Electronic Supporting Information for

Organocatalysis for New Chiral Fullerene-based Materials

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General Methods and Materials

The commercially available reagents and solvents were used without further purification. Alkynoates 1a-f† and allenes 3a-h†† were previously described in the literature. 1H NMR and 13C NMR spectra were recorded on a BRUKER AVANCE-300 and -700 in CDCl3, or a BRUKER AVANCE AMX-700 in CDCl3 at 23°C, and referenced to CDCl3; coupling constants (\(J\)) are reported in Hz and the chemical shifts (\(\delta\)) in ppm. Mass spectra were reported on a BRUKER-ULTRAFLEX III (MALDI-TOF). Reactions were monitored by thin-layer chromatography carried out on 0.2 mm TLC-aluminium sheets of silica gel (Merck, TLC Silica gel 60 F254). Flash column chromatographies were performed using silica gel (230-400 mesh). The ee values were determined by HPLC. For ee values and conversions, chiral HPLC column Pirkle Covalent (R,R) Whelk-02 10/100 FEC (4.6 x 250 mm), Pirkle Covalent (R,R) Whelk-01 5/100 (4.6 x 250 mm) were used. All these values were monitored in a 320 nm spectrophotometer detector. Cyclic voltammograms (CV) were recorded on a potentiotstat/galvanostat AUTOLAB with PGSTAT30 equipped with a software GPES for windows version 4.8 in a conventional three compartment cell. Measurements were carried out using a GCE (glassy carbon electrode) as working electrode, an Ag/AgNO3 reference electrode, and a platinum wire as counter electrode. Bu4NPF6 was used as supporting electrolyte and o-DCB/MeCN (4:1) mixture as solvent.
Experimental Procedures and Characterizations

General procedure for the enantioselective [3+2] cycloaddition of alkynoates/allenoates 1a-f/3a-h to [60]fullerene:

In an ordinary vial under Ar atmosphere, a suspension of the corresponding alkynoates/allenoates 1a-f/3a-h (1.0 eq.) and 2-[(11bS)-3H-binaphtho[2,1-c:1’,2’-e]phosphepin-4(5H)-yl]ethanamine (0.1 eq.) in 1.0 mL of dry toluene is prepared. After 15 min. of stirring at room temperature, [60]fullerene (1.07 eq, 0.017 mmol) is added and the mixture is stirred at room temperature for two hours. Finally, the solvent is evaporated under vacuum and dark residue is then purified by silica-gel column chromatography using CS₂ as eluent (for recovering unreacted [60]fullerene). Then, mixtures of solvents (indicated in each case) are used affording desired cyclopenteno[4,5:1,2][60]fullerene derivatives 2a-j. Conversions and ee are determined by HPLC analysis using Pirkle Covalent (R,R) Whelk-02 and Pirkle Covalent (R,R) Whelk-01 as chiral columns (conditions and enantiomers retention times are indicated in each case). For the synthesis of the racemic compounds (2a-j) the same procedure was used replacing the optically pure phosphine P-XII by racemic dppe (1,2-bis(diphenylphosphine)ethane).

Synthesis of \((3R)\)-1-ethoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (2a)

The adduct 2a was prepared according to the previously described general procedure.[88] Conversion: 42%. ee: 86% (Pirkle Covalent (R,R) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min). This adduct 2a was also prepared by using ethyl 4-phenyl-3-butynoate 1a (2.9 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1’,2’-e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 31%; ee: 88%. \(^1\)H NMR (700 MHz, CDCl\(_3\)) \(\delta\) 1.46 (t, 3H, \(J=7.1\) Hz), 4.45-4.53 (m, 2H), 6.06 (d, 1H, \(J=2.4\) Hz), 7.37-7.41 (m, 1H), 7.47-7.53 (m, 2H), 7.72 (d, 2H, \(J=7.3\) Hz), 7.89 (d, 1H, \(J=2.4\) Hz) ppm. \(^{13}\)C NMR (175 MHz, CDCl\(_3\)) \(\delta\) 14.6, 29.7, 61.4, 63.6, 76.0, 128.3, 129.2, 129.7, 134.1, 135.5, 135.8, 134.0, 137.9, 139.1, 139.4, 138.5, 140.3, 141.6, 141.7, 141.8, 141.9, 142.1, 142.2, 142.41, 142.44, 142.62, 142.64, 142.68,
Synthesis of 1-ethoxycarbonyl-3-(2,2-diethoxycarbonyl-4-pentenyl)-1-cyclopenteno[4,5:1,2][60]fullerene (2b)

The adduct 2b was prepared according to the general procedure using triethyl oct-7-en-2-yne-1,5,5-tricarboxylate 1c (5.1 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 19% (eluent: hexane:CH$_2$Cl$_2$, 1:1).

$^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 1.35 (t, $J$ = 7.1 Hz, 3H), 1.42 (td, $J$ = 7.1, 2.4 Hz, 6H), 2.85 (dd, $J$ = 14.3, 12.0 Hz, 1H), 3.04 (qd, $J$ = 14.6, 7.4 Hz, 2H), 3.24 (dd, $J$ = 14.4, 2.9 Hz, 1H), 4.36-4.28 (m, 2H), 4.45-4.37 (m, 4H), 4.87 (dt, $J$ = 11.9, 2.6 Hz, 1H), 5.17 (d, $J$ = 10.1 Hz, 1H), 5.25 (d, $J$ = 17.0 Hz, 1H), 5.77 (ddt, $J$ = 17.1, 10.1, 7.4 Hz, 1H), 7.68 (d, $J$ = 2.3 Hz, 1H) ppm. $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 14.2, 14.2, 14.3, 29.7, 38.0, 38.3, 53.2, 57.0, 61.4, 61.97, 61.99, 74.9, 76.1, 120.3, 131.6, 134.0, 135.7, 135.7, 136.1, 136.2, 139.2, 139.3, 139.8, 140.0, 141.6, 141.7, 141.9, 141.96, 142.02, 142.2, 142.3, 142.4, 142.5, 142.6, 142.70, 142.74, 142.8, 143.07, 143.12, 144.4, 144.46, 144.49, 144.54, 144.8, 145.05, 145.13, 145.4, 145.5, 145.6, 145.9, 145.98, 146.01, 146.02, 146.1, 146.2, 146.25, 146.32, 146.37, 146.43, 146.8, 147.3, 147.4, 148.1, 148.4, 150.8, 151.2, 152.0, 156.7, 163.6, 170.8, 171.4 ppm. HRMS (ESI POS.): [M]$^+$ Calc. for C$_{77}$H$_{34}$NaO$_6$: 1067.14706; found: 1067.14442

Synthesis of (3R)-1-tert-butoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (2e)

The adduct 2e was prepared according to the general procedure using tert-butyl-4-phenyl-3-butynoate 1e (3.4 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 19% (eluent: hexane:CH$_2$Cl$_2$, 1:1).
e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 49% (eluent: hexane:CH₂Cl₂, 3:1). ee: 60% (Pirkle Covalent (R,R) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min; tᵣ for the major (3R) isomer: 4.29 min, tᵣ for the minor (3S) isomer: 5.07 min). ^1H NMR (700 MHz, CDCl₃) δ 1.65 (s, 9H), 6.02 (d, J = 2.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H), 7.80 (d, J = 2.5 Hz, 1H) ppm.

Synthesis of (3S)-1-ethoxycarbonyl-3-benzyl-1-cyclopenteno[4,5:1,2][60]fullerene (2d)

The adduct 2d was prepared according to the general procedure using ethyl 5-phenylpenta-2,3-dienoate 3b (3.2 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 67% (eluent: hexane:CH₂Cl₂, 1:1). ee: 84% (Pirkle Covalent (R,R) Whelk-01, hexane/2-propanol 95:5, flow rate 3.00 mL/min; tᵣ for the major (3S) isomer: 14.46 min, tᵣ for the minor (3R) isomer: 17.95 min). ^1H NMR (700 MHz, CDCl₃) δ 1.38 (t, J = 7.1 Hz, 3H), 3.93 (dd, J = 13.2, 5.7 Hz, 1H), 4.45-4.36 (m, 2H), 3.47-3.39 (m, 1H), 5.10 (ddd, J = 11.7, 5.7, 2.3 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.53 (d, J = 7.3 Hz, 2H), 7.62 (d, J = 2.4 Hz, 1H) ppm. ^13C NMR (176 MHz, CDCl₃) δ 14.3, 29.7, 31.0, 41.9, 53.5, 59.3, 61.4, 74.0, 127.0, 129.0, 129.2, 134.2, 135.7, 135.9, 136.1, 138.7, 139.2, 139.3, 139.6, 140.2, 141.6, 141.7, 141.9, 142.0, 142.1, 142.2, 142.3, 142.4, 142.65, 142.71, 142.8, 143.09, 143.11, 143.2, 144.4, 144.47, 144.49, 144.50, 144.53, 144.8, 145.1, 145.2, 145.3, 145.37, 145.40, 145.5, 145.6, 145.98, 146.02, 146.1, 146.2, 146.26, 146.32, 146.33, 146.37, 146.42, 147.3, 147.4, 148.27, 148.33, 150.8, 151.0, 152.7, 156.9, 163.8 ppm. HRMS (ESI POS.): [M]+ Calc. for C₇₃H₁₄NaO₂: 945.08860; found: 945.08892.
Synthesis of $(3S)$-1-ethoxycarbonyl-3-methyl-1-cyclopenteno[4,5:1,2][60]fullerene (2e)

The adduct 2e was prepared according to the previously described general procedure.\textsuperscript{[iii]} Conversion: 20%. \textit{ee}: 93% (Pirkle Covalent (\textit{R,R}) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min). \textsuperscript{i}H NMR (700 MHz, CDCl\textsubscript{3}) \textit{δ} 1.43 (t, 3H, \textit{J} = 7.1 Hz), 2.01 (d, 3H, \textit{J} = 7.5 Hz), 4.40-4.48 (m, 2H), 4.90 (dq, 1H, \textit{J} = 7.1 Hz), 7.78 (d, 1H, \textit{J} = 2.3 Hz) ppm. \textsuperscript{13}C NMR (175 MHz, CDCl\textsubscript{3}) \textit{δ} 14.3, 20.4, 52.3, 61.4, 74.4, 76.7, 135.3, 135.7, 136.0, 139.1, 139.3, 139.9, 140.2, 141.58, 141.61, 191.4, 192.0, 142.17, 142.21, 142.25, 143.1, 144.45, 144.51, 144.99, 145.02, 145.15, 145.19, 145.3, 145.37, 145.38, 145.5, 145.6, 145.94, 145.98, 146.02, 146.1, 146.21, 146.24, 146.31, 146.34, 146.37, 147.3, 147.4, 148.2, 148.4, 149.7 (CH), 150.8, 151.2, 153.2, 157.1, 163.9 ppm.

Synthesis of $(3S)$-1-ethoxycarbonyl-3-ethyl-1-cyclopenteno[4,5:1,2][60]fullerene (2f)

The adduct 2f was prepared according to the previously described general procedure.\textsuperscript{[iii]} Conversion: 70%. \textit{ee}: 92% (Pirkle Covalent (\textit{R,R}) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min). \textsuperscript{i}H NMR (700 MHz, CDCl\textsubscript{3}) \textit{δ} 1.44 (t, 3H, \textit{J} = 7.1 Hz), 1.51 (t, 3H, \textit{J} = 7.3 Hz), 2.22-2.33 (m, 1H), 2.54-2.70 (m, 1H), 4.35-4.50 (m, 2H), 4.90 (dq, 1H, \textit{J} = 7.1 Hz), 7.93 (d, 1H, \textit{J} = 2.4 Hz) ppm. \textsuperscript{13}C NMR (175 MHz, CDCl\textsubscript{3}) \textit{δ} 13.5, 14.7, 29.6, 30.1, 59.9, 61.7, 74.9, 128.7, 136.1, 136.3, 136.4, 139.7, 140.1, 143.6, 141.2, 140.1, 140.6, 141.2, 141.97, 142.02, 142.4, 142.6, 142.8, 143.2, 143.5, 144.85, 144.93, 145.3, 145.7, 145.91, 145.93, 146.37, 146.39, 146.62, 146.64, 147.7, 148.0, 148.69, 148.77, 151.3, 151.6, 153.5, 157.7, 164.2 ppm.

Synthesis of $(3S)$-1-ethoxycarbonyl-3-isopropyl-1-cyclopenteno[4,5:1,2][60]fullerene (2g)

The adduct 2g was prepared according to the previously described general procedure.\textsuperscript{[iv]} Conversion: 42%. \textit{ee}: 80% (Pirkle Covalent (\textit{R,R}) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min). \textsuperscript{i}H NMR
(700 MHz, CDCl₃) δ 1.44 (t, 3H, J = 7.1 Hz), 1.49 (d, 3H, J = 6.7 Hz), 1.55 (d, 3H, J = 6.9 Hz), 2.91-3.01 (m, 1H), 4.40-4.50 (m, 2H), 4.79 (t, 1H, J = 2.6 Hz), 7.87 (d, 1H, J = 2.5 Hz) ppm. ¹³C NMR (175 MHz, CDCl₃) δ 14.7, 19.8, 24.5, 30.1, 31.9, 61.7, 64.7, 75.2, 135.7, 136.3, 137.1, 139.6, 140.0, 140.58, 142.0, 142.1, 142.28, 142.31, 142.32, 142.33, 142.7, 142.83, 142.89, 143.04, 143.11, 143.2, 143.52, 143.57, 144.84, 144.89, 144.93, 145.1, 145.37, 145.48, 145.59, 145.7, 145.90, 145.92, 146.3, 146.38, 146.42, 146.51, 146.57, 146.63, 146.71, 146.75, 146.78, 146.96, 147.67, 147.75, 148.6, 151.6, 153.5, 158.3 ppm.

Synthesis of 1-ethoxycarbonyl-3-(4-formylphenyl)-1-cyclopenteno[4,5:1,2][60]fullerene (2h)

The adduct 2h was prepared according to the general procedure using ethyl 4-(4-formylphenyl)-2,3-butadienoate 3f (3.4 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 31% (eluent: hexane:CH₂Cl₂, 1:1). ¹H NMR (700 MHz, CDCl₃) δ 1.46 (t, J = 7.1 Hz, 3H), 4.50 (dddd, J = 18.0, 10.9, 7.1, 3.8 Hz, 2H), 6.14 (d, J = 2.4 Hz, 1H), 7.87 (d, J = 2.5 Hz, 1H), 7.91 (d, J = 8.1 Hz, 2H), 8.02 (d, J = 8.1 Hz, 2H), 10.08 (s, 1H) ppm. ¹³C NMR (176 MHz, CDCl₃) δ 14.3, 28.7, 29.7, 61.7, 63.4, 75.6, 76.4, 130.4, 130.5, 134.3, 135.66, 135.71, 135.8, 136.1, 138.90, 138.94, 139.2, 139.4, 139.6, 140.3, 141.6, 141.7, 141.9, 142.0, 142.1, 142.2, 142.4, 142.5, 142.68, 142.71, 142.74, 143.1, 144.46, 144.49, 144.7, 145.1, 145.17, 145.24, 145.4, 145.6, 145.7, 145.8, 145.9, 146.0, 146.1, 146.17, 146.22, 146.23, 146.27, 146.30, 146.35, 146.39, 146.41, 147.3, 147.4, 147.9, 148.3, 150.0, 150.5, 152.8, 156.4, 163.5, 191.8 ppm. HRMS (ESI POS.): [M]+ Calc. for C₇₃H₁₁O₃: 935.0714; found: 935.0677.

Synthesis of (3S)-1-tert-butoxycarbonyl-3-benzyl-1-cyclopenteno[4,5:1,2][60]fullerene (2i)

The adduct 2i was prepared according to the general procedure using tert-butyl 5-phenyl-2,3-pentadienoate 3g (3.6 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 31% (eluent: hexane:CH₂Cl₂, 1:1). ¹H NMR (700 MHz, CDCl₃) δ 1.46 (t, J = 7.1 Hz, 3H), 4.50 (dddd, J = 18.0, 10.9, 7.1, 3.8 Hz, 2H), 6.14 (d, J = 2.4 Hz, 1H), 7.87 (d, J = 2.5 Hz, 1H), 7.91 (d, J = 8.1 Hz, 2H), 8.02 (d, J = 8.1 Hz, 2H), 10.08 (s, 1H) ppm. ¹³C NMR (176 MHz, CDCl₃) δ 14.3, 28.7, 29.7, 61.7, 63.4, 75.6, 76.4, 130.4, 130.5, 134.3, 135.66, 135.71, 135.8, 136.1, 138.90, 138.94, 139.2, 139.4, 139.6, 140.3, 141.6, 141.7, 141.9, 142.0, 142.1, 142.2, 142.4, 142.5, 142.68, 142.71, 142.74, 143.1, 144.46, 144.49, 144.7, 145.1, 145.17, 145.24, 145.4, 145.6, 145.7, 145.8, 145.9, 146.0, 146.1, 146.17, 146.22, 146.23, 146.27, 146.30, 146.35, 146.39, 146.41, 147.3, 147.4, 147.9, 148.3, 150.0, 150.5, 152.8, 156.4, 163.5, 191.8 ppm. HRMS (ESI POS.): [M]+ Calc. for C₇₃H₁₁O₃: 935.0714; found: 935.0677.
ethylphosphine-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 28% (eluent: hexane:CH₂Cl₂, 1:1). ee: 80% (Pirkle Covalent (R,R) Whelk-01, hexane/2-propanol 98:2, flow rate 2.00 mL/min; tᵣ for the major (3S) isomer: 9.94 min, tᵣ for the minor (3R) isomer: 12.01 min). ¹H NMR (700 MHz, CDCl₃) δ 1.58 (s, 9H), 3.49-3.38 (m, 1H), 3.92 (dd, J= 13.3, 5.6 Hz, 1H), 5.06 (ddd, J= 11.6, 5.6, 2.3 Hz, 1H), 7.36 (t, J= 7.3 Hz, 1H), 7.46 (t, J= 7.6 Hz, 2H), 7.52 (d, J= 7.2 Hz, 2H), 7.54 (d, J= 2.3 Hz, 1H) ppm. ¹³C NMR (176 MHz, CDCl₃) δ 21.6, 28.3, 42.0, 59.1, 74.2, 82.5, 125.4, 127.0, 128.3, 129.0, 129.1, 129.3, 134.2, 135.7, 136.1, 137.5, 137.8, 138.8, 139.1, 139.2, 139.7, 140.3, 141.6, 141.7, 141.96, 141.99, 142.05, 142.06, 142.2, 142.27, 142.30, 142.4, 142.69, 142.74, 142.8, 143.1, 143.2, 144.46, 144.48, 144.54, 144.9, 145.1, 145.2, 145.3, 145.36, 145.39, 145.5, 145.58, 146.0, 146.05, 146.14, 146.2, 146.3, 146.35, 146.36, 146.39, 146.44, 146.5, 147.3, 147.4, 148.4, 148.6, 151.0, 151.2, 152.9, 157.1, 162.9 ppm. HRMS (ESI POS.): [M]+ Calc. for C₇₅H₁₈O₂: 950.1312; found: 950.1270.

Synthesis of (3R)-1-benzyloxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (2j)

The adduct 2j was prepared according to the previously described general procedure. Conversion: 37%. ee: 99% (Pirkle Covalent (R,R) Whelk-01, hexane/2-propanol 98:2, flow rate 2.00 mL/min). ¹H NMR (700 MHz, CDCl₃) δ 5.42 (d, 1H, J= 12.2), 5.48 (d, 1H, J= 12.2), 6.05 (d, 1H, J= 2.5 Hz), 7.35-7.45 (m, 4H), 7.45-7.52 (m, 4H), 7.70 (d, 2H, J= 7.2 Hz), 7.93 (d, 1H, J= 2.5 Hz) ppm. ¹³C NMR (175 MHz, CDCl₃) δ 31.3, 64.0, 67.7, 76.3, 128.7, 129.0, 129.1, 129.6, 130.1, 134.5, 135.6, 135.9, 136.2, 136.4, 138.09, 138.10, 139.5, 139.76, 139.79, 140.0, 140.7, 141.96, 142.05, 142.07, 142.19, 142.27, 142.33, 142.53, 142.59, 142.61, 142.90, 142.83, 143.01, 143.04, 143.07, 143.10, 143.45, 144.75, 144.83, 144.84, 144.88, 145.19, 145.39, 145.43, 145.50, 145.69, 145.74, 145.76, 145.9, 146.02, 146.05, 146.23, 146.29, 146.35, 146.38, 146.52, 146.58, 146.61, 146.64, 146.72, 146.78, 147.08, 147.10, 147.7, 147.8, 148.3, 148.8, 150.7, 151.2, 154.0, 157.3, 163.8 ppm.
The adduct 5 was prepared according to the general procedure using methyl 2-((tert-butoxycarbonyl)oxy)(phenyl)methylacrylate 4 (4.6 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 36% (eluent: hexane:CH₂Cl₂, 1:1). ee: 57% (Pirkle Covalent (R,R) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min; tᵣ for the major (3S) isomer: 9.33 min, tᵣ for the minor (3R) isomer: 51.48 min).¹¹H NMR (700 MHz, CDCl₃) δ 3.92 (s, 3H), 6.24 (d, J= 1.8 Hz, 1H), 7.35 (t, J= 7.5 Hz, 1H), 7.41 (s, 1H), 7.54 (s, 1H), 7.66 (s, 1H), 7.79 (s, 1H), 8.12 (d, J= 1.8 Hz, 1H) ppm. ¹³C NMR (176 MHz, CDCl₃) δ 29.7, 52.4, 63.1, 74.7, 127.9, 134.2, 135.5, 136.2, 136.9, 138.5, 139.4, 140.2, 140.4, 140.6, 141.0, 141.7, 141.78, 141.81, 141.82, 141.98, 142.02, 142.1, 142.2, 142.3, 142.5, 142.58, 142.61, 142.67, 142.73, 143.1, 143.2, 144.3, 144.4, 144.49, 144.52, 145.0, 145.1, 145.2, 145.4, 145.46, 145.49, 145.53, 145.6, 145.65, 145.70, 145.79, 145.82, 145.9, 146.06, 146.08, 146.12, 146.2, 146.4, 146.5, 147.4, 147.5, 150.9, 151.1, 153.9, 156.4, 164.6 ppm. HRMS (ESI POS.): [M]+ Calc. for C₇₁H₁₀O₂: 894.0686; found: 894.0682.

The adduct 7a was prepared according to the general procedure using ethyl-2,3-pentadienoate 3c (91.5 μL, 0.556 mmol), [70]fullerene (500 mg, 0.595 mmol) and dppe (26 mg, 0.056 mmol). Conversion: 46% (eluent: hexane:CH₂Cl₂, 1:1). ¹¹H NMR (700 MHz, CDCl₃) δ 1.59 (t, J= 7.2 Hz, 3H), 1.68 (d, J= 7.5 Hz, 3H), 4.21 (qd, J= 7.5, 2.2 Hz, 1H), 4.57 (q, J= 7.1 Hz, 2H), 7.34 (d, J= 2.2 Hz, 1H) ppm. ¹³C NMR (176 MHz, CDCl₃) δ 14.6, 20.5, 30.0, 50.3, 61.5, 67.4, 131.39, 131.41, 131.43, 131.5, 133.6, 133.9, 134.0, 135.3, 135.9, 137.5, 140.0, 140.1, 140.2, 140.4, 142.9, 143.15, 143.29, 143.31, 143.34, 143.38, 143.44, 143.7, 145.65, 145.76, 145.80, 146.0, 146.2, 146.9, 147.03, 147.09, 147.2, 147.5, 147.80, 148.82, 148.88, 148.9, 149.14, 149.15, 149.41, 149.42, 149.77, 149.84, 149.99, 150.01, 150.08, 150.42, 150.45, 150.54, 150.58, 150.71, 150.72, 151.21, 151.22, 151.5, 151.6, 156.2, 156.3, 156.9, 161.2, 163.7 ppm. HRMS (ESI POS.): [M]+ Calc. for C₇₀H₈O₂: 966.0681; found: 966.0655.
Synthesis of 1-ethoxycarbonyl-3-phenyl-1-cyclopenteno[3,4:25',8'][70]fullerene (7b)

The adduct 7b was prepared according to the general procedure using ethyl 4-phenyl-2,3-butadienoate 3a (41.9 mg, 0.223 mmol), [70]fullerene (200 mg, 0.238 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1',2'-e]phosphepin-4(5H)-yl]ethanamine (8 mg, 0.022 mmol).

Conversion: 58% (eluent: hexane:CH$_2$Cl$_2$, 1:1). ee: 76% (Pirkle Covalent (R,R) Whelk-01, hexane/methanol 98:2, flow rate 2.50 mL/min; $t_R$ for the major (3S) isomer: 8.05 min, $t_R$ for the minor (3R) isomer: 10.09 min). $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 1.61 (t, $J = 7.2$ Hz, 3H), 4.62 (qq, $J = 10.7$, 7.2 Hz, 2H), 5.32 (d, $J = 2.4$ Hz, 1H), 7.28–7.26 (m, 1H), 7.38–7.32 (m, 4H), 7.43 (d, $J = 2.4$ Hz, 1H) ppm. $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 14.6, 61.1, 61.7, 69.0, 69.1, 128.3, 129.0, 129.3, 131.2, 131.37, 131.42, 131.44, 131.46, 131.54, 133.1, 133.8, 133.9, 134.0, 135.4, 136.8, 138.3, 139.4, 139.8, 140.1, 140.3, 140.4, 142.7, 143.2, 143.29, 143.30, 143.32, 143.37, 143.44, 143.46, 143.50, 144.5, 145.3, 145.6, 145.9, 146.2, 146.7, 147.00, 147.02, 147.1, 147.47, 147.53, 148.7, 148.77, 148.80, 148.9, 149.10, 149.11, 149.29, 149.34, 149.6, 149.7, 149.88, 149.91, 150.1, 150.45, 150.46, 150.52, 150.6, 150.65, 150.70, 151.0, 151.3, 151.45, 151.50, 151.52, 156.4, 157.5, 161.1, 163.7 ppm. HRMS (ESI POS.): [M]+ Calc. for C$_{82}$H$_{12}$O$_2$: 1028.0837; found: 1028.0786.

Synthesis of 1-ethoxycarbonyl-3-phenyl-1-cyclopenteno[3,4:8',25'][70]fullerene (7b’)

The adduct 7b’ was prepared according to the general procedure using ethyl 4-phenyl-2,3-butadienoate 3a (41.9 mg, 0.223 mmol), [70]fullerene (200 mg, 0.238 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1',2'-e]phosphepin-4(5H)-yl]ethanamine (8 mg, 0.022 mmol).

Conversion: 6% (eluent: hexane:CH$_2$Cl$_2$, 1:1). $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 1.32 (t, $J = 7.1$ Hz, 6H), 4.36–4.26 (m, 2H), 5.60 (d, $J = 2.4$ Hz, 1H), 7.44 (d, $J = 2.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.62 (t, $J = 7.7$ Hz, 2H), 7.70 (d, $J = 7.3$ Hz, 2H) ppm. $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 14.2, 29.8, 61.4, 65.0, 128.5, 129.4, 130.0, 131.1, 131.2, 131.56, 131.64, 132.5, 132.8, 133.8, 136.7, 137.2, 137.7, 138.8, 139.1, 139.8, 140.1, 140.3, 143.0, 143.22, 143.24, 143.29, 143.30, 143.4, 143.5, 145.2, 146.0, 146.1, 146.3, 146.4, 146.6, 146.98, 147.02, 147.03, 147.4, 147.5, 147.6, 148.2, 148.6, 148.7, 148.75, 148.78,
149.16, 149.19, 149.27, 149.30, 149.5, 149.7, 149.8, 150.1, 150.68, 150.70, 150.8, 150.85, 150.88, 151.3, 151.4, 151.5, 154.3, 155.2, 155.4, 155.8, 163.2 ppm.
Representative NMR spectra of cyclopenteno[4,5:1,2][60]fullerene derivatives 2a-j

$^1$H-NMR, $^{13}$C-NMR spectra of 1-ethoxycarbonyl-3-(2,2-diethoxycarbonyl-4-pentenyl)-1-cyclopenteno[4,5:1,2][60]fullerene (2b)
$^1$H-NMR, $^{13}$C-NMR spectra of 1-tert-butoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (2c)
$^1$H-NMR, $^{13}$C-NMR of 1-ethoxycarbonyl-3-benzyl-1-cyclopenteno[4,5:1,2][60]fullerene (2d)
$^1$H-NMR, $^{13}$C-NMR spectra 1-ethoxycarbonyl-3-(4-formylphenyl)-1-cyclopenteno[4,5:1,2][60]fullerene (2h)
$^1$H-NMR, $^{13}$C-NMR spectra 1-tert-butoxycarbonyl-3-benzyl-1-cyclopenteno[4,5:1,2][60]fullerene (2i)
$^1$H-NMR, $^{13}$C-NMR spectra of 1-ethoxycarbonyl-3-methyl-1-cyclopenteno[3,4:25',8'][70]fullerene (7a)
$^1$H-NMR, $^{13}$C-NMR spectra of 1-ethoxycarbonyl-3-phenyl-1-cyclopenteno[3,4:25',8'][70]fullerene (7b)
$^{1}$H-NMR, $^{13}$C-NMR spectra of 1-ethoxycarbonyl-3-phenyl-1-cyclopenteno[3,4-:8’:25’][70]fullerene (7b’)

[Diagram of NMR spectra and chemical structure]
Representative HPLC chromatograms of racemic and enantioenriched cyclopenteno[4,5:1,2][60]fullerene derivatives 2c-d, 2i, 5 and 7b.

HPLC chromatograms of 1-tert-butoxycarbonyl-3-phenyl-1-cyclopenteno[4,5,1,2][60]fullerene (2c)
Pirkle Covalent (R,R) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min.

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HPLC chromatograms of 1-ethoxycarbonyl-3-benzyl-1-cyclopenteno[4,5:1,2][60]fullerene (2d) Pirkle Covalent (R,R) Whelk-01, hexane/2-propanol 95:5, flow rate 3.00 mL/min.
HPLC chromatograms of 1-tert-butoxycarbonyl-3-benzyl-1-cyclopenteno[4,5:1,2][60]fullerene (2i) 
Pirkle Covalent ($R,R$) Whelk-01, hexane/2-propanol 98:2, flow rate 2.00 mL/min.
HPLC chromatograms of 2-methoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (5)
Pirkle Covalent (R,R) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min.
HPLC chromatograms of 1-ethoxycarbonyl-3-phenyl-1-cyclopenteno[3,4:25',8'][70]fullerene (7b) Pirkle Covalent (R,R) Whelk-01, hexane/methanol 98:2, flow rate 3.00 mL/min.

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**Electrochemistry**

Cyclic voltammograms were recorded on a potentiostat/galvanostat AUTOLAB with PGSTAT30 equipped with a software GPES for windows version 4.8 in a conventional three compartment cell. Measurements of $2b$-$d$, $2h$-$i$ were carried out using o-DCB/MeCN (4:1) containing Bu$_4$N$^+$PF$_6^-$ (0.1M) as a supporting electrolyte at room temperature, along with pristine C$_{60}$ as a reference. Glassy carbon, platinum wire, and Ag/Ag$^+$ electrodes were used as working, counter, and reference electrodes, respectively (Table S1).

Table S1. Reduction Potentials for the Cyclopenteno[60]fullerenes 2b-d, 2h-i, and Pristine[60]fullerene$^a$

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$^a$ Potential in volts vs ferrocene/ferrocenium measured with cyclic voltammetry in o-DCB/MeCN (4:1) containing Bu$_4$N$^+$PF$_6^-$ (0.1M) as a supporting electrolyte. Glassy carbon, platinum wire, and Ag/Ag$^+$ electrodes were used as working, counter, and reference electrodes, respectively.

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