

Supporting Information

Mechanochemical transformation of tetraaryl[3]cumulenes to benzofulvenes via electrophilic iodocyclization

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General information

Mechanochemical reactions were carried out using grinding vessels in a POWTEQ GT 300 mill. Both jars and balls are made of stainless. The heat gun HAKKO FV-310 with temperature control function was used for high-temperature ball milling reactions. NMR spectra were recorded on a JEOL resonance JNM-ECZ-400 in CDCl₃ solutions. Chemical shifts are reported in parts per million (ppm) relative to TMS as an internal standard. The melting point was measured on a Yanaco MP-J13 micro melting-point apparatus and uncorrected. A high-resolution mass spectrum was recorded in a ThermoFisher Exactive. X-Ray single crystallographic analysis was conducted using a Rigaku R-AXIS RAPID II.

General Procedure for Mechanochemical Iodocyclization Reactions of Tetraaryl[3]cumulenes:

Tetraaryl[3]cumulene **1** (0.3 mmol) and *N*-iodosuccinimide (2.2 eq.) were placed in a ball milling vessel (stainless, 10 mL) loaded with two grinding balls (stainless, diameter: 15 mm). After the vessel was closed in the air without purging with inert gas, the vessel was placed in the ball mill (POWTEQ GT 300, 30 min at 25 Hz). After the reaction was quenched by saturated Na₂S₂O₃ aq., the reaction mixture was extracted with dichloromethane. Then, the organic layer was dried over MgSO₄ and concentrated *in vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents to give the corresponding benzofulvene **2**. The structures of **2**, except for **2g**, were determined by ¹H NMR spectroscopy with reference to our previous report. The structure of **2g** was determined by ¹H and ¹³C NMR spectroscopy, HRMS, and X-ray single crystallographic analysis.

2a: ¹H NMR (CDCl₃): δ = 6.46 (d, *J* = 7.9 Hz, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 7.03–7.11 (m, 2H), 7.28–7.30 (m, 2H), 7.37–7.49 (m, 13H).

This compound is known: F. Yagishita, K. Hoshi, Y. Yoshida, S. Ueta, K. Minagawa, Y. Imada, Y. Kawamura, *Eur. J. Org. Chem.* **2021**, 235–238.

2b: ¹H NMR (CDCl₃): δ = 2.07 (s, 3H), 2.40 (s, 3H), 2.41 (s, 3H), 2.45 (s, 3H), 6.32 (s, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 7.14–7.28 (m, 10H), 7.40 (d, *J* = 7.9 Hz, 2H).

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2c: ¹H NMR (CDCl₃): δ = 3.48 (s, 3H), 3.87 (s, 6H), 3.88 (s, 3H), 6.17 (d, *J* = 2.6 Hz, 1H), 6.61 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.9 Hz, 2H).

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2f: $^1\text{H NMR}$ (CDCl_3): δ = 3.42 (s, 3H), 3.86 (s, 3H), 6.00 (d, J = 2.3 Hz, 1H), 6.61 (dd, J = 8.2, 2.3 Hz, 1H), 6.99–7.02 (m, 3H), 7.29–7.31 (m, 2H), 7.37–7.46 (m, 10H).

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2g: $^1\text{H NMR}$ (CDCl_3): δ = 2.41 (s, 3H), 2.43 (s, 3H), 3.44 (s, 3H), 3.87 (s, 3H), 6.06 (d, J = 2.3 Hz, 1H), 6.60 (d, J = 8.3, 2.3 Hz, 1H), 6.99–7.03 (m, 3H), 7.18–7.28 (m, 8H), 7.46 (d, J = 8.6 Hz, 2H).

This compound is known: F. Yagishita, K. Hoshi, Y. Yoshida, S. Ueta, K. Minagawa, Y. Imada, Y. Kawamura, *Eur. J. Org. Chem.* **2021**, 235–238.

2h: orange solid; mp 184.0–185.0 °C; $^1\text{H NMR}$ (CDCl_3): δ = 3.50 (s, 3H), 3.87 (s, 3H), 6.07 (d, J = 2.3 Hz, 1H), 6.62 (dd, J = 8.2, 2.3 Hz, 1H), 6.99–7.03 (m, 3H), 7.20 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.42–7.45 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3): δ = 55.0, 55.3, 85.1, 109.4, 112.8, 113.7, 120.8, 128.3, 128.4, 129.1, 130.8, 132.5, 134.5, 135.4, 135.6, 136.5, 139.1, 139.5, 139.7, 140.7, 146.7, 153.7, 158.1, 159.6; HRMS (ESI-MS) m/z calcd for $\text{C}_{30}\text{H}_{21}\text{O}_2\text{Cl}_2\text{I}+\text{H}$ 611.0036 found 611.0031.

Single crystal X-ray structure analysis:

Crystal data of **2h**: monoclinic space group $P2_1/n$, a = 10.48395(19) Å, b = 10.77886(19) Å, c = 22.9750(4) Å, β = 102.103(7)°, V = 2538.58(10) Å³, Z = 4, ρ = 1.599 Mg/m³, in the final least-squares refinement cycles on F^2 , the model converged at R_1 = 0.0300, wR_2 = 0.0782, and GOF = 1.053 for 4636 reflections CCDC2340176.

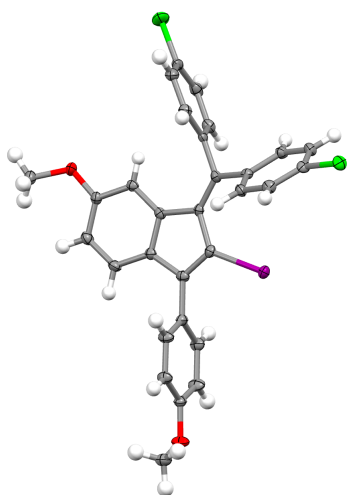


Figure S1. ORTEP drawing of **2h** and thermal ellipsoids at 50% probability,

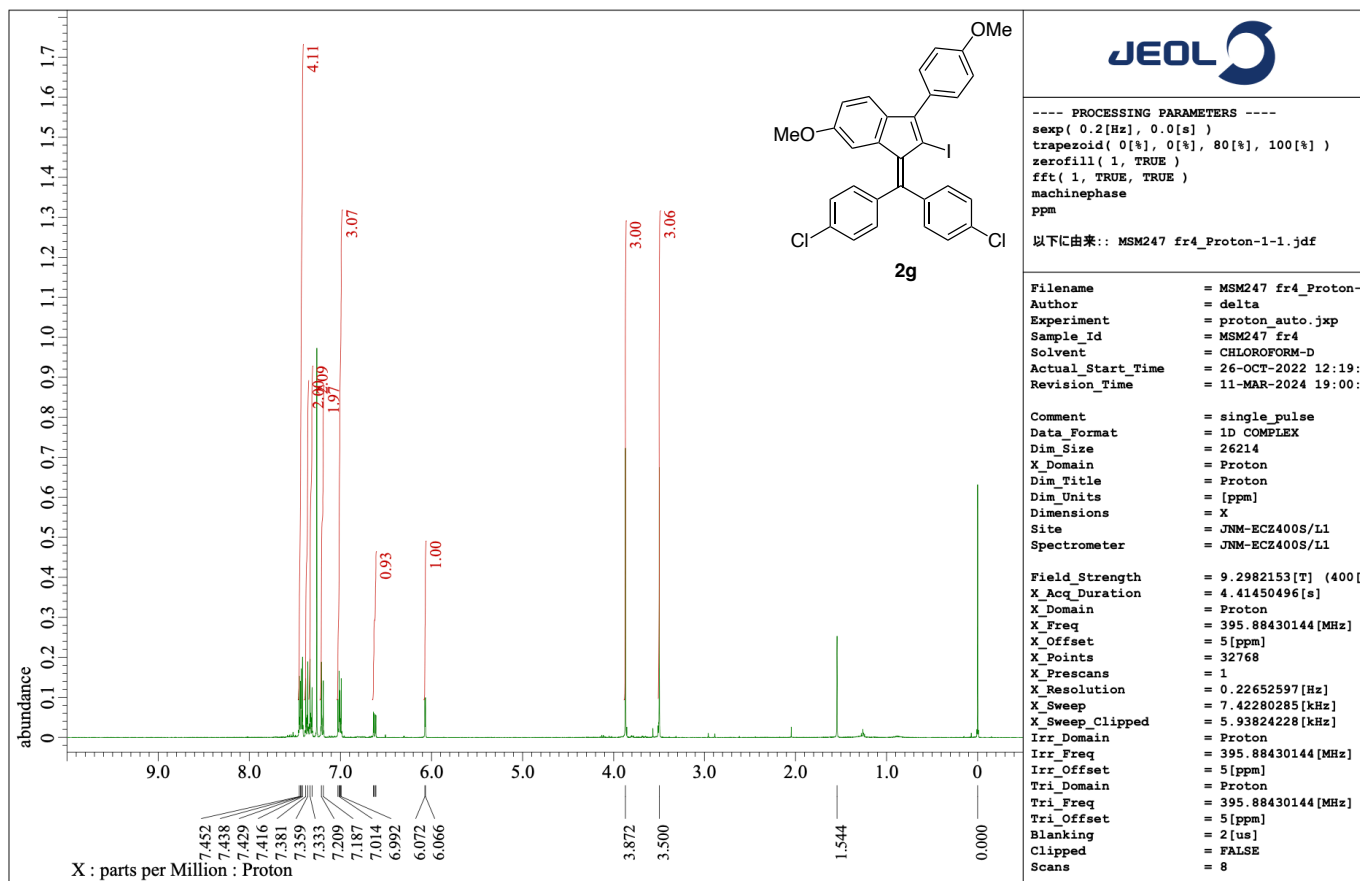
Mechanochemical Iodocyclization Reactions of 1a under high-temperature conditions:

Tetraphenyl[3]cumulene **1** (0.3 mmol) and *N*-iodosuccinimide (1.2 equiv.) were placed in a ball milling vessel (stainless, 10 mL) loaded with two grinding balls (stainless, diameter: 15 mm). After the vessel was closed in the air without purging with inert gas, the vessel was placed in the ball mill (POWTEQ GT 300, 30 min at 25 Hz) and a heat gun (the preset temperature at 245 °C). After 30 min, the jar was then cooled rapidly with cold water and opened. Then, the reaction was quenched by saturated Na₂S₂O₃ aq., and the reaction mixture was extracted with dichloromethane. After the organic layer was dried over MgSO₄ and concentrated *in vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 0.27 mmol of **2a** was separated in 90% yield.

Mechanochemical Suzuki–Miyaura Cross-Coupling Reaction:

Benzofulvene **2a** (0.3 mmol), *p*-methoxyphenylboronic acid (0.6 mmol, 2.0 equiv.), tetrakis(triphenylphosphine)palladium (0.015 mmol, 5 mol%), and K₂CO₃ (1.5 mmol, 5.0 equiv.) were placed in a ball milling vessel (stainless, 5 mL) loaded with two grinding balls (stainless, diameter: 10 mm). Then, 38 µL of mixtures of toluene and H₂O (9 : 1) were added via a syringe. After the vessel was closed in the air without purging with inert gas, the vessel was placed in the ball mill (POWTEQ GT 300, 30 min at 25 Hz) and a heat gun (the preset temperature at 245 °C). After 30 min, the jar was then cooled rapidly with cold water and opened. The reaction mixture was poured into water and extracted with ethyl acetate, then the organic layer was dried over MgSO₄, and concentrated *in vacuo*. The residual mixture was subjected to chromatography on silica gel using mixtures of ethyl acetate and hexane as eluents, and 0.294 mmol of **3** was separated in 98% yield.

¹H NMR of 2h



¹³C NMR of 2h

