Supporting Information

Effects of the alkyl substituent in the π-donor heteroatom on the kinetic and thermodynamic acidities of Fischer thiocarbene complexes.

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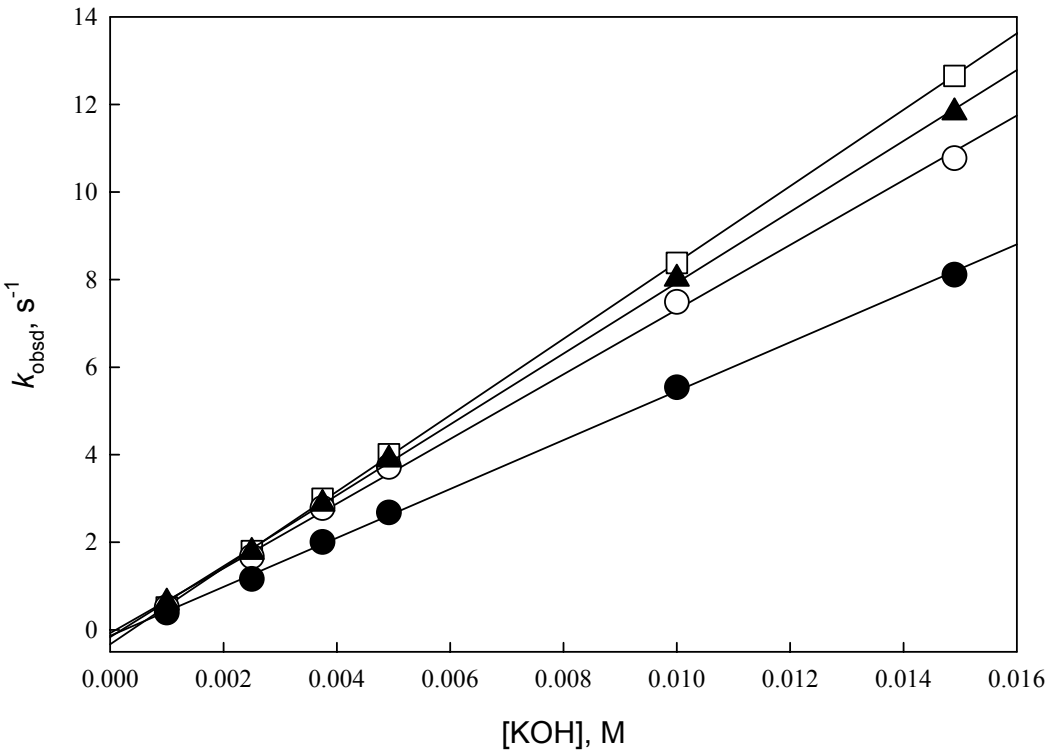


Figure S1. Plots for the proton transfer reaction from **5-Cr-*i*Pr** (□), **5-Cr-*t*But** (▲),**5-Cr-*n*But**(○) and **5-Cr-*c*Hex** (●) to KOH.

Table S1. Reaction of **5-W-*i*Pr** with morpholine buffers.[a]

pH	[Buffer], M	k_{obsd} , s^{-1} [b]
7.80	0.0250	15.90 ± 0.05
	0.0375	21.34 ± 0.07
	0.0500	27.9 ± 0.1
	0.0625	34.2 ± 0.2
	0.0750	40.1 ± 0.4
	0.0875	47.0 ± 0.3
	0.100	53.4 ± 0.8
8.30	0.0125	6.90 ± 0.04
	0.0250	13.27 ± 0.06
	0.0375	20.11 ± 0.07
	0.0500	26.6 ± 0.1
	0.0625	32.9 ± 0.2
	0.0750	39.7 ± 0.2
	0.1000	50.8 ± 0.6
8.50	0.0125	6.78 ± 0.03
	0.0250	13.38 ± 0.06
	0.0375	19.23 ± 0.07
	0.0500	26.5 ± 0.2
	0.0625	32.8 ± 0.2
	0.0750	39.5 ± 0.5
	0.1000	51.6 ± 0.7
8.88	0.0125	6.46 ± 0.03
	0.0250	13.02 ± 0.09
	0.0375	19.1 ± 0.1
	0.0500	26.5 ± 0.1
	0.0625	33.8 ± 0.1
	0.0750	40.5 ± 0.3

	0.1000	54.7 ± 0.4

pH	[Buffer], M	k_{obsd} , s^{-1} [b]
9.00	0.0125	6.34 ± 0.04
	0.0250	13.0 ± 0.1
	0.0375	18.86 ± 0.08
	0.0500	25.82 ± 0.07
	0.0625	32.44 ± 0.07
	0.0750	38.54 ± 0.09
	0.1000	51.2 ± 0.2
9.27	0.0125	6.10 ± 0.02
	0.0250	13.01 ± 0.08
	0.0375	19.85 ± 0.09
	0.0500	26.45 ± 0.09
	0.0625	32.47 ± 0.09
	0.0750	38.62 ± 0.09
	0.1000	49.0 ± 0.4
9.40	0.0125	6.30 ± 0.07
	0.0250	12.8 ± 0.2
	0.0375	19.4 ± 0.2
	0.0500	25.1 ± 0.2
	0.0625	32.2 ± 0.2
	0.0750	37.9 ± 0.3
	0.1000	51.8 ± 0.6

[a]Acetonitrile:Water (1:1 V/V), 25ºC, μ = 0.1 M (KCl), [**5-W-*i*Pr**] = 1.00 x 10^{-4} M.. [b] Monitored at 436 nm in a stopped-flow apparatus.

Characterization of the Fischer carbene complexes.

5-Cr-*n*Bu: ^{1}H NMR δ 0.97 (t, 3H, $SCH_2CH_2CH_2CH_3$), 1.52 – 1.41 (m, 2H, $SCH_2CH_2CH_2CH_3$), 1.74 – 1.62 (m, 2H, $SCH_2CH_2CH_2CH_3$), 3.16 (t, 2H, $SCH_2CH_2CH_2CH_3$), 3.56 (s, 3H, CH_3). ^{13}C NMR δ 13.5 ($SCH_2CH_2CH_2CH_3$), 21.9 ($SCH_2CH_2CH_2CH_3$), 29.1 ($SCH_2CH_2CH_2CH_3$), 42.3 ($SCH_2CH_2CH_2CH_3$), 45.8 (CH_3), 216.3 (CO, equatorial), 227.2 (CO, axial), 366.4 (C=). FT IR (cm^{-1}) 2971.4 w, 2940.9 w, 2874.7 w, 2065.1 m, 1932.7 s, 1118.0 w, 781.9 w, 659.7 w, 456.0 w. UV-vis (50% MeCN – 50% Water): λ_{max} = 450 nm (ε ≈ 11330 $M^{-1}cm^{-1}$). These values compare well with the ones reported in the literature.[64]

5-Cr-*i*Pr: ^{1}H NMR δ 1.34– 1.38 (d, 6H, $SCH(CH_3)_2$), 3.62 (s, 3H, CH_3), 3.88 – 4.02 (m, 1H, $SCH(CH_3)_2$). ^{13}C NMR δ 21.6 ($SCH(CH_3)_2$), 45.2 ($SCH(CH_3)_2$), 45.7 (CH_3), 216.3 (CO, equatorial), 227.2 (CO, axial), 364.5 (C=). FT IR (cm^{-1}) 2986.7 w, 2930.7 w, 2869.6 w, 2060.0 m, 1993.8 m, 1932.7 s, 1240.4 w, 771.7 w, 649.5 w, 456.0 w. UV-vis (50% MeCN – 50% Water): λ_{max} = 451 nm (ε ≈ 9370 $M^{-1}cm^{-1}$). HRMS (nitrobenzyl alcohol): calcd for $C_{10}H_{10}CrO_5S$ 293.9654, obtained 293.9643.

5-Cr-*t*Bu: ^{1}H NMR δ 1.54 (s, 9H, ($SC(CH_3)_3$)), 3.80 (s, 3H, CH_3). ^{13}C NMR δ 30.0 ($SC(CH_3)_3$), 46.2 ($SC(CH_3)_3$), 60.7 (CH_3), 216.4 (CO, equatorial), 227.1 (CO, axial), 368.0 (C=). FT-IR (cm^{-1}) 2971.4 w, 2065.1 m, 1998.9 m, 1907.2 s, 1474.4 w, 1168.9 w, 1123.1 w, 1056.9 w, 751.3 w, 659.7 m, 537.0 w. UV-vis (50% MeCN – 50% Water): λ_{max} = 457 nm (ε ≈ 6260 $M^{-1}cm^{-1}$). HRMS (nitrobenzyl alcohol): calcd for $C_{11}H_{12}CrO_5S$ 307.9811, obtained 307.9807.

5-Cr-*c*Hex: ^{1}H NMR δ 1.32 – 1.97 (m, 11H, SC_6H_{11}), 3.60 (s, 3H, CH_3). ^{13}C NMR δ 25.1, 25.6, 31.5, 45.1 (SC_6H_{11}), 54.0 (CH_3), 216.3 (CO, equatorial), 227.2 (CO, axial), 364.3 (C=). FT-IR (cm^{-1}) 2930.7 s, 2859.4 s, 2075.2 m, 1942.9 s, 1454 m, 1265.6 m, 990.7 m, 859.7 m, 659.9 w. UV-vis (50% MeCN – 50% Water): λ_{max} = 450 nm (ε ≈ 7520 M^{-1} cm^{-1}).

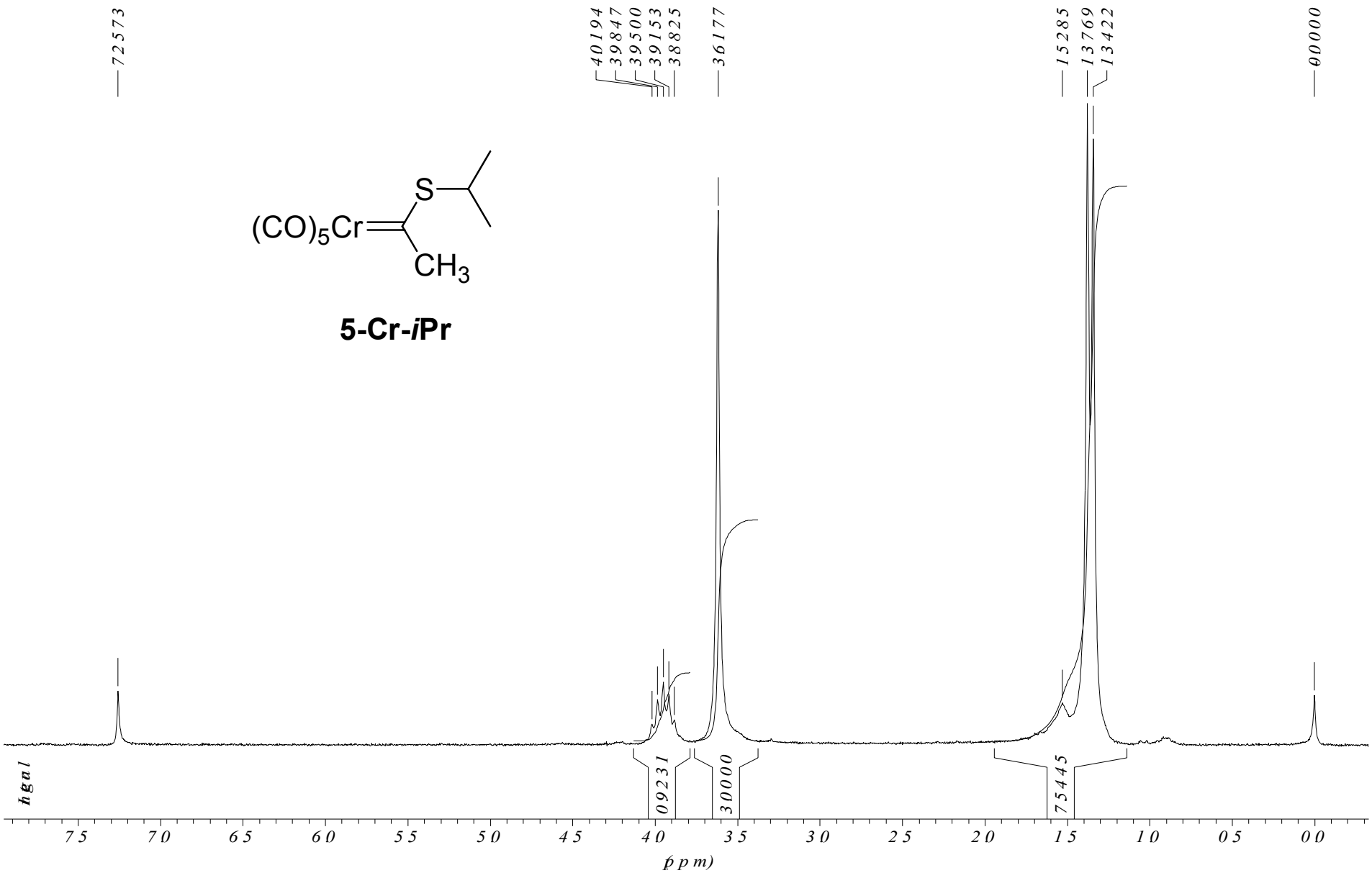
5-W-*n*Bu: ^{1}H NMR δ 0.97 (t, 3H, $SCH_2CH_2CH_2CH_3$), 1.44 – 1.50 (m, 2H, $SCH_2CH_2CH_2CH_3$), 1.67 – 1.73 (m, 2H, $SCH_2CH_2CH_2CH_3$), 3.00 (t, 2H, $SCH_2CH_2CH_2CH_3$), 3.37 (s, 3H, CH_3). ^{13}C NMR δ 13.6 ($SCH_2CH_2CH_2CH_3$), 22.0 ($SCH_2CH_2CH_2CH_3$), 28.7 ($SCH_2CH_2CH_2CH_3$), 42.8 ($SCH_2CH_2CH_2CH_3$), 47.8 (CH_3), 197.7 (CO, equatorial), 207.4 (CO, axial), 332.3 (C=). FT IR (cm^{-1}) 2962.4 w, 2914.9 w,

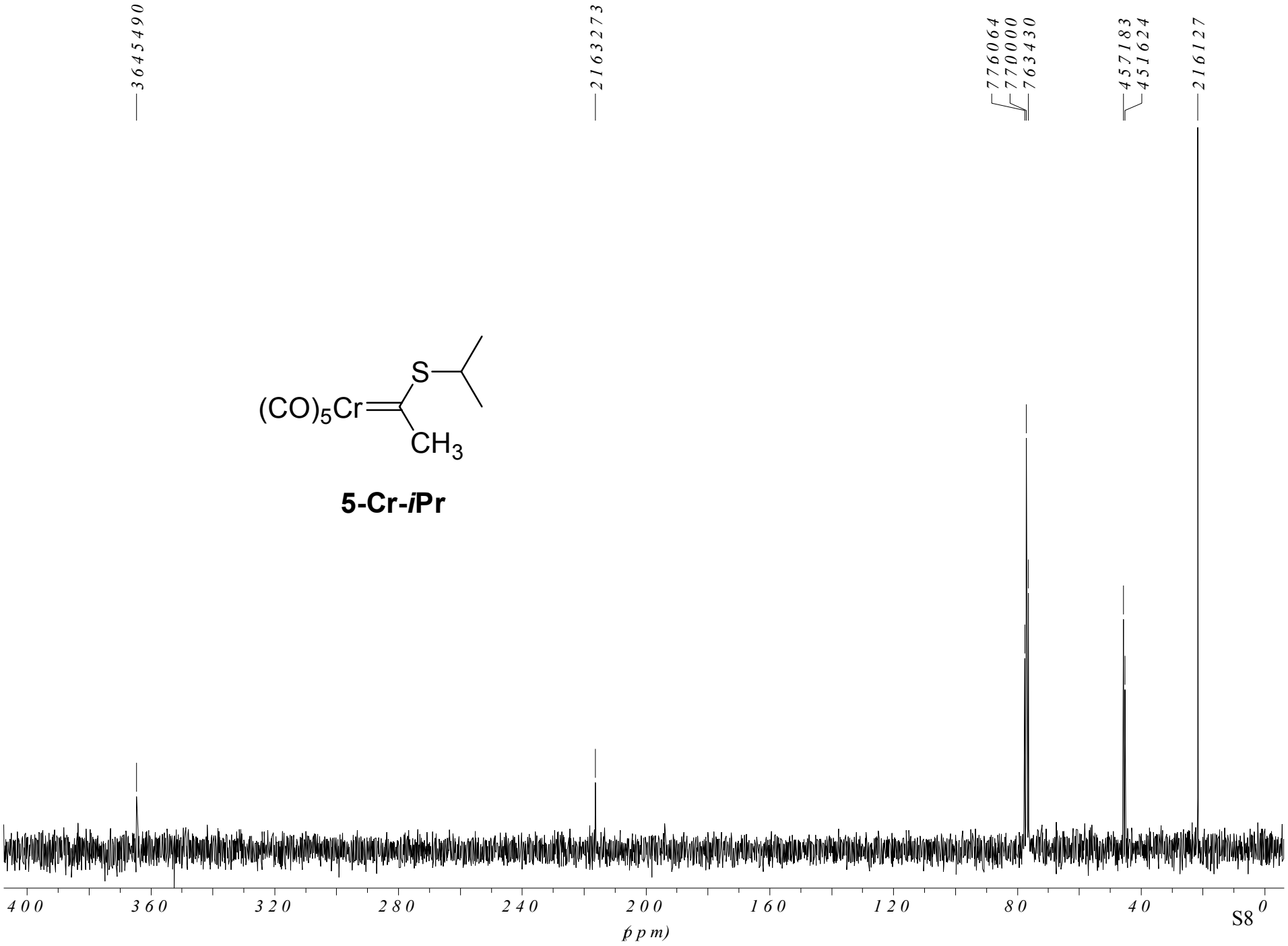
2067.3 m, 1940.6 s, 1263.4 w, 1093.1 w, 1017.8 w, 942.6 w, 887.1 w, 804.0 w, 570.3 w. UV-vis (50% MeCN – 50% Water): λ_{max} = 435 nm (ε ≈ 10779 $M^{-1}cm^{-1}$). HRMS (nitrobenzyl alcohol): calcd for $C_{11}H_{12}O_5SW$ 440.9988, obtained 440.9981.

5-W-*i*Pr: ^{1}H NMR δ 1.37– 1.39 (d, 6H, SCH(C*H*$_3$)$_2$), 3.44 (s, 3H, C*H*$_3$), 3.75 – 3.86 (m, 1H, SC*H*(CH$_3$)$_2$). ^{13}C NMR δ 21.3 (SCH(*C*H$_3$)$_2$), 46.4 (S*C*H(CH$_3$)$_2$), 47.2 (*C*H$_3$), 197.7 (CO, equatorial), 207.3 (CO, axial), 330.5 (C=). FT IR (cm^{-1}) 2976.4 w, 2064.9 m, 1980.1 m, 1936.6 s, 1338.4 w, 1238.5 w, 1108.3, 1041.7 w, 764.4 w, 598.0 w, 570.3 w, 423.8 w. UV-vis (50% MeCN – 50% Water): λ_{max} = 436 nm (ε ≈ 11500 $M^{-1}cm^{-1}$). HRMS (nitrobenzyl alcohol): calcd for $C_{10}H_{10}O_5SW$ 426.9831, obtained 426.9812.

5-W-*t*Bu: ^{1}H NMR δ 1.56 (s, 9H, (SC(C*H*$_3$)$_3$)), 3.64 (s, 3H, C*H*$_3$). ^{13}C NMR δ 29.8 (SC(*C*H$_3$)$_3$), 48.0 (S*C*(CH$_3$)$_3$), 61.6 (*C*H$_3$), 197.3 (CO, equatorial), 207.2 (CO, axial), 334.5 (C=). FT-IR (cm^{-1}) 2998.0 w, 2958.4 w, 2067.3 m, 1992.1 m, 1956.4 s, 1928.7 s,1897.0 s, 1370.3 w, 1342.6 w, 1156.4 w, 1116.8 w, 1069.3 w, 934.7 w, 764.4 m, 594.1 m, 578.2 m. UV-vis (50% MeCN – 50% Water): λ_{max} = 441 nm (ε ≈ 14627 $M^{-1}cm^{-1}$). HRMS (nitrobenzyl alcohol): calcd for $C_{11}H_{12}O_5SW$ 440.9988, obtained 440.9978.

5-W-*c*Hex: ^{1}H NMR δ 1.31 – 2.08 (m, 11H, SC$_6$*H*$_{11}$), 3.43 (s, 3H, C*H*$_3$). ^{13}C NMR δ 25.1, 25.6, 31.2, 47.1 (S*C*$_6$H$_{11}$), 54.4 (*C*H$_3$), 197.7 (CO, equatorial), 207.3 (CO, axial), 330.3 (C=). FT IR (cm^{-1}) 2935.8 w, 2859.4 w, 2080.3 m, 1988.7 m, 1932.3 s, 1917.4 s, 1895.1 s, 1443.8 w, 1102.7 w, 776.8 m, 593.5 m, 573.5 m. UV-vis (50% MeCN-50% Water): λ_{max}= 437 (ε≈ 11954 $M^{-1}s^{-1}$).). HRMS (nitrobenzyl alcohol): calcd for $C_{13}H_{14}O_5SW$ 467.0144, obtained 467.0147.





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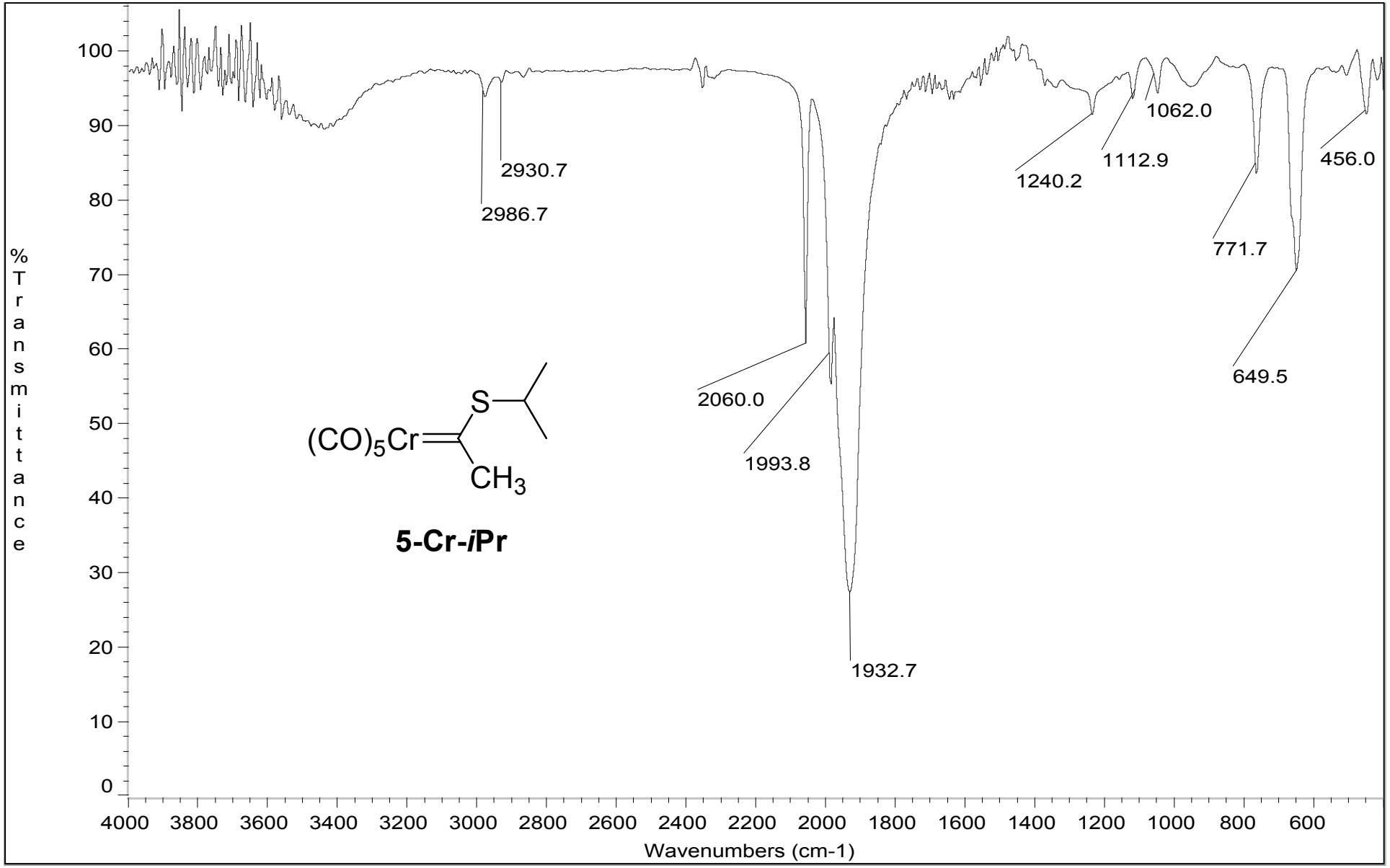

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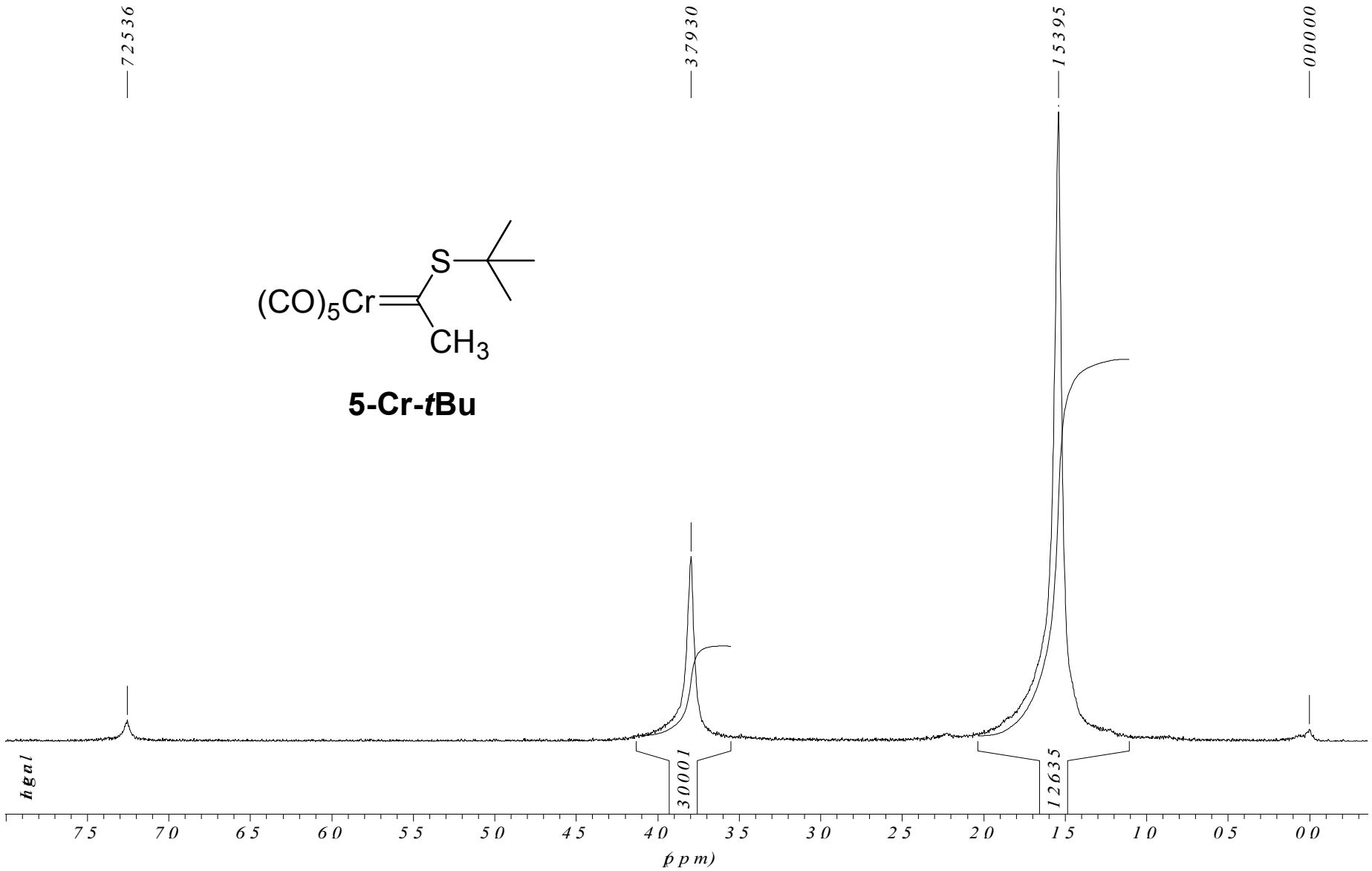

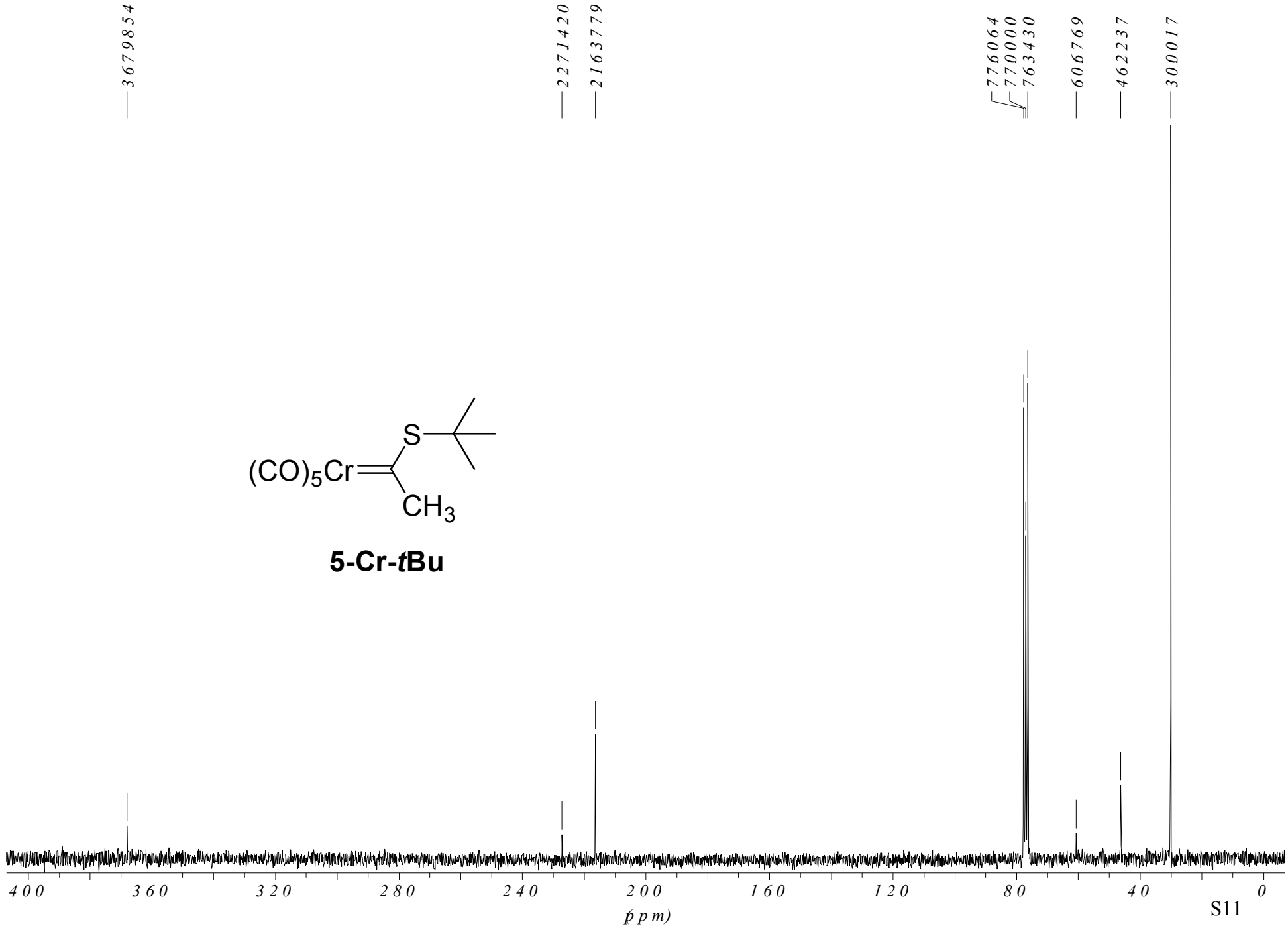

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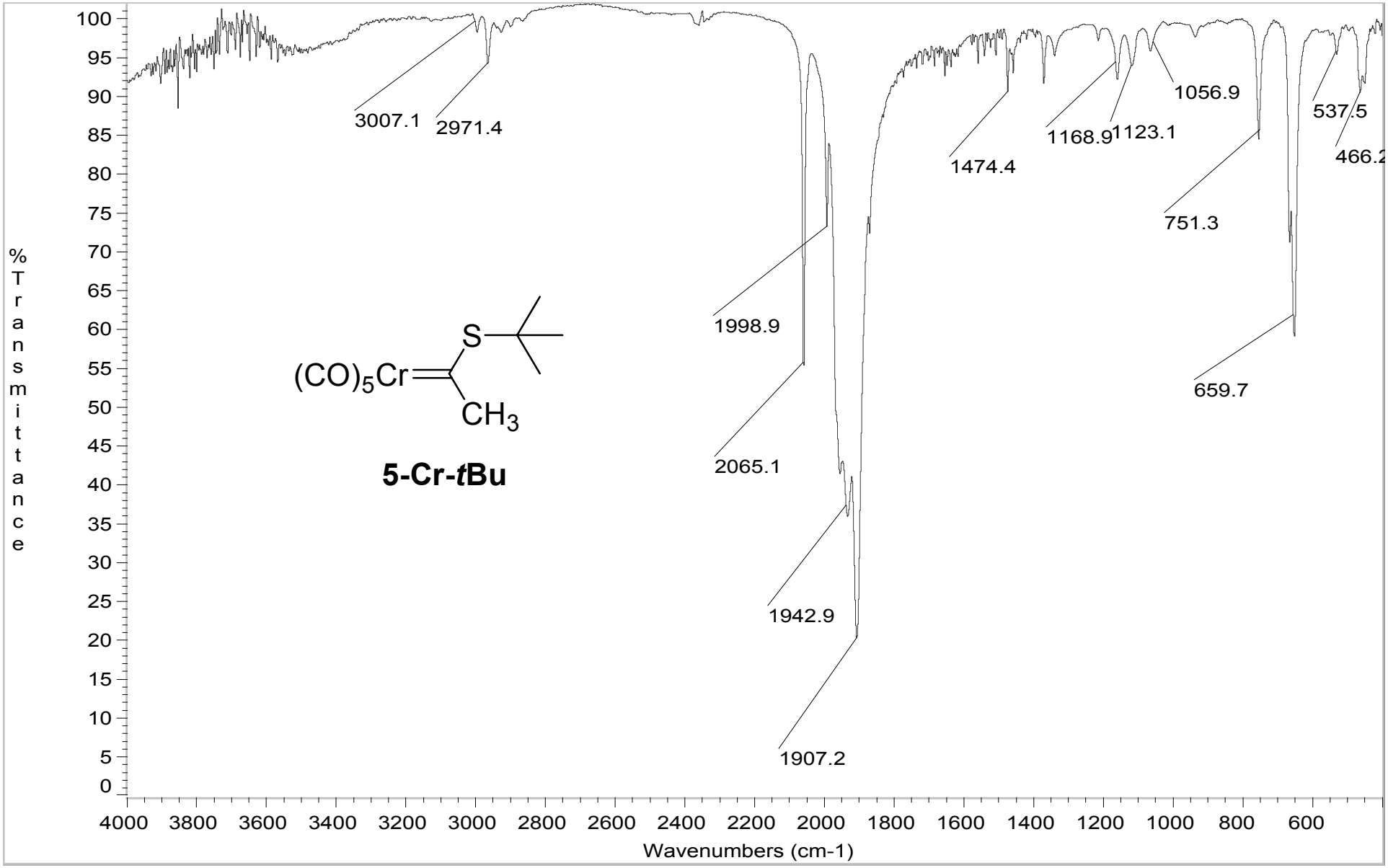

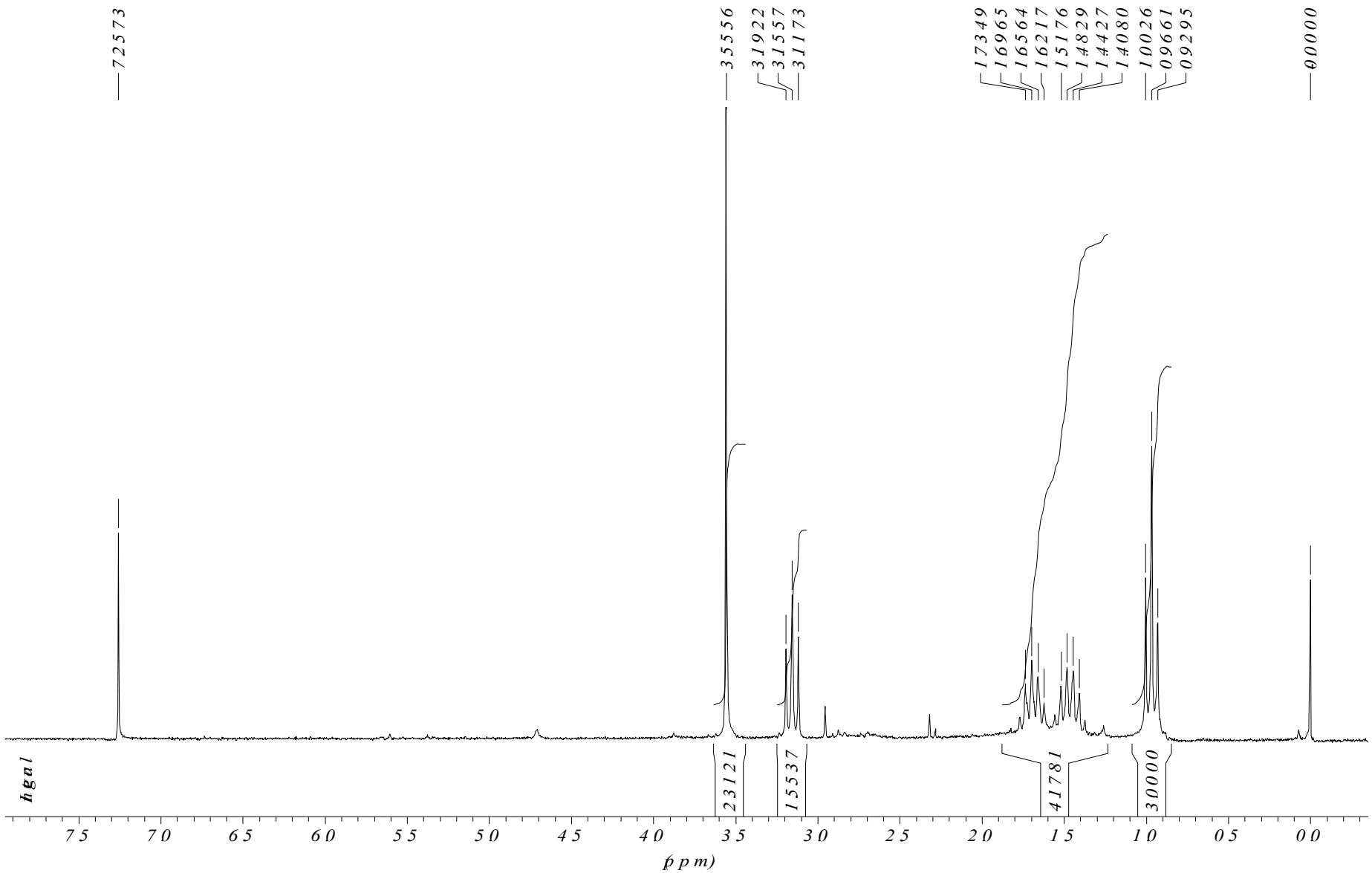

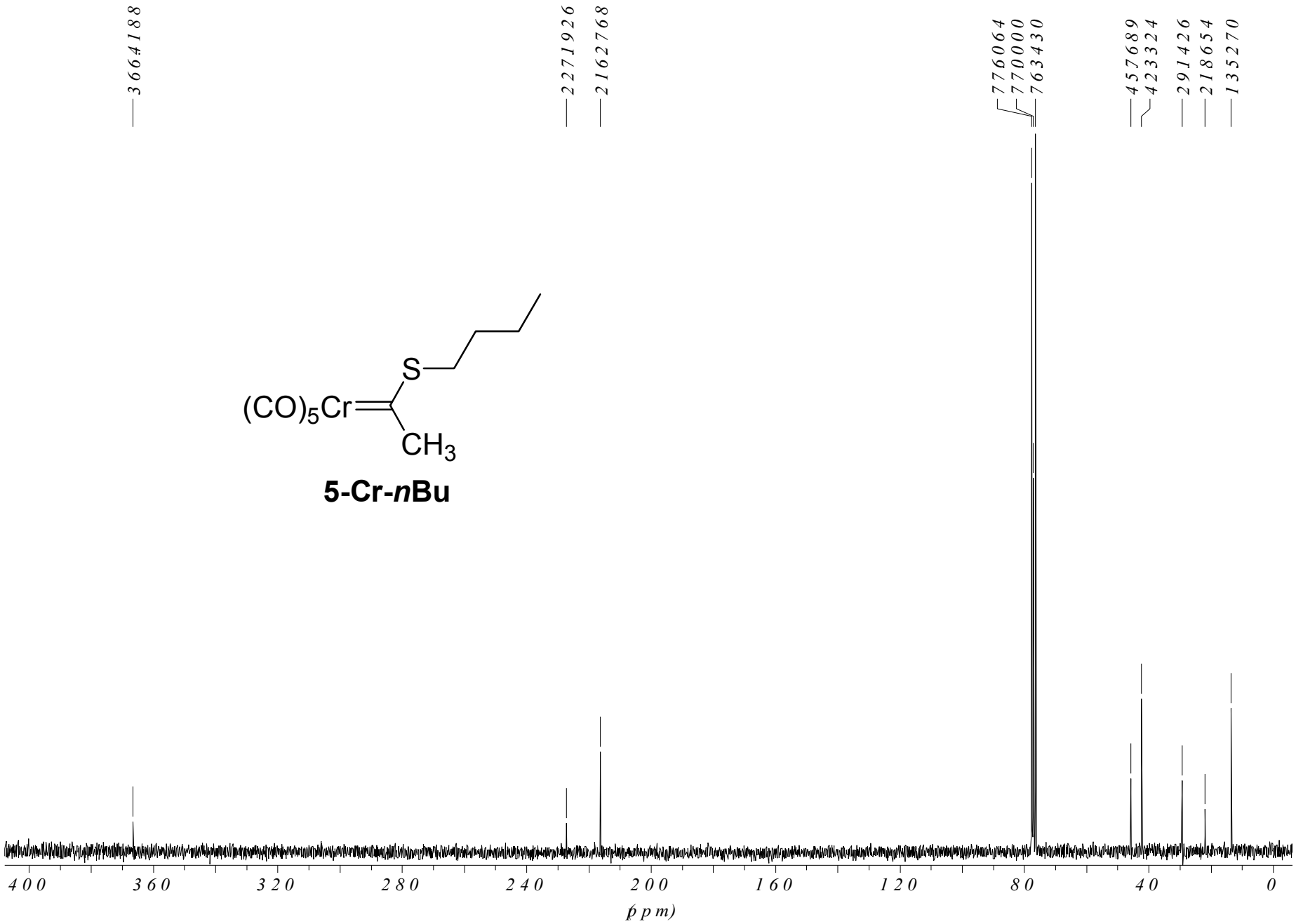

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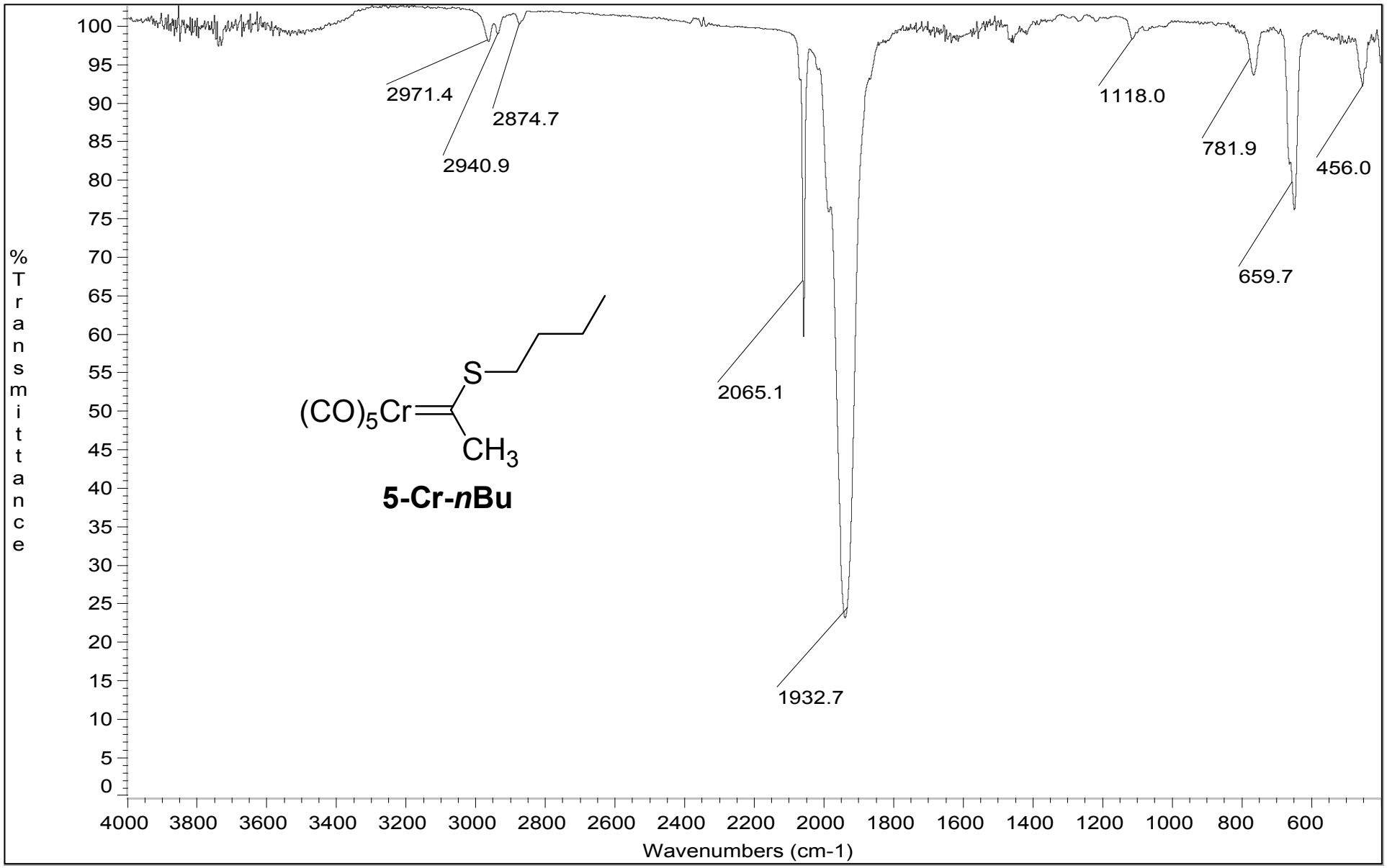

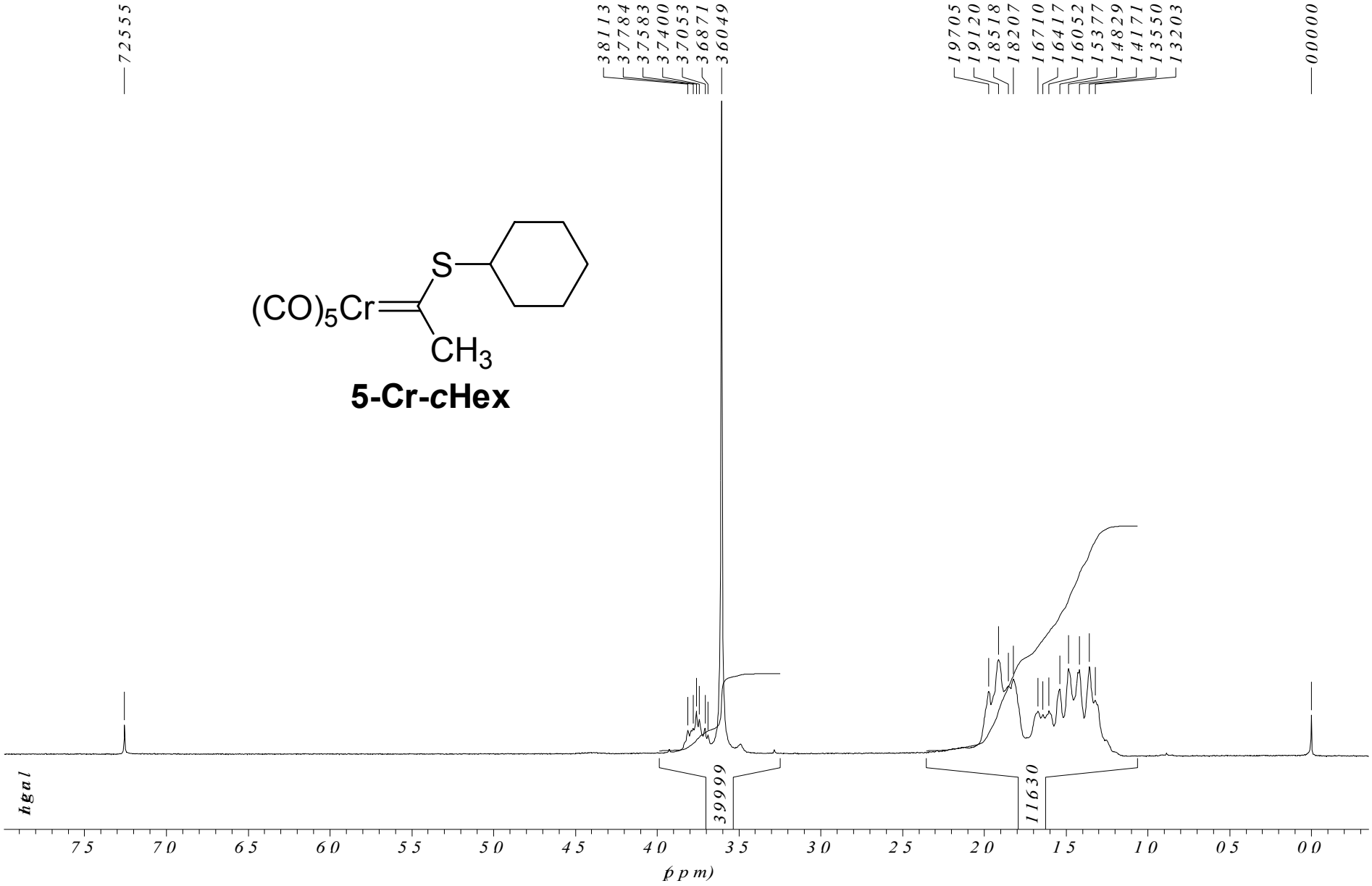

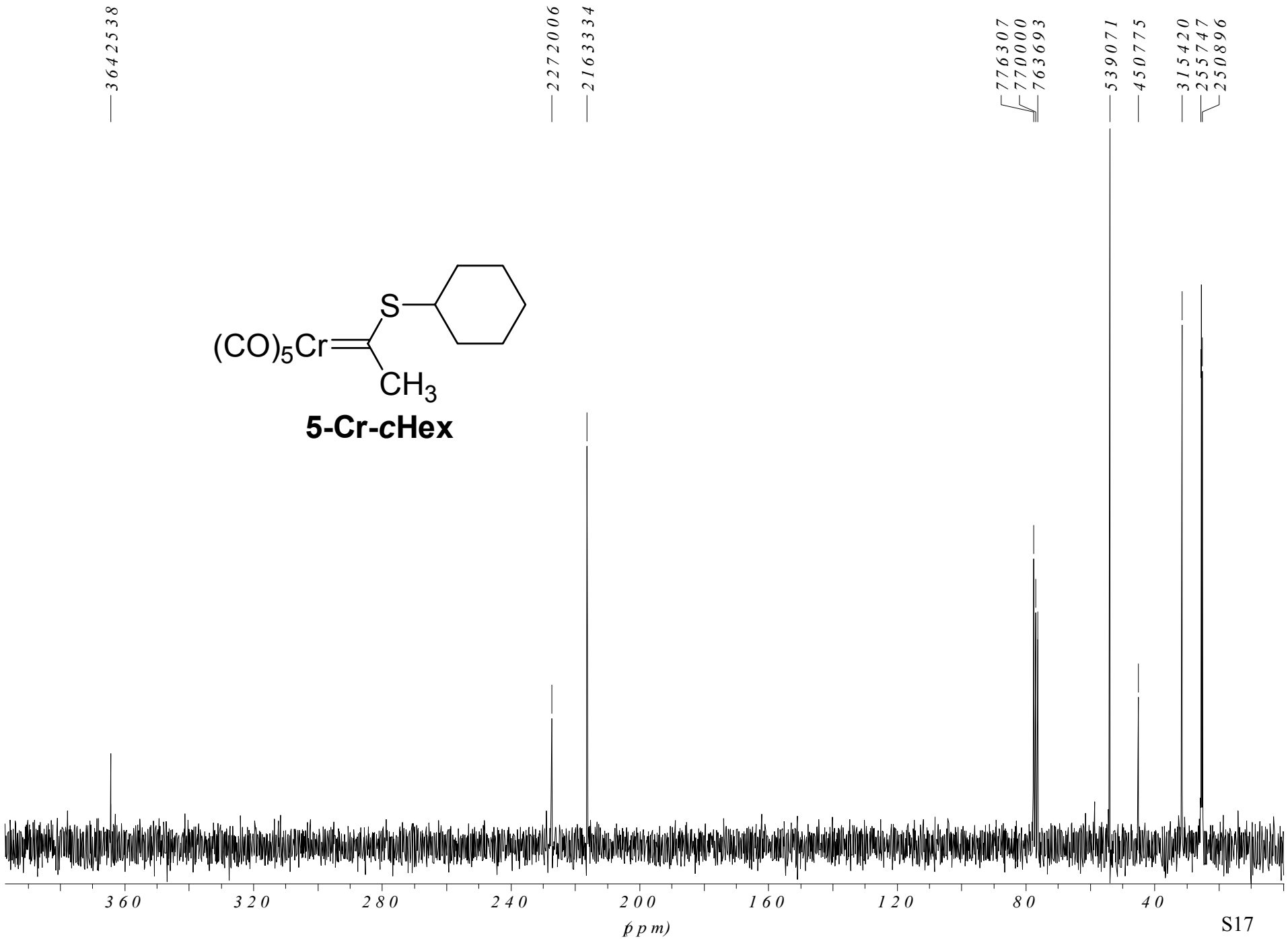

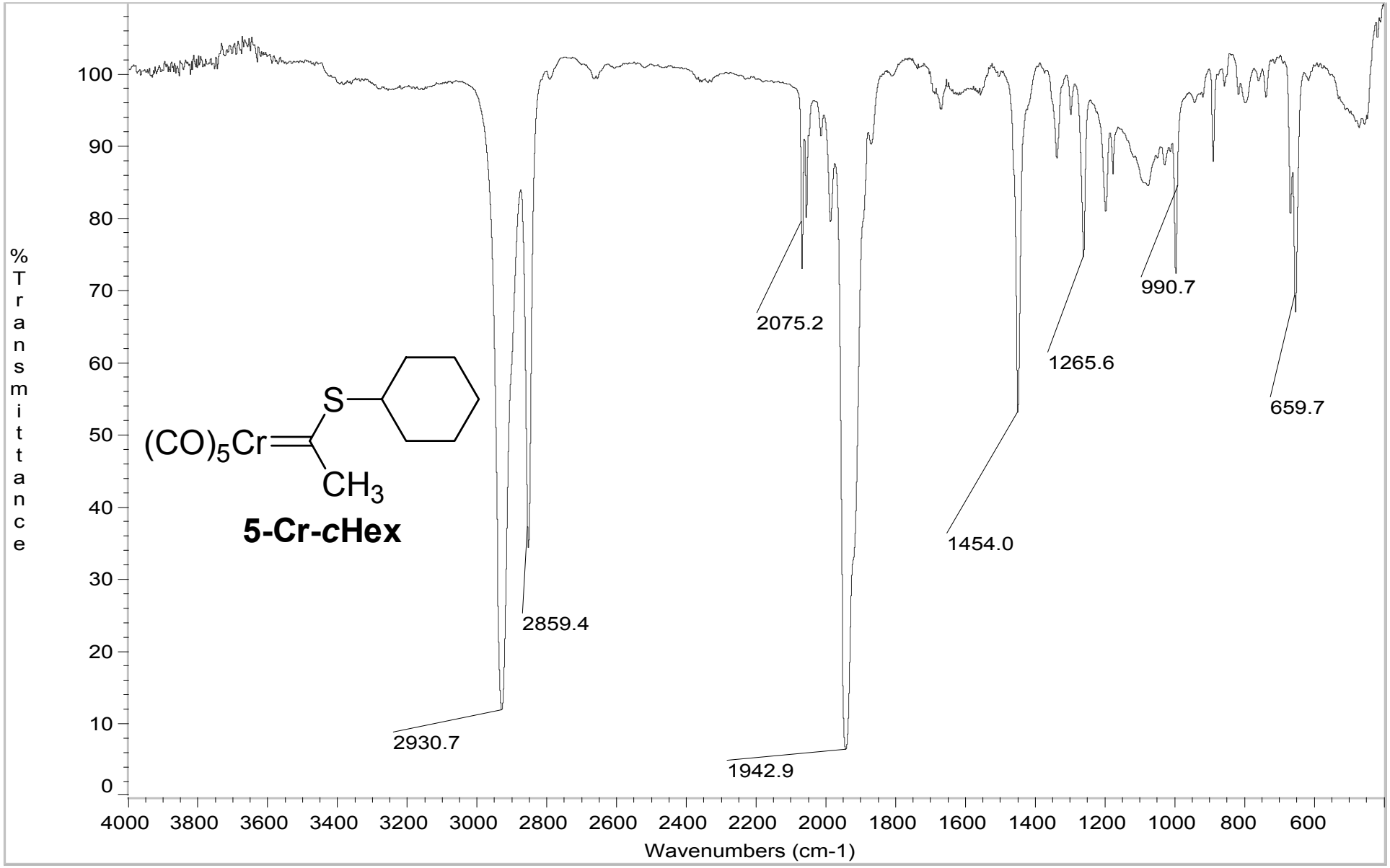

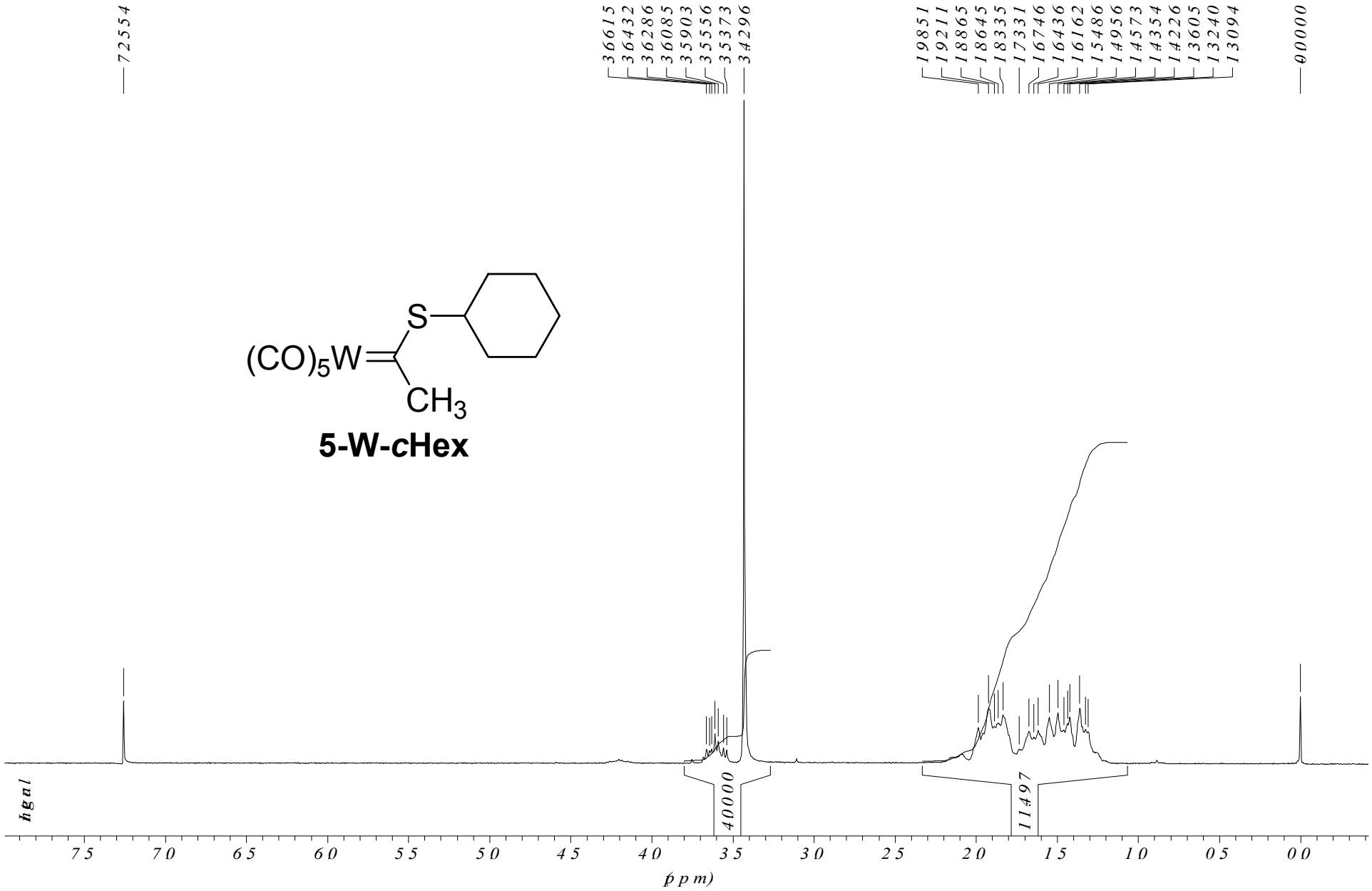

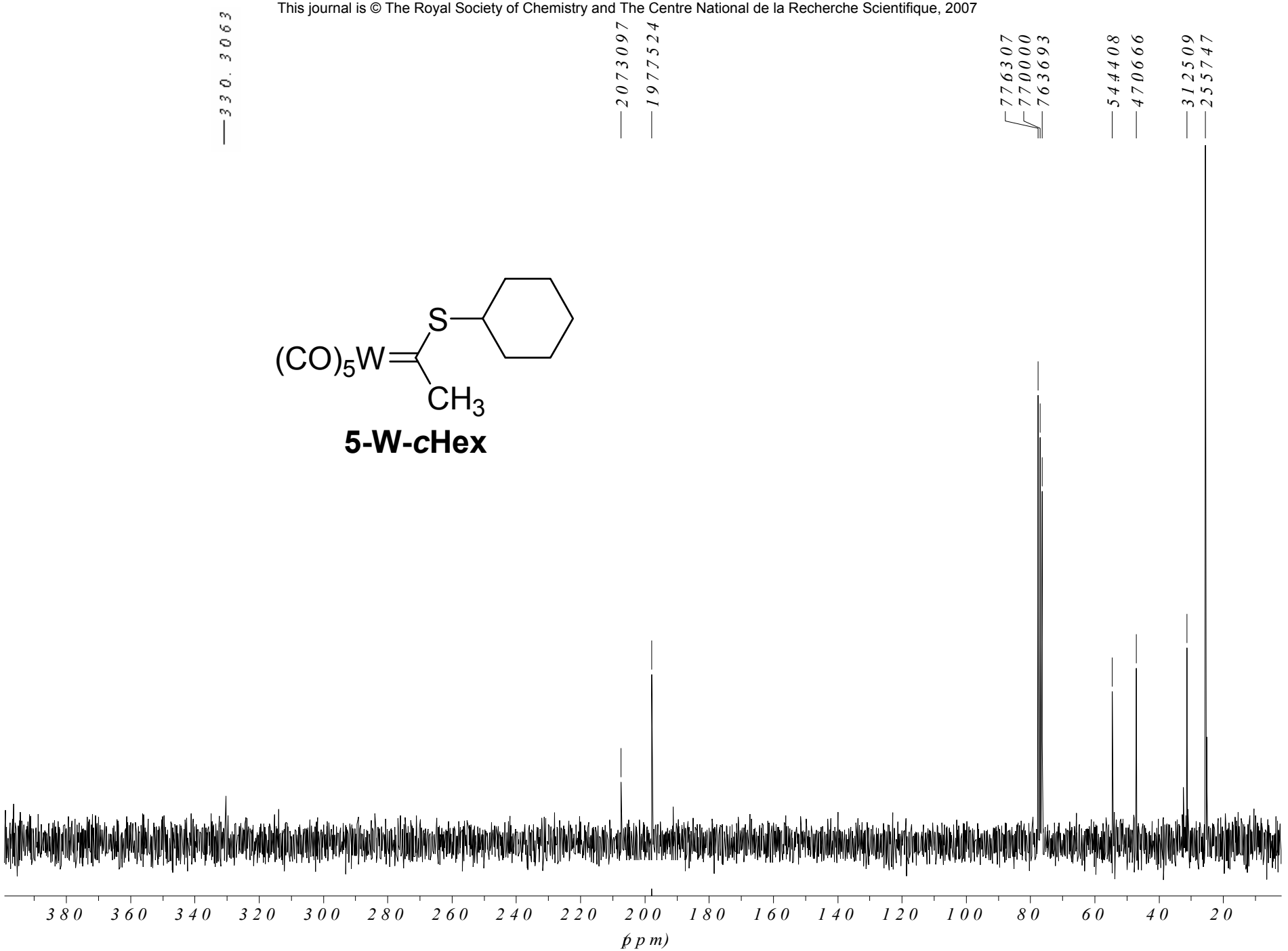

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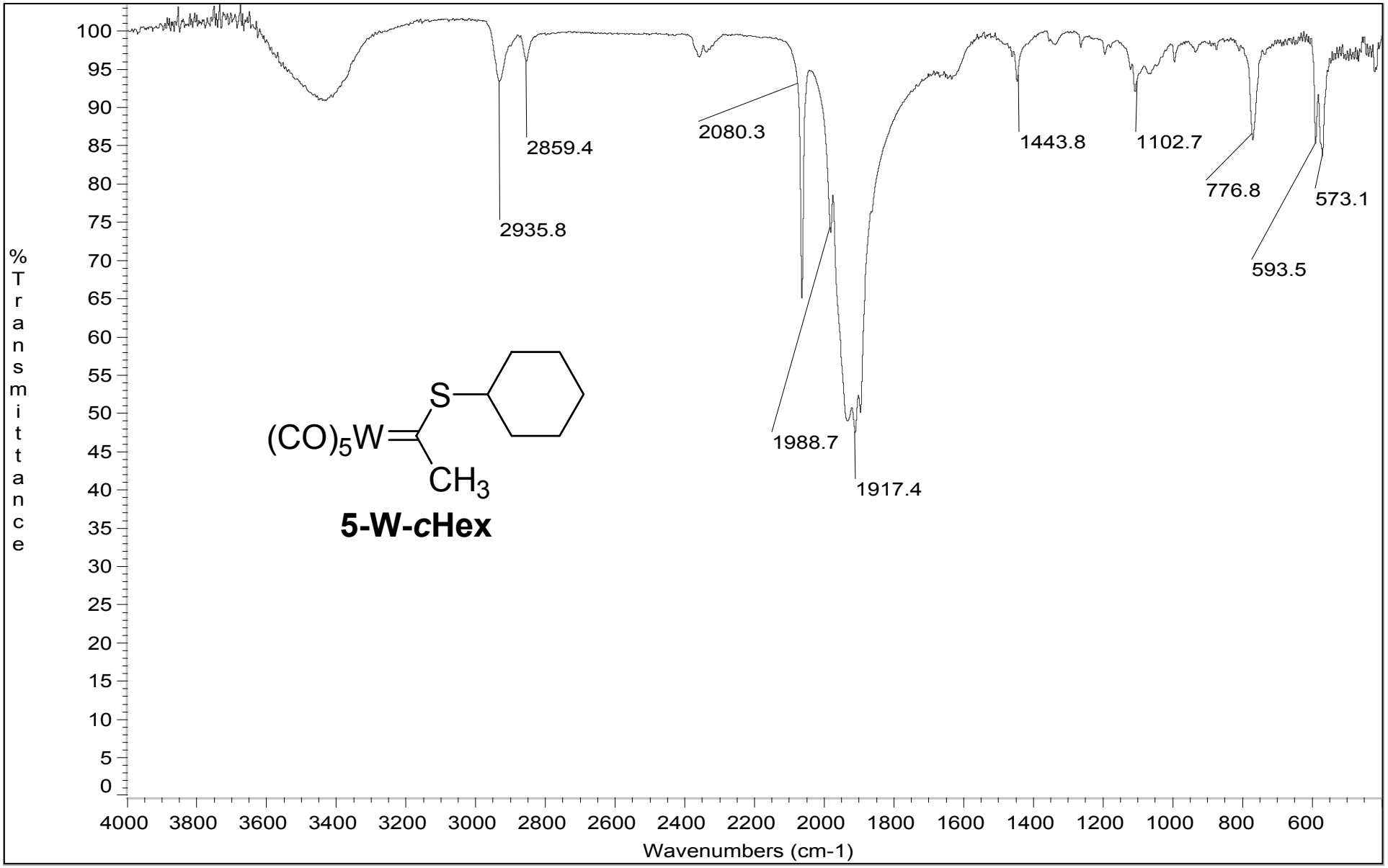

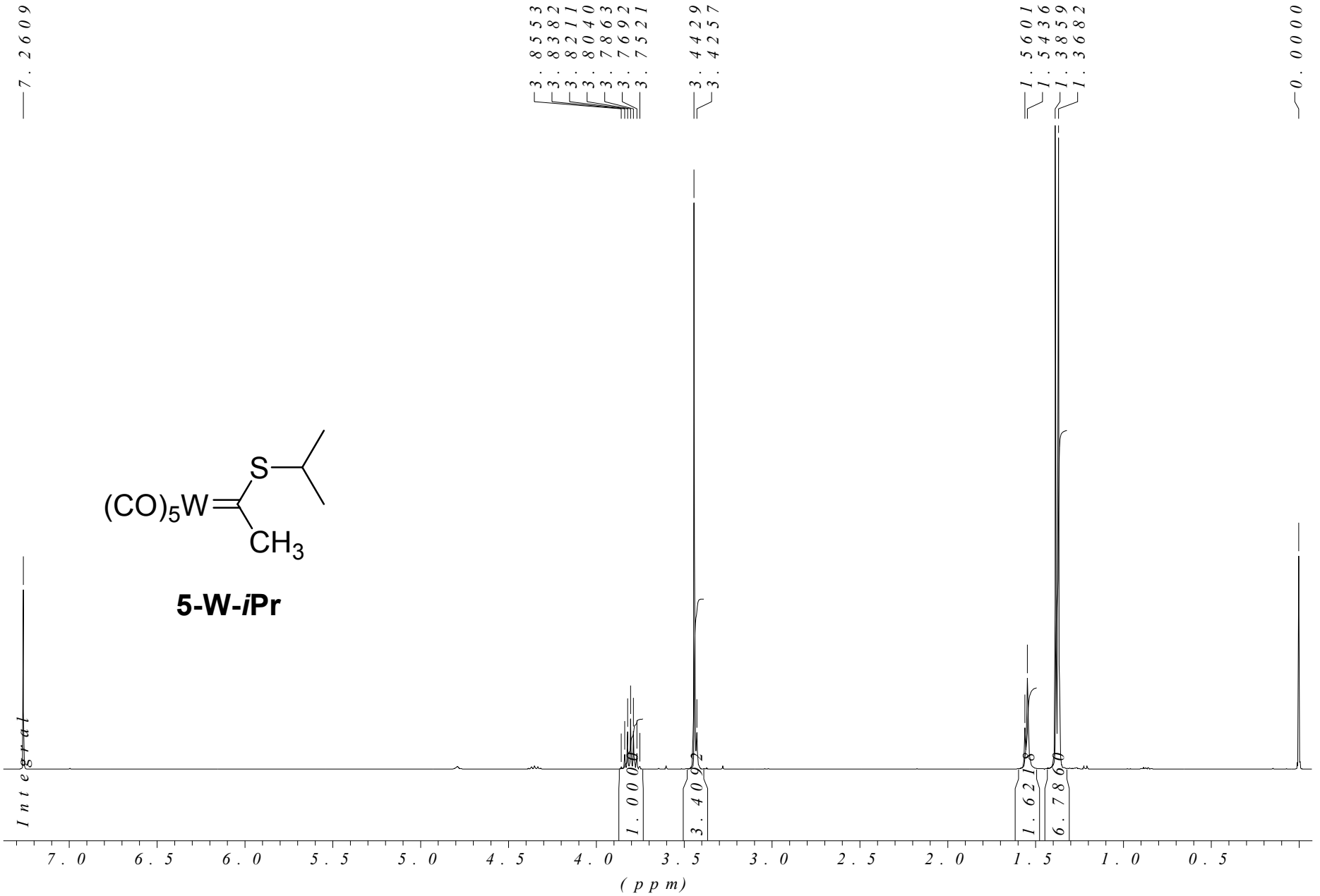

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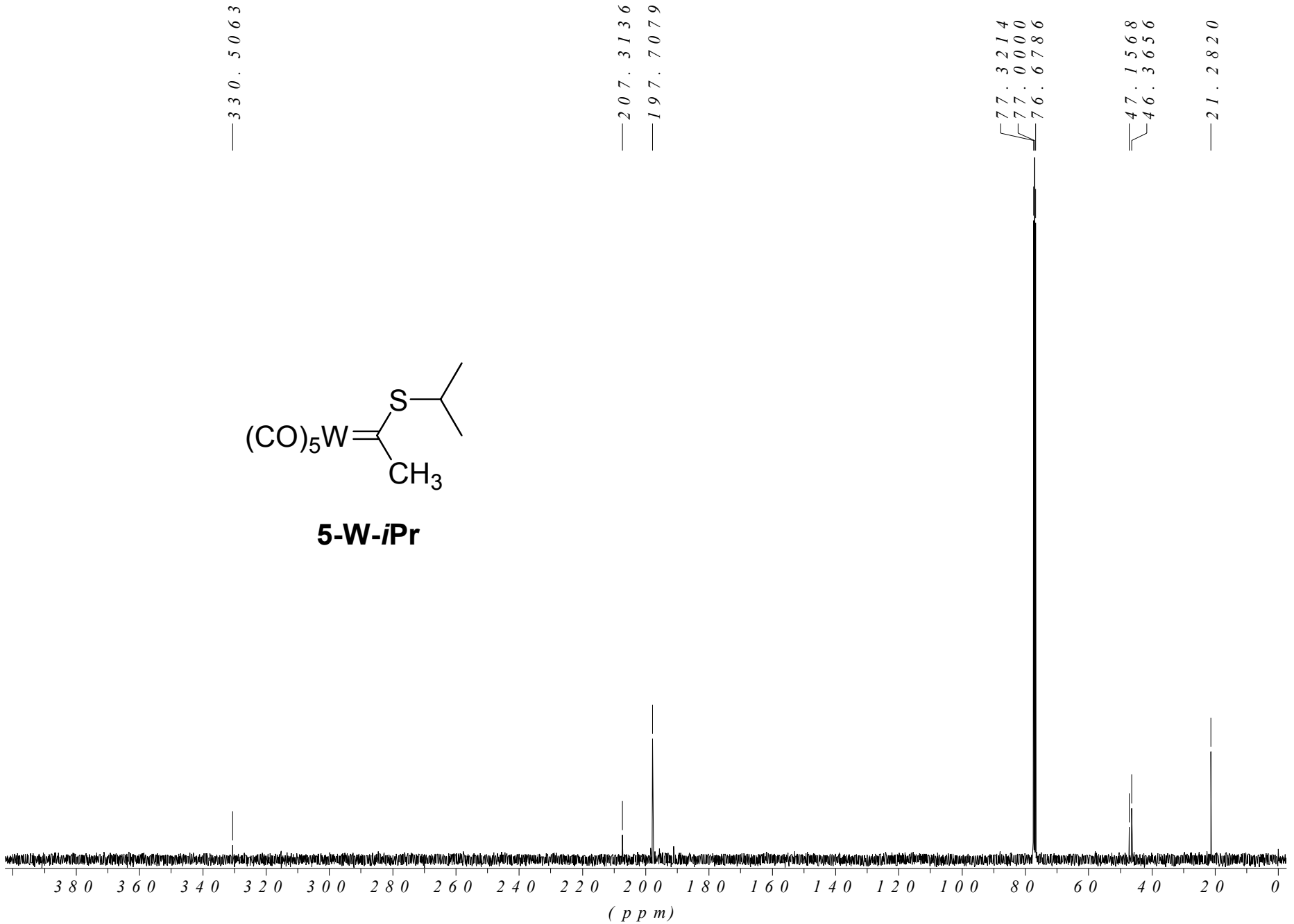

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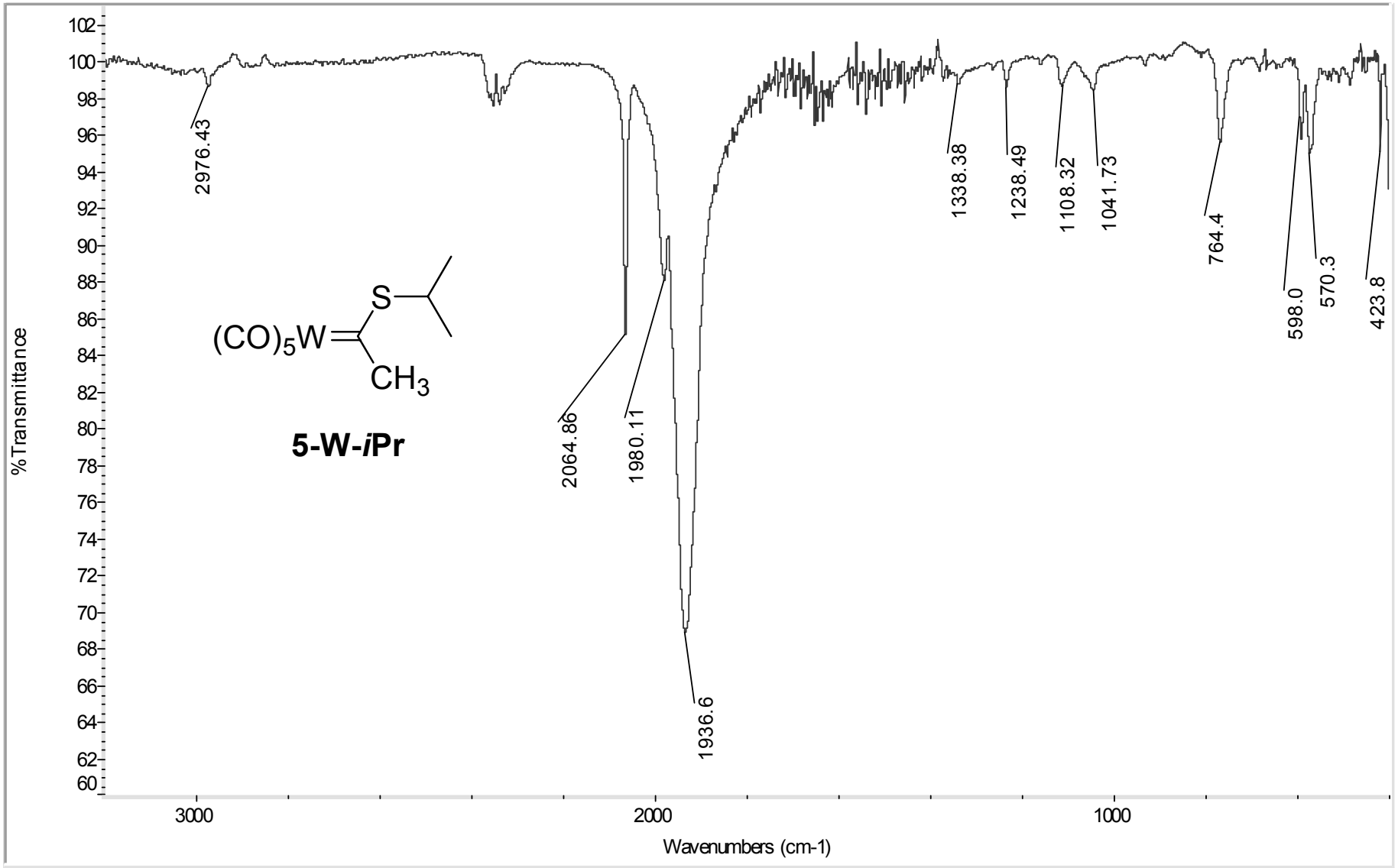

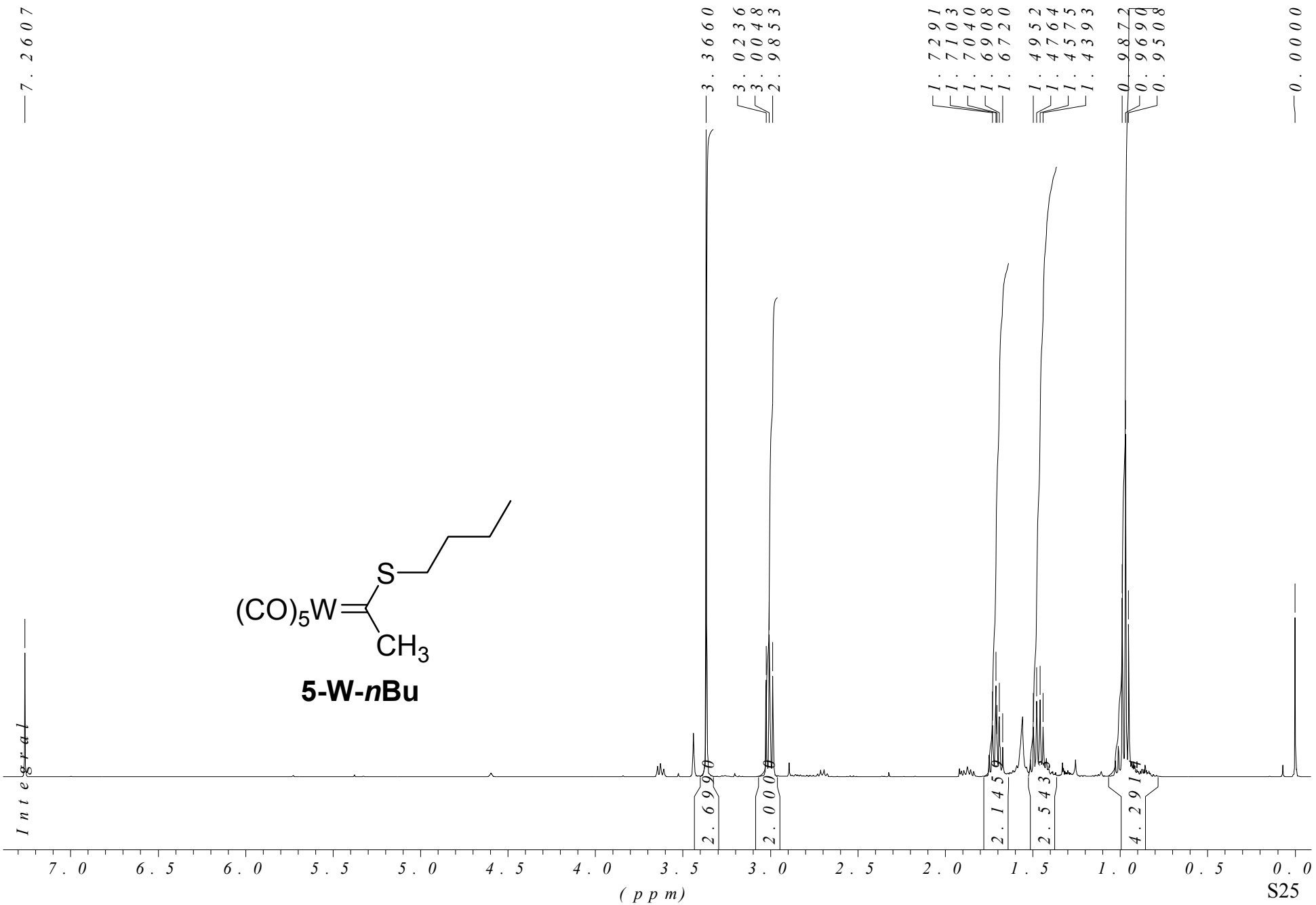

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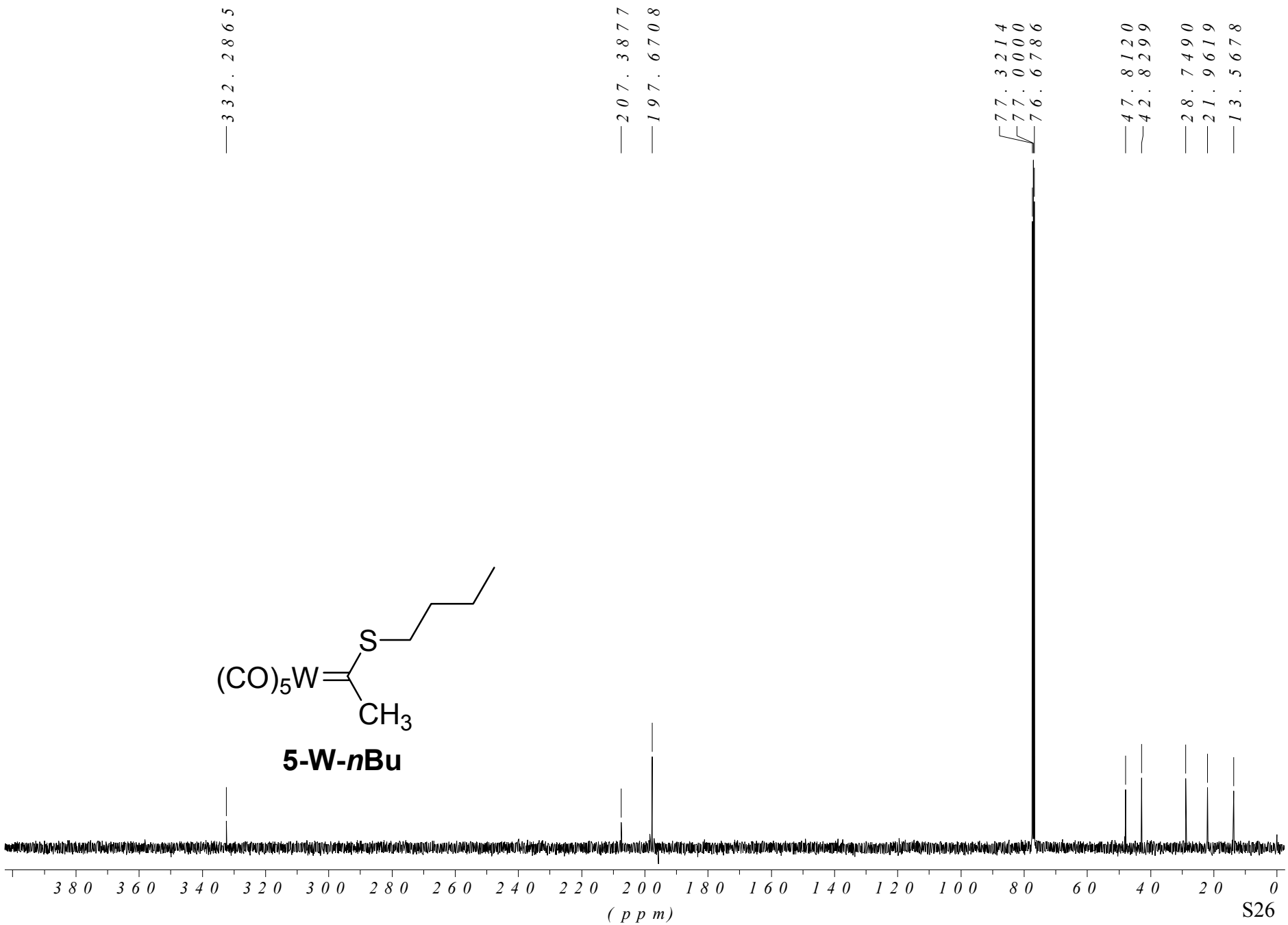

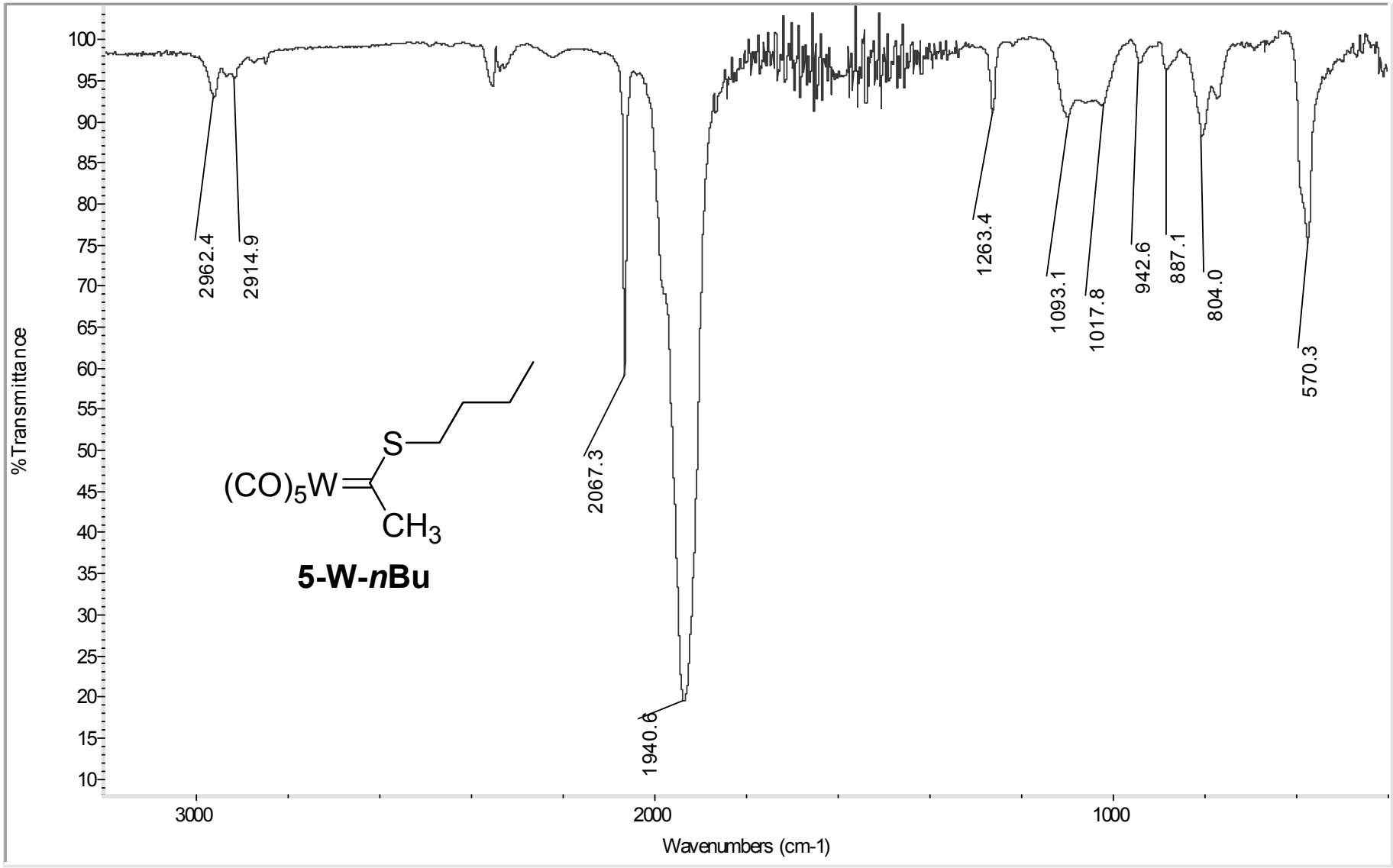

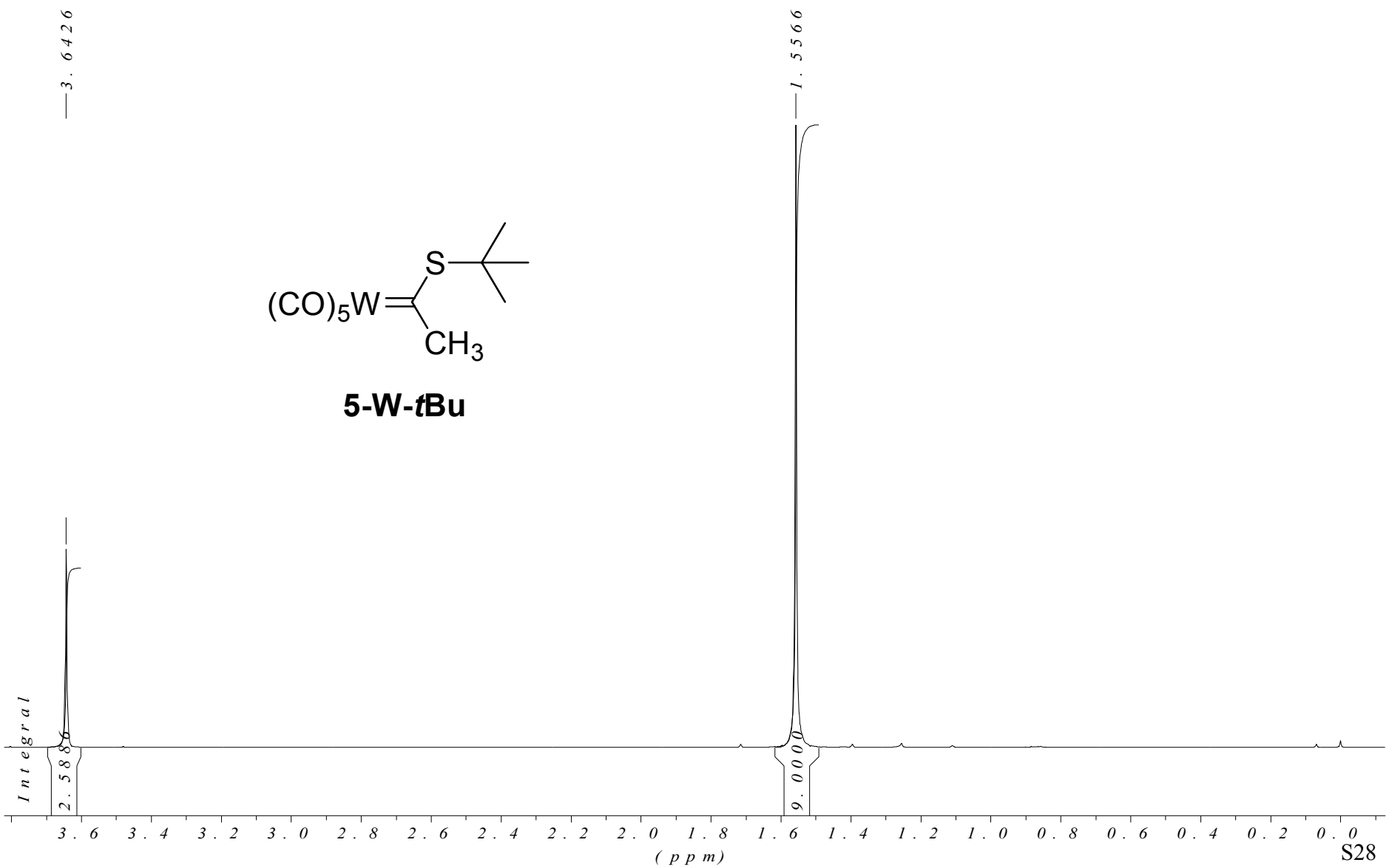

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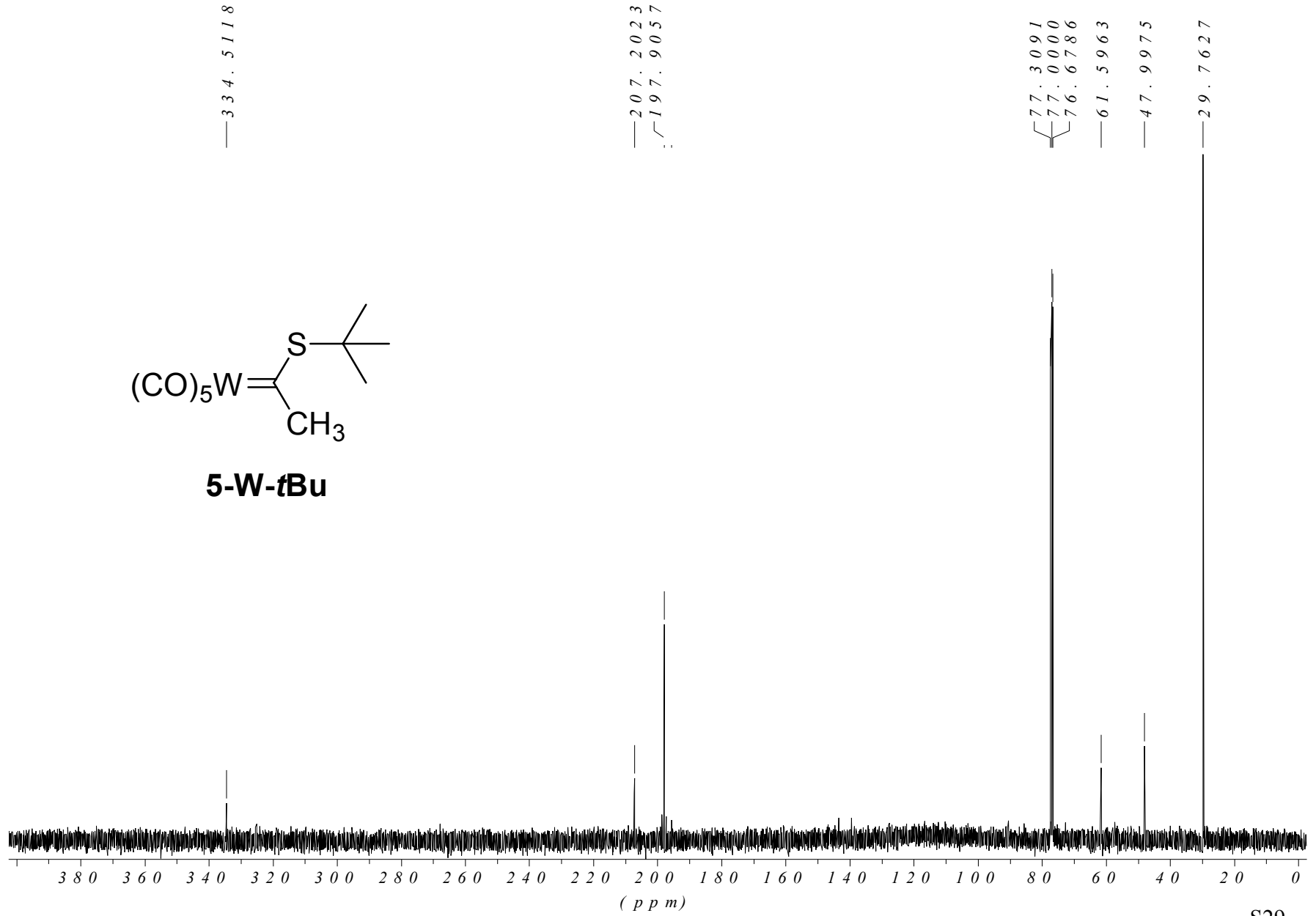

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