

Electronic Supplementary Information

Synthesis of spiro[indolenine]-methanofullerenes via Deoxofluor promoted deoxidated cyclopropanation of 1,2-(3-indole)fullerenols

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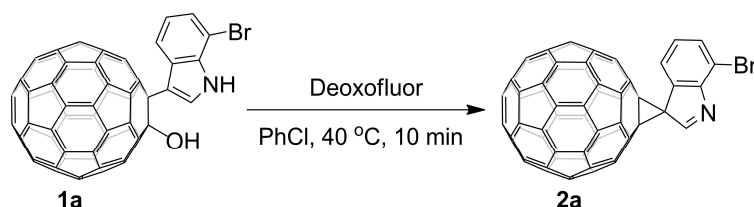
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General Methods

Deoxofluor and solvents were obtained from commercial suppliers and used without further purification. 1,2-(3-indole)fullerenols **1a-1e** were prepared according to our previous work (reference 8c, *Org. Lett.*, 2021, 23, 1302-1308). All reactions were carried out using a standard Schlenk technique under an argon or nitrogen atmosphere. ¹H NMR and proton-decoupled ¹³C NMR spectra were recorded on 400 MHz (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR), and 600 MHz (600 MHz for ¹H NMR, 150 MHz for ¹³C NMR) NMR spectrometers. ¹H NMR spectra were referenced to residual DMSO at 2.50 ppm and residual acetone at 2.05 ppm, and ¹³C NMR spectra were referenced to residual DMSO at 39.52 ppm and residual acetone at 29.85 ppm. Column chromatography was carried out employing silica gel G.

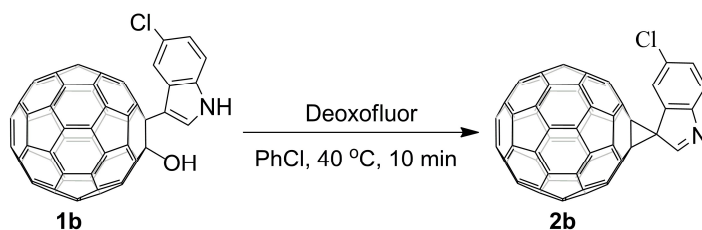
1. Experimental Procedures and Spectral Data of 2a-2e

Synthesis of 2a



1a (18.6 mg, 0.02 mmol), Deoxofluor (36 μ L, 0.20 mmol) were dissolved in chlorobenzene (5 mL) at 40°C under N₂ atmosphere. After 10 minutes of reaction, the color of the solution changed gradually from brown to deep red. Then, petroleum ether was added to the mixture to precipitate the product. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted **1a** (1.3 mg) and **2a** (14.8 mg, 81 %) as black amorphous solid. ¹H NMR (400 MHz, CS₂/d₆-acetone) δ 9.01 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 7.2 Hz, 1H), 7.77-7.72 (m, 2H); ¹³C NMR (150 MHz, CS₂/d₆-acetone) (all 2C unless indicated) δ 166.45, 156.74, 148.12, 146.04, 145.99, 145.95, 145.70, 145.54, 145.53, 145.47, 145.43, 145.40, 145.35, 145.28, 145.02, 144.53, 143.80, 143.78, 143.71, 143.67, 142.78, 142.67, 142.15, 141.99, 139.33, 138.10, 135.70, 133.32, 125.97, 124.4, 121.81, 74.50, 50.51. FT-IR ν /cm⁻¹ (KBr) 1540, 1508, 1458, 1411, 1185, 1132, 861, 772, 740, 697, 548, 523; UV-vis (CHCl₃) λ_{max} /nm 383, 430, 456, 686; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]⁻ calcd for C₆₈H₄BrN 912.9527; found 912.9532.

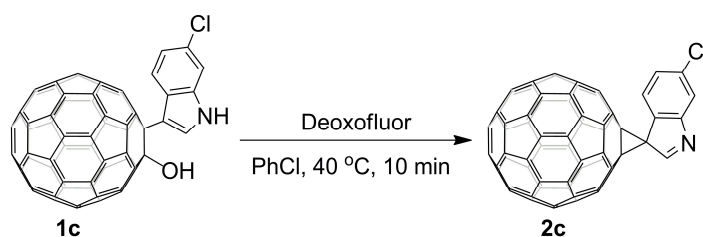
Synthesis of 2b



1b (17.8 mg, 0.02 mmol), Deoxofluor (36 μ L, 0.20 mmol) were dissolved in

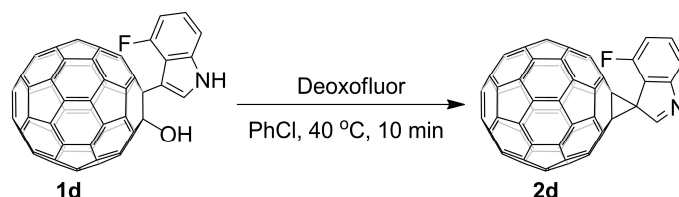
chlorobenzene (5 mL) at 40°C under N₂ atmosphere. After 10 minutes of reaction, the color of the solution changed gradually from brown to deep red. Then, petroleum ether was added to the mixture to precipitate the product. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted **1b** (1.1 mg) and **2b** (13.5 mg, 76 %) as black amorphous solid. ¹H NMR (400 MHz, CS₂/d₆-acetone) δ 9.09 (s, 1H), 8.17 (s, 1H), 7.88(d, *J* = 8 Hz, 1H), 7.63(d, *J* = 8.4 Hz, 1H); ¹³C NMR (150 MHz, CS₂/d₆-acetone) (all 2C unless indicated) δ 166.65, 156.39, 148.20, 146.10, 146.07, 146.00, 145.78, 145.60, 145.57, 145.46, 145.40, 145.35, 144.59, 143.86, 143.83, 143.76, 143.72, 142.84, 142.7, 142.18, 142.03, 139.42, 138.21, 135.44, 133.62, 130.40, 124.10, 123.25, 74.57, 50.63. FT-IR ν/cm⁻¹ (KBr) 1542, 1508, 1458, 1427, 1189, 1156, 861, 816, 742, 703, 552, 524; UV-vis (CHCl₃) λ_{max}/nm 385, 431, 454, 687; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]⁻ calcd for C₆₈H₄ClN 869.0032; found 869.0038.

Synthesis of 2c



1c (17.8 mg, 0.02 mmol), Deoxofluor (36 μL, 0.20 mmol) were dissolved in chlorobenzene (5 mL) at 40°C under N₂ atmosphere. After 10 minutes of reaction, the color of the solution changed gradually from brown to deep red. Then, petroleum ether was added to the mixture to precipitate the product. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted **1c** (1.2 mg) and **2c** (12.3 mg, 71 %) as black amorphous solid. ¹H NMR (400 MHz, CS₂/d₆-acetone) δ 9.15 (s, 1H), 8.21 (d, *J* = 8 Hz, 1H), 7.90 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (150 MHz, CS₂/d₆-acetone) (all 2C unless indicated) δ 168.01, 158.96, 148.25, 146.25, 146.08, 146.07, 146.0, 145.81, 145.5, 145.55, 145.4, 145.36, 145.06, 144.58, 143.86, 143.81, 143.7, 143.71, 142.86, 142.79, 142.73, 142.62, 142.12, 142.04, 139.44, 138.20, 136.29, 132.1, 127.46, 123.6, 123.6, 74.59, 50.68. FT-IR ν/cm⁻¹ (KBr) 1576, 1543, 1450, 1427, 1184, 1064, 887, 808, 740, 689, 589, 556, 526; UV-vis (CHCl₃) λ_{max}/nm 388, 431, 456, 689; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]⁻ calcd for C₆₈H₄ClN 869.0032; found 869.0029.

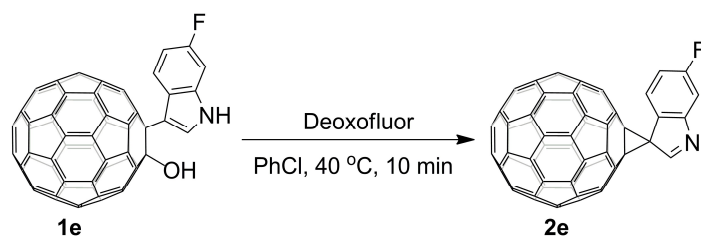
Synthesis of 2d



1d (17.4 mg, 0.02 mmol), Deoxofluor (36 μL, 0.20 mmol) were dissolved in chlorobenzene (5 mL) at 40°C under N₂ atmosphere. After 10 minutes of reaction, the

color of the solution changed gradually from brown to deep red. Then, petroleum ether was added to the mixture to precipitate the product. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted **1d** (2.0 mg) and **2d** (11.4 mg, 67 %) as black amorphous solid. ¹H NMR (400 MHz, CS₂/d₆-acetone) δ 9.12 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.65-7.61 (m, 1H), 7.22 (t, *J* = 9.2 Hz, 1H); ¹³C NMR (150 MHz, CS₂/d₆-acetone)(all 2C unless indicated) δ 167.43, 148.96, 147.67, 146.12, 146.05, 146.01, 145.97, 145.91, 145.57, 145.52, 145.48, 145.37, 144.69, 144.54, 144.04, 143.81, 143.7, 143.66, 143.63, 143.57, 142.79, 142.77, 142.47, 142.39, 142.29, 141.81, 141.46, 137.84, 132.00, 131.9, 119.79, 119.7, 115.72, 115.5, 73.28, 51.56. FT-IR ν/cm⁻¹ (KBr) 1624, 1590, 1556, 1508, 1476, 1424, 1240, 1185, 1001, 787, 740, 700, 556, 523; UV-vis (CHCl₃) λ_{max}/nm 386, 430, 457, 687; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]⁻ calcd for C₆₈H₄FN 853.0328; found 853.0331.

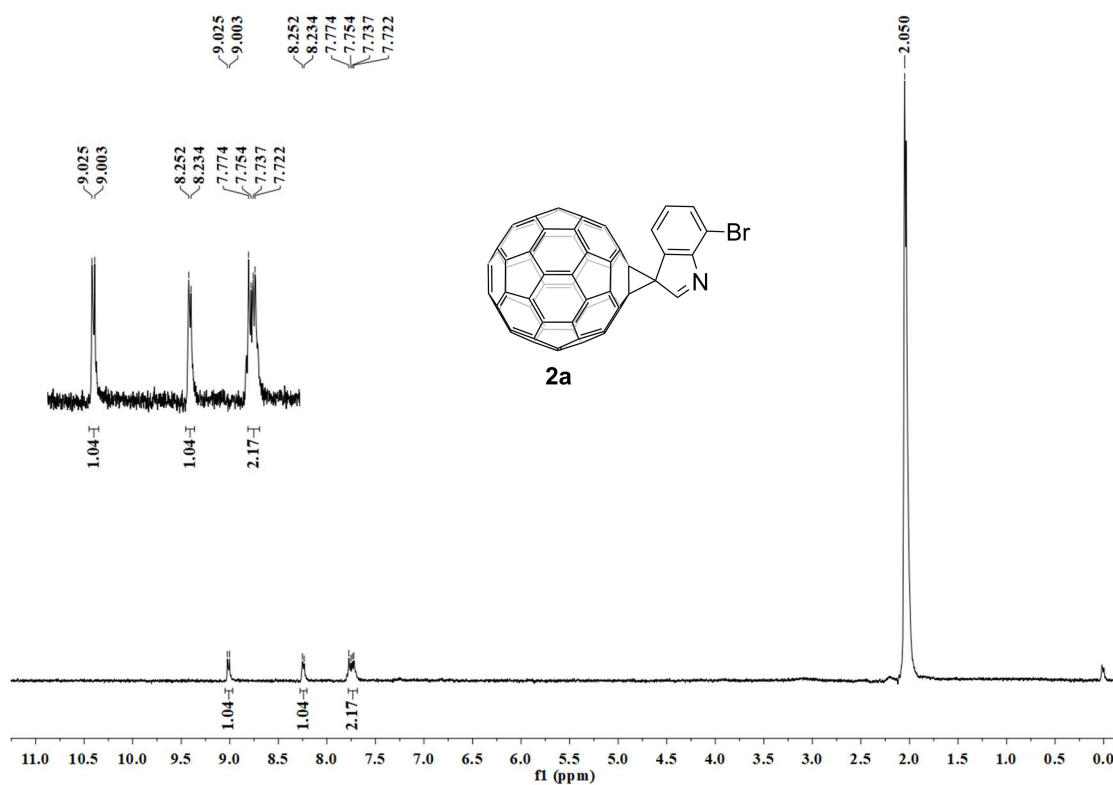
Synthesis of **2e**



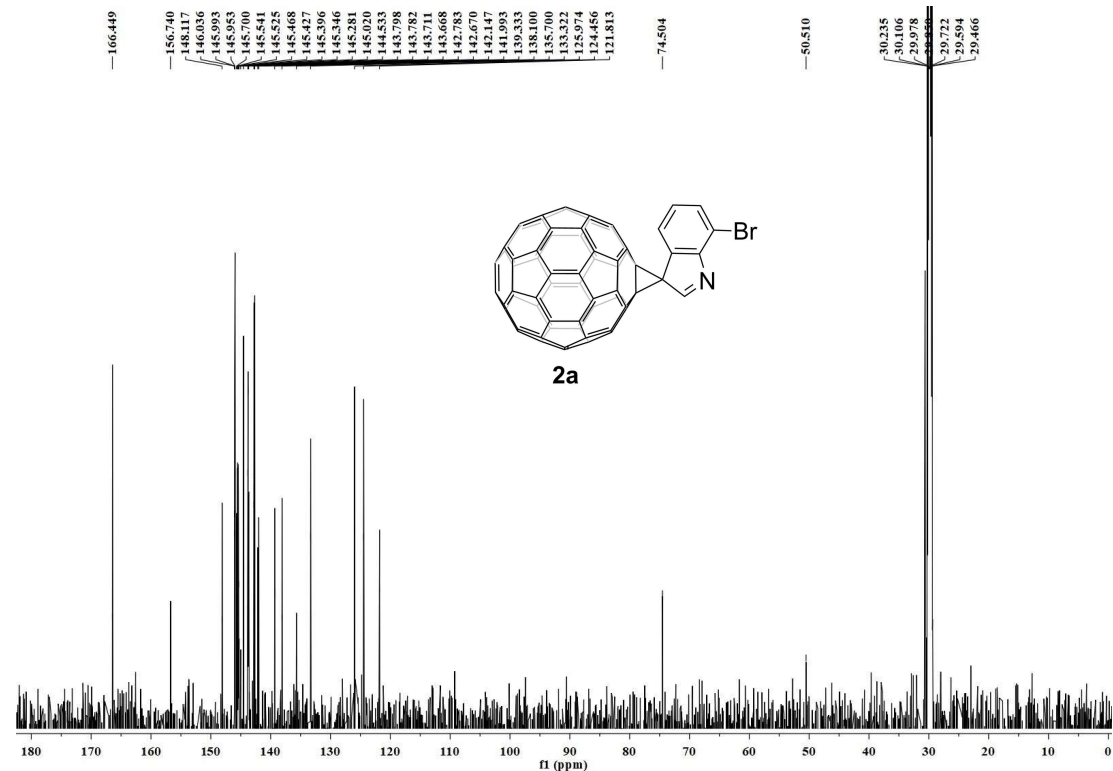
1e (17.4 mg, 0.02 mmol), Deoxofluor (36 μL, 0.20 mmol) were dissolved in chlorobenzene (5 mL) at 40°C under N₂ atmosphere. After 10 minutes of reaction, the color of the solution changed gradually from brown to deep red. Then, petroleum ether was added to the mixture to precipitate the product. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted **1e** (1.5 mg) and **2e** (11.1 mg, 65 %) as black amorphous solid. ¹H NMR (600 MHz, CS₂/d₆-DMSO) δ 9.66 (s, 1H), 8.71 (dd, *J* = 8.4, 5.4 Hz, 1H), 8.10 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.70 (td, *J* = 8.4, 2.4 Hz, 1H); ¹³C NMR (150 MHz, CS₂/d₆-acetone) (all 2C unless indicated) δ 168.61, 148.48, 146.51, 146.16, 146.07, 145.96, 145.72, 145.65, 145.60, 145.54, 145.49, 145.44, 144.67, 143.95, 143.89, 143.82, 143.78, 142.9, 142.88, 142.82, 142.74, 142.17, 142.09, 139.55, 138.29, 123.91, 123.84, 114.39, 114.23, 111.09, 110.93, 74.73, 50.66. FT-IR ν/cm⁻¹ (KBr) 1624, 1588, 1558, 1514, 1476, 1424, 1239, 1187, 1001, 790, 743, 702, 558, 526; UV-vis (CHCl₃) λ_{max}/nm 388, 430, 459, 686. HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]⁻ calcd for C₆₈H₄FN 853.0328; found 853.0334.

2. NMR Spectra of 2a-2e

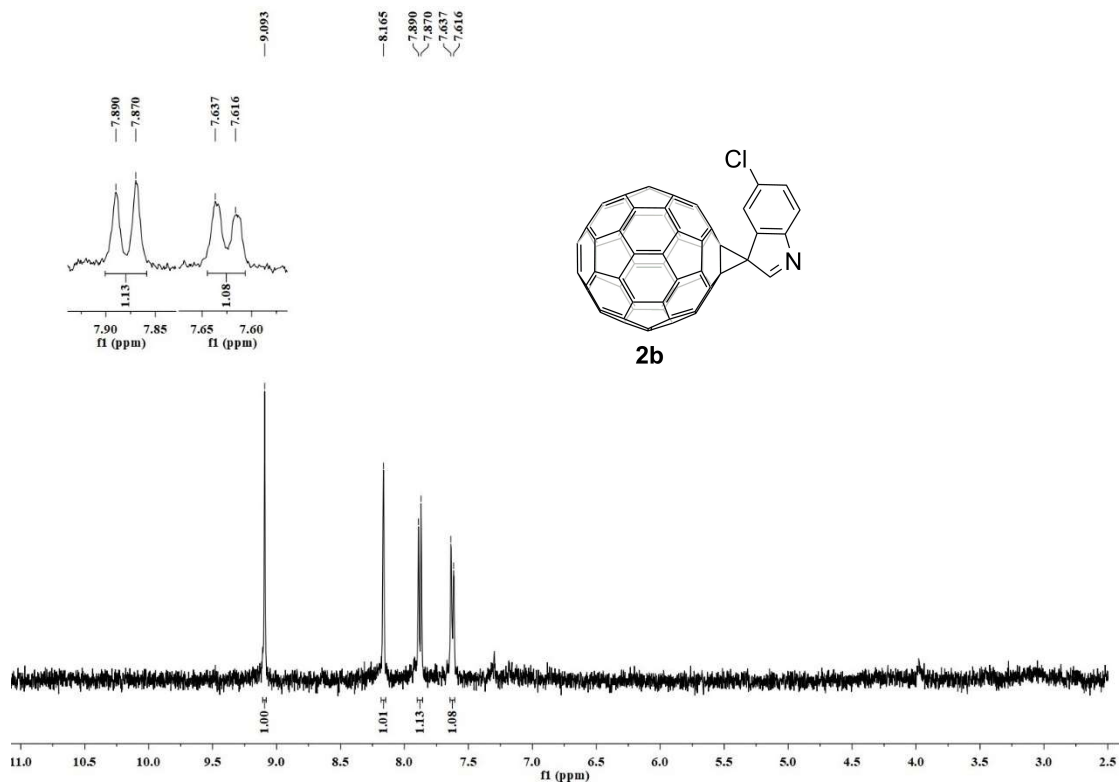
¹H NMR (400 MHz, CS₂/d₆-acetone) of compound 2a



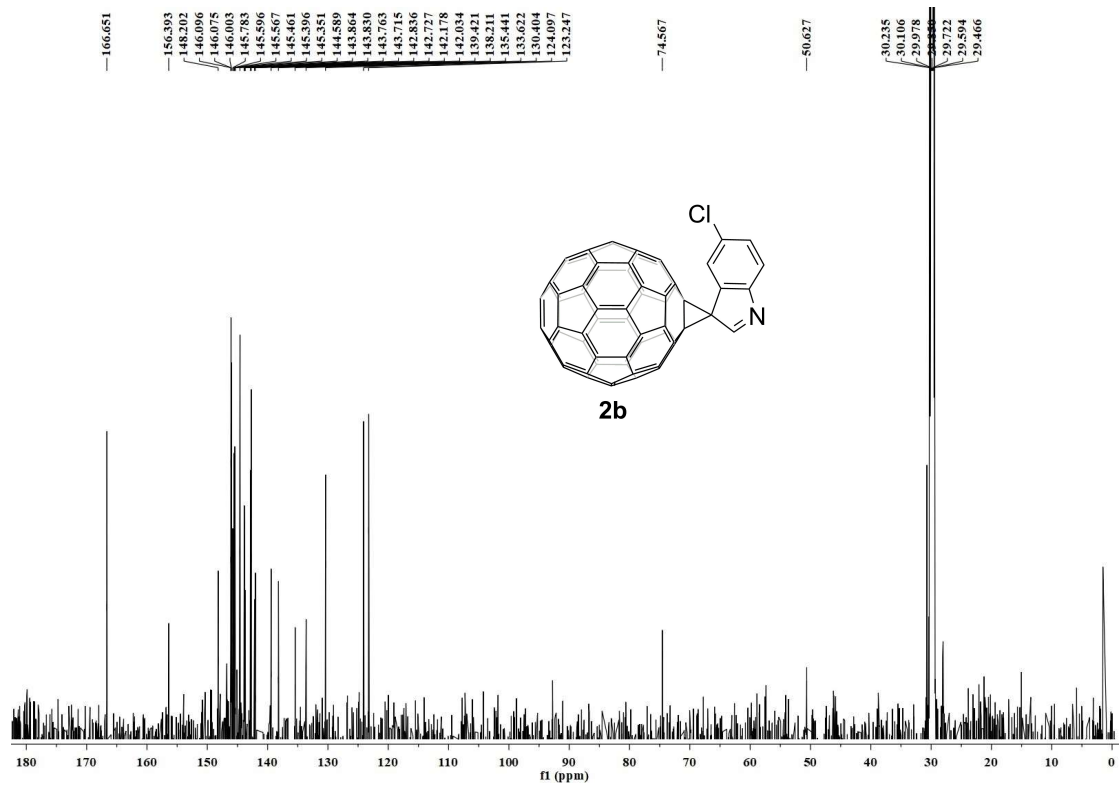
¹³C NMR (150 MHz, CS₂/d₆-acetone) of compound 2a



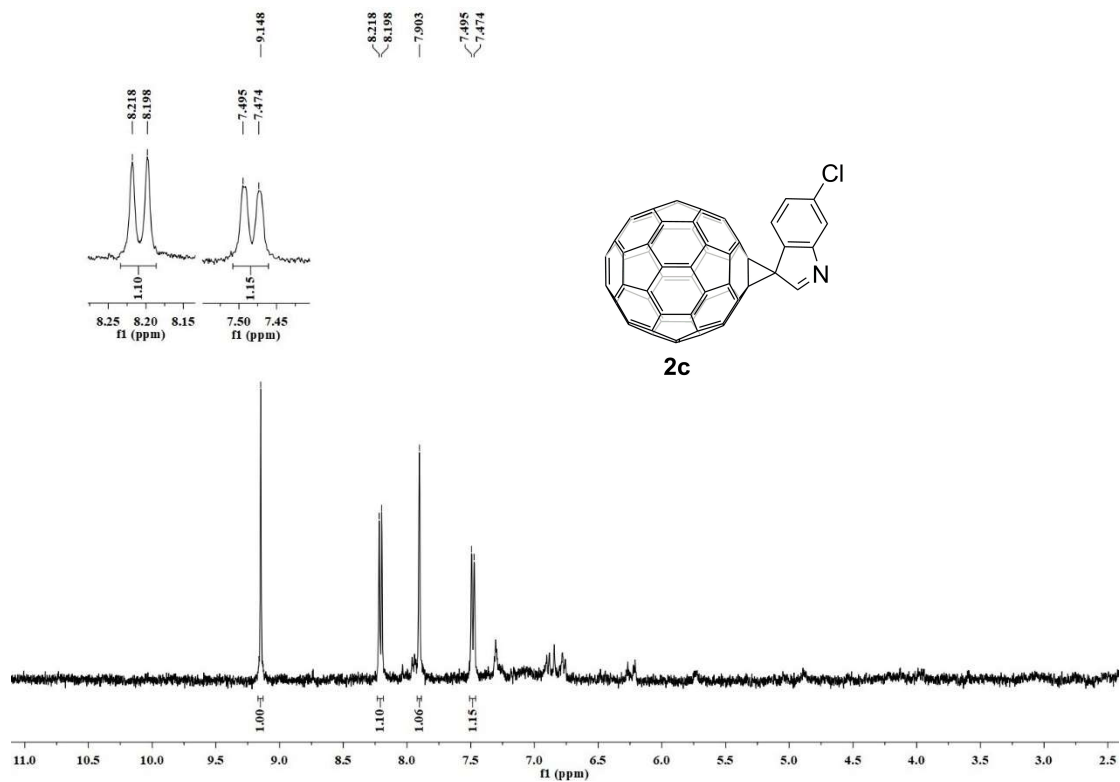
^1H NMR (400 MHz, CS_2/d_6 -acetone) of compound 2b



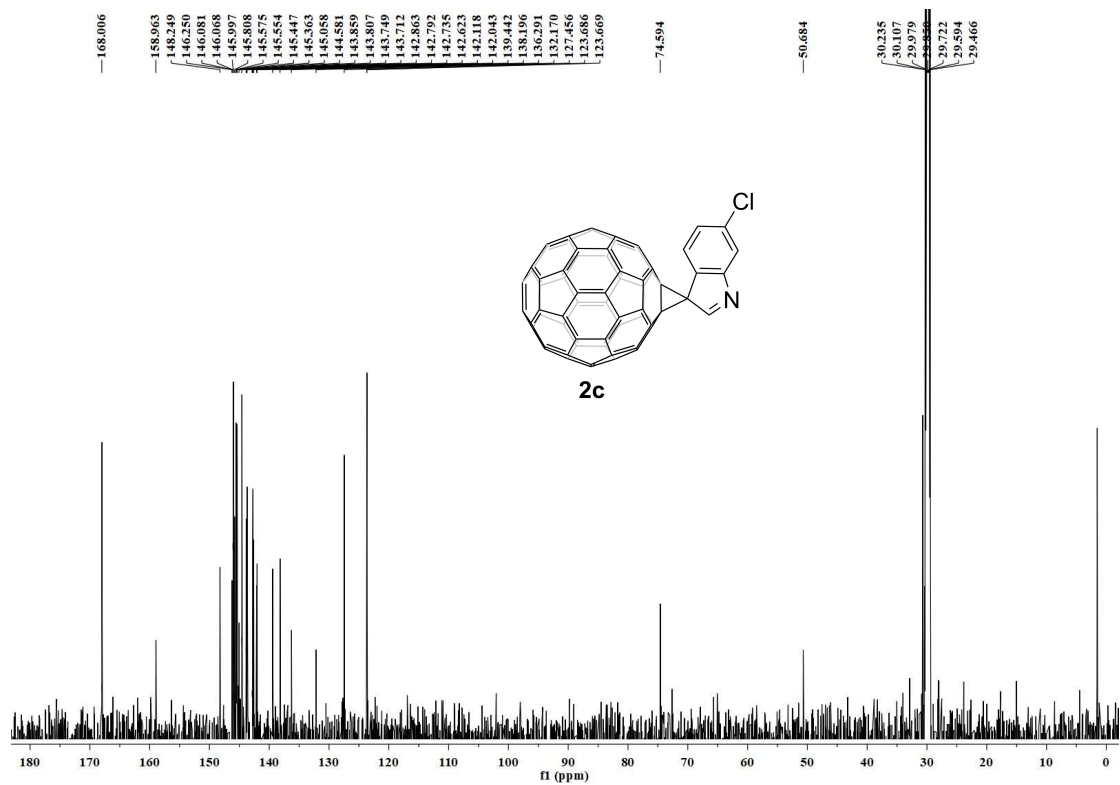
^{13}C NMR (150 MHz, CS_2/d_6 -acetone) of compound 2b



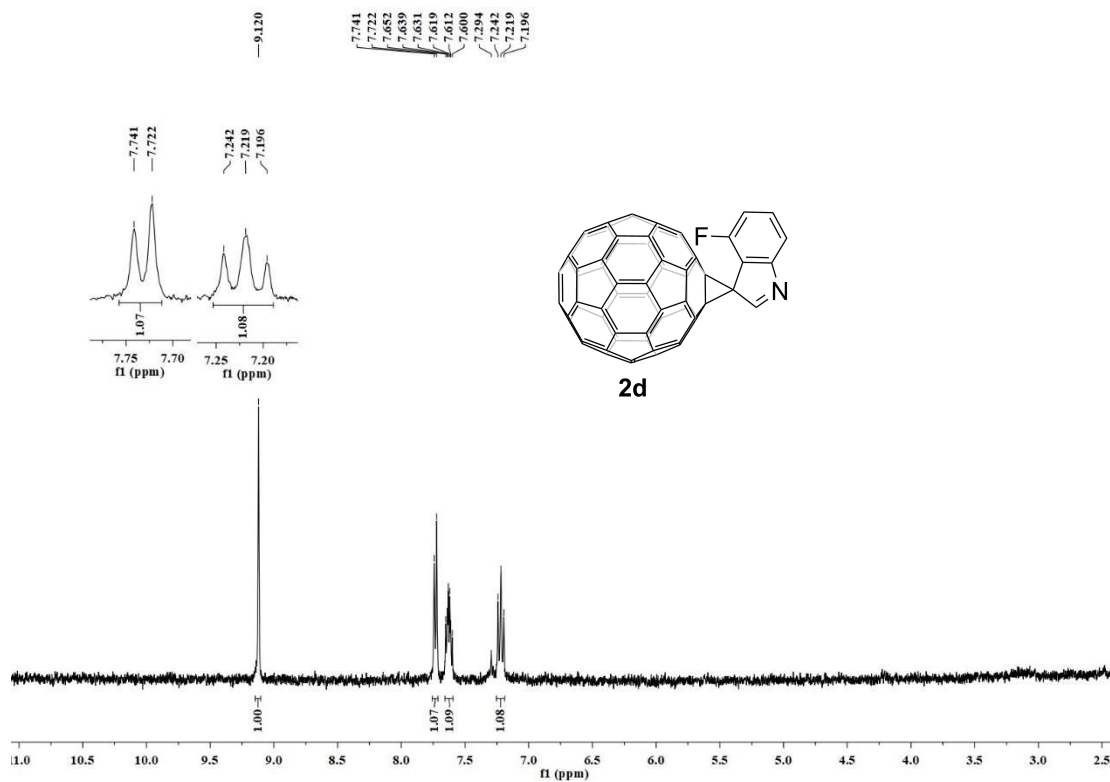
^1H NMR (400 MHz, CS_2/d_6 -acetone) of compound **2c**



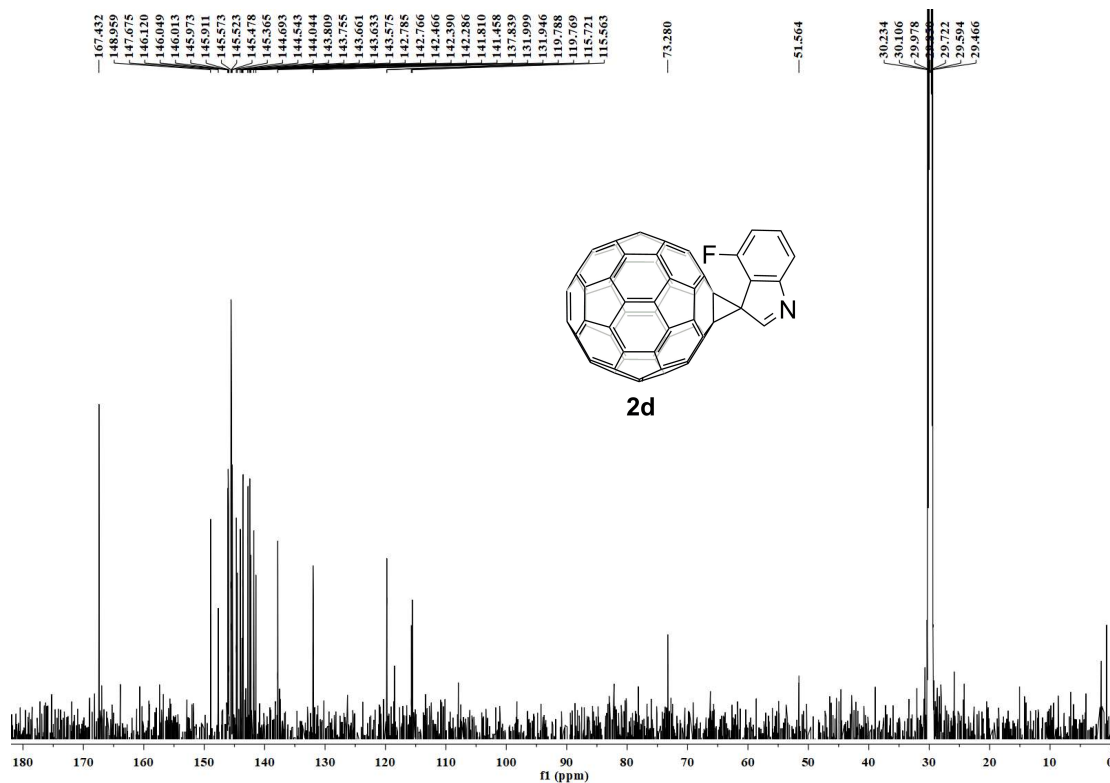
^{13}C NMR (150 MHz, CS_2/d_6 -acetone) of compound **2c**



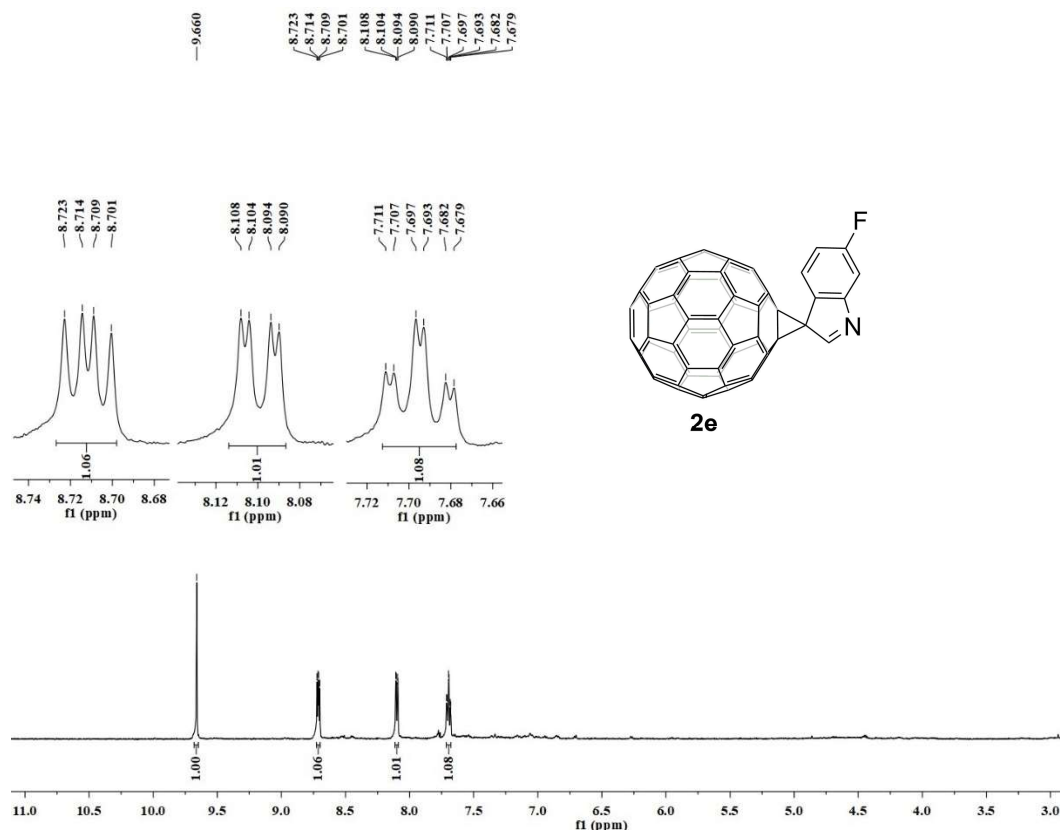
^1H NMR (400 MHz, CS_2/d_6 -acetone) of compound 2d



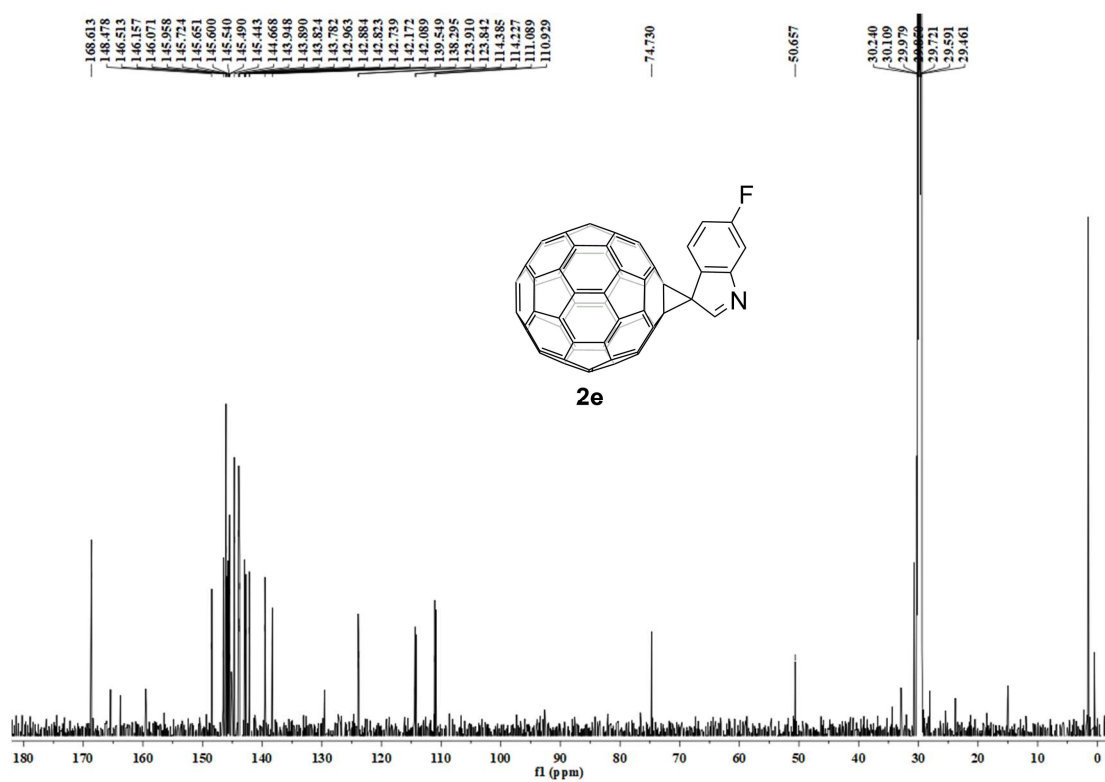
^{13}C NMR (150 MHz, CS_2/d_6 -acetone) of compound 2d



¹H NMR (400 MHz, CS₂/d₆-DMSO) of compound 2e



¹³C NMR (150 MHz, CS₂/d₆-acetone) of compound 2e



3. Single-Crystal X-Ray Crystallography of 2a

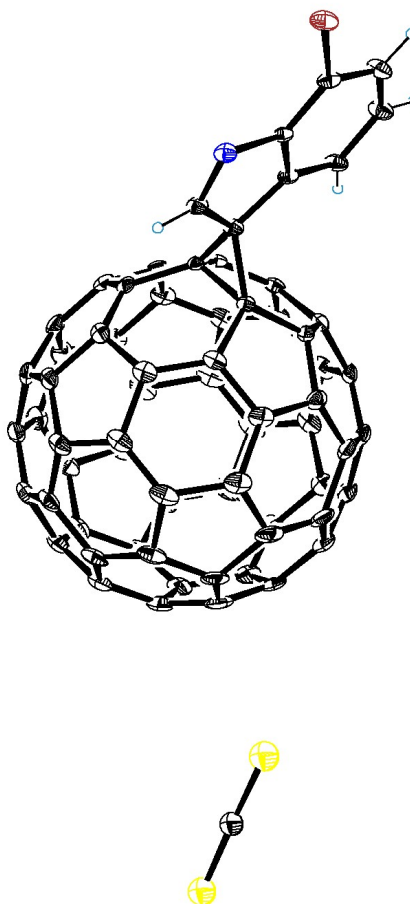


Figure S1 ORTEP diagram of **2a** with 20% thermal ellipsoids.

Black block crystals of **2a** suitable for X-ray diffraction were obtained from the slow evaporation of a solution containing CS₂ and *n*-hexane. Single-crystal X-ray diffraction data were collected on a diffractometer (DECTRIS PILATUS 300K, STOE & Cie GmbH) equipped with a CCD area detector using graphite-monochromated Cu K α radiation ($\lambda = 1.54184$ Å). The structure was solved with direct methods using SHELXS-97 and refined with full-matrix least-squares refinement using the SHELXL-97 program within OLEX2. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2298884.

Table 1 Crystal data and structure refinement for 2a	
Identification code	2a
Empirical formula	C ₆₈ H ₄ BrN ₂ S ₂
Formula weight	992.76
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	17.9648(10)
b/Å	14.7598(7)

c/Å	13.8606(8)
$\alpha/^\circ$	90
$\beta/^\circ$	100.983(4)
$\gamma/^\circ$	90
Volume/Å ³	3607.9(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.828
μ/mm^{-1}	3.127
F(000)	1972.0
Crystal size/mm ³	0.03 × 0.02 × 0.01
Radiation	CuK α ($\lambda = 1.54186$)
2 Θ range for data collection/ $^\circ$	10.032 to 138.802
Index ranges	-21 \leq h \leq 21, -17 \leq k \leq 10, -16 \leq l \leq 13
Reflections collected	20007
Independent reflections	6585 [$R_{\text{int}} = 0.0575$, $R_{\text{sigma}} = 0.0577$]
Data/restraints/parameters	6585/0/643
Goodness-of-fit on F ²	1.044
Final R indexes [$ I > 2\sigma(I)$]	$R_1 = 0.0752$, $wR_2 = 0.1970$
Final R indexes [all data]	$R_1 = 0.1087$, $wR_2 = 0.2269$
Largest diff. peak/hole / e Å ⁻³	1.28/-1.30

5. UV-vis absorption spectra of compounds 2a-2e

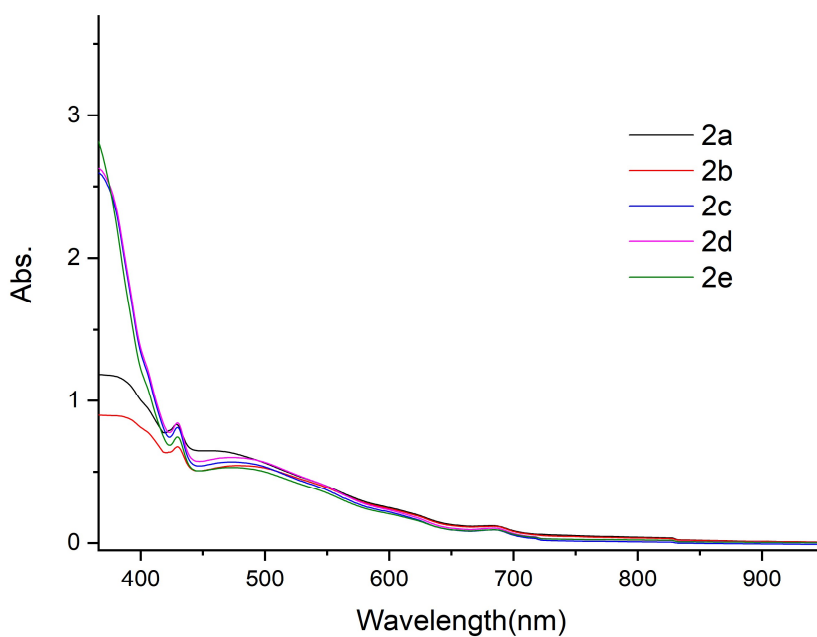


Figure S2. UV-vis spectra of **2a-2e** in CHCl₃