Supplementary Material for Organic & Biomolecular Chemistry

ENOLS AND THIOENOLS OF SUBSTITUTED CYANO MONOTHIOCARBONYLMALONAMIDES. STRUCTURES, ENOLIZATION VS. THIOENOLIZATION, EQUILIBRIA AND CONFORMATIONS

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Supplementary Data

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Table S1. **^{1}H NMR Spectral Data (in ppm) of R^3NHCSCH(CN)CONR^{1}R^2 (Amide)/ R^3NHCSC(CN)=C(OH)NR^{1}R^2 (Enol)/ R^3NHC(SH)=C(CN)CONR^{1}R^2 (Thioenol) (Systems 12/11/13) in Several Solvents at Room Temperature**

R^3	CONR^{1}R^2	Solvent	Amide, Enol or Thioenol	CONR^{1}R$^{2\ a,\ b}$	$R^{3\ b}$	NH[a]	CH, OH or SH[a]
Ph	$CONMe_2$	$CDCl_3$	Amide	3.09; 3.28	7.24-7.44 (m); 7.77 (d, J = 7.7 Hz)	10.60	5.33
			Enol	3.27	ov amide signals	8.49	16.64
			Thioenol	3.13	ov amide signals	12.40	4.58
		THF-d_8	Amide	2.98; 3.20	7.23 (t, J = 7.3 Hz); 7.36 (t, J = 7.7 Hz); 7.73 (d, J = 7.7 Hz)	11.18	5.59
			Enol	3.20 (ov amide signals)	ov amide signals	9.37	16.84
		CD_3CN	Amide	2.96; 3.09	7.33 (t, J = 7.3 Hz); 7.45 (t, J = 8.1 Hz); 7.67 (d, J = 8.1 Hz)	10.45	5.45
			Enol	3.20	ov amide signals	8.81	16.55
		DMSO-d_6		2.89; 3.00	7.29 (t, J = 7.2 Hz); 7.44 (t, J = 7.5 Hz); 7.76 (d, J = 7.8 Hz)	12.07	5.80
p-An	$CONMe_2$	$CDCl_3$	Amide	3.07 (s); 3.27	3.82 (s), 6.92 (d, J = 8.9 Hz), 7.65 (d, J = 8.9 Hz)	10.51	5.33
			Enol	3.25	3.82 (s, ov), 6.92 (d, ov), 7.25 (d, J = 8.2 Hz)	8.43	16.61
			Thioenol	3.11	3.82 (s, ov), 7.15 (d, J = 8.8 Hz), 7.25 (d, ov)	12.14	4.53
		THF-d_8	Amide	2.97; 3.20	3.77 (s), 6.91 (d, J = 8.8 Hz), 7.62 (d, J = 8.9 Hz)	11.05	5.56
			Enol	3.20 (ov)	3.79 (s), 6.91 (d, ov), 7.22 (d, J = 8.3 Hz)	9.27	16.87
		CD_3CN	Amide	2.96; 3.08	3.80 (s), 6.96 (d, J = 8.7 Hz), 7.56 (d, J = 8.8 Hz)	10.34	5.42
			Enol	3.19	3.81 (s), 6.96 (d, ov), 7.20 (d, J = 8.9 Hz)	8.72	16.57

		DMSO-d_6	Amide	2.89; 2.99	3.77 (s); 6.99 (d, J = 8.9 Hz); 7.67 (d, J = 8.8 Hz)	11.96	5.75
1-Np		CCl_4	Amide	2.77; 2.99	7.10-7.26 (m); 7.42-7.52 (m); 7.71 (d, J = 7.5 Hz)	10.45	5.01
			Enol	2.97	7.10-7.26 (ov); 7.42-7.52 (ov); 7.64 (d, J = 8.3 Hz)	8.33	16.56
			Thioenol	2.82	7.10-7.26 (ov); 7.42-7.52 (ov); 7.59 (d, J = 8.1 Hz)	12.77	4.29
		$CDCl_3$	Amide	3.12; 3.31	7.43-7.62 (m); 7.85-7.98 (m)	10.81	5.49
			Enol	3.29	ov amide signals	8.71	16.64
			Thioenol	3.17	ov amide signals	12.72	4.50
		C_6D_6	Amide	2.05; 2.22	7.08-7.57 (m); 7.91 (d, J = 7.9 Hz); 8.19 (d, J = 7.8 Hz)	11.13	5.09
			Enol	2.34	6.90-6.95 (m); 8.00 (d, J = 8.0 Hz)	8.86	17.29
			Thioenol	2.70	ov	13.19	4.27
		THF-d_8	Amide	3.05; 3.27	7.48-7.53 (m); 7.64 (d, J = 7.3 Hz); 7.35 (d, J = 8.2 Hz); 7.89-7.91 (m); 8.06 (d, J = 6.9 Hz)	11.42	5.79
			Enol	3.23	ov amide signals	9.71	16.89
			Thioenol	3.11	ov amide signals	12.98	5.17
		$(CD_3)_2CO$	Amide	3.05; 3.31	7.50-7.58 (m); 7.67 (d, J = 7.9 Hz); 7.94 (d, J = 8.0 Hz); 7.96-8.10 (m)	11.28	5.91
			Enol	3.27	ov amide signals	9.56	16.72
			Thioenol	3.11	ov amide signals	12.85	5.02
		CD_3CN	Amide	3.03; 3.20	7.44-7.64 (m); 7.84-8.00 (m)	10.53	5.65
			Enol	3.23	ov amide signals	9.05	16.52
			Thioenol	3.08	ov amide signals	12.55	5.11
		DMF-d_7	Amide	3.05; 3.30	7.58-7.67 (m); 7.99-8.09 (m);	12.28	6.22

					8.19 (d, J = 8.1 Hz)		
		DMSO-d_6	Amide	2.97; 3.16	7.50-7.61 (m); 7.95 (d, J = 7.3 Hz); 8.01 (t, J = 6.5 Hz)	12.18	6.08
Me	$CONMe_2$	$CDCl_3$	Amide	3.01; 3.24	3.17 (d, J = 4.9 Hz)	9.00	5.29
			Enol	3.19	3.14 (d, J = 4.4 Hz)	7.26	16.42
		THF-d_8	Amide	2.92; 3.19	3.08 (d, J = 4.6 Hz)	9.56	5.51
			Enol	3.16	3.08 (d, ov)	7.97	16.62
		CD_3CN	Amide	2.92; 3.04	3.09 (d, J = 4.8 Hz)	8.90	5.34
		DMSO-d_6	Amide	2.85; 2.93	3.01 (d, J = 4.4 Hz)	10.44	5.64
Et	$CONMe_2$	$CDCl_3$	Amide	3.04; 3.25	1.31 (t, J = 7.4 Hz); 3.67 (m)	8.73	5.24
			Enol	3.21	1.31 (ov); 3.67 (ov)	7.00	16.49
		THF-d_8	Amide	4.55; 4.80	2.82 (t, J = 7.2 Hz); 5.27 (m)	11.16	7.08
			Enol	4.23	2.82 (t, ov); 5.27 (ov)	9.50	18.26
		CD_3CN	Amide	2.92; 3.03	1.21 (t, J = 7.3 Hz); 3.63 (m)	8.88	5.28
		DMSO-d_6	Amide	2.85; 2.91	1.15 (t, J = 7.2 Hz); 3.55 (m)	10.48	5.57
i-Pr		CCl_4	Amide	2.70; 2.93	0.97 (d, J = 6.6 Hz); 0.99 (d, J = 6.6 Hz); 4.15 (M, J = 6.8 Hz)	8.17	4.73
			Enol	2.89	1.03 (D, J = 6.5 Hz); 4.22 (M, J = 6.7 Hz)	6.39	16.28
		$CDCl_3$	Amide	3.01; 3.21	1.25 (d, J = 6.4 Hz); 1.34 (d, J = 6.4 Hz); 4.48 (oct, J = 6.4 Hz)	8.62	5.22
			Enol	3.18	1.25 (d, J = 6.4 Hz); 4.59 (oct, J = 6.4 Hz)	6.81	16.49
		THF-d_8	Amide	2.93; 3.16	1.21 (d, J = 6.5 Hz); 1.25 (d, J = 6.4 Hz); 4.57 (oct, J = 6.4 Hz)	9.30	5.41
			Enol	3.15	1.23 (d, J = 6.5 Hz); ov	7.30	16.65
		CD_3CN	Amide	2.91; 2.99	1.23 9d, J = 6.5 Hz); 1.25 (d, J = 6.5 Hz); 4.50 (oct, J = 6.5	8.79	5.24

					Hz)		
		DMSO-d_6	Amide	2.84; 2.87	1.17 (d, J = 6.8 Hz); 1.19 (d, J = 6.8 Hz); 4.38 (oct. J = 6.8 Hz)	10.42 (d, J = 6.0 Hz)	5.49
t-Bu		CCl_4	Amide	2.70; 2.92	1.23 (s)	8.23	4.62
			Enol	2.87	1.25 (s)	6.60	16.39
		$CDCl_3$	Amide	3.01; 3.20	1.52 (s)	8.67	5.10
			Enol	3.15	1.55 (s)	6.97	16.62
		THF-d_8	Amide	2.95; 3.13	1.52 (s)	9.09	5.27
		CD_3CN	Amide	2.91; 2.99	1.52 (s)	8.70	5.17
		DMSO-d_6	Amide	2.83; 2.85	1.48 (s)	10.01	5.54
Ph	CONHMe	$CDCl_3$	Amide	2.88 (d, ov thioenol signal); 7.75	ov thioenol signals	10.84	5.05
			Enol	3.01 (d, J = 5.2 Hz); 6.32	ov thioenol signals	8.21	16.85
			Thioenol	2.88 (d, J = 5.2 Hz); 5.97	7.23-7.45 (m)	12.80	4.45
		THF-d_8	Amide	2.78 (d, J = 5.3 Hz); 7.84	ov enol signals	11.29	5.03
			Enol	2.91 (d, J = 5.3 Hz); 7.60	7.19-7.43 (m)	9.20	17.09
			Thioenol	2.77 (ov amide); 6.87	ov enol signals	13.19	6.89
		CD_3CN	Amide	2.77 (d, J = 5.4 Hz); 7.03	ov enol signals	10.53	5.05
			Enol	2.91 (d, J = 5.3 Hz); 6.80	7.31-7.46 (m); 7.70 (d, J = 7.7 Hz)	8.61	16.85
			Thioenol	2.89 (d, ov); 6.30	ov enol signals	12.80	6.80
		DMSO-d_6	Amide	2.69 (s); 8.18	7.25; 7.41; 7.74	11.97	5.35
p-An		$CDCl_3$	Amide	2.92 (d, J = 4.9 Hz); [c]	3.75 (s, ov); 7.15 (d, ov); 7.62 (d, J = 8.6 Hz)	10.54	4.93

			Enol	3.02 (d, J = 4.8 Hz); 6.08	3.82 (s, ov); 6.39 (d, ov); 7.25 (d, J = 8.4 Hz)	8.10	16.85
			Thioenol	2.88 (d, J = 4.8 Hz); 5.88	3.83 (s); 6.93 (d, J = 8.7 Hz); 7.15 (d, J = 8.7 Hz)	12.52	4.39
		THF-d_8	Amide	2.78 (d, J= 4.7 Hz); 7.82 (br)	3.78 (s, ov); 6.91 (d, ov); 7.67 (d, J = 8.9 Hz)	11.15	5.01
			Enol	2.91 (d, J = 4.8 Hz); 7.52 (br)	3.76 (s); 6.87 (d, J = 8.5 Hz); 7.20 (d, J = 8.4 Hz)	9.11	17.12
			Thioenol	2.76 (d, ov); 6.83 (br)	3.73 (s, ov); 6.95 (d, J = 8.6 Hz); 7.16 (d, ov)	12.88	4.85
		CD_3CN	Amide	2.77 (d, J = 4.7 Hz); 6.97 (ov)	3.80 (s); 6.95 (d, J = 8.6 Hz); 7.61 (d, J = 8.6 Hz)	10.37	5.01
			Enol	2.90 (d, J = 4.4 Hz); 6.73 (br)	3.79 (s); 6.90 (d, J = 8.4 Hz); 7.21 (d, J = 8.2 Hz)	8.51	16.86
			Thioenol	2.75 (d, ov); 6.23 (br)	3.77 (s); 6.95 (ov); 7.61 (ov)	12.59	4.56
		DMSO-d_6	Amide	2.69 (d, J = 4.6 Hz); 8.16 (br)	3.76 (s); 6.97 (d, J = 8.2 Hz); 7.47 (d, J = 8.9 Hz)	11.86	5.29 (s, br)
1-Np		$CDCl_3$	Amide	2.98 (d, J = 4.8 Hz); 8.01	ov thioenol signals	9.19	[c]
			Enol	3.03 (d, J = 4.8 Hz); 6.20	ov thioenol signals	8.37	16.83
			Thioenol	2.93 (d, J = 4.8 Hz); 5.97	7.39-7.64 (m); 7.84-7.95 (m)	13.05	4.34
		$(CD_3)_2CO$	Amide	2.82 (d, J = 5.0 Hz); 8.17	ov amide signals	11.69	5.64
			Enol	2.89 (d, J = 5.0 Hz); 8.04	7.42-7.74 (m); 7.87-7.96 (m)	9.45	16.98
			Thioenol	2.90 (ov); [c]	ov enol signals	13.45	6.80
		THF-d_8	Amide	2.85 (d, J = 4.0 Hz); 8.07	ov enol signals	11.55	5.30

			Enol	2.94 (d, J = 4.0 Hz); 7.66	7.44-7.50 (m); 7.83-7.89 (m)	9.53	17.11
			Thioenol	2.88 (ov); 6.98	ov enol signals	13.51	6.97
		CD_3CN	Amide	2.84; 7.43	ov enol signals	10.92	5.36
			Enol	2.93; 6.83	7.44 (d, J = 7.6 Hz); 7.52-7.63 (m); 7.83-7.85 (m); 7.91-7.96 (m)	8.84	16.79
			Thioenol	2.88; [c]	ov enol signals	13.12	6.34
		DMSO-d_6	Amide	2.77; 8.48	7.31-7.64 (m); 7.75-7.98 (m)	12.33	5.65
Me		$CDCl_3$	Amide	3.17 (d, J = 4.5 Hz); 9.17	2.86 (d, J = 4.6 Hz)	7.06	4.88
			Enol	3.13 (d, J = 4.6 Hz); 6.90	2.96 (d, J = 4.5 Hz)	6.13	16.59
			Thioenol	3.07 (d, J = 4.7 Hz); 5.82	2.80 (d, J = 4.6 Hz)	11.02	4.55
		C_6D_6	Amide	2.47 (d, J = 4.6 Hz); 8.35	2.08 (d, J = 4.8 Hz)	5.78	4.17
			Enol	2.47 (d, J = 4.6 Hz); 6.40	1.99 (d, J = 4.7 Hz)	5.24	17.20
			Thioenol	2.18	1.81 (weak signal)	11.04	[c]
		THF-d_8	Amide	3.07 (d, J = 4.6 Hz); 9.62	2.73 (d, J = 4.8 Hz)	7.74	4.85
			Enol	3.04 (d, J = 4.6 Hz); 7.74	2.87 (d, J = 4.7 Hz)	7.30	16.74
		CD_3CN	Amide	3.08 (d, J = 4.7 Hz); 8.95	2.74 (d, J = 4.7 Hz)	6.94	4.88
			Enol	3.03 (d, J = 4.6 Hz); 7.26	2.86 (d, J = 4.8 Hz)	6.55	16.60
		DMSO-d_6	Amide	2.99 (d, J = 4.5 Hz); 10.34	2.64 (d, J = 4.6 Hz)	8.12	5.11

Et		$CDCl_3$	Amide	2.86 (d, J = 4.8 Hz); 9.07	1.27 (t, J = 7.3 Hz); 3.39 (m)	7.10	4.88
			Enol	2.95 (d, J = 4.9 Hz); 6.70	1.24 (t, J = 7.3 Hz); 3.65 (m)	6.18	16.64
			Thioenol	2.80 (d, J = 4.8 Hz); 5.85	1.28 (t, J = 7.2 Hz); 3.65 (ov)	11.07	4.55
		THF-d_8	Amide	2.87 (d, J = 4.6 Hz); 9.60	1.19 (t, J = 7.4 Hz); 3.61 (m, ov)	7.71	4.82
			Enol	2.74 (d, J = 4.4 Hz); 7.63	1.17 (t, J = 7.2 Hz); 3.61 (m)	7.31	16.79
		CD_3CN	Amide	2.74 (d, J = 4.5 Hz); 8.93	1.21 (t, J = 7.3 Hz); 3.60 (m)	6.92	4.84
			Enol	2.87 (d, J = 4.6 Hz); 7.18	1.18 (t, J = 7.4 Hz); 3.60 (m, ov)	6.55	16.66
		DMSO-d_6	Amide	2.65 (d, J = 4.3 Hz); 10.34	1.15 (t, J = 7.5 Hz); 3.51 (m)	8.08	5.08
i-Pr		$CDCl_3$	Amide	2.86 (d, J = 4.7 Hz); 7.05	1.27 (d, J = 6.4 HZ); 4.47 (oct, J = 6.6 HZ)	8.91	4.85
			Enol	2.95 (d, J = 4.9 Hz); 6.17	1.24 (d, J = 6.6 Hz); 4.54 (oct, J = 6.6 Hz)	6.44 (d, J = 6.8 Hz)	16.68 (d, J = 1.5 Hz)
			Thioenol	2.80 (d, J = 5.8 Hz); 5.84	1.24 (d, ov); 3.77 (oct, J = 6.8 Hz)	11.14	5.84
		THF-d_8	Amide	2.74 (d, J = 4.6 Hz); 7.70	1.22 (d, J = 6.8 Hz); 4.51 (oct, J = 6.8 Hz)	9.46	4.77
			Enol	2.87 (d, J = 4.6 Hz); 7.05	1.22 (d, J = 6.8 Hz, ov); 4.58 (oct, J = 6.7 Hz)	7.37	16.78
		CD_3CN	Amide	2.74 (d, J = 5.0 Hz); 6.91	1.23 (d, J = 6.6 Hz); 1.24 (d, J = 6.6 Hz); 4.46 (oct, J = 6.6 Hz)	8.83	4.80

			Enol	2.86 (d, J = 4.9 Hz); 6.56	1.23 (d, ov); 4.53 (oct, J = 6.7 Hz)	6.78	16.68
		DMSO-d_6	Amide	2.64 9d, J = 4.8 Hz); 8.03	1.18 (d, J = 6.6 Hz); 4.36 (oct, J = 6.6 Hz)	10.23	5.03
t-Bu		CCl_4	Amide	2.58 (d, J = 4.9 Hz); 6.51	1.23 (s)	8.38	4.21
			Enol	2.66 (d, J = 4.9 Hz); 5.59	1.24 (s)	6.14	16.57 (d, J = 1.8 Hz)
			Thioenol	2.47 (d, J = 4.8 Hz); 5.30	1.17 (s)	11.44	4.47
		$CDCl_3$	Amide	2.87 (d, J = 4.8 Hz); 7.04	1.53 (s)	8.74	4.79
			Enol	2.94 (d, J = 4.8 Hz); 6.05	1.54 (s)	6.55	16.88 (d, J = 1.2 Hz)
			Thioenol	2.81 (d, J = 4.8 Hz); 5.81	1.47 (s)	11.61	4.79 (ov)
		C_6D_6	Amide	2.04 (s); 5.59	1.27 (ov)	8.75	4.09
			Enol	1.93 (d, J = 4.9 Hz); 5.13	1.27 (s)	6.69	17.43 (d, J = 1.6 Hz)
			Thioenol	2.26 (s); 7.21	1.27 (ov)	12.02	5.44 (br)
		THF-d_8	Amide	2.75 (d, J = 4.8 Hz); 7.79	1.51 (s)	9.25	4.76
			Enol	2.86 (d, J = 4.8 Hz); 6.74	1.53 (s)	7.42	16.80
		CD_3CN	Amide	2.74 (d, J = 4.9 Hz); 7.91 (s)	1.51	8.73	4.79
			Enol	2.85; 6.54	1.52 (s)	6.69	16.77
		DMF-d_7	Amide	2.73 (d, J = 4.6 Hz); 8.09	1.51 (s)	9.89	5.24
		DMSO-d_6	Amide	2.64 (d, J = 2.1 Hz);	1.47 (s)	9.77	5.13

				8.00			
Ph	$CONH_2$	$CDCl_3$	Enol	5.55 (br)	ov thioenol signals	8.31	16.61
			Thioenol	5.74	7.22 (s); 7.30-7.46 (m)	12.70	4.47
		THF-d_8	Amide	9.53	ov enol signals	11.25	5.02
			Enol	7.77	7.02-7.61 (m)	9.28	16.49
p-An		$CDCl_3$	Enol	5.38 (br)	3.84 (s); 6.93 (d, J = 8.2 Hz); 7.26 (d, ov the $CDCl_3$ signal)	8.22	16.59
			Thioenol	5.67 (br)	3.84 (s, ov); 6.93 (d, ov); 7.16 (d, J = 8.3 Hz)	12.45	4.42
		THF-d_8	Amide	7.38 (ov); 7.68 (ov)	3.76 (s); 6.87 (ov); 7.20 (ov)	11.20	5.01
			Enol	7.38 (br); 7.68 (br)	3.76 (s,ov); 6.87 (d, J = 8.8 Hz); 7.20 (d, J = 8.8 Hz)	9.19	16.54
		CD_3CN	Amide	7.58 (br)	3.80 (s, ov); 6.93 (ov)	10.38	5.03
		CD_3CN	Enol	6.6 (br)	3.80 (s); 6.93 (d, J = 8.8 Hz); 7.21 (d, J = 8.7 Hz)	8.66	16.43
1-Np [d]		THF-d_8	Enol	7.85	7.45-7.82 (m)	9.64	16.56
i-Pr		$CDCl_3$	Amide	5.56 (br)	1.43 (d, J = 6.2 Hz); 4.49 (m)	8.54	5.02
			Enol	5.77	1.27 (d, J = 6.3 Hz); 4.55 (m, J = 5.6 Hz)	6.60	16.46
			Thioenol	[c]	1.27 (ov); 4.55 (ov)	11.21	4.14
		THF-d_8	Amide	7.2 (ov)	1.33 (d, J = 6.2 Hz); 4.51 (m, J = 5.8 Hz)	9.49	5.30
			Enol	7.34 (br)	1.22 (d, J = 6.4 Hz); 4.59 (m, J = 5.9 Hz)	7.16	16.18
		DMSO-d_6	Amide	6.20; 10.2	1.25 (d, J = 6.3 Hz); 3.71 (m, J = 5.6 Hz)	10.36	4.42
t-Bu		$CDCl_3$	Amide	5.87	1.52 (s)	8.35	4.75
			Enol	5.60	1.56 (s)	6.73	16.66
			Thioenol	5.40	1.48 (s)	11.58	4.88
		C_6D_6	Amide	5.22	1.04 (s)	8.20	4.29

			Enol	4.13	1.20 (s)	6.72	17.02
			Thioenol	ov	1.18 (s, ov)	11.89	3.87
		THF-d_8	Amide	7.11	1.51 (s)	9.21	4.75
			Enol	7.39 (br)	1.54 (s)	6.84	16.19
		CD_3CN	Amide	6.27; 6.37	1.52 (s)	8.62	4.80
			Enol	6.61	1.50 (s)	6.79	16.43
		DMF-d_7	Amide	7.69	1.52 (s)	9.88	5.26
		DMSO-d_6	Amide	7.46; 7.60	1.47 9s)	9.75	5.12
Ph	CONHPr-*i*	$CDCl_3$	Amide	1.20 (d, ov); 4.08 (m, ov); 7.76 (d, J = 6.5 Hz)	7.16 – 7.42 (ov)	11.04	5.17
			Enol	1.27 (d, J = 6.6 Hz); 4.13 (m, J = 6.6 Hz); 5.92 (d, J = 7.1 Hz)	7.16-7.42 (m)	8.28	16.82
			Thioenol	1.20 (d, J = 6.5 Hz); 4.08 (m, J = 6.5 Hz); 5.72 (d, J = 7.0 Hz)	7.16-7.42 (ov)	12.85	4.70
		THF-d_8	Amide	(dd, $J_1 = J_2$ = 6.6 Hz); 4.02 (oct, J = 6.9 Hz); 7.72 (d, J = 6.6 Hz)	7.07 – 7.50 (ov)	11.35	5.04
			Enol	1.26 (d, J = 6.6 Hz); 4.15 (octet, J = 6.6 Hz); 7.80 (d, J = 6.8 Hz)	7.07 – 7.50 (m)	9.19	17.11
			Thioenol	1.17 (ov); 4.02 (ov); 7.96 (d, J = 6.6 Hz)	7.07 – 7.50 (ov)	13.17	6.5
		CD_3CN	Amide	1.16 (d, J = 6.5 Hz); 3.97 (oct, J = 6.8 Hz); 6.97	7.15 – 7.71 (m)	10.60	5.06
			Enol	1.25 (d, J = 6.4 Hz); 4.13 (oct, J = 6.0 Hz);	7.15 – 7.71 (m, ov)	8.65	16.88

				8.48			
			Thioenol	1.16 (ov); 3.97 (ov); 8.36	7.15-7.71 (m, ov)	12.89	5.98
		$DMSO-d_6$	Amide	1.11 (d, J = 6.1 Hz); 3.89 (oct, J= 6.2 Hz); 8.15 (s, br)	7.25 (t, J = 6.1 Hz); 7.41 (t, J = 7.1 Hz); 7.76 (d, J = 7.5 Hz)	11.89	5.29
i-Pr		$CDCl_3$	Amide	1.16 (d, J = 6.0 Hz); 3.98 (oct, J = 6.2 Hz); 8.92	1.16 (d, ov); 4.50 (ov)	6.82	4.84
			Enol	1.22 (d, J = 6.5 Hz); 4.08 (oct, J = 6.9 Hz); 5.65	1.23 (d, J = 6.5 Hz); 4.54 (oct, J = 6.6 Hz)	6.45	16.64
			Thioenol	1.22 (ov); 4.08 (ov)	1.22 (ov); 4.54 (ov)	11.27	5.52
		$THF-d_8$	Amide	1.22 (d, J = 6.6 Hz); 3.95 (oct, J = 6.6 Hz); 7.51	1.22 (d, ov); 4.53 (oct, J = 6.4 Hz)	9.42	4.76
			Enol	1.12 (d, J = 6.4 Hz); 4.10 (oct, J = 6.5 Hz); 7.05	1.14 (d, J = 6.5 Hz); 4.57 (oct, J = 4.5 Hz)	6.95	16.79
		CD_3CN	Amide	1.13 (d, J = 6.6 Hz); 3.93 (oct, J = 6.5 Hz); 6.75	1.23 (d, J = 6.7 Hz); 4.49 (oct, J = 6.7 Hz)	8.77	4.76
			Enol	1.13 (ov); 4.07 (oct, J= 6.6 Hz); 6.22	1.23 (ov); 4.49 (ov)	5.97	16.69
		$DMSO-d_6$	Amide	1.08 (dd, J_1 = 6.5 Hz, J_2 = 6.4 Hz); 3.81 (oct, J = 6.5 Hz); 7.94	1.17 (dd, J_1 = 6.8 Hz, J_2 = 7.5 Hz); 4.34 (oct, J = 6.9 Hz)	10.08	4.97
i-Pr	$CONHCHPh_2$	$CDCl_3$	Amide	ov enol signals	ov enol signals; 4.14 (oct, J = 6.8 Hz)	8.18	4.81
			Enol	6.14-6.26 (m, CH,	1.29 (d, J = 6.2 Hz); 4.56 (d, J	6.51 (d,	16.94

				NH); 7.17-7.54 (m)	= 6.8 Hz)	J = 7.2 Hz)	
			Thioenol	ov enol signals	1.30 (d, J = 6.8 Hz); 3.81 (oct, J = 6.8 Hz)	11.05	4.62
		THF-d_8	Amide	6.29 (d, J = 7.7 Hz, CH); 8.51 (s); 7.22-7.30 (m)	1.20 (d, J = 6.6 Hz); 1.22 (d, J = 6.4 Hz); 4.56 (oct, J = 6.9 Hz)	9.48	5.03
			Enol	6.18 (d, J = 8.0 Hz), CH); 6.88 (s); Ph ov amide signals	ov amide signals	7.76	17.07
		CD_3CN	Amide	6.08 (d, J = 7.5 Hz); 7.26-7.43 (m); 7.69	1.21 (dd, , $J_1 = J_2$ = 6.6 Hz); 4.48 (oct, J = 6.5 Hz)	8.79	4.97
		DMSO-d_6	Amide	6.06 (d, J = 7.9 Hz); 9.00 (s); 7.19-7.36 (m)	1.14 (d, J = 6.3 Hz); 1.20 (d, J = 6.3 Hz); 4.38 (oct, J = 6.4 Hz)	10.20	5.26
t-Bu		$CDCl_3$	Amide	ov enol signals; 7.71 (s, NH)	1.47 (s)	8.50	4.79
			Enol	6.13-6.27 (m, CH); 6.06 (d, J = 7.3 Hz, NH); 7.2-7.37 (m, Ph)	1.56 (s)	6.65	17.09
			Thioenol	ov enol signals	1.51 (s)	11.52	4.83
		THF-d_8	Amide	6.20 (d, J = 7.9 Hz, CH); 8.66 (d, J = 7.8 Hz); 7.12-7.32 (m)	1.49 (s)	9.18	4.95
			Enol	6.29 (d, J = 7.8 Hz, CH); 6.85 (d, J = 7.8 Hz); ov Ph signals	1.55 (s)	7.85	17.09
		CD_3CN	Amide	6.08 (d, J = 7.4 Hz); 7.22-7.411 (m); 7.76 (s, br)	1.48 (s)	8.67	4.98

		DMSO-d_6	Amide	6.05 (d, J = 7.7 Hz, CH); 9.00 (d, J = 7.7 Hz); 7.27-7.37 (m, Ph)	1.45 (s)	9.71	5.26
t-Bu	CONHPh	$CDCl_3$	Amide	ov; 8.20 (s, NH)	1.56 (s)	8.67	4.86
			Enol	ov; 6.74 (s, NH)	1.59 (s)	7.78	17.30
			Thioenol	7.09-7.51 (m); 7.72 (s, NH)	1.51 (s)	11.61	4.90
		CD_3CN	Amide	7.14 (t, J = 7.4 Hz); 7.36 (t, J = 8.2 Hz); 7.52 (d, J = 8.0 Hz); 8.52 (s, br)	1.54 (s)	8.70	4.99
		DMSO-d_6	Amide	7.09 (t, J = 6.8 Hz); 7.33 (t, J = 7.3 Hz); 7.53 (d, J = 7.0 Hz); 9.84 (s, NH)	1.47 (s)	10.21	5.30

[a] A singlet unless otherwise stated; [b] ov= Overlaps; [c] Not observed; [d] Decomposed during the measurement of the spectrum in CD_3CN and DMSO-d_6.

Table S2. ^{13}**C NMR Spectral Data (in ppm) of R^3NHCSCH(CN)CONR^{1}R^2 (Amide)/ R^3NHCSC(CN)=C(OH)NR^{1}R^2 (Enol)/ R^3NHC(SH)=C(CN)CONR^{1}R^2 (Thioenol), (Systems 12/11/13) in Several Solvents at Room Temperature**

R^3	COR^{1}R^2	Solvent	Amide, Enol or Thioenol	CH or =C$_\beta$^{a}	CN^a	NR^{1}R^2	R^3	C=O or C=S	=C$_\alpha$ or C=O
Ph	CONMe$_2$	$CDCl_3$	Amide	51.26 (d, J = 142.4 Hz)	113.85 (d, J = 11.0 Hz)	36.80 (q, J = 140.1 Hz); 38.56 (q, J = 139.3 Hz)	122.90 (d, J = 162.0 Hz); 127.30 (d, J = 162.8 Hz); 128.87 (d, J = 162.0 Hz); 137.88 (s)	183.54 (d, J = 7.8 Hz), C=S)	162.31 (m, C=O)
			Enol	68.09	119.44	39.73 (q, J = 140 Hz)	126.48 (d, J = 162.8 Hz); 127.19 (d, J = 162.2 Hz); 128.80 (d, J = 1 62.8 Hz); 137.41 (s)	188.35 (s, C=S)	171.15 (s, C$_\alpha$)
			Thioenol	72.60	120.52	38.07 (w)	125.74 (d, J = 162.3 Hz); 127.70 (ov); 129.44 (ov); 137.54 (s)	167.72 (s, C=O)	167.98 (s, C$_\alpha$)
		THF-d$_8$	Amide	51.63 (d, J = 141.6 Hz)	114.00 (d, J = 11.0 Hz)	35.19 (1, J = 138.5 Hz); 37.34 (q, J = 138.5 Hz)	123.46 (d, J = 162.0 Hz); 126.49 (d, J = 162.0 Hz); 128.29 (d, J = 161.2 Hz); 139.14 (t, J = 8.6 Hz)	186.40 (d, J = 7.1 Hz, C=S)	161.82 (m, C=O)
			Enol	68.09	118.20	38.86 (w)	126.26 (w); 126.60 (w); 128.16 (w); 139.02 (w)	[b]	[b]
		CD_3CN	Amide	52.06 (d, J = 141.8 Hz)	114.63 (d, J = 11.0 Hz)	35.90 (q, J = 139.2 Hz); 37.51 (q, J = 139.3 Hz)	123.90 (d, J = 162.0 Hz); 127.37 (d, J = 162.3 Hz); 128.93 (d, J = 161.4 Hz); 138.45 (s)	187.63 (d, J = 7.1 Hz, C=S)	161.72 (m, C=O)

			Enol	[b]	[b]	39.40 (w)	[b]; 127.07 (w); 128.67 (w); [b]	[b]	[b]
		DMSO-d_6	Amide	53.38 (d, J = 138.5 Hz)	116.50 (d, J = 11.0 Hz)	36.47 (q, J = 139.3 Hz); 37.59 (q, J = 140.1 Hz)	123.57 (d, J = 162.0 Hz); 127.26 (d, J = 163.5 Hz); 129.26 (d, J = 162.0 Hz); 139.31 (s)	187.96 (d, J = 6.5 Hz, C=S)	161.73 (m, C=O)
p-An		$CDCl_3$	Amide	50.98 (d, J = 142.7 Hz)	113.96 (d, J = 10.7 Hz)	36.77 (q, J = 140.0 Hz); 38.55 (q, J = 139.4 Hz)	55.35 (q, J = 144.1 Hz); 113.90 (d, J = 161.4 Hz); 124.61 (d, J = 160.9 Hz); 130.87 (t, J = 9.1 Hz); 158.26 (s)	183.16 (d, J = 7.0 Hz, C=S)	162.24 (m, J = 3.1 Hz, C=O)
			Enol	67.61	119.52	39.68 (q, J = 137.2 Hz)	55.29 (q, J = 144.0 Hz); 113.95 (d, J = 160.7 Hz); 128.09 (d, J = 161.0 Hz); 130.1 (t, J = 9.4 Hz); 158.49 (s)	188.67 (s, C=S)	171.03 (s, C_α)
			Thioenol	71.69	120.71	[b]	55.36 (q, ov); 114.53 (d, J = 160.3 Hz); 127.54 (d, J = 160.1 Hz); 130.2 (ov); 159.02 (s)	168.08 (s, C=O)	168.73 (s, C_α)
		THF-d_8	Amide	51.42 (d, J = 141.1 Hz)	114.11 (d, J = 10.2 Hz)	35.50 (q, J = 140.2 Hz); 37.37 (q, J = 140.0 Hz)	54.60 (q, J = 143.8 Hz); 113.35 (d, J = 162.1 Hz); 124.96 (d, J = 162.3 Hz); 132.02 (t, J = 9.6 Hz); 158.24 (s)	185.78 (d, J = 7.0 Hz), C=S)	161.87 (m, J = 3.2 Hz, C=O)
			Enol	67.58	118.08	38.75 (q, w)	54.60 (ov); 114.11 (d, J = 160.8 Hz); 128.07 (d, J = 160.5 Hz); 131.2 (s); 158.60 (s)	189.03 (s, C=S)	171.53 (s, C_α)

		CD_3CN	Amide	51.90 (d, J = 138.3 Hz)	114.71 (d, J = 9.9 Hz)	35.90 (q, J = 139.8 Hz); 37.51 (q, J = 140.1 Hz)	55.19 (q, J = 144.5 Hz); 113.93 (d, J = 161.8 Hz); 125.47 (d, J = 160.8 Hz); 131.37 (t, J = 11.1 Hz); 158.52 (s)	187.09 (d, J = 6.9 Hz, C=S)	161.77 (m, C=O)
			Enol	[b]	[b]	138.5 (q, vw)	55.19 (ov); 114.79 (vw); 127.89 (vw); 128.60 (vw)	188.0 (vw, C=S)	[b]
		DMSO-d_6	Amide	53.14 (d, J = 136.5 Hz)	115.69 (d, J = 11.6 Hz)	36.47 (q, J = 140.0 Hz); 37.56 (q, J = 140.5 Hz)	55.79 (q, J = 144.4 Hz); 114.32 (d, J = 161.5 Hz); 125.11 (d, J = 162.0 Hz); 132.29 (t, J = 10.7 Hz); 158.05 (s)	187.04 (d, J = 6.4 Hz, C=S)	161.78 (m, C=O)
1-Np		$CDCl_3$	Amide	50.62 (d, J = 143.2 Hz)	114.01 (d, J = 11.0 Hz)	36.86 (q, J = 140.1 Hz); 38.63 (q, J = 139.3 Hz)	121.22; 123.38; 125.04; 126.49; 127.15; 128.10; 128.48; 128.57; 133.42; 134.09	186.19 (d, J = 7.1 Hz, C=S)	162.30 (m, C=O)
			Enol	67.90	119.64	39.72 (q, J = 140.1 Hz)	122.19; 124.44; 125.1; 126.30; 126.97; 128.35; 128.40; 129.49; 133.80; 134.21	189.88 (s, C=S)	171.06 (s, C_α)
			Thioenol	72.58	120.54	38.19 (q, J = 139.5 Hz)	122.3; 125.17; 126.35; 126.82; 127.42; 128.51; 128.72; 130.10; 133.54; 134.13	168.22 (s, C=O)	169.34 (s, C_α)
		C_6D_6	Amide	50.36 (d, J = 140.8 Hz)	114.34 (d, J = 11.0 Hz)	35.55 (q, J = 140.1 Hz); 36.94 (q, J = 141.3 Hz)	121.46; 123.30; 125.02; 126.15; 126.85; 127.52; 127.84; 128.42; 133.93; 134.20	186.44 (d, J = 7.0 Hz)	162.22 (m, C=O)
			Enol	68.23	119.34	38.45 (ov)	122.49; 123.89; 125.06; 126.02; 126.54; 126.61;	190.34 9s, C=S)	170.89 (s, C_α)

							128.23; 130.54; 133.99; 134.29		
			Thioenol	73.29	120.15	37.39 (w)	122.23; 123.30; 124.91; 126.68; 129.62; 134.10; 134.25	168.25 (s, C=O)	169.15 (s, C_α)
		THF-d_8[c]	Amide	51.24 (d, J = 142.4 Hz)	114.24 (d, J = 11.0 Hz)	35.61 (q, J = 139.3 Hz); 37.54 (q, J = 139.3 Hz)	122.46; 124.35; 125.00; 126.00; 126.22; 127.82; 128.04; 129.21; 134.31; 135.51	189.26 (d, J = 7.0 Hz, C=S)	161.89 (m, C=O)
			Enol	67.75	118.21	38.90 (q, J = 140.1 Hz)	122.81; 125.83; 126.06; 126.41; 127.70; 127.98; 130.71; 134.29; 135.20	190.30 (s, C=S)	171.61 (S, C_α)
		$(CD_3)_2CO$[c]	Amide	51.27 (d, J = 139.3 Hz)	114.49 (d, J = 11.0 Hz)	35.78 (q, J = 139.3 Hz); 37.54 (q, J = 139.3 Hz)	122.46; 124.55; 125.32; 126.34; 126.60; 128.22; 128.29; 129.04; 134.30; 135.06	190.21 (d, J = 7.0 Hz)	161.92 (m, C=O)
			Enol	67,.81	118.48	39.15 (w)	122.86; 126.11; 126.55; 127.99	[b]	[b]
		CD_3CN[c,d]	Amide	51.21 (d, J = 139.6 Hz)	114.70 (d, J = 10.9 Hz)	35.99 (q, J = 139.0 Hz); 37.80 (q, J = 139.0 Hz)	122.25; 124.87; 125.55; 126.62; 126.95; 128.45; 128.61; 128.92; 134.21; 134.72	190.60 (d, J = 7.0 Hz, C=S)	161.87 (m, C=O)
		DMF-d_7	Amide	52.13 (d, J = 138.3 Hz)	115.37 (d, J = 11.4 Hz)	35.92 (q, J = 139.0 Hz); 37.53 (q, J = 139.0 Hz)	123.11; 124.93; 125.75; 126.65; 126.78; 128.37; 128.56; 129.33; 134.53; 135.91	191.74 (d, J = 7.1 Hz, C=S)	162.11 (m, C=O)
		DMSO-d_6	Amide	52.18 (d, J = 134.9 Hz)	115.68 (d, J = 11.6 Hz)	36.57 (q, J = 136.9 Hz); 37.96 (q, J = 137.6 Hz)	123.29; 125.04; 126.11; 126.98; 127.10; 128.55; 128.77; 129.11; 134.33; 135.71	191.50 (d, J = 6.8 Hz, C=S)	162.05 (m, C=O)

Me		$CDCl_3$	Amide	50.17 (d, J = 142.5 Hz)	114.04 (d, J = 10.4 Hz)	36.76 (q, J = 139.3 Hz); 38.68 (q, J = 139.8 Hz)	33.58 (q, J = 140.6 Hz)	186.65 (m, C=S)	161.94 (m, C=O)
			Enol	66.570	119.85	39.63 (q, J = 139.8 Hz)	31.31 (q, J = 141.6 Hz)	189.08 (s, C=S)	173.24 (s, C_α)
		THF-d_8[d]	Amide	50.42 (d, J = 142.3 Hz)	114.25 (d, J = 10.4 Hz)	35.38 (q, J = 140.1 Hz); 37.53 (q, J = 140.0 Hz)	32.78 (q, J = 139.8 Hz)	187.99 (m, C=S)	161.64 (m, C=O)
		CD_3CN	Amide	50.82 (d, J = 141.8 Hz)	114.82 (d, J = 10.8 Hz)	35.79 (q, J = 140.0 Hz); 37.59 (q, J = 141.0 Hz)	32.97 (q, J = 140.8 Hz)	188.56 (m, C=S)	161.73 (m, C=O)
		DMSO-d_6	Amide	51.48 (d, J = 136.9 Hz)	115.74 (d, J = 11.3 Hz)	36.45 (q, J = 141.6 Hz); 37.72 (q, J = 141.3 Hz)	33.68 (q, J = 142.2 Hz)	189.05 (m, C=S)	161.79 (m, C=O)
Et		$CDCl_3$	Amide	50.16 (d, J = 142.4 Hz)	114.01 (d, J = 10.6 Hz)	36.72 (q, J = 139.8 Hz); 38.59 (q, J = 139.6 Hz)	12.44 (q, J = 127.7 Hz); 41.65 (t, J = 140.5 Hz)	185.63 (m, C=S)	161.91 (m, C=O)
			Enol	66.55	119.72	39.60 (q, J = 139.8 Hz)	13.68 (q, J = 127.3 Hz); 41.65 (q, ov)	187.73 (s, C=S)	170.87 (s, C_α)
		THF-d_8[d]	Amide	50.60 (d, J = 142.4 Hz)	114.21 (d, J = 11.0 Hz)	35.41 (q, J = 138.5 Hz); 37.47 (q, J = 138.5 Hz)	11.57 (q, J = 127.6 Hz); 40.97 (t, J = 140.9 Hz)	187.22 (m, J = 7.0 Hz, C=S)	161.67 (m, C=O)
		CD_3CN	Amide	51.05 (d, J = 139.3 Hz)	114.84 (d, J = 11.0 Hz)	35.78 (q, J = 139.5 Hz);	11.55 (q, J = 127.7 Hz); 41.27 (t, J = 142.8 Hz)	187.71 (m, J = 6.8 Hz, C=S)	161.71 (m,

						37.48 (q, J = 139.0 Hz)			C=O)
		DMSO-d_6	Amide	51.81 (d, J = 141.2 Hz)	115.76 (d, J = 10.7 Hz)	36.43 (q, J = 139.8 Hz); 37.54 (q, J = 138.8 Hz)	12.66 (q, J = 127.3 Hz); 41.35 (t, J = 141.7 Hz)	188.09 (m, J = 6.8 Hz, C=S)	161.76 (m, C=O)
i-Pr		$CDCl_3$	Amide	50.15 (d, J = 142.4 Hz)	113.96 (d, J = 10.2 Hz)	36.72 (q, J = 140.1 Hz); 38.53 (q, J = 139.3 Hz)	20.58 (q, J = 127.5 Hz); 48.39 (d, J 142.4 Hz)	184.44 (d of d, J_1 = 7.0 Hz, J_2 = 7.8 Hz)	161.92 (m, C=O)
			Enol	66.56	119.66	39.60 (q, J = 141.6 Hz)	21.90 (q, J = 127.5 Hz); 45.80 (d, J = 142.4 Hz)	186.41 (d, J = 3.1 Hz)	171.00 (s, C_α)
		THF-d_8	Amide	50.39 (d, J = 140.9 Hz)	114.08 (d, J = 10.2 Hz)	35.38 (q, J = 142.4 Hz); 37.30 (q, J = 141.6 Hz)	19.56 (q, J = 126.8 Hz); 47.97 (d, J = 142.4 Hz)	186.38 (d of d, J_1 = 7.0 Hz, J_2 = 7.0 Hz)	161.66 (m, C=O)
			Enol	66.95 (w)	[b]	38.73 (w)	20.82 (w); 45.40 (w)	[b]	[b]
		CD_3CN	Amide	51.22 (d, J = 137.7 Hz)	114.88 (d, J = 11.7 Hz)	35.78 (q, J = 142.4 Hz); 37.32 (q, J = 142.4 Hz)	19.54 (q, J = 128.3 Hz); 19.60 (q, J = 128.3 Hz); 48.35 (d, J = 140.1 Hz)	186.82 (d, J = 7.0 Hz)	161.69 (d, C=O)
		DMSO-d_6	Amide	52.06 (d, J 137.7 Hz)	115.78 (d, J = 11.0 Hz)	36.41 (q, J = 138.5 Hz); 37.32 (q, J = 138.5 Hz)	20.58 (q, J = 127.6 Hz); 20.77 (q, J = 128.3 Hz); 48.08 (d, J = 141.6 Hz)	187.07 (d of d, J_1 = 7.0 Hz), J_2 = 7.0 Hz)	161.72 (m, C=O)
t-Bu		$CDCl_3$	Amide	51.98 (d, J = 143.2 Hz)	114.23 (d, J = 11.0 Hz)	36.65 (q, J = 140.1 Hz); 38.47 (q, J = 139.3 Hz)	26.85 (q, J = 127.6 Hz); 56.46 (s)	184.34 (d, J = 7.0 Hz, C=S)	162.37 (m, C=O)

			Enol	67.21	120.04	39.57 (q, J = 140.1 Hz)	28.58 (q, J = 128.3 Hz); 55.45 (s)	187.26 (s, C=S)	171.55 (s, C_α)
		THF-d_8	Amide	51.66 (d, J = 141.7 Hz)	114.38 (d, J = 10.9 Hz)	35.39 (q, J = 139.0 Hz); 37.16 (q, J = 139.0 Hz)	26.14 (q, J = 128.7 Hz); 55.66 (s)	186.35 (d, j = 7.5 Hz)	162.50 (m, C=O)
		CD_3CN	Amide	52.93 (d, J = 138.5 Hz)	115.20 (d, J = 111.0 Hz)	35.81 (q, J = 141.6 Hz); 37.29 (q, J = 141.6 Hz)	26.10 (q, J = 129.1 Hz); 56.43 (s)	186.85 (d, J = 7.0 Hz)	162.12 (m, C=O)
		DMSO-d_6	Amide	53.82 (d, J = 137.7 Hz)	116.10 (d, J = 11.0 Hz)	36.41 (q, J = 141.6 Hz); 37.20 (q, J = 141.6 Hz)	27.02 (q, J = 126.8 Hz); 56.31 (s)	187.69 (d, J = 6.9 Hz)	161.90 (m, C=O)
Ph	CONHMe	$CDCl_3$[e]	Enol	67.80	118.12	26.16 (q, J = 139.3 Hz)	125.66 (d, J = 162.8 Hz); 127.93 (d, J = 162.8 Hz); 129.52 (d, J = 156.6 Hz); 137.33 (s)	186.27 (s, C=S)	171.98 (s, C_α)
			Thioenol	72.88	120.33	27.46 (q, J = 140.1 Hz)	126.32 (d, J = 162.8 Hz); 127.21 (d, J = 162.0 Hz); 128.85 (d, J = 162.0 Hz); 137.07 (s)	165.89 (s, C=O)	167.43 (s, C_α)
		THF-d_8[c]	Amide	55.22 (d, J = 142.4 Hz)	114.38 (d, J = 9.4 Hz)	26.19 (q, J = 140.1 Hz)	122.91 (d, J = 162.0 Hz); 126.35 (d, J = 161.8 Hz); 128.29 (d, J = 161.2 Hz); 139.23 (s)	186.62 (ov, C=S)	161.67 (m, C=O)
			Enol	67.68	116.44	26.59 (q, J = 140.1 Hz)	126.45 (d, J = 161.2 Hz); 126.79 (d, J = 162.0 Hz); 128.06 (d, J = 160.4 Hz); 138.62 (s)	186.68 (s, C=S)	171.97 (s, C_α)

		CD_3CN[c]	Amide	55.06	114.98	26.81	123.67; 127.32; 128.91; 138.50	186.71 (C=S)	161.58 (C=O)
			Enol	67.83	118.58	26.46	126.99; 127.22; 128.60; 137.99	187.77 (C=S)	171.91 (C_α)
		DMSO-d_6	Amide	55.48	114.67	27.25 (q, J = 139.3 Hz)	123.73 (d, J = 161.2 Hz); 126.90 (d, J = 161.2 Hz); 129.07 (d, J = 161.2 Hz); 139.60 (s)	187.52 (C=S)	161.49 (C=O)
			Thioenol	73.60	116.32	30.49 (q, J = 141.6 Hz)	123.03 (d, J = 162.8 Hz); 127.41 (d, J = 162.7 Hz); 130.44 (d, J = 162.8 Hz)	166.46 (C=O)	167.42 (C_α)
p-An		$CDCl_3$[e]	Enol	67.37	118.20	27.45 (q, J = 140.5 Hz)	55.36 (q, J = 144.0 Hz); 114.08 (d, J = 160.6Hz); 128.06 (d, J = 161.3 Hz); 129.78 (t, J = 9.2 Hz); 158.63 (m)	186.64 (s, C=S)	171.93 (s, C_α)
			Thioenol	72.21	120.49	26.13 (q, J = 138.8 Hz)	55.45 (q, J = 144.2 Hz); 114.64 (d, J = 160.0 Hz); 127.68 (d, J = 162.5 Hz); 130.06 (t, J = 8.9 Hz); 159.23 (m)	166.85 (s, C=O)	167.51 (m, C_α)
		THF-d_8	Amide	55.02 (d, J = 139.7 Hz)	114.47 (d, J = 10.2 Hz)	26.26 (q, J = 138.8 Hz)	54.62 (q, J = 143.8 Hz); 113.34 (d, J = 161 Hz); 124.47 (d, J = 162.2 Hz); 132.13 (t, J = 9.2 Hz); 158.13 (m)	185.86 (d, J = 7.0 Hz, C=S)	161.77 (m, C=O)
			Enol	67.10	116.68	26.61 (q, J = 139.8 Hz)	54.55 (q, J = 143.7 Hz); 113.29 (d, J = 160 Hz); 128.28 (d, J = 161 Hz); 131.19 9t, J = 9.2 Hz);	186.97 (s, C=S)	171.91 (s, C_α)

							158.38 (m)		
			Thioenol	72.60	119.12	25.34 (w)	54.74 (q, J = 144.1 Hz); 114.30 9d, J = 160.5 Hz); 127.44 (d, J = 159.9 Hz); 130.62 (w); 159.77 (w)	166.28 (s, C=O)	167.32 (s, C_α)
		CD_3CN[c]	Amide	55.19 (d, J = 138.8 Hz)	115.08 (d, J = 10.3 Hz)	26.46 (q, J = 139.0 Hz)	54.86 (q, J = 143.2 Hz); 113.89 (d, J = 161.0 Hz); 125.22 (d, J = 161.8 Hz); 131.51 (t, J = 9.4 Hz); 158.48	187.12 (s, C=S)	161.64 (m, C=O)
			Enol	67.32	116.87	26.79 (q, J = 138.9 Hz)	55.13 (q, J = 143.3 Hz); 113.70 (d, J = 162.8 Hz); 128.74 (d, J = 161.9 Hz); 130.66 (t, J = 9.5 Hz); 158.61	186.95 (m, C=S)	171.87 (s, C_α)
		DMSO-d_6	Amide	55.76 (ov)	115.10 (d, J = 10.1 Hz)	27.24 (q, J = 140.0 Hz)	55.76 (q, J = 142.8 Hz); 114.0 (d, J = 162.3 Hz); 128.2 (d, J = 161.3 Hz); 132.1 (t, j = 9.6 Hz); 158.31	186.82 (s, C=S)	161.27 (s, C=O)
1-Np		$CDCl_3$[e]	Enol	67.72	118.17	27.56 (q, J = 141.6 Hz)	12219; 125.27; 126.35; 126.45; 126.94; 128.51; 128.72; 130.17; 133.09; 134.19	187.97 (s, C=S)	172.06 (s, C_α)
			Thioenol	73.04	120.32	26.27 (q, J = 140.1 Hz)	122.25; 124.66; 125.13; 127.06; 127.53; 128.41; 128.96; 129.63; 133.63; 134.28	167.52 (s, C=O)	167.69 (s, C_α)
		THF-d_8	Amide	54.46	114.59	26.31	122.45; 124.17; 126.25; 126.98; 127.93; 130.82;	189.56 (s, C=S)	161.89 (m,

							134.52; 135.50		C=O)
			Enol	67.39	116.69	26.64	122.87; 124.96; 125.77; 125.99; 126.49; 127.67; 127.93; 130.92; 134.26; 135.08	188.23 (m, C=S)	172.04 (s, C_α)
			Thioenol	73.02	118.32	25.50	[b]	167.50 (s, C=O)	168.02 (s, C_α)
		CD_3CN[c]	Amide	54.29 (d, J = 143.0 Hz)	[b]	26.46 (q, J = 141.6 Hz)	Overlap enol signals	188.31 (m, C=S)	161.79 (s, C=O)
			Enol	67.66	116.89	26.85 (q, J = 141.6 Hz)	122.45-128.41 (m); 130.78; 134.16; 134.47	190.01 (s, C=S)	171.97 (s, C_α)
		DMSO-d_6	Amide	54.52 (d, J = 142.7 Hz)	115.23	27.28 (q, J = 139.6 Hz)	122.65; 123.31; 124.57; 125.96; 126.77; 126.89; 127.79; 129.18; 134.25; 135.95	187.23 (C=S)	162.05 (C=O)
Me		$CDCl_3$	Amide	54.15 9d, J = 139.9 Hz)	114.37 (d, j = 10.3 Hz)	33.70 (q, J = 138.7 Hz)	27.27 (q, J = 138.5 Hz)	187.67 (m, C=S)	161.61 (m, C=O)
			Enol	66.03	118.58	30.84 (q, J = 139.2 Hz)	27.34 (q, J = 139.3 Hz)	187.36 (q, J = 4.5 Hz, C=S)	171.63 (m, C_α)
			Thioenol	70.20	121.45	32.13 (q, ov)	26.05 (q, ov)	167.77 (s, C=O)	1732.26 (s, C_α)
		C_6D_6[c]	Amide	53.88 (d, J = 140.7 Hz)	116.72 (d, J = 9.9 Hz)	32.66 (q, J = 139.8 Hz)	32.66 (q, ov)	189.16 (m, C=S)	161.60 (m, C=O)
			Enol	66.39	118.06	30.05 (q, J = 138.9 Hz)	26.29 (q, J = 140.2 Hz)	187.69 (m, C=S)	171.60 (m, C_α)
		THF-d_8	Amide	53.74 (d, J = 140.8 Hz)	114.28 (d, J = 9.8 Hz)	32.75 (q, J = 140.9 Hz)	26.08 (q, J = 141.2 Hz)	188.55 (m, C=S)	161.49 (m, C=O)

			Enol	65.76	116.86	30.11 (q, J = 140.8 Hz)	26.44 (q, ov)	187.26 (q, J = 4.7 Hz, C=S)	171.44 (m, C_α)
		CD_3CN	Amide	53.70 (d, J = 139.2 Hz)	114.87 (d, J = 10.4 Hz)	33.02 (q, J = 141.1 Hz)	26.38 (q, J = 140.9 Hz)	188.93 (m, C=S)	161.60 (m, C=O)
			Enol	65.77	117.23	30.23 (vw)	26.63 (vw)	186.97 (s, C=S)	171.45 (s, C_α)
		DMSO-d_6	Amide	53.36 (d, J = 137.6 Hz)	115.88 (d, J = 9.7 Hz)	33.77 (q, J = 140.6 Hz)	27.15 (1, J = 138.8 Hz)	189.06 (m, C=S)	161.63 (s, C=O)
Et		$CDCl_3$	Amide	54.21 (d, J = 137.0 Hz)	114.44 (d, J = 10.1 Hz)	27.25 (q, J = 140.1 Hz)	12.44 (q, J = 127.1 Hz); 41.96 (t, J = 141.1 Hz)	186.62 (m, C=S)	161.66 (m, C=O)
			Enol	65.98	118.54	27.32 (q, J = 140.3 Hz)	13.83 (q, J = 127.3 Hz); 38.81 (t, J = 141.3 Hz)	186.06 (m, C=S)	171.71 (s, C_α)
			Thioenol	70.05	Not observed	26.02 (q, J = 140.0 Hz)	14.53 (q, J = 127.7 Hz); 40.92 (t, J = 141.0 Hz)	166.45 (s, C=O)	167.80 (s, C_α)
		THF-d_8	Amide	53.83 (d, J – 138.7 Hz)	114.32 (d, J = 10.3 Hz)	26.11 (q, J = 140.8 Hz)	11.62 (q, J = 126.8 Hz); 41.11 9t, J = 141.2 Hz)	187.70 (m, C=S)	161.52 (m, C=O)
			Enol	65.86	116.84	26.45 (q, J = 140.3 Hz)	13.20 (q, J = 126.9 Hz); 38.21 (t, J = 141.2 Hz)	186.08 (m, C=S)	171.55 (m, C_α)
		CD_3CN	Amide	53.83 (d, J = 137.9 Hz)	114.96 (d, J = 10.7 Hz)	26.38 (q, J = 139.2 Hz)	11.60 (q, J = 127.5 Hz); 41.48 (t, J = 141.1 Hz)	188.03 (m, C=S)	161.58 (m, C=O)
			Enol	65.90	Not observed	26.65 (q, J = 139.4 Hz)	13.17 (q, J = 127.3 Hz); 38.40 (t, J = 141.0 Hz)	185.81 (m, C=S)	171.5 (m, C_α)
		DMSO-d_6	Amide	53.48 (d, J = 137.7 Hz)	115.94 (d, J = 10.2 Hz)	127.18 (q, J = 138.8 Hz)	12.79 (q, J = 127.1 Hz); 41.59 (t, J = 141.2 Hz)	188.07 (m, C=S)	161.61 (m, C=O)

i-Pr		$CDCl_3$	Amide	54.29 (d, J = 141.6 Hz)	114.45 (d, J = 11.0 Hz)	27.24 (q, J = 140.1 Hz)	20.54 (q, J = 128.3 Hz); 20.61 (q, ov); 48.76 (d, J = 142.4 Hz)	185.45 (m, C=S)	161.66 (s, C=O)
			Enol	65.95	118.47	27.30 (q, J = 140.8 Hz)	21.99 (q, J = 126.8 Hz); 45.47 (d, J = 141.6 Hz)	184.75 (d, J = 3.9 Hz)	171.75 (m, C_α)
			Thioenol	69.82	121.61	25.98 (q, J = 139.3 Hz)	22.88 (q, J = 127.5 Hz); [b]	165.07 (s, C=O)	167.84 (s, C_α)
		THF-d_8	Amide	53.78 (d, J = 139.7 Hz)	114.40 (d, J = 10.0 Hz)	26.10 (q, J = 140.5 Hz)	19.67 (q, J = 128.3 Hz); 19.72 (q, ov); 47.96 (d, J = 140.5 Hz)	185.14 (d, J = 36. Hz, C=S)	161.51 (s, C=O)
			Enol	66.05	116.69	26.48 (q, J = 140.5 Hz)	20.87 (q, J = 126.8 Hz); 45.22 (d, J = 141.2 Hz)	186.90 (m, C=S)	171.63 (s, C_α)
		CD_3CN	Amide	53.86 (d, J = 138.4 Hz)	115.04 (d, J = 10.5 Hz)	26.38 (q, J = 139.2 Hz)	19.65 (q, J = 127.9 Hz); 48.48 (d, J = 142.6 Hz)	187.06 (m, C=S)	161.54 (m, C=O)
			Enol	65.95	118.57	26.66 (q, J = 139.8 Hz)	20.89 (q, J = 127.9 Hz); 45.59 (d, J = 142.6 Hz)	184.72 (s, C=S)	171.64 (s, C_α)
		DMSO-d_6	Amide	53.53 (d, J = 138.8 Hz)	116.95 (d, J = 10.5 Hz)	27.14 (q, J = 138.5 Hz)	20.81 (q, J = 128.3 Hz); 48.22 (d, J = 142.1 Hz)	187.05 (s, C=S)	161.58 (s, C=O)
t-Bu		$CDCl_3$	Amide	56.11 (d, J = 139.2 Hz)	114.64 (d, J = 9.5 Hz)	27.25 (q, J = 138.3 Hz)	29.50 (q, J = 127.5 Hz); 56.86 (s)	185.31 (s, C=S)	162.09 (s, C=O)
			Enol	66.65	118.90	26.96 (q, J = 140.9 Hz)	28.76 (q, J = 128.3 Hz); 55.45 (s)	185.67 (s, C=S)	172.18 (s, C_α)
			Thioenol	70.69	121.78	26.08 (w)	[b]; 54.91 (s)	164.80 (s, C=O)	168.01 (s, C_α)
		C_6D_6[c]	Amide	55.82 (d, J = 140.1 Hz)	[b]	26.43 (q, J = 139.8 Hz)	[b]; 55.42 (s)	[b]	162.10 (s, C=O)
			Enol	67.17	118.44	26.23 (q, J = 139.8 Hz)	28.21 (q, J = 129.2 Hz); 54.93 (s)	186.21 (s, C=S)	172.09 (s, C_α)

		THF-d_8	Amide	54.83 (d, J = 140.1 Hz)	114.62 9d, J = 10.2 Hz)	26.10 (q, J = 139.3 Hz)	26.14 (q, J = 128.3 Hz); 55.62 (s)	186.88 (d, J = 7.0 Hz)	162.26 (m, C=O)
			Enol	66.88	117.24	26.40 9q, J = 139.3 Hz)	27.94 (q, J = 127.5 Hz); 54.75 (s)	186.00 (s, C=S)	171.79 (s, C_α)
		CD_3CN	Amide	55.31 (d, J = 138.3 Hz)	115.25 9d, J = 10.2 Hz)	26.40 9q, J = 139.6 Hz)	26.12 (q, J = 127.4 Hz); 56.42 (s)	187.08 (d, J = 7.5 Hz)	162.05 (s, C=O)
			Enol	66.72	117.42	26.58 (w)	27.93 (q, J = 138.7 Hz); [b]	[b]	171.83 (s, C_α)
		DMF-d_8	Amide	55.19 (d, J = 139.8 Hz)	115.92 (d, J = 10.7 Hz)	26.64 9q, J = 127.6 Hz)	26.56 (q, J = 129.8 Hz); 56.19 (s)	188.19 (d, J = 6.4 Hz)	162.17 (m, C=O)
		DMSO-d_6	Amide	55.04 (d, J = 139.3 Hz)	116.19 (d, J = 10.7 Hz)	27.11 (q, J = 137.7 Hz)	27.11 (q, J = 128.3 Hz); 56.20 9s)	187.62 (m, C=S)	161.88 (m, C=O)
p-An	$CONH_2$	THF-d_8[c]	Enol	67.16	116.52	-	54.50 (q, J = 143.6 Hz); 113.28 (d, J = 160.2 Hz); 128.24 (d, J = 161.4 Hz); 131.28 (s); 158.41 (s)	188.03 (s, C=S)	173.61 (s, C_α)
		CD_3CN	Enol	[b]	117.20	-	55.15; 113.80; 128.67; 131.5; 158.71	188 (C=S)	173.0 (C_α)
1-Np[f]		CD_3CN, DMSO-d_6							
i-Pr		$CDCl_3$[c, e]	Enol	66.51	117.77	-	21.93; 45.84	185.4 (s, C=S)	172.92 (s, C_α)
		THF-d_8	Amide	60.88	[b]	-	19.51; 19.58; 48.14	187.28 (s, C=S)	[b]

			Enol	66.22	116.63	-	20.78; 43.30	185.87 (s, C=S)	173.14 (s, C_α)
		DMSO-d_6	Amide	53.34 (d, J = 137.8 Hz)	113.5 (d, J = 9.9 Hz)	-	22.41 (q, J = 127.2 Hz); 44.63 (d, J = 143.7 Hz)	186.84 (s, C=S)	171.41 (s, C_α)
t-Bu		$CDCl_3$[e]	Enol	67.19	118.09		28.62 (q, J = 128.2 Hz); 55.81(s)	186.22 (s, C=S)	173.26 (s, C_α)
			Thioenol	70.12	121.52		29.42 (q, J = 127.9 Hz); 55.19 (s)	166.01 (s, C=O)	169.38 (s, C_α)
		THF-d_8	Amide	54.65 (d, J = 138.9 Hz)	114.73 (d, J = 10.3 Hz)		26.16 (q, J = 126.9 Hz); 55.58 (s)	187.07(s, C=S)	163.72 (s, C=O)
			Enol	67.02	117.17		27.86 (q, J = 127.6 Hz); 54.84 (s)	186.85 (s, C=S)	173.35 (s, C_α)
		CD_3CN	Amide	55.38	114.93		26.10; 55.48	186.67(s, C=S)	162.62 (s, C=O)
			Enol	66.87	118.60		27.77; 55.89	185.87 (s, C=S)	172.85 (s, C_α)
		DMF-d_7	Amide	55.52 (d, J = 140.6 Hz)	116.07 (d, J = 9.2 Hz)		26.55 (q, J = 126.6 Hz); 56.17 (s)	188.41 (s, C=S)	163.39 (s, C=O)
		DMSO-d_6	Amide	55.56 (d, J = 139.6 Hz)	116.27 (d, J = 9.5 Hz)		27.07 (q, J = 126.7 Hz); 56.22 (s)	187.80 (s, C=S)	162.99 (s, C=O)
Ph	CONHPr-*i*	$CDCl_3$[e]	Enol	67.65	117.94	22.40 (q, J = 127.1 Hz); 43.76 (d, J = 142.8 Hz)	126.20 (d, J = 161.2 Hz); 127.04 (d, J = 162.3 Hz); 128.71 (d, J = 161.8 Hz); 137.04	186.30 (m, C=S)	170.55 (m,, C_α)
			Thioenol	72.89	120.21	22.60 (q, J = 126.4 Hz); 41.50 (d, J = 138.2 Hz)	125.72 (d, J = 163.0 Hz); 127.75 (d, J = 162.1 Hz); 129.40 (d, J = 161.9 Hz); 137.26	165.77 (s, C=O)	165.95 (m, C_α)
		THF-d_8[c]	Amide	54.73 (d, J = 141.3 Hz)	114.33 (d, J = 10.3 Hz)	21.11 (q, J = 127.1 Hz);	122.96 (d, J = 162.5); 126.41 (d, J = 161.9	186.51 (m, C=S)	160.58 (m,

						21.15 (q, J = 127.1 Hz); 42.44 (d, J = 139.2 Hz)	Hz); 128.30 (d, J = 162.0 Hz); 139.12		C=O)
			Enol	67.65	116.45	21.36 (q, J = 126.8 Hz); 43.45 (d, J = 140.2 Hz)	126.23 (d, J = 161.3 Hz); 126.73 (d, J = 162.0 Hz); 128.10 (d, J = 161.7 Hz); 138.51	186.83 (m, C=S)	170.72 (m, C_{α})
		CD_3CN[a]	Amide	54.91 (d, J = 140.9 Hz)	114.97 (d, J = 10.8 Hz)	21.08 (q, J = 126.8 Hz); 42.81 (d, J = 140.4 Hz)	123.65 (d, J = 160.7 Hz); 127.26 (d, J = 161.3 Hz); 128.88 (d, J = 160.6 Hz); 138.55	186.79 (m, C=S)	160.25 (m, C=O)
			Enol	67.72	116.77	21.35 (q, J = 127.1 Hz); 43.90 (d, J = 140.1 Hz)	126.99 (d, J = 161.6 Hz); 127.22 (d, J = 161.3 Hz); 128.58 (d, J = 160.9 Hz); 137.90	187.79 (m, C=S)	170.58 (m, C_{α})
		DMSO-d_6	Amide	55.11 (d, J = 140.2 Hz)	114.52 (d, J = 10.2 Hz)	22.39 (q, J = 126.7 Hz); 42.38 (d, J = 139.9 Hz)	123.59 (d, J = 161.8 Hz); 126.99 (d, J = 162.0 Hz); 129.13 (d, J = 161.3 Hz); 139.58	187.81 (m, C=S)	160.23 (m, C=O)
i-Pr		$CDCl_3$[c]	Amide	54.42 (d, J = 139.2 Hz)	114.39 (d, J = 10.8 Hz)	22.40 (q, ov); 43.07 (d, ov)	21.82 (q, ov); 48.60 (d, ov)	185.75 (s, C=S)	160.14 (s, C=O)
			Enol	65.93	118.28	22.50 9q, J = 127.1 Hz); 43.55 (d, J = 141.8 Hz)	21.95 (q, J = 127.2 Hz); 45.39 (d, J = 142.0 Hz)	184.81 (s, C=S)	170.41 (s, C_{α})
		THF-d_8	Amide	53.53 (d, J = 140.9 Hz)	114.27 9d, J = 10.2 H)	21.07 (q, J = 127.2 Hz); 21.13 (q, ov); 42.28 (d, J = 140.6 Hz)	19.64 (q, J =- 127.2 Hz); 19.67 (q, ov); 47.97 (d, J = 142.0 Hz)	186.83 (m, C=S)	160.32 (m, C=O)

			Enol	66.04	116.67	21.42 (q, J = 126.9 Hz); 43.28 (d, J = 141.5 Hz)	20.88 (q, J = 126.9 Hz); 45.22 (d, J = 141.0 Hz)	185.25 (d, J = 3.5 Hz, C=S)	170.38 (s, C_α)
		CD_3CN	Amide	53.92 (d, J = 140.6 Hz)	115.02 (d, J 10.1 Hz)	21.10 (q, J = 126.8 Hz); 42.70 (d, J = 140.2 Hz)	19.61 (q, J = 127. 0Hz); 19.67 (q, ov); 48.44 (d, J = 141.8 Hz)	187.18 (s, C=S)	160.19 (s, C=O)
			Enol	[b]	[b]	21.60 (q, J = 126.9 Hz); 43.8 (w)	20.91 (q, ov); 45.50 (w)	[b]	[b]
		DMSO-d_6	Amide	53.91 (d, J = 140.9 Hz)	115.93 (d, J = 10.3 Hz)	22.32 (q, J = 126.6 Hz); 42.21 (d, J = 141.8 Hz)	20.66 (q, J = 128.0 Hz); 20.79 (q, ov); 48.15 (d, J = 142.0 Hz)	187.18 (s, C=S)	160.0 (s, C=O)
i-Pr	CONHC-HPh_2	CD_3CN	Amide	54.00 (d, J = 139.8 Hz)	114.80 (d, J = 10.2 Hz)	58.06 (d, J =); 127.12; 127.26; 127.61; 127.66; 128.68; 128.71; 141.04; 141.10	19.62 (q, J = 126.8 Hz); 48.60 (d, J = 142.1 Hz)	186.98	160.20
i-Pr	CONHC-HPh_2	$CDCl_3$[e]	Enol	66.48	117.93	58.65 (d, J = 142.2 Hz); 127.20; 128.10; 128.94; 139.79	22.02 (q, J = 126.8 Hz); 45.70 (d, J = 139.3 Hz)	184.82 (s, C=S)	170.62 (s, C_α)
			Thioenol	69.93	121.45	58.20 (ov); 127.25; 128.74; 128.83; 140.28	22.87 (q, J = 130.5 Hz); 48.94 (d, J = 139.9 Hz)	165.71 (s, C=O)	166.70 (s, C_α)
		THF-d_8	Amide	53.59 (d, J = 139.6 Hz)	114.08 (d, J = 10.2 Hz)	57.49 (d, J = 141.8 Hz); 126.54-128.47 (m); 141.20	19.62 (q, J = 127.2 Hz); 48.20 (d, J = 140.1 Hz)	186.63 (m, C=S)	160.23, (m, C=O)

			Enol	66.93	116.33	58.19 (d, J = 142.9 hz); 126.54-128.47 (ov); 140.63	20.79 (q, J = 127.0 Hz); 45.44 (d, J = 141.0 Hz)	185.28 (s, C=S)	170.68 (s, C_α)
		CD_3CN	Amide	53.99 (d, J = 140.0 Hz)	114.80 (d, J = 10.3 Hz)	58.06 (d, J = 141.2 Hz); 127.12; 127.26; 127.61; 127.66; 128.68; 128.71; 141.04; 141.10	19.62 (q, J = 126.8 Hz); 48.60 (d, J = 140.2 Hz)	186.98 (s, C=S)	160.20 (s, C=O)
		DMSO-d_6	Amide	54.16 (d, J = 137.6 Hz)	115.87 (d, J = 10.4 Hz)	57.46 (d, J = 139.5 Hz); 127.51-129.10 (m); 141.90	20.69 (q, J = 128.0 Hz); 20.90 (q, J = 126.7 Hz); 48.30 (d, J = 144.4 Hz)	186.86 (s, C=S)	160.18 (s, C=O)
t-Bu		$CDCl_3$	Amide	56.91 (d, J = 137.7 Hz)	114.25 (d, J = 9.6 Hz)	58.25 (d, J = 137.2 Hz); 125.98-128.89 (ov); 141.34	26.88 (q, J =127.3 Hz); 55.07 (s)	185.20 (m, C=S)	160.35 (m, C=O)
			Enol	67.03	118.35	58.47 (d, J = 142.0 Hz); 125.98-128.89 (m); 139.86	28.71 (q, J = 127.2 Hz); 55.65 (s)	185.52 (s, C=S)	170.95 (m, C_α)
			Thioenol	70.67	121.66	57.07 (d, J = 139.4 Hz); 125.98-128.89 (ov); 140.41	29.46 (q, J =128.0 Hz); 56.69 (s)	165.35 (s, C=O)	166.38 (s, C_α)
		THF-d_8[d]	Amide	54.79 (d, J = 142.0 Hz)	114.38 (d, J = 10.4 Hz)	57.50 (d, J = 140.3 Hz); 127.13; 127.18; 127.25; 127.41; 128.22; 140.99	26.12 (q, J =127.1 Hz); 55.81 (s)	186.57 (m, C=S)	161.19 (m, C=O)

		CD_3CN	Amide	55.59 (d, J = 141.3 Hz)	115.09 (d, J = 10.2 Hz)	57.99 (d, J = 140.8 Hz); 127.12; 127.26; 127.36; 127.61; 128.60; 128.68; 140.90; 141.12	26.10 (q, J = 127.3 Hz); 56.58 (s)	187.08 (s, C=S)	160.64 (s, C=O)
		DMSO-d_6	Amide	56.08 (d, J = 139.9 Hz)	116.12 (d, J = 10.8 Hz)	57.33 (d, J = 141.0 Hz); 127.45; 127.65; 127.88; 128.80; 129.0; 141.89	27.05 (q, J = 126.9 Hz); 56.30 (s)	187.34 (s, C=S)	160.36 (s, C=O)
t-Bu	CONHPh	$CDCl_3$	Amide	[b]	114.51 (d, J = 10.3 Hz)	120.33; 121.57; 125.67; 136.44	26.82 (q, J = 126.9 Hz); 58.16 (s)	185.10 (s, C=S)	158.79 (s, C=O)
			Enol	67.84	118.31	122.38; 124.48; 126.03; 135.39	28.78 (q, J =127.2 Hz); 55.94 (s)	185.43 (s, C=S)	170.41 (s, C_α)
			Thioenol	71.31	120.43	120.93; 129.05; 129.26; 137.33	29.55 (q, J =127.6 Hz); 55.43 (s)	165.92 (s, C=O)	165.92 (ov, C_α)
		CD_3CN	Amide	56.10 (d, J = 138.3 Hz)	114.91 (d, J = 10.2 Hz)	119.71 (d, J = 164.0 Hz); 124.49 (d, J = 160.3 Hz); 128.95 (d, J = 163.1 Hz); 138.04 (s)	26.10 (q, J = 129.3 Hz); 56.79 (s)	186.94 (s, C=S)	160.76 (s, C=O)
		DMSO-d_6	Amide	56.25	116.38	119.69; 124.35; 129.36; 138.82	27.17; 56.25 (ov)	187.23 (C=S)	161.44 (C=O)

[a] A singlet unless otherwise stated. [b] Signal was not observed. [c] Thioenol signals were not observed. [d] Enol signals were not observed. [e] Amide signals were not observed. [f] Decomposed in CD_3CN and DMSO-d_6. ov = Overlaps other signals; w = weak signal. vw = Very weak signal.

Table S3. Selected ^{13}C NMR Spectral Data (in ppm) for **11/12/13** Systems in $CDCl_3$ at Room Tempereture

Compd.		Enol, **11**			Amide-thioamide, **12**			Thioamide, **13**		
Number	R^3	C=S, C_α(E)[a]	C≡N[a]	C_β[a]	C=S, C=O	C≡N[b]	CH[c]	C=O, C_α(TE)[a]	C≡N[a]	C_β[a]
11a/12a/13a	Ph	188.35, 171.15	119.44	68.09	183.54, 162.31	113.85	51.26	167.72, 167.98	120.52	72.60
11b/12b/13b	*p*-An	188.67, 171.03	119.50	67.61	183.16, 162.24	113.96	50.98	168.08, 168.73	120.70	71.69
11c/12c/13c	1-Np	189.88, 171.06	119.64	67.90	186.19, 162.30	114.01	50.62	168.22, 169.34	120.54	72.58
11d/12d/13d	Me	189.10, 170.82	119.85	66.56	186.65, 161.94	114.04	50.17	[d]	[d]	[d]
11e/12e/13e	Et	187.73, 170.87	119.71	66.54	185.63, 161.91	114.00	50.16	[d]	[d]	[d]
11f/12f/13f	*i*-Pr	186.41, 171.00	119.66	66.56	184.44, 161.92	113.96	50.15	[d]	[d]	[d]
11g/12g/13g	*t*-Bu	187.26, 171.55	120.04	67.21	184.34, 162.37	114.23	51.98			
11h/12h/13h	Ph	186.27, 171.98	118.12	67.80	[e]	[e]	[e]	165.89, 167.43	120.33	72.88
11i/12i/13i	*p*-An	186.64, 171.93	118.20	67.37	[e]	[e]	[e]	166.85, 167.51	120.49	72.21
11j/12j/13j	1-Np	187.97, 172.06	118.17	67.72	[f]	[f]	[f]	167.52, 167.69	120.32	73.04
11k/12k/13k	Me	187.36, 171.63	118.58	66.03	187.67, 161.61	114.37	54.15	167.77, 173.26	121.45	70.20
11l/12l/13l	Et	186.06, 171.71	118.54	65.98	186.62, 161.66	114.44	54.21	166.45, 167.80	121.48	70.05

11m/12m/13m	*i*-Pr	184.75, 171.75	118.47	65.95	185.45, 161.66	114.45	54.29	165.07, 167.84	121.61	69.82
11n/12n/13n	*t*-Bu	185.67, 172.18	118.90	66.65	185.31, 162.09	114.64	56.11	164.80, 168.01	121.78	70.69
11s/12s/13s	*t*-Bu	186.22, 173.26	118.08	67.19	[f]	[f]	[f]	166.01, 169.38	121.52	70.12
11t/12t/13t	Ph	186.30, 170.55	117.94	67.65	184.50, [e]	[e]	55.00	165.77, 165.95	120.21	72.90
11u/12u/13u	*i*-Pr	184.81, 170.41	118.28	65.93	185.75, 160.14	114.39	54.43	[e]	[e]	[e]
11v/12v/13v	*i*-Pr	184.82, 170.62	117.93	66.48	185.50, 160.22	114.19	58.65	165.71, 166.25	121.45	69.93
11w/12w/13w	*t*-Bu	185.52, 170.95	118.35	67.03	185.40,160.35	114.25	58.47	165.35, 166.38	121.66	70.67
11x/12x/13x	*t*-Bu	185.43, 170.41	118.31	67.84	185.00, 158.78	114.51	55.43	165.92,165.92	121.57	71.31

[a] Singlet. [b] Doublet, J= 9.5-11.0 Hz. [c] Doublet, J= 139.2-143.2 Hz. [d] The thioenol was not observed. [e] The signal was not observed. [f] The amide was not observed.

Table S4. Structures of the Solid Tautomers of I (*i*-PrNH(C=Z)CH(CN)$CONMe_2$), II (PhNH(C=Z)CH(CN)CONHMe) and III (*p*-AnNH(C=Z)CH(CN)CONHMe) and Comparison of Selected Bond Lengths and Angles

Compd.	I			II			III		
Species	Z= O	Z= S	Δ_{OS}	Z= O	Z= S	Δ_{OS}	Z= O	Z= S	Δ_{OS}
% Enol[a]	80	12		90	46[b]		90	43[c]	
Structure	Amide	Amide		Amide	Enol		Enol	Enol	
Bond	length, Å								
C(1)-C(2)	1.532(4)	1.5416	0.0096	1.543(3)	1.4257	0.1173	1.401(5)	1.422(3)	0.021
C(2)-C(3)	1.545(3)	1.5442	0.003	1.547(3)	1.4265	0.1205	1.440(5)	1.423(3)	0.017
C(1)-O(1)	1.220(3)	1.2292	0.0092	1.224(3)	1.3009	0.0769	1.301(4)	1.305(3)	0.004
C(1)-N(1)	1.335(3)	1.3297	0.0053	1.312(3)	1.3181	0.0061	1.327(5)	1.315(3)	0.012
Z(1)-H					1.06		1.17(5)	1.14	0.03
Angle	deg, °								
O1C1C2	119.9(2)	119.67	0. 23	118.9(2)	122.67	3.77	119.4(3)	122.7	3.3
C1C2C3	109.8(2)	112.30	2.5	107.45	124.86	17.41	119.4(3)	124.6	5.2
OHZ					160(2)		159(4)	159(2)	0

[a] In $CDCl_3$. [b] 50% Thioenol. [c] 53% Thioenol.

Table S5. δ(OH) Values and the Differences Δ_{os} (ppm), K_{Enol} Values and $K_{Z=O}/K_{Z=S}$ Ratios for $R^3NH(C{=}Z)C(CN){=}C(OH)NR^1R^2$ for Z = O and Z = S in $CDCl_3$

Compound		δ(ZH)			K_{Enol}		
NR^1R^2	R^3	Z = O	Z = S	Δ_{os}	Z = O	Z = S[a]	$K_{Z=O}/K_{Z=S}$[a]
NMe_2	Ph	17.79	16.64	1.15	4.00	0.40(0.67)	10.0(5.97)
	p-An	17.88	16.62	1.26	4.00	0.38(0.63)	10.5(6.4)
	i-Pr	18.18	16.49	1.69	4.00	0.14(0.15)	28.6(26.7)
	t-Bu	18.42	16.62	1.62	2.70	0.04(0.04)	67.5 (67.5)
NHMe	Ph	17.65	16.83	0.82	9.00	11.5(24.0)	0.78(0.38)
	p-An	17.71	16.81	0.90	9.00	11.7(25.9)	0.77(0.35)
	i-Pr	17.73	16.68	1.05	11.5	2.87(3.35)	4.01(3.43)
	t-Bu	17.80	16.88	0.92	5.25	1.18(1.64)	4.45(3.20)
NH_2	Ph	17.32	16.63	0.69	≥50	≥50(≥50)	-
	i-Pr	17.53	16.48	1.05	≥50	≥50(≥50)	-
	t-Bu	19.59	16.66	0.93	≥50	10.6(14.1)	-
NHPr-*i*	*i*-Pr	17.76	16.64	1.12	8.06	3.15(3.47)	2.57(2.33)

[a] Data in parentheses are related to K_{Total} or to values based on K_{Total}.

Table S6. Analytical Data, mp's and Yield for "formal" $R^1R^2NCOCH(CN)CSNHR^3$

Compound					Calculated %			Found		
R^1R^2	R^3	Formula	mp, ˚C	yield, %	C	H	N	C	H	N
Me_2	Ph	$C_{12}H_{13}N_3OS$	139-40	64	58.30	5.26	17.00	58.18	5.35	17.09
Me_2	*p*-An	$C_{13}H_{15}N_3O_2S$	135-6	72	56.32	5.42	15.16	56.36	5.49	15.11
Me_2	1-Np	$C_{16}H_{15}N_3OS$	140-1	79	64.65	5.05	14.14	64.48	5.04	14.35
Me_2	Me	$C_7H_{11}N_3OS$	138-9	78	45.41	5.95	22.70	45.67	6.10	22.41
Me_2	Et	$C_8H_{13}N_3OS$	131-2	51	48.24	6.53	21.11	47.88	6.35	20.67
Me_2	*i*-Pr	$C_9H_{15}N_3OS$	147-9	92	50.70	7.04	19.72	50.30	7.06	19.42
Me_2	*t*-Bu	$C_{10}H_{17}N_3OS$	144-5	85	52.86	7.49	18.50	53.05	7.37	18.27
H Me	Ph	$C_{11}H_{11}N_3OS$	153-5[a]	80	56.65	4.72	18.03	56.29	4.77	17.76
H Me	*p*-An	$C_{12}H_{13}N_3O_2S$	143-5	57	54.75	4.94	15.97	54.62	4.93	16.02
H Me	1-Np	$C_9H_{15}N_3OS$	158-60	89	63.60	4.59	14.84	63.30	4.65	14.98
H Me	Me	$C_6H_9N_3OS$	139-41[b]	77	42.11	5.26	24.56	42.39	5.26	24.46
H Me	Et	$C_7H_{11}N_3OS$	135-6	34	45.41	5.95	22.70	45.48	6.02	22.93
H Me	*i*-Pr	$C_8H_{13}N_3OS$	130-2	81	48.24	6.53	21.11	47.99	6.56	21.31
H Me	*t*-Bu	$C_9H_{15}N_3OS$	149-50	82	50.70	7.04	19.72	50.75	7.11	19.61
H_2	Ph	$C_{10}H_9N_3OS$	183-4 dec[c]	72	54.79	4.11	19.18	54.91	4.15	19.31
H_2	*p*-An	$C_{11}H_{11}N_3O_2S$	165-6[d]	51	53.01	4.42	16.87	52.87	4.39	17.06
H_2	1-Np	$C_{14}H_{11}N_3OS$	185-6 dec	78	62.45	4.09	15.61	62.17	4.18	15.57

H_2	*i*-Pr	$C_7H_{11}N_3OS$	145-6	68	45.41	5.95	22.70	45.86	6.03	21.21
H_2	*t*-Bu	$C_8H_{13}N_3OS$	159-60 dec	63	48.24	6.53	21.11	47.90	6.60	20.96
H *i*-Pr	Ph	$C_{13}H_{15}N_3OS$	128-30	80	59.77	5.75	16.09	59.58	5.69	15.92
H *i*-Pr	*i*-Pr	$C_{10}H_{17}N_3OS$	157-8	74	52.86	7.49	18.50	52.82	7.46	18.24
H Ph	*t*-Bu	$C_{14}H_{17}N_3OS$	147-8 dec	87	61.09	6.18	15.25	59.95	5.91	15.04
H $CHPh_2$	*i*-Pr	$C_{20}H_{21}N_3OS$	163-4	89	68.38	5.98	11.96	67.96	6.05	11.85
H $CHPh_2$	*t*-Bu	$C_{21}H_{23}N_3OS$	166-8	73	69.04	6.30	11.51	69.14	6.33	11.23

[a] lit. [10a] mp 154-6 °C. [b] lit. [10c] mp 136 °C for the enol isomer and 142 °C for the amide isomer. [c] lit. [10d] mp 186-7 °C. [d] lit. [10f] mp 166-7 °C.

Spectral data and procedures for formation of several products.

(a) 11a-g/12a-g/13a-g. NMR spectral data of **11f/12f** δ_H (400 MHz, 298 K, $CDCl_3$) (**Amide 12f**): 1.25, 1.34 (2x3H, d, J = 6.4, *i*-Pr-*Me*), 3.01(3H, s, NMe), 3.21 (3H, s, NMe), 4.48 (1H, oct, J = 6.4, *i*-Pr-C*H*), 5.22 (1H, s, CH), 8.62 (1H, s, NH). (**Enol 11f**): 1.25 (*i*-Pr-*Me*, overlaps a **12f** signal), 3.18 (0.9 H, s, NMe), 4.59 (0.15 H, oct, J = 6.4, *i*-Pr-C*H*), 6.81 (0.13 H, s, NH), 16.49 (0.14 H, s, OH).

The *tert*-butyl derivative **11g**, mp 144-5 ˚C was prepared similarly to the preparation of **11f/12f** in 85% yield. The ethyl derivative **11e**, mp 131-2 ˚C (0.51 g, 51%) was similarly obtained from 0.56 g, (15 mmol) of cyanoacetamide and ethyl isothiocyanate (0.44 mL, 5 mmol). The phenyl and *p*-anisyl derivatives **11a** and **11b**, mp 139-40 ˚C and 135-6˚C, respectively, were prepared similarly, in 64 and 72% yield, respectively. In these cases the solid was dissolved immediately after adding the more reactive isothiocyanates. The 1-naphthyl derivative **11c**, was similarly prepared except that after completing the isothiocyanate addition, all the Na salt had been dissolved. However, after starting to heat the solution a white precipitate of the Na salt $[1\text{-NpNHCHC(CN)CONMe}_2]^-Na^+$ was obtained.

δ_H (300 MHz, 298 K, DMSO): 2.95 (6H, s, NMe_2), 7.42 (1H, t, J = 7.8), 7.51 (2H, m. Ar), 7.61 (1H, d, J = 8.4 Hz, Ar), 7.89 (1H, d, J = 7.2, Ar)), 8.06 (1H, d, J = 7.8, Ar), 8.37 (1H, d, J = 7.8, Ar), 13.09 (1H, s, NH). The solution of the salt in DMF (5 mL) was added dropwise to an ice-cold solution of 6% HCl (100 mL), the yellow solid formed was filtered and washed with cold water (500 mL), giving 2.35 g (79%) of **11c**, mp 140-1 ˚C. The spectral and analytical data for all the compounds are given in Tables 3, S1-S3 and S6.

(b) 11h-n/12h-n/13h-n. The *p*-anisyl derivative **11i**, mp 143-5 ˚C was obtained, similarly to **11j** in 57% yield and the isopropyl derivative **11m**, 132-4 ˚C was obtained in 81% yield. The *tert*-butyl derivative **11n** (1.75 g, 82%) was similarly obtained from *N*-methylcyanoacetamide (0.98 g, 10 mmol) and *tert*-butyl isothiocyanate (1.16 mL, 10 mmol) in dry THF, but after 4 hrs reflux most of the solvent was evaporated. The concentrated THF solution of the Na salt (5 mL) was added dropwise into an ice-cold solution of 6% HCl, giving pure white **11n**, mp 149-50 ˚C.

The δ_H (400 Hz, 298 K, $CDCl_3$) displayed signals in a ratio of 45:37:18 of **11n**:**12n**:**13n**, respectively. (**12n**): 1.53 (7.9 H, s, *t*-Bu), 2.87 (2.6 H, d, J = 4.8, NMe), 4.79 (0.84 H, s, CH), 7.05 (0.8 H, s, NH), 8.74 (0.78 H, s, NH). (**11n**): 1.54 (8.7 H, s, *t*-Bu), 2.94 (3.0 H, d, J = 4.8, NMe), 6.05 (0.98 H, s, NH), 6.55 (0.98 H, s, NH), 16.88 (0.98 H, d, J = 1.2, OH). (**13n**): 1.47 (3.7 H, s, *t*-Bu), 2.81 (1.3 H, d, J = 4.8, NMe), 4.79 (0.35 H, s, SH), 5.81 (0.4 H, s, NH), 11.61 (0.35 H, s, NH). δ_C (100.133 MHz, 298 K, $CDCl_3$). (**12n**): 27.25 (q, J = 138.3, NMe), 29.50 (q, J = 127.5, Me), 56.11 (d, J = 139.2, CH), 56.86 (s, *C*Me_3), 114.64 (d, J = 9.5, CN), 162.09 (s, C=O), 185.31 (s, C=S). (**11n**): 26.96 (q, J = 140.9, NMe), 28.76 (q, J = 128.3, Me), 55.45 (s, *C*Me_3), 66.65 (s, C_β), 118.90 (s, CN): 172.18 (s, C_α), 185.67 (s, C=S). (**13n**): 26.08 (w, CNMe), 28.76 (overlaps an **11n** signal), 54.91 (s, *C*Me_3), 70.69 (s, C_β), 121.78 (s, CN), 164.80 (s, C=O), 168.01 (s, C_α).

The ethyl derivative, mp 135-6 ˚C, was prepared similarly in 34% yield. The spectral and analytical data for all the compounds are given in Tables 3, S1-S3 and S6.

(c) 11o-s/12o-s/13o-s. The phenyl derivative **11o**, mp 183-4 ˚C, was formed in 72% yield, the *p*-anisyl derivative **11p**, mp 165-6 ˚C, was obtained in 51% yield, and the 1-naphthyl derivative **11g**, mp 185-6 ˚C (dec), was obtained in 78% yield. The *i*-Pr derivative **11r**, mp 145-6 ˚C (dec), and the *t*-Bu derivatives **11s**, mp 159-60 ˚C (dec), were obtained in 68% and 63% yield, respectively. Attempt to crystallize these five compounds for X-ray diffraction analysis gave different heterocyclic products. The spectral and analytical data for all the compounds are given in Tables 3, S1-S3 and S6.