Supporting Information-I

Discovery of 2-Aminobuta-1,3-enynes in Asymmetric Organocascade Catalysis: Construction of Drug-like Spirocyclic Cyclohexanes Having Five to Six Contiguous Stereocenters

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General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by

irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received. Ynones **1a-e** was prepared according to the literature procedure.[1]

General Experimental Procedures

Procedure A: General procedure for the primary amine/acid-catalyzed asymmetric cascade *r*-M reaction: In an ordinary glass vial equipped with a magnetic stirring bar was added 0.05 mmol of catalyst primary amine **4e** and 0.075 mmol 2-fluoro benzoic acid **5b** in toluene (1.0 mL) were stirred at 25 °C for 5 min and then 0.5 mmol of ynone **1**, 0.25 mmol of aldehyde **2**, 0.25 mmol of 1,3-indandione **3** were added and the reaction mixture was stirred at ambient temperature for 24–36 h. The crude reaction mixture was treated with saturated aqueous ammonium chloride solution; the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure products **6** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure B: General procedure for the diamine/acid-catalysed asymmetric cascade *r*-M reaction: In an ordinary glass vial equipped with a magnetic stirring bar, was added 0.05 mmol of chiral diamine **4b** and 0.075 mmol of benzoic acid **5a** in toulene (1.0 mL) were stirred at 25 °C for 5 min and then 0.5 mmol of ynone **1**, 0.25 mmol of aldehyde **2**, 0.25 mmol of 1,3-indandione **3** were added and stirred at ambient temperature for 48 h. The crude reaction mixture was treated with saturated aqueous ammonium chloride solution; then the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure products **7** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure C: General procedure for the pyrrolidine-catalysed racemic cascade *r*-M reaction: In an ordinary glass vial equipped with a magnetic stirring bar, was added 0.06 mmol of pyrrolidine, 0.6 mmol of ynone **1**, 0.3 mmol of aldehyde **2**, 0.3 mmol of indanedione **3** in brine solution (3.0 mL) and stirred at ambient temperature for 48 h. The crude reaction mixture was treated with saturated aqueous ammonium chloride solution; then the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined

organic layers were dried (Na_2SO_4), and concentrated. Pure racemic products **6** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure D: General procedure for the reduction of chiral *r*-M products 6: In an oven dried round bottom flask, $NaBH_4$ (0.75 mmol) was added to the stirred solution of *r*-M product **6** (0.5 mmol) in dry methanol (2.0 mL) at 0 °C. Slowly reaction mixture was brought to room temperature and stirred for 0.5 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure chiral allylic alcohols **8** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure E: General procedure for the selective oxidation of chiral allylic alcohols 8: In an oven dried round bottom flask, *m*-CPBA (1.2 equiv., 0.24 mmol) was added to a stirred solution of allylic alcohol **8** (1.0 equiv., 0.2 mmol) in dry CH_2Cl_2 at 0 °C. After complete consumption of the substrate **8** (as monitored by TLC), the reaction mixture was diluted with CH_2Cl_2, washed with 10% aqueous K_2CO_3 solution, and brine, and dried with Na_2SO_4. Evaporation of solvent under reduced pressure gave crude product, which was purified by column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate to yield the secondary α-hydroxy chiral epoxides **9**.

Procedure F: General procedure for the cyclopropanation of chiral allylic alcohols 8:[2] To a solution of 60 mg (0.13 mmol) of chiral allylic alcohol **8ae** in 2.0 mL of anhydrous CH_2Cl_2 at -10 °C was added dropwise 5.0 equiv. (0.65 mmol) of 1.0 M diethylzinc solution followed by 5.0 equiv. (0.65 mmol) of diiodomethane. The cooling bath was allowed to warm to rt over 3 h and the mixture was stirred for an additional 1 h, after which time TLC analysis showed complete consumption of starting material. A saturated aq. NH_4Cl (5 mL) was added and mixture was diluted with ether (10 mL) and 10% aq. HCl (5 mL). The layers were separated and the organic layer was then successively washed with saturated aq. Na_2SO_3 (5 mL), saturated aq. $NaHCO_3$ (5 mL) and saturated aq. NaCl (5 mL). The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure gave crude product **10ae**, which was purified by column chromatography (silica gel, hexane/ethyl acetate).

Procedure G: General procedure for the Suzuki coupling on chiral *r*-M product 6ae:[3] A 25 mL round bottom flask equipped with magnetic stir bar was added solution of $Pd(PPh_3)_4$ (3.80 mg, 0.0033 mmol) in toluene (0.8 mL) and boronic acid (**a-b**) (16.56 mg, 0.12 mmol) in EtOH (0.35 mL) were added

to a solution of sodium succinate hexahydrate (170 mg, 0.63 mmol) and chiral *r*-M product **6ae** (68.4 mg, 0.15 mmol) in toluene (0.8 mL) and H_2O (0.7 mL) under nitrogen atmosphere. The resulting mixture was stirred at 80 °C for 1 h. The addition of boronic acid (8.28 mg, 0.06 mmol) in the EtOH (0.35 mL) and $Pd(PPh_3)_4$ (1.9 mg, 0.00165 mmol) in toluene (0.4 mL) were repeated for further three times at 60 min intervals. Then mixture was stirred for further 4 h. Then reaction was cooled to 25 °C and the crude reaction mixture was worked up with mixture of H_2O and Et_2O. The aqueous layer was extracted with Et_2O (2 x 5 mL) and the combined organic layers were washed with 1.0 M NaOH, brine and dried over Na_2SO_4, and concentrated under reduced pressure to gave crude product, which was purified by column chromatography (silica gel, hexane/ethyl acetate).

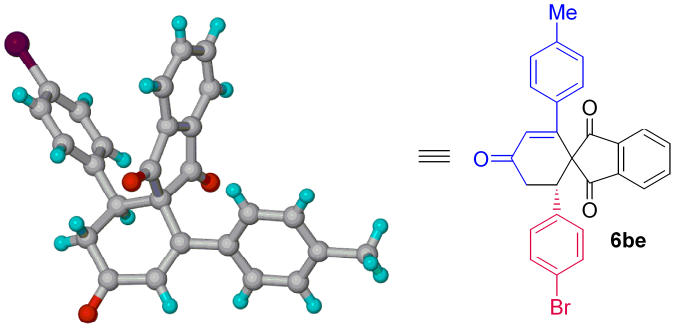


Figure S1. Crystal structure of functionalized spiro-cyclohexanone (**6be**).

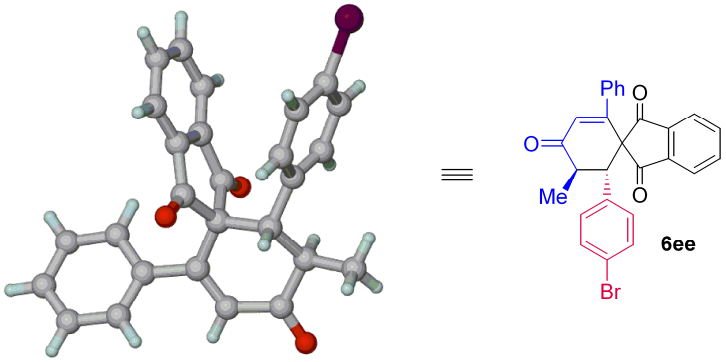
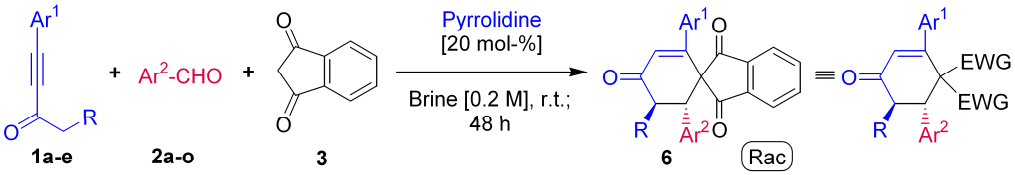
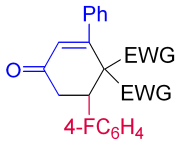


Figure S2. Crystal structure of functionalized spiro-cyclohexanone (**6ee**).

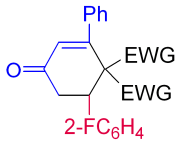
Table S1. Synthesis of racemic spirane products **6**.[a-c]



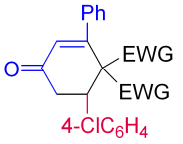
1a-e **2a-o** **3** **6**



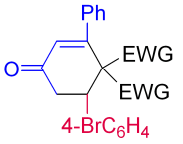
6ab, 75%



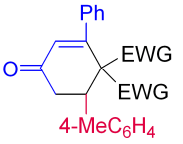
6ac, 65%



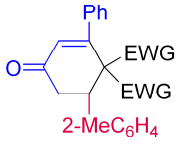
6ad, 60%



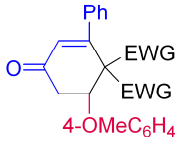
6ae, 65%



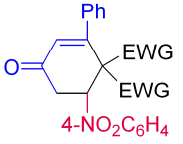
6af, 67%



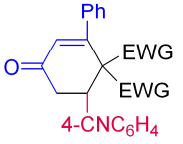
6ag, 55%



6ah, 50%



6ai, 75%



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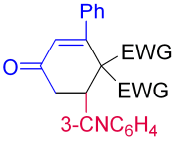
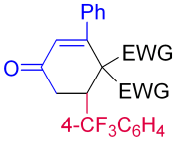
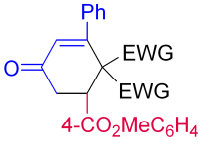


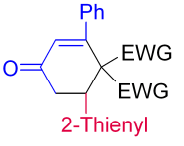
6ak, 60%



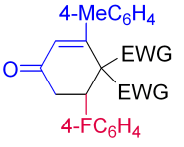
6al, 70%



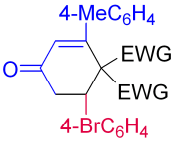
6am, 50%



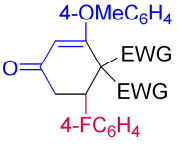
6an, 40%



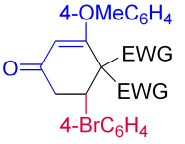
6bb, 50%



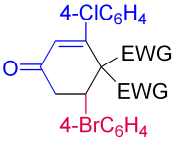
6be, 50%



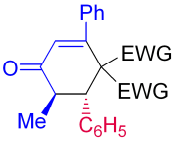
6cb, 40%



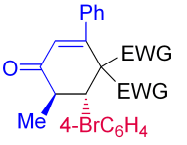
6ce, 50%



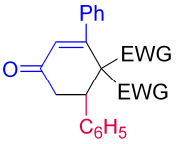
6de, 50%



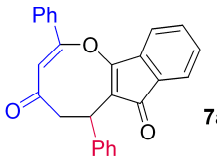
6ea, 70%
>99% *de*



6ee, 75%
>99% *de*

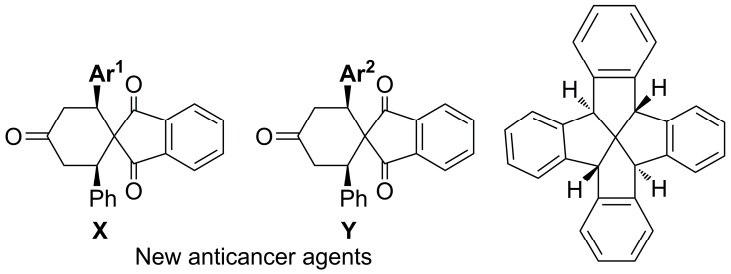


6aa, 65%



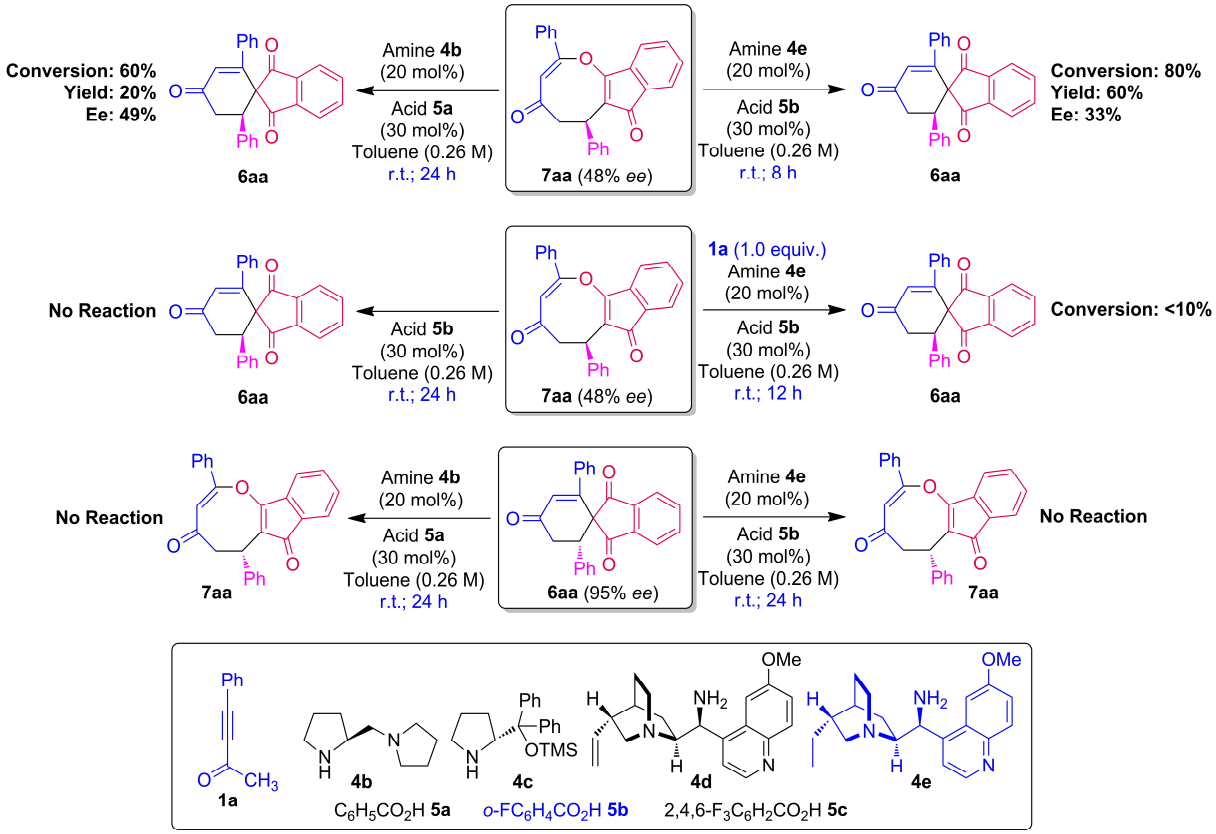
7aa,[d] 60%

[a] Reactions were carried out in brine (0.2 M) with 2 equiv. of **1a-e** relative to the **2a-o** (0.2 mmol) and **3** (0.2 mmol) in the presence of 20-mol% of catalyst pyrrolidine. [b] Yield refers to the column purified product. [c] Ratio or *de* is based on HPLC analysis. [d] DL-diamine **4b** (20 mol-%)/**5a** (30 mol-%) used as catalyst in toluene (0.25 M).

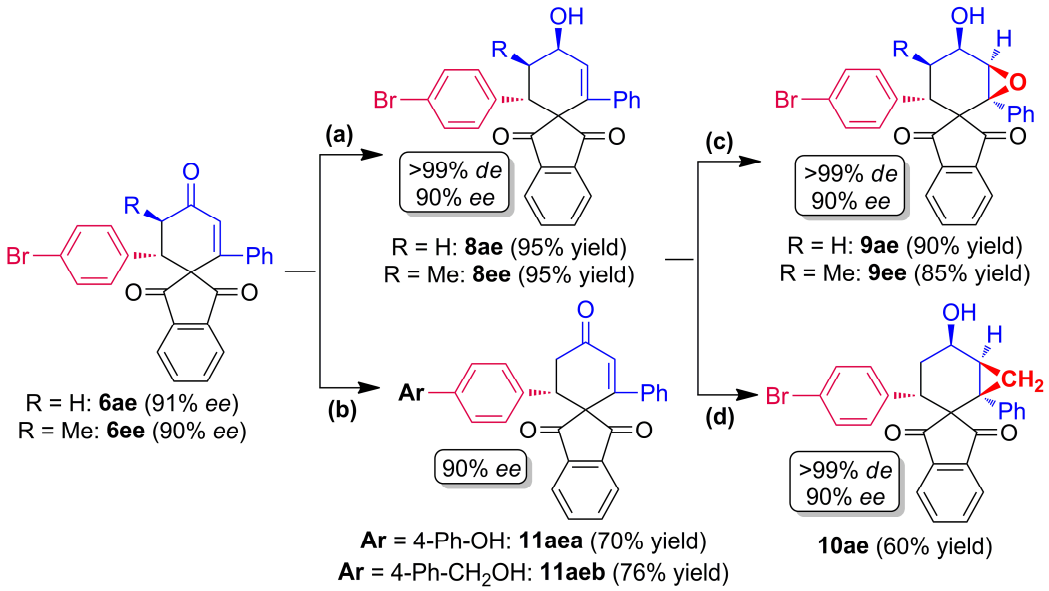


(S-1)

Eq-S1: Medicinally important products containing spiro-cyclohexanone scaffolds.



Scheme S1. Controlled experiments to test the interconversion of **6aa** and **7aa**.



Scheme 1 **Synthesis of drug-like spiranes for anticancer studies.** *Reaction conditions:* (**a**) $NaBH_4$ (1.5 equiv.), dry CH_3OH (0.25 M), 0-25 °C, 0.5 h; (**b**) **Ar**-$B(OH)_2$ (2.0 equiv.), $Pd(PPh_3)_4$ (0.055 equiv.), $C_6H_5CH_3$ (2 mL), sodium succinate (4.2 equiv.), $C_6H_5CH_3$:H_2O (1.14:1; 1.5 mL), EtOH (1.4 mL), 90 °C, 8 h; (**c**) *m*CPBA (1.2 equiv.), CH_2Cl_2 (0.2 M), 0-25 °C, 2 h; (**d**) CH_2I_2 (5.0 equiv.), Et_2Zn (5.0 equiv.), CH_2Cl_2 (0.065 M), −10 °C to 25 °C, 4 h.

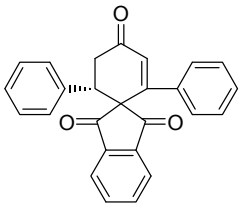
Results and discussion for Scheme 1:

With the medicinal applications in mind, we explored the utilization of spiranes **6** bearing aryl bromide in the synthesis of functionalized chiral spiranes **8-11** *via* simple transformations (Scheme 1). Selective reduction of chiral spirotriones (+)-**6ae**/(+)-**6ee** with 1.5 equiv. of $NaBH_4$ in dry CH_3OH at 0-25 °C for 0.5 h furnished the allylic alcohols (+)-**8ae**/(+)-**8ee** in each 95% yield with 90% *ee* and >99% *de* respectively (Scheme 1). Interestingly, selective oxidation of the resulting pure allylic alcohols (+)-**8ae**/(+)-**8ee** with 1.2 equiv. of *m*CPBA in dry CH_2Cl_2 at 0-25 °C for 2 h furnished the chiral epoxides (−)-**9ae**/(−)-**9ee** in 90/85% yield with 90% *ee* and >99% *de* respectively. Simmons–Smith cyclopropanation of the chiral allylic alcohol (+)-**8ae** with each 5.0 equiv. of CH_2I_2 and Et_2Zn in dry CH_2Cl_2 at −10 to 25 °C for 4 h furnished the cyclopropane alcohol (−)-**10ae** in 60% yield with 90% *ee* and >99% *de*. These high-yielding reactions on **6ae**/**6ee** produces five to six contiguous stereogenic centers and the resulting chiral spiranes **8-10** could be good compounds for the anticancer studies.[4]

Given our interest to synthesize library of chiral biphenyls to study the cell functions,[5c] herein we combined the asymmetric *r*-M reaction with Suzuki coupling to generate the optically pure biphenyl-substituted spirotriones **11** without racemization. Interestingly, Pd-catalyzed Suzuki reaction of (+)-**6ae** bearing aryl bromide with 4-hydroxyphenylboronic acid (**a**), $Pd(PPh_3)_4$ and sodium succinate in

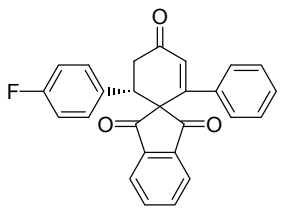
toluene/ethanol/water (4:2:1) at 90 °C for 8 h furnished the product (+)**-11aea** in 70% yield without racemization (Scheme 1). Another biphenyl-based chiral spirotrione (+)**-11aeb** was also prepared in 76% yield with 90% *ee*. Compounds (+)**-11aea** and (+)**-11aeb** are drug-like molecules for the treatment of cancer cells, which is emphasizing the value of this *r*-M and Suzuki coupling approach to the pharmaceuticals.[4]

(*S*)-1',3'-diphenylspiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6aa): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:15, flow rate 1.0 mL/min, λ = 254 nm), t_R = 10.82 min (major), t_R = 15.84 min (minor). Mp 175 °C; **$[\alpha]_D^{25}$ = +44.44° (*c* = 0.20 g/100 mL, $CHCl_3$, >99 % *ee*);** IR (Neat): ν_{max} 3061, 2924, 2855, 1740, 1703, 1595, 1495, 1454, 1410, 1329, 1254, 1163, 1078, 1024, 918, 885, 764, 737 and 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (1H, d, *J* = 7.6 Hz), 7.64 (1H, t, *J* = 7.2 Hz), 7.58-7.52 (2H, m), 7.19 (1H, t, *J* = 7.2 Hz), 7.12 (2H, t, *J* = 7.2 Hz), 6.98-6.94 (7H, m), 6.50 (1H, s), 4.12 (1H, dd, *J* = 14.4, 3.2 Hz), 3.70 (1H, t, *J* = 15.2 Hz), 2.67 (1H, dd, *J* = 16.8, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.0 (C, C=O), 198.3 (C, C=O), 197.6 (C, C=O), 156.1 (C), 142.8 (C), 142.2 (C), 137.4 (C), 136.3 (C), 135.6 (2 x CH), 132.3 (CH), 129.1 (CH), 128.5 (2 x CH), 128.3 (2 x CH), 128.2 (2 x CH), 127.9 (CH), 126.5 (2 x CH), 123.2 (CH), 122.9 (CH), 65.0 (C), 48.5 (CH), 38.4 (CH_2); LRMS m/z 379.00 ($M + H^+$), calcd for $C_{26}H_{18}O_3$ 378.13; Anal. calcd for $C_{26}H_{18}O_3$ (378.13): C, 82.52; H, 4.79; Found: C, 82.45; H, 4.71%.



6aa

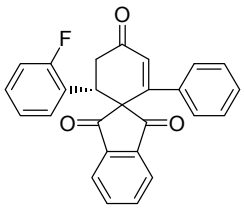
(*S*)-1'-(4-fluorophenyl)-3'-phenylspiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6ab): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 12.59 min (major), t_R = 14.55 min (minor). Mp 110 °C; **$[\alpha]_D^{25}$ = +57.91° (*c* = 0.52 g/100 mL, $CHCl_3$, 92% *ee*);** IR (Neat): ν_{max} 3059, 2897, 1734, 1699, 1605, 1510, 1445, 1404, 1339, 1298, 1242, 1163,1032, 934, 901, 830, 793, 770, 735, 694 and 648 cm^{-1};



6ab

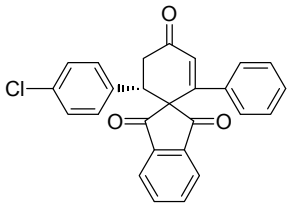
^{1}H NMR ($CDCl_3$) δ 7.84 (1H, d, *J* = 7.6 Hz), 7.69 (1H, t, *J* = 7.2 Hz), 7.62 (1H, t, *J* = 7.6 Hz), 7.57 (1H, d, *J* = 7.6 Hz), 7.20 (1H, t, *J* = 7.2 Hz), 7.13 (2H, t, *J* = 7.6 Hz), 7.00-6.93 (4H, m), 6.69 (2H, t, *J* = 8.8 Hz), 6.49 (1H, s), 4.12 (1H, dd, *J* = 14.8, 3.6 Hz), 3.66 (1H, t, *J* = 15.2 Hz), 2.66 (1H, dd, *J* = 16.8, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.0 (C, C=O), 198.4 (C, C=O), 197.2 (C, C=O), 162.1 (C, d, *J* = 196.7 Hz), 156.0 (C), 142.9 (C), 142.2 (C), 137.4 (C), 135.94 (CH), 135.91 (CH), 132.4 (C, d, *J* = 2.6 Hz), 132.3 (CH), 130.0 (2 x CH, d, *J* = 6.5 Hz), 129.2 (CH), 128.6 (2 x CH), 126.7 (2 x CH), 123.3 (CH), 123.0 (CH), 115.3 (2 x CH, d, *J* = 17.1 Hz), 65.0 (C), 47.6 (CH), 38.7 (CH_2); LRMS m/z 397.00 (M + H^+), calcd for $C_{26}H_{17}FO_3$ 396.12; Anal. calcd for $C_{26}H_{17}FO_3$ (396.12): C, 78.78; H, 4.32; Found: C, 78.65; H, 4.41%.

(*R*)-1'-(2-fluorophenyl)-3'-phenylspiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6ac): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 10.50 min (major), t_R = 13.67 min (minor). Mp 195 °C; **$[\alpha]_D^{25}$ = +91.88° (*c* = 0.21 g/100 mL, $CHCl_3$, 93% *ee*);** IR (Neat): ν_{max} 3057, 2924, 2853, 1742, 1707, 1676, 1595, 1493, 1454, 1330, 1264, 1196, 1101, 1024, 887, 762, 739 and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.90 (1H, d, *J* = 7.2 Hz), 7.70 (1H, br t, *J* = 7.6 Hz), 7.63–7.60 (2H, m), 7.21 (1H, t, *J* = 7.2 Hz), 7.14 (2H, t, *J* = 7.6 Hz), 7.07 (1H, t, *J* = 7.6 Hz), 6.98–6.94 (3H, m), 6.82 (1H, t, *J* = 7.6 Hz), 6.72 (1H, t, *J* = 9.2 Hz), 6.53 (1H, s), 4.50 (1H, dd, *J* = 14.4, 3.6 Hz), 3.65 (1H, t, *J* = 16.8 Hz), 2.64 (1H, dd, *J* = 16.8, 4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 198.7 (C, C=O), 198.1 (C, C=O), 197.1 (C, C=O), 160.0 (C, d, *J* = 248 Hz), 156.3 (C), 142.6 (C), 142.3 (C), 137.5 (C), 135.8 (CH), 135.7 (CH), 132.4 (CH), 129.7 (CH, d, *J* = 9 Hz), 129.5 (CH, d, *J* = 4 Hz), 129.2 (CH), 128.6 (2 x CH), 126.6 (2 x CH), 124.1 (CH, d, *J* = 3 Hz), 123.8 (C, d, *J* = 14 Hz), 123.4 (CH), 123.1 (CH), 115.8 (CH, d, *J* = 22.8 Hz), 64.4 (C), 41.4 (CH), 38.5 (CH_2); LRMS m/z 397.00 (M + H^+), calcd for $C_{26}H_{17}FO_3$ 396.12; Anal. calcd for $C_{26}H_{17}FO_3$ (396.12): C, 78.78; H, 4.32; Found: C, 78.70; H, 4.40%.



6ac

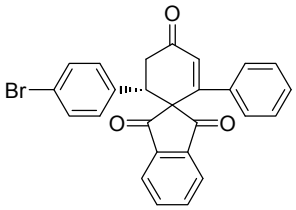
(*S*)-1'-(4-chlorophenyl)-3'-phenylspiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6ad): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 15.26 min (major), t_R = 21.44 min (minor). Mp 145 °C; **$[\alpha]_D^{25}$ = +59.26° (*c* = 0.54 g/100 mL, $CHCl_3$, 93% *ee*);** IR (Neat): ν_{max} 3057, 2920, 1734, 1701,



6ad

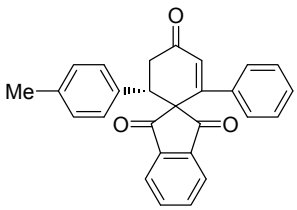
1674, 1591, 1489, 1252, 1092, 1015 and 887 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (1H, d, *J* = 7.6 Hz), 7.70 (1H, t, *J* = 7.2 Hz), 7.63 (1H, t, *J* = 7.2 Hz), 7.57 (1H, d, *J* = 7.6 Hz), 7.20 (1H, t, *J* = 7.2 Hz), 7.13 (2H, t, *J* = 7.6 Hz), 6.99–6.92 (6H, m), 6.81 (1H, s), 4.11 (1H, dd, *J* = 14.8, 3.6 Hz), 3.66 (1H, t, *J* = 16.4 Hz), 2.64 (1H, dd, *J* = 17.2, 4.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.9 (C, C=O), 198.3 (C, C=O), 197.2 (C, C=O), 156.0 (C), 142.8 (C), 142.2 (C), 137.3 (C), 136.1 (2 x CH), 135.1 (C), 133.9 (C), 132.3 (CH), 129.7 (2 x CH), 129.2 (CH), 128.6 (4 x CH), 126.7 (2 x CH), 123.4 (CH), 123.1 (CH), 64.8 (C), 47.6 (CH), 38.5 (CH_2); LRMS m/z 413.00 ($M + H^+$), calcd for $C_{26}H_{17}ClO_3$ 412.09; Anal. calcd for $C_{26}H_{17}ClO_3$ (412.09): C, 75.64; H, 4.15; Found: C, 75.51; H, 4.19%.

(*S*)-1'-(4-bromophenyl)-3'-phenylspiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6ae): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 14.56 min (major), t_R = 24.82 min (minor). Mp 102 °C; **$[\alpha]_D^{25}$ = +57.68° (*c* = 0.20 g/100 mL, $CHCl_3$, 92% *ee*);** IR (Neat): ν_{max} 3059, 2920, 2849, 1740, 1703, 1674, 1593, 1489, 1445, 1412, 1352, 1330, 1254, 1163, 1076, 1011, 887, 824, 762, 737, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (1H, d, *J* = 7.6 Hz), 7.70 (1H, t, *J* = 6.8 Hz), 7.63 (1H, t, *J* = 7.6 Hz), 7.57 (1H, d, *J* = 7.2 Hz), 7.18 (1H, d, *J* = 7.2 Hz), 7.14–7.10 (4H, m), 6.94–6.87 (4H, m), 6.47 (1H, s), 4.10 (1H, dd, *J* = 14.4, 3.2 Hz), 3.66 (1H, t, *J* = 14.8 Hz), 2.64 (1H, dd, *J* = 16.8, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.8 (C, C=O), 198.2 (C, C=O), 197.1 (C, C=O), 156.0 (C), 142.8 (C), 142.1 (C), 137.3 (C), 136.0 (2 x CH), 135.6 (C), 132.2 (CH), 131.5 (2 x CH), 130.0 (2 x CH), 129.2 (CH), 128.5 (2 x CH), 126.6 (2 x CH), 123.4 (CH), 123.0 (CH), 122.0 (C), 64.7 (C), 47.6 (CH), 38.4 (CH_2); LRMS m/z 456.00 (M^+), calcd for $C_{26}H_{17}BrO_3$ 456.04; Anal. calcd for $C_{26}H_{17}BrO_3$ (456.04): C, 68.29; H, 3.75; Found: C, 68.35; H, 3.71%.



6ae

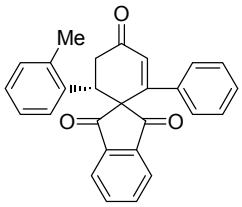
(*S*)-3'-phenyl-1'-(*p*-tolyl)spiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6af): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 11.89 min (major), t_R = 19.95 min (minor). Mp 145 °C; **$[\alpha]_D^{25}$ = +49.74° (*c* = 0.50 g/100 mL, $CHCl_3$, 93% *ee*);** IR (Neat): ν_{max} 3057, 2919, 1738, 1701, 1667, 1593, 1443, 1333, 1250, 885, 814, 789, 762, 732 and 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.83 (1H, d, *J* = 7.6 Hz), 7.65 (1H, t, *J* = 6.8 Hz), 7.59–7.53 (2H, m), 7.19 (1H, t, *J* = 7.2 Hz), 7.12 (2H, t, *J* = 7.6 Hz),



6af

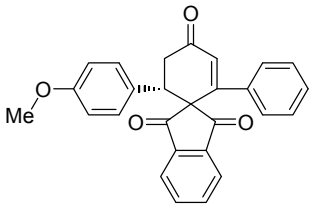
6.94 (2H, d, *J* = 7.6 Hz), 6.87 (2H, d, *J* = 8 Hz), 6.78 (2H, d, *J* = 7.6 Hz), 6.48 (1H, s), 4.09 (1H, dd, *J* = 14.4, 3.2 Hz), 3.68 (1H, t, *J* = 15.2 Hz), 2.64 (1H, dd, *J* = 16.8, 3.6 Hz), 2.06 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.2 (C, C=O), 198.5 (C, C=O), 197.9 (C, C=O), 156.2 (C), 143.0 (C), 142.4 (C), 137.7 (C), 137.6 (C), 135.7 (2 x CH), 133.4 (C), 132.4 (CH), 129.1 (CH), 129.0 (2 x CH), 128.6 (2 x CH), 128.2 (2 x CH), 126.6 (2 x CH), 123.3 (CH), 123.0 (CH), 65.2 (C), 48.3 (CH), 38.8 (CH_2), 20.8 (CH_3); LRMS m/z 393.00 (M + H$^+$), calcd for $C_{27}H_{20}O_3$ 392.14; Anal. calcd for $C_{27}H_{20}O_3$ (392.14): C, 82.63; H, 5.14; Found: C, 82.48; H, 5.09%.

(*S*)-3'-phenyl-1'-(*o*-tolyl)spiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6ag): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 9.04 min (major), t_R = 15.06 min (minor). Mp 180 °C; **$[\alpha]_D^{25}$ = +189.67° (*c* = 0.13 g/100 mL, $CHCl_3$, 98% *ee*);** IR (Neat): ν_{max} 3061, 2920, 2853, 1737, 1699, 1674, 1591, 1485, 1464, 1310, 1256, 889, 756, 700, 584 and 552 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.95 (1H, d, *J* = 7.6 Hz), 7.70 (1H, t, *J* = 7.2 Hz), 7.58 (1H, t, *J* = 7.2 Hz), 7.51 (1H, d, *J* = 7.6 Hz), 7.22–7.12 (3H, m), 7.04 (1H, d, *J* = 7.6 Hz), 6.96 (2H, d, *J* = 7.6 Hz), 6.90 (1H, d, *J* = 7.2 Hz), 6.85–6.78 (2H, m), 6.52 (1H, s), 4.49 (1H, dd, *J* = 14.4, 3.6 Hz), 3.58 (1H, t, *J* = 14.4 Hz), 2.60 (1H, dd, *J* = 17.2, 4.0 Hz), 2.24 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.5 (C, C=O), 199.1 (C, C=O), 197.8 (C, C=O), 156.9 (C), 142.8 (2 x C), 137.6 (C), 136.2 (C), 135.74 (CH), 135.70 (CH), 135.2 (C), 132.4 (CH), 131.2 (CH), 129.1 (CH), 128.6 (2 x CH), 127.6 (CH), 126.9 (CH), 126.6 (2 x CH), 126.0 (CH), 123.4 (CH), 122.9 (CH), 64.7 (C), 43.6 (CH), 40.0 (CH_2), 19.5 (CH_3); LRMS m/z 393.00 (M + H$^+$), calcd for $C_{27}H_{20}O_3$ 392.14; Anal. calcd for $C_{27}H_{20}O_3$ (392.14): C, 82.63; H, 5.14; Found: C, 82.56; H, 5.18%.



6ag

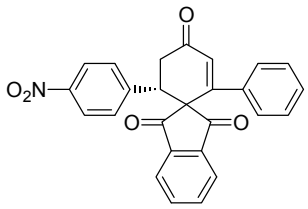
(*S*)-1'-(4-methoxyphenyl)-3'-phenylspiro[cyclohex[3']ene-2',2'-indene]-1,3',5'-trione (6ah): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 13.69 min (major), t_R = 18.55 min (minor). Mp 115 °C; **$[\alpha]_D^{25}$ = +30.78° (*c* = 0.12 g/100 mL, $CHCl_3$, 98% *ee*);** IR (Neat): ν_{max} 3057, 2926, 2849, 1736, 1703, 1672, 1611, 1514, 1443, 1256, 1182, 1032, 887, 831, 764, 737 and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.84 (1H, d, *J* = 7.6 Hz), 7.67 (1H, t, *J* = 6.8 Hz), 7.61–7.55 (2H, m), 7.20 (1H, t, *J* = 7.2 Hz), 7.13 (2H, t, *J* = 7.6 Hz), 6.93 (4H, m), 6.52 (2H, d, *J* = 8.8 Hz), 6.49 (1H, s), 4.09 (1H, dd, *J* = 14.8, 3.6



6ah

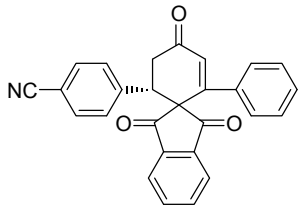
Hz), 3.66 (1H, t, *J* = 16.8 Hz), 3.60 (3H, s, OC*H*$_3$), 2.64 (1H, dd, *J* = 16.8, 4.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.4 (C, C=O), 198.6 (C, C=O), 197.8 (C, C=O), 159.0 (C), 156.2 (C), 143.0 (2 x C), 142.4 (C), 137.6 (C), 135.7 (2 x CH), 132.4 (CH), 129.4 (2 x CH), 129.1 (CH), 128.6 (2 x CH), 126.6 (2 x CH), 123.3 (CH), 123.0 (CH), 113.7 (2 x CH), 65.2 (C), 55.1 (CH_3, OCH_3), 47.9 (CH), 38.9 (CH_2); LRMS m/z 409.00 ($M + H^+$), calcd for $C_{27}H_{20}O_4$ 408.14; Anal. calcd for $C_{27}H_{20}O_4$ (408.14): C, 79.40; H, 4.94; Found: C, 79.32; H, 4.98%.

(*S*)-1'-(4-nitrophenyl)-3'-phenylspiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6ai): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 29.12 min (major), t_R = 39.07 min (minor). Mp 160 °C; **$[\alpha]_D^{25}$ = +57.42° (*c* = 0.41 g/100 mL, $CHCl_3$, 94% *ee*);** IR (Neat): ν_{max} 3063, 2924, 2857, 2205,1740, 1703, 1597, 1522, 1493, 1445, 1348, 1256, 1182, 1111, 889, 858, 812, 764, 737 and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.84–7.81 (3H, m), 7.65 (1H, t, *J* = 7.2 Hz), 7.57 (1H, t, *J* = 7.6 Hz), 7.51 (1H, d, *J* = 7.6 Hz), 7.18 (2H, d, *J* = 8.4 Hz), 7.13 (1H, t, *J* = 7.2 Hz), 7.06 (2H, t, *J* = 7.6 Hz), 6.88 (2H, d, *J* = 7.2 Hz), 6.43 (1H, s), 4.23 (1H, dd, *J* = 14.4, 3.6 Hz), 3.68 (1H, t, *J* = 16.0 Hz), 2.64 (1H, dd, *J* = 16.8, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.1 (C, C=O), 197.6 (C, C=O), 196.0 (C, C=O), 155.6 (C), 147.1 (C), 143.7 (C), 142.3 (C), 141.6 (CH), 136.8 (C), 136.2 (C), 136.2 (2 x CH), 132.0 (CH), 129.3 (2 x CH), 129.1 (CH), 128.4 (2 x CH), 126.4 (2 x CH), 123.3 (2 x CH), 123.0 (CH), 64.2 (C), 47.3 (CH), 37.9 (CH_2); LRMS m/z 422.00 ($M - H^+$), calcd for $C_{26}H_{17}NO_5$ 423.11; Anal. calcd for $C_{26}H_{17}NO_5$ (423.11): C, 73.75; H, 4.05; N, 3.31; Found: C, 73.65; H, 4.09; N, 3.38%.



6ai

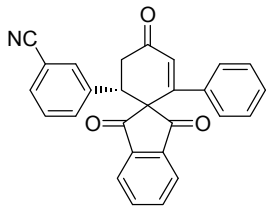
(*S*)-4-(1',3',5-trioxo-1-phenyl-1',3'-dihydrospiro[cyclohex[6]ene-2,2'-inden]-3-yl)benzonitrile (6aj): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 29.51 min (major), t_R = 33.55 min (minor). Mp 145 °C; **$[\alpha]_D^{25}$ = +61.81° (*c* = 0.50 g/100 mL, $CHCl_3$, 90% *ee*);** IR (Neat): ν_{max} 3067, 2915, 2228 (C≡N), 1738 (C=O), 1701 (C=O), 1667, 1589,1410, 1327, 1233, 1020, 882, 839, 781, 762, 743, 692 and 565 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.84 (1H, d, *J* = 7.6 Hz), 7.71 (1H, t, *J* = 6.8 Hz), 7.64 (1H, t, *J* = 7.6 Hz), 7.56 (1H, d, *J* = 7.6 Hz), 7.31 (2H, d, *J* = 8 Hz), 7.21–7.10 (5H, m), 6.91 (2H, d, *J* = 7.2 Hz), 6.48 (1H, s), 4.18 (1H, dd, *J* = 14.8, 3.6 Hz), 3.69 (1H, t, *J* = 15.2 Hz), 2.66 (1H, dd, *J* = 16.8, 3.6



6aj

Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.5 (C, C=O), 197.9 (C, C=O), 196.5 (C, C=O), 155.8 (C), 142.6 (C), 142.0 (2 x C), 137.1 (C), 136.4 (2 x CH), 132.3 (CH), 132.2 (2 x CH), 129.3 (CH), 129.2 (2 x CH), 128.7 (2 x CH), 126.7 (2 x CH), 123.5 (CH), 123.2 (CH), 118.0 (C, *C*≡N), 112.0 (C), 64.5 (C), 47.9 (CH), 38.0 (CH_2); LRMS m/z 402.00 ($M - H^+$), calcd for $C_{27}H_{17}NO_3$ 403.12; Anal. calcd for $C_{27}H_{17}NO_3$ (403.12): C, 80.38; H, 4.25; N, 3.47; Found: C, 80.26; H, 4.32; N, 3.41%.

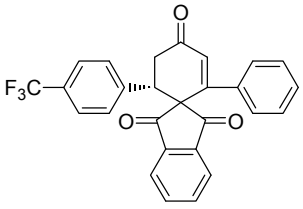
(*S*)-3-(1',3',5-trioxo-1-phenyl-1',3'-dihydrospiro[cyclohex[6]ene-2,2'-inden]-3-yl)benzonitrile (6ak):



6ak

Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 25.20 min (major), t_R = 28.75 min (minor). Mp 135 °C; **$[\alpha]_D^{25}$ = +56.61° (*c* = 0.46 g/100 mL, $CHCl_3$, 87% *ee*);** IR (Neat): ν_{max} 3067, 2922, 2853, 2230 (C≡N), 1738 (C=O), 1703 (C=O), 1593, 1429, 1250, 1159, 1024, 882, 762 and 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.89 (1H, d, *J* = 7.6 Hz), 7.71 (1H, t, *J* = 7.2 Hz), 7.63 (1H, t, *J* = 7.2 Hz), 7.58 (1H, d, *J* = 7.2 Hz), 7.30–7.27 (3H, m), 7.22–7.11 (4H, m), 6.93 (2H, d, *J* = 7.2 Hz), 6.49 (1H, s), 4.16 (1H, dd, *J* = 14.8, 3.6 Hz), 3.68 (1H, t, *J* = 16.0 Hz), 2.66 (1H, dd, *J* = 16.4, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.4 (C, C=O), 197.9 (C, C=O), 196.4 (C, C=O), 155.7 (C), 142.6 (C), 141.9 (C), 138.2 (C), 137.0 (C), 136.2 (2 x CH), 132.8 (CH), 132.2 (CH), 131.7 (2 x CH), 129.3 (2 x CH), 128.6 (2 x CH), 126.6 (2 x CH), 123.4 (CH), 123.2 (CH), 117.9 (C, *C*≡N), 112.6 (C), 64.5 (C), 47.5 (CH), 38.0 (CH_2); LRMS m/z 402.00 ($M - H^+$),calcd for $C_{27}H_{17}NO_3$ 403.12; Anal. calcd for $C_{27}H_{17}NO_3$ (403.12): C, 80.38; H, 4.25; N, 3.47; Found: C, 80.25; H, 4.32; N, 3.41%.

(*S*)-3'-phenyl-1'-(4-(trifluoromethyl)phenyl)spiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6al):

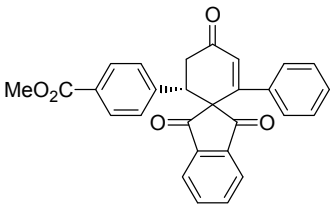


6al

Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 14.50 min (major), t_R = 18.86 min (minor). Mp 90 °C; **$[\alpha]_D^{25}$ = +57.78° (*c* = 0.50 g/100 mL, $CHCl_3$, 91% *ee*);** IR (Neat): ν_{max} 3059, 2915, 2207, 1734, 1699, 1674, 1595, 1424, 1330, 1233, 1165, 1128, 1067, 885, 785, 760, 692 and 604 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.83 (1H, d, *J* = 7.6 Hz), 7.67 (1H, t, *J* = 7.2 Hz), 7.62–7.54 (2H, m), 7.26 (2H, d, *J* = 7.6 Hz), 7.21–7.11 (5H, m), 6.94 (2H, d, *J* = 7.6 Hz), 6.49 (1H, s), 4.19 (1H, dd, *J* = 14.8, 3.6 Hz), 3.71 (1H, t, *J* = 15.2 Hz), 2.67 (1H, dd, *J* = 16.4, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.7 (C, C=O), 198.1 (C, C=O), 196.8 (C, C=O), 156.0 (C), 142.8 (C), 142.1 (C), 140.6 (C), 137.2 (C), 136.1 (2 x

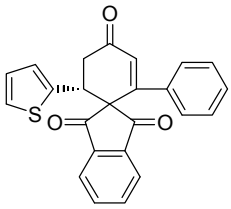
CH), 132.3 (CH), 130.1 (C, q, *C*F_3), 129.3 (CH), 128.8 (2 x CH), 128.6 (2 x CH), 126.7 (2 x CH), 125.4 (2 x CH), 125.4 (C), 123.4 (CH), 123.1 (CH), 64.7 (C), 48.0 (CH), 38.2 (CH_2); LRMS m/z 447.00 (M + H^+), calcd for $C_{27}H_{17}F_3O_3$ 446.11; Anal. calcd for $C_{27}H_{17}F_3O_3$ (446.11): C, 72.64; H, 3.84; Found: C, 72.51; H, 3.91%.

(*S*)-methyl 4-(1',3',5-trioxo-1-phenyl-1',3'-dihydrospiro[cyclohex[6]ene-2,2'-inden]-3-yl)benzoate (6am): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 14.90 min (major), t_R = 19.39 min (minor). Mp 85 °C; **$[\alpha]_D^{25}$ = +71.78° (*c* = 0.50 g/100 mL, $CHCl_3$, 95% *ee*);** IR (Neat): ν_{max} 3059, 2919, 2851, 1703, 1680, 1607, 1437, 1285, 1186, 1111, 1019, 889, 737 and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (1H, d, *J* = 7.6 Hz), 7.68–7.63 (3H, m), 7.59–7.52 (2H, m), 7.18 (1H, t, *J* = 7.2 Hz), 7.13–7.07 (4H, m), 6.93 (2H, d, *J* = 7.6 Hz), 6.48 (1H, s), 4.18 (1H, dd, *J* = 14.8, 4.0 Hz), 3.79 (3H, s, CO_2CH_3), 3.71 (1H, t, *J* = 15.2 Hz), 2.66 (1H, dd, *J* = 16.4, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.7 (C, C=O), 198.1 (C, C=O), 197.0 (C, C=O), 166.3 (C, O-C=O), 156.0 (C), 142.8 (C), 142.1 (C), 141.6 (C), 137.3 (C), 136.1 (2 x CH), 132.3 (CH), 129.7 (C), 129.6 (2 x CH), 129.2 (CH), 128.6 (2 x CH), 128.5 (2 x CH), 126.7 (2 x CH), 123.4 (CH), 123.1 (CH), 64.7 (C), 52.1 (CH_3, CO_2Me), 48.1 (CH), 38.3 (CH_2); LRMS m/z 437.00 (M + H^+), calcd for $C_{28}H_{20}O_5$ 436.46; Anal. calcd for $C_{28}H_{20}O_5$ (436.46): C, 77.05; H, 4.62; Found: C, 77.18; H, 4.58%.



6am

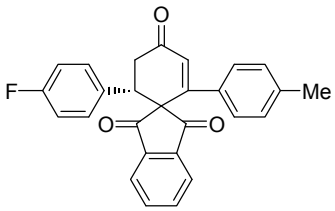
(*R*)-1-phenyl-3-(thiophen-2-yl)spiro[cyclohex[6]ene-2,2'-indene]-1',3',5-trione (6an): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 14.04 min (major), t_R = 16.26 min (minor). Mp 205 °C; **$[\alpha]_D^{25}$ = +42.08° (*c* = 0.17 g/100 mL, $CHCl_3$, 96% *ee*);** IR (Neat): ν_{max} 2917, 1734, 1705, 1676, 1597, 1262, 885 and 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (1H, d, *J* = 7.2 Hz), 7.73–7.69 (1H, m), 7.65 (2H, m), 7.20 (1H, t, *J* = 7.2 Hz), 7.13 (2H, t, *J* = 7.6 Hz), 6.93 (2H, d, *J* = 7.2 Hz), 6.87 (1H, d, *J* = 4.8 Hz), 6.69 (1H, d, *J* = 3.2 Hz), 6.60 (1H, dd, *J* = 8.4, 3.6 Hz), 6.48 (1H, s), 4.45 (1H, dd, *J* = 14.8, 4.0 Hz), 3.61 (1H, t, *J* = 14.8 Hz), 2.83 (1H, dd, *J* = 17.2, 4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.2 (C, C=O), 198.0 (C, C=O), 196.6 (C, C=O), 156.1 (C), 143.2 (C), 142.4 (C), 139.4 (C), 137.4 (C), 135.8 (2 x CH), 132.3 (CH), 129.2 (CH), 128.6 (2 x CH), 127.2 (CH), 126.6 (2 x CH), 126.5 (CH), 124.9 (CH), 123.5 (CH), 123.1 (CH), 65.1 (C),



6an

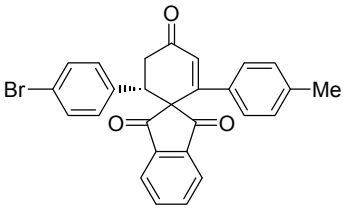
43.8 (CH), 40.1 (CH_2); LRMS m/z 385.00 ($M + H^+$), calcd for $C_{24}H_{16}O_3S$ 384.08; Anal. calcd for $C_{24}H_{16}O_3S$ (384.08): C, 74.98; H, 4.19; Found: C, 74.87; H, 4.23%.

(*S*)-1'-(4-fluorophenyl)-3'-(p-tolyl)spiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6bb): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 11.58 min (major), t_R = 20.83 min (minor). Mp 200 °C; **$[\alpha]_D^{25}$ = +42.27° (*c* = 0.60 g/100 mL, $CHCl_3$, 94% *ee*);** IR (Neat): ν_{max} 3067, 2920, 2855, 1738, 1699, 1672, 1601, 1510, 1233, 889, 835, 814, 785, 754, 588, 550 and 498 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (1H, d, *J* = 7.6 Hz), 7.69 (1H, t, *J* = 7.2 Hz), 7.62 (1H, t, *J* = 7.2 Hz), 7.57 (1H, d, *J* = 7.2 Hz), 6.97 (2H, br t, *J* = 8.8 Hz), 6.92 (2H, d, *J* = 8.0 Hz), 6.82 (2H, d, *J* = 8.0 Hz), 6.68 (2H, t, *J* = 8.4 Hz), 6.48 (1H, S), 4.10 (1H, dd, *J* = 14.8, 3.6 Hz), 3.64 (1H, t, *J* = 16.0Hz), 2.63 (1H, dd, *J* = 16.4, 3.6 Hz), 2.20 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.2 (C, C=O), 198.4 (C, C=O), 197.3 (C, C=O), 162.1 (C, d, *J* = 246 Hz), 156.2 (C), 142.9 (C), 142.2 (C), 139.4 (C), 135.9 (2 x CH), 134.6 (C), 132.4 (C, d, *J* = 3 Hz), 131.9 (CH), 130.0 (2 x CH, d, *J* = 8.0 Hz), 129.3 (2 x CH), 126.4 (2 x CH), 123.4 (CH), 123.0 (CH), 115.3 (2 x CH, d, *J* = 21.2 Hz), 64.9 (C), 47.8 (CH), 38.7 (CH_2), 21.2 (CH_3); LRMS m/z 409.00 ($M - H^+$), calcd for $C_{27}H_{19}FO_3$ 410.13; Anal. calcd for $C_{27}H_{19}FO_3$ (410.13): C, 79.01; H, 4.67; Found: C, 79.15; H, 4.61%.



6bb

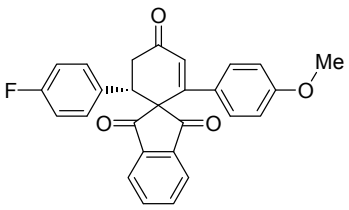
(*S*)-1'-(4-bromophenyl)-3'-(p-tolyl)spiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6be): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 12.25 min (major), t_R = 18.95 min (minor). Mp 170 °C; **$[\alpha]_D^{25}$ = +33.56° (*c* = 0.46 g/100 mL, $CHCl_3$, 92% *ee*);** IR (Neat): ν_{max} 3057, 2920, 2857, 1740, 1701,1665, 1590, 1489, 1327, 1242,1011, 887, 810, 764, 586 and 542 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.86 (1H, d, *J* = 7.5 Hz), 7.72 (1H, t, *J* = 7.5 Hz), 7.65 (1H, t, *J* = 7.5 Hz), 7.59 (1H, d, *J* = 7.5 Hz), 7.14 (2H, d, *J* = 8.0 Hz), 6.94 (2H, d, *J* = 8.0 Hz), 6.89 (2H, d, *J* = 9.0 Hz), 6.83 (2H, d, *J* = 8.0 Hz), 6.49 (1H, s), 4.09 (1H, dd, *J* = 14.5, 3.5 Hz), 3.65 (1H, t, *J* = 15 Hz), 2.64 (1H, dd, *J* = 17.0, 4.0 Hz), 2.22 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.0 (C, C=O), 198.3 (C, C=O), 197.1 (C, C=O), 156.1 (C), 142.9 (C), 142.2 (C), 139.4 (C), 136.02 (CH), 136.00 (CH), 135.7 (C), 134.5



6be

(C), 131.9 (CH), 131.5 (2 x CH), 130.0 (2 x CH), 129.3 (2 x CH), 126.6 (2 x CH), 123.4 (CH), 123.1 (CH), 122.0 (C), 64.7 (C), 47.8 (CH), 38.4 (CH_2), 21.1 (CH_3); LRMS m/z 470.00 (M^+), calcd for $C_{27}H_{19}BrO_3$ 470.05; Anal. calcd for $C_{27}H_{19}BrO_3$ (470.05): C, 68.80; H, 4.06; Found: C, 68.71; H, 4.12%.

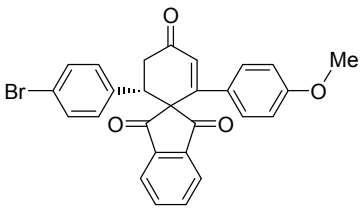
(*S*)-1'-(4-fluorophenyl)-3'-(4-methoxyphenyl)spiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6cb):



6cb

Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 16.51 min (major), t_R = 26.76 min (minor). Mp 195 °C; **$[\alpha]_D^{25}$ = +21.06° (*c* = 0.26 g/100 mL, $CHCl_3$, 94% *ee*);** IR (Neat): ν_{max} 3077, 3013, 2926, 2849, 1738, 1699, 1672, 1605, 1510, 1416, 1331, 1290, 1250, 1179, 1117, 1032, 897, 839, 787 and 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (1H, d, *J* = 7.6 Hz), 7.71 (1H, t, *J* = 7.2 Hz), 7.65 (1H, t, *J* = 7.2 Hz), 7.60 (1H, d, *J* = 7.2 Hz), 6.99 (2H, br t, *J* = 8.4 Hz), 6.90 (2H, d, *J* = 8.4 Hz), 6.69 (2H, t, *J* = 8.4 Hz), 6.66 (2H, d, *J* = 8.4 Hz), 6.50 (1H, s), 4.11 (1H, dd, *J* = 14.8, 3.6 Hz), 3.71 (3H, s, OC*H*$_3$), 3.64 (1H, t, *J* = 16.8 Hz), 2.65 (1H, dd, *J* = 16.4, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.4 (C, C=O), 198.5 (C, C=O), 197.3 (C, C=O), 162.1 (C, d, *J* = 246.1 Hz), 160.4 (C), 155.8 (C), 142.9 (C), 142.2 (C), 135.97 (CH), 135.92 (CH), 132.4 (C, d, *J* = 3.0 Hz), 131.6 (CH), 130.0 (2 x CH, d, *J* = 8.0 Hz), 129.8 (C), 128.1 (2 x CH), 123.4 (CH), 123.0 (CH), 115.3 (2 x CH, d, *J* = 21.2 Hz), 114.1 (2 x CH), 65.0 (C), 55.2 (CH_3, O*C*H$_3$), 47.9 (CH), 38.6 (CH_2); LRMS m/z 427.00 (M + H^+), calcd for $C_{27}H_{19}FO_4$ 426.13; Anal. calcd for $C_{27}H_{19}FO_4$ (426.13): C, 76.05; H, 4.49; Found: C, 76.15; H, 4.41%.

(*S*)-1'-(4-bromophenyl)-3'-(4-methoxyphenyl)spiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6ce):

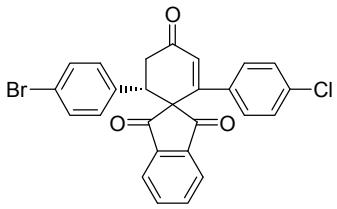


6ce

Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 19.08 min (major), t_R = 29.07 min (minor). Mp 140 °C; **$[\alpha]_D^{25}$ = +10.42° (*c* = 0.50 g/100 mL, $CHCl_3$, 95% *ee*);** IR (Neat): ν_{max} 2922, 2853, 1742, 1703, 1651, 1602, 1512, 1460, 1258, 1175, 1024, 884 and 820 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.86 (1H, d, *J* = 8.0 Hz), 7.73 (1H, t, *J* = 7.5 Hz), 7.66 (1H, t, *J* = 7 Hz), 7.61 (1H, d, *J* = 7.5 Hz), 7.13 (2H, d, *J* = 8 Hz), 6.88 (4H, d, *J* = 8.5 Hz), 6.65 (2H, d, *J* = 8.5 Hz), 6.48 (1H, s), 4.08 (1H, dd, *J* = 14.5, 3.5 Hz), 3.70 (3H, s, OC*H*$_3$), 3.63 (1H, t, *J* = 16.5 Hz), 2.63 (1H, dd, *J* = 17.0, 4.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.1 (C, C=O), 198.4 (C, C=O), 197.1 (C, C=O), 160.4 (C), 155.7 (C), 142.9 (C), 142.1 (C), 136.1 (CH), 136.0 (CH), 135.7 (C), 131.5 (2 x CH), 130.0 (2 x CH), 129.7 (C), 128.1 (2 x CH),

123.4 (CH), 123.1 (CH), 122.0 (C), 114.1 (3 x CH), 64.8 (C), 55.2 (CH_3, OCH_3), 47.9 (CH), 38.4 (CH_2); LRMS m/z 486.00 (M^+), calcd for $C_{27}H_{19}BrO_4$ 486.05; Anal. calcd for $C_{27}H_{19}BrO_4$ (486.05): C, 66.54; H, 3.93; Found: C, 66.48; H, 3.88%.

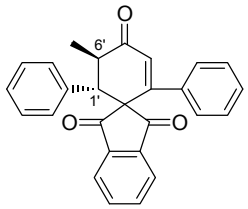
(*S*)-1'-(4-bromophenyl)-3'-(4-chlorophenyl)spiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6de):



6de

Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 15.38 min (major), t_R = 23.65 min (minor). **$[\alpha]_D^{25}$ = +15.24° (*c* = 0.17 g/100 mL, $CHCl_3$, 91% *ee*);** IR (Neat): ν_{max} 3067, 2924, 2857, 1736, 1703, 1674, 1591, 1489, 1252, 1094, 1013, 889, 818 and 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (1H, d, *J* = 7.6 Hz), 7.73 (1H, t, *J* = 7.2 Hz), 7.66 (1H, t, *J* = 7.2 Hz), 7.60 (1H, d, *J* = 7.2 Hz), 7.13 (2H, d, *J* = 8.8 Hz), 7.11 (2H, d, *J* = 8.8 Hz), 6.87 (4H, d, *J* = 8.0 Hz), 6.44 (1H, s), 4.08 (1H, dd, *J* = 14.4, 3.2 Hz), 3.64 (1H, t, *J* = 16 Hz), 2.64 (1H, dd, *J* = 16.8, 3.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.8 (C, C=O), 198.1 (C, C=O), 196.9 (C, C=O), 154.7 (C), 142.7 (C), 142.1 (C), 136.3 (2 x CH), 135.8 (C), 135.4 (2 x C), 132.7 (CH), 131.6 (2 x CH), 130.0 (2 x CH), 128.9 (2 x CH), 128.1 (2 x CH), 123.5 (CH), 123.2 (CH), 122.1 (C), 64.7 (C), 47.7 (CH), 38.4 (CH_2); LRMS m/z 493.00 (M+2 + H^+), calcd for $C_{26}H_{16}BrClO_3$ 490.00; Anal. calcd for $C_{26}H_{16}BrClO_3$ (490.00): C, 63.50; H, 3.28; Found: C, 63.41; H, 3.22%.

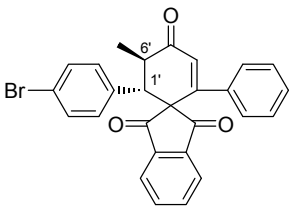
(1'*S*,6'*R*)-6'-methyl-1',3'-diphenylspiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6ea): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 90:10, flow rate 0.6 mL/min, λ = 254 nm), t_R = 12.10 min (major), t_R = 23.91 min (minor). Mp 195 °C; **$[\alpha]_D^{25}$ = +95.3° (*c* = 0.20 g/100 mL, $CHCl_3$, 99% *ee*; >99% *de*);** IR (Neat): ν_{max} 3027, 2930, 1740, 1707, 1667, 1591, 1493, 1455, 1375, 1331, 1273, 1236, 878, 766, 700, 592, 546 and 527 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.83 (1H, d, *J* = 7.6 Hz), 7.64 (1H, t, *J* = 7.2 Hz), 7.54 (1H, t, *J* = 7.2 Hz), 7.49 (1H, d, *J* = 7.2 Hz), 7.20 (1H, t, *J* = 7.2 Hz), 7.11 (2H, t, *J* = 7.6 Hz), 6.96–6.93 (7H, m), 6.49 (1H, s), 3.78 (1H, d, *J* = 13.2 Hz), 3.65 (1H, quintet, *J* = 7.2 Hz), 1.01 (3H, d, *J* = 6.8 Hz, CHC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.2 (C, C=O), 199.8 (C, C=O), 198.9 (C, C=O), 154.8 (C), 142.9 (C), 142.6 (C), 137.5 (C), 135.8 (C), 135.6 (2 x CH), 132.1 (CH), 129.1 (CH), 128.5 (3 x CH), 128.4 (3 x CH), 127.7 (CH), 126.7 (2 x CH),



6ea

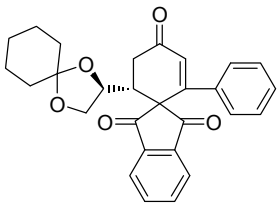
123.2 (CH), 123.0 (CH), 65.5 (C), 55.1 (CH), 40.3 (CH), 12.7 (CH_3); LRMS m/z 393.00 ($M + H^+$), calcd for $C_{27}H_{20}O_3$ 392.14; Anal. calcd for $C_{27}H_{20}O_3$ (392.14): C, 82.63; H, 5.14; Found: C, 82.45; H, 5.21%.

(1'*S*,6'*R*)-1'-(4-bromophenyl)-6'-methyl-3'-phenylspiro[cyclohex[3']ene-2',2'-indene]-1',3',5'-trione (6ee): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 16.47 min (major), t_R = 21.64 min (minor). Mp 125 °C; **$[\alpha]_D^{25}$ = +67.79° (*c* = 1.15 g/100 mL, $CHCl_3$, 90% *ee*; >99% *de*);** IR (Neat): ν_{max} 3059, 2973, 2933, 2876, 1738, 1703, 1669, 1487, 1445, 1337, 1265, 1238, 1072, 1009, 909, 878, 820, 783, 766, 747, 702 and 548 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.83 (1H, d, *J* = 7.6 Hz), 7.68 (1H, t, *J* = 7.2 Hz), 7.59 (1H, t, *J* = 7.2 Hz), 7.52 (1H, d, *J* = 7.6 Hz), 7.27–7.07 (5H, m), 6.91–6.86 (4H, m), 6.45 (1H, s), 3.76 (1H, d, *J* = 17.6 Hz), 3.63–3.55 (1H, m), 0.98 (3H, d, *J* = 6.8 Hz, $CHCH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.9 (C, C=O), 199.2 (C, C=O), 198.8 (C, C=O), 154.7 (C), 142.7 (C), 142.4 (C), 137.2 (C), 136.0 (2 x CH), 135.1 (C), 131.9 (CH), 131.6 (2 x CH), 129.1 (CH), 128.5 (4 x CH), 126.8 (2 x CH), 123.3 (CH), 123.1 (CH), 121.8 (C), 65.2 (C), 54.2 (CH), 40.2 (CH), 12.7 (CH_3); LRMS m/z 470.00 (M^+), calcd for $C_{27}H_{19}BrO_3$ 470.05; Anal. calcd for $C_{27}H_{19}BrO_3$ (470.05): C, 68.80; H, 4.06; Found: C, 68.71; H, 4.12%.



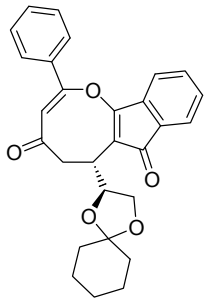
6ee

(*R*)-1-phenyl-3-((*S*)-1,4-dioxaspiro[4.5]decan-2-yl)spiro[cyclohex[6]ene-2,2'-indene]-1',3',5-trione (6ao): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 120 °C; **$[\alpha]_D^{25}$ = –15.82° (*c* = 0.28 g/100 mL, $CHCl_3$, >99% *ee*, >99 *de*);** IR (Neat): ν_{max} 3061, 2934, 2859, 1757, 1744, 1713, 1674, 1597, 1447, 1256, 1161, 1107, 939, 887, 847, 764, 737 and 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.12 (1H, d, *J* = 7.6 Hz), 7.94–7.82 (3H, m), 7.22 (1H, t, *J* = 7.2 Hz), 7.14 (2H, t, *J* = 7.6 Hz), 6.91 (2H, d, *J* = 7.6 Hz), 6.39 (1H, s), 3.87–3.80 (2H, m), 3.62 (1H, t, *J* = 6 Hz), 3.28 (1H, dd, *J* = 17.2, 14.0 Hz), 3.02 (1H, br d, *J* = 13.6 Hz), 2.55 (1H, dd, *J* = 17.2, 3.6 Hz), 1.70–1.35 (6H, m), 1.18–1.07 (4H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 201.2 (C, C=O), 197.9 (C, C=O), 196.1 (C, C=O), 156.9 (C), 143.5 (C), 142.2 (C), 137.4 (C), 136.2 (CH), 135.6 (CH), 132.2 (CH), 129.1 (CH), 128.5 (2 x CH), 126.6 (2 x CH), 123.9 (CH), 123.0 (CH), 110.8 (C, O-*C*-O), 73.0 (CH), 65.7 (CH_2), 62.7 (C), 46.1 (CH), 35.3 (CH_2), 33.7 (CH_2), 32.3 (CH_2), 24.9 (CH_2), 23.8 (CH_2), 23.3 (CH_2); LRMS m/z 441.00 ($M - H^+$), calcd for $C_{28}H_{26}O_5$ 442.18; Anal. calcd for $C_{28}H_{26}O_5$ (442.18): C, 76.00; H, 5.92; Found: C, 76.18; H, 5.86%.



6ao

(*R*,*Z*)-2-phenyl-6-((*S*)-1,4-dioxaspiro[4.5]decan-2-yl)-5,6-dihydroindeno[1,2-b]oxocine-4,7-dione (7ao):

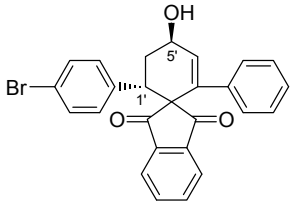


7ao

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as viscous liquid. **$[\alpha]_D^{25}$ = –59.02° (*c* = 0.43 g/100 mL, $CHCl_3$, >99% *ee*, >99 *de*);** IR (Neat): ν_{max} 3063, 2936, 2859, 1711, 1661, 1609, 1449, 1368, 1331, 1263, 1163, 1103, 928, 862, 764, 735 and 692 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.91–7.89 (2H, m), 7.57–7.52 (3H, m), 7.44–7.42 (1H, m), 7.23–7.22 (2H, m), 6.87–6.85 (1H, m), 6.32 (1H, s), 4.40 (1H, q, *J* = 6.0 Hz), 4.06 (1H, t, *J* = 8.0 Hz), 3.94 (1H, t, *J* = 6.5 Hz), 3.67 (1H, t, *J* = 12.0 Hz), 3.16–3.11 (1H, m), 2.79 (1H, dd, *J* = 11.5, 5.0 Hz), 1.67–1.55 (6H, m), 1.42–1.38 (4H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 201.1 (C, C=O), 194.1 (C, C=O), 173.6 (C), 163.1 (C), 140.3 (C), 133.4 (CH), 133.3 (C), 131.2 (CH), 130.4 (C), 129.8 (CH), 129.1 (2 x CH), 125.8 (2 x CH), 122.4 (CH), 122.1 (C), 119.4 (CH), 114.2 (CH), 110.2 (C, O-*C*-O), 77.0 (CH), 67.4 (CH_2), 40.7 (CH_2), 36.1 (CH_2), 35.2 (CH), 34.7 (CH_2), 25.2 (CH_2), 24.0 (CH_2), 23.8 (CH_2); LRMS m/z 441.00 ($M - H^+$), calcd for $C_{28}H_{26}O_5$ 442.18; Anal. calcd for $C_{28}H_{26}O_5$ (442.18): C, 76.00; H, 5.92; Found: C, 76.12; H, 5.88%.

(*S*,*Z*)-2,6-diphenyl-5,6-dihydroindeno[1,2-b]oxocine-4,7-dione (7aa): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm), t_R = 10.70 min (major), t_R = 14.45 min (minor). Mp 105 °C; **$[\alpha]_D^{25}$ = +51.8° (*c* = 0.62 g/100 mL, $CHCl_3$, 91% *ee*);** IR (Neat): ν_{max} 3057, 2924, 2853, 1726, 1653, 1632, 1613, 1493, 1447, 1362, 1325, 1262, 1072, 968, 862, 775, 762, 733, 702 and 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 (2H, br s), 7.58 (3H, br s), 7.47 (2H, d, *J* = 7.2 Hz), 7.36 (3H, t, *J* = 6.8 Hz), 7.28–7.19 (3H, m), 6.93 (1H, d, *J* = 6.4 Hz), 6.39 (1H, s), 4.21 (1H, dd, *J* = 12.4, 4.8 Hz), 3.99 (1H, t, *J* = 11.6 Hz), 2.88 (1H, dd, *J* = 10.8, 4.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.8 (C, C=O), 193.6 (C, C=O), 172.7 (C), 164.8 (C), 141.1 (2 x C), 140.6 (C), 133.4 (CH), 131.3 (CH), 130.2 (C), 129.5 (CH), 129.0 (2 x CH), 128.8 (2 x CH), 127.5 (2 x CH), 127.1 (CH), 125.7 (2 x CH), 125.1 (C), 122.3 (CH), 119.4 (CH), 114.9 (CH), 47.0 (CH), 31.8 (CH_2); LRMS m/z 379.00 ($M + H^+$), calcd for $C_{26}H_{18}O_3$ 378.13; Anal. calcd for $C_{26}H_{18}O_3$ (378.13): C, 82.52; H, 4.79; Found: C, 82.45; H, 4.71%.

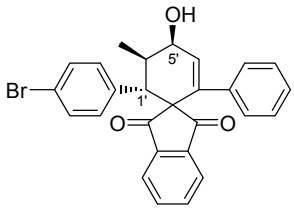
(1'*S*,5'*R*)-1'-(4-bromophenyl)-5'-hydroxy-3'-phenylspiro[cyclohex[3']ene-2',2'-indene]-1',3'-dione (8ae):



8ae

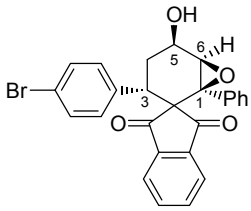
Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 30.82 min (major), t_R = 36.92 min (minor). **$[\alpha]_D^{25}$ = +6.22° (*c* = 0.50 g/100 mL, $CHCl_3$, 90% *ee*; >99 *de*);** IR (Neat): ν_{max} 3416 (OH), 3060, 2930, 2865, 1738 (C=O), 1701 (C=O), 1593, 1491, 1443, 1410, 1350, 1252, 1051, 1032, 889, 824, 764, 737, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (1H, d, *J* = 7.2 Hz), 7.59–7.54 (3H, m), 7.07 (2H, d, *J* = 6.8 Hz), 7.04–6.99 (3H, m), 6.89 (2H, d, *J* = 7.6 Hz), 6.84 (2H, d, *J* = 8.0 Hz), 6.28 (1H, s), 4.71 (1H, br s, C*H*OH), 3.60 (1H, d, *J* = 13.6 Hz, ArC*H*), 2.95 (1H, br s, O*H*), 2.83 (1H, q, *J* = 12.8 Hz), 2.26 (1H, dd, *J* = 12.0, 6.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 202.4 (C, C=O), 201.7 (C, C=O), 142.6 (C), 142.3 (C), 139.1 (C), 137.54 (C), 137.50 (CH), 137.0 (C), 135.7 (CH), 135.6 (CH), 131.2 (2 x CH), 130.0 (2 x CH), 128.1 (2 x CH), 127.8 (2 x CH), 127.6 (CH), 122.9 (CH), 122.6 (CH), 121.3 (C), 67.6 (O*C*H), 64.5 (C), 46.1 (CH), 33.4 (CH_2); LRMS m/z 459.00 ($M + 2 - H^+$), calcd for $C_{26}H_{19}BrO_3$ 458.05; Anal. calcd for $C_{26}H_{19}BrO_3$ (458.05): C, 67.99; H, 4.17; Found: C, 67.83; H, 4.21%.

(1'*S*,5'*R*,6'*R*)-1'-(4-bromophenyl)-5'-hydroxy-6'-methyl-3'-phenylspiro[cyclohex[3']ene-2',2'-indene]-1',3'-dione (8ee): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as viscous liquid. **$[\alpha]_D^{25}$ = +19.46° (*c* = 0.68 g/100 mL, $CHCl_3$, 90% *ee*; >99% *de*);** IR (Neat): ν_{max} 3462 (OH), 2974, 2928, 2868, 1740 (C=O), 1701 (C=O), 1591, 1489, 1240, 1031, 764 and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.72 (1H, d, *J* = 7.2 Hz), 7.60 (1H, t, *J* = 6.4 Hz), 7.55–7.50 (2H, m), 7.09–7.01 (5H, m), 6.89 (2H, d, *J* = 6.8 Hz), 6.81 (2H, br s), 6.22 (1H, s), 4.19 (1H, br s, C*H*OH), 3.35 (1H, d, *J* = 12.4 Hz, ArC*H*), 2.85–2.78 (1H, m), 2.41 (1H, br s, O*H*), 0.92 (3H, d, *J* = 6.4 Hz, CHCH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 202.2 (C, C=O), 202.0 (C, C=O), 142.6 (C), 142.5 (C), 139.0 (C), 136.8 (C), 136.6 (CH), 135.8 (C), 135.6 (CH), 135.6 (CH), 131.2 (2 x CH), 128.1 (3 x CH), 127.9 (3 x CH), 127.6 (CH), 122.9 (CH), 122.7 (CH), 121.1 (C), 73.9 (CH), 65.1 (C), 52.6 (CH), 36.1 (CH), 16.1 (CH_3); LRMS m/z 472.00 (M^+), calcd for $C_{27}H_{21}BrO_3$ 472.07; Anal. calcd for $C_{27}H_{21}BrO_3$ (472.07): C, 68.51; H, 4.47; Found: C, 68.51; H, 4.43%.



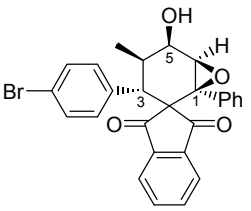
8ee

(1*S*,3*S*,5*R*,6*R*)-3-(4-bromophenyl)-5-hydroxy-1-phenyl-7-oxaspiro[bicyclo[4.1.0]heptane-2,2'-indene]-1',3'-dione (9ae): Prepared by following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as gummy solid. **$[\alpha]_D^{25}$ = –81.40° (*c* = 0.50 g/100 mL, $CHCl_3$, 90% *ee*; >99% *de*);** IR (Neat): ν_{max} 3430 (OH), 3061, 2930, 1744 (C=O), 1705 (C=O), 1593, 1489, 1449, 1426, 1258, 1180, 1049, 1011, 947, 870, 824, 770, 737, 700 and 669 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73 (1H, d, *J* = 7.6 Hz), 7.59 (1H, t, *J* = 7.6 Hz), 7.49 (1H, t, *J* = 7.2 Hz), 7.39 (1H, d, *J* = 7.6 Hz), 7.13 (2H, d, *J* = 8.4 Hz), 7.03–6.98 (5H, m), 6.92 (2H, d, *J* = 8.4 Hz), 4.53–4.49 (1H, m), 3.60–3.56 (2H, m), 2.93 (1H, q, *J* = 12.8 Hz), 2.08–2.04 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.8 (C, C=O), 197.8 (C, C=O), 143.1 (C), 142.2 (C), 137.5 (C), 136.2 (C), 135.7 (CH), 135.5 (CH), 131.2 (2 x CH), 130.6 (2 x CH), 128.4 (2 x CH), 128.3 (CH), 127.7 (2 x CH), 122.8 (CH), 122.7 (CH), 121.2 (C), 68.7 (CH), 67.7 (C), 61.8 (CH), 60.2 (C), 44.0 (CH), 30.2 (CH_2); LRMS m/z 475.00 ($M + H^+$), calcd for $C_{26}H_{19}BrO_4$ 474.05; Anal. calcd for $C_{26}H_{19}BrO_4$ (474.05): C, 65.70; H, 4.03; Found: C, 65.81; H, 4.08%.



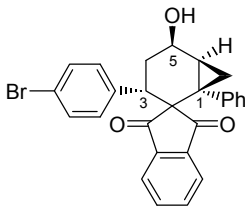
9ae

(1*S*,3*S*,4*R*,5*R*,6*R*)-3-(4-bromophenyl)-5-hydroxy-4-methyl-1-phenyl-7-oxaspiro[bicyclo[4.1.0]heptane-2,2'-indene]-1',3'-dione (9ee): Prepared by following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as viscous liquid. **$[\alpha]_D^{25}$ = –59.36° (*c* = 0.54 g/100 mL, 90% *ee*; >99% *de*);** IR (Neat): ν_{max} 3482 (OH), 3061, 2971, 2930, 2876, 1742 (C=O), 1705 (C=O), 1593, 1489, 1449, 1412, 1352, 1258, 1047, 1013, 945, 903, 880, 770, 737 and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.74 (1H, d, *J* = 7.6 Hz), 7.59 (1H, t, *J* = 7.2 Hz), 7.48 (1H, t, *J* = 7.6 Hz), 7.36 (1H, d, *J* = 7.6 Hz), 7.22 (1H, br s), 7.05–6.97 (7H, m), 6.68 (1H, br s), 4.01 (1H, d, *J* = 8.8 Hz), 3.59 (1H, br s), 3.29 (1H, d, *J* = 12.0 Hz), 2.92–2.85 (1H, m), 0.91 (3H, d, *J* = 6.8 Hz, CHC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.5 (C, C=O), 198.2 (C, C=O), 142.9 (C), 141.9 (C), 136.2 (C), 135.6 (CH), 135.5 (C), 135.4 (CH), 132.6 (CH), 131.2 (CH), 131.0 (2 x CH), 128.3 (3 x CH), 127.7 (2 x CH), 122.7 (2 x CH), 121.1 (C), 74.5 (CH), 67.3 (C), 61.7 (CH), 61.3 (C), 50.8 (CH), 32.8 (CH), 15.3 (CH_3); LRMS m/z 489.00 ($M + H^+$), calcd for $C_{27}H_{21}BrO_4$ 488.06; Anal. calcd for $C_{27}H_{21}BrO_4$ (488.06): C, 66.27; H, 4.33; Found: C, 66.15; H, 4.38%.



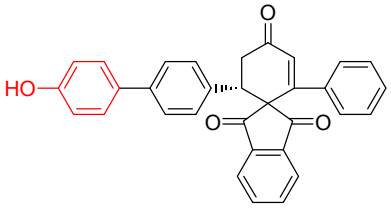
9ee

(1*R*,3*S*,5*R*,6*S*)-3-(4-bromophenyl)-5-hydroxy-1-phenylspiro[bicyclo[4.1.0]heptane-2,2'-indene]-1',3'-dione (10ae): Prepared by following the procedure **F** and purified by column chromatography using EtOAc/hexane and isolated as viscous liquid. **$[\alpha]_D^{25}$ = –72.08° (*c* = 0.23 g/100 mL, $CHCl_3$, 90% *ee*; >99% *de*);** IR (Neat): ν_{max} 3426 (OH), 3057, 2932, 1740 (C=O), 1701 (C=O), 1593, 1489, 1411, 1350, 1258, 1119, 1040, 876, 826, 799, 770, 737, 702 and 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.76 (1H, d, *J* = 7.6 Hz), 7.63 (1H, t, *J* = 7.2 Hz), 7.52 (1H, t, *J* = 7.6 Hz), 7.32 (1H, d, *J* = 7.6 Hz), 7.12 (2H, d, *J* = 8 Hz), 7.00–6.73 (7H, m), 4.68 (1H, m), 3.46 (1H, d, *J* = 13.6 Hz), 2.43 (1H, q, *J* = 12.8 Hz), 2.21 (1H, t, *J* = 5.6 Hz), 2.05–1.98 (2H, m), 1.89 (1H, br s, OH), 0.87 (1H, dd, *J* = 8.8, 6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 201.9 (2 x C, C=O), 142.7 (C), 142.4 (C), 142.2 (C), 138.3 (C), 135.4 (CH), 135.3 (CH), 131.1 (2 x CH), 131.0 (CH), 130.7 (2 x CH), 127.7 (2 x CH), 127.0 (2 x CH), 122.7 (CH), 122.5 (CH), 121.0 (C), 68.0 (CH), 58.4 (C), 44.3 (CH), 36.6 (C), 30.9 (CH_2), 26.8 (CH), 12.4 (CH_2); LRMS m/z 471.00 ($M - H^+$), calcd for $C_{27}H_{21}BrO_3$ 472.07; Anal. calcd for $C_{27}H_{21}BrO_3$ (472.07): C, 68.51; H, 4.47; Found: C, 68.42; H, 4.52%.



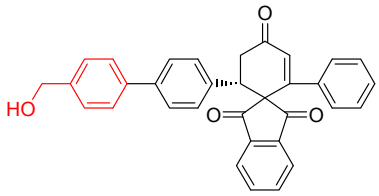
10ae

(*S*)-3'-(4'-hydroxy-[1,1'-biphenyl]-4-yl)-1'-phenylspiro[cyclohex[6']ene-2',2'-indene]-1',3',5'-trione (11aea): Prepared by following the procedure **G** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 23.72 min (major), t_R = 34.53 min (minor). Mp 125 °C; **$[\alpha]_D^{25}$ = +34.83° (*c* = 0.68 g/100 mL, $CHCl_3$, 90% *ee*);** IR (Neat): ν_{max} 3028 (OH), 2917, 1740 (C=O), 1704 (C=O), 1663, 1591, 1499, 1445, 1331, 1252, 1024, 887, 824, 762, 696, and 527 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (1H, d, *J* = 7.6 Hz), 7.64–7.61 (1H, m), 7.56–7.55 (2H, m), 7.24–7.12 (7H, m), 7.03 (2H, d, *J* = 8.0 Hz), 6.96 (2H, d, *J* = 7.6 Hz), 6.83 (2H, d, *J* = 8.4 Hz), 6.52 (1H, s), 4.16 (1H, dd, *J* = 14.8, 3.6 Hz), 3.73 (1H, t, *J* = 16.4 Hz), 2.71 (1H, dd, *J* = 16.8, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.4 (C, C=O), 198.6 (C, C=O), 198.4 (C, C=O), 157.0 (C), 156.0 (C), 143.0 (C), 142.3 (C), 140.5 (C), 137.4 (C), 135.9 (2 x CH), 134.5 (C), 132.2 (CH), 132.1 (C), 129.3 (CH), 128.7 (4 x CH), 128.0 (2 x CH), 126.6 (2 x CH), 126.4 (2 x CH), 123.4 (CH), 123.1 (CH), 115.8 (2 x CH), 65.2 (C), 48.3 (CH), 38.6 (CH_2); LRMS m/z 471.00 ($M + H^+$), calcd for $C_{32}H_{22}O_4$ 470.15; Anal. calcd for $C_{32}H_{22}O_4$ (470.15): C, 81.69; H, 4.71; Found: C, 81.57; H, 4.82%.



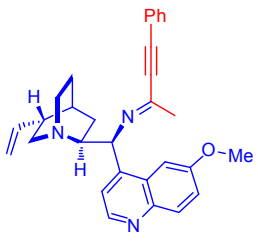
11aea

(*S*)-3'-(4'-(hydroxymethyl)-[1,1'-biphenyl]-4-yl)-1'-phenylspiro[cyclohex[6']ene-2',2'-indene]-1',3',5'-trione (11aeb): Prepared by following the procedure **G** and purified by column chromatography using EtOAc/hexane and isolated as viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 28.86 min (major), t_R = 33.99 min (minor). **$[\alpha]_D^{25}$ = +26.44° (*c* = 0.78 g/100 mL, $CHCl_3$, 90% *ee*);** IR (Neat): ν_{max} 3540 (OH), 2922, 2855, 1732 (C=O), 1698 (C=O), 1667, 1590, 1497, 1404, 1323, 1252, 1044, 812, 777, 762, 694, 594 and 569 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.83 (1H, d, *J* = 7.6 Hz), 7.64–7.60 (1H, m), 7.55 (2H, br s), 7.37–7.31 (4H, m), 7.20 (3H, m), 7.13 (2H, t, *J* = 7.6 Hz), 7.04 (2H, d, *J* = 8 Hz), 6.95 (2H, d, *J* = 7.6 Hz), 6.50 (1H, s), 4.69 (2H, s, CH_2OH), 4.15 (1H, dd, *J* = 14.4, 3.2 Hz), 3.71 (1H, t, *J* = 15.2 Hz), 2.68 (1H, dd, *J* = 16.4, 3.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.2 (C, C=O), 198.4 (C, C=O), 197.7 (C, C=O), 156.3 (C), 143.0 (C), 142.3 (C), 140.4 (2 x C), 139.3 (C), 137.5 (C), 135.8 (2 x CH), 135.5 (C), 132.4 (CH), 129.2 (CH), 128.8 (2 x CH), 128.6 (2 x CH), 127.4 (2 x CH), 126.9 (4 x CH), 126.6 (2 x CH), 123.4 (CH), 123.0 (CH), 65.1 (C), 64.9 (CH_2), 48.3 (CH), 38.5 (CH_2); LRMS m/z 485.00 ($M + H^+$), calcd for $C_{33}H_{24}O_4$ 484.00; Anal. calcd for $C_{33}H_{24}O_4$ (484.00): C, 81.80; H, 4.99; Found: C, 81.65; H, 5.06%.



11aeb

(*S*,*E*)-1-(6-methoxyquinolin-4-yl)-N-(4-phenylbut-3-yn-2-ylidene)-1-((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methanamine (A'): ^1H NMR ($CDCl_3$) δ 8.73 (1H, d, *J* = 4.4 Hz), 8.01 (1H, d, *J* = 9.2 Hz), 7.77 (1H, br s), 7.56–7.53 (1H, m), 7.41–7.32 (6H, m), 5.83–5.74 (1H, m), 5.64 (1H, d, *J* = 9.6 Hz), 4.96 (2H, m), 3.65 (3H, s, OCH_3), 3.37–3.32 (1H, m), 3.26 (1H, dd, *J* = 14.0, 10.4 Hz), 2.84–2.75 (2H, m), 2.62 (2H, br s), 2.29 (3H, s, CH_3), 1.62–1.56 (3H, m), 1.41–1.36 (1H, m), 0.89–0.85 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 157.6 (C), 151.2 (C), 147.7 (CH), 145.7 (C), 144.8 (C), 141.7 (CH), 131.7 (2 x CH), 131.7 (CH), 129.7 (CH), 128.6 (2 x CH), 128.4 (C), 121.8 (CH), 121.4 (CH), 121.2 (C), 114.3 (CH_2), 102.7 (CH), 96.3 (C), 83.7 (C), 61.3 (CH), 56.2 (CH_2), 55.3 (CH_3, OCH_3), 41.2 (CH_2), 39.8 (CH), 28.3 (CH_2), 28.0 (2 x CH), 27.7 (CH_3), 25.2 (CH_2); LRMS m/z 450.70 ($M + H^+$), calcd for $C_{30}H_{31}N_3O$ (449.5868).



A'

References:

1. a) S. Rondeau-Gagne, C. Curutchet, F. Grenier, G. D. Scholes, *Tetrahedron* **2010,** *66,* 4230-4242; b) A. Zanka, *Organic Process Research & Development* **1998**, *2,* 60-62.
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3. M. Prieto, S. Mayor, K. Rodriguez, P. Lloyd-Williams, E. Giralt, *J. Org. Chem.* **2007,** *72*, 1047-1050.
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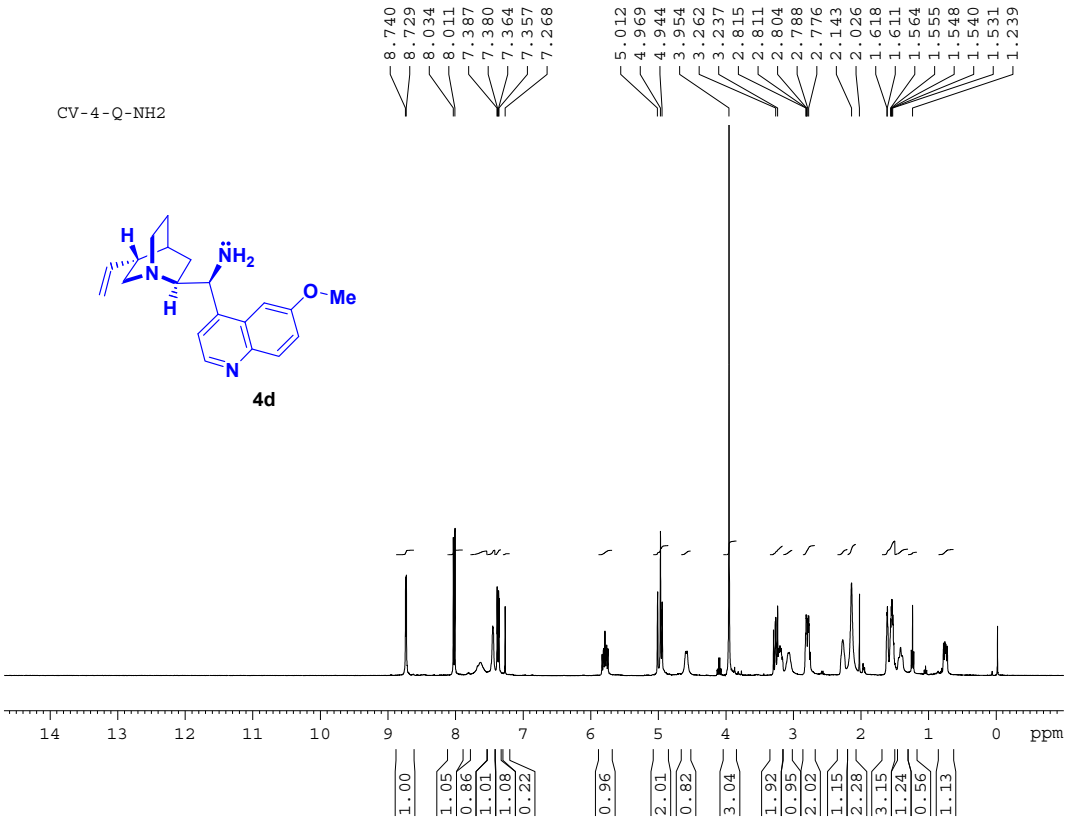
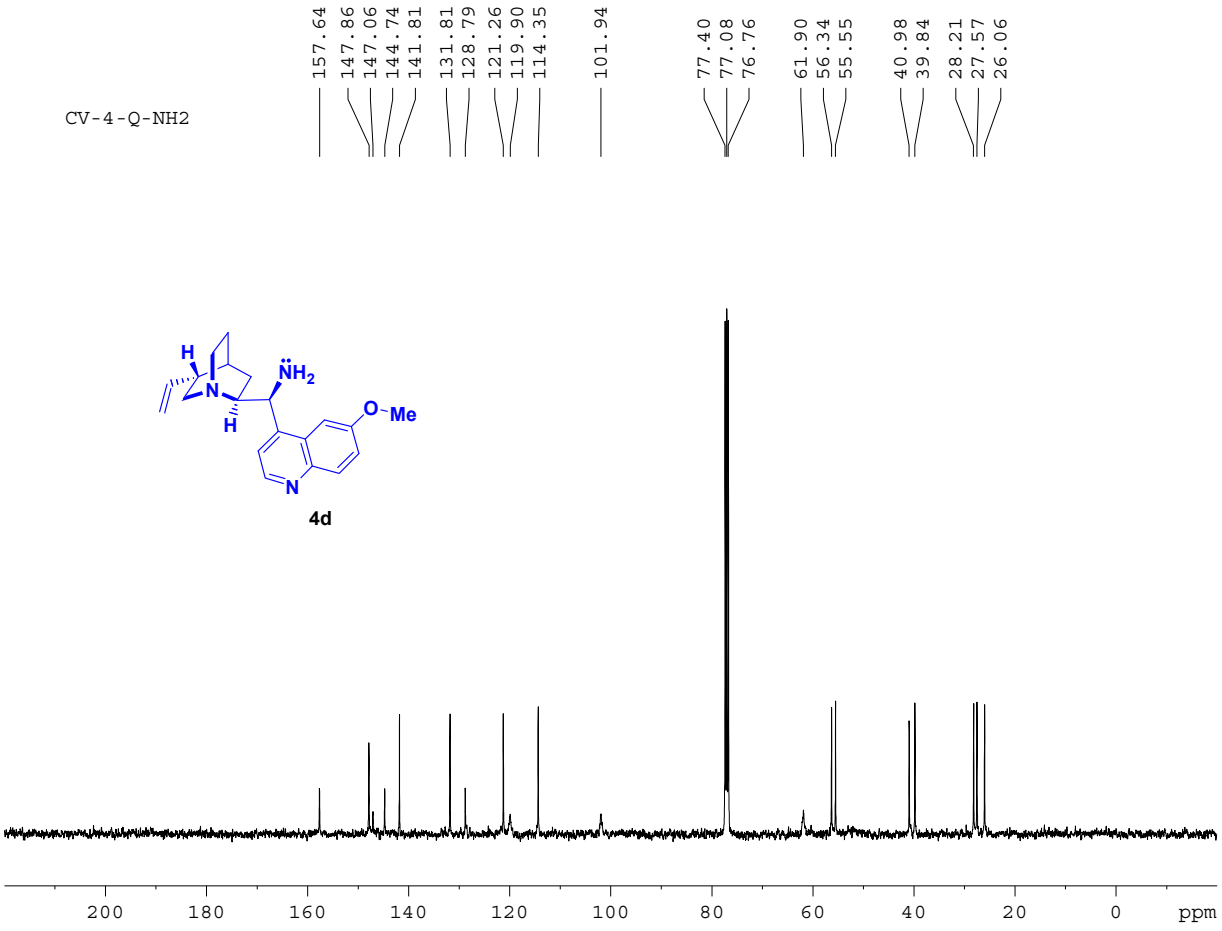
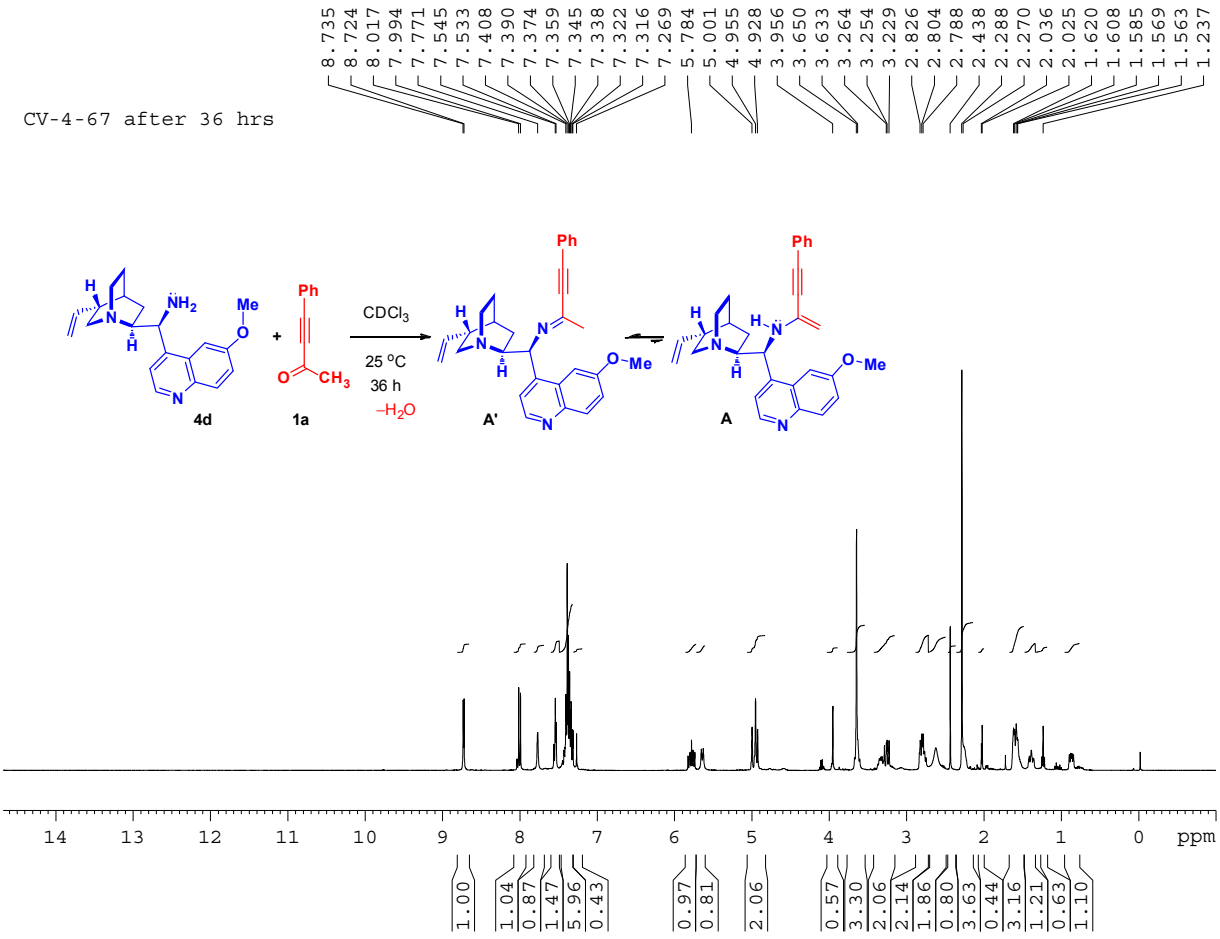
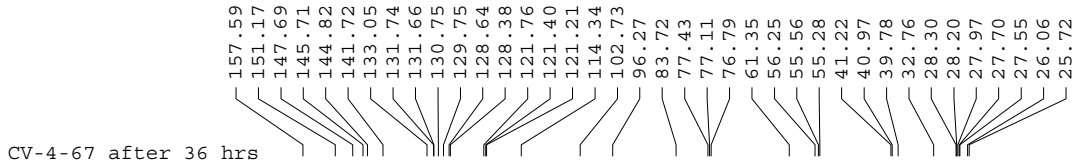
Spectra's for the controlled NMR experiments to prove *in situ* formation of 2-aminobuta-1,3-enyne:




CV-4-Q-NH2
157.64
147.86
147.06
144.74
141.81
131.81
128.79
121.26
119.90
114.35
101.94
77.40
77.08
76.76
61.90
56.34
55.55
40.98
39.84
28.21
27.57
26.06
H
N
H
NH2
O
Me
N
4d
200
180
160
140
120
100
80
60
40
20
0
ppm


CV-4-67 after 36 hrs
8.735
8.724
8.017
7.994
7.771
7.545
7.533
7.408
7.390
7.374
7.359
7.345
7.338
7.322
7.316
7.269
5.784
5.001
4.955
4.928
3.956
3.650
3.633
3.264
3.254
3.229
2.826
2.804
2.788
2.438
2.288
2.270
2.036
2.025
1.620
1.608
1.585
1.569
1.563
1.237
CDCl3
25 °C
36 h
–H2O
4d
1a
A'
A
ppm
1.00
1.04
0.87
1.47
5.96
0.43
0.97
0.81
2.06
0.57
3.30
2.06
2.14
1.86
0.80
3.63
0.44
3.16
1.21
0.63
1.10


157.59
151.17
147.69
145.71
144.82
141.72
133.05
131.74
131.66
130.75
129.75
128.64
128.38
121.76
121.40
121.21
114.34
102.73
96.27
83.72
77.43
77.11
76.79
61.35
56.25
55.56
55.28
41.22
40.97
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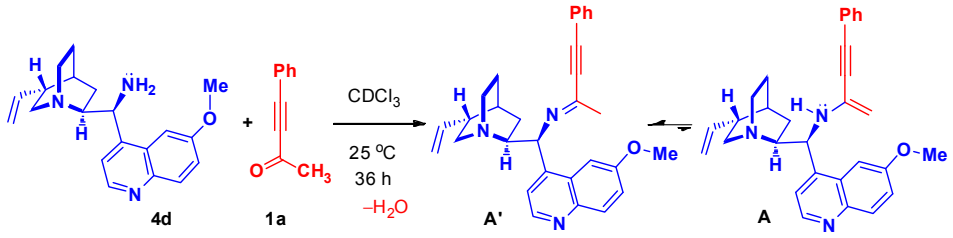
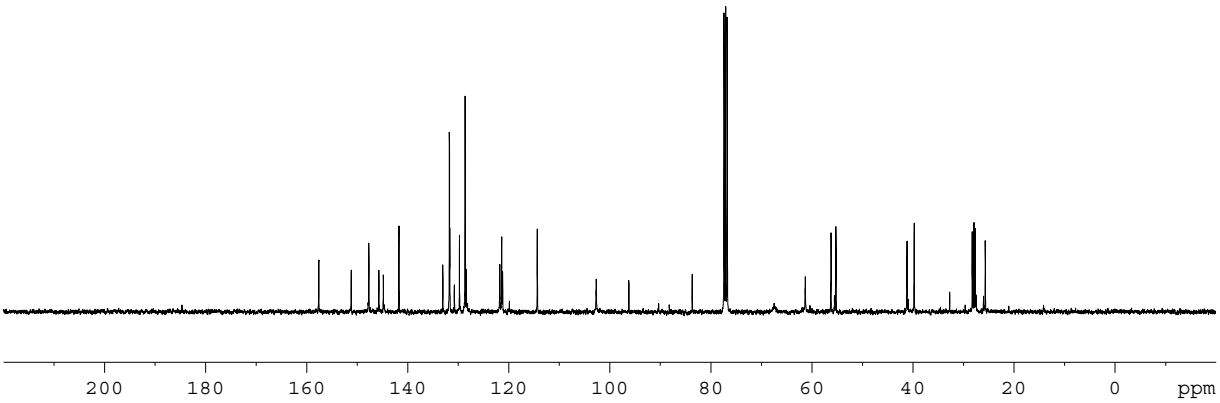
28.30
28.20
27.97
27.70
27.55
26.06
25.72
CV-4-67 after 36 hrs


Ph
CDCl3
25 °C
36 h
–H2O
4d
1a
A'
A


200
180
160
140
120
100
80
60
40
20
0
ppm

Check CIF/PLATON (standard) for Datablock: DBR-12a [6be]

Bond precision: C-C = 0.0042 A Wavelength=1.54184

Cell: a=8.5036(15) b=12.3169(10) c=21.639(4)

alpha=90 beta=90 gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2266.4(6)	2266.4(6)
Space group	P 21 21 21	P2(1)2(1)2(
Hall group	P 2ac 2ab	?
Moiety formula	C27 H19 Br O3	?
Sum formula	C27 H19 Br O3	C27 H19 Br O3
Mr	471.32	471.33
Dx,g cm-3	1.381	1.381
Z	4	4
Mu (mm-1)	2.674	2.674
F000	960.0	960.0
F000'	959.74	
h,k,lmax	10,15,26	10,15,26
Nref	2591[4537]	4488
Tmin,Tmax	0.374,0.586	0.400,0.617
Tmin'	0.283	

Correction method= MULTI-SCAN

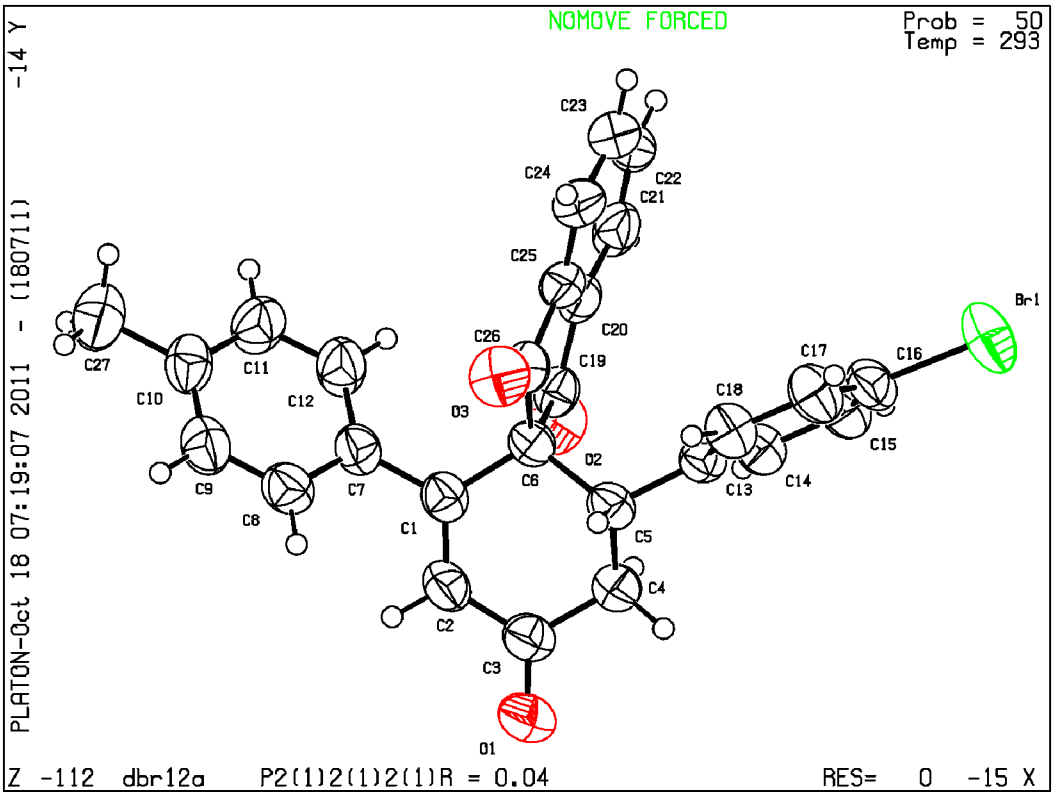
Data completeness= 1.73/0.99 Theta(max)= 73.110

R(reflections)= 0.0355(3736) wR2(reflections)= 0.0964(4488)

S = 1.051 Npar= 286

PLATON version of 18/07/2011; check.def file version of 04/07/2011

Datablock DBR-12a - ellipsoid plot



Check CIF/PLATON (standard) for Datablock: DBR-09-09-11 [6ee]

Bond precision: C-C = 0.0073 A Wavelength=1.54184

Cell: a=8.0571(2) b=11.5261(2) c=12.1322(2)

alpha=90 beta=99.462(2) gamma=90

Temperature: 298 K

	Calculated	Reported
Volume	1111.35(4)	1111.35(4)
Space group	P 21	P 1 21 1
Hall group	P 2yb	?
Moiety formula	C27 H19 Br O3	?
Sum formula	C27 H19 Br O3	C27 H19 Br O3
Mr	471.32	471.33
Dx,g cm-3	1.408	1.408
Z	2	2
Mu (mm-1)	2.727	2.727
F000	480.0	480.0
F000'	479.87	
h,k,lmax	9,14,14	9,14,14
Nref	2220[4216]	3712
Tmin,Tmax	0.366,0.466	0.394,0.516
Tmin'	0.277	

Correction method= MULTI-SCAN

Data completeness= 1.67/0.88 Theta(max)= 70.030

R(reflections)= 0.0684(3457) wR2(reflections)= 0.1932(3712)

S = 1.041 Npar= 281

PLATON version of 18/07/2011; check.def file version of 04/07/2011

Datablock DBR-09-09-11 - ellipsoid plot