Scalable synthesis of multi-substituted aryl-phosphonates: exploring the limits of isoretical expansion and the synthesis of new triazene-based phosphonates

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**Supplemental Materials**

***IR data***

**1,3,5-*Tris*(4-bromophenyl)benzene (TBPB, 3a).** FTIR (cm-1): 3045, 1591, 1493, 1648, 1589, 1488, 1440, 1365, 1257, 1238, 1200, 1064, 1005, 942, 869, 805, 690.

***Tris*(4’-bromo-[1,1’-biphenyl]-4-yl)-1,3,5-benzene (TBBPB) (5a).** FTIR (cm-1): 3017, 1601, 1491, 1443, 1194, 1005, 857, 802, 720.

**(*E*)-1,3-*bis*(4’-bromo-[1,1’-biphenyl]-4-yl)but-2-en-1-one (DBBPE) (6a).** FTIR (cm-1): 3094, 3081, 1642, 1590, 1455, 1365, 1311, 1252, 1176, 1047, 1010, 981, 912, 857, 803, 739.

**1,3,5-*tris*(4-bromo-2-methylphenyl)triazine (8a).** FTIR (cm-1): 3005, 2945, 2371, 2347, 1593, 1559, 1517, 1430, 1389, 1342, 1253, 1195, 1150, 1084, 1027, 866, 805.

**4,4’-bis(diisopropyl phosphonate) biphenyl (1b).** FTIR (cm-1): 2973, 2944, 2891, 2355, 2340, 1596, 1384, 1249, 1167, 1139, 1096, 961, 876, 813, 764, 748, 700.

**Diisopropyl (*E*)-(4’-(4-(4’-(diisopropoxyphosphoryl)-[1,1’-biphenyl]-4-yl)-4-oxobut-2-en-2-yl)-[1,1’-biphenyl]-4-yl)phosphonate (6b).** FTIR (cm-1): 2991, 2937, 2883, 1638, 1583, 1409, 1362, 1225, 1155, 1107, 1081, 963, 867, 809, 741, 679.

**Hexaisopropyl((1,3,5-triazine-2,4,6-triyl)*tris*(([1,1’-biphenyl]-4’-4-diyl)))*tris*(phosphonate) (7b).** FTIR (cm-1): 2988, 2941, 2873, 1500, 1361, 1243, 1175, 1138, 1096, 1058, 968, 882, 804, 775, 694.

**1,3,5-*tris*(diisopropyl 2-methylphenyl-4-phosphonato)triazine (8b).** FTIR (cm-1): 3015, 2959, 2892, 2209, 1520, 1465, 1396, 1250, 1177, 1148, 1103, 963, 905, 842, 789, 708.

**Biphenyl-4,4’-di(phosphonic acid) (1c).** FTIR (cm-1): 3500-2000, 2365, 2343, 1594, 1130, 1117, 1000, 93, 809, 705. CHN analysis calcd. (%): C 45.86, H 3.82; found: C 45.14, H 3.80.

**3,3’,5,5’-Tetra(phosphoric acid)-1,1’-biphenyl (2c).** FTIR (cm-1): 3750-3350, 3008, 2953, 2903, 1428, 1345, 1211, 1141, 1103, 1063, 965, 850, 795, 717, 656. CHNS analysis calcd. (%): C 30.38, H 2.95; found C 30.47, H 2.92.

**1,3,5-Benzene-tri-*p*-phenylphosphonic acid (3c).** FTIR (cm-1): 3500-2000, 2357, 2325, 1204, 1111, 1055, 99, 937, 795, 730, 681. CHNS analysis calcd (%): C 22.64, H 2.83; found: C 22.30, H 2.84.

**1,3,5-*Tris*(phenyl-4-phosphonic acid)benzene (BBTPA) (4c).** FTIR (cm-1): 3600-2000, 2375, 2339, 1590, 1133, 1051, 982, 919, 815, 721, 686.

**((1,3,5-triazine-2,4,6-triyl)*tris*(3-methylbenzene-4,1,-diyl))*tris*(phosphonic acid) (MBTTPA) (8c).** FTIR (cm-1): 3700-2000, 2988, 2939, 1560, 1503, 1375, 1341, 1141, 1099, 977, 883, 807, 793, 681.

***Computational data***

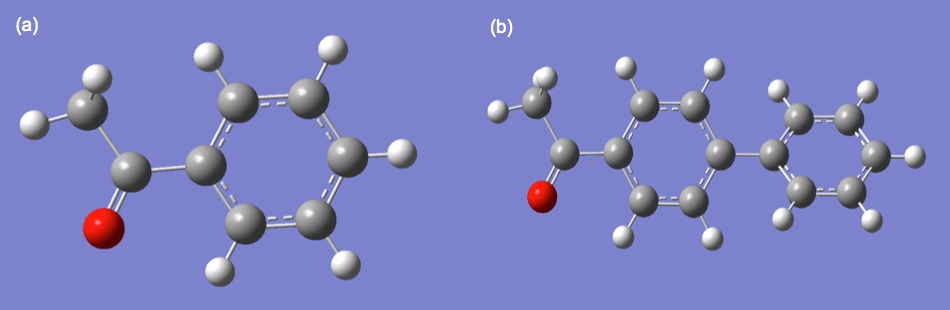
**Table S 1:** Selected calculated structural parameters for R(CH3)C=C(H)C(O)R intermediate using RB3LYP method and 6-31G\*\* basis set.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| R | O=C (Å) | C=C (Å) | O…Me (Å) | O=C-C (°) | C-C=C (°) | C=C-C (°) | Σ(X-C-C) (°) |
| Ph | 1.26293 | 1.3659 | 2.81671 | 122.03680 | 125.88735 | 123.34808 | 371.27223 |
| Bi-phenyl | 1.26346 | 1.36566 | 2.85974 | 122.26606 | 126.43491 | 123.52476 | 372.22573 |

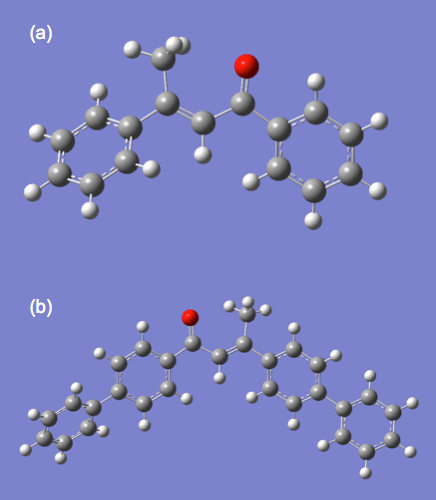
**Table S 2:** Calculated total energy (Hartree) for optimized structures using RB3LYP method and 6-31G\*\* basis set.a

|  |  |  |  |
| --- | --- | --- | --- |
| R | RC(O)CH3 | R(CH3)C=C(O)R | C6H3R3 |
| Ph | -384.814612 | -693.210538 | -925.24701 |
| Bi-phenyl | -615.827943 | -1155.237226 | -1618.255426 |

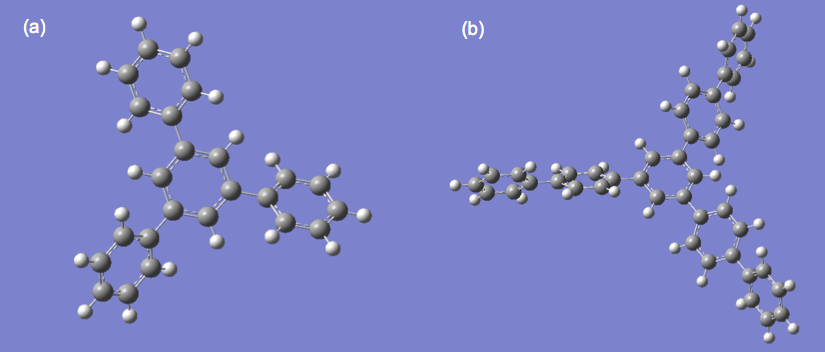
a Energy for H2O = -76.401391 Hartree.



**Figure S 1:** Calculated structures of (a) PhC(O)CH3 and (b) (biphen)C(O)CH3. Calculations of all structures was carried out at the RB3LYP level with the 6-31G\*\* basis set



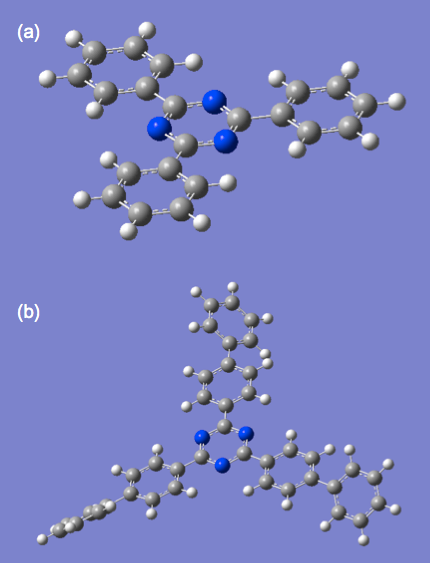
**Figure S 2.** Calculated structures of (a) Ph(CH3)C=C(H)C(O)Ph and (b) (biphen)(CH3)C=C(H)C(O)(biphen). Calculations of all structures was carried out at the RB3LYP level with the 6-31G\*\* basis set.



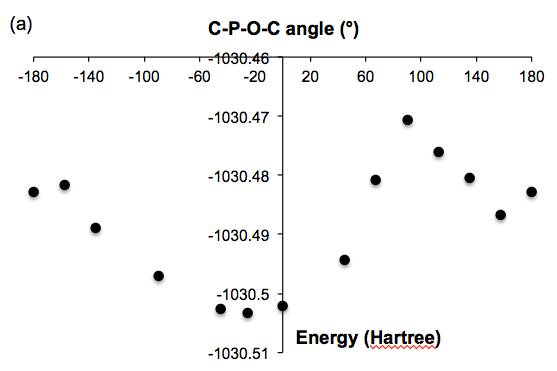
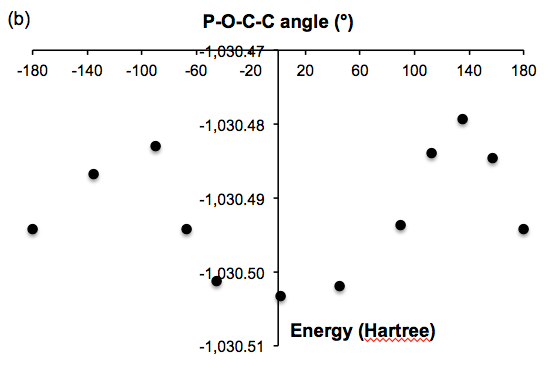
**Figure S 3:** Calculated structures of (a) C6H3Ph and (b) C6H3(biphen). Calculations of all structures was carried out at the RB3LYP level with the 6-31G\*\* basis set.

**Table S 3:** Calculated total energy (Hartree) for optimized structures using RB3LYP method and 6-31G\*\* basis set.

|  |  |  |  |
| --- | --- | --- | --- |
| Entry | R | R-C≡N | N3C3R3 |
| 1 | Ph | -324.423785 | -973.337598 |
| 2 | Bi-phenyl | -555.437023 | -1666.377571 |



**Figure S 4:** Calculated structures of (a) C3N3Ph and (b) C3N3(biphen). Calculations of all structures was carried out at the RB3LYP level with the 6-31G\*\* basis set.

**Figure S 5:** Plot of calculated total energy (Hartree) of C6H5P(O)(OiPr)2 as a function of the (a) C-P-O-C and (b) C-C-P=O torsional angle.