Supplementary Information

Fullerene Cations-mediated Demethylation/Cyclization to 5- and 7-Membered Cyclo[60]fullerene Derivatives

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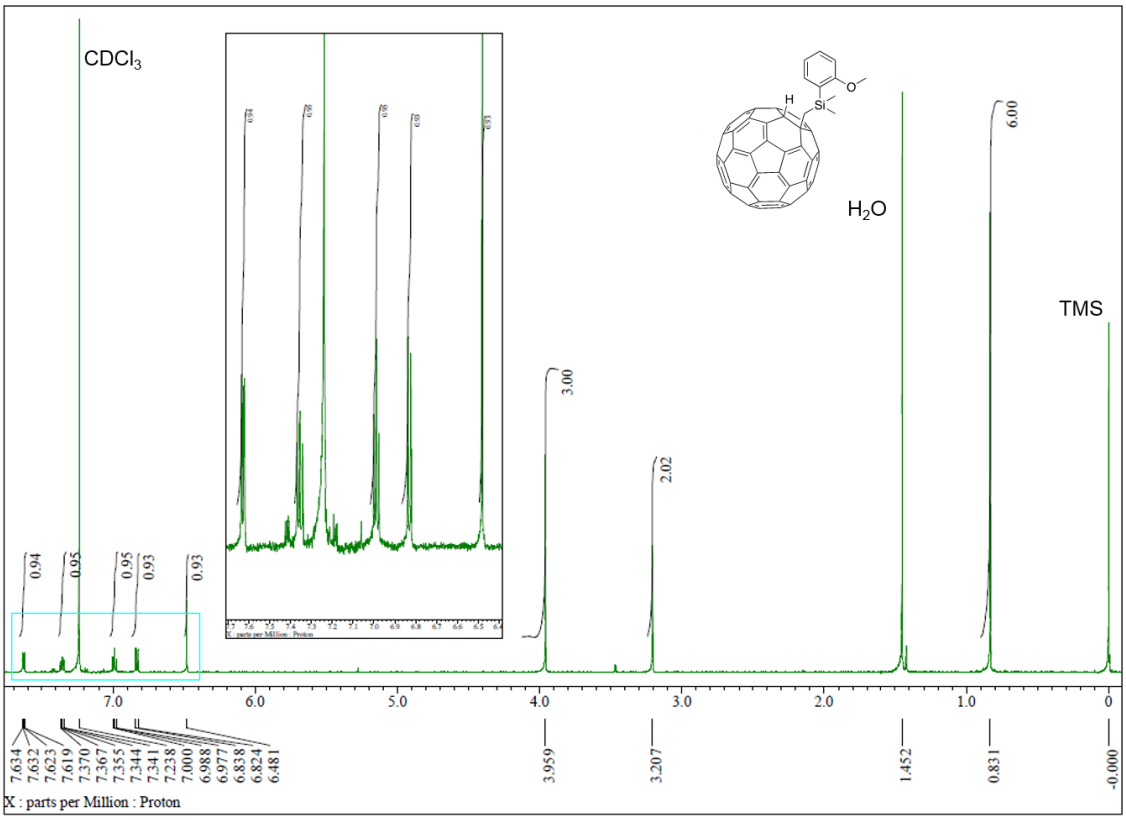

Figure S1. ^{1}H NMR spectrum for $C_{60}(CH_2SiMe_2C_6H_4\text{-}OMe\text{-}2)H$.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 0.83 (s, 6H, $SiMe_2$), 3.21 (s, 2H, CH_2), 3.96 (s, 3H, OCH_3), 6.48 (s, 1H, C_{60}-H), 6.83 (d, J = 8.4 Hz, 1H, C_6H_4), 6.99 (t, J = 7.2 Hz, 1H, C_6H_4), 7.36 (td, J = 7.5 Hz, J = 0.2 Hz, 1H, C_6H_4), 7.63 (dd, J = 7.2 Hz, J = 1.2 Hz, 1H, C_6H_4).

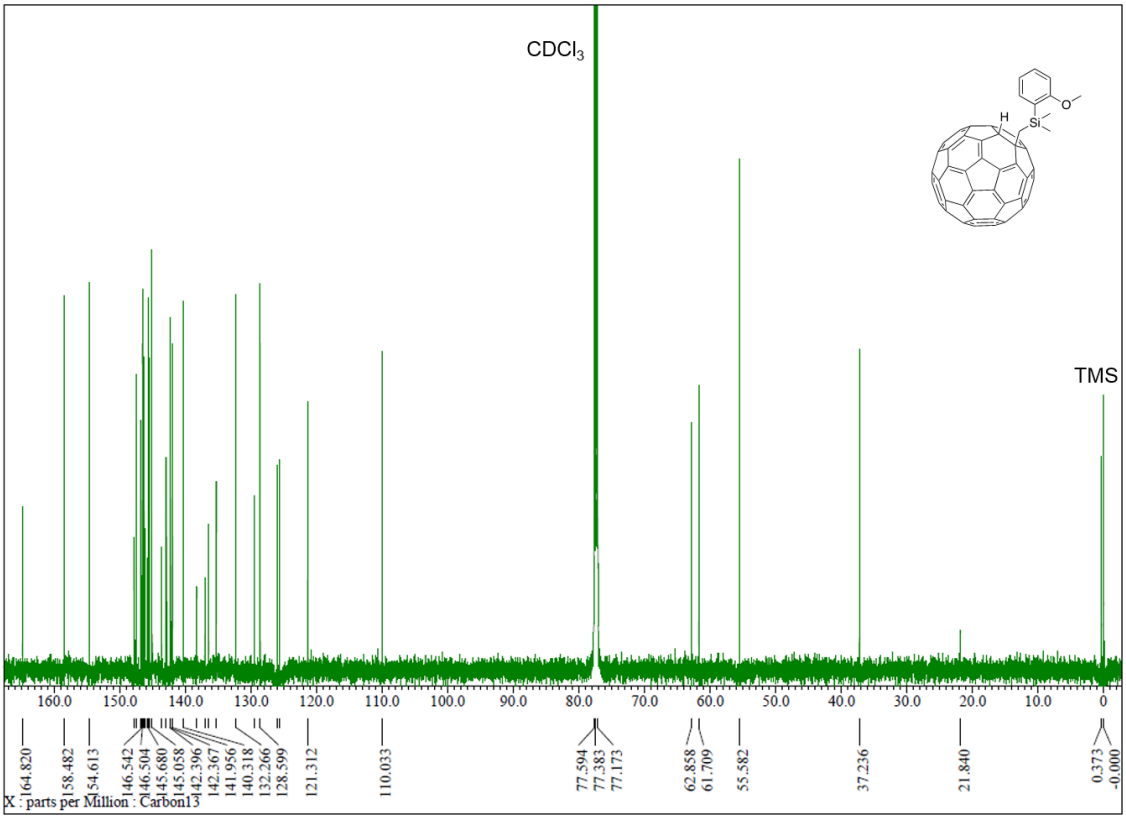

Figure S2. ^{13}C NMR spectrum for $C_{60}(CH_2SiMe_2C_6H_4\text{-}OMe\text{-}2)H$.

^{13}C NMR (150 MHz, $CDCl_3/CS_2$): δ 0.37, 21.84, 37.24, 55.58, 61.71, 62.86, 110.03, 121.31, 125.66, 125.95, 128.59, 129.40, 132.26, 135.23, 136.44, 136.99, 140.31, 140.33, 141.95, 142.23, 142.33, 142.36, 142.39, 142.87, 143.60, 145.05, 145.50, 145.67, 145.72, 146.19, 146.26, 146.49, 146.53, 146.60, 146.72, 147.37, 147.66, 147.81, 154.61, 158.48, 164.82.

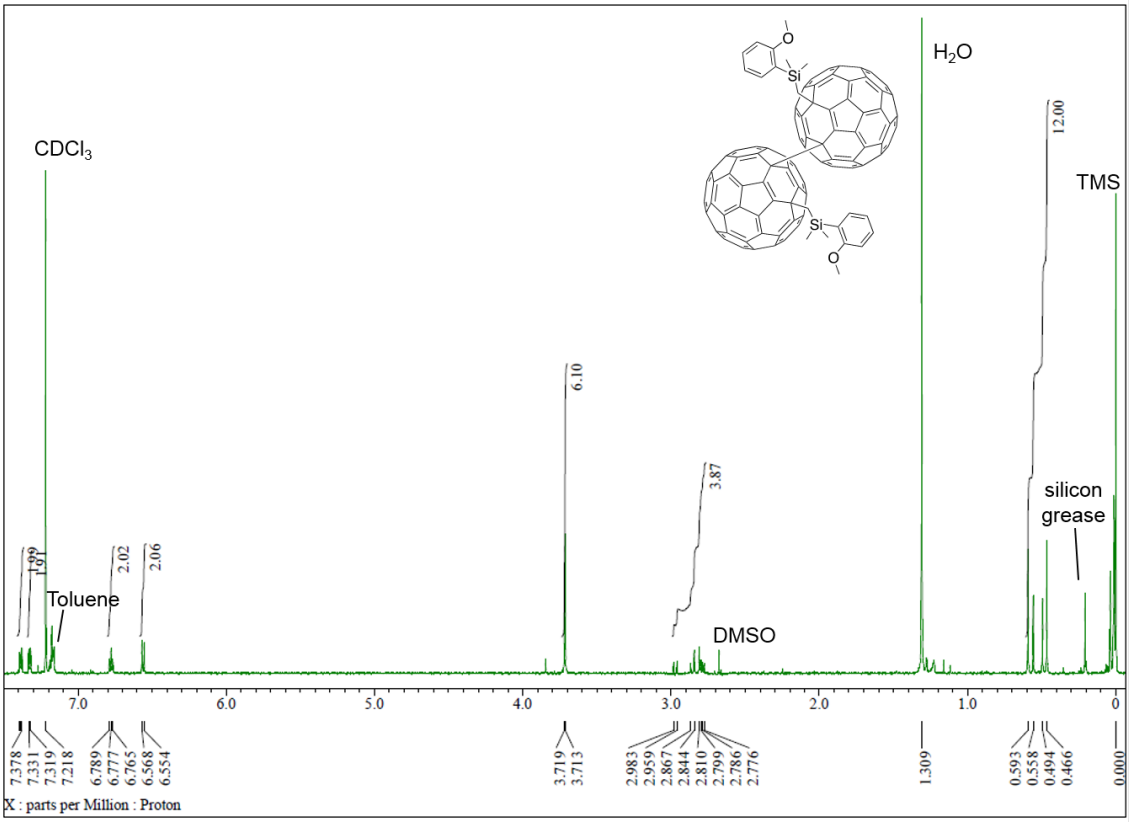

Figure S3. ^{1}H NMR spectrum for $\{C_{60}CH_2SiMe_2C_6H_4\text{-}OMe\text{-}2\}_2$

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 0.47–0.59 (m, 12H, $SiMe_2$), 2.78–2.98 (m, 4H, CH_2), 3.71–3.72 (br, 6H, OCH_3), 6.56 (d, J = 8.4 Hz, 2H, C_6H_4), 6.78 (t, J = 7.2 Hz, 2H, C_6H_4), 7.32–7.33 (m, 2H, C_6H_4), 7.38–7.39 (m, 2H, C_6H_4).

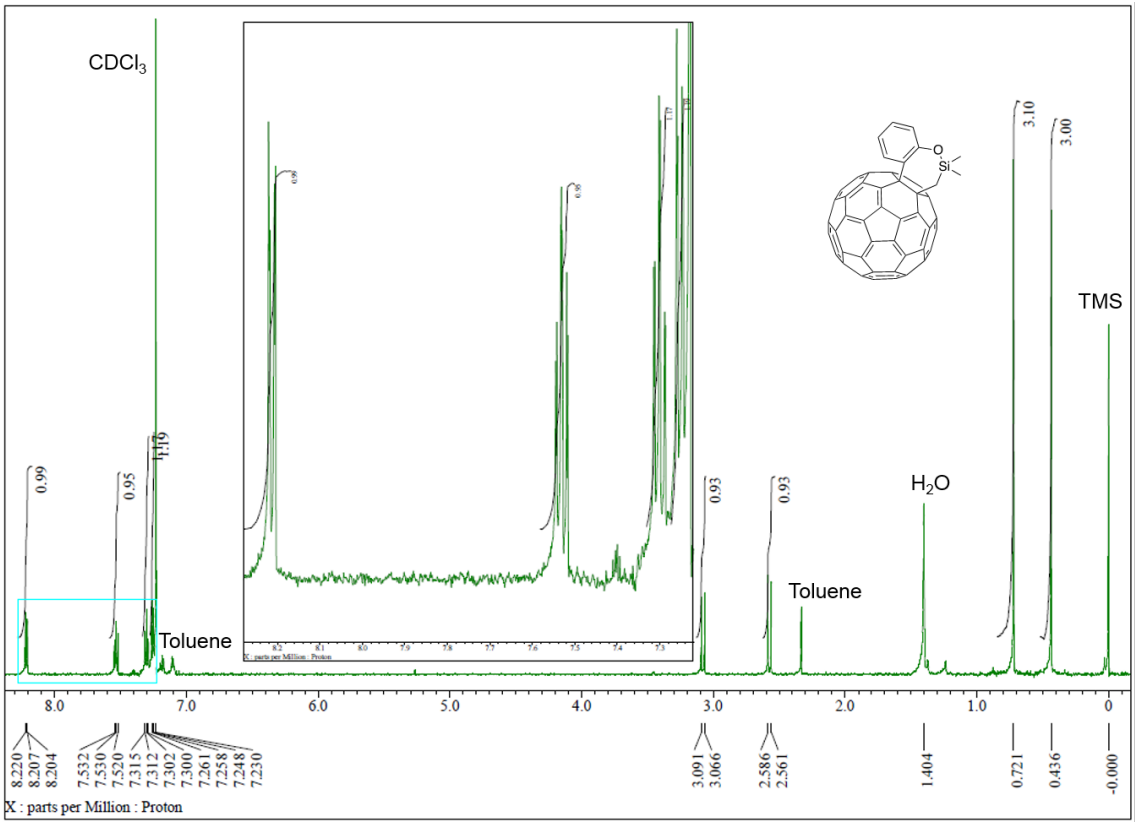

Figure S4. ^{1}H NMR spectrum for **3a**.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 0.44 (s, 3H, CH_3), 0.72 (s, 3H, CH_3), 2.57 (d, J = 15.0 Hz, 1H, CH_2), 3.08 (d, J = 15.0 Hz, 1H, CH_2), 7.25 (dd, J = 7.8 Hz, J = 1.8 Hz, 1H, C_6H_4), 7.30 (td, J = 7.5 Hz, J = 1.8 Hz, 1H, C_6H_4), 7.53 (td, J = 7.5 Hz, J = 1.8 Hz, 1H, C_6H_4), 8.21 (dd, J = 7.8 Hz, J = 1.8 Hz, 1H, C_6H_4).

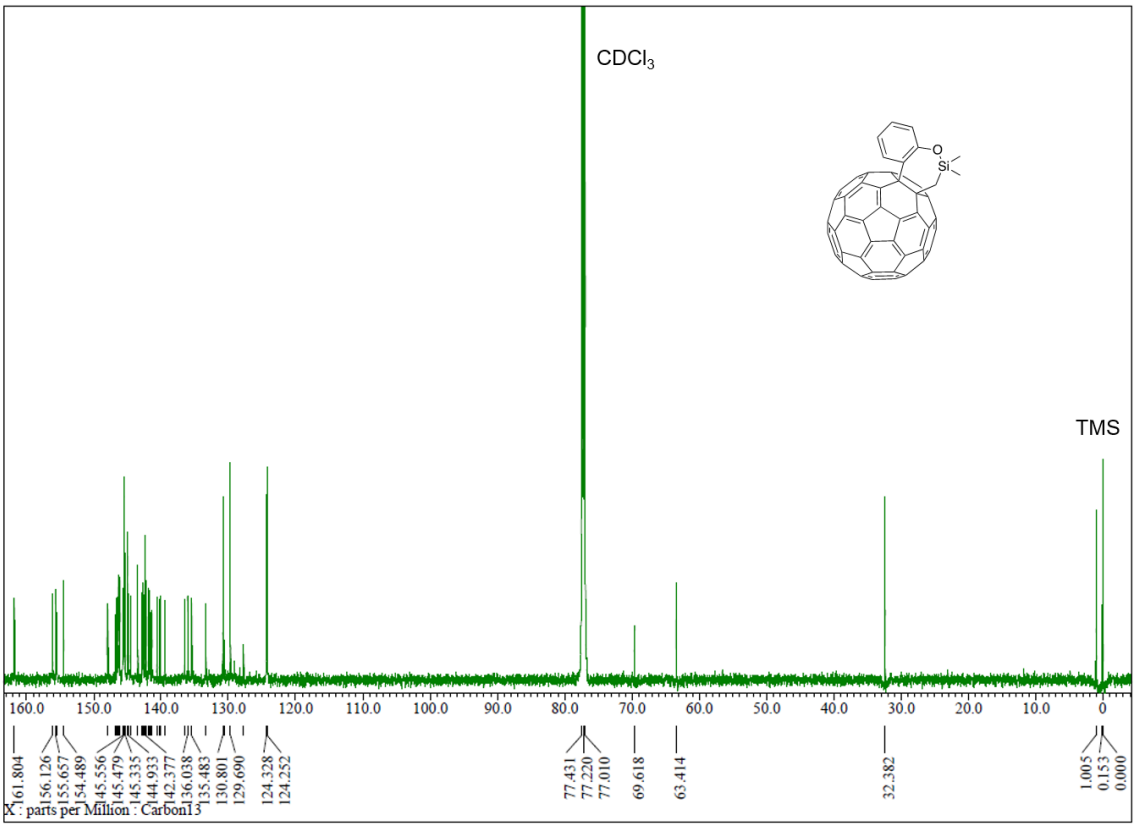

Figure S5. ^{13}C NMR spectrum for **3a**.

^{13}C NMR (150 MHz, $CDCl_3/CS_2$): δ 0.15, 1.01, 32.38, 63.41, 69.62, 124.25, 124.33, 127.72, 129.11, 129.69, 130.59, 130.80, 133.32, 135.43, 135.48, 136.04, 136.51, 139.42, 140.14, 140.24, 140.59, 141.35, 141.48, 141.69, 141.77, 141.88, 141.90, 142.21, 142.23, 142.26, 142.38, 142.51, 142.67, 142.70, 142.77, 142.80, 143.43 (two peaks, overlapped), 144.55 (two peaks, overlapped), 144.85, 144.93, 144.97 (two peaks, overlapped), 145.34 (two peaks, overlapped), 145.48 (two peaks, overlapped), 145.56, 145.60, 145.68, 146.10, 146.12, 146.27, 146.31 (two peaks, overlapped), 146.34, 146.37, 146.44, 146.50, 146.59, 146.72, 147.88, 147.99, 154.49, 155.53, 155.66, 156.13, 161.80.

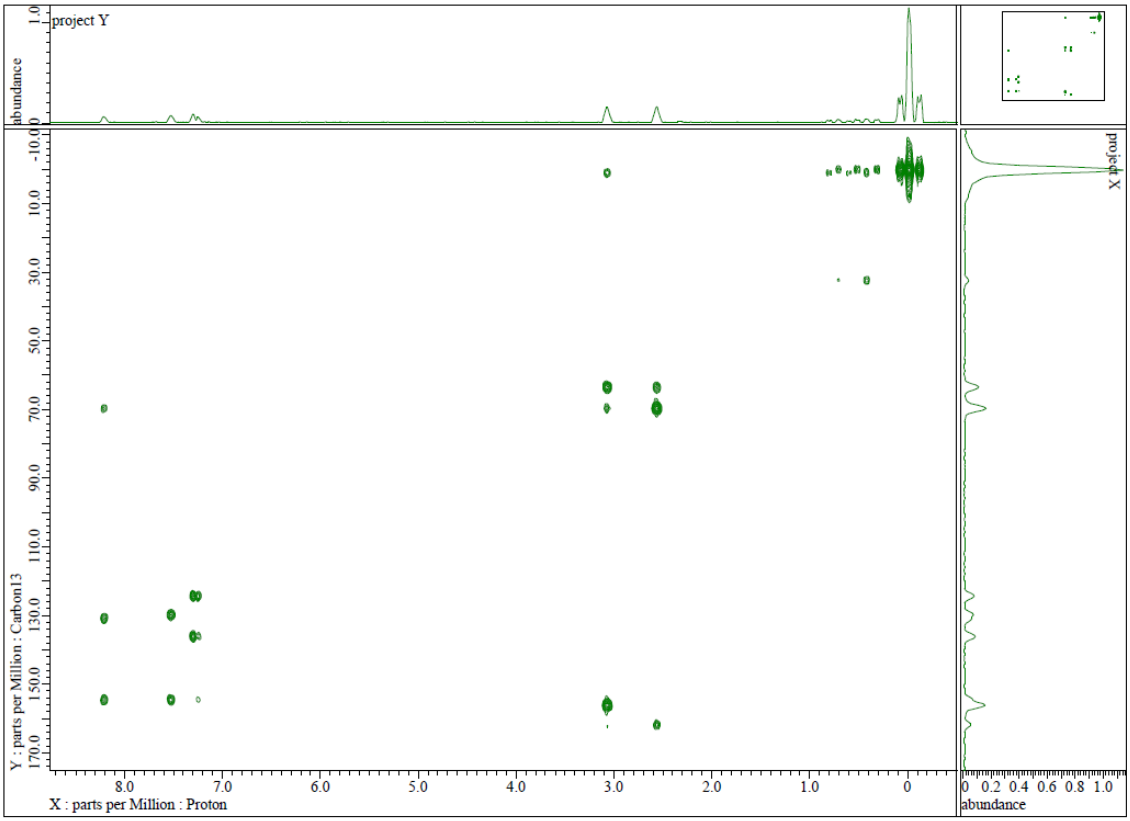

Figure S6. HMBC NMR spectrum for **3a**.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$)^{13}C NMR (150 MHz, $CDCl_3/CS_2$)

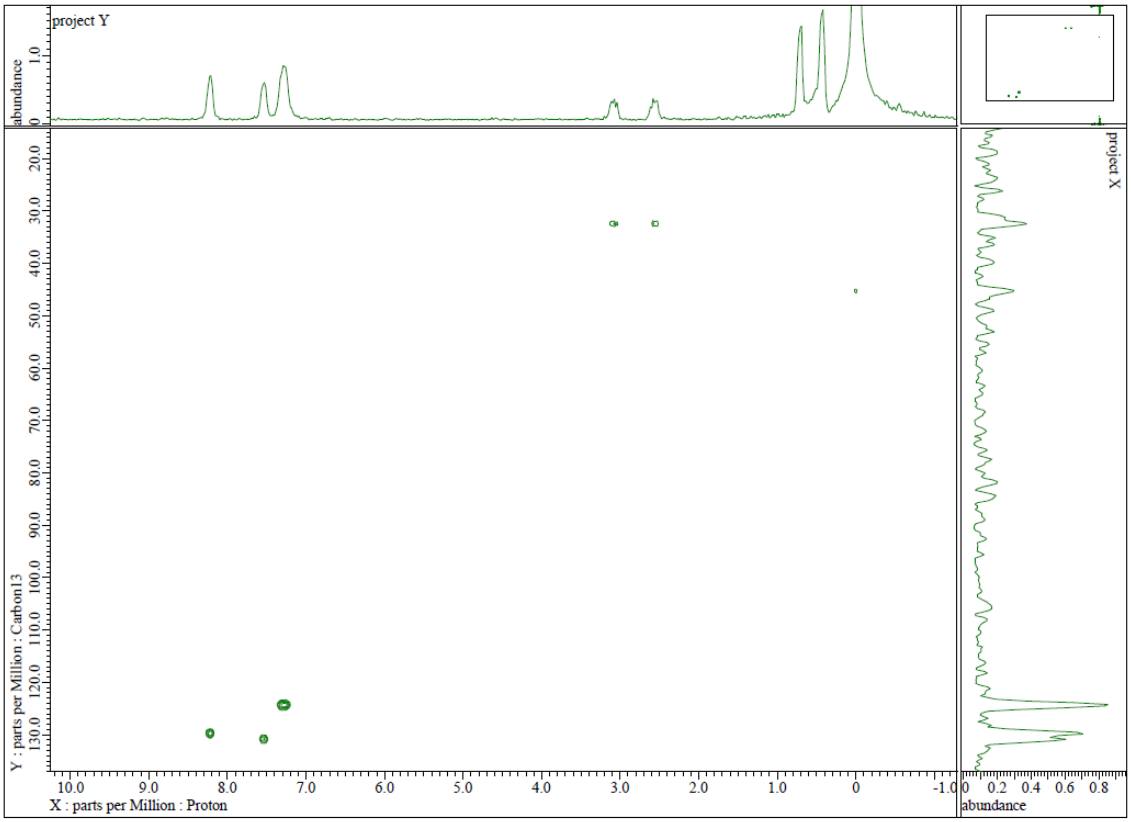

Figure S7. HMQC NMR spectrum for **3**a.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$)^{13}C NMR (150 MHz, $CDCl_3/CS_2$)

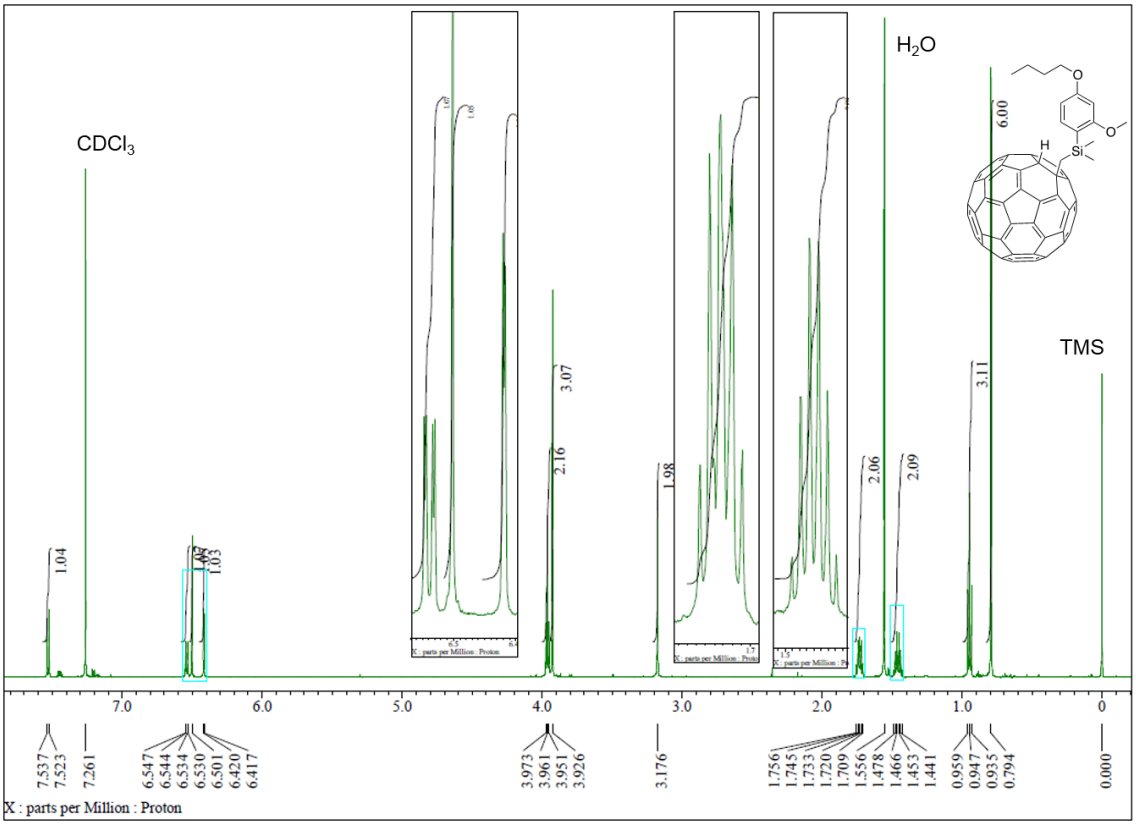

Figure S8. ^{1}H NMR spectrum for $C_{60}(CH_2SiMe_2C_6H_3\text{-}OMe\text{-}2\text{-}OBu\text{-}4)H$.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 0.79 (s, 6H, $SiMe_2$), 0.95 (t, J = 7.2 Hz, 3H, $OCH_2CH_2CH_2CH_3$), 1.46 (sext, J = 7.2 Hz, 2H, $OCH_2CH_2CH_2CH_3$), 1.73 (quin, J = 6.6 Hz, 2H, $OCH_2CH_2CH_2CH_3$), 3.18 (s, 2H, CH_2), 3.93 (s, 3H, OCH_3), 3.96 (t, J = 7.2 Hz, 2H, $OCH_2CH_2CH_2CH_3$), 6.42 (d, J = 1.8 Hz, 1H, C_6H_3), 6.50 (s, 1H, C_{60}-H), 6.54 (dd, J = 8.1 Hz, J = 1.8 Hz, 1H, C_6H_3), 7.53 (d, J = 8.4 Hz, 1H, C_6H_3).

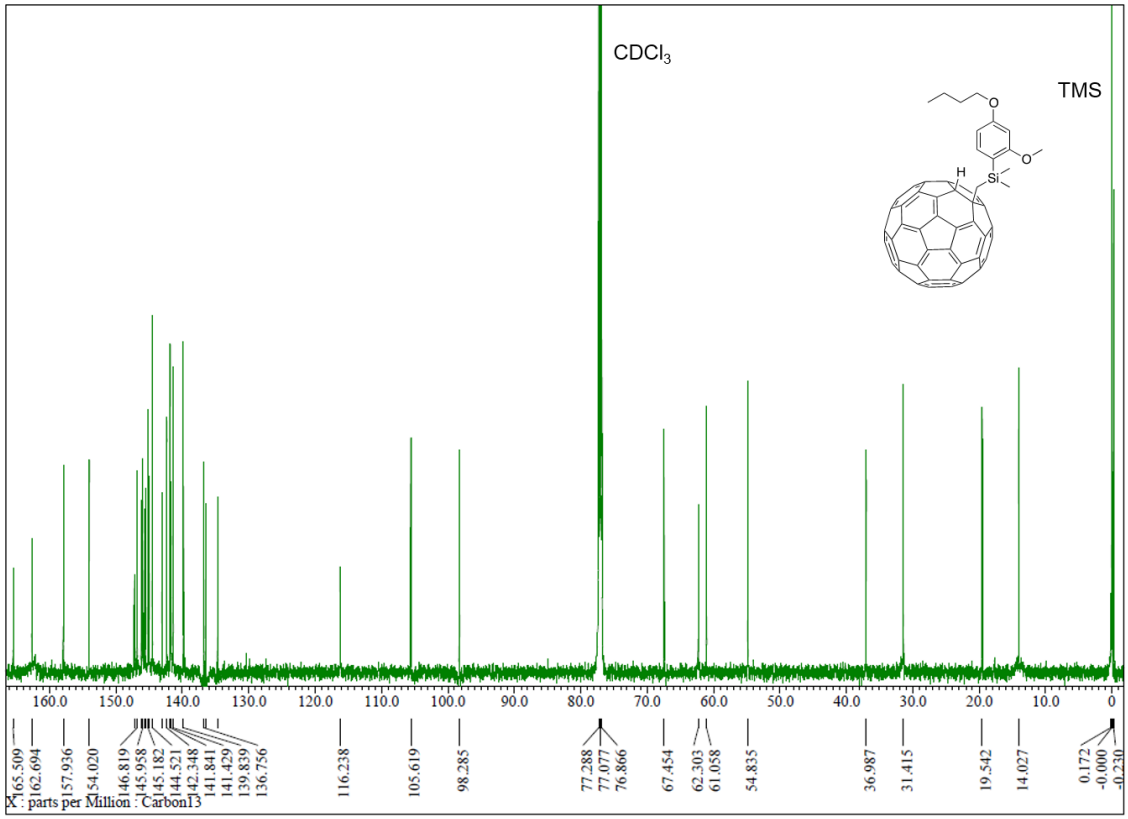

Figure S9. ^{13}C NMR spectrum for $C_{60}(CH_2SiMe_2C_6H_3\text{-}OMe\text{-}2\text{-}OBu\text{-}4)H$..

^{13}C NMR (150 MHz, $CDCl_3/CS_2$): δ -0.23, 14.03, 19.54, 31.42, 36.99, 54.84, 61.06, 62.30, 67.45, 98.29, 105.62, 116.24, 134.69, 136.49, 136.76, 139.84 (two peaks, overlapped), 141.43 (two peaks, overlapped), 141.72, 141.81, 141.84 (two peaks, overlapped), 142.35 (two peaks, overlapped), 143.10, 144.52 (two peaks, overlapped), 145.00, 145.12, 145.19 (two peaks, overlapped), 145.58, 145.70, 145.96, 146.00, 146.07, 146.20, 146.82, 147.10, 147.23, 154.02, 157.94, 162.69, 165.51.

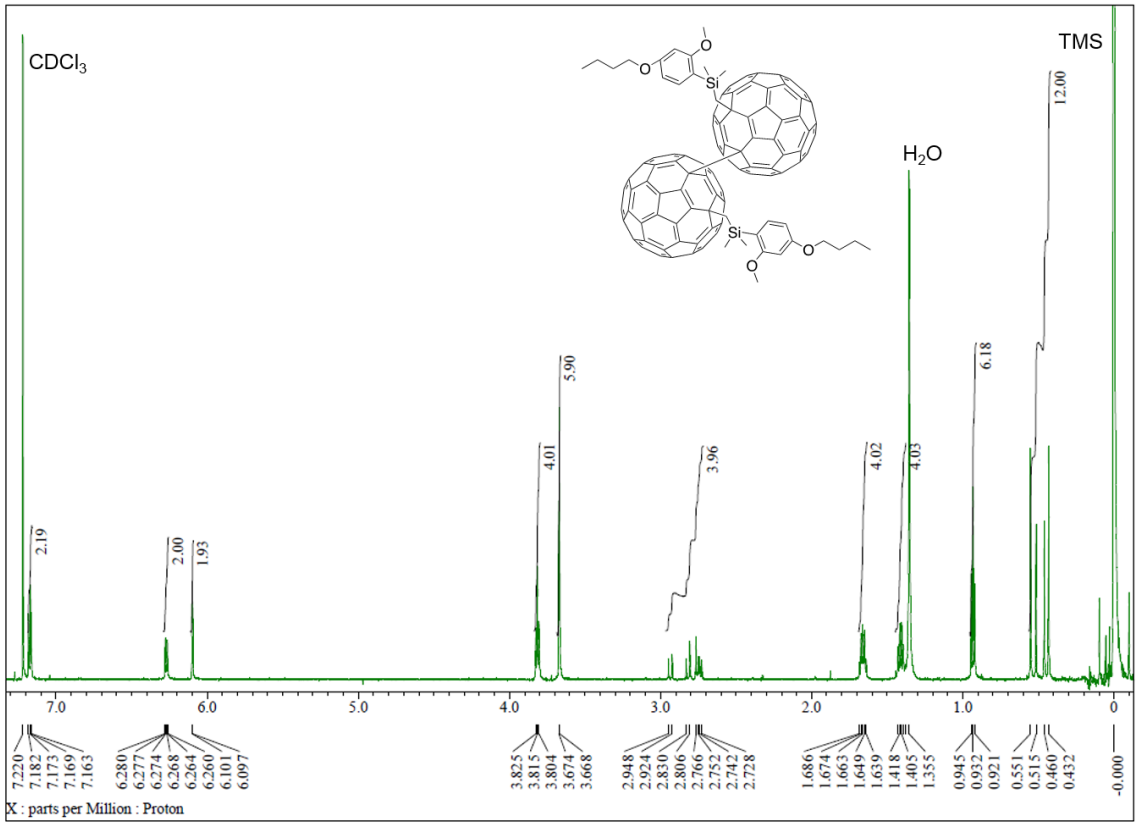

Figure S10. ^{1}H NMR spectrum for $\{C_{60}CH_2SiMe_2C_6H_3\text{-}OMe\text{-}2\text{-}OBu\text{-}4\}_2$.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 0.43–0.55 (m, 12H, $SiMe_2$), 0.93 (t, J = 7.8 Hz, 6 H, $OCH_2CH_2CH_2CH_3$), 1.44 (sext, J = 7.2 Hz, 4H, $OCH_2CH_2CH_2CH_3$), 1.66 (quin, J = 7.2 Hz, 4H, $OCH_2CH_2CH_2CH_3$), 2.74–2.95 (m, 4H, CH_2), 3.67 (d, J = 3.6 Hz, 6H, OCH_3), 3.82 (t, J = 6.6 Hz, 4H, $OCH_2CH_2CH_2CH_3$), 6.10 (d, J = 2.4 Hz, 2H, C_6H_3), 6.27 (td, J = 7.8 Hz, J = 1.8 Hz, 2H, C_6H_3), 7.16–7.18 (m, 2H, C_6H_3).

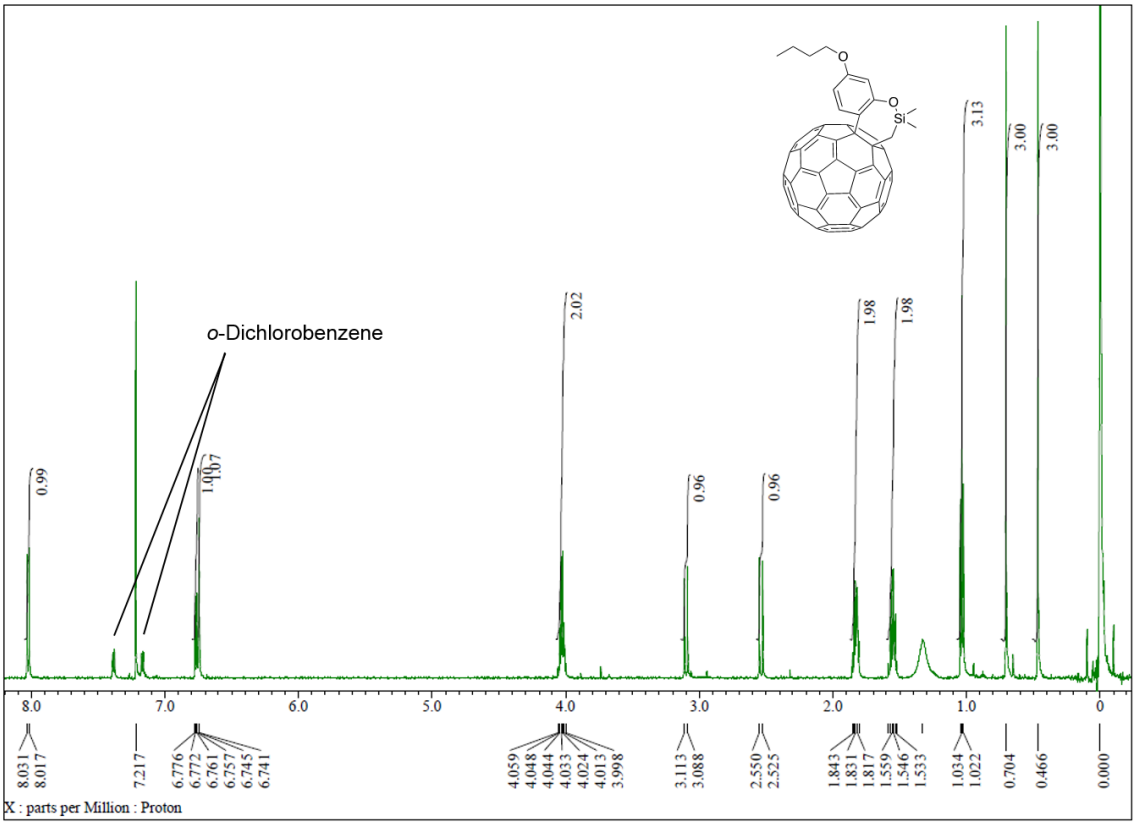

Figure S11. ^{1}H NMR spectrum for **3b**.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 0.47 (s, 3H, CH_3), 0.70 (s, 3H, CH_3), 1.03 (t, J = 7.8 Hz, 3H, $OCH_2CH_2CH_2CH_3$), 1.55 (sext, J = 7.8 Hz, 2H, $OCH_2CH_2CH_2CH_3$), 1.83 (quin, J = 6.6 Hz, 2H, $OCH_2CH_2CH_2CH_3$), 2.54 (d, J = 15.0 Hz, 1H, CH_2), 3.10 (d, J = 15.0 Hz, 1H, CH_2), 4.00–4.06 (m, 2H, $OCH_2CH_2CH_2CH_3$), 6.74 (d, J = 2.4 Hz, 1H, C_6H_3), 6.77 (dd, J = 9.0 Hz, J = 2.4 Hz, 1H, C_6H_3), 8.02 (d, J = 8.4 Hz, 1H, C_6H_3).

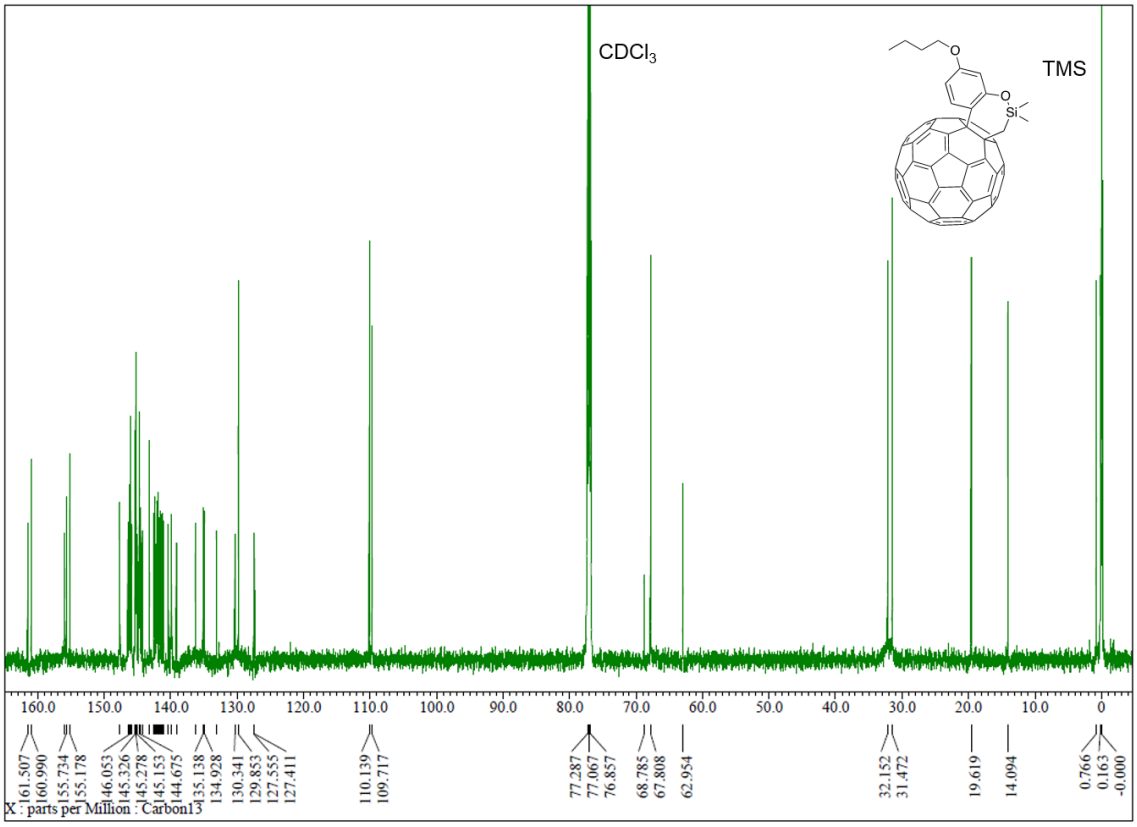

Figure S12. ^{13}C NMR spectrum for **3b**.

^{13}C NMR (150 MHz, $CDCl_3/CS_2$): δ 0.16, 0.77, 14.09, 19.62, 31.47, 32.15, 62.95, 67.81, 68.80, 109.73, 110.14, 127.41, 127.56, 129.85, 130.34, 133.13, 134.93, 135.14, 136.29, 139.17, 139.87, 139.95, 140.32, 141.07, 141.22, 141.44, 141.48, 141.65, 141.68, 141.95, 141.98, 142.02, 142.11, 142.16, 142.26 (two peaks, overlapped), 142.40, 142.43, 142.50, 142.55, 143.17 (two peaks, overlapped), 144.32, 144.52, 144.68, 142.71, 142.77, 145.11, 145.15, 145.19, 145.21, 145.28, 145.33, 145.41, 145.84, 145.88, 146.02, 146.05 (two peaks, overlapped), 146.11, 146.16, 146.25, 146.32, 146.47 (two peaks, overlapped), 147.63, 147.72, 155.18, 155.69, 155.73, 156.07, 160.99, 161.51.

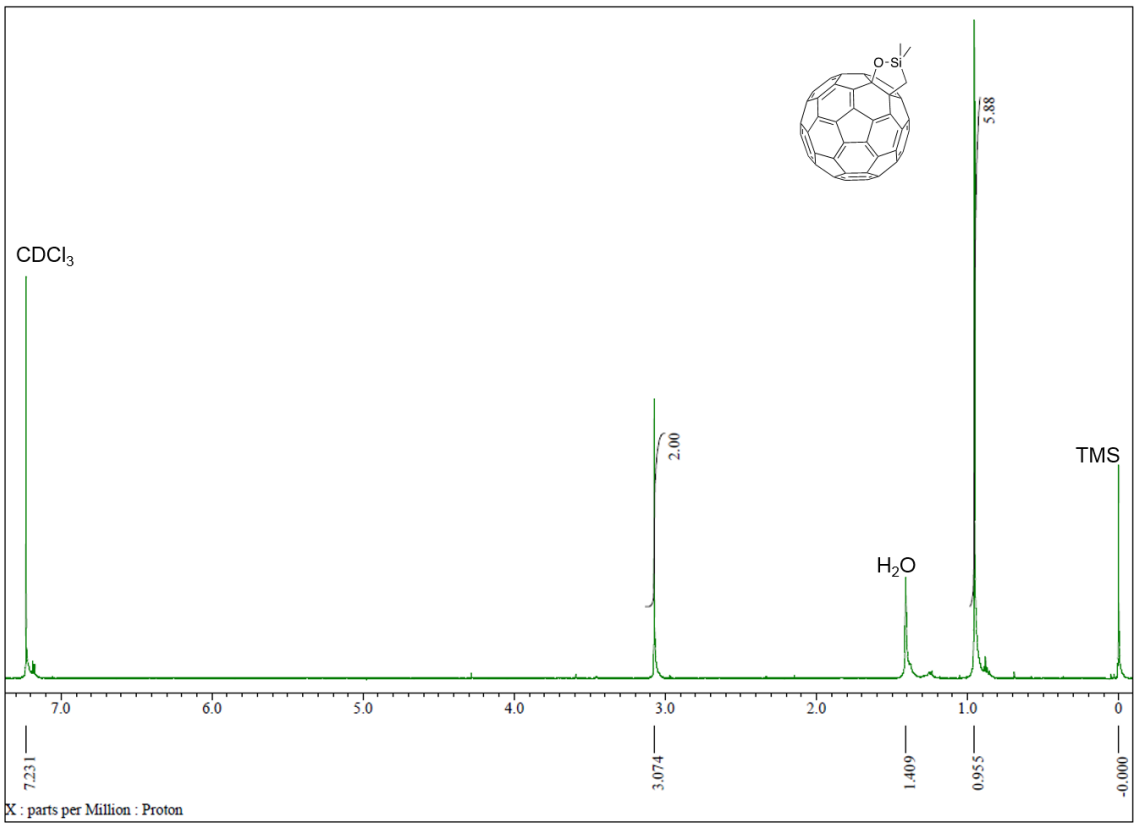

Figure S13. ^{1}H NMR spectrum for **5**.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 0.96 (s, 6H, $2CH_3$), 3.07 (s, 2H, CH_3).

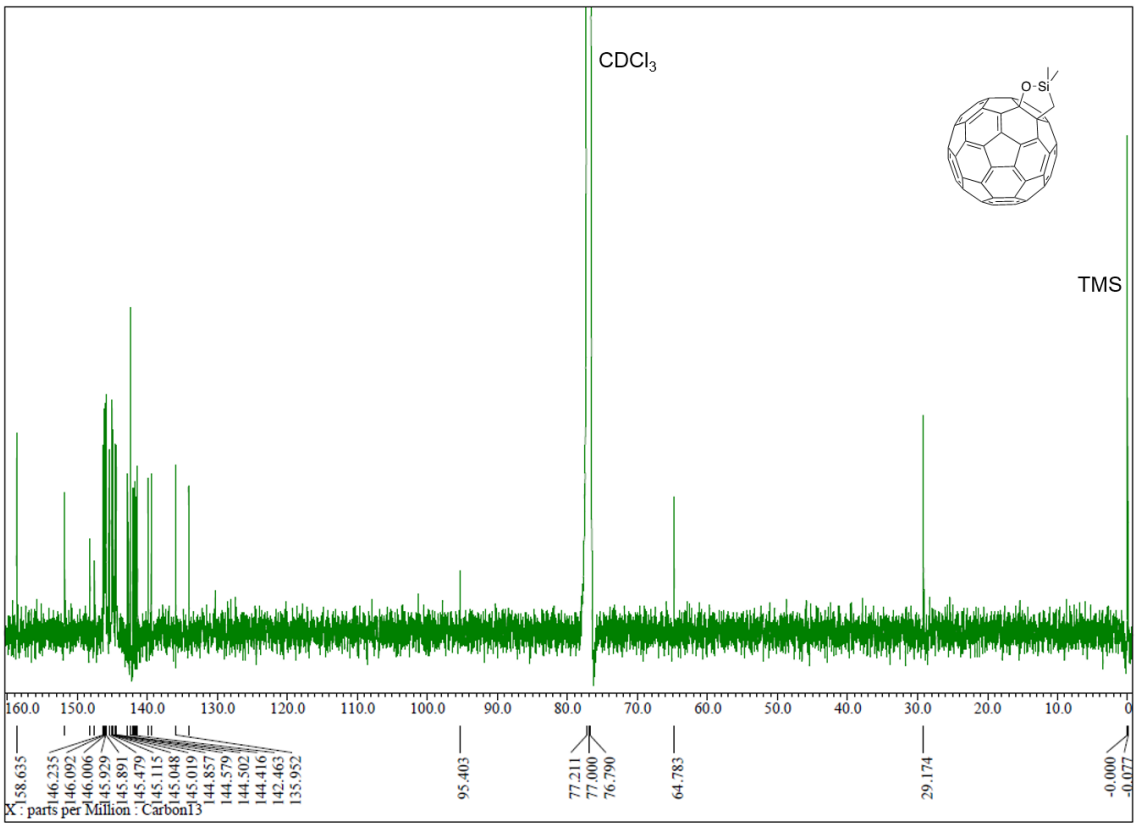

Figure S14. ^{13}C NMR spectrum for **5**.

^{13}C NMR (150 MHz, $CDCl_3/CS_2$): δ -0.08, 29.17, 64.78, 95.40, 134.10, 135.95, 139.46, 139.90, 141.38, 141.62, 141.80, 141.98, 142.08, 142.39, 142.46, 142.80, 144.42, 144.50, 144.58, 144.86, 145.02, 145.05, 145.08, 145.12, 145.48, 145.89, 145.93, 146.01, 146.09, 146.24, 147.53, 148.18, 151.80, 158.63.

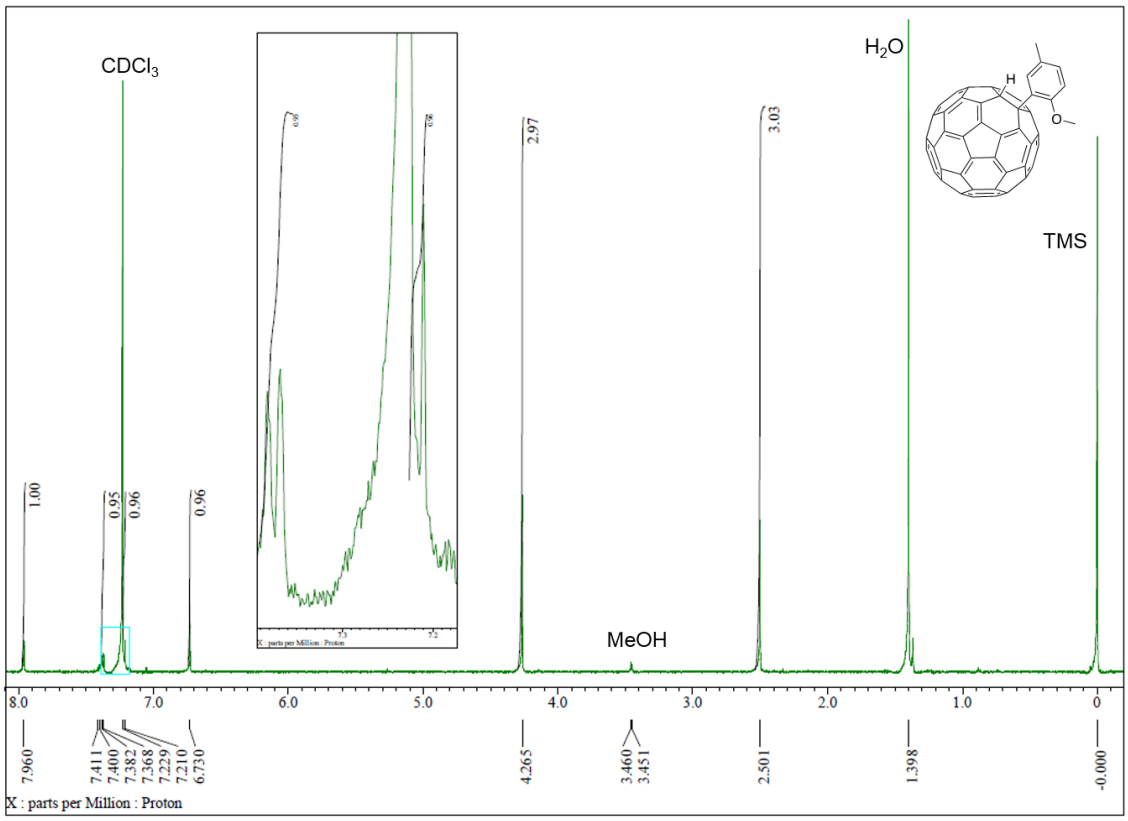

Figure S15. ^{1}H NMR chart for $C_{60}(C_6H_4$-OMe-2-Me-5)H.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 2.50 (s, 3H, CH_3), 4.27 (s, 3H, OCH_3), 6.73 (s, 1H, C_{60}-H), 7.22 (d, J = 6.0 Hz, 1H, C_6H_3), 7.38 (d, J = 8.4 Hz, 1H, C_6H_3), 7.96 (s, 1H, C_6H_3).

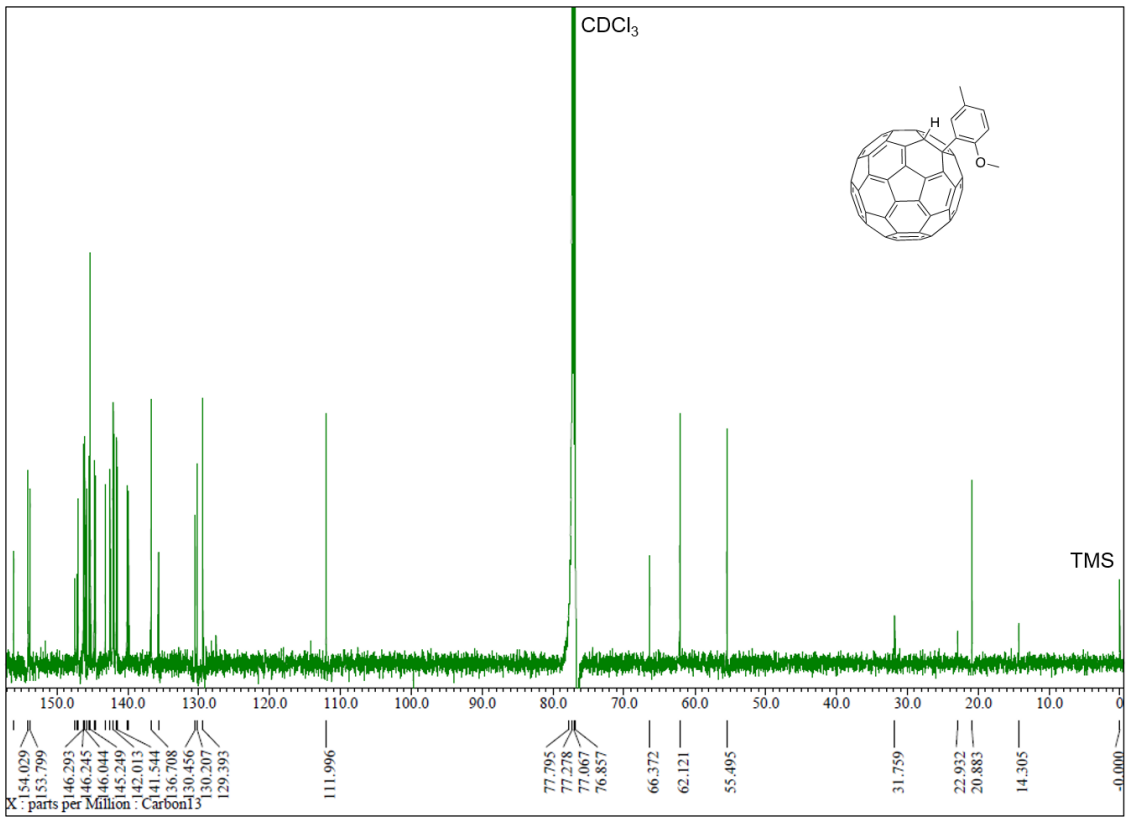

Figure S16. ^{13}C NMR chart for $C_{60}(C_6H_4$-OMe-2-Me-5)H.

^{13}C NMR (150 MHz, $CDCl_3$ / CS_2): δ 14.31, 20.88, 22.93, 31.76, 55.50, 62.12, 66.37, 112.00, 129.39, 130.21, 130.46, 135.69, 136.71, 139.89, 140.14, 141.53, 141.54, 141.67, 142.01, 142.11, 142.48, 142.52, 143.18, 144.55, 144.77, 145.25, 145.43, 145.80, 146.02, 146.04, 146.20, 146.25, 146.29, 147.03, 147.15, 147.40, 153.80, 154.03, 156.09.

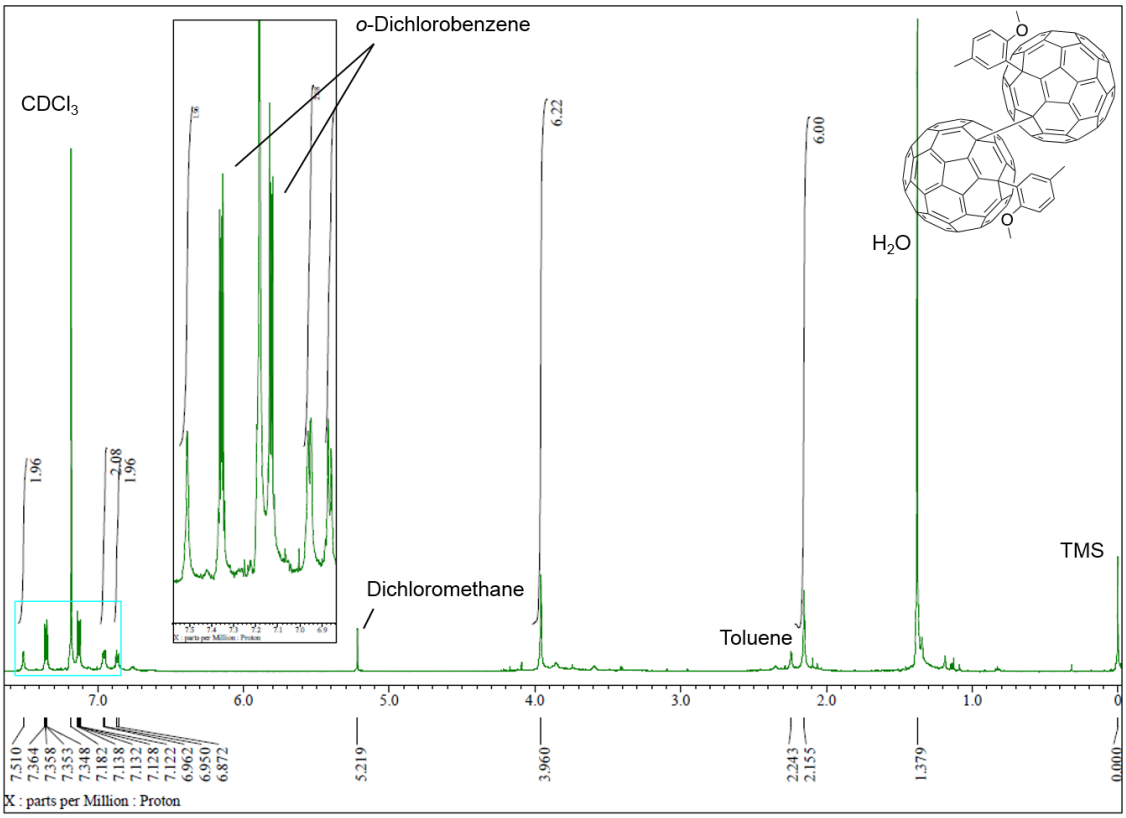

Figure S17. ^{1}H NMR chart for $\{C_{60}(C_6H_4\text{-MeO-2-Me-5})\}_2$

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 2.16 (s, 6H, CH_3), 3.96 (S, 6H, OCH_3), 6.87 (d, J = 7.8 Hz, 2H, C_6H_3), 6.96 (d, J = 7.2 Hz, 2H, C_6H_3), 7.51 (s, 2H, C_6H_3).

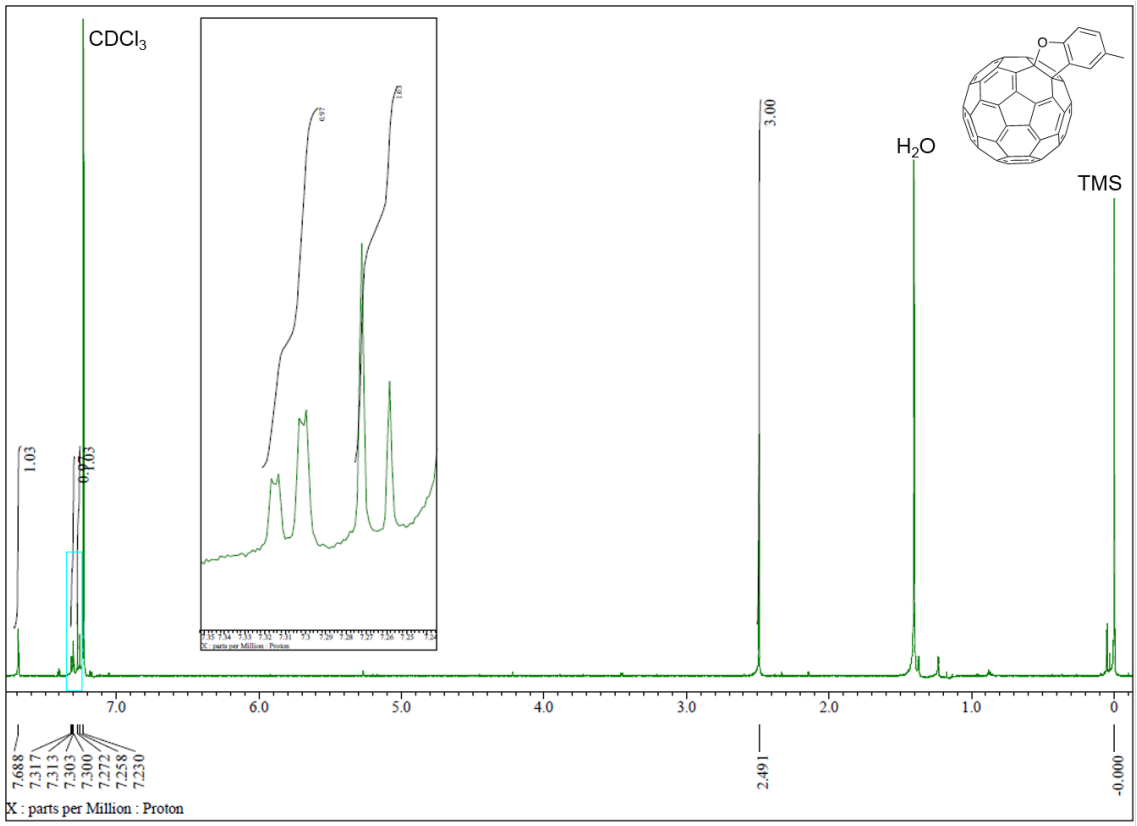

Figure S18. ^{1}H NMR chart for **6**.

^{1}H NMR (600 MHz, $CDCl_3/CS_2$): δ 2.49 (s, 3H, CH_3), 7.27 (d, J = 8.4 Hz, 1H, C_6H_3), 7.31 (d, J = 7.8 Hz, J = 8.4 Hz, 1H, C_6H_3), 7.69 (s, 1H, C_6H_3).

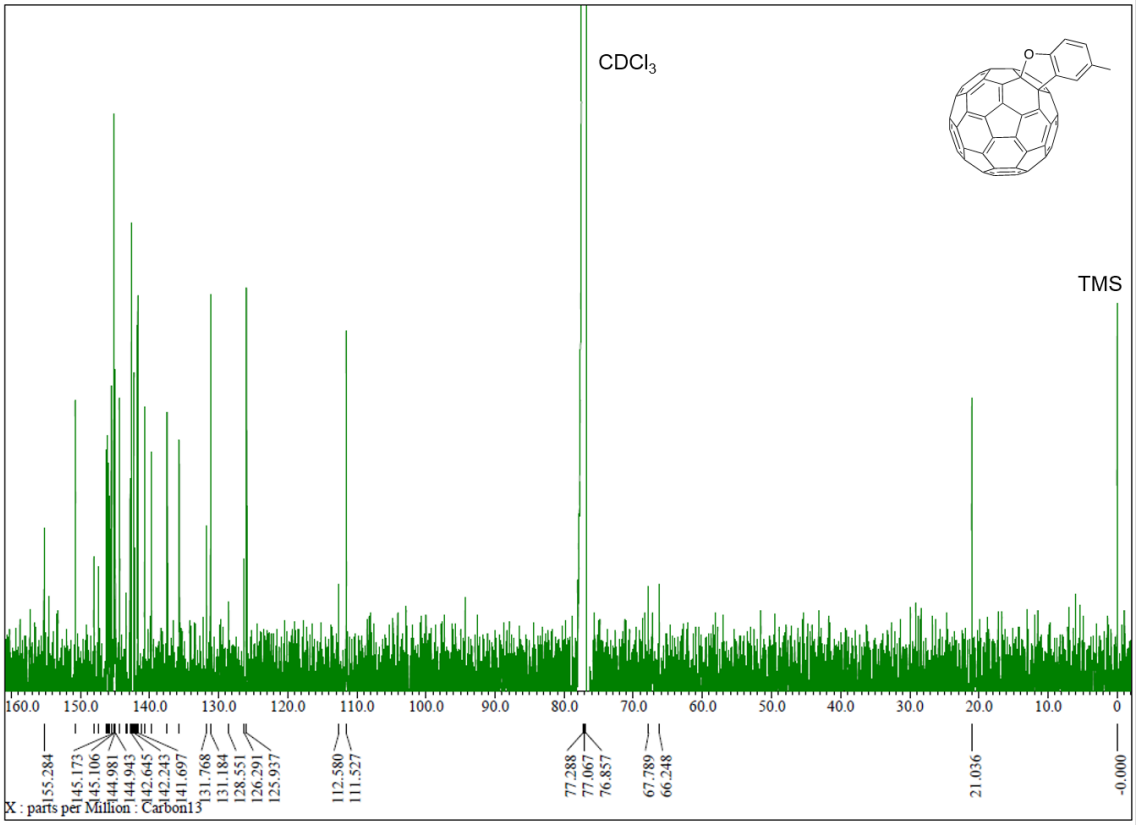

Figure S19. ^{13}C NMR chart for **6**.

^{13}C NMR (150 MHz, $CDCl_3/CS_2$): δ 21.04, 66.25, 67.79, 111.53, 112.58, 125.94, 126.29,128.55, 131.18, 131.77, 135.67, 137.41, 139.71, 140.71, 141.70, 142.07, 142.21, 142.24, 142.61, 142.65, 142.84, 143.39, 144.30, 144.37, 144.94, 144.98, 145.11, 145.17, 145.45, 145.56, 145.86, 145.97, 146.07, 146.14, 146.22, 147.32, 148.06, 150.74, 155.28.

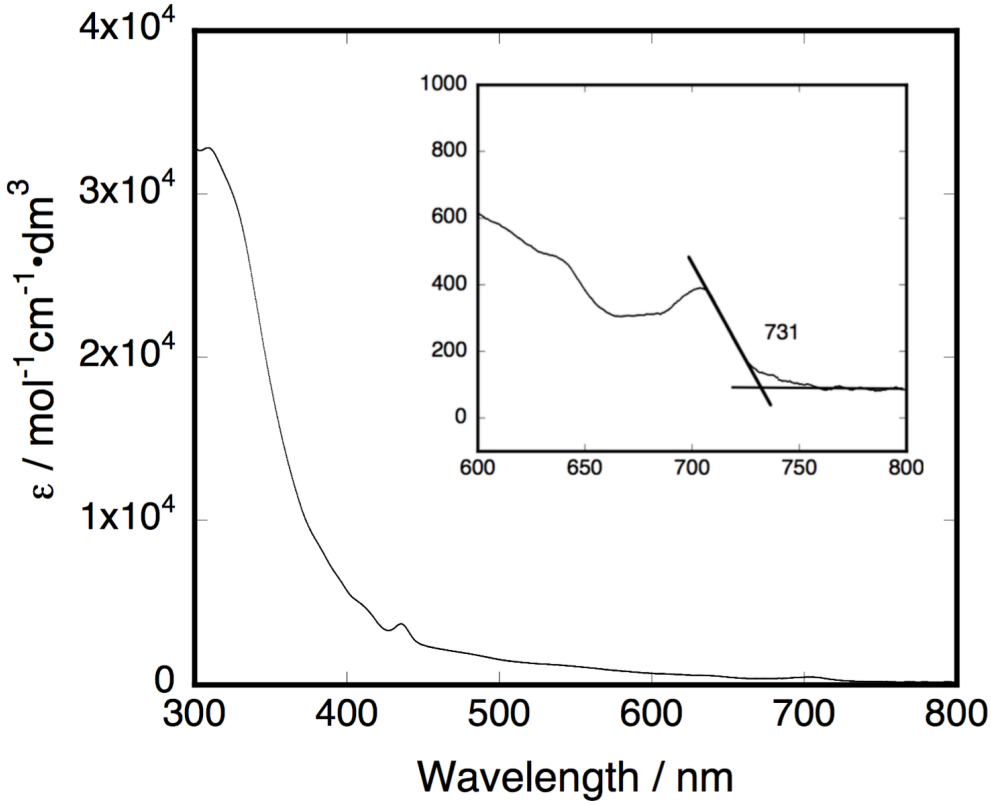

Figure S20. UV-vis absorption spectrum for **3**a in CH_2Cl_2.

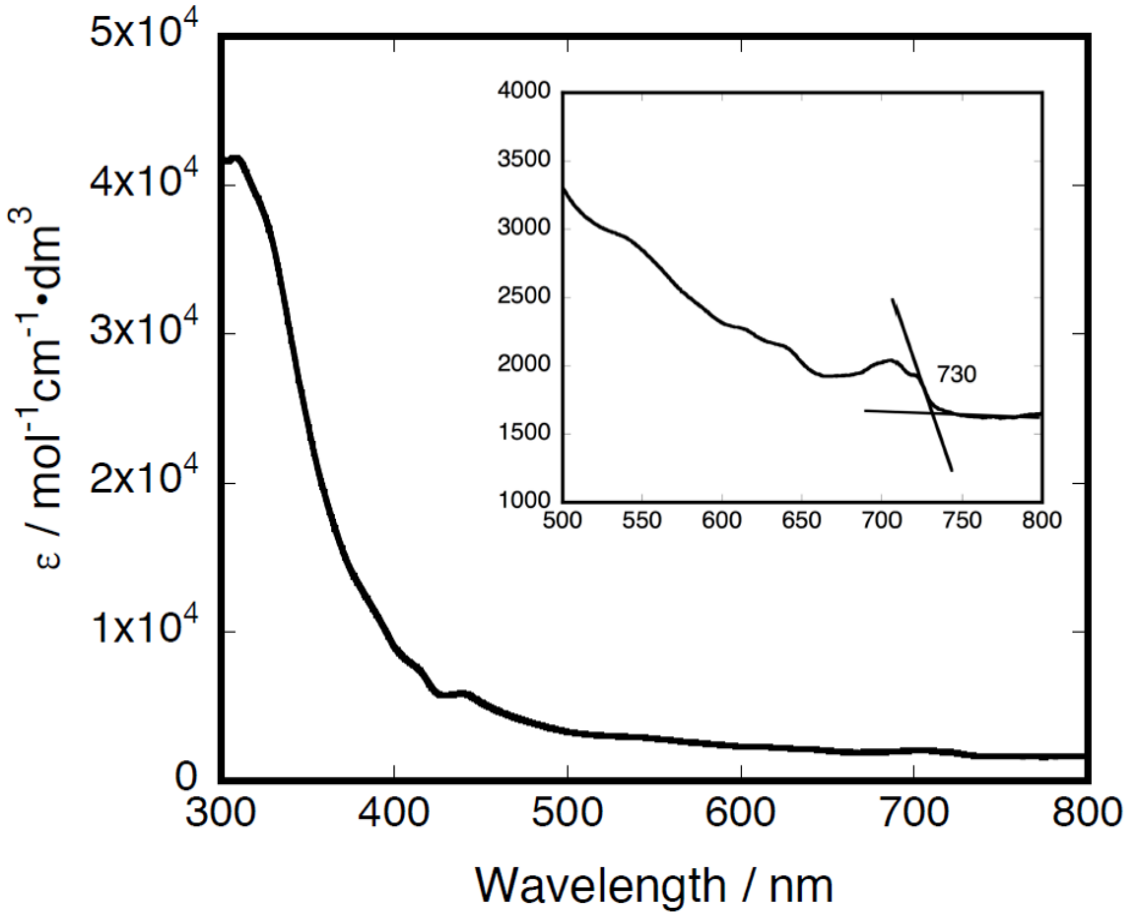

Figure S21. UV-vis absorption spectrum for **3b** in CH_2Cl_2.

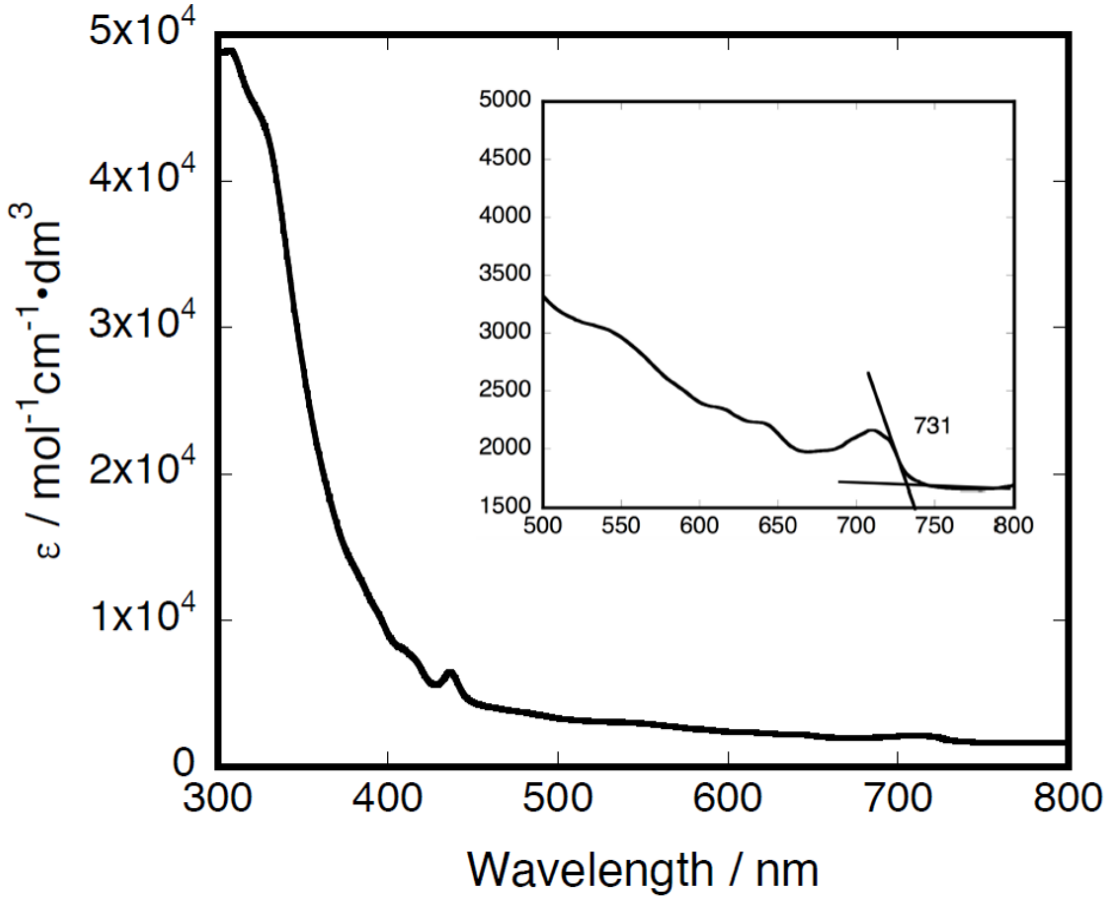

Figure S22. UV-vis absorption spectrum for **2** in CH_2Cl_2.

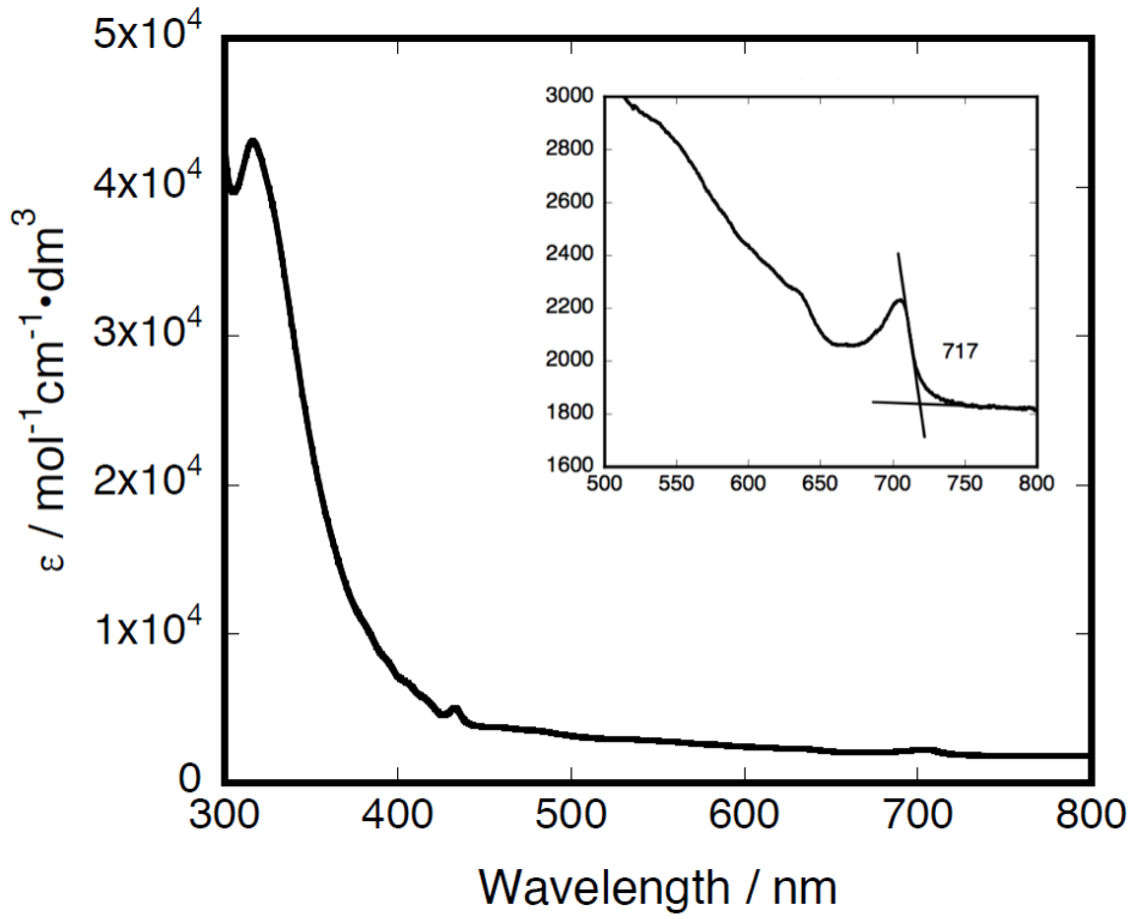

Figure S23. UV-vis absorption spectrum for **5** in ODCB.

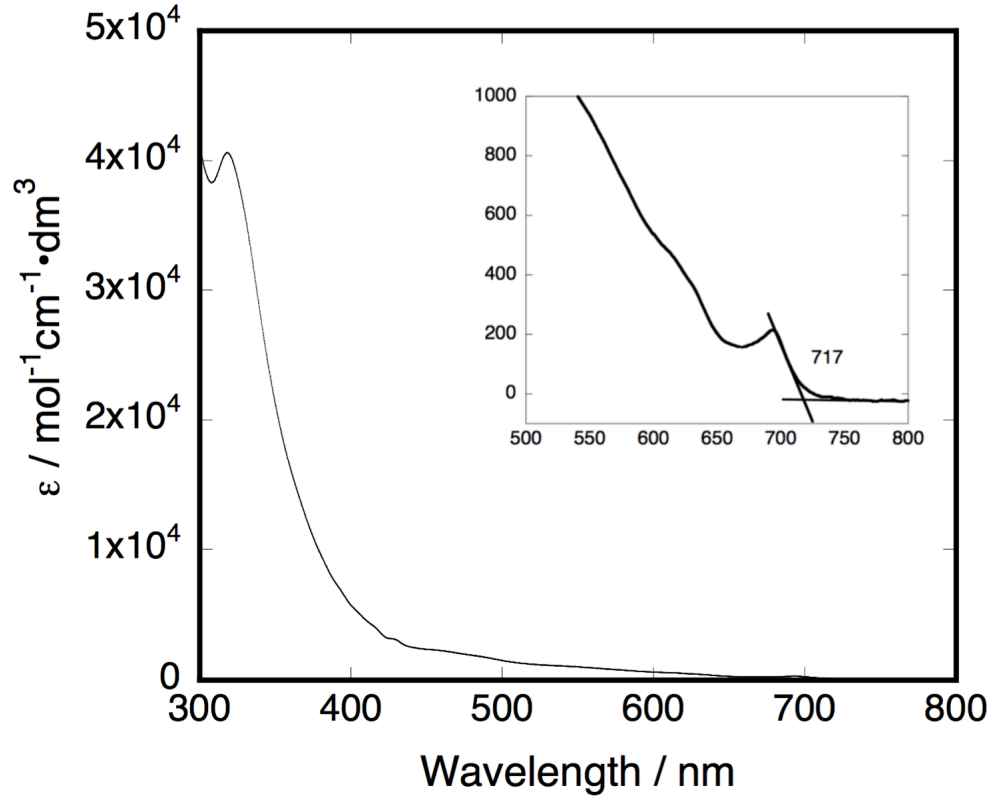

Figure S24. UV-vis absorption spectrum for **6** in ODCB.

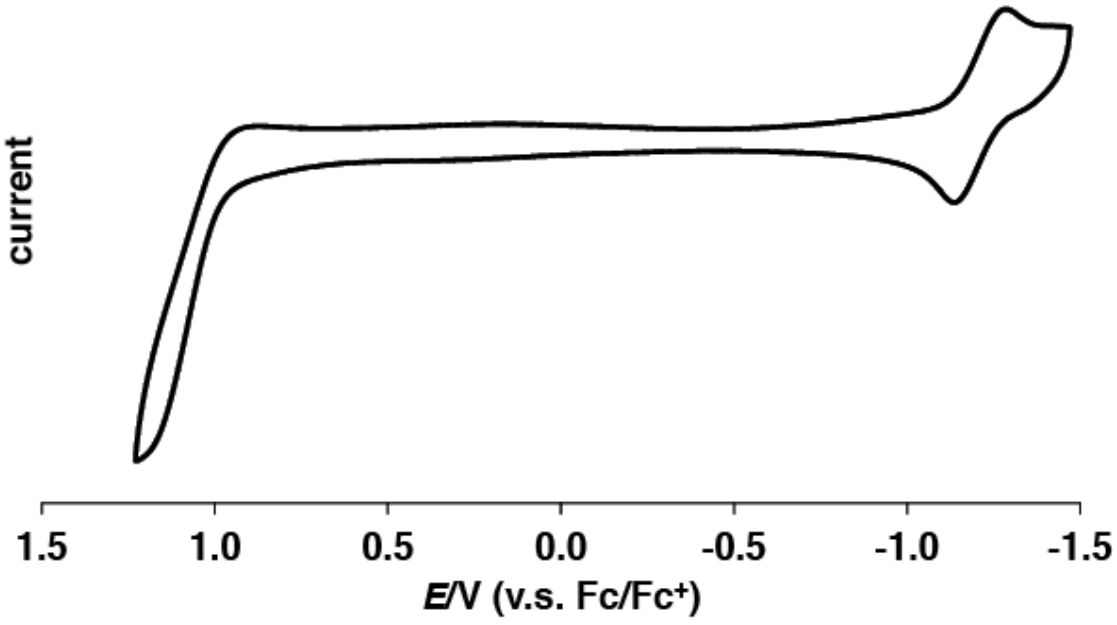

Figure S25. CV for **3a** in ODCB.

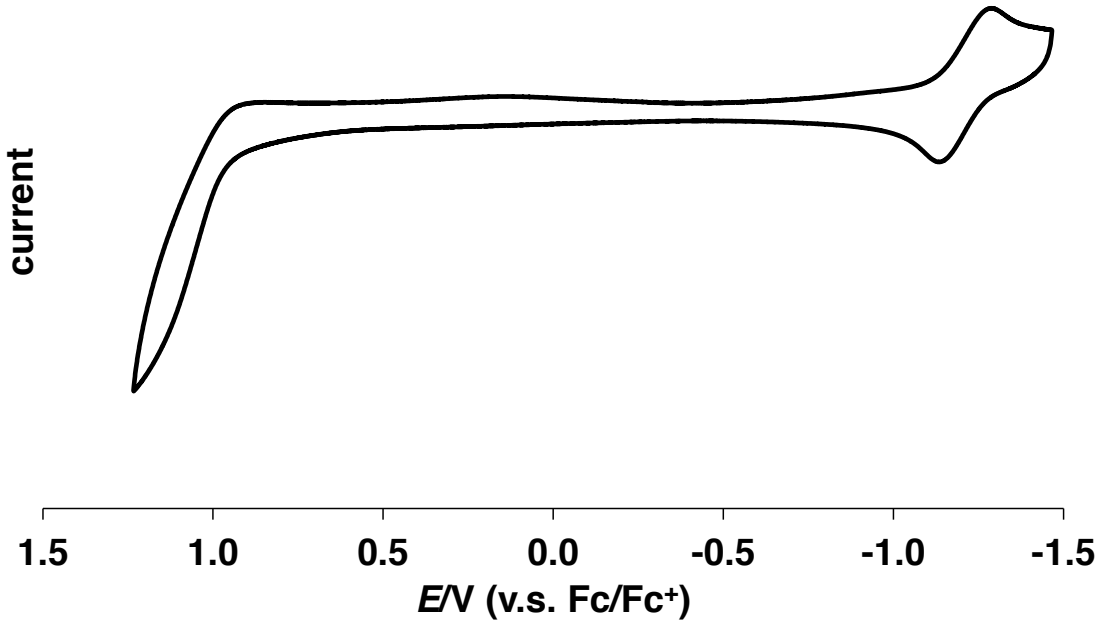

Figure S26. CV for **3b** in ODCB.

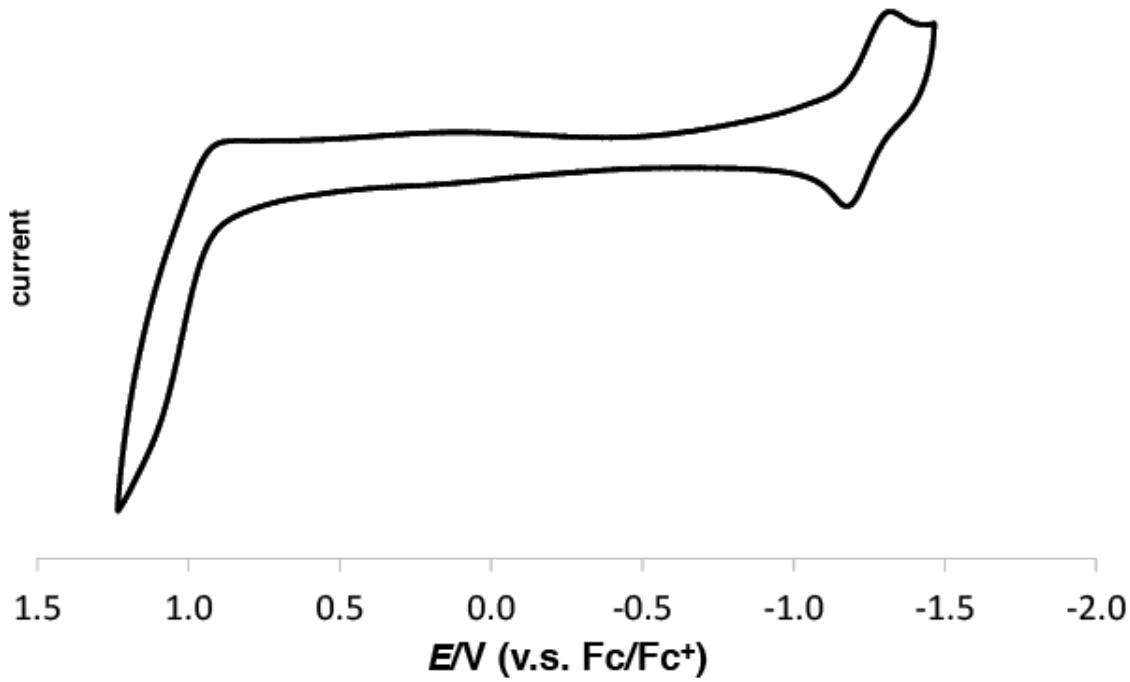

Figure S27. CV for **2** in ODCB.

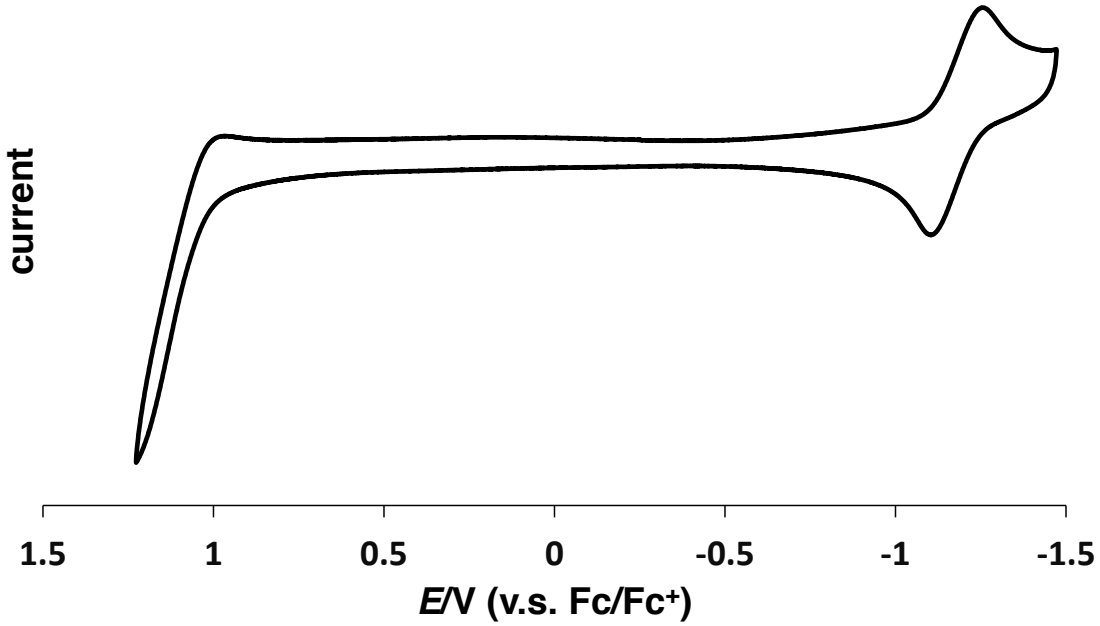

Figure S28. CV for **5** in ODCB.

Table S1. Photovoltaic parameters of DPP(TBFu)$_2$: **5**

D:A ratio	SVA time	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [–]	PCE [%]
5:2	30 sec	0.87	0.66	0.27	0.16
	90 sec	0.82	0.96	0.24	0.19
	120 sec	0.89	2.06	0.39	0.71
5:3	30 sec	0.90	4.71	0.50	2.12
	90 sec	0.90	3.25	0.45	1.31
	120 sec	0.90	1.58	0.31	0.44
5:4	30 sec	0.90	2.64	0.40	0.96
	90 sec	0.90	2.81	0.35	0.89
	120 sec	0.90	2.11	0.38	0.71

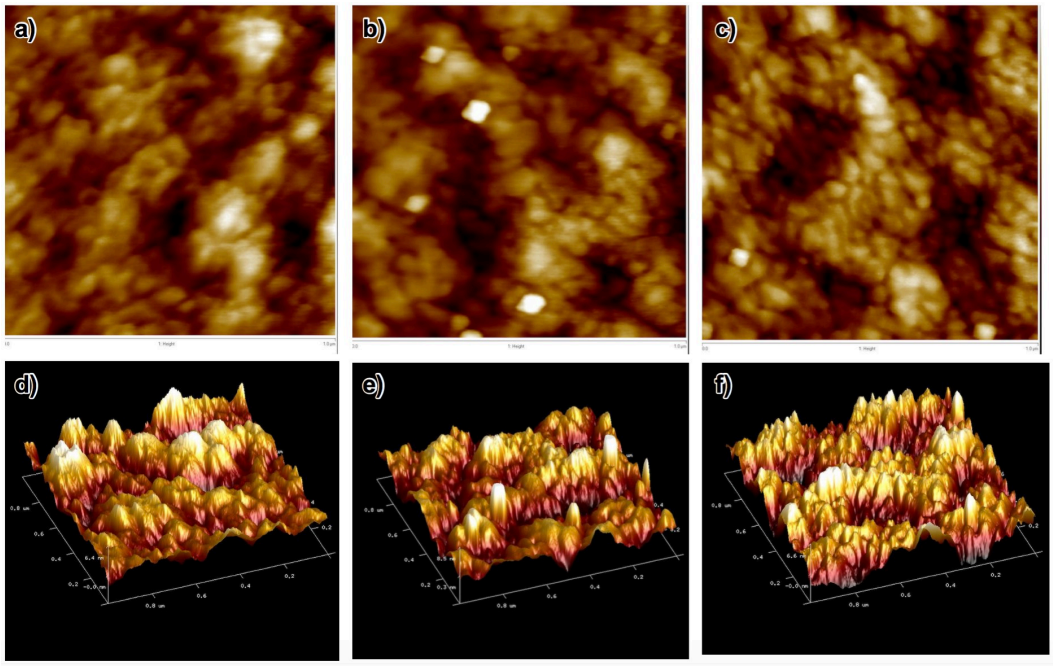

Figure S29. 1 mm square AFM height (a, b, c) and 3D (d, e, f) images of thin films of DPP(TBFu)$_2$:**3** = 5:3 with SVA in CH_2Cl_2 for 30 sec (a, d), for 90 sec (b, e), DPP:(TBFu)$_2$:**5**= 5:4 with SVA in CH_2Cl_2 for 30 sec (c, f). Root-mean-square roughness values (R_q) were 1.77 nm, 2.36 nm, and 2.12 nm, respectively.

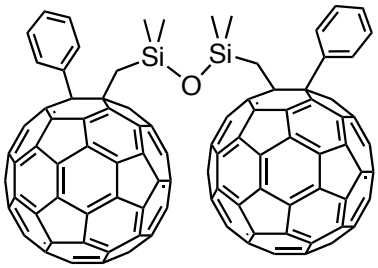

Figure S30. Molecular structure of dehydrated product of **2**.

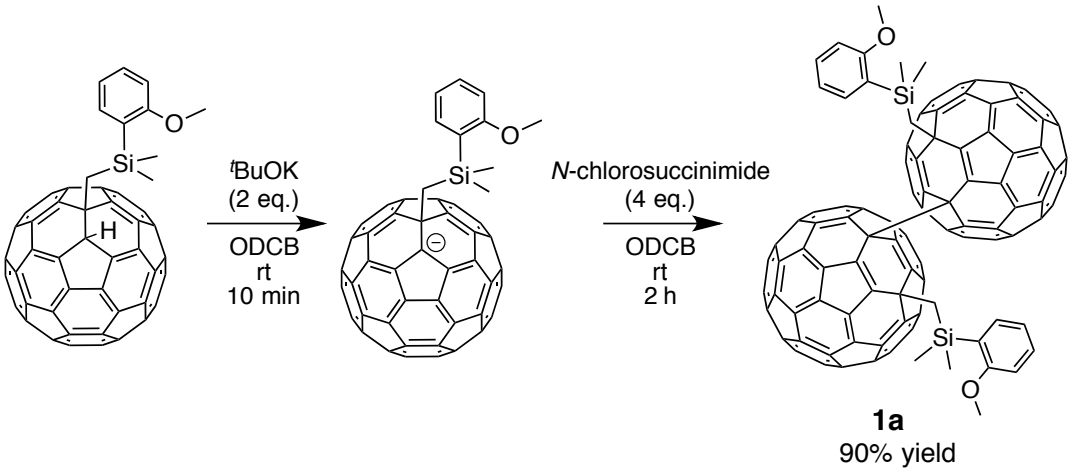

Figure S31. Synthetic scheme of dimer **1a**.