Supporting Information

Efficient Construction of Biaryls and Macrocyclic Cyclophanes via Electron-transfer Oxidation of Lipshutz Cuprates

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Contents

1. Materials and Methods	 S2
2. Preparation of Bis(4-bromo-3-thienyl)dimethylsilane (4a)	 S4
3. Preparation of Bis(3-bromo-2-thienyl)methane (4b)	 S4
4. Preparation of Bis(2-bromophenyl)ether (4c)	 S5
5. X-ray Structural Analysis of 5a	 S5
6. X-ray Structural Analysis of 5c	 S5
7. TABLE S1. Summaries of Crystallographic Data of 5a and 5c	 S6
8. Figure S1. ¹ H NMR spectrum of 5a (500 MHz)	 S7
9. Figure S2. ¹³ C NMR spectrum of 5a (100 MHz)	 S7
10. Figure S3. ¹ H NMR spectrum of 5b (400 MHz)	 S8
11. Figure S4. ¹³ C NMR spectrum of 5b (100 MHz)	 S8
12. Figure S5. ¹ H NMR spectrum of 5c (500 MHz)	 S9
13. Figure S6. ¹³ C NMR spectrum of 5c (100 MHz)	 S9
14. Theoretical Methods	 S10
15. TABLE S2. Optimized geometries and energies for 5a (at B3LYP/6-31G(d))	 S10
16. TABLE S3. Optimized geometries and energies for 5b (at B3LYP/6-31G(d))	 S13
17. TABLE S4. Optimized geometries and energies for 5c (at B3LYP/6-31G(d))	 S17
18. TABLE S5. Optimized geometries and energies for 12a-12c (at B3LYP/6-31G(d))	 S20
19. References	 S23

1. Materials and Methods.

^1H NMR (500 MHz or 400 MHz) and ^{13}C NMR (125 MHz or 100 MHz) spectra were recorded in CDCl_3 with SiMe_4 as an internal standard. UV-vis spectra were measured in ethanol. Mass spectra were measured with DI- or GC-mass spectrometer (EI, 70 eV). Tetrahydrofuran and ether were dried over benzophenone ketyl (sodium/benzophenone). Acetonitrile was dried and distilled from calcium hydride, and triethylamine was dried and distilled from molecular sieves. Copper(I) cyanide, copper(I) thiocyanate, and copper(I) chloride were dried by vacuum at room temperature for at least 24 h. Copper(I) iodide was recrystallized from anhydrous THF, and then dried by vacuum. Tetracyanoquinodimethane, *p*-benzoquinone, 2,5-dimethyl-1,4-benzoquinone, 2,6-dimethyl-1,4-benzoquinone, and tetramethyl-1,4-benzoquinone were commercially available and were used after recrystallization from benzene. The biaryls **3a**,¹ **3b**,¹ **3c**,¹ **3d**,² **3e**,³ **3f**,⁴ **3g**,⁵ **3h**,⁵ **3i**,⁵ **3j**,¹ **3k**,¹ **3l**,¹ **3m**,⁵ **3n**,⁶ **3o**,^{6,7} **3p**,⁸ **3q**,⁸ and **3r**⁸ were known compounds. The compounds **4a**,⁸ **4b**,⁹ and **4c**¹⁰ were prepared according to the reported procedures.

4,4'-Dichlorobiphenyl (3a)¹: ^1H NMR (CDCl_3 , 500 MHz) δ 7.46 (d, J = 8.4 Hz, 4H), 7.39 (d, J = 8.4 Hz, 4H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 138.4, 133.7, 129.0, 128.2; EI-MS m/z 223 (M^+).

Biphenyl (3b)¹: ^1H NMR (CDCl_3 , 500 MHz) δ 7.61 (dd, J = 8.4 Hz and 1.0 Hz, 4H), 7.45 (t, J = 7.8 Hz, 4H), 7.36 (t, J = 7.3 Hz, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 141.2, 128.7, 127.2, 127.1; EI-MS m/z 154 (M^+).

4,4'-Difluorobiphenyl (3c)¹: ^1H NMR (CDCl_3 , 500 MHz) δ 7.48-7.45 (m, 4H), 7.11 (t, J = 8.7 Hz, 4H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.4, 161.4, 136.4, 136.3, 128.6, 128.5, 115.7, 115.6; EI-MS m/z 190 (M^+).

4,4'-Dimethoxybiphenyl (3d)²: ^1H NMR (CDCl_3 , 500 MHz) δ 7.38 (d, J = 8.8 Hz, 4H), 6.86 (d, J = 8.8 Hz, 4H), 3.73 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 158.7, 133.4, 127.7, 114.1, 55.3; EI-MS m/z 214 (M^+).

3,3'-Dimethoxybiphenyl (3e)³: ¹H NMR (CDCl₃, 500 MHz) δ 7.41-7.39 (m, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.20 (s, 2H), 6.96 (d, J = 8.1 Hz, 2H), 3.91 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 159.8, 142.5, 129.7, 119.6, 112.8, 112.7, 55.2; EI-MS m/z 214 (M^+).

2,2'-Dimethoxybiphenyl (3f)⁴: ¹H NMR (CDCl₃, 500 MHz) δ 7.36-7.31 (m, 2H), 7.25-7.23 (m, 2H), 7.02-6.99 (m, 4H), 3.78 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ 157.0, 131.4, 128.6, 127.7, 120.3, 111.0, 55.7; EI-MS m/z 214 (M^+).

4,4'-Dimethylbiphenyl (3g)⁵: ¹H NMR (CDCl₃, 500 MHz) δ 7.48 (d, J = 8.0 Hz, 4H), 7.23 (d, J = 8.0 Hz, 4H), 2.39 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 138.3, 136.7, 129.4, 126.8, 21.0; EI-MS m/z 182 (M^+).

3,3'-Dimethylbiphenyl (3h)⁵: ¹H NMR (CDCl₃, 500 MHz) δ 7.47 (s, 2H), 7.46 (dd, J = 11.0 and 0.6 Hz, 2H), 7.38 (dt, J = 1.6 and 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 2.48 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ 141.3, 138.2, 128.6, 127.94, 127.87, 124.2, 21.5; EI-MS m/z 182 (M^+).

2,2'-Dimethylbiphenyl (3i)⁵: ¹H NMR (CDCl₃, 500 MHz) δ 7.26-7.20 (m, 6H), 7.10 (d, J = 7.0 Hz, 2H), 2.05 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 141.5, 135.8, 129.8, 129.2, 127.1, 125.5, 19.8; EI-MS m/z 182 (M^+).

4,4'-Dibromobiphenyl (3j)¹: ¹H NMR (CDCl₃, 500 MHz) δ 7.46 (d, J = 8.4 Hz, 4H), 7.31 (d, J = 8.4 Hz, 4H); ¹³C NMR (CDCl₃, 125 MHz) δ 138.9, 132.0, 128.5, 121.9; EI-MS m/z 316 (M^+ + 4), 314 (M^+ + 2), 312 (M^+).

3,3'-Dibromobiphenyl (3k)¹: ¹H NMR (CDCl₃, 500 MHz) δ 7.71-7.68 (m, 2H), 7.49-7.41 (m, 4H), 7.29 (t, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 141.7, 130.8, 130.4, 130.1, 125.7, 123.0; EI-MS m/z 316 (M^+ + 4), 314 (M^+ + 2), 312 (M^+).

2,2'-Dibromobiphenyl (3l)¹: ¹H NMR (CDCl₃, 500 MHz) δ 7.68-7.66 (m, 2H), 7.39-7.36 (m, 2H), 7.28-7.24 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz): δ 142.0, 132.6, 131.0, 129.4, 127.1, 123.5; EI-MS m/z 316 (M^+ + 4), 314 (M^+ + 2), 312 (M^+).

2,2',4,4',6,6'-Hexamethylbiphenyl (3m)⁵: ¹H NMR (CDCl₃, 500 MHz) δ 6.96 (s, 4H), 2.35 (s, 6H), 1.89 (s, 12H); ¹³C NMR (CDCl₃, 125 MHz) δ 137.0, 136.0, 135.4, 128.2, 21.1, 19.8; EI-MS m/z 238 (M^+).

1,1'-Binaphthyl (3n)⁵: ¹H NMR (CDCl₃, 500 MHz) δ 7.93-7.91 (m, 4H), 7.57-7.54 (m, 2H), 7.48-7.42 (m, 4H), 7.38 (d, J = 8.5 Hz, 2H), 7.27-7.24 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 138.4, 133.5, 132.8, 128.1, 127.85, 127.79, 126.5, 125.9, 125.8, 125.4; EI-MS m/z 254 (M^+).

2,2'-Binaphthyl (3o)^{6,7}: ¹H NMR (CDCl₃, 500 MHz) δ 8.18 (s, 2H), 7.97-7.93 (m, 4H), 7.90-7.88 (m, 4H), 7.55-7.49 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz) δ 138.4, 133.7, 132.6, 128.5, 128.2, 127.6, 126.3, 126.1, 126.0, 125.7; EI-MS m/z 254 (M^+).

2,2'-Bithiophene (3p)⁸: ¹H NMR (CDCl₃, 500 MHz) δ 7.20 (dd, J = 5.2 and 0.9 Hz, 2H), 7.17 (dd, J = 3.5 and 0.9 Hz, 2H), 7.01 (dd, J = 5.2 and 3.5 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 137.4, 127.7, 124.3, 123.7; EI-MS m/z 166 (M^+).

3,3'-Bithiophene (3q)⁸: ¹H NMR (CDCl₃, 500 MHz) δ 7.37 (dd, J = 2.8 and 1.6 Hz, 2H), 7.35-7.32 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz) δ 137.2, 126.3, 126.0, 119.8; EI-MS m/z 166 (M^+).

4,4'-Dibromo-3,3'-bithienyl (3r)⁸: ¹H NMR (CDCl₃, 500 MHz) δ 7.38 (d, J = 3.4 Hz, 2H), 7.35 (d, J = 3.4 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 135.1, 125.5, 123.3, 112.3; EI-MS m/z 326 (M^+ + 4), 324 (M^+ + 2), 322 (M^+).

2. Preparation of Bis(4-bromo-3-thienyl)dimethylsilane (4a)

The compound **4a** was prepared according to the reported method⁸: colorless crystals; ¹H NMR (CDCl₃, 400 MHz) δ 7.37 (d, J =3.0 Hz, 2H), 7.32 (d, J =3.0 Hz, 2H), 0.70 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 138.3, 135.6, 124.2, 115.4, -1.5; EI-MS m/z 386 (M^+ + 4), 384 (M^+ + 2), 382 (M^+).

3. Preparation of Bis(3-bromo-2-thienyl)methane (4b)

The compound **4b** was prepared according to the reported method⁹: colorless crystals; ¹H NMR (CDCl₃, 500 MHz) δ 7.18 (d, J =5.4 Hz, 2H), 6.93 (d, J =5.4 Hz, 2H), 4.26 (s, 2H); EI-MS m/z 340 (M^+ + 4), 338 (M^+ + 2), 336 (M^+).

4. Preparation of Bis(2-bromophenyl)ether (4c)

The compound **4c** was prepared according to the reported method¹⁰: colorless oil; ¹H NMR (CDCl₃, 400 MHz) δ 7.63 (d, J =8.0 Hz, 2H), 7.24 (t, J =7.8 Hz, 2H), 7.02 (t, J =7.8 Hz, 2H), (d, J =8.0 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 153.1, 133.8, 128.5, 125.0, 119.4, 114.2; EI-MS m/z 332 ($M^+ + 4$), 330 ($M^+ + 2$), 328 (M^+).

5. X-ray Structural Analysis of 5a

Single crystal of **5a** (C₂₀H₂₀S₄Si₂) suitable for X-ray analysis was prepared by recrystallization from n-hexane. Diffraction data was collected on a Rigaku AFC7R diffractometer at -120 °C with graphite monochromated Mo-K α (λ = 0.71069 Å) radiation. Detail of the X-ray diffraction study are summarized in Table S1. For a structure analysis and refinement, computations were performed using the teXsan¹¹ crystallographic software package of Molecular Structure Corporation. Neutral atom scattering factors were taken from Cromer and Waber.¹² Anomalous dispersion effects were included in F_{cal} ¹³; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.¹⁴ The structure was solved by direct methods (SIR92). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but not refined. The weighting scheme $\omega = 1/\sigma^2(F_0)$ with $\sigma(F_0)$ from counting statistics gave satisfactory agreement analyses.

6. X-ray Structural Analysis of 5c

Single crystal of **5c** (C₂₄H₁₆O₂) suitable for X-ray analysis was prepared by recrystallization from n-hexane. Diffraction data was collected on a Rigaku AFC7R diffractometer at ambient temperature with graphite monochromated Mo-K α (λ = 0.71069 Å) radiation. For a structure analysis and refinement, computations were performed in a similar manner as to **5a**. Detail of the X-ray diffraction study are summarized in Table S1.

7. TABLE S1. Summaries of Crystallographic Data of 5a and 5c

	5a	5c
empirical formula	C ₂₀ H ₂₀ S ₄ Si ₂	C ₂₄ H ₁₆ O ₂
fw	444.79	336.39
crystal syst	monoclinic	orthorhombic
space group	C2/c (#15)	P2 ₁ 2 ₁ 2 ₁ (#19)
cryst color	colorless	colorless
lattice params		
<i>a</i> (Å)	27.190(3)	11.358(2)
<i>b</i> (Å)	11.435(1)	15.466(4)
<i>c</i> (Å)	14.976(2)	9.749(2)
β (°)	113.257(9)	
<i>V</i> (Å ³)	4278.0(10)	1712.5(6)
<i>Z</i>	8	4
<i>D</i> _{calc} (g•cm ⁻³)	1.381	1.305
μ (MoK α) (cm ⁻¹)	5.59	0.82
<i>F</i> (000)	1856.00	704.00
radiation	graphite monochromated Mo-K α (λ = 0.71069 Å)	graphite monochromated Mo-K α (λ = 0.71069 Å)
temp (°C)	-120	25
scan type	ω	ω -2 θ
2 θ max (°)	55.0	55.0
no. of reflns measd		
total	5273	2266
unique	4919	2246
no. of observns	4919 (All)	1518 (I > σ (I))
structure soln	direct methods (SIR92)	direct methods (SIR92)
refinement	full-matrix least squares	full-matrix least squares
reflection / parameter ratio	20.84	6.43
residuals: <i>R</i> ; <i>R</i> _{<i>I</i>}	0.048; 0.032	0.083; 0.061
goodness of fit (GOF)	1.16	1.93
max shift/error in final cycle	1.196	0.001
maximum peak		
in final diff map (e•Å ⁻³)	0.00	0.00
minimum peak		
in final diff map (e•Å ⁻³)	0.00	0.00

8. Figure S1. ^1H NMR spectrum of **5a** (500 MHz).

9. Figure S2. ^{13}C NMR spectrum of **5a** (100 MHz).

10. Figure S3. ^1H NMR spectrum of **5b** (400 MHz).

11. Figure S4. ^{13}C NMR spectrum of **5b** (100 MHz).

12. **Figure S5.** ¹H NMR spectrum of **5c** (500 MHz).

13. **Figure S6.** ¹³C NMR spectrum of **5c** (100 MHz).

14. Theoretical Methods

The GAUSSIAN 98¹⁴ series of programs was used for all DFT calculations. All molecules were fully optimized using the B3LYP¹⁵ levels of theory with the 6-31G(d) basis set. The optimized geometries and energies are shown in Table S2.

15. TABLE S2. Optimized geometries and energies for 5a (at B3LYP/6-31G(d)).

5a (*D*₂-conformer)

HF=-2945.9553632

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	0.000000	0.000000	2.473591
2	6	0	-2.408232	1.351397	1.733721
3	6	0	-1.084706	1.141911	1.429531
4	6	0	-0.681155	1.957111	0.299176
5	6	0	-1.698854	2.738928	-0.183528
6	16	0	-3.173966	2.511998	0.695431
7	6	0	-1.132213	-1.035126	3.585203
8	1	0	-2.992871	0.884570	2.515445
9	1	0	-1.654289	3.438795	-1.007555
10	1	0	-1.698665	-0.403644	4.280693
11	1	0	-0.534177	-1.730206	4.186105
12	1	0	-1.847338	-1.624307	3.001710
13	6	0	2.408232	-1.351397	1.733721
14	6	0	1.084706	-1.141911	1.429531
15	6	0	0.681155	-1.957111	0.299176
16	6	0	1.698854	-2.738928	-0.183528
17	16	0	3.173966	-2.511998	0.695431
18	6	0	1.132213	1.035126	3.585203
19	1	0	2.992871	-0.884570	2.515445
20	1	0	1.654289	-3.438795	-1.007555

21	1	0	1.698665	0.403644	4.280693
22	1	0	0.534177	1.730206	4.186105
23	1	0	1.847338	1.624307	3.001710
24	14	0	0.000000	0.000000	-2.473591
25	6	0	2.408232	1.351397	-1.733721
26	6	0	1.084706	1.141911	-1.429531
27	6	0	0.681155	1.957111	-0.299176
28	6	0	1.698854	2.738928	0.183528
29	16	0	3.173966	2.511998	-0.695431
30	6	0	1.132213	-1.035126	-3.585203
31	1	0	2.992871	0.884570	-2.515445
32	1	0	1.654289	3.438795	1.007555
33	1	0	1.698665	-0.403644	-4.280693
34	1	0	0.534177	-1.730206	-4.186105
35	1	0	1.847338	-1.624307	-3.001710
36	6	0	-2.408232	-1.351397	-1.733721
37	6	0	-1.084706	-1.141911	-1.429531
38	6	0	-0.681155	-1.957111	-0.299176
39	6	0	-1.698854	-2.738928	0.183528
40	16	0	-3.173966	-2.511998	-0.695431
41	6	0	-1.132213	1.035126	-3.585203
42	1	0	-2.992871	-0.884570	-2.515445
43	1	0	-1.654289	-3.438795	1.007555
44	1	0	-1.698665	0.403644	-4.280693
45	1	0	-0.534177	1.730206	-4.186105
46	1	0	-1.847338	1.624307	-3.001710

5a (C_{2h}-conformer)

HF=-2945.9459511

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	14	0	1.539207	1.488811	0.000000
2	6	0	-0.051142	2.499339	0.000000
3	6	0	2.988767	2.711011	0.000000
4	1	0	-0.960980	1.895666	0.000000
5	1	0	3.971516	2.226109	0.000000
6	6	0	2.987319	-0.017710	1.911354
7	6	0	1.727977	0.391403	1.537668
8	6	0	0.731437	-0.135168	2.453876
9	6	0	1.282604	-0.901076	3.451879
10	16	0	3.002657	-1.022515	3.323474
11	1	0	-0.076791	3.144696	0.886182
12	1	0	2.942644	3.354909	0.886211
13	1	0	3.930032	0.219645	1.435693
14	1	0	0.754930	-1.401394	4.252822
15	6	0	2.987319	-0.017710	-1.911354
16	6	0	1.727977	0.391403	-1.537668
17	6	0	0.731437	-0.135168	-2.453876
18	6	0	1.282604	-0.901076	-3.451879
19	16	0	3.002657	-1.022515	-3.323474
20	1	0	-0.076791	3.144696	-0.886182
21	1	0	2.942644	3.354909	-0.886211
22	1	0	3.930032	0.219645	-1.435693
23	1	0	0.754930	-1.401394	-4.252822
24	14	0	-1.539207	-1.488811	0.000000
25	6	0	0.051142	-2.499339	0.000000
26	6	0	-2.988767	-2.711011	0.000000
27	1	0	0.960980	-1.895666	0.000000
28	1	0	-3.971516	-2.226109	0.000000
29	6	0	-2.987319	0.017710	1.911354
30	6	0	-1.727977	-0.391403	1.537668
31	6	0	-0.731437	0.135168	2.453876
32	6	0	-1.282604	0.901076	3.451879
33	16	0	-3.002657	1.022515	3.323474

34	1	0	0.076791	-3.144696	0.886182
35	1	0	-2.942644	-3.354909	0.886211
36	1	0	-3.930032	-0.219645	1.435693
37	1	0	-0.754930	1.401394	4.252822
38	6	0	-2.987319	0.017710	-1.911354
39	6	0	-1.727977	-0.391403	-1.537668
40	6	0	-0.731437	0.135168	-2.453876
41	6	0	-1.282604	0.901076	-3.451879
42	16	0	-3.002657	1.022515	-3.323474
43	1	0	0.076791	-3.144696	-0.886182
44	1	0	-2.942644	-3.354909	-0.886211
45	1	0	-3.930032	-0.219645	-1.435693
46	1	0	-0.754930	1.401394	-4.252822

16. TABLE S3. Optimized geometries and energies for 5b (at B3LYP/6-31G(d)).

5b (C_{2h} -conformer)

HF=-2285.8574372

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.128076	1.264416	0.000000
2	1	0	-2.102142	1.774051	0.000000
3	1	0	-1.343694	0.191793	0.000000
4	16	0	-0.162401	3.262865	1.760182
5	6	0	0.545448	2.798525	3.272593
6	6	0	0.588529	1.443658	3.402424
7	6	0	0.046718	0.738231	2.269978
8	6	0	-0.403884	1.595463	1.286352
9	1	0	0.903960	3.552470	3.960458
10	1	0	1.007730	0.935211	4.264036
11	16	0	-0.162401	3.262865	-1.760182
12	6	0	0.545448	2.798525	-3.272593

13	6	0	0.588529	1.443658	-3.402424
14	6	0	0.046718	0.738231	-2.269978
15	6	0	-0.403884	1.595463	-1.286352
16	1	0	0.903960	3.552470	-3.960458
17	1	0	1.007730	0.935211	-4.264036
18	6	0	1.128076	-1.264416	0.000000
19	1	0	2.102142	-1.774051	0.000000
20	1	0	1.343694	-0.191793	0.000000
21	16	0	0.162401	-3.262865	1.760182
22	6	0	-0.545448	-2.798525	3.272593
23	6	0	-0.588529	-1.443658	3.402424
24	6	0	-0.046718	-0.738231	2.269978
25	6	0	0.403884	-1.595463	1.286352
26	1	0	-0.903960	-3.552470	3.960458
27	1	0	-1.007730	-0.935211	4.264036
28	16	0	0.162401	-3.262865	-1.760182
29	6	0	-0.545448	-2.798525	-3.272593
30	6	0	-0.588529	-1.443658	-3.402424
31	6	0	-0.046718	-0.738231	-2.269978
32	6	0	0.403884	-1.595463	-1.286352
33	1	0	-0.903960	-3.552470	-3.960458
34	1	0	-1.007730	-0.935211	-4.264036

5b (C₂-conformer)

HF=-2285.8562164

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	16	0	0.803483	3.476235	-1.905046
2	6	0	-0.638815	4.265521	-1.359857
3	6	0	-1.361538	3.452789	-0.538898

4	6	0	-0.769496	2.156653	-0.333970
5	6	0	0.426675	2.020267	-1.012465
6	6	0	-1.411742	1.156354	0.546914
7	6	0	-1.884476	1.496998	1.862960
8	6	0	-2.468065	0.453658	2.516572
9	16	0	-2.468065	-0.982787	1.543816
10	6	0	-1.669349	-0.159348	0.227358
11	6	0	-1.418047	-0.873881	-1.074124
12	1	0	-0.869327	5.271649	-1.683028
13	1	0	-2.307653	3.739978	-0.092346
14	1	0	-1.757891	2.483077	2.296695
15	1	0	-2.881512	0.434713	3.515955
16	1	0	-1.097437	-0.123415	-1.806268
17	1	0	-2.369352	-1.264996	-1.458282
18	16	0	-0.803483	-3.476235	-1.905046
19	6	0	0.638815	-4.265521	-1.359857
20	6	0	1.361538	-3.452789	-0.538898
21	6	0	0.769496	-2.156653	-0.333970
22	6	0	-0.426675	-2.020267	-1.012465
23	6	0	1.411742	-1.156354	0.546914
24	6	0	1.884476	-1.496998	1.862960
25	6	0	2.468065	-0.453658	2.516572
26	16	0	2.468065	0.982787	1.543816
27	6	0	1.669349	0.159348	0.227358
28	6	0	1.418047	0.873881	-1.074124
29	1	0	0.869327	-5.271649	-1.683028
30	1	0	2.307653	-3.739978	-0.092346
31	1	0	1.757891	-2.483077	2.296695
32	1	0	2.881512	-0.434713	3.515955
33	1	0	1.097437	0.123415	-1.806268
34	1	0	2.369352	1.264996	-1.458282

5b (D_2 -conformer)

HF=-2285.846054

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
<hr/>					
1	6	0	0.000000	0.000000	2.307558
2	6	0	-0.890328	0.931966	1.513958
3	6	0	-0.642611	1.662289	0.373072
4	6	0	-1.772552	2.453215	-0.027232
5	6	0	-2.849833	2.324037	0.799830
6	16	0	-2.513938	1.219374	2.091004
7	1	0	-0.634318	-0.597555	2.977390
8	1	0	-1.759033	3.093447	-0.902982
9	1	0	-3.814998	2.806982	0.729285
10	6	0	0.890328	-0.931966	1.513958
11	6	0	0.642611	-1.662289	0.373072
12	6	0	1.772552	-2.453215	-0.027232
13	6	0	2.849833	-2.324037	0.799830
14	16	0	2.513938	-1.219374	2.091004
15	1	0	0.634318	0.597555	2.977390
16	1	0	1.759033	-3.093447	-0.902982
17	1	0	3.814998	-2.806982	0.729285
18	6	0	0.000000	0.000000	-2.307558
19	6	0	0.890328	0.931966	-1.513958
20	6	0	0.642611	1.662289	-0.373072
21	6	0	1.772552	2.453215	0.027232
22	6	0	2.849833	2.324037	-0.799830
23	16	0	2.513938	1.219374	-2.091004
24	1	0	0.634318	-0.597555	-2.977390
25	1	0	1.759033	3.093447	0.902982
26	1	0	3.814998	2.806982	-0.729285
27	6	0	-0.890328	-0.931966	-1.513958

28	6	0	-0.642611	-1.662289	-0.373072
29	6	0	-1.772552	-2.453215	0.027232
30	6	0	-2.849833	-2.324037	-0.799830
31	16	0	-2.513938	-1.219374	-2.091004
32	1	0	-0.634318	0.597555	-2.977390
33	1	0	-1.759033	-3.093447	0.902982
34	1	0	-3.814998	-2.806982	-0.729285

17. TABLE S4. Optimized geometries and energies for 5c (at B3LYP/6-31G(d)).

5c (C_2 -conformer)

HF=-1074.6279437

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	1.195375	-1.351868	0.550552
2	6	0	1.605380	-1.896556	1.779087
3	6	0	2.314487	-1.145714	2.713676
4	6	0	2.634778	0.183573	2.432331
5	6	0	2.254154	0.748014	1.217167
6	6	0	1.544871	-0.014702	0.287786
7	8	0	1.244018	0.488780	-0.961178
8	6	0	0.718513	1.760895	-1.099042
9	6	0	1.371289	2.590951	-2.011452
10	6	0	0.893208	3.874540	-2.264819
11	6	0	-0.241838	4.331752	-1.594876
12	6	0	-0.893208	3.493940	-0.692399
13	6	0	-0.444814	2.188676	-0.423956
14	1	0	1.329848	-2.922055	2.008621
15	1	0	2.605170	-1.592703	3.659968
16	1	0	3.186923	0.780625	3.152995
17	1	0	2.509338	1.774391	0.972601

18	1	0	2.255631	2.206384	-2.509739
19	1	0	1.408703	4.512145	-2.977620
20	1	0	-0.628848	5.329009	-1.783629
21	1	0	-1.797670	3.837274	-0.198112
22	6	0	-1.195375	1.351868	0.550552
23	6	0	-1.605380	1.896556	1.779087
24	6	0	-2.314487	1.145714	2.713676
25	6	0	-2.634778	-0.183573	2.432331
26	6	0	-2.254154	-0.748014	1.217167
27	6	0	-1.544871	0.014702	0.287786
28	8	0	-1.244018	-0.488780	-0.961178
29	6	0	-0.718513	-1.760895	-1.099042
30	6	0	-1.371289	-2.590951	-2.011452
31	6	0	-0.893208	-3.874540	-2.264819
32	6	0	0.241838	-4.331752	-1.594876
33	6	0	0.893208	-3.493940	-0.692399
34	6	0	0.444814	-2.188676	-0.423956
35	1	0	-1.329848	2.922055	2.008621
36	1	0	-2.605170	1.592703	3.659968
37	1	0	-3.186923	-0.780625	3.152995
38	1	0	-2.509338	-1.774391	0.972601
39	1	0	-2.255631	-2.206384	-2.509739
40	1	0	-1.408703	-4.512145	-2.977620
41	1	0	0.628848	-5.329009	-1.783629
42	1	0	1.797670	-3.837274	-0.198112

5c (D_2 -conformer)

HF=-1074.6183671

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	8	0	0.000000	0.000000	2.152977
2	6	0	0.922677	0.807361	1.515263
3	6	0	2.148630	0.925255	2.176282
4	6	0	3.140288	1.762254	1.674448
5	6	0	2.914614	2.482704	0.500231
6	6	0	1.686478	2.367398	-0.146740
7	6	0	0.662535	1.543279	0.345641
8	1	0	2.300877	0.345712	3.081258
9	1	0	4.089263	1.844407	2.197320
10	1	0	3.683245	3.135234	0.096367
11	1	0	1.493555	2.936148	-1.052335
12	6	0	-0.922677	-0.807361	1.515263
13	6	0	-2.148630	-0.925255	2.176282
14	6	0	-3.140288	-1.762254	1.674448
15	6	0	-2.914614	-2.482704	0.500231
16	6	0	-1.686478	-2.367398	-0.146740
17	6	0	-0.662535	-1.543279	0.345641
18	1	0	-2.300877	-0.345712	3.081258
19	1	0	-4.089263	-1.844407	2.197320
20	1	0	-3.683245	-3.135234	0.096367
21	1	0	-1.493555	-2.936148	-1.052335
22	8	0	0.000000	0.000000	-2.152977
23	6	0	0.922677	-0.807361	-1.515263
24	6	0	2.148630	-0.925255	-2.176282
25	6	0	3.140288	-1.762254	-1.674448
26	6	0	2.914614	-2.482704	-0.500231
27	6	0	1.686478	-2.367398	0.146740
28	6	0	0.662535	-1.543279	-0.345641
29	1	0	2.300877	-0.345712	-3.081258
30	1	0	4.089263	-1.844407	-2.197320
31	1	0	3.683245	-3.135234	-0.096367
32	1	0	1.493555	-2.936148	1.052335
33	6	0	-0.922677	0.807361	-1.515263
34	6	0	-2.148630	0.925255	-2.176282

35	6	0	-3.140288	1.762254	-1.674448
36	6	0	-2.914614	2.482704	-0.500231
37	6	0	-1.686478	2.367398	0.146740
38	6	0	-0.662535	1.543279	-0.345641
39	1	0	-2.300877	0.345712	-3.081258
40	1	0	-4.089263	1.844407	-2.197320
41	1	0	-3.683245	3.135234	-0.096367
42	1	0	-1.493555	2.936148	1.052335

18. TABLE S5. Optimized geometries and energies for 12a-12c (at B3LYP/6-31G(d)).

12a (C_{2h} -conformer)

HF=-388.2056866

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	0.445220	1.594442	0.000000
2	1	0	1.152816	0.762679	0.000000
3	1	0	1.037159	2.525019	0.000000
4	6	0	-0.376936	1.584041	1.267594
5	6	0	-0.376936	0.633833	2.215850
6	1	0	-0.996771	2.466057	1.433472
7	1	0	-0.958959	0.826306	3.119496
8	6	0	-0.376936	1.584041	-1.267594
9	6	0	-0.376936	0.633833	-2.215850
10	1	0	-0.996771	2.466057	-1.433472
11	1	0	-0.958959	0.826306	-3.119496
12	6	0	-0.445220	-1.594442	0.000000
13	1	0	-1.152816	-0.762679	0.000000
14	1	0	-1.037159	-2.525019	0.000000
15	6	0	0.376936	-1.584041	1.267594

16	6	0	0.376936	-0.633833	2.215850
17	1	0	0.996771	-2.466057	1.433472
18	1	0	0.958959	-0.826306	3.119496
19	6	0	0.376936	-1.584041	-1.267594
20	6	0	0.376936	-0.633833	-2.215850
21	1	0	0.996771	-2.466057	-1.433472
22	1	0	0.958959	-0.826306	-3.119496

12b (C_2 -conformer)

HF=-388.1994106

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	-1.449569	0.755658	-0.726131
2	6	0	-0.568789	1.993294	-0.655302
3	6	0	0.568789	2.183767	0.035707
4	6	0	1.314433	1.232587	0.873020
5	6	0	1.663461	-0.028402	0.576639
6	1	0	-1.080850	0.056929	-1.486793
7	1	0	-2.435531	1.085476	-1.084925
8	1	0	-0.938478	2.844699	-1.226282
9	1	0	0.989926	3.191036	0.008956
10	1	0	1.651001	1.631627	1.831740
11	1	0	2.204244	-0.596191	1.333708
12	6	0	1.449569	-0.755658	-0.726131
13	6	0	0.568789	-1.993294	-0.655302
14	6	0	-0.568789	-2.183767	0.035707
15	6	0	-1.314433	-1.232587	0.873020
16	6	0	-1.663461	0.028402	0.576639
17	1	0	1.080850	-0.056929	-1.486793
18	1	0	2.435531	-1.085476	-1.084925
19	1	0	0.938478	-2.844699	-1.226282

20	1	0	-0.989926	-3.191036	0.008956
21	1	0	-1.651001	-1.631627	1.831740
22	1	0	-2.204244	0.596191	1.333708

12c (D_2 -conformer)

HF=-388.1810833

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	0.000000	0.000000	2.299988
2	6	0	-0.896722	0.947918	1.526644
3	6	0	-0.634122	1.596525	0.386125
4	1	0	-0.635507	-0.592048	2.976777
5	1	0	-1.878710	1.108058	1.971255
6	1	0	-1.432684	2.219839	-0.022816
7	6	0	0.896722	-0.947918	1.526644
8	6	0	0.634122	-1.596525	0.386125
9	1	0	0.635507	0.592048	2.976777
10	1	0	1.878710	-1.108058	1.971255
11	1	0	1.432684	-2.219839	-0.022816
12	6	0	0.000000	0.000000	-2.299988
13	6	0	0.896722	0.947918	-1.526644
14	6	0	0.634122	1.596525	-0.386125
15	1	0	0.635507	-0.592048	-2.976777
16	1	0	1.878710	1.108058	-1.971255
17	1	0	1.432684	2.219839	0.022816
18	6	0	-0.896722	-0.947918	-1.526644
19	6	0	-0.634122	-1.596525	-0.386125
20	1	0	-0.635507	0.592048	-2.976777
21	1	0	-1.878710	-1.108058	-1.971255
22	1	0	-1.432684	-2.219839	0.022816

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