Supporting Information

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An Atom-Economical and Stereoselective Domino Synthesis of Functionalised Dienes

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**General Methods:** All glassware was oven dried at 80 °C before use and all reactions were performed under an atmosphere of argon unless otherwise stated. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-FTIR spectrometer. Wavelengths (v) are reported in cm⁻¹. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). Accurate mass determinations were obtained on a Brucker APEX III FT-MS (7 T magnet). All ¹H-NMR and ¹³C-NMR experiments were recorded using Bruker DPX-300, AV-400, AV-500 and AV-600 spectrometers at 300 K. Chemical shifts (δ) are quoted in ppm and coupling constants (J) are quoted in Hz. The 7.27, 7.23, 5.99 and 2.05 ppm resonance of residual CDCl₃, CDCl₂CHCl₂, C₆D₅H and CD₃COCD₂H for proton spectra and 128.0, 77.16, 73.8 and 29.84 ppm resonance of C₆D₆, CDCl₃, CDCl₂CDCl₂, and CD₃COCD₃ for carbon spectra were used as internal references. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminium plates coated with keiselgel F₂₅₄ with 0.2 mm thickness. Visualisation was achieved by a combination of ultraviolet light (254 nm) and acidic potassium permanganate or anisaldehyde. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.).

Microwave reactions were performed using a Discover SP CEM microwave.

All the reactions were performed using a stock ethereal solution of bicyclic lactone 1 prepared according to the literature in a concentration typically ranging from 0.15M to 0.25M. No significant change in yields depending on the concentration of 1 was noted in the reactions reported on this study (provided that the concentration is in the range 0.15-0.25M).
1. General procedure for lactone preparation:

2-pyrone (500 mg, 5.2 mmol) was dissolved in degassed Et₂O (150 mL) and the resulting solution was irradiated at –10 ºC using a water-cooled mercury arc lamp (Hanovia, 450 W) with a quartz filter. The reaction progress was followed by ¹H-NMR and usually 24 to 36h was required to reach completion. After warming to room temperature, the solution was concentrated under vacuum in a cold bath to reach a volume of 5-10 mL and the concentration of 1 was repeatedly assayed by ¹H-NMR. Solutions of 1 were stored at 4 ºC and did not show any signs of decomposition after several weeks.

The synthesis of 3-substituted-2-pyrone was performed in accordance to the reported literature.¹[1]

2-oxabicyclo[2.2.0]hex-5-en-3-one (1a)

Data of the ¹H-NMR spectra of 1a matches those reported in the literature.² ¹H-NMR (500 MHz, CDCl₃) δ 6.73 (app. t, J 3.5, 1H), 6.54 (app. t, J 1.9, 1H), 5.29 (dd, J 4.5, 1.9, 1H), 4.39 (s, 1H).

4-methyl-2-oxabicyclo[2.2.0]hex-5-en-3-one (1b)

Data of the $^1$H-NMR spectra of 1b matches those reported in the literature.\textsuperscript{[3]} $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 6.73 (dd, $J$ 4.5, 2.5, 1H), 6.55 (d, $J$ 2.5, 1H), 5.15 (d, $J$ 4.5, 1H), 1.45 (s, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta$ 172.9, 145.9, 139.9, 76.0, 66.7, 11.4.

4-butyl-2-oxabicyclo[2.2.0]hex-5-en-3-one (1c)

Compound 1c was obtained as a yellow solution in diethyl ether in quantitative yield according to the general procedure. $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.70 (dd, $J$ = 4.4, $J$ = 2.4, 1H), 6.51 (d, $J$ = 2.4, 1H), 5.13 (d, $J$ = 4.4, 1H), 1.88-1.81 (m, 2H), 1.45-1.33 (m, 4H), 0.91 (t, $J$ 7.1, 3H).

4-(p-tolyl)-2-oxabicyclo[2.2.0]hex-5-en-3-one (1d)

Compound 1d was obtained as a yellow solution in diethylether in quantitative yield according to the general procedure. $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.22 (m, 4H), 6.97 (dd, $J$

4.2, 2.7, 1H), 6.76 (d, J 2.7, 1H), 5.33 (d, J 4.2, 1H), 2.36 (s, 3H). 13C-NMR (125 MHz, CDCl3) δ 171.0, 144.8, 141.5, 138.6, 129.9 (2C), 128.2, 126.6 (2C), 73.2, 21.4; FTIR (neat) νmax 3030, 1810, 830; HRMS (ESI) exact mass calculated for [M] (C_{12}H_{10}O_{2}) requires m/z 186.0679, found m/z 186.0681.

2. Preparation of (E,Z)-5-aryloxy-dienes:

To a stirred suspension of sodium hydride (60% in mineral oil, 6.5 mg, 0.16 mmol, 1.0 equiv) in THF (1.0 mL) was added dropwise a solution of the desired substituted phenol (0.17 mmol, 1.1 equiv) in THF (0.2 mL) at room temperature. In a schlenk flask, Pd(PPh3)4 (9.0 mg, 8 μmol, 5 mol%) was evacuated/backfilled with Ar three times and dissolved in THF (2.0 mL). The phenolate sodium salt solution was added to the solution of Pd(PPh3)4 and the mixture was cooled to 0 °C. After 5 min, an ethereal solution of lactone (0.20 M in Et2O, 0.8 mL, 0.16 mmol, 1.0 eq) was added dropwise and the mixture was stirred at 0 °C for 3 hours. The solution was quenched with H2O (2 mL) and Et2O (2 mL) was added to the mixture. The organic phase was extracted three times with saturated NaHCO3. The combined aqueous phases were then acidified using 1M HCl and extracted three times with EtOAc. The combined organic phases were washed with brine, dried over MgSO4 and the solvent was removed under vacuum to give the corresponding diene 2.

(2Z,4E)-5-(mesityloxy)penta-2,4-dienoic acid (2a)

Compound 2a was obtained as colourless crystals in 98% yield according to the general procedure. 1H-NMR (500 MHz, CD3COCD3) δ 7.13 (d, J = 12.4, 1H), 6.86 (s, 2H), 6.83 (app.
$t, J = 11.6, 1H), 6.88 \text{ (app. t, } J = 11.6, 1H), 5.43 \text{ (d, } J = 11.6, 1H), 2.20 \text{ (s, 3H), } 2.01 \text{ (s, 6H); }$

$^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 168.1, 158.2, 150.6, 143.4, 135.6, 130.3 (2C), 130.2, 113.4, 107.1 (2C), 20.8, 16.1 (2C); FTIR (neat) $\nu_{\text{max}}$ 2923, 1684, 1621, 1592, 1445, 1193, 1162, 937, 823; HRMS (ESI) exact mass calculated for [M-H]$^-$ (C$_{14}$H$_{15}$O$_3$) requires $m/z$ 231.1025, found $m/z$ 231.1027. The structure of compound (Z,E)-2a was confirmed through single-crystal X-ray analysis (see below).

Crystal structure analysis of compound (Z,E)-2a crystallized from acetone (CCDC 878396)

(2Z,4E)-5-(4-(trifluoromethyl)phenoxy)penta-2,4-dienoic acid (2b)

![Diagram of compound 2b](image)

Compound 2b was obtained as colourless crystals in 98% yield according to the general procedure. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.76 (d, $J = 8.4$, 2H), 7.54 (d, $J = 11.9$, 1H), 7.43 (app. t, $J = 11.9$, 1H), 7.36 (d, $J = 8.4$, 2H), 6.82 (app. t, $J = 11.3$, 1H), 5.66 (d, $J = 11.3$, 1H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 167.8, 159.8, 153.2, 141.8, 128.2 (q, $J_{C-F}$ 4, 2C), 126.1 (q, $J_{C-F}$ 33), 125.1 (q, $J_{C-F}$ 270), 118.1 (2C), 116.3, 112.2; $^{19}$F-NMR (376 MHz, CD$_3$COCD$_3$) $\delta$ -62.3; FTIR (neat) $\nu_{\text{max}}$ 2924, 1689, 1599, 1453, 1209, 1129, 1107, 1062, 927, 822; HRMS (ESI) exact mass calculated for [M-H]$^-$ (C$_{12}$H$_8$O$_3$F$_3$) requires $m/z$ 257.0429,
found m/z 257.0431. The structure of compound (Z,E)-2b was confirmed through single-crystal X-ray analysis (see below).

![Crystal structure analysis of compound (Z,E)-2b crystallized from acetone (disordered CF₃ group) (CDCC 878394)](image)

(2Z,4E)-2-(p-tolyl)-5-(4-(trifluoromethyl)phenoxy) penta-2,4-dienoic acid (2c)

Compound 2c was obtained as a yellow oil in 81% yield according to the general procedure.

$^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.77 (d, $J = 8.8$, 2H), 7.55 (d, $J = 11.8$, 1H), 7.36 (d, $J = 8.8$, 2H), 7.33 (d, $J = 8.1$, 2H), 7.17 (d, $J = 8.1$, 2H), 7.02 (app. t, $J = 11.8$, 1H), 6.91 (d, $J = 11.8$, 1H), 2.32 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 168.9, 160.2, 151.3, 137.8, 136.6, 133.5, 132.3, 129.6 (2C), 128.4 (2C), 128.2 (q, $J_{C-F}$ 4, 2C), 125.8 (q, $J_{C-F}$ 33), 125.3 (q, $J_{C-F}$ 271), 117.9 (2C), 113.6, 21.1; $^{19}$F-NMR (375 MHz, CD$_3$COCD$_3$) $\delta$ = -61.7; FTIR (neat) $\nu_{\text{max}}$ 2925, 1684, 1606, 1321, 1235, 1158, 1103, 1064, 839, 821; HRMS (ESI) exact mass calculated for [M+Na]$^+$ (C$_{19}$H$_{15}$F$_3$O$_3$Na) requires m/z 371.0870, found m/z 371.0866.
(2Z,4E)-5-(perfluorophenoxy)penta-2,4-dienoic acid (2d)

![Chemical Structure](image)

Compound 2d was obtained as a yellow oil in 51% yield according to the general procedure. 

$^1$H-NMR (300 MHz, CD$_3$COCD$_3$); $\delta$ 7.39 (d, $J = 12.3$, 1H), 7.30 (app. t, $J = 11.6$, 1H), 6.77 (app. t, $J = 11.3$, 1H), 5.67 (d, $J = 11.3$, 1H); $^{13}$C-NMR (75 MHz, CD$_3$COCD$_3$) $\delta$ 167.6, 155.7, 140.4, 117.4, 110.2; (C$^{IV}$ from pentafluoro phenol not detected by $^{13}$C-NMR); $^{19}$F-NMR (375 MHz, CD$_3$COCD$_3$) $\delta$ -157.5 (2F), -162.3, -164.6 (2F); FTIR (neat) $\nu_{\text{max}}$ 2927, 1628, 1599, 1512, 1223, 1171, 1106, 997, 978, 927; HRMS (ESI) exact mass calculated for [M-H]$^-$ (C$_{11}$H$_4$F$_5$O$_3$) requires m/z 279.0083, found m/z 279.0086.

(2Z,4E)-5-(p-tolyloxy)penta-2,4-dienoic acid (2e)

![Chemical Structure](image)

Compound 2e was obtained as colourless crystals in 88% yield according to the general procedure. 

$^1$H-NMR: (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.37 (d, $J = 11.9$, 1H), 7.28 (dd, $J = 11.9$, $J = 11.5$, 1H), 7.20 (d, $J = 8.3$, 2H), 7.02 (d, $J = 8.3$, 2H), 6.78 (dd, $J = 11.9$, $J = 11.5$, 1H), 5.57 (d, $J = 11.5$, 1H), 2.30 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 168.1, 155.7, 155.2, 142.8, 134.3, 131.1 (2C), 117.9 (2C), 114.6, 110.2, 20.5; FTIR (neat) $\nu_{\text{max}}$ 3028, 2925, 2969, 1677, 1630, 1591, 1501, 1443, 1206, 930; HRMS (ESI) exact mass calculated for [M-H]$^-$ (C$_{12}$H$_{11}$O$_3$) requires m/z 203.0715, found m/z 203.0714.
(2Z,4E)-2-(p-tolyl)-5-(p-tolyloxy)penta-2,4-dienoic acid (2g)

Compound 2g was obtained as a yellow oil in 49% yield according to the general procedure. 

\[ ^1\text{H-NMR (500 MHz, CD}_3\text{COCD}_3) \delta 7.39 (d, J = 11.6, 1H), 7.32 (d, J = 8.0, 2H), 7.20 (d, J = 8.4, 2H), 7.15 (d, J = 8.0, 2H), 7.03 (d, J = 8.4, 2H), 6.95-6.86 (m, 2H), 2.31 (s, 3H), 2.30 (s, 3H) ; ^{13}\text{C-NMR (125 MHz, CD}_3\text{COCD}_3) \delta 169.0, 155.4, 153.7, 137.5, 137.1, 135.2, 134.1, 131.1 (2C), 130.4, 129.5 (2C), 128.4 (2C), 117.7 (2C), 111.6, 21.1, 20.6; \text{FTIR (neat) } \nu_{\text{max}} 2923, 1765, 1698, 1512, 1220, 819; \text{HRMS (ESI) exact mass calculated for [M+Na]^+ (C}_{19}\text{H}_{18}\text{O}_3\text{Na}) requires } m/z 317.1149, \text{found } m/z 317.1148. \]

(2Z,4E)-5-(3,5-dimethylphenoxy)penta-2,4-dienoic acid (2h)

Compound 2h was obtained as colourless crystals in 89% yield according to the general procedure. 

\[ ^1\text{H-NMR (500 MHz, CD}_3\text{COCD}_3) \delta 7.39 (d, J = 12.0, 1H), 7.30 (app. td, J = 12.0, J = 1.0, 1H), 6.81-6.75 (m, 4H), 5.57 (d, J = 11.3, 1H), 2.29 (s, 6H); ^{13}\text{C-NMR (125 MHz, CD}_3\text{COCD}_3) \delta 168.1, 157.3, 155.4, 142.9, 140.5 (2C), 126.5, 115.5 (2C), 114.7, 110.5, 21.2 (2C); \text{FTIR (neat) } \nu_{\text{max}} 3029, 2923, 1632, 1584, 1446, 1174, 932; \text{HRMS (ESI) exact mass calculated for [M]^+ (C}_{13}\text{H}_{14}\text{O}_3) requires } m/z 218.0942, \text{found } m/z 218.0943. \]
(2Z,4E)-5-(3,5-dimethylphenoxy)-2-methylpenta-2,4-dienoic acid (2i)

![Chemical Structure](image)

Compound 2i was obtained as colourless crystals in 97% yield according to the general procedure. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) δ 7.22 (d, $J = 12.1$, 1H), 7.15 (app. t, $J = 11.5$, 1H), 6.78 (s, 1H), 6.72 (s, 2H), 6.72 (d, $J = 11.5$, 1H), 2.28 (s, 6H), 1.94 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) δ 169.0, 157.6, 152.5, 140.5, 137.9, 126.1, 123.4, 115.3 (3C), 111.9, 21.3, 21.0 (2C); FTIR (neat) $\nu_{\text{max}}$ 2924, 2856, 1681, 1592, 1177, 947; HRMS (ESI) exact mass calculated for [M]$^+$ (C$_{14}$H$_{16}$O$_3$) requires $m/z$ 232.1097, found $m/z$ 232.1099. The structure of compound (Z,E)-3i was confirmed through single-crystal X-ray analysis (see below).

Crystal structure analysis of compound (Z,E)-2i crystallized from acetone (Cambridge Crystallographic Data Centre number: 878398).
(2Z,4E)-5-(4-methoxyphenoxy)penta-2,4-dienoic acid (2j)

Compound \(2j\) was obtained as colourless crystals in 64% yield according to the general procedure. \(^1\)H-NMR (500 MHz, CD\(_3\)COCD\(_3\)) \(\delta\) 7.32 (d, \(J = 12.2\), 1H), 7.24 (dd, \(J = 12.2, J = 11.5\), 1H), 7.07 (d, \(J = 9.1\), 2H), 6.95 (d, \(J = 9.1\), 2H), 6.76 (dd, \(J = 12.2, J = 11.5\), 1H), 5.55 (d, \(J = 11.5\), 1H), 3.78 (s, 3H); \(^{13}\)C-NMR (125 MHz, CD\(_3\)COCD\(_3\)) \(\delta\) 168.1, 156.6 (2C), 142.8 (2C), 119.4 (2C), 115.9 (2C), 114.6, 109.9, 56.0; FTIR (neat) \(\nu\)\(_{\text{max}}\) 2933, 2837, 1679, 1632, 1505, 1198, 1131, 930, 825; HRMS (ESI) exact mass calculated for [M-H] \((\text{C}_{12}\text{H}_{11}\text{O}_4)\) requires \(m/z\) 219.0664, found \(m/z\) 219.0663. The structure of compound \((Z,E)-2j\) was confirmed through single-crystal X-ray analysis (see below).

Crystal structure analysis of compound \((Z,E)-2j\) crystallized from acetone
(Cambridge Crystallographic Data Centre number: 878394).
(2Z,4E)-5-(4-methoxyphenoxy)-2-methylpenta-2,4-dienoic acid (2k)

![Chemical structure of 2k](image)

Compound 2k was obtained as colourless crystals in 71% yield according to the general procedure. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) δ 7.18 (d, $J = 12.1$, 1H), 7.11 (app. t, $J = 11.7$, 1H), 7.07 (d, $J = 9.1$, 2H), 6.96 (d, $J = 9.1$, 2H), 6.61 (app. td, $J = 11.7$, $J = 1.3$, 1H), 3.80 (s, 3H), 1.96 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) δ 168.8, 157.3, 153.8, 151.5, 138.2, 123.3, 119.3 (2C), 116.0 (2C), 111.3, 55.9, 21.0; FTIR (neat) ν$_{max}$ 2957, 2931, 2836, 1671, 1627, 1505, 1214, 1176, 1103, 944; HRMS (ESI) exact mass calculated for [M-H]$^-$ (C$_{13}$H$_{13}$O$_4$) requires m/z 233.0820, found m/z 233.0819.

(Z)-2-((E)-3-(4-methoxyphenoxy)allylidene)hexanoic acid (2l)

![Chemical structure of 2l](image)

Compound 2l was obtained as a yellow oil in 44% yield according to the general procedure. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) δ 7.19 (d, $J = 12.1$, 1H), 7.07-7.02 (m, 3H), 6.93 (d, $J = 9.1$, 2H), 6.56 (d, $J = 11.5$, 1H), 3.78 (s, 3H), 2.30 (t, $J = 7.8$, 2H), 1.49-1.43 (m, 2H), 1.37-1.29 (m, 2H), 0.91 (t, $J = 7.1$, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) δ 168.9, 157.2, 153.8, 151.5, 138.4, 128.3, 119.3 (2C), 115.8 (2C), 111.4, 56.0, 35.2, 32.7, 23.1, 14.3; FTIR (neat) ν$_{max}$ 2957, 2931, 2861, 1676, 1631, 1503, 1206, 1169, 1113, 1035, 952; HRMS (ESI) exact mass calculated for [M+Na]$^+$ (C$_{16}$H$_{20}$ONa) requires m/z 299.1252, found m/z 299.1254.
(2Z,4E)-5-(2-methoxyphenoxy)penta-2,4-dienoic acid (2m)

Compound 2m was obtained as yellow solid in 97% yield according to the general procedure.  
$^{1}H$-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.25 (d, $J = 12.2$, 1H), 7.21-7.19 (m, 2H), 7.13-7.10 (m, 2H), 6.96 (app. t, $J = 7.7$, 1H), 6.74 (app. t, $J = 11.3$, 1H), 5.53 (d, $J = 11.3$, 1H), 3.84 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 168.0, 157.6, 151.4, 146.0, 143.0, 126.4, 121.7, 120.4, 114.2, 114.0, 109.1, 56.1; FTIR (neat) $\nu$$_{\text{max}}$ 3036, 2924, 2573, 1691, 1633, 1590, 1497, 1199, 1179, 1103; HRMS (ESI) exact mass calculated for [M-H]$^-$ (C$_{12}$H$_{11}$O$_4$) requires $m/z$ 219.0664, found $m/z$ 219.0663.

(2Z,4E)-5-(2-methoxyphenoxy)-2-(p-tolyl)penta-2,4-dienoic acid (2n)

Compound 2n was obtained as a yellow oil in 90% yield according to the general procedure.  
$^{1}H$-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.33-7.27 (m, 3H), 7.20-7.11 (m, 5H), 6.98 (ddd, $J = 8.5$, $J = 6.7$, $J = 1.8$, 1H), 6.85 (d, $J = 4.9$, 1H), 6.84 (d, $J = 6.5$, 1H) 3.86 (s, 3H), 2.33 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 168.9, 155.2, 151.1, 146.0, 143.0, 135.0, 129.8, 129.2 (2C), 128.1 (2C), 125.8, 121.4, 119.7, 113.7, 110.2, 56.0, 20.8; FTIR (neat) $\nu$$_{\text{max}}$ 2923, 1678, 1627, 1583, 1499, 1257, 1212, 1137; HRMS (ESI) exact mass calculated for [M+Na]$^+$ (C$_{19}$H$_{18}$O$_4$Na) requires $m/z$ 333.1094, found $m/z$ 333.1097.
(2Z,4E)-5-(4-(methylthio)phenoxy)penta-2,4-dienoic acid (2o)

![Chemical structure of 2o]

Compound 2o was obtained as a yellow solid in 67% yield according to the general procedure. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.36 (d, $J = 12.5$, 1H), 7.29-7.24 (m, 3H), 7.07 (d, $J = 8.1$, 2H), 6.74 (app. t, $J = 11.4$, 1H), 5.56 (d, $J = 11.4$, 1H), 2.44 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 167.9, 155.2, 142.6, 134.7, 129.3 (2C), 118.7 (3C), 115.1, 110.7, 16.4; FTIR (neat) $\nu_{\text{max}}$ 2916, 2573, 1627, 1490, 1213, 1137, 922; HRMS (ESI) exact mass calculated for [M-H]$^-$ (C$_{12}$H$_{11}$O$_3$S) requires $m/z$ 235.0433, found $m/z$ 235.0434.

(2Z,4E)-5-(4-(methylthio)phenoxy)-2-(p-tolyl)penta-2,4-dienoic acid (2p)

![Chemical structure of 2p]

Compound 2p was obtained as a yellow oil in 81% yield according to the general procedure. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.42 (d, $J = 11.0$, 1H), 7.35-7.31 (m, 4H), 7.16 (d, $J = 8.3$, 2H), 7.12 (d, $J = 8.6$, 2H), 6.95-6.88 (m, 2H), 2.48 (s, 3H), 2.32 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 169.0, 155.5, 153.2, 137.7, 137.0, 134.8, 134.4, 131.0, 129.6 (2C), 129.5 (2C), 128.5 (2C), 118.6 (2C), 112.1, 21.1, 16.5; FTIR (neat) $\nu_{\text{max}}$ 2922, 1678, 1628, 1583, 1488, 1219, 1158, 818; HRMS (ESI) exact mass calculated for [M+H]$^+$ (C$_{19}$H$_{18}$O$_3$S) requires $m/z$ 349.0870, found $m/z$ 349.0869.
(2Z,4E)-5-((4-methoxynaphthalen-1-yl)oxy)penta-2,4-dienoic acid (2q)

![Chemical structure of 2q](image)

Compound 2q was obtained as colourless crystals in 43% yield according to the general procedure. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 8.24 (d, $J$ = 8.2, 1H), 8.07 (d, $J$ = 8.2, 1H), 7.62-7.56 (m, 2H), 7.47 (d, $J$ = 12.1, 1H), 7.37 (app. td, $J$ = 11.9, $J$ = 1.0, 1H), 7.17 (d, $J$ = 8.2, 1H), 6.91 (d, $J$ = 8.2, 1H), 6.81 (t, $J$ = 11.6, 1H), 5.58 (d, $J$ = 11.4, 1H), 4.02 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 167.9, 157.1, 153.2, 146.7, 142.9, 127.7, 127.4, 127.1, 127.0, 123.0, 122.0, 114.7, 113.2, 110.1, 104.1, 56.2; FTIR (neat) $\nu_{\text{max}}$ 2934, 2571, 1677, 1620, 1589, 1390, 1221, 1176, 1092, 922; HRMS (ESI) exact mass calculated for [M+Na]$^+$ (C$_{16}$H$_{14}$O$_4$Na) requires $m/z$ 293.0787, found $m/z$ 293.0784. The structure of compound (Z,E)-2q was confirmed through single-crystal X-ray analysis (see below).

Crystal structure analysis of compound (Z,E)-2q crystallized from Acetone (Cambridge Crystallographic Data Centre number: 878397).
Background reaction on the lactone 1a:
Diene 2i was not observed when the reaction was performed in absence of Pd catalyst according to the general procedure (p. S4).

Background reaction on the 2-pyrone:
When 2-pyrone was submitted to the optimized reaction conditions reported on p. S4 (in presence of phenoxide anion, with and without Pd cat.), no reaction was observed.

![Chemical structure](image)

Procedure for isomerisation of (Z,E) diene (2j) to (E,E) diene (2E,4E)-5-(4-methoxyphenoxy)penta-2,4-dienoic acid (2j')

(2Z,4E)-5-(4-methoxyphenoxy)penta-2,4-dienoic acid (2j) was dissolved in THF (1 mL) and a catalytic amount of I₂ (10 mol%) was added to the solution. The mixture was stirred at room temperature for 2h. H₂O (5 mL) and EtOAc (5 mL) were added to the reaction mixture and the organic phase was extracted three times with saturated NaHCO₃. The combined aqueous phases were acidified to pH 1 using 1M HCl and extracted three times with EtOAc. Solvent was removed under vacuum to give the (E,E) diene 2j’ in 22% yield. ¹H-NMR (300 MHz, CD₃COCD₃) δ 7.40 (d, J = 11.8, 1H), 7.37 (dd, J = 15.3, J = 11.6, 1H), 7.08 (d, J = 9.0, 2H), 6.96 (d, J = 9.0, 2H), 6.06 (app. t, J = 11.9, 1H), 5.82 (d, J = 15.2, 1H), 3.79 (s, 3H); ¹³C-NMR (75 MHz, CD₃COCD₃) δ 168.0, 157.2, 155.5, 151.0, 143.1, 119.4 (2C), 118.4, 115.8 (2C), 110.6, 56.0. HRMS (ESI) exact mass calculated for [M]+ (C₁₂H₁₂O₄) requires m/z 220.0734, found m/z 293.0736.
3. Ring opening of cyclobutenes

\((2Z,4E)-7\text{-ethoxy-6-(ethoxycarbonyl)-6-methyl-7-oxohepta-2,4-dienoic acid ((Z,E)-5)}\)

A stirred solution of cyclobutenes cis-4 \(^{[4]}\) (50.0 mg) was heated in toluene at 110 °C for 30 min. The solvent was removed under vacuum to give (Z,E)-5 as a white solid in essentially quantitative yield (NMR internal standard yield). \(^1\)H-NMR (400 MHz, CD\(_3\)COCD\(_3\)) \(\delta \) 7.53 (ddd, \(J = 15.9, \ J = 11.1, \ J = 0.9, \) 1H), 6.76 (app.td, \(J = 11.1, \ J = 0.9, \) 1H), 6.51 (app. dt, \(J = 15.9, \ J = 0.9, \) 1H), 5.75 (app. dt, \(J = 11.1, \ J = 0.9, \) 1H), 4.19 (q, \(J = 7.1, \) 4H), 1.56 (s, 3H), 1.23 (t, \(J = 7.1, \) 6H); \(^{13}\)C-NMR (100 MHz, CD\(_3\)COCD\(_3\)) \(\delta \) 170.9 (2C), 167.3, 144.7, 141.3, 127.7, 119.5, 62.3 (2C), 56.9, 20.8, 14.3 (2C); FTIR (neat) \(v_{\text{max}} \) 2985, 2939, 1728, 1692, 1253, 1107, 1016, 858.

\((2E,4E)-7\text{-ethoxy-6-(ethoxycarbonyl)-6-methyl-7-oxohepta-2,4-dienoic acid ((E,E)-5)}\)

A stirred solution of cyclobutenes cis-4 \(^{[3]}\) (50.4 mg) was heated in toluene at 110 °C for 2 hours. The solvent was removed under vacuum to give (E,E)-5 as a white solid in essentially quantitative yield (NMR internal standard yield). \(^1\)H-NMR (400 MHz, CD\(_3\)COCD\(_3\)) \(\delta \) 7.31 (ddd, \(J = 15.4, \ J = 10.6, \ J = \ 0.6, \) 1H), 6.60 (app.dt, \(J = 15.8, \ J = 0.6, \) 1H), 6.42 (ddd, \(J = 15.8, \ J = 10.6, \ J = 0.6, \) 1H), 6.00 (app. dt, \(J = 15.4, \ J = 0.6, \) 1H), 4.19 (q, \(J = 7.1, \) 4H), 1.56 (s, 3H), 1.23 (t, \(J = 7.1, \) 6H); \(^{13}\)C-NMR (100 MHz, CD\(_3\)COCD\(_3\)) \(\delta \) 170.7 (2C), 167.6, 144.7, 140.5, 129.6, 123.4, 62.3 (2C), 56.8, 20.5, 14.3 (2C); FTIR (neat) \(v_{\text{max}} \) 2985, 2939, 1727, 1691, 1108, 1014, 858, 827The structure of compound (E,E)-5 was confirmed through single-crystal X-ray analysis (see below).

---

4. Kinetic studies of electrocyclic ring opening of cyclobuenes.

Samples of cyclobutene cis-4, cis-6, cis-8, trans-4, trans-6, trans-8 were dissolved in CDCl2CDCl2 (0.04 M) and heated to 90 °C in an Avance III 500 spectrometer (499.89MHz) equipped with a BBFOplus 1H/BB (incl. 19F) probehead with z-gradient from Bruker Biospin GmbH. The conversion of the cyclobutene starting material into the corresponding diene was monitored recording the 1H-NMR spectra over time.

Preparation of the starting materials.

Compounds cis-4, cis-8, trans-4, trans-8 were prepared following a procedure described in the literature and their spectroscopic properties match those reported.\textsuperscript{3,4} Compounds 6 were prepared starting from the corresponding free carboxylic acid 4 according to the following procedure: carboxylic acid 4 (100.0 mg, 0.37 mmol) was dissolved in dichlorometane (3.7 mL) and the resulting solution was cooled to 0 °C. DMF (1 drop) followed by oxalyl chloride (48 μL, 0.55 mmol, 1.5 equiv.) were added dropwise, the resulting mixture was stirred for 30 min and then dry MeOH (375 μL, 9.2 mmol, 25 equiv.)
was added dropwise. After 30 min at 0 °C, the solvent was removed under vacuum and the product was purified by column chromatography (pentane/EtOAc: 95/5) to give ester 6.

diethyl 2-(cis-4-(methoxycarbonyl)cyclobut-2-en-1-yl)-2-methylmalonate (cis-6)

![cis-6_diagram]

Compound cis-6 was obtained in 80% yield according to the procedure. Spectroscopic properties in agreement with those reported in the literature.\(^\text{[4]}\)

diethyl 2-(trans-4-(methoxycarbonyl)cyclobut-2-en-1-yl)-2-methylmalonate (trans-6)

![trans-6_diagram]

Compound trans-6 was obtained in 84% yield according to the procedure. \(^1\)H-NMR (500 MHz, CD\(_3\)COCD\(_3\)) \(\delta\) 6.22 (d, \(J = 2.6\), 1H), 6.13 (d, \(J = 2.6\), 1H), 4.18-4.12 (m, 4H), 3.64 (s, 3H), 3.57 (s, 1H), 3.43 (s, 1H), 1.37 (s, 3H), 1.21 (t, \(J = 7.1\), 6H); \(^13\)C-NMR (125 MHz, CD\(_3\)COCD\(_3\)) \(\delta\) 172.8, 171.8, 171.5, 140.8, 136.3, 62.0 (2C), 55.3, 52.0, 51.5, 48.3, 17.6, 14.5 (2C).
Kinetic data

\[
\begin{array}{c|c}
\text{Time (min)} & \text{Conversion} \\
0 & 0 \\
2.2 & 0.085 \\
4.2 & 0.160 \\
6.3 & 0.230 \\
8.5 & 0.291 \\
10.8 & 0.372 \\
13.1 & 0.425 \\
15.4 & 0.471 \\
17.6 & 0.517 \\
19.9 & 0.568 \\
22.1 & 0.601 \\
24.4 & 0.639 \\
26.6 & 0.672 \\
28.9 & 0.705 \\
31.2 & 0.735 \\
42.5 & 0.848 \\
53.9 & 0.909 \\
65.2 & 0.947 \\
76.6 & 0.961 \\
130.8 & 1.000 \\
198.8 & 1.000 \\
206.4 & 1.000 \\
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\]

Calculated $t_{1/2} = 16.3$ min
### Table 1: Time and Conversion

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Calculated $t_{1/2} = 40.6$ min
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Calculated $t_{1/2} = 198.0$ min
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Calculated $t_{1/2} = 105.0$ min
\[
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50.4 & 0.274 \\
80.8 & 0.395 \\
111.2 & 0.496 \\
121.3 & 0.528 \\
141.6 & 0.583 \\
161.8 & 0.626 \\
182.1 & 0.670 \\
202.3 & 0.713 \\
222.6 & 0.746 \\
242.8 & 0.778 \\
253 & 0.783 \\
283.4 & 0.823 \\
364.4 & 0.892 \\
455.5 & 0.935 \\
\end{array}
\]

Calculated \( t_{1/2} = 113.6 \text{ min} \)
(1E,3E)-5,5-diethyl 1-methyl hexa-1,3-diene-1,5,5-tricarboxylate ((E,E)-7)

\[
\begin{align*}
&\text{\textsuperscript{1}H-NMR (500 MHz, CD\textsubscript{3}COCD\textsubscript{3}) } \delta 7.31 (dd, J = 15.4, 10.8, 1H), 6.61 (d, J = 15.8, 1H), 6.69 (dd, J = 15.8, J = 10.8, 1H), 6.02 (d, J = 15.4, 1H), 4.19 (q, J = 7.1, 4H), 3.69 (s, 3H), 1.56 (s, 3H), 1.23 (t, J = 7.1, 6H); \\
&\text{\textsuperscript{13}C-NMR (125 MHz, CD\textsubscript{3}COCD\textsubscript{3}) } \delta 170.8 (2C), 167.3, 144.6, 140.9, 129.6, 123.0, 62.4 (2C), 56.9, 51.8, 20.6, 14.4 (2C).
\end{align*}
\]

(1Z,3E)-5,5-diethyl 1-methyl hexa-1,3-diene-1,5,5-tricarboxylate ((Z,E)-7)

\[
\begin{align*}
&\text{\textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{2}CDCl\textsubscript{2}) } \delta 7.46 (dd, J = 15.8, J = 11.1, 1H), 6.64 (app. t, J = 11.3, 1H), 6.46 (d, J = 15.8, 1H), 5.73 (d, J = 11.3, 1H), 4.20 (q, J = 7.1, 4H), 3.71 (s, 3H), 1.62 (s, 3H), 1.25 (t, J = 7.1, 6H); \\
&\text{\textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{2}CDCl\textsubscript{2}) } \delta 170.4 (2C), 166.5, 143.8, 140.3, 126.9, 118.1, 62.0 (2C), 56.0, 51.4, 19.7, 14.0 (2C).
\end{align*}
\]

diethyl 2-((1E,3E)-5-(benzylamino)-5-oxopenta-1,3-dienyl)-2-methylmalonate ((E,E)-9)

\[
\begin{align*}
&\text{\textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{2}CDCl\textsubscript{2}) } \delta 7.36-7.33 (m, 2H), 7.31-7.27 (m, 3H), 7.25 (dd, J = 15.0, 10.9, 1H), 6.48 (d, J = 15.7, 1H), 6.23 (dd, J = 15.7, J = 10.9, 1H), 5.91 (d, J = 15.0, 1H), 5.86 (t, J = 5.7, 1H), 4.50 (d, J = 5.7, 2H), 4.19 (q, J = 7.1, 4H), 1.58 (s, 3H), 1.25 (t, J = 7.1, 6H); \\
&\text{\textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{2}CDCl\textsubscript{2}) } \delta 170.3 (2C), 165.3, 140.2, 138.3, 138.0, 128.7 (2C), 128.5, 127.6 (2C), 127.5, 124.5, 62.0 (2C), 55.8, 43.5, 19.9, 14.0 (2C).
\end{align*}
\]
diethyl 2-((1E,3Z)-5-(benzylamino)-5-oxopenta-1,3-dienyl)-2-methylmalonate ((Z,E)-9)

$^1$H-NMR (500 MHz, CD$_3$COCD$_3$) \( \delta \) 7.86 (dd, \( J = 16.0, J = 11.0 \), 1H), 7.71 (br s, 1H), 7.31 (app.d, \( J = 4.3 \), 1H), 7.23 (m, 1H), 6.51 (dd, \( J = 11.2, J = 11.0 \), 1H), 6.36 (d, \( J = 16.0 \), 1H), 5.88 (d, \( J = 11.2 \), 1H), 4.43 (d, \( J = 6.0 \), 2H), 4.19 (q, \( J = 7.1 \), 4H), 1.55 (s, 3H), 1.23 (t, \( J = 7.1 \), 6H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) \( \delta \) 171.1 (2C), 166.3, 140.5, 138.9, 129.3 (2C), 128.6, 128.6 (2C), 127.8, 122.9, 119.5, 62.3 (2C), 56.8, 43.4, 20.8, 14.3 (2C).
5. Comparison of $^1$H-NMR data for dienes

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<th>$\delta$(H$_4$) (ppm)</th>
<th>$\delta$(H$_5$) (ppm)</th>
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6. Domino electrocyclic ring opening / Diels-Alder cycloaddition

Cycloadduct 10

A microwave tube containing trans-6 (70.8 mg, 0.25 mmol, 1 equiv.), o-xylene (2.5 mL) and N-phenylmaleimide (215.6 mg, 1.25 mmol, 5 equiv.) was purged with Ar and heated at 220 °C for 6 hours in a microwave oven (200 W). The solvent was removed under vacuum and the product was purified by column chromatography (pentane/EtOAc: 75/25) to afford cycloadduct 10 (87 mg, 76%). FTIR (neat) v_{max} 3063, 2985, 2953, 1709, 1500, 1384, 1185, 1105, 1019, 733, 699;\(^1\)H-NMR (600 MHz, CD$_3$COCD$_3$) δ 7.45-7.41 (m, H$_{21, 23}$), 7.36 (m, H$_{22}$), 7.29-7.25 (m, H$_{20, 24}$), 6.34 (dt, J = 9.7, J = 3.1, H$_5$), 6.30 (dt, J = 9.7, J = 3.1, H$_4$), 4.19 (q, J = 7.1, 2H$_{17}$), 4.15 (ddd, J = 9.1, J = 4.9, J = 0.7, H$_7$), 4.12-4.02 (m, 2H$_{14}$), 3.80 (ddd, J = 8.9, J = 8.2, J = 0.5, H$_2$), 3.76 (s, 3H$_{10}$), 3.36 (m, H$_6$), 3.01 (m, H$_3$), 1.82 (s, 3H$_{12}$), 1.22 (t, J = 7.1, 3H$_{18}$), 1.20 (t, J = 7.1, 3H$_{18}$);\(^{13}\)C-NMR (150 MHz, CD$_3$COCD$_3$) δ 177.1 (C$_1$), 177.0 (C$_8$), 173.0 (C$_{16}$), 171.7 (C$_9$), 171.1 (C$_{13}$), 133.5 (C$_{19}$), 131.7 (C$_4$), 129.4 (C$_{21}$, C$_{23}$), 128.9 (C$_{22}$), 127.8 (C$_{20}$, C$_{24}$), 125.9 (C$_5$), 62.4 (C$_{17}$), 61.3 (C$_{14}$), 55.3 (C$_{11}$), 52.2 (C$_{10}$), 45.5 (C$_7$), 44.2 (C$_3$), 41.0 (C$_2$), 39.7 (C$_6$), 20.5 (C$_{12}$), 14.2 (C$_{15}$), 14.2 (C$_{18}$); HRMS exact mass calculated for [M+Na]$^+$ (C$_{24}$H$_{27}$NO$_8$Na) requires m/z 480.1629, found m/z 480.1635.

The relative stereochemistry of compound 10 was determined by analogy with compound A synthesized in an analogous way starting from sorbic acid methyl ester (o-xylene, 5 equiv. and N-phenylmaleimide, 2 hours, 220 °C, 82% yield). In particular the almost identical diagnostic coupling constant of protons 2 and 7 in compound 10 and A as well as similar NOE effects clearly indicate that these two compounds have the same relative stereochemistry. The structure of A was unambiguously determined by single-crystal X-ray analysis (see below).
Following the same procedure, compound A was isolated in 79% yield. FTIR (neat) $\nu_{\text{max}}$ 2993, 1725, 1701, 1198, 1053, 759, 716, 706, 695, 685; $^1$H-NMR (600 MHz, CDCl$_3$) $\delta$ 7.44-7.39 (m, H$_{21}$, H$_{23}$), 7.35 (m, H$_{22}$), 7.20-7.19 (m, H$_{20}$, H$_{24}$), 6.45 (dt, $J = 9.4$, $J = 3.3$, H$_5$), 5.85 (dt, $J = 9.4$, $J = 3.3$, H$_4$), 3.88 (dd, $J = 8.9$, $J = 5.8$, H$_7$), 3.83 (s, 3H$_{10}$), 3.28 (dd, $J = 8.9$, $J = 7.5$, H$_3$), 3.21 (m, H$_6$), 2.51 (m, H$_3$), 1.47 (d, $J = 7.4$, 3H$_{11}$); $^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$ 176.3 (C$_1$), 175.9 (C$_8$), 171.2 (C$_9$), 134.8 (C$_4$), 131.6 (C$_{19}$), 129.2 (C$_{21}$, C$_{23}$), 128.8 (C$_{22}$), 126.5 (C$_5$, C$_{20}$, C$_{24}$), 52.5 (C$_{10}$), 44.0 (C$_2$), 43.9 (C$_7$), 40.6 (C$_6$), 31.7 (C$_3$), 16.8 (C$_{11}$); HRMS exact mass calculated for [M+Na]$^+$ (C$_{17}$H$_{17}$NO$_4$Na) requires $m/z$ 322.1050, found $m/z$ 322.1050.

Crystal structure analysis of compound A crystallized from CH$_2$Cl$_2$/Heptane
(Cambridge Crystallographic Data Centre number: 866301).
Synthesis of the cyclobutenes starting material for intramolecular domino electrocyclic ring opening / Diels-Alder cycloaddition

Compound \textit{trans-11a} and \textit{trans-11b} were synthesized according to literature procedure. \[^3\]

\textbf{4-(1-ethoxy-2-(ethoxycarbonyl)-1-oxohex-5-en-2-yl)cyclobut-2-ene carboxylic acid (\textit{trans-11a})}

\begin{center}
\includegraphics[width=0.2\textwidth]{trans-11a.png}
\end{center}

Compound \textit{trans–11a} was obtained in 66\% isolated yield. FTIR (neat) ν\textsubscript{max} 2983, 1727, 1373, 1238, 1045, 915, 719; \(^1\)H-NMR (300 MHz, CD\textsubscript{3}COCD\textsubscript{3}) δ 6.28 (dt, \(J = 2.8, J = 1.1\), 1H), 6.12 (dt, \(J = 2.8, J = 0.9\), 1H), 5.81 (m, 1H), 5.03 (m, 1H), 4.95 (m, 1H), 4.24-4.14 (m, 4H), 3.66 (m, 1H), 3.54 (m, 1H), 2.16-1.95 (m, 4H), 1.25 (t, \(J = 7.1\), 3H), 1.24 (t, \(J = 7.1\), 3H); \(^{13}\)C-NMR (75 MHz, CD\textsubscript{3}COCD\textsubscript{3}) δ 173.2, 171.0, 170.8, 141.1, 138.7, 135.6, 115.4, 61.8, 61.8, 59.6, 49.4, 48.4, 32.7, 29.5, 14.4, 14.4; HRMS exact mass calculated for [M+Na]\(^+\) (C\textsubscript{16}H\textsubscript{22}O\textsubscript{6}Na) requires \(m/z\) 333.1308, found \(m/z\) 333.1308.

\textbf{4-(1-ethoxy-2-(ethoxycarbonyl)-1-oxohept-6-en-2-yl)cyclobut-2-ene carboxylic acid (\textit{trans-11b})}

\begin{center}
\includegraphics[width=0.2\textwidth]{trans-11b.png}
\end{center}

Compound \textit{trans–11b} was obtained in 70\% isolated yield. FTIR (neat) ν\textsubscript{max} 2982, 1726, 1371, 1238, 1045, 914, 718; \(^1\)H-NMR (300 MHz, CD\textsubscript{3}COCD\textsubscript{3}) δ 6.26 (dt, \(J = 2.8, J = 1.1\), 1H), 6.10 (dt, \(J = 2.8, J = 0.9\), 1H), 5.78 (m, 1H), 5.00 (m, 1H), 4.93 (m, 1H), 4.22-4.12 (m, 4H), 3.63 (m, 1H), 3.52 (m, 1H), 2.09-2.01 (m, 2H), 1.99-1.87 (m, 2H), 1.44 (m, 1H), 1.31 (m, 1H), 1.23 (t, \(J = 7.1\), 3H), 1.22 (t, \(J = 7.1\), 3H); \(^{13}\)C-NMR (75 MHz, CD\textsubscript{3}COCD\textsubscript{3}) δ 173.2, 171.2,
170.9, 141.2, 139.1, 135.5, 115.3, 61.7, 61.7, 59.8, 49.4, 48.4, 34.6, 32.7, 24.5, 14.4, 14.4; HRMS exact mass calculated for [M+Na]$^+$ (C$_{17}$H$_{24}$O$_6$Na) requires $m/z$ 347.1471, found $m/z$ 347.1433.

Intramolecular domino electrocyclic ring opening / Diels-Alder cycloaddition

**Cycloadduct 13a/13a***

A microwave tube containing *trans-11a* (81.5 mg, 0.26 mmol) and toluene (5.2 mL) was purged with Ar and heated at 180 °C for 2 hours in a microwave oven (200 W). The solvent was removed under vacuum and the product was purified by column chromatography (toluene/EtOAc/CH$_3$COOH: 80/20/0.5) to afford the desired cycloadduct **13a** in 63% yield as a whitish solid (57/43* mixture of diastereoisomers). FTIR (neat) $\nu_{\text{max}}$ 2982, 2934, 2872, 1720, 1695, 1252, 1231, 1094, 1014, 912, 723; $^1$H-NMR (600 MHz, C$_6$D$_6$) $\delta$ 6.05 (dt, $J = 10.0, J = 2.0, 1H$), 5.89 (tt, $J = 10.2, J = 2.3, J = 1.0, 1H$), 5.79 (ddd, $J = 10.2, J = 4.1, J = 2.8, 1H$), 5.74 (dddd, $J = 10.2, J = 4.4, J = 3.0, J = 1.1, 1H$), 4.22-4.05 (m, 4H, 4H*), 3.25 (m, 1H), 3.19 (m, 1H*), 3.00 (m, 1H), 2.55 (m, 1H), 2.49 (dt, $J = 14.0, J = 8.6, 1H$), 2.45 (m, 1H*), 2.34 (m, 1H*), 2.33 (m, 1H), 2.02 (ddd, $J = 14.0, J = 10.4, J = 2.5, 1H$), 1.95-1.80 (m, 3H, 2H*), 1.63 (m, 1H), 1.48 (dt, $J = 12.6, J = 7.0, 1H$), 1.45 (dt, $J = 12.8, J = 11.2, 1H$), 1.26 (m, 1H*), 1.19 (t, $J = 7.1, 3H$), 1.18 (t, $J = 7.1, 3H$), 1.16 (t, $J = 7.1, 3H$), 1.14 (t, $J = 7.1, 3H$); $^{13}$C-NMR (150 MHz, CD$_3$COCD$_3$) $\delta$ 175.1, 174.7, 172.5, 172.4, 171.4, 171.3, 130.1, 127.9, 127.8, 126.4, 64.3, 61.8, 61.6, 61.6, 61.5, 61.1, 50.6, 44.9, 41.8, 41.7, 38.3, 37.5, 34.1, 32.9, 31.0, 30.2, 29.1, 14.4, 14.3, 14.3, 14.3; HRMS exact mass calculated for [M+Na]$^+$ (C$_{16}$H$_{22}$O$_6$Na) requires $m/z$ 333.1308, found $m/z$ 333.1306.
Cycloadduct 13b

A microwave tube containing trans-11b (56.5 mg, 0.17 mmol) and toluene (3.5 mL) was purged with Ar and heated at 180 °C for 2 hours in a microwave oven (200 W). The solvent was removed under vacuum and the product was purified by column chromatography (toluene/EtOAc/CH₃COOH: 90/10/0.5) to afford the desired cycloadduct 13b (43.3 mg, 77% contaminated with 10% of an unidentified by-product). This material was crystallized from pentane to afford pure compound 13b as a white solid (33.7 mg, 60%, single diastereisomer). FTIR (neat) ν max 2978, 2934, 1723, 1696, 1446, 1249, 1016, 921, 764; ¹H-NMR (600 MHz, C₆D₆) δ 5.97 (dddd, J = 10.4, J = 4.0, J = 3.0, J = 1.3, 1H), 5.57 (d, J = 10.4, 1H), 3.98-3.89 (m, 4H), 3.40 (m, 1H), 2.65 (m, 1H), 2.42 (m, 1H), 2.35-2.30 (m, 2H), 1.87 (td, J = 13.7, J = 3.5, 1H), 1.72 (dddd, J = 14.3, J = 8.6, J = 3.8, 1H), 1.44 (dt, J = 13.5, J = 3.6, 1H), 1.35 (qd, J = 12.6, J = 3.6, 1H), 1.31 (m, 1H), 1.07 (m, 1H), 0.89 (t, J = 7.1, 3H), 0.87 (t, J = 7.1, 3H); ¹³C-NMR (150 MHz, C₆D₆) δ 180.9, 170.8, 170.6, 128.3, 126.0, 61.2, 61.0, 59.0, 39.4, 37.9, 30.6, 29.0, 27.6, 25.8, 22.5, 14.0, 14.0; HRMS: exact mass calculated for [M+Na]+ (C₁₇H₂₄O₆Na) requires m/z 347.1471, found m/z 347.1433. The structure of 13b was confirmed by single-crystal X-ray analysis (see below).

Crystal structure analysis of compound 13b crystallized from CH₂Cl₂/Heptanes (Cambridge Crystallographic Data Centre number: 866302).
7. Diels-Alder reactions of push-pull aryloxy-dienes

**General procedure for methyl ester formation:**

![Diagram of chemical reaction](image)

An ethereal solution of diazomethane\(^5\) was added dropwise to a stirred solution of crude acid 2 in THF until complete consumption of the starting material was observed by TLC. Excess CH\(_2\)N\(_2\) was quenched by addition of a few drops of acetic acid and the solvent was removed under vacuum. The product was then purified by column chromatography (pentane/EtOAc: 95/5) to afford the methyl esters 14.

**(2Z,4E)-methyl 5-(4-methoxyphenoxy)penta-2,4-dienoate (14a)**

![Compound 14a](image)

Compound 14a was obtained as a colourless oil in 50% yield. \(^1\)H-NMR (300 MHz, CD\(_3\)COCD\(_3\)) \(\delta\) 7.34 (d, \(J = 12.0, 1H\)), 7.21 (td, \(J = 11.7, J = 0.9, 1H\)), 7.08 (d, \(J = 9.2, 2H\)), 6.95 (d, \(J = 9.2, 2H\)), 6.75 (app. t, \(J = 11.7, 1H\)), 5.53 (d, \(J = 11.2, 1H\)), 3.79 (s, 3H), 3.65 (s, 3H); \(^13\)C-NMR (75 MHz, CD\(_3\)COCD\(_3\)) \(\delta\) 167.3, 157.0, 142.9, 119.5 (2C), 118.4, 115.8 (2C), 115.5, 114.0, 109.7, 56.0, 51.0; FTIR (neat) \(\nu_{\text{max}}\) 3076, 2942, 2838, 1702, 1634, 1504, 1439, 1164, 1130, 833; HRMS (DE) exact mass calculated for [M+H]\(^+\) (C\(_{13}\)H\(_{15}\)O\(_4\)) requires \(m/z\) 235.0968, found \(m/z\) 235.0970.

(2Z,4E)-methyl 5-(p-tolyloxy)penta-2,4-dienoate (14b)

Compound 14b was obtained as a colourless oil in 50% yield. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.40 (d, $J = 12.0$, 1H), 7.26 (app. td, $J = 11.7$, $J = 1.0$, 1H), 7.21 (d, $J = 8.3$, 2H), 7.03 (d, $J = 8.3$, 2H), 6.77 (app. t, $J = 11.7$, 1H), 5.55 (d, $J = 11.4$, 1H), 3.65 (s, 3H), 2.31 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 167.6, 156.2, 143.0, 134.7, 131.4 (2C), 118.1 (2C), 117.1, 114.4, 110.3, 51.1, 20.7; FTIR (neat) $\nu_{max}$ 2945, 1701, 1636, 1604, 1501, 1440, 1221, 1162, 926; HRMS (ESI) exact mass calculated for [M+Na]$^+$ (C$_{13}$H$_{15}$O$_3$Na) requires $m/z$ 241.0831, found $m/z$ 241.0835.

General procedure for Diels-Alder reactions of 4-aryloxy-dienyl methyl esters:

Diene methyl ester 14 (0.07 mmol) and N-Phenyl maleimide (0.36 mmol, 5.0 equiv.) in toluene (2 mL) were heated under reflux for 24h. Solvents were removed under vacuum and the product was purified by column chromatography on silica gel (pentane/EtOAc: 9/1) to afford cycloadduct 15.
methyl-7-(4-methoxyphenoxy)-1,3-dioxo-2-phenyl-2,3,3a,4,7,7a-hexahydro-1H-isooindole-4-carboxylate (15a)

Compound 15a (single diastereoisomer) was obtained as a pale yellow oil in 98% yield. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.50-7.37 (m, H$_{21}$, H$_{23}$), 7.44-7.37 (m, H$_{22}$), 7.32 (d, $J$ = 7.7, H$_{20}$, H$_{24}$), 6.90 (d, $J$ = 8.9, H$_{12}$, H$_{16}$), 6.83 (d, $J$ = 8.9, H$_{13}$, H$_{15}$), 6.51 (m, H$_4$), 6.20 (dd, $J$ = 9.5, 1.9, H$_3$), 5.27 (t, $J$ = 4.6, H$_3$), 4.09 (dd, $J$ = 9.8, $J$ = 6.8, H$_2$), 3.80 (s, 3H$_{10}$), 3.75 (m, H$_6$), 3.74 (s, 3H$_{17}$), 3.45 (dd, $J$ = 10.2, 3.7, H$_2$); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 179.0 (C$_8$), 175.9 (C$_{1}$), 173.8 (C$_9$), 155.8 (C$_{14}$), 152.0 (C$_{11}$), 133.9 (C$_8$), 132.1 (C$_3$), 129.9 (C$_4$), 129.8 (C$_{21}$, C$_{23}$), 129.1 (C$_{22}$), 127.9 (C$_{20}$, C$_{24}$), 118.2 (C$_{12}$, C$_{16}$), 115.5 (C$_{13}$, C$_{15}$), 70.3 (C$_3$), 55.9 (C$_{17}$), 53.1 (C$_{10}$), 45.4 (C$_2$), 41.1 (C$_6$), 39.7 (C$_7$). MS (EI) $m/z$ (%) = 252 (35), 124 (100), 119 (39); FTIR (neat) $\nu_{\text{max}}$ 2954, 1710, 1504, 1383, 1196, 1212, 1172, 1030, 822, 753, 691; HRMS (ESI) exact mass calculated for [M+Na]$^+$ (C$_{23}$H$_{21}$NO$_6$Na) requires $m/z$ 430.1263, found $m/z$ 430.1261.

methyl-1,3-dioxo-2-phenyl-7-(p-tolyloxy)-2,3,3a,4,7,7a-hexahydro-1H-isooindole-4-carboxylate (15b)

Compound 15b (dr = 85:15) was obtained as a pale yellow oil in 80%. Data for major isomer: $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.50-7.36 (m, 3H), 7.33-7.31 (m, 2H), 7.07 (d, $J$ 8.2, 2H), 6.85 (d, $J$ 8.8, 2H), 6.55 (qd, $J$ 5.3, 3.7, 1H), 6.19 (dd, $J$ 9.6, 2.6, 1H), 5.34 (dd, $J$ 6.0, 4.1,
1H), 4.10 (dd, J = 10.8, J = 6.9, 1H), 3.80 (s, 3H), 3.72 (m, 1H), 3.46 (dd, J = 10.8, J = 4.1, 1H), 2.23 (s, 3H); 13C-NMR (125 MHz, CD3COCD3) δ 178.9, 175.8, 173.7, 155.8, 133.9, 132.1, 131.6, 130.8 (2C), 129.9, 129.8 (2C), 129.1, 127.8 (2C), 116.6 (2C), 69.5, 53.1, 45.3, 41.1, 39.7, 20.6; FTIR (neat) νmax 3029, 2953, 1710, 1499, 1507, 1382, 1224, 1173; HRMS (ESI) exact mass calculated for [M+Na]+ (C23H21NO5Na) requires m/z 414.1310, found m/z 414.1312.

8. Intramecular Diels-Alder reactions of 4-aryloxy-dienyl methyl esters

Preparation of O-allyl-phenol

o-allyl phenol and 2-allyl-6-methoxyphenol were purchased from Aldrich. Methyl 3-allyl-4-hydroxybenzoate, 2-allyl-3,5-dimethoxyphenol and (3-allyl-4-hydroxyphenyl)(phenyl) methanone were synthesized according to the scheme below:

General procedure for O-allylation of phenols:

The desired phenol (1 equiv.) was dissolved in acetone (0.2 M), K2CO3 (2 equiv.) and allyl bromide (1.2 equiv.) were added. The resulting mixture was heated at reflux until complete consumption of the starting material was detected by TLC (3 – 24 hours). The reaction mixture was allowed to cool to room temperature and the solid was filtered off. The solvent was removed under vacuum to afford a crude residue which was used in the next step without further purification.

General procedure for Claisen rearrangement:

The desired O-allyl phenol was poured in a microwave tube, purged with Ar and heated in a microwave oven (200 W) at 200 °C. The product was purified by column chromatography or crystallized to afford the O-allyl phenols.
methyl 3-allyl-4-hydroxybenzoate

![Methyl 3-allyl-4-hydroxybenzoate](image)

The reaction was stopped after 10h, although the starting material was not completely consumed. The product was purified by crystallization from pentane to afford methyl 3-allyl-4-hydroxybenzoate (65% yield).  

2-allyl-3,5-dimethoxyphenol

![2-allyl-3,5-dimethoxyphenol](image)

The reaction was stopped after 5h and the product was purified by column chromatography (pentane/EtOAc: 97/3 to 95/5) to afford 2-allyl-3,5-dimethoxyphenol (76% yield). $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 8.11 (s, 1H), 6.11 (d, $J = 2.2$, 1H), 6.09 (d, $J = 2.2$, 1H), 5.88 (m, 1H), 4.93 (d, $J = 16.6$, 1H), 4.83 (d, $J = 9.9$, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.30 (d, $J = 6.4$, 2H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 160.4, 160.1, 157.0, 138.2, 113.8, 107.6, 94.5, 90.9, 55.8, 55.3, 27.6.

(3-allyl-4-hydroxyphenyl)(phenyl)methanone

![3-allyl-4-hydroxyphenyl)(phenyl)methanone](image)

The reaction was stopped after 20h, although the starting material was not completely consumed. The product was purified by column chromatography (pentane/EtOAc: 9/1) to afford (3-allyl-4-hydroxyphenyl)(phenyl)methanone (62% yield). $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 155.4, 155.2, 153.8, 152.0, 108.9, 106.5, 106.1, 89.4, 82.6, 73.1, 70.7, 33.3, 27.9.

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CD$_3$COCD$_3$) $\delta$ 9.25 (br s, 1H), 7.73-7.71 (m, 2H), 7.66 (d, $J = 2.2$, 1H), 7.61 (ddd, $J = 7.4$, $J = 6.6$, $J = 2.0$, 1H), 7.56 (dd, $J = 8.2$, $J = 2.2$, 1H), 7.54-7.51 (m, 2H), 6.98 (d, $J = 8.2$, 1H), 6.03 (m, 1H), 5.09 (d, $J = 17.3$, 1H), 5.03 (d, $J = 10.0$, 1H), 3.44 (d, $J = 6.7$, 2H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 195.3, 160.3, 139.6, 137.3, 133.3, 132.5, 131.4, 130.2 (2C), 130.1, 129.1 (2C), 127.6, 116.1, 115.4, 34.8.

**Preparation of dienes 2r-v**

Dienes 2r-v were synthesized according to the general procedure reported at page S5. After work-up the crude material was carried to the next step without any further purification. The $^1$H-NMR internal standard yields (internal standard = 1,3,5-trimethoxybenzene) are listed below:

Crude carboxylic acid 2 was dissolved in dichloromethane (0.1 M) and the resulting solution was cooled to 0 °C. DMF (1 drop) followed by oxalyl chloride (2 equiv. assuming a quantitative yield of formation of the carboxylic acids 2r-v in the Tsuji-Trost reaction) were added dropwise and the resulting mixture was stirred for 30 min at 0 °C. MeOH (25 equiv.) was added dropwise and after 30 min at 0 °C, the reaction mixture was quenched with a saturated solution of NaHCO$_3$ and diluted with CH$_2$Cl$_2$. The layers were separated and the aqueous phase was extracted 3 times with CH$_2$Cl$_2$. The combined organic layers were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under vacuum and the product was purified by column chromatography (pentane/EtOAc: 98/2) to give ester 16a-e.
(2Z,4E)-methyl 5-(2-allylphenoxy)penta-2,4-dienoate (16a)

![16a](image)

Compound 16a was obtained in 33% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.37 (d, $J = 12.1$, 1H), 7.32-7.22 (m, 3H), 7.18-7.10 (m, 2H), 6.78 (app. t, $J = 11.5$, 1H), 5.97 (m, 1H), 5.56 (d, $J = 11.2$, 1H), 5.05 (d, $J = 16.5$, 1H), 5.03 (d, $J = 9.2$, 1H), 3.65 (s, 3H), 3.41 (d, $J = 6.5$, 2H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 167.4, 156.5, 155.0, 142.7, 137.3, 131.4, 131.1, 128.7, 125.4, 118.1, 116.2, 114.2, 110.1, 51.0, 34.7; FTIR (neat) $\nu_{\text{max}}$ 1708, 1635, 1488, 1439, 1165, 1146, 930; HRMS exact mass calculated for [M+Na]$^+$ (C$_{15}$H$_{16}$O$_3$Na) requires $m/z$ 267.0992, found $m/z$ 267.0989.

methyl 3-allyl-4-(((1E,3Z)-5-methoxy-5-oxopenta-1,3-dien-1-yl)oxy)benzoate (16b)

![16b](image)

Compound 16b was obtained in 46% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.95-7.90 (m, 2H), 7.49 (d, $J = 12.0$, 1H), 7.37 (app. t, $J = 11.7$, 1H), 7.25 (d, $J = 8.4$, 1H), 6.81 (app. t, $J = 11.7$, 1H), 5.99 (m, 1H), 5.62 (d, $J = 11.2$, 1H), 5.10 (d, $J = 15.9$, 1H), 5.08 (d, $J = 8.7$, 1H), 3.86 (s, 3H), 3.67 (s, 3H), 3.48 (d, $J = 6.7$, 2H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 167.3, 166.5, 158.5, 154.4, 142.0, 136.7, 132.6, 131.0, 130.4, 126.8, 116.8, 116.7, 115.4, 111.6, 52.3, 51.1, 34.5; FTIR (neat) $\nu_{\text{max}}$ 1710, 1638, 1604, 1437, 1165, 1140; HRMS exact mass calculated for [M+Na]$^+$ (C$_{17}$H$_{18}$O$_5$Na) requires $m/z$ 325.1046, found $m/z$ 325.1047.
(2Z,4E)-methyl 5-(2-allyl-3,5-dimethoxyphenoxy)penta-2,4-dienoate (16c)

Compound 16c was obtained in 43% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.33 (d, $J = 12.2$, 1H), 7.25 (app. t, $J = 11.9$, 1H), 6.75 (app. t, $J = 11.9$, 1H), 6.42 (d, $J = 2.2$, 1H), 6.35 (d, $J = 2.2$, 1H), 5.86 (m, 1H), 5.55 (d, $J = 11.2$, 1H), 4.91 (d, $J = 17.1$, 1H), 4.88 (d, $J = 9.9$, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.65 (s, 3H), 3.30 (d, $J = 6.2$, 2H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 167.4, 160.8, 160.0, 156.5, 156.2, 142.8, 137.4, 114.7, 114.1, 111.4, 110.0, 96.1, 95.5, 56.2, 55.8, 51.0, 27.7; FTIR (neat) $\nu_{\text{max}}$ 1709, 1581, 1438, 1416, 1145, 993, 932, 816; HRMS exact mass calculated for [M+Na]$^+$ (C$_{17}$H$_{20}$O$_5$Na) requires m/z 327.1208, found m/z 327.1211.

(2Z,4E)-methyl 5-(2-allyl-6-methoxyphenoxy)penta-2,4-dienoate (16d)

Compound 16d was obtained in 44% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.19-7.13 (m, 2H), 7.04-6.97 (m, 2H), 6.86 (d, $J = 7.9$, 1H), 6.69 (app. t, $J = 11.5$, 1H), 5.93 (m, 1H), 5.47 (d, $J = 11.2$, 1H), 5.05 (d, $J = 18.7$, 1H), 5.01 (d, $J = 11.8$, 1H), 3.82 (s, 3H), 3.61 (s, 3H), 3.34 (d, $J = 6.6$, 2H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 167.5, 159.6, 152.4, 143.3, 143.2, 137.2, 134.0, 126.9, 122.7, 116.3, 113.0, 112.0, 107.3, 56.3, 50.9, 34.6; FTIR (neat) $\nu_{\text{max}}$ 1708, 1632, 1476, 1439, 1274, 1162, 994, 928, 815, 757; HRMS exact mass calculated for [M+Na]$^+$ (C$_{16}$H$_{18}$O$_5$Na) requires m/z 297.1097, found m/z 297.1099.
(2Z,4E)-methyl 5-(2-allyl-6-methoxyphenoxy)penta-2,4-dienoate (16e)

Compound 16e was obtained in 65% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.77-7.75 (m, 3H), 7.73 (dd, $J = 8.2$, 2.2, 1H), 7.66 (m, 1H), 7.57-7.52 (m, 3H), 7.41 (dd, $J = 12.0$, 1.0, 1H), 7.30 (d, $J = 8.4$, 1H), 6.83 (app. t, $J = 11.6$, 1H), 6.01 (m, 1H), 5.63 (d, $J = 11.2$, 1H), 5.13-5.06 (m, 2H), 3.68 (s, 3H), 3.51 (d, $J = 6.6$, 2H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 195.4, 167.5, 158.3, 154.6, 142.2, 138.8, 136.7, 134.3, 133.3, 132.9 (2C), 131.2, 131.1, 130.5 (2C), 129.3 (2C), 119.9, 115.5, 111.8, 34.8. FTIR (neat) $\nu_{max}$ 3080, 2949, 1637, 1192, 1162, 1135;

**General procedure for intramolecular Diels-Alder reaction**

A microwave tube containing diene 16a-e and toluene (0.1 M) was purged with Ar and heated at 180 °C for 20 hours in a microwave oven (200 W). The solvent was removed under vacuum and the product was purified by column chromatography. All intramolecular Diels-Alder reactions described in this section were performed on a 0.5 mmol scale.

**Cycloadducts 17a/17a***

Some unreacted diene was observed in the $^1$H-NMR of the crude reaction mixture. The product was purified by column chromatography (pentane/EtOAc from 98/2 to 95/5) to afford cycloadducts 17a/17a* (79/21* mixture of diastereomers, 52%). The product was obtained in 60% isolated yield based on the recovered starting material. $^1$H-NMR (600 MHz, CDCl$_3$) $\delta$ 7.13-7.03 (m, 2H, 2H*), 6.89-6.83 (m, 2H, 1H*), 6.81 (d, $J = 8.2$, 1H*), 6.10 (ddd, $J = 10.0$, $J = 4.3$, $J = 2.2$, 1H*), 6.04 (dd, $J = 10.0$, $J = 4.1$, 1H*), 6.01 (dm, $J = 10.2$, 1H), 5.96 (dm, $J = 10.2$, 1H), 4.53 (t, $J = 3.9$, 1H*), 4.27 (dm, $J = 9.6$, 1H), 3.74 (s, 3H), 3.73 (s, 3H*), 3.39 (m, 1H), 3.30 (m, 1H*), 3.02 (dd, $J = 16.6$, $J = 6.6$, 1H*), 2.78 (dd, $J = 16.0$, $J = 4.9$, 1H),
2.64 (dd, $J = 16.0, J = 12.0, 1H$), 2.62 (dd, $J = 16.5, J = 4.4, 1H^*$), 2.40 (m, 1H*), 2.26 (dddd, $J = 13.4, J = 5.7, J = 2.9, J = 1.3, 1H$), 2.03-1.94 (m, 1H, 2H*), 1.68 (dt, $J = 13.1, J = 11.5, 1H$); $^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$ 173.9, 173.8*, 155.1, 153.4*, 129.9, 129.8*, 129.5, 129.2*, 128.7*, 127.5, 127.3*, 127.2, 122.3, 120.7, 120.5*, 120.4*, 117.0, 116.6*, 76.0, 69.8, 52.3 (1C+1C*), 42.5, 40.2*, 34.2, 32.1, 29.9, 28.8*, 28.4*, 25.9*; FTIR (neat) $\nu_{\text{max}}$ 1736, 1579, 1488, 1454, 1440, 1236, 1176, 1051, 931; HRMS exact mass calculated for [M+Na]$^+$ (C$_{15}$H$_{16}$O$_3$Na) requires $m/z$ 267.0992, found $m/z$ 267.0990.

A mixture of diastereomers 17a and 17a* was repetedly purified by column chromatography and crystallization to yield an analytically pure sample of the main diastereomer 17a. Crystals suitable for X-ray crystallographic analysis were prepared by crystallization from dichloromethane/heptane.

Crystal structure analysis of the major isomer 17a crystallized from CH$_2$Cl$_2$/Heptanes (Cambridge Crystallographic Data Centre number: 887606).
Cycloadducts 17b/17b*

Some unreacted diene was observed in the $^1$H-NMR of the crude reaction mixture. The product was purified by column chromatography (toluene/EtOAc from 98/2 to 95/5) to afford cycloadducts 17b/17b* (78/22* mixture of diastereomers, 42%). The product was obtained in 54% isolated yield based on the recovered starting material. $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.81-7.75 (m, 2H, 2H*), 6.85 (d, $J = 8.7$, 1H), 6.80 (d, $J = 9.1$, 1H*), 6.10-6.03 (m, 2H*), 6.03-5.95 (m, 2H), 4.61 (m, 1H*), 4.32 (dm, $J = 9.8$, 1H), 3.87 (s, 3H), 3.86 (s, 3H*), 3.74 (s, 3H), 3.73 (s, 3H*), 3.38 (m, 1H), 3.29 (m, 1H*), 3.02 (dd, $J = 16.7$, $J = 6.5$, 1H*), 2.81 (dd, $J = 16.1$, $J = 4.9$, 1H), 2.64 (dd, $J = 16.4$, $J = 12.2$, 1H, 1H*), 2.43 (m, 1H*), 2.29 (m, 1H), 2.03-1.87 (m, 1H, 2H*), 1.69 (app q, $J = 12.0$ 1H); $^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta$ 173.7, 173.6*, 167.1*, 167.0, 159.2, 157.6*, 132.0, 131.9*, 129.4, 129.0, 128.9*, 128.7*, 127.6 (1C+1C*), 122.5, 122.3*, 122.2, 120.1*, 117.0, 116.5*, 76.7, 70.6*, 52.3 (1C+1C*), 52.0, 51.0*, 42.4, 40.1*, 34.0, 31.9, 29.8, 28.6*, 28.1*, 25.7*; FTIR (neat) $\nu_{\text{max}}$ 2957, 2924, 1729, 1707, 1613, 1578, 1494, 1437, 1319, 1161, 1094, 1034, 837, 767, 699; HRMS exact mass calculated for [M+Na]$^+$ (C$_{17}$H$_{18}$O$_5$Na) requires $m/z$ 325.1046, found $m/z$ 325.1044.

Cycloadducts 17c/17c*

The product was purified by column chromatography (toluene/EtOAc from 98/2 to 95/5) to afford cycloadducts 17c/17c* (78/22* mixture of diastereomers, 65%). $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 6.10 (d, $J = 2.2$, 1H), 6.07 (d, $J = 2.2$, 1H*), 6.00 (d, $J = 2.2$, 1H), 5.98-5.94 (m, 3H*), 5.94-5.88 (m, 2H), 4.48 (m, 1H*), 4.15 (dd, $J = 9.6$, $J = 3.3$, 1H), 3.78 (s, 3H), 3.77 (s, 3H*), 3.72 (s, 3H), 3.71 (s, 3H*), 3.69 (s, 3H), 3.68 (s, 3H*), 3.41 (m, 1H), 3.33 (m, 1H*), 2.71 (dd, $J = 16.4$, $J = 5.2$, 1H), 2.69 (m, 1H*), 2.38 (dd, $J = 16.7$, $J = 5.3$, 1H*), 2.31 (m, 1H*), 2.23 (dddd, $J = 13.2$, $J = 5.7$, $J = 2.6$, 1H), 2.16 (dd, $J = 16.2$, $J = 12.0$, 1H), 1.98-1.88.

S49
(m, 2H*), 1.80 (m, 1H), 1.63 (app q, \( J = 12.0 \) 1H); \(^{13}\)C-NMR (125 MHz, CD\textsubscript{3}COCD\textsubscript{3}) \( \delta \) 174.0, 173.9*, 160.5, 160.3*, 159.5*, 159.5, 157.2, 155.3*, 129.9, 129.9*, 129.3*, 128.3, 104.4, 102.2*, 94.3, 94.1*, 92.0, 91.7*, 76.6, 70.5*, 55.7, 55.7*, 55.5, 55.4*, 52.1 (C, C*), 43.1, 40.6*, 34.7, 30.6, 28.6*, 27.0*, 26.9, 22.9*; FTIR (neat) \( \nu_{\text{max}} \) 2942, 2927, 1735, 1618, 1586, 1494, 1213, 1197, 1142, 1117, 1054, 806; HRMS exact mass calculated for [M+Na]\(^+\) (C\textsubscript{17}H\textsubscript{20}O\textsubscript{5}Na) requires \( m/z \) 327.1205, found \( m/z \) 327.1203.

**Cycloadducts 17d/17d**

Some unreacted diene was observed in the \(^1\)H-NMR of the crude reaction mixture. The product was purified by column chromatography (toluene/EtOAc from 98/2 to 95/5) to afford cycloadducts 17d/17d* (79/21* mixture of diastereomers, 57%). The product was obtained in 67% isolated yield based on the recovered starting material. Data for 17d: \(^1\)H-NMR (500 MHz, CD\textsubscript{3}COCD\textsubscript{3}) \( \delta \) 6.78-6.74 (m, 2H), 6.66 (t, \( J = 4.6 \) 1H), 5.98 (dm, \( J = 10.4 \) 1H), 5.93 (dm, \( J = 10.4 \) 1H), 4.23 (dm, \( J = 9.5 \) 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.44 (m, 1H), 2.77 (dd, \( J = 16.0 \), \( J = 5.1 \) 1H), 2.63 (dd, \( J = 16.0 \), \( J = 12.3 \) 1H), 2.25 (m, 1H), 1.92 (m, 1H), 1.65 (app q, \( J = 13.0 \) 1H); \(^{13}\)C-NMR (125 MHz, CD\textsubscript{3}COCD\textsubscript{3}) \( \delta \) 174.0, 149.7, 145.7, 130.0, 128.2, 124.0, 122.4, 120.8, 110.7, 76.8, 56.0, 52.2, 43.0, 34.9, 32.5, 30.5; FTIR (neat) \( \nu_{\text{max}} \) 2925, 2839, 1733, 1583, 1481, 1259, 1089, 1036, 926, 763, 729; HRMS exact mass calculated for [M+Na]\(^+\) (C\textsubscript{16}H\textsubscript{18}O\textsubscript{4}Na) requires \( m/z \) 297.1097, found \( m/z \) 297.1100.
Some unreacted diene was observed in the $^1$H-NMR of the crude reaction mixture. The product was purified by column chromatography (toluene/EtOAc from 98/2 to 95/5) to afford cycloadducts 17e/17e* (79/21* mixture of diastereomers, 48%). The product was obtained in 55% isolated yield based on the recovered starting material. $^1$H-NMR (500 MHz, CD$_3$COCD$_3$) $\delta$ 7.75-7.70 (m, 2H, 3H*), 7.68-7.50 (m, 5H, 4H*), 6.92 (d, $J = 8.4$, 1H), 6.86 (d, $J = 8.4$, 1H*), 6.05-6.00 (m, 2H*), 6.00-5.95 (m, 2H), 4.74 (m, 1H*), 4.41 (dd, $J = 9.6$, $J = 3.6$, 1H), 3.70 (s, 3H), 3.69 (s, 3H*), 3.46 (m, 1H), 3.36 (m, 1H*), 3.04 (dd, $J = 16.6$, $J = 6.2$, 1H*), 2.87 (dd, $J = 16.1$, $J = 4.8$, 1H), 2.77-2.68 (m, 1H, 1H*), 2.45 (m, 1H*), 2.28 (m, 1H), 2.04-1.87 (m, 1H, 2H*), 1.69 (app q, $J = 12.9$, 1H); $^{13}$C-NMR (125 MHz, CD$_3$COCD$_3$) $\delta$ 195.2, 195.2*, 173.8, 173.7*, 159.9, 158.5*, 139.4*, 139.3, 133.4, 133.2*, 132.6, 132.5*, 130.8*, 130.7*, 130.6, 130.2 (2C), 130.2 (2C), 129.6*, 129.4, 129.2*, 129.1 (3C), 129.1 (2C)*, 128.7, 123.6, 121.5*, 117.4, 116.9*, 77.5, 71.7*, 52.2*, 52.2, 43.0, 40.3*, 34.8, 32.3, 30.3, 29.0*, 28.6*, 26.6*. FTIR (neat) $\nu_{\text{max}}$ 3044, 2951, 1732, 1648, 1602, 1572, 1236, 1118; HRMS (ESI) exact mass calculated for [M+H]$^+$ (C$_{22}$H$_{20}$O$_4$Na) requires $m/z$ 371.1253, found $m/z$ 371.1253.

Cycloadducts 17e/17e*
MeO-\begin{align*} &\text{O} \\ &\text{HO} \\ &\text{O} \\ &\text{2j}\end{align*}
MeO

2k
\[
\text{O}
\]

\[
\text{OH}
\]

\[
\text{OMe}
\]

2n
MeS-\_\begin{array}{c} \text{Me}\_\text{S} \\
\end{array} \_\text{O} \_\text{S} \text{MeS}_\text{2p}
MeO-\[\text{O}
\begin{align*}
\text{HO-}\[\text{2q}
\end{align*}

ppm

167.97
157.14
153.17
146.72
142.89
127.75
127.97
127.07
122.93
122.06
117.19
117.14
104.10
104.00
56.19
trans-6
trans-6

\[
\begin{align*}
\text{COOMe} & \\
\text{COOEt} & \\
\text{COOEt} & \\
\end{align*}
\]
(Z,E)-5
(Z,E)-7
(E,E)-7
\[\text{EtOOC COOEt} \quad \text{COMe}\]

\[(E,E)-7\]
Relevant NOE interaction
trans-11b
No NOE observed between:
- K and H;
- M and D

Relevant NOE interaction
No NOE observed between:
- K and H;
- L and E

Relevant NOE interaction
17a  Major diastereoisomer
17a* Minor diastereoisomer
Major diastereomer
17a

Relevant NOE interaction

Minor diastereomer
17a*

Relevant NOE interaction
**17b**

Major diastereoisomer

**17b**

Minor diastereoisomer

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
17c
Major diastereoisomer

17c*
Minor diastereoisomer

ppm
17d
Major diastereoisomer

17d*
Minor diastereoisomer
Crystallographic data

\((2Z,4E)-5\text{-}(\text{mesityloxy})\text{penta-2,4-dienoic acid (2a) CDCC 878396}}\)

Crystal structure analysis of 2a crystallized from acetone.

Crystal data and structure refinement.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>7417</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>{14}\text{H}</em>{16}\text{O}_3)</td>
</tr>
<tr>
<td>Color</td>
<td>colourless</td>
</tr>
<tr>
<td>Formula weight</td>
<td>232.27 g \cdot \text{mol}^{-1}</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>TRICLINIC</td>
</tr>
<tr>
<td>Space group</td>
<td>(P\overline{1}, \text{ (no. 2)})</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>8.2022(9) Å</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>90.033(2)°</td>
</tr>
<tr>
<td>b</td>
<td>11.0487(12) Å</td>
</tr>
<tr>
<td>(\beta)</td>
<td>94.313(2)°</td>
</tr>
<tr>
<td>c</td>
<td>28.058(3) Å</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>99.031(2)°</td>
</tr>
<tr>
<td>Volume</td>
<td>2503.9(5) Å</td>
</tr>
<tr>
<td>(Z)</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.232 \text{Mg} \cdot \text{m}^{-3}</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.086 mm(^{-1})</td>
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<tr>
<td>(F(000))</td>
<td>992 e</td>
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<tr>
<td>Crystal size</td>
<td>0.18 x 0.08 x 0.08 mm(^3)</td>
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<tr>
<td>(\theta) range for data collection</td>
<td>1.46 to 34.65°</td>
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<tr>
<td>Index ranges</td>
<td>-13 \leq h \leq 13, -17 \leq k \leq 17, -44 \leq l \leq 44</td>
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<tr>
<td>Reflections collected</td>
<td>90815</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>21317 [(R_{\text{int}} = 0.0561)]</td>
</tr>
<tr>
<td>Reflections with (I&gt;2\sigma(I))</td>
<td>13153</td>
</tr>
<tr>
<td>Completeness to (\theta = 27.50^\circ)</td>
<td>100.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Gaussian</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.00 and 0.997</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>21317 / 0 / 629</td>
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<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.024</td>
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<tr>
<td>Final R indices [I&gt;2\sigma(I)]</td>
<td>R$_i$ = 0.0529      \quad wR$^2$ = 0.1261</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R$_i$ = 0.1024 \quad wR$^2$ = 0.1485</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.457 and -0.266 e \cdot \text{Å}^{-3}</td>
</tr>
</tbody>
</table>
(2Z,4E)-5-(4-(trifluoromethyl)phenoxy)penta-2,4-dienoic acid (2b) CDCC 878394

Crystal structure analysis of 2b crystallized from acetone.

**Crystal data and structure refinement.**

- **Identification code**: 7364
- **Empirical formula**: C₁₂H₉F₃O₃
- **Color**: colourless
- **Formula weight**: 258.19 g · mol⁻¹
- **Temperature**: 100 K
- **Wavelength**: 1.54184 Å
- **Crystal system**: MONOCLINIC
- **Space group**: P2₁/c, (no. 14)
- **Unit cell dimensions**: 
  - a = 7.8605(3) Å, α = 90°.
  - b = 13.6495(5) Å, β = 91.990(2)°.
  - c = 10.5353(4) Å, γ = 90°.
- **Volume**: 1129.67(7) Å³
- **Z**: 4
- **Density (calculated)**: 1.518 Mg · m⁻³
- **Absorption coefficient**: 1.236 mm⁻¹
- **F(000)**: 528 e
- **Crystal size**: 0.28 x 0.09 x 0.08 mm³
- **θ range for data collection**: 5.31 to 67.10°.
- **Index ranges**: -9 ≤ h ≤ 9, -15 ≤ k ≤ 16, -12 ≤ l ≤ 12
- **Reflections collected**: 24991
- **Independent reflections**: 2000 [R:int = 0.0450]
- **Reflections with I>2σ(I)**: 1793
- **Completeness to θ = 67.10°**: 98.9 %
- **Absorption correction**: Gaussian
- **Max. and min. transmission**: 0.91 and 0.77
- **Refinement method**: Full-matrix least-squares on F²
<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data / restraints / parameters</td>
<td>2000 / 0 / 174</td>
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<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.068</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>$R_i = 0.0641$, $wR^2 = 0.1453$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_i = 0.0698$, $wR^2 = 0.1493$</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.0015(4)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.661 and -0.492 e · Å^-3</td>
</tr>
</tbody>
</table>
(2Z,4E)-5-(3,5-dimethylphenoxy)-2-methylpenta-2,4-dienoic acid (2i) CDCC 878398

Crystal structure analysis of 2i crystallized from acetone.

Crystal data and structure refinement.

Identification code 7401
Empirical formula C13H14O4
Color colourless
Formula weight 234.24 g · mol⁻¹
Temperature 100 K
Wavelength 0.71073 Å
Crystal system MONOCLINIC
Space group P2₁/c, (no. 14)
Unit cell dimensions
a = 14.1580(12) Å  α = 90°.
b = 10.4838(5) Å  β = 105.598(7)°.
c = 8.1386(7) Å  γ = 90°.
Volume 1163.52(15) Å³
Z 4
Density (calculated) 1.337 Mg · m⁻³
Absorption coefficient 0.099 mm⁻¹
F(000) 496 e
Crystal size 0.46 x 0.33 x 0.16 mm³
θ range for data collection 2.99 to 37.00°.
Index ranges -23 ≤ h ≤ 23, -17 ≤ k ≤ 17, -13 ≤ l ≤ 13
Reflections collected 45164
Independent reflections 5898 [R(int) = 0.0489]
Reflections with I>2σ(I) 4669
Completeness to θ = 27.50° 99.8 %
Absorption correction Gaussian
Max. and min. transmission 0.98 and 0.95
Refinement method: Full-matrix least-squares on $F^2$

Data / restraints / parameters: 5898 / 0 / 157

Goodness-of-fit on $F^2$: 1.058

Final $R$ indices [$I > 2\sigma(I)$]: $R_I = 0.0427$, $wR^2 = 0.1086$

$R$ indices (all data): $R_I = 0.0603$, $wR^2 = 0.1193$

Largest diff. peak and hole: 0.643 and -0.260 e·Å$^{-3}$
(2Z,4E)-5-(4-methoxyphenoxy)penta-2,4-dienoic acid (2j) CDCC 878395

Crystal structure analysis of 2j crystallized from acetone.

**Crystal data and structure refinement.**

- Identification code: 7373
- Empirical formula: C_{12}H_{12}O_{4}
- Color: colourless
- Formula weight: 220.22 g · mol⁻¹
- Temperature: 100 K
- Wavelength: 0.71073 Å
- Crystal system: ORTHORHOMBIC
- Space group: Pbcn, (no. 60)
- Unit cell dimensions:
  - a = 29.196(7) Å, α = 90°.
  - b = 9.3405(15) Å, β = 90°.
  - c = 7.9764(14) Å, γ = 90°.
- Volume: 2175.2(7) Å³
- Z: 8
- Density (calculated): 1.345 Mg · m⁻³
- Absorption coefficient: 0.101 mm⁻¹
- F(000): 928 e
- Crystal size: 0.3 x 0.19 x 0.14 mm³
- θ range for data collection: 2.79 to 32.11°.
- Index ranges: -43 ≤ h ≤ 43, -13 ≤ k ≤ 13, -11 ≤ l ≤ 11
- Reflections collected: 43914
- Independent reflections: 3802 [R_{int} = 0.0611]
- Reflections with I>2σ(I): 2626
- Completeness to θ = 31.00°: 99.9 %
- Absorption correction: Gaussian
- Max. and min. transmission: 0.991 and 0.98
- Refinement method: Full-matrix least-squares on F²
<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data / restraints / parameters</td>
<td>3802 / 0 / 147</td>
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<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.041</td>
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<tr>
<td>Final R indices [$I&gt;2\sigma(I)$]</td>
<td>$R_1 = 0.0455$</td>
</tr>
<tr>
<td></td>
<td>$wR^2 = 0.0999$</td>
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<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.0794$</td>
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<td></td>
<td>$wR^2 = 0.1159$</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.290 and -0.265 e · Å$^{-3}$</td>
</tr>
</tbody>
</table>
(2Z,4E)-5-((4-methoxynaphthalen-1-yl)oxy)penta-2,4-dienoic acid (2q) CDCC 878397

Crystal structure analysis of 2q crystallized from acetone.

Crystal data and structure refinement.
Identification code 7418
Empirical formula C_{16}H_{14}O_4
Color colourless
Formula weight 270.27 g · mol⁻¹
Temperature 100 K
Wavelength 0.71073 Å
Crystal system MONOCLINIC
Space group P2₁/n, (no. 14)
Unit cell dimensions
\[a = 8.6390(18) \text{ Å} \quad \alpha = 90°.\]
\[b = 4.8905(13) \text{ Å} \quad \beta = 96.394(18)°.\]
\[c = 31.875(8) \text{ Å} \quad \gamma = 90°.\]
Volume 1338.3(6) Å³
Z 4
Density (calculated) 1.341 Mg · m⁻³
Absorption coefficient 0.096 mm⁻¹
F(000) 568 e
Crystal size 0.66 x 0.13 x 0.06 mm³
θ range for data collection 2.89 to 31.75°.
Index ranges -12 ≤ h ≤ 12, -7 ≤ k ≤ 4, -41 ≤ l ≤ 46
Reflections collected 10747
Independent reflections 4178 \[R_{int} = 0.0439\]
Reflections with l>2σ(I) 2799
Completeness to θ = 27.50° 98.7 %
Absorption correction Gaussian
Max. and min. transmission 0.99 and 0.98
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4178 / 0 / 183
Goodness-of-fit on F² 1.045
Final R indices [I>2\sigma(I)] R₁ = 0.0659 \quad wR² = 0.1589
R indices (all data) R₁ = 0.1048 \quad wR² = 0.1830
Largest diff. peak and hole 0.411 and -0.366 e \cdot Å⁻³
Crystal structure analysis of \((E,E)-5\) crystallized from DCM/Heptane.

**Crystal data and structure refinement.**

<table>
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<th>Value</th>
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<td>Identification code</td>
<td>7505</td>
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<tr>
<td>Empirical formula</td>
<td>(C_{13}H_{18}O_6)</td>
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<tr>
<td>Color</td>
<td>colourless</td>
</tr>
<tr>
<td>Formula weight</td>
<td>(270.27 \text{ g \cdot mol}^{-1})</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>MONOCLINIC</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/c), (no. 14)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 12.1829(16) \text{ Å}) (\alpha = 90^\circ).</td>
</tr>
<tr>
<td></td>
<td>(b = 9.3750(12) \text{ Å}) (\beta = 91.501(2)^\circ).</td>
</tr>
<tr>
<td></td>
<td>(c = 12.2675(16) \text{ Å}) (\gamma = 90^\circ).</td>
</tr>
<tr>
<td>Volume</td>
<td>1400.6(3) Å³</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.282 \text{ Mg \cdot m}^{-3})</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.102 mm⁻¹</td>
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<tr>
<td>(F(000))</td>
<td>576 e</td>
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<tr>
<td>Crystal size</td>
<td>0.30 x 0.19 x 0.02 mm³</td>
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<td>(\theta) range for data collection</td>
<td>1.67 to 30.55°.</td>
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<tr>
<td>Index ranges</td>
<td>(-17 \leq h \leq 17, -13 \leq k \leq 13, -17 \leq l \leq 17)</td>
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<tr>
<td>Reflections collected</td>
<td>38377</td>
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<tr>
<td>Independent reflections</td>
<td>4280 [(R_{int} = 0.0354)]</td>
</tr>
<tr>
<td>Reflections with (l&gt;2\sigma(l))</td>
<td>3667</td>
</tr>
<tr>
<td>Completeness to (\theta = 27.50^\circ)</td>
<td>100.0 %</td>
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<td>Absorption correction</td>
<td>Gaussian</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.00 and 0.97</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
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<td>------------------------------------</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on $F^2$</td>
<td>1.062</td>
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<tr>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.470 and -0.182 e · Å$^{-3}$</td>
</tr>
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</table>
Crystal structure analysis of A crystallized from DCM/Heptane.

**Crystal data and structure refinement.**

- **Identification code**: 7585
- **Empirical formula**: $\text{C}_{17}\text{H}_{17}\text{N}\text{O}_{4}$
- **Color**: colorless
- **Formula weight**: 299.32 g \(\cdot\) mol\(^{-1}\)
- **Temperature**: 100 K
- **Wavelength**: 0.71073 Å
- **Crystal system**: MONOCLINIC
- **Space group**: \(\text{P2}_1/c\), (no. 14)
- **Unit cell dimensions**: 
  - \(a = 9.845(2)\) Å \(\alpha = 90^\circ\)
  - \(b = 15.130(4)\) Å \(\beta = 95.633(4)^\circ\)
  - \(c = 9.818(2)\) Å \(\gamma = 90^\circ\)
- **Volume**: 1455.4(6) Å\(^3\)
- **Z**: 4
- **Density (calculated)**: 1.366 Mg \(\cdot\) m\(^{-3}\)
- **Absorption coefficient**: 0.098 mm\(^{-1}\)
- **F(000)**: 632 e
- **Crystal size**: 0.25 x 0.08 x 0.06 mm\(^3\)
- **θ range for data collection**: 2.08 to 30.51°
- **Index ranges**: 
  - \(-14 \leq h \leq 14, -21 \leq k \leq 21, -14 \leq l \leq 14\)
- **Reflections collected**: 39991
- **Independent reflections**: 4431 [\(R_{int} = 0.0796\)]
- **Reflections with I\(>2\sigma(I)\)**: 4027
- **Completeness to θ = 27.50°**: 100.0 %
- **Absorption correction**: Gaussian
- **Max. and min. transmission**: 1.00 and 0.89
- **Refinement method**: Full-matrix least-squares on $F^2$
- **Data / restraints / parameters**: 4431 / 0 / 201
- **Goodness-of-fit on $F^2$**: 1.131
<table>
<thead>
<tr>
<th></th>
<th>( R_1 = 0.0434 )</th>
<th>( wR^2 = 0.1068 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Final R indices [I&gt;2( \sigma (I) )]</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>( R_1 = 0.0471 )</td>
<td>( wR^2 = 0.1096 )</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>0.415 and -0.236 e ( \cdot ) ( \text{Å}^{-3} )</td>
<td></td>
</tr>
</tbody>
</table>
Crystal structure analysis of 13b crystallized from DCM/Heptane.

Crystal data and structure refinement.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>7633</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{17}H_{24}O_{6}</td>
</tr>
<tr>
<td>Color</td>
<td>colourless</td>
</tr>
<tr>
<td>Formula weight</td>
<td>324.36 g · mol^{-1}</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>TRICLINIC</td>
</tr>
<tr>
<td>Space group</td>
<td>P¯1, (no. 2)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 8.269(2) Å, b = 10.113(3) Å, c = 10.652(3) Å</td>
</tr>
<tr>
<td></td>
<td>α = 100.932(4)°, β = 101.789(4)°, γ = 100.590(4)°</td>
</tr>
<tr>
<td>Volume</td>
<td>832.9(4) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.293 Mg · m^{-3}</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.097 mm^{-1}</td>
</tr>
<tr>
<td>F(000)</td>
<td>348 e</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.30 x 0.14 x 0.08 mm³</td>
</tr>
<tr>
<td>θ range for data collection</td>
<td>2.01 to 30.51°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>23194</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5081 [R_{int} = 0.0337]</td>
</tr>
<tr>
<td>Reflections with I&gt;2σ(I)</td>
<td>4242</td>
</tr>
<tr>
<td>Completeness to θ = 27.50°</td>
<td>100.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Gaussian</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.99 and 0.98</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
</tbody>
</table>
Data / restraints / parameters: 5081 / 0 / 211

Goodness-of-fit on $F^2$: 1.034

Final R indices [$I > 2\sigma(I)$]: $R_I = 0.0370$  $wR^2 = 0.0942$

R indices (all data): $R_I = 0.0470$  $wR^2 = 0.1003$

Largest diff. peak and hole: 0.405 and -0.190 e · Å$^{-3}$
Crystal structure analysis of 17a crystallized from DCM/Heptane.

**Crystal data and structure refinement.**

- **Identification code**: 7640
- **Empirical formula**: C_{15}H_{16}O_{3}
- **Color**: colorless
- **Formula weight**: 244.28 g · mol\(^{-1}\)
- **Temperature**: 100 K
- **Wavelength**: 1.54184 Å
- **Crystal system**: MONOCLINIC
- **Space group**: \(\text{P2}_1/\text{c, (no. 14)}\)
- **Unit cell dimensions**:
  - \(a = 10.2678(4)\) Å, \(\alpha = 90^\circ\)
  - \(b = 13.6678(5)\) Å, \(\beta = 103.345(2)^\circ\)
  - \(c = 8.7688(3)\) Å, \(\gamma = 90^\circ\)

- **Volume**: 1197.37(8) Å\(^3\)
- **Z**: 4
- **Density (calculated)**: 1.355 Mg · m\(^{-3}\)
- **Absorption coefficient**: 0.759 mm\(^{-1}\)
- **F(000)**: 520 e
- **Crystal size**: 0.254 x 0.252 x 0.187 mm\(^3\)
- **\(\theta\) range for data collection**: 4.43 to 62.38°.
- **Index ranges**: -11 ≤ \(h\) ≤ 11, -15 ≤ \(k\) ≤ 15, -10 ≤ \(l\) ≤ 10
- **Reflections collected**: 25643
- **Independent reflections**: 1893 [\(R_{int} = 0.0461\)]
- **Reflections with I>2\(\sigma(I)\)**: 1779
- **Completeness to \(\theta = 62.38^\circ\)**: 99.4 %
- **Absorption correction**: Gaussian
- **Max. and min. transmission**: 0.32 and 0.14
- **Refinement method**: Full-matrix least-squares on F\(^2\)
Data / restraints / parameters 1893 / 0 / 164
Goodness-of-fit on $F^2$ 1.059
Final R indices [I>2$\sigma$(I)] $R_1 = 0.0327$  $wR^2 = 0.0873$
R indices (all data) $R_1 = 0.0345$  $wR^2 = 0.0887$
Largest diff. peak and hole 0.200 and -0.172 e·Å$^{-3}$