Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Modification of Nonlinear Optical Dyes for Dye Sensitized Solar Cells: a New Use for a Familiar Acceptor

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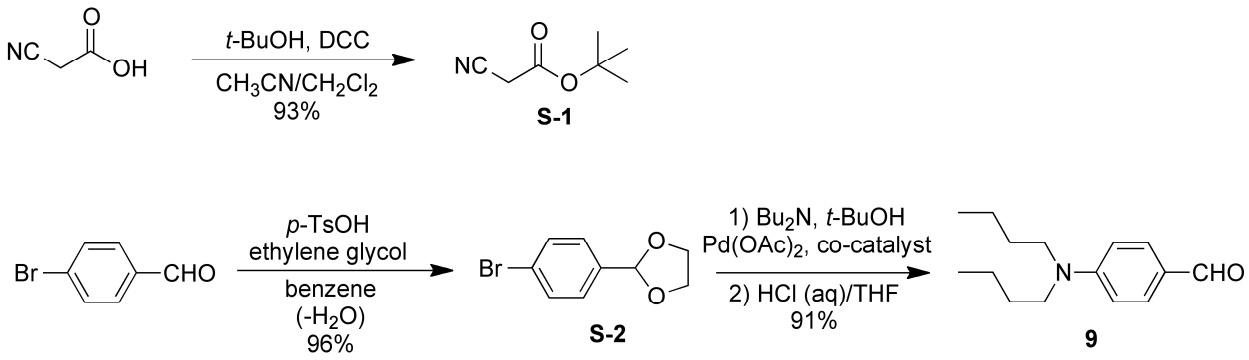
Synthetic Details



Scheme S1. Synthesis of *tert*-butyl-2-cyanoacetate and of 4-(dibutylamino)benzaldehyde.

***tert*-butyl 2-cyanoacetate (S-1)**[1] – In a flask was placed cyanoacetic acid (5.000 g, 58.8 mmol), *t*-butanol (5.54 mL, 58.8 mmol), and acetonitrile (40 mL). The solution was cooled in an ice bath and DCC (59 mL, 1 M in methylene chloride) was added drop-wise over 20 min. The

reaction was allowed to slowly warm to room temperature overnight. After removal of the DCU precipitate by filtration through a plug of silica, the desired product was collected by distillation under reduced pressure (6 mTorr) and mild heating to obtain a clear, colorless liquid (7.728 g, 93%) whose NMR spectra matched that in the literature.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.36 (s, 2H), 1.50 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.17, 113.31, 83.23, 27.13, 25.25.

2-(4-bromophenyl)-1,3-dioxolane (S-2)[2] – In a flask fitted with a Dean-Stark setup was introduced benzene (150 mL), *p*-bromobenzaldehyde (3.000 g, 16.20 mmol), ethylene glycol (10 mL), and *p*-toluenesulfonic acid monohydrate (0.150 g, 0.80 mmol). The reaction was heated to 105 °C overnight. Heat was removed and upon cooling to room temperature the reaction was diluted with methylene chloride (100 mL) and washed with saturated aqueous $NaHCO_3$ (50 mL), water (50 mL), and brine (50 mL). The organic phase was dried over $MgSO_4$, filtered, and solvent removed under reduced pressure to give an oil that solidified as yellow-white needles upon standing (3.560 g, 96%) and whose spectra matched that in the literature.[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 5.78 (s, 1H), 4.07 (m, 4H).

4-(dibutylamino)benzaldehyde (S-3)[4] – In a flask under inert atmosphere was combined **5** (3.00 g, 13.10 mmol), $Pd(OAc)_2$ (0.029 g, 0.13 mmol), 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene HBF_4 (0.063 g, 0.13 mmol), potassium *t*-butoxide (2.204 g, 19.64 g), dibutylamine (2.43 mL, 14.4 mmol), and THF (15 mL). The reaction was refluxed for 24 h, then cooled to room temp and filtered through a plug of silica eluting with ethyl acetate. Solvent was removed under reduced pressure yielding a brown oil that was dissolved in THF (50 mL) and HCl (1 M aqueous, 100 mL) and stirred at 60 °C overnight. Upon cooling to room temperature,

the reaction was extracted with 1:1 hexanes/ethyl acetate (3 x 50 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (50 mL), brine (50 mL), dried over $MgSO_4$, filtered, and solvent removed under reduced pressure. The resulting oil was chromatographed on silica eluting with a hexanes/methylene chloride gradient to give a clear, brown oil upon removal of solvent (2.773 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.70 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 3.35 (t, J = 7.7 Hz, 4H), 1.60 (m, 4H), 1.39 (m, 4H), 0.98 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 152.4, 131.9, 124.3, 110.4, 50.5, 29.0, 20.0, 13.7.

Synthetic References:

(1) Nahmany, M.; Melman, A., *Org. Lett.* **2001**, *3* (23), 3733-3735.
(2) Bartholomew, G. P.; Rumi, M.; Pond, S., J. K.; Perry, J. W.; Tretiak, S.; Bazan, G. C., *J. Am. Chem. Soc.* **2004**, *126* (37), 11529-11542.
(3) Chen, C.-T.; Weng, S.-S.; Kao, J.-Q.; Lin, C.-C.; Jan, M.-D., *Org. Lett.* **2005**, *7* (15), 3343-3346.
(4) (a) Stauffer, S. R.; Lee, S.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F., *Org. Lett.* **2000**, *2* (10), 1423-1426; (b) Plater, J. M.; Jackson, T., *Tetrahedron* **2003**, *59* (25), 4673-4685.

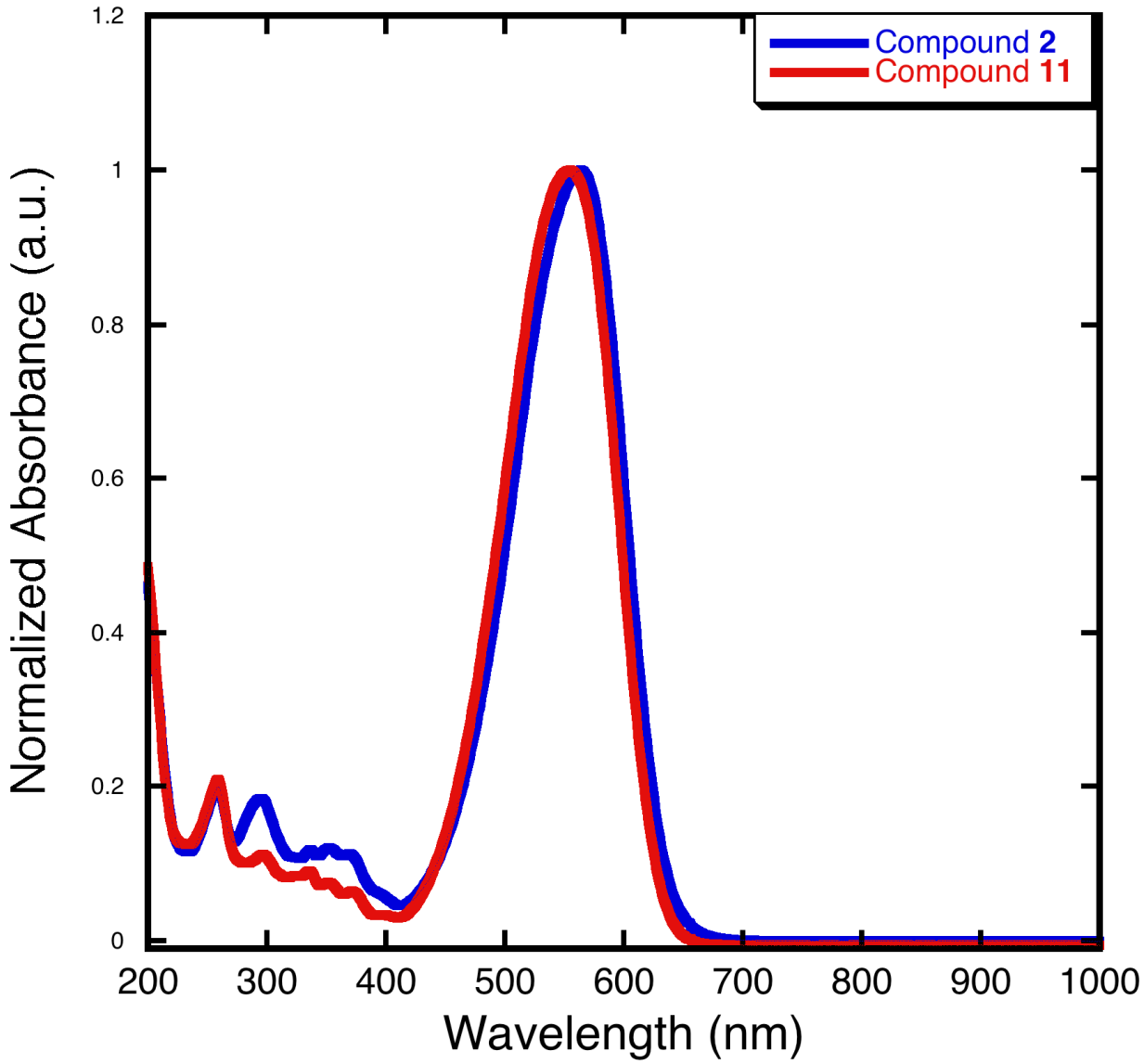


Figure S1. Normalized UV-Vis absorption of spectra of **2** and **11** in acetonitrile. The concentration of both compounds is ~10^{-5} M.

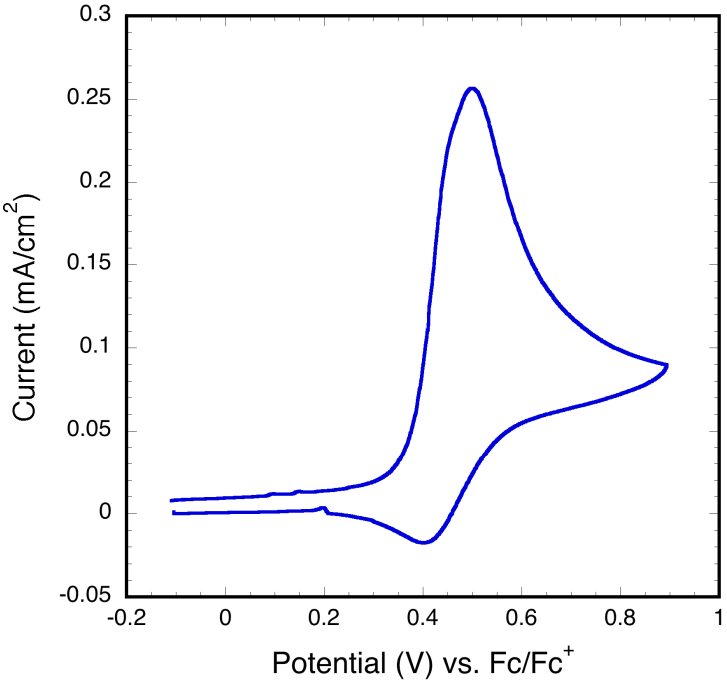


Figure S2. CV data of dye **2** adsorbed on a nanocrystalline TiO_2 electrode. Tetrabutylammonium hexafluorophosphoate (0.1 M) was the supporting electrolyte; a Pt flag was used as the counter electrode, and $Ag/AgNO_3$ in acetonitrile was used as the reference electrode. The scan rate was 20 mV/s.

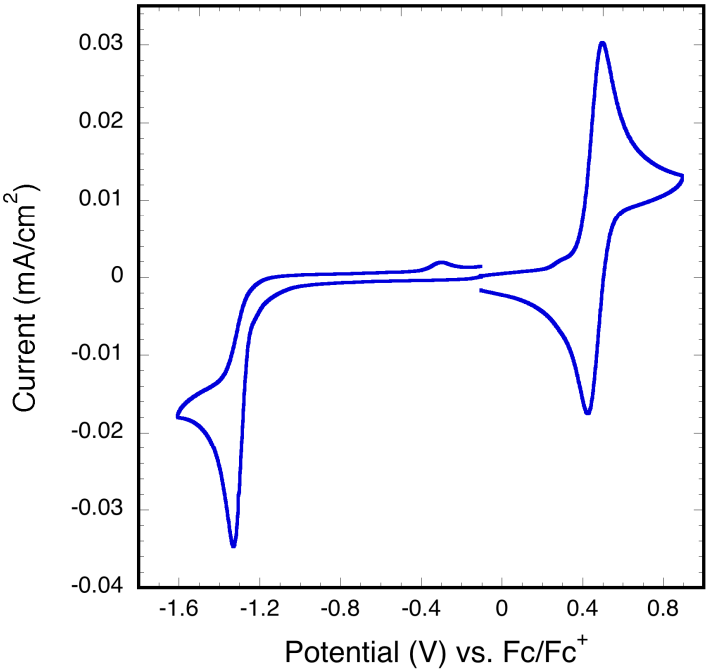


Figure S3. CV data of **11**. The concentration of **11** was 3.0 mM in acetonitrile. Tetrabutylammonium hexafluorophosphoate (0.10 M) was the supporting electrolyte; A Pt button served as the working electrode, a Pt flag was used as the counter electrode, and $Ag/AgNO_3$ was used as the reference electrode. The scan rate was 20 mV/s.

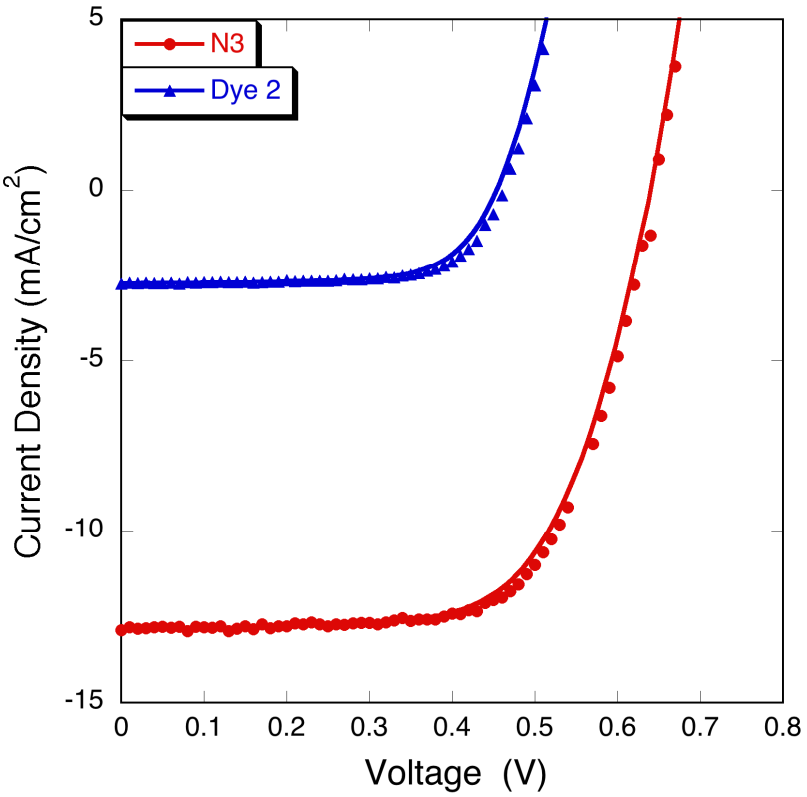


Figure S4. J-V Curves for the data in Table 1.

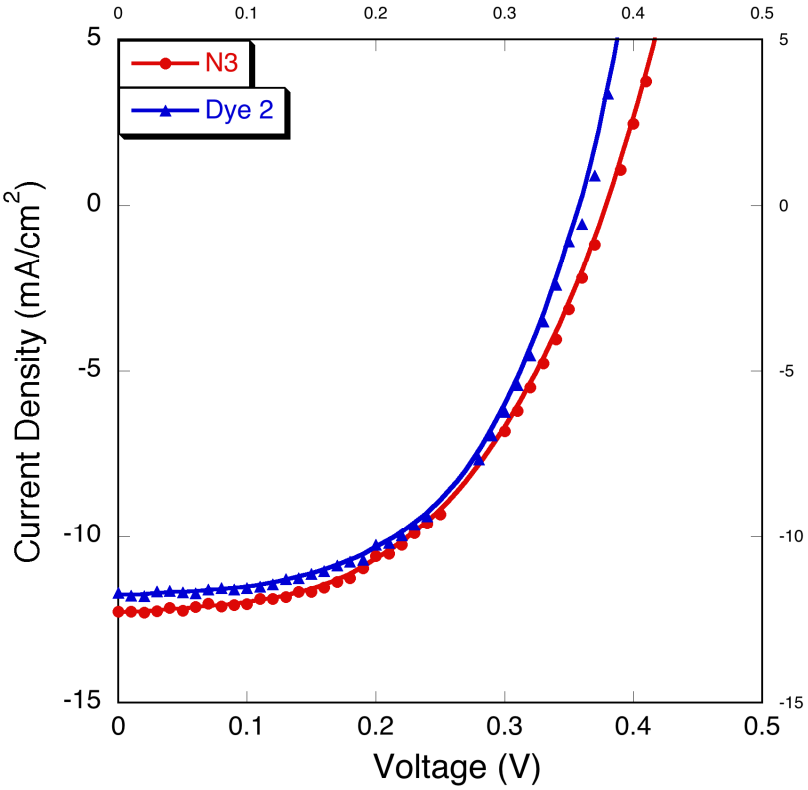


Figure S5. J-V curves for the data in Table 2.

Figure S6. ^{1}H NMR spectrum of *tert*-butyl 2-cyanoacetate (compound **S-1**).

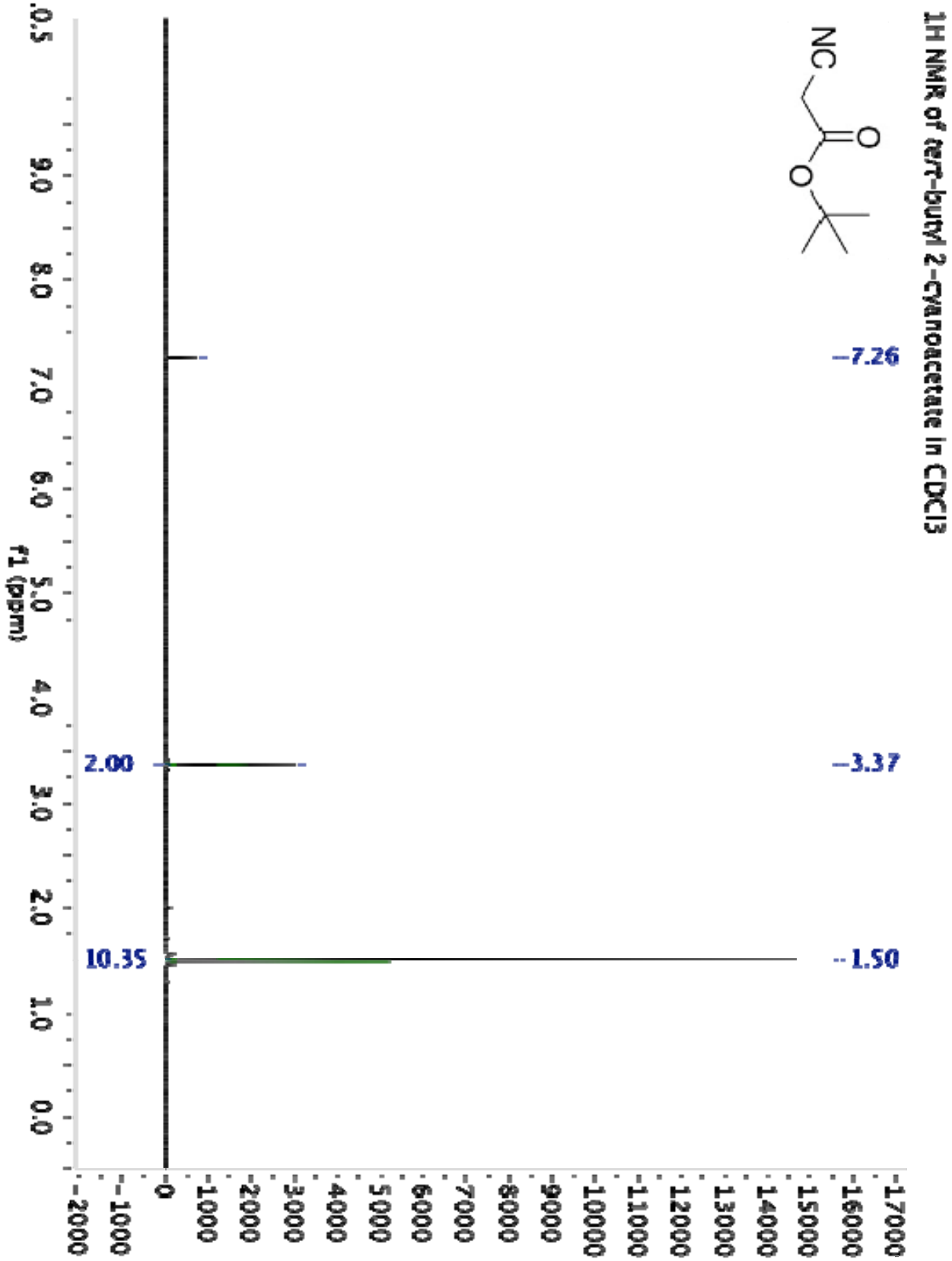


Figure S7. ^{13}C NMR spectrum of *tert*-butyl 2-cyanoacetate (compound **S-1**).

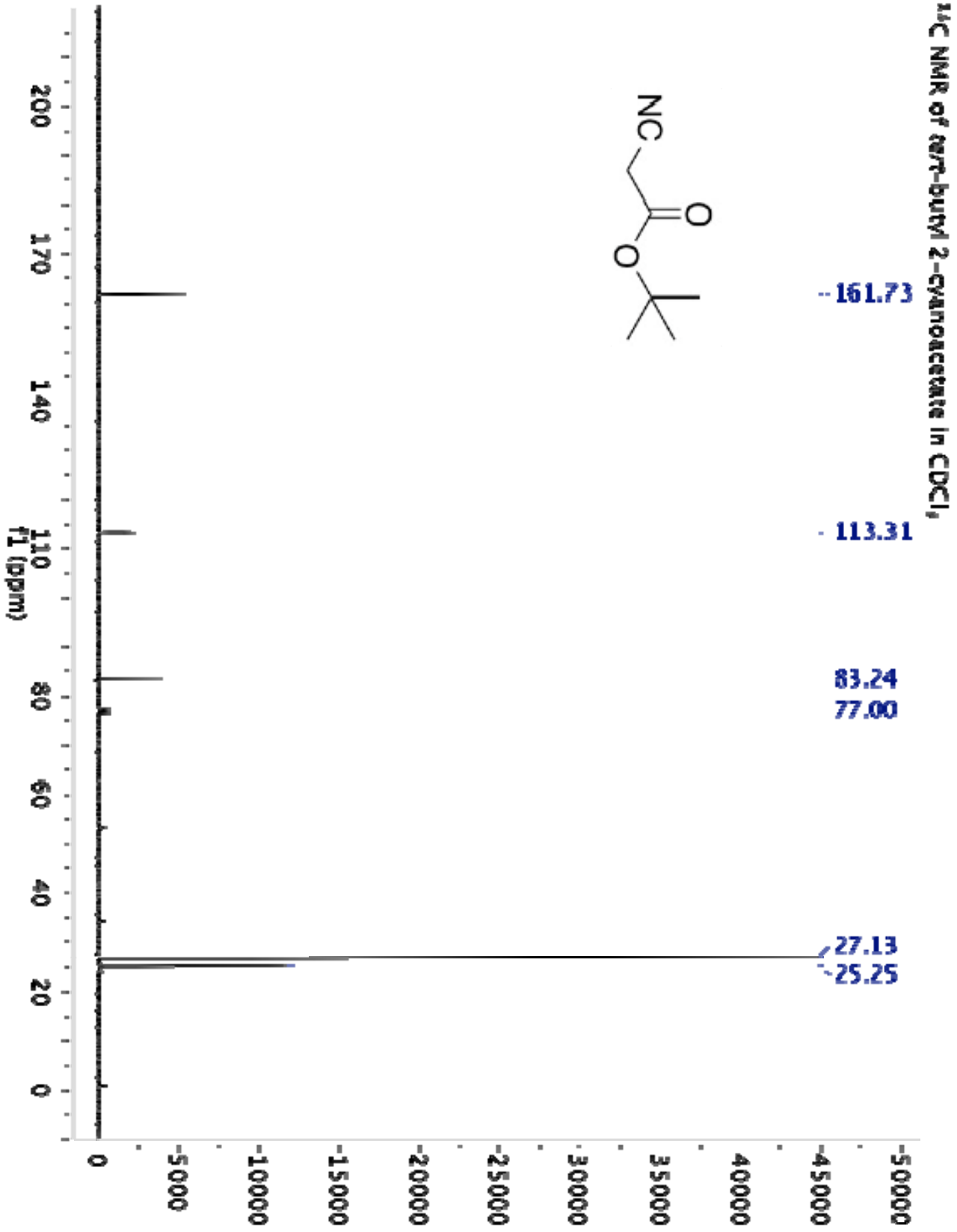


Figure S8. ^{1}H NMR spectrum of 4-(dibutylamino)benzaldehyde (compound **9**).

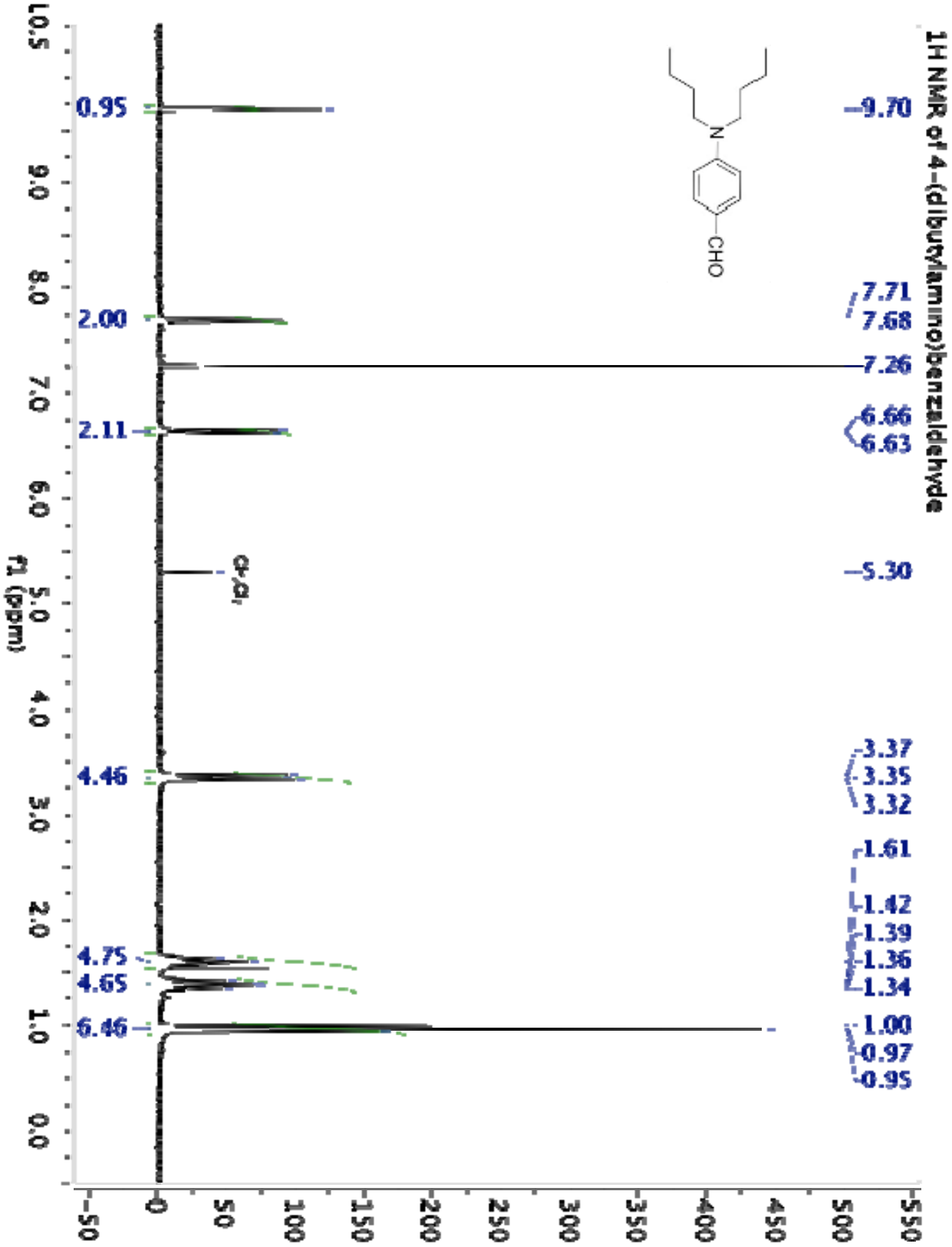


Figure S9. ^{13}C NMR spectrum of 4-(dibutylamino)benzaldehyde (compound **9**).

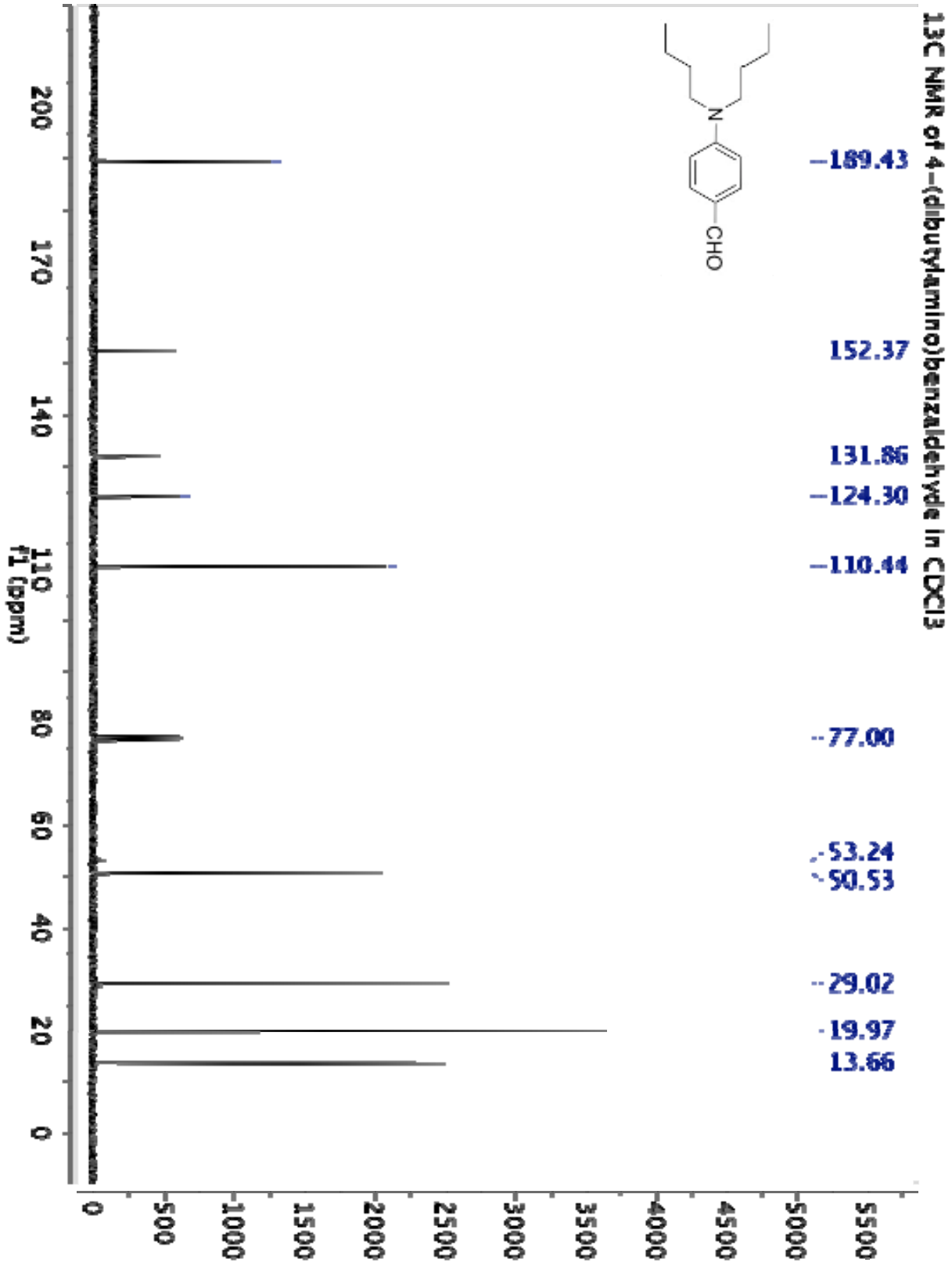


Figure S10. ^{1}H NMR spectrum of 2-(3-(*tert*-butyldimethylsilyloxy)-3-methylbutan-2-ylidene)propanedinitrile (compound **8**).

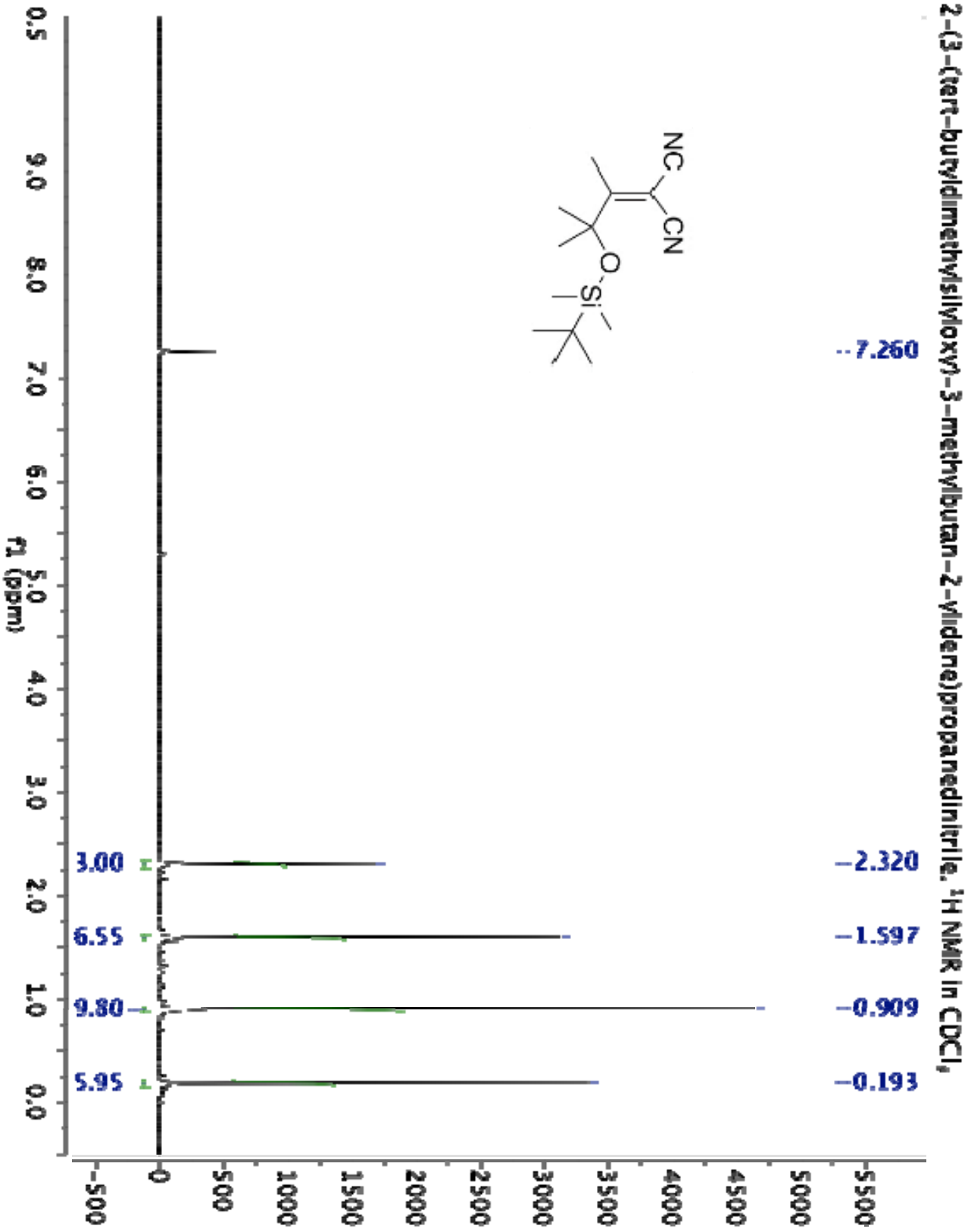


Figure S11. ^{13}C NMR of 2-(3-(*tert*-butyldimethylsilyloxy)-3-methylbutan-2-ylidene)propanedinitrile (compound **8**).

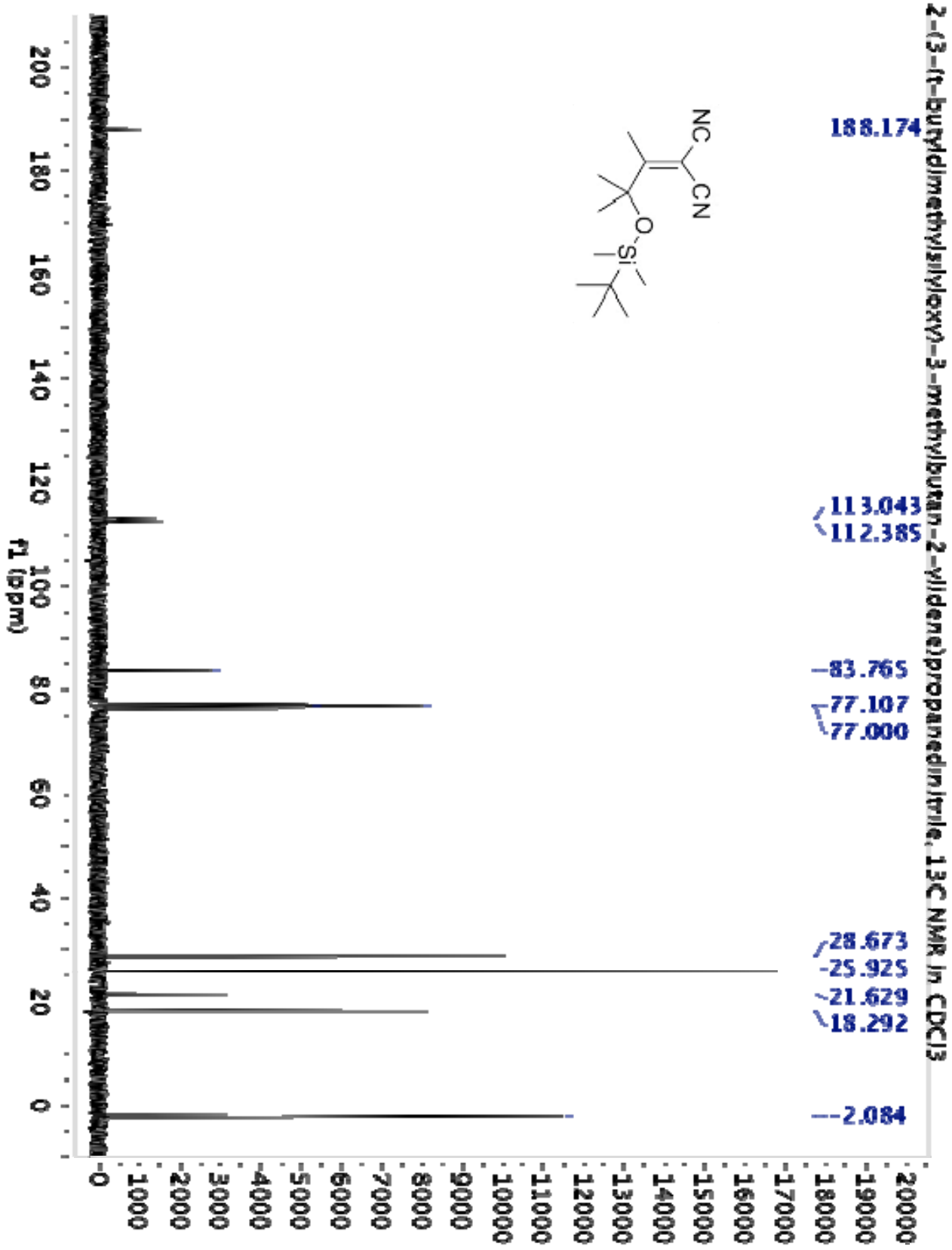


Figure S12. ^{1}H NMR spectrum of 2-imino-4,5,5-trimethyl-2,5-dihydrofuran-3-carbonitrile (compound **5**).

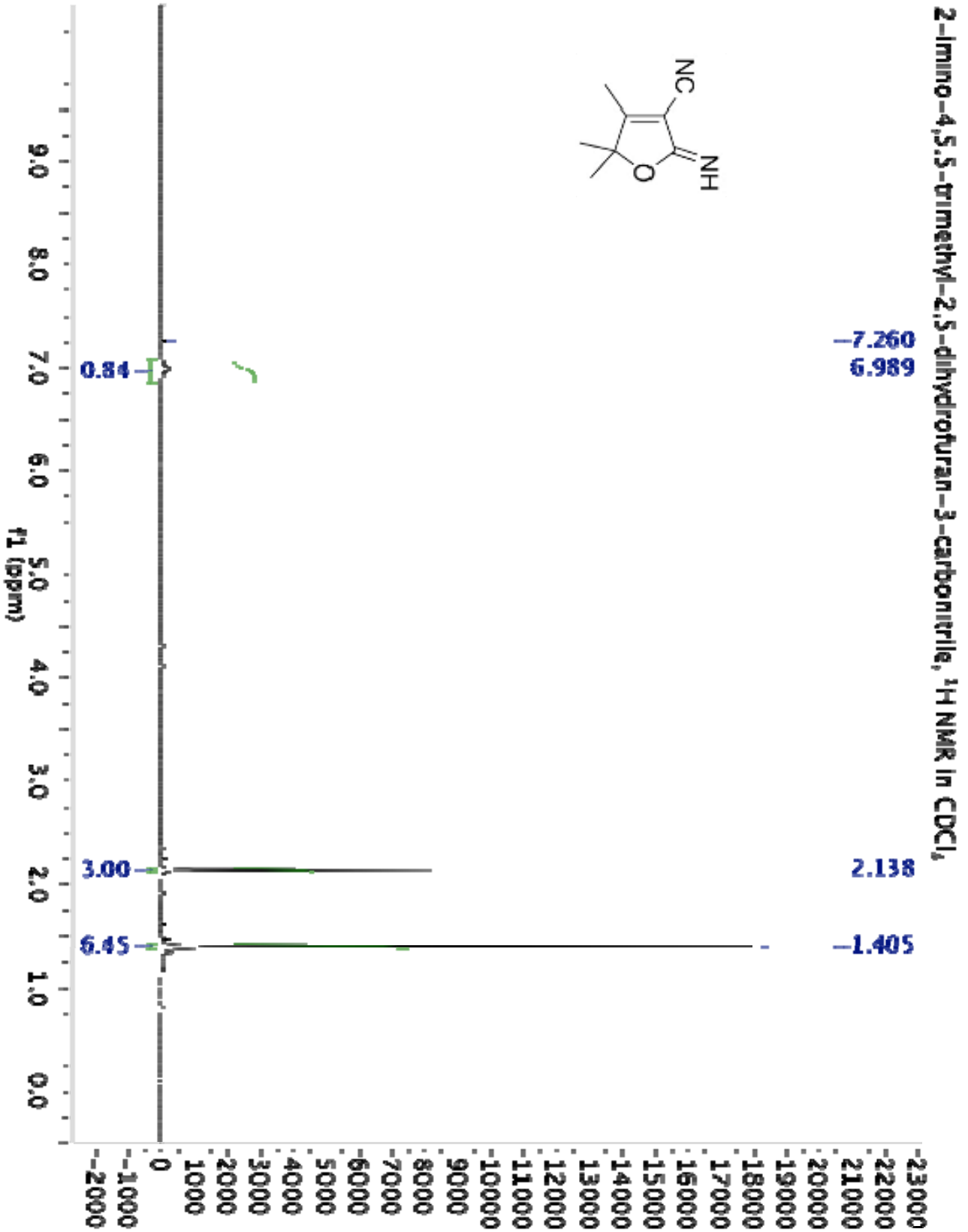


Figure S13. ^{13}C NMR spectrum of 2-imino-4,5,5-trimethyl-2,5-dihydrofuran-3-carbonitrile (compound **5**).

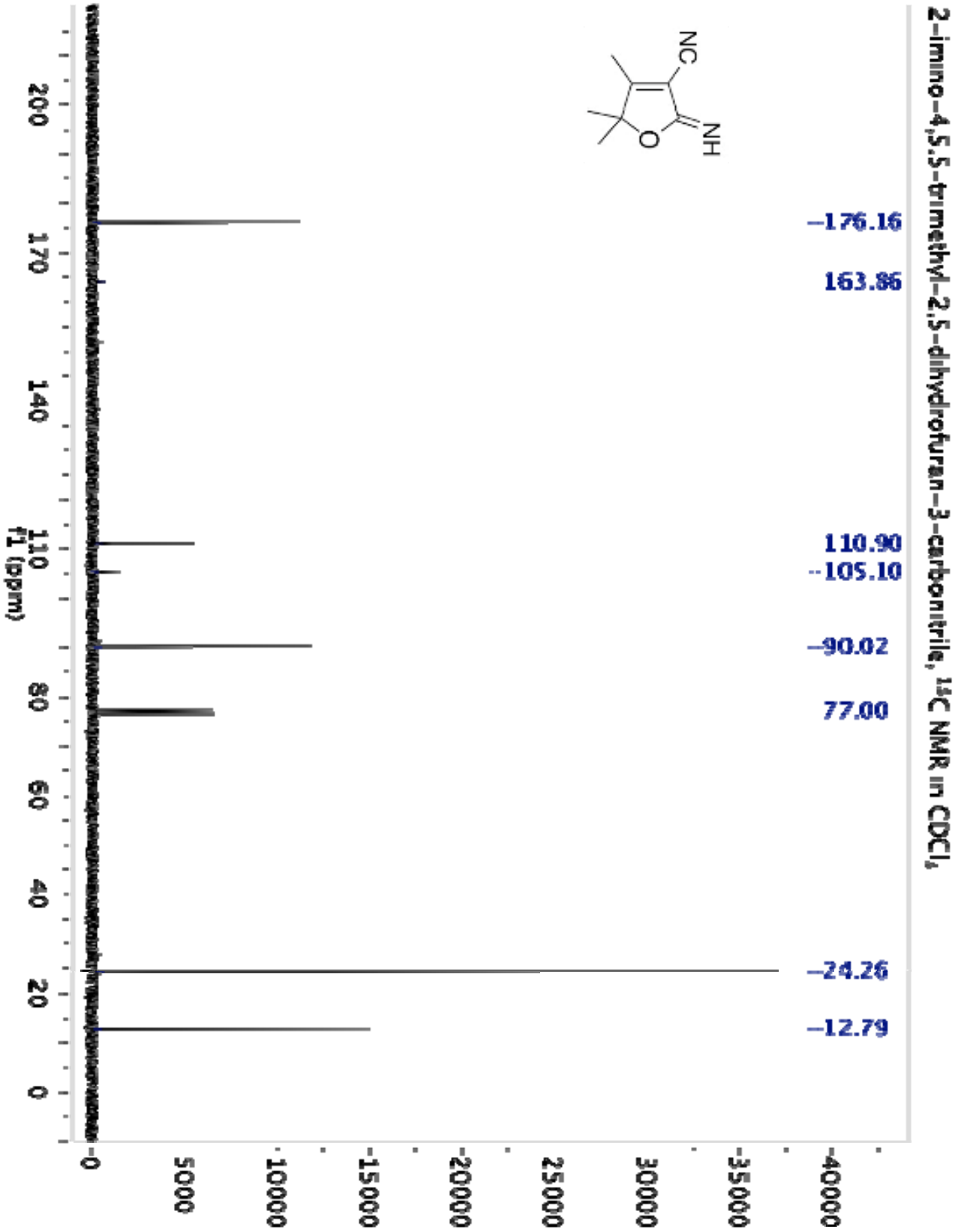


Figure S14. ^{1}H NMR spectrum of (*E*)- and (*Z*)- *tert*-butyl 2-cyano-2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)ethanoate (compound **10**). The peak at ~2.10 ppm is acetic acid contaminant.

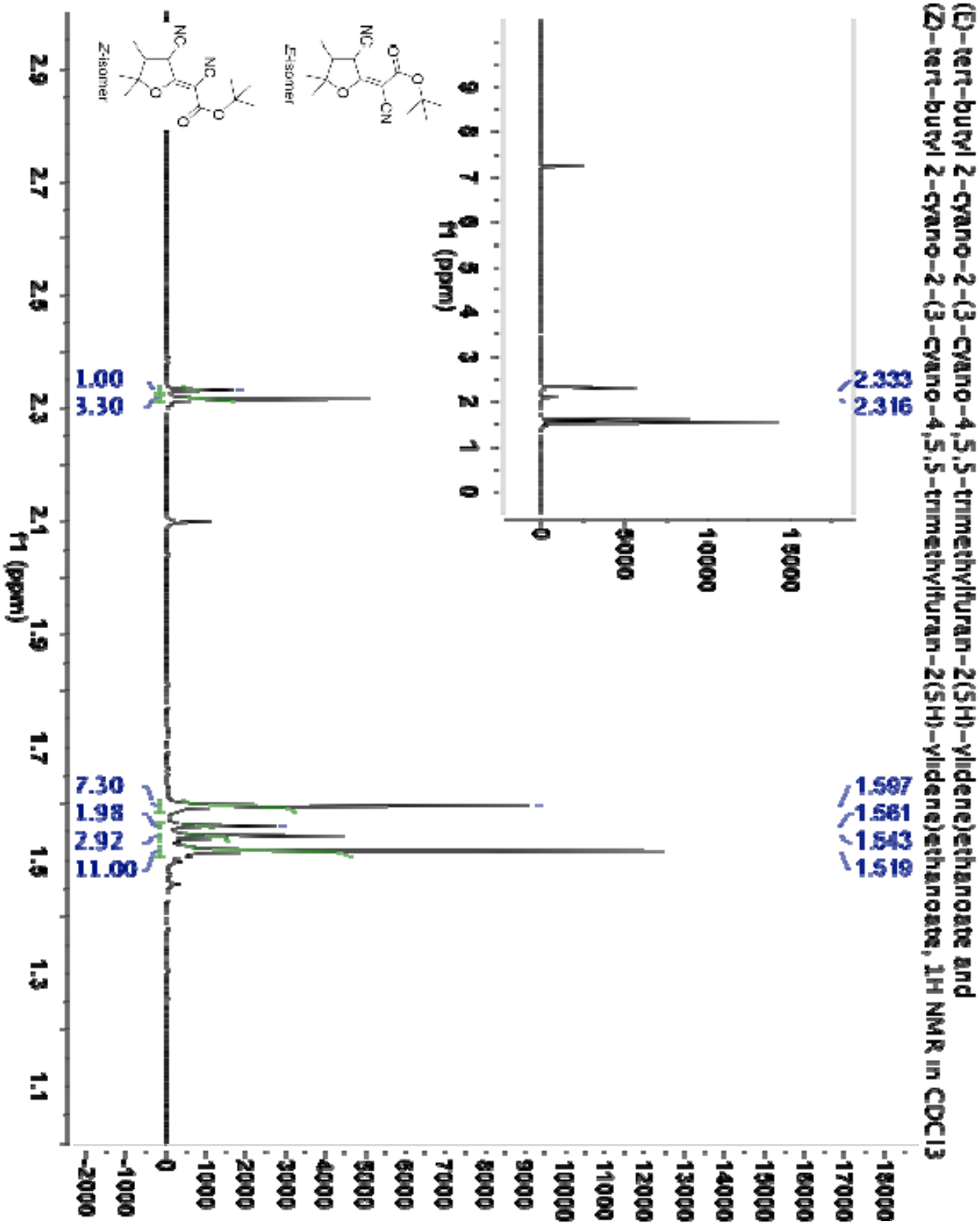


Figure S15. ^{1}H NMR spectrum of (*E*)-*tert*-butyl 2-cyano-2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)ethanoate (compound **10**).

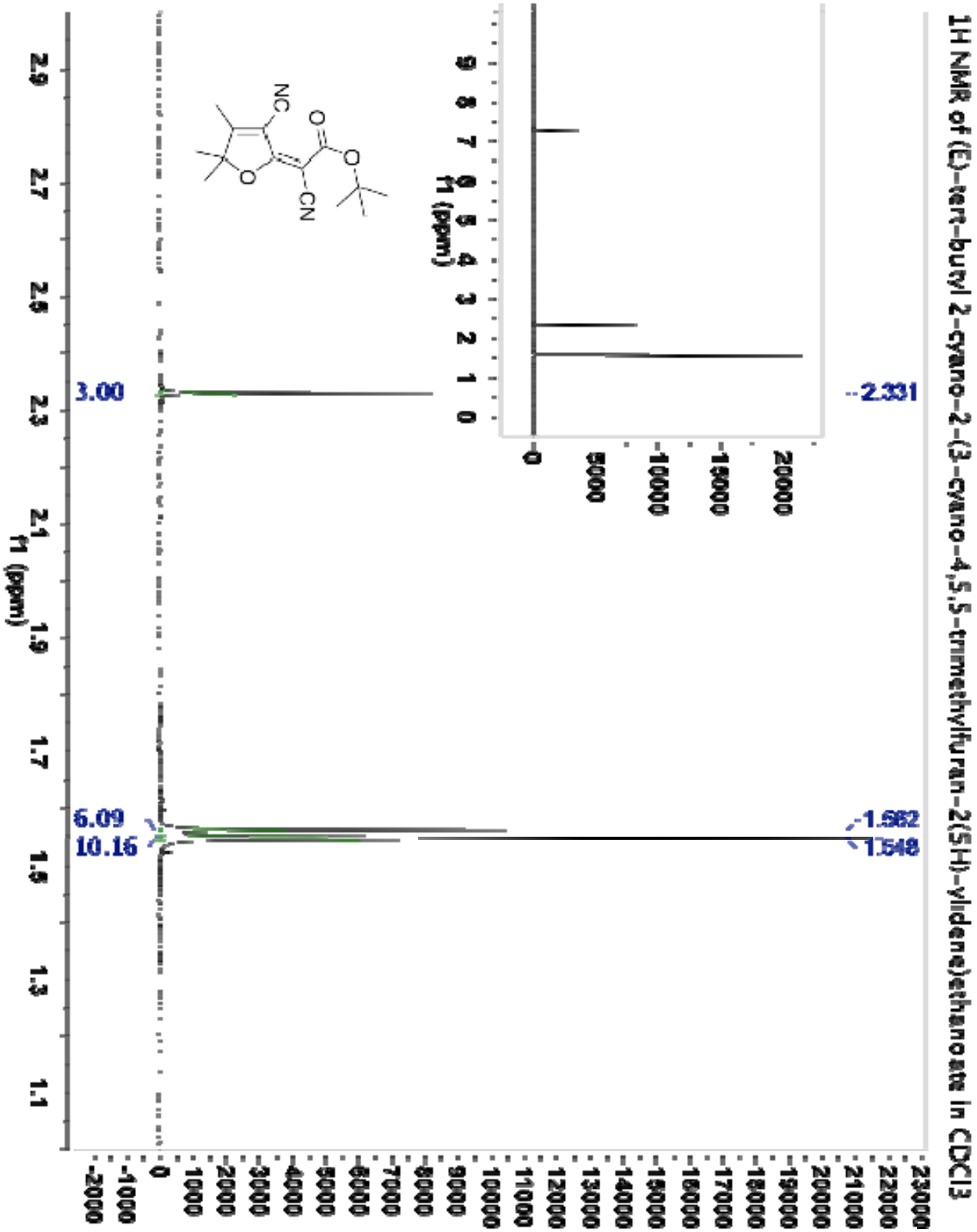


Figure S16. ^{13}C NMR spectrum of (*E*)-*tert*-butyl 2-cyano-2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)ethanoate (compound **10**).

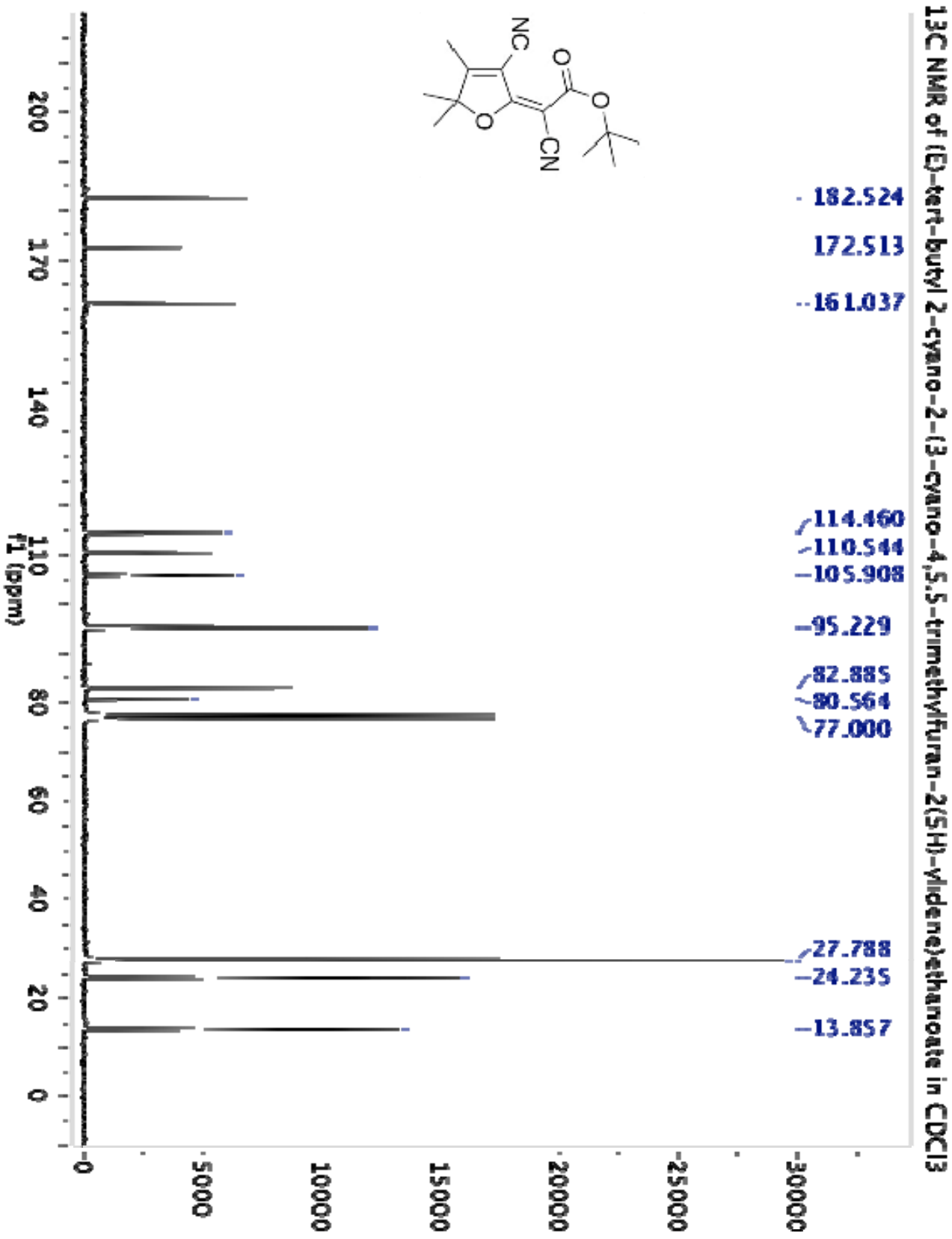


Figure S17. ^{1}H NMR spectrum of (*E*)- and (*Z*)-*tert*-butyl-2-cyano-2-(3-cyano-4-(4-(dibutylamino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)ethanoate (compound **11**).

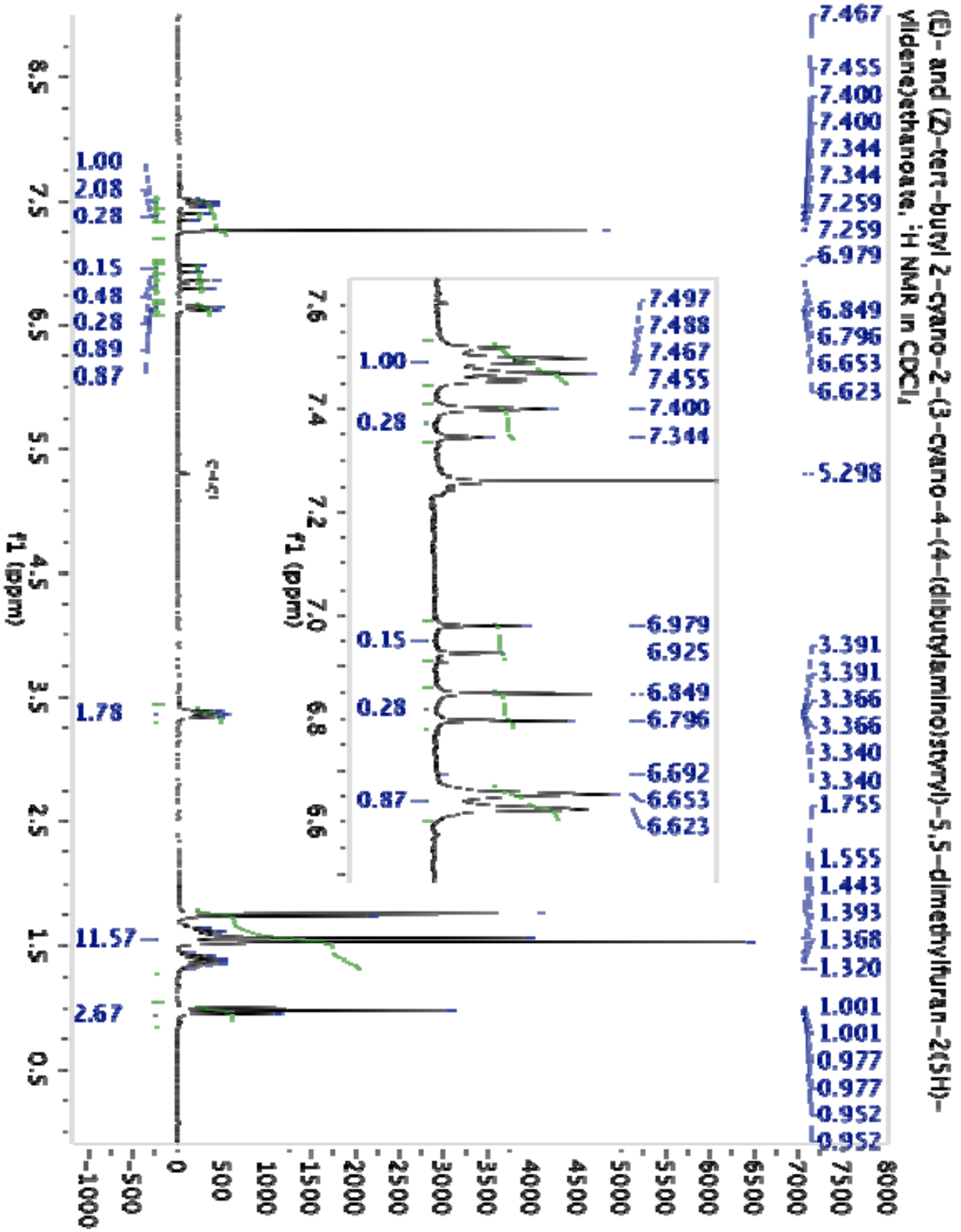


Figure S18. ^{1}H NMR spectrum of (*Z*)-*tert*-butyl-2-cyano-2-(3-cyano-4-(4-(dibutylamino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)ethanoate (compound **11**).

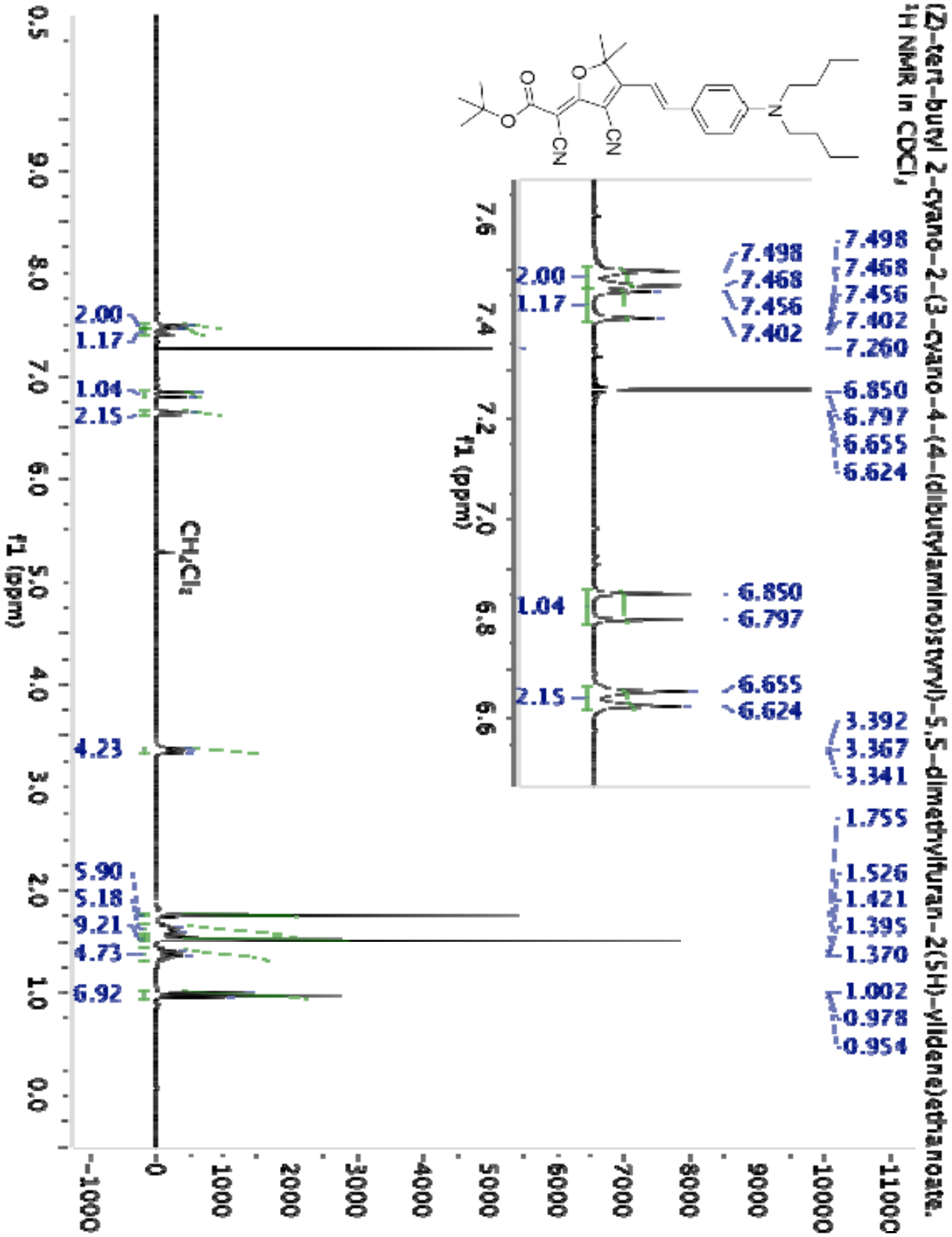


Figure S19. ^{13}C NMR spectrum of (*Z*)-*tert*-butyl-2-cyano-2-(3-cyano-4-(4-(dibutylamino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)ethanoate (compound **11**).

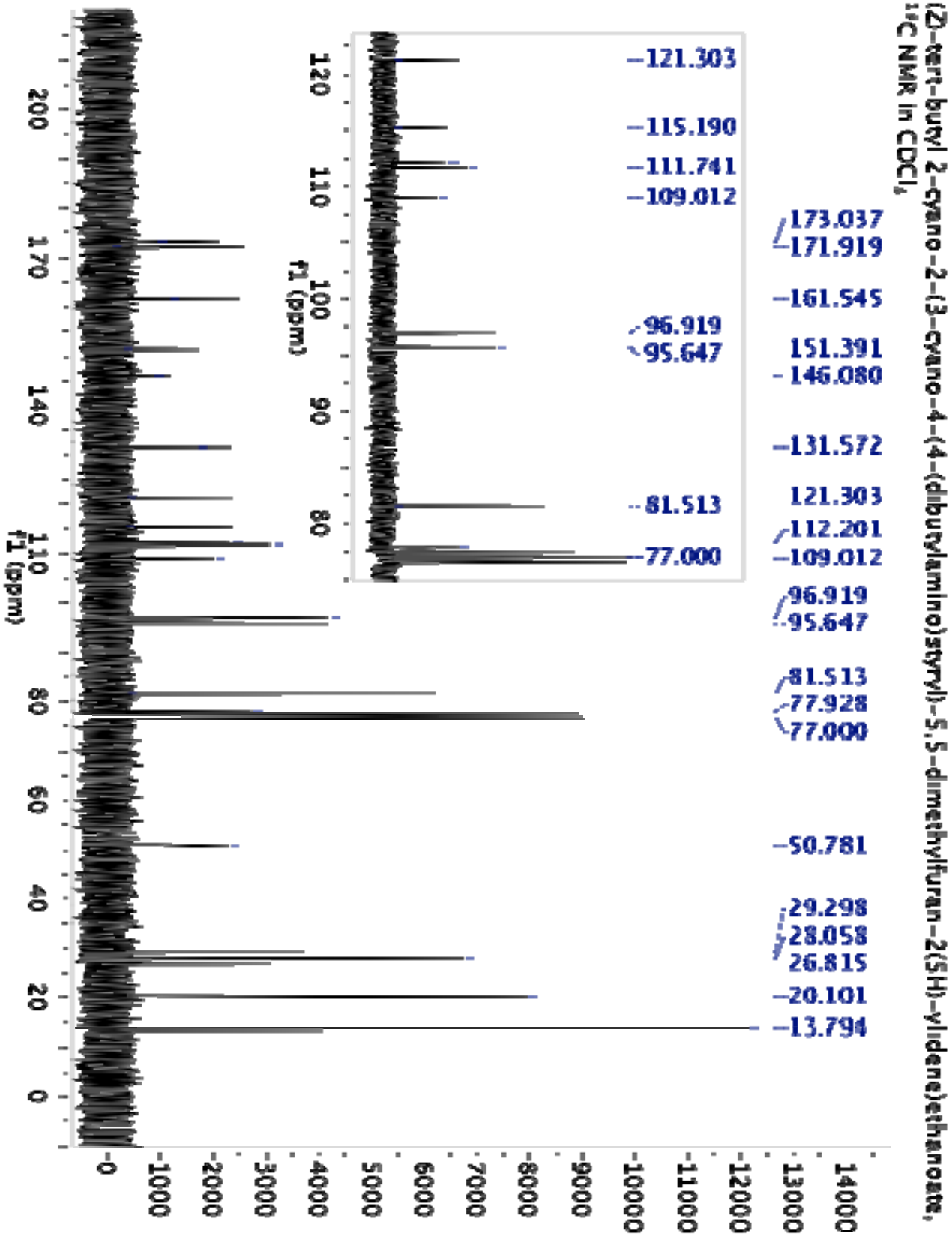


Figure S20. ^{1}H NMR spectrum of (*E*)- and (*Z*)-2-cyano-2-(3-cyano-4-((*E*)-4-(dibutylamino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)ethanoic acid (compound **2**) in DMSO.

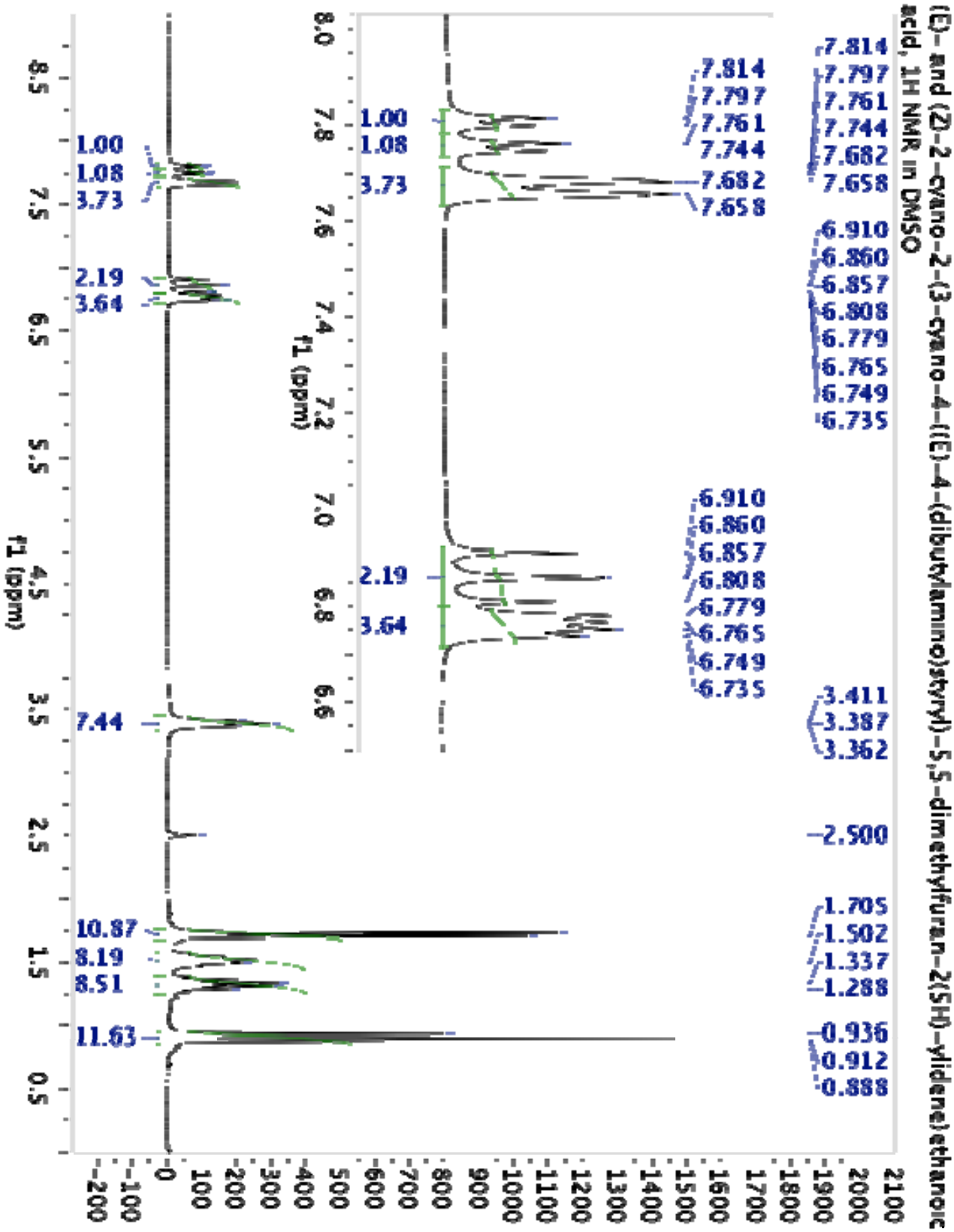


Figure S21. ^{13}C NMR spectrum of (*E*)- and (*Z*)-2-cyano-2-(3-cyano-4-((*E*)-4-(dibutylamino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)ethanoic acid (compound **2**) in DMSO.

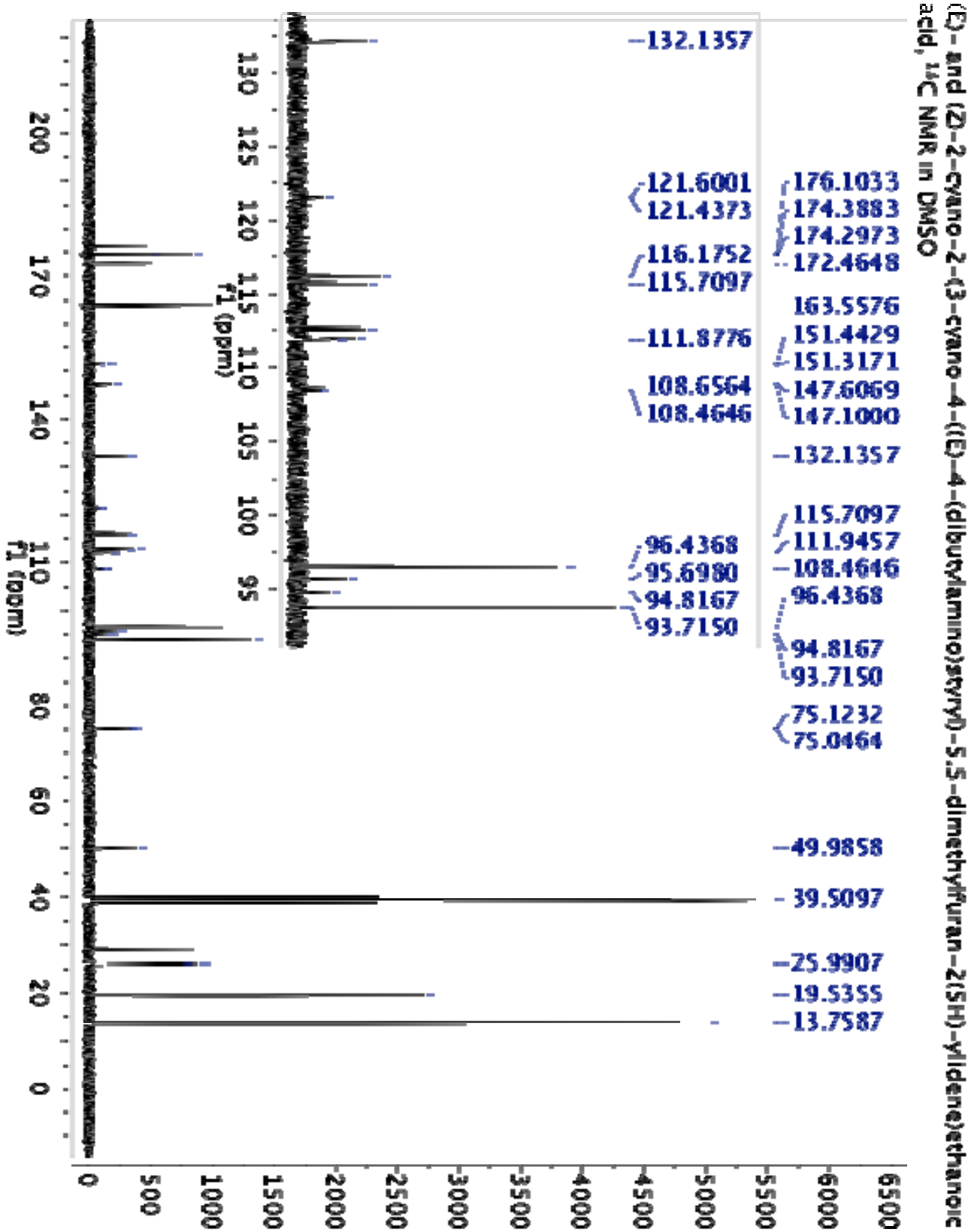


Table S1. Crystal data and structure refinement for Compound **10**.

Identification code	p9	
Empirical formula	C15 H18 N2 O3	
Formula weight	274.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pca2(1)	
Unit cell dimensions	a = 13.1063(16) Å	a= 90°.
	b = 11.6040(14) Å	b= 90°.
	c = 9.9901(13) Å	g = 90°.
Volume	1519.3(3) Å^3	
Z	4	
Density (calculated)	1.199 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	584	
Crystal size	0.25 x 0.25 x 0.15 mm^3	
Theta range for data collection	1.75 to 29.00°.	
Index ranges	-17<=h<=17, -15<=k<=15, -13<=l<=13	
Reflections collected	20898	
Independent reflections	4020 [R(int) = 0.0464]	
Completeness to theta = 29.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9875 and 0.9792	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4020 / 1 / 181	
Goodness-of-fit on F^2	1.146	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1024	
R indices (all data)	R1 = 0.0496, wR2 = 0.1060	
Absolute structure parameter	0.9(9)	
Largest diff. peak and hole	0.257 and -0.176 e.Å^{-3}	

Table S2. Crystal data and structure refinement for **11**.

Identification code	paul10	
Empirical formula	C30 H39 N3 O3	
Formula weight	489.64	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.680(3) Å	a= 90°.
	b = 8.7927(15) Å	b= 97.770(3)°.
	c = 19.636(3) Å	g = 90°.
Volume	2853.5(8) Å^3	
Z	4	
Density (calculated)	1.140 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	1056	
Crystal size	0.40 x 0.17 x 0.08 mm^3	
Theta range for data collection	1.23 to 26.00°.	
Index ranges	-20<=h<=20, -10<=k<=10, -24<=l<=24	
Reflections collected	32231	
Independent reflections	5619 [R(int) = 0.0923]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9941 and 0.9711	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5619 / 0 / 325	
Goodness-of-fit on F^2	0.911	
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1230	
R indices (all data)	R1 = 0.0895, wR2 = 0.1560	
Largest diff. peak and hole	0.261 and -0.275 e.Å^{-3}	