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Supporting Information

Rhodium-Mediated Enantioselective Synthesis of a Benzopicene-Based Phospha[9]helicene: Structure-Properties Relationship of Triphenylene- and Benzopicene-Based Carbo- and Phosphahelicenes

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I. Theoretical Calculations

All calculations were carried out using the Gaussian 09 program.[1] Full optimizations were performed with wB97XD,[2] the 6-31G(d) basis set, and the integral equation formalism polarizable continuum model (IEFPCM, chloroform).[3]

Pictorial representatiosn of frontier molecular orbitals of carbo[7]helicene **1**, phospha[7]helicene **2**, carbo[9]helicene **3**, and phospha[9]helicene **4** are shown in Figure S1, Figure S2, Figure S3, and Figure S4, respectively.

Cartesian coordinates of optimized [7]helicene **1**, phospha[7]helicene **2**, [9]helicene **3** and phospha[9]helicene **4** are shown in Table S1.

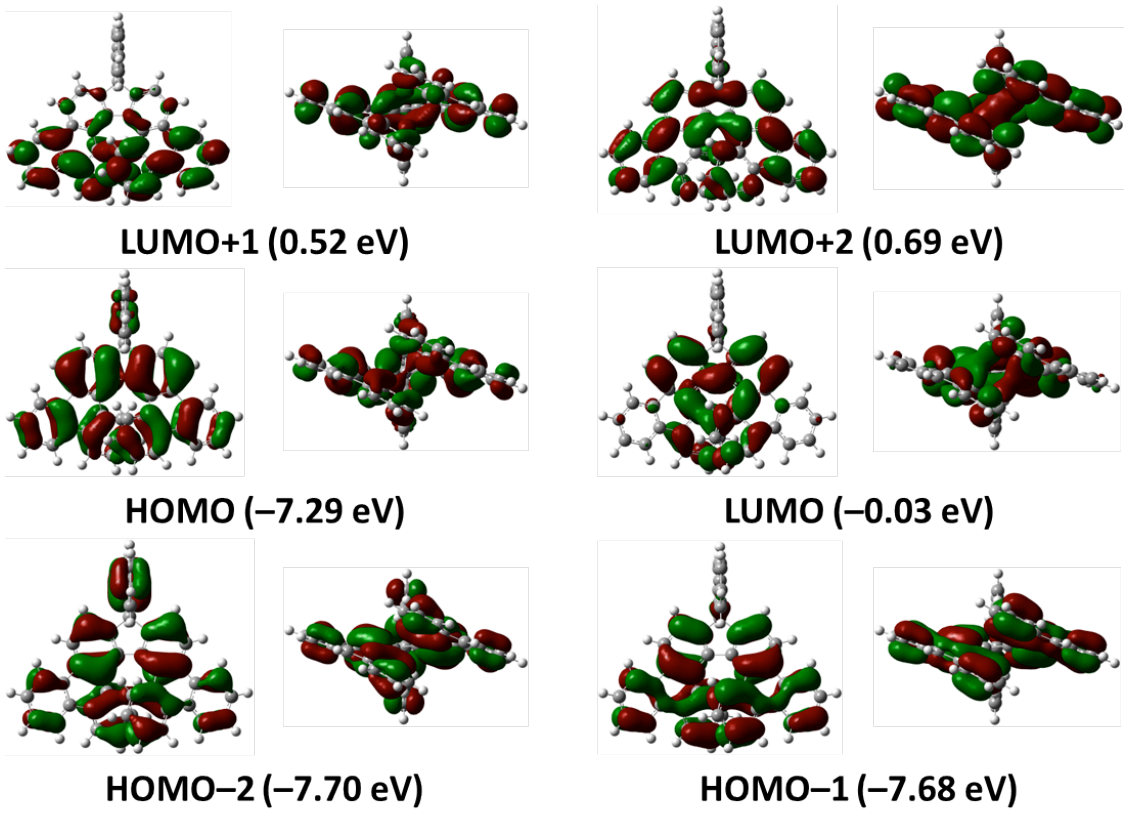

Figure S1. Pictorial representation of frontier molecular orbitals of carbo[7]helicene **1.**

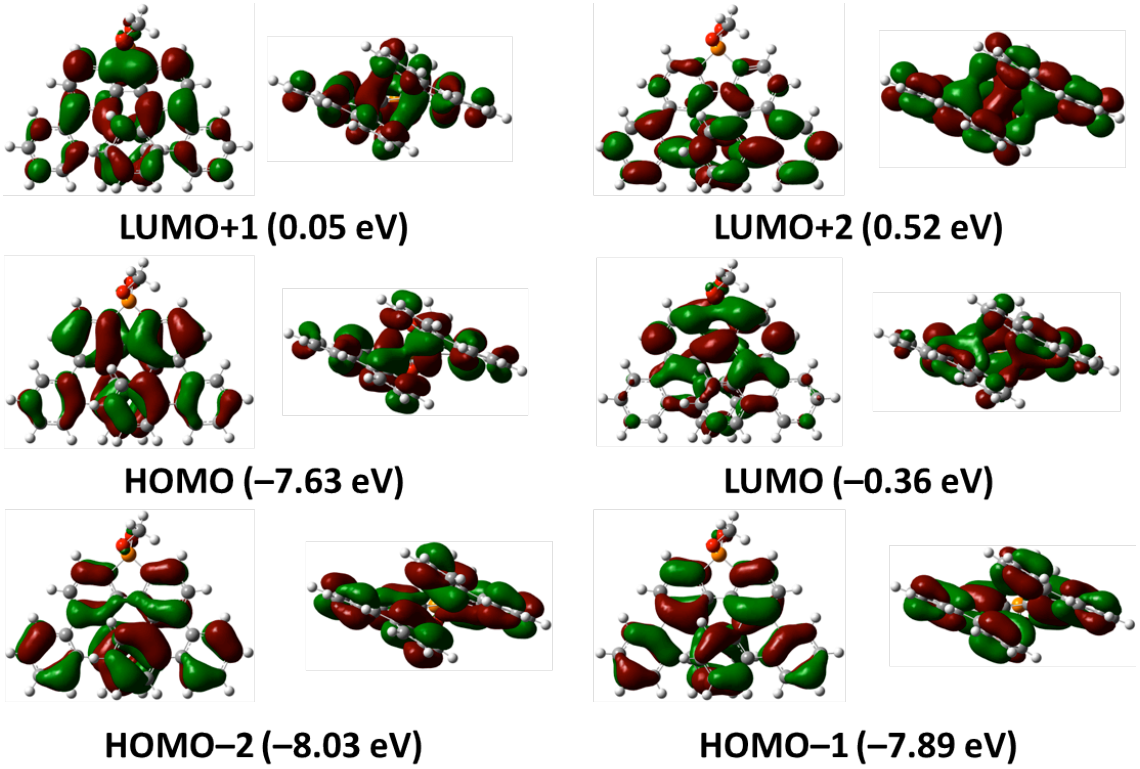

Figure S2. Pictorial representation of frontier molecular orbitals of phospha[7]helicene **2**.

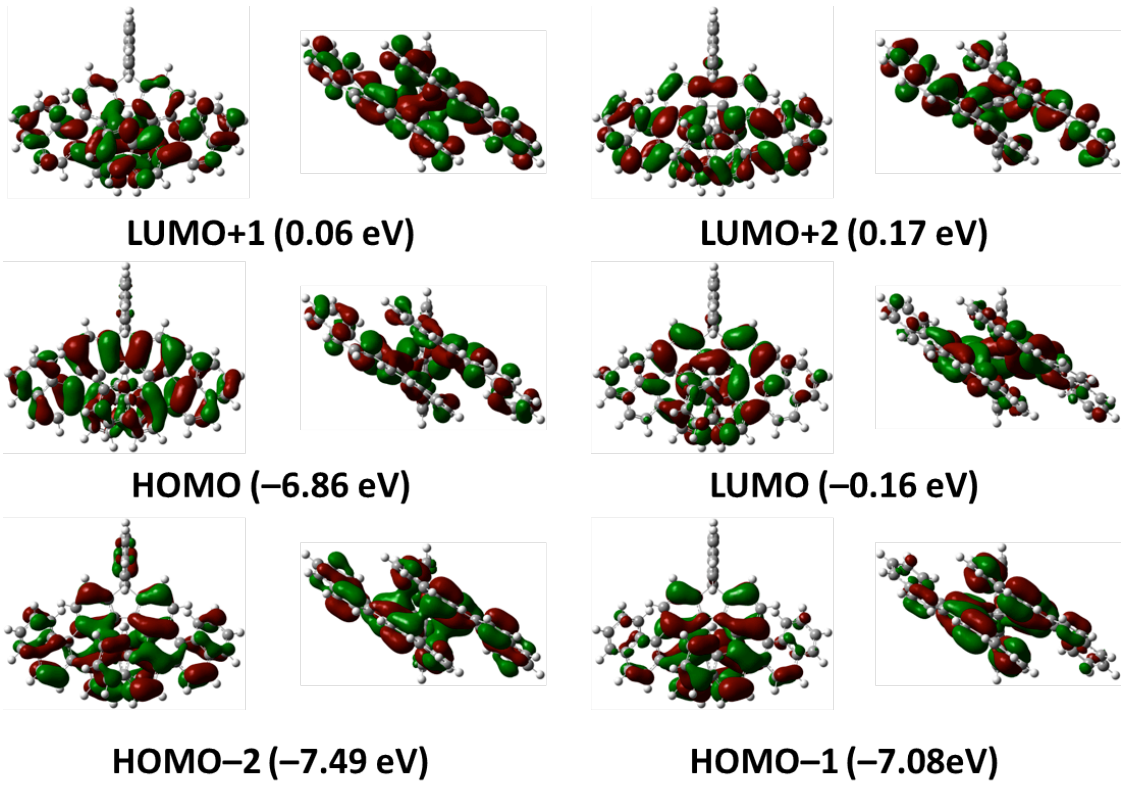

Figure S3. Pictorial representation of frontier molecular orbitals of carbo[9]helicene **3**.

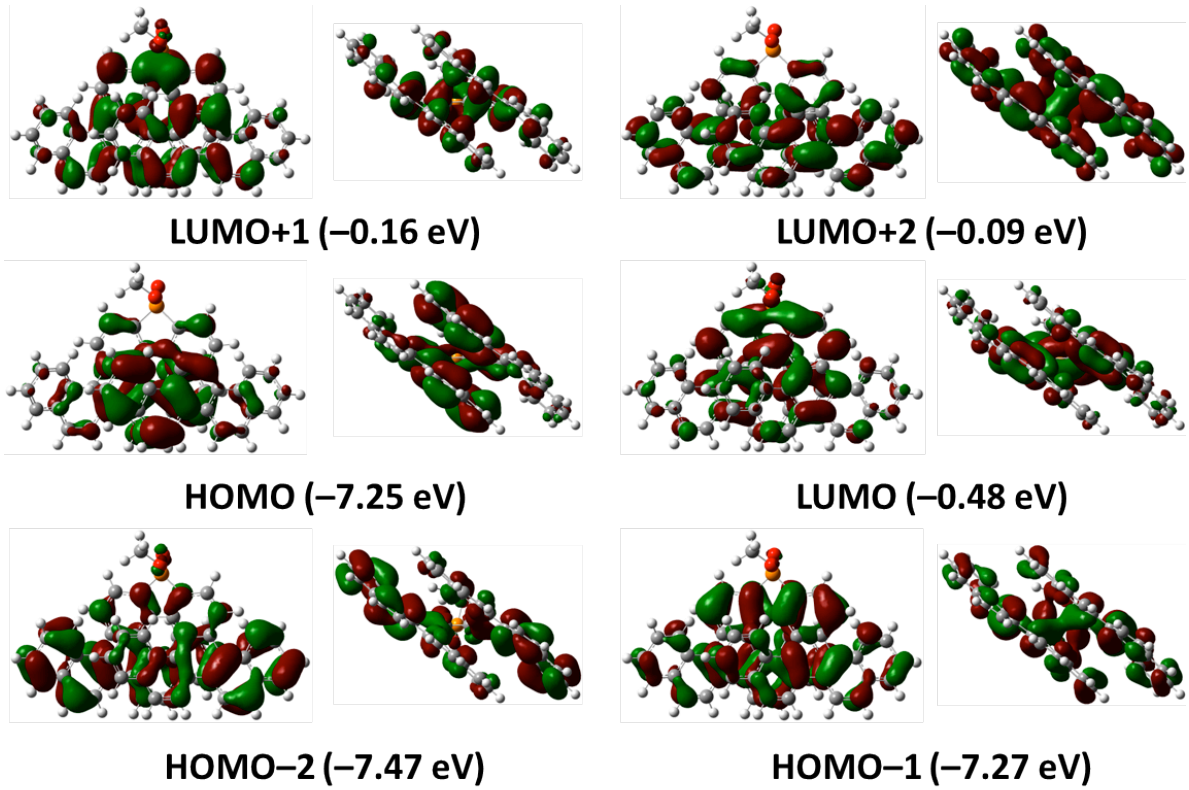

Figure S4. Pictorial representation of frontier molecular orbitals of phospha[9]helicene **4**.

Table S1. Cartesian coordinates of optimized [7]helicene **1**, phospha[7]helicene **2**, [9]helicene **3** and phospha[9]helicene **4**.

[7]helicene **1**

C 2.69473 0.00015 0.00058
C 1.73554 -1.16959 0.00263
C 1.73544 1.1698 -0.00089
C 0.40951 -0.74271 0.08952
C 0.40945 0.74278 -0.08816
C -0.60024 -1.70482 0.35742
C -0.6003 1.70476 -0.35639
C -0.28441 -3.06686 0.13645
C -1.91057 -1.38396 0.92971
C -2.95971 -2.32381 0.8687
C -1.37886 -4.04536 0.03211
C -2.70826 -3.65004 0.29662
C -2.1134 -0.19028 1.64441
C -4.20612 -1.98208 1.42428
C 1.05901 -3.4497 -0.03914
C -1.14647 -5.35596 -0.42714
C -3.7516 -4.56176 0.05233
C -1.91034 1.3838 -0.92924
C -0.2847 3.06685 -0.13521
C -1.37933 4.04522 -0.03131
C -2.95962 2.32352 -0.86868
C -2.70855 3.64981 -0.29655
C 1.05859 3.44982 0.04089
C -1.14726 5.35582 0.42812
C -2.11272 0.19011 -1.64405
C -4.20577 1.98159 -1.42472
C -3.75206 4.56152 -0.05293
C 2.07486 2.51575 0.03505
H 1.31872 4.4966 0.14083
H 3.11526 2.82082 0.09735
C 2.07515 -2.51552 -0.03307
H 1.31925 -4.49647 -0.13896
H 3.11561 -2.82042 -0.09517
C -2.18322 -6.24486 -0.63565
H -0.13918 -5.68252 -0.65701
H -1.97158 -7.24619 -0.99782
C -3.50075 -5.8408 -0.40448
H -4.78104 -4.26099 0.21055
H -4.32508 -6.52304 -0.58779
C -4.40744 -0.76759 2.05122
H -5.02614 -2.69042 1.39583
H -5.38023 -0.53004 2.4708
C -3.34247 0.1269 2.18564
H -1.28584 0.49428 1.78301
H -3.47276 1.06279 2.71994
C -3.34153 -0.12724 -2.18578
H -1.28501 -0.49433 -1.78235
H -3.47147 -1.06315 -2.72013
C -4.40669 0.76708 -2.05173
H -5.02591 2.68981 -1.39656
H -5.3793 0.52938 -2.47165
C -2.18415 6.24468 0.63602
H -0.14011 5.68238 0.65863
H -1.97277 7.246 0.99835
C -3.50152 5.84057 0.40401
H -4.78139 4.26076 -0.2118
H -4.32599 6.52281 0.58675
C 3.65698 0.0254 -1.17986
C 3.35436 0.05383 -2.53173
C 4.98545 0.01541 -0.73667
C 4.40413 0.07132 -3.45033
H 2.32079 0.06386 -2.86724
C 6.03264 0.03381 -1.65289
C 5.7304 0.06151 -3.01332
H 4.18837 0.09374-4.51421
H 7.0664 0.02726 -1.31901
H 6.53551 0.07625 -3.74186
C 4.98642 -0.01499 0.7347
C 3.65855 -0.02502 1.17965
C 6.03491 -0.03336 1.64946
C 3.35783 -0.05345 2.53196
C 5.73456 -0.06109 3.01028
H 7.06817 -0.02678 1.31403
C 4.40885 -0.07094 3.44908
H 2.32472 -0.06348 2.86891
H 6.54061 -0.07581 3.73777
H 4.19456 -0.09337 4.51326

phospha[7]helicene **2**

P 0.53724 3.94816 -0.331
C -0.92856 2.91158 -0.23641
C 1.65579 2.53059 -0.29989
C -0.55409 1.56663 -0.29135
C 0.91509 1.36719 -0.06839
O 0.65707 4.93234 -1.44258
C -1.54248 0.59272 -0.56609
C 1.59133 0.19862 0.34955
C -2.89244 0.9487 -0.34321
C -1.24934 -0.73778 -1.10543
C -2.18974 -1.7738 -0.95548
C -3.88194 -0.12777 -0.17385
C -3.49592 -1.47496 -0.35725
C -0.09194 -0.9717 -1.86878
C -1.87545 -3.04769 -1.46257
C -3.23479 2.30751 -0.20939
C -5.18297 0.14475 0.28709
C -4.4053 -2.49316 -0.02188
C 0.94341 -0.90287 1.06616
C 2.97999 0.11572 0.09231
C 3.61378 -1.21315 0.09168
C 1.54383 -2.17539 1.07975
C 2.86406 -2.35204 0.46358
C 3.69017 1.28302 -0.24053
C 4.92444 -1.39488 -0.38618
C -0.21498 -0.6856 1.83283
C 0.89044 -3.22047 1.75716
C 3.43408 -3.6255 0.29167
C 3.04656 2.50313 -0.35199
H 4.76355 1.2496 -0.38233
H 3.61526 3.40867 -0.53854
C -2.26696 3.29423 -0.24497
H -4.27255 2.60344 -0.11537
H -2.5463 4.34262 -0.22845
C -6.07186 -0.87114 0.58278
H -5.5013 1.16796 0.44854
H -7.06671 -0.63064 0.9443
C -5.67454 -2.20292 0.44082
H -4.11086 -3.5324 -0.11444
H -6.35593 -3.00881 0.69523
C -0.69129 -3.28117 -2.13587
H -2.58363 -3.86239 -1.36385
H -0.47476 -4.27338 -2.51956
C 0.19641 -2.22652 -2.36673
H 0.58251 -0.15122 -2.08212

H 1.10152 -2.38507 -2.94431
C -0.83919 -1.72209 2.49737
H -0.62316 0.31469 1.91319
H -1.73923 -1.53232 3.07347
C -0.29518 -3.00785 2.43484
H 1.33246 -4.20978 1.7869
H -0.77765 -3.83244 2.95046
C 5.47662 -2.6546 -0.5196
H 5.51802 -0.54053 -0.68959
H 6.48769 -2.76403 -0.89909
C 4.71919 -3.78158 -0.19142
H 2.85733 -4.51192 0.53009
H 5.13363 -4.77696 -0.31746
O 0.61832 4.59355 1.15067
C 1.78858 5.33466 1.51217
H 2.64574 4.66092 1.61771
H 2.00734 6.10481 0.7676
H 1.57632 5.80318 2.47295

[9]helicene **3**

C -0.00018 3.06312 0.0002
C 1.08494 2.10519 0.42926
C -1.08521 2.10505 -0.42887
C 0.66911 0.77896 0.33413
C -0.6692 0.77886 -0.33373
C 1.53142 -0.2489 0.8278
C -1.5313 -0.24909 -0.82749
C 2.90928 0.0901 0.91594
C 1.13107 -1.58615 1.23978
C 2.10176 -2.59399 1.30727
C 3.90823 -0.96754 0.86214
C 3.51112 -2.28196 1.11658
C -0.21645 -1.89814 1.67819
C 1.68235 -3.94661 1.49835
C 3.27116 1.44856 1.06392
C 5.27747 -0.71984 0.44049
C 4.51052 -3.29701 1.24542
C -1.13072 -1.58629 -1.23945
C -2.90921 0.08969 -0.91584
C -3.90804 -0.9681 -0.86221
C -2.10122 -2.5943 -1.30694
C -3.51066 -2.28249 -1.11642
C -3.27124 1.44809 -1.06386
C -5.27743 -0.72056 -0.441
C 0.21686 -1.89803 -1.67784
C -1.68156 -3.94684 -1.49802
C -4.50984 -3.29775 -1.24528
C -2.35048 2.45608 -0.88969
H -4.28369 1.69547 -1.35804
H -2.61685 3.49715 -1.04508
C 2.35025 2.45642 0.8899
H 4.28365 1.69602 1.35793
H 2.61644 3.49753 1.04531
C 6.24703 -1.74592 0.60699
C 5.69681 0.44736 -0.25417
C 7.59626 -1.51983 0.24495
C 5.82879 -3.02587 1.0676
H 4.23034 -4.30018 1.53904
H 6.57504 -3.80145 1.21674
C 0.37513 -4.27232 1.66636
H 2.40636 -4.74908 1.44809
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C -0.60714 -3.25582 1.81276
C -1.16128 -0.91571 2.06406
C -1.94501 -3.58146 2.13406
C 0.60782 -3.25564 -1.81236
C 1.16151 -0.91544 -2.0637
C 1.94578 -3.58103 -2.13355
C -0.37427 -4.27232 -1.66598
H -2.4054 -4.74946 -1.44785
H -0.07137 -5.3128 -1.74518
C -6.24681 -1.74677 -0.60782
C -5.69718 0.44659 0.2535
C -7.59623 -1.52078 -0.24639
C -5.82821 -3.02675 -1.068
H -4.22942 -4.30099 -1.53843
H -6.5743 -3.80248 -1.21719
C 7.98143 -0.34237 -0.34659
H 9.01644 -0.18088 -0.63177
C 7.00665 0.6323 -0.63231
H 7.28377 1.53161 -1.1741
H 8.31845 -2.3139 0.4166
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C -2.86488 -2.59694 2.39717
H -3.89436 -2.85037 2.63047
C -2.45043 -1.2517 2.40397
H -3.15401 -0.47086 2.67669
H -2.22683 -4.63003 2.18295
H 1.61644 4.56233 -4.21623
H 0.4716 7.4361 -1.22721
H 1.3389 6.90884 -3.49127
C -0.26345 5.35449 0.68724
C -0.42096 4.02626 1.10245
C -0.59235 6.40289 1.54106
C -0.90438 3.72644 2.36602
C -1.07926 6.10277 2.81211
H -0.47348 7.43608 1.22711
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H -1.02295 2.69399 2.68393
H -1.34047 6.90879 3.49125
H -1.61433 4.56227 4.21654

phospha[9]helicene **4**

P -0.11372 4.17618 -0.3292
C 1.17523 3.01839 0.17003
C -1.2908 2.86152 -0.71949
C 0.63485 1.73723 0.17684
C -0.66176 1.63477 -0.54603
O 0.11668 5.19655 -1.38962
C 1.32353 0.68824 0.83212
C -1.26991 0.45117 -1.03396
C 2.72807 0.83157 0.91697

C 0.69022 -0.49686 1.38118
C 1.46661 -1.64337 1.55461
C 3.53419 -0.38211 0.98204
C 2.90764 -1.58824 1.32571
C -0.68294 -0.49091 1.84633
C 0.80924 -2.86457 1.90527
C 3.25842 2.14523 0.92672
C 4.92828 -0.4046 0.57684
C 3.70856 -2.75734 1.50739
C -0.55791 -0.76315 -1.39159
C -2.68006 0.48502 -1.13649
C -3.40675 -0.77213 -1.00881
C -1.25901 -1.97045 -1.38014
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H 4.59131 -0.80706 -2.88407
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H -7.3639 -3.0898 -0.36175
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H -1.71017 6.38931 0.50769
H -2.59831 4.91407 1.00501
H -1.78381 5.92389 2.2291

II. References

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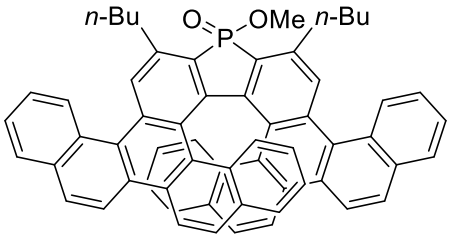
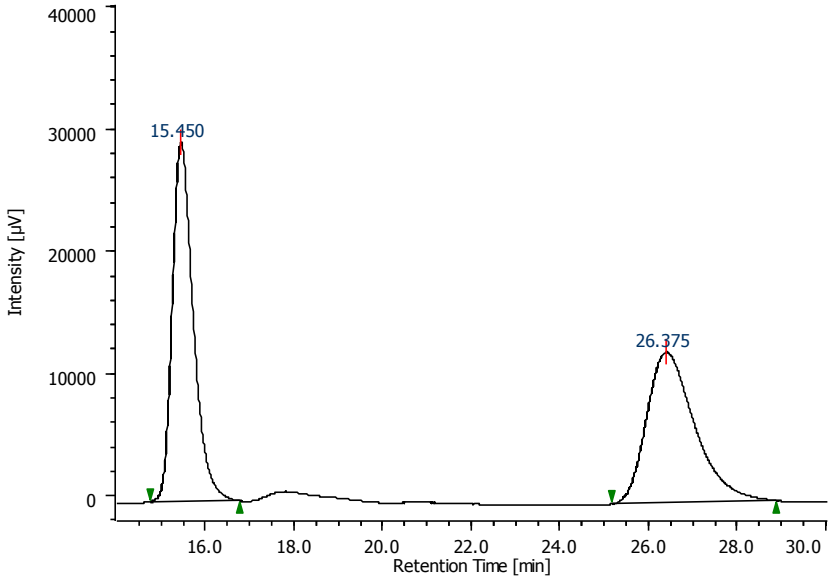
3. J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.

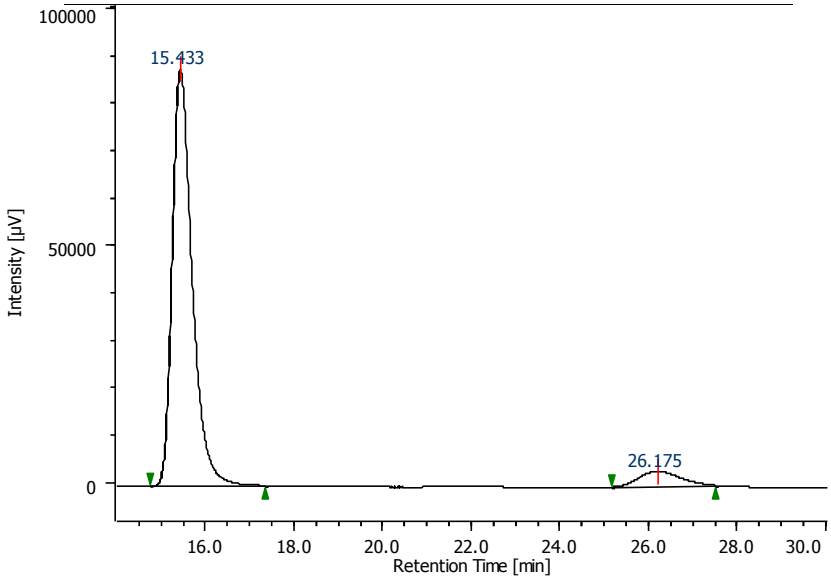
III. Chiral HPLC Charts

Phospha[9]helicene (–)-**4**





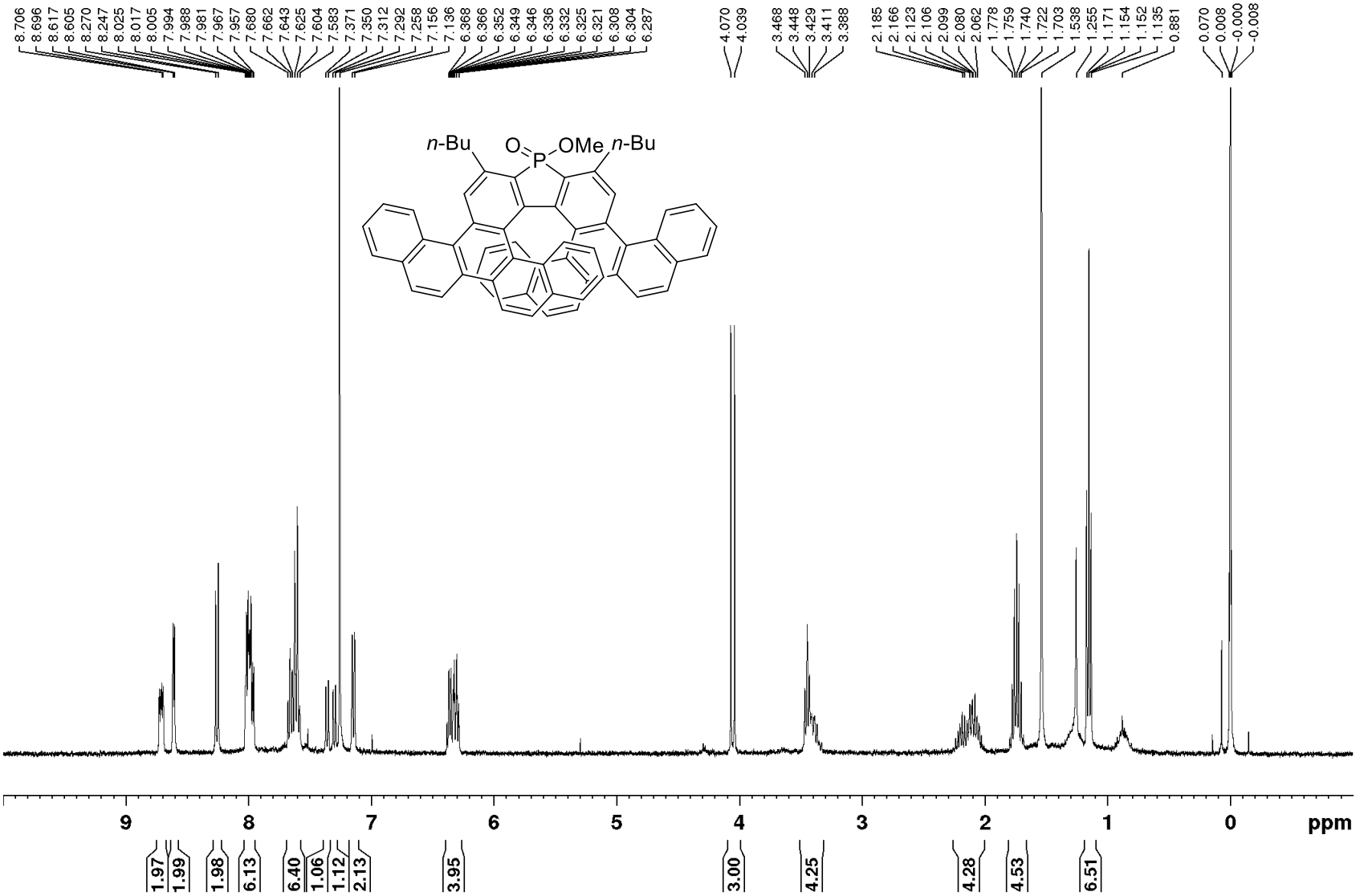
Peak No.	Retention Time (min)	Area (%)
1	15.450	50.958
2	26.375	49.042



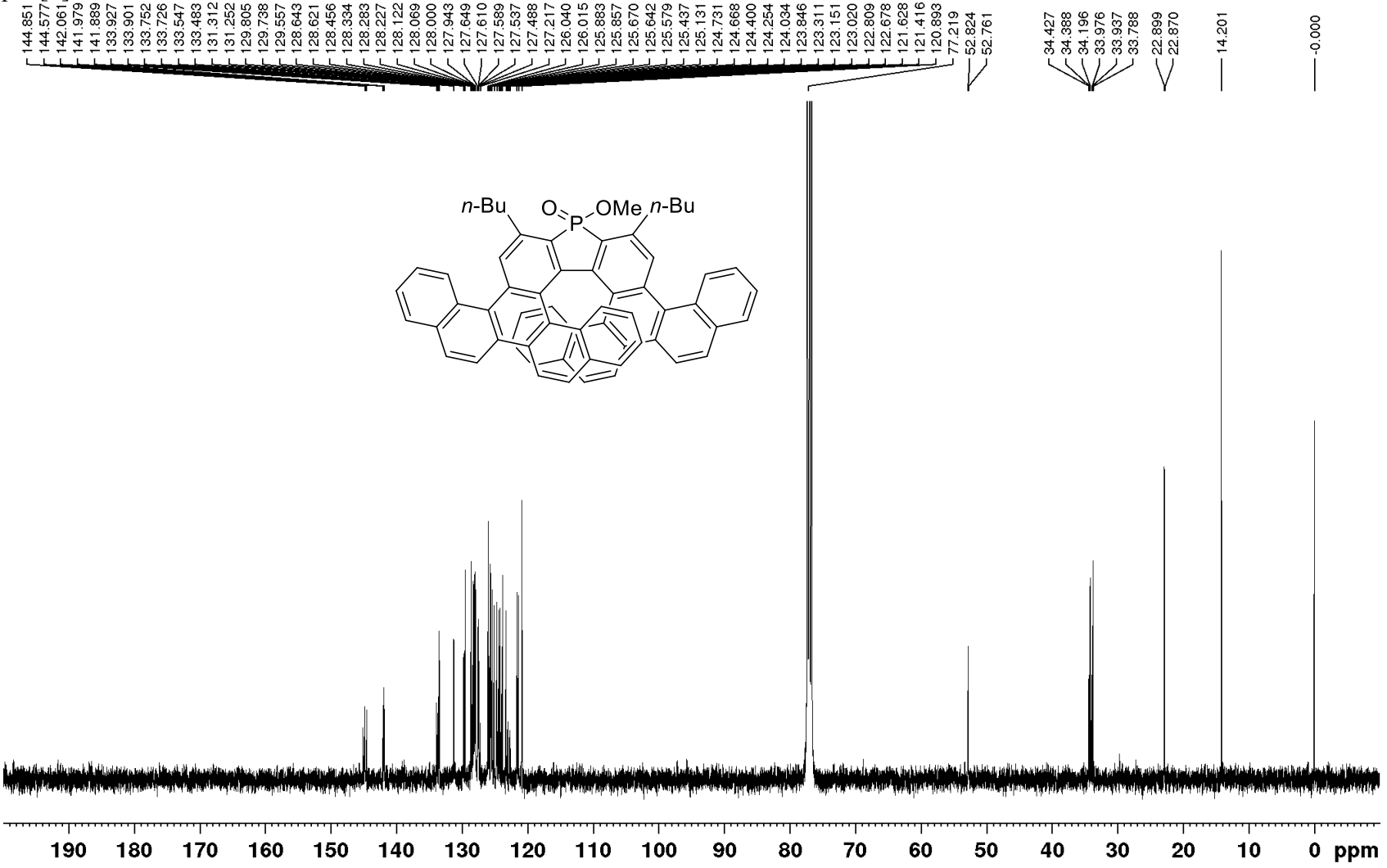
Peak No.	Retention Time (min)	Area (%)
1	15.433	93.026
2	26.175	6.974

IV. ^{1}H, ^{13}C, and ^{31}P NMR Spectra

Phospha[9]helicene **4**



Phospha[9]helicene **4**



Phospha[9]helicene **4**