Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Selective C-C coupling at a Pt(IV) centre: 100% preference for sp^2-sp^3 over sp^3-sp^3.

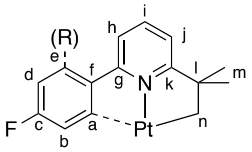
Paul A Shaw and Jonathan P Rourke*

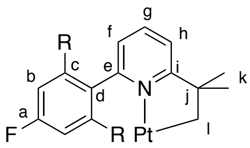
Department of Chemistry, Warwick University, Coventry. UK CV4 7AL.

Email: j.rourke@warwick.ac.uk

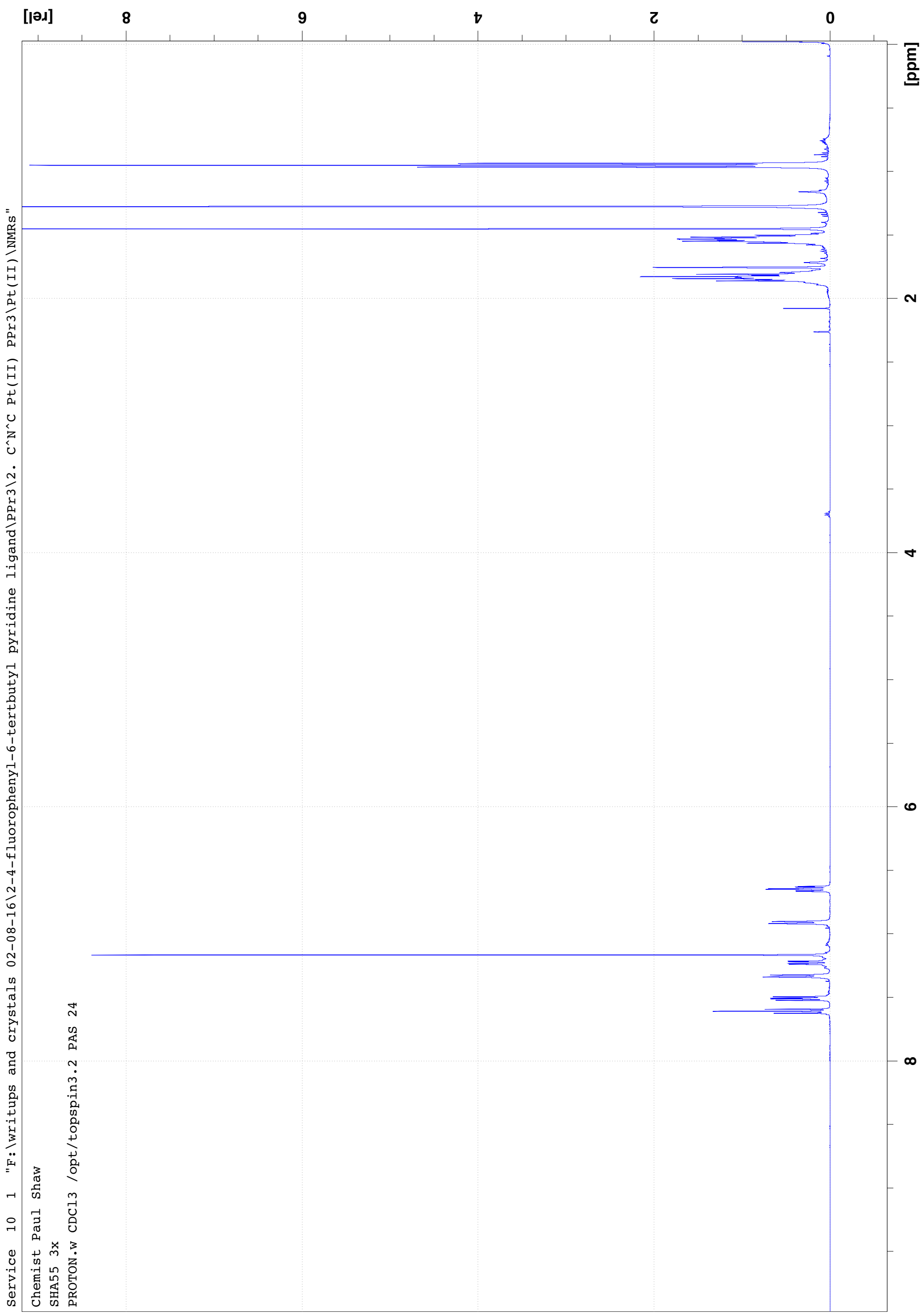
Contents

The leftmost labelling scheme was used for all complexes except **Me$_2$-3** and **Bn$_2$-3**, for which the right hand scheme was used:

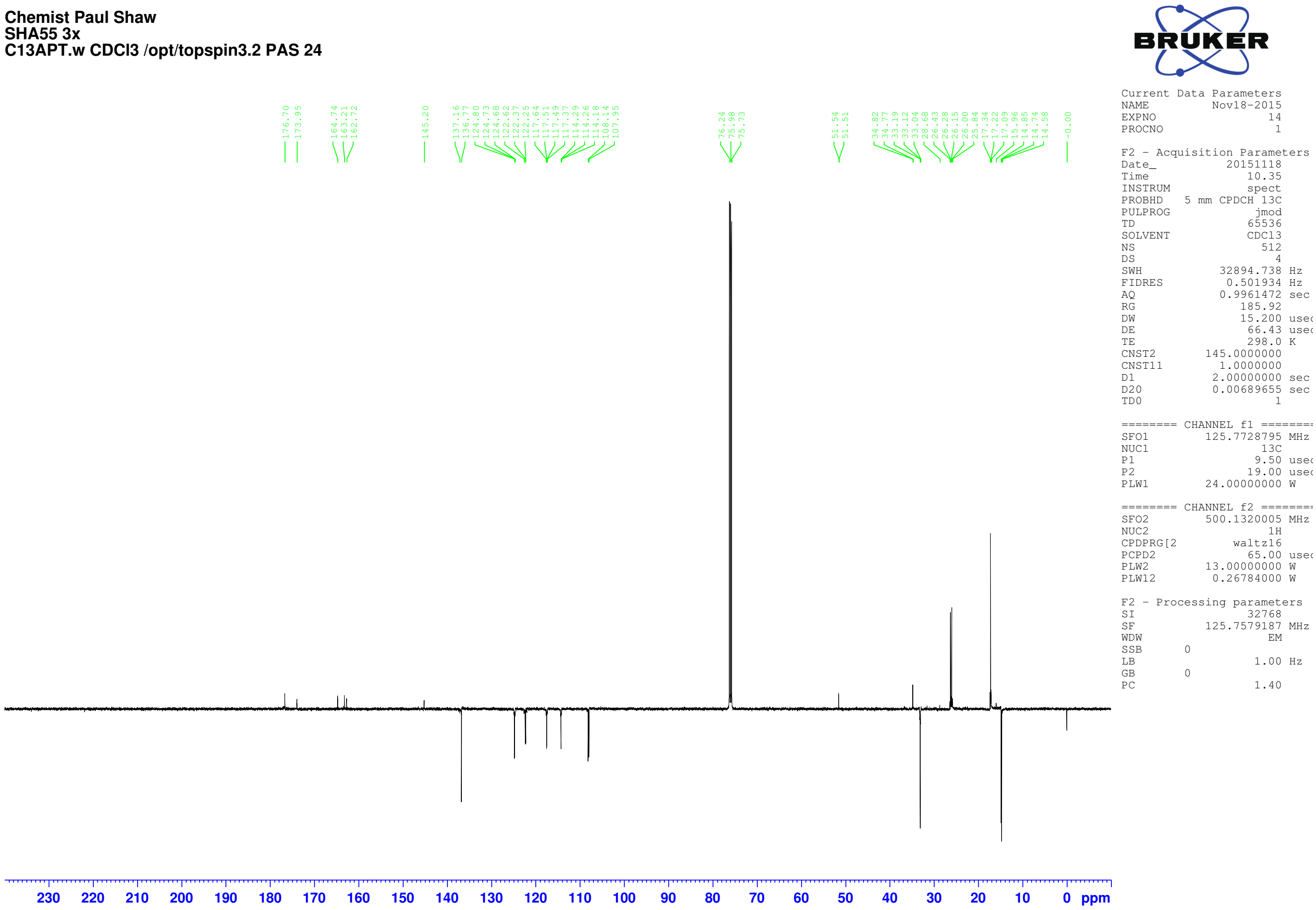




Complex 1



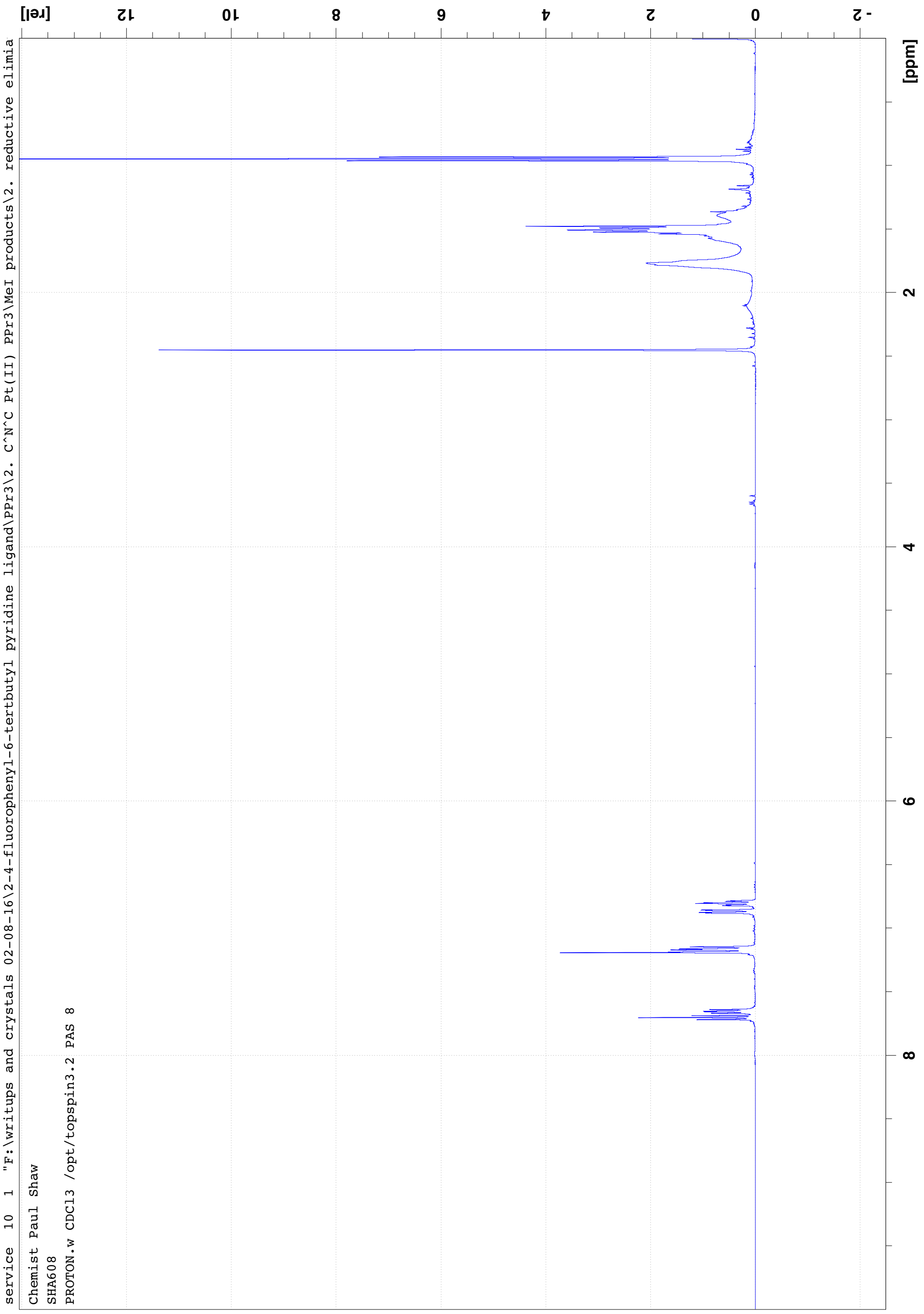
δ_H = 7.63 (1H, t, $^3J_{H\text{-}H}$ = 8 Hz, H_i), 7.43 (1H, dd, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}F}$ = 5 Hz, H_e), 7.36 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, H_h), 7.25 (1H, dd, $^3J_{H\text{-}F}$ = 9.5, $^4J_{H\text{-}H}$ = 2.5 Hz, $^3J_{H\text{-}Pt}$ = 29 Hz, H_b), 6.93 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, H_j), 6.67 (1H, td, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 9.5, $^4J_{H\text{-}H}$ = 2.5 Hz, H_d), 1.86 (6H, m, PCH_2), 1.78 (2H, s, $^2J_{H\text{-}H}$ = 39 Hz, H_n), 1.56 (6H, m, $PCH_2$$CH_2$), 1.30 (6H, s H_m), 0.97 (9H, t, $^3J_{H\text{-}H}$ = 7.5, PCH_2CH_2*Me*) ppm.



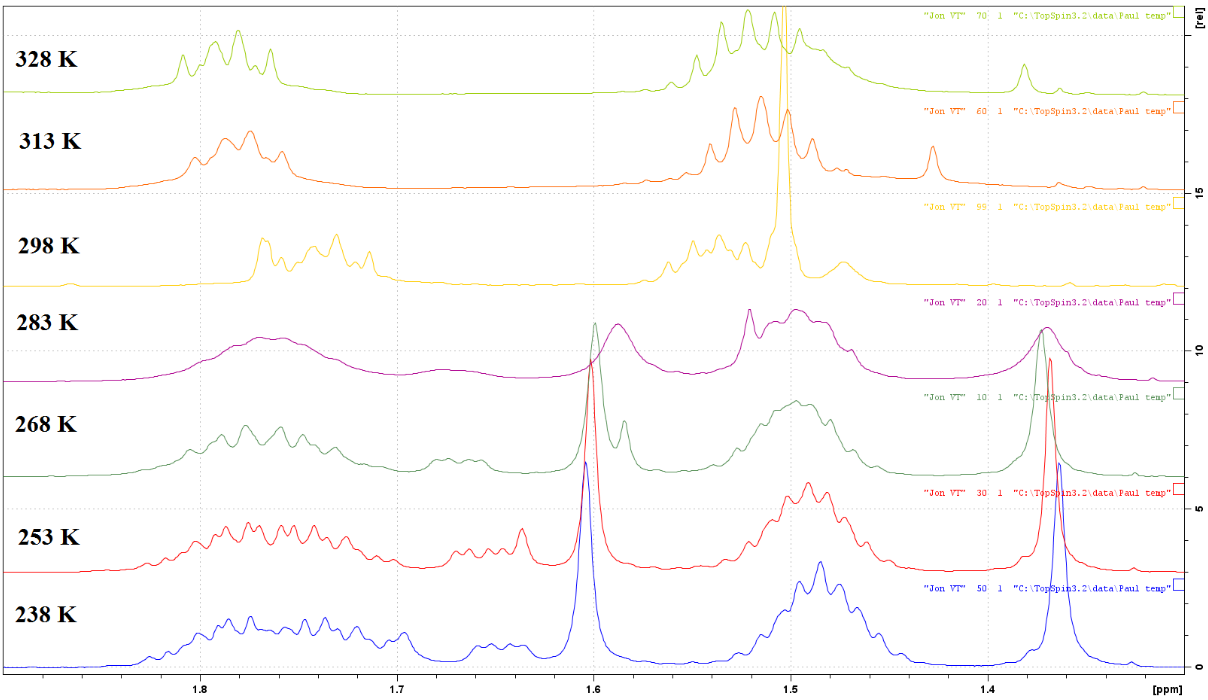
δ_C = 14.79 (d, $^3J_{C\text{-}P}$ = 15.5 Hz, PCH_2CH_2Me), 15.63 (s, $^3J_{C\text{-}Pt}$ = 32.5 Hz, PCH_2CH_2), 26.14 (d, $^1J_{C\text{-}P}$ = 35.63, $^2J_{C\text{-}Pt}$ = 37.5 Hz, PCH_2), 33.11 (s, $^3J_{C\text{-}Pt}$ = 18.5 Hz, C_m), 34.79 (d, $^2J_{C\text{-}P}$ = 6 Hz, $^1J_{C\text{-}Pt}$ = 466 Hz, C_n), 51.52, (d, $^3J_{C\text{-}P}$ = 3.5 Hz, $^2J_{C\text{-}Pt}$ = 21 Hz, C_l), 108.05 (d, $^2J_{C\text{-}F}$ = 22 Hz, C_d), 114.28 (d, $^4J_{C\text{-}P}$ = 3 Hz, $^3J_{C\text{-}Pt}$ = 25.5 Hz, C_h), 117.50 (d, $^4J_{C\text{-}P}$ = 2.5 Hz, $^3J_{C\text{-}Pt}$ = 33 Hz, C_j), 122.31 (d, $^2J_{C\text{-}F}$ = 15 Hz, $^2J_{C\text{-}Pt}$ = 64.5 Hz, C_b), 124.77 (d, $^3J_{C\text{-}F}$ = 9 Hz, $^3J_{C\text{-}Pt}$ = 30 Hz, C_e), 136.76 (s, C_i), 145.20 (m, $^2J_{C\text{-}Pt}$ = 26 Hz, C_f), 163.22 (s, $^2J_{C\text{-}Pt}$ = 52 Hz, H_g), 163.72 (d, $^2J_{C\text{-}F}$ = 254.5 Hz, $^3J_{C\text{-}Pt}$ = 52 Hz, C_c), 173.95 (m, $^1J_{C\text{-}Pt}$ = 686 Hz, C_a), 176.22 (s, $^2J_{C\text{-}Pt}$ = 19 Hz, H_k) ppm.

δ_F = -111.69 ($^4J_{F\text{-}Pt}$ = 26.5 Hz) ppm. δ_P = 0.44 ($^1J_{P\text{-}Pt}$ = 3813 Hz) ppm. δ_{Pt} = -4026 (d, $^1J_{Pt\text{-}P}$ = ~3700 Hz) ppm.

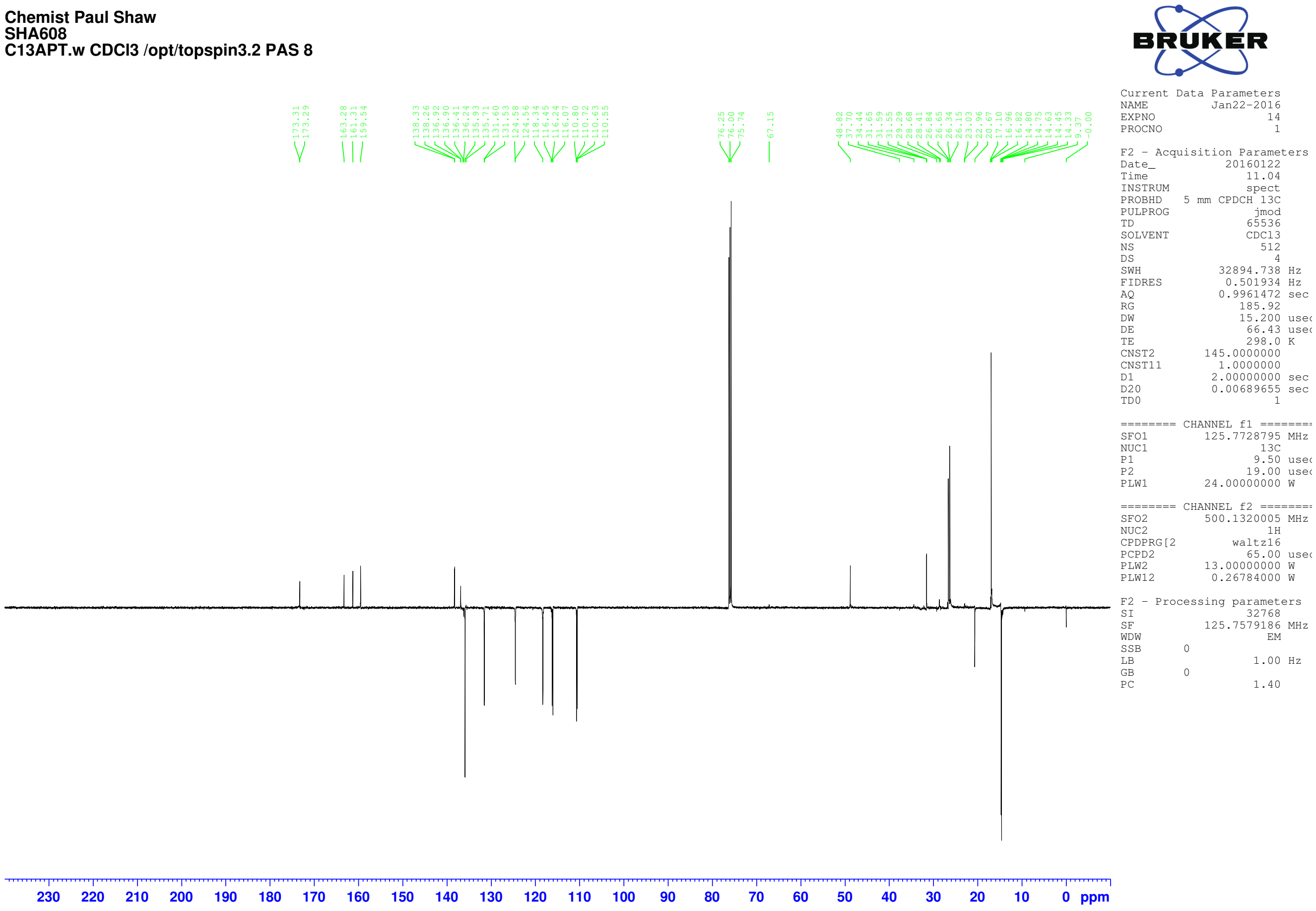
Complex Me-3



δ_H = 7.70 (1H, t, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 8 Hz, H_i), 7.65 (1H, dd, $^3J_{H\text{-}H}$ = 8.5 Hz, $^4J_{H\text{-}F}$ = 6 Hz, H_a), 6.16 (2H, m, $H_{h,j}$), 6.86 (1H, dd, $^3J_{H\text{-}H}$ = 10 Hz, $^4J_{H\text{-}H}$ = 2.5 Hz, H_d), 6.80 (1H, td, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 8 Hz, $^4J_{H\text{-}H}$ = 2.5 Hz, H_b), 2.45 (3H, s, Me), 1.77 (6H, m, P*CH₂*) 1.49 (14H, m, $H_{m,n}$, PCH_2*CH_2*), 0.95 (9H, t, $^3J_{H\text{-}H}$ = 7 Hz, PCH_2CH_2*Me*) ppm.



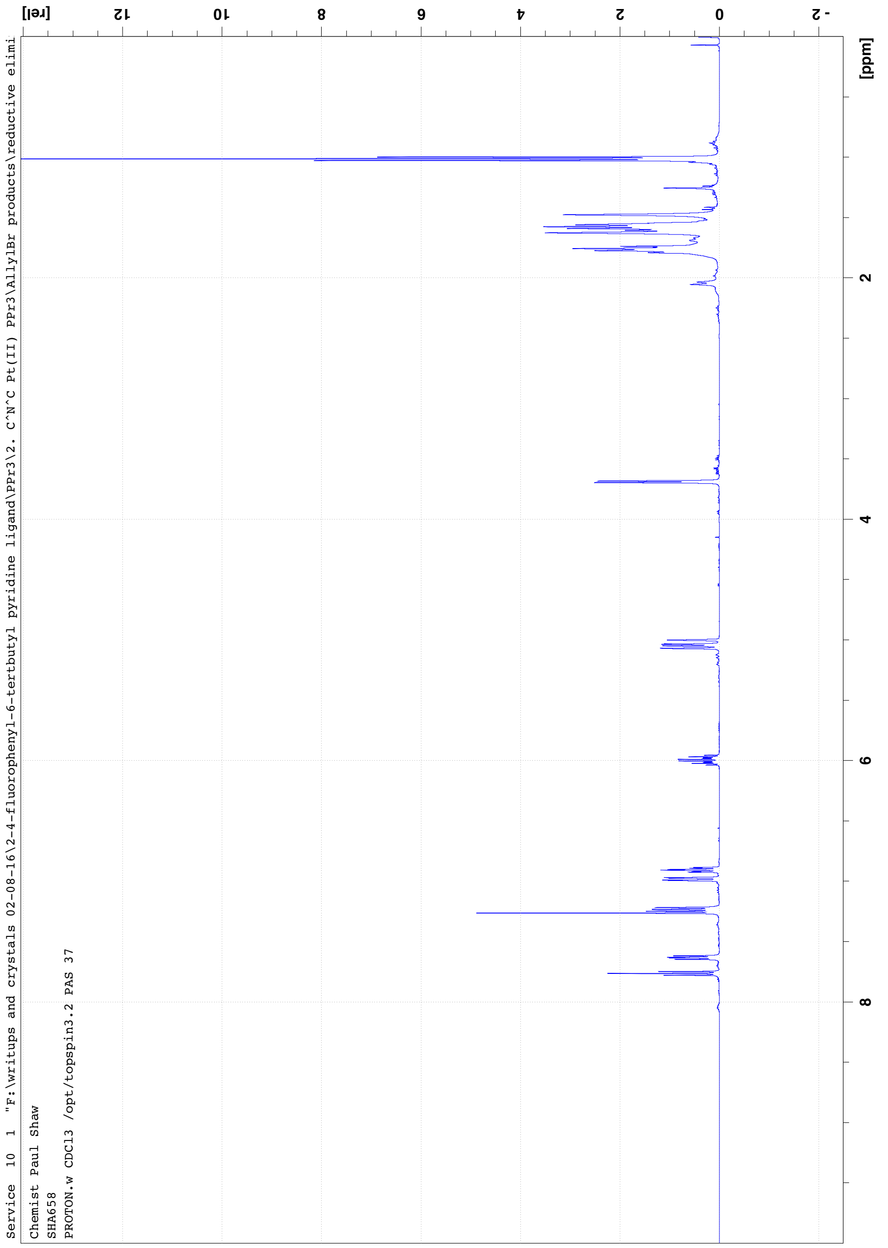
(600 MHz) Note that at 298 K PCH_2 is broader than normal, without its characteristic shape. See ESI. H_m is split into two broad peaks separated by 85 Hz. At 328 K, H_m has coalesced to form one broad lump hidden under $PCH_2$$CH_2$, and P$CH_2$ has regained its characteristic shape. Lowering the temperature to 268 K, H_m now comprises of two distinct peaks (1.44 and 1.66). Two new peaks also appear which correspond to H_n. These peaks are at 1.74 (1H, dd, $^2J_{H\text{-}H}$ = 10 Hz, $^3J_{H\text{-}P}$ = 3.5 Hz) and 2.21 (1H, d, $^2J_{H\text{-}H}$ = 10 Hz, $^2J_{H\text{-}Pt}$ = ~43 Hz) which were previously hidden under $PCH_2$$CH_2$. Lowering the temperature further to 238 K we see PCH_2 beginning to separate into 2 peaks. Using a separation of 131 Hz and a coalescence temperature of 313 K for H_m we can calculate a barrier of 62.9 kJmol^{-1}; a coalescence temperature of 298 would equate to a barrier of 59.9 kJmol^{-1}; variations in the peak separation make a similar difference in calculated value, hence our estimate of an uncertainty of ±5 kJmol^{-1}.



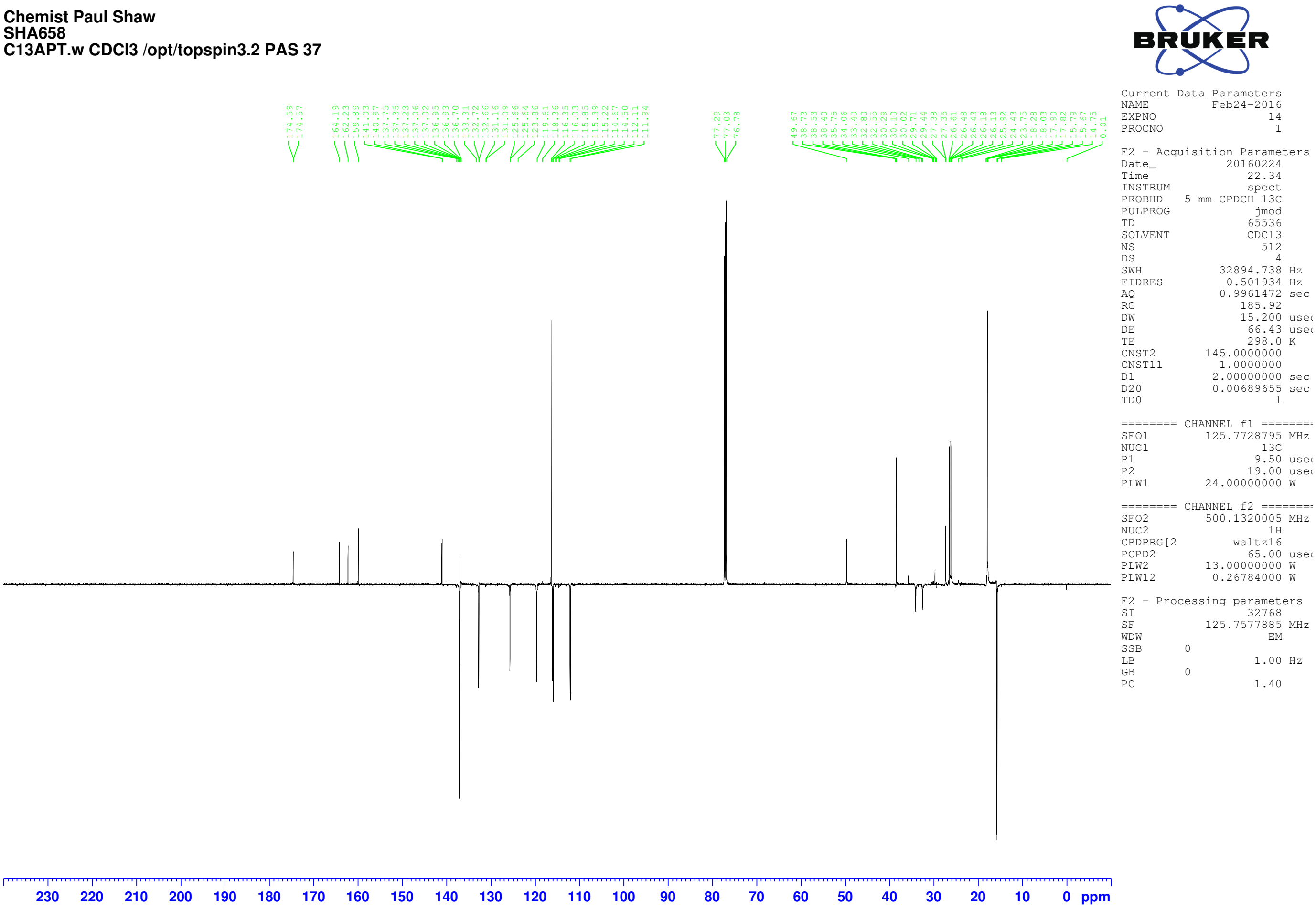
δ_C = 14.68 (d, $^3J_{C\text{-}P}$ = 15 Hz, PCH$_2$CH$_2$*Me*), 16.96 (s, $^3J_{C\text{-}Pt}$ = 35 Hz, PCH$_2$*CH$_2$*), 20.67 (s, Me), 26.49 (d, $^1J_{C\text{-}P}$ = 38 Hz, $^2J_{C\text{-}Pt}$ = 38 Hz, P*CH$_2$*), 31.58 (d, $^2J_{C\text{-}P}$ = 4 Hz, $^1J_{C\text{-}Pt}$ = 727 Hz, C_n), 48.83 (s, C_l), 110.64 (d, $^2J_{C\text{-}F}$ = 20 Hz, C_b), 116.18 (d, $^2J_{C\text{-}F}$ = 22 Hz, C_d), 118.35 (s, $^3J_{C\text{-}Pt}$ = 20 Hz, C_j), 124.57 (d, $^4J_{C\text{-}P}$ = 4 Hz, C_h), 134.56 (d, $^3J_{C\text{-}F}$ = 10 Hz, C_a), 135.9 (s, C_i), 136.91 (d, $^4J_{C\text{-}F}$ = 8 Hz, C_f), 138.31 (d, $^3J_{C\text{-}F}$ = 3 Hz, C_e), 159.57 (s, C_k), 162.22 (d, $^1J_{C\text{-}F}$ = 251 Hz, C_c), 173.30 (d, $^3J_{C\text{-}P}$ = 3 Hz, C_g) ppm. Note that at 298 K C_m does not show a resonance. This is probably due to broadness of this peak at this temperature.

δ_F = -113.28 ppm. δ_P = -2.05 ($^1J_{P\text{-}Pt}$ = 4303 Hz) ppm. δ_{Pt} = -4339 (d, $^1J_{Pt\text{-}P}$ = ~4300 Hz) ppm.

Complex Allyl-3



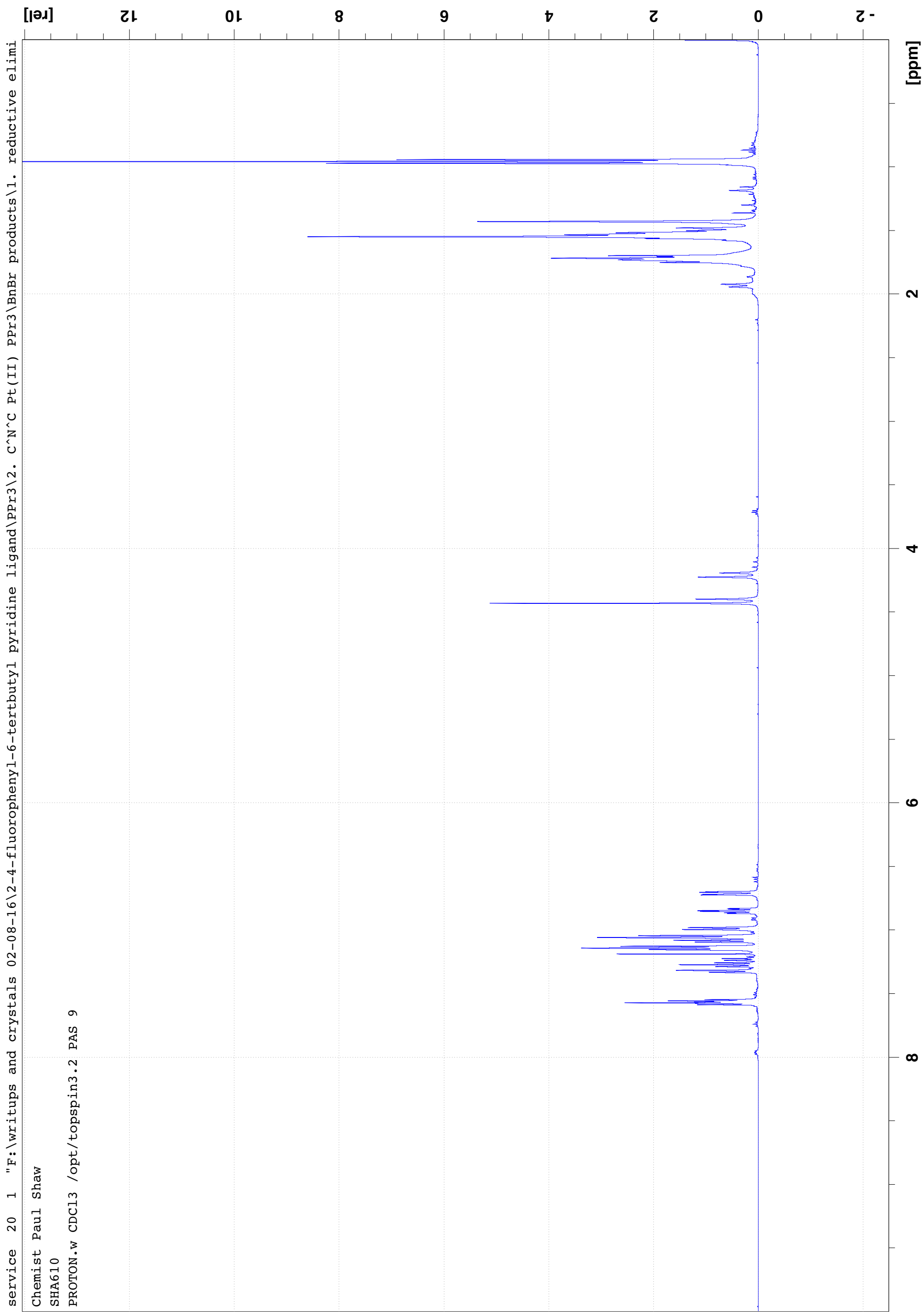
δ_H = 7.76 (1H, t, $^3J_{H\text{-}H}$ = 7.5 Hz, H_i), 7.63 (1H, dd, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}F}$ = 6 Hz, H_a), 7.26 (1H, d, $^3J_{H\text{-}H}$ = 7.5 Hz, H_j), 7.23 (1H, d, $^3J_{H\text{-}H}$ = 7.5 Hz, H_h), 6.98 (1H, dd, $^3J_{H\text{-}F}$ = 10 Hz, $^4J_{H\text{-}H}$ = 2 Hz, H_d), 6.90 (1H, td, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 8 Hz, $^4J_{H\text{-}H}$ = 2 Hz, H_b), 5.99 (1H, ddt, $^3J_{H\text{-}Htrans}$ = 17 Hz, $^3J_{H\text{-}Hcis}$ = 10 Hz, $^3J_{H\text{-}H}$ = 6.5 Hz, H_{allyl}), 5.06 (1H, dd, $^3J_{H\text{-}H}$ = 10 Hz, $^3J_{H\text{-}H}$ = 1.5 Hz, H_{allyl}), 5.01 (1H, dd, $^3J_{H\text{-}H}$ = 17 Hz, $^3J_{H\text{-}H}$ = 1.5 Hz, H_{allyl}), 3.69 (2H, d, $^3J_{H\text{-}H}$ = 6.5 Hz, H_{allyl}), 2.05 (1H, d, $^2J_{H\text{-}H}$ = 9.5 Hz, $^2J_{H\text{-}Pt}$ = 60 Hz, H_n), 1.77 (6H, m, P*CH₂*), 1.68 (1H, d, $^2J_{H\text{-}H}$ = 9.5 Hz, H_n), 1.63 (3H, s, H_m), 1.58 (6H, m, $PCH_2\mathit{CH_2}$), 1.48 (3H, s, H_m), 1.01 (9H, t, $^3J_{H\text{-}H}$ = 6 Hz, $PCH_2CH_2\mathit{Me}$) ppm. Note that at 298K both H_m and H_n have separated into two peaks each, separated by 75 Hz and 183 Hz respectively (600 MHz spectrometer).



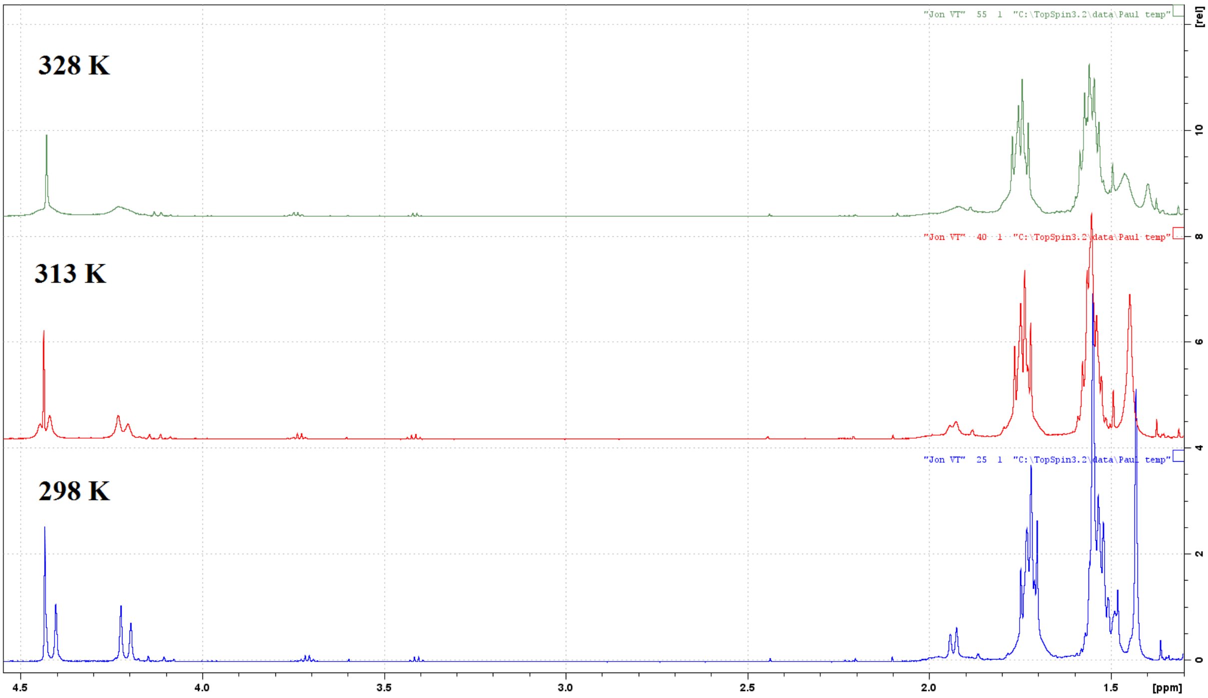
δ_C = 15.73 (d, $^3J_{C\text{-}P}$ = 15 Hz, PCH$_2$CH$_2$*Me*), 17.91 (s, $^3J_{C\text{-}Pt}$ = 32 Hz, PCH$_2$*CH$_2$*), 26.27 (d, $^1J_{C\text{-}P}$ = 37 Hz, $^2J_{C\text{-}Pt}$ = 46 Hz, P*CH$_2$*), 27.39 (d, $^2J_{C\text{-}P}$ = 5 Hz, $^1J_{C\text{-}Pt}$ = 746 Hz, C$_n$), 32.58 (s, $^3J_{C\text{-}Pt}$ = 59 Hz, H$_m$), 34.07 (s, $^3J_{C\text{-}Pt}$ = 33 Hz, H$_m$), 38.49 (s, C$_{allyl}$), 49.72 (s, $^2J_{C\text{-}Pt}$ = 23.5 Hz, C$_l$), 112.08 (d, $^2J_{C\text{-}F}$ = Hz, C$_b$), 115.96 (d, $^2J_{C\text{-}F}$ = Hz, C$_d$), 116.37 (s, C$_{allyl}$), 119.62 (s, $^3J_{C\text{-}Pt}$ = 25 Hz, C$_j$), 125.67 (d, $^4J_{C\text{-}P}$ = 4 Hz, C$_h$), 132.71 (d, $^3J_{C\text{-}F}$ = 9.5 Hz, C$_h$), 136.95 (m, C$_f$), 137.05 (m, C$_{i,allyl}$), 141.01 (d, $^3J_{C\text{-}F}$ = 8.5 Hz, C$_e$), 159.90 (s, C$_g$), 163.21 (d, $^1J_{C\text{-}F}$ = 249 Hz, C$_c$), 174.60 (s, C$_k$) ppm.

δ_F = -113.00 ppm. δ_P = -1.2 ($^1J_{P\text{-}Pt}$ = 4330 Hz) ppm. δ_{Pt} = -4214 (d, $^1J_{Pt\text{-}P}$ = ~4350 Hz) ppm.

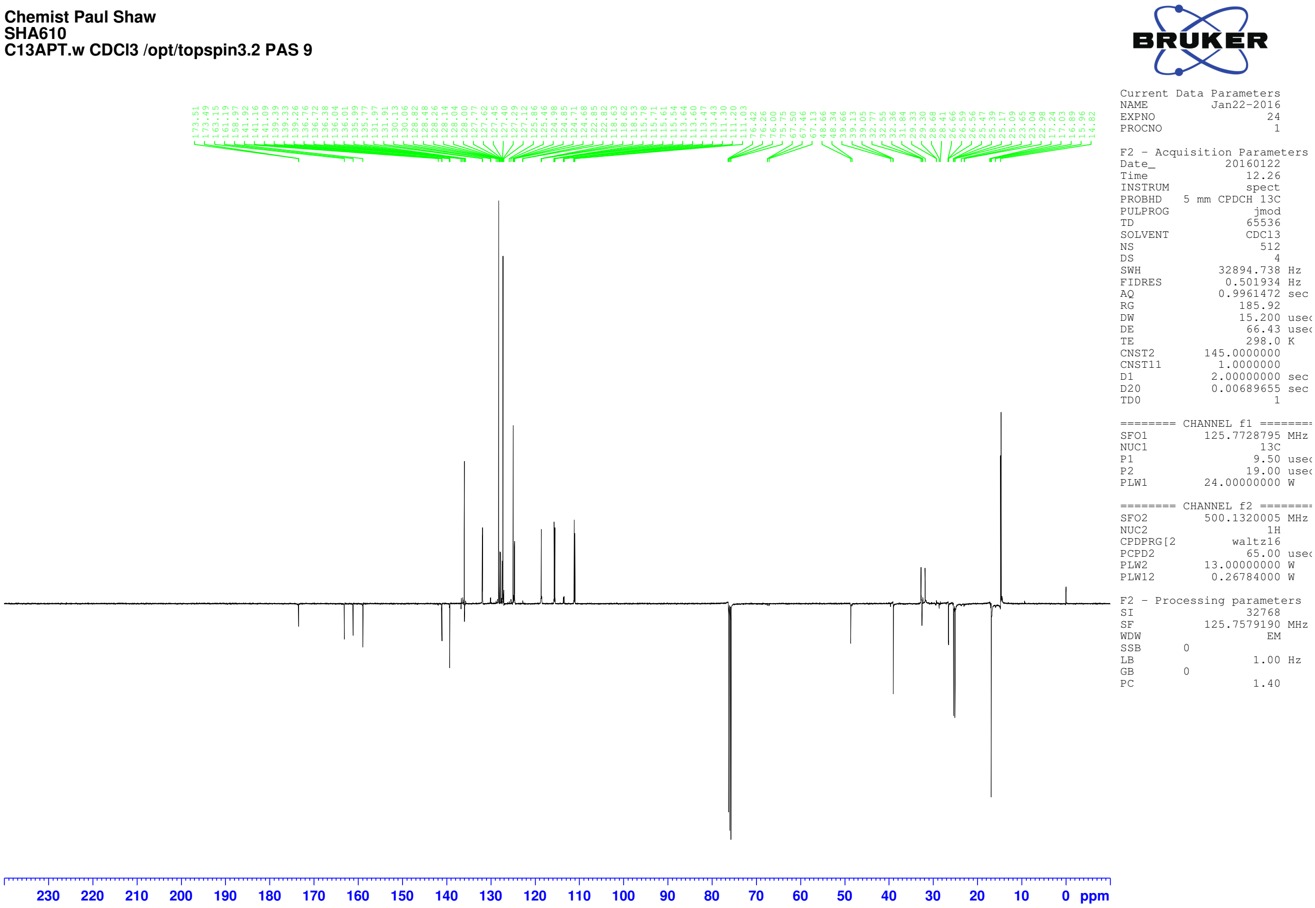
Complex Bn-3



δ_H = 7.57 (2H, m, $H_{a,i}$), 7.14 (3H, m, H_j, Bn-*m*), 7.08 (1H, m, Bn-*p*), 7.05 (2H, d, $^3J_{H-H}$ = 7.5 Hz, Bn-*o*), 6.99 (2H, d, $^3J_{H-H}$ = 7.5 Hz, H_h), 6.85 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_b), 6.70 (1H, td, $^3J_{H-F}$ = 10 Hz, $^4J_{H-H}$ = 2.5 Hz, H_b), 4.41 (1H, d, $^2J_{H-H}$ = 16.5 Hz, H_o), 2.41 (1H, d, $^2J_{H-H}$ = 16.5 Hz, Bn-CH_2), 1.93 (1H, d, $^2J_{H-H}$ = 10.5 Hz, $^2J_{H-Pt}$ = 51 Hz, H_n), 1.72 (7H, m, H_n, PCH_2), 1.53 (9H, m, H_m, PCH_2CH_2), 1.43 (3H, s, H_m), 0.96 (9H, t, $^3J_{H-H}$ = 7 Hz, PCH_2CH_2Me) ppm.



Note that at 298K the Bn-CH_2, H_m and H_n resonances have separated into 2 peaks each, separated by 103, 60 and 102 Hz respectively (600 MHz spectromter). By 328K, multiplicity is lost in all cases due to broadening of the peaks. Using a separation of 102 Hz and a coalescence temperature of 338 K we can calculate a barrier of 68.0 $kJmol^{-1}$; in line with our previous calculation our estimate of the uncertainty in this is ±5 $kJmol^{-1}$.

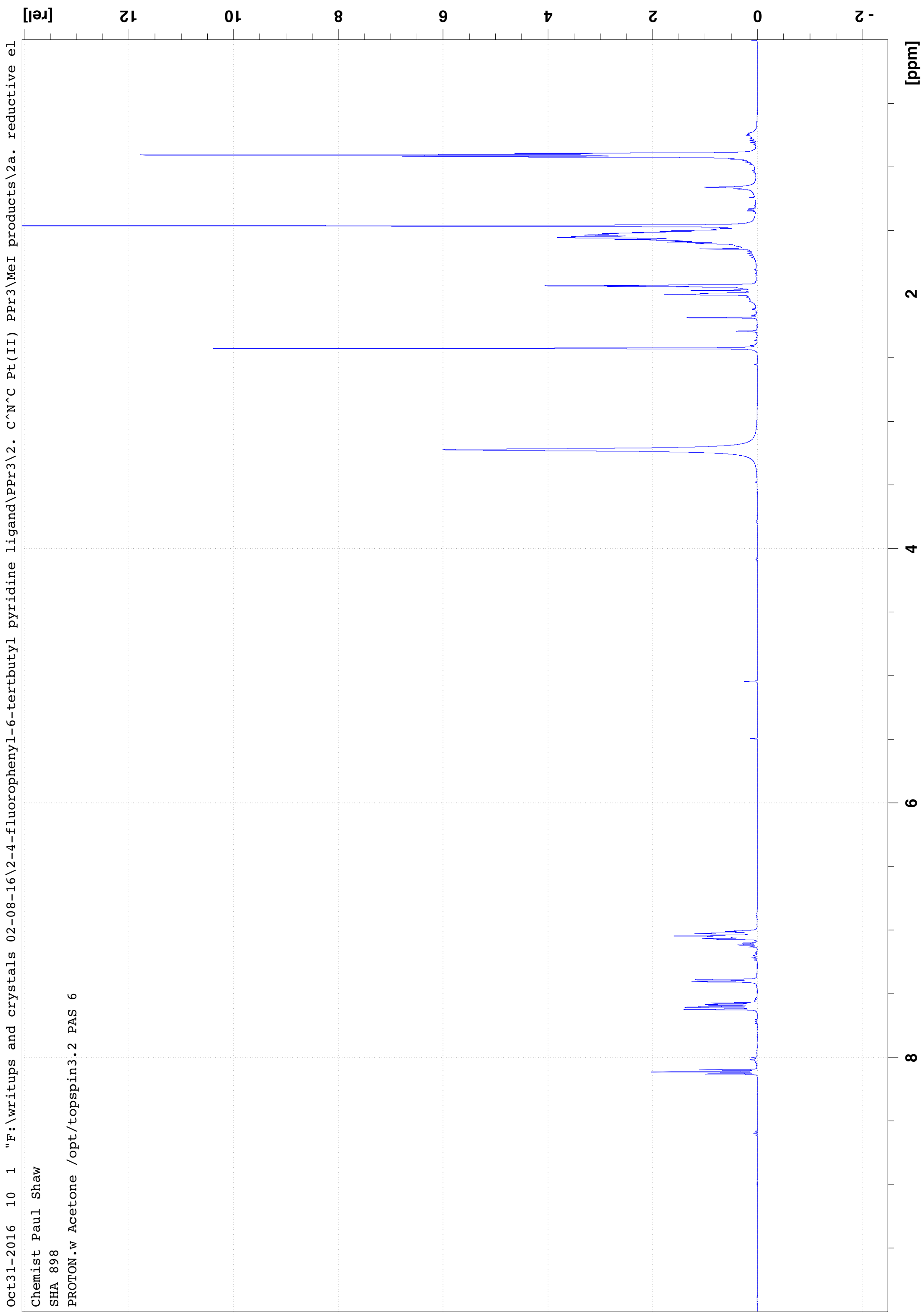


δ_C = 15.70 (d, $^3J_{C\text{-}P}$ = 14.5 Hz, $PCH_2CH_2\mathit{Me}$), 17.89 (s, $^3J_{C\text{-}Pt}$ = 31 Hz, $PCH_2\mathit{CH_2}$), 26.22 (d, $^3J_{C\text{-}P}$ = 38 Hz, $^2J_{C\text{-}Pt}$ = 38 Hz, $P\mathit{CH_2}$), 27.57 (d, $^2J_{C\text{-}P}$ = 5 Hz, $^1J_{C\text{-}Pt}$ = 741 Hz, C_n), 32.83 (s, C_m), 33.81 (s, C_m), 40.05 (s, Bn-$\mathit{CH_2}$), 49.66 (s, C_l), 112.13 (d, $^2J_{C\text{-}F}$ = 20 Hz, C_b), 116.64 (d, $^2J_{C\text{-}F}$ = 21 Hz, C_d), 119.64 (s, $^3J_{C\text{-}Pt}$ = 24 Hz, C_j), 125.69 (d, $^4J_{C\text{-}P}$ = 3.5 Hz, C_h), 125.98 (s, Bn-*p*), 128.32 (s, Bn-*m*), 129.26 (s, Bn-*o*), 132.94 (d, $^3J_{C\text{-}F}$ = 8.5 Hz, C_a), 136.94 (d, $^3J_{C\text{-}F}$ = 3 Hz, C_f), 137.03 (s, C_i), 140.33 (s, Bn-*i*), 142.12 (d, $^3J_{C\text{-}F}$ = 8 Hz, C_b), 159.95 (s, C_g), 163.13 (d, $^1J_{C\text{-}F}$ = 247 Hz, C_c), 174.49 (d, $^2J_{C\text{-}P}$ = 3 Hz, C_k) ppm.

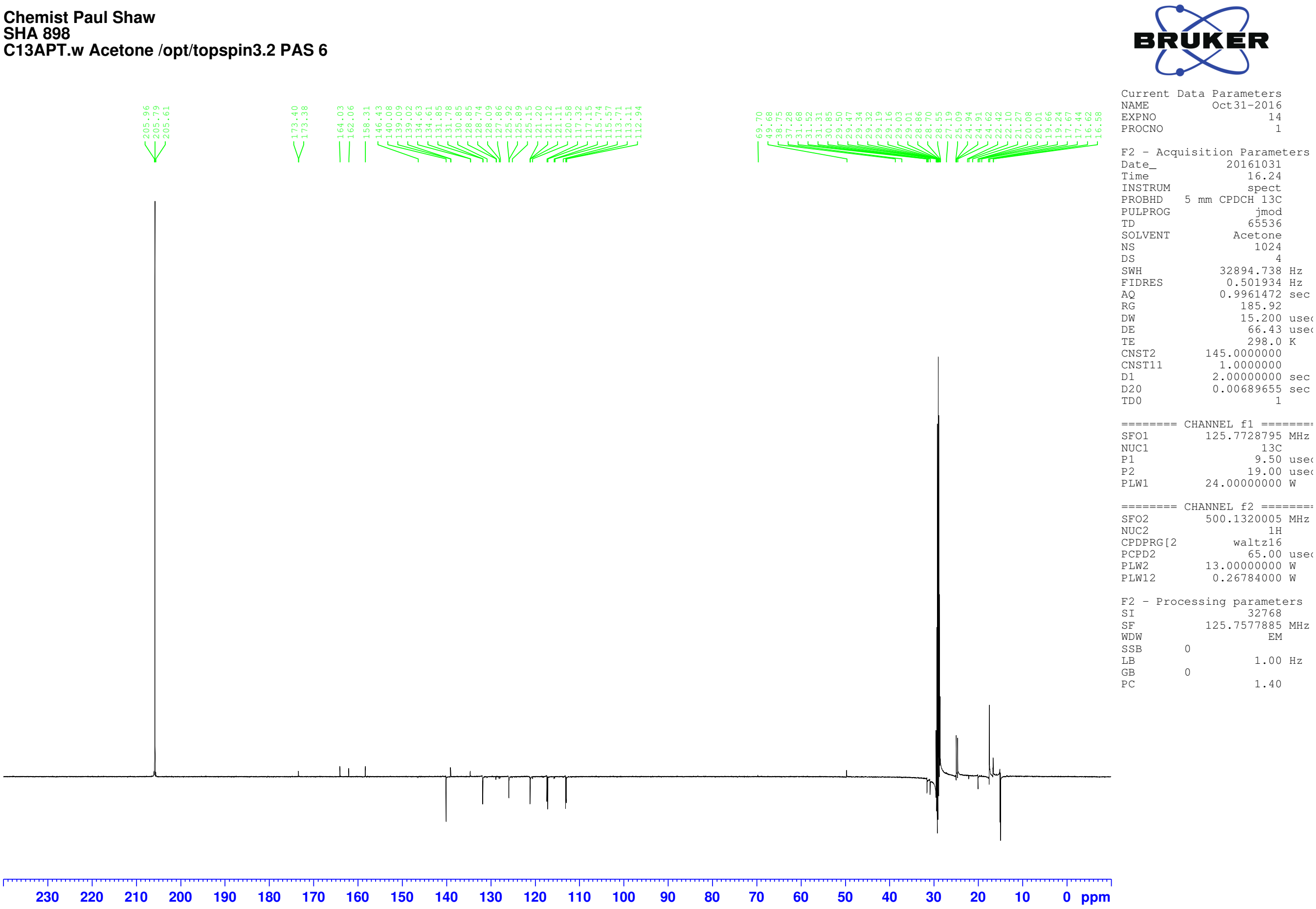
Note that at 298 K C_m is split into 2 peaks separated by 114 Hz (500 MHz spectrometer).

δ_F = -112.82 ppm. δ_P = -1.05 ($^1J_{P\text{-}Pt}$ = 4318 Hz) ppm. δ_{Pt} = -4219 (d, $^1J_{Pt\text{-}P}$ = ~4300 Hz) ppm.

Complex Me-4

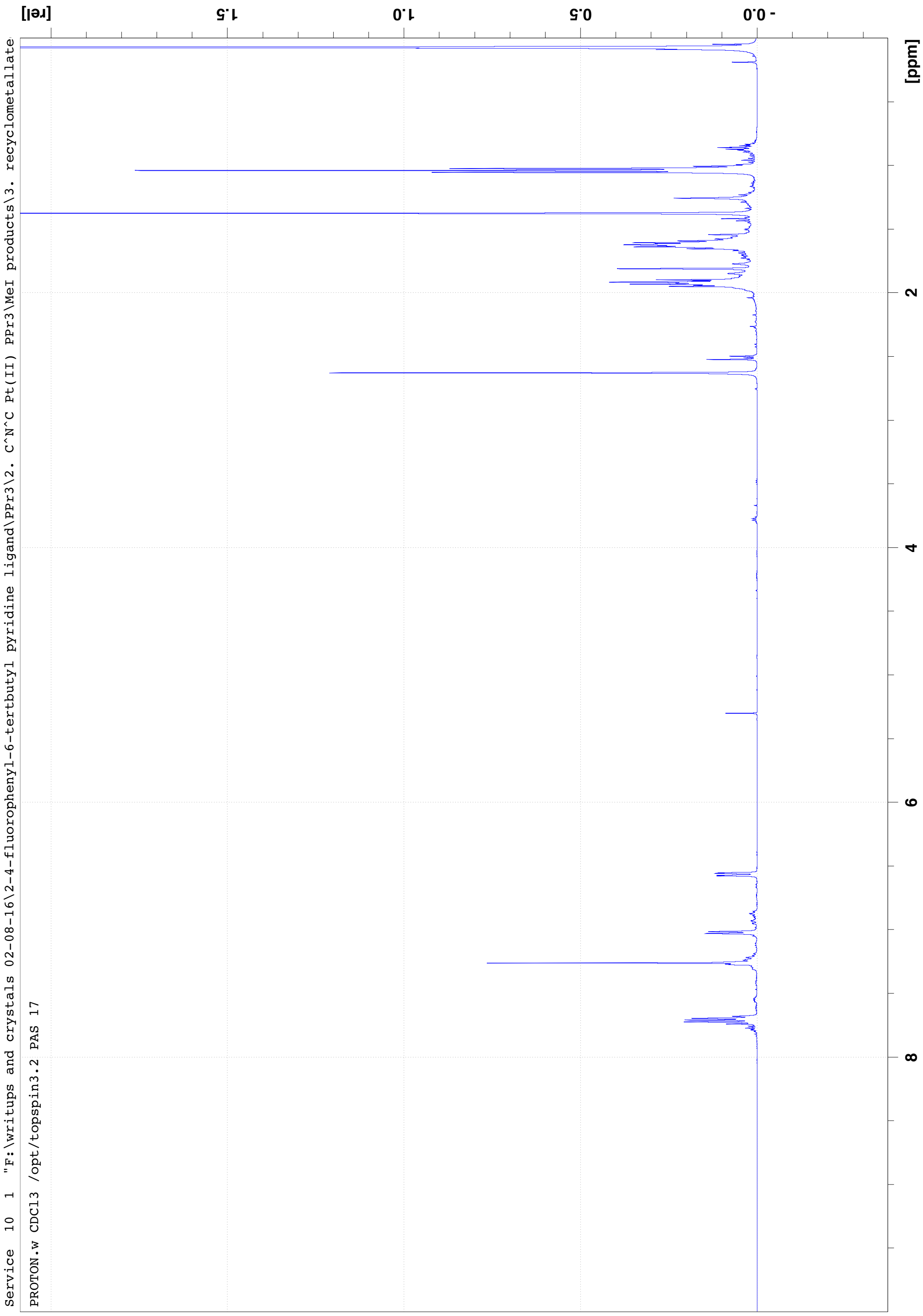


δ_H (Acetone-d$_6$) = 8.11 (1H, t, $^3J_{H\text{-}H}$ = 8 Hz, H$_i$), 7.59 (2H, m, H$_{j,a}$), 7.40 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, H$_h$), 7.04 (2H, m, H$_{b,d}$), 2.42 (3H, s, Me), 2.00 (2H, m, $^2J_{H\text{-}Pt}$ = ~32 Hz, H$_n$), 1.54 (12H, m, P*CH$_2$*, PCH$_2$*CH$_2$*), 0.91 (9H, t, $^3J_{H\text{-}H}$ = 7 Hz, PCH$_2$CH$_2$*Me*) ppm.

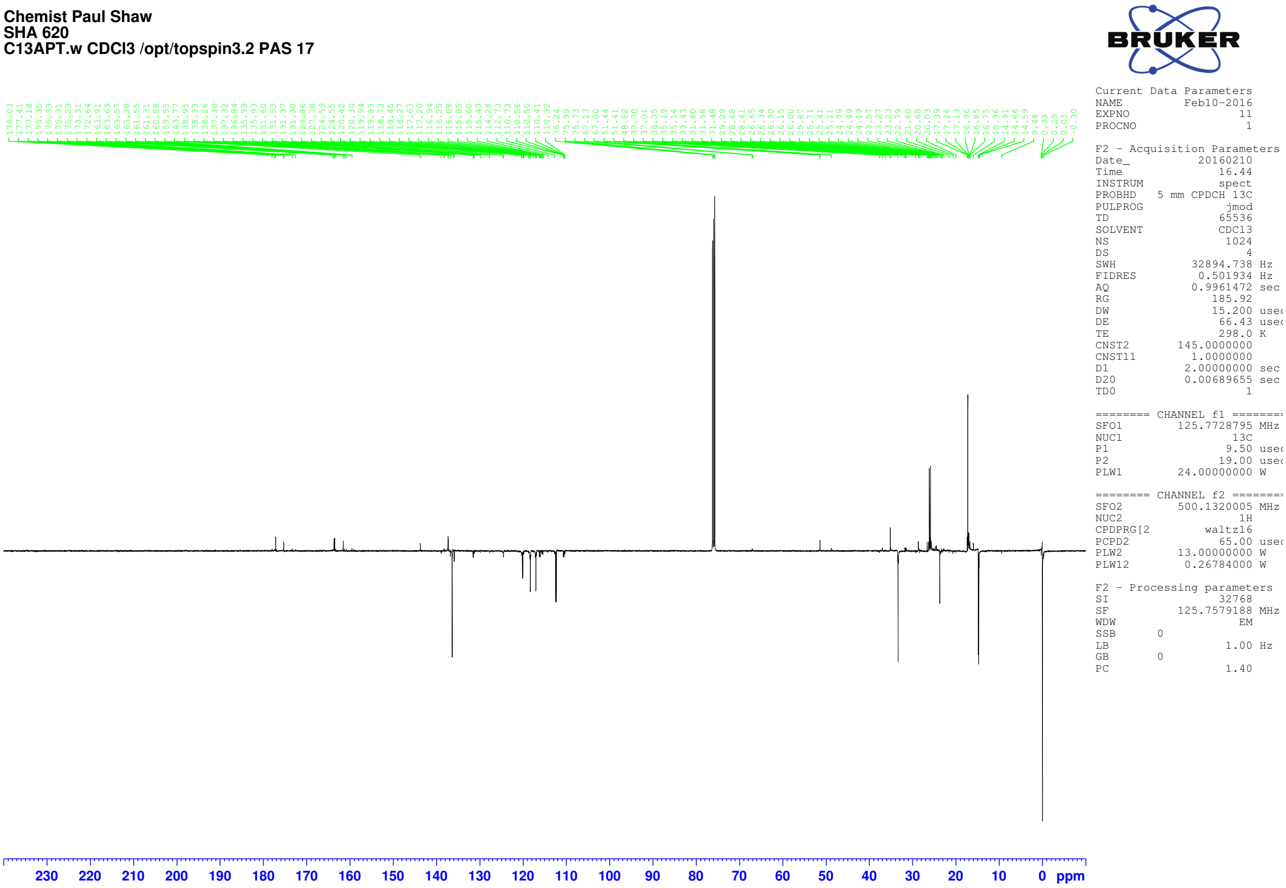


δ_C = 15.01 (d, $^3J_{C\text{-}P}$ = 15.5 Hz, PCH_2CH_2*Me*), 16.61 (d, $^2J_{C\text{-}P}$ = 5.5 Hz, $^1J_{C\text{-}Pt}$ = 765 Hz, C_n), 17.45 (s, $^3J_{C\text{-}Pt}$ = 30 Hz, PCH_2*CH_2*), 20.03 (s, Me), 24.77 (d, $^1J_{C\text{-}P}$ = 38 Hz, $^2J_{C\text{-}Pt}$ = 42 Hz, P*CH_2*), 31.21 (s, C_m), 49.68 (s, C_l), 113.04 (d, $^2J_{C\text{-}F}$ = 25 Hz, C_b), 117.25 (d, $^2J_{C\text{-}F}$ = 22 Hz, C_d), 121.13 (s, C_j), 125.93 (s, C_h), 131.83 (d, $^3J_{C\text{-}F}$ = 8.5 Hz, C_a), 134.63 (s, C_f), 139.07 (d, $^3J_{C\text{-}F}$ = 8.5 Hz, C_e), 140.10 (s, C_i), 158.35 (s, C_g), 163.02 (d, $^1J_{C\text{-}F}$ = 245 Hz, C_c), 173.43 (s, C_k) ppm. δ_F (Acetone-d_6) = -114.13 ppm. δ_P (Acetone-d_6) = 3.00 ($^1J_{P\text{-}Pt}$ = 4272 Hz) ppm. δ_{Pt} (Acetone-d_6) = -4116 (d, $^1J_{Pt\text{-}P}$ = ~4400 Hz) ppm.

Complex Me-1



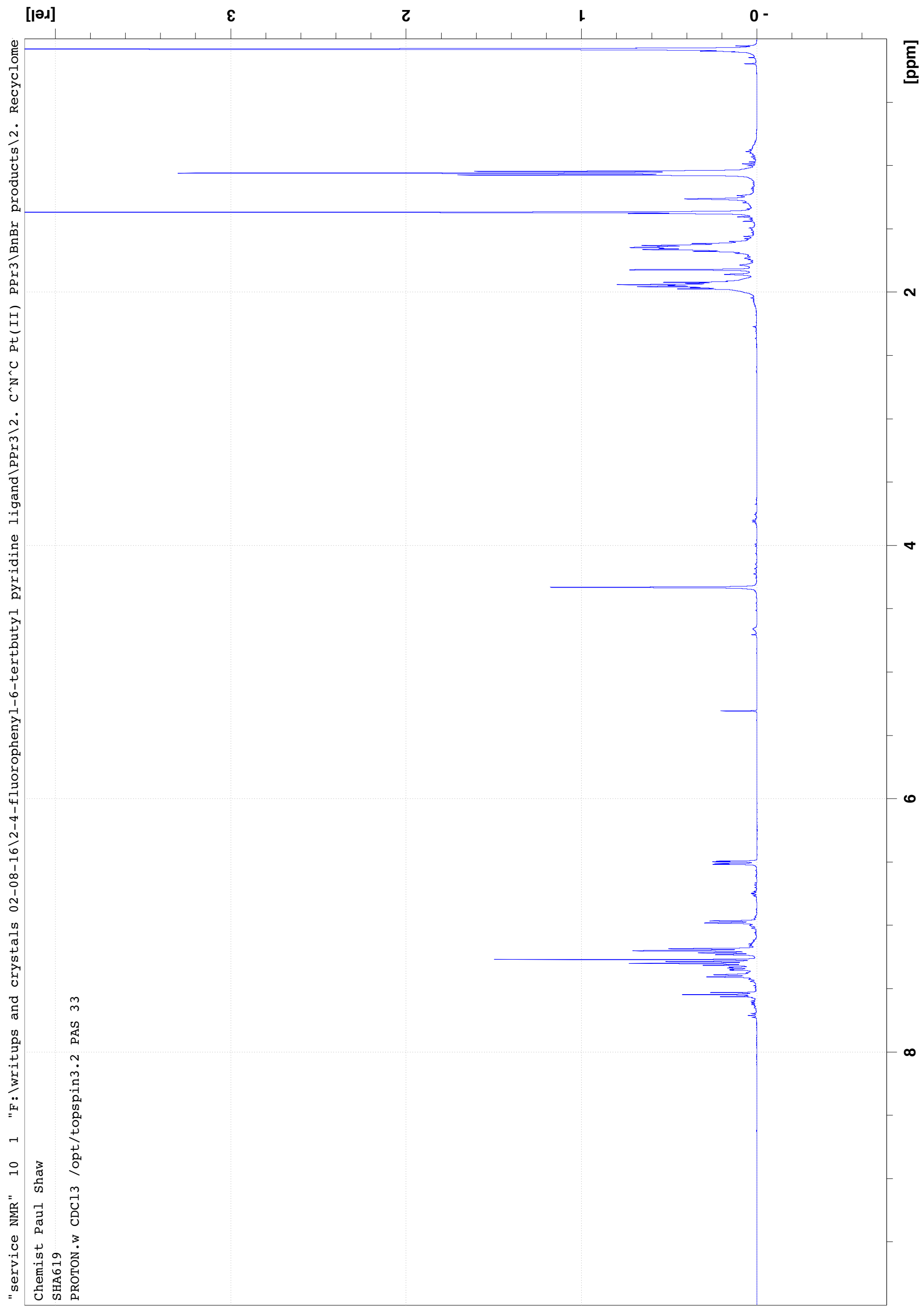
δ_H = 7.71 (2H, m, $H_{h,i}$), 7.25 (1H, m, H_b), 7.02 (1H, d, $^3J_{H\text{-}H}$ = 8.5 Hz, H_j), 6.56 (1H, dd, $^3J_{H\text{-}H}$ = 9.5 Hz, $^5J_{H\text{-}P}$ = 2 Hz, H_d), 2.63 (3H, s, Me), 1.92 (6H, m, P*CH$_2$*), 1.81 (2H, s, $^2J_{H\text{-}Pt}$ = 37 Hz, H_n), 1.62 (6H, m, PCH_2*CH$_2$*), 1.37 (6H, s, H_m), 1.04 (9H, t, $^3J_{H\text{-}H}$ = 7 Hz, PCH_2CH_2*Me*) ppm.



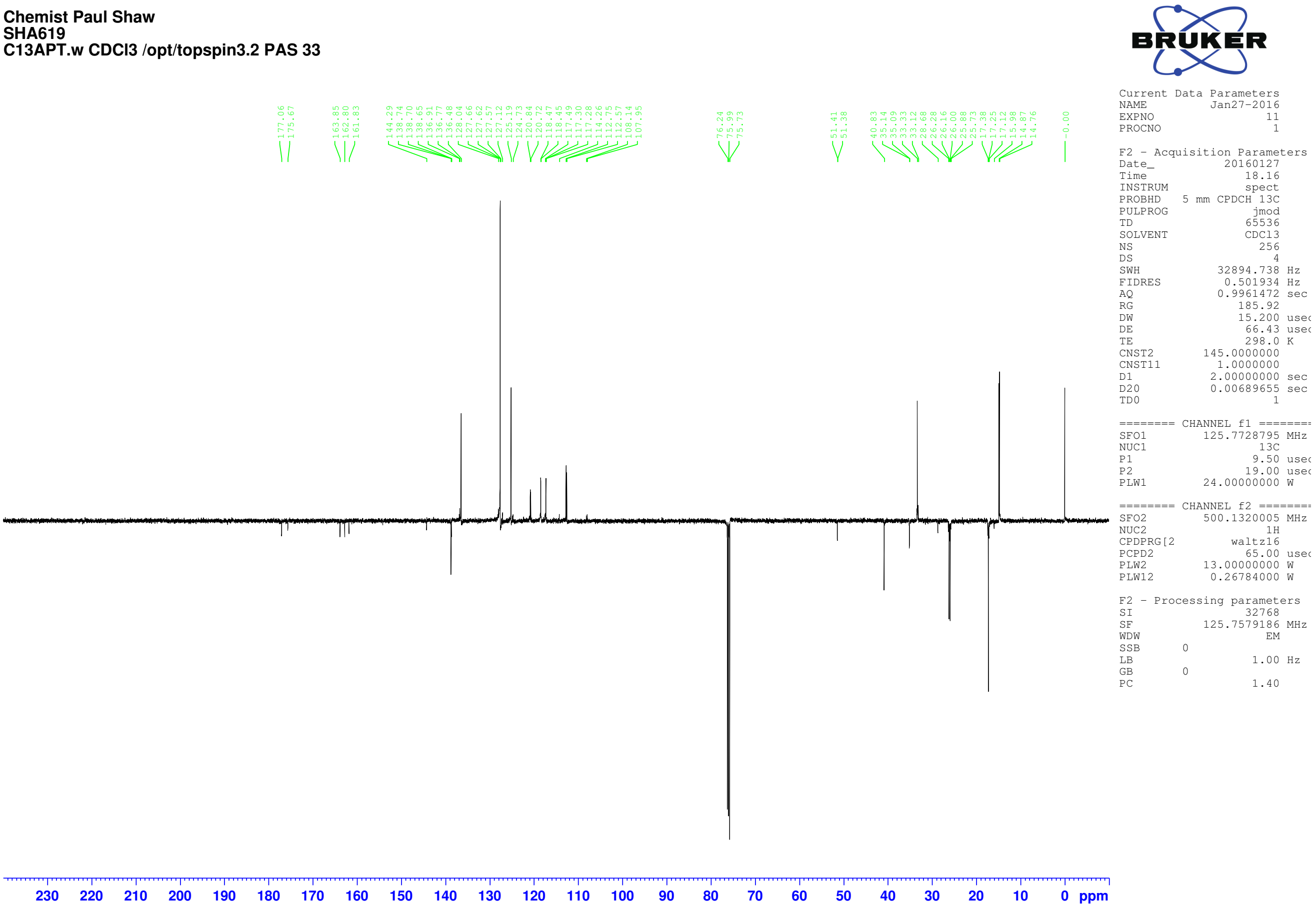
δ_C = 14.81 (d, $^3J_{C\text{-}P}$ = 14.5 Hz, $PCH_2CH_2\mathit{Me}$), 17.27 (s, $^3J_{C\text{-}Pt}$ = 32 Hz, $PCH_2\mathit{CH_2}$), 23.73 (s, Me), 26.01 (d, $^1J_{C\text{-}P}$ = 35 Hz, $^2J_{C\text{-}Pt}$ = 35 Hz, $P\mathit{CH_2}$), 33.36 (s, $^3J_{C\text{-}Pt}$ = 18 Hz, C_m), 35.18 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, $^1J_{C\text{-}Pt}$ = 460 Hz, C_n), 51.43 (d, $^3J_{C\text{-}P}$ = 4 Hz, C_l), 112.42 (d, $^3J_{C\text{-}F}$ = 21.5 Hz, C_d), 117.06 (d, $^4J_{C\text{-}P}$ = 3 Hz, $^3J_{C\text{-}Pt}$ = 31 Hz, C_h), 118.36 (d, $^4J_{C\text{-}P}$ = 3 Hz, $^3J_{C\text{-}Pt}$ = 23 Hz, C_j), 120.13 (d, $^2J_{C\text{-}F}$ = 14 Hz, $^2J_{C\text{-}Pt}$ = 60 Hz, C_b), 136.42 (s, C_i), 137.37 (d, $^3J_{C\text{-}F}$ = 7.5 Hz, $^3J_{C\text{-}Pt}$ = 31 Hz, C_e), 143.77 (s, $^2J_{C\text{-}Pt}$ = 29 Hz, C_f), 162.55 (d, $^1J_{C\text{-}F}$ = 254 Hz, $^3J_{C\text{-}Pt}$ = 55 Hz, C_c), 163.69 (s, $^2J_{C\text{-}Pt}$ = 54 Hz, C_g), 175.35 (m, $^1J_{C\text{-}Pt}$ = 680 Hz, C_a), 177.22 (s, $^2J_{C\text{-}Pt}$ = 54.5 Hz, C_k) ppm.

δ_F = -114.13 ($^4J_{F\text{-}Pt}$ = 28 Hz) ppm. δ_P = 0.96 ($^1J_{P\text{-}Pt}$ = 3820 Hz) ppm. δ_{Pt} = -3995 (d, $^1J_{Pt\text{-}P}$ = ~3900 Hz) ppm.

Complex Bn-1



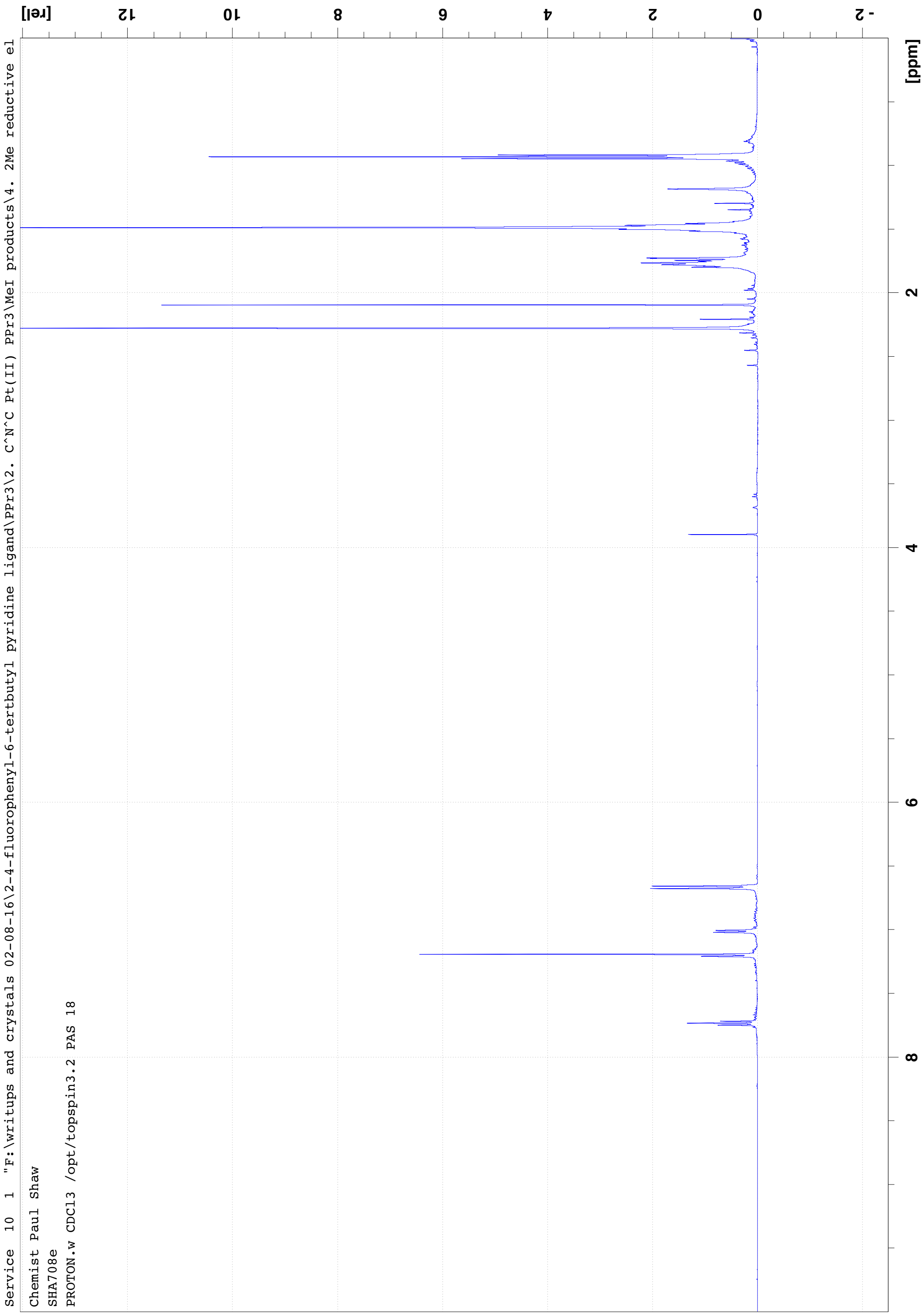
δ_H = 7.55 (1H, t, $^3J_{H\text{-}H}$ = 7.5 Hz, H_i), 7.41 (1H, d, $^3J_{H\text{-}H}$ = 7.5 Hz, H_h), 7.35 (d, 1H, $^3J_{H\text{-}F}$ = 8 Hz, $^4J_{H\text{-}H}$ = 2 Hz, $^3J_{H\text{-}Pt}$ = #20 Hz, H_b), 7.31 (3H, m, Bn-*m,p*), 7.20 (2H, d, $^3J_{H\text{-}H}$ = 8.5 Hz, Bn-*o*), 6.98 (1H, d, $^3J_{H\text{-}H}$ = 7.5 Hz, H_j), 6.51 (1H, dd, $^3J_{H\text{-}F}$ = 10 Hz, $^4J_{H\text{-}H}$ = 2 Hz, H_d), 4.34 (2H, s, Bn-CH_2), 1.95 (6H, m, PCH_2), 1.83 (2H, s, $^2J_{H\text{-}Pt}$ = 37 Hz, H_n), 1.66 (6H, m, PCH_2CH_2), 1.38 (6H, s, C_m), 1.07 (9H, t, $^3J_{H\text{-}H}$ = 7 Hz, PCH_2CH_2Me) ppm.



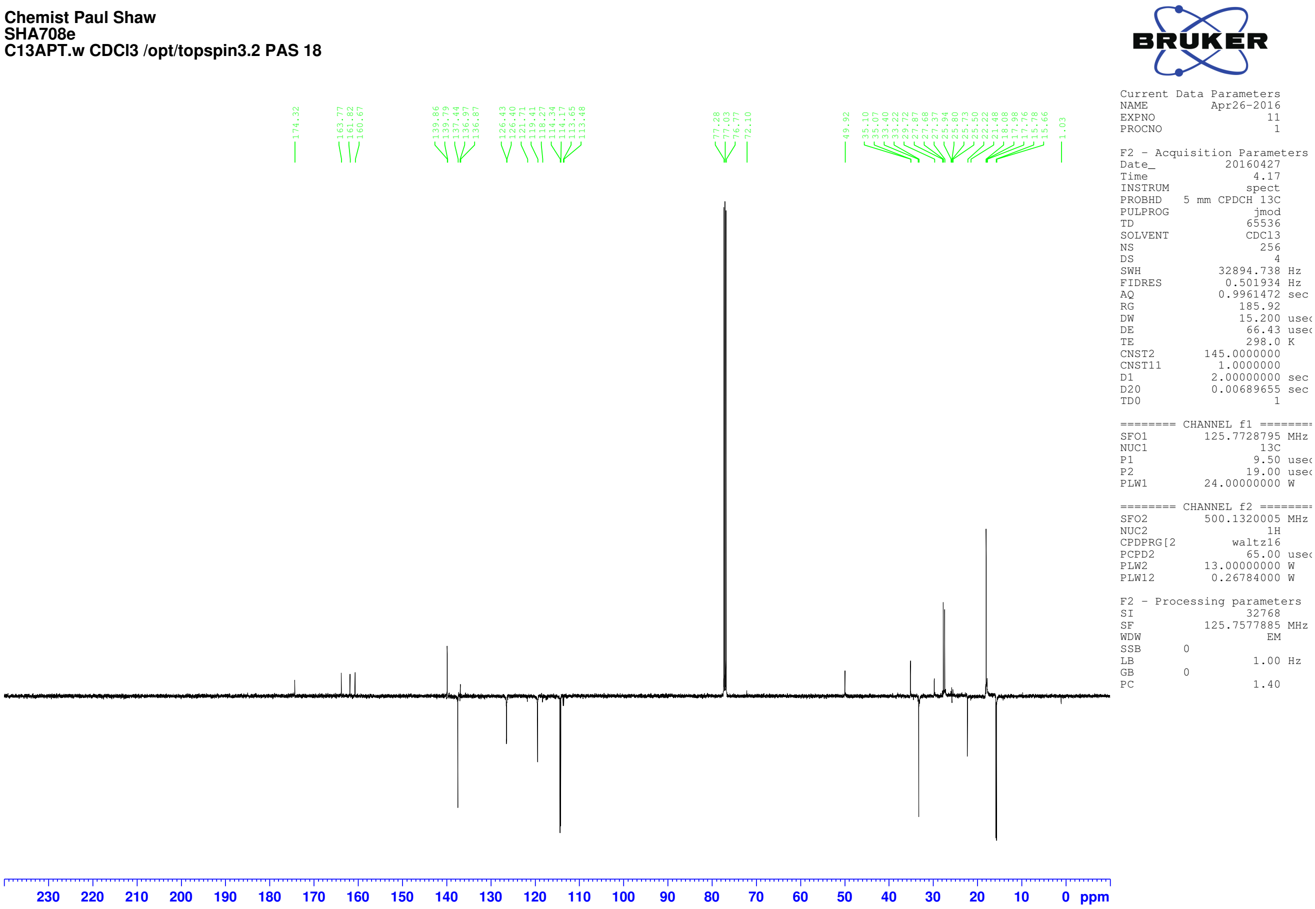
δ_C = 14.79 (d, $^3J_{C\text{-}P}$ = 14 Hz, PCH_2CH_2*Me*), 17.26 (s, $^3J_{C\text{-}Pt}$ = 30.5 Hz, PCH_2*CH₂*), 26.00 (d, $^1J_{C\text{-}P}$ = 36 Hz, $^2J_{C\text{-}Pt}$ = 36 Hz, P*CH₂*), 33.36 (s, $^3J_{C\text{-}Pt}$ = 17 Hz, C_m), 35.17 (s, C_n), 40.86 (s, Bn-*CH₂*), 51.44 (s, C_l), 112.69 (d, $^2J_{C\text{-}F}$ = 24 Hz, C_d), 117.35 (s, C_j), 118.52 (s, C_h), 120.83 (d, $^2J_{C\text{-}F}$ = 16 Hz, C_b), 125.29 (s, Bn-*p*), 127.69 (s, Bn-*o*,*m*), 136.46 (s, C_i), 138.82 (s, Bn-*i*), 144.28 (s, C_f), 162.82 (s, C_g), 162.85 (d, $^1J_{C\text{-}F}$ = 253 Hz, C_c), 175.66 (m, C_a), 177.07 (s, C_k) ppm.

δ_F = -113.66 ($^4J_{F\text{-}Pt}$ = 26.5 Hz) ppm. δ_P = 0.86 ($^1J_{P\text{-}Pt}$ = 3813 Hz) ppm. δ_{Pt} = -3987 (d, $^1J_{Pt\text{-}P}$ = ~3850 Hz) ppm.

Complex Me_2-3



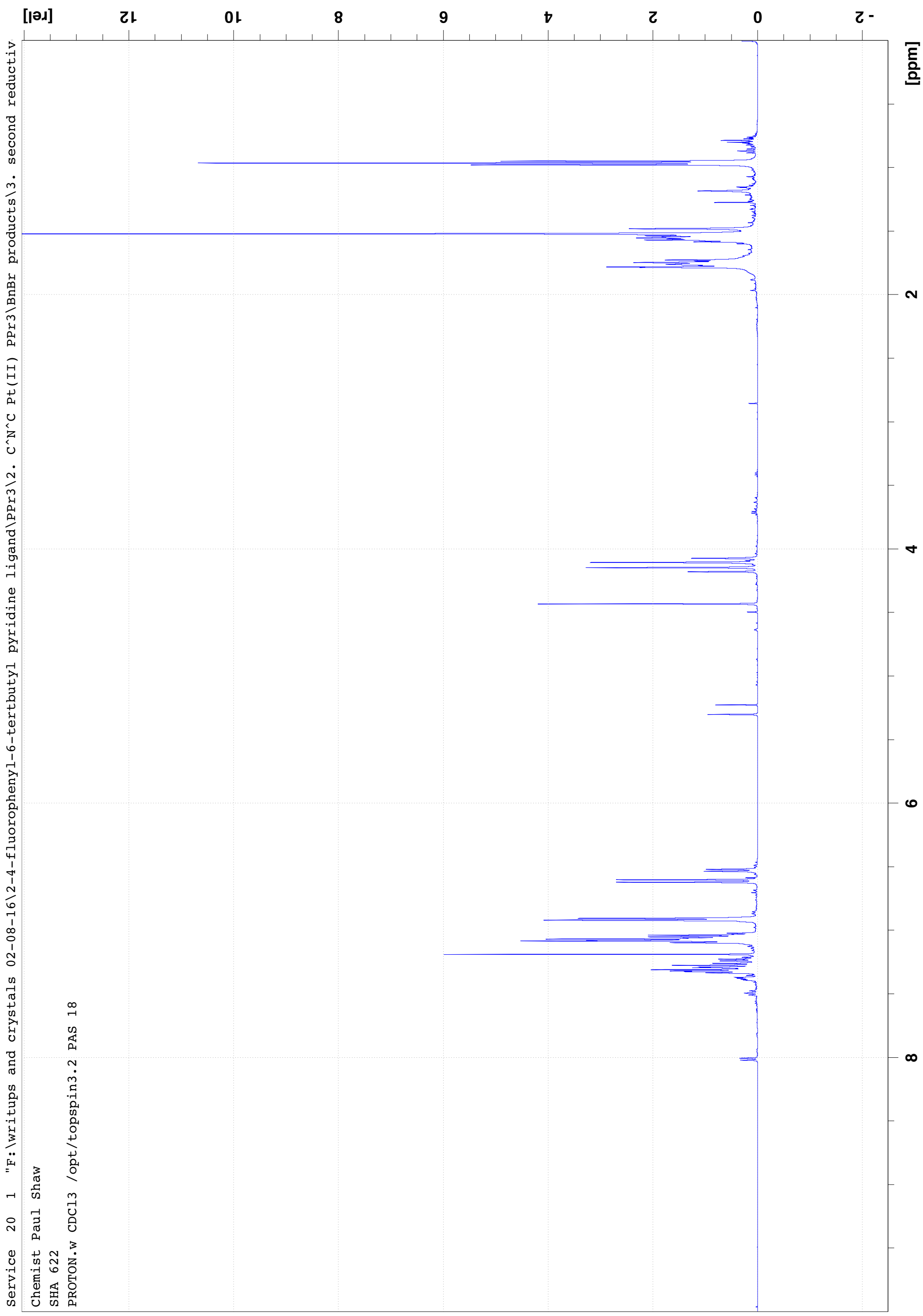
δ_H = 7.80 (1H, t, $^3J_{H\text{-}H}$ = 8 Hz, H_g), 7.27 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, H_h), 7.08 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, H_f), 6.73 (2H, d, $^3J_{H\text{-}F}$ = 9.5 Hz, H_b), 2.35 (6H, s, Me), 1.83 (8H, m, H_l, P*CH*$_2$), 1.56 (12H, m, H_k, PCH_2*CH*$_2$), 0.99 (9H, t, $^3J_{H\text{-}H}$ = 7 Hz, PCH_2CH_2*Me*) ppm.



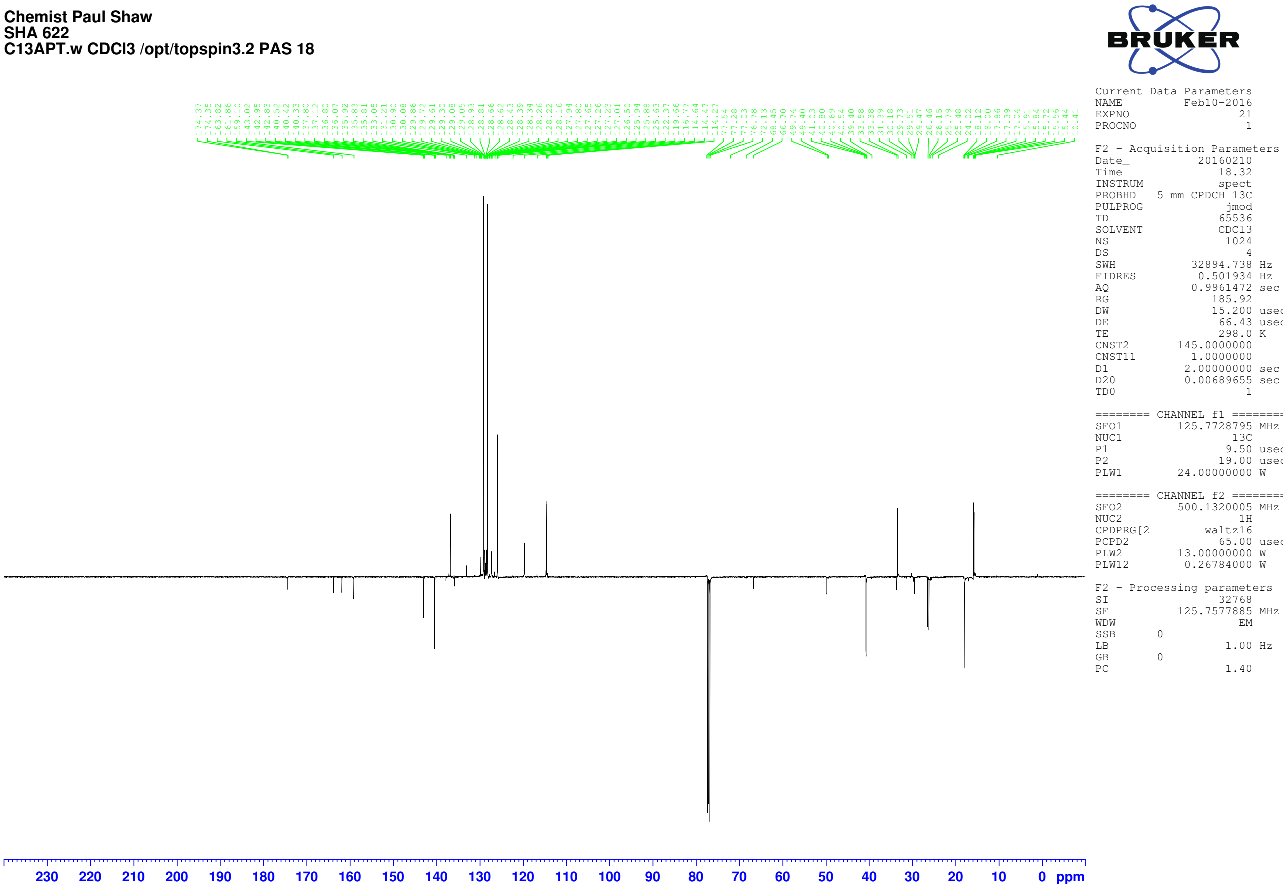
δ_C = 15.76 (d, $^3J_{C-P}$ = 18 Hz, $PCH_2CH_2\mathit{Me}$), 18.00 (s, $^3J_{C-Pt}$ = 30 Hz, $PCH_2\mathit{CH_2}$) 22.24 (s, Me), 27.57 (d, $^1J_{C-P}$ = 35 Hz, $^2J_{C-Pt}$ = 48 Hz, $P\mathit{CH_2}$), 33.23 (s, $^3J_{C-Pt}$ = 44 Hz, C_k), 35.16 (s, $^1J_{C-Pt}$ = 727 Hz, C_l), 49.98 (s, C_j), 114.22 (d, $^2J_{C-F}$ = 23 Hz, C_b), 119.42 (s, C_h), 126.44 (s, C_f), 136.86 (s, C_d), 137.44 (s, C_g), 139.83 (d, $^3J_{C-F}$ = 10 Hz, C_c), 160.69 (s, C_e), 162.80 (d, $^1J_{C-F}$ = 254 Hz, C_a), 174.32 (s, C_i) ppm.

δ_F = -114.84 ppm. δ_P = -1.80 ($^1J_{P-Pt}$ = 4292 Hz) ppm. δ_{Pt} = -4382 (d, $^1J_{Pt-P}$ = ~4300 Hz) ppm.

Complex Bn_2-3



δ_H = 7.32 (1H, t, $^3J_{H\text{-}H}$ = 8.5 Hz, H_g), 7.07 (7H, m, H_h, Bn-*m,p*), 6.91 (4H, d, $^3J_{H\text{-}H}$ = 8 Hz, Bn-*o*), 6.61 (2H, d, $^3J_{H\text{-}F}$ = 10 Hz, H_b), 6.53 (2H, d, $^3J_{H\text{-}H}$ = 8.5 Hz, H_f), 4.16 (2H, d, $^2J_{H\text{-}H}$ = 16 Hz, Bn-CH_2), 4.09 (2H, d, $^2J_{H\text{-}H}$ = 16 Hz, Bn-CH_2), 1.75 (8H, m, H_l, PCH_2), 1.55 (6H, m, PCH_2CH_2), 1.52 (6H, m, H_k), 0.96 (9H, t, $^3J_{H\text{-}H}$ = 7 Hz, PCH_2CH_2*Me*) ppm.



δ_C = 15.80 (d, $^3J_{C\text{-}P}$ = 16 Hz, $PCH_2CH_2\mathit{Me}$), 18.02 (s, $^3J_{C\text{-}Pt}$ = 27 Hz, $PCH_2\mathit{CH_2}$), 26.35 (d, $^1J_{C\text{-}P}$ = 37 Hz, $^2J_{C\text{-}Pt}$ = 34 Hz, $P\mathit{CH_2}$), 29.50 (d, $^2J_{C\text{-}P}$ = 4 Hz, C_l), 33.40 (s, C_k), 40.69 (s, C_m), 49.60 (s, C_j), 114.56 (d, $^2J_{C\text{-}F}$ = 22 Hz, C_b), 119.66 (s, C_f), 125.88 (s, Bn-*p*), 127.26 (s, C_h), 128.18 (s, Bn-*m*), 129.09 (s, Bn-*o*), 135.83 (s, C_d), 136.81 (s, C_g), 140.44 (s, C_n), 143.01 (d, $^3J_{C\text{-}F}$ = 8 Hz, C_c), 159.11 (s, C_e), 162.85 (d, $^1J_{C\text{-}F}$ = 247 Hz, C_a), 174.50 (s, C_i) ppm.

δ_F = -113.65 ppm. δ_P = -0.93 ($^1J_{P\text{-}Pt}$ = 4298 Hz) ppm. δ_{Pt} = -4250 (d, $^1J_{Pt\text{-}P}$ = ~4300 Hz) ppm.