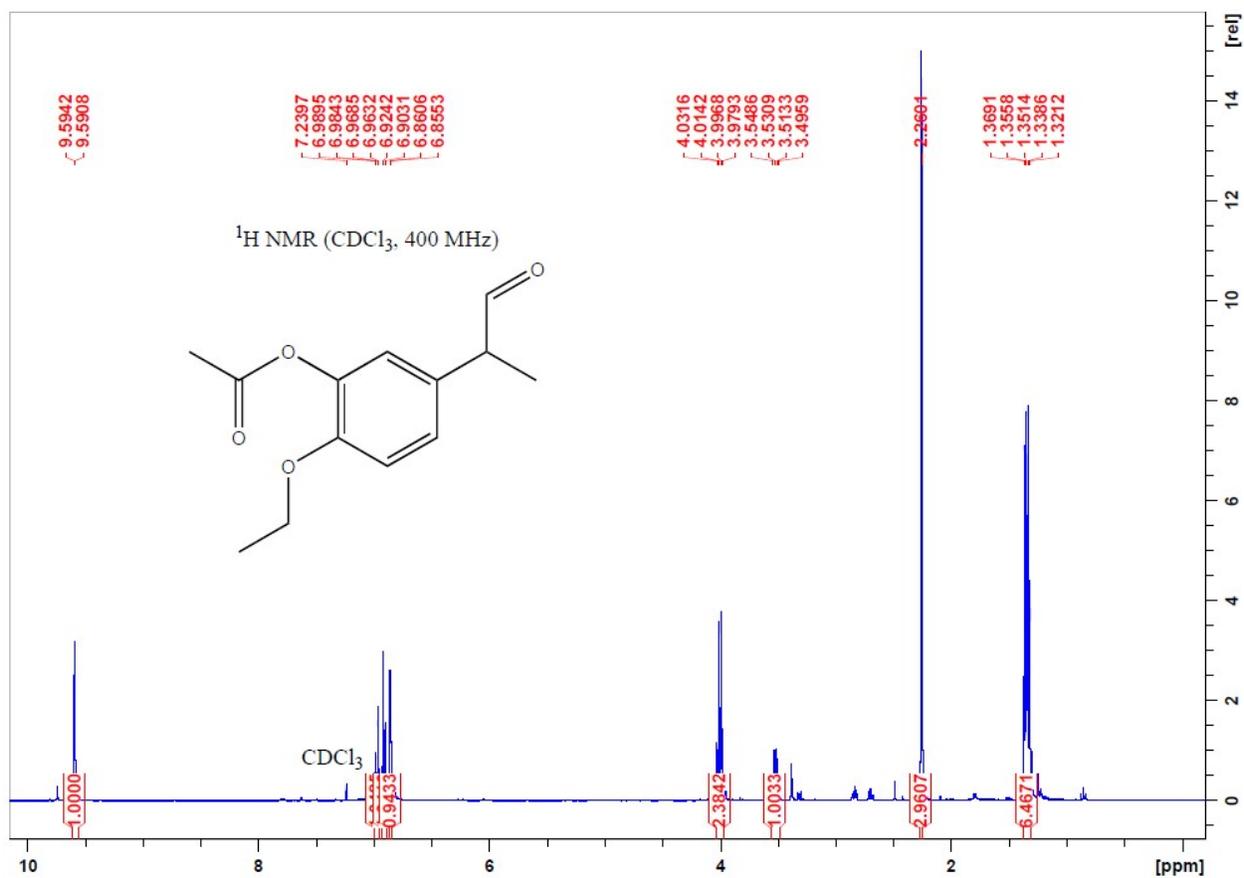


Figure S13. ¹H-NMR spectrum of **3f (iso)**.

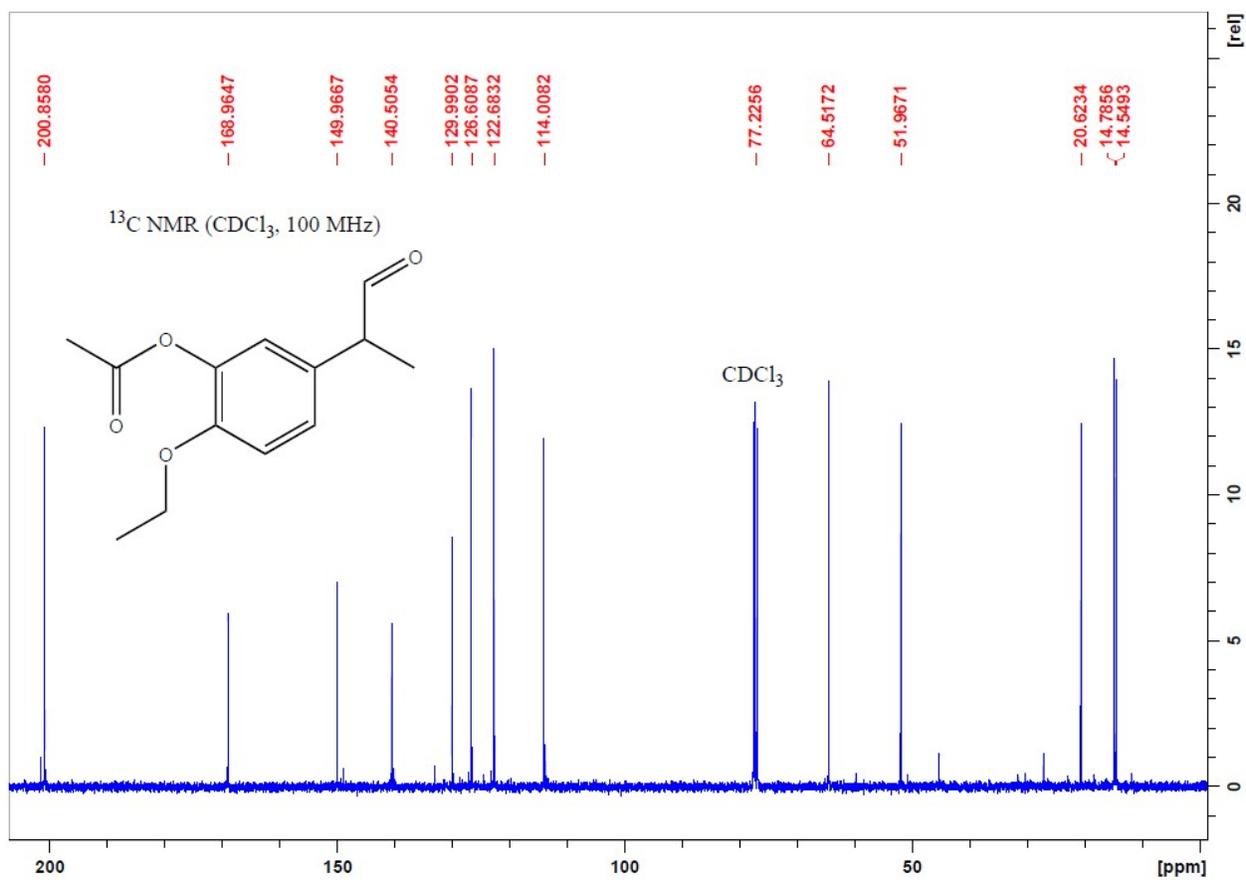


Figure S14. ¹³C-NMR spectrum of **3f (iso)**.

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