Supporting Information

Ruthenium(II) complexes with η^6-coordinated 3-phenylpropanol and 2-phenylethanol as catalysts for the tandem isomerization/Claisen rearrangement of diallyl ethers in water

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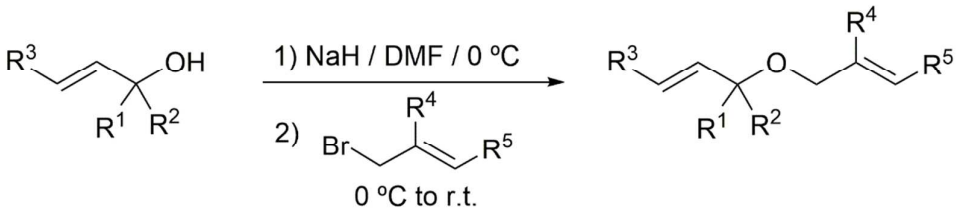
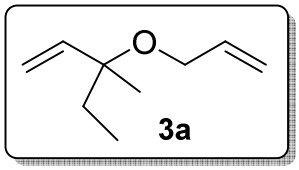
Contents

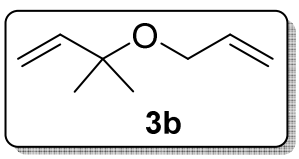
General procedure for the preparation of diallyl ethers 3a-l: Under argon atmosphere, a solution of the corresponding allylic alcohol (25 mmol) in 25 mL of DMF was added to a suspension of sodium hydride (0.90 g, 38 mmol) cooled at 0 ºC, and the resulting mixture stirred for 30 min. Then, the appropriate allyl bromide derivative (33 mmol) was added dropwise, and the mixture stirred at 0 ºC for 30 min and additional 4 h at room temperature. After this time, the reaction mixture was quenched with brine (30 mL) and the aqueous solution extracted with diethyl ether (3 x 30 mL). The combined organic extracts were washed with distilled water (3 x 10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was applied directly onto a silica gel column and chromatographed (10:1 hexane/EtOAc as eluent) to afford the pure diallyl ether as a colourless oil. All the allylic alcohols employed were obtained from commercial suppliers and used as received, with the exception of 1-vinylcyclohexan-1-ol,[1] 2-phenylbut-3-en-2-ol[1] and (*E*)-2-methyl-4-phenylbut-3-en-2-ol,[2] which were prepared by following the methods reported in the literature.



Scheme S1: Procedure employed for the synthesis of diallyl ethers **3a-l**.

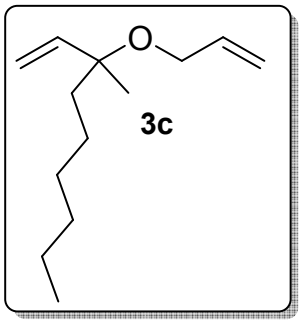


3-(Allyloxy)-3-methylpent-1-ene (3a): Yield: 2.945 g (84%). ^{1}H NMR ($CDCl_3$): δ = 5.99-5.86 (m, 1H, CH_2CH=), 5.78 (dd, 1H, $^3J_{HH}$ = 17.4 and 10.2 Hz, C_qCH=), 5.20-5.11 (m, 4H, C_qCH=CH_2 and CH_2CH=CH_2), 3.85 (d, 2H, $^3J_{HH}$ = 5.4 Hz, OCH_2), 1.60 (q, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3), 1.25 (s, 3H, CH_3), 0.89 (t, 3H, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 142.9 (s, C_qCH=), 136.0 (s, CH_2CH=), 115.5 (s, =CH_2), 114.6 (s, =CH_2), 77.9 (s, C_q), 63.5 (s, OCH_2), 32.5 (s, CH_2CH_3), 21.5 (s, CH_3), 8.0 (s, CH_2CH_3) ppm. HRMS (ESI): *m/z* 141.1277, [M+H$^+$] (calcd for $C_9H_{17}O$: 141.1279).

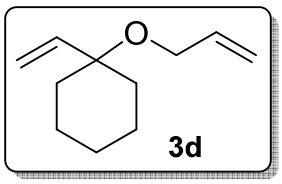


3-(Allyloxy)-3-methylbut-1-ene (3b):[3] Yield: 2.618 g (83%). ^{1}H NMR (C_6D_6): δ = 6.00-5.90 (m, 1H, CH_2CH=), 5.83 (dd, 1H, $^3J_{HH}$ = 17.4 and 10.8 Hz, C_qCH=), 5.39 (d, 1H, $^3J_{HH}$ = 17.4 Hz,

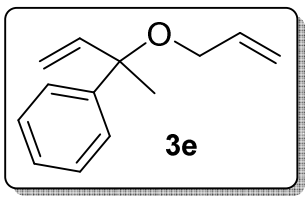
$C_qCH=CH_2$), 5.15-5.04 (m, 3H, $C_qCH=CH_2$ and $CH_2CH=CH_2$), 3.87-3.85 (m, 2H, OCH_2), 1.28 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 144.1 (s, $C_qCH=$), 136.5 (s, $CH_2CH=$), 114.3 (s, $=CH_2$), 113.2 (s, $=CH_2$), 74.9 (s, C_q), 63.7 (s, OCH_2), 25.5 (s, CH_3) ppm.



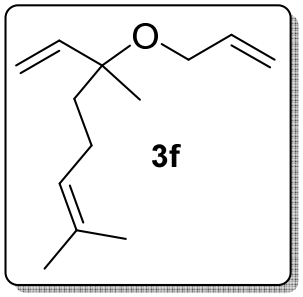
3-(Allyloxy)-3-methylnon-1-ene (3c): Yield: 4.319 g (88%). ^1H NMR (C_6D_6): δ = 6.03-5.95 (m, 1H, $CH_2CH=$), 5.82 (dd, 1H, $^3J_{HH}$ = 17.1 and 10.5 Hz, $C_qCH=$), 5.43 (d, 1H, $^3J_{HH}$ = 17.1 Hz, $C_qCH=CH_2$), 5.18-5.11 (m, 3H, $C_qCH=CH_2$ and $CH_2CH=CH_2$), 3.87-3.85 (m, 2H, OCH_2), 1.64-1.25 (m, 13H, CH_2 and CH_3), 0.97 (t, 3H, $^3J_{HH}$ = 6.6 Hz, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 143.6 (s, $C_qCH=$), 136.5 (s, $CH_2CH=$), 114.2 (s, $=CH_2$), 113.8 (s, $=CH_2$), 77.2 (s, C_q), 63.3 (s, OCH_2), 40.5 (s, CH_2), 32.0 (s, CH_2), 30.0 (s, CH_2), 23.7 (s, CH_2), 22.8 (s, CH_2), 22.0 (s, CH_3), 14.0 (s, CH_2CH_3) ppm. HRMS (ESI): *m/z* 197.1903, $[M+H^+]$ (calcd for $C_{13}H_{25}O$: 197.1905).



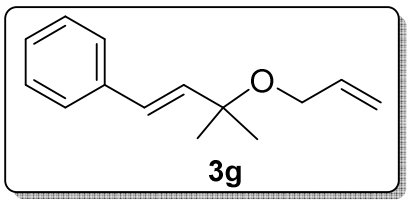
1-(Allyloxy)-1-vinylcyclohexane (3d):[3] Yield: 3.284 g (79%). ^1H NMR (C_6D_6): δ = 6.12-5.98 (m, 1H, $CH_2CH=$), 5.78 (dd, 1H, $^3J_{HH}$ = 17.1 and 10.5 Hz, $C_qCH=$), 5.43 (d, 1H, $^3J_{HH}$ = 17.1 Hz, $C_qCH=CH_2$), 5.18-5.11 (m, 3H, $C_qCH=CH_2$ and $CH_2CH=CH_2$), 3.85-3.82 (m, 2H, OCH_2), 1.51-1.01 (s, 10H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 143.7 (s, $C_qCH=$), 136.4 (s, $CH_2CH=$), 114.3 (s, $=CH_2$), 114.0 (s, $=CH_2$), 75.5 (s, C_q), 62.6 (s, OCH_2), 34.4 (s, CH_2), 22.8 (s, CH_2), 21.8 (s, CH_2) ppm.



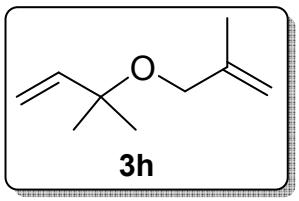
(2-(Allyloxy)but-3-en-2-yl)benzene (3e):[4] Yield: 4.236 g (90%). ^1H NMR (C_6D_6): δ = 7.31-7.16 (m, 5H, Ph), 6.04 (dd, 1H, $^3J_{HH}$ = 17.6 and 10.8 Hz, $C_qCH=$), 6.02-5.92 (m, 1H, $CH_2CH=$), 5.43 (d, 1H, $^3J_{HH}$ = 17.6 Hz, $C_qCH=CH_2$), 5.36-5.13 (m, 3H, $C_qCH=CH_2$ and $CH_2CH=CH_2$), 3.87-3.84 (m, 2H, OCH_2), 1.57 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 145.1 (s, C_{ipso}), 143.3 (s, $C_qCH=$), 136.0 (s, $CH_2CH=$), 128.1 (s, CH_{ortho} or CH_{meta}), 126.9 (s, CH_{para}), 126.3 (s, CH_{ortho} or CH_{meta}), 114.6 (s, $=CH_2$), 113.7 (s, $=CH_2$), 72.9 (s, C_q), 63.8 (s, OCH_2), 24.5 (s, CH_3) ppm.



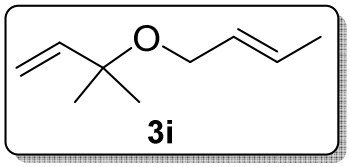
3-(Allyloxy)-3,7-dimethylocta-1,6-diene (3f):[5] Yield: 3.935 g (81%). ^{1}H NMR (C_6D_6): δ = 6.09-5.92 (m, 1H, CH_2CH=CH_2), 5.80 (dd, 1H, $^{3}J_{HH}$ = 17.4 and 6.8 Hz, C_qCH=), 5.45 (dd, 1H, $^{3}J_{HH}$ = 17.6 Hz, $^{2}J_{HH}$ = 1.6 Hz, C_qCH=CH_2), 5.31-5.28 (m, 1H, CH=$C(CH_3)_2$), 5.20-5.11 (m, 3H, C_qCH=CH_2 and CH_2CH=CH_2), 3.87 (d, 2H, $^{3}J_{HH}$ = 4.4 Hz, OCH_2), 2.28-2.22 (m, 2H, CH_2CH=$C(CH_3)_2$), 1.76 (s, 3H, CH=$C(CH_3)_2$), 1.72-1.68 (m, 2H, C_qCH_2), 1.66 (s, 3H, CH=$C(CH_3)_2$), 1.24 (s, 3H, C_qCH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 143.4 (s, C_qCH=), 136.5 (s, CH_2CH=CH_2), 130.8 (s, CH=$C(CH_3)_2$), 125.0 (s, CH=$C(CH_3)_2$), 114.3 (s, =CH_2), 113.9 (s, =CH_2), 77.0 (s, C_q), 63.3 (s, OCH_2), 40.3 (s, C_qCH_2), 25.6 (s, CH_3), 22.6 (s, CH_2CH=), 22.1 (s, CH_3), 17.4 (s, CH_3) ppm.



(*E*)-(3-(Allyloxy)-3-methylbut-1-en-1-yl)benzene (3g):[6] Yield: 3.945 g (78%). ^{1}H NMR (C_6D_6): δ = 7.25-7.14 (m, 5H, Ph), 6.55 (d, 1H, $^{3}J_{HH}$ = 16.2 Hz, =C*H*Ph), 6.27 (d, 1H, $^{3}J_{HH}$ = 16.2 Hz, C*H*=CHPh), 6.06-6.00 (m, 1H, C*H*=CH_2), 5.43 (d, 1H, $^{3}J_{HH}$ = 17.2 Hz, CH=C*H*$_2$), 5.16 (d, 1H, $^{3}J_{HH}$ = 10.4 Hz, CH=C*H*$_2$), 3.90 (br, 2H, OCH_2), 1.39 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 137.1 (s, C_{ipso}), 136.6 (s, *C*H=CHPh), 135.7 (s, *C*H=CH_2), 129.0 (s, CH_{para}), 128.5 (s, CH_{ortho} or CH_{meta}), 127.4 (s, CH_{ortho} or CH_{meta}), 126.5 (s, =*C*HPh), 114.4 (s, =CH_2), 74.9 (s, C_q), 63.8 (s, OCH_2), 26.4 (s, CH_3) ppm.

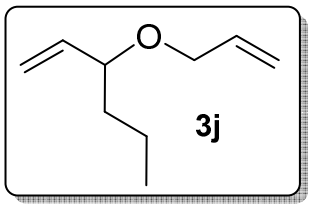


3-Methyl-3-((2-methylallyl)oxy)but-1-ene (3h):[7] Yield: 3.945 g (78%). ^{1}H NMR (C_6D_6): δ = 5.89 (dd, 1H, $^{3}J_{HH}$ = 17.6 and 10.8 Hz, C_qCH=CH_2), 5.29-5.27 (m, 1H, C_q=C*H*$_2$), 5.15 (dd, 1H, $^{3}J_{HH}$ = 17.4 Hz, $^{2}J_{HH}$ = 1.5 Hz, CH=C*H*$_2$), 5.08 (dd, 1H, $^{3}J_{HH}$ = 10.8 Hz, $^{2}J_{HH}$ = 1.5 Hz, CH=C*H*$_2$), 4.99-4.96 (m, 1H, C_q=C*H*$_2$), 3.80 (s, 2H, OCH_2), 1.78 (s, 3H, C*H*$_3$C=), 1.31 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 144.3 (s, CH=), 143.5 (s, C_q=), 113.2 (s, C_q=*C*H$_2$), 110.3 (s, CH=*C*H$_2$), 74.9 (s, C_q), 66.6 (s, OCH_2), 25.8 (s, CH_3), 19.5 (s, *C*H$_3$C=) ppm.

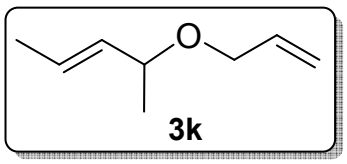


(*E*)-3-(But-2-en-1-yloxy)-3-methylbut-1-ene (3i): Yield: 2.629 g (75%). ^{1}H NMR (C_6D_6): δ = 5.90 (dd, 1H, $^{3}J_{HH}$ =

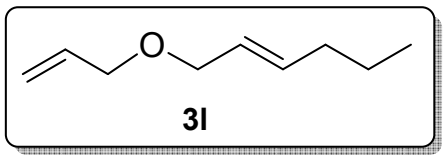
17.4 and 10.8 Hz, C*H*=CH_2), 5.73-5.70 (m, 2H, CH=CH), 5.15 (dd, 1H, $^3J_{HH}$ = 17.4 Hz, $^2J_{HH}$ = 1.5 Hz, CH=C*H*$_2$), 5.09 (dd, 1H, $^3J_{HH}$ = 10.8 Hz, $^2J_{HH}$ = 1.5 Hz, CH=C*H*$_2$), 3.89-3.86 (m, 2H, OCH_2), 1.68-1.65 (m, 3H, CH=CHC*H*$_3$), 1.31 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 144.4 (s, *C*H=CH_2), 129.6 (s, *C*H=$CHCH_3$), 126.1 (s, CH=*C*HCH_3), 113.1 (s, CH=*C*H_2), 74.8 (s, C_q), 63.5 (s, OCH_2), 25.9 (s, CH_3), 17.5 (s, CH=CH*C*H_3) ppm. HRMS (ESI): *m/z* 141.1276, [M+H^+] (calcd for $C_9H_{17}O$: 141.1279).



3-(Allyloxy)hex-1-ene (3j):[8] Yield: 3.015 g (86%). ^1H NMR (C_6D_6): δ = 6.03-5.90 (m, 1H, CH_2C*H*=CH_2), 5.72 (ddd, 1H, $^3J_{HH}$ = 17.7, 7.5 and 1.0 Hz, CHC*H*=CH_2), 5.40-5.33 (m, 1H, CHCH=C*H*$_2$), 5.19-5.10 (m, 3H, CH_2CH=C*H*$_2$ and CHCH=C*H*$_2$), 4.13-4.07 (m, 1H, OCH_2), 3.86-3.79 (m, 1H, OCH_2), 3.72-3.65 (m, 1H, OCH), 1.75-1.44 (m, 4H, CH_2), 1.01-0.95 (m, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 139.7 (s, CH*C*H=CH_2), 135.8 (s, CH_2*C*H=CH_2), 116.0 (s, =CH_2), 115.3 (s, =CH_2), 80.3 (s, OCH), 60.9 (s, OCH_2), 37.9 (s, CH*C*H_2), 18.6 (s, *C*H_2CH_3), 14.0 (s, CH_3) ppm.



(*E*)-4-(Allyloxy)pent-2-ene (3k): Yield: 2.776 g (88%). ^1H NMR (C_6D_6): δ = 6.05-5.94 (m, 1H, C*H*=CH_2), 5.57-5.35 (m, 2H, CH=CH), 5.39 (d, 1H, $^3J_{HH}$ = 19.2 Hz, CH=C*H*$_2$), 5.18-5.13 (m, 1H, CH=C*H*$_2$), 4.11-4.02 (m, 1H, OCH), 3.88-3.77 (m, 2H, OCH_2), 1.62 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH=CHC*H*$_3$), 1.34 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 136.0 (s, *C*H=CH_2), 134.0 (s, *C*H=$CHCH_3$), 126.7 (s, CH=*C*HCH_3), 115.3 (s, CH=*C*H_2), 75.8 (s, OCH), 68.6 (s, OCH_2), 21.7 (s, CH_3), 17.3 (s, CH=CH*C*H_3) ppm. HRMS (ESI): *m/z* 127.1124, [M+H^+] (calcd for $C_8H_{15}O$: 127.1123).



(*E*)-1-(Allyloxy)hex-2-ene (3l):[9] Yield: 2.100 g (83%). ^1H NMR (C_6D_6): δ = 6.01-5.90 (m, 1H, C*H*=CH_2), 5.71-5.66 (m, 2H, CH=CH), 5.36 (ddt, 1H, $^3J_{HH}$ = 17.4 Hz, $^2J_{HH}$ = $^4J_{HH}$ = 1.8 Hz, CH=C*H*$_2$), 5.15 (ddt, 1H, $^3J_{HH}$ = 10.5 Hz, $^4J_{HH}$ = 2.1 Hz, $^2J_{HH}$ = 1.8 Hz, CH=C*H*$_2$), 3.96-3.92 (m, 4H, OCH_2), 2.04-1.97 (m, 2H, =$CHCH_2$), 1.40-1.36 (m, 2H, CH_2), 0.99 (t, 3H, $^3J_{HH}$ = 6.6 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 135.5 (s, *C*H=CH_2), 133.2 (s,

CH=CH), 127.2 (s, CH=CH), 115.6 (s, CH=*C*H_2), 70.7 (s, OCH_2), 70.5 (s, OCH_2), 34.4 (s, =CH*C*H_2), 22.4 (s, CH_2), 13.5 (s, CH_3) ppm.

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(8) Ishii, Y.; Sakaguchi, S.; Nakano, T. *Jpn. Kokai Tokkyo Koho* JP 2001253843, 2001.

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NMR spectra of the novel diallyl ethers 3a, 3c, 3i and 3k.

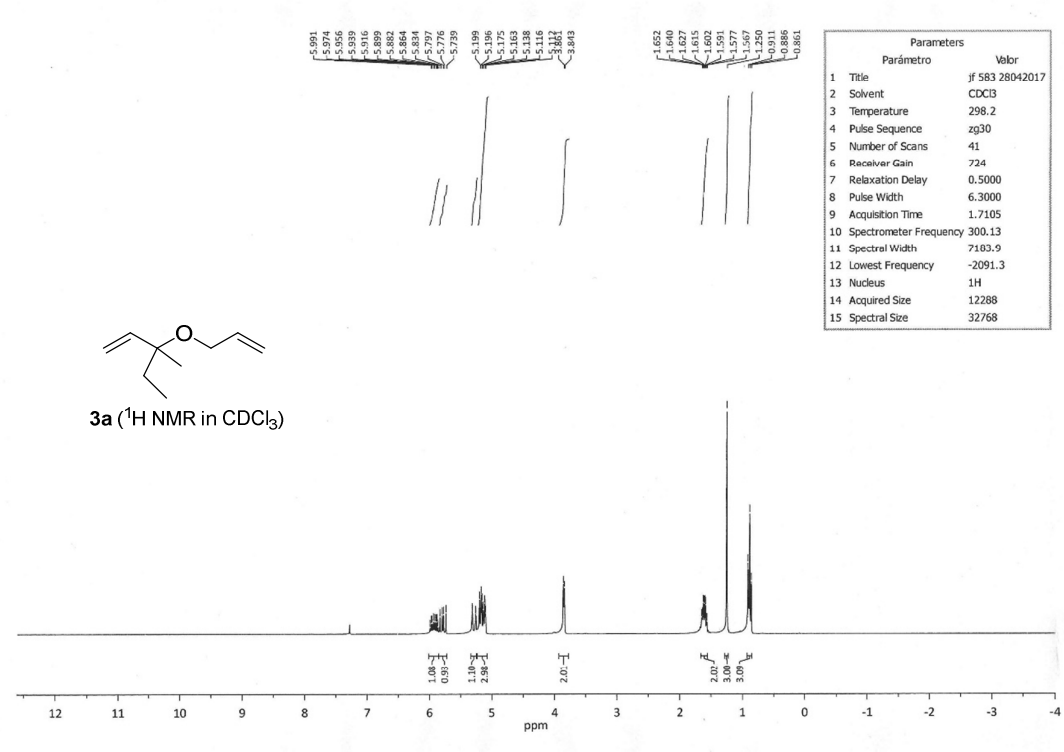

Figure S1: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 3-(allyloxy)-3-methylpent-1-ene, **3a**.

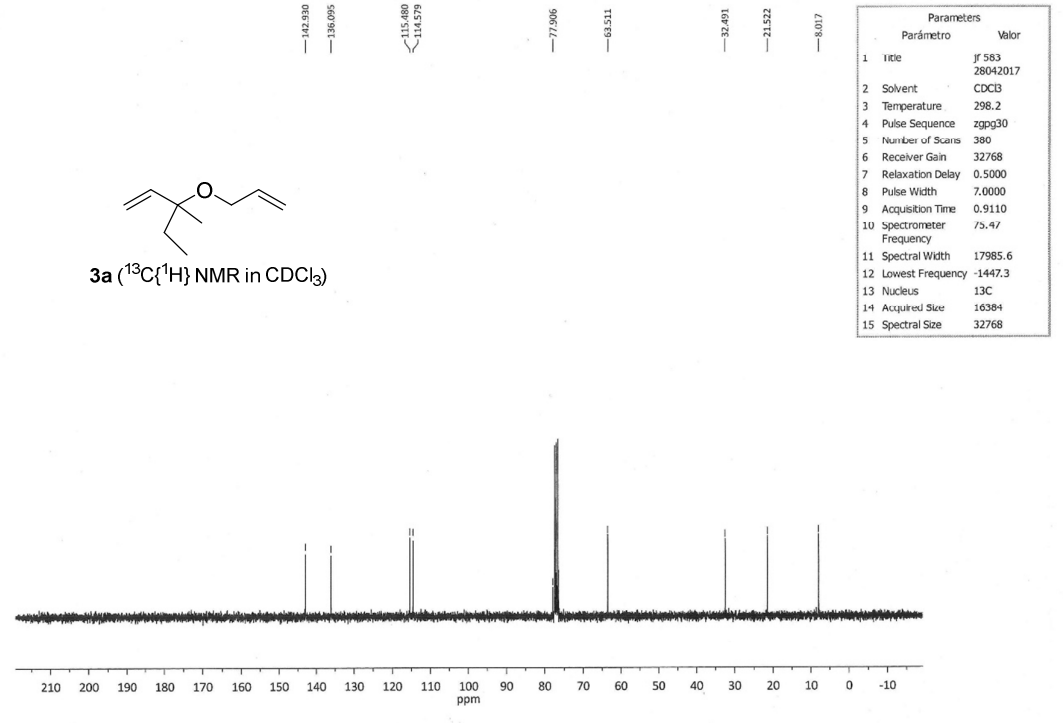

Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz, $CDCl_3$) of 3-(allyloxy)-3-methylpent-1-ene, **3a**.

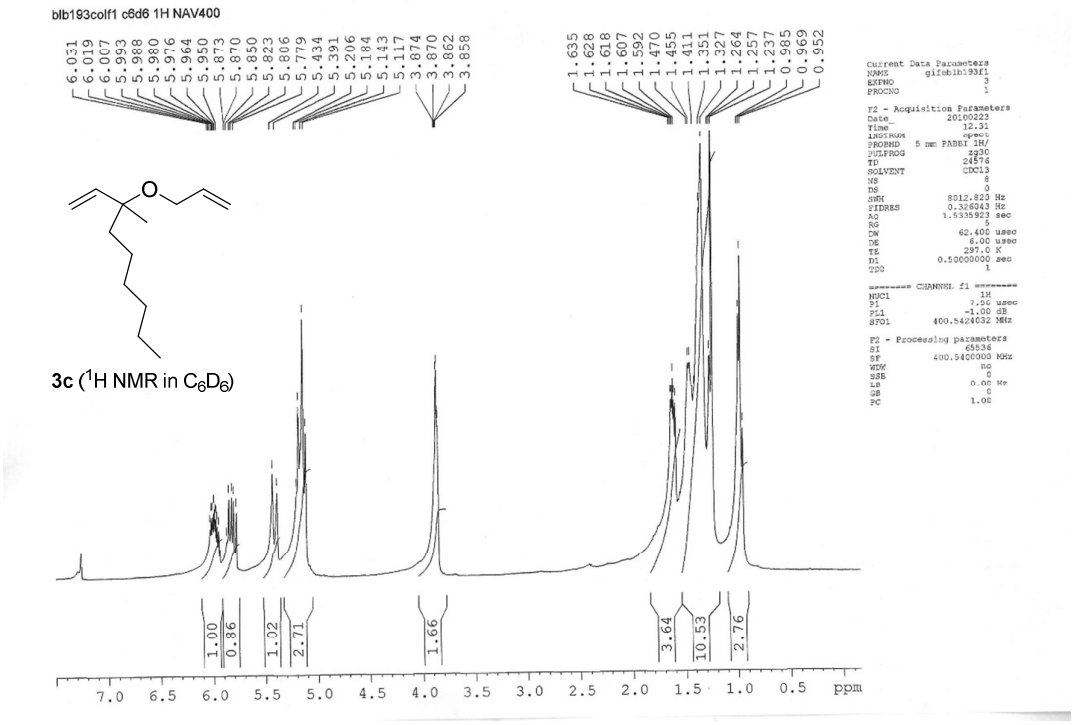

Figure S3: ^{1}H NMR spectrum (400 MHz, C_6D_6) of 3-(allyloxy)-3-methylnon-1-ene, **3c**.

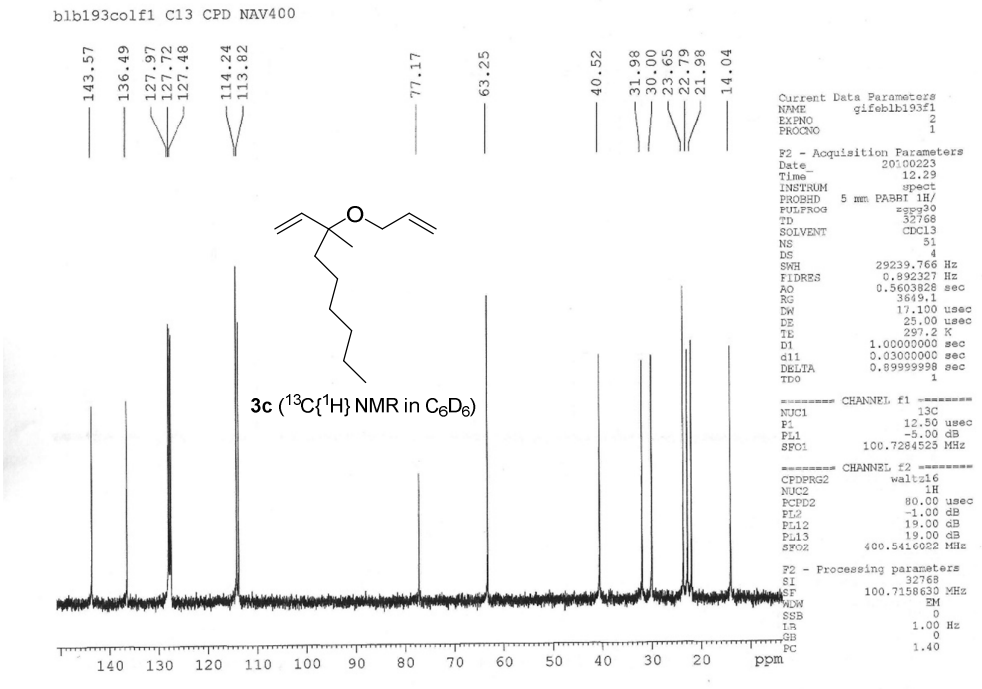

Figure S4: ^{13}C{^{1}H} NMR spectrum (100.7 MHz, C_6D_6) of 3-(allyloxy)-3-methylnon-1-ene, **3c**.

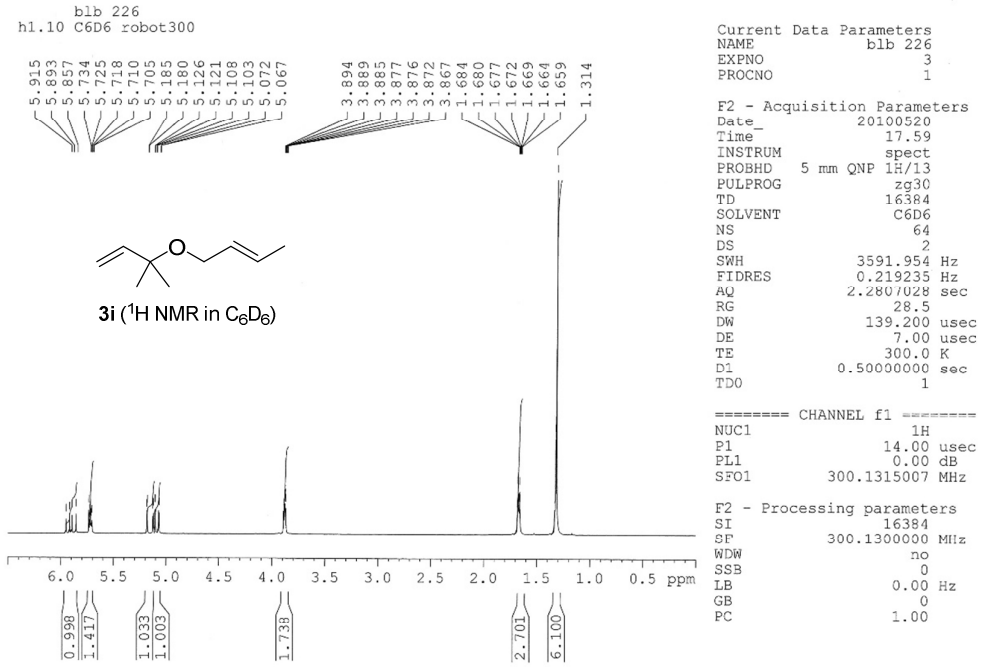

Figure S5: ^{1}H NMR spectrum (300 MHz, C_6D_6) of (*E*)-3-(but-2-en-1-yloxy)-3-methylbut-1-ene, **3i**.

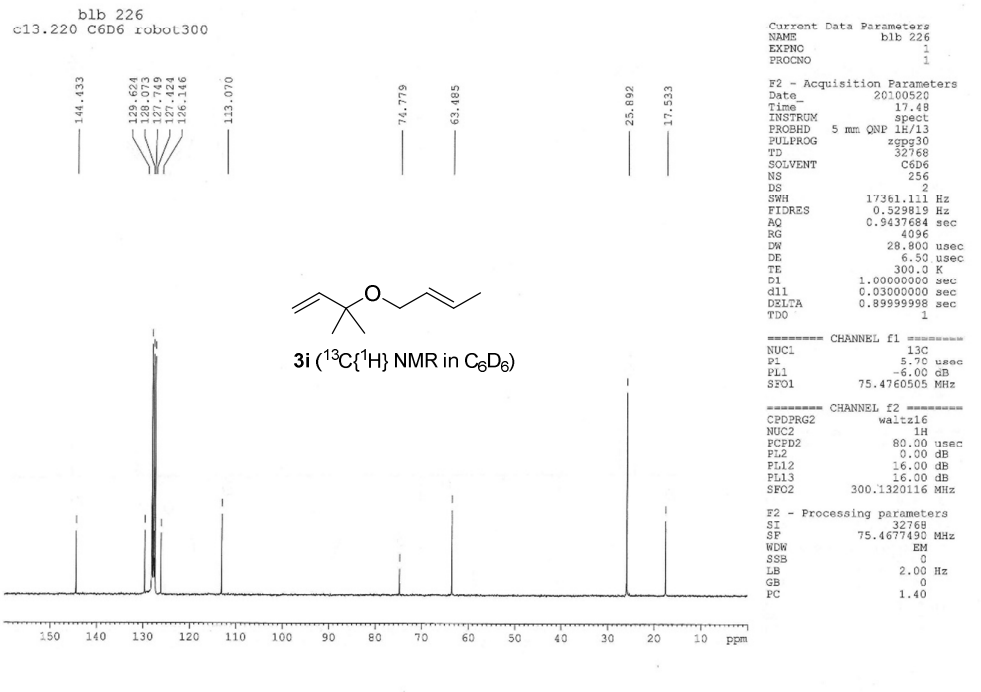

Figure S6: ^{13}C{^{1}H} NMR spectrum (75.5 MHz, C_6D_6) of (*E*)-3-(but-2-en-1-yloxy)-3-methylbut-1-ene, **3i**.

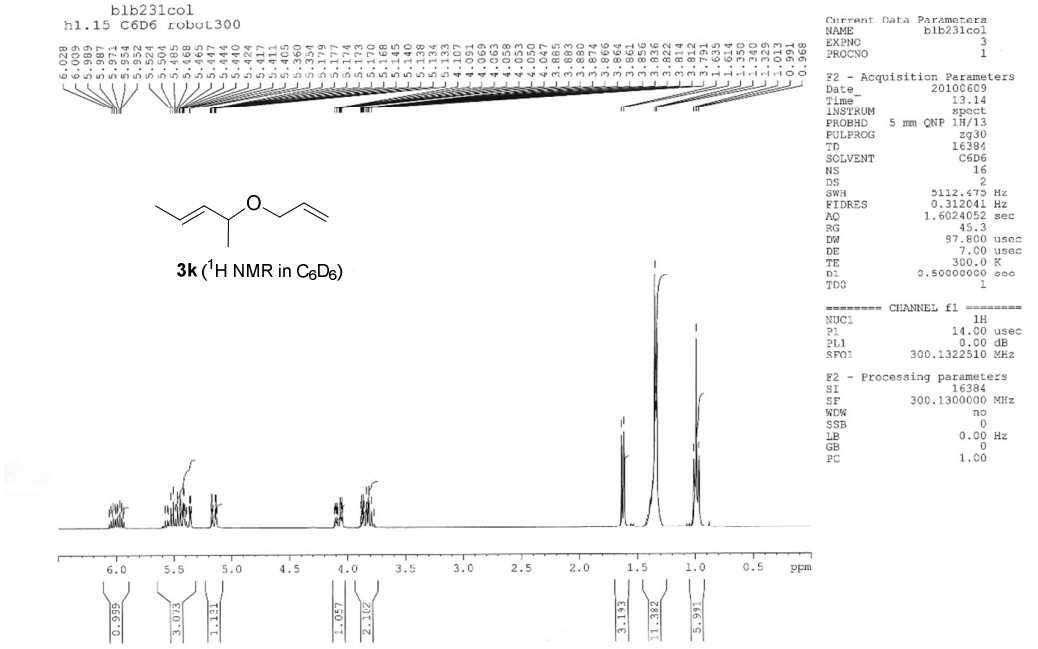

Figure S7: ^{1}H NMR spectrum (300 MHz, C_6D_6) of (*E*)-4-(allyloxy)pent-2-ene, **3k**.

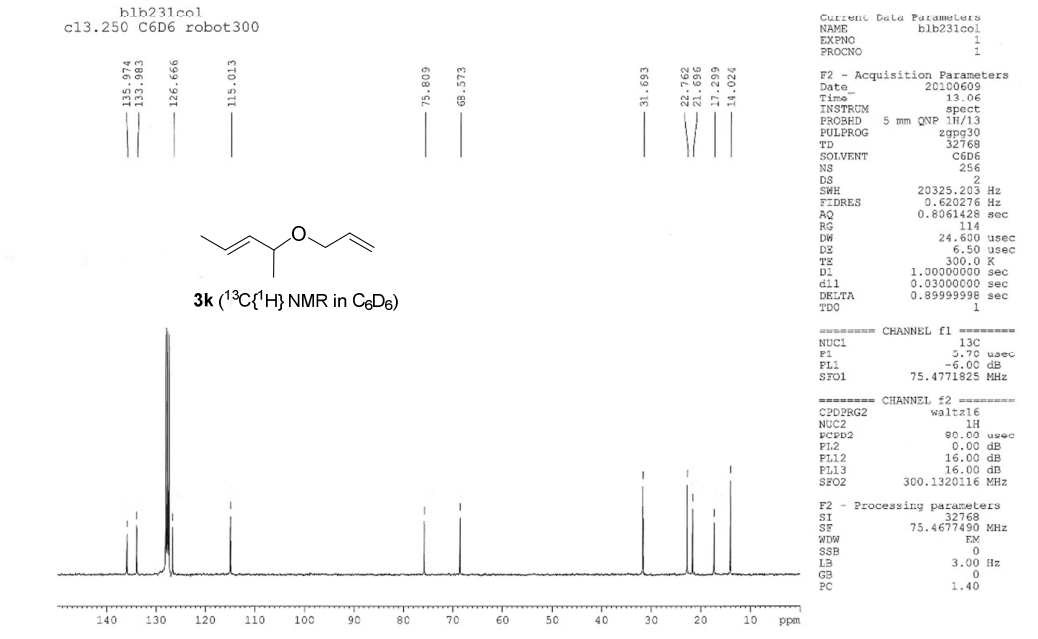

Figure S8: ^{13}C{^{1}H} NMR spectrum (75.5 MHz, C_6D_6) of (*E*)-4-(allyloxy)pent-2-ene, **3k**.

NMR spectra of the novel γ,δ-unsaturated aldehydes 4a, 4c, 4e and 4g.

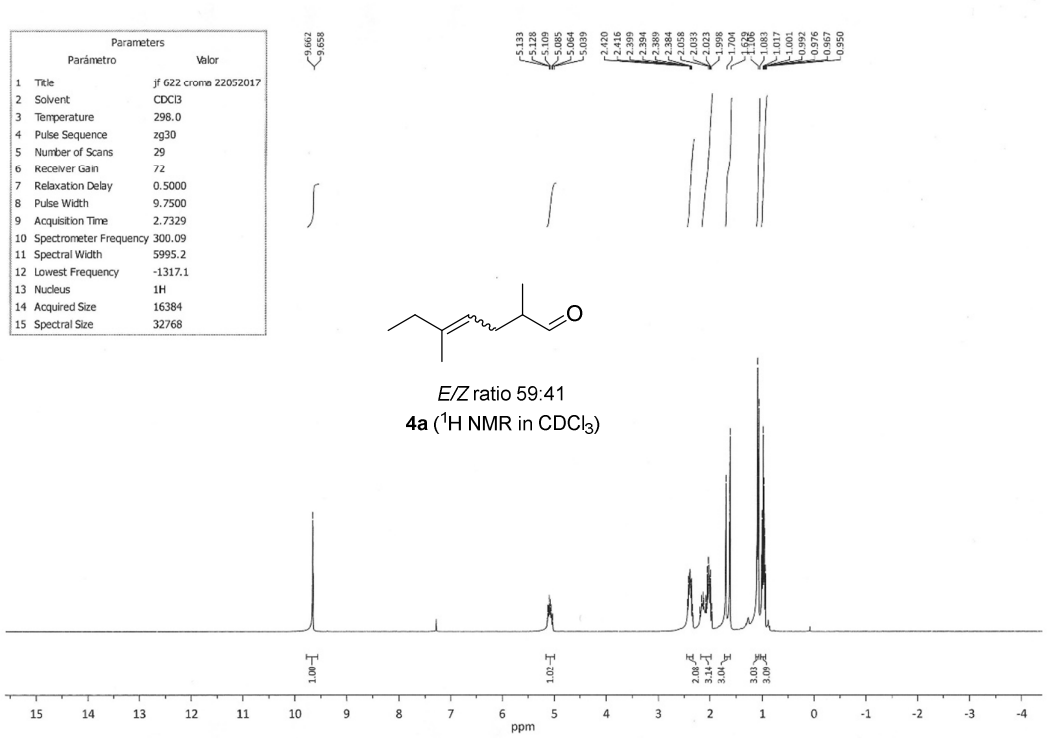

Figure S9: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 2,5-dimethylhept-4-enal, **4a**.

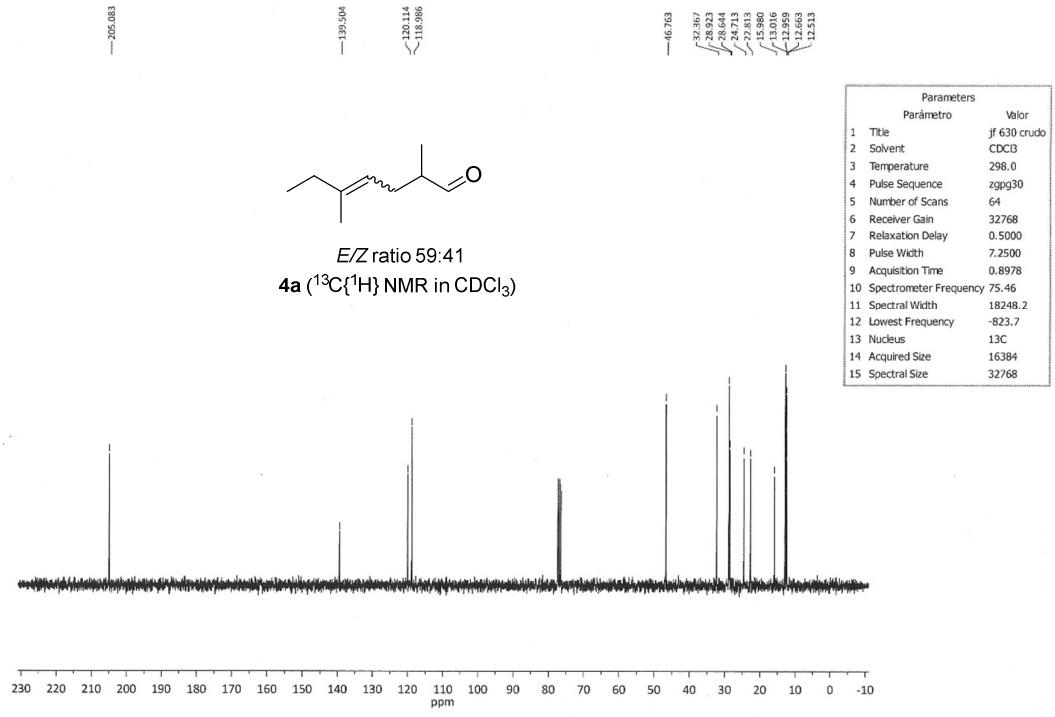

Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz, $CDCl_3$) of 2,5-dimethylhept-4-enal, **4a**.

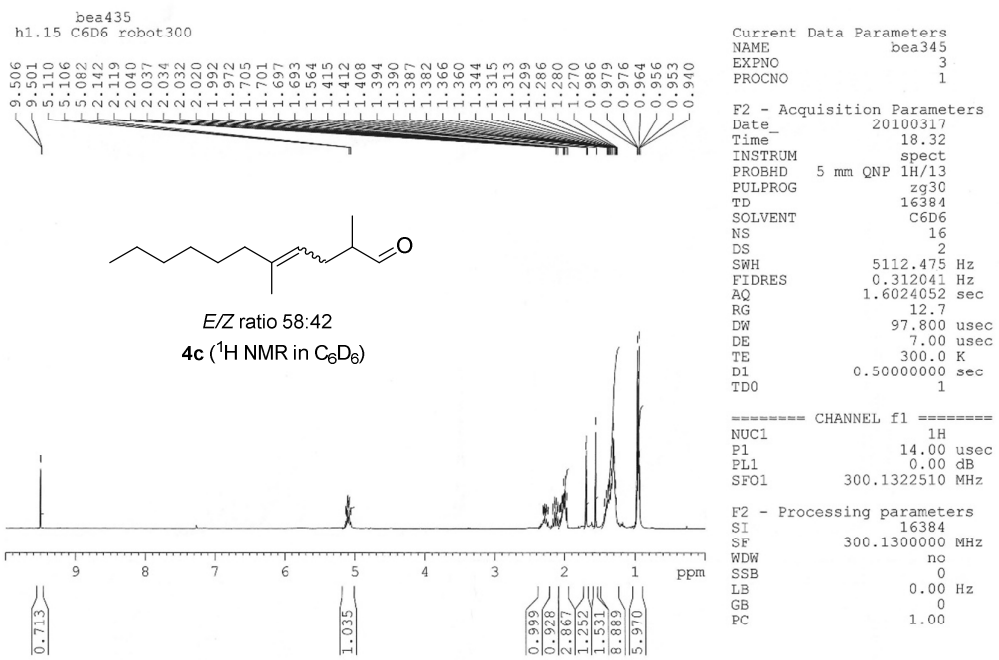

Figure S11: ^{1}H NMR spectrum (300 MHz, C_6D_6) of 2,5-dimethylundec-4-enal, **4c**.

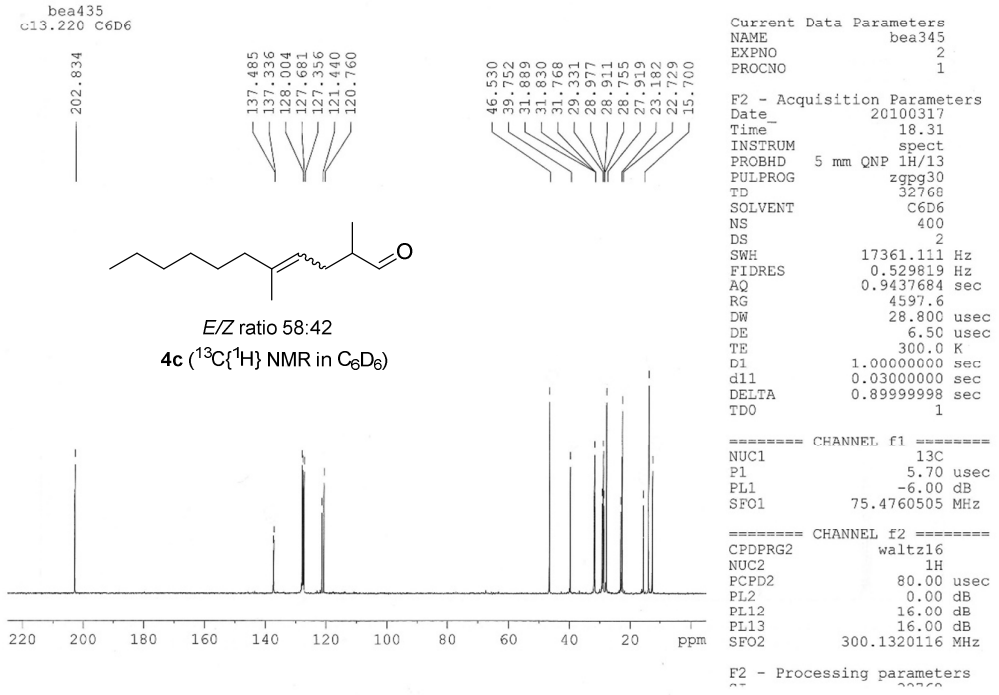

Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz, C_6D_6) of 2,5-dimethylundec-4-enal, **4c**.

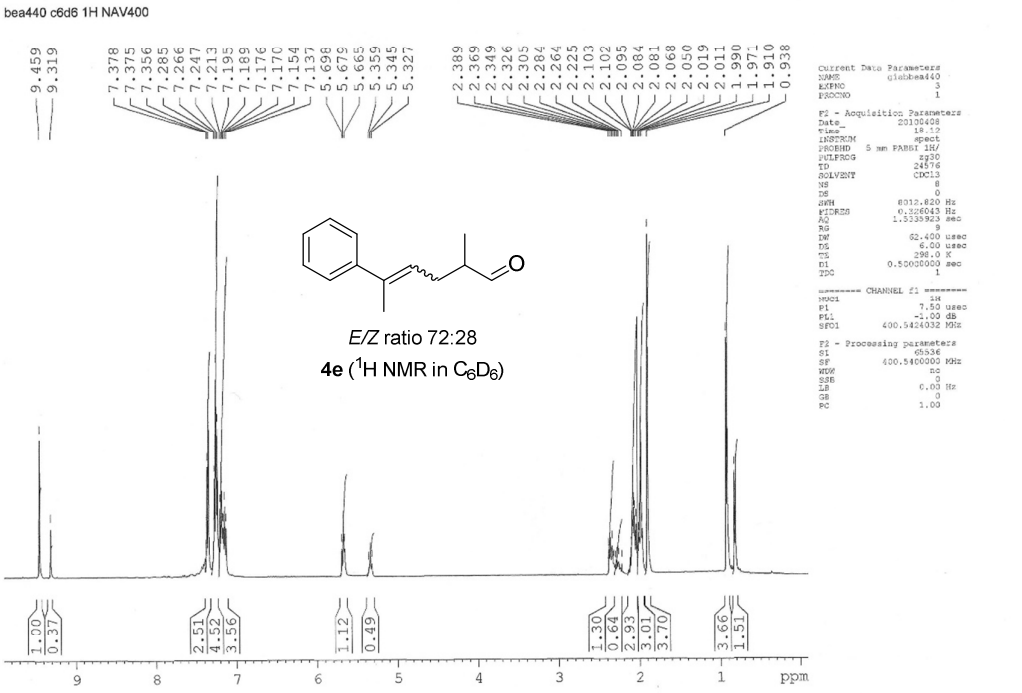

Figure S13: ^{1}H NMR spectrum (400 MHz, C_6D_6) of 2-methyl-5-phenylhex-4-enal, **4e**.

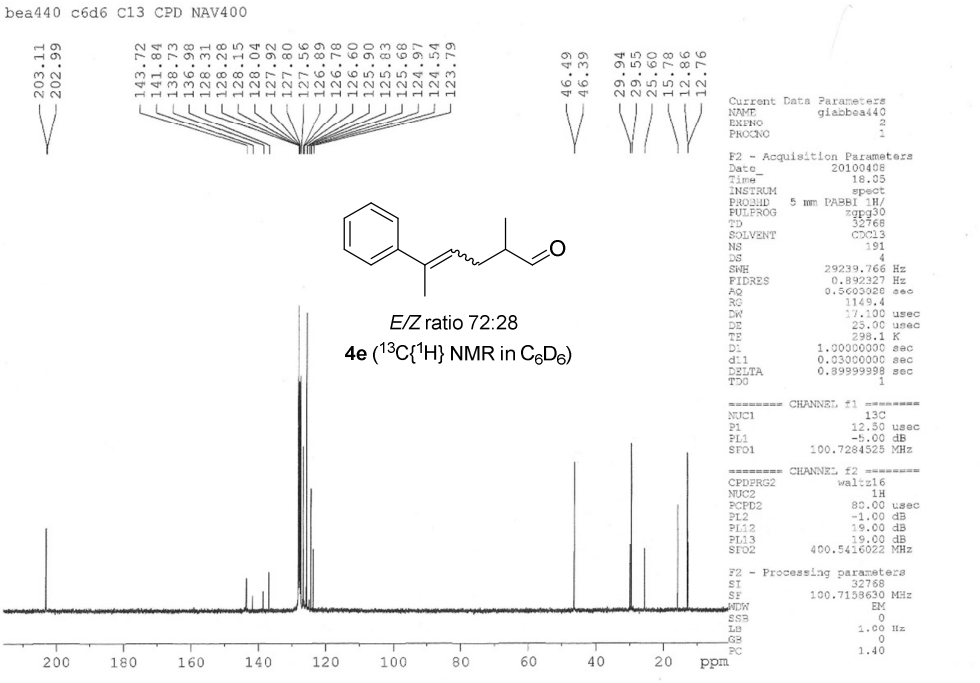

Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz, C_6D_6) of 2-methyl-5-phenylhex-4-enal, **4e**.

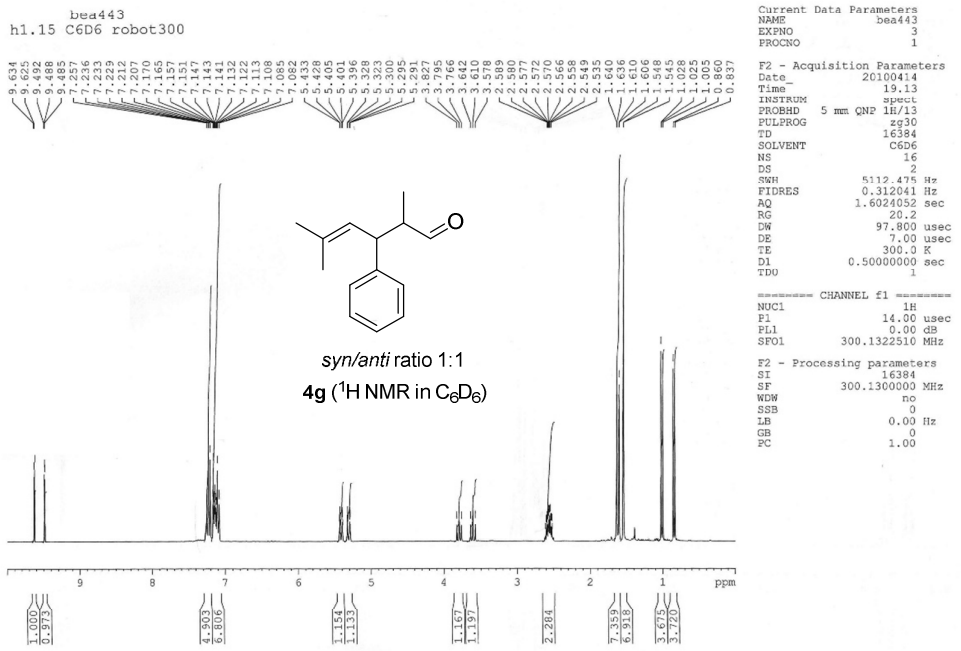

Figure S15: ^{1}H NMR spectrum (300 MHz, C_6D_6) of 2,3-dimethyl-3-phenylhex-4-enal, **4g**.

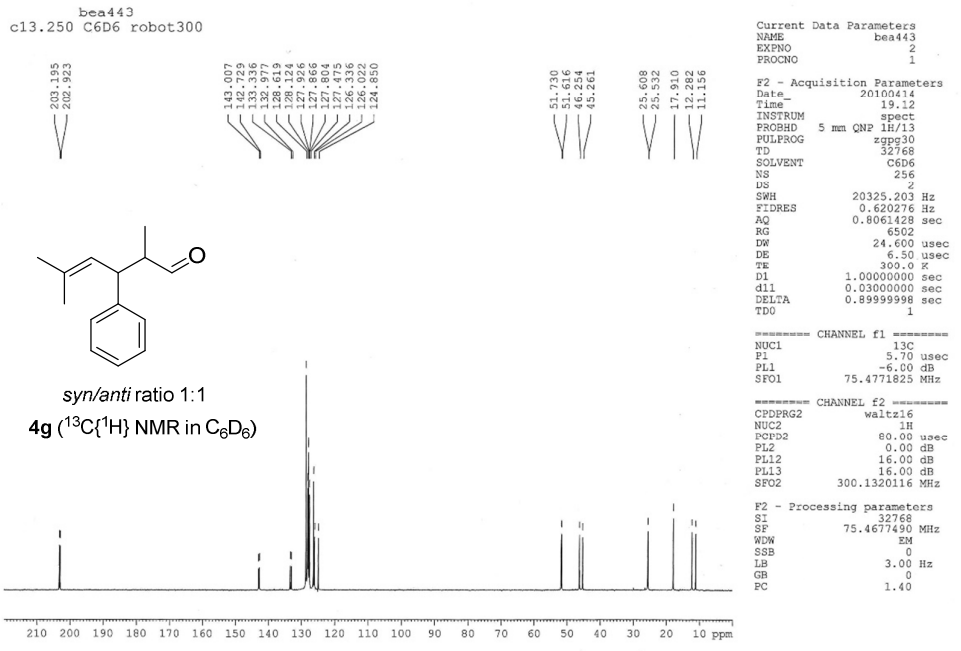

Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz, C_6D_6) of 2,3-dimethyl-3-phenylhex-4-enal, **4g**.