

## Supporting Information

### Metallacarborane Synthons for Molecular Construction—Oligofunctionalization of Cobalt Bis(1,2-dicarbollide) on Boron and Carbon Atoms with Extendable Ligands

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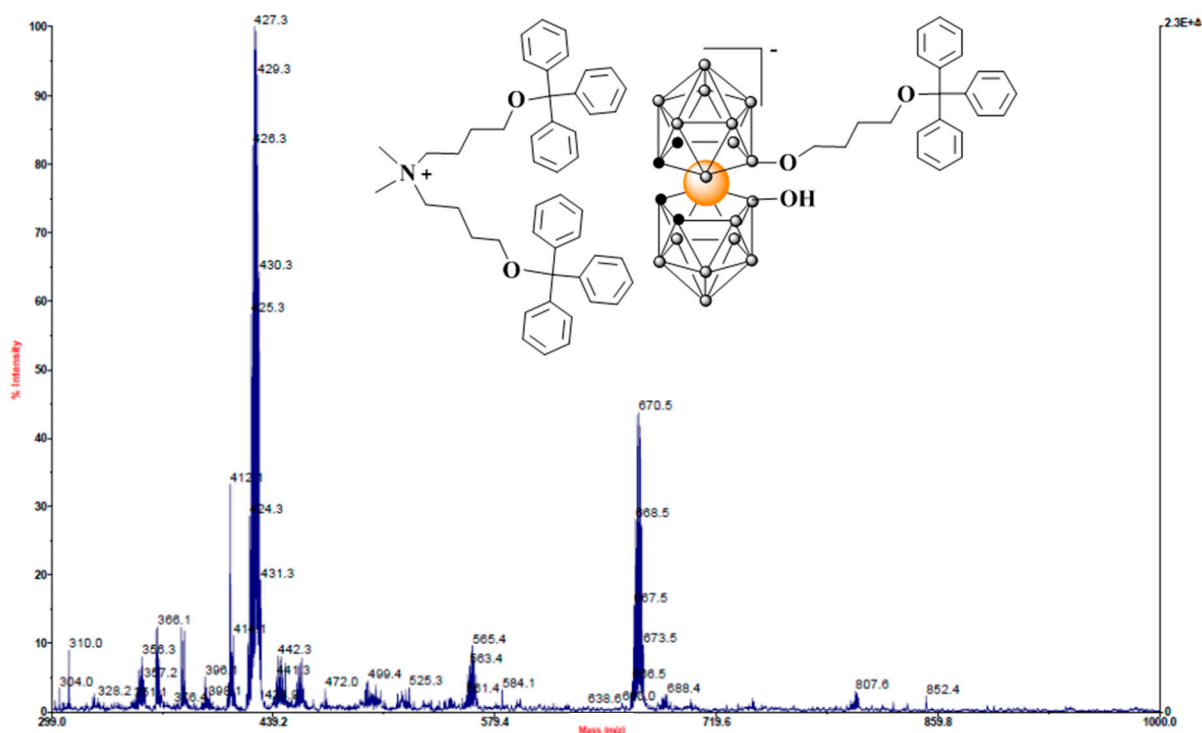
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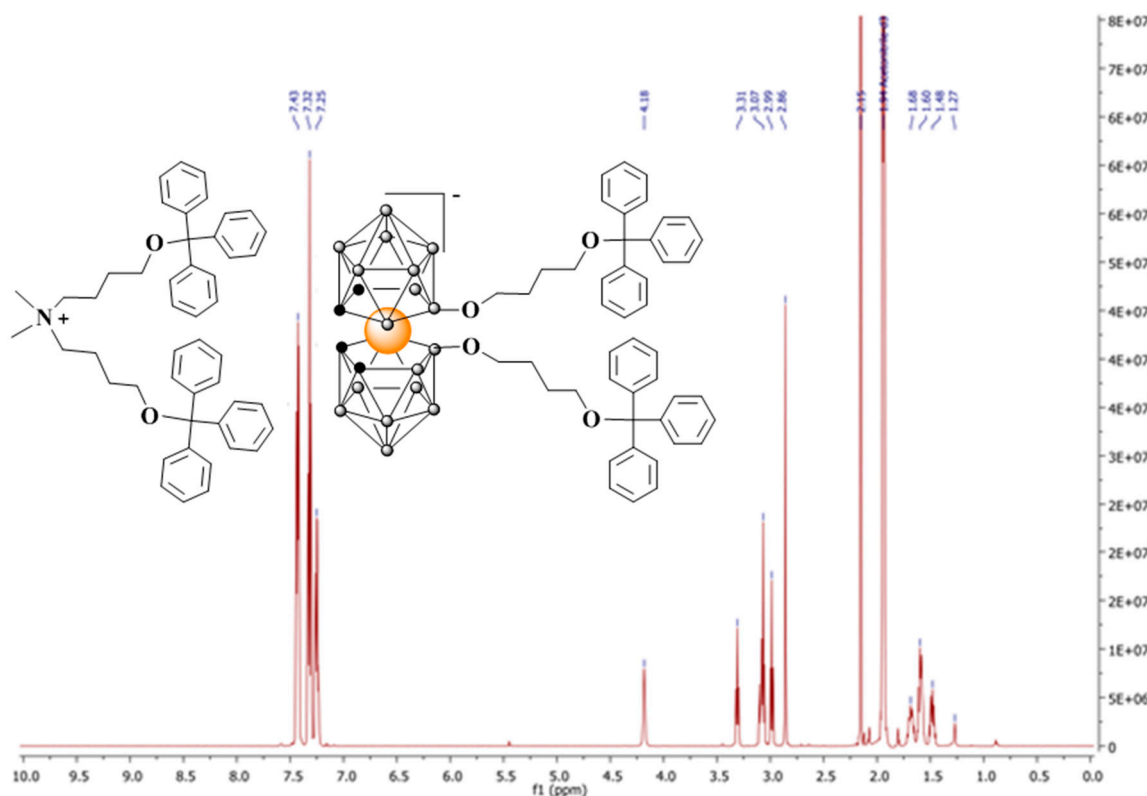
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| <b>Figure S57.</b> <sup>11</sup> B{ <sup>1</sup> H} NMR spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>3</sub> OCPh <sub>3</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ] HNEt <sub>3</sub> (16) .....                    | 33 |
| <b>Figure S58.</b> <sup>11</sup> B NMR spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>3</sub> OCPh <sub>3</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ] HNEt <sub>3</sub> (16) .....                                     | 33 |
| <b>Figure S59.</b> <sup>31</sup> P{ <sup>1</sup> H} NMR spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>3</sub> OCPh <sub>3</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ] HNEt <sub>3</sub> (16) .....                    | 34 |
| <b>Figure S60.</b> <sup>31</sup> P NMR spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>3</sub> OCPh <sub>3</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ] HNEt <sub>3</sub> (16) .....                                     | 34 |
| <b>Figure S61.</b> MS (ESI) spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>3</sub> OCPh <sub>3</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ] HNEt <sub>3</sub> (16) .....  | 35 |
| <b>Figure S62.</b> FT-IR spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>3</sub> OCPh <sub>3</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ] HNEt <sub>3</sub> (16) .....   | 35 |
| <b>Figure S63.</b> UV-VIS spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>3</sub> OCPh <sub>3</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ] HNEt <sub>3</sub> (16) .....  | 35 |
| <b>Figure S64.</b> <sup>1</sup> H NMR spectrum of 4-(1,3-bis(trityloxy)propan-2-yloxy)butyl-4-methylbenzenesulfonate (20) .....   | 36 |
| <b>Figure S65.</b> <sup>13</sup> C{ <sup>1</sup> H} NMR spectrum of 4-(1,3-bis(trityloxy)propan-2-yloxy)butyl-4-methylbenzenesulfonate (20) .....   | 36 |
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| <b>Figure S67.</b> FT-IR spectrum of spectrum of 4-(1,3-bis(trityloxy)propan-2-yloxy)butyl-4-methylbenzenesulfonate (20) .....  | 37 |
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| <b>Figure S70.</b> <sup>13</sup> C{ <sup>1</sup> H} NMR spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>4</sub> OCH(CH <sub>2</sub> OTr) <sub>2</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ]HNEt <sub>3</sub> (21) ..... | 38 |
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| <b>Figure S72.</b> <sup>11</sup> B NMR spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>4</sub> OCH(CH <sub>2</sub> OTr) <sub>2</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ]HNEt <sub>3</sub> (21) .....                  | 39 |
| <b>Figure S73.</b> <sup>31</sup> P{ <sup>1</sup> H} NMR spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>4</sub> OCH(CH <sub>2</sub> OTr) <sub>2</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ]HNEt <sub>3</sub> (21) ..... | 40 |
| <b>Figure S74.</b> <sup>31</sup> P NMR spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>4</sub> OCH(CH <sub>2</sub> OTr) <sub>2</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ]HNEt <sub>3</sub> (21) .....                  | 40 |
| <b>Figure S75.</b> MS (ESI) spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>4</sub> OCH(CH <sub>2</sub> OTr) <sub>2</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ]HNEt <sub>3</sub> (21) .....                             | 41 |
| <b>Figure S76.</b> MS (ESI) spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>4</sub> OCH(CH <sub>2</sub> OTr) <sub>2</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ]HNEt <sub>3</sub> (21) .....                             | 41 |
| <b>Figure S77.</b> UV-VIS spectrum of spectrum of [8,8'-O <sub>2</sub> P(O)S(CH <sub>2</sub> ) <sub>4</sub> OCH(CH <sub>2</sub> OTr) <sub>2</sub> -3,3'-Co(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> ) <sub>2</sub> ]HNEt <sub>3</sub> (21) .....                   | 41 |



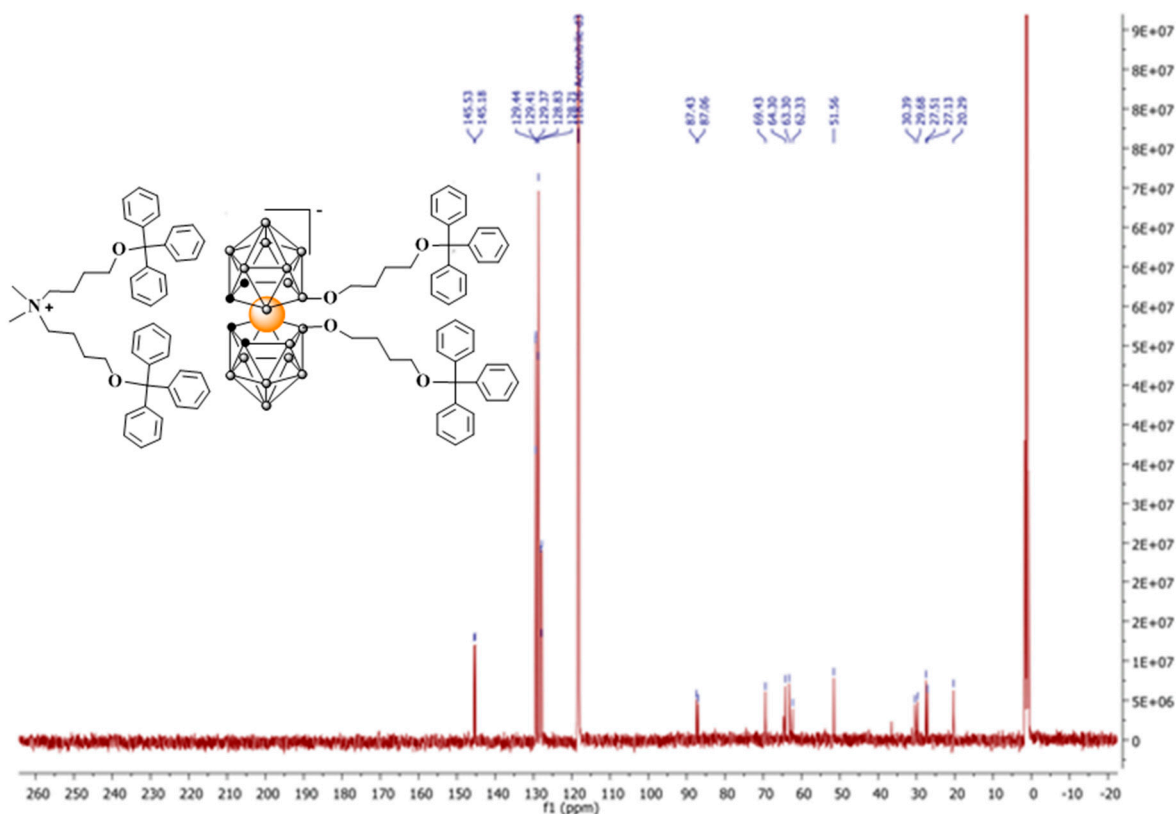




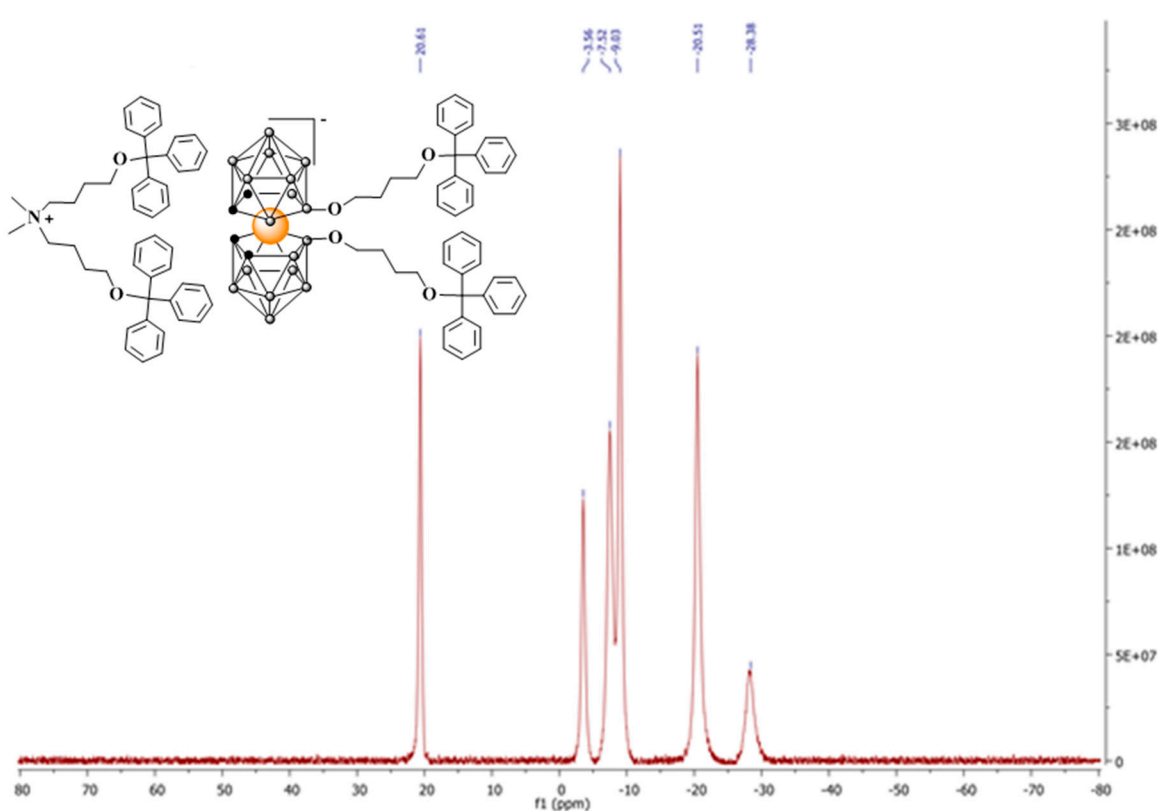
**Figure S1.** MS (ESI) spectrum of 3,3'-Co{[(8-O(CH<sub>2</sub>)<sub>4</sub>OCPh<sub>3</sub>]-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}(8'-OH-1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>4</sub>OPh<sub>3</sub>]<sub>2</sub> (**5**).



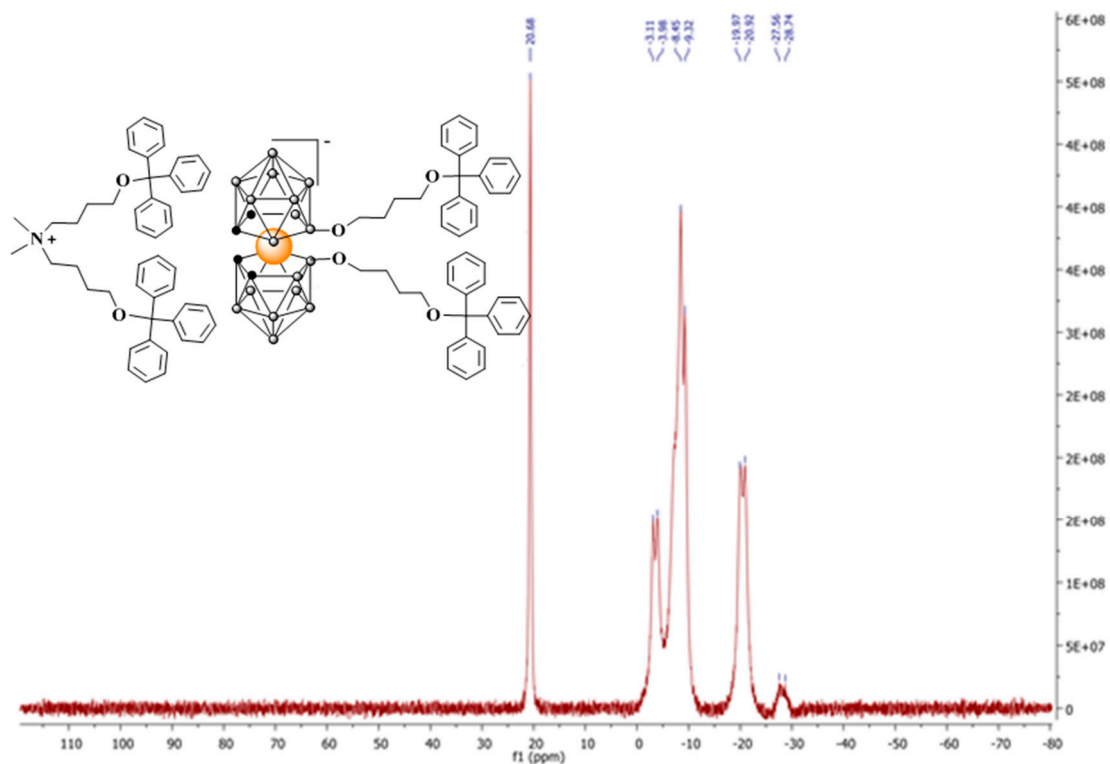
**Figure S2.** <sup>1</sup>H NMR spectrum of 3,3'-Co[(8-O(CH<sub>2</sub>)<sub>4</sub>OCPh<sub>3</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)]<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>4</sub>OPh<sub>3</sub>]<sub>2</sub> (**7**).



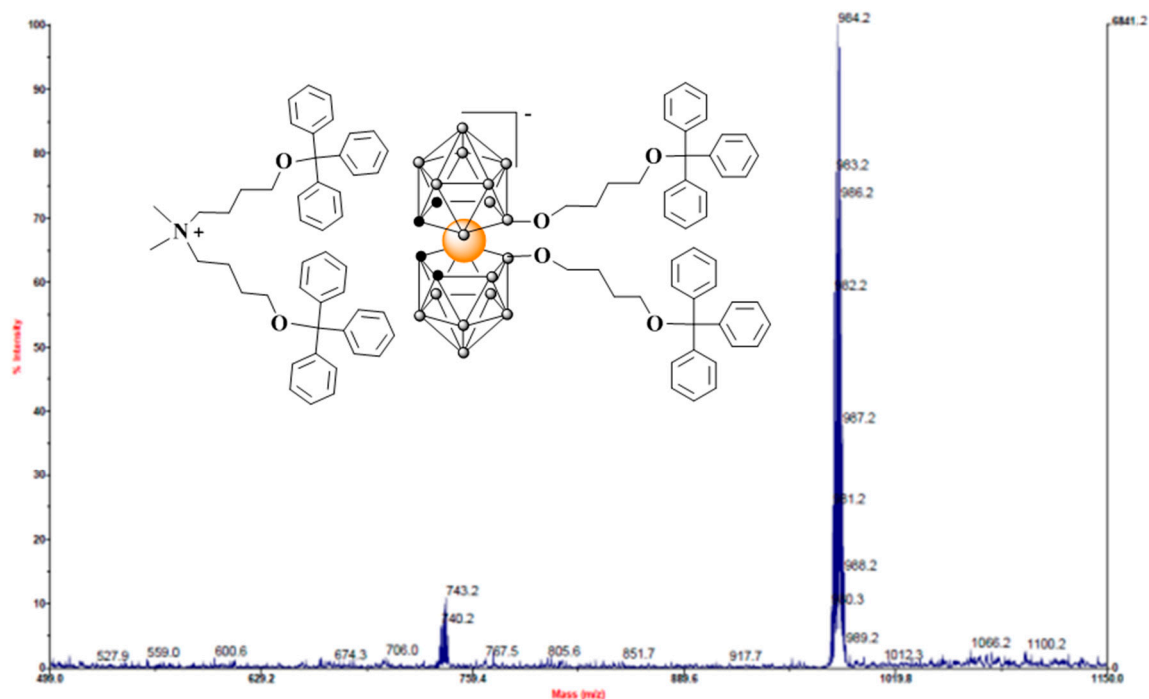
**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $3,3'\text{-Co}[(8\text{-O}(\text{CH}_2)_4\text{OCPh}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})]_2(\text{CH}_3)_2\text{N}[(\text{CH}_2)_4\text{OPh}_3]_2$  (**7**).



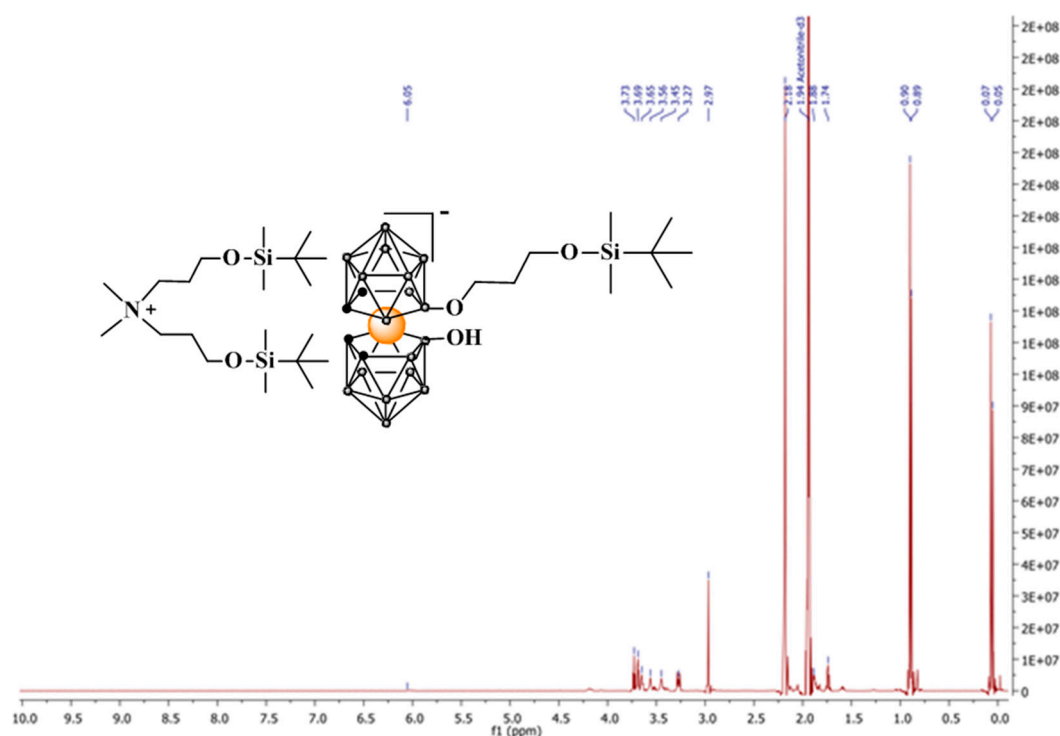
**Figure S4.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $3,3'\text{-Co}[(8\text{-O}(\text{CH}_2)_4\text{OCPh}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})]_2(\text{CH}_3)_2\text{N}[(\text{CH}_2)_4\text{OPh}_3]_2$  (**7**).



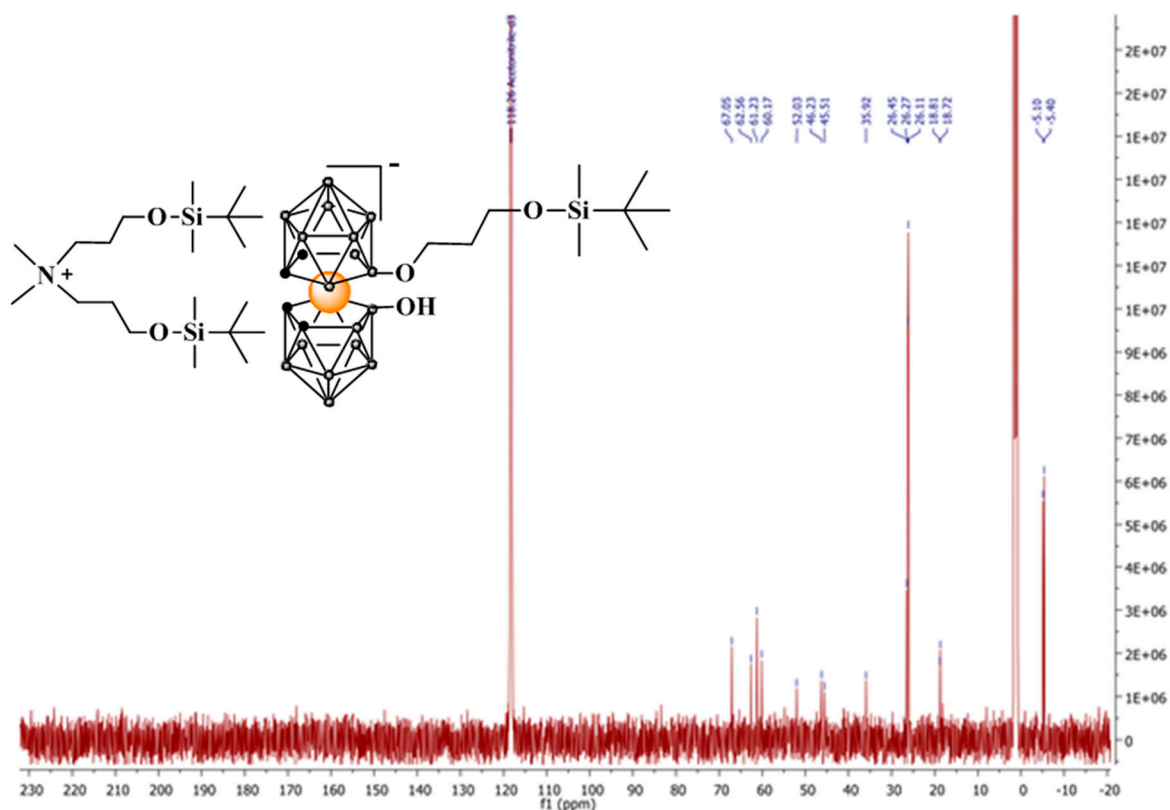
**Figure S5.**  $^{11}\text{B}$  NMR spectrum of  $3,3'\text{-Co}[(8\text{-O}(\text{CH}_2)_4\text{OCPh}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})]_2(\text{CH}_3)_2\text{N}[(\text{CH}_2)_4\text{OPh}_3]_2$  (**7**).



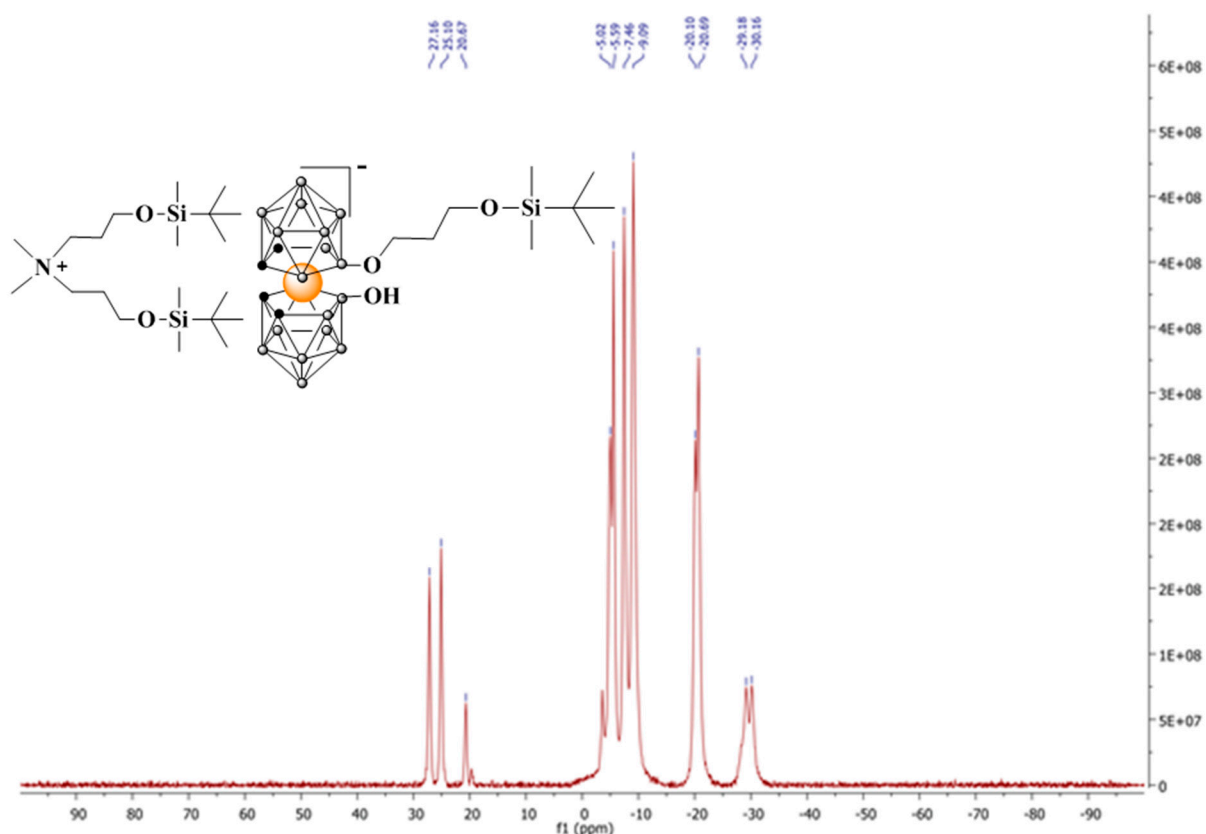
**Figure S6.** MS (ESI) spectrum of  $3,3'\text{-Co}[(8\text{-O}(\text{CH}_2)_4\text{OCPh}_3\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})]_2(\text{CH}_3)_2\text{N}[(\text{CH}_2)_4\text{OPh}_3]_2$  (**7**).



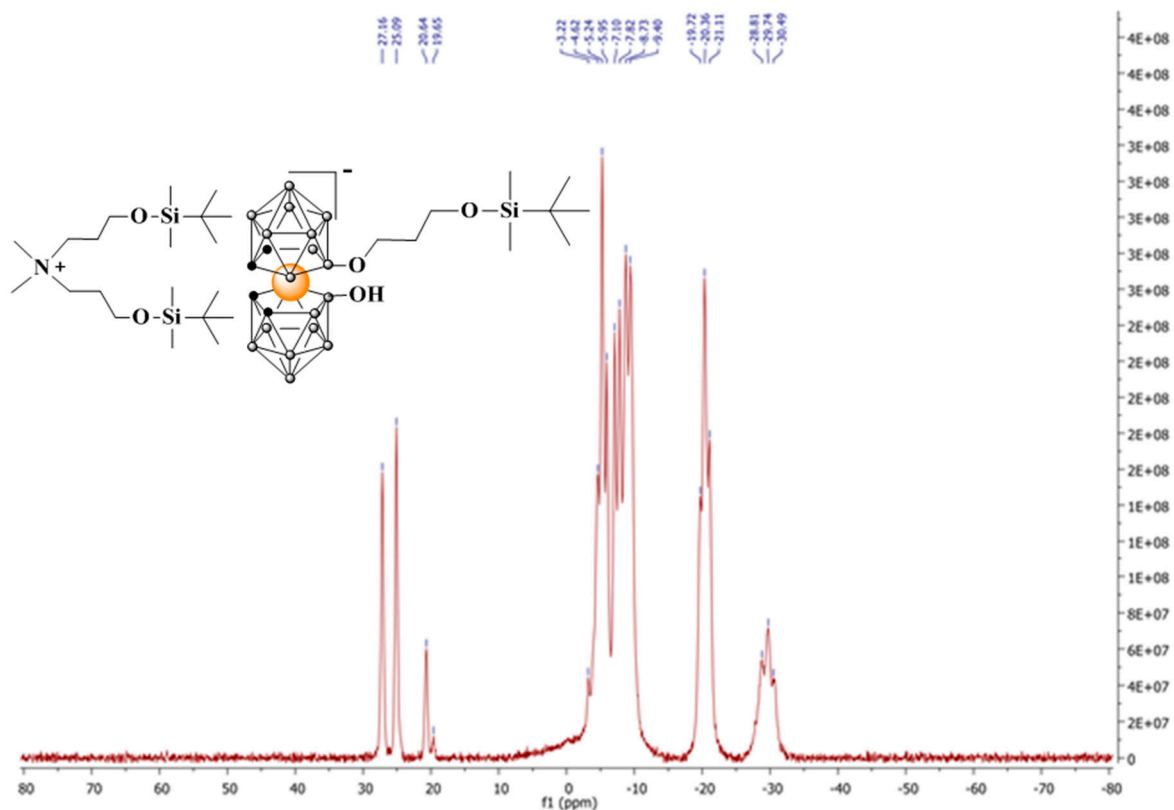
**Figure S7.**  $^1\text{H}$  NMR spectrum of 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS]-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>(8'-OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>) (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS]<sub>2</sub> (**6**).



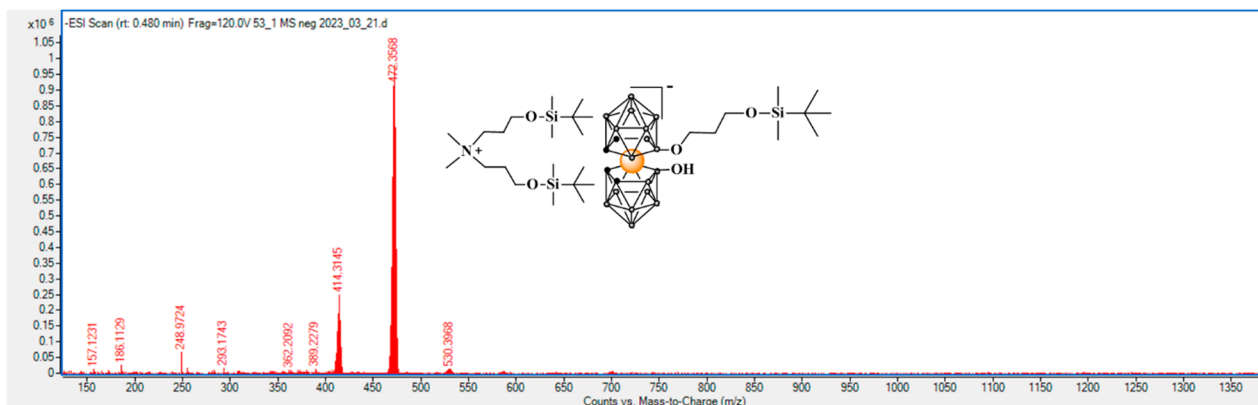
**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS]-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>(8'-OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>) (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS]<sub>2</sub> (**6**).



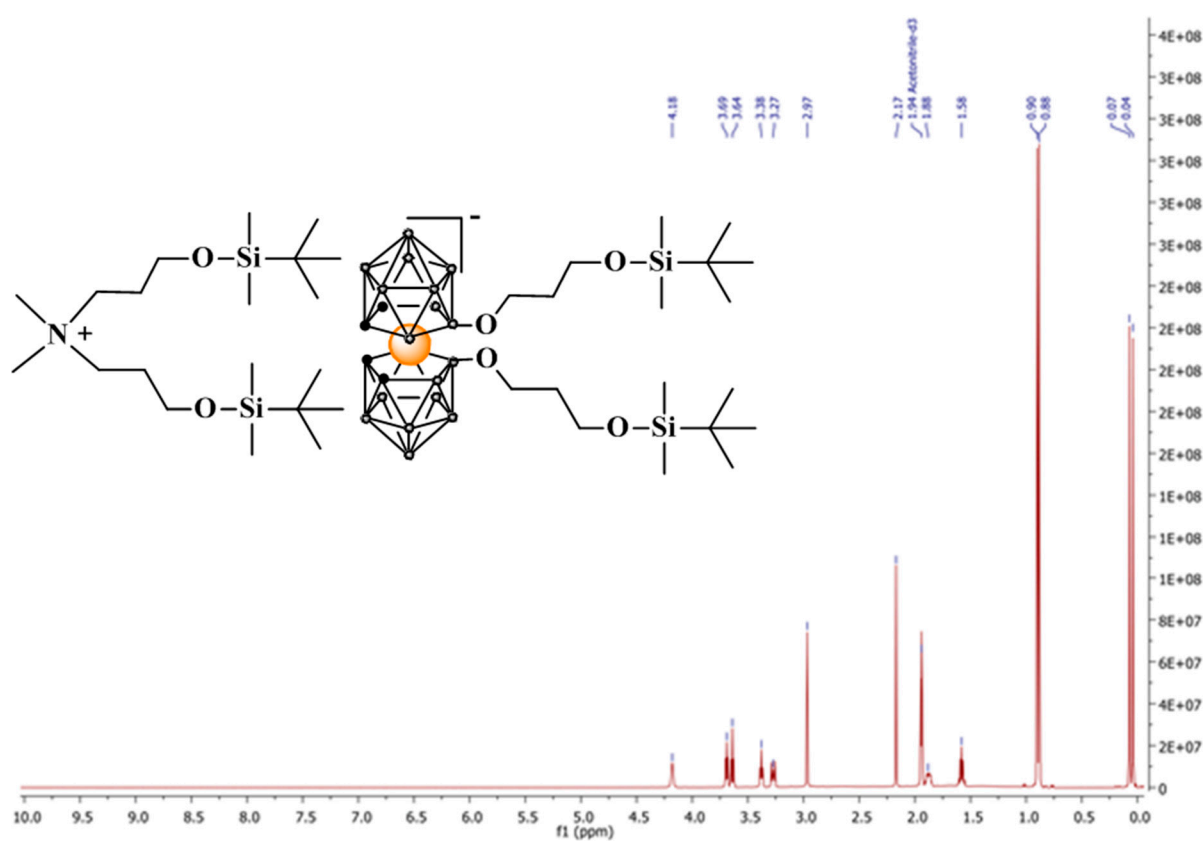
**Figure S9.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS]-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>(8'-OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>) (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS]<sub>2</sub> (**6**).



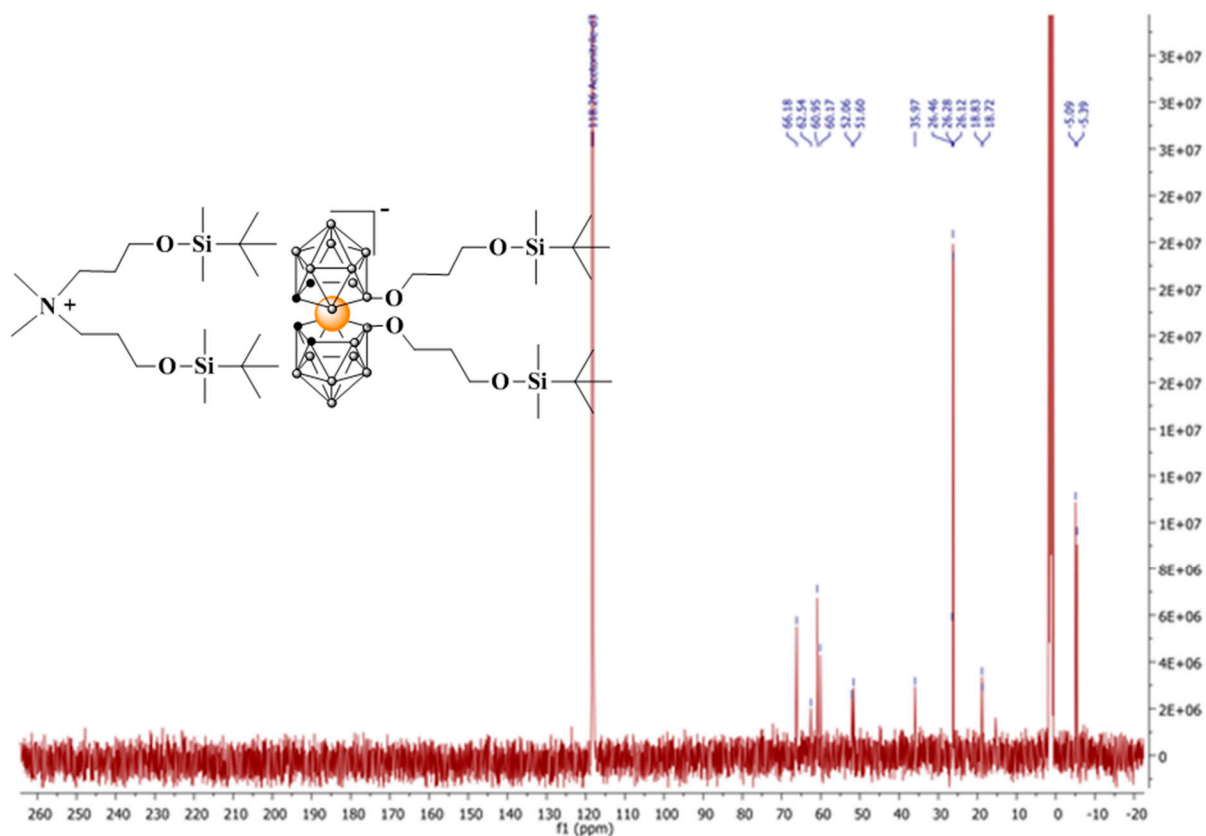
**Figure S10.**  $^{11}\text{B}$  NMR spectrum of 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS]-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>(8'-OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>) (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS]<sub>2</sub> (**6**).



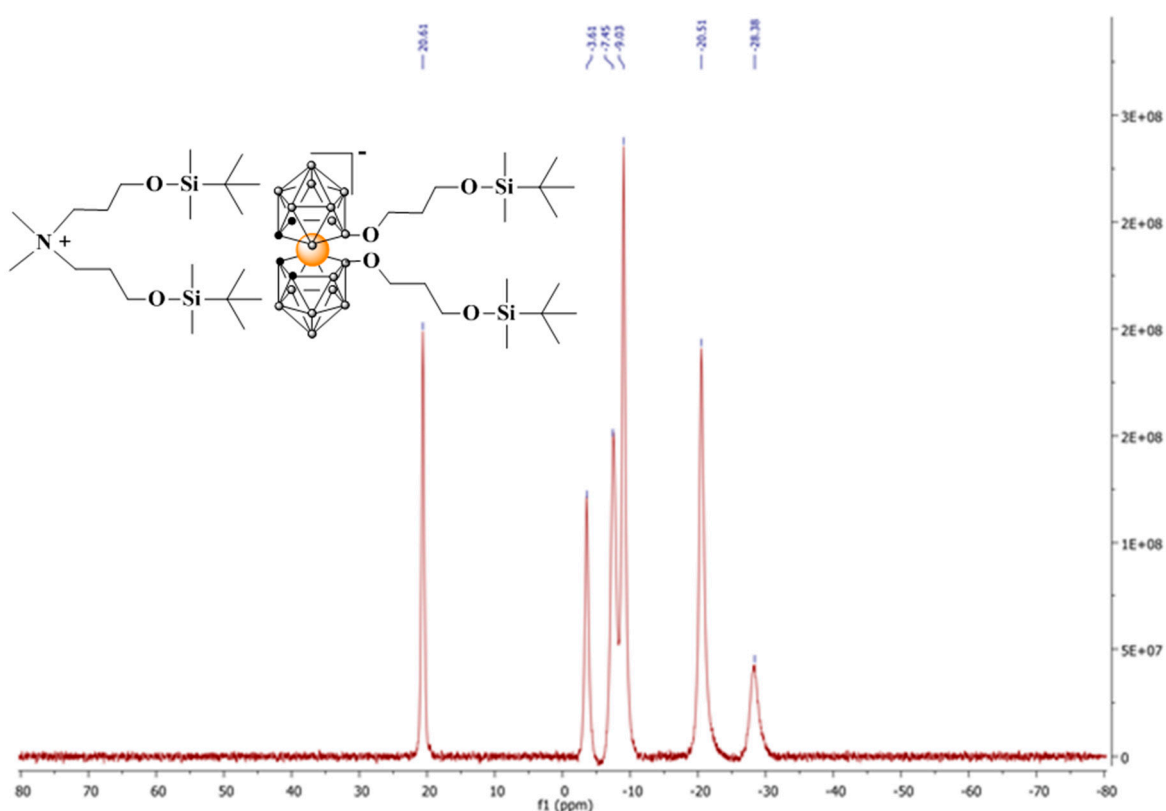
**Figure S11.** MS(ESI) spectrum of 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS]-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(8'-OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>) (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS)]<sub>2</sub> (**6**).



**Figure S12.** <sup>1</sup>H NMR spectrum 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS]-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)]<sub>2</sub> (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS)]<sub>2</sub> (**8**).

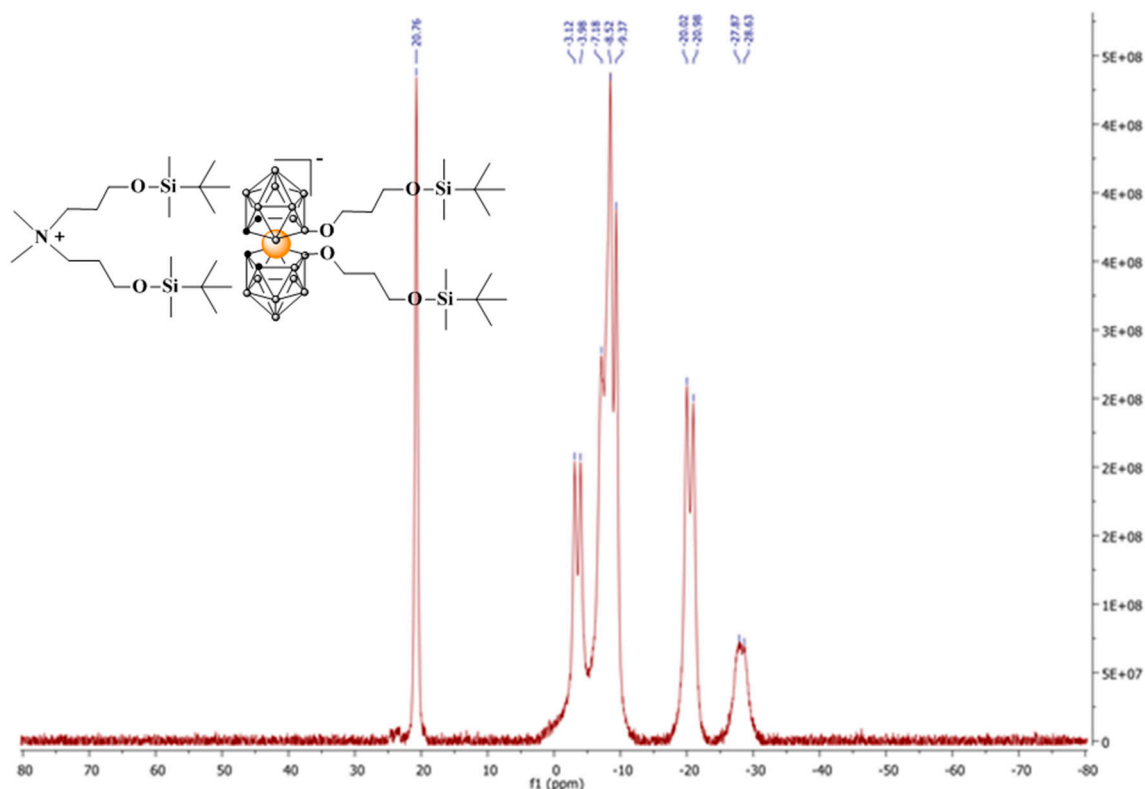


**Figure S13.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sub>2</sub> (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS]<sub>2</sub> (**8**).

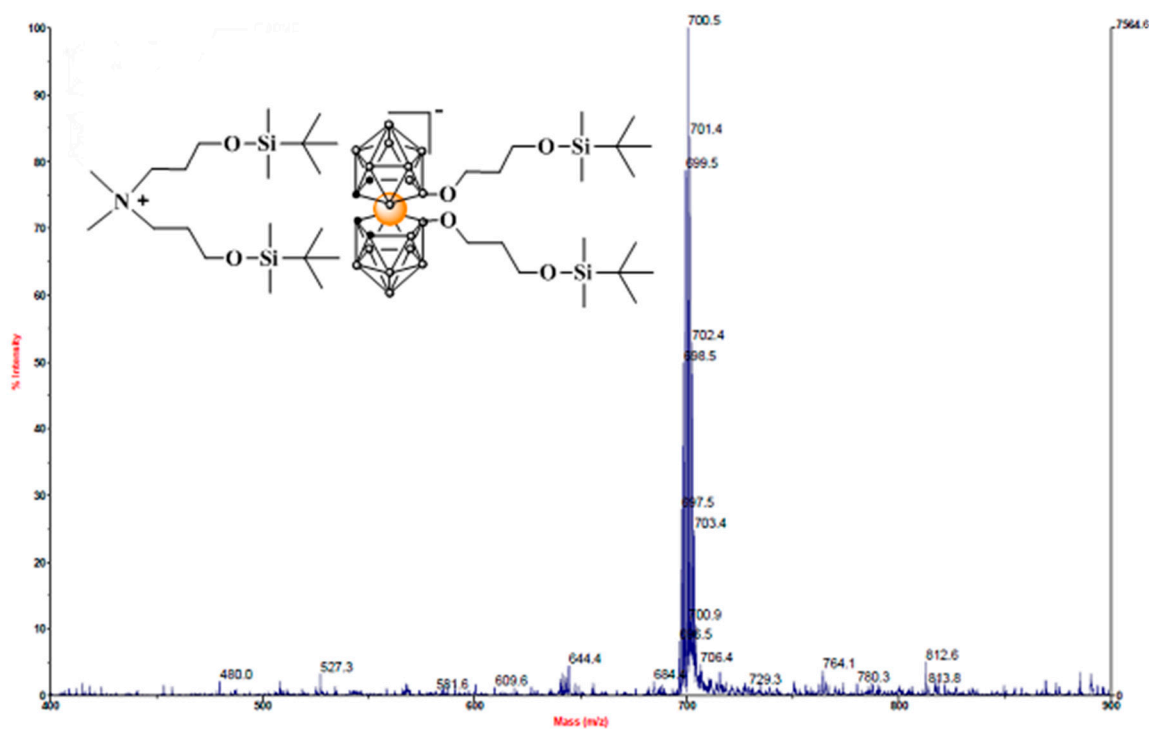


**Figure S14.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sub>2</sub> (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS]<sub>2</sub> (**8**).

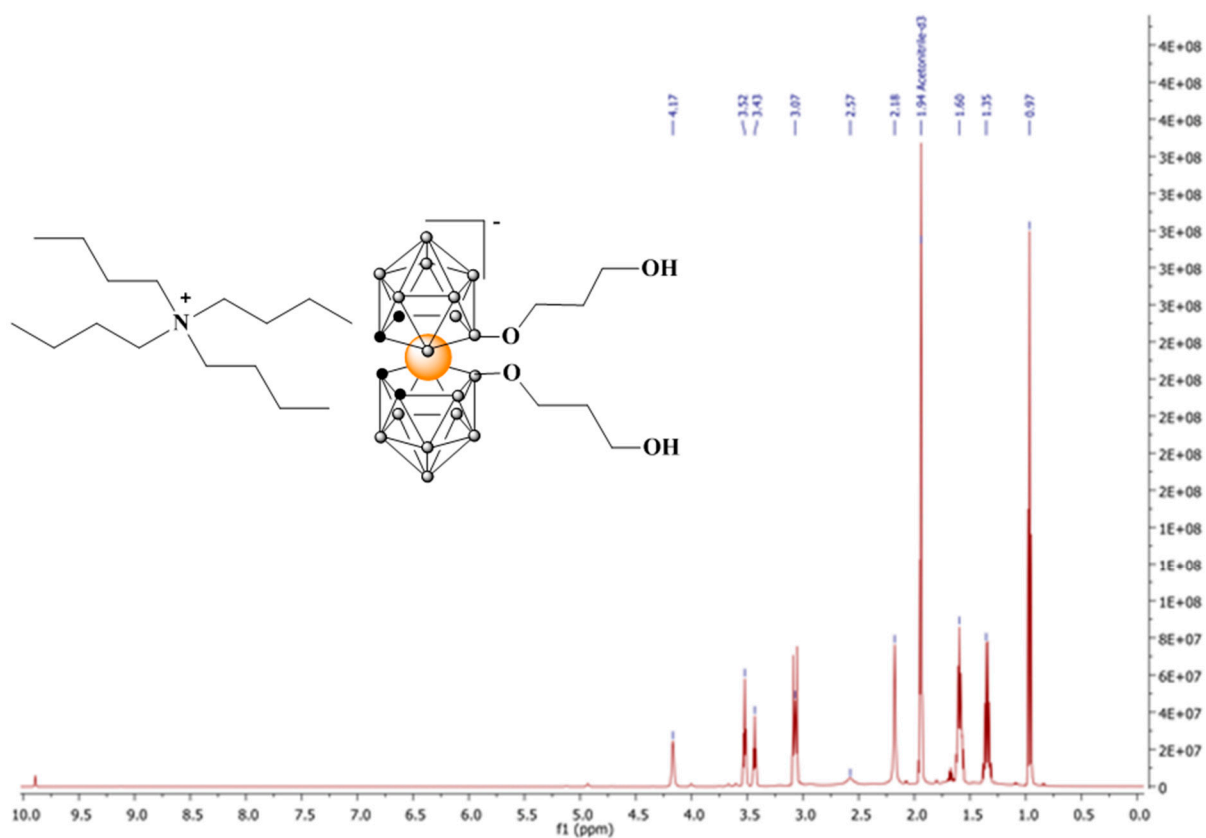




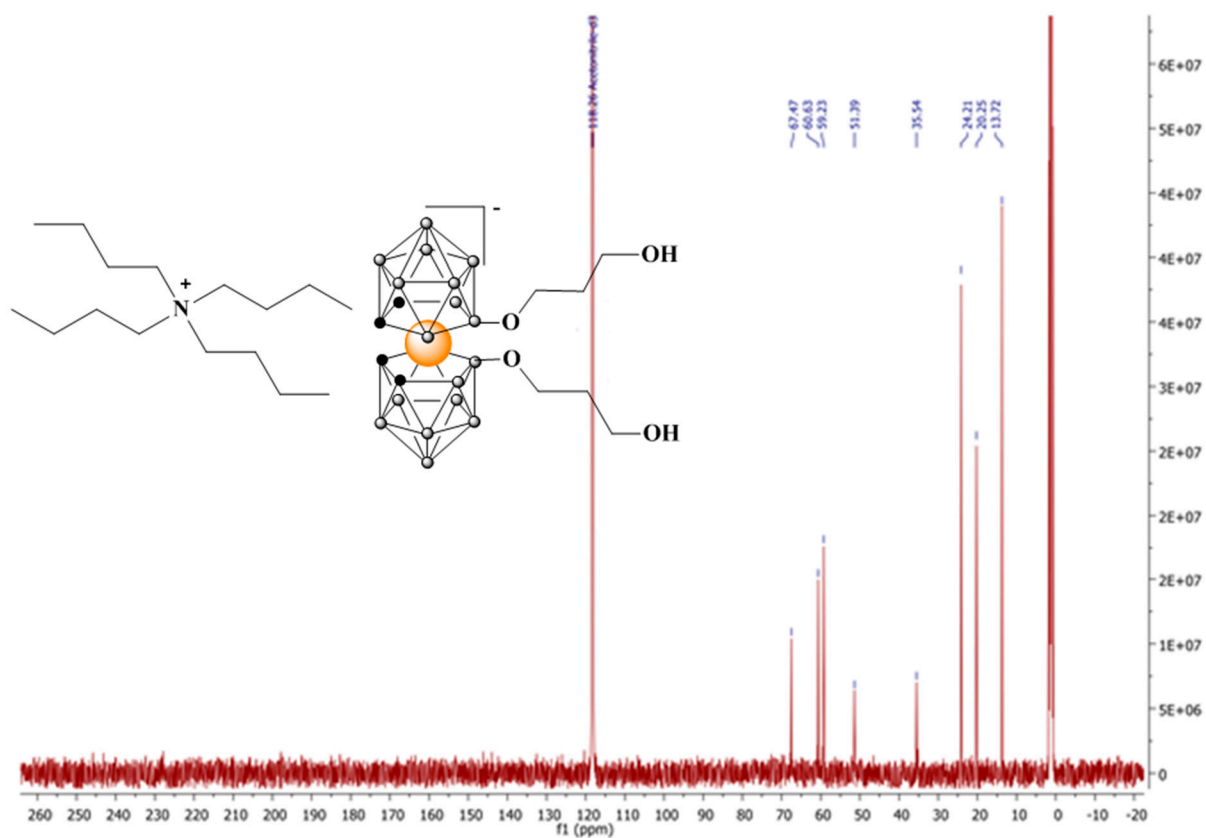
**Figure S15.**  $^{11}\text{B}$  NMR spectrum of 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sub>2</sub> (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS]<sub>2</sub> (**8**).



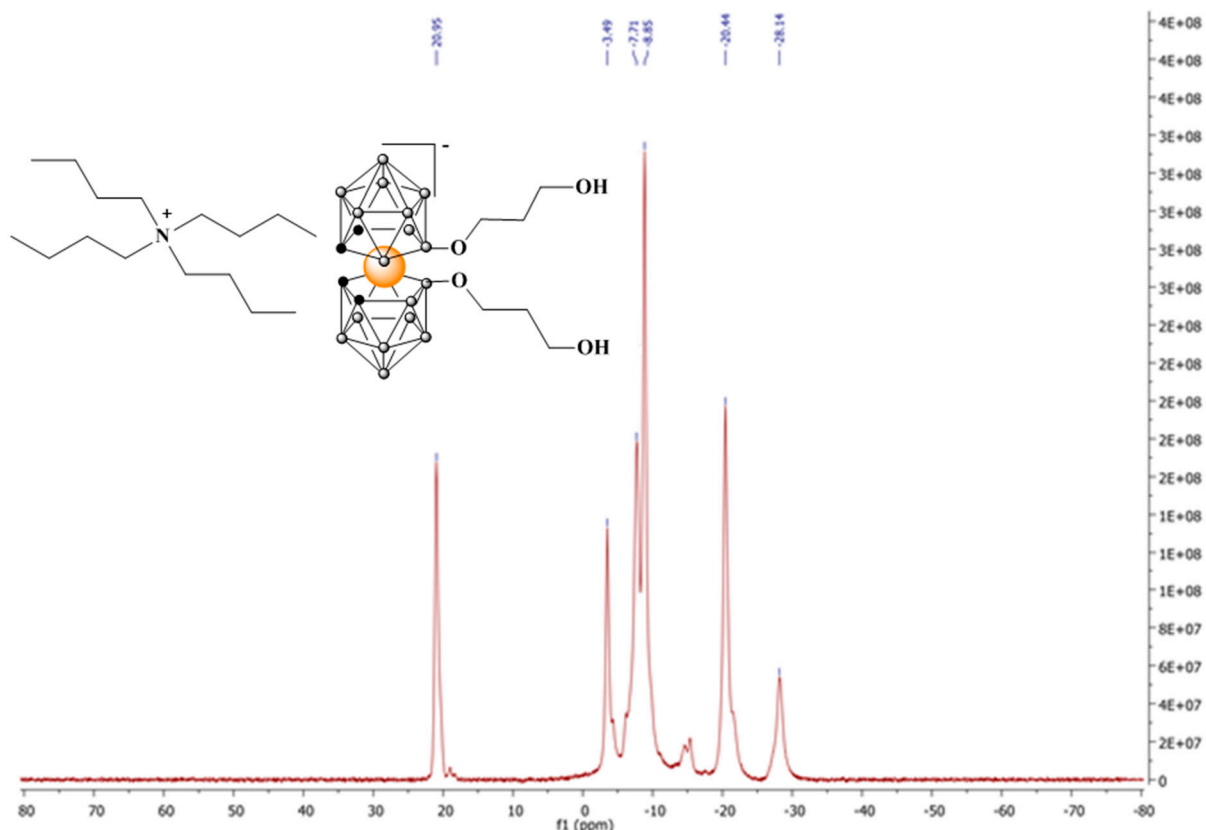
**Figure S16.** MS(ESI) spectrum of 3,3'-Co[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sub>2</sub> (CH<sub>3</sub>)<sub>2</sub>N[(CH<sub>2</sub>)<sub>3</sub>OTBDMS]<sub>2</sub> (**8**).



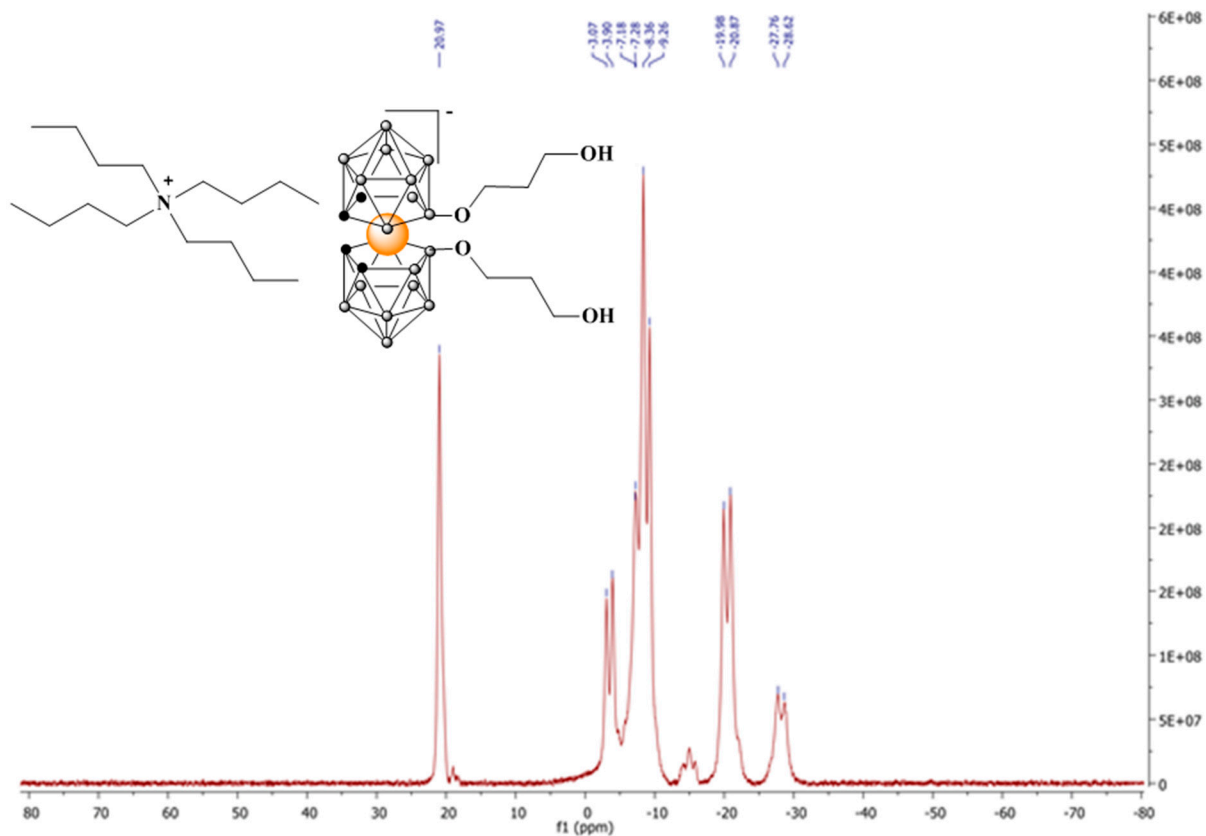
**Figure S17.** <sup>1</sup>H NMR spectrum of [3,3'-Co(8-O(CH<sub>2</sub>)<sub>3</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] TBA (9).



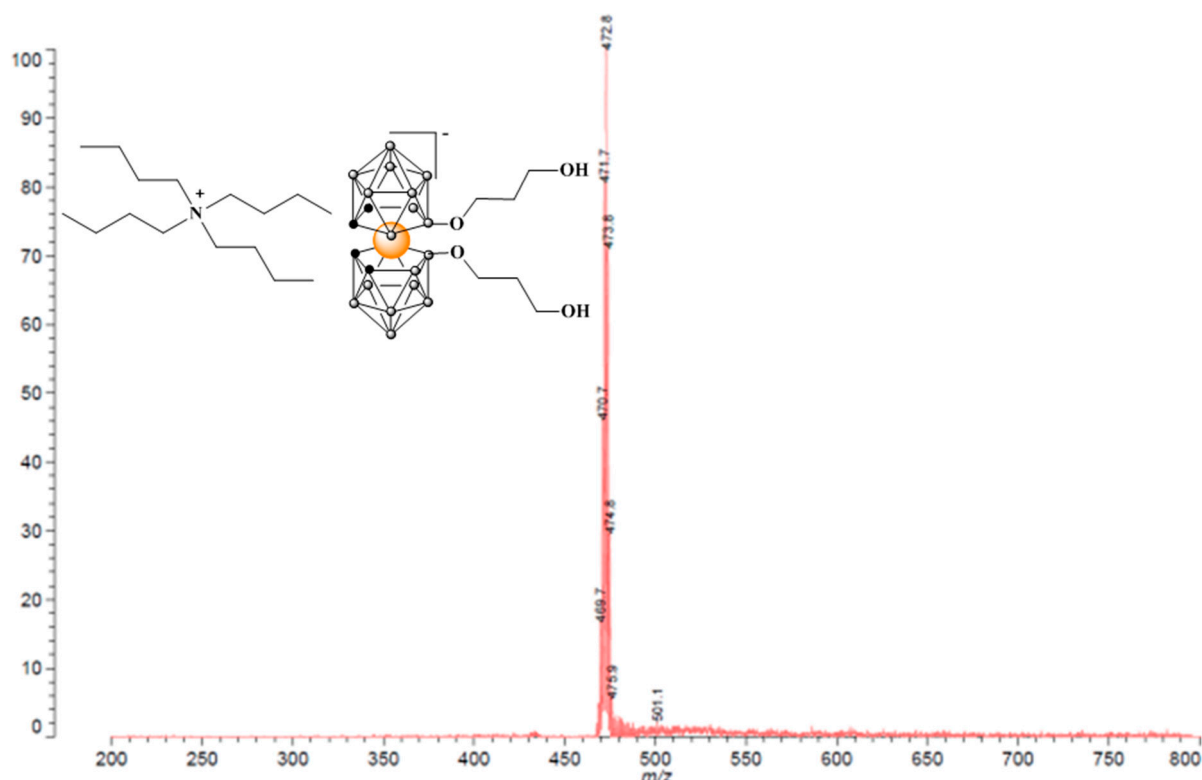
**Figure S18.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [3,3'-Co(8-O(CH<sub>2</sub>)<sub>3</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] TBA (9).



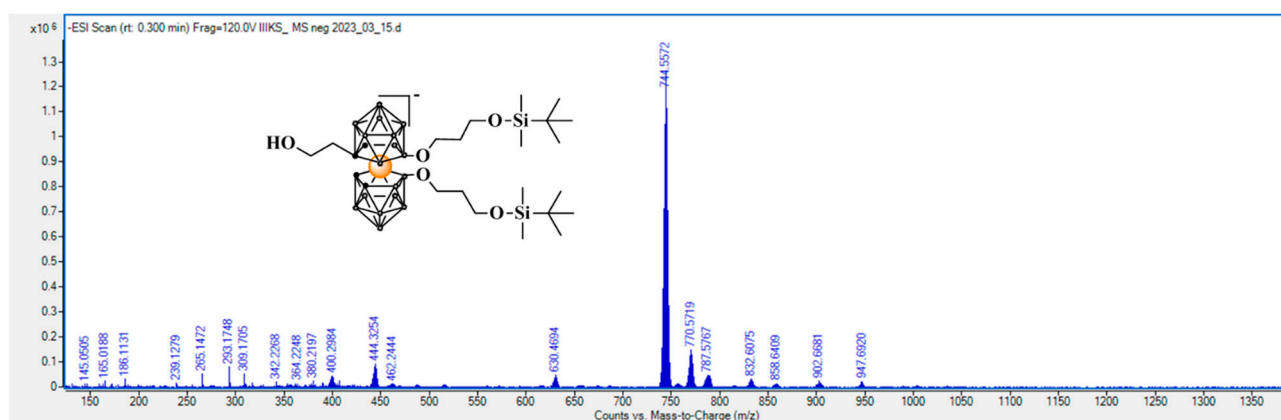
**Figure S19.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[3,3'\text{-Co(8-O(CH}_2)_3\text{OH-1,2-C}_2\text{B}_9\text{H}_{10})_2]$  TBA (**9**).



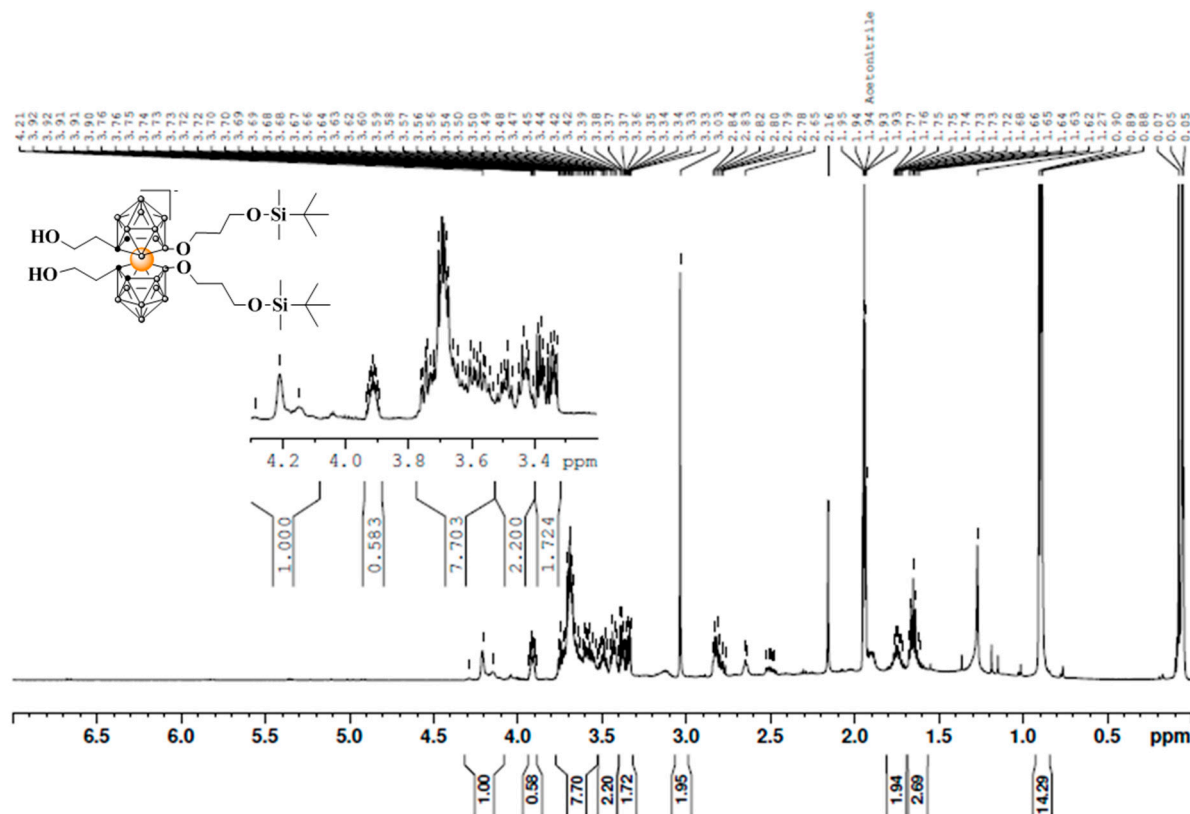
**Figure S20.**  $^{11}\text{B}$  NMR spectrum of  $[3,3'\text{-Co(8-O(CH}_2)_3\text{OH-1,2-C}_2\text{B}_9\text{H}_{10})_2]$  TBA (**9**).



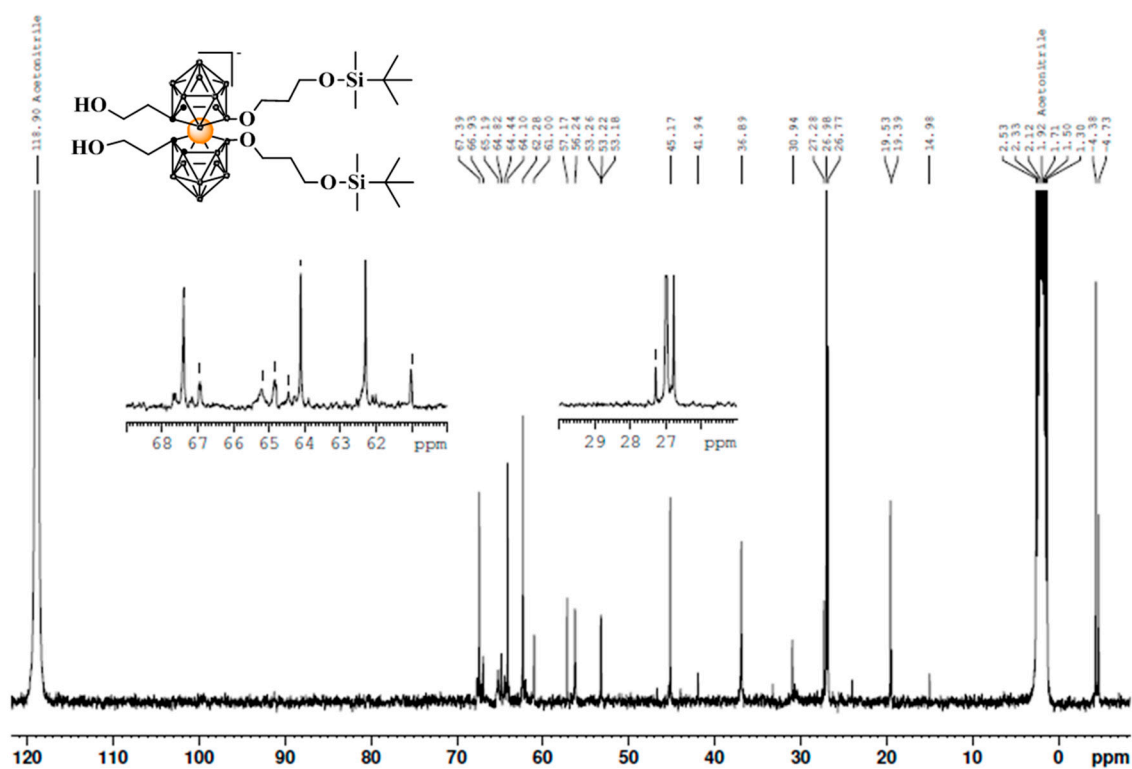
**Figure S21.** MS(ESI) spectrum of [3,3'-Co(8-O(CH<sub>2</sub>)<sub>3</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] TBA (9).



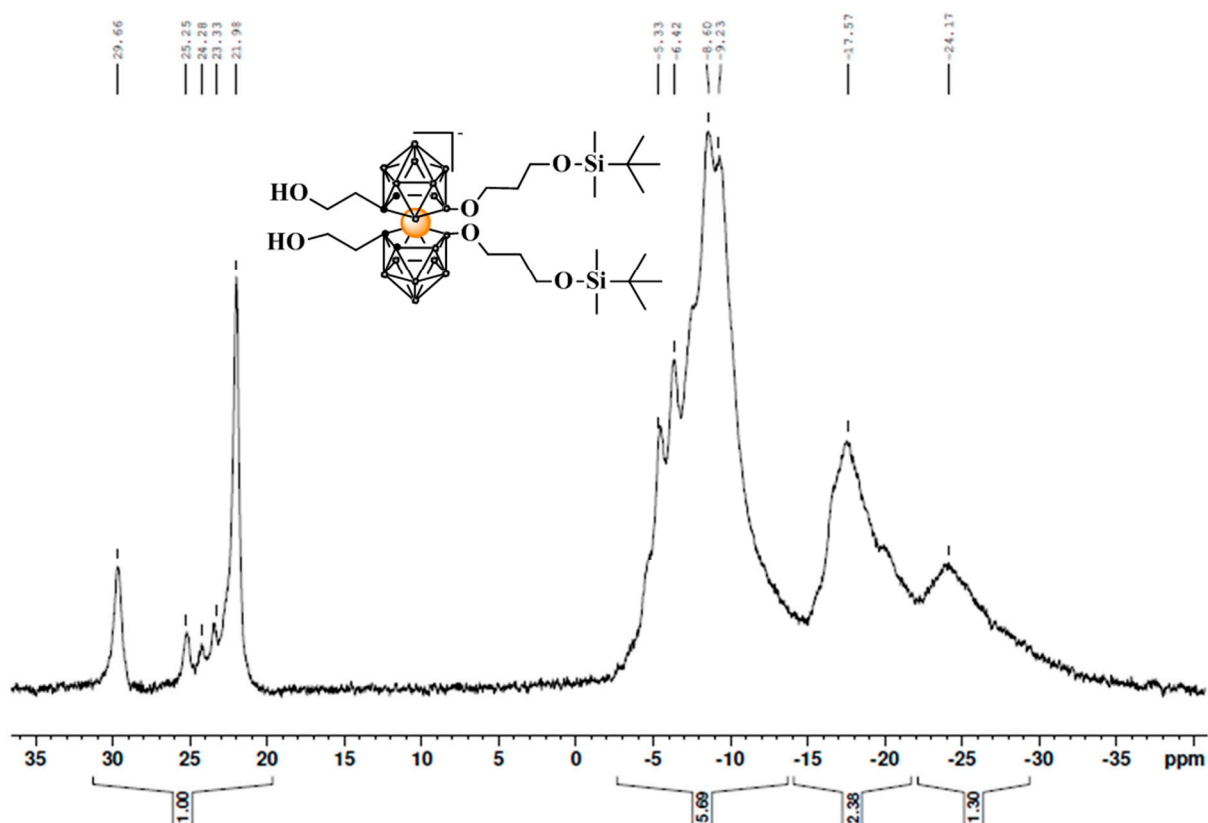
**Figure S22.** MS (ESI) spectrum of 3,3'-Co{[8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1-(CH<sub>2</sub>)<sub>2</sub>OH]-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>}[8'-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]- (10).



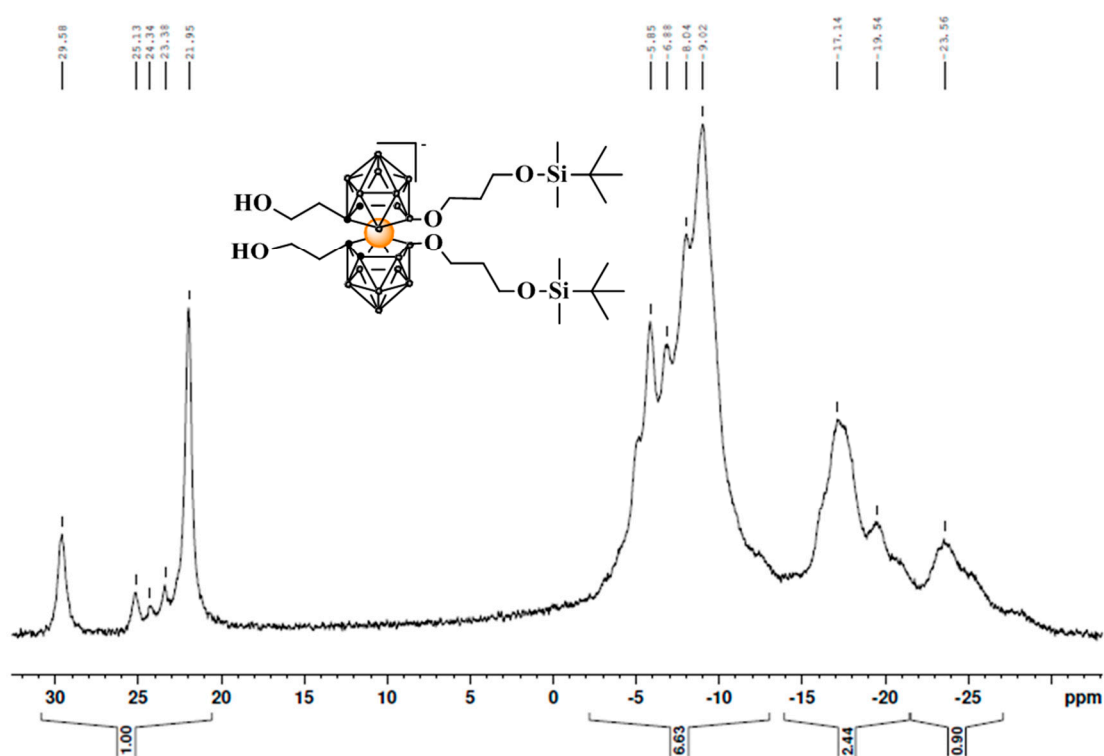
**Figure S23.**  $^1\text{H}$  NMR spectrum of 3,3'-Co[(8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1-(CH<sub>2</sub>)<sub>2</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)]<sub>2</sub><sup>-</sup> (**11**).



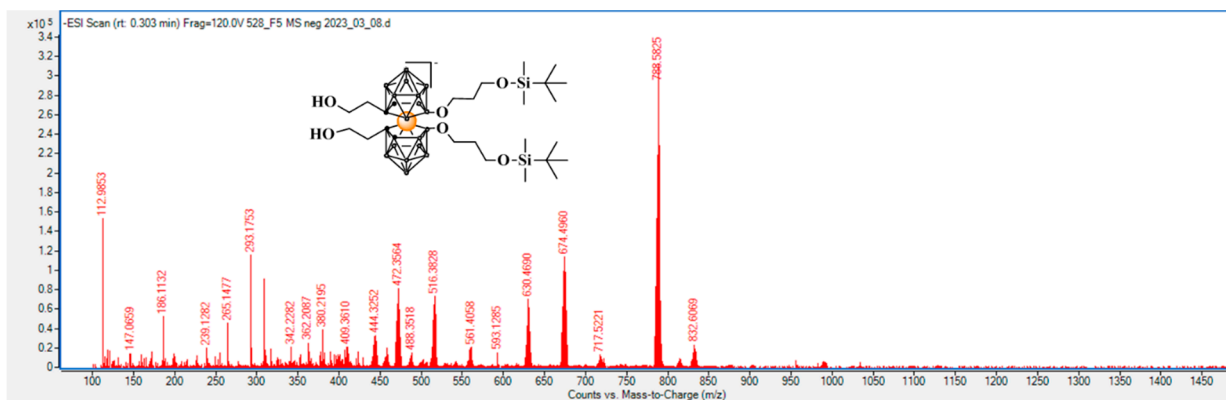
**Figure S24.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3,3'-Co[(8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1-(CH<sub>2</sub>)<sub>2</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)]<sub>2</sub><sup>-</sup> (**11**).



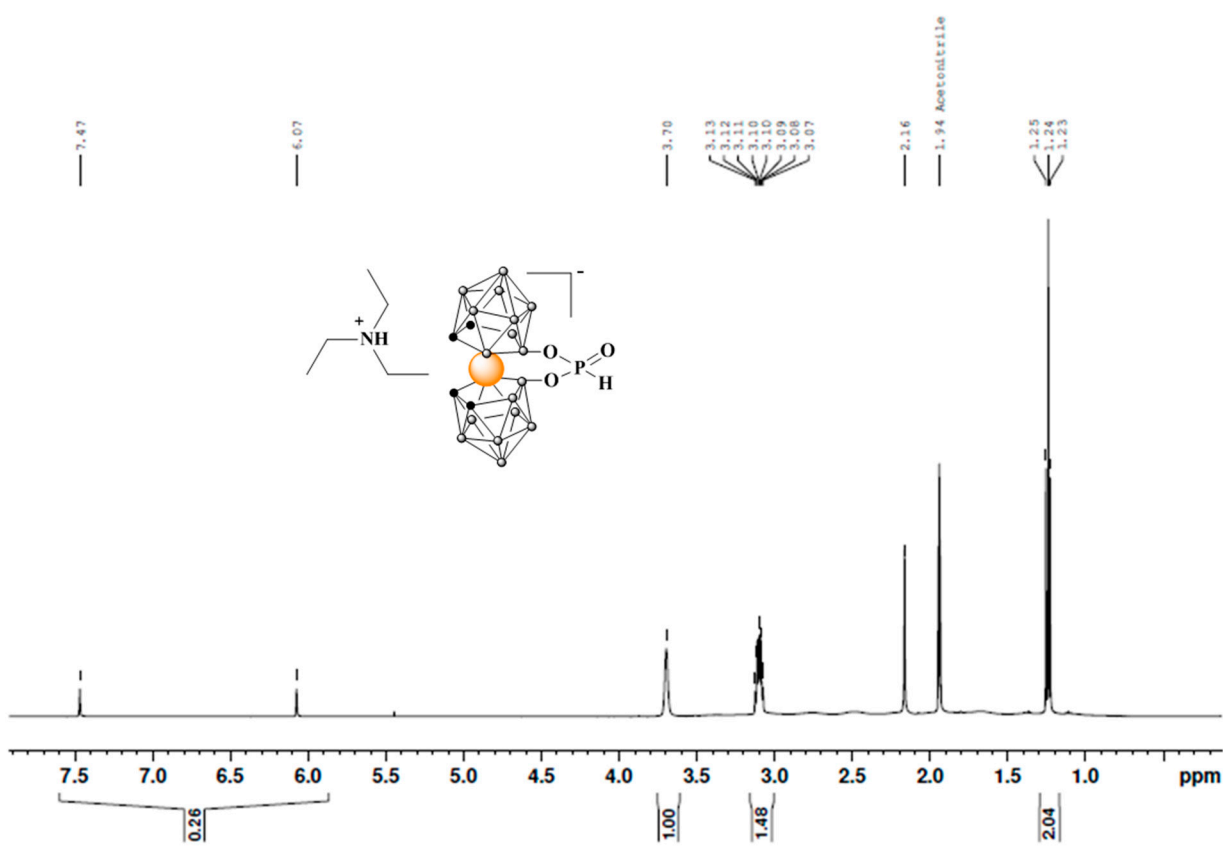
**Figure S25.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3,3'-Co[(8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1-(CH<sub>2</sub>)<sub>2</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)]<sub>2</sub><sup>-</sup> (**11**).



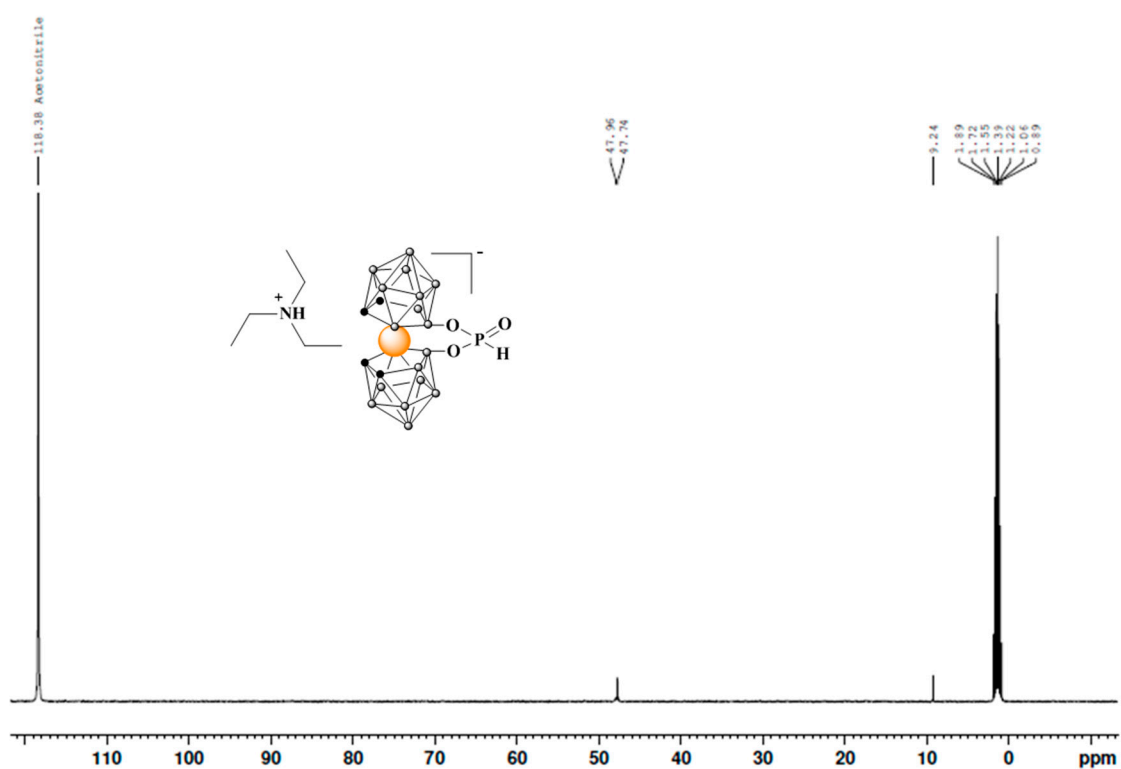
**Figure S26.**  $^{11}\text{B}$  NMR spectrum of 3,3'-Co[(8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1-(CH<sub>2</sub>)<sub>2</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)]<sub>2</sub><sup>-</sup> (**11**).



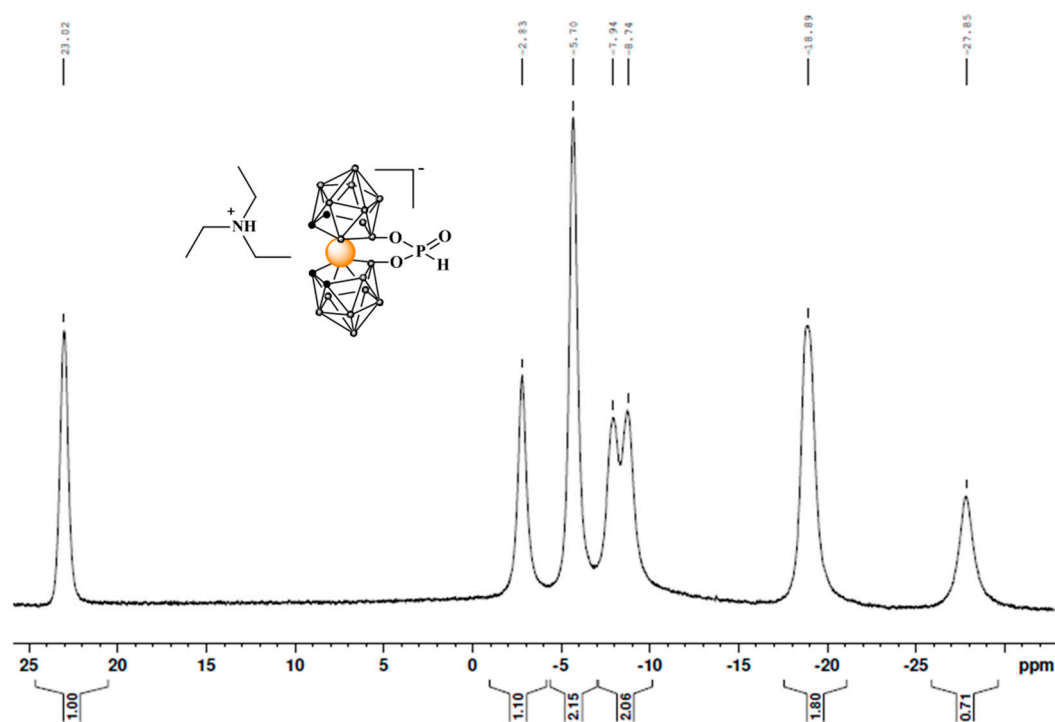
**Figure S27.** MS (ESI) spectrum of 3,3'-Co[(8-O(CH<sub>2</sub>)<sub>3</sub>OTBDMS-1-(CH<sub>2</sub>)<sub>2</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)]<sub>2</sub><sup>-</sup> (**11**).



**Figure S28.** <sup>1</sup>H NMR spectrum of 8,8'-bridged [8,8'-O<sub>2</sub>P(O)H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> H-phosphonate (**12**).

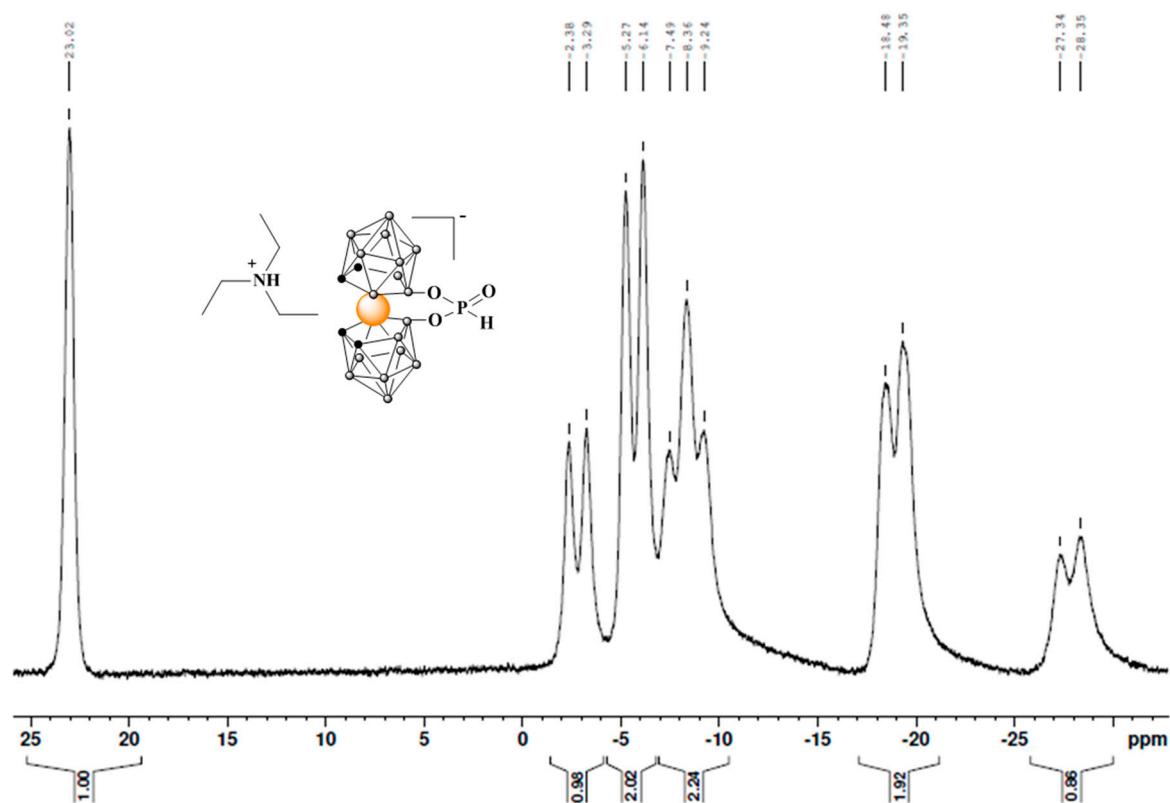


**Figure S29.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum 8,8'-bridged [8,8'-O<sub>2</sub>P(O)H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> H-phosphonate (**12**).

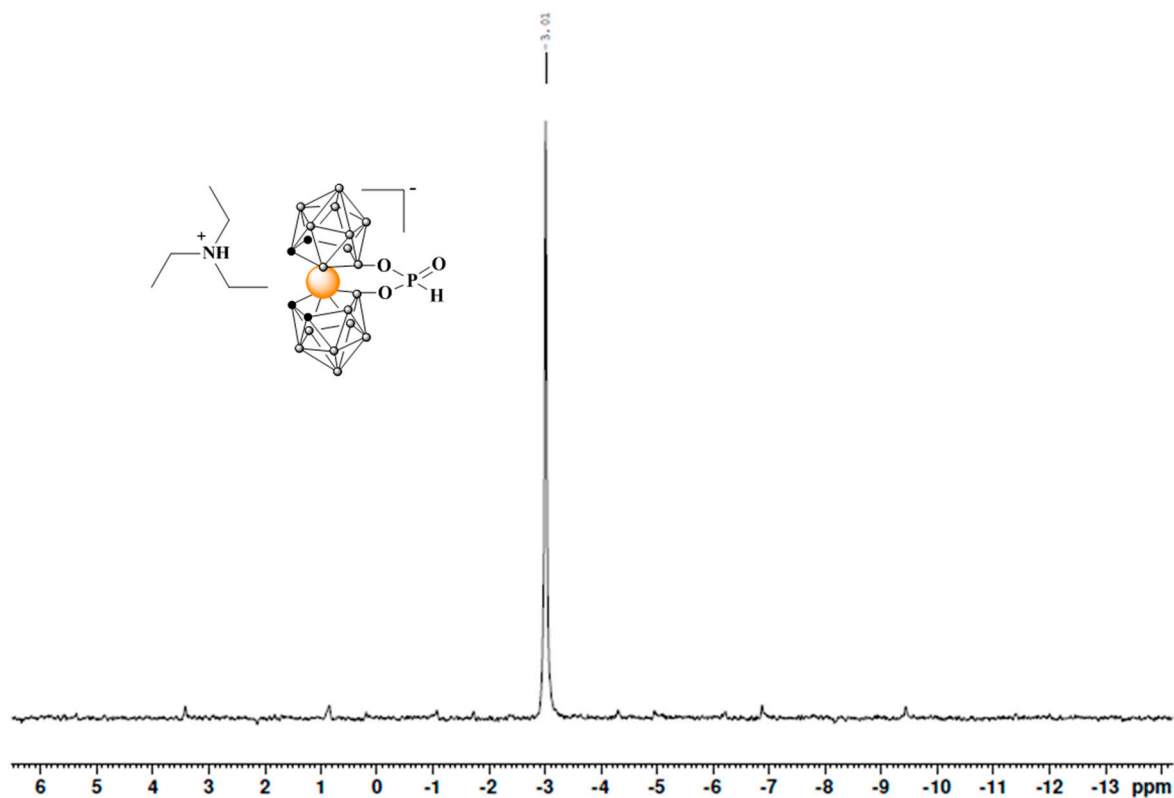


**Figure S30.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 8,8'-bridged [8,8'-O<sub>2</sub>P(O)H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> H-phosphonate (**12**).

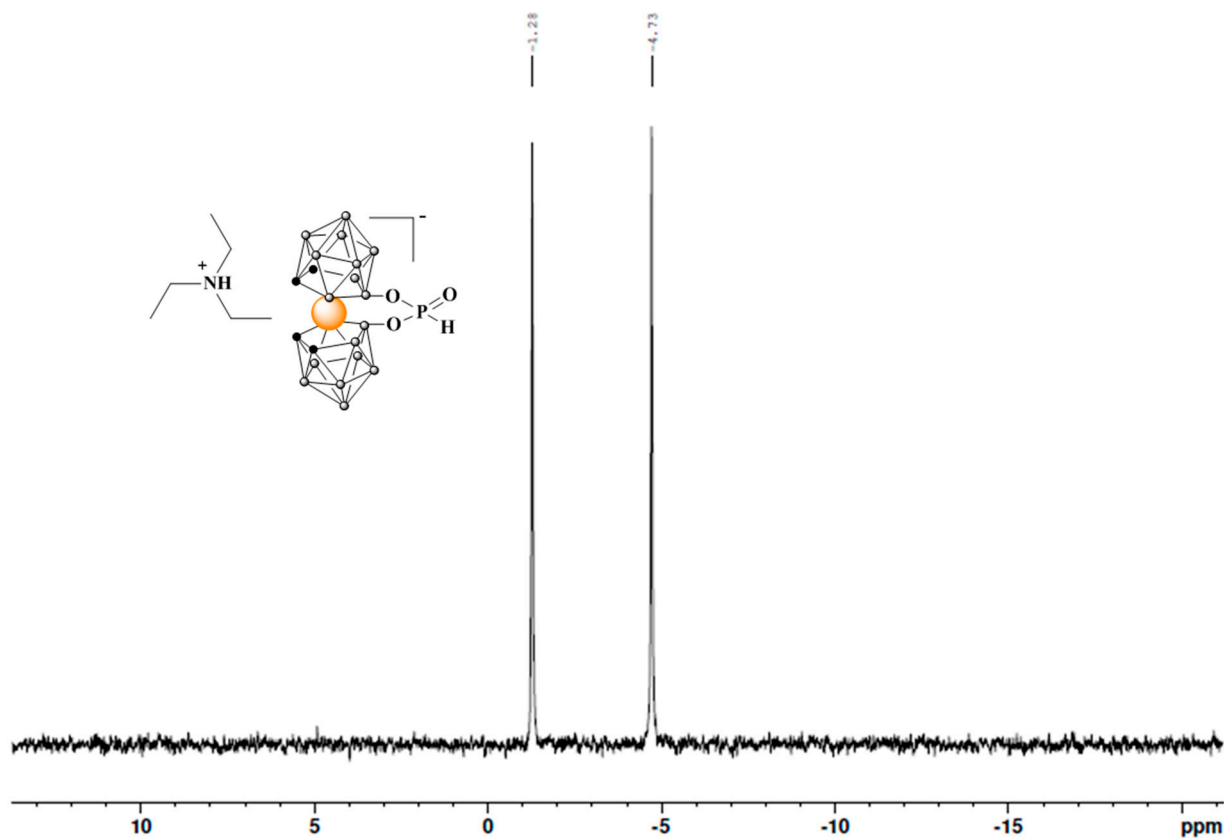




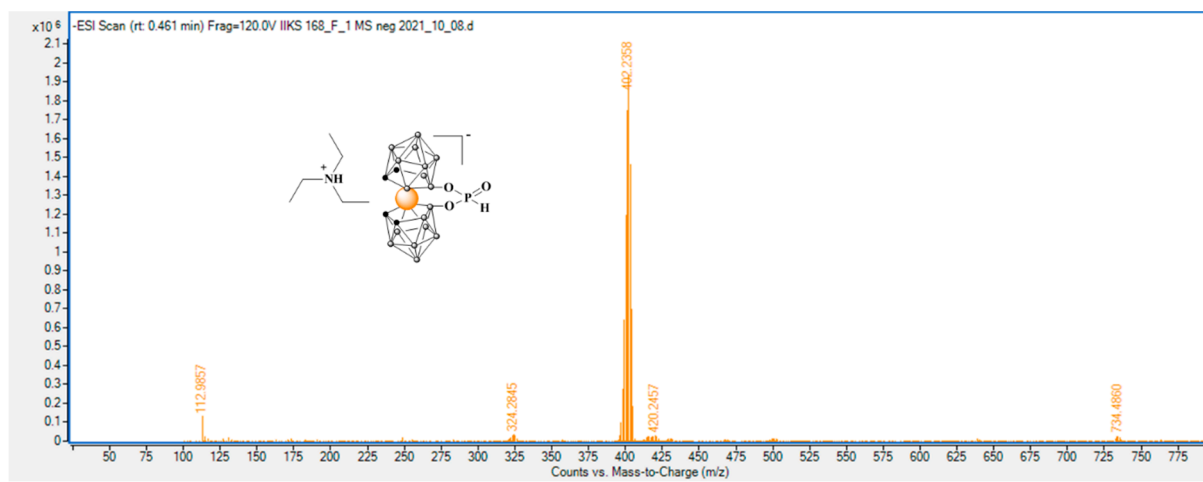
**Figure S31.**  $^{11}\text{B}$  NMR spectrum of 8,8'-bridged  $[8,8'\text{-O}_2\text{P(O)H-3,3'}\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]$   $\text{HNEt}_3$  H-phosphonate (**12**).



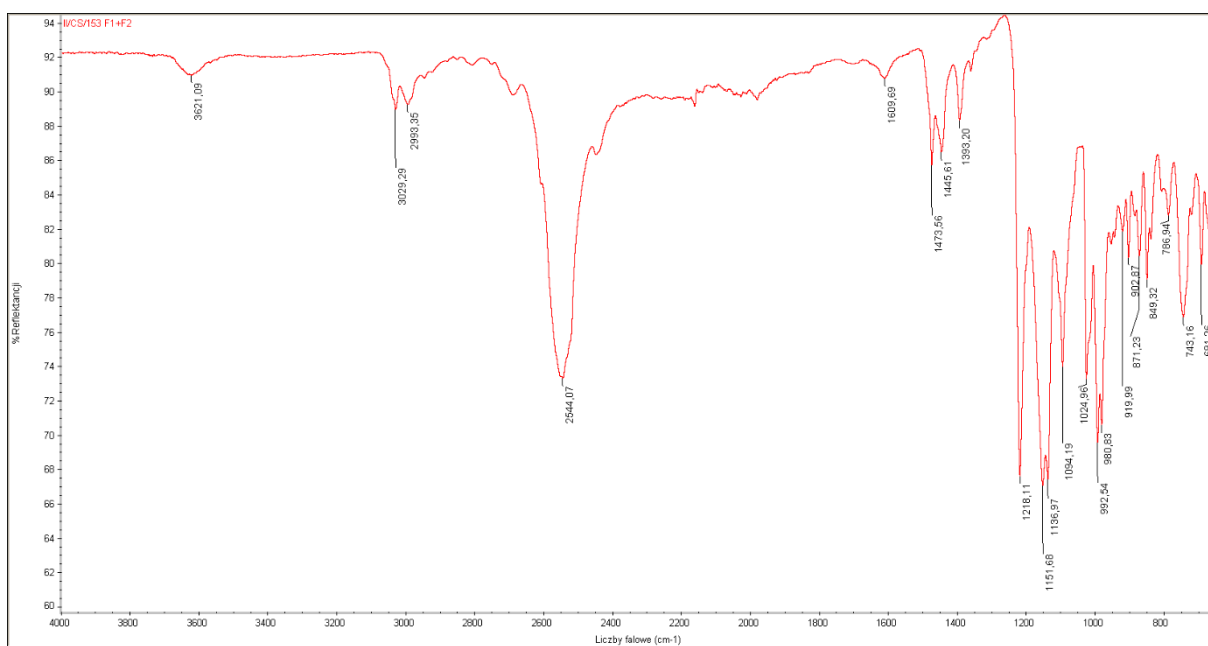
**Figure S32.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of 8,8'-bridged  $[8,8'\text{-O}_2\text{P(O)H-3,3'}\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]$   $\text{HNEt}_3$  H-phosphonate (**12**).



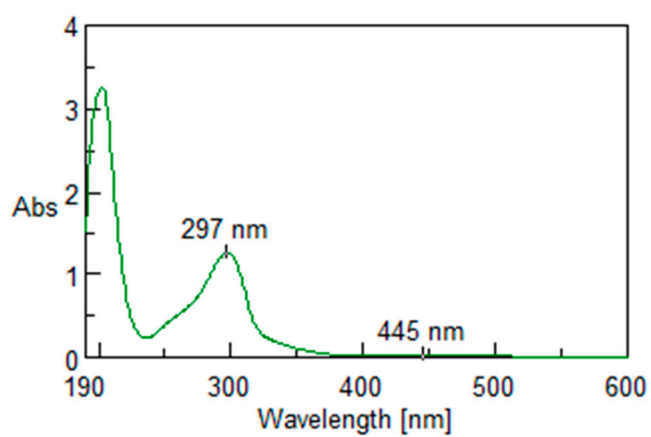
**Figure S33.**  $^{31}\text{P}$  NMR spectrum of 8,8'-bridged  $[8,8'\text{-O}_2\text{P(O)H-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$   $\text{HNEt}_3$  H-phosphonate (**12**).



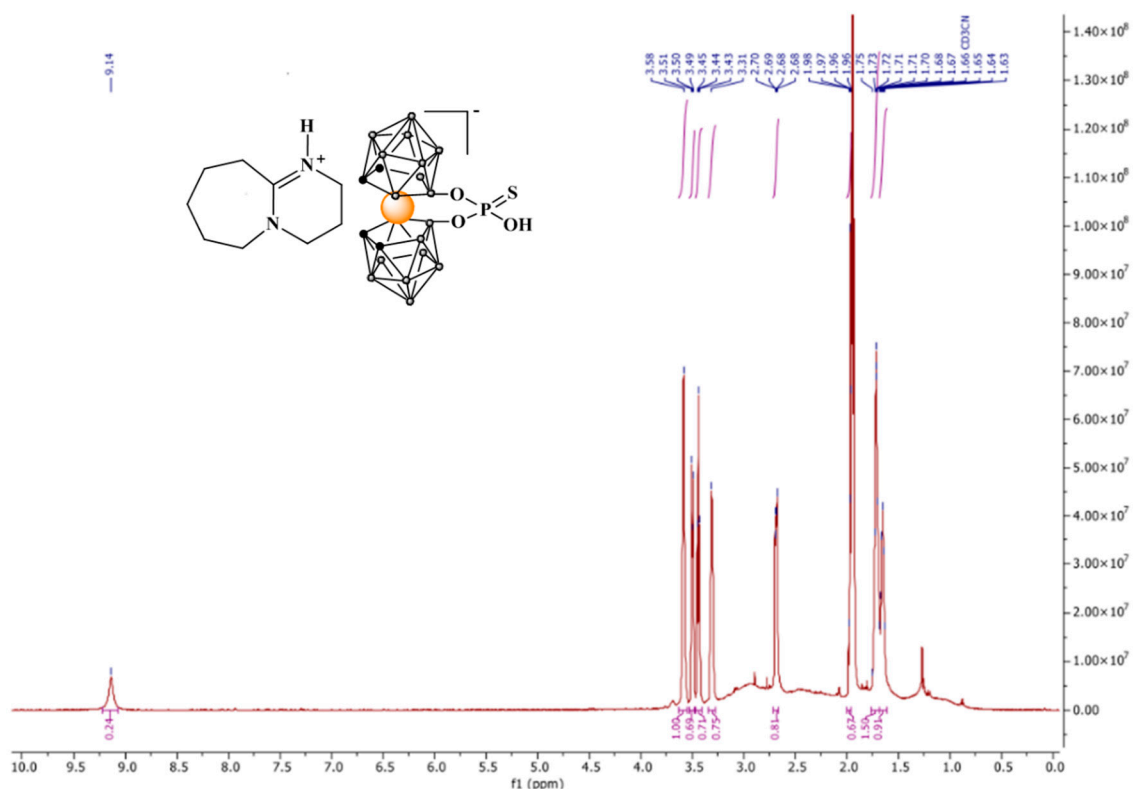
**Figure S34.** MS (ESI) spectrum of 8,8'-bridged  $[8,8'\text{-O}_2\text{P(O)H-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$   $\text{HNEt}_3$  H-phosphonate (**12**).



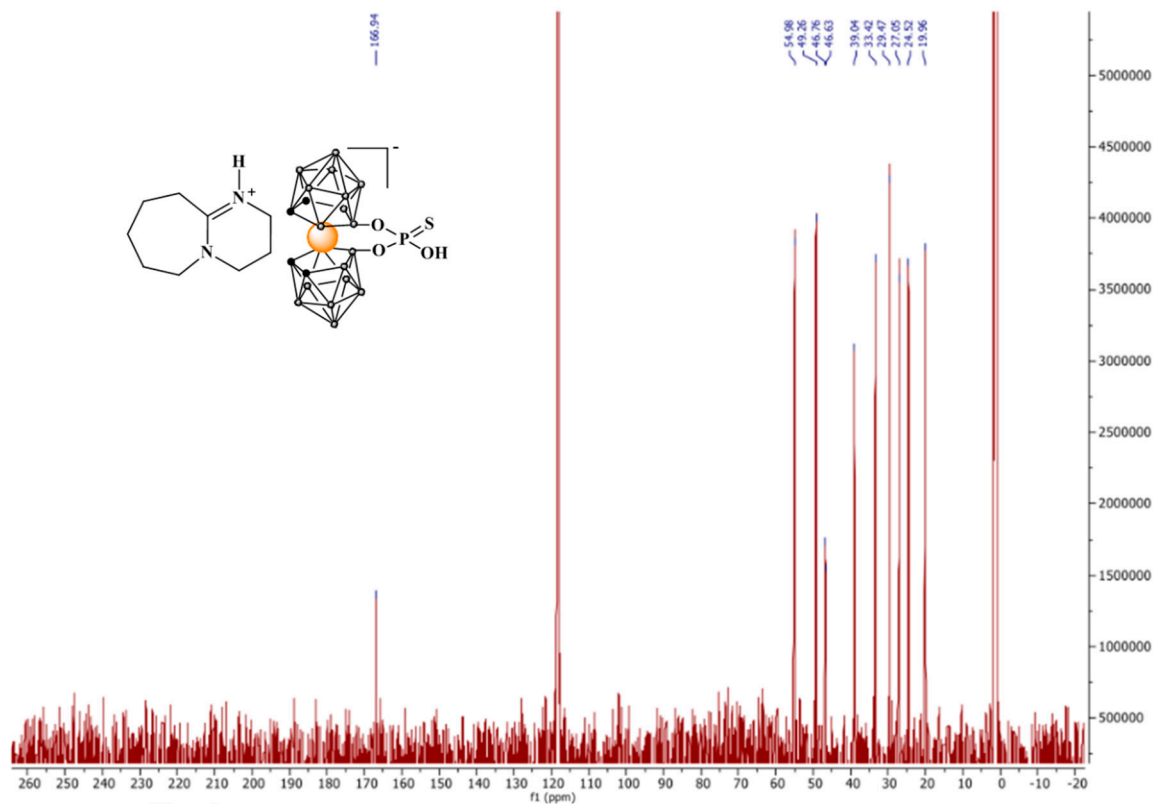
**Figure S35.** FT-IR spectrum of 8,8'-bridged [8,8'-O<sub>2</sub>P(O)H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNet<sub>3</sub> H-phosphonate (**12**).



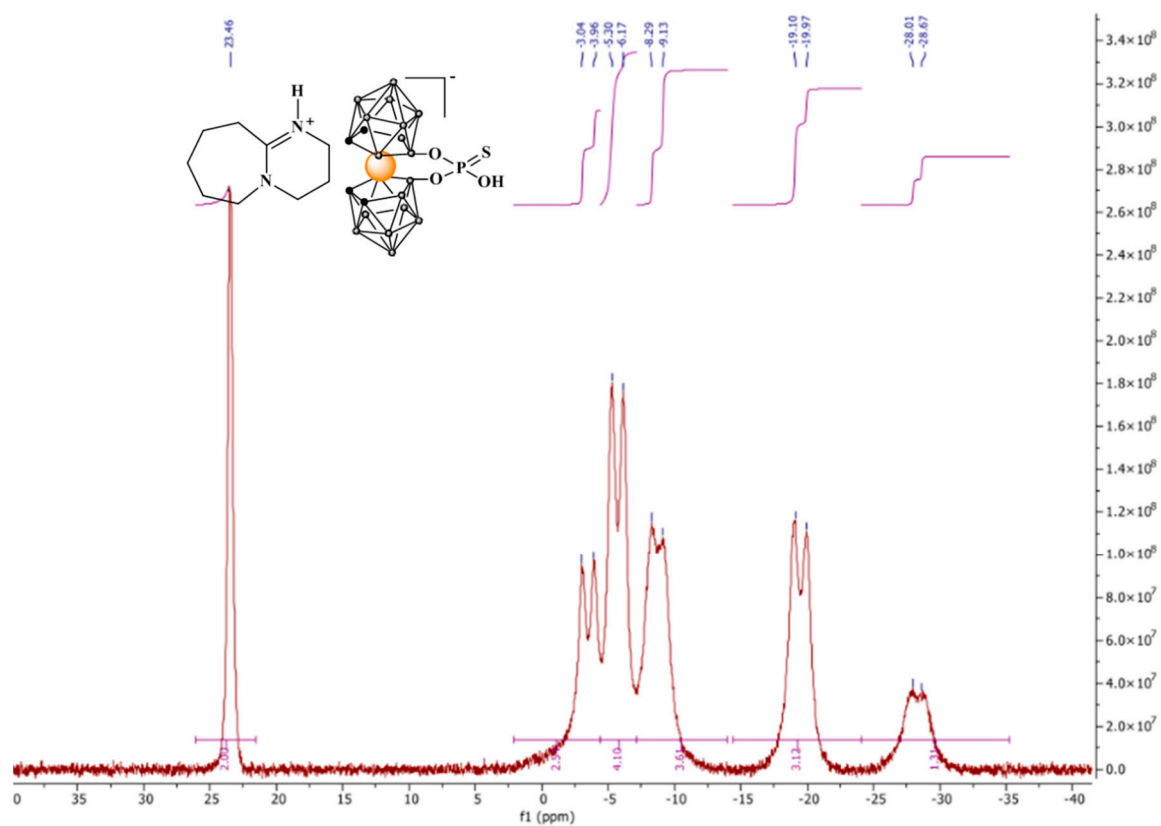
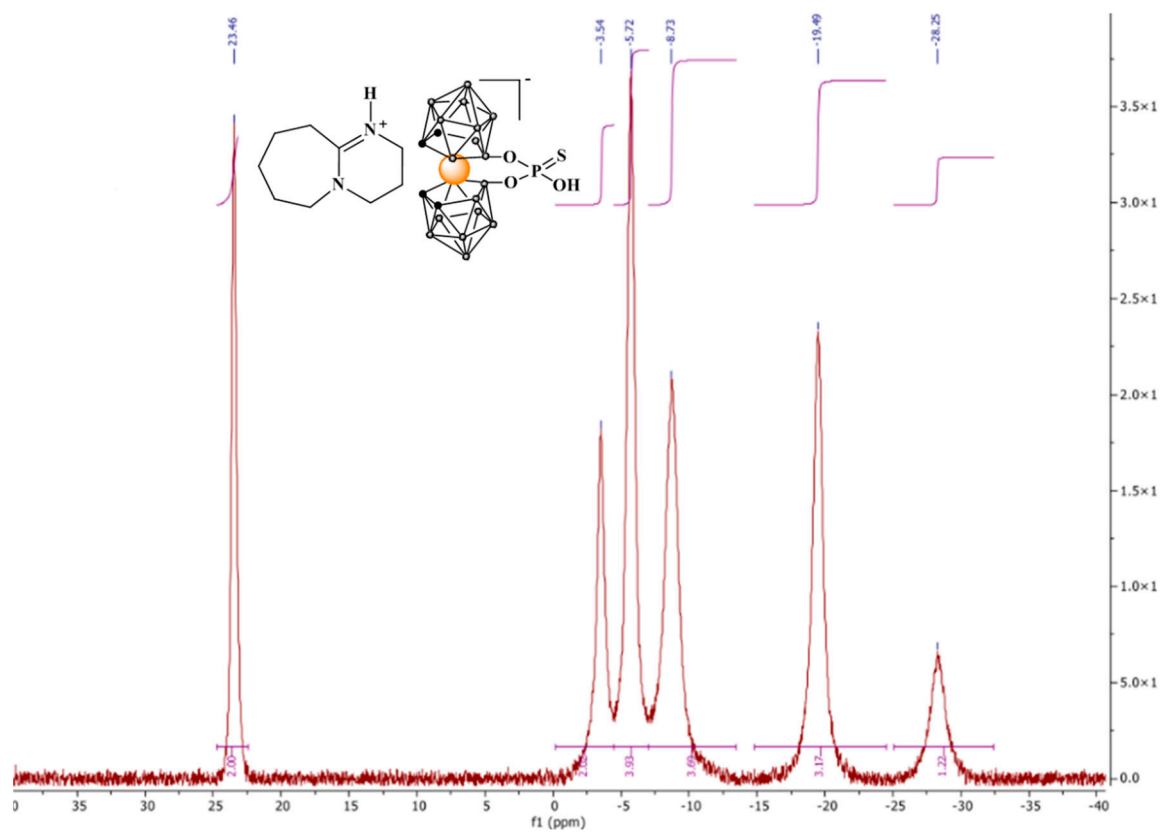
**Figure S36.** UV-VIS spectrum of 8,8'-bridged [8,8'-O<sub>2</sub>P(O)H-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNet<sub>3</sub> H-phosphonate (**12**).

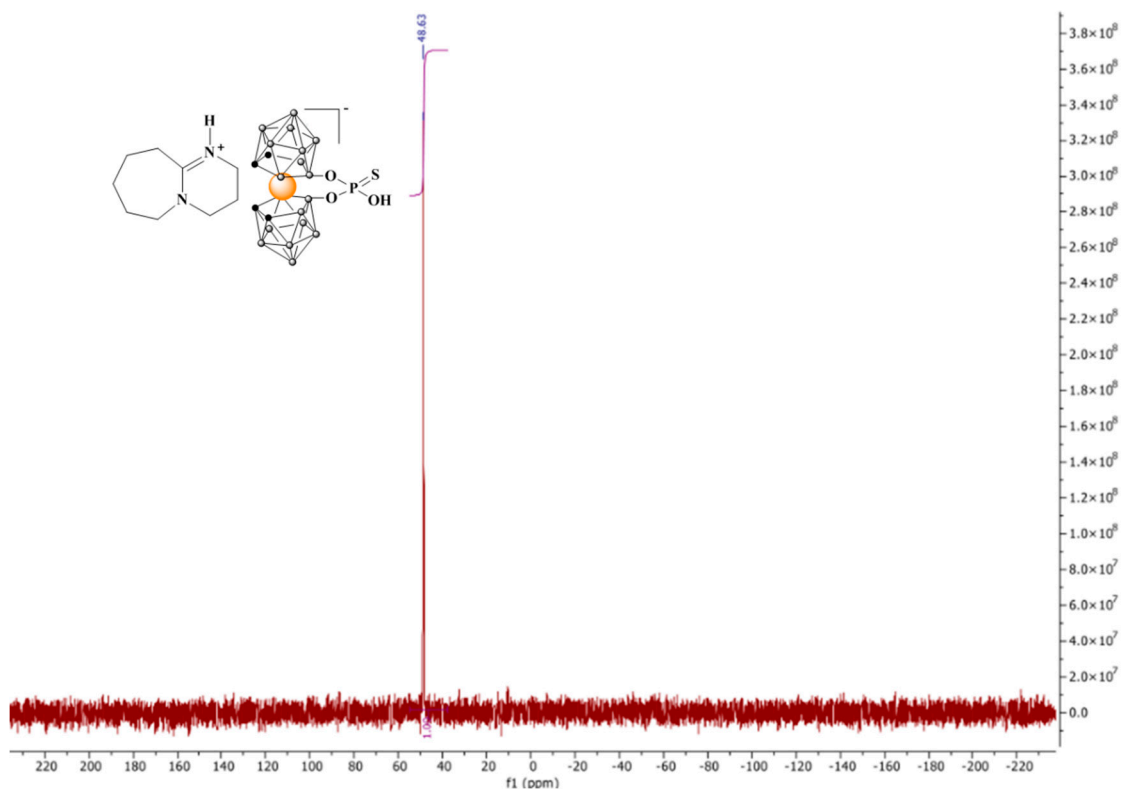


**Figure S37.**  $^1\text{H}$  NMR spectrum of 8,8'-bridged  $[8,8'\text{-O}_2\text{P}(\text{O})\text{SH-3,3'}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  HDBU phosphorothioate (**13**).

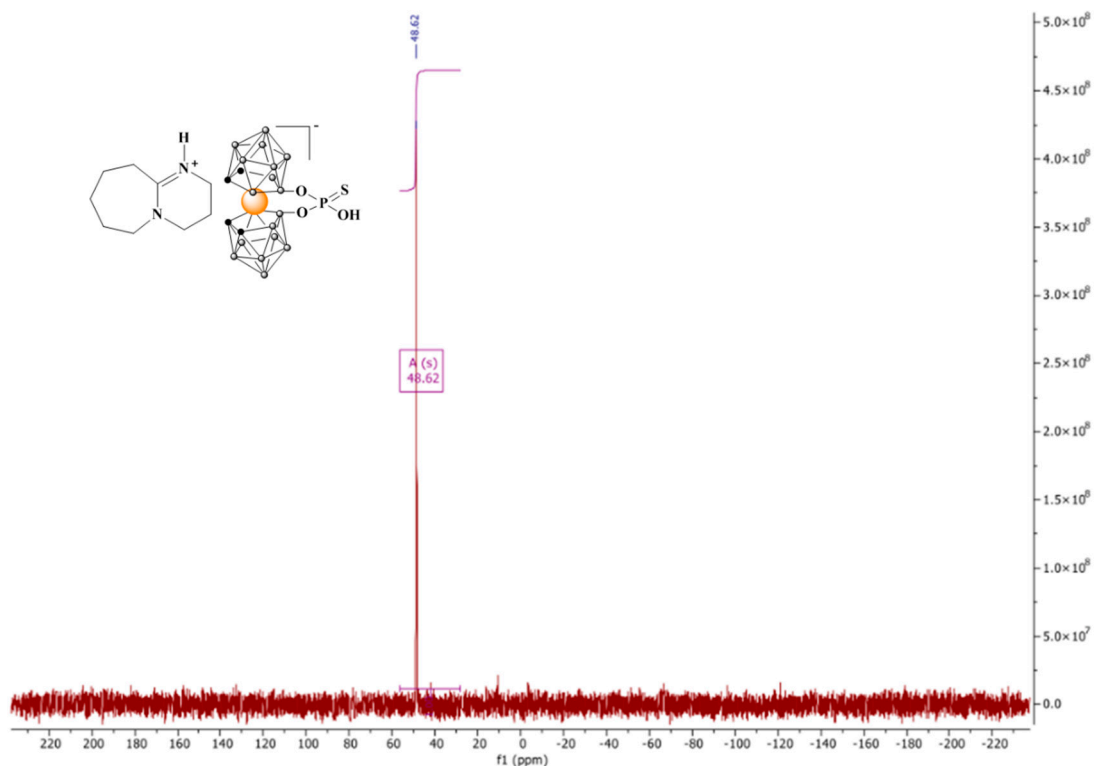


**Figure S38.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 8,8'-bridged  $[8,8'\text{-O}_2\text{P}(\text{O})\text{SH-3,3'}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  HDBU phosphorothioate (**13**).

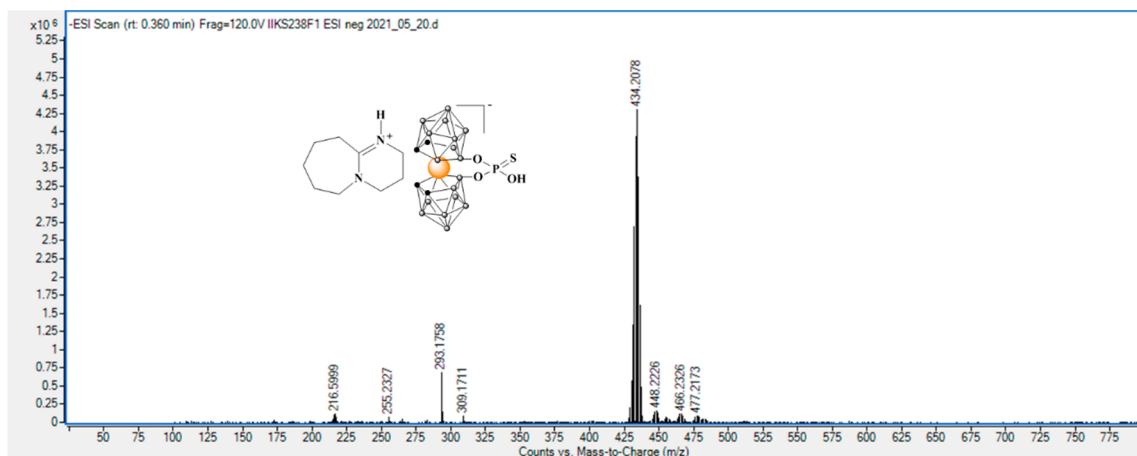




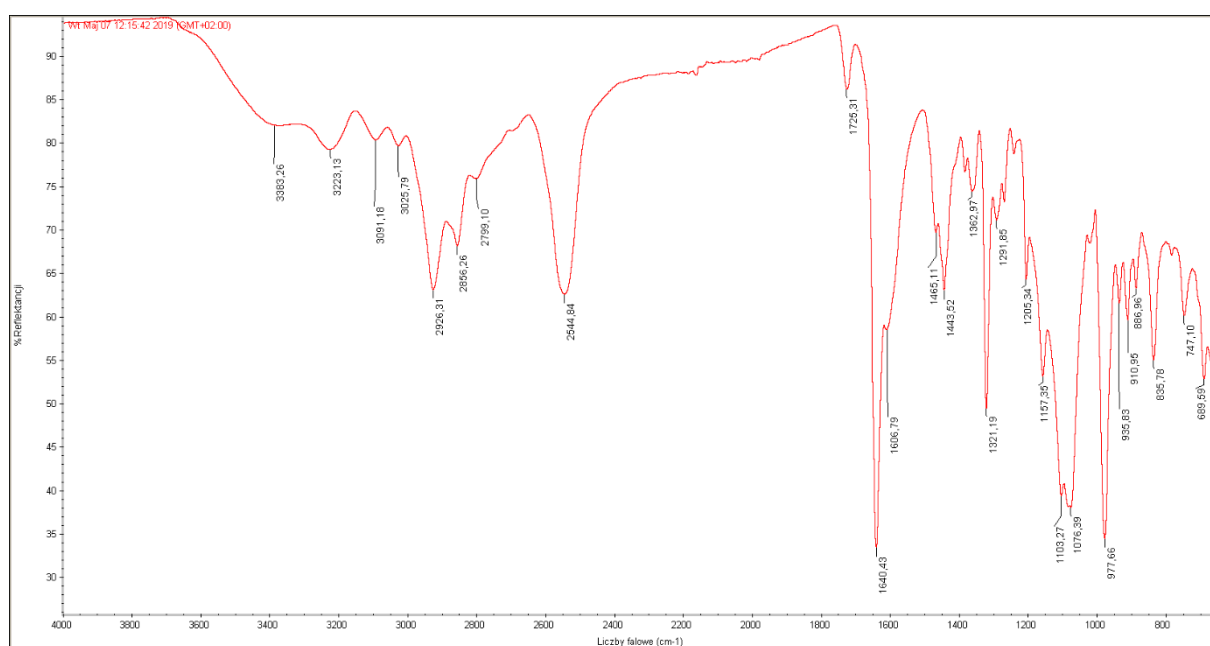
**Figure S41.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of 8,8'-bridged [8,8'-O<sub>2</sub>P(O)SH-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HDBU phosphorothioate (**13**).



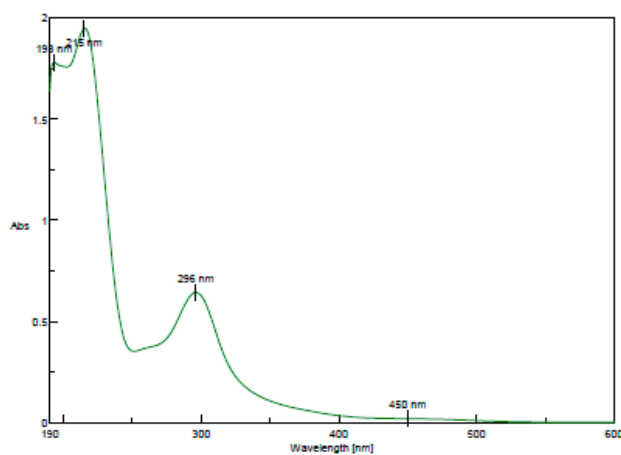
**Figure S42.**  $^{31}\text{P}$  NMR spectrum of 8,8'-bridged [8,8'-O<sub>2</sub>P(O)SH-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HDBU phosphorothioate (**13**).



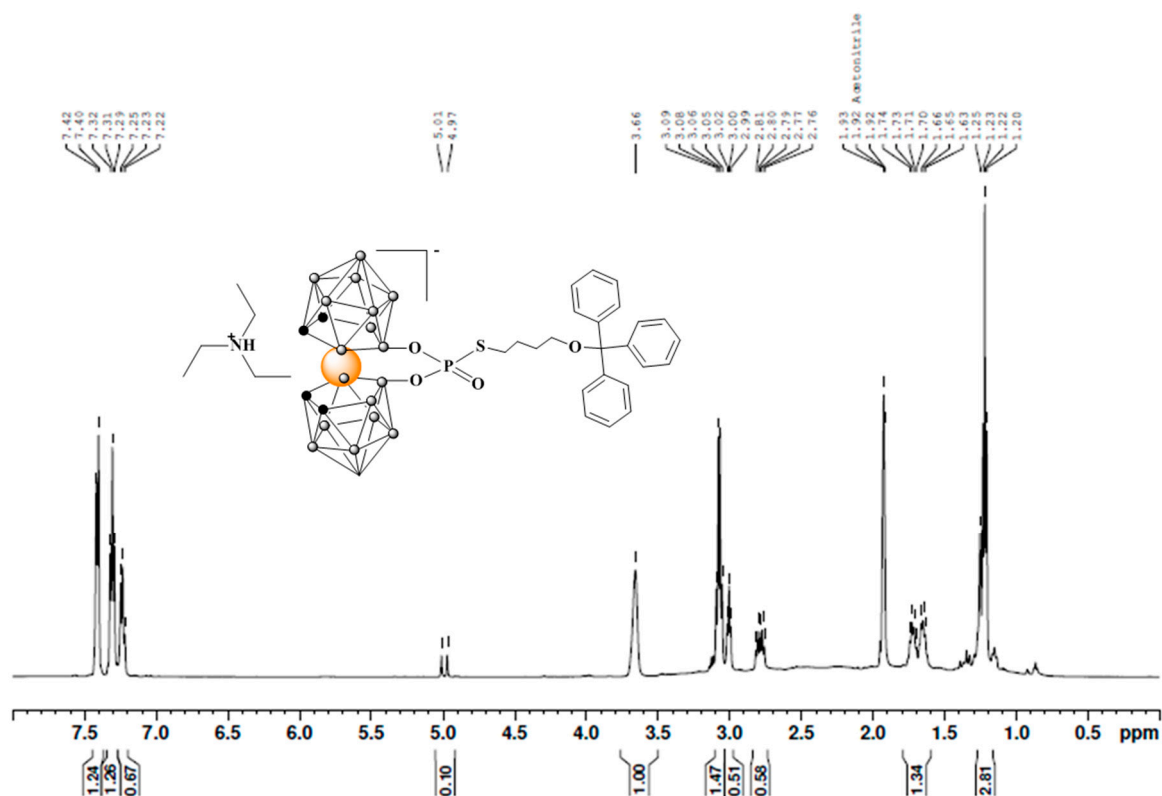
**Figure S43.** MS (ESI) spectrum of 8,8'-bridged [8,8'-O<sub>2</sub>P(O)SH-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HDBU phosphorothioate (**13**).



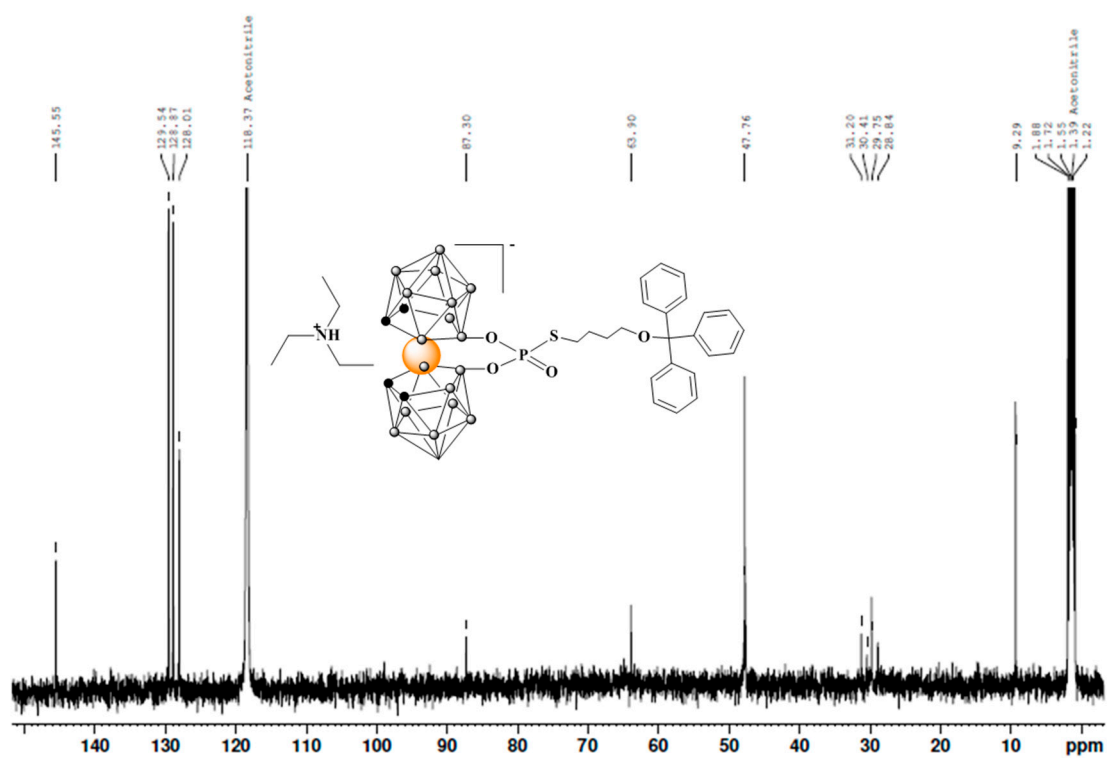
**Figure S44.** FT-IR spectrum of 8,8'-bridged [8,8'-O<sub>2</sub>P(O)SH-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HDBU phosphorothioate (**13**).



**Figure S45.** UV-VIS spectrum of spectrum of 8,8'-bridged [8,8'-O<sub>2</sub>P(O)SH-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HDBU phosphorothioate (**13**).

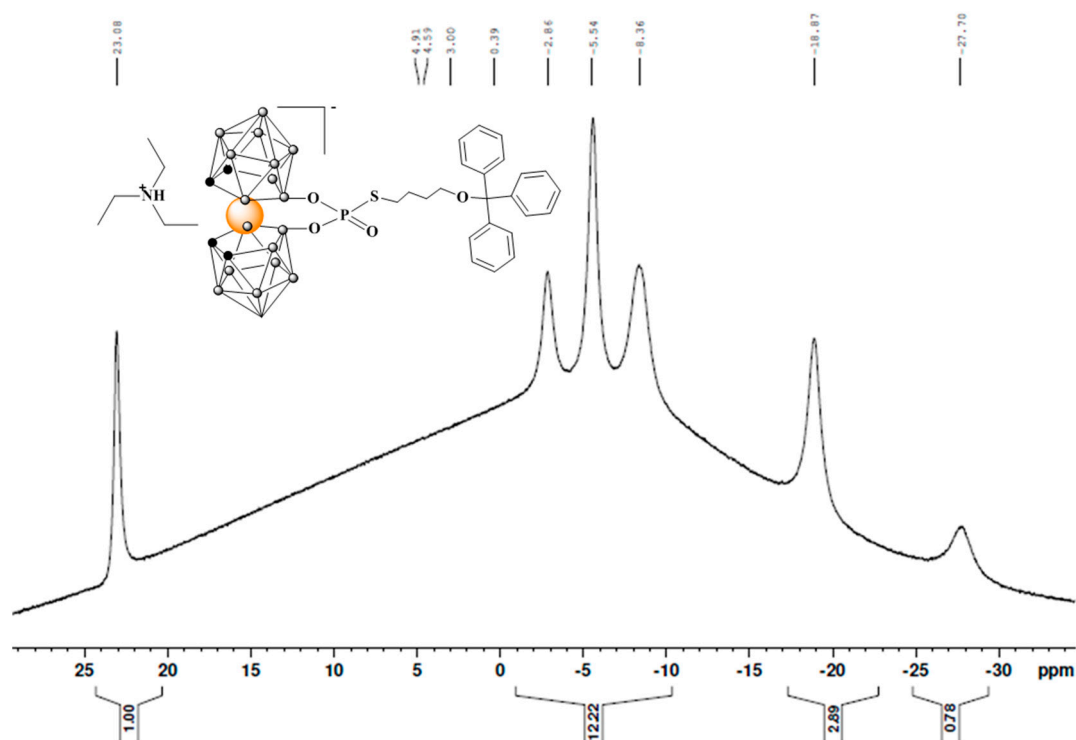


**Figure S46.** <sup>1</sup>H NMR spectrum of [8,8'-O<sub>2</sub>P(O)S(CH<sub>2</sub>)<sub>4</sub>OCPh<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> (15).

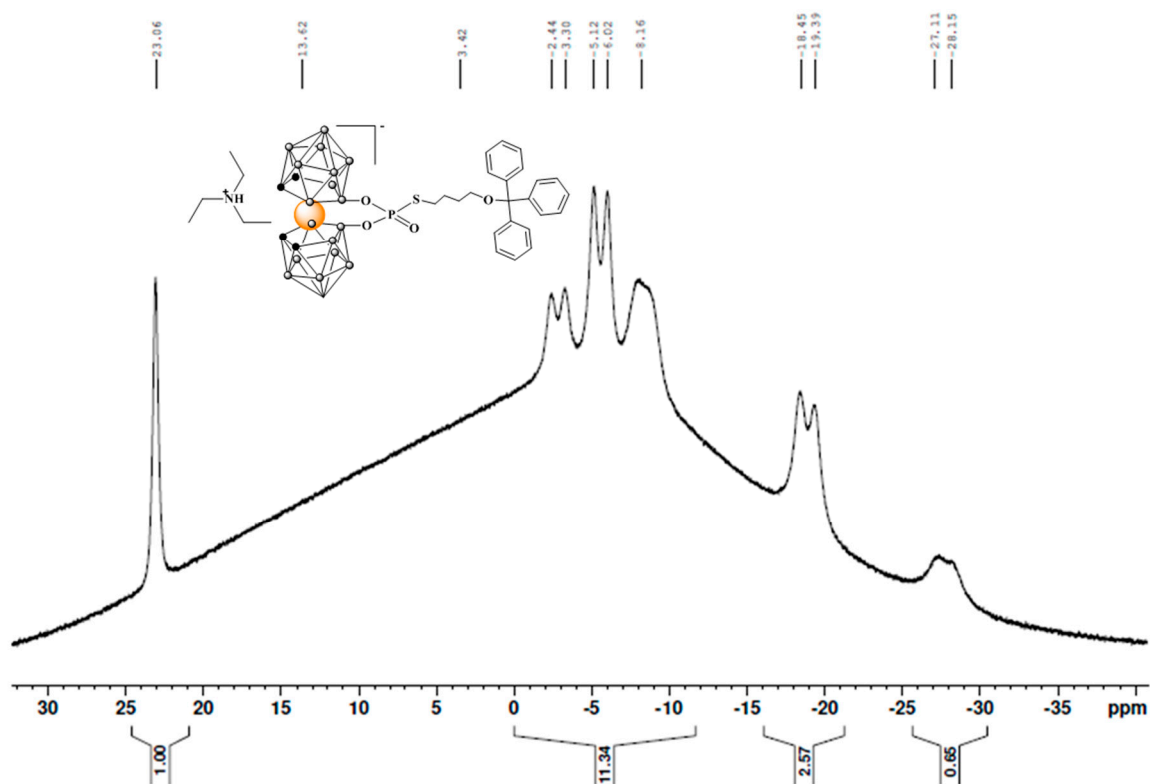


**Figure S47.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [8,8'-O<sub>2</sub>P(O)S(CH<sub>2</sub>)<sub>4</sub>OCPh<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> (15).

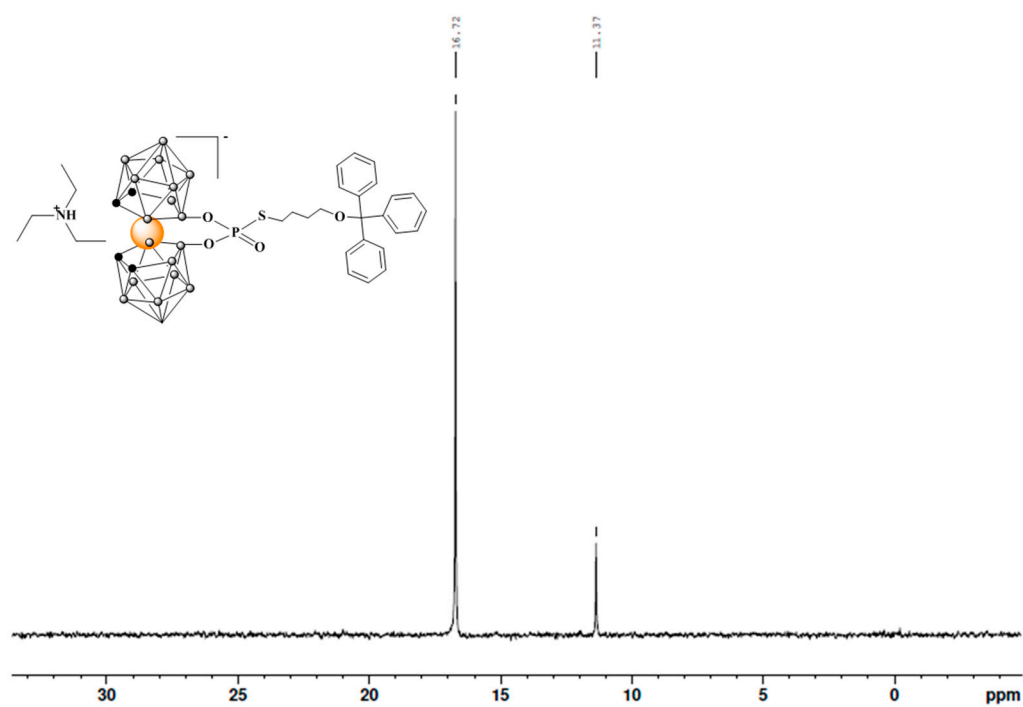




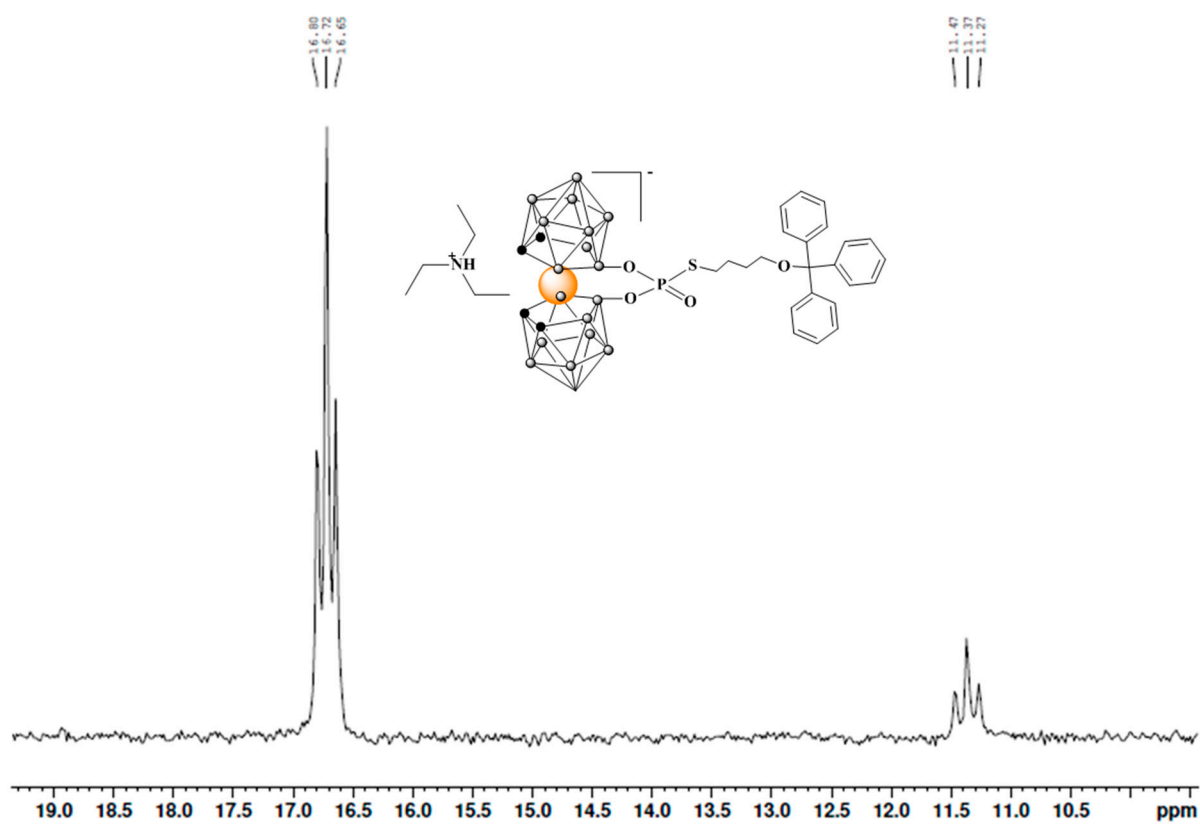
**Figure S48.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_4\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**15**).



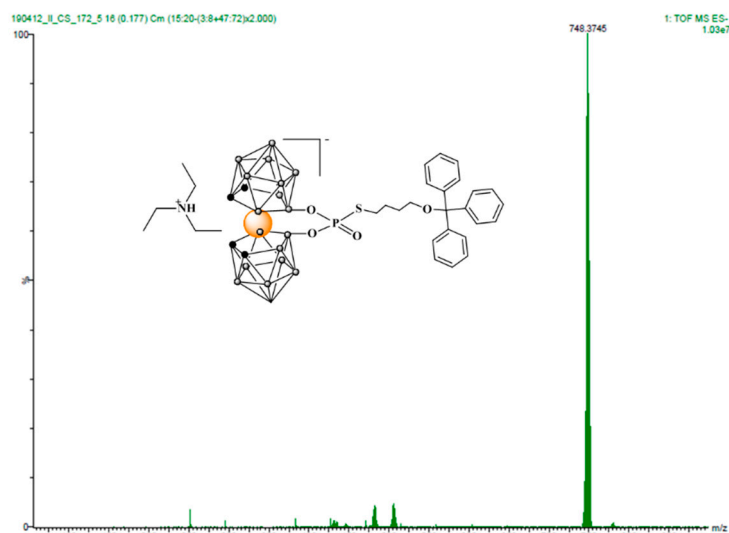
**Figure S49.**  $^{11}\text{B}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_4\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**15**).



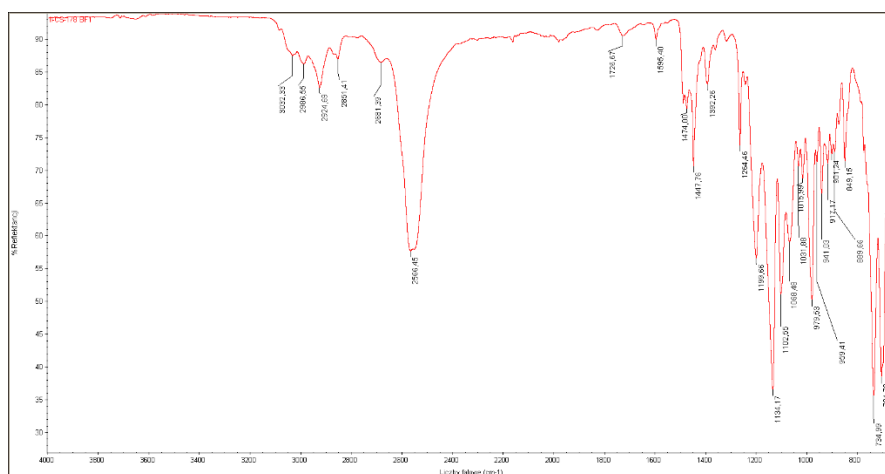
**Figure S50.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_4\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$   $\text{HNEt}_3$  (**15**).



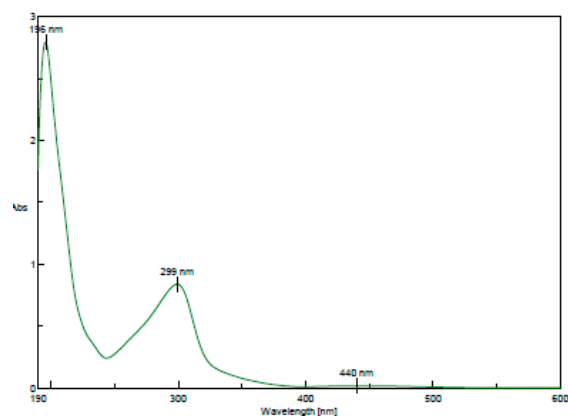
**Figure S51.**  $^{31}\text{P}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_4\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$   $\text{HNEt}_3$  (**15**).



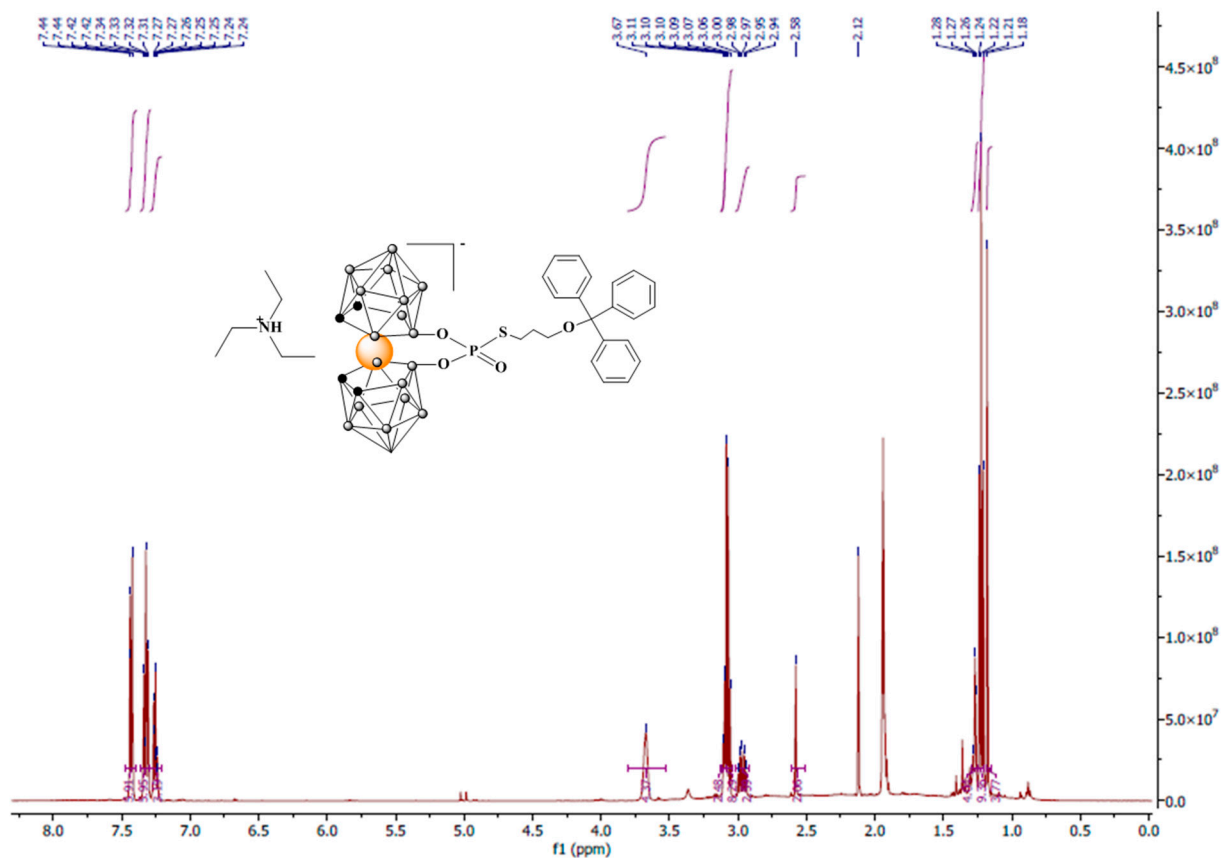
**Figure S52.** MS (ESI) spectrum of [8,8'-O<sub>2</sub>P(O)S(CH<sub>2</sub>)<sub>4</sub>OCPh<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> (**15**).



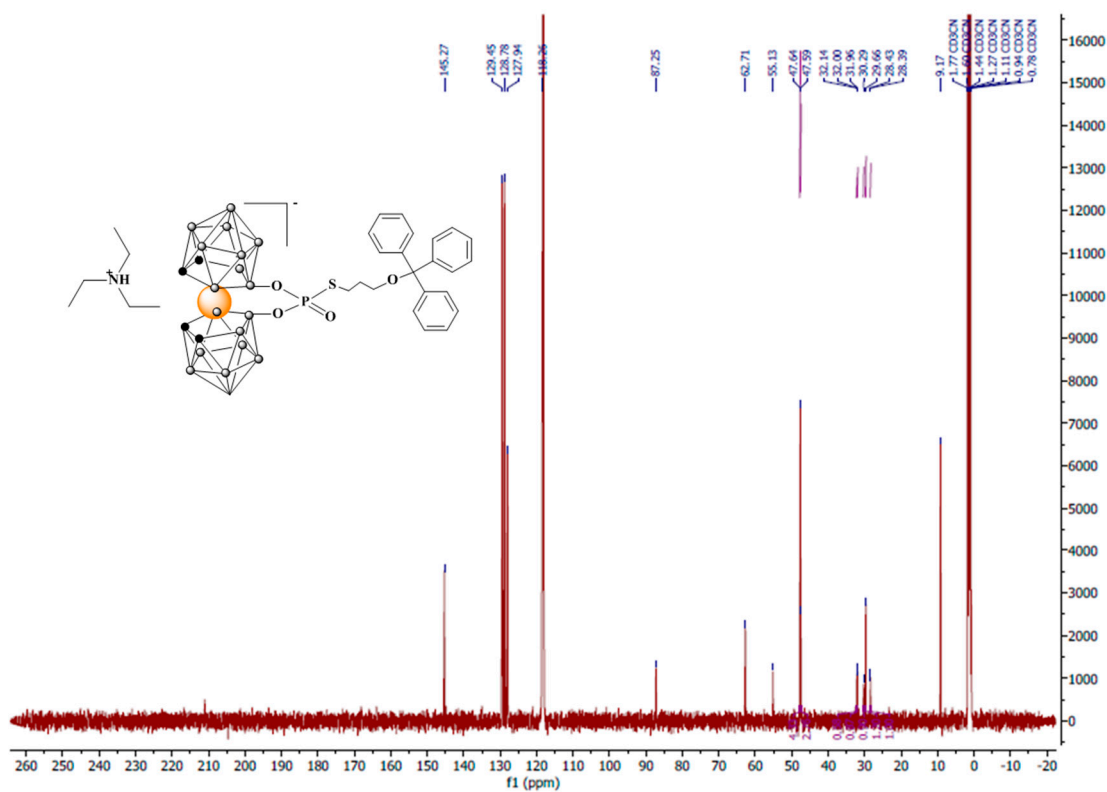
**Figure S53.** FT-IR spectrum of [8,8'-O<sub>2</sub>P(O)S(CH<sub>2</sub>)<sub>4</sub>OCPh<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> (**15**).



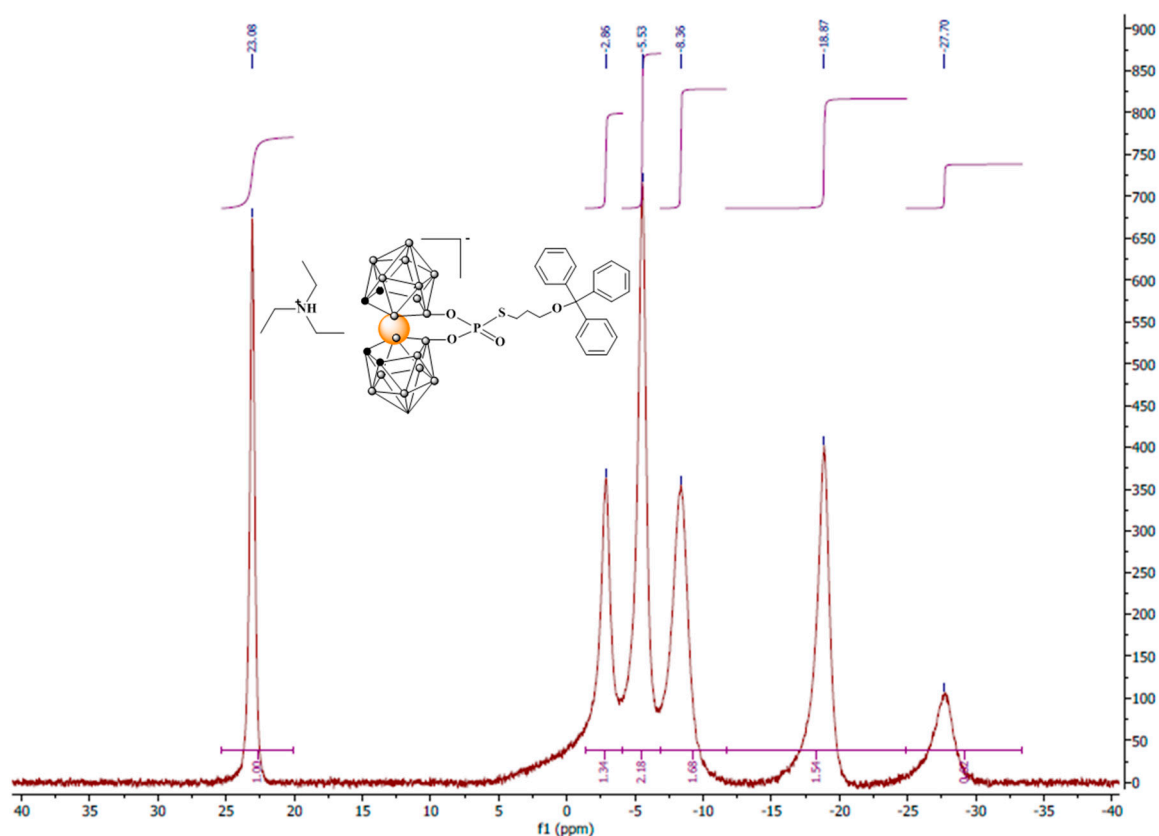
**Figure S54.** UV-VIS spectrum of [8,8'-O<sub>2</sub>P(O)S(CH<sub>2</sub>)<sub>4</sub>OCPh<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> (**15**).



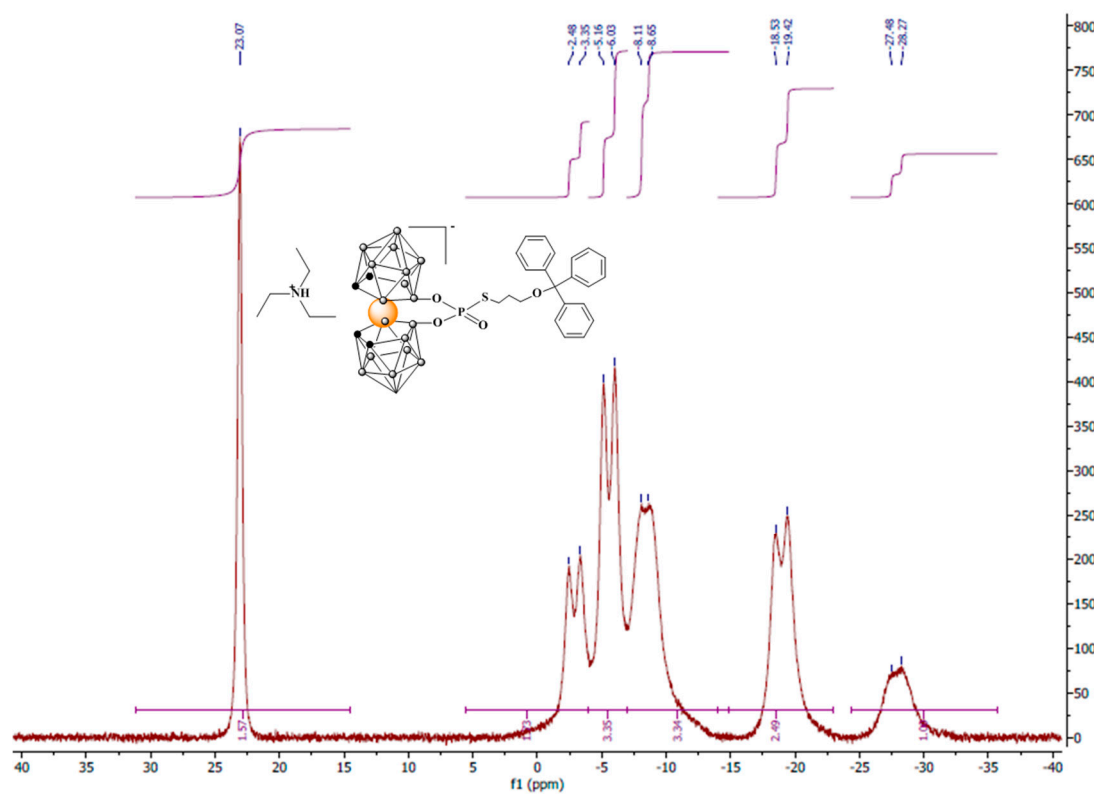
**Figure S55.**  $^1\text{H}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_3\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2] \text{HNEt}_3$  (16).



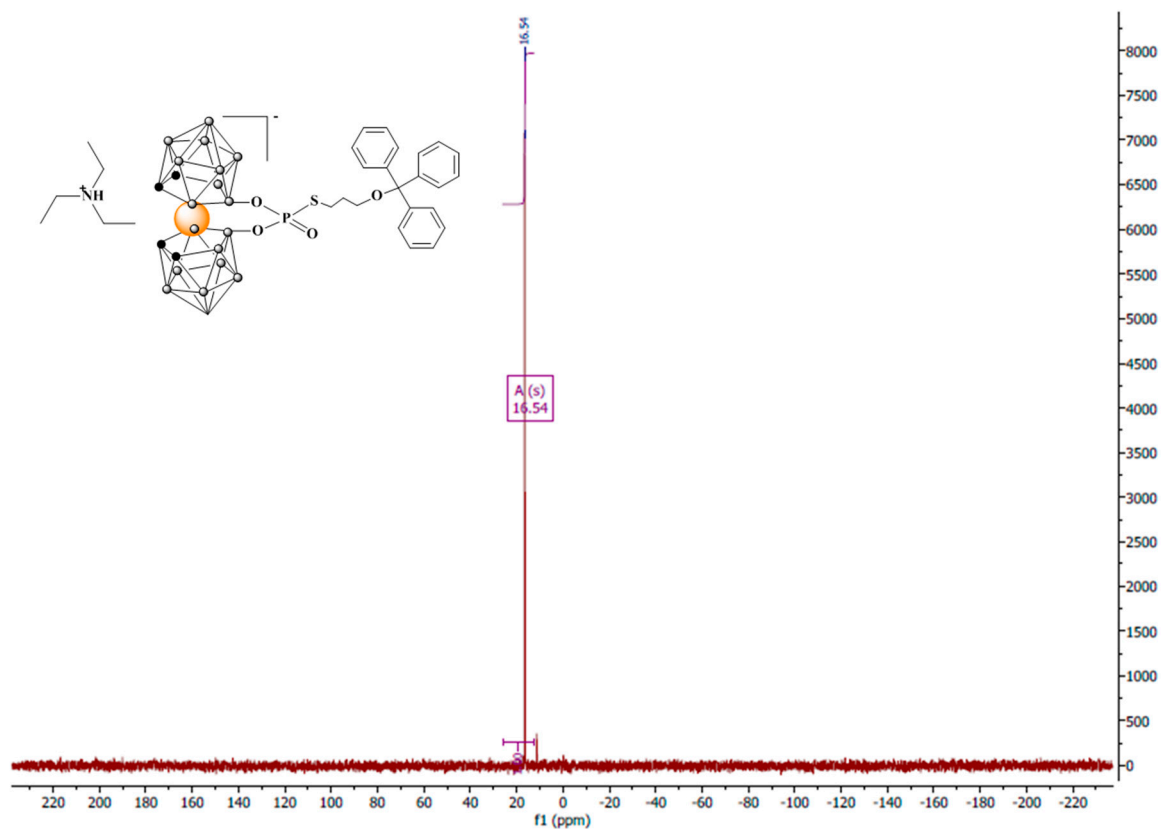
**Figure S56.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_3\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2] \text{HNEt}_3$  (16).



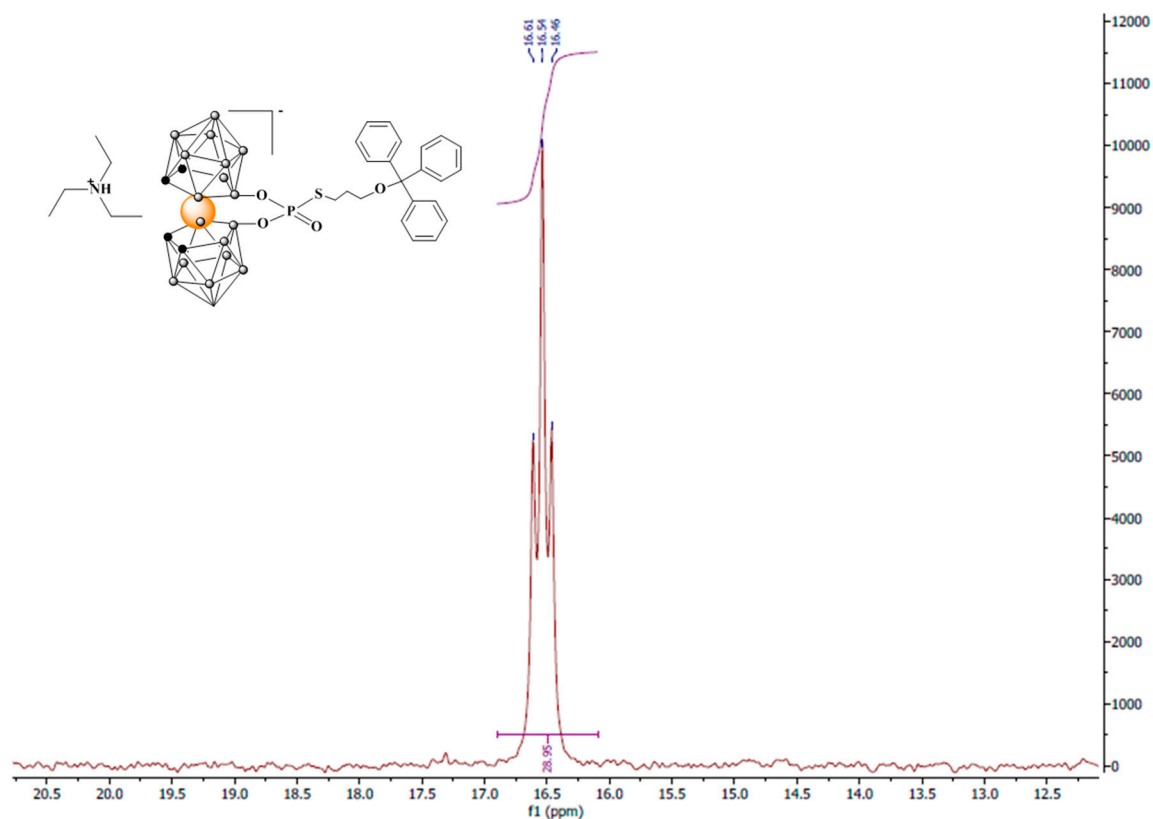
**Figure S57.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_3\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**16**).



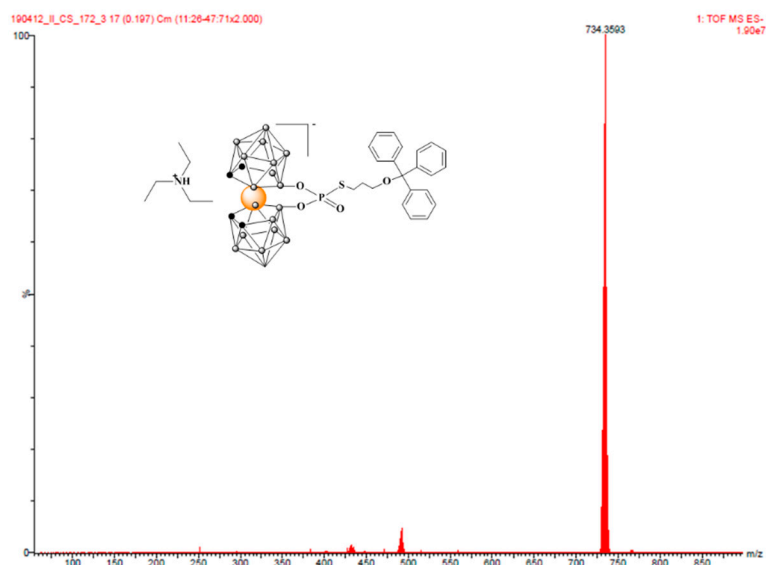
**Figure S58.**  $^{11}\text{B}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_3\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**16**).



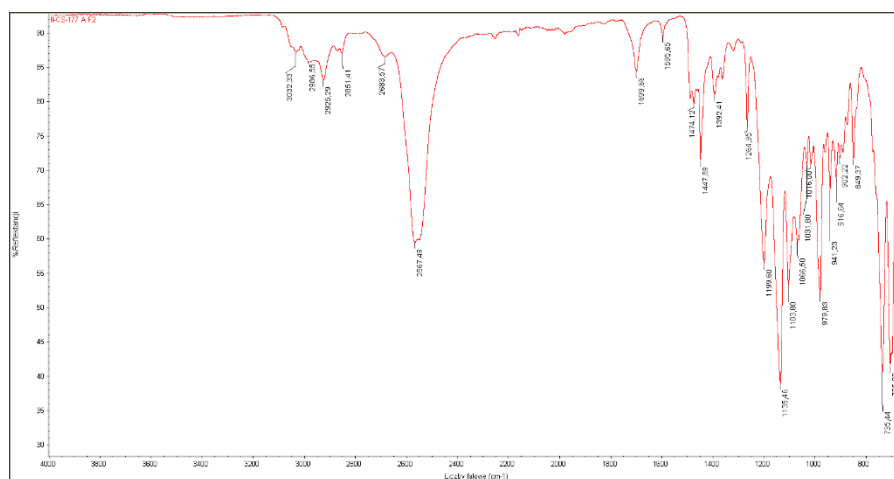
**Figure S59.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_3\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**16**).



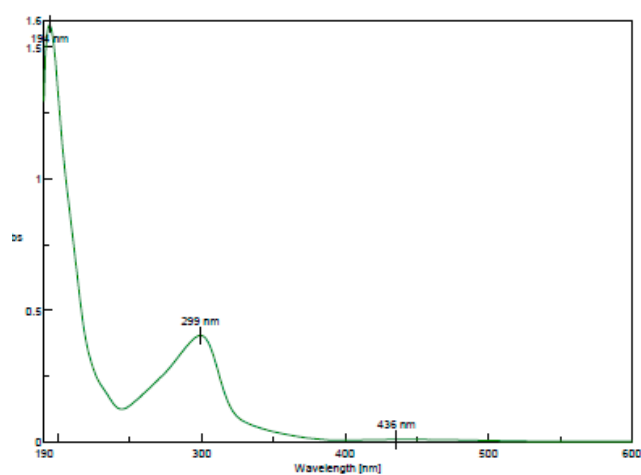
**Figure S60.**  $^{31}\text{P}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_3\text{OCPh}_3\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**16**).



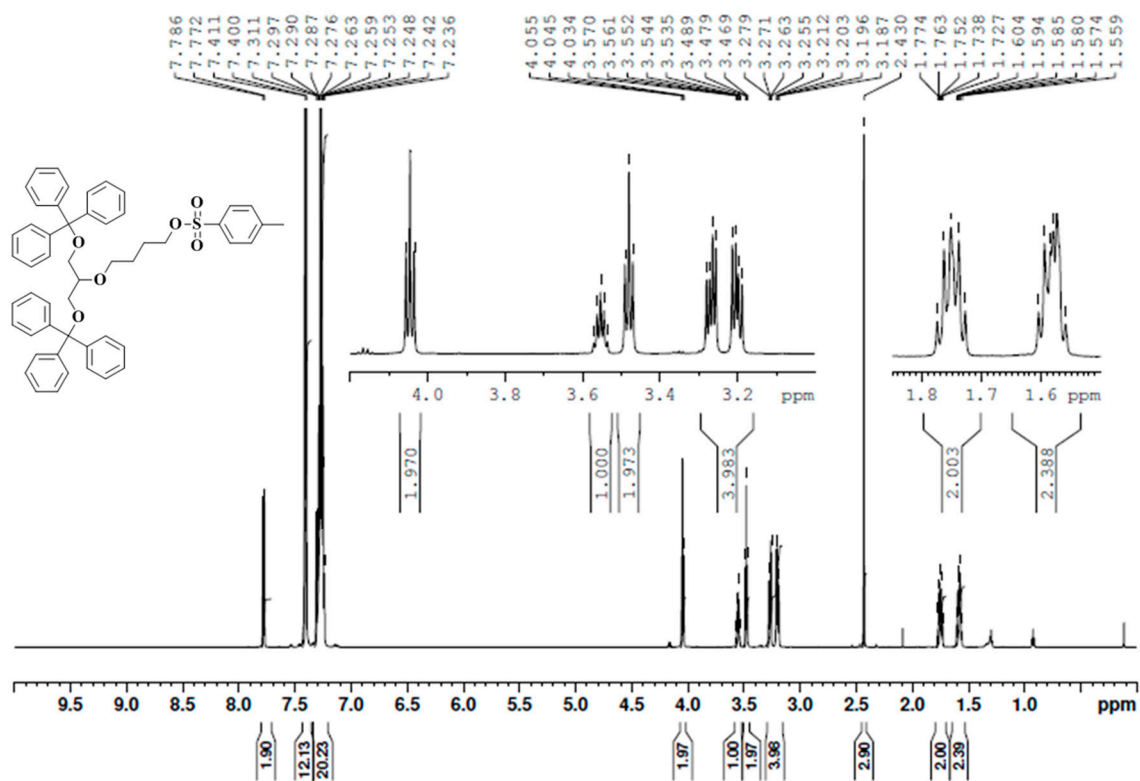
**Figure S61.** MS (ESI) spectrum of [8,8'-O<sub>2</sub>P(O)S(CH<sub>2</sub>)<sub>3</sub>OCPh<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> (**16**).



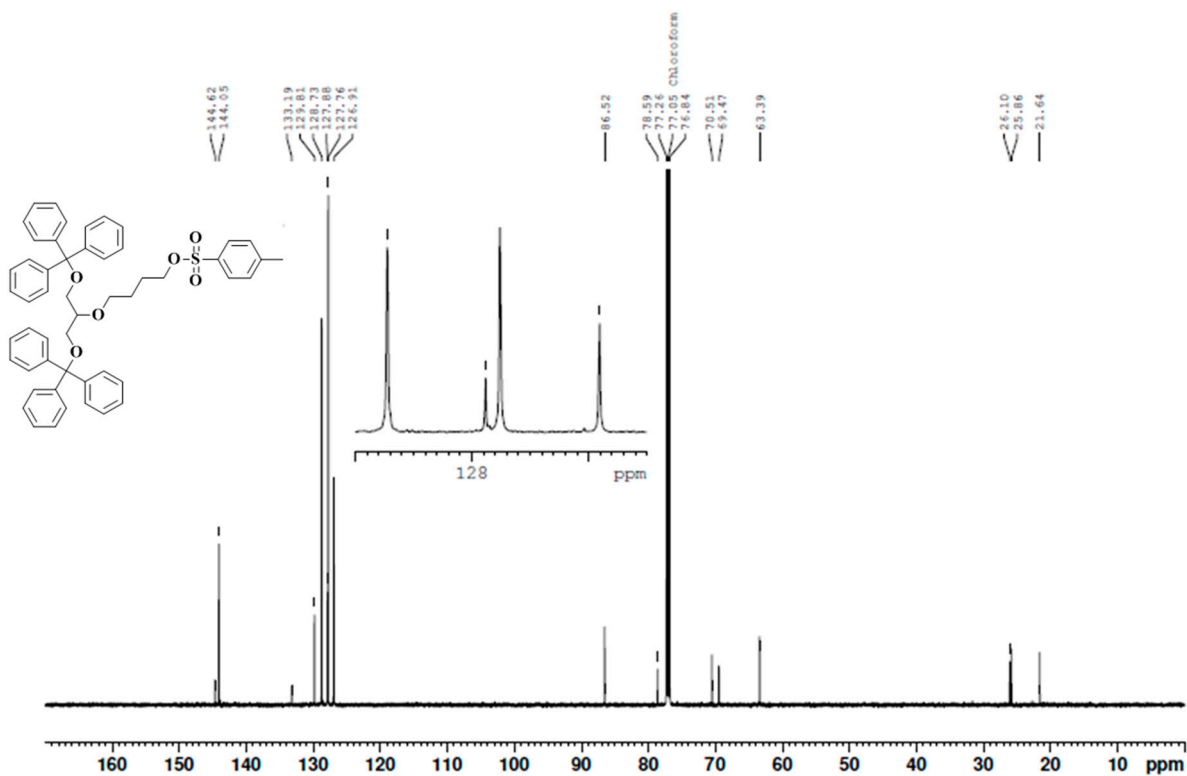
**Figure S62.** FT-IR spectrum of [8,8'-O<sub>2</sub>P(O)S(CH<sub>2</sub>)<sub>3</sub>OCPh<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> (**16**).



**Figure S63.** UV-VIS spectrum of [8,8'-O<sub>2</sub>P(O)S(CH<sub>2</sub>)<sub>3</sub>OCPh<sub>3</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] HNEt<sub>3</sub> (**16**).

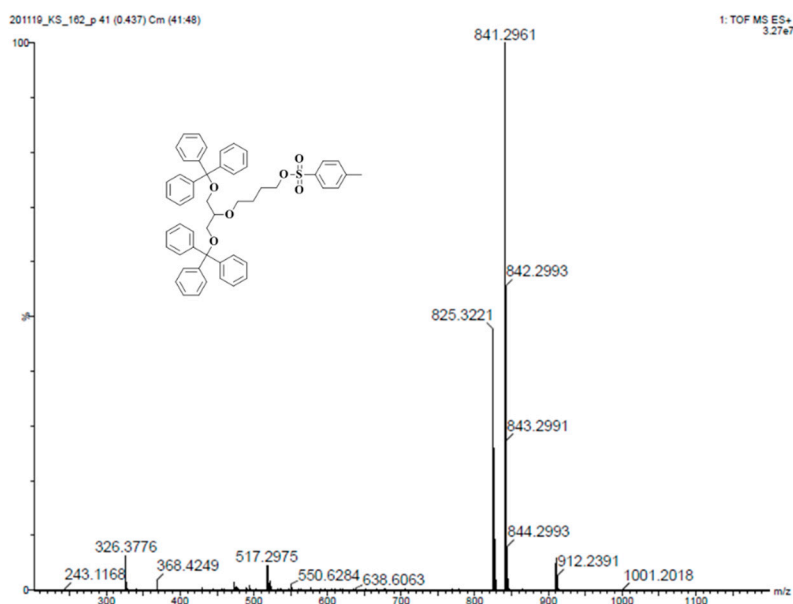


**Figure S64.**  $^1\text{H}$  NMR spectrum of 4-(1,3-bis(trityloxy)propan-2-yloxy)butyl 4-methylbenzenesulfonate (**20**).

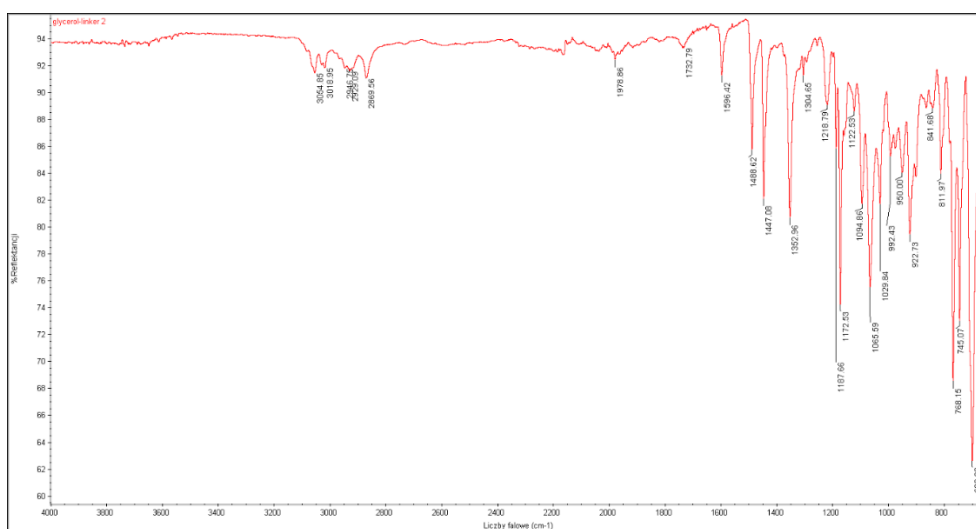


**Figure S65.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 4-(1,3-bis(trityloxy)propan-2-yloxy)butyl 4-methylbenzenesulfonate (**20**).

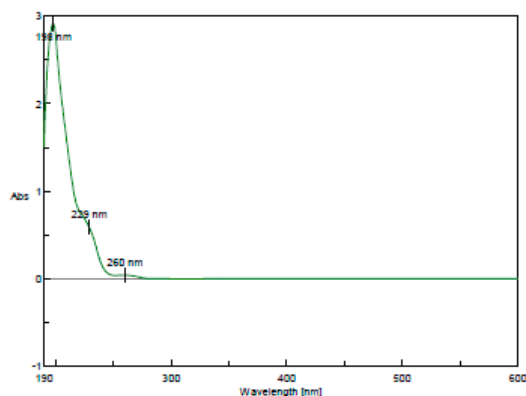




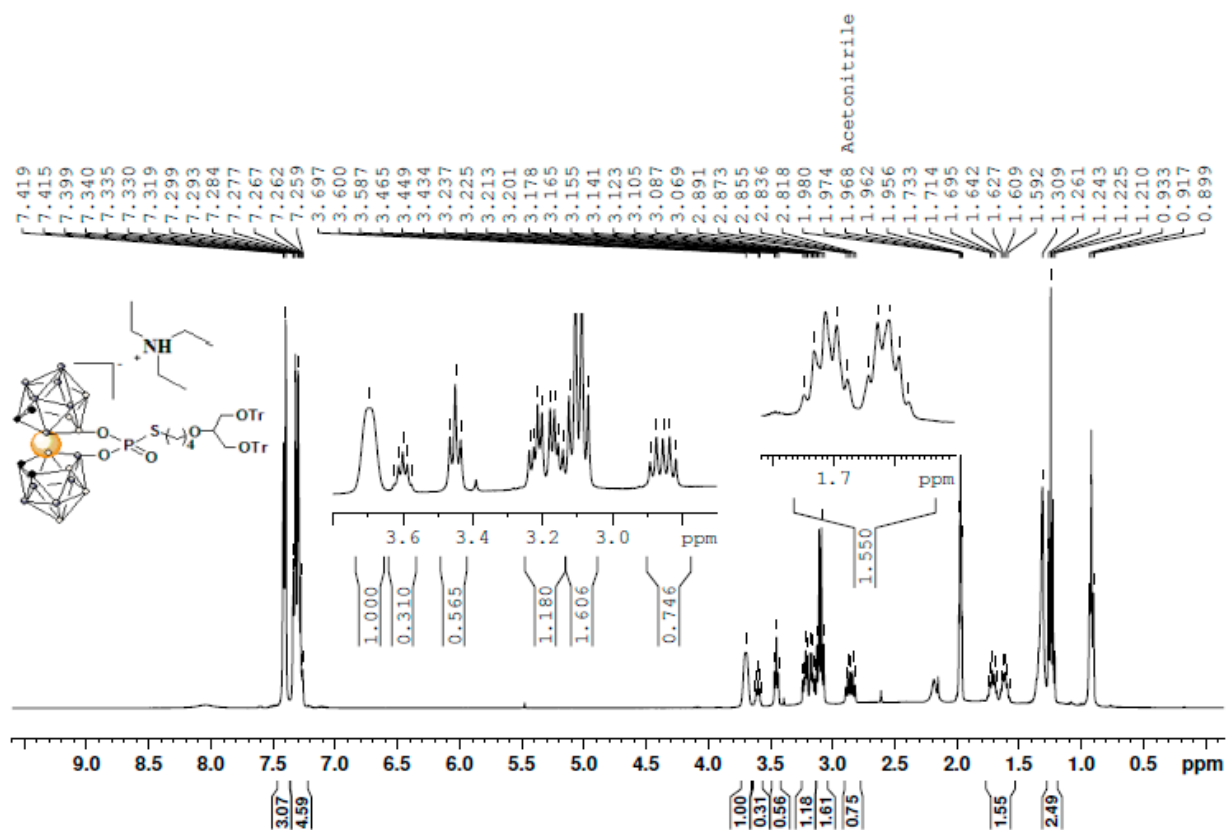
**Figure S66.** MS (ESI) spectrum of 4-(1,3-bis(trityloxy)propan-2-yloxy)butyl 4-methylbenzenesulfonate (**20**).



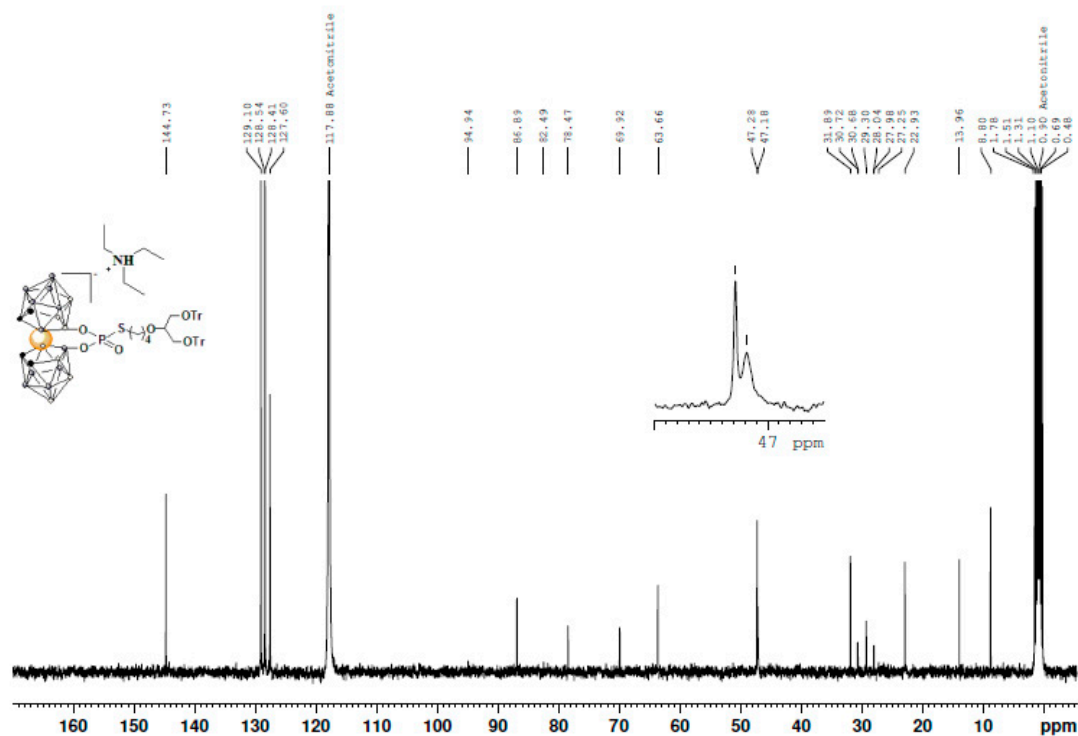
**Figure S67.** FT-IR spectrum of spectrum of 4-(1,3-bis(trityloxy)propan-2-yloxy)butyl 4-methylbenzenesulfonate (**20**).



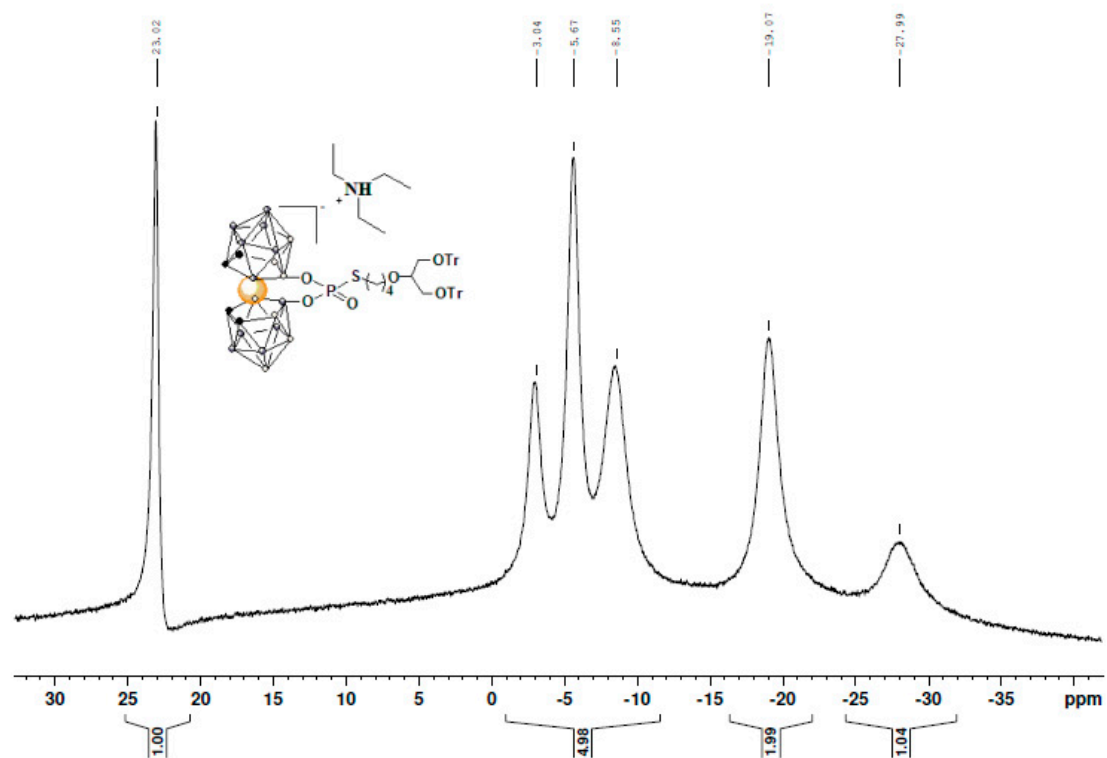
**Figure S68.** UV-VIS spectrum of 4-(1,3-bis(trityloxy)propan-2-yloxy)butyl 4-methylbenzenesulfonate (**20**).



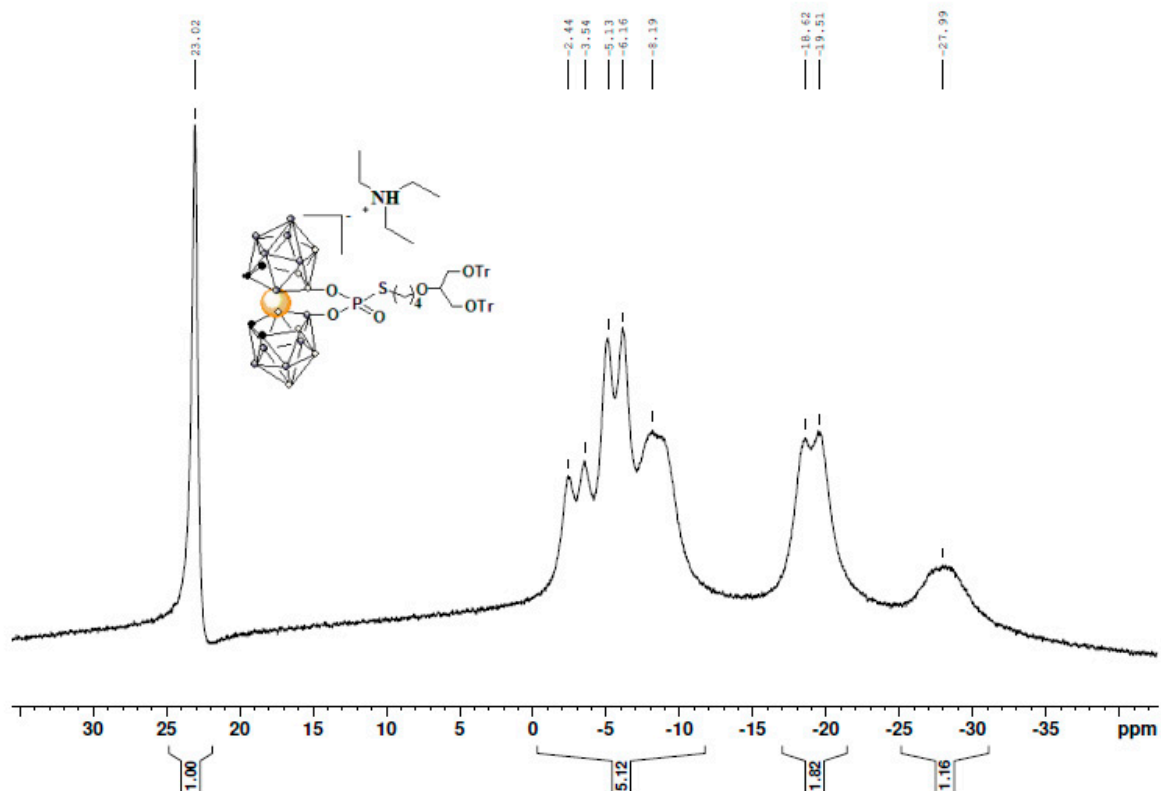
**Figure S69.**  $^1\text{H}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OTr})_2\text{-}3,3'\text{-Co}(\text{1,2-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**21**).



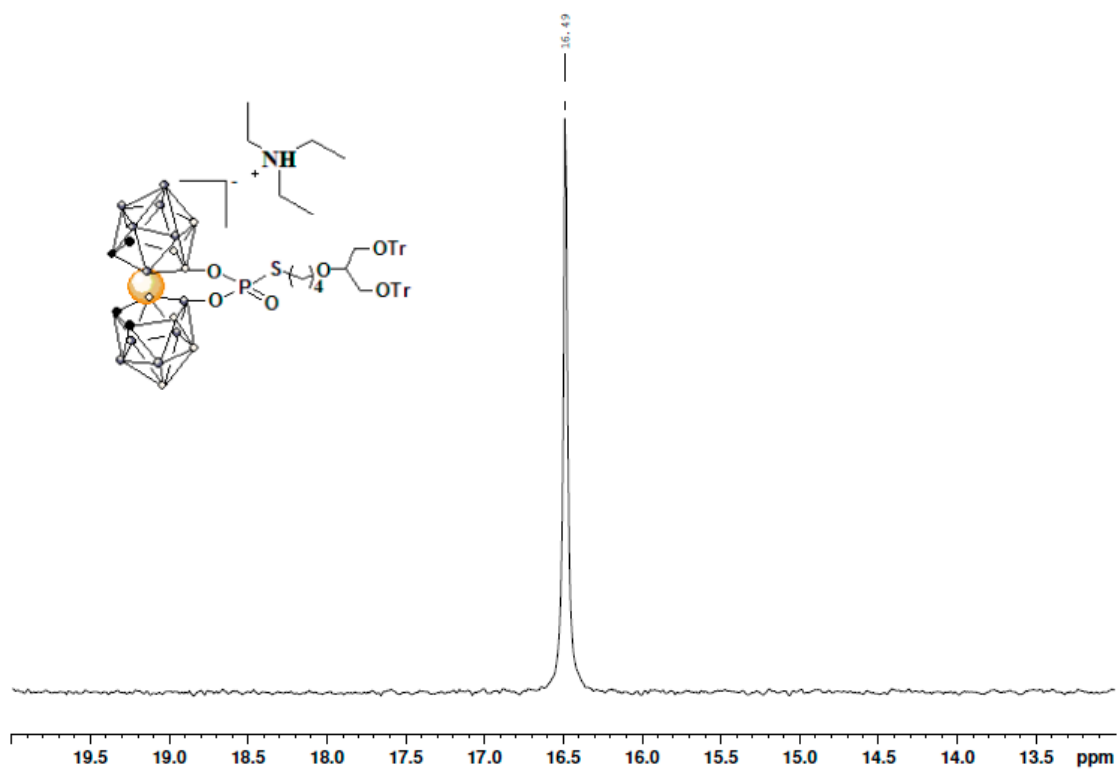
**Figure S70.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OTr})_2\text{-}3,3'\text{-Co}(\text{1,2-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**21**).



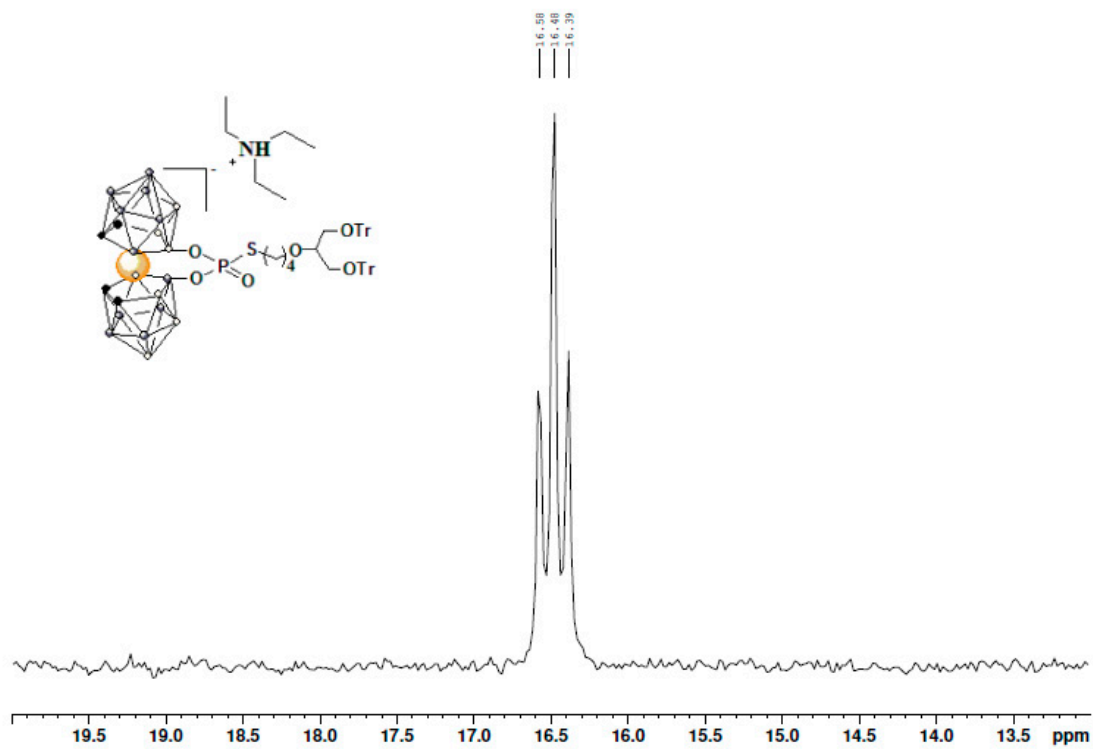
**Figure S71.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P(O)S(CH}_2)_4\text{OCH(CH}_2\text{OTr)}_2\text{-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2\text{]HNEt}_3$  (**21**).



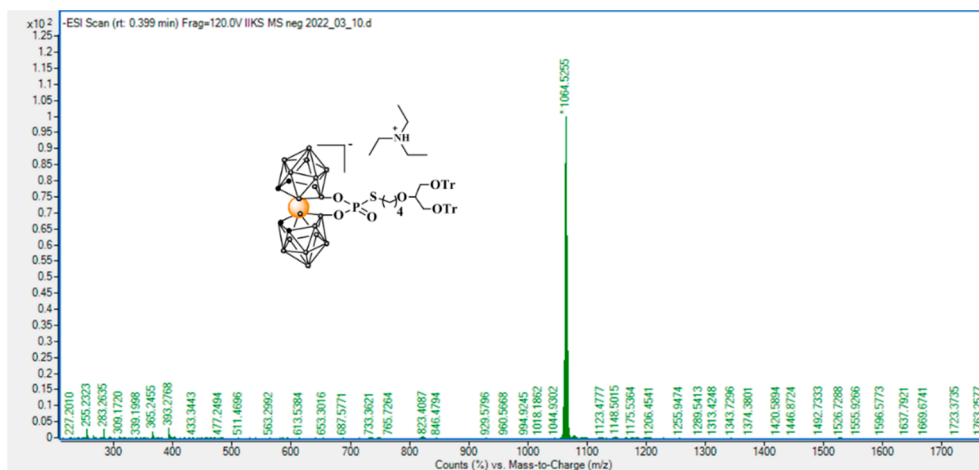
**Figure S72.**  $^{11}\text{B}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P(O)S(CH}_2)_4\text{OCH(CH}_2\text{OTr)}_2\text{-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2\text{]HNEt}_3$  (**21**).



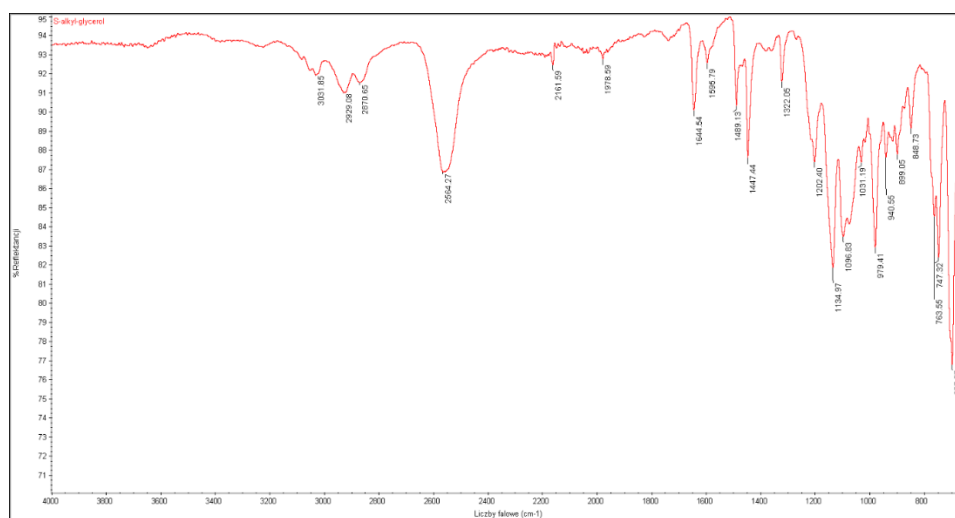
**Figure S73.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OTr})_2\text{-}3,3'\text{-Co}(\text{1,2-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**21**).



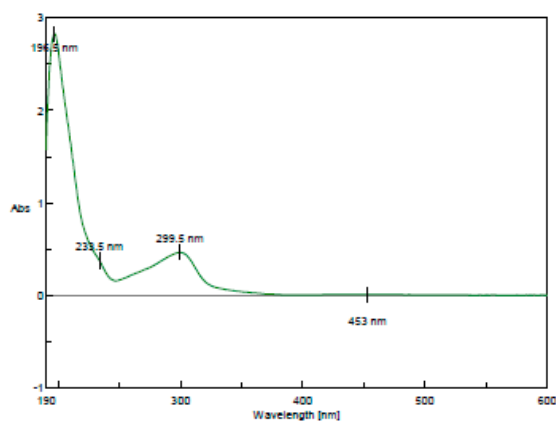
**Figure S74.**  $^{31}\text{P}$  NMR spectrum of  $[8,8'\text{-O}_2\text{P}(\text{O})\text{S}(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OTr})_2\text{-}3,3'\text{-Co}(\text{1,2-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**21**).



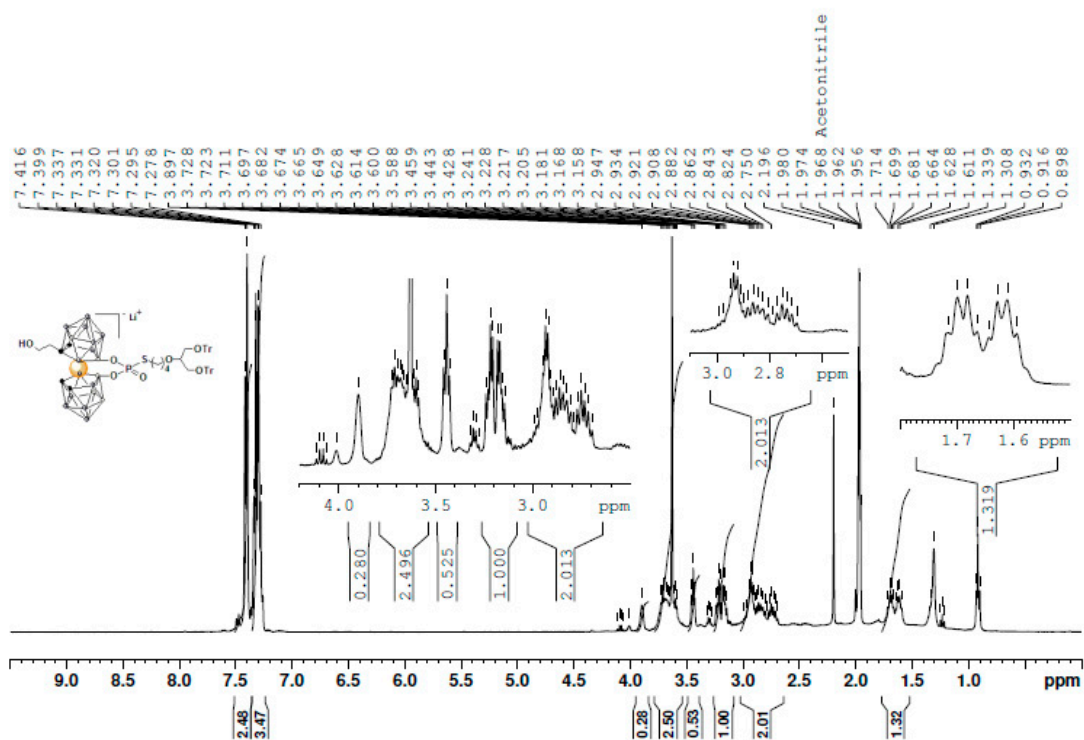
**Figure S75.** MS (ESI) spectrum of  $[8,8'\text{-O}_2\text{P(O)S(CH}_2)_4\text{OCH(CH}_2\text{OTr)}_2\text{-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**21**).



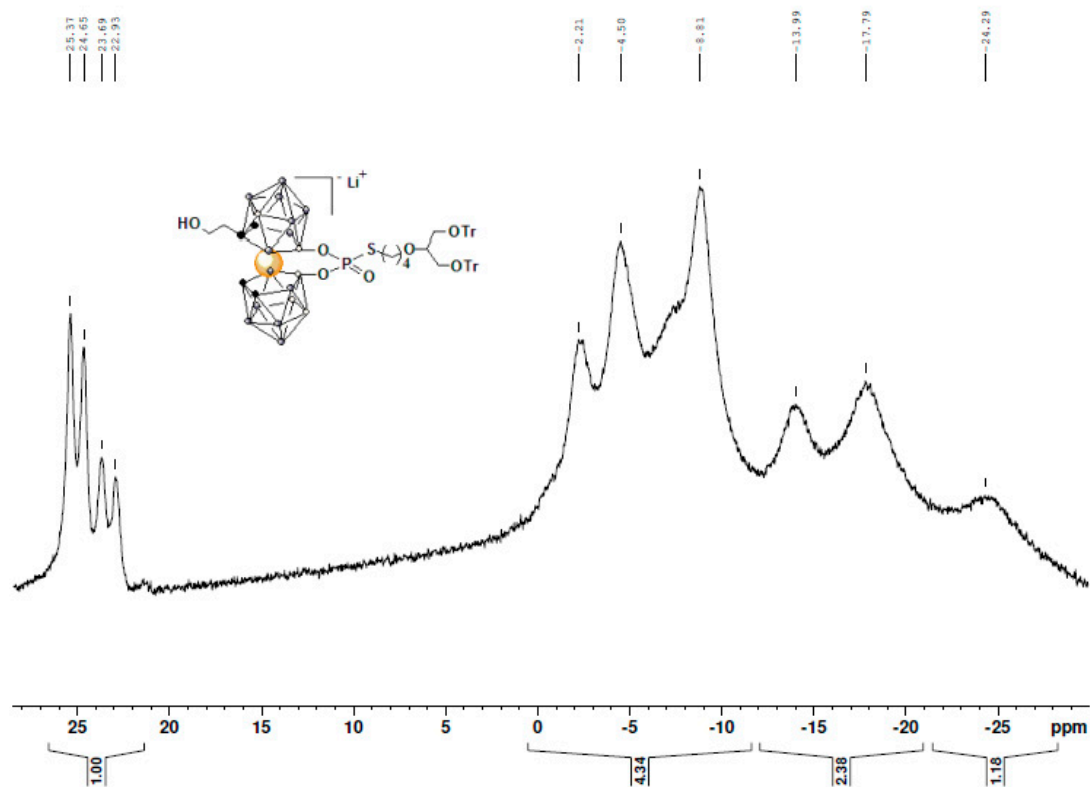
**Figure S76.** MS (ESI) spectrum of  $[8,8'\text{-O}_2\text{P(O)S(CH}_2)_4\text{OCH(CH}_2\text{OTr)}_2\text{-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**21**).



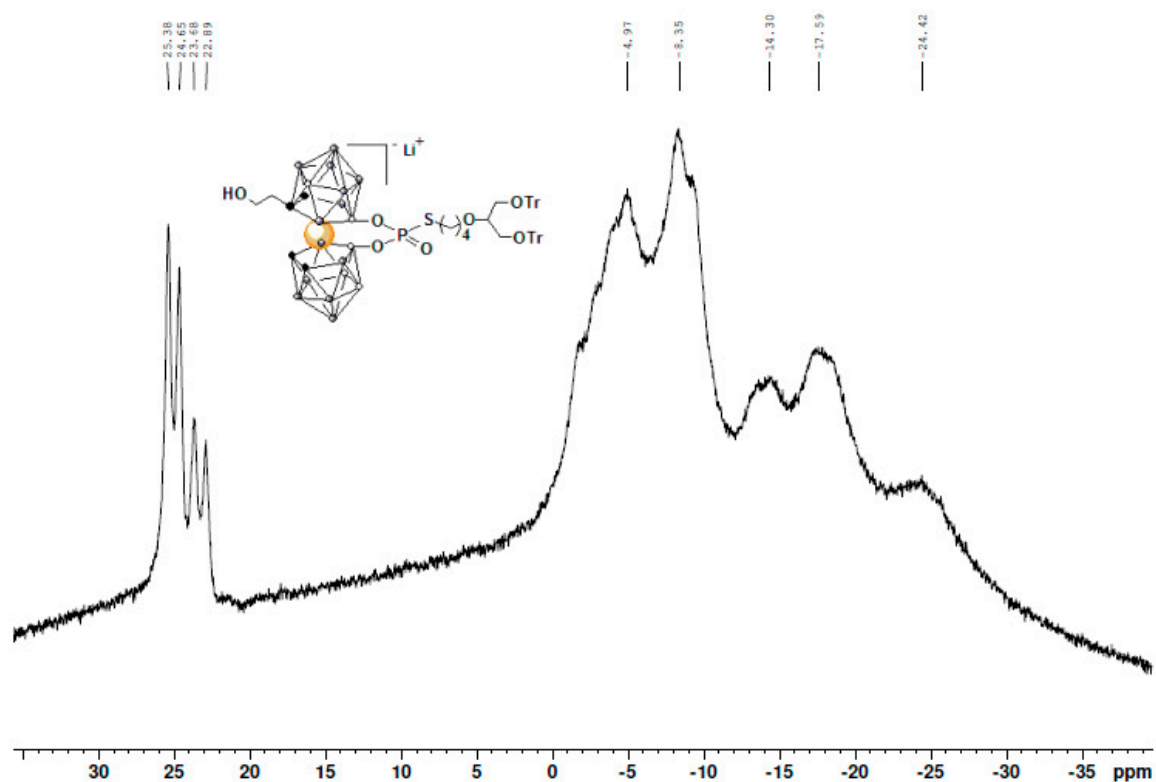
**Figure S77.** UV-VIS spectrum of spectrum of  $[8,8'\text{-O}_2\text{P(O)S(CH}_2)_4\text{OCH(CH}_2\text{OTr)}_2\text{-}3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]\text{HNEt}_3$  (**21**).



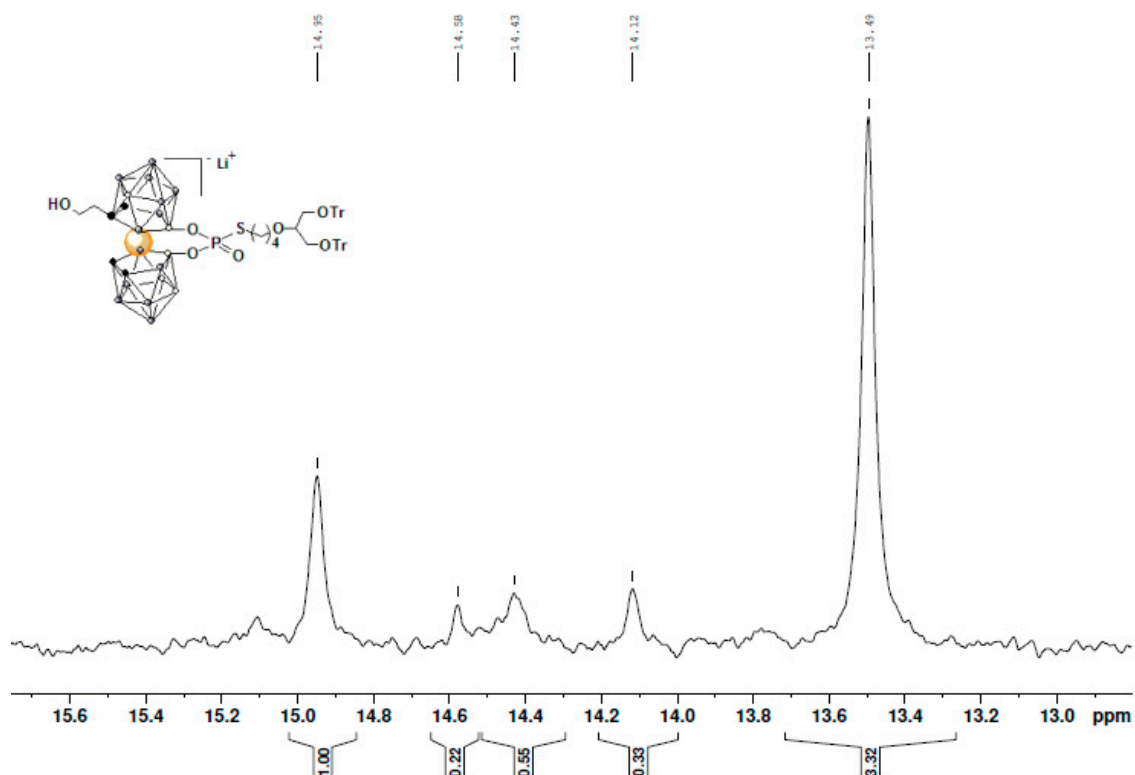
**Figure S78.** <sup>1</sup>H NMR spectrum of {8,8'-O<sub>2</sub>P(O)S[(CH<sub>2</sub>)<sub>4</sub>OCH(CH<sub>2</sub>OCPh<sub>3</sub>)<sub>2</sub>]-3,3'-Co[1-(CH<sub>2</sub>)<sub>2</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]}(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)} (**22**).



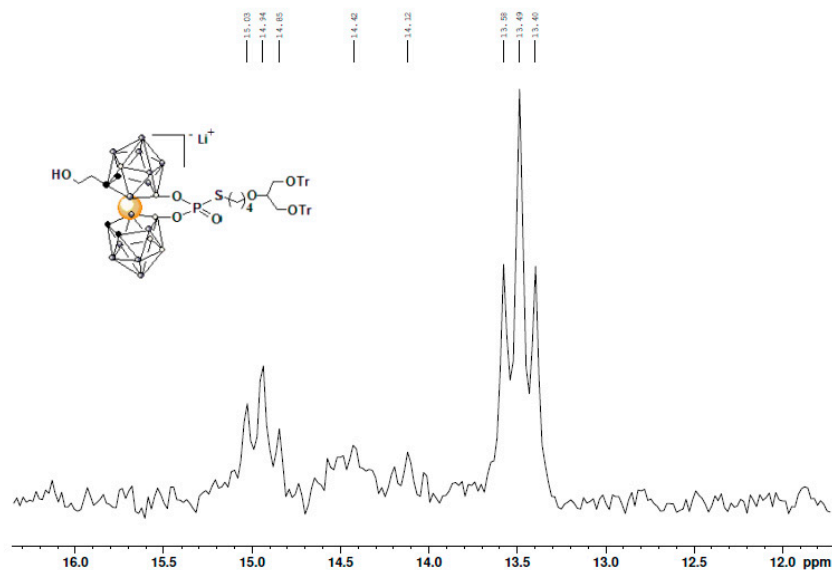
**Figure S79.** <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of {8,8'-O<sub>2</sub>P(O)S[(CH<sub>2</sub>)<sub>4</sub>OCH(CH<sub>2</sub>OCPh<sub>3</sub>)<sub>2</sub>]-3,3'-Co[1-(CH<sub>2</sub>)<sub>2</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]}(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)} (**22**).



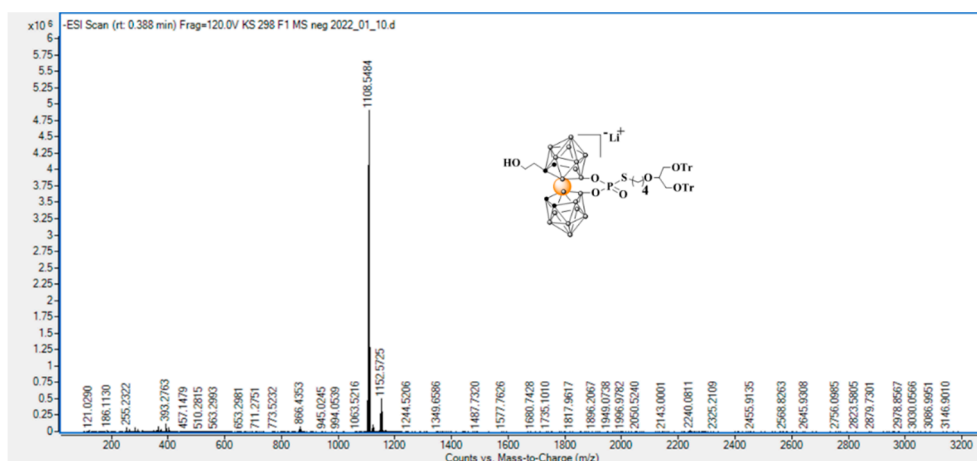
**Figure S80.**  $^{11}\text{B}$  NMR spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-}3,3'\text{-Co}[1\text{-(CH}_2)_2\text{OH-}1,2\text{-C}_2\text{B}_9\text{H}_{10}]\}(1',2'\text{-C}_2\text{B}_9\text{H}_{10})\}$  (**22**).



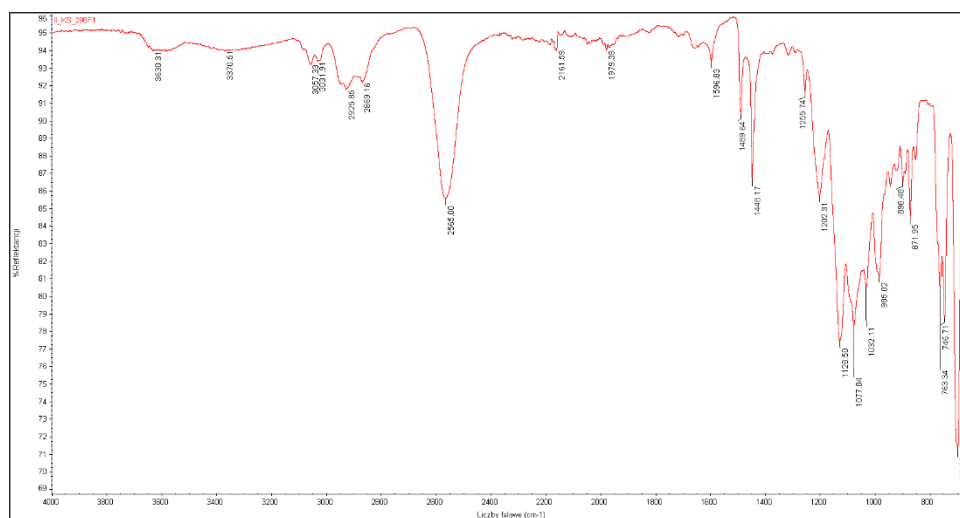
**Figure S81.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-}3,3'\text{-Co}[1\text{-(CH}_2)_2\text{OH-}1,2\text{-C}_2\text{B}_9\text{H}_{10}]\}(1',2'\text{-C}_2\text{B}_9\text{H}_{10})\}$  (**22**).



**Figure S82.**  $^{31}\text{P}$  NMR spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-3,3'-Co}[1\text{-(CH}_2)_2\text{OH-1,2-C}_2\text{B}_9\text{H}_{10}]\text{(1',2'-C}_2\text{B}_9\text{H}_{10})\}$  (**22**).

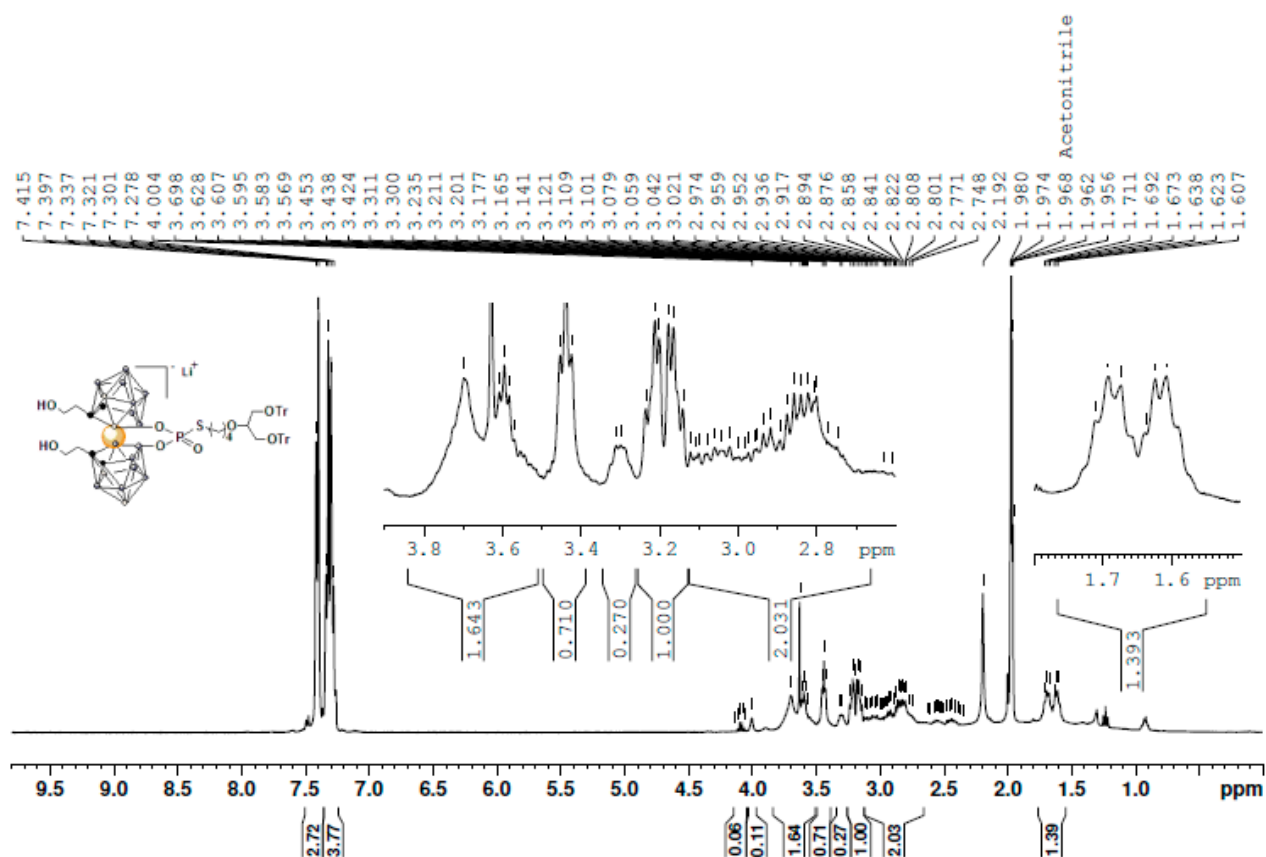


**Figure S83.** MS (ESI) spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-3,3'-Co}[1\text{-(CH}_2)_2\text{OH-1,2-C}_2\text{B}_9\text{H}_{10}]\text{(1',2'-C}_2\text{B}_9\text{H}_{10})\}$  (**22**).

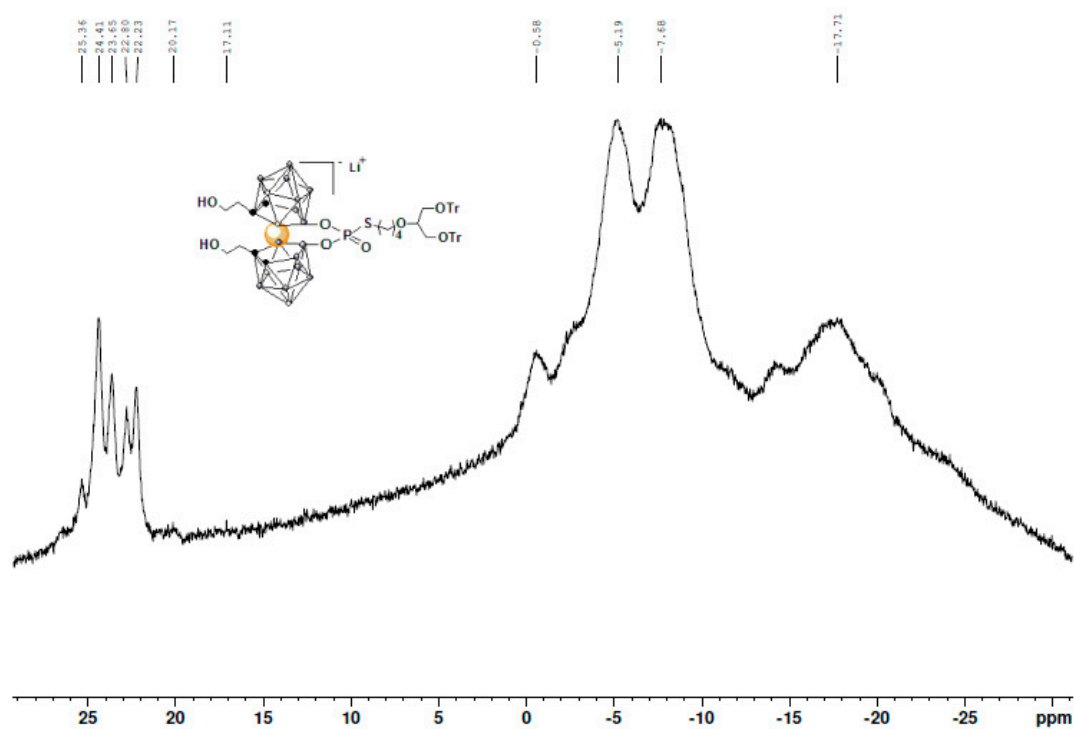


**Figure S84.** FT-IR spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-3,3'-Co}[1\text{-(CH}_2)_2\text{OH-1,2-C}_2\text{B}_9\text{H}_{10}]\text{(1',2'-C}_2\text{B}_9\text{H}_{10})\}$  (**22**).

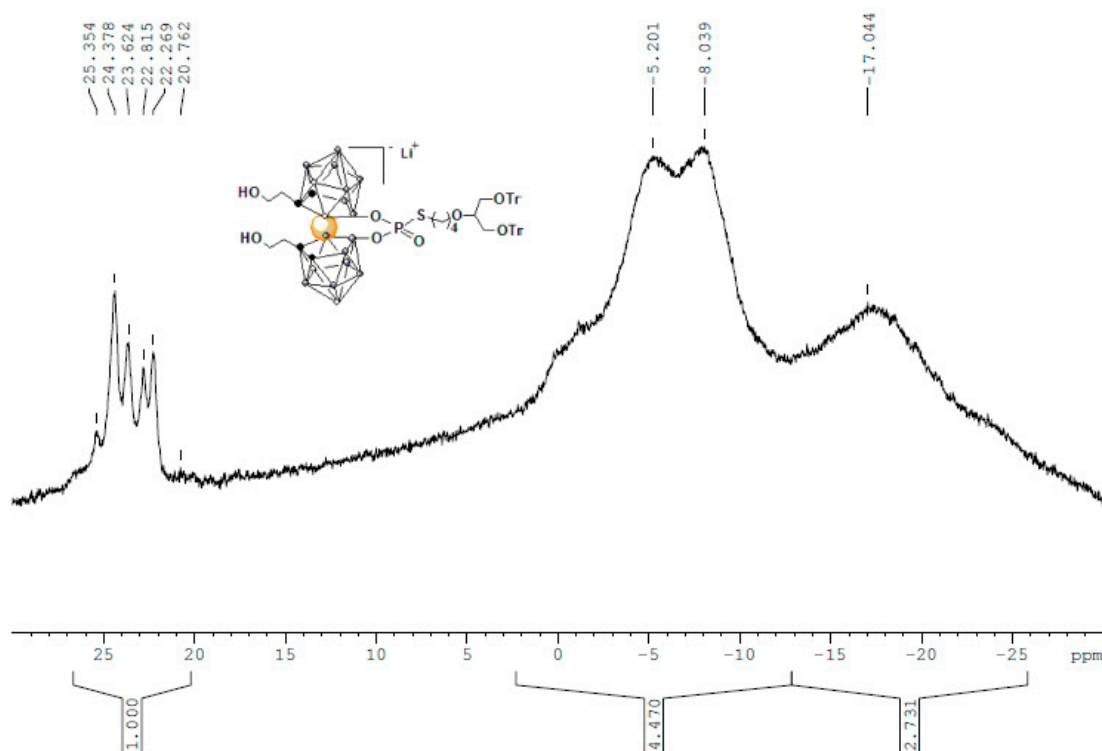




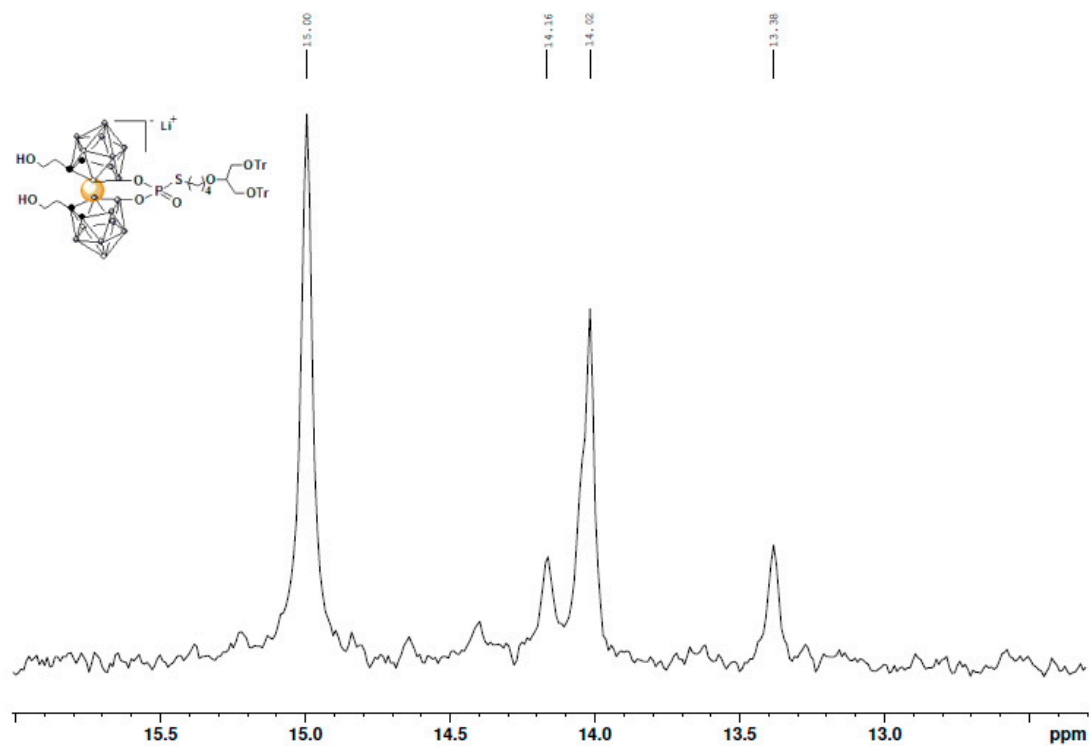
**Figure S85.** <sup>1</sup>H NMR spectrum of {8,8'-O<sub>2</sub>P(O)S[(CH<sub>2</sub>)<sub>4</sub>OCH(CH<sub>2</sub>OCPh<sub>3</sub>)<sub>2</sub>]-3,3'-Co[1-(CH<sub>2</sub>)<sub>2</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>][1'-(CH<sub>2</sub>)<sub>2</sub>OH-1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]} HNEt<sub>3</sub> (**23**).



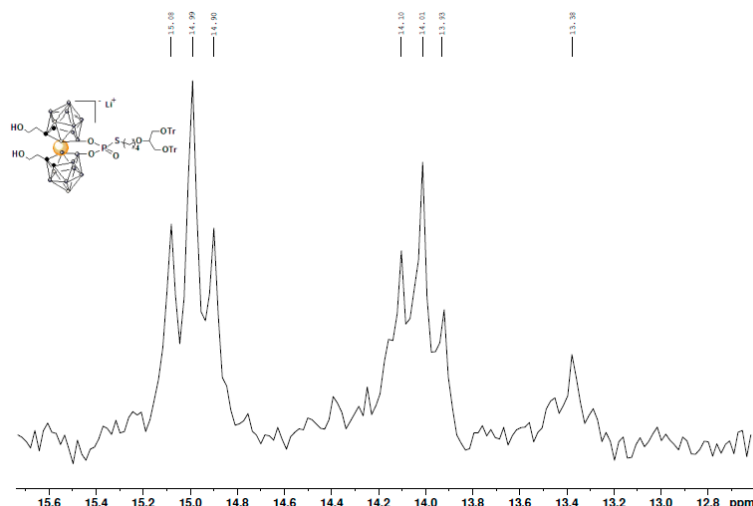
**Figure S86.** <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of {8,8'-O<sub>2</sub>P(O)S[(CH<sub>2</sub>)<sub>4</sub>OCH(CH<sub>2</sub>OCPh<sub>3</sub>)<sub>2</sub>]-3,3'-Co[1-(CH<sub>2</sub>)<sub>2</sub>OH-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>][1'-(CH<sub>2</sub>)<sub>2</sub>OH-1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]} HNEt<sub>3</sub> (**23**).



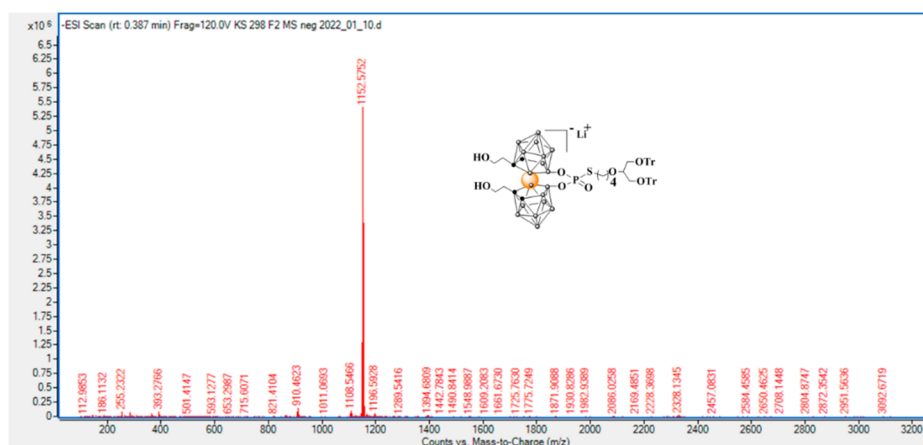
**Figure S87.**  $^{11}\text{B}$  NMR spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-}3,3'\text{-Co}[1\text{-(CH}_2)_2\text{OH-}1,2\text{-C}_2\text{B}_9\text{H}_{10}][1'\text{-(CH}_2)_2\text{OH-}1',2'\text{-C}_2\text{B}_9\text{H}_{10}]\}$   $\text{HNEt}_3$  (**23**).



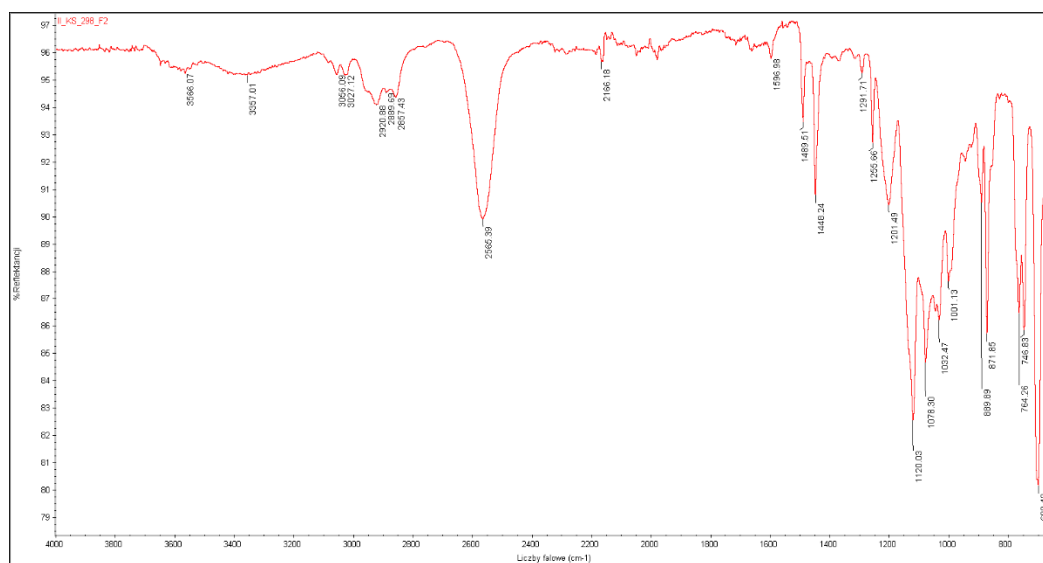
**Figure S88.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-}3,3'\text{-Co}[1\text{-(CH}_2)_2\text{OH-}1,2\text{-C}_2\text{B}_9\text{H}_{10}][1'\text{-(CH}_2)_2\text{OH-}1',2'\text{-C}_2\text{B}_9\text{H}_{10}]\}$   $\text{HNEt}_3$  (**23**).



**Figure S89.**  $^{31}\text{P}$  NMR spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-}3,3'\text{-Co}[1\text{-(CH}_2)_2\text{OH-}1,2\text{-C}_2\text{B}_9\text{H}_{10}]\text{ [}1'\text{-(CH}_2)_2\text{OH-}1',2'\text{-C}_2\text{B}_9\text{H}_{10}]\}$   $\text{HNEt}_3$  (**23**)



**Figure S90.** ESI (MS) spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-}3,3'\text{-Co}[1\text{-(CH}_2)_2\text{OH-}1,2\text{-C}_2\text{B}_9\text{H}_{10}]\text{ [}1'\text{-(CH}_2)_2\text{OH-}1',2'\text{-C}_2\text{B}_9\text{H}_{10}]\}$   $\text{HNEt}_3$  (**23**).



**Figure S91.** FT-IR spectrum of  $\{8,8'\text{-O}_2\text{P}(\text{O})\text{S}[(\text{CH}_2)_4\text{OCH}(\text{CH}_2\text{OCPh}_3)_2]\text{-}3,3'\text{-Co}[1\text{-(CH}_2)_2\text{OH-}1,2\text{-C}_2\text{B}_9\text{H}_{10}]\text{ [}1'\text{-(CH}_2)_2\text{OH-}1',2'\text{-C}_2\text{B}_9\text{H}_{10}]\}$   $\text{HNEt}_3$  (**23**).