Supporting Information

For

Dimethylphosphinate bridged Binuclear Rh(I) Catalysts for the Alkoxycarbonylation of Aromatic C–H bonds

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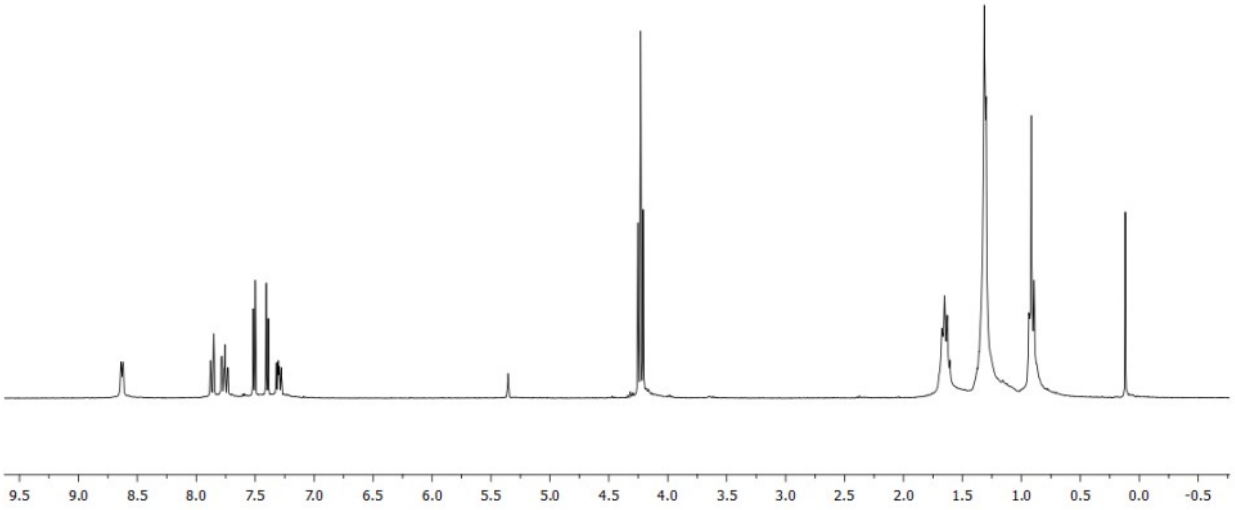
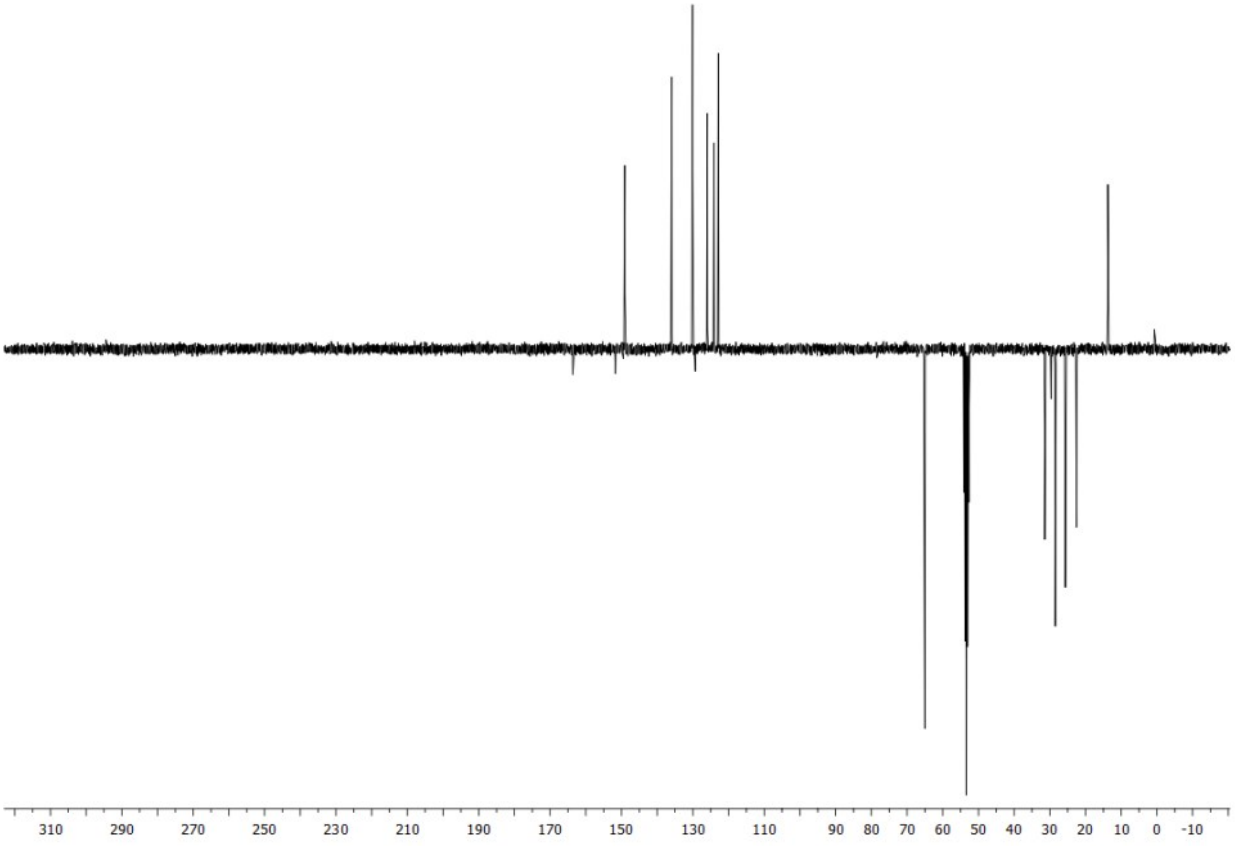
Hexyl-2-(pyridin-2-yl)thiophene-3-carboxylate

^{1}H NMR



^{13}C NMR-APT



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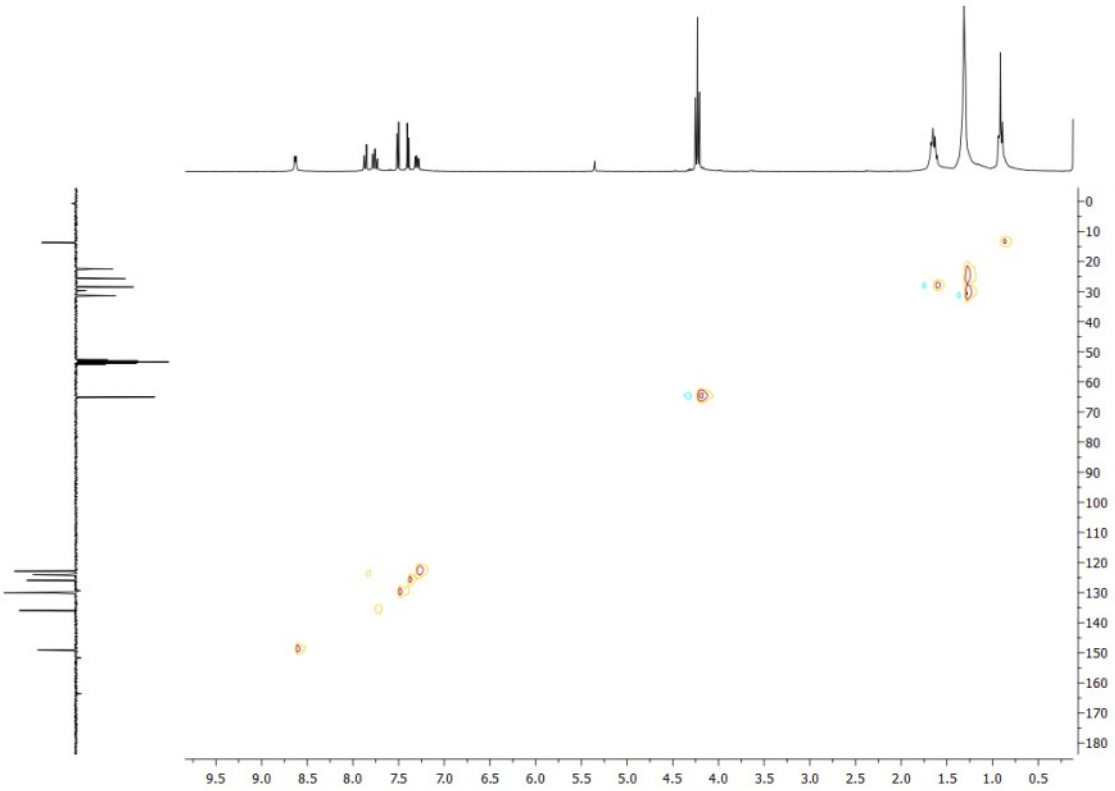

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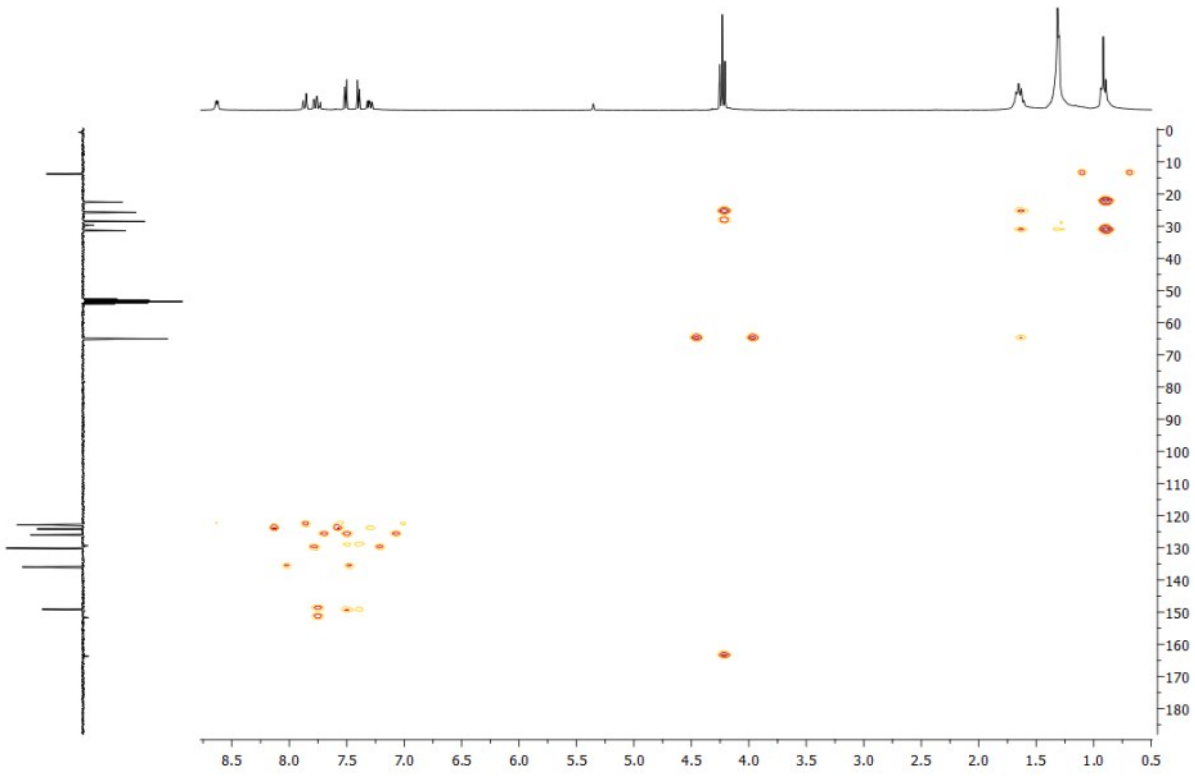

Complex 1

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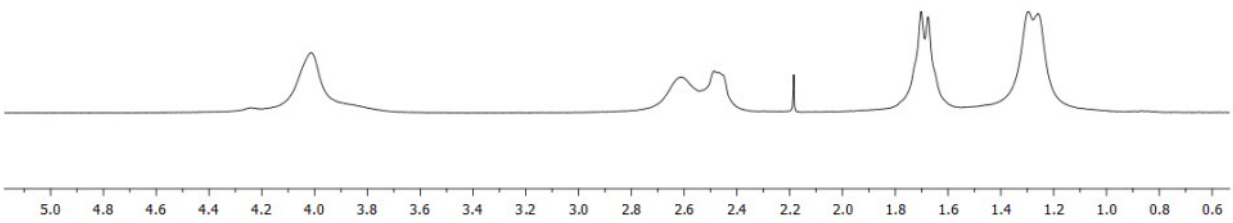

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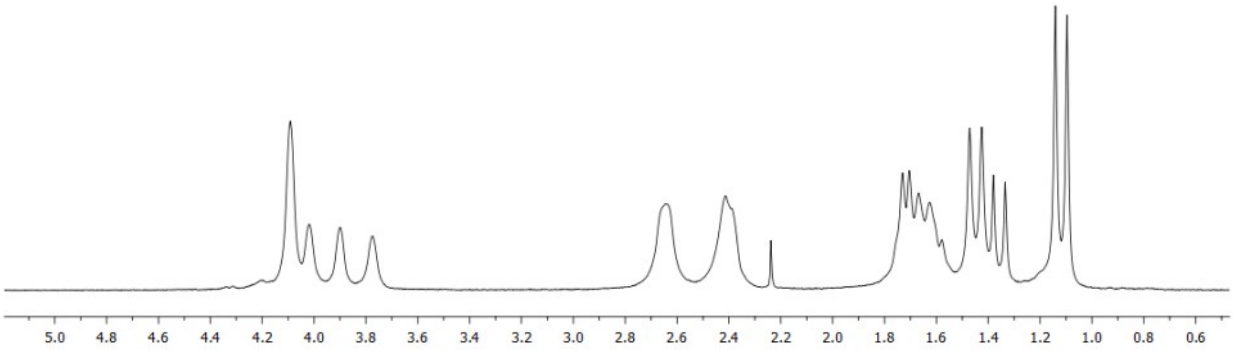

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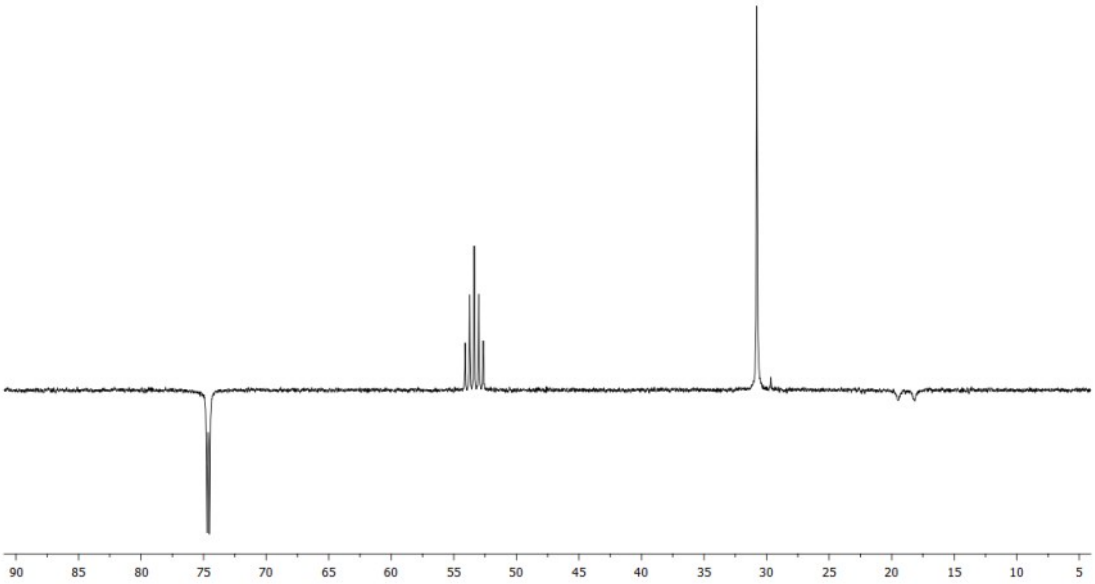

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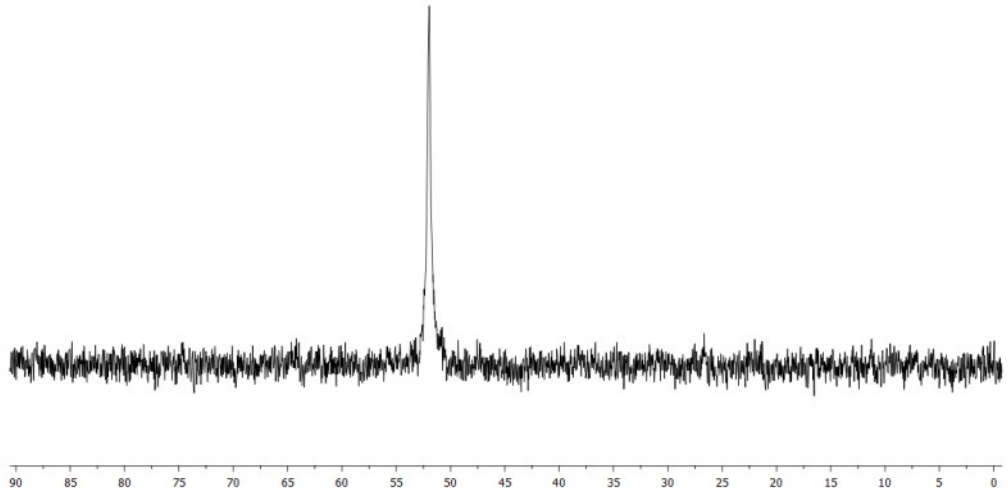

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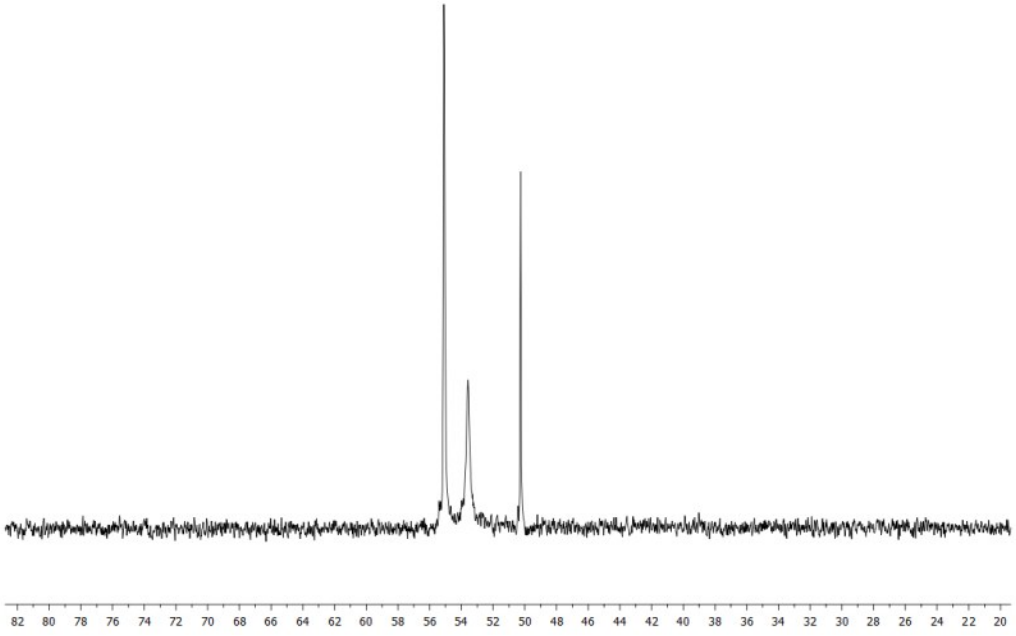

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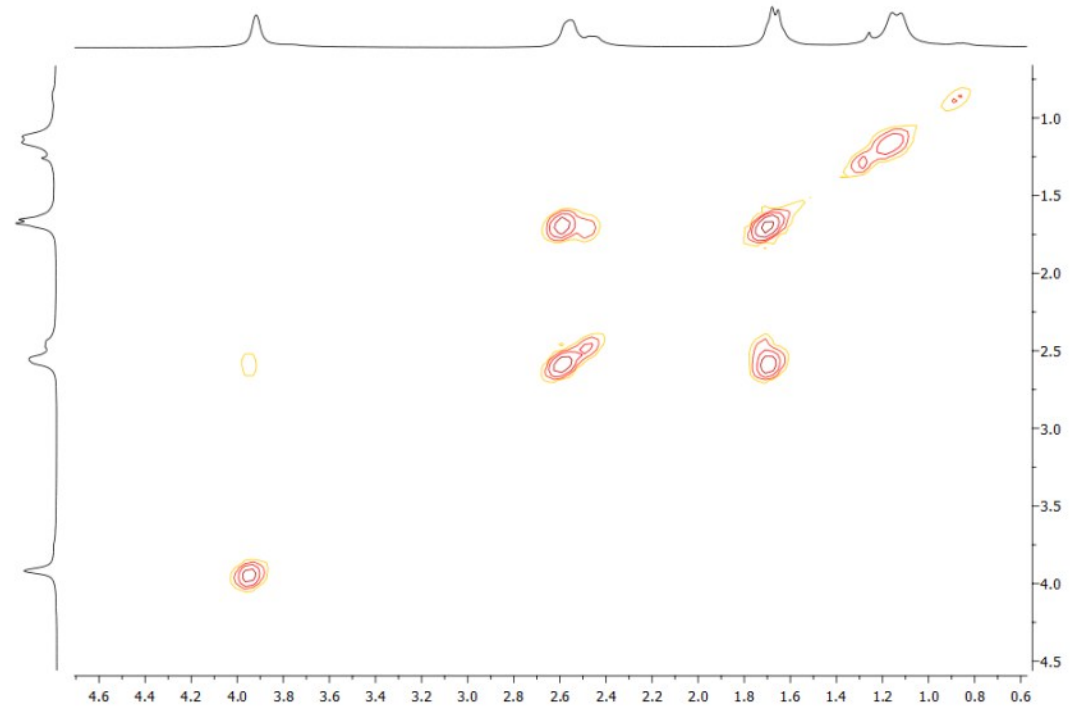

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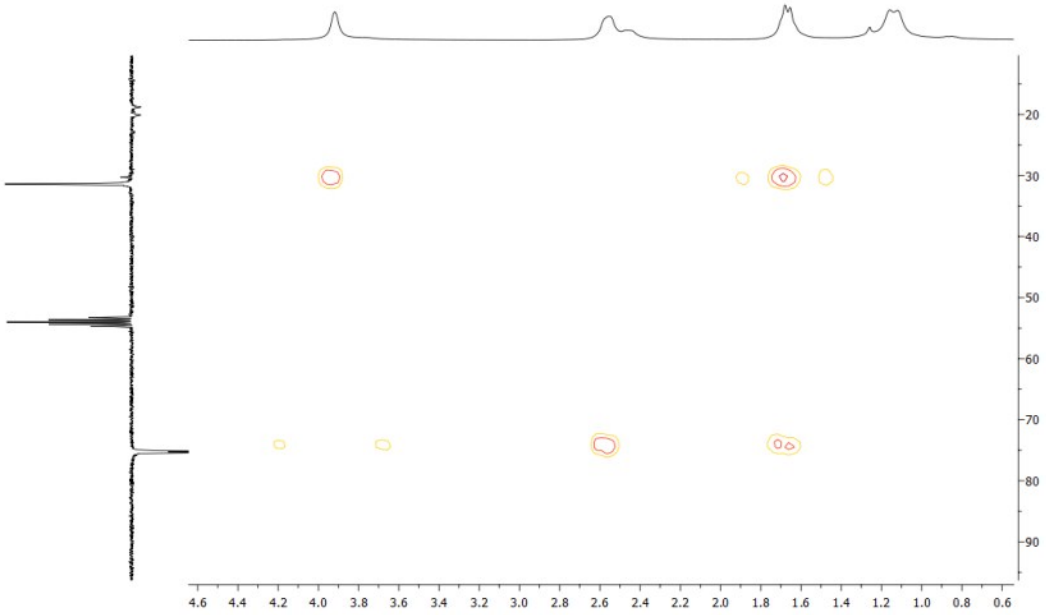

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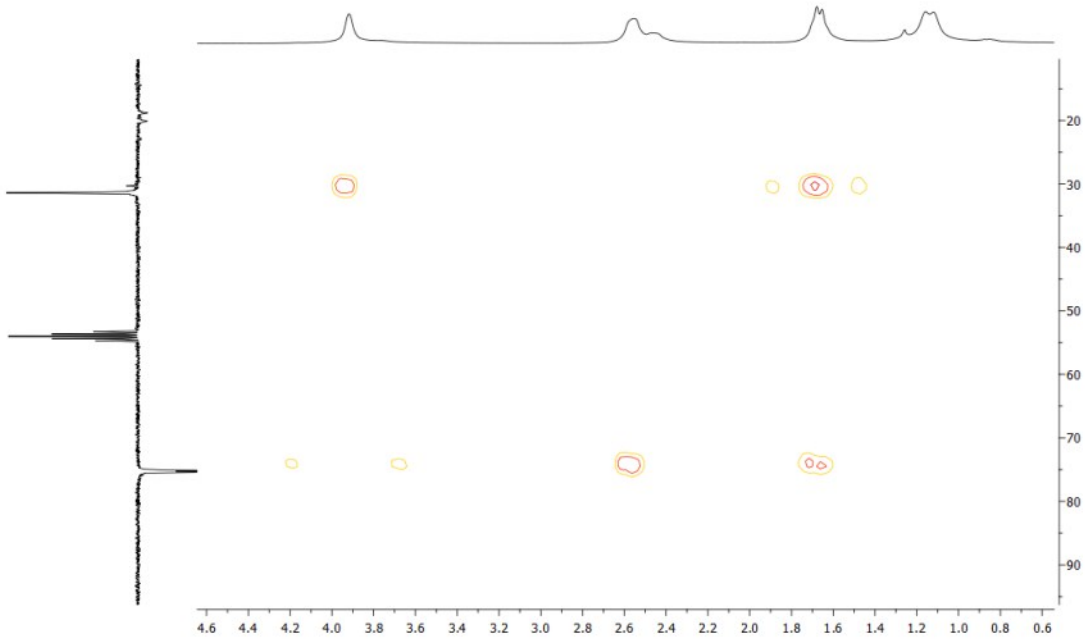
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0.6

Complex 2

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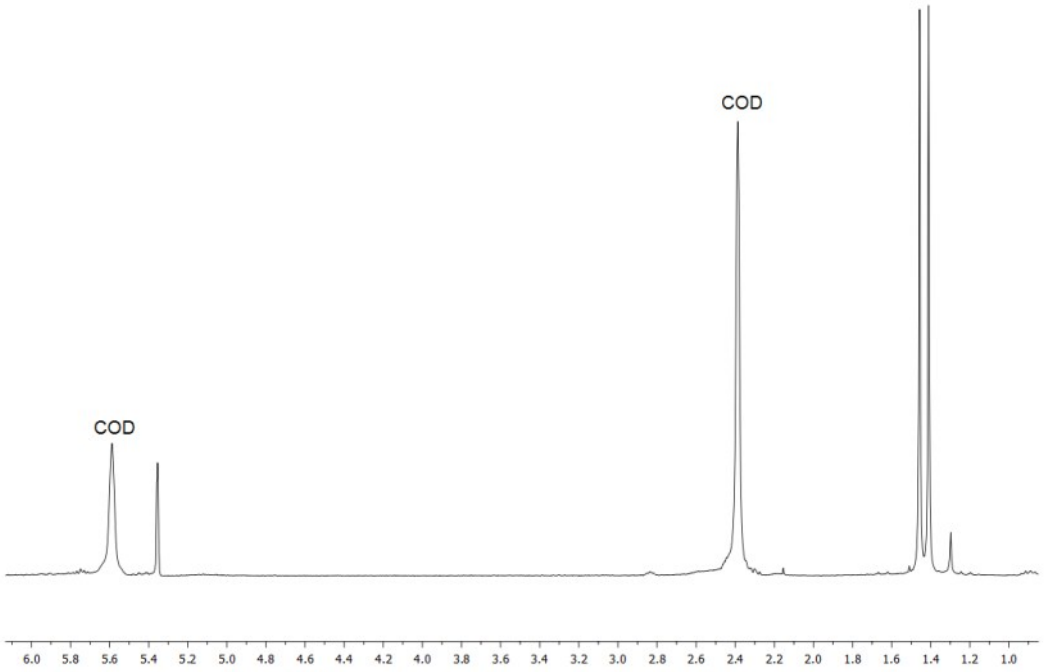

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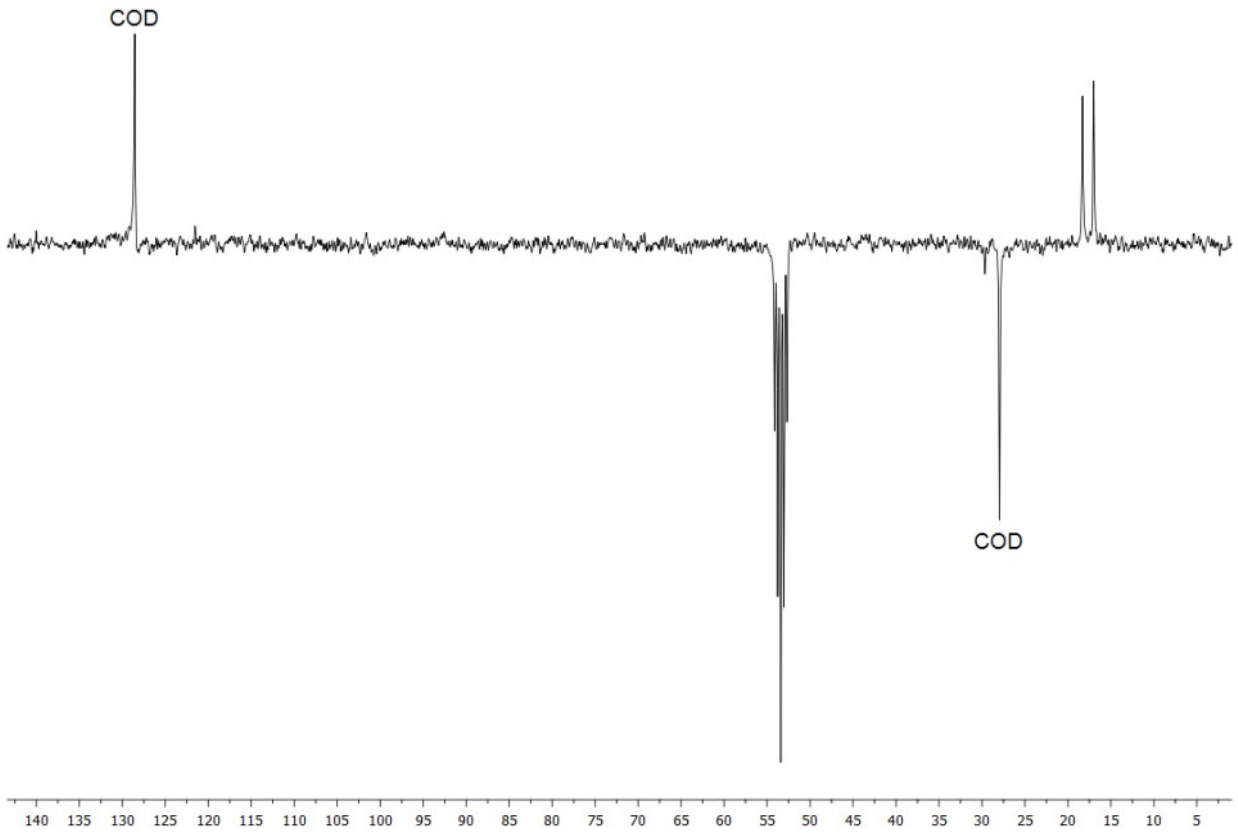

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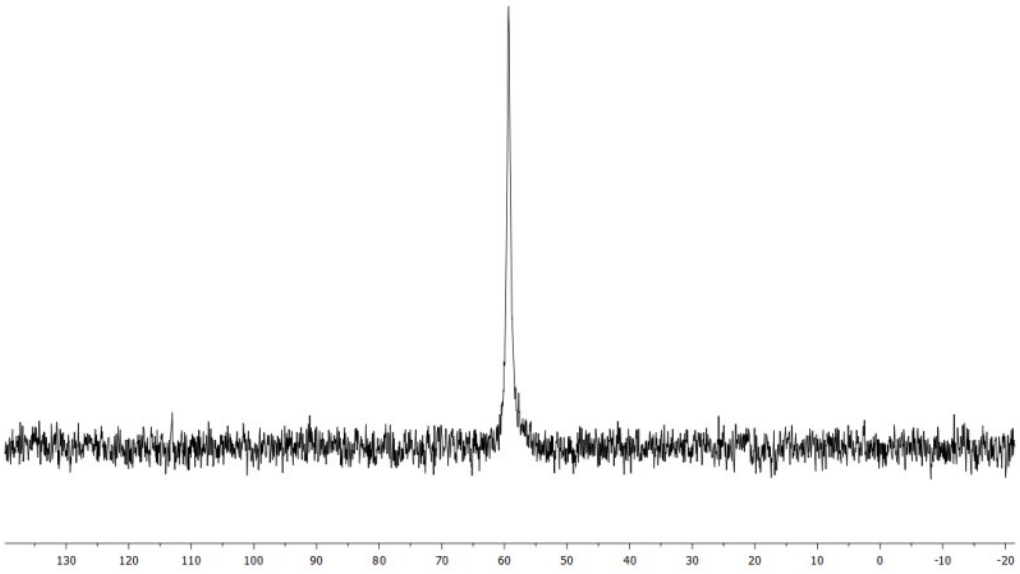

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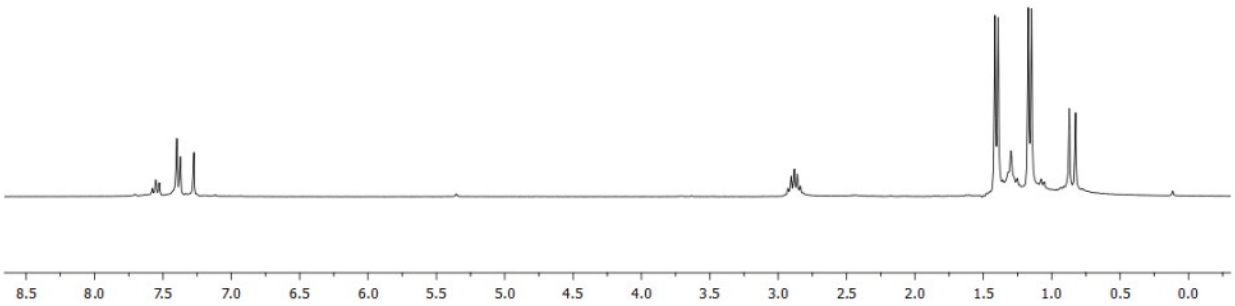

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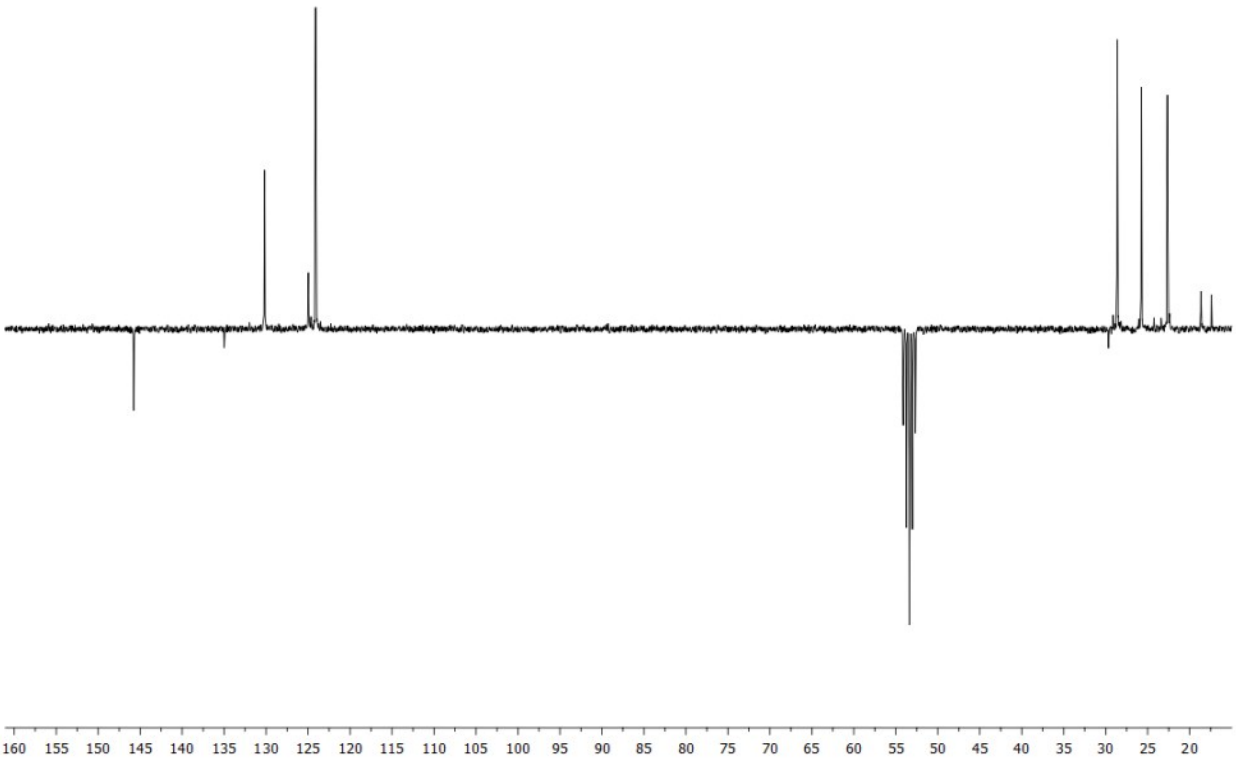

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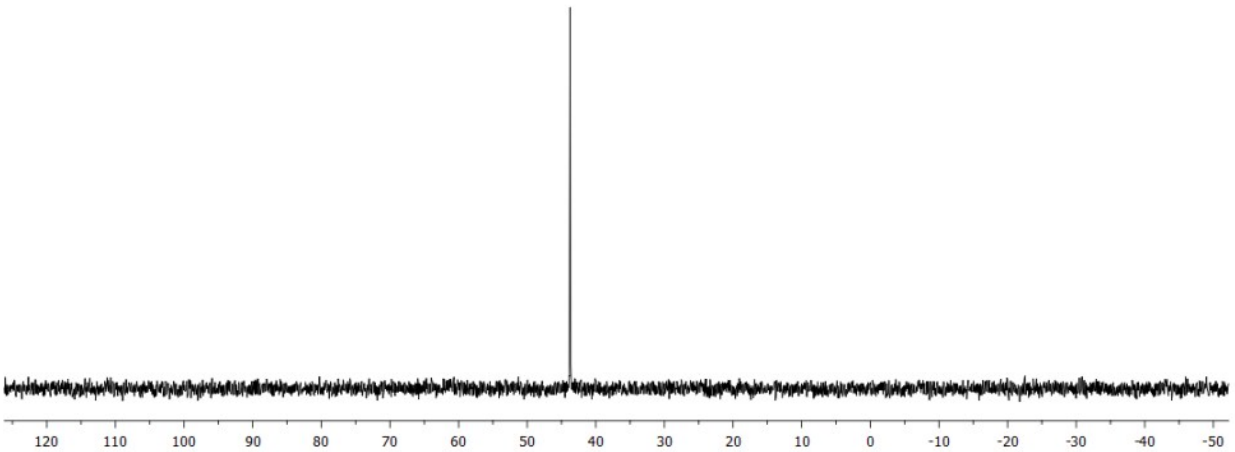

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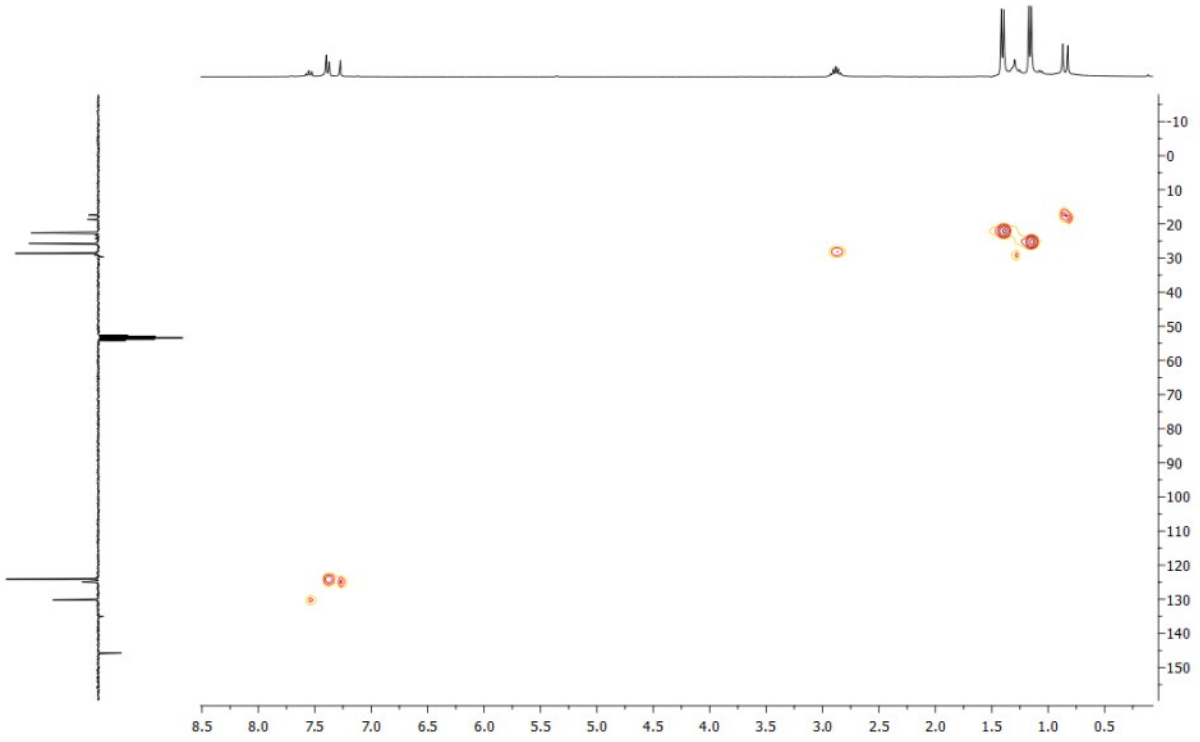

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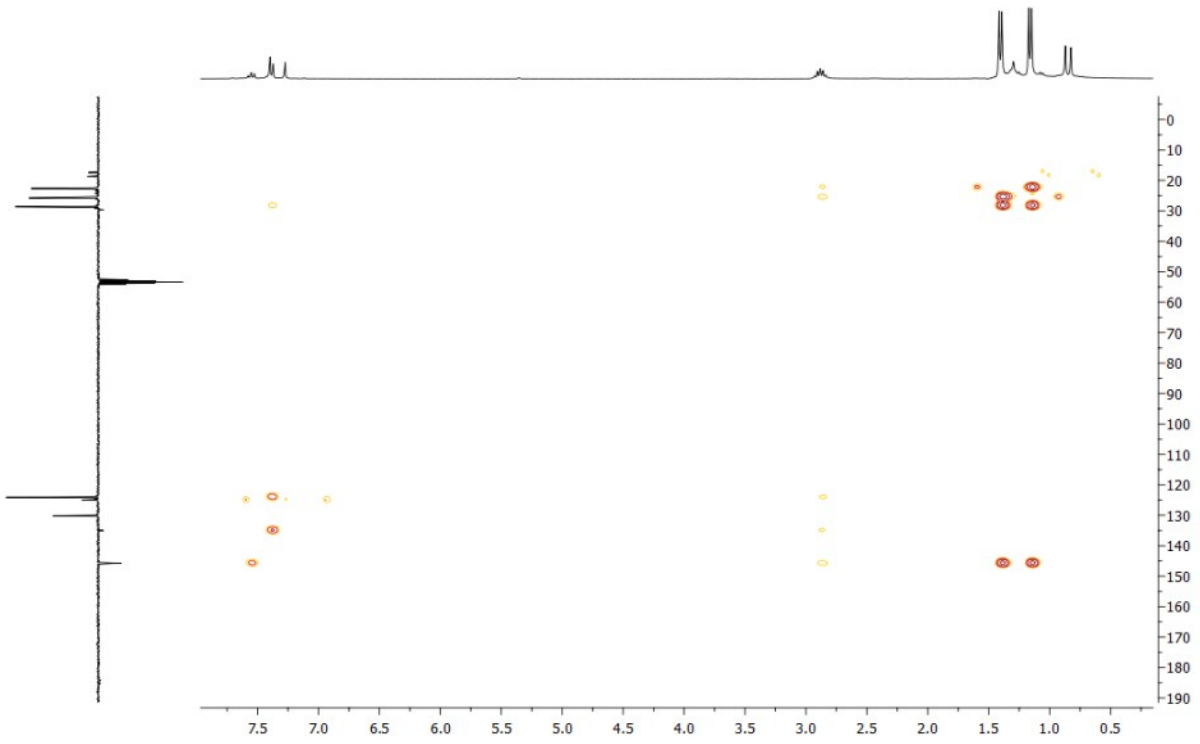

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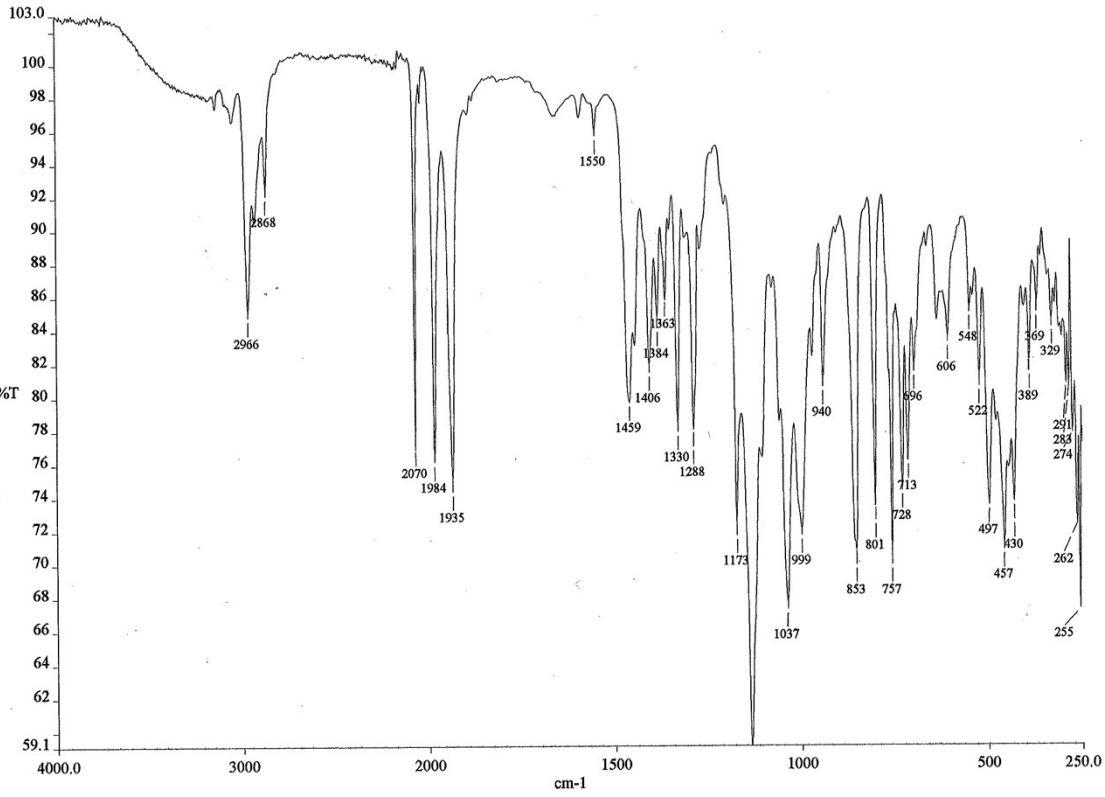
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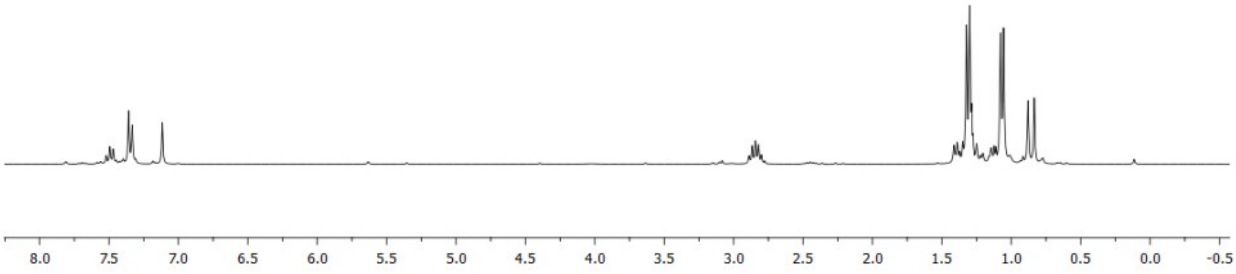
Complex 5a

^{1}H NMR



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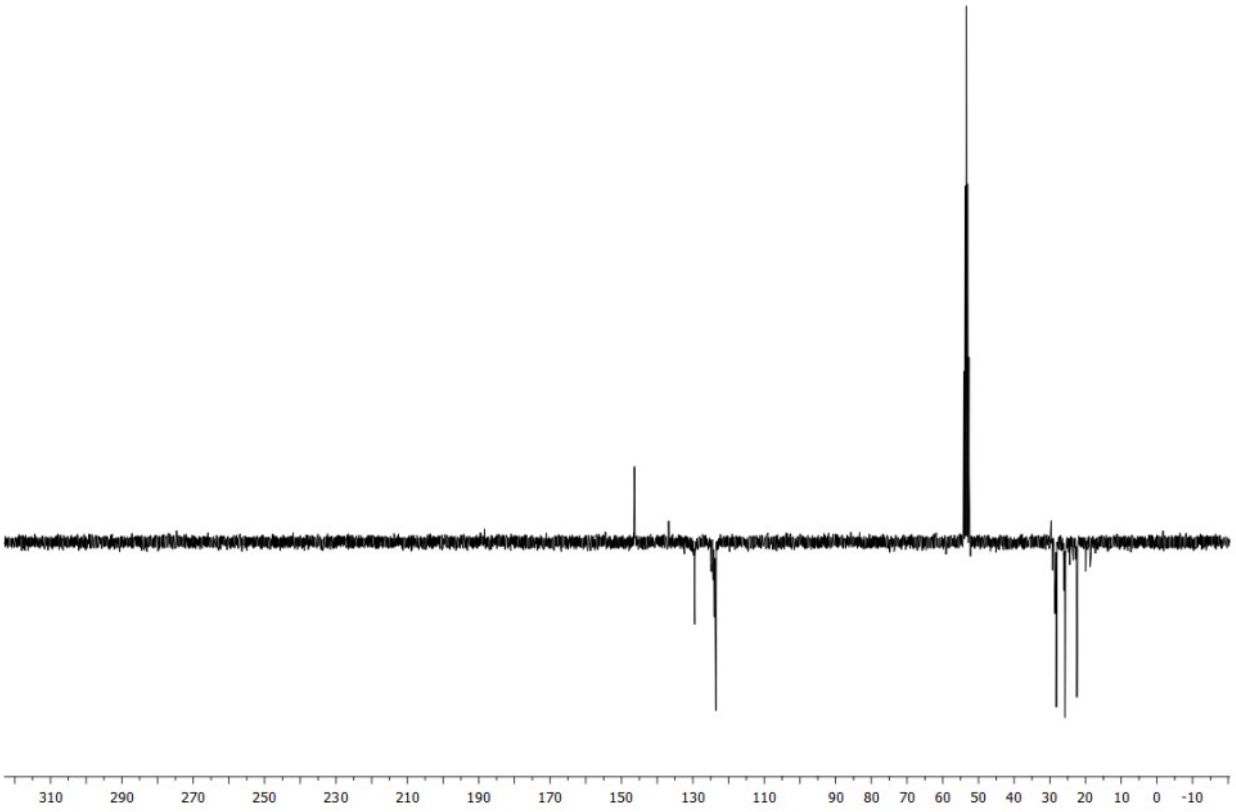
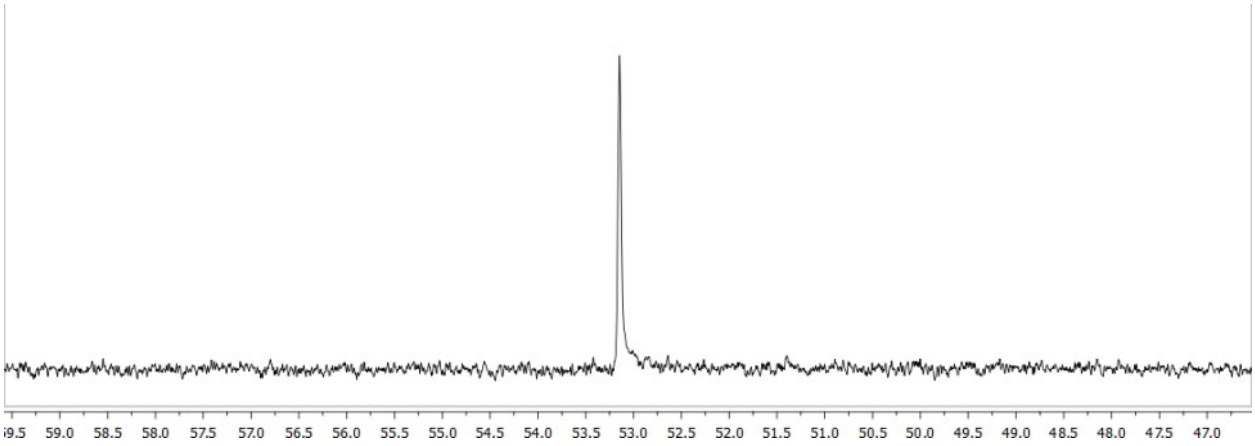


^{31}P NMR



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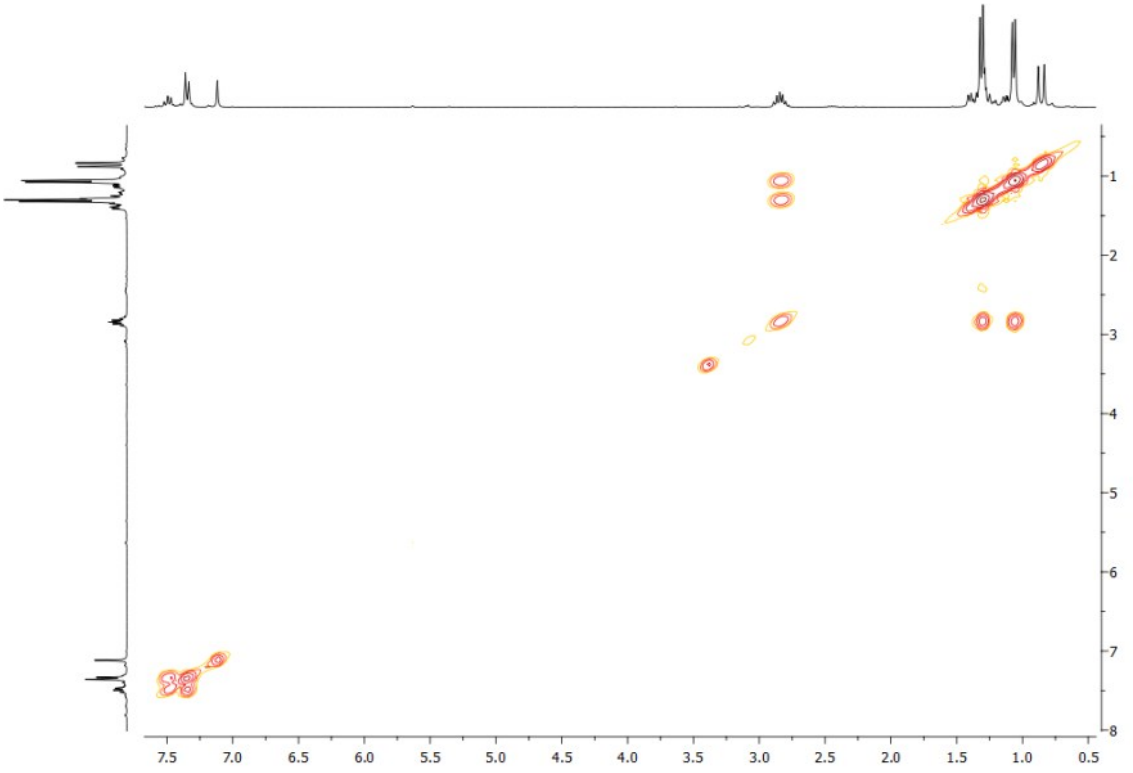

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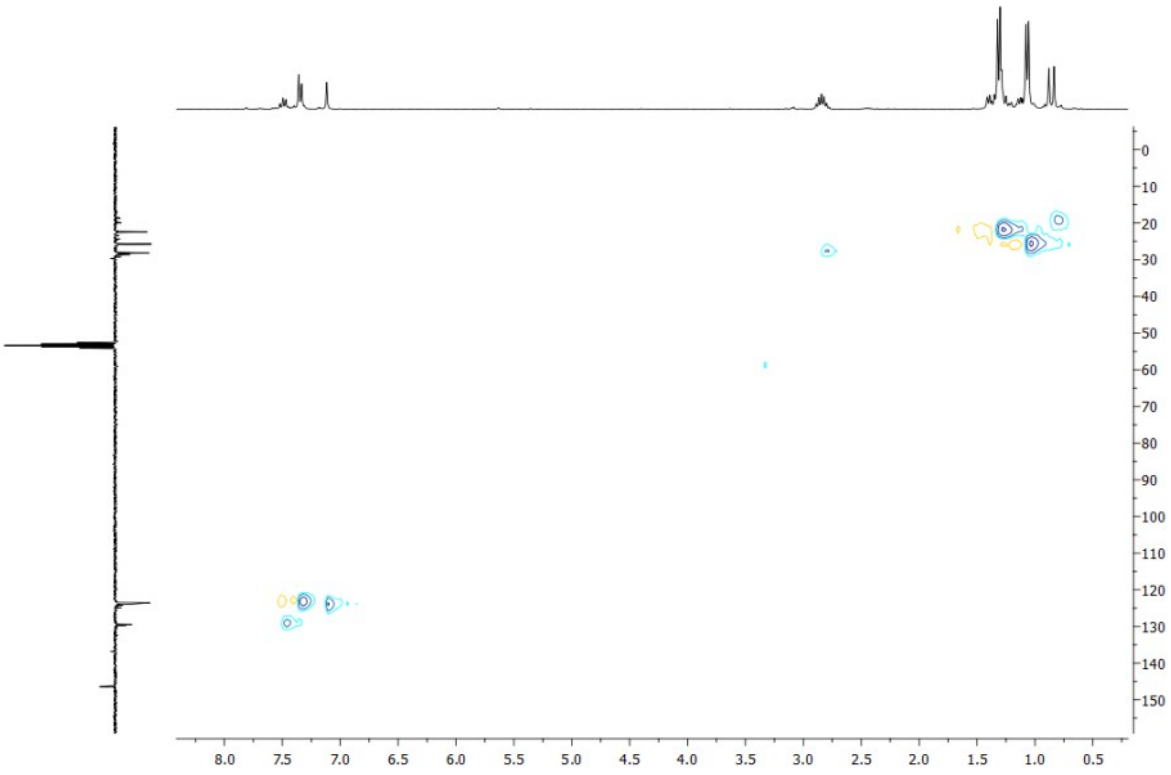

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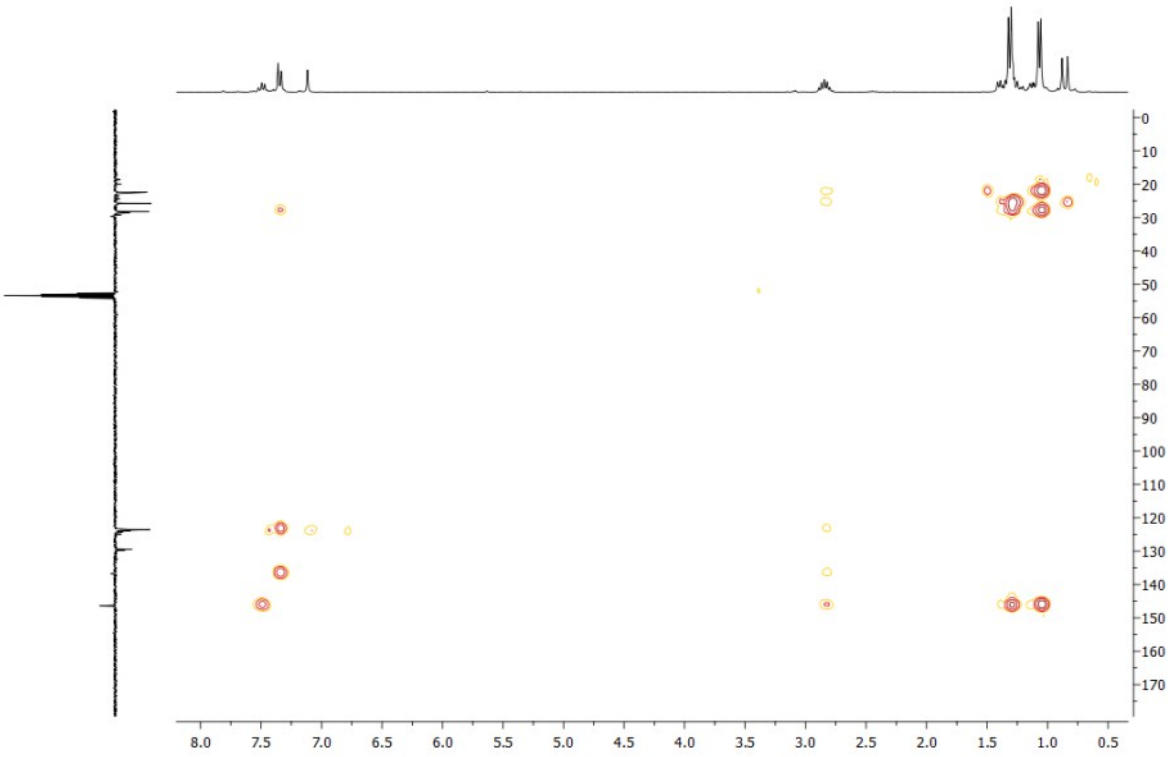

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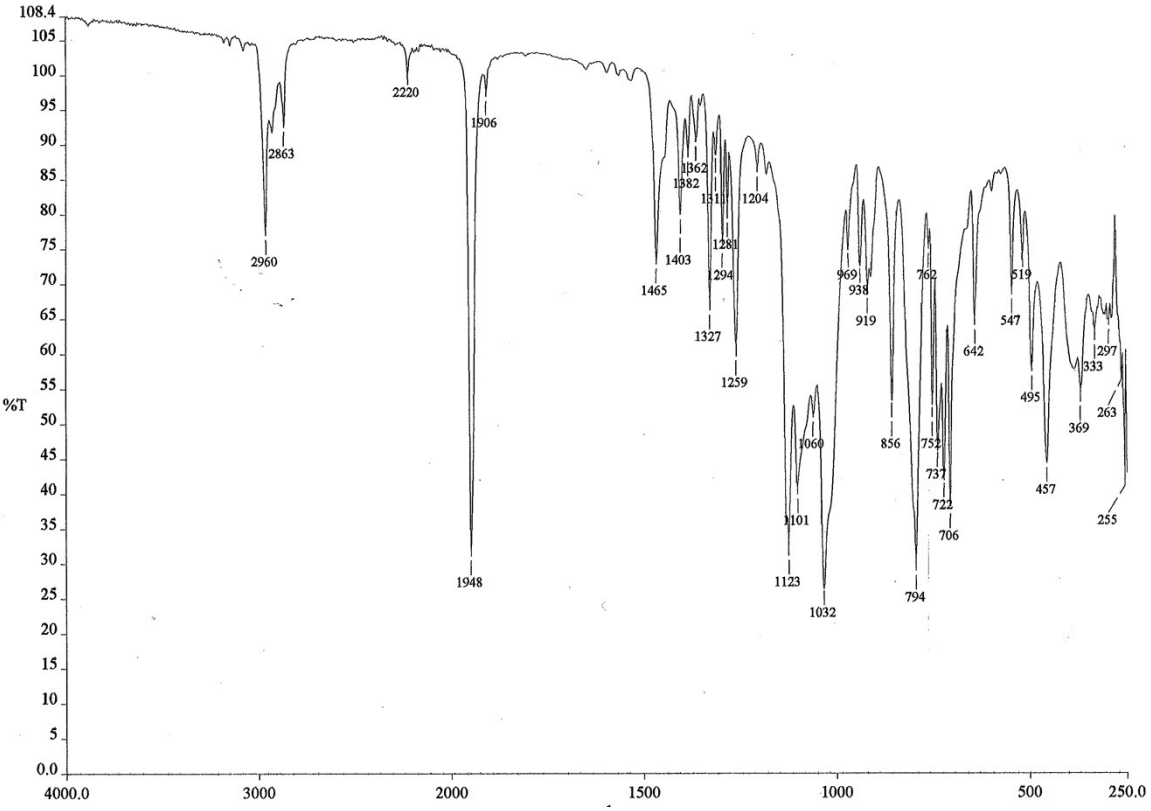
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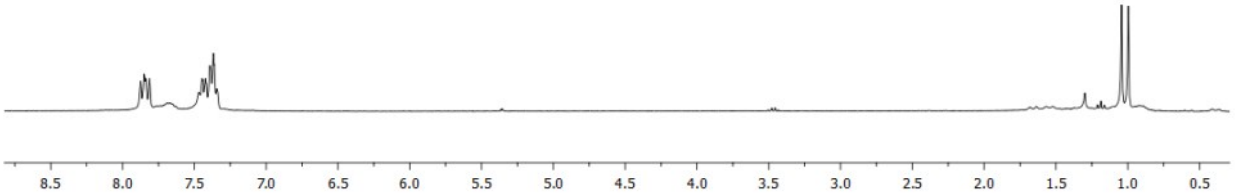
Complex 5b

^{1}H NMR



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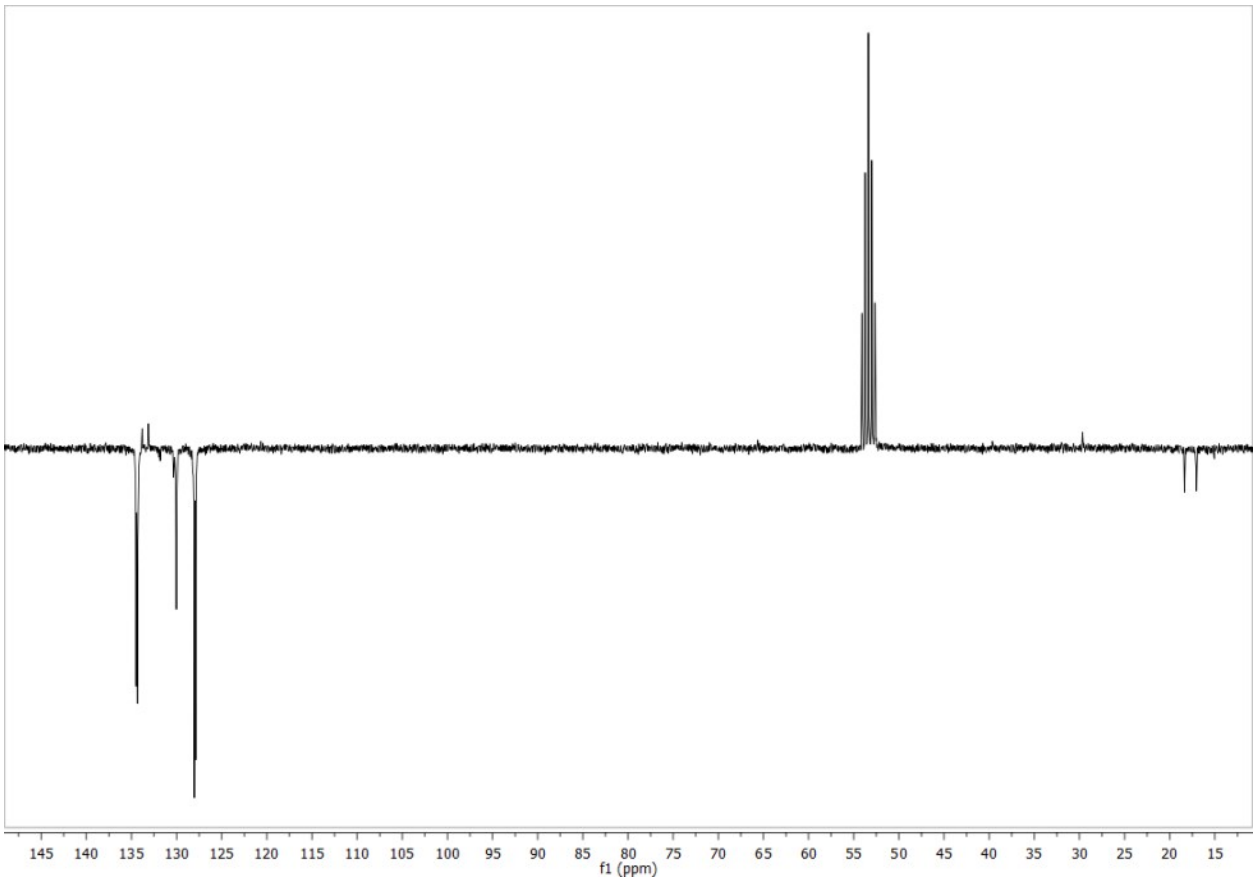

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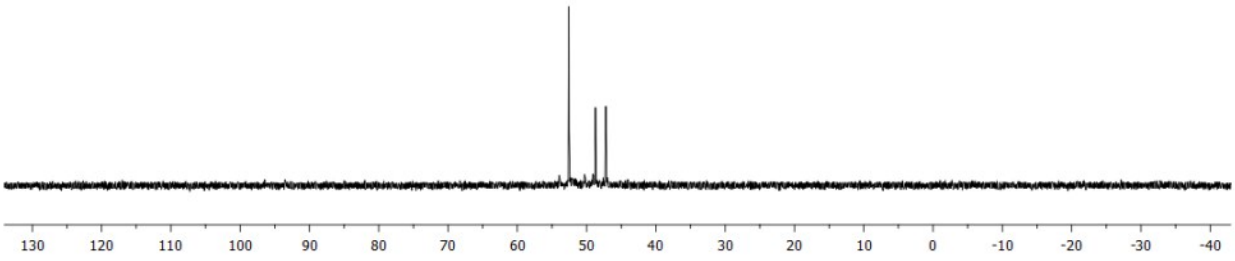

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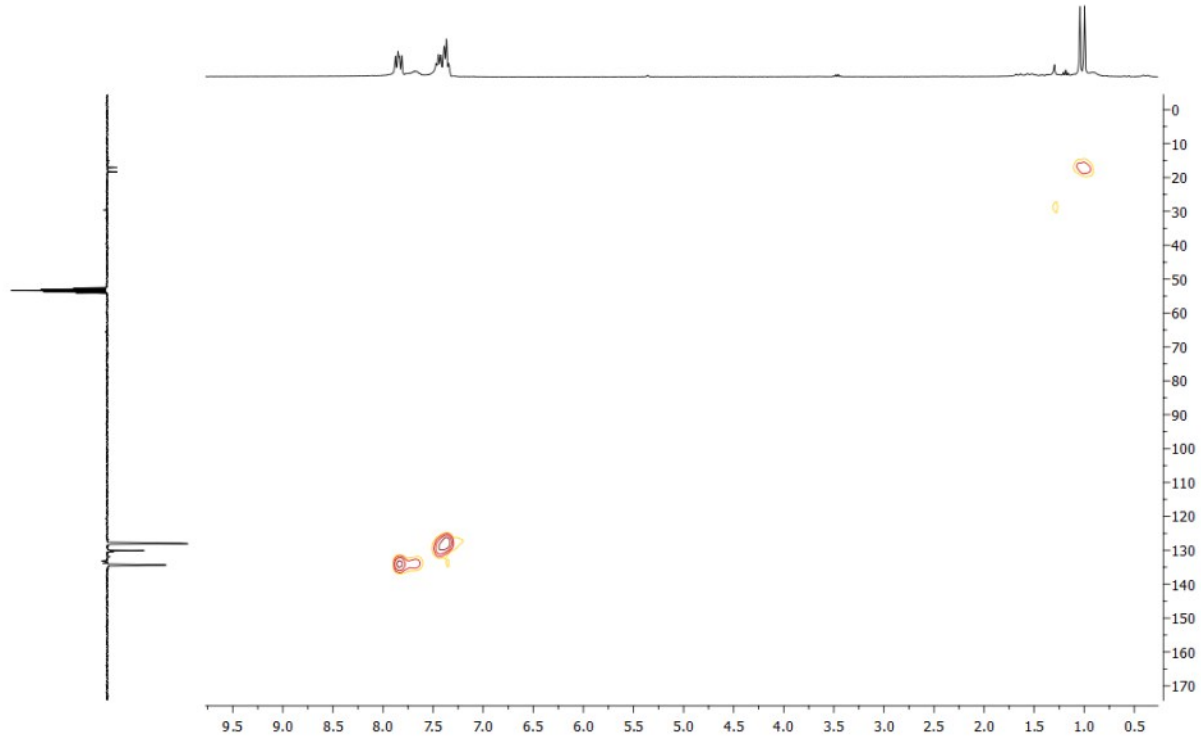

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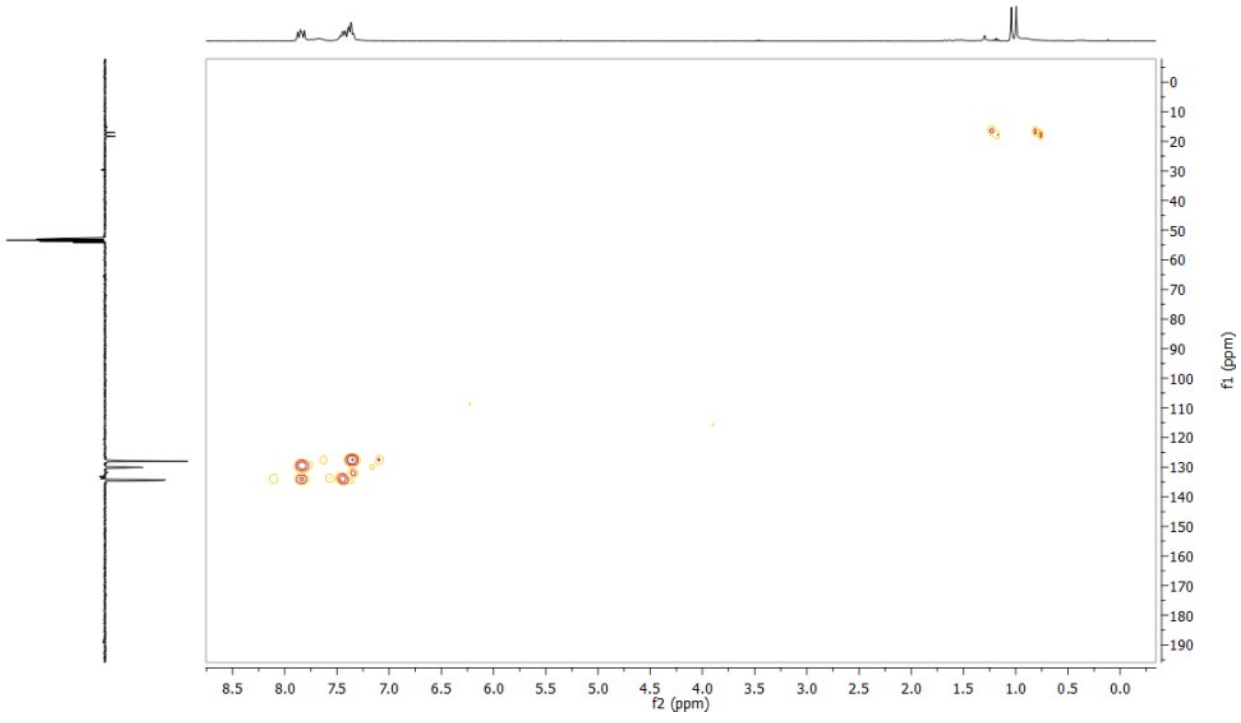

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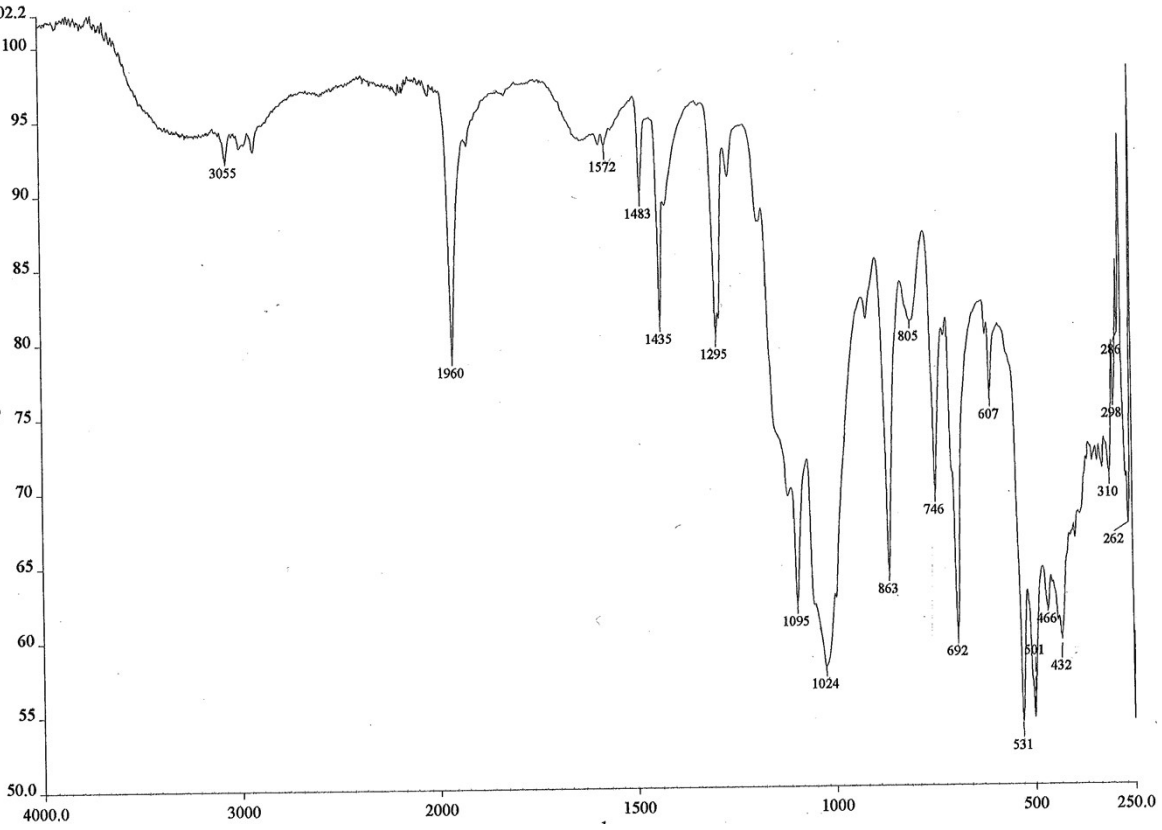
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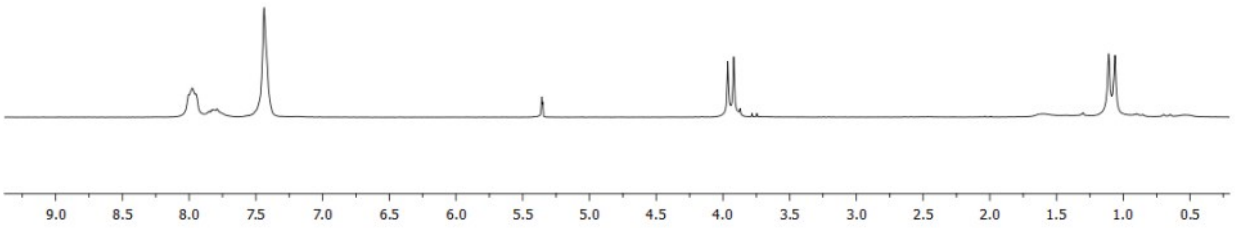
Complex 5c

^{1}H NMR



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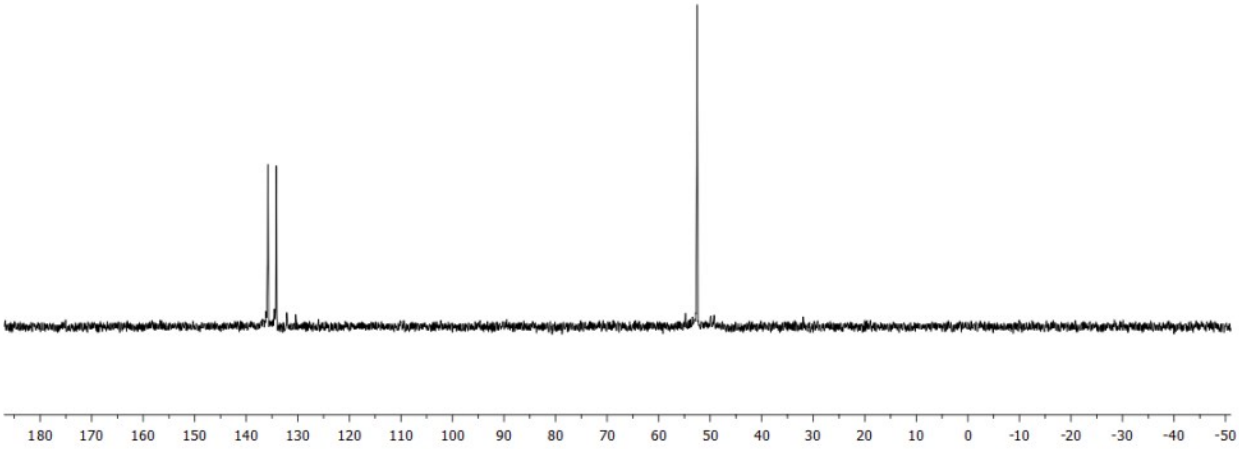

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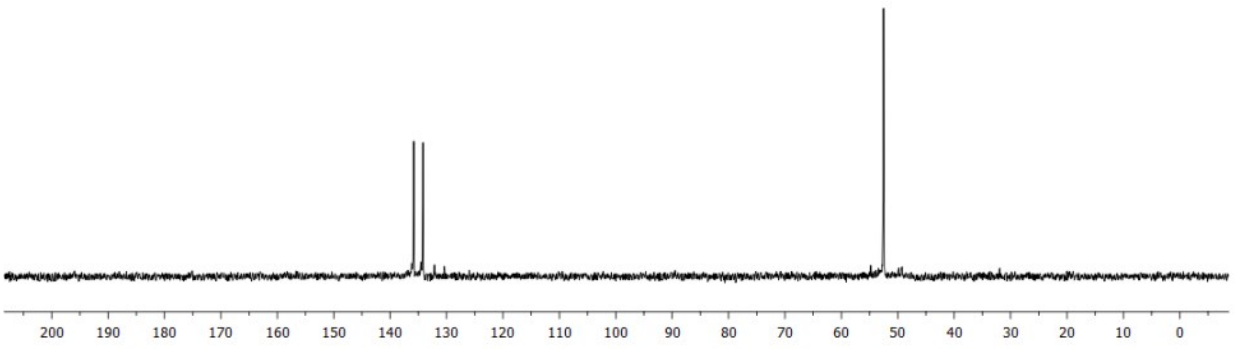

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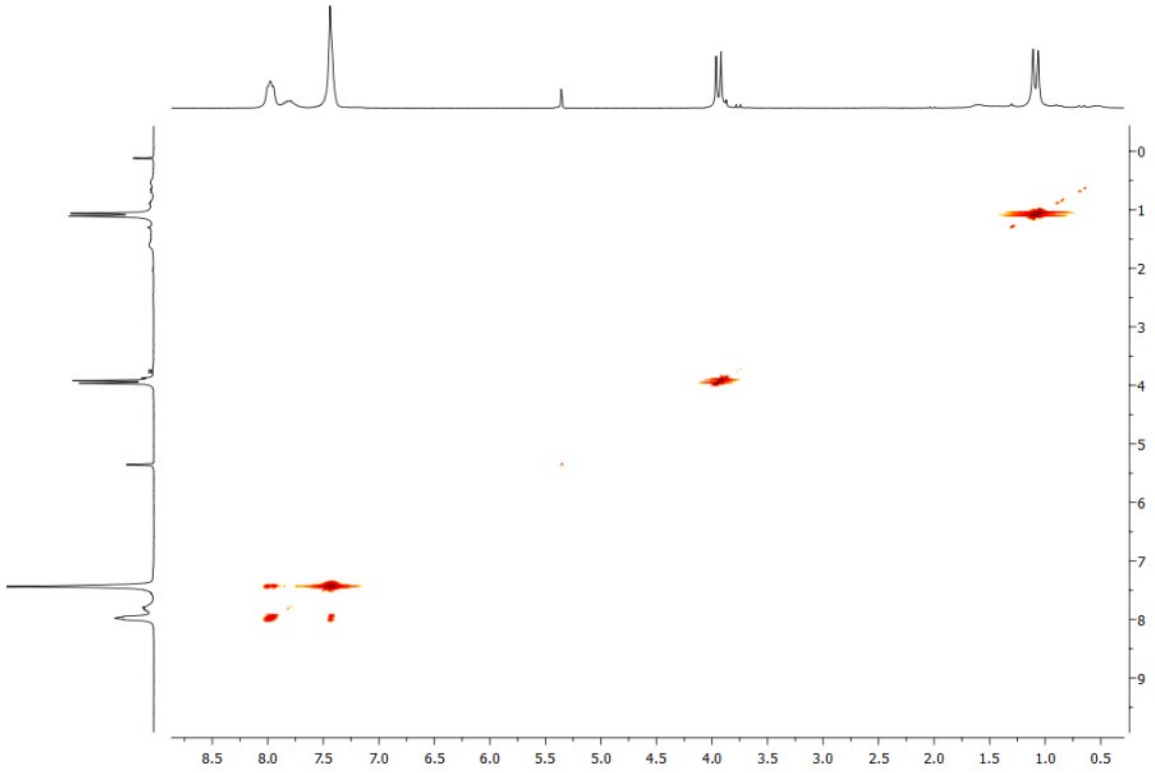

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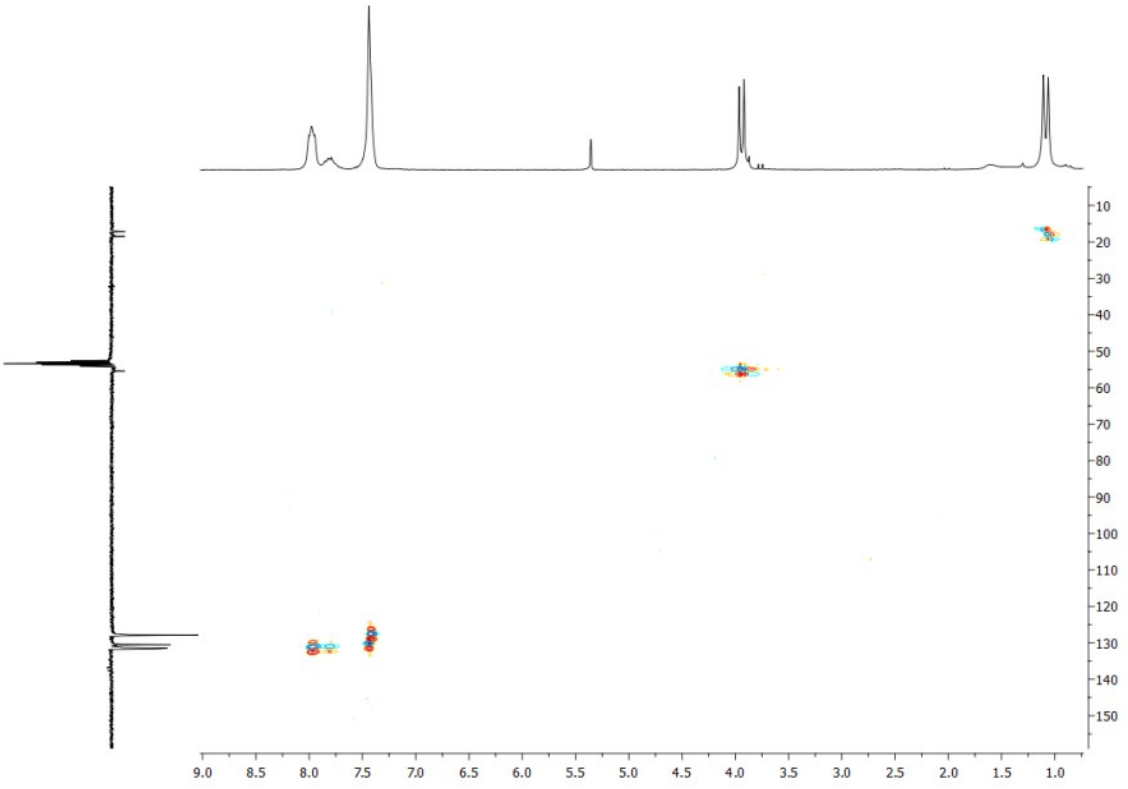

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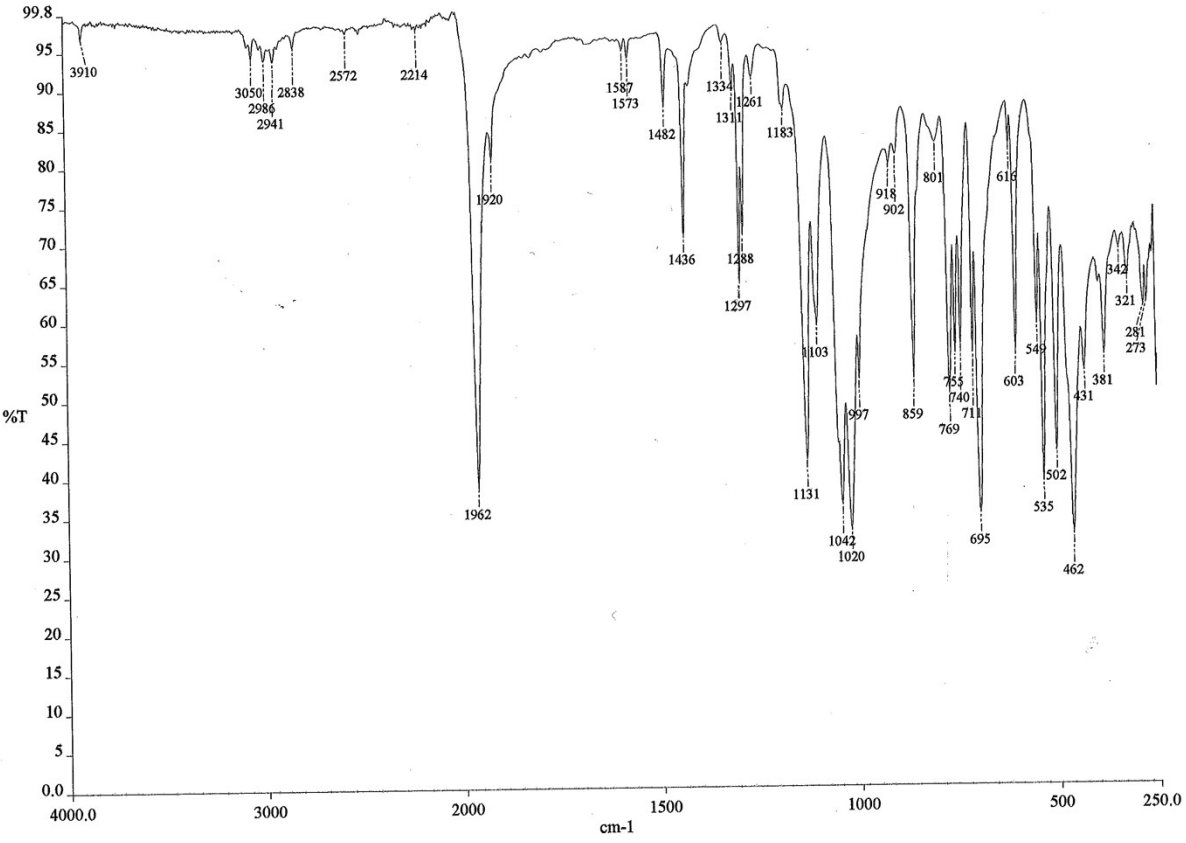
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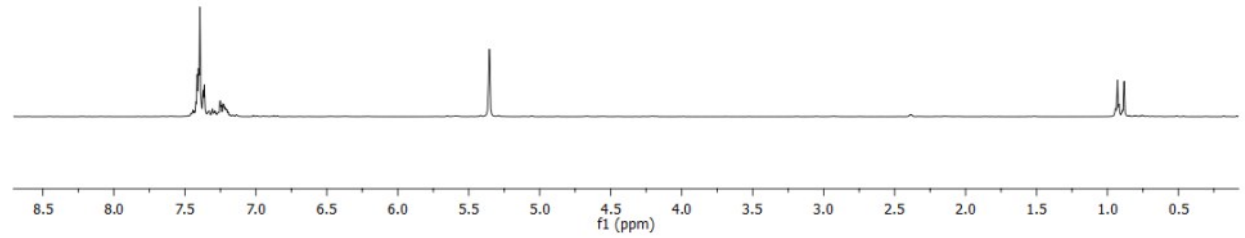
Complex 5d

^{1}H NMR



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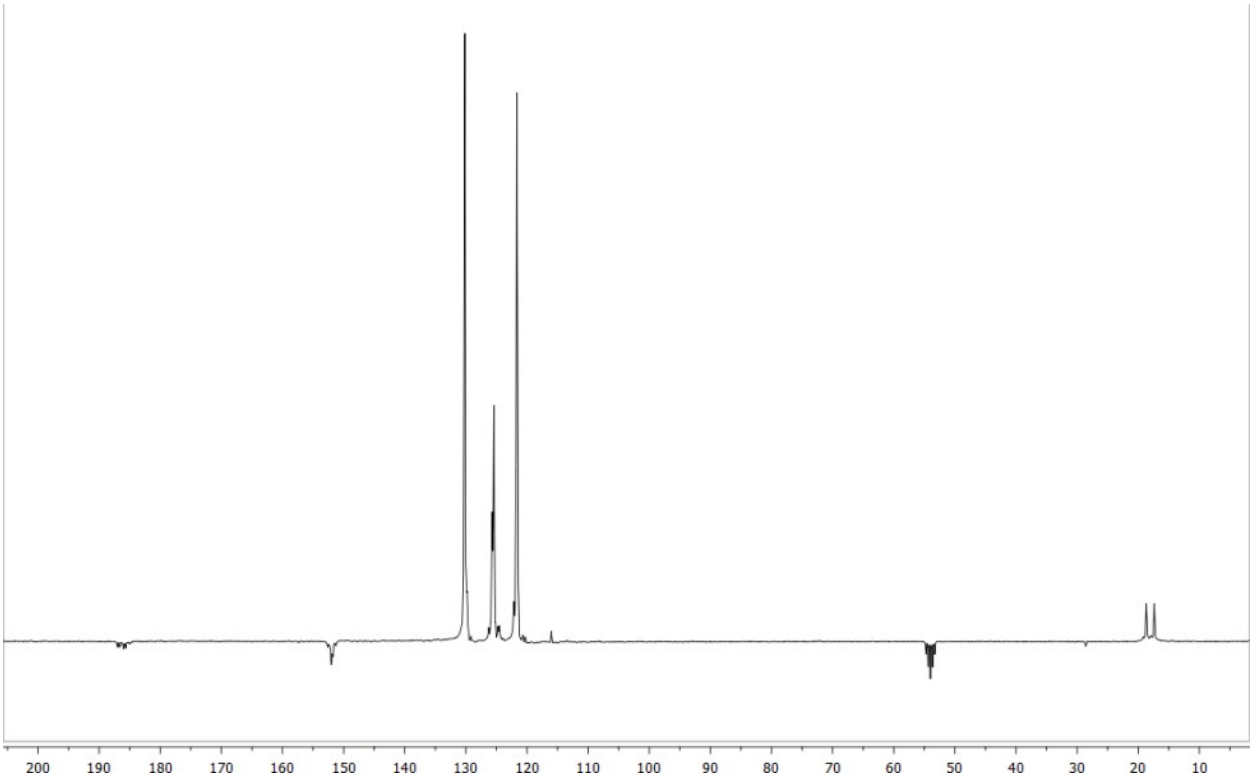

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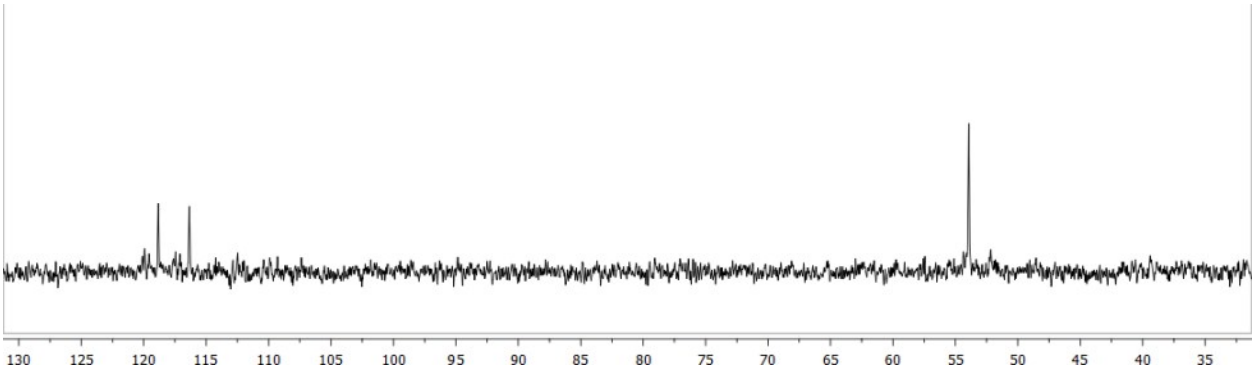

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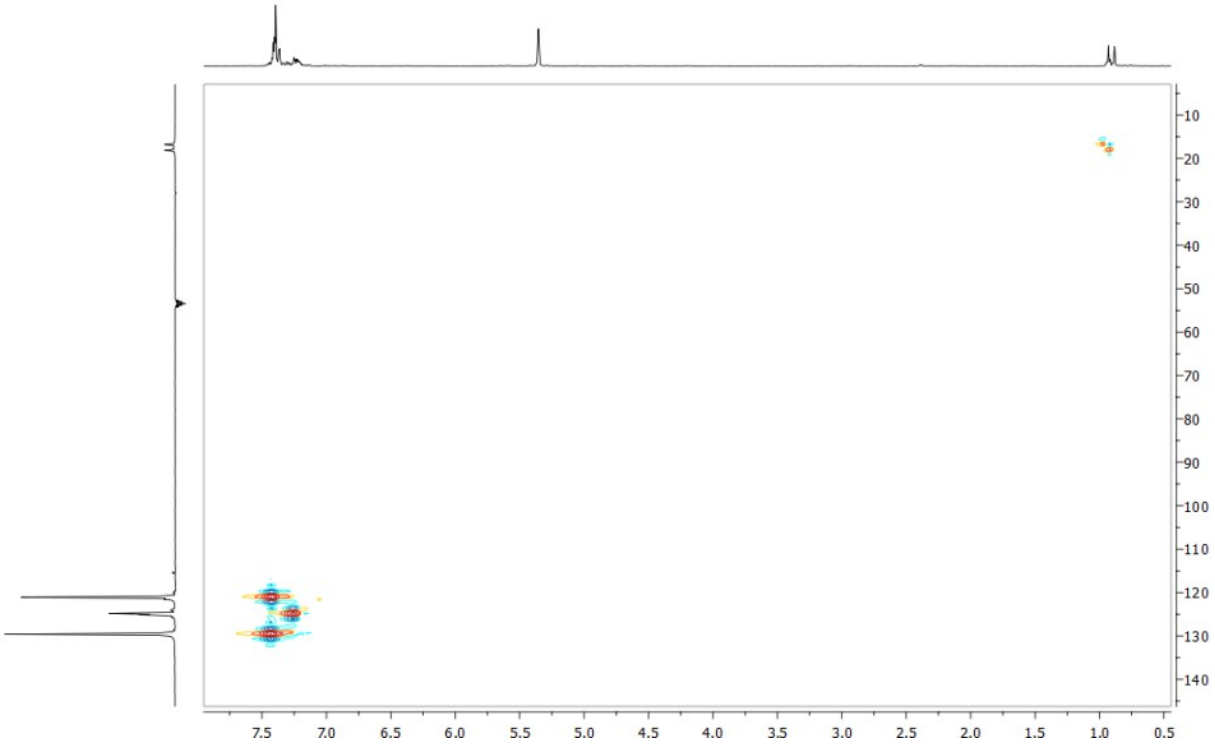

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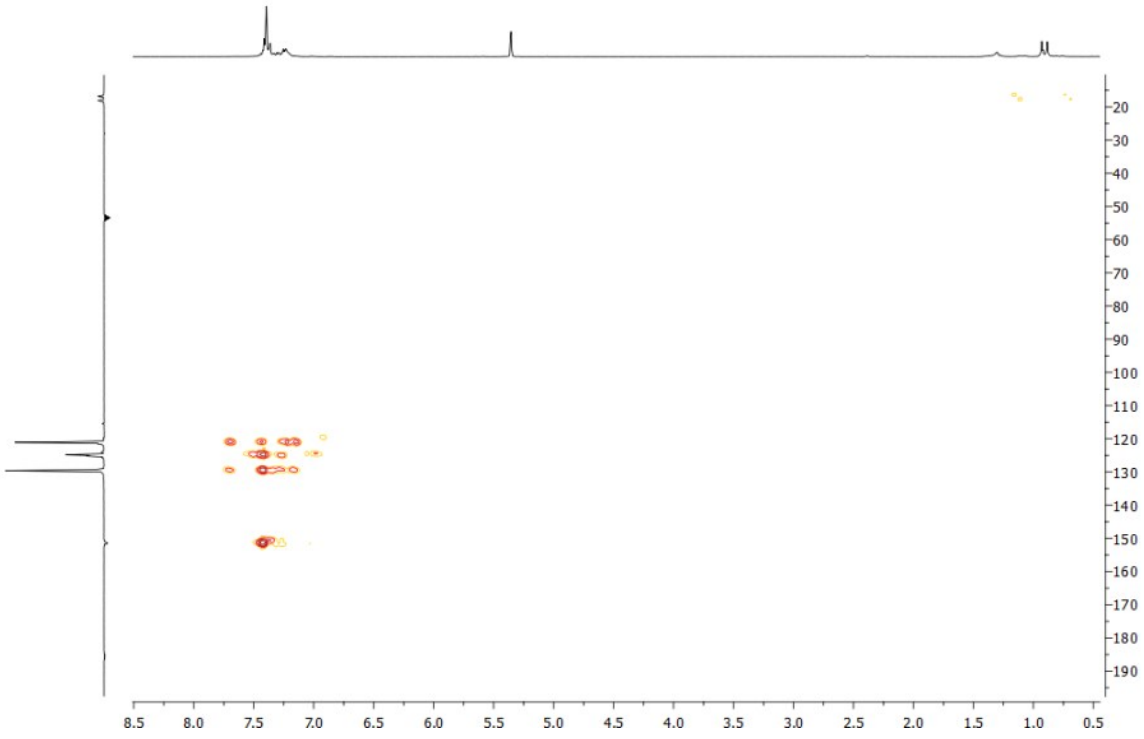

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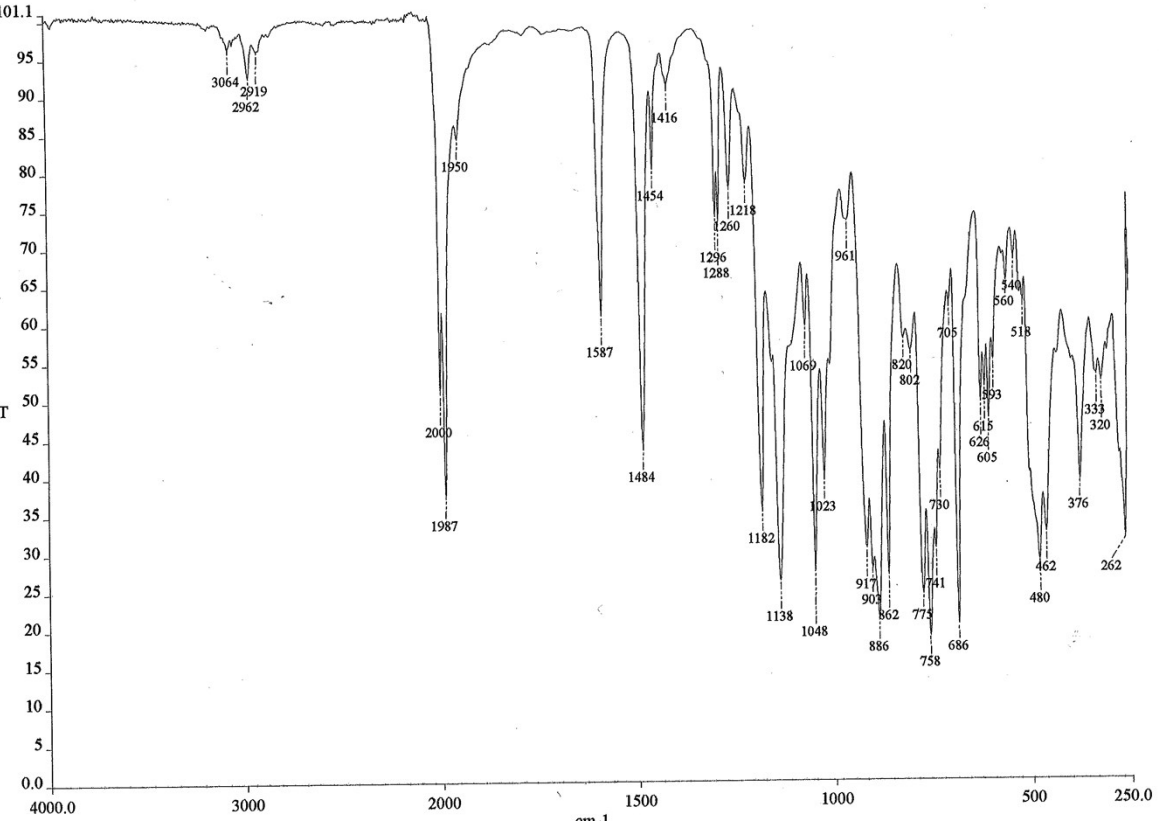
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X-Ray Data

Crystal data, data collection and refinement parameters for compounds **1**, **4**, **5a** and **5c** were collected on a Bruker Kappa APEX2 diffractometer equipped with an area detector and graphite monochromated Mo Kα radiation (0.71073 Å). Data reduction was carried out with the APEX2 software.[S1] All the structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXL-97 and WinGX programs.[S2] Non-hydrogen atoms were refined anisotropically. H atoms were positioned geometrically and refined with isotropic displacement parameters according to the riding model. Distance and angle calculations were performed using the SHELXL-97 and WinGX programs.[S2]

Crystal data for compound **1**: $[C_{20}H_{36}O_4P_2Rh_2]$, triclinic, *P–1*, a = 9.5370(15) Å, b = 9.7552(15) Å, c = 14.656(2) Å, α = 103.267(2)º, β = 95.938(2)º, γ = 117.358(2)º, Z = 2, M_r = 608.25, V = 1143.8(3) Å^3, D_{calcd} = 1.766 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, T = 100 K, μ = 1.606 mm^{-1}, 12054 reflections collected, 5799 unique (R_{int} = 0.0783), 4355 observed, $R1(F_o)$ = 0.0393 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.0862 (all data), GOF = 1.063. CCDC 1496354.

Crystal data for compound **4**: $[C_{31}H_{42}N_2O_4PRh]$, orthorhombic, $P2_12_12_1$, a = 10.5240(14) Å, b = 15.865(2) Å, c = 19.108(3) Å, Z = 4, M_r = 640.55, V = 3190.4(7) Å^3, D_{calcd} = 1.334 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, T = 100 K, μ = 0.621 mm^{-1}, 42996 reflections collected, 8401 unique (R_{int} = 0.0419), 7828 observed, $R1(F_o)$ = 0.0256 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.0602 (all data), GOF = 1.026. CCDC 1496355.

Crystal data for compound **5a**: $[C_{62}H_{88}Cl_4N_4O_6P_2Rh_2]$, monoclinic, $P2_1/c$, a = 12.7954(8) Å, b = 17.1516(10) Å, c = 16.0830(10) Å, β = 107.3960(10)º, Z = 2, M_r = 1394.92, V = 3368.2(4) Å^3, D_{calcd} = 1.375 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, T = 100 K, μ = 0.745 mm^{-1}, 82380 reflections collected, 8426 unique (R_{int} = 0.1104), 5954 observed, $R1(F_o)$ = 0.0451 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.0890 (all data), GOF = 1.024. CCDC 1496356.

Crystal data for compound **5c**: $[C_{32}H_{38}O_8P_4Rh_2]$, monoclinic, *C2/c*, a = 19.9476(11) Å, b = 9.3438(5) Å, c = 20.4044(11) Å, β = 109.9100(10)º, Z = 4, M_r = 880.32, V = 3575.8(3) Å^3, D_{calcd} = 1.635 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, T = 100 K, μ = 1.149 mm^{-1}, 21038 reflections collected, 28.597 unique (R_{int} = 0.0259), 25.000 observed, $R1(F_o)$ = 0.0234 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.0595 (all data), GOF = 1.024. CCDC 1496357.

[S1] APEX2 Bruker AXS Inc., Madison, Wisconsin, USA, 2011.

[S2] a) G. M. Sheldrick, SHELXS-97 and SHELXL-97; University of Göttingen, Germany, 1997; b) L. J. Farrugia, WinGX; University of Glasgow, Great Britain, 1998.