Supporting Information for

Hydroindation of allenes and its application to radical cyclization

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Analysis. IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All 1H and 13C NMR spectra were recorded with a JEOL JMT C-400/54/SS (400 and 100 MHz, respectively) in deuteriochloroform (CDCl3) containing 0.03% (w/v) of tetramethylsilane as internal standard. Mass spectra were recorded on a JEOL JMS-DS-303 spectrometer. Column chromatography was performed by using MERCK Silica gel 60. Purification of products by recycle GPC system was performed by JAPAN ANALYTICAL INDUSTRY CO., LTD. LC-908. Yields were determined by 1H NMR using internal standard. Stereochemistry of products was determined by NOE-difference spectrum or coupling constant of 1H NMR.
Materials:

Di-n-butyltin dihydride (n-Bu₂SnH₂) was prepared by the reduction of di-n-butyltin dichloride (n-Bu₂SnCl₂) with LiAlH₄.¹ Di-n-butyliodotin hydride (n-Bu₂SnIH) was synthesized in situ by the redistribution reaction between Bu₂SnI₂ and Bu₂SnH₂.²

THF was purchased in dehydrated form.

Undeca-1,2-diene (Octyllallene) (1a) was prepared according to the known procedures.³

4-Methyl-4-Phenyl-penta-1,2-diene (1d) was prepared according to our reported method.⁴ To the mixture of InCl₃ (0.275 g, 1.25 mmol) and propargyl trimethylsilane (68% purity 8.40g, 50.8 mmol) and chlorotrimethylsilane (1.39 g, 12.8 mmol) in dry dichloromethane (45 mL) was added dropwise 2-phenyl-propan-2-ol (2.98 g, 22 mmol) at 0 °C under nitrogen. After stirring at 0 °C for 2 h, the reaction mixture was warmed up to rt and then diluted with saturated NaHCO₃(aq) and extracted by Hexane/AcOEt= 9/1. The combined organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography eluting with hexane and then distilled under reduced pressure (100 °C/ 8 mmHg, 1.87 g, 54% yield).

\[
\text{HO} + \text{TMS} \xrightarrow{\text{InCl₃ (5 mol\%)} \text{Me₃SiCl (50 mol\%)} \text{CH₂Cl₂, 0 °C, 2 h}} \text{Ph} \quad 1b \quad 54%
\]

4-Benzyloxy-buta-1,2-diene (Benzyloxymethylallene) (1e) was prepared by following procedures.

To a solution of KOH (33.7 g, 600 mmol) in DMSO (200 mL) was added dropwise propargyl alcohol (11.2 g, 200 mmol) at 0 °C. The resulting solution was stirred at 0 °C to room temperature for 4 h. The solution was cooled to 0 °C and benzyl bromide (34.21 g, 200 mmol) was added. After stirring at rt for 14 h, water was added, and extracted by Et₂O. The combined organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by distillation under reduced pressure to give alkyne S₁ as colorless oil (47 °C/ 0.07 mmHg, 24.3 g, 86% yield).

Under nitrogen atmosphere to a mixture of CuBr (7.16 g, 50 mmol), paraformaldehyde (7.51 g, 250 mmol) and diisopropylamine (20.2 g, 200 mmol) in dioxane (380 mL) was added alkyne S₁ (14.6 g, 100 mmol). The resulting solution was refluxed for 18 h. After the reaction, the solution was filtered by celite and concentrated under reduced pressure. The resulting mixture was diluted by water (30 mL), AcOEt (70 mL) and 6M HCl (100 mL) and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over MgSO₄, filtered and concentrated. The residue was purified by distillation under reduced pressure to give 1e as colorless oil (82 °C/ 1.6 mmHg, 11.1 g, 70% yield).

\[
\text{OH} \xrightarrow{\text{KOH (3 eq)} \text{DMSO, 0 °C to rt, 2 h}} \text{Ph} \xrightarrow{\text{Ph} \text{Br (1 eq)} \text{0 °C to rt, 14 h}} \text{S₁} \quad 86%
\]

\[
\text{S₁} \xrightarrow{\text{CuBr (0.5 eq)} \text{(CH₂O)₅ (2.5 eq)} \text{iPr₂NH (2 eq)} \text{dioxane, reflux, 18 h}} \text{1e} \quad 70%
\]

Vinylidene-cyclohexane (1f) was prepared according to the known procedures.\(^5\) Cyclonona-1,2-diene (1g) was prepared according to the known procedures.\(^6\)

Allenene 5b was prepared from cinnamyl bromide and propargyl alcohol by following procedures.

To a mixture of propargyl alcohol (10.1 g, 180 mmol) and K\(_2\)CO\(_3\) (24.9 g, 180 mmol) in acetone (75 mL) was added cinnamyl bromide (29.6 g, 150 mmol) at room temperature. The mixture was refluxed for 12 h. After the resulting mixture was cooled to room temperature, water was added and extracted by AcOEt. The combined organic layer was dried over MgSO\(_4\), filtered and concentrated. The residue was purified by silica gel column chromatography eluting with Hexane/AcOEt= 95/5 and distilled to give enyne S2 as colorless oil (14.1 g, 55% yield).

Under nitrogen atmosphere to a solution of CuBr (5.88 g, 41 mmol), paraformaldehyde (6.16 g, 205 mmol) and diisopropylamine (16.6 g, 164 mmol) in dioxane (300 mL) was added enyne S2 (14.1 g, 82 mmol). The resulting solution was refluxed for 15 h. After the reaction, the solution was filtrated by cerite and concentrated under reduced pressure. The resulting mixture was diluted by water (30 mL), AcOEt (70 mL) and 6M HCl (100 mL) and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over MgSO\(_4\), filtered and concentrated. The residue was purified by distillation under reduced pressure to give 8b as colorless oil (76 °C/ 0.05 mmHg, 7.17 g, 47% yield).

\[
\begin{align*}
\text{Br} & \quad + \quad \begin{array}{c}
\text{OH} \\
\text{(1.2 eq)}
\end{array} \\
& \xrightarrow{\text{K}_2\text{CO}_3 (1.2 \text{ eq})} \text{acetone, reflux, 12 h} \quad \text{S2 55%}
\end{align*}
\]

Allenene 8c was prepared by following procedures.

Under nitrogen atmosphere to a solution of phosphorous ylide S4 (52.3 g, 150 mmol) in CH\(_2\)Cl\(_2\) (80 mL) was added dropwise aldehyde S3 (21.1 g, 150 mmol) at 10 °C over a period of 45 min. The resulting solution was stirred at 10 °C for 1 h. After the reaction, the solution was concentrated under reduced pressure. The precipitated white solid was filtered using hexane and the solution was concentrated under reduced pressure to give ester S5 including small amount of aldehyde (31.3 g, ca. >99% yield).

Under nitrogen atmosphere to a solution of crude ester S5 (29.5 g, 140 mmol) in toluene (200 mL) was added dropwise aldehyde diisobutylaluminium hydride (207 mL, 1.5 M in toluene, 310 mmol) at -78 °C. The resulting solution was warmed up to room temperature over a period of 1 h. After the reaction, the solution was cooled by iced-bath and 2M HCl in water (400 mL) was added.

dropwise slowly. The resulting mixture was extracted by CH₂Cl₂. The combined organic layer was dried over MgSO₄, filtered and concentrated. The precipitated solid was recrystallized by hexane to give alcohol S₆ as white solid (19.4 g, 85% yield).

To a suspension of 60% NaH in oil (4.8 g, 120 mmol) in THF (150 mL) was added dropwise a solution of alcohol S₆ (18.6 g, 110 mmol) in THF (50 mL) at 0 °C. The resulting solution was stirred at 0 °C to room temperature for 4 h. The solution was cooled by iced-bath and propargyl bromide (14.3 g, 120 mmol) was added. After stirring at 0 °C to room temperature for 18 h, water was added, and extracted by Et₂O. The combined organic layer was dried over MgSO₄, filtered and concentrated to give enyne S₇ with small amount of impurities (22.0 g, ca. 97% yield).

Under nitrogen atmosphere to a mixture of CuBr (5.74 g, 40 mmol), paraformaldehyde (6.01 g, 200 mmol) and diisopropylamine (16.2 g, 160 mmol) in dioxane (300 mL) was added crude enyne S₇ (16.3 g, 79 mmol). The resulting solution was refluxed for 21 h. After the reaction, the solution was filtrated by celite and concentrated under reduced pressure. The resulting mixture was diluted by AcOEt (100 mL) and 6M HCl (100 mL) and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography eluting with Hexane/AcOEt= 95/5 and distilled under reduced pressure to give 8c as colorless oil (102 ℃/ 0.10 mmHg, 8.56 g, 49% yield).
Allenenes 8d and 8e were prepared by similar procedures with 8c from aldehydes S8 and S9 instead of S3.

![Allenene 8a](attachment:image)

Allenene 8a was prepared by following procedures.

To a suspension of 60% NaH in oil (4.6 g, 115 mmol) in THF (230 mL) was added dropwise diethyl malonate (S10) (27.7 g, 174 mmol) at 0 °C. The resulting solution was stirred at 0 °C to room temperature for 3 h. The solution was cooled by iced-bath and cinnamyl bromide (25.0 g, 127 mmol) was added. After stirring at 0 °C to room temperature for 16 h, 1M HCl aq was added, and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over MgSO₄, filtered and concentrated. Excess S10 was removed from residue by distillation under reduced pressure (62 °C/ 3 mmHg). The residue was purified by silica gel column chromatography eluting with Hexane/AcOEt= 95/5 to give diester S11 including small amount of impurities (26.7 g, ca. 84% yield).

To a suspension of 60% NaH in oil (4.24 g, 106 mmol) in THF (200 mL) was added dropwise diester S11 (26.5 g, 96 mmol) at 0 °C. The resulting solution was stirred at 0 °C to room temperature for 3 h. The solution was cooled by iced-bath and propargyl bromide (12.6 g, 106 mmol) was added. After stirring at 0 °C to room temperature for 38 h, 1M HCl aq was added, and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over MgSO₄, filtered and concentrated to give crude enyne S12 including small amount of impurities (29.7 g, ca. 98% yield).

Under nitrogen atmosphere to a mixture of CuBr (6.89 g, 48 mmol), paraformaldehyde (7.15 g, 238 mmol) and diisopropylamine (19.2 g, 190 mmol) in dioxane (360 mL) was added crude enyne S12 (29.9 g, 95 mmol). The resulting solution was refluxed for 27 h. After the reaction, the solution was filtrated by celite and concentrated under reduced pressure. To the resulting mixture was diluted by water (30 mL), AcOEt (70 mL), and 6M HCl (100 mL) and extracted by AcOEt. The combined organic layer was washed by sodium bicarbonate aq and brine, and dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography eluting with Hexane/AcOEt= 95/5 and distilled under reduced pressure to give 8a including small amount of impurities as colorless oil (150 °C/ 0.07 mmHg, 4.9 g, 16% yield).
Unless otherwise noted, materials obtained from commercial supplier were used without further purification.
Typical experimental procedures:

Hydroindation of allenes using HInCl₂ (InCl₃/Et₃SiH system)

The 10 mL of round bottom flask charged with InCl₃ (0.442 g, 2 mmol) was heated at 110 °C in vacuo for 1 h. After nitrogen was filled, MeCN (2 mL) and Et₃SiH (0.233 g, 2.0 mmol) was added and the mixture was stirred at rt for 5 min. Then allenes (1.0 mmol) and Et₃B (0.1 mL, 1M solution in hexane, 0.1 mmol) were added successively. The resulting mixture was stirred at rt for 2 h. After 1M HCl aq was added, the reaction mixture was extracted with ether (10 mL x 3). The combined organic layer was dried over MgSO₄ and concentrated. Product was determined by ¹H NMR. Purification was performed by silica gel column chromatography eluting with hexane. Further purification was performed by distillation under reduced pressure.

Radical cyclization of allenenes using HInCl₂ (InCl₂OMe/PhSiH₃ system)

A 30 mL of round bottom flask charged with InCl₃ (0.442 g, 2.0 mmol) and NaOMe (0.108 g, 2.0 mmol) was dried by heating at 110 °C under reduced pressure for 1 h. After nitrogen was filled, THF (10 mL) was added to dissolve InCl₃. The resulting mixture was stirred at rt for 0.5 h. Then PhSiH₃ (0.260 g, 2.4 mmol), allene 8b (1.0 mmol) and Et₃B (0.1 mL, 1M solution in hexane, 0.1 mmol) were added successively, and the resulting solution was stirred at rt for 20 h. After 1M HCl aq was added, the reaction mixture was extracted with ether (10 mL x 3). The combined organic layer was dried over MgSO₄ and concentrated. Cyclized product was determined by ¹H NMR. Purification was performed by silica gel column chromatography eluting with hexane. Further purification was performed by distillation under reduced pressure.

Radical cyclization of allenenes and successive coupling (InCl₂OMe/PhSiH₃ system)

A 30 mL of round bottom flask charged with InCl₃ (0.442 g, 2.0 mmol) and NaOMe (0.108 g, 2.0 mmol) was dried by heating at 110 °C under reduced pressure for 1 h. After nitrogen was filled, THF (10 mL) was added to dissolve InCl₃. The resulting mixture was stirred at rt for 0.5 h. Then PhSiH₃ (0.260 g, 2.4 mmol), allenene 8b (1.0 mmol) and Et₃B (0.1 mL, 1M solution in hexane, 0.1 mmol) were added successively, and the resulting solution was stirred at rt for 20 h. After DMF (2 mL) was added, THF was removed under reduced pressure. Then aryl iodide (0.204 g, 1.0 mmol), Pd(Ph₃P)₄ (0.046 g, 4 mol%) and LiI (3.0 mmol) were added and the mixture was stirred at 100 °C for 5 h. After the reaction, resulting solution was filtrated by celite. After concentration of the filtrate, yield of product 12b was determined by ¹H NMR (36% yield). Further purification was performed by silica gel column chromatography eluting with hexane/AcOEt = 9/1.
Radical cyclization of allenene 8b using Bu₂SnIH

A 30 mL of round bottom flask was dried by flame under reduced pressure. After nitrogen was filled, THF (10 mL) was added. Bu₂SnH₂ (0.234 g, 1.0 mmol) and Bu₂SnI₂ (0.486 g, 1.0 mmol) were added successively to generate Bu₂SnIH (2.0 mmol) by the redistribution reaction. To the mixture was added allene 8b (0.186 g, 1.0 mmol) and resulting mixture was stirred at rt for 20 h. To the resulting solution was added CHCl₃ (5 mL) to completely decompose the remained tin hydride and volatiles were removed under reduced pressure. Products were determined by ¹H NMR. Purification was performed by recycle GPC eluting with CHCl₃.
Physical and spectral data:
Starting materials
buta-2,3-dienyloxymethyl-benzene (1e)

Colorless liquid
bp 82 °C/ 1.6 mmHg
IR (neat) 1955 (C=C=C) cm⁻¹

¹H NMR (CDCl₃, 400 MHz) δ 7.35-7.26 (m, 5H, g, h and i), 5.28 (tt, J = 7.0 and 6.5 Hz, 1H, c), 4.80 (dt, J = 6.5 and 2.4 Hz, 1H, a), 4.54 (s, 2H, e), 4.07 (dt, J = 7.0 and 2.4 Hz, 2H, d)

¹³C NMR (CDCl₃, 100 MHz) δ 209.32 (b), 138.04 (f), 128.36, 127.85, 127.62 (i), 87.69 (c), 75.69 (a), 71.79 (e), 67.85 (d)

MS (CI) m/z 161 (M⁺ + H, 23), 143 (100), 131 (42), 91 (CH₂Ph, 53)

HRMS calcd for C₁₁H₁₃O: 161.0966, found: m/z 161.0970 (CI, (M⁺ + H), + 0.3 mmu)

(E)-diethyl 2-(buta-2,3-dienyl)-2-cinnamylmalonate (8a)

Colorless liquid
bp 150 °C/ 0.07 mmHg
IR (neat) 1955 (C=C=C) cm⁻¹, 1732 (C=O) cm⁻¹

¹H NMR (CDCl₃, 400 MHz) δ 7.32-7.19 (m, 5H, j, k and l), 6.45 (d, J = 15.7 Hz, 1H, h), 6.04 (dt, J = 15.7 and 7.7 Hz, 1H, g), 5.00 (tt, J = 8.0 and 6.7 Hz, 1H, c), 4.69 (dt, J = 6.7 and 2.4 Hz, 2H, a), 4.20 (q, J = 7.2 Hz, 4H, n), 2.84 (dd, J = 7.7 and 1.2 Hz, 2H, f), 2.66 (dt, J = 8.0 and 2.4 Hz, 2H, d), 1.25 (t, J = 7.2 Hz, 6H, o)

¹³C NMR (CDCl₃, 100 MHz) δ 210.12 (b), 170.62 (m), 137.09 (i), 134.09 (h), 128.47 (k), 127.36 (l), 126.17 (j), 123.87 (g), 84.28 (c), 74.66 (a), 61.34 (n), 57.89 (e), 36.08 (f), 32.09 (d), 14.12 (o)

MS (EI, 70 eV) m/z 328 (M⁺, 0.3), 254 (39), 181 (97), 180 (53), 141 (32), 128 (23), 117 (CH₂CH=CHPh, 100), 115 (62), 91 (74)

HRMS calcd for C₂₀H₂₄O₄: 328.1675, found: m/z 328.1669 (EI, (M⁺), - 0.6 mmu)

Anal. calcd for C₂₀H₂₄O₄: C, 73.15; H, 7.37, found: C, 73.11; H, 7.37.
(\textit{E})-3-buta-2,3-dienyloxy-propenyl)benzene (8b)

![Chemical structure of (\textit{E})-3-buta-2,3-dienyloxy-propenyl)benzene (8b)]

Colorless liquid
bp 87 °C/ 0.07 mmHg
IR (neat) 1955 (C\textsubscript{C}C) cm\textsuperscript{-1}, 1115 (C-O-C) cm\textsuperscript{-1}, 1080 (C-O-C) cm\textsuperscript{-1}
\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \delta 7.40-7.22 (m, 5H, \textit{i}, \textit{j} and \textit{k}), 6.61 (d, \textit{J} = 15.9 Hz, 1H, \textit{g}), 6.29 (dt, \textit{J} = 15.9 and 6.0 Hz, 1H, \textit{f}), 5.28 (tt, \textit{J} = 7.0 and 6.8 Hz, 1H, \textit{c}), 4.81 (dt, \textit{J} = 6.8 and 2.4 Hz, 2H, \textit{a}), 4.17 (dd, \textit{J} = 6.0 and 1.4 Hz, 2H, \textit{e}), 4.07 (dt, \textit{J} = 7.0 and 2.4 Hz, 2H, \textit{d})
\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \delta 209.21 (\textit{b}), 136.56 (\textit{h}), 132.51 (\textit{g}), 128.43 (\textit{j}), 127.57 (\textit{k}), 126.37 (\textit{i}), 125.71 (\textit{f}), 87.62 (\textit{c}), 75.62 (\textit{a}), 70.29 (\textit{e}), 67.72 (\textit{d})
MS (CI) m/z 187 (\textit{M}^+ + \textit{H}, 1), 156 (4), 133 (PhCH=CHCH\textsubscript{2}O, 6), 118 (10), 117 (100)
HRMS calcld for C\textsubscript{13}H\textsubscript{14}O + H: 187.1123, found: m/z 187.1120 (CI, (\textit{M}^+ + \textit{H}), - 0.3 mmu)

1-((\textit{E})-3-buta-2,3-dienyloxy-propenyl)-4-chloro-benzene (8c)

![Chemical structure of 1-((\textit{E})-3-buta-2,3-dienyloxy-propenyl)-4-chloro-benzene (8c)]

Colorless liquid
bp 102 °C/ 0.10 mmHg
IR (neat) 1955 (C\textsubscript{C}C) cm\textsuperscript{-1}, 1115 (C-O-C) cm\textsuperscript{-1}, 1092 (C-O-C) cm\textsuperscript{-1}
\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \delta 7.32-7.26 (m, 4H), 6.57 (d, \textit{J} = 15.9 Hz, 1H, \textit{g}), 6.27 (dt, \textit{J} = 15.9 and 6.0 Hz, 1H, \textit{f}), 5.28 (tt, \textit{J} = 6.8 and 6.8 Hz, 1H, \textit{c}), 4.81 (dt, \textit{J} = 6.8 and 2.4 Hz, 2H, \textit{a}), 4.16 (dd, \textit{J} = 6.0 and 1.4 Hz, 2H, \textit{d})
\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \delta 209.32 (\textit{b}), 135.14 (\textit{h}), 132.51 (\textit{g}), 128.43 (\textit{j}), 127.57 (\textit{k}), 126.37 (\textit{i}), 125.71 (\textit{f}), 87.58 (\textit{c}), 75.75 (\textit{a}), 70.19 (\textit{e}), 67.98 (\textit{d})
MS (CI) m/z 221 (\textit{M}^+ + \textit{H}, 0.7), 153 (33), 151 (ClC\textsubscript{6}H\textsubscript{4}CH=CHCH\textsubscript{2}, 100)
HRMS calcld for C\textsubscript{13}H\textsubscript{13}ClO + H: 221.0733, found: m/z 221.0726 (CI, (\textit{M}^+ + \textit{H}), - 0.7 mmu)
1-((E)-3-buta-2,3-dienyloxy-propenyl)-4-methoxy-benzene (8d)

Colorless liquid

bp 121 °C/ 0.03 mmHg

IR (neat) 1955 (C=C=C) cm⁻¹, 1250 (C-O-C) cm⁻¹, 1103 (C-O-C) cm⁻¹, 1080 (C-O-C) cm⁻¹, 1038 (C-O-C) cm⁻¹

¹H NMR (CDCl₃, 400 MHz) δ 7.33 (d, J = 8.9 Hz, 2H, j), 6.85 (d, J = 8.9 Hz, 2H, i), 6.55 (d, J = 15.9 Hz, 1H, g), 6.16 (dt, J = 15.9 and 6.3 Hz, 1H, f), 5.28 (tt, J = 7.0 and 6.8 Hz, 1H, c), 4.80 (dt, J = 6.8 and 2.4 Hz, 2H, a), 4.15 (dd, J = 6.3 and 1.2 Hz, 2H, e), 4.06 (dt, J = 7.0 and 2.4 Hz, 2H, d), 3.80 (s, 3H, l)

¹³C NMR (CDCl₃, 100 MHz) δ 209.27 (b), 159.24 (k), 132.41 (g), 129.39 (h), 127.65 (i), 123.44 (f), 113.90 (j), 87.71 (c), 75.66 (a), 70.61 (e), 67.68 (d), 55.23 (l)

MS (EI, 70 eV) m/z 216 (M⁺, 6), 186 (41), 185 (M⁺ - OMe, 56), 171 (27), 163 (M⁺ - CH₂CH=C=CH₂, 26), 147 (MeOC₆H₄CH=CHCH₂, 92), 135 (100), 134 (24), 131 (29), 121 (75), 115 (31), 105 (31), 103 (36), 91 (39), 77 (25)

HRMS calcd for C₁₄H₁₆O₂: 216.1150, found: m/z 216.1145 (EI, (M⁺), - 0.5 mmu)
1-(3-buta-2,3-dienyloxy-propenyl)-naphthalene (8e)

These compounds were obtained as mixture of stereoisomers. \((E\text{-isomer:Z-isomer} = 94:6)\); See NMR spectrum. The observed data was shown below.

\((E\text{-isomer})\)

Pale yellow liquid
bp 122 °C/ 0.04 mmHg
IR (neat) 1955 (C=C=C) cm\(^{-1}\), 1115 (C-O-C) cm\(^{-1}\), 1076 (C-O-C) cm\(^{-1}\)
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.12 (d, \(J = 7.2\) Hz, 1H), 7.85 (d, \(J = 7.2\) Hz, 1H), 7.78 (d, \(J = 8.2\) Hz, 1H), 7.61, (d, \(J = 7.0\) Hz, 1H), 7.53-7.42 (m, 3H, \(j\), \(m\) and \(n\)), 7.37 (d, \(J = 15.5\) Hz, 1H, \(g\)), 6.32 (dt, \(J = 15.5\) and 6.0 Hz, 1H, \(f\)), 5.32 (tt, \(J = 7.0\) and 6.5 Hz, 1H, \(c\)), 4.83 (dt, \(J = 6.5\) and 2.4 Hz, 2H, \(a\)), 4.28 (dd, \(J = 6.0\) and 1.4 Hz, 2H, \(e\)), 4.14 (dt, \(J = 7.0\) and 2.4 Hz, 2H, \(d\))
\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 209.34 (b), 134.45, 133.53, 131.09, 129.69 (g), 129.04 (f), 128.47, 127.97, 125.97, 125.71, 125.57, 123.92, 123.76, 87.72 (c), 75.74 (a), 70.53 (e), 67.89 (d)
MS (EI, 70 eV) m/z 236 (M\(^+\), 3), 206 (48), 205 (21), 167 (NpCH=CHCH\(_2\), 47), 166 (27), 165 (81), 155 (100), 154 (21), 153 (NpCH=CH, 46), 152 (58)
HRMS calcd for C\(_{17}\)H\(_{16}\)O: 236.1201, found: m/z 236.1191 (EI, (M\(^+\)), - 1.0 mmu)

\((Z\text{-isomer})\)

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.13 (d, \(J = 11.6\) Hz, 1H, \(g\)), 6.11 (dt, \(J = 11.6\) and 6.5 Hz, 1H, \(f\)), 5.17 (tt, \(J = 7.0\) and 6.5 Hz, 1H, \(c\)), 4.63 (dt, \(J = 6.5\) and 2.4 Hz, 2H, \(a\)), 3.95 (dt, \(J = 7.0\) and 2.4 Hz, 2H, \(d\))
\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 130.19, 130.08, 128.32, 127.83, 126.55, 126.04, 125.85, 125.11, 124.81, 87.57, 75.51, 70.26, 66.52
MS (EI, 70 eV) m/z 236 (M\(^+\), 5), 206 (43), 168 (32), 167 (NpCH=CHCH\(_2\), 59), 166 (33), 165 (95), 155 (100), 154 (24), 153 (NpCH=CH, 60), 152 (65), 128 (22)
HRMS calcd for C\(_{17}\)H\(_{16}\)O: 236.1201, found: m/z 236.1213 (EI, (M\(^+\)), + 1.2 mmu)
Products

$\text{((E)}$-1,1-dimethyl-but-2-enyl)-benzene (6d-$\text{E}$)

Colorless liquid
IR (neat) 1597 (C=C) cm$^{-1}$

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.35 (d, $J = 8.0$ Hz, 2H, g), 7.29 (dd, $J = 8.0$ and 7.5 Hz, 2H, h), 7.17 (t, $J = 7.5$ Hz, 1H, i), 5.64 (dq, $J = 15.5$ and 1.4 Hz, 1H, c), 5.45 (dq, $J = 15.5$ and 6.3 Hz, 1H, b), 1.71 (dd, $J = 6.3$ and 1.4 Hz, 3H, a), 1.38 (s, 6H, e)

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 149.40 (f), 141.08 (c), 127.97 (h), 126.11 (g), 125.57 (i), 120.95 (b), 40.27 (d), 28.86 (e), 18.03 (a)

MS (EI, 70 eV) m/z 160 ($\text{M}^+$, 39), 145 ($\text{M}^+ \text{-CH}_3$, 100), 117 (22)

HRMS calcld for C$_{12}$H$_{16}$: 160.1252, found: m/z 160.1257 (EI, ($\text{M}^+$), + 0.5 mmu)

$\text{((Z)}$-1,1-dimethyl-but-2-enyl)-benzene (6d-$\text{Z}$)

Colorless liquid
IR (neat) 1601 (C=C) cm$^{-1}$

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.39 (d, $J = 8.0$ Hz, 2H, g), 7.28 (dd, $J = 8.0$ and 7.2 Hz, 2H, h), 7.16 (t, $J = 7.2$ Hz, 1H, i), 5.69 (dq, $J = 11.4$ and 1.7 Hz, 1H, c), 5.41 (dq, $J = 11.4$ and 7.2 Hz, 1H, b), 1.43 (s, 6H, e), 1.20 (dd, $J = 7.2$ and 1.7 Hz, 3H, a)

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 150.42 (f), 140.56 (c), 127.99 (h), 126.11 (g), 125.26, 124.77, 39.92 (d), 31.12 (e), 14.19 (a)

MS (EI, 70 eV) m/z 160 ($\text{M}^+$, 36), 145 ($\text{M}^+ \text{-CH}_3$, 100), 117 (23)

HRMS calcld for C$_{12}$H$_{16}$: 160.1252, found: m/z 160.1250 (EI, ($\text{M}^+$), - 0.2 mmu)
(2-methylpent-4-en-2-yl)-benzene (7d)\(^7\)

\[
\begin{align*}
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_3 &\quad \text{C} \quad \\
&\quad \text{H} \quad \\
\end{align*}
\]

\((E)-((\text{but-2-enyloxy})\text{methyl})\text{-benzene (6e-E)}\)\(^8\)

\[
\begin{align*}
\text{CH}_2\text{CH} &\quad \text{O} \quad \\
&\quad \text{C} \quad \\
\end{align*}
\]

\((\text{but-3-enyloxy})\text{methyl}-\text{benzene (7e)}\)\(^9\)

\[
\begin{align*}
\text{CH}_2\text{CH} &\quad \text{O} \quad \\
&\quad \text{C} \quad \\
\end{align*}
\]

\((E)-2\text{-ido-undec-2-ene (2a''-E)}\)

No NOE was observed at \(c\)-H (6.15 ppm) by irradiation at \(a\)-H (2.36 ppm).

\[
\begin{align*}
\text{H} &\quad \text{Me} \quad a \quad c \quad d \quad e \quad f \quad g \quad h \quad i \quad j \quad k \\
\text{a} &\quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e} \quad \text{f} \quad \text{g} \quad \text{h} \quad \text{i} \quad \text{j} \quad \text{k} \\
\end{align*}
\]

0.4\% NOE

Colorless liquid

IR (neat) 1635 (C=C) cm\(^{-1}\)

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 6.15 (t, \(J = 7.5\) Hz, 1H, \(c\)), 2.36 (s, 3H, \(a\)), 2.01 (dt, \(J = 7.5\) and 7.2 Hz, 2H, \(d\)), 1.37-1.22 (m, 12H), 0.88 (t, \(J = 7.2\) Hz, 3H, \(k\))

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 141.55 (\(c\)), 93.37 (\(b\)), 31.85, 30.65, 29.36, 29.22, 29.06, 28.88, 27.43 (\(a\)), 22.65 (\(j\)), 14.10 (\(k\))

MS (EI, 70 eV) m/z 280 (M\(^+\), 87), 181 (21), 168 (27), 97 (58), 83 (46), 69 (57), 55 (100), 41 (31)

HRMS calcd for C\(_{11}\)H\(_{21}\)I: 280.0688, found: m/z 280.0702 (EI, (M\(^+\)), + 1.4 mmu)


**(Z)-2-iodo-undec-2-ene (2a''-Z) and 2-iodo-undec-1-ene (3a'')**

6.6% NOE was observed at $c$-H (5.40 ppm) by irradiation at $a$-H (2.49 ppm) in 2a''-Z.

These compounds were not purely isolated and were obtained as mixture of regionisomers (2a''-Z: 3a'' = 63:37). See NMR spectrum. The observed data was shown below.

**Colorless liquid**

IR (neat) 1651 (C=C) cm$^{-1}$, 1616 (C=C) cm$^{-1}$

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 6.00 (s, 1H, a, 3a''), 5.68 (s, 1H, a, 3a''), 5.40 (t, $J = 6.8$ Hz, 1H, c, 2a''-Z), 2.49 (s, 3H, a, 2a''-Z), 2.37 (t, $J = 7.0$ Hz, 2H, c, 3a''), 2.07 (dt, $J = 7.0$ and 6.8 Hz, 2H, d, 2a''-Z), 1.55-1.28 (m, 26H, 2a''-Z, 3a''), 0.88 (t, $J = 7.0$ Hz, 6H, k, 2a''-Z, 3a'')

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 135.58 (c, 2a''-Z), 125.10 (a, 3a''), 112.88 (b, 3a''), 100.69 (b, 2a''-Z), 45.30 (c, 3a''), 36.57 (d, 2a''-Z), 33.49 (a, 2a''-Z), 31.87, 29.49, 29.46, 29.32, 29.27, 29.25, 29.17, 29.06, 28.36, 28.15, 22.67, 14.11 (k, 2a''-Z, 3a'')

MS (EI, 70 eV) m/z 280 (M$^+$, 67), 168 (47), 97 (67), 83 (54), 69 (58), 57 (CH$_2$CH$_2$CH$_2$CH$_3$, 23), 55 (100), 43 (CH$_2$CH$_2$CH$_3$, 21), 41 (38)

HRMS calcd for C$_{11}$H$_{21}$I: 280.0688, found: m/z 280.0682 (EI, (M$^+$), - 0.6 mmu)
diethyl 3-benzyl-4-vinyl-cyclopentane-1,1-dicarboxylate (9a)

(major)
Colorless liquid
IR (neat) 1732 (C=O) cm\(^{-1}\)
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.30-7.14 (m, 5H), 5.69 (ddd, \(J = 17.1, 10.2\) and 8.2 Hz, 1H, \(b\)), 5.09 (dd, \(J = 17.1\) and 1.9 Hz, 1H, \(a\)), 5.05 (dd, \(J = 10.2\) and 1.9 Hz, 1H, \(a\)), 4.22-4.09 (m, 4H, \(n\) and \(n'\)), 2.92 (dd, \(J = 13.5\) and 3.6 Hz, 1H, \(h\)), 2.50 (dd, \(J = 13.5\) and 7.5 Hz, 1H, \(f\)), 2.36-2.21 (m, 3H), 2.05 (dd, \(J = 13.5\) and 10.9 Hz, 1H), 2.00-1.87 (m, 2H), 1.23 (t, \(J = 7.0\) Hz, 3H, \(o\)), 1.19 (t, \(J = 7.0\) Hz, 3H, \(o'\))
\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 172.63 (m), 172.47 (m'), 140.74 (i), 139.96 (b), 128.81, 128.24, 125.83 (l), 115.83 (a), 61.41 (n), 61.36 (n'), 58.21 (e), 50.04 (c), 46.71 (g), 40.30, 39.56, 39.17, 14.00 (o), 13.96 (o')
MS (EI, 70 eV) m/z 330 (M\(^+\), 28), 256(52), 239 (36), 211 (26), 183 (33), 182 (20), 173 (36), 165 (63), 143 (79), 91 (CH\(_2\)Ph, 100)
HRMS calcld for C\(_{20}\)H\(_{26}\)O\(_4\): 330.1831, found: m/z 330.1813 (EI, (M\(^+\)), - 1.8 mmu)

(minor)
This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after GPC were shown below.
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 5.85 (ddd, \(J = 17.1, 10.3\) and 8.5 Hz, 1H, \(b\)), 5.08 (dd, \(J = 10.3\) and 1.9 Hz, 1H, \(a\)), 5.04 (dd, \(J = 17.1\) and 1.9 Hz, 1H, \(a\)), 2.51 (dd, \(J = 14.0\) and 7.2 Hz, 1H), 2.08 (dd, \(J = 13.8\) and 8.2 Hz, 1H), 1.24 (t, \(J = 7.0\) Hz, 3H, \(o\)), 1.21 (t, \(J = 7.0\) Hz, 3H, \(o'\))
\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 172.77 (m), 172.69 (m'), 141.16 (i), 138.10 (b), 128.87, 128.22, 125.75 (l), 115.84 (a), 61.45 (n), 61.42 (n'), 58.75 (e), 46.57, 44.81, 38.80, 38.24, 36.30, 14.02 (o), 13.97 (o')
MS (EI, 70 eV) m/z 330 (M\(^+\), 22), 256 (59), 239 (49), 229 (24), 184 (23), 183 (37), 182 (30), 173 (46), 165 (65), 143 (56), 91 (CH\(_2\)Ph, 100)
HRMS calcld for C\(_{20}\)H\(_{26}\)O\(_4\): 330.1831, found: m/z 330.1820 (EI, (M\(^+\)), - 1.1 mmu)
3-benzyl-4-vinyl-tetrahydrofuran (9b)

The stereochemistry of the products was determined by NOE observation. 5.2% NOE was observed at f-H (2.31-2.22 ppm) by irradiation at b-H (5.69 ppm). 0.3% NOE was observed at g-H (2.91 ppm) by irradiation at b-H (5.69 ppm).

Colorless liquid
IR (neat) 1639 (C=C) cm⁻¹, 1053 (C-O-C) cm⁻¹

1H NMR (CDCl₃, 400 MHz) δ 7.27 (dd, J = 7.5 and 7.4 Hz, 2H, j), 7.19 (t, J = 7.4 Hz, 1H, k), 7.14 (d, J = 7.5, 2H, i), 5.69 (ddd, J = 17.1 and 10.1 and 8.5 Hz, 1H, b), 5.08 (dd, J = 17.1 and 1.7 Hz, 1H, a), 5.05 (dd, J = 10.1 and 1.7 Hz, 1H, a), 4.03 (dd, J = 8.2 and 8.2 Hz, 1H, d), 3.88 (dd, J = 8.5 and 7.5 Hz, 1H, e), 3.54 (dd, J = 8.2 and 8.7 Hz, 1H, d), 3.53 (dd, J = 8.5 and 7.9 Hz, 1H, e), 2.91 (dd, J = 13.8 and 4.8 Hz, 1H, g), 2.88-2.48 (m, 2H, c and g), 2.31-2.22 (m, 1H, f)

13C NMR (CDCl₃, 100 MHz) δ 140.28 (h), 137.85 (b), 128.62 (i), 128.38 (j), 116.46 (a), 73.35 (e), 72.85 (d), 50.32 (c), 47.24 (f), 37.75 (g)

MS (EI, 70 eV) m/z 188 (M⁺, 1), 157 (27), 129 (30), 104 (32), 92 (51), 91 (PhCH₂, 100)

HRMS calcd for C₁₃H₁₆O: 188.1201, found: m/z 188.1210 (EI, (M⁺), + 0.9 mmu)

Anal. calcd for C₁₃H₁₆O: C, 82.94; H, 8.57, found: C, 82.92; H, 8.31.

(minor) cis-3-benzyl-4-vinyl-tetrahydrofuran (9b-cis)

This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after GPC were shown below.

1H NMR (CDCl₃, 400 MHz) δ 5.89 (ddd, J = 17.1 and 10.3 and 9.4 Hz, 1H, b), 3.96 (dd, J = 8.5 and 6.5 Hz, 1H), 3.81 (dd, J = 8.6 and 7.2 Hz, 1H), 3.74 (dd, J = 8.5 and 4.8 Hz, 1H), 2.78 (dd, J = 13.5 and 5.3 Hz, 1H, g)

13C NMR (CDCl₃, 100 MHz) δ 140.78, 136.13, 128.75, 128.49, 125.97, 116.88, 72.67, 71.93, 46.74, 44.82, 34.25

MS (EI, 70 eV) m/z 188 (M⁺, 2), 157 (27), 105 (25), 104 (29), 92 (47), 91 (CH₂Ph, 100)

HRMS calcd for C₁₃H₁₆O: 188.1201, found: m/z 188.1198 (EI, (M⁺), - 0.3 mmu)
The stereochemistry of the products was determined by comparison of $^1$H NMR spectrum with 9b. These compounds were not purely isolated and were obtained as mixture of diastereomers. (9c-trans:9c-cis = 83:17); See NMR spectrum. The observed data was shown below.

Colorless liquid

IR (neat) 1639 (C=C) cm$^{-1}$, 1095 (C-O-C) cm$^{-1}$, 1053 (C-O-C) cm$^{-1}$

Anal. calcd for C$_{13}$H$_{15}$ClO: C, 70.11; H, 6.79; Cl, 15.92, found: C, 69.84; H, 6.58; Cl, 16.20.

(major) trans-3-(4-methoxyphenylmethyl)-4-vinyltetrahydrofuran (9c-trans)

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.24 (d, $J = 8.2$ Hz, 2H, j), 7.07 (d, $J = 8.2$ Hz, 2H, i), 5.67 (ddd, $J = 17.0$, 10.1 and 8.5 Hz, 1H, b), 5.05 (dd, $J = 10.1$ and 1.7 Hz, 1H, a), 4.02 (ddd, $J = 17.0$, 10.1 and 1.7 Hz, 1H, d), 3.86 (dd, $J = 8.5$ and 7.5 Hz, 1H, e), 3.54 (dd, $J = 8.5$ and 8.5 Hz, 1H, d), 3.49 (dd, $J = 8.5$ and 8.2 Hz, 1H, e), 2.87 (dd, $J = 13.8$ and 5.1 Hz, 1H, g), 2.56-2.46 (m, 2H, c and g), 2.28-2.18 (m, 1H, f)

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 138.69 (h), 137.69 (b), 131.87 (k), 129.95 (i), 128.50 (j), 116.60 (a), 73.17 (e), 72.85 (d), 50.26 (c), 47.13 (f), 37.13 (g)

MS (EI, 70 eV) m/z 222 (M$,^+$, 9), 138 (27), 125 (CH$_2$C$_6$H$_4$Cl, 100), 91 (22)

HRMS calcld for C$_{13}$H$_{15}$ClO: 222.0811, found: m/z 222.0808 (EI, (M$^+$), - 0.3 mmu)

(minor) cis-3-(4-methoxyphenylmethyl)-4-vinyltetrahydrofuran (9c-cis)

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.86 (ddd, $J = 17.0$, 10.1 and 9.2 Hz, 1H, b), 5.16 (dd, $J = 10.1$ and 1.7 Hz, 1H, a), 5.10 (dd, $J = 17.0$ and 1.7 Hz, 1H, a), 3.96 (dd, $J = 8.5$ and 6.5 Hz, 1H), 3.80 (dd, $J = 8.5$ and 7.0 Hz, 1H), 3.74 (dd, $J = 8.5$ and 4.8 Hz, 1H), 2.74 (dd, $J = 13.5$ and 5.6 Hz, 1H, g)

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 139.20, 135.94, 131.75, 117.10, 72.69, 71.81, 46.66, 44.71, 33.62

MS (EI, 70 eV) m/z 222 (M$,^+$, 3), 167 (32), 139 (30), 138 (29), 127 (36), 125 (CH$_2$C$_6$H$_4$Cl, 100), 91 (20)

HRMS calcld for C$_{13}$H$_{15}$ClO: 222.0811, found: m/z 222.0818 (EI, (M$^+$), + 0.7 mmu)
3-(4-methoxyphenylmethyl)-4-vinyl-tetrahydrofuran (9d)

The stereochemistry of the products was determined by comparison of $^1$H NMR spectrum with 9b.

(major) trans-3-(4-methoxyphenylmethyl)-4-vinyl-tetrahydrofuran (9d-trans)

Colorless liquid
IR (neat) 1639 (C=C) cm$^{-1}$, 1250 (C-O-C) cm$^{-1}$, 1111 (C-O-C) cm$^{-1}$, 1038 (C-O-C) cm$^{-1}$

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.06 (d, $J = 8.7$ Hz, 2H, i), 6.82 (d, $J = 8.7$ Hz, 2H, j), 5.69 (ddd, $J = 17.0$, 10.1 and 8.5 Hz, 1H, b), 5.08 (dd, $J = 17.0$ and 1.4 Hz, 1H, a), 5.05 (dd, $J = 10.1$ and 1.4 Hz, 1H, a), 4.02 (dd, $J = 8.5$ and 8.2 Hz, 1H, d), 3.87 (dd, $J = 8.5$ and 7.5 Hz, 1H, e), 3.79 (s, 3H, l), 3.54 (dd, $J = 8.5$ and 8.5 Hz, 1H, d), 3.51 (dd, $J = 8.5$ and 8.2 Hz, 1H, e), 2.85 (dd, $J = 13.8$ and 4.8 Hz, 1H, g), 2.56-2.43 (m, 2H, c and g), 2.28-2.18 (m, 1H, f)

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 157.89 (k), 137.92 (b), 132.32 (h), 129.53 (i), 116.39 (a), 113.73 (j), 73.34 (e), 72.85 (d), 55.19 (l), 50.21 (c), 46.73 (f), 36.80 (g)

MS (EI, 70 eV) m/z 218 (M$^+$, 16), 121 (CH$_2$C$_6$H$_4$OMe, 100)

HRMS calcd for C$_{14}$H$_{18}$O$_2$: 218.1307, found: m/z 218.1313 (EI, (M$^+$), + 0.6 mmu)

(minor) cis-3-(4-methoxyphenylmethyl)-4-vinyl-tetrahydrofuran (9d-cis)

This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after GPC were shown below.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.88 (ddd, $J = 16.9$, 10.4 and 9.2 Hz, 1H, b), 5.15 (dd, $J = 10.4$ and 1.9 Hz, 1H, a), 5.11 (dd, $J = 16.9$ and 1.9 Hz, 1H, a), 3.96 (dd, $J = 8.5$ and 6.8 Hz, 1H), 2.72 (dd, $J = 13.5$ and 5.6 Hz, 1H, g)

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 136.20, 132.80, 129.52, 116.81, 72.70, 71.98, 46.73, 45.04, 33.32

MS (EI, 70 eV) m/z 218 (M$^+$, 14), 163 (22), 148 (24), 121 (CH$_2$C$_6$H$_4$OMe, 100)

HRMS calcd for C$_{14}$H$_{18}$O$_2$: 218.1307, found: m/z 218.1309 (EI, (M$^+$), + 0.2 mmu)
3-(naphthalene-1-ylmethyl)-4-vinyl-tetrahydrofuran (9e)

The stereochemistry of the products was determined by comparison of $^1$H NMR spectrum with 9b.

**major** trans-3-(naphthalene-1-ylmethyl)-4-vinyltetrahydrofuran (9e-trans)
Colorless liquid

IR (neat) 1639 (C=O) cm$^{-1}$, 1065 (C-O-C) cm$^{-1}$, 1041 (C-O-C) cm$^{-1}$

$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.97 (d, $J = 8.2$ Hz, 1H), 7.84 (d, $J = 8.5$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 7.53-7.45 (m, 2H), 7.37 (dd, $J = 8.2$ and 7.0 Hz, 1H), 7.27 (d, $J = 7.0$ Hz, 1H), 5.73 (ddd, $J = 17.0$, 10.0 and 8.5 Hz, 1H, $b$), 5.14 (dd, $J = 17.0$ and 1.7 Hz, 1H, $a$), 5.10 (dd, $J = 10.1$ and 1.7 Hz, 1H, $a$), 4.07 (dd, $J = 8.5$ and 8.0 Hz, 1H, $d$), 3.80 (dd, $J = 8.5$ and 7.5 Hz, 1H, $e$), 3.60 (dd, $J = 8.5$ and 8.2 Hz, 1H, $e$), 3.54 (dd, $J = 8.5$ and 8.5 Hz, 1H, $d$), 3.45 (dd, $J = 14.0$ and 4.6 Hz, 1H, $g$), 2.85 (dd, $J = 14.0$ and 9.9 Hz, 1H, $g$), 2.65 (ddd, $J = 8.5$, 8.5, 8.2 and 8.0 Hz, 1H, $c$), 2.50-2.40 (m, 1H, $f$)

$^{13}$C NMR (CDCl$_3$, 100 MHz) δ 137.80 ($b$), 136.43, 133.84 ($g$), 131.67, 128.80, 127.02, 126.21, 125.87, 125.52, 125.39, 123.48, 116.72 ($a$), 73.58 ($e$), 72.90 ($d$), 50.85 ($c$), 46.20 ($f$), 34.98 ($g$)

MS (EI, 70 eV) m/z 238 (M$^+$, 32), 142 (100), 141 (CH$_2$Np, 96)

HRMS calcd for C$_{17}$H$_{18}$O: 238.1358, found: m/z 238.1362 (EI, (M$^+$), + 0.4 mmu)

**minor** cis-3-(naphthalene-1-ylmethyl)-4-vinyltetrahydrofuran (9e-cis)
This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after GPC were shown below.

$^1$H NMR (CDCl$_3$, 400 MHz) δ 6.03 (ddd, $J = 16.9$, 10.1 and 9.2 Hz, 1H, $b$), 3.99 (dd, $J = 8.5$ and 7.0 Hz, 1H), 3.31 (dd, $J = 13.8$ and 4.3 Hz, 1H), 3.05-2.98 (m, 1H)

$^{13}$C NMR (CDCl$_3$, 100 MHz) δ 136.78, 136.12, 133.90, 131.74, 128.84, 126.92, 126.42, 123.55, 117.26 ($a$), 72.46, 72.06, 47.08, 43.83, 31.22 ($g$)

MS (EI, 70 eV) m/z 238 (M$^+$, 35), 155 (28), 142 (88), 141 (CH$_2$Np, 100), 115 (25)

HRMS calcd for C$_{17}$H$_{18}$O: 238.1358, found: m/z 238.1371 (EI, (M$^+$), + 1.3 mmu)
3-benzyl-4-(1-(4-nitrophenyl)-vinyl)-tetrahydrofuran (12b)

\[ \text{NO}_2 \]

(major)
Yellow liquid
IR (neat) 1597 (C=C) cm\(^{-1}\), 1516 (NO\(_2\)) cm\(^{-1}\), 1346 (NO\(_2\)) cm\(^{-1}\), 1111 (C-O-C) cm\(^{-1}\), 1061 (C-O-C) cm\(^{-1}\)

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.09 (d, \(J = 8.9\) Hz, 2H, \(n\)), 7.31-7.19 (m, 5H), 7.10 (d, \(J = 8.2\) Hz, 2H, \(i\)), 5.45 (s, 1H, \(a\)), 5.38 (s, 1H, \(a\)), 4.15 (dd, \(J = 8.7\) and 7.2 Hz, 1H, \(d\)), 4.01 (dd, \(J = 8.5\) and 7.0 Hz, 1H, \(e\)), 3.77 (dd, \(J = 8.7\) and 6.0 Hz, 1H, \(d\)), 3.65 (dd, \(J = 8.5\) and 6.0 Hz, 1H, \(e\)), 3.03 (ddd, \(J = 7.2, 6.8\) and 6.0 Hz, 1H, \(c\)), 2.81 (dd, \(J = 13.8\) and 7.2 Hz, 1H, \(g\)), 2.70 (dd, \(J = 13.8\) and 8.0 Hz, 1H, \(g\)), 2.57-2.48 (m, 1H, \(f\))

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 148.15, 147.48, 146.88, 139.63 (h), 128.68, 128.47, 127.06, 126.32 (k), 123.48 (n), 115.56 (a), 73.04, 73.00, 48.79 (c), 46.85 (f), 38.96 (g)

MS (EI, 70 eV) m/z 309 (M\(^+\), 1), 218 (M\(^+\) - CH\(_2\)Ph, 33), 130 (35), 92 (45), 91 (PhCH\(_2\), 100)

HRMS calcd for C\(_{19}\)H\(_{19}\)NO\(_3\): 309.1365, found: m/z 309.1359 (EI, (M\(^+\)), - 0.6 mmu)

(minor)
This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture after silica gel column chromatography were shown below.

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 5.61 (s, 1H, \(a\)), 5.28 (s, 1H, \(a\))

MS (EI, 70 eV) m/z 309 (M\(^+\), 5), 278 (36), 177 (24), 160 (20), 146 (22), 133 (26), 132 (21), 131 (23), 130 (78), 129 (22), 128 (24), 117 (100), 115 (37), 105 (92), 92 (21), 91 (PhCH\(_2\), 98)

HRMS calcd for C\(_{19}\)H\(_{19}\)NO\(_3\): 309.1365, found: m/z 309.1364 (EI, (M\(^+\)), - 0.1 mmu)
1e

$\begin{align*}
\text{1H NMR} \\
5.435 \\
1.000 \\
2.093 \\
2.089 \\
2.088 \\
7.35 \\
7.34 \\
7.30 \\
7.29 \\
7.28 \\
7.27 \\
7.26 \\
5.32 \\
5.30 \\
5.28 \\
5.26 \\
5.25 \\
4.82 \\
4.81 \\
4.81 \\
4.80 \\
4.80 \\
4.79 \\
4.54 \\
4.08 \\
4.07 \\
4.06 \\
4.06 \\
4.05 \\
0.00
\end{align*}$

$\begin{align*}
\text{13C NMR} \\
209.32 \\
138.04 \\
128.36 \\
127.85 \\
127.62 \\
87.69 \\
77.32 \\
77.00 \\
76.68 \\
75.69 \\
71.79 \\
67.85
\end{align*}$
6d-\(E\)

\[\text{\foreignlanguage{en}{1H NMR}}\]

\[\text{\foreignlanguage{en}{13C NMR}}\]
6d-Z

$^1$H NMR

$^{13}$C NMR
2a''-\textit{E}

\textbf{\textsuperscript{1}H NMR}

\textbf{\textsuperscript{13}C NMR}
**2a''-Z and 3a''**

![Structural formulas of 2a''-Z and 3a''](image)

**1H NMR**

![1H NMR spectrum image](image)

**13C NMR**

![13C NMR spectrum image](image)
**8a**

**1H NMR**

**13C NMR**
$^{1}H$ NMR

$^{13}C$ NMR
8c

$^1$H NMR

$^1$C NMR

$^1$H NMR

$^1$C NMR

S29
$^{1}$H NMR

$^{13}$C NMR
8e

(E/Z = 94/6)

$^1$H NMR

$^{13}$C NMR
9a-major

$^1$H NMR

$^{13}$C NMR
9b-trans

$^1$H NMR

$^1$C NMR
**9c (trans/cis = 83/17)**

\[ \text{trans} / \text{cis} = 83/17 \]

**H NMR**

**C NMR**
**9d-trans**

\[ \text{OMe} \]

**\(^1\)H NMR**

**\(^{13}\)C NMR**
**9e-trans**

\begin{center}
\includegraphics[width=0.5\textwidth]{diagram.png}
\end{center}

**1H NMR**

\begin{center}
\includegraphics[width=\textwidth]{1H_NMR.png}
\end{center}

**13C NMR**

\begin{center}
\includegraphics[width=\textwidth]{13C_NMR.png}
\end{center}
12b-major

\[
\begin{align*}
\text{NO}_2 \\
\end{align*}
\]

\[^1H\text{ NMR}\]

\[^{13}C\text{ NMR}\]