

Role of the Hydrophobicity on the Thermodynamic and Kinetic Acidity of Fischer Thiocarbene Complexes.

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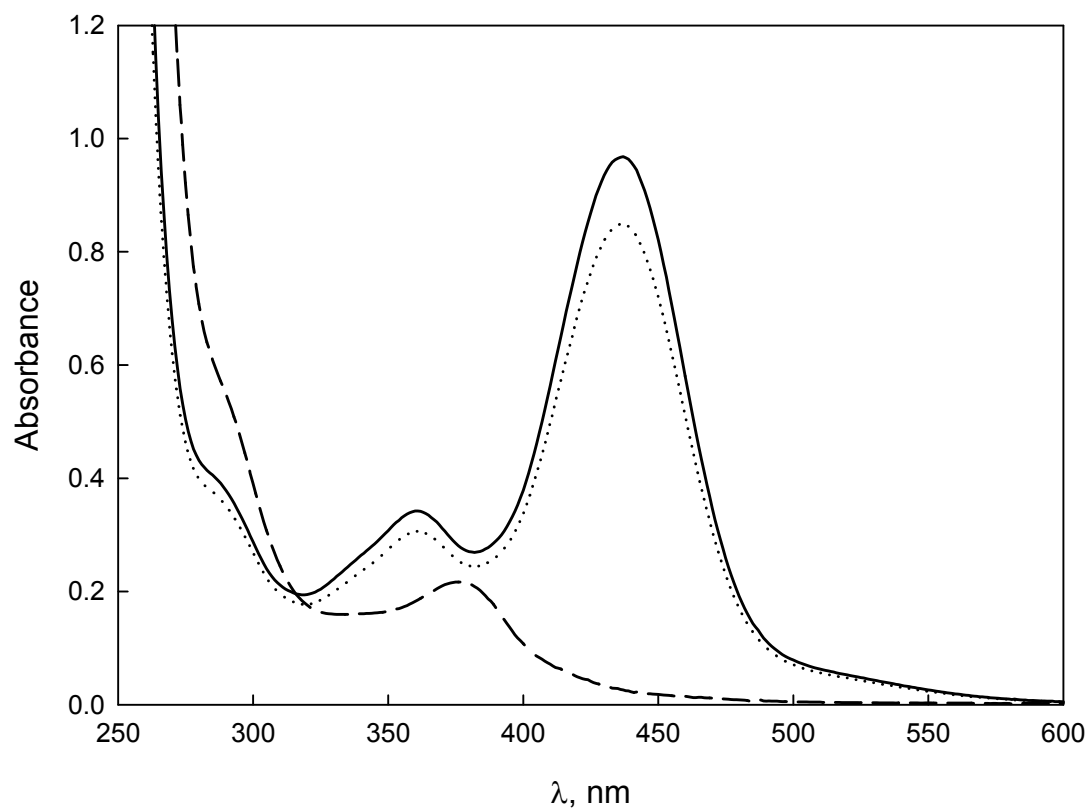


Fig. S1. UV-vis spectra of (—) 1×10^{-4} M **W-Sc-Hex** in 50% MeCN – 50% water at 25°C, (---) the corresponding anion obtained in 5×10^{-4} M KOH and (···) recovery upon acidification.

Table S1. Proton transfer reaction of KOH with **W-Sn-Bu**.^a

[KHO], M ^b	k_{obs} , s ⁻¹
0.0010	0.882 ± 0.002
0.0025	2.372 ± 0.005
0.0050	4.80 ± 0.01
0.0100	8.26 ± 0.02
0.0175	17.17 ± 0.05
0.0250	25.4 ± 0.1
0.0375	37.15 ± 0.06

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [W-Sn-Bu] = 1.00 x 10⁻⁴ M. Monitored at 436 nm in a stopped-flow apparatus. ^b These values have been computed as 10^{-(15,19-pH)}.

Table S2. Proton transfer reaction of morpholine with **W-Sn-Bu**.^a

pH	[Buffer], M	[MorfH ⁺], M	k_{obs} , s ⁻¹
7.80	0.0250	0.0222	20.68 ± 0.03
	0.0375	0.0333	25.41 ± 0.06
	0.0500	0.0444	32.73 ± 0.08
	0.0625	0.0555	40.4 ± 0.2
	0.0750	0.0666	48.5 ± 0.2
	0.0875	0.0777	56.1 ± 0.4
	0.1000	0.0888	61.0 ± 0.3
8.30	0.0125	0.0089	12.73 ± 0.03
	0.0250	0.0179	16.80 ± 0.02
	0.0375	0.0268	24.37 ± 0.03
	0.0500	0.0358	32.3 ± 0.1
	0.0625	0.0447	39.8 ± 0.3
	0.0750	0.0536	48.3 ± 0.2
	0.1000	0.0715	61.9 ± 0.3
8.50	0.0125	0.0077	12.75 ± 0.04
	0.0250	0.0153	16.37 ± 0.01
	0.0375	0.0230	23.82 ± 0.03
	0.0500	0.0307	32.3 ± 0.2
	0.0625	0.0383	39.6 ± 0.1
	0.0750	0.0460	47.7 ± 0.2
	0.1000	0.0613	63.0 ± 0.4
8.88	0.0125	0.00498	11.21 ± 0.07

	0.0250	0.00995	15.8 ± 0.1
	0.0375	0.01493	23.3 ± 0.1
	0.0500	0.01990	32.5 ± 0.1
	0.0625	0.02488	40.8 ± 0.2
	0.0750	0.02985	48.0 ± 0.3
	0.1000	0.03980	61.9 ± 0.4
9.00	0.0125	0.00417	7.96 ± 0.03
	0.0250	0.00835	15.9 ± 0.1
	0.0375	0.01252	23.50 ± 0.08
	0.0500	0.01669	32.04 ± 0.09
	0.0625	0.02087	40.6 ± 0.1
	0.0750	0.02504	48.2 ± 0.3
	0.1000	0.03339	63.9 ± 0.5
9.27	0.0125	0.00265	9.95 ± 0.05
	0.0250	0.00530	15.45 ± 0.09
	0.0375	0.00795	23.31 ± 0.07
	0.0500	0.01060	32.70 ± 0.06
	0.0625	0.01326	40.5 ± 0.2
	0.0750	0.01591	49.0 ± 0.2

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), $[\mathbf{W-Sn-Bu}] = 1.00 \times 10^{-4}$ M. Monitored at 436 nm in a stopped-flow apparatus.

Table S3. Proton transfer reaction of Piperidine with $\mathbf{W-Sn-Bu}$.^a

[Buffer], M	[B], M	$k_{\text{obs}}, \text{s}^{-1}$
0.0125	0.00625	42.7 ± 0.3
0.0250	0.01250	107.0 ± 0.5
0.0375	0.01875	171 ± 1
0.0500	0.02500	233 ± 1
0.0625	0.03125	317 ± 3
0.0750	0.03750	411 ± 4
0.1000	0.05000	618 ± 7

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), $[\mathbf{W-Sn-Bu}] = 1.00 \times 10^{-4}$ M, pH = 11.01. Monitored at 436 nm in a stopped-flow apparatus.

Table S4. Proton transfer reaction of Piperazine with **W-Sn-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	9.9 ± 0.1
0.0250	0.01250	23.2 ± 0.2
0.0375	0.01875	36.5 ± 0.2
0.0500	0.02500	48.69 ± 0.08
0.0625	0.03125	64.4 ± 0.2
0.0750	0.03750	77 ± 1
0.1000	0.05000	106.7 ± 0.7

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sn-Bu**] = 1.00 x 10⁻⁴ M, pH = 9.97.

Monitored at 436 nm in a stopped-flow apparatus.

Table S5. Proton transfer reaction of HEPA with **W-Sn-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	5.61 ± 0.06
0.0250	0.01250	11.4 ± 0.1
0.0375	0.01875	17.0 ± 0.1
0.0500	0.02500	22.8 ± 0.2
0.0625	0.03125	29.11 ± 0.09
0.0750	0.03750	35.5 ± 0.1
0.1000	0.05000	47.3 ± 0.3

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sn-Bu**] = 1.00 x 10⁻⁴ M, pH = 9.33.

Monitored at 436 nm in a stopped-flow apparatus.

Table S6. Proton transfer reaction of n-butylamine with **W-Sn-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	15.7 ± 0.1
0.0250	0.01250	32.37 ± 0.06
0.0375	0.01875	48.3 ± 0.2
0.0500	0.02500	66.3 ± 0.2
0.0625	0.03125	84.4 ± 0.4
0.0750	0.03750	103.0 ± 0.7
0.1000	0.05000	140.7 ± 0.4

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sn-Bu**] = 1.00 x 10⁻⁴ M, pH = 10.40.

Monitored at 436 nm in a stopped-flow apparatus.

Table S7. Proton transfer reaction of MeOCH₂CH₂NH₂ with **W-Sn-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	3.36 ± 0.05
0.0250	0.01250	6.71 ± 0.02
0.0375	0.01875	10.87 ± 0.06
0.0500	0.02500	14.43 ± 0.05
0.0625	0.03125	17.70 ± 0.05
0.0750	0.03750	22.19 ± 0.09
0.1000	0.05000	29.81 ± 0.04

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sn-Bu**] = 1.00×10^{-4} M, pH = 9.39. Monitored at 436 nm in a stopped-flow apparatus.

Table S8. Proton transfer reaction of Benzylamine with **W-Sn-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	8.93 ± 0.04
0.0250	0.01250	20.2 ± 0.1
0.0375	0.01875	30.84 ± 0.06
0.0500	0.02500	42.0 ± 0.1
0.0625	0.03125	54.0 ± 0.2
0.0750	0.03750	65.9 ± 0.2
0.1000	0.05000	92.2 ± 0.8

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sn-Bu**] = 1.00×10^{-4} M, pH = 9.12. Monitored at 436 nm in a stopped-flow apparatus.

Table S9. Proton transfer reaction of Furfurylamine with **W-Sn-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	6.26 ± 0.04
0.0250	0.01250	12.9 ± 0.1
0.0375	0.01875	19.39 ± 0.06
0.0500	0.02500	26.02 ± 0.06
0.0625	0.03125	32.3 ± 0.1
0.0750	0.03750	38.6 ± 0.2
0.1000	0.05000	51.4 ± 0.2

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sn-Bu**] = 1.00×10^{-4} M, pH = 8.58. Monitored at 436 nm in a stopped-flow apparatus.

Table S10. Proton transfer reaction of EtOCOCH₂NH₂ with **W-Sn-Bu**.^a

[Buffer], M	[HB ⁺], M	$k_{\text{obs.}} \text{ s}^{-1}$
0.0125	0.00625	11.23 ± 0.04
0.0250	0.01250	20.75 ± 0.06
0.0375	0.01875	28.32 ± 0.09
0.0500	0.02500	37.8 ± 0.2
0.0625	0.03125	45.4 ± 0.3
0.0750	0.03750	53.2 ± 0.4
0.1000	0.05000	66.3 ± 0.5

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1 \text{ M}$ (KCl), [**W-Sn-Bu**] = $1.00 \times 10^{-4} \text{ M}$, pH = 7.43.

Monitored at 436 nm in a stopped-flow apparatus.

Table S11. Proton transfer reaction of KOH with **W-St-Bu**.^a

[KOH], M ^b	$k_{\text{obs.}} \text{ s}^{-1}$
0.0010	0.767 ± 0.002
0.0025	2.669 ± 0.005
0.0050	5.34 ± 0.01
0.0100	11.9 ± 0.1
0.0175	22.18 ± 0.03
0.0250	31.7 ± 0.3
0.0375	48.5 ± 0.8

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1 \text{ M}$ (KCl), [**W-St-Bu**] = $1.00 \times 10^{-4} \text{ M}$. Monitored at 441 nm in a stopped-flow apparatus. ^b These values have been computed as $10^{-(15.19-\text{pH})}$.

Table S12. Proton transfer reaction of morpholine with **W-St-Bu**.^a

pH	[Buffer], M	[MorfH ⁺], M	$k_{\text{obs.}} \text{ s}^{-1}$
7.80	0.0250	0.0222	10.11 ± 0.01
	0.0375	0.0333	15.45 ± 0.01
	0.0500	0.0444	20.42 ± 0.03
	0.0625	0.0555	25.69 ± 0.04
	0.0750	0.0666	30.47 ± 0.06
	0.0875	0.0777	35.5 ± 0.1
	0.1000	0.0888	40.12 ± 0.09
8.30	0.0125	0.0089	6.61 ± 0.01
	0.0250	0.0179	10.24 ± 0.01

	0.0375	0.0268	15.36 ± 0.02
	0.0500	0.0358	20.38 ± 0.03
	0.0625	0.0447	25.58 ± 0.04
	0.0750	0.0536	30.92 ± 0.05
	0.1000	0.0715	41.3 ± 0.4
8.50	0.0125	0.0077	7.79 ± 0.04
	0.0250	0.0153	10.85 ± 0.03
	0.0375	0.0230	15.31 ± 0.02
	0.0500	0.0307	21.26 ± 0.03
	0.0625	0.0383	26.3 ± 0.1
	0.0750	0.0460	31.54 ± 0.04
	0.1000	0.0613	40.8 ± 0.2
8.88	0.0125	0.00498	5.12 ± 0.02
	0.0250	0.00995	10.01 ± 0.03
	0.0375	0.01493	15.01 ± 0.06
	0.0500	0.01990	21.0 ± 0.1
	0.0625	0.02488	26.3 ± 0.1
	0.0750	0.02985	31.6 ± 0.1
	0.1000	0.03980	43.2 ± 0.2
9.00	0.0125	0.00417	7.15 ± 0.02
	0.0250	0.00835	10.9 ± 0.05
	0.0375	0.01252	15.99 ± 0.08
	0.0500	0.01669	21.69 ± 0.09
	0.0625	0.02087	28.44 ± 0.06
	0.0750	0.02504	33.44 ± 0.06
	0.1000	0.03339	44.3 ± 0.2
9.27	0.0125	0.00265	5.475 ± 0.008
	0.0250	0.00530	11.21 ± 0.05
	0.0375	0.00795	16.6 ± 0.1
	0.0500	0.01060	22.83 ± 0.05
	0.0625	0.01326	27.9 ± 0.1
	0.0750	0.01591	33.7 ± 0.1

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), $[\mathbf{W-Sr-Bu}] = 1.00 \times 10^{-4}$ M. Monitored at 441 nm in a stopped-flow apparatus.

Table S13. Proton transfer reaction of piperidine with **W-St-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	27.1 ± 0.1
0.0250	0.01250	70.3 ± 0.5
0.0375	0.01875	102.9 ± 0.6
0.0500	0.02500	143.0 ± 0.8
0.0625	0.03125	179.9 ± 0.5
0.0750	0.03750	223 ± 1
0.1000	0.05000	317 ± 2

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-St-Bu**] = 1.00 x 10⁻⁴ M, pH = 11.01.

Monitored at 441 nm in a stopped-flow apparatus.

Table S14. Proton transfer reaction of piperazine with **W-St-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	7.06 ± 0.02
0.0250	0.01250	16.4 ± 0.1
0.0375	0.01875	25.2 ± 0.2
0.0500	0.02500	33.5 ± 0.1
0.0625	0.03125	43.17 ± 0.09
0.0750	0.03750	52.47 ± 0.09
0.1000	0.05000	71.8 ± 0.3

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-St-Bu**] = 1.00 x 10⁻⁴ M, pH = 9.97.

Monitored at 441 nm in a stopped-flow apparatus.

Table S15. Proton transfer reaction of HEPA with **W-St-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	3.38 ± 0.01
0.0250	0.01250	6.96 ± 0.04
0.0375	0.01875	10.35 ± 0.04
0.0500	0.02500	14.0 ± 0.2
0.0625	0.03125	16.91 ± 0.09
0.0750	0.03750	20.8 ± 0.1
0.1000	0.05000	28.29 ± 0.09

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-St-Bu**] = 1.00 x 10⁻⁴ M, pH = 9.33.

Monitored at 441nm in a stopped-flow apparatus.

Table S16. Proton transfer reaction of n-butylamine with **W-St-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	12.57 ± 0.05
0.0250	0.01250	26.23 ± 0.08
0.0375	0.01875	39.96 ± 0.07
0.0500	0.02500	54.8 ± 0.1
0.0625	0.03125	70.7 ± 0.9
0.0750	0.03750	87.1 ± 0.1
0.1000	0.05000	112.7 ± 0.4

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-St-Bu**] = 1.00×10^{-4} M, pH = 10.40.

Monitored at 441 nm in a stopped-flow apparatus.

Table S17. Proton transfer reaction of MeOCH₂CH₂NH₂ with **W-St-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	2.90 ± 0.01
0.0250	0.01250	5.77 ± 0.02
0.0375	0.01875	9.18 ± 0.03
0.0500	0.02500	12.79 ± 0.07
0.0625	0.03125	15.77 ± 0.09
0.0750	0.03750	20.0 ± 0.2
0.1000	0.05000	26.89 ± 0.09

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-St-Bu**] = 1.00×10^{-4} M, pH = 9.39.

Monitored at 441 nm in a stopped-flow apparatus.

Table S18. Proton transfer reaction of benzyamine with **W-St-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	6.96 ± 0.05
0.0250	0.01250	14.84 ± 0.07
0.0375	0.01875	23.64 ± 0.06
0.0500	0.02500	32.20 ± 0.05
0.0625	0.03125	41.8 ± 0.1
0.0750	0.03750	50.2 ± 0.3
0.1000	0.05000	70.5 ± 0.4

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-St-Bu**] = 1.00×10^{-4} M, pH = 9.12.

Monitored at 441 nm in a stopped-flow apparatus.

Table S19. Proton transfer reaction of furfurylamine with **W-St-Bu**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	5.27 ± 0.05
0.0250	0.01250	10.73 ± 0.08
0.0375	0.01875	15.64 ± 0.09
0.0500	0.02500	21.4 ± 0.1
0.0625	0.03125	26.66 ± 0.06
0.0750	0.03750	32.4 ± 0.2
0.1000	0.05000	43.0 ± 0.4

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-St-Bu**] = 1.00×10^{-4} M, pH = 8.58.

Monitored at 441 nm in a stopped-flow apparatus.

Table S20. Proton transfer reaction of EtOCOCH₂NH₂ with **W-St-Bu**.^a

[Buffer], M	[HB ⁺], M	k_{obs} , s ⁻¹
0.0125	0.00625	9.232 ± 0.009
0.0250	0.01250	17.48 ± 0.04
0.0375	0.01875	25.15 ± 0.06
0.0500	0.02500	34.5 ± 0.6
0.0625	0.03125	40.1 ± 0.6
0.0750	0.03750	47.6 ± 0.3
0.1000	0.05000	60.9 ± 0.7

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-St-Bu**] = 1.00×10^{-4} M, pH = 7.43.

Monitored at 441 nm in a stopped-flow apparatus.

Table S21. Proton transfer reaction of KOH with **W-Sc-Hex**.^a

[KHO], M ^b	k_{obs} , s ⁻¹
0.0010	0.528 ± 0.002
0.0025	1.651 ± 0.002
0.0050	3.485 ± 0.009
0.0100	7.41 ± 0.06
0.0175	13.8 ± 0.2
0.0250	19.9 ± 0.4
0.0375	28.8 ± 0.4

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00×10^{-4} M. Monitored at 436 nm in a stopped-flow apparatus. ^b These values have been computed as $10^{-(15,19-\text{pH})}$.

Table S22. Proton transfer reaction of morpholine with **W-Sc-Hex**.^a

pH	[Buffer], M	[MorfH ⁺], M	k_{obs} , s ⁻¹
7.80	0.0250	0.0222	18.43 ± 0.03
	0.0375	0.0333	25.94 ± 0.03
	0.0500	0.0444	34.96 ± 0.07
	0.0625	0.0555	43.0 ± 0.2
	0.0750	0.0666	51.0 ± 0.2
	0.0875	0.0777	59.9 ± 0.2
	0.1000	0.0888	69.4 ± 0.2
8.30	0.0125	0.0089	12.2 ± 0.1
	0.0250	0.0179	16.05 ± 0.04
	0.0375	0.0268	23.77 ± 0.05
	0.0500	0.0358	31.2 ± 0.2
	0.0625	0.0447	38.6 ± 0.2
	0.0750	0.0536	46.2 ± 0.1
	0.1000	0.0715	60.0 ± 0.3
8.50	0.0125	0.0077	11.50 ± 0.02
	0.0250	0.0153	15.84 ± 0.05
	0.0375	0.0230	22.69 ± 0.08
	0.0500	0.0307	30.58 ± 0.06
	0.0625	0.0383	37.8 ± 0.2
	0.0750	0.0460	45.7 ± 0.3
	0.1000	0.0613	59.9 ± 0.5
8.88	0.0125	0.00498	8.19 ± 0.05
	0.0250	0.00995	13.0 ± 0.1
	0.0375	0.01493	20.77 ± 0.07
	0.0500	0.01990	29.1 ± 0.1
	0.0625	0.02488	35.5 ± 0.2
	0.0750	0.02985	43.4 ± 0.2
	0.1000	0.03980	56.1 ± 0.4
9.00	0.0125	0.00417	10.10 ± 0.07
	0.0250	0.00835	14.28 ± 0.06
	0.0375	0.01252	21.4 ± 0.2
	0.0500	0.01669	28.7 ± 0.1
	0.0625	0.02087	36.6 ± 0.1

	0.0750	0.02504	43.4 ± 0.2
	0.1000	0.03339	56.3 ± 0.4
9.27	0.0125	0.00265	8.22 ± 0.05
	0.0250	0.00530	13.45 ± 0.09
	0.0375	0.00795	20.07 ± 0.08
	0.0500	0.01060	28.0 ± 0.1
	0.0625	0.01326	34.28 ± 0.04
	0.0750	0.01591	41.2 ± 0.1

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00×10^{-4} M. Monitored at 436 nm in a stopped-flow apparatus.

Table S23. Proton transfer reaction of piperidine with **W-Sc-Hex**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	36.1 ± 0.2
0.0250	0.01250	88.0 ± 0.3
0.0375	0.01875	127.4 ± 0.6
0.0500	0.02500	181 ± 2
0.0625	0.03125	229 ± 1
0.0750	0.03750	313 ± 3
0.1000	0.05000	457 ± 6

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00×10^{-4} M, pH = 11.01. Monitored at 436 nm in a stopped-flow apparatus.

Table S24. Proton transfer reaction of piperazine with **W-Sc-Hex**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	7.6 ± 0.1
0.0250	0.01250	17.97 ± 0.07
0.0375	0.01875	28.3 ± 0.1
0.0500	0.02500	39.0 ± 0.1
0.0625	0.03125	49.9 ± 0.2
0.0750	0.03750	60.0 ± 0.3
0.1000	0.05000	87 ± 1

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00×10^{-4} M, pH = 9.97. Monitored at 436 nm in a stopped-flow apparatus.

Table S25. Proton transfer reaction of HEPA with **W-Sc-Hex**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	4.52 ± 0.05
0.0250	0.01250	9.1 ± 0.1
0.0375	0.01875	14.6 ± 0.2
0.0500	0.02500	19.1 ± 0.3
0.0750	0.03750	29.1 ± 0.7
0.1000	0.05000	40.2 ± 0.7

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00 x 10⁻⁴ M, pH = 9.33.

Monitored at 436 nm in a stopped-flow apparatus.

Table S26. Proton transfer reaction of n-butylamine with **W-Sc-Hex**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	11.75 ± 0.05
0.0250	0.01250	24.04 ± 0.08
0.0375	0.01875	35.62 ± 0.09
0.0500	0.02500	51.5 ± 0.1
0.0625	0.03125	65.6 ± 0.2
0.0750	0.03750	81.0 ± 0.3
0.1000	0.05000	104.6 ± 0.4

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00 x 10⁻⁴ M, pH = 10.40.

Monitored at 436 nm in a stopped-flow apparatus.

Table S27. Proton transfer reaction of MeOCH₂CH₂NH₂ with **W-Sc-Hex**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	2.86 ± 0.04
0.0250	0.01250	5.61 ± 0.02
0.0375	0.01875	9.07 ± 0.05
0.0500	0.02500	12.42 ± 0.06
0.0625	0.03125	15.97 ± 0.08
0.0750	0.03750	19.44 ± 0.07
0.1000	0.05000	26.3 ± 0.1

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00 x 10⁻⁴ M, pH = 9.39.

Monitored at 436 nm in a stopped-flow apparatus.

Table S28. Proton transfer reaction of benzylamine with **W-Sc-Hex**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	7.81 ± 0.04
0.0250	0.01250	16.87 ± 0.05
0.0375	0.01875	26.66 ± 0.05
0.0500	0.02500	36.15 ± 0.08
0.0625	0.03125	45.9 ± 0.2
0.0750	0.03750	55.7 ± 0.2
0.1000	0.05000	76.4 ± 0.3

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00×10^{-4} M, pH = 9.12.

Monitored at 436 nm in a stopped-flow apparatus.

Table S29. Proton transfer reaction of furfurylamine with **W-Sc-Hex**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	6.3 ± 0.2
0.0250	0.01250	12.3 ± 0.1
0.0375	0.01875	17.7 ± 0.1
0.0500	0.02500	24.0 ± 0.2
0.0625	0.03125	28.7 ± 0.2
0.0750	0.03750	35.0 ± 0.2
0.1000	0.05000	45.1 ± 0.4

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00×10^{-4} M, pH = 8.58.

Monitored at 436 nm in a stopped-flow apparatus.

Table S30. Proton transfer reaction of EtOCOCH₂NH₂ with **W-Sc-Hex**.^a

[Buffer], M	[HB ⁺], M	k_{obs} , s ⁻¹
0.0125	0.00625	11.52 ± 0.05
0.0250	0.01250	22.02 ± 0.07
0.0375	0.01875	30.0 ± 0.1
0.0500	0.02500	42.8 ± 0.3
0.0625	0.03125	50.3 ± 0.1
0.0750	0.03750	58.8 ± 0.6
0.1000	0.05000	74.2 ± 0.4

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Sc-Hex**] = 1.00×10^{-4} M, pH = 7.43.

Monitored at 436 nm in a stopped-flow apparatus.

Table S31. Proton transfer reaction of KOH with **W-Si-Pr**.^a

[KHO], M	$k_{\text{obs.}} \text{ s}^{-1}$
0.0010	0.737 ± 0.001
0.0025	2.441 ± 0.007
0.0050	5.13 ± 0.03
0.0100	11.38 ± 0.04
0.0175	21.2 ± 0.2
0.0250	29.6 ± 0.1
0.0375	45.5 ± 0.8

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1 \text{ M}$ (KCl), $[\text{W-Si-Pr}] = 1.00 \times 10^{-4} \text{ M}$. Monitored at 436 nm in a stopped-flow apparatus. ^b These values have been computed as $10^{-(15,19-\text{pH})}$.

Table S32. Proton transfer reaction of morpholine with **W-Si-Pr**.^a

pH	[Buffer], M	[MorfH ⁺], M	$k_{\text{obs.}} \text{ s}^{-1}$
7.80	0.0250	0.0222	15.904
	0.0375	0.0333	21.343
	0.0500	0.0444	27.945
	0.0625	0.0555	34.197
	0.0750	0.0666	40.072
	0.0875	0.0777	46.965
	0.1000	0.0888	53.434
8.30	0.0125	0.0089	6.90
	0.0250	0.0179	13.27
	0.0375	0.0268	20.11
	0.0500	0.0358	26.64
	0.0625	0.0447	32.89
	0.0750	0.0536	39.67
	0.1000	0.0715	50.81
8.5	0.0125	0.0077	6.78
	0.0250	0.0153	13.38
	0.0375	0.0230	19.23
	0.0500	0.0307	26.48
	0.0625	0.0383	32.82
	0.0750	0.0460	39.25
	0.1000	0.0613	51.62

8.88	0.0125	0.0050	6.46 ± 0.03
	0.0250	0.0099	13.02 ± 0.09
	0.0375	0.0149	19.1 ± 0.1
	0.0500	0.0199	26.5 ± 0.1
	0.0625	0.0249	33.8 ± 0.1
	0.0750	0.0299	40.5 ± 0.3
	0.1000	0.0398	54.7 ± 0.4
9.0	0.0125	0.0042	6.34 ± 0.04
	0.0250	0.0083	13.0 ± 0.1
	0.0375	0.0125	18.86 ± 0.08
	0.0500	0.0167	25.82 ± 0.07
	0.0625	0.0209	32.44 ± 0.07
	0.0750	0.0250	38.54 ± 0.09
	0.1000	0.0334	51.2 ± 0.2
9.27	0.0125	0.0027	6.10 ± 0.02
	0.0250	0.0053	13.01 ± 0.08
	0.0375	0.0080	19.85 ± 0.09
	0.0500	0.0106	26.45 ± 0.09
	0.0625	0.0133	32.47 ± 0.09
	0.0750	0.0159	38.62 ± 0.09
	0.1000	0.0212	49.0 ± 0.4
9.40	0.0125	0.0021	6.30
	0.0250	0.0042	12.78
	0.0375	0.0062	19.40
	0.0500	0.0083	25.15
	0.0625	0.0104	32.21
	0.0750	0.0125	37.94
	0.1000	0.0166	51.83

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), $[\mathbf{W-Si-Pr}] = 1.00 \times 10^{-4}$ M. Monitored at 436 nm in a stopped-flow apparatus.

Table S33. Proton transfer reaction of piperidine with **W-Si-Pr**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	28.6 ± 0.4
0.0250	0.01250	74.9 ± 0.3
0.0375	0.01875	104.8 ± 0.8
0.0500	0.02500	152.3 ± 0.6
0.0625	0.03125	198 ± 1
0.0750	0.03750	246 ± 2
0.1000	0.05000	336 ± 2

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), **[W-Si-Pr]** = 1.00 x 10⁻⁴ M, pH = 11.01.

Monitored at 436 nm in a stopped-flow apparatus.

Table S34. Proton transfer reaction of piperazine with **W-Si-Pr**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	8.05 ± 0.09
0.0250	0.01250	19.24 ± 0.08
0.0375	0.01875	29.1 ± 0.2
0.0500	0.02500	40.7 ± 0.2
0.0625	0.03125	52.1 ± 0.1
0.0750	0.03750	65.1 ± 0.4
0.1000	0.05000	92 ± 1

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), **[W-Si-Pr]** = 1.00 x 10⁻⁴ M, pH = 9.97.

Monitored at 436 nm in a stopped-flow apparatus.

Table S35. Proton transfer reaction of HEPA with **W-Si-Pr**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	4.59 ± 0.01
0.0250	0.01250	10.1 ± 0.2
0.0375	0.01875	14.41 ± 0.09
0.0500	0.02500	19.76 ± 0.08
0.0625	0.03125	24.45 ± 0.03
0.0750	0.03750	29.26 ± 0.07
0.1000	0.05000	40.14 ± 0.07

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), **[W-Si-Pr]** = 1.00 x 10⁻⁴ M, pH = 9.33.

Monitored at 436 nm in a stopped-flow apparatus.

Table S36. Proton transfer reaction of n-butylamine with **W-Si-Pr**.^a

[Buffer], M	[HB ⁺], M	k_{obs} , s ⁻¹
0.0125	0.00625	11.64 ± 0.06
0.0250	0.01250	24.4 ± 0.2
0.0375	0.01875	36.9 ± 0.2
0.0500	0.02500	51.0 ± 0.7
0.0625	0.03125	62.8 ± 0.2
0.0750	0.03750	80.2 ± 0.7
0.1000	0.05000	99.9 ± 0.3

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Si-Pr**] = 1.00 x 10⁻⁴ M, pH = 10.40.

Monitored at 436 nm in a stopped-flow apparatus.

Table S37. Proton transfer reaction of MeOCH₂CH₂NH₂ with **W-Si-Pr**.^a

[Buffer], M	[B], M	k_{obs} , s ⁻¹
0.0125	0.00625	2.79 ± 0.01
0.0250	0.01250	5.71 ± 0.03
0.0375	0.01875	9.02 ± 0.04
0.0500	0.02500	12.28 ± 0.09
0.0625	0.03125	15.30 ± 0.07
0.0750	0.03750	19.08 ± 0.03
0.1000	0.05000	26.0 ± 0.1

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Si-Pr**] = 1.00 x 10⁻⁴ M, pH = 9.39.

Monitored at 436 nm in a stopped-flow apparatus.

Table S38. Proton transfer reaction of benzylamine with **W-Si-Pr**.^a

[Buffer], M	[HB ⁺], M	k_{obs} , s ⁻¹
0.0125	0.00625	6.64 ± 0.05
0.0250	0.01250	14.43 ± 0.06
0.0375	0.01875	23.1 ± 0.1
0.0500	0.02500	32.3 ± 0.3
0.0625	0.03125	40.5 ± 0.2
0.0750	0.03750	49.7 ± 0.4
0.1000	0.05000	68.8 ± 0.3

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Si-Pr**] = 1.00 x 10⁻⁴ M, pH = 9.12.

Monitored at 436 nm in a stopped-flow apparatus.

Table S39. Proton transfer reaction of furfurilamine with **W-Si-Pr**.^a

[Buffer], M	[HB ⁺], M	k_{obs} , s ⁻¹
0.0125	0.00625	5.22 ± 0.09
0.0250	0.01250	10.41 ± 0.08
0.0375	0.01875	15.52 ± 0.07
0.0500	0.02500	21.6 ± 0.3
0.0625	0.03125	26.50 ± 0.04
0.0750	0.03750	31.7 ± 0.1
0.1000	0.05000	41.1 ± 0.2

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Si-Pr**] = 1.00×10^{-4} M, pH = 8.58.

Monitored at 436 nm in a stopped-flow apparatus.

Table S40. Proton transfer reaction of EtOCOCH₂NH₂ with **W-Si-Pr**.^a

[Buffer], M	[HB ⁺], M	k_{obs} , s ⁻¹
0.0125	0.00625	8.93 ± 0.03
0.0250	0.01250	17.00 ± 0.04
0.0375	0.01875	23.42 ± 0.08
0.0500	0.02500	32.55 ± 0.08
0.0625	0.03125	39.75 ± 0.09
0.0750	0.03750	46.5 ± 0.2
0.1000	0.05000	58.1 ± 0.2

^aAcetonitrile:Water (1:1 V/V), 25°C, $\mu = 0.1$ M (KCl), [**W-Si-Pr**] = 1.00×10^{-4} M, pH = 7.43.

Monitored at 436 nm in a stopped-flow apparatus.

Cartesian coordinates (in Å) and total energy (in a. u. non corrected zero-point vibrational energies included) of all the stationary points discussed in the text in gas phase. All calculation have been performed at the B3LYP/LANLDZ&6-31+G(d) level of theory.

Cr-SMe

E = -1169.1218991

C 1.27042200 0.51168100 -0.00287400
S 2.45683400 -0.70810800 -0.00019100
C 1.77176100 1.93336600 -0.00297200
C 4.13423600 0.04782800 -0.00098700
H 2.37407000 2.13532800 0.89526000
H 2.42527400 2.12626600 -0.86619500
H 0.95480100 2.65572200 -0.02881500
H 4.83560300 -0.79084100 0.00964300
H 4.30307500 0.64331300 -0.90213300
H 4.29620900 0.66067000 0.88965400
Cr -0.70933900 -0.03148300 0.00001900
C -1.00204100 1.29103300 1.34378100
O -1.18445000 2.08764200 2.15906900
C -2.56491200 -0.43556300 0.00214800
O -3.69532800 -0.67245100 0.00335200
C -0.40908600 -1.34199400 1.36133100
O -0.23692400 -2.13001000 2.18492200
C -0.99657600 1.26439900 -1.37064600
O -1.17436900 2.04557700 -2.20170000
C -0.40913000 -1.36970000 -1.33419600
O -0.23921300 -2.17468800 -2.14168600

Cr-SMe⁻

E = -1168.60427

C 1.29396700 0.63154700 -0.06561400
S 2.45809600 -0.71653700 -0.01352000
C 1.72966600 1.90832600 -0.12908100
C 4.13812000 0.02016100 -0.06507800
H 2.78140000 2.20207100 -0.15252000
H 1.02212100 2.73531000 -0.16091500
H 4.84679200 -0.81464200 -0.03335800
H 4.29894600 0.59006600 -0.98757500
H 4.31761900 0.67363600 0.79654000
Cr -0.80721200 -0.05160400 -0.01572800

C -1.03886000 1.29052000 1.29552000
O -1.18248000 2.11448000 2.10080300
C -2.59287700 -0.51789700 0.02148600
O -3.72896100 -0.80110100 0.04461700
C -0.41266300 -1.28909300 1.37026300
O -0.23749000 -2.04577000 2.23305200
C -1.08703100 1.21362700 -1.39220300
O -1.26377500 1.98964100 -2.23762400
C -0.43743300 -1.36023700 -1.34132000
O -0.27109900 -2.15984700 -2.16622300

Cr-Si-Pr

E= -1247.7510433

C -0.71581700 0.54796500 -0.31195000
S -1.95340000 -0.56030500 0.02782500
C -1.08539800 1.92055400 -0.81018300
C -3.66393600 0.13313300 -0.28646800
C -4.10599300 1.07504700 0.83726400
C -4.59285700 -1.07886400 -0.43219800
Cr 1.23683200 -0.04986300 0.02380500
C 1.56376300 0.30069700 -1.82254100
O 1.74597000 0.52006200 -2.94133500
C 3.05234500 -0.51796800 0.29981700
O 4.16173400 -0.79612600 0.46482500
C 0.86580100 -1.88019300 -0.39755100
O 0.69157500 -2.99148400 -0.65196300
C 1.68495800 1.74739300 0.46676400
O 1.98238000 2.82812500 0.74621400
C 0.81420700 -0.39642300 1.85541600
O 0.54227900 -0.60017500 2.95744600
H -2.04227400 1.98590800 -1.33974800
H -1.14739200 2.59105300 0.06053500
H -0.29983300 2.32582600 -1.45309500
H -3.62640900 0.66872500 -1.24078500
H -3.44982100 1.94576100 0.93041300
H -4.11854100 0.55499100 1.80206200
H -5.12170400 1.43958800 0.63596700
H -5.61457700 -0.73387300 -0.63234400
H -4.61687700 -1.67762800 0.48618500
H -4.28607600 -1.73000500 -1.25744600

Cr-Si-Pr

E= -1247.2328809

C -0.70748500 0.61321900 -0.37573800
S -1.94132100 -0.55541300 0.17061100
C -1.04900500 1.76882600 -0.98463200
C -3.62703200 0.13088300 -0.19583100
C -4.04767500 1.20353900 0.81646300
C -4.61697100 -1.04045200 -0.22059300
Cr 1.34884300 -0.08597000 0.05227600
C 1.73906200 0.46834200 -1.71235000
O 1.98385100 0.80713300 -2.79559500
C 3.10112000 -0.57461800 0.36553400
O 4.21664500 -0.87356800 0.55893400
C 0.93425600 -1.81349800 -0.62044100
O 0.74388300 -2.87825000 -1.04166000
C 1.63337200 1.66994500 0.69293800
O 1.80989300 2.74750400 1.08756200
C 0.84650800 -0.60830900 1.80873300
O 0.60425100 -0.92415800 2.89904200
H -2.07366100 2.09173200 -1.18211900
H -0.28087800 2.46000600 -1.32778400
H -3.58132700 0.57133500 -1.19975000
H -3.31087700 2.01078800 0.87114300
H -4.14154800 0.76687400 1.81887500
H -5.02034700 1.64063000 0.54009700
H -5.63503300 -0.67805400 -0.42575200
H -4.63658900 -1.55964200 0.74683000
H -4.34872400 -1.77280900 -0.99011300

Cr-Sn-Bu

E= -1287.0655851

C 0.16458400 0.71753800 -0.00016400
S 1.50540600 -0.32841400 -0.00013700
C 0.46387400 2.19562800 -0.00016500
C 3.08494200 0.64058900 -0.00007600
C 4.27108000 -0.33037100 0.00002900
C 5.62078600 0.40535500 0.00003500
Cr -1.72739900 -0.09072200 0.00001000
C -2.19422500 1.16700700 1.35604000
O -2.48126600 1.92459000 2.17863500
C -3.50793200 -0.74742900 0.00020300
O -4.59476400 -1.13921500 0.00031500

C -1.24546900 -1.35822400 1.34901800
O -0.96407700 -2.12144000 2.16612700
C -2.19394700 1.16597600 -1.35708700
O -2.48075900 1.92295900 -2.18031300
C -1.24549000 -1.35935100 -1.34795700
O -0.96421800 -2.12327900 -2.16444000
C 6.81717300 -0.55394400 0.00003200
H 1.05802200 2.47810500 0.88116300
H 1.05961900 2.47804600 -0.88041700
H -0.44599800 2.79742500 -0.00095800
H 3.10674800 1.28185200 -0.88805500
H 3.10661600 1.28189200 0.88787500
H 4.21117700 -0.98464400 -0.88041000
H 4.21111600 -0.98453500 0.88054500
H 5.67664600 1.06207800 0.87989500
H 5.67665100 1.06209100 -0.87981600
H 6.80700800 -1.20125700 -0.88582700
H 6.80696300 -1.20132500 0.88584000
H 7.76494700 -0.00334600 0.00007900

Cr-Sn-Bu⁻

E= -1286.5467661

C 0.16495300 0.84223400 -0.04630700
S 1.50288300 -0.33568500 -0.02108200
C 0.41741300 2.16880200 -0.07666600
C 3.07858400 0.61988100 -0.04255000
C 4.27701200 -0.33459300 -0.02019300
C 5.62779100 0.39832200 -0.03702000
Cr -1.82339600 -0.12417900 -0.02116200
C -2.25582900 1.16737600 1.28994000
O -2.52447900 1.95969100 2.09499400
C -3.52804500 -0.83249500 -0.00134200
O -4.61423900 -1.26988600 0.01128500
C -1.26827900 -1.29652500 1.36622100
O -0.98997700 -2.02085700 2.22960600
C -2.25593200 1.09703700 -1.39806300
O -2.52432300 1.84589400 -2.24376500
C -1.27048400 -1.36788500 -1.34587300
O -0.99414200 -2.13691600 -2.17037000
C 6.83044400 -0.55439000 -0.01433400
H 1.41635900 2.60954600 -0.08778900
H -0.40054100 2.88739500 -0.09198800
H 3.10847500 1.24742800 -0.94305500

H 3.10759600 1.28776600 0.82846200
H 4.22029900 -1.01174600 -0.88455700
H 4.21990900 -0.97079700 0.87471500
H 5.68337100 1.07739900 0.82654300
H 5.68388300 1.03596600 -0.93159400
H 6.81941500 -1.22523700 -0.88356800
H 6.81991300 -1.18269500 0.88615300
H 7.78116100 -0.00532100 -0.02778400

Cr-St-Bu

E= -1287.0611138

C -0.52794100 0.60225300 0.03618600
S -1.72583200 -0.59221800 -0.00718900
C -0.89565900 2.06288400 0.05319200
C -3.54756000 -0.02924000 0.00432100
C -3.93160100 0.56974200 1.36545500
C -4.28020000 -1.37032600 -0.19507800
Cr 1.44427800 -0.05178100 -0.00144900
C 1.90100000 1.49043900 -1.02149900
O 2.20271700 2.41366900 -1.64699100
C 3.27086000 -0.55086700 -0.02318800
O 4.38803200 -0.84686000 -0.03521800
C 1.10872200 -1.01661500 -1.61744700
O 0.89250300 -1.59367300 -2.59221100
C 1.69334700 0.91498500 1.62325100
O 1.83226100 1.50531100 2.60593000
C 1.05621700 -1.63073200 1.00922900
O 0.86751700 -2.58787700 1.62424400
C -3.86664800 0.91330100 -1.16417700
H -0.95388200 2.40635000 -0.99097900
H -1.85092200 2.29773300 0.52907700
H -0.11117100 2.65670400 0.52879300
H -3.43754400 1.52445400 1.56597300
H -3.68988000 -0.11626300 2.18423400
H -5.01492200 0.75036600 1.38608200
H -5.36269800 -1.19112800 -0.18646400
H -4.05102200 -2.08260600 0.60552100
H -4.02202700 -1.83546000 -1.15287200
H -4.95225700 1.07545200 -1.20550400
H -3.55732600 0.48070400 -2.12191200
H -3.39320400 1.89244900 -1.05964900

Cr-St-Bu⁻

E= -1286.5428524

C -0.56424500 0.72477900 0.13491700
S -1.73308200 -0.59537300 -0.11037900
C -0.90075200 2.01333100 0.35516100
C -3.54194200 -0.06167400 -0.03297700
C -3.90733000 0.49496000 1.35273300
C -4.31347600 -1.37346900 -0.26718800
Cr 1.51282200 -0.06349500 0.02399700
C 1.85800400 1.45194800 -1.05224500
O 2.07799400 2.37936000 -1.71522800
C 3.27651800 -0.60143000 -0.04661000
O 4.39954800 -0.93023200 -0.08884900
C 1.09992900 -1.04279500 -1.55136800
O 0.91280100 -1.64158000 -2.52784100
C 1.79859400 0.94892400 1.59506500
O 1.97839500 1.56762500 2.56087000
C 1.06424000 -1.55655500 1.11165000
O 0.86129400 -2.47595700 1.79037300
C -3.88630800 0.93098000 -1.15543500
H -1.91928400 2.39737100 0.40763500
H -0.12631100 2.76556400 0.49708200
H -3.33894400 1.39530500 1.59902200
H -3.70234000 -0.24882600 2.13120000
H -4.97967300 0.74578700 1.38984800
H -5.39627500 -1.17877500 -0.24369700
H -4.08281500 -2.11488200 0.50712700
H -4.06641800 -1.81209400 -1.24137600
H -4.95849500 1.18305200 -1.12294200
H -3.66717900 0.49312800 -2.13601500
H -3.31623200 1.85982400 -1.07388900

Cr-Sc-Hex

E = -1364.4888128

C 0.06963500 0.40195200 0.40248600
S -1.13761200 -0.58571800 -0.26895400
C -0.36853100 1.51763700 1.31976800
C -2.85100600 -0.05020700 0.24537600
C -3.72604100 -1.31483900 0.31988300
C -5.17712900 -0.95503600 0.68880900
C -5.77032000 0.08098200 -0.27825500
Cr 2.04165000 -0.02247500 -0.03223800

C 2.25570000 1.81849700 -0.48254300
O 2.38300500 2.93334600 -0.75487200
C 3.87841800 -0.33611800 -0.38377400
O 4.99956200 -0.52135000 -0.59365300
C 1.63124900 -0.41679800 -1.85881900
O 1.40707200 -0.65268300 -2.96506800
C 2.47220900 0.34762100 1.78764500
O 2.74664000 0.56358200 2.88846800
C 1.78093400 -1.86423900 0.41134100
O 1.62171900 -2.97340900 0.68324200
C -4.88699200 1.33541400 -0.36138000
C -3.43538600 0.98118800 -0.73491800
H -1.22003600 2.09018000 0.93281900
H -0.68166900 1.08716100 2.28365700
H 0.44786400 2.21114200 1.52820400
H -2.77269200 0.38482500 1.24793100
H -3.30924700 -2.01879100 1.05028600
H -3.71358200 -1.82423500 -0.65478500
H -5.78758600 -1.86689300 0.69685800
H -5.20107900 -0.55408600 1.71334000
H -5.86051600 -0.36635800 -1.27951300
H -6.78597500 0.35338600 0.03570700
H -5.29103700 2.04214500 -1.09733900
H -4.89759300 1.85462500 0.60891100
H -2.81490700 1.88537300 -0.75769500
H -3.41016500 0.56019600 -1.75006600

Cr-Sc-Hex⁻

E= -1363.9696918

C 0.05380100 0.48581100 0.47995500
S -1.12167500 -0.69034000 -0.17253100
C -0.34321400 1.55399000 1.20362000
C -2.83226300 -0.15655600 0.29926900
C -3.75758500 -1.38555000 0.26909700
C -5.20577400 -1.01327700 0.63794900
C -5.75138200 0.11545300 -0.25237100
Cr 2.13882200 -0.04812800 -0.03531400
C 2.32575000 1.77823100 -0.48644100
O 2.44413500 2.89929600 -0.76433600
C 3.91049900 -0.40554300 -0.41135100
O 5.03751300 -0.62244800 -0.64338000
C 1.64079900 -0.40626800 -1.83342000
O 1.39986800 -0.61628000 -2.94926300

C 2.51836700 0.33731900 1.77626100
O 2.75564000 0.57318800 2.88804900
C 1.82951900 -1.85838300 0.45155000
O 1.70561900 -2.97120000 0.75740200
C -4.82291000 1.34081900 -0.23036800
C -3.37982800 0.95848500 -0.60810600
H -1.38177200 1.79705400 1.43923100
H 0.38962800 2.25029300 1.60798800
H -2.78015500 0.20961200 1.33423500
H -3.37537500 -2.15394400 0.95243900
H -3.74109400 -1.82601500 -0.73982000
H -5.85154500 -1.90069600 0.56657900
H -5.23648700 -0.68798000 1.68965900
H -5.83653200 -0.25181700 -1.28726800
H -6.76628600 0.39526500 0.06601700
H -5.19940600 2.11552100 -0.91396100
H -4.83201400 1.78397500 0.77797100
H -2.72203900 1.83337600 -0.56257800
H -3.35603400 0.60257500 -1.64872500

W-SMe

E= -1150.6912223

C -1.34821700 0.53027000 -0.00004300
C -1.84725900 1.95412100 0.00066600
H -2.47414500 2.15478300 -0.88053100
H -2.47418200 2.15382000 0.88206100
H -1.02496300 2.67117000 0.00108600
S -2.54067000 -0.69065100 -0.00109100
C -4.21257200 0.07497800 -0.00104600
H -4.91877700 -0.75972600 -0.00153900
H -4.37527400 0.67950300 0.89516900
H -4.37496400 0.68028800 -0.89678900
C 2.76099600 -0.48634400 0.00001400
O 3.89142500 -0.73134200 -0.00002400
C 0.42353200 -1.47647200 1.44320800
O 0.24274900 -2.28416100 2.24773100
C 1.08222900 1.38393500 1.45254900
O 1.27489300 2.18322800 2.26476300
C 1.08240100 1.38465600 -1.45166200
O 1.27517800 2.18436900 -2.26343200
C 0.42325900 -1.47571900 -1.44373300
O 0.24222600 -2.28296700 -2.24864600
W 0.75152200 -0.03885500 0.00007600

W-SMe⁻

E= -1150.174732

C -1.37227900 0.64976700 0.06028700
C -1.81157000 1.92799100 0.09220300
H -2.86313200 2.22179300 0.11094800
H -1.10245100 2.75438500 0.10081400
S -2.53945600 -0.70112800 0.04635100
C -4.21771300 0.03834600 0.08165000
H -4.92784300 -0.79565200 0.07159600
H -4.37660700 0.63124100 0.98986900
H -4.39702500 0.67031300 -0.79587300
C 2.77309300 -0.57047200 -0.01675400
O 3.90801800 -0.86692600 -0.03741400
C 0.45369200 -1.46426900 1.45501800
O 0.28807500 -2.26818200 2.27750400
C 1.17995600 1.32836800 1.49552800
O 1.38385200 2.10981500 2.33138700
C 1.14378000 1.39266300 -1.40392800
O 1.32706400 2.21049800 -2.20916200
C 0.41799400 -1.40012900 -1.46848800
O 0.23200200 -2.16747600 -2.32099000
W 0.83408100 -0.04684500 0.01877100

W-Si-Pr

E= -1229.3204093

C -0.75930800 0.44969000 0.38273700
C 3.29291200 -0.51575900 -0.39463700
O 4.40889700 -0.75607600 -0.58342500
C 1.69059500 -0.04624300 1.97441400
O 1.91226400 -0.02658700 3.10890000
C 1.74696800 1.92913300 -0.15453500
O 1.99632200 3.05652300 -0.20948300
C 0.94275600 -0.13383800 -2.07782900
O 0.74137300 -0.16776500 -3.21410300
C 0.87104900 -2.09394100 0.04161700
O 0.62265400 -3.22033000 0.08803000
C -1.16192000 1.47520100 1.41663700
H -1.62188800 0.96920700 2.27925600
H -0.29767200 2.02900100 1.78705000
H -1.89798100 2.19638700 1.03968600
S -2.00662500 -0.35888700 -0.45029400

C -3.69736100 0.25724200 0.06451400
H -3.62632700 0.55389300 1.11516600
C -4.13020100 1.44967600 -0.79608300
H -5.12382200 1.79361100 -0.48051700
H -3.43878000 2.29448800 -0.71316400
H -4.19025200 1.16745100 -1.85349500
C -4.66081700 -0.92954200 -0.06033700
H -4.36890500 -1.75980100 0.59090900
H -5.67217300 -0.61191500 0.22182600
H -4.70448300 -1.30224900 -1.09080400
W 1.31259100 -0.08097600 -0.04917400

W-Si-Pr⁻

E= -1228.8032269

C -0.78456700 0.58728000 0.42602100
C 3.28772400 -0.58259100 -0.43811200
O 4.40432300 -0.87371700 -0.64951500
C 1.73859300 0.01940900 1.94895900
O 1.94589000 0.07384100 3.09121000
C 1.83694100 1.91495000 -0.24578600
O 2.10798100 3.04072600 -0.34778600
C 0.93778100 -0.13088500 -2.06894700
O 0.73030400 -0.15922800 -3.21173700
C 0.88080800 -2.05452600 0.13356800
O 0.65451300 -3.18827100 0.24964700
C -1.13942100 1.60960800 1.23574900
H -0.37607700 2.20429400 1.73528700
H -2.16716300 1.90716400 1.45355100
S -2.01476100 -0.42857000 -0.38356300
C -3.70291600 0.19811600 0.06573100
H -3.68003700 0.43270000 1.13752200
C -4.08510200 1.45526800 -0.72546900
H -5.06119000 1.84283900 -0.39311800
H -3.33999700 2.24674200 -0.59971300
H -4.15460200 1.22690600 -1.79656800
C -4.70509300 -0.94000200 -0.16519400
H -4.46721300 -1.81245400 0.45338400
H -5.72500800 -0.60852700 0.07899400
H -4.70133000 -1.26039400 -1.21549500
W 1.38137100 -0.07229000 -0.06501300

W-Sn-Bu

E= -1268.634833

C -0.21770100 0.73705400 -0.00107500
C 3.72554500 -0.80871800 0.00197400
O 4.81409200 -1.20085500 0.00281800
C 1.27795600 -1.47783300 1.44672400
O 0.99067500 -2.25158300 2.25394000
C 2.30696300 1.26872100 1.45052800
O 2.60220300 2.03764000 2.26158300
C 2.30778600 1.26424500 -1.45351200
O 2.60360700 2.03060300 -2.26678100
C 1.27841900 -1.48204500 -1.44195300
O 0.99128000 -2.25806900 -2.24703000
C -0.52210700 2.21538100 -0.00333900
H -1.11756500 2.49626100 -0.88418300
H -1.11583300 2.49906700 0.87779300
H 0.38946700 2.81505800 -0.00513100
S -1.55860400 -0.31647000 0.00066300
C -3.13695700 0.65282300 -0.00065600
H -3.15867000 1.29543800 0.88630400
H -3.15908600 1.29245400 -0.88976400
C -4.32393800 -0.31723600 0.00122300
H -4.26434400 -0.97007000 0.88274300
H -4.26483600 -0.97286700 -0.87825200
C -5.67284500 0.41997000 0.00043700
H -5.72815700 1.07543200 -0.88038600
H -5.72773400 1.07806300 0.87932200
C -6.87037700 -0.53790500 0.00214100
H -6.86078400 -1.18393700 0.88893300
H -7.81748600 0.01382600 0.00153800
H -6.86118200 -1.18656200 -0.88273500
W 1.79360800 -0.10074000 0.00046500

W-Sn-Bu⁻

E= -1268.1171477

C -0.21914800 0.86670600 -0.05132800
C 3.72581900 -0.89885200 0.00556700
O 4.81071200 -1.34505700 0.02067800
C 1.29041400 -1.40605900 1.46948600
O 1.00930400 -2.14228500 2.32339100
C 2.38033300 1.26536400 1.40027000
O 2.67432700 2.05170100 2.20406100
C 2.39711100 1.19643200 -1.49922000
O 2.70247700 1.94247300 -2.33655600

C 1.29805500 -1.46995000 -1.45538600
O 1.01890400 -2.24165700 -2.27801800
C -0.47975300 2.19295100 -0.08947200
H -1.48017700 2.62973700 -0.10228800
H 0.33710200 2.91289900 -0.11005400
S -1.55636700 -0.31720500 -0.01812700
C -3.13409000 0.63344500 -0.04374200
H -3.16451100 1.30530900 0.82414200
H -3.16566500 1.25662900 -0.94719300
C -4.33069800 -0.32334500 -0.01672600
H -4.27163700 -0.95606800 0.88049700
H -4.27344200 -1.00355000 -0.87862300
C -5.68264500 0.40733900 -0.03505200
H -5.74030800 1.04208600 -0.93157300
H -5.73880900 1.08897800 0.82643500
C -6.88367200 -0.54729900 -0.00871600
H -6.87154300 -1.17293100 0.89359200
H -7.83522500 0.00023300 -0.02309700
H -6.87220200 -1.22062000 -0.87600900
W 1.87456200 -0.11932400 -0.02040000

W-St-Bu

E= -1268.6300525

C -0.57309600 0.59691800 0.11619800
C 3.49737400 -0.60867800 -0.04283500
O 4.61647900 -0.90239400 -0.07695500
C 1.05108300 -1.93710800 0.77069800
O 0.81498300 -2.98678300 1.19042000
C 1.76420000 0.65198000 1.93159200
O 1.89874800 1.06687500 3.00204200
C 2.02872600 1.76583600 -0.74261400
O 2.33482100 2.79493700 -1.17329000
C 1.22544400 -0.80714300 -1.88564100
O 1.04762700 -1.21950100 -2.94915500
C -0.94832100 2.02961900 0.40146100
H -0.98247500 2.56680600 -0.55854100
H -1.91641500 2.16714500 0.88903900
H -0.17816200 2.51865500 1.00301700
S -1.77157200 -0.56485600 -0.19921100
C -3.58983700 0.00275200 -0.13186400
C -4.32156400 -1.26784600 -0.60683000
H -5.40329700 -1.08441600 -0.59212800
H -4.03915800 -1.54058100 -1.62970700

H -4.11706800 -2.12386000 0.04604300
C -4.01254400 0.33340900 1.30748200
H -3.52143700 1.22810200 1.70035800
H -5.09550700 0.51527300 1.33124800
H -3.79643300 -0.49838500 1.98629700
C -3.86937700 1.15478700 -1.10670900
H -4.95299800 1.32751300 -1.15518000
H -3.40155000 2.09228300 -0.79723800
H -3.52356300 0.91403100 -2.11788000
W 1.51671500 -0.07362400 0.02021400

W-St-Bu⁻

E= -1268.113022

C -0.61299900 0.69835200 0.25073800
C 3.48694700 -0.65955500 -0.08542400
O 4.61013200 -0.98996200 -0.15999500
C 1.06080900 -1.85746000 0.93813000
O 0.81856200 -2.87094800 1.45172700
C 1.90797800 0.72462900 1.90238300
O 2.11291600 1.17874800 2.95255300
C 1.99792400 1.72392400 -0.82414400
O 2.24610800 2.74616500 -1.31820800
C 1.19067300 -0.86395800 -1.80963100
O 1.03334800 -1.31122600 -2.87031400
C -0.96273800 1.91506500 0.72327200
H -1.98299100 2.28394800 0.82137400
H -0.19358500 2.61610400 1.04415400
S -1.77586900 -0.53670800 -0.30467300
C -3.58612000 -0.02064600 -0.18269100
C -4.34464600 -1.24911200 -0.71858700
H -5.42833700 -1.06055200 -0.68971000
H -4.06403400 -1.46935700 -1.75549500
H -4.13673600 -2.14012600 -0.11418300
C -4.00451100 0.23116800 1.27510700
H -3.44582700 1.05402400 1.72790700
H -5.07737900 0.47707600 1.32396100
H -3.82996200 -0.66277500 1.88467700
C -3.89278400 1.18887500 -1.08117700
H -4.96846600 1.42467600 -1.04332300
H -3.33862800 2.08054800 -0.77742900
H -3.62619000 0.97160900 -2.12179400
W 1.57070500 -0.07758500 0.04966600

W-Sc-Hex

E= -1346.0579164

C -0.03051400 0.28553600 0.47009900
C -4.11595800 -0.29868700 -0.49357900
O -5.23990700 -0.43653800 -0.73225400
C -1.81658300 -2.08275600 -0.18845900
O -1.63965000 -3.22095600 -0.26428700
C -1.70274600 0.10208000 -2.07324400
O -1.47910300 0.18104400 -3.20332300
C -2.41126000 1.98992100 0.05572200
O -2.57672500 3.13182400 0.12489100
C -2.55827500 -0.21468100 1.94457900
O -2.81610600 -0.31008400 3.06778300
C 0.40995800 1.10753000 1.65878800
H -0.42678400 1.65417800 2.09706900
H 0.81029600 0.44102900 2.43800500
H 1.20248100 1.82530100 1.41354000
S 1.18308200 -0.44593000 -0.47522100
C 2.89347300 -0.01981400 0.13939400
C 3.80641400 -1.22084100 -0.16827600
C 3.42054000 1.26932100 -0.51475400
H 2.82977500 0.10796500 1.22584400
C 5.25773900 -0.93046200 0.25705500
H 3.77906900 -1.43141500 -1.24746200
H 3.43176100 -2.11804700 0.33899800
C 4.87198300 1.55293600 -0.08458900
H 3.37651700 1.15669000 -1.60728400
H 2.77623300 2.12058600 -0.26340200
C 5.79236900 0.35975700 -0.38321500
H 5.89281400 -1.78409900 -0.01173000
H 5.30306800 -0.84064300 1.35285800
H 5.23386000 2.45480000 -0.59446700
H 4.89628700 1.77239000 0.99358100
H 6.80872000 0.56637600 -0.02452000
H 5.86607600 0.22190100 -1.47239400
W -2.12204200 -0.04634100 -0.05973900

W-Sc-Hex⁻

E= -1345.5399775

C 0.00274600 0.39833800 0.54401400
C -4.11443100 -0.32597300 -0.56011700
O -5.24199300 -0.49535200 -0.83583800

C -1.84729800 -2.04810000 -0.09248400
O -1.70714300 -3.20154500 -0.09908600
C -1.68496100 0.10550100 -2.06372200
O -1.44702300 0.18610700 -3.19802400
C -2.47148300 2.00433900 -0.03699700
O -2.64141500 3.15389200 -0.01308600
C -2.61825800 -0.13156200 1.92161100
O -2.86951900 -0.19103800 3.05483100
C 0.40372300 1.26111700 1.50378400
H -0.33056700 1.82746200 2.07460500
H 1.44287200 1.45066500 1.78066600
S 1.18466400 -0.56719200 -0.39267500
C 2.89569500 -0.10581400 0.14631700
C 3.85753600 -1.24948300 -0.21996000
C 3.37208000 1.22143500 -0.46819700
H 2.87474000 -0.01379900 1.24133400
C 5.30622700 -0.92202100 0.18873700
H 3.81662800 -1.42278700 -1.30638500
H 3.52741200 -2.17977100 0.25876700
C 4.81492300 1.55673200 -0.04776800
H 3.32015600 1.13524900 -1.56358300
H 2.68898400 2.02993500 -0.18611500
C 5.78163100 0.41534600 -0.40291000
H 5.97671900 -1.73609800 -0.12313000
H 5.36710000 -0.87075300 1.28713300
H 5.13924200 2.49257400 -0.52530500
H 4.84703900 1.73383800 1.03891200
H 6.79767900 0.64702000 -0.05146300
H 5.84139800 0.32354800 -1.49887100
W -2.18853400 -0.02297000 -0.07699600

Table S41. Contribution of solvation free energy for Fischer carbene complexes in acetonitrile (kcal/mol).^a

	neutral				anion			
	ΔG_{cav}	ΔG_{dis}	ΔG_{rep}	ΔG_{el}	ΔG_{cav}	ΔG_{dis}	ΔG_{rep}	ΔG_{el}
Cr-SMe	25.43	-16.83	2.48	-5.51	24.60	-16.50	2.44	-37.95
Cr-Si-Pr	28.84	-19.87	3.11	-5.71	27.93	-19.58	3.10	-37.68
Cr-St-Bu	30.27	-20.81	3.21	-5.49	29.36	-20.56	3.22	-37.55
Cr-Sn-Bu	31.08	-21.63	3.24	-5.64	30.39	-21.29	3.20	-38.27
Cr-Sc-Hex	32.35	-23.27	3.58	-5.51	31.41	-22.90	3.55	-38.00
W-SMe	27.00	-16.99	2.55	-5.43	26.24	-16.65	2.51	-37.04
W-Si-Pr	30.51	-20.02	3.17	-5.60	29.71	-19.77	3.19	-36.63
W-St-Bu	31.90	-20.97	3.28	-5.53	30.99	-20.71	3.29	-36.45
W-Sn-Bu	32.75	-21.77	3.30	-5.59	31.98	-21.47	3.28	-37.19
W-Sc-Hex	34.00	-23.47	3.67	-5.42	33.20	-23.17	3.65	-36.98

^a All values have computed in CPCM model, UAKS cavities and 250 tesserae per sphere with an average area of 0.3 \AA^2 were used.

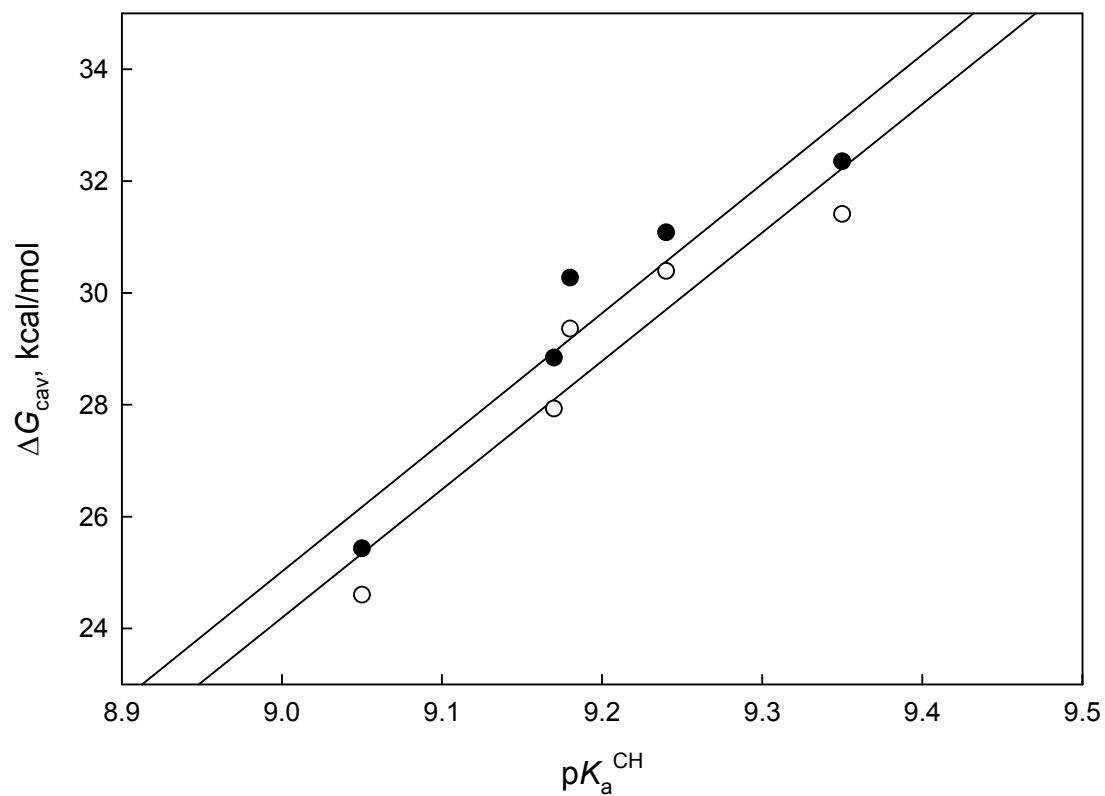


Fig. S2. Plot of ΔG_{cav} (in kcal/mol) vs. pK_a^{CH} for (●) neutral Fischer carbenes **Cr-SR**, slope = (23 ± 4) kcal/mol $r^2 = 0.907867$; and (○) Anions of the Fischer carbenes **Cr-SR**, slope = (23 ± 4) kcal/mol $r^2 = 0.900524$.

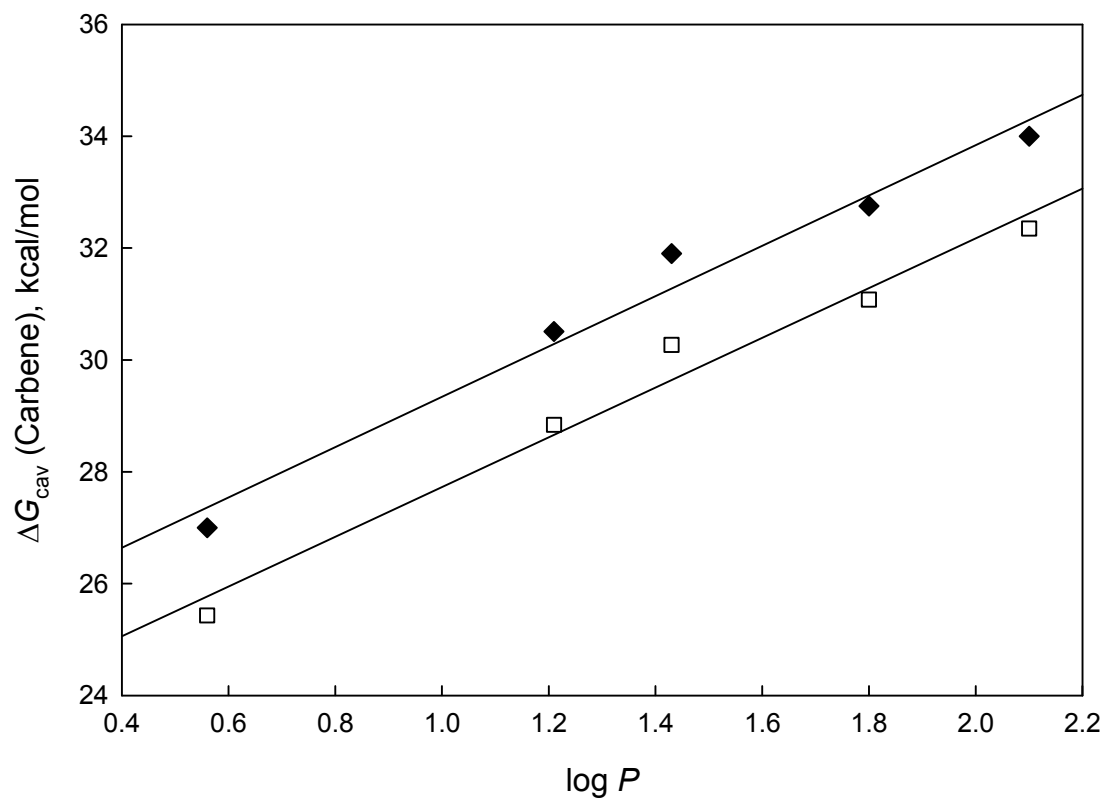


Fig S3. Plot of ΔG_{cav} (in kcal/mol) vs. $\log P$ for the neutral Fischer carbenes (□) **Cr-SR**, slope = (4.4 ± 0.4) kcal/mol $r^2 = 0.977564$; and (◆) **W-SR**, slope = (4.5 ± 0.4) kcal/mol $r^2 = 0.976042$.

Spectroscopic characterization of the Fischer carbenes **W-SR**.

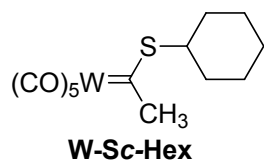
W-Sn-Bu: ^1H NMR δ 0.97 (t, 3H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.44 – 1.50 (m, 2H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.67 – 1.73 (m, 2H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.00 (t, 2H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.37 (s, 3H, CH_3). ^{13}C NMR δ 13.6 ($\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 22.0 ($\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 28.7 ($\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 42.8 ($\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 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): $\lambda_{\text{max}} = 435$ nm ($\epsilon \approx 10779 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (nitrobenzyl alcohol): calcd for $\text{C}_{11}\text{H}_{12}\text{O}_5\text{SW}$ 440.9988, obtained 440.9981.

W-Si-Pr: ^1H NMR δ 1.37– 1.39 (d, 6H, $\text{SCH}(\text{CH}_3)_2$), 3.44 (s, 3H, CH_3), 3.75 – 3.86 (m, 1H, $\text{SCH}(\text{CH}_3)_2$). ^{13}C NMR δ 21.3 ($\text{SCH}(\text{CH}_3)_2$), 46.4 ($\text{SCH}(\text{CH}_3)_2$), 47.2 (CH_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): $\lambda_{\text{max}} = 436$ nm ($\epsilon \approx 11500 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (nitrobenzyl alcohol): calcd for $\text{C}_{10}\text{H}_{10}\text{O}_5\text{SW}$ 426.9831, obtained 426.9812.

W-St-Bu: ^1H NMR δ 1.56 (s, 9H, $\text{SC}(\text{CH}_3)_3$), 3.64 (s, 3H, CH_3). ^{13}C NMR δ 29.8 ($\text{SC}(\text{CH}_3)_3$), 48.0 ($\text{SC}(\text{CH}_3)_3$), 61.6 (CH_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): $\lambda_{\text{max}} = 441$ nm ($\epsilon \approx 14627 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (nitrobenzyl alcohol): calcd for $\text{C}_{11}\text{H}_{12}\text{O}_5\text{SW}$ 440.9988, obtained 440.9978.

W-Sc-Hex: ^1H NMR δ 1.31 – 2.08 (m, 11H, SC_6H_{11}), 3.43 (s, 3H, CH_3). ^{13}C NMR δ 25.1, 25.6, 31.2, 47.1 (SC_6H_{11}), 54.4 (CH_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): $\lambda_{\text{max}} = 437$ nm ($\epsilon \approx 11954 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (nitrobenzyl alcohol): calcd for $\text{C}_{13}\text{H}_{14}\text{O}_5\text{SW}$ 467.0144, obtained 467.0147.

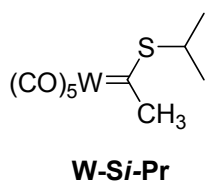
NMR and FT-IR Spectra



NMR ^1H (CDCl_3) A1

NMR ^{13}C (CDCl_3) A2

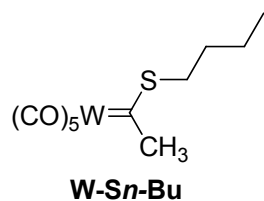
FT-IR (KCl) A3



NMR ^1H (CDCl_3) B1

NMR ^{13}C (CDCl_3) B2

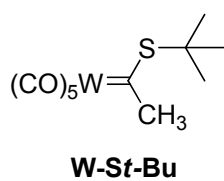
FT-IR (KCl) B3



NMR ^1H (CDCl_3) C1

NMR ^{13}C (CDCl_3) C2

FT-IR (KCl) C3

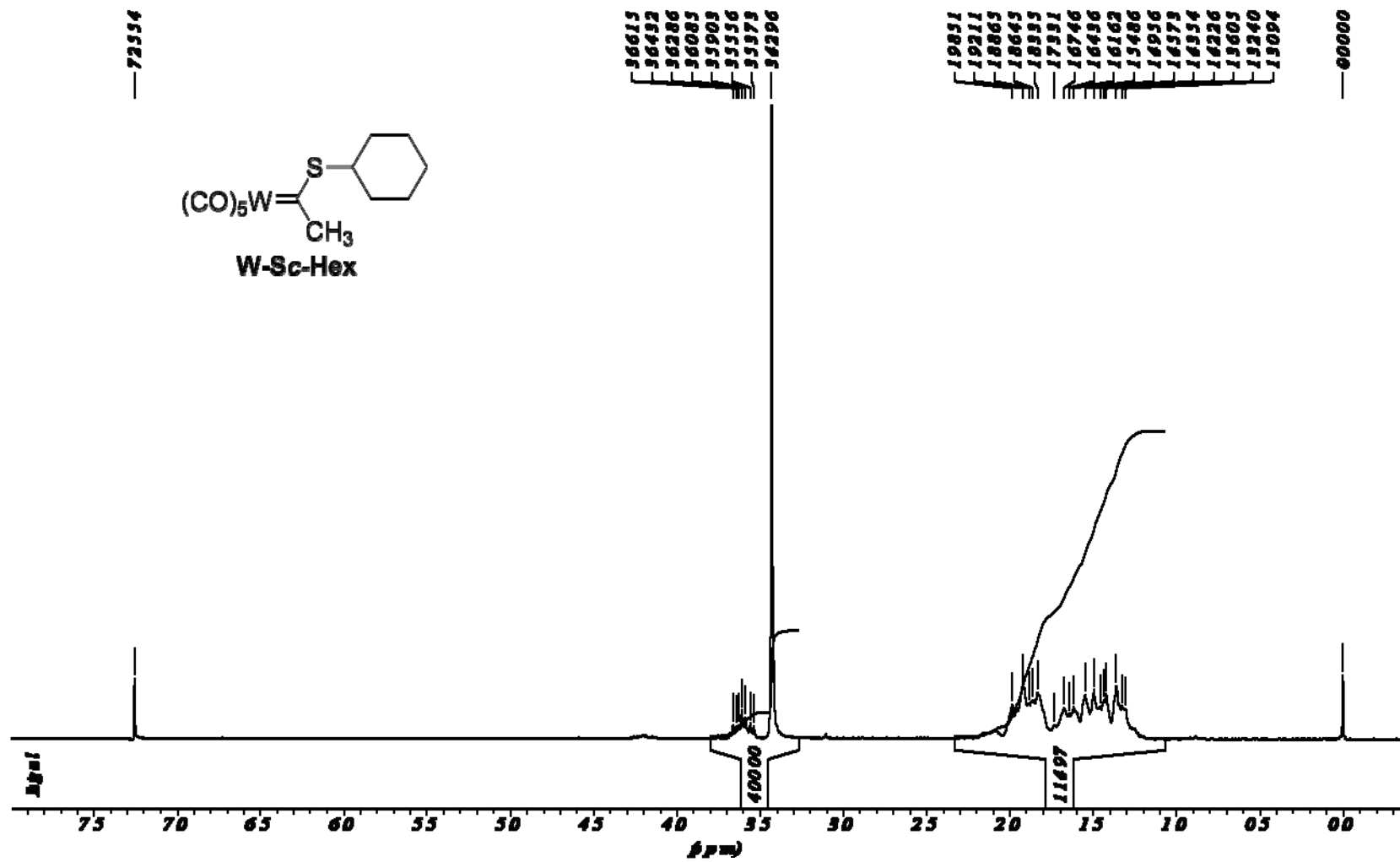


NMR ^1H (CDCl_3) D1

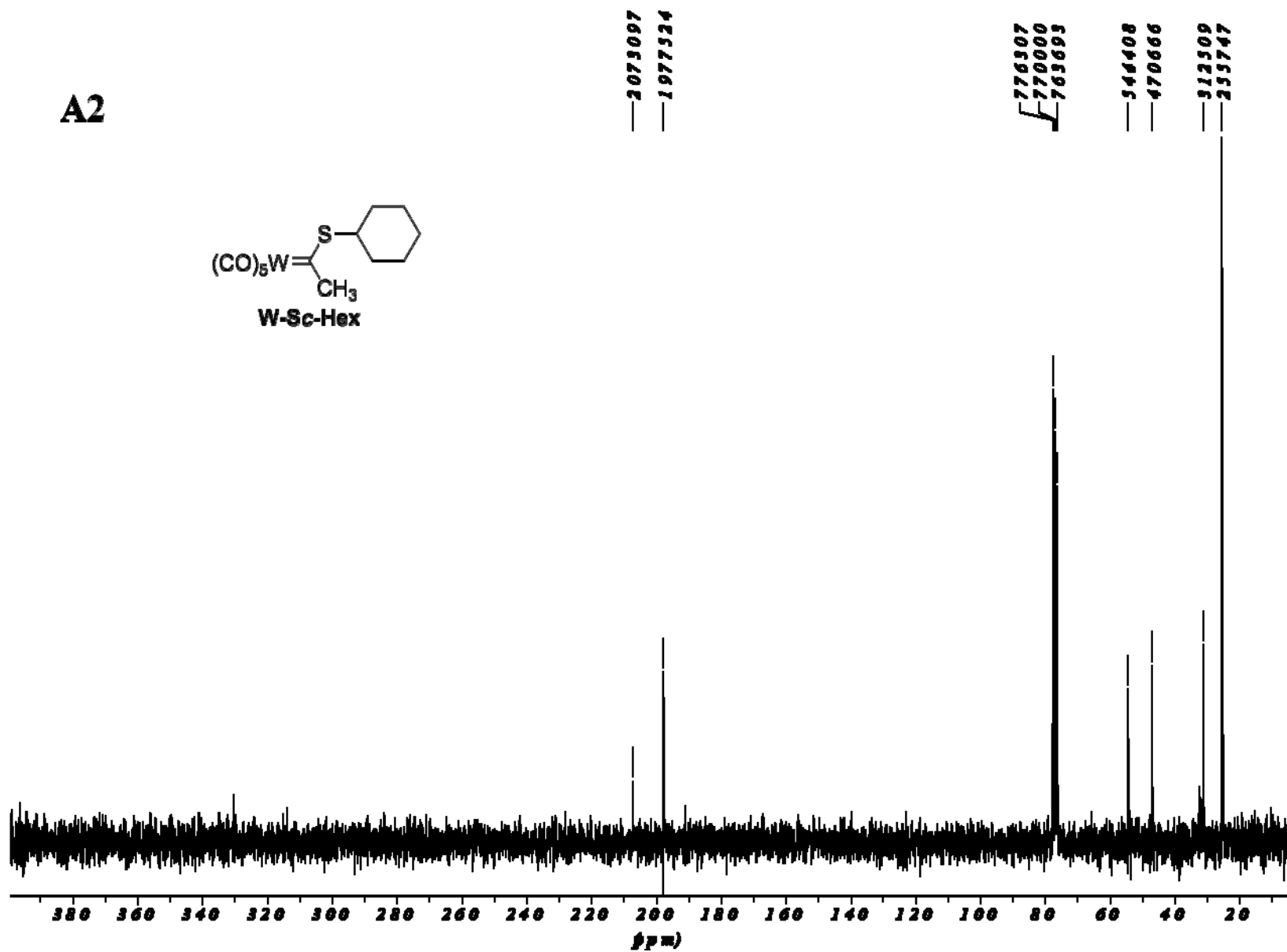
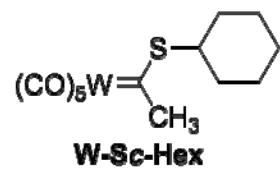
NMR ^{13}C (CDCl_3) D2

FT-IR (KCl) D3

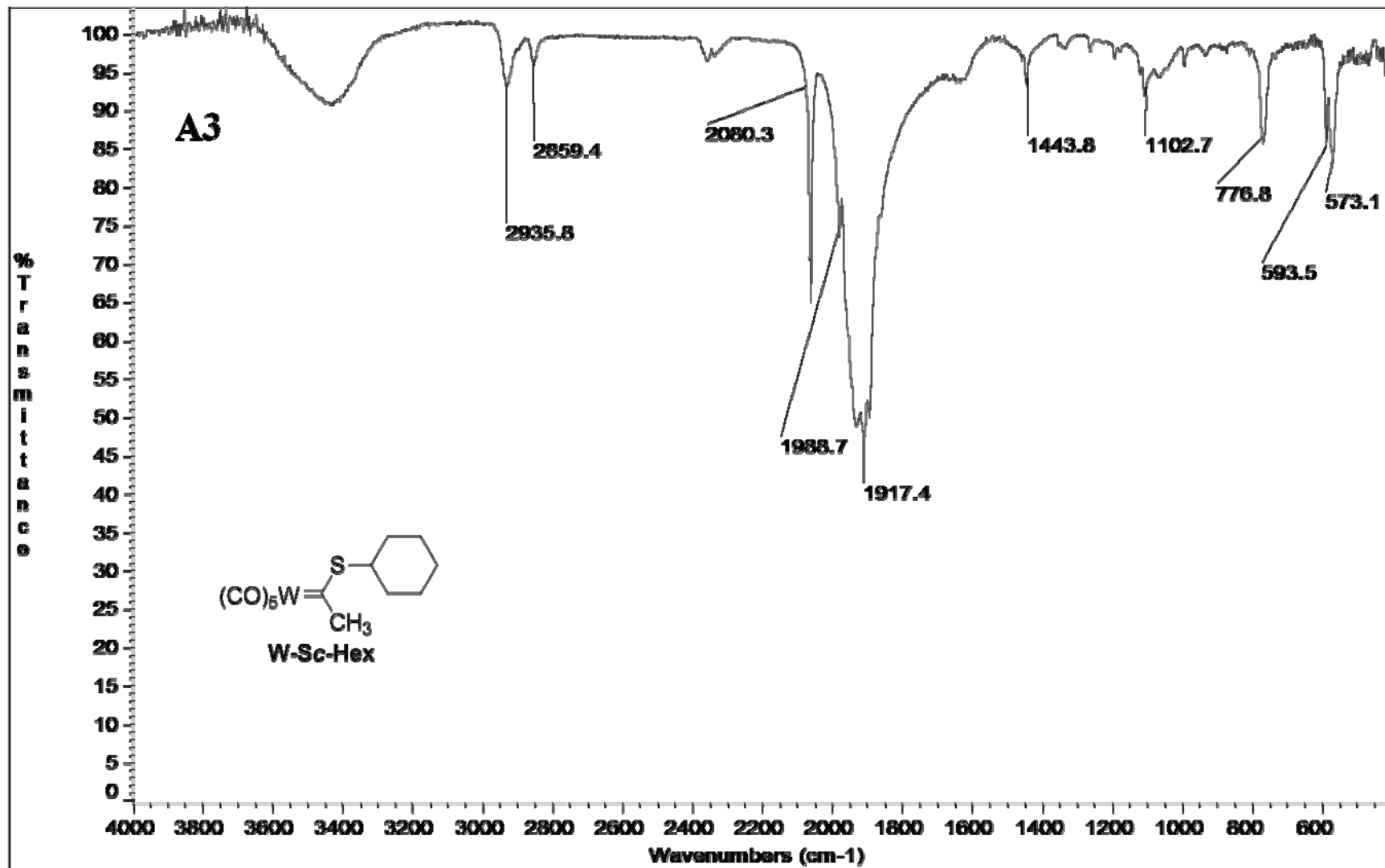
A1

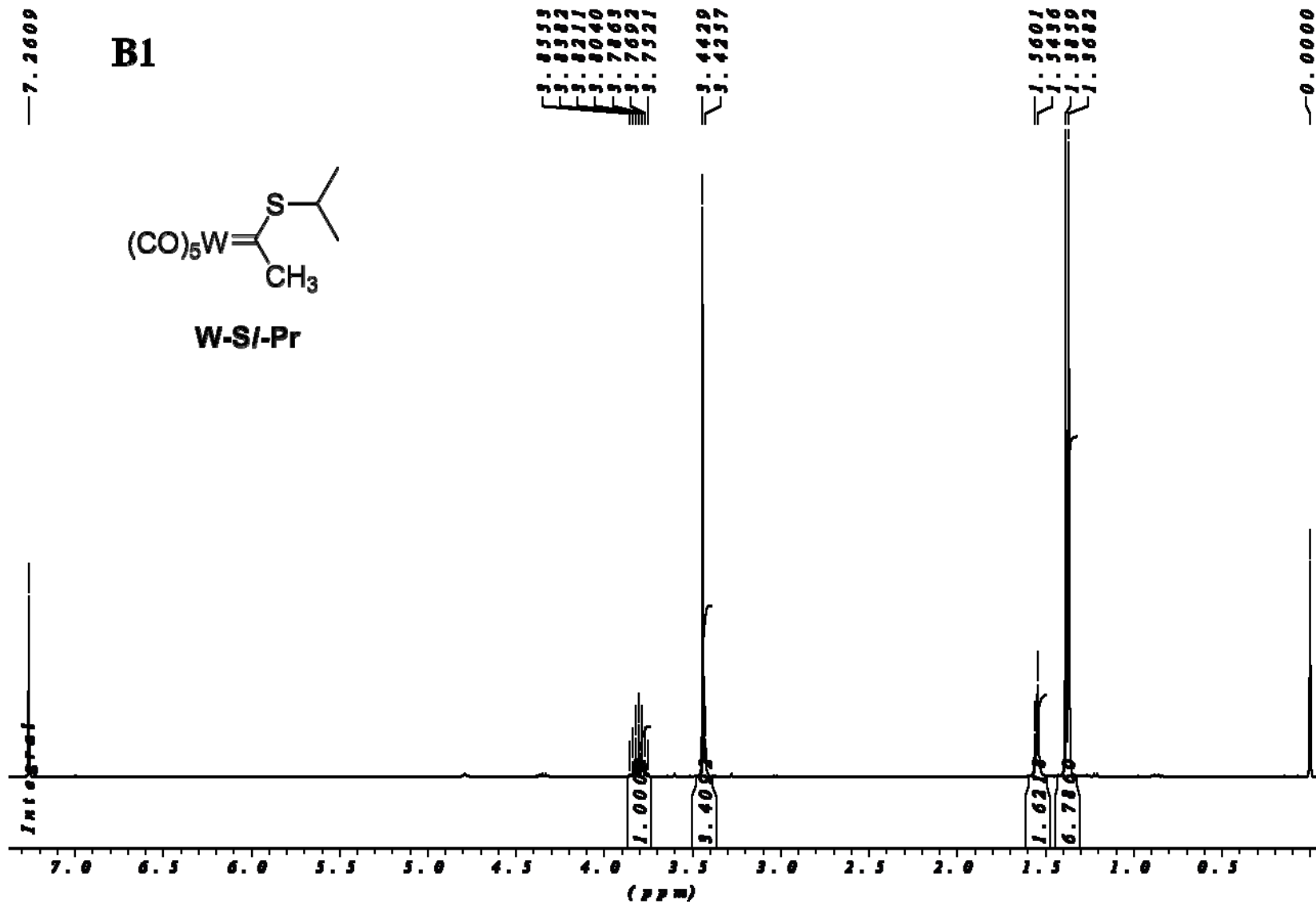


A2

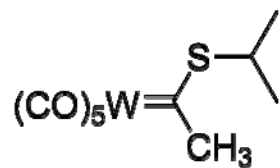


S42

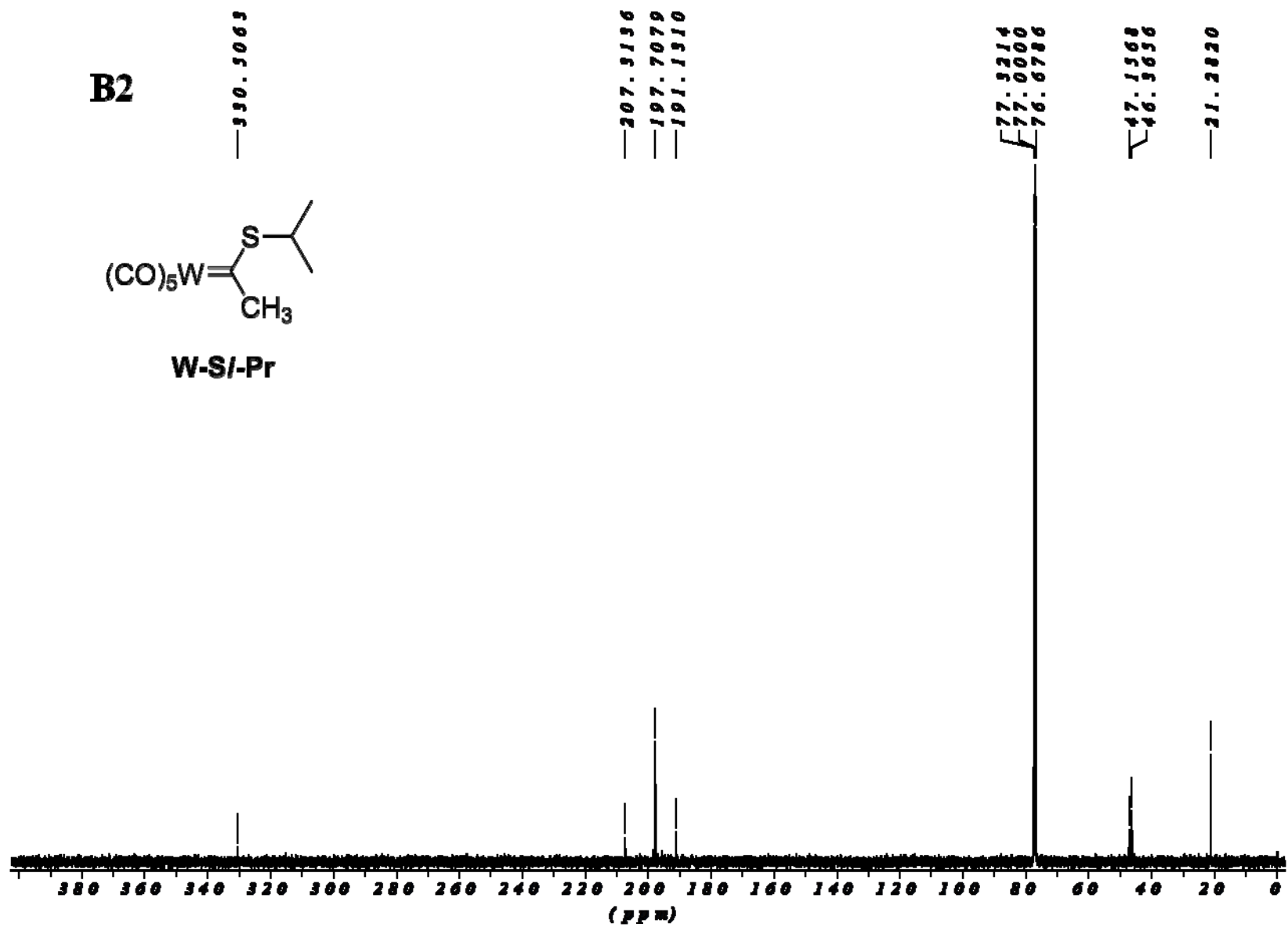


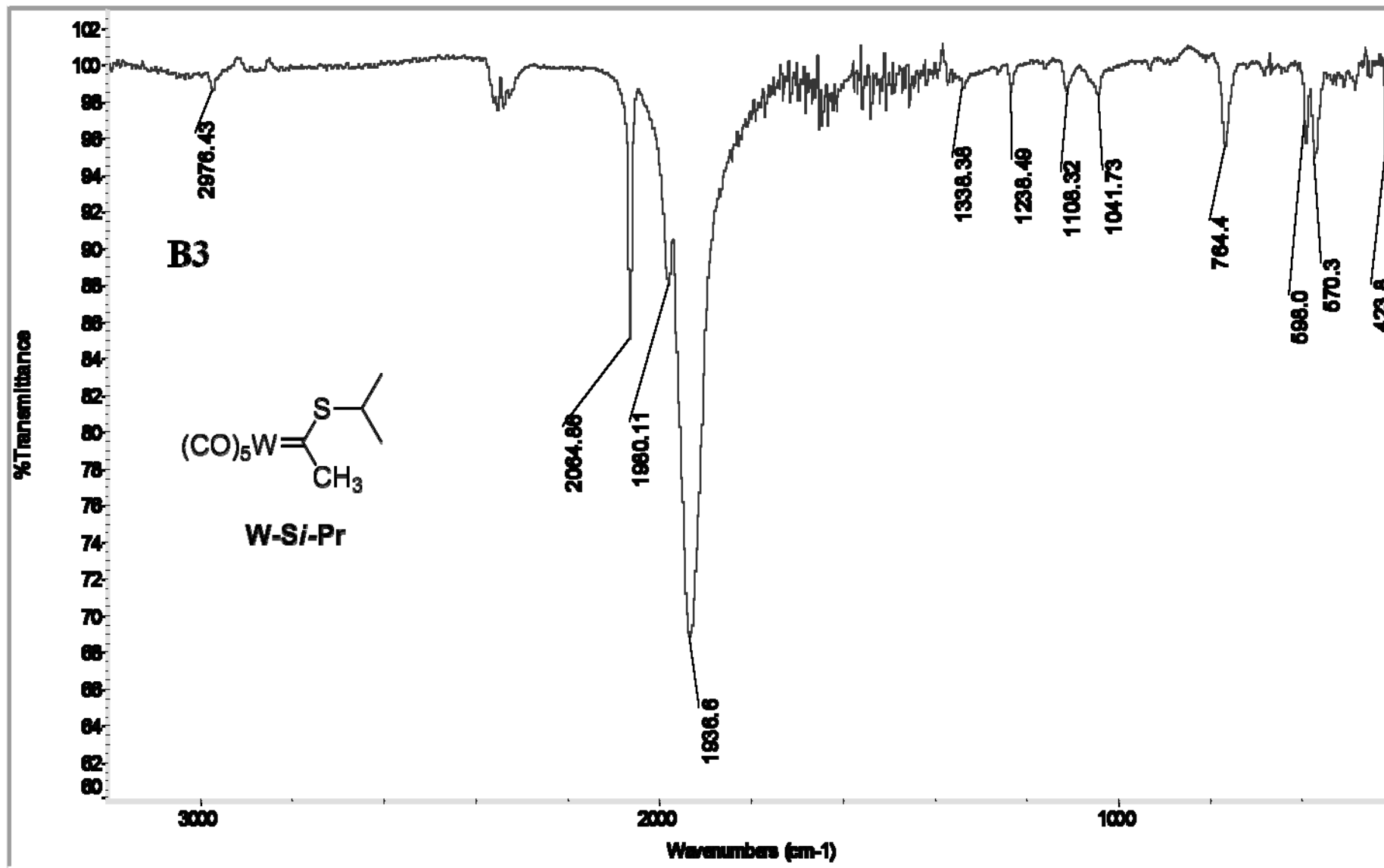


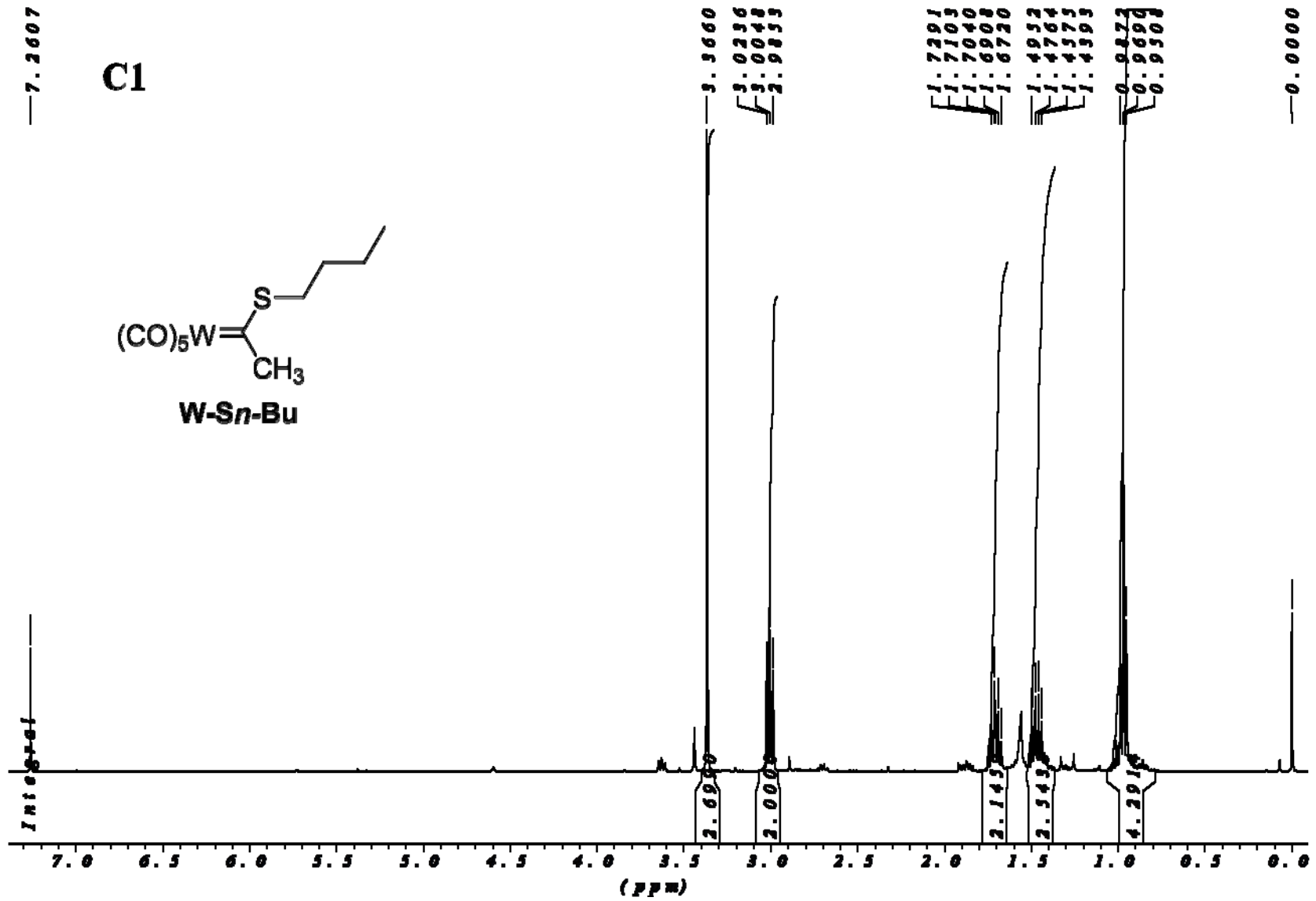
B2

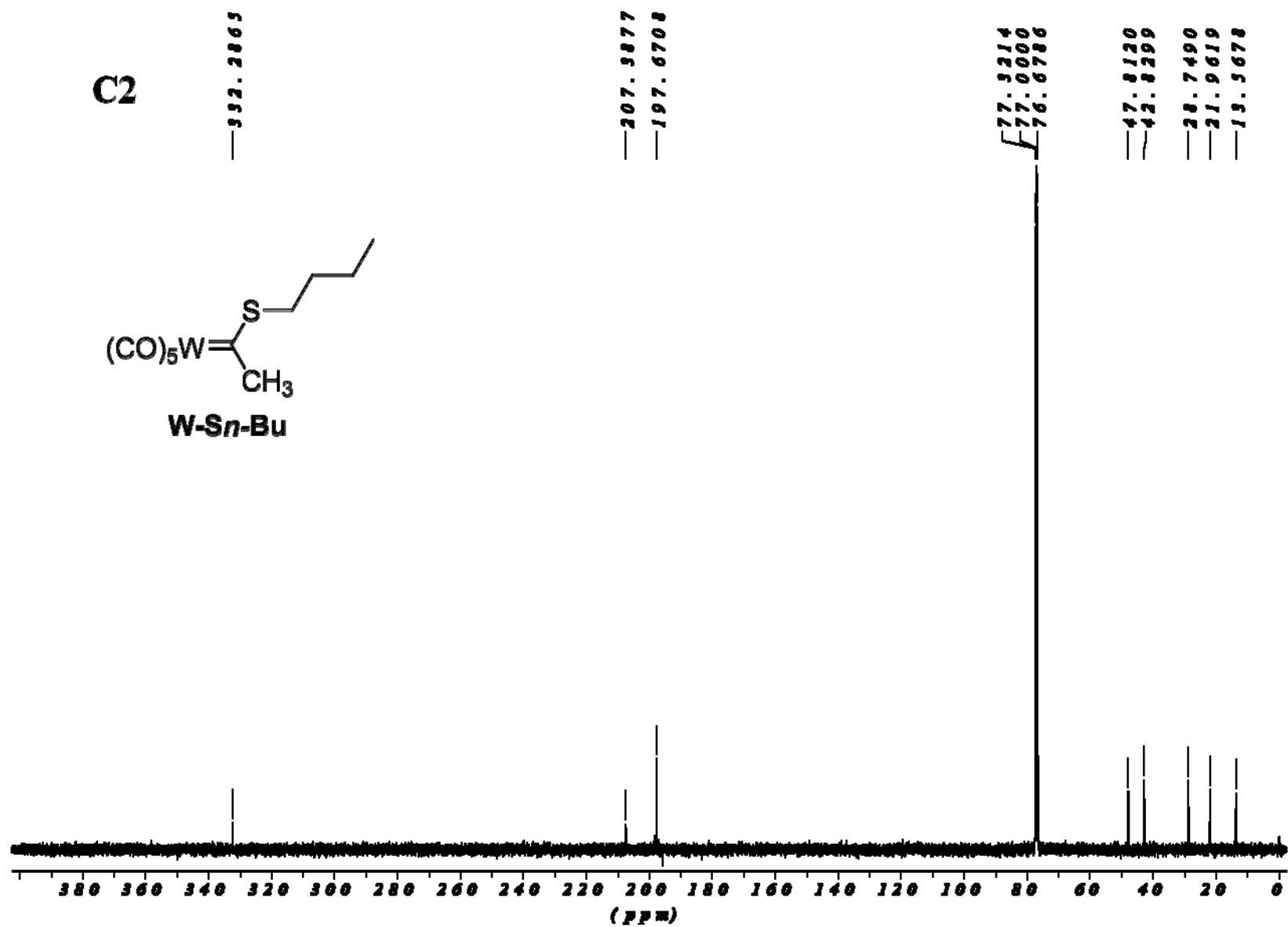


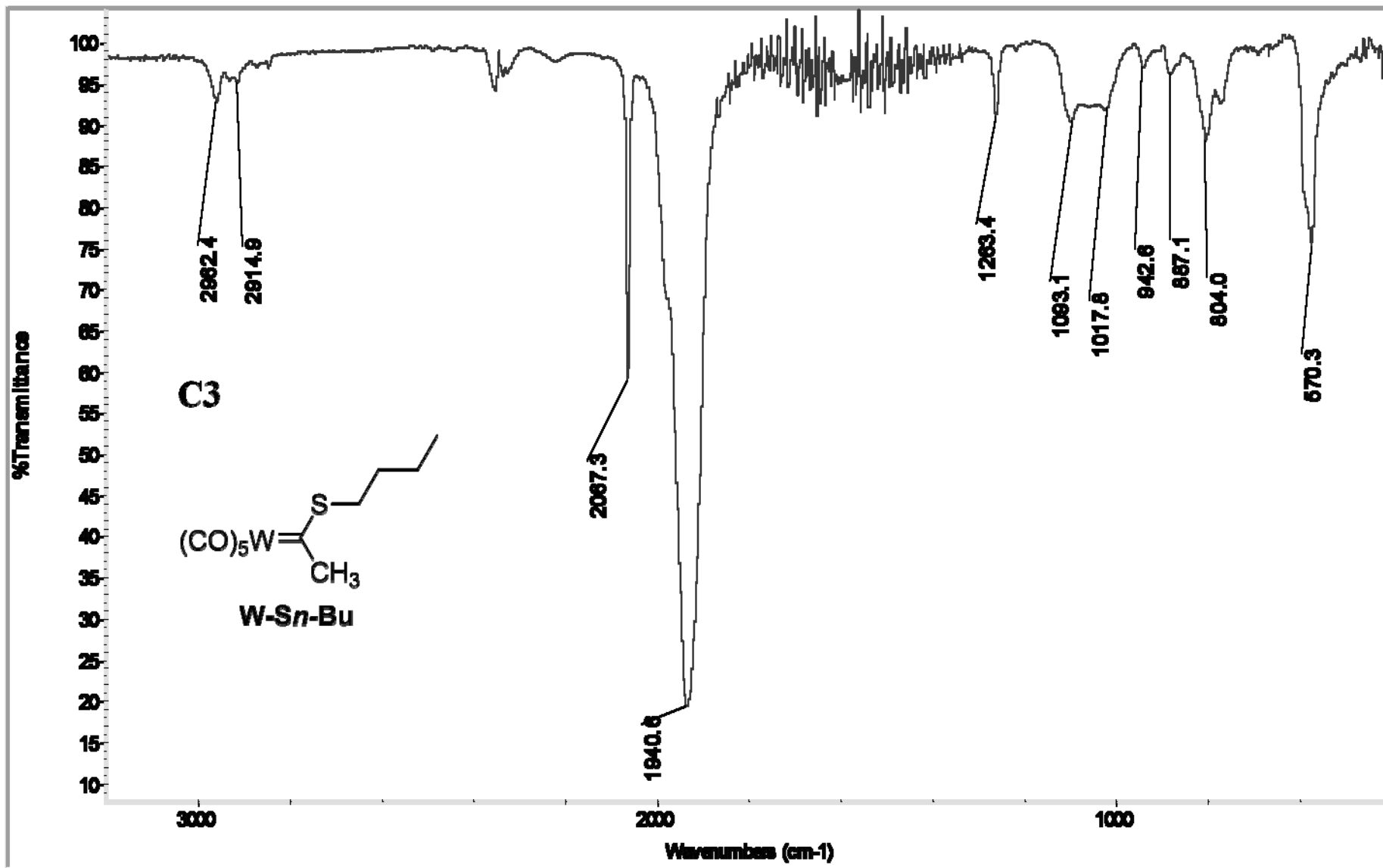
W-Si-Pr

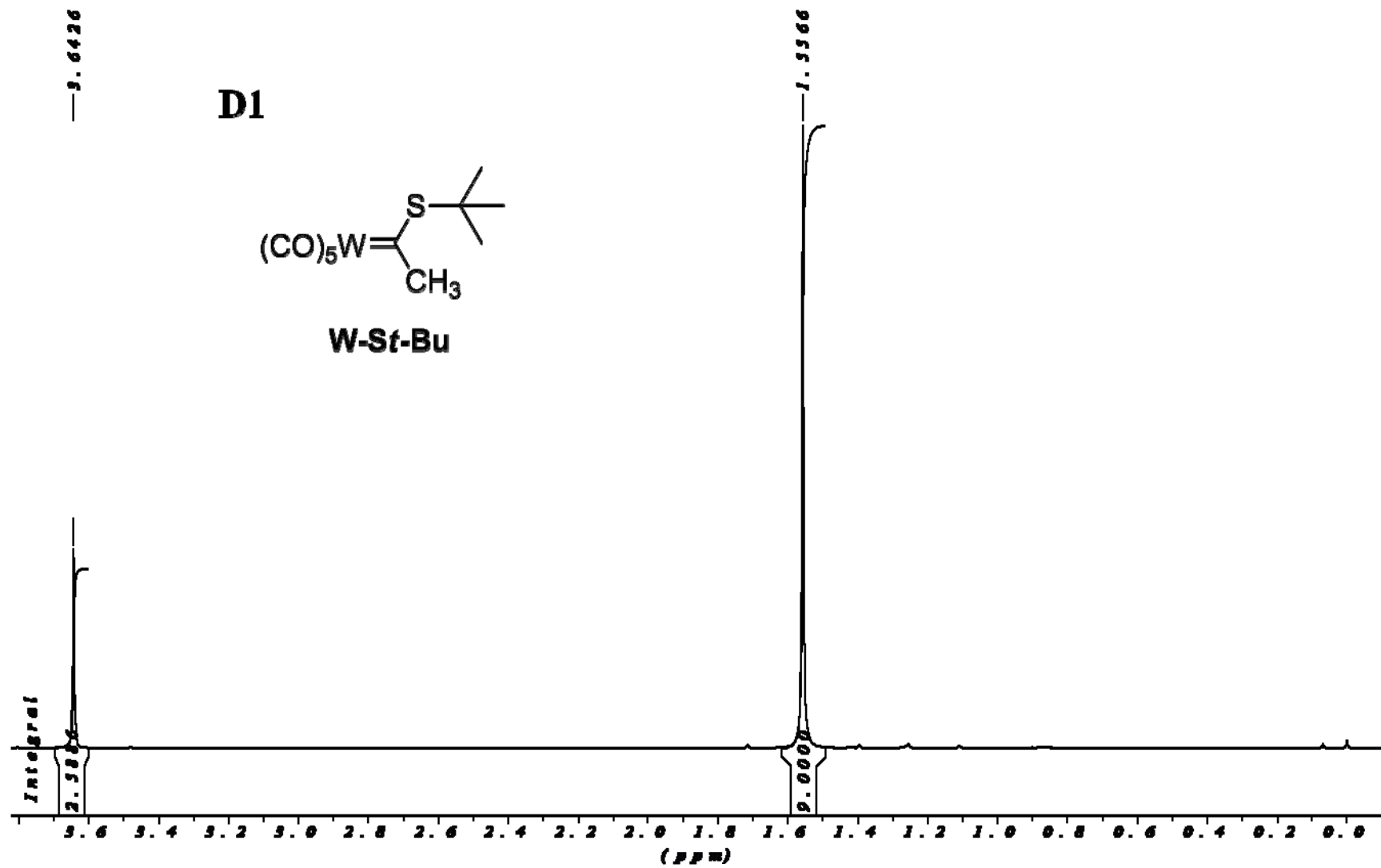




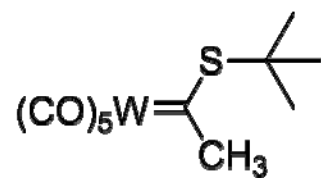








D2



W-Sf-Bu

