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Supporting Information

Reevaluation of the Pd/C-Catalyzed Decarbonylation of Aliphatic Aldehydes

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General Information

Pd/C (10 wt. % loading) was purchased from Sigma Aldrich. All aldehydes were obtained from commercial sources and used without further purification, except for the hydrocinnamaldehyde which was distilled prior to use since it is highly unstable. Unless stated otherwise, solvents and other reagents were obtained from commercial sources and used without further purification. Dry-flash chromatography was performed on SiO₂ (0.018–0.032 mm). IR spectra were recorded on a Thermo-Scientific Nicolet 6700 FT-IR Diamond Crystal instrument. ¹H and ¹³C NMR spectra were recorded on a Bruker Ultrashield Avance III spectrometer (at 500 and 125 MHz, respectively) using CDCl₃ (unless stated otherwise) as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in parts per million (ppm) on the (δ) scale. Chemical shifts were calibrated relative to those of the solvent. GC-MS spectra of the synthesized compounds were acquired on an Agilent Technologies 7890A apparatus equipped with a DB-5 MS column (30 m \times 0.25 mm \times 0.25 μ m), a 5975C MSD and FID detector. The selected values are as follows: carrier gas was He (1.0 mL/min), temperature linearly increased from 40 – 315 °C (10 °C/min), injection volume: 1 μL, temperature: 250 °C, temperature (FID detector): 300 °C, and EI mass spectra range: m/z 40-550. For determination of NMR and GC-MS yield, the internal standard (naphthalene or methyl benzoate) was added to the reaction mixture after the workup. Compound 10 was analyzed by high resolution tandem mass spectrometry using LTQ Orbitrap XL (Thermo Fisher Scientific Inc., USA) mass spectrometer. The sample was dissolved in MeCN and it was injected directly. Ionization was done in positive mode on heated electrospray ionization (HESI) probe. HESI parameters were: spray voltage 4.7 kV, vaporizer temperature 60 °C, sheath and auxiliary gas flow 24 and 10 (arbitrary units), respectively, capillary voltage 49 V, capillary temperature 275 °C, tube lens voltage 80 V, resolution (at m/z 400): 30000.

Compounds 3,3-diphenylpropanal (1b),¹ 2-(adamantan-1-yl)acetaldehyde (1j),² 2-(4-methoxyphenyl)octanal (1n)³ and 3α , 7α , 12α -triacetoxy-5 β -cholan-24-al (4)^{4,5} were synthesized according to the previously reported procedures.

General procedure A for decarbonylation of aliphatic aldehydes

Decarbonylation of 3-phenylpropanal to ethylbenzene (2a) [CAS Reg. No. 100-41-4]

Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves (3–4 Å, 100 mg), aldehyde 1a (50 μ L, 0.38 mmol), Pd/C (20 mg, 5 mol% Pd), and cyclohexane (1 mL) and the sealed tube was heated at 130 °C for 24 h. The reaction

mixture was cooled to room temperature, filtered through a pad of Celite, and washed with CH_2Cl_2 (15 – 20 mL). Compound **2a** was obtained, GC-MS yield: 67%, based on naphthalene as a standard. GC-MS: m/z = 106.1 [M]⁺.

NMR spectroscopic analysis:

General procedure B for decarbonylation of aliphatic aldehydes

Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves (3–4 Å, 100 mg), aldehyde **1a** (40 μ L, 0.30 mmol), Pd/C (16 mg, 5 mol% Pd), and C₆D₆ (1 mL) and the sealed tube was heated at 130 °C for 24 h. The reaction mixture was cooled to room temperature, filtered through a short pad of SiO₂ to remove the catalyst, and the SiO₂ was washed with C₆D₆ (2 × 0.5 mL). Compound **2a** was obtained, NMR yield: 78%, based on methyl benzoate as a standard. ¹H NMR (500 Hz, C₆D₆) = 7.10-7.00 (m, 5H), 2.43 (q, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 3H). ¹³C (125 Hz, C₆D₆) = 144.28, 128.59, 128.09, 125.91, 29.15, 15.80.

Decarbonylation of 3,3-diphenylpropanal to 1,1-diphenylethane (2b)⁶

Following the general procedure A for the decarbonylation, compound **2b** was obtained after column chromatography (SiO₂: hexane) as a colorless oil. Alongside the desired product, ${}^{1}H$ NMR analysis showed the formation of a side product, 1,1-diphenylethylene **3b**. The ratio between the main product and the side product was determined by ${}^{1}H$ NMR (78% **2b**, 6% **3b**). 1,1-Diphenylethane: ${}^{1}H$ NMR (500 Hz, CDCl₃) δ 7.29 - 7.15 (m, 10H), 4.15 (q, J = 7 Hz, 1H), 1.64 (d, J = 7 Hz, 3H); ${}^{13}C$ (125 Hz, CDCl₃) δ 146.35, 128.33, 127.60, 125.99, 44.75, 21.83; GC-MS m/z 182.1 [M] $^{+}$.

1,1-Diphenylethylene: ¹H NMR (500 Hz, CDCl₃) δ 7.35 - 7.30 (m, 10H), 5.46 (s, 2H).

Decarbonylation of 2,2-diphenylacetaldehyde to diphenylmethane (2c) [CAS Reg. No. 101-81-5]

Following the general procedure A for decarbonylation, compound **2c** was obtained after dry-flash column chromatography (SiO₂: hexane) as a colorless oil in 69% yield. Diphenylmethane 1 H NMR (500 Hz, CDCl₃) = 7.31-7.27 (m, 4H), 7.22-7.18 (m, 6H), 4.00 (s, 2H). GC-MS: m/z = 168.0 [M]^{+} .

Decarbonylation of phenylacetaldehyde to toluene (2d) [CAS Reg. No. 108-88-3]

Following the general procedure A for decarbonylation, compound **2d** was obtained. GC-MS yield: 82%, based on naphthalene as a standard. GC-MS: $m/z = 92.0 \text{ [M]}^+$.

Decarbonylation of octanal to *n***-heptane (2e)** [CAS Reg. No. 142-82-5]

Following the general procedure A for decarbonylation, compound **2e** was obtained. GC-MS yield: 64%, based on naphthalene as a standard. GC-MS: $m/z = 100.0 \text{ [M]}^+$.

Decarbonylation of nonanal to *n***-octane (2f)** [CAS Reg. No. 111-65-9]

Following the general procedure A for decarbonylation, compound **2f** was obtained. GC-MS yield: 50%, based on naphthalene as a standard. GC-MS: $m/z = 114.1 \text{ [M]}^+$.

Decarbonylation of decanal to *n***-nonane (2g)** [CAS Reg. No. 111-84-2]

Following the general procedure A for decarbonylation, compound 2g was obtained. GC-MS yield: 54%, based on naphthalene as a standard. GC-MS: $m/z = 128.1 \text{ [M]}^+$.

Decarbonylation of undecanal to *n***-decane (2h)** [CAS Reg. No. 124-18-5]

Following the general procedure A for decarbonylation, compound **2h** was obtained. GC-MS yield: 99%, based on naphthalene as a standard. GC-MS: $m/z = 142.1 [M]^+$.

Decarbonylation of cyclohexanecarbaldehyde to cyclohexane (2i) [CAS Reg. No. 110-82-7]

Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves (3–4 Å, 100 mg), aldehyde **1i** (40 μ L, 0.33 mmol), Pd/C (18 mg, 5 mol% Pd), and C_6D_6 (1 mL) and the sealed tube was heated at 130 °C for 24 h. The reaction mixture was cooled to room temperature, filtered through a short pad of SiO₂ to remove the catalyst, and the SiO₂ was washed with C_6D_6 (2 × 0.5 mL). Compound **2i** was obtained, NMR yield: 74%, based on naphthalene as a standard. ¹H NMR (500 Hz, C_6D_6) = 1.41 (s, 12H). ¹³C (125 Hz, C_6D_6) = 27.18.

General procedure C for decarbonylation of aliphatic aldehydes

Decarbonylation of 2-(adamantan-1-yl)acetaldehyde to 1-methyladamantane (2j)⁷

Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves (3–4 Å, 100 mg), aldehyde **1j** (180 mg, 1.01 mmol), Pd/C (107 mg, 10 mol% Pd), and cyclohexane (1 mL) and the sealed tube was heated at 130 °C for 48 h. The

reaction mixture was cooled to room temperature, filtered through a pad of Celite, washed with CH_2Cl_2 (15 – 20 mL) and the solvents were removed under the reduced pressure. The crude product was purified by dry-flash column chromatography (SiO₂: pentane) to afford product **2j** as a colorless powder (119 mg, 78 %). IC (ATR) = 2900, 2844, 1453 cm⁻¹. ¹H NMR (500 Hz, CDCl₃) = 1.92 (s, 3H), 1.70 - 1.55 (m, 6H), 1.50 - 1.41 (m, 6H), 0.76 (s, 3H). ¹³C (125 Hz, CDCl₃) = 44.64, 36.94, 31.44, 29.80, 28.89. GC-MS: m/z = 150.1 [M]⁺.

Deuterium labeling experiment

$[1D_1]$ 1-methyladamantane (d-2j)

Round-bottom flask, purged with argon and equipped with a magnetic stir bar was charged with aldehyde **1j** (452 mg, 2.53 mmol) and MeOH (7 mL). NaBD₄ (106 mg, 2.53, 1 equiv) was added to the solution in portions, over 5 minutes. The resulting mixture was stirred at room temperature for 3h. The reaction was quenched with H₂O (15 mL) and the mixture was extracted with Et₂O (2 × 20 mL). The organic solution was dried over anhydrous Na₂SO₄, filtered and the solvents were removed under the reduced pressure. The crude product was used in the next reaction without further purification. Compound **10** was obtained as a colorless powder (396 mg, 86%). Mp = 65–68 °C. IC (ATR) = 3300, 2902, 2846, 1450 cm⁻¹. ¹H NMR (500 Hz, CDCl₃) = 3.64 (t, J = 7.5 Hz, 1H), 1.90 (s, 3H), 1.66 (d, J = 12.0 Hz, 3H), 1.59 (d, J = 12.0 Hz, 3H), 1.54 – 1.41 (m, 7H), 1.34 (d, J = 7.5 Hz, 2H). ¹³C (125 Hz, CDCl₃) = 58.31 (t, J = 21.6 Hz), 47.05, 42.72, 37.03, 31.79, 28.59. GC-MS: m/z = 181.1 [M]⁺.

Alcohol **10** (100 mg, 0.55 mmol) was dissolved in CH_2Cl_2 (8 mL) and PCC (178 mg, 0.83 mmol, 1.5 equiv) was added to the solution. The resulting mixture was stirred at room temperature for 2 hour. The mixture was filtered through a pad of SiO_2 and the SiO_2 was washed with CH_2Cl_2 (20 mL). The solvent was removed under the reduced pressure to yield a pure d-1j (95 mg, 96%) as a colorless oil. IC (ATR) = 2903, 2849, 1707, 1450 cm⁻¹. ¹H NMR (500 Hz, CDCl₃) = 9.87 (m, 0.15 H), 2.12 (m, 2H), 1.99 (s, 3H), 1.76 – 1.64 (m, 12H). ¹³C (125 Hz, CDCl₃) = 203. 61 (C–H), 203.32 (t, J = 26.1 Hz, C–D), 57.06 (t, J = 3.5 Hz), 42.70, 36.60, 33.28, 28.43. GC-MS: m/z = 179.1 [M]⁺.

Following the general procedure C for decarbonylation, compound d-2j was obtained after dry-flash column chromatography (SiO₂: pentane) as a colorless foam (49 mg, 61%). IC (ATR) = 2955, 2924, 2853, 1460 cm⁻¹. ¹H NMR (500 Hz, CDCl₃) = 1.92 (s, 3H), 1.71-1.57 (m, 6H), 1.47-1.42 (m, 6H), 0.76 (s, CH₃), 0.74 (t, J = 1.5 Hz, CH₂D). ¹³C (125 Hz,CDCl₃) = 44.61, 36.92, 31.43, 31.11 (t, J = 18.9 Hz, CH₂D), 29.76, 28.87. GC-MS: m/z = 151.1 [M]⁺.

Decarbonylation of adamantane-1-carbaldehyde to adamantane (2k) [CAS Reg. No. 281-23-2]

Following the general procedure C for decarbonylation, compound **2k** was obtained after dry-flash column chromatography (SiO₂: pentane) as a colorless powder (88 mg, 54%). IC (ATR) = 2904, 2848, 1450 cm⁻¹. ¹H NMR (500 Hz, CDCl₃) = 1.87 (s, 4H), 1.75 (s, 12H). ¹³C (125 Hz, CDCl₃) = 37.75, 28.35. GC-MS: $m/z = 136.0 \text{ [M]}^+$.

Decarbonylation of undec-10-enal to dec-1-ene (21) [CAS Reg. No. 872-05-9]

Following the general procedure A for decarbonylation, compound **21** was obtained. GC-MS yield: 72%, based on naphthalene as a standard. GC-MS: $m/z = 140.2 \text{ [M]}^+$.

Decarbonylation of 3-(3-chlorophenyl)propionaldehyde to 1-chloro-3-ethylbenzene (2m) [CAS Reg. No. 620-16-6]

Following the general procedure B for decarbonylation, compound **2m** was obtained, NMR yield: 51%, based on methyl benzoate as a standard. 1 H NMR (500 Hz, C_6D_6) = 7.15-7.00 (m, 2H), 6.85-6.83 (m, 1H), 6.73-6.70 (m, 1H), 2.22 (q, J = 7.5 Hz, 2H), 0.91 (t, J = 7.5 Hz, 3H).

Decarbonylation of 2-(4-methoxyphenyl)octanal to 1-heptyl-4-methoxybenzene (2n)⁸

Following the general procedure A for decarbonylation, compound **2n** was obtained after dry-flash column chromatography (SiO₂: pentane) as a colorless oil (35 mg, 95%). IC (ATR) = 2998, 2955, 2927, 2854, 1612, 1513, 1462, 1299, 1246, 1178, 1040, 827 cm⁻¹. ¹H NMR (500 Hz, CDCl₃) = 7.12 - 7.05 (m, 2H), 6.86 - 6.77 (m, 2H), 3.78 (s, 3H), 2.59 - 2.50 (m, 2H), 1.60 - 1.53 (m, 2H), 1.35 - 1.21 (m, 8H), 0.92 - 0.85 (m, 3H). ¹³C (125 Hz, CDCl₃) = 157.58, 135.07, 129.22, 113.63, 55.23, 35.03, 31.83, 31.76, 29.24, 29.18, 22.66, 14.08. GC-MS: m/z = 206.1 [M]⁺.

Decarbonylation of 2-(4-acetylphenyl)octanal (10) to 4-n-heptylacetophenone (20)9

Dry glass reaction tube equipped with a magnetic stir bar was charged with Pd(OAc)₂ (5 mg, 0.02 mmol, 4 mol%), rac-BINAP (20 mg, 0.03 mmol, 6 mol%), Cs_2CO_3 (208 mg, 0.64 mmol) and 4-bromoacetophenone (106 mg, 0.53 mmol, 1 equiv). The reaction tube was evacuated and backfilled with argon followed by the addition of octanal (100 μ L, 0.64 mmol, 1.2 equiv) and 1,4-dioxane (2 mL) and the sealed reaction tube was heated at 80 °C for 9 h. The reaction mixture was cooled to room temperature, filtered through a pad of Celite, washed with EtOAc (25 mL) and the solvents were removed under reduced pressure. The crude product was purified by dry-flash column chromatography (SiO₂: hexane/ethyl acetate = 9/1) to afford 2-(4-acetylphenyl)octanal **1o** as a yellow oil (45 mg, 34%). IC (ATR) = 3401, 2928, 2858, 1683, 1608, 1462, 1415, 1360, 1270 cm⁻¹. ¹H NMR (500 Hz, CDCl₃) = 9.69 (d, J = 2 Hz, 1H), 7.97 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 3.60 – 3.55 (m, 1H), 2.61 (s, 3H), 2.15 – 2.05 (m, 1H), 1.80 – 1.70 (m, 1H), 1.40 – 1.15 (m, 8H), 0.90 – 0.80 (m, 3H). ¹³C (125 Hz, CDCl₃) = 200.14, 197.58, 142.03, 136.37, 128.99, 59.13, 31.50, 29.75, 29.03, 27.00, 26.58, 22.51, 13.98. GC-MS: m/z = 246.2 [M]⁺. HRMS (HESI) m/z ([M + H]⁺) calcd for $C_{16}H_{23}O_2$: 247.16980, found 247.16864.

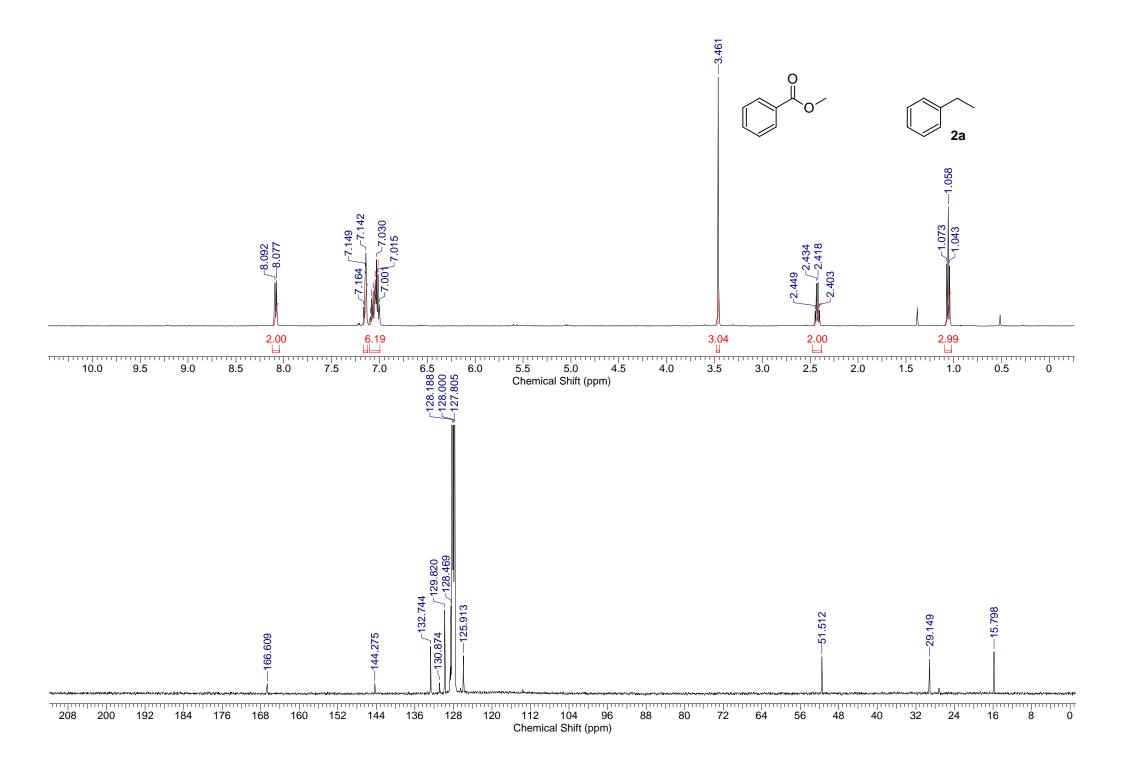
Following the general procedure A for decarbonylation, compound **20** was obtained after dry-flash column chromatography (SiO₂: pentane/EtOAc = 95/5) as a yellow oil (64 mg, 76%). IC (ATR) = 2956, 2928, 2856, 1684, 1606, 1462, 1412, 1358, 1268, 1182 cm⁻¹. ¹H NMR (500 Hz, CDCl₃) = 7.88 (d, J = 8 Hz, 2H), 7.26 (d, J = 8 Hz, 2H), 2.70 – 2.60 (m, 2H), 2.58 (s, 3H), 1.70 – 1.55 (m, 2H), 1.40 – 1.20 (m, 8H), 0.95 – 0.80 (m, 3H). ¹³C (125 Hz, CDCl₃) = 197.85, 148.81, 134.88, 128.56, 128.43, 35.95, 31.73, 31.08, 29.18, 29.08, 26.48, 22.60, 14.04. GC-MS: m/z = 218.2 [M]⁺.

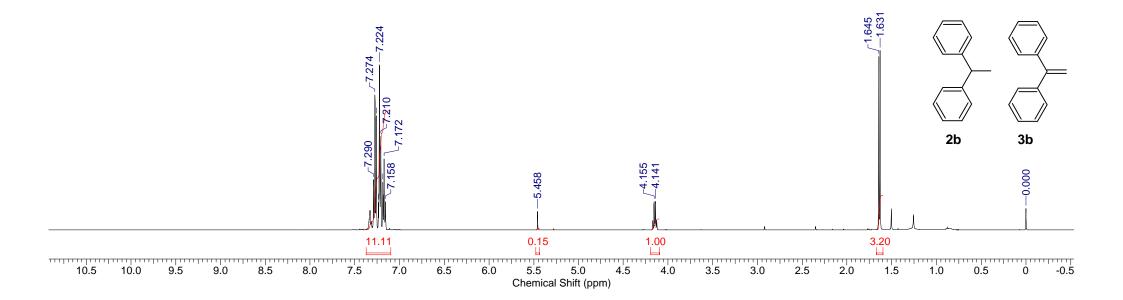
Decarbonylation of 3α , 7α , 12α -triacetoxy- 5β -cholan-24-al to 3α , 7α , 12α -triacetoxy-24-nor- 5β -cholane (5) 10

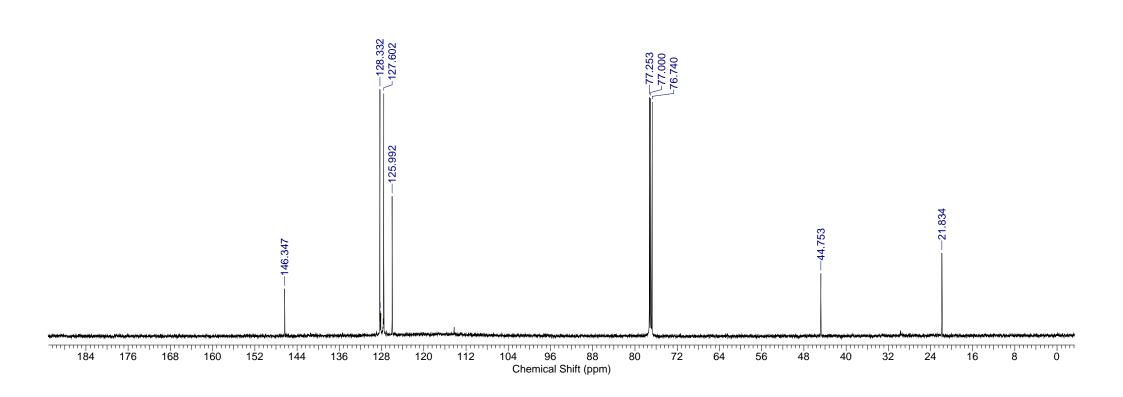
Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves (3–4 Å, 100 mg), aldehyde **4** (46 mg, 0.09 mmol), Pd/C (5 mg, 5 mol% Pd), and cyclohexane (1 mL) and the sealed tube was heated at 130 °C for 24 h. The reaction mixture was cooled to room temperature, filtered through a pad of Celite, washed with CH₂Cl₂ (15 – 20 mL) and the solvents were removed under the reduced pressure. The residue was dissolved in EtOH (2 mL) and the solution was purged with argon, followed by addition of Pd/C (4 mg). The reaction mixture, connected to a balloon of hydrogen, was stirred at room temperature overnight. The reaction mixture was filtered through short pad of SiO₂, to remove

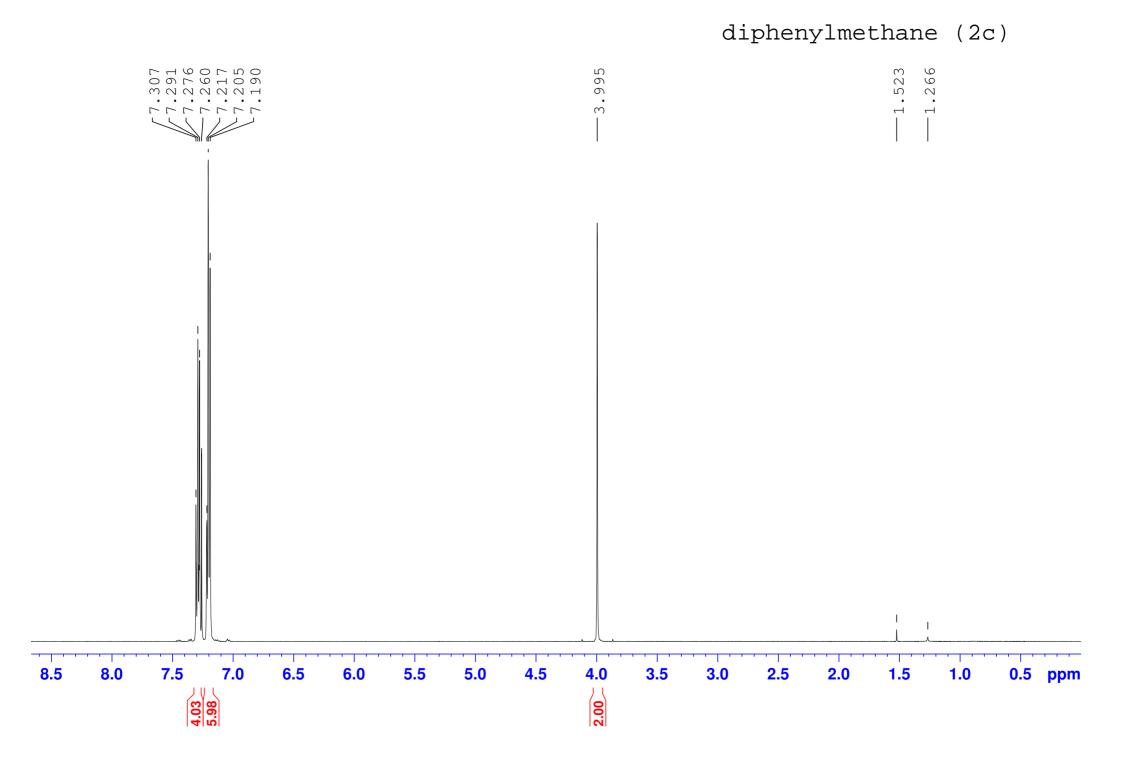
the catalyst, and SiO₂ was washed with CH₂Cl₂ (25 mL). The solvents were removed under the reduced pressure to afford the pure **5** as a colorless oil (37 mg, 85%). IC (ATR) = 2958, 2872, 1733, 1376, 1249, 1025, 736 cm⁻¹. ¹H NMR (500 Hz, CDCl₃) = 5.01 (s, 1H), 4.95- 4.90 (m, 1H), 4.63 – 4.54 (m, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.01 – 1.37 (m, 16H), 1.33 – 1.22 (m, 4H), 1.25 – 0.99 (m, 3H), 0.92 (s, 3H), 0.84 – 0.78 (m, 5H), 0.73 (s, 3H). ¹³C (125 Hz, CDCl₃) = 170.53, 170.49, 170.35, 75.51, 74.09, 70.74, 47.21, 44.96, 43.34, 40.95, 37.75, 36.24, 34.69, 34.61, 34.33, 31.25, 28.90, 28.06, 27.16, 26.87, 25.55, 22.83, 22.54, 21.59, 21.45, 21.38, 17.23, 12.19, 10.22.

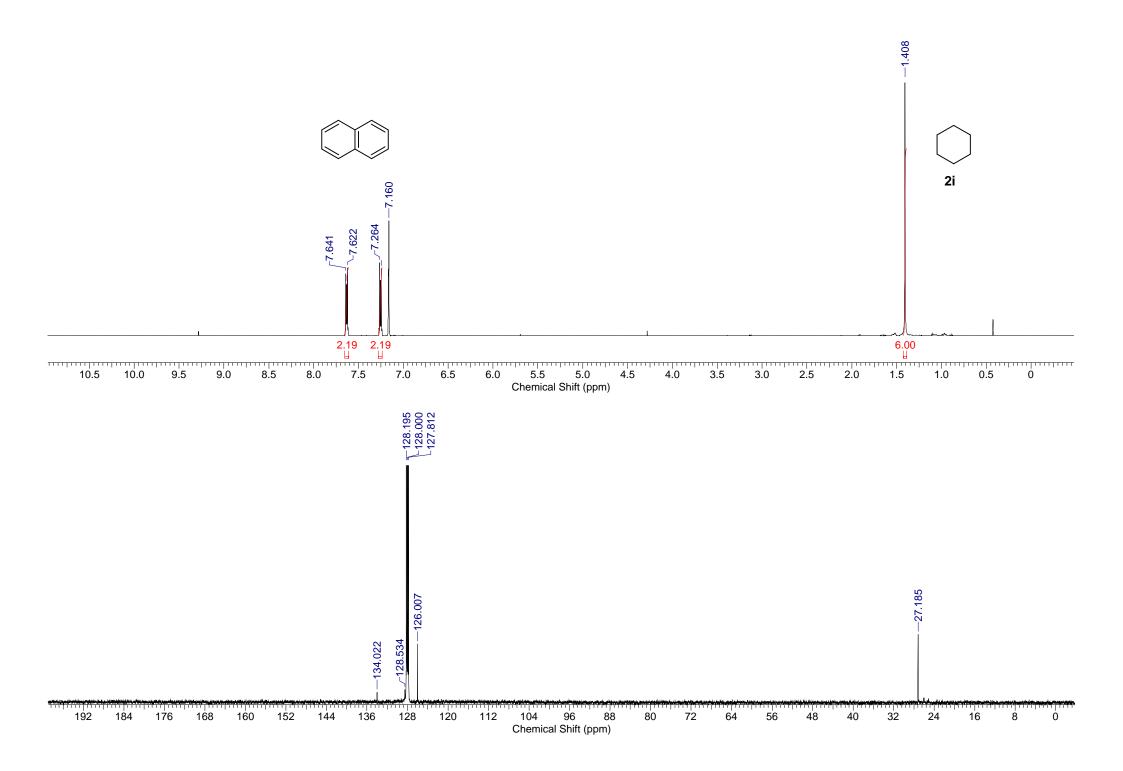
Decarbonylation of (±)-citronellal to 2,6-dimethylhept-2-ene (7) [CAS Reg. No. 5557-98-2], **2,6-dimethylheptane (8)** [CAS Reg. No. 1072-05-5] **and** *p*-cimene (9) [CAS Reg. No. 99-87-6] Following the general procedure A for decarbonylation, compounds 7, **8** and **9** were obtained. GC-MS yield of **7**: 36%, based on naphthalene as a standard. GC-MS: m/z = 126.1 [M]⁺. GC-MS yield of **8**: 8%, based on naphthalene as a standard. GC-MS: m/z = 128.1 [M]⁺. GC-MS yield of **9**: 23%, based on naphthalene as a standard. GC-MS: m/z = 134.1 [M]⁺.



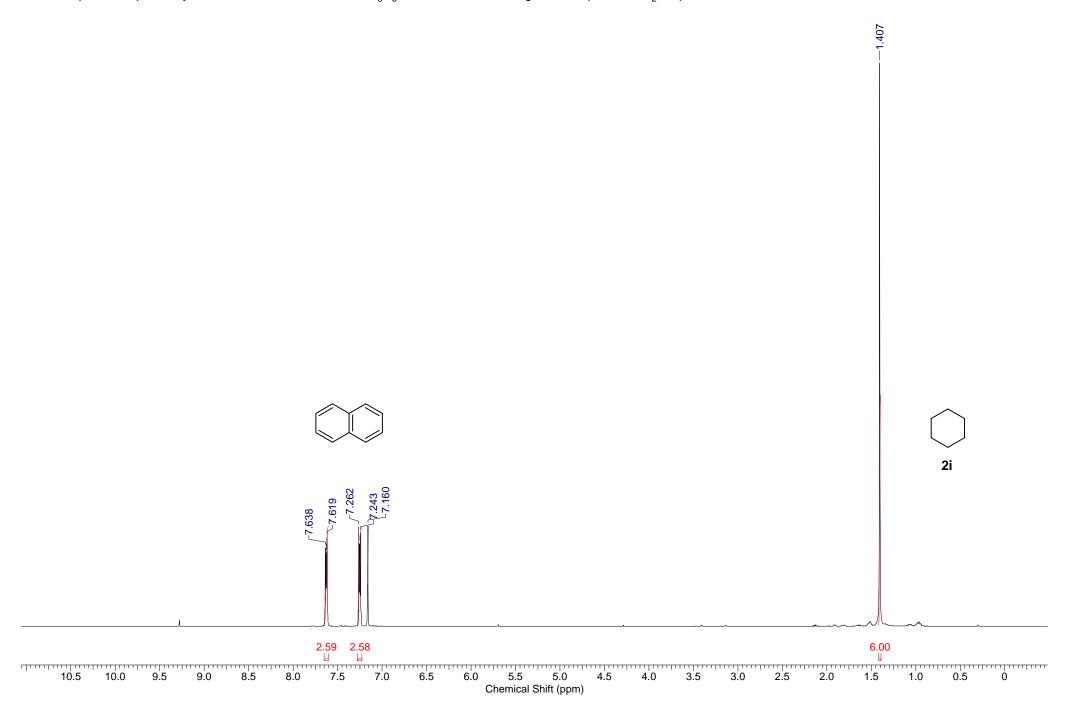


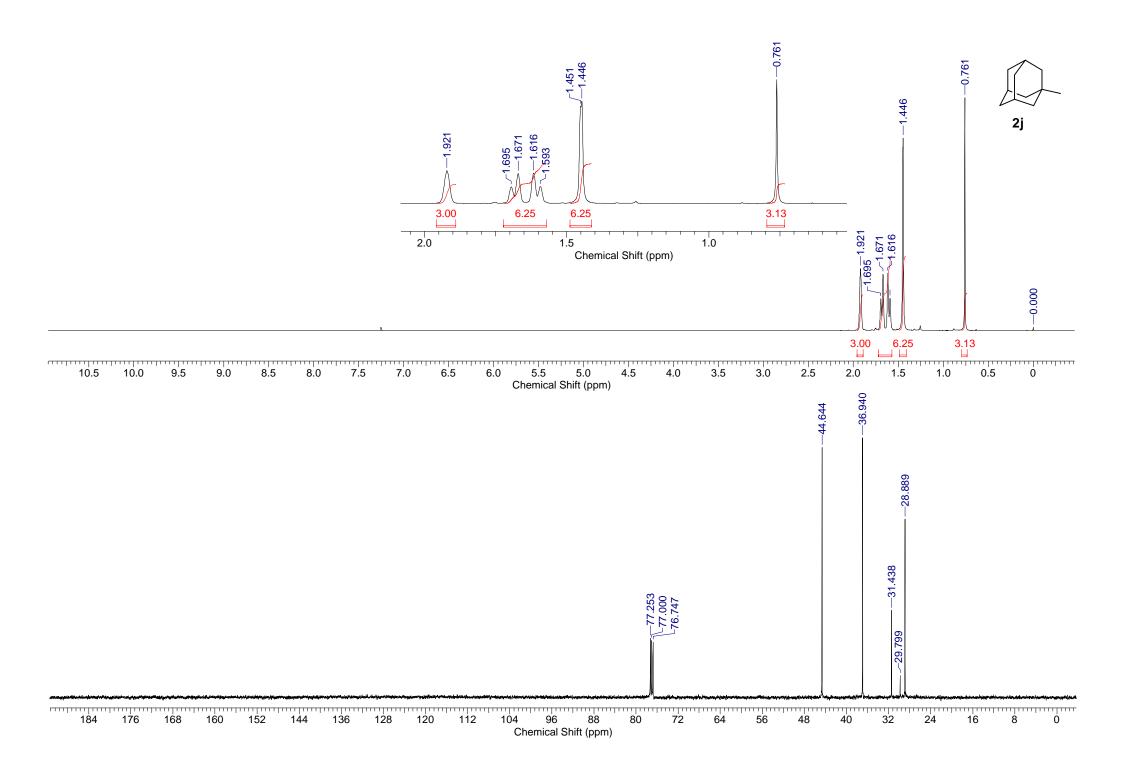


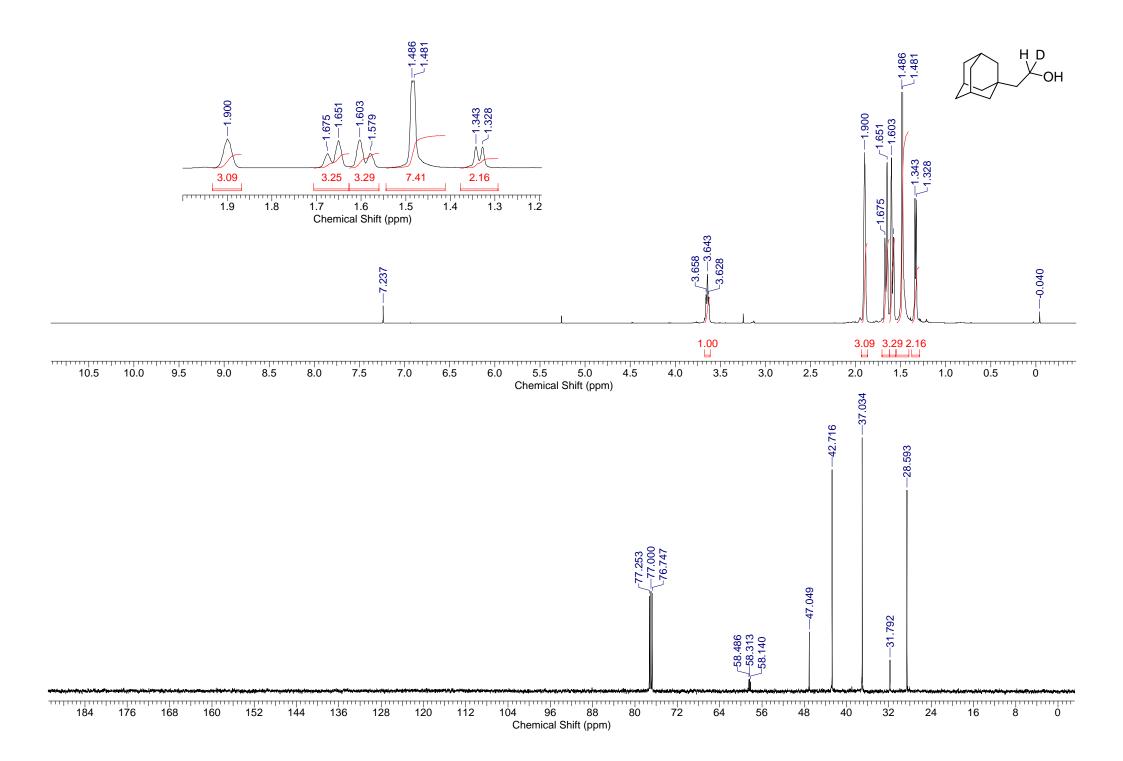


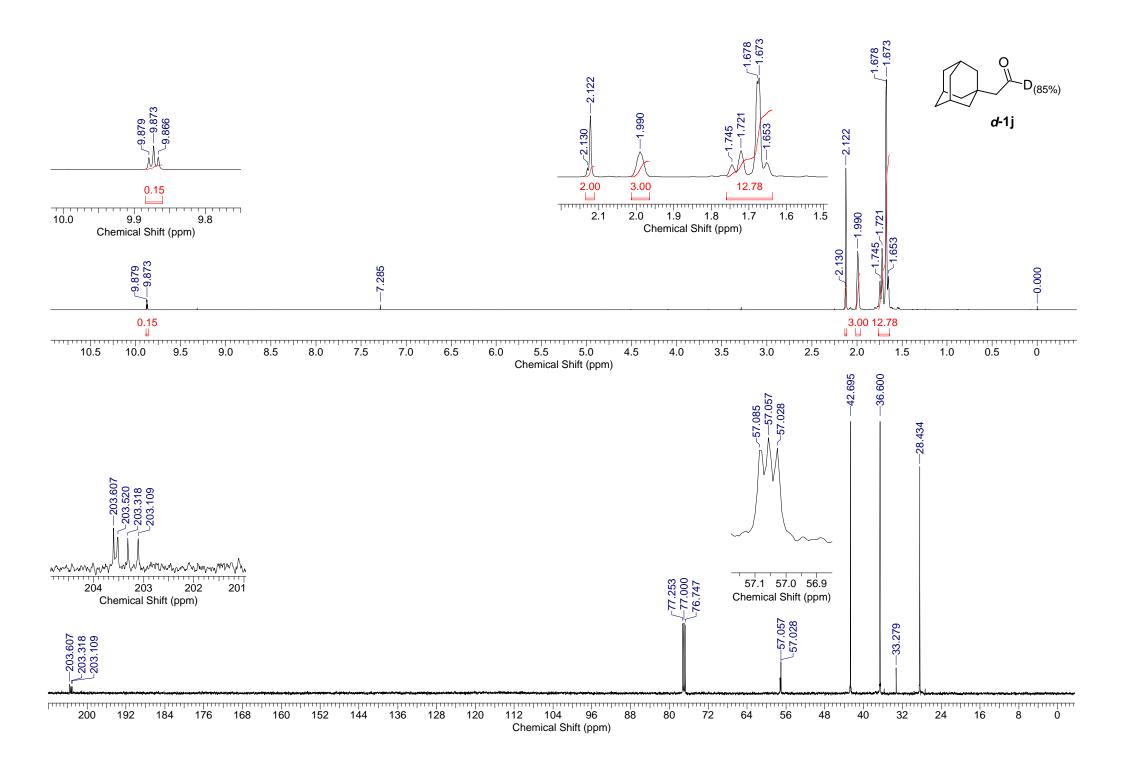


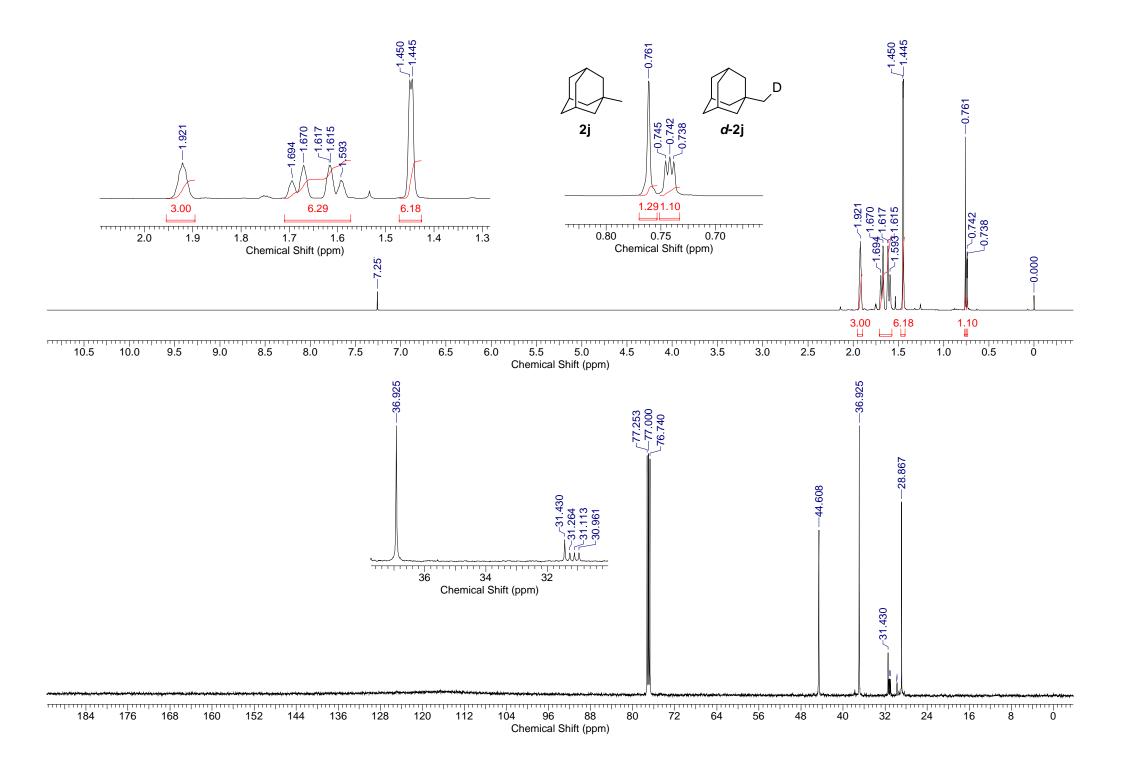
¹H NMR spectroscopic analysis of the reaction mixtures in C₆D₆ before filtration through a short pad of SiO₂; naphthalene was used as an internal standard

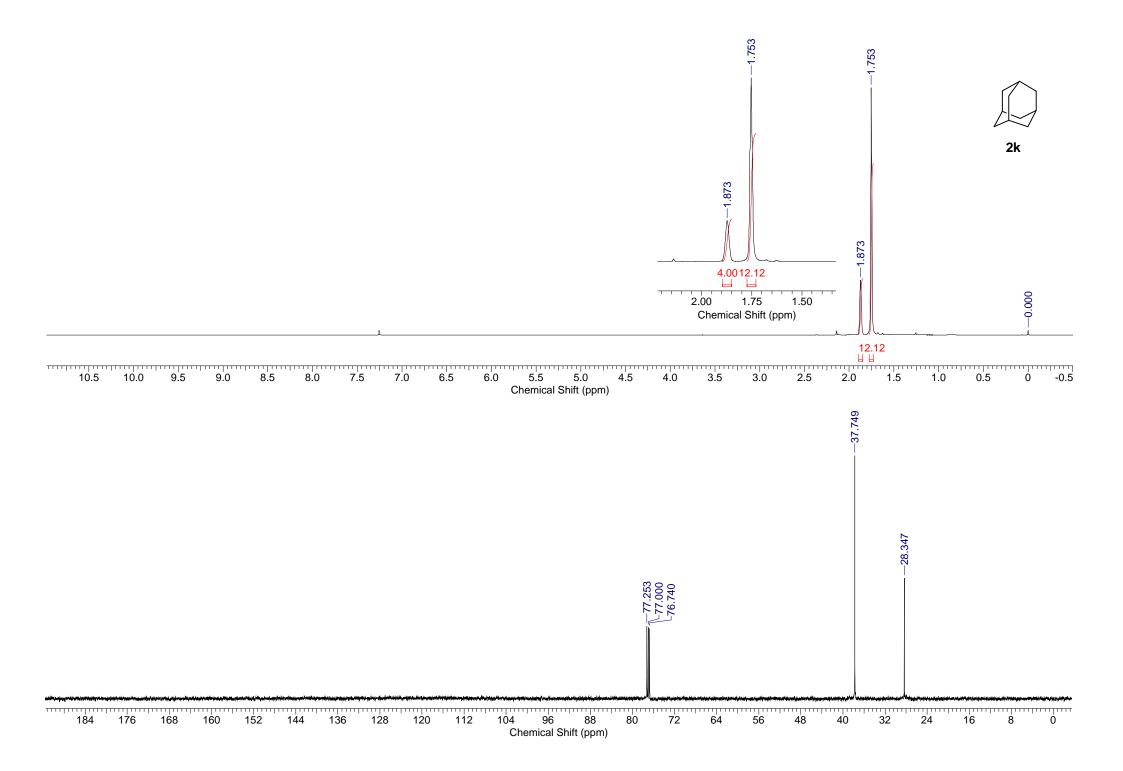




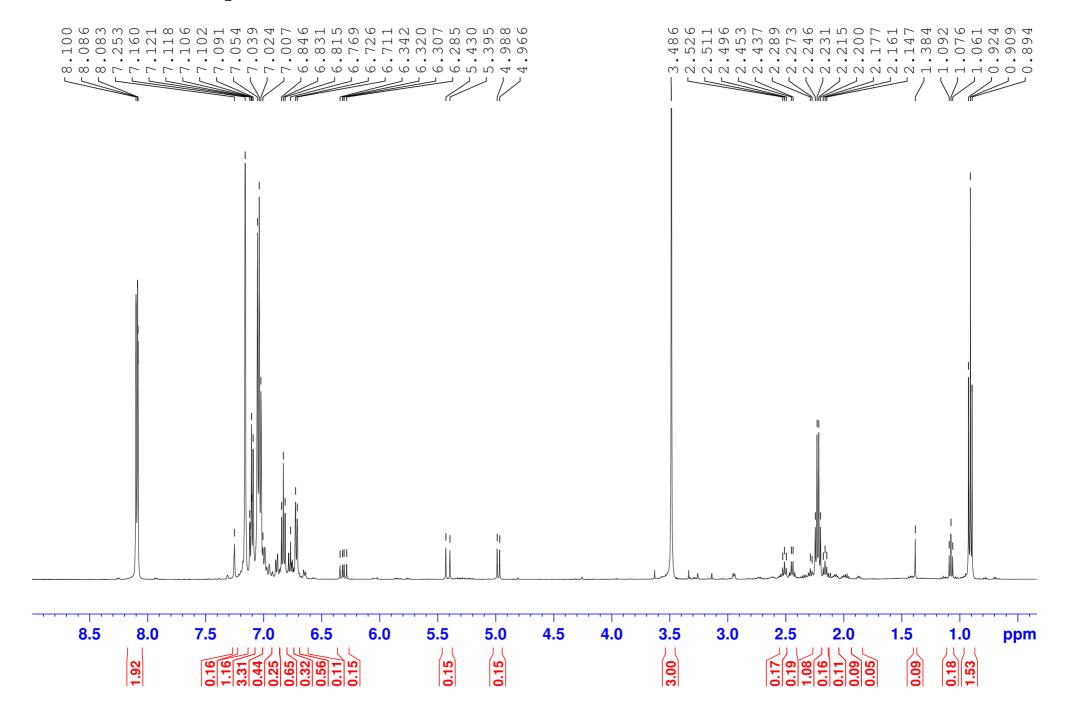


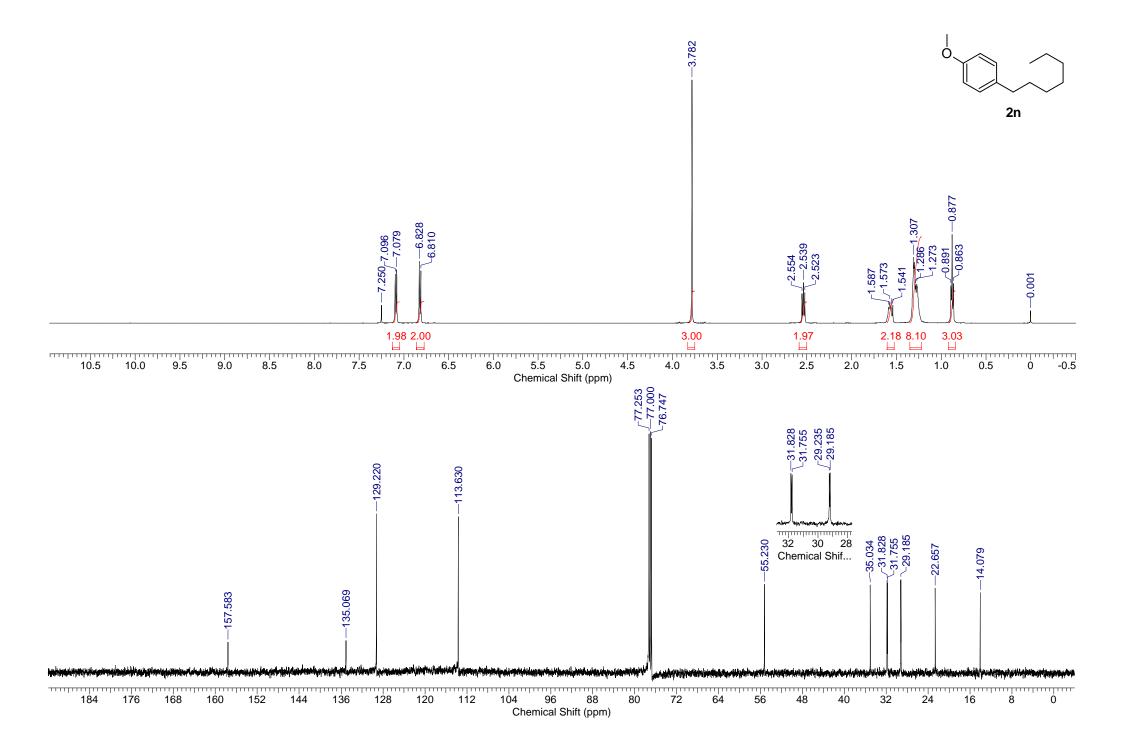


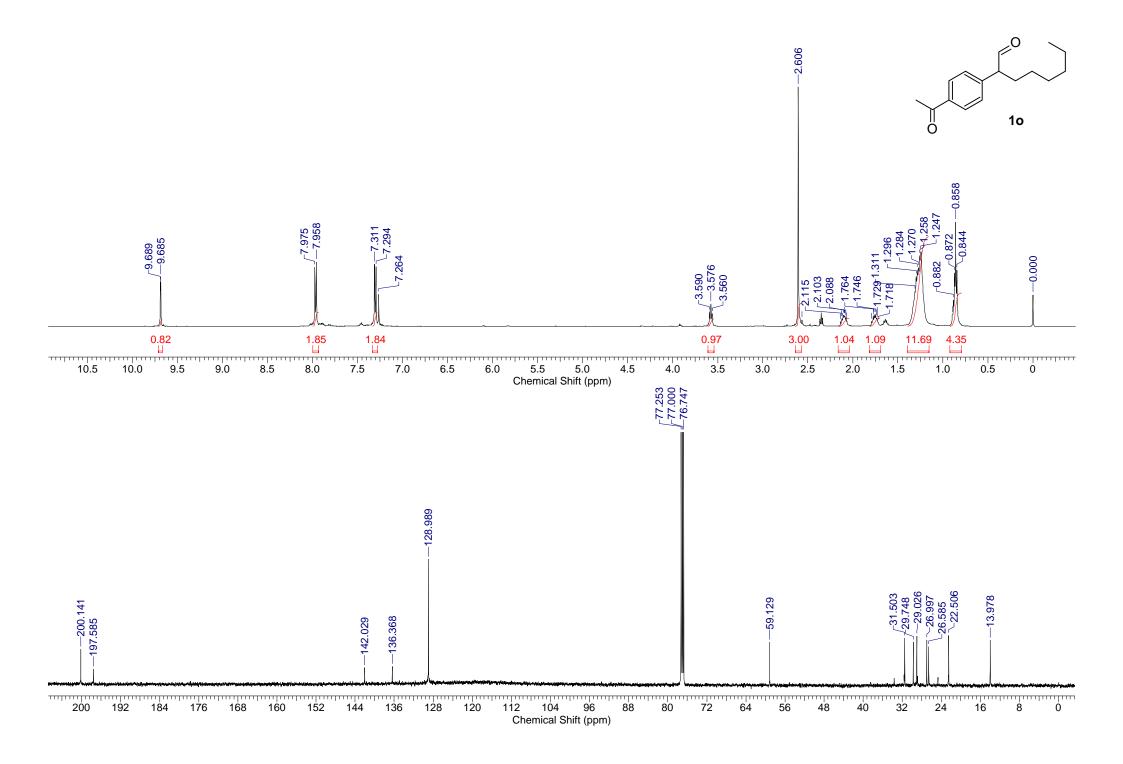


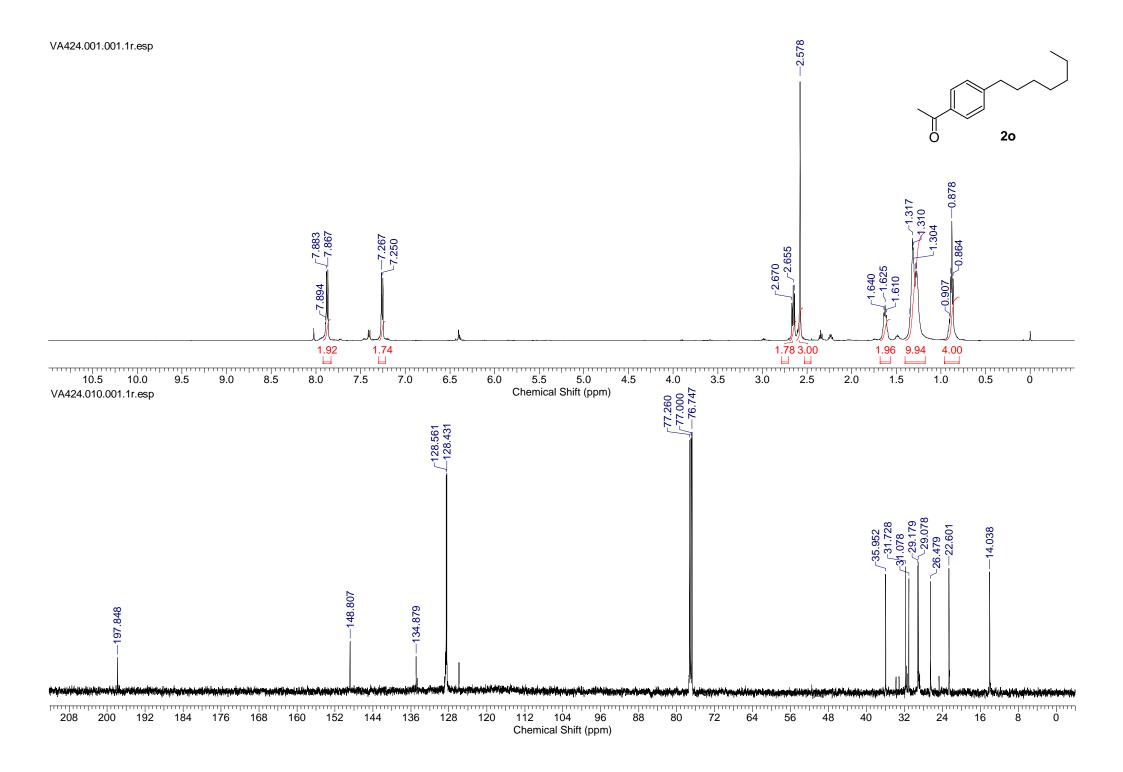


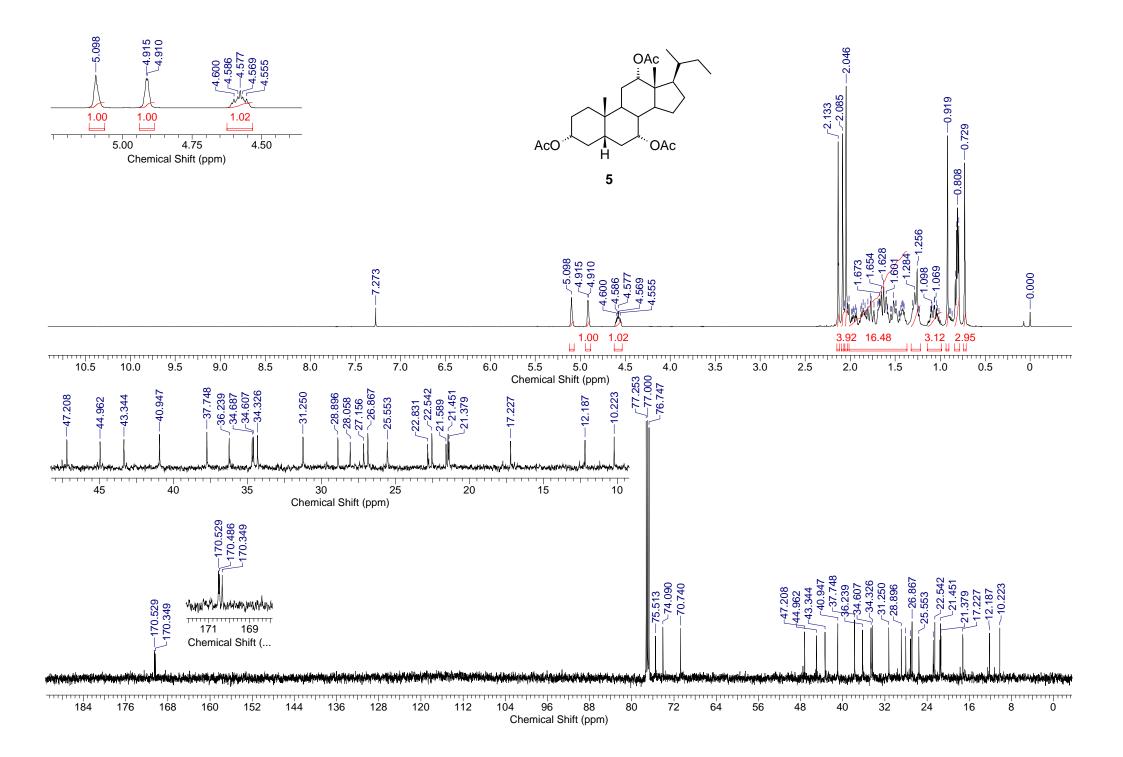
1-chloro-3-ethylbenzene (2m)

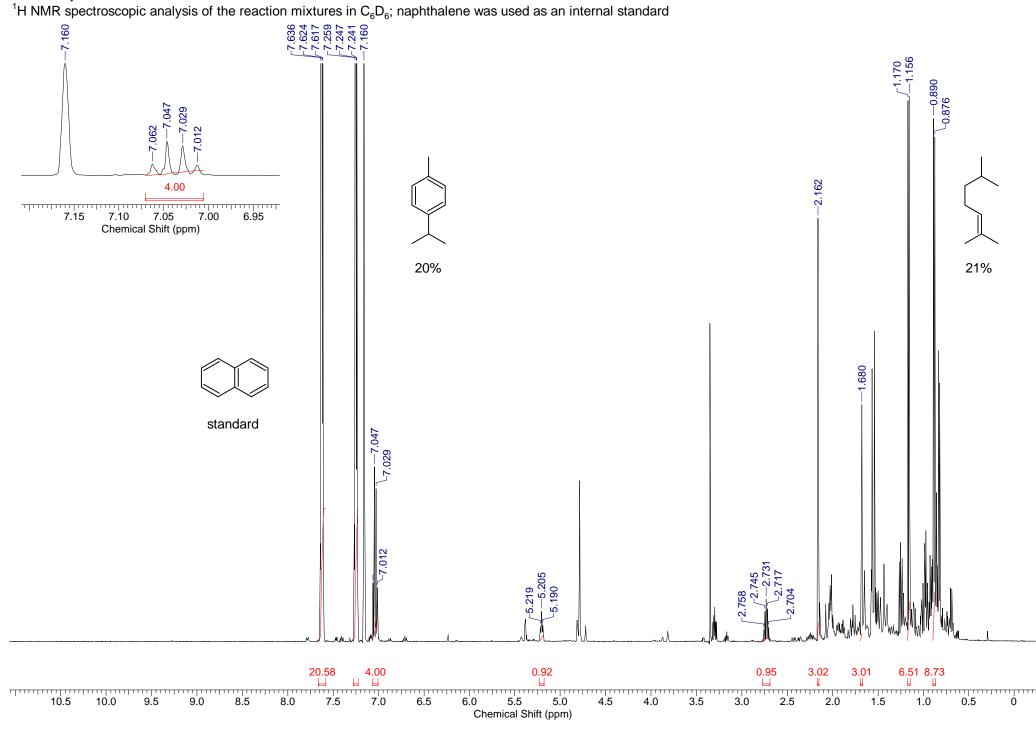


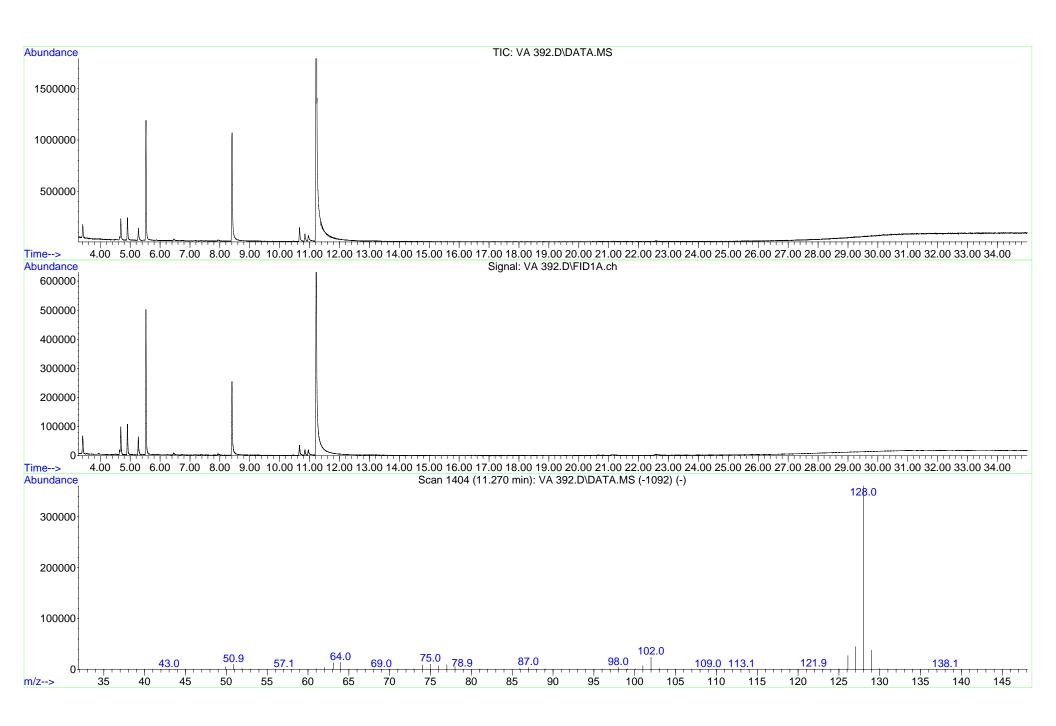


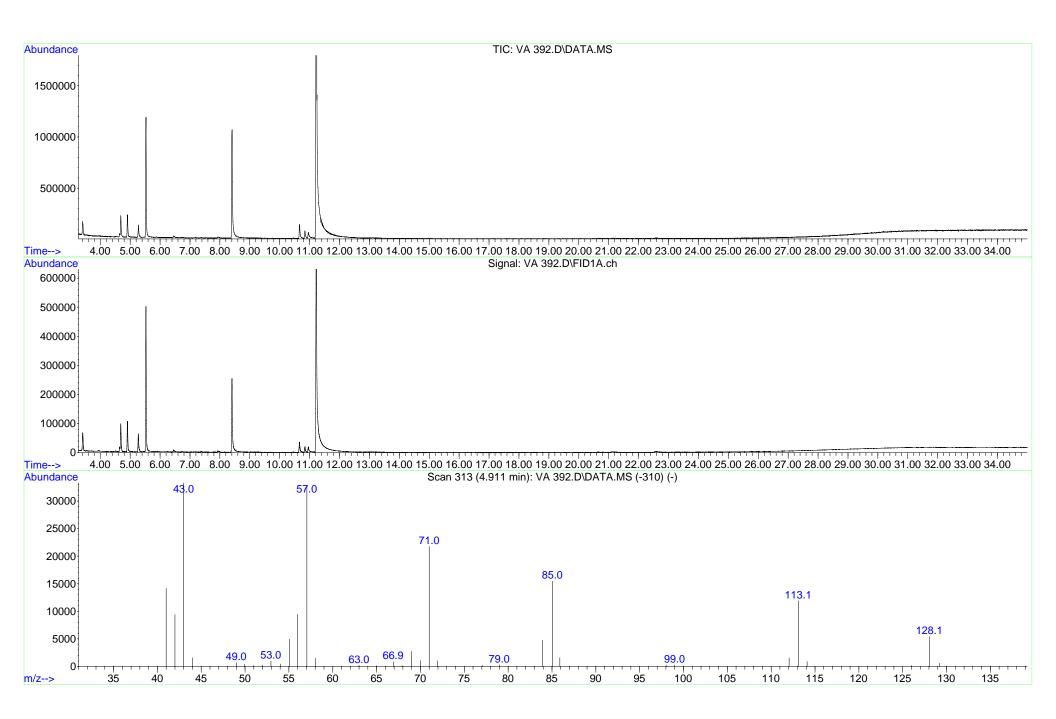


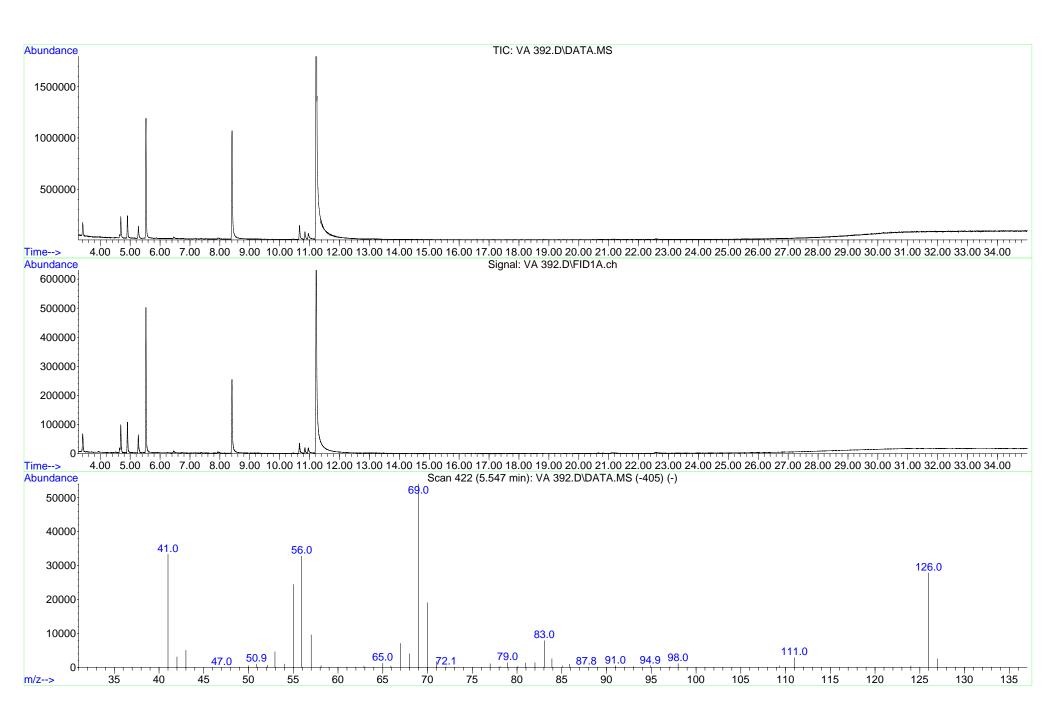


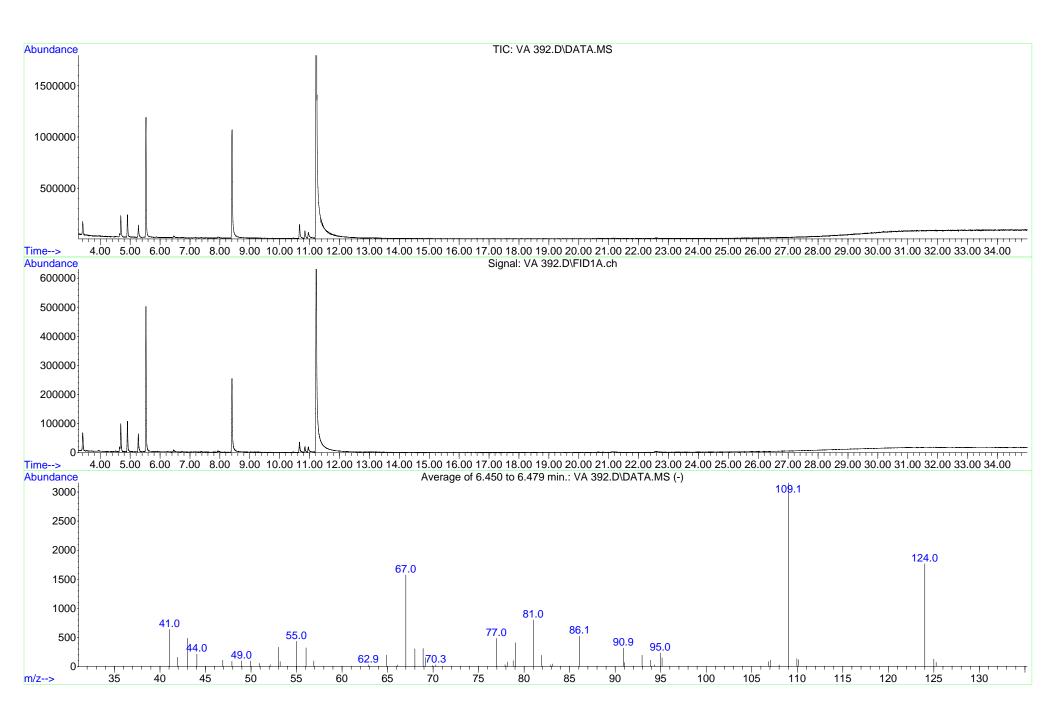


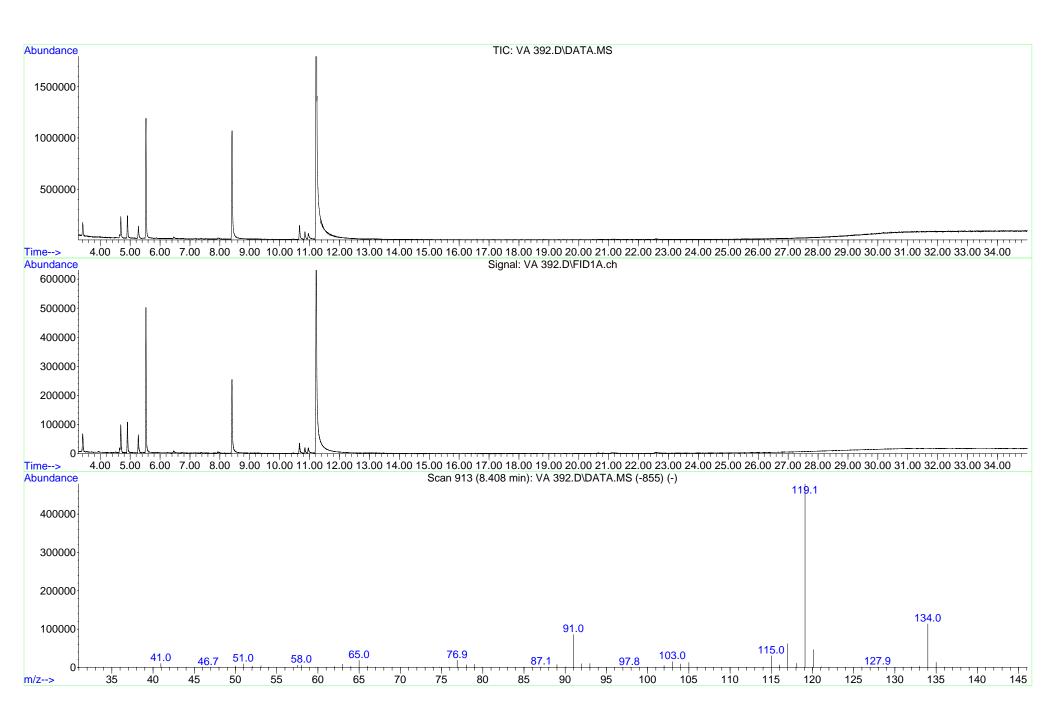


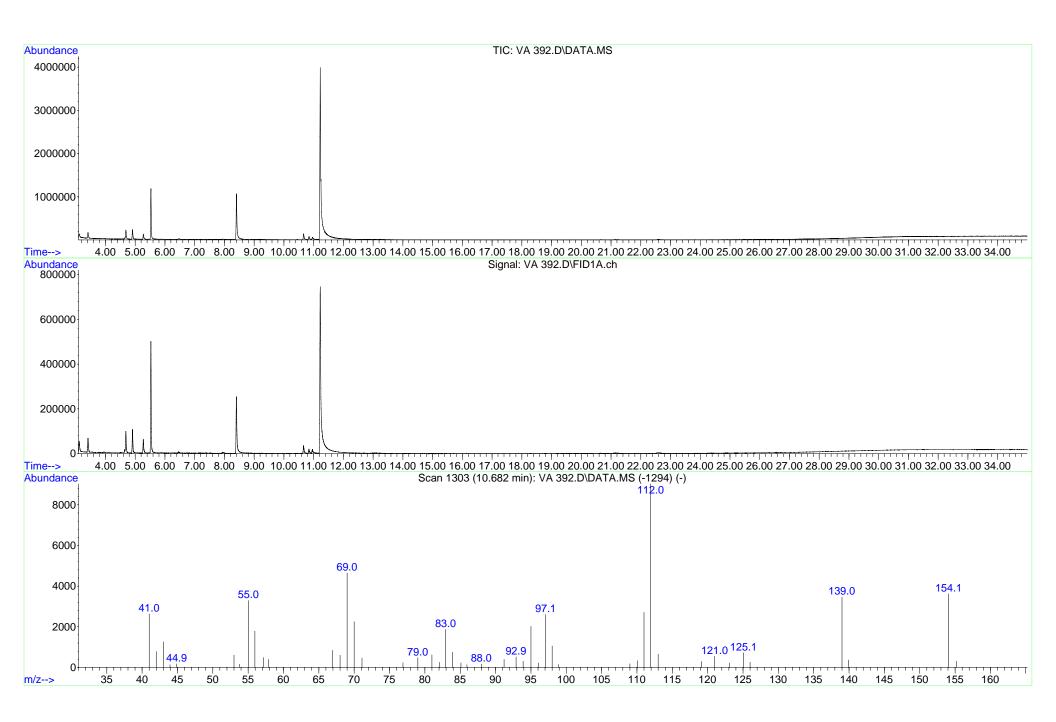












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