Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

The Triple-Bond Metathesis of Aryldiazonium Salts: A Prospect for Dinitrogen Cleavage

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anie_201506546_sm_miscellaneous_information.pdf

CRYSTALLOGRAPHIC SECTION

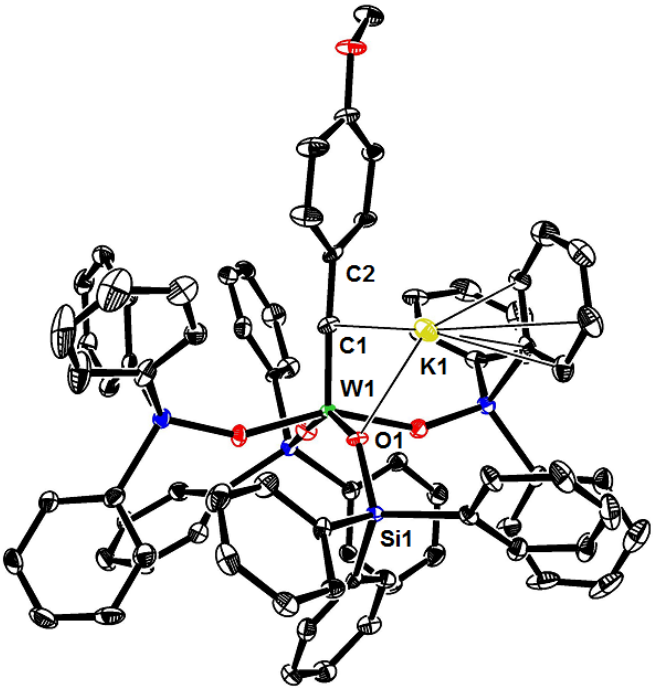


Figure S-1. Structure of the tungsten alkylidyne ate-complex **5**; co-crystallized CH_2Cl_2 is not shown for clarity; color code: W = green, O = red, Si = blue, K = yellow; **CCDC- 1412622**

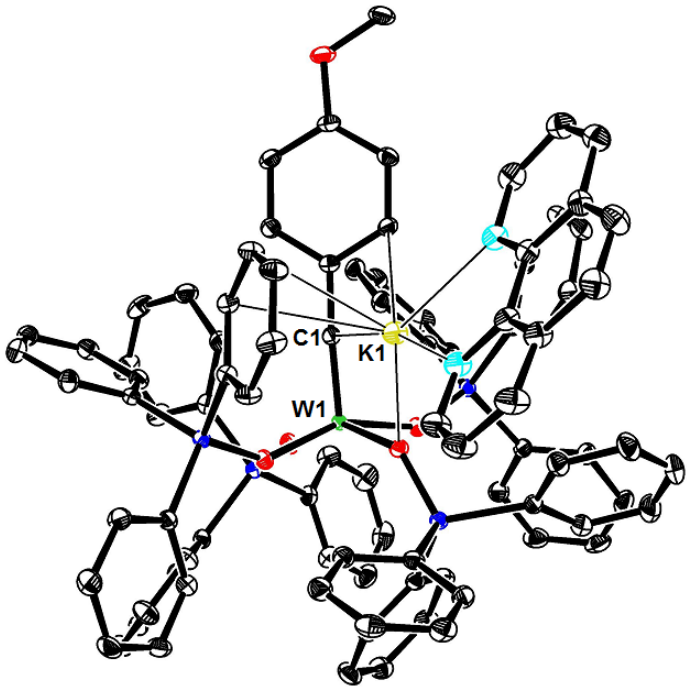


Figure S-2. Structure of the tungsten ate-complex **6a** (co-crystallized CH_2Cl_2 is not shown for clarity); color code: W = green, O = red, Si = blue, K = yellow, N = cyan; **CCDC- 1412623**

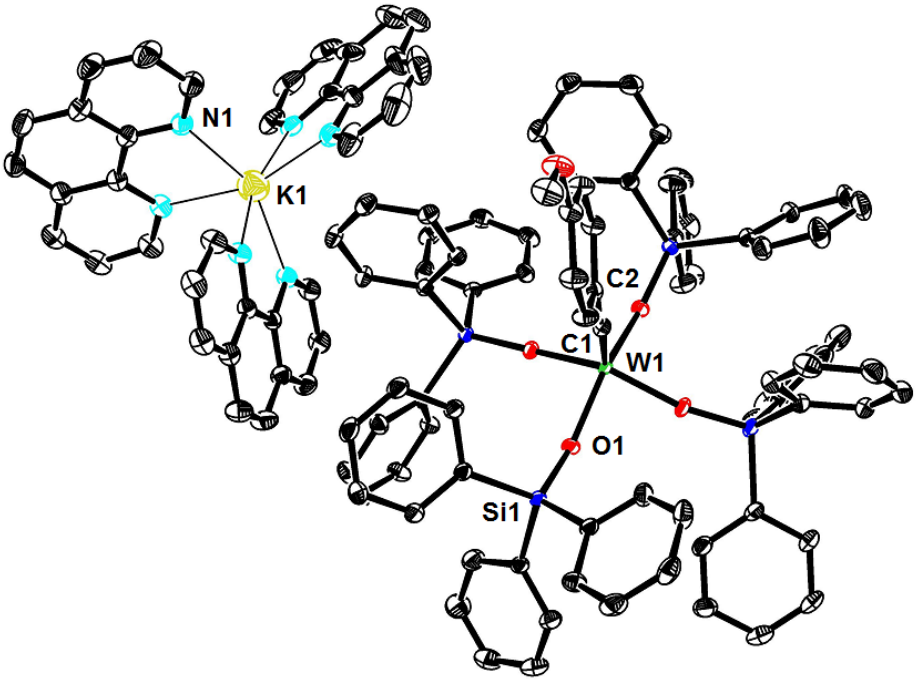


Figure S-3. Structure of the tungsten ate-complex **6b** (co-crystallized CH_2Cl_2 is not shown for clarity); color code: W = green, O = red, Si = blue, K = yellow, N = cyan; **CCDC- 1412652**

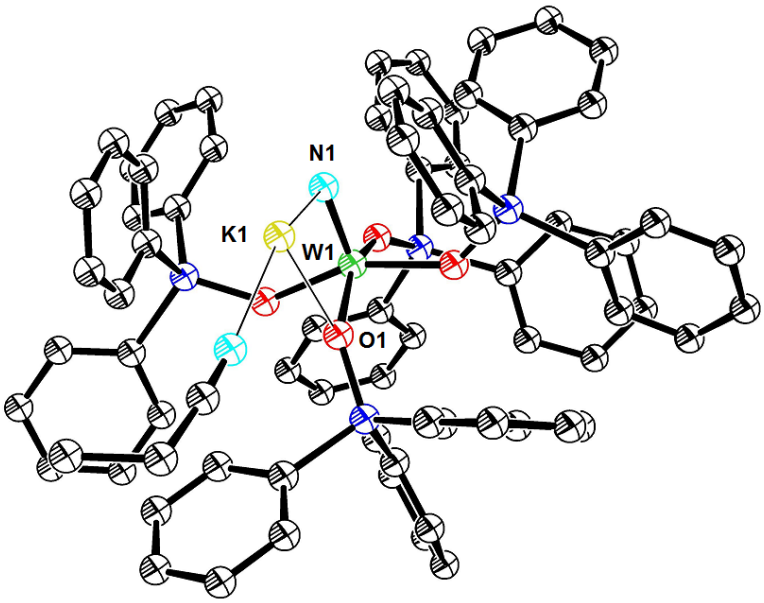


Figure S-4. Structure of the tungsten nitride ate-complex **7·EtCN** in the solid state; color code: W = green, O = red, Si = blue, K = yellow, N = cyan; **CCDC- 1412624**

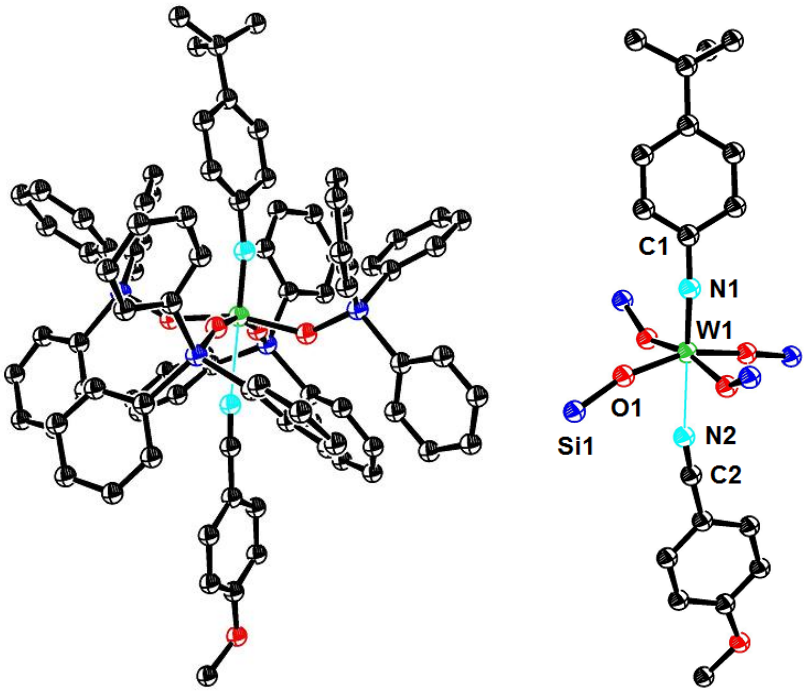


Figure S-5. Structure of the metathesis product **9b** in the solid state; the disorder of the *tert*-butyl group over two positions is not shown for clarity; color code: W = green, O = red, Si = blue, K = yellow, N = cyan; **CCDC- 1412625**

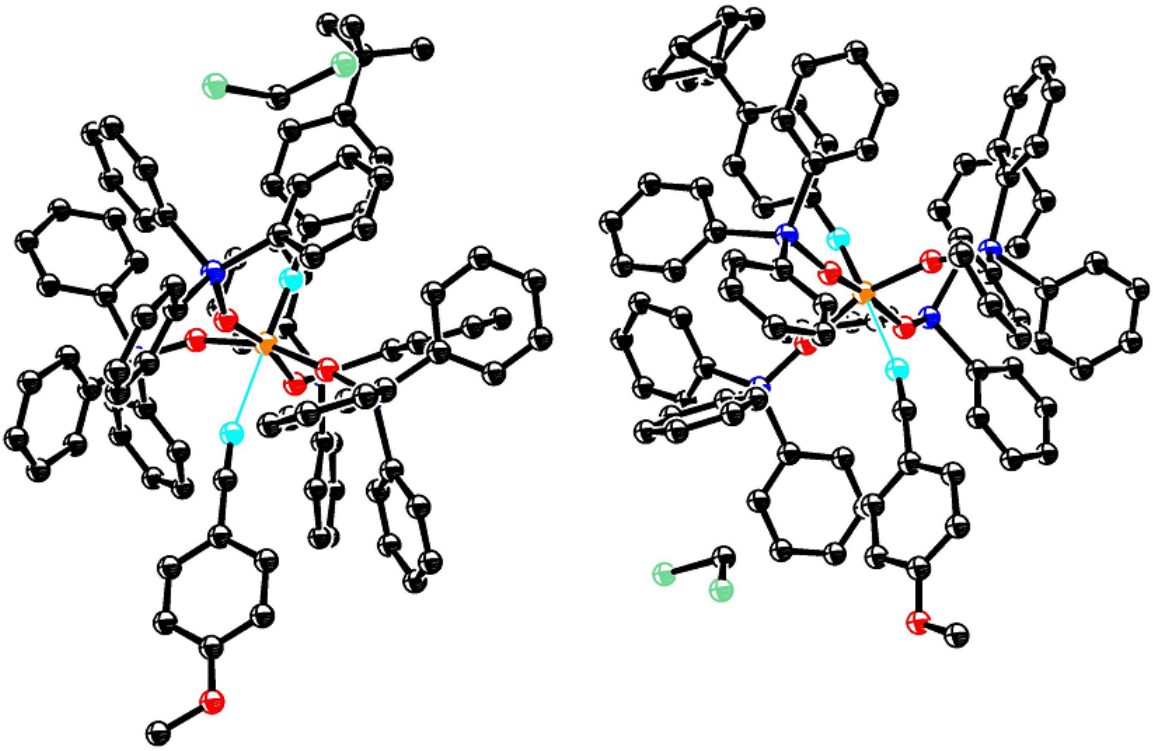


Figure S-6. Structure of the metathesis product **10** in the solid state, showing the two independent molecules in the unit cell and the co-crystallized CH_2Cl_2; color code: Mo = orange, O = red, Si = blue, K = yellow, N = cyan; **CCDC- 1412626**

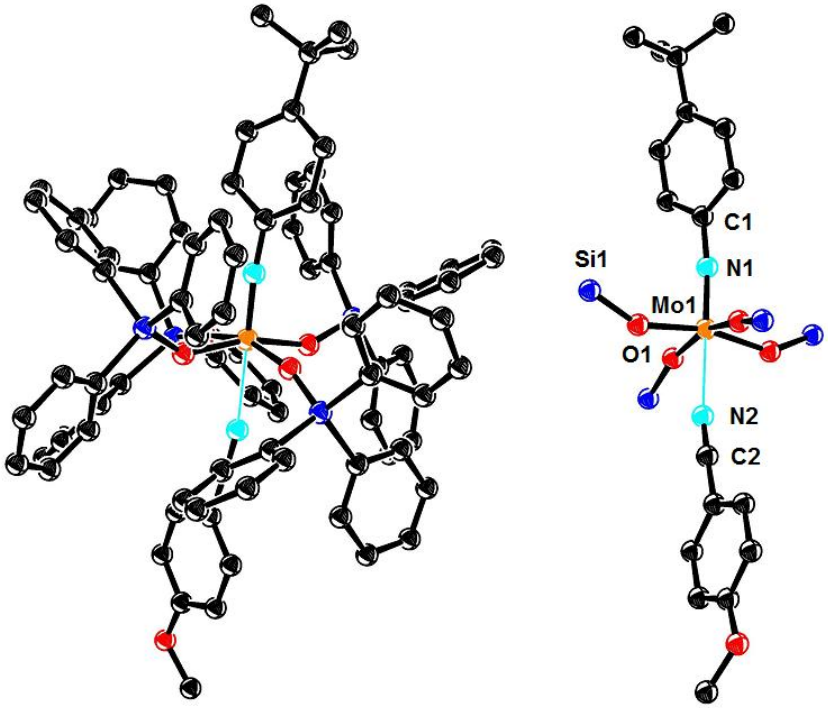


Figure S-7. Structure of one of the two independent molecules of **10** in the unit cell (depicted in Figure S-6); color code: Mo = orange, O = red, Si = blue, K = yellow, N = cyan; **CCDC- 1412626**

X-ray Crystal Structure Analysis of Complex 5: $C_{164}H_{142}Cl_8K_2O_{10}Si_8W_2$, M_r = 3226.99 g · mol^{-1}, orange prism, crystal size 0.25 x 0.12 x 0.08 mm, monoclinic, space group $P2_1/n$, a = 13.6369(15) Å, b = 20.0740(18) Å, c = 27.376(2) Å, β = 99.771(10)°, V = 7385.3(12) Å^3, T = 100 K, Z = 2, D_{calc} = 1.451 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 1.882 mm^{-1}, Empirical absorption correction (T_{min} = 0.72, T_{max} = 0.88), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.70 < θ < 27.50°, 65707 measured reflections, 16948 independent reflections, 15249 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.067 [$I > 2\sigma(I)$], wR_2 = 0.171, 872 parameters, H atoms riding, S = 1.308, residual electron density 4.5 / -3.2 e Å^{-3}. **CCDC- 1412622**.

X-ray Crystal Structure Analysis of Complex 6a: $C_{93}H_{77}Cl_2KN_2O_5Si_4W$, M_r = 1708.78 g · mol^{-1}, red plate, crystal size 0.27 x 0.15 x 0.05 mm, monoclinic, space group $P2_1/c$, a = 16.348(2) Å, b = 25.430(3) Å, c = 19.302(3) Å, β = 92.892(2)°, V = 8014.4(18) Å^3, T = 100 K, Z = 4, D_{calc} = 1.416 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 1.675 mm^{-1}, Empirical absorption correction (T_{min} = 0.70, T_{max} = 0.93), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 1.48 < θ < 30.51°, 227218 measured reflections, 24478 independent reflections, 21038 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.023 [$I > 2\sigma(I)$], wR_2 = 0.055, 983 parameters, H atoms riding, S = 1.019, residual electron density 1.2 / -1.3 e Å^{-3}. **CCDC- 1412623**.

X-ray Crystal Structure Analysis of Complex 6b: $C_{80}\,H_{67}\,O_5\,Si_4\,W \cdot C_{36}\,H_{24}\,K\,N_6 \cdot 1.5\,C\,H_2\,Cl_2$, M_r = 1562.78 g · mol^{-1}, orange prism, crystal size 0.24 x 0.21 x 0.14 mm, triclinic, space group $P\bar{1}$, a = 14.7528(17) Å, b = 17.1029(10) Å, c = 20.776(6) Å, α = 87.485(6)°, β = 78.533(11)°, γ = 82.209(8)°, V = 5089.3(15) Å^3, T = 100 K, Z = 2, D_{calc} = 1.378 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 1.360 mm^{-1}, Empirical absorption correction (T_{min} = 0.60, T_{max} = 0.74), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.62 < θ < 33.09°, 151511 measured reflections, 38556 independent reflections, 34270 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.100 [$I > 2\sigma(I)$], wR_2 = 0.293, 1250 parameters, H atoms riding, S = 1.098, residual electron density 4.0 / -3.1 e Å^{-3}. **CCDC- 1412652**.

X-ray Crystal Structure Analysis of Complex 7·EtCN: $C_{75}\,H_{65}\,K\,N_2\,O_4\,Si_4\,W$, M_r = 1393.60 g · mol^{-1}, colorless prism, crystal size 0.12 x 0.08 x 0.05 mm, monoclinic, space group $P2_1/c$, a = 18.6289(19) Å, b = 14.2871(12) Å, c = 25.032(7) Å, β = 101.306(18)°, V = 6533(2) Å^3, T = 100 K, Z = 4, D_{calc} = 1.417 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 1.957 mm^{-1}, Empirical absorption correction (T_{min} = 0.80, T_{max} = 0.90), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.599 < θ < 33.221°, 143201 measured reflections, 24867 independent reflections, 20217 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.042 [$I > 2\sigma(I)$], wR_2 = 0.118, 785 parameters, H atoms riding, S = 1.169, residual electron density 3.1 / -2.9 e Å^{-3}. **CCDC- 1412624**.

X-ray Crystal Structure Analysis of Complex 9b: $C_{91}\,H_{82}\,Cl_2\,N_2\,O_5\,Si_4\,W$, M_r = 1650.69 g · mol^{-1}, yellow plate, crystal size 0.08 x 0.07 x 0.02 mm, orthorhombic, space group *Pbca*, a = 15.9596(14) Å, b = 20.994(3) Å, c = c = 46.933(7) Å, V = 15725(3) Å^3, T = 100 K, Z = 8, D_{calc} = 1.394 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 1.653 mm^{-1}, Empirical absorption correction (T_{min} = 0.85, T_{max} = 0.96), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.663 < θ < 30.361°, 252053 measured reflections, 23664 independent reflections, 11117 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.067 [$I > 2\sigma(I)$], wR_2 = 0.169, 947 parameters, H atoms riding, S = 1.016, residual electron density 4.1 / -2.5 e Å^{-3}. **CCDC- 1412625**.

X-ray Crystal Structure Analysis of Complex 10: $C_{91}\,H_{82}\,Cl_2\,Mo\,N_2\,O_5\,Si_4$, M_r = 1562.78 g · mol^{-1}, colorless plate, crystal size 0.14 x 0.11 x 0.06 mm, monoclinic, space group $P2_1/c$, a = 47.070(8) Å, b = 15.847(2) Å, c = 21.004(3) Å, β = 90.897(10)°, V = 15666(4) Å^3, T = 100 K, Z = 8, D_{calc} = 1.325 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.352 mm^{-1}, Empirical absorption correction (T_{min} = 0.96, T_{max} = 0.98), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.607 < θ < 27.103°, 199841 measured reflections, 33915 independent reflections, 23568 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.100 [$I > 2\sigma(I)$], wR_2 = 0.293, 1889 parameters, H atoms riding, twinning law and batch scale factor [1 0 0 0 -1 0 0 0 -1] and 0.097(1), S = 1.828, residual electron density 2.5 / -1.1 e Å^{-3}. **CCDC- 1412626**.

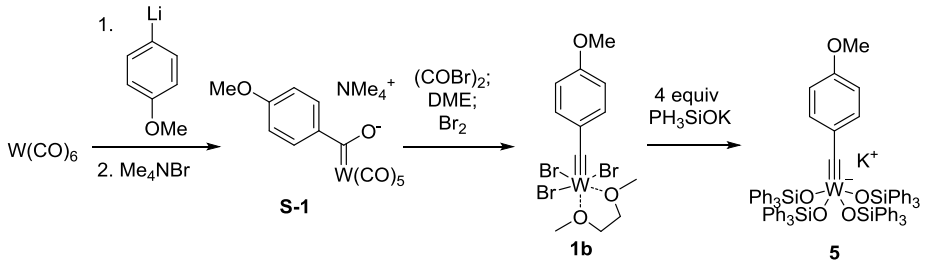
General. Unless stated otherwise, all reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: Et_2O (Mg/anthracene), CH_2Cl_2, pentane, toluene (Na/K); propionitrile, 1,2-dimethoxyethane (CaH_2), pyridine were dried by an adsorption solvent purification system based on molecular sieves. 1,10-phenanthroline was dried by sublimation. Celite was dried overnight at 120 °C under high vacuum. Flash column chromatography: Merck silica gel 60 (40–63 μm) with HPLC grade solvents. NMR: Spectra were recorded on Bruker DPX 300, AV400, AV500 or AVIII 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 54.00 ppm; residual $CHDCl_2$: δ_H = 5.32 ppm; [D_6]-acetone: δ_C = 206.26 ppm; residual [D_5]-acetone: δ_H = 2.05 ppm); [D_6]-DMSO: δ_C = 39.52 ppm; residual [D_5]-DMSO: δ_H = 2.50 ppm); IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}; High resolution mass spectrometry: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).

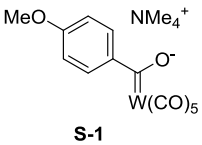
The Mo-alkylidyne ate complex **2** and neutral Mo-alkylidyne complex **3**[1] were prepared according to the literature.

Upon indication of decomposition (color change, irreproducible yields) the aryldiazonium salts were repurified by dissolution into acetone and precipitation with diethyl ether.

Starting metal complexes

Note**:** *The complexes carrying Ph_3SiO-ligands contained ≤ 10% of silanolate impurities even after recrystallization; fully satisfactory elemental analyses were therefore not obtained. The NMR spectra, however, confirm an acceptable purity of the bulk material***.**



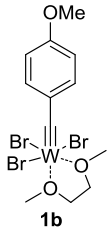


To a solution of 4-iodoanisole (4.68 g, 20.0 mmol) in Et_2O, stirring at −78 °C, was added a solution of *n*BuLi in pentane (1.6 M, 12.5 mL, 20.0 mmol) over 2 min. After stirring 20 min at this temperature, the mixture was warmed to 0 °C, then added by addition funnel to a refluxing mixture of $W(CO)_6$ (7.04 g, 20 mmol) in

[1] Heppekausen, J.; Stade, R.; Kondoh, A.; Seidel, G.; Goddard, R.; Fürstner, A. *Chem. Eur. J.* **2012**, *18*, 10281-10299.

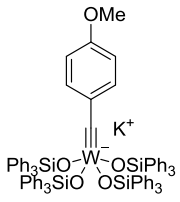
Et_2O (200 mL) over 5 min. Upon addition of the generated aryllithium reagent, the refluxing mixture became dark orange in color. Stirring was continued at reflux temperature for 45 min; the mixture was then cooled to ambient temperature and was concentrated to dryness under vacuum.

To the resultant thick orange paste was added a solution of Me_4NBr (4.62 g, 30 mmol) in H_2O (50 mL). The mixture was stirred 30 min, then the precipitate was collected by filtration, washing alternately with H_2O and Et_2O (2 x 40 mL each), then dried under vacuum, leaving the desired product **S-1** as a bright orange solid (9.31 g, 87% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.60 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.34 (s, 12H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 281.9, 207.9, 204.0, 191.9, 160.8, 150.3, 128.6, 112.8, 56.7, 55.6 ppm.



1b

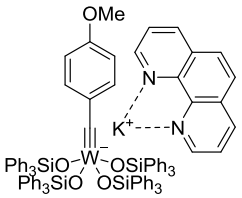
To a solution of Fischer carbene **S-1** (4.56 g, 8.47 mmol), stirring in CH_2Cl_2 at −78 °C, was added by cannula a solution of oxalyl bromide (820 µL, 8.73 mmol) in CH_2Cl_2 (5 mL) held at −78 °C. After stirring at this temperature for 15 min, the violet solution was allowed to warm until it reached an internal temperature of around −20 °C, at which point it had become dark yellow in color. The reaction mixture was cooled again to −78 °C, then filtered at −78 °C through Celite using a jacketed filter into a receiving flask held at −78 °C and containing 1,2-dimethoxyethane (4.54 mL, 44.0 mmol). To the resulting orange solution was added dropwise through an addition funnel a solution of Br_2 (450 ul, 8.73 mmol) in CH_2Cl_2 (5 mL). After 15 min stirring at −78 °C, the reaction mixture was warmed to ambient temperature, then filtered through Celite. The brown-green filtrate was concentrated until persistent green precipitate was observed. Pentane (300 mL) was added by addition funnel over 1 h, resulting in the formation of more green precipitate. The precipitate was collected by filtration and dried under vacuum to give the desired alkylidyne **1b** as a green solid (4.40 g, 82% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.32 (s, 3H), 4.17-4.14 (m, 2H), 4.06-4.03 (m, 2H), 3.97 (s, 3H), 3.90 (s, 3H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 332.9, 163.9, 140.1, 136.7, 132.0, 114.2, 111.4, 79.9, 76.8, 70.6, 60.8, 55.7 ppm.



5

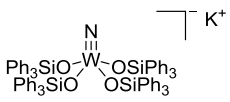
To a solution of complex **1b** (2.27 g, 3.59 mmol) in toluene (50 mL), stirring at 0 °C, was added a solution of Ph_3SiOK (5.64 g, 17.9 mmol) in toluene (50 mL) over 10 min. The mixture was warmed to ambient temperature and stirred an additional 2 h, then filtered through Celite. The filtrate was concentrated to dryness and the residue was taken up in diethyl ether (50 mL). The resulting suspension was stirred for 15 min before pentane (50 mL) was added. The precipitate was collected by filtration. CH_2Cl_2 (10 mL) was added to the precipitate and the solution was separated from any remaining insoluble material. To the filtrate was added pentane (50 mL), and the precipitate was collected by filtration and dried under vacuum, to give the desired alkylidyne **5** as a pink solid (2.98 g, 58% yield). In some instances, some fractional equivalent of DME remained in the complex. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 (dd, *J* = 7.9, 1.2 Hz, 24H), 7.20 (tt, *J* = 7.4, 1.3 Hz, 12H), 6.94 (t, *J* = 7.7 Hz,

24H), 6.50 (d, *J* = 8.8 Hz, 2H), 5.57 (d, *J* = 8.8 Hz, 2H), 3.71 (s, 3H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 260.9, 158.1, 140.4, 139.1, 136.4, 134.2, 129.1, 127.7, 112.5, 55.6 ppm.



6a

To a solution of **5** (120 mg, 0.0831 mmol) in CH_2Cl_2 (10 mL) was added 1,10-phenanthroline (15.0 mg, 0.0831 mol). The reaction mixture was stirred for 3 h at ambient temperature. Pentane (50 mL) was added, the resulting precipitate was collected by filtration, dissolved in a minimum of CH_2Cl_2 (2 mL) and reprecipitated with pentane (10 mL). The precipitate was collected by filtration and dried under vacuum to give the phenanthroline adduct **6a** as an orange solid (121 mg, 90% yield). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.33 (dd, J = 8.1, 1.7 Hz, 2H), 7.92 (dd, *J* = 4.4, 1.5 Hz, 2H), 7.90 (s, 2H), 7.45 (m, 26H), 7.06 (tt, *J* = 7.4, 2.6 Hz, 12H), 6.85 (t, *J* = 7.6 Hz, 24H), 6.53 (d, *J* 0 8.8 Hz, 2H), 5.73 (d, *J* = 8.8 Hz, 2H) ppm; ^{13}C NMR (150 MHz, CD_2Cl_2) δ 262.6, 157.9, 150.5, 146.1, 140.9, 139.3, 137.2, 136.4, 134.8, 129.4, 127.5, 127.3, 123.7, 112.3, 55.6 ppm.



7

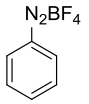
To a mixture of the tungsten alkylidyne **5** (1.12 g, 0.727 mmol) in toluene (5 mL) was added propionitrile (270 µL, 3.75 mmol). The pink reaction mixture quickly became homogeneous and was heated to 60 °C with stirring for 3 h, by which point the mixture had become yellow in color. The mixture was cooled to ambient temperature and concentrated to dryness under high vacuum. The residue was taken up in 3:1 Et_2O/ CH_2Cl_2 (40 mL) and insoluble material filtered off through Celite. The filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH_2Cl_2 (5 mL), and the product was precipitated by addition of pentane (~150 mL). Recrystallization by slow diffusion of pentane into a concentrated solution of the material in CH_2Cl_2 furnished single crystals of the propionitrile adduct **7**·EtCN suitable for X-ray diffraction. As the EtCN ligand in **7**·EtCN, however, is labile and can be removed in high vacuum, the material was spectroscopically characterized as the EtCN-free complex **7** after it had been dried in high vacuum; yellow powder (680 mg, 70% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.45 – 7.37 (m, 24H), 7.26-7.22 (m, 12H), 7.06 – 6.97 (m, 24H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 138.3, 136.5, 129.5, 127.9 ppm.

General procedure for the preparation of aryldiazonium salts

Note: *Though the tetrafluoroborate salts of aryldiazoniums are typically nonexplosive, care should nonetheless be taken to avoid potential detonation from friction or from impact of the dry compounds*.

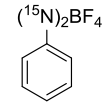
Performed open to atmosphere: To a aqueous solution of HBF_4 (48% *w/w*, 3.2 mL, 25 mmol), stirring vigorously at 0 °C, was added aniline (10 mmol), and precipitation was observed. *tert*-Butyl methyl ether was added until the biphasic mixture was free of heterogeneity (~5 mL). An aqueous solution of $NaNO_2$ (696 mg, 10.1 mmol in 3 mL H_2O) was then added dropwise over 2 min and the reaction

was stirred at 0 °C for an additional 20 min. The mixture was allowed to warm to ambient temperature and stirred an additional 30 min, by which point the crude product had precipitated. The precipitate was collected by filtration, washing with cold H_2O (2 x 3 mL) and *tert*-butyl methyl ether (2 x 10 mL). The solid material was then dissolved in acetone, and precipitated by addition of *tert*-butyl methyl ether. The aryldiazonium was isolated by filtration and dried under vacuum.



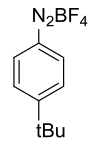
8a

The product **8a** was isolated as a colorless solid (1.53 g, 80% yield). ^{1}H NMR (300 MHz, Acetone-d_6) δ 8.92 – 8.81 (m, 2H), 8.40 (ddt, J = 8.0, 7.4, 1.2 Hz, 1H), 8.16 – 8.05 (m, 2H) ppm; ^{13}C NMR (75 MHz, Acetone-d_6) δ 142.2, 133.6, 132.4, 116.4 ppm; IR (film): $\bar{\nu}$ = 3107, 2294, 1570, 1462, 1311, 1290, 1173, 1025, 989, 943, 755, 665, 530, 522, 453 cm^{-1}. HRMS (ESI+) *m/z*: calcd for $C_6H_5N_2$: 105.0447; found: 105.0448.



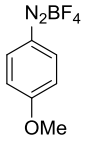
$^{15}N_2$-8a

The procedure was modified, employing ^{15}N-labeled aniline and ^{15}N-labeled sodium nitrite on a 2.0 mmol scale. The product **$^{15}N_2$-8a** was isolated as a colorless solid (205 mg, 53% yield). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.86 – 8.77 (m, 2H), 8.37 (tt, J = 7.8, 1.3 Hz, 1H), 8.08 (tt, J = 7.8, 1.3 Hz, 2H).ppm; ^{13}C NMR (101 MHz, Acetone-d_6) δ 142.0, 133.4 (d, $J_{C\text{-}N}$ = 2.2 Hz), 132.2 (d, $J_{C\text{-}N}$ = 3.2 Hz), 116.2 (dd, $J_{C\text{-}N}$ = 9.9, 5.7 Hz) ppm; ^{15}N NMR (61 MHz, Acetone-d_6) δ -66.2, −148.9 ppm; IR (film): $\bar{\nu}$ = 3107, 2217, 1570, 1461, 1311, 1290, 1173, 1027, 990, 944, 756, 665, 522, 446 cm^{-1}. HRMS (ESI+) *m/z*: calcd for $C_6H_5{}^{15}N_2$: 107.0388; found: 107.0392.



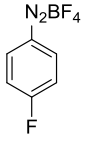
8b

The reaction was run on a 6.88 mmol scale, and the product **8b** was isolated as a colorless solid (798 mg, 47% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 – 8.53 (m, 2H), 7.86 – 7.79 (m, 2H), 1.36 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 132.9, 129.1, 110.6, 36.9, 30.6 ppm; IR (film): $\bar{\nu}$ = 3016, 2966, 2273, 1574, 1480, 1417, 1373, 1269, 1036, 841, 768, 721, 619, 543, 520 cm^{-1}. HRMS (ESI+) *m/z*: calcd for $C_{10}H_{13}N_2$: 161.1073; found: 161.1073.



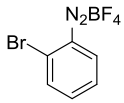
8c

The product **8c** was isolated as a colorless solid (1.31 g, 59% yield). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.84 – 8.76 (m, 2H), 7.60 – 7.53 (m, 2H), 4.18 (d, J = 0.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Acetone-d_6): δ = 170.6, 137.0, 118.4, 103.7, 58.0 ppm; IR (film): $\bar{\nu}$ = 3119, 2685, 2250, 1582, 1568, 1493, 1442, 1343, 1288, 1197, 1099, 1033, 841, 807, 685, 522, 498 cm^{-1}. HRMS (ESI+) *m/z*: calcd for $C_7H_7N_2O$: 135.0553; found: 135.0553.



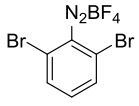
8d

The product **8d** was isolated as a colorless solid (820 mg, 39% yield). ^{1}H NMR (300 MHz, Acetone-d_6) δ 9.02 – 8.90 (m, 2H), 7.93 – 7.82 (m, 2H) ppm; ^{13}C NMR (101 MHz, Acetone-d_6) δ 170.3 (d, $J_{C\text{-}F}$ = 268.8 Hz), 138.0 (d, $J_{C\text{-}F}$ = 12.3 Hz), 120.5 (d, $J_{C\text{-}F}$ = 25.6 Hz), 112.1 (d, $J_{C\text{-}F}$ = 3.0 Hz) ppm; ^{19}F NMR (282 MHz, Acetone-d_6) δ −86.9 ppm; IR (film): $\bar{\nu}$ = 3115, 2294, 1932, 1579, 1484, 1431, 1250, 1167, 1012, 850, 836, 685, 525 cm^{-1}. HRMS (ESI+) *m/z*: calcd for $C_6H_4N_2F$: 123.0353; found: 123.0355.



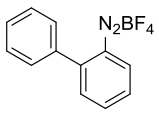
8e

The product **8e** was isolated as a tan solid (1.36 g, 50% yield). ^{1}H NMR (300 MHz, Acetone-d_6) δ 8.94 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.31 (app t, *J* = 8.0 Hz, 1H), 8.09 (app t, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (101 MHz, Acetone-d_6) δ 143.2, 136.3, 136.2, 131.3, 125.3, 118.7 ppm; IR (film): ν̄ = 3096, 2288, 1562, 1468, 1302, 1269, 1051, 1033, 772, 656 cm^{-1}. HRMS (ESI+) *m/z*: calcd for $C_6H_4N_2Br$: 182.9552; found: 182.9553.



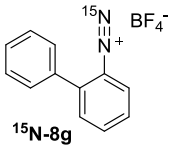
8f

The product **8f** was isolated as a pale yellow solid (2.01 g, 57% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (d, *J* = 8.2 Hz, 2H), 8.07 (t, *J* = 8.2 Hz, 1H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.5, 134.4, 126.7, 121.2 ppm; IR (film): ν̄ = 3105, 3076, 2276, 1556, 1545, 1446, 1284, 1221, 1157, 1022, 802, 739, 521, 405 cm^{-1}. HRMS (ESI+) *m/z*: calcd for $C_6H_3N_2Br_2$: 260.8658; found: 260.8659.



8g

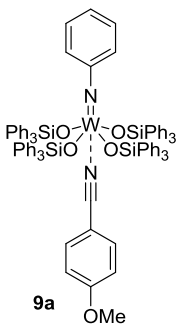
The reaction was run on a 4.10 mmol scale, and the product **8g** was isolated as a colorless solid (771 mg, 70% yield). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.92 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.43 (app td, *J* = 7.8, 1.3 Hz, 1H), 8.11 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.06 (ddd, *J* = 8.4, 7.8, 1.2 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.74 – 7.68 (m, 3H) ppm; ^{13}C NMR (101 MHz, Acetone-d_6) δ 146.4, 142.4, 134.7, 133.9, 133.2, 131.9, 131.3, 130.7, 129.5, 114.7 ppm; IR (film): ν̄ = 3103, 2267, 1590, 1557, 1471, 1293, 1030, 785, 759, 718, 705, 520, 496, 456 cm^{-1}. HRMS (ESI+) *m/z*: calcd for $C_{12}H_9N_2$: 181.0760; found: 181.0761.



^{15}N-8g

The procedure was modified, employing ^{15}N-labeled sodium nitrite, and the reaction was run on a 1.87 mmol scale, and the product **^{15}N-8g** was isolated as a colorless solid (375 mg, 74% yield). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.95 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.45 (app td, *J* = 7.8, 1.3 Hz, 1H), 8.13 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.08 (ddd, *J* = 8.4, 7.8, 1.2 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.76 – 7.69 (m, 3H) ppm; ^{13}C NMR (101 MHz, Acetone-d_6) δ 146.5, 142.6, 134.9, 134.0, 133.3, 132.1, 131.5, 130.8, 129.7, 114.9 (d, $J_{C\text{-}N}$ = 6.0 Hz) ppm; IR (film): ν̄ = 3103, 2234, 1591, 1557, 1471, 1293, 1031, 784, 759, 718, 705, 520, 495, 455 cm^{-1}. HRMS (ESI+) *m/z*: calcd for $C_{12}H_9N^{15}N$: 182.0731; found: 182.0732.

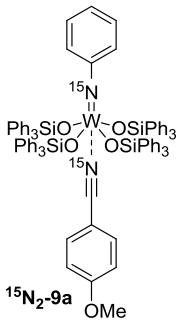
Synthesis of imido complexes



9a

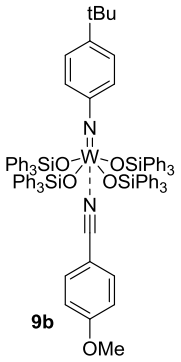
To aryldiazonium **8a** (18.8 mg, 0.098 mmol) in CH_2Cl_2 (2 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne **5** (142 mg, 0.098 mmol) in CH_2Cl_2 (2 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color, and the color dissipated to the original pink color within seconds. The mixture was warmed to ambient temperature and stirred 1 h, by which time it had become yellow in color. The reaction mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH_2Cl_2 and the product precipitated with pentane. The precipitate was collected by

filtration, giving **9a** as a yellow solid (127 mg, 86% yield, by NMR contains ~10% impurity). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.24-7.14 (m, 41H), 7.10 (t, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.85-6.80 (m, 24 H), 6.34 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 164.5, 153.3, 137.6, 136.4, 136.1, 135.8, 129.5, 129.0, 127.8, 127.5, 117.6, 115.5, 101.7, 56.3 ppm.



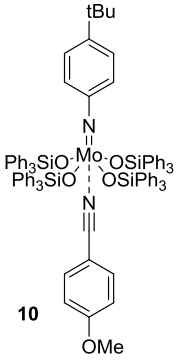
$^{15}N_2$-9a

To aryldiazonium **$^{15}N_2$-8a** (10.8 mg, 0.0557 mmol) in CH_2Cl_2 (2 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne **5** (80.4 mg, 0.0557 mmol) in CH_2Cl_2 (2 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become yellow in color. The reaction mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH_2Cl_2 and the product precipitated with pentane. The precipitate was collected by filtration, giving **$^{15}N_2$-9a** a yellow solid (65 mg, 77% yield). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.22-7.16 (m, 38H), 7.11 (t, *J* = 7.2 Hz, 2H), 6.95 (m, 2H), 6.85-6.80 (m, 25 H), 6.35 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H) ppm; ^{13}C NMR (151 MHz, CD_2Cl_2) δ 164.3, 153.1 ($J_{C\text{-}W,C\text{-}N}$ = 38.0, 10.7 Hz) 137.5, 136.1, 134.7, 129.2, 128.9, 127.6, 127.3 ($J_{C\text{-}N}$ = 2.0 Hz), 127.3, 117.5 ($J_{C\text{-}N}$ = 25 Hz), 115.3, 101.6, 44.3 ppm; ^{15}N NMR (61 MHz, CD_2Cl_2) δ −0.6 ($J_{W\text{-}N}$ = 135 Hz), −145.0 ppm.



9b

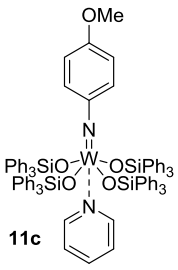
To aryldiazonium **8b** (37.8 mg, 0.152 mmol) in CH_2Cl_2 (3 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne **5** (220 mg, 0.152 mmol) in CH_2Cl_2 (3 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become yellow in color. The reaction mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH_2Cl_2 and the product precipitated with pentane. The precipitate was collected by filtration, giving **9b** as a yellow solid (200 mg, 84% yield). X-ray quality single crystals were grown by layered diffusion with CH_2Cl_2 and pentane.^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.27 (d, *J* = 12.0 Hz, 2H), 7.24-7.15 (m, 36H), 7.10 (d, *J* = 12.0 Hz), 6.94 (d, *J* = 8.0 Hz, 2H), 6.88-6.81 (m, 24H), 6.31 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 1.30 (s, 9H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 164.4, 151.2, 150.9, 137.7, 136.3, 129.4, 128.7, 128.8, 124.2, 117.6, 115.4, 115.3, 101.9, 56.3, 34.7, 31.8 ppm.



10

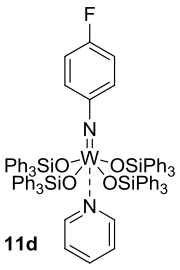
To aryldiazonium **8b** (35.5 mg, 0.143, mmol) in CH_2Cl_2 (3 mL) stirring at 0 °C was added dropwise a solution of the molybdenum alkylidyne **2** (194 mg, 0.143 mmol) in CH_2Cl_2 (3 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become orange/brown in color. The mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH_2Cl_2 and the product precipitated with pentane.

The precipitate was collected by filtration, giving **10** as an orange solid (172 mg, 81% yield). X-ray quality single crystals were grown by layered diffusion with CH_2Cl_2 and pentane. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.30 (d, *J* = 7 Hz, 2H), 7.23-7.17 (m, 24H), 6.96 (d, *J* = 9 Hz, 2H), 6.92 (d, *J* = 7 Hz, 2H), 6.90-6.83 (m, 24H), 6.45 (d, *J* = 9 Hz, 2H), 3.86 (s, 3H), 1.37 (s, 9H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 163.8, 153.6, 153.5, 137.6, 136.3, 134.7, 129.5, 128.1, 127.8, 124.9, 118.5, 115.2, 103.1, 56.2, 35.2, 31.4 ppm.



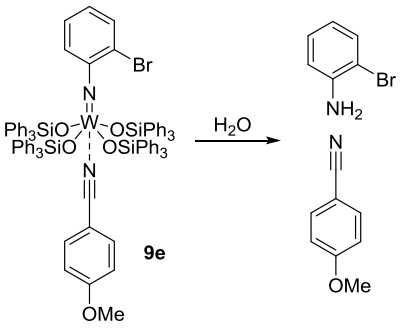
11c

To aryldiazonium **8c** (21.5 mg, 0.097 mmol) in CH_2Cl_2 (3 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne **5** (140 mg, 0.097 mmol) in CH_2Cl_2 (3 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become orange in color. Pyridine (39 ul, 0.485 mmol) was then added and the reaction mixture was stirred an additional 30 min. The reaction mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH_2Cl_2 and the product precipitated by addition of pentane and cooling to −20 °C. The precipitate was collected by filtration, washing with 10 mL cold 1:1 pentane/Et_2O, giving **11c** as a yellow solid (118 mg, 82% yield). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.88 (s, 2H), 7.58 (t, *J* = 7 Hz, 1H), 7.25-7.16 (m, 12H), 7.12-7.03 (m, 24H), 6.93 (t, *J* = 7 Hz, 2H), 6.85 (t, *J* = 8 Hz, 24H), 6.62 (d, *J* = 9 Hz, 2H), 6.42 (d, *J* = 9 Hz, 2H), 3.81 (s, 3H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.3, 151.2, 147.1, 137.8, 136.7, 135.5, 131.6, 129.5, 127.8, 124.0, 112.6, 56.0 ppm.

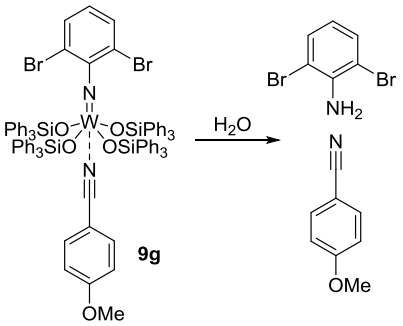


11d

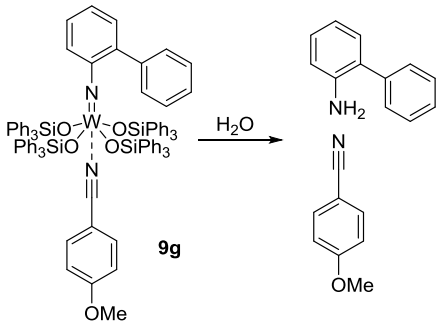
To aryldiazonium **8d** (25.0 mg, 0.119 mmol) in CH_2Cl_2 (3 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne **5** (172 mg, 0.119 mmol) in CH_2Cl_2 (3 mL) over 2 min. Upon contact, the reaction mixture immediately became purple in color. The reaction mixture was warmed to ambient temperature and stirred 1 h, by which time it had become yellow in color. Pyridine (48 ul, 0.590 mmol) was then added and the reaction mixture was stirred an additional 30 min. The mixture was filtered through Celite, the filtrate was concentrated to dryness, the residue was redissolved in a minimum of CH_2Cl_2 and the product precipitated by addition of pentane and cooling to −20 °C. The precipitate was collected by filtration, washing with 10 mL cold 1:1 pentane/Et_2O, giving **11d** as a yellow solid (124 mg, 71% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.88 (br s, 2H), 7.65-7.55 (m, 1H),7.25-7.15 (m, 12H), 7.12-7.00 (m, 24H), 6.95-6.87 (m, 2H), 6.88-6.73 (m, 26H),6.42-6.35 (m, 2H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 151.3, 149.6, 138.8, 137.6, 136.7, 131.6 (d, *J* = 8 Hz), 129.6, 127.9, 124.1, 114.4 (d, *J* = 23 Hz) ppm (carbon at para position not observed); ^{19}F NMR (282 MHz, CD_2Cl_2) δ −113.70.



To aryldiazonium **8e** (11.9 mg, 0.0439 mmol) in CH_2Cl_2 (1 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne **5** (63.4 mg, 0.0439 mmol) in CH_2Cl_2 (1 mL) over 2 min. The mixture was warmed to ambient temperature (remained deep purple for ~20 min) and stirred 1 h, by which time it had become yellow in color. To the reaction mixture containing complex **9e** was added drops of H_2O and stirring was continued for 30 min. The mixture was concentrated to dryness and the residue purified by flash column chromatography on SiO_2 (1:1 to 3:1 benzene/hexanes), giving 2-bromoaniline (5.5 mg, 73% yield) and 4-methoxybenzonitrile (3.0 mg, 51% yield). ^{1}H NMR spectra were in good agreement with the literature data.[2,3]



To aryldiazonium **8g** (28.1 mg, 0.0803 mmol) in CH_2Cl_2 (2 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne **5** (116 mg, 0.803 mmol) in CH_2Cl_2 (2 mL) over 2 min. The mixture was warmed to ambient temperature and stirred 1 h, by which time it had become dark yellow in color. To the reaction mixture containing complex **9g** was added drops of H_2O and stirring was continued for an additional 30 min. The mixture was concentrated to dryness and the residue purified by flash column chromatography on SiO_2 (1:1 to 3:1 benzene/hexanes), giving 2,6-dibromoaniline (12.0 mg, 60% yield) and 4-methoxybenzonitrile (6.0 mg, 56% yield). ^{1}H NMR spectra were in good agreement with the literature data.[2,4]

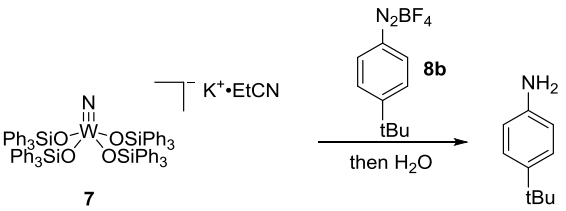


To aryldiazonium **8g** (21.9 mg, 0.0817 mmol) in CH_2Cl_2 (3 mL) stirring at 0 °C was added dropwise a solution of the tungsten alkylidyne **5** (118 mg, 0.0817 mmol) in CH_2Cl_2 (1 mL) over 2 min. The reaction mixture was warmed to ambient temperature and stirred 3 h, by which time it had become orange in color. To the reaction mixture containing complex **9g** was added drops of H_2O and stirring continued for an additional 30 min. The mixture was concentrated to dryness and the residue purified by flash column chromatography on SiO_2 (1:1 benzene/hexanes to separate from PH_3SiOH, then 9:1 hexanes/*tert*-butyl methyl ether), giving 2-aminobiphenyl (7.0 mg, 51% yield)

[2] 4-Methoxybenzonitrile: Wang, Z.; Chang, S. *Org. Lett.* **2013**, *15*, 1990-1993.
[3] 2-Bromoaniline: Kelley, S. M.; Lipschutz, B. H. *Org. Lett.* **2014**, *16*, 98-101.
[4] 2,6-Dibromoaniline: Morrison, M. D.; Hanthorn, J. J.; Pratt, D. A. *Org. Lett.* **2009**, *11*, 1051-1054.

and 4-methoxybenzonitrile (10.0 mg, 92% yield). ^{1}H NMR spectra were in good agreement with the literature data.[2,5]

Reaction of the tungsten nitride complx 7 with aryldiazonium 8b

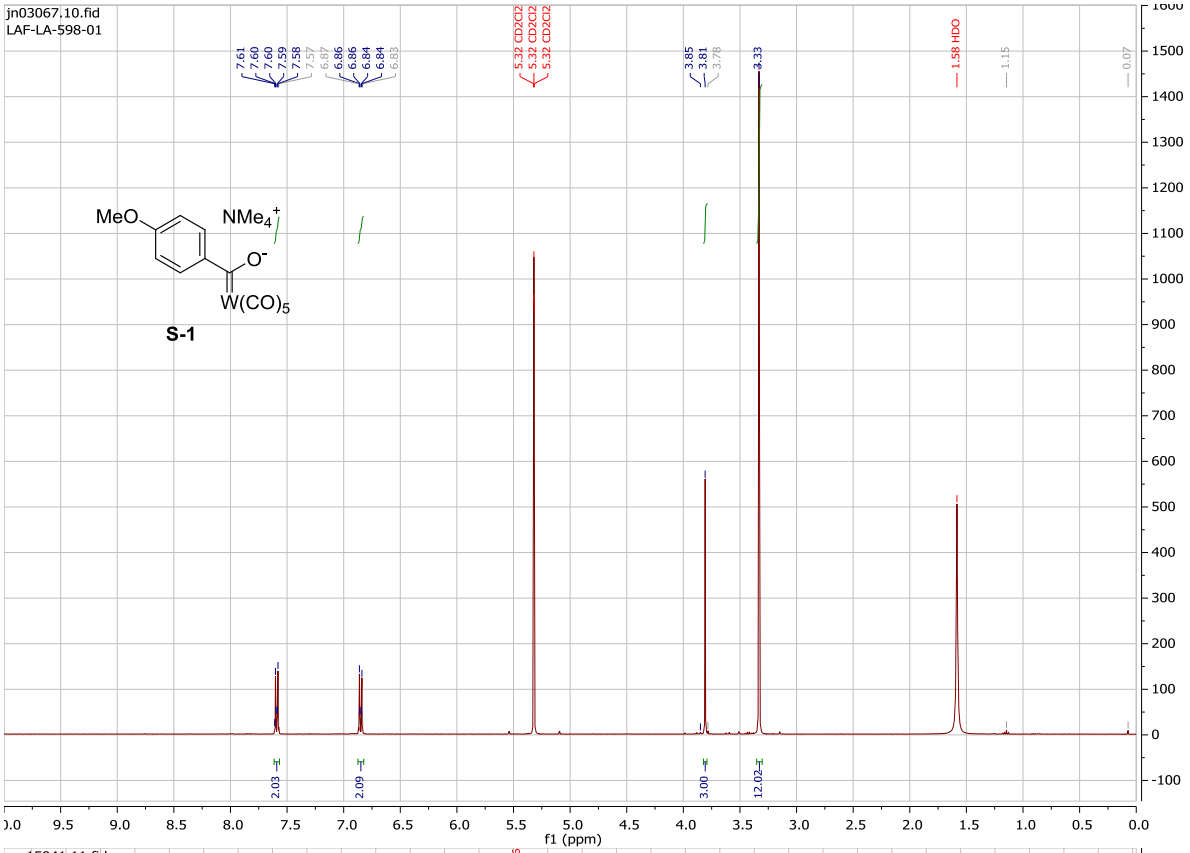


To aryldiazonium **8b** (13.9 mg, 0.0560 mmol) in DCM (2 mL) stirring at −20 °C was added dropwise a solution of the tungsten nitride **7** (75.0 mg, 0.560 mmol) in CH_2Cl_2 (2 mL) over 2 min. The reaction mixture was warmed to ambient temperature and stirred 2 h, by which time it had become brown in color. To the reaction mixture was added drops of H_2O and the reaction mixture was stirred an additional 30 min. The reaction mixture was concentrated to dryness and purified by flash column chromatography on SiO_2 (4:1 hexanes/*tert*-butyl methyl ether), giving 4-*tert*-butylaniline **12b** (6.0 mg, 72% yield). ^{1}H NMR spectra were in good agreement with the literature values.[2,6,7]

[5] 2-Aminobiphenyl: Green, R. A.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2013**, *54*, 3839-3843.

[6] 4-*tert*-Butylpyridine: Qi, H.-L.; Chen, D.-S.; Ye, J.-S.; Huang, J.-M. *J. Org. Chem.* **2013**, *78*, 7482-7487.

[7] GC/MS and IR inspection of the crude material suggest that small amounts of (*tert*-butyl)phenyl azide are also present; studies into this interesting side reaction are underway.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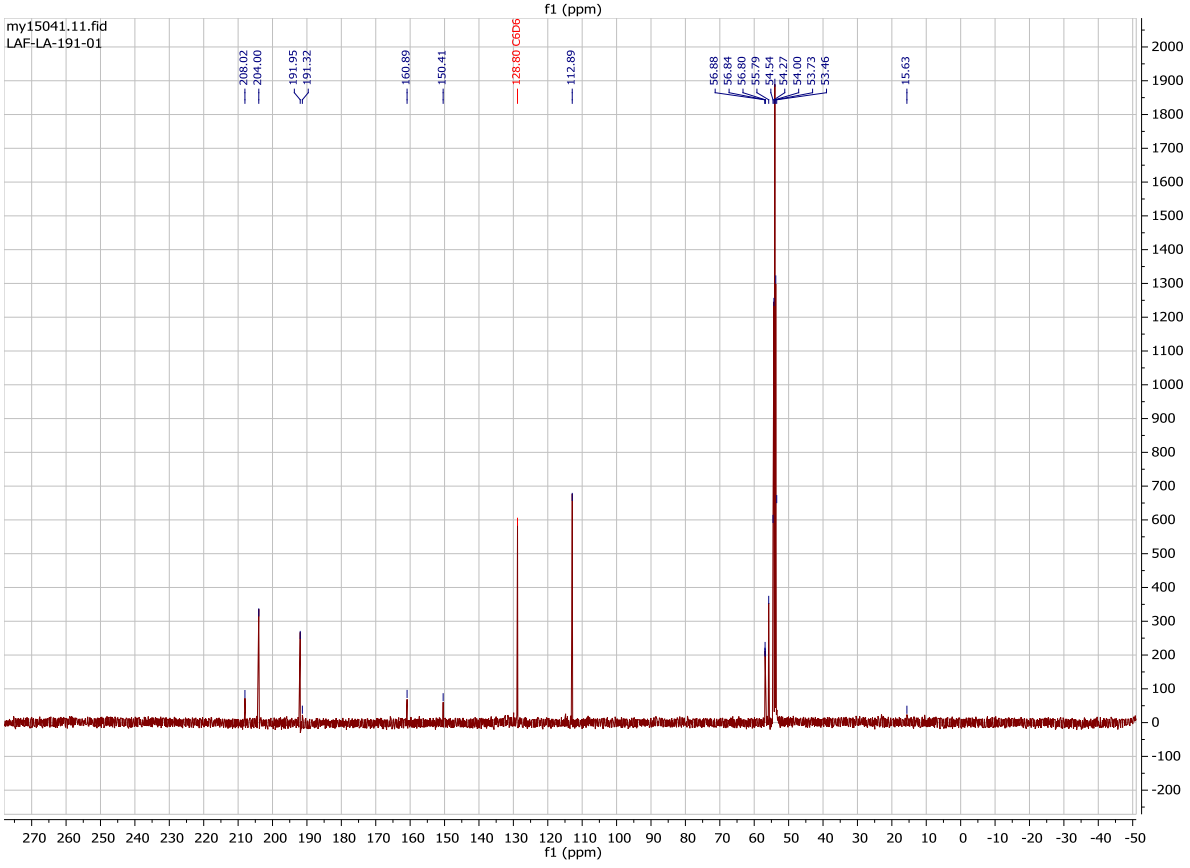
O-
W(CO)5
S-1
f1 (ppm)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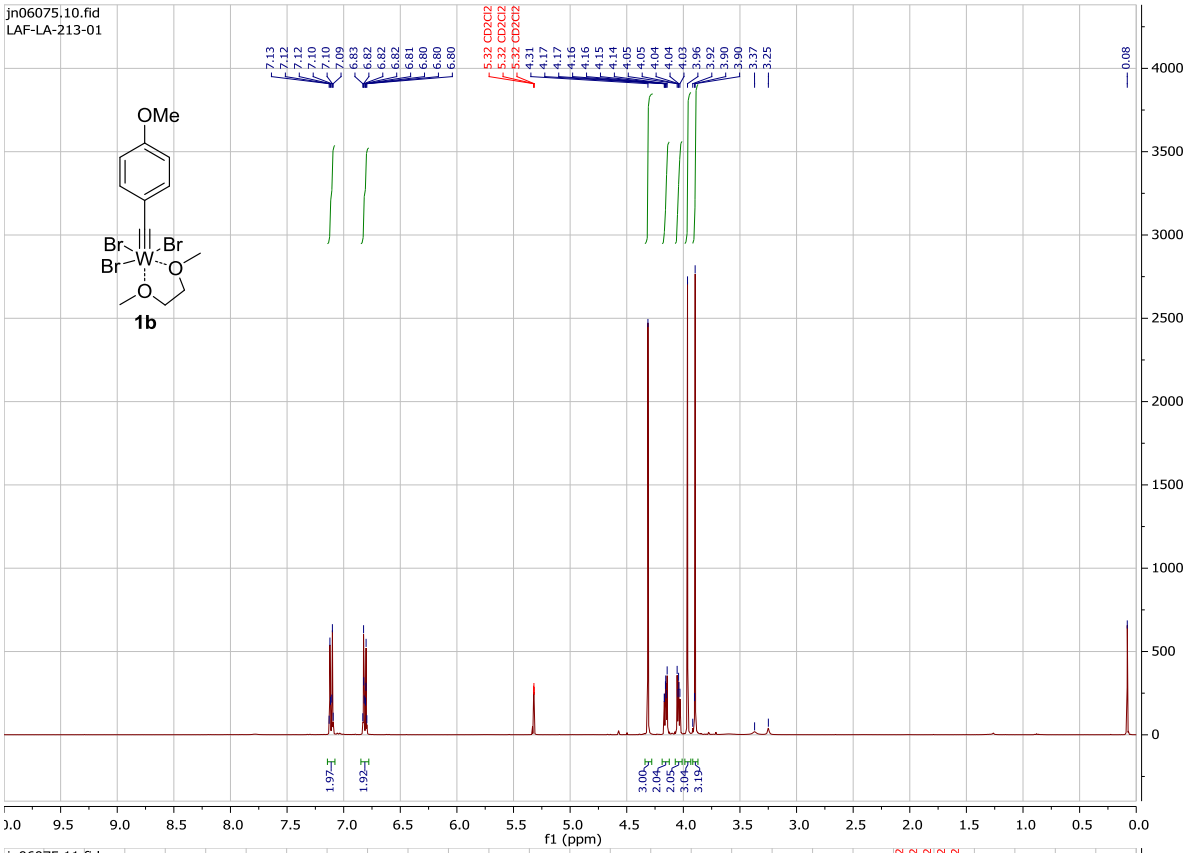
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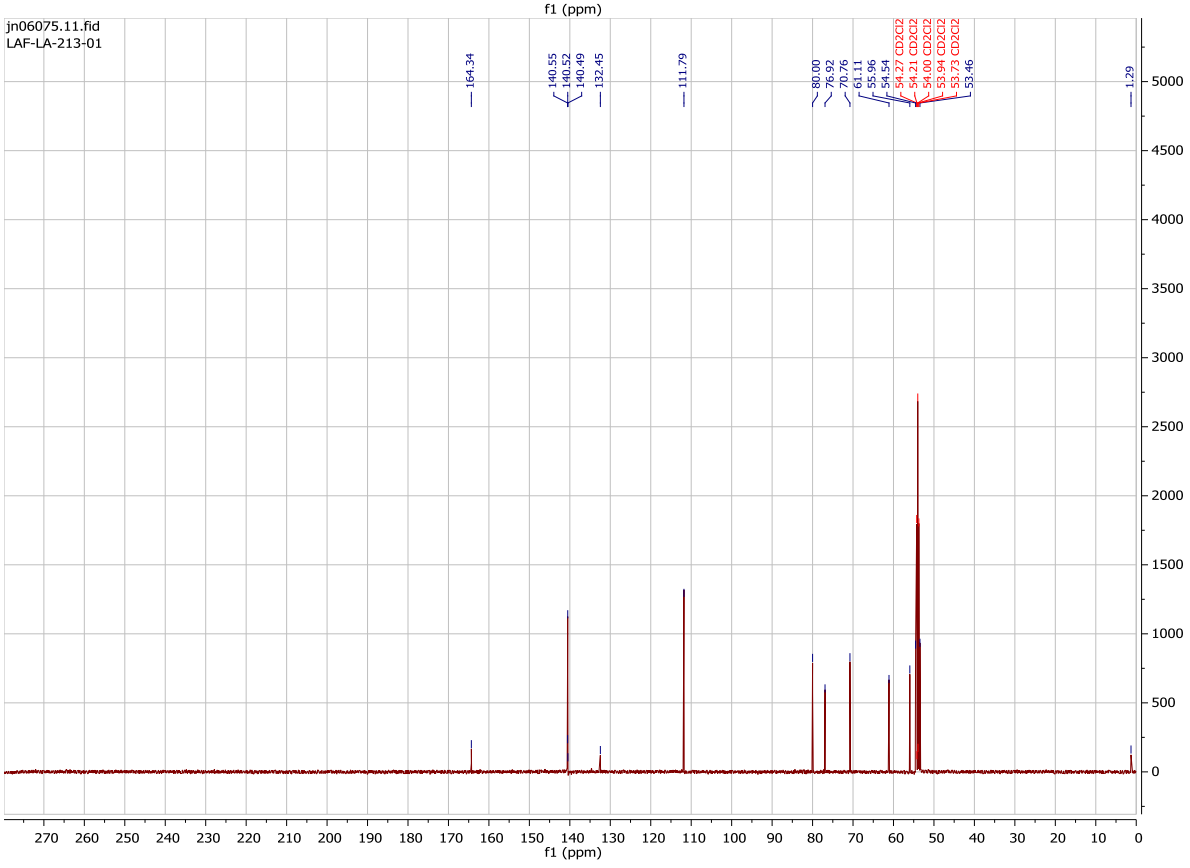
Br
W
Br
O
O
1b
f1 (ppm)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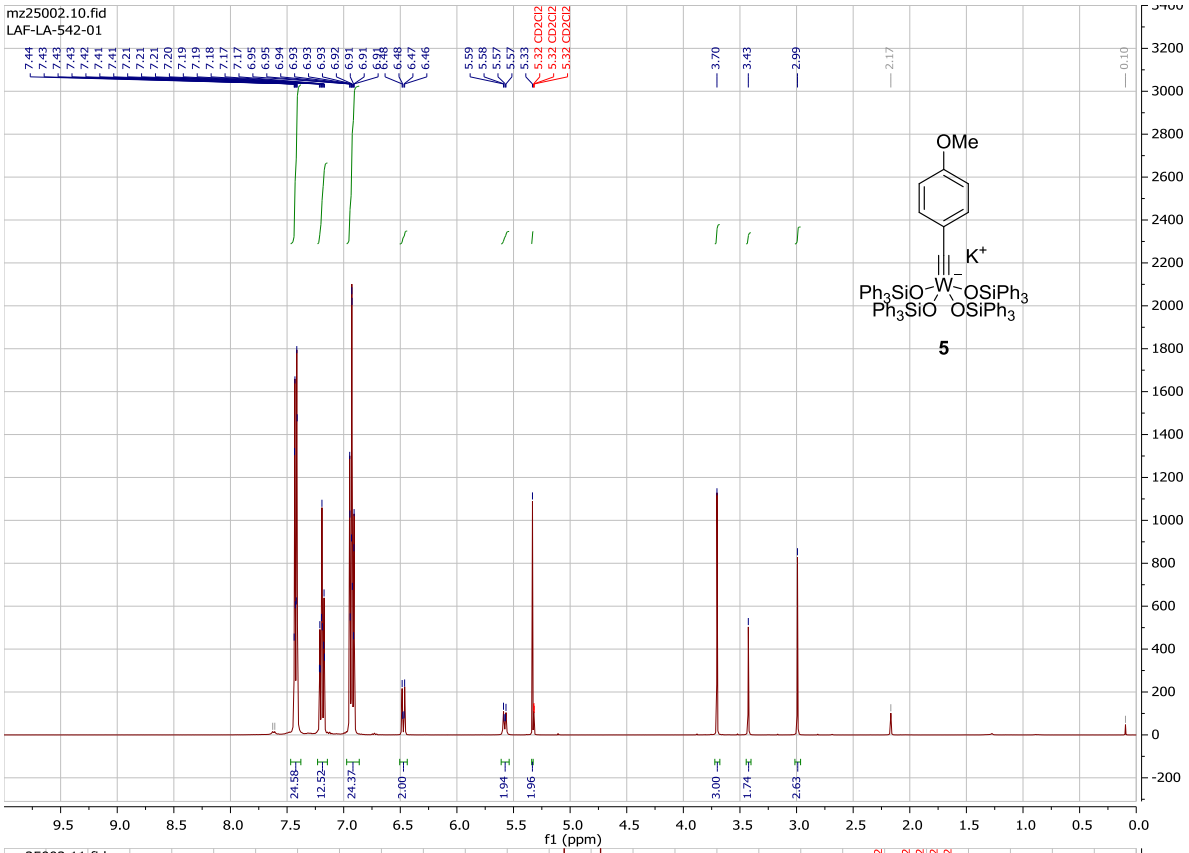
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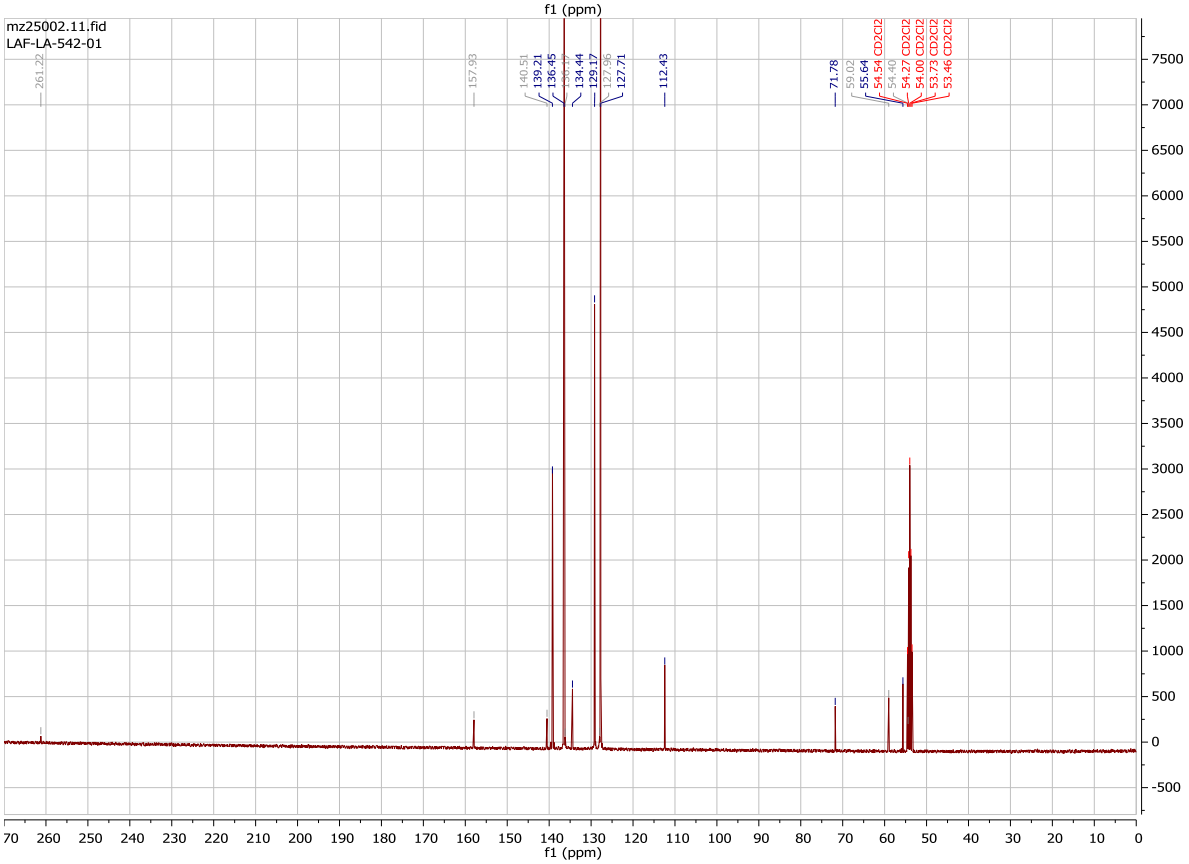
OSiPh3
Ph3SiO
OSiPh3
5
f1 (ppm)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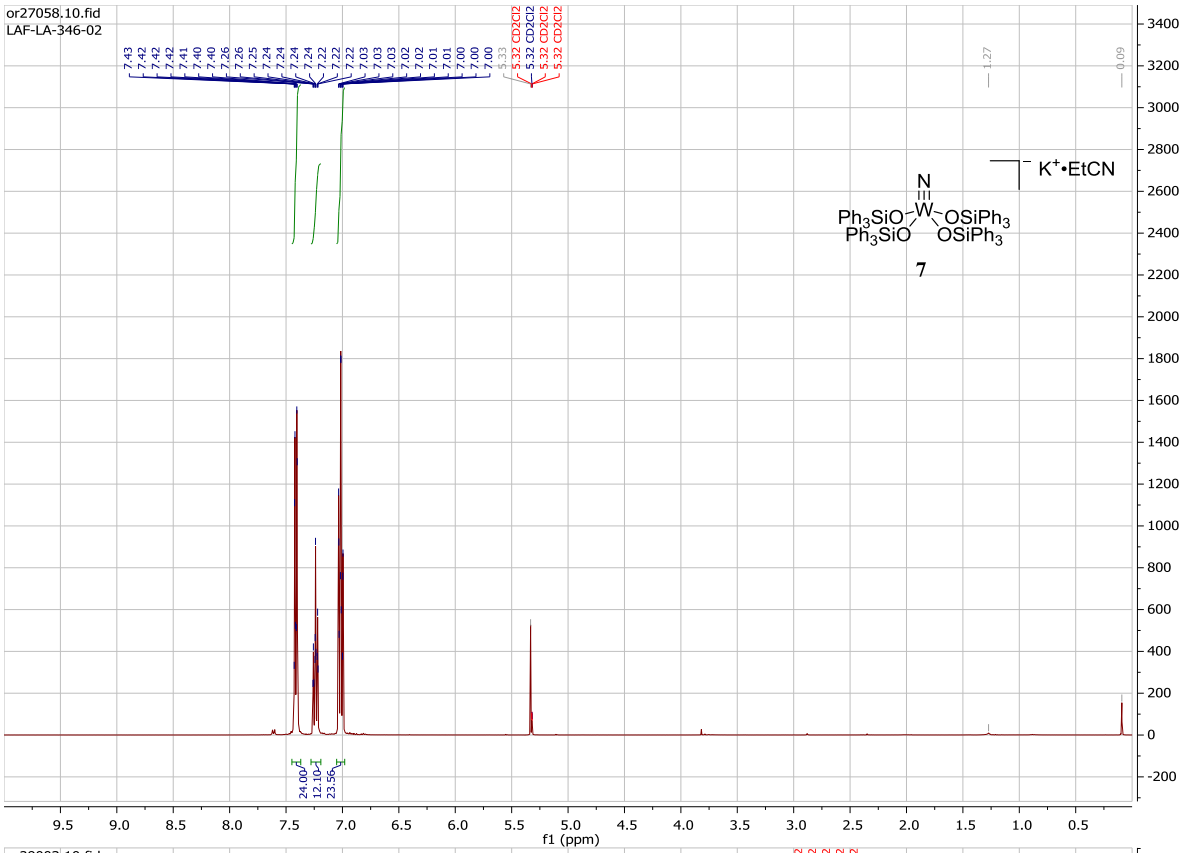
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7.42
7.41
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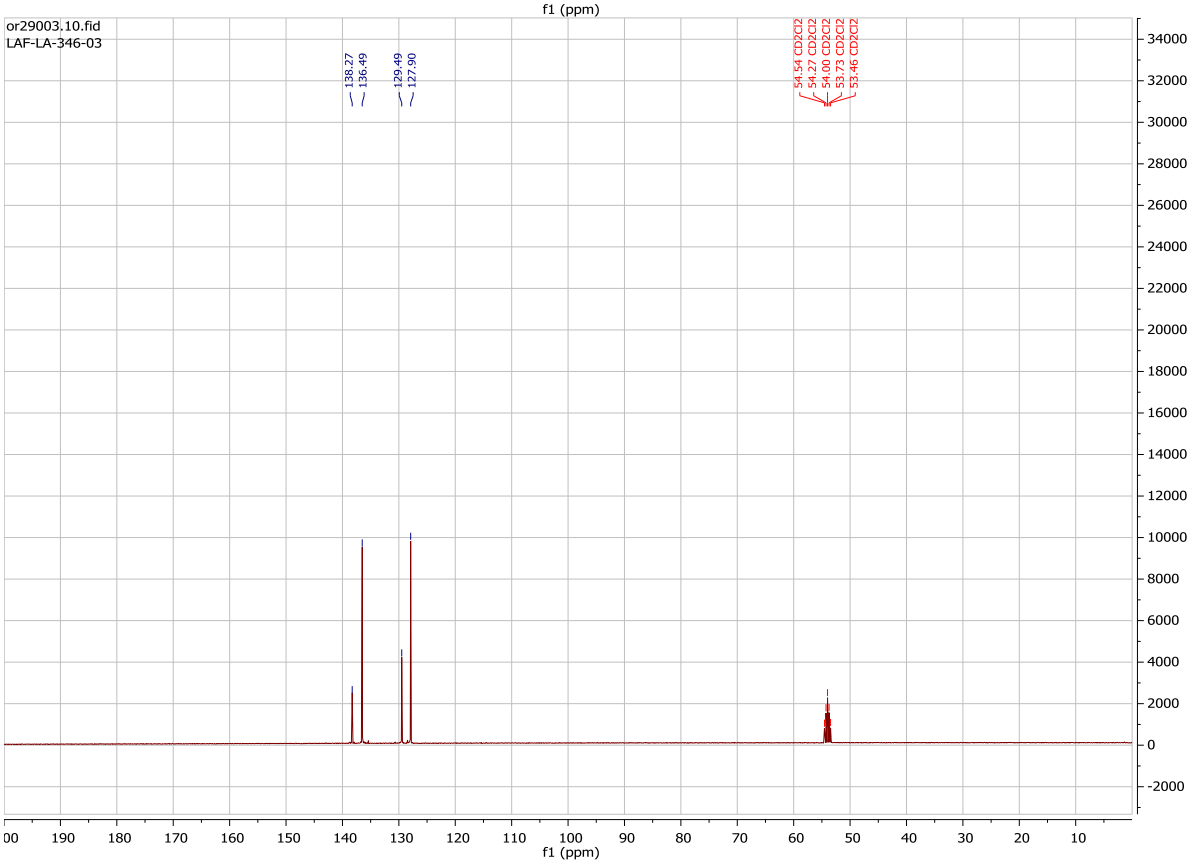
7.24
7.24
7.24
7.24
7.22
7.22
7.22
7.03
7.03
7.03
7.02
7.02
7.02
7.01
7.01
7.00
7.00
7.00
5.33
5.32 CD2Cl2
5.32 CD2Cl2
5.32 CD2Cl2
5.32 CD2Cl2
5.32 CD2Cl2
1.27
0.09
K+•EtCN
N
W
Ph3SiO
Ph3SiO
OSiPh3
OSiPh3
7
24.00
12.10
23.56
f1 (ppm)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136.49
129.49
127.90
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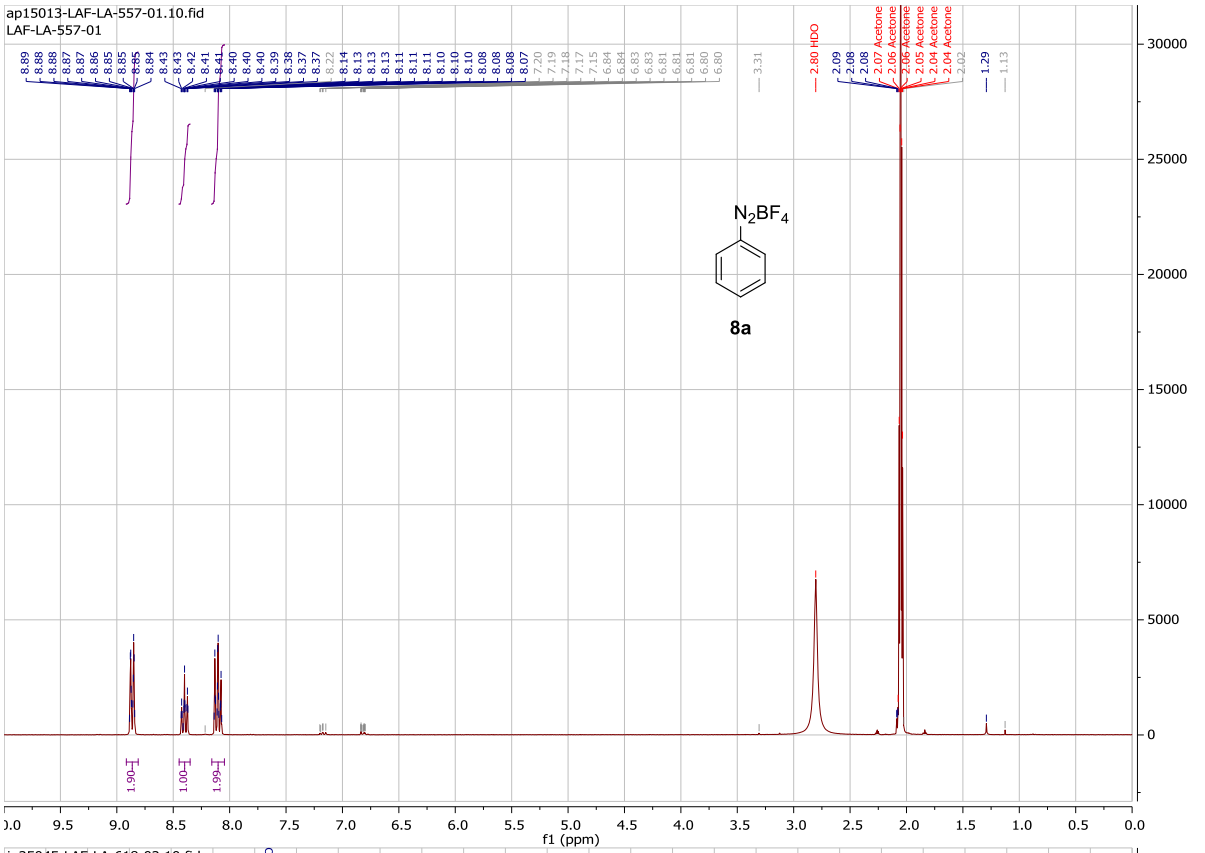
53.73 CD2Cl2
53.46 CD2Cl2
f1 (ppm)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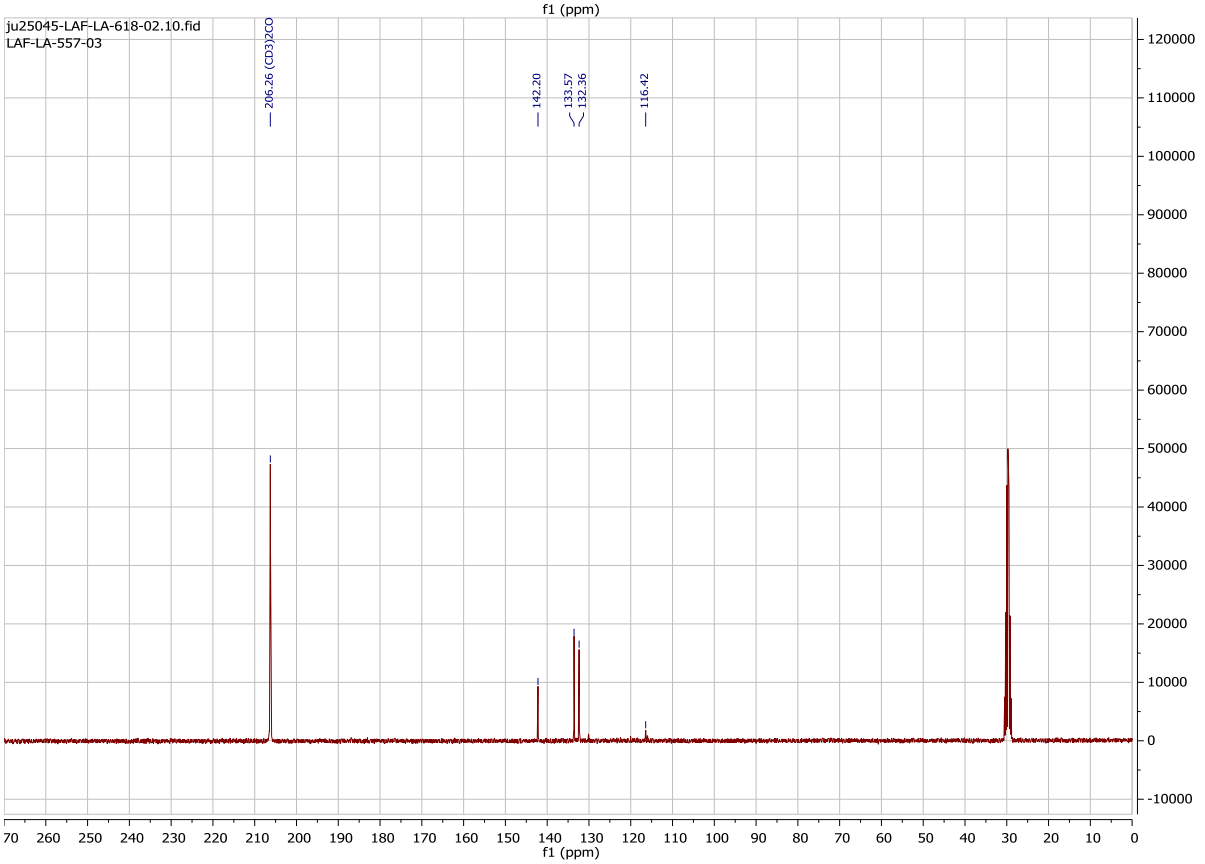
2.07 Acetone
2.06 Acetone
2.05 Acetone
2.04 Acetone
1.29
3.31
1.90
1.00
1.99
f1 (ppm)

N_2BF_4

8a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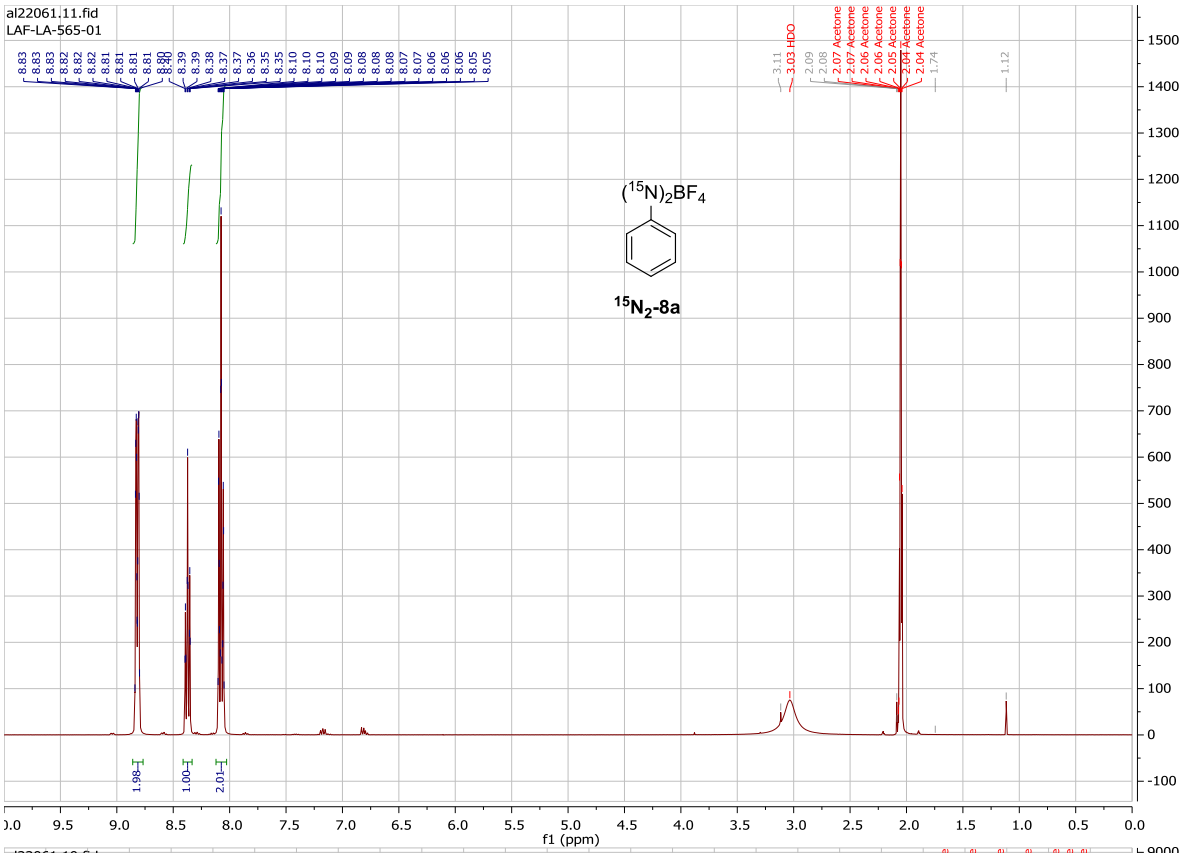
132.36
116.42
f1 (ppm)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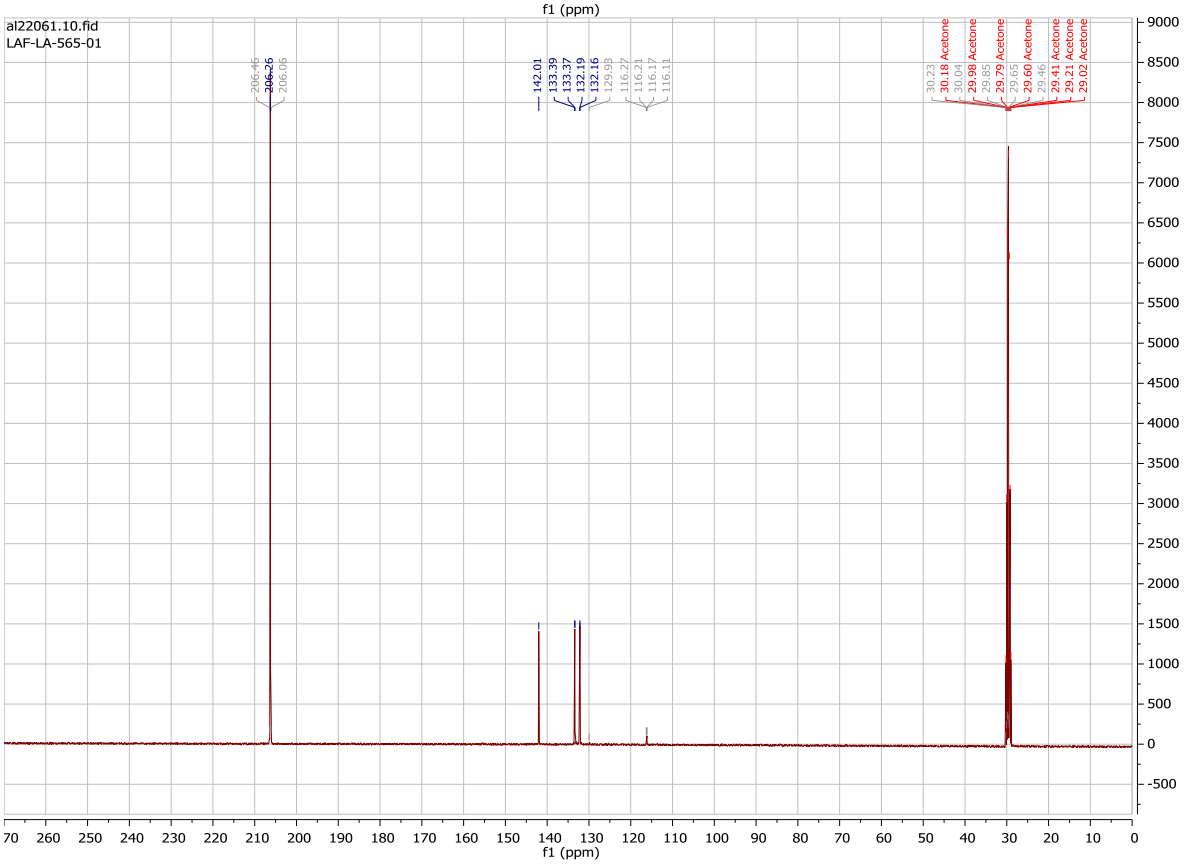
$(^{15}N)_2BF_4$
$^{15}N_2$-8a
f1 (ppm)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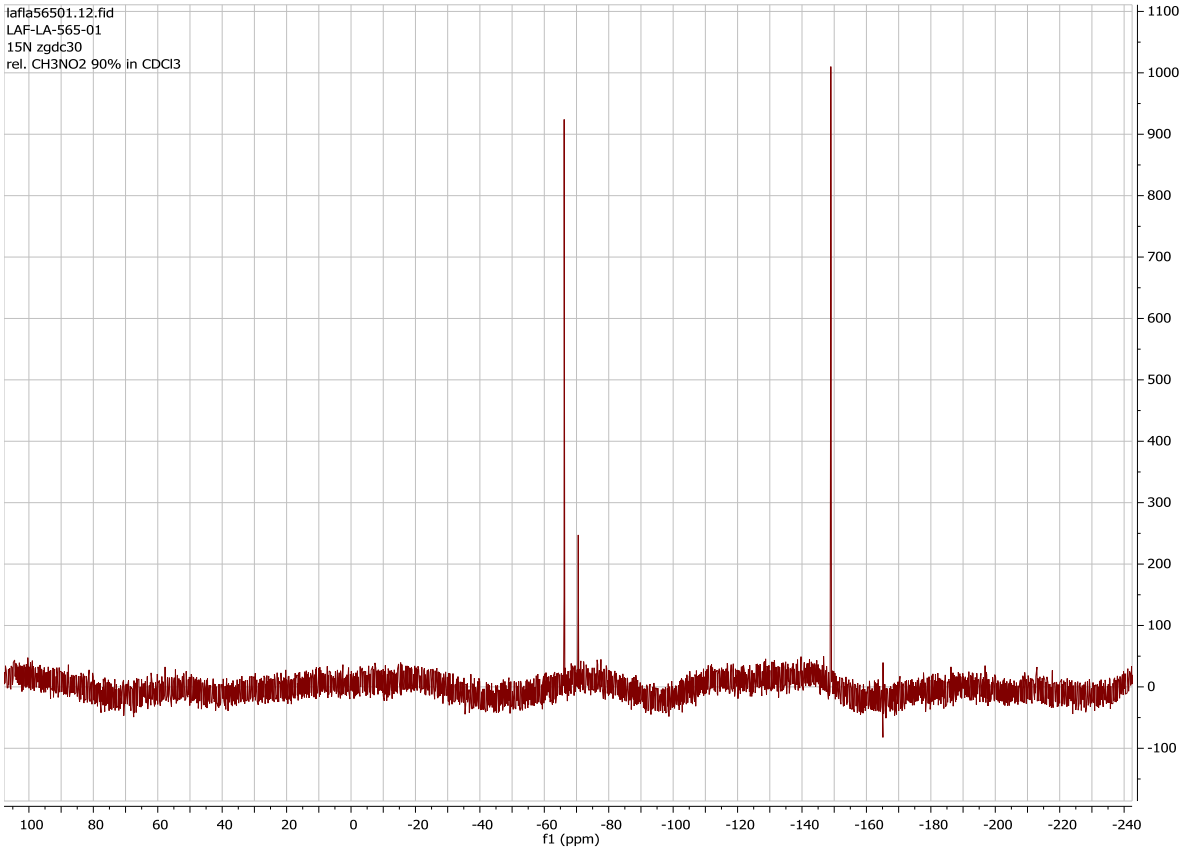
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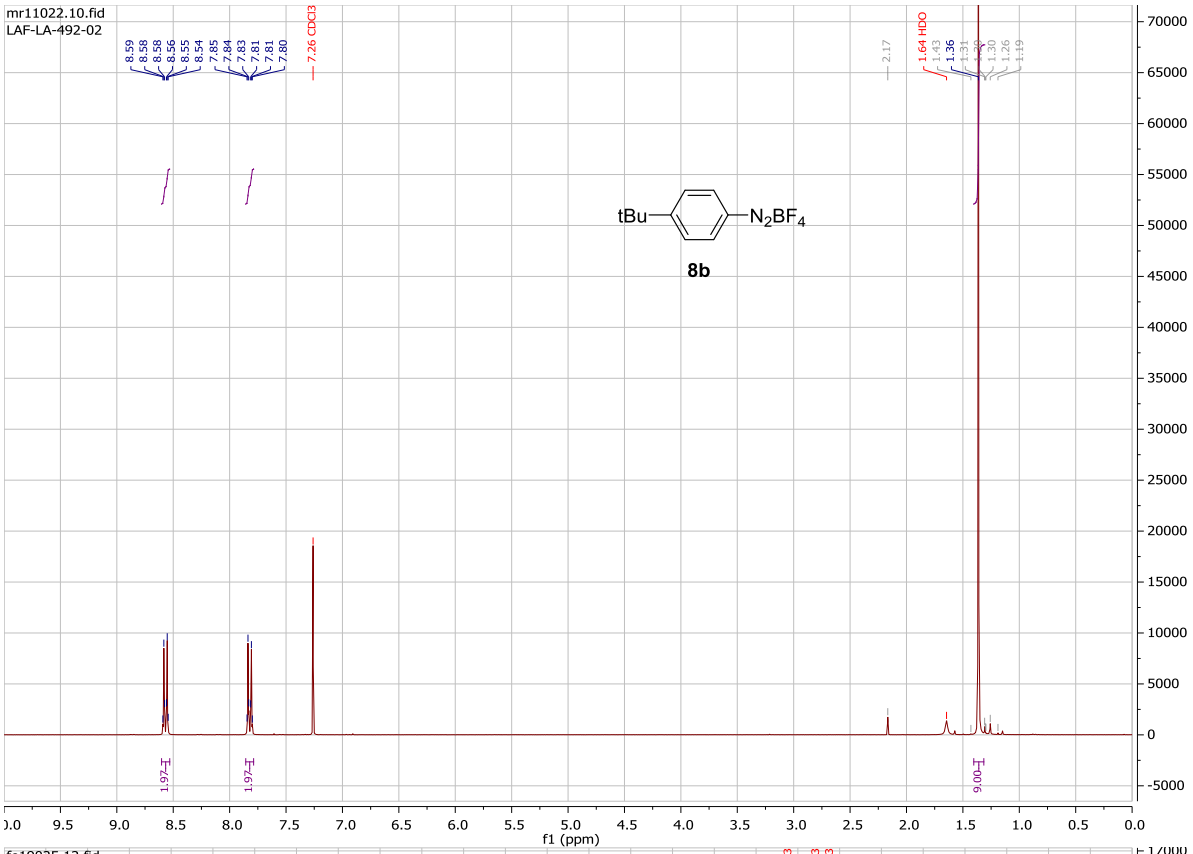
15N zgdc30
rel. CH3NO2 90% in CDCl3
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)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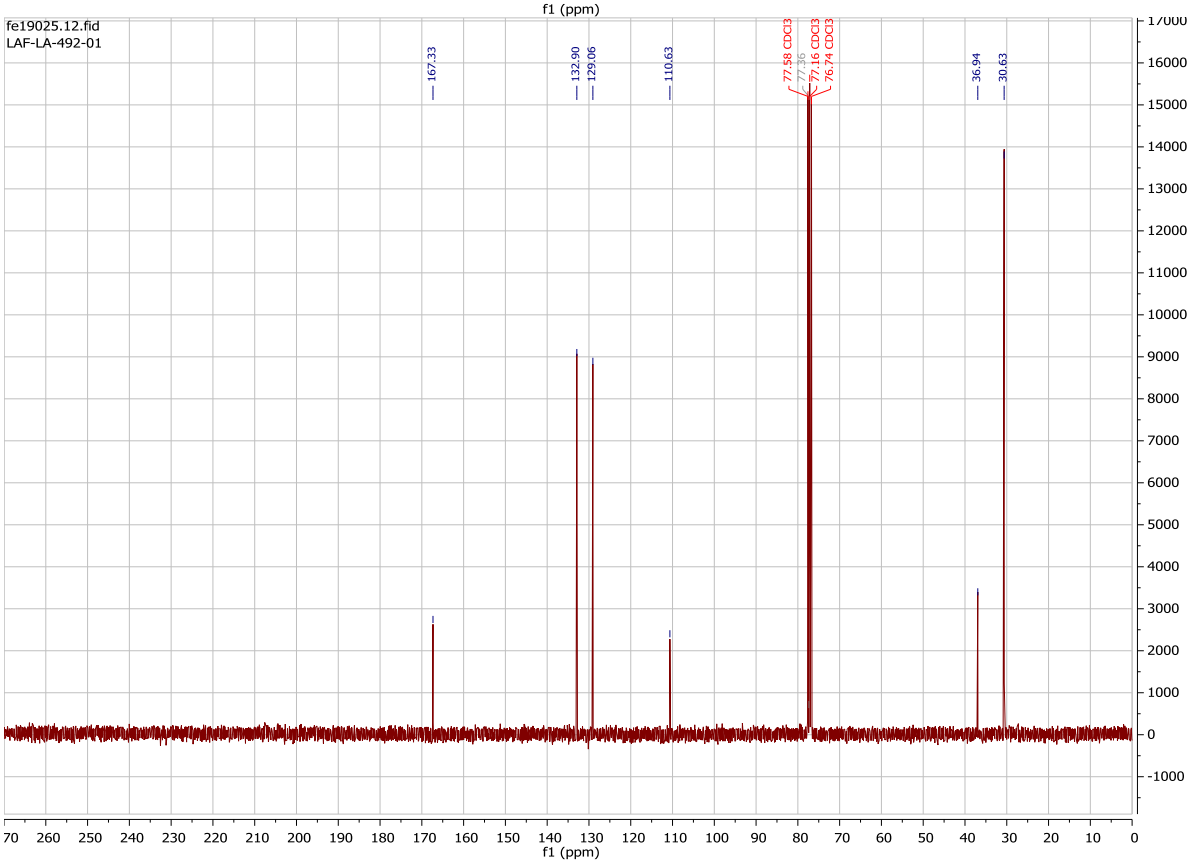
8.59
8.58
8.58
8.56
8.55
8.54
7.85
7.84
7.83
7.81
7.81
7.80
7.26 CDCl3
2.17
1.64 H2O
1.43
1.36
1.31
1.30
1.26
1.19
tBu
N2BF4
8b
1.97
1.97
9.00
f1 (ppm)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132.90
129.06
110.63
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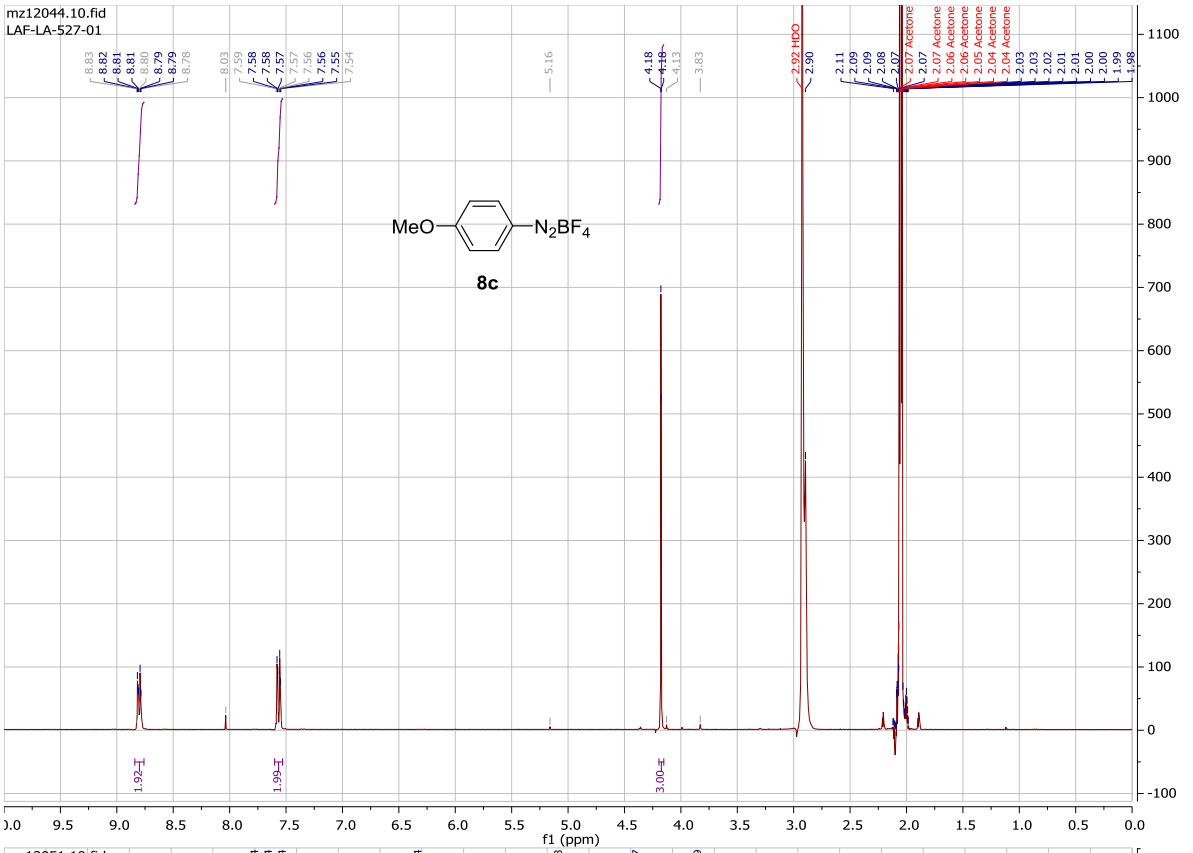
77.36
77.16 CDCl3
76.74 CDCl3
36.94
30.63
f1 (ppm)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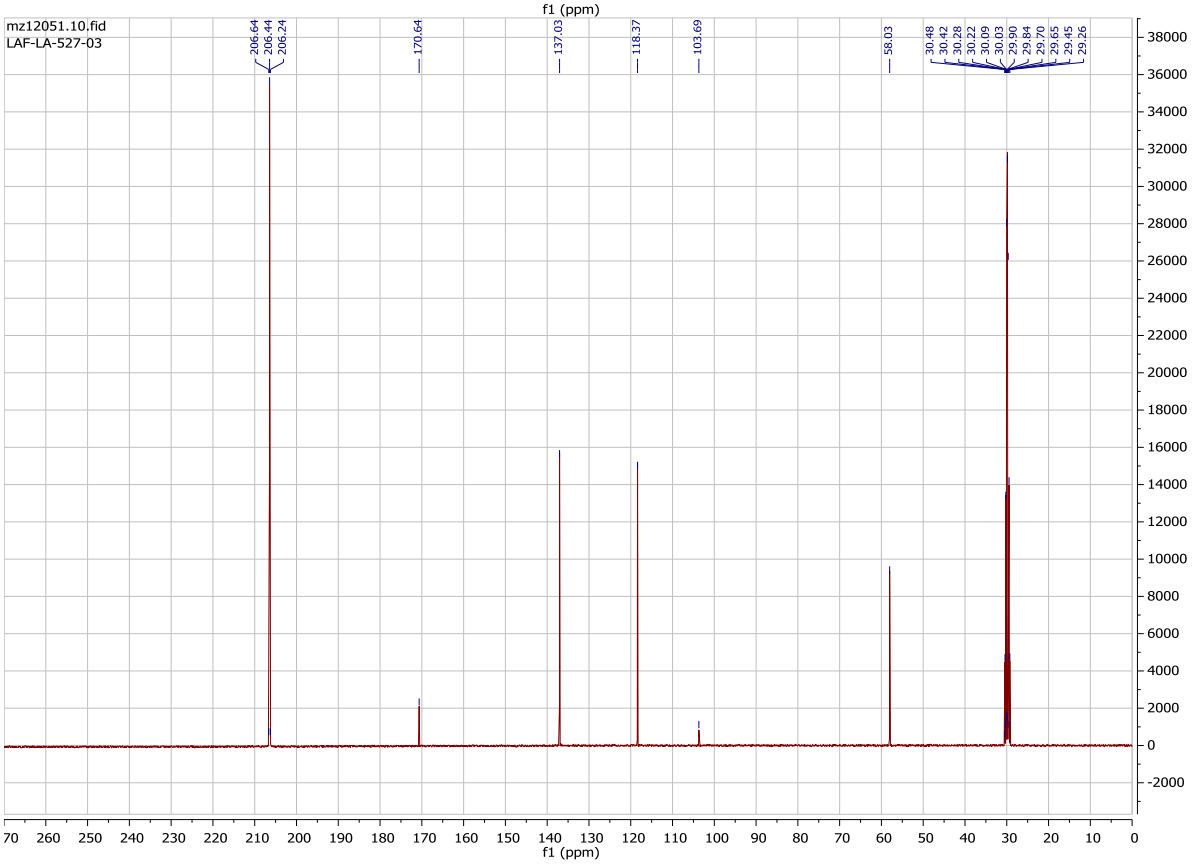
N_2BF_4
8c
f1 (ppm)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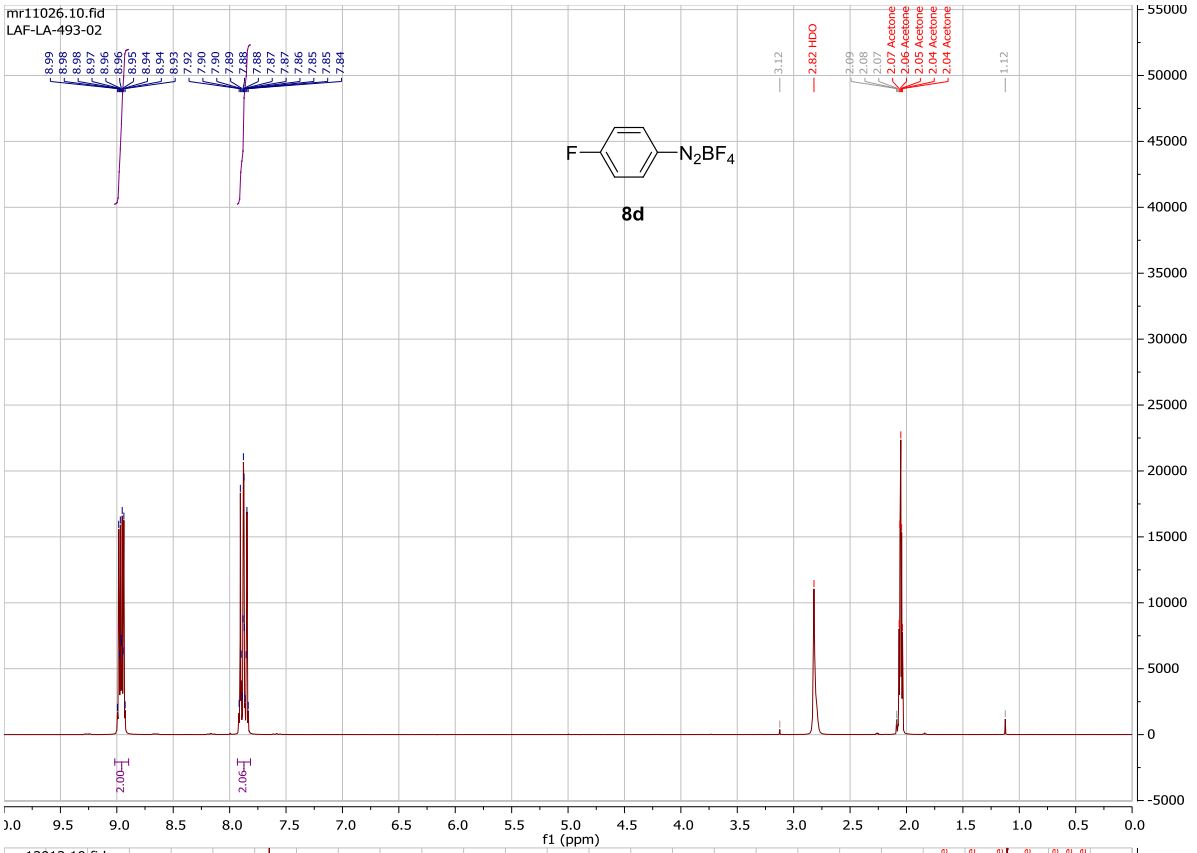
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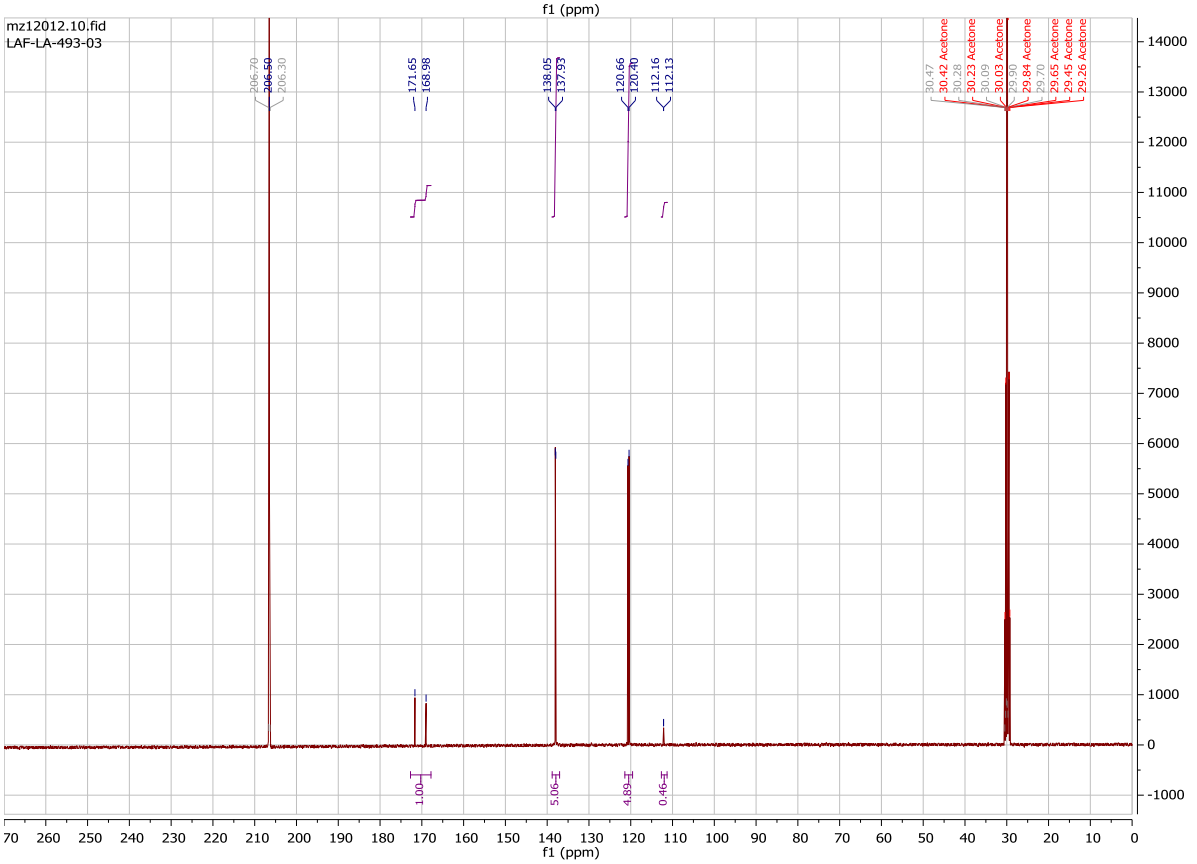
7.92 7.90 7.90 7.89 7.88 7.88 7.87 7.87 7.86 7.85 7.85 7.84
3.12
2.82 HDO
2.09 2.08 2.07
2.07 Acetone 2.06 Acetone 2.05 Acetone 2.04 Acetone 2.04 Acetone
1.12
F
N2BF4
8d
2.00
2.06
f1 (ppm)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171.65 168.98
138.05 137.93
120.66 120.40
112.16 112.13
30.47 30.42 Acetone 30.28 30.23 Acetone 30.09 30.03 Acetone 29.90 29.84 Acetone 29.70 29.65 Acetone 29.45 Acetone 29.26 Acetone
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5.06
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0.46
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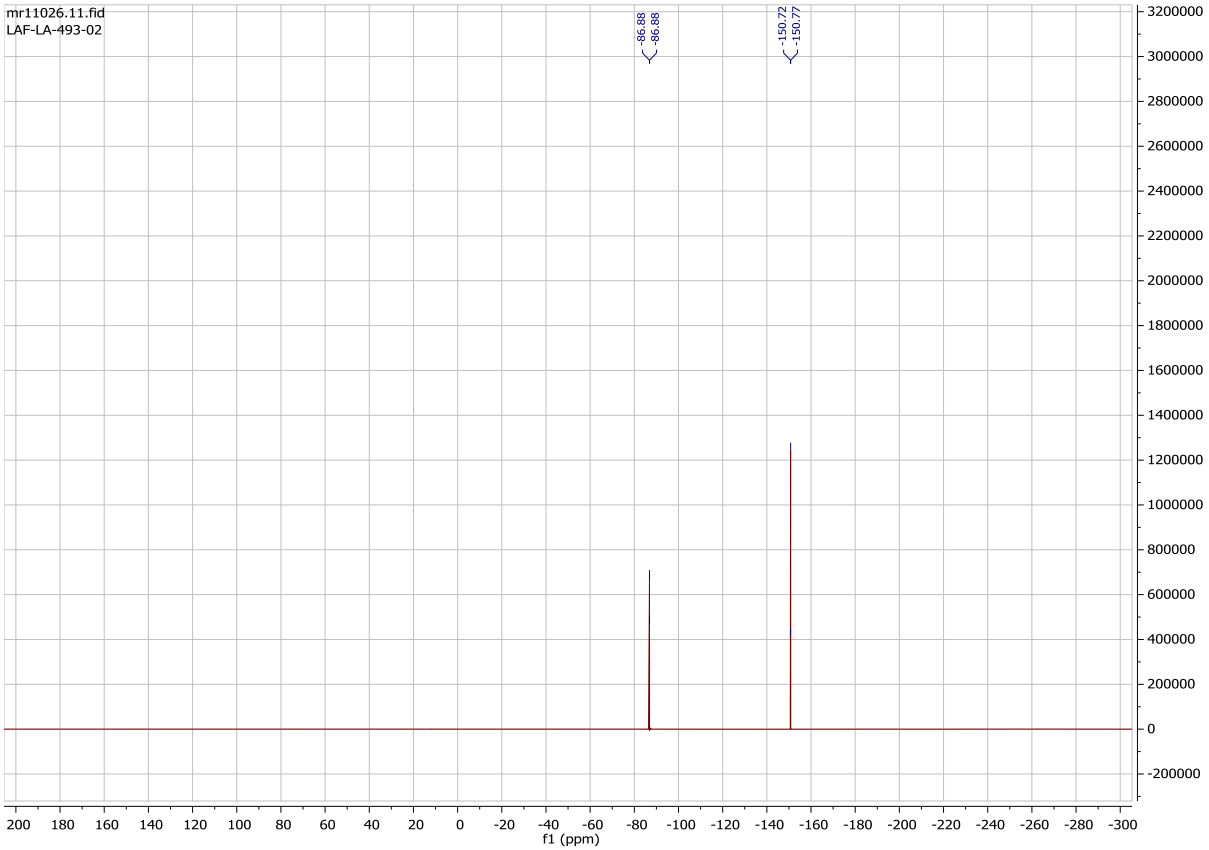
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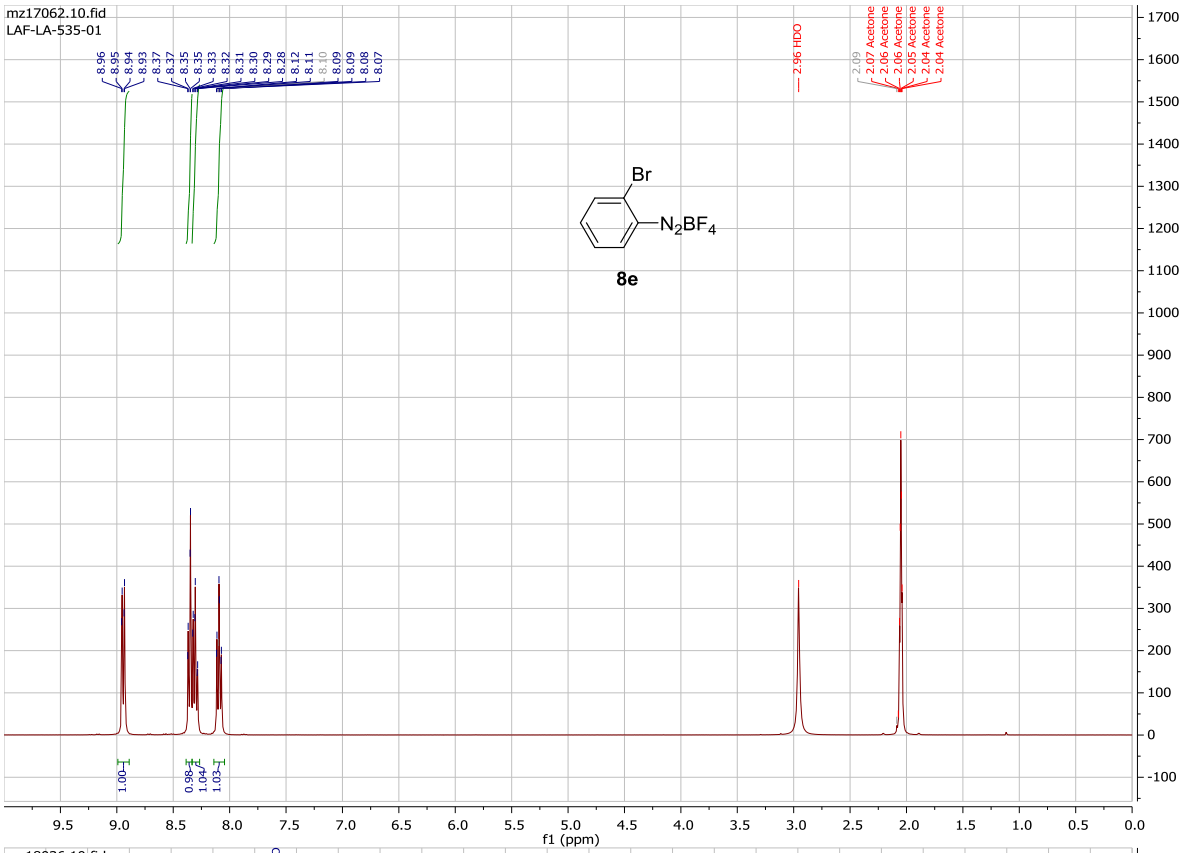
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)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8.31
8.30
8.29
8.28
8.12
8.11
8.10
8.09
8.09
8.08
8.07
2.96 HDO
2.09
2.07 Acetone
2.06 Acetone
2.06 Acetone
2.05 Acetone
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2.04 Acetone
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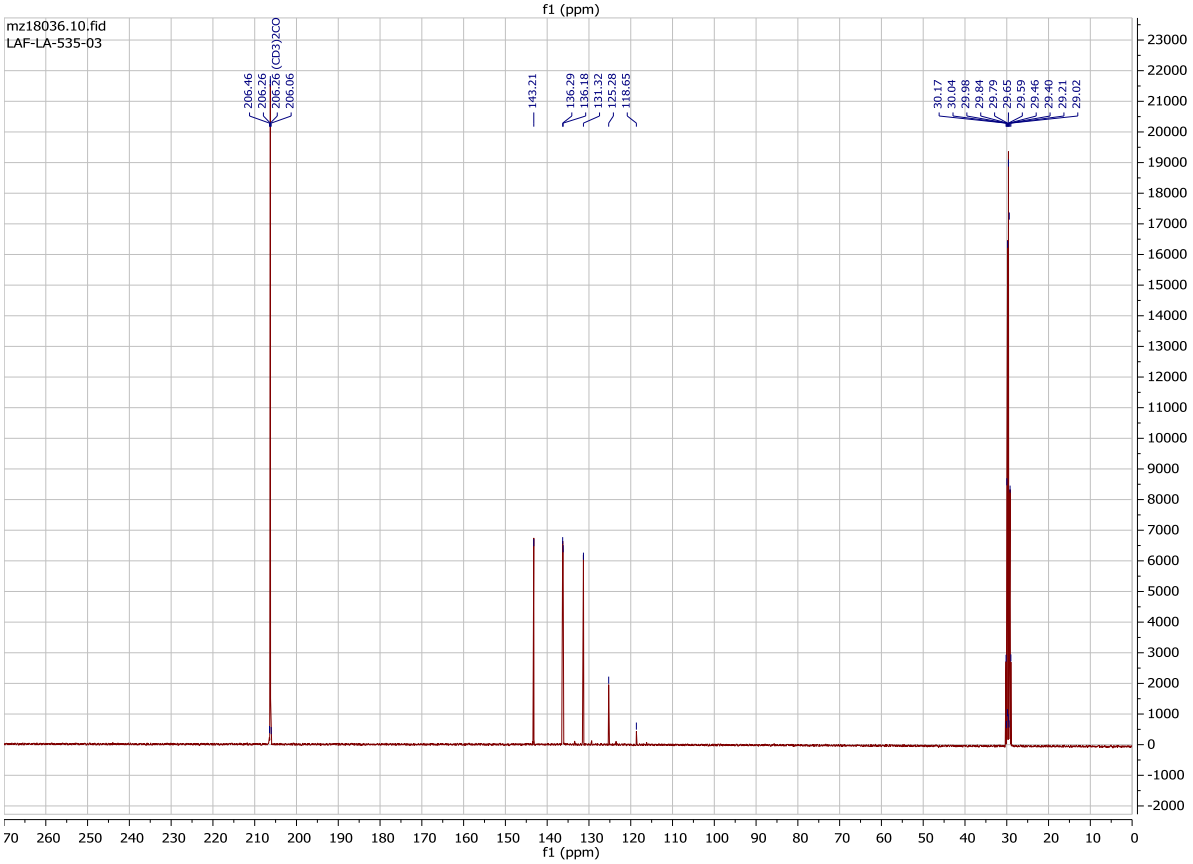
N2BF4
8e
1.00
0.98
1.04
1.03
f1 (ppm)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206.26
206.26 (CD3)2CO
206.06
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136.29
136.18
131.32
125.28
118.65
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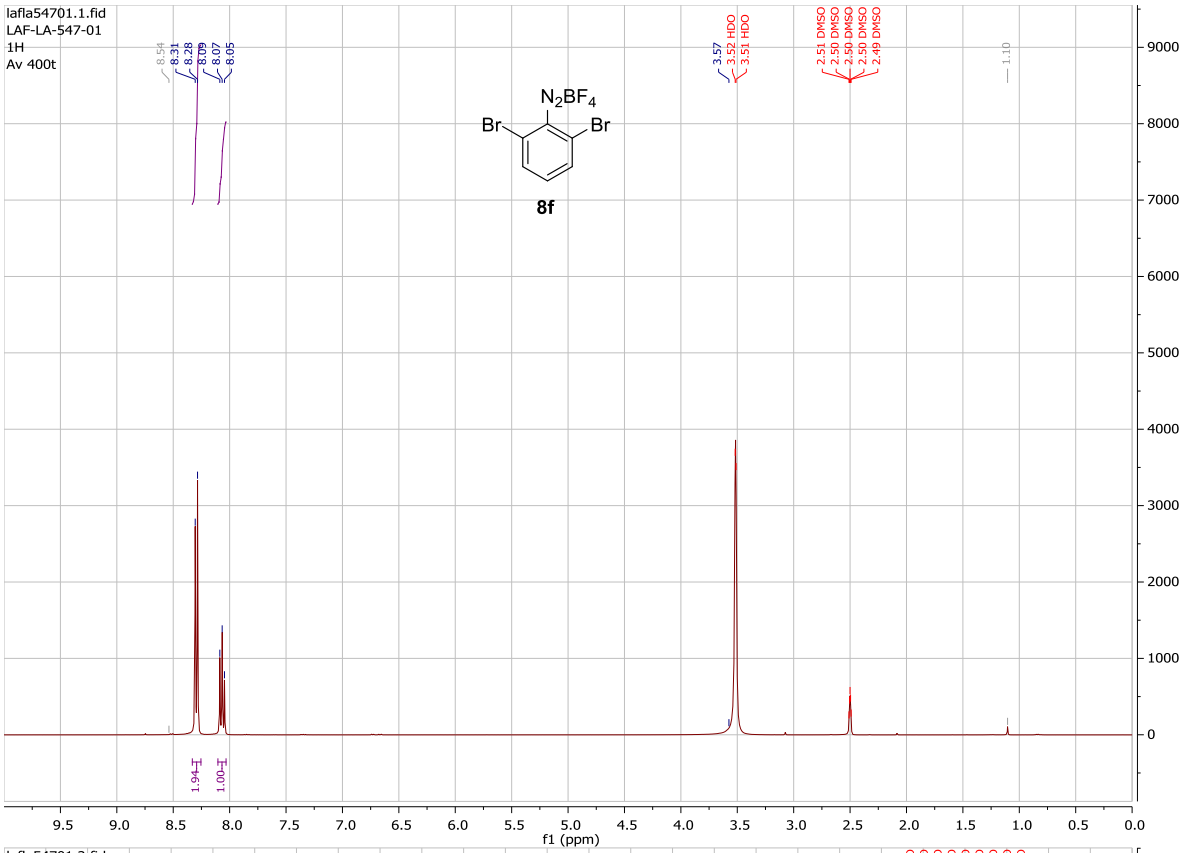
29.59
29.46
29.40
29.21
29.02
f1 (ppm)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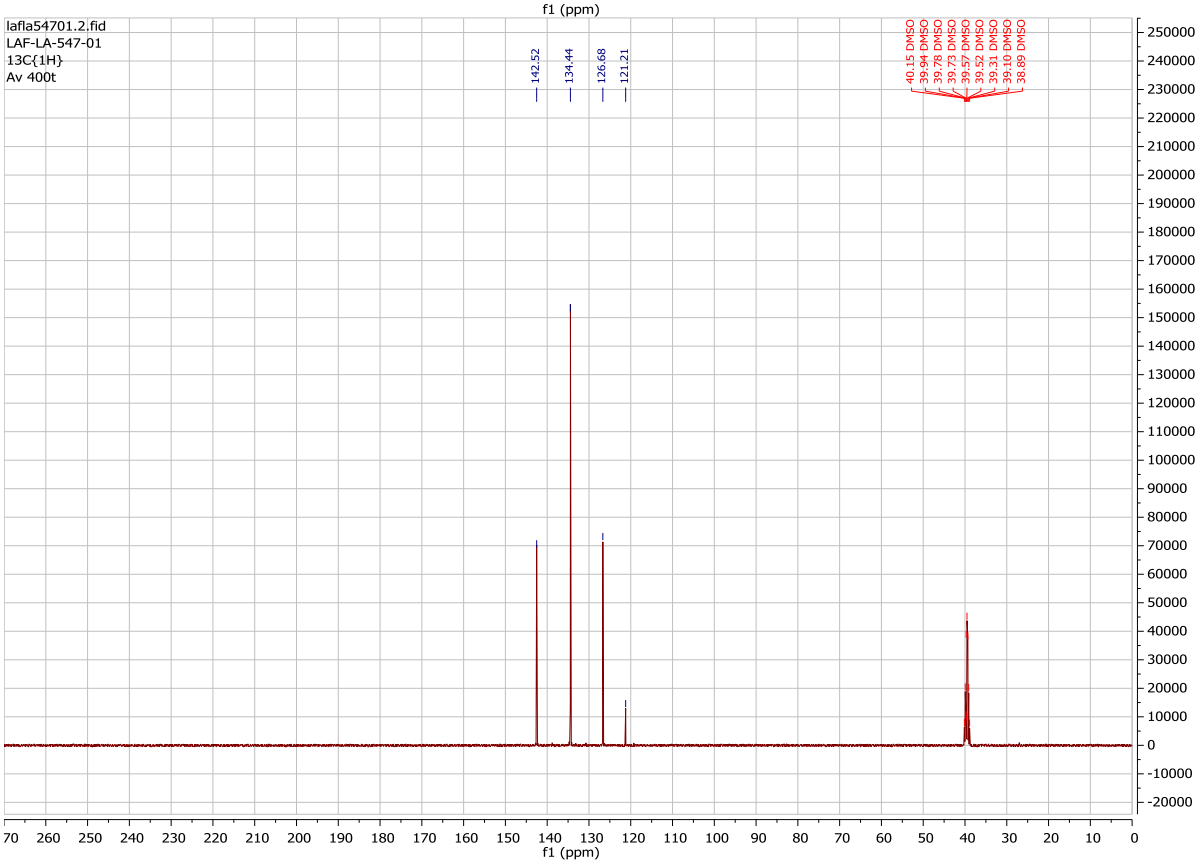
1H
Av 400t
8.54
8.31
8.28
8.09
8.07
8.05
3.57
3.52 HDO
3.51 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
1.10
1.94
1.00
f1 (ppm)

N2BF4
Br
Br

8f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121.21
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39.31 DMSO
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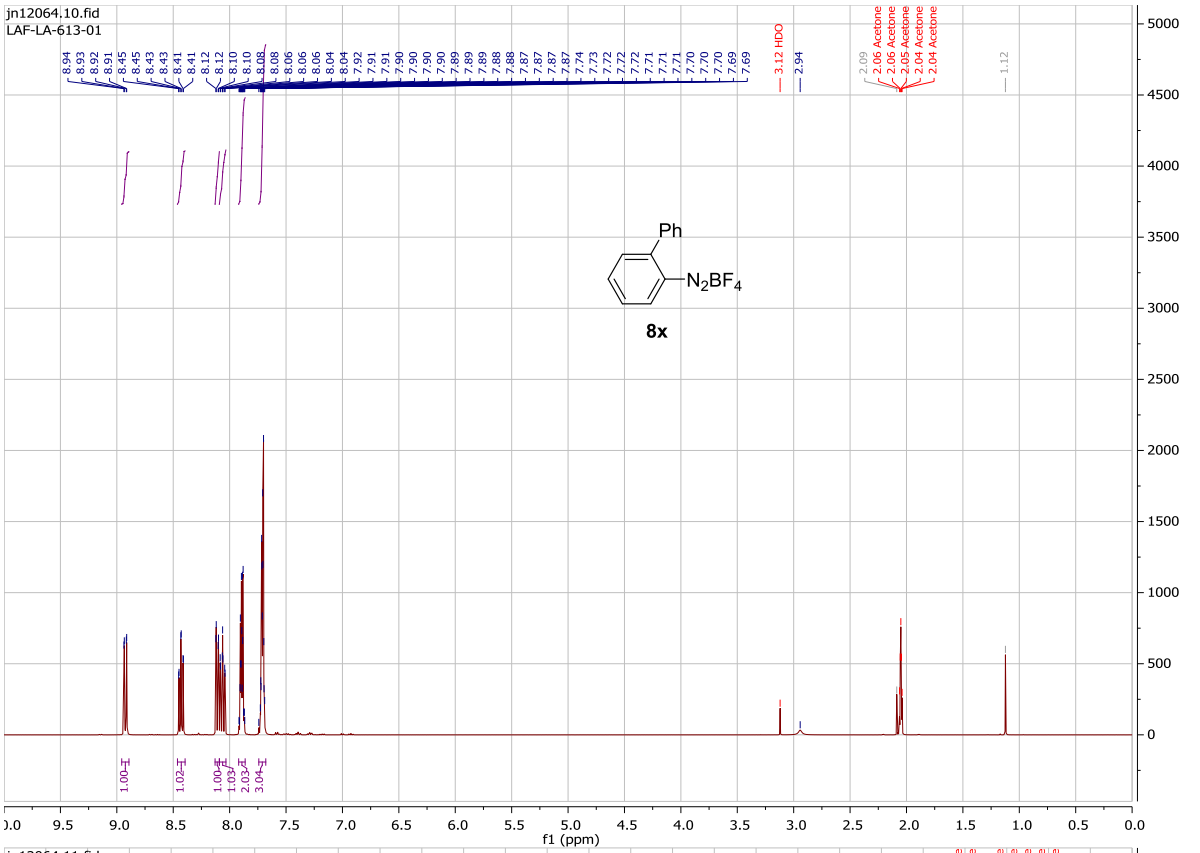
38.89 DMSO
f1 (ppm)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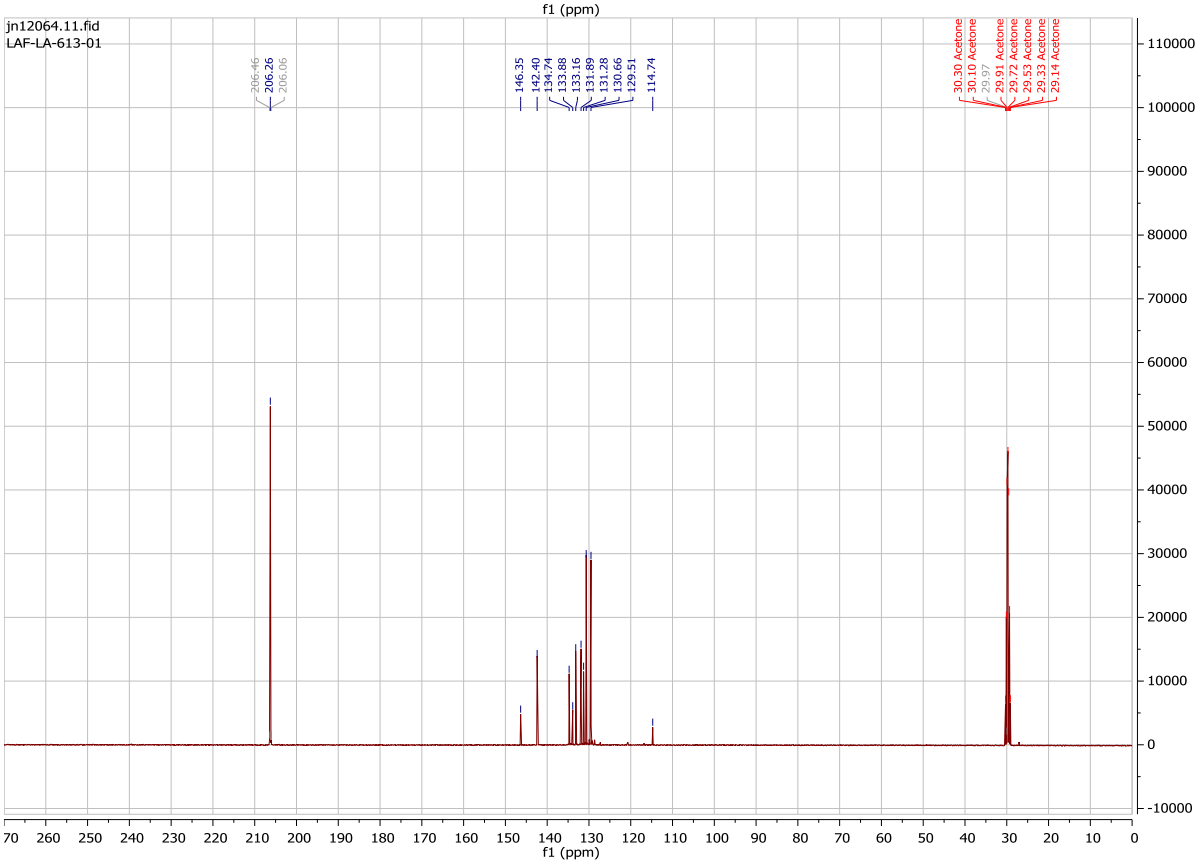
8x
f1 (ppm)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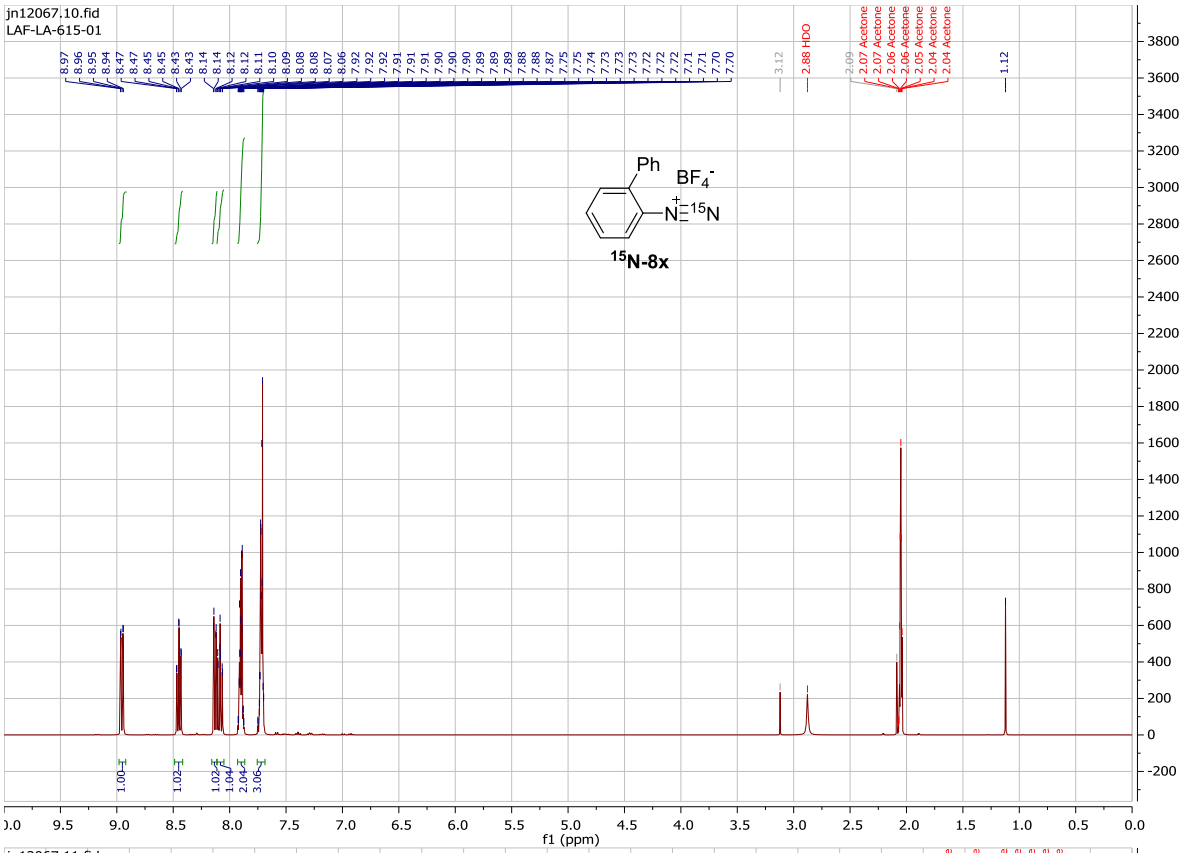
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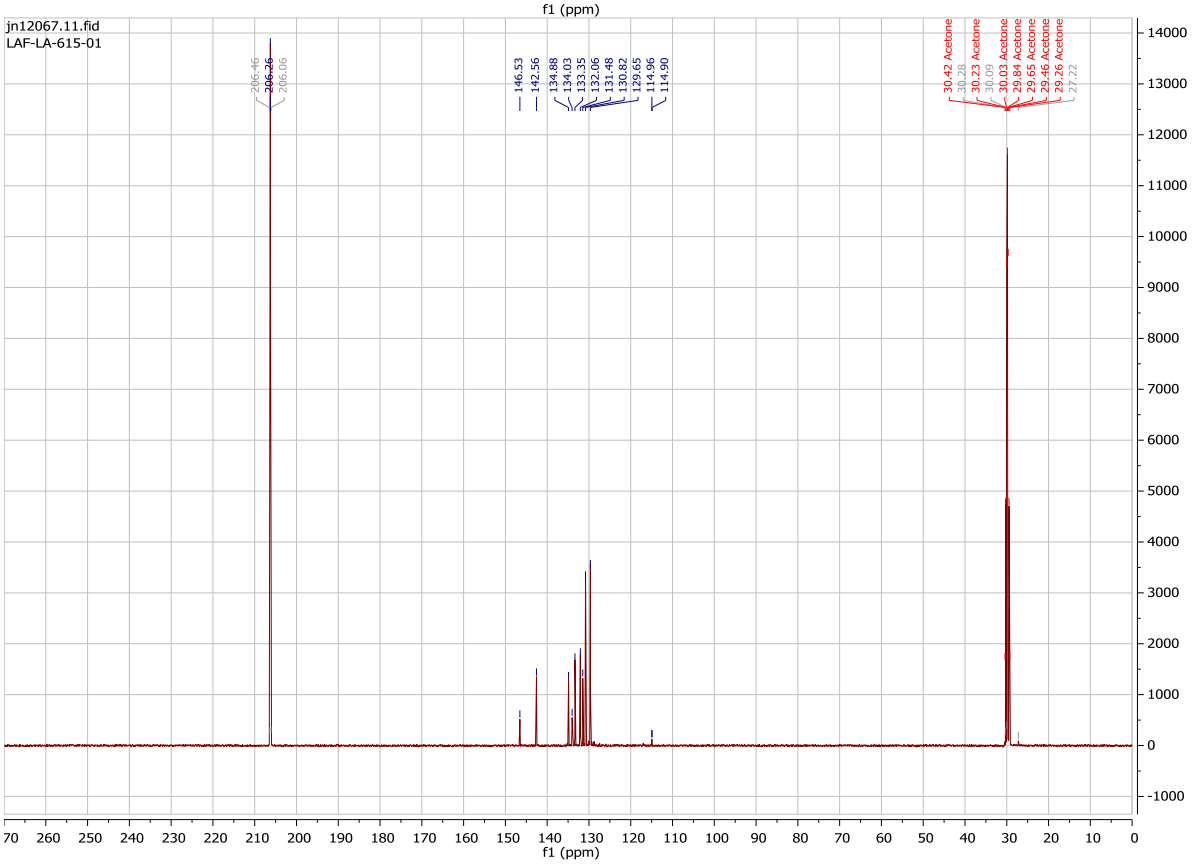
Ph
BF4-
N+
15N
15N-8x
f1 (ppm)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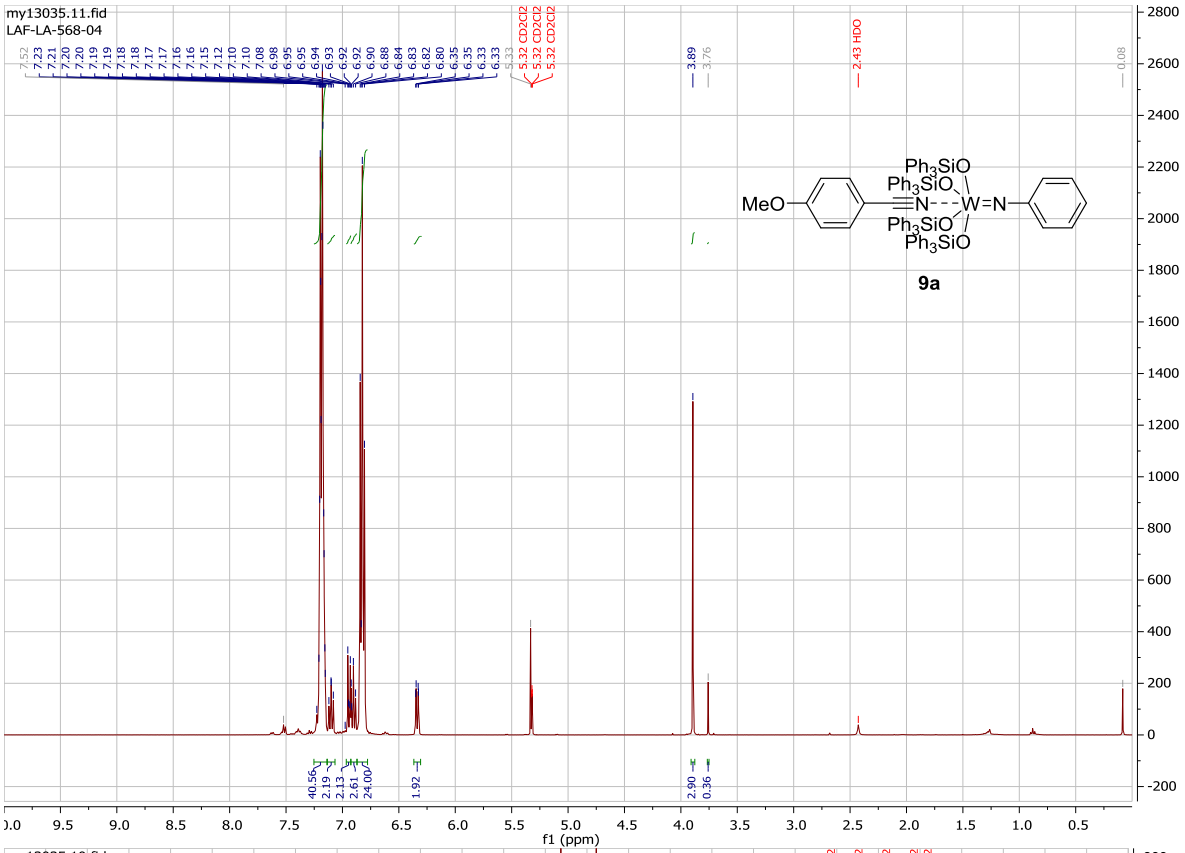
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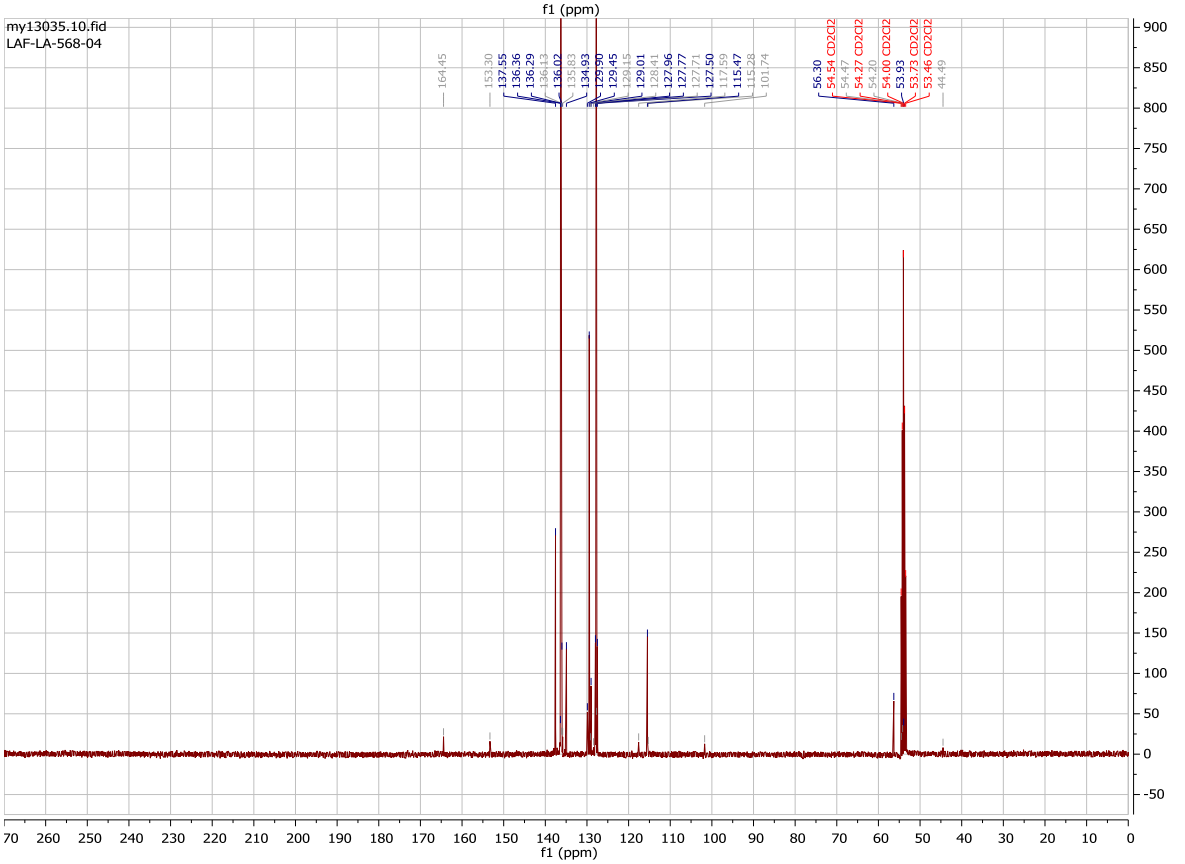
9a
f1 (ppm)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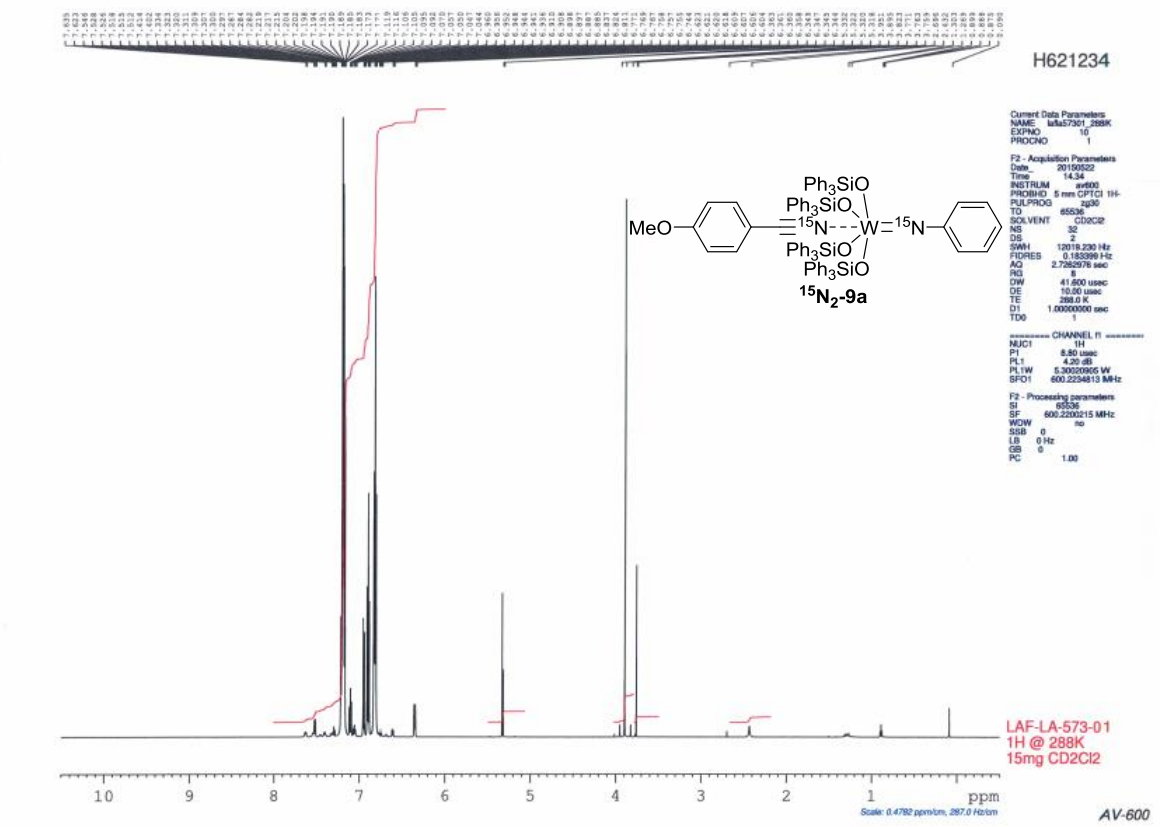
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Ph3SiO
15N
W
15N
Ph3SiO
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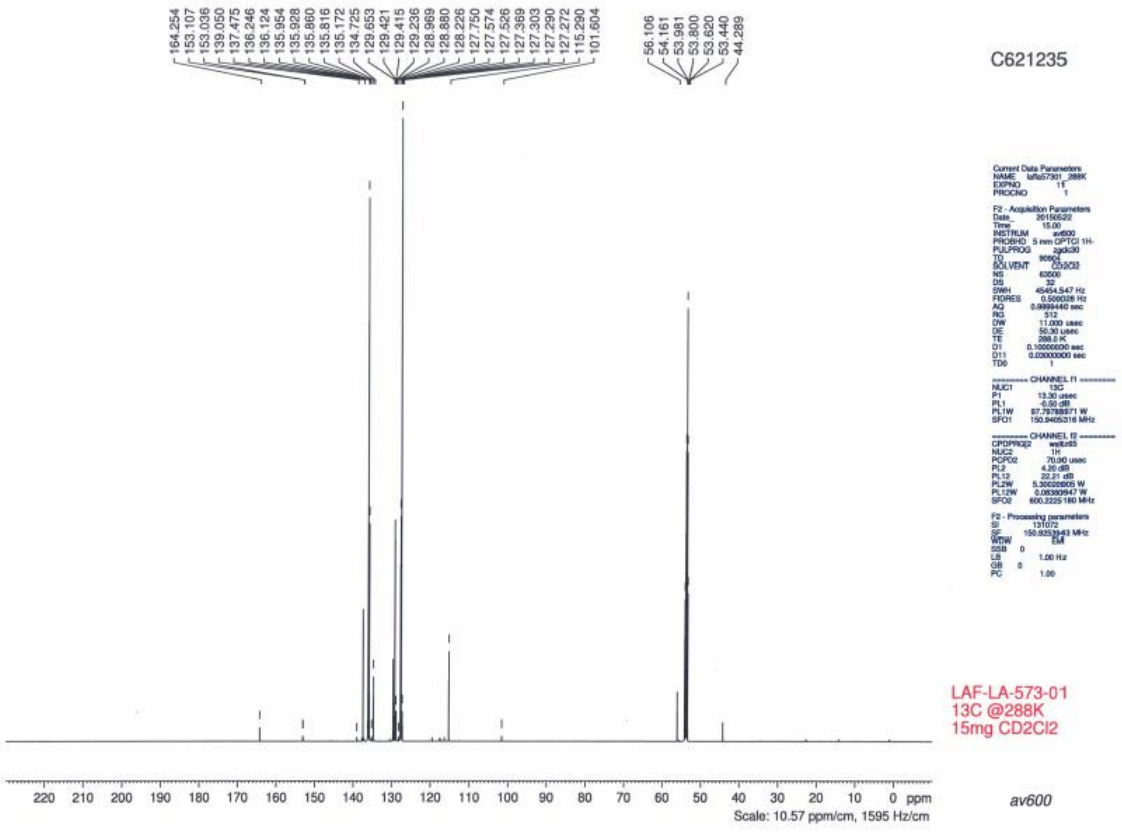
15N2-9a
LAF-LA-573-01
1H @ 288K
15mg CD2Cl2
AV-600


C621235
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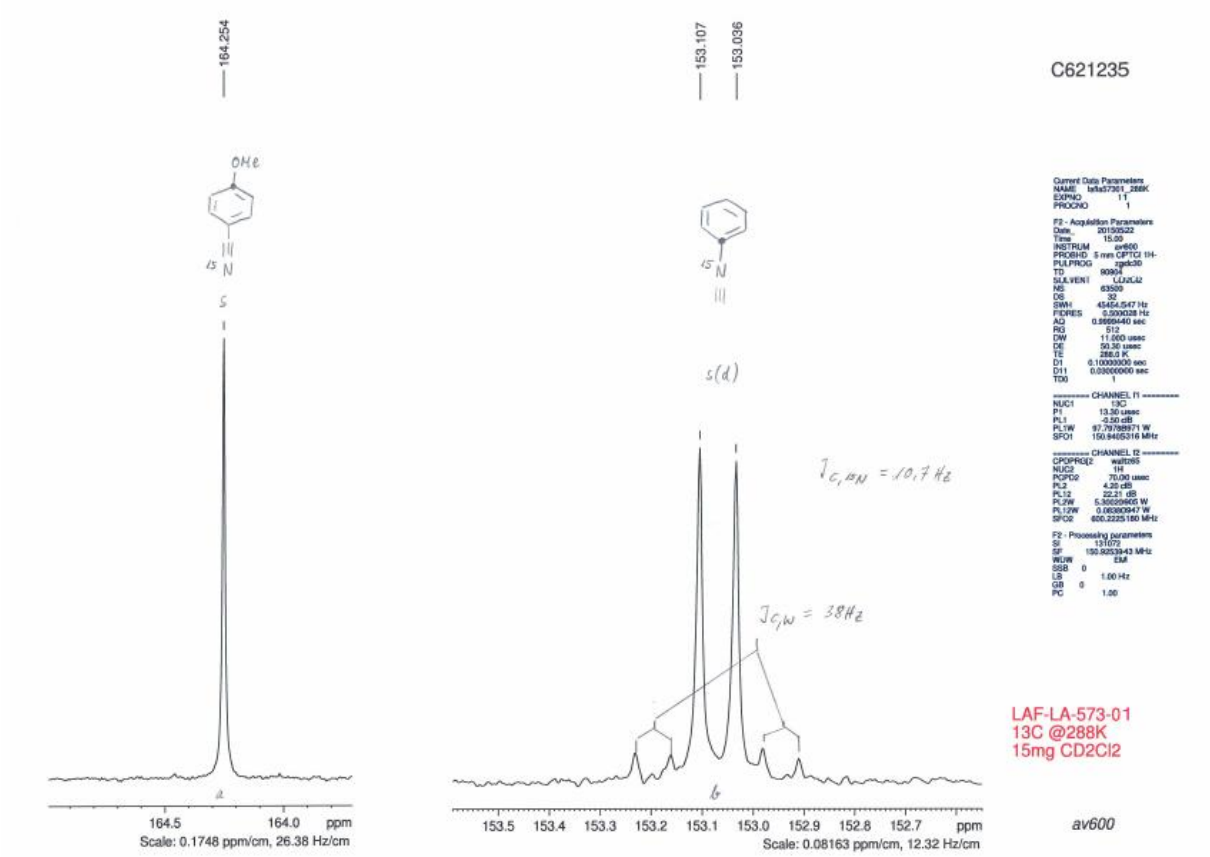
13C @288K
15mg CD2Cl2
av600
Scale: 10.57 ppm/cm, 1595 Hz/cm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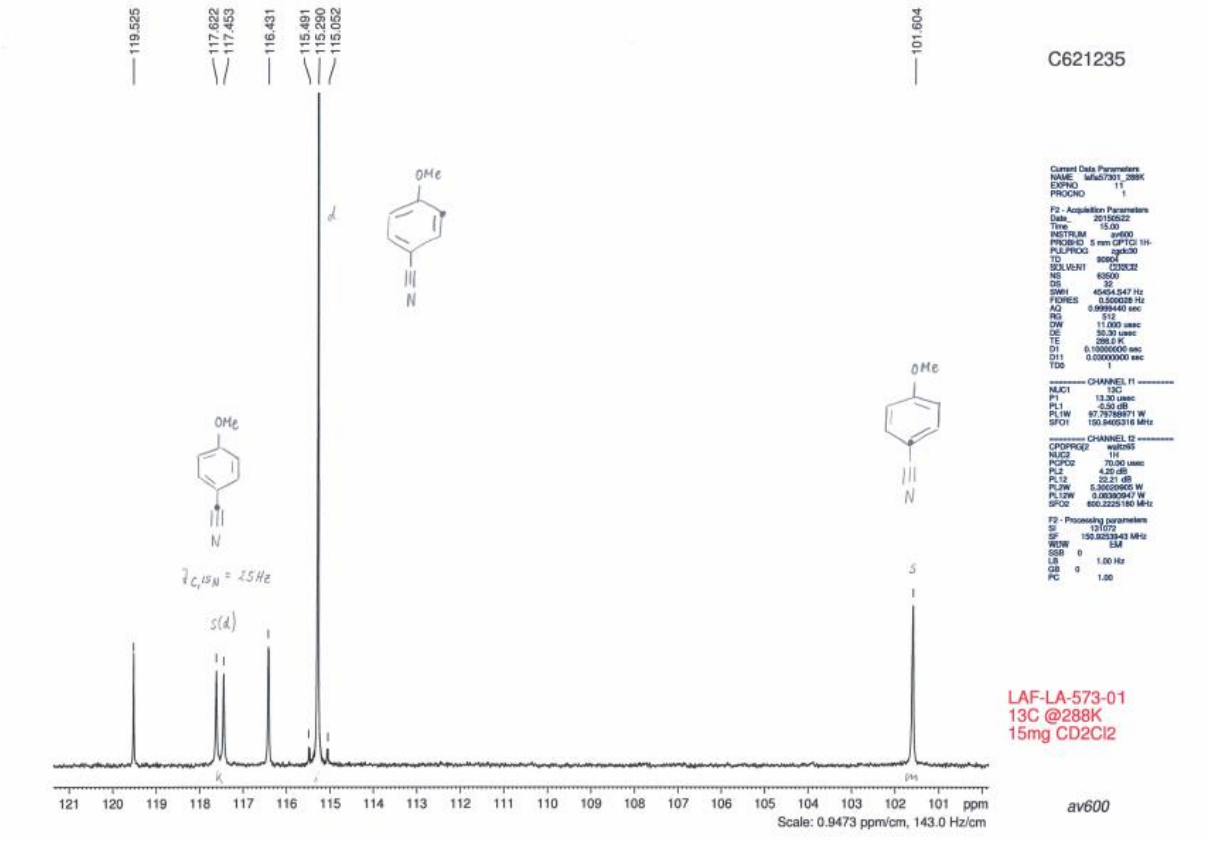
153.107
153.036
C621235
OMe
15N
s
s(d)
$J_{C,15N}$ = 10.7 Hz
$J_{C,W}$ = 3.8Hz
a
b
164.5
164.0
ppm
Scale: 0.1748 ppm/cm, 26.38 Hz/cm
153.5 153.4 153.3 153.2 153.1 153.0 152.9 152.8 152.7 ppm
Scale: 0.08163 ppm/cm, 12.32 Hz/cm
LAF-LA-573-01
13C @288K
15mg CD2Cl2
av600


119.525
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117.453
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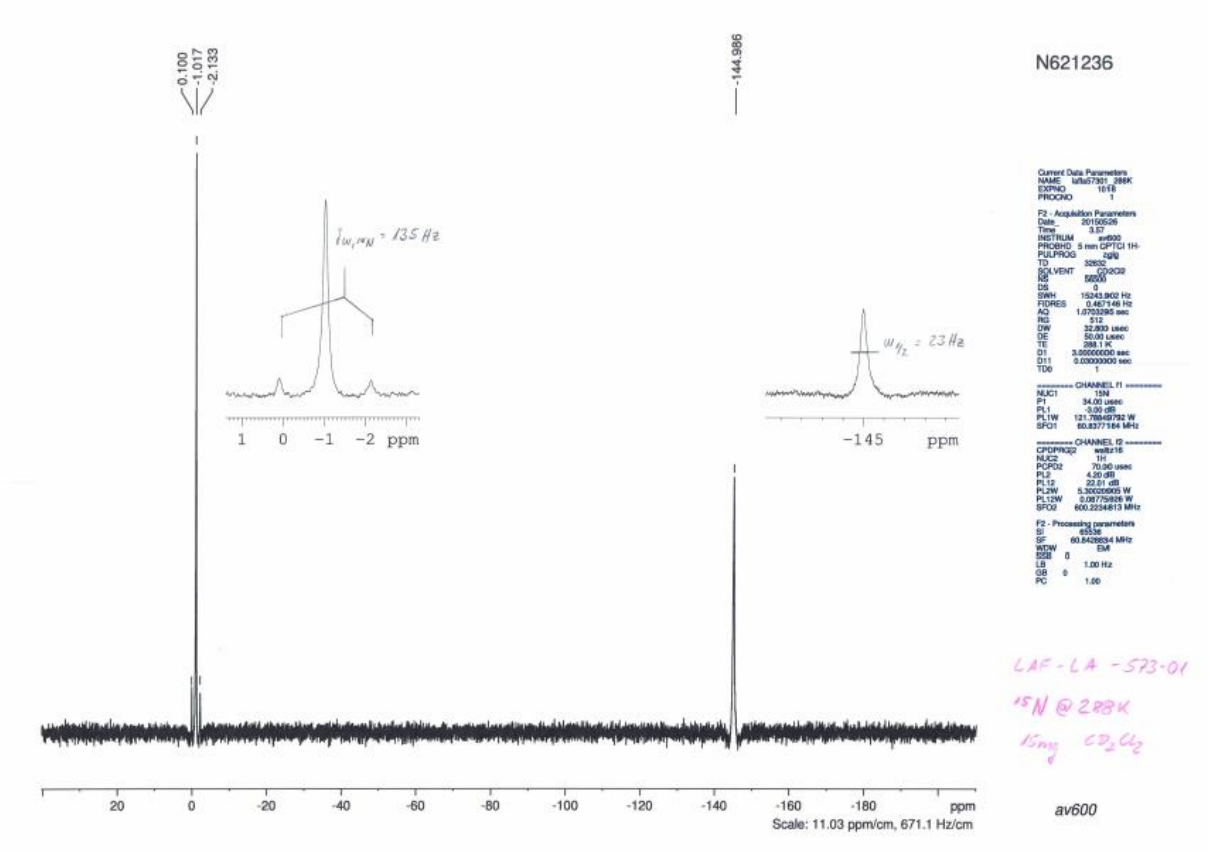
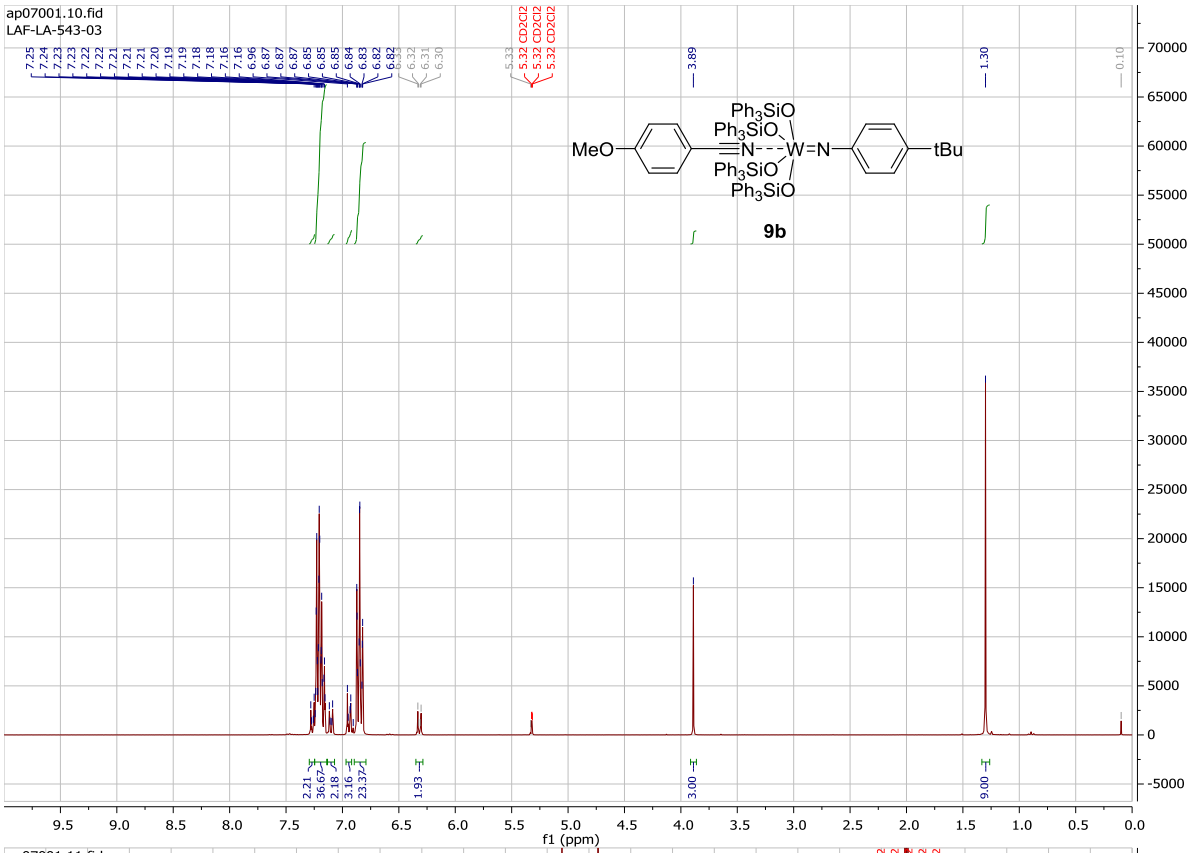
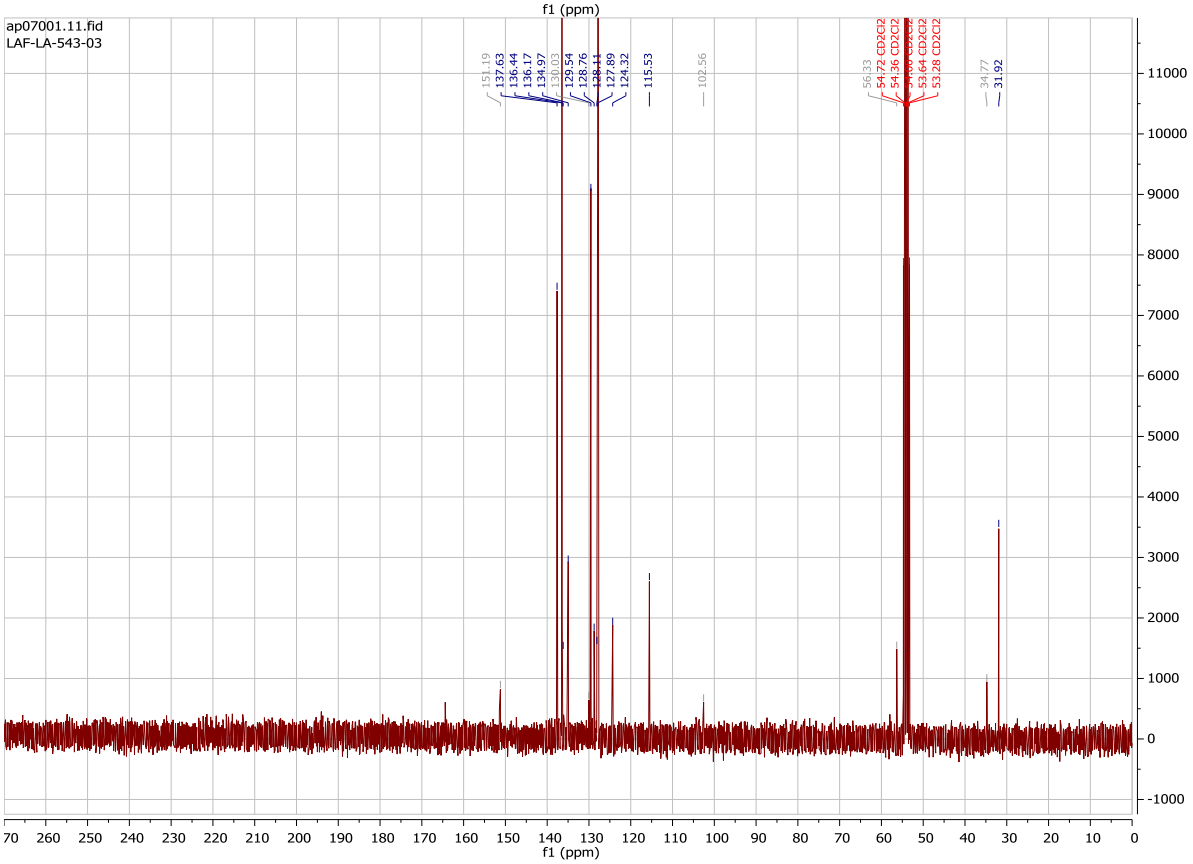
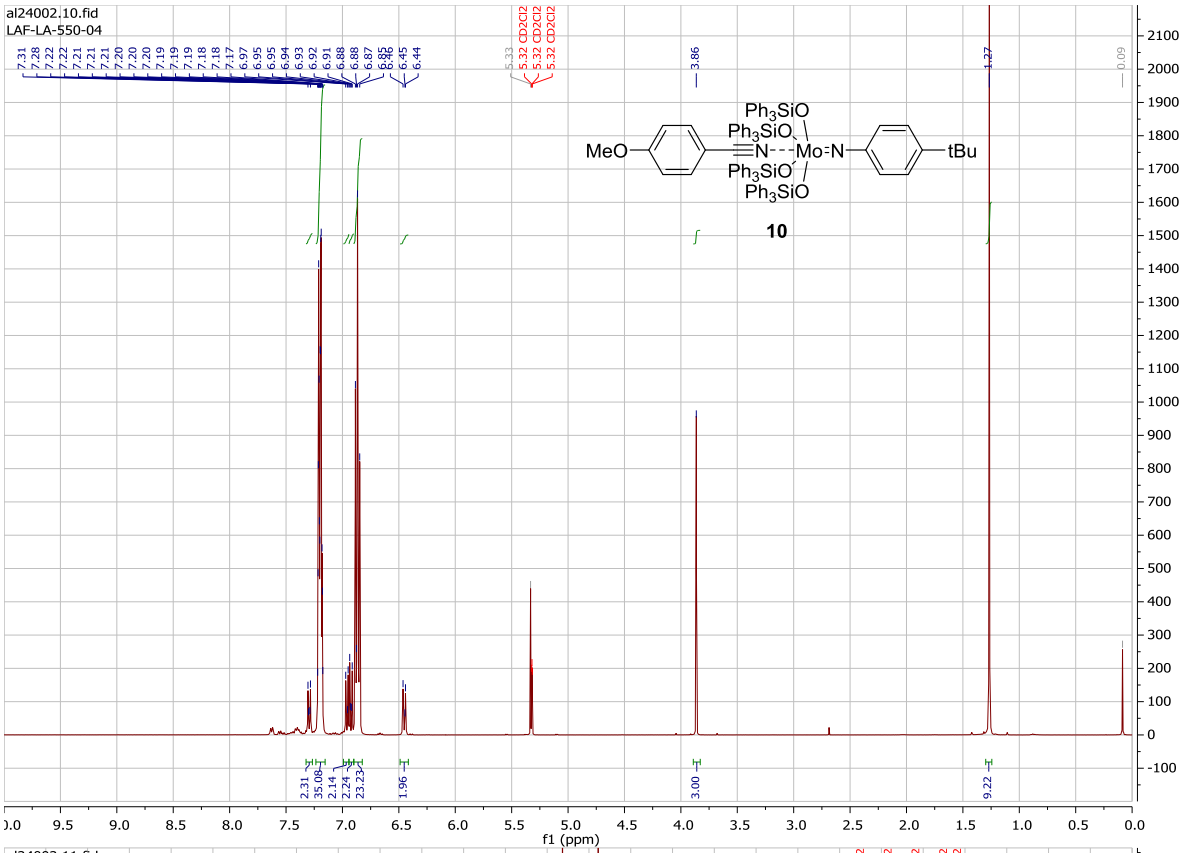
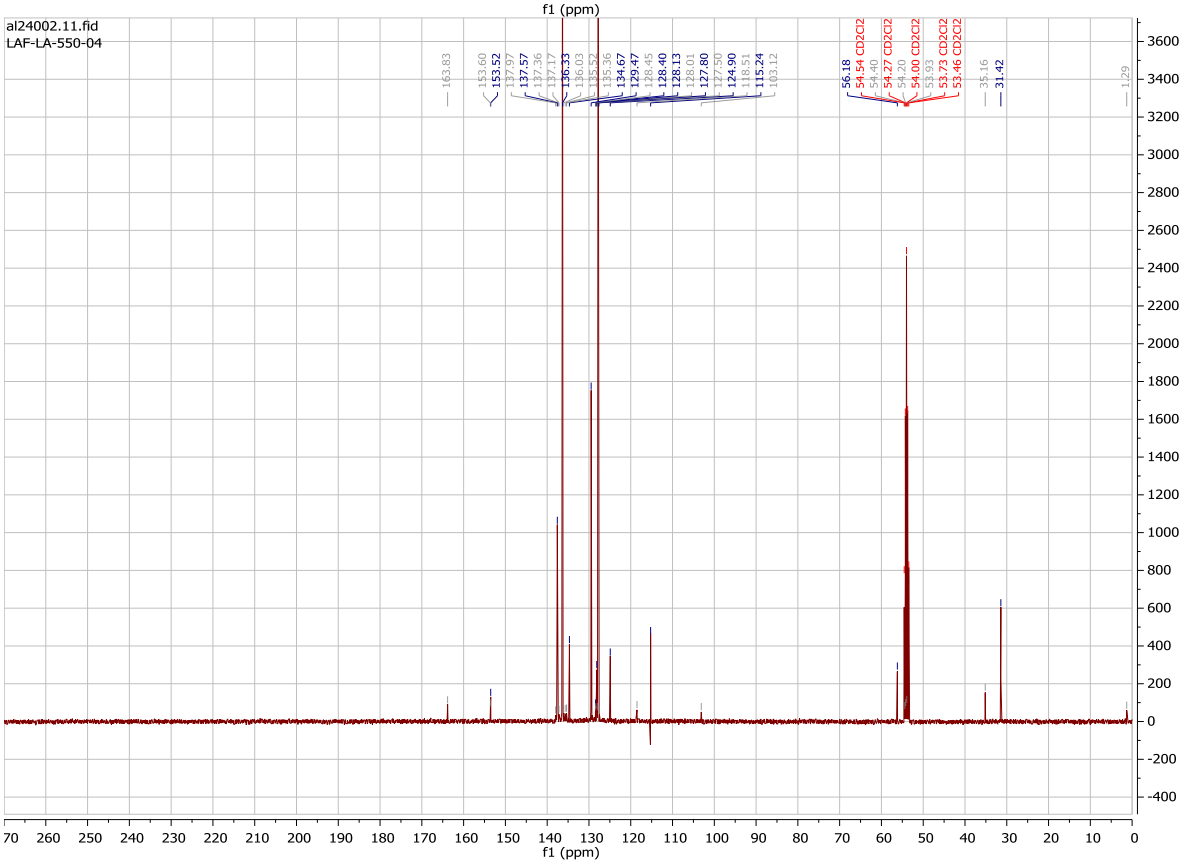
115.290
115.052
101.604
C621235
OMe
N
d
s
$J_{C,15N}$ = 2.5Hz
s(d)
121 120 119 118 117 116 115 114 113 112 111 110 109 108 107 106 105 104 103 102 101 ppm
Scale: 0.9473 ppm/cm, 143.0 Hz/cm
LAF-LA-573-01
13C @288K
15mg CD2Cl2
av600

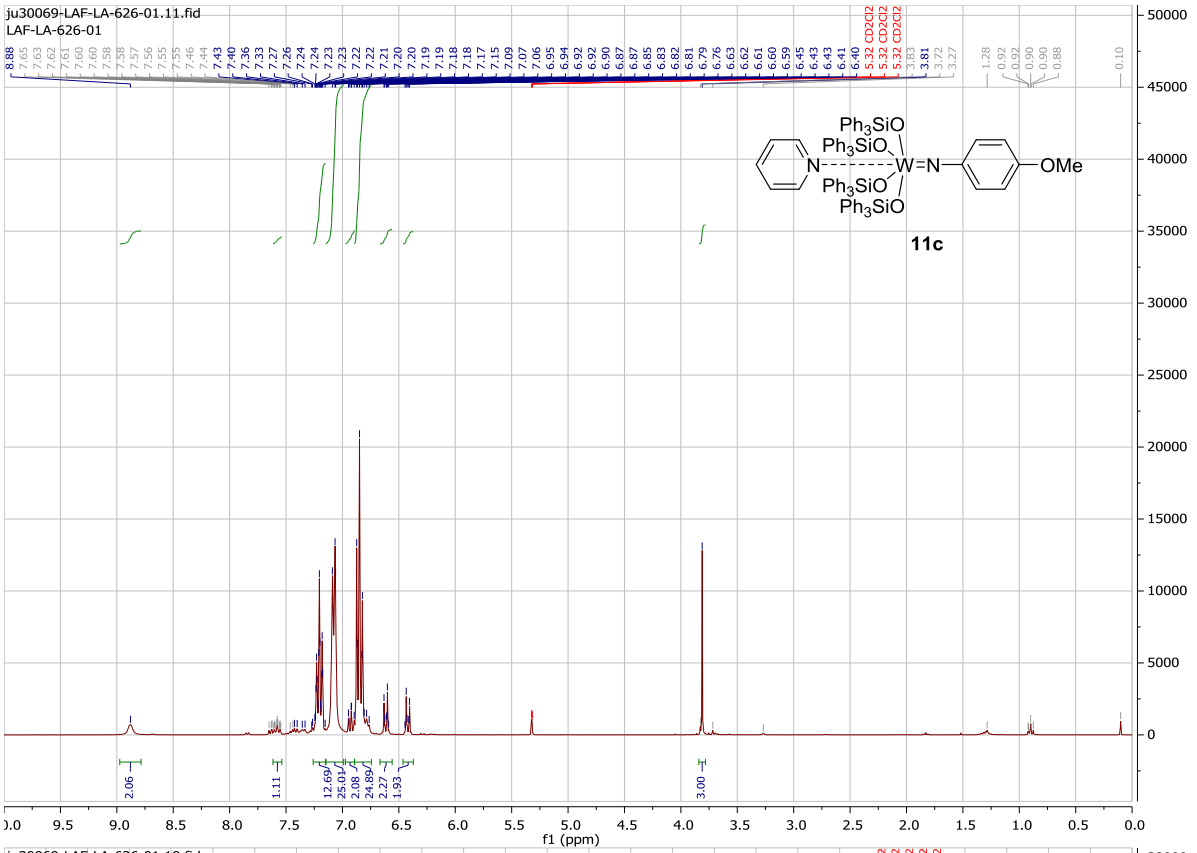

0.100
-1.017
-2.133
-144.986
N621236
$J_{W_1/2\,^{15}N}$ = 135 Hz
W_{H_z} = 23 Hz
1 0 -1 -2 ppm
-145 ppm
Current Data Parameters
NAME lafla57301_288K
EXPNO 1018
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150526
Time 3.57
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zgig
TD 32632
SOLVENT CD2Cl2
NS 58800
DS 0
SWH 15243.902 Hz
FIDRES 0.467148 Hz
AQ 1.0703295 sec
RG 512
DW 32.800 usec
DE 50.00 usec
TE 288.1 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 15N
P1 34.00 usec
PL1 -3.00 dB
PL1W 121.78949792 W
SFO1 60.8377184 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 4.20 dB
PL12 22.01 dB
PL2W 5.30020605 W
PL12W 0.08775826 W
SFO2 600.2234813 MHz
F2 - Processing parameters
SI 65536
SF 60.8428834 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
LAF-LA-573-01
15N @ 288K
15mg CD2Cl2
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 ppm
Scale: 11.03 ppm/cm, 671.1 Hz/cm
av600

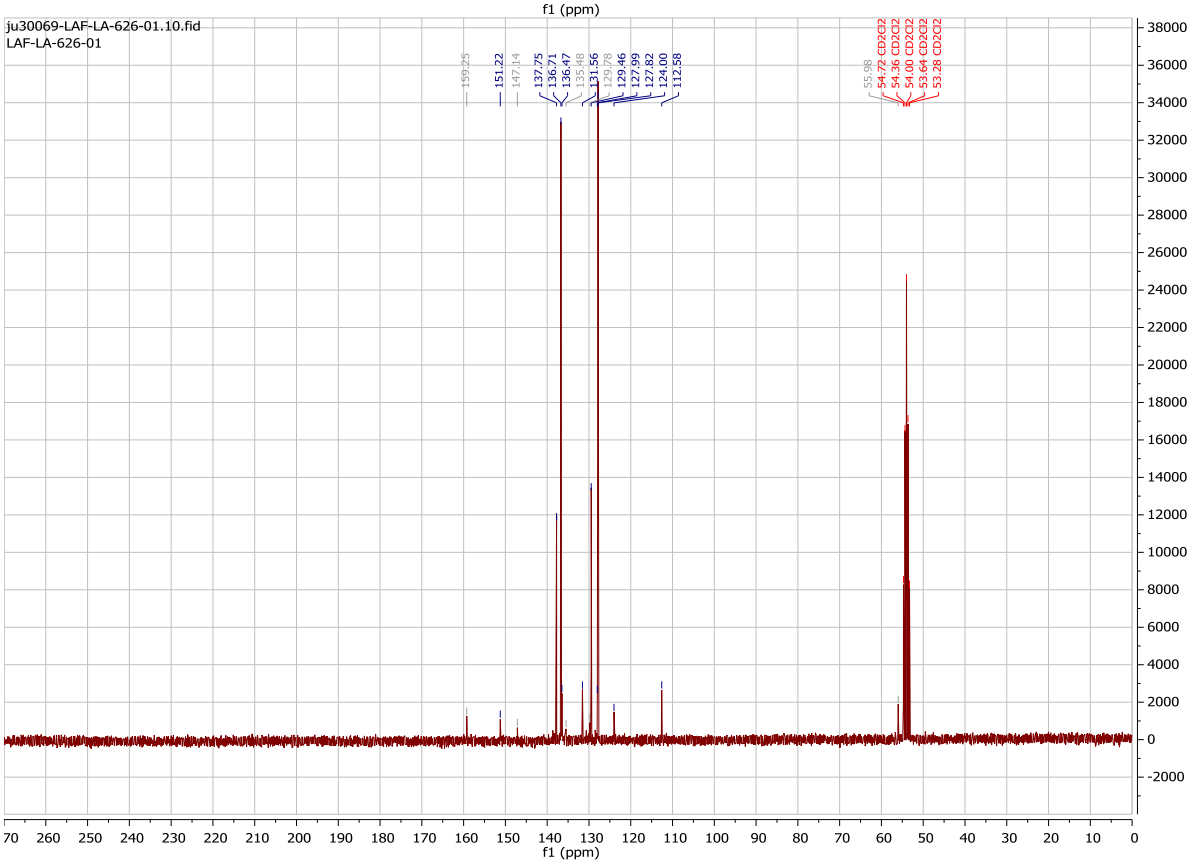

ap07001.10.fid
LAF-LA-543-03
MeO
tBu
W
N
Ph3SiO
Ph3SiO
Ph3SiO
Ph3SiO
9b
f1 (ppm)

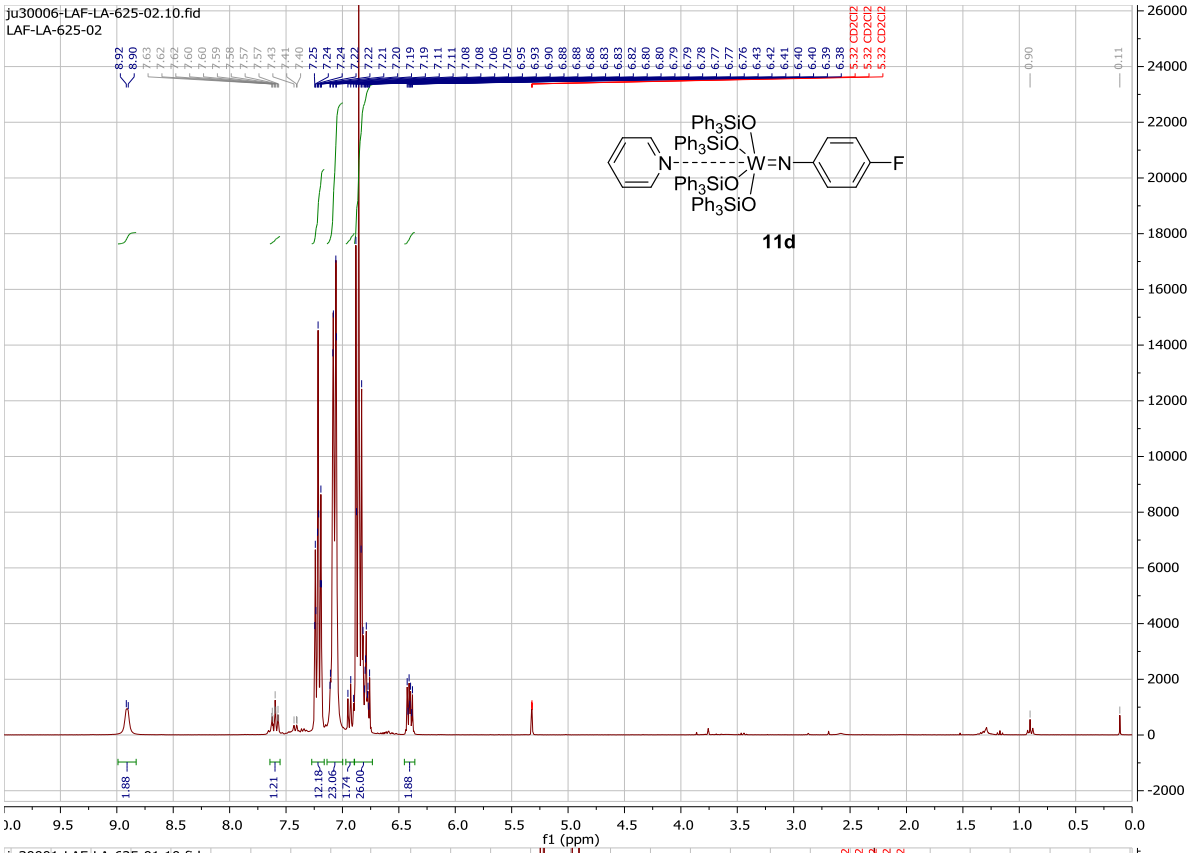

ap07001.11.fid
LAF-LA-543-03
f1 (ppm)

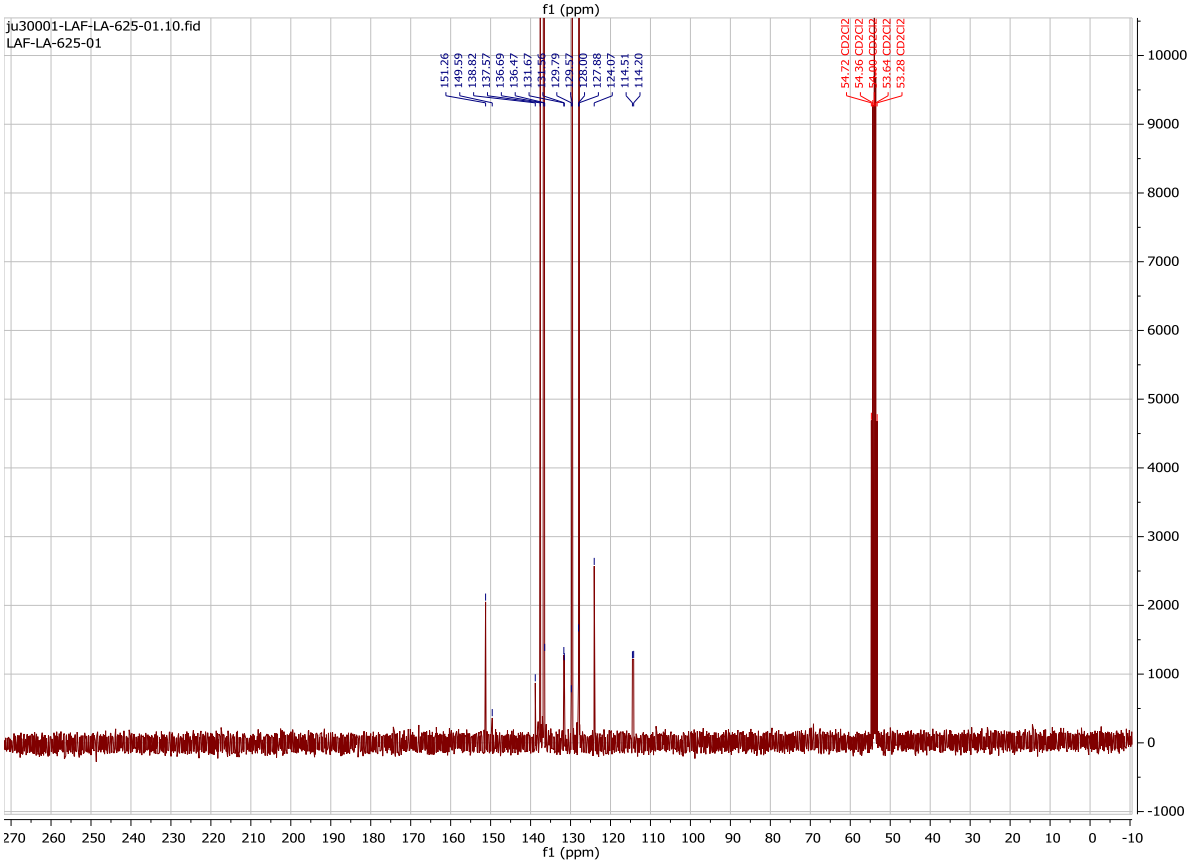

al24002.10.fid
LAF-LA-550-04
MeO
tBu
Mo
N
Ph3SiO
Ph3SiO
Ph3SiO
Ph3SiO
10
f1 (ppm)

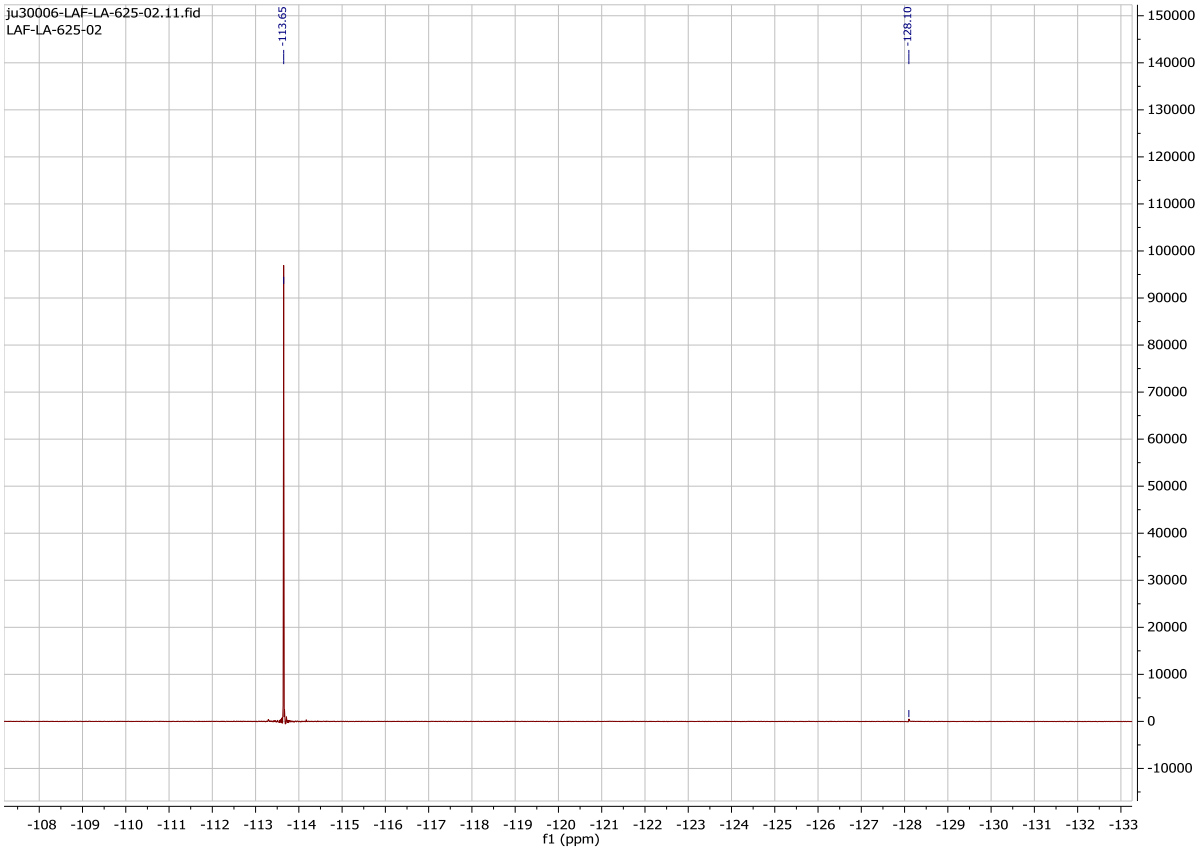

al24002.11.fid
LAF-LA-550-04
f1 (ppm)


ju30069-LAF-LA-626-01.11.fid
LAF-LA-626-01
Ph3SiO
Ph3SiO
N
W=N
OMe
Ph3SiO
Ph3SiO
11c
f1 (ppm)


ju30069-LAF-LA-626-01.10.fid
LAF-LA-626-01
f1 (ppm)


ju30006-LAF-LA-625-02.10.fid
LAF-LA-625-02
Ph3SiO
Ph3SiO
N
W=N
F
Ph3SiO
Ph3SiO
11d
f1 (ppm)


ju30001-LAF-LA-625-01.10.fid
LAF-LA-625-01
f1 (ppm)



Low temperature ^{13}C NMR of showing a carbene formed on reaction of ^{15}**N-8g** with **5**