

Supporting Information

Selective α,δ -hydrocarboxylation of conjugated dienes utilizing CO₂ and electrosynthesis

1.0 General Experimental

Reagents: Commercially available materials (electrolytes, reducing agents, dienes) were used without further purification. Anthracene (**1j**), *trans,trans*-1,4-diphenyl-1,3-butadiene (**1i**), hexa-2,4-diene (**1k**), 2,3-dimethylbutadiene (**1l**) and cyclohexadiene (**1m**) were purchased from commercial sources and used as received. Anhydrous N,N-dimethylformamide and THF were purchased from Sigma-Aldrich and dried over 3Å molecular sieves prior to use. Tetraethylammonium iodide was also purchased from Sigma-Aldrich. Deuterated solvents were purchased from Fluorochem UK Ltd.

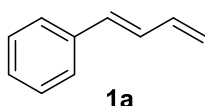
Analytical Methods: All infrared spectra were obtained using a Perkin-Elmer Spectrum 65 FT-IR spectrophotometer; thin film spectra were acquired using sodium chloride plates. All ¹H and ¹³C NMR spectra were measured at 400 and 100 MHz using a Bruker Avance 400 MHz spectrometer, a Jeol ECS 400 MHz spectrometer or at 500 and 125 MHz on a Jeol ECZ 500 MHz spectrometer. The solvent used for NMR spectroscopy was CDCl₃ (unless stated otherwise) using TMS (tetramethylsilane) as the internal reference. Chemical shifts are given in parts per million (ppm) and J values are given in Hertz (Hz).

Analysis by GCMS utilised a Shimadzu QP2020, GC-2010 Plus, using a 15 m x 0.25 mm DB-5 column and an electron impact low resolution mass spectrometer, acids were converted to their corresponding methyl esters using TMSdiazomethane prior to sampling. Melting points were recorded using a Stuart Scientific melting point apparatus SMP3 and are uncorrected. All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored by GCMS or using thin layer chromatography (TLC) on aluminium backed plates with Merck Kiesel 60 F254 silica gel. TLC visualised by UV radiation at a wavelength of 254 nm. Purification by column chromatography used Apollo Scientific 60 40-63µm silica gel.

Electrode electrochemical reactions were carried out using a 10mL reaction vial using a carbon anode and a stainless steel cathode supplied by IKA and the current was supplied from an IKA ElectraSyn 2.0

2.0 Procedure for preparing 1,3-dienes via Wittig reaction

General Procedure I: A suspension of allyltriphenylphosphonium bromide (10 mmol) in 50 mL of THF under inert atmosphere was cooled at 0 °C with an ice bath. Then, n-BuLi (10 mmol, 4 mL, 2.5M in hexanes) was added dropwise. The reaction was stirred for 1hr at 0 °C and then the corresponding aldehyde (8 mmol dissolved in 5 mL of THF) was added dropwise. The reaction was stirred for 12 hours at room temperature. After this time, it was quenched with 10 mL of methanol and 10 g silica gel was added. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using hexane on silica gel.

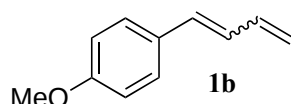


(E)-buta-1,3-dien-1-ylbenzene (1a). Following the general procedure I, but using methyltriphenylphosphonium bromide (3.58 g, 10 mmol) and *trans*-cinnamaldehyde (1.0mL, 8 mmol) to give **1a** (0.9 g, 86.5% yield). Colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.33-7.31 (m, 2H), 7.25-7.21 (m, 2H), 7.16-7.12 (m, 1H), 6.71 (ddt, J = 15.5, 10.5, 0.8 Hz, 1H), 6.50 – 6.38 (m, 2H), 5.25 (dd, J = 17.2, 0.6 Hz, 1H), 5.10 (dd, J = 10.4, 0.6).

¹³C NMR (101 MHz, CDCl₃) δ 137.3, 137.2, 132.9, 129.7, 128.7, 127.7, 126.5, 117.7 ppm.

Spectral data is in agreement with the literature.¹

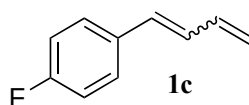


(*E,Z*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (1b). Following the general procedure I using 4-methoxybenzaldehyde (0.97 mL, 8 mmol), affording **1b** (1.1 g, 86% yield) as a mixture of isomers (*E*:*Z* = 1.6:1). Yellow liquid

¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.7 Hz, 2H, *E* isomer), 7.18 (d, *J* = 8.5 Hz, 2H, *Z* isomer), 6.83 (d, *J* = 8.8 Hz, 2H, *Z* isomer), 6.78 (d, *J* = 8.7 Hz, 2H, *E* isomer), 6.57 (d, *J* = 15.7 Hz, 1H, *E* isomer), 6.38 (dt, *J* = 16.8, 10.3 Hz, 1H, *E* isomer), 6.09 (d, *J* = 11.5 Hz, 1H, *Z* isomer), 5.27 (ddt, *J* = 16.9, 1.8, 0.8 Hz, 1H, *Z* isomer), 5.18 (dd, *J* = 16.0, 0.8 Hz, 1H, *E* isomer), 5.10 (dddd, *J* = 10.2, 2.1, 1.4, 0.9 Hz, 1H, *Z* isomer), 5.00 (d, *J* = 9.3 Hz, 1H, *E* isomer), 3.70 (s, 3H, *E* isomer), 3.69 (s, 3H, *Z* isomer) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 159.4 (*E* isomer), 158.8 (*Z* isomer), 137.5 (*E* isomer), 133.5 (*Z* isomer), 132.5 (*E* isomer), 130.4 (*Z* isomer), 130.3 (*Z* isomer), 130.2 (*Z* isomer), 130.1 (*E* isomer), 129.5 (*Z* isomer), 119.1 (*Z* isomer), 127.9 (*E* isomer), 127.8 (*E* isomer), 116.6 (*E* isomer), 114.2 (*E* isomer), 113.8 (*Z* isomer), 55.3 (*Z* isomer), 55.3 (*E* isomer) ppm.

Spectral data is in agreement with the literature.²



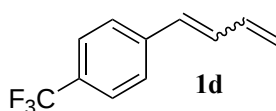
(*E,Z*)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (1c). Following the general procedure I using 4-fluorobenzaldehyde (0.85 mL, 8 mmol), affording **1c** (0.9 g, 76% yield) as a mixture of isomers (*E*:*Z* = 1:1.5). Yellow liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.38-7.34 (m, 2H, *E* isomer), 7.28 (dddd, *J* = 8.6, 5.4, 2.7, 1.6 Hz, 2H, *Z* isomer), 7.06-6.98 (m, 2H), 6.83 (dddd, *J* = 16.8, 11.2, 10.1, 1.1 Hz, 1H, *Z* isomer), 6.73-6.67 (m, 1H, *E* isomer), 6.52 (d, *J* = 15.6 Hz, 1H, *E* isomer), 6.48 (dt, *J* = 16.9, 10.3 Hz, 1H, *E* isomer), 6.40 (d, *J* = 11.5 Hz, 1H, *Z* isomer), 6.25 (t, *J* = 11.3 Hz, 1H, *Z* isomer), 5.35 (dd, *J* = 16.9, 1.8, 1H, *Z* isomer), 5.25-5.23 (m, 1H), 5.17 (dd, *J* = 9.6, 1.2 Hz, 1H, *E* isomer) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 162.2 (d, *J* = 240.0 Hz, *E* isomer), 159.7 (d, *J* = 194.4 Hz, *Z* isomer), 135.9 (*E* isomer), 132.3 (d, *J* = 3.5 Hz, *E* isomer), 132.2 (d, *J* = 3.5 Hz, *Z* isomer), 131.7 (*Z* isomer), 130.5 (*E* isomer), 129.5 (d, *J* = 1.3 Hz, *Z* isomer), 129.4 (d, *J* = 7.9 Hz, *Z* isomer), 128.3 (d, *J* = 7.6 Hz, *E* isomer), 128.1 (*Z* isomer), 126.8 (d, *J* = 34.4 Hz, *E* isomer), 118.8 (*Z* isomer), 116.6 (*E* isomer), 114.4 (d, *J* = 37.6 Hz, *E* isomer), 114.0 (d, *J* = 32.5 Hz, *Z* isomer) ppm.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.0 (*E* isomer), -114.6 (*Z* isomer) ppm.

Spectral data is in agreement with the literature.²

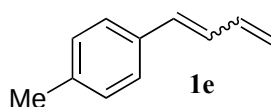


(*E,Z*)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (1d). Following the general procedure I using 4-trifluoromethylbenzaldehyde (1.09 mL, 8 mmol), affording **1d** (0.95 g, 60% yield) as a mixture of isomers (*E:Z* = 1:1). Yellow liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.2 Hz, 2H, *Z* isomer), 7.49 (d, *J* = 8.8 Hz, 2H, *E* isomer), 7.41(d, *J* = 8.5 Hz, 2H, *E* isomer), 7.34 (d, *J* = 8.5 Hz, 2H, *Z* isomer), 6.82-6.69 (m, 1H), 6.50 (d, *J* = 15.7 Hz, 1H, *E* isomer), 6.47 (dt, *J* = 16.9, 9.9 Hz, 1H, *E* isomer), 6.42 (d, *J* = 11.6 Hz, 1H, *Z* isomer), 6.27 (t, *J* = 11.4 Hz, 1H, *Z* isomer), 5.39 (ddt, *J* = 16.8, 1.7, 0.8 Hz, 1H, *Z* isomer), 5.33 (d, *J* = 16.9 Hz, 1H, *E* isomer), 5.24 (dtd, *J* = 10.2, 1.6, 0.9 Hz, 1H, *Z* isomer), 5.18 (m, 1H, *E* isomer) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 140.9 (*Z* isomer), 140.6 (*E* isomer), 136.7 (*E* isomer), 132.6 (*Z* isomer), 132.5 (*Z* isomer), 132.0 (*E* isomer), 131.2 (*E* isomer), 129.5 (*E* isomer), 129.2 (*Z* isomer), 128.8 (*E* isomer), 126.5 (*Z* isomer), 125.6 (q, *J* = 3.9 Hz, *E* isomer), 125.2 (q, *J* = 3.9 Hz, *Z* isomer), 122.9 (*E* isomer), 121.2 (*Z* isomer), 119.4 (*Z* isomer) ppm.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.3 ppm.



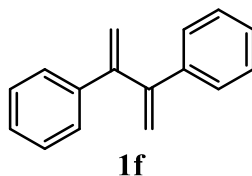
(*E,Z*)-1-(buta-1,3-dien-1-yl)-4-methylbenzene (1e). Following the general procedure I using 4-methylbenzaldehyde (0.92 mL, 8 mmol), affording **1e** (0.95 g, 82.4% yield) as a mixture of isomers (*E:Z* = 1.6:1). Colorless liquid

¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 8 Hz, 2H, *E* isomer), 7.13 (d, *J* = 8.4 Hz, 2H, *Z* isomer), 7.04 (d, *J* = 8 Hz, 2H, *E* isomer), 7.02 (d, *J* = 8 Hz, 2H, *Z* isomer), 6.80 (dd, *J* = 15.7, 10.6 Hz, 1H, *E* isomer), 6.65 (dd, *J* = 15.6, 10.4 Hz, 1H, *Z* isomer), 6.44 (d, *J* = 15.9 Hz, 1H, *E* isomer), 6.44 (d, *J* = 15.6 Hz, 1H, *Z* isomer), 6.34 (m, 2H), 5.27 (ddt, *J* = 16.9, 1.7, 0.8 Hz, 1H, *Z* isomer), 5.23 (dd, *J* = 16.1, 0.8 Hz, 1H, *E* isomer), 5.11 (dddd, *J* = 10.5, 2.2, 1.4, 0.9 Hz, 1H, *Z* isomer), 5.04 (d, *J* = 9.5 Hz, 1H, *E* isomer), 2.25 (s, 3H, *E* isomer), 2.23 (s, 3H, *Z* isomer).

¹³C NMR (101 MHz, CDCl₃) δ 137.6 (*E* isomer), 137.4 (*Z* isomer), 136.9 (*E* isomer), 134.6 (*Z* isomer), 134.5 (*E* isomer), 133.5 (*Z* isomer), 132.9 (*Z* isomer), 130.5 (*Z* isomer), 130.3 (*E* isomer), 129.4 (*Z* isomer), 129.3 (*Z* isomer), 129.1 (*E* isomer), 128.8 (*E* isomer), 126.5 (*E* isomer), 119.3 (*E* isomer), 117.1 (*Z* isomer), 21.3 (*Z* isomer), 21.3 (*E* isomer) ppm.

Spectral data is in agreement with the literature.¹

Spectral data is in agreement with the literature.³

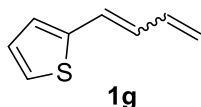


2,3-Diphenyl-1,3-butadiene (1f). Following the general procedure I but using methyltriphenylphosphonium bromide (7.16 g, 20 mmol) and benzil (1.68 g, 8 mmol), affording **1f** (1.2 g, 73% yield). Colorless solid.

¹H NMR (400 MHz, CDCl₃) δ 7.40 - 7.38 (m, 4H), 7.38 - 7.21 (m, 6H), 5.54 (d, *J* = 1.6 Hz, 2H), 5.31 (d, *J* = 1.6 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 149.9, 140.2, 128.2, 127.5, 116.4.

Spectral data is in agreement with the literature.⁶

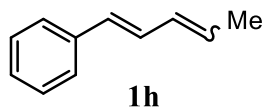


(*E,Z*)-2-(buta-1,3-dien-1-yl)thiophene (1g). Following the general procedure I using 2-thiophenecarboxaldehyde (0.75 mL, 8 mmol), affording **1g** (0.9 g, 87% yield) as a mixture of isomers (*E:Z* = 1:1.5). Yellow liquid.

¹H NMR (500 MHz, CDCl₃) δ 7.17 (dd, *J* = 5.5, 1.5 Hz, 1H, *E* isomer), 7.09 (dd, *J* = 5.5, 1.5 Hz, 1H, *Z* isomer), 7.01 (m, 1H), 6.93 – 6.85 (m, 1H), 6.60–6.48 (m, 1H), 6.40 – 6.30 (m, 1H), 6.04 (td, *J* = 11.1, 0.9 Hz, 1H), 5.31 (ddd, *J* = 16.9, 1.8, 0.9 Hz, 1H, *Z* isomer), 5.21 (d, *J* = 16.8 Hz, 1H, *E* isomer), 5.05 (m, 1H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ 142.6, 140.3, 136.7, 133.3, 129.4, 128.5, 128.4, 127.6, 127.0, 126.8, 126.1, 125.8, 124.6, 122.6, 120.2, 117.6 ppm.

Spectral data is in agreement with the literature.⁵

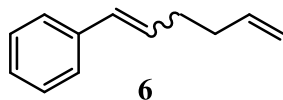


(*E,Z*)-Penta-1,3-dien-1-ylbenzene (1h). Following the general procedure I but using ethyltriphenylphosphonium bromide (3.71 g, 10 mmol) and cinnamaldehyde (1 mL, 8 mmol), affording **1h** (1.2 g, 83% yield) as a mixture of isomers (*E:Z* = 1:1.6). Colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8 Hz, 2H, *Z* isomer), 7.32 (d, *J* = 7.2 Hz, 2H, *E* isomer), 7.28 – 7.22 (m, 2H), 7.18 – 7.14 (m, 1H), 7.07 (ddd, *J* = 15.6, 11.2, 4.4 Hz, 1H, *Z* isomer), 6.70 (dd, *J* = 15.6, 12 Hz, 1H, *E* isomer), 6.48 (d, *J* = 15.6 Hz, 1H, *Z* isomer), 6.37 (d, *J* = 16 Hz, 1H, *E* isomer), 6.20 – 6.13 (m, 1H), 5.77 (dq, *J* = 13.9, 6.8 Hz, 1H, *E* isomer), 5.68 (dq, *J* = 10.7, 7.2 Hz, 1H, *Z* isomer), 1.82 (dd, *J* = 7.2, 1.6 Hz, 3H, *Z* isomer), 1.77 (dd, *J* = 6.8, 1.0 Hz, 3H, *E* isomer) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 137.9, 132.2, 130.4, 130.1, 130.0, 129.5, 128.8, 128.7, 127.5, 127.2, 126.6, 126.4, 124.3, 18.6, 13.8.

Spectral data is in agreement with the literature.⁴

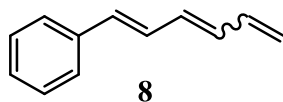


(*E,Z*)-1,5-Hexadien-1-ylbenzene (6). Following the general procedure I but using benzaldehyde (0.82mL, 8 mmol) and 4-Pentenyltriphenylphosphonium bromide, affording **6** (1.0 g, 80% yield) as a mixture of isomers (*E:Z* = 1:1). Colorless liquid

¹H NMR (500 MHz, CDCl₃) δ 7.37–7.20 (5H,m), 6.44 (1H,m), 5.85 (1H, m), 5.69 (1H, m), 5.05 (2H, m), 2.44 (2H,m), 2.23 (2H,m).

¹³C NMR (126 MHz, CDCl₃) δ 138.1, 137.8, 137.1, 132.1, 130.3, 130.2, 129.3, 128.8, 128.5, 128.3, 128.2, 126.9, 126.6, 126.0, 115.0, 34.0, 33.6, 32.5, 28.0 ppm.

Spectral data is in agreement with the literature.¹⁹



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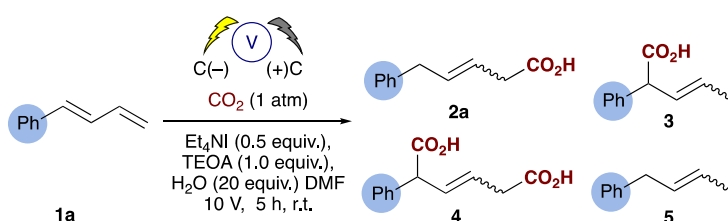
(1E,3(E,Z))-(hexa-1,3,5-trien-1-yl)benzene (8). Following the general procedure I using *trans*-cinnamaldehyde (1.0mL, 8 mmol), affording **8** (1.0 g, 80% yield) as a mixture of isomers (*E*:*Z* = 1:1). White solid

¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, *J* = 7.6 Hz, 2H, *E* isomer), 7.28 (d, *J* = 7.2 Hz, 2H, *Z* isomer), 7.22 (t, *J* = 7.0 Hz, 2H, *E* isomer), 7.19 (t, *J* = 7.2 Hz, 2H, *Z* isomer), 7.15 – 7.09 (m, 1H), 6.84 (dd, *J* = 15.6, 10.2 Hz, 1H, *E* isomer), 6.70 (dd, *J* = 15.4, 10.2 Hz, 1H, *Z* isomer), 6.48 (d, *J* = 15.9 Hz, 1H, *E* isomer), 6.44 (d, *J* = 15.6 Hz, 1H, *Z* isomer), 6.36 – 6.21 (m, 2H), 6.07 (t, *J* = 11.0 Hz, 1H, *E* isomer), 5.98 (t, *J* = 11.0 Hz, 1H, *Z* isomer), 5.21 (dd, *J* = 16.9, 1.2 Hz, 1H, *Z* isomer), 5.17 (dd, *J* = 16.1, 0.8 Hz, 1H, *E* isomer), 5.11 (dddd, *J* = 10.5, 2.2, 1.4, 0.9 Hz, 1H, *Z* isomer), 5.02 (d, *J* = 9.5 Hz, 1H, *E* isomer).

¹³C NMR (126 MHz, CDCl₃) δ 137.4 (*E* isomer), 137.4 (*Z* isomer), 137.2 (*E* isomer), 133.9 (*E* isomer), 133.7 (*E* isomer), 133.6 (*E* isomer), 133.1 (*Z* isomer), 132.3 (*Z* isomer), 130.5 (*Z* isomer), 130.3 (*Z* isomer), 128.9 (*E* isomer), 128.8 (*E* isomer), 128.8 (*Z* isomer), 127.9 (*E* isomer), 127.7 (*Z* isomer), 126.7 (*E* isomer), 126.5 (*Z* isomer), 124.1 (*Z* isomer), 118.5 (*E* isomer), 117.6 (*Z* isomer) ppm.

Spectral data is in agreement with the literature.⁷

3.0 Electrocarboxylation of dienes using a non-sacrificial electrochemical cell (Initial Procedure)



(E)-buta-1,3-dien-1-ylbenzene (1a). (130 mg, 1.0 mmol) was added to a solution of Et₄NI (128 mg, 0.5 mmol) and TEOA (1.0 mmol) in DMF (5 mL). The resulting mixture was flushed with CO₂ for 10 min and then electrolysed at a constant voltage of 10 V (current fluctuated from 60-100 mA) in a single compartment cell containing a carbon cathode and carbon anode with a constant CO₂ flow with stirring for 5h. The crude reaction mixture was acidified by addition of HCl/H₂O (1:1, 2 mL) and extracted with diethyl ether (3 x 5 mL) to afford an amber oil. ¹H NMR analysis showed the presence of three major components **2a**, **3** and **4** in a ratio of 1.7: 1: 1 and amount of reduced product **5** around 10% (detected by GCMS).

4.0 Optimisation Screening

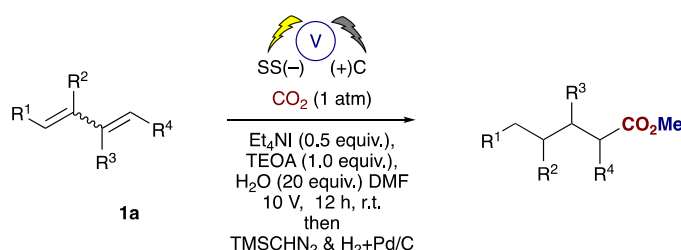
Electrode screening: The above procedure has been repeated by using different electrodes and the product analysed by GCMS.

Entry	Anode	Cathode	Ratio 2a : 3 : 4 : 5
1	C	C	1.7 : 1 : 1 : 1
2	C	Ni	0 : 0 : 0 : 1
3	C	Cu	3.8 : 1 : 1 : 2
4	C	SS	9 : 1 : 1 : 1
5	SS	SS	3.1 : 1 : 1 : 0

Water additive screen: The above procedure has been repeated but using a graphite electrode at anode and stainless steel at cathode with different amount of water.

Entry	Water amount	Ratio 2a : 3 : 4 : 5
1	5 eq.	9 : 1 : 0.82 : 0.7
2	10 eq.	9 : 1 : 0.74 : 0.7
3	15 eq.	9 : 1 : 0.69 : 0.65
4	20 eq.	9 : 1 : 0.51 : 0.6
5	1 mL	0

5.0 Optimised Procedure Used



General Procedure II: Substrate (1.0 mmol) was added to a solution of Et_4NI (128 mg, 0.5 mmol) and TEOA (149 mg, 1.0 mmol) in DMF (5 mL) and H_2O (360 μL , 20.0 mmol). The resulting mixture was flushed with CO_2 and kept under a positive pressure of CO_2 . The mixture was electrolysed at a constant voltage of 10V (current fluctuated from 60-100 mA) in a single compartment cell containing a stainless-steel cathode and carbon anode with stirring for 4h for substrates **1a-i**. The crude reaction mixture was acidified by addition of $\text{HCl}/\text{H}_2\text{O}$ (1:1, 2 mL) and extracted with diethylether (3 x 5mL). The combined organic phases were washed with brine, dried over MgSO_4 and filtered. The solvent was then removed under vacuum and it was dissolved in a 1:1 $\text{MeOH}:\text{Et}_2\text{O}$ mixture. 1 mL of trimethylsilyldiazomethane 2M solution in hexane was added and the reaction was stirred and after 30 minutes silica gel was added, and solvent was removed under vacuum. The monoacids were purified by column chromatography (hexane/ EtOAc mixtures), and the product was directly reduced by mixing it with 10% Pd/C (10.6 mg, 5 mol%) in 50 mL Methanol and stirred at room temperature for 24 h under 50 psi of hydrogen gas flow. The solution was filtered through celite and the solvent was removed under reduced pressure and the preparative TLC was used to separate the two acids.



Methyl 5-phenylpentanoate (2a') and Methyl 2-phenylpentanoate (3a') General procedure II was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**) (130.0 mg, 1.0 mmol), affording **2a'** and **3a'** (100.0 mg, 56.8% yield with ratio 9:1 respectively). Colorless oil.

^1H NMR (400 MHz, CDCl_3)

for **2a'** δ 7.28 – 7.14 (m, 5H), 3.65 (s, 3H), 2.61 (t, J = 7.2 Hz, 2H), 2.32 (t, J = 6.8 Hz, 2H), 1.68 – 1.60 (m, 4H).

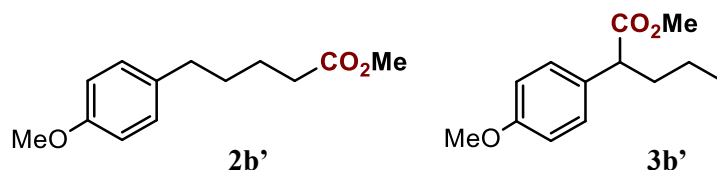
for **3a'** δ 7.30 - 7.15 (m, 5H), 3.63 (s, 3H), 3.54 (t, J = 7.6 Hz, 1H), 2.02 (m, 1H), 1.73 (m, 1H), 1.25 (m, 2H), 0.89 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3)

for **2a'** δ 174.1, 142.2, 128.4, 128.3, 125.8, 51.5, 35.6, 34.0, 30.9, 24.6.

for **3a'** δ 174.7, 139.3, 128.6, 128.0, 127.2, 51.9, 51.4, 35.7, 20.8, 13.8.

Spectral data is in agreement with the literature.^{11, 12}



Methyl 5-(4-methoxyphenyl)pentanoate (2b') and **Methyl 2-(4-methoxyphenyl)pentanoate (3b')**. General procedure II was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (**1b**) (160.0 mg, 1.0 mmol), affording **2b'** & **3b'** (120.0 mg, 58.2% yield with ratio 8.2:1 respectively). Colorless oil.

¹H NMR (400 MHz, CDCl₃)

for **2b'** δ 7.07 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.64 (s, 3H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.31 (t, *J* = 6.8 Hz, 2H), 1.65 – 1.58 (m, 4H).

for **3b'** δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H), 3.63 (s, 3H), 3.49 (t, *J* = 7.6 Hz, 1H), 2.00 (m, 1H), 1.71 (m, 1H), 1.22 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃)

for **2b'** δ 174.2, 157.8, 134.2, 129.3, 113.8, 55.3, 51.5, 34.6, 34.0, 31.2, 24.6.

for **3b'** δ 175.0, 158.7, 131.4, 128.9, 114.0, 55.3, 51.9, 50.5, 35.7, 20.7, 13.8.

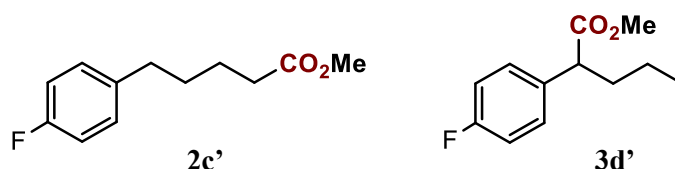
IR (neat, cm⁻¹)

for **3b'** 2959, 1733, 1611, 1512, 1436, 1257, 1100, 1034, 829, 794.

HRMS ESI,

for **3b'** (C₁₃H₁₈NaO₃) [M+Na]⁺ calculated 245.1154, found 245.1151.

Spectral data for **2b'** is in agreement with the literature.¹⁰



Methyl 5-(4-fluorophenyl)pentanoate (2c') and **Methyl 2-(4-fluorophenyl)pentanoate (3c')**. General procedure II was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (**1c**) (148.0 mg, 1.0 mmol), affording **2c'** & **3c'** (98.0 mg, 50.5% yield with ratio 6.2:1 respectively). Colorless oil.

¹H NMR (400 MHz, CDCl₃)

for **2c'** δ 7.10 (dd, *J* = 8.8, 5.6, 2.8 Hz, 2H), 6.94 (t, *J* = 8.8 Hz, 2H), 3.65 (s, 3H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.31 (t, *J* = 6.8 Hz, 2H), 1.68 – 1.58 (m, 4H).

for **3c'** δ 7.27 (d, *J* = 5.2 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 3.64 (s, 3H), 3.52 (t, *J* = 7.6 Hz, 1H), 2.01 (m, 1H), 1.69 (m, 1H), 1.26 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃)

for **2c'** δ 174.0, 137.7 (d, *J* = 3.8 Hz), 129.7 (d, *J* = 7.6 Hz), 115.1 (d, *J* = 21.0 Hz), 51.5, 34.8, 33.9, 31.0, 24.5.

for **3c'** δ 174.5, 134.9, 129.4, 115.5, 115.3, 52.0, 50.6, 35.8, 20.7, 13.8.

¹⁹F NMR (375 MHz, CDCl₃)

for **2c'** δ -117.7.

for **3c'** δ -115.5.

IR (neat, cm^{-1})

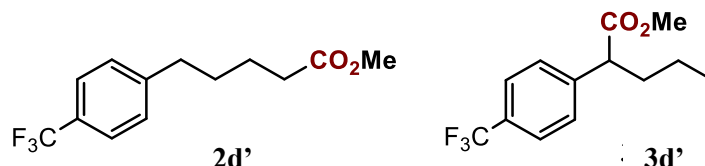
for **2c'** 2948, 1736, 1601, 1509, 1436, 1363, 1219, 1157, 1097, 823.

for **3c'** 2961, 1733, 1643, 1510, 1463, 1260, 1095, 1019, 798.

HRMS ESI,

for **2c'** ($\text{C}_{12}\text{H}_{15}\text{FNaO}_2$) $[\text{M}+\text{Na}]^+$ calculated 233.0954, found 233.0951.

for **3c'** ($\text{C}_{12}\text{H}_{15}\text{FNaO}_2$) $[\text{M}+\text{Na}]^+$ calculated 233.0954, found 233.0955.



Methyl 5-(4-(trifluoromethyl)phenyl)pentanoate (2d') and **Methyl 2-(4-(trifluoromethyl)phenyl)pentanoate (3d')**. General procedure II was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (**1d**) (198.0 mg, 1.0 mmol), affording **2d'** & **3d'** (110.0 mg, 45.0% yield with ratio 1:5.5 respectively). Colorless oil.

^1H NMR (500 MHz, CDCl_3)

for **2d'** δ 7.47 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 3.60 (s, 3H), 2.63 (t, J = 7.0 Hz, 2H), 2.28 (t, J = 7.0 Hz, 2H), 1.63 – 1.58 (m, 4H).

for **3d'** δ 7.56 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 3.65 (s, 3H), 3.61 (t, J = 8.0 Hz, 1H), 2.03 (m, 1H), 1.75 (m, 1H), 1.26 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3)

for **2d'** δ 173.9, 146.2, 128.7, 125.3, 125.3, 125.2, 51.6, 35.4, 33.8, 30.6, 24.5.

for **3d'** δ 173.9, 143.2, 129.7, 128.4, 125.6, 125.5, 52.1, 51.2, 35.6, 20.7, 13.7.

^{19}F NMR (475 MHz, CDCl_3)

for **2d'** δ -62.4.

for **3d'** δ -62.4.

IR (neat, cm^{-1})

for **2d'** 2918, 1732, 1673, 1463, 1325, 1161, 1125, 1067, 1018, 801.

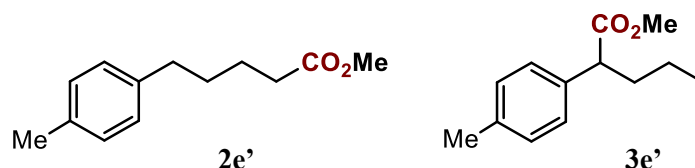
for **3d'** 2923, 1737, 1619, 1462, 1419, 1165, 1126, 1068, 1019, 800.

HRMS ESI,

for **2d'** ($\text{C}_{13}\text{H}_{15}\text{F}_3\text{NaO}_2$) $[\text{M}+\text{Na}]^+$ calculated 283.0922, found 283.0919.

for **3d'** ($\text{C}_{13}\text{H}_{15}\text{F}_3\text{NaO}_2$) $[\text{M}+\text{Na}]^+$ calculated 283.0922, found 283.0921.

Spectral data is in agreement with the literature.^{8,9}



Methyl 5-(*p*-tolyl)pentanoate (2e') and **Methyl 2-(*p*-tolyl)pentanoate (3e')**. General procedure II was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-methylbenzene (**1e**) (144.0 mg, 1.0 mmol), affording **2e'** & **3e'** (108.0 mg, 56.8% yield with ratio 7.4:1 respectively). Faint yellow oil.

^1H NMR (400 MHz, CDCl_3)

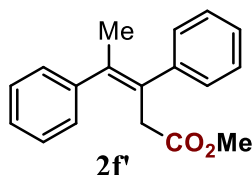
for **2e'** δ 7.07 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 3.64 (s, 3H), 2.57 (t, J = 7.6 Hz, 2H), 2.31 (t, J = 7.2 Hz, 2H), 2.30 (s, 3H), 1.67 – 1.57 (m, 4H).

for **3e'** δ 7.17 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 3.62 (s, 3H), 3.50 (t, J = 7.2 Hz, 1H), 2.31 (s, 3H), 2.00 (m, 1H), 1.72 (m, 1H), 1.25 (m, 2H), 0.88 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3)

for **2e'** δ 174.2, 139.1, 135.2, 129.0, 128.3, 51.5, 35.1, 34.0, 31.0, 24.6, 21.0.

for **3e'** δ 174.8, 136.8, 136.3, 129.3, 127.8, 51.9, 51.0, 35.6, 21.1, 20.7, 13.8.



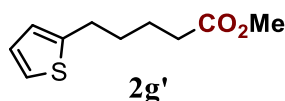
Methyl 3,4-diphenylpent-3-enoate (2f'). General procedure II was followed (without hydrogenation step) using 2,3-Diphenyl-1,3-butadiene (**1f**) (206.0 mg, 1.0 mmol), affording **2f'** (150.0 mg, 59.5% yield). Colorless solid.

^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.24 (m, 10H), 3.52 (s, 3H), 3.26 (s, 2H), 1.89 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.3, 143.5, 141.9, 138.0, 130.2, 128.8, 128.4, 128.2, 127.9, 126.9, 126.8, 51.6, 41.1, 22.8.

IR (neat, cm^{-1}) 2918, 1736, 1600, 1492, 1436, 1163, 1015, 701.

HRMS ESI, ($\text{C}_{18}\text{H}_{18}\text{NaO}_2$) [$\text{M}+\text{Na}$] $^+$ *calculated* 289.3298, *found* 289.3299.

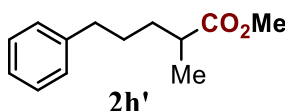


Methyl 5-(thiophen-2-yl)pentanoate (2g'). General procedure II was followed using (*E,Z*)-2-(buta-1,3-dien-1-yl)thiophene (**1g**) (136.0 mg, 1.0 mmol), affording **2g'** (100.0 mg, 54.9% yield). Yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.05 (dd, J = 4.8, 1.2 Hz, 1H), 6.85 (dd, J = 5.2, 3.6 Hz, 1H), 6.72 (d, J = 4.4 Hz, 1H), 3.60 (s, 3H), 2.78 (t, J = 7.2 Hz, 2H), 2.28 (t, J = 7.2 Hz, 2H), 1.70 – 1.60 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 173.0, 143.9, 125.7, 123.2, 121.9, 50.5, 32.8, 30.2, 28.5, 23.3.

Spectral data is in agreement with the literature.¹⁰

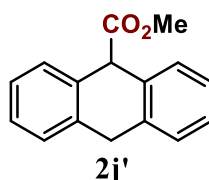


Methyl 2-methyl-5-phenylpentanoate (2h'). General procedure II was followed using (*E,Z*)-Penta-1,3-dien-1-ylbenzene (**1h**) (144.0 mg, 1.0 mmol), affording **2h'** (110.0 mg, 57.8% yield). Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 7.22 – 7.09 (m, 5H), 3.59 (s, 3H), 2.54 (t, J = 7.5 Hz, 2H), 2.40 (six, J = 7.0 Hz, 1H), 1.68 – 1.60 (m, 1H), 1.58 – 1.51 (m, 2H), 1.43 – 1.36 (m, 1H), 1.08 (d, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 177.2, 142.2, 128.4, 128.3, 125.8, 51.5, 39.4, 35.8, 33.4, 29.1, 17.1.

Spectral data is in agreement with the literature.⁹

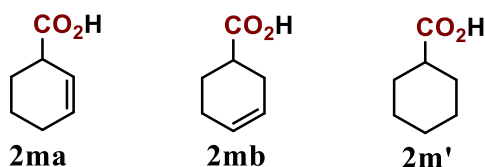


Methyl 9,10-dihydroanthracene-10-carboxylate (2j'). General procedure II was followed (without hydrogenation step) using Anthracene (178.1 mg, 1.0 mmol), affording **2j'** (140.0 mg, 62.5% yield). White solid.

¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.23 (m, 8H), 5.00 (s, 1H), 4.32 (d, J = 18.5 Hz, 1H), 3.90 (d, J = 18.0 Hz, 1H), 3.58 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 172.4, 136.7, 133.8, 128.3, 128.1, 127.5, 126.4, 52.9, 52.4, 35.7.

Spectral data is in agreement with the literature.¹⁵



2-Cyclohexene-1-carboxylic acid (2ma) and 3-Cyclohexene-1-carboxylic acid (2mb). General procedure II was followed using Cyclohexa-1,3-diene (**1m**) (80.0 mg, 1.0 mmol), affording **2ma** & **2mb** (100.0 mg, 79.3% yield with ratio 1.65:1 respectively) without methylation and hydrogenation steps. Colorless oil. And after hydrogenation step, **Cyclohexane carboxylic acid (2m')** was obtained.

¹H NMR (400 MHz, CDCl₃)

for **2ma&2mb** δ 10.93 (br, 1H), 5.89-5.64 (m, 2H), 3.12 (m, 1H, **3ka** C-H), 2.60 (m, 1H, **3kb** C-H), 2.26-1.53 (m, 6H).

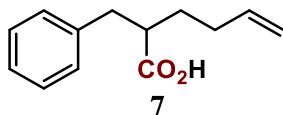
for **2m'** δ 9.05 (br, 1H), 2.26 (m, 1H), 1.92-1.15 (m, 10H).

¹³C NMR (101 MHz, CDCl₃)

for **2ma&2mb** δ 182.4, 181.2, 130.2, 126.8, 125.0, 123.6, 40.9, 39.1, 27.2, 25.1, 24.8, 24.6, 24.3, 20.7.

for **2m'** δ 182.2, 43.2, 28.9, 25.8, 25.4.

Spectral data is in agreement with the literature.^{16,17,18}

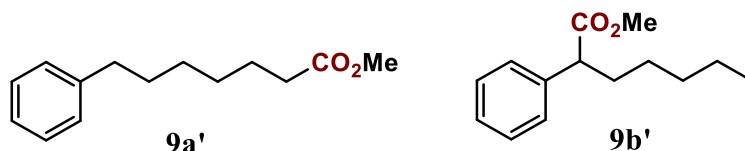


2-Benzylhex-5-enoic Acid (7). General procedure II was followed (without hydrogenation and methylation steps) using (*E,Z*)-1,5-Hexadien-1-ylbenzene (**6**) (158.1 mg, 1.0 mmol), affording **7** (150.0 mg, 73.5% yield). Colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 11.22 (br, 1H), 7.32 – 7.16 (m, 5H), 5.73 (m, 1H), 4.98 (m, 2H), 2.97 (m, 1H), 2.73 (m, 2H), 2.11 (m, 2H), 1.78 (m, 1H), 1.74 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 181.1, 138.9, 137.5, 128.9, 128.5, 126.5, 115.5, 46.7, 38.1, 31.4, 30.7.

Spectral data is in agreement with the literature.²⁰



Methyl 7-phenylheptanoate (9a') and **Methyl 2-phenylheptanoate (9b')**. General procedure II was followed using (1*E*,3(*E*,*Z*))-hexa-1,3,5-trien-1-yl)benzene (**8**) (156.0 mg, 1.0 mmol), affording **9a'** & **9b'** (120.0 mg, 59.4% yield with ratio 6:1 respectively). Colorless oil.

¹H NMR (400 MHz, CDCl₃)

for **9b'** δ 7.37 - 7.27 (m, 5H), 3.69 (s, 3H), 3.57 (t, *J* = 7.6 Hz, 1H), 2.09 (m, 1H), 1.80 (m, 1H), 1.25 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H).

for **9a'** δ 7.24 - 7.09 (m, 5H), 3.60 (s, 3H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.23 (t, *J* = 7.6 Hz, 2H), 1.59 - 1.52 (m, 4H), 1.30 - 1.26 (m, 4H).

¹³C NMR (101 MHz, CDCl₃)

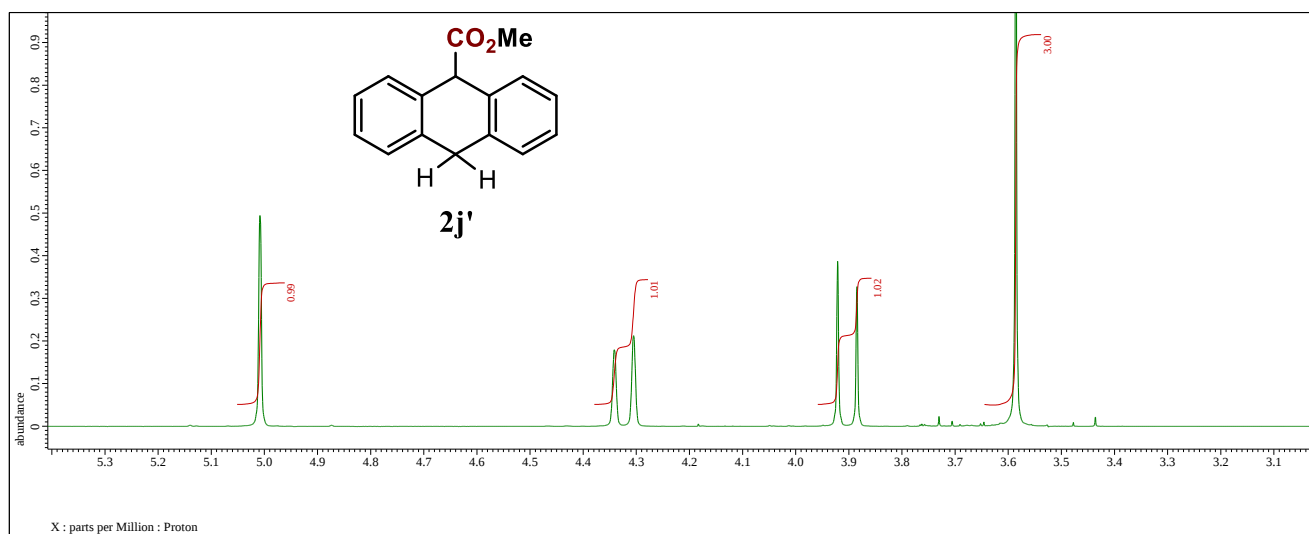
for **9b'** δ 174.7, 139.3, 128.6, 127.9, 127.2, 51.9, 51.7, 33.6, 31.6, 27.3, 22.5, 14.0.

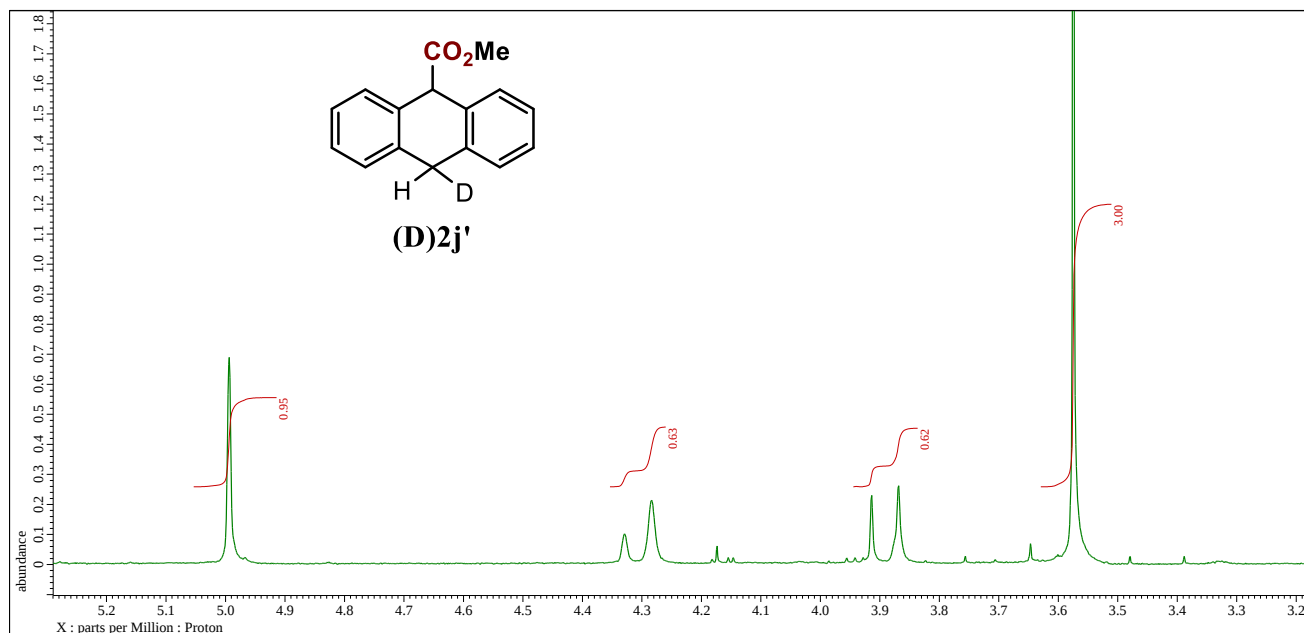
for **9a'** δ 174.3, 142.7, 128.4, 128.3, 125.6, 51.5, 35.9, 34.1, 31.3, 29.0, 28.9, 24.9.

Spectral data is in agreement with the literature.^{13,14}

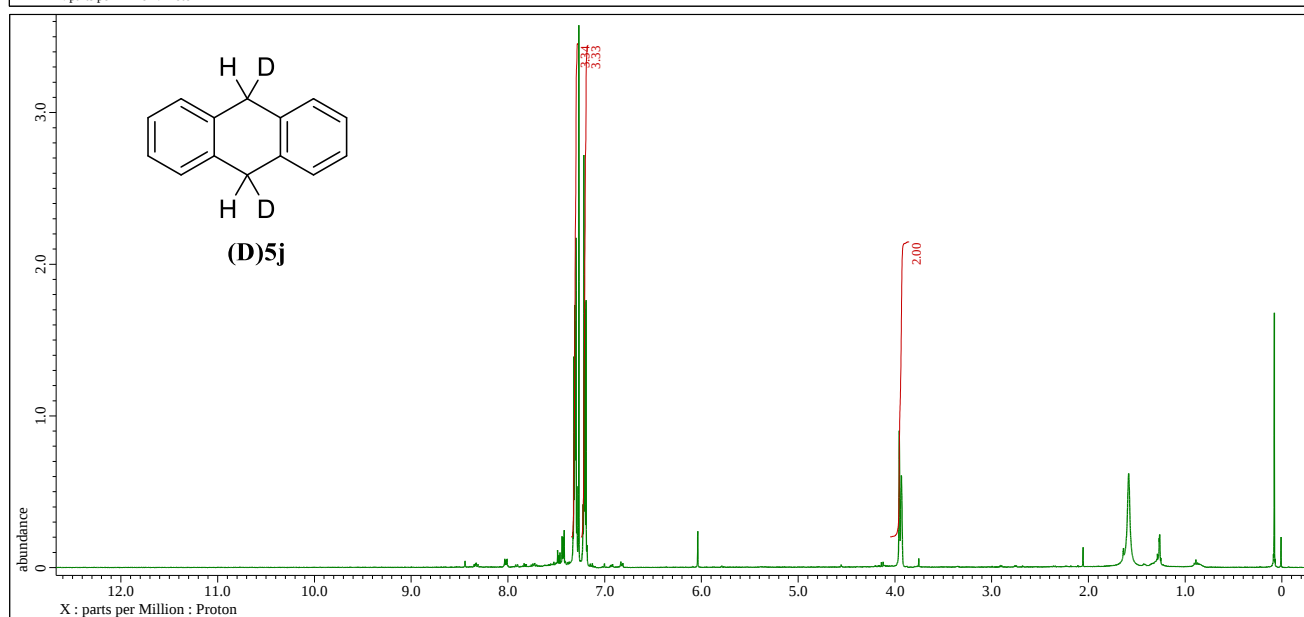
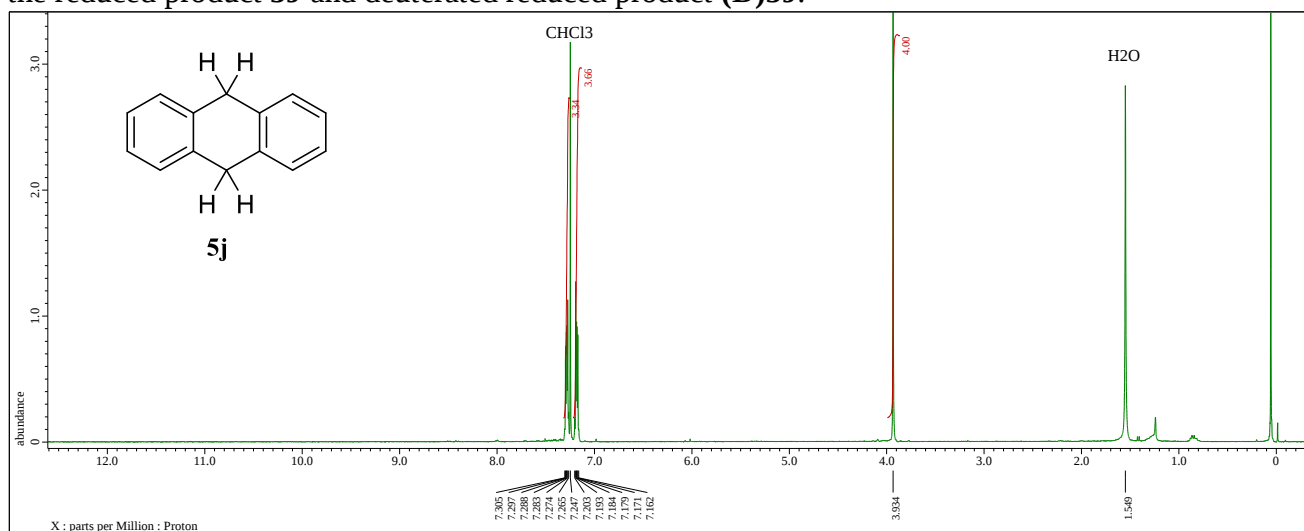
Deuterium Labelling Studies

Following the general procedure II but using D₂O instead of H₂O and starting with Anthracene affording the deuterated product (**D**)**2j'**.



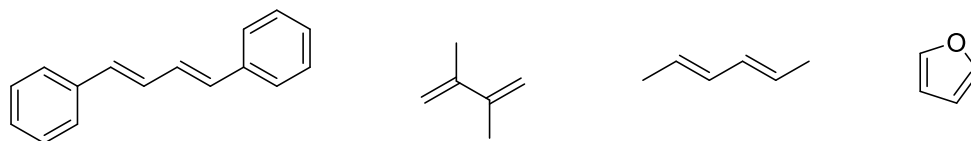


Following the general procedure II but using D_2O or H_2O and no CO_2 starting with Anthracene affording the reduced product **5J** and deuterated reduced product **(D)5J**.



Unsuccessful substrates

The following compounds were tested under the optimized reaction conditions. In all cases, we observed no conversion to product or less than 30% yield of the corresponding carboxylic acid derivatives.



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