Supporting Information for:

The first molecular dumbbell consisting of an endohedral $Sc_3N@C_{80}$ and an empty C_{60}-fullerene building block

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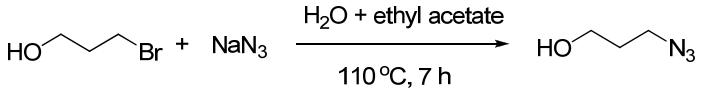
Content

General considerations

All chemicals were purchased from chemical suppliers and were used as received. C_{60} (99.0 %) was purchased from IOLITEC nanomaterials. $Sc_3N@I_h$-C_{80} was supplied by Luna Innovations (95.0 %). Malonates precursors were synthesized according to reported literature procedures as specified below. HPLC isolation was carried out using Cosmosil 5-Buckyprep (4.6 × 250 mm) column with toluene as eluent. NMR spectra were recorded with Bruker Avance 400 (400 MHz) or Jeol EX 400 (400 MHz) spectrometers. Chemical shifts are given in ppm and referenced to residual solvent signals and reported relative to external $SiMe_4$. HRMS were recorded with Bruker microTOF II focus and Shimadzu AXIMA Confidence maXis 4G instruments. MALDI-TOF HRMS were recorded with an UltrafleXtreme TOF/TOF (Bruker Daltonics). UV/vis-NIR spectroscopy was recorded in a Varian Cary 5000 spectrophotometer.

S1. Synthesis of clickable malonates

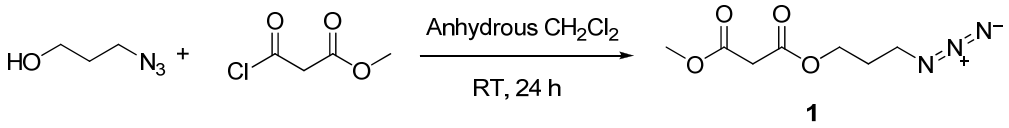
S1.1 Synthesis of azidomalonate (1)[1]



Scheme S1. Synthesis of 3-azido-1-propanol.

Azido malonate **1** was synthesized in two steps: 1) Synthesis of precursor 3-aizdo-1-propanol. 2.00 g (14.5 mmol) of 3-bromo-1-propanol were dissolved in 5.0 mL ethyl acetate to react with excess sodium azide (3.00 g, 46 mmol), which was dissolved in 5.0 mL distilling water, at 110 °C for 7 h (Scheme S1). The obtained product dissolved in ethyl acetate was washed with water for three times and dried over anhydrous sodium sulfate. After evaporation of inorganic solvent, a transparent liquid product was obtained in a yield of 95%. The structure was characterized by proton NMR spectroscopy as shown in Fig. S1.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm) δ = 3.61 (t, J = 6.0 Hz, 2H), 3.34 (t, J = 6.8 Hz, 2H), 3.04 (s, 1H), 1.73 (m, 2H).



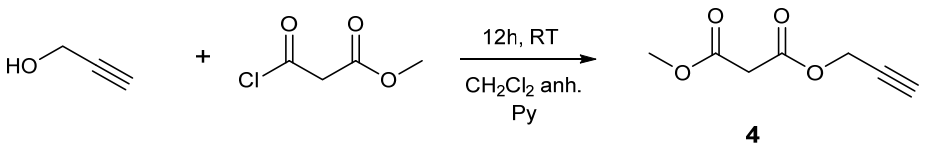
Scheme S2. Synthesis of azido malonate **1**.

2) The generated 3-azido-1-proponal (1.56 g, 15.4 mmol) was dissolved in anhydrous CH_2Cl_2 together with pyridine (1.22 g, 15.4 mmol), into which methyl malonyl chloride (2.10 g, 15.4 mmol) was gradually added within 10 min at room temperature (Scheme S2). After 24 h, the reaction was terminated and treated with brine. Afterwards, the obtained product was purified by column chromatography on silica gel eluted by hexane/ethyl acetate (v/v = 4/1) to give ultimate azidomalonate **1** (72%), whose structure was elucidated by ^{1}H and ^{13}C NMR spectroscopy as shown in Fig. S2, S3.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm). δ = 4.20 (t, J = 6.4 Hz, 2H), 3.70 (s, 3H), 3.35 (t, J = 6.4 Hz, 2H), 3.35 (s, 2H), 1.88 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm), δ = 166.7, 166.2, 62.2, 52.4, 47.9, 41.1, 27.9.

S1.2 Synthesys of methyl prop-2-yn-1-yl malonate or alkynyl malonate (4)[2]



4

Scheme S3. Synthesis of alkynyl malonate **4**

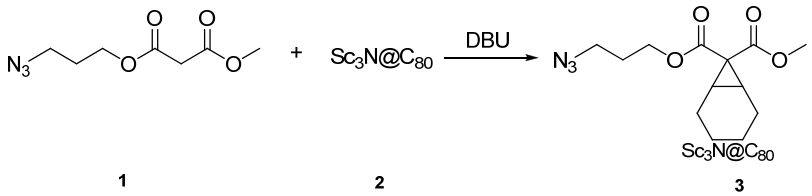
Prop-2-yn-1-ol (785.0 mg, 815 µL, 14 mmol) was dissolved in anhydrous CH_2Cl_2 (75.0 mL) at 0 °C under inert atmosphere. Subsequently, pyridine (1.25 mL, 15.4 mmol) and methyl malonyl chloride (1.90 g, 1.5 mL, 14 mmol) dissolved in anhydrous CH_2Cl_2 (25.0 mL) were added dropwise and the mixture was stirred for 24 h (0 °C to RT). The product was washed with H_2O and extracted with CH_2Cl_2 (3 × 50.0 mL), the combined organic fractions were dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the crude was chromatographically purified (SiO_2, hexane : EtOAc = 8 : 1 → 5 : 1) to obtain **4** as yellowish oil (2.120 g, 97%)

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 4.72 (d, J = 2.5 Hz, 2H, CH_2CCH), 3.73 (s, 3H, OCH_3), 3.41 (s, 2H, COCH_2CO), 2.48 (t, J = 2.5 Hz, 1H, CH alkyne)

^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 166.44 (*C*O), 165.65 (*C*O), 76.90 (*C*CH), 75.41(C*C*H), 52.88 (*C*H_2CCH), 52.60 (O*C*H_3), 40.96 (COCH_2CO).

S2. Synthesis of fullerene precursors

S2.1 Bingel-Hirsch reaction of $Sc_3N@I_h$-C_{80}.



Scheme S4. Schematic synthesis of **3** via Bingel-Hirsch reaction of $Sc_3N@I_h$-C_{80}.

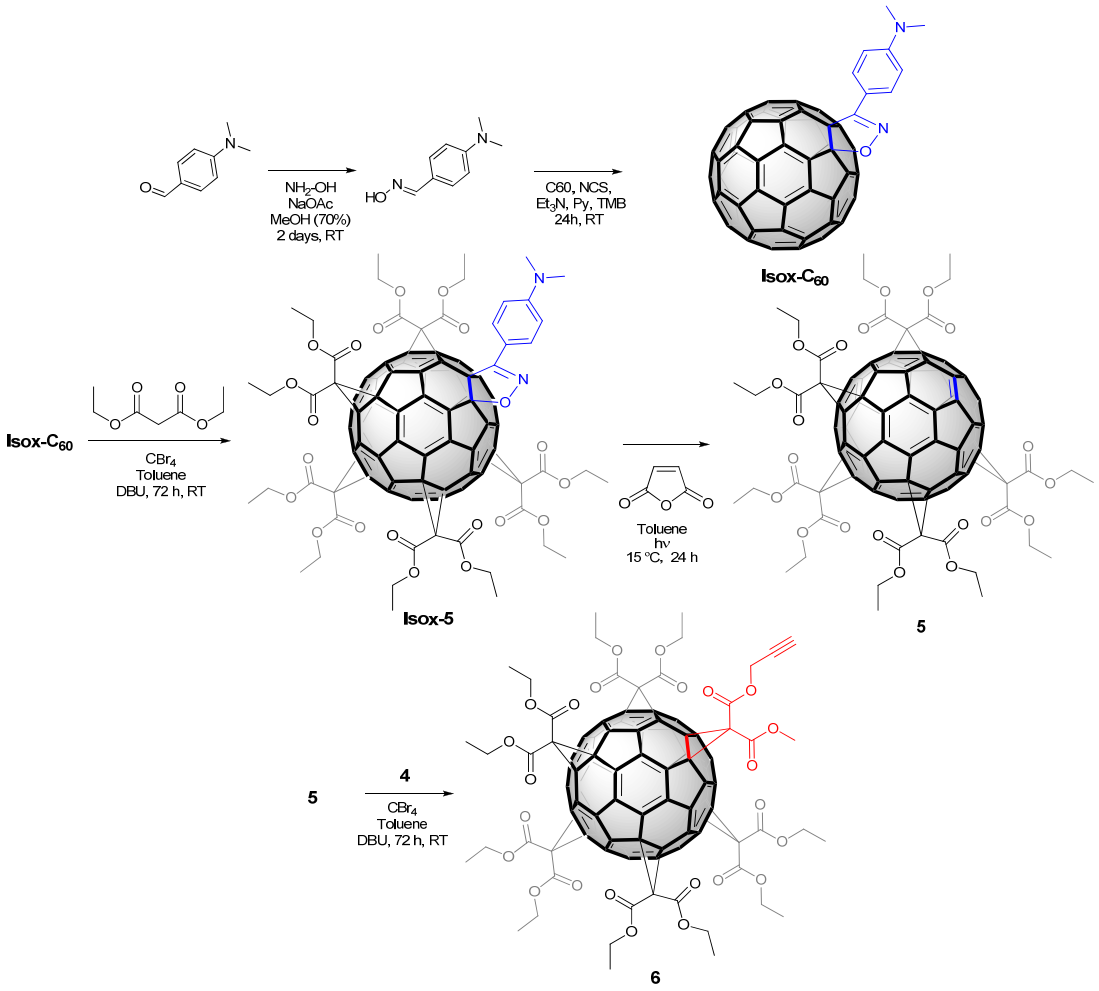
The Bingel-Hirsch reaction of compound **2** $Sc_3N@I_h$-C_{80} (10.0 mg, 9 μmol) with excess of azidomalonate **1** (36.2 mg, 180 μmol) was carried out at 60 °C in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) (10 μL, 66 μmol) in 10.0 mL mixed solvent of *o*-DCB/DMF (4 : 1) for 8 h under a nitrogen atmosphere (scheme S4). As discussed in previous report, by adding partial polar solvent such as DMF, the reaction occurs facilely.[3] Under this reaction condition one major monoadduct (named as compound **3**) was generated along with some unreacted $Sc_3N@I_h$-C_{80} in a proportion of 2 : 3 according to the integrated peak areas of high performance liquid chromatogram (HPLC) (Fig. S6(a)). Thus the yield was estimated to be 36% which is in accordance with that of previous reported analogue of $Sc_3N@I_h$-C_{80} utilizing the identical reaction (Bingel-Hirsch reaction). One step isolation readily gave rise to the pure **3** as further confirmed by matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectroscopic analysis showing an ionic peak at m/z = 1308 (Fig. S6(b)). Additionally, both ^{1}H (Fig. S7) and ^{13}C NMR spectroscopy (Fig. S8) were performed to further unambiguously elucidate its structure.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm) δ = 4.59 (q, J = 6.0 Hz, 2H), 4.11 (s, 3H), 3.50 (t, J = 6.4 Hz, 2H), 2.09 (t, J = 6.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$/CS_2 (v/v=1 : 1), TMS, ppm), δ = 152.76, 152.69, 151.34, 151.29, 151.15, 151.05, 150.40, 150.39, 150.23, 150.19, 149.52, 149.38, 148.79, 147.36, 145.70, 145.61, 145.44, 145.21, 145.16, 145.09, 145.57, 144.52, 144.51 (2C), 144.43, 144.41, 143.98, 14 3.92, 143.77, 143.64, 143.31, 143.17, 142.91, 142.58, 142.29, 142.20, 142.12, 142.03, 141.67, 141.27, 141.21, 141.10, 140.63, 140.58, 140.51, 140.39, 140.29, 140.27, 139.95, 139.86, 139.14, 139.04, 139.02, 138.40, 138.31, 138.29, 138.15, 138.06, 137.30, 137.22, 136.34, 134.93, 134.85, 134.80, 134.77, 134.43(2C), 134.29, 134.20, 133.88, 131.36, 126.82, 125.37, 125.20, 124.95, 124.89, 122.84(2C), 89.04, 86.24. For attached group: δ = 163.76, 163.19, 64.31, 57.06, 47.62, 29.89, 28.17.

S2.2 Alkynyl-C_{60} derivative (6)

Fullerene **6** was synthesized following the approach depicted in scheme S5



Scheme S5. Synthesis of clickable hexakis-fullerene **6**.

Synthesis of isoxazolino protected -C_{60}.

The synthesis was performed according to the method previously described in the literature:[4]

4-(N,N-Dimethylamino)benzaldoxime:

$NH_2OH{\cdot}HCl$ (2.779 g, 40 mmol) and NaOAc (3.281 g, 40 mmol) were added under ambient conditions to a stirred solution of 4-(*N,N*-dimethylamino)benzaldehyde (3.045 g, 20 mmol) in 70%-methanol (90.0 mL). The solution was stirred for 48 h and the solvent was removed under reduced pressure. After extraction with CH_2Cl_2 (50.0 mL) and 10%-$NaHCO_3$ solution (50.0 mL), the organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo*. The product was obtained as a white solid which was used without further purifications. (3.201 g, 19.5 mmol, 98%)

^{1}H NMR (400 MHz, RT, $CDCl_3$, ppm): δ = 2.98 (s, 6H, N-CH_3), 6.67 (d, 2H, ^3J = 8.9 Hz, *meta*-H), 7.43 (d, 2H, ^3J = 8.9 Hz, *ortho*-H), 8.03 (s, 1H, *H*-CN)

^{13}C NMR (100 MHz, RT, $CDCl_3$, ppm): δ = 40.17 (N(CH_3)$_2$), 111.98 (*meta*-*C*), 119.72 (*C*-CN), 128.33

(*ortho-C*), 150.51 (*C*=N), 151.56 (*C*-NMe_2)

MS (ESI) m/z = 165 $[M+H]^+$

3´-(4-N,N-Dimethylaminophenyl)isoxazolo[4´,5´:1,2][60]-fullerene (Isox-C_{60}):

4-(*N,N*-Dimethylamino)benzaldoxime (602 mg, 3.7 mmol) was dissolved in chloroform (200.0 mL) and pyridine (0.5 mL, 6.2 mmol) under argon atmosphere. After cooling down to 0°C, N-chlorosuccinimide (530 mg, 4.0 mmol) was added to the stirred solution. C_{60}-Fullerene (2.000 g, 2.8 mmol) was previously dissolved in 1,2,4-trimethylbenzene (250.0 mL) and triethylamine (1.6 mL, 12.3 mmol) under argon atmosphere and sonication, this solution was afterwards poured onto the oxime-solution. The reaction mixture was stirred overnight at 0°C→ RT. After that it was concentrated *in vacuo* to 50.0 mL and purified by column chromatography with toluene as eluent, to recover first the non reacted C_{60} followed by **Isox-C_{60}** (664 mg, 0.8 mmol, 29%) as a dark brown solid.

^{1}H NMR (400 MHz, RT, $CDCl_3$: CS_2, 1:1, ppm): δ = 3.04 (s, 6H, N-CH_3), 6.73 (d, 2H, ^3J = 8.9 Hz, *meta*-H), 8.09 (d, 2H, ^3J = 8.9 Hz, *ortho*-H)

^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1:1, ppm) δ = 153.19 ((1C, *C*=N)), 151.68 (C ipso), 148.00, 147.50, 147.05, 146.63, 146.51, 146.47, 146.42, 146.22, 146.16, 145.82, 145.76, 145.73, 145.55, 145.46, 145.39, 145.17, 144.72, 144.39, 143.23, 143.09, 142.76, 142.73, 142.67, 142.58, 142.40, 141.92, 140.51, 140.46, 137.17, 136.94 (58C, C_{60}-sp^2), 130.29 (2C, *C*H Ar), 116.53 (C ipso), 112.24 (2C, *C*H Ar), 103.85 (1C, C_{60}-isoxazolino C-O), 79.58 (1C, C_{60}-isoxazolino (C-C)), 40.19 (2C; N(CH_3)$_2$).

MS (MALDI-TOF, DHB) m/z = 881 $[M]^+$

Synthesis of pentakis-adduct precursor (Isox-5)

The Bingel-Hirsch reaction was carried out following the methodology previously described in our group[5]. **Isox-C_{60}** (150 mg, 0.170 mmol) was dissolved in dry toluene (250.0 mL) together with CBr_4 (5.65 g, 17 mmol) and diethyl malonate (285 µL, 1.170 mmol). The solution was stirred for 1 h under exclusion of light and nitrogen atmosphere at RT. Subsequently, DBU (0.5 mL 3.4 mmol) dissolved in toluene (10.0 mL) was added over 5 min and the reaction mixture was stirred for additional 72 h. The crude product was plug-filtered (SiO_2; toluene : EtOAc = 9 : 1) and purified by column chromatography (SiO_2; toluene : EtOAc = 95 : 5) to obtain fullerene **Isox-5** (107 mg, 38%) as a yellow-orange solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.87 (d, *J* = 9.1 Hz, 2H, Ar), 6.68 (d, *J* = 9.1 Hz, 2H, Ar), 4.45 – 4.14 (m, 20H, CH_2), 2.97 (s, 6H, N(CH_3)$_2$), 1.43 – 1.24 (m, 30H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 164.22, 164.15, 164.07, 163.86, 163.80, 163.77 (10C, *C*O) 154.78 (1C, $C_{isoxazolino}$), 151.54 (1C, Ar), 147.09, 146.98, 146.74, 146.53, 146.27, 146.18, 145.71, 145.63, 145.53, 144.30, 143.96, 143.46, 142.41, 142.01, 141.51, 141.43, 140.60, 139.89, 139.69, 139.41 (48 C, C_{60}-*sp2*), 129.76 (2C, *C*H Ar), 116.75 (1C, *C* ipso), 111.77 (2C, *C*H Ar), 101.63 (1C, C_{60}-isoxazolino C-O),77.36 (1C, C_{60}-isoxazolino (C-C), 69.99, 69.32, 68.14, 67.53 (10C, C_{60} *sp3* Bingel), 63.13, 63.05, 62.59 (10 C, *C*H_2), 45.54, 45.39, 44.67, 41.92 (5C, CO*C*CO), 40.16 (2C, N(CH_3)$_2$), 14.14, 14.08 (10C, *C*H_3).

MS (MALDI-TOF, DHB): *m/z* = 1511.3248 [(M-isoxazoline)]$^+$

Synthesis of pentakisadduct (5)

The protected fullerene **Isox-5** (75 mg, 0.045 mmol) was dissolved in dry toluene (30.0 mL) together with maleic anhydride (134 mg, 1.35 mmol) under nitrogen atmosphere. The reaction mixture was irradiated with a halogen lamp (500 W) while cooling down to 15 °C for 24 h. The mixture was purified by silica plug (toluene : EtOAc = 95 : 5) to obtain pentakisadduct **5** (43 mg, 63%) as an orange solid which was further precipitated from DCM into pentane.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 4.47 – 4.30 (m, 16H, CH_2), 4.25 (q, *J* = 7.1 Hz, 4H, CH_2), 1.42 – 1.32 (m, 24H, CH_3), 1.26 (t, *J* = 7.1 Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 164.18, 164.06, 163.53, (10C, *C*O), 148.74, 147.13, 146.29, 145.94, 145.30, 144.81, 144.49, 144.42, 144.25, 143.33, 142.54, 140.04, 139.93 (50C, C_{60}-sp^2), 70.06, 69.63, 69.53, 69.30 (10C, C_{60}-sp^3) 63.12, 63.10, 62.88 (10C, *C*H_2), 54.05, 45.78, 45.10 (5C, COCCO), 14.22, 14.16, 14.14, 14.04 (10C, *C*H_3)

MS (MALDI-TOF, DCTB): *m/z* = 1511.2803 $[M]^+$

Synthesis of C_{60}-alkynyl hexakisadduct (6)

Pentakisadduct **5** (24 mg, 15.9 µmol) was dissolved in dry toluene (25.0 mL) together with CBr_4 (11 mg, 33.1 µmol) and malonate **4** (7 mg, 44.8 µmol). The solution was stirred for 1 h under exclusion of light and nitrogen atmosphere at RT. Subsequently, DBU (10 µL 66.9 µmol) dissolved in toluene (1.0 mL) was added over 5 min and the reaction mixture was stirred for 72 h. The crude product was plug-filtered (SiO_2; toluene : EtOAc = 95 : 5 → 9 : 1) and purified through column chromatography (SiO_2; toluene : EtOAc = 95 : 5) to obtain fullerene **6** (20 mg, 76%) as a yellow solid which was further precipitated from DCM into pentane.

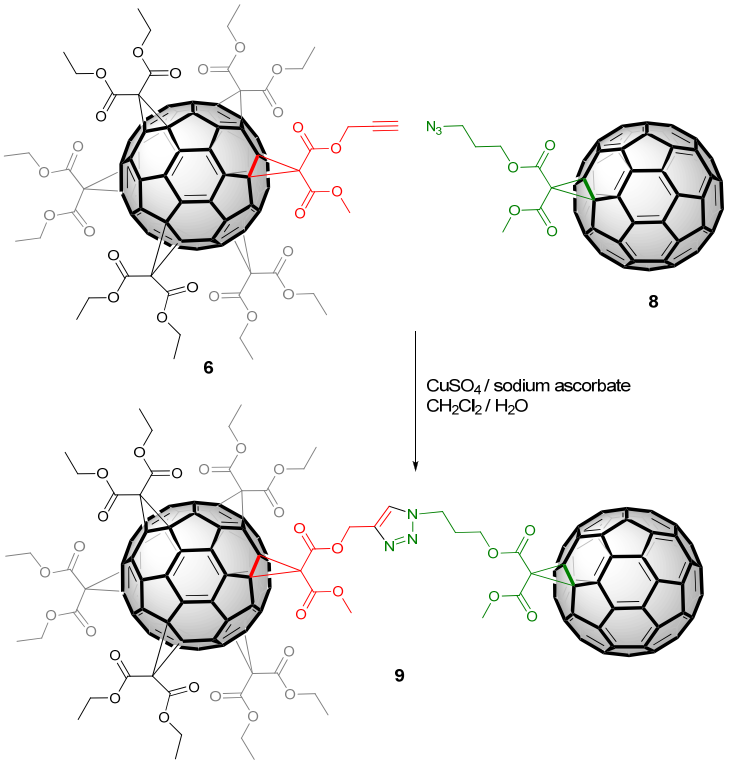
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 4.85 (d, *J* = 2.5 Hz, 2H, (CH_2CCH)), 4.33 (q, *J* = 7.1 Hz, 20H, CH_2), 3.88 (s, 3H, OCH_3), 2.53 (t, *J* = 2.5 Hz, 1H, C*H*alkyne), 1.32 (t, *J* = 7.1 Hz, 30H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 164.16, 163.95, 163.92, 163.31 (12C, *C*O), 146.15, 146.05, 146.03, 145.95, 145.91, 145.85, 141.32, 141.26, 140.94, 140.86, (48C, C_{60}-sp^2), 77.36, 76.26 (2C, *C*CH and C*C*H), 69.26, 69.25, 69.22, 69.18, 68.96 (12C, C_{60}-sp^3), 63.02 (10C, *C*H_2), 54.14, 53.86 (2C, *C*H_2CCH and OCH_3), 45.54 (6C, CO*C*CO), 14.20 (10C, *C*H_3).

HRMS (APPI) m/z: Calculated for $C_{102}H_{56}O_{24}$ 1664.3162, found 1664.3169.

S3. Synthesis of dimer C_{60} - C_{60} via click reaction.

To a solution of azido-fullerene **8**[1] (11.0 mg, 12 µmol) and [5:1] C_{60} fullerene **6** (20.0 mg, 12 µmol) in CH_2Cl_2 (1.2 mL), was added a solution of $CuSO_4 \cdot 5H_2O$ (0.9 mg, 3.6 µmol) and sodium ascorbate (2.1 mg, 10 µmol) in water (1.2 mL) followed by DIPEA (10 µL, 57 µmol). After stirring for 4 days at RT, a saturated aqueous solution of EDTA (1.0 mL) was added, the mixture was vigorously stirred for another 10 min, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent was concentrated at reduced pressure without drying completely. The crude was purified by flash column chromatography (CH_2Cl_2 : MeOH = 100 : 0.5 → 100 : 1) to afford dimer **9** (16.6 mg, 54%) as a brown solid which was further precipitated from DCM into pentane.



Scheme S6. Synthesis of ***dimer C_{60} - C_{60}*** **9**.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.72 (s, 1H, *1,2,3*-triazole), 5.44 (s, 2H, OC*H*$_2$-triazole), 4.61 (t, *J* = 7.0 Hz, 2H, NC*H*$_2$), 4.56 (t, *J* = 5.9 Hz, 2H, OC*H*$_2$), 4.39 – 4.28 (m, 20H, C*H*$_2$), 4.14 (s, 3H, OC*H*$_3$), 3.81 (s, 3H, OC*H*$_3$), 2.55 - 2.40 (m, 2H, $NCH_2CH_2CH_2O$), 1.37 – 1.28 (m, 30H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 164.30, 164.04, 163.67 (12C, *C*O), 145.98, 145.53, 145.44, 145.36, 145.28, 145.24, 145.17, 145.08, 144.93, 144.13, 143.28, 142.43, 142.37, 142.11, 141.39, 141.31, 141.07, 141.02, 139.59, 138.94 (108C, C_{60}-sp^2 and C quaternary triazole), 124.68 (*C*H-triazole), 71.45, 69.23, 69.01 (14C, C_{60}-sp^3), 63.77 (CH_2O), 63.03 (10C, CH_2), 60.01 (OCH_2-triazole), 54.40 (OCH_3), 53.85 (OCH_3), 47.07 (NCH_2), (CH2, 45.47, 44.91 (6C, CO*C*CO), 29.51 ($NCH_2CH_2CH_2O$), 14.12 (10C, CH_3).

MS (MALDI-TOF, DHB): *m/z* = 2608.2955 $[M+Na]^+$

S4. Synthesis of dumbbell-7

To a solution of fullerene **6** (4.5 mg, 2.7 μmol) and azido $Sc_3N@I_h$-C_{80} **3** (2.0 mg, 1.5 μmol) in CH_2Cl_2 (1.0 mL), was added an aqueous solution (1.0 mL) of $CuSO_4 \cdot 5H_2O$ (0.11 mg, 0.45 μmol, 0.3 eq), sodium ascorbate (0.26 mg, 1.35 μmol, 0.9 eq) and DIPEA (10 μL, 57 μmol). After stirring for 4 days at RT under nitrogen atmosphere, a saturated aqueous solution of EDTA (1.0 mL) was added and prolonged reaction for another 10 min, it was terminated by phases separation. Besides, the aqueous layer was extracted with CH_2Cl_2 (2 × 5.0 mL) and altogether organic layers were combined, dried over Na_2SO_4, and the solvent was concentrated at reduced pressure without drying completely. The crude was purified by flash column chromatography (toluene : EtOAc = 100 : 0 → 95 : 5) to recover first non-reacted azido $Sc_3N@I_h$-C_{80} **3**, followed by fullerene **6** and last compound dumbbell-**7** as a brown solid.

^{1}H NMR (400 MHz, CD_2Cl_2, TMS, ppm) δ = 7.69 (s, 1H, 1,2,3-triazole), 5.42 (s, 2H, OCH_2-triazole) 4.57 - 4.45 (m, 2H, CH_2) 4.41-4.26 (m, 20 H, CH_2CH$_3$) 4.12 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.63 – 3.49(m, 2H, CH_2), 2.48-2.39 (m, 2H, CH_2), 1.40-1.27 (m, 30H, CH_2CH_3). Noteworthy, the peak located at 1.31 ppm is overlapped with residual solvent hexane and H_2O, consequently, the corresponding integral is not accurate.

MS (MALDI-TOF, DCTB): *m/z* = 2972.4561 $[M]^+$

S5. ^{1}H, ^{13}C NMR spectroscopy and UV/vis-NIR spectroscopy

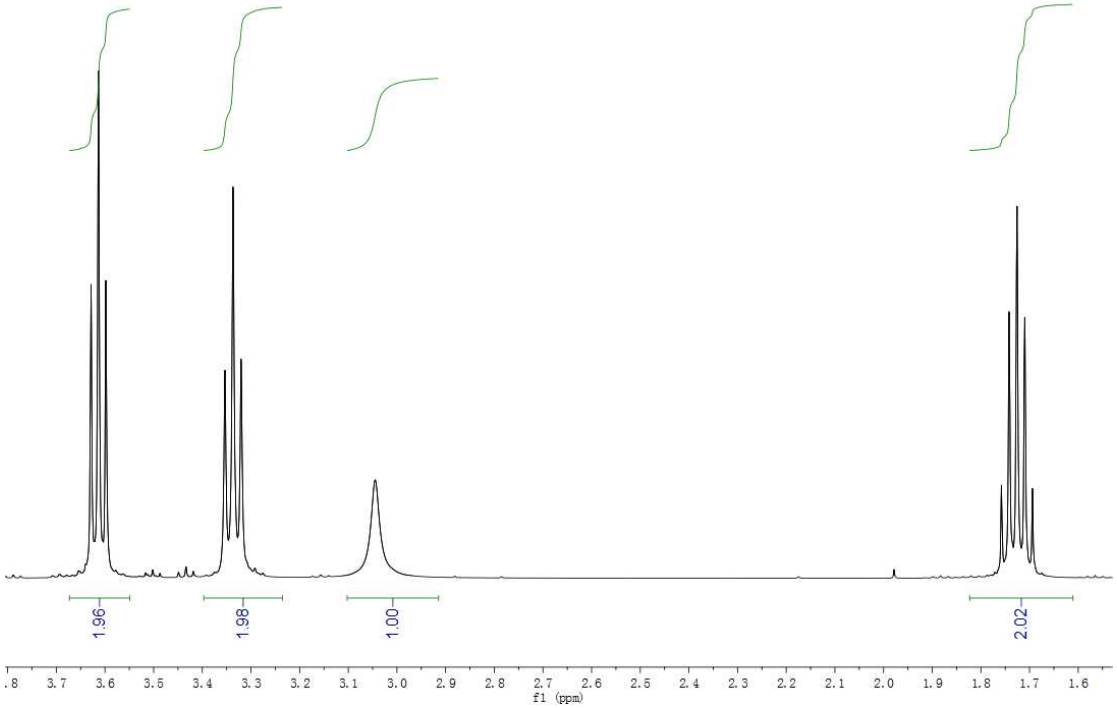


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-azido-1-propanol.

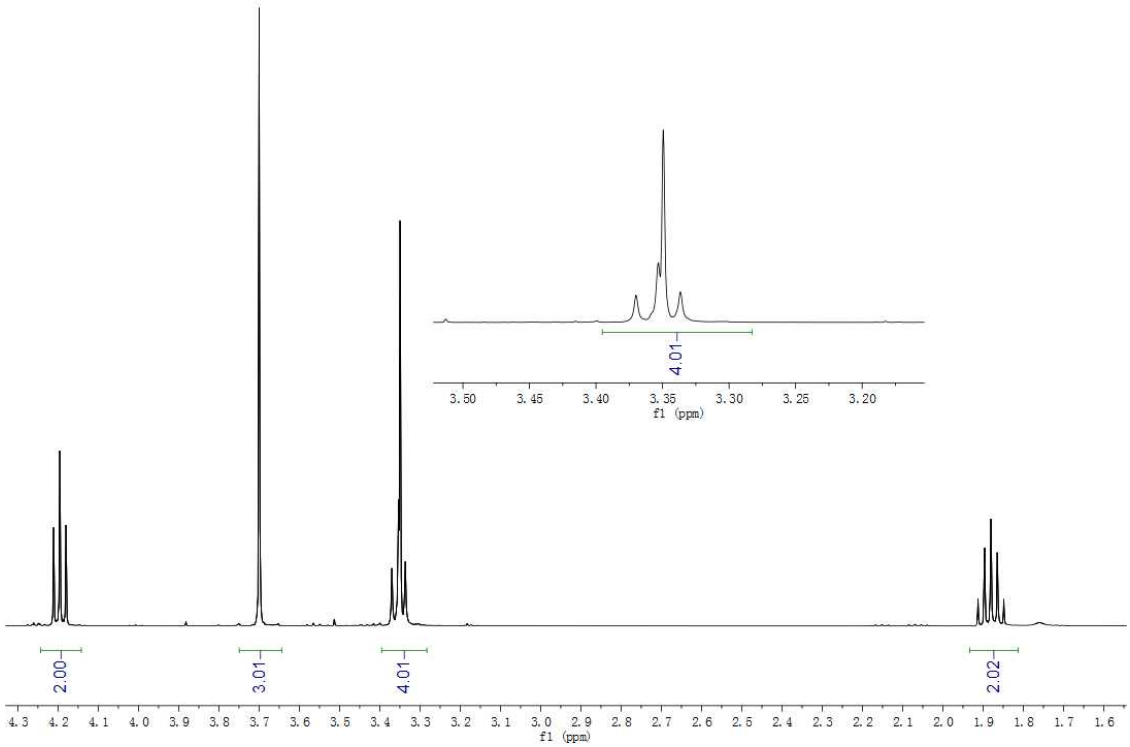


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of azido malonate **1**.

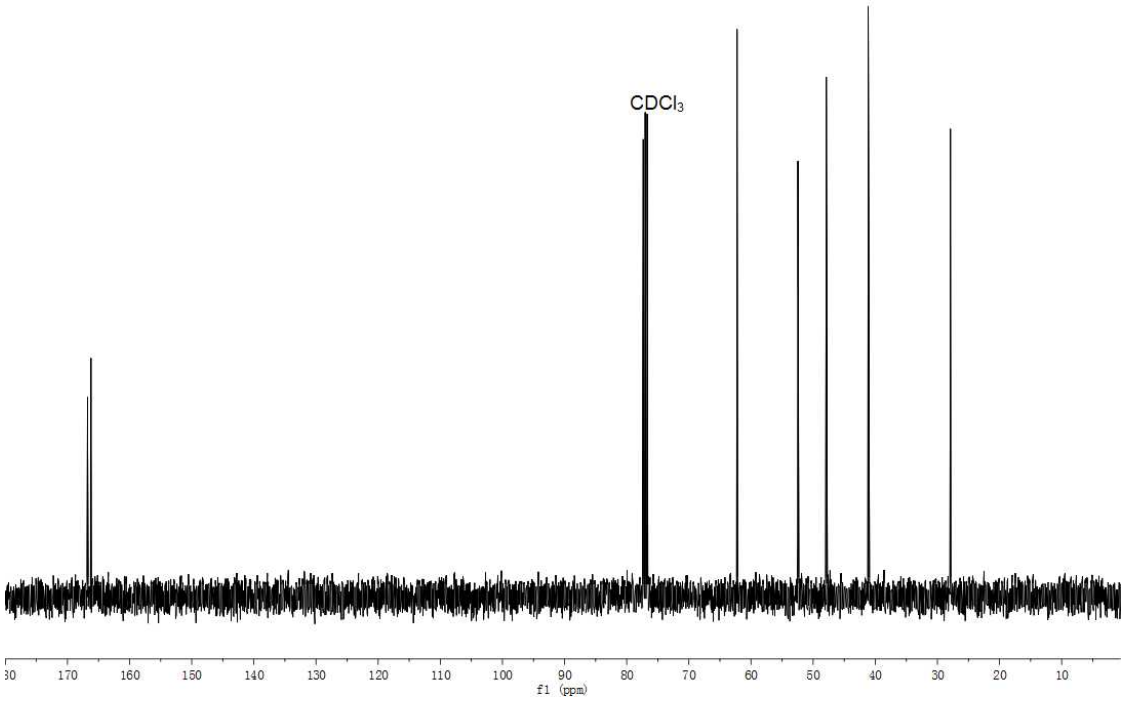


Figure S3. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of azido malonate **1**.

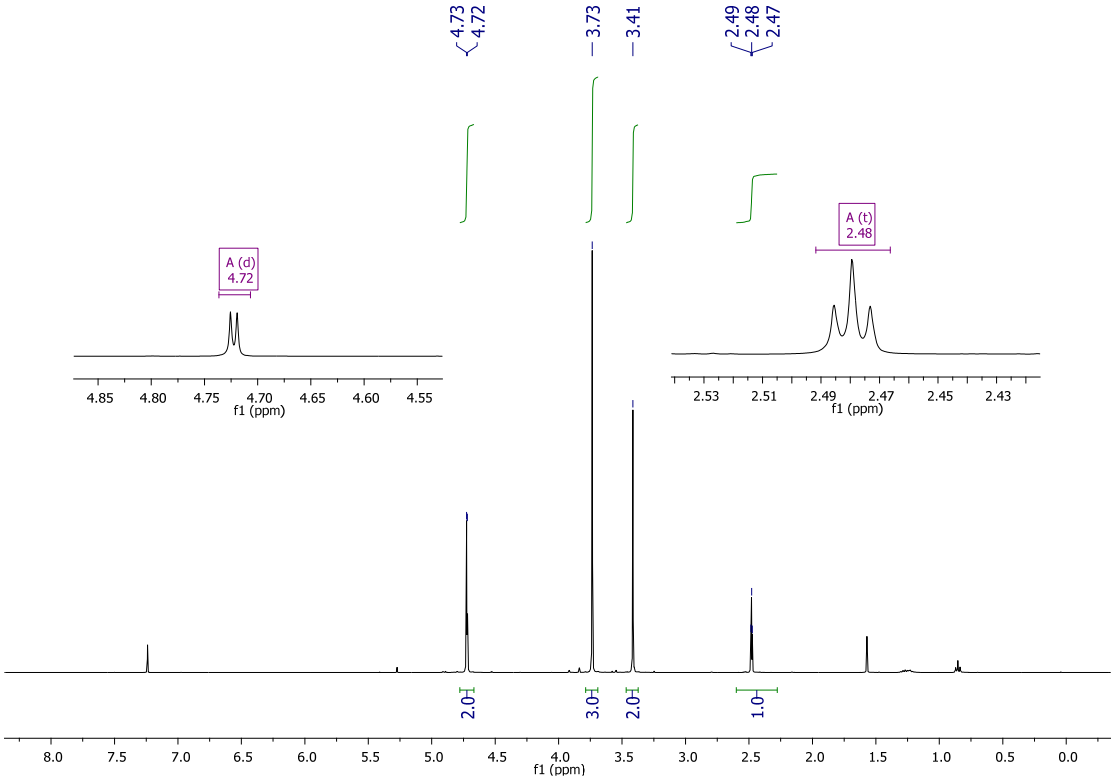


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of alkyne **4**

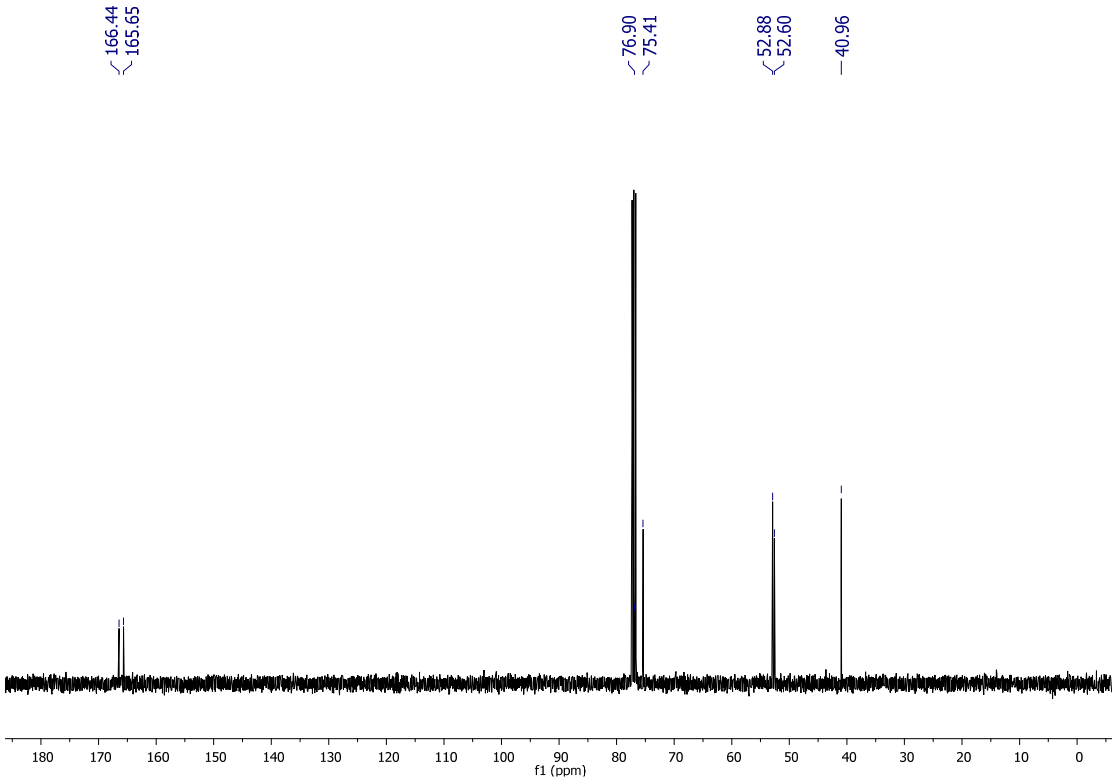


Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of alkyne **4**

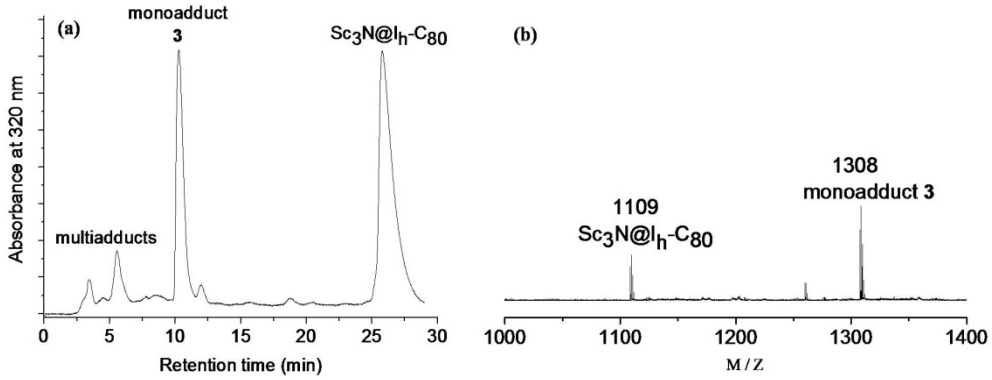


Figure S6. (a) HPLC isolation of compound **3** (4.6 × 250 mm Buckyprep column; flow rate 5.0 ml/min; injection volume 2 ml; toluene as eluent; 40 °C); (b) MALDI-TOF mass spectrum of **3**.

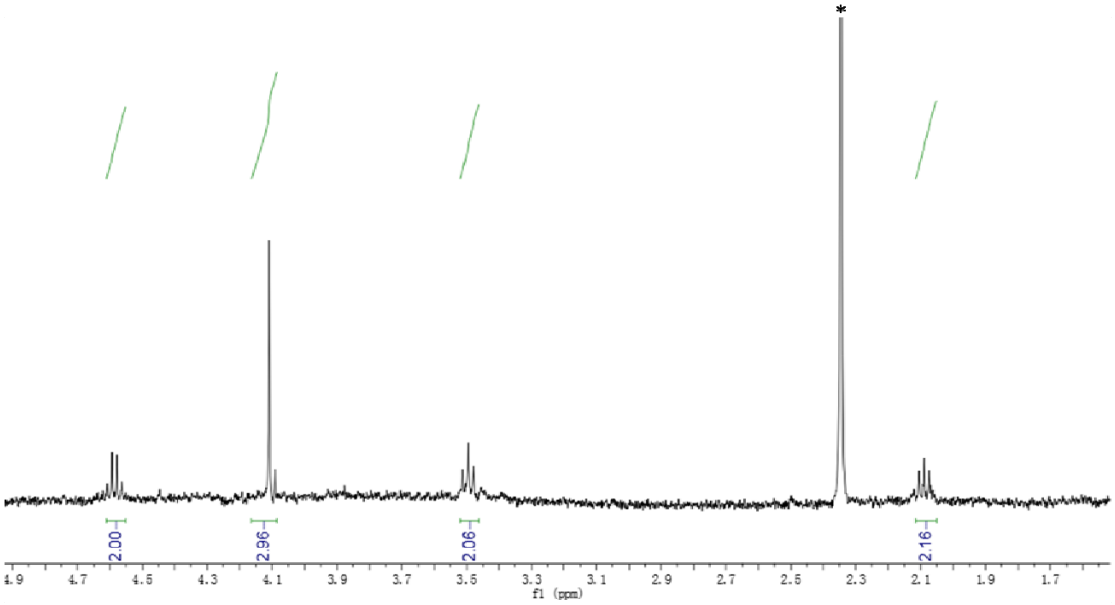


Figure S7. ^{1}H NMR spectrum of **3**.The peak labeled by asterisk denotes the residual toluene.

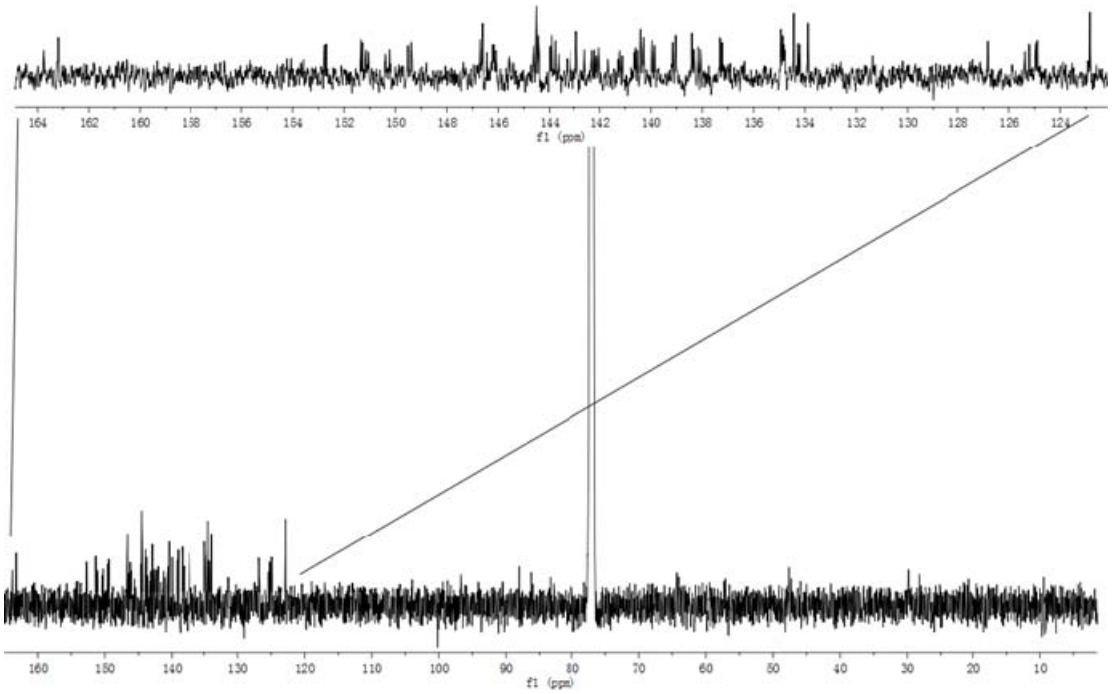


Figure S8. ^{13}C NMR spectrum of **3**.

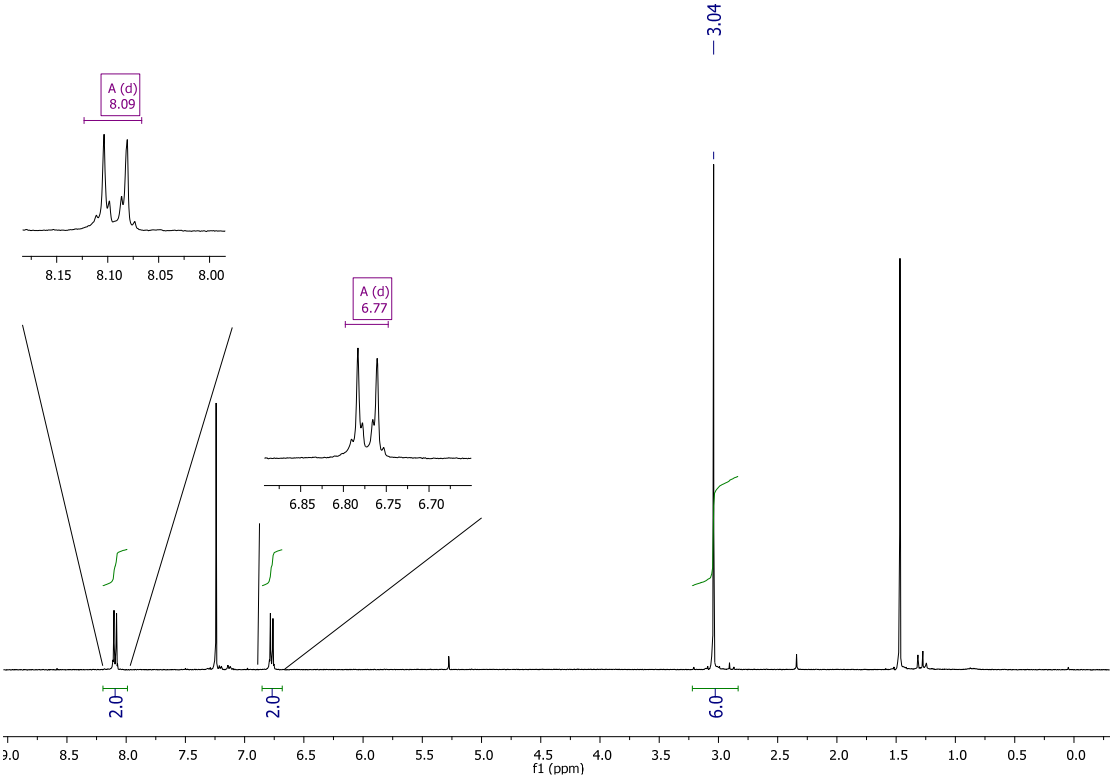


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of isoxazolino fullerene.

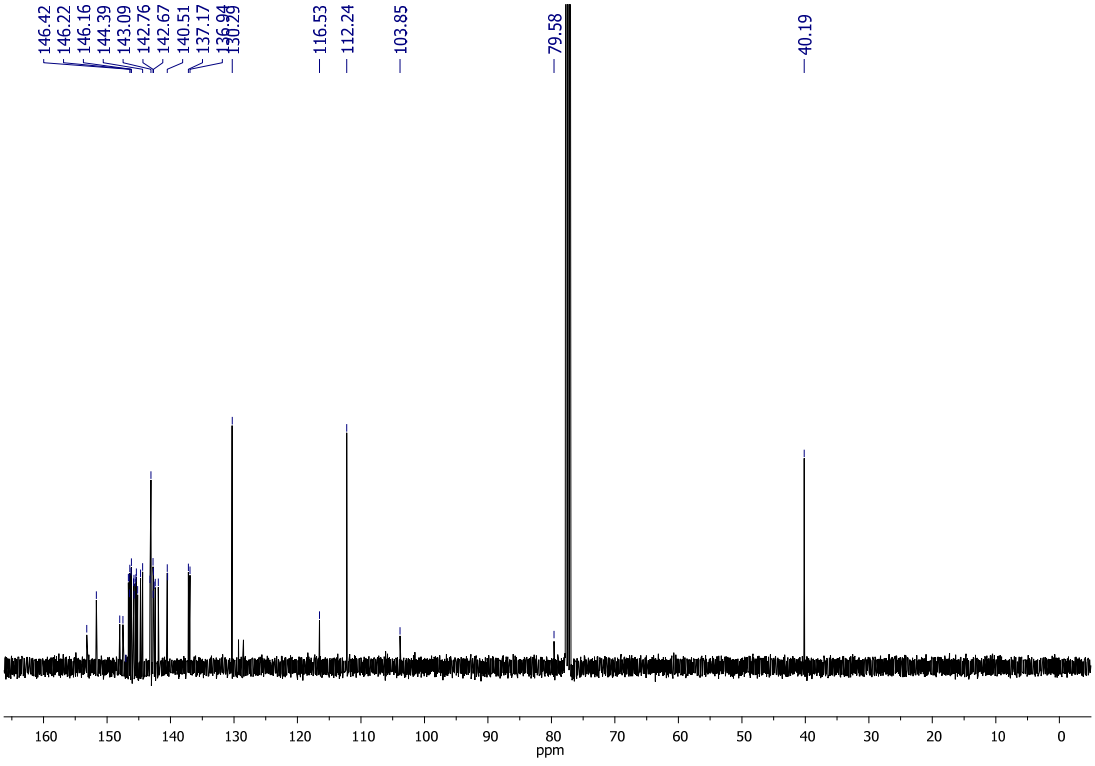


Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of isoxazolino fullerene.

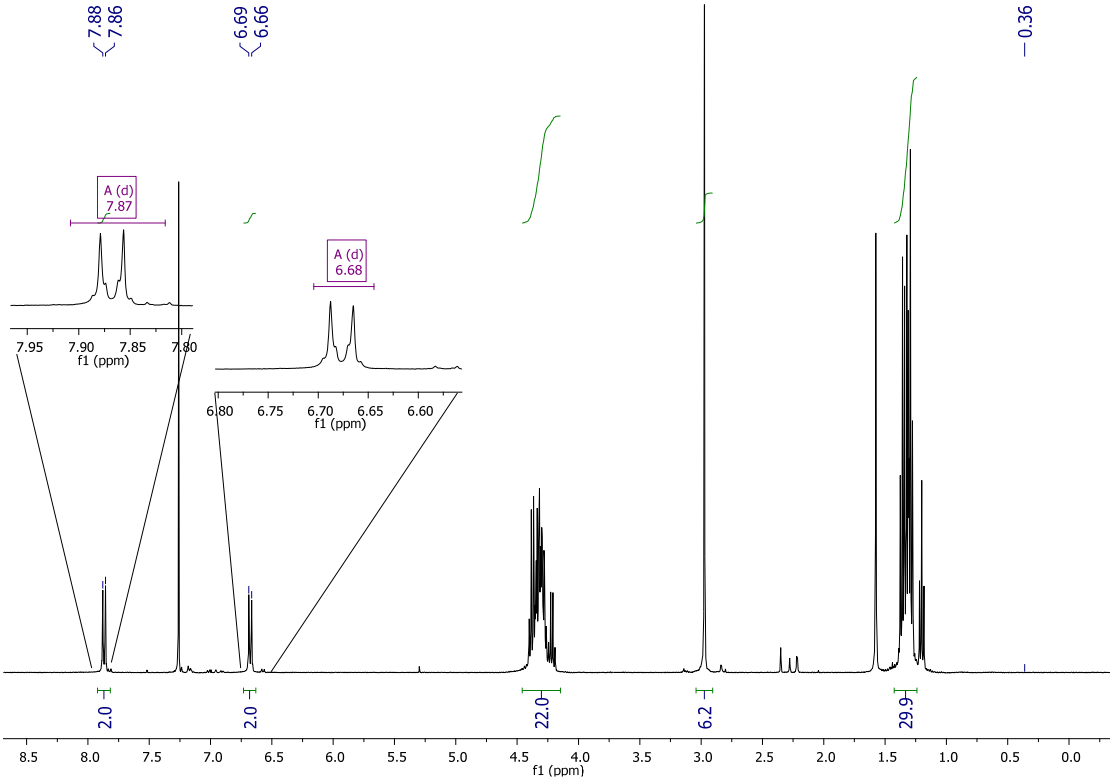


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of [5:1] fullerene **(Isox-5)**.

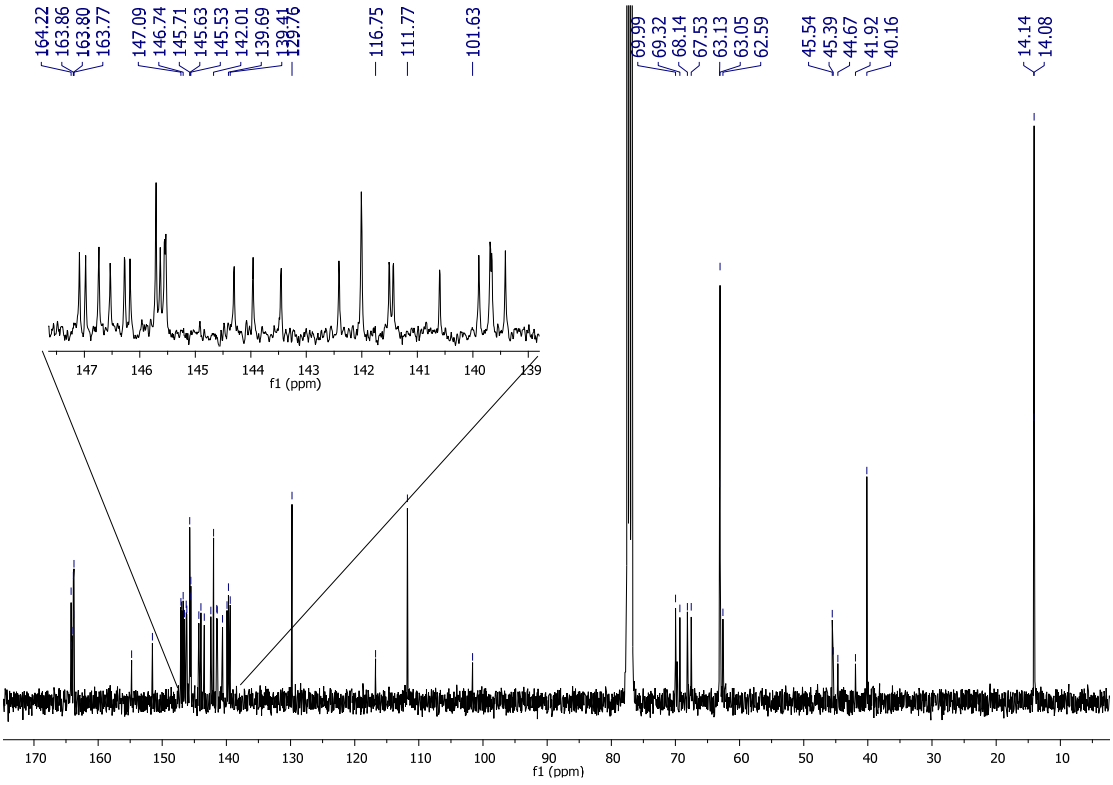


Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) of [5:1] fullerene **(Isox-5)**.

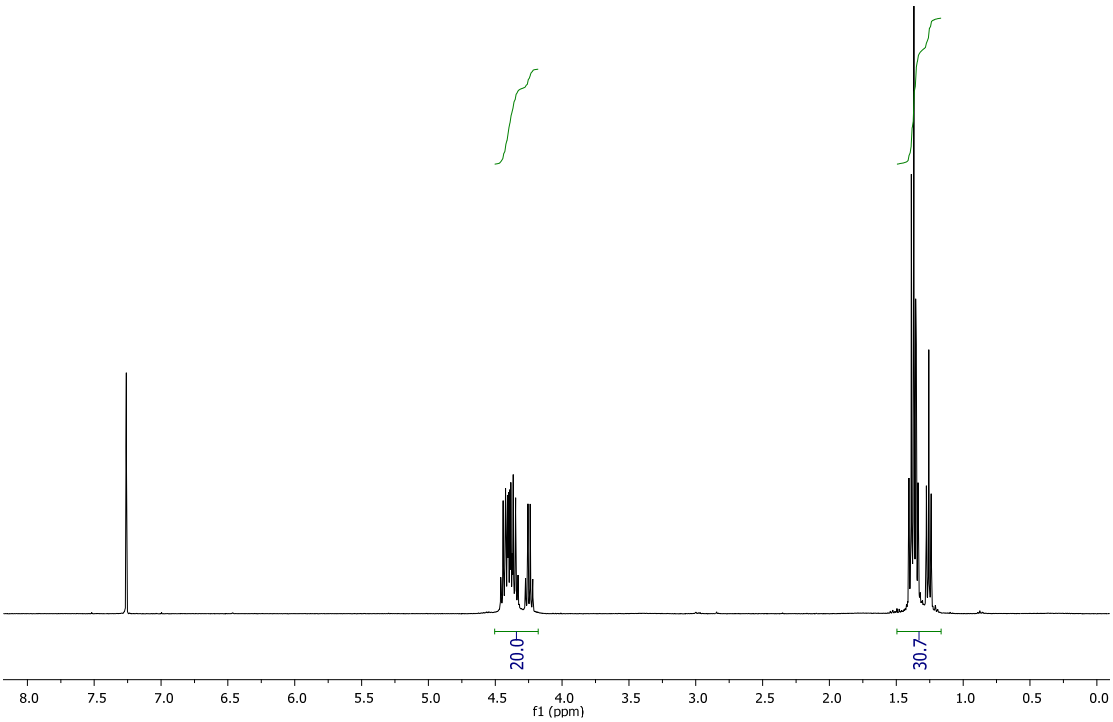


Figure S13 ^{1}H NMR (400 MHz, $CDCl_3$) of [5:0] fullerene **5**.

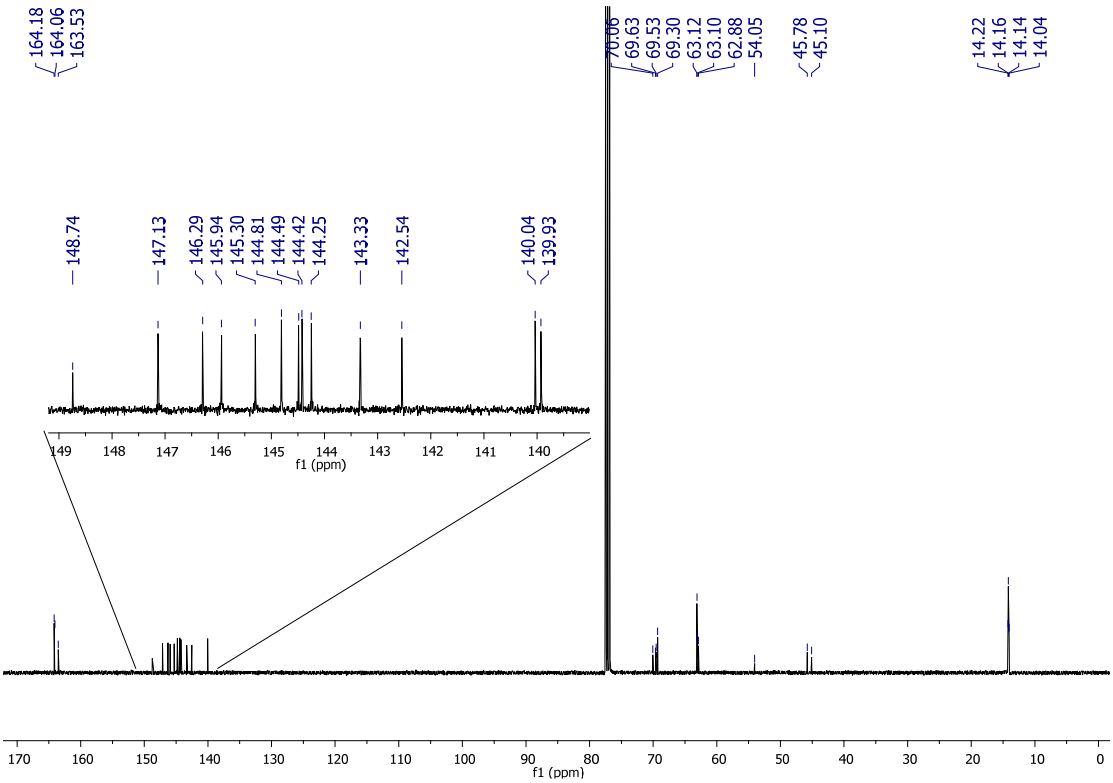


Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) of [5:0] fullerene **5**.

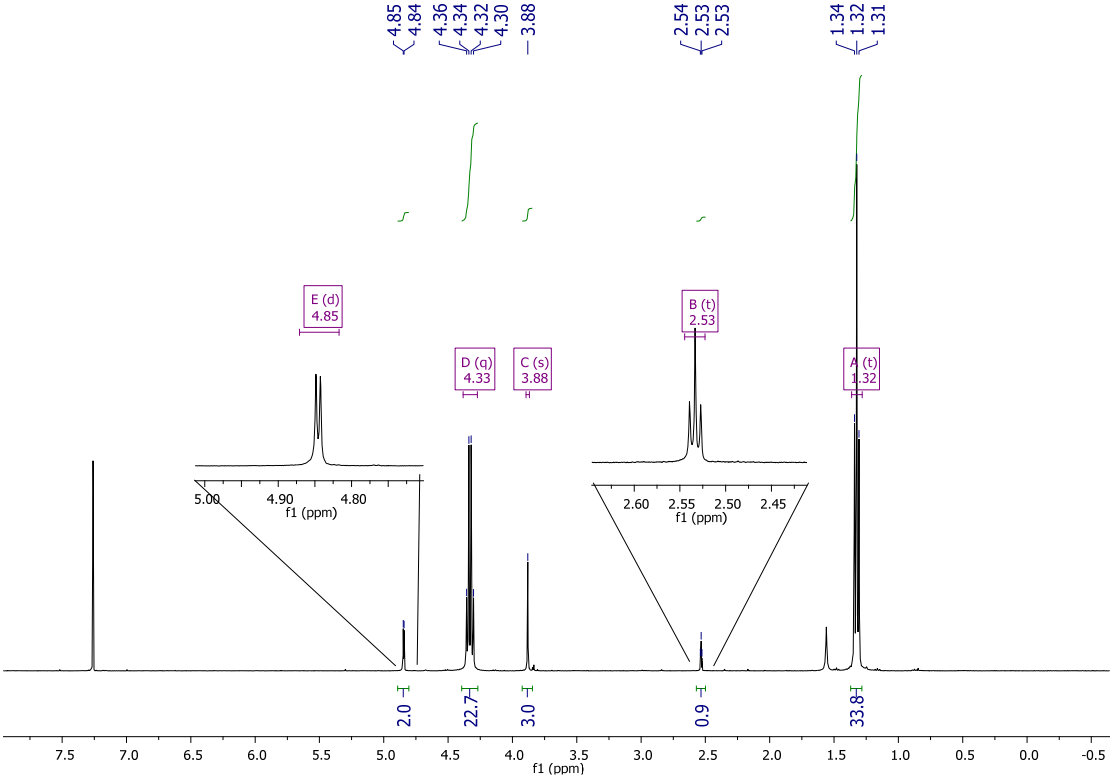


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of [5:1] fullerene **6**.

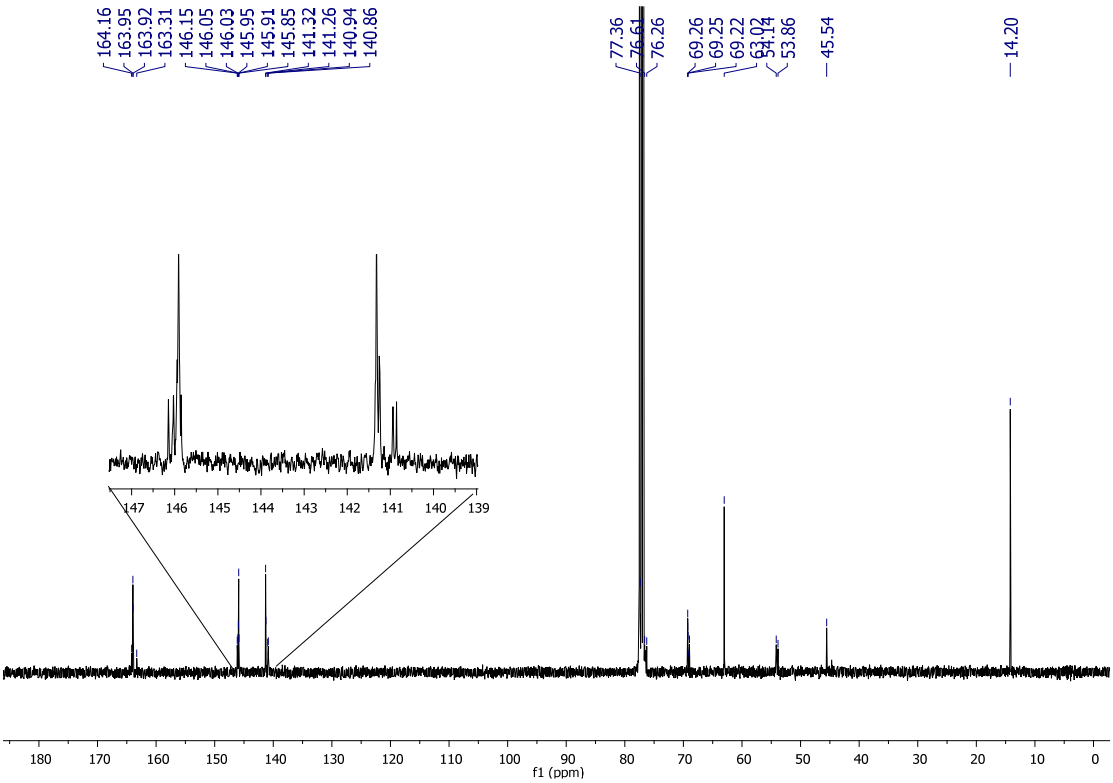


Figure S16. ^{13}C NMR (100 MHz, $CDCl_3$) of [5:1] fullerene **6.** Noteworthy, the C_{60}-sp^2 signals for the [5:1] are distributed in two groups of signals instead of only two signals as it is characteristic for the hexakisadduct due to the presence of two different malonates around the fullerene.

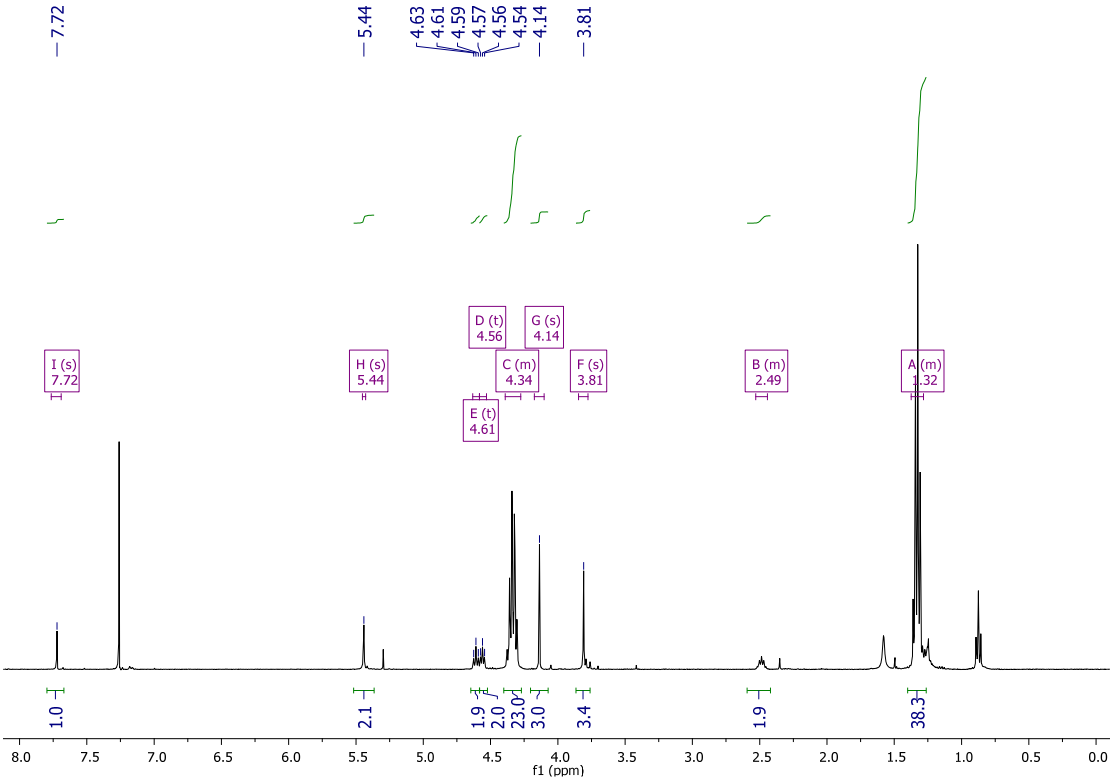


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) of dimer C_{60}-C_{60} fullerene **9**.

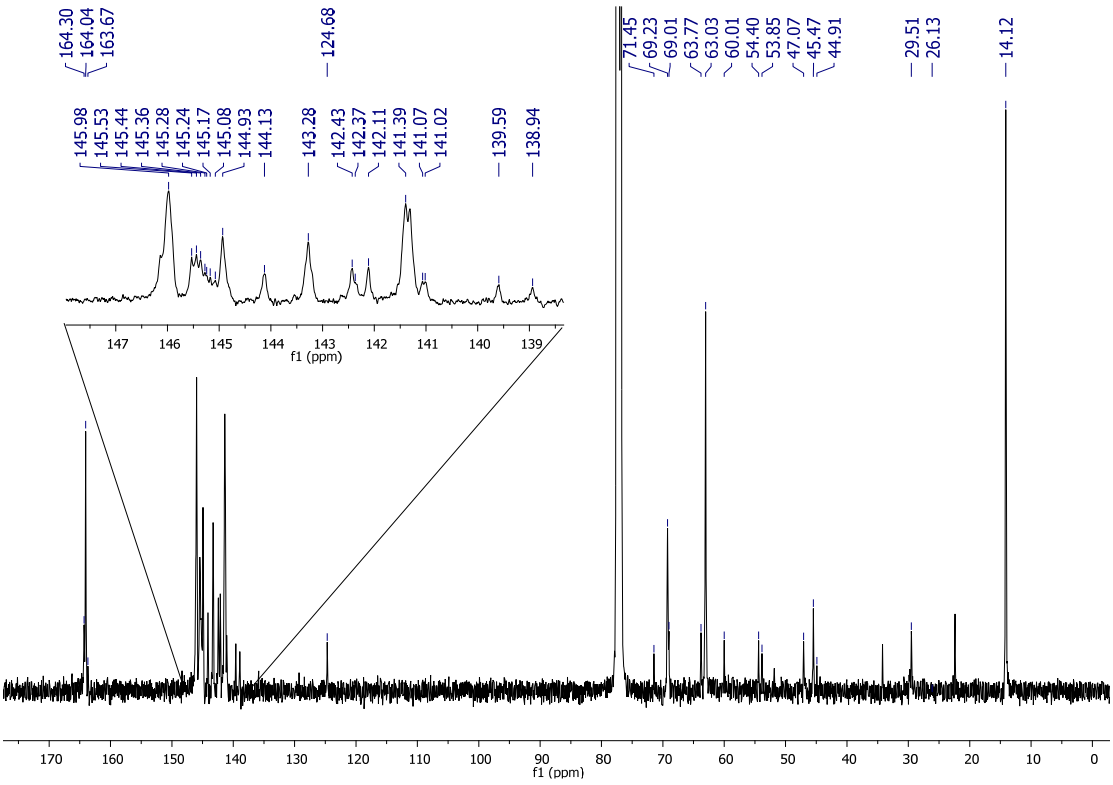


Figure S18A. ^{13}C NMR (101 MHz, $CDCl_3$) of dimer C_{60}-C_{60} fullerene **9**.

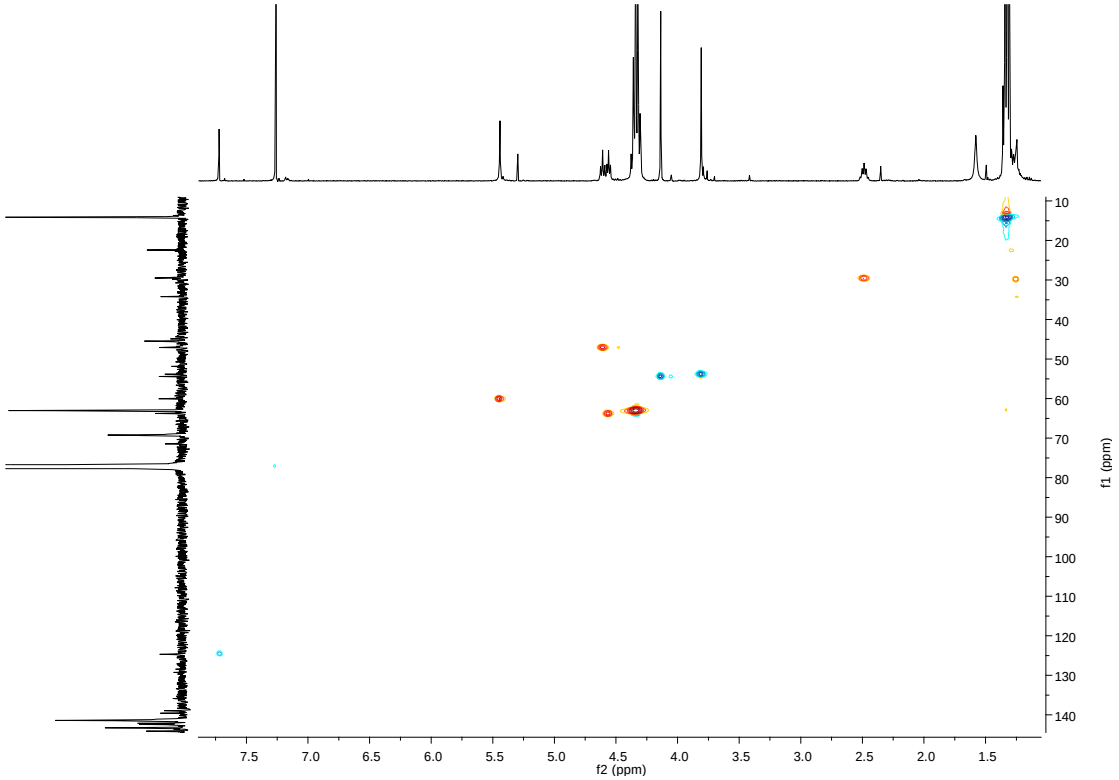


Figure S18B. HSQC ($CDCl_3$) of dimer C_{60}-C_{60} fullerene **9**.

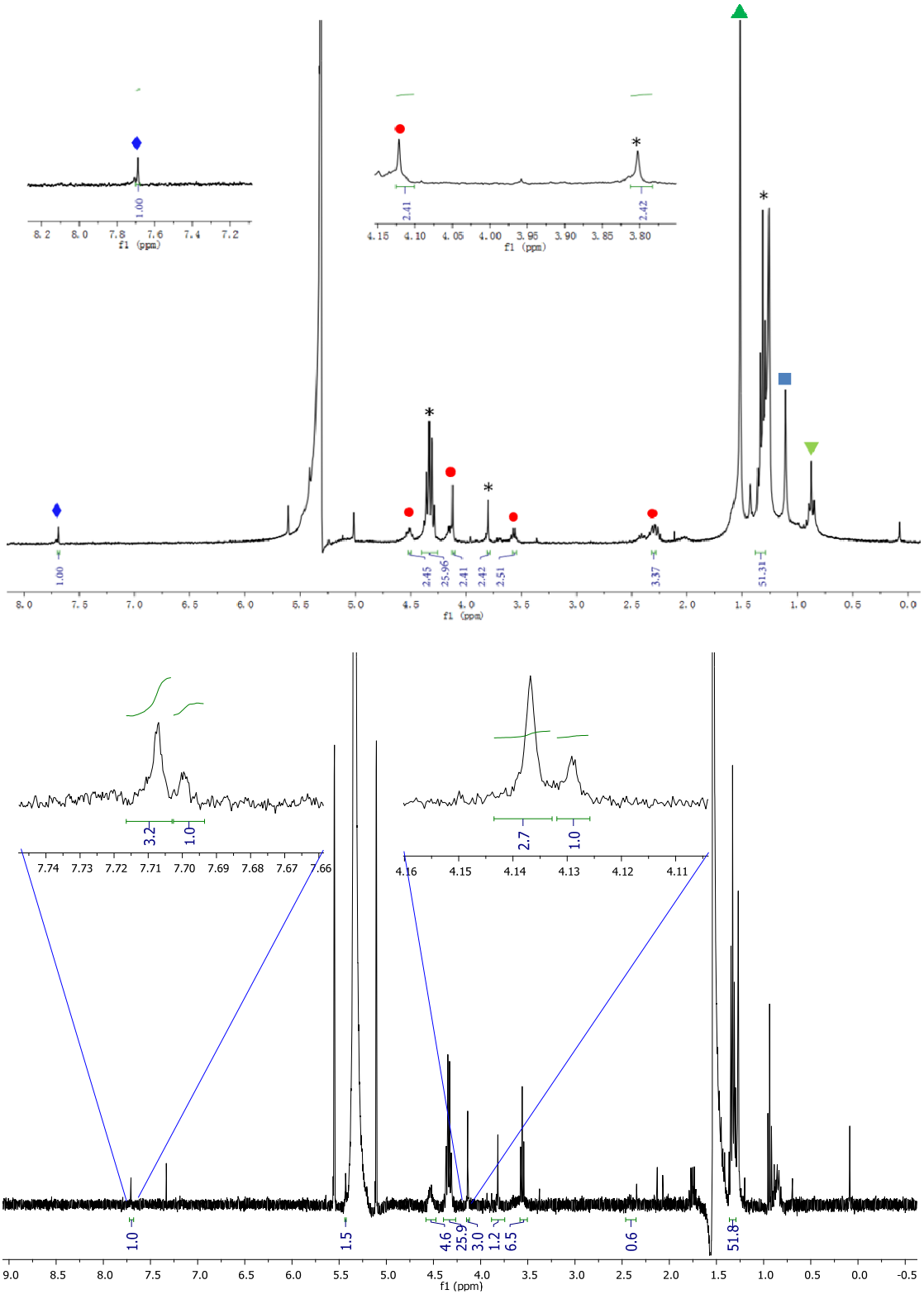


Figure S19. (upper) ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of pure dumbell-**7**. The peaks labeled by red circle indicate the signals resulting from **3**. The peaks labeled by asterisk denote the signals originating from **6**. The peak labeled by blue diamond is corresponding to proton of 1,2,3-triazole. The peak labeled by triangle denotes H_2O. The peaks labeled by reverse triangle and square indicate hexane and unknown impurity, respectively. (down) ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of mixture of two isomers of dumbbell, which indicates that the two isomers are in an approximate ratio of 3:1 as estimated from the integral area of two peaks located at 7.71, 4.14 ppm.

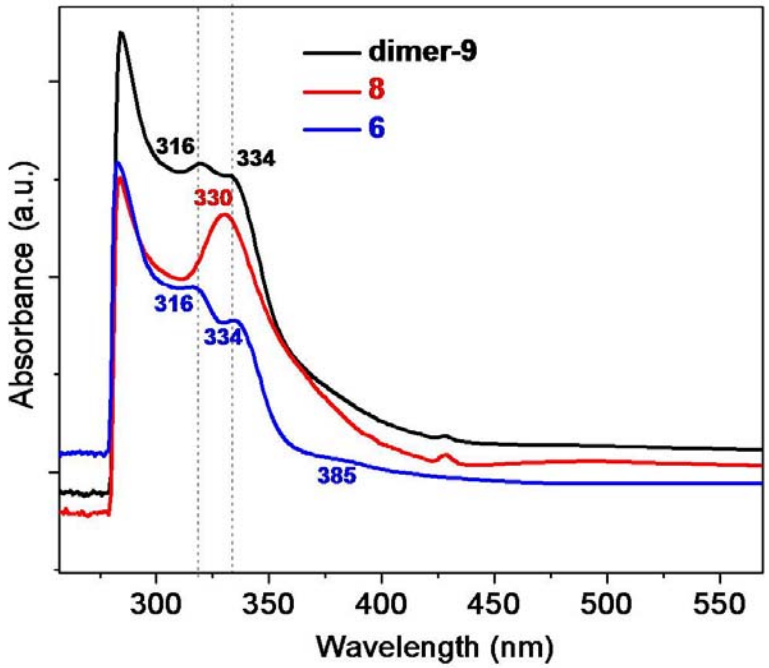


Fig. S20 UV-vis-NIR spectrum of dimer-**9** dissolved in toluene in comparison with those of **6** and **8**.

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