Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Lewis Acid Base Chemistry of Bestmann's Ylide, Ph_3PCCO, and its Bulkier Analogue, $(Cyclohexyl)_3PCCO$

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1. General Remarks

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk or cannula techniques or in a Vacuum Atmospheres OMNI inert atmosphere dry box containing an atmosphere of purified nitrogen. Toluene and hexanes were distilled under nitrogen from alkali metals and stored over 4 Å molecular sieves prior. Acetonitrile was stored over 4 Å molecular sieves prior to use. All deuterated solvents were purchased from Cambridge Isotope Labs. C_6D_6, C_7D_8, CD_2Cl_2 and $CDCl_3$ were dried and stored over 4 Å molecular sieves prior to use. $NaN(SiMe_3)_2$ (Alfa Aesar), Ph_3CBF_4 (Alfa Aesar), Ph_3CBr (Alfa Aesar) and $AlMe_3$ (Acros, 1M solution in heptane) were purchased form commercial sources and used without further purification. Ph_3PCCO [1], $B(C_6F_5)_3$ [2] and $Al(C_6F_5)_3$ [3] were synthesized according to the literature procedure and stored in the glove box. The ^{1}H-, ^{13}C-, ^{11}B- ^{19}F-, and ^{31}P-NMR spectra were obtained from a JOEL ECS 400 and Varian 500. All measurements, unless noted otherwise, were carried out at 298 K and NMR chemical shifts were given in ppm. The ^{11}B NMR spectra referenced to H_3BO_3 in D_2O (δ = 36 ppm), the ^{31}P NMR referenced to H_3PO_4 in D_2O (δ = 0 ppm), ^{19}F NMR spectrum was referenced to $C_6H_5CF_3$ in C_6D_6 (δ = 62.3 ppm), The ^{1}H-NMR spectra were referenced to the residual protonated solvent for ^{1}H and the ^{13}C-NMR spectra were referenced to the deuterated solvent peaks. The following abbreviations were used to describe peak multiplicities in the reported NMR spectroscopic data: “s” for singlet, “d” for doublet, “t” for triplet, “q” for quartet, “m” for multiplet and “br” for broadened resonances. The Raman spectra were recorded on a Bruker Optics Senterra dispersive Raman microscope spectrometer with a spectral resolution of 3-5 cm^{-1} using 785 nm laser excitation. Elemental analyses were performed using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

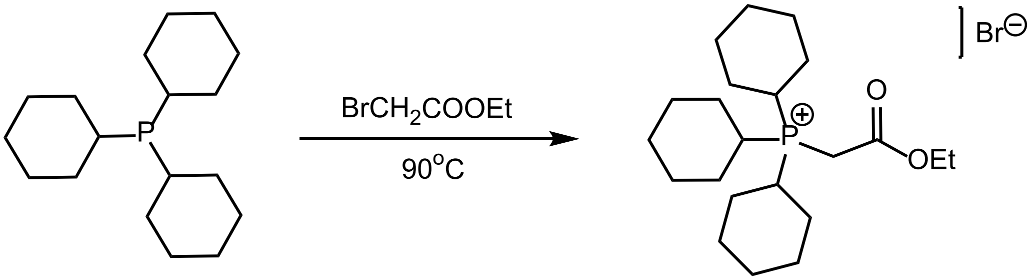
[1] R. Schobert, *Organic Syntheses*, **2005**, *82*, 140.

[2] S. Lancaster, *ChemSpider SyntheticPages*, **2003**, doi:10.1039/SP215.

[3] S. P. Lewis, US 75885991 B2, **2008**.

2. Synthetic Procedures

2.1 [(Cyclohexyl)$_3$PCH$_2$COOEt]Br



A 50 ml Schlenk flask equipped with a magnetic stir bar was charged with tricyclohexylphosphine (2 g, 7.13 mmol) under nitrogen atmosphere. To this solution, bromoethyl acetate (0.82 ml, 7.13 mmol) was slowly added with stirring. Afterwards, the reaction mixture was heated for ca. one hour at 90°C. After cooling to room temperature, ca. 20 mL of hexanes were added and the resulting white suspension was centrifuged (Note: filtration is also possible but should be done under nitrogen or quickly on the bench without nitrogen as the product is hygroscopic). The solid was washed twice with hexanes, centrifuged and dried under vacuum to give 3.0 g (96%) of the title compound. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.27 (t, $^3J_{H\text{-}H}$ = 8 Hz, CH$_3$, 3 H), 1.29-1.30 (m, cyclohexyl, 6 H), 1.38-1.57 (m, cyclohexyl, 13 H), 1.76-1.79 (m, cyclohexyl, 3 H), 1.89-1.92 (m, cyclohexyl, 5 H), 2.04-2.06 (m, cyclohexyl, 6 H), 2.83 (m, cyclohexyl, 3 H), 4.00 (d, $^2J_{P\text{-}H}$ = 12 Hz, PCH$_2$, 2 H), 4.19 (q, $^3J_{H\text{-}H}$ = 8 Hz, OCH$_2$, 2 H) ppm. ^{13}C{H} NMR (CDCl$_3$, 100.6 MHz): 14.3 (CH$_3$), 23.4 (d, $^1J_{P\text{-}C}$ = 45.3 Hz, PCH$_2$), 25.7 (CH$_2$), 26.7 (d, $^2J_{P\text{-}C}$ = 12.1 Hz, CH$_2$), 27.4 (d, $^3J_{P\text{-}C}$ = 4.0 Hz, CH$_2$), 30.8 (d, $^1J_{P\text{-}C}$ = 39 Hz, CH), 63.1 (OCH$_2$), 166.1 (d, $^3J_{P\text{-}C}$ = 3 Hz, CO) ppm. ^{31}P NMR [CDCl$_3$, 161.9 MHz]: δ 33.7 ppm. Anal. Calc. for $C_{22}H_{40}BrO_2P$ (447.438): C, 59.06; H, 9.01; Found C, 57.67; H, 9.07.

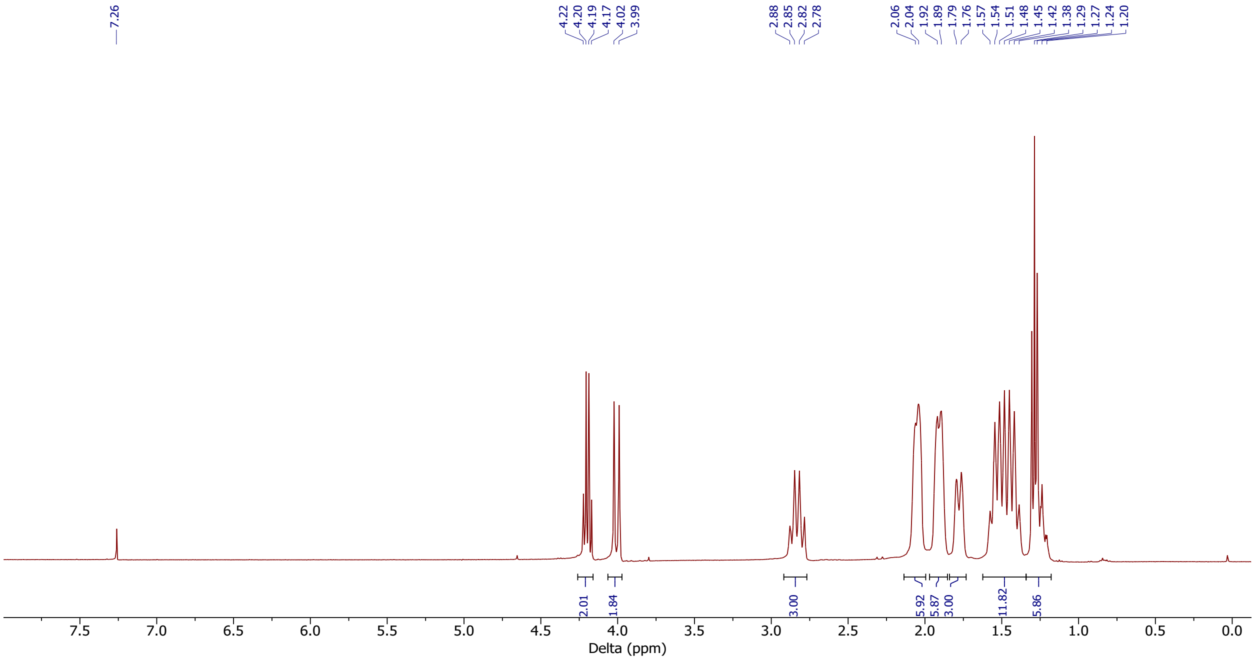


Figure S1.^{1}H NMR spectrum of [(cyclohexyl)$_3$PCH$_2$COOEt]Br in CDCl$_3$.

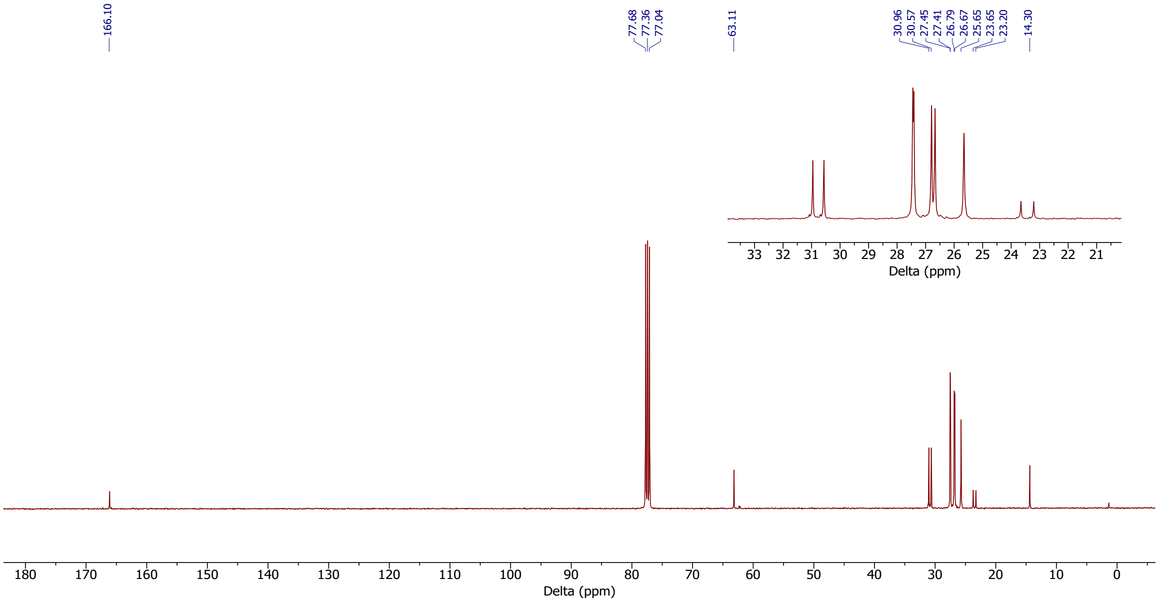


Figure S2.^{13}C NMR spectrum of [(cyclohexyl)$_3$PCH$_2$COOEt]Br in CDCl$_3$.

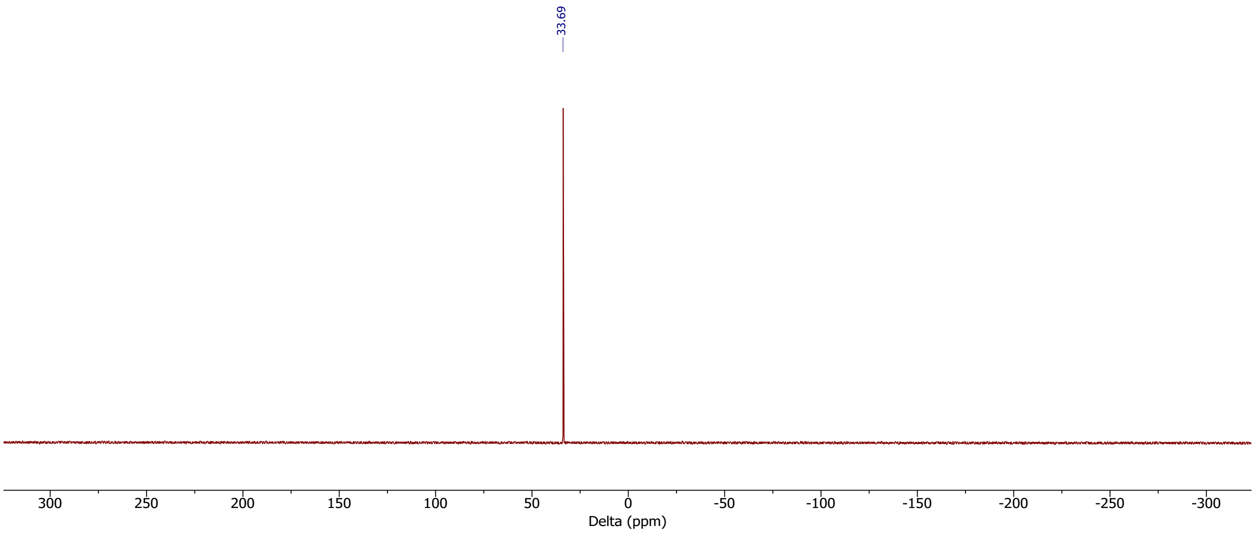
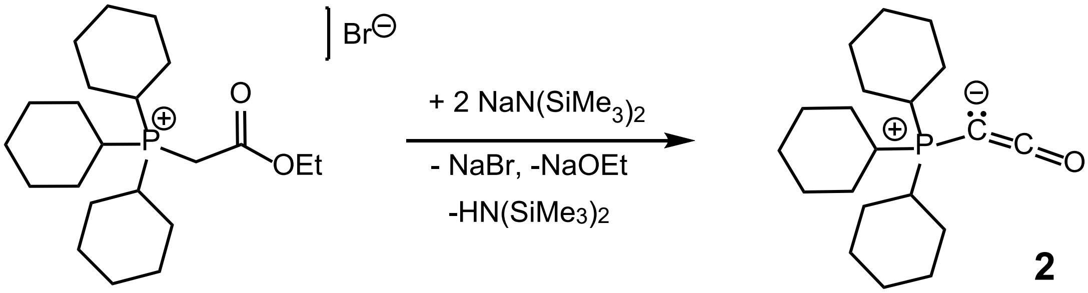


Figure S3. ^{31}P NMR spectrum of [(cyclohexyl)$_3$PCH$_2$COOEt]Br in CDCl$_3$.

2.2 (Cyclohexyl)$_3$PCCO (**2**)



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In the glove box, a 50 mL Schlenk flask equipped with a magnetic stir bar was charged with [(cyclohexyl)$_3$PCH$_2$COOEt]Br (2 g, 4.47 mmol) and 20 ml of dry toluene. Then sodium bis(trimethylsilyl)amide (1.64 g, 8.95 mmol) was added portion wise with stirring. Then the flask was taken from the glove box, attached to the Schlenk line and heated at 90ºC for 3 hours. After cooling to room temperature, the resulting suspension was centrifuged and the solution was decanted off. The precipitate was washed twice with toluene, centrifuged and all washings were combined. Then all the solvent was removed under vacuum and the remaining solid was dried under vacuum (ca. 8-10 hrs.) until hexamethyldisilazane [HN(SiMe$_3$)$_2$] was fully removed. Subsequently, the crude product was recrystallized from toluene to give 990 mg (70%) of analytically pure **2**. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 0.95-1.02 (b, cyclohexyl, 9 H), 1.23-1.26 (m, cyclohexyl, 6 H), 1.48 (b, cyclohexyl, 3 H), 1.56-1.65 (m, cyclohexyl, 9 H), 1.74-1.77 (m, cyclohexyl, 6 H) ppm. ^{13}C{H} NMR (C$_6$D$_6$, 100.6 MHz): 26.7 (CH$_2$), 27.6 (d, $^2J_{P\text{-}C}$ = 13 Hz, CH$_2$), 27.9 (d, $^3J_{P\text{-}C}$ = 3.02 Hz, CH$_2$), 35.6 (d, $^1J_{P\text{-}C}$ = 57 Hz, CH), -17.5 (d, $^1J_{P\text{-}C}$ = 177 Hz, P=C), 145.5 (d, $^2J_{P\text{-}C}$ = 39 Hz, CO) ppm. ^{31}P NMR [C$_6$D$_6$, 161.9 MHz]: δ 20.5 ppm. Anal. Calc. for C$_{20}$H$_{33}$OP (320.457): C, 74.96; H, 10.38; Found C, 72.66; H, 10.49.

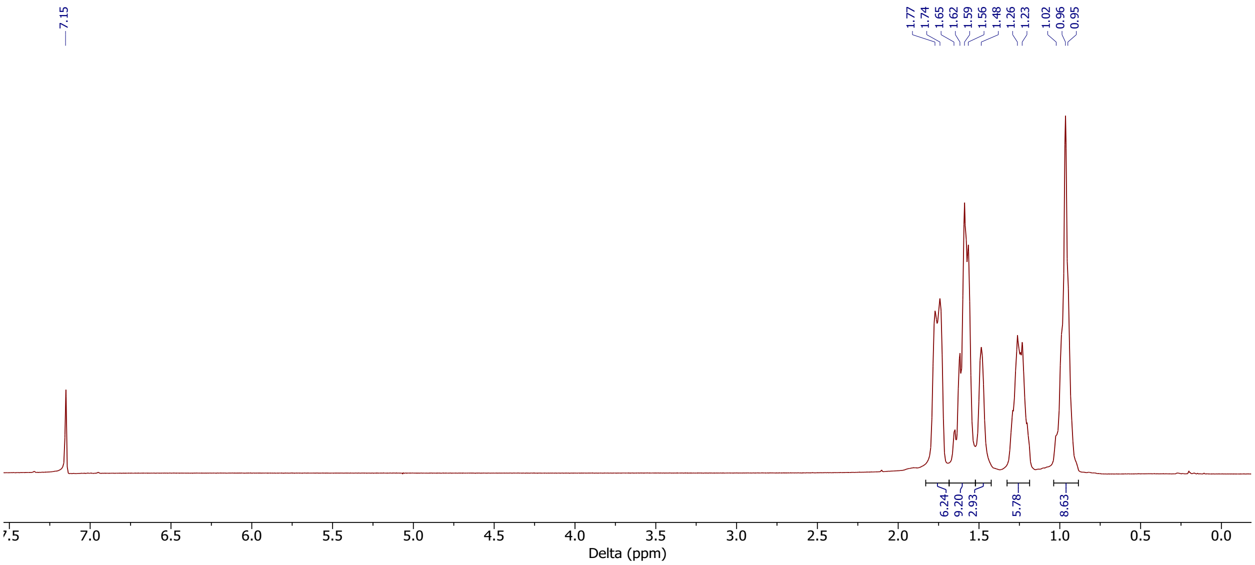


Figure S4. ^{1}H NMR spectrum of **2** in C_6D_6.

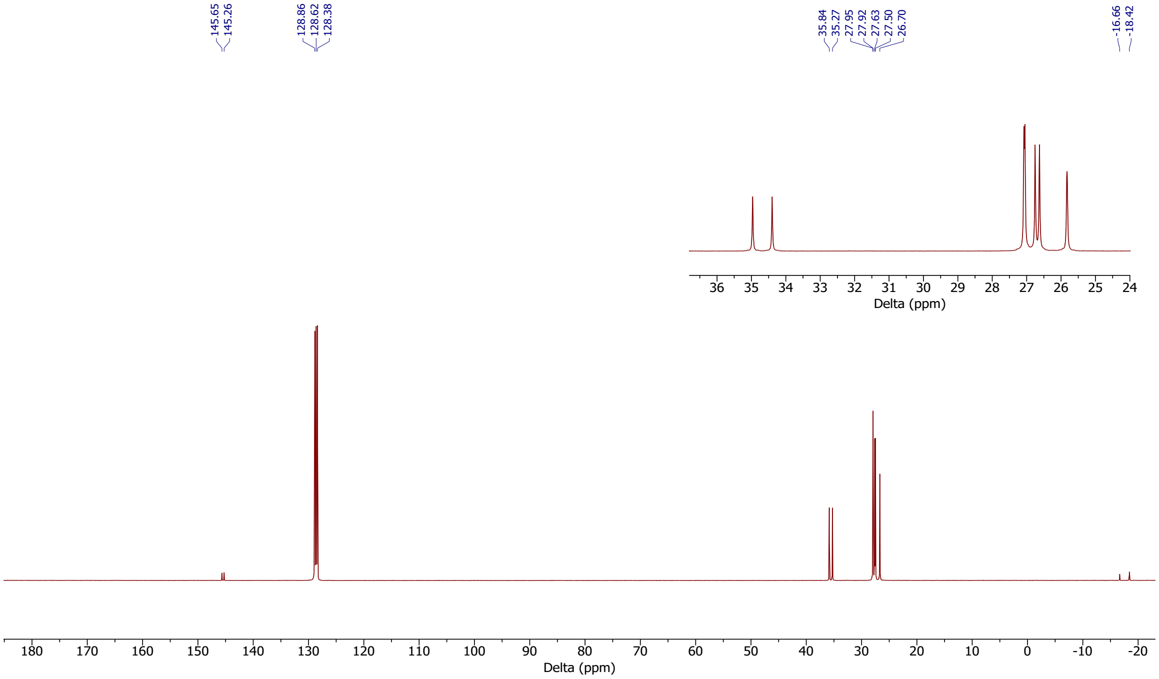


Figure S5. ^{13}C NMR spectrum of **2** in C_6D_6.

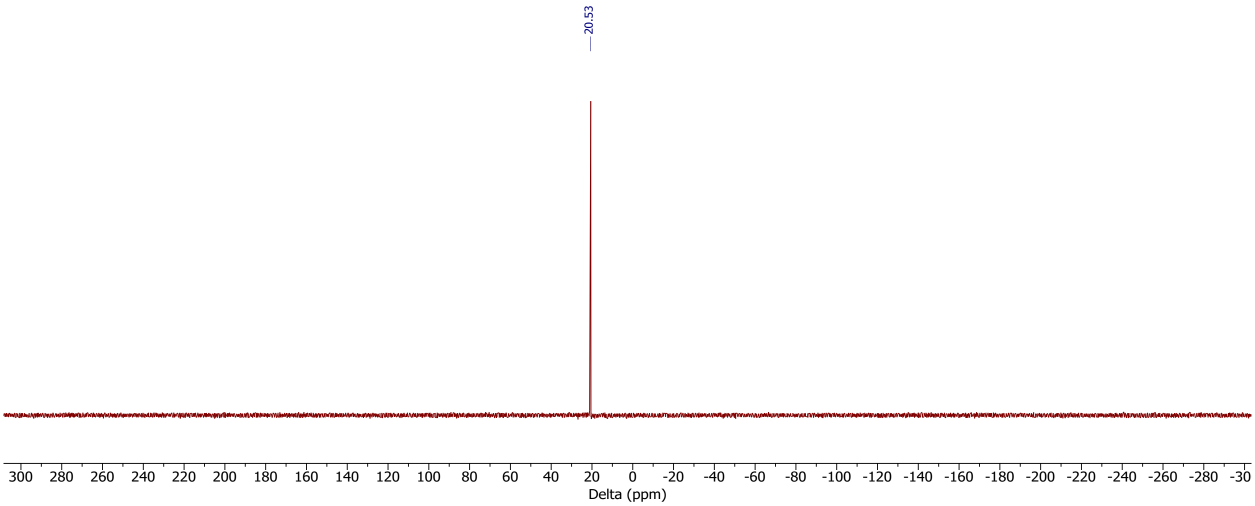
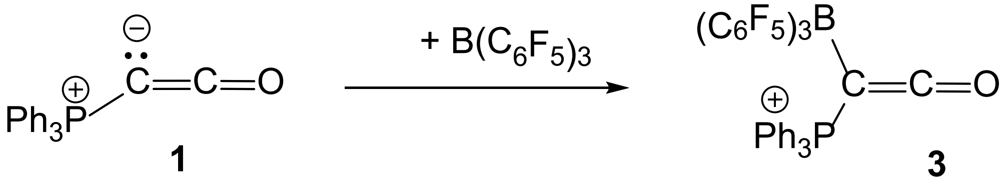


Figure S6. ^{31}P NMR spectrum of **2** in C_6D_6.

2.3 Synthesis of **3**



In a Glove box, a 25 mL Schlenk flask was charged with **1** (300 mg, 0.99 mmol) and 2 ml of toluene. Subsequently, $B(C_6F_5)_3$ (510 mg, 0.99 mmol) was added to the flask. The formation of **3** was confirmed by ^{11}B, ^{19}F and ^{31}P NMR spectroscopy. Then, the toluene was removed under vacuum to leave raw **3** as a solid material, which was washed twice with hexanes and dried under vacuum (yield 80%). ^{1}H NMR (C_6D_6, 400 MHz): δ 6.72-6.76 (m, arom. H, 6 H), 6.86-6.90 (m, arom. H, 3 H), 7.17-7.20 (m, arom. H, 6 H) ppm. $^{13}C\{H\}$ NMR (C_6D_6, 100.6 MHz): 122.1 (d, $^{1}J_{P\text{-}C}$ = 92 Hz, ipso-C-P), 130.1 (d, $^{2}J_{P\text{-}C}$ = 13 Hz, arom. CH), 134.1 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, arom. CH), 134.9 (d, $^{4}J_{P\text{-}C}$ = 3 Hz, arom. CH), 137.9 (m, $^{1}J_{C\text{-}F}$ = 254 Hz, ortho-CF), 140.3 (m, $^{1}J_{C\text{-}F}$ = 251 Hz, para-CF), 149.1 (m, $^{1}J_{C\text{-}F}$ = 246 Hz, meta-CF), 171.9 (d, $^{2}J_{P\text{-}C}$ = 10 Hz, CO) ppm. ^{11}B NMR (C_6D_6, 128.4 MHz): δ -14.4 ppm. ^{31}P NMR [C_6D_6, 161.9 MHz]: δ 29.9 ppm. ^{19}F NMR (C_6D_6, 376.3 MHz): δ -130.2 (m, ortho-F, 6 F), -158.8 (m, para-F, 3 F), -164.2 (m, meta-F, 6 F) ppm. Anal. Calc. for $C_{38}H_{15}BF_{15}OP$ (814.297): C, 56.05; H, 1.86; Found C, 56.45; H, 1.98.

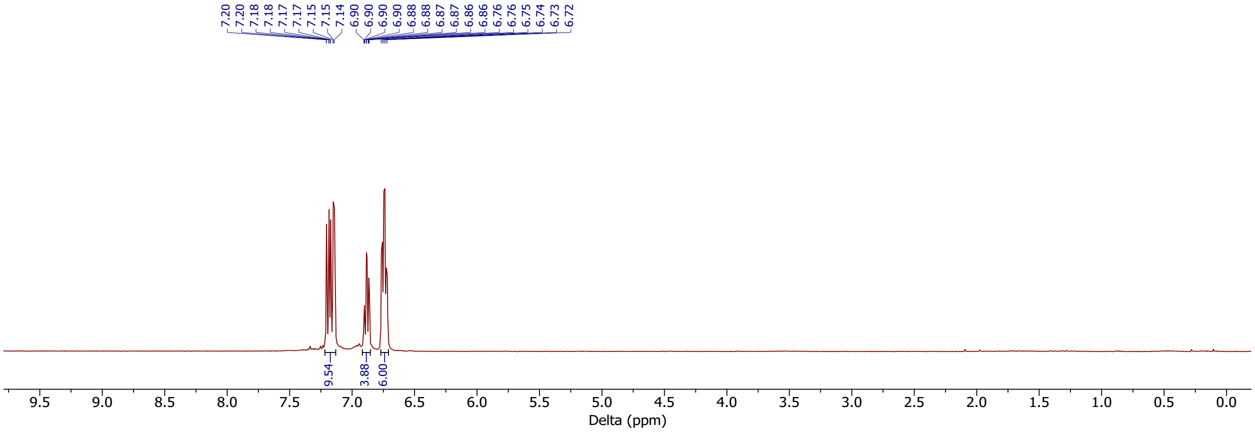


Figure S7. ^{1}H NMR spectrum of **3** in C_6D_6.

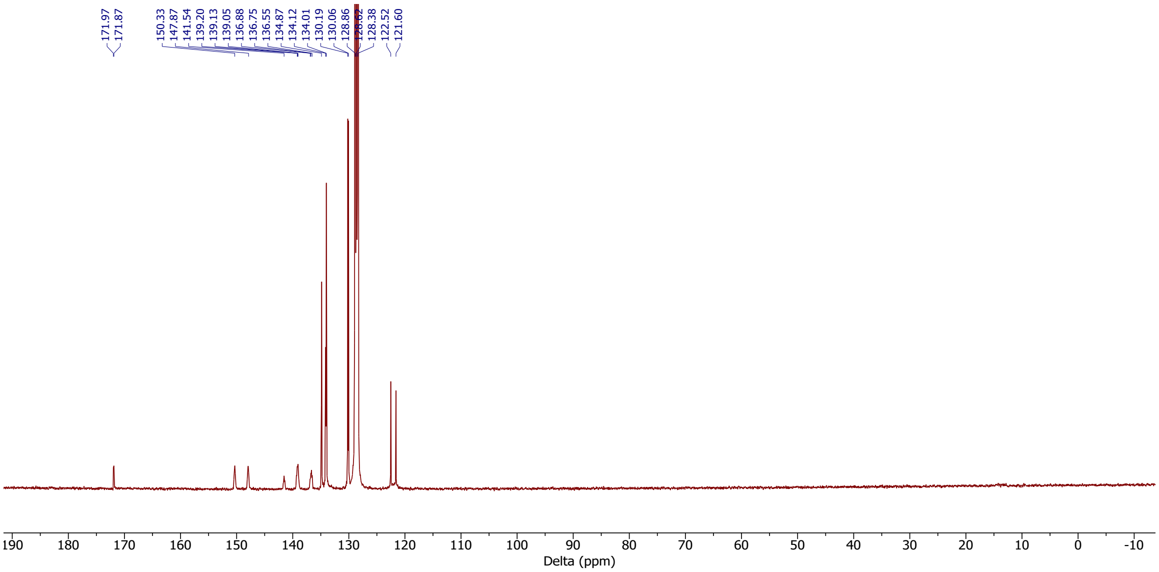


Figure S8. ^{13}C NMR spectrum of **3** in C_6D_6.

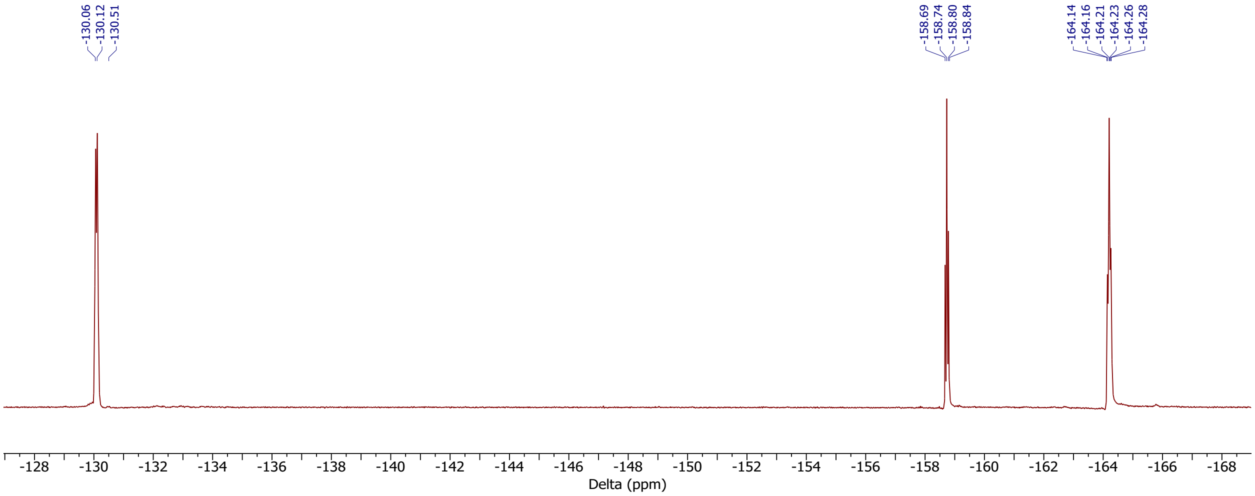


Figure S9. ^{19}F NMR spectrum of **3** in C_6D_6.

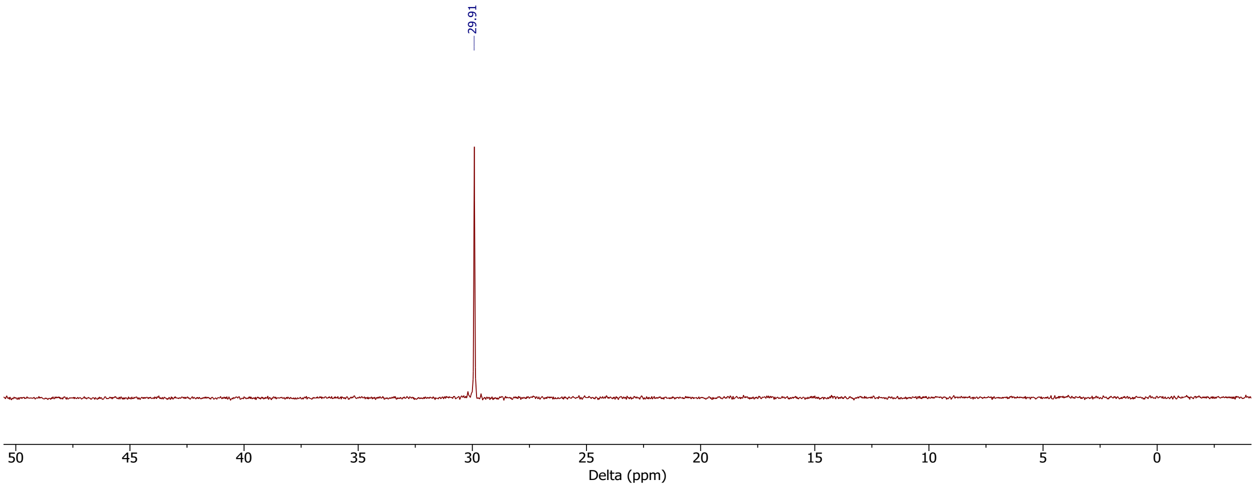


Figure S10. ^{31}P NMR spectrum of **3** in C_6D_6.

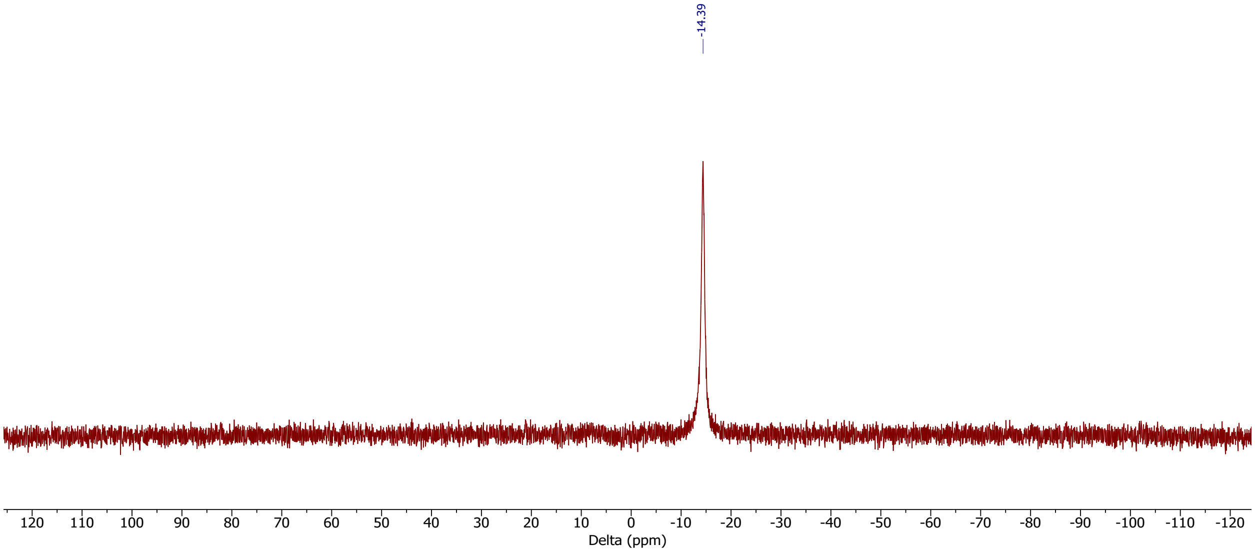
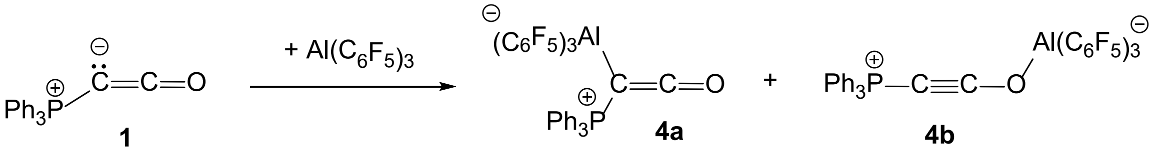


Figure S11. ^{11}B NMR spectrum of **3** in C_6D_6.

2.4 Reaction of ylide **1** with $Al(C_6F_5)_3$



In a Glove box, a J-Young NMR tube was charged with **1** (50 mg, 0.16 mmol) and 0.5 mL of C_6D_6. Then $Al(C_6F_5)_3$×(toluene)$_{1/3}$ (92 mg, 0.16 mmol) was added and the resulting solution analyzed by NMR spectroscopy. ^1H NMR (C_6D_6, 400 MHz): δ 6.86-6.91 (m, arom. H, 6 H), 7.11-7.15 (m, arom. H, 3 H), 7.21-7.26 (m, arom. H, 6 H) ppm. $^{13}C\{H\}$ NMR (C_6D_6, 100.6 MHz): 115.6 (br, ipso-C), 124.7 (d, $^1J_{P\text{-}C}$ = 106 Hz, P-C), 130.1 (d, $^2J_{P\text{-}C}$ = 13 Hz, CH), 133.2 (d, $^3J_{P\text{-}C}$ = 12 Hz, CH), 133.7 (CH), 137.5 (m, $^1J_{C\text{-}F}$ = 249 Hz, ortho-CF), 142.4 (m, $^1J_{C\text{-}F}$ = 270 Hz, para-CF), 151.3 (m, $^1J_{C\text{-}F}$ = 232 Hz, meta-CF) ppm. ^{31}P NMR [C_6D_6, 161.9 MHz]: δ 10.1 ppm. ^{19}F NMR (C_6D_6, 376.3 MHz): δ -122.4 (m, ortho-F, 6 F), -153.8 (m, para-F, 3 F), -162.0 (m, meta-F, 6 F) ppm. ^{31}P NMR [C_6D_6, 161.9 MHz, 213K]: δ ~28, ~4 ppm.

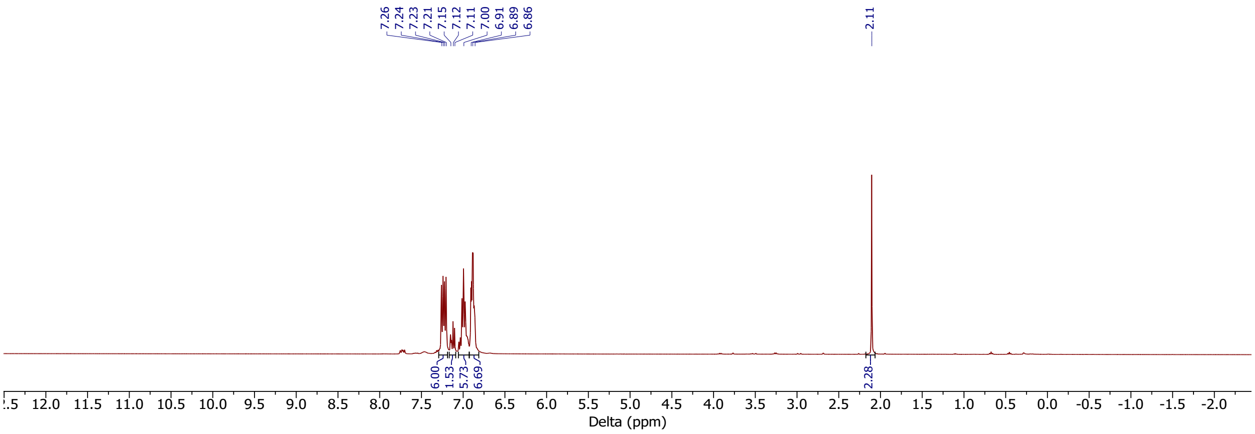


Figure S12. ^1H NMR spectrum in C_6D_6 at room temperature.

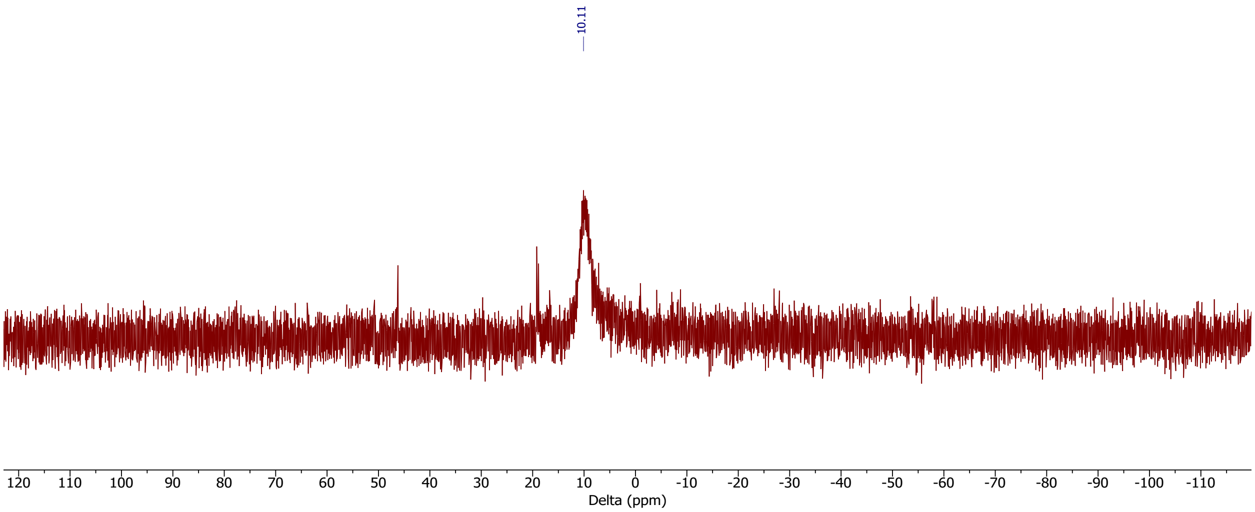


Figure S13. ^{31}P NMR Spectrum in C_6D_6 at room temperature.

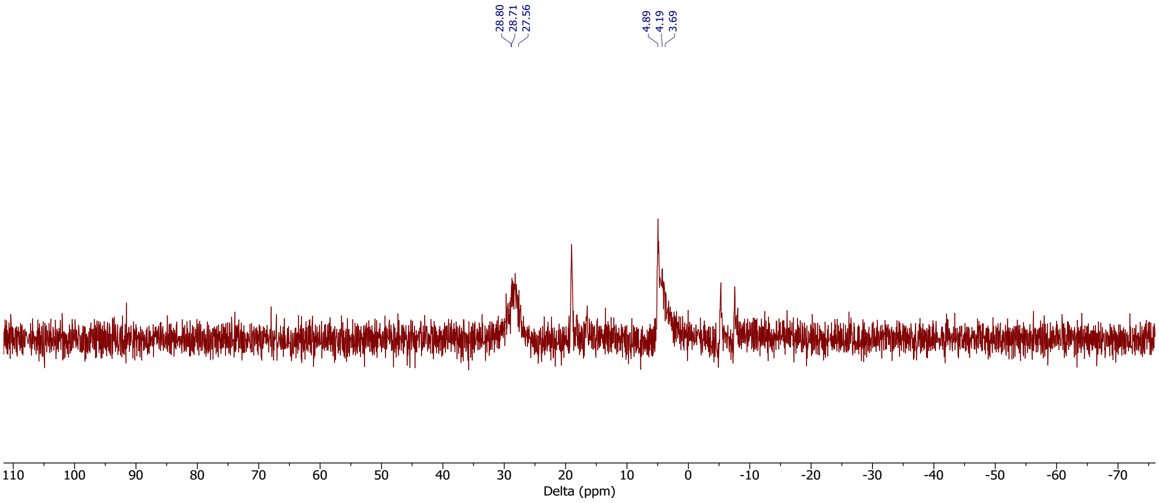


Figure S14. ^{31}P NMR spectrum in toluene at -60°C.

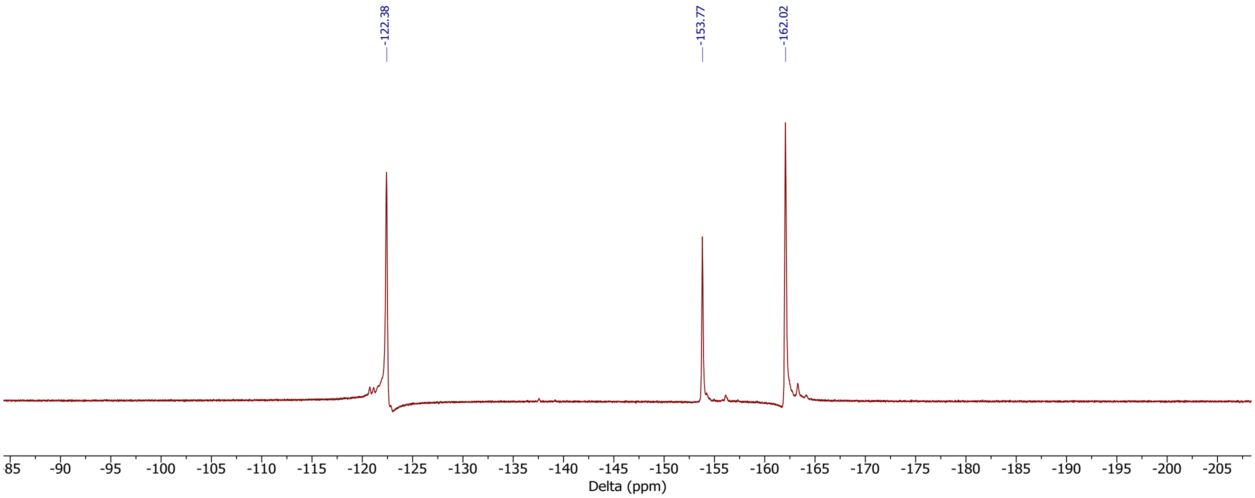


Figure S15. ^{19}F NMR spectrum in C_6D_6 at room temperature.

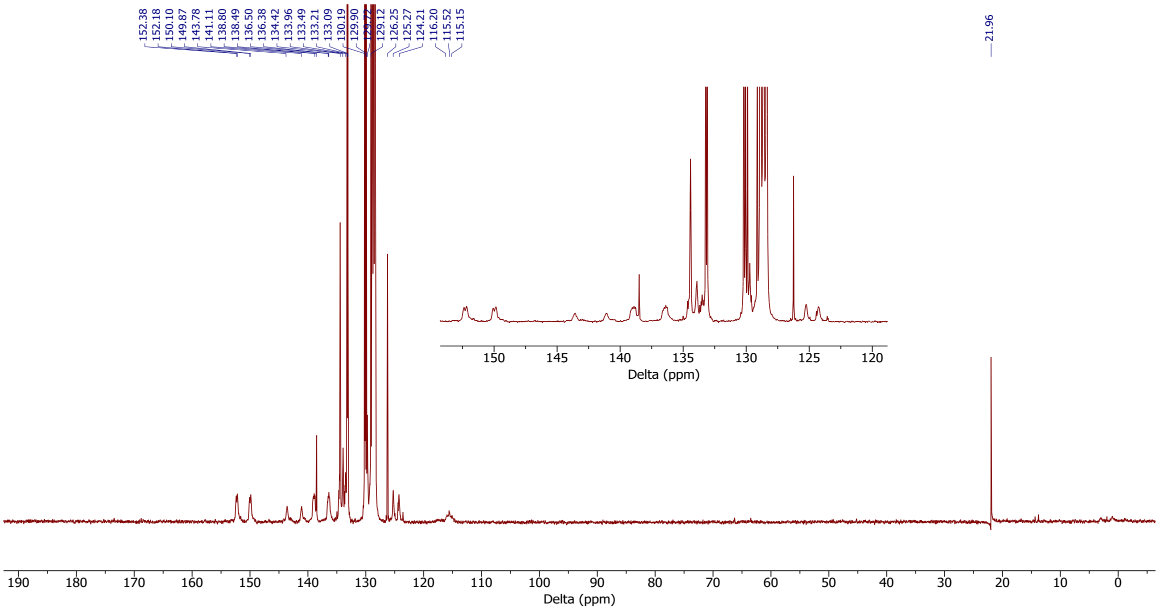
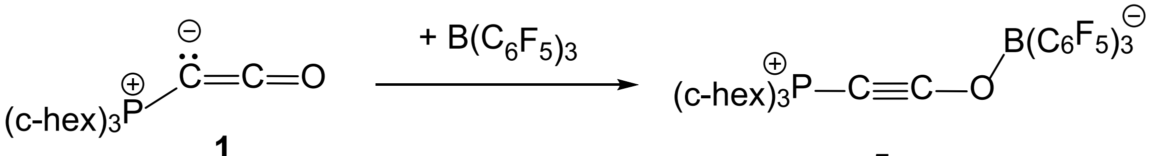


Figure S16. ^{13}C NMR spectrum in C_6D_6 at room temperature.

2.5 Synthesis of **5**



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In a Glove box, a 25 mL Schlenk flask was charged with **2** (50 mg, 0.16 mmol) and 0.5 ml of toluene and $B(C_6F_5)_3$ (80 mg, 0.16 mmol) was subsequently added. The immediate formation of Lewis acid base adduct **5** was confirmed by NMR spectroscopy. Then, the solvent was removed under vacuum, the solid residue washed twice with hexanes and dried under vacuum. Yield 80%. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.75-0.77 (m, cyclohexyl, 14 H), 1.23-1.60 (m, cyclohexyl, 19 H) ppm. ^{13}C{H} NMR (C_6D_6, 125.7 MHz): 5.2 (d, $^1J_{P\text{-}C}$ = 200.0 Hz, P=C), 25.6 (CH_2), 26.8 (d, $^2J_{P\text{-}C}$ = 13.8 Hz, CH_2), 27.2 (d, $^3J_{P\text{-}C}$ = 2.5 Hz, CH_2), 32.1 (d, $^1J_{P\text{-}C}$ = 52.8 Hz, CH), 125.3 (d, $^1J_{P\text{-}C}$ = 40.22 Hz, CO), 119.5 (ipso-C), 138.2 (m, $^1J_{C\text{-}F}$ = 254 Hz, ortho-CF), 140.9 (m, $^1J_{C\text{-}F}$ = 251 Hz, para-CF), 149.4 (m, $^1J_{C\text{-}F}$ = 242 Hz, meta-CF) ppm. ^{11}B NMR (C_6D_6, 128.4 MHz): δ 0.3 ppm. ^{31}P NMR [C_6D_6, 161.9 MHz]: δ 23.9 ppm. ^{19}F NMR (C_6D_6, 376.3 MHz): δ -133.3 (m, ortho-F, 6 F), -157.9 (m, para-F, 3 F), -164.6 (m, meta-F, 6 F) ppm. Anal. Calc. for $C_{38}H_{33}BF_{15}OP$ (832.441): C, 54.83; H, 4.00; Found C, 53.85; H, 3.78.

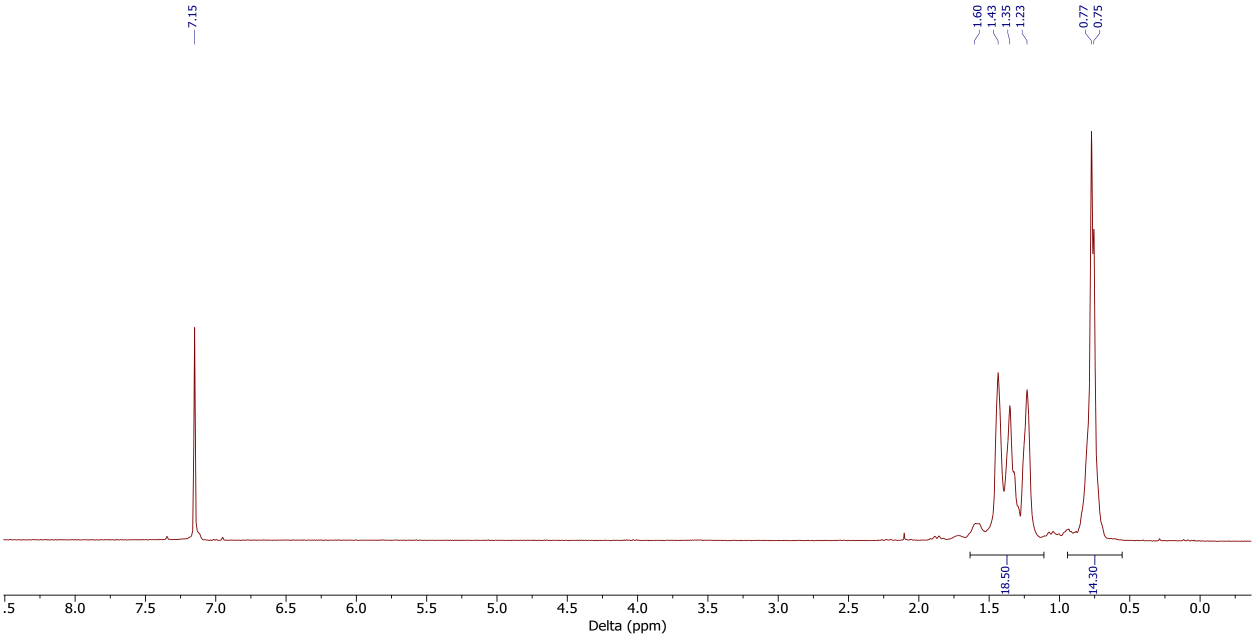


Figure S17. ^{1}H NMR spectrum of **5** in C_6D_6.

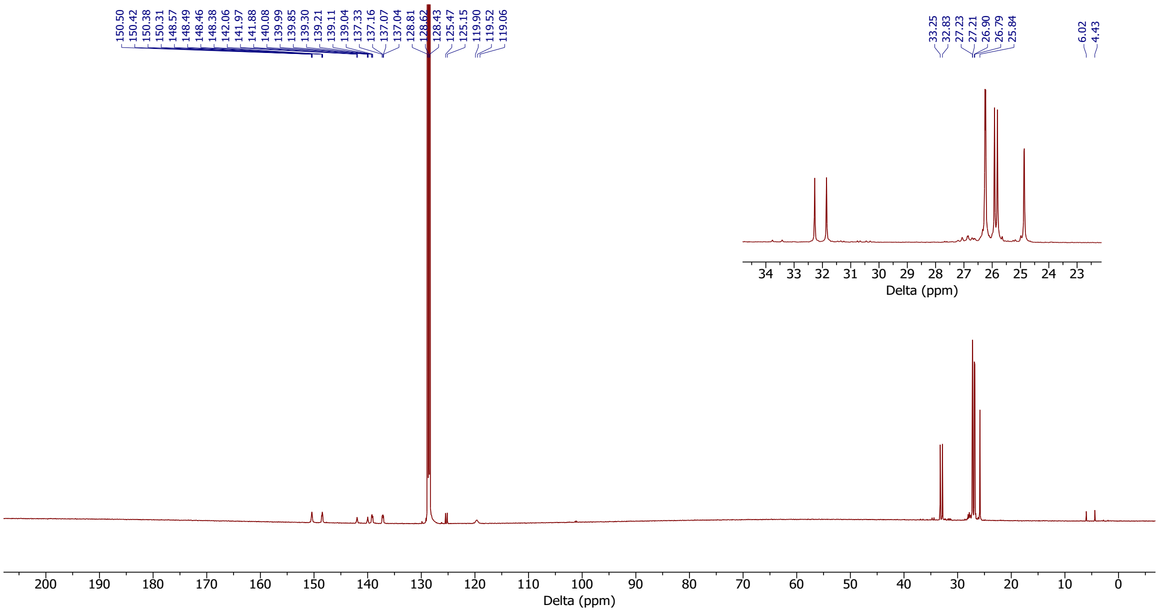


Figure S18. ^{13}C NMR spectrum of **5** in C_6D_6.

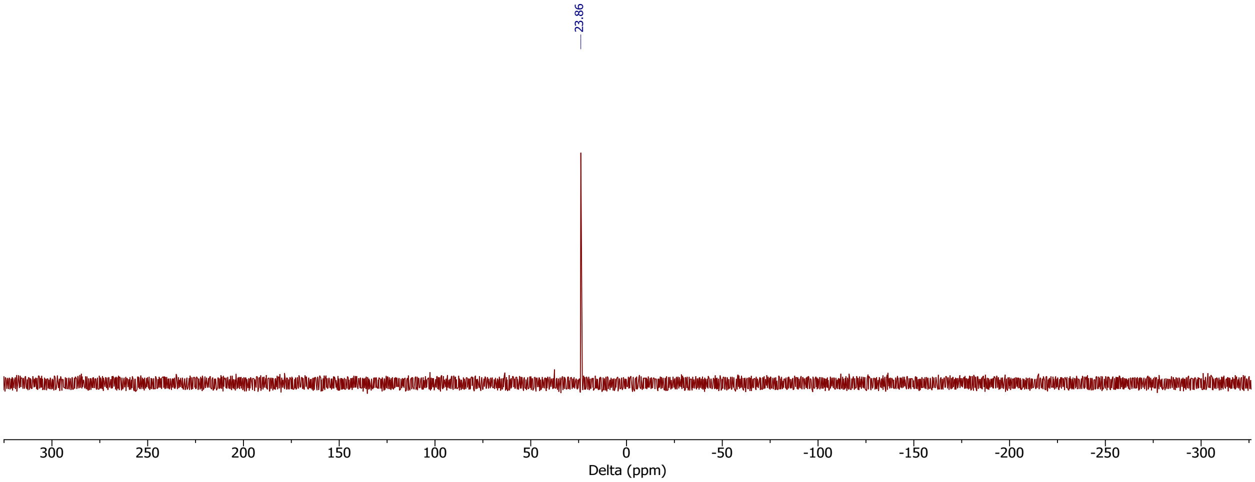


Figure S19. ^{31}P NMR spectrum of **5** in C_6D_6.

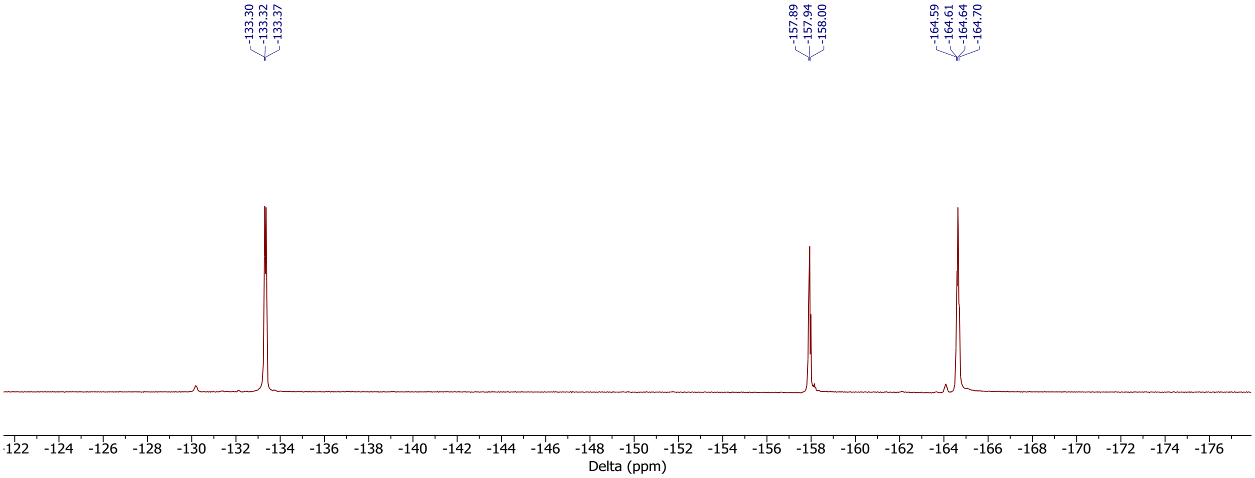


Figure S20. ^{19}F NMR spectrum of **5** in C_6D_6.

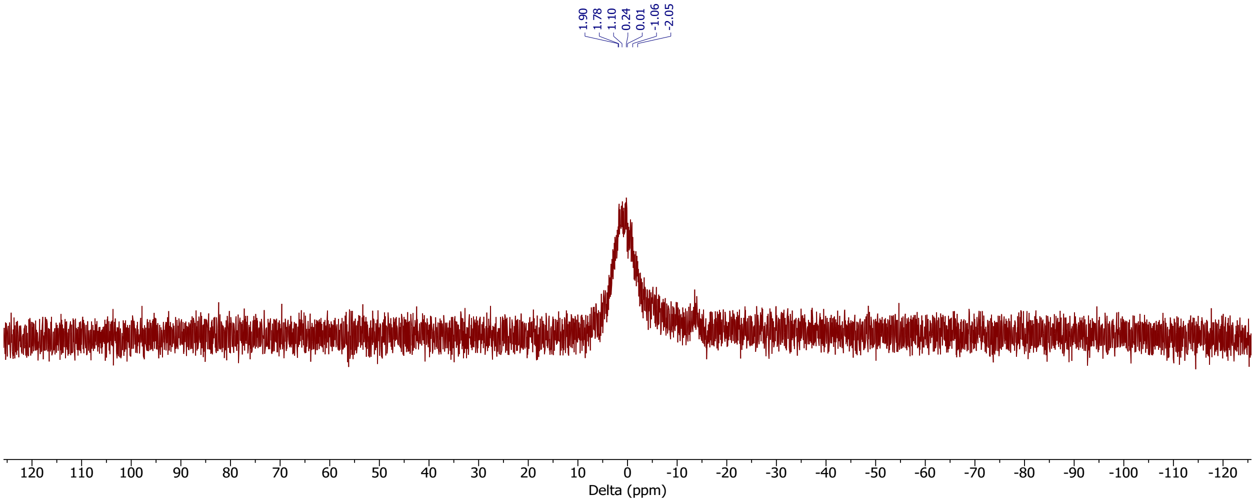
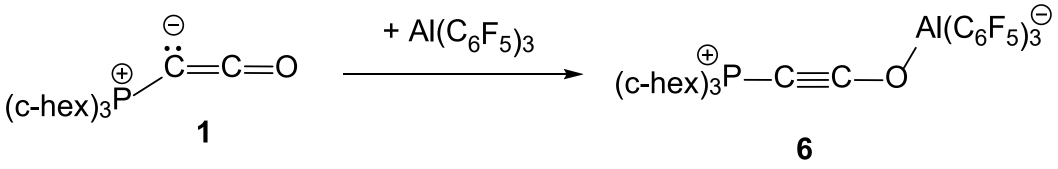


Figure S21. ^{11}B NMR spectrum of **5** in C_6D_6.

2.6 Synthesis of **6**



In a Glove box, a Schlenk flask was charged with **2** (50 mg, 0.16 mmol) and 0.5 ml of toluene and $Al(C_6F_5)_3{\times}(toluene)_{1/3}$ (90 mg, 0.16 mmol) was subsequently added. Upon concentration of the solution, crystals precipitated, which were collected, washed with hexanes twice and dried under vacuum. Yield 65%. ^{1}H NMR (toluene-D_8, 400 MHz): δ 0.75-0.94 (m, cyclohexyl, 14 H), 1.35-1.64 (m, cyclohexyl, 19 H) ppm. ^{13}C{H} NMR (toluene-D_8, 100.6 MHz): 0.0 (d, $^1J_{P\text{-}C}$ = 202.0 Hz, P=C), 26.4 (CH_2), 27.4 (d, $^2J_{P\text{-}C}$ = 13.1 Hz, CH_2), 27.8 (d, $^3J_{P\text{-}C}$ = 3.0 Hz, CH_2), 33.7 (d, $^1J_{P\text{-}C}$ = 53.2 Hz, CH), 124.5 (d, $^1J_{P\text{-}C}$ = 41.2 Hz, CO), 116 (ipso-C), 138.2 (m, $^1J_{C\text{-}F}$ = 241 Hz, ortho-CF), 142.8 (m, $^1J_{C\text{-}F}$ = 243 Hz, para-CF), 151.7 (m, $^1J_{C\text{-}F}$ = 237 Hz, meta-CF) ppm. ^{31}P NMR [toluene-D_8, 161.9 MHz]: δ 24.5 ppm. ^{19}F NMR (toluene-D_8, 376.3 MHz): δ -122.6 (m, ortho-F, 6 F), -154.2 (m, para-F, 3 F), -162.3 (m, meta-F, 6 F) ppm. The results from combustion analysis were unsatisfactory due to partial decomposition of **6**.

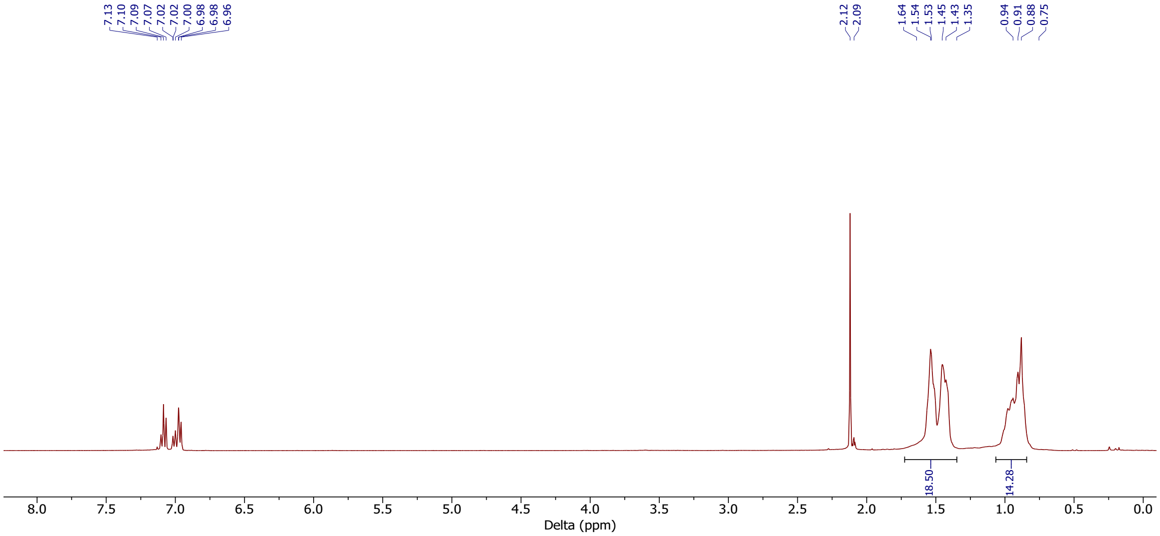


Figure S22. ^{1}H NMR spectrum of **6** in toluene-d8.

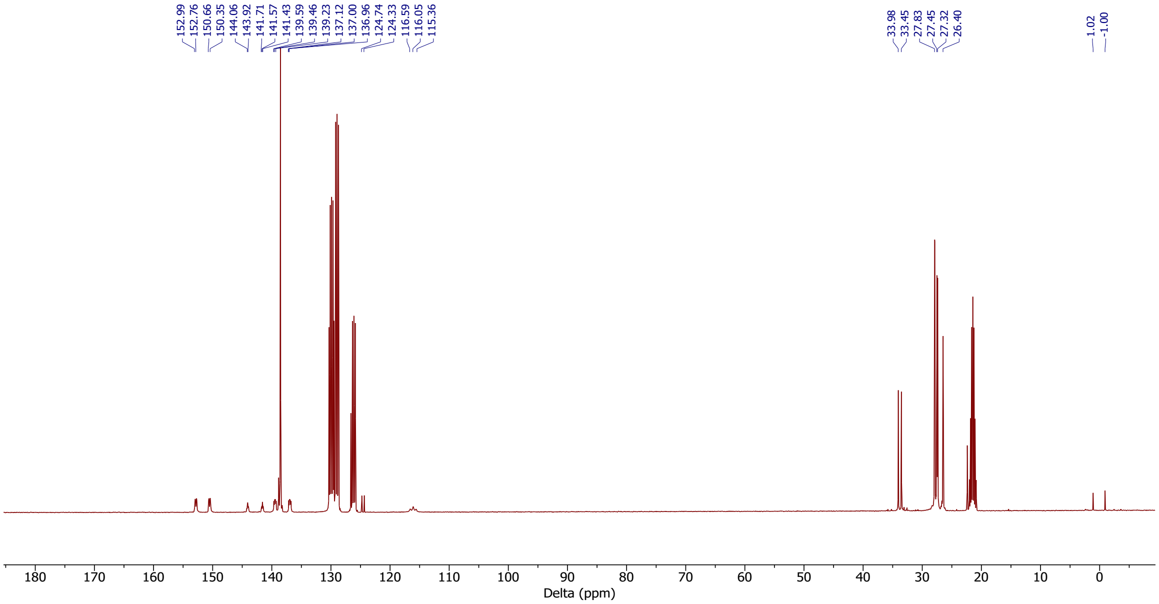


Figure S23. ^{13}C NMR spectrum of **6** in toluene-d8.

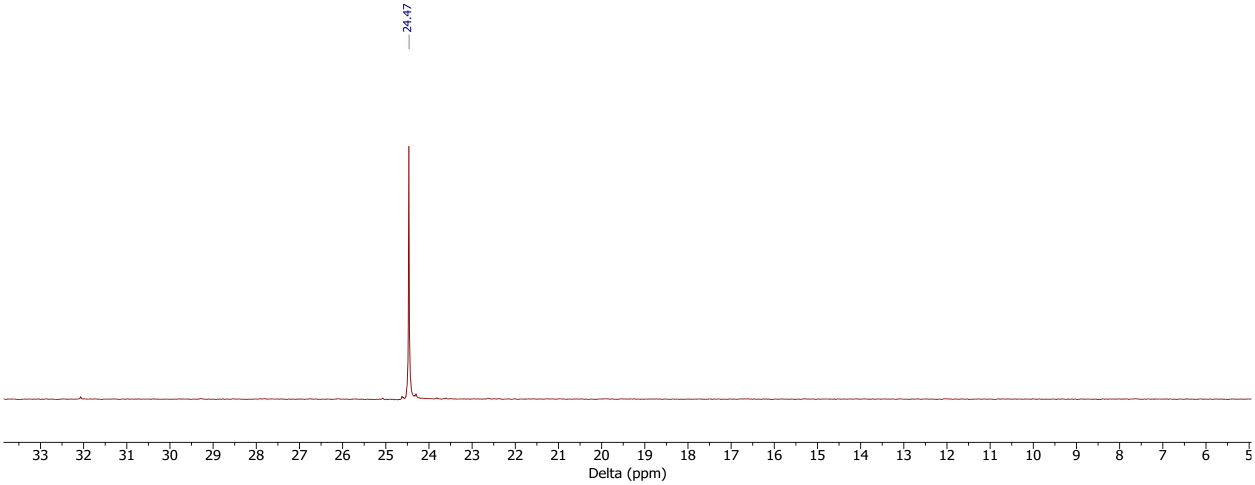


Figure S24. ^{31}P NMR spectrum of **6** in toluene-d8.

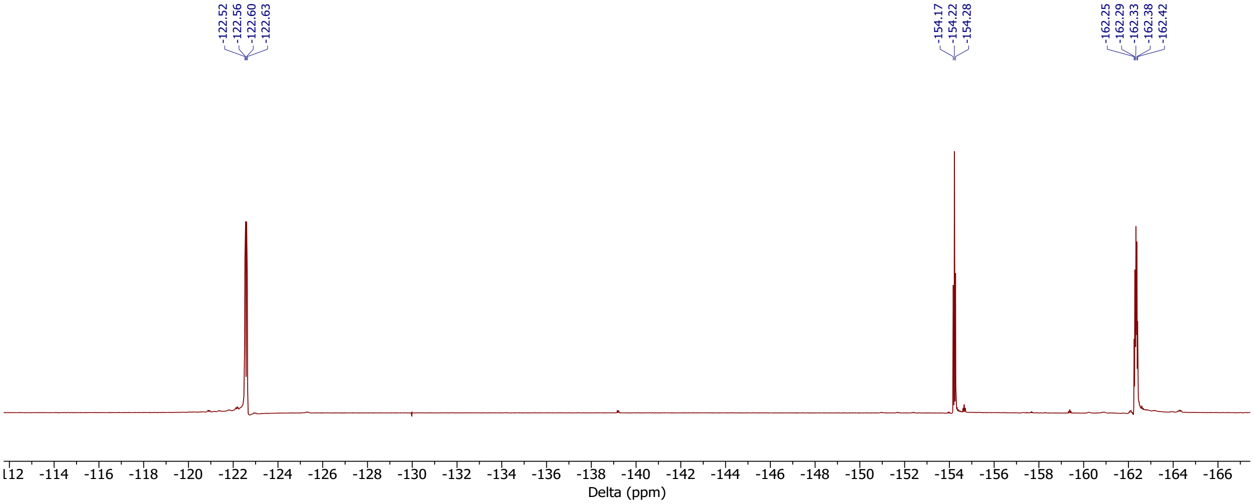
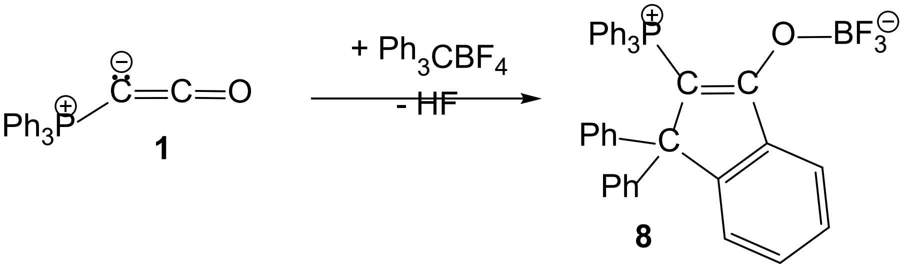


Figure S25. ^{19}F NMR spectrum of **6** in toluene-d8.

2.7 Synthesis of **8**



A 25 mL Schlenk flask equipped with a magnetic stir bar was charged with **1** (200 mg, 0.66 mmol) and acetonitrile (3 mL). Then Ph_3CBF_4 (218 mg, 0.66 mmol) was added and the mixture stirred until all solid material had dissolved. Colorless crystals formed upon standing the solution overnight without stirring. After decantation of the solvent, the crystals were washed twice with acetonitrile and dried under vacuum to give analytically pure **8**×$(CH_3CN)_{0.5}$. Yield 62%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.96-8.27 (m, arom. H, 29 H) ppm. ^{13}C{H} NMR (CD_2Cl_2, 125.7 MHz): 65.7 (d, $^2J_{P\text{-}C}$ = 10.1 Hz, trityl-C), 98.0 (d, $^1J_{P\text{-}C}$ = 102 Hz, P=C), 122.1 (d, $^1J_{P\text{-}C}$ = 92 Hz, ipso-C), 124.9 (d, $^4J_{P\text{-}C}$ = 2.5 Hz, ***C***H=CH-CH), 125.8 (q, CH-CH=***C***H, $J_{P\text{-}F}$ = 6.3 Hz), 127.8 (m-C), 128.2, 129.9 (C=***C***H-***C***H=C), 127.8 (meta-CH), 128.9 (d, $^2J_{P\text{-}C}$ = 21.4 Hz, ortho-CH), 129.9 (d, $^3J_{P\text{-}C}$ = 13.8 Hz, meta-CH), 131.3 (para-CH), 134.2 (d, $^4J_{P\text{-}C}$ = 2.5 Hz, ortho-CH), 135.2 (d, $^4J_{P\text{-}C}$ = 11.3 Hz, para-CH), 135.8 (d, $^3J_{P\text{-}C}$ = 13.8 Hz, ***C***=C), 142.0 (ipso-C), 159.1 (d, $^3J_{P\text{-}C}$ = 12.6 Hz, C=***C***), 177.6 (CO) ppm. ^{11}B NMR (CD_2Cl_2, 128.4 MHz): δ -2.2 ppm. ^{31}P NMR [CD_2Cl_2, 161.9 MHz]: δ 16.5 ppm. ^{19}F NMR (CD_2Cl_2, 376.3 MHz): δ -146.2 ppm. Anal. Calc. for $C_{39}H_{29}BF_3OP$×$(CH_3CN)_{0.5}$ (632.965): C, 75.90; H, 4.86; Found C, 74.82; H, 4.75.

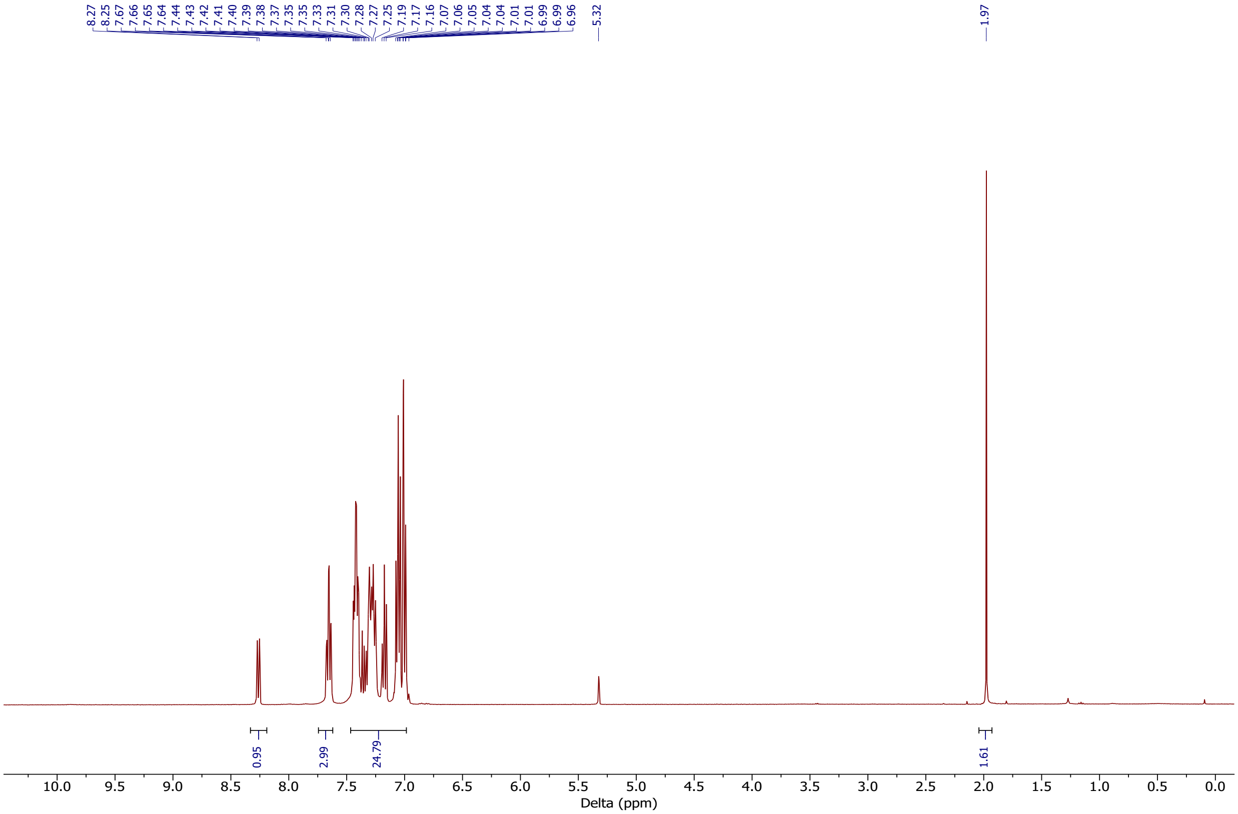


Figure S26. ^1H NMR spectrum of **8** in CD_2Cl_2.

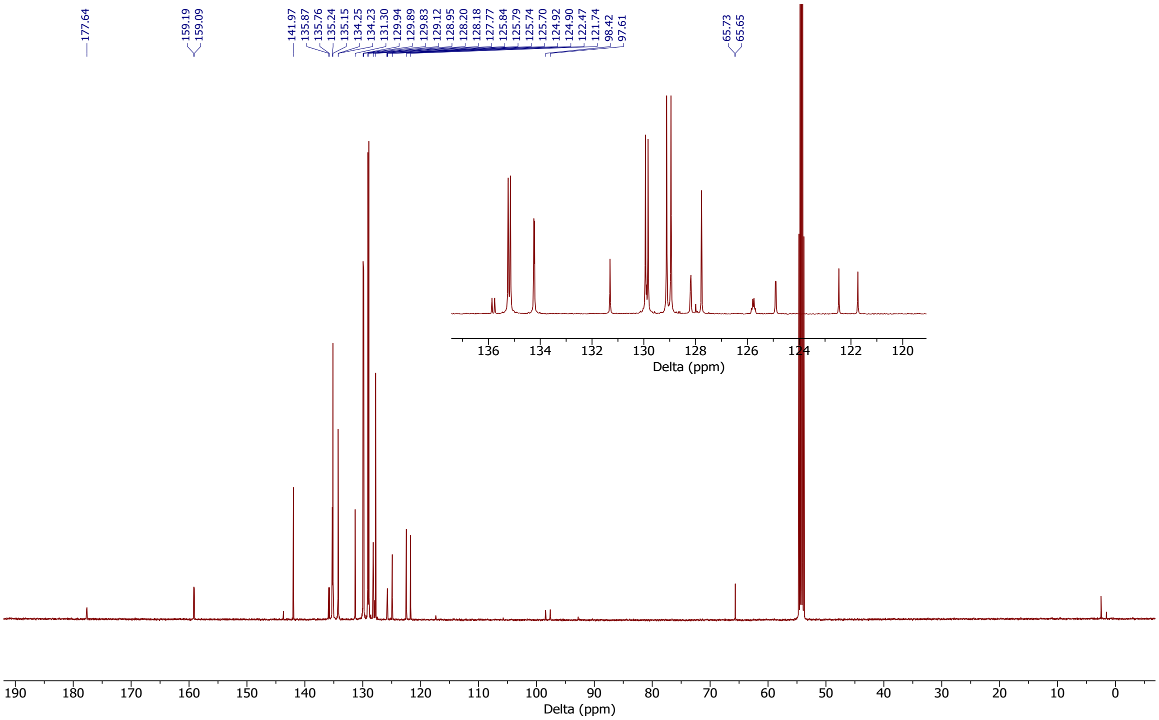


Figure S27. ^{13}C NMR spectrum of **8** in CD_2Cl_2.

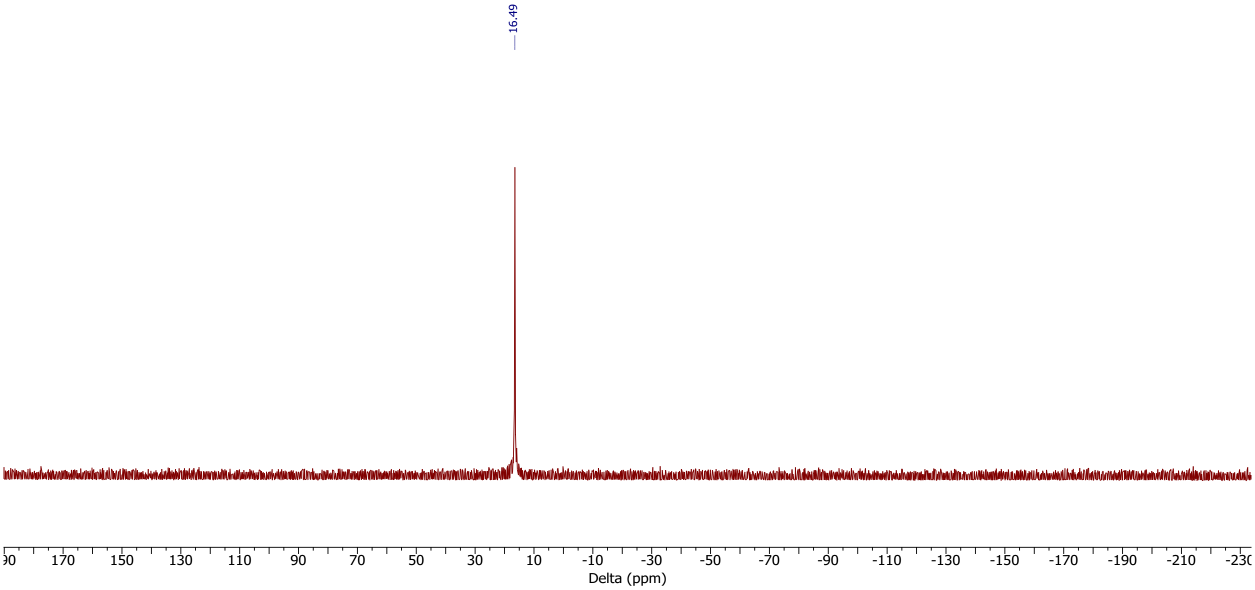


Figure S28. ^{31}P NMR spectrum of **8** in CD_2Cl_2.

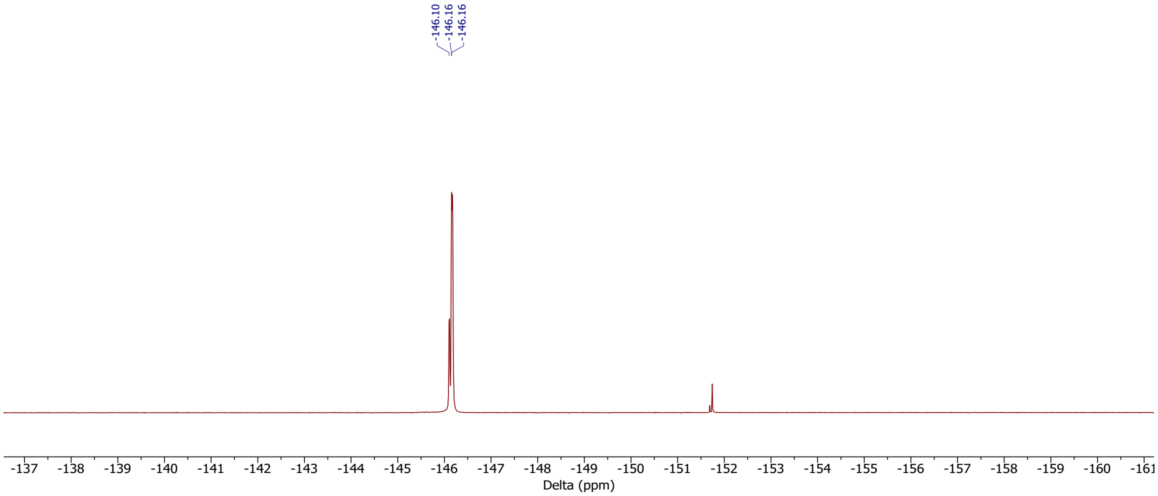


Figure S29. ^{19}F NMR spectrum of **8** in CD_2Cl_2.

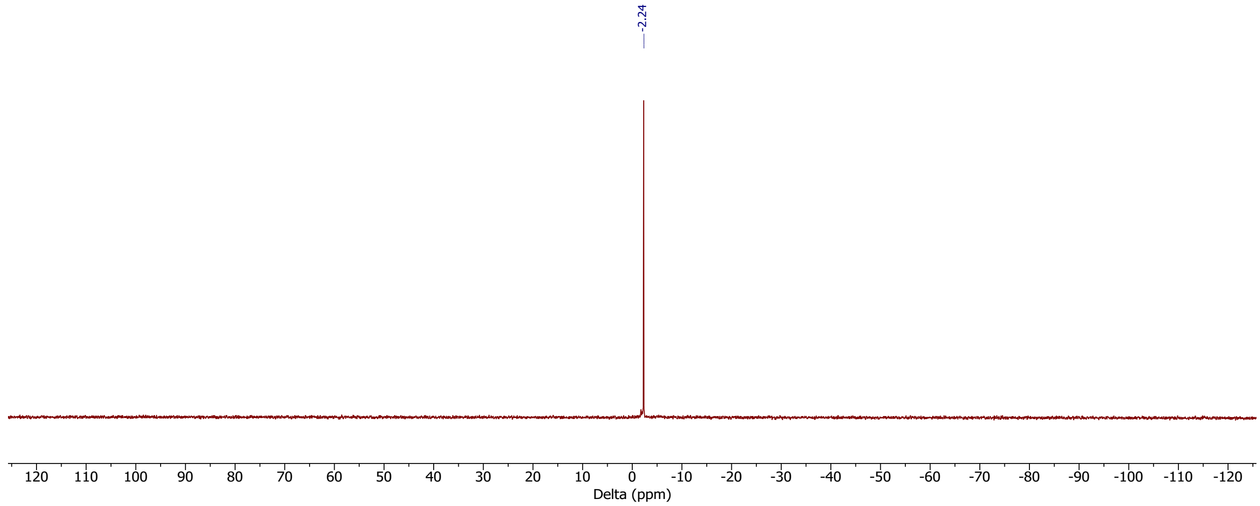
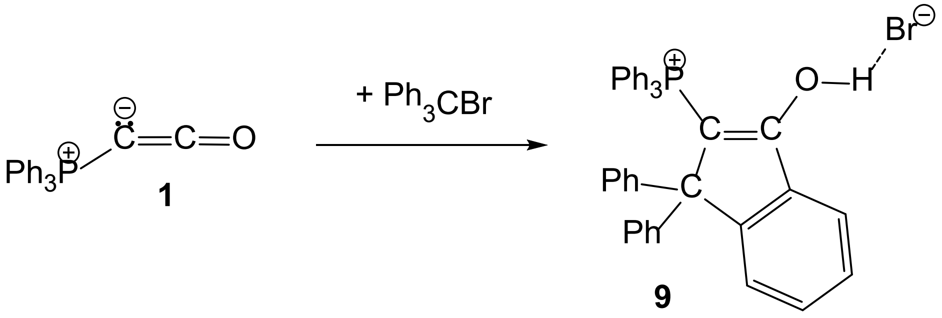


Figure S30. ^{11}B NMR spectrum of **8** in CD_2Cl_2.

2.8 Synthesis of **9**



A 25 mL Schlenk flask equipped with a magnetic stir bar was charged with **1** (200 mg, 0.66 mmol) and acetonitrile (3 mL). Then Ph_3CBr (218 mg, 0.66 mmol) was added and the mixture stirred until all solid material dissolved. Colorless crystals formed upon standing the solution overnight without stirring. The solvent was decanted off, the crystals washed twice with acetonitrile and dried under vacuum for several hours. Yield 53%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.97-7.62 (m, 29 H) ppm. ^{13}C{H} NMR (CD_2Cl_2, 100.6 MHz): 66.2 (b, trityl-C),122.5 (b, ipso-C), 123.4, 125.0, 127.9,128.6 (CH), 127.6 (meta-CH), 128.9 (d, $^2J_{P\text{-}C}$ = 27 Hz, ortho-CH), 129.9 (d, $^3J_{P\text{-}C}$ = 13 Hz, meta-CH), 131.3 (para-CH), 135.1 (d, $^4J_{P\text{-}C}$ = 10 Hz, para-CH), 134.1 (ortho-CH), 137.6 (C=C), 143.1 (ipso-C), 158.6 (d, $^3J_{P\text{-}C}$ = 12 Hz, C=C) ppm. ^{31}P NMR [CD_2Cl_2, 161.9 MHz]: δ 15.7 ppm. IR (solid-state): ν = 3300 cm^{-1} (OH). Anal. Calc. for $C_{39}H_{29}BF_3OP$ (625.546): C, 74.88; H, 4.83; Found C, 75.02; H, 4.68 (Note! To fully remove acetonitrile for elemental analysis, the sample was dried under vacuum at 80°C for ca. 1 day).

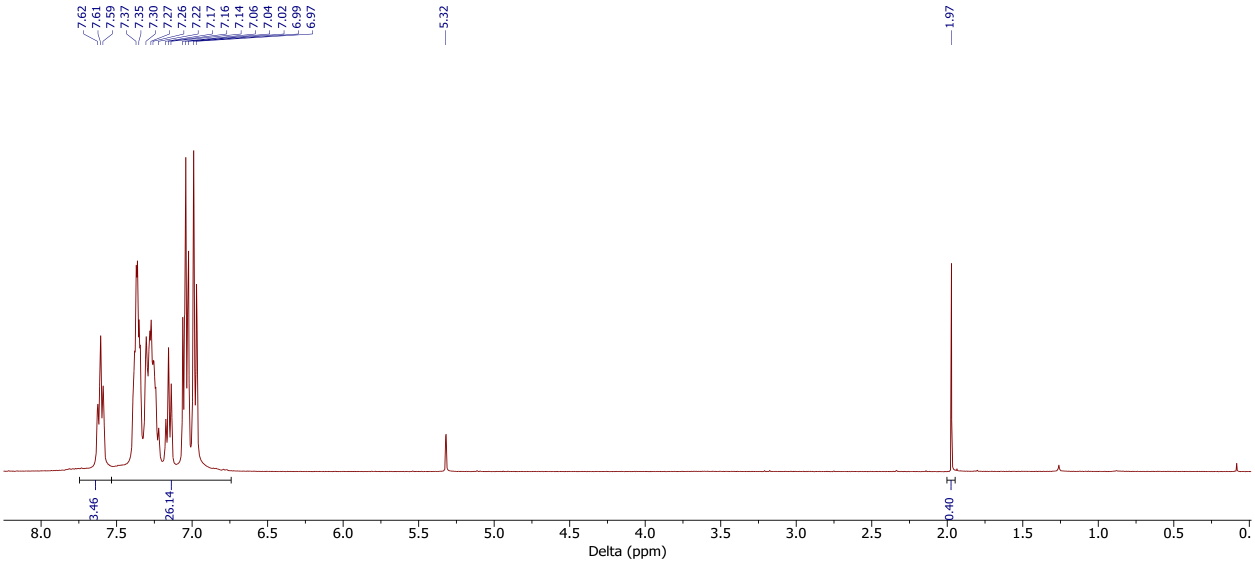


Figure S31. ^{1}H NMR spectrum of **9** in CD_2Cl_2.

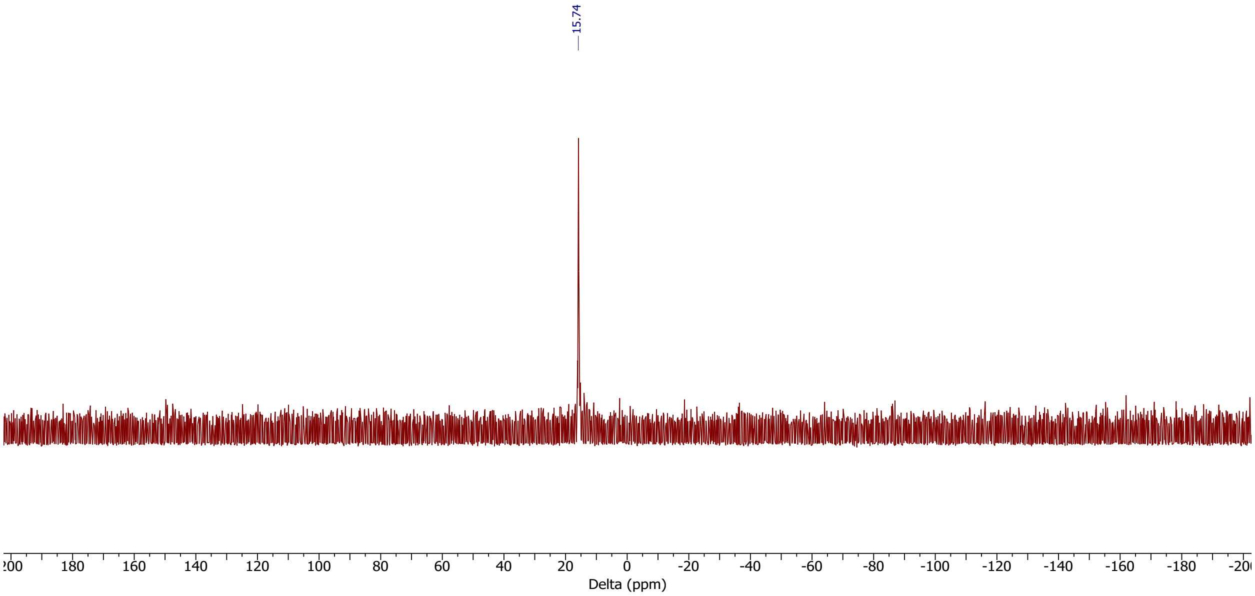


Figure S32. ^{31}P NMR spectrum of **9** in CD_2Cl_2.

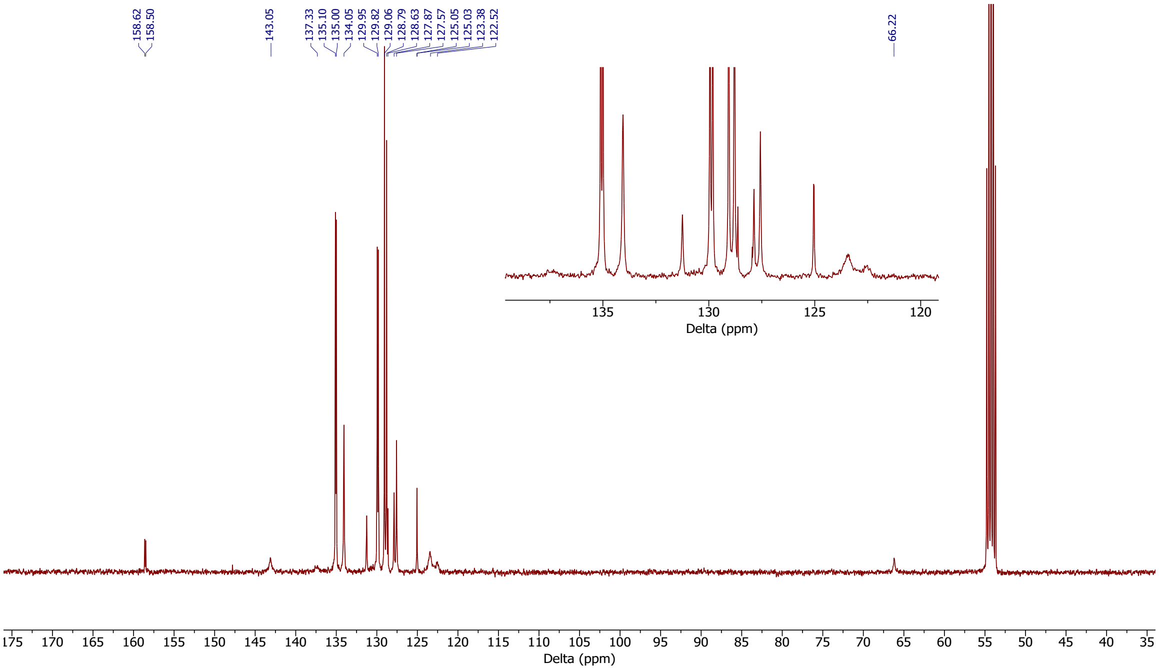
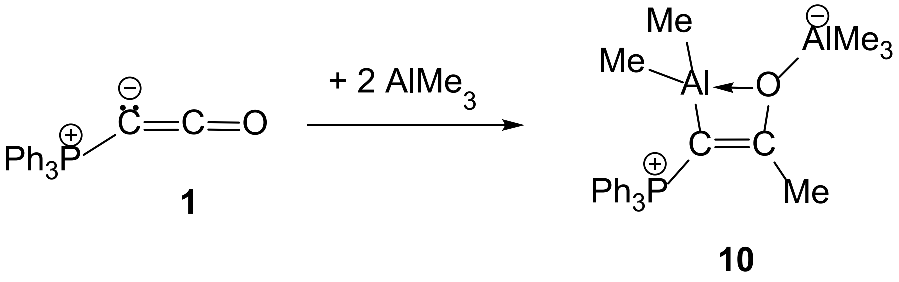


Figure S33. ^{13}C NMR spectrum of **9** in CD_2Cl_2.

2.9 Synthesis of **10**



In a Glove box, a J-Young NMR tube was charged with **1** (50 mg, 0.16 mmol) and 0.4 ml of C_6D_6. A heptane solution of $AlMe_3$ (1 M, 0.32 mmol, 0.32 ml) was added slowly. Upon concentration of the solution, crystals of **10** precipitated, which were collected, washed with hexanes twice and finally dried under vacuum. Yield 90% ^{1}H NMR (C_6D_6, 400 MHz): δ 1.77 (d, $^4J_{P\text{-}H}$ = 0.4 Hz, CH_3), -0.03 [s, $Al(CH_3)_2$, 6 H], -0.11 [s, $Al(CH_3)_3$, 9 H], 6.89-6.94 (m, arom. CH, 6 H), 7.01-7.06 (m, arom. CH, 3 H), 7.18-7.24 (m, 6H) ppm. ^{13}C{H} NMR (C_6D_6, 100.6 MHz): -5.7 [$Al(CH_3)_3$], -7.2 [$Al(CH_3)_2$], 22.8 (d, $^3J_{P\text{-}C}$ = 4.0 Hz, CH_3), 96.7 (d, $^1J_{P\text{-}C}$ = 73.4 Hz, P=C), 125.6 (d, $^1J_{P\text{-}C}$ = 91.2 Hz, CH), 130.2 (d, $^2J_{P\text{-}C}$ = 13.1 Hz, CH), 133.6 (d, $^3J_{P\text{-}C}$ = 10.1 Hz, CH), 133.8 (d, $^4J_{P\text{-}C}$ = 2.0 Hz, CH), 178.8 (d, $^2J_{P\text{-}C}$ = 10.1 Hz, CO) ppm. ^{31}P NMR [C_6D_6, 161.9 MHz]: δ 11.3 ppm. The results from combustion analysis were unsatisfactory due to decomposition of **10**.

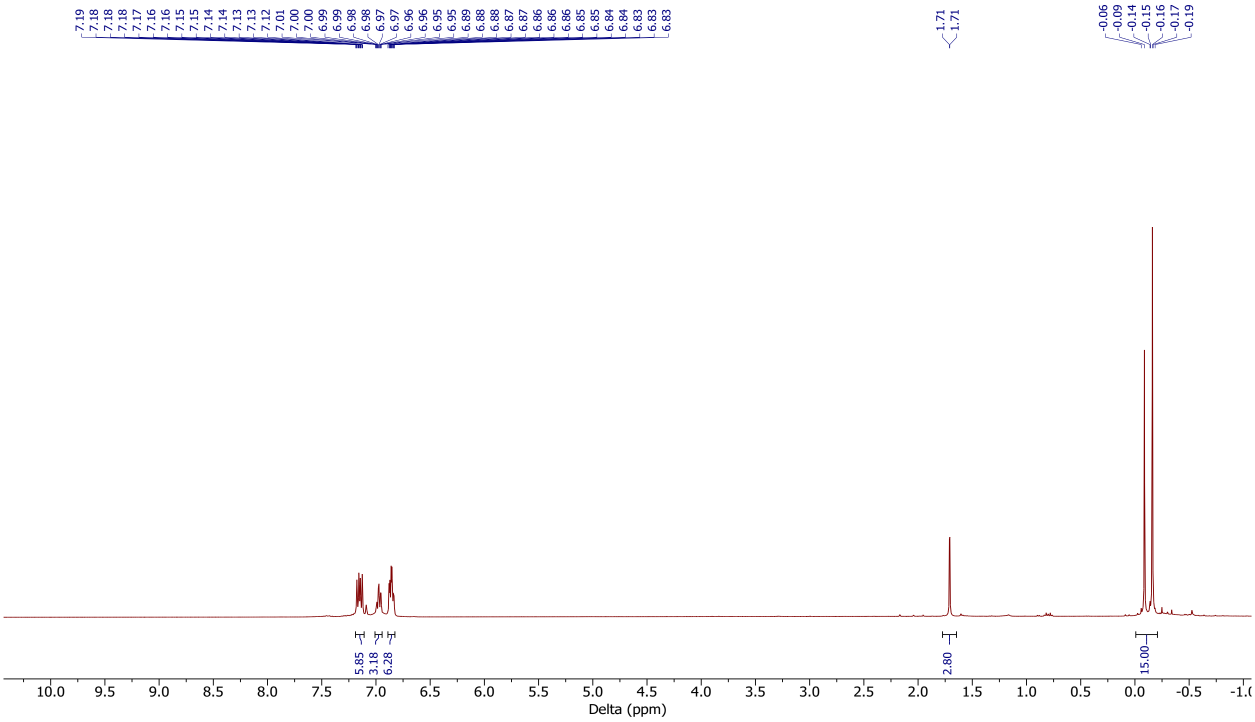


Figure S34. ^{1}H NMR spectrum of **10** in C_6D_6.

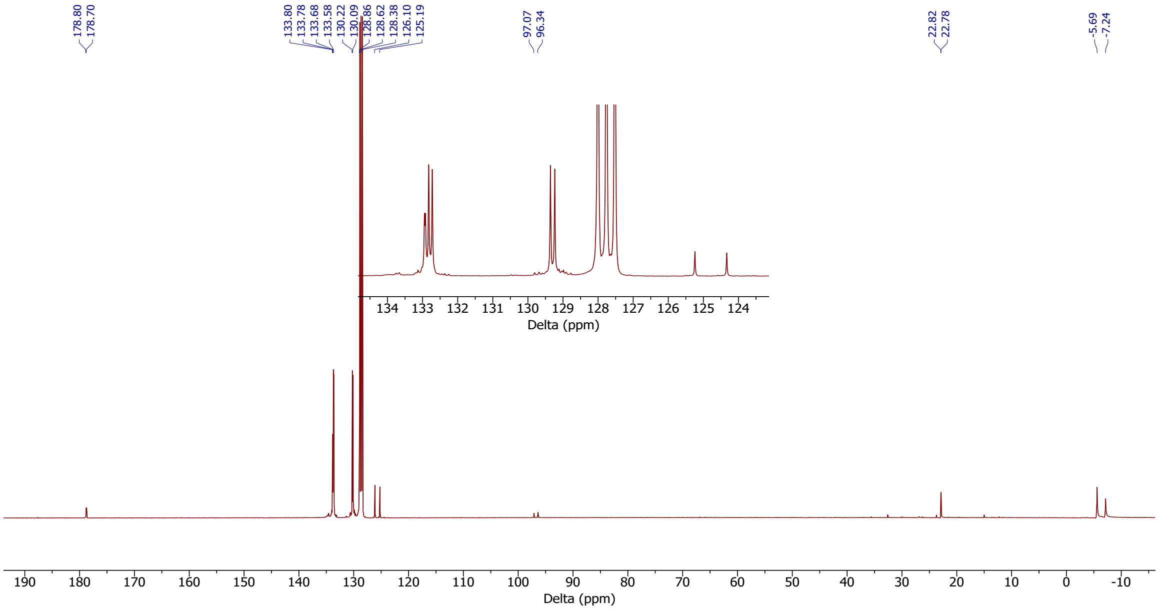


Figure S35. ^{13}C NMR spectrum of **10** in C_6D_6.

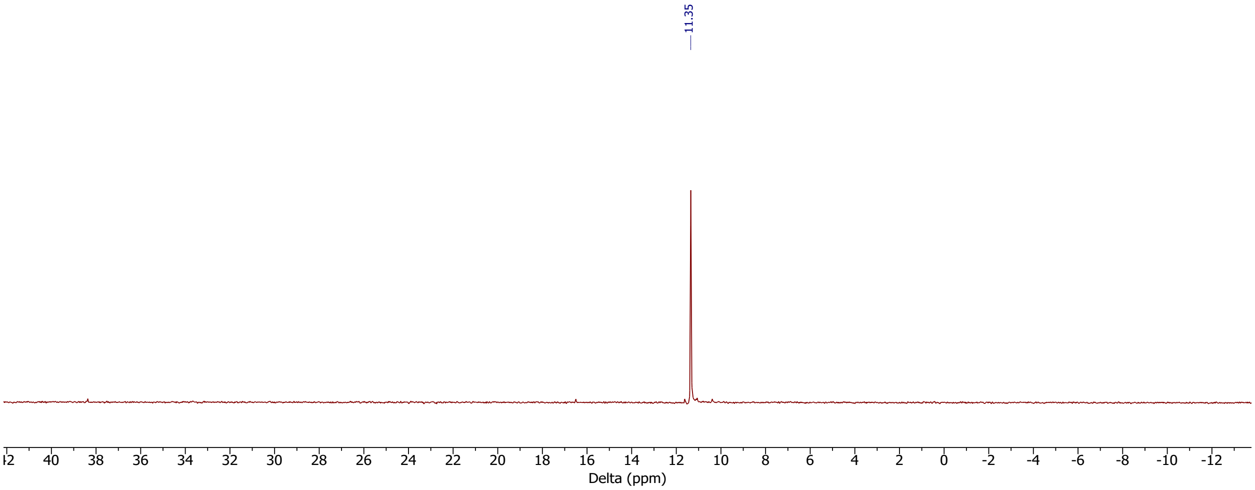
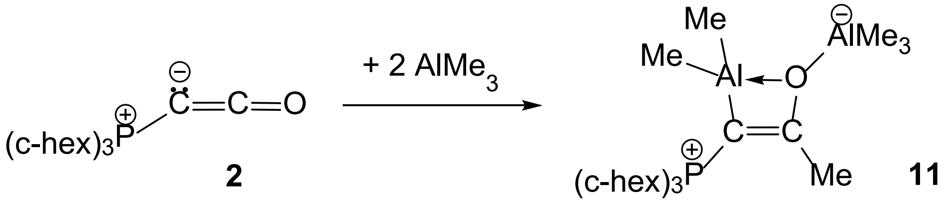


Figure S36. ^{31}P NMR spectrum of **10** in C_6D_6.

2.10 Synthesis of **11**



In a Glove box, a J-Young NMR tube was charged with **2** (50 mg, 0.16 mmol) and 0.4 ml of C_6D_6. To this solution, a heptane solution of $AlMe_3$ (1M, 0.32 mmol, 0.32 ml) was added slowly. Upon concentration of the solution, crystals of **11** precipitated, which were collected, washed twice with hexanes and finally dried under vacuum. Yield 88%. ^1H NMR (C_6D_6, 400 MHz, 333 K): δ 2.20 (d, $^4J_{P\text{-}H}$ = 4.0 Hz, CH_3, 3 H), -0.11 [s, $Al(CH_3)_2$, 6 H], -0.08 [s, $Al(CH_3)_3$, 9 H] 0.89-0.98 (m, cyclohexyl, 8 H), 1.05-7.1.14 (m, cyclohexyl, 7 H), 1.48-1.69 (m, cyclohexyl, 18 H) ppm. $^{13}C\{H\}$ NMR (C_6D_6, 100.6 MHz, 333 K): 33.7 (d, $^1J_{P\text{-}C}$ = 49.2 Hz, CH), 27.5 (d, $^2J_{P\text{-}C}$ = 12 Hz, CH_2), 27.7 (d, $^3J_{P\text{-}C}$ = 3.0 Hz, CH_2), 26.4 (CH_2), 94.7 (d, $^1J_{P\text{-}C}$ = 63.3 Hz, P=C), 25.00 (d, $^3J_{P\text{-}C}$ = 2.00 Hz, CH_3), -5.6 [$Al(CH_3)_3$], -6.7 [$Al(CH_3)_2$], 174.5 (d, $^2J_{P\text{-}C}$ = 6.0 Hz, CO) ppm. ^{31}P NMR [C_6D_6, 161.9 MHz, 333 K]: δ 22.6 ppm. The results from combustion analysis were unsatisfactory due to decomposition of **11**. Determination of the solid-state structure of **11** by X-ray crystallography was attempted. Owing to the poor quality of the collected data set, only connectivity could be confirmed (see also below).

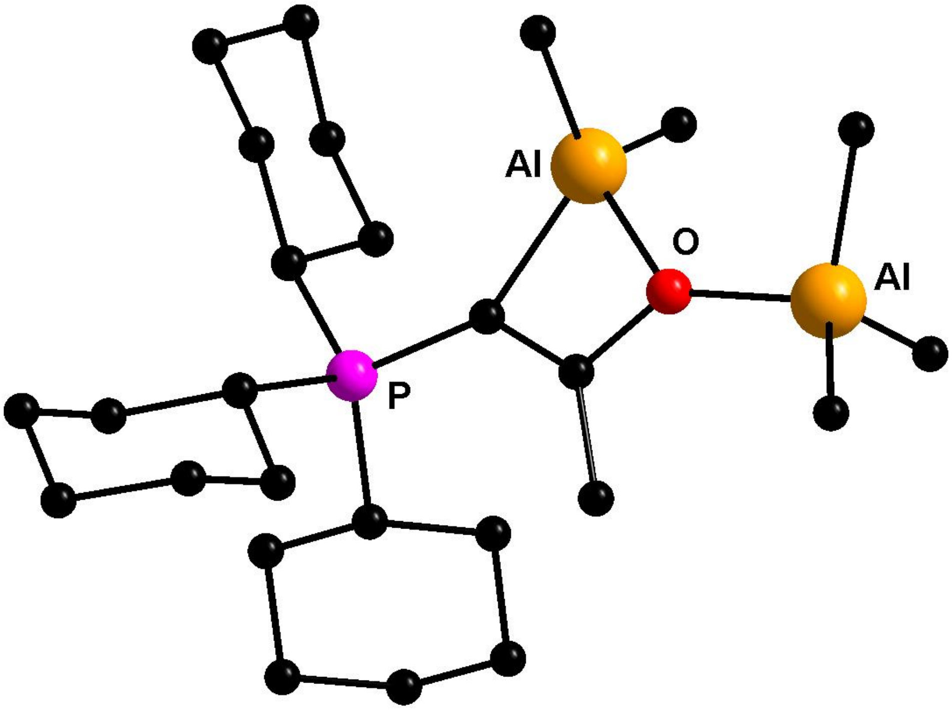


Figure S37. Solid-state structure of **11** (black = carbon, H atoms omitted).

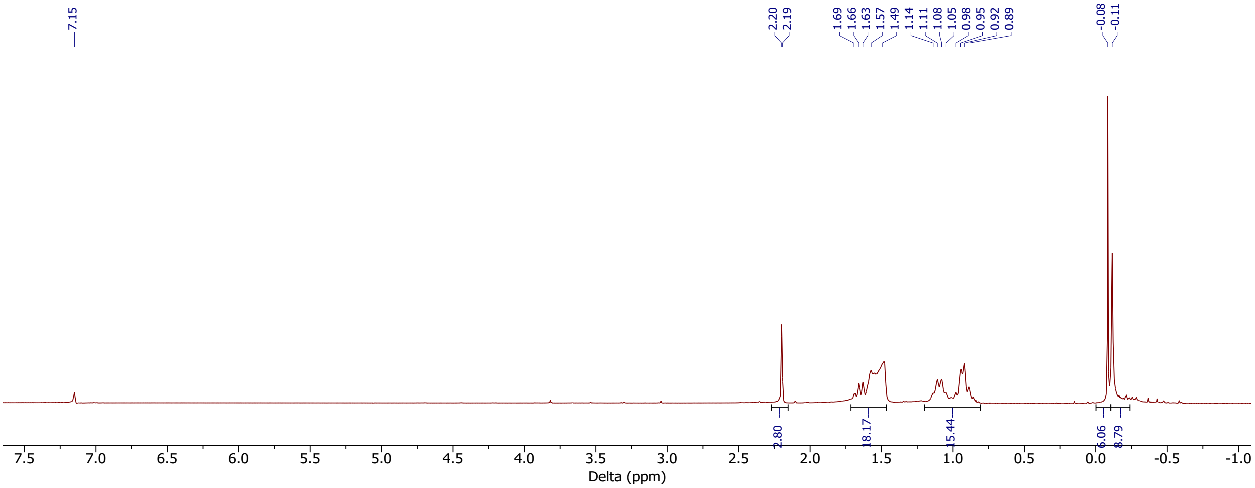


Figure S38. ^{1}H NMR spectrum of **11** in C_6D_6.

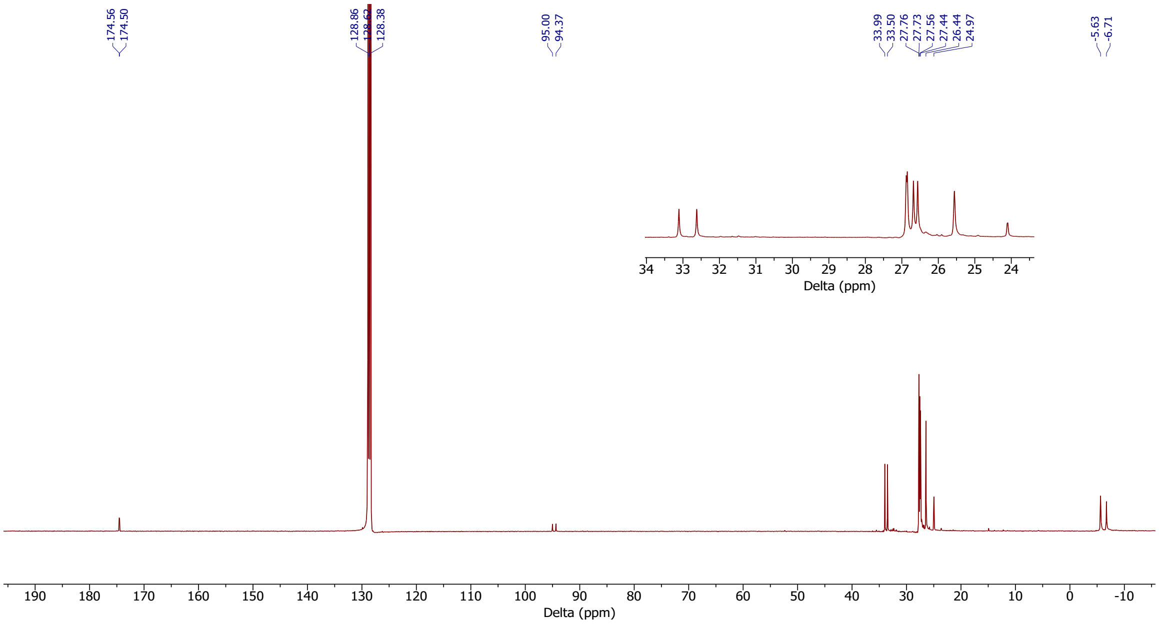


Figure S39. ^{13}C NMR spectrum of **11** in C_6D_6.

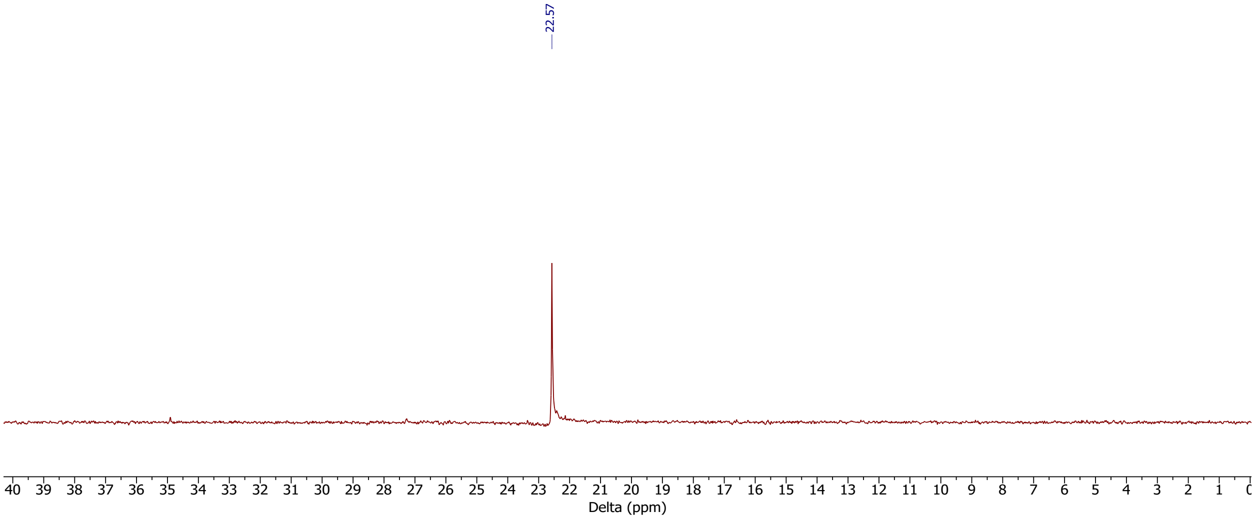


Figure S40. ^{31}P NMR spectrum of **11** in C_6D_6.

3. X-ray crystallography

X-ray diffraction data for compounds **1**, **2**, **3**, **5**, **6**, **8**, **9**, and **10** were obtained on a Bruker Smart Apex II CCD diffractometer, using graphite-monochromated Mo-Kα radiation ($\boldsymbol{\lambda}$ = 0.71073 Å) at 100 K. Intensity data were collected using ω-steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All the data were corrected for Lorentz polarization effects. A multi-scan absorption corrections were applied using SADABS [4]. Structures were solved by direct methods (SHELXS) [4] and refined by full-matrix least-squares against F^2 (SHELXL) [5]. All hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. In the structures of **3** and **7**, highly disordered interstitial solvent molecules were treated as diffuse scattering with Platon/SQUEEZE [6, 7]. For compounds **3**, **5**, **8**, and **9** the rigid-bond restraint RIGU was applied globally during the final refinements to help restrain slight positional disorder.

CCDC1881945-1881952 (**1**, **2**, **3**, **5**, **6**, **8**, **9**, **10**) contain the supplementary crystallographic data for this paper. These data can be obtained from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

[4] Krause *et al.*, **2015**, SADABS v2014/5.

[5] G. M. Sheldrick, *Acta Crystallogr.*, **2008**, *A64*, 112.

[6] A. L. Spek, *J. Appl. Cryst.* , 2003, *36*, 7.

[7] A. L. Spek, *Acta Cryst.*, **2009**, *D65*, 148.

Table 1. Crystallographic data for complexes **1-3** and **5**.

	1	**2**	**3**	**5**
Formula	$C_{20}H_{15}OP$	$C_{20}H_{33}OP$	$C_{44}H_{29}BF_{15}OP$	$C_{45}H_{41}BF_{15}OP$
Molecular weight	302.29	320.43	900.45	924.56
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	10.703(10)	14.1064(19)	11.9223(18)	11.2805(14)
b (Å)	10.124(9)	14.0310(19)	17.418(3)	13.0713(17)
c (Å)	14.561(13)	19.066(3)	19.227(3)	15.639(2)
β (°)	93.534(14)	107.466(2)	102.096(2)	110.532(2)
Volume (Å^3)	1575(2)	3599.7(8)	3904.2(10)	2065.1(5)
Z	4	8	4	2
ρ_{calcd} (g cm^{-3})	1.275	1.183	1.532	1.487
Temperature (K)	100	100	100	100
μ (mm^{-1})	0.173	0.154	0.179	0.171
Reflections collected	21843	41888	37581	21668
Unique reflections (R_{int})	3466 (0.0303)	8008 (0.0359)	7159 (0.0796)	7602 (0.0543)
R_1 [I>2σ(I)]	0.0336	0.0341	0.0507	0.0483
wR_2 (all data)	0.0857	0.0897	0.1312	0.1135
Goodness-of-fit on F^2	1.055	1.034	1.025	1.021

Table 2. Crystallographic data for complexes **6** and **8-10**.

	6	**8**	**9**	**10**
Formula	$C_{38}H_{33}AlF_{15}OP$	$C_{46}H_{37}BF_3OP$	$C_{43}H_{36}BrN_2OP$	$C_{26}H_{33}Al_2OP$
Molecular weight	848.59	704.53	707.62	446.45
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	11.1971(15)	9.7980(10)	10.3865(8)	8.6481(10)
b (Å)	15.351(2)	18.6088(18)	13.6653(10)	22.635(3)
c (Å)	21.663(3)	20.228(2)	14.2202(11)	13.7034(16)
β (°)	94.574(2)	95.8660(10)	90.9690(10)	90.665(2)
Volume (Å^3)	3711.8(9)	3528.1(6)	1790.3(2)	2682.3(5)
Z	4	4	2	4
ρ_{calcd} (g cm^{-3})	1.519	1.326	1.313	1.106
Temperature (K)	100	100	100	100
μ (mm^{-1})	0.205	0.131	1.229	0.182
Reflections collected	39040	55003	31758	28610
Unique reflections (R_{int})	7615 (0.0335)	12997 (0.1132)	7925 (0.0320)	5483 (0.0321)
R_1 [$I>2\sigma(I)$]	0.0348	0.0539	0.0312	0.0407
wR_2 (all data)	0.0850	0.1334	0.0789	0.1126
Goodness-of-fit on F^2	1.012	0.977	1.034	1.043

4. Computational data

Quantum chemical calculations based on density functional theory (DFT) were carried out for geometry optimization and frequency calculations of **1** and **2**. Calculations were performed by means of the B3-LYP [8] functional and the triple-ζ valence polarization basis set (def2-TZVP) [9] using the Turbomole [10] program suite. Dispersion interactions were explicitly included in the calculations by using the empirical formalism D3 developed by Grimme [11]. The C=C=O stretching frequency values were corrected by a scale factor of 0.9662 [12].

Table 3. Calculated distances, angles and C=C=O stretching frequencies of the central PCCO units of **1** and **2**.

Comp.	Distance [Å]			Angle [°]		Frequency [cm^{-1}]	
	P-C	C-C	C-O	P-C-C	C-C-O	C=C=O asym.	C=C=O sym.
1	1.648	1.272	1.177	140.8	176.1	2128	1448
2	1.653	1.269	1.181	144.1	176.3	2126	1448

Cartesian coordinates of **1**:

P	0.5723174	0.0943782	0.0827289
O	3.5071691	1.1011434	2.4270248
C	2.1078554	0.5182362	0.5054225
C	2.8019962	0.8160127	1.5287914
C	0.1901208	0.6298705	-1.6151010
C	0.9792061	1.6190834	-2.2022931
H	1.8230527	2.0154508	-1.6513790
C	0.6889703	2.0732554	-3.4840129
H	1.3077075	2.8387867	-3.9351513
C	-0.3877424	1.5424814	-4.1858307
H	-0.6110046	1.8950466	-5.1851842
C	-1.1742401	0.5507103	-3.6065594

H	-2.0078801	0.1284855	-4.1535645
C	-0.8865443	0.0942513	-2.3267657
H	-1.4969028	-0.6854478	-1.8894298
C	-0.7364282	0.7880984	1.1489348
C	-0.7105317	0.4565038	2.5079292
H	0.0494879	-0.2171606	2.8852662
C	-1.6477748	0.9943000	3.3773921
H	-1.6192796	0.7324588	4.4275486
C	-2.6167269	1.8747074	2.9013806
H	-3.3449377	2.2981466	3.5818543
C	-2.6434374	2.2130973	1.5543574
H	-3.3912119	2.9017692	1.1812095
C	-1.7075088	1.6714300	0.6779235
H	-1.7354724	1.9435016	-0.3686646
C	0.2925790	-1.7093139	0.1002422
C	-0.9716009	-2.2617075	0.3187791
H	-1.8171919	-1.6197417	0.5306613
C	-1.1465823	-3.6406076	0.2872359
H	-2.1280934	-4.0622471	0.4646861
C	-0.0621563	-4.4750073	0.0377224
H	-0.1990266	-5.5490933	0.0164639
C	1.2005178	-3.9292027	-0.1731034
H	2.0486645	-4.5767422	-0.3568158
C	1.3796783	-2.5522381	-0.1397803
H	2.3626852	-2.1212682	-0.2835935

Cartesian coordinates of **2**:

P	-5.1969014	2.5961084	13.4050748
O	-8.1711186	4.8302473	12.1407374
C	-6.1990692	3.9028816	13.2566878
C	-7.2251124	4.3489669	12.6588374

C	-3.7456284	3.0772663	14.4371154
C	-3.0306122	4.3172318	13.8732242
C	-1.9440567	4.8033194	14.8383710
C	-0.9445836	3.6918910	15.1710143
C	-1.6556373	2.4471098	15.7076051
C	-2.7377674	1.9568735	14.7378741
C	-4.5018012	1.9614072	11.7939128
C	-4.1139669	0.4706321	11.7822130
C	-3.4250739	0.0976631	10.4640435
C	-4.3029718	0.4384663	9.2576939
C	-4.7179525	1.9114109	9.2754314
C	-5.4017596	2.2943764	10.5914563
C	-6.0046614	1.1701088	14.2652291
C	-7.2909100	0.7603985	13.5243934
C	-7.9924762	-0.4097597	14.2204651
C	-8.2934439	-0.0884834	15.6853152
C	-7.0191175	0.3154565	16.4284710
C	-6.3075835	1.4861071	15.7409128
H	-4.2163795	3.3815762	15.3787162
H	-2.5642466	4.0702771	12.9124757
H	-3.7592034	5.1057837	13.6809430
H	-1.4263693	5.6640301	14.4071220
H	-2.4180794	5.1538774	15.7622510
H	-0.2062365	4.0471272	15.8947450
H	-0.3899147	3.4242303	14.2635244
H	-2.1218513	2.6824002	16.6713295
H	-0.9352026	1.6463762	15.8944165
H	-3.2369477	1.0780050	15.1528714
H	-2.2570126	1.6389277	13.8067677
H	-3.5797515	2.5429883	11.6771220
H	-3.4622748	0.2231002	12.6213812

H	-5.0138575	-0.1414175	11.8920978
H	-2.4766131	0.6418695	10.3883223
H	-3.1765265	-0.9672200	10.4675948
H	-3.7785947	0.2005532	8.3284628
H	-5.2018085	-0.1887995	9.2805454
H	-5.3848618	2.1303290	8.4377178
H	-3.8287288	2.5386170	9.1391208
H	-6.3487275	1.7532417	10.6795941
H	-5.6511361	3.3553174	10.5957330
H	-5.2965522	0.3357213	14.2279695
H	-7.9630134	1.6228395	13.4882765
H	-7.0718664	0.4951685	12.4881585
H	-8.9145155	-0.6535283	13.6859255
H	-7.3538250	-1.2995246	14.1680538
H	-8.7629060	-0.9455283	16.1751374
H	-9.0146241	0.7357182	15.7317017
H	-6.3388456	-0.5439740	16.4718590
H	-7.2485023	0.5842419	17.4630728
H	-5.3865836	1.7149479	16.2820327
H	-6.9361128	2.3804772	15.7891728

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5. IR and Raman data

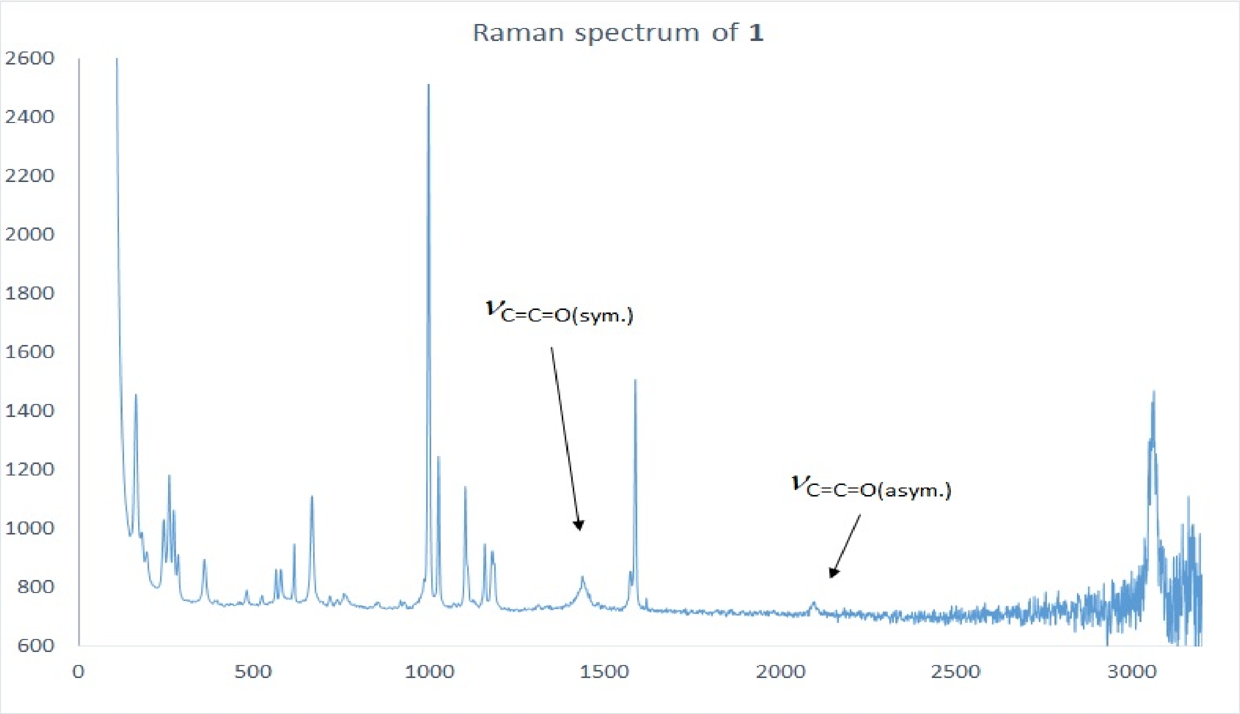


Figure S41. Raman spectrum of **1** (conditions: 785 nm, 25 mW, 5 s).

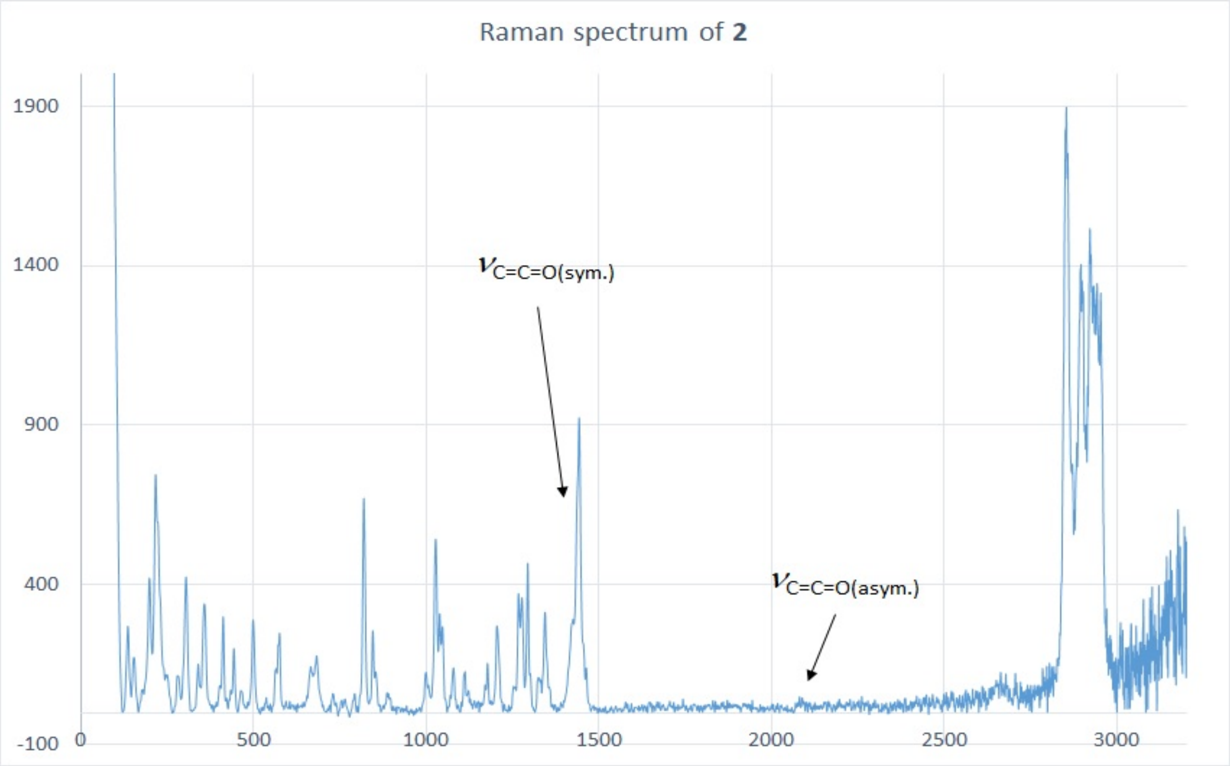


Figure S42. Raman spectrum of **2** (conditions: 785 nm, 25 mW, 5 s).

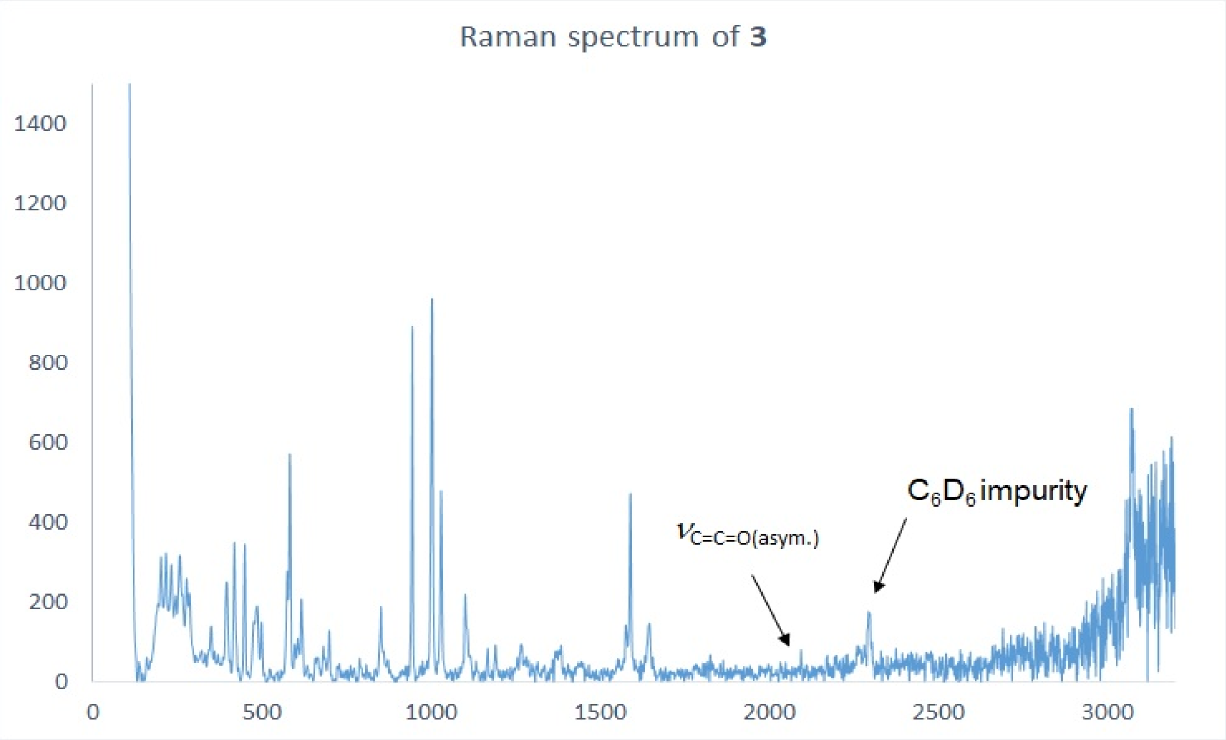


Figure S43. Raman spectrum of **3** (conditions: 785 nm, 25 mW, 20 s).

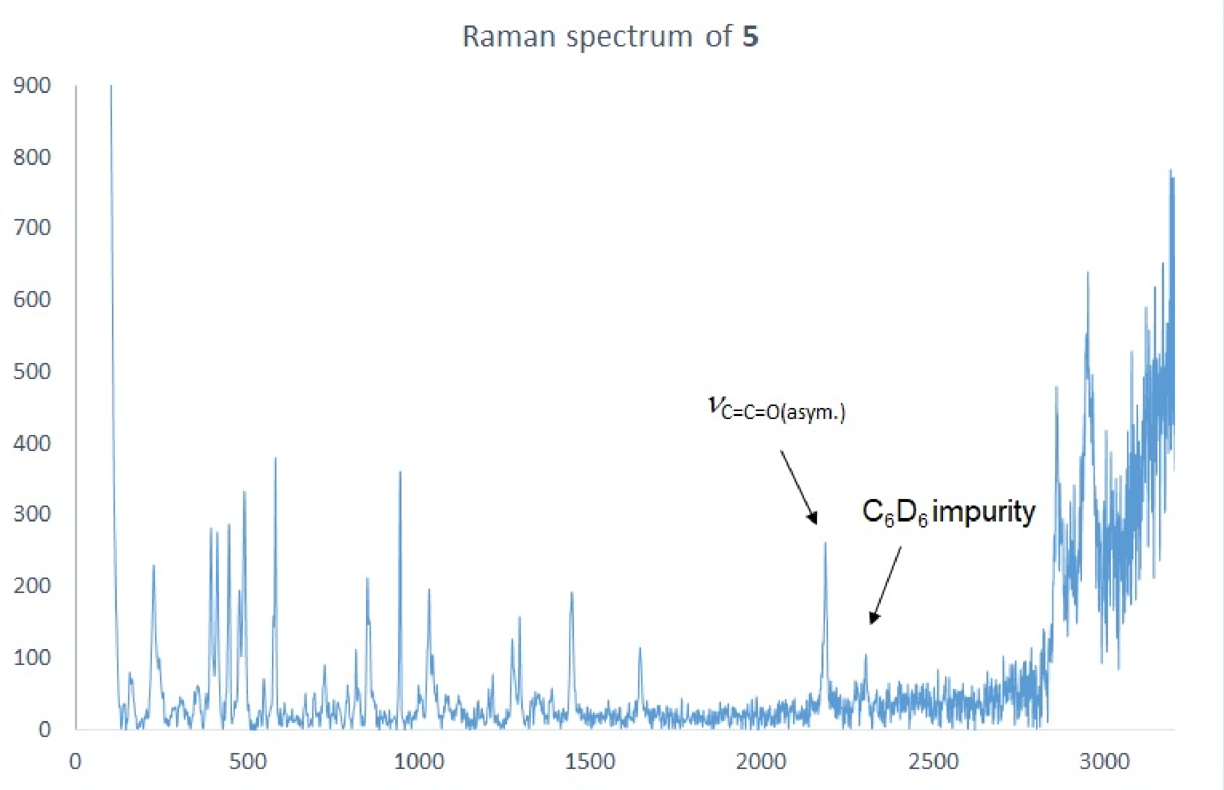


Figure S44. Raman spectrum of **5** (conditions: 785 nm, 25 mW, 20 s).

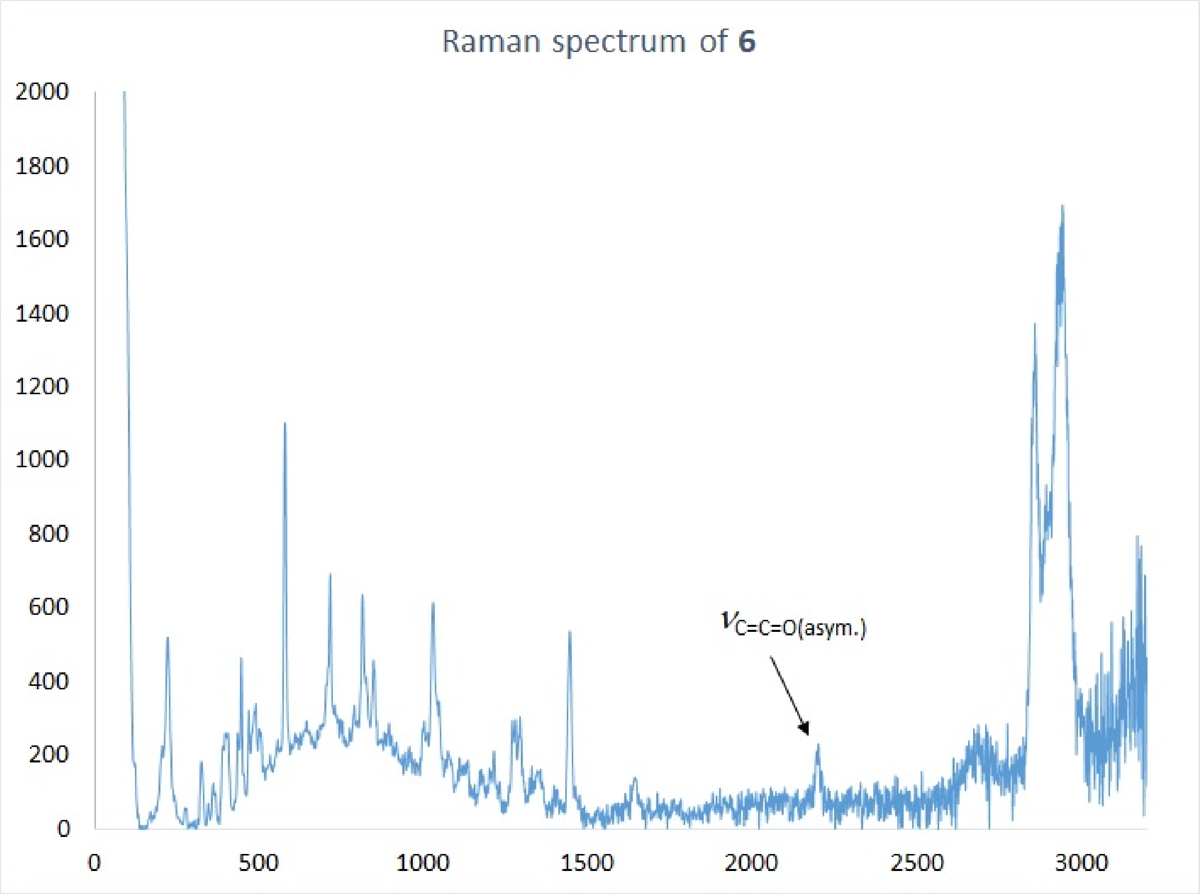
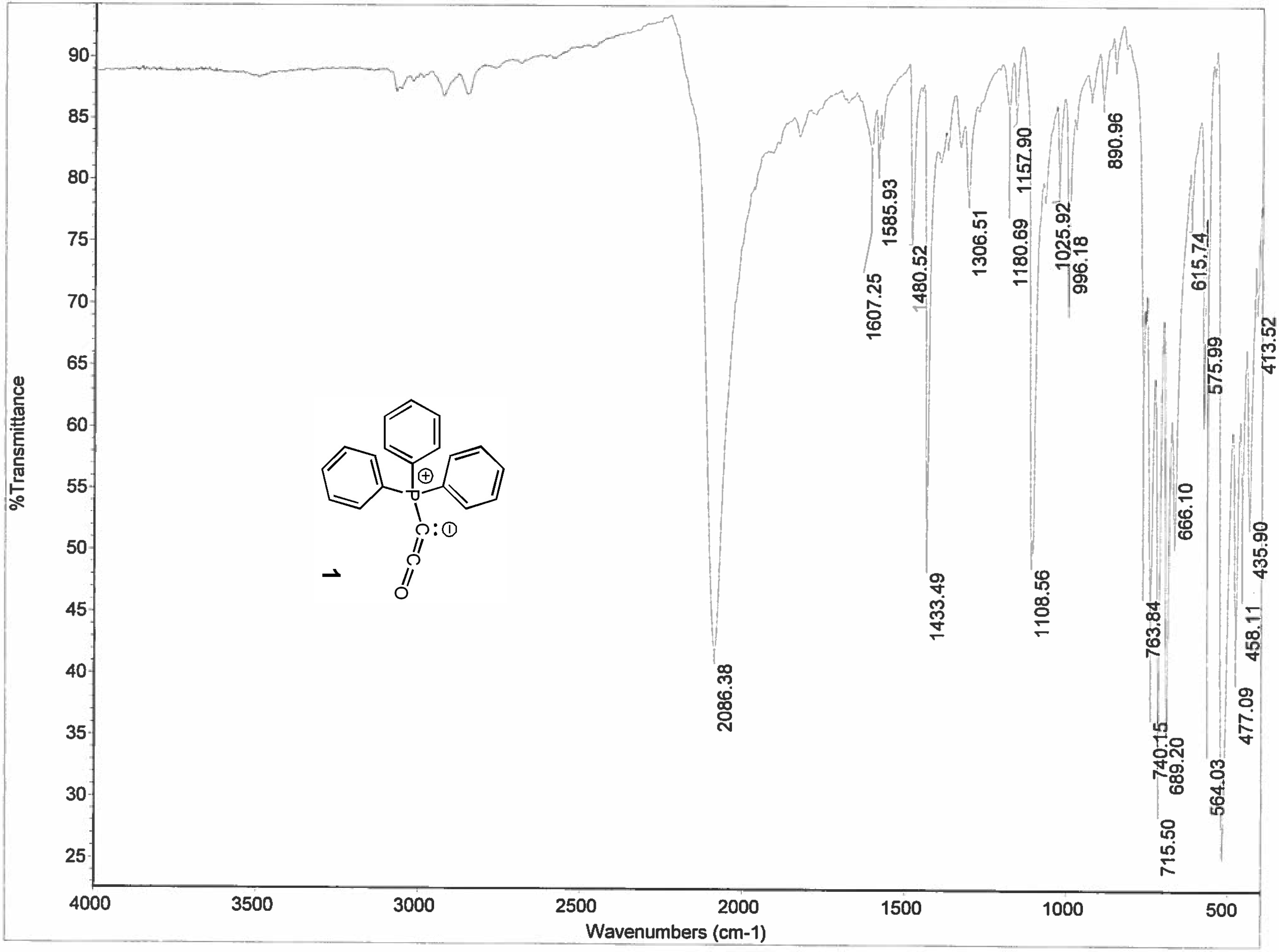


Figure S45. Raman spectrum of **6** (conditions: 785 nm, 25 mW, 20 s).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75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
2086.38
1607.25
1585.93
1480.52
1433.49
1306.51
1180.69
1157.90
1108.56
1025.92
996.18
890.96
763.84
740.15
715.50
689.20
666.10
615.74
575.99
564.03
477.09
458.11
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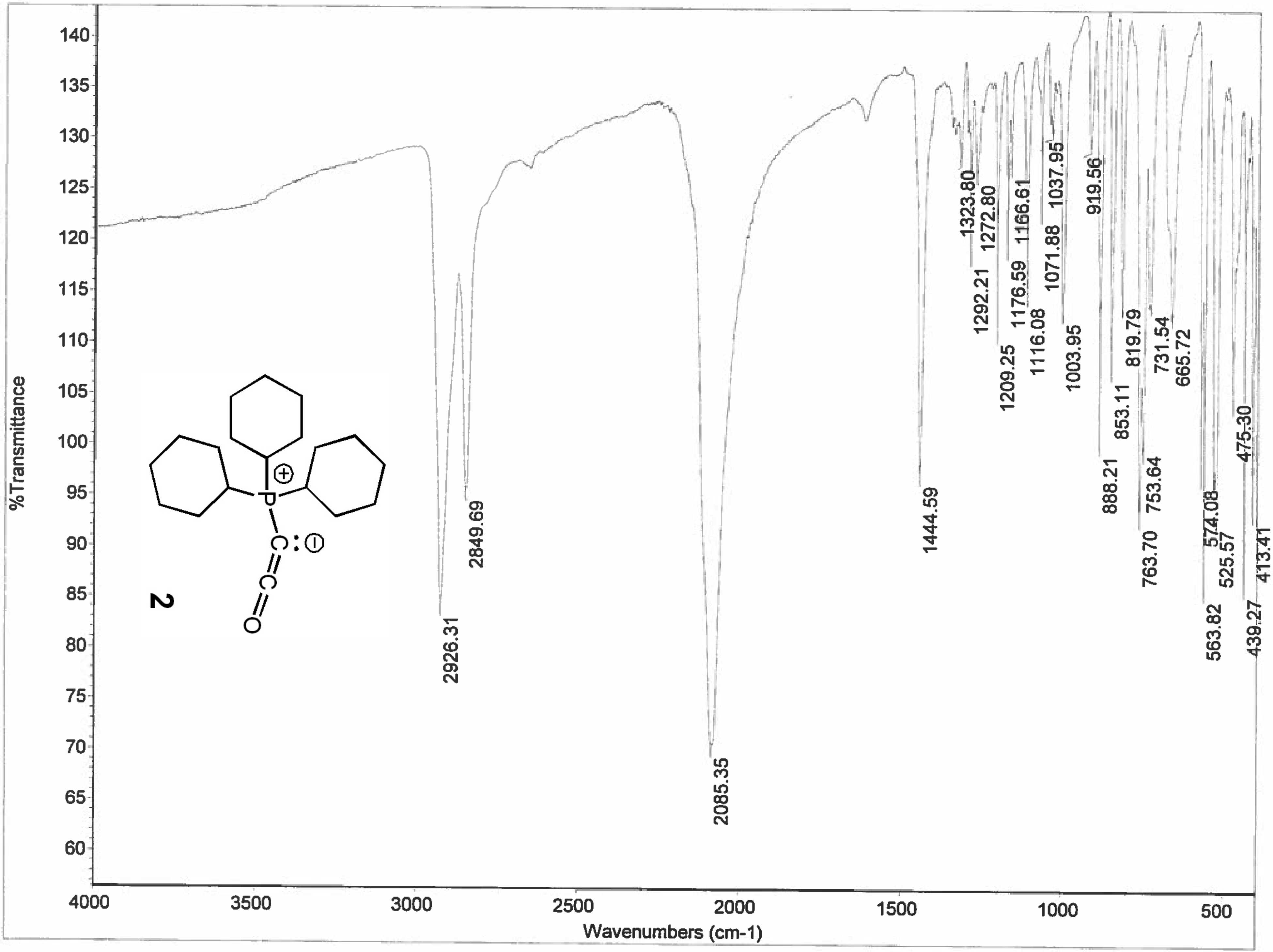
413.52
P
C
C
O
1



2

%Transmittance
Wavenumbers (cm-1)
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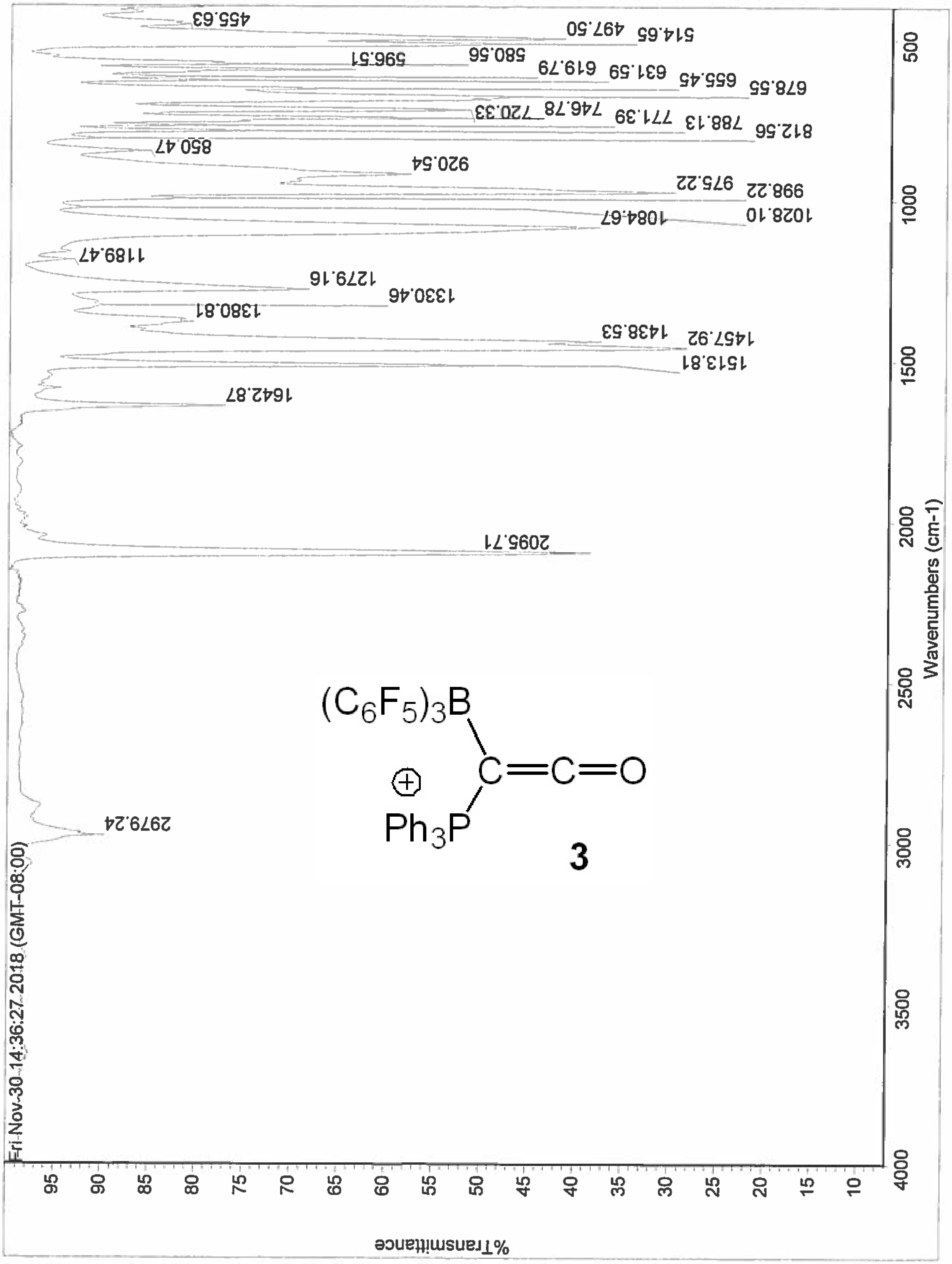
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
4000
3500
3000
2500
2000
1500
1000
500
2926.31
2849.69
2085.35
1444.59
1323.80
1292.21
1272.80
1209.25
1176.59
1166.61
1116.08
1071.88
1037.95
1003.95
919.56
888.21
853.11
819.79
763.70
753.64
731.54
665.72
574.08
563.82
525.57
475.30
439.27
413.41
P
C
C
O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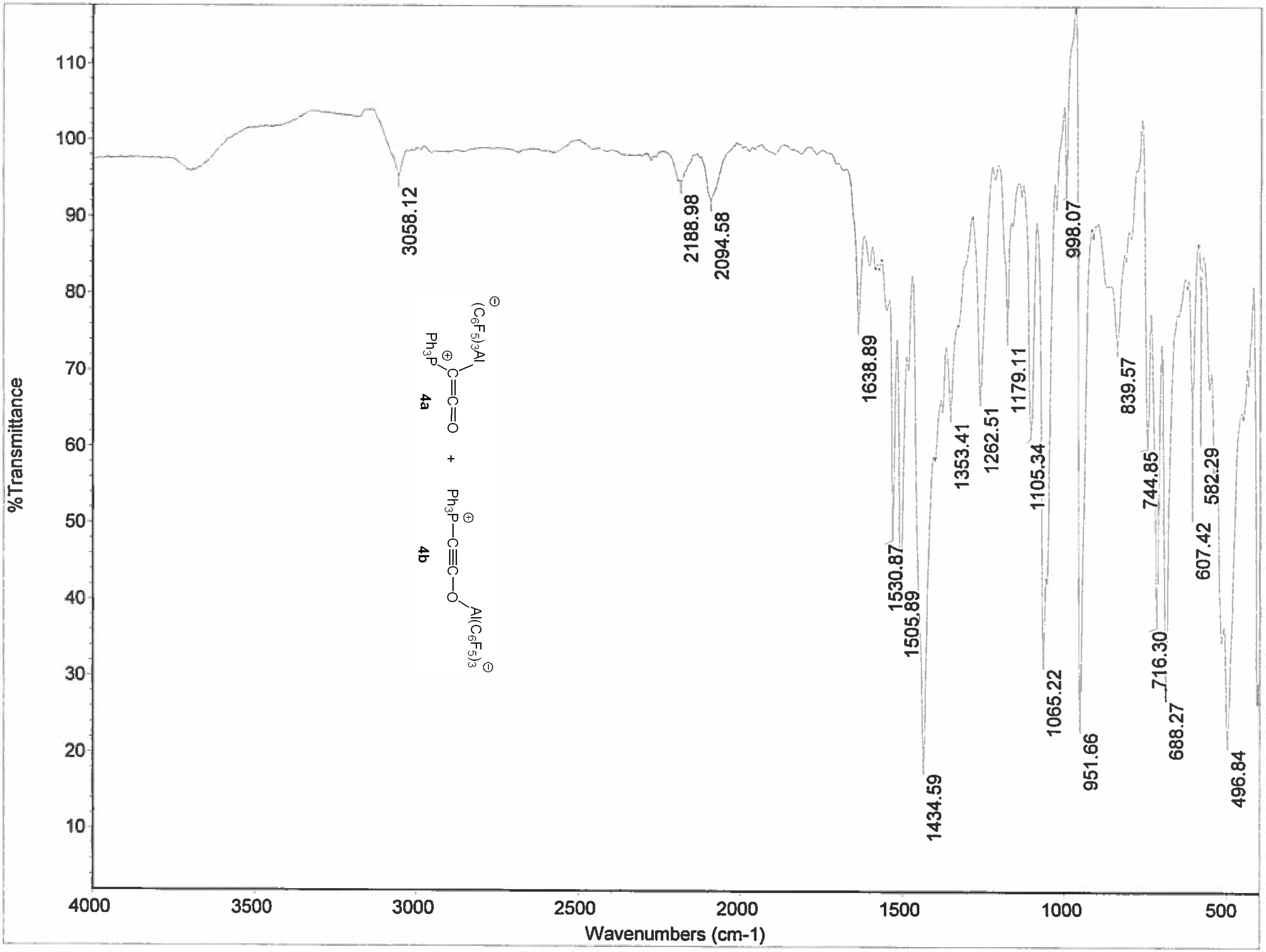
65
60
55
50
45
40
35
30
25
20
15
10
4000
3500
3000
2500
2000
1500
1000
500
2979.24
2095.71
1642.87
1513.81
1457.92
1438.53
1380.81
1330.46
1279.16
1189.47
1084.67
1028.10
998.22
975.22
920.54
850.47
812.56
788.13
771.39
746.78
720.33
678.55
655.45
631.59
619.79
596.51
580.56
514.65
497.50
455.63
$(C_6F_5)_3B$
C=C=O
Ph_3P
⊕
3

3Y+AlCF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20
10
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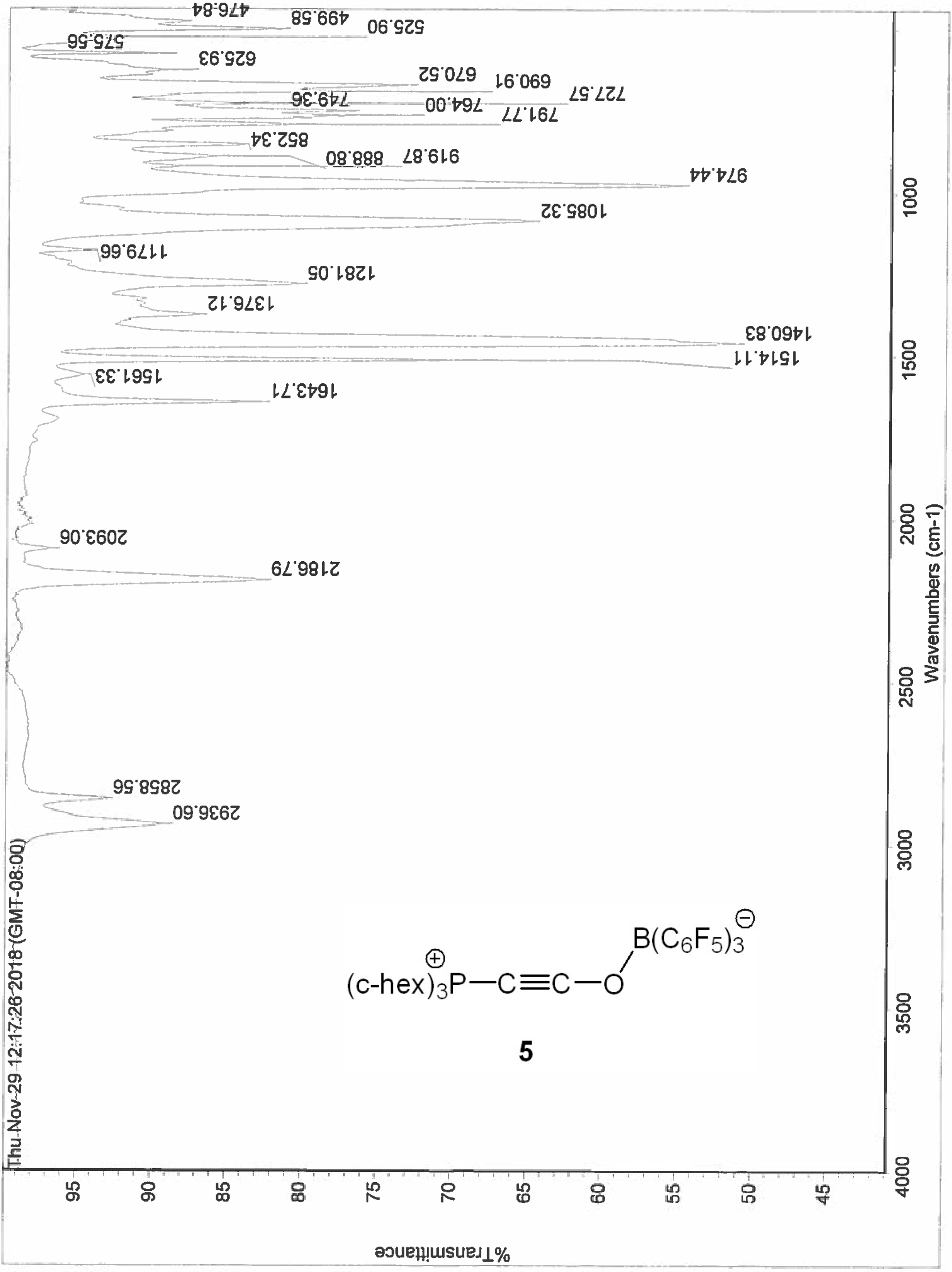
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3058.12
2188.98
2094.58
1638.89
1530.87
1505.89
1434.59
1353.41
1262.51
1179.11
1105.34
1065.22
998.07
951.66
839.57
744.85
716.30
688.27
607.42
582.29
496.84
(C6F5)3Al
Ph3P
4a
+
Ph3P
Al(C6F5)3
4b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3000
2500
2000
1500
1000
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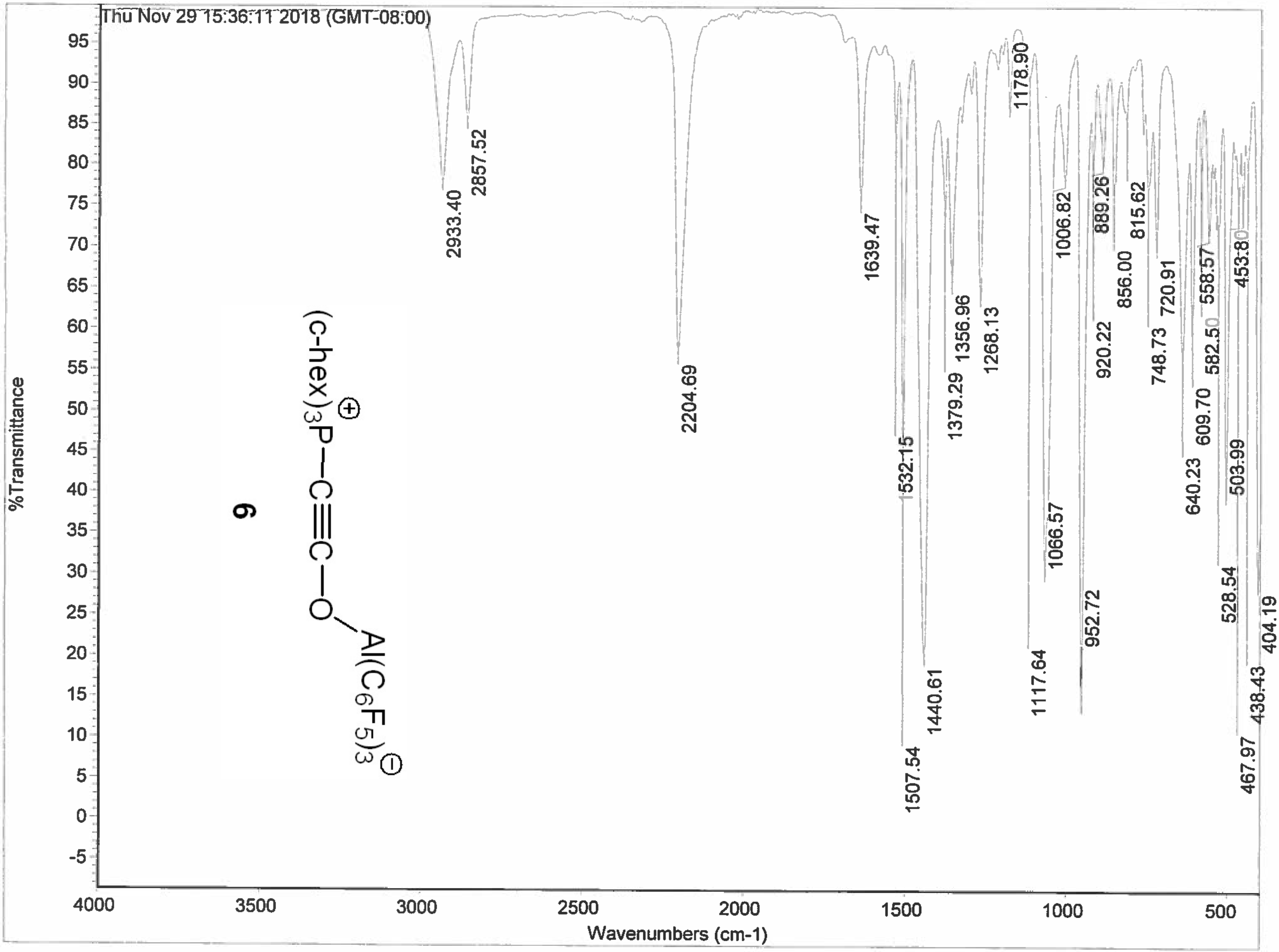
2858.56
2186.79
2093.06
1643.71
1561.33
1514.11
1460.83
1376.12
1281.05
1179.66
1085.32
974.44
919.87
888.80
852.34
791.77
764.00
749.36
727.57
690.91
670.52
625.93
575.56
525.90
499.58
476.84
(c-hex)$_3$P$^{\oplus}$—C≡C—O—B(C$_6$F$_5$)$_3^{\ominus}$

5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30
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20
15
10
5
0
-5
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
2933.40
2857.52
2204.69
1639.47
1532.15
1507.54
1440.61
1379.29
1356.96
1268.13
1178.90
1117.64
1066.57
1006.82
952.72
920.22
889.26
856.00
815.62
748.73
720.91
640.23
609.70
582.50
558.57
528.54
503.99
467.97
453.80
438.43
404.19
(c-hex)3P—C≡C—O—Al(C6F5)3
6