Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis of an expanded pincer ligand and its bimetallic coinage metal complexes

Supplementary information

Andie R Delaney, Li-Juan Yu, Michelle L Coote, Annie L Colebatch

Table of contents

Synthetic procedures:

Synthesis of [Cu_2(μ-Cl)$_2$(tBu-PONNOP)] (**1a**): **L** (70.7 mg, 0.157 mmol) and CuCl (32.3 mg, 0.326 mmol) were added to a 10 mL J. Young flask. THF (3 mL) was added and the suspension stirred for 4 hours. The reaction was filtered and the solid extracted with DCM (3 mL). Solvent was removed in vacuo to give **1a** as an orange powder (33.0 mg, 0.051 mmol, 33%). ^{1}H NMR (d_2-DCM, 400 MHz): δ = 1.33 (d, $^3J_{PH}$ = 14.6 Hz, 36 H, CH_3), 7.12 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, H3/6), 8.19 (d, $^3J_{HH}$ = 8.6 Hz, 4 H, H4/5). ^{31}P{^{1}H} NMR (d_2-DCM, 162 MHz): δ_P = 131.1 (br s). ^{13}C{^{1}H} NMR (d_2-DCM, 151 MHz): δ_C = 27.4 (d, $^2J_{PC}$ = 10.6 Hz, CH_3), 36.8 (s, *t*Bu-C), 112.7 (s, C3/6), 117.9 (s, C4a), 141.4 (s, C4/5), 149.9 (s, C8a), 164.6 (s, C2/7). MS (ESI+): 611.1 [M–Cl]$^+$.

Synthesis of [Ag_2(NCMe)$_2$(tBu-PONNOP)][PF_6]$_2$ (**5b**) : A solution of **L** (51.4 mg, 0.114 mmol) in MeCN (5 mL) was transferred via cannula into a flask containing $AgPF_6$ (66.6 mg, 0.263 mmol). The mixture was stirred for 3 hours before removing solvent in vacuo. DCM (3 mL) was added, causing precipitation of a brown solid that was removed through filtration. The yellow filtrate was put under vacuum with heating to 40˚C to give (**5b**) as an oily yellow solid (63.7 mg, 0.06 mmol, 54% [based on formulation with two bound molecules of MeCN]). ^{1}H NMR (d_2-DCM, 800 MHz): δ = 1.38 (d, $^3J_{PH}$ = 14.9 Hz, 36 H, CH_3), 2.36 (s, 8H, MeCN), 7.31 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, H3/6), 8.45 (d, $^3J_{HH}$ = 8.6 Hz, 4 H, H4/5). ^{31}P{^{1}H} NMR (d_2-DCM, 162 MHz): δ_P = −144.5 (h, $^1J_{PF}$ = 706.6 Hz, PF_6), 143.2 (br d, $^1J_{AgP}$ ≈ 647 Hz, *t*Bu-PONNOP). ^{19}F{^{1}H} NMR (d_2-DCM, 376 MHz) = −72.9 (d, $^1J_{PF}$ = 706.4 Hz). ^{13}C{^{1}H} NMR (d_2-DCM, 201 MHz): δ_C = 2.87 (s, MeCN-CH_3), 27.3 (d, $^2J_{PC}$ = 10.7 Hz, CH_3), 37.4 (d, $^1J_{PC}$ = 4.6 Hz, *t*Bu-C), 114.9 (s, C3/6), 119.2 (s, C4a), 122.6 (s, MeCN-C), 143.3 (s, C4/5), 150.7 (s, C8a), 164.4 (s, C2/7). MS (ESI+): 701.1 [M–2PF_6+Cl]$^+$.

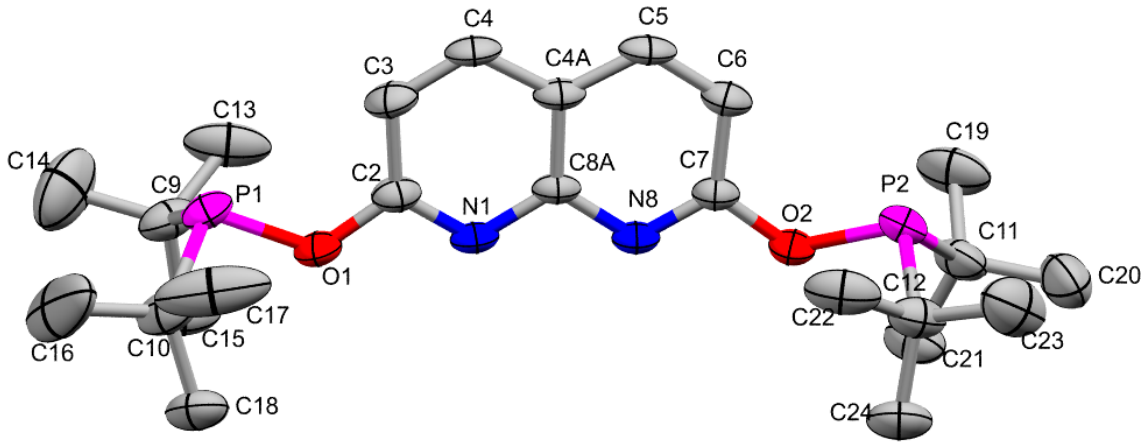

Figure S1. Solid-state structure of **L** (50% displacement ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): P1–O1 1.673(4), P2–O2 1.681(4), O1–C2 1.367(6), O2–C7 1.376(6), P1–C9 1.864. P1–C10 1.865(5), P2–C11 1.862(6), P2–C12 1.854(5), N1–C2 1.311(7), N1–C8A 1.360(6), N8–C7 1.303(6), N8–C8A 1.369(7), C2–C3 1.424(7), C3–C4 1.357(7), C4–C4A 1.412(8), C4A–C5 1.405(7), C5–C6 1.362(8), C6–C7 1.419(6), C2–O1–P1 124.8(3), C7–O2–P2 123.8(3), O1–P1–C9 98.6(2), O1–P1–C10 95.9(2), C9–P1–C10 112.8(3), O2–P2–C11 96.7(2), O2–P2–C12 99.6(2), C11–P2–C12 113.3(3).

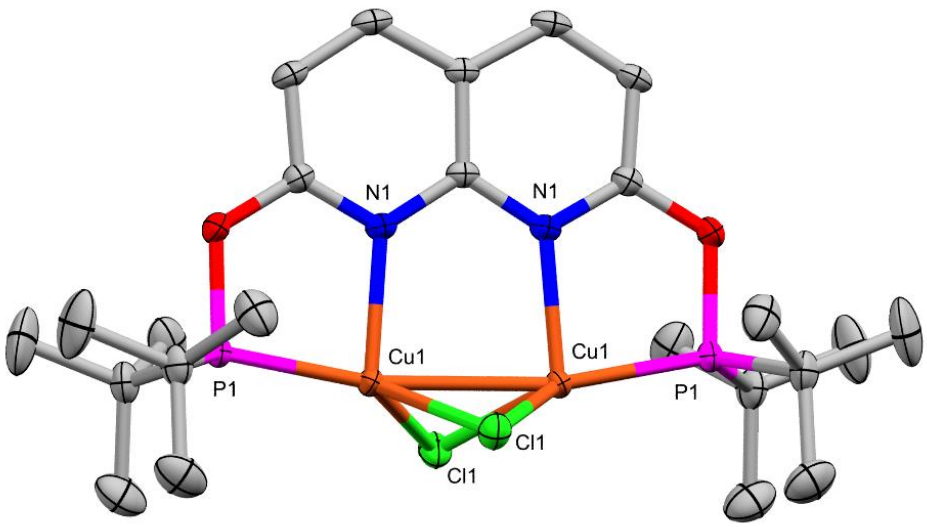

Figure S2. Solid-state structure of **1a** (50% displacement ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): Cu1–Cl1 2.3488(6), Cu1–N1 2.135(3), Cu1–P1 2.1614(6), Cu1···Cu1 2.6251(4), P1–Cu1–N1 83.77(6), P1–Cu1–Cl1 127.63(3), Cl1–Cu1–Cl1 98.82(3).

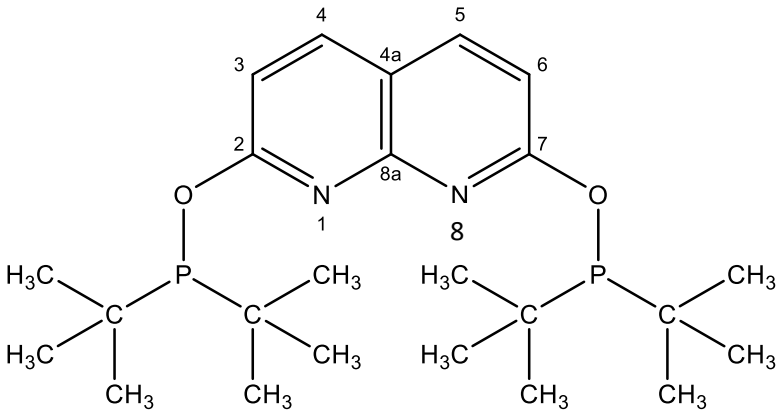

Figure S3. Numbering scheme used in all NMR assignments.

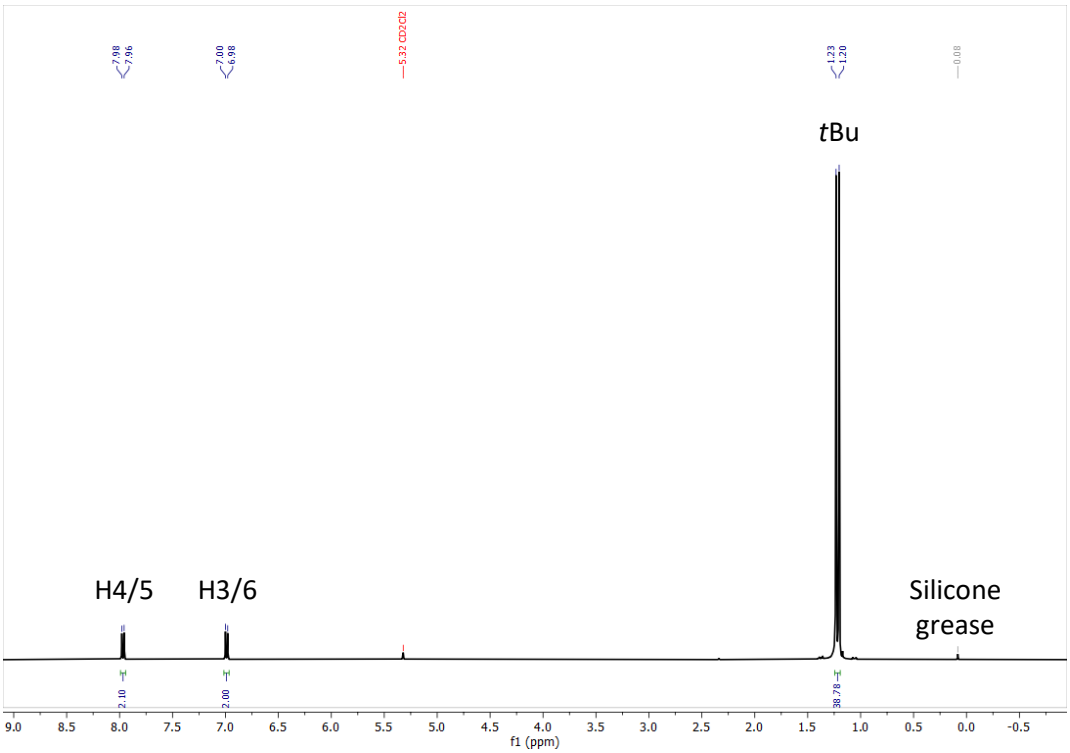

Figure S4. ^{1}H NMR spectrum of **L**. (CD_2Cl_2, 400 MHz, 298 K)

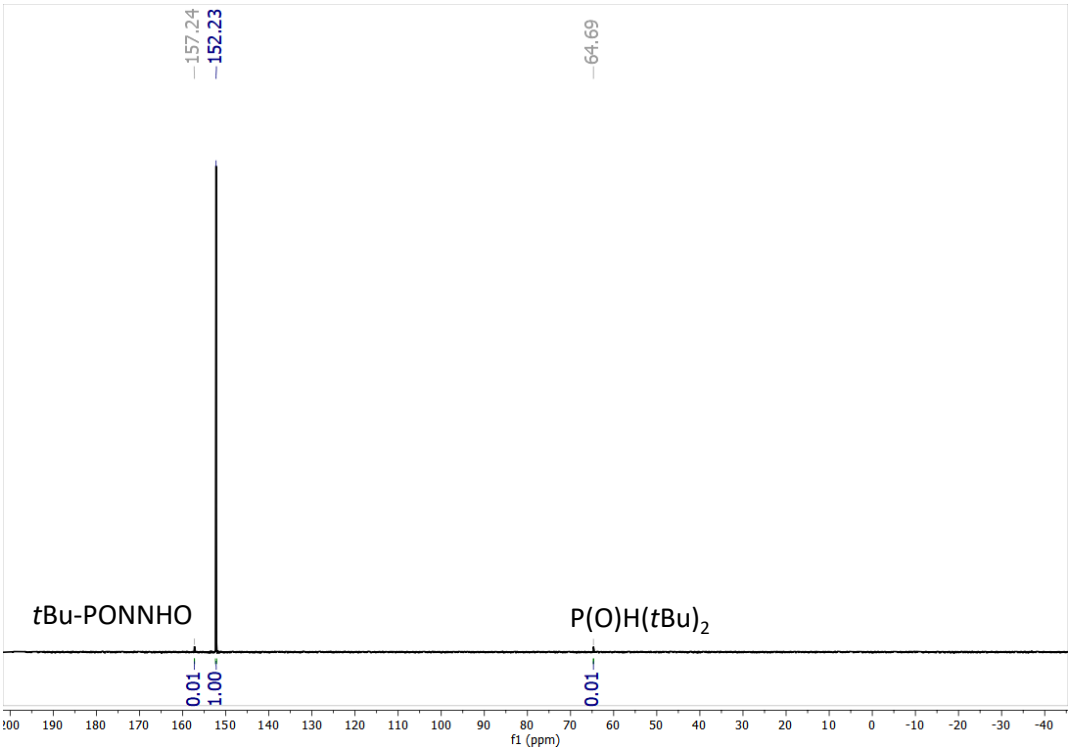

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **L**. (CD_2Cl_2, 162 MHz, 298 K). Vey small amounts of decomposition to tBu-PONNHO and P(O)H(*t*Bu)$_2$ are noted.

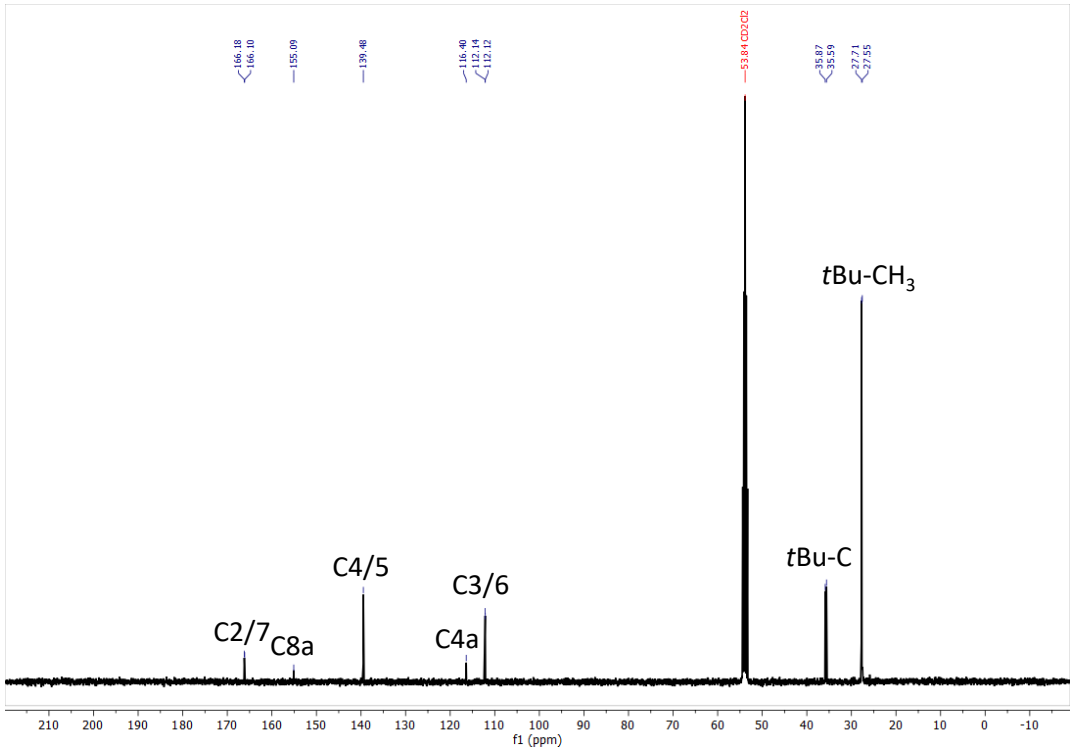

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **L**. (CD_2Cl_2, 101 MHz, 298 K)

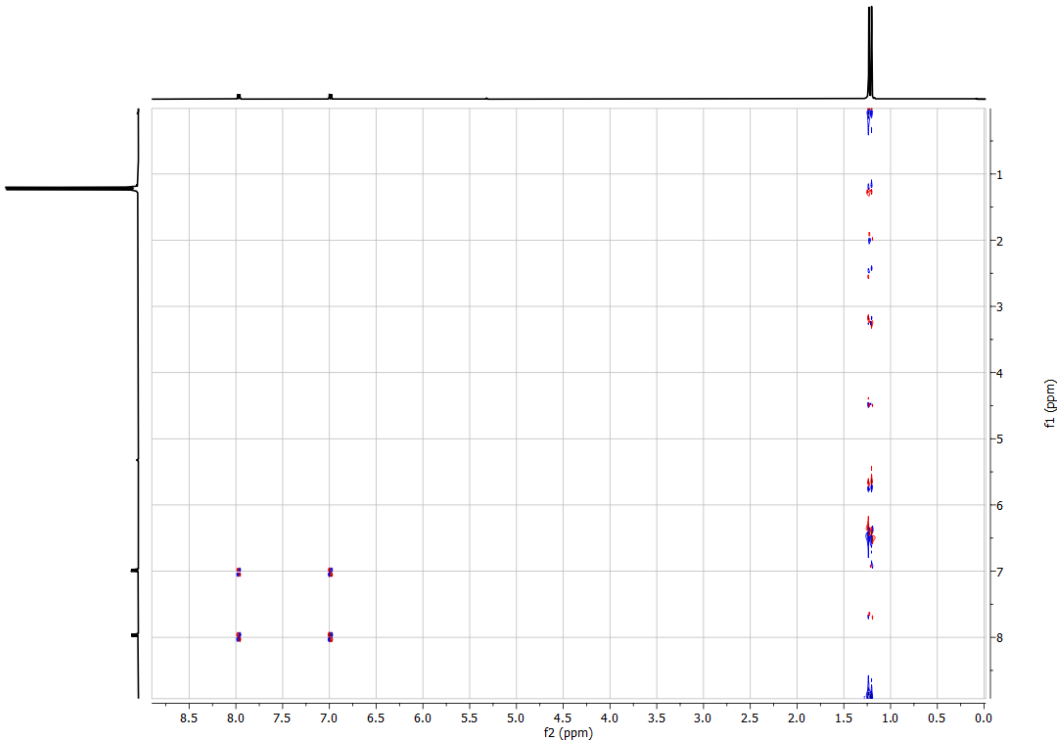

Figure S7. ^{1}H-^{1}H COSY NMR spectrum of **L**. (CD_2Cl_2, 400 MHz, 298 K)

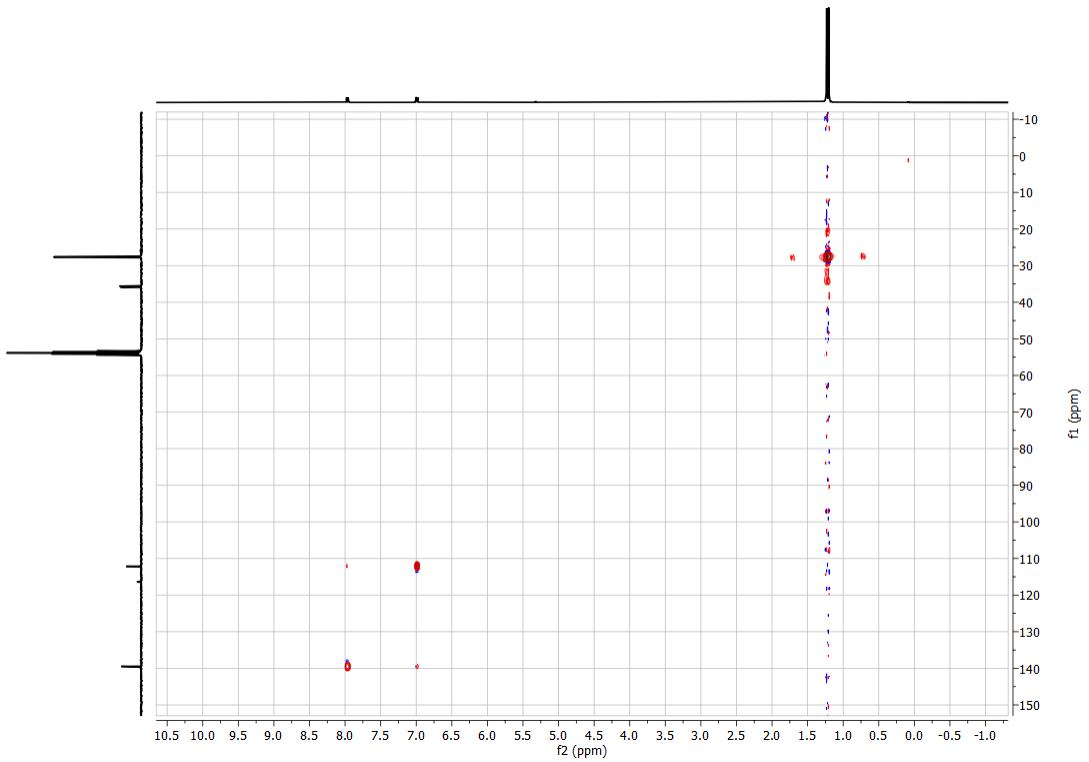

Figure S8. ^{1}H-^{13}C HSQC NMR spectrum of **L**. (CD_2Cl_2, 400, 101 MHz, 298 K)

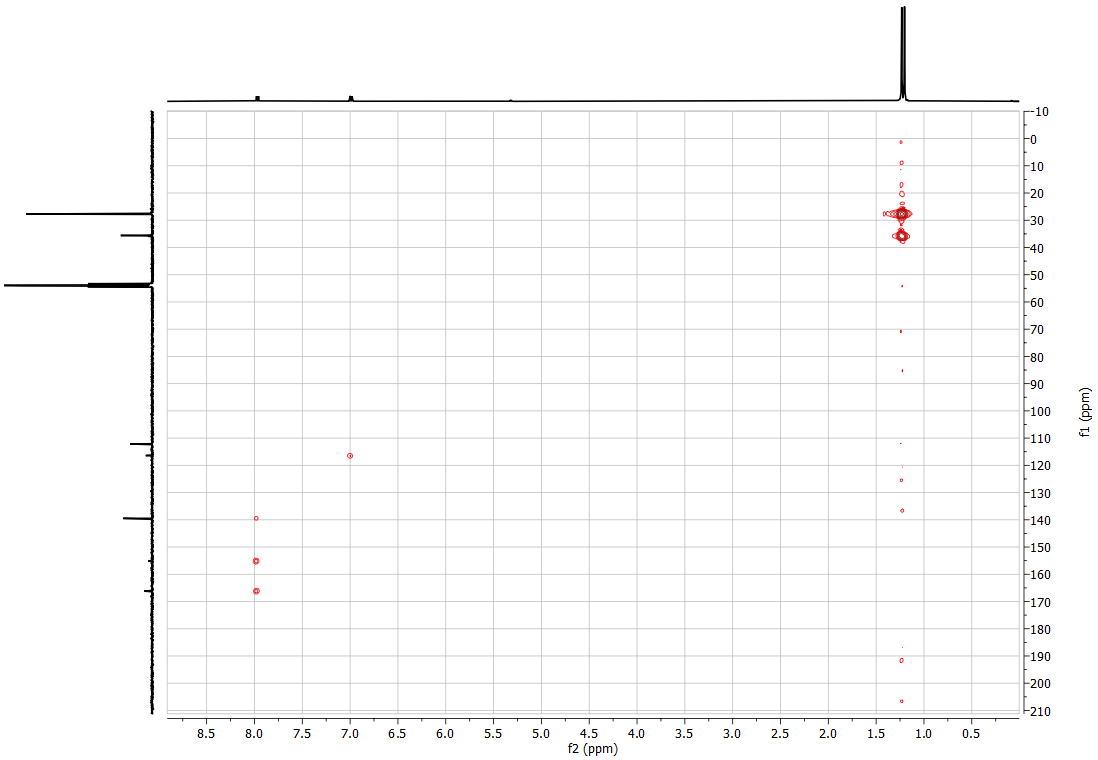

Figure S9. ^{1}H-^{13}C HMBC NMR spectrum of **L**. (CD_2Cl_2, 400, 101 MHz, 298 K)

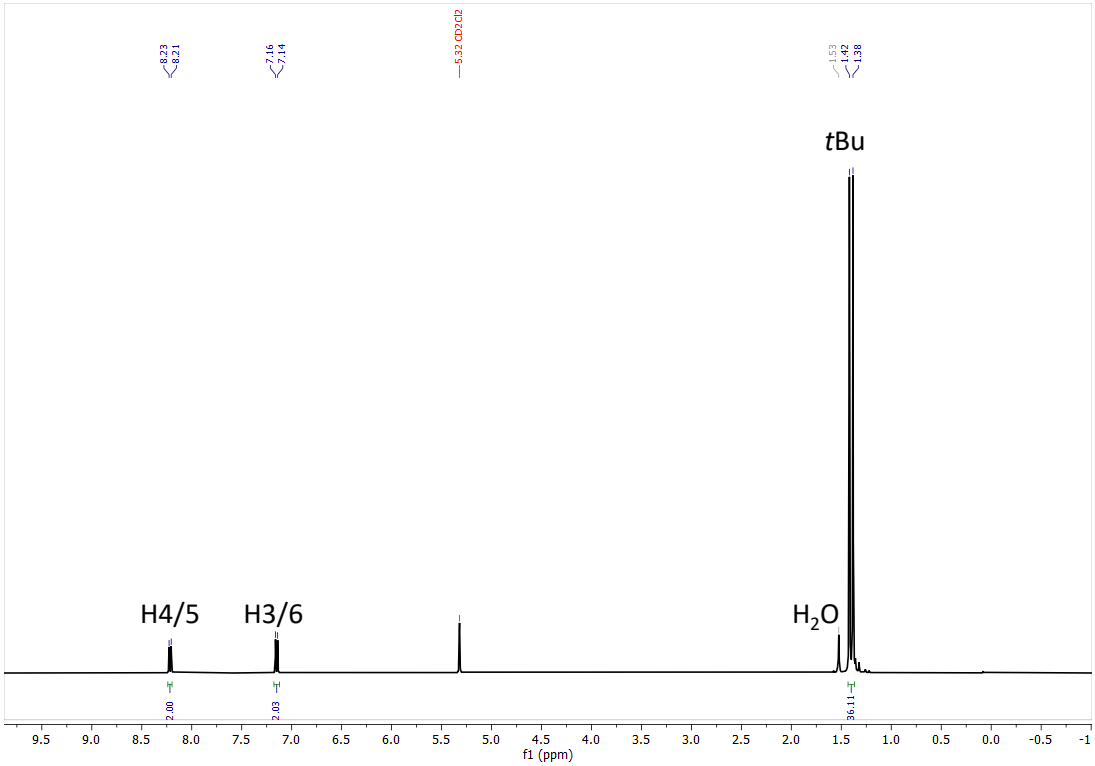

Figure S10. ^{1}H NMR spectrum of **1**. (CD_2Cl_2, 400 MHz, 298 K)

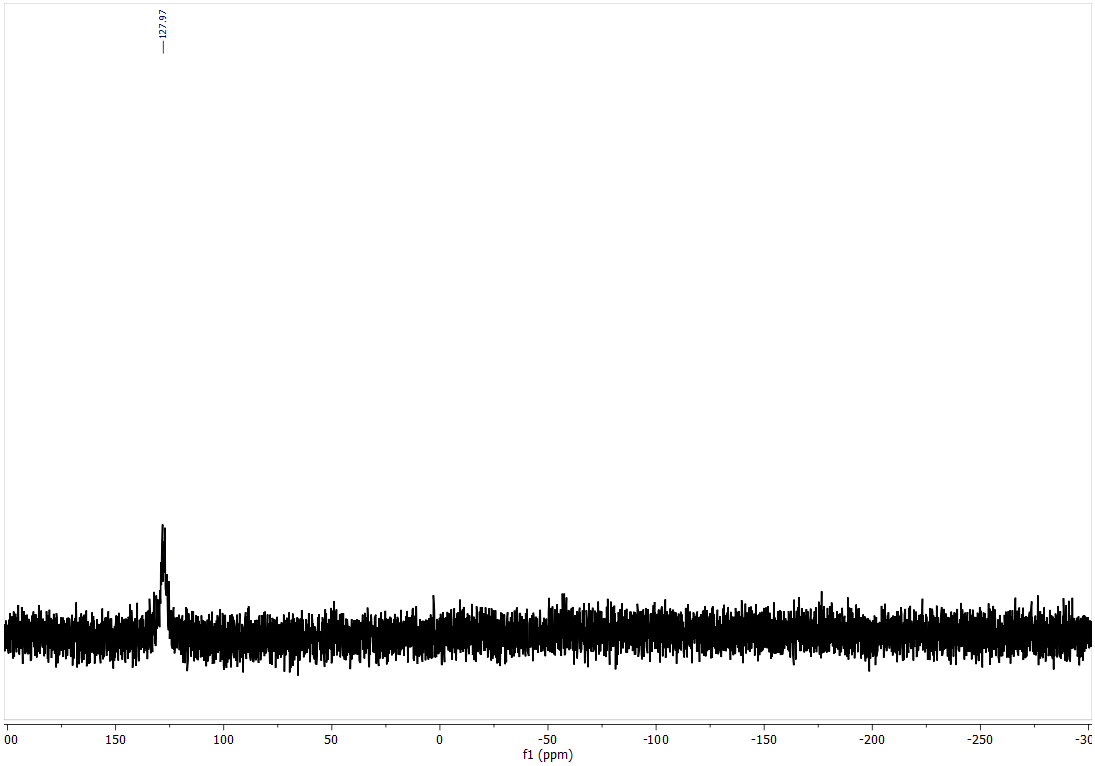

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **1**. (CD_2Cl_2, 162 MHz, 298 K)

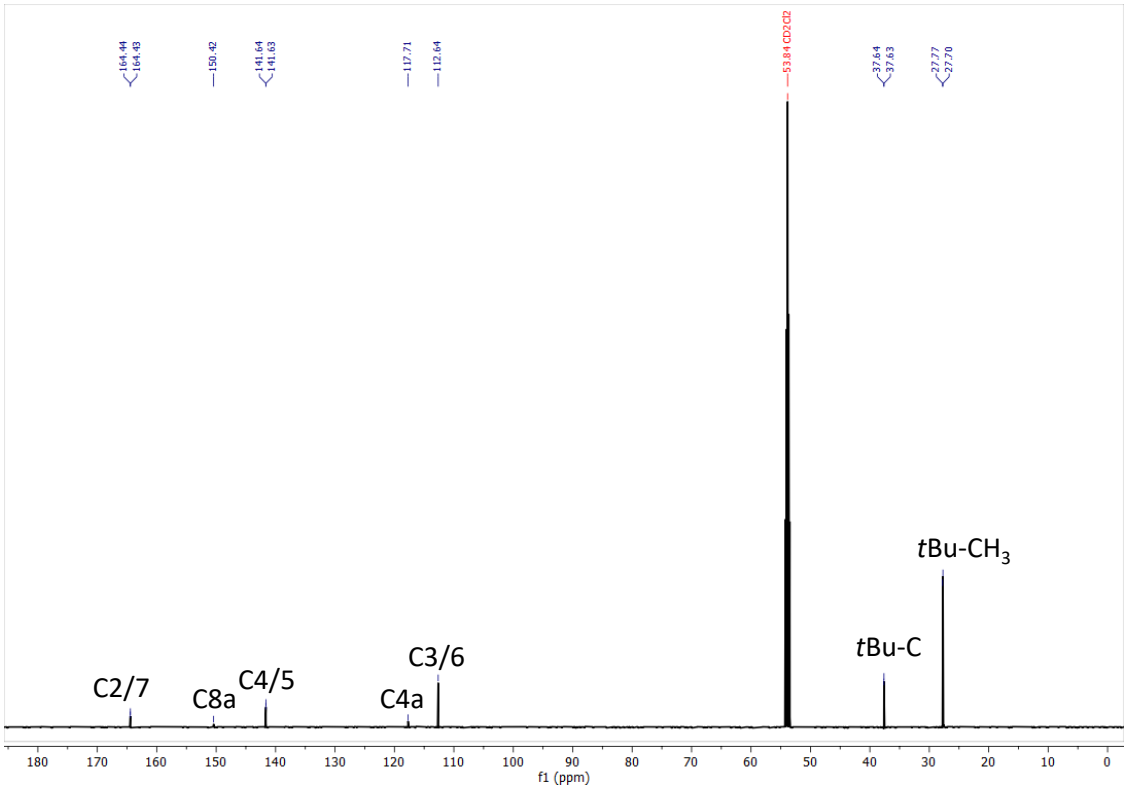

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **1**. (CD_2Cl_2, 151 MHz, 298 K)

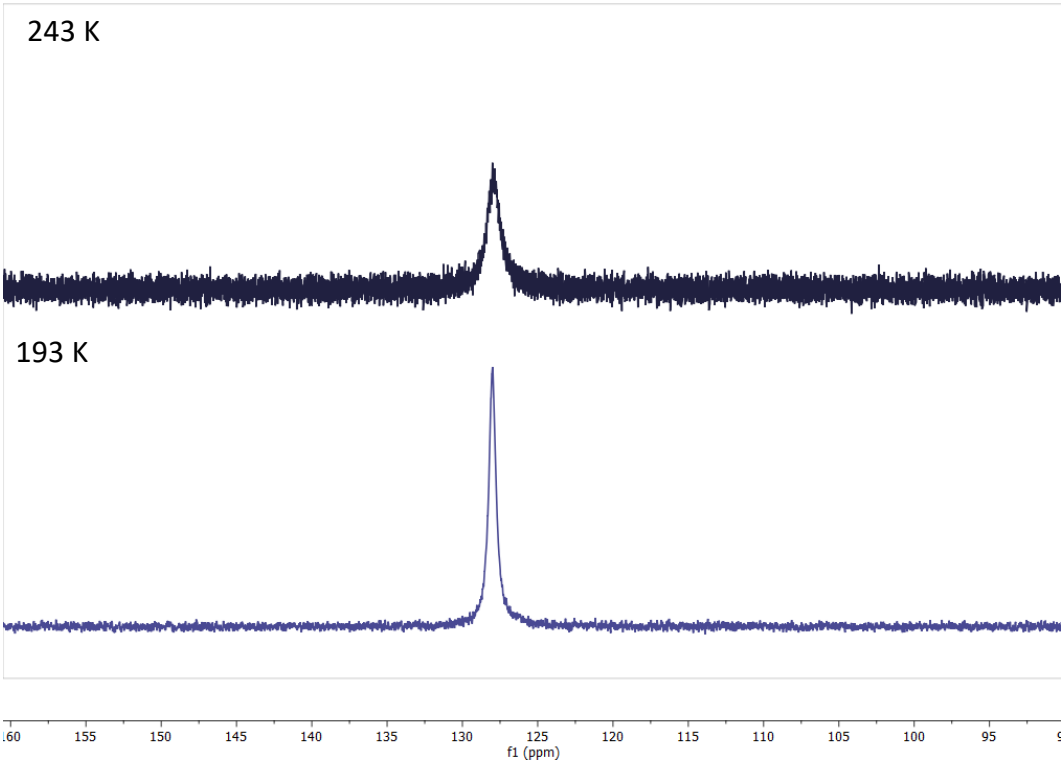

Figure S13. Variable temperature $^{31}P\{^{1}H\}$ NMR spectrum of **1**. (CD_2Cl_2, 162 MHz)

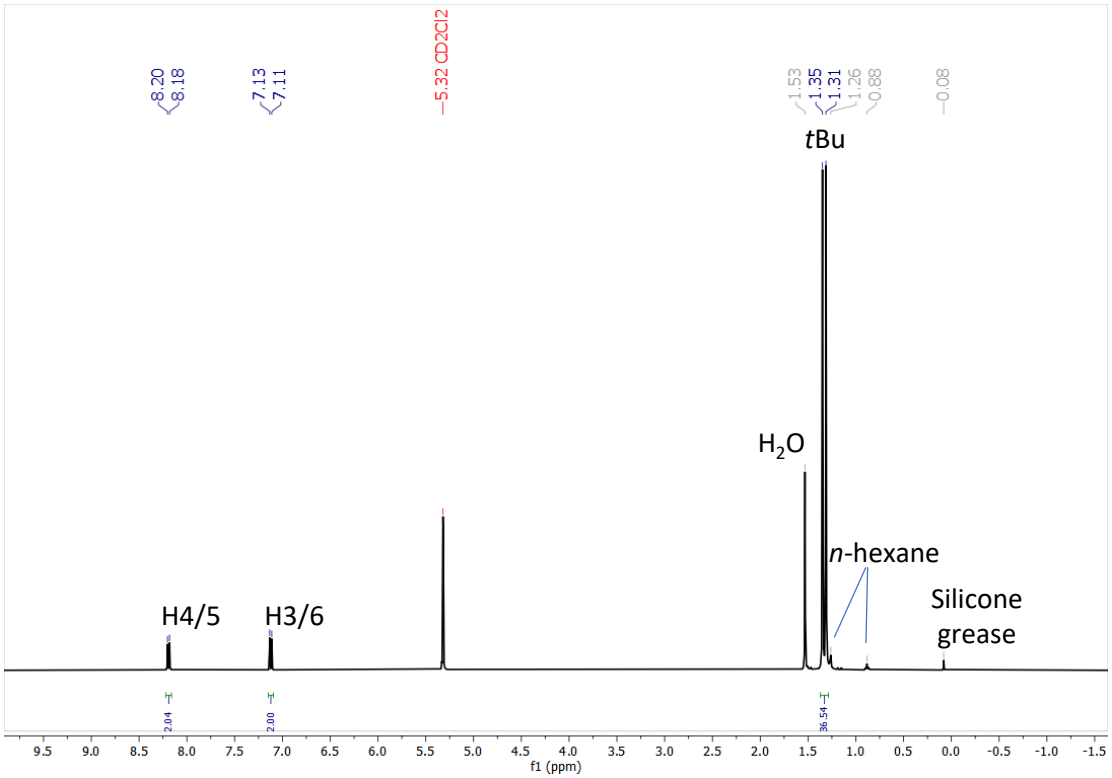

Figure S14. ^{1}H NMR spectrum of **1a**. (CD_2Cl_2, 400 MHz, 298 K)

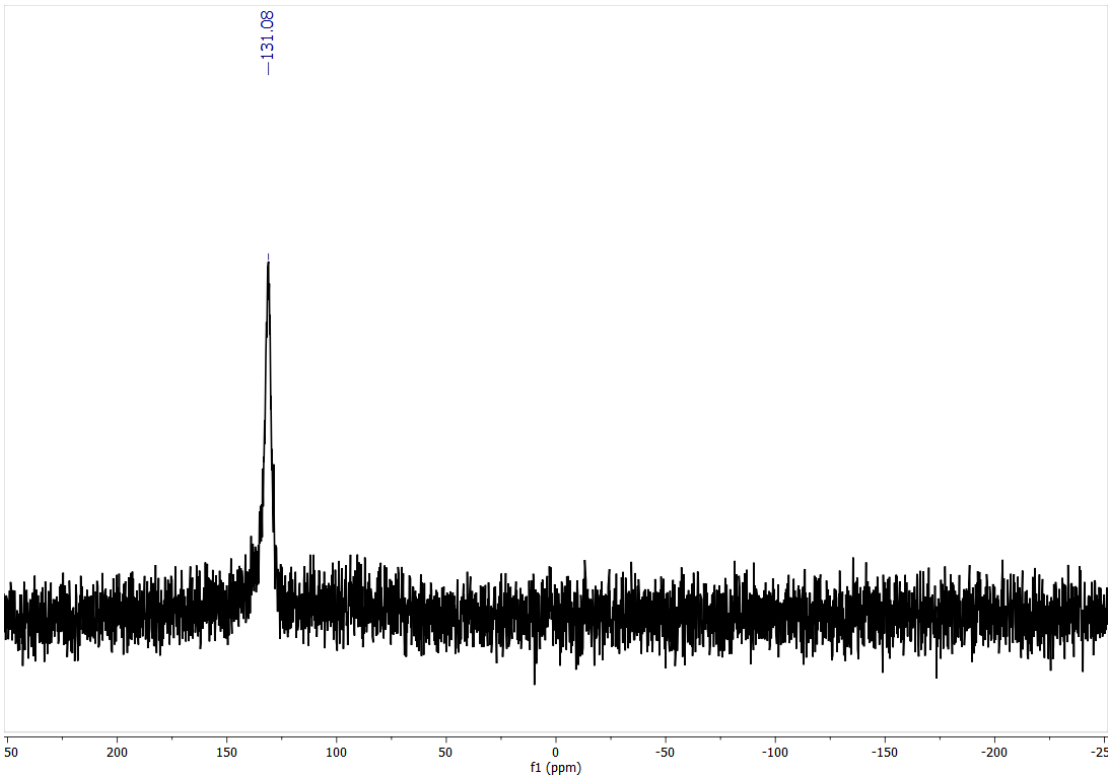

Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **1a**. (CD_2Cl_2, 162 MHz, 298 K)

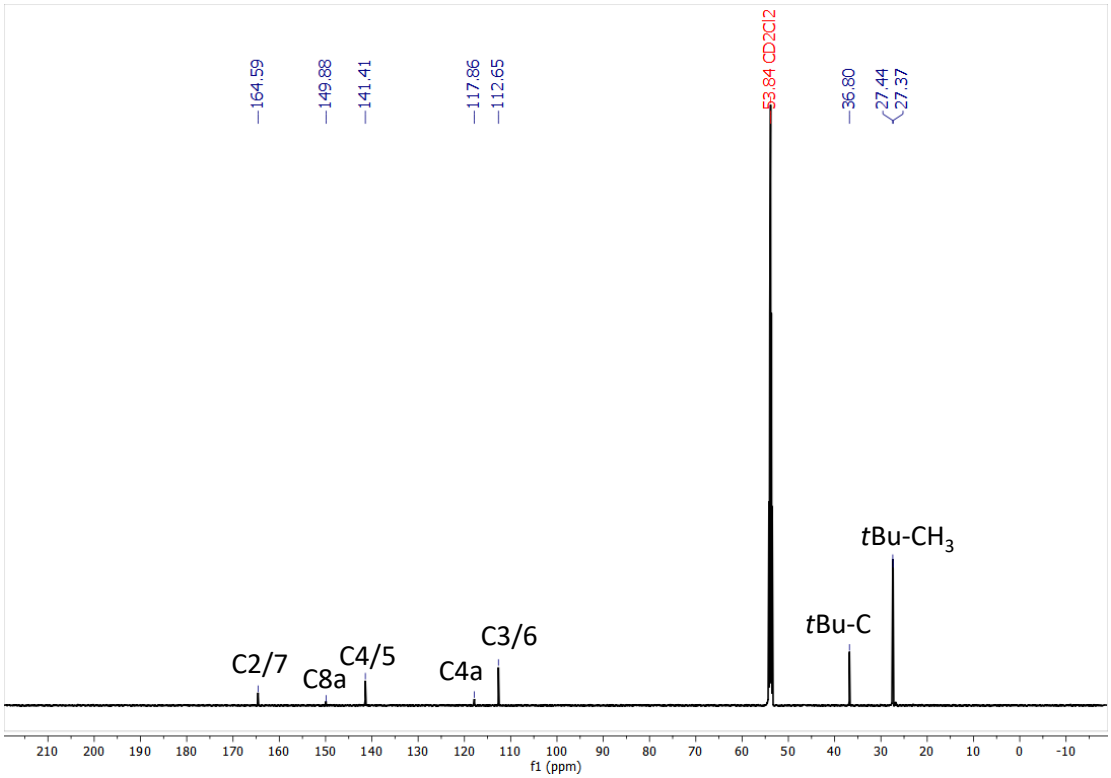

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **1a**. (CD_2Cl_2, 151 MHz, 298 K)

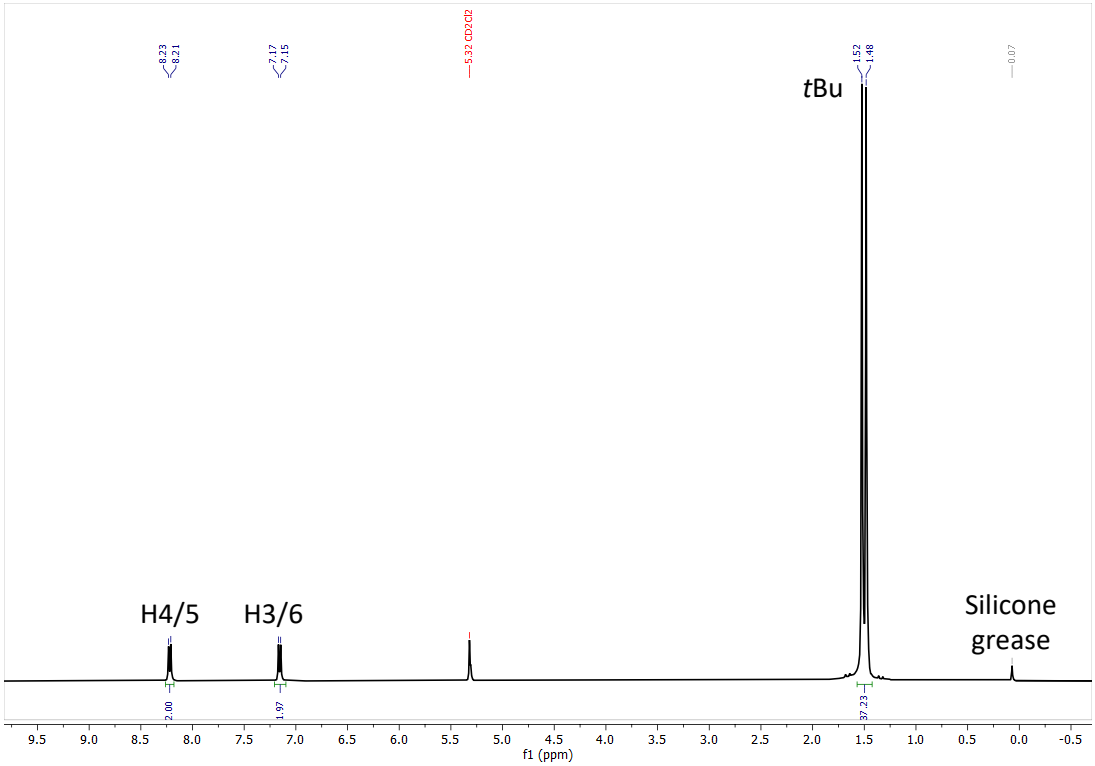

Figure S17. ^{1}H NMR spectrum of **2**. (CD_2Cl_2, 400 MHz, 298 K)

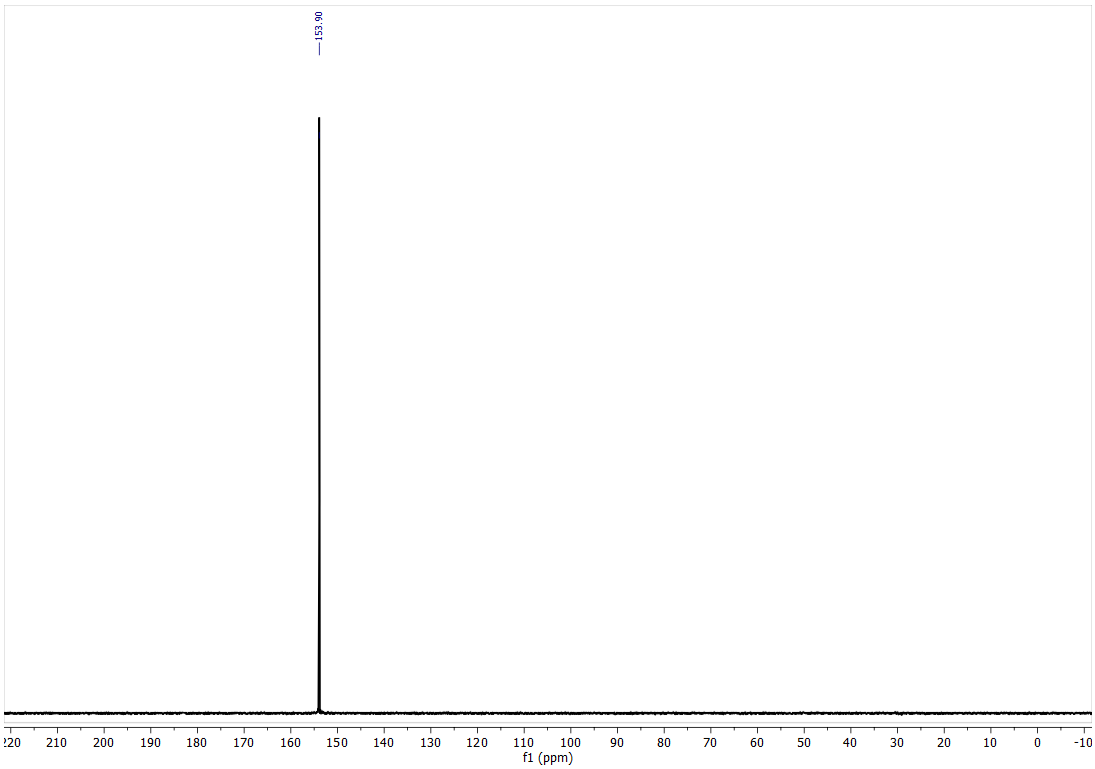

Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **2**. (CD_2Cl_2, 162 MHz, 298 K)

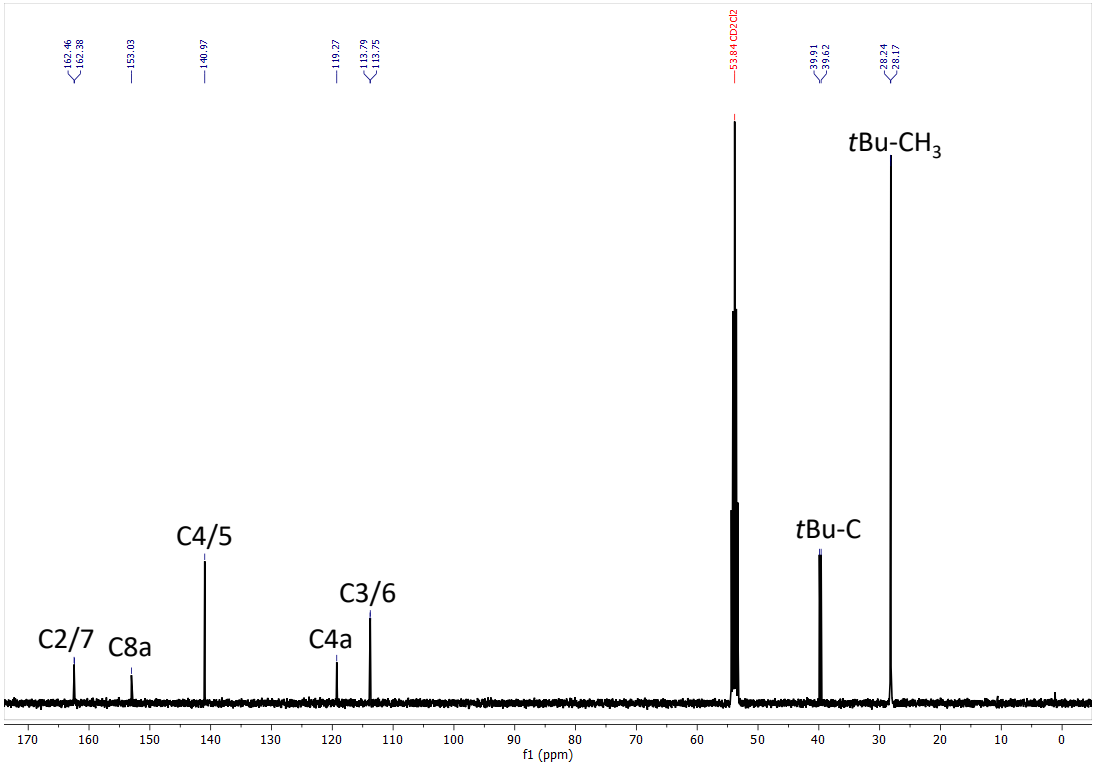

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **2**. (CD_2Cl_2, 101 MHz, 298 K)

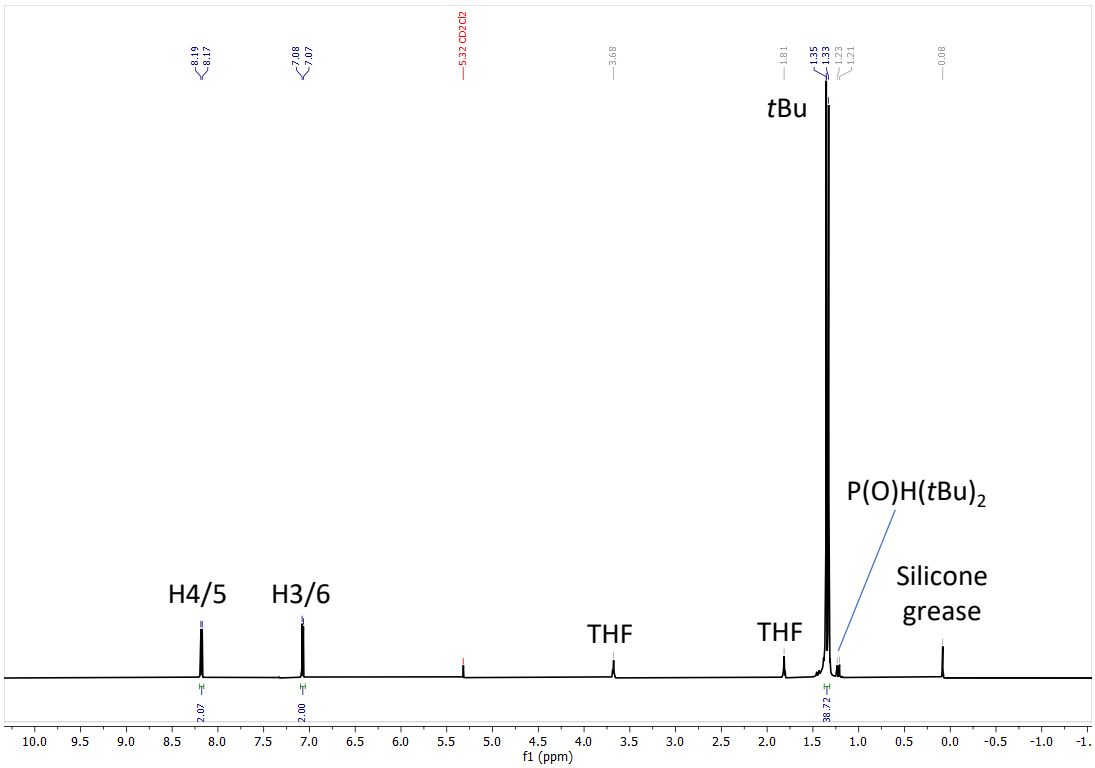

Figure S20. ^{1}H NMR spectrum of **3**. (CD_2Cl_2, 600 MHz, 298 K). Note that presence of P(O)H(*t*Bu)$_2$ is due to decomposition of uncomplexed ligand, and addition of water to this NMR did not increase the amount of P(O)H(*t*Bu)$_2$ present.

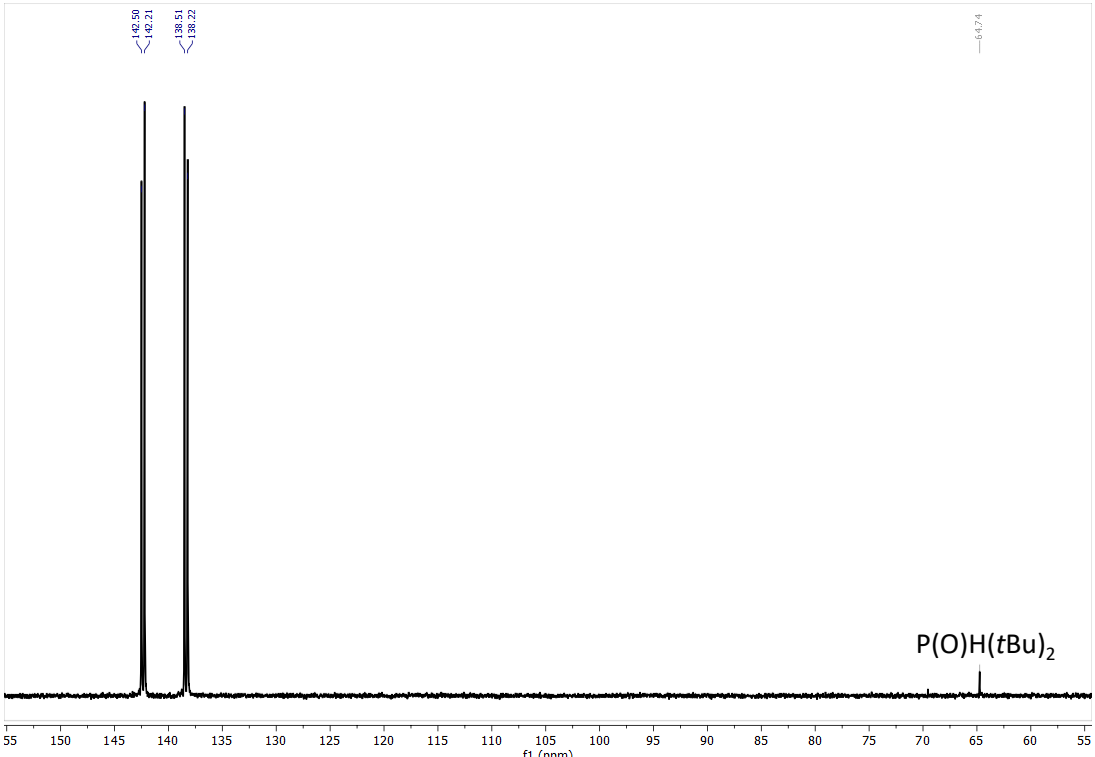

Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of **3**. (CD_2Cl_2, 162 MHz, 298 K). Note that presence of P(O)H(tBu)$_2$ is due to decomposition of uncomplexed ligand, and addition of water to this NMR did not increase the amount of P(O)H(tBu)$_2$ present.

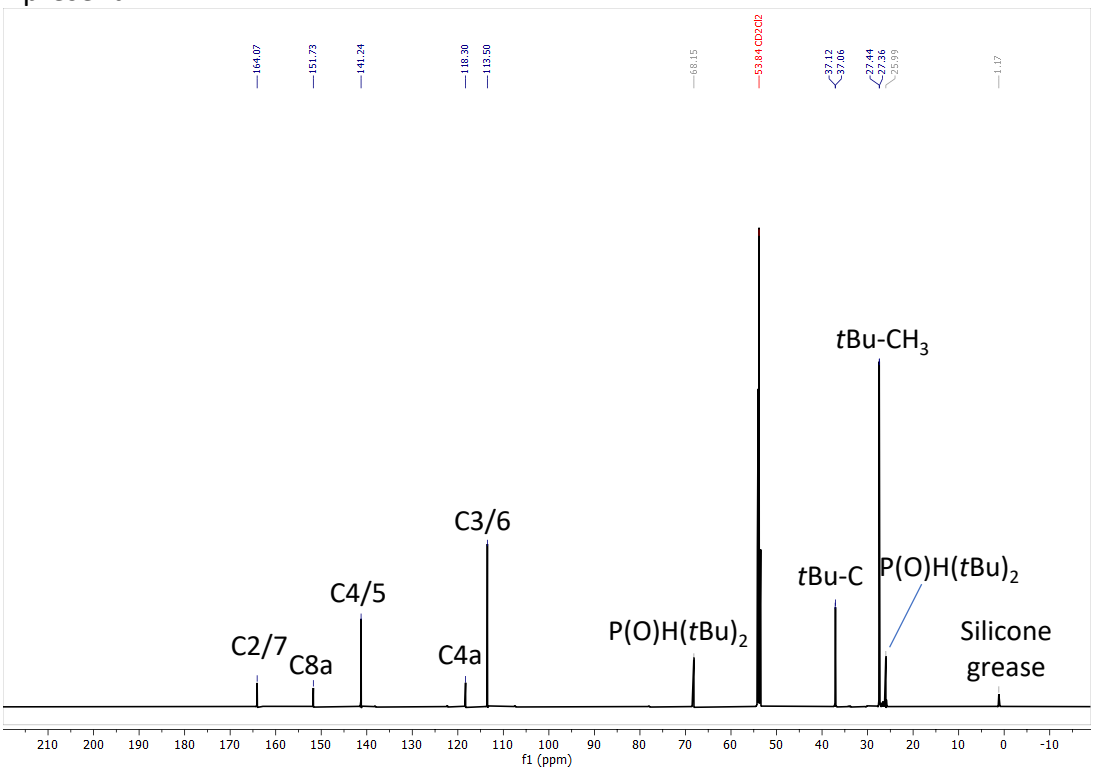

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **3**. (CD_2Cl_2, 151 MHz, 298 K). Note that presence of P(O)H(tBu)$_2$ is due to decomposition of uncomplexed ligand, and addition of water to this NMR did not increase the amount of P(O)H(tBu)$_2$ present.

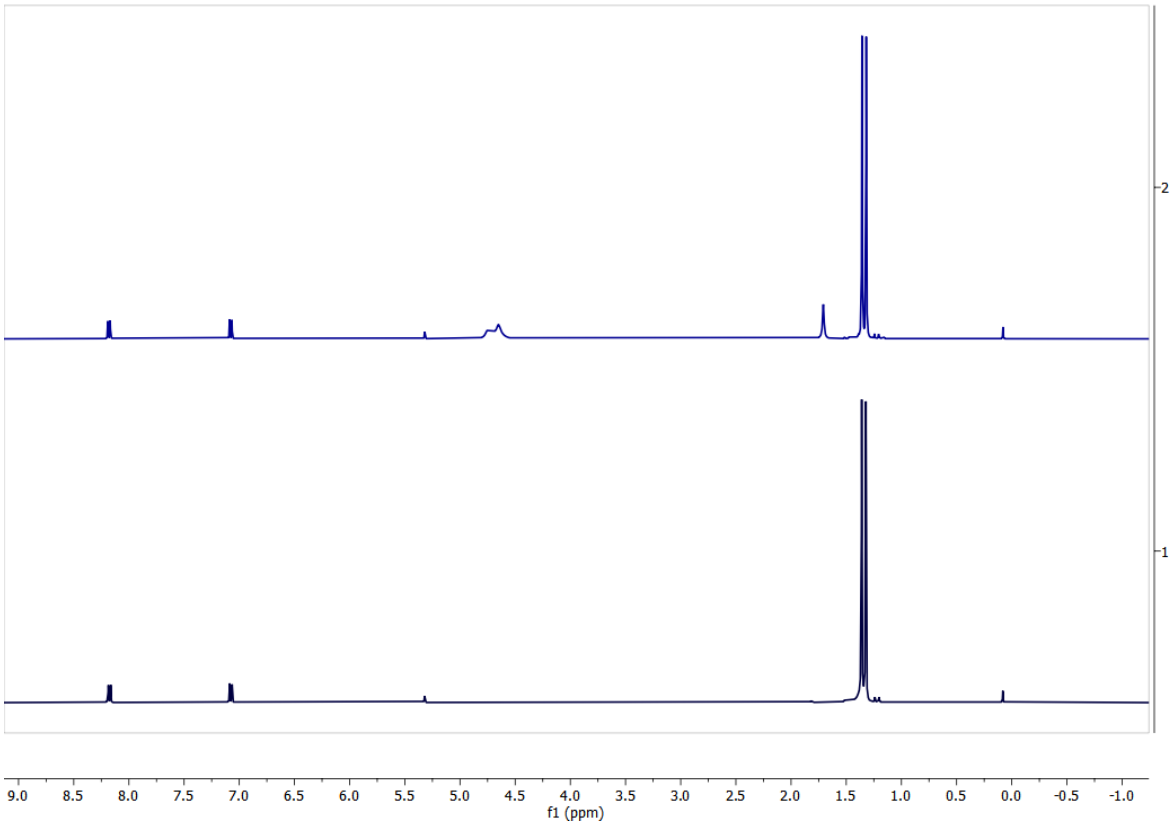

Figure S23. ^{1}H NMR spectrum of **3**. (CD_2Cl_2, 400 MHz, 298 K). Bottom spectrum is before addition of water, top spectrum is with addition of water taken after 1 hour. No change in the peaks corresponding to **3** is observed.

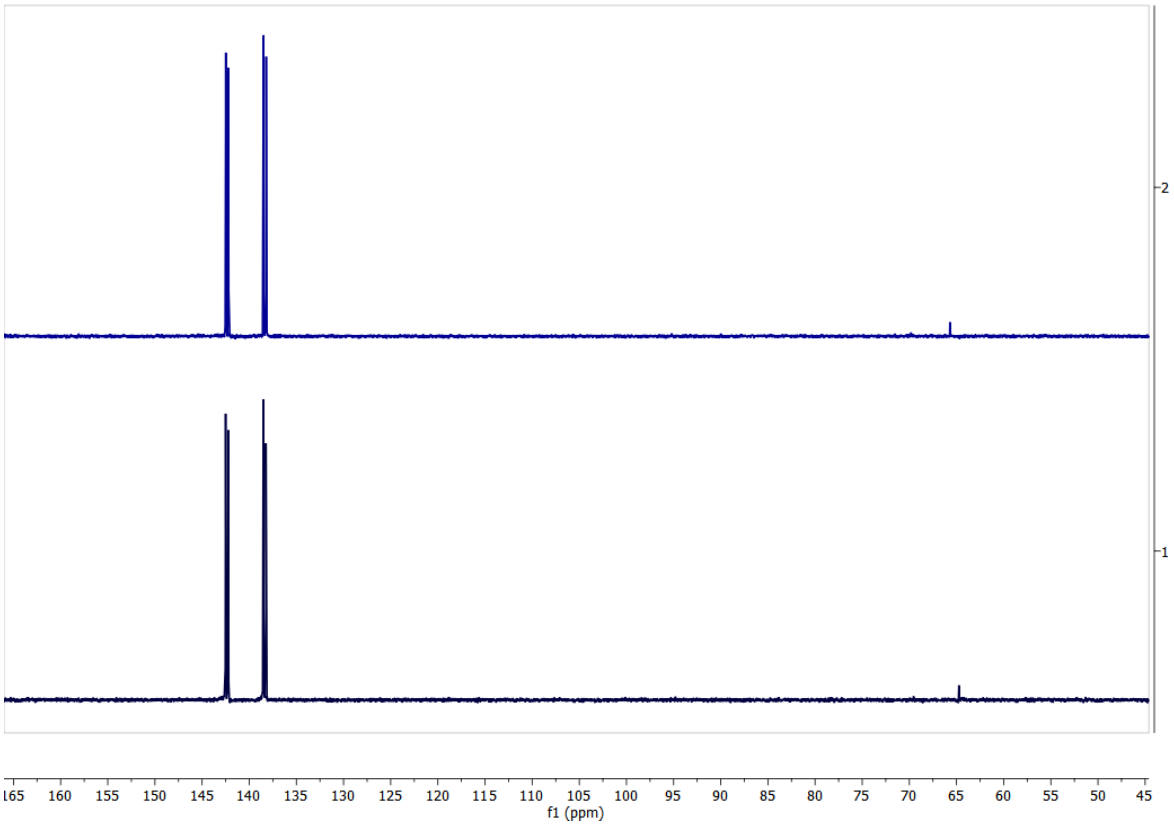

Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of **3**. (CD_2Cl_2, 162 MHz, 298 K). Bottom spectrum is before addition of water, top spectrum is with addition of water taken after 1 hour. No change in the peaks corresponding to **3** is observed.

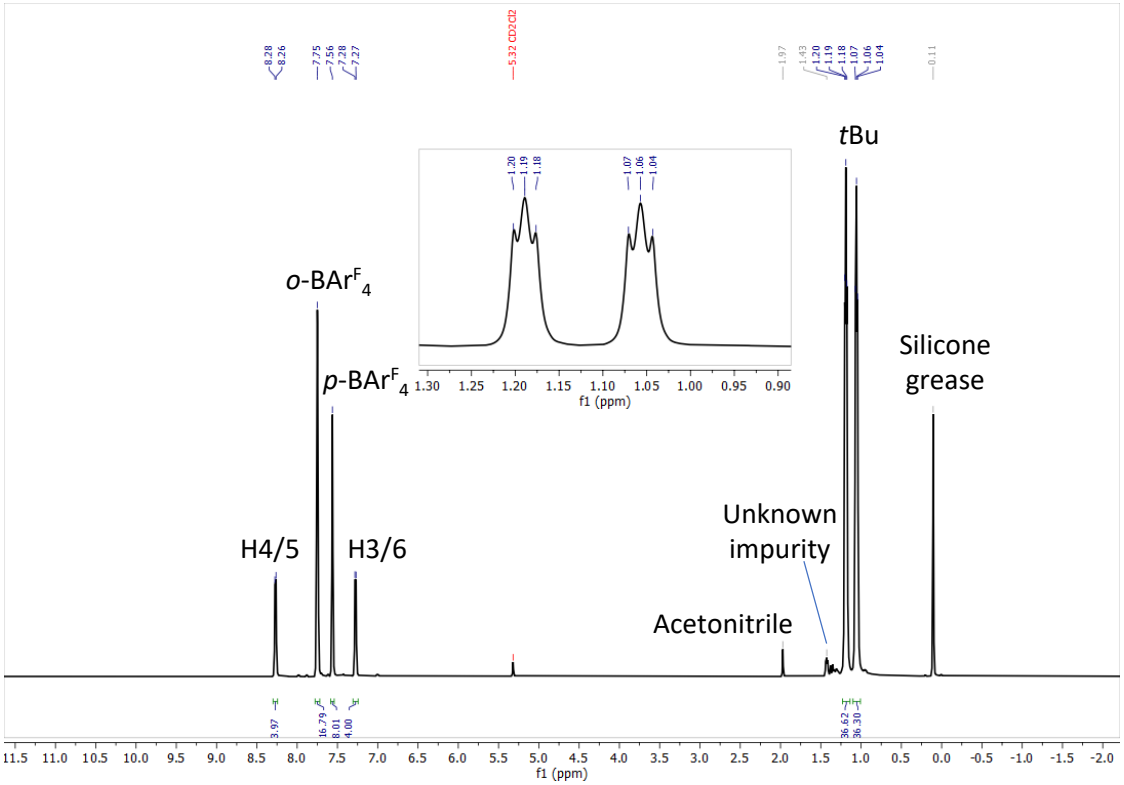

Figure S25. ^{1}H NMR spectrum of **4**. (CD_2Cl_2, 600 MHz, 298 K)

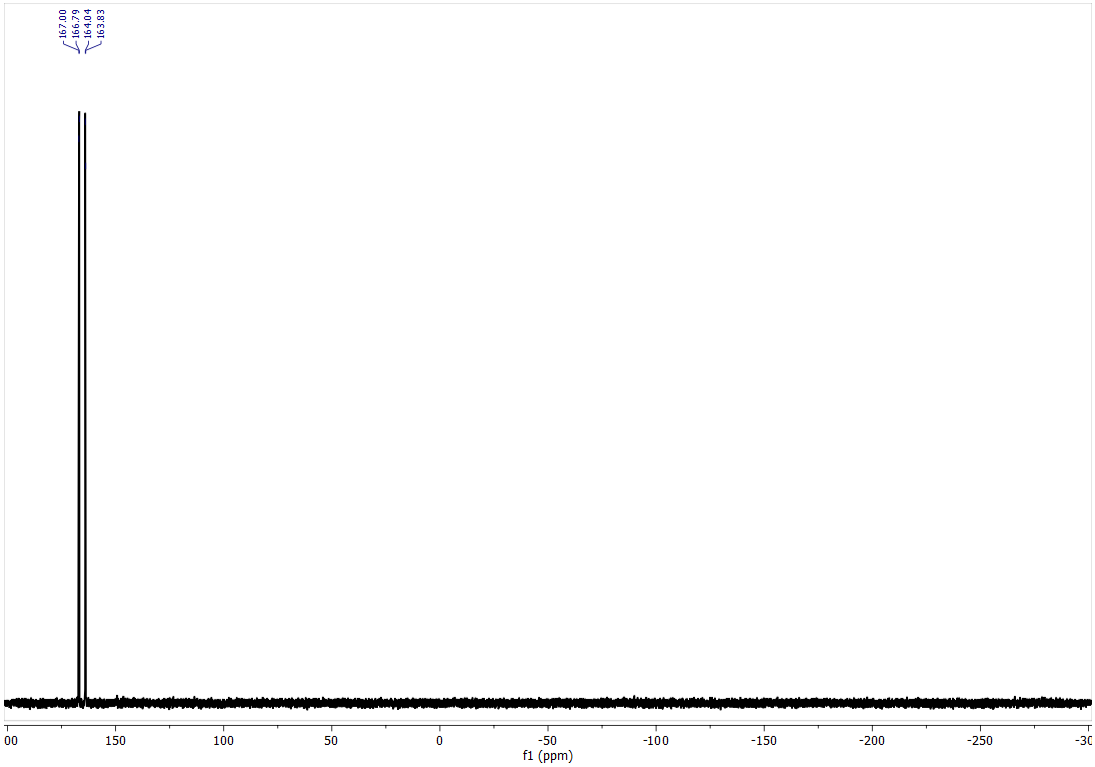

Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum of **4**. (CD_2Cl_2, 162 MHz, 298 K)

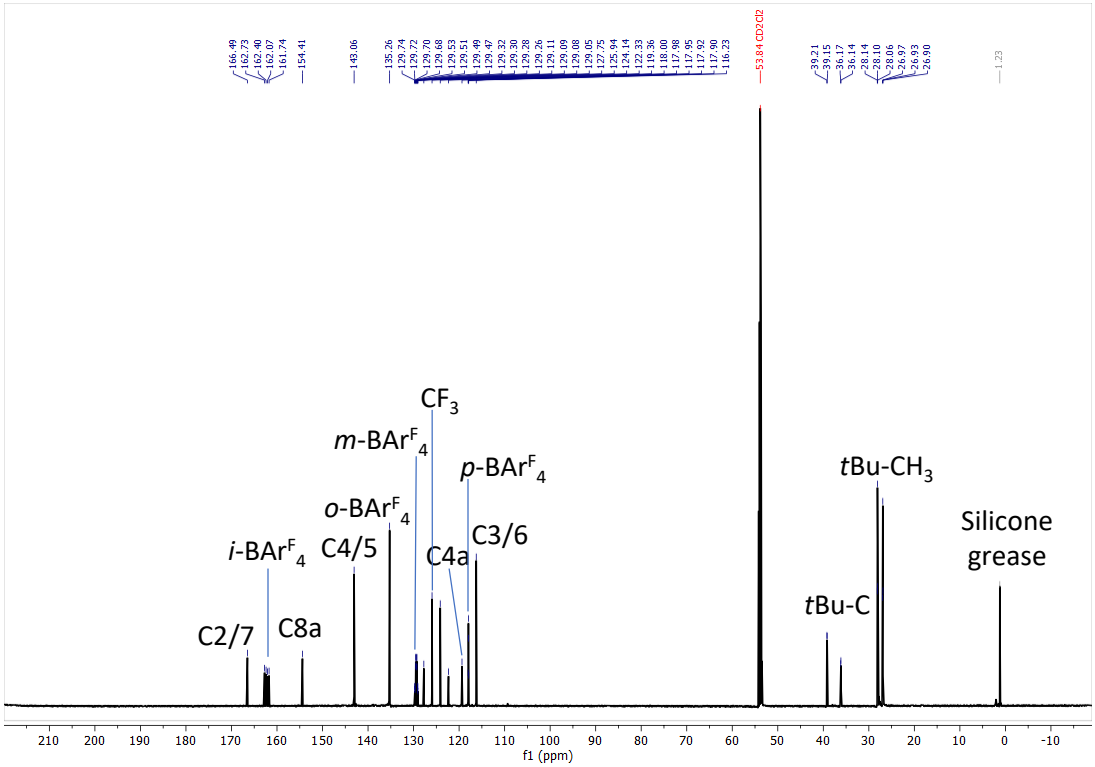

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **4**. (CD_2Cl_2, 151 MHz, 298 K)

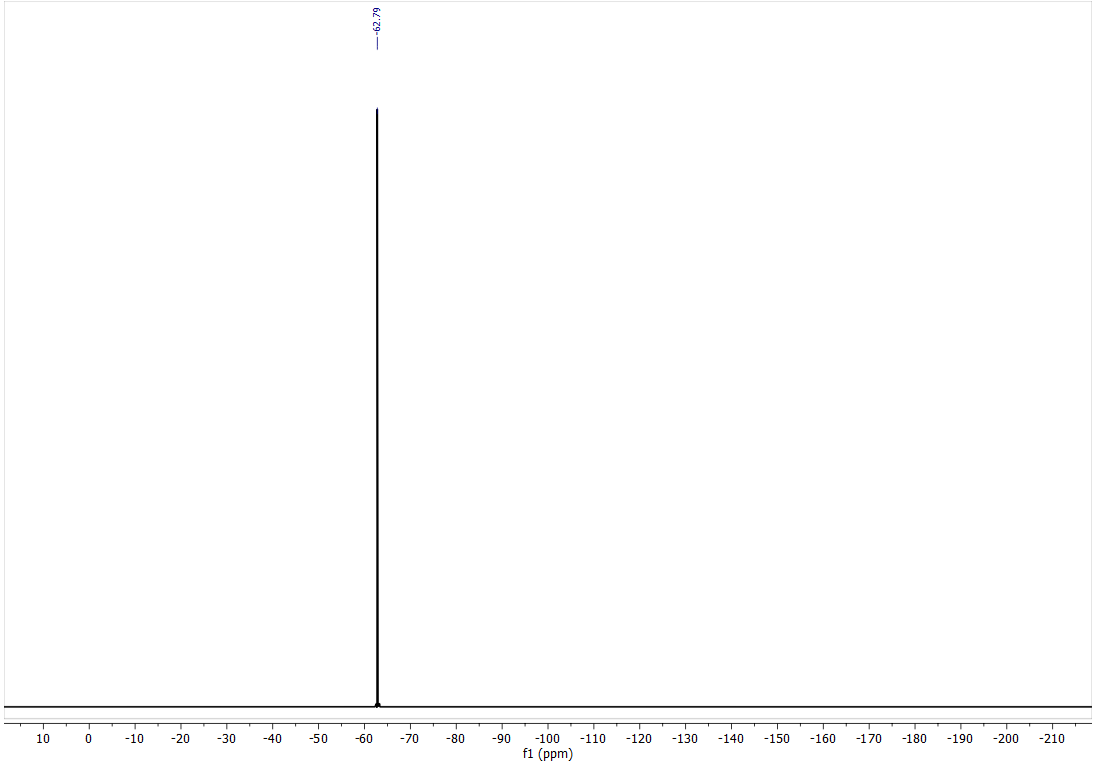

Figure S28. $^{19}F\{^{1}H\}$ NMR spectrum of **4**. (CD_2Cl_2, 376 MHz, 298 K)

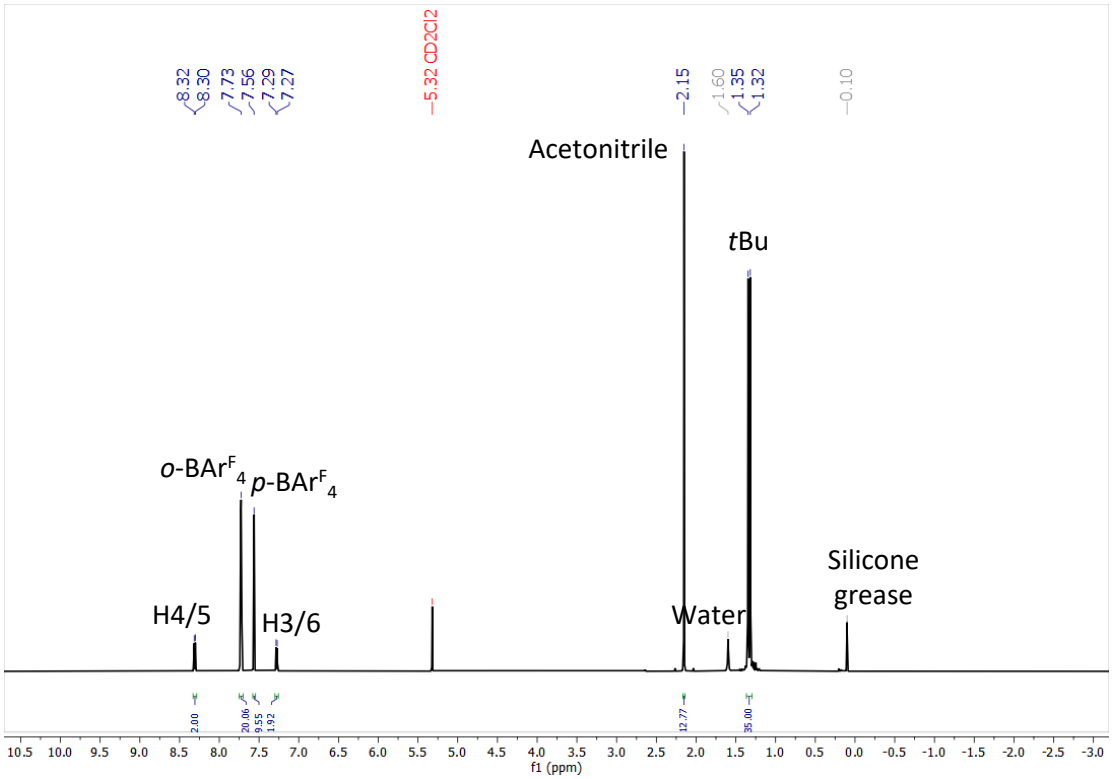

Figure S29. ^{1}H NMR spectrum of **5a**. (CD_2Cl_2, 600 MHz, 298 K).

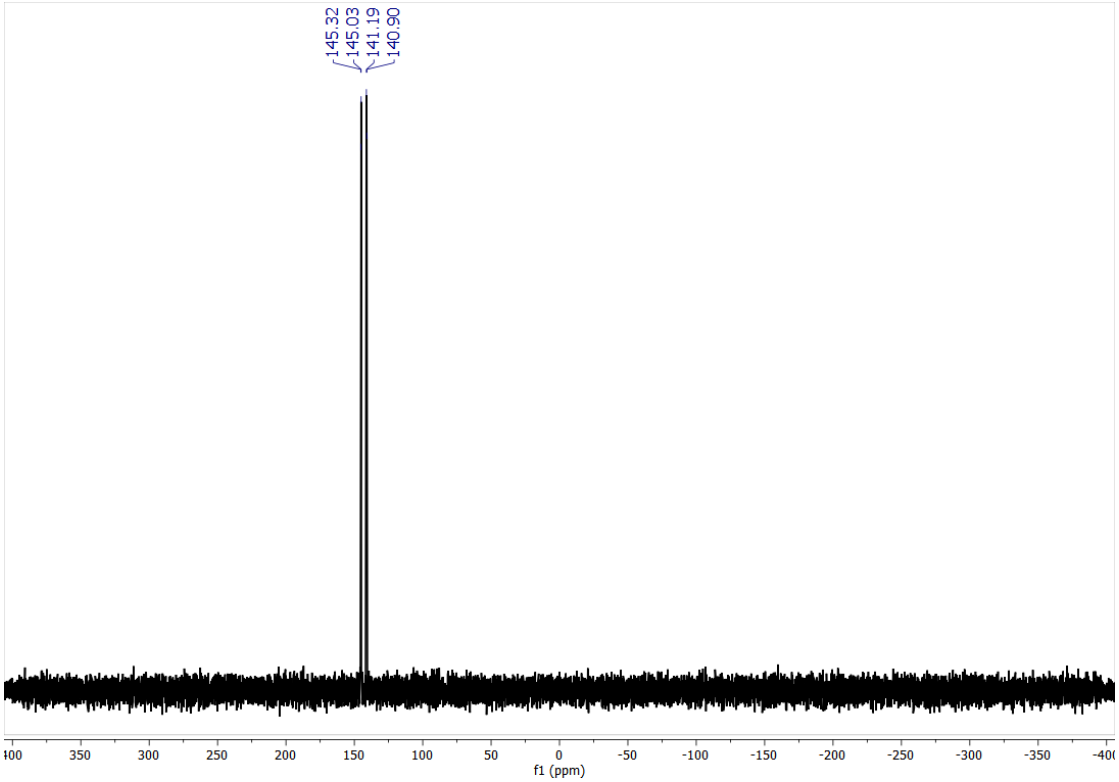

Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of **5a**. (CD_2Cl_2, 162 MHz, 298 K)

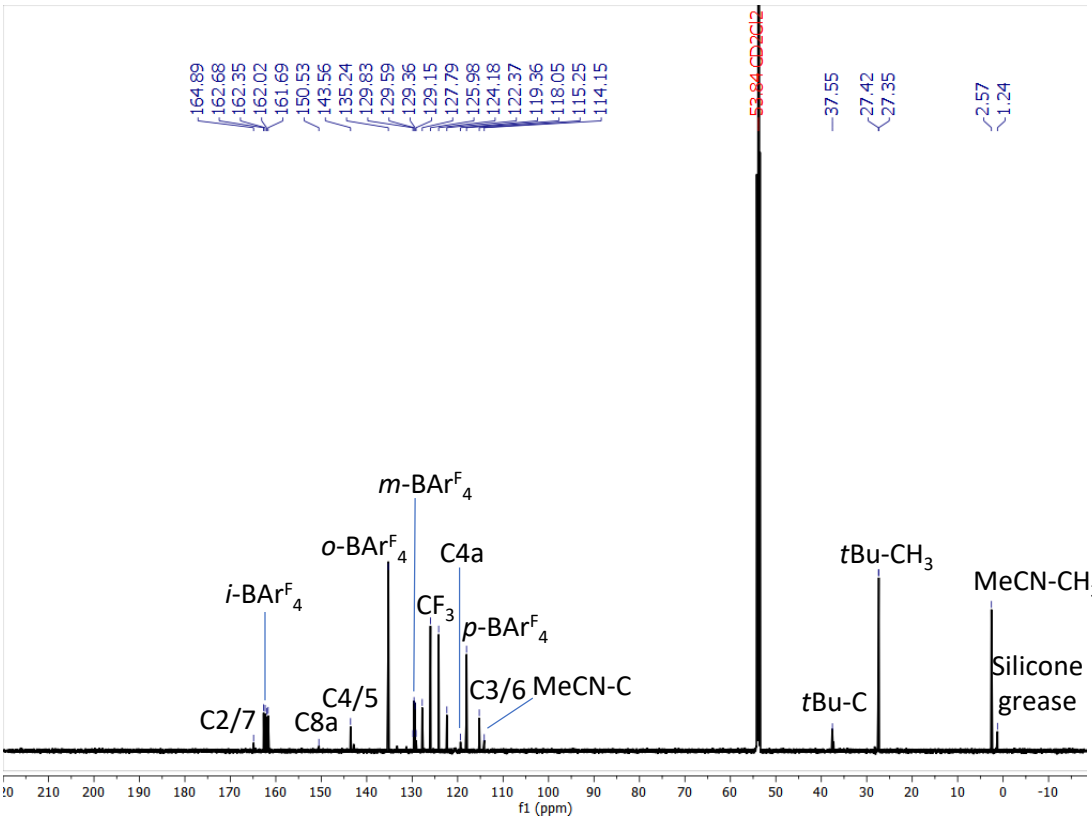

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **5a**. (CD_2Cl_2, 151 MHz, 298 K).

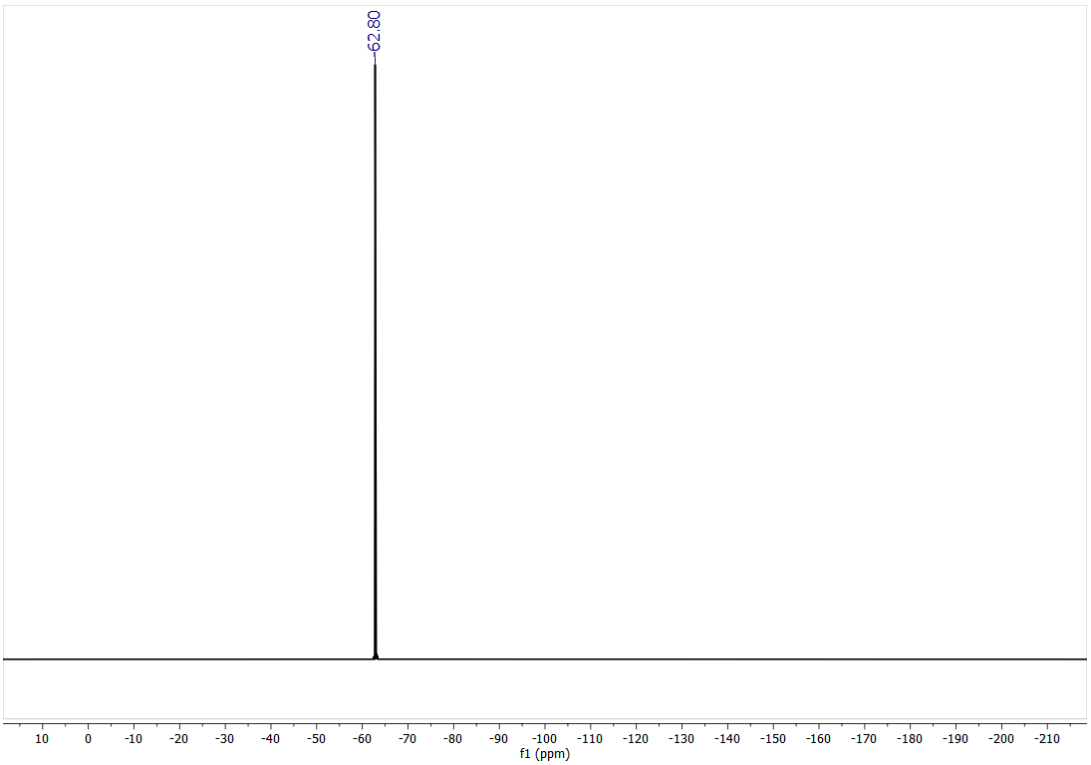

Figure S32. $^{19}F\{^{1}H\}$ NMR spectrum of **5a**. (CD_2Cl_2, 376 MHz, 298 K)

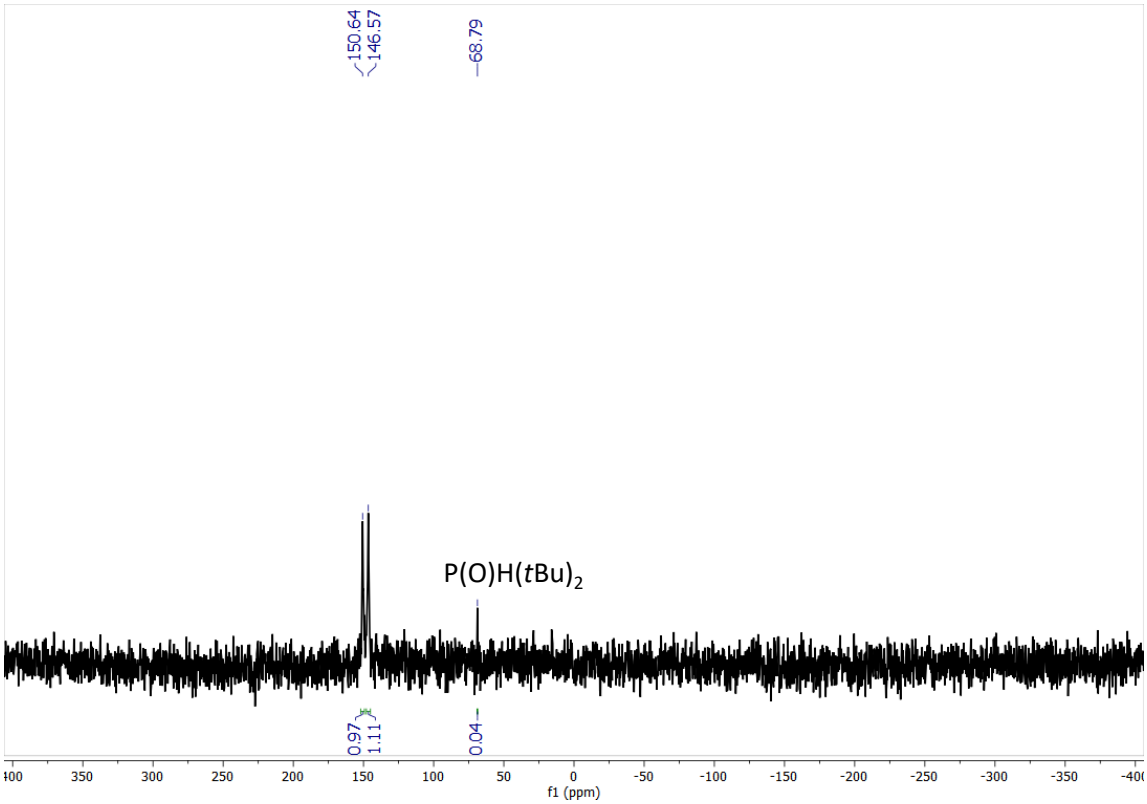

Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum of **5a** monitoring decomposition after standing in a d_3-MeCN/H_2O solution for 31 hours. (CD_3CN, 162 MHz, 298 K).

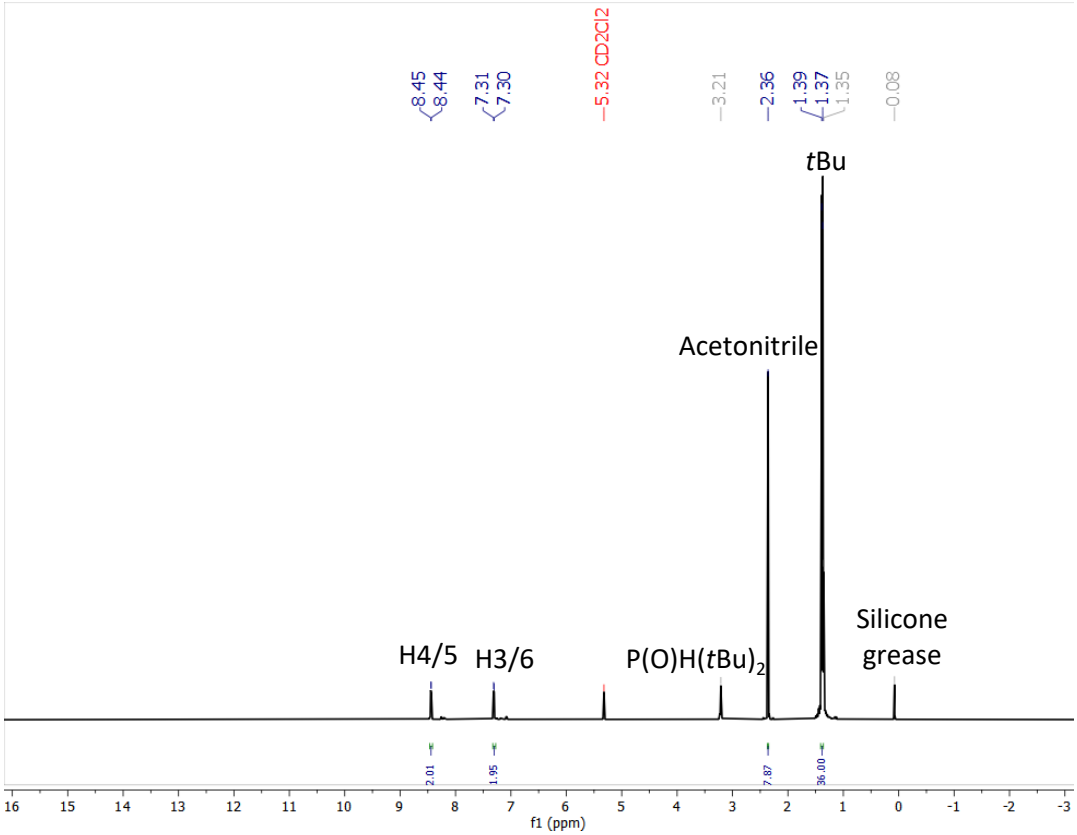

Figure S34. ^{1}H NMR spectrum of **5b**. (CD_2Cl_2, 800 MHz, 298 K).

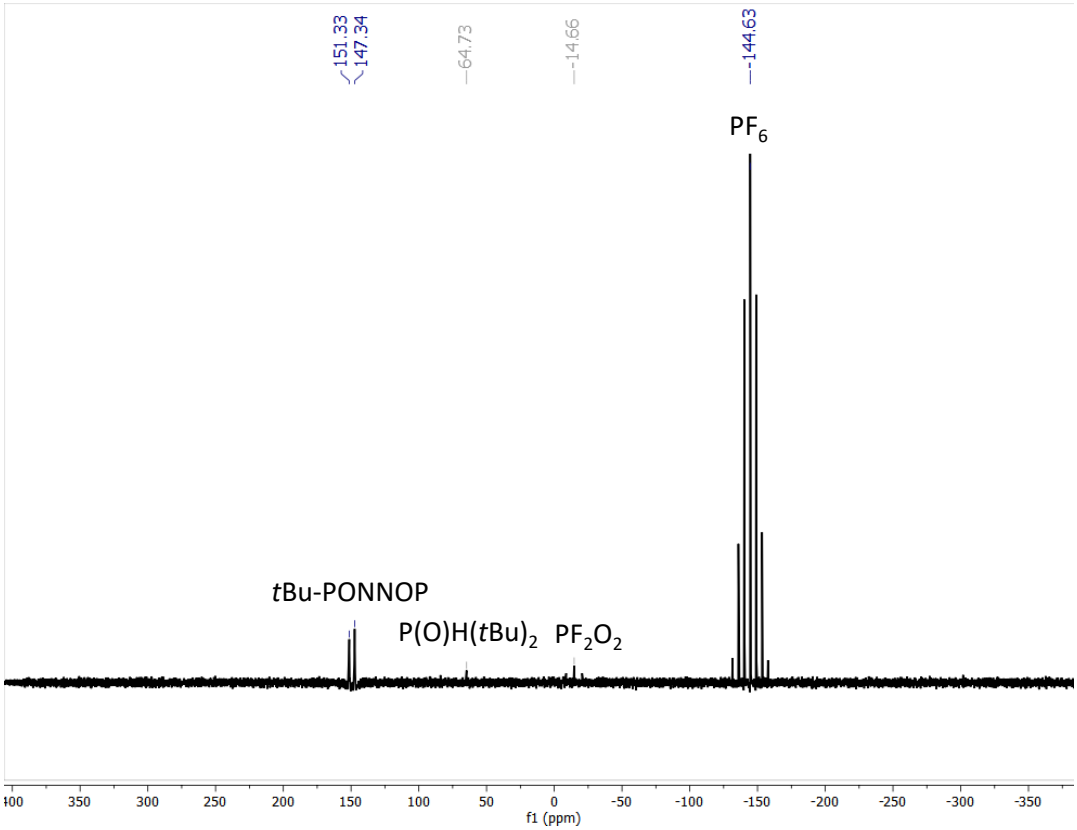

Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum of **5b**. (CD_2Cl_2, 162 MHz, 298 K)

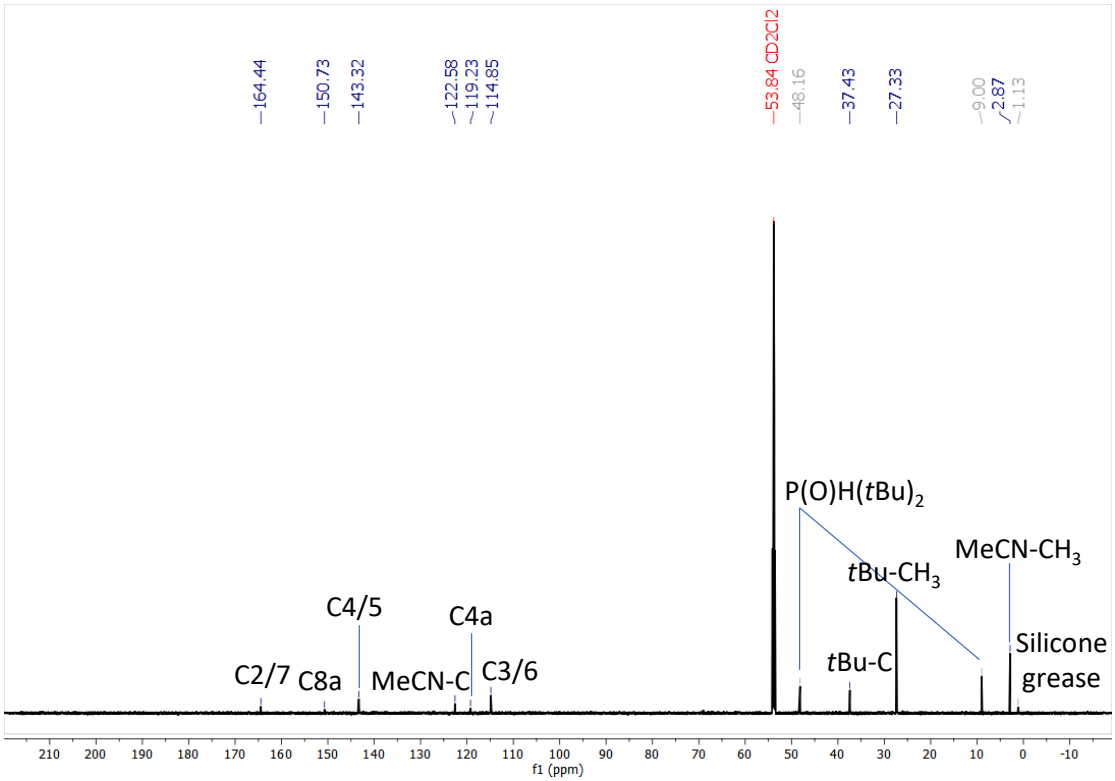

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of **5b**. (CD_2Cl_2, 201 MHz, 298 K)

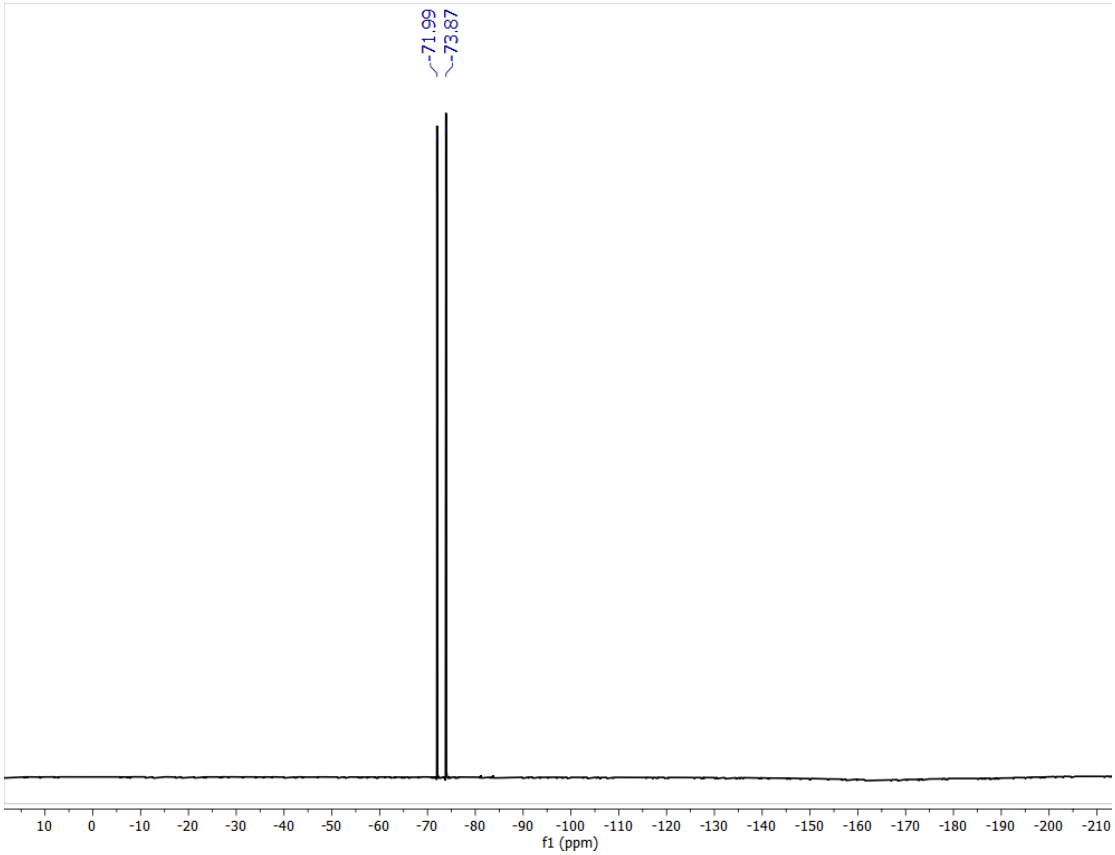

Figure S37. $^{19}F\{^{1}H\}$ NMR spectrum of **5b**. (CD_2Cl_2, 376 MHz, 298 K).

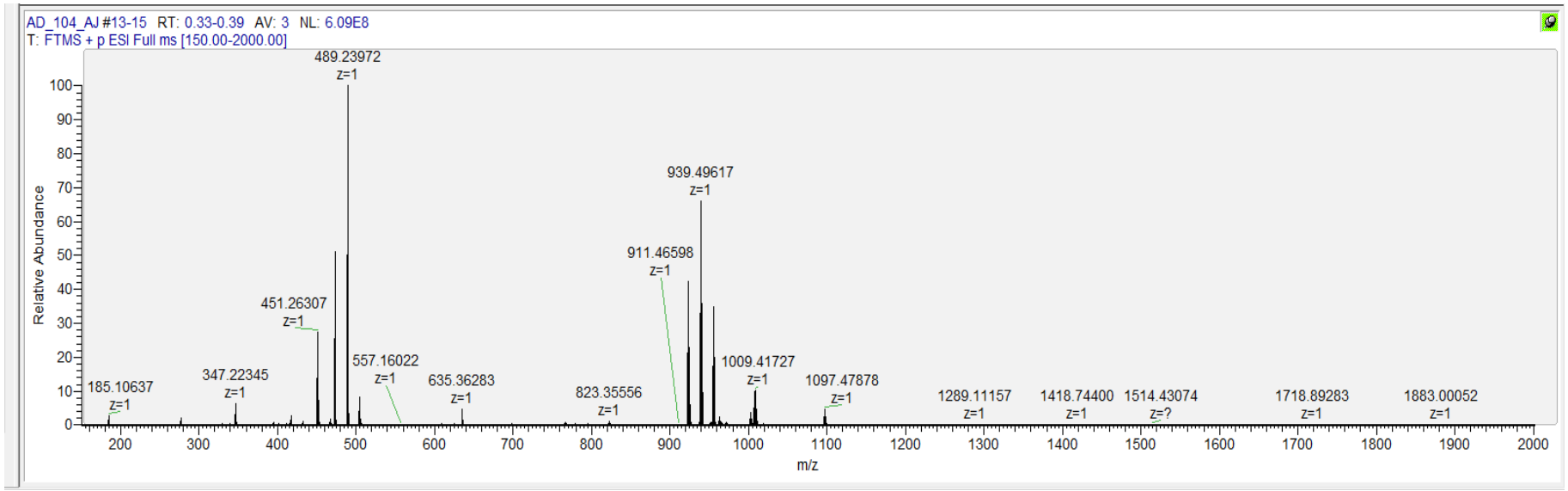

Figure S38. HRMS (ESI+) of **L**, full spectrum

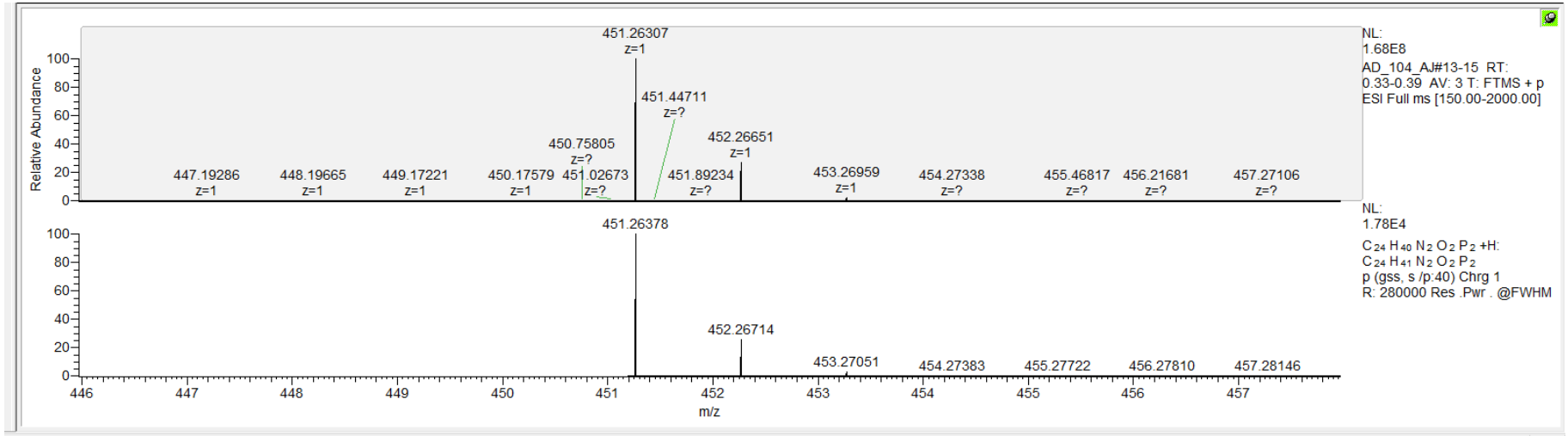

Figure S39. HRMS (ESI+) of **L**, $[M+H]^+$

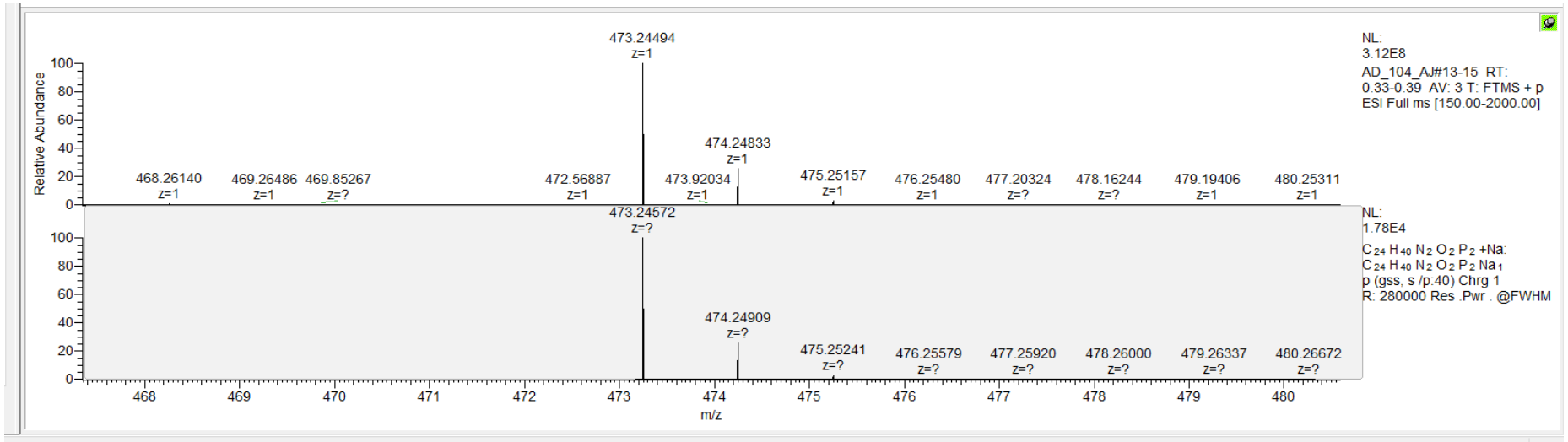

Figure S40. HRMS (ESI+) of **L**, $[M+Na]^+$

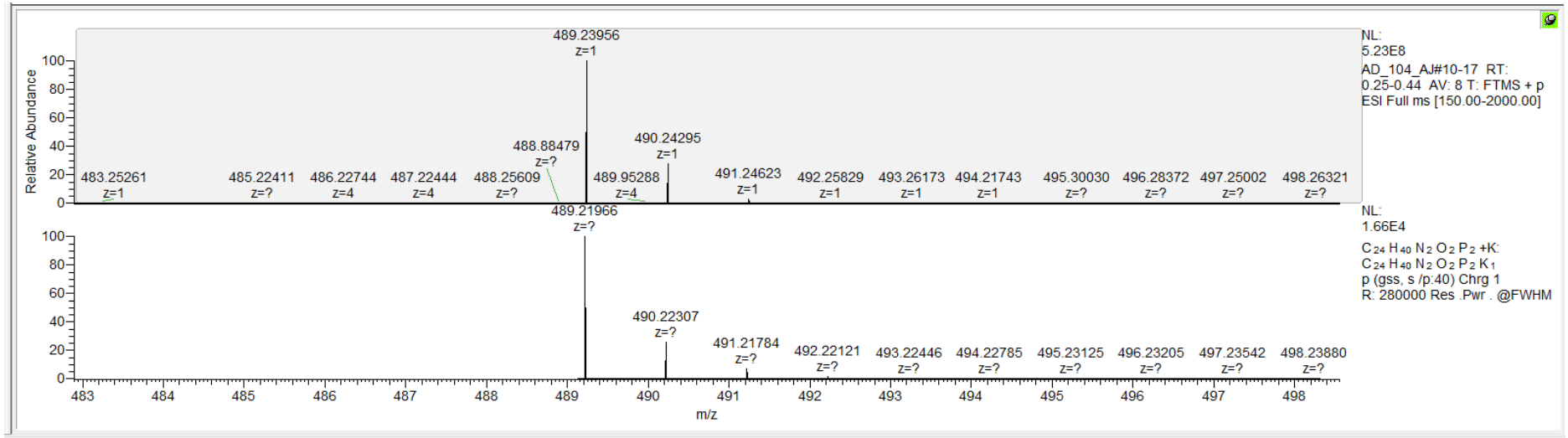

Figure S41. HRMS (ESI+) of **L**, $[M+K]^+$

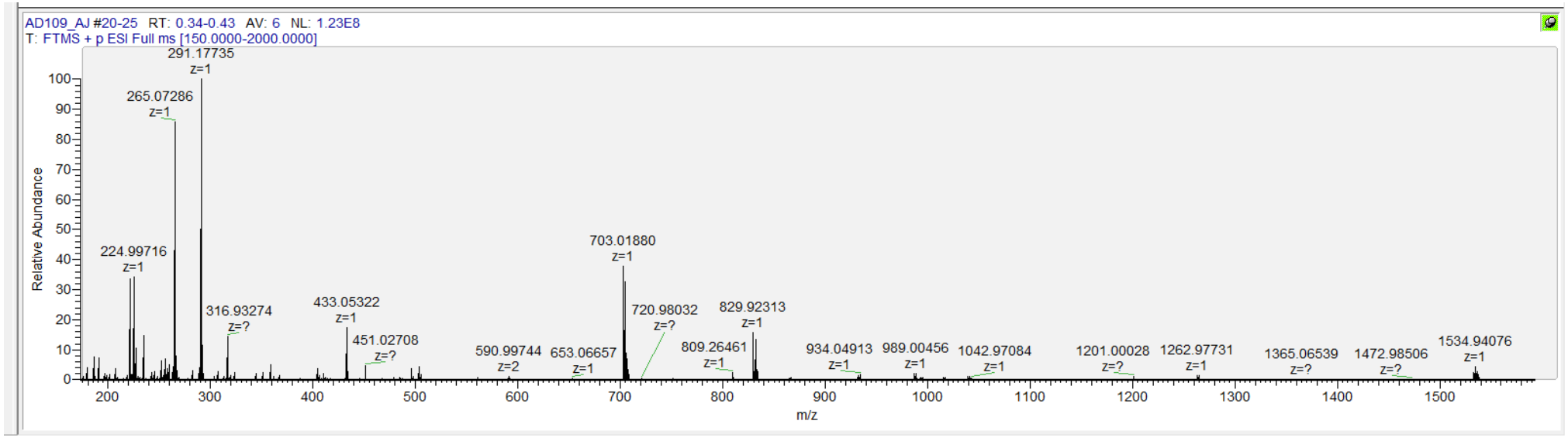

Figure S42. HRMS (ESI+) of **1**, full spectrum

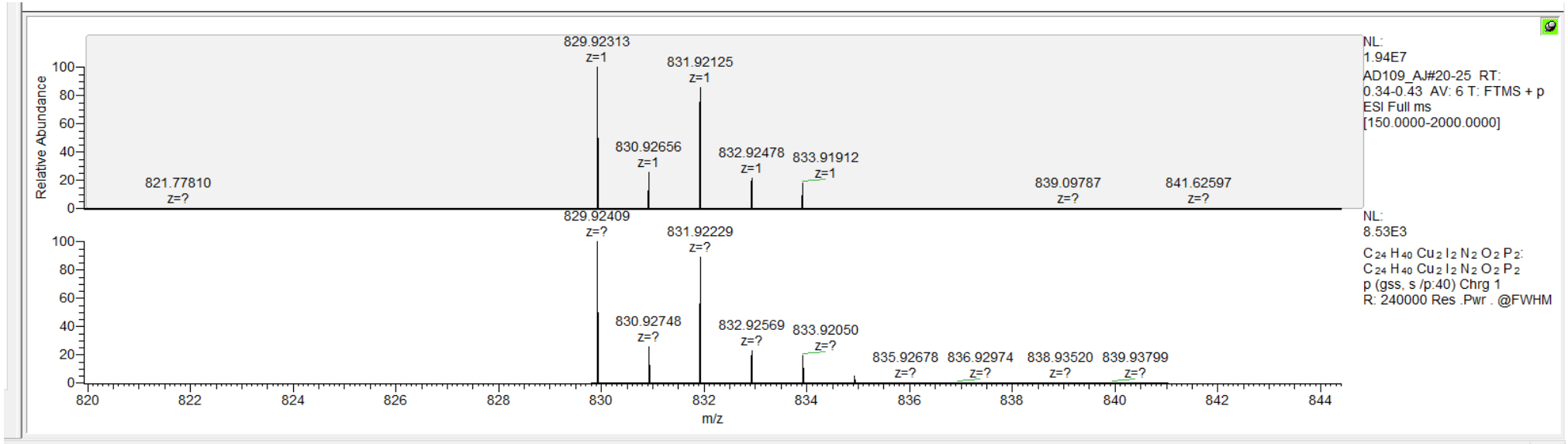

Figure S43. HRMS (ESI+) of **1**, $[M+H]^+$

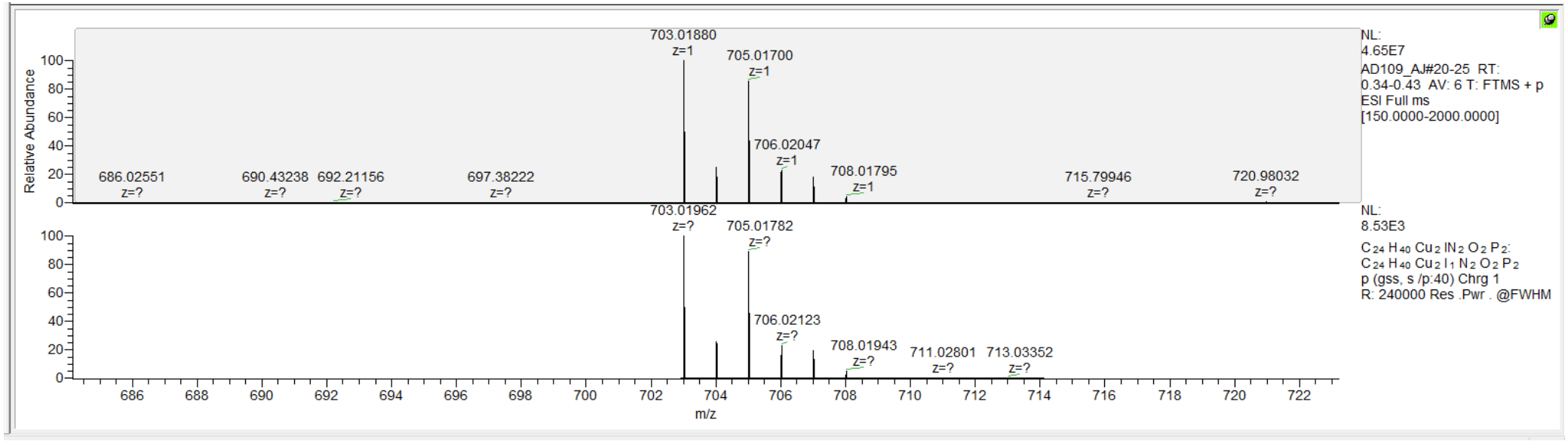

Figure S44. HRMS (ESI+) of **1**, $[M\text{-}I]^+$

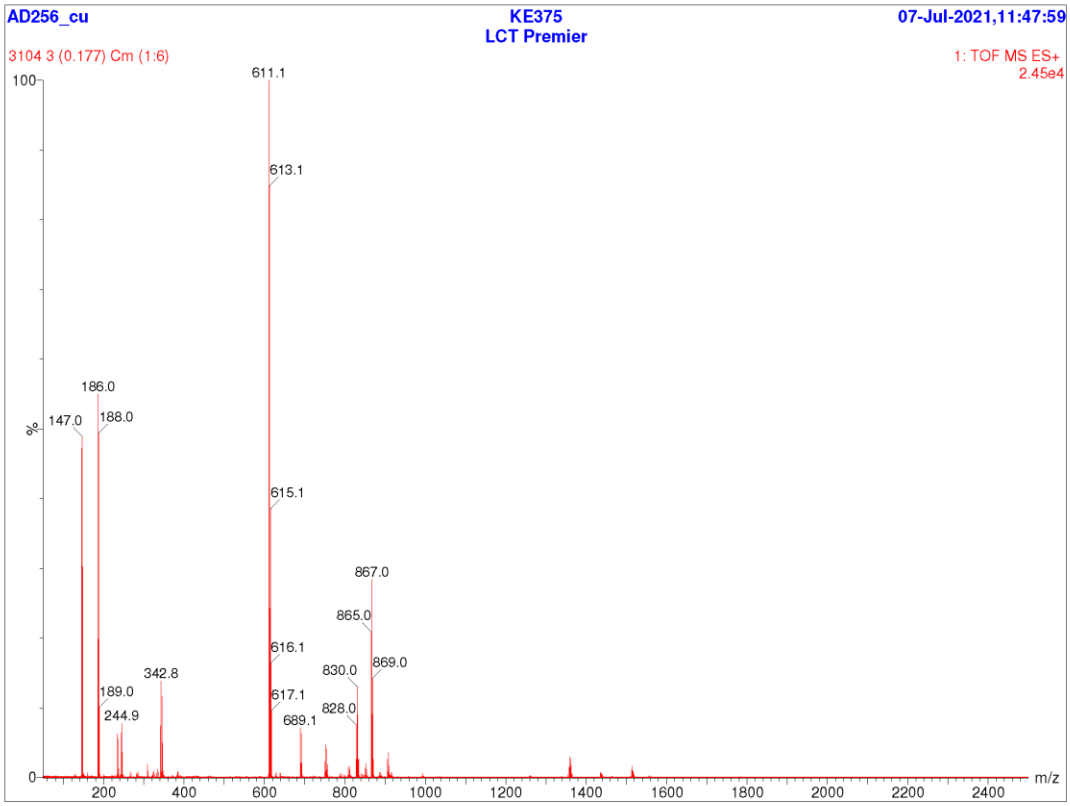

Figure S45. LRMS (ESI+) of **1a**, full spectrum.

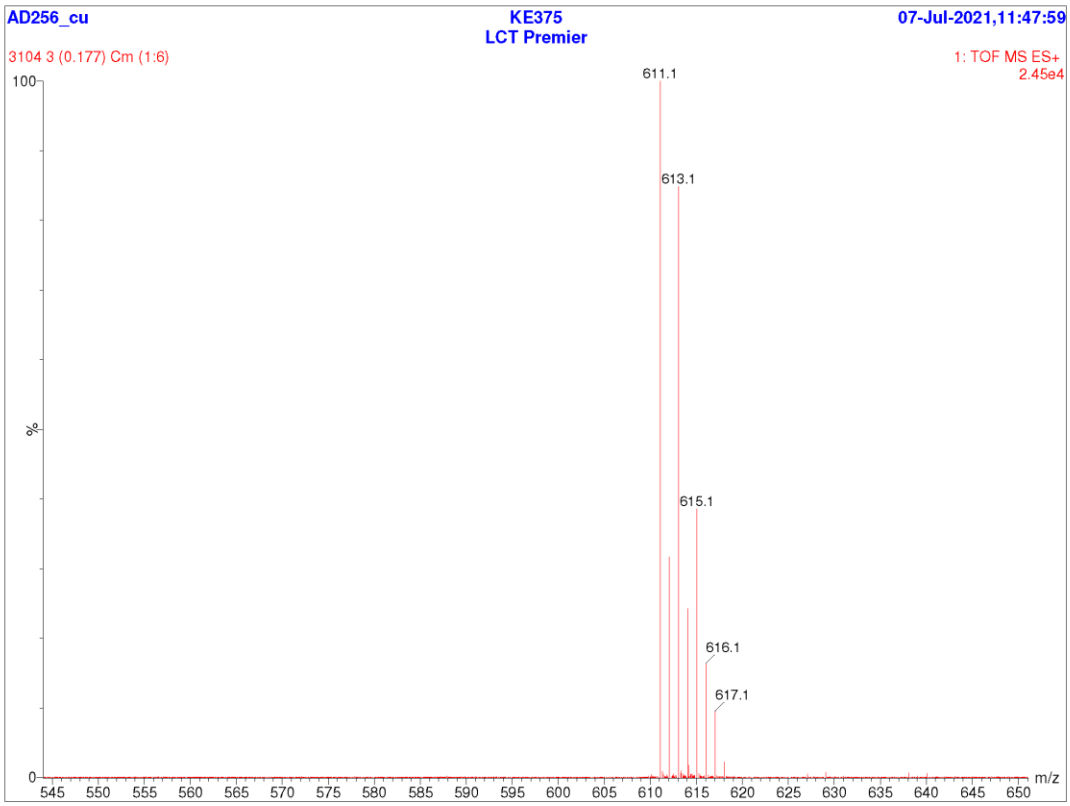

Figure S46. LRMS (ESI+) of **1a**, 611.1 $[M\text{-}Cl]^+$.

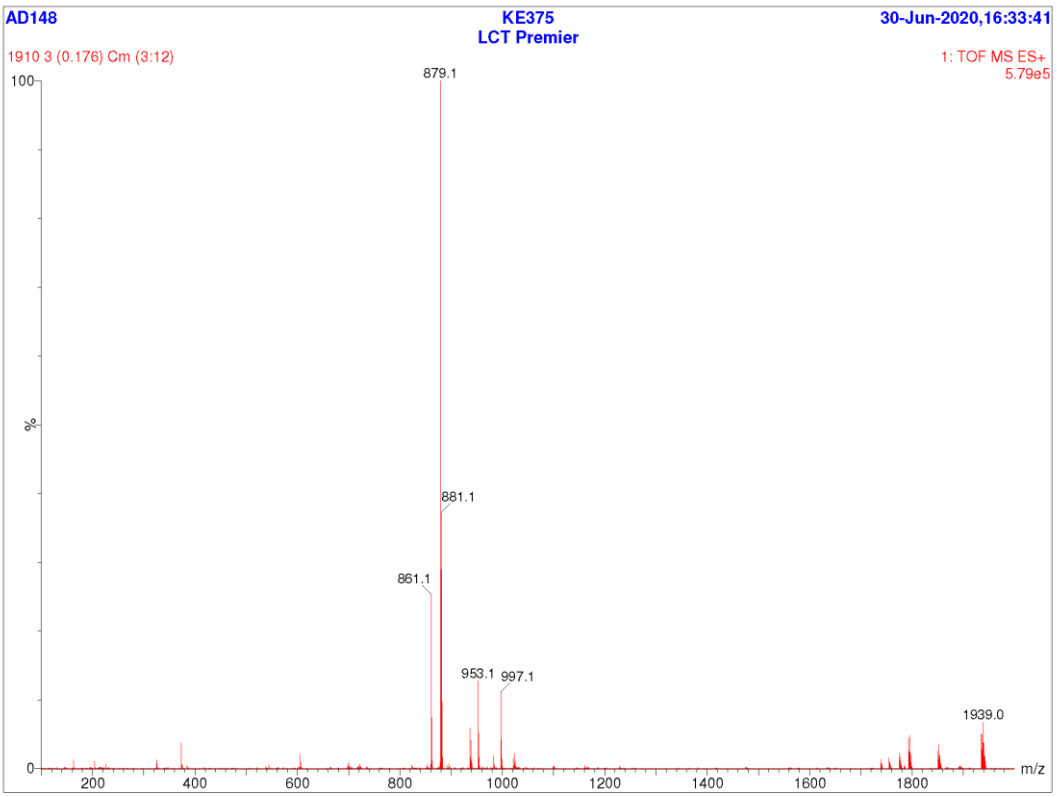

Figure S47. LRMS (ESI+) of **2**, full spectrum.

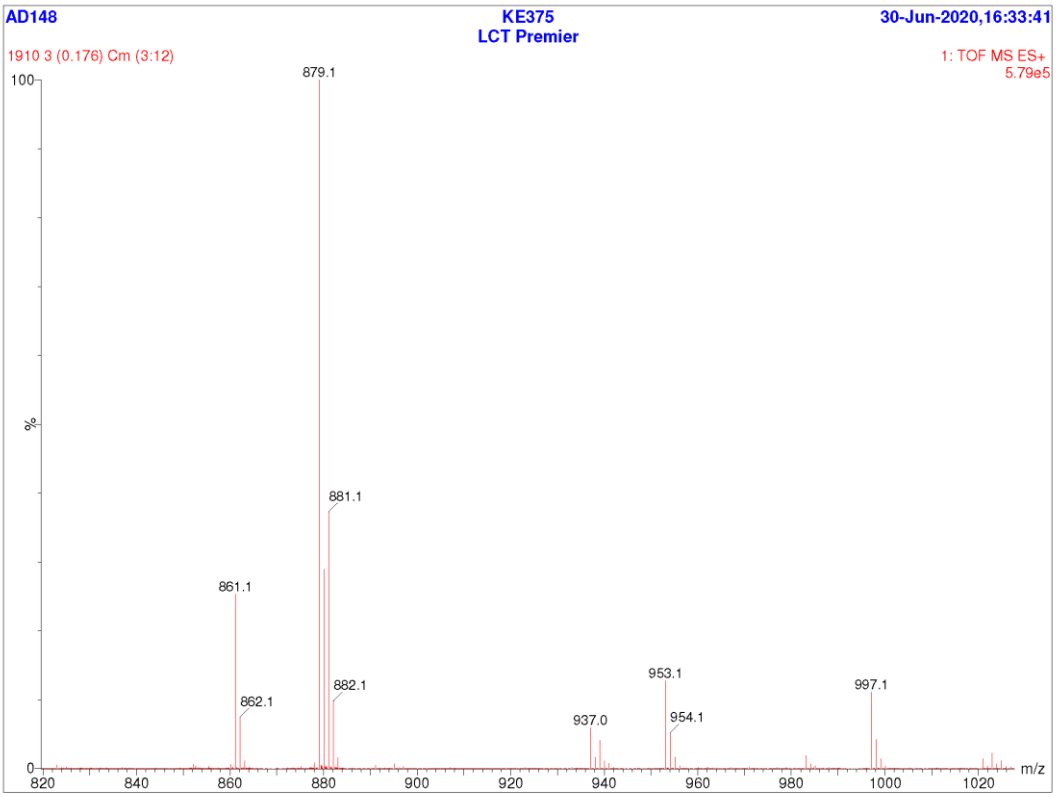

Figure S48. LRMS (ESI+) of **2**, 879.1 $[M\text{-}Cl]^+$, 937.0 $[M+Na]^+$, 953.1 $[M+K]^+$.

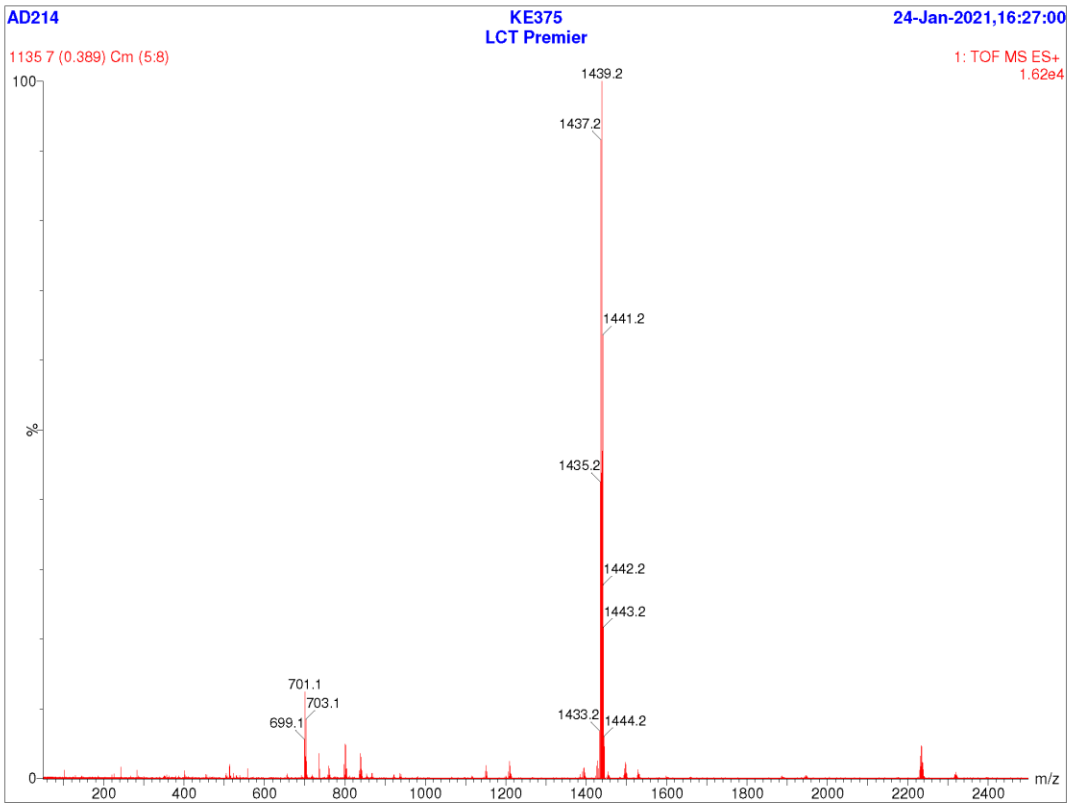

Figure S49. LRMS (ESI+) of **3**, full spectrum.

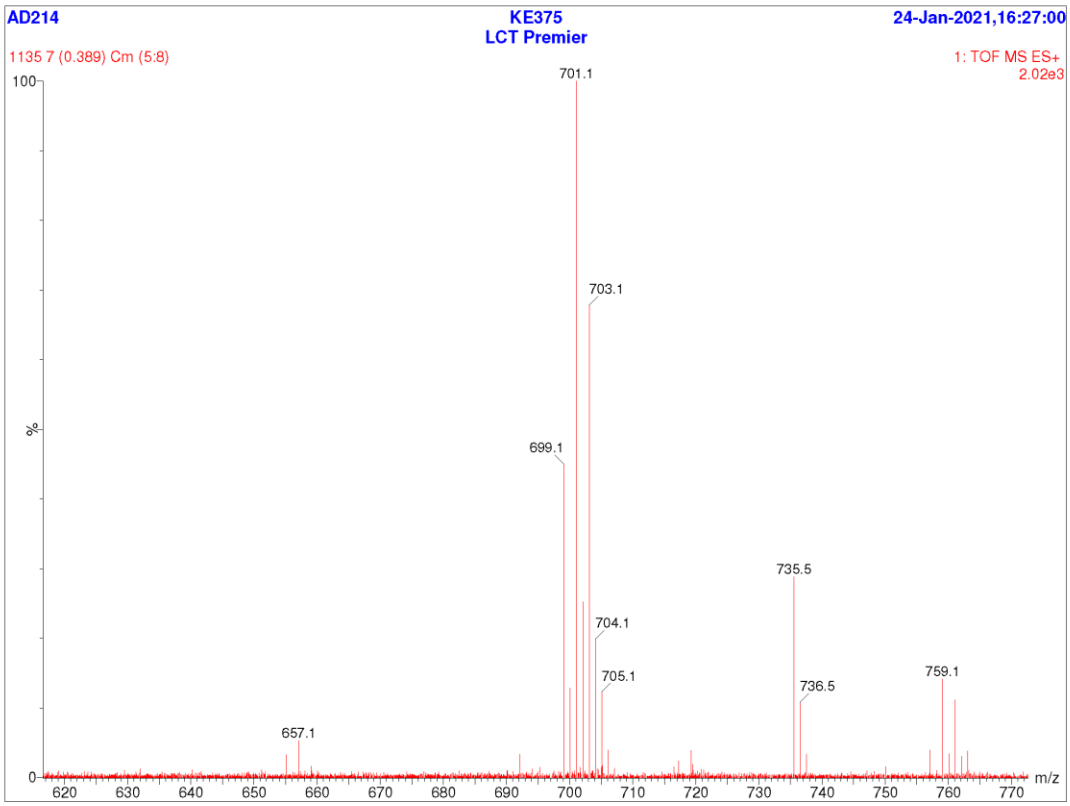

Figure S50. LRMS (ESI+) of **3**, 701.1 $[M\text{-}Cl]^+$.

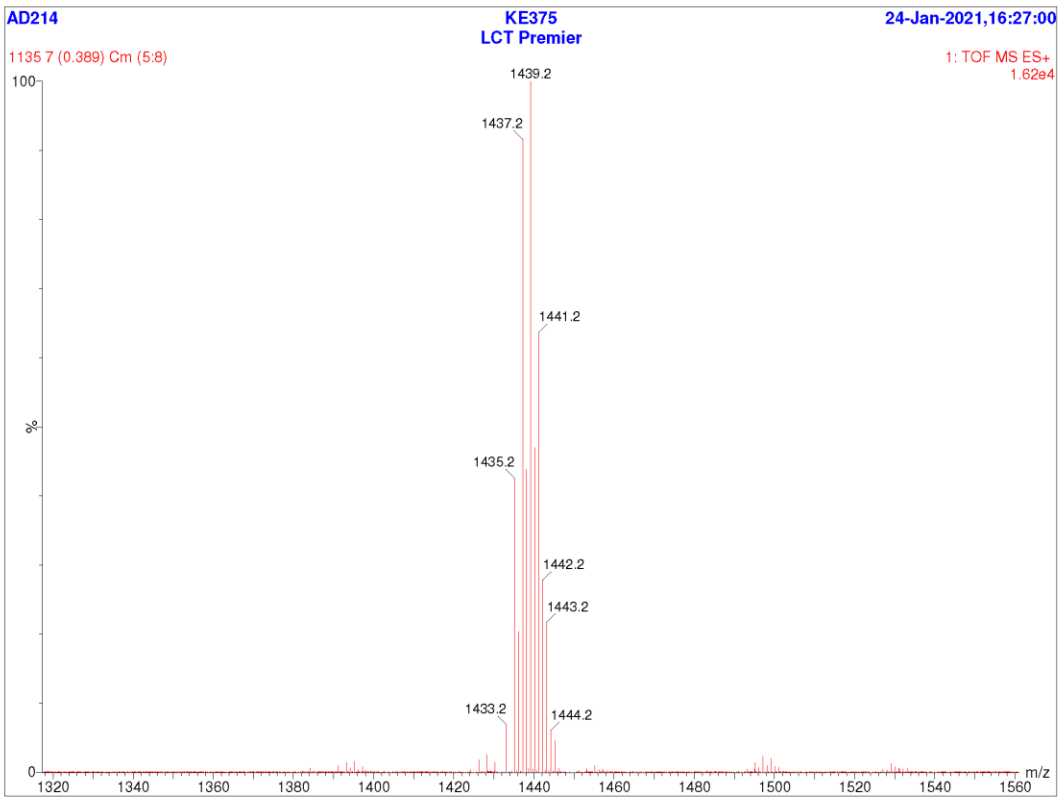

Figure S51. LRMS (ESI+) of **3**, 1439.2 $[2M\text{-}Cl]^+$.

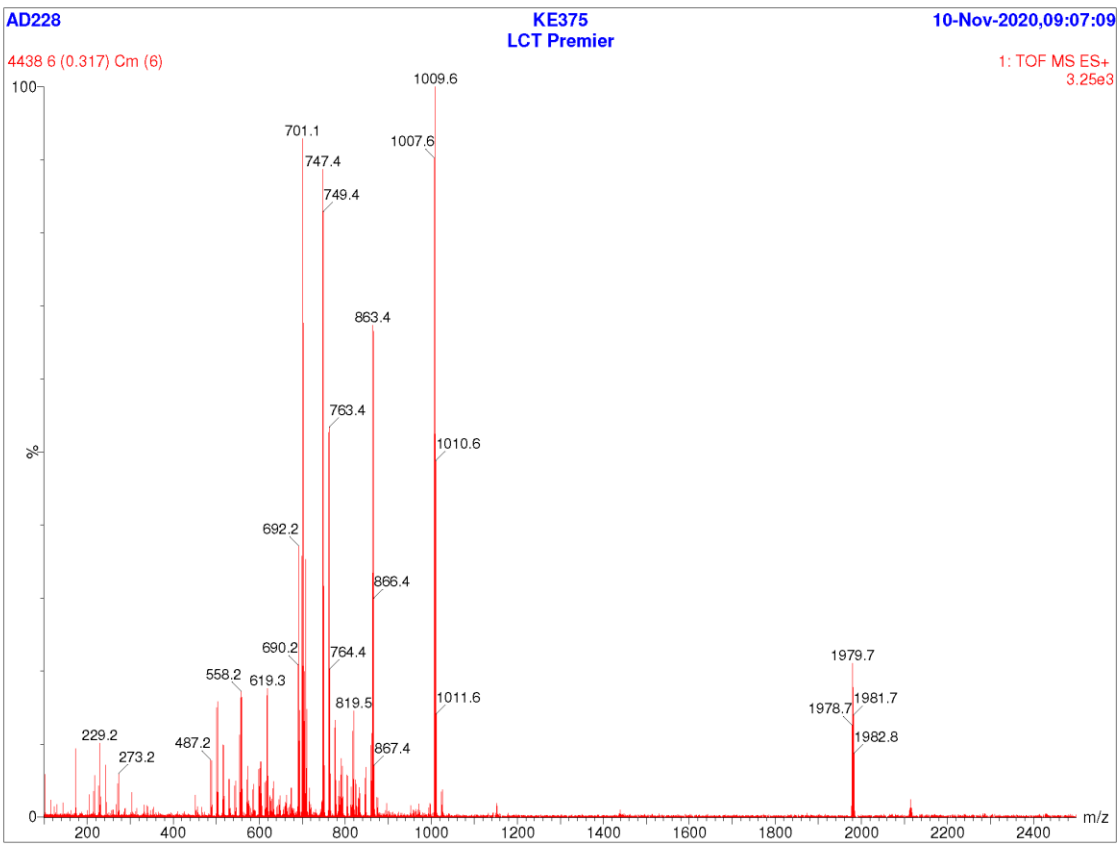

Figure S52. LRMS (ESI+) of **4**, full spectrum.

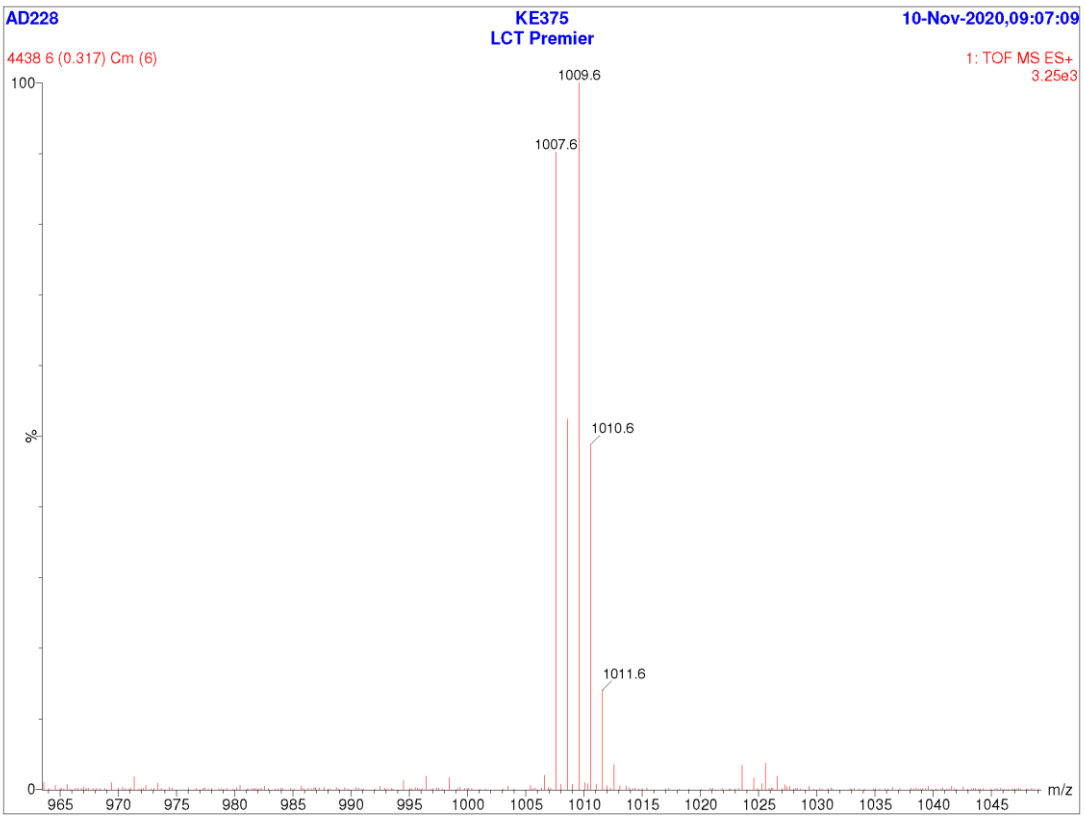

Figure S53. LRMS (ESI+) of **4**, 1009.6 $[M\text{-}Ag\text{-}2BAr^{F}_{4}]^{+}$.

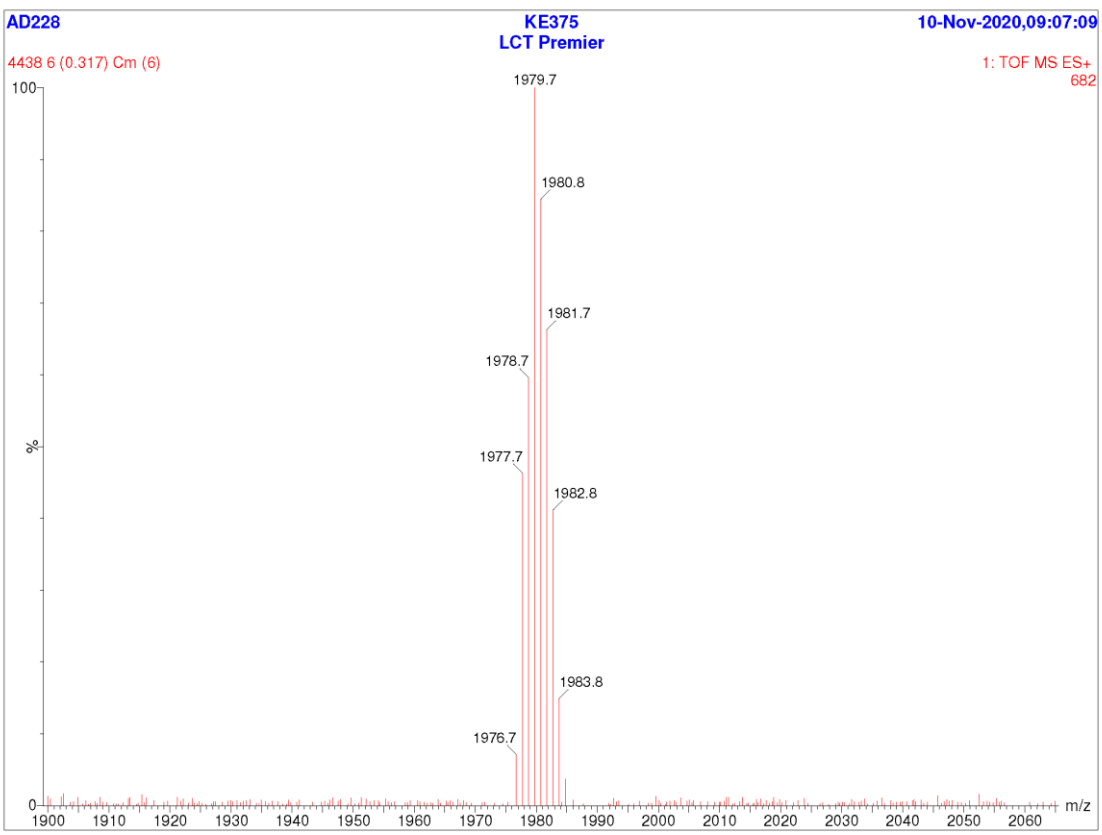

Figure S54. LRMS (ESI+) of **4**, 1979.7 $[M\text{-}BAr^{F}_{4}]^{+}$.

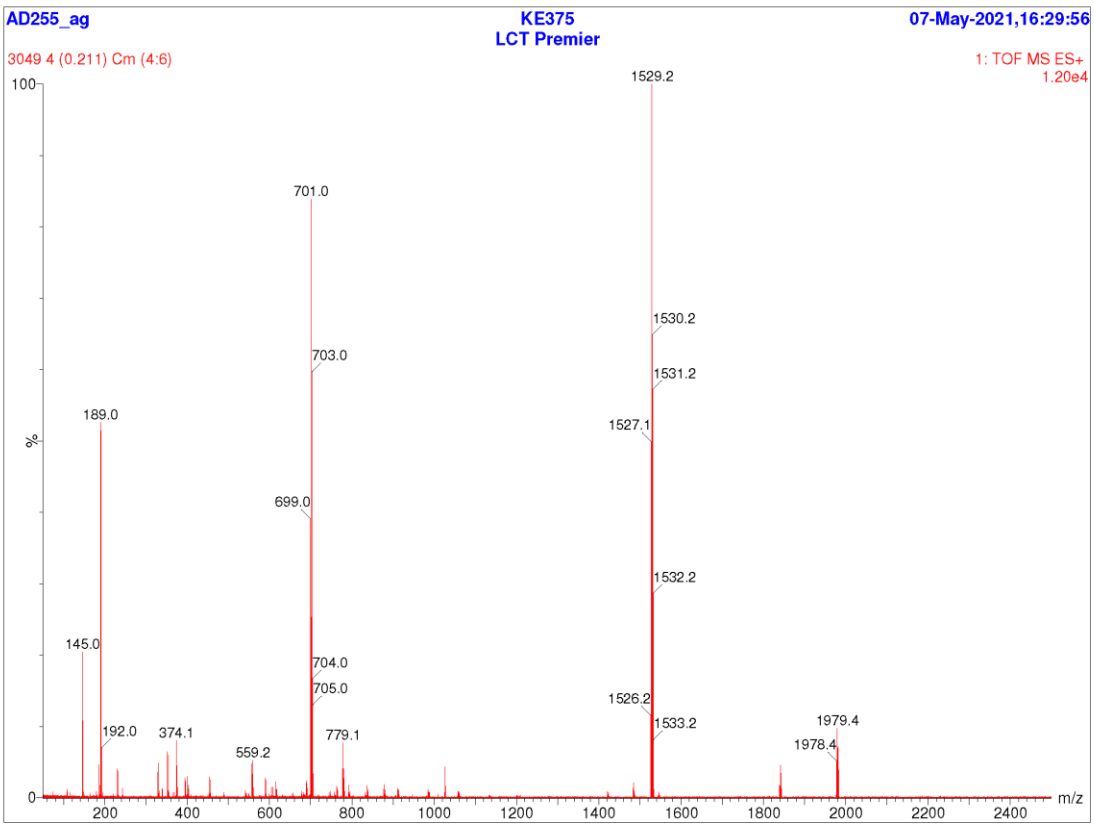

Figure S55. LRMS (ESI+) of **5a**, full spectrum.

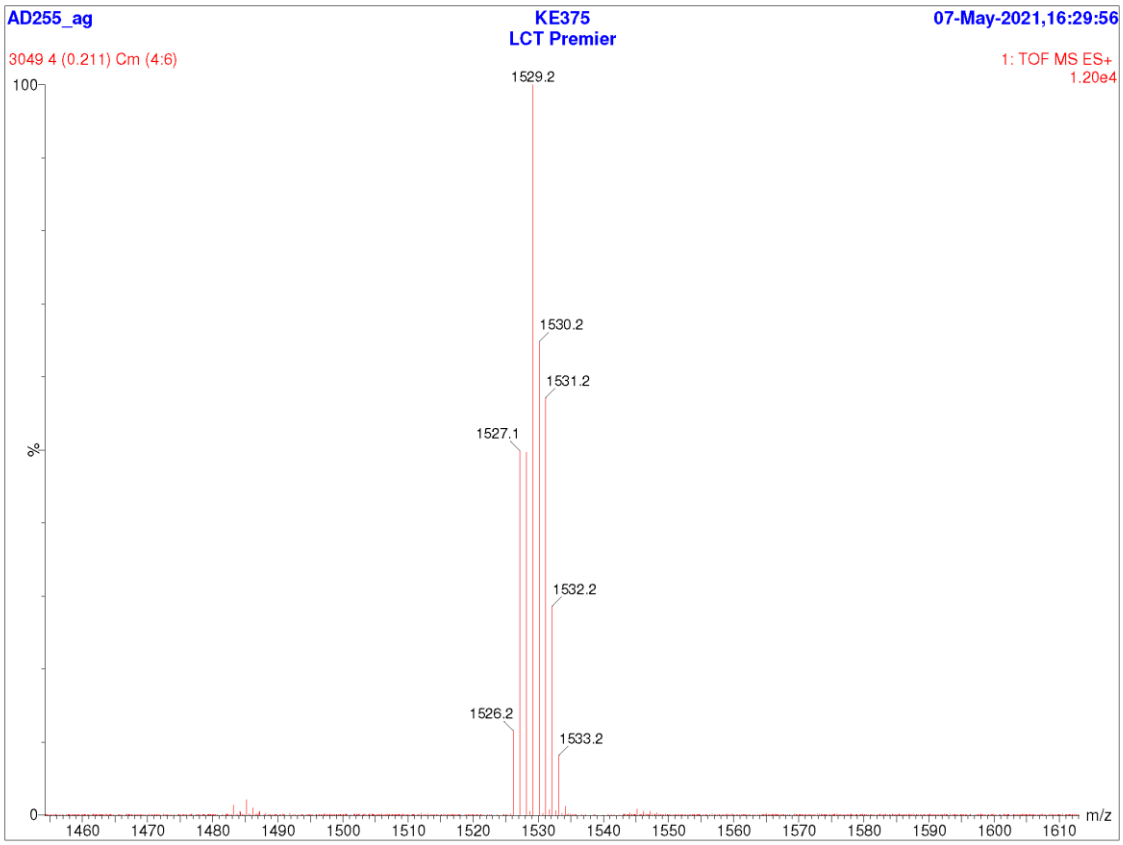

Figure S56. LRMS (ESI+) of **5a**, 1529.2 $[M\text{-}BAr^{F}_{4}]^{+}$.

	*t*Bu-PONNOP (**L**)	$[Cu_2(\mu\text{-}I)_2(t\text{Bu-PONNOP})]$ (**1**)	$[Cu_2(\mu\text{-}Cl)_2(t\text{Bu-PONNOP})]$ (**1a**)	$[Au_2Cl_2(t\text{Bu-PONNOP})].CH_2Cl_2$ (**2**.CH_2Cl_2)	$[Ag_2(\mu\text{-}Cl)_2(t\text{Bu-PONNOP})]$. MeCN (**3**.MeCN)	$[Ag_2(t\text{Bu-PONNOP})_2][BAr^F{}_4]_2$ (**4**)
CCDC number	2086142	2086145	2099166	2086146	2086143	2086144
Empirical formula	$C_{24}H_{40}N_2O_2P_2$	$C_{24}H_{40}Cu_2I_2N_2O_2P_2$	$C_{24}H_{40}Cu_2Cl_2N_2O_2P_2$	$C_{25}H_{42}Au_2Cl_4N_2O_2P_2$	$C_{28}H_{46}Ag_2Cl_2N_4O_2P_2$	$C_{112}H_{104}Ag_2B_2F_{48.01}N_4O_4P_4$
Formula weight	450.52	831.40	648.50	1000.28	819.27	2843.42
Temperature/K	150.00(10)	150.00(10)	150.15(10)	149.98(11)	150.00(10)	150.01(10)
Crystal system	triclinic	Tetragonal	tetragonal	orthorhombic	monoclinic	triclinic
Space group	P-1	$P\text{-}42_1m$	P-421m	Pbca	P2/n	P-1
a/Å	6.3190(7)	13.19560(10)	13.1203(3)	14.4412(6)	12.2144(4)	16.8129(10)
b/Å	14.4208(18)	13.19560(10)	13.1203(3)	19.7582(8)	9.5605(3)	20.1783(13)
c/Å	15.1492(15)	8.87860(10)	8.6767(4)	24.0737(11)	15.3894(3)	21.3753(14)
α/°	83.368(9)	90	90	90	90	74.616(6)
β/°	87.909(8)	90	90	90	92.463(2)	70.234(6)
γ/°	77.724(10)	90	90	90	90	66.202(6)
Volume/Å^3	1339.8(3)	1545.98(3)	1493.63(10)	6869.0(5)	1795.44(8)	6173.9(8)
Z	2	2	2	8	2	2
ρ_{calc}g/cm^3	1.117	1.786	1.442	1.934	1.515	1.530
μ/mm^{-1}	1.627	18.530	1.733	8.962	11.194	4.145
F(000)	488.0	816.0	672.0	3824.0	832.0	2864.0
Crystal size/mm^3	0.21 × 0.127 × 0.029	0.596 × 0.199 × 0.146	0.889 × 0.428 × 0.211	0.344 × 0.275 × 0.135	0.29 × 0.199 × 0.146	0.162 × 0.138 × 0.074
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.136 to 141.918	9.478 to 147.642	6.944 to 64.92	3.384 to 64.92	9.056 to 141.976	7.046 to 142.892
Index ranges	-6 ≤ h ≤ 7, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18	-16 ≤ h ≤ 15, -16 ≤ k ≤ 16, -10 ≤ l ≤ 11	-19≤ h ≤ 19, -19 ≤ k ≤ 19, -12 ≤ l ≤ 12	-16 ≤ h ≤ 21, -27 ≤ k ≤ 29, -30 ≤ l ≤ 35	-14 ≤ h ≤ 14, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18	-20 ≤ h ≤ 19, -24 ≤ k ≤ 18, -24 ≤ l ≤ 26
Reflections collected	8311	17949	20453	29294	5966	34050
Independent reflections	8311 [R_{int} = N/A, R_{sigma} = 0.0460]	1667 [R_{int} = 0.0903, R_{sigma} = 0.0329]	2623 [R_{int} = 0.0416, R_{sigma} = 0.0281]	10978 [R_{int} = 0.0436, R_{sigma} = 0.0574]	5966 [R_{int} = N/A, R_{sigma} = 0.0180]	22812 [R_{int} = 0.0264, R_{sigma} = 0.0545]
Data/restraints/parameters	8311/0/284	1667/0/96	2623/0/96	10978/0/356	5966/0/190	22812/766/1838
Goodness-of-fit on F^2	1.111	1.144	1.107	1.024	0.993	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0658, wR_2 = 0.1776	R_1 = 0.0401, wR_2 = 0.0986	R_1 = 0.0259, wR_2 = 0.0529	R_1 = 0.0367, wR_2 = 0.0596	R_1 = 0.0238, wR_2 = 0.0609	R_1 = 0.0514, wR_2 = 0.1253
Final R indexes [all data]	R_1 = 0.0971, wR_2 = 0.1889	R_1 = 0.0402, wR_2 = 0.0987	R_1 = 0.0309, wR_2 = 0.0554	R_1 = 0.0619, wR_2 = 0.0694	R_1 = 0.0263, wR_2 = 0.0617	R_1 = 0.0809, wR_2 = 0.1489
Largest diff. peak/hole / e Å^{-3}	0.65/-0.31	1.69/-1.73	0.29/-0.38	0.98/-1.33	0.54/-0.74	1.40/-1.38
Flack parameter	N/A	-0.011(4)	-0.019(6)	N/A	N/A	N/A

Table S1. X-ray crystallographic data.

Methodology Validation

We firstly benchmarked three different levels of theory to choose the best methodology to accurately predict the parameters of the crystal structures of compounds 1–4. The results are shown in Table S1. The mean signed deviation (MAD) between the calculated and experimental bond distances is used to verify how good the level of theory is. As seen Level 2 gave best agreement and then was used for the following NBO analysis.

Table S2. Benchmark results with these four levels of theory.[a]

Compounds	Bond distances (Å)	Exp.	Level 1	Level 2	Level 3
4	Ag1----Ag2	4.90276	4.49988	4.82192	4.90534
	Ag1---P1A	2.4111	2.45373	2.39678	2.38794
	Ag1---P1C	2.4122	2.45532	2.39572	2.39034
	Ag1----N1A	2.7274	2.58252	2.63503	2.65693
	Ag1----N1C	2.6983	2.57785	2.63008	2.66181
	Ag2---P2A	2.4351	2.46244	2.39997	2.39349
	Ag2---P2C	2.4402	2.46581	2.40261	2.3910
	Ag2---N8A	2.5663	2.60014	2.67952	2.69247
	Ag2---N8C	2.5623	2.58423	2.65672	2.71991
	MAD(Å)		0.096	0.061	0.059
3	Ag1---P1	2.37517	2.39229	2.32739	2.34037
	Ag1---N1	2.6643	2.73494	2.7558	2.73662
	Ag1---Cl	2.51777	2.49885	2.42827	2.44052
	Ag1---Cl1'	2.62858	2.49885	2.7665	2.88229
	Ag1---Ag1	3.05044	2.96207	3.0714	3.12332
	MAD(Å)		0.065	0.078	0.102
2	P1---Au1	2.2201	2.27592	2.23683	2.24208
	Au1---Cl1	2.2861	2.35597	2.30025	2.32721
	P2---Au2	2.2231	2.27596	2.23676	2.24208
	Au2---Cl2	2.2961	2.35599	2.30032	2.32759
	Au1---N1	3.2743	3.16304	3.2118	3.24413
	Au2---N8	3.1313	3.16307	3.21156	3.23735
	Au1---Au2	6.09628	5.92385	6.05244	6.17926
	MAD(Å)		0.079	0.034	0.037
1	Cu1---I1	2.63298	2.64448	2.6384	2.6578
	Cu1---N1	2.1166	2.14143	2.1317	2.10762
	Cu1---P1	2.2011	2.19311	2.19459	2.20927
	Cu1---Cu1	2.56009	2.53524	2.55176	2.57654
	MAD(Å)		0.017	0.009	0.015

[a]The geometries were optimized at BP86-D3BJ/6-31G(d)-SDD (SDD[1] for metal atoms and Rassolov corrected 6-31G(d)[2] for all other atoms) in gas phase (denoted as Level 1), BP86-D3BJ/Def2TZVP in gas phase (denoted as Level 2), and BP86-D3BJ/Def2TZVP in DCM phase with CPCM solvent model.[3]

[1] Fuentealba, P.; Preuss, H.; Stoll, H.; Von Szentpály, L. A proper account of core-polarization with pseudopotentials: single valence-electron alkali compounds. Chem. Phys. Lett. 1982, 89, 418−422

[2] Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. 6-31G* basis set for third-row atoms. J. Comput. Chem. 2001, 22, 976−984.

[3] Barone, V.; Cossi, M. Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. J. Phys. Chem. A 1998, 102, 1995−2001.

Gaussian Optimized Structures

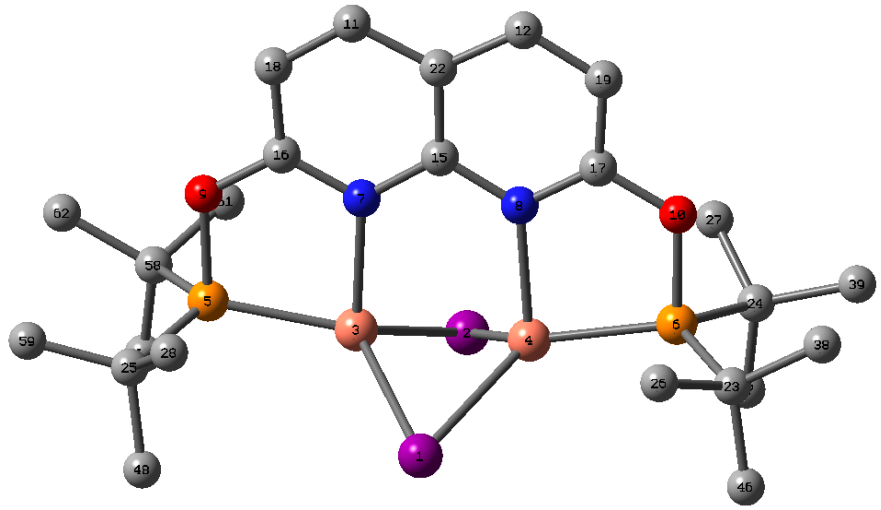

Figure S57. Optimized structure of compound 1 at BP86-D3BJ/Def2-TZVP level of theory in gas phase.

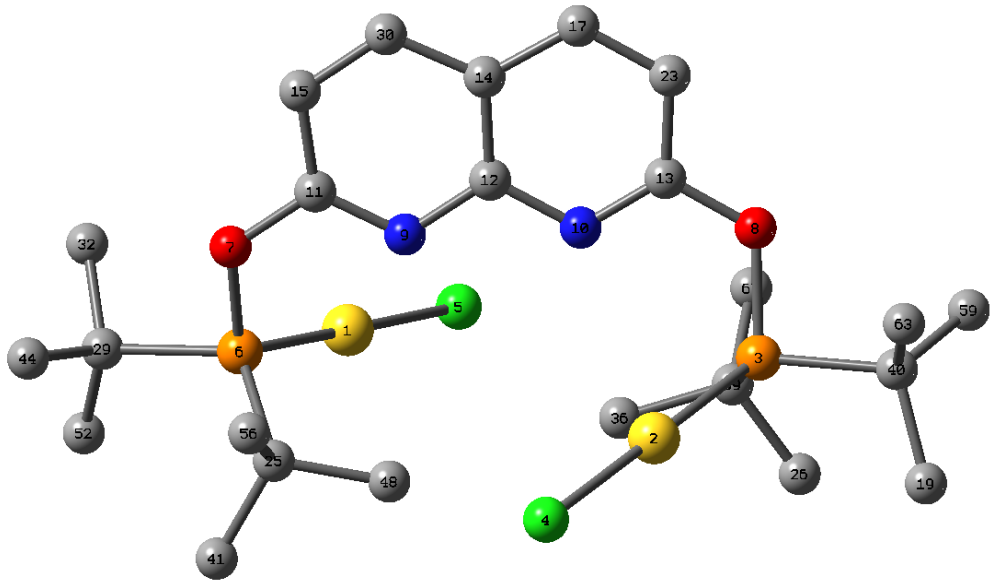

Figure S58. Optimized structure of compound 2 at BP86-D3BJ/Def2-TZVP level of theory in gas phase.

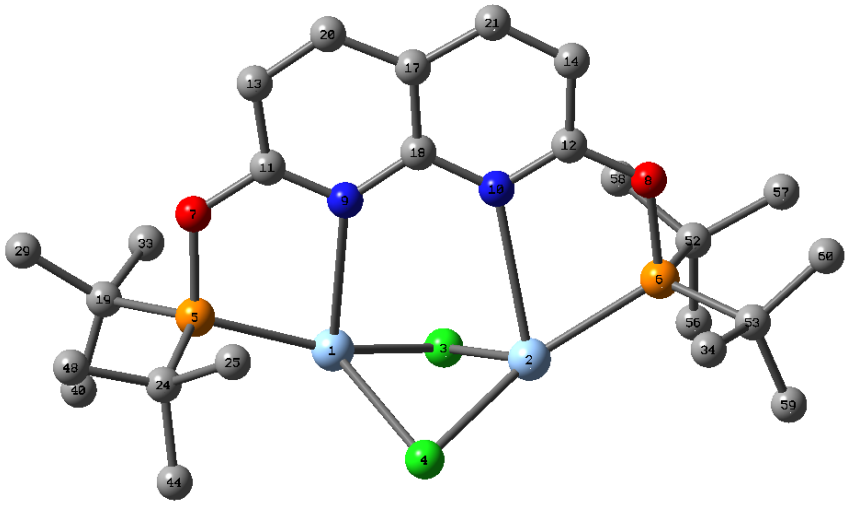

Figure S59. Optimized structure of compound 3 at BP86-D3BJ/Def2-TZVP level of theory in gas phase.

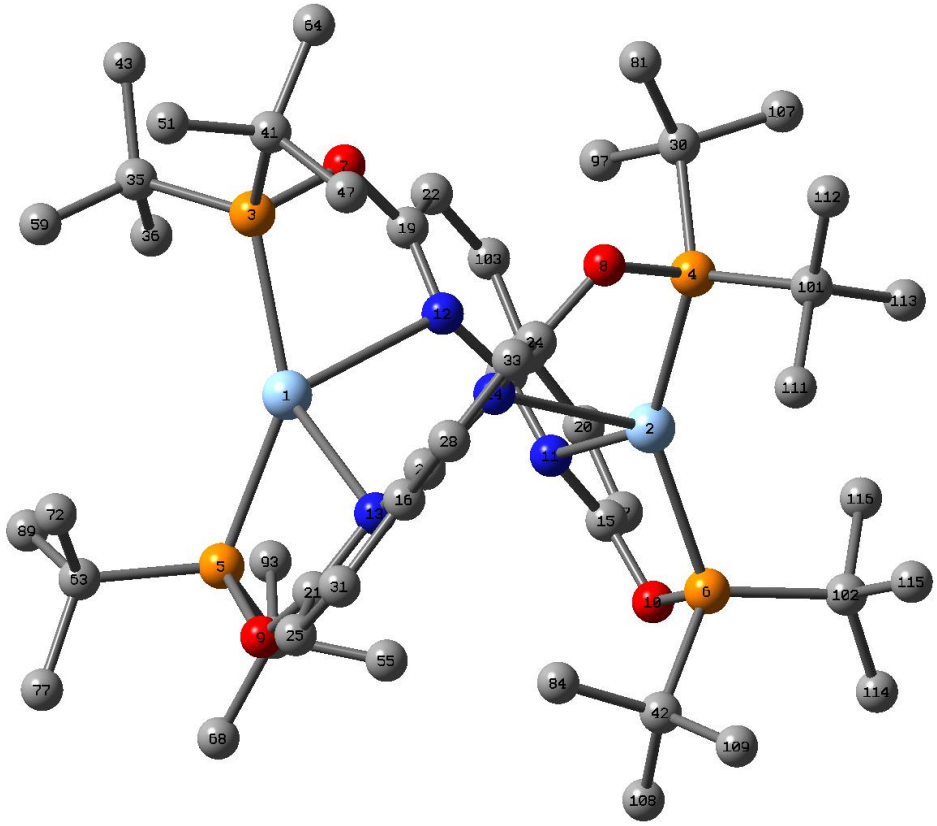

Figure S60. Optimized structure of compound 4 at BP86-D3BJ/Def2-TZVP level of theory in gas phase.

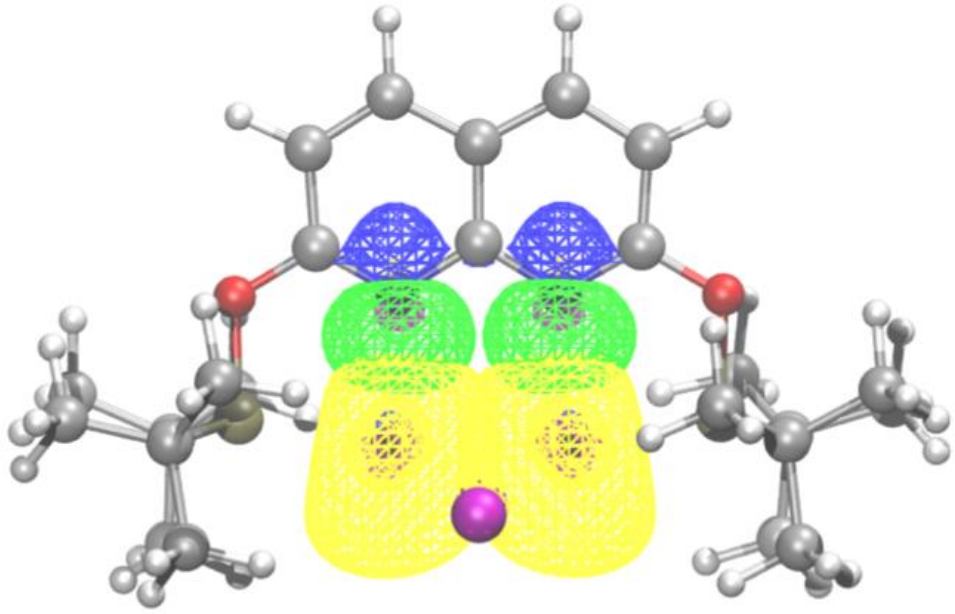

Figure S61. NBO plot of the major Cu···N bonding interactions in 1. Isosurface value = 0.05.

Table S2. Electronic energies for compounds 1–4.[a]

Compound	Ee (a.u.)	Img
1	-5759.63015465	0
2	-3074.58607467	0
3	-3097.01306199	0
4	-4058.07952332	0

[a]The energies are electronic energies without inclusion of zero-point vibrational energy. The Img column lists the number of imaginary frequencies.

Raw data of NBO analysis for compounds 1, 3 and 4

Table S3. Second order perturbative estimates of donor-acceptor interactions in the NBO basis of compound 1.

Donor NBO —— Acceptor NBO		E(2) (kcal/mol)
83. LP (1)Cu 3	186. BD*(1) N 7- C 15	0.16
83. LP (1)Cu 3	445. RY (1) N 7	0.55
83. LP (1)Cu 3	447. RY (3) N 7	0.08
84. LP (2)Cu 3	446. RY (2) N 7	0.26
85. LP (3)Cu 3	186. BD*(1) N 7- C 15	0.19
85. LP (3)Cu 3	187. BD*(1) N 7- C 16	0.08
85. LP (3)Cu 3	190. BD*(1) N 8- C 17	0.05
85. LP (3)Cu 3	445. RY (1) N 7	0.11
86. LP (4)Cu 3	188. BD*(2) N 7- C 16	0.32
87. LP (5)Cu 3	186. BD*(1) N 7- C 15	0.14
87. LP (5)Cu 3	187. BD*(1) N 7- C 16	0.27
87. LP (5)Cu 3	445. RY (1) N 7	0.59
88. LP (1)Cu 4	189. BD*(1) N 8- C 15	0.16
88. LP (1)Cu 4	471. RY (1) N 8	0.55
88. LP (1)Cu 4	473. RY (3) N 8	0.08
89. LP (2)Cu 4	191. BD*(2) N 8- C 17	1.25
89. LP (2)Cu 4	472. RY (2) N 8	0.26
90. LP (3)Cu 4	187. BD*(1) N 7- C 16	0.05
90. LP (3)Cu 4	189. BD*(1) N 8- C 15	0.19
90. LP (3)Cu 4	190. BD*(1) N 8- C 17	0.08
90. LP (3)Cu 4	471. RY (1) N 8	0.11
91. LP (4)Cu 4	191. BD*(2) N 8- C 17	0.33
92. LP (5)Cu 4	189. BD*(1) N 8- C 15	0.14
92. LP (5)Cu 4	190. BD*(1) N 8- C 17	0.28
92. LP (5)Cu 4	471. RY (1) N 8	0.6
95. LP (1) N 7	**177. LV (1)Cu 3**	**20.96**
95. LP (1) N 7	331. RY (3)Cu 3	2.46
95. LP (1) N 7	333. RY (5)Cu 3	0.08
95. LP (1) N 7	335. RY (7)Cu 3	0.3
95. LP (1) N 7	337. RY (9)Cu 3	0.25
95. LP (1) N 7	342. RY (14)Cu 3	0.17
95. LP (1) N 7	347. RY (19)Cu 3	0.09
96. LP (1) N 8	177. LV (1)Cu 3	0.49
96. LP (1) N 8	330. RY (2)Cu 3	0.09
96. LP (1) N 8	337. RY (9)Cu 3	0.06
97. LP (1) O 9	177. LV (1)Cu 3	0.61

108. BD (1) N 7- C 15	177. LV (1)Cu 3	1.00
109. BD (1) N 7- C 16	177. LV (1)Cu 3	2.21
109. BD (1) N 7- C 16	331. RY (3)Cu 3	0.12
109. BD (1) N 7- C 16	340. RY (12)Cu 3	0.05
110. BD (2) N 7- C 16	332. RY (4)Cu 3	0.05
110. BD (2) N 7- C 16	336. RY (8)Cu 3	0.11
111. BD (1) N 8- C 15	177. LV (1)Cu 3	0.15
112. BD (1) N 8- C 17	177. LV (1)Cu 3	0.06
95. LP (1) N 7	178. LV (1)Cu 4	0.49
95. LP (1) N 7	360. RY (2)Cu 4	0.08
95. LP (1) N 7	367. RY (9)Cu 4	0.06
96. LP (1) N 8	**178. LV (1)Cu 4**	**20.97**
96. LP (1) N 8	361. RY (3)Cu 4	2.47
96. LP (1) N 8	363. RY (5)Cu 4	0.08
96. LP (1) N 8	365. RY (7)Cu 4	0.3
96. LP (1) N 8	367. RY (9)Cu 4	0.3
96. LP (1) N 8	370. RY (12)Cu 4	0.06
96. LP (1) N 8	372. RY (14)Cu 4	0.17
96. LP (1) N 8	377. RY (19)Cu 4	0.08

Table S4. Second order perturbative estimates of donor-acceptor interactions in the NBO basis of compound 3.

Donor NBO —— Acceptor NBO		E(2) (kcal/mol)
57. LP (1)Ag 1	171. BD*(2) N 9- C 11	0.1
57. LP (1)Ag 1	461. RY (1) N 9	0.06
58. LP (2)Ag 1	171. BD*(2) N 9- C 11	0.09
58. LP (2)Ag 1	172. BD*(1) N 9- C 18	0.06
58. LP (2)Ag 1	461. RY (1) N 9	0.18
58. LP (2)Ag 1	462. RY (2) N 9	0.05
59. LP (3)Ag 1	461. RY (1) N 9	0.08
59. LP (3)Ag 1	172. BD*(1) N 9- C 18	0.06
59. LP (3)Ag 1	461. RY (1) N 9	0.08
62. LP (1)Ag 2	174. BD*(2) N 10- C 12	0.1
62. LP (1)Ag 2	487. RY (1) N 10	0.06
63. LP (2)Ag 2	174. BD*(2) N 10- C 12	0.09
63. LP (2)Ag 2	175. BD*(1) N 10- C 18	0.06
63. LP (2)Ag 2	487. RY (1) N 10	0.18
63. LP (2)Ag 2	488. RY (2) N 10	0.05
64. LP (3)Ag 2	487. RY (1) N 10	0.08
81. LP (1) N 9	**159. LV (1)Ag 1**	**5.86**
81. LP (1) N 9	237. RY (1)Ag 1	0.08
81. LP (1) N 9	238. RY (2)Ag 1	0.16
81. LP (1) N 9	239. RY (3)Ag 1	0.57
81. LP (1) N 9	240. RY (4)Ag 1	0.11
81. LP (1) N 9	241. RY (5)Ag 1	0.07
81. LP (1) N 9	243. RY (7)Ag 1	0.09
81. LP (1) N 9	245. RY (9)Ag 1	0.17
81. LP (1) N 9	246. RY (10)Ag 1	0.14
81. LP (1) N 9	247. RY (11)Ag 1	0.14

81. LP (1) N 9	248. RY (12)Ag 1	0.28
81. LP (1) N 9	249. RY (13)Ag 1	0.15
81. LP (1) N 9	250. RY (14)Ag 1	0.17
81. LP (1) N 9	251. RY (15)Ag 1	0.05
81. LP (1) N 9	252. RY (16)Ag 1	0.07
81. LP (1) N 9	256. RY (20)Ag 1	0.1
81. LP (1) N 9	258. RY (22)Ag 1	0.27
81. LP (1) N 9	259. RY (23)Ag 1	0.17
81. LP (1) N 9	261. RY (25)Ag 1	0.1
82. LP (1) N 10	159. LV (1)Ag 1	0.07
82. LP (1) N 10	242. RY (6)Ag 1	0.23
82. LP (1) N 10	243. RY (7)Ag 1	0.08
82. LP (1) N 10	246. RY (10)Ag 1	0.07
82. LP (1) N 10	251. RY (15)Ag 1	0.09
92. BD (1) N 9- C 11	159. LV (1)Ag 1	0.70
92. BD (1) N 9- C 11	239. RY (3)Ag 1	0.21
92. BD (1) N 9- C 11	240. RY (4)Ag 1	0.06
92. BD (1) N 9- C 11	243. RY (7)Ag 1	0.06
92. BD (1) N 9- C 11	245. RY (9)Ag 1	0.08
92. BD (1) N 9- C 11	246. RY (10)Ag 1	0.08
92. BD (1) N 9- C 11	248. RY (12)Ag 1	0.09
92. BD (1) N 9- C 11	250. RY (14)Ag 1	0.05
92. BD (1) N 9- C 11	256. RY (20)Ag 1	0.09
92. BD (1) N 9- C 11	258. RY (22)Ag 1	0.1
92. BD (1) N 9- C 11	259. RY (23)Ag 1	0.1
92. BD (1) N 9- C 11	261. RY (25)Ag 1	0.07
94. BD (1) N 9- C 18	239. RY (3)Ag 1	0.1
94. BD (1) N 9- C 18	240. RY (4)Ag 1	0.12
94. BD (1) N 9- C 18	243. RY (7)Ag 1	0.05
94. BD (1) N 9- C 18	245. RY (9)Ag 1	0.07
94. BD (1) N 9- C 18	246. RY (10)Ag 1	0.17
94. BD (1) N 9- C 18	256. RY (20)Ag 1	0.12
94. BD (1) N 9- C 18	258. RY (22)Ag 1	0.12
94. BD (1) N 9- C 18	259. RY (23)Ag 1	0.15
94. BD (1) N 9- C 18	261. RY (25)Ag 1	0.09
94. BD (1) N 9- C 18	266. RY (30)Ag 1	0.05
95. BD (1) N 10- C 12	242. RY (6)Ag 1	0.06
97. BD (1) N 10- C 18	242. RY (6)Ag 1	0.07
82. LP (1) N 10	**160. LV (1)Ag 2**	**5.86**
82. LP (1) N 10	267. RY (1)Ag 2	0.08
82. LP (1) N 10	268. RY (2)Ag 2	0.16
82. LP (1) N 10	269. RY (3)Ag 2	0.57
82. LP (1) N 10	270. RY (4)Ag 2	0.11
82. LP (1) N 10	271. RY (5)Ag 2	0.07
82. LP (1) N 10	273. RY (7)Ag 2	0.09
82. LP (1) N 10	275. RY (9)Ag 2	0.17
82. LP (1) N 10	276. RY (10)Ag 2	0.14
82. LP (1) N 10	277. RY (11)Ag 2	0.14
82. LP (1) N 10	278. RY (12)Ag 2	0.28
82. LP (1) N 10	279. RY (13)Ag 2	0.15

82. LP (1) N 10 280. RY (14)Ag 2	0.17
82. LP (1) N 10 281. RY (15)Ag 2	0.05
82. LP (1) N 10 282. RY (16)Ag 2	0.07
82. LP (1) N 10 286. RY (20)Ag 2	0.1
82. LP (1) N 10 288. RY (22)Ag 2	0.27
82. LP (1) N 10 289. RY (23)Ag 2	0.17
82. LP (1) N 10 291. RY (25)Ag 2	0.1
92. BD (1) N 9- C 11 272. RY (6)Ag 2	0.06
94. BD (1) N 9- C 18 272. RY (6)Ag 2	0.07
95. BD (1) N 10- C 12 160. LV (1)Ag 2	0.70
95. BD (1) N 10- C 12 269. RY (3)Ag 2	0.21
95. BD (1) N 10- C 12 270. RY (4)Ag 2	0.06
95. BD (1) N 10- C 12 273. RY (7)Ag 2	0.06
95. BD (1) N 10- C 12 275. RY (9)Ag 2	0.08
95. BD (1) N 10- C 12 276. RY (10)Ag 2	0.08
95. BD (1) N 10- C 12 278. RY (12)Ag 2	0.09
95. BD (1) N 10- C 12 280. RY (14)Ag 2	0.05
95. BD (1) N 10- C 12 286. RY (20)Ag 2	0.09
95. BD (1) N 10- C 12 288. RY (22)Ag 2	0.1
95. BD (1) N 10- C 12 289. RY (23)Ag 2	0.1
95. BD (1) N 10- C 12 291. RY (25)Ag 2	0.07
97. BD (1) N 10- C 18 269. RY (3)Ag 2	0.1
97. BD (1) N 10- C 18 270. RY (4)Ag 2	0.12
97. BD (1) N 10- C 18 273. RY (7)Ag 2	0.05
97. BD (1) N 10- C 18 275. RY (9)Ag 2	0.07
97. BD (1) N 10- C 18 276. RY (10)Ag 2	0.17
97. BD (1) N 10- C 18 286. RY (20)Ag 2	0.12
97. BD (1) N 10- C 18 288. RY (22)Ag 2	0.12
97. BD (1) N 10- C 18 289. RY (23)Ag 2	0.15
97. BD (1) N 10- C 18 291. RY (25)Ag 2	0.09
97. BD (1) N 10- C 18 296. RY (30)Ag 2	0.05
99. BD (1) C 12- C 14 160. LV (1)Ag 2	0.19

Table S5. Second order perturbative estimates of donor-acceptor interactions in the NBO basis of compound 4

Donor NBO —— Acceptor NBO	E(2) (kcal/mol)
85. LP (1)Ag 1 719. RY (1) N 12	0.18
86. LP (2)Ag 1 719. RY (1) N 12	0.15
86. LP (2)Ag 1 721. RY (3) N 12	0.09
87. LP (3)Ag 1 286. BD*(1) N 12- C 17	0.12
87. LP (3)Ag 1 288. BD*(2) N 12- C 19	0.15
87. LP (3)Ag 1 719. RY (1) N 12	0.17
89. LP (5)Ag 1 287. BD*(1) N 12- C 19	0.06
89. LP (5)Ag 1 288. BD*(2) N 12- C 19	0.06
89. LP (5)Ag 1 719. RY (1) N 12	0.13
89. LP (5)Ag 1 721. RY (3) N 12	0.15
85. LP (1)Ag 1 290. BD*(2) N 13- C 21	0.06
85. LP (1)Ag 1 745. RY (1) N 13	0.18
85. LP (1)Ag 1 748. RY (4) N 13	0.06

86. LP (2)Ag 1 290. BD*(2) N 13- C 21	0.33
86. LP (2)Ag 1 745. RY (1) N 13	0.08
87. LP (3)Ag 1 290. BD*(2) N 13- C 21	0.1
87. LP (3)Ag 1 291. BD*(1) N 13- C 23	0.06
87. LP (3)Ag 1 745. RY (1) N 13	0.11
88. LP (4)Ag 1 290. BD*(2) N 13- C 21	0.23
88. LP (4)Ag 1 745. RY (1) N 13	0.06
89. LP (5)Ag 1 289. BD*(1) N 13- C 21	0.06
89. LP (5)Ag 1 745. RY (1) N 13	0.14
89. LP (5)Ag 1 747. RY (3) N 13	0.2
90. LP (1)Ag 2 693. RY (1) N 11	0.2
91. LP (2)Ag 2 693. RY (1) N 11	0.1
91. LP (2)Ag 2 695. RY (3) N 11	0.08
92. LP (3)Ag 2 284. BD*(2) N 11- C 15	0.08
92. LP (3)Ag 2 285. BD*(1) N 11- C 17	0.08
92. LP (3)Ag 2 693. RY (1) N 11	0.11
93. LP (4)Ag 2 284. BD*(2) N 11- C 15	0.21
94. LP (5)Ag 2 283. BD*(1) N 11- C 15	0.05
94. LP (5)Ag 2 693. RY (1) N 11	0.11
94. LP (5)Ag 2 695. RY (3) N 11	0.14
91. LP (2)Ag 2 294. BD*(2) N 14- C 24	0.41
91. LP (2)Ag 2 771. RY (1) N 14	0.11
91. LP (2)Ag 2 773. RY (3) N 14	0.06
92. LP (3)Ag 2 292. BD*(1) N 14- C 23	0.11
92. LP (3)Ag 2 294. BD*(2) N 14- C 24	0.15
92. LP (3)Ag 2 771. RY (1) N 14	0.14
93. LP (4)Ag 2 294. BD*(2) N 14- C 24	0.06
94. LP (5)Ag 2 771. RY (1) N 14	0.07
94. LP (5)Ag 2 773. RY (3) N 14	0.13
107. LP (1) N 11 263. LV (1)Ag 1	0.21
108. LP (1) N 12 263. LV (1)Ag 1	**7.51**
108. LP (1) N 12 417. RY (1)Ag 1	0.43
108. LP (1) N 12 418. RY (2)Ag 1	0.07
108. LP (1) N 12 419. RY (3)Ag 1	0.12
108. LP (1) N 12 420. RY (4)Ag 1	0.4
108. LP (1) N 12 422. RY (6)Ag 1	0.38
108. LP (1) N 12 424. RY (8)Ag 1	0.07
108. LP (1) N 12 429. RY (13)Ag 1	0.11
108. LP (1) N 12 431. RY (15)Ag 1	0.2
108. LP (1) N 12 432. RY (16)Ag 1	0.11
108. LP (1) N 12 433. RY (17)Ag 1	0.07
108. LP (1) N 12 434. RY (18)Ag 1	0.18
108. LP (1) N 12 435. RY (19)Ag 1	0.4
108. LP (1) N 12 437. RY (21)Ag 1	0.51
108. LP (1) N 12 438. RY (22)Ag 1	0.06
108. LP (1) N 12 439. RY (23)Ag 1	0.11
108. LP (1) N 12 440. RY (24)Ag 1	0.05
131. BD (1) N 11- C 17 263. LV (1)Ag 1	0.18
132. BD (1) N 12- C 17 263. LV (1)Ag 1	0.11
132. BD (1) N 12- C 17 417. RY (1)Ag 1	0.05

132. BD (1) N 12- C 17	418. RY (2)Ag 1	0.07
132. BD (1) N 12- C 17	420. RY (4)Ag 1	0.06
132. BD (1) N 12- C 17	421. RY (5)Ag 1	0.11
132. BD (1) N 12- C 17	422. RY (6)Ag 1	0.14
132. BD (1) N 12- C 17	435. RY (19)Ag 1	0.07
132. BD (1) N 12- C 17	437. RY (21)Ag 1	0.16
132. BD (1) N 12- C 17	446. RY (30)Ag 1	0.05
133. BD (1) N 12- C 19	263. LV (1)Ag 1	0.43
133. BD (1) N 12- C 19	422. RY (6)Ag 1	0.09
133. BD (1) N 12- C 19	435. RY (19)Ag 1	0.13
133. BD (1) N 12- C 19	437. RY (21)Ag 1	0.12
134. BD (2) N 12- C 19	263. LV (1)Ag 1	0.62
134. BD (2) N 12- C 19	417. RY (1)Ag 1	0.08
134. BD (2) N 12- C 19	422. RY (6)Ag 1	0.07
107. LP (1) N 11	**264. LV (1)Ag 2**	**7.33**
107. LP (1) N 11	448. RY (2)Ag 2	0.07
107. LP (1) N 11	450. RY (4)Ag 2	0.43
107. LP (1) N 11	451. RY (5)Ag 2	0.31
107. LP (1) N 11	452. RY (6)Ag 2	0.25
107. LP (1) N 11	461. RY (15)Ag 2	0.31
107. LP (1) N 11	464. RY (18)Ag 2	0.08
107. LP (1) N 11	465. RY (19)Ag 2	0.41
107. LP (1) N 11	467. RY (21)Ag 2	0.4
107. LP (1) N 11	468. RY (22)Ag 2	0.09
107. LP (1) N 11	469. RY (23)Ag 2	0.21
108. LP (1) N 12	264. LV (1)Ag 2	0.25
129. BD (1) N 11- C 15	264. LV (1)Ag 2	1.44
129. BD (1) N 11- C 15	448. RY (2)Ag 2	0.07
129. BD (1) N 11- C 15	451. RY (5)Ag 2	0.07
129. BD (1) N 11- C 15	452. RY (6)Ag 2	0.13
129. BD (1) N 11- C 15	461. RY (15)Ag 2	0.08
129. BD (1) N 11- C 15	465. RY (19)Ag 2	0.2
129. BD (1) N 11- C 15	467. RY (21)Ag 2	0.19
129. BD (1) N 11- C 15	469. RY (23)Ag 2	0.1
130. BD (2) N 11- C 15	264. LV (1)Ag 2	0.6
130. BD (2) N 11- C 15	451. RY (5)Ag 2	0.09
131. BD (1) N 11- C 17	264. LV (1)Ag 2	0.1
131. BD (1) N 11- C 17	448. RY (2)Ag 2	0.06
131. BD (1) N 11- C 17	450. RY (4)Ag 2	0.06
131. BD (1) N 11- C 17	452. RY (6)Ag 2	0.14
131. BD (1) N 11- C 17	465. RY (19)Ag 2	0.07
131. BD (1) N 11- C 17	467. RY (21)Ag 2	0.13
131. BD (1) N 11- C 17	469. RY (23)Ag 2	0.05
132. BD (1) N 12- C 17	264. LV (1)Ag 2	0.19
109. LP (1) N 13	**263. LV (1)Ag 1**	**8.01**
109. LP (1) N 13	418. RY (2)Ag 1	0.12
109. LP (1) N 13	420. RY (4)Ag 1	0.54
109. LP (1) N 13	421. RY (5)Ag 1	0.44
109. LP (1) N 13	422. RY (6)Ag 1	0.31
109. LP (1) N 13	424. RY (8)Ag 1	0.08

109. LP (1) N 13	431. RY (15)Ag 1	0.14
109. LP (1) N 13	432. RY (16)Ag 1	0.25
109. LP (1) N 13	434. RY (18)Ag 1	0.34
109. LP (1) N 13	435. RY (19)Ag 1	0.41
109. LP (1) N 13	437. RY (21)Ag 1	0.56
109. LP (1) N 13	438. RY (22)Ag 1	0.17
109. LP (1) N 13	439. RY (23)Ag 1	0.12
109. LP (1) N 13	440. RY (24)Ag 1	0.06
109. LP (1) N 13	446. RY (30)Ag 1	0.05
110. LP (1) N 14	263. LV (1)Ag 1	0.32
135. BD (1) N 13- C 21	263. LV (1)Ag 1	1.7
135. BD (1) N 13- C 21	417. RY (1)Ag 1	0.09
135. BD (1) N 13- C 21	418. RY (2)Ag 1	0.1
135. BD (1) N 13- C 21	421. RY (5)Ag 1	0.13
135. BD (1) N 13- C 21	422. RY (6)Ag 1	0.17
135. BD (1) N 13- C 21	432. RY (16)Ag 1	0.07
135. BD (1) N 13- C 21	434. RY (18)Ag 1	0.12
135. BD (1) N 13- C 21	435. RY (19)Ag 1	0.26
135. BD (1) N 13- C 21	437. RY (21)Ag 1	0.31
135. BD (1) N 13- C 21	438. RY (22)Ag 1	0.06
135. BD (1) N 13- C 21	439. RY (23)Ag 1	0.05
135. BD (1) N 13- C 21	440. RY (24)Ag 1	0.06
135. BD (1) N 13- C 21	446. RY (30)Ag 1	0.06
136. BD (2) N 13- C 21	263. LV (1)Ag 1	0.55
136. BD (2) N 13- C 21	421. RY (5)Ag 1	0.08
137. BD (1) N 13- C 23	263. LV (1)Ag 1	0.08
137. BD (1) N 13- C 23	418. RY (2)Ag 1	0.09
137. BD (1) N 13- C 23	420. RY (4)Ag 1	0.06
137. BD (1) N 13- C 23	422. RY (6)Ag 1	0.19
137. BD (1) N 13- C 23	435. RY (19)Ag 1	0.09
137. BD (1) N 13- C 23	437. RY (21)Ag 1	0.17
137. BD (1) N 13- C 23	446. RY (30)Ag 1	0.05
138. BD (1) N 14- C 23	263. LV (1)Ag 1	0.2
109. LP (1) N 13	264. LV (1)Ag 2	0.18
110. LP (1) N 14	**264. LV (1)Ag 2**	**6.72**
110. LP (1) N 14	447. RY (1)Ag 2	0.17
110. LP (1) N 14	448. RY (2)Ag 2	0.06
110. LP (1) N 14	449. RY (3)Ag 2	0.05
110. LP (1) N 14	450. RY (4)Ag 2	0.35
110. LP (1) N 14	452. RY (6)Ag 2	0.32
110. LP (1) N 14	454. RY (8)Ag 2	0.06
110. LP (1) N 14	461. RY (15)Ag 2	0.27
110. LP (1) N 14	465. RY (19)Ag 2	0.37
110. LP (1) N 14	467. RY (21)Ag 2	0.39
110. LP (1) N 14	469. RY (23)Ag 2	0.19
137. BD (1) N 13- C 23	264. LV (1)Ag 2	0.16
138. BD (1) N 14- C 23	264. LV (1)Ag 2	0.09
138. BD (1) N 14- C 23	448. RY (2)Ag 2	0.06
138. BD (1) N 14- C 23	450. RY (4)Ag 2	0.07
138. BD (1) N 14- C 23	451. RY (5)Ag 2	0.07

138. BD (1) N 14- C 23	452. RY (6)Ag 2	0.14
138. BD (1) N 14- C 23	465. RY (19)Ag 2	0.08
138. BD (1) N 14- C 23	467. RY (21)Ag 2	0.14
138. BD (1) N 14- C 23	469. RY (23)Ag 2	0.06
139. BD (1) N 14- C 24	264. LV (1)Ag 2	1.33
139. BD (1) N 14- C 24	452. RY (6)Ag 2	0.12
139. BD (1) N 14- C 24	461. RY (15)Ag 2	0.06
139. BD (1) N 14- C 24	465. RY (19)Ag 2	0.15
139. BD (1) N 14- C 24	467. RY (21)Ag 2	0.13
139. BD (1) N 14- C 24	469. RY (23)Ag 2	0.07
140. BD (2) N 14- C 24	264. LV (1)Ag 2	0.57
140. BD (2) N 14- C 24	447. RY (1)Ag 2	0.06

Optimized coordinates for compounds 1–4

1

I	-0.041514	-1.372882	2.124033
I	0.040849	-1.401326	-2.105253
Cu	-1.275424	-0.434313	-0.033186
Cu	1.275309	-0.434121	0.039176
P	-3.440960	-0.078815	-0.015339
P	3.441005	-0.078801	0.014380
N	-1.157602	1.693855	0.000666
N	1.157228	1.693665	-0.017921
O	-3.477474	1.657146	0.025067
O	3.477122	1.656705	-0.041358
C	-1.254436	4.496849	0.003909
C	1.254237	4.496571	-0.044464
H	-1.286888	5.588486	0.003256
H	1.286769	5.588174	-0.052830
C	-0.000162	2.408871	-0.011646
C	-2.318267	2.346068	0.018490
C	2.317913	2.345664	-0.040902
C	-2.416884	3.761939	0.025409
C	2.416633	3.761420	-0.059658
H	-3.403155	4.223242	0.042874
H	3.402938	4.222493	-0.080786
C	-0.000118	3.836631	-0.017577
C	4.471711	-0.283777	1.569641
C	4.367954	-0.452618	-1.575114
C	-4.371718	-0.438771	1.575133
C	3.570037	0.256538	2.698603
C	3.616648	0.331470	-2.670358
C	-3.623503	0.355503	2.665124
H	3.420007	1.342136	2.607510
H	3.795727	1.412180	-2.585731
H	-3.803291	1.435272	2.570642
H	4.062649	0.064932	3.665545
H	3.984266	-0.001512	-3.654100
H	-3.992987	0.030771	3.650925
H	2.584078	-0.230163	2.709215
H	2.532742	0.143022	-2.636196
H	-2.539356	0.167738	2.634951
C	5.807990	0.469924	1.599802
C	5.855448	-0.087395	-1.613212
H	6.557484	0.028794	0.933545
H	6.454184	-0.732976	-0.957042
H	6.211857	0.433383	2.624980
H	6.229833	-0.227343	-2.640867
H	5.678678	1.527356	1.329967
H	6.030931	0.960682	-1.333066
C	4.674034	-1.796612	1.761373
C	4.171800	-1.962500	-1.817467
C	-4.175144	-1.946295	1.831289
H	3.718148	-2.339120	1.700309
H	3.104581	-2.228855	-1.825748
H	-3.107735	-2.211677	1.845010
H	5.103956	-1.981819	2.758709
H	4.598891	-2.224793	-2.798824
H	-4.604966	-2.200401	2.813608
H	5.365269	-2.216028	1.016285
H	4.678474	-2.573903	-1.057352
H	-4.679043	-2.564718	1.074998
C	-4.466952	-0.297751	-1.571816
C	-5.859500	-0.074069	1.606268
C	-4.663885	-1.812588	-1.753328
C	-3.563724	0.237391	-2.702056
C	-5.805432	0.451506	-1.611077
H	-6.456346	-0.726193	0.954876
H	-6.236270	-0.204373	2.634321
H	-6.034846	0.971172	1.315671
H	-3.706278	-2.351373	-1.686573
H	-5.355202	-2.229106	-1.006671
H	-5.091245	-2.006203	-2.750173
H	-2.575522	-0.244929	-2.705267
H	-4.051992	0.035459	-3.669094
H	-3.419158	1.324397	-2.619405
H	-6.205787	0.407408	-2.637333
H	-6.555698	0.011985	-0.944632
H	-5.680415	1.510986	-1.347272

2

Au	10.370613	13.250503	8.582094
Au	10.282679	11.905557	14.482557
P	9.116536	13.813466	14.538045
Cl	11.466068	9.933879	14.422928
Cl	9.942963	15.506654	8.716450
P	10.768178	11.053175	8.451348
O	9.362092	10.107415	8.539076
O	7.478739	13.614332	14.141930
N	8.654816	11.235020	10.401307
N	8.020281	12.424166	12.262941
C	8.366856	10.420431	9.412946
C	7.669877	11.578238	11.265108
C	7.103221	12.785398	13.130040
C	6.335414	11.075830	11.131048
C	7.089370	9.843047	9.187752
H	6.936589	9.168103	8.346779
C	5.374653	11.510029	12.080561
H	4.344884	11.153094	12.007840
C	10.121257	14.600298	17.017955
H	10.761688	13.711244	16.915306
H	9.915058	14.746031	18.089915

H	10.679602	15.473488	16.662656
C	5.745721	12.370974	13.090401
H	5.045352	12.724977	13.845583
C	11.902642	10.379690	9.800290
C	10.726672	16.079334	14.115829
H	10.239389	16.695550	14.882434
H	11.547398	15.513792	14.580206
C	11.217709	10.499234	6.718053
C	6.077359	10.182930	10.058955
H	5.073016	9.774143	9.927422
C	10.025656	10.919706	5.831335
H	9.109415	10.374995	6.090855
H	10.276755	10.697131	4.782306
H	9.826308	11.998601	5.914596
C	10.529155	14.460124	12.240623
H	11.410627	13.934950	12.635529
H	9.908534	13.737158	11.701375
C	9.747745	15.154411	13.370965
C	8.782081	14.408516	16.283718
C	13.359265	10.365435	9.303621
H	13.537349	9.630312	8.508196
H	13.679159	11.357113	8.952460
C	11.428721	8.981910	6.611045
H	12.300639	8.639991	7.183595
H	11.600685	8.716803	5.555560
H	10.545601	8.428841	6.958385
C	11.827935	11.344750	10.997577
H	12.201734	12.341875	10.724060
H	12.447352	10.943750	11.813692
H	10.804792	11.449803	11.372579
C	12.459316	11.275737	6.244165
H	12.332708	12.358497	6.394775
H	12.592342	11.098329	5.165396
H	13.377652	10.959394	6.751056
C	11.461582	8.974286	10.235755
H	10.459521	8.990575	10.682747
H	11.468375	8.252265	9.407774
C	7.929011	15.684805	16.327970
H	8.449140	16.550489	15.897560
H	7.697824	15.925767	17.377947
H	6.977750	15.550323	15.795471
C	8.022115	13.254131	16.972059
H	7.037143	13.084569	16.519693
H	7.877130	13.516177	18.031949
H	8.594032	12.315258	16.926345
C	8.580749	15.959140	12.779483
H	7.930592	15.326064	12.162417
H	8.995800	16.735834	12.119267
H	7.969974	16.448596	13.550309
H	14.001408	10.097009	10.156555
H	10.862147	15.222887	11.520979
H	11.174885	16.759368	13.375189
H	12.155619	8.619407	11.012781

3

Ag	-1.468839	-1.085607	-0.447990
Ag	1.468874	-1.085511	0.448292
Cl	0.283858	-1.913961	-1.910305
Cl	-0.283865	-1.913253	1.910903
P	-3.546211	-0.130235	-0.013765
P	3.546212	-0.130239	0.013673
O	-3.472518	1.574889	-0.067897
O	3.472531	1.574893	0.067558
N	-1.154351	1.618335	-0.018777
N	1.154366	1.618337	0.018357
C	-2.299288	2.265409	-0.051595
C	2.299300	2.265413	0.051273
C	-2.416086	3.683108	-0.068634
C	2.416092	3.683110	0.068453
H	-3.403767	4.141487	-0.097516
H	3.403770	4.141491	0.097406
C	0.000003	3.763702	-0.000099
C	0.000006	2.330463	-0.000174
C	-4.856508	-0.343682	-1.338634
C	-1.255619	4.421538	-0.038291
C	1.255623	4.421539	0.038164
H	-1.291827	5.513400	-0.042517
H	1.291826	5.513401	0.042506
C	-4.171037	-0.375942	1.735586
C	-3.134449	0.337659	2.629116
H	-3.182759	1.429626	2.514444
H	-2.110434	-0.007919	2.421576
H	2.110138	-0.008369	-2.421541
C	-6.042683	0.627103	-1.253576
H	-5.703669	1.670779	-1.211425
H	-6.663413	0.509829	-2.156742
H	-6.681795	0.434231	-0.384544
C	-4.100426	-0.101514	-2.661938
C	4.100760	-0.101042	2.661775
H	-3.248135	-0.787480	-2.774477
H	3.248457	-0.786955	2.774550
H	-4.793365	-0.261208	-3.503643
H	-3.720433	0.928478	-2.726456
H	3.720813	0.928976	2.726148
C	-5.330182	-1.805234	-1.286148
H	-5.963349	-2.000371	-0.409472
H	-5.925791	-2.024977	-2.186302
H	-4.480488	-2.505418	-1.267961
C	-4.109797	-1.888355	2.022824
H	-3.095505	-2.282882	1.863833
H	-4.375152	-2.056470	3.078896
H	-4.815095	-2.461032	1.405310

C	-5.571053	0.180572	2.015773
H	-6.353719	-0.396033	1.503839
H	-5.770664	0.116353	3.097957
H	-5.658983	1.235698	1.720571
C	4.170826	-0.376209	-1.735714
C	4.856668	-0.343483	1.338424
H	-3.361380	0.097228	3.679960
H	4.793798	-0.260605	3.503423
C	4.109589	-1.888664	-2.022730
C	5.570795	0.180306	-2.016143
C	3.134114	0.337234	-2.629227
C	5.330296	-1.805059	1.286158
C	6.042862	0.627249	1.253038
H	3.095329	-2.283194	-1.863546
H	4.374799	-2.056917	-3.078816
H	4.814990	-2.461236	-1.405238
H	5.770280	0.115949	-3.098342
H	5.658733	1.235473	-1.721090
H	6.353533	-0.396212	-1.504223
H	3.360953	0.096684	-3.680064
H	3.182381	1.429217	-2.514694
H	5.963374	-2.000372	0.409457
H	5.925987	-2.024651	2.186295
H	4.480583	-2.505226	1.268183
H	6.681871	0.434183	0.383972
H	6.663691	0.510139	2.156157
H	5.703875	1.670927	1.210716

4

Ag	-2.400069	-0.008118	0.103889
Ag	2.418776	0.053518	-0.056740
P	-3.118246	2.199902	-0.486300
P	2.988422	2.332310	0.435669
P	-3.051971	-2.265315	0.577830
P	3.186242	-2.180018	-0.498136
O	-2.239229	2.584867	-1.884290
O	2.117278	2.720227	1.833685
O	-2.169324	-2.762929	1.935768
O	2.196267	-2.768863	-1.742306
N	0.721212	-0.982109	-1.818540
N	-0.826075	0.748817	-1.862563
N	-0.740383	-0.932563	1.929875
N	0.755441	0.844267	1.889497
C	1.364463	-1.951592	-2.449568
C	0.110456	-0.086691	4.051098
C	-0.087944	-0.165733	-2.551017
C	-0.153502	-0.259718	-3.977849
C	-1.504933	1.649934	-2.553406
C	0.516236	-1.343018	-4.601237
C	-1.358900	-1.888905	2.603519
C	-1.524689	1.729453	-3.968589
C	0.044172	-0.059499	2.621490
C	1.413222	1.788816	2.540918
C	-1.253019	-2.082016	4.003789
H	-1.768040	-2.919377	4.472201
C	1.252146	-2.219711	-3.836962
C	0.814098	0.958115	4.701912
H	0.853492	0.986550	5.792619
C	2.460967	3.718206	-0.712253
C	-0.540273	-1.151830	4.725013
H	-0.478675	-1.220358	5.812920
C	1.440669	1.926635	3.951465
H	1.981455	2.758398	4.400377
C	-4.848192	2.281928	-1.201160
C	-4.857794	1.223268	-2.323795
H	-4.230429	1.516075	-3.175530
H	-5.888237	1.106184	-2.691470
H	-4.515399	0.240462	-1.960958
C	-2.597059	-3.529073	-0.722191
C	-2.689626	3.650066	0.620966
C	2.942523	-3.504463	0.803006
C	-5.210526	3.656441	-1.778372
H	-5.303623	4.422034	-0.997329
H	-6.184385	3.588479	-2.287444
H	-4.470708	3.994593	-2.516701
C	-1.455516	3.192352	1.418364
H	-1.703201	2.354330	2.085861
H	-1.090313	4.027653	2.036109
H	-0.635808	2.865558	0.766721
C	-3.840832	3.902115	1.609246
H	-4.722466	4.338968	1.124242
H	-3.494754	4.617340	2.371063
H	-4.143566	2.984595	2.136107
C	-1.065349	-3.644541	-0.653044
H	-0.583094	-2.656389	-0.634116
H	-0.708022	-4.179954	-1.546503
H	-0.750266	-4.208143	0.233854
C	-5.849349	1.848925	-0.115570
H	-5.558581	0.892788	0.343000
H	-6.835952	1.706339	-0.582048
H	-5.963569	2.593151	0.680164
C	-4.777957	-2.453389	1.269916
C	-2.360276	4.921998	-0.175016
H	-1.506101	4.768118	-0.846448
H	-2.096852	5.721129	0.535173
H	-3.208848	5.273964	-0.773808
C	-3.230709	-4.915882	-0.562127
H	-3.014909	-5.355446	0.420654
H	-2.809658	-5.586912	-1.327308
H	-4.318083	-4.895876	-0.709794
C	-4.905055	-1.319223	2.308512
H	-4.243022	-1.483958	3.170719

H	-5.939281	-1.290115	2.683432
H	-4.668943	-0.334895	1.876686
H	3.179488	4.687124	-2.497592
C	-5.044265	-3.795316	1.968496
H	-5.099552	-4.632716	1.265633
H	-6.013175	-3.734898	2.487685
H	-4.276448	-4.018611	2.721100
C	2.056399	4.987163	0.053868
H	1.212608	4.800283	0.729719
H	1.747179	5.751693	-0.675710
C	1.744440	-3.016651	1.636844
H	1.999008	-2.104764	2.196727
H	1.462508	-3.796345	2.361549
H	0.870561	-2.795189	1.013512
H	3.992322	-1.660123	-3.305721
C	-5.763138	-2.220263	0.112050
H	-5.542602	-1.291201	-0.435501
H	-6.782739	-2.132042	0.516751
H	-5.762702	-3.054093	-0.603055
C	-2.997050	-2.901552	-2.073798
H	-4.080298	-2.740629	-2.160098
H	-2.696590	-3.582900	-2.884466
H	-2.491947	-1.936878	-2.234339
C	1.253119	3.158263	-1.482205
H	1.553452	2.330852	-2.141303
H	0.815480	3.953493	-2.105678
H	0.471476	2.778595	-0.812828
C	4.725875	2.536453	1.102903
C	4.844867	-2.264534	-1.361550
C	-0.876709	0.741617	-4.674546
H	0.452068	-1.467507	-5.684024
H	-2.079525	2.530329	-4.454964
H	1.782834	-3.068809	-4.265117
C	3.582903	4.022481	-1.718362
C	2.636709	-4.880813	0.192529
C	4.180253	-3.573373	1.712406
H	2.882595	5.402643	0.643429
C	4.833942	1.488398	2.230542
C	5.009223	3.935739	1.665132
C	5.722298	2.169822	-0.012572
C	5.208779	-3.668479	-1.861375
C	5.920881	-1.717427	-0.405588
C	4.709311	-1.297935	-2.556908
H	-0.914112	0.721407	-5.765490
H	4.432428	4.537712	-1.253836
H	3.949918	3.114670	-2.220028
H	2.475527	-5.598449	1.011913
H	1.729663	-4.858452	-0.424062
H	3.461368	-5.258336	-0.423832
H	3.933129	-4.191828	2.588833
H	5.039884	-4.037974	1.213841
H	4.479250	-2.581936	2.084883
H	4.183252	1.727236	3.082211
H	4.581100	0.477147	1.872922
H	5.871240	1.467183	2.596978
H	4.271926	4.224247	2.426633
H	5.022208	4.702598	0.879726
H	6.001699	3.939093	2.141696
H	5.428326	1.248046	-0.536739
H	6.711367	1.994061	0.436667
H	5.832025	2.966367	-0.756272
H	4.419720	-4.091273	-2.498034
H	5.402587	-4.362682	-1.033322
H	6.129594	-3.610556	-2.462097
H	5.600489	-0.783098	0.078211
H	6.192015	-2.433970	0.377019
H	6.830163	-1.495300	-0.984327
H	5.688456	-1.204516	-3.050169
H	4.397286	-0.291453	-2.233673