Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

Synthesis of optically pure [60]fullerene *e,e,e,*-tris adducts

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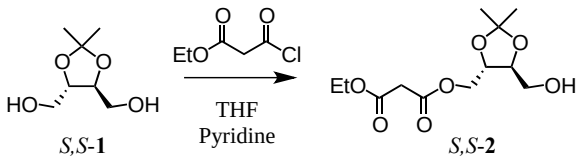
Experimental section

General. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from E. Merck. IR spectra (cm^{-1}) were recorded on a Perkin–Elmer Spectrum One Spectrophotometer. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference. MALDI-TOF-MS were obtained on a Bruker ULTRAFLEX TOF/TOF mass spectrometer with a dithranol matrix. CD spectra were recorded at 25°C on a Jasco J-810 circular dichroism spectrometer.

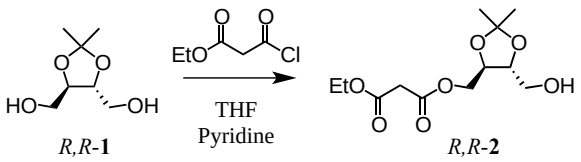
Compound *S,S*-2



S,S-**1** *S,S*-**2**

A solution of ethyl malonyle chloride (0.80 mL, 6.25 mmol) in anhydrous THF (60 mL) was added dropwise over 1 h to a stirred solution of (*4S,5S*)-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (*S,S*-**1**) (2.03 g, 12.50 mmol) and pyridine (0.95 mL, 11.75 mmol) in anhydrous THF (20 mL) at 0°C. The mixture was then stirred at room temperature overnight. The resulting mixture was filtered to remove the salts and concentrated. Column chromatography (SiO_2, CH_2Cl_2) gave *S,S*-**2** (1.21 g, 70%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.31 (t, J = 7 Hz, 3H), 1.44 (s, 3H), 1.45 (s, 3H), 1.93 (m, 1H), 3.45 (s, 2H), 3.67 (m, 1H), 3.86 (m, 1H), 3.98 (m, 1H), 4.40-4.15 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.0, 26.9, 27.0, 41.4, 61.7, 61.8, 64.9, 74.8, 78.3, 109.9, 166.3, 166.35.

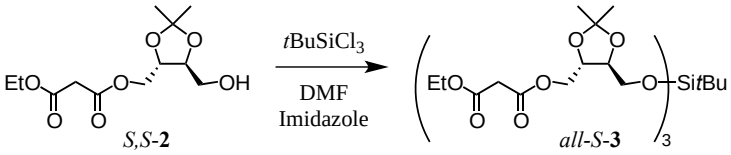
Compound *R,R*-2



R,R-**1** *R,R*-**2**

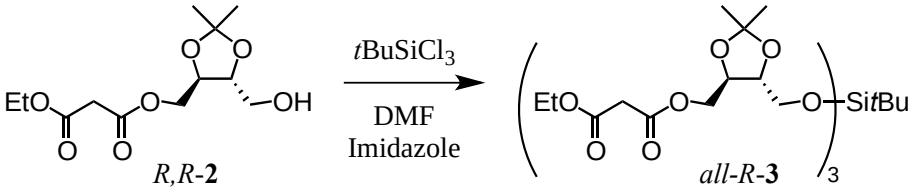
As described for *S,S*-**2** starting from (*4R,5R*)-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (*R,R*-**1**) (2.00 g, 12.33 mmol), pyridine (1.00 mL, 12.33 mmol) and ethyl malonyle chloride (0.79 mL, 6.17 mmol). Column chromatography (SiO_2, CH_2Cl_2) gave *R,R*-**2** (1.31 g, 77%) as a colorless oil. ^1H and ^{13}C-NMR data rigorously identical to those described for the corresponding enantiomer *S,S*-**2**.

Compound *all-S*-3



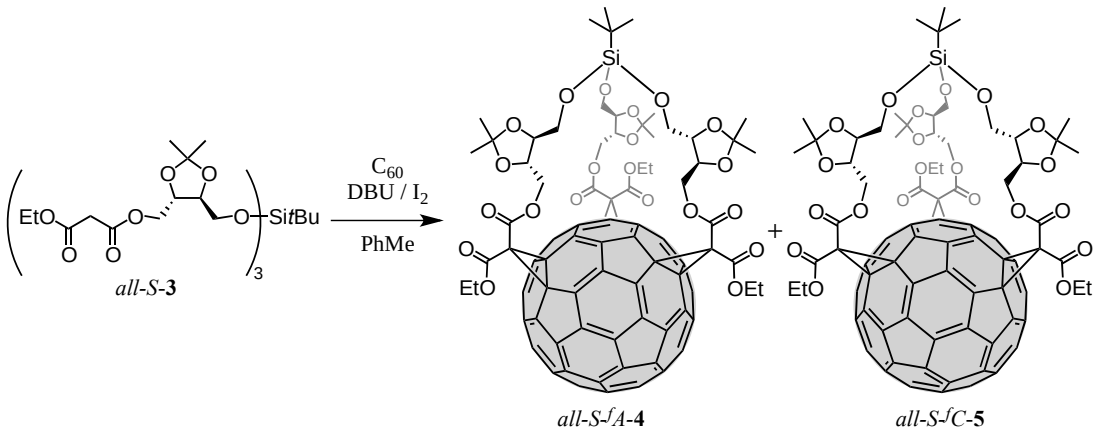
A mixture of *S,S*-**2** (1.14 g, 4.10 mmol), imidazole (262 mg, 3.85 mmol) and *t*$BuSiCl_3$ (248 mg, 1.30 mmol) in anhydrous DMF (10 mL) was stirred at 0°C for 1 h. The mixture was then allowed to warm slowly to room temperature and stirred for 12 h at this temperature, then H_2O (50 mL) was added. The aqueous layer was extracted with Et_2O (3 x). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated. Column chromatography (SiO_2, CH_2Cl_2) gave *all-S*-**3** (460 mg, 39%) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): 1.00 (s, 9H), 1.30 (t, *J* = 7 Hz, 9H), 1.43 (s, 18H), 3.45 (s, 6H), 3.92-4.05 (m, 9H), 4.15-4.27 (m, 12H), 4.42-4.49 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.0, 17.8, 26.2, 26.9, 27.1, 41.3, 61.6, 63.3, 65.2, 109.9, 166.2, 166.4.

Compound *all-R*-3



As described for *all-S*-**3** starting from *R,R*-**2** (1.00 g, 3.62 mmol), imidazole (269 mg, 3.96 mmol) and *t*$BuSiCl_3$ (217 mg, 1.13 mmol). Column chromatography (SiO_2, CH_2Cl_2) gave *all-R*-**3** (538 mg, 52 %) as a colorless oil. ^1H and ^{13}C NMR data rigorously identical to those described for the corresponding enantiomer *all-S*-**3**.

Compounds *all-S-^{f}A*-4 and *all-S-^{f}C*-5



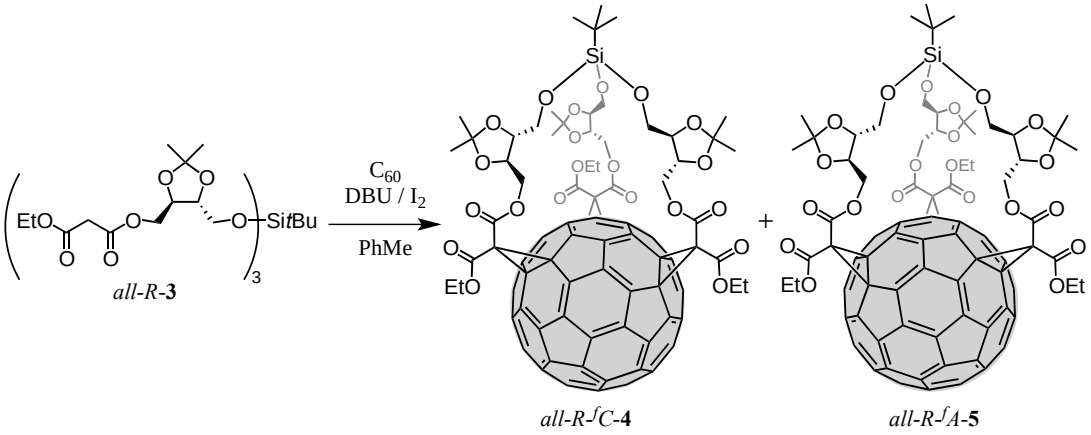
DBU (0.56 mL, 3.75 mmol) was added to a stirred solution of C_{60} (536 mg, 0.75 mmol), *all-S*-**3** (460 mg, 0.50 mmol) and I_2 (444 mg, 1.75 mmol) in toluene (1.2 L) at -15 °C. After 1 h, the mixture was filtered through a short plug of SiO_2, eluting first with toluene (to remove unreacted C_{60}), then with CH_2Cl_2. Gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) followed by column chromatography (SiO_2, cyclohexane/EtOAc 80:20) gave *all-S-^{f}A*-**4** (59.4 mg, 7%) and *all-S-^{f}C*-**5** (41.4 mg, 5%).

Data for all-S-^{f}A-**4**. Red solid. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.00 (s, 9H), 1.41 (t, *J* = 7 Hz, 9H), 1.415 (br s, 9H), 1.49 (br s, 9H), 3.69 (d, *J* = 5 Hz, 6H), 3.92 (td, *J* = 8 Hz and 5 Hz, 3H), 4.09 (br d, *J* = 8 Hz, 3H), 4.35-4.51 (m, 9H), 4.57 (dd, *J* = 13 Hz and 2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 14.1, 18.0, 26.5, 26.7, 27.2, 52.8, 62.2, 63.4, 63.8, 70.1, 70.8, 75.5, 75.7, 109.7, 141.7, 141.7, 142.0, 142.6, 143.0, 143.3, 143.5, 144.1, 144.2, 145.8, 146.2, 146.25, 146.3, 146.4, 146.8, 146.9, 146.9, 147.0, 162.6, 162.7. IR (neat): 1750 (C=O). MALDI-TOF-MS: 1647.31 ($[M+Na]^+$, calcd for $C_{100}H_{60}O_{21}SiNa$: 1647.33), 1624.33 ($[M]^+$, calcd for $C_{100}H_{60}O_{21}Si$: 1624.34).

Data for all-S-^{f}C-**5** Red solid. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.05 (s, 9H), 1.40 (t, *J* = 7 Hz, 9H), 1.42 (s, 18H), 3.69 (dd, *J* = 11 Hz and 2 Hz, 3H), 3.81-3.90 (m, 6H), 4.30-4.50 (m, 15H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.0, 18.4, 26.8, 26.9, 27.3, 52.8, 62.5, 63.3, 68.2, 70.0, 70.7, 75.3, 78.1, 110.1, 141.0, 141.8, 142.2, 142.8, 143.3 (2C), 143.4, 143.7, 144.3, 145.7, 146.3, 146.4 (2C), 146.5, 146.7, 146.85 (2C), 146.9, 163.0, 163.6. IR (neat): 1749 (C=O). MALDI-

TOF-MS: 1647.3 ($[M+Na]^+$, calcd for $C_{100}H_{60}O_{21}SiNa$: 1647.33), 1624.3 ($[M]^+$, calcd for $C_{100}H_{60}O_{21}Si$: 1624.34).

Compounds *all-R-*^{f}*C*-4 and *all-R-*^{f}*A*-5

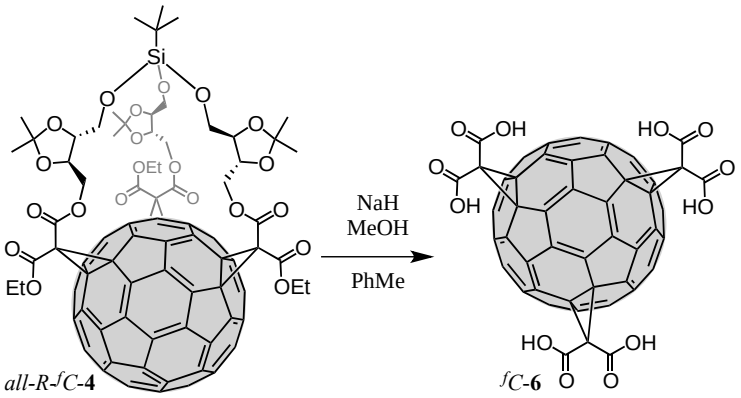


As described for *all-S-*^{f}*A*-**4** and *all-S-*^{f}*C*-**5** starting from C_{60} (468 mg, 0.65 mmol), *all-R*-**3** (538 mg, 0.59 mmol) and I_2 (524 mg, 2.07 mmol). Gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) followed by column chromatography (SiO_2, cyclohexane/EtOAc 80:20) gave *all-R-*^{f}*C*-**4** (80.1 mg, 9%) and *all-R-*^{f}*A*-**5** (81.6 mg, 9%).

Data for all-R-^{f}*C*-**4**. Red solid. ^{1}H and ^{13}C NMR, IR, MS and UV/vis data rigorously identical to those described for the corresponding enantiomer *all-S-*^{f}*A*-**4**.

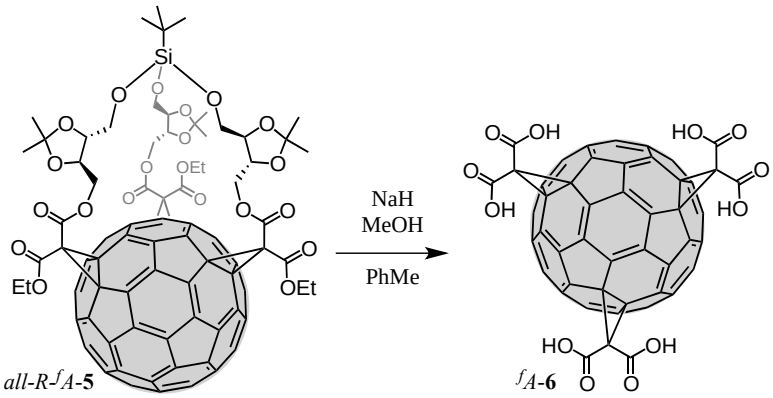
Data for all-R-^{f}*A*-**5**. Red solid. ^{1}H and ^{13}C NMR, IR, MS and UV/vis data rigorously identical to those described for the corresponding enantiomer *all-S-*^{f}*C*-**5**.

Compound ^{f}*C*-6



A solution of *all-R-*^{f}*C*-**4** (70.3 mg, 0.04 mmol) and NaH (60% dispersion in mineral oil, 19.2 mg, 0.80 mmol) in toluene (10 mL) was stirred at 60°C for 3 h. Then, MeOH (1 mL) was added. After 1 h, the resulting precipitate was collected by centrifugation, washed with toluene, an aqueous 2M H_2SO_4 solution and water. Finally, drying *in vacuo* at 60°C overnight gave ^{f}*C*-**6** (31.5 mg, 77 %) as a red solid. The analytical data of ^{f}*C*-**6** were in complete agreement with literature data.[1]

Compound ^{f}*A*-6



A solution of *all-R-*^{f}*A*-**5** (75.3 mg, 0.046 mmol) and NaH (60% dispersion in mineral oil, 22.2 mg, 0.93 mmol) in toluene (10 mL) was stirred at 60°C for 3 h. Then, MeOH (1 mL) was added. After 1 h, the resulting precipitate was collected by centrifugation, washed with toluene, an aqueous 2M H_2SO_4 solution and water. Finally, drying *in vacuo* at 60°C overnight gave ^{f}*A*-**6** (39.3 mg, 87%) as a red solid. The analytical data of ^{f}*A*-**6** were in complete agreement with literature data.[1]

X-Ray crystal structure of *all-S-*^{f}*A*-4.

Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of hexane into a 1:1 $CHCl_3/CH_2Cl_2$ solution of *all-S-*^{f}*A*-**4**. Data were collected at 173 K on a Bruker APEX-II CCD diffractometer (Cu-Kα radiation, λ = 1.54178 Å). The structure was solved by direct methods (SHELXS-97) and refined against F^2 using the SHELXL-97 software. The non-hydrogen atoms were refined anisotropically, using weighted full-matrix

[1] I. Lamparth and A. Hirsch, *Chem. Commun*., 1994, 1727-1728.

least-squares on F^2. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. Crystallographic data: formula: *all-S-*^{f}*A-***4**.$(CHCl_3)_2$.(CH_2Cl_2): $C_{100}H_{60}O_{21}Si(CHCl_3)_2(CH_2Cl_2)$ (M = 1949.23 g.mol^{-1}); crystal system: orthorhombic, space group P $2_12_12_1$; *a* = 14.8066(6) Å; *b* = 21.8262(9) Å; *c* = 26.1967(11) Å; α = 90.00°; β = 90.00°; γ = 90.00°; V = 8462.2(6) Å^3; Z = 4; F(000) = 4000; a total of 50199 reflections collected; 2.64° < θ < 66.76°, 14531 independent reflections with 13512 having I > 2σ(I); 1163 parameters; final results: $R_1(F^2)$ = 0.1200; $wR_2(F^2)$ = 0.3274, Flack parameter: 0.16(3); Goof = 1.546

The moderate $R_1(F^2)$ value (0.1200) results mainly from the disorder of some CO_2Et and Me groups. The structure is however in no doubt. Importantly, the absolute configuration of the stereogenic C atoms of the dioxolane subunits (C-67, C-68, C-79, C-80, C-91, C-92) is known thus allowing the relative determination of the absolute configuration of the chiral *e,e,e* fullerene addition pattern.

Fig. S1. TLC (eluent: cyclohexane/EtOAc 8:2) of *all-R-*^{f}*A*-**5** (left), *all-R-*^{f}*C*-**4** (centre) and both compounds (right).

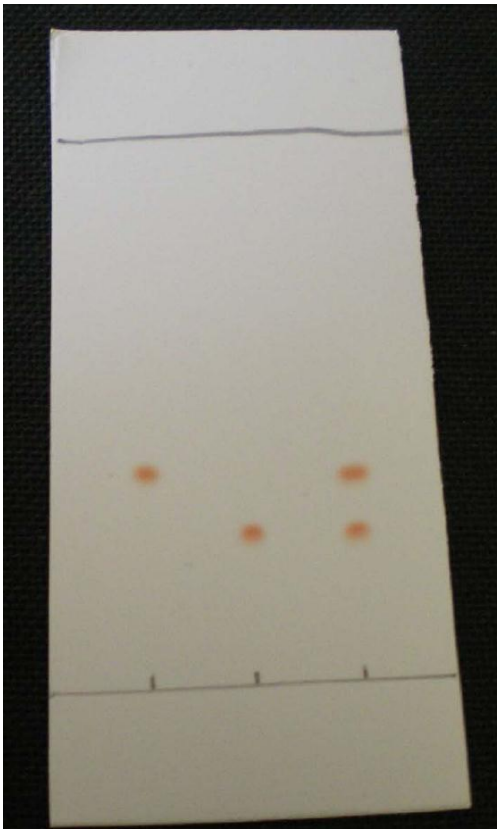


Fig. S2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound *all-S-*^{f}*A*-**4**.

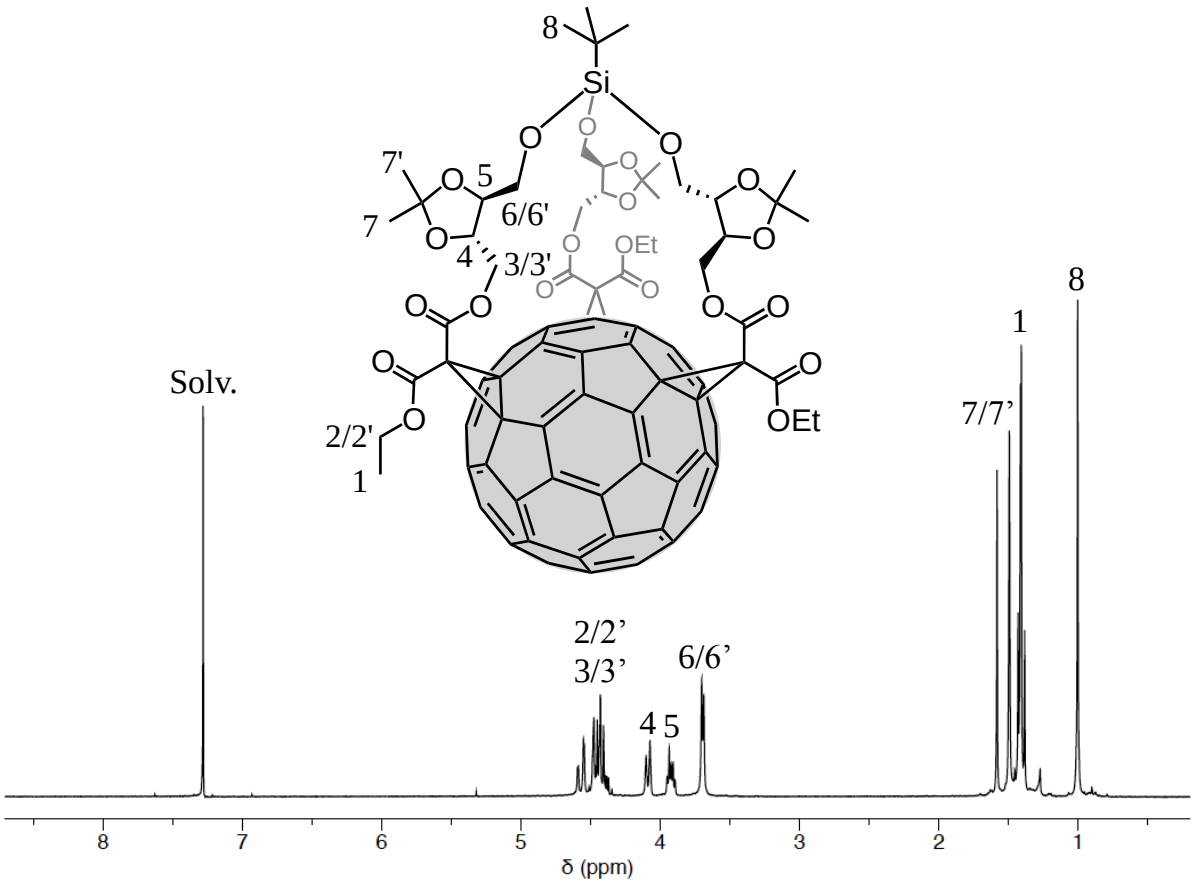


Fig. S3. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound *all-S-*^{f}*A*-**4**.

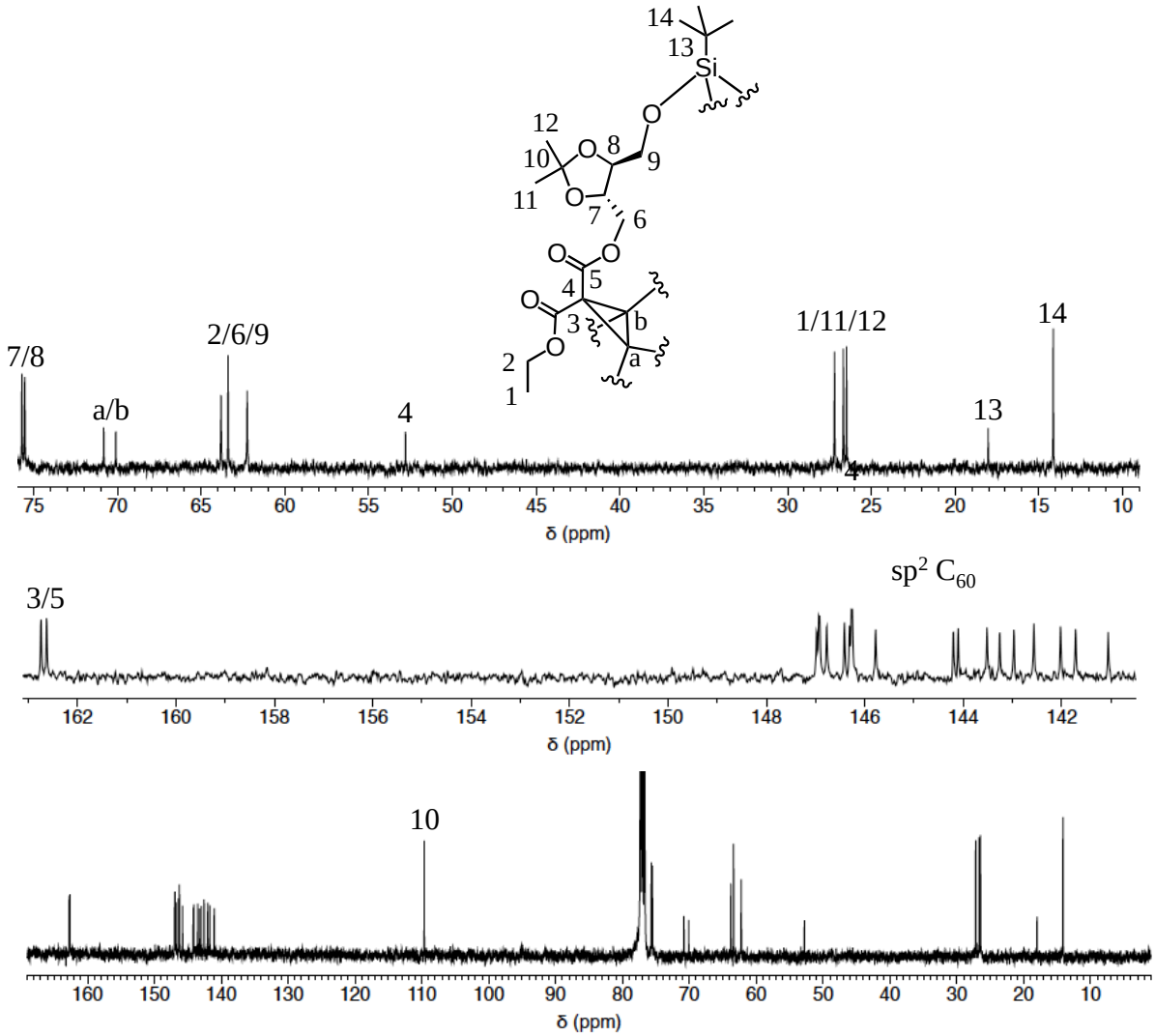
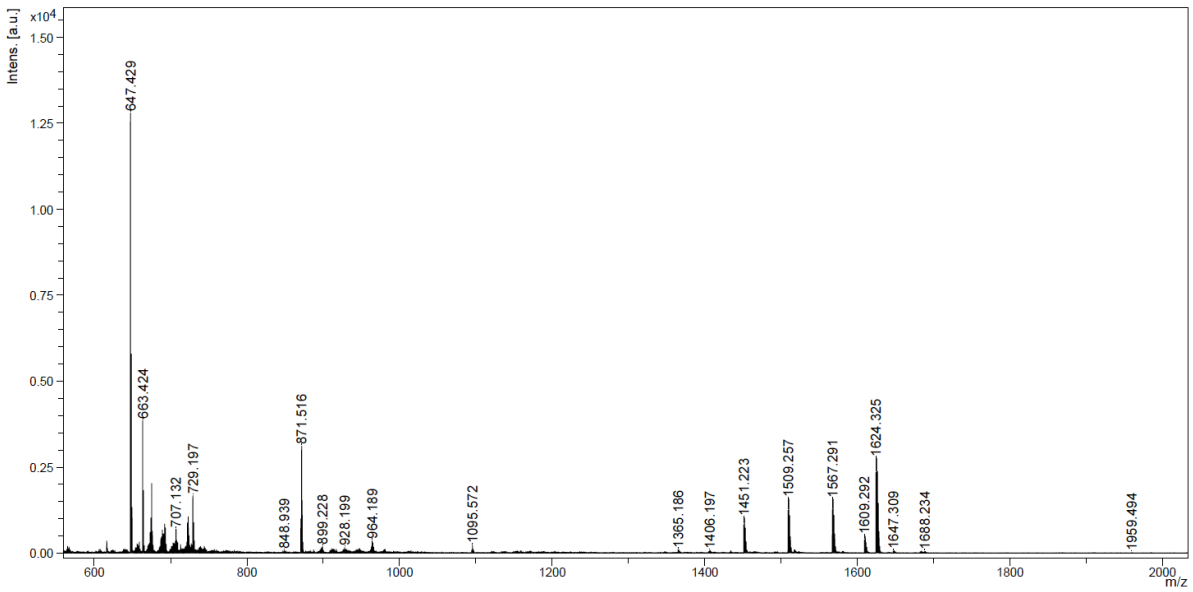


Fig. S4. MALDI-TOF mass spectrum of compound *all-S-*^{f}*A*-**4**.



1647.3: $[M + Na]^+$, calcd for $C_{100}H_{60}O_{21}SiNa$: 1647.33

1624.3: $[M]^+$, calcd for $C_{100}H_{60}O_{21}Si$: 1624.34

1567.3: $[M - t\text{Bu}]^+$, calcd for $C_{96}H_{51}O_{21}Si$: 1567.27

1509.3: $[M - t\text{BuSiOCH}_2]^+$, calcd for $C_{95}H_{49}O_{20}$: 1509.28

1451.2: $[M - t\text{BuSiOCH}_2 - \text{OC}(\text{CH}_3)_2]^+$, calcd for $C_{92}H_{43}O_{19}$: 1451.24

Fig. S5. IR spectrum (neat) of compound *all-S-*^{f}*A*-**4**.

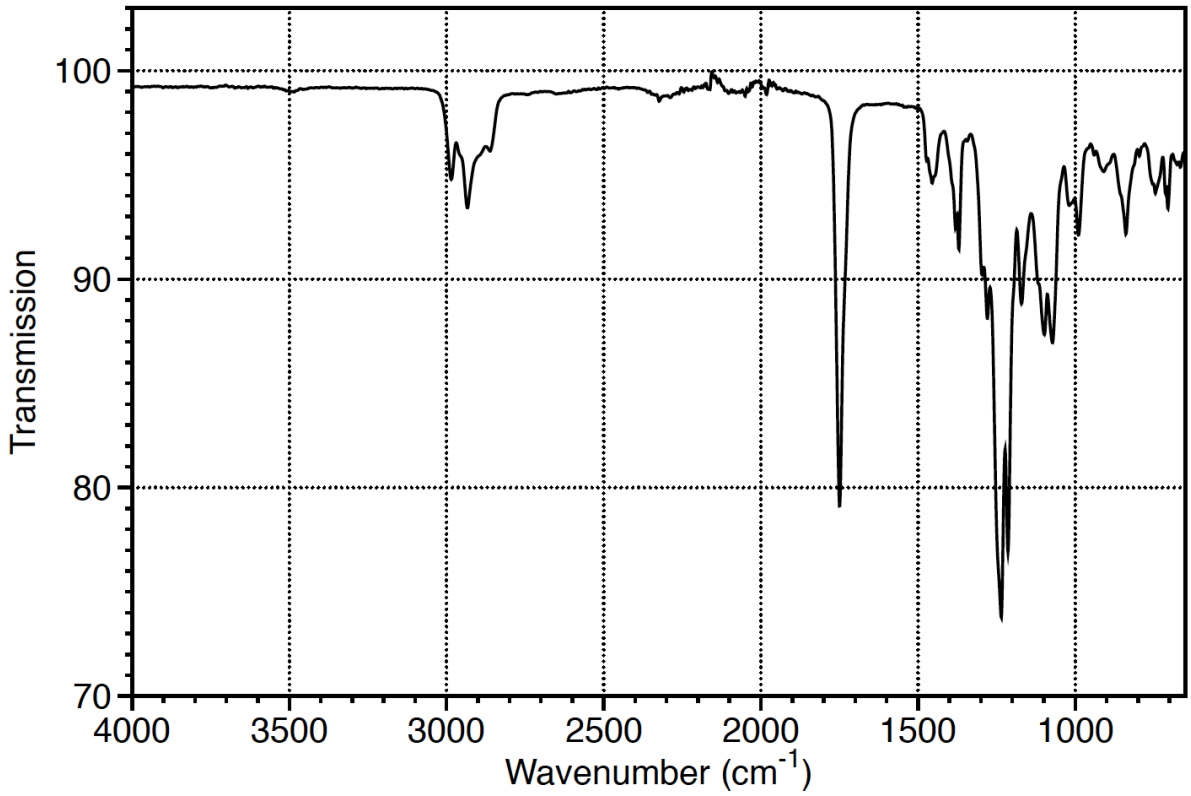


Fig. S6. Absorption spectrum of compound *all-S-*^{f}*A*-**4** (CH_2Cl_2).

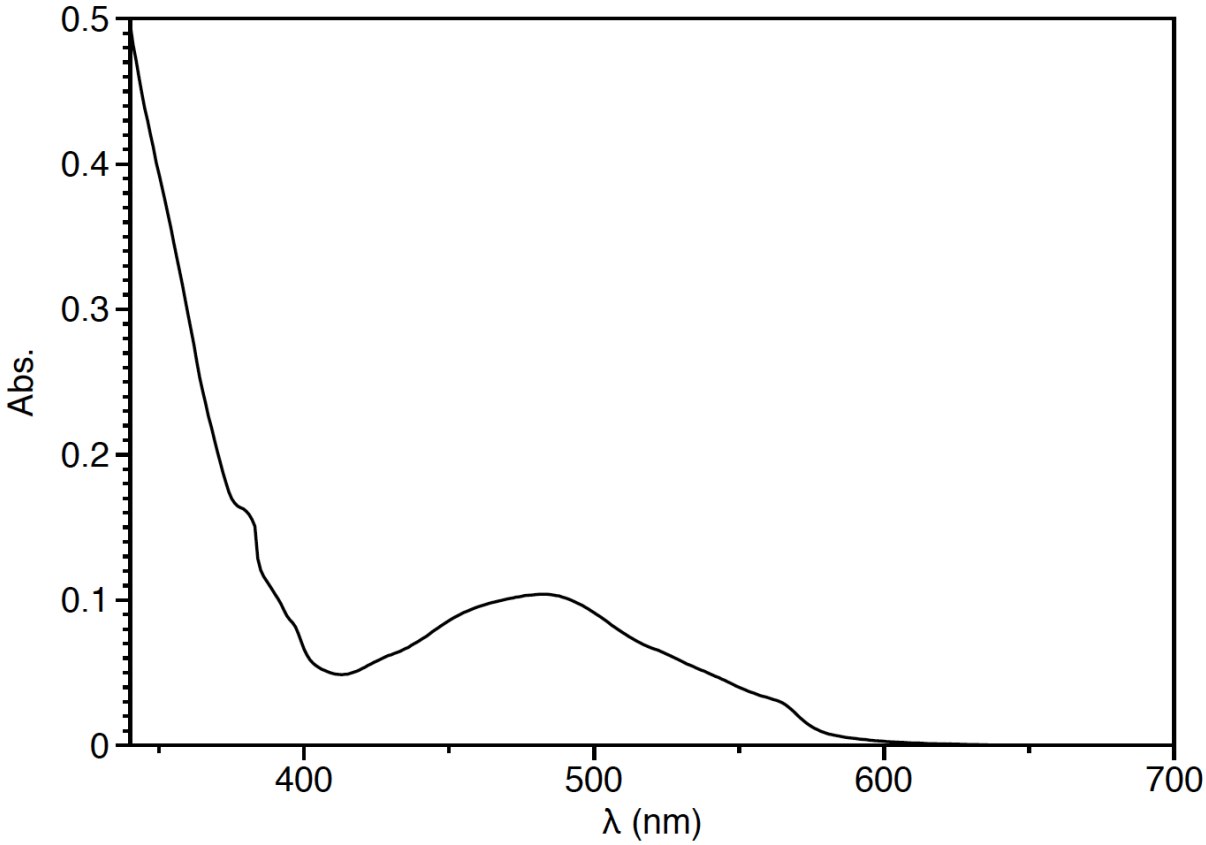


Fig. S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound *all-S-*^{f}*C*-**5**.

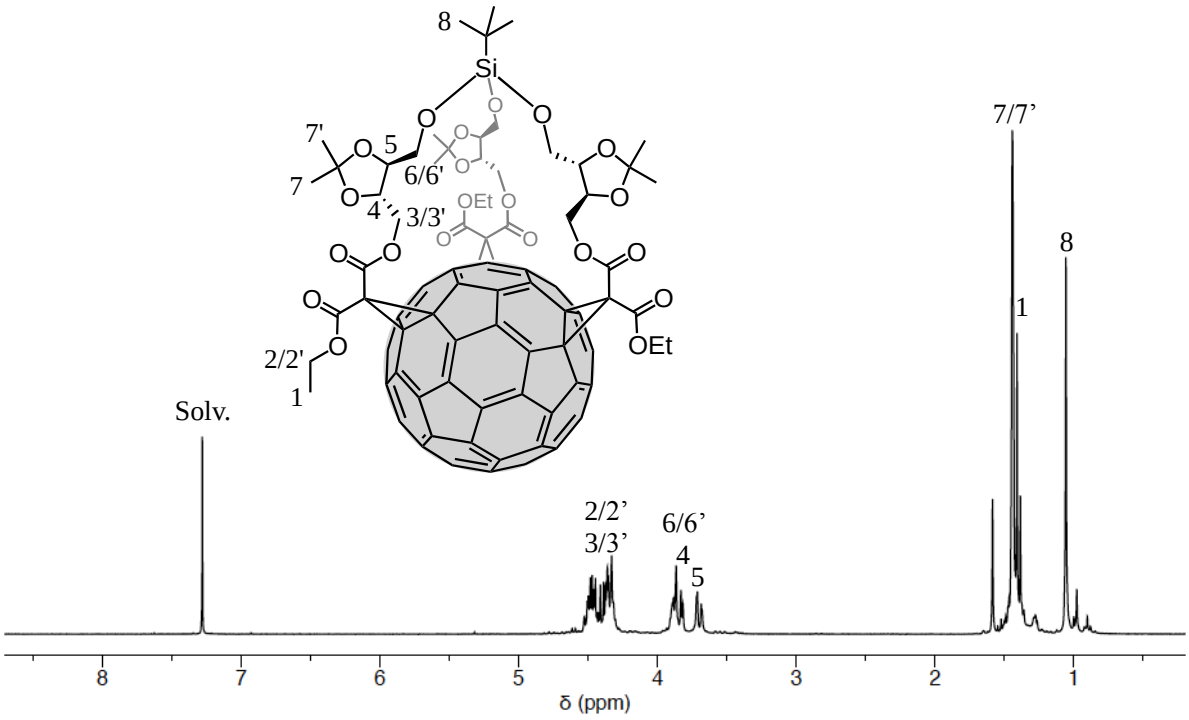


Fig. S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound *all-S-*^{f}*C*-**5**.

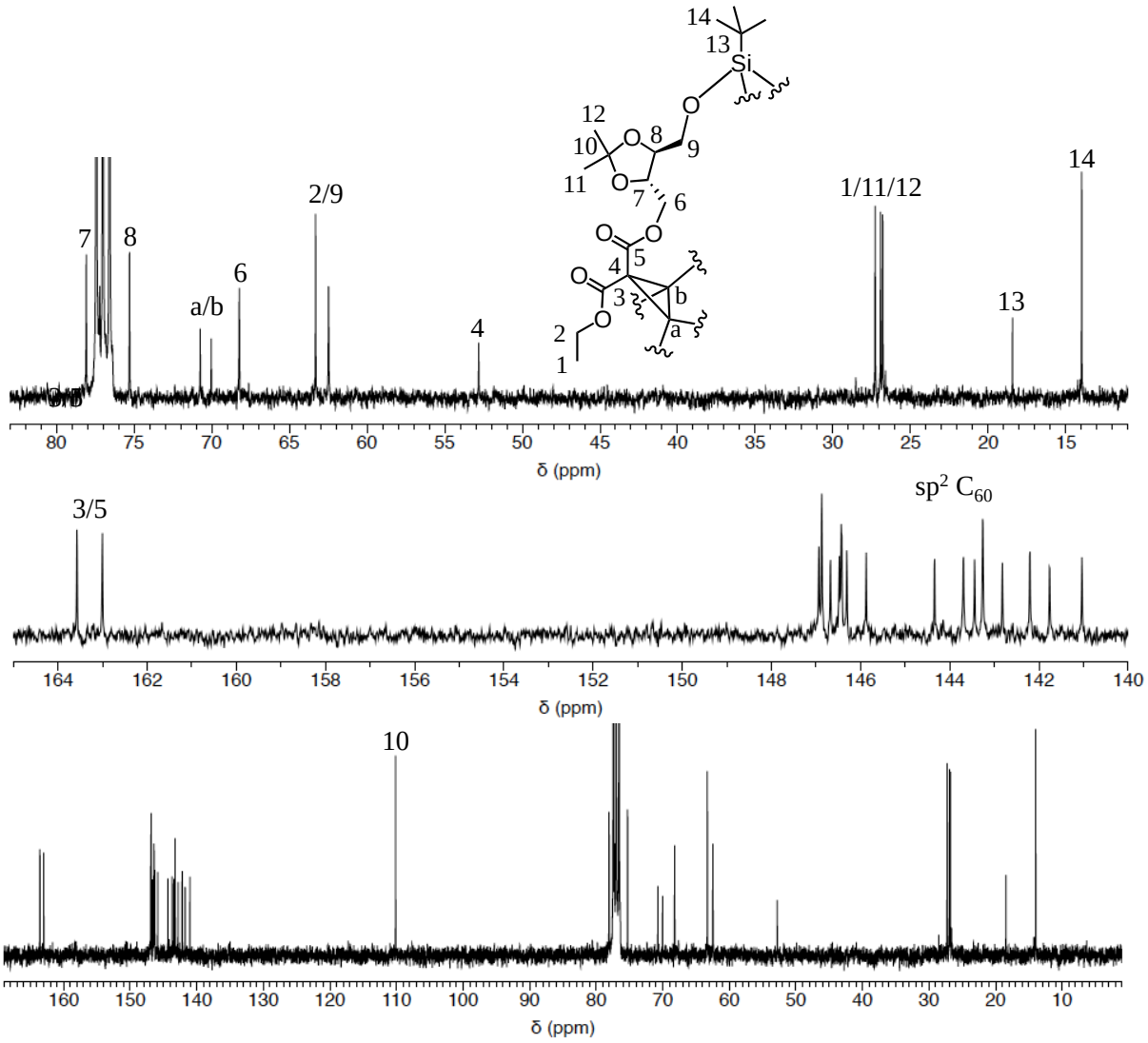
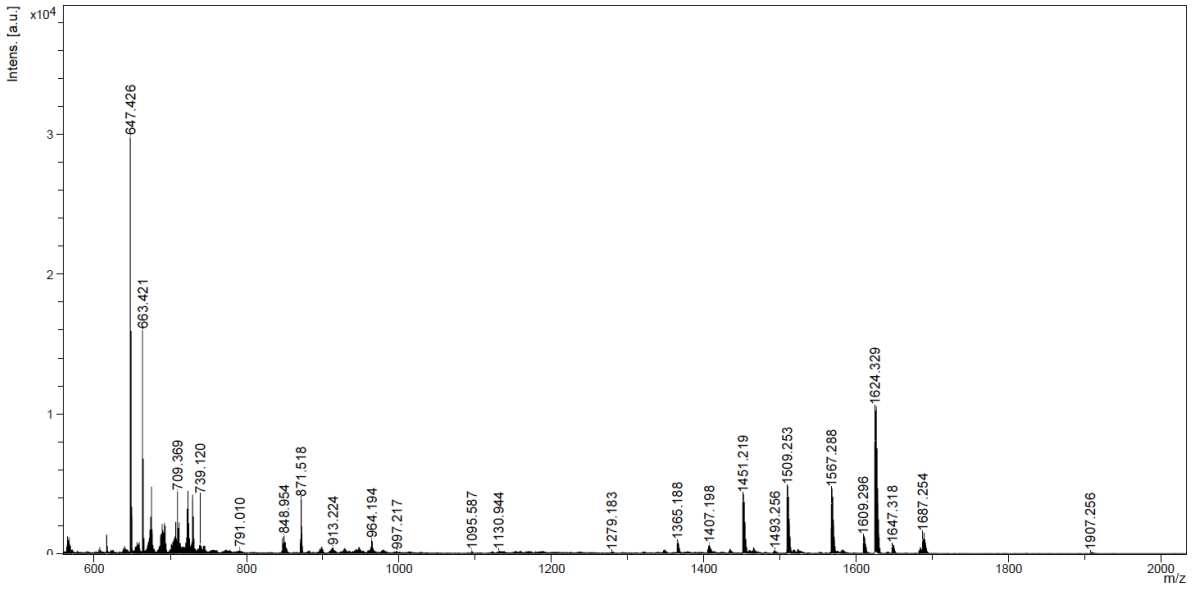


Fig. S9. MALDI-TOF mass spectrum of compound *all-S-*^{f}*C*-**5**.



1647.3: $[M + Na]^+$, calcd for $C_{100}H_{60}O_{21}SiNa$: 1647.33

1624.3: $[M]^+$, calcd for $C_{100}H_{60}O_{21}Si$: 1624.34

1567.3: $[M - t\text{Bu}]^+$, calcd for $C_{96}H_{51}O_{21}Si$: 1567.27

1509.3: $[M - t\text{BuSiOCH}_2]^+$, calcd for $C_{95}H_{49}O_{20}$: 1509.28

1451.2: $[M - t\text{BuSiOCH}_2 - \text{OC}(\text{CH}_3)_2]^+$, calcd for $C_{92}H_{43}O_{19}$: 1451.24

Fig. S10. IR spectrum (neat) of compound *all-S-*^{f}*C*-**5**.

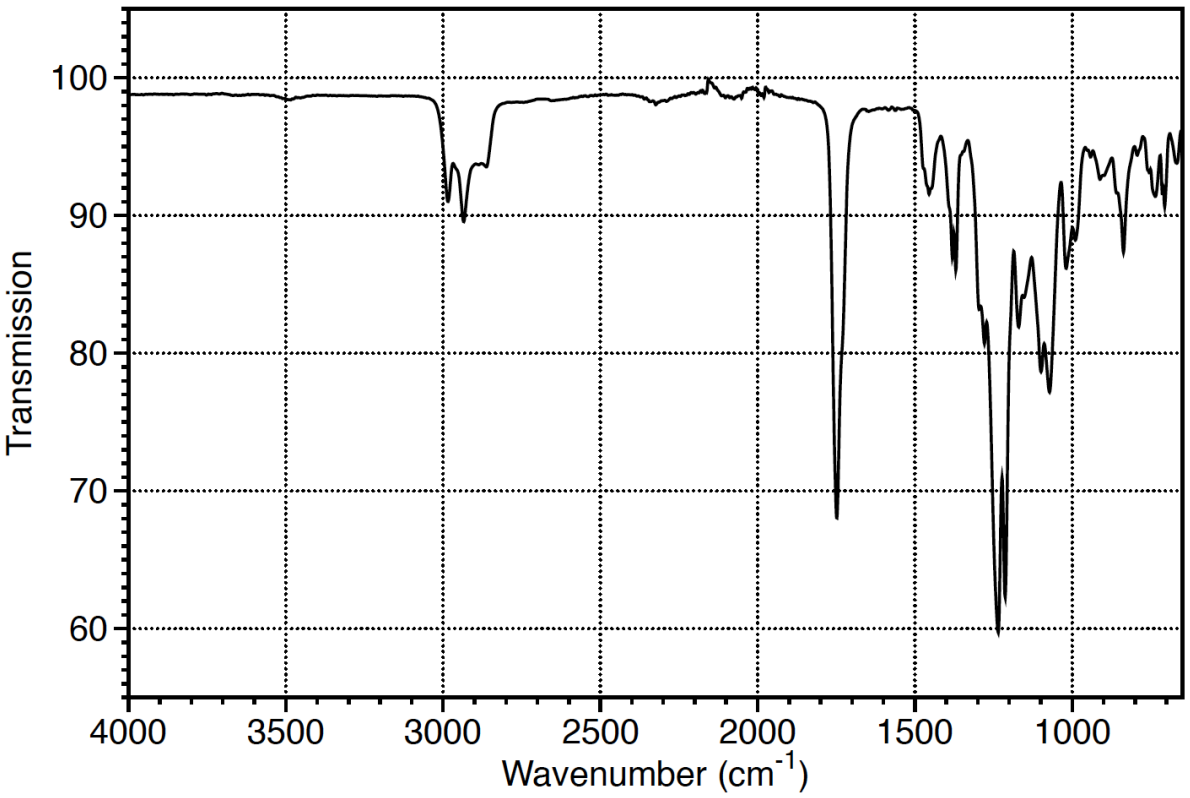


Fig. S11. Absorption spectrum of compound *all-S-*^{f}*C*-**5** (CH_2Cl_2).