Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2023

ELECTRONIC SUPPORTING INFORMATION

Electronic Supporting Information for:

C–H Activation in Bimetallic Rhodium Complexes to Afford N-Heterocyclic Carbene Pincer Complexes.

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Anthony F. Hill*[a] and Lachlan J. Watson[a]

Experimental

General Considerations

Unless otherwise stated, experimental work was carried out at room temperature under a dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques with dried and degassed solvents.

NMR spectra were obtained on a Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C at 100.6 MHz, ^{19}F at 376.5 MHz, ^{31}P at 162 MHz), a Bruker Avance 600 (^{1}H at 600.0 MHz, ^{13}C at 150.9 MHz), a Bruker Avance 700 (^{1}H at 700.0 MHz, ^{13}C at 176.1 MHz, ^{31}P at 283 MHz) or a Bruker Avance 800 (1H at 800.1 MHz, ^{13}C at 201.2 MHz) spectrometers at the temperatures indicated. Chemical shifts (δ) are reported in ppm with coupling constants given in Hz and are referenced to the solvent peak, or external references (85% H_3PO4 in H_2O for ^{31}P). The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), m (multiplet), br (broad) and combinations thereof for more highly coupled systems. In some cases, distinct peaks were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra, but to the level of accuracy that is reportable (i.e. 2 decimal places for ^{1}H NMR, 1 decimal place for ^{13}C NMR) they are reported as having the same chemical shift. The abbreviation 'napth' is used to refer to the naphthalene backbone of the dihydroperimidine based ligand, while 'i' (*ipso*), 'o' (*ortho*), 'm' (*meta*), and 'p' (*para*) refer to positions on the phenyl rings of PPh_2 groups. Extreme insolubility in many samples resulted in low quality NMR acquisitions, and as a result some resonances may not be unequivocally assigned.

Infrared spectra were obtained using a PerkinElmer Spectrum One FT-IR spectrometer. The strengths of IR absorptions are denoted by the abbreviations vs (very strong), s (strong), m (medium), w (weak), sh (shoulder) and br (broad).

Elemental microanalytical data were provided by Macquarie University. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or methanol as the matrix.

Data for X-ray crystallography were collected with an Agilent Xcalibur CCD diffractometer or an Agilent SuperNova CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) and the CrysAlis PRO software.[1] The structures were solved by intrinsic phasing and refined by full-matrix least-squares on F^2 using the SHELXS or SHELXT and SHELXL programs.[2] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[3] Structural data for **2a** were collected at the Australian Synchrotron using the MX2 beamline using silicon double crystal monochromated synchrotron radiation at 100 K. Raw frame data were collected using BluIce[4] and data reduction, interframe scaling, unit cell refinement and absorption corrections were processed using XDS.[5]

The synthesis of the pro-ligands 1,8-bis(R-phosphinomethyl)-2,3-dihydroperimidine (di-R-H_2Pm, R = phenyl, cyclohexyl) and the rhodium complexes [RhCl(RPm)] have been reported previously.[6] The reagents $[RhCl(CO)(PPh_3)_2]$,[7] $[RhCl(CS)(PPh_3)_2]$,[8] $[RhH(CO)(PPh_3)_3]$,[9] $[Rh(CO)(PPh_3)_2]_2$,[10,11] potassium graphite (KC_8),[12] and triphenylcyclopropenium hexafluorophosphate[13,14] were prepared according to literature procedures. The remaining reagents were purchased from commercial sources.

Computational Details

Computational studies were performed by using the *SPARTAN20*® suite of programs.[15] Geometry optimisation (gas phase) for diatomics and metal complexes was performed at the DFT level of theory using the exchange functionals ωB97X-D of Head-Gordon.[16,17] The Los Alamos effective core potential type basis set (LANL2Dζ) of Hay and Wadt [18-20] was used for I, Mo and W while Pople 6-31G* basis sets[21] were used for all other atoms. Frequency calculations were performed for all compounds to

---

[a] *Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, ACT 2601, Australia.*
* Corresponding author. E-mail: a.hill@anu.edu.au

CCDC 2222022-2222025.2222038, 2222051 and 22225520 contain the supplementary crystallographic data for this paper, and are available free of charge from The Cambridge Crystallographic Data Centre.

confirm that each optimized structure was a local minimum and also to identify vibrational modes of interest. Cartesian atomic coordinates are provided below.

Synthetic Procedures

Synthesis of [RhCl(CO)(μ-PhH$_2$Pm)]$_2$ (2a). A solution of [RhCl(CO)(PPh$_3$)$_2$] (644 mg, 0.932 mmol) and PhH$_2$Pm (528 mg, 0.932 mmol) was heated to 50 °C in THF (20 mL) for 1.5 hours resulting in an off-white suspension. The solvent was removed under reduced pressure, and the sample suspended in CH$_2$Cl$_2$ (15 mL) and treated with ethanol (20 mL) before selectively removing the CH$_2$Cl$_2$ under reduced pressure to afford an off-white precipitate. The suspension was filtered and the solid washed with ethanol (20 mL), petroleum spirits (60–80 °C, 40 mL) and diethyl ether (30 mL) before drying *in vacuo*. Yield: 560 mg (0.382 mmol, 82%). IR (CH$_2$Cl$_2$, cm^{-1}): 1980 ν_{CO}, 1590 $\nu_{C=C}$. IR (ATR, cm^{-1}): 1978 ν_{CO}, 1591 $\nu_{C=C}$. ^{1}H NMR (700 MHz, CDCl$_3$, 298 K): δ_H = 7.80 (s.br, 8 H, PPh$_2$), 7.31, 7.21 (2 x s.br, overlap with CHCl$_3$ peak, 12 H, PPh$_2$), 6.85 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, napthC*H*), 6.74 (dd, 2 H, $^3J_{HH}$ = 7.81 Hz, napthC*H*), 5.98 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, napthC*H*), 5.33 (m, 4 H, NC*H*$_2$P), 4.79 (s.br, 2 H, NC*H*$_2$N). The compound was insufficiently soluble in any organic solvent to unequivocally identify any peaks in the ^{13}C{^{1}H} or 2D ^{1}H–^{13}C HSQC or HMBC NMR spectra. ^{31}P{^{1}H} NMR (283 MHz, CDCl$_3$, 298 K): δ_P = 18.5 (d.br, $^1J_{RhP}$ = 124 Hz). MS (ESI, +ve ion, *m/z*): Found: 1429.1781. Calcd. for $C_{76}H_{64}{}^{35}ClN_4P_4Rh_2O_2$ [M–Cl]$^+$: 1429.1779. Anal. Found: C 62.37 H 4.44 N 3.81 %. Calcd. for $C_{76}H_{64}Cl_2N_4P_4Rh_2O_2$: C 62.27 H 4.40 N 3.82 %. Crystals suitable for structural determination were grown by slow evaporation of a saturated chloroform solution at 25 °C and measured at the Australian Synchrotron on the MX$_2$ beamline. Low data completion ratio is due to the limitations of the instrument available at the Australian Synchrotron operating under rotation data collection with a fixed detector and affects some high angle data. *Crystal Data for* $C_{76}H_{64}Cl_2N_4O_2P_4Rh_2$ (M_w =1465.91 gmol^{-1}): triclinic, space group *P*-1 (no. 2), a = 11.403(2), b = 12.569(3), c = 12.798(3) Å, α = 108.38(3), β = 106.46(3), γ = 93.84(3)°, V = 1644.5(7) Å^3, Z = 1, T = 100(2) K, μ(Synchrotron) = 0.732 mm^{-1}, D_{calc} = 1.480 Mgm^{-3}, 30342 reflections measured (3.466° ≤ 2Θ ≤ 64.204°), 8517 unique (R_{int} = 0.0563, R_{sigma} = 0.0613) which were used in all calculations. The final R_1 was 0.0521 ($I > 2\sigma(I)$) and wR_2 was 0.1575 (all data) for 406 refined parameters without restraints. CCDC 2222552.

Synthesis of [RhCl(CO)(μ-CyH$_2$Pm)]$_2$ (2b). A suspension of [RhCl(CO)(PPh$_3$)$_2$] (100 mg, 0.145 mmol) and CyH$_2$Pm (86 mg, 0.145 mmol) was stirred in THF (10 mL) for 2 hours before removing the solvent under reduced pressure. The sample was partially dissolved in CH$_2$Cl$_2$ (10 mL) before adding ethanol (20 mL), then removing the CH$_2$Cl$_2$ selectively under reduced pressure to afford an off-white precipitate. The suspension was filtered and the solid washed with petroleum spirits (60–80 °C, 10 mL) and diethyl ether (10 mL) before drying *in vacuo*. Yield: 83 mg (0.055 mmol, 76%). IR (CH$_2$Cl$_2$, cm^{-1}): 1955 ν_{CO}, 1608 $\nu_{C=C}$. IR (ATR, cm^{-1}): 1954 ν_{CO}, 1591 $\nu_{C=C}$. ^{1}H NMR (700 MHz, C$_6$D$_{12}$, 298 K): δ_H = 7.17 (dd, 2 H, $^3J_{HH}$ = 7.8 Hz, napthC*H*), 7.04 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, napthC*H*), 6.63 (s.br, 2 H, napthC*H*), 5.06 (3 x s.br, 6 H, NC*H*$_2$P and NC*H*$_2$N). The compound was insufficiently soluble in any organic solvent to usefully identify any resonances in the ^{13}C{^{1}H} or 2D ^{1}H–^{13}C{^{1}H} HSQC or HMBC NMR spectra. ^{31}P{^{1}H} NMR (283 MHz, C$_6$D$_{12}$, 298 K): δ_P = 42.76, 34.52 (2 x s.br). MS (ESI, +ve ion, m/z): Found: 1477.5537. Calcd. for $C_{76}H_{112}{}^{35}ClN_4O_2P_4Rh_2$ [M–Cl]$^+$: 1477.5534. Anal. Found: C 60.30 H 7.34 N 3.72 %. Calcd. for $C_{76}H_{112}Cl_2N_4O_2P_4Rh_2$: C 60.28 H 7.45 N 3.70 %. Insolubility of the complex precluded recrystallisation for X-ray diffraction studies.

Synthesis of [RhCl(CS)(μ-PhH$_2$Pm)]$_2$ (3a). An orange solution of [RhCl(CS)(PPh$_3$)$_2$] (135 mg, 0.191 mmol) and PhH$_2$Pm (108 mg, 0.191 mmol) in THF (20 mL) was stirred for 1.5 hours. The solvent was removed under reduced pressure, and the sample dissolved in the minimal CH$_2$Cl$_2$ (*ca.* 10 mL). Addition of *n*-hexane (30 mL) and selective removal of CH$_2$Cl$_2$ under reduced pressure afforded a light orange precipitate. The suspension was filtered and the solid washed with *n*-hexane (30 mL), ethanol (5 mL) and diethyl ether (15 mL) before drying *in vacuo*. Yield: 108 mg (0.0739 mmol, 78%). IR (CH$_2$Cl$_2$, cm^{-1}): 1592 $\nu_{C=C}$, 1312 ν_{CS}. IR(ATR, cm^{-1}): 1591 $\nu_{C=C,}$ 1311 ν_{CS}. ^{1}H NMR (700 MHz, CDCl$_3$, 298 K): δ_H = 7.86 (s.br, 8 H, PPh$_2$), 7.29, 7.21 (2 x s.br, 12 H, PPh$_2$), 6.85 (d, 2 H, $^3J_{HH}$ = 7.9 Hz, napthC*H*), 6.76 (dd, 2 H, $^3J_{HH}$ = 7.6 Hz, napthC*H*), 6.05 (d, 2 H, $^3J_{HH}$ = 7.4 Hz, napthC*H*), 5.40 (s.br, 4 H, NC*H*$_2$P), 4.83 (s.br, 2 H, NC*H*$_2$N). The compound was insufficiently soluble in any organic solvent to identify the CS carbon resonance by ^{13}C{^{1}H} or ^{1}H–^{13}C HMBC spectroscopy. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 298 K): δ_C = 142.1, 135.1 (napth*C*), 135.0 (napth*C* or PPh$_2$), 132.3 (d, J_{PC} = 10 Hz, PPh$_2$), 132.1, 130.8, 130.7, 130.6, 130.5 (napth*C* or PPh$_2$), 128.6 (d, J_{PC} = 12 Hz, PPh$_2$), 128.2 (PPh$_2$), 116.9, 115.3, 104.7 (napth*C*H), 67.3 (N*C*H$_2$N), 50.5 (m, N*C*H$_2$P). ^{31}P{^{1}H} NMR (163 MHz, CDCl$_3$, 298 K): δ_P = 19.6 (d.br, $^1J_{RhP}$ = 137 Hz). MS (ESI, +ve ion, *m/z*): Found: 713.0816. Calcd. for $C_{38}H_{32}N_2P_2RhS$ [M – 2Cl]$^{2+}$: 713.0817. Anal. Found: C 60.91 H 4.28 N 3.77 S 3.81 %. Calcd. for $C_{76}H_{64}Cl_2N_4P_4Rh_2S_2$: C 60.93 H 4.28 N 3.74 S 4.28 %. Crystals suitable for structural determination were grown from liquid diffusion of ethanol into a saturated CDCl$_3$ solution at 5 °C. The crystals suffer from modulated disorder from a rotating chloroform solvate influencing the ligand backbone. The modulation could not be successfully modelled, but a twofold disorder model is adequate to extract some structural information. Low data completion ratio is due to the limitations of the instrument available at the Australian Synchrotron operating under rotation data collection with a fixed detector and affects some high angle data. *Crystal Data for* $C_{39}H_{33}Cl_4N_2P_2RhS$ (M_w =868.38 gmol^{-1}): triclinic, space group *P*-1 (no. 2), a = 12.1459(6), b = 12.7759(8), c = 13.1675(7) Å, α = 70.396(5), β = 77.844(4), γ = 84.928(4)°, V = 1881.32(19) Å^3, Z = 2, T = 150.0(1) K, μ(Cu Kα) = 7.852 mm^{-1}, D_{calc} = 1.533 Mgm^{-3}, 13600 reflections measured (7.346° ≤ 2Θ ≤ 147.404°), 7420 unique (R_{int} = 0.0342, R_{sigma} = 0.0466) which were used in all calculations. The final R_1 was 0.0505 ($I > 2\sigma(I)$) and wR_2 was 0.1413 (all data) for 739 refined parameters with 625 restraints. CCDC 2222051.

Synthesis of [RhCl(CS)(μ-CyH$_2$Pm)]$_2$ (3b). A suspension of [RhCl(CO)(PPh$_3$)$_2$] (90 mg, 0.127 mmol) and CyH$_2$Pm (75 mg, 0.127 mmol) was stirred in THF (10 mL) for an hour before removing the solvent under reduced pressure. The sample was partially dissolved in CH_2Cl_2 (15 mL) before adding ethanol (20 mL) and filtering to afford a pale orange solid. The solid was washed with petroleum spirits (60–80 °C, 20 mL) and diethyl ether (10 mL) before drying *in vacuo*. Yield: 68 mg (0.044 mmol, 69%). IR (CH_2Cl_2, cm^{-1}): 1607 $\nu_{C=C}$, ν_{CS} obscured by solvent background. IR (ATR, cm^{-1}): 1591 $\nu_{C=C}$, 1283 ν_{CS}. The compound was too insoluble in any organic solvent to obtain useful NMR data. This also precluded crystallographic analysis. MS (ESI, +ve ion, *m/z*): Found: 1509.5090. Calcd. for $C_{76}H_{112}{}^{35}ClN_4P_4Rh_2S_2$ $[M{-}Cl]^+$: 1509.5077. Anal. Found: C 59.24 H 7.13 N 3.64 S 3.79 %. Calcd. for $C_{76}H_{112}Cl_2N_4P_4Rh_2S_2$: C 59.02 H 7.30 N 3.62 S 4.15 %.

Syntheses of [Rh₂(μ-CO)₂(PhH₂Pm)₂].Et₂O (4). (a) *Method 1; KC_8 reduction:* A suspension of **2a** (256 mg, 0.175 mmol) and KC_8 (180 mg, 1.33 mmol) in benzene (10 mL) was stirred for 4-12 hours at room temperature and the reaction progress monitored regularly by ^1H NMR spectroscopy. Immediately after consumption of the staring material and concomitant formation of a dark red colour, the suspension was filtered through diatomaceous earth, washing with benzene (~ 10 mL) until the filtrate ran clear. The solvent was condensed to ~4 mL under reduced pressure, and diethyl ether (10 mL) added to afford a red-orange precipitate. The solid was collected by filtration, washing with *n*-hexane (3 x 15 mL) and diethyl ether (2 x 5 mL), before drying *in vacuo*. Yield: 42 mg (0.029 mmol, 17%). (b) *Method 2; ligand substitution:* A solution of $[Rh(CO)(PPh_3)_2]_2$ in benzene was prepared by bubbling CO through a solution of $[RhH(CO)(PPh_3)_3]$ (250 mg, 0.272 mmol) in benzene (10 mL) for 30 mins. To the orange solution was added PhH_2Pm (154 mg, 0.271 mmol), causing a darker colour and some effervescence. After stirring for 16 hours, the solvent was condensed to ~4 mL under reduced pressure and diethyl ether (4 mL) added to afford a very small amount of off-white precipitate. The red filtrate was collected, and diethyl ether (6 mL) added before leaving the flask to sit for an hour to form large red crystals. The product was collected by filtration and washed with *n*-hexane (3 x 15 mL) and diethyl ether (2 x 5 mL) before drying *in vacuo*. Yield: 121 mg (0.0824 mmol, 61%). IR (THF, cm^{-1}): 1738 ν_{CO}, 1593 $\nu_{C=C}$. IR (ATR, cm^{-1}) 1736 ν_{CO}, 1591 $\nu_{C=C}$. ^1H NMR (700 MHz, C_6D_6, 298 K): δ_H = 8.05 (m, 8 H, *o*-PPh_2), 7.44, 7.36 (2 x m, 8 H, *o*-PPh_2), 7.29 (s.br, 2 H, NC*H*···Rh), 7.32, 7.27 (2 x m, 4 H, napthC*H*), 7.23-6.78 (series of multiplets, 24 H, *m*-PPh_2 and *p*-PPh_2), 6.67-6.62 (m, 8 H, napthC*H*), 4.57, 4.38 (2 x s.br, 2 x 2 H, NC*H₂*P), 4.13 (d, 2 H, $^2J_{HH}$ = 12 Hz, terminal NCHN), 3.88, 3.80 (2 x s.br, 2 x 2 H, NC*H₂*P), 3.27 (q, 2 H, $^3J_{HH}$ = 7 Hz, Et_2O), 1.12 (t, 3 H, $^3J_{HH}$ = 7 Hz, Et_2O). Overlapping peaks prevent accurate integrations and assignments of some ^1H NMR signals. Some positions were determined using 2-D NMR techniques, while others could not be assigned with confidence. $^{31}P\{^1H\}$ NMR (283 MHz, C_6D_6, 298 K): δ_P = 24.09 (d, $^1J_{RhP}$ = 186 Hz), 18.69 (d, $^1J_{RhP}$ = 201 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K): δ_P = 24.07 (d, $^1J_{RhP}$ = 186 Hz), 18.77 (d, $^1J_{RhP}$ = 201 Hz). $^{13}C\{^1H\}$ NMR (176 MHz, C_6D_6, 298 K): δ_C = 238.5 (m, Rh_2CO), 146.2, 145.4 (2 x s.br, napthC), 137.70 (t.br, $^1J_{PC}$ = 34 Hz, *i*-PPh_2), 136.9 (d, $^1J_{PC}$ = 31 Hz, *i*-PPh_2), 136.5 (napthC), 133.9 (br m, *o*-PPh_2), 132.7 (d, o-PPh_2), 129.6-127.0 (series of peaks unassigned by 2D experiments, napthC, *m*-PPh_2, *p*-PPh_2), 120.8 (brs, napthC*H*), 119.9 (napthC), 119.4 (s.br, napthC*H*), 110.7, 107.5 (2 x br s, napthC*H*), 65.9 (s, Et_2O), 64.0 (br m, N_2CH_2), 52.4 (d.br, $^1J_{PC}$ = 23 Hz, NC*H₂*P), 50.02 (d.br, $^1J_{PC}$ = 26 Hz, NC*H₂*P), 15.60 (Et_2O). The sensitivity of this compound precluded mass spectrometric analysis. Anal. Found: C 65.63 H 4.71 N 4.12 %. Calcd. for $C_{76}H_{62}N_4O_2P_4Rh_2$: C 65.43 H 4.62 N 4.02 %. Crystals suitable for structural determination were grown from liquid diffusion of diethyl ether into a saturated benzene solution of the sample at room temperature. *Crystal Data for* $C_{84}H_{84}N_4O_4P_4Rh_2$ (M_w =1541.23 $gmol^{-1}$): monoclinic, space group I2/a (no. 15), a = 26.9934(4), b = 12.76730(10), c = 23.3601(4) Å, β = 115.376(2)°, V = 7273.9(2) Å^3, Z = 4, T = 150.0(1) K, μ(Cu Kα) = 4.929 mm^{-1}, D_{calc} = 1.407 Mgm^{-3}, 21222 reflections measured (7.816° ≤ 2Θ ≤ 147.844°), 7280 unique (R_{int} = 0.0207, R_{sigma} = 0.0209) which were used in all calculations. The final R_1 was 0.0292 ($I > 2\sigma(I)$) and wR_2 was 0.0770 (all data) for 444 refined parameters without restraints. CCDC 2222038.

Syntheses of [Rh(CO)(PhPm)]X (X = BF₄, PF₆) (5). *(a) Method 1, synthesis of [Rh(CO)(PhPm)]BF₄*: A solution of **1a** (250 mg, 0.356 mmol) and $AgBF_4$ (83 mg, 0.427 mmol) in acetonitrile (15 mL) was stirred for 1 hour in the absence of light before bubbling CO through the solution for 1.5 hours. The solution was stirred for a further hour, then the solvent removed under reduced pressure. The product was extracted through a small diatomaceous earth plug (3 x 5 cm) with the minimal CH_2Cl_2 (~20 mL), and the solvent removed under reduced pressure. The product was then extracted through an identical diatomaceous earth plug using the minimal ethanol (20 mL) to which n-hexane (100 mL) was added to afford a bright yellow solid. Following filtration, the solid was washed with toluene (2 x 15 mL), *n*-hexane (2 x 20 mL) and Et_2O (2 x 20 mL) before drying *in vacuo*. Yield: 189 mg (242 mmol, 68 %). IR (CH_2Cl_2, cm^{-1}) 2029 ν_{CO}, 1586 $\nu_{C=C}$. IR (ATR, cm^{-1}) 2025 ν_{CO}, 1583 $\nu_{C=C}$. ^1H NMR (800 MHz, $(CD_3)_2CO$, 298 K): δ_H = 7.96 (m, 8 H, *o*-PPh_2), 7.65 (m, 4 H, *p*-PPh_2), 7.62 (m, 8 H, *m*-PPh_2), 7.56 (d, 2 H, $^3J_{HH}$ = 8 Hz, napthC*H*), 7.46 (t, 2 H, $^3J_{HH}$ = 8 Hz, napthC*H*), 7.29 (d, 2 H, $^3J_{HH}$ = 8 Hz, napthC*H*), 5.48 (t^v, $^{2,4}J_{PH}$ = 3 Hz, NC*H₂*P). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 298 K): δ_P = 36.90 (d, $^1J_{RhP}$ = 132 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K): δ_F = –152.3 (s). $^{13}C\{^1H\}$ NMR (201 MHz, $(CD_3)_2CO$, 298 K): δ_C = 209.2 (dt, $^1J_{RhC}$ = 47, $^2J_{PC}$ = 10 Hz, N*C*N, assigned on the basis of coupling to the NCH_2P protons in the HMBC experiment), 195.5 (dt, $^1J_{RhC}$ = 58, $^2J_{PC}$ = 13 Hz, *C*O), 135.0 (napthC), 134.7 (napthC), 133.9 (vt, $^2J_{PC}$ = 7 Hz, *o*-PPh_2), 132.7 (*p*-PPh_2), 131.40 (napthC), 131.0 (vt, $^1J_{PC}$ = 25 Hz, *i*-Ph), 130.2 (vt, $^3J_{PC}$ = 6 Hz, *m*-PPh_2), 129.04 (napthC*H*), 123.6 (napthC*H*), 120.8 (napthC), 109.9 (napthC*H*), 61.6 (vt, $^{1,3}J_{PC}$ = 17 Hz, NC*H₂*P). MS (ESI, +ve ion, m/z): Found: 695.0891. Calcd. for $C_{38}H_{30}N_2OP_2{}^{103}Rh$ $[M - BF_4]^+$: 695.0888. Anal. Found: C 58.74 H 4.53 N 3.41 %. Calcd. for $C_{38}H_{30}BF_4N_2OP_2Rh$: C 58.76 H 4.54 N 3.61 %. (b) *Method 2, synthesis of [Rh(CO)(PhPm)]PF₆*: To a solution of **4** in benzene was added excess $[C_3Ph_3]PF_6$. Crystals suitable for structural determination deposited immediately from the benzene reaction mixture. Crude $^{31}P\{^1H\}$ NMR spectroscopy estimates 78% conversion alongside two unknown rhodium-containing products. IR (CH_2Cl_2, cm^{-1}) 2030

ν_{CO}, 1586 $\nu_{C=C}$. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ_H = 7.80 (m, 8 H, PPh$_2$), 7.58 (m, 12 H, PPh$_2$), 7.20, 7.19 (2 x s.br, 2 x 2 H, napthC*H*), 6.99 (t, $^3J_{HH}$ = 4.3 Hz, napthC*H*), 4.96 (t^v, $^{2,4}J_{HP}$ = 2.8 Hz, NC*H*$_2$P). ^{31}P{^{1}H} NMR (283 MHz, CDCl$_3$, 298 K): δ_P = 36.24 (d, $^1J_{PRh}$ = 132 Hz), –144.1 (sept, $^1J_{FP}$ = 713 Hz, PF$_6$). MS (ESI, +ve ion, m/z): Found: 695.0902. Calcd. for $C_{38}H_{30}N_2OP_2{}^{103}Rh$ [M – PF$_6$]$^+$: 695.0888. *Crystal Data for* $C_{44}H_{36}F_6N_2OP_3Rh$ (M_w = 918.57 gmol^{-1}): monoclinic, space group *P*2$_1$/n (no. 14), *a* = 15.2904(3), *b* = 16.1205(5), *c* = 19.0392(6) Å, β = 105.181(3)°, *V* = 4529.2(2) Å^3, *Z* = 4, T = 150.0(1) K, μ(Cu Kα) = 4.553 mm^{-1}, D_{calc} = 1.347 Mgm^{-3}, 17713 reflections measured (8.606° ≤ 2Θ ≤ 145.874°), 8798 unique (R_{int} = 0.0365, R_{sigma} = 0.0595) which were used in all calculations. The final R_1 was 0.0450 (I > 2σ(I)) and wR_2 was 0.1163 (all data) for 564 refined parameters with 310 restraints. CCDC 2222025.

Synthesis of [Rh(CO)(C≡CSiMe$_3$)(μ-PhH$_2$Pm)]$_2$ (6). To a solution of lithium trimethylsilylacetylide (0.288 mmol) in THF (15 mL) at -78 °C was added **2a** (210 mg, 0.144 mmol) and stirred for an hour before allowing the flask to warm to room temperature and stirring for 16 h. Solvent was reduced to 4 mL under reduced pressure, and Et$_2$O (15 mL) added to afford a small amount of yellow precipitate (unreacted **2a**). The filtrate was collected by cannula filtration, and *n*-hexane (10 mL) added before leaving the flask at -20 °C overnight, affording a bright yellow precipitate. The product was collected by filtration, washed with Et$_2$O (2 x 3 mL), n-hexane (3 x 15 mL) and dried *in vacuo*. Yield: 142 mg (0.089 mmol, 62%). IR (CH$_2$Cl$_2$, cm^{-1}): 1986 ν_{CO}, 1590 $\nu_{C≡C}$. IR (ATR, cm-1): 1975 ν_{CO}, 1589 $\nu_{C=C}$. The C≡C stretch was not observed perhaps due to overlap with the CO stretch. ^{1}H NMR (700 MHz, CD$_2$Cl$_2$, 213 K): δ_H = 8.18-6.64 (series of broad multiplets, 56 H, napthC*H* and PPh$_2$), 6.47 (2 H, NC*H*$_2$N or NC*H*$_2$P), 6.20 (d, 2 H, napthC*H*), 6.16, 5.80, 5.34, 4.69, 4.38, 4.25, (8 x m, 8 x 1 H, NC*H*$_2$P and NC*H*$_2$N), 0.09 (18 H, SiMe$_3$). ^{31}P{^{1}H} NMR (283 MHz, CD$_2$Cl$_2$, 213 K): δ_P = 27.4 ($^2J_{RhP}$ = 288 Hz, $^1J_{RhP}$ = 130 Hz), 15.9 ($^2J_{RhP}$ = 288 Hz, $^1J_{RhP}$ = 131 Hz). The complex was insufficiently soluble to acquire useful ^{13}C NMR data. Peaks were not observed at 298 K due to broadening, the sample precipitated over time at lower temperatures and decomposed at higher temperatures. Anal. found: C 65.00; H 5.177, N 3.74. Calcd. for $C_{86}H_{82}N_4O_2P_4Rh_2Si_2$: C 64.98; H 5.20; N 3.52. *Crystal Data for* $C_{98}H_{94}N_4O_2P_4Rh_2Si_2$ (M_w =1745.65 gmol^{-1}): triclinic, space group *P*-1 (no. 2), *a* = 12.7185(5), *b* = 14.3038(6), *c* = 14.4821(6) Å, *α* = 64.079(4), *β* = 66.091(4), *γ* = 74.274(4)°, *V* = 2152.08(18) Å^3, *Z* = 1, *T* = 150.0(1) K, μ(Cu Kα) = 4.472 mm^{-1}, D_{calc} = 1.347 Mgm^{-3}, 16125 reflections measured (7.192° ≤ 2Θ ≤ 147.388°), 8522 unique (R_{int} = 0.0362, R_{sigma} = 0.0590) which were used in all calculations. The final R_1 was 0.0346 (I > 2σ(I)) and wR_2 was 0.0808 (all data) for 508 refined parameters without restraints. CCDC 2222024.

Synthesis of [Rh(C≡CSiMe$_3$)(PhPm)] (7). To a solution of ethynyltrimethylsilane (0.043 mL, 0.299 mmol) in THF (20 mL) at –78 °C was added ^{n}BuLi (1.6 M, 0.20 mL, 0.314 mmol) and stirred, warming to room temperature over 45 mins. This solution was slowly added to a suspension of **1a** (0.200 g, 0.285 mmol) in THF (20 mL) at –78 °C while stirring. The solution was warmed to room temperature and stirred for 3 hours, causing the orange suspension to turn clear red. The solvent was reduced to 5 mL and n-hexane added (60 mL) to afford a bright orange precipitate. This was collected by filtration, and the solid ultrasonically triturated in Et$_2$O (20 mL) for 5 minutes. The solid was isolated by filtration and washed with another 15 mL of Et$_2$O before drying *in vacuo*. Yield: 165 mg (0.217 mmol, 76%). IR (CH$_2$Cl$_2$, cm^{-1}) 2001 $\nu_{C≡C}$, 1584 $\nu_{C=C}$. IR (ATR, cm^{-1}) 1995 $\nu_{C≡C}$, 1580 $\nu_{C=C}$. ^{1}H NMR (800 MHz, C$_6$D$_6$, 298 K): δ_H = 8.21 (m, 8 H, *o*-PPh$_2$), 7.19 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, napthC*H*), 7.11 (m, 8 H, J_{HH} = 7.6 Hz, *m*-PPh$_2$), 7.05 (dd, 2 H, $^3J_{HH}$ = 6.9 Hz, napthC*H*), 7.03 (m, 4 H, J_{HH} = 6.4 Hz, *p*-PPh$_2$), 6.12 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, napthC*H*), 4.32 (s, 4 H, NC*H*$_2$P), 0.45 (s, 9 H, SiCH$_3$). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, 298 K): δ_P = 28.64 (d, $^1J_{Rh}$P = 155 Hz). ^{31}C{^{1}H} NMR (201 MHz, C$_6$D$_6$, 298 K): δ_C = 218.4 (m, N*C*N, weak peak identified by HMBC), 135.9 (t^v, $^{1,3}J_{CP}$ = 20 Hz, *i*-PPh$_2$), 135.2 (t.br, $^3J_{CP}$ = 5 Hz, Rh*C*CSiMe$_3$), 134.8 (napth*C*), 134.0 (m, Rh*C*CSiMe$_3$, tentatively assigned by HMBC NMR), 133.9 (t^v, $^{2,4}J_{PC}$ = 7 Hz, *o*-PPh$_2$), 130.0 (*p*-PPh$_2$), 128.7 (t^v, $^{3,5}J_{PC}$ = 5 Hz, *m*-PPh$_2$), 128.4 (napthC*H*), 120.2 (napthC*H*), 118.6 (napth*C*), 106.5 (napthC*H*), 60.7 (t^v, $^{2,4}J_{CP}$ = 15 Hz, N*C*H$_2$P), 2.5 (s, SiMe$_3$). The final napthC resonance was obscured by the solvent peak. MS (ESI, +ve ion, *m/z*): Found: 763.1336. Calcd. for $C_{42}H_{38}N_2SiP_2Rh$ [M–H]$^+$: 763.1335. Found: 779.1287. Calcd. for $C_{42}H_{38}N_2SiOP_2Rh$ [M–H+O]$^+$: 779.1284. Anal. Found: C 67.76 H 5.31 N 3.30 %. Calcd. for $C_{48}H_{42}N_2OP_2RhSi$: C 67.37 H 4.95 N 3.27 %. Crystals suitable for structural determination formed upon standing a saturated benzene solution at room temperature overnight. *Crystal Data for* $C_{51}H_{48}N_2P_2RhSi$ (M_w =881.85 gmol^{-1}): monoclinic, space group *P*2$_1$/c (no. 14), *a* = 9.59280(10), *b* = 22.3888(2), *c* = 20.17120(10) Å, *β* = 95.3060(10)°, *V* = 4313.63(6) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(Cu Kα) = 4.450 mm^{-1}, D_{calc} = 1.358 Mgm^{-3}, 44676 reflections measured (7.898° ≤ 2Θ ≤ 147.96°), 8691 unique (R_{int} = 0.0281, R_{sigma} = 0.0213) which were used in all calculations. The final R_1 was 0.0316 (I > 2σ(I)) and wR_2 was 0.0879 (all data) for 537 refined parameters without restraints. CCDC 2222023.

Synthesis of [Rh(C≡CPh)(PhPm)] (8). To a solution of ethynylbenzene (0.046 mL, 0.42 mmol) in THF (20 mL) at –78 °C was added ^{n}BuLi (1.6 M, 0.21 mL, 0.34 mmol) and stirred, warming to room temperature over 45 mins. This solution was slowly added to an orange suspension of **1a** (0.215 g, 0.306 mmol) in THF (15 mL) at –78 °C while stirring. The solution was warmed to room temperature and stirred for 3 hours, turning clear red. The solvent was reduced to 5 mL and n-hexane (60 mL) added to afford a bright orange precipitate. This was collected by filtration, and the solid sonicated in Et$_2$O (20 mL) for 5 minutes. The solid was isolated by filtration and dried in vacuo. Yield: 170 mg (0.221 mmol, 72%). IR (CH$_2$Cl$_2$, cm^{-1}) 2065 $\nu_{C≡C}$, 1585 $\nu_{C=C}$. IR (ATR, cm^{-1}) 2060 $\nu_{C≡C}$, 1579 $\nu_{C=C}$. 1H NMR (800 MHz, C$_6$D$_6$, 298 K): δ_H = 8.23 (m, 8 H, o-PPh$_2$), 7.67 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, o-CCC$_6$H$_5$), 7.19 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, napthCH), 7.15 (m, 2 H, m-CCC$_6$H$_5$), 7.06 (t, 8 H, $^3J_{HH}$ = 7 Hz, m-PPh$_2$), 7.04 (t, 2 H, $^3J_{HH}$ obscured due to overlap with PPh$_2$ group, napthCH), 6.99 (t, 4 H, $^3J_{HH}$ = 7 Hz, p-PPh$_2$), 6.97 (t, 1 H, $^3J_{HH}$ = 7 Hz, p-CCC$_6$H$_5$), 6.13 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, napthCH), 4.33 (s, 4 H, NCH$_2$PPh$_2$). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, 298 K): δ_P = 29.41 (d, $^1J_{PRh}$ = 154 Hz). ^{13}C{^{1}H} NMR (201 MHz, C$_6$D$_6$, 298 K): δ_C = 217.4 (NCN, resonance too weak to observe in 1-D NMR was identified by HMBC NMR), 135.9 (t^v, $^{1,3}J_{CP}$ = 21 Hz, i-PPh$_2$), 135.3, 134.8

(napthC), 133.8 (m, o-PPh$_2$), 131.5 (napthC), 131.05 (i-CCPh), 130.0 (m, p-PPh$_2$), 128.8 (m-PPh$_2$), 128.7 to 127.7 (overlapping peaks obscured by solvent peak, napthCH, CCPh, o-CCPh, p-CCPh), 124.3 (m-CCPh), 120.1, 118.5, 106.8, 106.3 (napthCH and napthC), 60.6 (v^t, $^3J_{CP}$ = 15 Hz, NCH$_2$P). MS (ESI, +ve ion, m/z): Found: 768.1326. Calcd. for $C_{45}H_{38}N_2P_2{}^{103}Rh$ [M]$^+$: 768.1331. Found: 791.1222. Calcd. for $C_{45}H_{38}N_2P_2{}^{103}RhNa$ [M+Na]$^+$: 791.1228. Anal. Found: C 69.93 H 5.255 N 3.77 %. Calcd. for $C_{45}H_{38}N_2P_2Rh$: C 70.04 H 4.96 N 3.63 %. Crystals suitable for structural determination were grown by slow diffusion of pentane into a saturated benzene solution at room temperature. Crystal Data for $C_{51}H_{41}N_2P_2Rh$ (M_w =846.71 gmol^{-1}): monoclinic, space group $P2_1/n$ (no. 14), a = 9.81730(10), b = 25.6987(3), c = 16.1102(2) Å, β = 97.0220(10)°, V = 4033.99(8) Å^3, Z = 4, T = 150.0(1) K, μ(Cu Kα) = 4.464 mm^{-1}, D_{calc} = 1.394 Mgm^{-3}, 29911 reflections measured (6.88° ≤ 2Θ ≤ 148.26°), 8097 unique (R_{int} = 0.0277, R_{sigma} = 0.0252) which were used in all calculations. The final R_1 was 0.0314 (I > 2σ(I)) and wR_2 was 0.0840 (all data) for 505 refined parameters without restraints. CCDC 2222022.

References

1 *CrysAlis PRO*, Agilent Technologies Ltd, Yarnton, Oxfordshire, England, 2014.

2 (a) G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2008, **64**, 112; (b) G. M. Sheldrick, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 2015, 71, 3.

3 (a) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453; (b) C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466.

4 T. M. McPhillips, S. E. McPhillips, H.-J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis, P. Kuhn, Journal of Synchrotron Radiation, 2002, **9**, 401.

5 W. Kabsch, *J. Appl. Crystallogr.*, 1993, **26**, 795-800.

6 A. F. Hill and C. M. A. McQueen, *Organometallics*, 2012, **31**, 8051.

7 D. Evans, J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1990, **28**, 79.

8 M. Kubota and C. O. M. Ho, *Inorg. Synth.*, 1979, **19**, 204.

9 N. Ahmad, J. J. Levison and S. D. Robinson, *Inorg. Synth.*, 1990, **28**, 81.

10 W. Rand Kenan Jr, P. Singh, C. B. Dammann and D. J. Hodgson, *Inorg. Chem.*, 1973, **12**, 1335.

11 D. Evans, G. Yagupsky and G. Wilkinson, *J. Chem. Soc. (A),* 1968, 2660.

12 D. M. Ottmers and H. F. Rase, *Carbon N Y*, 1966, **4**, 125.

13 R. P. Hughes, J. W. Reisch and A. L. Rheingold, *Organometallics*, 1985, **4**, 1754.

14 R. Breslow and R. Xu, *Org. Synth.,* 1997, **74**, 72.

15 *Spartan 20*® (2020) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A.

16 J. D. Chai and M. Head-Gordon, *J Chem Phys.*, 2008, **128**, 084106.

17 J. D. Chai and M. Head-Gordon, *Phys Chem Chem Phys*, 2008, **10**, 6615-6620.

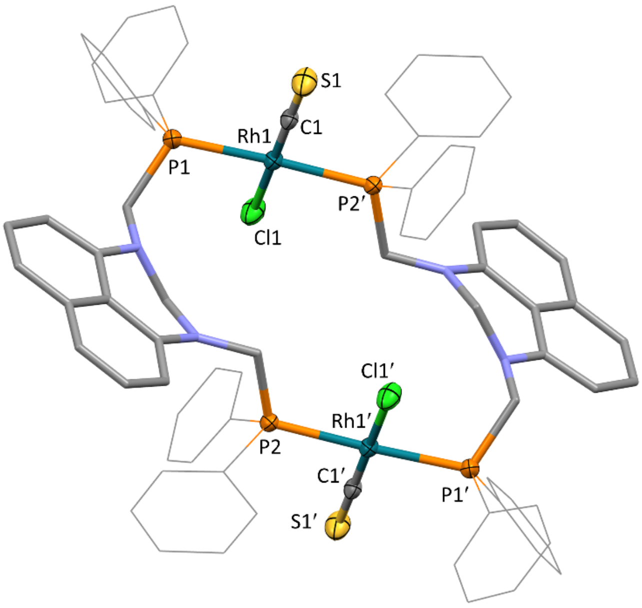
18 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283.

19 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299-310.

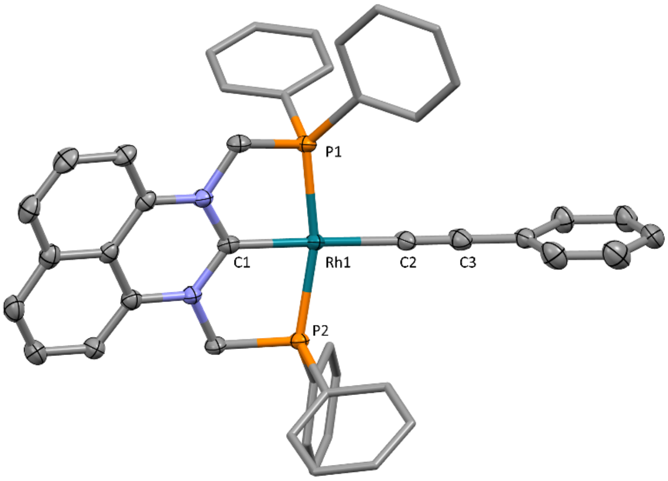
20 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284-298.

21 W. J. Hehre, R. Ditchfeld and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.

Additional Crystal Data



Molecular structure of **3a** in a crystal of **3a**·(CHCl$_3$). (30% displacement ellipsoids, naphthalene and phenyl groups simplified, hydrogen atoms and solvent omitted for clarity, only one-half of the C$_2$-symmetric molecule is unique). Selected distances [Å] and angles [°]: Rh1–C1 1.786(5), C1–S1 1.549(5), Rh1–Cl1 2.3817(12), Rh1–P1 2.3200(10), Rh1–P2 2.3285(11), Cl1–Rh1–C1 177.36(15), P1–Rh1–P2′ 177.22(4), Rh1–C1–S1 178.2(3).

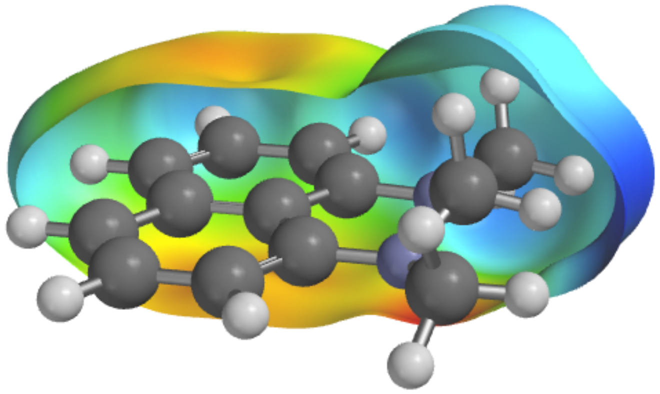


Molecular structure of **8** in a crystal of **8**·(C$_6$H$_6$). (50% displacement ellipsoids, naphthalene and phenyl groups simplified, hydrogen atoms and solvent omitted for clarity). Selected distances [Å] and angles [°]: Rh1–C1 1.999(3), Rh1–C2 2.043(3), C2–C3 1.204(4), Rh1–P1 2.2305(6), Rh1–P2 2.2233(6), C1–Rh1–C2 173.71(11), Rh1–C2–C3 171.5(3), P1–Rh1–P2 165.52(3).

Computational Results

1. 1,3-dimethyl-2,3-dihydro-1*H*-perimidine

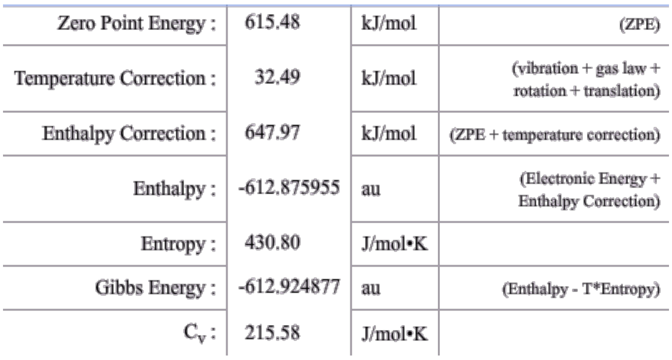
Electrostatic Potential Surface



Cartesian Coordinates

Atom	x	y	z
H	3.359002	0.036368	-2.671278
C	2.411906	0.007619	-2.139844
H	1.231231	0.187788	-3.916117
C	1.235078	0.095823	-2.833894
C	1.241711	-0.152493	-0.026171
C	-0.003501	0.059425	-2.142348
C	2.428248	-0.111193	-0.735113
C	-0.002027	-0.057798	-0.728408
C	-1.243671	0.121748	-2.828992
H	3.382191	-0.162975	-0.224022
C	-2.419503	0.057904	-2.130283
H	-1.242107	0.213733	-3.911222
H	-3.367868	0.106533	-2.658031
C	-2.433058	-0.060635	-0.725514
H	-3.385825	-0.092802	-0.210953
C	-1.244914	-0.125981	-0.021155
N	-1.185700	-0.278495	1.362668
N	1.184094	-0.305638	1.357103
C	-2.402618	-0.131431	2.127647
H	-2.857405	0.868220	2.028894
H	-2.183000	-0.312611	3.182998
H	-3.137417	-0.876838	1.810421
C	2.407029	-0.187784	2.117661
H	2.886103	0.800225	2.016043
H	3.121357	-0.952000	1.798019
H	2.187116	-0.362521	3.174071
C	0.007132	0.262430	1.976779
H	0.020162	1.372629	1.917776
H	0.006254	-0.019251	3.033266

Thermodynamic Properties at 298.15 K

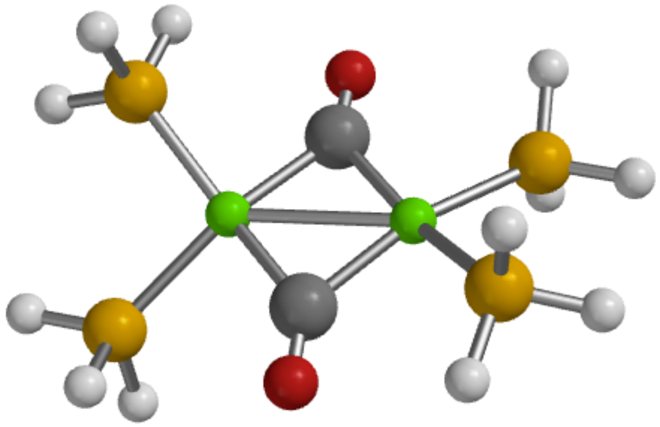


Zero Point Energy :	615.48	kJ/mol	(ZPE)
Temperature Correction :	32.49	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	647.97	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-612.875955	au	(Electronic Energy + Enthalpy Correction)
Entropy :	430.80	J/mol•K	
Gibbs Energy :	-612.924877	au	(Enthalpy - T*Entropy)
C_v :	215.58	J/mol•K	

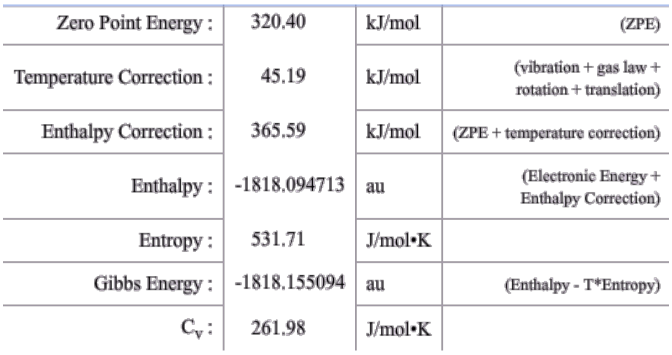
2. [$Rh_2(\mu\text{-}CO)_2(PH_3)_4$]*(Rh–Rh)*

Cartesian Coordinates

Atom	x	y	z
Rh	0.391384	1.294974	0.185677
Rh	-0.350599	-1.301115	-0.213765
C	-0.979758	0.433348	-1.001682
C	1.106112	-0.450663	0.878486
O	-1.770053	0.769728	-1.815207
O	1.984911	-0.803088	1.587203
P	0.107220	3.208408	-1.141705
H	0.659776	3.147973	-2.438564
H	0.616774	4.480585	-0.799278
H	-1.183779	3.625631	-1.522793
P	1.408433	2.347260	2.015181
H	2.423810	1.700793	2.751336
H	0.556718	2.644240	3.102348
H	2.017794	3.620819	1.943045
P	-2.413361	-2.236621	-0.826080
H	-3.369205	-2.378729	0.203127
H	-2.549311	-3.543335	-1.350247
H	-3.242543	-1.578384	-1.756401
P	0.842043	-3.311907	0.016030
H	2.033208	-3.405648	-0.734753
H	0.318120	-4.575032	-0.340462
H	1.392307	-3.689239	1.258505

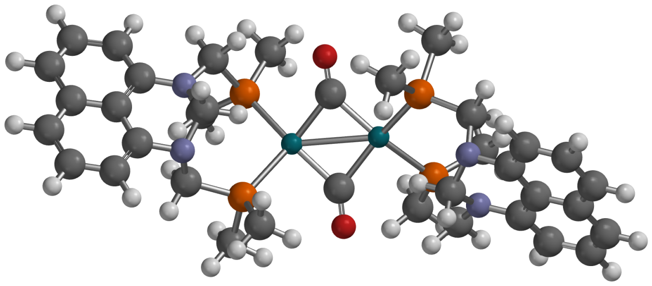


Thermodynamic Properties at 298.15 K

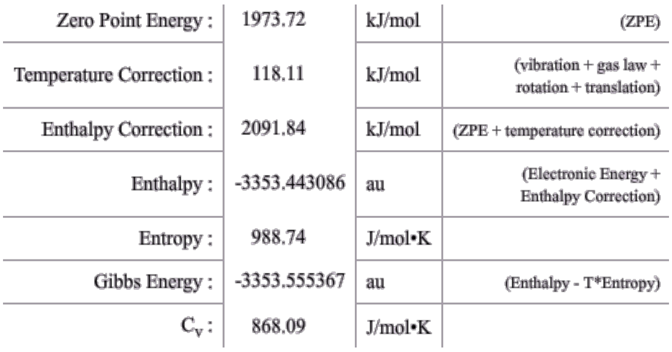


Zero Point Energy :	320.40	kJ/mol	(ZPE)
Temperature Correction :	45.19	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	365.59	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1818.094713	au	(Electronic Energy + Enthalpy Correction)
Entropy :	531.71	J/mol•K	
Gibbs Energy :	-1818.155094	au	(Enthalpy - T*Entropy)
C_v :	261.98	J/mol•K	

3. [$Rh_2(\mu\text{-}CO)_2(MeH_2Pm)_2$]*(Rh–Rh)*



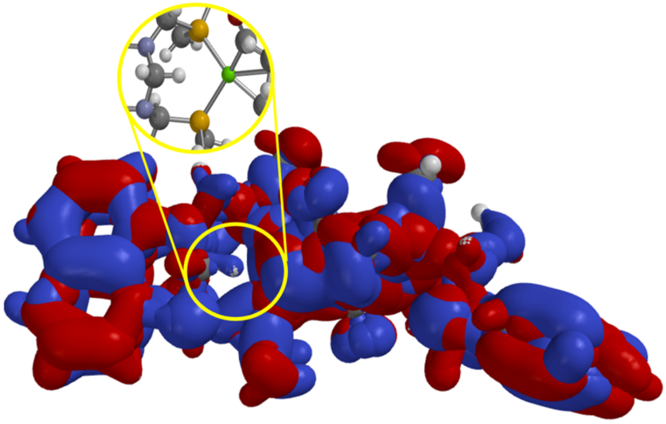
Thermodynamic Properties at 298.15 K



Zero Point Energy :	1973.72	kJ/mol	(ZPE)
Temperature Correction :	118.11	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	2091.84	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3353.443086	au	(Electronic Energy + Enthalpy Correction)
Entropy :	988.74	J/mol•K	
Gibbs Energy :	-3353.555367	au	(Enthalpy - T*Entropy)
C_v :	868.09	J/mol•K	

Cartesian Coordinates

Atom	x	y	z
Rh	1.348682	-0.046792	1.076250
P	2.844071	1.419987	2.134769
P	2.830927	-1.473775	-0.050118
O	-0.130130	-2.651958	0.827456
N	4.446448	2.064565	0.014377
N	4.421517	0.262976	-1.579715
C	7.752386	1.989042	-1.674124
C	6.411011	1.681748	-1.319873
C	5.743147	0.621714	-1.998638
C	3.743298	1.450421	-1.103977
H	2.728521	1.200946	-0.784199
H	3.682877	2.150204	-1.949613
C	6.499386	3.346775	0.446276
H	6.057748	3.906840	1.261696
C	4.482857	-0.842381	-0.614655
H	5.062397	-0.570955	0.282643
H	5.010345	-1.669675	-1.100843
C	-0.043090	-1.470434	0.955416
C	5.768438	2.399011	-0.247301
C	6.371961	-0.079697	-2.998043
H	5.831955	-0.875436	-3.502308
C	8.367665	1.251205	-2.718342
H	9.390557	1.493670	-2.993371
C	7.832324	3.633326	0.085882
H	8.366432	4.395174	0.646781
C	8.450364	2.992433	-0.954295
H	9.474078	3.228808	-1.228821
C	7.695553	0.242970	-3.361096
H	8.180599	-0.312881	-4.158103
Rh	-1.351564	0.043681	1.077015
P	-2.846308	-1.433785	2.125709
P	-2.829516	1.471516	-0.055251
O	0.125768	2.651794	0.831664
N	-4.433669	-2.066633	-0.007080
N	-4.420644	-0.258262	-1.594720
C	-7.756932	-1.973463	-1.660353
C	-6.410811	-1.672099	-1.319587
C	-3.617702	-2.706102	1.001912
H	-2.800470	-3.285888	0.551006
H	-4.214682	-3.395523	1.600157
C	-5.744351	-0.617356	-2.007320
C	-3.738859	-1.446566	-1.127247
H	-2.722802	-1.197036	-0.810970
H	-3.681959	-2.142889	-1.976043
C	-6.495104	-3.320590	0.461963
H	-6.052220	-3.872529	1.282254
C	-4.482465	0.842211	-0.624049
H	-5.061690	0.567424	0.272416
H	-5.008763	1.672423	-1.106583
C	0.040127	1.470419	0.958074
C	-5.761835	-2.387523	-0.249481
C	-6.377030	0.082101	-3.005471
H	-5.837814	0.874538	-3.515733
C	-8.376388	-1.238550	-2.704327
H	-9.402715	-1.477150	-2.969741
C	-7.832801	-3.600977	0.115093
H	-8.367803	-4.352755	0.688596
C	-8.454955	-2.966877	-0.927095
H	-9.482289	-3.199340	-1.191209
C	-7.704407	-0.237290	-3.357864
H	-8.192921	0.316537	-4.154160
C	3.640141	2.698313	1.034848
H	4.252779	3.356328	1.652362
H	2.836974	3.308678	0.598539
C	-3.364756	2.995824	0.821609
H	-2.463099	3.537957	1.120266
H	-3.919472	2.725207	1.724901
H	-3.986366	3.641446	0.191258
C	-2.160491	2.140125	-1.629758
H	-1.219449	2.654077	-1.419661
H	-2.864012	2.834181	-2.102598
H	-1.967039	1.308446	-2.312049
C	-4.337583	-0.766538	2.970030
H	-4.038700	0.025353	3.662598
H	-4.871303	-1.547308	3.522858
H	-5.015978	-0.339622	2.227039
C	-2.135281	-2.522150	3.426897
H	-1.737368	-1.899661	4.233089
H	-1.308822	-3.091597	2.995244
H	-2.882526	-3.210156	3.838210
C	3.365687	-2.995469	0.831873
H	3.990428	-3.641489	0.205019
H	2.463916	-3.538323	1.128901
H	3.917057	-2.721646	1.736230
C	2.166537	-2.147036	-1.624248
H	2.870862	-2.843066	-2.093047
H	1.975668	-1.317266	-2.309580
H	1.224493	-2.659898	-1.415601
C	2.131315	2.504602	3.437814
H	2.879921	3.185144	3.858898
H	1.723816	1.879322	4.237033
H	1.311292	3.082030	3.004466
C	4.322296	0.732978	2.986477
H	5.008148	0.316858	2.244030
H	4.012585	-0.069592	3.661690
H	4.851583	1.502657	3.558677

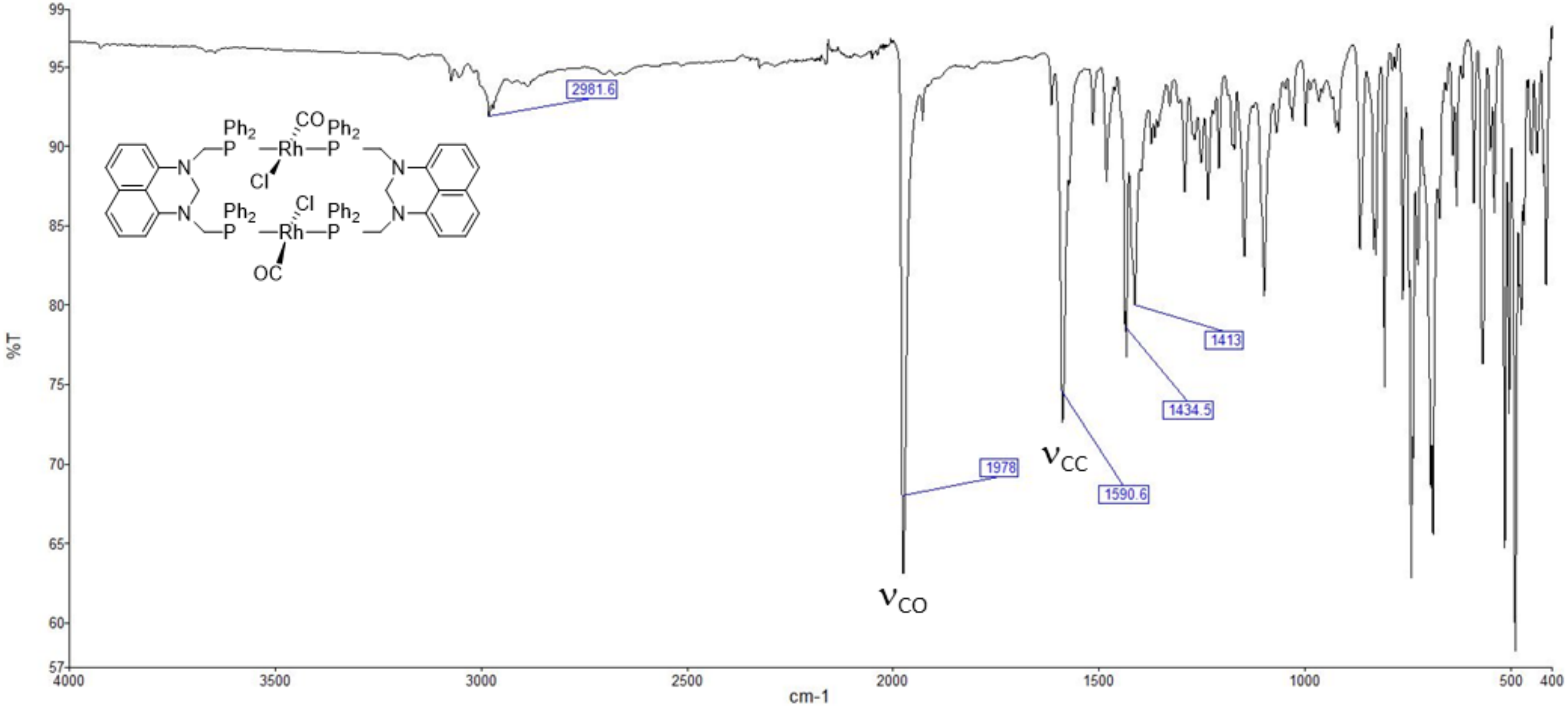


Superposition of 30 HOMOs indicating no effective overlap between C–H and Rh

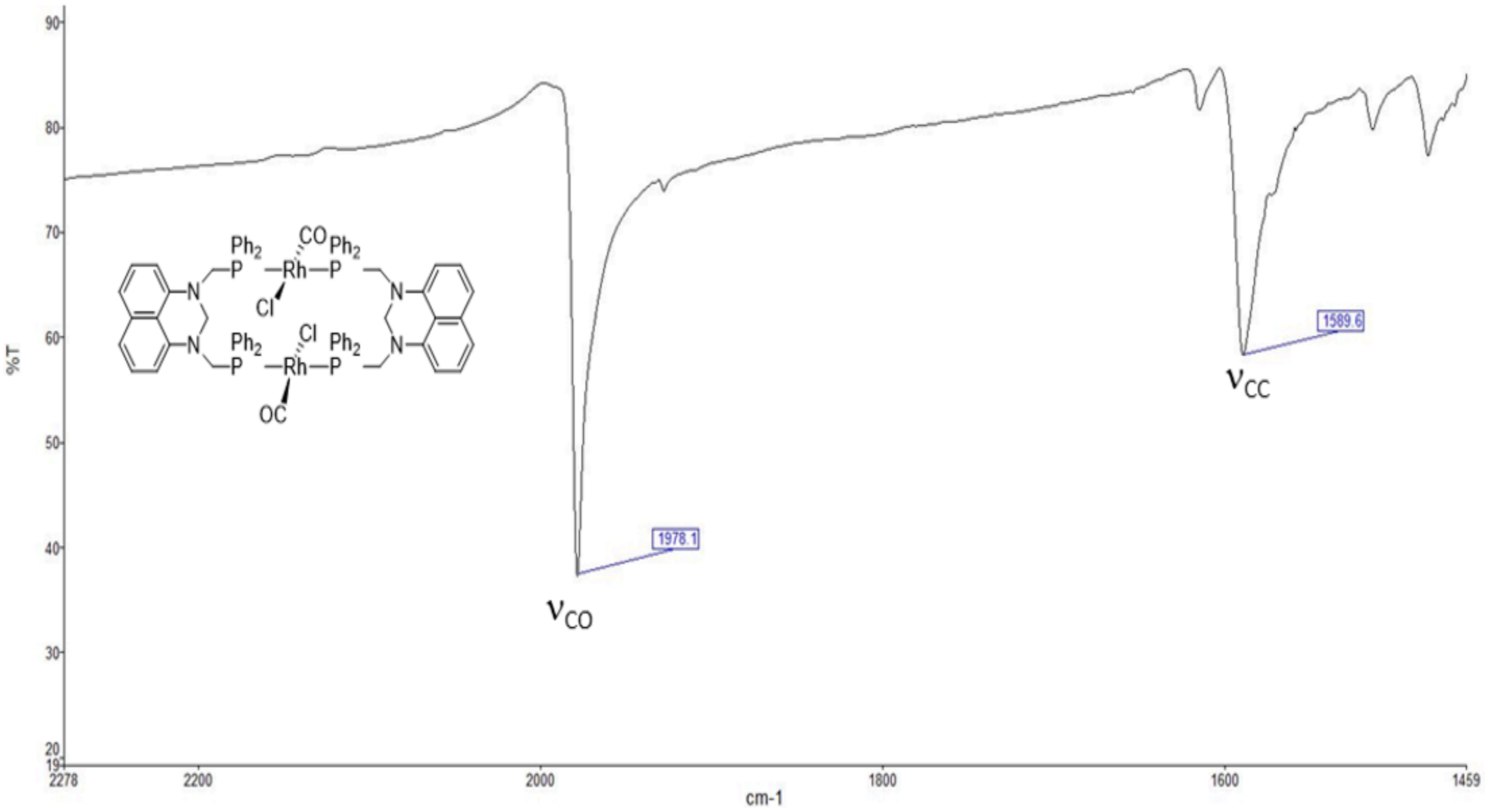
Table of selected inconclusive reaction conditions.

Complex	Reagent	Solvent	Temperature (°C)	Observation
2a	DMAD	Toluene	25	No reaction.
3a	Methyl propiolate	Toluene	25	No reaction.
2a	DMAD	Toluene	110	Loss of all ^{1}H and ^{31}P NMR signals other than DMAD.
3a	Methyl propiolate	Toluene	110	^{31}P NMR singlets at 24.5 ppm, 10.7 ppm. Small ^{1}H signals at 12, 9 ppm, messy ^{1}H NMR resonances between 5 and 6 ppm.
2a	CO	CH_2Cl_2	25	Loss of all ^{1}H and ^{31}P NMR signals. IR too broad to assign peaks.
2a	H_2	CH_2Cl_2	25	Loss of all ^{1}H and ^{31}P NMR signals. IR too broad to assign peaks.
3a	H_2	CH_2Cl_2	25	Too insoluble to observe ^{31}P signals. Variety of ^{1}H signals between 5 and 6 ppm indicating no major product. Nothing separable on workup.
2a	$C_3Ph_3PF_6$	CH_2Cl_2	25	No observable reaction.
2a	Diphenylacetylene	Toluene	110	No observable reaction.
2a	$AgPF_6$	MeCN	25	Highly sensitive and insoluble yellow product which turned brown before NMR acquisition. No ^{31}P peaks of the brown product were observed.
2a	TBAF, 1,4-bis-trimethylsilylbutadiyne			Too insoluble to observe ^{31}P NMR resonances. Multiple ^{1}H peaks between 4.5 and 7.0 ppm due to several PhH_2Pm ligand systems. None correspond to that of **6**. Nothing separable on workup.
3a	KC_8	Toluene	25	Clean formation of a new, still insoluble, symmetrical product (δ_P = 17.2, $^{1}J_{RhP}$ = 188 Hz) which decomposed over time or upon workup.
4	CO_2	THF	25	Lack of repeatability in results. By $^{31}P\{^{1}H\}$ NMR we have observed sharp doublets at 23.7 ppm (78 Hz), 19.45 ppm (125 Hz), 22.18 ppm (155 Hz), 26.12 ppm (193 Hz) and 20.22 ppm (140 Hz). There are also singlets at 25.0 ppm (unknown) and -26 ppm

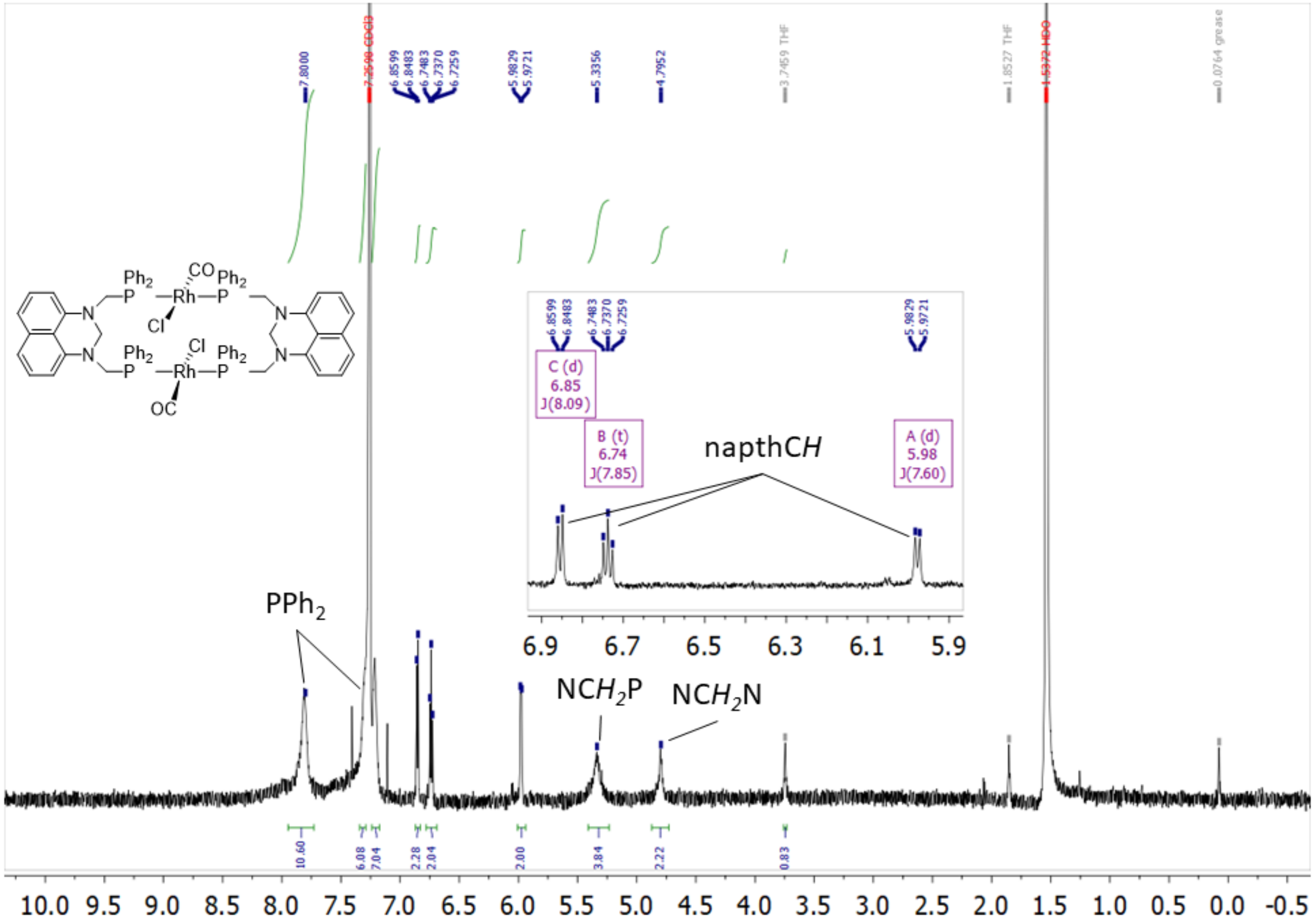
				(Free PhH_2Pm ligand). Proved inseparable and prone to further reaction with atmosphere of .
4	CS_2	THF	25	Loss of all NMR resonances presumably due to extreme broadening or precipitation from the mixture (no major ppt was observed by eye however) nothing separable on workup.
4	H_2	THF	25	Busy forest of ^{31}P NMR peaks between 5 and 45 ppm, unknown splitting. At least 7 resonances between -8 and -13 ppm by ^{1}H NMR indicative of metal hydride species.
4	Dimethylacetylene dicarboxylate	THF	25	By $^{31}P\{^{1}H\}$ NMR singlets at 10.3 and 25.9 ppm were observed along with two doublets of doublets (49.9 ppm, 159 and 14 Hz), (26.9 ppm, 124 and 14 Hz couplings). Over time rearranged to 4 new doublets and 6 singlets. No species proved separable for purification.
4	1,4-diphenylbutadiyne	THF	25	Various broad peaks between 0 and 60 ppm by $^{31}P\{^{1}H\}$ NMR spectroscopy. One sharp singlet at 25 ppm. ^{1}H NMR dominated by excess organic reagent.
4	1,4-bis(trimethylsilyl)butadiyne	THF	25	Too insoluble to observe ^{31}P NMR resonances. Multiple ^{1}H peaks between 4.5 and 7.0 ppm due to several PhH_2Pm ligand systems. Nothing separable on workup.
4	S_8	THF	25	Loss of all NMR resonances, possibly due to precipitation, difficult to know due to excess S_8 in solution. Nothing separable on workup.
4	Ferrocenium hexafluorophosphate	C_6D_6	25	Slow (multi-day), clean conversion to **5**.
5	benzaldehyde	-	110	Decomposition. Loss of starting material signals and formation of $^{31}P\{^{1}H\}$ NMR singlets at 43.9 and 28.7 ppm.



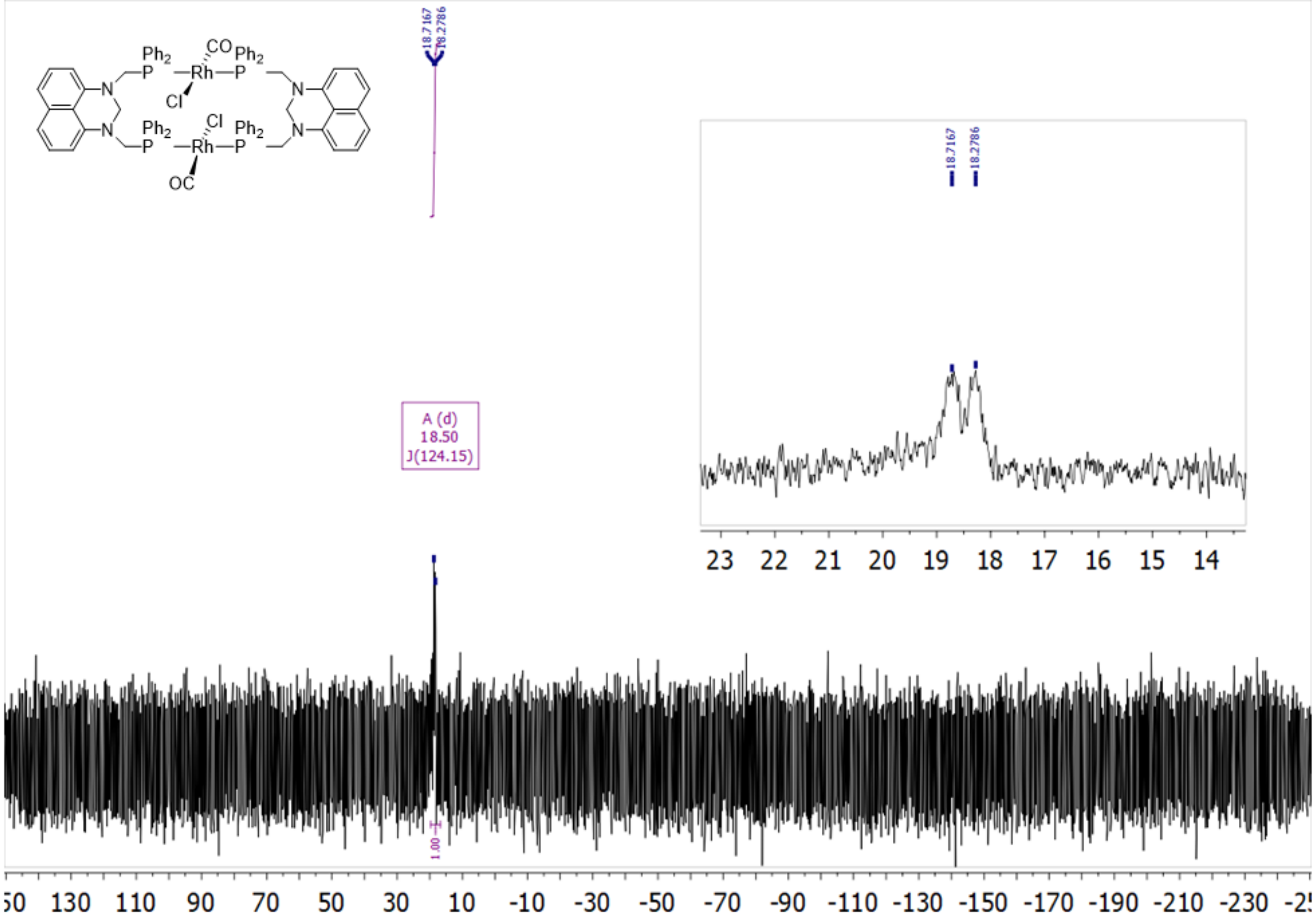
IR (ATR, cm^{-1}) for [RhCl(CO)(μ-PhH$_2$Pm)]$_2$ (**2a**).



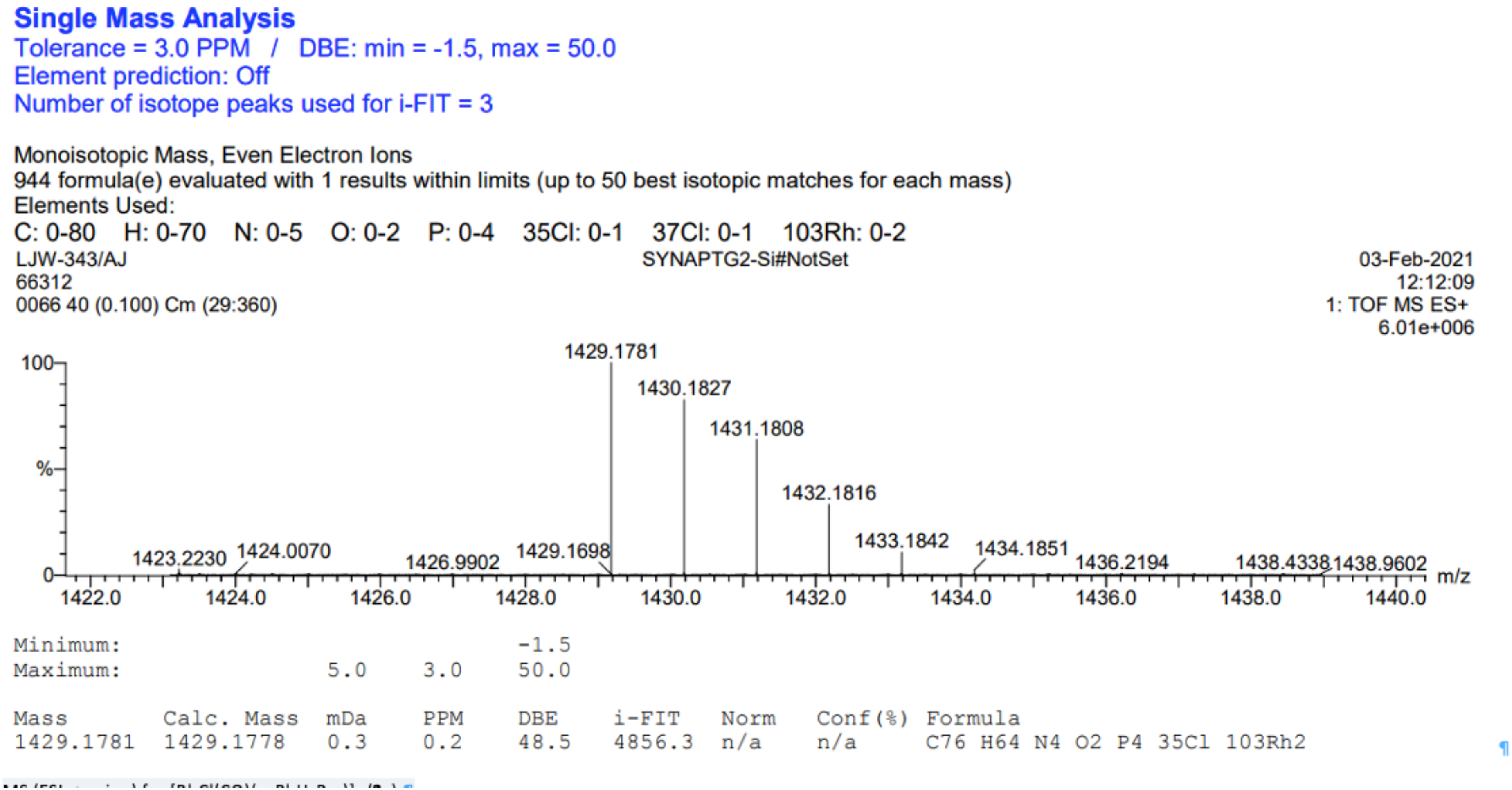
IR (CH_2Cl_2, cm^{-1}) for $[RhCl(CO)(\mu\text{-}PhH_2Pm)]_2$ (**2a**).



^{1}H NMR (700 MHz, CDCl$_3$, 298K) for [RhCl(CO)(μ-PhH$_2$Pm)]$_2$ (**2a**).



$^{31}P\{^1H\}$ NMR (283 MHz, $CDCl_3$, 298 K) for $[RhCl(CO)(\mu\text{-}PhH_2Pm)]_2$ (**2a**).



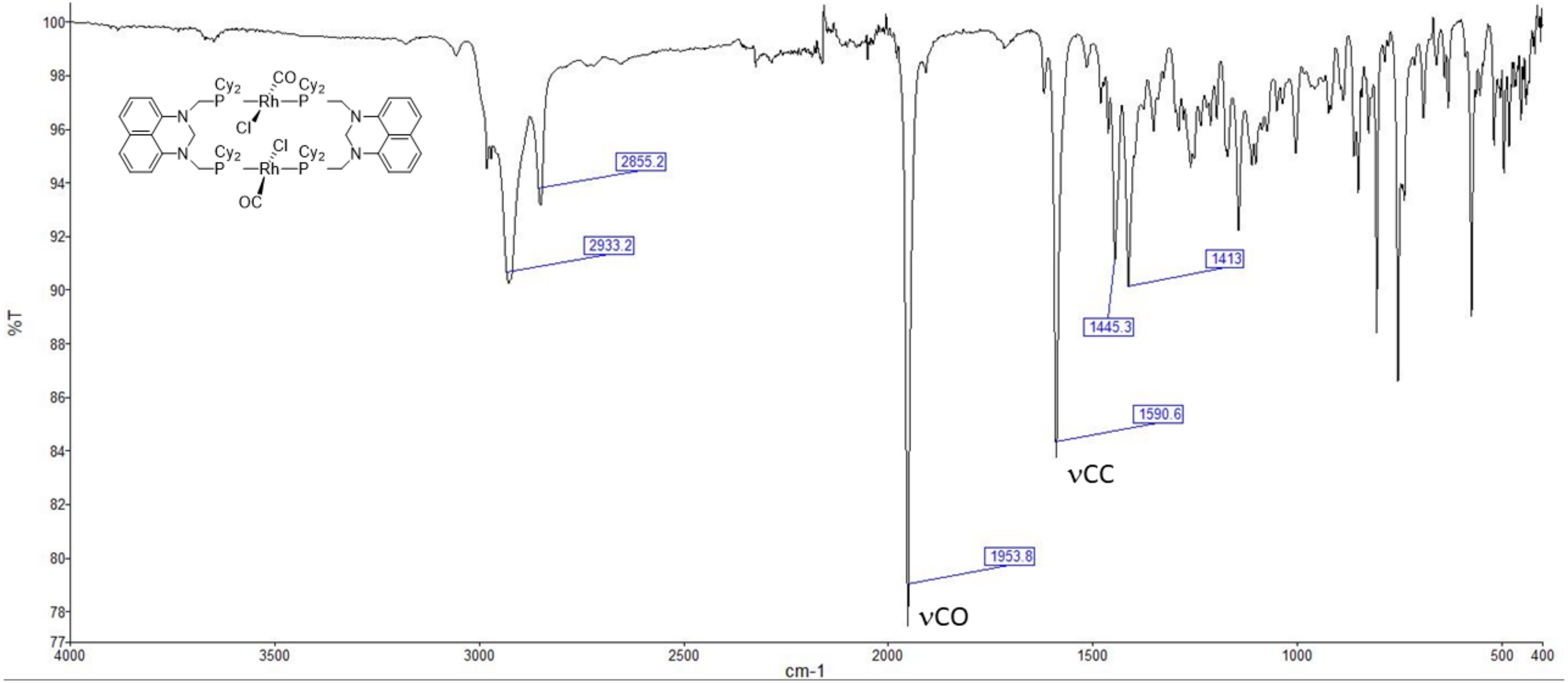
Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
944 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-80 H: 0-70 N: 0-5 O: 0-2 P: 0-4 35Cl: 0-1 37Cl: 0-1 103Rh: 0-2

LJW-343/AJ SYNAPTG2-Si#NotSet 03-Feb-2021
66312 12:12:09
0066 40 (0.100) Cm (29:360) 1: TOF MS ES+
6.01e+006

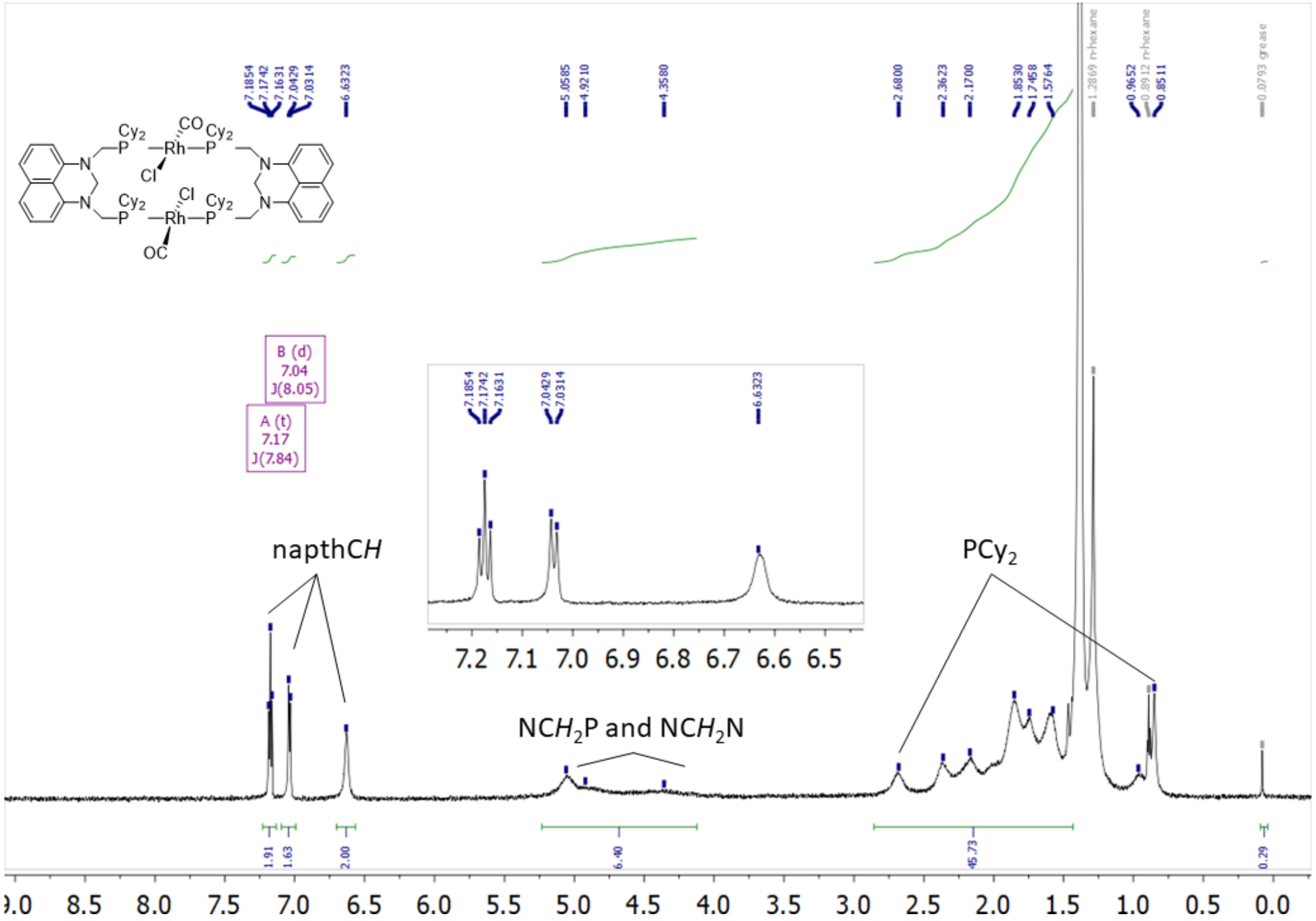
```
Minimum:                                 -1.5
Maximum:                5.0      3.0     50.0

Mass          Calc. Mass   mDa      PPM      DBE      i-FIT    Norm     Conf(%)  Formula
1429.1781     1429.1778    0.3      0.2      48.5     4856.3   n/a      n/a      C76 H64 N4 O2 P4 35Cl 103Rh2
```

MS (ESI, +ve ion) for $[RhCl(CO)(\mu\text{-}PhH_2Pm)]_2$ (**2a**).

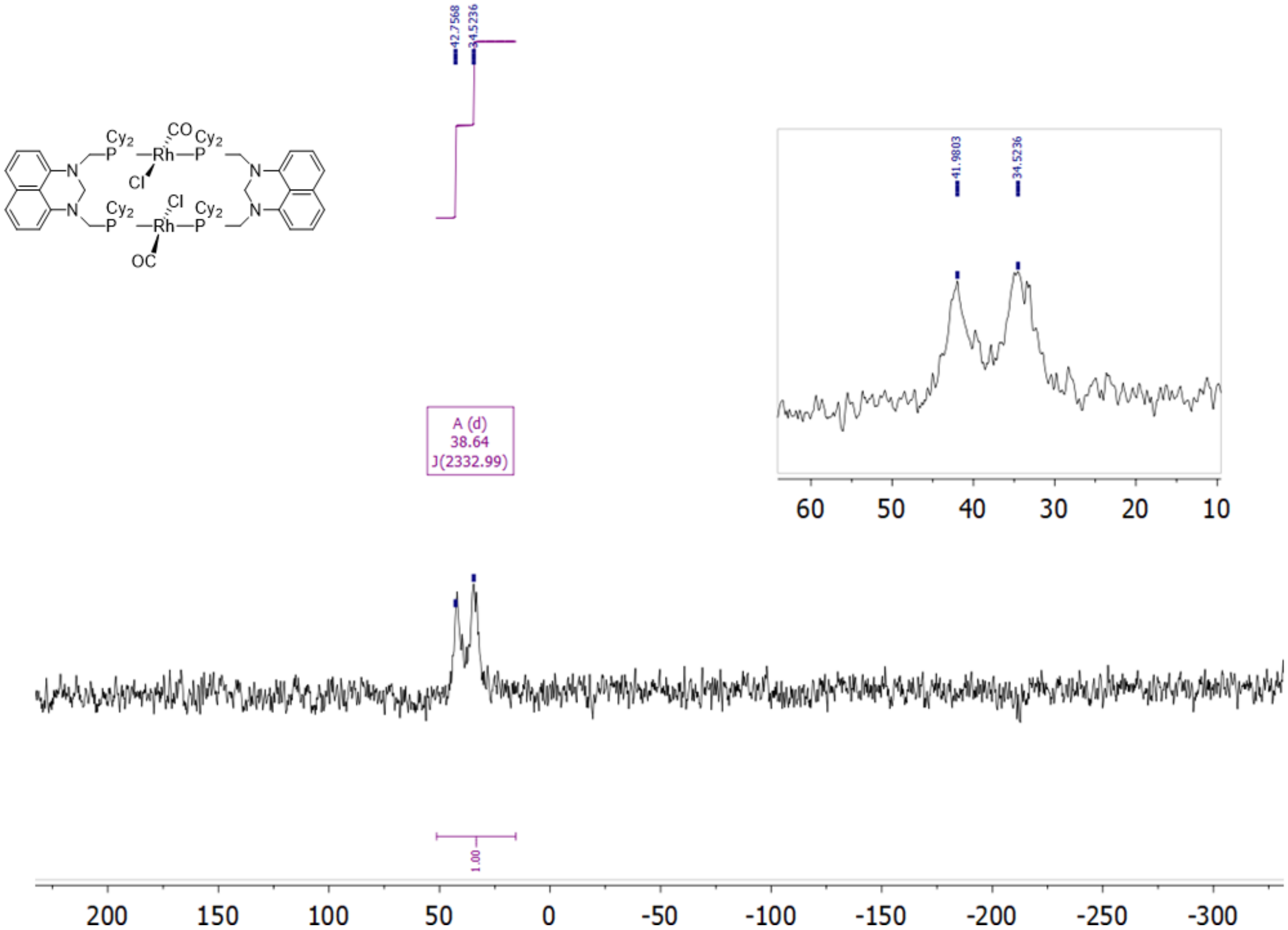


IR (ATR, cm^{-1}) for [RhCl(CO)(μ-CyH$_2$Pm)]$_2$ (**2b**).

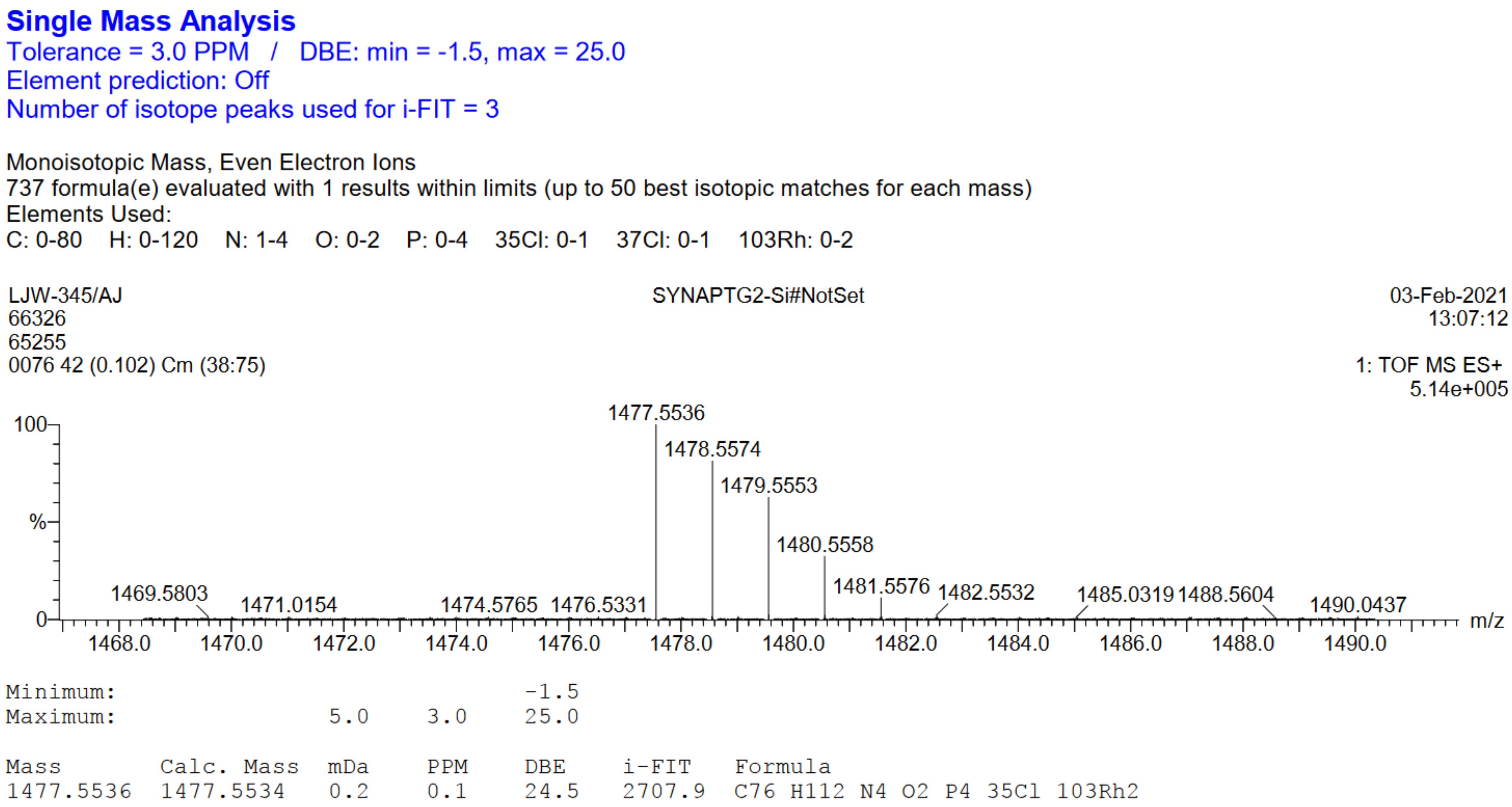
IR (CH_2Cl_2, cm^{-1}) for $[RhCl(CO)(\mu\text{-}CyH_2Pm)]_2$ (**2b**).



^{1}H NMR (700 MHz, C_6D_{12}, 298K) for $[RhCl(CO)(\mu\text{-}CyH_2Pm)]_2$ (**2b**).



$^{31}P\{^{1}H\}$ NMR (283 MHz, C_6D_{12}, 298 K) for $[RhCl(CO)(\mu\text{-}CyH_2Pm)]_2$ (**2b**).



Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 25.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
737 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-80 H: 0-120 N: 1-4 O: 0-2 P: 0-4 35Cl: 0-1 37Cl: 0-1 103Rh: 0-2

LJW-345/AJ
66326
65255
0076 42 (0.102) Cm (38:75)

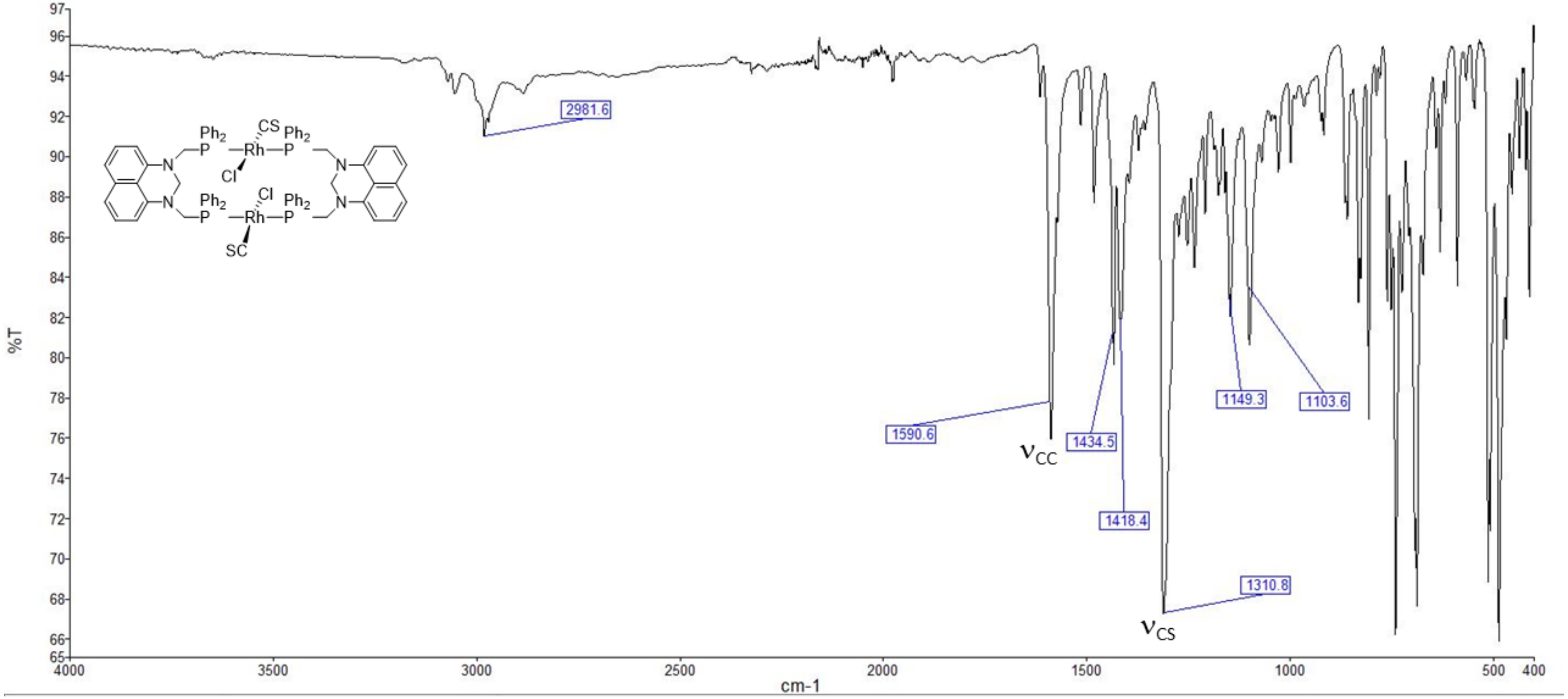
SYNAPTG2-Si#NotSet

03-Feb-2021
13:07:12

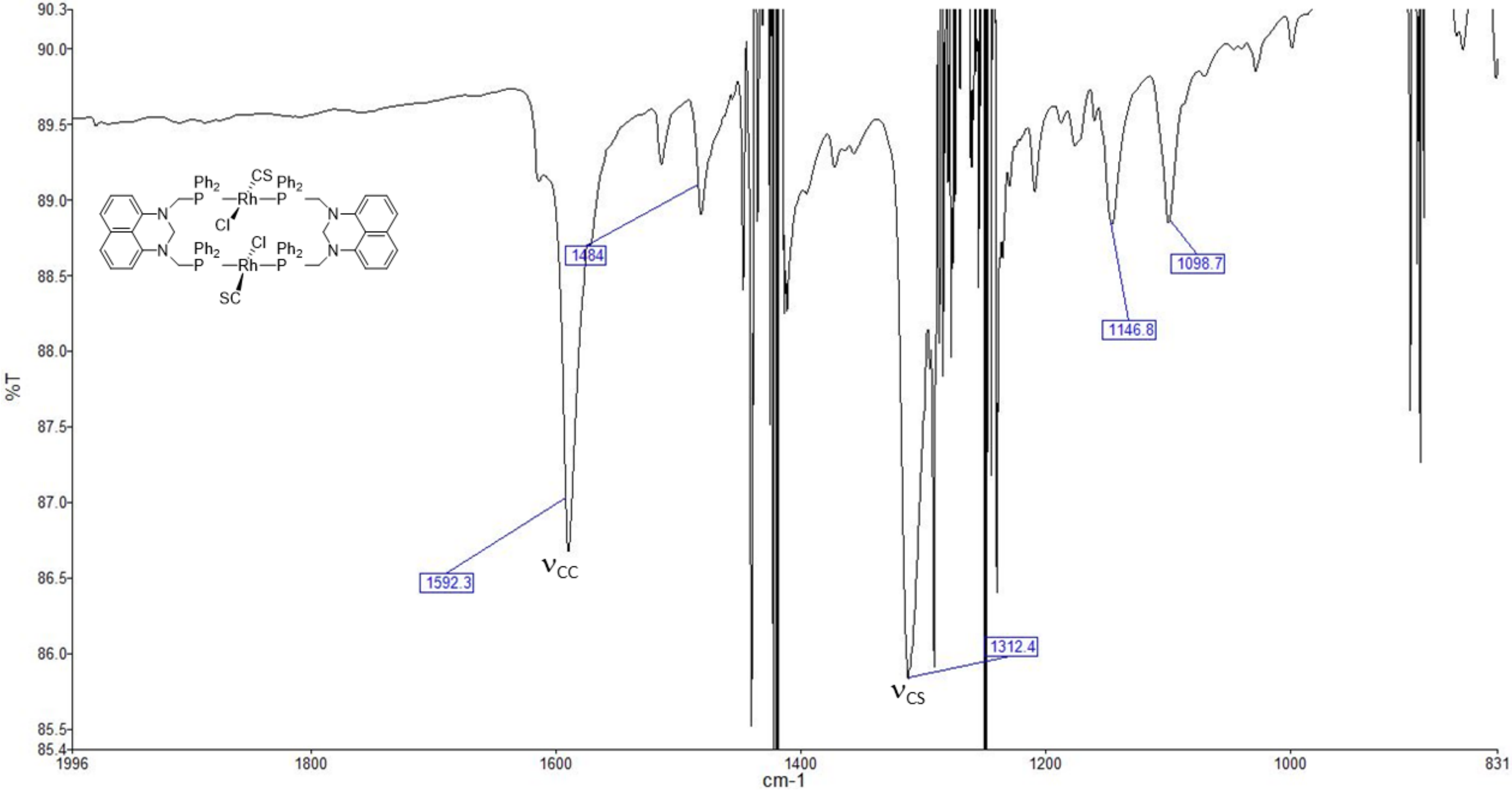
1: TOF MS ES+
5.14e+005

```
Minimum:                                 -1.5
Maximum:                   5.0     3.0   25.0

Mass        Calc. Mass  mDa    PPM    DBE     i-FIT    Formula
1477.5536   1477.5534   0.2    0.1    24.5    2707.9   C76 H112 N4 O2 P4 35Cl 103Rh2
```

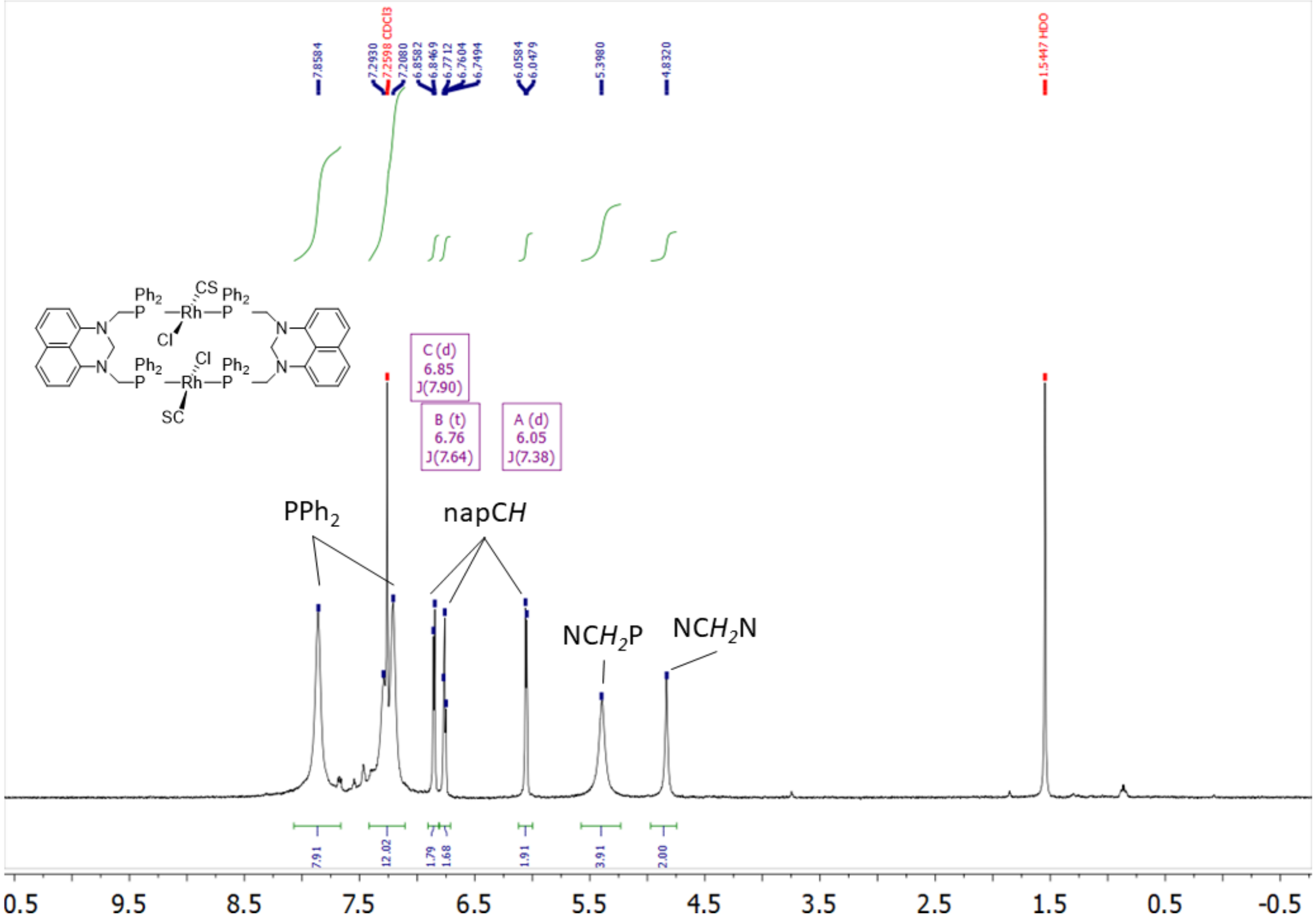
MS (ESI, +ve ion) for $[RhCl(CO)(\mu\text{-}CyH_2Pm)]_2$ (**2b**).



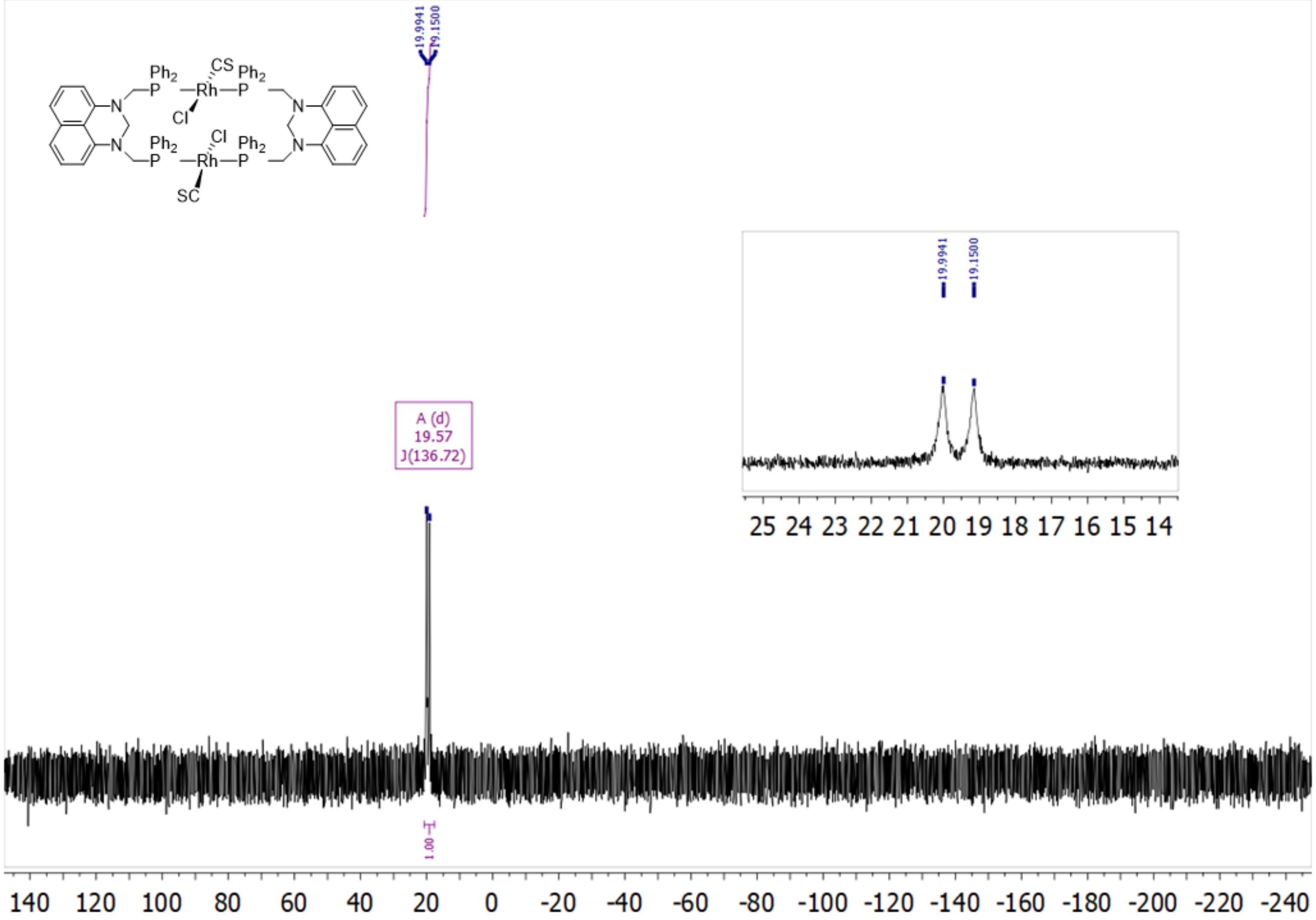
IR (ATR, cm^{-1}) for [RhCl(CS)(μ-PhH$_2$Pm)]$_2$ (**3a**).



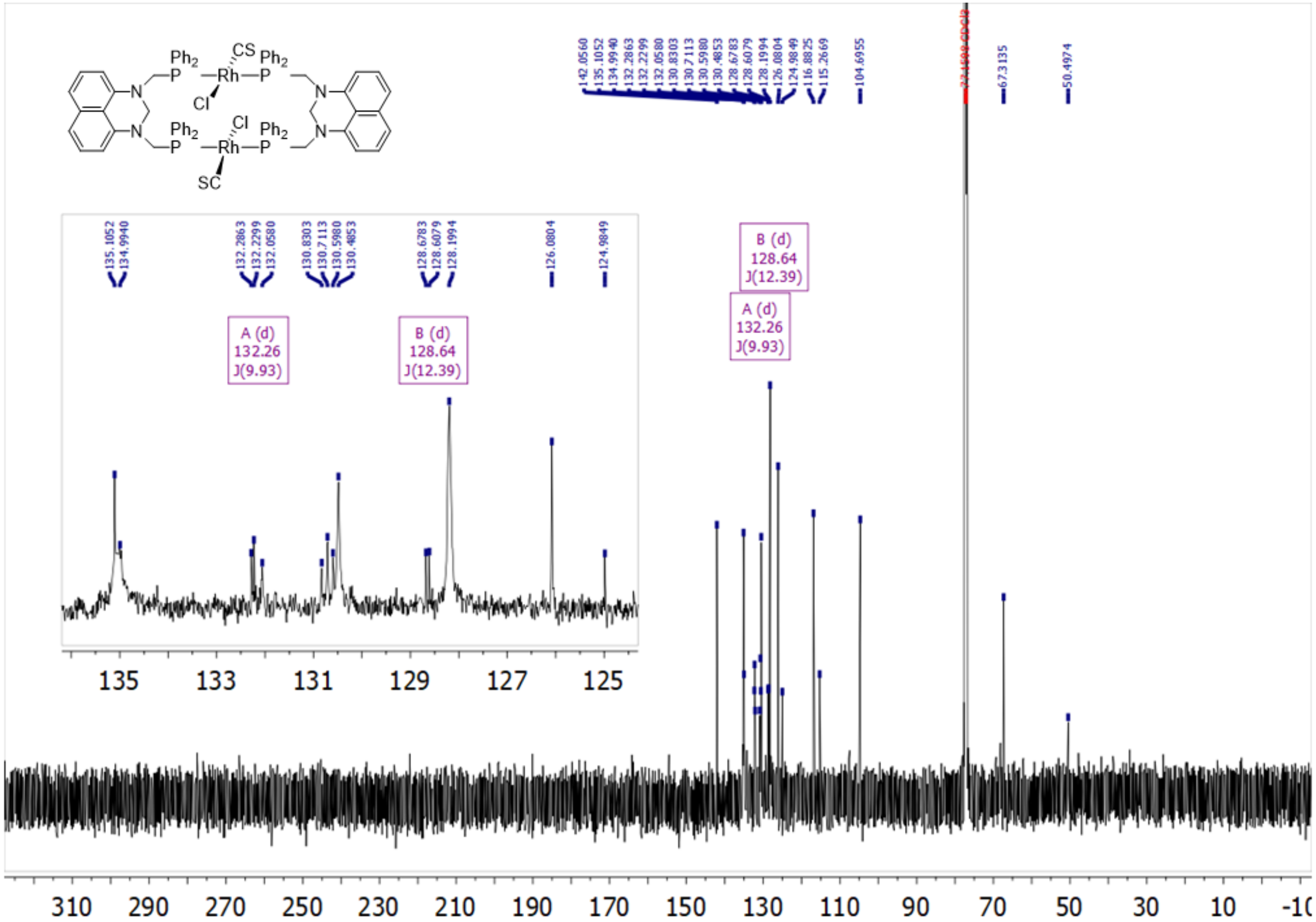
IR (CH_2Cl_2, cm^{-1}) for $[RhCl(CS)(\mu\text{-}PhH_2Pm)]_2$ (**3a**).



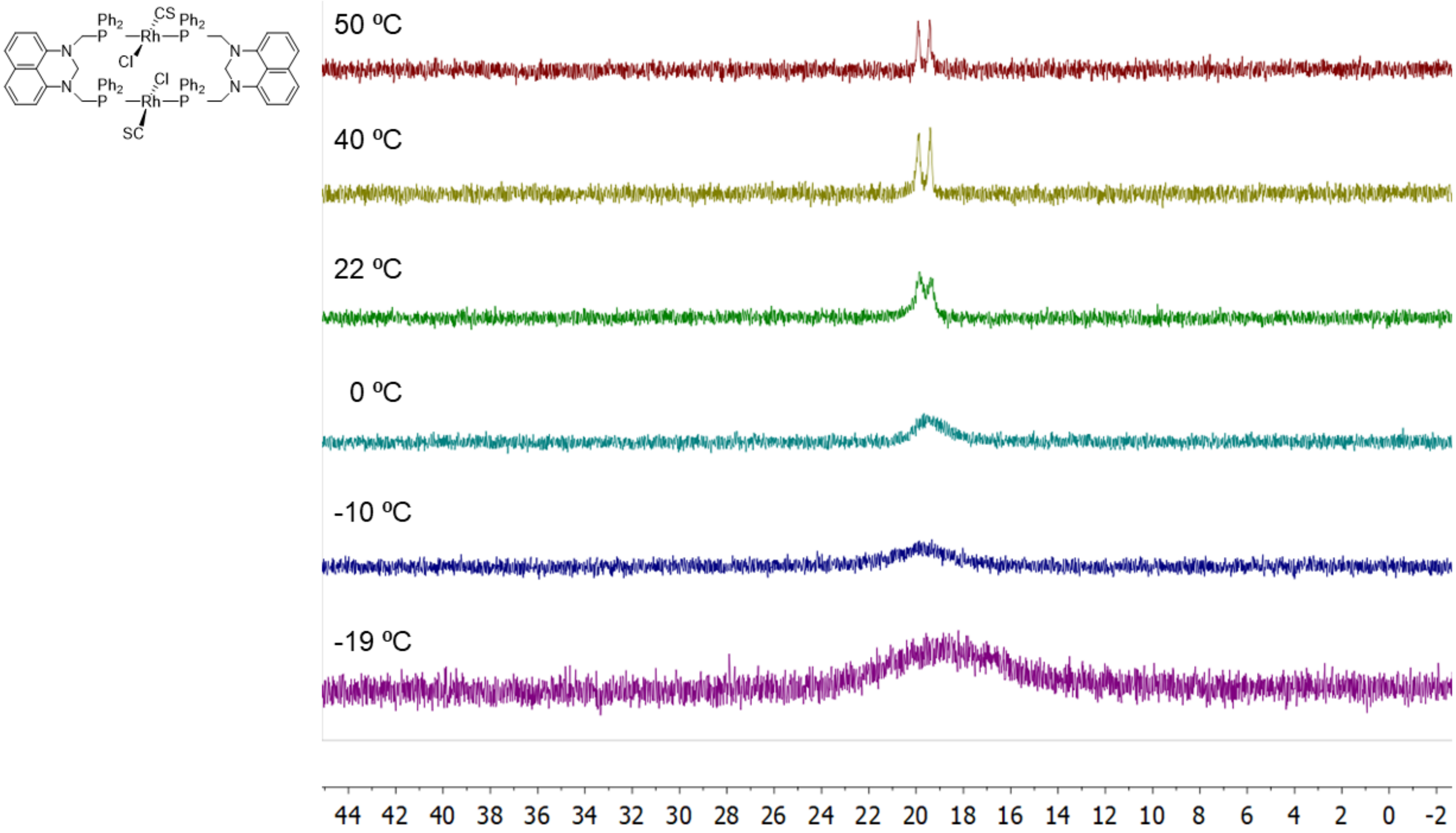
^{1}H NMR (700 MHz, $CDCl_3$, 298K) for $[RhCl(CS)(\mu\text{-}PhH_2Pm)]_2$ (**3a**).



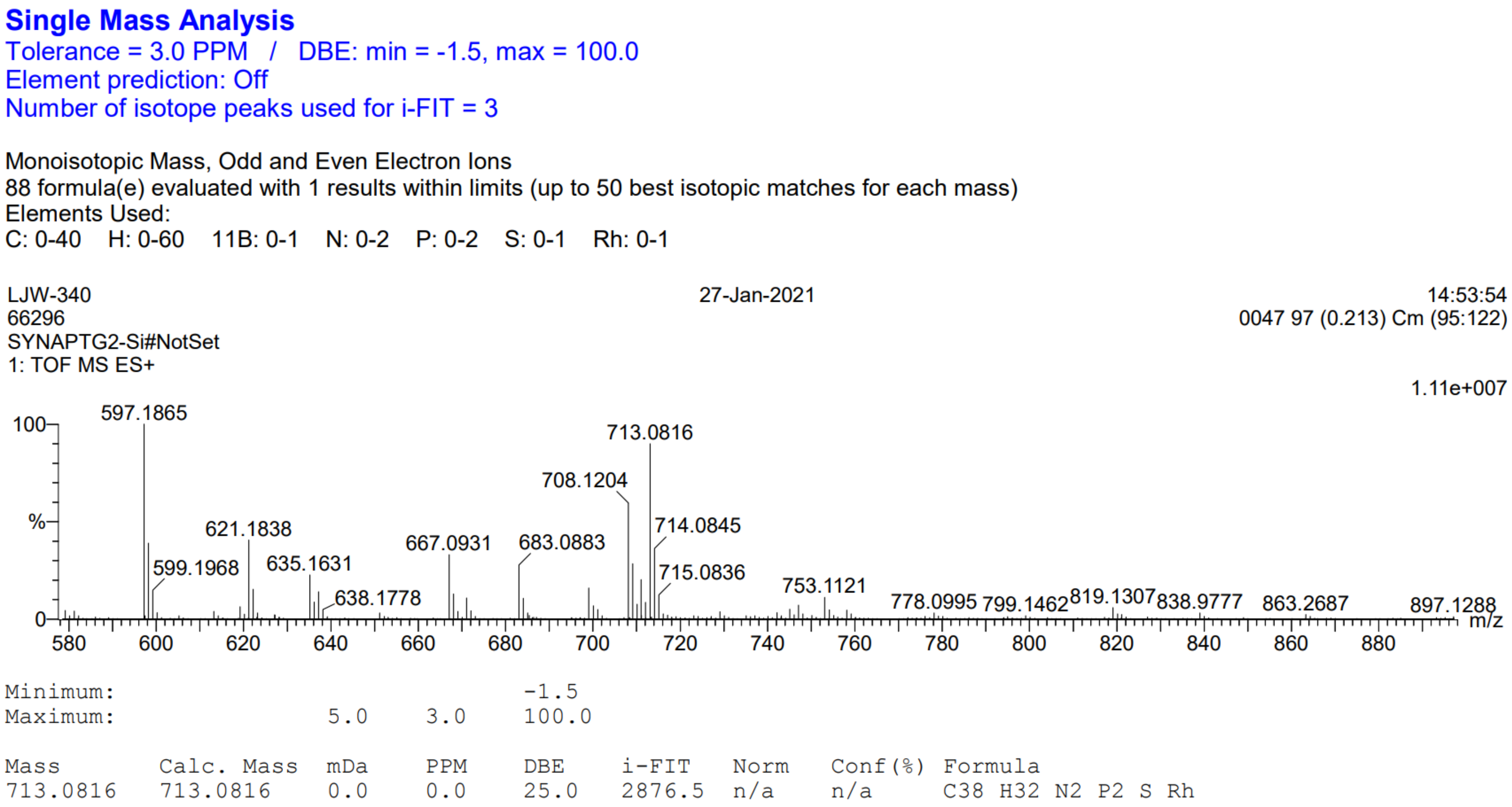
$^{31}P\{^1H\}$ NMR (163 MHz, $CDCl_3$, 298 K) for $[RhCl(CS)(\mu\text{-}PhH_2Pm)]_2$ (**3a**).



$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) for $[RhCl(CS)(\mu\text{-}PhH_2Pm)]_2$ (**3a**).



Variable temperature $^{31}P\{^1H\}$ NMR (163 MHz, $CDCl_3$, 298 K) for $[RhCl(CS)(\mu\text{-}PhH_2Pm)]_2$ (**3a**).



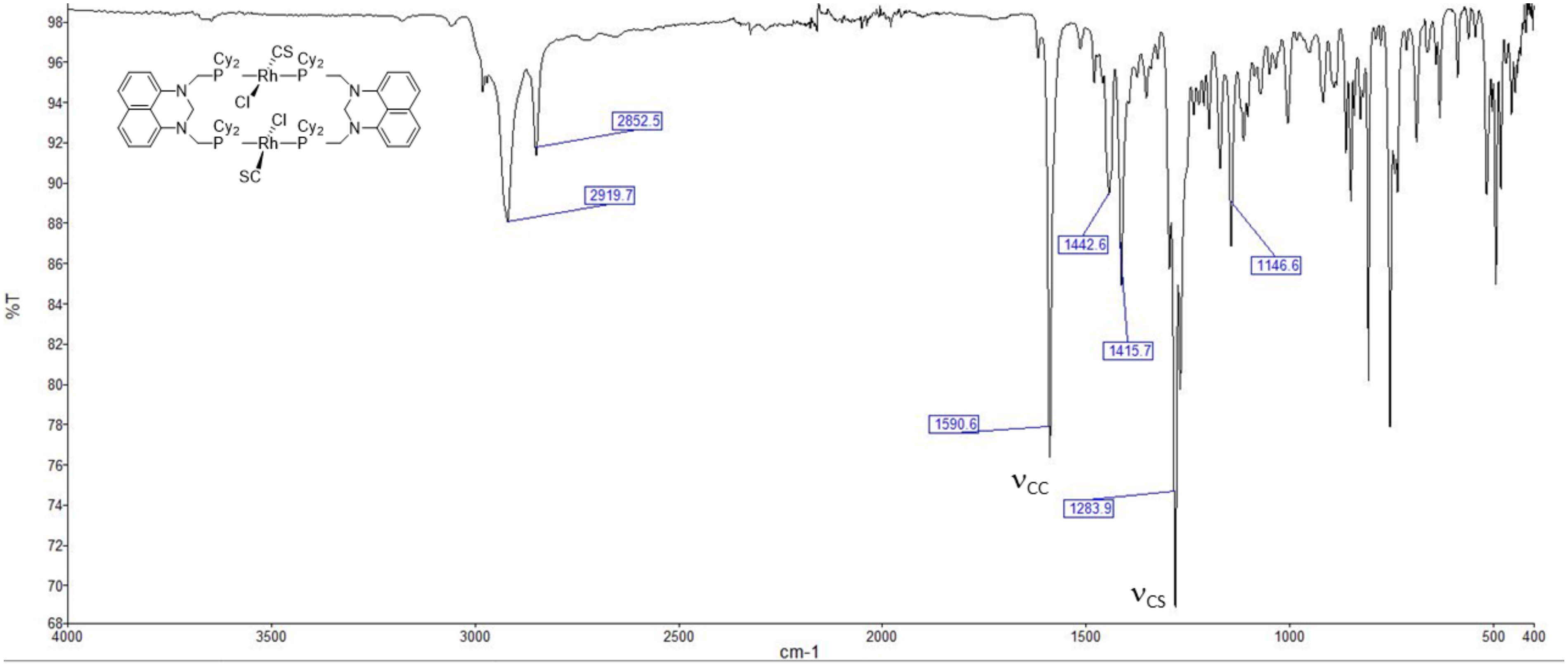
Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
88 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-40 H: 0-60 11B: 0-1 N: 0-2 P: 0-2 S: 0-1 Rh: 0-1

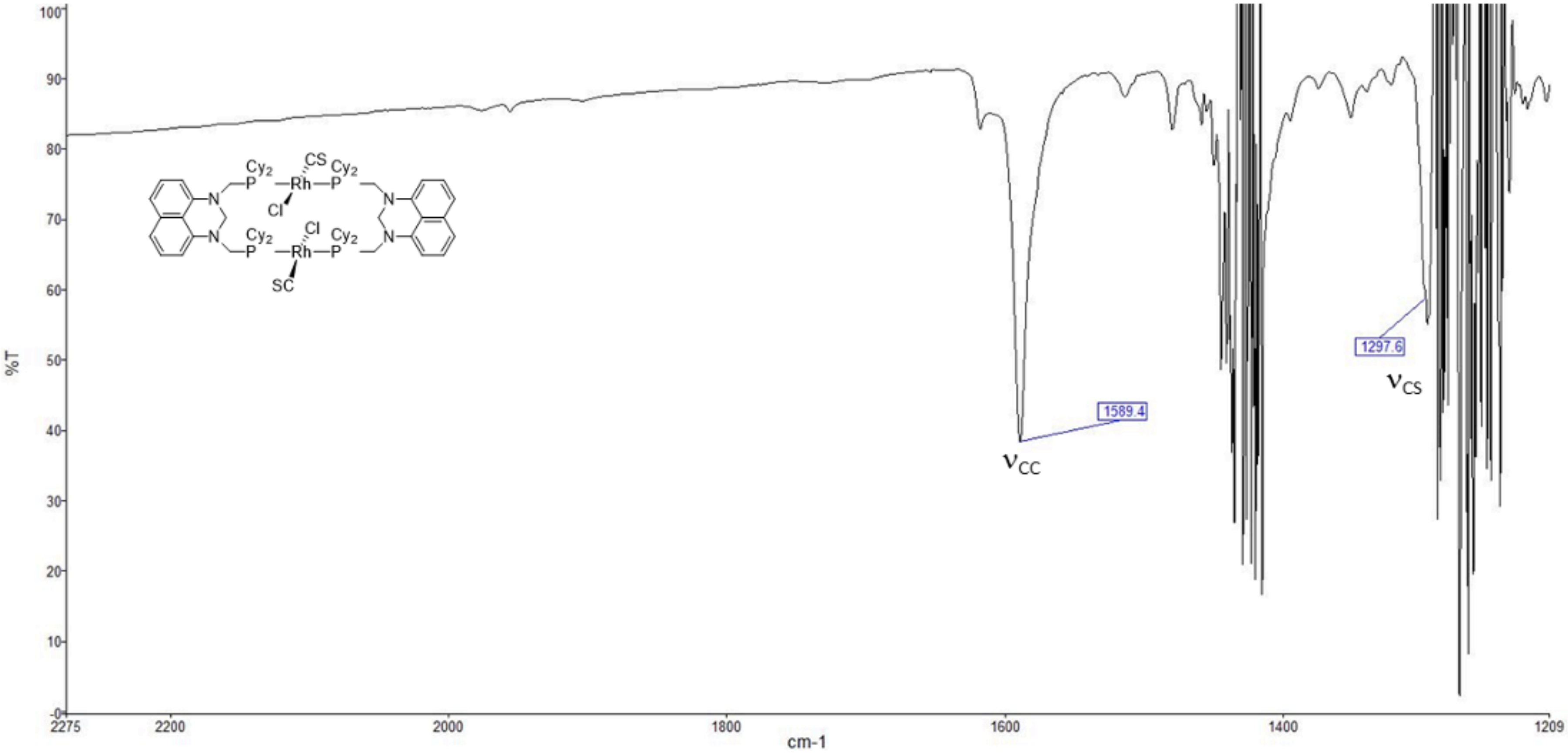
LJW-340 27-Jan-2021 14:53:54
66296 0047 97 (0.213) Cm (95:122)
SYNAPTG2-Si#NotSet
1: TOF MS ES+ 1.11e+007

```
Minimum:                              -1.5
Maximum:                  5.0    3.0   100.0

Mass       Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula
713.0816   713.0816    0.0    0.0    25.0   2876.5  n/a    n/a      C38 H32 N2 P2 S Rh
```

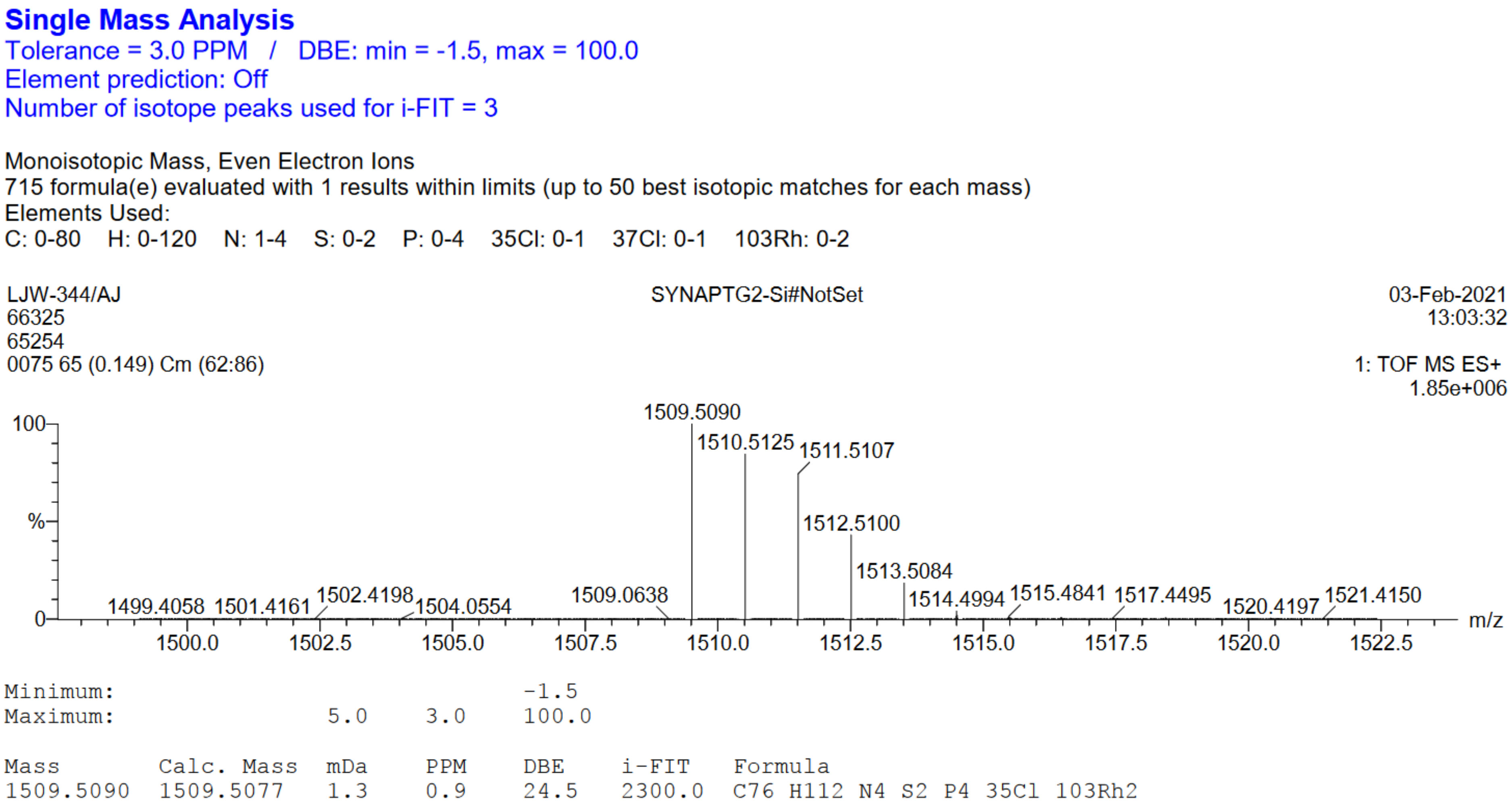
MS (ESI, +ve ion) for $[RhCl(CS)(\mu\text{-}PhH_2Pm)]_2$ (**3a**).



IR (ATR, cm^{-1}) for [RhCl(CS)(μ-CyH$_2$Pm)]$_2$ (**3b**).



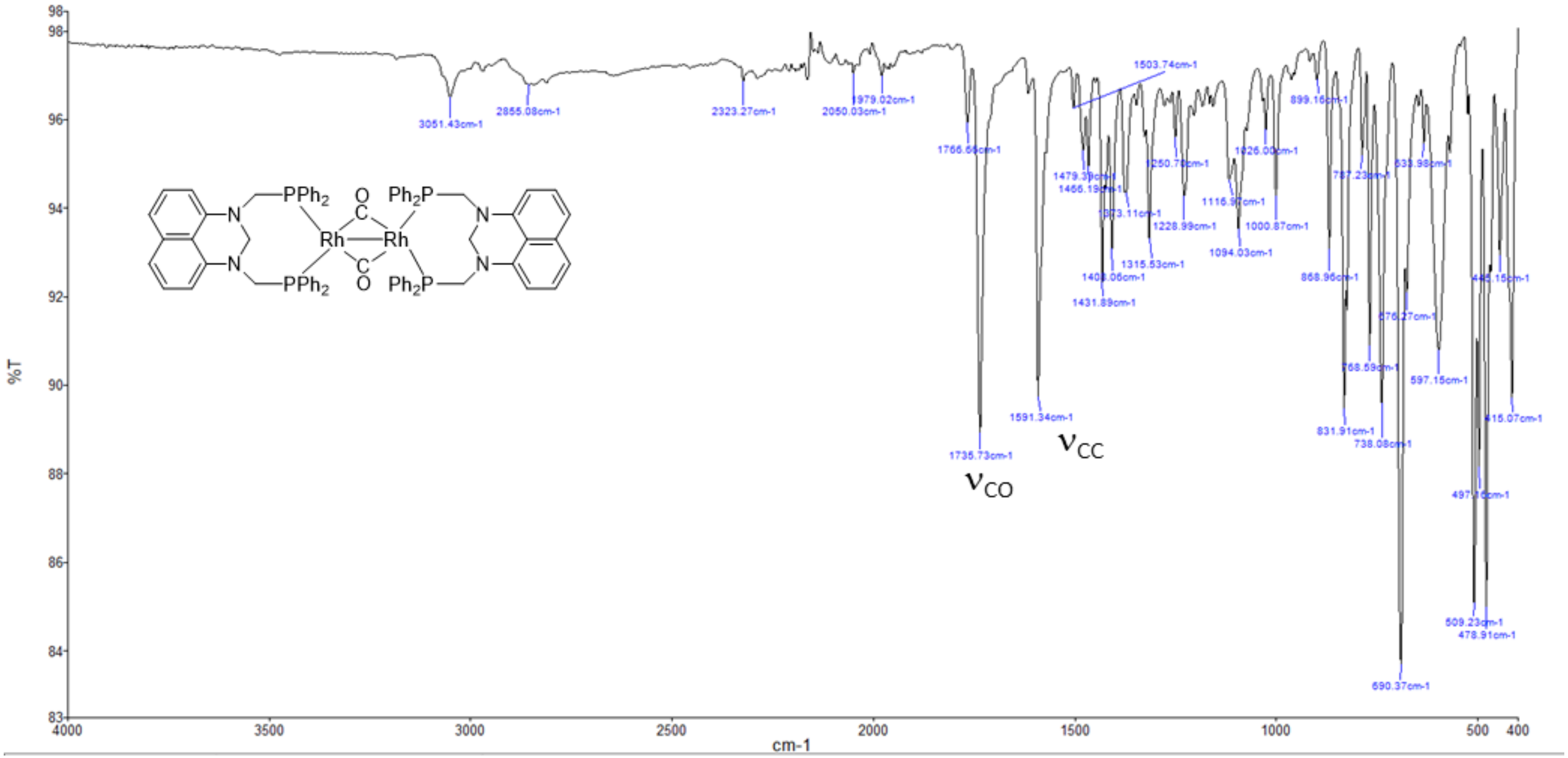
IR (CH_2Cl_2, cm^{-1}) for $[RhCl(CS)(\mu\text{-}CyH_2Pm)]_2$ (**3b**).



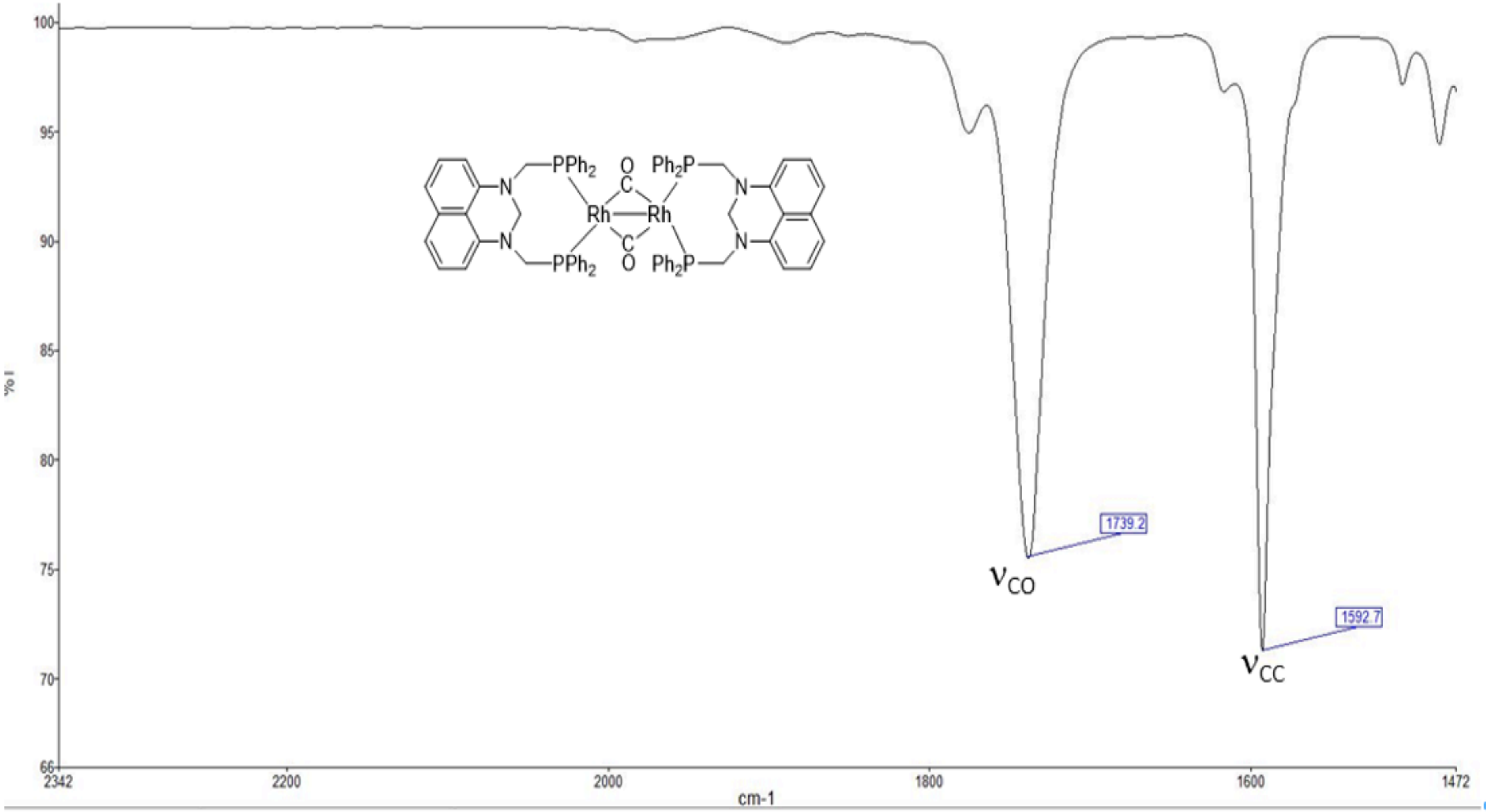
```
Single Mass Analysis
Tolerance = 3.0 PPM   /   DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
715 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-80   H: 0-120   N: 1-4   S: 0-2   P: 0-4   35Cl: 0-1   37Cl: 0-1   103Rh: 0-2

LJW-344/AJ                                   SYNAPTG2-Si#NotSet                              03-Feb-2021
66325                                                                                           13:03:32
65254
0075 65 (0.149) Cm (62:86)                                                                 1: TOF MS ES+
                                                                                               1.85e+006
```

```
Minimum:                            -1.5
Maximum:              5.0    3.0   100.0

Mass       Calc. Mass  mDa    PPM   DBE    i-FIT   Formula
1509.5090  1509.5077   1.3    0.9   24.5   2300.0  C76 H112 N4 S2 P4 35Cl 103Rh2
```

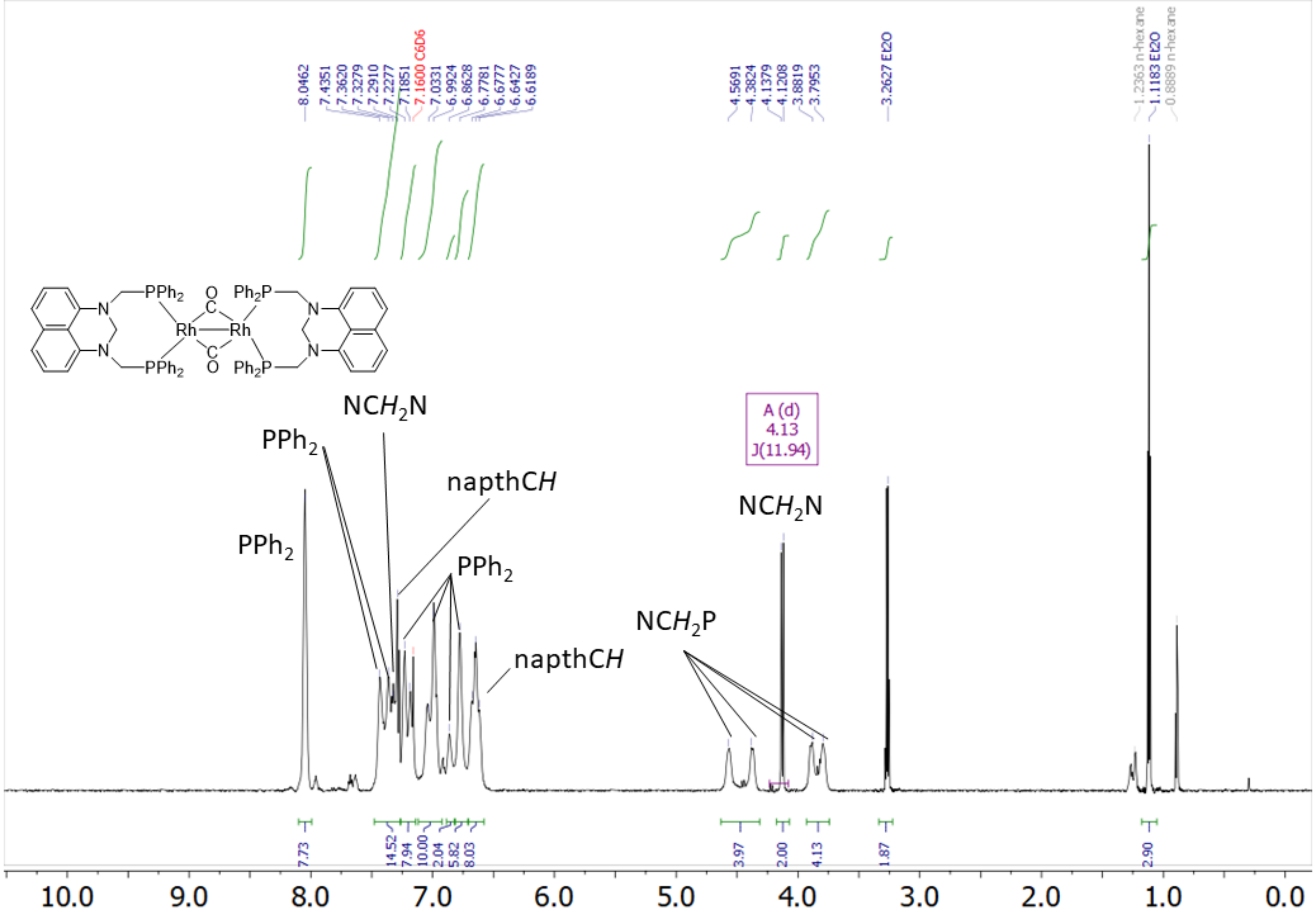
MS (ESI, +ve ion) for [RhCl(CS)(μ-CyH$_2$Pm)]$_2$ (**3b**).



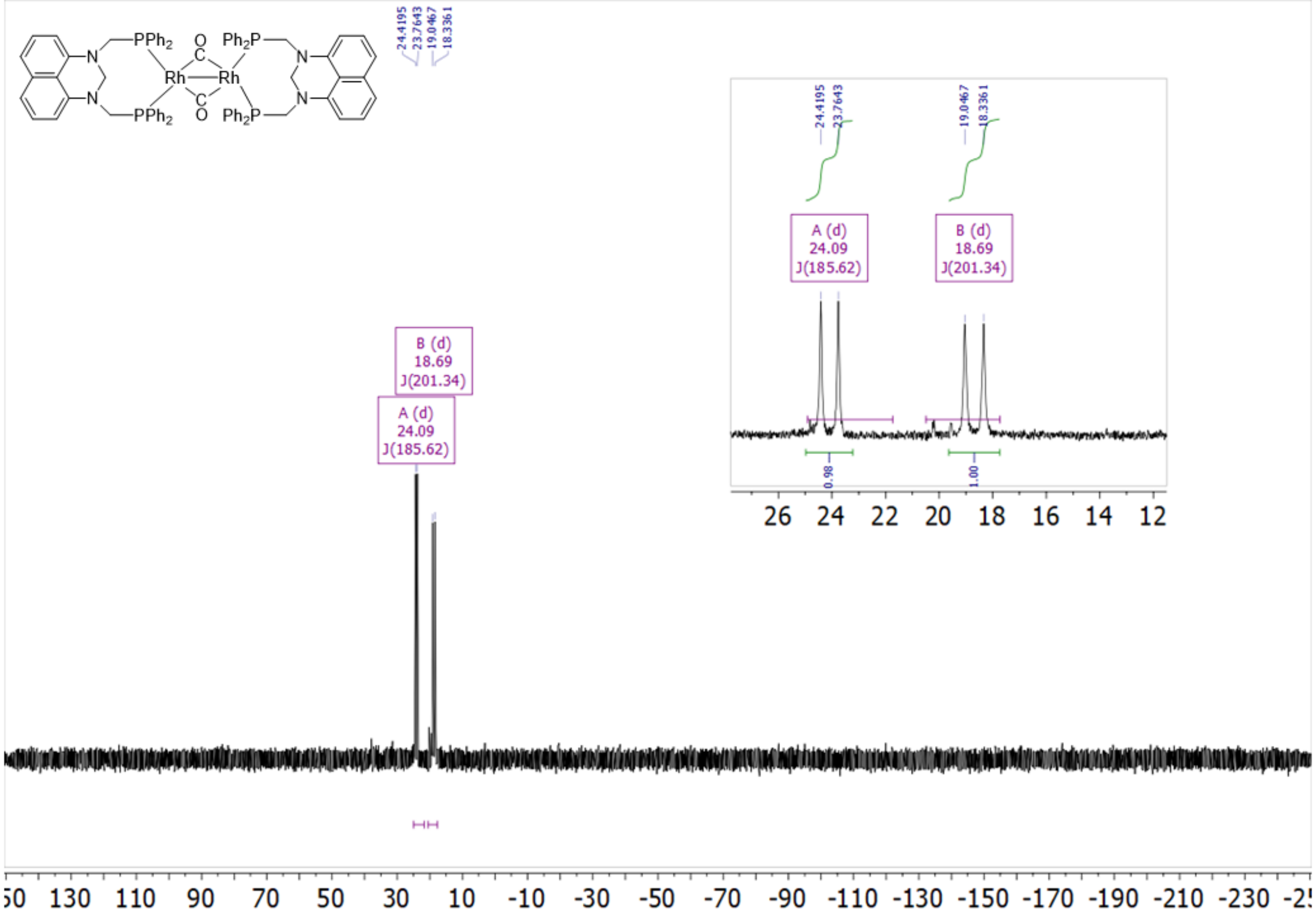
IR (ATR, cm-1) for [Rh_2(μ-CO)$_2$(PhH_2Pm)$_2$] (**4**).



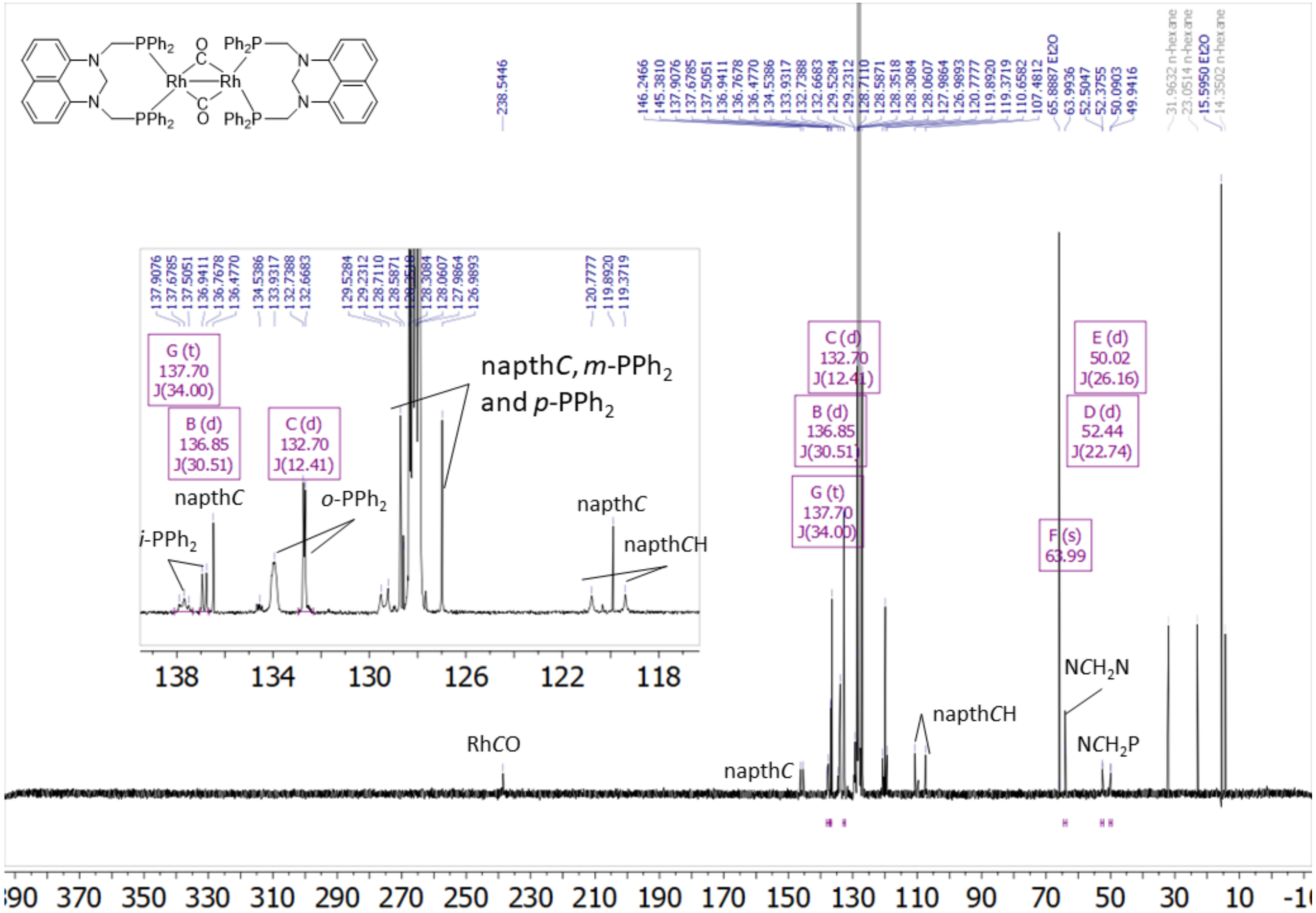
IR (THF, cm-1) for [Rh$_2$(μ-CO)$_2$(PhH$_2$Pm)$_2$] (**4**).



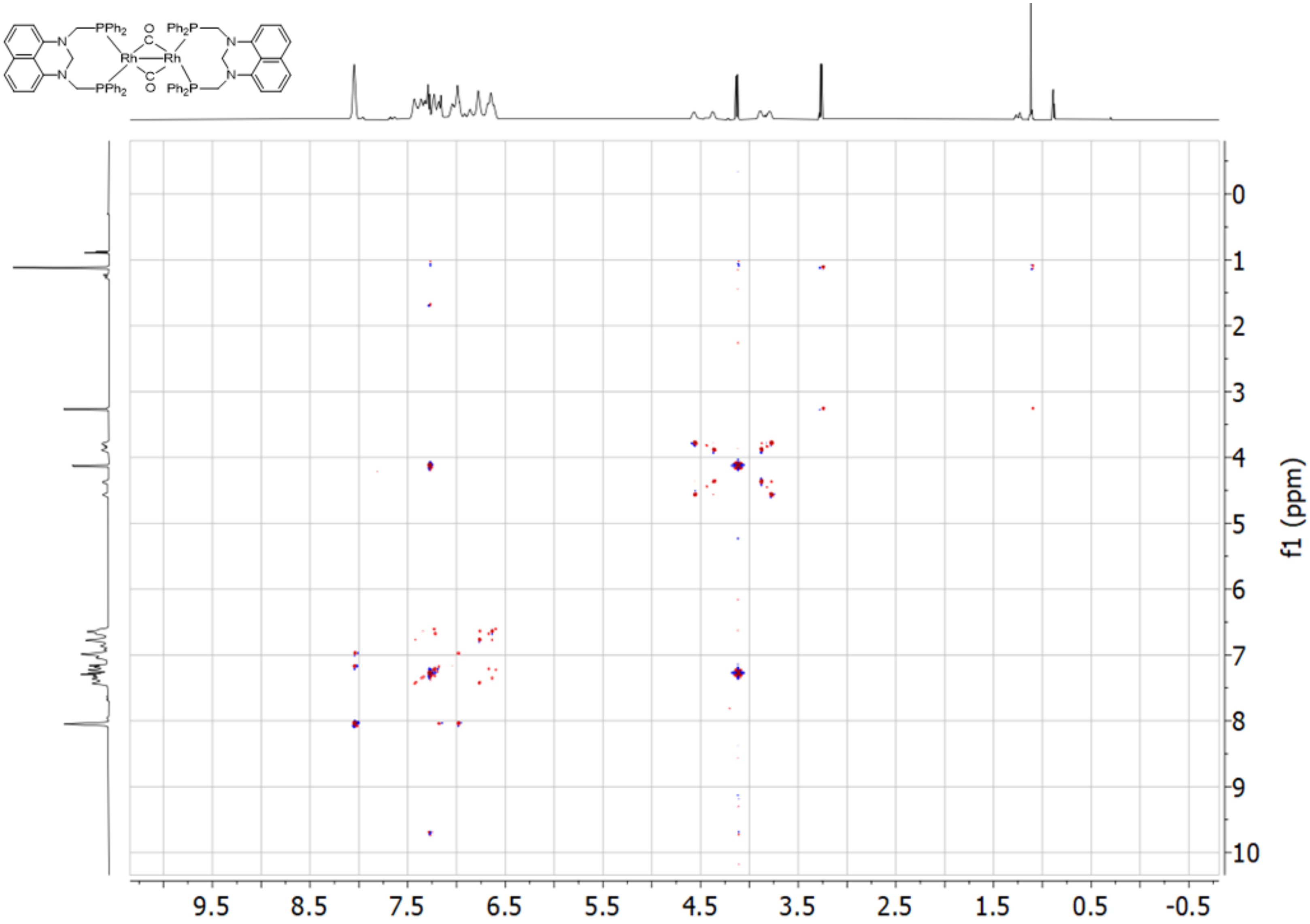
^{1}H NMR (700 MHz, C_6D_6, 298 K) for [$Rh_2(\mu\text{-}CO)_2(PhH_2Pm)_2$] (**4**).



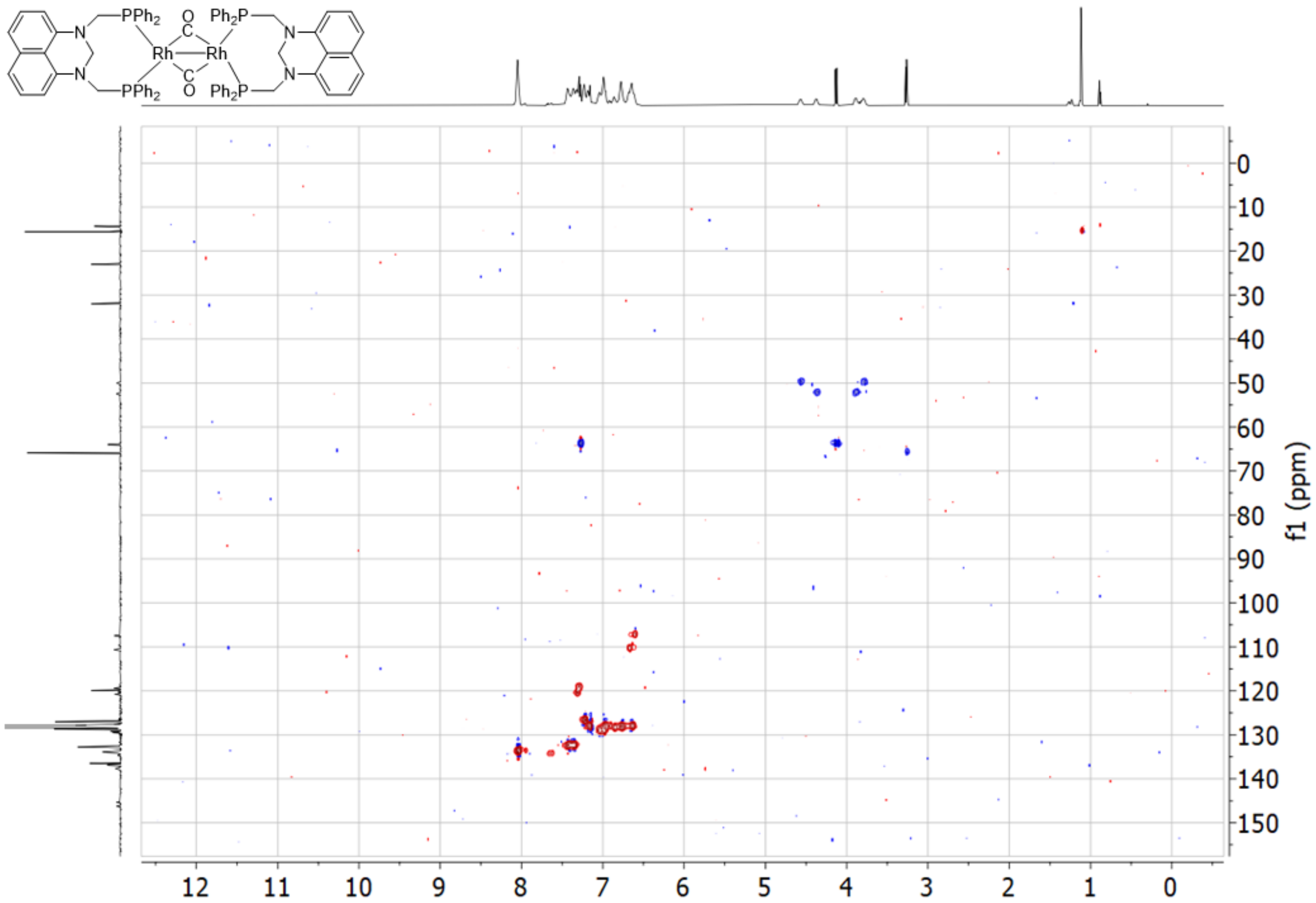
$^{31}P\{^1H\}$ NMR (283 MHz, C_6D_6, 298 K) for $[Rh_2(\mu\text{-CO})_2(PhH_2Pm)_2]$ (**4**).



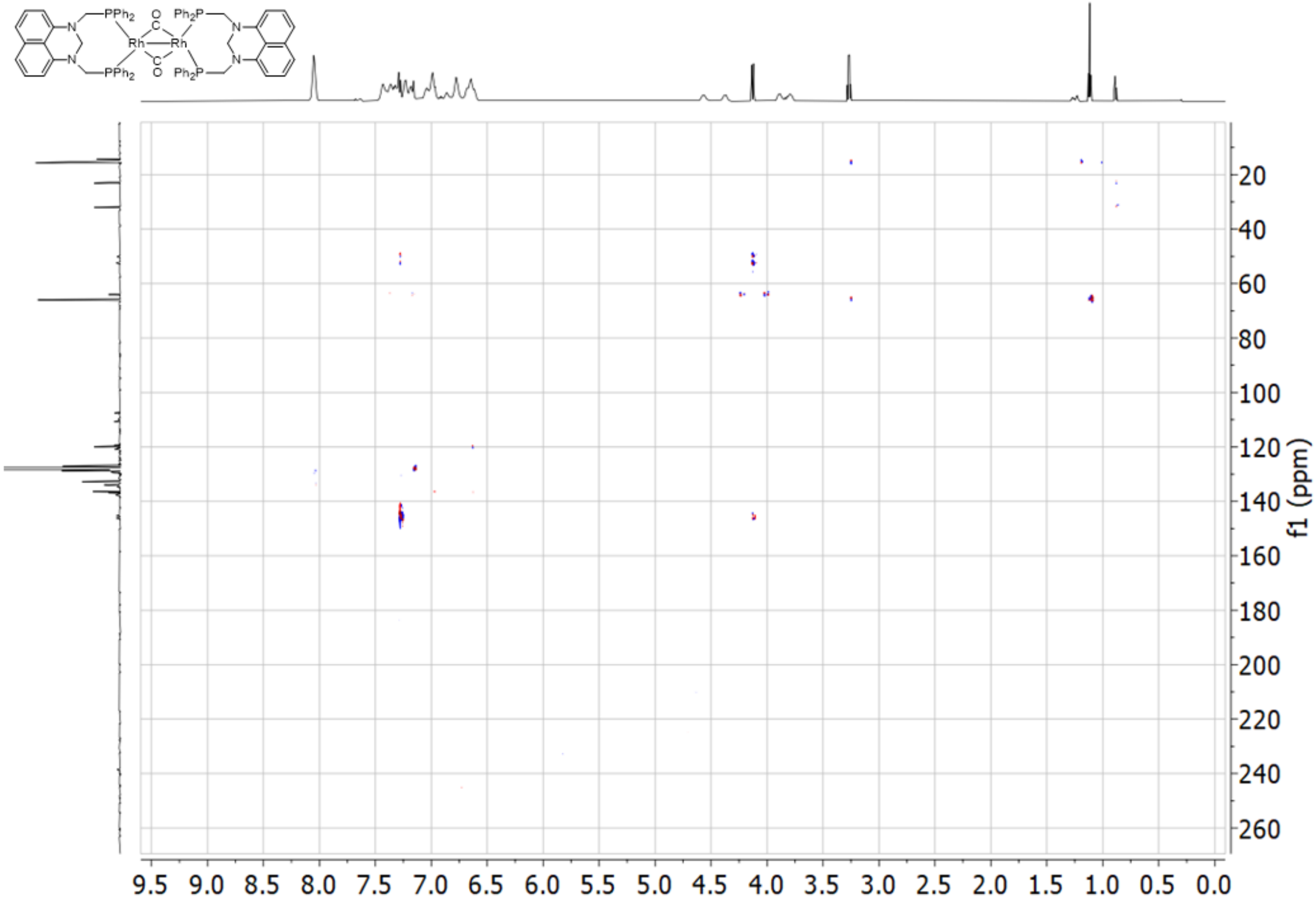
$^{13}C\{^{1}H\}$ NMR (176 MHz, C_6D_6, 298 K) for $[Rh_2(\mu\text{-}CO)_2(PhH_2Pm)_2]$ (**4**).



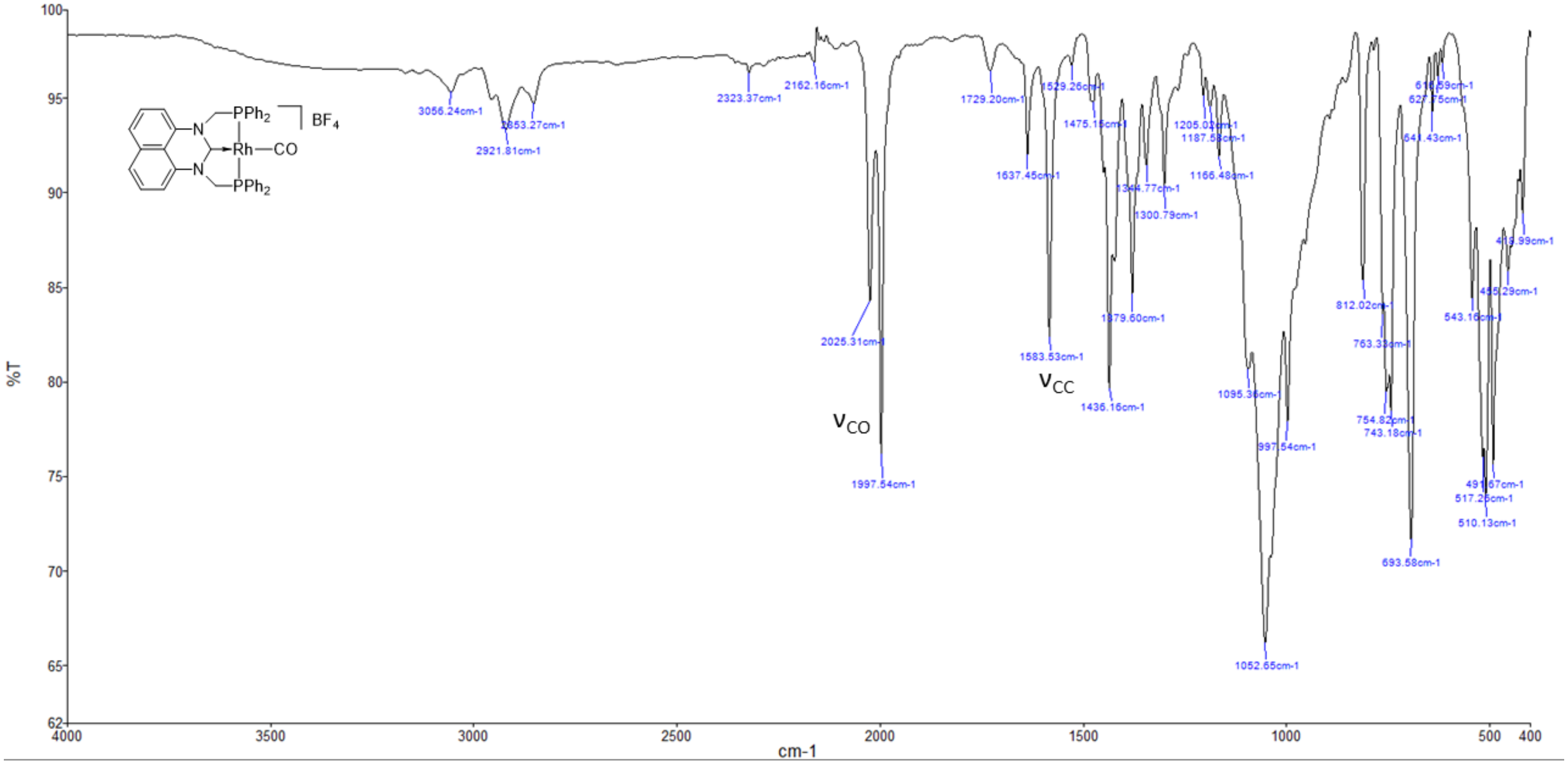
COSY NMR (C_6D_6, 298 K) for [$Rh_2(\mu\text{-}CO)_2(PhH_2Pm)_2$] (**4**).



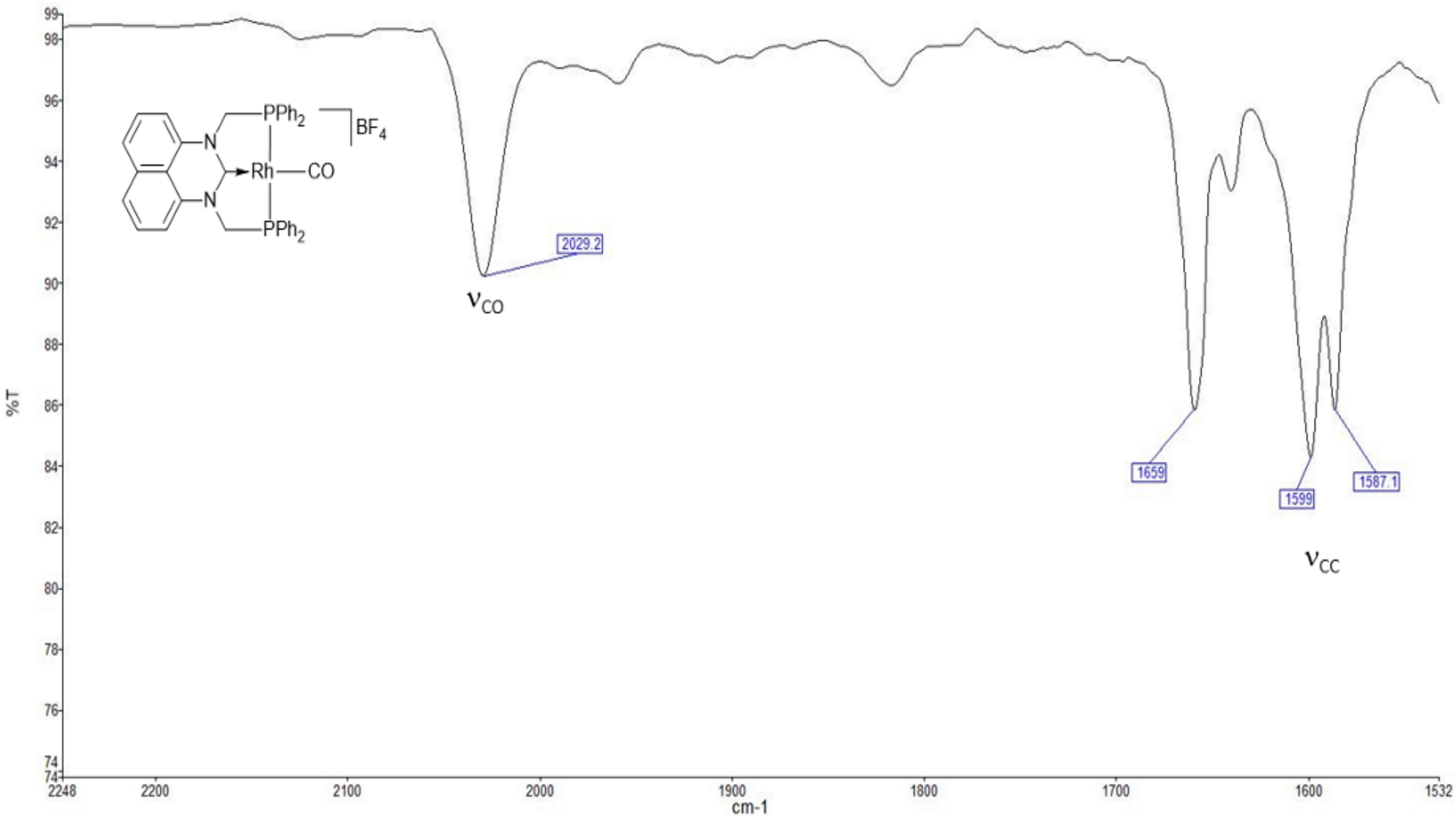
HSQC NMR (C_6D_6, 298 K) for $[Rh_2(\mu\text{-}CO)_2(PhH_2Pm)_2]$ (**4**).



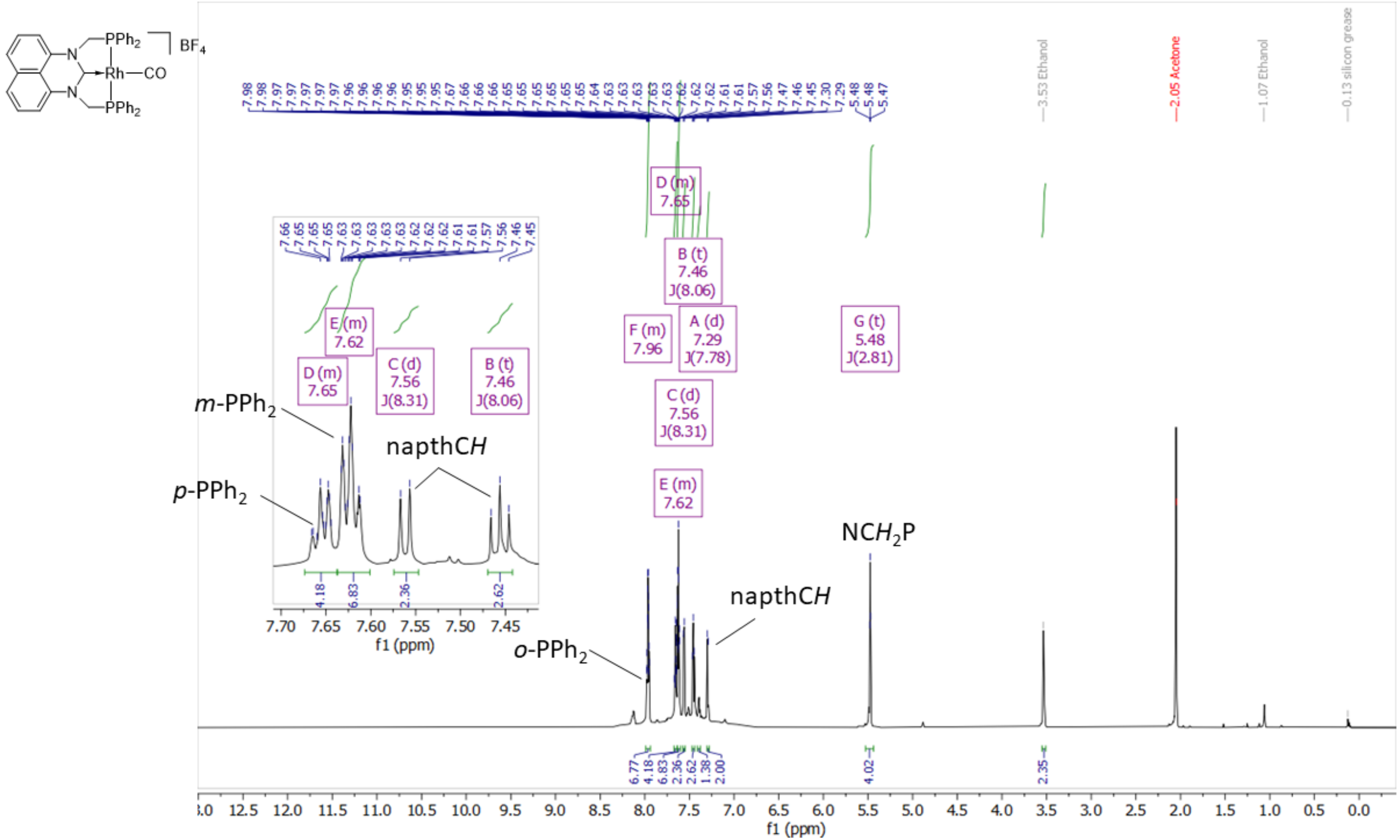
HMBC NMR (C_6D_6, 298 K) for $[Rh_2(\mu\text{-}CO)_2(PhH_2Pm)_2]$ (**4**).



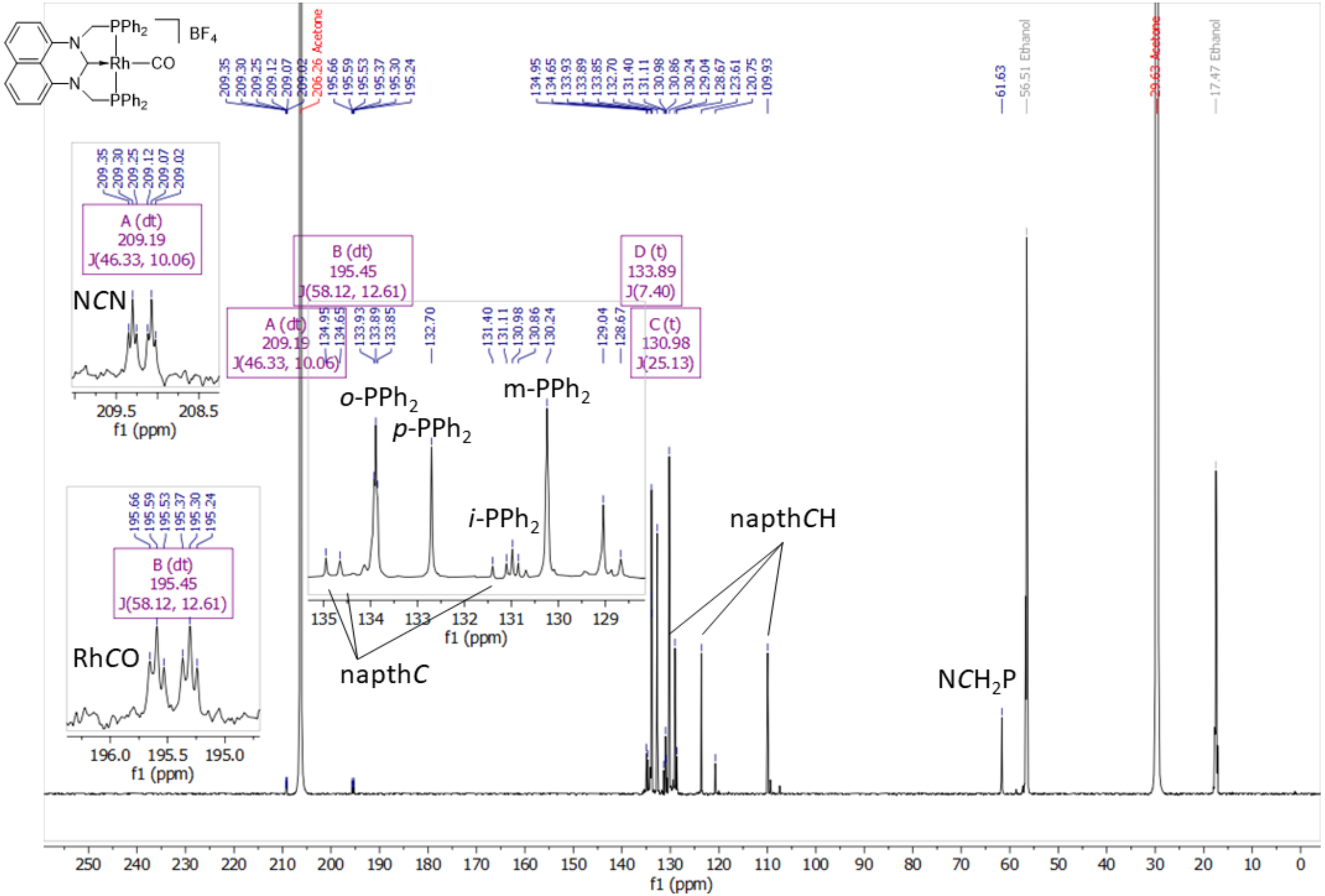
IR (ATR, cm-1) for [Rh(CO)(PhPm)]BF_4 (**5**).



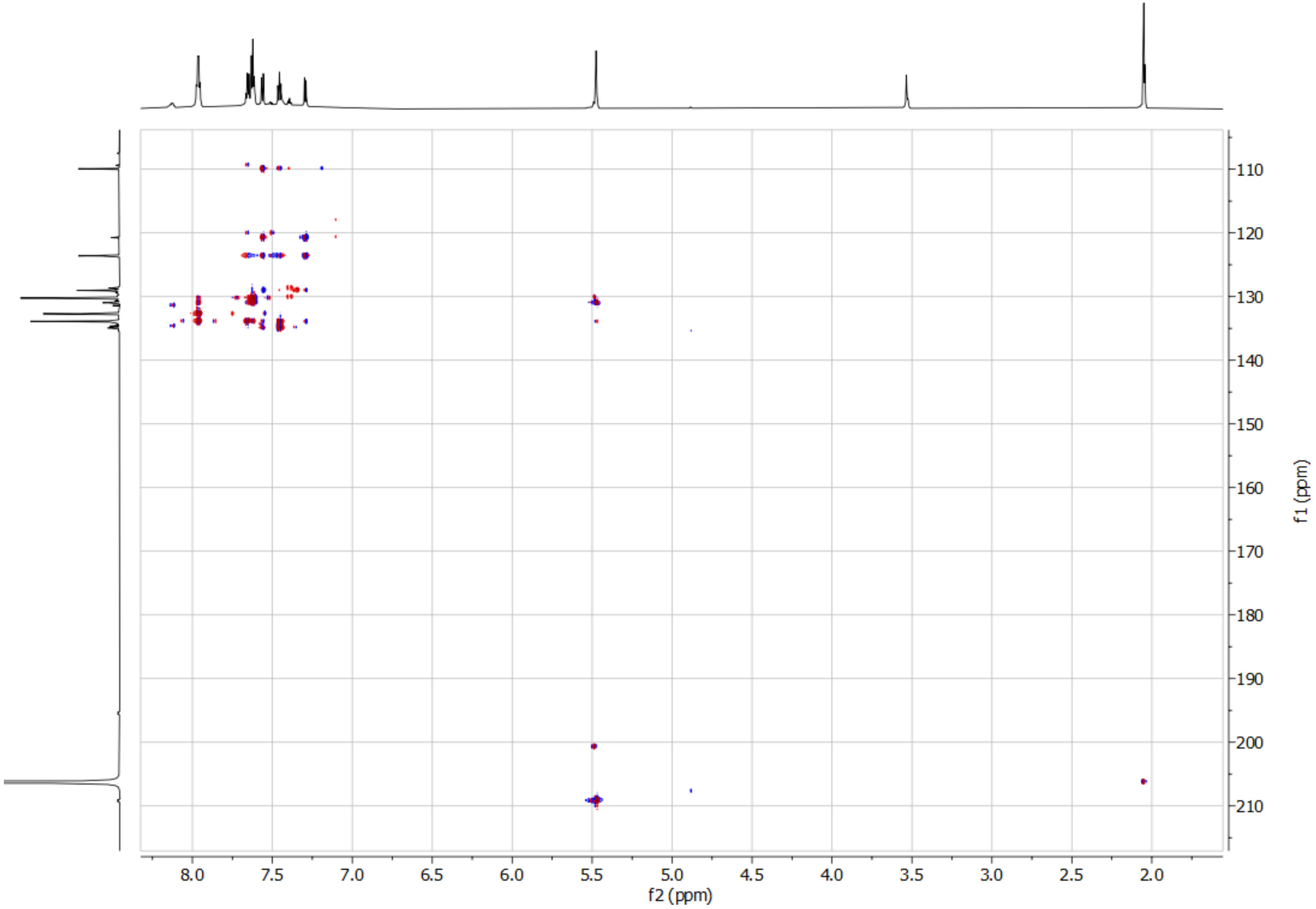
IR (CH_2Cl_2, cm^{-1}) for $[Rh(CO)(PhPm)]BF_4$ (**5**).



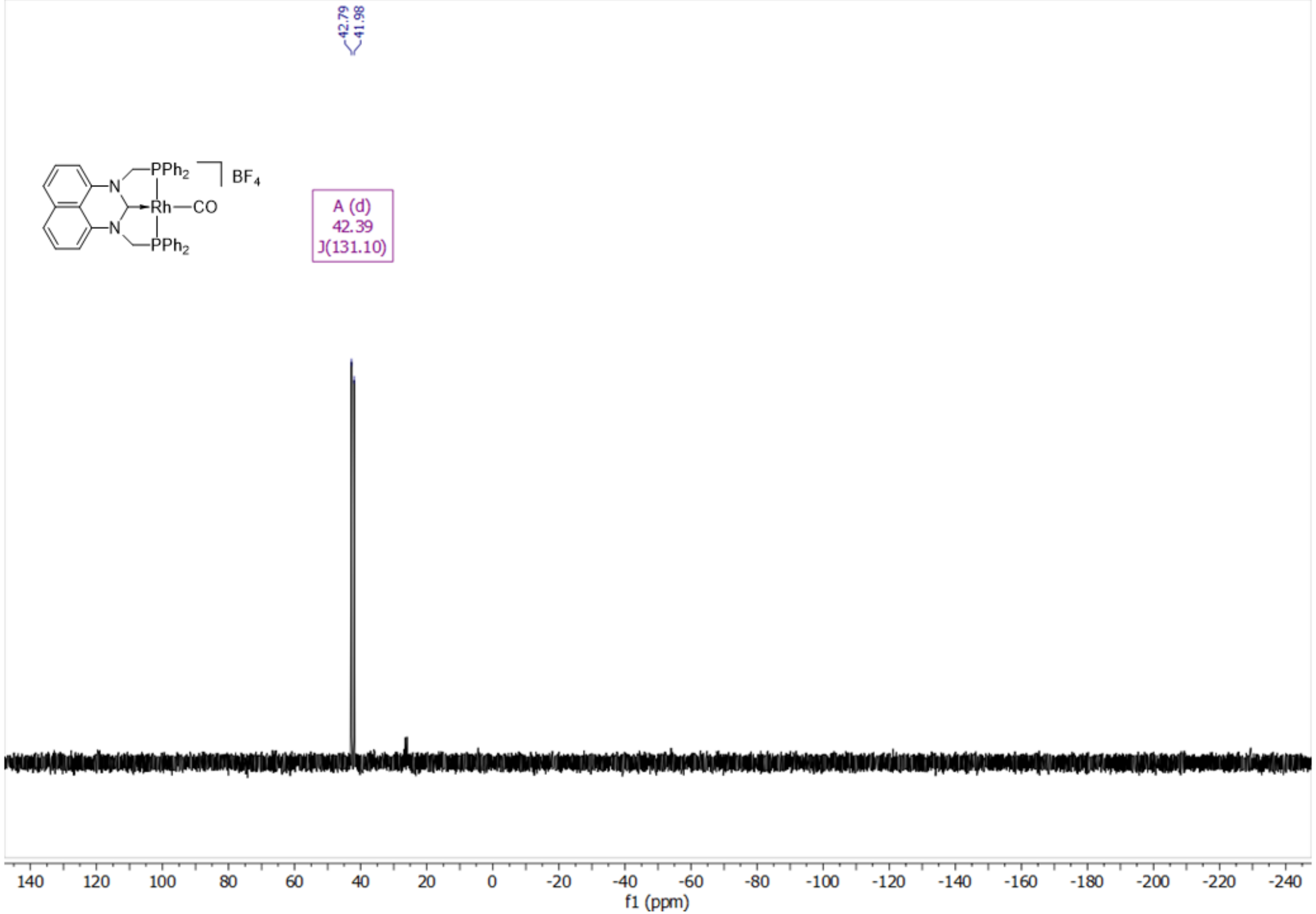
^{1}H NMR (800 MHz, $(CD_3)_2CO$, 298 K for $[Rh(CO)(PhPm)]BF_4$ (**5**).



$^{13}C\{^1H\}$ NMR (201 MHz, $(CD_3)_2CO$, 298 K) for $[Rh(CO)(PhPm)]BF_4$ (**5**).



HMBC NMR ($(CD_3)_2CO$, 298 K) for $[Rh(CO)(PhPm)]BF_4$ (**5**).



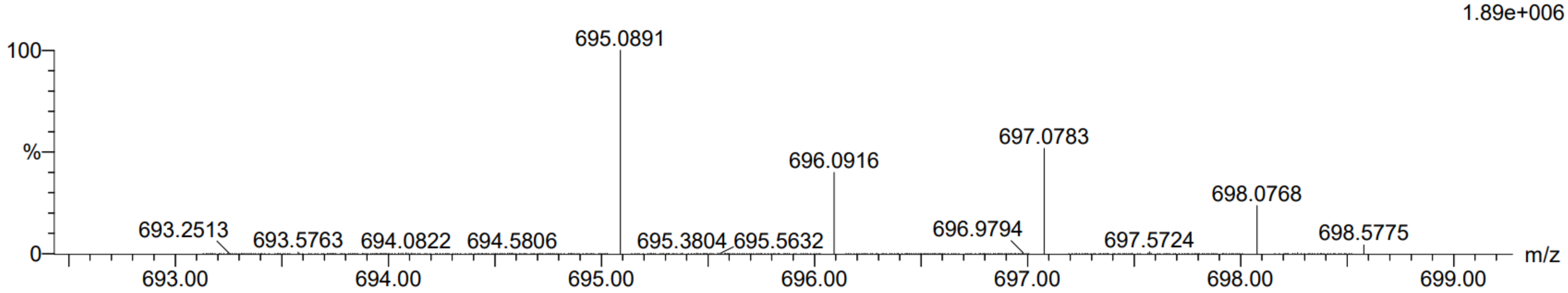
$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298 K) for $[Rh(CO)(PhPm)]BF_4$ (**5**).

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

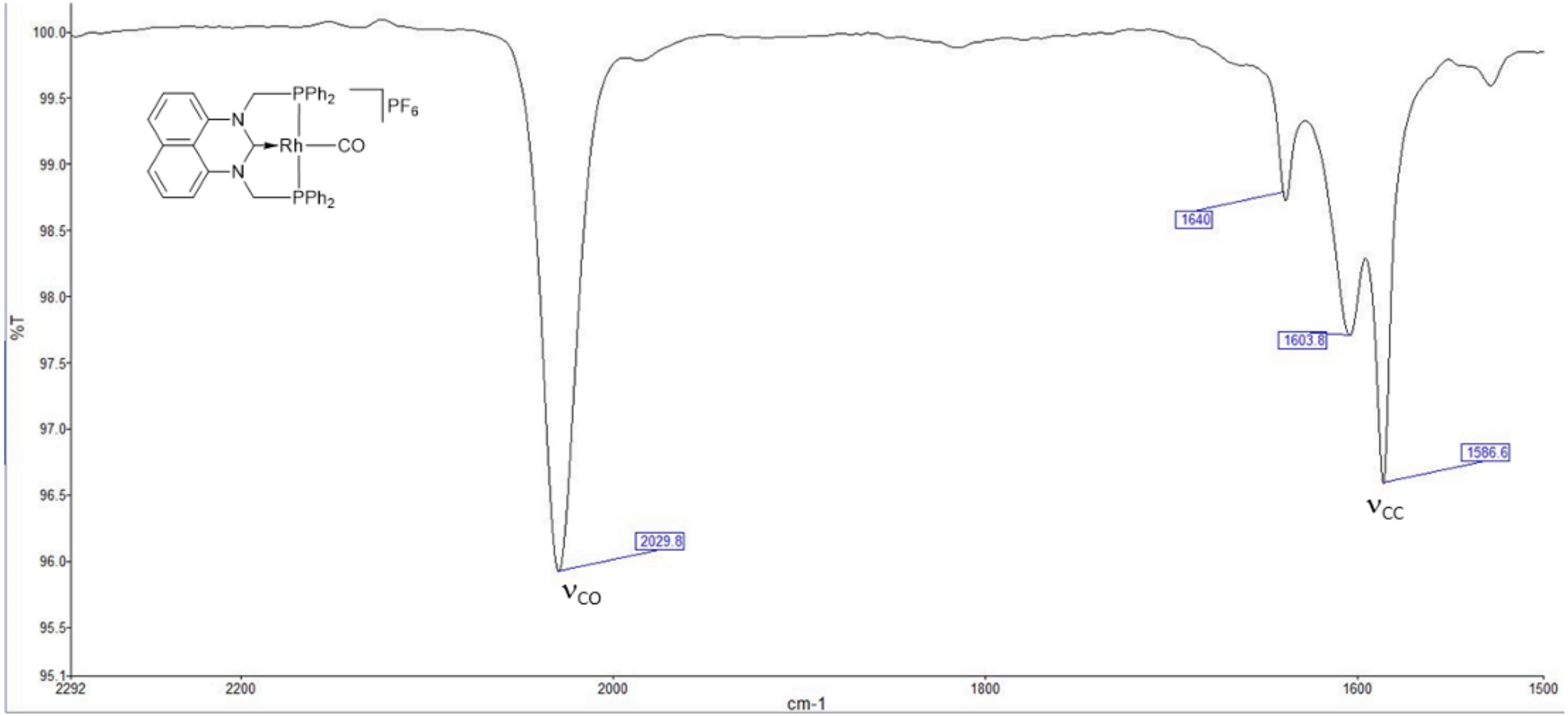
Monoisotopic Mass, Odd and Even Electron Ions
77 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-40 H: 0-40 N: 0-2 O: 0-3 P: 0-2 103Rh: 0-1

LJW-499/AJ SYNAPTG2-Si#NotSet 05-May-2022
67014 13:07:50
2365A 197 (0.412)
1: TOF MS ES+

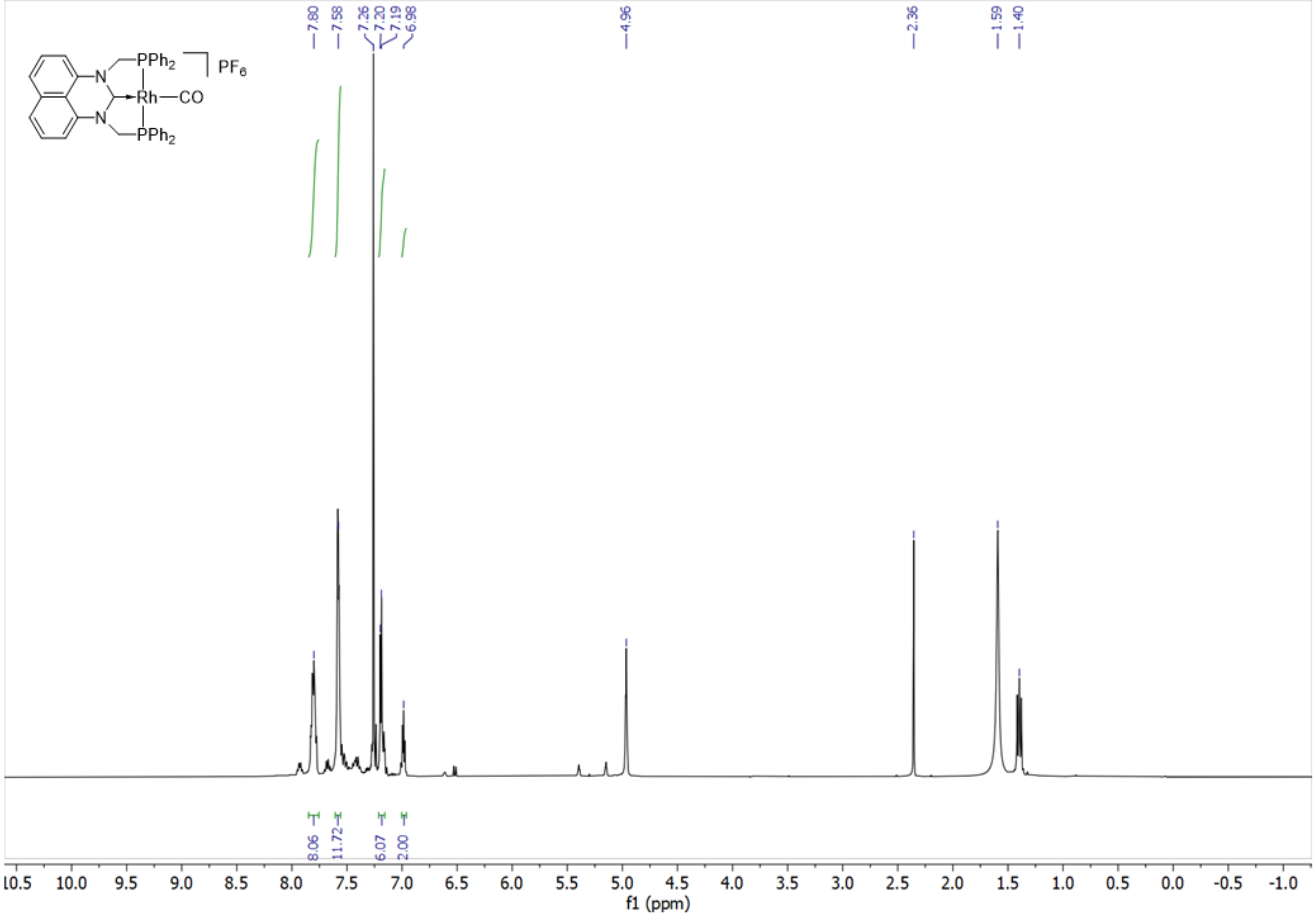


```
Minimum:                          -1.5
Maximum:              25.0   3.0   50.0

Mass       Calc. Mass  mDa    PPM    DBE    i-FIT   Formula
695.0891   695.0888    0.3    0.4    26.0   1439.5  C38 H30 N2 O P2 103Rh
```

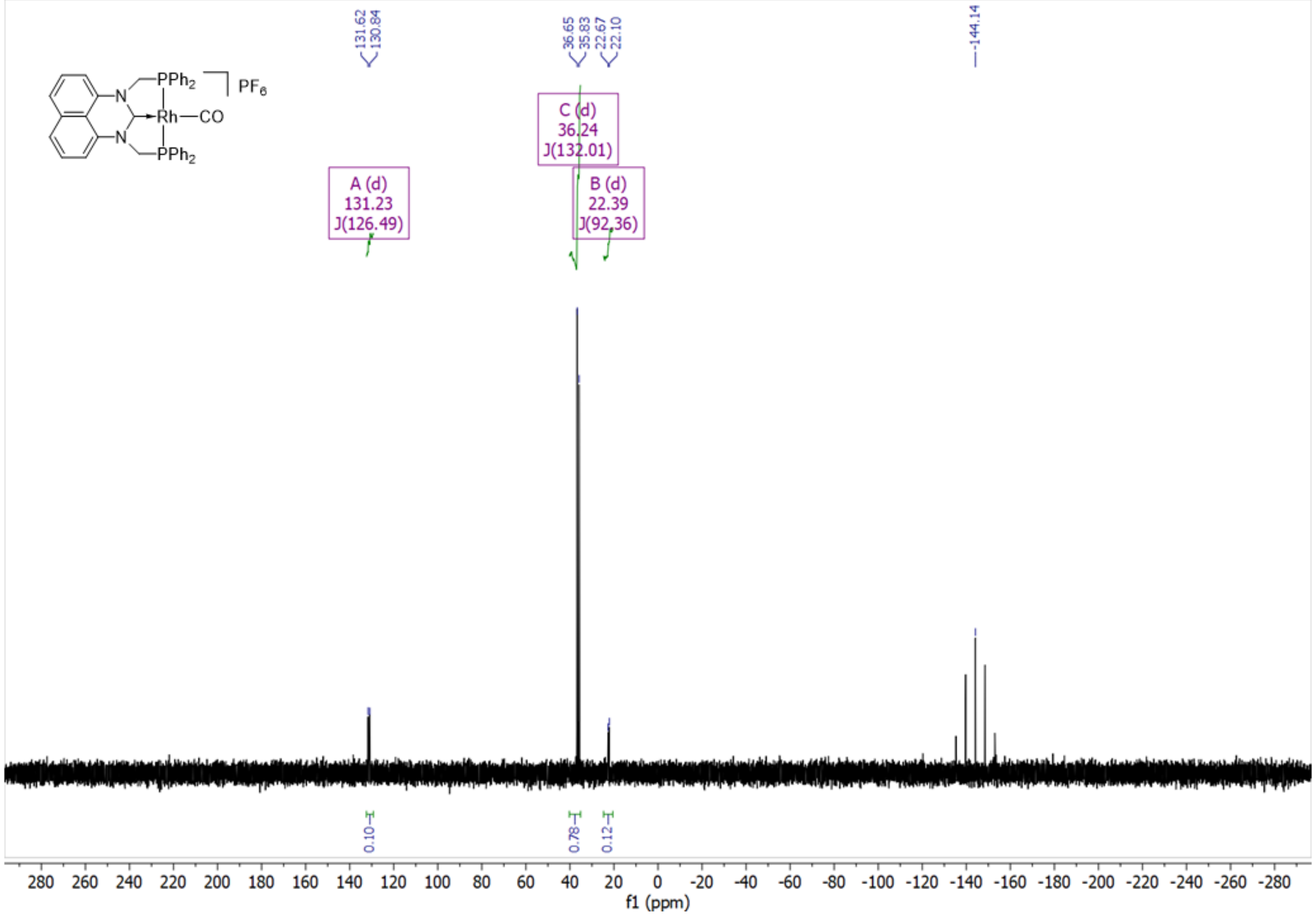
MS (ESI, +ve ion) for [Rh(CO)(PhPm)]BF_4 (**5**).



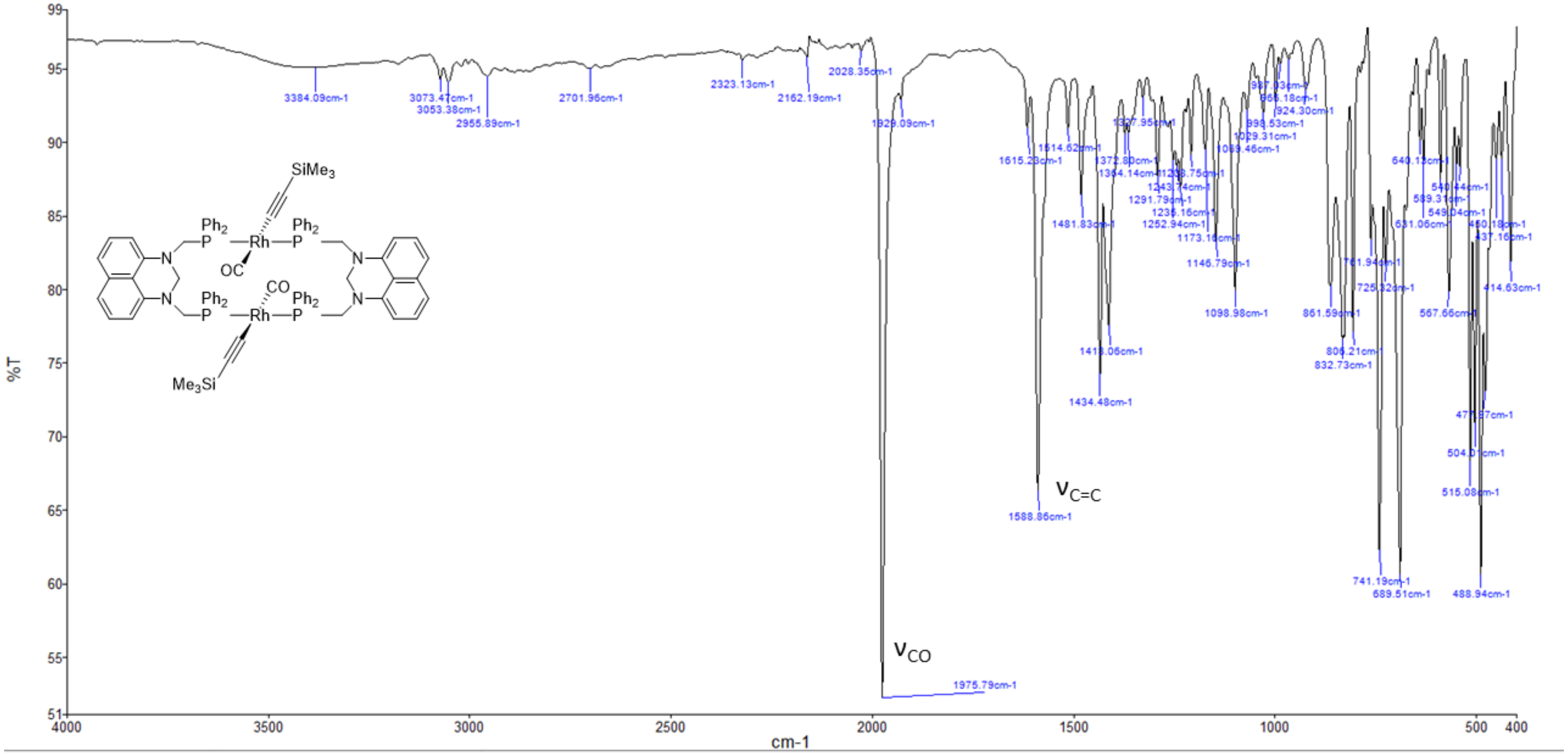
IR (ATR, cm^{-1}) for [Rh(CO)(PhPm)]PF_6 (**5**).



^{1}H NMR (400 MHz, $CDCl_3$, 298 K) for [Rh(CO)(PhPm)]PF_6 (**5**).



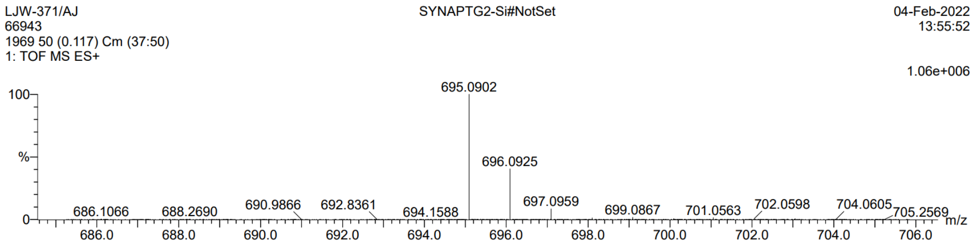
$^{31}P\{^{1}H\}$ NMR (283 MHz, $CDCl_3$, 298 K) for [Rh(CO)(PhPm)]PF_6 (**5**).



IR (ATR, cm^{-1}) for [Rh(CO)(C≡CSiMe$_3$)(μ-PhH$_2$Pm)]$_2$ (**6**).

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 28.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

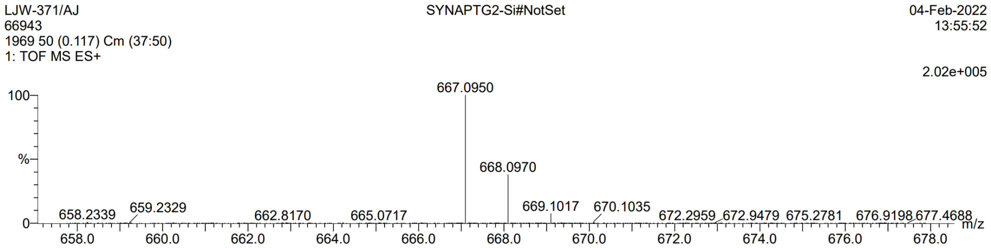
Monoisotopic Mass, Odd and Even Electron Ions
847 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-5 P: 0-2 103Rh: 0-1



```
Minimum:                        -1.5
Maximum:           25.0    3.0   28.0

Mass      Calc. Mass  mDa    PPM    DBE    i-FIT  Norm   Conf(%) Formula
695.0902  695.0888    1.4    2.0    26.0   881.2  n/a    n/a     C38 H30 N2 O P2 103Rh
```

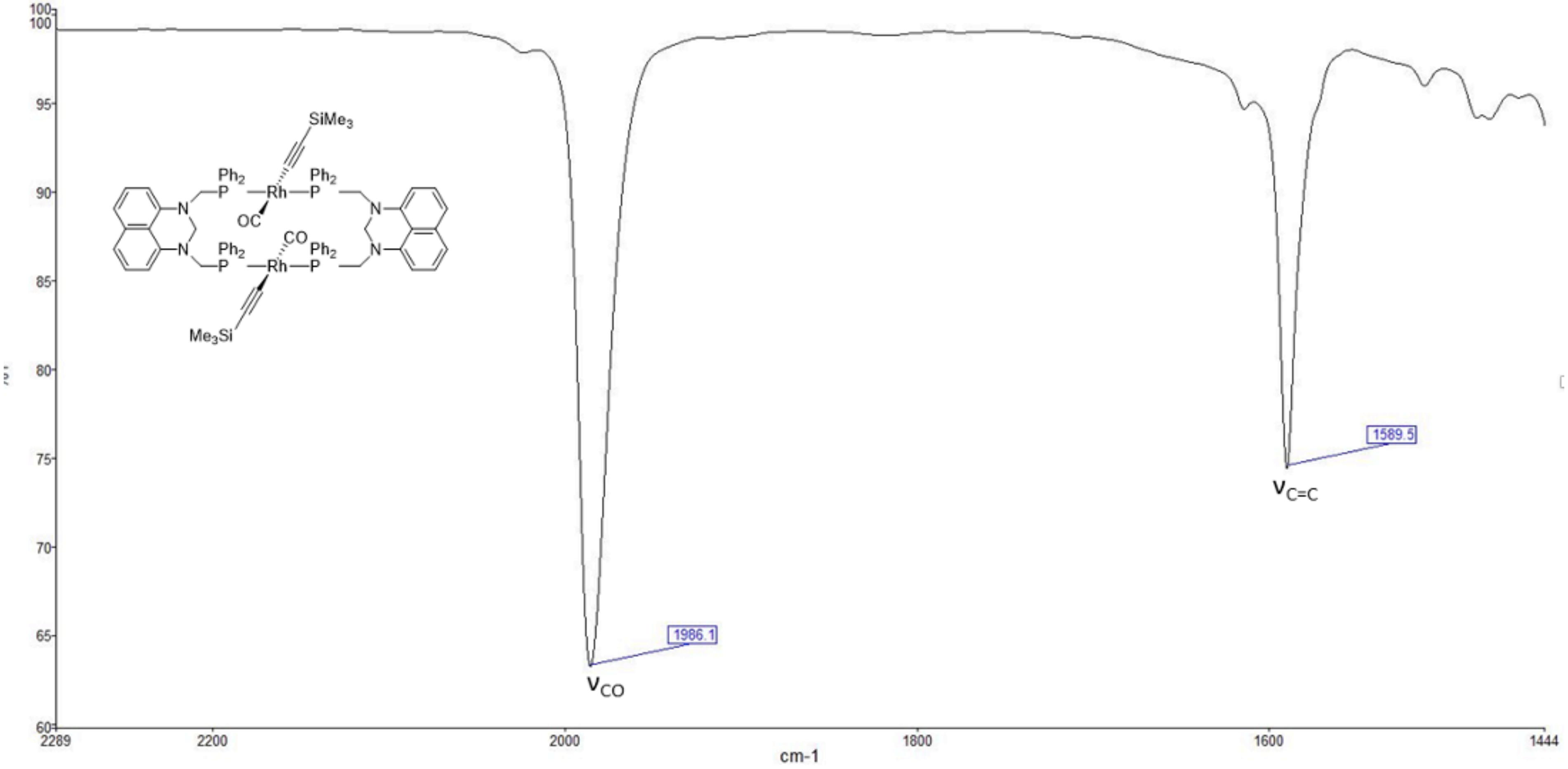
Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 28.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
903 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-5 P: 0-2 103Rh: 0-1

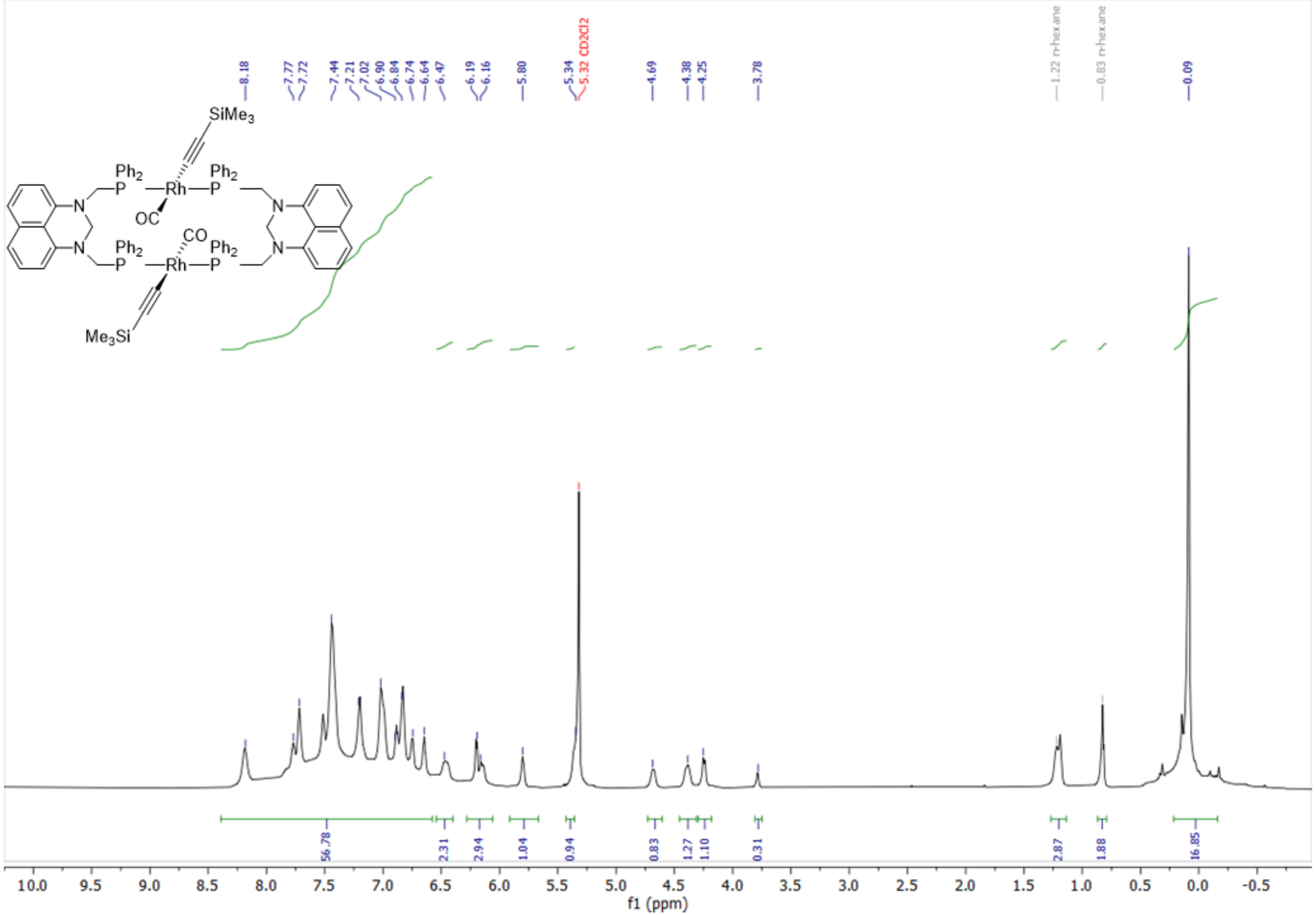


```
Minimum:                        -1.5
Maximum:           25.0    3.0   28.0

Mass      Calc. Mass  mDa    PPM    DBE    i-FIT  Norm   Conf(%) Formula
667.0950  667.0939    1.1    1.6    25.0   662.9  n/a    n/a     C37 H30 N2 P2 103Rh
```

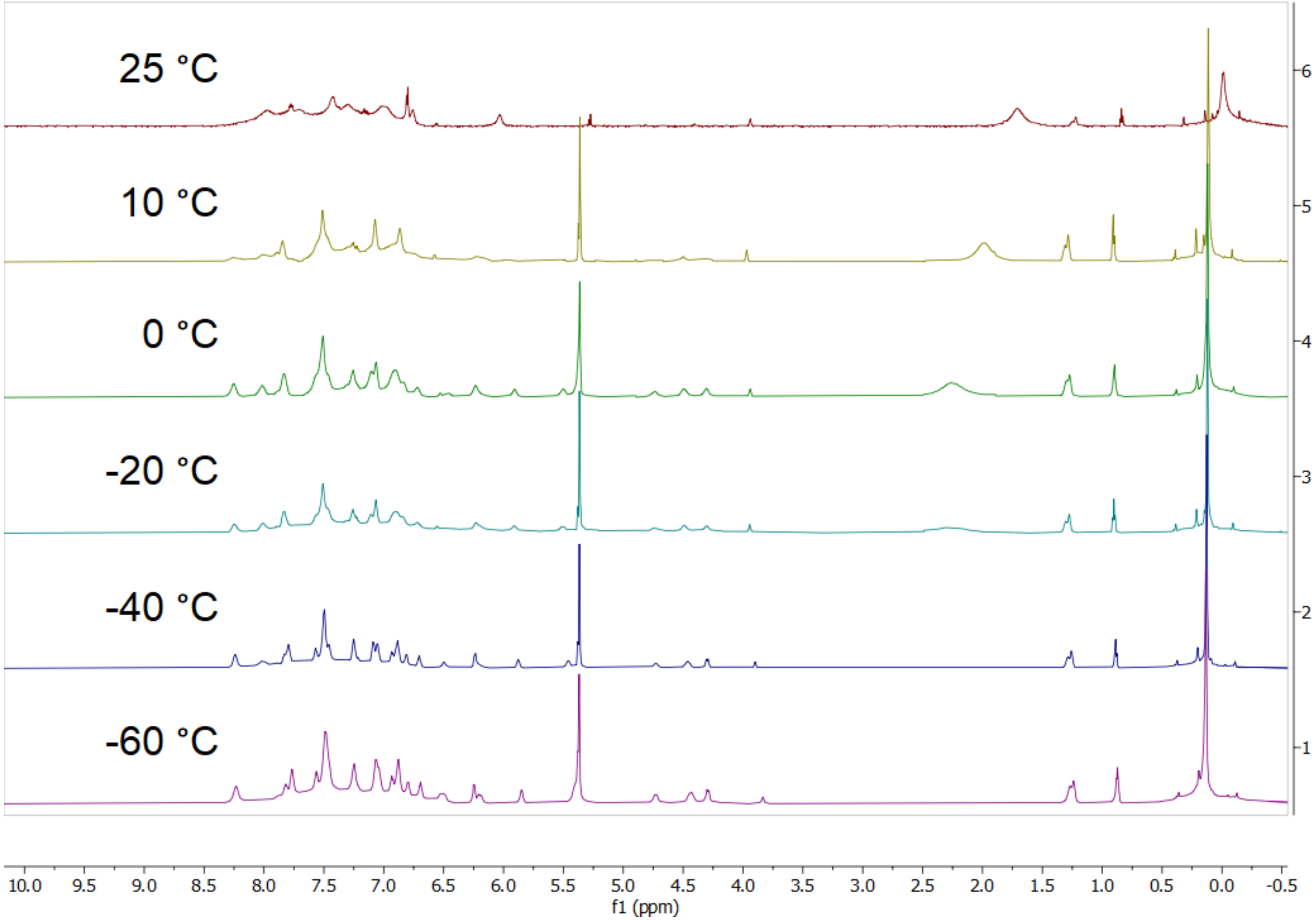
MS (ESI, +ve ion) for [Rh(CO)(PhPm)]PF$_6$ (**5**).



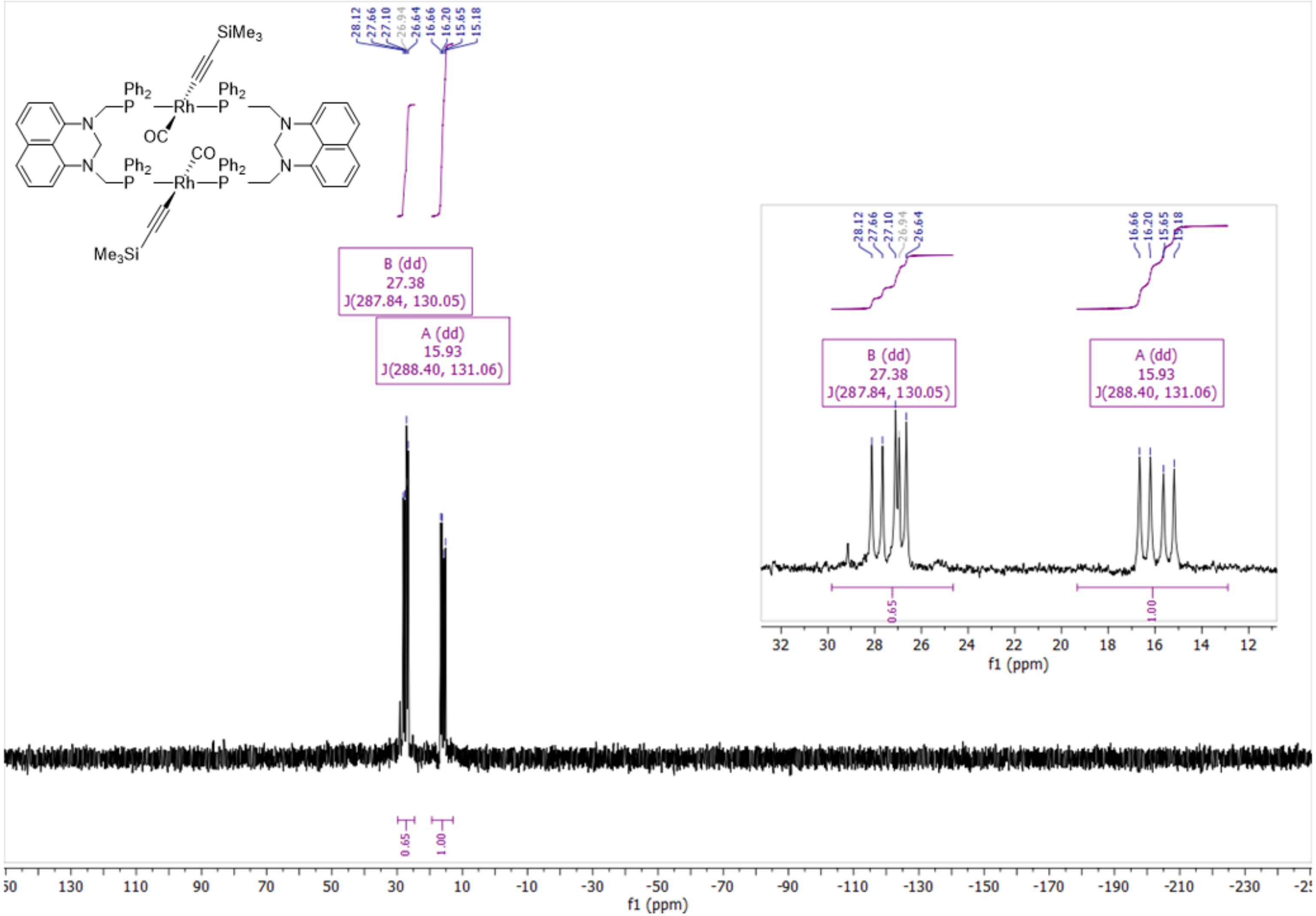
IR (CH_2Cl_2, cm^{-1}) for $[Rh(CO)(C{\equiv}CSiMe_3)(\mu\text{-}PhH_2Pm)]_2$ (**6**).



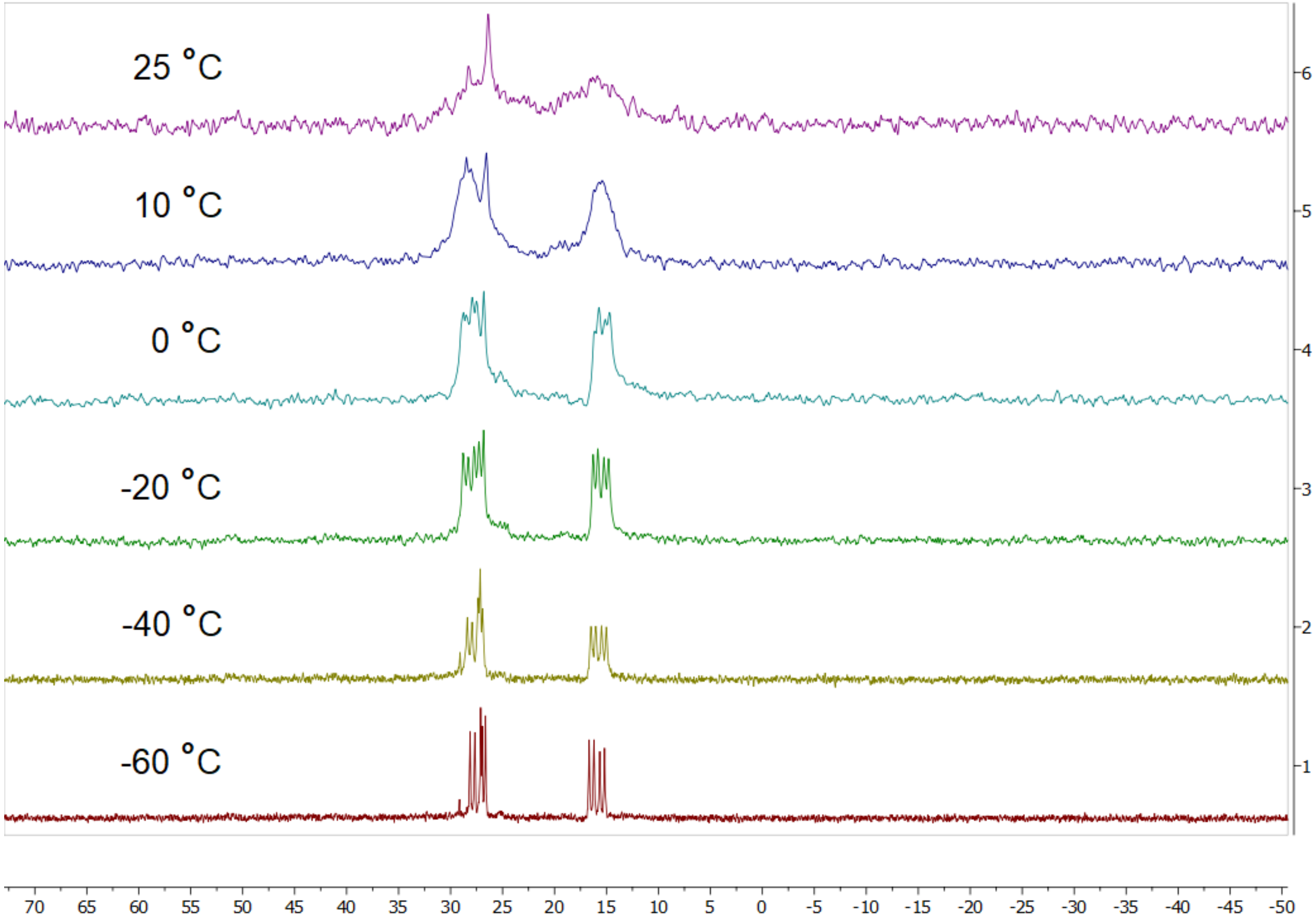
^{1}H NMR (700 MHz, CD_2Cl_2, 213 K) for [Rh(CO)(C≡C$SiMe_3$)(μ-PhH_2Pm)]$_2$ (**6**).



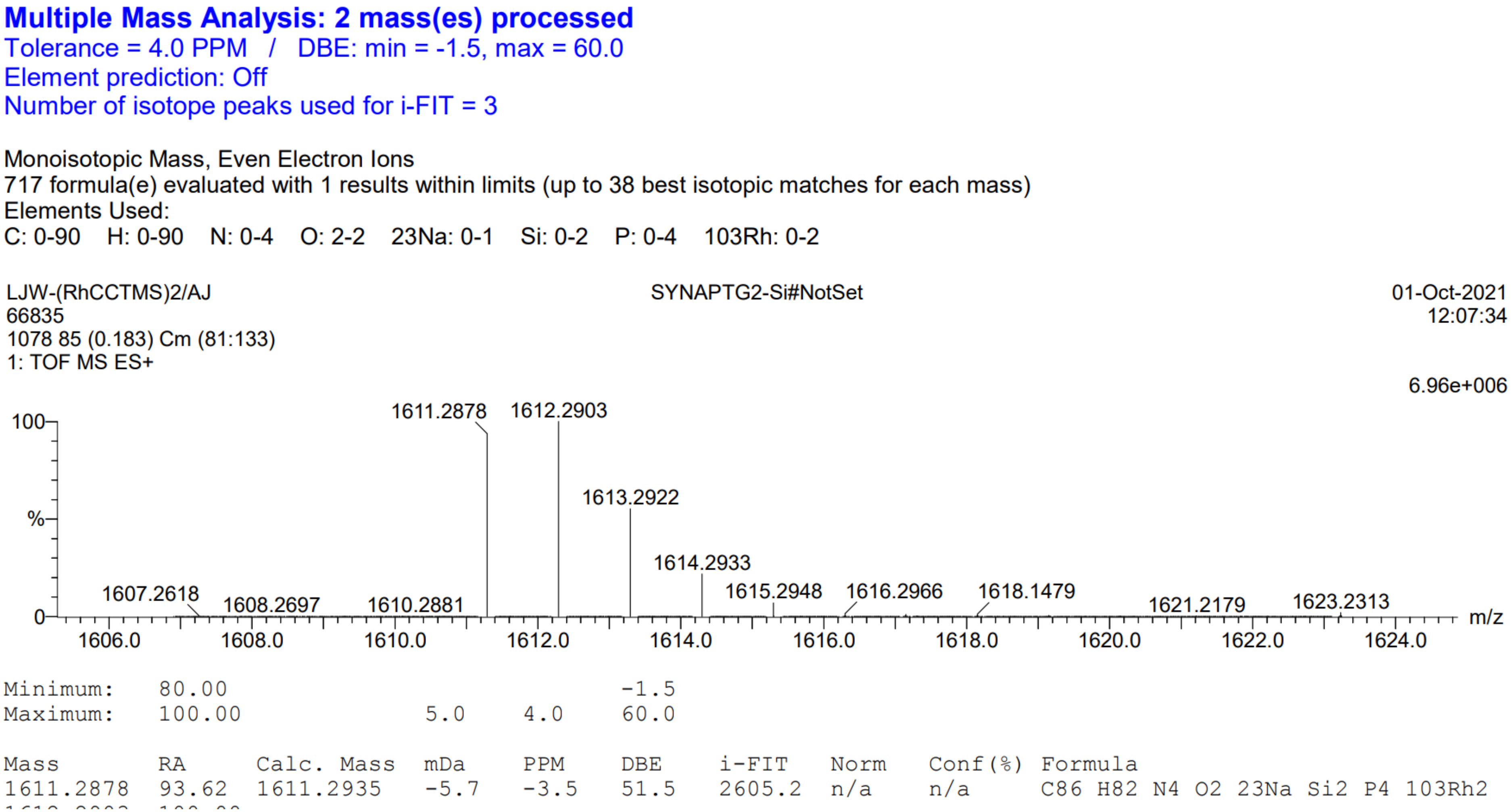
Variable temperature ^{1}H NMR (700 MHz, CD_2Cl_2) for [Rh(CO)(C≡CSiMe$_3$)(μ-PhH$_2$Pm)]$_2$ (**6**).



$^{31}P\{^1H\}$ NMR (283 MHz, CD_2Cl_2, 213 K) for $[Rh(CO)(C{\equiv}CSiMe_3)(\mu\text{-}PhH_2Pm)]_2$ (**6**).



Variable temperature $^{31}P\{^1H\}$ NMR (700 MHz, CD_2Cl_2) for $[Rh(CO)(C{\equiv}CSiMe_3)(\mu\text{-}PhH_2Pm)]_2$ (**6**).



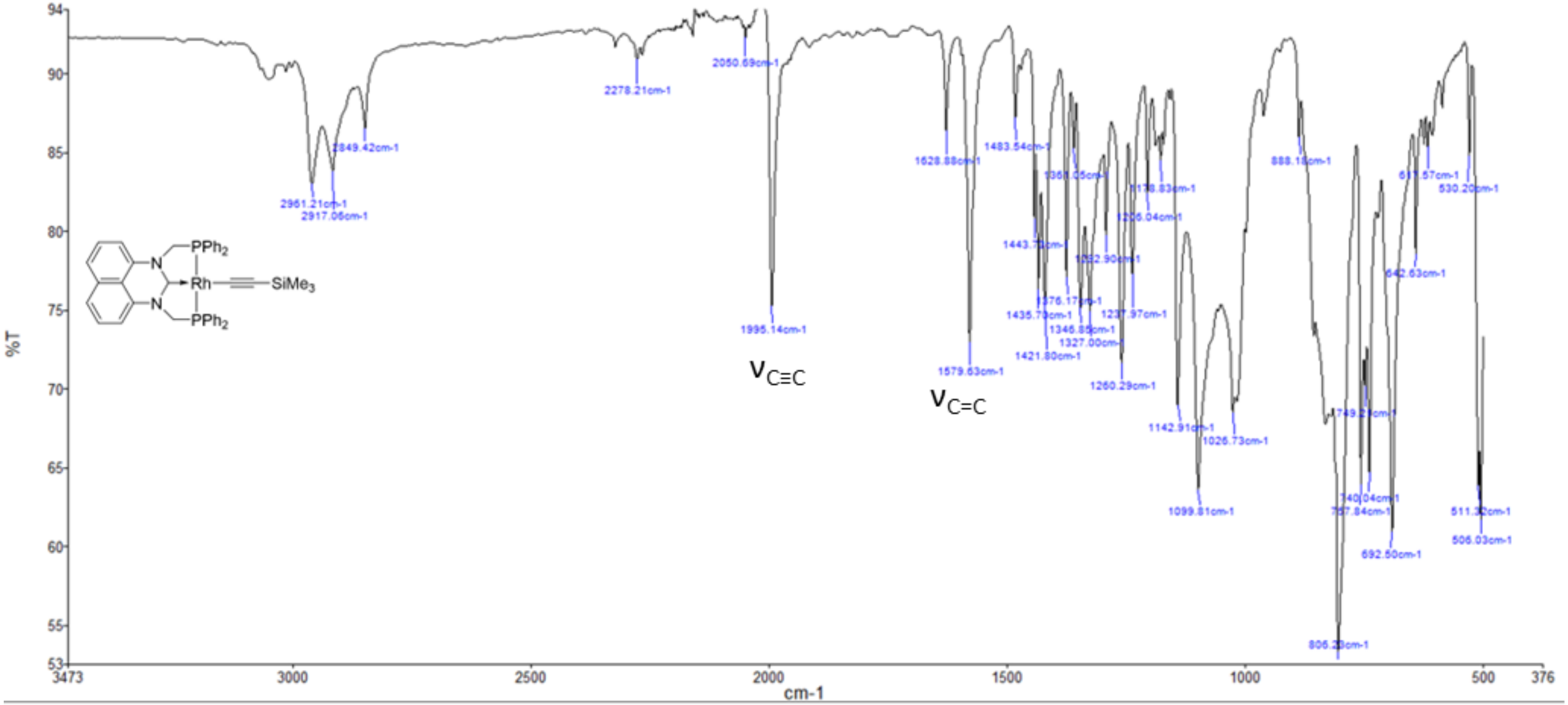
Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 4.0 PPM / DBE: min = -1.5, max = 60.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
717 formula(e) evaluated with 1 results within limits (up to 38 best isotopic matches for each mass)
Elements Used:
C: 0-90 H: 0-90 N: 0-4 O: 2-2 23Na: 0-1 Si: 0-2 P: 0-4 103Rh: 0-2

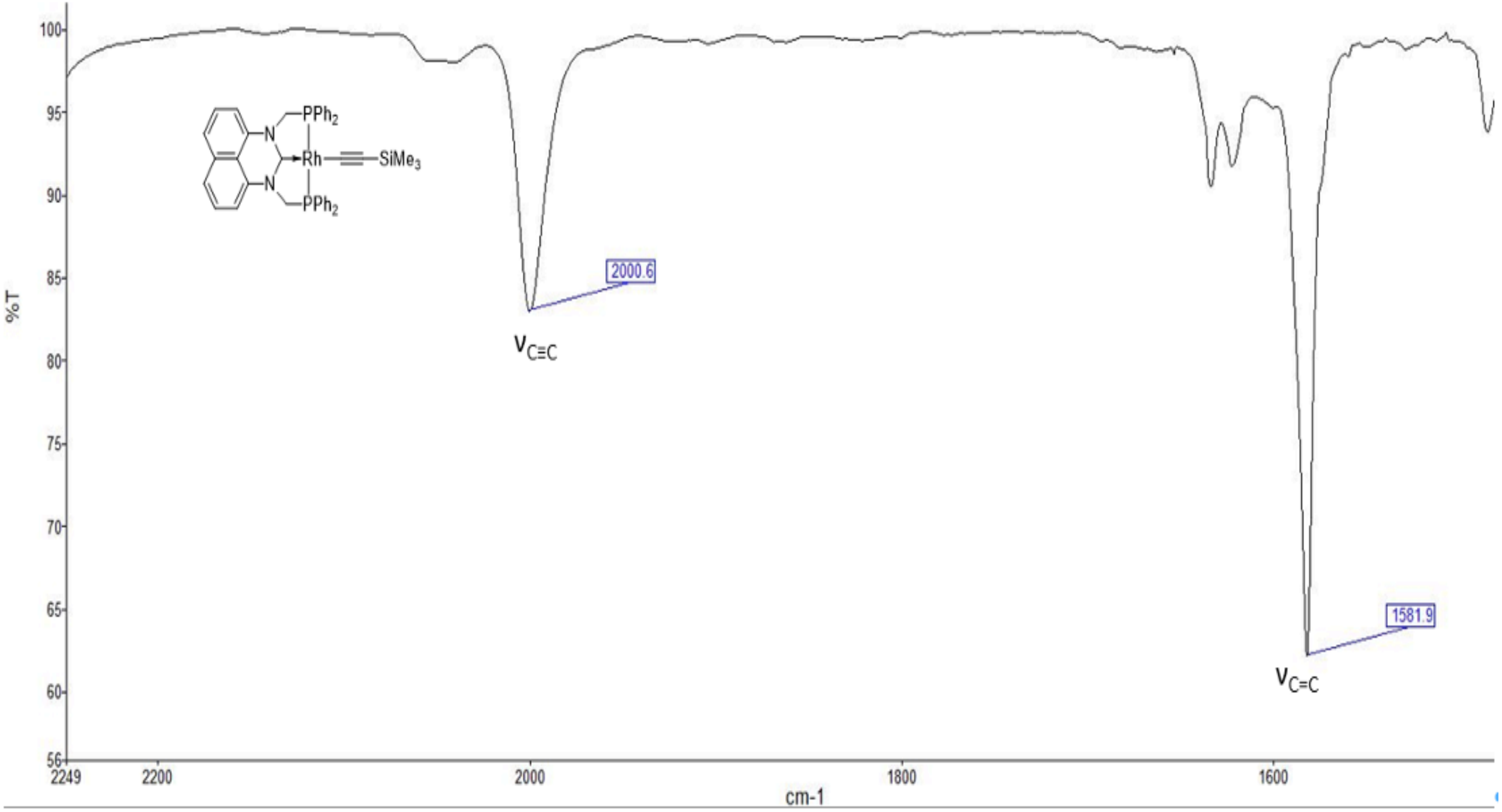
LJW-(RhCCTMS)2/AJ SYNAPTG2-Si#NotSet 01-Oct-2021
66835 12:07:34
1078 85 (0.183) Cm (81:133)
1: TOF MS ES+

```
Minimum:    80.00                             -1.5
Maximum:    100.00              5.0     4.0   60.0

Mass        RA      Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula
1611.2878   93.62   1611.2935   -5.7   -3.5   51.5   2605.2  n/a    n/a      C86 H82 N4 O2 23Na Si2 P4 103Rh2
```

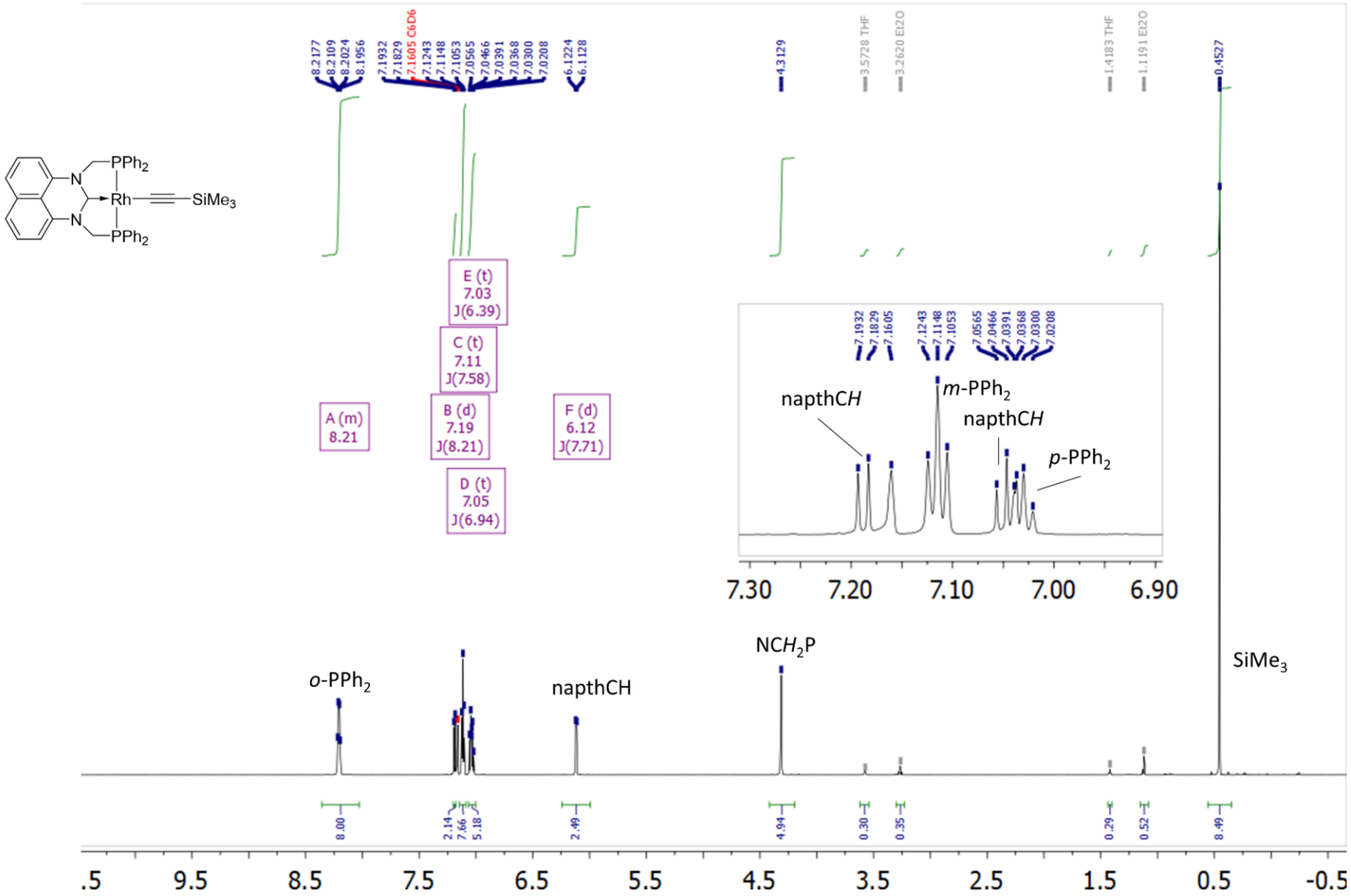
MS (ESI, +ve ion) for $[Rh(CO)(C{\equiv}CSiMe_3)(\mu\text{-}PhH_2Pm)]_2$ (**6**).



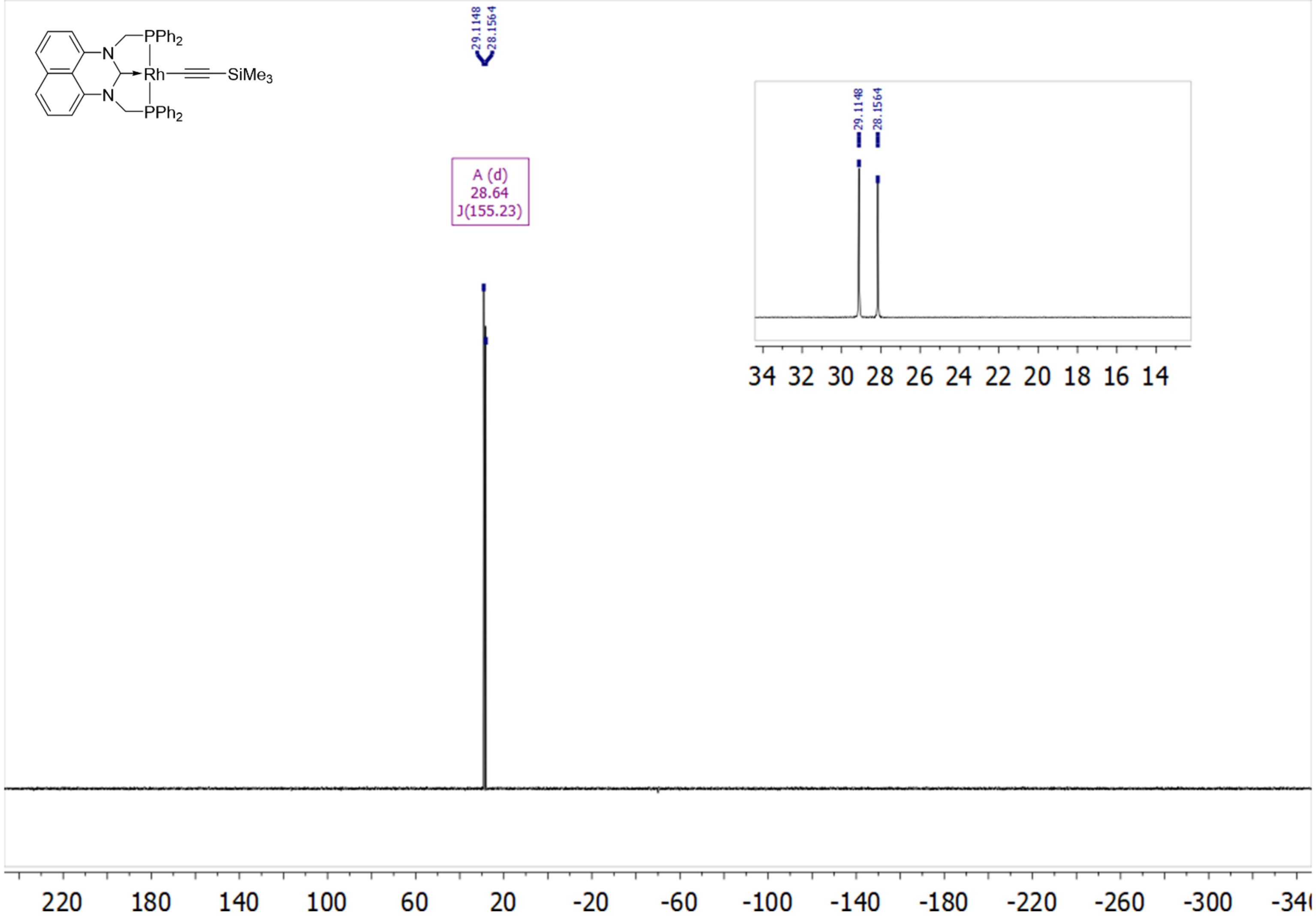
IR (ATR, cm^{-1}) for [Rh(C≡CSiMe$_3$)(PhPm)] (**7**).



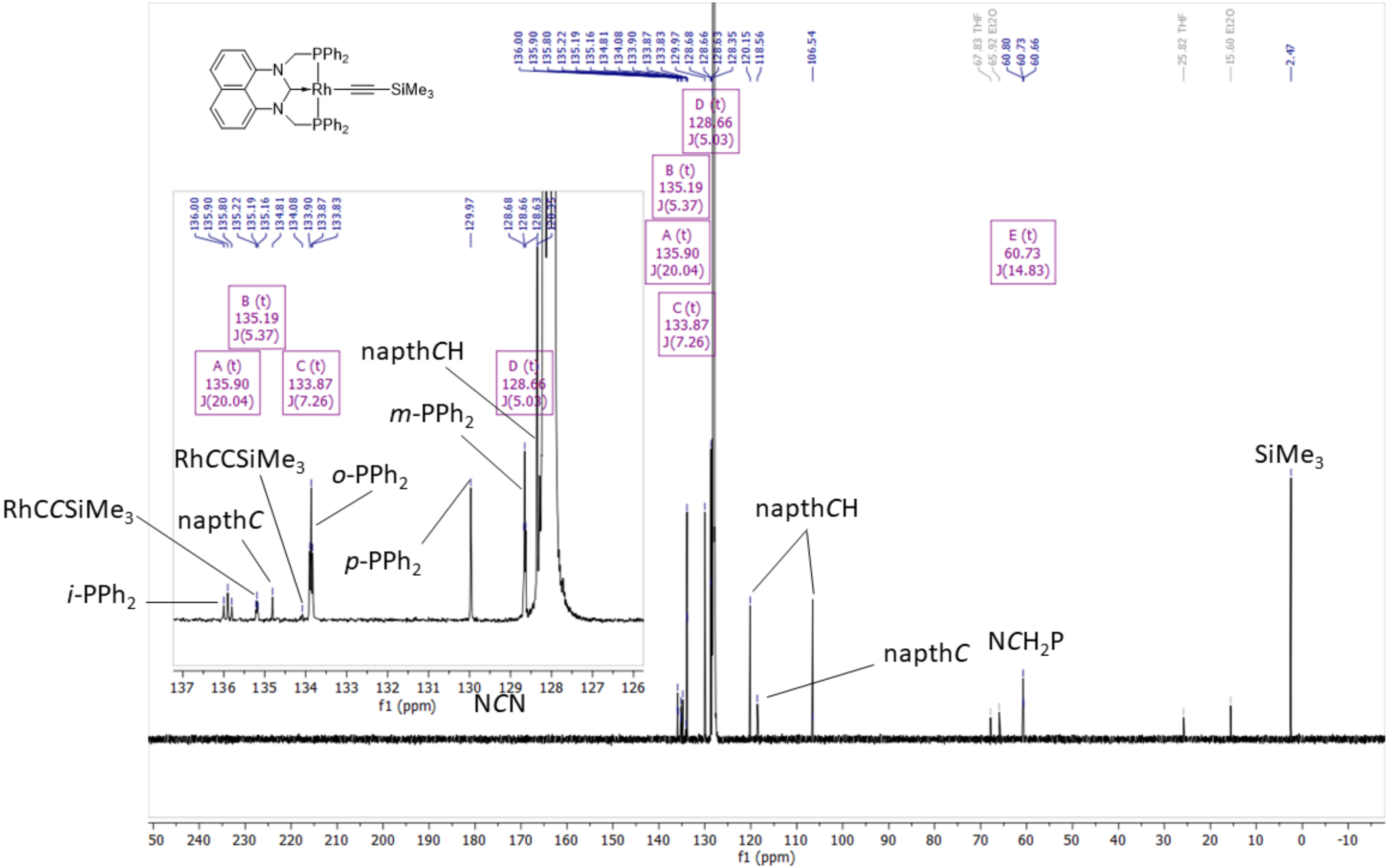
IR (CH_2Cl_2, cm^{-1}) for [Rh(C≡CSiMe$_3$)(PhPm)] (**7**).



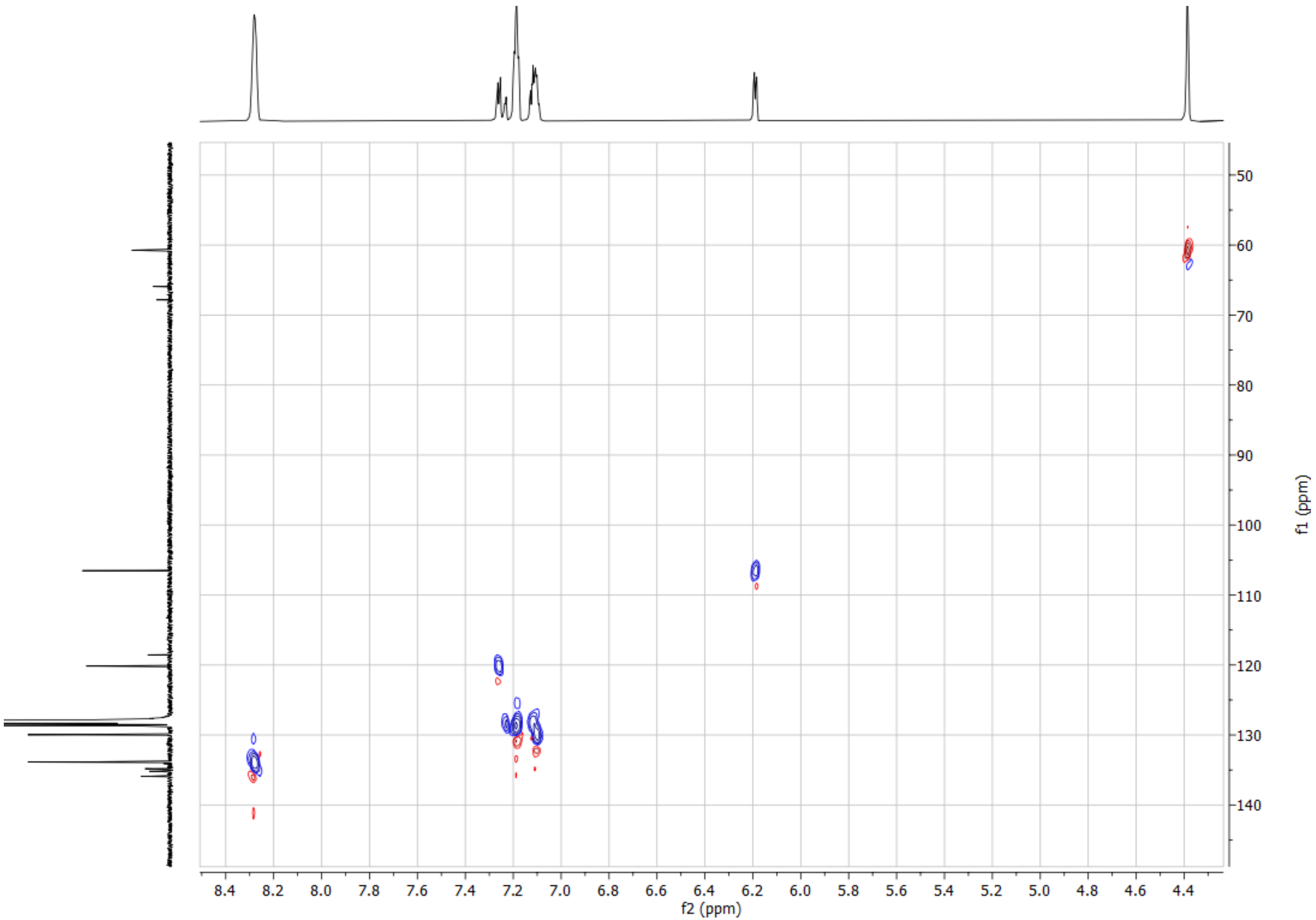
^{1}H NMR (800 MHz, C_6D_6, 298K) for [Rh(C≡CSiMe$_3$)(PhPm)] (**7**).



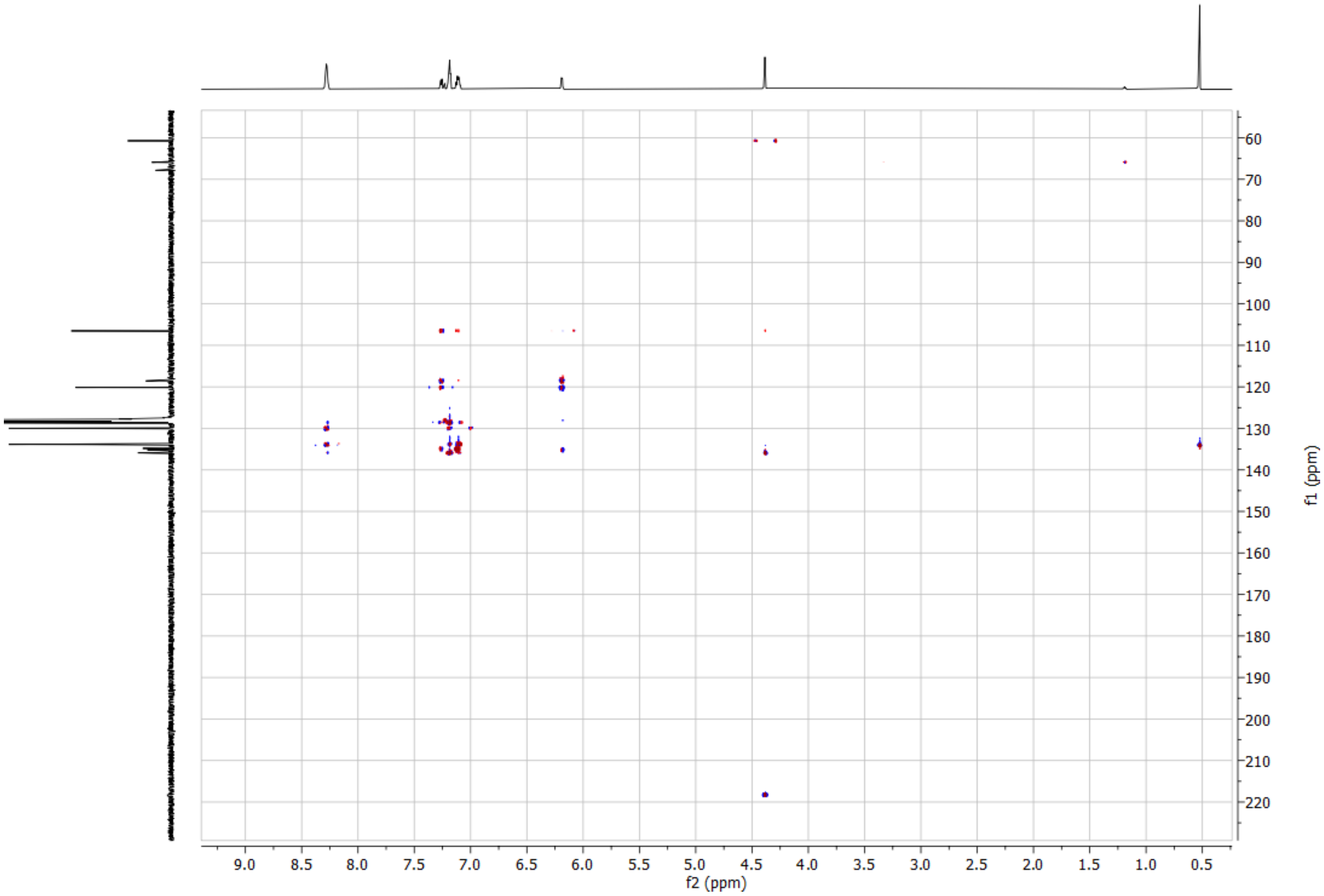
$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298K) for [Rh(C≡CSiMe$_3$)(PhPm)] (**7**).



$^{13}C\{^1H\}$ NMR (201 MHz, C_6D_6, 298K) for [Rh(C≡CSiMe$_3$)(PhPm)] (**7**).



HSQC NMR (C_6D_6, 298K) for [Rh(C≡CSiMe$_3$)(PhPm)] (**7**).



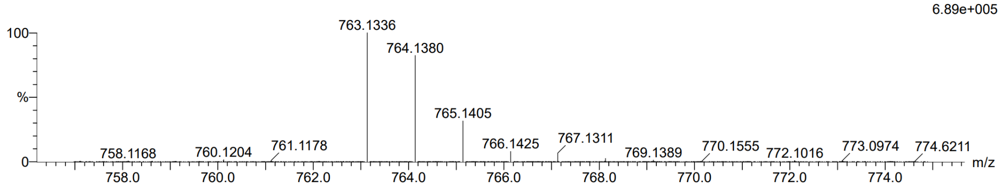
HMBC NMR (C_6D_6, 298K) for [Rh(C≡CSiMe$_3$)(PhPm)] (**7**).

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 30.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
69 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-2 Si: 0-1 P: 0-2 103Rh: 0-1

LJW-361/AJ SYNAPTG2-Si#NotSet 19-Mar-2021
66498 14:31:32
0278 64 (0.143) Cm (64:85)
1: TOF MS ES+



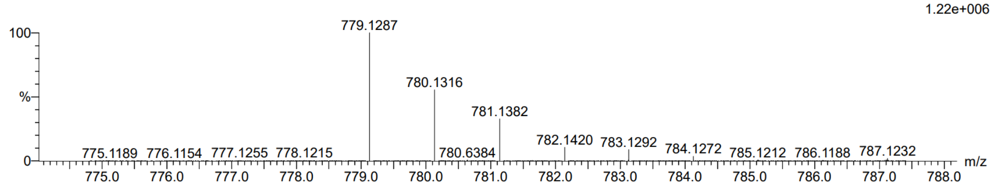
```
Minimum:                         -1.5
Maximum:              5.0    3.0  30.0

Mass       Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula
763.1336   763.1335    0.1    0.1    27.0   1856.2  n/a    n/a      C42 H38 N2 Si P2 103Rh
```

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 30.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

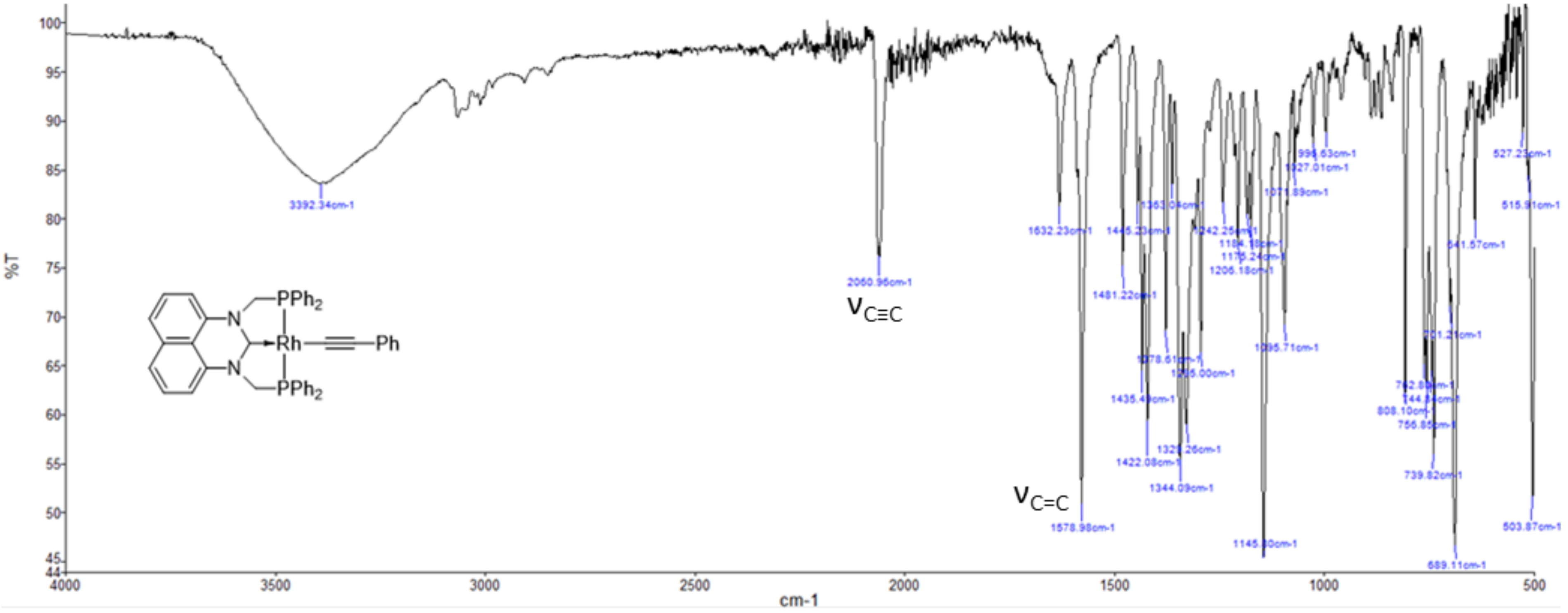
Monoisotopic Mass, Odd and Even Electron Ions
390 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-2 O: 0-4 Si: 0-1 P: 0-2 103Rh: 0-1

LJW-361/AJ SYNAPTG2-Si#NotSet 19-Mar-2021
66498 14:31:32
0278 64 (0.143) Cm (64:85)
1: TOF MS ES+

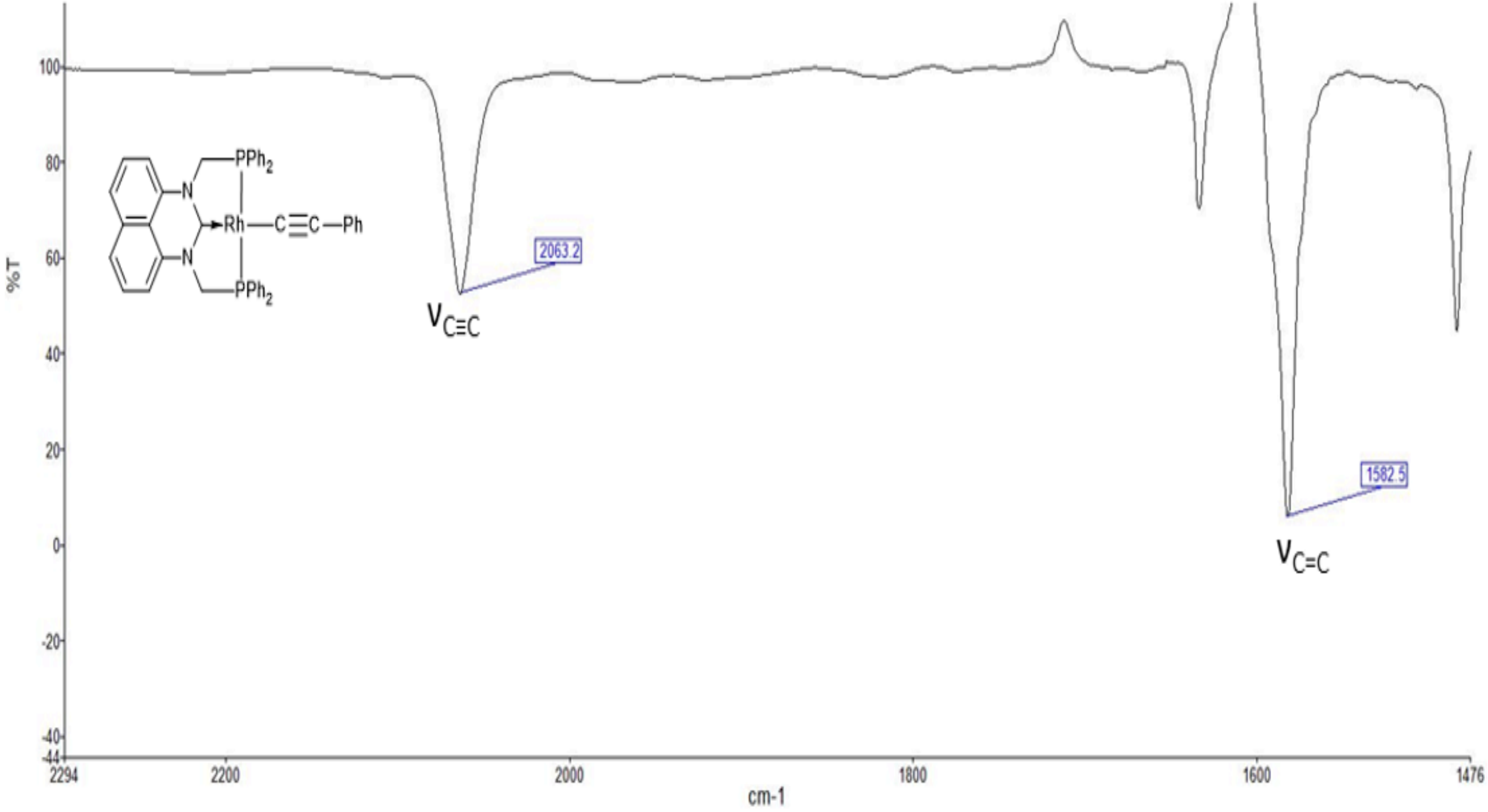


```
Minimum:                         -1.5
Maximum:              5.0    3.0  30.0

Mass       Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula
779.1287   779.1284    0.3    0.4    27.0   1891.0  n/a    n/a      C42 H38 N2 O Si P2 103Rh
```

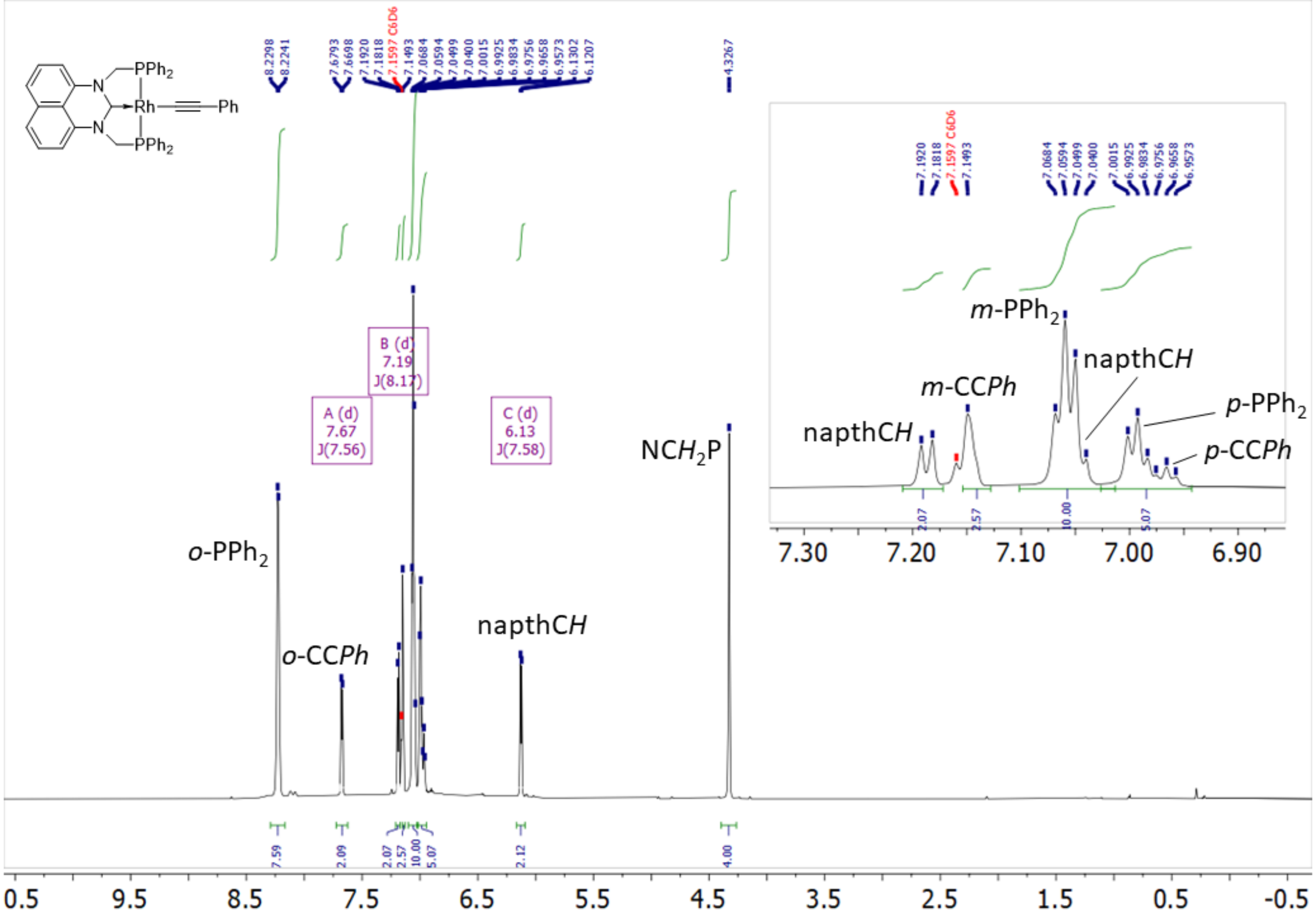
MS (ESI, +ve ion) for $[Rh(C{\equiv}CSiMe_3)(PhPm)]$ (**7**).



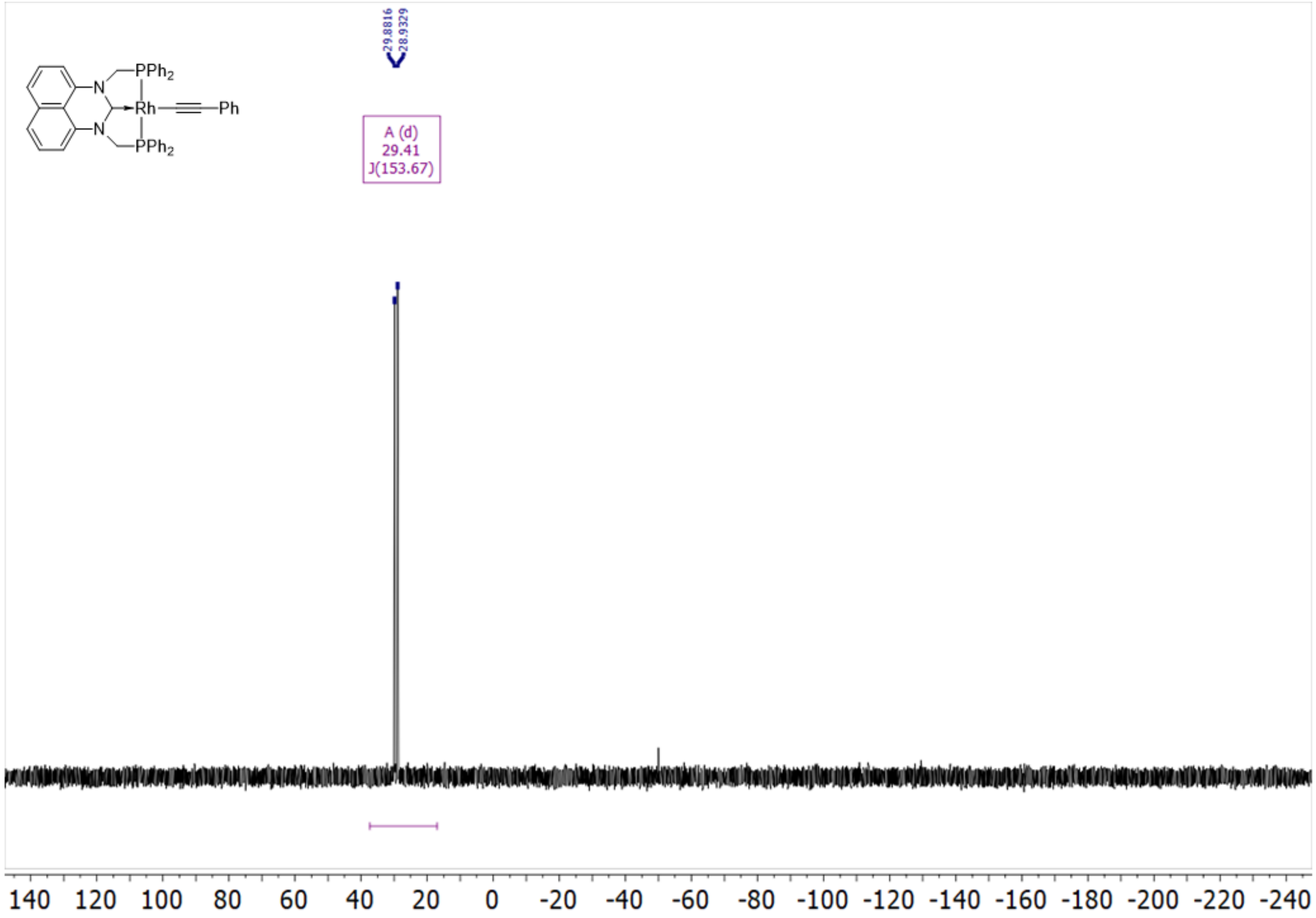
IR (ATR, cm^{-1}) for [Rh(C≡CPh)(PhPm)] (**8**).



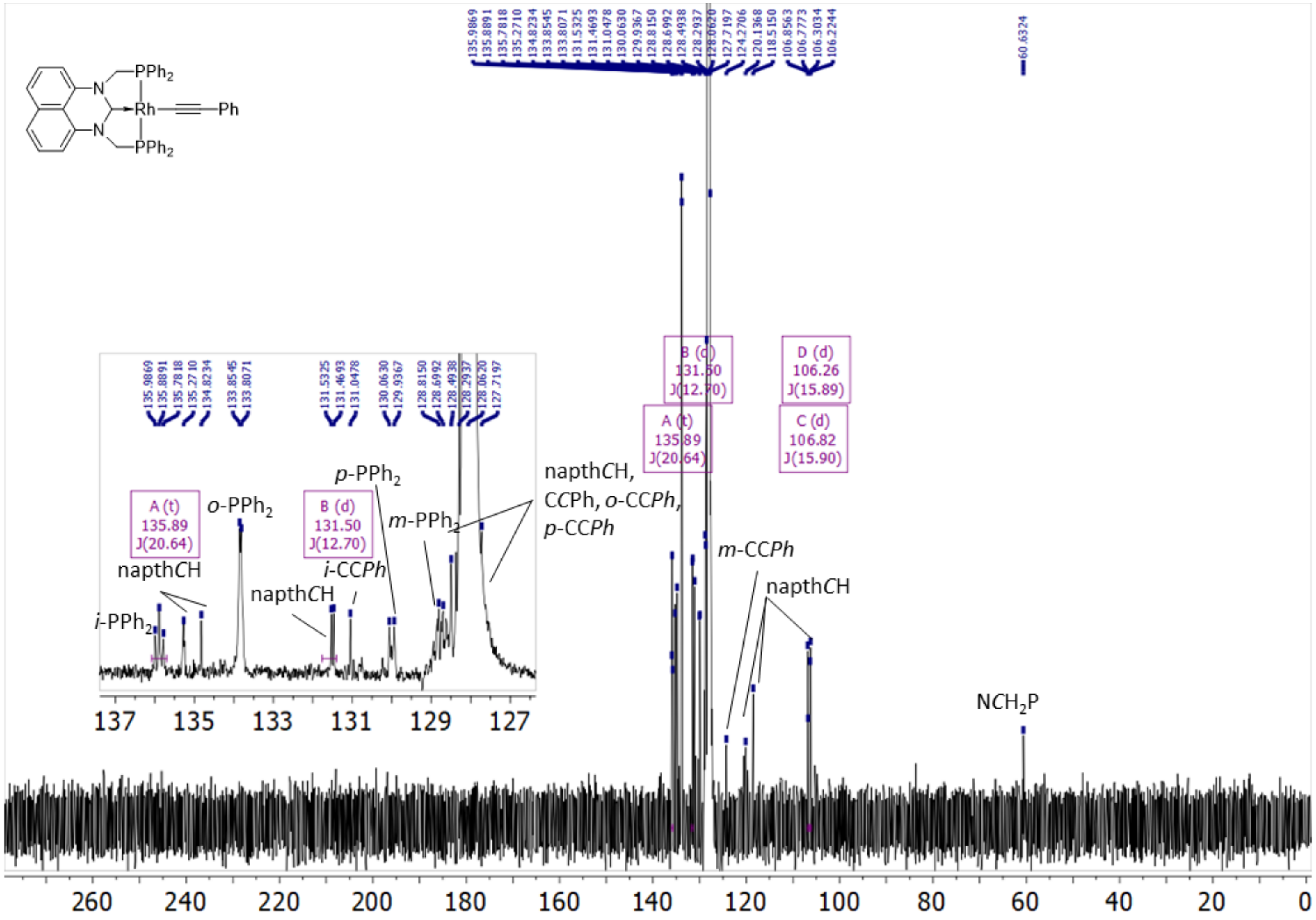
IR (CH_2Cl_2, cm^{-1}) for [Rh(C≡CPh)(PhPm)] (**8**).



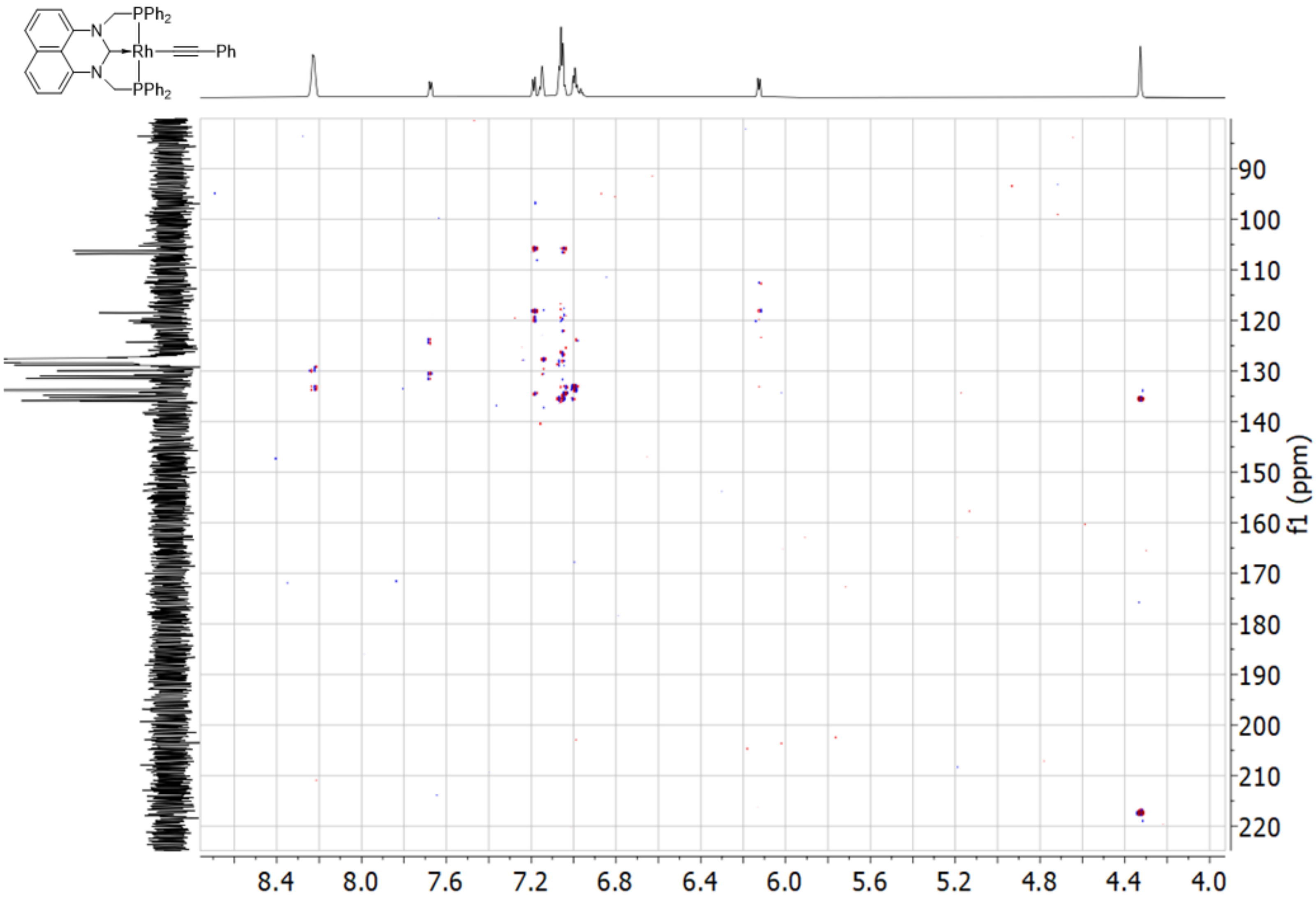
^{1}H NMR (800 MHz, C_6D_6, 298K) for [Rh(C≡CPh)(PhPm)] (**7**).



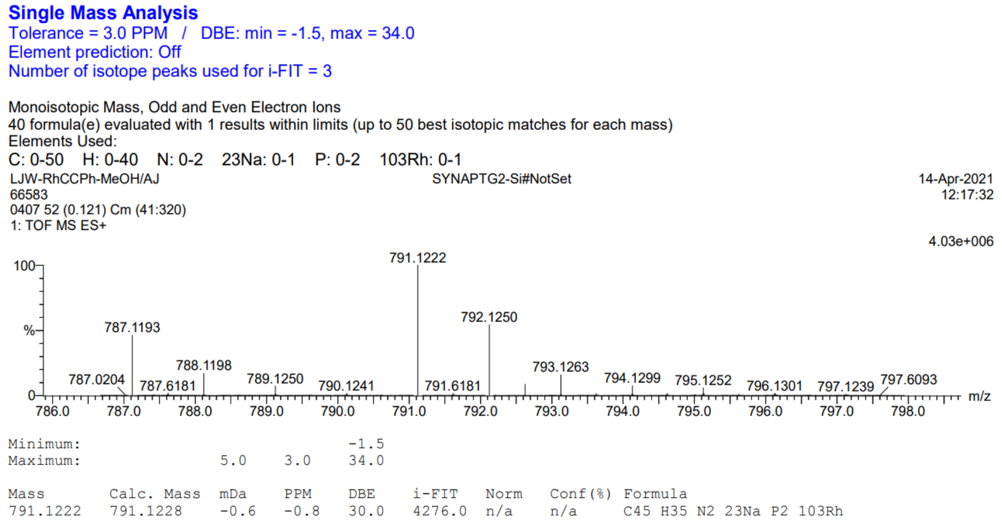
^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298K) for [Rh(C≡CPh)(PhPm)] (**8**).



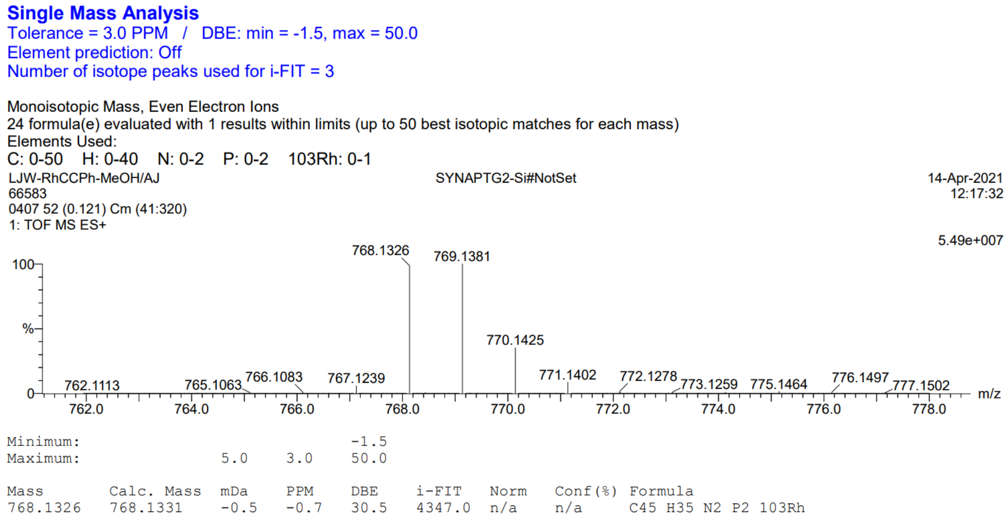
$^{13}C\{^{1}H\}$ NMR (201 MHz, C_6D_6, 298K) for [Rh(C≡CPh)(PhPm)] (**8**).



^{1}H-^{13}C HMBC (C_6D_6, 298K) for [Rh(C≡CPh)(PhPm)] (**8**).



```
Single Mass Analysis
Tolerance = 3.0 PPM   /   DBE: min = -1.5, max = 34.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50    H: 0-40    N: 0-2    23Na: 0-1    P: 0-2    103Rh: 0-1
LJW-RhCCPh-MeOH/AJ                         SYNAPTG2-Si#NotSet                     14-Apr-2021
66583                                                                                12:17:32
0407 52 (0.121) Cm (41:320)
1: TOF MS ES+
                                                                                  4.03e+006

Minimum:                              -1.5
Maximum:              5.0     3.0     34.0

Mass       Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula
791.1222   791.1228    -0.6   -0.8   30.0   4276.0  n/a    n/a      C45 H35 N2 23Na P2 103Rh
```



```
Single Mass Analysis
Tolerance = 3.0 PPM   /   DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
24 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-50    H: 0-40    N: 0-2    P: 0-2    103Rh: 0-1
LJW-RhCCPh-MeOH/AJ                         SYNAPTG2-Si#NotSet                     14-Apr-2021
66583                                                                                12:17:32
0407 52 (0.121) Cm (41:320)
1: TOF MS ES+
                                                                                  5.49e+007

Minimum:                              -1.5
Maximum:              5.0     3.0     50.0

Mass       Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%)  Formula
768.1326   768.1331    -0.5   -0.7   30.5   4347.0  n/a    n/a      C45 H35 N2 P2 103Rh
```

MS (ESI, +ve ion) for [Rh(C≡CPh)(PhPm)] (**8**).