Supporting Information for:

Selective Palladium-catalysed Synthesis of Diesters: Alkoxycarbonylation of a CO_2-butadiene derived δ-lactone

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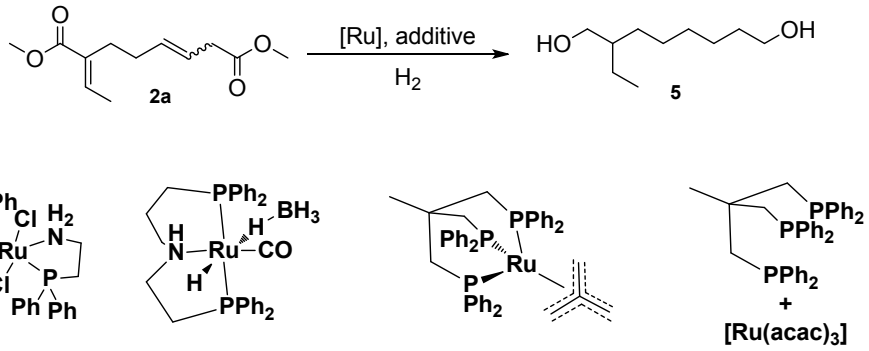
1. Hydrogenation of dimethyl 7-ethylideneoct-3-enedioate (2a) to 2-ethyloctane-1,8-diol (5) with homogeneous catalysts.

General procedure for hydrogenation of 2-ethyloctane-1,8-diol 5. Metal complex or catalyst precursor and ligand were quickly weighed in a 4 mL vial in the air. The vial was then sealed, connected to the atmosphere with a needle and evacuated and refilled with argon for three times. **2a** (0.5 mmol) and a stock solution of the solvent containing the appropriate additive were added. The vial was placed inside a 300 mL stainless steel Parr autoclave and the autoclave was flushed three times with nitrogen, pressurized with hydrogen and heated. After the reaction time, the autoclave was cooled with ice water and vented. The crude was analyzed by gas-chromatography.

Table S1. Hydrogenation of **2a** to **5**.[a]



Entry	Catalyst	Solvent	Additive (mol%)	CO (bar)	T (°C)	t (h)	5 Yield (%)
1	**c1**	THF	MeONa (10)	50	120	22	traces
2	**c2**	THF	-	50	120	22	8
3	**c3**	THF	-	70	150	22	2
4	**c4**	MeOH	MSA (10)	70	150	22	35
5	**c4**	MeOH	$HNTf_2$ (10)	70	150	22	69
6	**c4**	MeOH	MSA (5)/Zn (5)	70	150	24	42
7	**c4**	MeOH	$HNTf_2$ (5)/Zn (5)	70	150	24	91
8	**c4**	MeOH	MeONa	70	150	22	17
9	**c4**	dioxane	$HNTf_2$ (5)	70	150	22	24

[a]Reactions conditions: **2a** (0.5 mmol), metal complex (0.01mmol), ligand when added (0.02 mmol), solvent (2 mL). Conversion of **2a** was complete in all cases. Yields were determined by GC analysis using hexadecane as the internal standard.

2. Characterization of products and NMR spectra

Dimethyl 7-ethylideneoct-3-enedioate (2a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (q, J = 7.1 Hz, 1H, E/Z isomers), 5.56 – 5.38 (m, 2H, E/Z isomers), 3.65 (s, 3H, OCH_3, Z isomer), 3.64 (s, 3H, OCH_3, E isomer), 3.60 (s, 3H, OCH_3, Z isomer), 3.59 (s, 3H, OCH_3, E/Z isomers), 3.00 (d, J = 5.9 Hz, 2H, Z isomer), 2.94 (d, J = 5.1 Hz, 2H, E isomer), 2.35 – 2.24 (m, 2H, E/Z isomers), 2.12 – 1.97 (m, 2H, E/Z isomers), 1.73 (d, 3H, CHCH_3, Z isomer overlapped with the CHCH_3 signal of E isomer), 1.71 ppm (d, J = 7.1 Hz, 3H, CH_3, E isomer).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 172.3 (Z isomer), 168.15, 168.11 (Z isomer) , 138.2 (Z isomer), 138.0, 133.8, 132.3, 132.3 (Z isomer), 132.2 (Z isomer), 122.2, 121.6 (Z isomer), 51.82 (Z isomer), 51.76, 51.6, 37.91, 32.7 (Z isomer), 31.8, 26.7 (Z isomer), 26.15, 26.09 (Z isomer), 14.4 (Z isomer), 14.3 ppm.
GCMS-EI m/z (%) = 226 (M^+, 1), 194 (13), 179 (7), 162 (100), 147 (10), 134 (67), 120 (20), 107 (29), 93 (16), 91 (20), 81 (22), 71 (26), 59 (30).
ESI-HRMS calcd for $C_{12}H_{18}O_4Na$ $[M+Na]^+$: 249.10973; found: 227.10976.

Dibutyl 7-ethylideneoct-3-enedioate (2b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (q, *J* = 7.1 Hz, 1H, E/Z isomers), 5.71 – 5.27 (m, 2H, E/Z isomers), 4.11 – 3.92 (m, 4H, E/Z isomers), 2.99 (d, *J* = 5.4 Hz, 2H, Z isomer), 2.93 (d, *J* = 5.1 Hz, 2H, E isomer), 2.31 (t, *J* = 7.6 Hz, 2H, E/Z isomers), 2.16 – 1.90 (m, 2H, E/Z isomers), 1.73 (d, 3H, CHCH_3, Z isomer overlapped with the CHCH_3 signal of E isomer), 1.70 (d, *J* = 7.2 Hz, 3H, CH_3, E isomer), 1.63 – 1.45 (m, 4H, E/Z isomers), 1.43 – 1.15 (m, 4H, E/Z isomers), 0.86 ppm (m, 6H, E/Z isomers).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 171.8 (Z isomer), 167.6, 137.6 (Z isomer), 137.4, 133.5, 132.6, 132.5 (Z isomer), 132.0 (Z isomer), 122.3, 121.7 (Z isomer), 64.3, 64.1, 38.1, 32.8 (Z isomer), 31.8, 30.7, 30.6, 26.7 (Z isomer), 26.1, 26.0 (Z isomer), 19.2, 19.1, 14.2, 13.7, 13.6 ppm.
GCMS-EI m/z (%) = 310 (M^+, 1), 236 (7), 208 (6), 179 (11), 162 (100), 147 (8), 134 (50), 120 (11), 107 (22), 99 (13), 93 (12), 81 (13), 67 (5), 57 (27), 54 (26), 41 (39).
EI-HRMS calcd for $C_{18}H_{30}O_4$ $[M]^+$: 310.21386; found: 310.21401.

Bis(2-ethylhexyl) 7-ethylideneoct-3-enedioate (2c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (q, *J* = 7.1 Hz, 1H, E/Z isomers), 5.63 – 5.33 (m, 2H, E/Z isomers), 4.08 – 3.89 (m, 4H, E/Z isomers), 3.05 (d, *J* = 5.3 Hz, 2H, Z isomer), 2.99 (d, *J* = 5.3 Hz, 2H, Z isomer), 2.50 – 2.23 (m, 2H, E/Z isomers), 2.19 – 2.01 (m, 2H, E/Z isomers), 1.79 (d, 3H, CHCH_3, Z isomer overlapped with the CHCH_3 signal of E isomer), 1.76 (d, *J* = 7.2 Hz, 3H, CHCH_3, E isomer), 1.65 – 1.44 (m, 2H, E/Z isomers), 1.43 – 1.12 (m, 16H, E/Z isomers), 0.98 – 0.77 ppm (m, 12H, E/Z isomers).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 167.8, 137.8 (Z isomer), 137.6, 133.6, 132.6, 132.1 (Z isomer), 122.4, 121.7 (Z isomer), 67.0, 66.6, 38.9, 38.7, 38.2, 33.0 (Z isomer), 31.9, 30.6, 30.4, 28.98, 28.91, 26.8 (Z isomer), 26.3, 26.1 (Z isomer), 24.0, 23.8, 23.0, 14.4 (Z isomer), 14.3, 14.0, 11.1, 11.0 ppm.
GCMS-EI m/z (%) = 422 (M^+, 0.3), 292 (4), 264 (4), 198 (4), 180 (44), 162 (100), 152 (12), 134 (29), 107 (15), 81 (8), 71 (44), 57 (69), 43 (41).
EI-HRMS calcd for $C_{26}H_{46}O_4$ $[M]^+$: 422.33906; found: 422.33917.

Dibenzyl 7-ethylideneoct-3-enedioate (2d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 10H, E/Z isomers), 6.92 (q, *J* = 7.1 Hz, 1H, E/Z isomers), 5.67 – 5.43 (m, 2H, E/Z isomers), 5.16 (s, 2H, E/Z isomers), 5.10 (s, 2H, E/Z isomers), 3.07 (d, *J* = 5.2 Hz, 2H, Z isomer), 3.03 (d, *J* = 4.2 Hz, 2H, E isomer), 2.50 – 2.30 (m, 2H E/Z isomers), 2.21 – 2.08 (m, 2H E/Z isomers), 1.75 (d, *J* = 7.1 Hz, 3H, CHCH_3, Z isomer overlapped with the CHCH_3 signal of E isomer), 1.74 ppm (d, *J* = 7.2 Hz, 3H, CHCH_3, Z isomer overlapped with the CHCH_3 signal of E isomer).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 171.6 (Z isomer), 167.3, 138.5 (Z isomer), 138.4, 136.4, 135.9, 133.8, 132.3, 132.2 (Z isomer), 128.5, 128.2, 128.0, 127.9, 122.2, 121.6 (Z isomer), 66.3, 66.1, 38.0, 32.8 (Z isomer), 31.8, 26.8 (Z isomer), 26.1, 26.0 (Z isomer), 14.3 ppm.
GCMS-EI m/z (%) = 287 (2), 269 (3), 251 (3), 223 (2), 181 (2), 163 (4), 107 (2), 91 (100), 65 (7).
ESI-HRMS calcd for $C_{24}H_{26}O_4Na$ $[M+Na]^+$: 401.17233; found: 401.17243.

Diisopropyl 7-ethylideneoct-3-enedioate (2e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.81 (q, *J* = 7.1 Hz, 1H, E/Z isomers), 5.67 – 5.33 (m, 2H, E/Z isomers), 5.07 – 4.86 (m, 2H, E/Z isomers), 3.01 (d, *J* = 5.7 Hz, 2H, Z isomer), 2.94 (d, *J* = 5.2 Hz, 2H, E isomer), 2.38 – 2.28 (m, 2H, E/Z isomers), 2.20 – 2.02 (m, 2H, E/Z isomers), 1.76 (d, 3H, CHCH_3, Z isomer overlapped with the CHCH_3 signal of E isomer), 1.74 (d, *J* = 7.1 Hz, 3H, CHCH_3, E isomer), 1.30 – 0.81 ppm (m, 12H, E/Z isomers).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 167.2, 137.4 (Z isomer), 137.2, 133.6, 132.9, 132.0 (Z isomer), 122.4, 121.9 (Z isomer), 67.8, 67.8, 67.5, 67.4, 38.4, 33.2 (Z isomer), 31.8, 26.8 (Z isomer), 26.2, 26.1 (Z isomer), 21.9, 21.8, 14.3 (Z isomer), 14.3 ppm.

GCMS-EI m/z (%) = 285 (M^+, 0.3), 240 (2), 222 (5), 198 (4), 194 (4), 180 (25), 162 (67), 153 (11), 134 (46), 107 (27), 93 (16), 81 (16), 67 (7), 54 (35), 43 (100).

ESI-HRMS calcd for $C_{16}H_{26}O_4Na$ $[M+Na]^+$: 305.17233; found: 305.17229.

Dimethyl 2-ethylideneoctanedioate (3): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (q, *J* = 7.1 Hz, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 2.38 – 2.18 (m, 4H), 1.76 (d, *J* = 7.1 Hz, 3H), 1.67 – 1.55 (m, 2H), 1.45 – 1.20 ppm (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 168.4, 137.5, 133.2, 51.7, 51.5, 34.1, 29.1, 28.7, 26.3, 24.9, 14.3.ppm.

GCMS-EI m/z (%) = 228 (M^+, 1), 196 (81), 181 (9), 164 (55), 153 (8), 137 (43), 122 (15), 109 (39), 94 (51), 81 (49), 67 (45), 59 (100), 55 (59), 41 (41).

ESI-HRMS calcd for $C_{12}H_{20}O_4Na$ $[M+Na]^+$: 251.12538; found: 251.12543.

Dimethyl 2-ethyloctanedioate (4): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.61 (s, 3H), 3.60 (s, 3H), 2.32 – 2.14 (m, 3H), 1.49 (m, 6H), 1.32 – 1.12 (m, 4H), 0.82 ppm (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 174.1, 51.5, 51.3, 47.2, 34.0, 31.9, 29.1, 27.1, 25.5, 24.8, 11.8 ppm.

GCMS-EI m/z (%) = 199 (8), 171 (25), 166 (34), 157 (13), 138 (29), 129 (22), 114 (11), 102 (97), 97 (45), 87 (100), 69 (56), 59 (93), 55 (97), 41 (57).

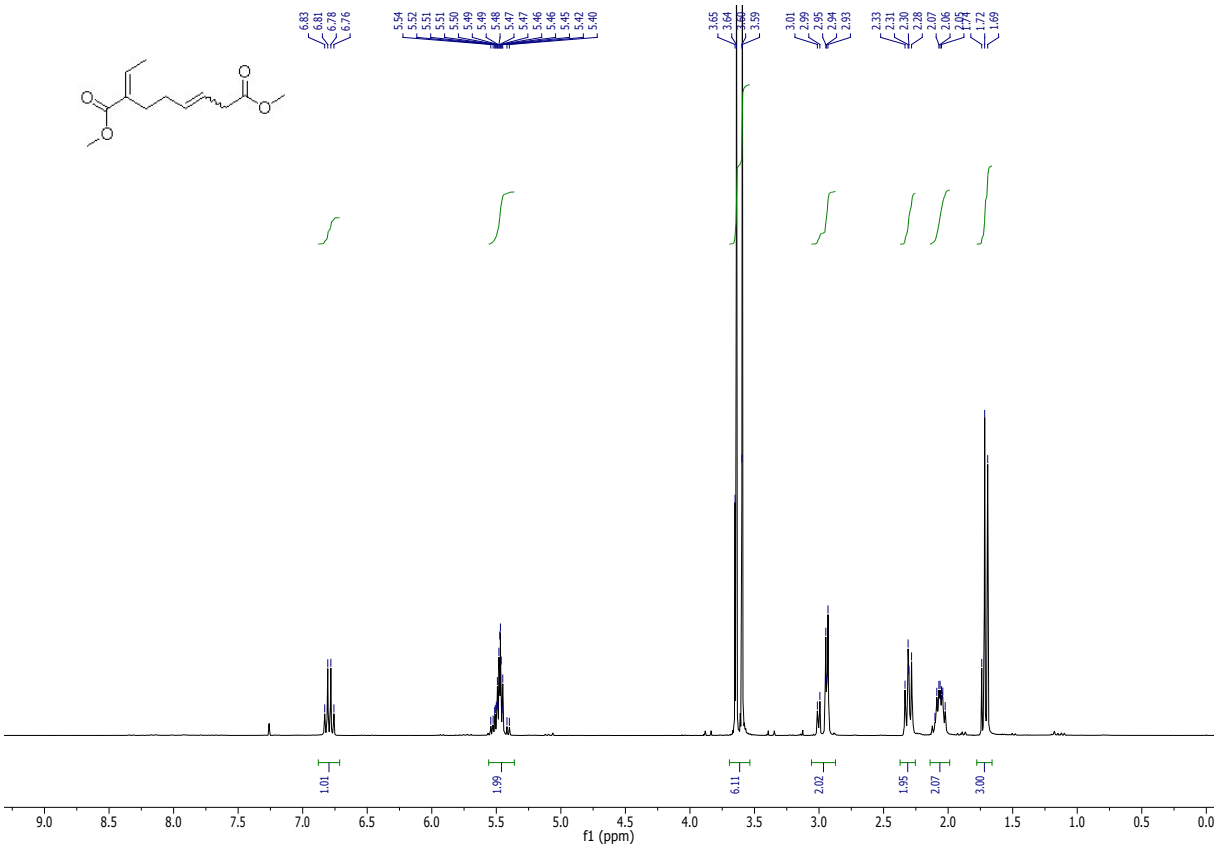
ESI-HRMS calcd for $C_{12}H_{22}O_4Na$ $[M+Na]^+$: 253.14103; found: 253.14109.

2-Ethyloctane-1,8-diol (5): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.6 Hz, 2H), 3.53 (d, *J* = 5.0 Hz, 2H), 2.42 (br s, 2H), 1.70 – 1.47 (m, 2H), 1.44 – 1.15 (m, 11H), 0.88 ppm (t, *J* = 7.3 Hz, 3H).

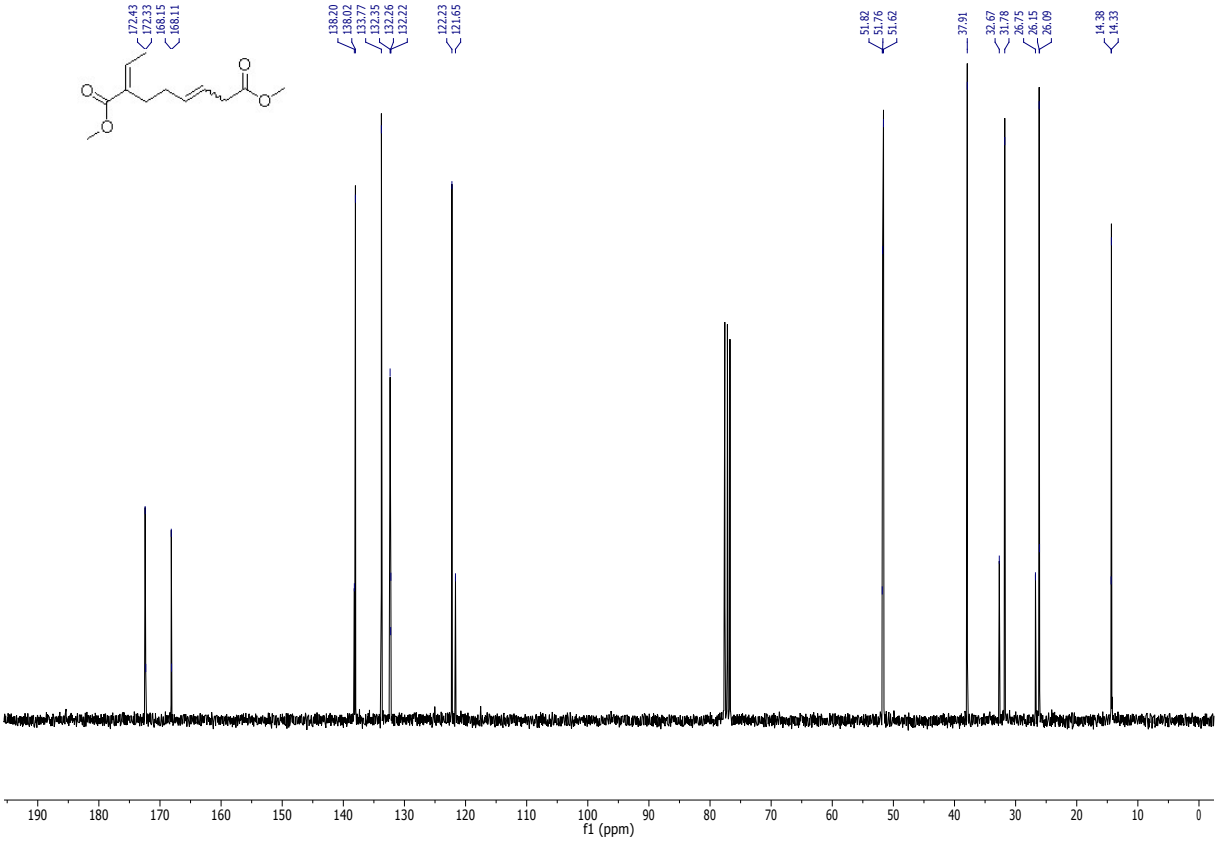
^{13}C NMR (75 MHz, $CDCl_3$) δ 65.0, 62.7, 41.9, 32.7, 30.3, 29.8, 26.8, 25.7, 23.3, 11.1.

GCMS-EI m/z (%) =172 (M^+, 0.3), 144 (2), 126 (16), 109 (24), 97 (52), 83 (61), 69 (88), 55 (100).

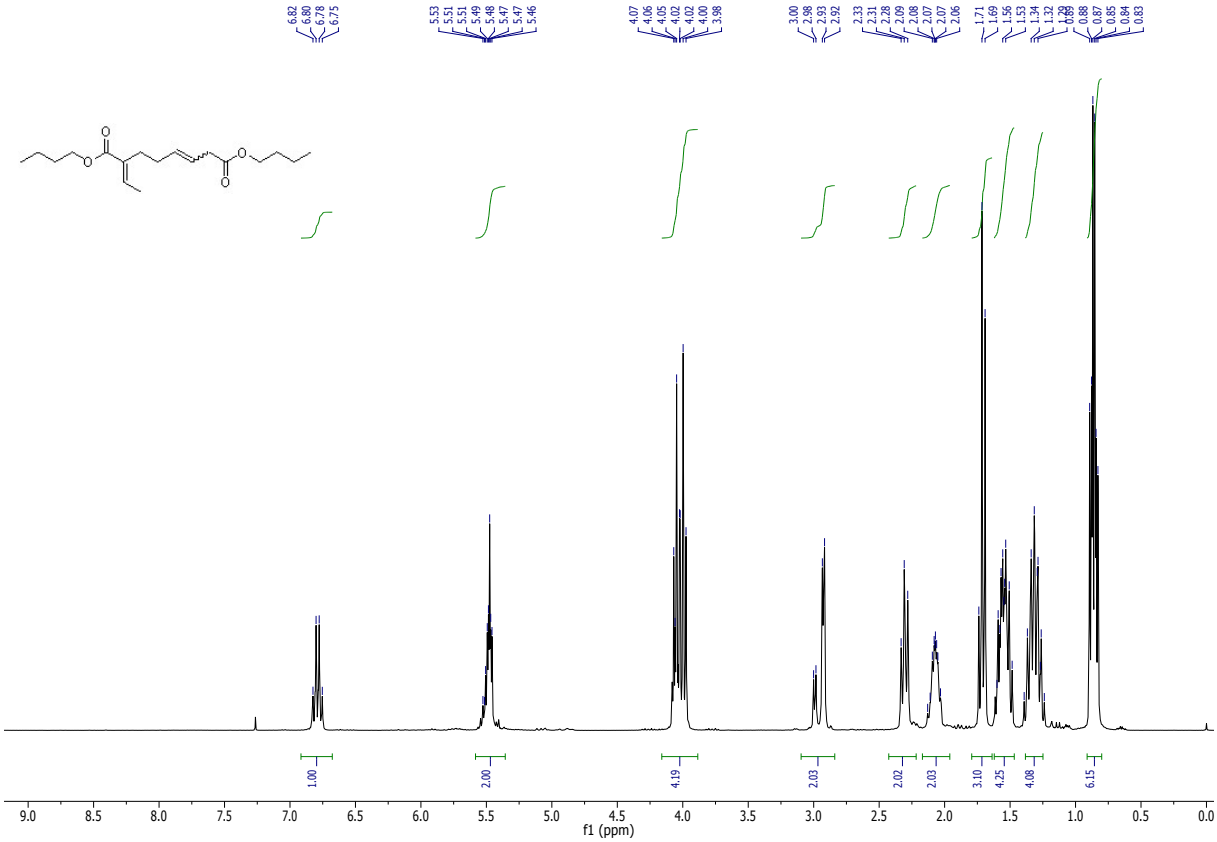
ESI-HRMS calcd for $C_{10}H_{23}O_2$ $[M+H]^+$: 175.16926; found: 175.16928.



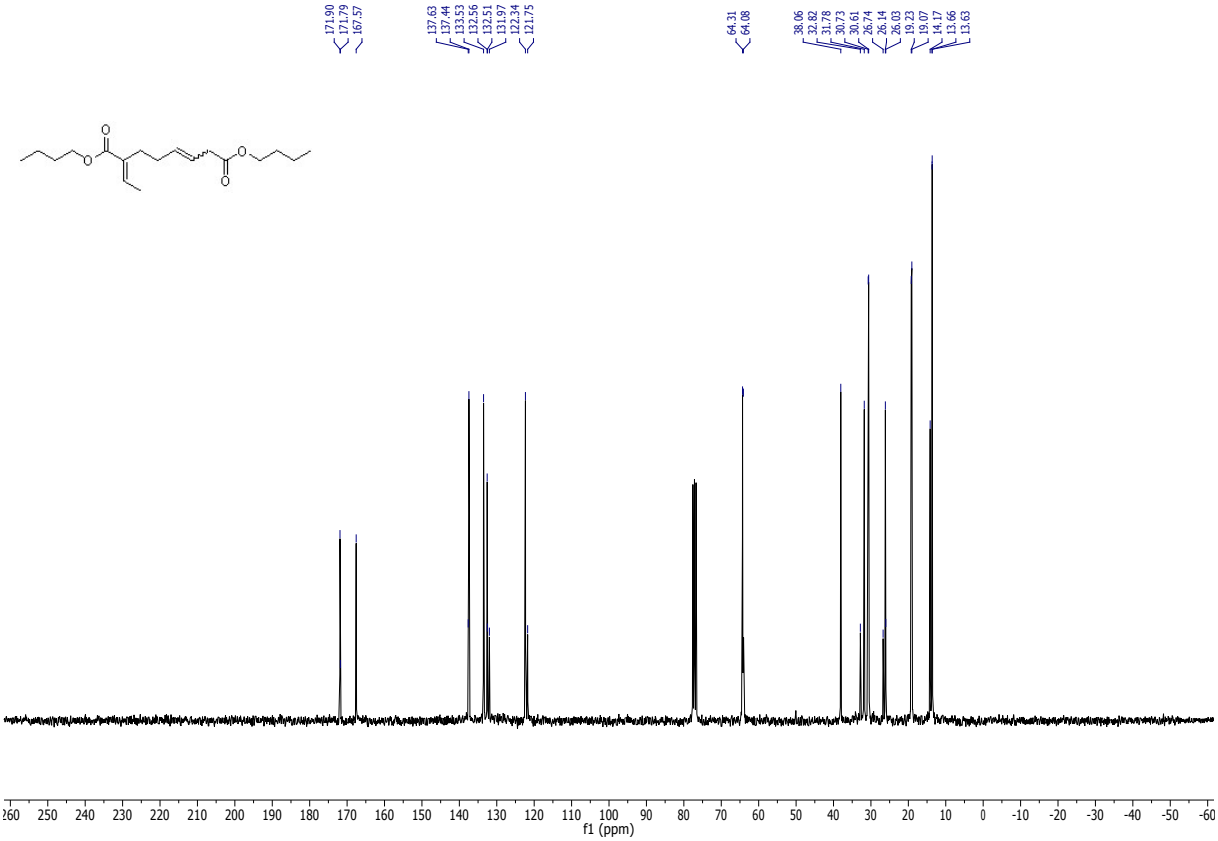
^{1}H NMR (300 MHz, $CDCl_3$) dimethyl 7-ethylideneoct-3-enedioate, **2a**.



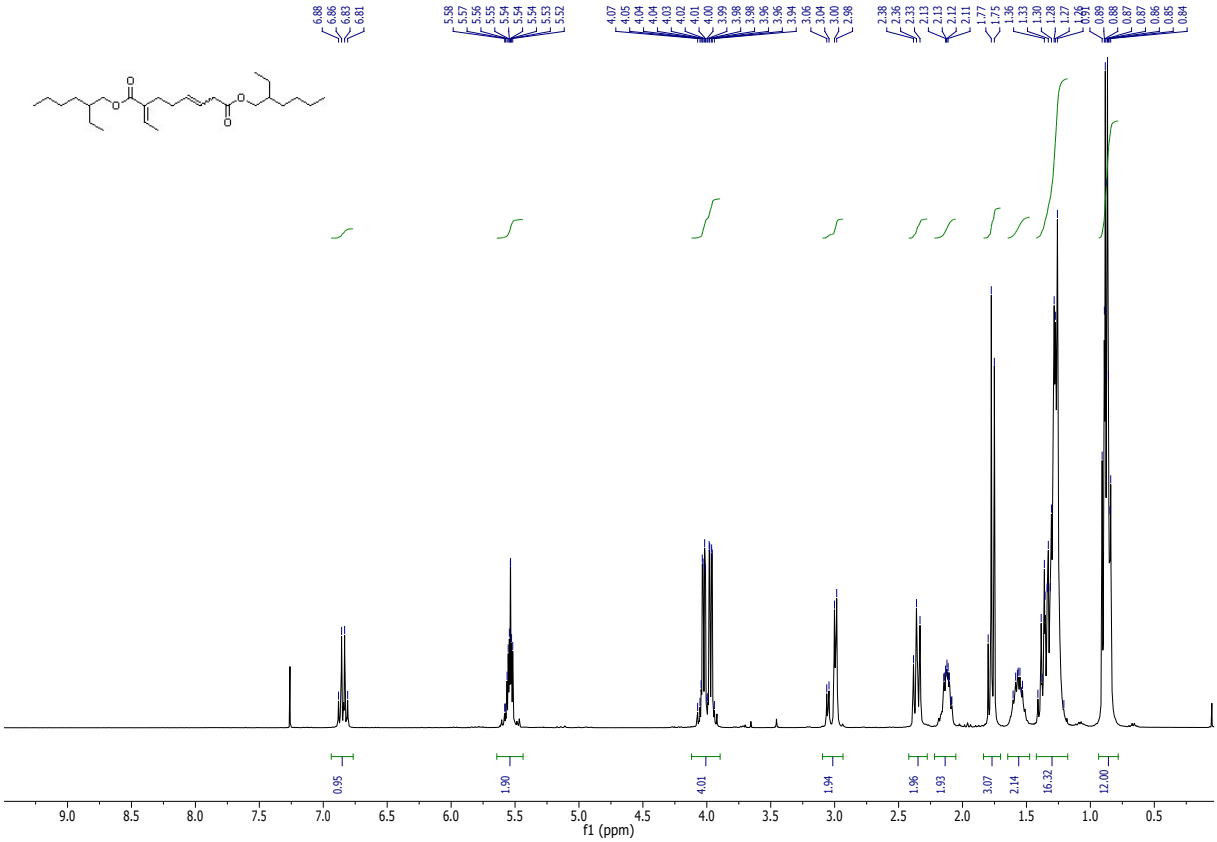
^{13}C NMR (75 MHz, $CDCl_3$) dimethyl 7-ethylideneoct-3-enedioate, **2a**.



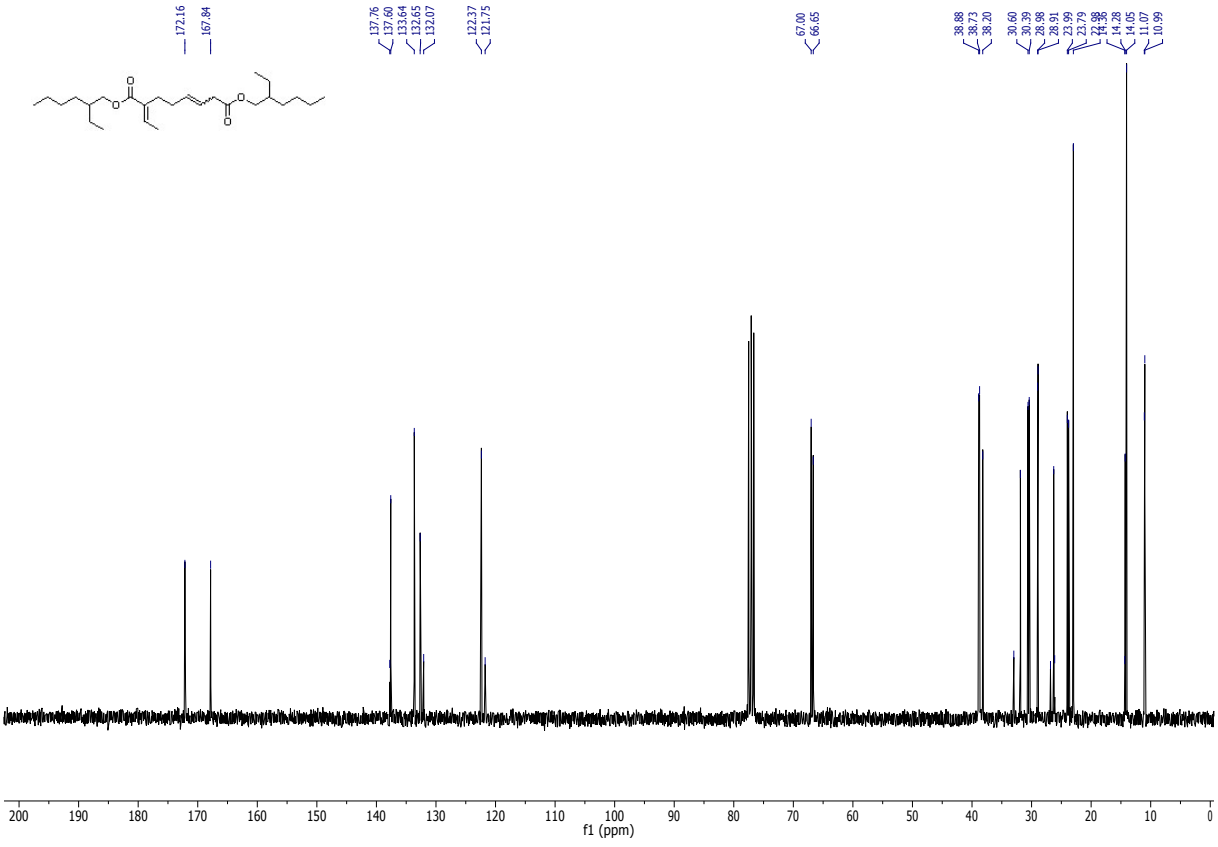
^{1}H NMR (300 MHz, $CDCl_3$) dibutyl 7-ethylideneoct-3-enedioate, **2b**.



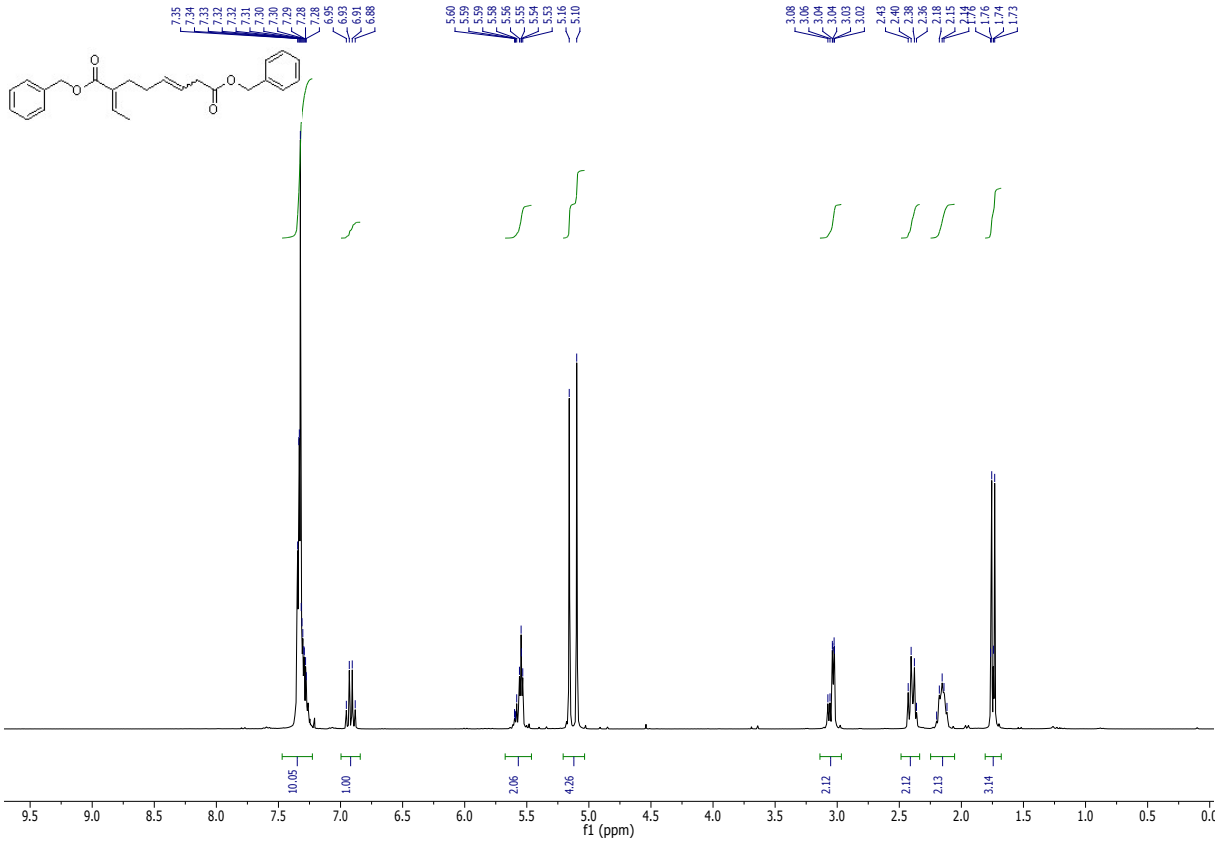
^{13}C NMR (75 MHz, $CDCl_3$) dibutyl 7-ethylideneoct-3-enedioate, **2b**.



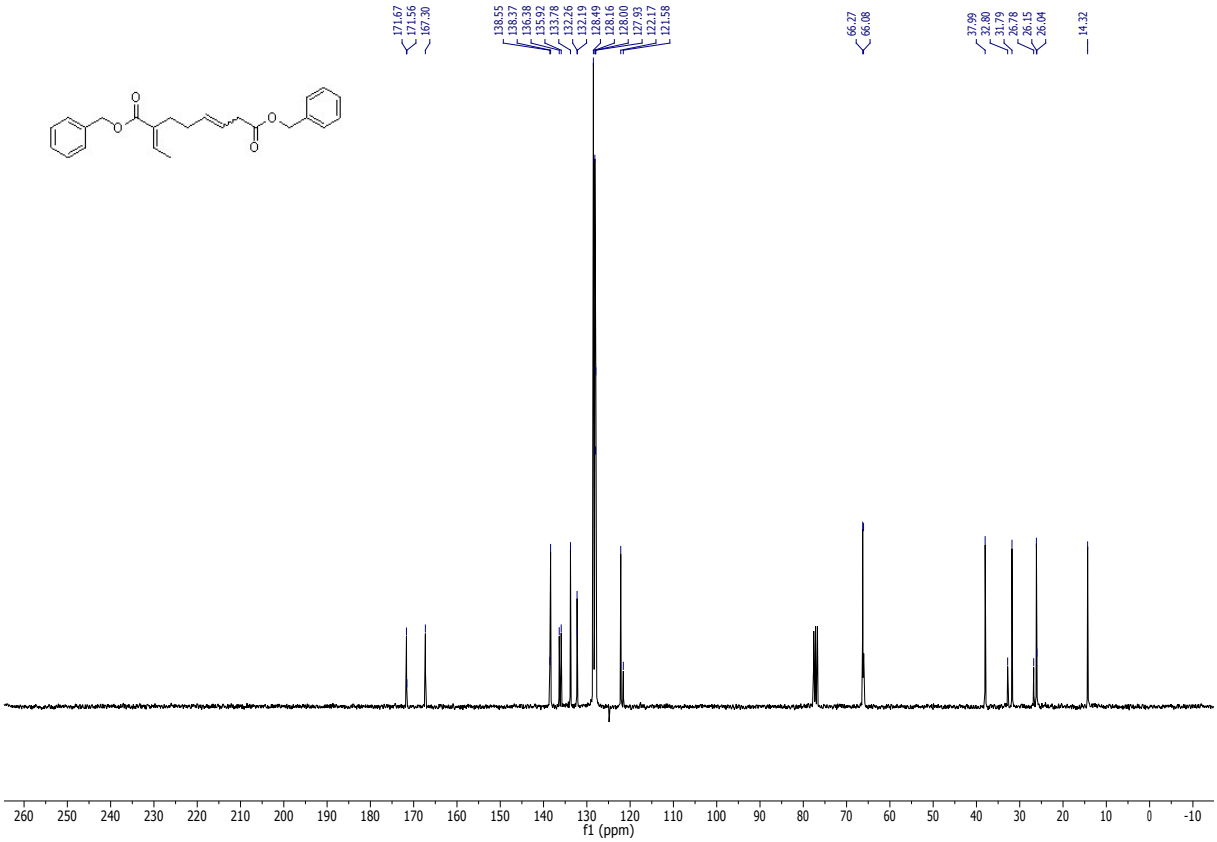
^{1}H NMR (300 MHz, $CDCl_3$) bis(2-ethylhexyl) 7-ethylideneoct-3-enedioate, **2c**.



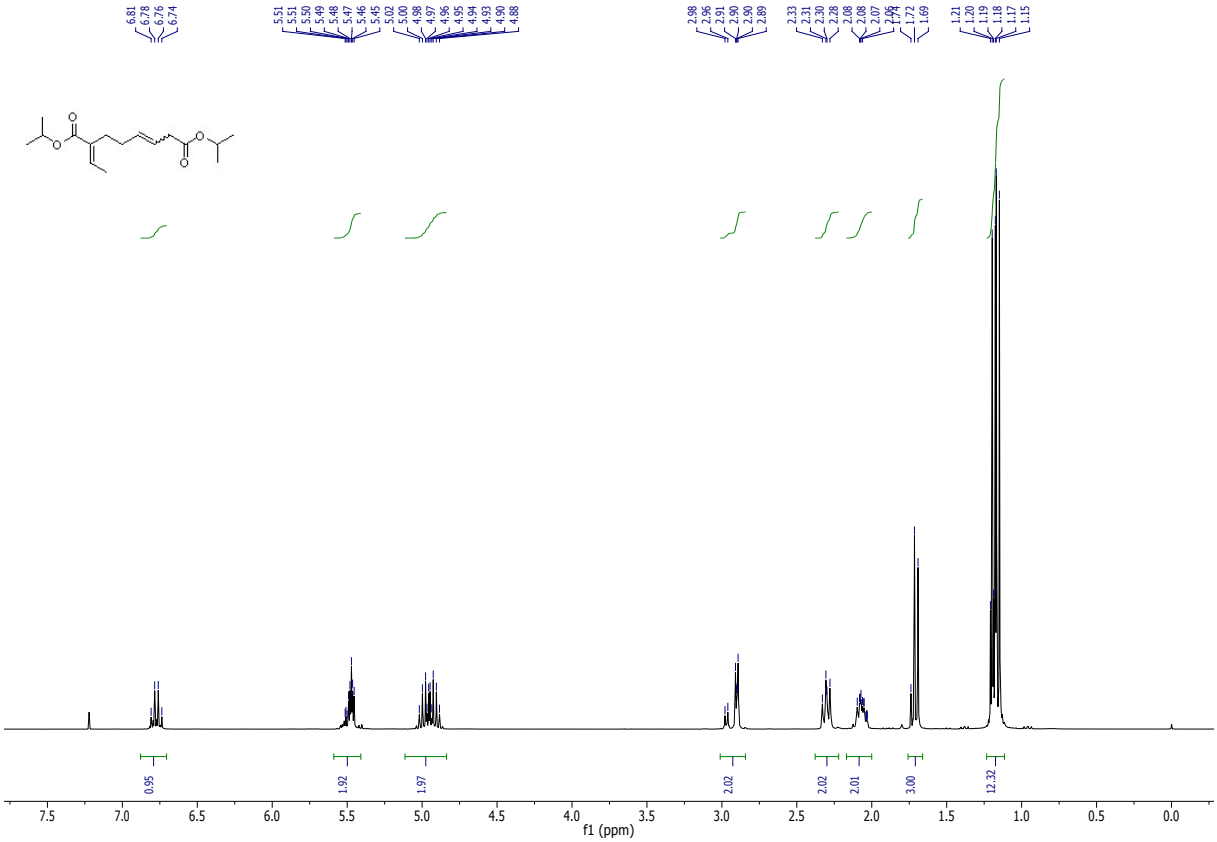
^{13}C NMR (75 MHz, $CDCl_3$) bis(2-ethylhexyl) 7-ethylideneoct-3-enedioate, **2c**.



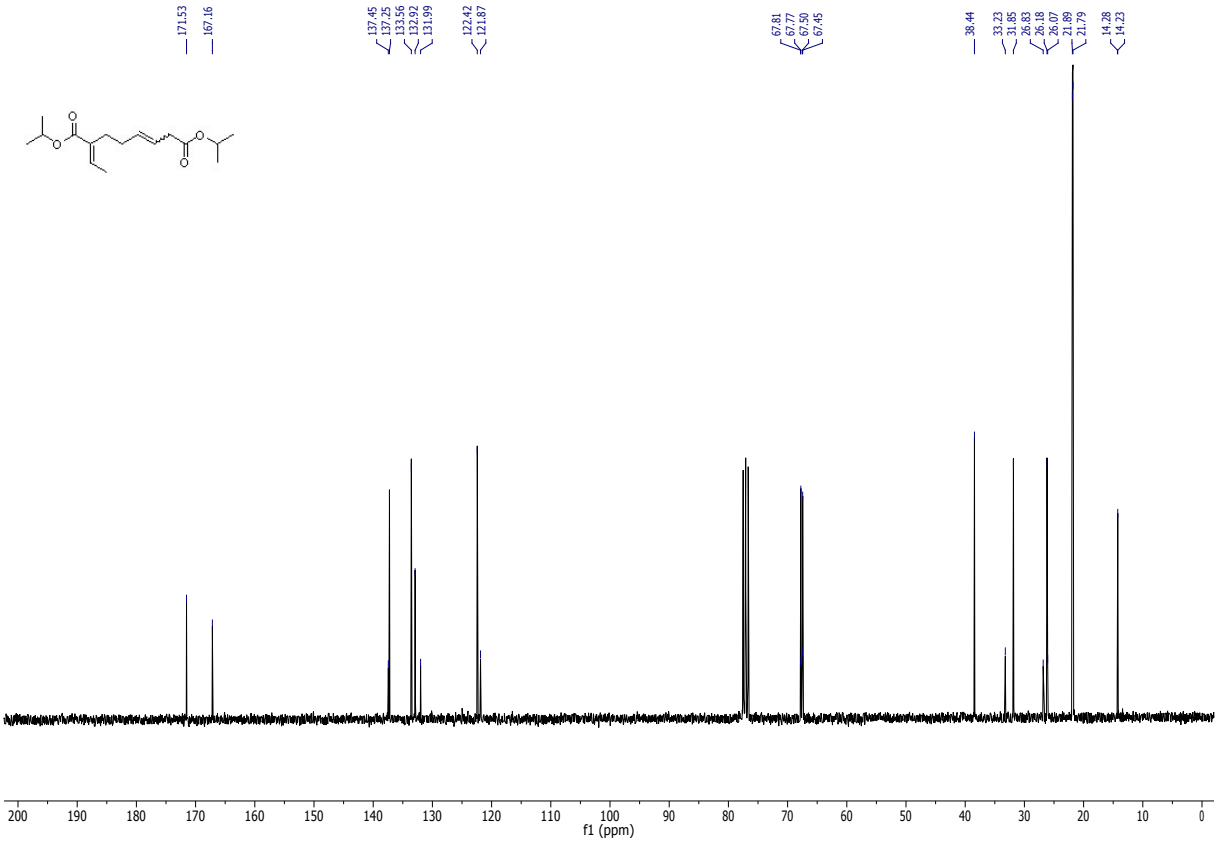
^{1}H NMR (300 MHz, $CDCl_3$) dibenzyl 7-ethylideneoct-3-enedioate, **2d**.



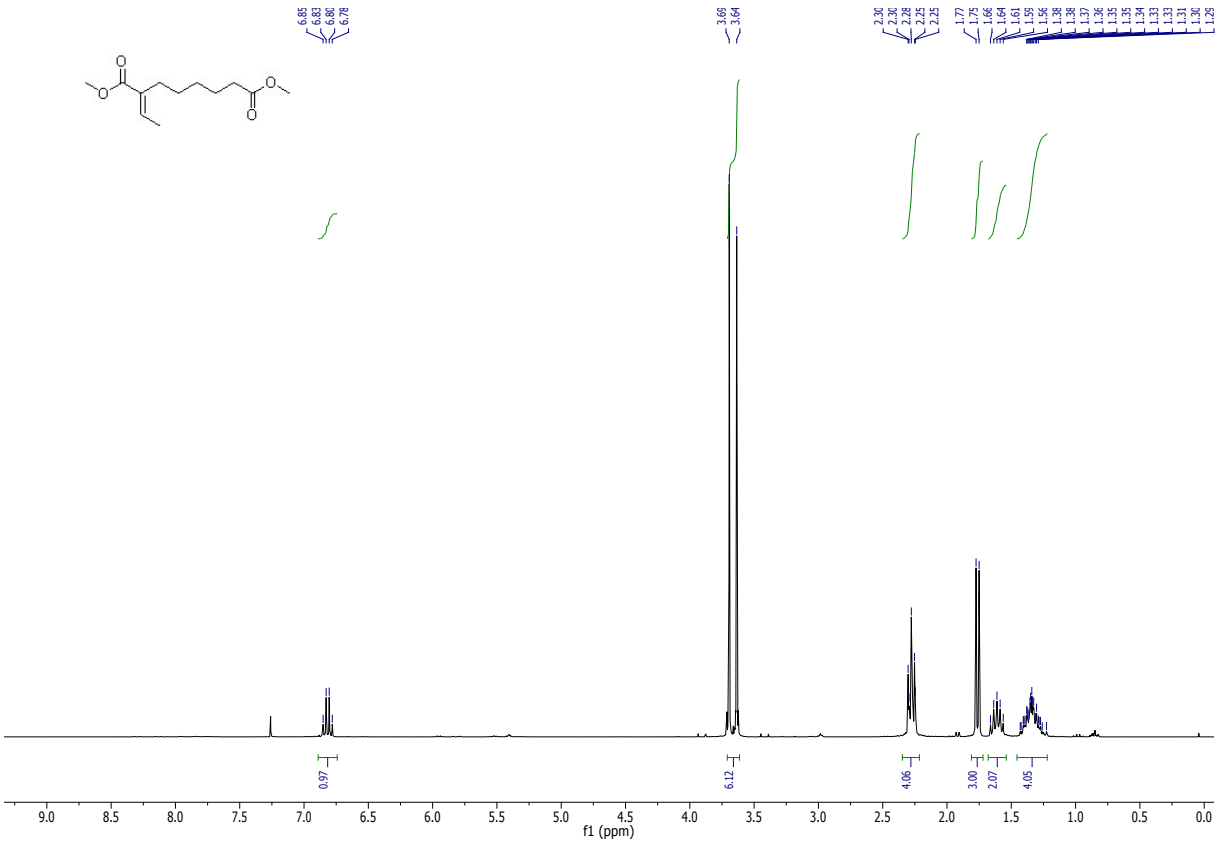
^{13}C NMR (75 MHz, $CDCl_3$) dibenzyl 7-ethylideneoct-3-enedioate, **2d**.



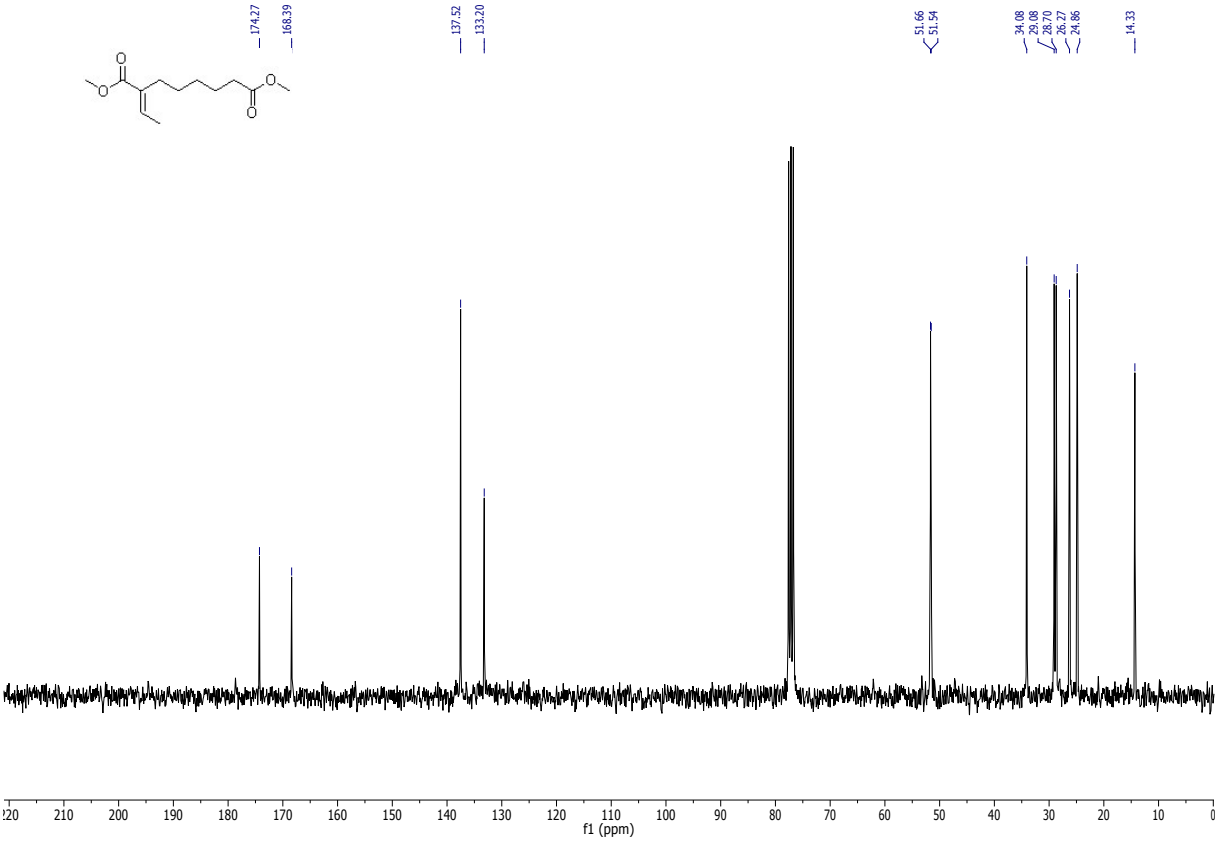
^{1}H NMR (300 MHz, $CDCl_3$) diisopropyl 7-ethylideneoct-3-enedioate, **2e**.



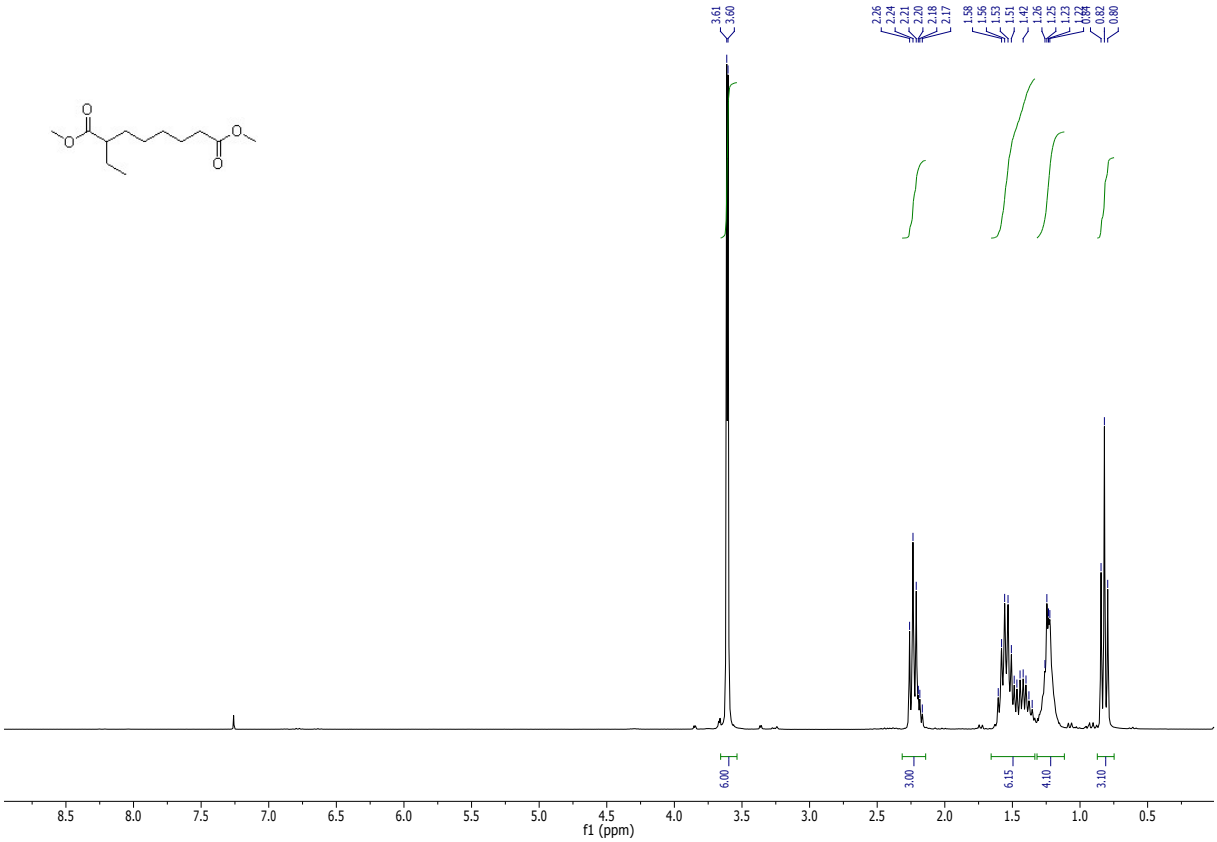
^{13}C NMR (75 MHz, $CDCl_3$) diisopropyl 7-ethylideneoct-3-enedioate, **2e**.



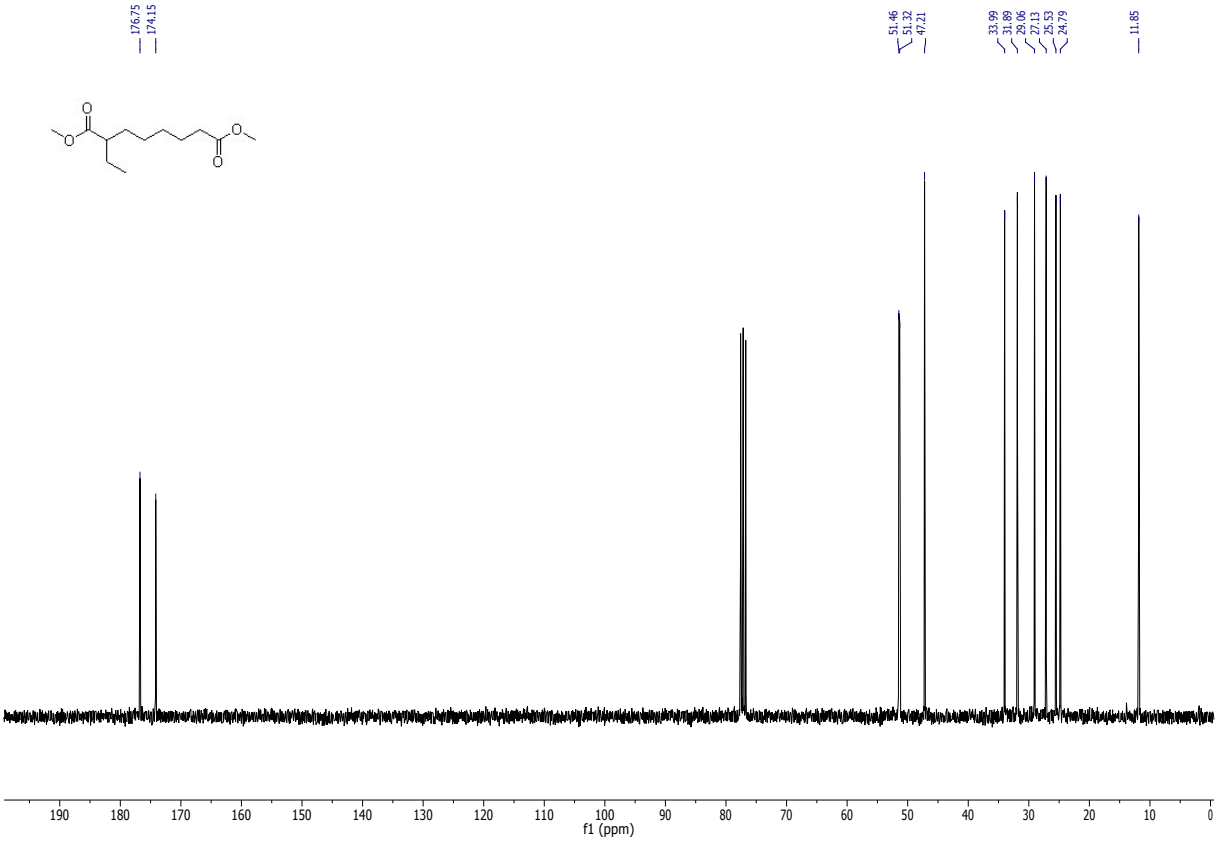
^{1}H NMR (300 MHz, $CDCl_3$) dimethyl 2-ethylideneoctanedioate, **3**.



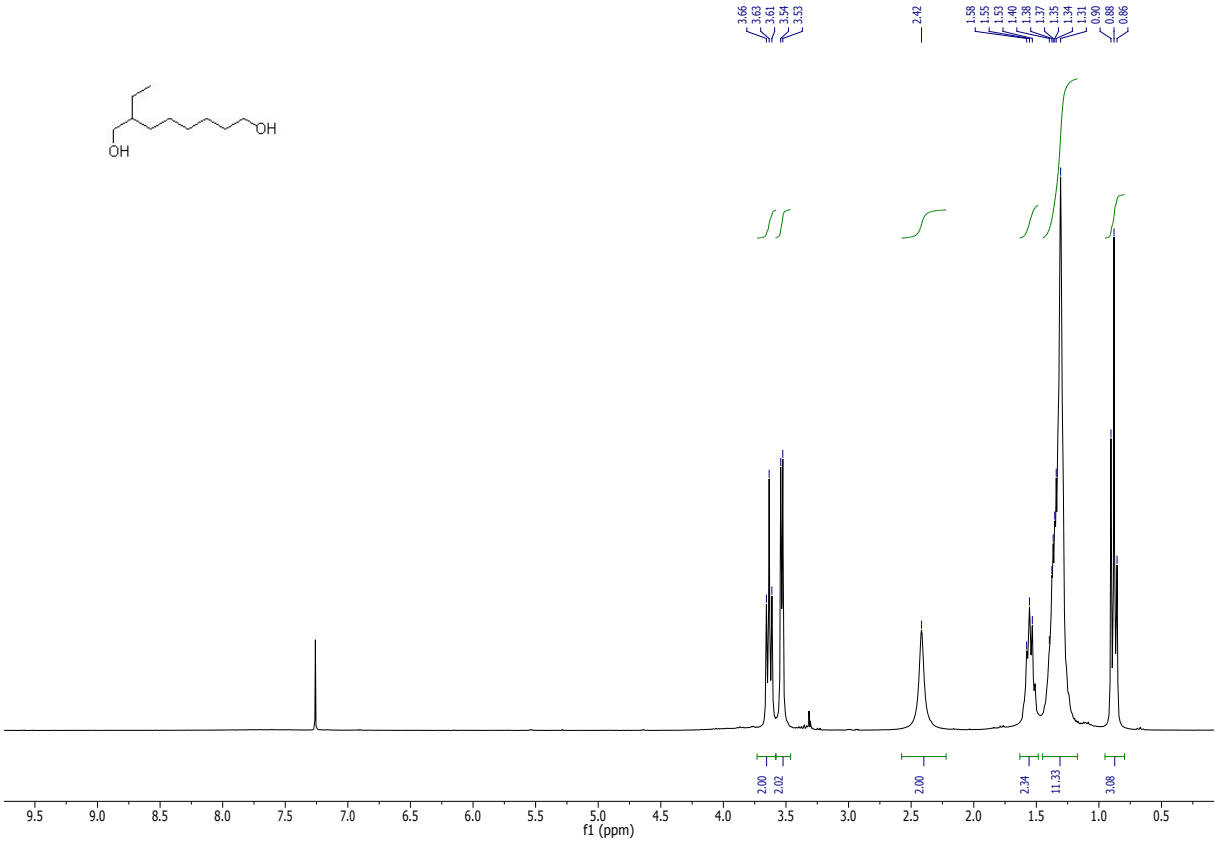
^{13}C NMR (75 MHz, $CDCl_3$) dimethyl 2-ethylideneoctanedioate, **3**.



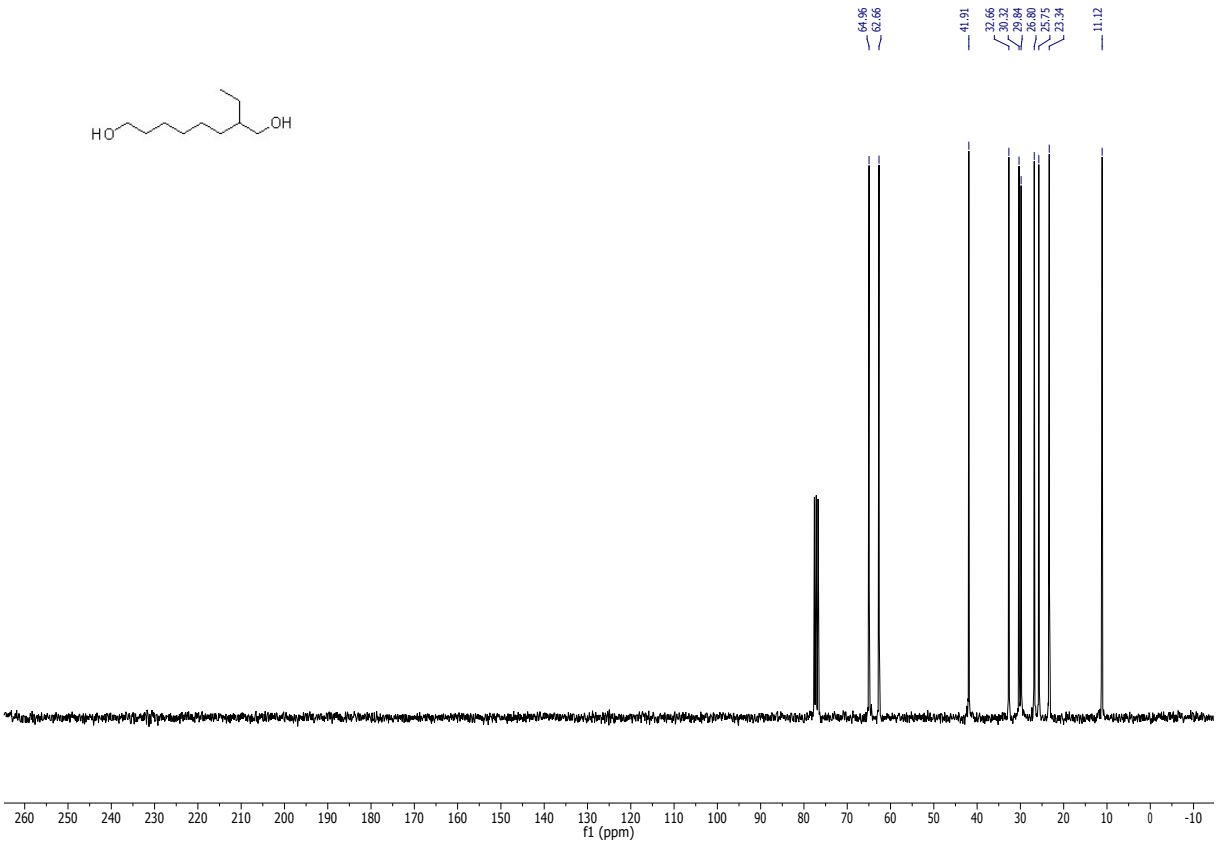
^{1}H NMR (300 MHz, $CDCl_3$) dimethyl 2-ethyloctanedioate, **4**.



^{13}C NMR (75 MHz, $CDCl_3$) dimethyl 2-ethyloctanedioate, **4**



^{1}H NMR (300 MHz, $CDCl_3$) 2-ethyloctane-1,8-diol, **5**.



^{13}C NMR (75 MHz, $CDCl_3$) 2-ethyloctane-1,8-diol, **5**.