Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2023

Electronic Supporting Information

for

Transition-Metal-Mediated Benzylation of C_{60} with Benzyl Chlorides

Li-Jun Xu,[a,b] Wei-Wei Yang,[a] Fu-She Han[a,b,*] and Xiang Gao,[a,b,*]

[a] Jilin Province Key Lab of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, China

[b] University of Science and Technology of China, Hefei, Anhui, 230026, China

Email: fshan@ciac.ac.cn; gx8802@yahoo.com

Table of Contents

In Situ Vis−NIR Measurement

The reaction mixture was transferred into a 0.1 × 1 cm cuvette under argon atmosphere every 30 minutes, and the cuvette was sealed with a rubber septum and parafilm for the Vis−NIR measurement.

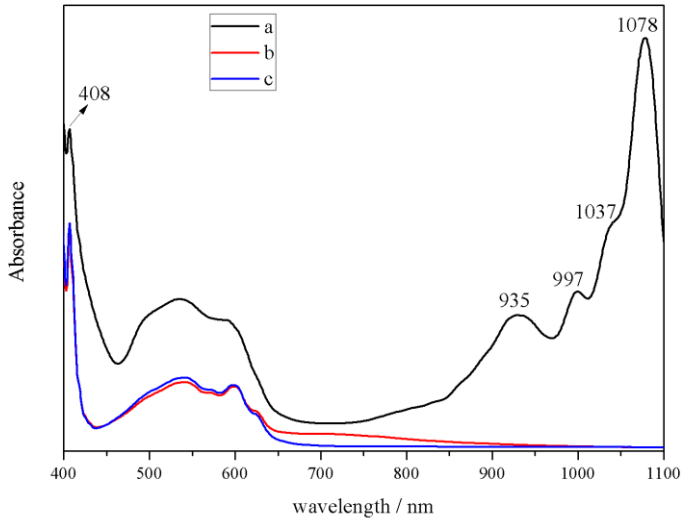


Figure S1. In situ Vis−NIR spectra of the reaction under different conditions: (a) without adding benzyl chloride (BnCl); (b) without adding benzyl chloride and Mn powder; (c) without adding benzyl chloride and $Cu(OAc)_2$. All measurements were carried out under Ar atmosphere with a 0.1 × 1 cm cuvette.

HPLC Charts of the Crude Reaction Mixture and Isolated Products

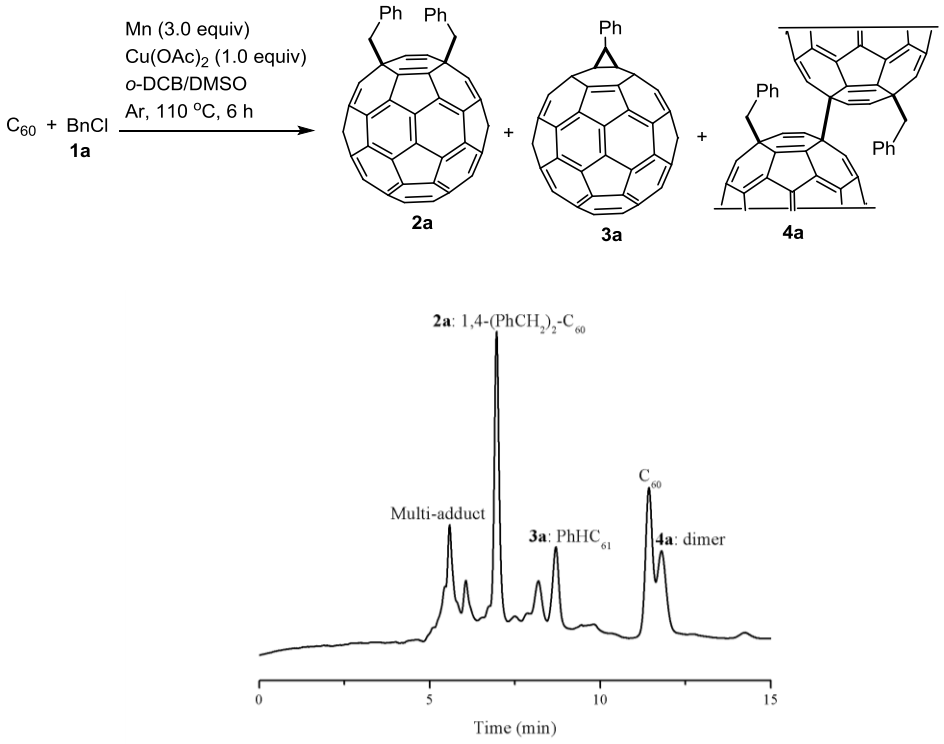


Figure S2. HPLC chart of the crude reaction mixture of C_{60} with **1a**. (LC98-I, toluene as eluent at a flow rate of 3.6 mL/min)

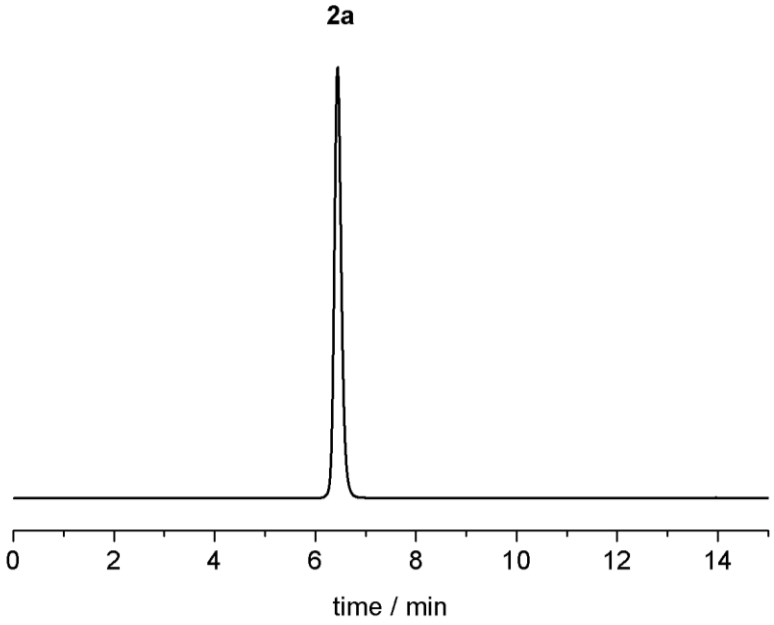


Figure S3. HPLC chart of **2a**. (LC98-II, toluene as eluent at a flow rate of 3.6 mL/min)

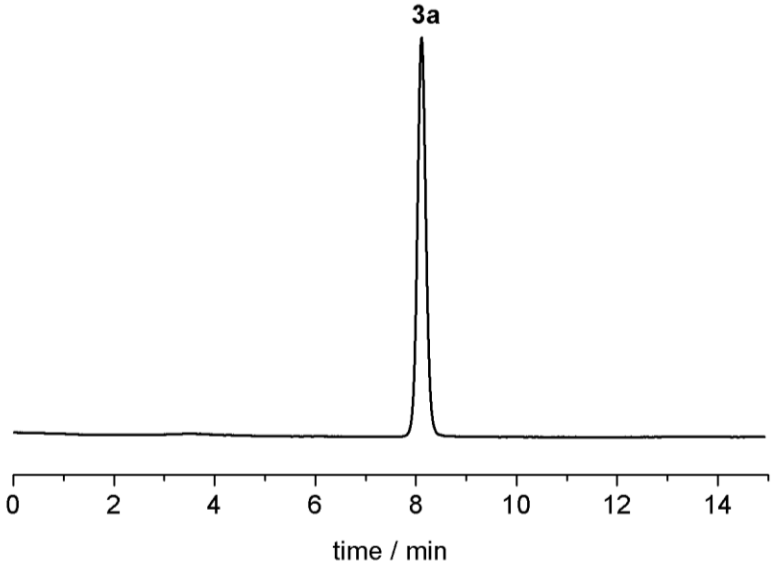


Figure S4. HPLC chart of **3a**. (LC98-II, toluene as eluent at a flow rate of 3.6 mL/min)

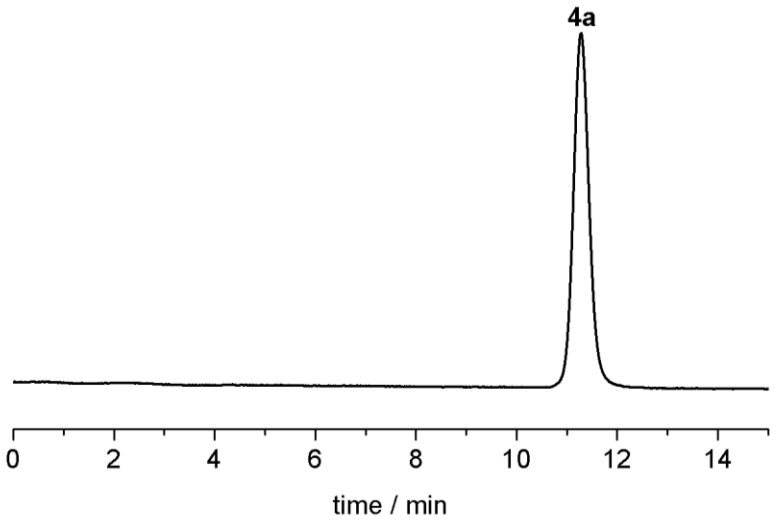


Figure S5. HPLC chart of **4a**. (LC98-II, toluene as eluent at a flow rate of 3.6 mL/min)

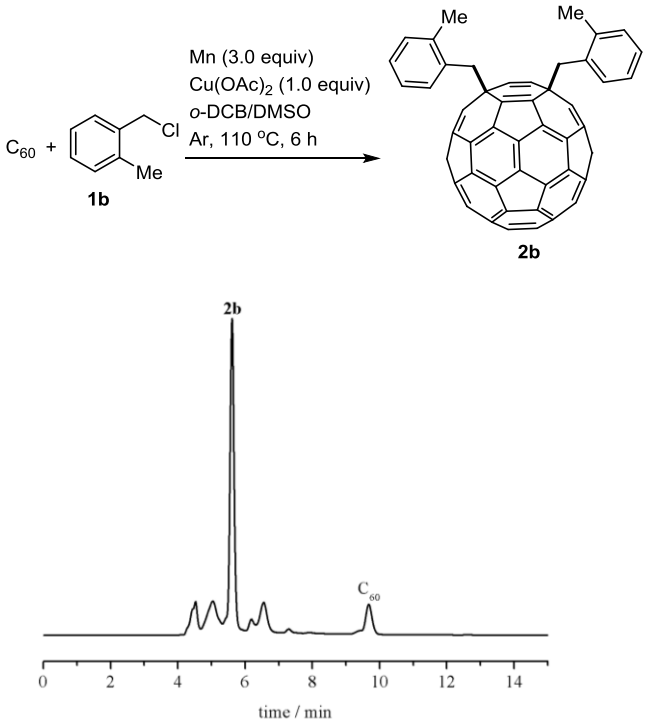


Figure S6. HPLC chart of the crude reaction mixture of C_{60} with **1b**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

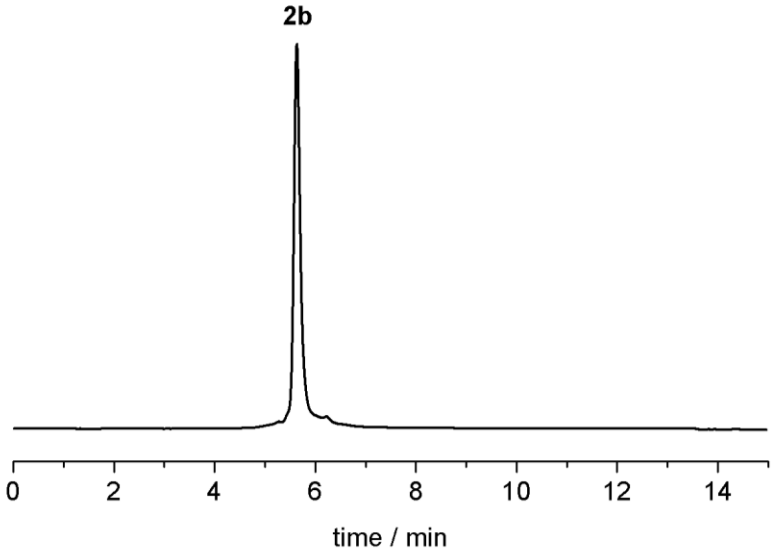


Figure S7. HPLC chart of **2b**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

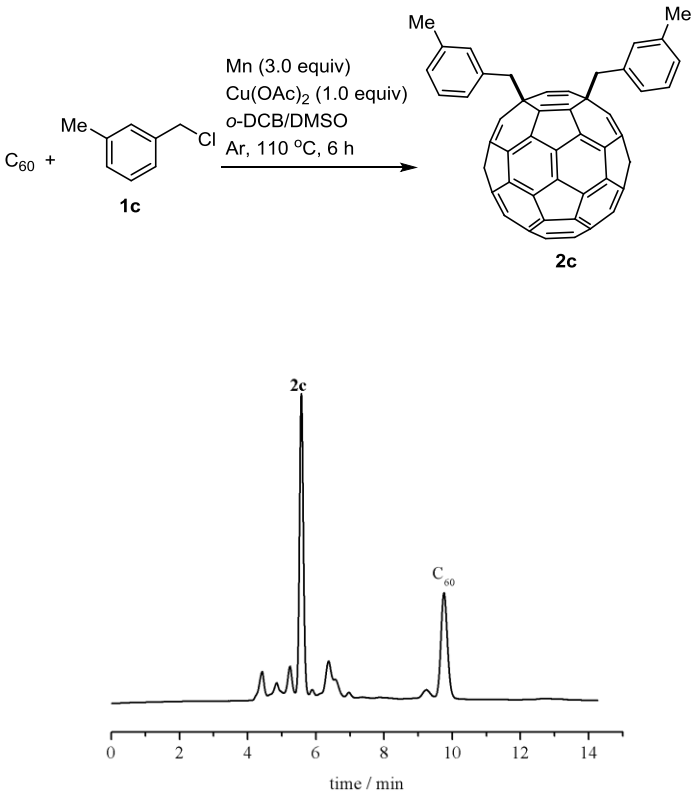


Figure S8. HPLC chart of the crude reaction mixture of C_{60} with **1c**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

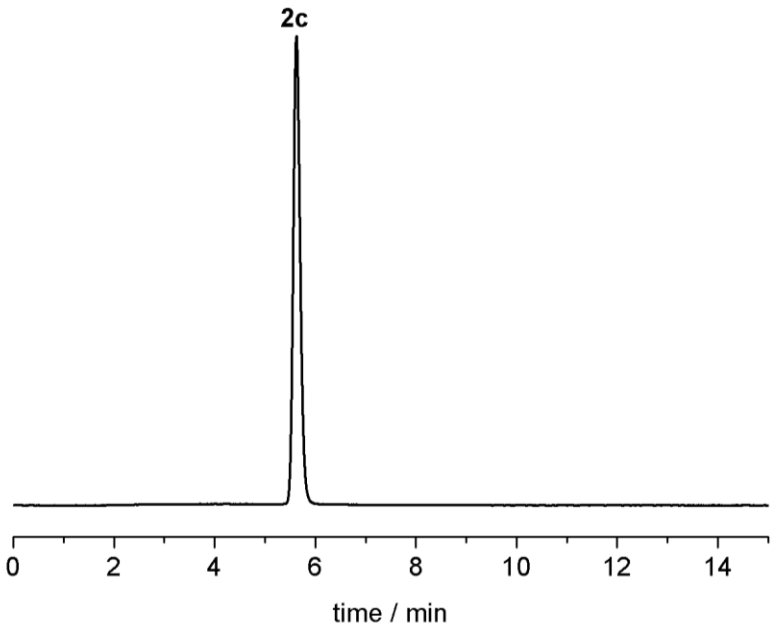


Figure S9. HPLC chart of **2c**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

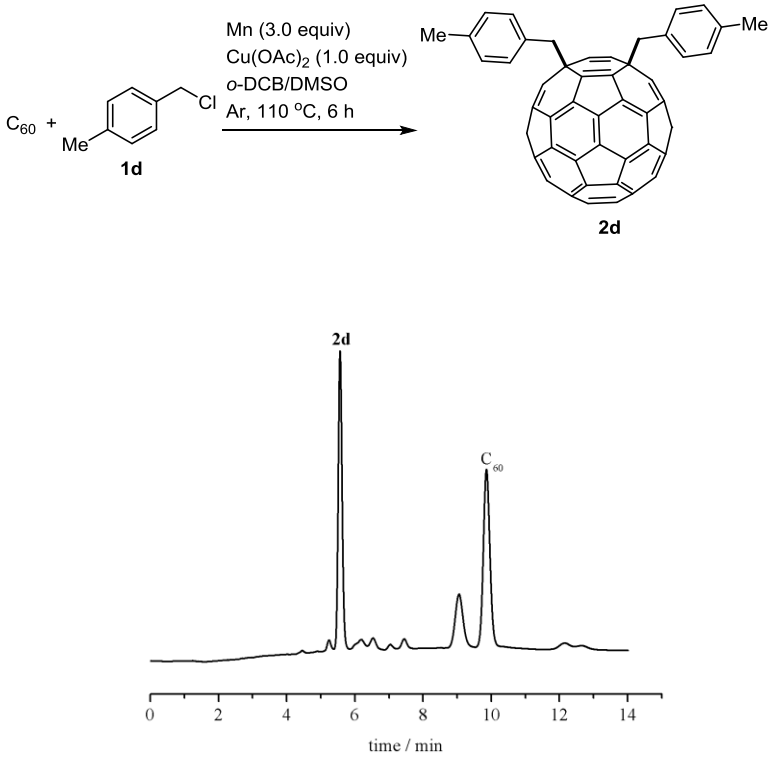


Figure S10. HPLC chart of the crude reaction mixture of C_{60} with **1d**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

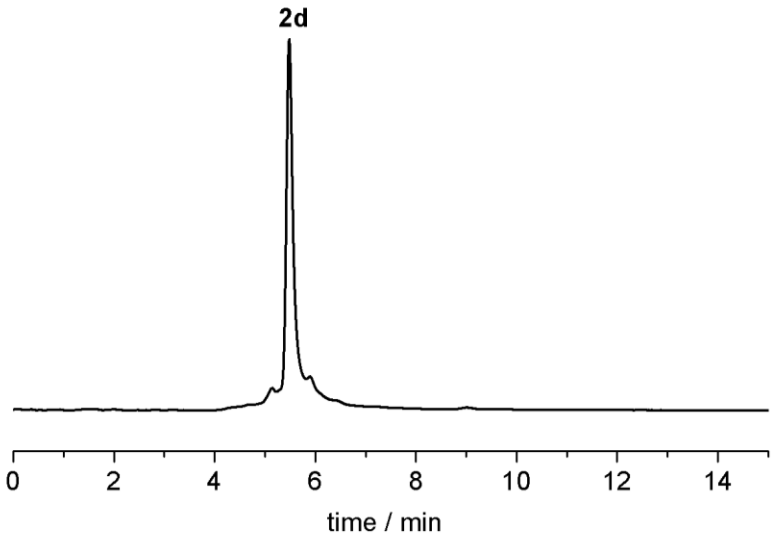


Figure S11. HPLC chart of **2d**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

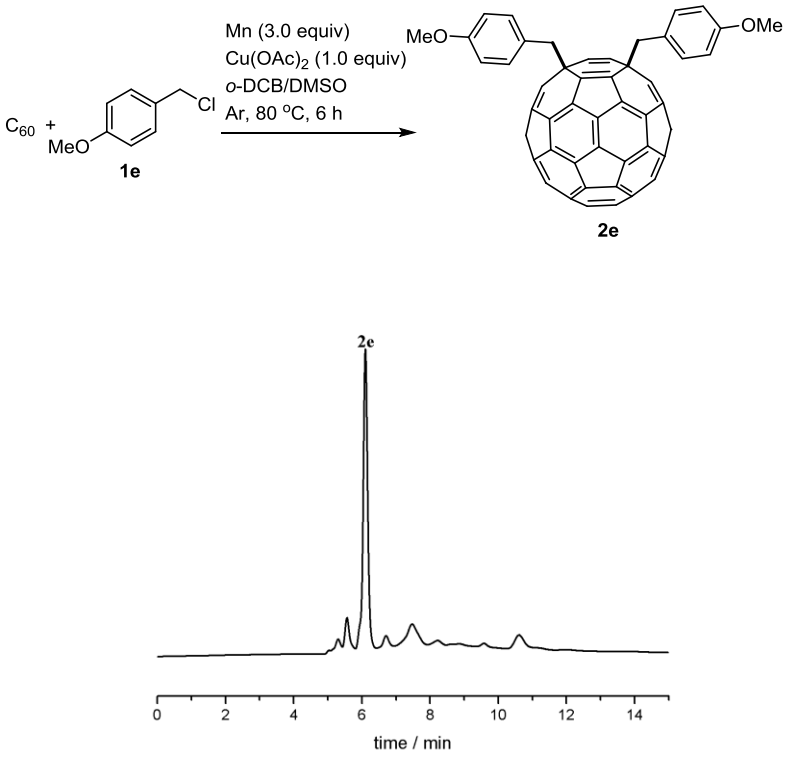


Figure S12. HPLC chart of the crude reaction mixture of C_{60} with **1e**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

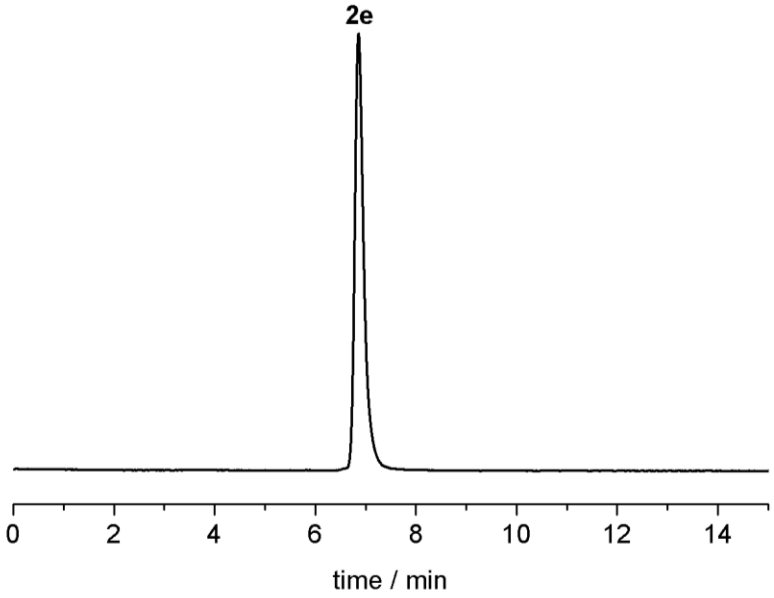
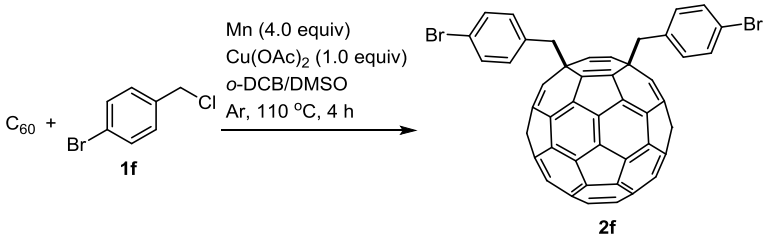


Figure S13. HPLC chart of **2e**. (LC98-II, toluene as eluent at a flow rate of 3.6 mL/min)



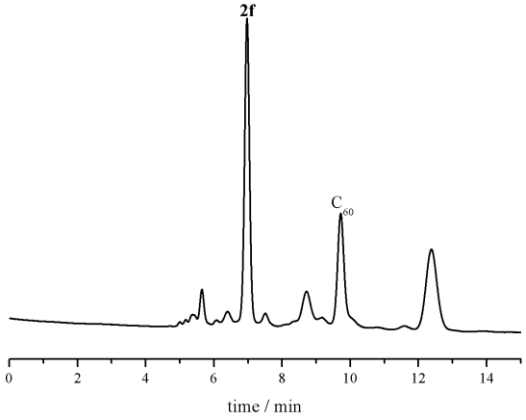


Figure S14. HPLC chart of the crude reaction mixture of C_{60} with **1f**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

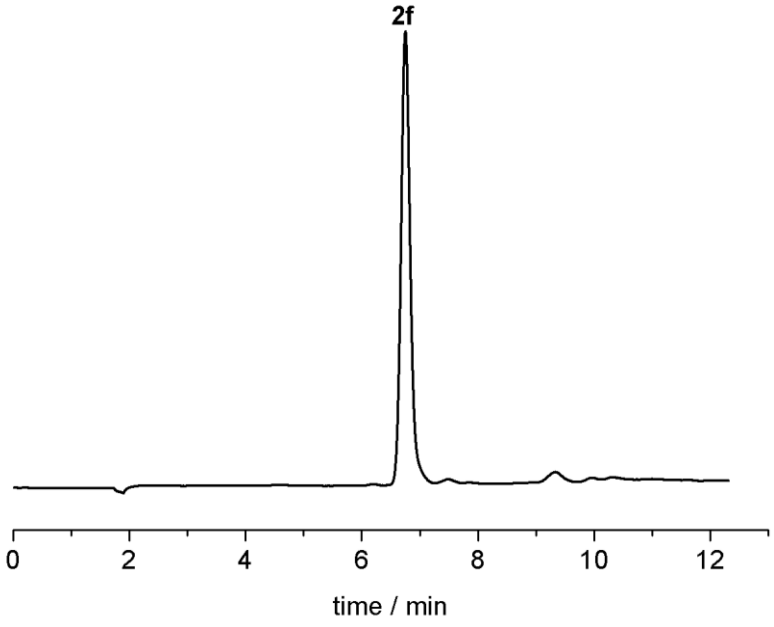


Figure S15. HPLC chart of **2f**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

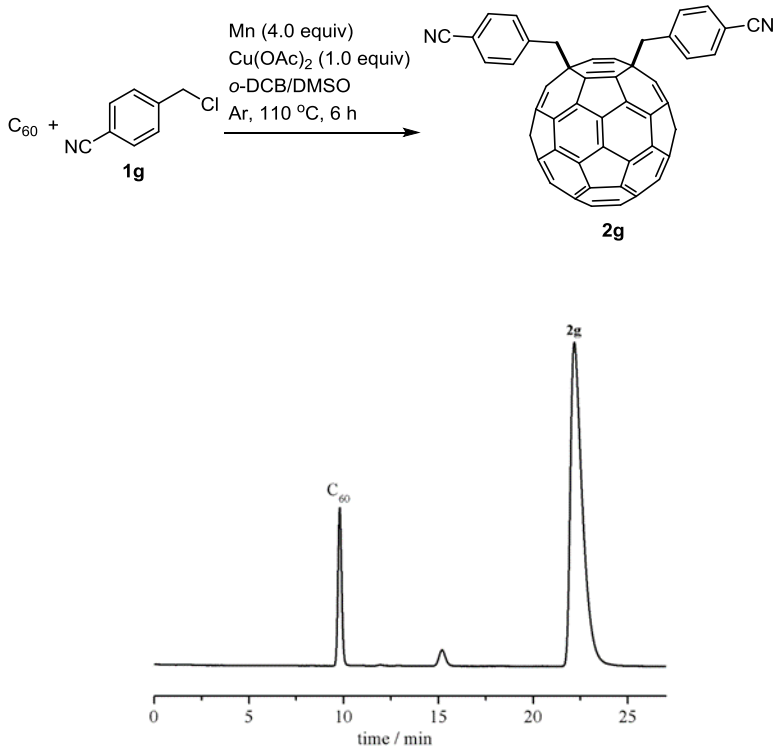


Figure S16. HPLC chart of the crude reaction mixture of C_{60} with **1g**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

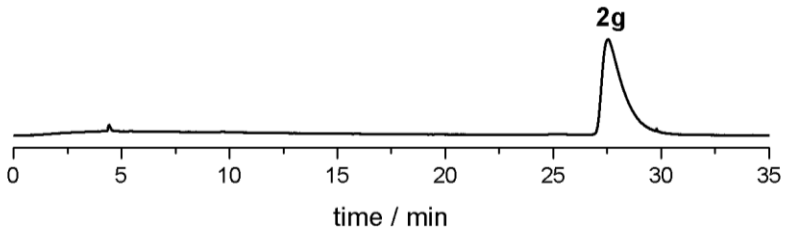


Figure S17. HPLC chart of **2g**. (LC98-II, toluene as eluent at a flow rate of 3.6 mL/min)

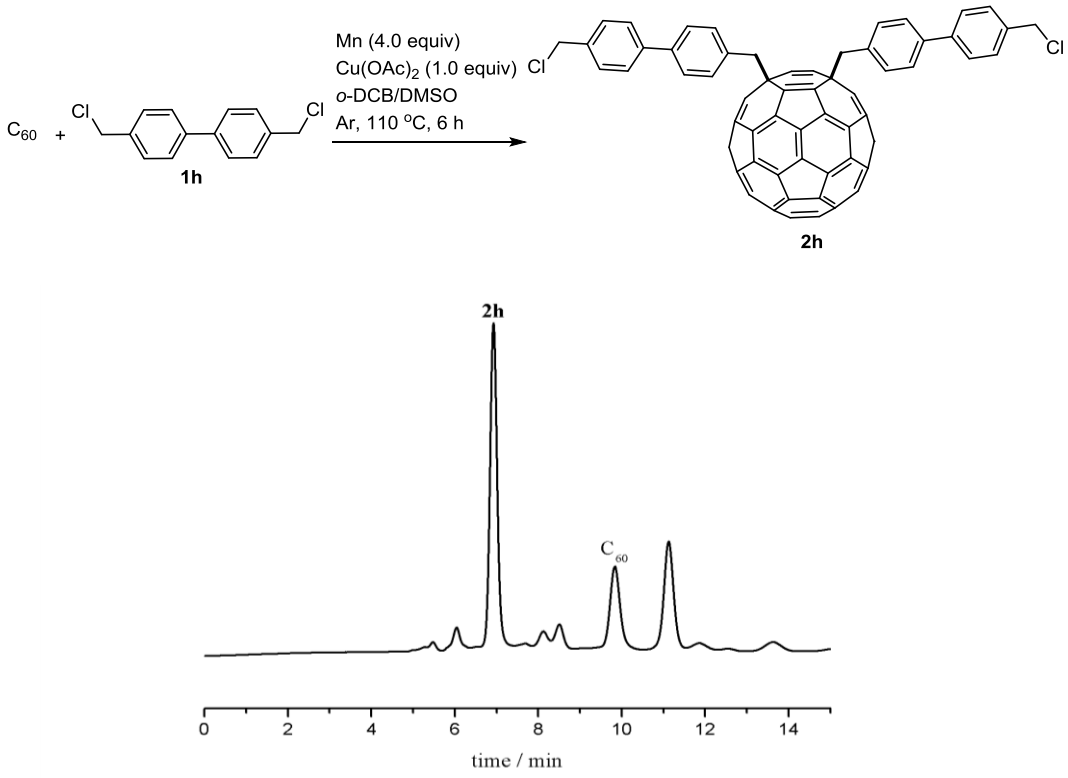


Figure S18. HPLC chart of the crude reaction mixture of C_{60} with **1h**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

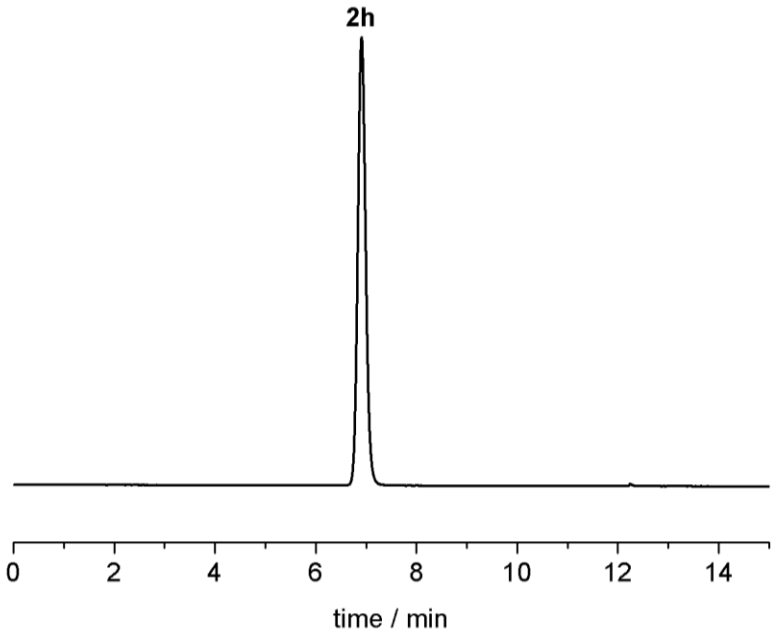
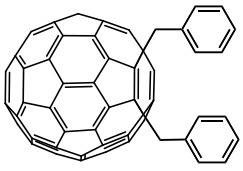


Figure S19. HPLC chart of **2h**. (LC98-II, toluene as eluent at a flow rate of 4.0 mL/min)

UV-Vis, HRMS, and NMR Spectra of the Products



2a

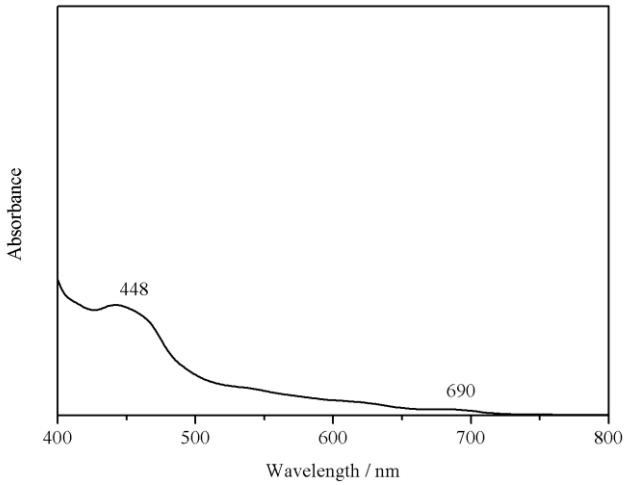


Figure S20. UV-Vis absorption spectrum of **2a** in toluene.

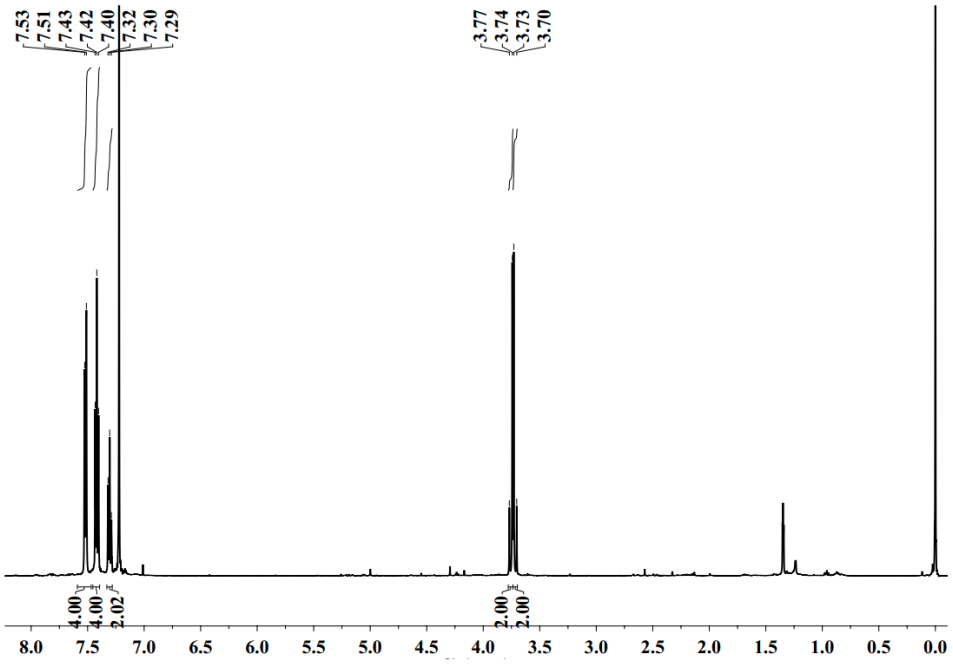
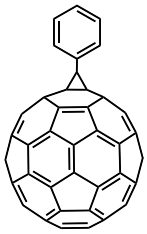


Figure S21. ^{1}H NMR spectrum of **2a** in $CS_2/CDCl_3$=1:1.



3a

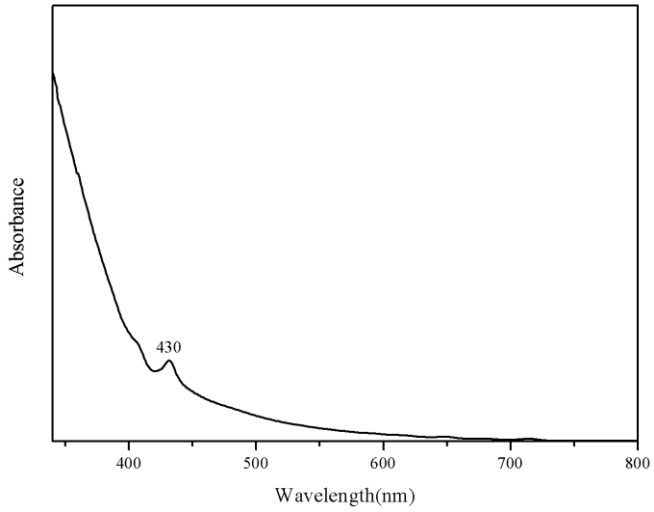


Figure S22. UV-vis absorption spectrum of **3a** in toluene.

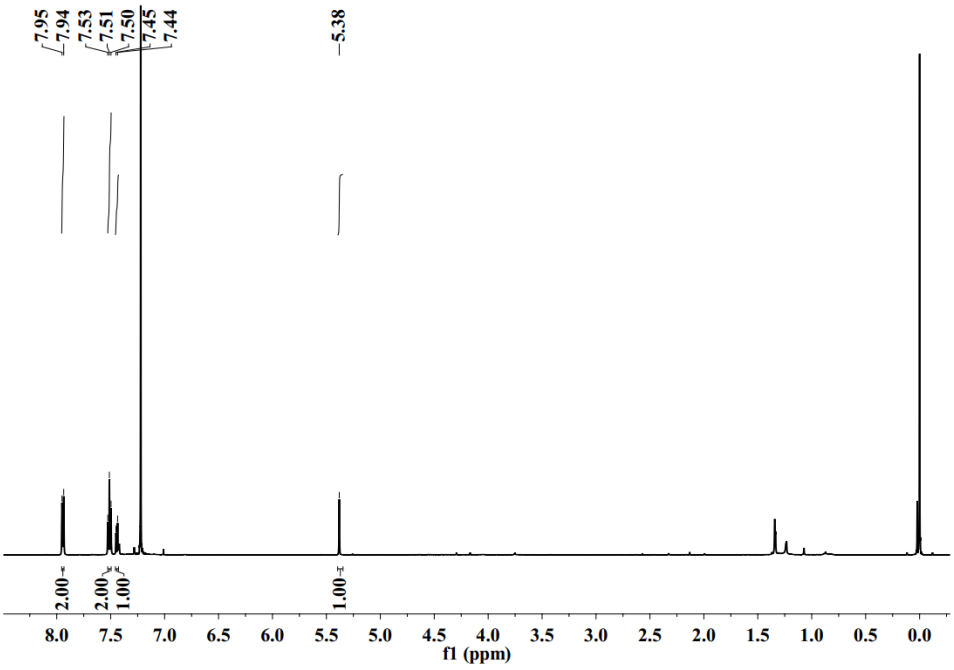
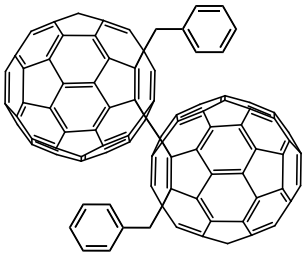


Figure S23. ^{1}H NMR spectrum of **3a** in $CS_2/CDCl_3$ = 1:1.



4a

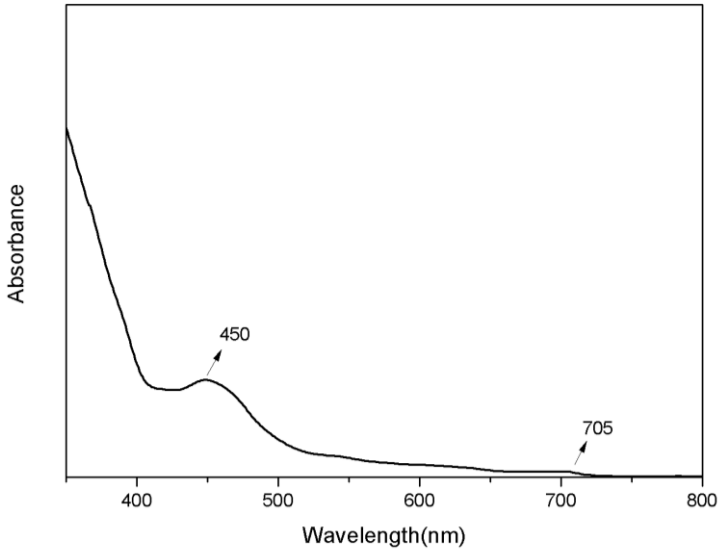


Figure S24. UV-Vis absorption spectrum of **4a** in toluene.

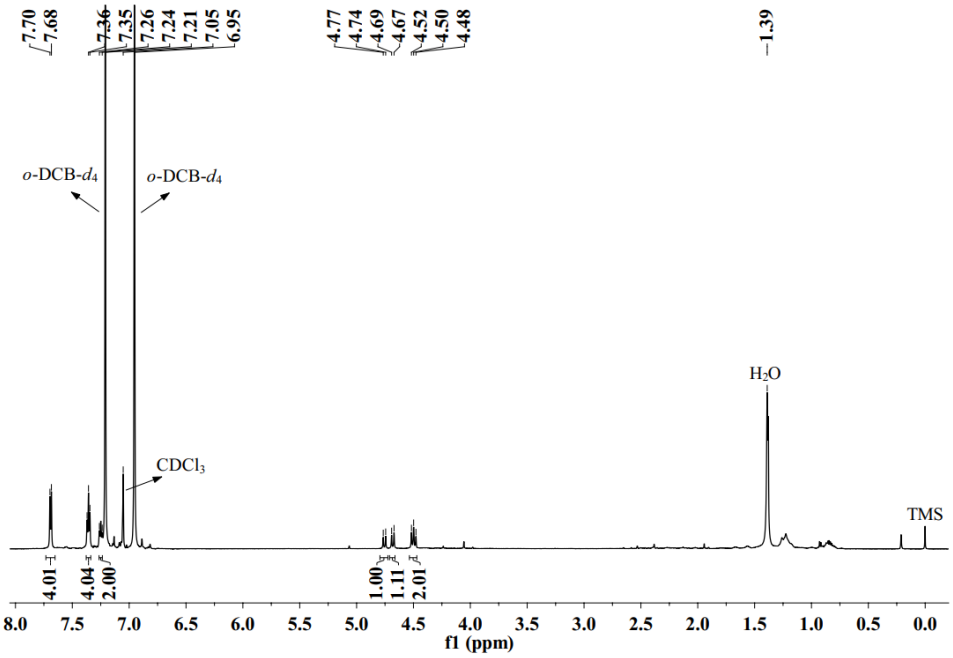
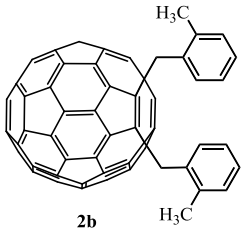


Figure S25. ^{1}H NMR spectrum of **4a** in *o*-DCB-d_4 and $CDCl_3$ (2 drops)**.**



2b

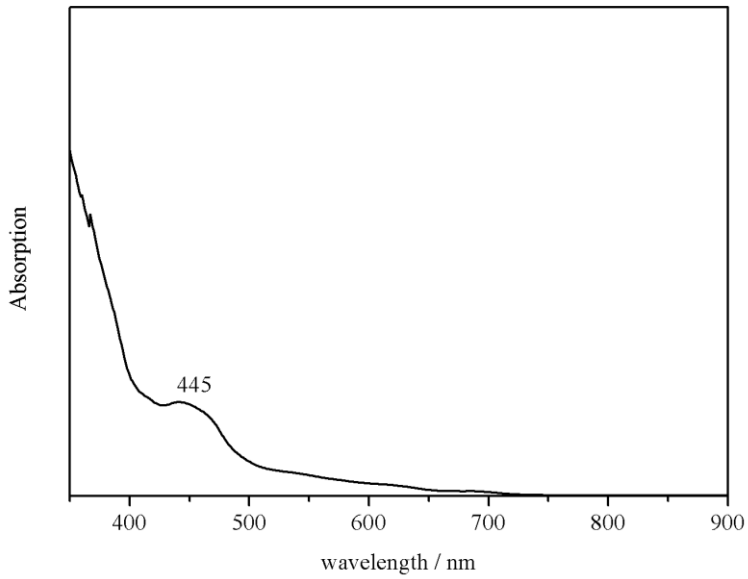


Figure S26. UV-Vis absorption spectrum of **2b** in toluene.

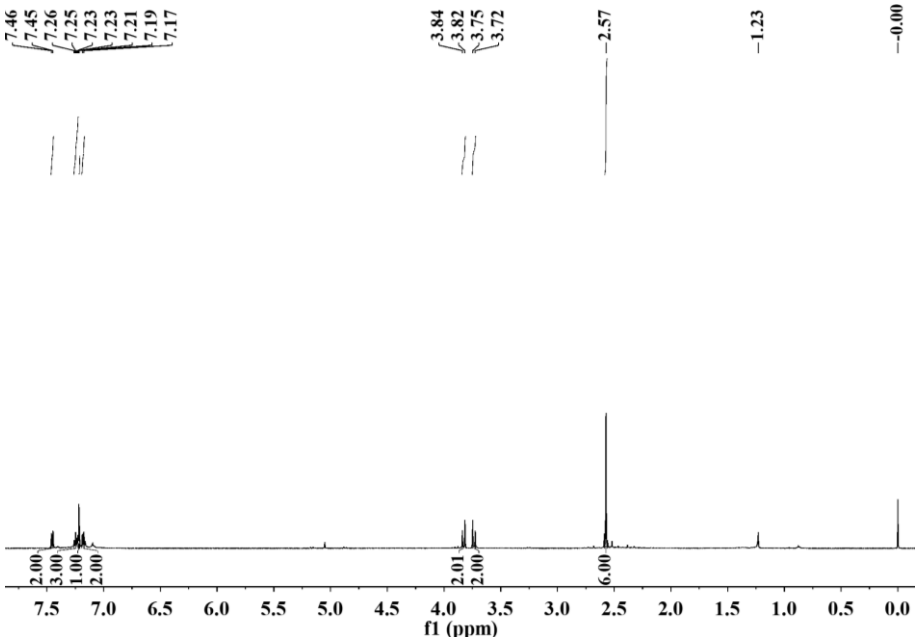


Figure S27. ^{1}H NMR spectrum of **2b** in $CS_2/CDCl_3$ = 1:1.

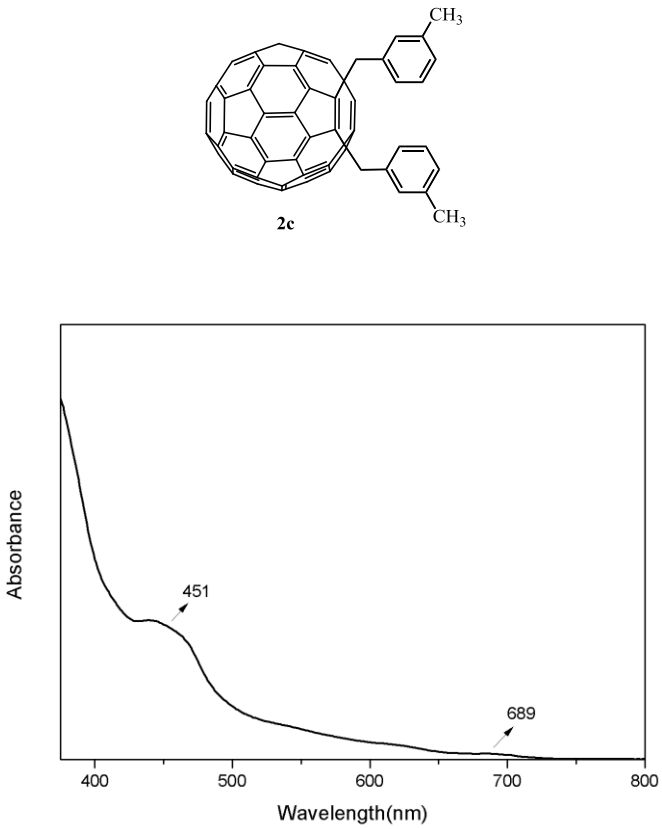
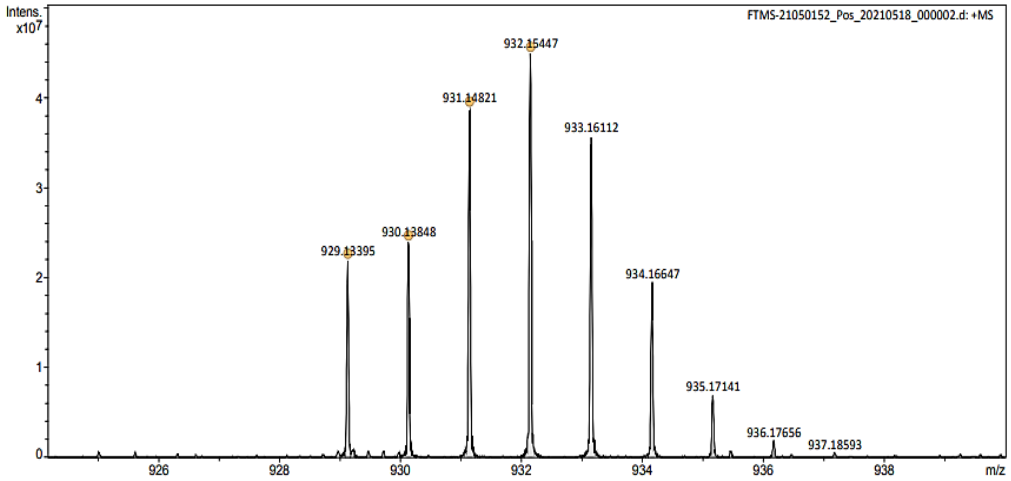


Figure S28. UV-Vis absorption spectrum of **2c** in toluene.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
929.133952	1	C76H17	100.00	929.132477	-1.6	-2.9	369.2	69.0	even	ok
930.138482	1	C76H18	41.10	930.140302	2.0	-2.0	365.7	68.5	odd	ok
931.148210	1	C76H19	100.00	931.148127	-0.1	-4.4	281.2	68.0	even	ok
932.154468	1	C76H20	47.10	932.155952	1.6	-2.3	55.1	67.5	odd	ok

Figure S29. HRMS of **2c**

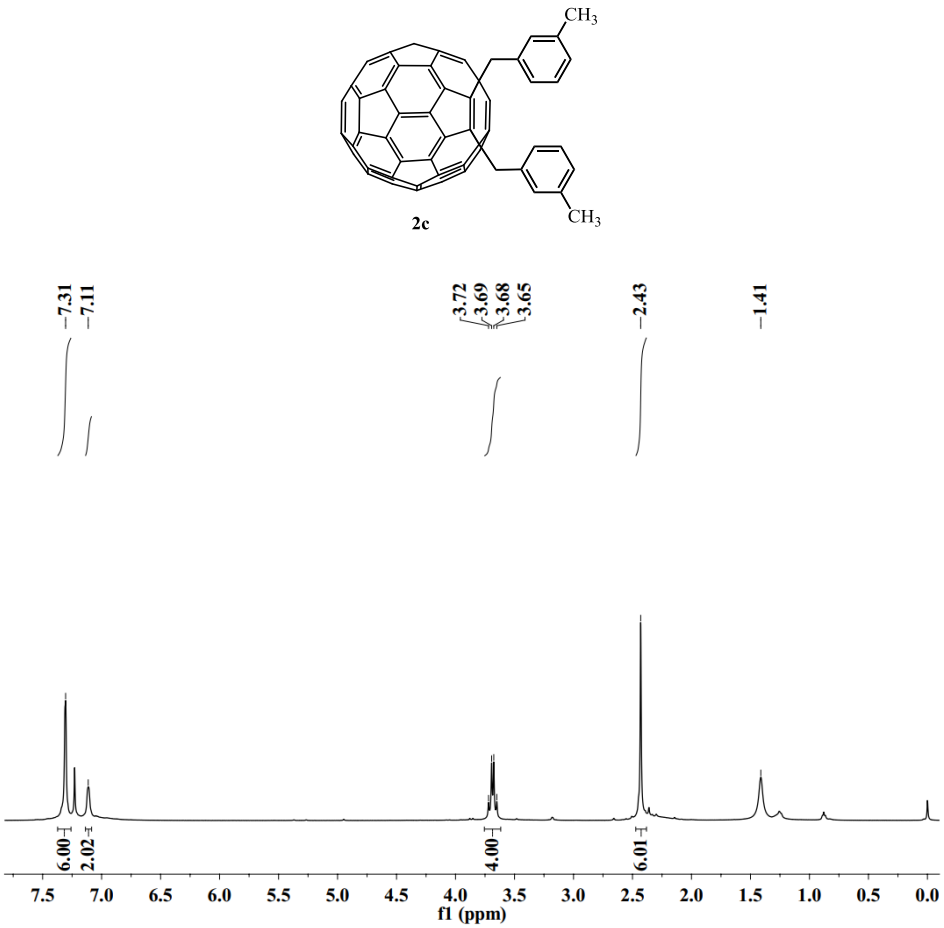


Figure S30. ^{1}H NMR spectrum of **2c** in $CDCl_3$.

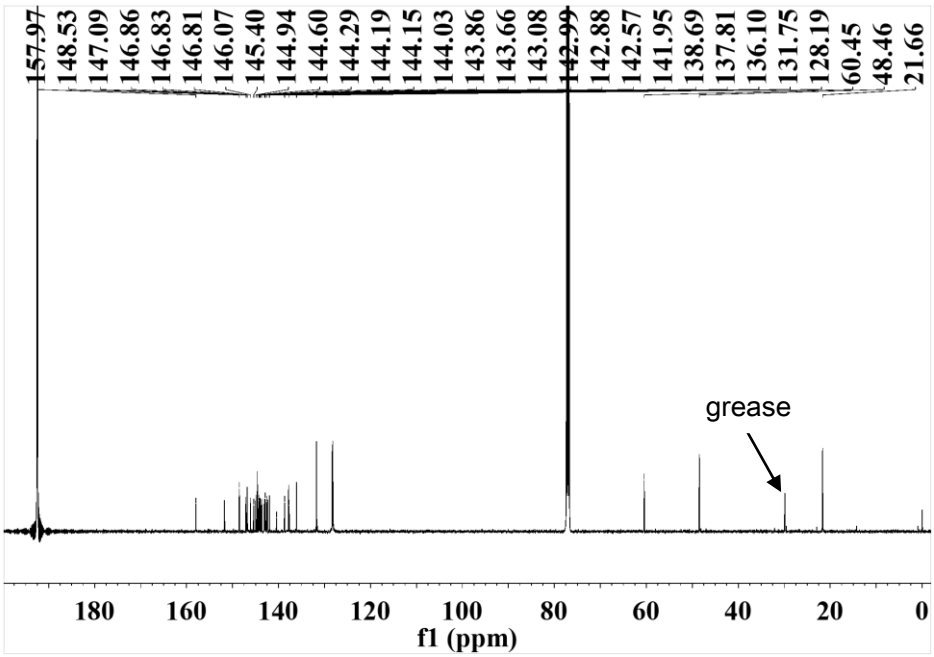
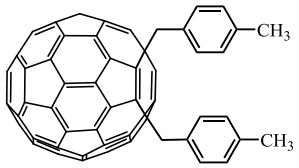


Figure S31. ^{13}C NMR spectrum of **2c** in $CS_2/CDCl_3$ = 1:1.



2d

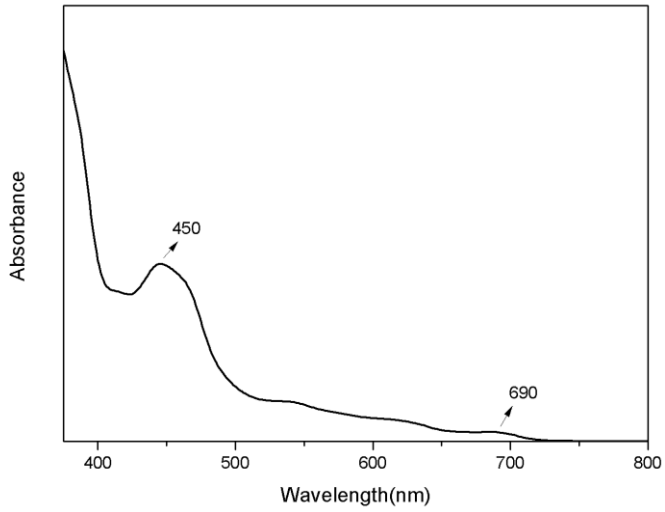
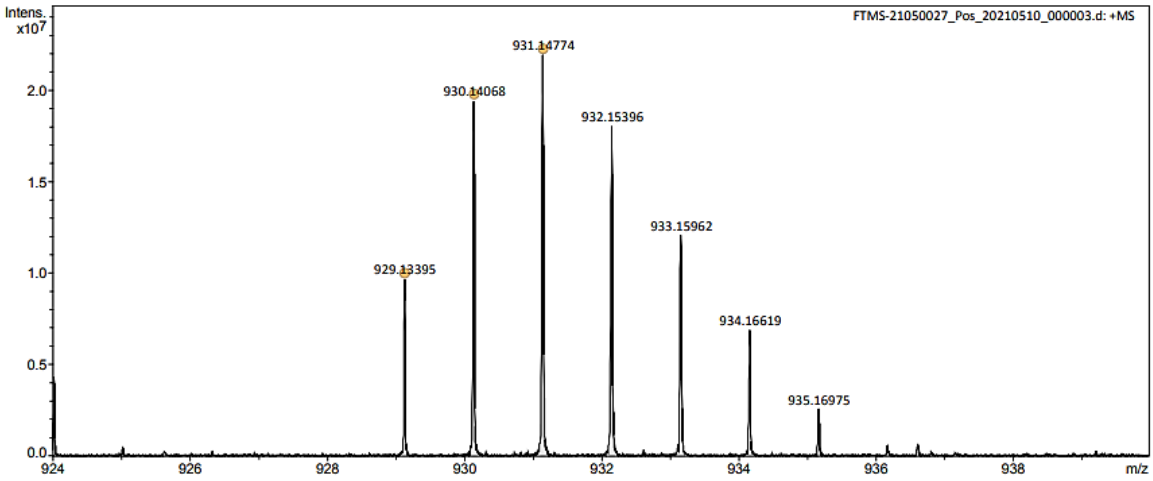


Figure S32. UV-Vis absorption spectrum of **2d** in toluene.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
929.133951	1	C76H17	100.00	929.132477	-1.6	-5.0	509.2	69.0	even	ok
930.140684	1	C76H18	100.00	930.140302	-0.4	-3.8	314.9	68.5	odd	ok
931.147737	1	C76H19	100.00	931.148127	0.4	-3.6	146.7	68.0	even	ok

Figure S33. HRMS of **2d**.

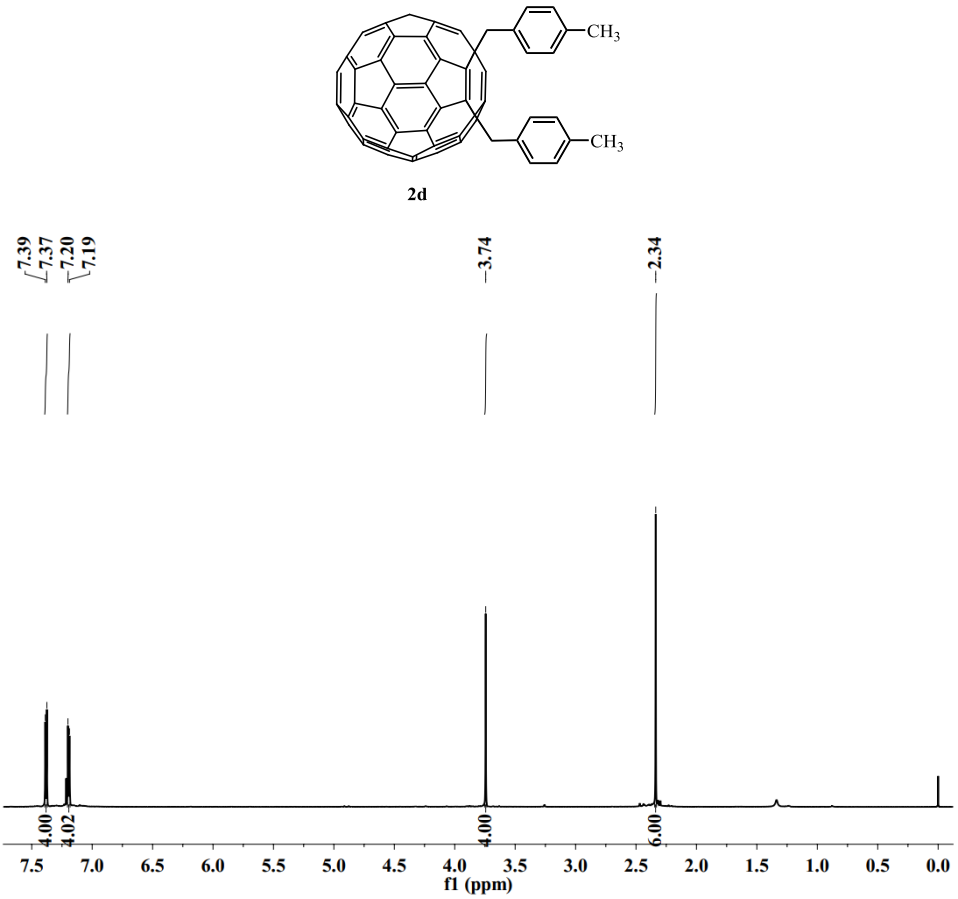


Figure S34. ^{1}H NMR spectrum of **2d** in $CS_2/CDCl_3$ = 1:1.

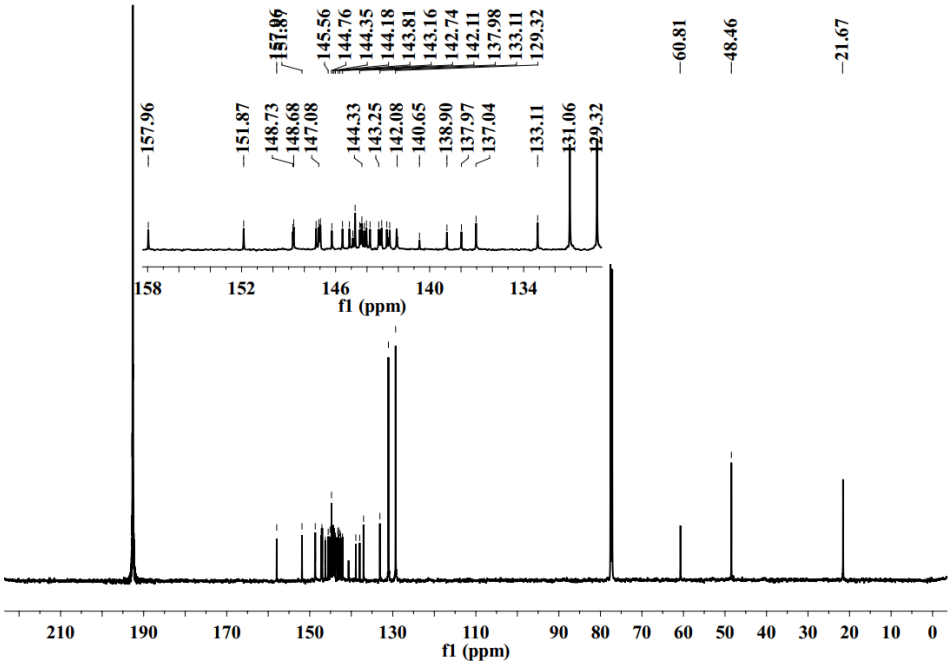
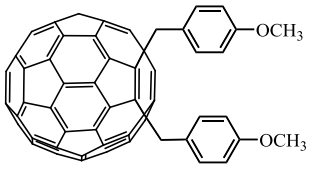


Figure S35. ^{13}C NMR spectrum of **2d** in $CS_2/CDCl_3$ = 1:1.



2e

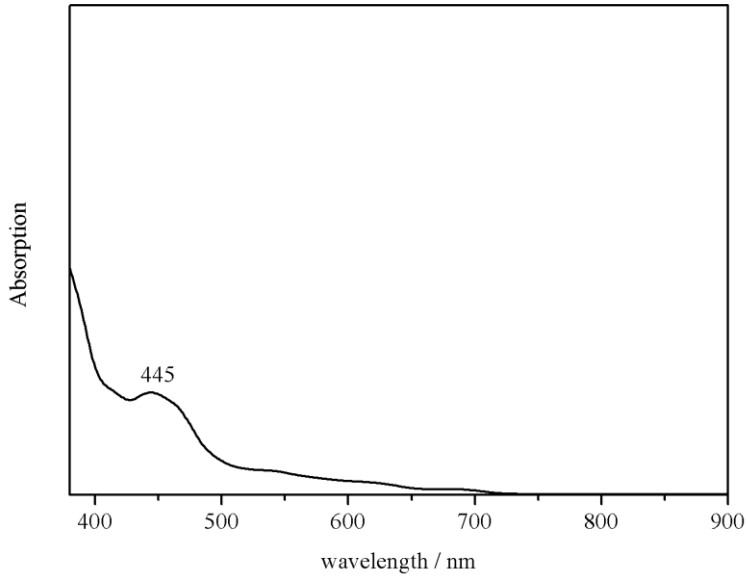
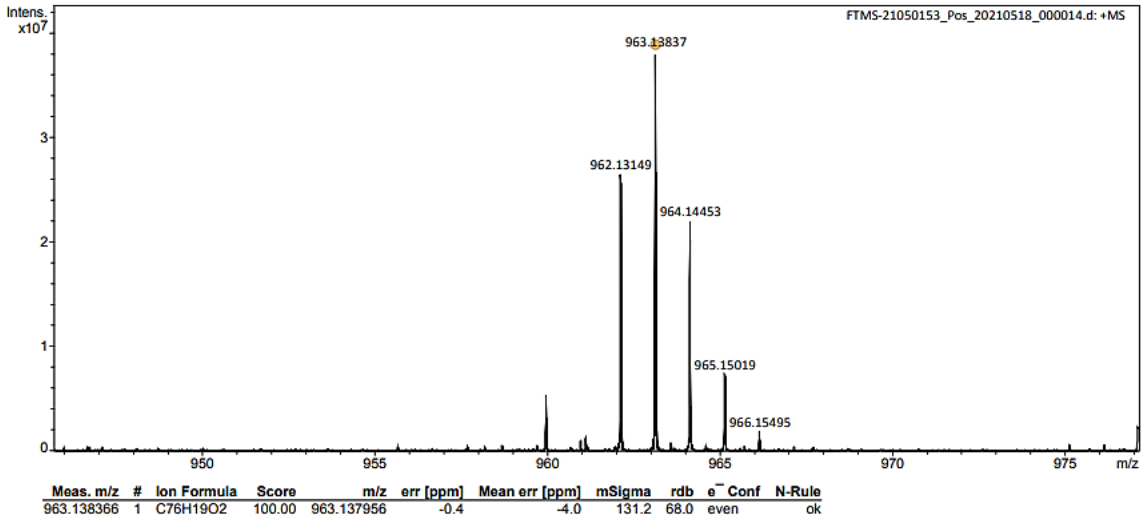
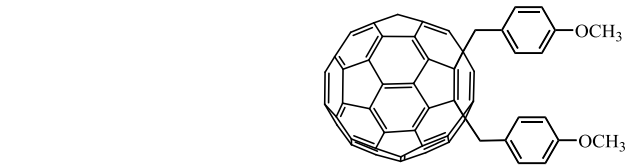


Figure S36. UV-Vis absorption spectrum of **2e** in toluene.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
963.138366	1	C76H19O2	100.00	963.137956	-0.4	-4.0	131.2	68.0	even	ok

Figure S37. HRMS of **2e**.



2e

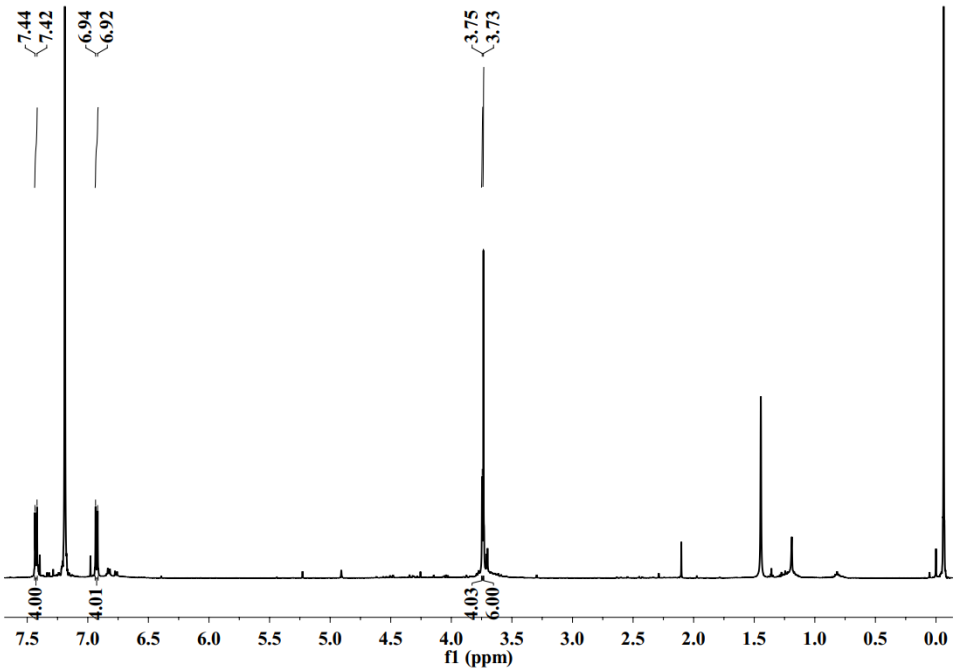


Figure S38. ^{1}H NMR spectrum of **2e** in $CS_2/CDCl_3$ = 1:1.

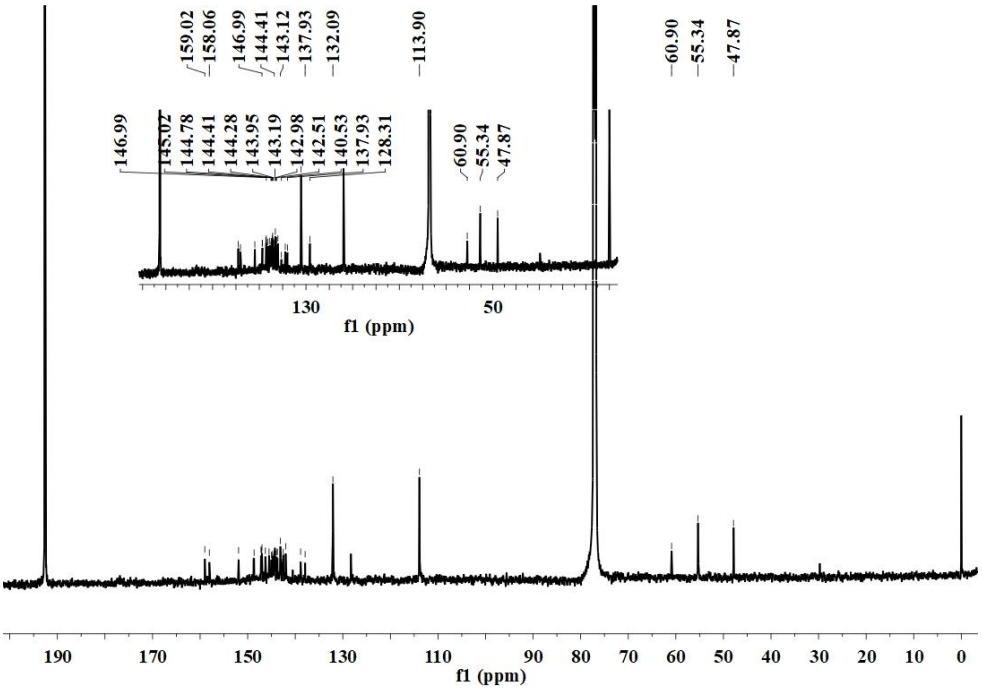
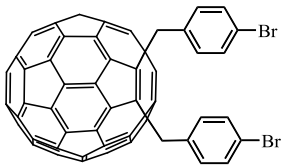


Figure S39. ^{13}C NMR spectrum of **2e** in $CS_2/CDCl_3$ = 1:1.



2f

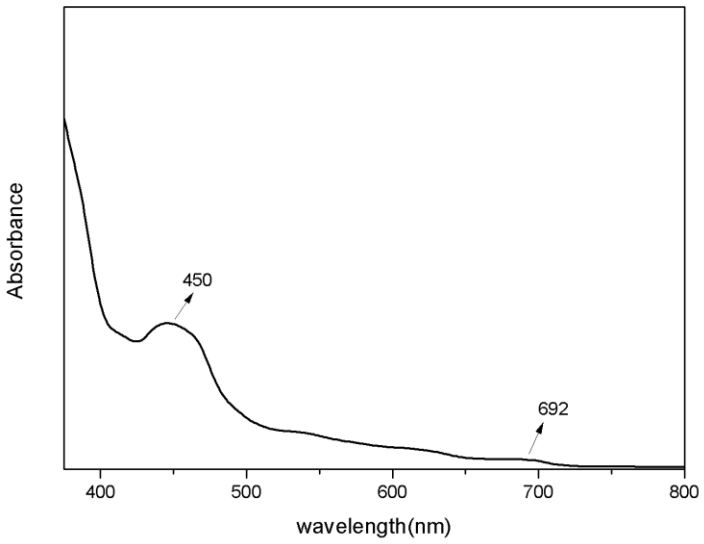


Figure S40. UV-Vis absorption spectrum of **2f** in toluene.

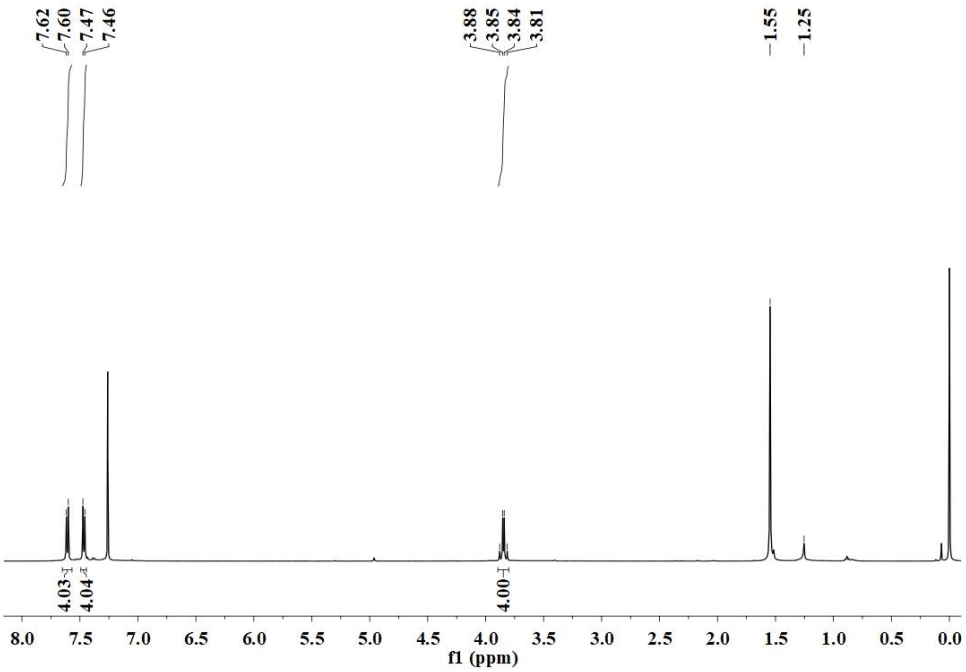
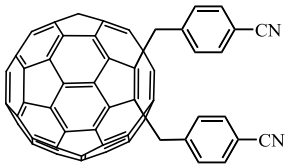


Figure S41. ^{1}H NMR spectrum of **2f** in $CDCl_3$.



2g

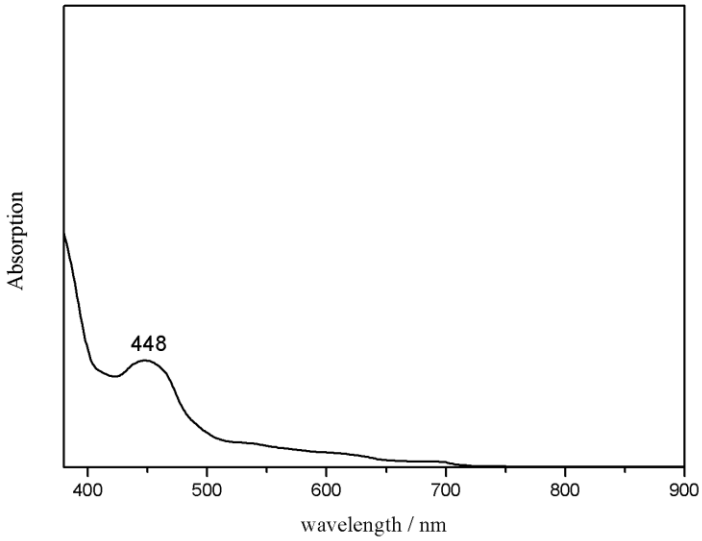
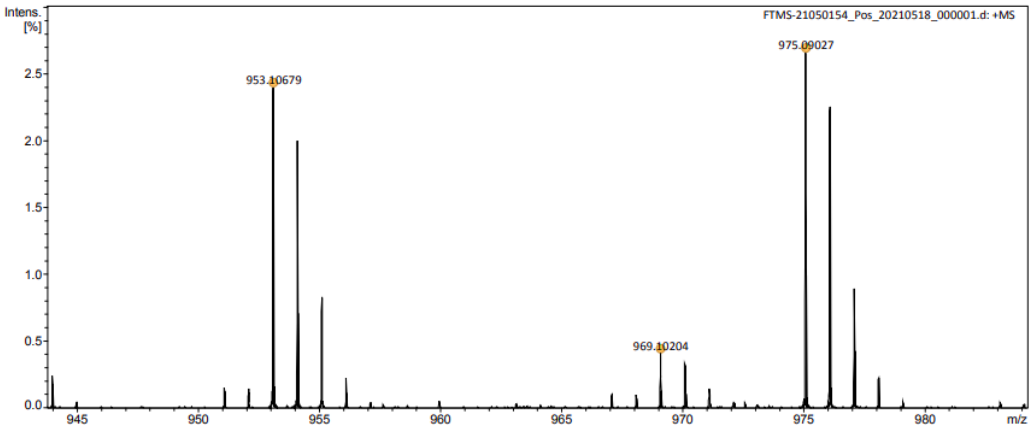


Figure S42. UV-Vis absorption spectrum of **2g** in toluene.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
953.106790	1	C76H13N2	100.00	953.107325	0.6	-0.0	4.1	72.0	even	ok
969.102045	1	C76H13N2O	100.00	969.102239	0.2	0.1	43.6	72.0	even	ok
975.090272	1	C76H12N2Na	100.00	975.089269	-1.0	-0.9	10.0	72.0	even	ok

Figure S43. HRMS of **2g**.

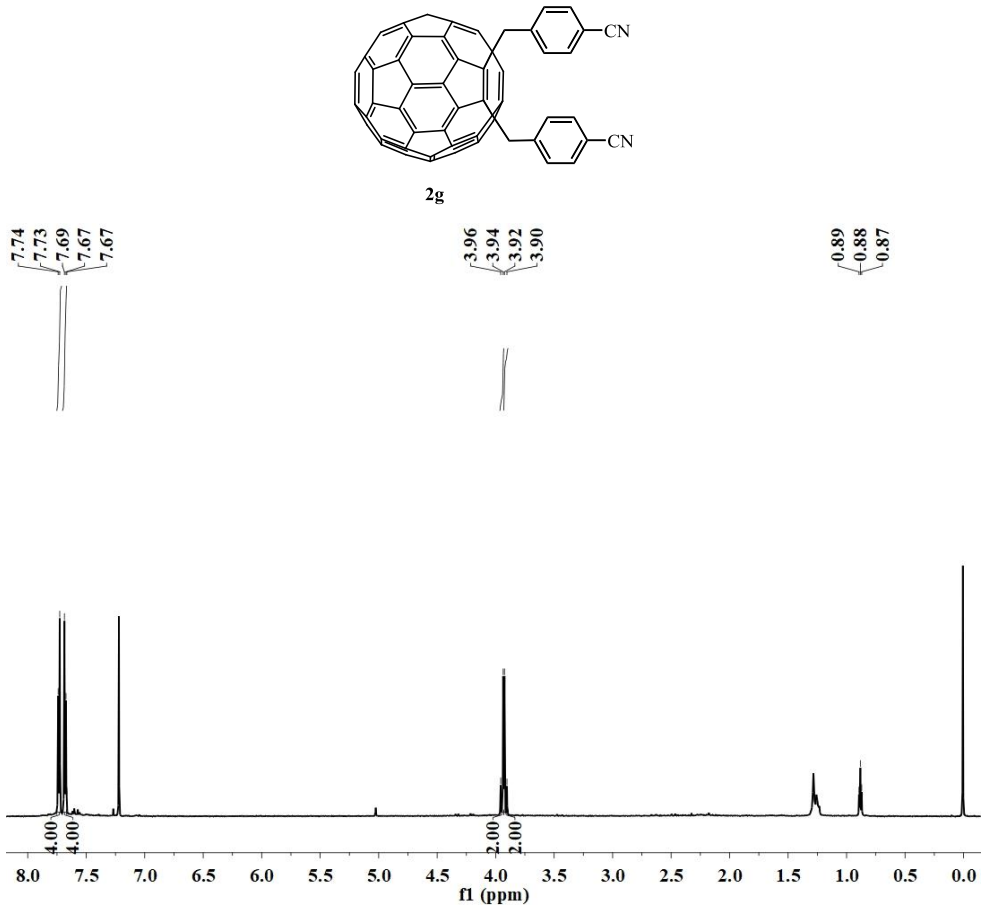


Figure S44. ^{1}H NMR spectrum of **2g** in $CS_2/CDCl_3$ = 1:1.

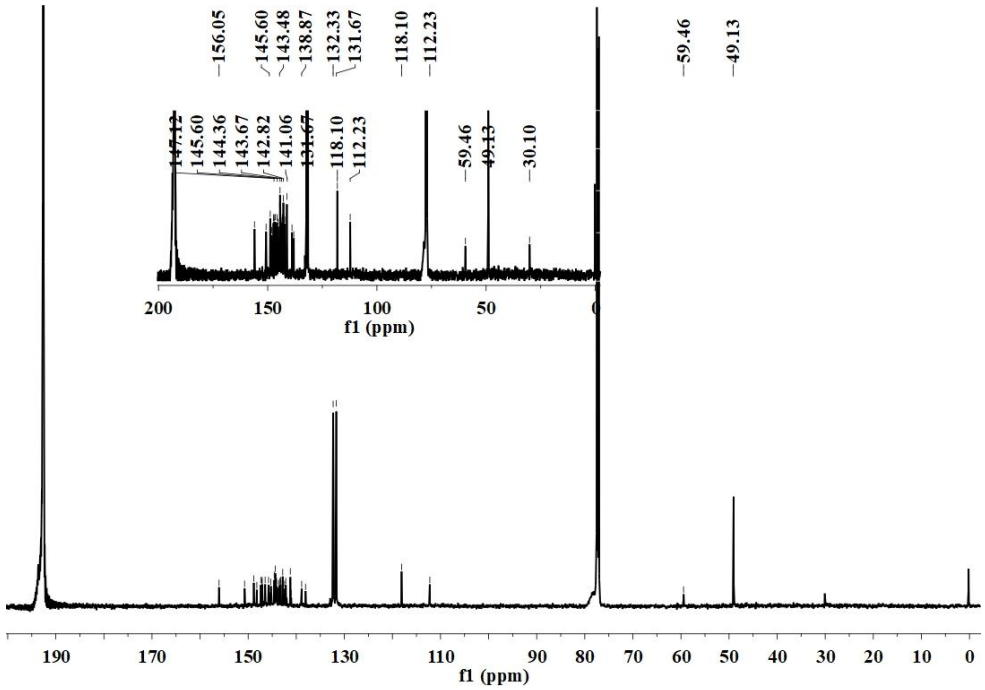
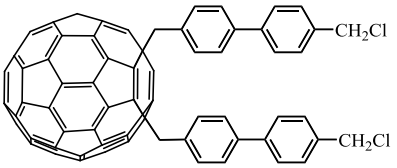


Figure S45. ^{13}C NMR spectrum of **2g** in $CS_2/CDCl_3$ = 1:1.



2h

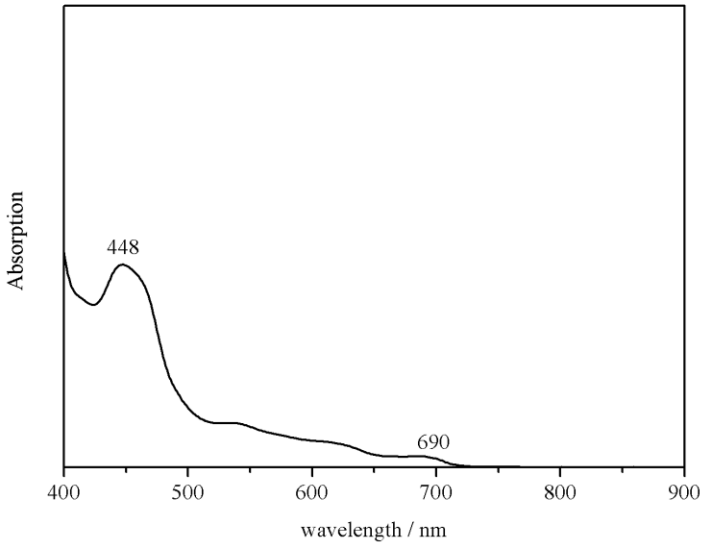


Figure S46. UV-Vis absorption spectrum of **2h** in toluene.

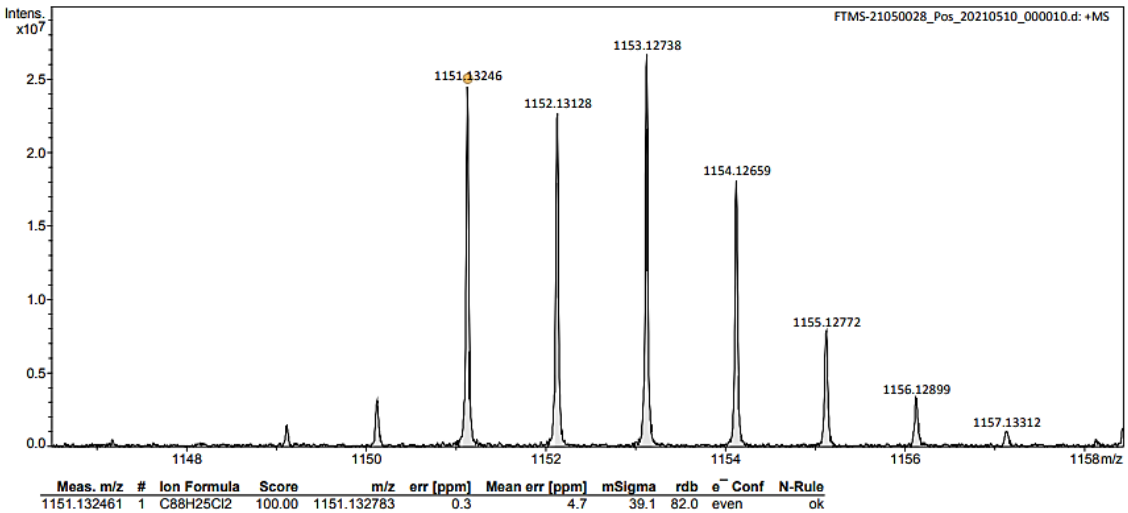


Figure S47. HRMS of **2h**.

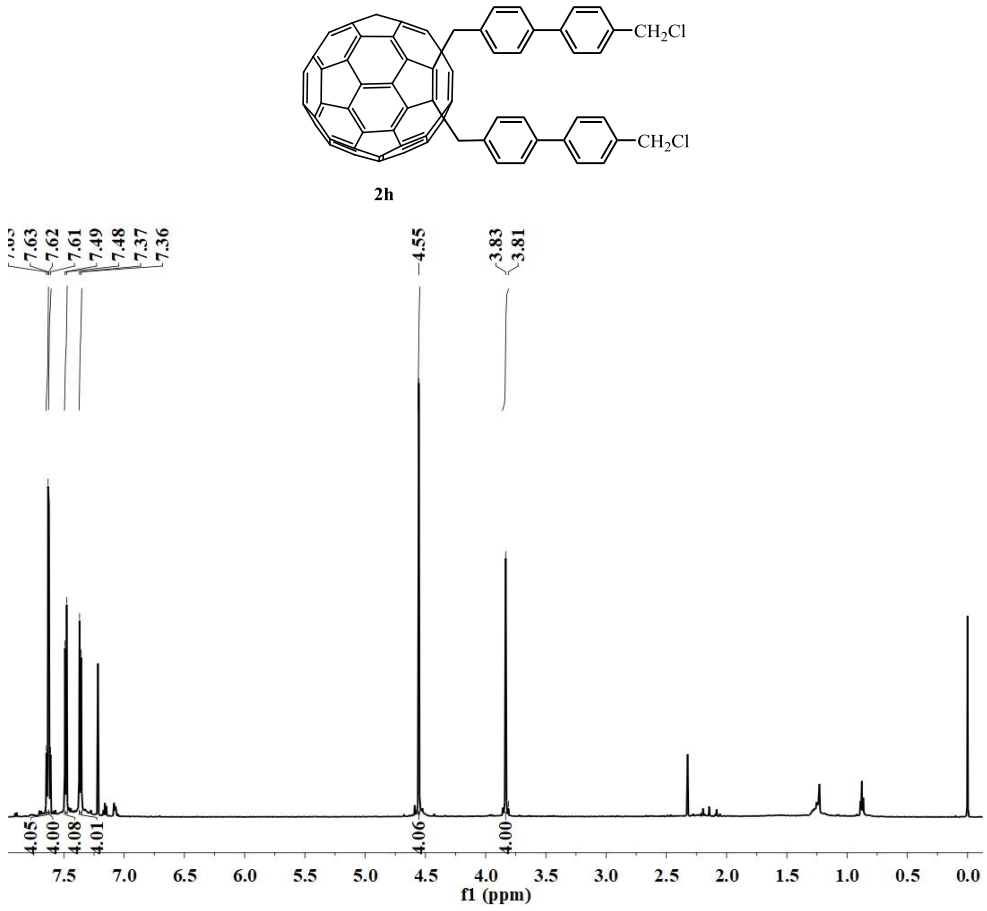


Figure S48. ^{1}H NMR spectrum of **2h** in $CS_2/CDCl_3$ = 1:1.

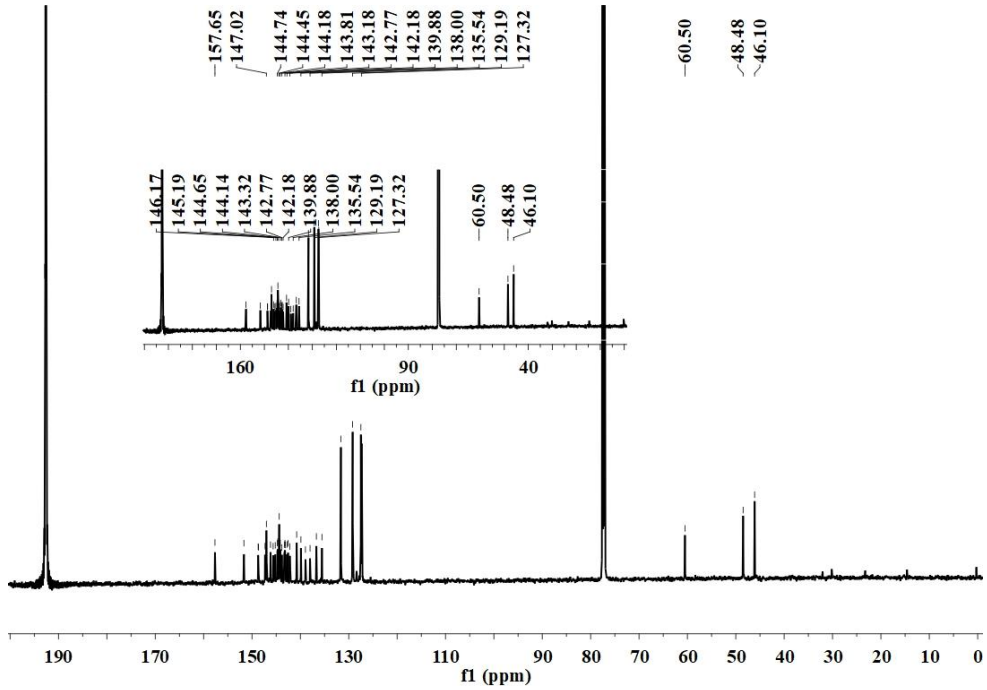


Figure S49. ^{13}C NMR spectrum of **2h** in $CS_2/CDCl_3$ = 1:1.