Electronic Supporting Information for

Organocatalysis for New Chiral Fullerene-based Materials

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General Methods and Materials

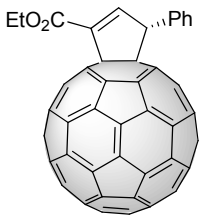
The commercially available reagents and solvents were used without further purification. Alkynoates **1a-f**[i] and allenes **3a-h**[ii]were previously described in the literature. ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCE-300 and -700 in $CDCl_3$, or a BRUKER AVANCE AMX-700 in $CDCl_3$ at 23ºC, and referenced to $CDCl_3$; coupling constants (*J*) are reported in Hz and the chemical shifts (δ) 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 F_{254}). 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 potentiostat/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 $Ag/AgNO_3$ reference electrode, and a platinum wire as counter electrode. $Bu_4N^+PF_6^-$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-[(11b*S*)-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 CS_2as 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).

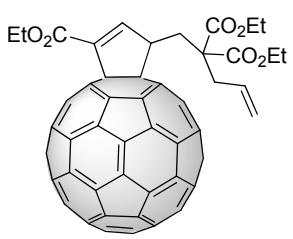
Synthesis of (3*R*)-1-ethoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (2a)



The adduct **2a** was prepared according to the previously described general procedure.[iii] 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, $CDCl_3$) δ 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, $CDCl_3$) δ 14.2, 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,

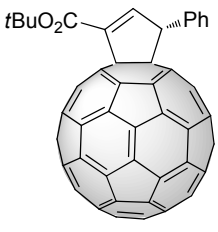
142.71, 143.07, 143.12, 144.36, 144.45, 144.46, 144.49, 144.8, 144.98, 145.02, 145.06, 145.11, 145.14, 145.31, 145.34, 145.36, 145.5, 145.6, 145.7, 1455.85, 145.89, 145.97, 145.99, 146.13, 146.19, 146.21, 146.24, 146.3, 146.4, 147.3, 147.4, 145.0, 148.5, 150.4, 151.0, 153.7, 157.0, 163.8 ppm.

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_2Cl_2, 1:1). ^{1}H NMR (700 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{77}H_{24}NaO_6$: 1067.14706; found: 1067.14442

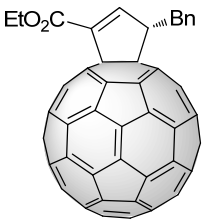
Synthesis of (3*R*)-1-*tert*-butoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (2c)



The adduct **2c** 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′-

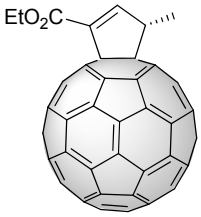
e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 49% (eluent: hexane:CH_2Cl_2, 3:1). *ee*: 60% (Pirkle Covalent (*R,R*) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min; t_R for the major (3*R*) isomer: 4.29 min, t_R for the minor (3*S*) isomer: 5.07 min). ^{1}H NMR (700 MHz, $CDCl_3$) 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. ^{13}C NMR (176 MHz, $CDCl_3$) δ 28.4, 29.7, 63.3, 76.2, 76.4, 82.8, 128.2, 129.1, 129.8, 134.1, 135.5, 135.8, 135.9, 139.0, 139.3, 139.46, 139.50, 139.7, 140.2, 141.6, 141.6, 141.7, 141.8, 141.93, 141.94, 142.0, 142.1, 142.21, 142.22, 142.39, 142.42, 142.62, 142.64, 142.68, 142.70, 143.07, 143.12, 144.36, 144.43, 144.5, 144.8, 144.97, 144.99, 145.1, 145.30, 145.31, 145.34, 145.4, 145.5, 145.6, 145.7, 145.9, 145.98, 145.99, 146.1, 146.17, 146.20, 146.23, 146.3, 146.4, 147.3, 147.4, 148.1, 148.7, 150.6, 151.2, 153.9, 157.2, 163.0 ppm. HRMS (MALDI+): [M]+ Calc. for $C_{74}H_{16}O_2$: 936.1150; found: 936.1165

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



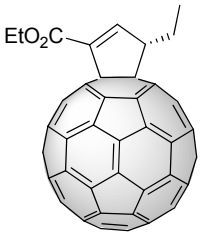
The adduct **2d** was prepared according to the general procedure using ethyl 5-phenylpenta-2,3-dienoate **3b** (3.2 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 67% (eluent: hexane:CH_2Cl_2, 1:1). *ee*: 84% (Pirkle Covalent (*R,R*) Whelk-01, hexane/2-propanol 95:5, flow rate 3.00 mL/min; t_R for the major (3*S*) isomer: 14.46 min, t_R for the minor (3*R*) isomer: 17.95 min).^{1}H NMR (700 MHz, $CDCl_3$) 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. ^{13}C NMR (176 MHz, $CDCl_3$) 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, 144.50, 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 $C_{73}H_{14}NaO_2$: 945.08860; found: 945.08892.

Synthesis of (3*S*)-1-ethoxycarbonyl-3-methyl-1-cyclopenteno[4,5:1,2][60]fullerene (2e)



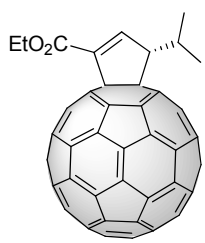
The adduct **2e** was prepared according to the previously described general procedure.[iii] Conversion: 20%. *ee*: 93% (Pirkle Covalent (*R,R*) Whelk-02, hexane/2-propanol 98:2,flow rate 3.00 mL/min). ^{1}H NMR (700 MHz, $CDCl_3$) δ 1.43 (t, 3H, *J*= 7.1 Hz), 2.01 (d, 3H, *J*= 7.5 Hz), 4.40-4.48 (m, 2H), 4.90 (dq, 1H, *J*= 7.1 Hz), 7.78 (d, 1H, *J*= 2.3 Hz) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) 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 (3*S*)-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.[iii] Conversion: 70%. *ee*: 92% (Pirkle Covalent (*R,R*) Whelk-02, hexane/2-propanol 98:2,flow rate 3.00 mL/min). ^{1}H NMR (700 MHz, $CDCl_3$) δ 1.44 (t, 3H, *J*= 7.1 Hz), 1.51 (t, 3H, *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, *J*= 7.1 Hz), 7.93 (d, 1H, *J*= 2.4 Hz) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) 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.

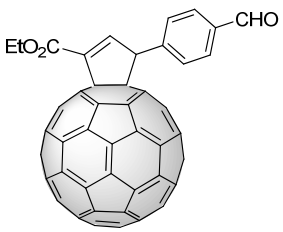
Synthesis of (3*S*)-1-ethoxycarbonyl-3-isopropyl-1-cyclopenteno[4,5:1,2][60]fullerene (2g)



The adduct **2g** was prepared according to the previously described general procedure.[iii] Conversion: 42%. *ee*: 80% (Pirkle Covalent (*R,R*) Whelk-02, hexane/2-propanol 98:2,flow rate 3.00 mL/min). ^{1}H NMR

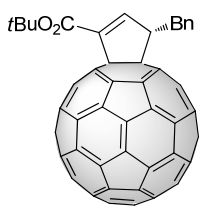
(700 MHz, $CDCl_3$) δ 1.44 (t, 3H, *J*= 7.1 Hz), 1.49 (d, 3H, *J*= 6.7 Hz), 1.55 (d, 3H, *J*= 6.9 Hz), 2.91-3.01(m, 1H), 4.40-4.50 (m, 2H), 4.79 (t, 1H, *J*= 2.6 Hz), 7.87 (d, 1H, *J*= 2.5 Hz) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 14.7, 19.8, 24.5, 30.1, 31.9, 61.7, 64.7, 75.2, 135.7, 136.3, 137.1, 139.6, 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:CH_2Cl_2, 1:1). ^1H NMR (700 MHz, $CDCl_3$) 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. ^{13}C NMR (176 MHz, $CDCl_3$) 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 $C_{73}H_{11}O_3$: 935.0714; found: 935.0677.

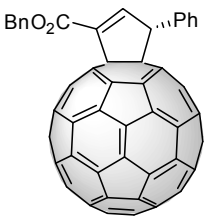
Synthesis of (3*S*)-1-*tert-but*oxycarbonyl-3-benzyl-1-cyclopenteno[4,5:1,2][60]fullerene (2i)



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′-

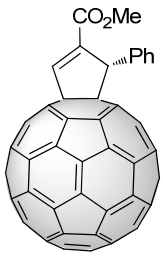
e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 28% (eluent: hexane:CH_2Cl_2, 1:1). *ee*: 80% (Pirkle Covalent (*R,R*) Whelk-01, hexane/2-propanol 98:2, flow rate 2.00 mL/min; t_R for the major (3*S*) isomer: 9.94 min, t_R for the minor (3*R*) isomer: 12.01 min).^{1}H NMR (700 MHz, $CDCl_3$) 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. ^{13}C NMR (176 MHz, $CDCl_3$) 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 $C_{75}H_{18}O_2$: 950.1312; found: 950.1270.

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



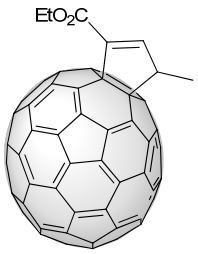
The adduct **2j** was prepared according to the previously described general procedure.[iii] Conversion: 37%. *ee*: 99% (Pirkle Covalent (*R,R*) Whelk-01, hexane/2-propanol 98:2, flow rate 2.00 mL/min). ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.42 (d, 1H, *J*= 12.2), 5.48 (d, 1H, *J*= 12.2), 6.05 (d, 1H, *J*= 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. ^{13}C NMR (175 MHz, $CDCl_3$) 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.

Synthesis of (3*S*)-2-methoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (5)



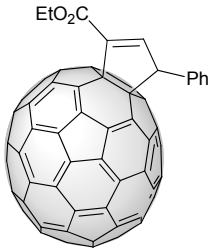
The adduct **5** was prepared according to the general procedure using methyl 2-(((tert-butoxycarbonyl)oxy)(phenyl)methyl)acrylate **4** (4.6 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl]ethanamine (0.6 mg, 0.002 mmol). Conversion: 36% (eluent: hexane:CH_2Cl_2, 1:1). *ee*: 57% (Pirkle Covalent (*R,R*) Whelk-02, hexane/2-propanol 98:2, flow rate 3.00 mL/min; t_R for the major (3*S*) isomer: 9.33 min, t_R for the minor (3*R*) isomer: 51.48 min).[iv] ^{1}H NMR (700 MHz, $CDCl_3$) 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. ^{13}C NMR (176 MHz, $CDCl_3$) 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 $C_{71}H_{10}O_2$: 894.0686; found: 894.0682.

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



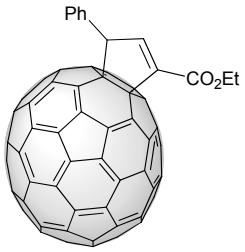
The adduct **7a** was prepared according to the general procedure using ethyl-2,3-pentadienoate **3c** (91.5μL, 0.556 mmol), [70]fullerene (500 mg, 0.595 mmol) and dppe (26 mg, 0.056 mmol). Conversion: 46% (eluent: hexane:CH_2Cl_2, 1:1). ^{1}H NMR (700 MHz, $CDCl_3$) δ 1.59 (t, *J*= 7.2 Hz, 3H), 1.68 (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. ^{13}C NMR (176 MHz, $CDCl_3$) 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 $C_{79}H_9O_2$: 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_2Cl_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 (3*S*) isomer: 8.05 min, t_R for the minor (3*R*) isomer: 10.09 min). ^{1}H NMR (700 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 145.7, 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, 156.2, 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´)

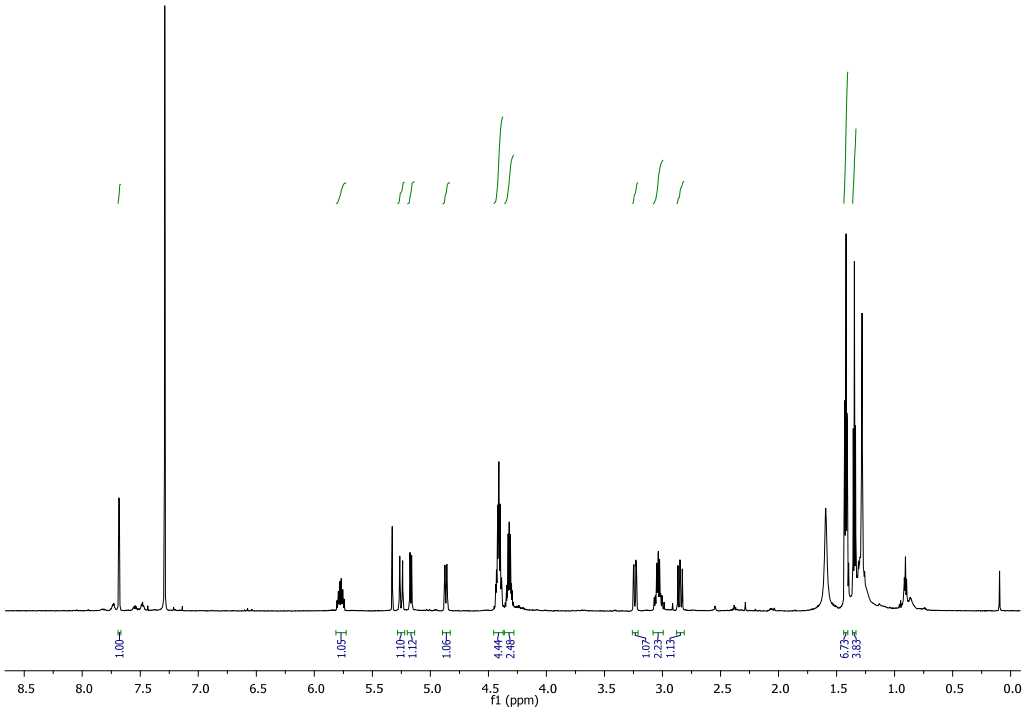


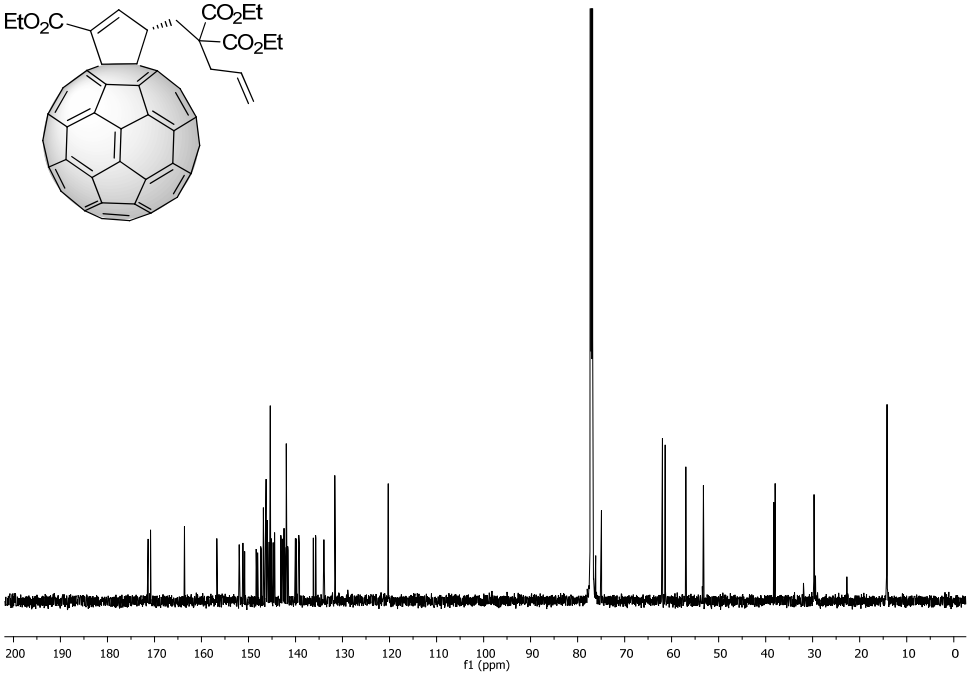
The adduct **7b´** was prepared according to the general procedure using ethyl 4-phenyl-2,3-butadienoate **3a** (41.9 mg, 0.223 mmol), [70]fullerene (200 mg, 0.238 mmol) and 2-[(11bS)-3H-binaphtho[2,1-c:1′,2′-e]phosphepin-4(5H)-yl]ethanamine (8 mg, 0.022 mmol). Conversion: 6% (eluent: hexane:CH_2Cl_2, 1:1). ^{1}H NMR (700 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

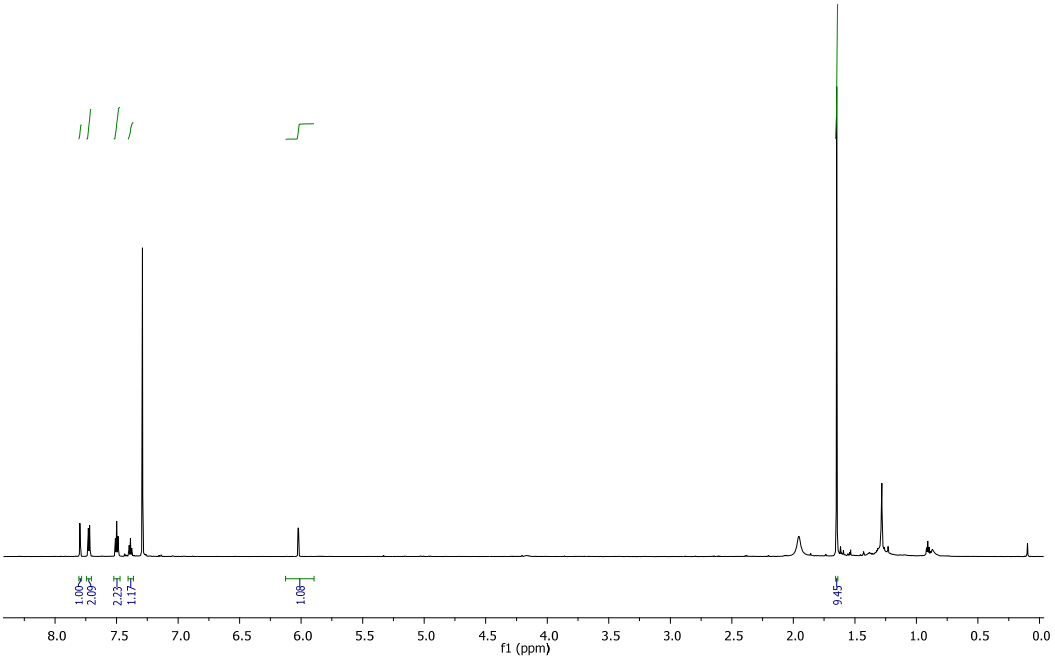
Representative NMR spectra of cyclopenteno[4,5:1,2][60]fullerene derivatives 2a-j

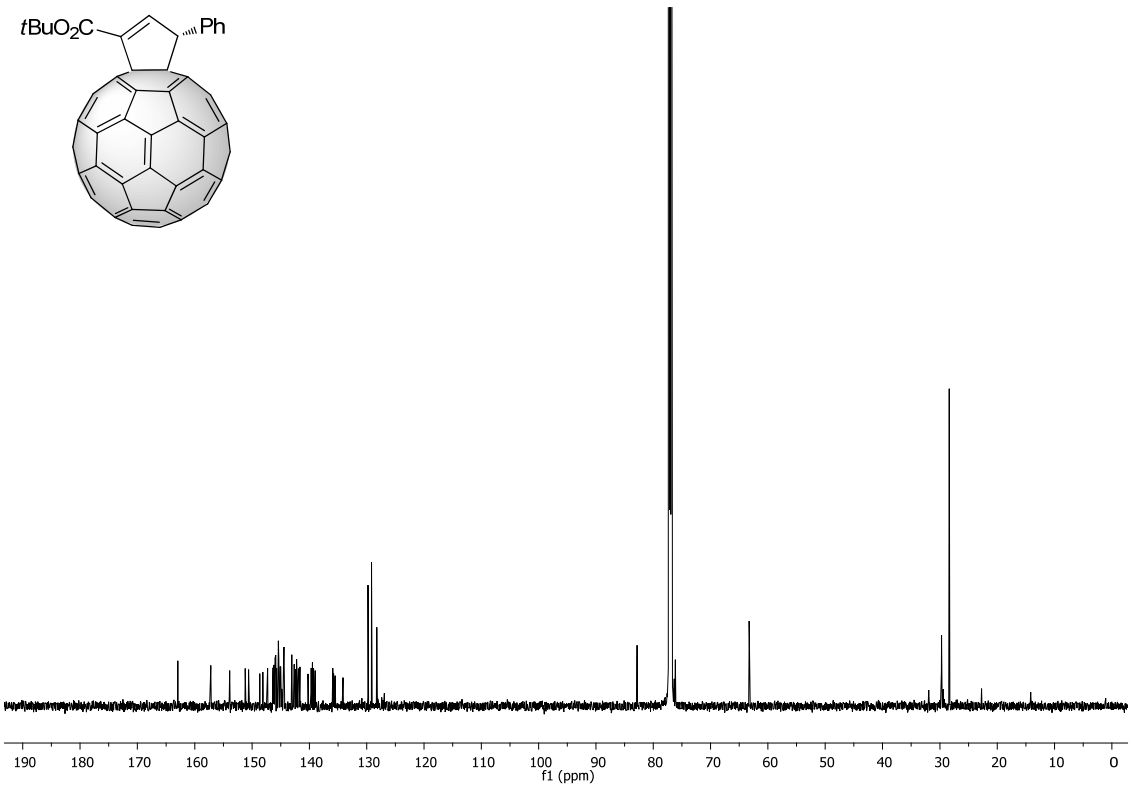
^{1}H-NMR,^{13}C-NMR spectra of 1-ethoxycarbonyl-3-(2,2-diethoxycarbonyl-4-pentenyl)-1-cyclopenteno[4,5:1,2][60]fullerene (**2b**)



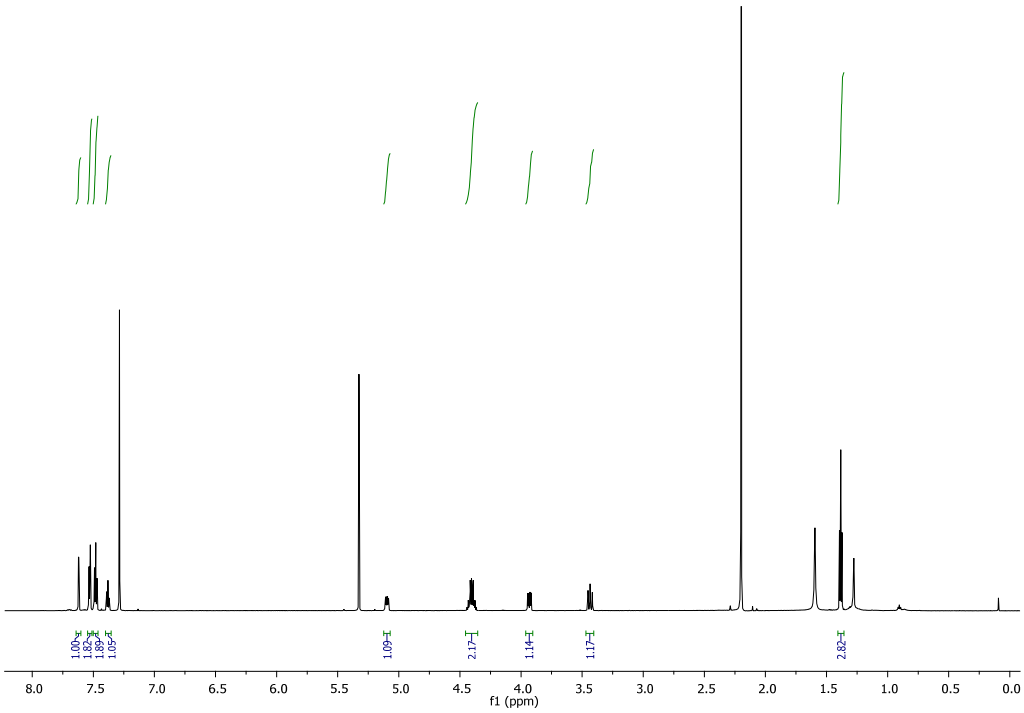


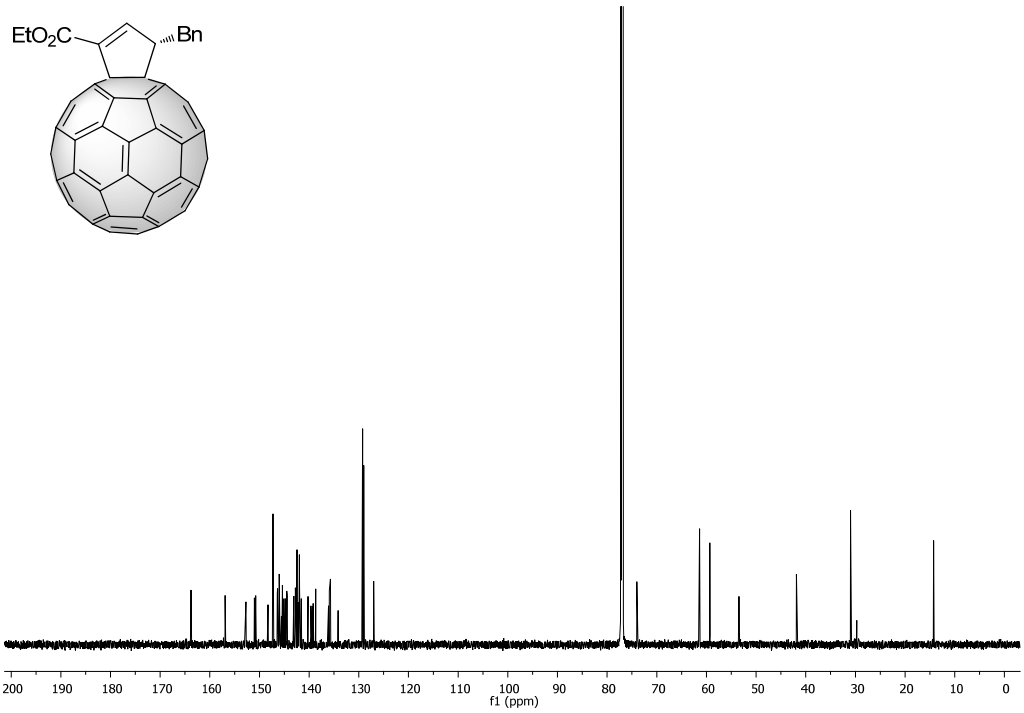
^{1}H-NMR,^{13}C-NMR spectra of 1-tert-butoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (**2c**)



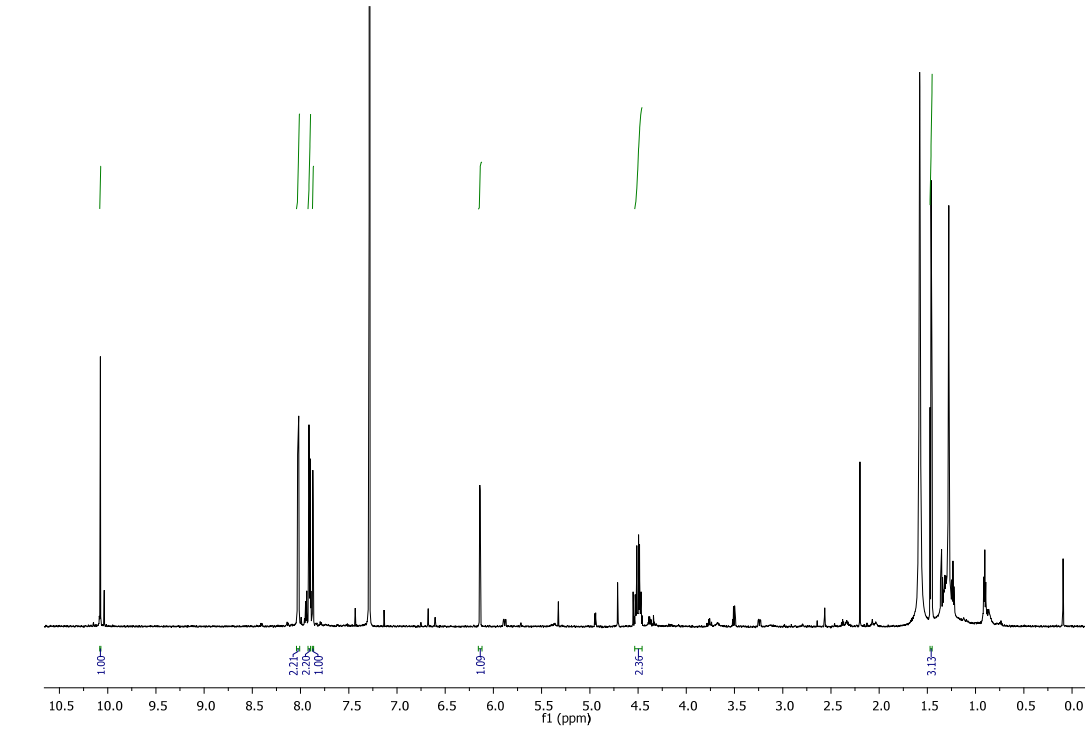


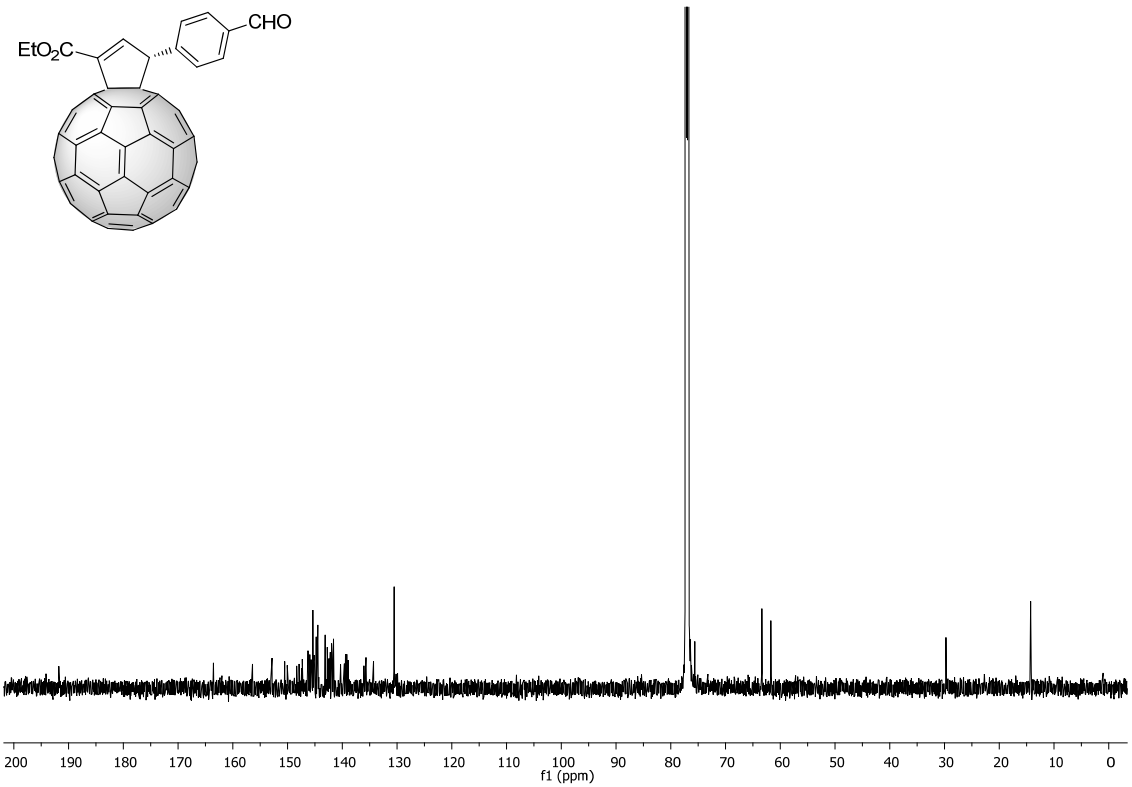
^{1}H-NMR,^{13}C-NMR of 1-ethoxycarbonyl-3-benzyl-1-cyclopenteno[4,5:1,2][60]fullerene (**2d**)



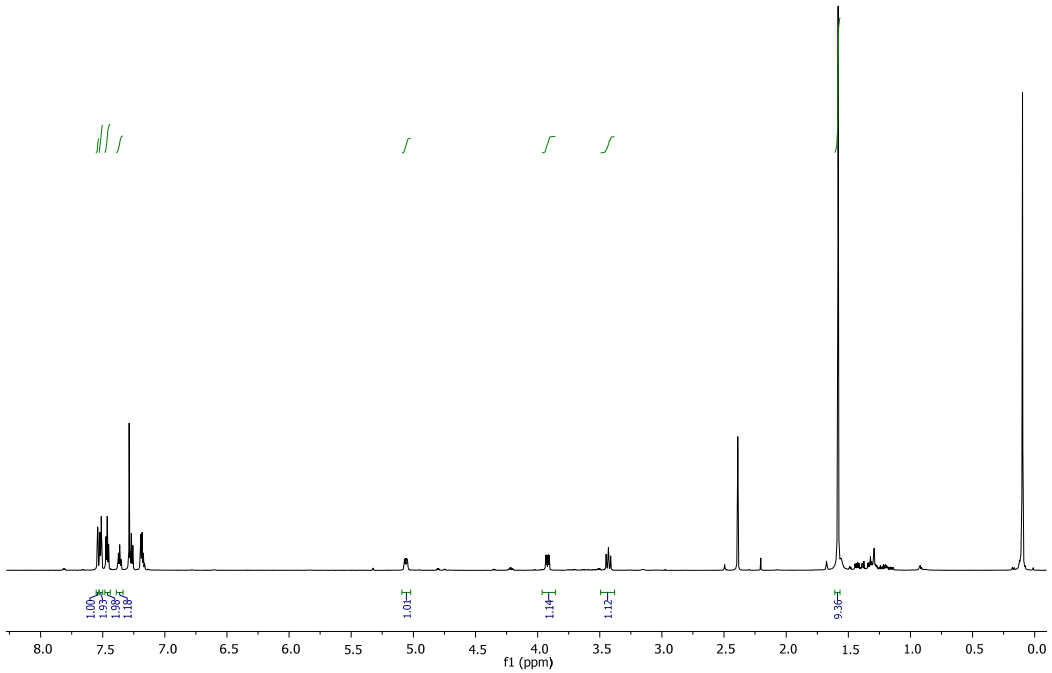


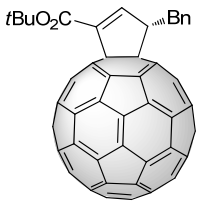
^{1}H-NMR,^{13}C-NMR spectra 1-ethoxycarbonyl-3-(4-formylphenyl)-1-cyclopenteno[4,5:1,2][60]fullerene (**2h**)

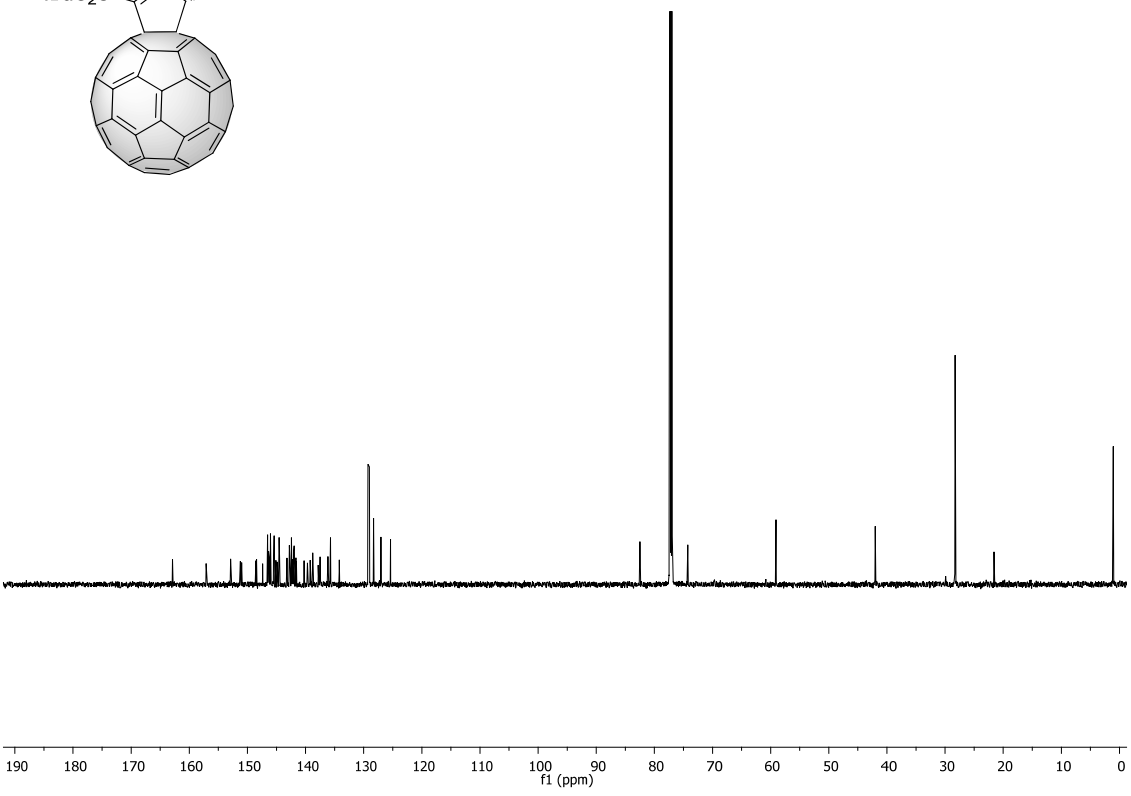




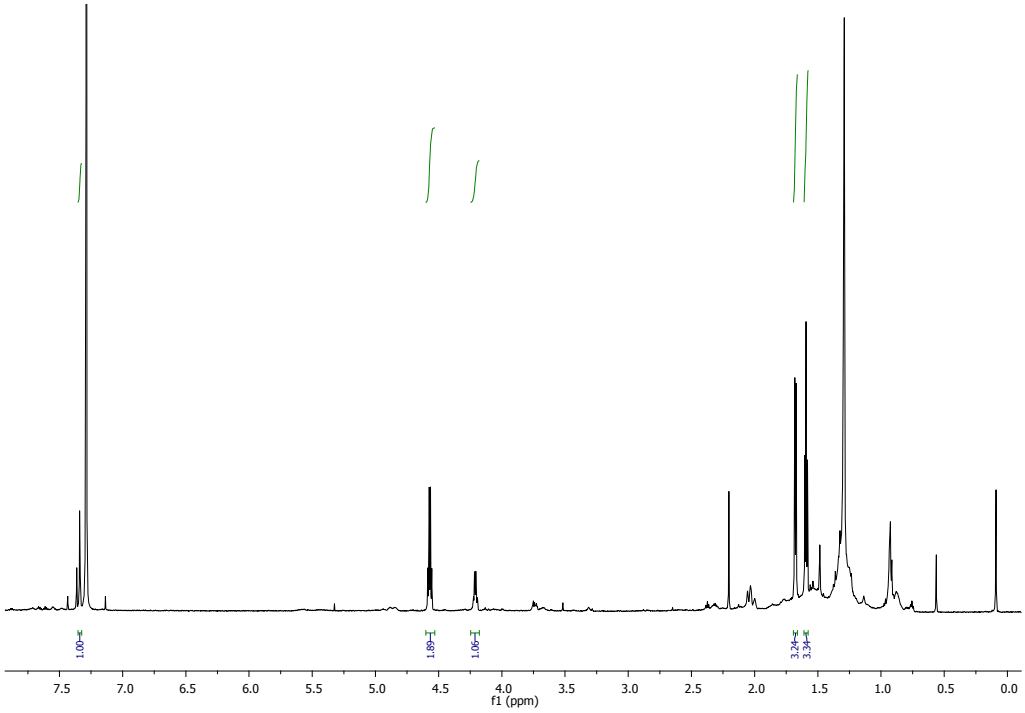
^{1}H-NMR,^{13}C-NMR spectra 1-*tert*-butoxycarbonyl-3-benzyl-1-cyclopenteno[4,5:1,2][60]fullerene (**2i**)

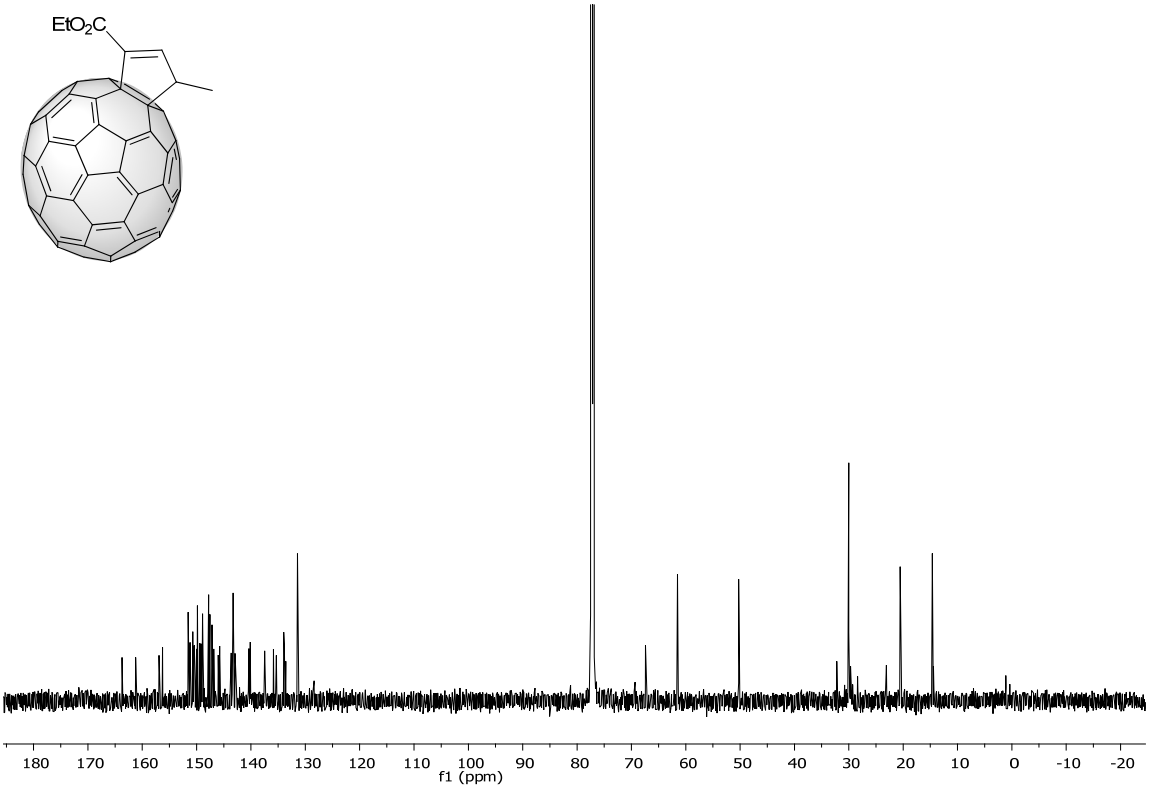




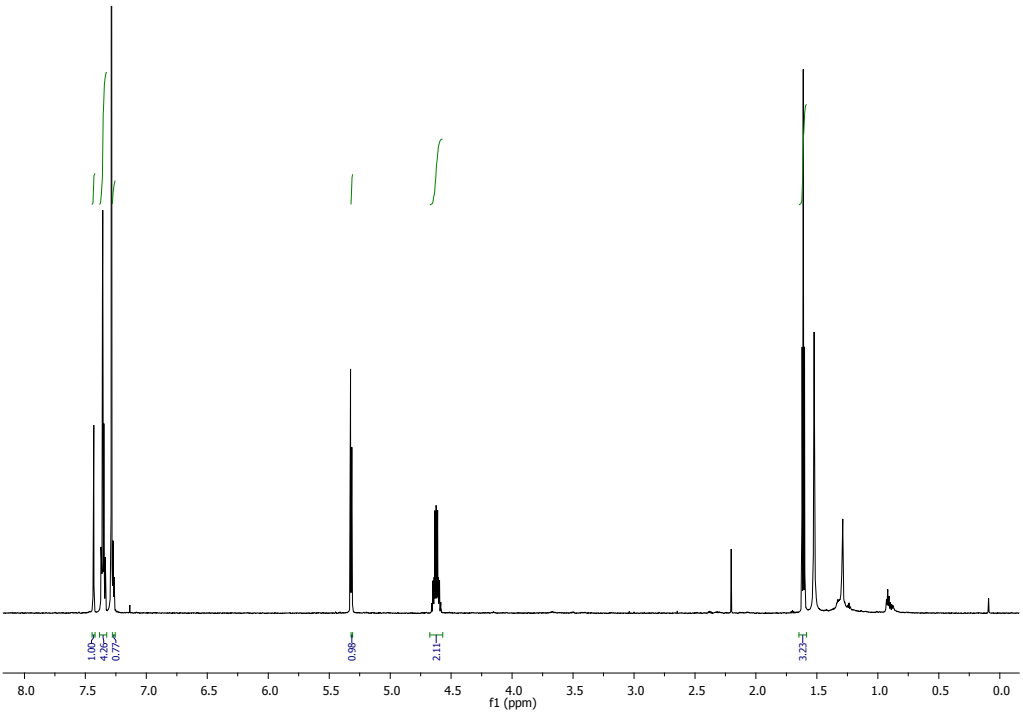


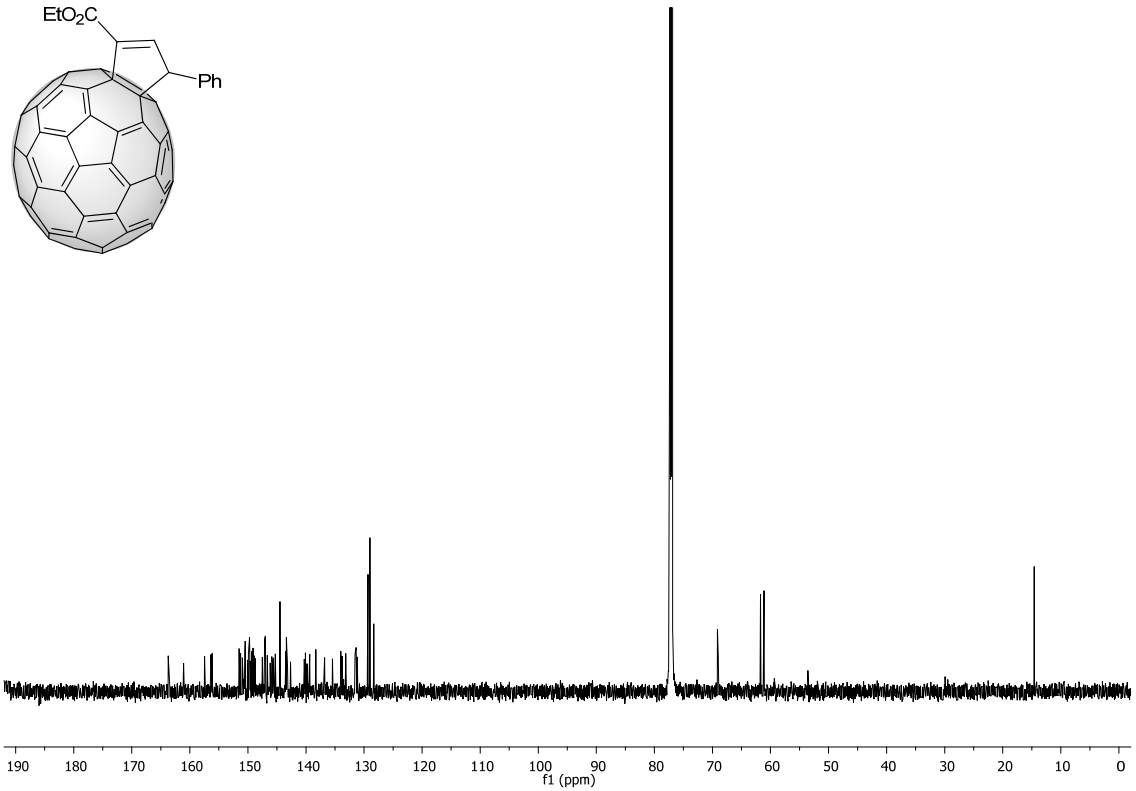
^{1}H-NMR,^{13}C-NMR spectra of 1-ethoxycarbonyl-3-methyl-1-cyclopenteno[3,4:25',8']][70]fullerene (7a)



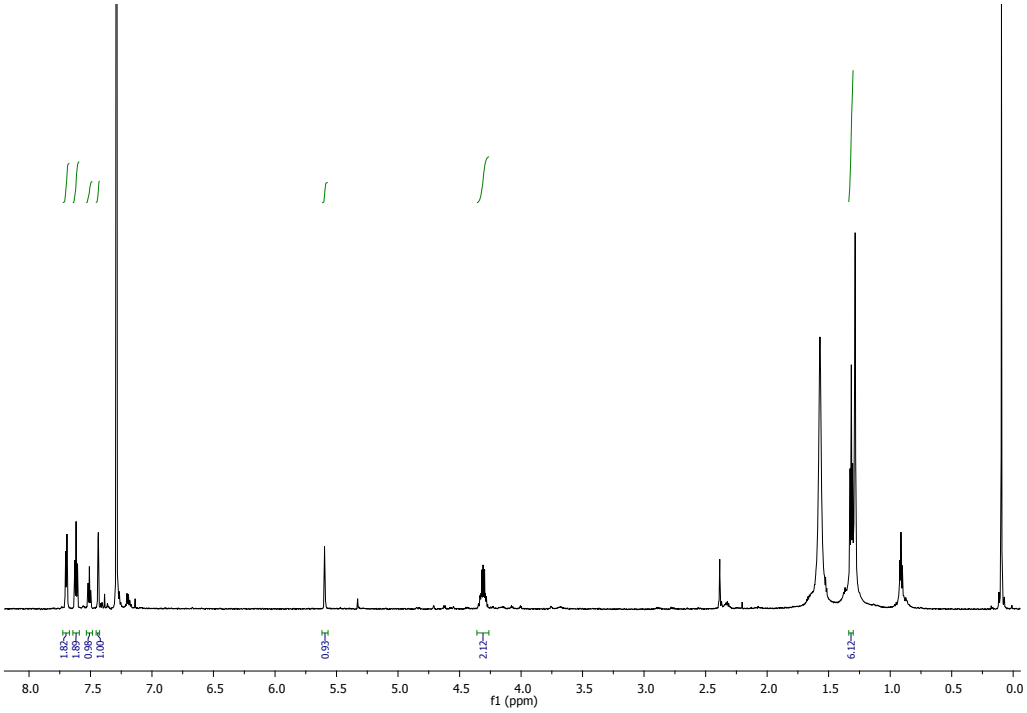


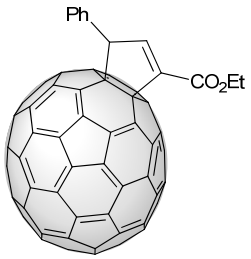
^{1}H-NMR,^{13}C-NMR spectra of 1-ethoxycarbonyl-3-phenyl-1-cyclopenteno[3,4:25',8'][70]fullerene (7b)

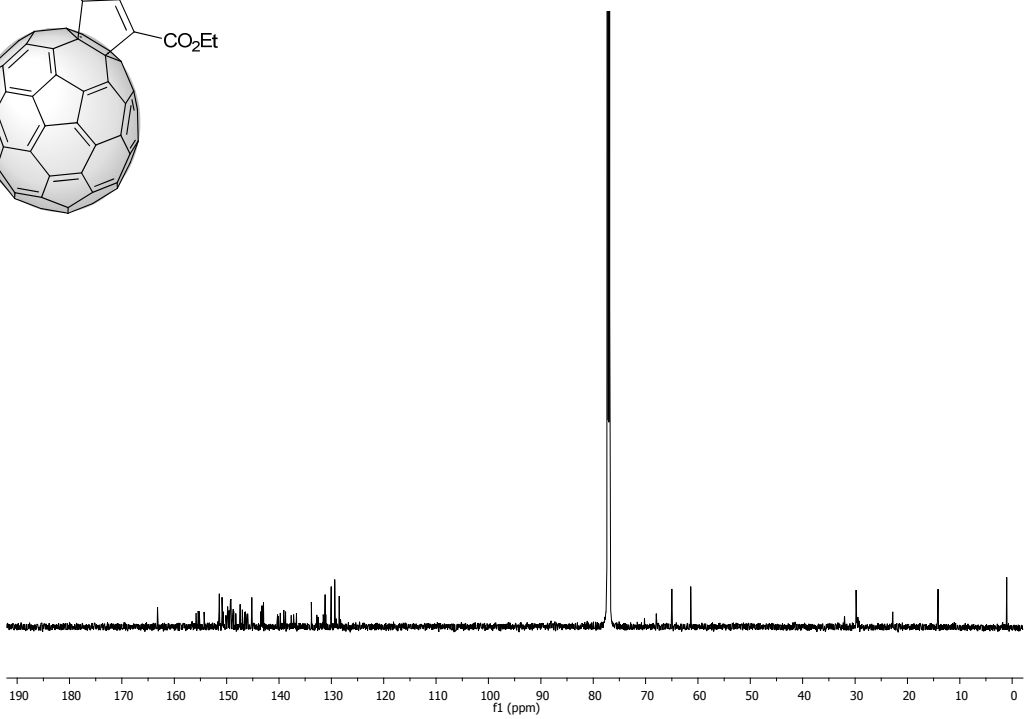




^{1}H-NMR,^{13}C-NMR spectra of 1-ethoxycarbonyl-3-phenyl-1-cyclopenteno[3,4:,8':25'][70]fullerene (7b´)



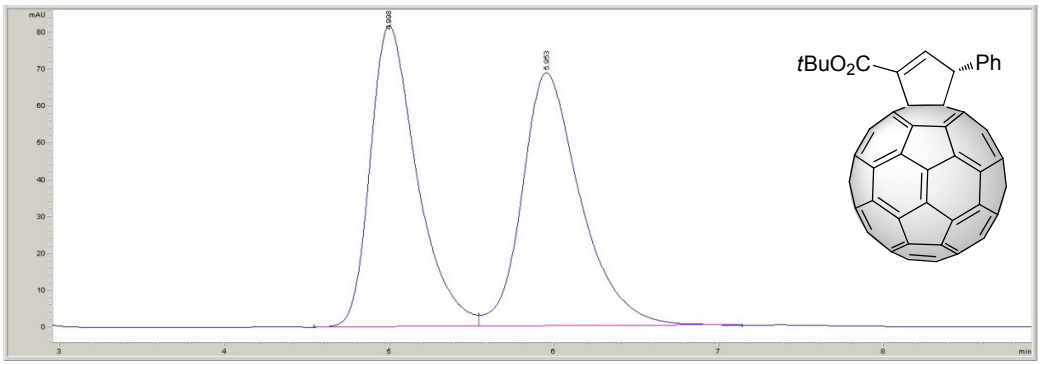




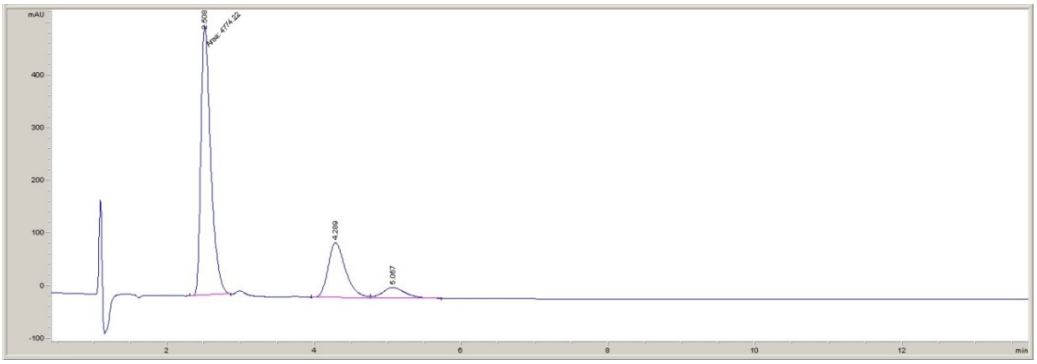
Representative HPLC chromatograms of racemic and enantioenriched cyclopenteno[4,5:1,2][60]fullerene derivatives 2c-d, 2i, 5 and 7b.

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.



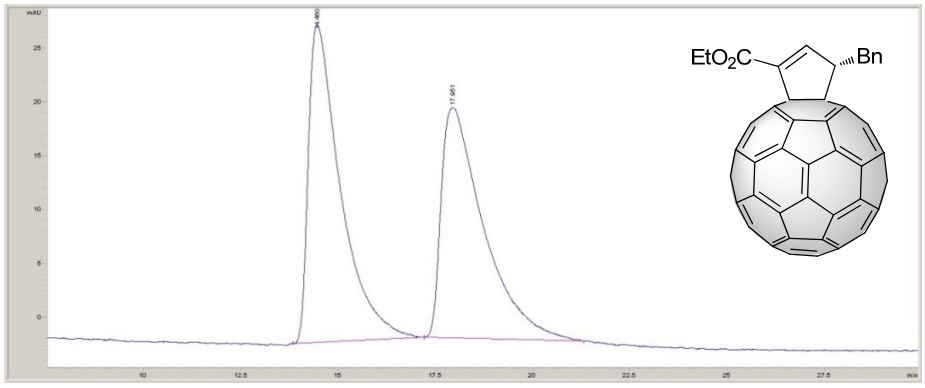
#	Time	Area	Height	Width	Area%	Symmetry
1	4.998	1610	81.9	0.2975	48.602	0.635
2	5.953	1702.6	68.8	0.3708	51.398	0.67



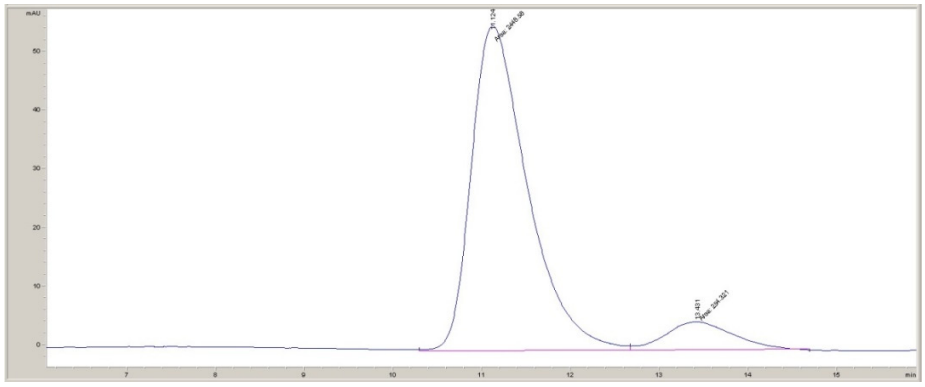
#	Time	Area	Height	Width	Area%	Symmetry
1	2.508	4774.2	513.7	0.1549	69.038	0.606
2	4.289	1723.7	104.3	0.2508	24.925	0.701
3	5.067	417.5	19.8	0.3162	6.037	0.78

#	Time	Area	Height	Width	Area%	Symmetry
1	4.289	1723.7	104.3	0.2508	80.501	0.701
2	5.067	417.5	19.8	0.3162	19.499	0.78

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.



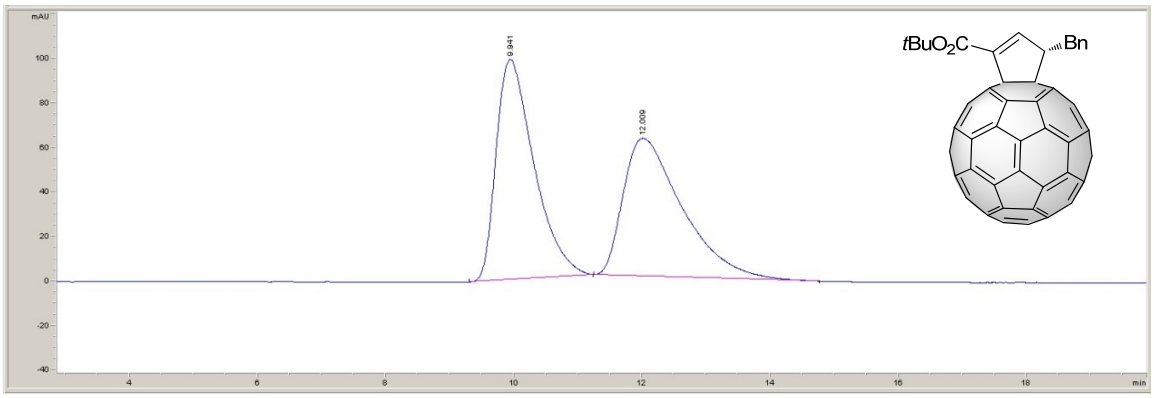
#	Time	Area	Height	Width	Area%	Symmetry
1	14.46	1697.6	29.5	0.7976	51.144	0.342
2	17.951	1621.7	21.4	1.0126	48.856	0.343



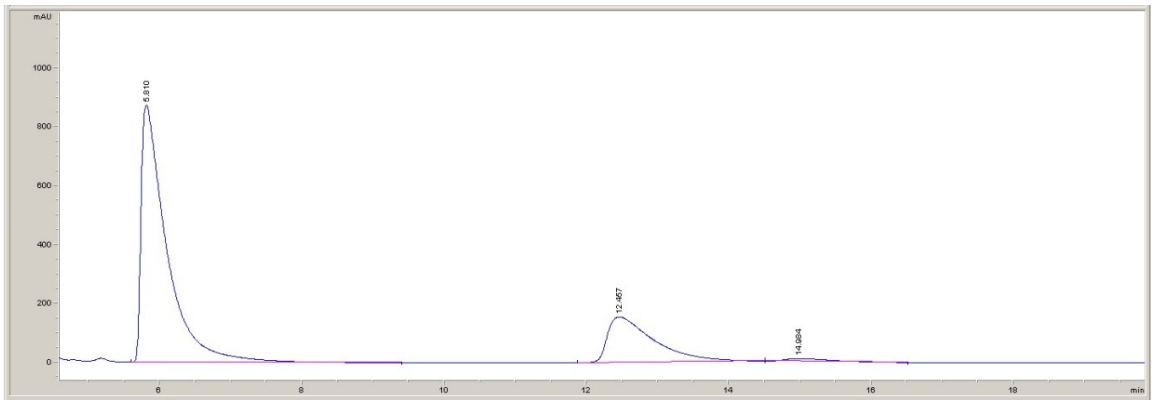
#	Time	Area	Height	Width	Area%	Symmetry
1	2.705	1391	143.7	0.1614	33.994	0.673
2	11.124	2446.6	55.4	0.7354	59.791	0.605
3	13.431	254.3	4.8	0.8859	6.215	0.872

#	Time	Area	Height	Width	Area%	Symmetry
1	11.124	2446.6	55.4	0.7354	90.584	0.605
2	13.431	254.3	4.8	0.8859	9.416	0.872

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.



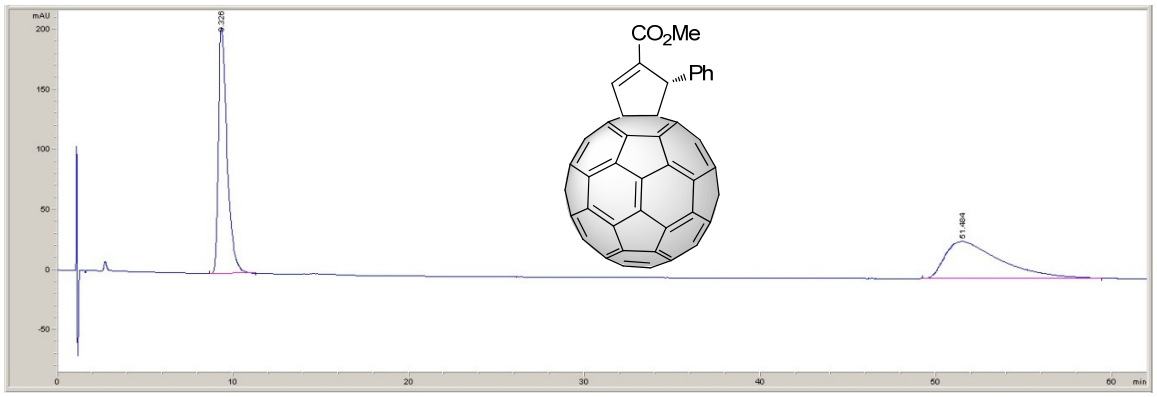
#	Time	Area	Height	Width	Area%	Symmetry
1	9.941	4057.3	98.9	0.6266	50.615	0.559
2	12.009	3958.7	61.9	0.9263	49.385	0.473



#	Time	Area	Height	Width	Area%	Symmetry
1	12.457	7505.3	157.2	0.7956	91.278	0.31
2	14.984	717.1	13.7	0.8737	8.722	0.617

#	Time	Area	Height	Width	Area%	Symmetry
1	5.81	21796	873.8	0.353	74.505	0.224
2	12.457	7016.8	155.1	0.6538	23.986	0.308
3	14.984	441.6	10	0.6149	1.509	0.436

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.

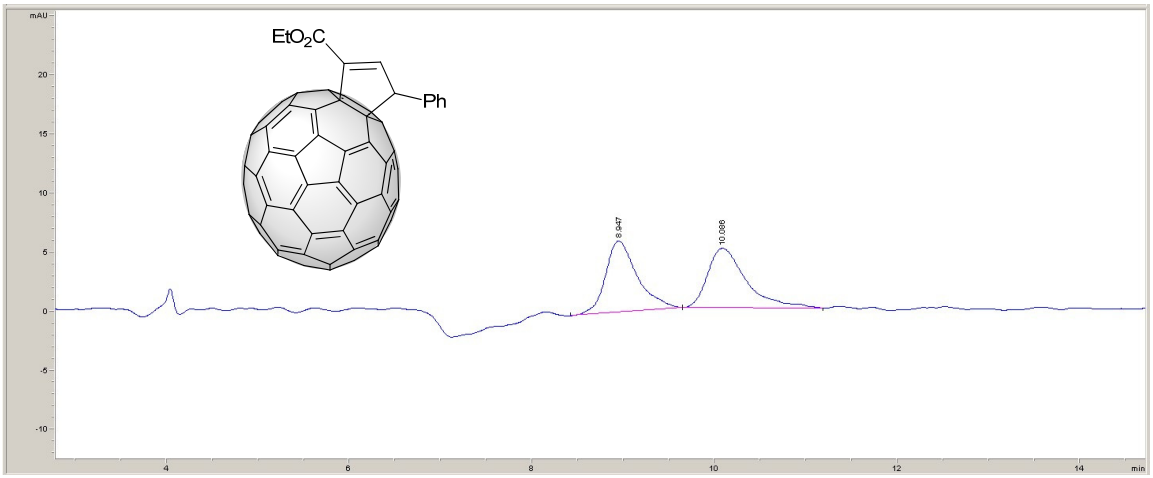


#	Time	Area	Height	Width	Area%	Symmetry
1	9.326	7045	205	0.521	51.452	0.526
2	51.484	6647.3	30.6	2.5366	48.548	0.448

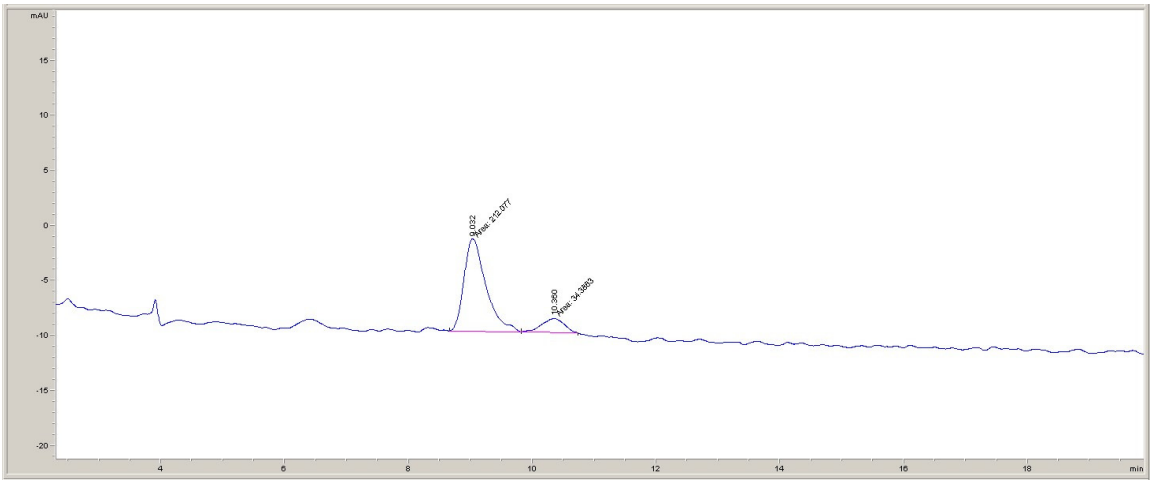
#	Time	Area	Height	Width	Area%	Symmetry
1	2.65	15031.6	1513	0.1656	63.370	0.511
2	9.614	1719.7	47.9	0.5979	7.250	0.687
3	50.822	6969.1	31.6	3.6786	29.380	0.405

#	Time	Area	Height	Width	Area%	Symmetry
1	9.614	1719.7	47.9	0.5979	19.792	0.687
2	50.822	6969.1	31.6	3.6786	80.208	0.405

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.



#	Time	Area	Height	Width	Area%	Symmetry
1	8.947	146.3	6	0.3451	49.685	0.674
2	10.086	148.2	5	0.4253	50.315	0.575



#	Time	Area	Height	Width	Area%	Symmetry
1	9.032	212.1	8.5	0.4179	86.048	0.621
2	10.36	34.4	1.3	0.432	13.952	1.38

Electrochemistry

Cyclic voltammograms were recorded on a potentiostat/galvanostatAUTOLAB with PGSTAT30 equipped with a software GPES for windows version 4.8in a conventional three compartment cell. Measurements of **2b-d, 2h-i** were carried out using*o*-DCB/MeCN (4:1) containing $Bu_4N^+PF_6^-$(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]

Product	$E_{1/2}^{red1}$/V	$E_{1/2}^{red2}$/V	$E_{1/2}^{red3}$/V
C_{60}	-1.027	-1.421	-1.877
2b	-1.118	-1.500	-2.025
2c	-1.133	-1.525	-2.050
2d	-1.107	-1.505	-2.019
2h	-1.081	-1.476	-2.003
2i	-1.114	-1.512	-2.039

[a] Potential in volts *vs*ferrocene/ferrocenium measured with cyclic voltammetry in *o*-DCB/MeCN (4:1) containing $Bu_4N^+PF_6^-$(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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[iii]J. Marco-Martínez, V. Marcos, S. Reboredo, S. Filippone and N. Martín, *Angew. Chem. Int. Ed.*, 2013, **52**, 5115.

[iv]H.-T. Yang, W.-L. Ren, C.-B. Miao, C.-P. Dong, Y. Yang, H.-T. Xi, Q. Meng, Y. Jiang and X.-Q. Sun, *J. Org. Chem.*, 2013, **78**, 1163.