

Electronic Supplementary Information

Ni-Catalyzed direct 1,4-difunctionalization of [60]fullerene with benzyl bromides

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General Information. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 400 MHz) spectrometers. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl_3 at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer. Preparative recycling HPLC was used a LC-2000 Plus instrument equipped with a Buckyprep column (4.6 mm x 250 mm, nakarai Tesque). HPLC analysis performed using toluene as an elution at 0.6 mL/min flow rate, detection at 320 nm in 16 °C. Column chromatography was carried out employing Slica gel 60 N (spherical, neutral, 40~100 m, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F₂₅₄ (Merk).

Materials. Anhydrous 1,2-dichlorobenzene (Aldrich), toluene, carbon disulfide, DMSO (WAKO), Ni catalysts (Aldrich), C_{60} (Aldrich), benzyl bromides (Aldrich), Mn (Mitsuwa's Pure Chem, 200mesh), CoCl_2 , dppf (Aldrich), benzyl bromides **1a-1i** were purchased and used as received. CoX_2 (ligand) were prepared following the reported literature.¹ The singly bonded fullerene dimer **4a** and hydrofullerene **3a** were prepared following the reported papers.^{2,3} The structure of products were determined by using ^1H NMR, ^{13}C NMR, HMRS, and UV-vis spectra, and authentic sample of **2g**.⁴

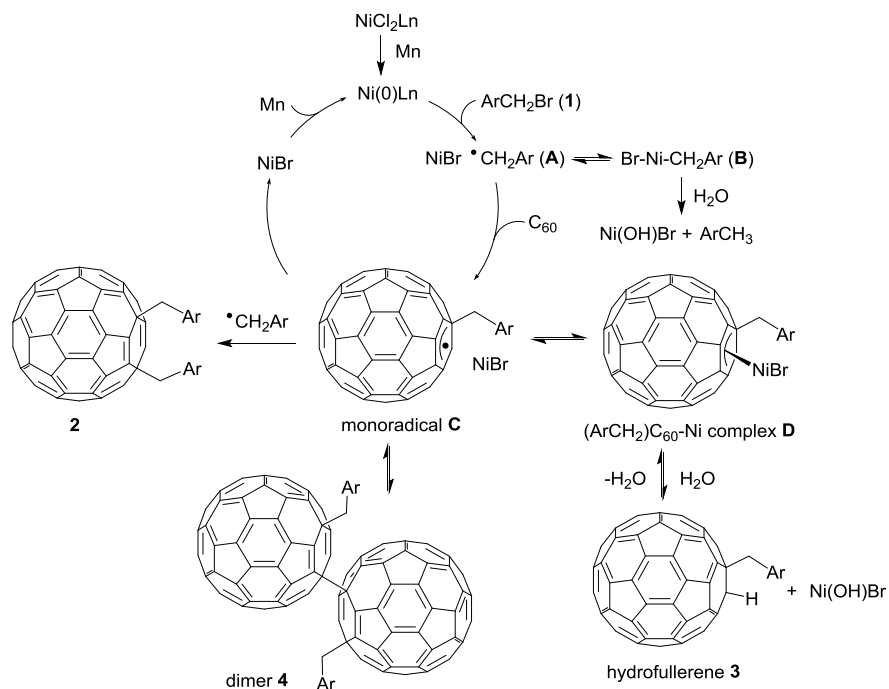
References:

1. R. J. McKinney, *Inorg. Chem.* **1982**, *21*, 2051.
2. S. Lu, T. Jin, E. Kwon, M. Bao and Y. Yamamoto, *Angew. Chem., Int. Ed.*, 2012, **51**, 802.
3. S. Lu, T. Jin, M. Bao and Y. Yamamoto, *J. Am. Chem. Soc.*, 2011, **133**, 12842.
4. K. M. Kadish, X. Gao, E. Van Caemelbecke, T. Hirasaka, T. Suenobu and S. Fukuzumi, *J. Phys. Chem. A*, 1998, **102**, 3898.

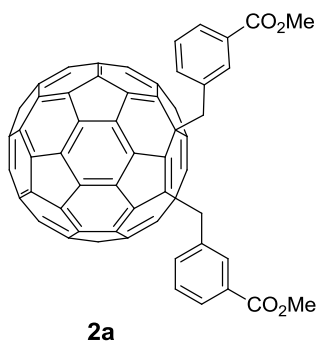
Representative procedure of Ni-catalyzed difunctionalization for synthesis of **2a**

To a mixture of 1,2-dichlorobenzene (4 mL) and DMSO (0.15 mL) solution were added NiCl_2dppe (0.8 mg, 5 mol%), Mn (2.4 mg, 1.5 equiv.), C_{60} (21.6 mg, 0.03 mmol), and methyl 3-(bromomethyl)benzoate (**1a**) (20.6 mg, 3 equiv.) under an argon atmosphere at rt. The reaction mixture was stirred at rt for 24 h. After monitoring by HPLC and TLC, the reaction mixture was purified directly through a silica gel chromatography using toluene as an eluent. The obtained product was washed with methanol and dried, affording the expected product **2a** in 58% yield (18 mg) as a dark brown solid.

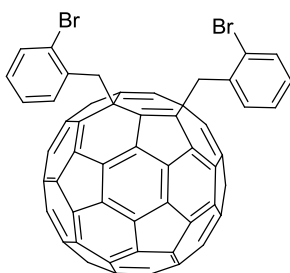
Scheme S1. Proposed reaction mechanism



Analytical data of 2

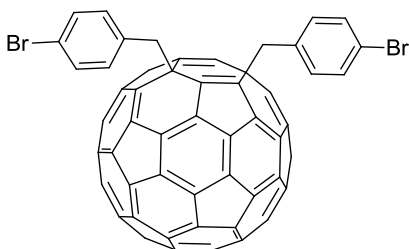


Dark brown solid; soluble solvents: CHCl_3 , toluene, ODCB; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 3.76 (2H, d, $J = 12.8$ Hz), 3.84 (2H, d, $J = 12.8$ Hz), 3.95 (6H, s), 7.56 (2H, dd, $J = 7.6, 7.6$ Hz), 7.78 (2H, d, $J = 7.6$ Hz), 8.01 (2H, d, $J = 7.6$ Hz), 8.21 (2H, s); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 48.14, 51.85, 59.79, 128.28, 128.57, 130.23, 131.65, 135.10, 136.22, 137.56, 138.43, 140.37, 141.67, 141.77, 142.10, 142.30, 142.33, 142.73, 142.77, 142.93, 143.35, 143.72, 143.80, 143.95, 144.01, 144.15, 144.30, 144.46, 144.79, 145.23, 145.49, 146.35, 146.61, 146.89, 148.07, 148.33, 150.93, 156.77, 165.93. HRMS (MALDI) calcd for $\text{C}_{78}\text{H}_{18}\text{O}_4$ $[\text{M}]^+$: 1018.1200, found 1018.1203.



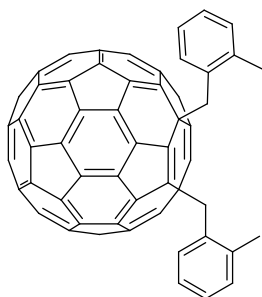
2b

Dark brown solid; soluble solvents: CHCl_3 , toluene, ODCB; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 3.94 (2H, d, $J = 13.2$ Hz), 4.19 (2H, d, $J = 13.2$ Hz), 7.24 (2H, ddd, $J = 8.0, 8.0, 1.6$ Hz), 7.46 (2H, ddd, $J = 8.0, 8.0, 1.2$ Hz), 7.69 (2H, dd, $J = 8.0, 1.2$ Hz), 7.21 (2H, dd, $J = 8.0, 1.6$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 47.33, 59.56, 126.31, 127.29, 129.15, 132.87, 133.46, 135.75, 137.72, 138.54, 140.41, 141.68, 141.84, 142.22, 142.34, 142.41, 142.79, 142.89, 142.99, 143.38, 143.73, 143.88, 144.05, 144.07, 144.13, 144.44, 144.56, 144.65, 144.85, 145.30, 145.65, 146.69, 146.73, 146.75, 146.94, 148.20, 148.42, 151.20, 156.72. HRMS (MALDI) calcd for $\text{C}_{74}\text{H}_{12}\text{Br}_2$ $[\text{M}]^+$: 1058.9334, found 1058.9386.



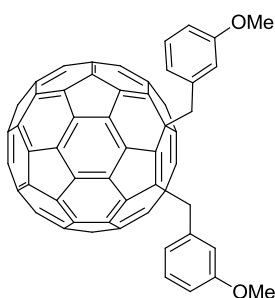
2c

Dark brown solid; soluble solvents: CHCl_3 , toluene, ODCB; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 3.84 (2H, d, $J = 12.8$ Hz), 3.88 (2H, d, $J = 12.8$ Hz), 7.47 (4H, d, $J = 8.0$ Hz), 7.60 (4H, d, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 48.15, 59.85, 121.80, 131.48, 132.35, 134.75, 137.73, 138.61, 140.51, 141.73, 141.82, 142.17, 142.39, 142.44, 142.84, 142.87, 143.04, 143.43, 143.84, 144.04, 144.05, 144.09, 144.18, 144.37, 144.45, 144.86, 145.33, 145.62, 146.49, 146.73, 146.99, 148.17, 148.43, 151.00, 156.72. HRMS (MALDI) calcd for $\text{C}_{74}\text{H}_{12}\text{Br}_2$ $[\text{M}]^+$: 1058.9379, found 1058.9381.



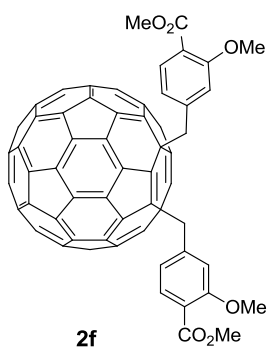
2d

Dark brown solid; soluble solvents: CHCl_3 , toluene, ODCB; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 2.62 (6H, s), 3.78 (2H, d, $J = 13.2$ Hz), 3.87 (2H, d, $J = 13.2$ Hz), 7.20-7.31 (6H, m), 7.50 (2H, d, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 20.68, 44.73, 60.20, 125.75, 127.49, 130.89, 131.70, 134.18, 136.74, 137.28, 138.45, 140.25, 141.64, 141.66, 142.11, 142.21, 142.30, 142.67, 142.70, 142.82, 143.32, 143.58, 143.71, 143.85, 143.90, 143.99, 144.23, 144.28, 144.42, 144.65, 145.12, 145.78, 146.47, 146.53, 146.56, 146.79, 148.12, 148.24, 151.44, 157.38. HRMS (MALDI) calcd for $\text{C}_{76}\text{H}_{18}$ $[\text{M}]^+$: 930.1403, found 930.1406.

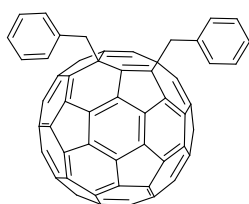


2e

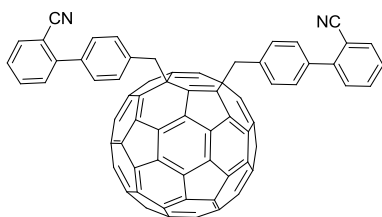
Dark brown solid; soluble solvents: CHCl_3 , toluene, ODCB; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 3.72 (2H, d, $J = 12.8$ Hz), 3.76 (2H, d, $J = 12.8$ Hz), 3.85 (6H, s), 6.85 (2H, d, $J = 8.0$ Hz), 7.08 (2H, s), 7.12 (2H, d, $J = 8.0$ Hz), 7.36 (2H, dd, $J = 8.0, 8.0$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 48.43, 54.75, 60.13, 111.93, 117.27, 123.21, 129.14, 137.29, 137.46, 138.43, 140.26, 141.67, 141.69, 142.12, 142.23, 142.30, 142.65, 142.72, 142.82, 143.38, 143.61, 143.75, 143.89, 143.92, 144.02, 144.27, 144.32, 144.42, 144.70, 145.14, 145.74, 146.51, 146.54, 146.57, 146.82, 148.19, 148.25, 151.35, 157.47, 159.15. HRMS (MALDI) calcd for $\text{C}_{76}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$: 962.1301, found 962.1257.



Dark brown solid; soluble solvents: CHCl_3 , toluene, ODCB; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 3.90 (6H, s), 3.91 (6H, s), 4.08 (2H, d, $J = 12.8$ Hz), 4.19 (2H, d, $J = 12.8$ Hz), 7.57 (2H, d, $J = 7.6$ Hz), 7.65 (2H, s), 7.73 (2H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 42.25, 51.72, 55.07, 59.17, 111.71, 121.80, 129.71, 130.57, 131.89, 137.11, 138.47, 140.25, 141.51, 141.61, 142.08, 142.20, 142.29, 142.58, 142.75, 142.77, 143.28, 143.42, 143.71, 143.82, 143.84, 143.99, 144.18, 144.25, 144.28, 144.51, 145.08, 145.57, 146.47, 146.49, 146.55, 146.73, 148.04, 148.18, 151.04, 157.13, 157.52, 165.72. HRMS (ESI) calcd for $\text{C}_{80}\text{H}_{22}\text{O}_6\text{Na}$ $[\text{M}]^+$: 1101.1309, found 1101.1309.

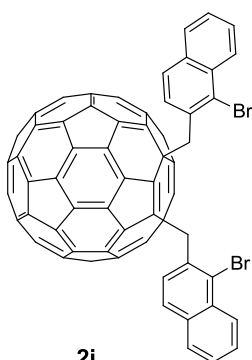


Dark brown solid; soluble solvents: CHCl_3 , toluene, ODCB; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 3.74 (2H, d, $J = 12.8$ Hz), 3.79 (2H, d, $J = 12.8$ Hz), 7.34 (2H, dd, $J = 7.6, 7.6$ Hz), 7.45 (4H, dd, $J = 7.6, 7.6$ Hz), 7.51 (4H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 48.44, 60.19, 127.26, 128.20, 130.74, 135.78, 137.46, 138.42, 140.22, 141.63, 141.68, 142.08, 142.20, 142.29, 142.63, 142.71, 142.81, 143.34, 143.61, 143.71, 143.87, 143.90, 143.99, 144.23, 144.28, 144.42, 144.68, 145.12, 145.71, 146.48, 146.52, 146.54, 146.81, 148.19, 148.23, 151.30, 157.39. HRMS (MALDI) calcd for $\text{C}_{74}\text{H}_{14}$ $[\text{M}]^+$: 902.1090, found 902.1093.



2h

Dark brown solid; soluble solvents: CHCl_3 , toluene, ODCB; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 3.81 (2H, d, $J = 13.2$ Hz), 3.88 (2H, d, $J = 13.2$ Hz), 7.38-7.45 (4H, m), 7.58-7.75 (12H, m); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 48.20, 60.11, 111.19, 117.99, 127.32, 128.24, 128.72, 129.76, 131.15, 132.63, 133.39, 136.69, 137.19, 137.56, 138.55, 140.37, 141.72, 141.81, 142.16, 142.30, 142.36, 142.76, 142.79, 142.93, 143.43, 143.80, 143.97, 143.99, 144.05, 144.24, 144.37, 144.50, 144.80, 145.23, 145.73, 146.48, 146.63, 146.91, 148.22, 148.34, 151.24, 157.28. HRMS (MALDI) calcd for $\text{C}_{88}\text{H}_{20}\text{N}_2$ $[\text{M}]^+$: 1104.1576, found 1104.1569.



2i

Dark brown solid; soluble solvents: CHCl_3 , toluene, ODCB; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 4.23 (2H, d, $J = 12.8$ Hz), 4.49 (2H, d, $J = 12.8$ Hz), 7.49 (2H, dd, $J = 8.0, 8.0$ Hz), 7.59 (2H, dd, $J = 8.0, 8.0$ Hz), 7.73 (2H, d, $J = 8.0$ Hz), 7.83 (2H, d, $J = 8.0$ Hz), 7.89 (2H, d, $J = 8.0$ Hz), 8.39 (2H, d, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 1/4$) δ 48.82, 59.62, 126.23, 126.57, 127.31, 127.53, 127.78, 128.05, 129.46, 132.48, 133.60, 133.72, 137.74, 138.56, 140.37, 141.65, 141.79, 142.15, 142.30, 142.36, 142.74, 142.85, 142.94, 143.36, 143.73, 143.83, 143.99, 144.03, 144.09, 144.40, 144.56, 144.61, 144.80, 145.24, 145.64, 146.63, 146.69, 146.72, 146.89, 148.19, 148.36, 151.12, 156.66. HRMS (MALDI) calcd for $\text{C}_{82}\text{H}_{16}\text{Br}_2$ $[\text{M}]^+$: 1157.9569, found 1157.9572.

NMR spectra

