

Access to Aryl Azides via Copper Powder-Catalyzed Cross-coupling of Arylboronic Acids with Hypervalent Azido-iodine Reagent ABZ(I)

Zhifang Yang,^a Feng-Huan Du,^b Chi Zhang,^{b,*} and Yunfei Du^{a,*}

^a Tianjin Key Laboratory for Modern Drug Delivery & High-Efficiency, School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China;
Email: duyunfeier@tju.edu.cn

^b State Key Laboratory of Elemento-Organic Chemistry, The Research Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China; zhangchi@nankai.edu.cn

Supporting Information

I	General Information	S1
II	Experimental Procedures and Spectroscopic Data	S2-S17
III	Computational Results	S18-S39
IV	References	S40-S42
V	NMR Spectra of Starting Materials and Products	S43-S95

I. General Information

^1H and ^{13}C NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer at 25 °C. Chemical shifts values are given in ppm and referred as the internal standard to TMS: 0.00 ppm. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), q (quadruple), dd (doublet of doublet), m (multiplet), etc. The coupling constants J , are reported in Hertz (Hz). High resolution mass spectrometry (HRMS) data were recorded on Q Exactive HF (Q ExactiveTM HF/UltiMateTM 3000 RSLCnano) using electron spray ionization (ESI) in positive (or negative) mode. Melting points were determined with a Micromelting point apparatus. TLC plates were visualized by exposure to ultraviolet light.

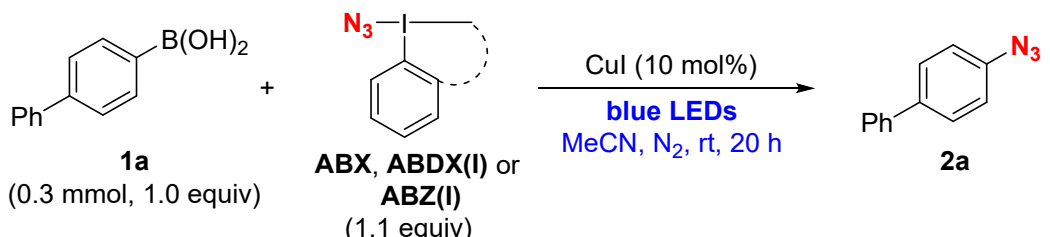
Reagents and solvents were purchased as reagent grade and were used without further purification. All reactions were performed in standard glassware, heated at 70 °C for 3 h before used. Flash column chromatography was performed over silica gel (200-300 m) using a mixture of ethyl acetate (EtOAc) and petroleum ether (PE).

II. Experimental Procedures and Spectroscopic Data

1. Optimization of the Reaction Conditions of **1a**.

To a 20 mL of Schlenk tube were added 4-biphenylboronic acid **1a** (0.3 mmol, 60 mg, 1.0 equiv), hypervalent azido-iodine reagent (0.33 mmol, 1.1 equiv) and copper catalyst (0.03 mmol, 10 mol%; Meryer, 99.9%, 200 mesh) under N₂ atmosphere, followed by addition of the solvent (4 mL). The tube was screw-capped and stirred at room temperature under visible-light irradiation with blue LED (5 W). After stirring for 20 h, the reaction mixture was diluted with dichloromethane, filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by silica gel chromatography (PE:EtOAc = 100:1) to afford **2a** as a white solid.

Table S1. Screening of Hypervalent Azido-iodine Reagents. ^a



The reaction scheme shows 4-biphenylboronic acid (**1a**) reacting with a hypervalent azido-iodine reagent (ABX, ABDX(I), or ABZ(I)) in the presence of CuI (10 mol%) in MeCN under N₂ at room temperature for 20 hours, irradiated with blue LEDs, to produce 4-azidobiphenyl (**2a**).

Entry	N ₃ source	Yield of 2a (%) ^b
1	ABZ(I)	93
2	ABDX(I)	31
3	ABX	0

^a Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), hypervalent azido-iodine reagent (0.33 mmol, 1.1 equiv), CuI (10 mol%), MeCN (4 mL), blue LED (5 W). ^b Isolated yield based on **2a**.

Table S2. Screening of Solvents. ^a

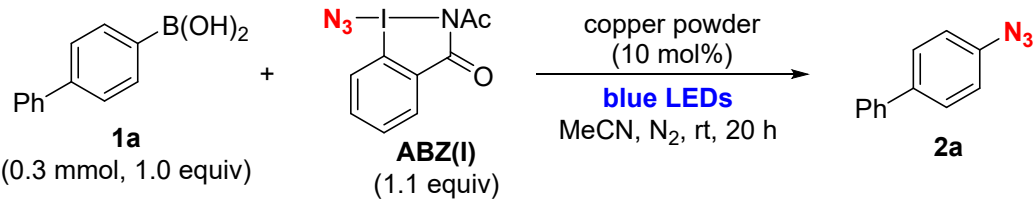
Entry	Solvent	Yield of 2a (%) ^b
1	MeCN	93 (78)^c
2	THF	11
3	1,4-dioxane	7
4	DMF	71
5	HFIP	0
6	toluene	0
7	CHCl ₃	85
8	DCE	88
9 ^d	MeCN/H ₂ O	trace

^a Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **ABZ(I)** (0.33 mmol, 1.1 equiv), CuI (10 mol%), solvent (4 mL), blue LED (5 W). ^b Isolated yield based on **2a**. ^c Wet acetonitrile (4 mL) was used as the solvent. ^d MeCN/H₂O (3.5 mL/0.5 mL) was used as the solvent.

Table S3. Screening of Copper Catalysts. ^a

Entry	Catalyst	Yield of 2a (%) ^b
1	CuI	93
2	CuBr	90
3	CuCl	83
4	Cu ₂ O	trace
5	CuBr ₂	56
6	Cu(OAc) ₂	64
7	Cu(OTf) ₂	78
8	copper powder	95
9	none	nd

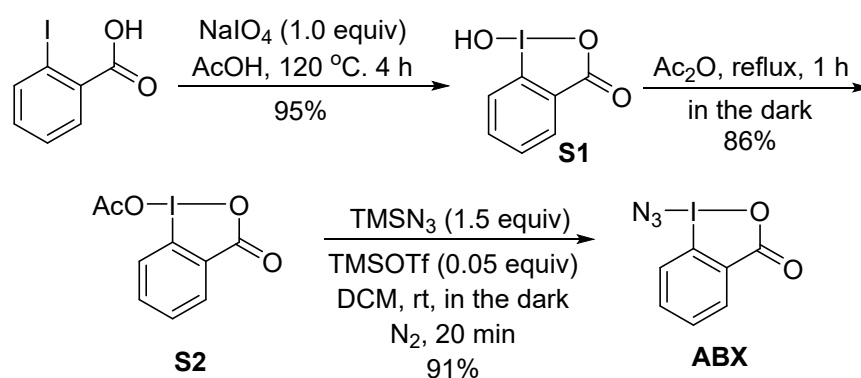
^a Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **ABZ(I)** (0.33 mmol, 1.1 equiv), Cu salt (10 mol%), acetonitrile (4 mL), blue LED (5 W). ^b Isolated yield based on **2a**. nd, not detected.

Table S4. Screening of Light Irradiation and Temperature. ^a

Entry	Conditions	Yield of 2a (%) ^b
1	standard condition	95
2	in the dark	36
3	in the dark under 60 °C	85
4	white LED (5 W)	74

^a Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **ABZ(I)** (0.33 mmol, 1.1 equiv), copper powder (10 mol%), acetonitrile (4 mL), blue LED (5 W). ^b Isolated yield based on **2a**.

2. Synthesis of and Characterization Data of Compounds **ABX**, **ABDX(I)** and **ABZ(I)**.



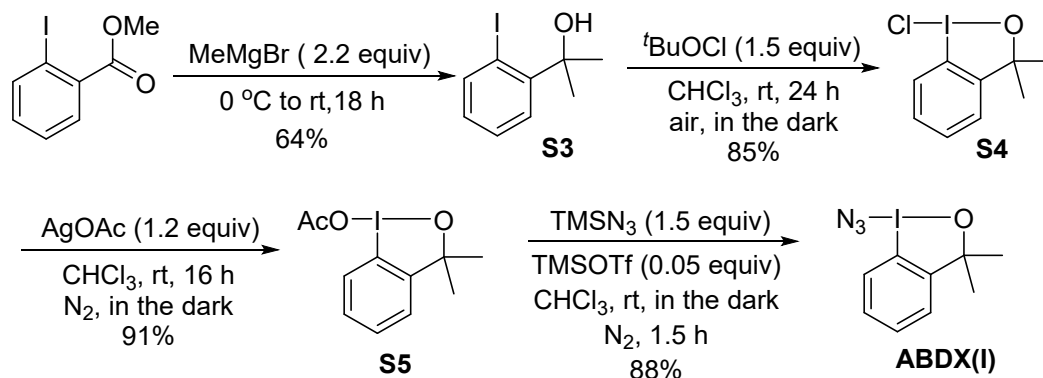
ABX was prepared according to the literature procedure.¹

Preparation of S1: To a 500 mL round-bottomed flask equipped with an stirrer bar were added 2-iodo benzoic acid (8.0 g, 32.2 mmol, 1.0 equiv), 2-iodobenzamide NaIO₄ (7.24 g, 33.8 mmol, 1.0 equiv), and 30% (v:v) aq. AcOH (48 mL) under air. The mixture was vigorously stirred at 120 °C and refluxed. After stirring for 4 h, the reaction mixture was cooled to room temperature and diluted with cold water (180 mL), protecting it from light. The mixture was then filtered and further washed with ice water and cold acetone, air dried in the dark overnight to give the pure compound **S1** (8.5 g, 95%) as a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.04 (s, 1H), 8.01 (dd, *J* = 7.6, 1.6 Hz,

1H), 7.96 (td, $J = 8.4, 1.2$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.70 (td, $J = 7.6, 1.2$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 168.2, 135.0, 132.0, 131.6, 130.9, 126.8, 120.9.

Preparation of S2: To a 500 mL round-bottomed flask equipped with an stirrer bar were added compound **S1** (8.5 g, 32.2 mmol, 1.0 equiv) and acetic anhydride (30 mL). Then the reaction mixture was stirred and reflux at 110 °C. Until the solution turned clear (without suspension), reaction was cool down to room temperature and white crystals started to form. The crystallization was continued at -18 °C. The crystals were then collected and dried overnight under high vacuum to give compound **S2** (8.5 g, 86%) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 8.19 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.96 (d, $J = 7.6$ Hz, 1H), 7.91 (td, $J = 8.8, 1.6$ Hz, 1H), 7.67 (td, $J = 8.0, 1.2$ Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.2, 168.1, 136.0, 132.9, 131.2, 129.2, 128.8, 118.2, 20.1.

Preparation of ABX: To a 150 mL two-necked round-bottomed flask equipped with a stirrer bar were added compound **S2** (1.00 g, 3.28 mmol, 1.00 equiv) and DCM (30 mL) under N_2 atmosphere, followed by the careful addition of TMSN_3 (4.9 mol, 0.66 mL, 1.5 equiv) and TMSOTf (0.16 mmol, 30 μL , 0.05 equiv). The reaction mixture was stirred at room temperature for 20 min in the dark. After the completion of the reaction, the mixture was then evaporated to give a yellow precipitate, which was washed a few times with hexane to give **ABX** (0.86 g, 91%) as a pure yellow crystal. ^1H NMR (400 MHz, CDCl_3) δ 8.33 – 8.29 (m, 1H), 8.02 – 7.97 (m, 2H), 7.81 – 7.76 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 136.2, 133.5, 131.8, 129.5, 126.5, 117.8.



ABDX(I) was prepared according to the literature procedure.¹⁻²

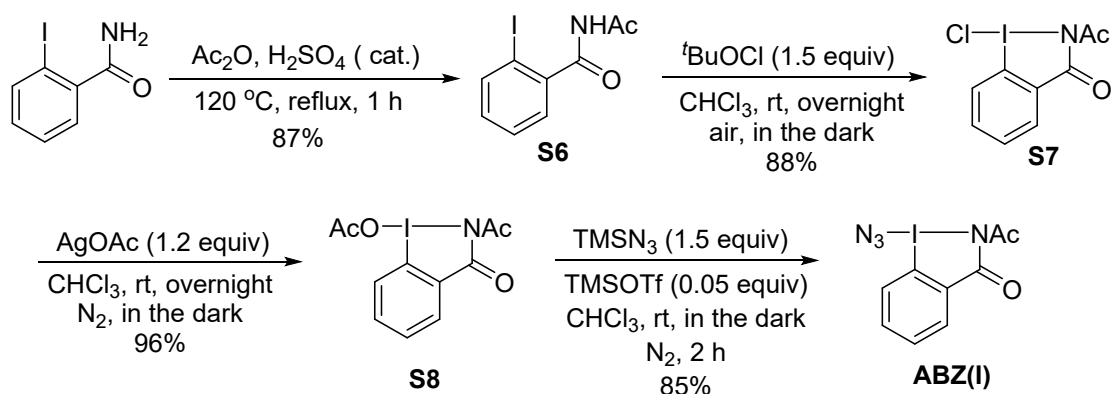
Preparation of S3: To a 500 mL round-bottomed flask equipped with a stirrer bar were added methyl 2-iodobenzoate (21 g, 80 mmol, 1.0 equiv) and 100 mL dry diethyl ether under N₂ atmosphere, then the solution was cooled down at 0 °C with an ice bath. Methylmagnesium bromide (176.0 mL, 176 mmol, c = 1.0 M, 2.20 equiv) was added dropwise and the reaction was stirred for 60 min at 0 °C. The reaction mixture was then allowed to warm to room temperature and it was further stirred for 20 h. When the reaction was completed, the reaction was quenched with sat. aq. NH₄Cl (150 mL) in an iced bath. The organic layer was separated and extracted with Et₂O (3 × 100 mL), water (2 × 200 mL), brine (1 × 100 mL) and the combined organic layers were dried over MgSO₄. The solvent was concentrated *in vacuum*. The residue was further purified by silica gel chromatography (PE:EtOAc = 10:1) to afford compound **S3** as yellow oil (13.44 g, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.32 (td, *J* = 8.2, 1.2 Hz, 1H), 6.90 (td, *J* = 7.6, 1.6 Hz, 1H), 1.76 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 148.4, 142.7, 128.6, 128.1, 126.7, 93.1, 73.6, 29.8.

Preparation of S4: To a 200 mL round-bottomed flask equipped with a stirrer bar were added compound **S3** (2.62 g, 10 mmol, 1.0 equiv), *t*-BuOCl (1.7 mL, 15 mmol, 1.5 equiv) and 100 mL CHCl₃. The reaction mixture was stirred at room temperature for 24 h in the dark under air. The precipitate was filtered and washed with *n*-hexane (50 mL) to give compound **S4** as a yellow solid (2.5 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ 8.01 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.16 (dd, *J* = 7.2, 1.6 Hz, 1H),

1.55 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 130.9, 130.4, 128.3, 126.0, 114.5, 85.1, 29.1.

Preparation of **S5**: To a 150 mL two-necked round-bottomed flask equipped with a stirrer bar were added compound **S4** (2.1 g, 7.1 mmol, 1.0 equiv), AgOAc (1.4 g, 8.5 mmol, 1.2 equiv) and 60 mL CHCl_3 under N_2 atmosphere. The reaction mixture was stirred at room temperature in the dark for 16 h. The mixture was filtered through a pad of Celite and washed with CHCl_3 (80 mL), then were concentrated in vacuum to give compound **S5** as a light white solid (2.1 g, 85%). ^1H NMR (400 MHz, CDCl_3) δ 7.80 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.57 – 7.41 (m, 2H), 7.18 (dd, $J = 7.2, 1.6$ Hz, 1H), 2.11 (s, 3H), 1.53 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 177.3, 149.3, 130.3, 129.9, 129.8, 126.1, 115.6, 84.5, 29.1, 21.4.

Preparation of **ABDX(I)**: To a 150 mL two-necked round-bottomed flask equipped with a stirrer bar were added compound **S5** (0.64 g, 2.0 mmol, 1.00 equiv) and CHCl_3 (25 mL) under N_2 atmosphere, followed by the careful addition of TMSN_3 (3 mol, 0.46 mL, 1.5 equiv) and TMSOTf (0.1 mmol, 18 μL , 0.05 equiv). The reaction mixture was stirred at room temperature for 1.5 h in the dark. When the reaction was completed, the reaction mixture was evaporated to give a yellow precipitate, which was washed a few times with hexane to give **ABDX(I)** (0.53 g, 88%) as a pure yellow crystal. ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.9$ Hz, 1H), 7.65 – 7.49 (m, 2H), 7.22 (d, $J = 6.9$ Hz, 1H), 1.53 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 130.8, 130.3, 127.8, 126.6, 114.1, 83.2, 29.4.



ABZ(I) was prepared according to the literature.²

Preparation of S6: To a 250 mL round-bottomed flask equipped with a stirrer bar were added 2-iodobenzamide (50 g, 0.2 mol, 1.0 equiv), acetic anhydride (100 mL), and 5 drops of conc. H₂SO₄. Then the reaction mixture was heated to 120 °C and refluxed in the dark. The reaction was monitored by TLC. After the starting material was consumed completely, the reaction mixture was cooled to room temperature and washed with sat. aq. NaHCO₃ and extracted with EtOAc (3 × 200 mL), dried over anhydrous MgSO₄ and concentrated *in vacuum*. The crude material was purified by flash column chromatography (PE: EtOAc = 5 :1) to give compound **S6** as a white solid (50 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ 8.59 (br, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 4.4 Hz, 2H), 7.20 – 7.12 (m, 1H), 2.54 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 167.7, 140.3, 134.0, 132.2, 128.3, 128.2, 91.9, 25.4.

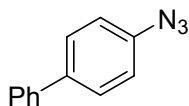
Preparation of S7: To a 250 mL round-bottomed flask equipped with a stirrer bar were added compound **S6** (5.3 g, 18.4 mmol, 1.0 equiv), *t*-BuOCl (3.2 mL, 28 mmol, 1.5 equiv) and 100 mL CHCl₃. The reaction mixture was stirred at room temperature overnight in the dark under air. The precipitate was filtered and washed with *n*-hexane (50 mL) to give compound **S7** as a white solid (5.2 g, 88%). ¹H NMR (400 MHz, CDCl₃) δ 8.49 (dd, *J* = 9.0, 0.4 Hz, 1H), 8.21 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.94 (td, *J* = 8.8, 1.6 Hz, 1H), 7.78 (td, *J* = 7.6, 0.8 Hz, 1H), 2.67 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 175.5, 161.5, 136.8, 134.4, 132.4, 131.6, 128.3, 114.0, 25.6.

Preparation of **S8**: To a 150 mL two-necked round-bottomed flask equipped with a stirrer bar were added compound **S7** (3.24 g, 10 mmol, 1.0 equiv), AgOAc (2.0 g, 12 mmol, 1.2 equiv) and 60 mL CHCl₃ under N₂ atmosphere. The reaction mixture was stirred at room temperature overnight in the dark. When the reaction was completed, the mixture was filtered through a pad of Celite and washed with CHCl₃ (80 mL). The solvent was concentrated in vacuum to give compound **S8** as a white solid (3.3 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.86 (td, *J* = 8.8, 1.6 Hz, 1H), 7.70 (td, *J* = 7.6, 0.8 Hz, 1H), 2.64 (s, 3H), 2.17 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.0, 176.2, 162.4, 136.3, 134.7, 132.1, 130.9, 130.3, 115.6, 25.7, 21.4.

Preparation of **ABZ(I)**: To a 150 mL two-necked round-bottomed flask equipped with a stirrer bar were added compound **S8** (2.6 g, 7.5 mmol, 1.00 equiv) and CHCl₃ (60 mL) under N₂ atmosphere. Followed the careful addition of TMSN₃ (11.3 mmol, 1.7 mL, 1.5 equiv) and TMSOTf (0.75 mmol, 136 μL, 0.05 equiv). The reaction mixture was stirred at room temperature for 2 h in the dark. When the reaction was completed, the reaction mixture was evaporated to give a yellow precipitate, which was washed a few times with hexanes to give **ABZ(I)** (2.1 g, 85%) as a pure yellow crystal. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.19 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 6.6 Hz, 1H), 8.00 (t, *J* = 7.7 Hz, 1H), 7.81 (t, *J* = 7.4 Hz, 1H), 2.52 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 175.8, 163.2, 136.8, 135.0, 131.9, 131.6, 129.0, 117.0, 26.1.

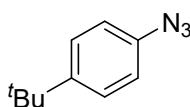
3. General Procedure and Characterization Data of Compounds 2a-2v.

To a 20 mL of Schlenk tube were added arylboronic acid **1** (0.3 mmol, 1.0 equiv), **ABZ(I)** (0.33 mmol, 1.1 equiv) and copper powder (0.03 mmol, 2 mg, 10 mol%) under N₂ atmosphere, followed by addition of acetonitrile (4 mL). The tube was screw-capped and stirred at room temperature under visible-light irradiation with blue LED (5 W). After stirring for 20 h, the reaction mixture was diluted with dichloromethane, filtered through a pad of Celite and concentrated in vacuum. The residue was purified with silica gel chromatography (PE/EtOAc) to afford **2**.



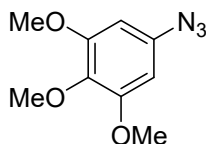
4-Azido-1,1'-biphenyl (**2a**).

The product **2a** (56 mg, 95% yield) [known compound]³ was purified with silica gel chromatography (PE:EtOAc = 80:1) as a light yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (t, *J* = 8.6 Hz, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 140.1, 139.1, 137.9, 128.8, 128.4, 127.3, 126.8, 119.4.



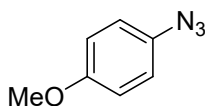
1-Azido-4-(*tert*-butyl)benzene (**2b**).

The product **2b** (46 mg, 85% yield) [known compound]⁴ was purified with silica gel chromatography (PE:EtOAc = 100:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 1.31 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 148.0, 137.1, 126.7, 118.6, 34.4, 31.3.



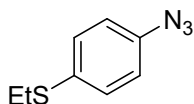
5-Azido-1,2,3-trimethoxybenzene (**2c**).

The product **2c** (51 mg, 82% yield) [known compound]⁴ was purified with silica gel chromatography (PE:EtOAc = 40:1) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 6.24 (s, 2H), 3.84 (s, 6H), 3.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 154.01, 135.59, 135.25, 96.31, 60.94, 56.11.



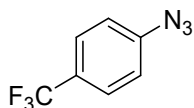
1-Azido-4-methoxybenzene (**2d**).

The product **2d** (38 mg, 84% yield) [known compound]³ was purified with silica gel chromatography (PE:EtOAc = 60:1) as yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 6.96 (d, *J* = 9.1 Hz, 2H), 6.89 (d, *J* = 9.1 Hz, 2H), 3.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.0, 132.3, 112.0, 115.1, 55.5.



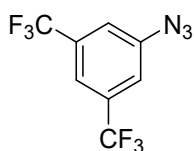
(4-Azidophenyl)(ethyl)sulfane (2e).

The product **2e** (41 mg, 76% yield) was purified with silica gel chromatography (PE:EtOAc = 20:1) as orange oil. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 2.91 (q, *J* = 7.3 Hz, 2H), 1.29 (t, *J* = 7.3 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 138.0, 132.6, 131.2, 119.5, 28.4, 14.3. MS (EI): *m/z* (%) 180.2 (M+H)⁺. HRMS (EI): Calcd. for C₈H₁₀N₃S: 180.2485 (M+H)⁺; Found: 180.0592.



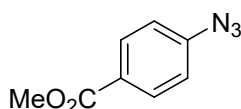
1-Azido-4-(trifluoromethyl)benzene (2f).

The product **2f** (35 mg, 63% yield) [known compound]⁵ was purified with silica gel chromatography (PE:EtOAc = 150:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.2 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) δ 143.7, 127.1 (q, *J* = 32.8 Hz), 127.0 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.0 Hz), 119.2.



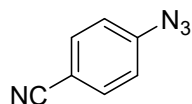
1-Azido-3,5-bis(trifluoromethyl)benzene (2g).

The product **2g** (43 mg, 56% yield) [known compound]⁵ was purified with silica gel chromatography (PE:EtOAc = 150:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.44 (s, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2 (s, 6F). ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 133.5 (q, *J* = 33.7 Hz), 122.8 (q, *J* = 271.2 Hz), 119.2 (q, *J* = 3.5 Hz), 118.5 (m).



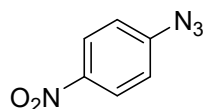
Methyl 4-azidobenzoate (2h).

The product **2h** (36 mg, 68% yield) [known compound]⁶ was purified with silica gel chromatography (PE:EtOAc = 30:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 144.7, 131.4, 126.6, 118.8, 52.1.



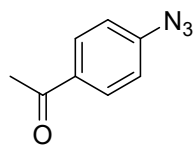
4-Azidobenzonitrile (**2i**).

The product **2i** (31 mg, 72% yield) [known compound]⁵ was purified with silica gel chromatography (PE:EtOAc = 30:1) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 133.8, 119.7, 118.4, 108.3.



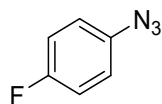
1-Azido-4-nitrobenzene (**2j**).

The product **2j** (23 mg, 46% yield) [known compound]³ was purified with silica gel chromatography (PE:EtOAc = 40:1) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 9.1 Hz, 2H), 7.14 (d, *J* = 9.1 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 144.6, 125.6, 119.4.



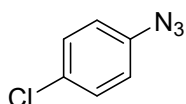
1-(4-Azidophenyl)ethan-1-one (**2k**).

The product **2k** (37 mg, 76% yield) [known compound]³ was purified with silica gel chromatography (PE:EtOAc = 40:1) as an orange solid. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 2.58 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.5, 144.9, 133.8, 130.2, 118.9, 26.5.



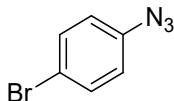
1-Azido-4-fluorobenzene (**2l**).

The product **2l** (22 mg, 54% yield) [known compound]⁴ was purified with silica gel chromatography (PE:EtOAc = 150:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.10 – 7.02 (m, 2H), 7.02 – 6.94 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -117.68 – -117.80 (m, 1F). ¹³C NMR (100 MHz, CDCl₃) δ 160.0 (d, *J* = 242.7 Hz), 135.8 (d, *J* = 2.8 Hz), 120.3 (d, *J* = 8.2 Hz), 116.6 (d, *J* = 23.0 Hz).



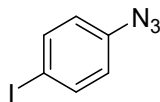
1-Azido-4-chlorobenzene (2m).

The product **2m** (24 mg, 52% yield) [known compound]⁵ was purified with silica gel chromatography (PE:EtOAc = 150:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 130.2, 129.8, 120.3.



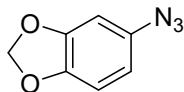
1-Azido-4-bromobenzene (2n).

The product **2n** (41 mg, 69% yield) [known compound]³ was purified with silica gel chromatography (PE:EtOAc = 150:1) as a light yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 139.2, 132.8, 120.6, 117.7.



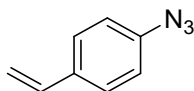
1-Azido-4-iodobenzene (2o).

The product **2o** (50 mg, 68% yield) [known compound]³ was purified with silica gel chromatography (PE:EtOAc = 150:1) as a brown solid. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 139.9, 138.7, 121.0, 88.2.



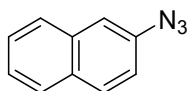
5-Azidobenzo[d][1,3]dioxole (2p).

The product **2p** (37 mg, 76% yield) [known compound]⁴ was purified with silica gel chromatography (PE:EtOAc = 80:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 6.77 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 2.2 Hz, 1H), 6.49 (dd, *J* = 8.2, 2.3 Hz, 1H), 5.97 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 148.7, 145.0, 133.8, 111.6, 108.8, 101.6, 100.7.



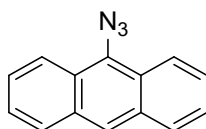
1-Azido-4-vinylbenzene (2q).

The product **2q** (35 mg, 81% yield) [known compound]⁷ was purified with silica gel chromatography (PE:EtOAc = 200:1) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.23 (d, *J* = 10.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 139.3, 135.8, 134.5, 127.6, 119.1, 113.6.



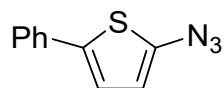
1-Azidonaphthalene (2r).

The product **2r** (45 mg, 88% yield) [known compound]⁴ was purified with silica gel chromatography (PE:EtOAc = 150:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (t, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.37 (m, 3H), 7.16 (dd, *J* = 8.8, 2.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 137.5, 134.0, 131.0, 129.9, 127.8, 126.98, 126.97, 125.4, 118.8, 115.8.



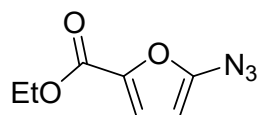
9-Azidoanthracene (2s).

The product **2s** (53 mg, 81% yield) [known compound]⁸ was purified with silica gel chromatography (PE:EtOAc = 100:1) as a brown solid. ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, *J* = 10.2 Hz, 3H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.64 – 7.42 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 131.8, 128.7, 126.3, 126.0, 125.5, 125.2, 122.5.



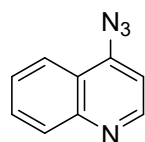
2-Azido-5-phenylthiophene (2t).

The product **2t** (39 mg, 64% yield) was purified with silica gel chromatography (PE:EtOAc = 120:1) as a white solid. m.p. 67 ~ 69 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 3.8 Hz, 1H), 6.99 (d, *J* = 3.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.4, 137.9, 133.5, 129.0, 127.9, 125.7, 124.5. MS (EI): *m/z* (%) 202.1 (M+H)⁺. HRMS (EI): Calcd. for C₁₀H₈N₃S: 202.0433 (M+H)⁺; Found: 202.0428.



Ethyl 5-azidofuran-2-carboxylate (2u).

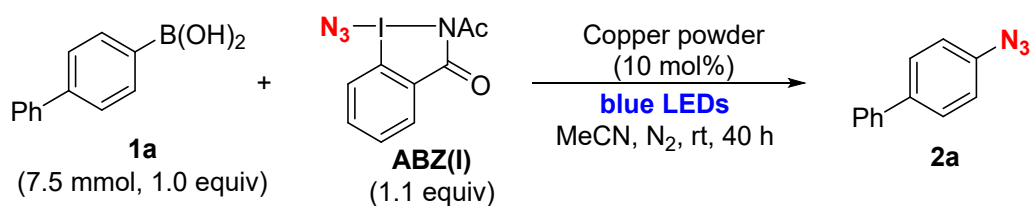
The product **2u** (32 mg, 59% yield) was purified with silica gel chromatography (PE:EtOAc = 30:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.03 (d, *J* = 3.5 Hz, 1H), 6.66 (d, *J* = 3.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.5, 149.9, 122.5, 119.8, 94.6, 61.2, 14.3. MS (EI): *m/z* (%) 182.1 (M+H)⁺. HRMS (EI): Calcd. for C₇H₈N₃O₃: 182.0560 (M+H)⁺; Found: 182.0551.



4-Azidoquinoline (2v).

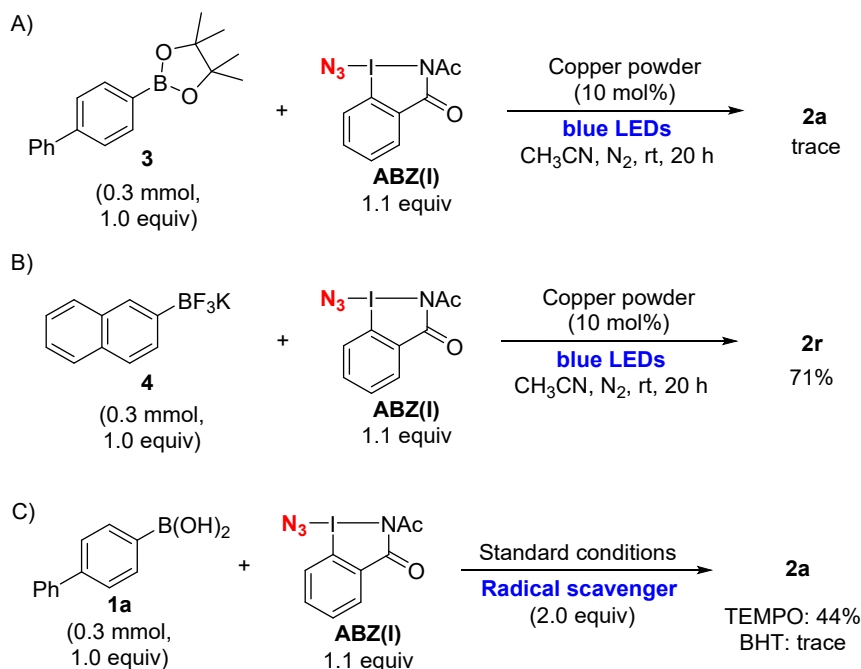
The product **2v** (33 mg, 65% yield) [known compound]⁹ was purified with silica gel chromatography (PE:EtOAc = 60:1) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (d, *J* = 4.6 Hz, 1H), 8.07 (t, *J* = 7.6 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 4.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.1, 149.0, 146.3, 130.5, 129.1, 126.6, 122.3, 121.6, 108.6.

4. Gram-scale synthesis of 2a.



To a 100 mL of Schlenk tube were added arylboronic acid **1a** (7.5 mmol, 1.49 g, 1.0 equiv), **ABZ(I)** (8.25 mmol, 2.72 g, 1.1 equiv) and copper powder (0.75 mmol, 48 mg, 0.10 equiv) under N₂ atmosphere, followed by addition of acetonitrile (60 mL). The tube was screw-capped and stirred at room temperature under visible-light irradiation with blue LED (5 W). After stirring for 40 h, the reaction mixture was diluted with dichloromethane, filtered through a pad of Celite and concentrated in vacuum. The residue was purified with silica gel chromatography (PE:EtOAc = 100:1) to afford **2a** (1.16 g, 79%).

5. Control experiments.



Procedure A: to a 20 mL of Schlenk tube were added 2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3** (0.3 mmol, 1.0 equiv), **ABZ(I)** (0.33 mmol, 1.1 equiv) and copper powder (0.03 mmol, 2 mg, 10 mol%) under N₂ atmosphere, followed by addition of acetonitrile (4 mL). The tube was screw-capped and stirred at

room temperature under visible-light irradiation with blue LED (5 W). After stirring for 20 h, only trace yield of azide **2a** was observed by TLC.

Procedure B: to a 20 mL of Schlenk tube were added trifluoro(naphthalen-2-yl)borate **4** (0.3 mmol, 1.0 equiv), **ABZ(I)** (0.33 mmol, 1.1 equiv) and copper powder (0.03 mmol, 2 mg, 10 mol%) under N₂ atmosphere, followed by addition of acetonitrile (4 mL). The tube was screw-capped and stirred at room temperature under visible-light irradiation with blue LED (5 W). After stirring for 20 h, the reaction mixture was diluted with dichloromethane, filtered through a pad of Celite and concentrated in vacuum. The residue was purified with silica gel chromatography (PE:EtOAc = 150:1) to afford **2r**.

Procedure C: to a 100 mL of Schlenk tube were added arylboronic acid **1a** (0.3 mmol, 59 mg, 1.0 equiv), **ABZ(I)** (0.33 mmol, 109 mg, 1.1 equiv), copper powder (0.03 mmol, 2 mg, 0.10 equiv) and TEMPO or BHT (0.6 mmol, 2.0 equiv) under N₂ atmosphere, followed by addition of acetonitrile (4 mL). The tube was screw-capped and stirred at room temperature under visible-light irradiation with blue LED (5 W). After stirring for 20 h, the reaction mixture was diluted with dichloromethane, filtered through a pad of Celite and concentrated in vacuum. The residue was purified with silica gel chromatography (PE:EtOAc = 80:1) to afford **2a**.

III. Computational Results

Computational Methods

Quantum chemical calculations were performed using the Gaussian 16 suite of programs.¹⁰ The MN15¹¹ was used for geometry optimizations and frequencies calculations, and a mixed basis set of SDD¹² for I and Cu and 6-31G(d,p)¹³ for other atoms in conjunction with the SMD¹⁴ implicit solvation model to account for the solvation effects of the acetonitrile. The recently corrected radius for iodine was used for SMD calculations.¹⁵ Optimized geometries were verified by frequency computations as minima (zero imaginary frequencies) or transition structures (a single imaginary frequency) at the same level of theory. Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structure and intermediate.¹⁶

More accurate electronic energies were obtained by single point energy calculations at the SMD-MN15/6-311++G(2df,2p)+SDD(I, Cu)¹⁷ level of theory. A factor of $RT\ln(24.46)$ was added to free energy for each species to account for the 1 atm to 1 M standard state change. All Gibbs energies in solution reported throughout the text are in kilocalories per mole, and the bond lengths are in angstroms. The structures were generated by CYLview.¹⁸

SMD-MN15/6-31G(d,p)+SDD(I, Cu) Calculated Cartesian Coordinates and Single Point Energies Calculated Using the SMD-MN15/6-311++G(2df,2p)+SDD(I, Cu)//SMD-MN15/6-31G(d,p)+SDD(I, Cu).

ABZ(I)

C	0.83088500	3.83057100	0.03905200
C	-0.41158700	3.21309800	0.15885100
C	-0.50829200	1.82220000	0.06617600
C	0.65930200	1.09580700	-0.14167700
C	1.90920400	1.67005300	-0.27224300
C	1.97961100	3.06498800	-0.17664600
H	0.90768900	4.91118000	0.11102800

H	-1.32276500	3.78171200	0.32311400
H	2.79557300	1.06980300	-0.44960700
H	2.94660000	3.54963700	-0.27479000
C	-1.82689100	1.13422000	0.18070800
O	-2.87909600	1.73167700	0.36349400
N	-1.67599500	-0.22758500	0.04990700
C	-2.62553600	-1.23299500	0.09042400
O	-2.22671900	-2.38813600	-0.04931100
C	-4.06783200	-0.87750600	0.29835200
H	-4.65173800	-1.79870900	0.29468600
H	-4.19135800	-0.34746100	1.24668800
H	-4.40745700	-0.20298200	-0.49221300
I	0.33260600	-1.02478000	-0.25885600
N	2.57224100	-1.31413500	-0.58509900
N	3.19997700	-1.53155000	0.44210300
N	3.83359000	-1.74398600	1.37723500
Zero-point correction=			0.156428 (Hartree/Particle)
Thermal correction to Energy=			0.171685
Thermal correction to Enthalpy=			0.172630
Thermal correction to Gibbs Free Energy=			0.112039
SCF Done: E(RMN15) = -727.296721069			

A

C	-2.67955500	-0.68053600	-0.00192200
C	-3.71759100	0.25472200	-0.00298000
C	-3.43891800	1.62328100	-0.00151200
C	-2.11843700	2.06177500	0.00135700
C	-1.06104100	1.14437400	0.00333600
C	-1.36960000	-0.21657800	0.00120100
H	-2.89640700	-1.74480600	-0.00388400

H	-4.74590900	-0.09518300	-0.00526500
H	-4.25081700	2.34438900	-0.00255200
H	-1.86903300	3.11939200	0.00248100
I	0.21977800	-1.64895000	-0.00166700
C	0.33654400	1.67906900	0.00667300
O	0.57366200	2.88618600	-0.00760100
N	1.28504900	0.70512100	0.03249600
C	2.66205200	0.68655900	0.00519700
O	3.28738300	-0.36388400	-0.00124500
C	3.34214100	2.04013800	-0.01258200
H	3.02759400	2.60583900	-0.89361800
H	3.04869100	2.62038300	0.86604000
H	4.42037200	1.87328400	-0.02417800
Zero-point correction=			0.141656 (Hartree/Particle)
Thermal correction to Energy=			0.154151
Thermal correction to Enthalpy=			0.155095
Thermal correction to Gibbs Free Energy=			0.097699
SCF Done: E(UMN15) =	-563.242533849		

Azido radical

N	0.00000000	0.00000000	1.18114900
N	0.00000000	0.00000000	0.00001200
N	0.00000000	0.00000000	-1.18116100
Zero-point correction=			0.009779 (Hartree/Particle)
Thermal correction to Energy=			0.012519
Thermal correction to Enthalpy=			0.013463
Thermal correction to Gibbs Free Energy=			-0.012124
SCF Done: E(UMN15) =	-163.998645976		

Copper powder

Cu	0.00000000	0.00000000	0.00000000
Zero-point correction=			0.000000 (Hartree/Particle)
Thermal correction to Energy=			0.001416
Thermal correction to Enthalpy=			0.002360
Thermal correction to Gibbs Free Energy=			-0.016509

SCF Done: E(UMN15) = -197.568839460

B

C	3.31914400	1.74943800	-0.56321700
C	2.50089800	2.84547700	-0.28467700
C	1.20529600	2.63976500	0.18217600
C	0.68897100	1.34646900	0.35431300
C	1.53724000	0.26707600	0.09250600
C	2.84363400	0.45309600	-0.36063900
H	4.33370800	1.89529900	-0.92334800
H	2.87333400	3.85646300	-0.42332600
H	0.56157400	3.48377700	0.41790400
H	3.48922800	-0.40042700	-0.54636000
I	0.93729600	-1.75646000	0.49542300
C	-0.74191000	1.24861900	0.84283700
O	-1.03920400	1.81380800	1.89859600
N	-1.56073100	0.58611700	-0.02029300
C	-2.89297400	0.33086700	0.21683900
O	-3.55119100	-0.22668500	-0.67273800
Cu	-1.08935500	-0.15042900	-1.79335000
C	-3.55431700	0.69460700	1.52348200
H	-3.00431000	0.26937000	2.36762900
H	-3.54719100	1.77858700	1.66540000
H	-4.57937600	0.31948500	1.50532900
Zero-point correction=			0.143506 (Hartree/Particle)

Thermal correction to Energy=	0.157662
Thermal correction to Enthalpy=	0.158606
Thermal correction to Gibbs Free Energy=	0.099295

SCF Done: E(RMN15) = -760.961992454

C

C	-1.92485700	3.20731000	-0.01750700
C	-0.69639000	3.42583800	0.60907100
C	0.07327400	2.34068200	1.02164200
C	-0.35977700	1.02572100	0.79480500
C	-1.59751600	0.83052800	0.17834700
C	-2.38787100	1.90668700	-0.22442100
H	-2.53511600	4.04695600	-0.33815000
H	-0.34134900	4.43808000	0.77945600
H	1.03031300	2.49590000	1.51666300
H	-3.35548900	1.73793100	-0.68804600
I	-2.39562200	-1.14296000	-0.07854700
C	0.56338600	-0.08822500	1.22972300
O	0.80104400	-0.26052800	2.42261900
N	1.11170800	-0.76472600	0.16981900
C	2.09737400	-1.73116300	0.26859700
C	2.41486700	-2.38063200	1.58873000
H	2.90237400	-1.64666600	2.23858000
H	1.50673000	-2.70425300	2.10289800
H	3.08208800	-3.22462000	1.40534300
O	2.70910200	-2.04091600	-0.75841000
Cu	1.18952400	0.03042900	-1.62944600
N	2.59526800	1.32955000	-1.20935500
N	3.11062800	1.28132300	-0.11621100
N	3.61184500	1.25988000	0.92612100

Zero-point correction=	0.156247 (Hartree/Particle)
Thermal correction to Energy=	0.173893
Thermal correction to Enthalpy=	0.174837
Thermal correction to Gibbs Free Energy=	0.106817

SCF Done: E(UMN15) = -924.991558826

1a

C	-2.68639600	1.12612900	0.43220900
C	-1.96800800	-0.00000500	0.00000900
C	-2.68640300	-1.12612600	-0.43221100
C	-4.08038300	-1.12618200	-0.43203700
C	-4.78329200	0.00001800	-0.00002700
C	-4.08037500	1.12620700	0.43200000
H	-2.14741100	1.99952900	0.79187700
H	-2.14742300	-1.99952800	-0.79188100
H	-4.61826000	-2.00522500	-0.77747100
H	-5.87001500	0.00002700	-0.00004100
H	-4.61824800	2.00526000	0.77741600
C	-0.48218000	-0.00001500	0.00002600
C	0.23745300	-1.17300400	0.28075500
C	0.23748400	1.17297400	-0.28069700
C	1.62973100	-1.16847900	0.27864100
H	-0.30125600	-2.08616100	0.52353800
C	1.62974700	1.16842200	-0.27858300
H	-0.30122200	2.08613000	-0.52349200
C	2.35666900	-0.00004700	0.00003200
H	2.16842800	-2.08624000	0.50511400
H	2.16849100	2.08614400	-0.50508400
B	3.92328400	0.00001000	0.00000200
O	4.56489400	1.17776000	-0.27642500

H	5.53348400	1.13422800	-0.26718400
O	4.56499900	-1.17768900	0.27637400
H	5.53358500	-1.13413300	0.26690100
Zero-point correction=			0.206532 (Hartree/Particle)
Thermal correction to Energy=			0.219153
Thermal correction to Enthalpy=			0.220097
Thermal correction to Gibbs Free Energy=			0.166732
SCF Done:	E(RMN15) = -638.800157473		

INT-1

C	1.24273300	-2.90452000	1.44964800
C	1.72764600	-2.08398500	0.43304200
C	2.77945200	-1.18994400	0.65543000
C	3.35725200	-1.13403000	1.93252500
C	2.87639900	-1.94293600	2.96057100
C	1.81694200	-2.82055700	2.72012600
H	0.42405400	-3.59317200	1.26121700
H	4.17405200	-0.43861200	2.11157800
H	3.32592300	-1.88718600	3.94765500
H	1.43654600	-3.45188600	3.51821200
I	0.82876900	-2.22484500	-1.50290000
C	3.24922100	-0.20880600	-0.39390800
O	4.25421900	-0.40033100	-1.06009100
N	2.42836800	0.91203700	-0.40672400
C	2.50533600	1.86097800	-1.33723900
O	1.78107500	2.91396900	-1.24001700
C	3.37537200	1.78349500	-2.55214300
H	4.42619800	1.85762500	-2.25836600
H	3.25200800	0.81522100	-3.04588500
H	3.11363400	2.60024900	-3.22548300

Cu	1.01962900	0.94630800	1.04278700
N	-0.11432900	0.24114200	2.44592300
N	-0.97279200	-0.50368600	2.03231000
N	-1.80868900	-1.21852800	1.66901300
C	-1.50073400	2.52100400	0.86655400
C	-0.49233400	2.30712200	-0.11596500
C	-0.77322600	1.33314600	-1.10329300
C	-1.97645900	0.63719200	-1.12612500
C	-2.97751400	0.89654000	-0.16883100
C	-2.71605200	1.85456800	0.83311200
H	-1.30880000	3.24935400	1.65280300
H	-0.03747200	1.13164400	-1.88043100
H	-2.16484200	-0.09032500	-1.91221600
H	-3.46412300	2.04474700	1.59911100
C	-4.27494100	0.18387200	-0.22017300
C	-5.46449400	0.83906400	0.13723300
C	-4.33843300	-1.15846900	-0.63038700
C	-6.68700100	0.17088600	0.08022000
H	-5.43247100	1.88388300	0.43751400
C	-5.56044300	-1.82615900	-0.68217300
H	-3.41947900	-1.68587500	-0.87938000
C	-6.73900900	-1.16316000	-0.32925400
H	-7.60007700	0.69500600	0.35013300
H	-5.59272000	-2.86760100	-0.99121500
H	-7.69167800	-1.68439500	-0.37170600
B	0.79354700	3.32787600	-0.08397800
O	1.41714100	3.15697700	1.21897700
H	2.17960500	3.74023700	1.34232000
O	0.48288900	4.69627400	-0.32477900
H	0.12912100	4.83186900	-1.21332800

Zero-point correction=	0.364214 (Hartree/Particle)
Thermal correction to Energy=	0.395248
Thermal correction to Enthalpy=	0.396193
Thermal correction to Gibbs Free Energy=	0.300339

SCF Done: E(UMN15) = -1563.81517475

TS-1

C	2.82883400	-2.49028000	1.32903500
C	2.82130900	-1.51038200	0.33983500
C	3.37069000	-0.24467800	0.56466000
C	3.93541100	0.03671600	1.81679900
C	3.94270100	-0.93377800	2.81773000
C	3.38970700	-2.19194100	2.57313400
H	2.40259100	-3.47120800	1.13991600
H	4.36105700	1.02147100	1.99535800
H	4.38100100	-0.70822700	3.78535100
H	3.39363400	-2.95195300	3.34937600
I	1.93828600	-1.97878400	-1.55253300
C	3.30789100	0.85379700	-0.46579000
O	4.25267500	1.15379100	-1.17098800
N	2.07311100	1.52244800	-0.43979700
C	1.61016200	2.15532800	-1.49955300
O	0.52080300	2.85610200	-1.39847600
C	2.20754200	2.12204700	-2.86677000
H	3.03341500	2.83910000	-2.91272400
H	2.61589900	1.13490800	-3.09578600
H	1.44233900	2.40614400	-3.59011800
Cu	0.86060400	0.93229400	1.10478800
N	0.26293700	-0.30682800	2.48731900
N	-0.45122200	-1.20072900	2.09360400

N	-1.14537900	-2.06189900	1.75252000
C	-1.98443000	1.49399700	1.33470500
C	-1.01432500	1.33311000	0.32499200
C	-1.31680200	0.51620400	-0.77698100
C	-2.59187600	-0.02994000	-0.92610000
C	-3.57655600	0.17422900	0.05647700
C	-3.25033300	0.93978700	1.19479200
H	-1.74643300	2.07868200	2.22219200
H	-0.57221200	0.34459900	-1.55484500
H	-2.83447400	-0.59920700	-1.82063800
H	-3.99062500	1.07496600	1.98027000
C	-4.93379400	-0.40491700	-0.09530300
C	-6.06069600	0.27963100	0.38984200
C	-5.12148900	-1.64508100	-0.72786200
C	-7.33812800	-0.25989300	0.24554300
H	-5.93646800	1.25218200	0.86028900
C	-6.39902900	-2.18450500	-0.86999900
H	-4.25816300	-2.19978400	-1.08807100
C	-7.51215900	-1.49403400	-0.38442300
H	-8.19904100	0.28829500	0.61933600
H	-6.52492800	-3.14922300	-1.35454400
H	-8.50798100	-1.91460700	-0.49654300
B	-0.20366000	3.20665900	-0.15635300
O	0.54358400	3.65576800	0.93060900
H	1.48112000	3.41121700	0.89612800
O	-1.36625900	3.91411200	-0.39647000
H	-1.87943100	3.54677900	-1.12930000
Zero-point correction=			0.362968 (Hartree/Particle)
Thermal correction to Energy=			0.393961
Thermal correction to Enthalpy=			0.394905

Thermal correction to Gibbs Free Energy= 0.297722

SCF Done: E(UMN15) = -1563.79070968

INT-2

C	-0.37846800	-3.03609700	0.90141500
C	-1.05586000	-2.14298500	0.07195600
C	-0.39916900	-1.51689700	-0.99732300
C	0.93992600	-1.85795500	-1.25072500
C	1.62535500	-2.74488500	-0.42824600
C	0.96749100	-3.32008600	0.66004700
H	-0.89622000	-3.52246900	1.72267500
H	1.43820200	-1.37374100	-2.08610300
H	2.66802500	-2.97551500	-0.62777600
H	1.49015500	-4.00753400	1.31908200
I	-3.16379900	-1.94219300	0.42946400
C	-0.95834800	-0.45426400	-1.88827200
O	-0.64426900	-0.37339300	-3.06198000
N	-1.75045100	0.54323600	-1.26234500
C	-2.83110000	0.95407200	-1.85604000
O	-3.48873200	1.99940700	-1.37157900
C	-3.51145600	0.32127600	-3.02143500
H	-3.31847200	0.92625800	-3.91410300
H	-3.16981100	-0.69760900	-3.20111800
H	-4.58813100	0.33678300	-2.83232500
Cu	-1.09156500	1.06781600	0.68181400
N	-1.38629900	1.45490400	2.56656500
N	-0.52672000	1.70775300	3.37304800
N	0.26905500	1.94775900	4.18052900
C	1.68507400	0.33286100	1.50519100
C	0.93822500	1.01257100	0.54734500

C	1.52623100	1.48372700	-0.62548300
C	2.88859800	1.25877800	-0.84550900
C	3.66282800	0.56161600	0.09660200
C	3.04608100	0.10661700	1.27326300
H	1.23028100	-0.03484400	2.42443200
H	0.93855800	1.99651900	-1.38718400
H	3.34769500	1.60254500	-1.77043800
H	3.63824500	-0.41720100	2.02118700
C	5.10605100	0.30575800	-0.15033700
C	5.69849300	-0.90200900	0.25219000
C	5.90597600	1.26335800	-0.79408500
C	7.05230500	-1.14389800	0.02008100
H	5.08672700	-1.66307900	0.73243200
C	7.25925300	1.02055500	-1.02807300
H	5.46705500	2.21270000	-1.09311100
C	7.83807900	-0.18366000	-0.62128000
H	7.49204700	-2.08736300	0.33338600
H	7.86421400	1.77715900	-1.52131000
H	8.89293100	-0.37229200	-0.80271200
B	-2.92661600	3.08123100	-0.64281300
O	-1.69460500	3.57946600	-0.91992500
H	-1.19815200	3.11408000	-1.61234200
O	-3.69020000	3.67280700	0.30261800
H	-4.54356100	3.23647100	0.44984300
Zero-point correction=			0.364490 (Hartree/Particle)
Thermal correction to Energy=			0.395991
Thermal correction to Enthalpy=			0.396935
Thermal correction to Gibbs Free Energy=			0.297767
SCF Done: E(UMN15) = -1563.80630040			

TS-2

C	-5.14761700	0.19126600	1.21646000
C	-6.47086800	-0.24312200	1.28211100
C	-7.30161300	-0.13783600	0.16409100
C	-6.79642100	0.40482100	-1.01973200
C	-5.47328000	0.84001800	-1.08609600
C	-4.62692100	0.74113900	0.03123900
H	-4.50023700	0.08245100	2.08430900
H	-6.85121700	-0.67122800	2.20607400
H	-8.33308600	-0.47628500	0.21492900
H	-7.43697000	0.49727300	-1.89308900
H	-5.09732400	1.28265500	-2.00566300
C	-3.21743400	1.19538500	-0.03105600
C	-2.46656600	1.07874300	-1.22060300
C	-2.59213900	1.74764000	1.10261600
C	-1.13377100	1.46711200	-1.26728300
H	-2.93040600	0.64482300	-2.10455300
C	-1.26353100	2.16302600	1.05987300
H	-3.16393700	1.87984500	2.01894100
C	-0.49090200	1.96456300	-0.10821600
H	-0.56951600	1.36007900	-2.19439300
H	-0.81693600	2.63300500	1.93488300
Cu	1.11780900	0.91603600	0.46259900
N	0.52709300	3.62312900	-0.59781900
N	1.36295900	3.27698200	-1.38542000
N	2.16413300	2.84573400	-2.12610400
C	-1.44365600	-2.03899300	-0.03896000
C	-0.05656000	-1.93283400	0.02696600
C	0.60448500	-1.86802700	1.25911800
C	-0.15037600	-1.93459800	2.43832700

C	-1.54014500	-2.01826000	2.38390300
C	-2.18349200	-2.06713600	1.14633500
H	-1.94798800	-2.09763600	-0.99906900
H	0.36855900	-1.89948000	3.39289900
H	-2.11751700	-2.05163300	3.30309200
H	-3.26676200	-2.13356800	1.09291200
I	1.03878500	-1.95914200	-1.81280300
C	2.08601100	-1.68774300	1.40657600
O	2.77876600	-2.45774900	2.04472100
N	2.56655700	-0.47095900	0.87543300
C	3.77963300	-0.37727100	0.40653000
O	4.25606900	0.82598200	0.13593000
C	4.70119000	-1.49411900	0.06440500
H	5.43346600	-1.60336700	0.87243700
H	4.17457900	-2.43970200	-0.06326100
H	5.24233600	-1.22370300	-0.84586900
B	3.93801900	2.01192500	0.86725500
O	3.79711000	1.99266600	2.21755900
H	3.86078600	1.11975000	2.63477800
O	3.89142300	3.18211100	0.19902300
H	3.76170300	3.07562000	-0.76259600
Zero-point correction=			0.362722 (Hartree/Particle)
Thermal correction to Energy=			0.393948
Thermal correction to Enthalpy=			0.394892
Thermal correction to Gibbs Free Energy=			0.296550

SCF Done: E(UMN15) = -1563.78054918

E-Cu⁰

Cu	0.86645000	0.68413700	-1.43355700
C	-3.06118800	0.54580500	-0.85806300

C	-1.93579600	0.20286700	-0.10949600
C	-1.32430900	1.12702600	0.74694300
C	-1.88744100	2.40693000	0.85805100
C	-2.99831500	2.76875200	0.10050600
C	-3.58002100	1.83847700	-0.76210500
H	-3.53617800	-0.18642200	-1.50417400
H	-1.42392200	3.11534300	1.53987800
H	-3.41132800	3.76930800	0.18753800
H	-4.45029900	2.10701600	-1.35425000
I	-1.30059000	-1.84412900	-0.18668300
C	-0.07992300	0.87580900	1.54710700
O	-0.01450800	1.15493500	2.73652200
N	1.01944500	0.48898600	0.78088700
C	1.90061200	-0.37479700	1.18452100
O	3.00769700	-0.53206800	0.46201700
C	1.77023800	-1.34082300	2.30982200
H	2.58857900	-1.18192900	3.01957200
H	0.81698200	-1.23569700	2.82627600
H	1.87433100	-2.35532500	1.90813700
B	3.54719400	0.43092900	-0.43505900
O	3.42629500	1.77418500	-0.23901600
H	2.73341900	2.00983400	0.39835700
O	4.39056000	-0.02560600	-1.39846100
H	4.43705200	-0.99264800	-1.43711800
Zero-point correction=			0.178891 (Hartree/Particle)
Thermal correction to Energy=			0.197186
Thermal correction to Enthalpy=			0.198131
Thermal correction to Gibbs Free Energy=			0.129035
SCF Done: E(UMN15) =	-937.458292991		

2a

C	-2.68727300	-1.04832200	0.42471800
C	-4.07370600	-0.90690700	0.45533600
C	-4.66701800	0.29394400	0.06169800
C	-3.86161000	1.35171900	-0.36422100
C	-2.47535000	1.20949900	-0.39778500
C	-1.86662400	0.00747300	-0.00312700
H	-2.23340000	-1.97898200	0.75729500
H	-4.69099600	-1.73406700	0.79608800
H	-5.74773800	0.40465900	0.08671400
H	-4.31365400	2.28829500	-0.68018600
H	-1.85808800	2.03058400	-0.75482000
C	-0.38979000	-0.14430200	-0.03775300
C	0.20346400	-1.37795000	-0.35112000
C	0.45486000	0.94142600	0.24281400
C	1.58531200	-1.52473600	-0.38294600
H	-0.42547300	-2.23038200	-0.59504500
C	1.83917900	0.80902600	0.21313900
H	0.02340900	1.90263000	0.51072000
C	2.40755800	-0.43016600	-0.10113700
H	2.04206200	-2.47797000	-0.63338700
H	2.47178100	1.66328400	0.44383000
N	3.80841500	-0.66489700	-0.15572800
N	4.55822800	0.29035300	0.08394500
N	5.33593900	1.09564700	0.28765300

Zero-point correction= 0.185480 (Hartree/Particle)

Thermal correction to Energy= 0.197127

Thermal correction to Enthalpy= 0.198071

Thermal correction to Gibbs Free Energy= 0.146588

SCF Done: E(RMN15) = -626.327589508

INT-3

C	0.48108900	-3.32992100	0.60312500
C	-0.42030800	-2.40085000	0.08151900
C	0.05513400	-1.19316400	-0.42439100
C	1.43168700	-0.89231600	-0.43454200
C	2.31328800	-1.84342300	0.08683000
C	1.84827000	-3.05013700	0.61237700
H	0.12785500	-4.27462600	1.00668400
H	-1.48685400	-2.61090600	0.06313200
H	-0.64050500	-0.46588400	-0.84553200
H	2.54613100	-3.76937200	1.03094700
I	4.42255400	-1.49355300	0.23459100
C	1.85584300	0.42159800	-1.04967600
O	2.78372600	0.48607100	-1.84443700
N	1.06964500	1.47009100	-0.59519700
C	0.97878400	2.62858400	-1.23348900
O	0.23829600	3.57566500	-0.77328800
Cu	-0.01061400	1.10421400	1.14854700
C	1.66878400	2.94853700	-2.52645600
H	2.74531200	3.03850000	-2.35619800
H	1.53078700	2.13992500	-3.24872000
H	1.27122400	3.88654600	-2.91564800
C	-5.38248200	-1.41765900	0.71511200
C	-6.16935500	-2.55677700	0.54486500
C	-5.94744300	-3.41048200	-0.53827400
C	-4.93036200	-3.11805900	-1.44962700
C	-4.14316800	-1.97913200	-1.27969600
C	-4.35886800	-1.11168200	-0.19574400
H	-5.57487400	-0.74616200	1.54914400

H	-6.96308400	-2.77328900	1.25533300
H	-6.56196100	-4.29706400	-0.67048900
H	-4.74429700	-3.78074500	-2.29093500
H	-3.33741600	-1.76737200	-1.98020800
C	-3.51073600	0.09576800	-0.02190800
C	-3.10139500	0.51783900	1.24825700
C	-3.08300800	0.84198100	-1.13785300
C	-2.26829800	1.63862800	1.39429000
H	-3.42164800	-0.03483700	2.12961000
C	-2.24210600	1.93982300	-0.98557200
H	-3.41878900	0.54997200	-2.13124500
C	-1.78902400	2.36553700	0.27984900
H	-2.00214800	1.96072900	2.40436000
H	-1.90913000	2.47617300	-1.87379100
B	-0.70151200	3.57191200	0.46996900
O	-1.34783800	4.84156200	0.52037600
H	-0.68938500	5.54205900	0.63088700
O	0.19665500	3.31047800	1.61690300
H	-0.22342400	3.63388900	2.42759400
Zero-point correction=			0.351338 (Hartree/Particle)
Thermal correction to Energy=			0.378909
Thermal correction to Enthalpy=			0.379853
Thermal correction to Gibbs Free Energy=			0.290361
SCF Done: E(RMN15) = -1399.78130841			

TS-3

C	3.25518800	-2.42538000	1.49111900
C	3.08414900	-1.42158000	0.53962100
C	3.74129500	-0.19136200	0.65660500
C	4.61254100	0.00468700	1.73633500

C	4.78283100	-0.98607500	2.70104600
C	4.09589400	-2.19488700	2.58275000
H	2.75201100	-3.38143300	1.38088000
H	5.13951800	0.95238800	1.81345800
H	5.45163100	-0.81604600	3.53953500
H	4.22262400	-2.97388400	3.32917300
I	1.92471100	-1.89610200	-1.20364200
C	3.54469500	0.95844200	-0.29332000
O	4.48018500	1.49445000	-0.86444200
N	2.22781800	1.41903100	-0.32203600
C	1.67578400	1.91810000	-1.40154600
O	0.49049100	2.46430800	-1.32651900
C	2.25546100	1.88251200	-2.77739400
H	2.75605800	2.83720900	-2.97328500
H	2.98885700	1.08291500	-2.88925300
H	1.44279800	1.76782100	-3.49800900
Cu	0.71794100	0.69564000	0.96953800
C	-2.14414300	1.05679500	1.53305200
C	-1.21970100	0.90004300	0.47505200
C	-1.71897700	0.25238900	-0.67676600
C	-3.04063000	-0.18754200	-0.78097200
C	-3.93648800	-0.01756900	0.28726700
C	-3.46261500	0.60936000	1.45256300
H	-1.83039000	1.56396100	2.44699700
H	-1.06020500	0.11356900	-1.53723400
H	-3.39086300	-0.64723700	-1.70387200
H	-4.13208400	0.73096700	2.30272300
C	-5.34416400	-0.48226200	0.18843700
C	-6.38257700	0.22964900	0.81169100
C	-5.67058800	-1.64550800	-0.52837400

C	-7.70373800	-0.20822800	0.72328000
H	-6.15321500	1.14559500	1.35174300
C	-6.99190200	-2.08249900	-0.61903400
H	-4.87813200	-2.22287800	-0.99942200
C	-8.01455000	-1.36642100	0.00730900
H	-8.49280000	0.36133300	1.20789300
H	-7.22179700	-2.98953400	-1.17251900
H	-9.04409300	-1.70772400	-0.06208700
B	-0.23427200	2.85032400	-0.09639500
O	0.49570500	3.39023200	0.95806400
H	1.41911800	3.09398800	0.96790800
O	-1.43844900	3.47666500	-0.35697400
H	-1.95244800	3.00277000	-1.02529200
Zero-point correction=			0.349735 (Hartree/Particle)
Thermal correction to Energy=			0.377517
Thermal correction to Enthalpy=			0.378461
Thermal correction to Gibbs Free Energy=			0.287837
SCF Done: E(RMN15) = -1399.74281971			

INT-4

C	1.16753600	-3.10934700	0.32643200
C	1.95942600	-1.97605200	0.15150800
C	2.58457300	-1.35818300	1.24346900
C	2.43005000	-1.92544100	2.51671400
C	1.62797300	-3.04799000	2.70442900
C	0.98977100	-3.63190100	1.60983900
H	0.69573700	-3.58790100	-0.52684500
H	2.93365800	-1.45363300	3.35634800
H	1.50390500	-3.46531400	3.69910900
H	0.36156300	-4.50792900	1.74347200

I	2.27664800	-1.31369300	-1.86018400
C	3.38405500	-0.09203600	1.17699900
O	4.46027900	0.02626400	1.73285000
N	2.70355700	0.98065600	0.56065100
C	3.35534700	1.90846200	-0.07919400
O	2.69146200	2.97222300	-0.50177800
C	4.79205200	1.89433600	-0.46864800
H	5.36870700	2.42915800	0.29423500
H	5.18081200	0.87840800	-0.54535000
H	4.90055500	2.42597600	-1.41626600
Cu	0.67229700	0.75669300	0.53267200
C	-2.17944300	1.50761900	0.80584600
C	-1.25117700	0.54160200	0.35417900
C	-1.82542200	-0.60819600	-0.23531200
C	-3.20502300	-0.78749200	-0.36215000
C	-4.10144600	0.18944000	0.09892800
C	-3.56177800	1.34497500	0.68573000
H	-1.81720500	2.42362000	1.27618600
H	-1.17531800	-1.39781200	-0.61943200
H	-3.59339500	-1.68373700	-0.84427600
H	-4.23295200	2.11102200	1.07186700
C	-5.57038300	0.00642600	-0.02983200
C	-6.41525100	1.10146600	-0.27654100
C	-6.15125200	-1.26696800	0.09202600
C	-7.79416900	0.92944800	-0.39650400
H	-5.98325200	2.09261700	-0.39621400
C	-7.52965300	-1.44035600	-0.03141900
H	-5.51719500	-2.12446400	0.30659600
C	-8.35804800	-0.34267700	-0.27567600
H	-8.42831000	1.79015300	-0.59419600

H	-7.95816700	-2.43412000	0.07268600
H	-9.43237000	-0.47737500	-0.37068700
B	1.47623900	3.47345300	0.05013200
O	1.27024000	3.54540000	1.39010000
H	1.94929300	3.12203700	1.93885500
O	0.56559400	4.00416800	-0.79733000
H	0.79187300	3.90180200	-1.73469200
Zero-point correction=			0.351140 (Hartree/Particle)
Thermal correction to Energy=			0.379586
Thermal correction to Enthalpy=			0.380530
Thermal correction to Gibbs Free Energy=			0.286957
SCF Done: E(RMN15) = -1399.76445340			

IV. References

1. S. Alazet, F. Le Vaillant, S. Nicolai, T. Courant, J. Waser, Divergent Access to (1,1) and (1,2)-Azidolactones from Alkenes using Hypervalent Iodine Reagents, *Chem. Eur. J.*, 2017, **23**, 9501-9504.
2. X.-G. Yang, K. Zheng, C. Zhang, Electrophilic Hypervalent Trifluoromethylthio-Iodine(III) Reagent, *Org. Lett.*, 2020, **22**, 2026-2031.
3. L. Ren, N. Jiao, PdCl₂ catalyzed efficient assembly of organic azides, CO, and alcohols under mild conditions: a direct approach to synthesize carbamates, *Chem. Commun.*, 2014, **50**, 3706-3709.
4. A. S. Kumar, M. A. Reddy, M. Knorn, O. Reiser, B. Sreedhar, Magnetically Recoverable CuFe₂O₄ Nanoparticles: Catalyzed Synthesis of Aryl Azides and 1,4-Diaryl-1,2,3-triazoles from Boronic Acids in Water, *Eur. J. Org. Chem.*, 2013, 4674-4680.
5. F. Sebest, L. Casarrubios, H. S. Rzepa, A. J. P. White, S. Díez-González, Thermal azide-alkene cycloaddition reactions: straightforward multi-gram access to Δ^2 -1,2,3-triazolines in deep eutectic solvents, *Green Chem.*, 2018, **20**, 4023-4035.
6. (a) V. Babin, A. Sallustrau, O. Loreau, F. Caillé, A. Goudet, H. Cahuzac, A. del Vecchio, F. Taran, D. Audisio, A general procedure for carbon isotope labeling of linear urea derivatives with carbon dioxide, *Chem. Commun.*, 2021, **57**, 6680-6683; (b) L. Gong, C. Li, F. Yuan, S. Liu, X. Zeng, Chromium-Catalyzed Selective Borylation of Vinyl Triflates and Unactivated Aryl Carboxylic Esters with Pinacolborane, *Org. Lett.*, 2022, **24**, 3227-3231.
7. L. M. Kammer, M. Krumb, B. Spitzbarth, B. Lipp, J. Kühnborn, J. Busold, O. M. Mulina, A. O. Terentev, T. Opatz, Photoredox-Catalyzed Four-Component Reaction for the Synthesis of Complex Secondary Amines, *Org. Lett.*, 2020, **22**, 3318-3322.
8. R. A. Valiulin, S. Mamidyala, M. G. Finn, Taming Chlorine Azide: Access to 1,2-Azidochlorides from Alkenes, *J. Org. Chem.*, 2015, **80**, 2740-2755.
9. E. Mendes, E. Cadoni, F. Carneiro, M. B. Afonso, H. Brito, J. Lavrado, D. J. V. A. dos Santos, J. B. Vitor, S. Neidle, C. M. P. Rodrigues, A. Paulo, Combining 1,3-Ditriazolylbenzene and Quinoline to Discover a New G-Quadruplex-Interactive Small

Molecule Active against Cancer Stem-Like Cells, *Chemmedchem*, 2019, **14**, 1325-1328.

10. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

11. H. S. Yu, X. He, S. Li, D. G. Truhlar, MN15: A Kohn-Sham global-hybrid exchange-correlation density functional with broad accuracy for multi-reference and single-reference systems and noncovalent interactions, *Chem. Sci.*, 2016, **7**, 5032-5051.

12. (a) G. Igel-Mann, H. Stoll, H. Preuss, Pseudopotentials for main group elements (IIIa through VIIa), *Mol. Phys.*, 1988, **65**, 1321-1328; (b) D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, Theoretical Chemistry Accounts: Theory Computation, and Modeling, *Theor. Chim. Acta.*, 1990, **77**, 123-141.

13. P. C. Hariharan, J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chim. Acta.*, 1973, **28**, 213-222.

14. A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions, *J. Phys. Chem. B.*, 2009, **113**, 6378-6396.

15. E. Engelage, N. Schulz, F. Heinen, S. M. Huber, D. G. Truhlar, C. J. Cramer, Refined SMD Parameters for Bromine and Iodine Accurately Model Halogen-Bonding

Interactions in Solution, *Chem. Eur. J.*, 2018, **24**, 15983-15987.

16. (a) K. Fukui, The path of chemical reactions - the IRC approach, *Acc. Chem. Res.*, 1981, **14**, 363-368; (b) K. Fukui, *J. Phys. Chem.*, 1970, **74**, 4161-4163.

17. (a) A. D. McLean, G. S. Chandler, Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, $Z=11-18$, *J. Chem. Phys.*, 1980, **72**, 5639-5648; (b) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions, *J. Chem. Phys.*, 1980, **72**, 650-654; (c) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements, *J. Chem. Phys.*, 1988, **89**, 2193-2218; (d) M. J. Frisch, J. A. Pople, J. S. Binkley, Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets, *J. Chem. Phys.*, 1984, **80**, 3265-3269.

18. CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke: Quebec, Canada, **2009** (<http://www.cylview.org>).

V. ^1H and ^{13}C NMR Spectra of Starting Materials and Products

