Selective Synthesis of *N*-Cyano Sulfilimines by Dearomatizing Stable Thionium Ions

Sang Mee Kim,[†‡] On-Yu Kang,[†¶] Hwan Jung Lim,*[†§] and Seong Jun Park,*[†]

[†]Department of Drug Discovery, Korea Research Institute of Chemical Technology (KRICT), 141 Gajeong-ro, Daejeon 34114, Republic of Korea

[‡]Department of Chemistry, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul 04107, Republic of Korea

[¶]Department of Chemistry, Sungkyunkwan University, 2066 Seobu-ro, Suwon 16419, Republic of Korea

[§]Department of Medicinal and Pharmaceutical Chemistry, University of Science & Technology, 217 Gajeong-ro, Daejeon 34113, Republic of Korea

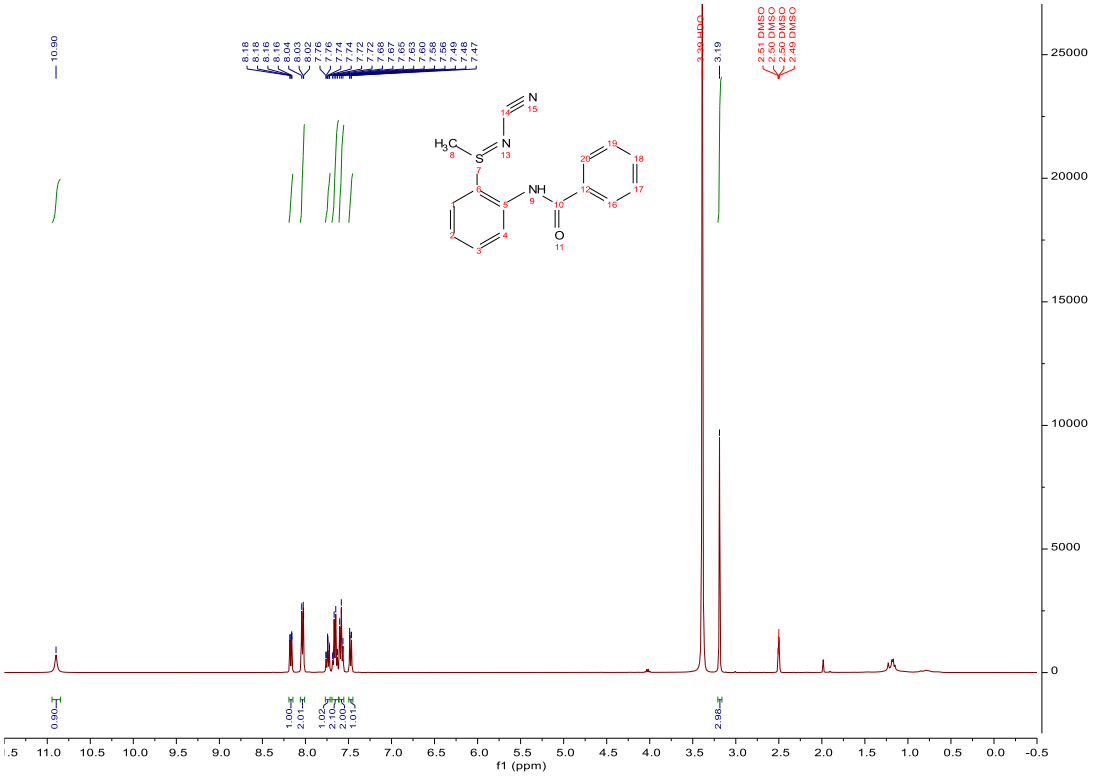
Email of corresponding author: Seong Jun Park – sjunpark@krict.re.kr

Supporting information

Contents

Figure S1 – S18. NMR spectroscopies of **2a** to **14**

Figure S1. ^{1}H and ^{13}C NMR spectroscopy of 2a



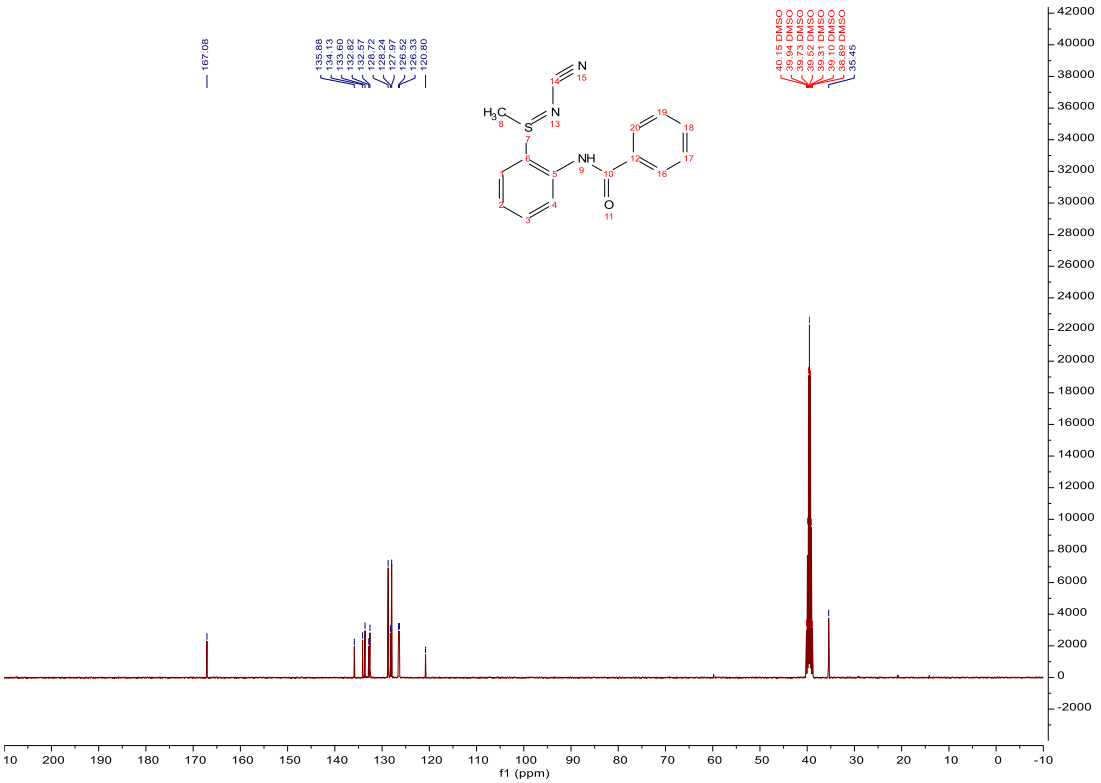
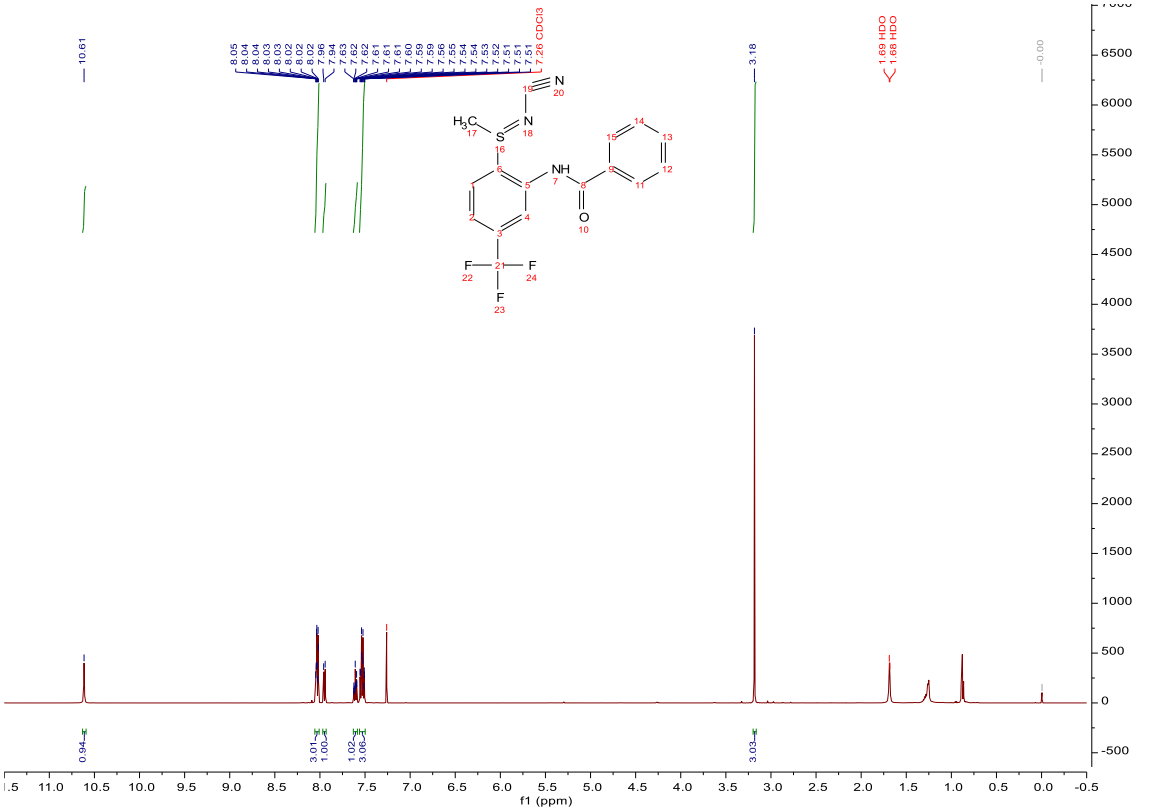


Figure S2. ^{1}H and ^{13}C NMR spectroscopy of 2b



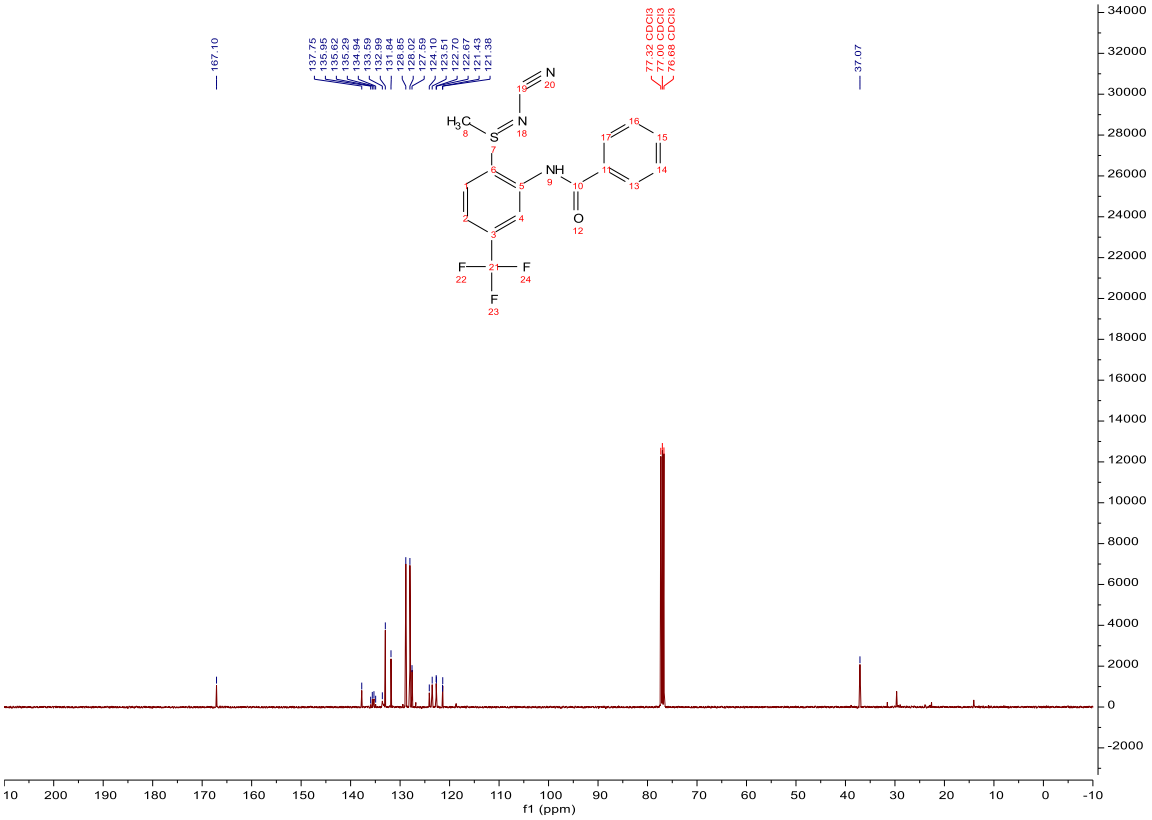


Figure S3. ^{19}F NMR spectroscopy of 2b

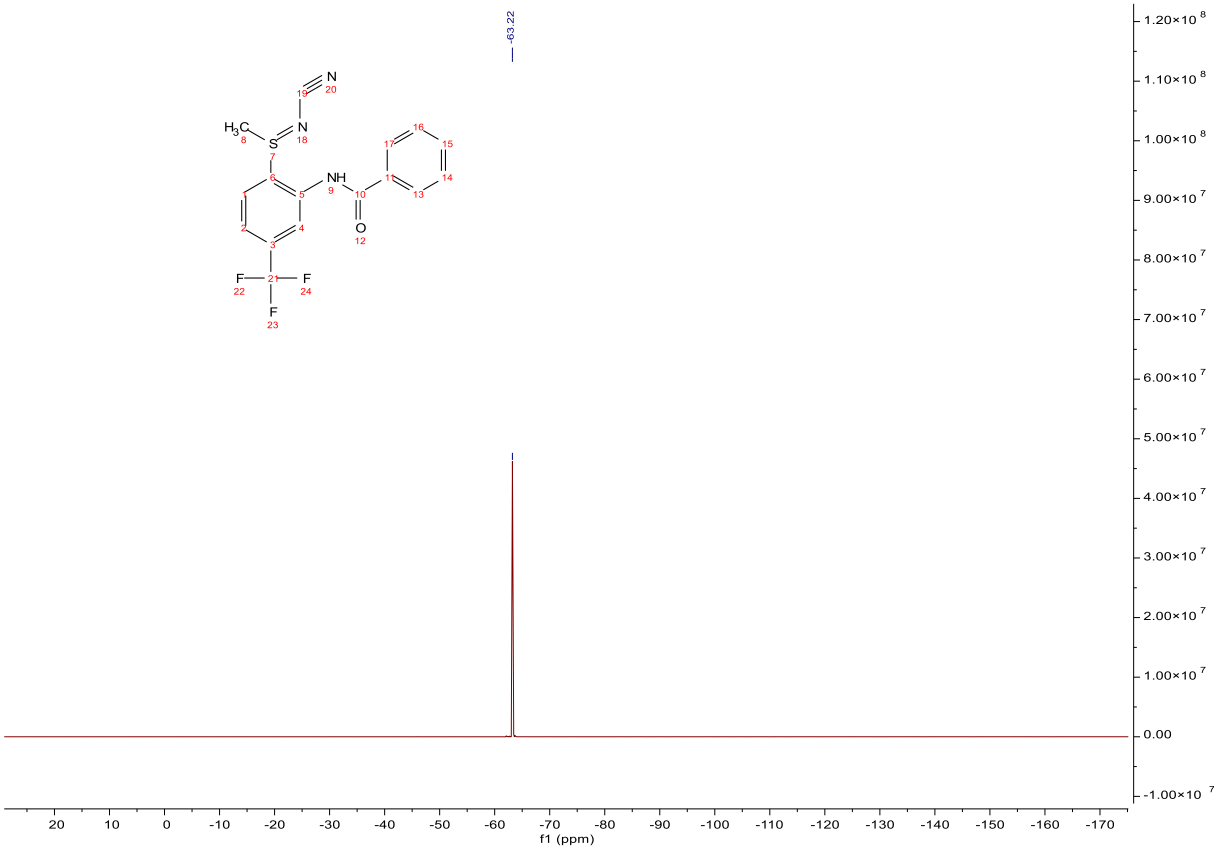
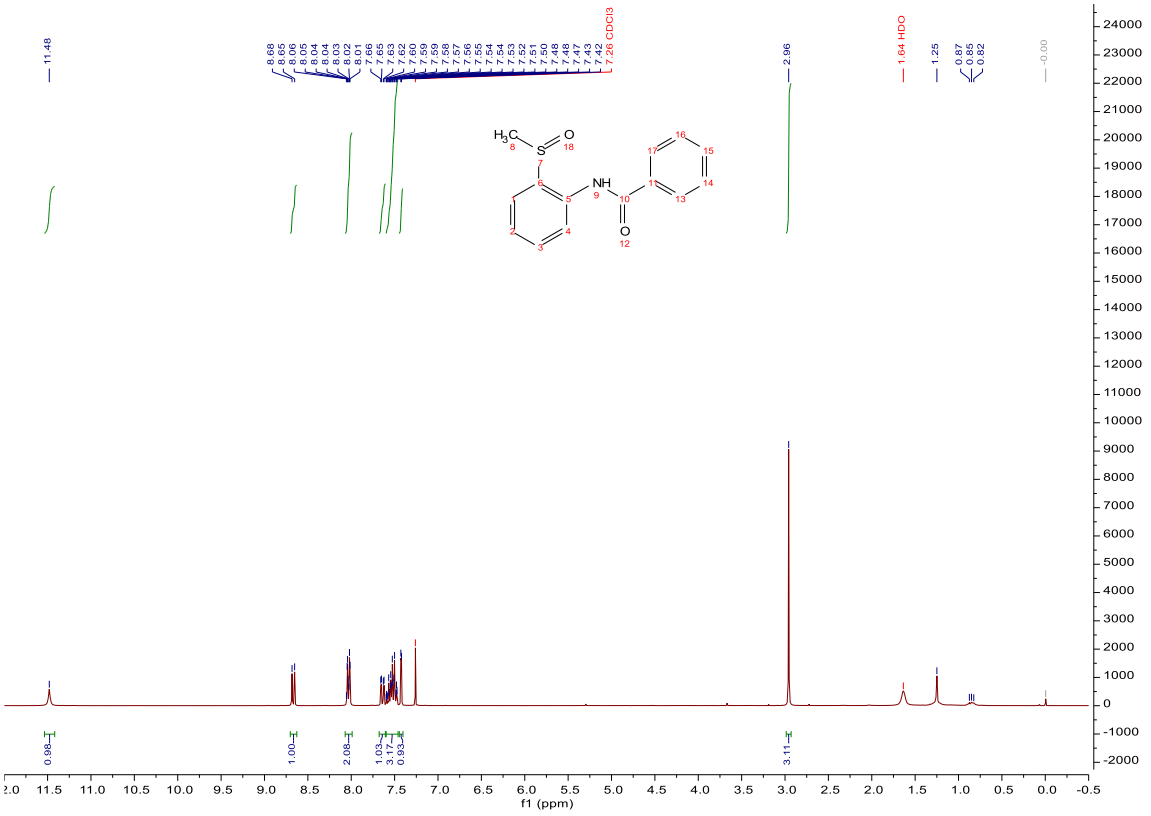


Figure S4. ^{1}H and ^{13}C NMR spectroscopy of 2c[1-3]



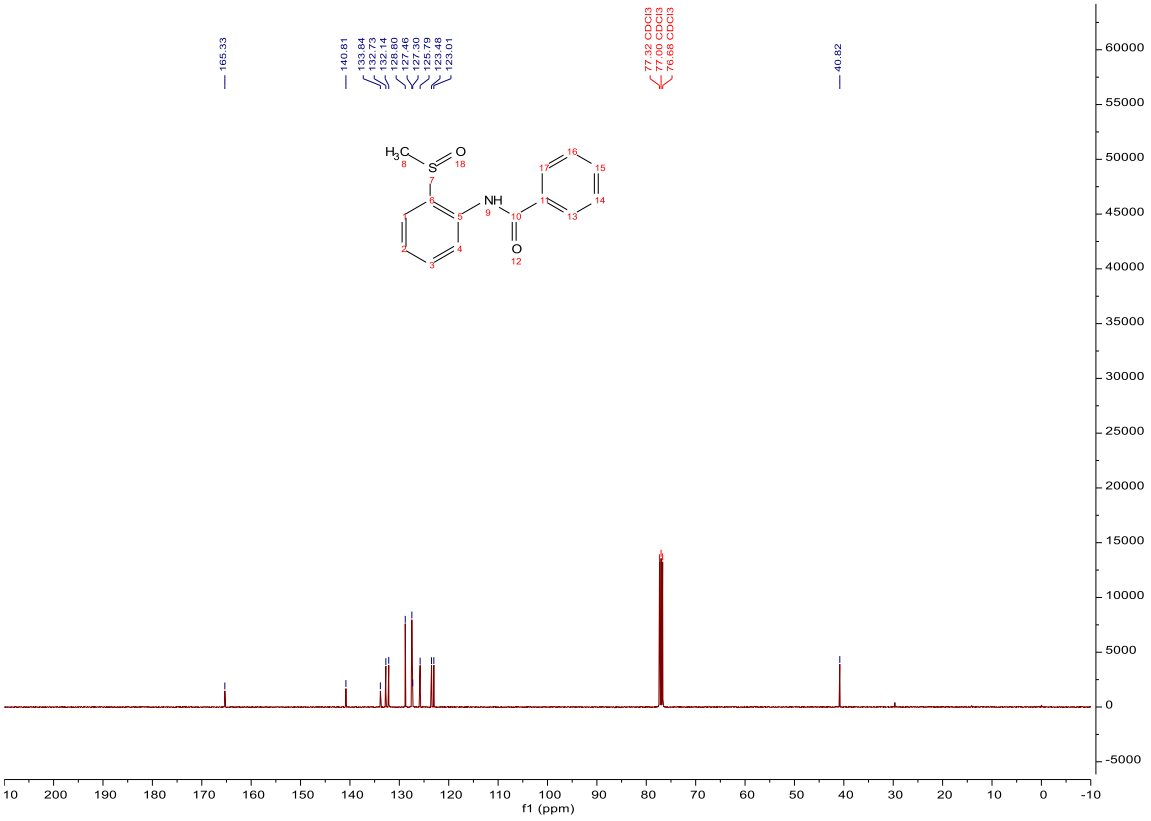
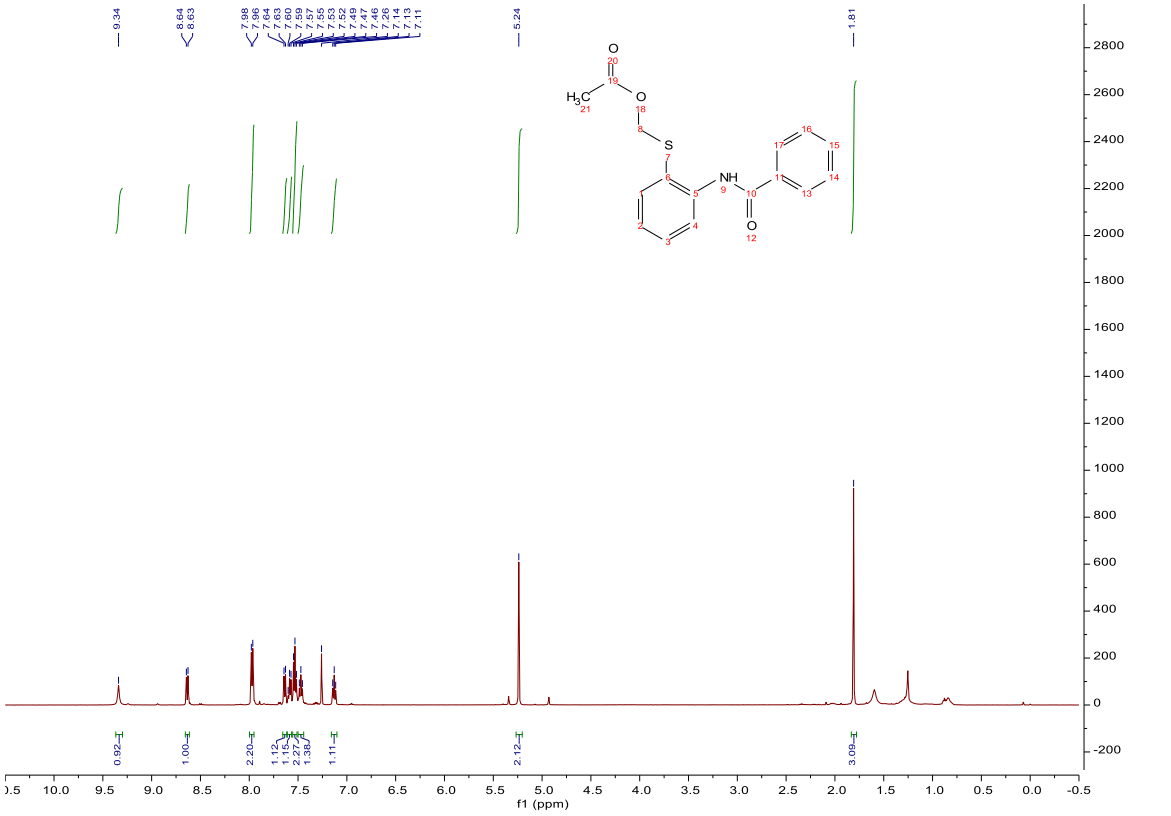


Figure S5. ^{1}H and ^{13}C NMR spectroscopy of 2d



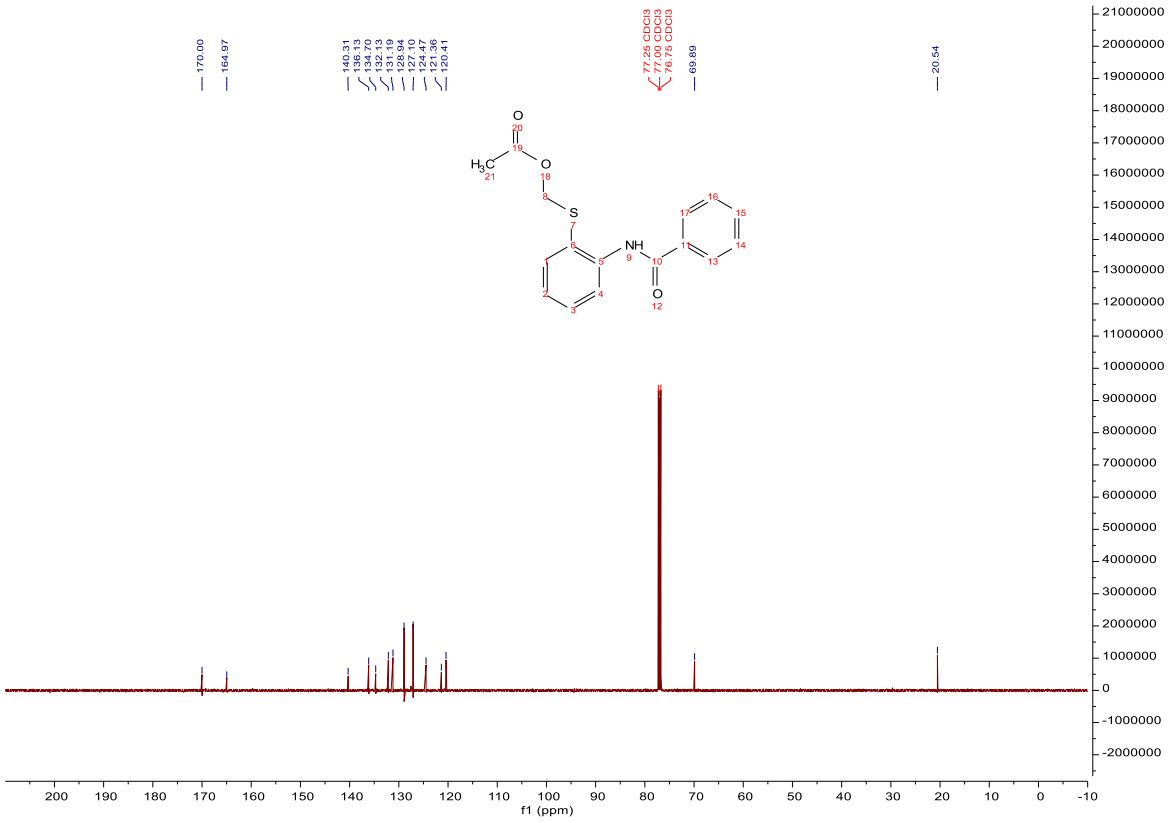


Figure S6. ^{1}H and ^{13}C NMR spectroscopy of 2e

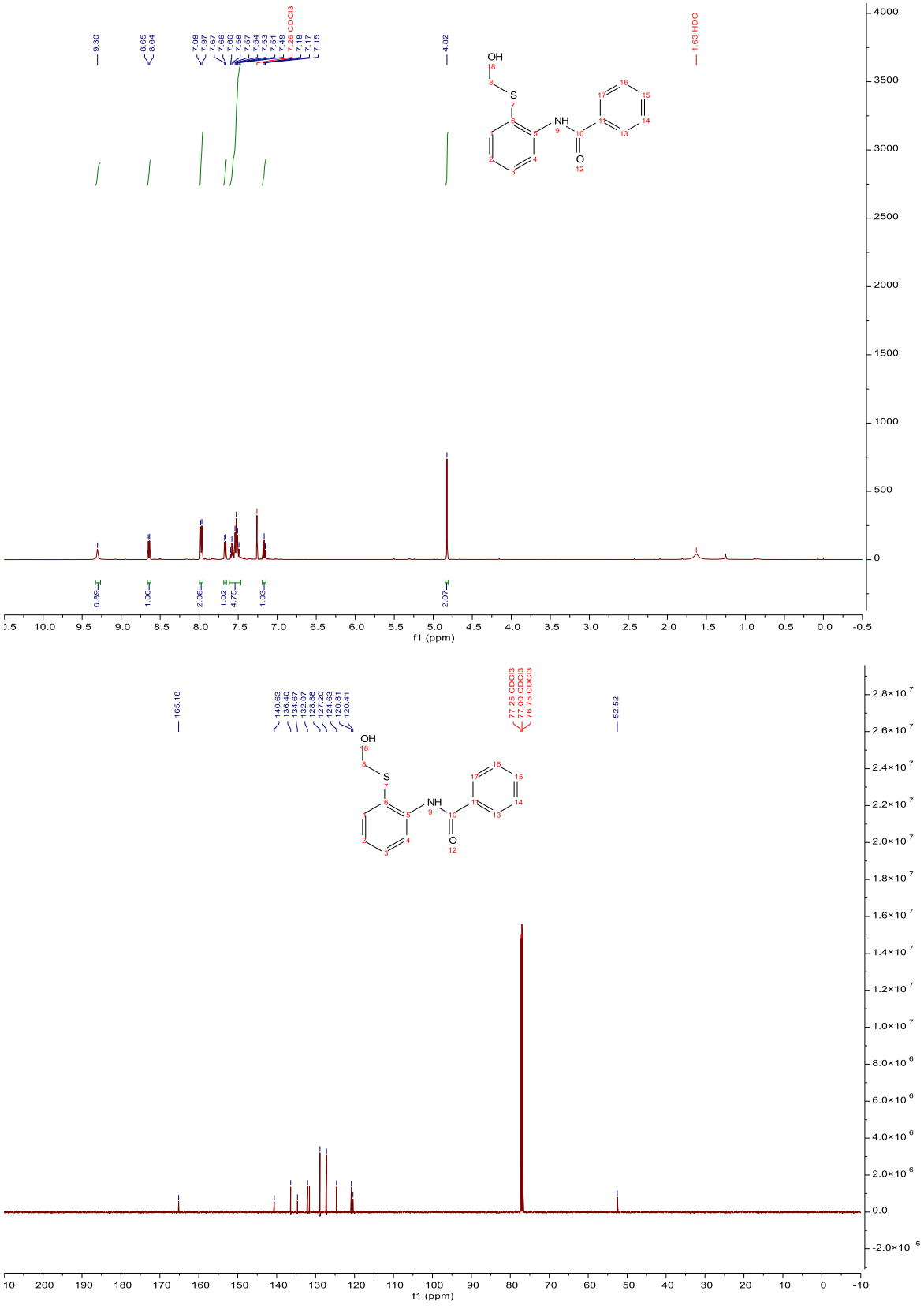
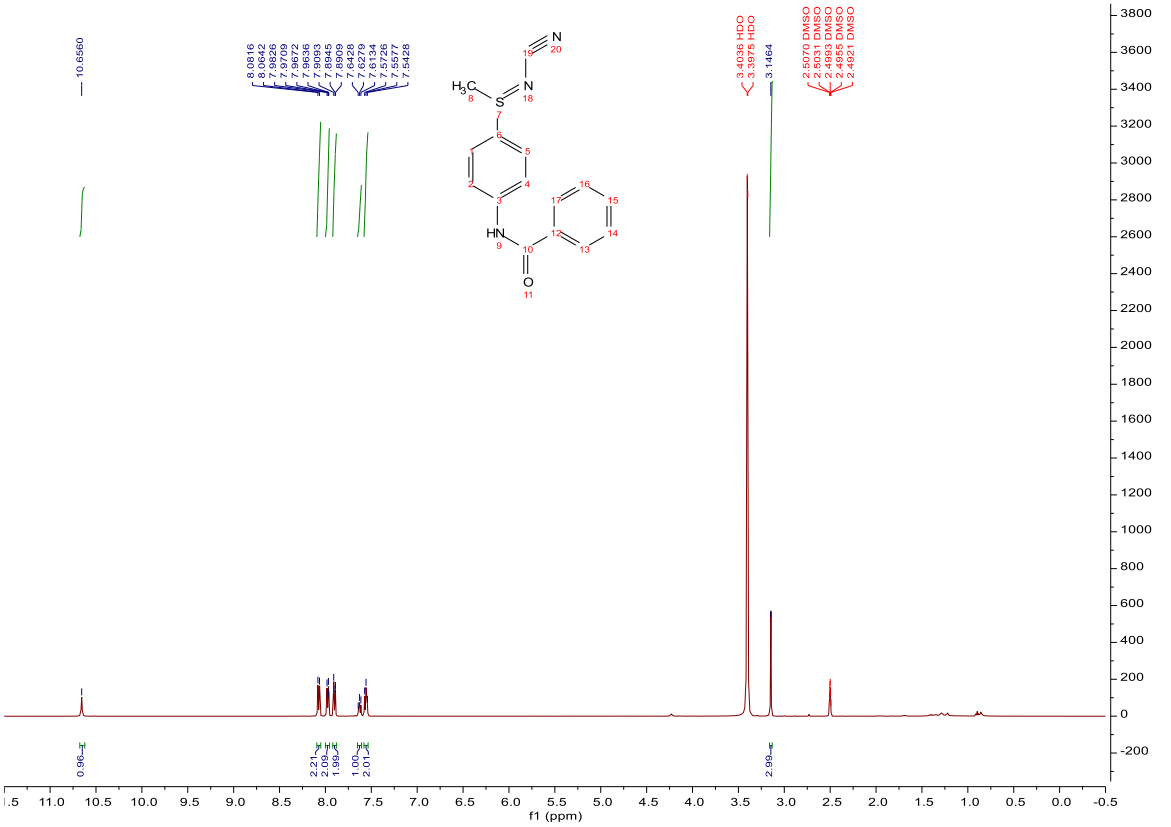


Figure S7. ^{1}H and ^{13}C NMR spectroscopy of 3



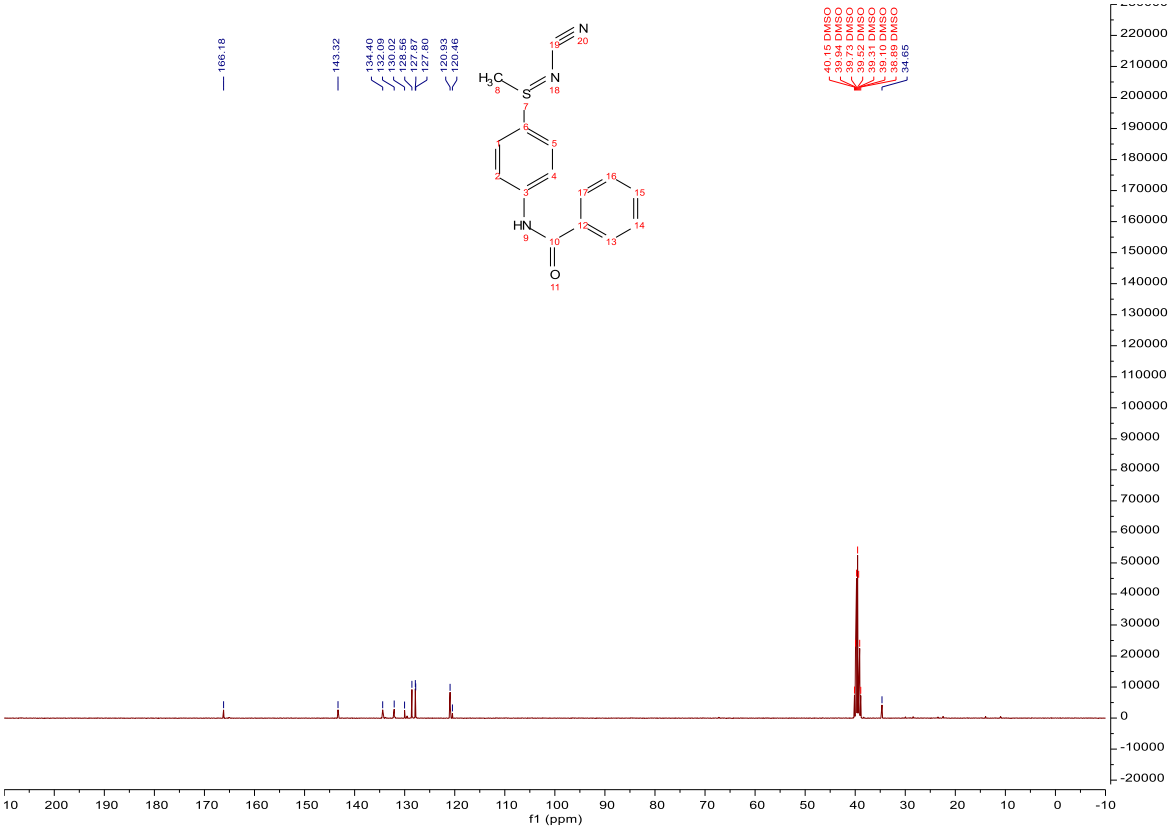


Figure S8. ^{1}H and ^{13}C NMR spectroscopy of 4

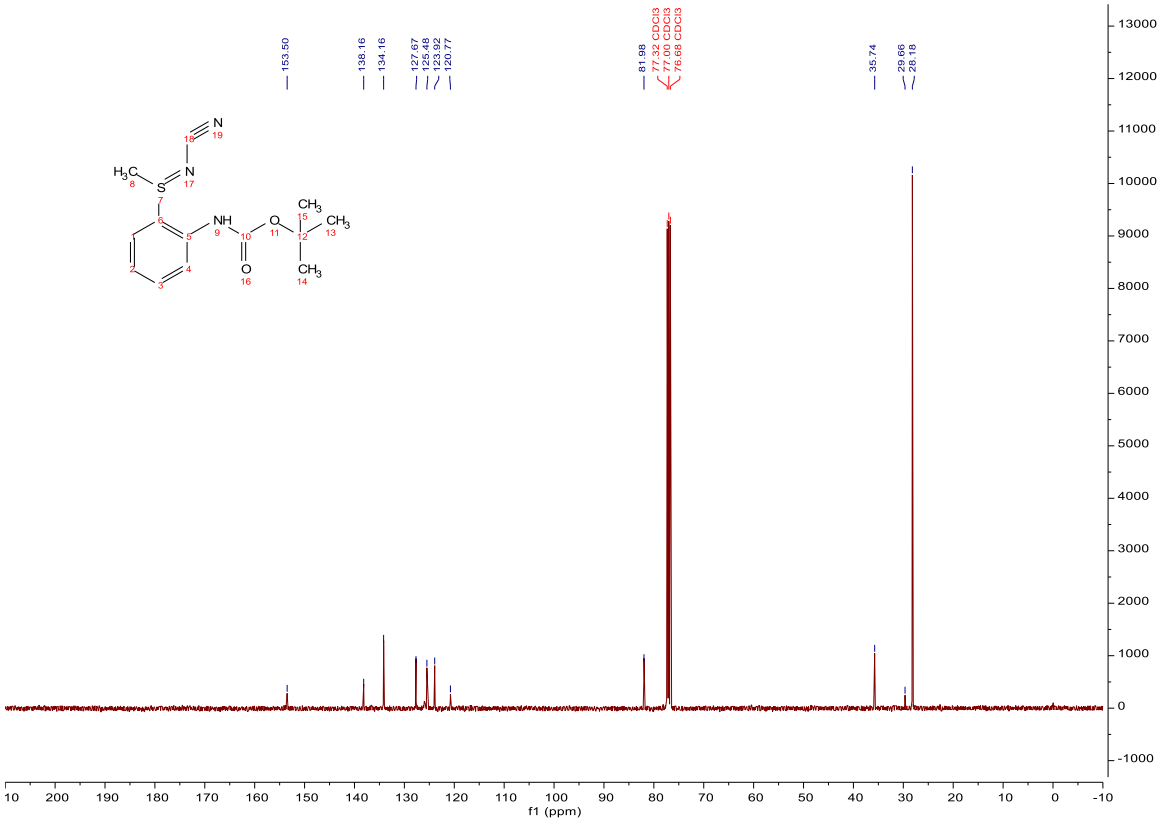


Figure S9. ^{1}H and ^{13}C NMR spectroscopy of 5

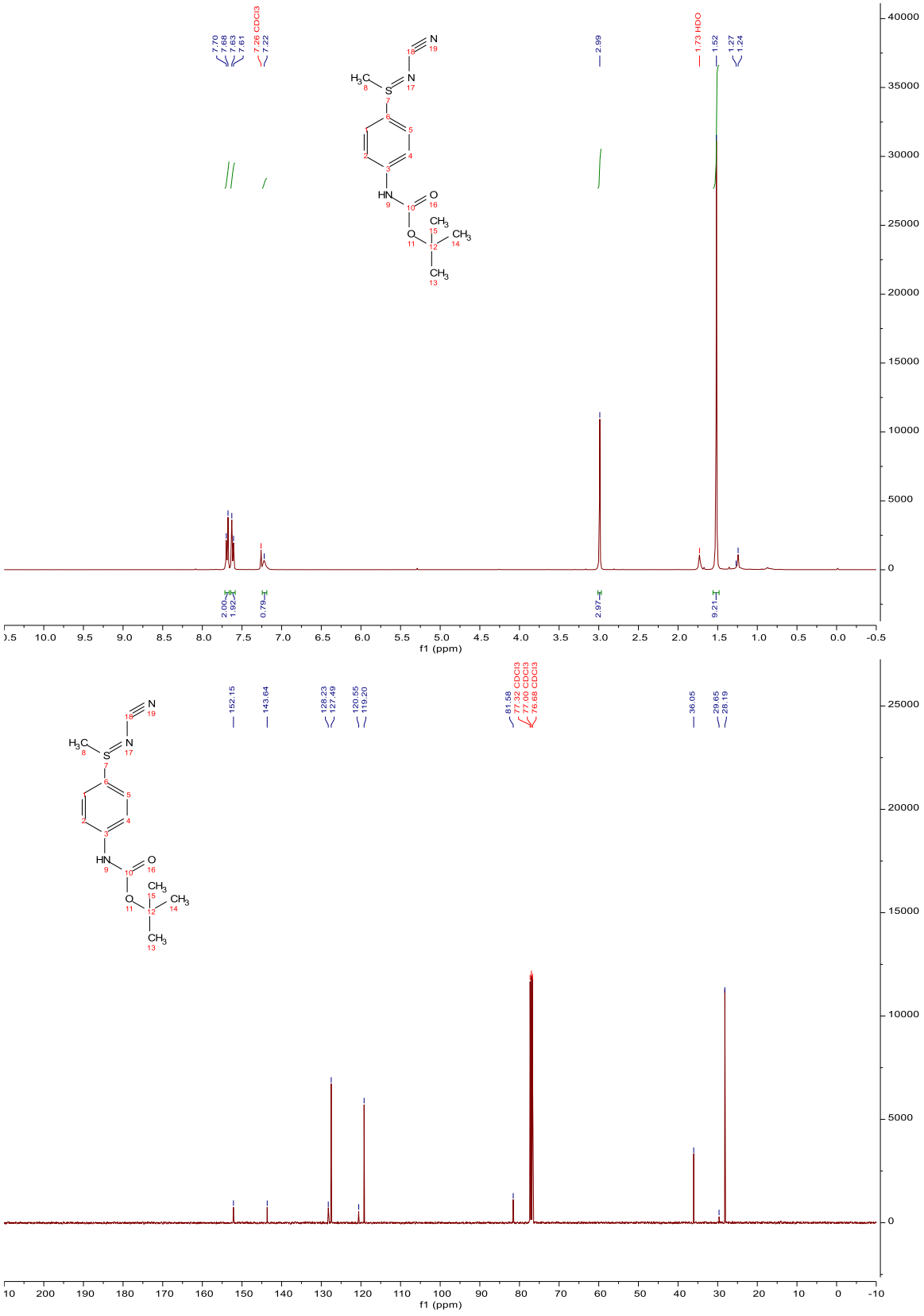
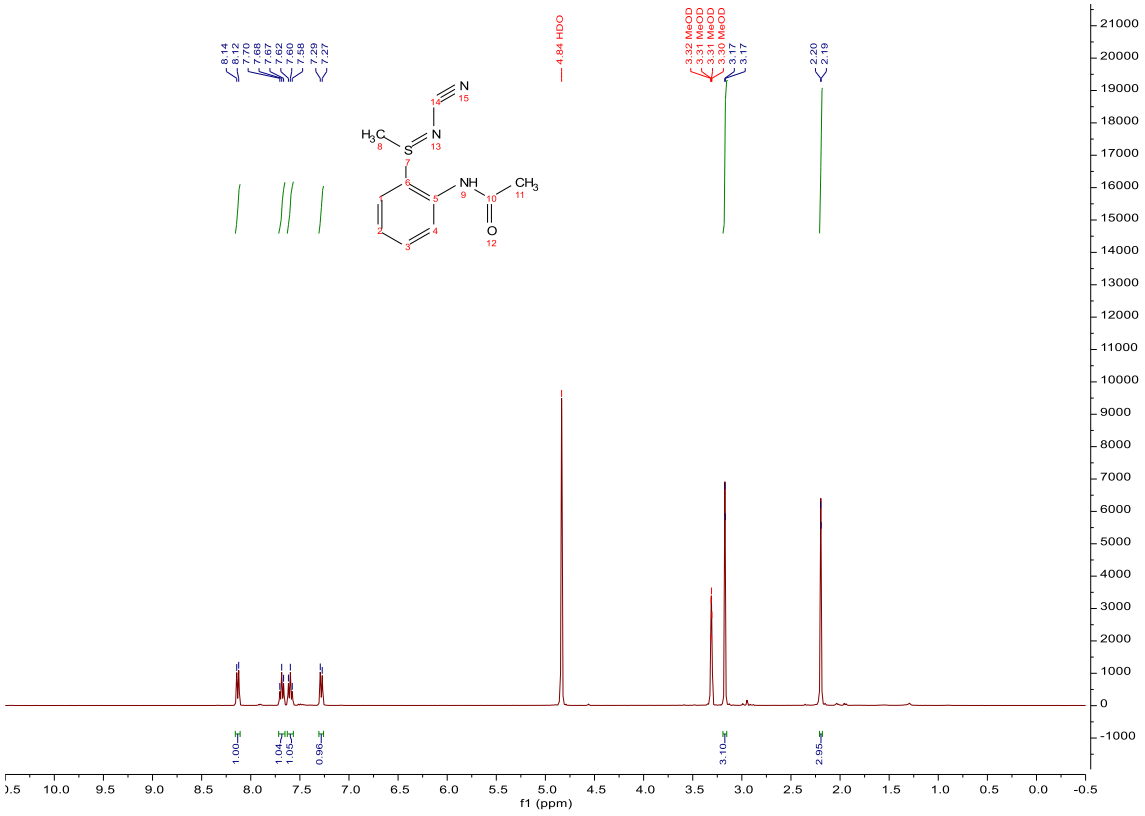


Figure S10. ^{1}H and ^{13}C NMR spectroscopy of 6



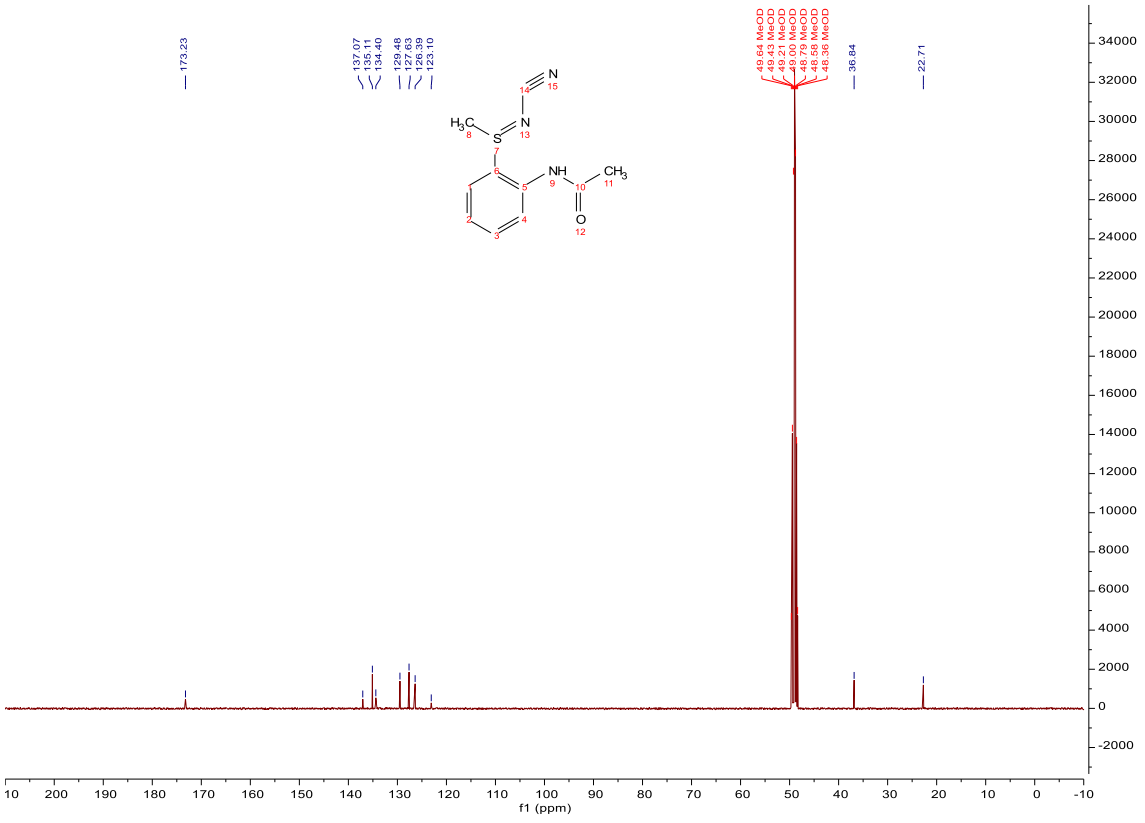


Figure S11. ^{1}H and ^{13}C NMR spectroscopy of 7

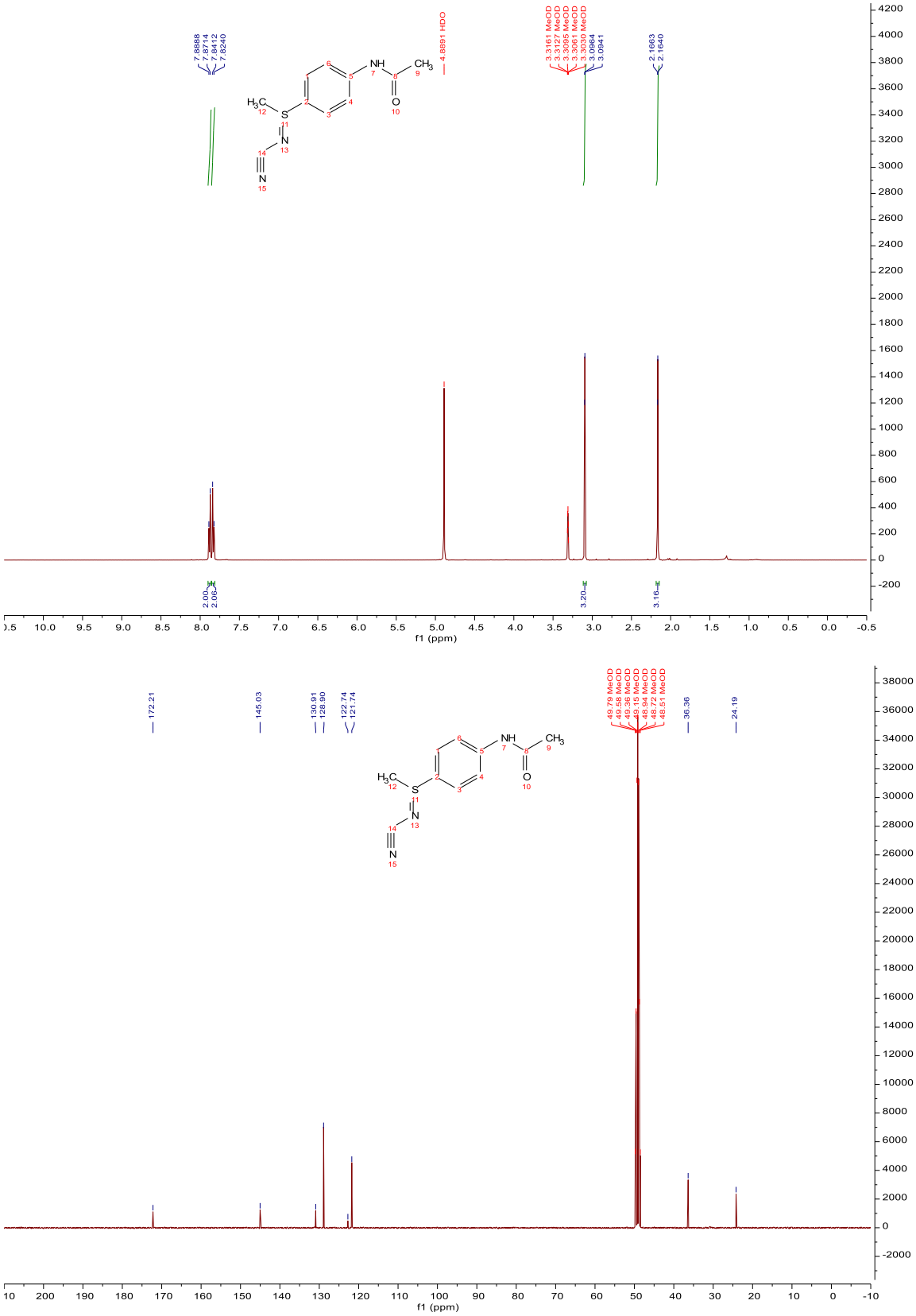
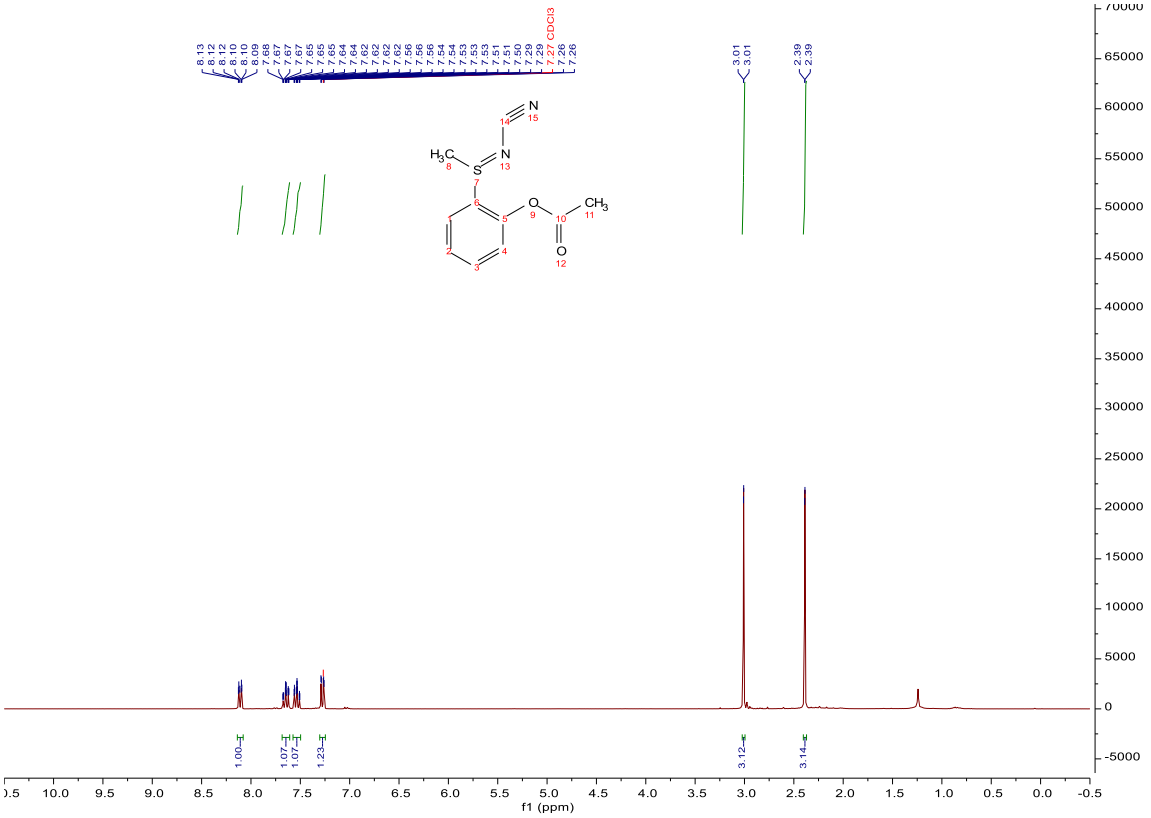


Figure S12. ^{1}H and ^{13}C NMR spectroscopy of 8



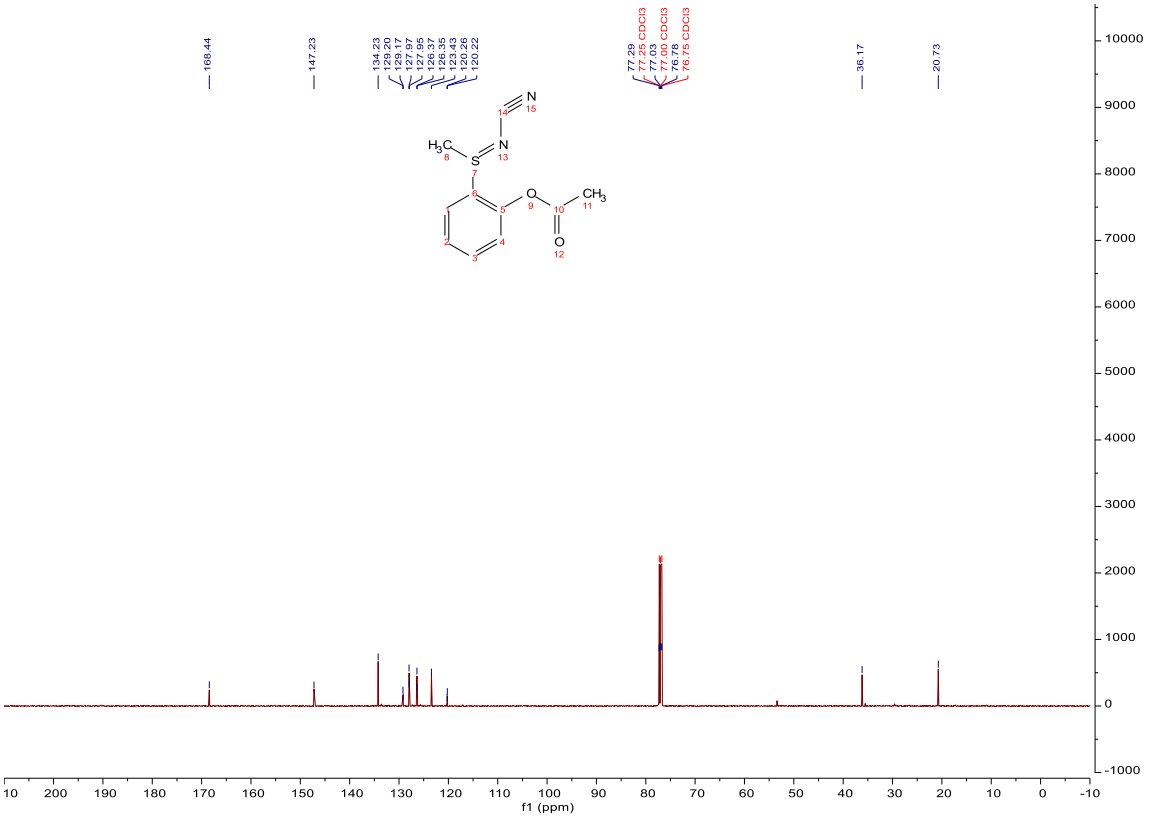
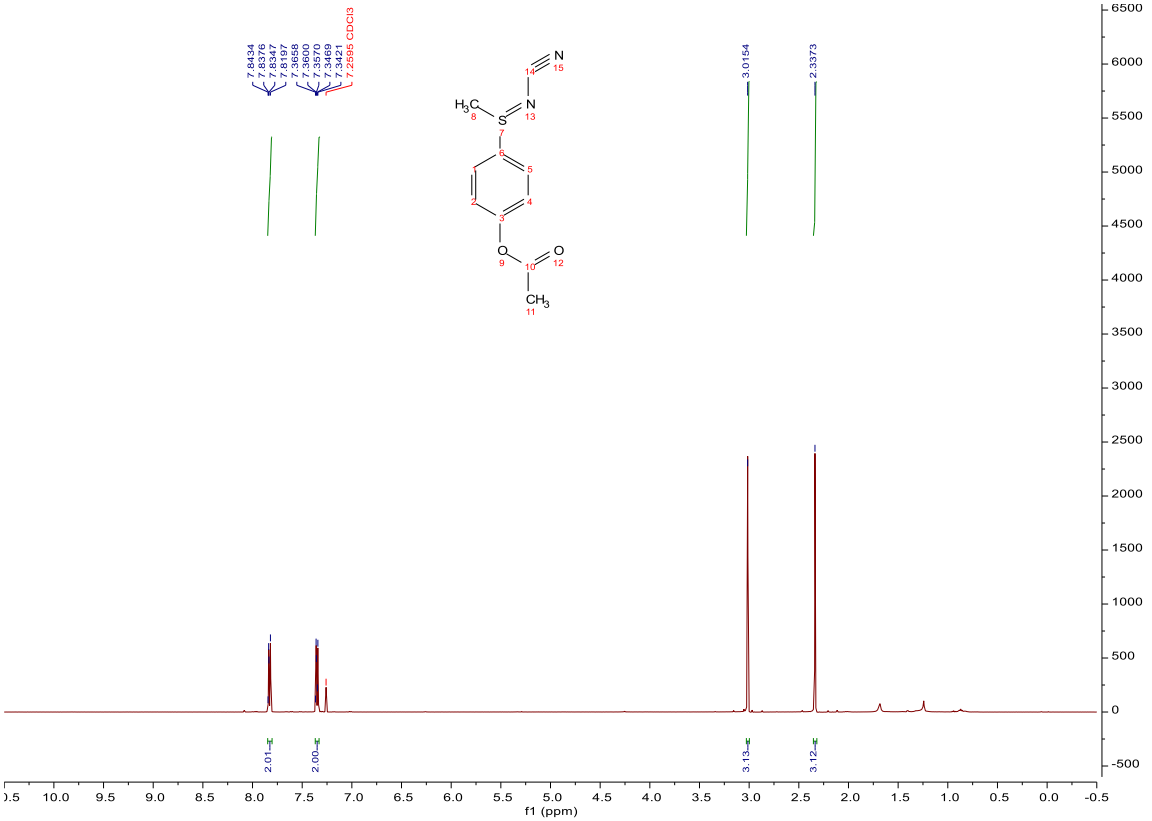


Figure S13. ^{1}H and ^{13}C NMR spectroscopy of 9



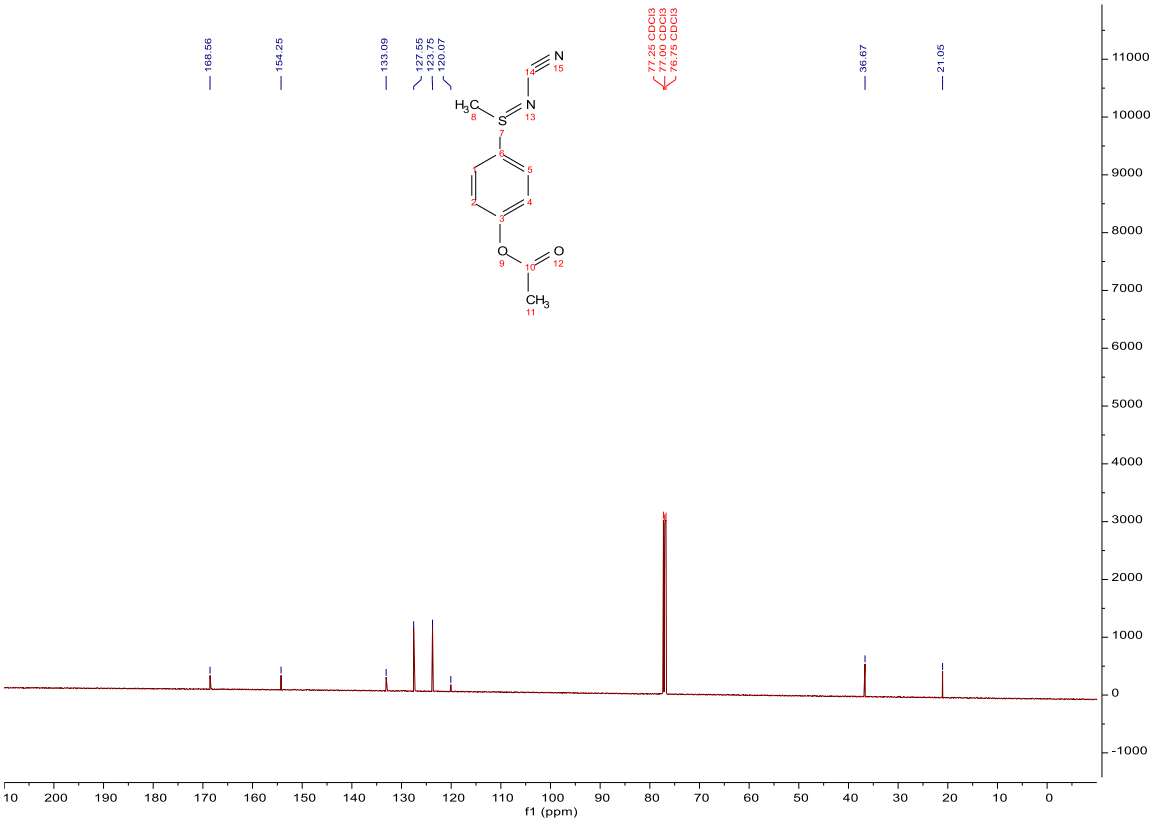


Figure S14. ^{1}H and ^{13}C NMR spectroscopy of 10

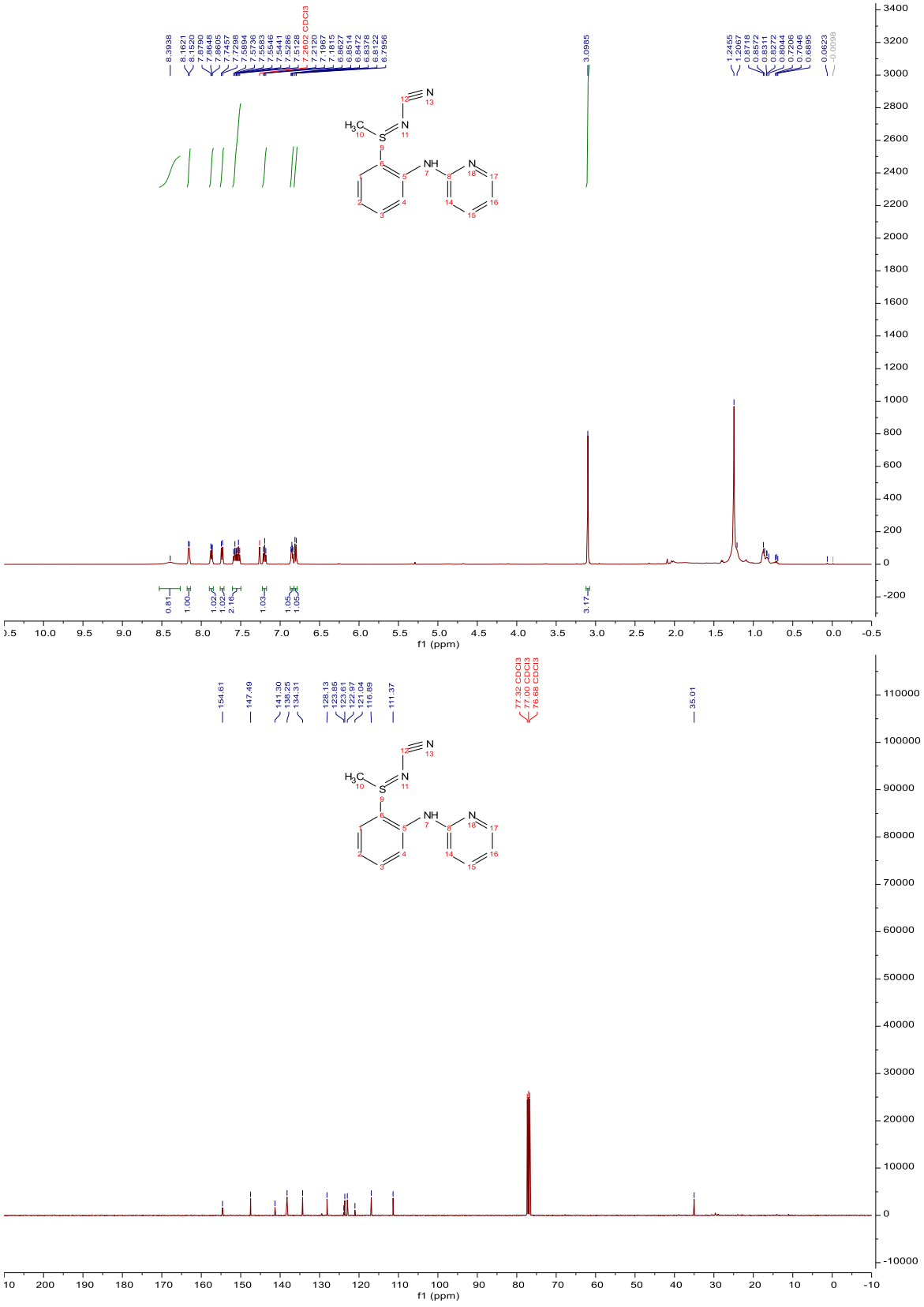


Figure S15. ^{1}H and ^{13}C NMR spectroscopy of 11

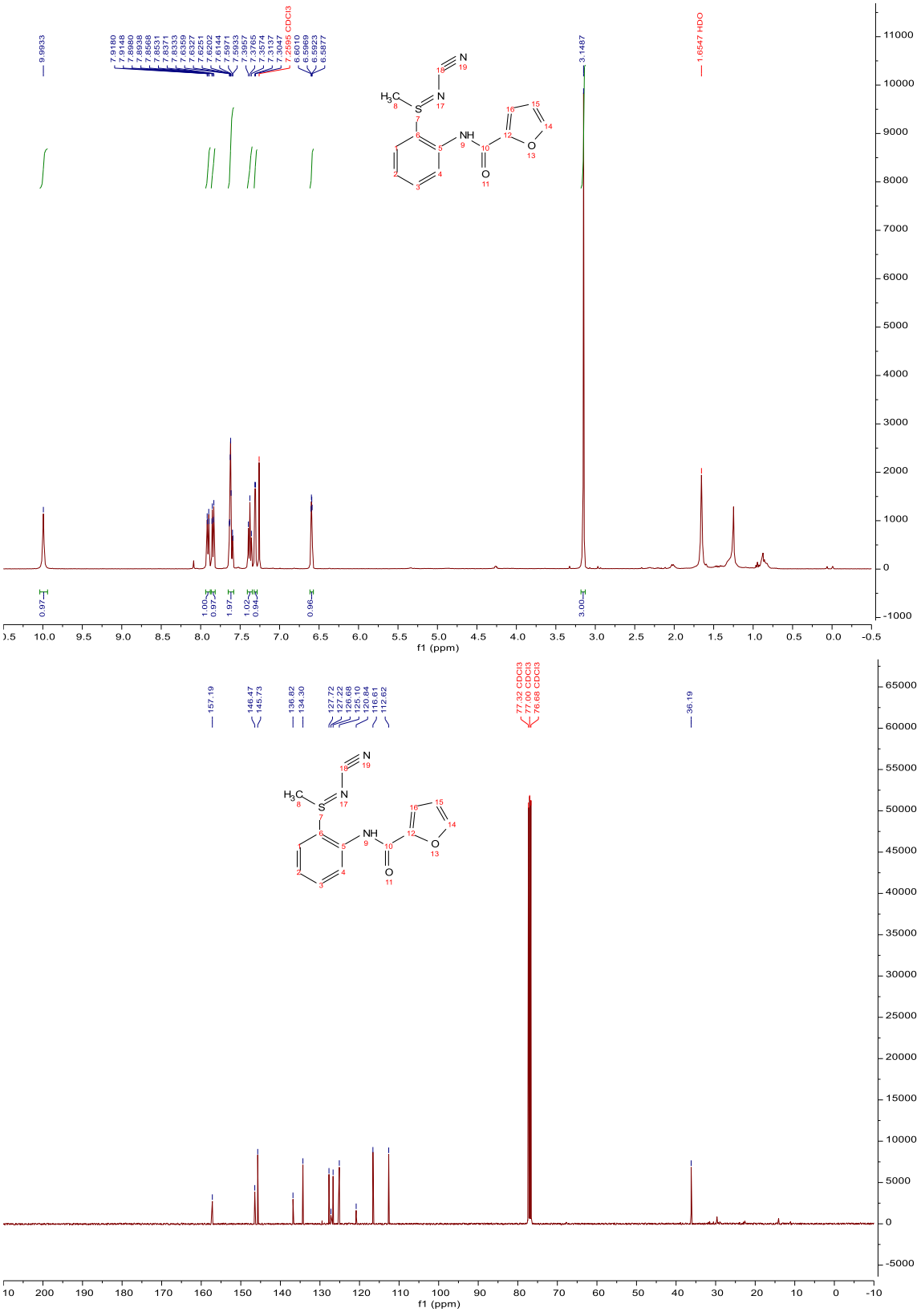


Figure S16. ^{1}H and ^{13}C NMR spectroscopy of 12

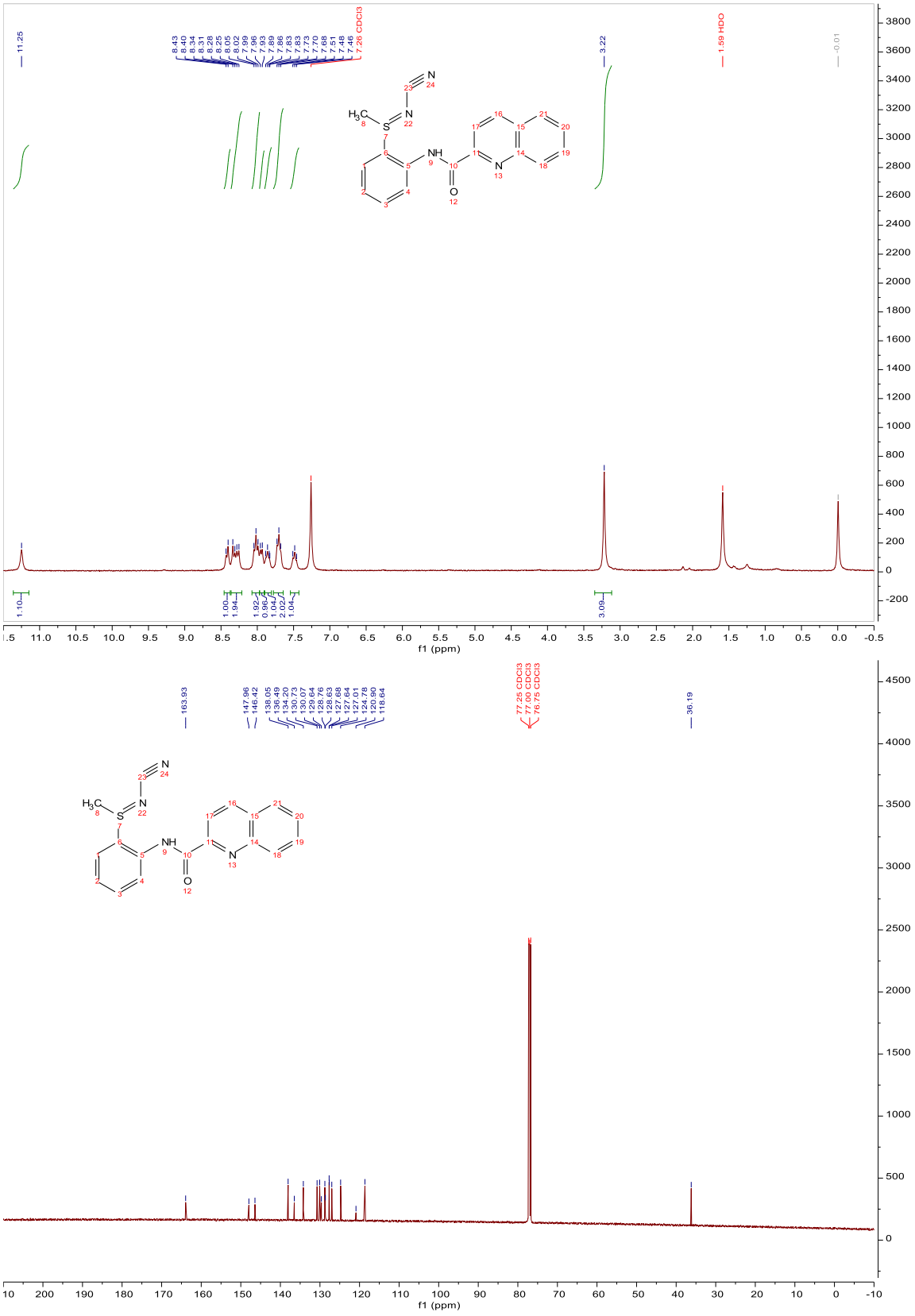
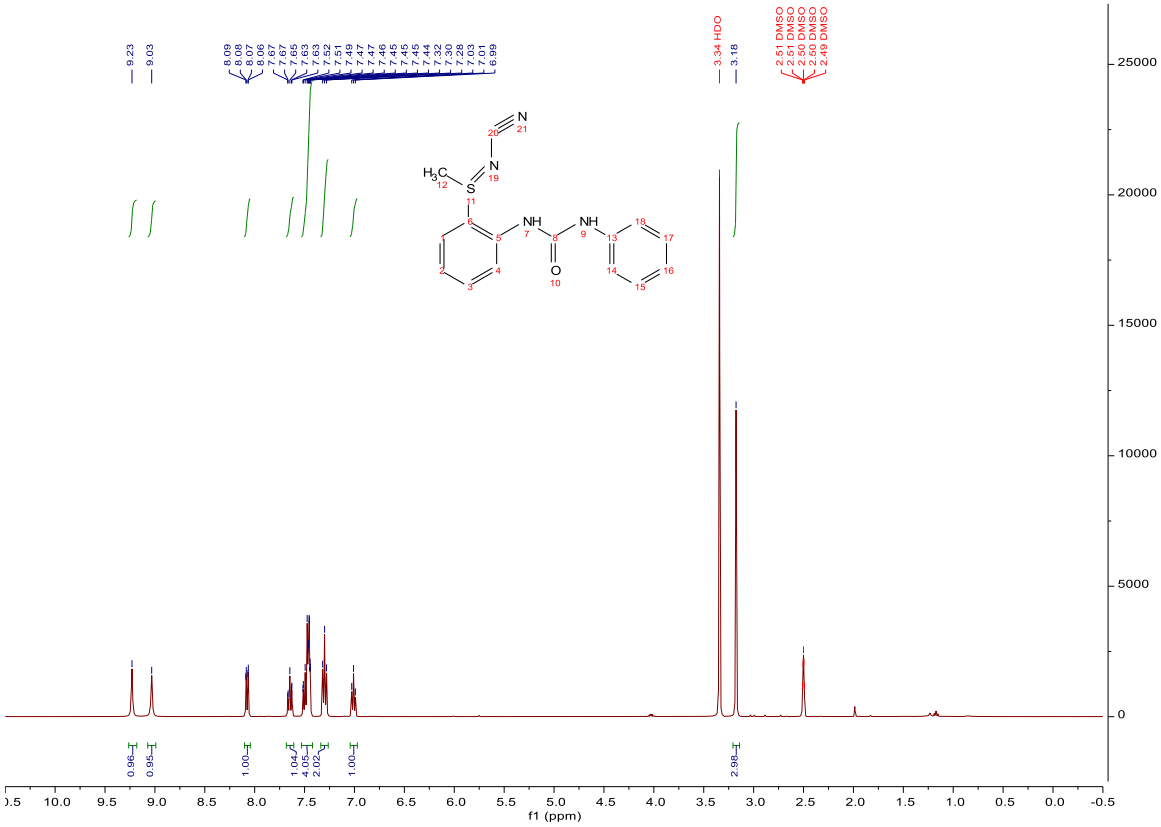


Figure S17. ^{1}H and ^{13}C NMR spectroscopy of 13



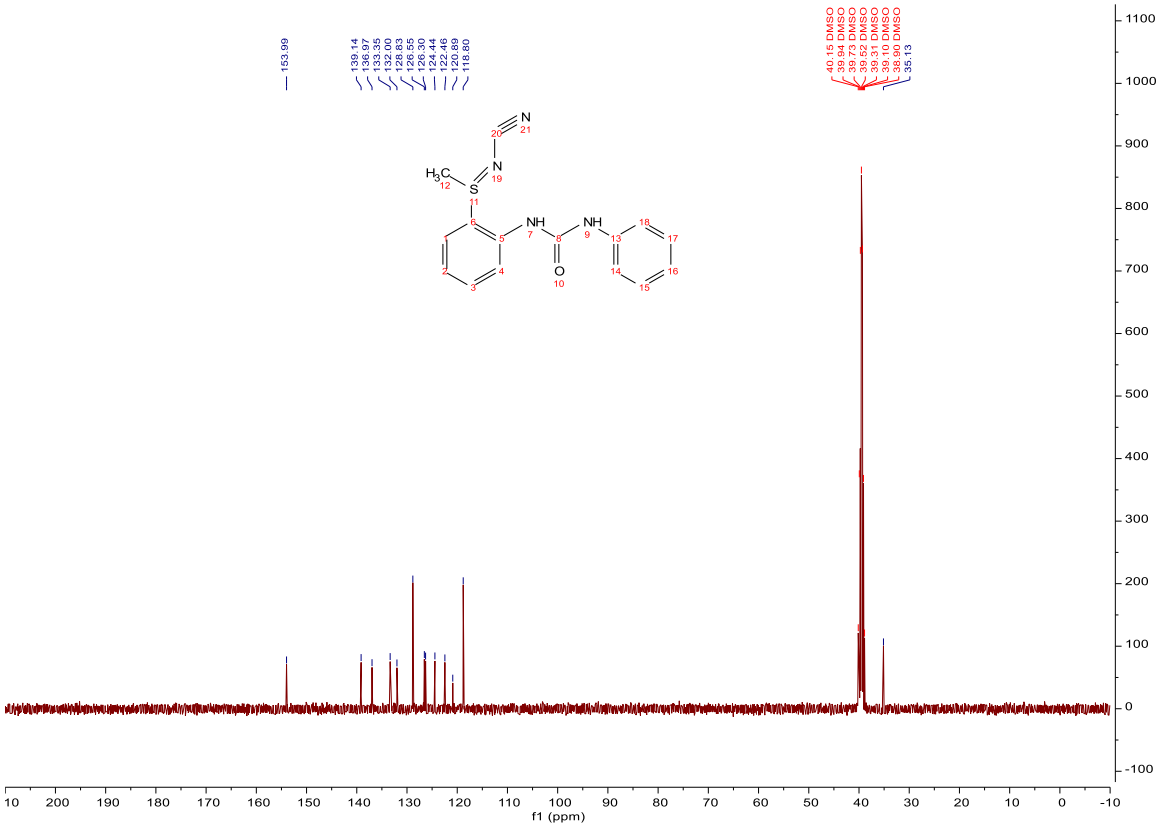
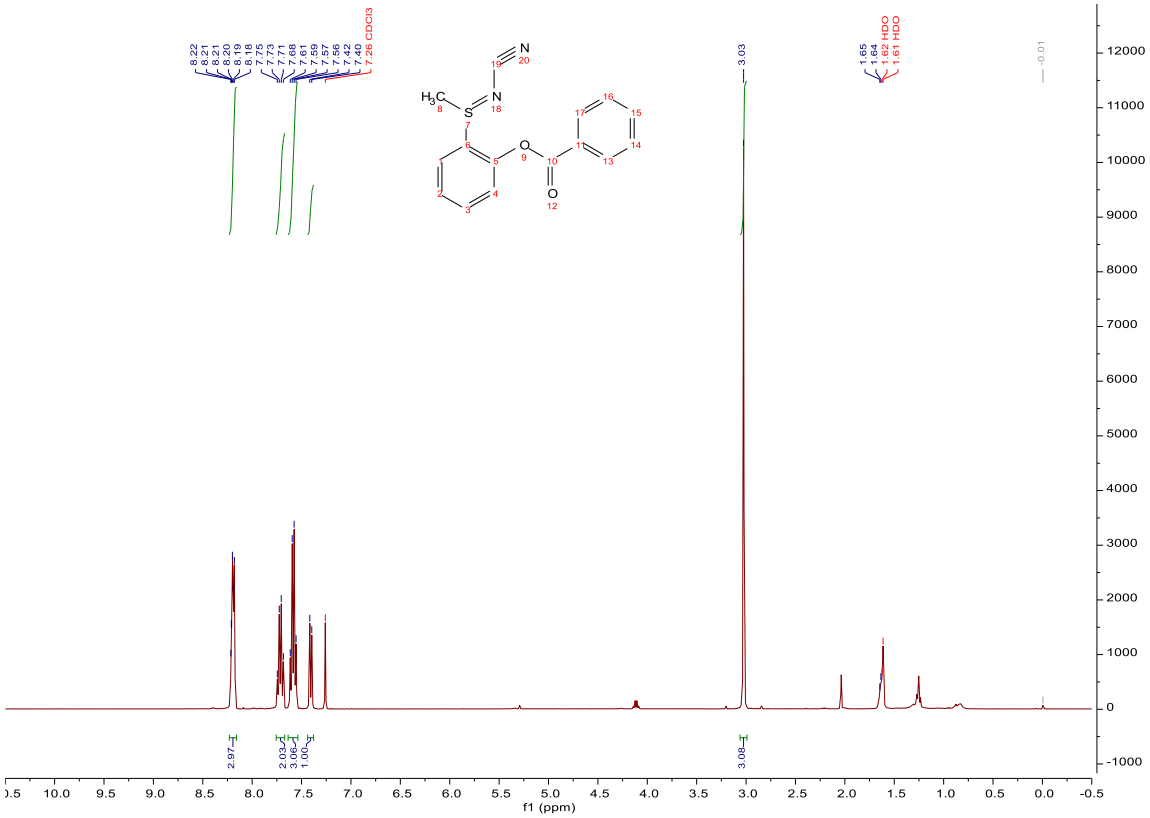


Figure S18. ^{1}H and ^{13}C NMR spectroscopy of 14



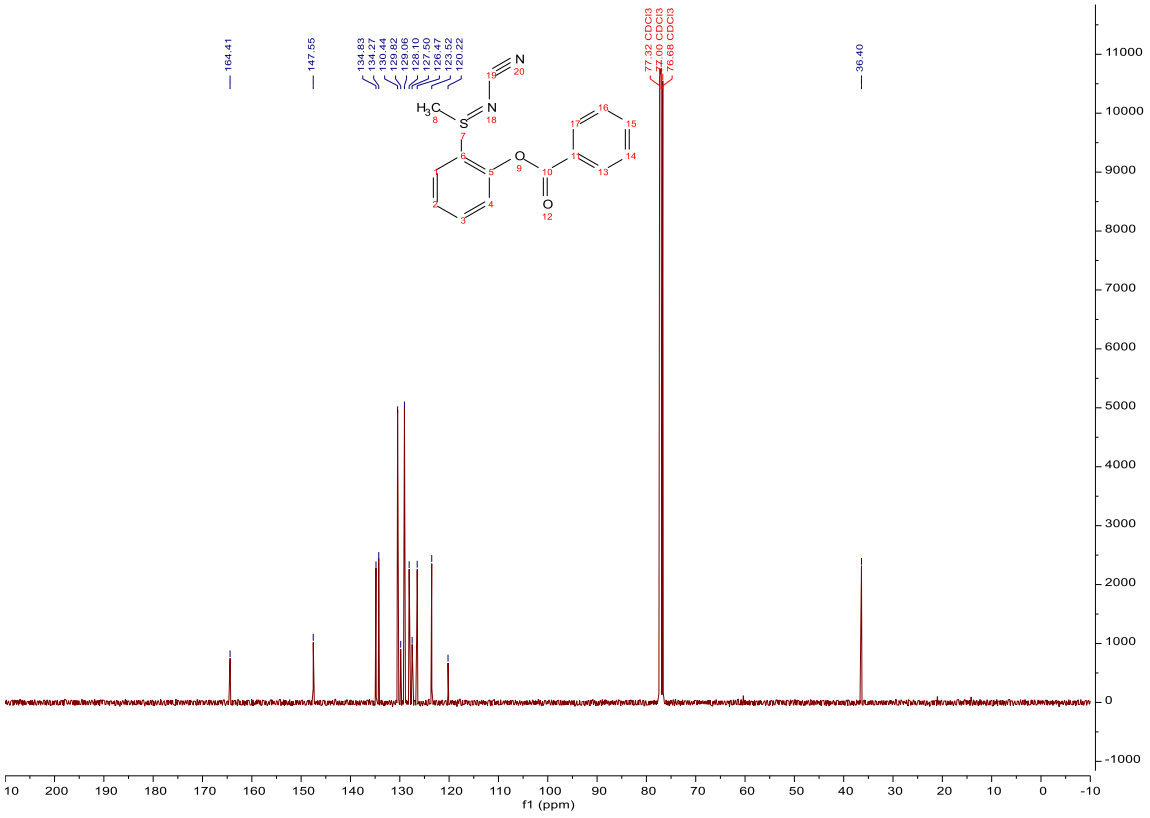
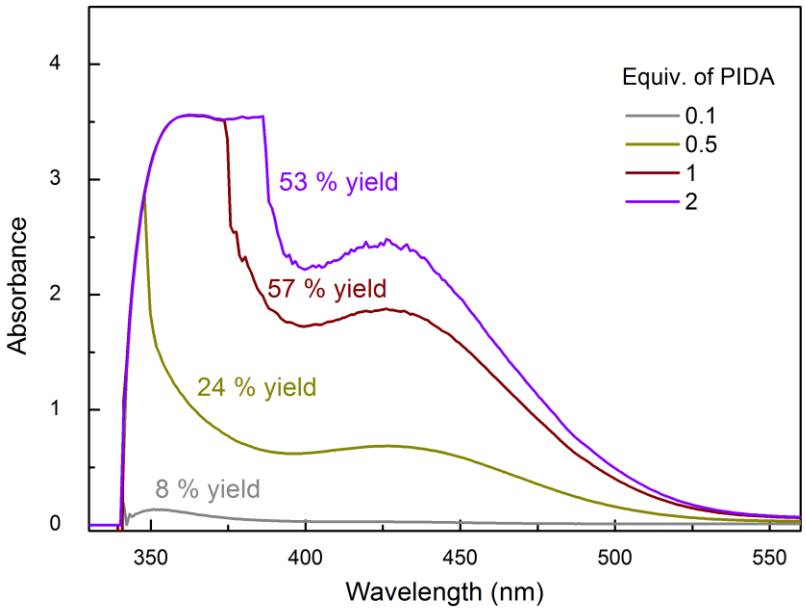
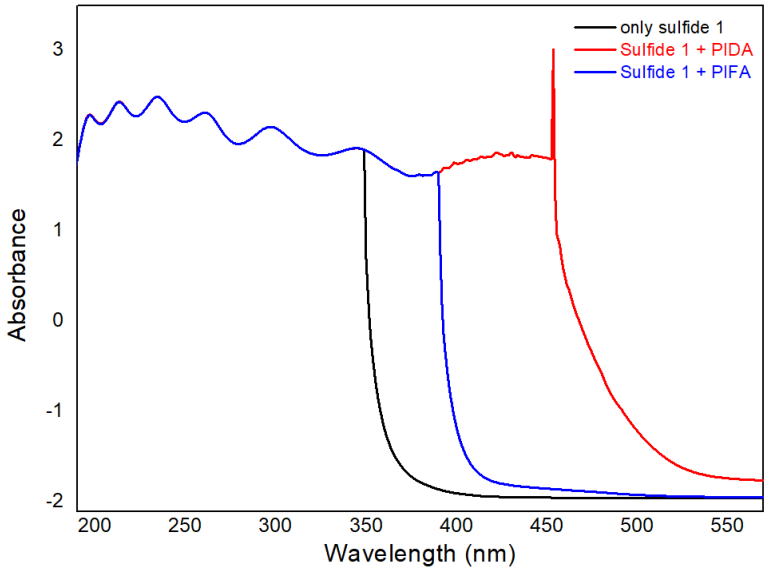


Figure S19. UV/vis spectroscopy studies for changing the amount of PIDA (a solution of sulfide **1** and PIDA in DMF)



Measurement procedure of UV-Vis spectroscopy. To a solution of sulfide **1** (50 mg, 0.2 mmol) in DMF (1 ml) was added $PhI(OAc)_2$ at RT. On shaking, a clear solution was obtained immediately. After remaining the resulting solution at RT for 10 minutes, measurement of UV absorption spectra was performed.

Figure S20. UV/vis spectroscopy studies of a solution of sulfide **1** with PIDA or PIFA in DMF



Measurement procedure of UV-Vis spectroscopy. To a solution of sulfide **1** (50 mg, 0.2 mmol) in DMF (1 ml) was added Iodine reagent (0.2 mmol) at RT. On shaking, a clear solution was obtained immediately. After remaining the resulting solution at RT for 10 minutes, measurement of UV absorption spectra was performed.

Figure 21. 2D DEPT NMR of sulfide **1** (700 MHz, DMF-d_7)

Figure S22 and Table S1. ^{1}H NMR studies of a solution of sulfide **1** with PIDA in deuterated DMF (dependent variable reaction time experiment)

Figure S22. ^{1}H NMR spectroscopy of a solution of sulfide **1** and PIDA in deuterated DMF

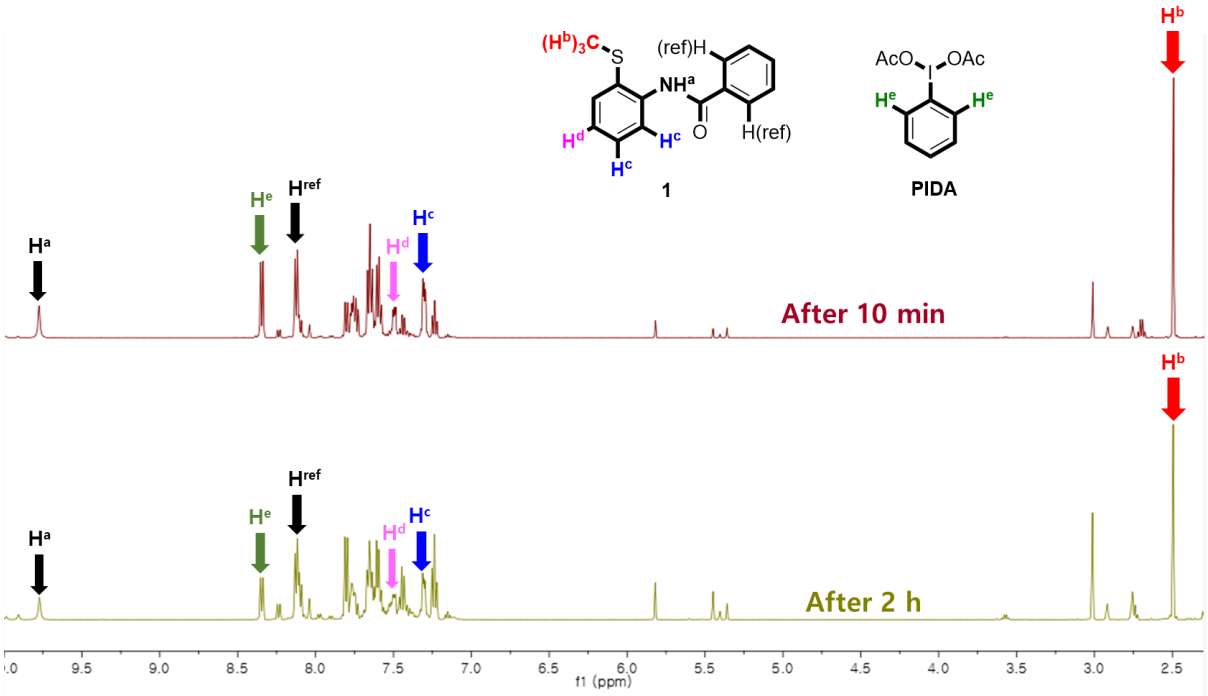


Table S1. Integral value of H^{a-e}

Time	H^{ref}	H^{a}	H^{b}	H^{c}	H^{d}	H^{e}
0	2.0	0.99	3.0	2.0	1.0	1.97
0.1 h	2.0	0.88	2.8	1.76	1.0	1.79
0.5 h	2.0	0.84	2.75	1.77	1.08	1.64
1 h	2.0	0.62	2.25	1.5	0.97	1.23
2 h	2.0	0.54	2.08	1.31	0.99	1.06
5 h	2.0	0.26	0.95	0.7	0.82	0.16

Figure 23. X-ray data of **2a**

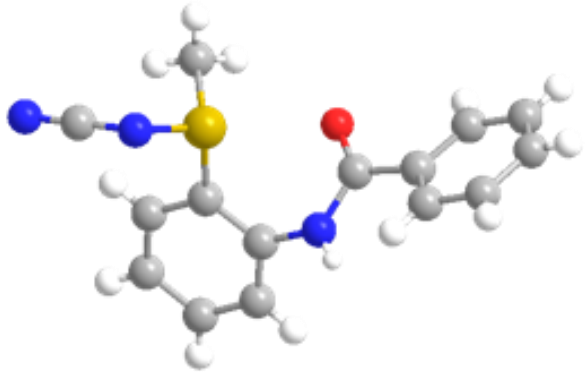


Table 1. Crystal data and structure refinement for SN-crystal

Identification code	20180201_0m	
Empirical formula	C15 H13 N3 O S	
Formula weight	283.34	
Temperature	296(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.8416(5) Å	α= 90°.
	b = 8.9737(6) Å	β= 103.688(5)°.
	c = 10.0972(7) Å	γ = 90°.
Volume	690.34(8) $Å^3$	
Z	2	
Density (calculated)	1.363 Mg/m^3	
Absorption coefficient	0.233 mm^{-1}	
F(000)	296	
Crystal size	0.26 x 0.08 x 0.04 mm^3	
Theta range for data collection	2.08 to 28.32°	
Index ranges	-10<=h<=10, -11<=k<=11, -13<=l<=13	
Reflections collected	12409	
Independent reflections	3325 [R(int) = 0.0673]	
Completeness to theta = 28.32°	99.8 %	
Absorption correction	Multi-scan	

Max. and min. transmission	0.9907 and 0.9419
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3325 / 1 / 181
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0706, wR2 = 0.1410
R indices (all data)	R1 = 0.1032, wR2 = 0.1532
Absolute structure parameter	-0.09(12)
Largest diff. peak and hole	0.652 and -0.249 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for SN-crystal. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	662(1)	2503(1)	2215(1)	40(1)
O(1)	1159(3)	58(3)	4134(3)	50(1)
N(1)	-280(4)	-823(4)	2066(3)	42(1)
N(2)	587(5)	3763(4)	1034(4)	51(1)
N(3)	-1171(5)	6055(4)	970(4)	67(1)
C(1)	1039(5)	-845(4)	3216(4)	39(1)
C(2)	2395(5)	-2043(4)	3270(4)	39(1)
C(3)	3358(5)	-2499(6)	4545(4)	51(1)
C(4)	4712(6)	-3510(5)	4648(5)	60(1)
C(5)	5103(6)	-4041(5)	3496(5)	57(1)
C(6)	4175(6)	-3630(5)	2234(4)	55(1)
C(7)	2806(5)	-2618(6)	2112(4)	45(1)
C(8)	-1706(5)	170(5)	1889(3)	41(1)
C(9)	-3389(5)	-393(5)	1564(4)	53(1)
C(10)	-4833(6)	541(5)	1357(4)	57(1)
C(11)	-4619(5)	2063(5)	1486(4)	52(1)
C(12)	-2952(5)	2655(5)	1800(4)	45(1)
C(13)	-1489(5)	1726(4)	1992(4)	37(1)
C(14)	-363(6)	4956(5)	1049(4)	50(1)
C(15)	887(6)	3483(5)	3792(4)	56(1)

Table 3. Bond lengths [Å] and angles [°] for SN-crystal.

S(1)-N(2)	1.634(4)
S(1)-C(13)	1.790(4)
S(1)-C(15)	1.792(4)
O(1)-C(1)	1.218(4)
N(1)-C(1)	1.361(4)
N(1)-C(8)	1.407(5)
N(1)-H(1A)	0.8600
N(2)-C(14)	1.306(6)
N(3)-C(14)	1.164(6)
C(1)-C(2)	1.503(5)
C(2)-C(7)	1.385(5)
C(2)-C(3)	1.391(5)
C(3)-C(4)	1.382(6)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.357(7)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.361(6)
C(5)-H(5A)	0.9300
C(6)-C(7)	1.388(6)
C(6)-H(6A)	0.9300
C(7)-H(7A)	0.9300
C(8)-C(9)	1.378(5)
C(8)-C(13)	1.408(6)
C(9)-C(10)	1.384(6)
C(9)-H(9A)	0.9300
C(10)-C(11)	1.379(7)
C(10)-H(10A)	0.9300
C(11)-C(12)	1.376(6)
C(11)-H(11A)	0.9300
C(12)-C(13)	1.394(5)
C(12)-H(12A)	0.9300
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600

N(2)-S(1)-C(13)	107.94(18)
N(2)-S(1)-C(15)	106.7(2)
C(13)-S(1)-C(15)	101.2(2)
C(1)-N(1)-C(8)	122.6(3)
C(1)-N(1)-H(1A)	118.7
C(8)-N(1)-H(1A)	118.7
C(14)-N(2)-S(1)	118.8(3)
O(1)-C(1)-N(1)	123.1(4)
O(1)-C(1)-C(2)	121.4(3)
N(1)-C(1)-C(2)	115.5(3)
C(7)-C(2)-C(3)	119.2(4)
C(7)-C(2)-C(1)	122.7(3)
C(3)-C(2)-C(1)	117.9(3)
C(4)-C(3)-C(2)	120.1(4)
C(4)-C(3)-H(3A)	119.9
C(2)-C(3)-H(3A)	119.9
C(5)-C(4)-C(3)	119.5(4)
C(5)-C(4)-H(4A)	120.3
C(3)-C(4)-H(4A)	120.3
C(4)-C(5)-C(6)	121.9(4)
C(4)-C(5)-H(5A)	119.1
C(6)-C(5)-H(5A)	119.1
C(5)-C(6)-C(7)	119.5(4)
C(5)-C(6)-H(6A)	120.3
C(7)-C(6)-H(6A)	120.3
C(2)-C(7)-C(6)	119.9(4)
C(2)-C(7)-H(7A)	120.1
C(6)-C(7)-H(7A)	120.1
C(9)-C(8)-N(1)	119.0(4)
C(9)-C(8)-C(13)	118.2(4)
N(1)-C(8)-C(13)	122.7(3)
C(8)-C(9)-C(10)	121.1(4)
C(8)-C(9)-H(9A)	119.4
C(10)-C(9)-H(9A)	119.4
C(11)-C(10)-C(9)	120.6(4)

C(11)-C(10)-H(10A)	119.7
C(9)-C(10)-H(10A)	119.7
C(12)-C(11)-C(10)	119.5(4)
C(12)-C(11)-H(11A)	120.3
C(10)-C(11)-H(11A)	120.3
C(11)-C(12)-C(13)	120.4(4)
C(11)-C(12)-H(12A)	119.8
C(13)-C(12)-H(12A)	119.8
C(12)-C(13)-C(8)	120.1(3)
C(12)-C(13)-S(1)	120.3(3)
C(8)-C(13)-S(1)	119.3(3)
N(3)-C(14)-N(2)	174.6(5)
S(1)-C(15)-H(15A)	109.5
S(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
S(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for SN-crystal. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	44(1)	23(1)	53(1)	-1(1)	12(1)	-2(1)
O(1)	61(2)	40(2)	45(1)	-9(1)	4(1)	7(2)
N(1)	48(2)	26(2)	46(2)	-5(2)	1(1)	4(2)
N(2)	69(2)	24(2)	65(2)	5(2)	26(2)	-3(2)
N(3)	71(3)	33(2)	87(3)	9(2)	1(2)	-4(2)
C(1)	49(2)	30(2)	36(2)	2(2)	7(2)	-6(2)
C(2)	41(2)	26(2)	47(2)	-1(2)	5(2)	-9(2)
C(3)	59(2)	40(2)	47(2)	-3(2)	0(2)	-1(3)
C(4)	63(3)	48(3)	57(3)	4(2)	-9(2)	11(3)
C(5)	54(3)	39(3)	74(3)	2(2)	7(2)	14(2)
C(6)	65(3)	43(3)	61(3)	-8(2)	21(2)	-1(2)
C(7)	48(2)	38(2)	49(2)	2(2)	10(2)	-9(2)
C(8)	45(2)	33(2)	42(2)	-1(2)	6(2)	-4(2)
C(9)	52(2)	31(2)	67(3)	1(2)	-1(2)	-5(2)
C(10)	45(2)	51(3)	69(3)	5(2)	3(2)	-9(2)
C(11)	44(2)	52(3)	62(3)	11(2)	16(2)	14(2)
C(12)	56(2)	22(2)	59(2)	4(2)	18(2)	6(2)
C(13)	43(2)	26(2)	42(2)	0(2)	10(2)	1(2)
C(14)	56(2)	35(2)	52(2)	7(2)	-1(2)	-18(2)
C(15)	67(3)	45(3)	53(2)	-10(2)	9(2)	-3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for SN-crystal.

	x	y	z	U(eq)
H(1A)	-242	-1440	1422	50
H(3A)	3090	-2123	5330	61
H(4A)	5350	-3825	5499	72
H(5A)	6032	-4705	3572	69
H(6A)	4455	-4022	1460	66
H(7A)	2167	-2328	1253	54
H(9A)	-3557	-1418	1482	63
H(10A)	-5957	138	1129	68
H(11A)	-5592	2685	1362	63
H(12A)	-2801	3682	1884	54
H(15A)	2013	3961	4031	84
H(15B)	788	2793	4496	84
H(15C)	-21	4221	3695	84

Table 6. Torsion angles [°] for SN-crystal.

C(13)-S(1)-N(2)-C(14)	65.1(3)
C(15)-S(1)-N(2)-C(14)	-43.0(4)
C(8)-N(1)-C(1)-O(1)	-5.6(5)
C(8)-N(1)-C(1)-C(2)	176.2(3)
O(1)-C(1)-C(2)-C(7)	-149.4(4)
N(1)-C(1)-C(2)-C(7)	28.9(5)
O(1)-C(1)-C(2)-C(3)	25.6(5)
N(1)-C(1)-C(2)-C(3)	-156.1(4)
C(7)-C(2)-C(3)-C(4)	0.3(6)
C(1)-C(2)-C(3)-C(4)	-174.9(4)
C(2)-C(3)-C(4)-C(5)	0.6(7)
C(3)-C(4)-C(5)-C(6)	-1.4(8)
C(4)-C(5)-C(6)-C(7)	1.1(7)
C(3)-C(2)-C(7)-C(6)	-0.5(6)
C(1)-C(2)-C(7)-C(6)	174.5(4)
C(5)-C(6)-C(7)-C(2)	-0.2(7)
C(1)-N(1)-C(8)-C(9)	-125.6(4)
C(1)-N(1)-C(8)-C(13)	56.3(5)
N(1)-C(8)-C(9)-C(10)	-178.9(4)
C(13)-C(8)-C(9)-C(10)	-0.7(6)
C(8)-C(9)-C(10)-C(11)	-0.7(7)
C(9)-C(10)-C(11)-C(12)	1.2(7)
C(10)-C(11)-C(12)-C(13)	-0.3(6)
C(11)-C(12)-C(13)-C(8)	-1.1(5)
C(11)-C(12)-C(13)-S(1)	173.1(3)
C(9)-C(8)-C(13)-C(12)	1.5(5)
N(1)-C(8)-C(13)-C(12)	179.7(3)
C(9)-C(8)-C(13)-S(1)	-172.7(3)
N(1)-C(8)-C(13)-S(1)	5.4(5)
N(2)-S(1)-C(13)-C(12)	-47.3(3)
C(15)-S(1)-C(13)-C(12)	64.6(3)
N(2)-S(1)-C(13)-C(8)	127.0(3)
C(15)-S(1)-C(13)-C(8)	-121.2(3)
S(1)-N(2)-C(14)-N(3)	-179(5)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for SN-crystal [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...N(3)#1	0.86	2.37	3.033(5)	133.7
N(1)-H(1A)...N(2)#2	0.86	2.44	3.105(5)	134.9

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x,y-1/2,-z