Supporting Information for

Synthesis of Functionalized Tetrahydrofurans from Alkenols and Olefins/Alkynes via Aerobic Oxidation – Radical Addition Cascades

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Contents

1 General Remarks

(i) The compound numbering in the Supporting information is consistent with that of the accompanying publication. (ii) References refer exclusively to the Supporting Information.

2 Instrumentation and Reagent Specification

^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded with FT-NMR DPX 400 and DMX 600 instruments (*Bruker*). Chemical shifts refer to the δ-scale (coupling constants J are given in Hz). The resonances of residual protons and the corresponding carbons of deuterated solvents ($CDCl_3$: δ_H 7.26, δ_C 77.0) were used as internal standards for ^{1}H-, and ^{13}C-NMR. ^{19}F-NMR chemical shifts were referenced versus α,α,α-Trifluorotoluene (δ_F −63.72) as internal standard.

Mass spectra (EI, 70 eV) were recorded with a Mass Selective Detector HP 6890 (*Hewlett Packard*).

Combustion analyses were performed with a vario Micro cube CHNS (*Elementar Analysentechnik / Hanau*).

Reaction progress was monitored via thin layer chromatography (TLC) on aluminium sheets coated with silica gel (60 F_{254}, *Machery-Nagel*). Compounds were detected by UV-light (254 nm) or by staining of developed TLC sheets with Ekkert's reagent.

IR spectra were recorded from pelletized samples in KBr using a FT-IR 1000 spectrometer (*Perkin Elmer*).

UV/Vis-spectra were recorded in 1 cm-quartz cuvettes with a Cary 100 spectrometer (*Varian*) at 20 °C using analytical grade solvents. Molar extinction coefficients (ε) are reported in m^2mol^{-1}.

GC/MS Analysis was performed with a HP 6890 Series (*Hewlett Packard*) with a ZB5 column (*Phenomenex*, 30 m × 0.25 mm, 0.25 μm). Temperature program: 40 °C (3 min), linear temperature rise (10 °C min^{-1}) to 280 °C, final temperature 280 °C (10 min).

All solvents were purified according to standard procedures.[1]

1-Phenylpent-4-en-1-ol (**1a**),[2,3] 1-phenylhex-4-en-1-ol (**1b**),[2] 2-phenylpent-4-en-1-ol (**1c**),[4] 3-phenylpent-4-en-1-ol (**1d**)[2,5] *cis*-2-allylcyclohexanol (**1e**)[6] , methyl 3-(2-hydroxy-cyclohex-1-yl)-prop-2-enoate (**1f**)[6,7], 1-phenylpent-4-en-1,3-diol (**1g**)[8] and bis-{4-[3,5-bis-(trifluoromethyl)-phenyl]-(2-oxo-κ*O*)-but-3-en-(4-olato-κ*O*)}-cobalt(II) (**3**)[7] were prepared according to published procedures.

3 Cobalt Complexes

Bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (4): A solution of benzoyltrifluoroacetone (2.01 g, 9.27 mmol) in EtOH (6.0 mL) was added to an aqueous solution of cobalt(II) acetate tetrahydrate (1.11 g, 4.46 mmol in 20 mL H_2O) and stirred at 20 °C for 1 h. The yellow precipitate was filtered and dried in vacuo. Yield: 2.32 g, 4.42 mmol, 99%; λ_{max} (EtOH) / nm (lg $\varepsilon/\varepsilon^*$) 252 (3.33), 319 (3.55); ν_{max} (KBr) / cm^{-1} 3383 (OH), 1608 (CO), 1574, 1535, 1490, 1460, 1433, 1288, 1252, 1186, 1163, 1132, 1077, 1026; δ_F ($CDCl_3$/acetone, 377 MHz) 6.1; Anal. calcd for $C_{20}H_{16}CoF_6O_6$ (525.26): C 45.73; H 3.07. Found: C 45.97; H 3.16.

4 Oxidation – Radical Addition Cascades

4.1 Comparing reactivity of cobalt(II) complexes in aerobic alkenol turnover

Cobalt complex **3** () or **4** () (15 µmol) was added to a solution of alcohol **1a** (0.5 mmol) in acrylonitrile (0.2 mL), CHD (0.8 mL) and toluene (1.0 mL). The reaction mixture was stirred at 60 °C while being exposed to laboratory atmosphere. Turnover of substrate **1a** was measured via GC in time intervals (Figure S1).

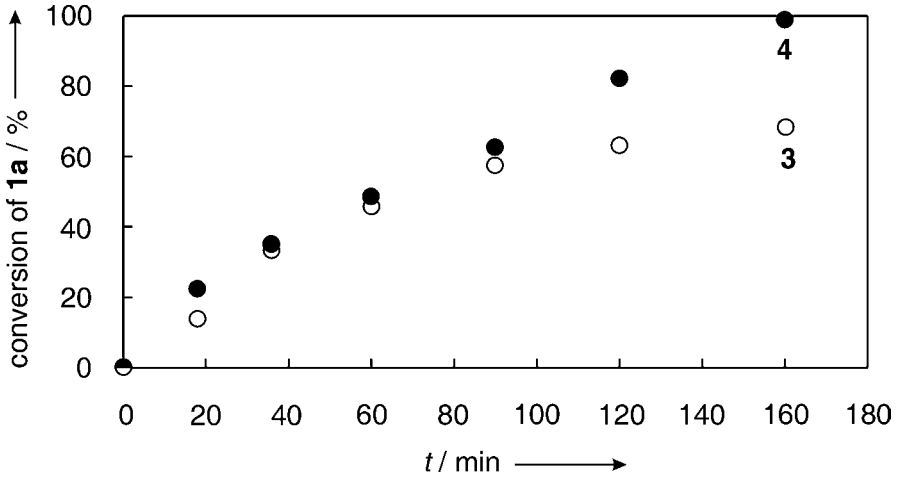

Figure S1. Time-dependency of 1-phenyl-4-penten-1-ol turnover using cobalt complexes **3**(○) and 4 (●) (60 °C, 3 mol % catalyst).

4.2 Oxidation of 1-phenylpent-4-en-1-ol (1a)

4.2.1 Reaction with acrylonitrile: A solution of alcohol **1a** (123 mg, 755 µmol) and Bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (11.8 mg, 22.5 µmol) in γ-terpinene (1.4 mL, 98%, 8.5 mmol), toluene (0.65 mL) and acrylonitrile (**2a**) (201 mg, 3.79 mmol) was stirred at 75 °C for 6 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified without further concentration by column chromatography [SiO_2, acetone/pentane = 1:10 → 1:5 (*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a)**. Yield: 20.0 mg (123 µmol, 16 %). Analytical data agree with published values.[2] **4-(*trans*-5-phenyltetrahydrofur-2-yl)-butyronitrile (6).** Yield: 71.0 mg (330 µmol, 44 %, *cis*:*trans* <1:99), R_f 0.36 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H (600 MHz, $CDCl_3$) 1.65–1.94 (6 H, m), 2.15–2.20 (1 H, m), 2.35–2.40 (1 H, m), 2.45 (2 H, td, J_t 7.0, J_d 2.0), 4.22 (1 H, quint, J 6.6), 4.99 (1 H, dd, J 8.2, 6.4), 7.24–7.31 (5 H, m). δ_C (150 MHz, $CDCl_3$) 17.2, 22.6, 32.5, 34.9, 35.1, 78.9, 80.3, 119.7 (CN), 125.5, 127.2, 128.3, 143.5. GC-MS (EI, 70 eV) *m/z* (%) 215 (52, M^+), 157 (17), 147 (61), 130 (42), 120 (93), 105 (100), 91 (98), 77 (52), 65 (17), 51 (30). Anal. calcd for $C_{14}H_{17}NO$ (215.29): C 78.10; H 7.96; N 6.51. Found: C 78.05; H 8.00; N 6.80. **[2-(*trans*-5-phenyltetrahydrofur-2-yl)-eth-1yl]-glutarodinitrile (10).** Yield: 29.7 mg (111 µmol, 15 %, *cis*:*trans* <1:99, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), R_f 0.24 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 600 MHz) 1.66–1.94 (6 H, m), 1.99 (2 H, dt, J_d 14.6, J_t 6.5), 2.16–2.22 (1 H, m), 2.35–2.40 (3 H, m), 2.52–2.65 (2 H, m), 2.83–2.90 (1 H, m), 4.19–4.25 (1 H, m), 4.97–5.01 (1 H, m), 7.24–7.35 (5 H, m). δ_C ($CDCl_3$, 150 MHz) 15.4, 28.2 / 28.4, 28.6 / 29.5, 30.6 / 31.2, 32.5 / 32.6, 33.2 / 33.7, 35.1 / 35.2, 78.5 / 79.3, 80.4, 118.0 (CN), 120.3 / 120.4 (CN), 125.6, 127.3, 128.4, 143.3.

4.2.2 Reaction with methyl acrylate: A solution of alcohol **1a** (122 mg, 751 µmol) and Bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (11.8 mg, 22.5 µmol) in γ-terpinene (1.4 mL, 98%, 8.5 mmol), toluene (0.5 mL) and methyl acrylate (**2b**) (330 mg, 3.79 mmol) was stirred at 75 °C for 6 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified without further concentration by column chromatography [SiO_2, acetone/pentane = 1:10 → 1:5

(*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a)**. Yield: 36.4 mg (224 µmol, 30 %). Analytical data agree with published values.[2]

Methyl 4-(*trans*-5-phenyltetrahydrofur-2-yl)-butyrate (7). Yield: 60.4 mg (243 µmol, 32 %, *cis*:*trans* <1:99), R_f 0.58 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.53–1.90 (6 H, m), 2.11–2.19 (1 H, m), 2.31–2.39 (3 H, m), 3.67 (3 H, s), 4.20 (1 H, quint, *J* 6.3), 4.98 (1 H, t, *J* 7.3), 7.22–7.34 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 21.7, 32.3, 34.0, 35.3, 35.4, 51.4 (Me), 79.5, 80.1, 125.5, 127.0, 128.2, 143.8, 174.0. GC-MS (70 eV, EI) *m/z* (%) 248 (2, M^+), 147 (53), 144 (56), 129 (44), 120 (100), 112 (50), 105 (48), 91 (89), 77 (30). **Dimethyl [2-(*trans*-5-phenyltetrahydrofur-2-yl)-eth-1-yl]-glutarate (11).** Yield: 33.7 mg (101 µmol, 13 %, *cis*:*trans* <1:99, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), R_f 0.32 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.47–1.73 (5 H, m), 1.77–1.96 (3 H, m), 2.10–2.17 (1 H, m), 2.29–2.40 (3 H, m), 2.43–2.49 (1 H, m), 3.67 (3 H, s), 3.68 (3 H, s), 4.11–4.20 (1 H, m), 4.97 (1 H, t, *J* 7.3), 7.21–7.37 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 27.0 / 27.2, 28.6 / 28.9, 31.7, 32.2 / 32.3, 33.5 / 33.8, 35.21 / 35.25, 44.5 / 44.7, 51.6 (Me), 79.4 / 79.6, 80.11 / 80.14, 125.5, 127.0, 128.2, 143.68 / 143.70, 173.35 / 173.38, 175.8 / 175.9. GC-MS (70 eV, EI) *m/z* (%) 334 (<1, M^+), 274 (10), 253 (13), 230 (20), 215 (40), 183 (22), 166 (34), 147 (86), 129 (53), 120 (66), 105 (75), 91 (100), 77 (30).

4.2.3 Reaction with methyl vinyl ketone: A solution of alcohol **1a** (163 mg, 1.00 mmol) and bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (15.8 mg, 30.1 µmol) in γ-terpinene (1.9 mL, 98%, 11.5 mmol), toluene (0.8 mL) and methyl vinyl ketone (**2c**) (355 mg, 5.06 mmol) was stirred at 75 °C for 7 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified without further concentration by column chromatography [SiO_2, acetone/pentane = 1:10 → 1:5 (*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a)**. Yield: 44.5 mg (274 µmol, 27 %). Analytical data agree with published values.[2] **5-(*trans*-2-phenyltetrahydrofur-5-yl)-pentan-2-one (8).** Yield: 73.0 mg (314 µmol, 31 %, *cis*:*trans* <1:99), R_f 0.40 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.49–1.76 (5 H, m), 1.79–1.89 (1 H, m), 2.09–2.18 (1 H, m), 2.13 (3 H, s), 2.32–2.39 (1 H, m), 2.49 (2 H, t, *J* 6.6), 4.18 (1 H, quint, *J* 6.5), 4.97 (1 H, dd, *J* 8.0, 6.6), 7.21–7.32 (5 H, m). δ_C ($CDCl_3$, 100

MHz) 20.5, 29.9 (Me), 32.4, 35.3, 35.4, 43.7, 79.6, 80.2, 125.5, 127.0, 128.3, 143.8, 209.1. GC-MS (70 eV, EI) *m/z* (%) 232 (3, M^+), 214 (4), 147 (44), 128 (57), 120 (64), 117 (38), 105 (45), 91 (100), 77 (34). **[3-(*trans*-2-phenyltetrahydrofur-5-yl)-eth-1-yl]-heptane-2,6-dione (12).** Yield: 38.7 mg (128 µmol, 13 %, *cis*:*trans* <1:99, 50/50-mixture of *rel*-3*S*/3*R*-diastereoisomers), R_f 0.20 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 600 MHz) 1.45–1.89 (8 H, m), 2.10–2.19 (7 H, m), 2.32–2.46 (3 H, m), 2.48–2.55 (1 H, m), 4.10–4.15 (1 H, m), 4.93–4.98 (1 H, m), 7.23–7.35 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 24.5 / 24.7, 27.8 / 28.0, 28.6 / 29.0, 30.0 (Me), 32.3 / 32.4 (Me), 33.5 / 33.6, 35.2, 40.77 / 40.82, 51.8 / 51.9, 79.5 / 79.7, 80.2, 125.5, 127.1, 128.3, 143.7, 208.1, 212.1 / 212.2. GC-MS (70 eV, EI) *m/z* (%) 302 (<1, M^+), 284 (12), 226 (4), 183 (30), 147 (57), 129 (46), 120 (35), 117 (32), 105 (46), 91 (100), 77 (30).

4.2.4 Reaction with methyl vinyl sulfone: A solution of alcohol **1a** (123 mg, 755 µmol) and bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (11.8 mg, 22.5 µmol) in cyclohexa-1,4-diene (0.9 mL, 9.2 mmol), toluene (0.9 mL) and methyl vinyl sulfone (**2d**) (459 mg, 4.24 mmol) was stirred at 75 °C for 16 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified without further concentration by column chromatography [SiO_2, acetone/pentane = 1:5 (*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a).** Yield: 24.3 mg (150 µmol, 20 %). Analytical data agree with published values.[2] **3-(*trans*-5-phenyltetrahydrofur-2-yl)-prop-1-yl methyl sulfone (9).** Yield: 87.1 mg (325 µmol, 43 %, *cis*:*trans* = <1:99), R_f 0.12 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 600 MHz) 1.65–1.71 (1 H, m), 1.75 (2 H, q, *J* 7.2), 1.83–1.90 (1 H, m), 1.96–2.10 (2 H, m), 2.14–2.19 (3 H, m), 2.34–2.39 (1 H, m), 2.90 (3 H, s), 3.06–3.17 (2 H, m), 4.22 (1 H, dt, J_d 14.1, J_t 6.1), 4.98 (1 H, dd, *J* 8.3, 6.7), 7.23–7.34 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 19.8, 32.4, 34.4, 35.2, 40.4 (Me), 54.8, 79.1, 80.3, 125.5, 127.2, 128.3, 143.4. GC-MS (70 eV, EI) *m/z* (%) 268 (2, M^+), 250 (2), 164 (8), 147 (20), 129 (20), 120 (100), 105 (31), 91 (42), 77 (16).

4.2.5 Reaction with fumaronitrile: A suspension of alcohol **1a** (164 mg, 1.01 mmol) and bis-{4-[3,5-bis-(trifluoromethyl)-phenyl]-(2-oxo-κ*O*)-but-3-en-(4-olato-κ*O*)}-cobalt(II) (**3**) (33.2 mg, 50.8 µmol) in cyclohexa-1,4-diene (1.0 mL, 10.2 mmol), toluene (1.6 mL) and

fumaronitrile (**2e**) (396 mg, 5.07 mmol) was stirred at 60 °C for 21 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. Unspent fumaronitrile was removed by filtration and the filtrate was purified by column chromatography [SiO_2, acetone/pentane = 1:5 → 1:3 (*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a)**. Yield: 3.1 mg (19.1 μmol, 2 %). Analytical data agree with published values.[2] **2-[(*trans*-5-phenyltetrahydrofur-2-yl)-methyl]-succinodinitrile (17a).** Yield: 161 mg (670 μmol, 66 %, *cis*:*trans* <1:99, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), R_f 0.22 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.69–1.78 (1 H, m), 1.86–2.11 (3 H, m), 2.24–2.30 (1 H, m), 2.37–2.42 (1 H, m), 2.80 (2 H, d, *J* 6.5, 3*-H), 2.83–2.95 (2 H, m, 3**-H), 3.21 (1 H, quint, *J* 6.5, 2*-H), 3.26–3.31 (1 H, m, 2**-H), 4.38–4.43 (1 H, m), 4.99–5.04 (1 H, m), 7.27–7.36 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 20.3 / 21.2, 25.8 / 26.5, 32.36 / 32.39, 34.7 / 35.0, 36.2 / 37.9, 75.7 / 76.6, 80.5 / 80.7, 115.7 / 116.0, 118.9 / 119.1, 125.4, 127.4, 128.3, 142.56 / 142.59. Anal. calcd for $C_{15}H_{16}N_2O$ (240.30): C 74.97; H 6.71; N 11.66. Found: C 74.63; H 6.50; N 11.62. GC-MS (70 eV, EI) *m/z* (%) 240 (31, M^+), 223 (6), 183 (12), 146 (14), 129 (9), 117 (32), 105 (100), 91 (44), 77 (37).

4.2.6 Reaction with dimethyl fumarate: A suspension of alcohol **1a** (168 mg, 1.04 mmol) and bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (15.8 mg, 30.0 μmol) in γ-terpinene (1.5 mL, 98%, 9.1 mmol), toluene (1.0 mL) and dimethylfumarate ((*E*)-**2f**) (720 mg, 5.00 mmol) was stirred at 60 °C for 20 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. Unspent dimethylfumarate was removed by filtration and the filtrate was purified by column chromatography [SiO_2, acetone/PE = 1:5 (*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a)**. Yield: 48.0 mg (296 μmol, 28 %). Analytical data agree with published values.[2] **dimethyl 2-[(*trans*-5-phenyltetrahydrofur-2-yl)-methyl]-succinate (18a).** Yield: 192 mg (625 μmol, 60 %, *cis*:*trans* <1:99, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), R_f 0.21 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.60–1.87 (3 H, m), 1.91–2.08 (1 H, m), 2.11–2.22 (1 H, m), 2.32– 2.40 (1 H, m), 2.58–2.82 (2 H, m), 3.01–3.13 (1 H, m), 3.66 / 3.70 (3 H, s), 3.67 (3 H, s), 4.20– 4.27 (1 H, m), 4.96 (1 H, t, *J* 7.3), 7.23–7.36 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 32.6, 35.0, 35.7 / 36.2, 37.8 / 38.0, 38.9 / 39.1, 51.7 (Me), 51.9 (Me), 77.1 / 77.7, 80.0, 125.4 / 125.5 , 127.0, 128.3, 143.5 / 143.6, 172.3, 175.2 / 175.3. Anal. calcd for $C_{17}H_{22}O_5$ (306.35): C 66.65; H 7.24. Found: C 66.21; H 7.13.

GC-MS (70 eV, EI) *m/z* (%) 306 (1, M^+), 274 (3), 246 (4), 225 (26), 202 (31), 187 (46), 170 (37), 155 (41), 147 (30), 129 (36), 120 (67), 105 (73), 91 (100), 77 (34).

4.2.7 Reaction with dimethyl maleate :A solution of alcohol **1a** (163 mg, 1.01 mmol) and bis-{4-[3,5-bis-(trifluoromethyl)-phenyl]-(2-oxo-κ*O*)-but-3-en-(4-olato-κ*O*)}-cobalt(II) (**3**) (32.9 mg, 50.4 μmol) in 1,4-cyclohexadiene (1.0 mL, 97% 10.2 mmol), toluene (1.3 mL) and dimethyl maleate ((*Z*)-**2f**) (755 mg, 5.24 mmol) was stirred at 60 °C for 6 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified without further concentration by column chromatography [SiO_2, acetone/pentane = 1:10 → 1:5 (*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a)**. Yield: 84.1 mg (518 μmol, 52 %). Analytical data agree with published values.[2] **dimethyl 2-[(*trans*-5-phenyltetrahydrofur-2-yl)-methyl]-succinate (18a).** Yield: 73.9 mg (241 μmol, 24 %, *cis*:*trans* <1:99, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), colorless oil.

4.2.8 Reaction with *N*-phenylmaleimide: A solution of alcohol **1a** (126 mg, 774 μmol) and bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (11.8 mg, 22.5 μmol) in γ-terpinene (1.4 mL, 98%, 8.5 mmol), toluene (0.2 mL) and *N*-phenylmaleimide (**2g**) (665 mg, 3.76 mmol) was stirred at 75 °C for 6 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified without further concentration by column chromatography [SiO_2, acetone/pentane = 1:10 → 1:5 → 1:3 (*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a)**. Yield: 8.3 mg (51.2 μmol, 7 %). Analytical data agree with published values.[2] **2-[(*trans*-5-phenyltetrahydrofur-2-yl)-methyl]-*N*-phenylsuccinimide (19).** Yield: 170 mg (505 μmol, 65 %, *cis*:*trans* <1:99, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), **Isomer 1:** R_f 0.16 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.71–1.80 (1 H, m), 1.85–1.95 (2 H, m), 2.20–2.33 (1 H, m), 2.37–2.45 (1 H, m), 2.85 (1 H, dd, *J* 18.3, 5.2), 3.09 (1 H, dd, *J* 18.3, 9.3), 3.30–3.36 (1 H, m), 4.30–4.36 (1 H, m), 5.04 (1 H, t, *J* 7.2), 7.24–7.41 (8 H, m), 7.47 (2 H, t, *J* 7.6). δ_C ($CDCl_3$, 100 MHz) 32.6, 34.7, 34.8, 36.9, 37.8, 76.6, 80.3, 125.5, 126.4, 127.2, 128.4, 128.5, 129.1, 132.0, 143.1, 175.7 (CO), 179.0 (CO). **Isomer 2:** R_f 0.13 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless crystalline solid. δ_H ($CDCl_3$, 400 MHz) 1.70–1.78 (1 H, m), 1.84–1.93 (1 H, m), 2.32–2.46 (3 H, m), 2.07–2.18

(2 H, m), 2.19–2.29 (1 H, m), 2.36–2.43 (1 H, m), 2.89–3.16 (3 H, m), 4.44–4.51 (1 H, m), 4.95 (1 H, t, *J* 7.2), 7.14 (2 H, d, *J* 8.1), 7.28–7.35 (8 H, m). δ_C ($CDCl_3$, 100 MHz) 32.4, 33.7, 34.8, 36.5, 38.5, 77.1, 80.1, 125.6, 126.5, 127.2, 128.2, 128.3, 128.9, 132.1, 142.9, 175.9 (CO), 179.2 (CO). Anal. calcd for $C_{21}H_{21}NO_3$ (335.40): C 75.20; H 6.31; N 4.18. Found: C 74.83; H 6.19; N 4.10. GC-MS (70 eV, EI): *m/z* (%) = 335 (18, M^+), 231 (80), 216 (100), 188 (73), 175 (65), 161 (52), 147 (25), 120 (74), 105 (62), 91 (98), 77 (55).

4.2.9 Reaction with ethyl propiolate: A solution of alcohol **1a** (164 mg, 1.01 mmol) and bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (15.8 mg, 30.0 μmol) in γ-terpinene (1.9 mL, 98%, 11.5 mmol), toluene (0.6 mL) and ethyl propiolate (**20a**) (505 mg, 5.04 mmol) was stirred at 75 °C for 7 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified without further concentration by column chromatography [SiO_2, acetone/pentane = 1:10 → 1:5 (*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a)**. Yield: 68.0 mg (419 μmol, 41 %). Analytical data agree with published values.[2] **Ethyl (*Z*)-4-(5-Phenyltetrahydrofur-2-yl)-but-2-en-oate (*Z*)-(21).** Yield: 56.7 mg (218 μmol, 22 %, *cis*:*trans* <1:99), R_f 0.46 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.29 (1 H, t, *J* 7.1), 1.70–1.79 (1 H, m), 1.82–1.91 (1 H, m), 2.12–2.19 (1 H, m), 2.34–2.42 (1 H, m), 2.93–3.08 (2 H, m), 4.18 (2 H, q, *J* 7.1), 4.36 (1 H, quint, *J* 6.6), 5.02 (1 H, t, *J* 7.2), 5.89 (1 H, d, *J* 11.6), 6.41 (1 H, dt, J_d 11.6, J_t 7.3), 7.22–7.33 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 14.2, 31.9, 35.17, 35.21, 59.8, 78.9, 80.5, 121.2, 125.6, 127.1, 128.3, 143.5, 146.3, 166.4. GC-MS (70 eV, EI) *m/z* (%) 260 (<1, M^+), 215 (5), 169 (5), 156 (5), 147 (100), 129 (57), 117 (20), 105 (25), 91 (95), 77 (21). **Ethyl (*E*)-4-(5-Phenyltetrahydrofur-2-yl)-but-2-en-oate (*E*)-(21).** Yield: 65.1 mg (250 μmol, 25 %, *cis*:*trans* <1:99), R_f 0.37 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.28 (1 H, t, *J* 7.1), 1.66–1.75 (1 H, m), 1.82–1.92 (1 H, m), 2.12–2.19 (1 H, m), 2.33–2.40 (1 H, m), 2.44–2.61 (2 H, m), 4.19 (2 H, q, *J* 7.1), 4.35 (1 H, quint, *J* 6.6), 5.02 (1 H, t, *J* 7.2), 5.93 (1 H, d, *J* 15.3), 7.00 (1 H, dt, J_d 15.3, J_t 7.6), 7.22–7.34 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 14.2, 31.9, 35.1, 38.7, 60.2, 78.1, 80.6, 123.5, 125.5, 127.1, 128.3, 143.3, 145.0, 166.4. GC-MS (70 eV, EI) *m/z* (%) 260 (6, M^+), 214 (1), 147 (100), 129 (45), 117 (12), 105 (20), 91 (64), 77 (8).

4.2.10 Reaction with dimethyl acetylenedicarboxylate: A solution of alcohol **1a** (164 mg, 1.01 mmol) and bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (15.8 mg, 30.0 μmol) in γ-terpinene (1.9 mL, 98%, 11.5 mmol), toluene (0.4 mL) and dimethyl acetylenedicarboxylate (**20b**) (727 mg, 5.01 mmol) was stirred at 75 °C for 7 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified without further concentration by column chromatography [SiO_2, acetone/pentane = 1:10 → 1:5 (*v*/*v*)]. ***trans*-2-methyl-5-phenyltetrahydrofuran (5a)**. Yield: 45.1 mg (278 μmol, 28 %). Analytical data agree with published values.[2] **Dimethyl 2-[(*trans*-5-phenyltetrahydrofuran-2-yl)methyl]-maleate (*Z*)-(22).** Yield: 59.6 mg (196 μmol, 19 %, *cis*:*trans* = <1:99), R_f 0.42 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.72–1.85 (2 H, m), 2.11–2.20 (1 H, m), 2.38–2.43 (1 H, m), 3.02 (1 H, dd, *J* 12.4, 4.8), 3.29 (1 H, dd, *J* 12.4, 8.4), 3.72 (3 H, s), 3.79 (3 H, s), 4.46 (1 H, quint, *J* 6.3), 4.96 (1 H, t, *J* 6.6), 6.84 (1 H, s), 7.20–7.32 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 31.4, 33.5, 34.6, 51.6 (Me), 52.5 (Me), 78.4, 79.9, 125.6, 127.0, 127.7, 128.2, 143.4, 144.7, 166.2, 167.4. GC-MS (70 eV, EI) *m/z* (%) 304 (4, M^+), 272 (4), 244 (3), 185 (12), 147 (100), 129 (45), 120 (24), 105 (22), 91 (72), 77 (16). **Dimethyl 2-[(*trans*-5-phenyltetrahydrofuran-2-yl)methyl]-fumarate (*E*)-(22).** Yield: 96.1 mg (316 μmol, 31 %, *cis*:*trans* = <1:99), R_f 0.21 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.68–1.77 (1 H, m), 1.82–1.91 (1 H, m), 2.14–2.21 (1 H, m), 2.35–2.42 (1 H, m), 2.59–2.76 (2 H, m), 3.73 (3 H, s), 3.82 (3 H, s), 4.39 (1 H, quint, *J* 6.6), 5.01 (1 H, t, *J* 7.3), 6.00 (1 H, s), 7.22–7.35 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 31.9, 35.0, 40.6, 51.8 (Me), 52.4 (Me), 77.1, 80.5, 121.8, 125.4, 127.1, 128.3, 143.2, 146.9, 165.3, 169.0. GC-MS (70 eV, EI) *m/z* (%) 304 (3, M^+), 272 (6), 244 (4), 185 (9), 147 (97), 129 (54), 120 (21), 105 (31), 91 (100), 77 (24).

4.3 Oxidation of 1-phenylhex-4-en-1-ol (1b)

4.3.1 Reaction with fumaronitrile: A solution of alcohol **1b** (181 mg, 1.03 mmol) and bis-{4-[3,5-bis-(trifluoromethyl)-phenyl]-(2-oxo-κ*O*)-but-3-en-(4-olato-κ*O*)}-cobalt(II) (**3**) (66.2 mg, 101 μmol)) in 1,4-cyclohexadiene (1.0 mL, 98%, 10.2 mmol), toluene (1.6 mL) and fumaronitrile (**2e**) (400 mg, 5.02 mmol), was stirred at 60 °C for 21 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. Unspent

fumaronitrile was removed by filtration and the filtrate was purified by column chromatography [SiO_2, acetone/pentane = 1:5 → 1:3 (*v*/*v*)]. **2-[1-(*trans*-5-phenyltetrahydrofur-2-yl)-eth-1-yl]-succinodinitrile (17b).** Yield: 150 mg (58 %, *cis*:*trans* <1:99, 50/50-mixture of *rel*-2*S*/2*R*- and *rel*-1'*S*/1'*R*-diastereoisomers), colorless oil. δ_H ($CDCl_3$, 400 MHz) (1 isomer) 1.13 (3 H, d, *J* 6.8), 1.71–1.91 (2 H, m), 2.08–2.15 (1 H, m), 2.23–2.29 (1 H, m), 2.36–2.42 (1 H, m), 2.85–2.93 (1 H, m), 3.11–3.20 (2 H, m), 4.13–4.19 (1 H, m), 5.03 (1 H, dd, *J* 8.4, 6.3), 7.28–7.37 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 15.1, 19.4, 32.3, 33.8, 35.0, 39.9, 81.2, 81.3, 116.8 (CN), 118.1 (CN), 125.3, 127.4, 128.4, 142.7. GC-MS (70 eV, EI) *m/z* (%) 254 (24, M^+), 197 (14), 171 (11), 147 (62), 129 (42), 117 (35), 105 (35), 91 (100), 77 (38).

4.4 Oxidation of 2-phenylpent-4-en-1-ol (1c)

4.4.1 Reaction with fumaronitrile: A solution of alcohol **1c** (174 mg, 1.07 mmol) and bis-{4-[3,5-bis-(trifluoromethyl)-phenyl]-(2-oxo-κ*O*)-but-3-en-(4-olato-κ*O*)}-cobalt(II) (**3**) (32.8 mg, 50.2 μmol)) in 1,4-cyclohexadiene (1.0 mL, 98%, 10.2 mmol), toluene (1.6 mL) and fumaronitrile (**2e**) (401 mg, 5.03 mmol), was stirred at 60 °C for 21 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. Unspent fumaronitrile was removed by filtration and the filtrate was purified by column chromatography [SiO_2, acetone/pentane = 1:5 → 1:3 (*v*/*v*)]. **2-[(4-phenyltetrahydrofur-2-yl)-methyl]-succinodinitrile (17c).** Yield: 149 mg (620 μmol, 58 %, *cis*:*trans* = 74:26, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), colorless oil. δ_H ($CDCl_3$, 600 MHz) 1.69–1.77 (1 H, m, *cis*), 1.94 (2 H, ddd, *J* 13.8, 10.2, 5.1, *trans*), 2.03–2.15 (3 H, m, *trans*, *cis*), 2.27 (1 H, dq, J_d 7.3, J_q 7.3, *trans*), 2.56 (1H, dq, J_d 7.3, J_q 6.5, *cis*), 2.82–2.97 (4 H, m, *cis*, *trans*), 3.21 (1 H, quint, *J* 6.5, *cis*/*trans*-2*-H), 3.29–3.29 (1 H, m, *cis*/*trans*-2**-H), 3.45–3.54 (2 H, m, *cis*, *trans*), 3.76 (1 H, td, J_t 8.3, J_d 3.2, *trans*), 3.83 (1 H, dt, J_d 14.9, J_t 8.5, *cis*), 4.17 (1 H, t, *J* 8.2, *cis*-THF-5*-H), 4.20–4.27 (2 H, m, *cis*-THF-5**-H, *trans*-THF-5*-H), 4.33–4.39 (1 H, m, *trans*-THF-5**-H) 7.23–7.34 (10 H, m, *cis*, *trans*). δ_C ($CDCl_3$, 100 MHz) 20.3 / 21.3 (*trans*), 20.4 / 21.1 (*cis*), 25.7 / 26.2 (*trans*), 26.1 / 26.6 (*cis*), 35.9 / 37.6 (*cis*), 36.4 / 38.0 (*trans*), 39.8 (*trans*), 40.8 / 41.0 (*cis*), 44.2 / 44.4 (*trans*), 45.1 / 45.2 (*cis*), 74.2 / 74.4 (*cis*), 74.7 / 74.8 (*trans*), 75.3 / 76.0 (*trans*), 76.2 / 76.9 (*cis*), 115.6 / 115.9 (CN), 118.7 / 118.9 (CN), 126.80 / 126.82, 127.1 / 127.2, 128.68 / 128.70, 141.3 / 141.4. Anal. calcd for $C_{15}H_{16}N_2O$ (240.30): C 74.97; H 6.71; N 11.66. Found: C 74.64; H 6.84; N

11.54. GC-MS (70 eV, EI) *m/z* (%) 240 (17, M^+), 209 (8), 156 (30), 147 (18), 129 (27), 117 (100), 108 (24), 91 (83), 77 (21).

4.4.2 Reaction with dimethyl fumarate: A solution of alcohol **1c** (151 mg, 929 μmol) and bis-{4-[3,5-bis-(trifluoromethyl)-phenyl]-(2-oxo-κ*O*)-but-3-en-(4-olato-κ*O*)}-cobalt(II) (**3**) (32.8 mg, 50.2 μmol)) in 1,4-cyclohexadiene (1.0 mL, 98%, 10.2 mmol), toluene (1.3 mL) and dimethyl fumarate (**2f**) (727 mg, 5.04 mmol), was stirred at 60 °C for 6 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. Unspent dimethyl fumarate was removed by filtration and the filtrate was purified by column chromatography [SiO_2, acetone/pentane = 1:5 (*v*/*v*)]. **Dimethyl 2-[(4-phenyltetrahydrofur-2-yl)-methyl]-succinate (18c).** Yield: 162 mg (530 μmol, 57 %, *cis*:*trans* = 73:27, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), R_f 0.28 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.60–2.18 (3 H, m), 2.41–2.52 (1 H, m), 2.57–2.81 (2 H, m), 3.00–3.11 (1 H, m), 3.38– 3.48 (1 H, m), 3.67–3.71 (6 H, m), 3.73–3.79 (1 H, m), 4.01–4.22 (2 H, m), 7.19–7.32 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 35.4 / 36.2 (*trans*), 35.5 / 36.3 (*cis*), 37.3 / 37.7 (*cis*), 37.6 / 37.9 (*trans*), 38.6 / 38.8 (*trans*), 38.8 / 39.1 (*cis*), 39.8 / 40.0 (*trans*), 41.1 (*cis*), 51.7 / 51.9 (Me), 51.8 / 51.9 (Me), 73.99 / 74.05 (*cis*), 74.48 / 74.53 (*trans*), 77.3 (*trans*), 77.5 / 78.1 (*cis*), 126.47 / 126.51, 127.1 / 127.2, 128.5, 142.0 / 142.3, 172.2 / 172.7, 175.1 / 175.2. Anal. calcd for $C_{17}H_{22}O_5$ (306.35): C 66.65; H 7.24. Found: C 66.44; H 7.38. GC-MS (70 eV, EI) *m/z* (%) 306 (1, M^+), 225 (13), 189 (9), 161 (31), 146 (88), 129 (45), 114 (58), 104 (22), 91 (100), 77 (16).

4.5 Oxidation of 3-phenylpent-4-en-1-ol (1d)

4.5.1 Reaction with fumaronitrile: A solution of alcohol **1d** (166 mg, 1.03 mmol) and bis-{4-[3,5-bis-(trifluoromethyl)-phenyl]-(2-oxo-κ*O*)-but-3-en-(4-olato-κ*O*)}-cobalt(II) (**3**) (32.6 mg, 49.9 μmol)) in 1,4-cyclohexadiene (1.0 mL, 98%, 10.2 mmol), toluene (1.6 mL) and fumaronitrile (**2e**) (400 mg, 5.02 mmol), was stirred at 60 °C for 24 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. Unspent fumaronitrile was removed by filtration and the filtrate was purified by column chromatography [SiO_2, acetone/pentane = 1:5 → 1:3 (*v*/*v*)].***trans*-2-methyl-3-phenyltetrahydrofuran (5d)**. Yield: 14.0 mg (86.3 μmol, 8 %, *cis*:*trans* = 3:97). Analytical data agree with published values.[9] **2-[(*trans*-3-phenyltetrahydrofur-2-yl)-**

methyl]-succinodinitrile (17d). Yield: 132 mg (548 μmol, 53 %, *cis*:*trans* = 3:97, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), colorless oil. δ_H ($CDCl_3$, 600 MHz) 1.81–2.03 (2 H, m), 2.12–2.20 (1 H, m), 2.39–2.44 (1 H, m), 2.73–2.99 (3 H, m), 3.12 (1 H, quint, *J* 6.5, 2*-H), 3.15–3.20 (1 H, m, 2**-H), 3.92–3.97 (1 H, m), 3.99–4.10 (1 H, m), 7.23–7.36 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 20.5 / 21.2, 25.9 / 26.6, 34.3 / 35.1, 35.2 / 35.8, 51.5 / 51.6, 67.9 / 68.0, 82.0 / 82.8, 115.6 / 115.9 (CN), 118.6 / 118.9 (CN), 127.2, 127.4, 128.9, 139.78 / 139.84. Anal. calcd for $C_{15}H_{16}N_2O$ (240.30): C 74.97; H 6.71; N 11.66. Found: C 74.75; H 6.81; N 11.78. GC-MS (70 eV, EI): *m/z* (%) = 240 (1, M^+), 147 (4), 128 (4), 117 (100), 115 (26), 91 (35), 77 (11).

4.5.2 Reaction with dimethyl fumarate: A solution of alcohol **1d** (168 mg, 1.03 mmol) and bis-{4-[3,5-bis-(trifluoromethyl)-phenyl]-(2-oxo-κ*O*)-but-3-en-(4-olato-κ*O*)}-cobalt(II) (**3**) (33.1 mg, 50.7 μmol)) in 1,4-cyclohexadiene (1.0 mL, 98%, 10.2 mmol), toluene (1.3 mL) and dimethyl fumarate (**2f**) (731 mg, 5.07 mmol), was stirred at 60 °C for 6 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. Unspent dimethyl fumarate was removed by filtration and the filtrate was purified by column chromatography [SiO_2, acetone/pentane = 1:5 (*v*/*v*)]. ***trans*-2-methyl-3-phenyltetrahydrofuran (5d)**. Yield: 45.9 mg (283 μmol, 27 %, *cis*:*trans* = 5:95). Analytical data agree with published values.[9] **Dimethyl 2-[(3-phenyltetrahydrofur-2-yl)-methyl]-succinate (18d).** Yield: 148 mg (484 μmol, 47 %, *cis*:*trans* = 5:95, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), R_f 0.25 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 400 MHz) 1.64–1.74 (1 H, m), 1.88–1.95 (1 H, m), 2.03–2.11 (1 H, m), 2.33–2.40 (1 H, m), 2.50– 2.59 (1 H, m), 2.63–2.73 (1 H, m), 2.89 (1 H, q, *J* 8.5), 2.80–3.04 (1 H, m), 3.60–3.66 (6 H, m), 3.79 (1 H, td, J_t 8.7, J_d 2.6, THF-2*-H), 3.85 (1 H, td, J_t 8.7, J_d 2.6, THF-2**-H), 3.93–4.03 (2 H, m), 7.21–7.30 (5 H, m). δ_C ($CDCl_3$, 100 MHz) 35.2 / 35.3, 35.4 / 35.6, 35.8 / 36.1, 38.8 / 39.0, 51.4 / 51.5, 51.7 (Me), 51.9 (Me), 67.56 / 67.60, 83.4 / 83.8, 126.8, 127.5, 128.7, 141.3, 172.2, 175.0, 175.3. Anal. calcd for $C_{17}H_{22}O_5$ (306.35): C 66.65; H 7.24. Found: C 66.25; H 7.30. GC-MS (70 eV, EI) *m/z* (%) 306 (1, M^+), 275 (6), 161 (12), 146 (20), 129 (5), 118 (100), 115 (21), 91 (45), 77 (8).

4.6 Oxidation of *cis*-2-allylcyclohexan-1-ol (1e)

4.6.1 Reaction with fumaronitrile: A suspension of alcohol **1e** (141 mg, 1.01 mmol) and bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (16.0 mg, 30.5 μmol) in cyclohexa-1,4-diene (1.5 mL, 15.3 mmol), toluene (1.0 mL) and fumaronitrile (**2e**) (391 mg, 4.92 mmol) was stirred at 60 °C for 20 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. Unspent fumaronitrile was removed by filtration and the filtrate was purified by column chromatography [SiO_2, acetone/pentane = 1:5 (*v*/*v*)]. ***rel*-(1*S*,6*S*,8*R*)-8-methyl-7-oxabicyclo[4.3.0]nonan (5e).** Yield: 4.0 mg (24.7 μmol, 22 %). Analytical data agree with published values.[7b] **2-({*rel*-(1*S*,6*S*,8*R*)-7-oxabicyclo[4.3.0]non-8-yl}-methyl)-succinodinitrile (17e).** Yield: 145 mg (666 μmol, 67 %, *cis*:*trans* = <1:99, 50/50-mixture of *rel*-2*S*/2*R*-diastereoisomers), R_f 0.26 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 600 MHz) 1.17–1.25 (2 H, m), 1.35–1.41 (2 H, m), 1.48–1.54 (1 H, m), 1.55–1.61 (2 H, m), 1.61–1.66 (1 H, m), 1.75–2.00 (4 H, m), 2.01–2.06 (1 H, m), 2.80–2.94 (2 H, m), 3.14–3.23 (1 H, m), 3.90–3.94 (1 H, m), 4.25–4.30 (1 H, m). δ_C ($CDCl_3$, 150 MHz) 20.2 / 21.3, 20.4, 23.84 / 23.86, 25.9 / 26.7, 27.3, 28.0, 37.1 / 37.9, 38.7, 38.8, 73.0 / 74.1, 76.7 / 76.8, 115.7 / 115.9 (CN), 119.0 / 119.2 (CN). GC-MS (70 eV, EI) *m/z* (%) 218 (3, M^+), 201 (14), 175 (67), 161 (18), 125 (29), 107 (35), 95 (20), 81 (100), 67 (39).

4.7 Oxidation of Methyl 3-(2-hydroxycyclohex-1-yl)-prop-2-enoate (1f)

4.7.1 Reaction with fumaronitrile: A suspension of alcohol **1f** (100 mg, 505 μmol) and bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (8.0 mg, 15.2 μmol) in cyclohexa-1,4-diene (0.5 mL, 5 mmol), toluene (1.0 mL) and fumaronitrile (**2e**) (202 mg, 2.53 mmol) was stirred at 60 °C for 20 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C. Unspent fumaronitrile was removed by filtration and the filtrate was purified by column chromatography [SiO_2, acetone/pentane = 1:5 (*v*/*v*)]. **Methyl 2-({ *rel*-(1*S*,6*S*,8*R*)-7-oxabicyclo[4.3.0]non-8-yl}-methyl)-acetate (5f).** Yield: 24.4 mg (123 μmol, 24 %, *cis*:*trans* = 17:83). δ_H ($CDCl_3$, 400 MHz) 1.10–1.61 (6 H, m), 1.62–1.72 (1 H, m), 1.81–1.94 (2 H, m), 1.62–1.72 (1 H, m), 1.61–1.66 (1 H, m), 2.43 (1 H, dd *J* 15.1, 6.3), 2.62 (1 H, dd, *J* 15.1, 7.2), 3.67 (3 H, s), 3.95 (1 H, q, *J* 4.8), 4.53 (1 H, quin, *J* 7.1). δ_C ($CDCl_3$, 100 MHz) 20.5, 23.9, 27.3, 28.1,

38.1, 38.3, 41.6, 51.6, 73.4, 76.7, 171.8. **Methyl 2-({ *rel*-(1*S*,6*S*,8*R*)-7-oxabicyclo[4.3.0]non-8-yl}-methyl)-3,4-dicyanobutanoate (17f).** Yield: 25.9 mg (93,7 µmol, 19 %, *cis*:*trans* = 25:75, 50/50-mixtures of *rel*-2*S*/2*R* and *rel*-3*S*/3*R* diastereoisomers), R_f 0.18 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless crystalline solid. δ_H ($CDCl_3$, 600 MHz) 1.14–1.96 (20 H, m, *cis/trans*), 2.04–2.10 (1 H, m, *trans*), 2.16–2.14 (1 H, m, *cis*), 2.75 (1 H, dd, *J* 9.7, 5.1, *trans*, *), 2.87–3.19 (5 H, m, *cis/trans*), 3.49 (1 H, ddd, *J* 8.1, 7.0, 4.4, *trans*, #), 3.59 (1 H, dt, *J* 7.2, 5.1, trans, ##), 3.68–3.72 (1 H, m, *cis*, #/##), 3.77 / 3.78 (3 H, s, Me, *trans*), 3.78 / 3.80 (3 H, s, Me, *cis*), 3.84–3.87 (1 H, m, *cis*), 3.95 (1 H, q, *J* 3.8, *trans*), 4.11–4.22 (1 H, m, *cis*, */**), 4.36 (1H, dt, *J* 9.7, 7.3, *trans*, *), 4.41 (1H, dt, *J* 9.2, 7.3, trans, **). δ_C ($CDCl_3$, 150 MHz) 19.0 / 19.7 (*trans*), 19.2 / 19.7 (*cis*), 20.0 (*trans*), 21.1 (*cis*), 23.4 / 23.5 (*cis*), 23.7 / 23.8 (*trans*), 27.2 (*trans*), 27.8 / 27.9 (*trans*), 28.5 / 28.7 (*cis*), 29.0 / 29.3 (*trans*), 29.1 / 29.4 (*cis*), 36.8 / 36.9 (*cis*), 37.2 / 37.3 (*cis*), 37.7 / 37.8 (*trans*), 37.8 / 37.9 (*trans*), 50.0 / 51.5 (*cis*), 50.9 / 52.3 (*trans*), 52.6 / 52.7 (*trans*), 52.7 / 53.1 (*cis*), 75.0 / 75.5 (*trans*), 75.8 / 76.3 (*cis*), 77.4 / 77.6 (*trans*), 78.1 / 78.2 (*cis*), 115.1 / 115.4 (*cis*), 115.6 / 116.0 (*trans*), 117.0 / 117.2 (*cis*), 117. / 117.4 (*trans*), 127.2 / 129.1 (*trans*), 128.1 / 129.5 (*cis*), 129.2 / 129.7 (*trans*), 130.1 / 130.4 (*cis*), 169.5 / 170.0 (*trans*), 169.6 / 169.9 (*cis*). GC-MS (70 eV, EI) *m/z* (%) 276 (<1, M^+), 236 (3), 222 (3), 203 (24), 197 (100), 165 (12), 95 (14), 74 (34), 67 (16).

4.8 Oxidation of *rel*-(1*R*,3*S*)-1-phenylpent-4-en-1,3-diol (1g)

4.8.1 Reaction with ethyl propiolate: A solution of *rel*-(1*R*,3*S*)-1-phenylpent-4-en-1,3-diol (**1g**) (193 mg, 1.08 mmol) and bis-[1,1,1-trifluoro-4-phenyl-2-(oxo-κ*O*)-but-3-en-4-(olato-κ*O*)]cobalt(II) dihydrate (**4**) (28.9 mg, 55.0 µmol) in cyclohexa-1,4-diene (1.5 mL, 15.3 mmol), toluene (1.5 mL) and ethyl propiolate (1.09 g, 10.8 mmol) was stirred at 60 °C for 16 h while being exposed to laboratory atmosphere. The reaction mixture was cooled to 20 °C and purified without further concentration by column chromatography [SiO_2, acetone/PE = 1:5 (*v*/*v*)]. **Ethyl 2-{*rel*-(2*R*,3a*S*,5*R*,6a*S*)-hexahydro-2-phenylfuro[3,2-b]fur-5-yl}-acetate (23).** Yield: 108 mg (390 µmol, 36 %, *cis*:*trans* = <1:99), R_f 0.37 [SiO_2, acetone/pentane = 1:5 (*v*/*v*)], colorless oil. δ_H ($CDCl_3$, 600 MHz) 1.28 (3 H, t, *J* 7.2), 1.81 (1 H, ddd, *J* 13.6, 9.4, 5.1), 1.90 (1H, ddd, *J* 13.6, 10.4, 4.6), 2.38 (1 H, dd, *J* 13.6,

5.1), 2.48–2.65 (3 H, m), 4.18 (2 H, q, *J* 7.2), 4.55–4.60 (1 H, m), 4.82 (1 H, t, *J* 4.6), 4.92 (1 H, t, *J* 4.6), 5.08 (1 H, dd, *J* 10.4, 5.1), 7.29–7.36 (5 H, m). δ_C ($CDCl_3$, 150 MHz) 14.2, 40.6, 40.9, 43.9, 60.6, 76.4, 81.3, 84.1, 84.2, 125.7, 127.5, 128.4, 141.7, 171.0. GC-MS (70 eV, EI) *m/z* (%) 276 (4, M^+), 258 (6), 189 (22), 117 (25), 105 (100), 91 (15), 77 (25).

5 NMR Spectra of Selected Compounds

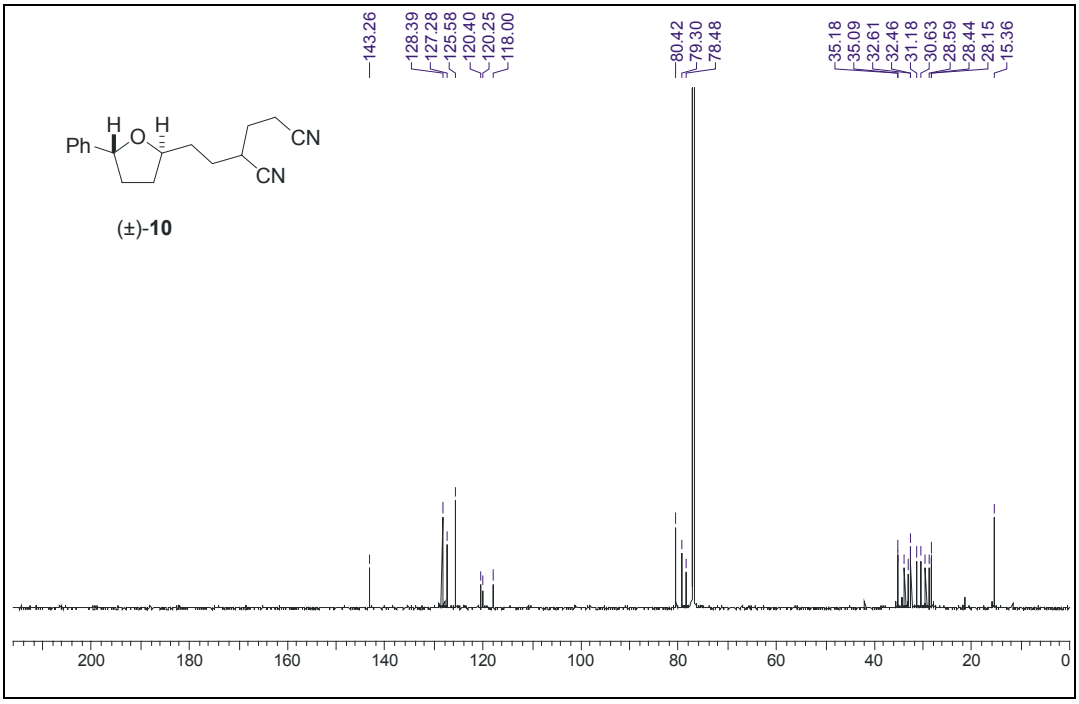

Figure S2. ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of [2-(*trans*-5-phenyltetrahydrofur-2-yl)-eth-1yl]-glutarodinitrile (**10**).

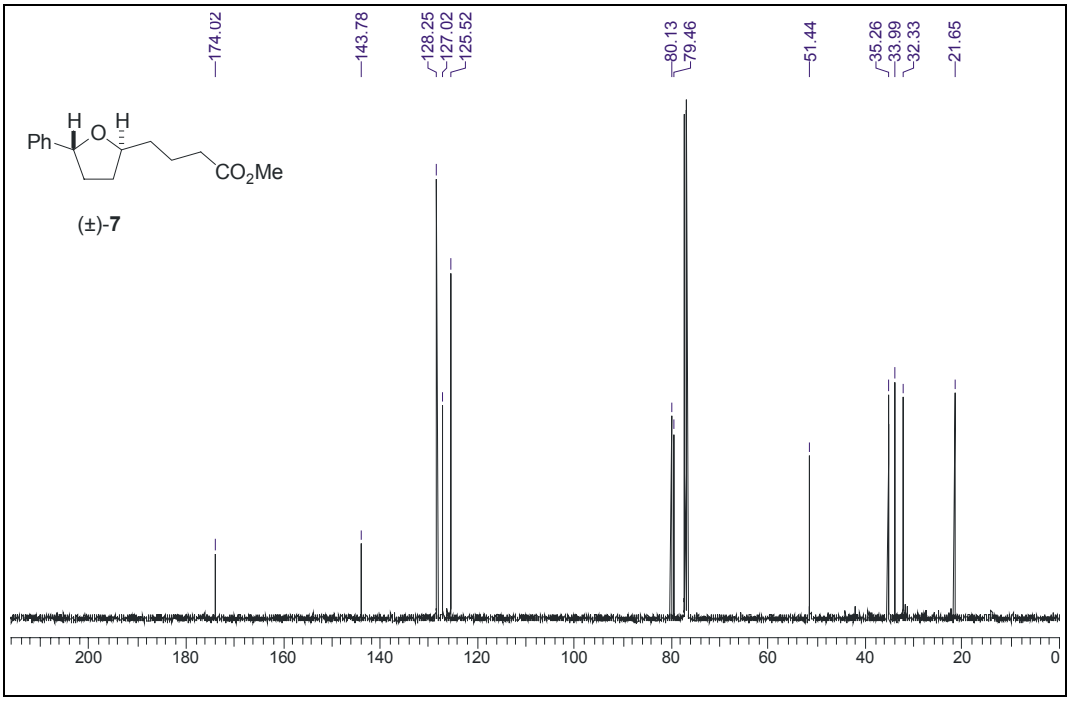

Figure S3. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Methyl 4-(*trans*-5-phenyltetrahydrofur-2-yl)-butyrate (**7**).

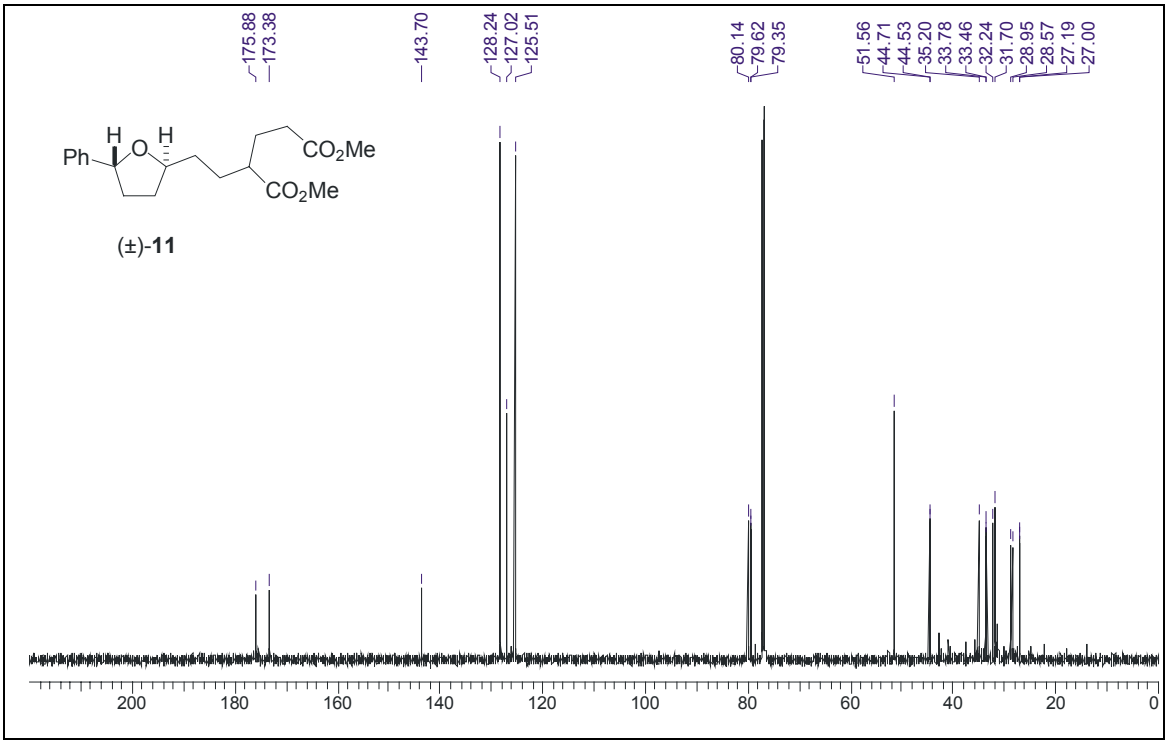

Figure S4. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Dimethyl [2-(*trans*-5-phenyltetrahydrofur-2-yl)-eth-1-yl]-glutarate (**11**).

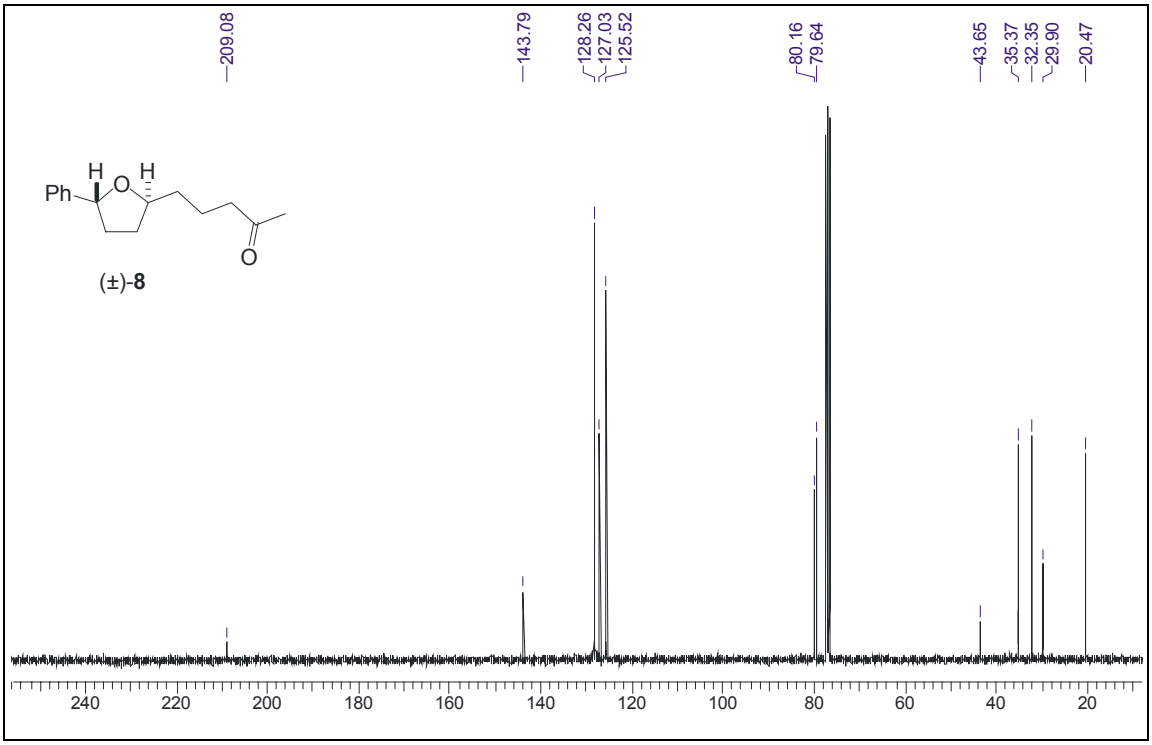

Figure S5. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 5-(*trans*-2-phenyltetrahydrofur-5-yl)-pentan-2-one (**8**).

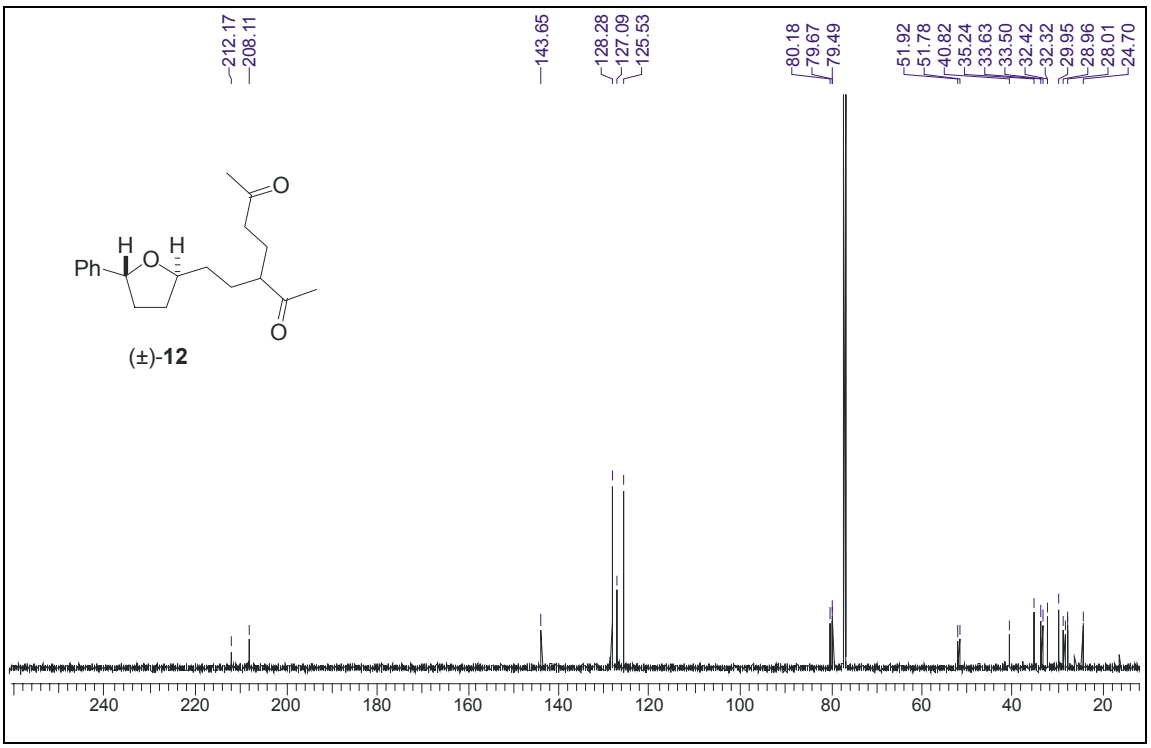

Figure S6. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of [3-(*trans*-2-phenyltetrahydrofur-5-yl)-eth-1-yl]-heptane-2,6-dione (**12**).

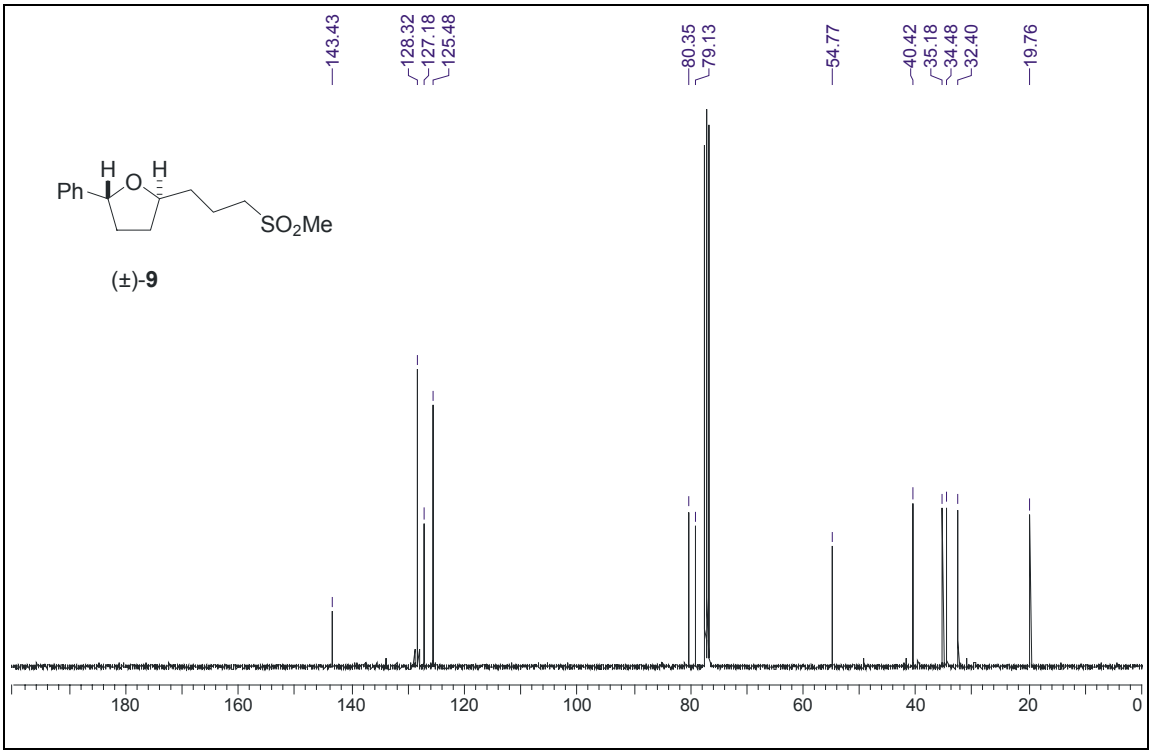

Figure S7. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 3-(*trans*-5-phenyltetrahydrofur-2-yl)-prop-1-yl methyl sulfone (**9**).

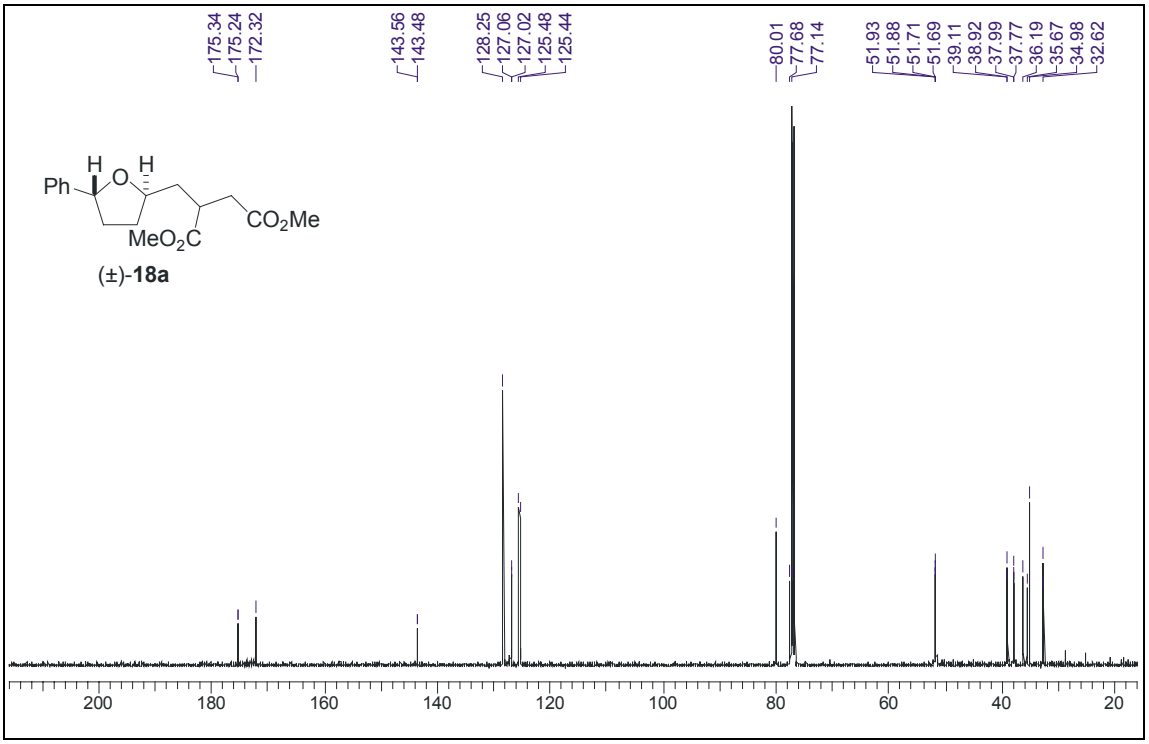

Figure S8. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of dimethyl 2-[(*trans*-5-phenyltetrahydrofur-2-yl)-methyl]-succinate (**18a**).

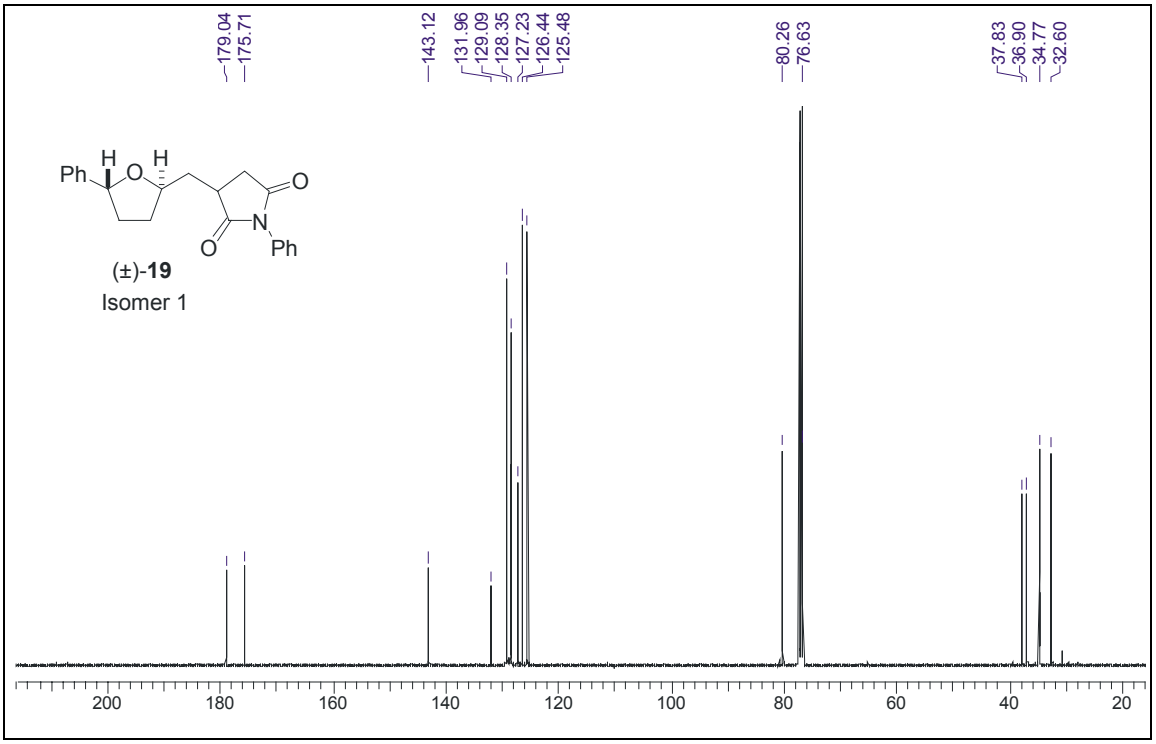

Figure S9. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 2-[(*trans*-5-phenyltetrahydrofur-2-yl)-methyl]-*N*-phenylsuccinimide (**19**) (Isomer 1).

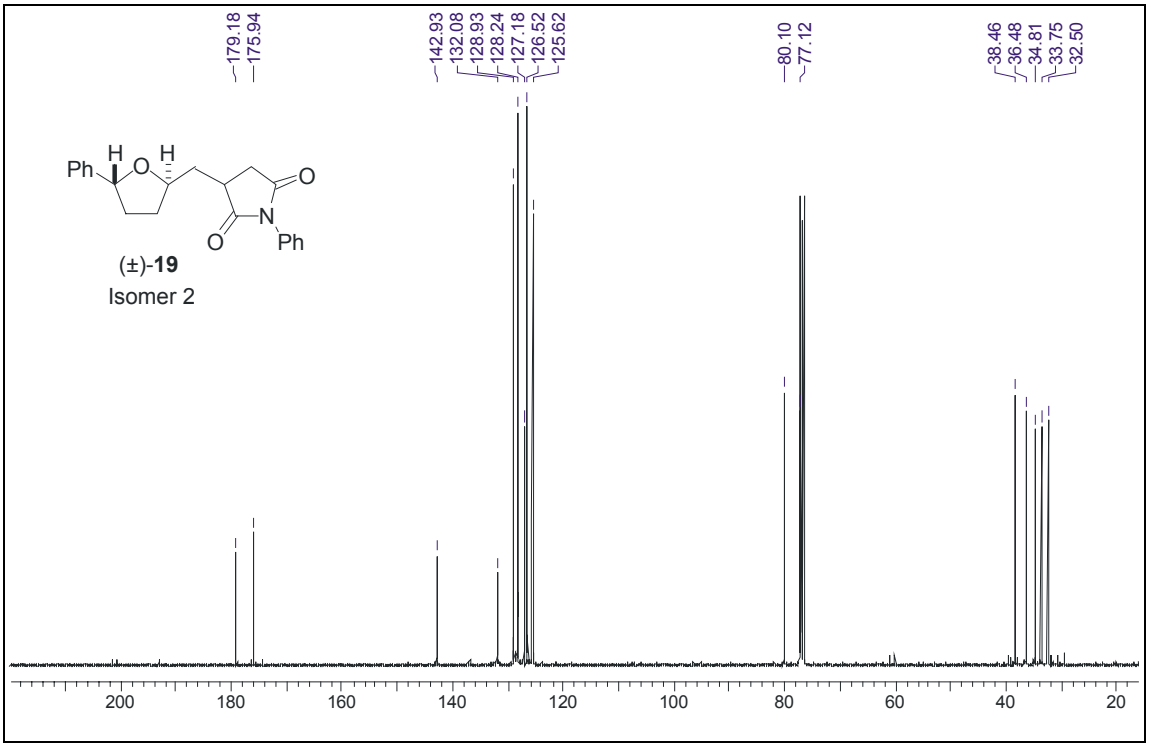

Figure S10. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of 2-[(*trans*-5-phenyltetrahydrofur-2-yl)-methyl]-*N*-phenylsuccinimide (**19**) (Isomer 2).

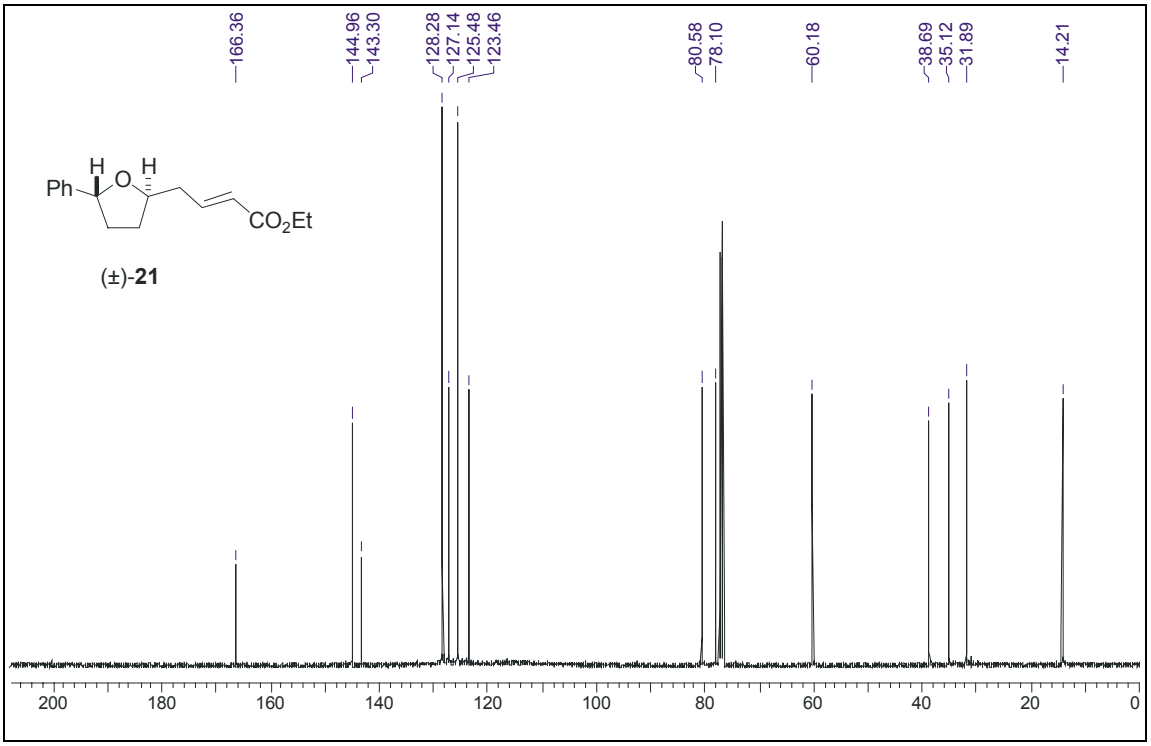

Figure S11. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of ethyl (*E*)-4-(5-Phenyltetrahydrofur-2-yl)-but-2-en-oate (**21**).

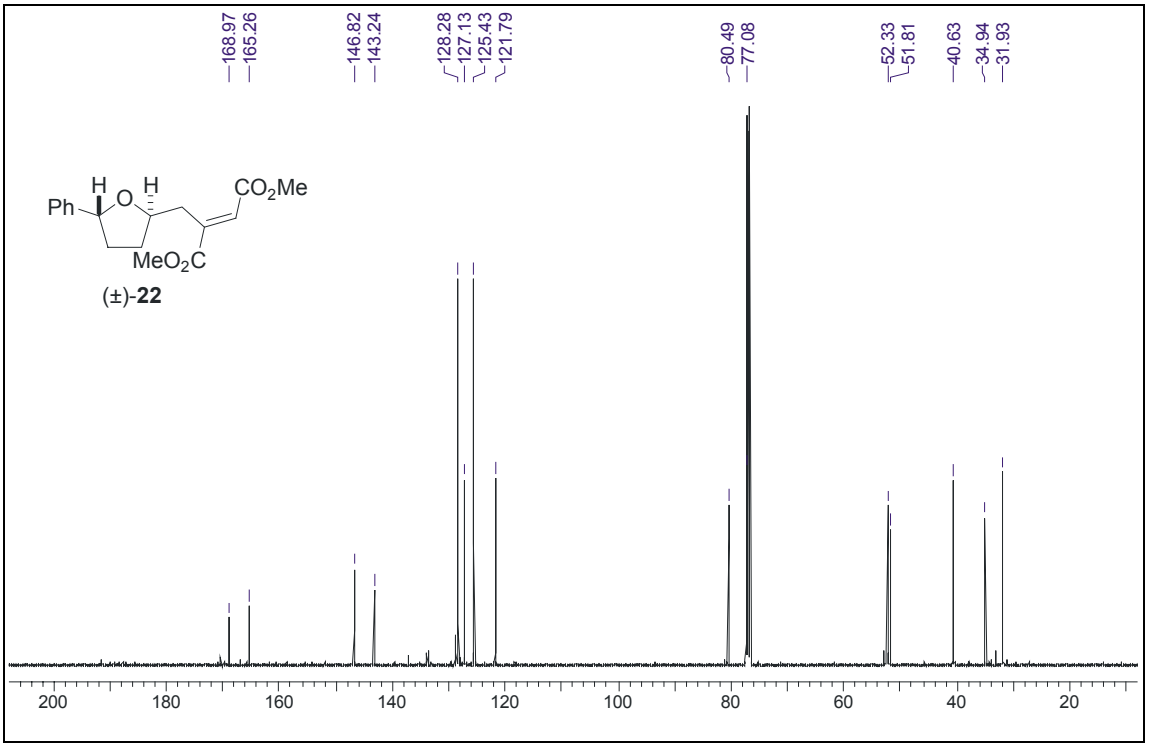

Figure S12. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Dimethyl 2-[(*trans*-5-phenyltetrahydrofuran-2-yl)methyl]-fumarate (**22**).

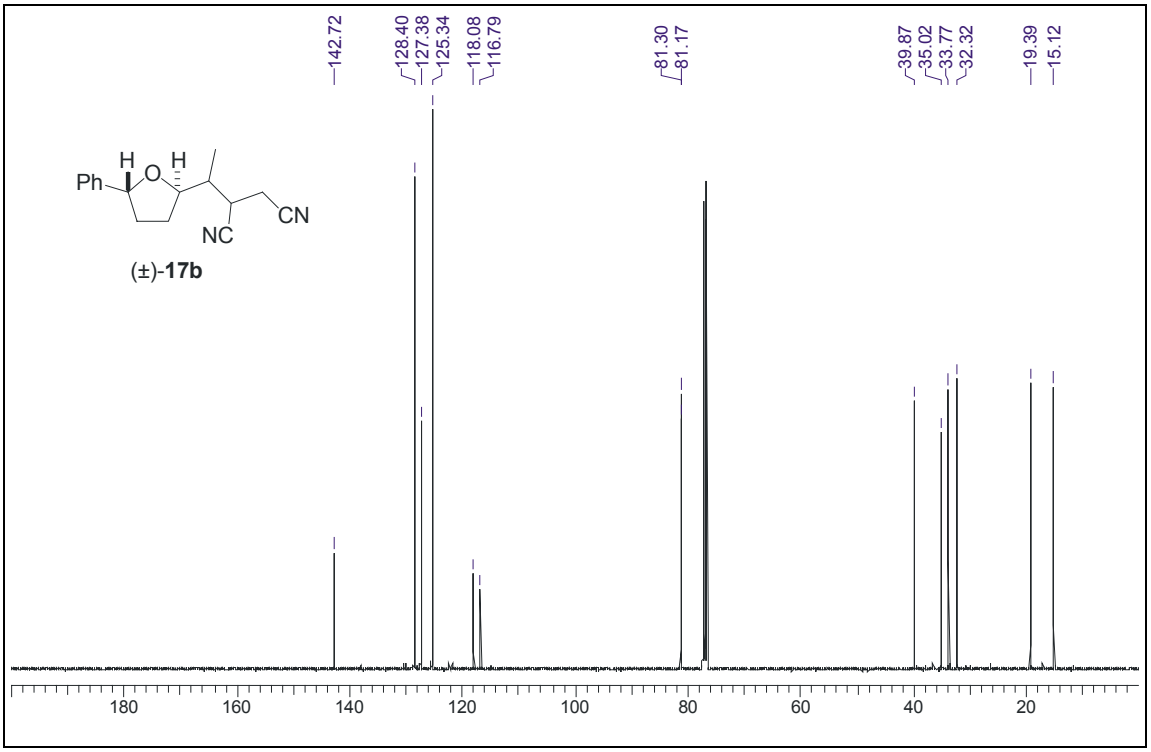

Figure S13. ^{13}C-NMR spectrum (100 MHz) of 2-[1-(*trans*-5-phenyltetrahydrofur-2-yl)-eth-1-yl]-succinodinitrile (**17b**) (1 isomer).

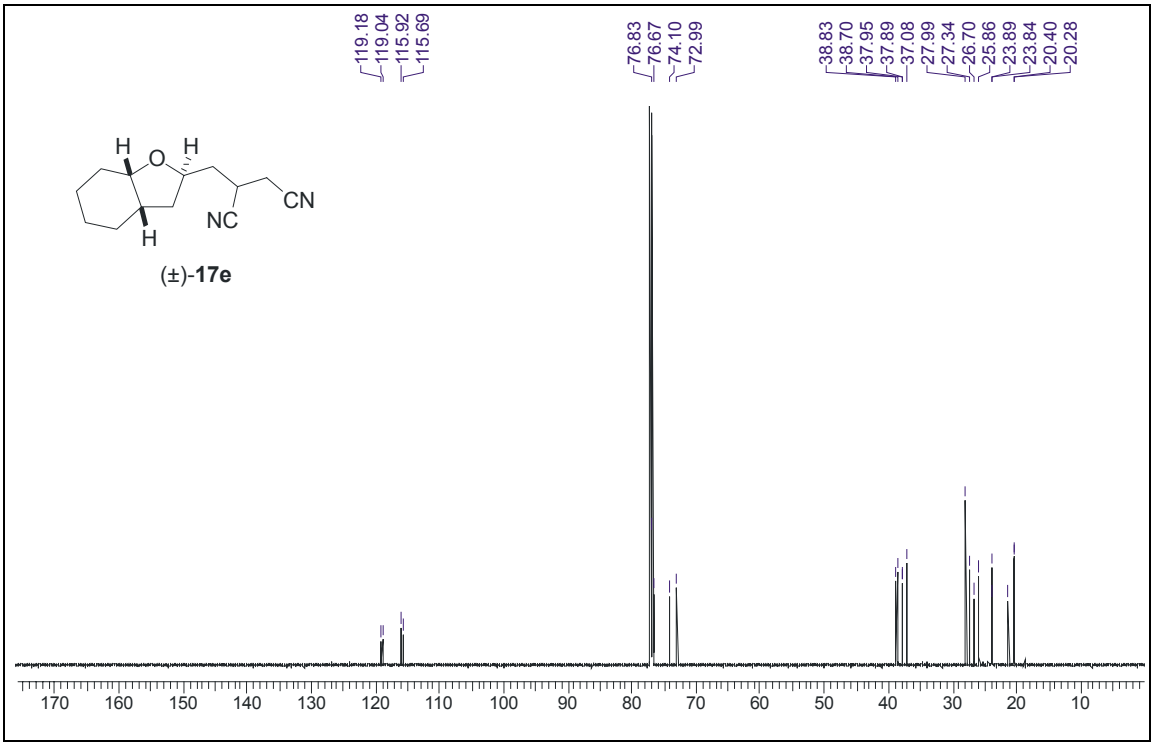

Figure S14. ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of 2-({rel-(1*S*,6*S*,8*R*)-7-oxabicyclo[4.3.0]non-8-yl}-methyl)-succinodinitrile (**17e**).

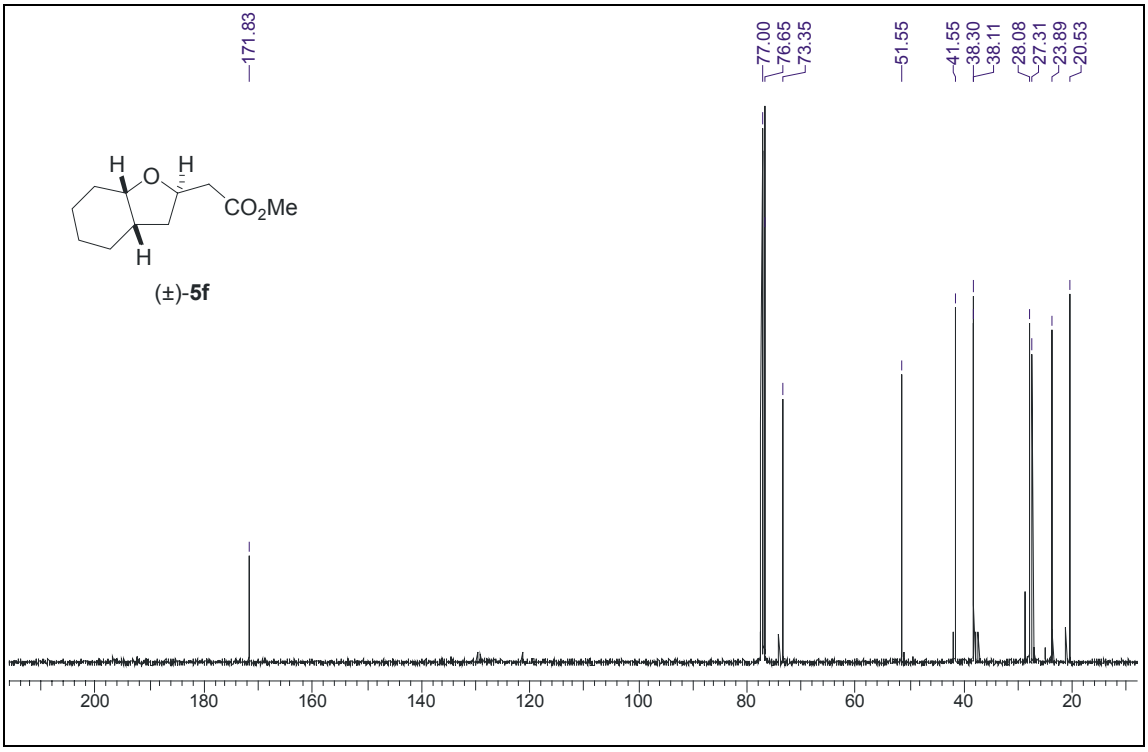

Figure S15. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of Methyl 2-({ *rel*-(1*S*,6*S*,8*R*)-7-oxabicyclo[4.3.0]non-8-yl}-methyl)-acetate (**5f**).

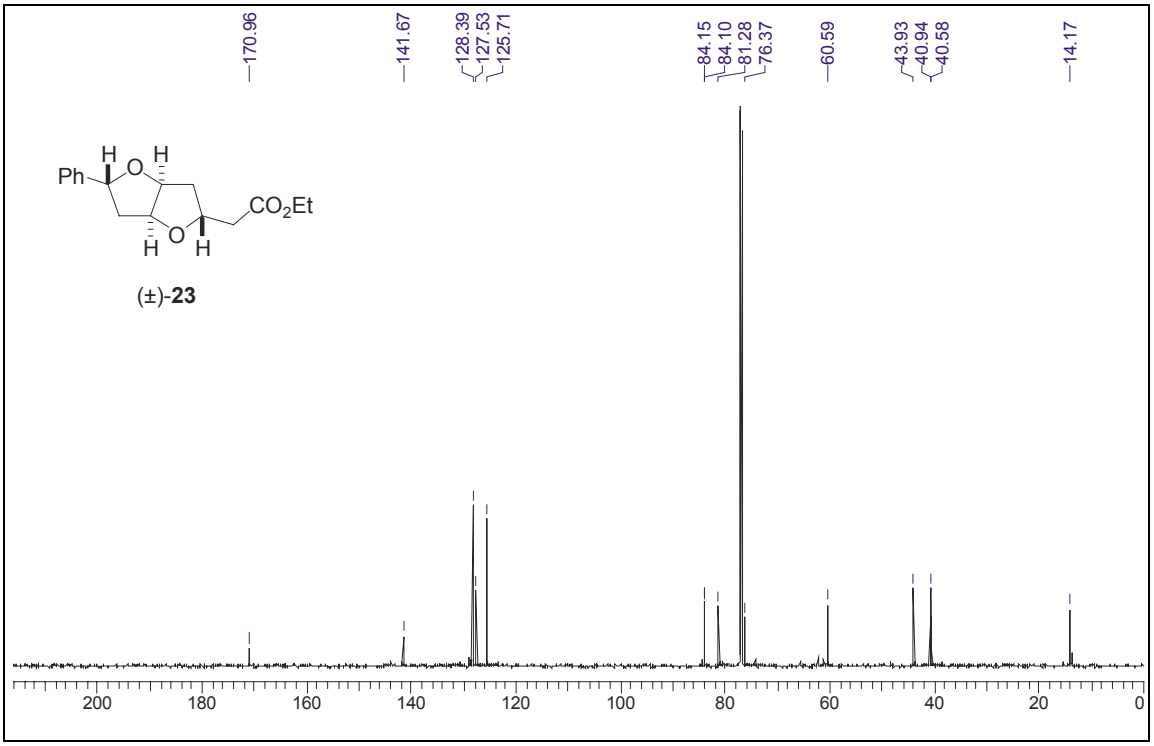

Figure S16. ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of ethyl 2-(*rel*-(2*R*,3a*S*,5*R*,6a*S*)-hexahydro-2-phenylfuro[3,2-b]furan-5-yl)acetate (**23**).

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