

Supporting Information for

NMR Descriptors of the Strained Metallacycles Formation in Organolithiums: Theoretical Study

Mark V. Kaplanskiy,^[b] Valerii V. Karpov,^[b,c] Elena Yu. Tupikina,^{*[b]} and Alexander S. Antonov^{*[a]}

Dedicated to Professor Alexander F. Pozharskii on the occasion of his 85th birthday.

-
- [a] Dr. A.S. Antonov
Institute of Organic Chemistry
University of Regensburg
D-93053 Regensburg, Germany
E-mail: Alexander.Antonov@chemie.uni-regensburg.de
- [b] M.V. Kaplanskiy, V.V. Karpov, Dr. E.Yu. Tupikina
Institute of Chemistry
St. Petersburg State University
198504 St. Petersburg, Russian Federation
- [c] V.V. Karpov (current address)
Institut für Chemie
Humboldt-Universität zu Berlin
10099 Berlin, Germany

Supporting information for this article is given via a link at the end of the document.

Table of Content

Table S1	NMR properties for monomeric and dimeric metallacycles	2
Table S2	Geometrical properties for monomeric and dimeric metallacycles	4
Table S3	Natural bond orbital (NBO) analysis for some carbanion metallacycles.	6
	Computational details	7
	Optimized geometrical structures of studied compounds in “balls and sticks” representation.	8

Table S1. NMR properties for monomeric and dimeric metallacycles. ${}^{\text{FC}}K_{\text{CLi}}$ – reduced Fermi–contact interaction term; ${}^{\text{SD}}K_{\text{CLi}}$ – reduced spin–dipole interaction term; ${}^{\text{PSO}}K_{\text{CLi}}$ – reduced paramagnetic spin–orbital interaction term; ${}^{\text{DSO}}K_{\text{CLi}}$ – reduced diamagnetic spin–orbital interaction term; ${}^1K_{\text{CLi}}$ – reduced spin–spin interaction constant; $\delta^{6,7}\text{Li}$ – lithium chemical shift which is independent on the isotope; $\delta^{13}\text{C}$ carbon chemical shift. Reduced spin–spin interaction constants and corresponding terms could be converted to observable values by multiplying it to corresponding nuclear g-factors*.

Compound	${}^{\text{FC}}K_{\text{CLi}}$, Hz	${}^{\text{SD}}K_{\text{CLi}}$, Hz	${}^{\text{PSO}}K_{\text{CLi}}$, Hz	${}^{\text{DSO}}K_{\text{CLi}}$, Hz	${}^1K_{\text{CLi}}$, Hz	$\delta^{6,7}\text{Li}$, ppm	$\delta^{13}\text{C}$, ppm
Monomers							
6a	13,367	0,071	−0,080	0,108	13,5	1,80	227,37
7a	13,355	0,021	−0,098	0,068	13,3	2,56	−1,80
8a	6,909	−0,059	−0,035	0,069	6,9	−0,09	173,99
9a							
10a	9,265	−0,001	−0,099	0,078	9,2	1,61	167,88
11a**	12,669	0,062	−0,079	0,107	12,8	2,36	200,49
12a	12,172	0,016	−0,103	0,083	12,2	2,14	24,10
13a	13,532	0,035	−0,089	0,086	13,6	1,60	212,56
14a	13,425	0,073	−0,082	0,109	13,5	2,26	228,44
15a	12,948	0,028	−0,103	0,086	13,0	2,10	30,31
16a	13,842	0,083	−0,057	0,088	14,0	1,11	263,95
17a	12,144	0,092	−0,077	0,122	12,3	2,45	240,58
18a	12,710	0,017	−0,106	0,089	12,7	1,90	26,08
19a	13,168	0,083	−0,063	0,093	13,3	1,00	269,36
20a	13,167	0,082	−0,084	0,123	13,3	2,31	235,74
6b	12,819	0,071	−0,080	0,110	12,9	1,69	229,50
7b	12,699	0,023	−0,097	0,069	12,7	2,34	−2,42
8b	6,820	−0,041	−0,058	0,071	6,8	−0,19	110,14
9b	6,417	−0,004	−0,085	0,078	6,4	1,47	27,73
10b	10,058	−0,008	−0,100	0,079	10,0	1,59	179,36
11b	10,045	0,011	−0,110	0,110	10,1	2,15	214,58
12b	11,425	0,015	−0,102	0,085	11,4	2,34	26,51
13b	12,812	0,029	−0,090	0,088	12,8	1,77	218,76
14b	12,510	0,071	−0,083	0,113	12,6	2,42	231,77
15b	11,857	0,029	−0,104	0,089	11,9	2,11	30,77
16b	13,228	0,072	−0,072	0,091	13,3	1,35	253,02
17b	11,806	0,097	−0,077	0,126	12,0	2,71	241,37
18b	12,035	0,017	−0,107	0,090	12,0	2,27	37,04
19b	12,913	0,082	−0,064	0,094	13,0	1,05	262,70
20b	12,650	0,091	−0,083	0,125	12,8	2,30	237,97
6c	12,452	0,075	−0,081	0,109	12,6	1,74	231,64
7c	12,185	0,025	−0,096	0,071	12,2	2,58	2,86
8c	7,258	−0,033	−0,086	0,080	7,2	0,74	75,42
9c	7,928	−0,007	−0,087	0,083	7,9	1,60	26,93
10c	8,868	−0,009	−0,108	0,082	8,8	1,58	208,82
11c	8,552	0,016	−0,118	0,114	8,6	2,45	233,17
12c	11,099	0,008	−0,103	0,087	11,1	2,62	25,54
13c	12,133	0,027	−0,090	0,090	12,2	2,06	221,08
14c	11,454	0,047	−0,089	0,117	11,5	2,81	237,21

15c	11,483	0,030	-0,106	0,091	11,5	2,56	31,35
16c	12,570	0,075	-0,048	0,093	12,7	1,55	258,21
17c	11,377	0,096	-0,070	0,128	11,5	3,03	240,18
18c	12,102	0,034	-0,107	0,091	12,1	2,29	29,60
19c	12,278	0,063	-0,065	0,095	12,4	1,18	256,78
20c	12,329	0,092	-0,086	0,128	12,5	2,50	237,41
6d	10,274	0,074	-0,065	0,100	10,4	2,89	240,64
7d	10,252	0,021	-0,080	0,061	10,3	3,39	-0,44
9d	7,419	-0,020	-0,090	0,077	7,4	2,94	31,35
8d	5,271	-0,015	-0,113	0,077	5,2	4,18	53,13
10d	7,158	-0,020	-0,117	0,079	7,1	2,90	208,23
11d	7,953	-0,030	-0,117	0,117	7,9	-0,31	230,42
12d	9,025	0,003	-0,093	0,082	9,0	3,78	33,11
13d	10,418	0,009	-0,090	0,084	10,4	3,47	213,11
14d	10,257	0,024	-0,103	0,116	10,3	2,68	242,97
15d	9,562	0,022	-0,094	0,084	9,6	3,80	34,36
16d	13,837	0,028	-0,071	0,091	13,9	1,11	199,92
17d	12,048	0,094	-0,068	0,122	12,2	2,32	233,69
18d	9,823	0,031	-0,093	0,085	9,8	3,19	32,78
19d	11,064	0,065	-0,057	0,088	11,2	2,35	249,44
20d	11,998	0,096	-0,067	0,125	12,2	2,34	238,85
Dimers							
21a	8,613	0,024	-0,095	0,114	8,7	2,02	201,06
22a	7,152	-0,002	-0,095	0,075	7,1	3,35	2,76
23a	1,405	-0,027	-0,046	0,063	1,4	0,77	107,05
24a	3,440	-0,007	-0,076	0,079	3,4	2,80	30,29
25a	3,337	-0,009	-0,107	0,104	3,3	2,79	181,13
26a	6,592	0,004	-0,101	0,091	6,6	3,12	29,53
27a	5,763	0,003	-0,103	0,116	5,8	3,45	198,66
28a	7,478	0,009	-0,105	0,092	7,5	2,70	28,78
29a	9,440	0,057	-0,098	0,135	9,5	2,18	207,42
30a	7,580	0,005	-0,112	0,096	7,6	2,76	37,30
31a	9,458	0,048	-0,108	0,135	9,5	2,01	203,06
21b	8,191	0,020	-0,092	0,114	8,2	2,26	201,61
22b	7,134	-0,002	-0,093	0,076	7,1	3,28	5,83
23b	1,397	-0,020	-0,062	0,072	1,4	1,55	75,72
24b	3,945	-0,007	-0,078	0,083	3,9	2,84	28,41
25b	2,884	-0,019	-0,110	0,111	2,9	2,29	192,38
26b	6,788	0,005	-0,103	0,093	6,8	3,54	32,93
27b	6,666	0,009	-0,105	0,120	6,7	3,77	200,87
28b	7,516	0,009	-0,107	0,096	7,5	2,96	30,15
29b	9,497	0,065	-0,093	0,136	9,6	2,19	204,73
30b	8,337	0,016	-0,108	0,097	8,3	3,02	40,25
31b	9,274	0,046	-0,111	0,137	9,3	2,28	225,21

*g-factor ^{13}C = 1.40482; g-factor ^6Li = 0.8220; g-factor ^7Li = 2.17096.

Table S2. Geometrical properties for monomeric and dimeric metallacycles. Metallacycle's size – describe formal size of the cycle; r_{CLi} – carbon and lithium interatomic distance; $\angle\alpha$ – intracycle valence angle X–C–Li, where X = C, N, O or F.

Compound	Metallacycle's size	r_{CLi} , Å	$\angle\alpha$, °
Monomers			
6a	0	2,074	
7a	0	2,092	
8a	3	2,022	62,3
9a	4		
10a	4	2,081	89,3
11a	4	2,067	117,3
12a	5	2,102	96,6
13a	5	2,061	106,8
14a	5	2,074	108,6
15a	6	2,091	108,6
16a	6	2,056	119,0
17a	6	2,033	125,0
18a	7	2,085	103,0
19a	7	2,078	122,8
20a	7	2,034	128,3
6b	0	2,079	90,6
7b	0	2,100	
8b	3	2,044	61,5
9b	4	2,144	84,9
10b	4	2,075	87,4
11b	4	2,079	88,6
12b	5	2,113	97,2
13b	5	2,074	104,6
14b	5	2,073	107,3
15b	6	2,086	107,8
16b	6	2,051	117,5
17b	6	2,014	122,1
18b	7	2,112	115,4
19b	7	2,077	124,0
20b	7	2,029	125,7
6c	0	2,095	
7c	0	2,115	
8c	3	2,024	67,6
9c	4	2,112	80,9
10c	4	2,064	86,3
11c	4	2,058	88,3
12c	5	2,099	100,4
13c	5	2,075	104,2
14c	5	2,074	104,8
15c	6	2,083	105,4
16c	6	2,069	114,3
17c	6	2,030	119,3
18c	7	2,121	114,8

19c	7	2,080	116,7
20c	7	2,029	126,7
6d	0	2,154	
7d	0	2,192	
8d	3	2,028	68,4
9d	4	2,108	75,6
10d	4	2,049	81,3
11d	4	2,034	77,6
12d	5	2,135	91,9
13d	5	2,107	100,0
14d	5	2,084	98,7
15d	6	2,126	101,4
16d	6	2,083	108,7
17d	6	2,052	117,3
18d	7	2,175	108,9
19d	7	2,131	118,7
20d	7	2,057	122,1
Dimers			
21a	0	2,167	
22a	0	2,174	
23a	3	2,227	56,8
24a	4	2,263	83,1
25a	4	2,264	80,4
26a	5	2,205	94,8
27a	5	2,272	96,2
28a	6	2,197	107,5
29a	6	2,096	122,4
30a	7	2,205	114,8
31a	7	2,122	131,3
21b	0	2,184	
22b	0	2,194	
23b	3	2,206	63,3
24b	4	2,246	78,6
25b	4	2,221	78,4
26b	5	2,199	97,0
27b	5	2,227	99,2
28b	6	2,188	106,6
29b	6	2,112	121,0
30b	7	2,181	110,1
31b	7	2,113	132,1

Table S3. Natural bond orbital (NBO) analysis for some carbanion metallacycles. Orbital types are divided into Lewis's orbitals and non-Lewis's orbitals. Core (CR), bond (BD) and lone pair (LP) orbitals correspond to former type; Lewis's low-valence (LV), anti-bond (BD*) and Rydberg's (Ry) orbitals correspond to later type. Occupancy describes the effective electrons number on the natural orbital; Hybridization describes the atomic orbital composition of the natural orbital; E – is the orbital interaction energy obtained by second order perturbation theory.

Complex	Orbital type*		Occupancy		Hybridization		E , kcal/mol
	C	Li	C	Li	C	Li	
7d	LP	Ry	1.907	0.188	sp ^{3.35}	s	31.04
8d	LP	LV	1.844	0.171	sp ^{4.97}	s	12.14
9d	LP	LV	1.828	0.232	sp ^{3.92}	s	25.37
12d	LP	LV	1.846	0.204	sp ^{3.50}	s	27.78
15d	LP	LV	1.852	0.196	sp ^{3.31}	s	29.90
18d	LP	LV	1.865	0.190	sp ^{3.34}	s	23.97

Computational details

All calculations were performed using Gaussian16 software version C.01. Geometries of all compounds were optimized to the minimum on the potential energy surface (PES) using B3LYP/def2-TZVP level of theory and PCM(Et₂O) scheme to include implicit solvent effects. For modeling explicit solvent effects, we used Me₂O instead of Et₂O to save computational time. We used dispersion correction GD3BJ to improve geometry description. Optimized geometries were checked for the absence of imaginary frequencies and were satisfied standard for Gaussian16 convergence criteria. For numerical integrations UltraFine grid was used.

In our previous work, we found that the combination of the WP04 functional and the aug-pcSseg-1 basis set gives accurate description of ¹J_{CLi}. We used this combination as well as PCM(Et₂O) scheme to calculate ¹J_{CLi}, carbon and lithium shielding constants values. The last two were then converted to chemical shifts using eq 1:

$$\delta = \sigma^{ref} - \sigma, \quad 1$$

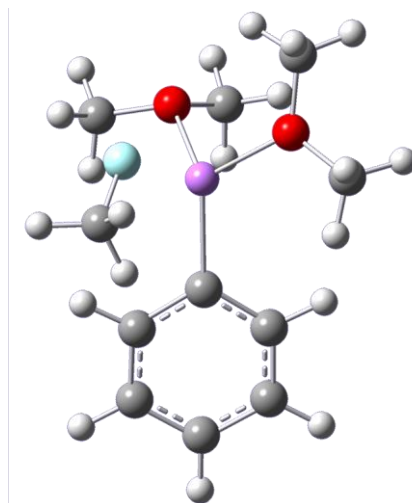
δ – carbon or lithium chemical shift value; σ – carbon or lithium shielding constant value; σ^{ref} – shielding constant value of the corresponding nuclear in a reference system. In case of carbon nuclear the reference system is tetramethylsilane and in case of lithium nuclear – lithium cation solvated by water molecules. In both cases the geometry optimization procedure and shielding calculations for the reference systems were performed in the same level of theory as for the studied complexes.

Optimized geometrical structures of studied compounds in “balls and sticks” representation.

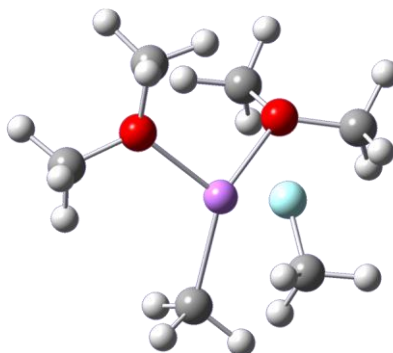
Compound

Structure

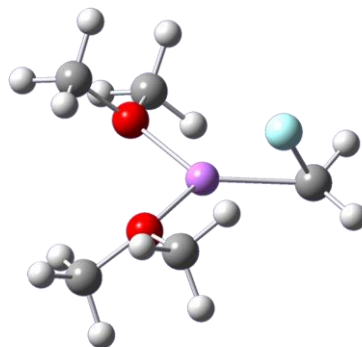
6a



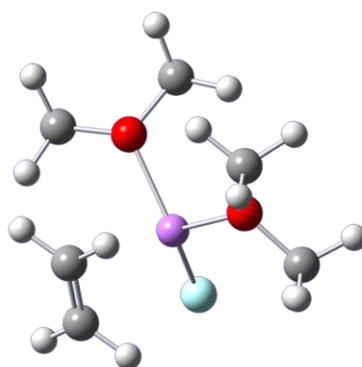
7a



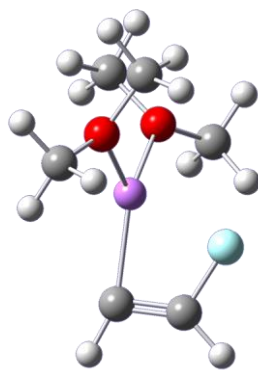
8a



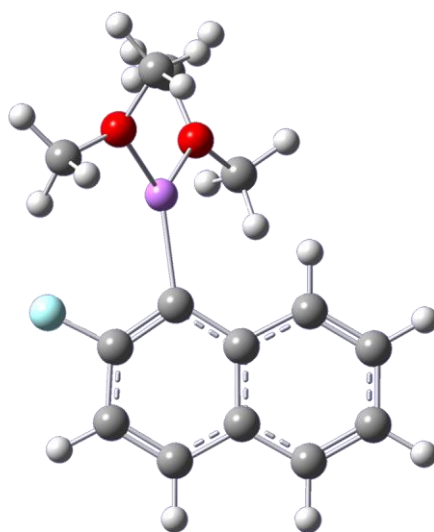
9a



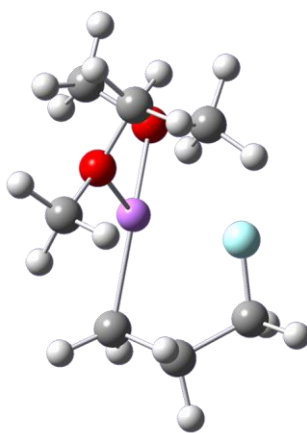
10a



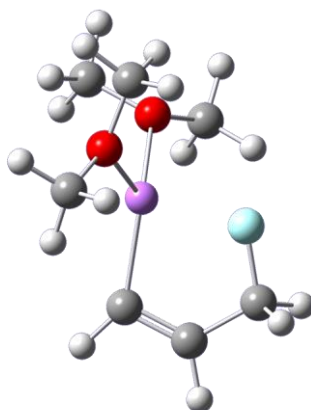
11a



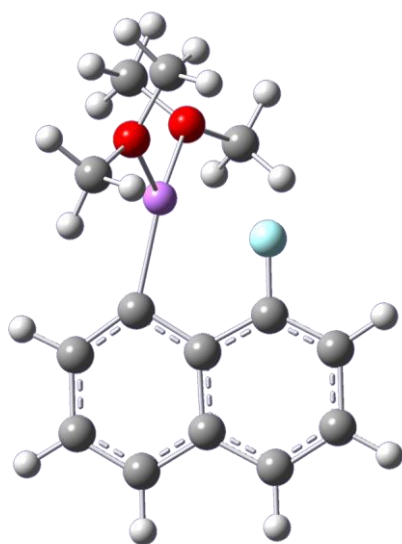
12a



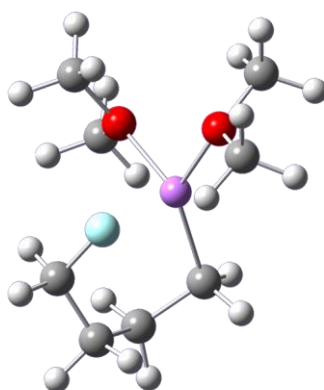
13a



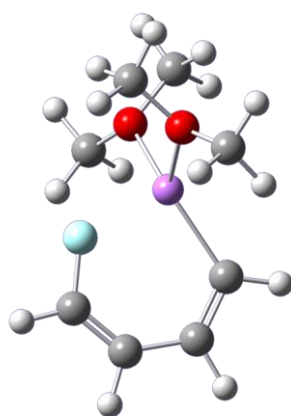
14a



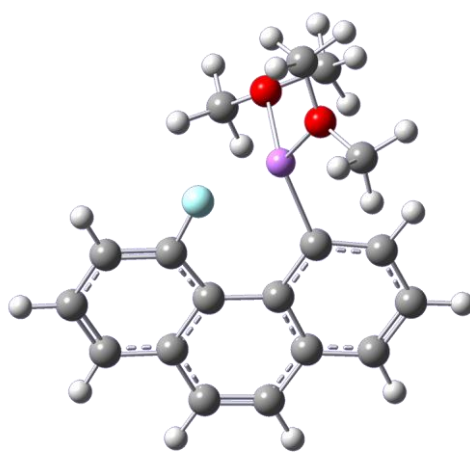
15a



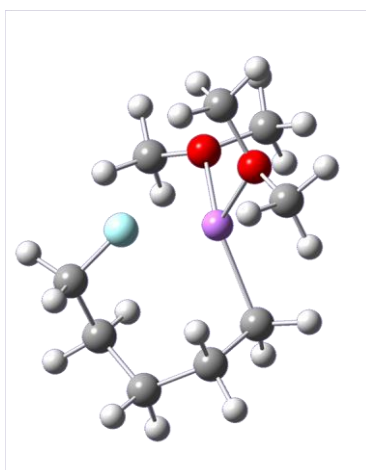
16a



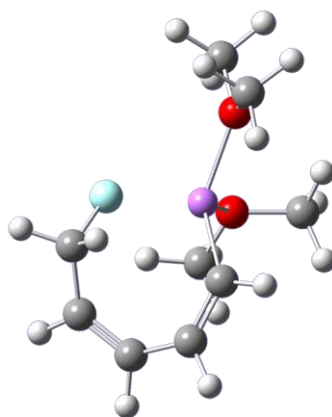
17a



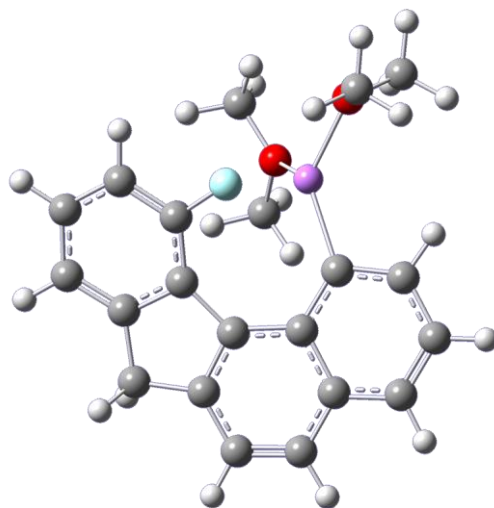
18a



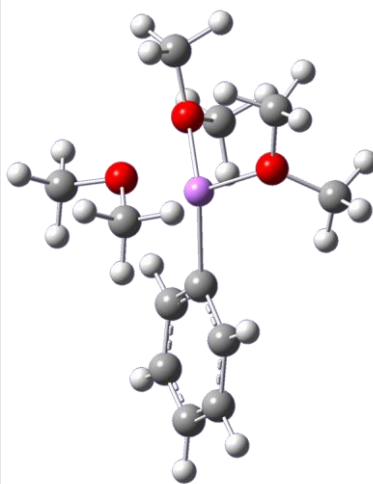
19a



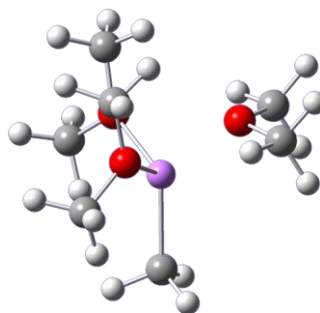
20a



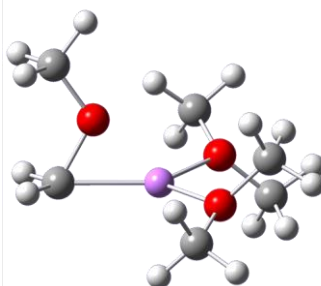
6b



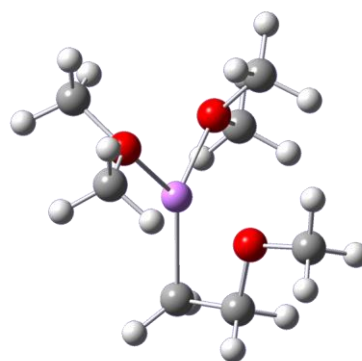
7b



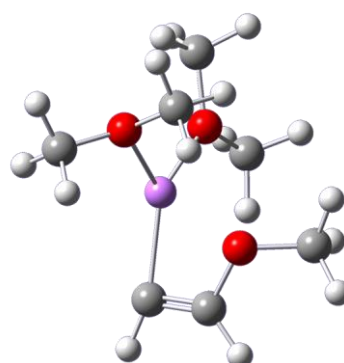
8b



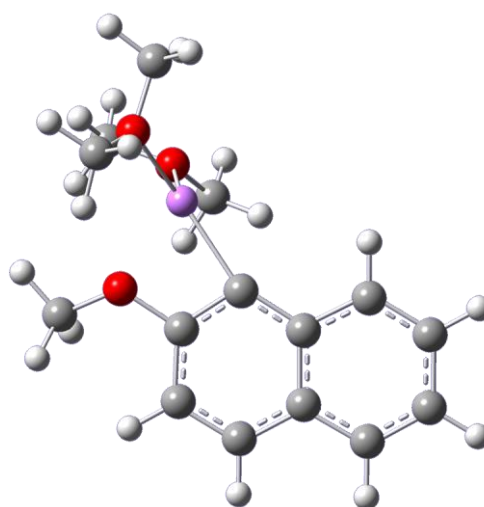
9b



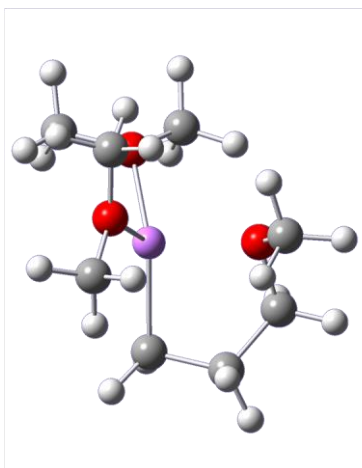
10b



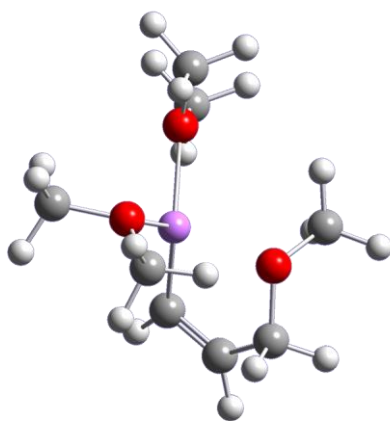
11b



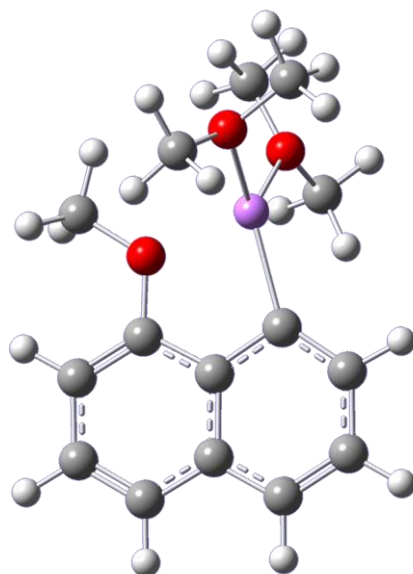
12b



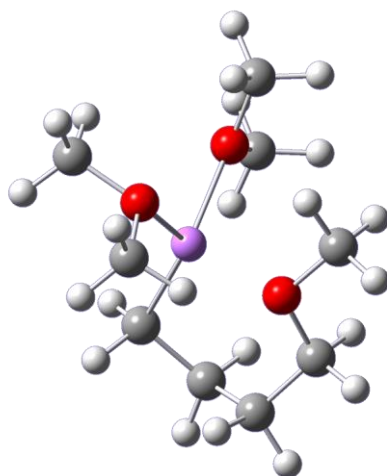
13b



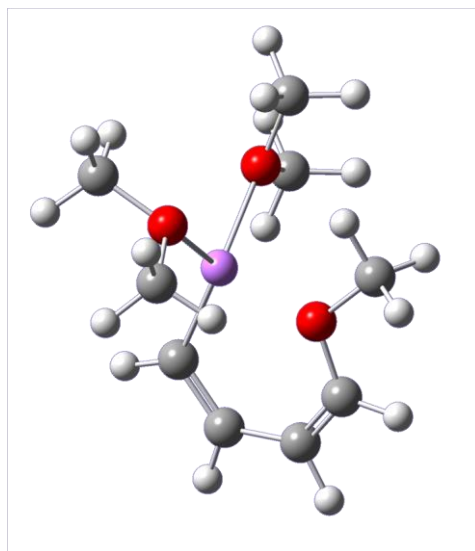
14b



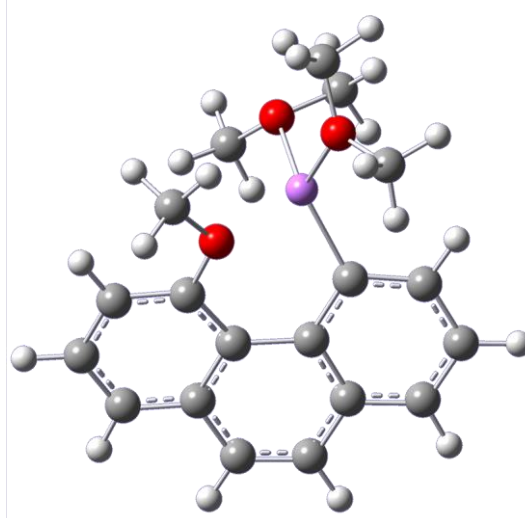
15b



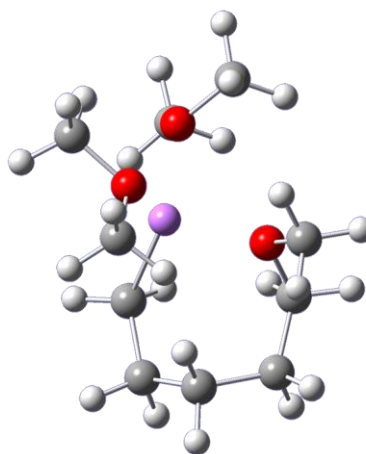
16b



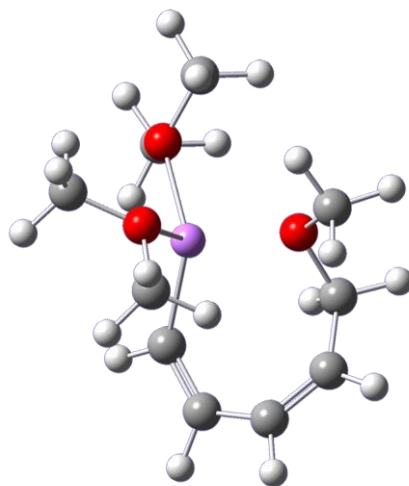
17b



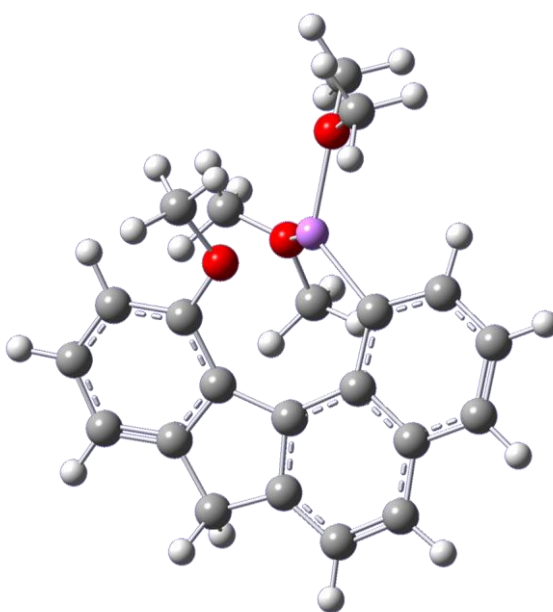
18b



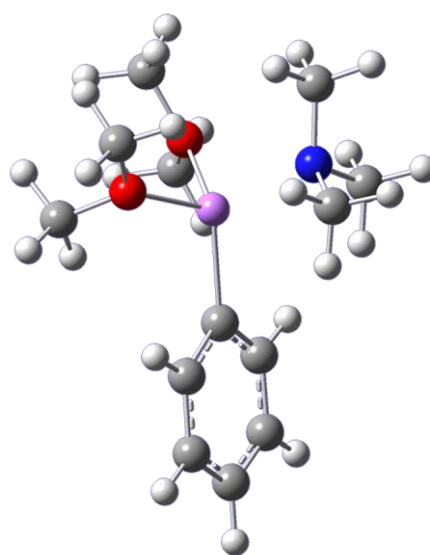
19b



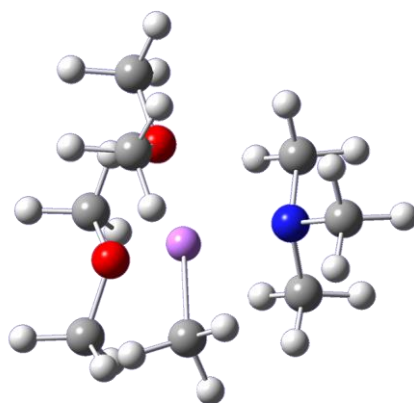
20b



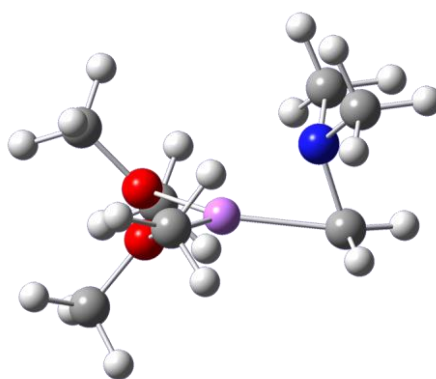
6c



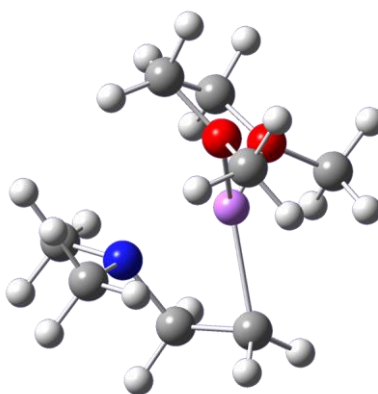
7c



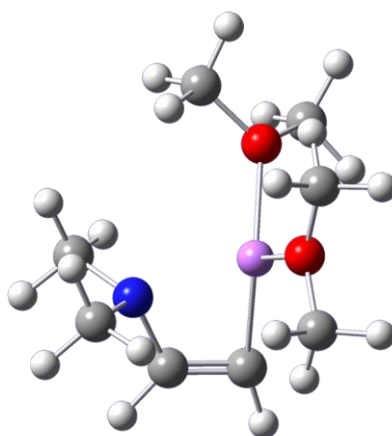
8c



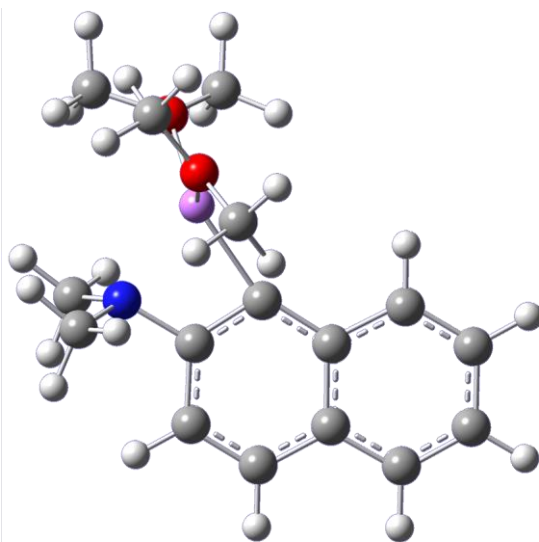
9c



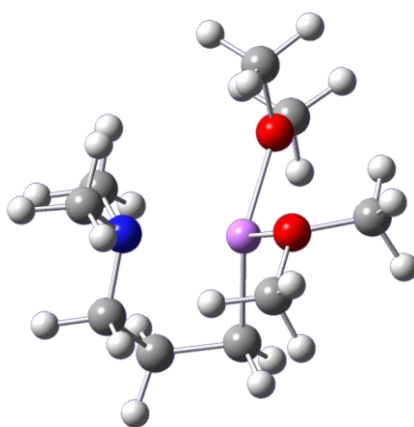
10c



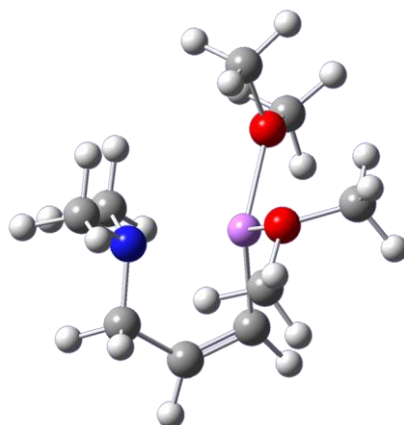
11c



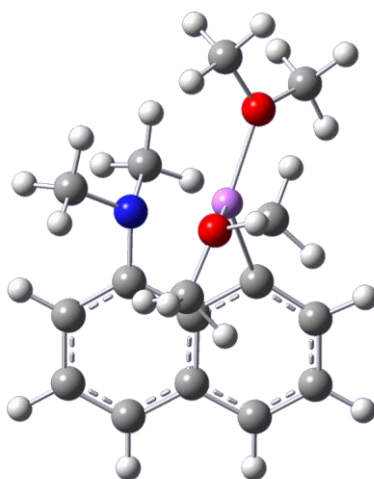
12c



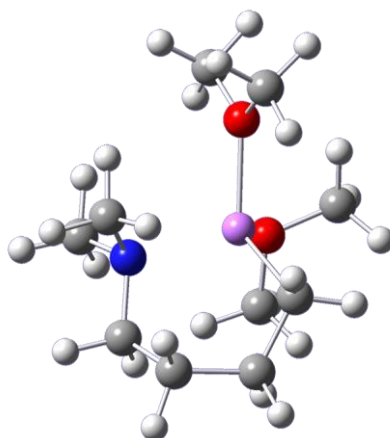
13c



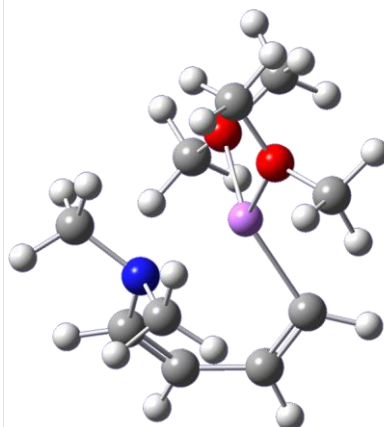
14c



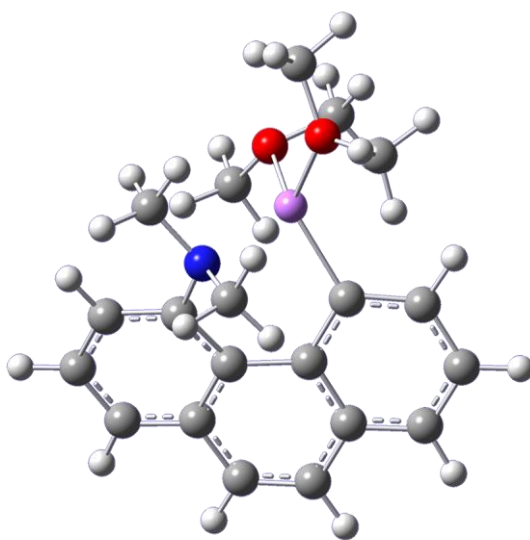
15c



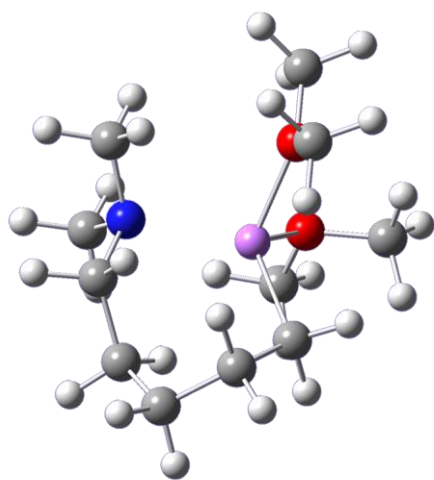
16c



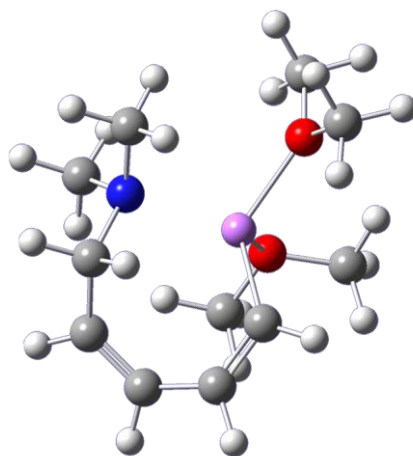
17c



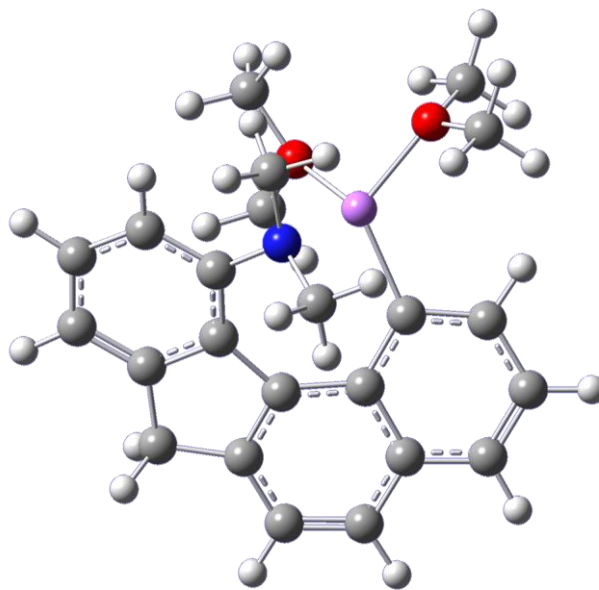
18c



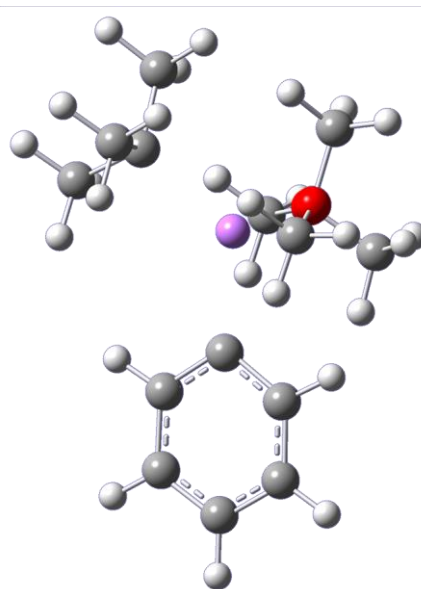
19c



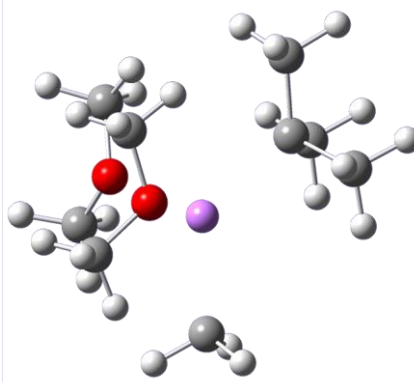
20c



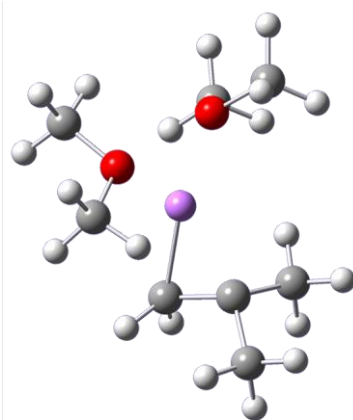
6d



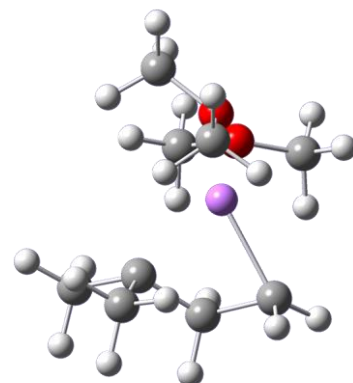
7d



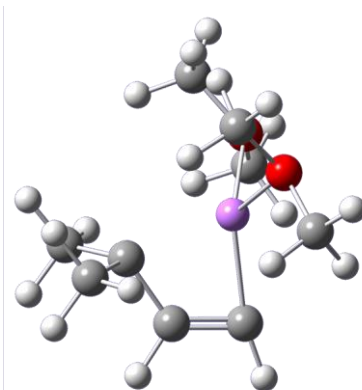
8d



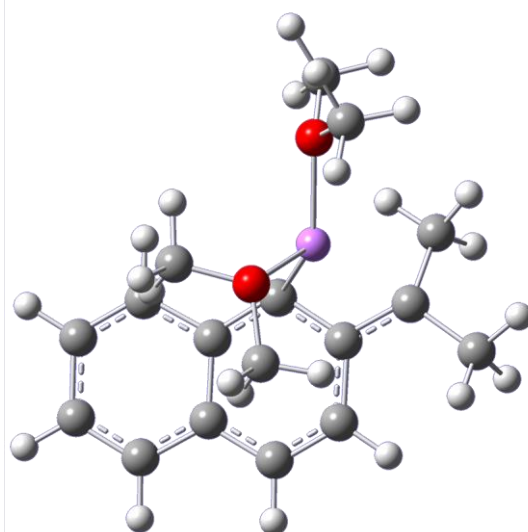
9d



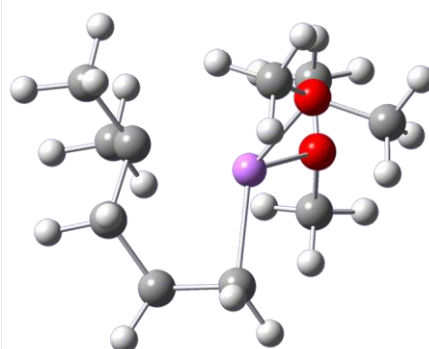
10d



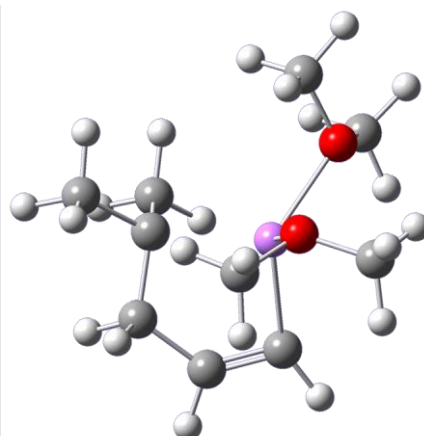
11d



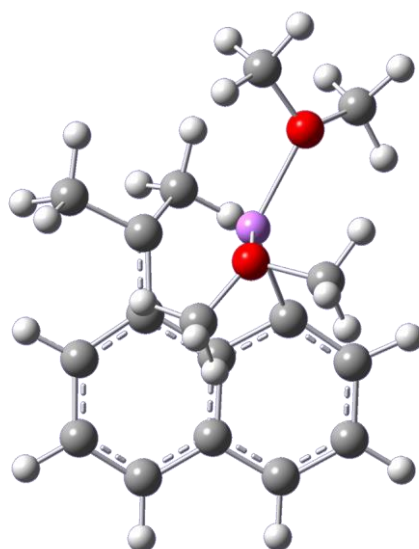
12d



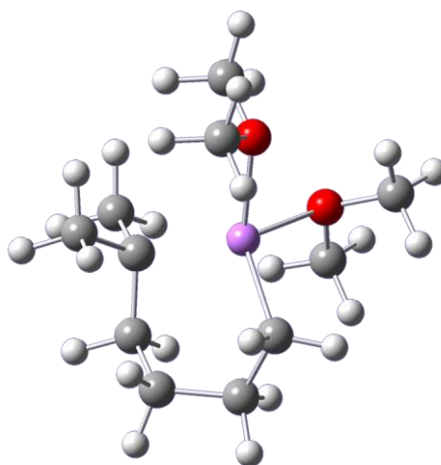
13d



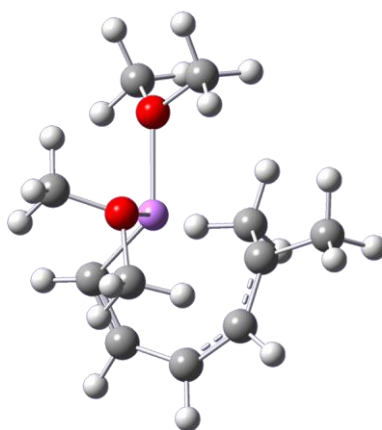
14d



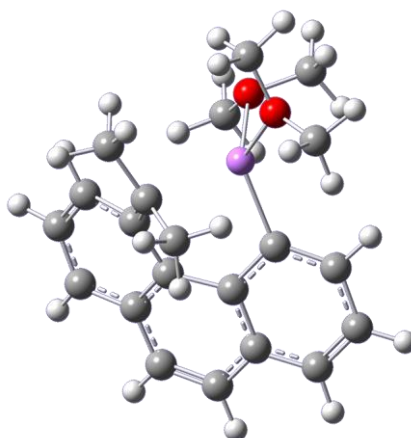
15d



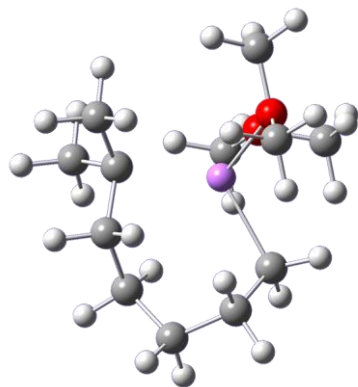
16d



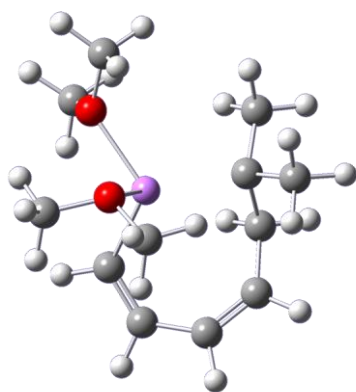
17d



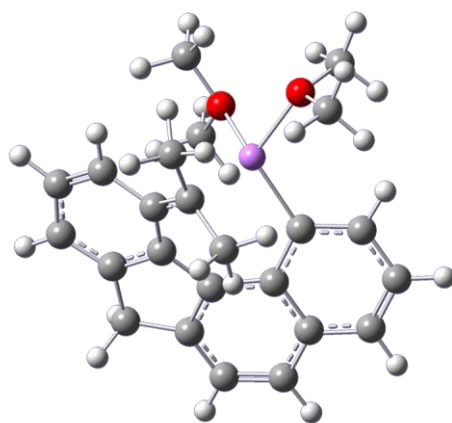
18d



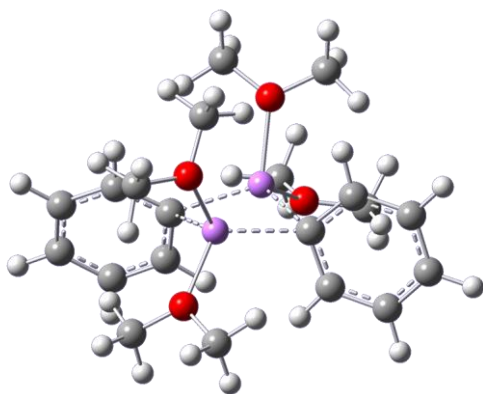
19d



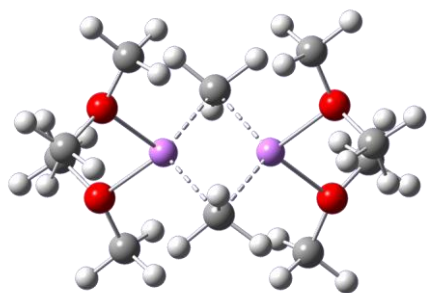
20d



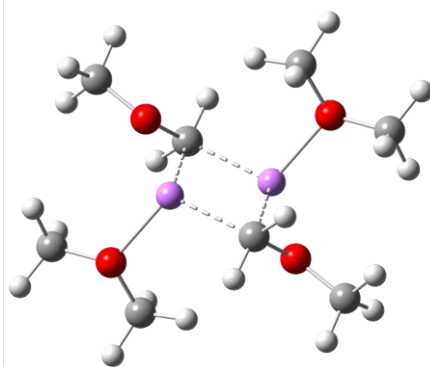
21a



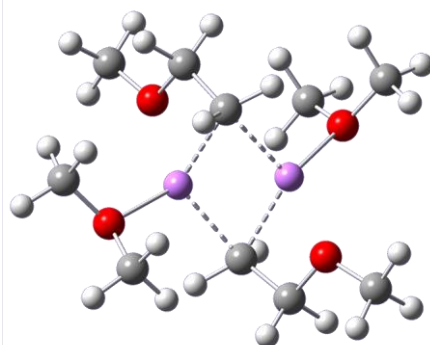
22a



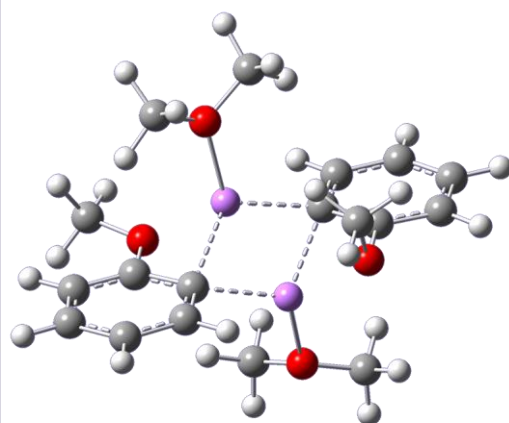
23a



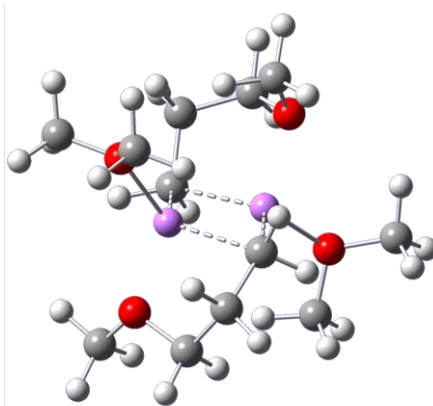
24a



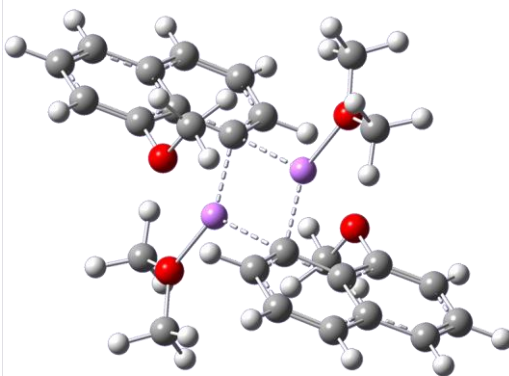
25a



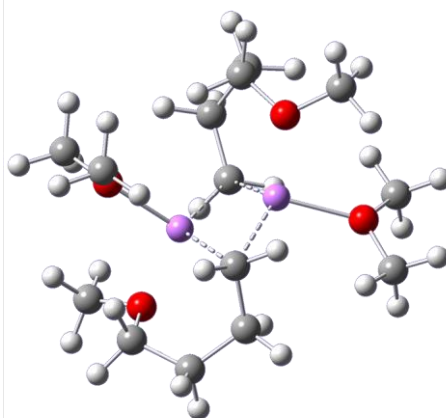
26a



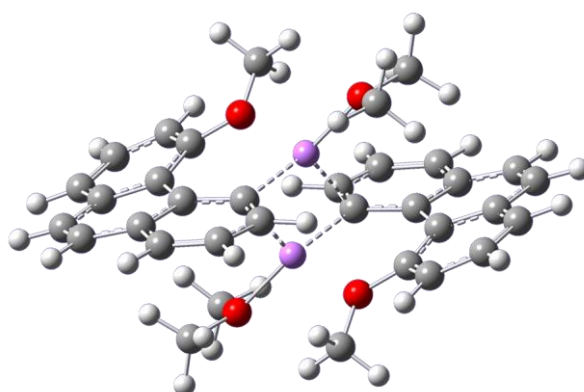
27a



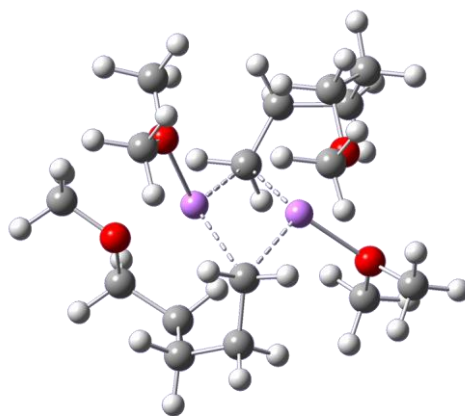
28a



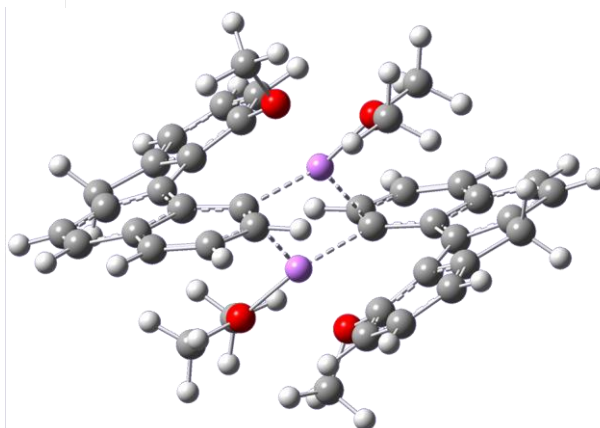
29a



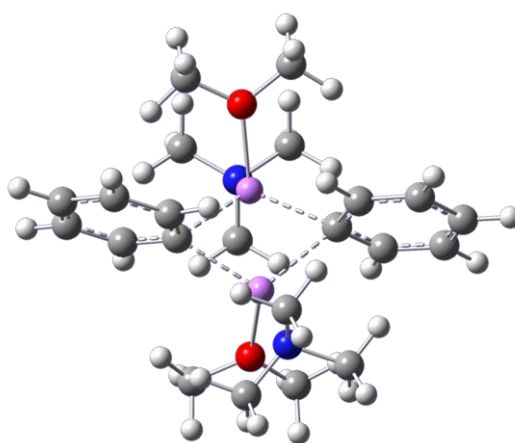
30a



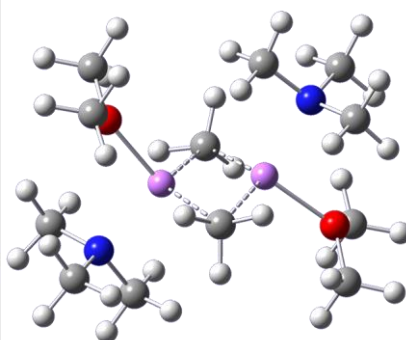
31a



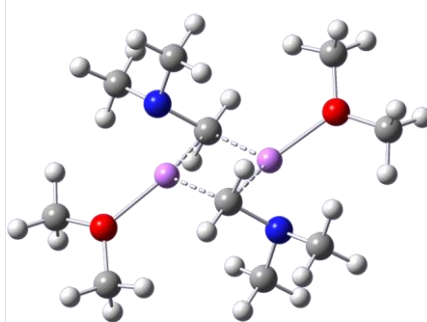
21b



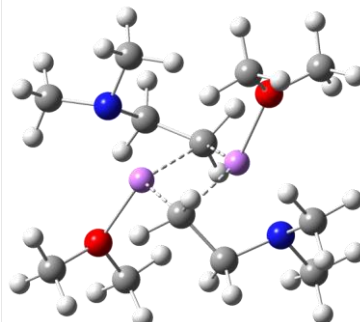
22b



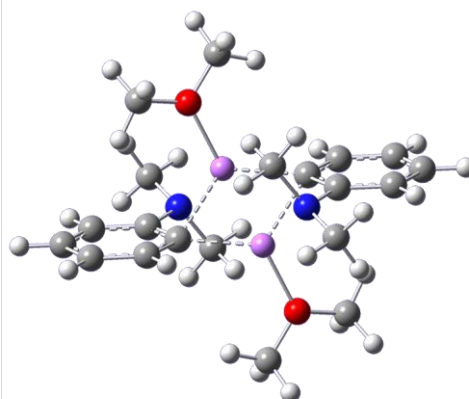
23b



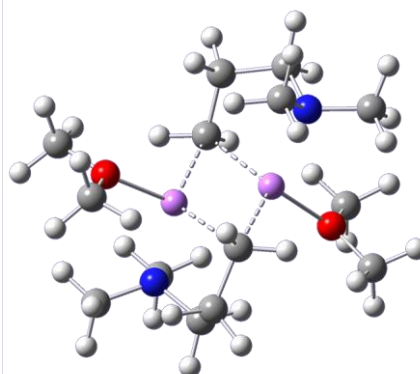
24b



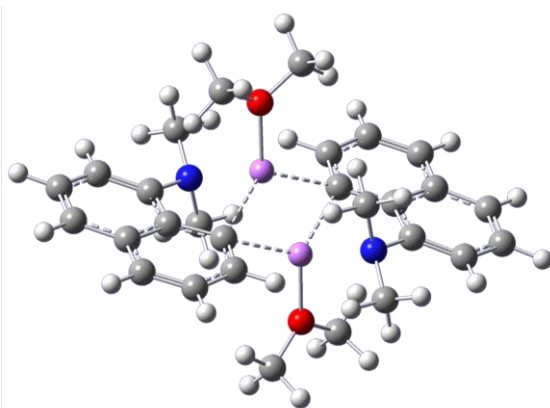
25b



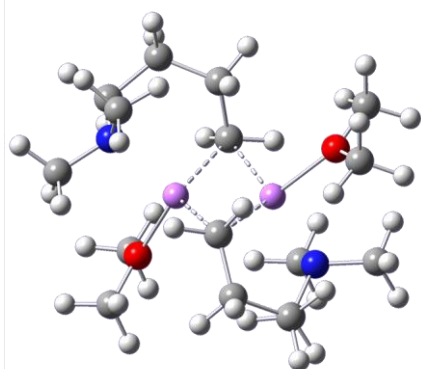
26b



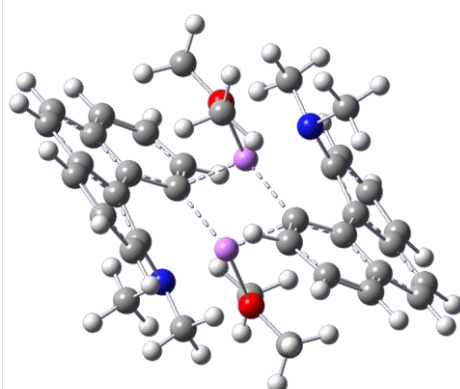
27b



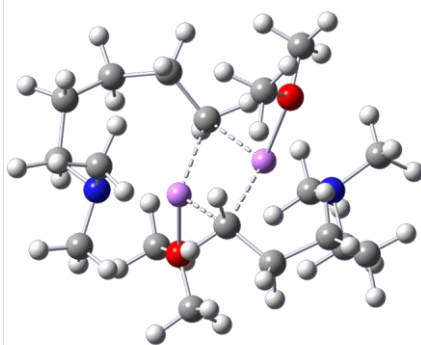
28b



29b



30b



31b

