Supporting Information

Palladium-Catalyzed Tetraallylation of C_{60} with Allyl Chloride and Allylstannane: Mechanism, Regioselectivity, and Enantioselectivity

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1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. $PdCl_2[P(OPh)_3]_2$[1] and phosphoramidites[2] was prepared according to procedure reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in flame-dried glassware with standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air. Preparative recycling HPLC was performed with a JAI LC-9204 instrument equipped with a Buckyprep column (20 mm × 250 mm, Nacalai Tesque) using toluene as an eluent. HPLC analysis was conducted on Shimadzu LC-20AB instrument equipped with a Buckyprep column (4.6 mm × 250 mm, Nacalai Tesque). LCMS analysis was conducted on a Waters Micromass LCT Premier (electrospray ionization time-of-flight mass spectrometry, ESI-TOFMS) equipped with a Buckyprep column (4.6 mm × 250 mm, Nacalai Tesque). Chiral HPLC analysis was conducted on Shimadzu LC-20AB instrument equipped with a CHIRAL-IB column (4.6 mm × 250 mm, DAICEL). High-resolution mass spectra (HRMS) were obtained from a Waters Micromass LCT Premier (electrospray ionization time-of-flight mass spectrometry, ESI-TOFMS). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JMN-GSX-270 (^{1}H 270 MHz, ^{13}C 67.8 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.0 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. The data of X-ray crystal structure analysis and the theoretical calculation are provided in our previous paper.[3]

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(1) Albinati, A.; Affolter, S.; Pregosin, P. S. *Organometallics* **1990**, *9*, 379.
(2) (a) Polet, D.; Alexakis, A. *Org. Lett.* **2002**, *9*, 1563. (b) Alonso, I.; Trillo, B.; López, F.; Montserrat, S.; Ujaque, G.; Castedo, L.; Lledós, A.; Mascareñas, J. L. *J. Am. Chem. Soc.* **2009**, *131*, 13020.
(3) Nambo, M.; Wakamiya, A.; Yamaguchi, S.; Itami, K. *J. Am. Chem. Soc.* **2009**, *131*, 15112.

2. Palladium-Catalyzed Tetraallylation of C_{60} (Scheme 4)

A 500-mL two-neck round-bottom flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To this flask were added $PdCl_2[P(OPh)_3]_2$ (160 mg, 0.2 mmol), C_{60} (1.44 g, 2 mmol), and dry *o*-dichlorobenzene (130 mL) under a stream of argon. Thereafter, allyl chloride (**1a**: 410 mL, 5 mmol) and allyltributyltin (**1b**: 1.5 mL, 4.9 mmol) were added to the mixture. After stirring the mixture at 50 °C for 11 h, the mixture was cooled to room temperature. The mixture was passed through a pad of silica gel with copious washings with toluene (~1.5 L). The filtrate was concentrated and subjected to preparative recycling HPLC equipped with a Buckyprep column (eluent: toluene) to afford $(CH_2{=}CHCH_2)_4C_{60}$ ((±)-**2**: 1.31 g, 74%) as dark brown solid. 1,2-$(CH_2{=}CHCH_2)_2C_{60}$ (**4**) was also isolated (127 mg, 8%).

Data of (±)-**2**:[3] ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.41 (dd, *J* = 13.5, 7.2 Hz, 1H), 3.49 (dd, *J* = 13.5, 7.2 Hz, 1H), 3.59 (d, *J* = 7.6 Hz, 2H), 3.67–3.73 (m, 3H), 3.82 (dd, *J* = 13.2, 6.9 Hz, 1H), 5.30–5.54 (m, 8H), 6.27–6.54 (m, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 41.97, 44.70, 44.94, 46.05, 55.30, 57.72, 60.86, 65.64, 119.55, 119.67, 119.94, 120.28, 132.68, 133.46, 133.60, 133.76, 134.41, 134.86, 135.95, 136.51, 139.94, 140.59, 141.18, 141.80, 142.31, 142.52, 142.63, 143.37, 143.53, 143.93, 144.09, 144.18, 144.24, 144.49, 144.51, 144.54, 144.61, 144.77, 145.03, 145.05, 145.32, 145.37, 145.39, 145.84, 145.92, 145.96, 146.24, 146.38, 146.52, 146.61, 146.66, 146.71, 146.89, 147.12, 147.33, 147.59, 147.79, 148.17, 148.80, 149.12, 149.18, 149.66, 150.17, 151.48, 154.29, 155.25, 155.87, 156.14, 160.07, 160.92. HRMS (ESI-TOF, negative) *m*/*z* calcd for $C_{72}H_{20}I$ $[M + I]^-$: 1011.0610, found 1011.0616.

Data of **4**:[3] ^{1}H NMR (270 MHz, $CDCl_3/CS_2$ = 1:1) δ 4.37 (dt, *J* = 6.9, 1.3 Hz, 4H), 5.46 (ddd, *J* = 10.2, 2.9, 1.3 Hz, 2H), 5.56 (ddd, *J* = 17.1, 2.9, 1.3 Hz, 2H), 6.66 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3/CS_2$ = 1:1) δ 44.51, 65.66, 119.73, 134.62, 135.75, 139.22, 141.24, 141.69, 142.06, 142.46, 143.07, 144.56, 145.18, 145.23, 145.81, 145.87, 146.07, 146.33, 147.50, 156.38. HRMS (ESI-TOF, negative) *m*/*z* calcd for $C_{66}H_{10}$ $[M]^-$: 802.0783, found 802.0782.

3. Palladium-Catalyzed Diallylation of C_{60} (Scheme 5)

A 10-mL Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To this flask were added $PdCl_2[P(OPh)_3]_2$ (2.4 mg, 3 mmol), C_{60} (21.6 mg, 30 mmol), and dry *o*-dichlorobenzene (2.0 mL) under a stream of argon. Thereafter, allyl chloride (**1a**: 3.0 mL, 36 mmol) and allyltributyltin (**1b**: 11 mL, 36 mmol) were added to the mixture. After stirring the mixture at 50 °C for 11 h, the mixture was cooled to room temperature. The mixture was passed through a pad of silica gel with copious washings with toluene (~30 mL). The filtrate was concentrated (~10 mL) and subjected to preparative recycling HPLC equipped with a Buckyprep column (eluent: toluene) to afford **2** (7.5 mg, 28%), 1,4-$(CH_2{=}CHCH_2)_2C_{60}$ (**3**: 6.8 mg, 28%), and 1,2-$(CH_2{=}CHCH_2)_2C_{60}$ (**4**: 2.3 mg, 10%). C_{60} was recovered in 29% yield (6.3 mg).

Data of **3**:[3] ^{1}H NMR (270 MHz, $CDCl_3/CS_2$ = 1:1) δ 3.77 (dd, *J* = 13.2, 7.2 Hz, 2H), 3.85 (dd, *J* = 13.2, 7.2 Hz, 2H), 5.51 (dm, *J* = 9.9 Hz, 2H), 5.57 (ddd, *J* = 16.8, 2.6, 1.3 Hz, 2H), 6.62 (ddt, *J* = 16.8, 9.9, 7.2 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3/CS_2$ = 1:1) δ 47.16, 58.75, 120.22, 132.93, 138.10, 138.76, 140.62, 141.80, 141.91, 142.29, 142.44, 142.50, 142.84, 142.99, 143.02, 143.58, 143.83, 143.91, 144.09, 144.14, 144.21, 144.56, 144.64, 144.97, 145.32, 145.74, 146.72, 146.76, 147.03, 147.07, 148.43, 148.45, 150.19, 151.22, 157.04. HRMS (ESI-TOF, negative) *m*/*z* calcd for $C_{66}H_{10}$ $[M]^-$: 802.0783, found 802.0775. These characterization data are consistent with literature values.[4]

The diallylation reactions of **3** and **4** (Scheme 5) were conducted following the procedure given above.

4. Palladium-Catalyzed Monoallylation of C_{60} (Scheme 7).

A 20-mL Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To this flask were added $PdCl_2(PhCN)_2$ (1.2 mg, 3 mmol), C_{60} (21.6 mg, 30 mmol), dry *o*-dichlorobenzene (3.0 mL), and saturated NH_4I aqueous solution (0.6 mL) under a stream of argon. Thereafter, allyltributyltin (**1b**: 37 mL, 120 mmol) was added to the mixture. After stirring the mixture at 80 °C for 11 h, the mixture was cooled to room temperature. The yields of 1-allyl-1,2-dihydro[60]fullerene (**5**) was determined to be 46% by HPLC analysis (Buckyprep column; toluene as eluent; flow rate 0.5 mL/min; UV detection at 326 nm) of this crude mixture using C_{70} as an internal standard. The mixture was passed through a pad of silica gel with copious washings with toluene (~30 mL). The filtrate was concentrated (~10 mL) and subjected to preparative recycling HPLC equipped with a Buckyprep column (eluent: toluene) to afford **5** (9.7 mg, 43%) as dark brown solid. C_{60} was recovered in 24% yield (5.2 mg).

Data of **5**:[3] ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.17 (dt, *J* = 7.2, 1.2 Hz, 2H), 5.76 (dm, *J* = 10.0 Hz, 1H), 5.91 (ddd, *J* = 17.3, 3.1, 1.2 Hz, 1H), 6.50 (s, 1H), 6.83 (ddt, *J* = 17.3, 10.0, 7.2 Hz, 1H). ^{13}C NMR (67.8 MHz, $CDCl_3/CS_2$ = 1:1) δ 50.96, 58.41, 64.05, 121.50, 133.18, 135.87, 136.13, 140.02, 140.78, 141.42, 141.69, 141.73, 141.80, 141.98, 142.34, 143.02, 144.34, 144.47, 145.14, 145.16, 145.23, 145.31, 145.55, 145.88, 145.94, 146.00, 146.15, 146.75, 146.87, 147.04, 147.20, 153.50, 155.09. HRMS (ESI-TOF, negative) *m*/*z* calcd for $C_{63}H_5$ $[M-H]^-$: 761.0391, found 761.0397. These characterization data are consistent with literature values.[4]

5. Palladium-Catalyzed C–H Allylation of 5 (Scheme 7).

A 50-mL glass Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To this flask were added $Pd_2(dba)_3 \cdot CHCl_3$ (1.7 mg, 3 μmol), $P(OPh)_3$ (3.1 μL, 12 μmol), and dry *o*-dichlorobenzene (6.0 mL) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, **5**

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[4] Meier, M. S.; Bergosh, R. G.; Gallagher, M. E.; Spielmann, H. P.; Wang, Z. *J. Org. Chem.* **2002**, *67*, 5946.

(11.4 mg, 15 μmol) and allyl methyl carbonate (**1c**: 3.5 mg, 31 μmol) were added to the flask under a stream of argon. After stirring at 80 °C for 18 h, the mixture was cooled to room temperature. The mixture was passed through a pad of silica gel with copious washings with toluene (~30 mL). The filtrate was concentrated (~10 mL) and subjected to preparative recycling HPLC equipped with a Buckyprep column (eluent: toluene) to afford **3** (7.8 mg, 65%) and **4** (1.3 mg, 11%).

6. Ruthenium-Catalyzed Ring-Closing Metathesis of 2 (Scheme 8).

A 10-mL glass Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To this flask were added **2** (14.0 mg, 16 μmol) and dry toluene (15 mL) at room temperature under a stream of argon. The Grubbs' catalyst $PhCH{=}RuCl_2(PCy_3)_2$ (1.4 mg, 1.6 μmol) was added to the flask under a stream of argon. After stirring the mixture at room temperature for 12 h, the mixture was passed through a pad of silica gel with copious washings with toluene (~15 mL). The filtrate was subjected to preparative recycling HPLC equipped with a Buckyprep column (eluent: toluene) to afford (±)-**6** (9.1 mg, 76%).

Data of (±)-**6**: ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 1:1) δ 3.24 (dd, *J* = 14.2, 6.1 Hz, 1H), 3.35–3.60 (m, 5H), 3.66 (dd, *J* = 13.6, 7.6 Hz, 1H), 3.70 (dd, *J* = 13.6, 7.6 Hz, 1H), 5,35 (d, *J* = 10.0 Hz, 1H), 5.39–5.44 (m, 1H), 5.48 (d, *J* = 10.0 Hz, 1H), 5.48–5.53 (m, 1H), 6.33–6.50 (m, 2H), 6.61–6.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1:1) δ 39.72, 39.97, 45.77, 45.96, 55.12, 58.21, 59.84, 65.10, 119.42, 119.95, 131.31, 131.96, 133.15, 133.69, 133.77, 133.94, 134.70, 136.00, 136.31, 140.31, 140.46, 141.34, 142.12, 142.29, 142.98, 143.17, 143.48, 143.68, 143.93, 144.09, 144.17, 144.26, 144.34, 144.36, 144.48, 144.62, 144.76, 144.82, 145.08, 145.15, 145.23, 145.56, 145.71, 146.07, 146.22, 146.35, 146.38, 146.41, 146.49, 146.56, 146.59, 146.81, 146.98, 147.39, 147.62, 147.70, 148.58, 148.91, 148.96, 149.44, 149.98, 151.12, 153.06, 155.03, 155.90, 156.56, 161.51, 162.83. HRMS (ESI-TOF, negative) *m*/*z* calcd for $C_{70}H_{16}$ $[M]^-$: 856.1257, found 856.1257.

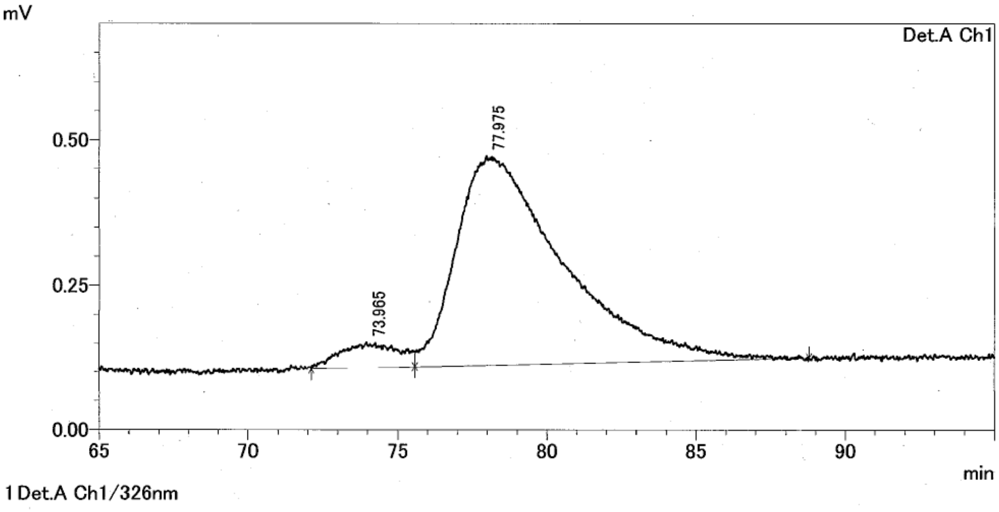
7. Rhodium-Catalyzed Hydrogenation of 2 (Scheme 8).

Compounds **2** (17.6 mg, 20 μmol), $RhCl(PPh_3)_3$ (3.6 mg, 4.0 μmol), and *o*-dichlorobenzene (2.0 mL) were placed into a 30-mL autoclave. After stirring the mixture under 50 atm H_2 at room temperature for 12 h, the mixture was passed through a pad of silica gel with copious washings with toluene (~15 mL). The filtrate was subjected to preparative recycling HPLC equipped with a Buckyprep column (eluent: toluene) to afford (±)-**7** (9.6 mg, 54%).

Data of (±)-**7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.6 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H), 1.25–1.31 (m, 6H), 1.90–2.17 (m, 8H), 2.59–2.96 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.69, 14.75, 14.82, 14.86, 20.29, 20.53, 20.74, 22.95, 39.61, 41.50, 42.59, 43.99, 55.78, 58.32, 61.47, 66.28, 132.23, 133.59, 134.68, 136.49, 139.64, 140.57, 141.03, 141.85, 141.94, 142.53, 142.63, 143.29, 143.86, 143.94, 144.08, 144.29, 144.42, 144.48, 144.78, 144.92, 145.04, 145.26, 145.28, 145.36, 145.78, 145.86, 145.90, 146.29, 146.34, 146.57, 146.61, 146.70, 146.87, 146.91, 147.08, 147.52, 147.70, 147.78, 148.29, 148.78, 149.06, 149.15, 149.58, 150.14, 151.73, 155.24, 156.06, 156.60, 156.62, 160.77, 162.72. HRMS (ESI-TOF, negative) *m*/*z* calcd for $C_{72}H_{28}$ $[M]^-$: 892.2196, found 892.2189.

8. Enantioselective Synthesis of 2 (Table 3, entry 9).

A 20-mL glass Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To this flask were added $PdCl_2(PhCN)_2$ (1.2 mg, 3 μmol), (*R*,*S*,*S*)-**L3** (3.2 mg, 6 μmol), and dry *o*-dichlorobenzene (6.0 mL) at room temperature under a stream of argon. After stirring the mixture at this temperature for 30 min, C_{60} (21.6 mg, 30 μmol), allyl chloride (**1a**: 6.1 μL, 75 μmol), and allyltributyltin (**1b**: 23 μL, 75 μmol) were added to the mixture at 0 °C. After the reaction mixture was stirred at 0 °C for 168 h, the mixture was passed through a pad of silica gel with copious washings with toluene (~30 mL). The filtrate was concentrated (~10 mL) and subjected to preparative recycling HPLC equipped with a Buckyprep column (eluent: toluene) to afford **2** (3.4 mg, 13%). The enantiomeric excess of **2** was determined to be 88% ee (see the chart below) by HPLC analysis (three directly connected CHIRAL-IB column; hexane/$CHCl_3$ (100:1) as eluent; flow rate 1.0 mL/min; UV detection at 326 nm). The retention times of enantiomers were 73.97 min (minor) and 77.98 min (major). $[\alpha]^{25}_{D}$ –8.9° (*c* 1.00, $CHCl_3$).



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1	73.965	5955	6.216
2	77.975	89845	93.784
合計		95800	100.000

9. ^{1}H and ^{13}C NMR Spectra of New Compounds

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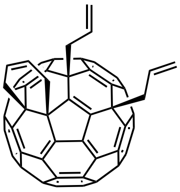

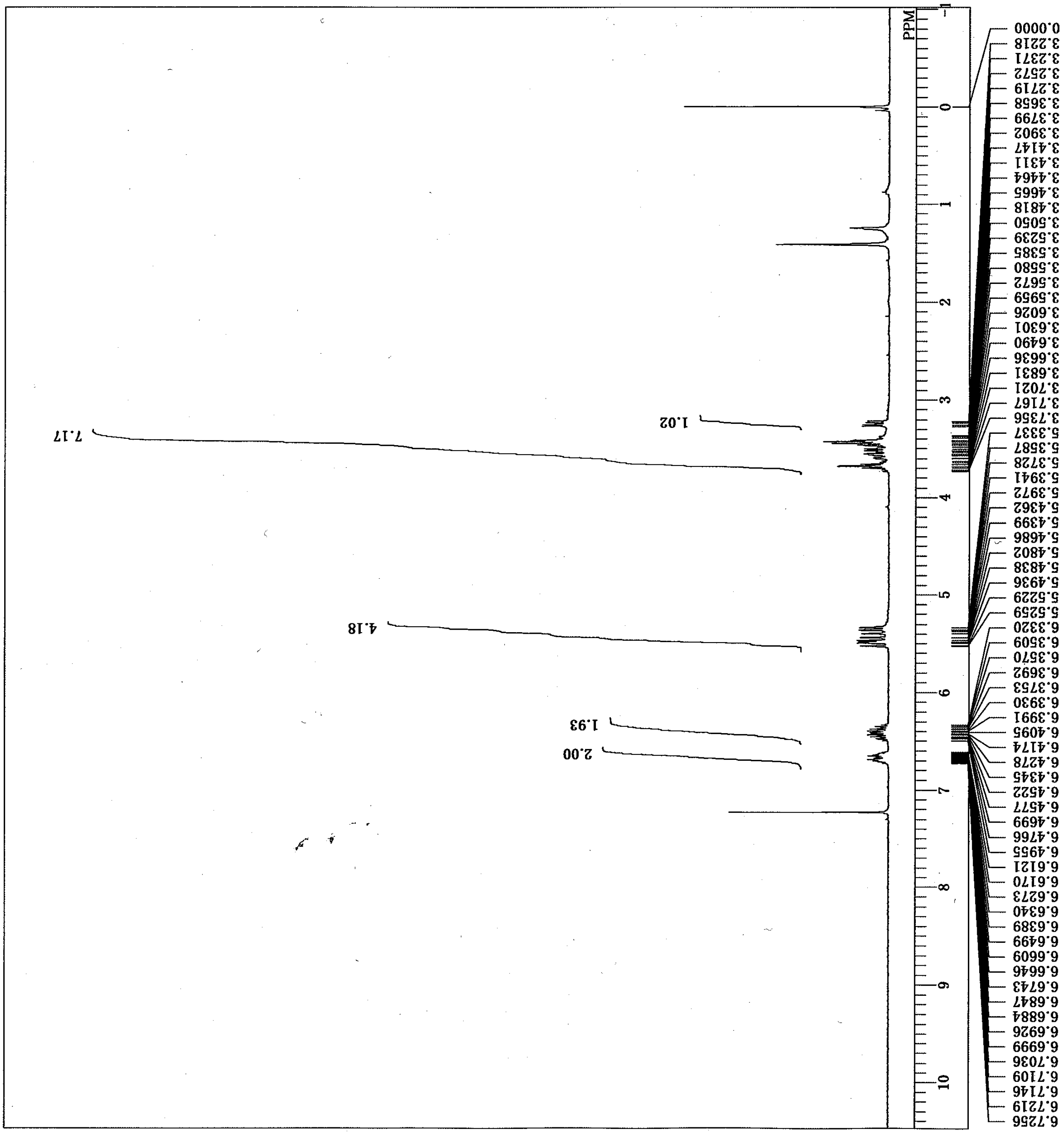

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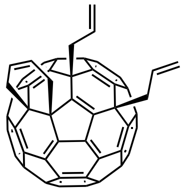

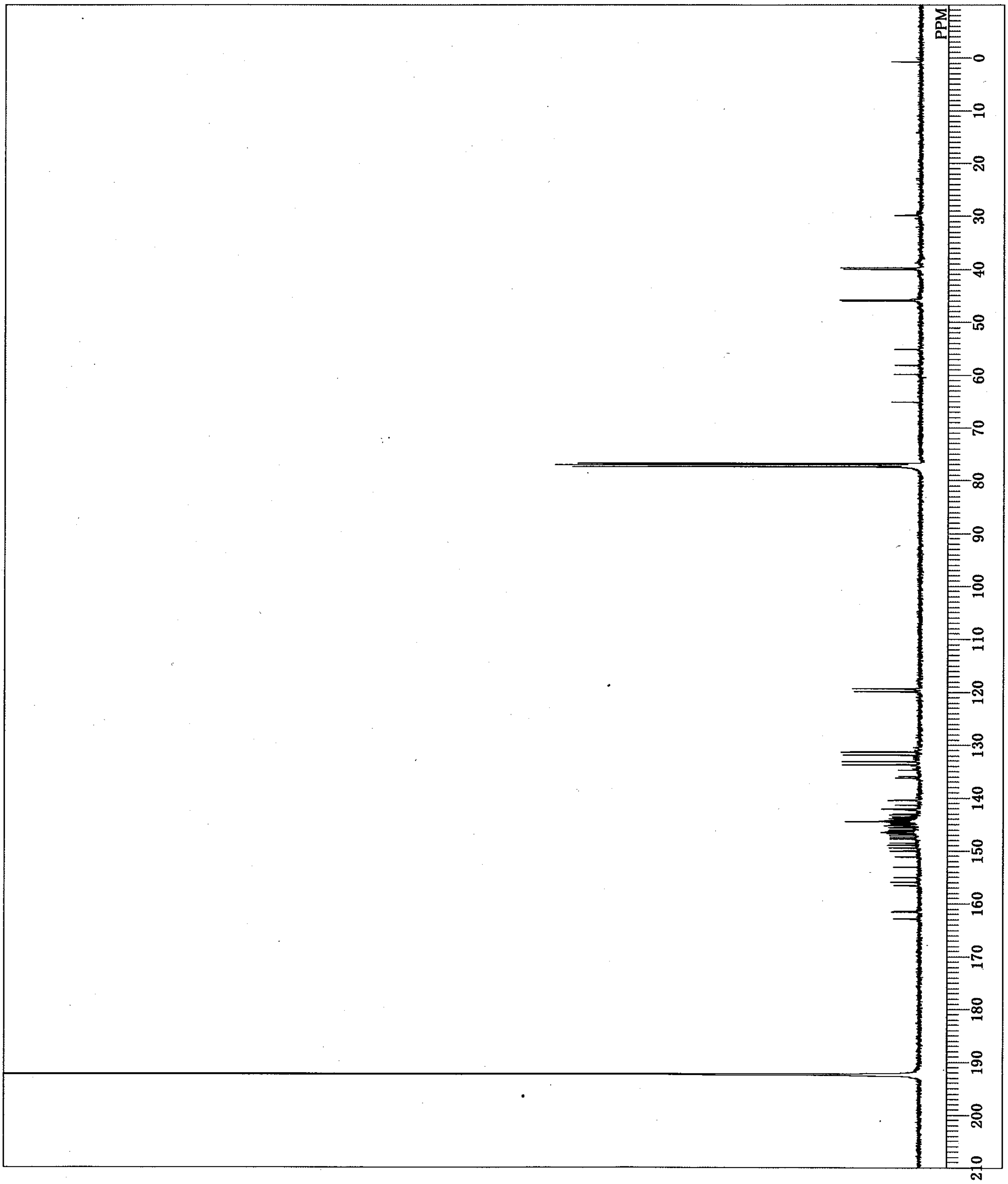

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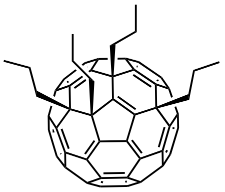

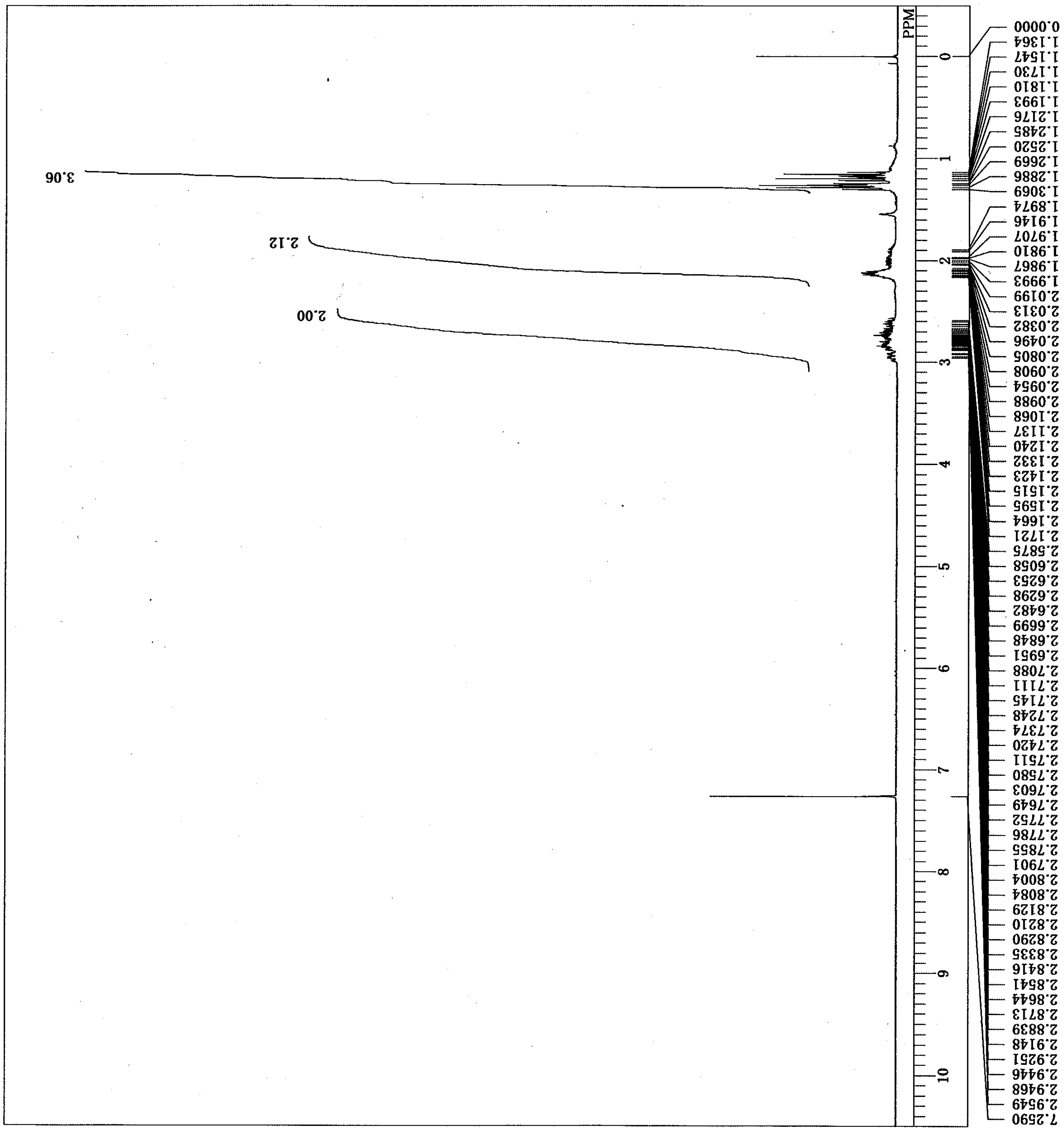

^{13}C NMR (100 MHz, $CDCl_3$) of 7