New Journal of Chemistry

Supporting Information

for

Conformation-induced light emission switching of *N*-acylhydrazone systems

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Contents

1. Absorption and emission properties in solutions of organic solvents and mixtures with water

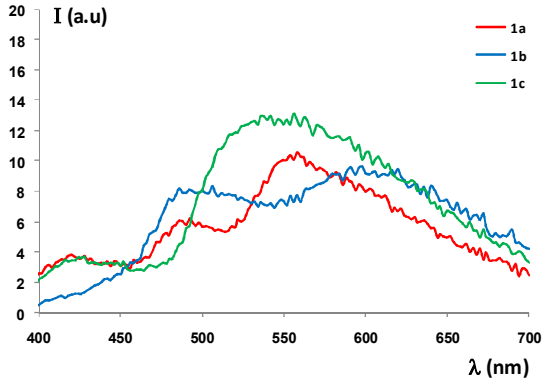

Figure S 1 Emission spectra of compounds **1a-c** at λ_{ex}=370nm

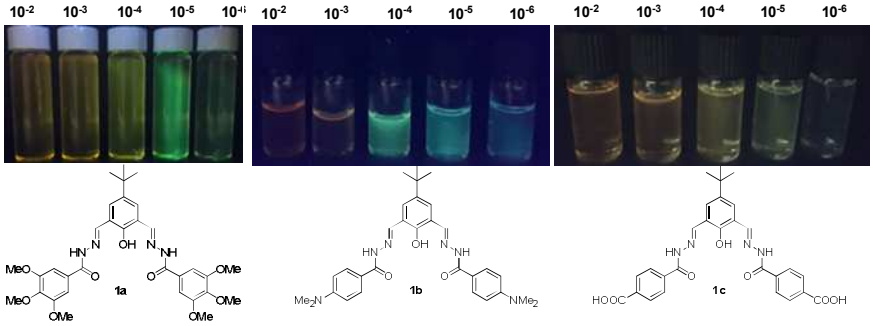

Figure S 2 Various concentrations of compounds **1a-c** in DMSO under UV light (365 nm)

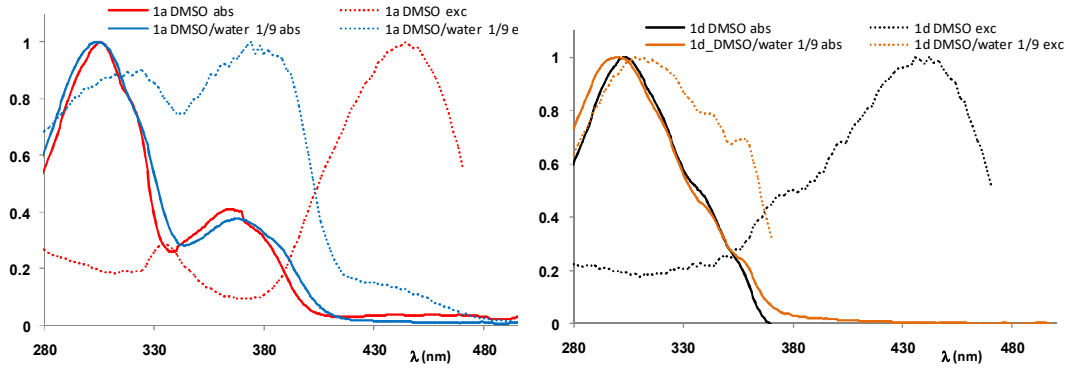

Figure S 3 Normalized absorption and excitation spectra of compounds **1a** and **1d** in DMSO and 90% water in DMSO

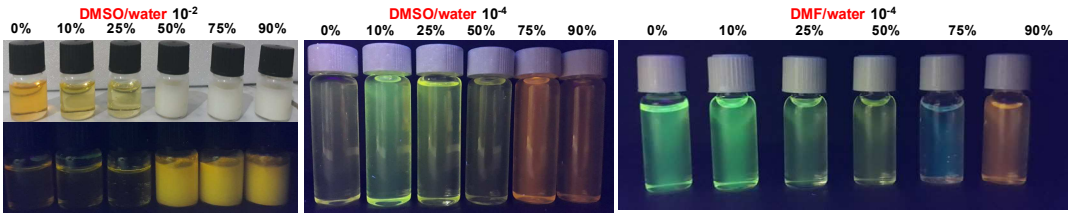

Figure S 4 Left: Solutions of **1a** in DMSO with increasing water content (10^{-2} M) under day light and UV light (365 nm). **Middle**: Solutions of **1a** in DMSO with increasing water content (10^{-4} M) under UV light (365 nm). **Right:** Solutions of **1a** in DMF with increasing water content (10^{-4} M) under UV light (365 nm).

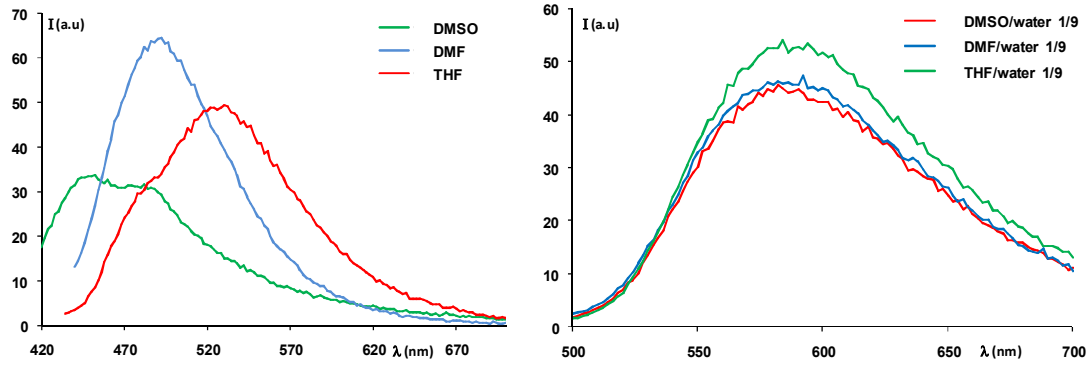

Figure S 5 Left: Emission spectra of compound **1a** (10^{-4} M) in various organic solvents (λ_{ex} = 370 nm).) **Right:** Emission spectra of compound **1a** (10^{-4} M) in various mixtures of organic solvents/water 1/9 v/v (λ_{ex} = 370 nm)

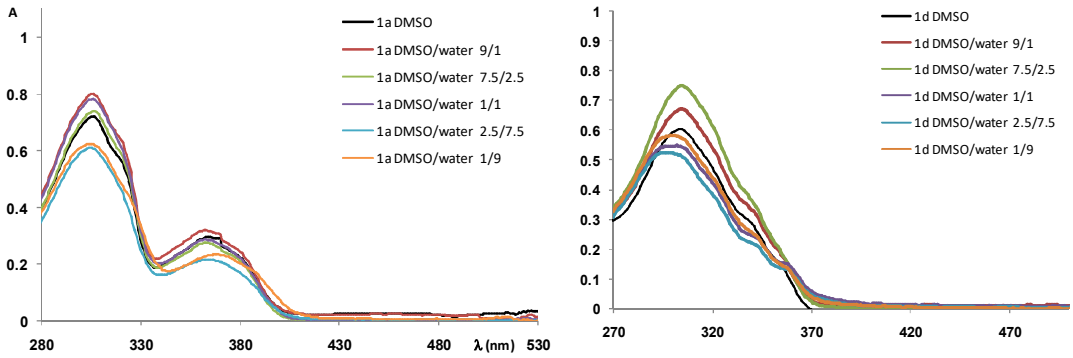

Figure S 6 Left Absorption spectra of compound **1a** in DMSO and various DMSO/water mixtures. **Right**: Absorption spectra of compound **1d** in DMSO and various DMSO/water mixtures

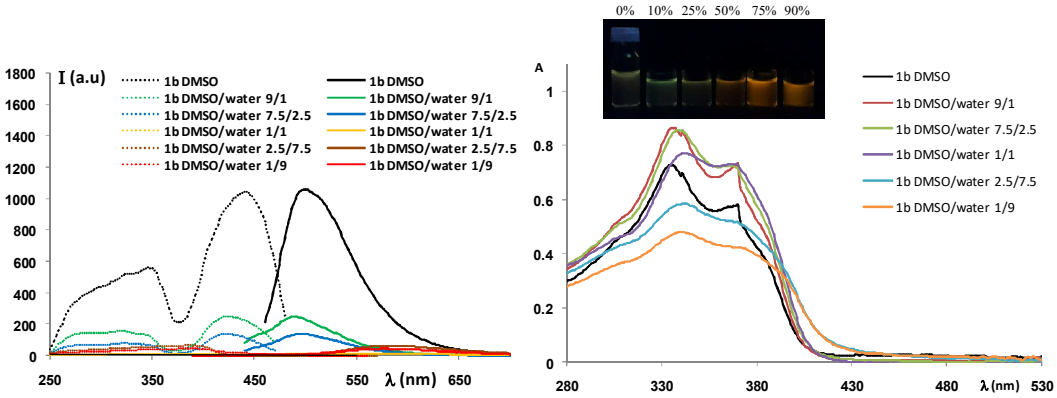

Figure S 7 Photo: Solutions of **1b** in DMSO with increasing water content (10^{-4} M) underUv light (365 nm). **Left**: Excitation and emission spectra of compound **1b** in DMSO and various DMSO/water mixtures. **Right** Absorption spectra of compound **1b** in DMSO and various DMSO/water mixtures

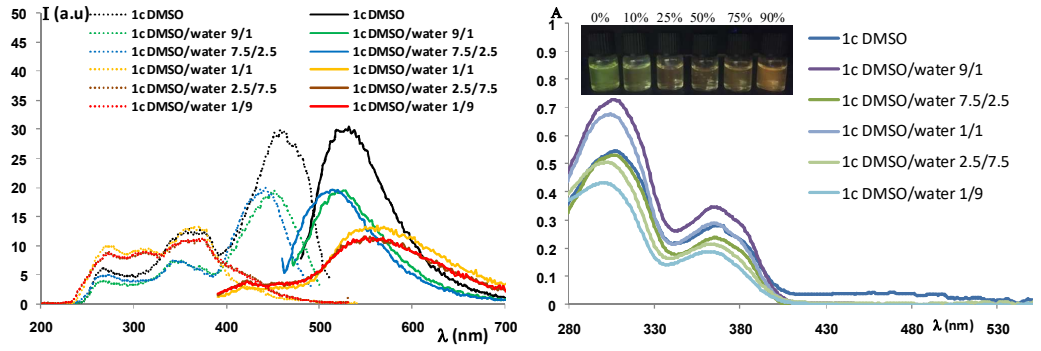

Figure S 8 Photo: Solutions of **1c** in DMSO with increasing water content (10^{-4} M) under UV light (365 nm). **Left**: Excitation and emission spectra of compound **1c** in DMSO and various DMSO/water mixtures. **Right** Absorption spectra of compound **1c** in DMSO and various DMSO/water mixtures

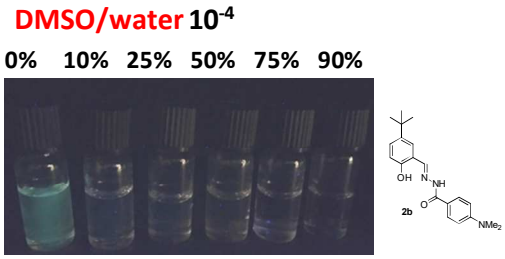

Figure S 9 Solutions of compound **2b** in DMSO with increasing amounts of water under UV light

Table S 1 Photophysical properties of compounds **1** in pure DMSO and various DMSO/water mixtures

	DMSO*		10% water in DMSO		25%water in DMSO		50%water in DMSO		75%water in DMSO		90%water in DMSO	
	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}
1a	370	440, 490, 552	370	444,484,548 wide band 400-700	370	450,470 wide band 400-700	370	450,550 wide band 400-700	370	590	370	588
	440	492	440	500	420	500	430	530				
1b	370	498 598	370	450,478 wide band 400-700	370	494 wide band 400-700	370	580 wide band 400-700	370	588	370	580
	440	500	420	490	422	494	402	580				
1c	370	550	370	420, 600 wide band 400-700	370	420, 584 wide band 400-700	370	562	370	548	370	550
	458	550	452	526	422	514						
1d	305	390, 494	305	396	305	396	305	358 396 422	305	396	305	396
	442	490	370	422	358	396						

* Quantum yields were calculated using fluoresceine as standard according to ref [1]

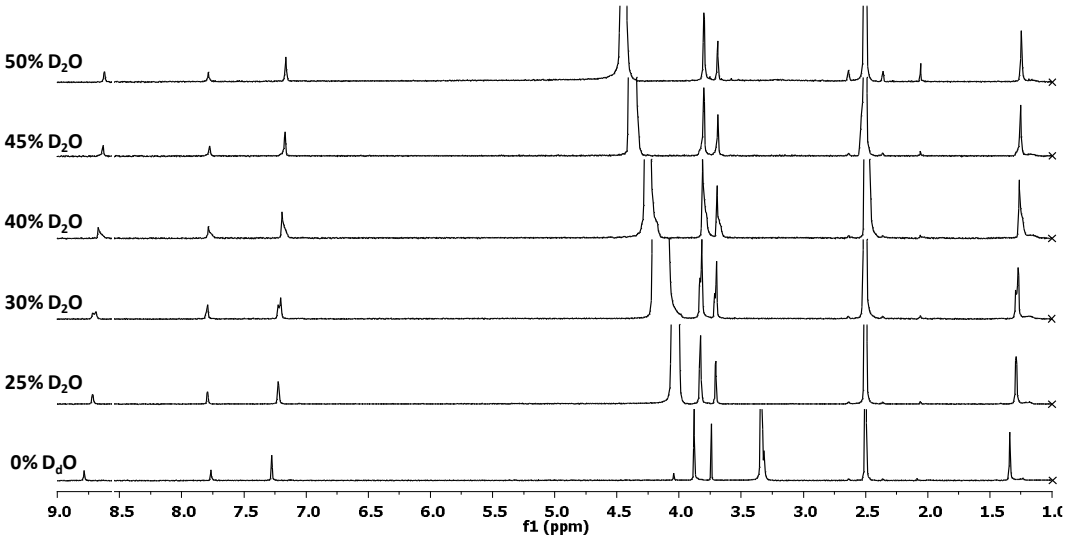

Figure S 10 Full ^{1}H NMR (500 MHz) spectra of compound **1a** in DMSO and increasing amounts of D_2O

[1] a) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107–1114 ; b) Brouwer, A. M. *Pure Appl. Chem.* **2011**, 83, 2213–2228.

2. Absorption and emission properties in solid state

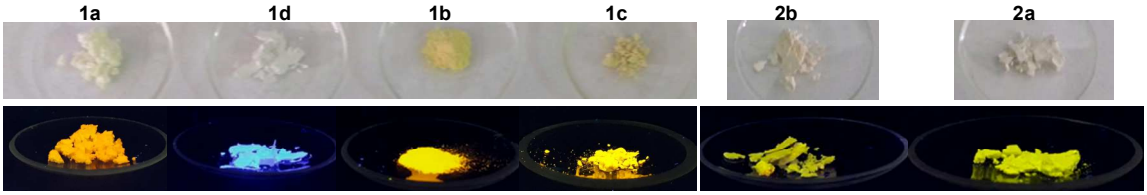

Figure S 11 Photos of solids **1**and **2**under day light and UV light

3. Absorption and emission spectra before and after irradiation experiments

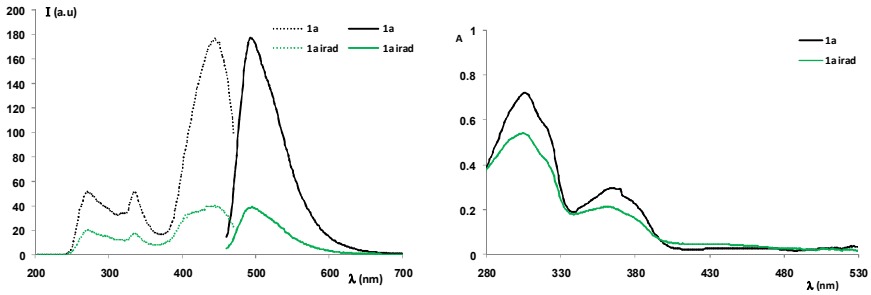

Figure S 12 Left: Excitation and emission spectra of compound **1a** in DMSO (2 x 10^{-5} M) before and after irradiation at 365 nm for 2h.
Right: UV-Vis spectra of **1a** in DMSO (2 x 10^{-5} M) before and after irradiation at 365 nm for 2h.

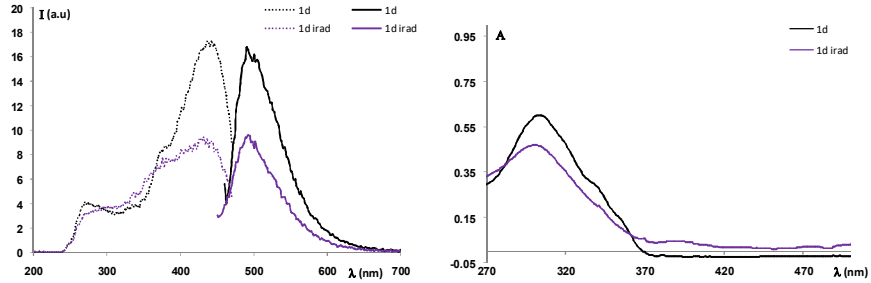

Figure S 13 Left: Excitation and emission spectra of compound **1d** in DMSO (2 x 10^{-5} M) before and after irradiation at 365 nm for 2h.
Right: UV-Vis spectra of **1d** in DMSO (2 x 10^{-5} M) before and after irradiation at 365 nm for 2h.

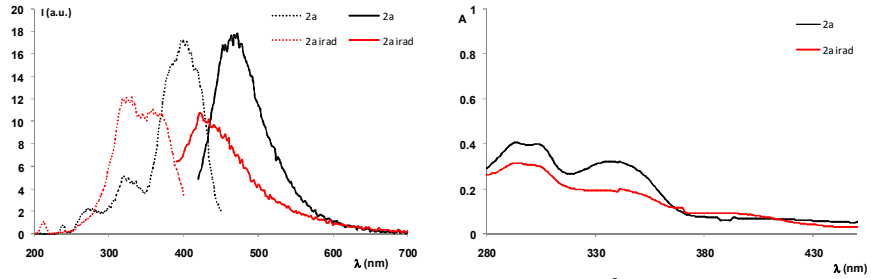

Figure S 14 Left: Excitation and emission spectra of compound **2a** in DMSO (2 x 10^{-5} M) before and after irradiation at 365 nm for 2h.
Right: UV-Vis spectra of **2a** in DMSO (2 x 10^{-5} M) before and after irradiation at 365 nm for 2h.

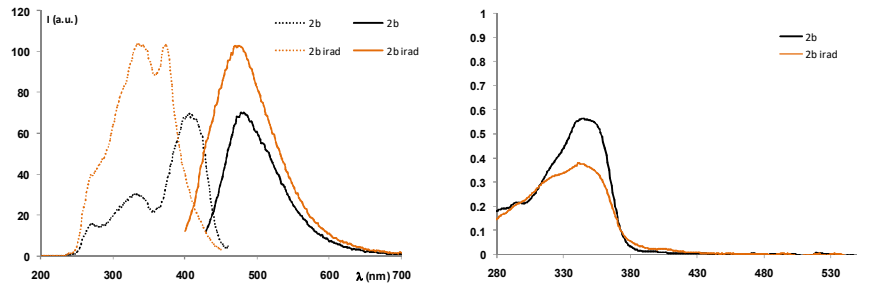

Figure S 15 Left: Excitation and emission spectra of compound **2b** in DMSO (2 x 10^{-5} M) before and after irradiation at 365 nm for 2h.
Right: UV-Vis spectra of **2b** in DMSO (2 x 10^{-5} M) before and after irradiation at 365 nm for 2h.

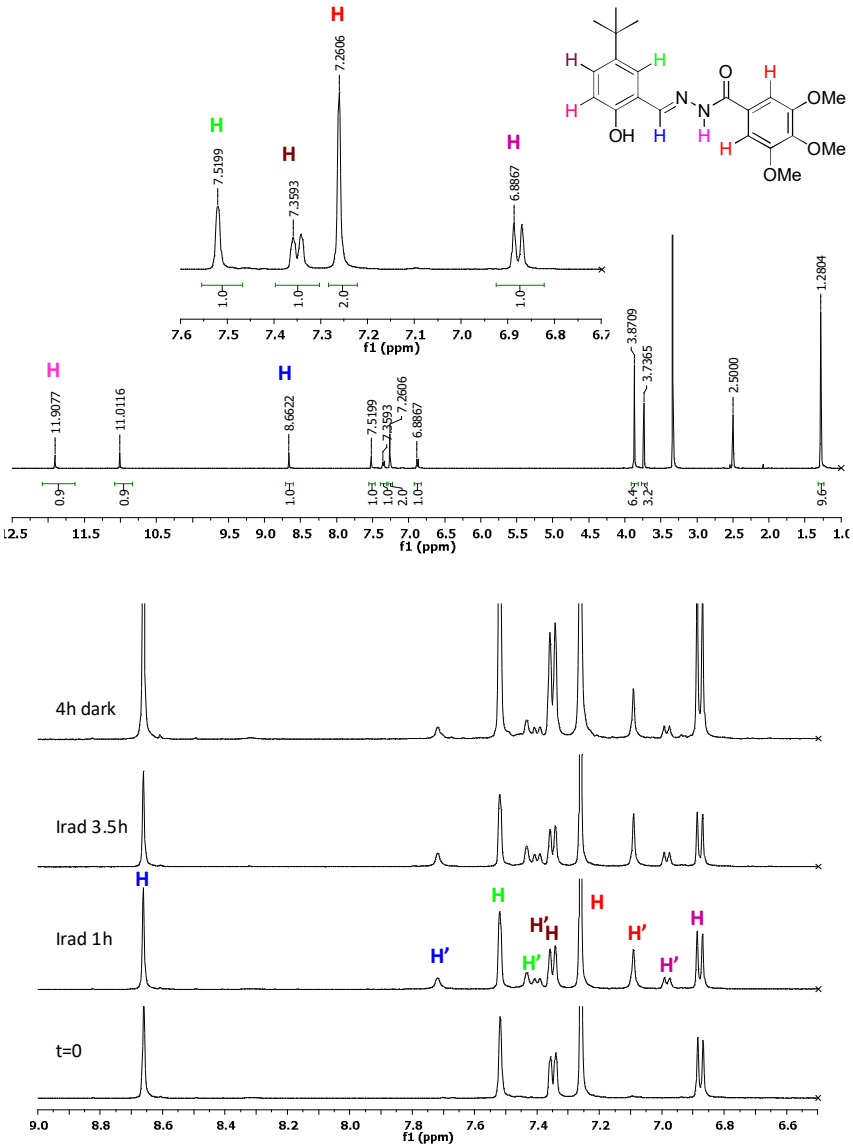

Figure S 16 Top: Full ^{1}H NMR spectrum (500 MHz,) of compound **2a** in DMSO-d_6 and assignment of the signals. **Bottom**: ^{1}H NMR spectra (500 MHz, fragments) of compound **2a** in DMSO-d_6 recorded before and after irradiation for the specified time.

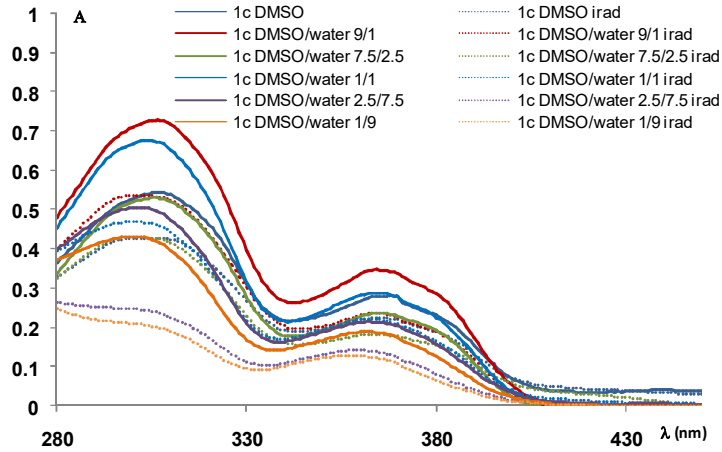

Figure S 17 UV-Vis spectra of **1c** in DMSO (2 x 10^{-5} M) and various mixtures DMSO/water before and after irradiation for 2h.

4. Crystallography

Table S 2 Selected bond lengths for compound **1b** (Å)

1b·DMSO		**1b·THF**	
C1-N1 = 1.443(4)	C14-C15 = 1.520(5)	C1-N1 = 1.443(8)	C19-C20 = 1.392(7)
C2-N1 = 1.438(4)	C18-C19 = 1.394(4)	C2-N1 = 1.457(7)	C19-C21 = 1.459(7)
C3-C4 = 1.376(4)	C19-C20 = 1.400(4)	C3-C4 = 1.365(7)	C20-O2 = 1.348(6)
C3-C8 = 1.384(4)	C19-C21 = 1.454(4)	C3-C8 = 1.382(7)	C21-N4 = 1.270(6)
C4-C5 = 1.399(4)	C20-O2 = 1.350(3)	C4-C5 = 1.395(8)	C22-O3 = 1.239(6)
C5-N1 = 1.370(4)	C21-N4 = 1.265(4)	C5-N1 = 1.363(7)	C22-N5 = 1.350(7)
C5-C6 = 1.392(4)	C22-O3 = 1.234(3)	C5-C6 = 1.393(8)	C22-C23 = 1.464(7)
C6-C7 = 1.374(4)	C22-N5 = 1.348(4)	C6-C7 = 1.366(7)	C23-C24 = 1.361(7)
C7-C8 = 1.388(4)	C22-C23 = 1.476(4)	C7-C8 = 1.370(7)	C23-C28 = 1.387(7)
C8-C9 = 1.470(4)	C23-C24 = 1.379(4)	C8-C9 = 1.494(7)	C24-C25 = 1.392(8)
C9-O1 = 1.227(4)	C23-C28 = 1.389(4)	C9-O1 = 1.223(6)	C25-C26 = 1.391(7)
C9-N2 = 1.365(4)	C24-C25 = 1.368(4)	C9-N2 = 1.378(7)	C26-N6 = 1.364(7)
C10-N3 = 1.271(4)	C25-C26 = 1.396(4)	C10-N3 = 1.266(6)	C26-C27 = 1.393(7)
C10-C11 = 1.449(4)	C26-N6 = 1.369(4)	C10-C11 = 1.450(7)	C27-C28 = 1.362(7)
C11-C12 = 1.393(4)	C26-C27 = 1.405(4)	C11-C12 = 1.403(7)	C29-N6 = 1.428(8)
C11-C20 = 1.404(4)	C27-C28 = 1.373(4)	C11-C20 = 1.413(7)	C30-N6 = 1.445(7)
C12-C13 = 1.390(4)	C29-N6 = 1.446(4)	C12-C13 = 1.385(7)	C31-C32 = 1.315(12)
C13-C18 = 1.378(4)	C30-N6 = 1.442(4)	C13-C18 = 1.382(7)	C31-O4 = 1.426(8)
C13-C14 = 1.534(4)	N2-N3 = 1.372(3)	C13-C14 = 1.517(8)	C32-C33 = 1.433(14)
C14-C17 = 1.497(5)	N4-N5 = 1.389(3)	C14-C15 = 1.504(8)	C33-C34 = 1.537(12)
C14-C16 = 1.509(5)		C14-C17 = 1.524(9)	C34-O4 = 1.357(9)
		C14-C16 = 1.528(9)	N2-N3 = 1.373(6)
		C18-C19 = 1.379(7)	N4-N5 = 1.377(6)

Table S 3 Crystallographic data, details of data collection and structure refinement parameters for compound **1b**

Compound	**1b·DMSO**	**1b·THF**
Chemical formula	$C_{32}H_{42}N_6O_4S$	$C_{34}H_{44}N_6O_4$
M (g mol^{-1})	606.77	600.75
Temperature, (K)	293(2)	293(2)
Wavelength, (Å)	0.71073	0.71073
Crystal system	*Monoclinic*	*Monoclinic*
Space group	$P2_1/c$	$P2_1/c$
a(Å)	10.9327(6)	11.036(2)
b(Å)	12.6897(9)	13.9465(18)
c(Å)	23.7448(11)	21.165(3)
α(°)	90	90
β(°)	99.417(4)	95.814(15)
γ(°)	90	90
V(Å^3)	3249.8(3)	3241.0(9)
Z	4	4
D_c (g cm^{-3})	1.240	1.231
μ (mm^{-1})	0.144	0.082
Goodness-of-fit on F^2	0.761	0.995
Final $R1$,wR_2 [$I>2\sigma(I)$]	0.0534, 0.1216	0.0830, 0.1731
$R1$, wR_2(all data)	0.1615, 0.1508	0.2500, 0.2465
Largest diff. peak and hole (eÅ^{-3})	0.541, -0.499	0.263, -0.216

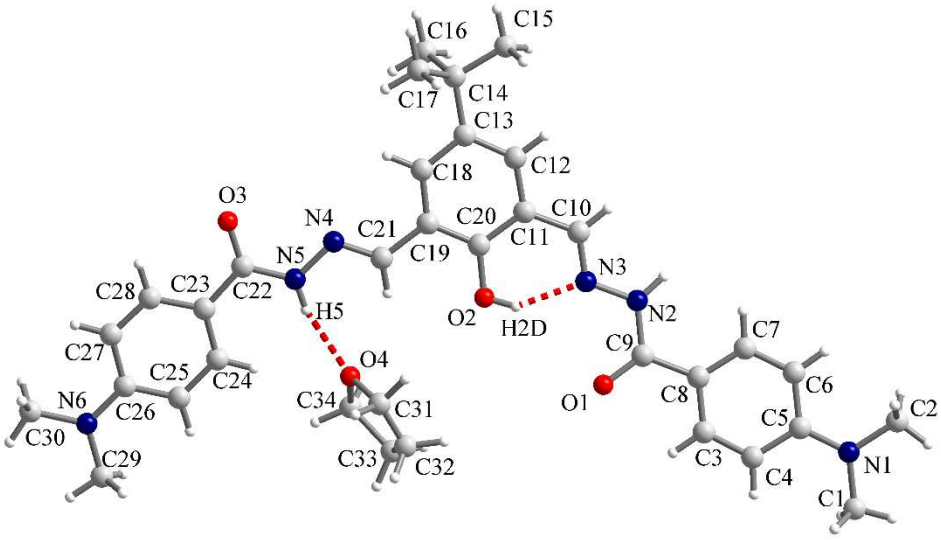

Figure S 18 View of the asymmetric unit in the crystal structure of compound **1b THF** along with the atoms labelling scheme (for clarity only the hydrogen atoms involved in hydrogen interactions were labelled).

5. Synthesis and NMR spectra

The aldehydes **3a-c** were synthesized according to previously described procedures[2] using Duff conditions (HMTA and TFA), while the hydrazides **4a-c**were either commercially available or readily synthesized from the corresponding carboxylic acids.

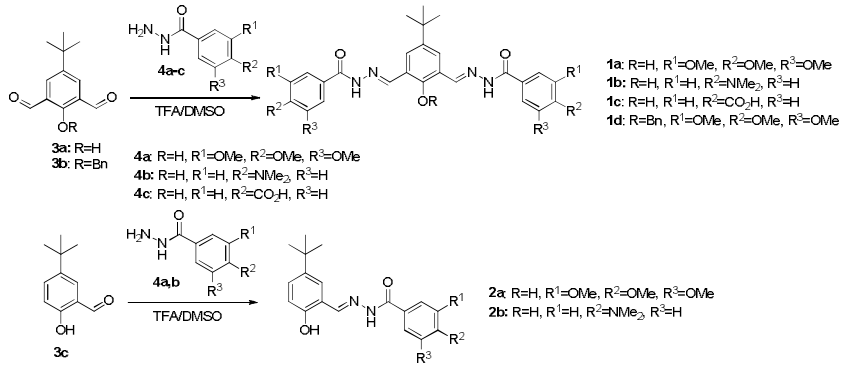

Figure S 19 Synthesis of *N*-acylhydrazones **1** and **2**

General experimental procedure for the synthesis of *N*-acylhydrazones. A mixture of the aldehyde (1 eq.) and the corresponding hydrazide (2 eq. for compounds **1** and 1 eq. for compounds **2**) were dissolved in DMSO (up to a 0.1-0.01 M final concentration) and a few drops of trifluoroacetic acid were added. The reaction mixture was heated at 100°C overnight. Water was added to the reaction mixture (up to 90%) and the resulting precipitate was filtered, washed with water and diethylether and dried to yield pure compounds.

(*N',N''E,N',N''E*)-*N',N''*-(5-*tert*-butyl-2-hydroxy-1,3-phenylene)bis(methan-1-yl-1-ylidene)bis(3,4,5-trimethoxybenzohydrazide) 1a. Light-yellow solid. Yield 88% (0.11 g). *m.p.* 277-281°C. R_f=0.6 (silica, EtOAc). ^{1}H RMN (500 MHz, DMSO-d_6): δ= 12.40 (s, 1H, O*H*), 12.00 (s, 1H, N*H*), 8.78 (s, 2H, C*H*N), 7.76 (s, 2H, H_{Ar}), 7.27 (s, 4H, H_{Ar}), 3.87 (s, 6H, OCH_3), 3.74 (s, 3H, OCH_3), 1.33 (s, 9H, *t*Bu) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ= 162.4; 154.7; 152.7; 146.4; 141.7; 140.6; 127.9; 126.8; 120.2; 119.6; 105.3; 60.2; 56.1; 33.9; 31.2 ppm. HRMS (APCI, +) m/z: calc. for $C_{32}H_{39}N_4O_9$ $[M+H]^+$ 623.2712 found 623.2710.

(*N',N''E,N',N''E*)-*N',N''*-(5-*tert*-butyl-2-hydroxy-1,3-phenylene)bis(methan-1-yl-1-ylidene)bis(4-(dimethylamino)benzohydrazide) 1b. Light-yellow solid. Yield 82% (0.434 g). *m.p.* 225-228°C. R_f=0.1 (silica, EtOAc:petroleum ether=1:1). ^{1}H RMN (500 MHz, DMSO-d_6): δ= 12.50 (s, 1H, N*H*), 11.84 (s, 1H, O*H*), 8.72 (s, 1H, C*H*N), 7.84 (d, 1H, ^3J=8.5 Hz, H_{Ar}), 7.70 (s, 2H, H_{Ar}), 6.77 (d, 1H, ^3J=8.5 Hz, H_{Ar}), 3.01 (s, 12H, N(CH_3)$_2$), 1.32 (s, 9H, *t*Bu) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ= 162.3; 155.1; 152.9; 146.6; 142.3; 129.3; 127.9; 119.4; 119.2; 111.2; 40.2; 34.2; 31.2 ppm. HRMS (APCI, +) m/z: calcd. $C_{30}H_{37}N_6O_3$ $[M+H]^+$: 529.2922, found: 529.2918.

4,4'-(2*E*,2'*E*)-2,2'-(5-*tert*-butyl-2-hydroxy-1,3-phenylene)bis(methan-1-yl-1-ylidene)bis(hydrazin-1-yl-2-ylidene)bis(oxomethylene)dibenzoic acid 1c. White solid. Yield 65% (0.167 g). *m.p.* 265-268°C. R_f=0.2 (silica, CH_2Cl_2:MeOH=1:1). ^{1}H RMN (500 MHz, DMSO-d_6): δ= 12.38 (s, 1H, O*H*), 12.31 (s, 2H, N*H*), 8.79 (s, 2H, C*H*N), 8.10-8.03 (overlapped peaks, 8H, H_{Ar}), 7.78 (s, 2H, H_{Ar}), 1.34 (s, 9H, *t*Bu) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ= 166.7; 162.3; 154.9; 147.1; 141.8; 136.7; 133.7; 129.4; 128.0; 127.1; 119.6; 34.0; 31.2; 31.1 ppm. HRMS (APCI, +) m/z: calc. for $C_{28}H_{27}N_4O_7$ $[M+H]^+$: 531.1874, found: 531.1862.

(*N',N''E,N',N''E*)-*N',N''*-(2-(benzyloxy)-5-*tert*-butyl-1,3-phenylene)bis(methan-1-yl-1-ylidene)bis(3,4,5-trimethoxybenzohydrazide) 1d. White solid. Yield 73% (0.519 g). *m.p.* 305.6-306.3°C. R_f=0.66 (silica, EtOAc). ^{1}H RMN (500 MHz, DMSO-d_6): δ= 11.85 (s, 2H, N*H*), 8.81 (s, 2H, C*H*N), 8.05 (s, 2H, H_{Ar}), 7.58 (d, 2H, ^3J=10.0 Hz, H_{Ar}), 7.44-7.36 (overlapped peaks, 3H, H_{Ar}), 4.93 (s, 2H, OCH_2), 3.88 (s, 12H, OCH_3), 3.73 (s, 6H, OCH_3), 1.37 (s, 9H, *t*Bu) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ= 162.9; 152.8; 154.8; 147.2; 143.0; 140,5; 136.1; 128.8;

[2] L.F. Lindoy, *Synthesis* **1998**, 1029-1032.

128.7; 128.4; 127.9; 105.3; 78.5; 60.2; 56.2; 34.4; 31.1; 30.7. HRMS (APCI, +) m/z: calc. for $C_{39}H_{45}N_4O_9$ $[M+H]^+$: 713.3181, found: 713.3174.

(*E*)-N'-(5-*tert*-butyl-2-hydroxybenzylidene)-2,3,4-trimethoxybenzohydrazide 2a. White solid. Yield 75% (0.325 g). *m.p.* 210-212°C. R_f=0.38 (silica, EtOAc: petroleum ether=1:1). ^{1}H RMN (500 MHz, DMSO-d_6): δ= 11.91 (s, 1H, N*H*), 11.01 (s, 1H, O*H*), 8.66 (s, 1H, C*H*N), 7.52 (s, 1H, H_{Ar}), 7.35 (d, 1H, ^3J=8.6 Hz, H_{Ar}), 7.26 (s, 2H, H_{Ar}), 6.87 (d, 2H, ^3J=8.6 Hz, H_{Ar}), 3.87 (s, 6H, OCH_3), 3.73 (s, 3H, OCH_3), 1.28 (s, 9H, *t*Bu) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ= 162.3; 155.3; 152.8; 148.4; 141.5; 140.6; 128.6; 128.0; 125.3; 118.0; 116.1; 105.2; 60.2; 56.1; 33.8; 31.3. HRMS (APCI, +) m/z: calc. for $C_{21}H_{27}N_2O_5$ $[M+H]^+$: 387.1914, found: 387.1909.

(*E*)-*N*'-(5-*tert*-butyl-2-hydroxybenzylidene)-4-(dimethylamino)benzohydrazide 2b. White solid. Yield 83% (0.314 g). *m.p.* 233-235°C. R_f=0.54 (silica, EtOAc: petroleum ether=1:1). ^{1}H RMN (500 MHz, DMSO-d_6): δ= 11.79 (s, 1H, N*H*), 11.30 (s, 1H, O*H*), 8.58 (s, 1H, C*H*N), 7.82 (d, 2H, ^3J=8.3 Hz, H_{Ar}), 7.44 (s, 1H, H_{Ar}), 7.32 (d, 1H, ^3J=8.6 Hz, H_{Ar}), 6.86 (d, 1H, ^3J=8.6 Hz, H_{Ar}), 6.77 (d, 2H, ^3J=8.3 Hz, H_{Ar}), 3.00 (s, 6H, CH_3) 1.27 (s, 9H, *t*Bu) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ= 162.6; 155.2; 152.6; 147.5; 141.4; 129.1; 128.1; 125.8; 118.8; 118.1; 116.0; 110.9, 40.1; 33.8, 31.3 ppm. HRMS (APCI, +) m/z: calc. for $C_{20}H_{26}N_3O_2$ $[M+H]^+$: 340.2020, found: 340.2017.

Figure S20 ^{1}H NMR spectrum of compound 1a

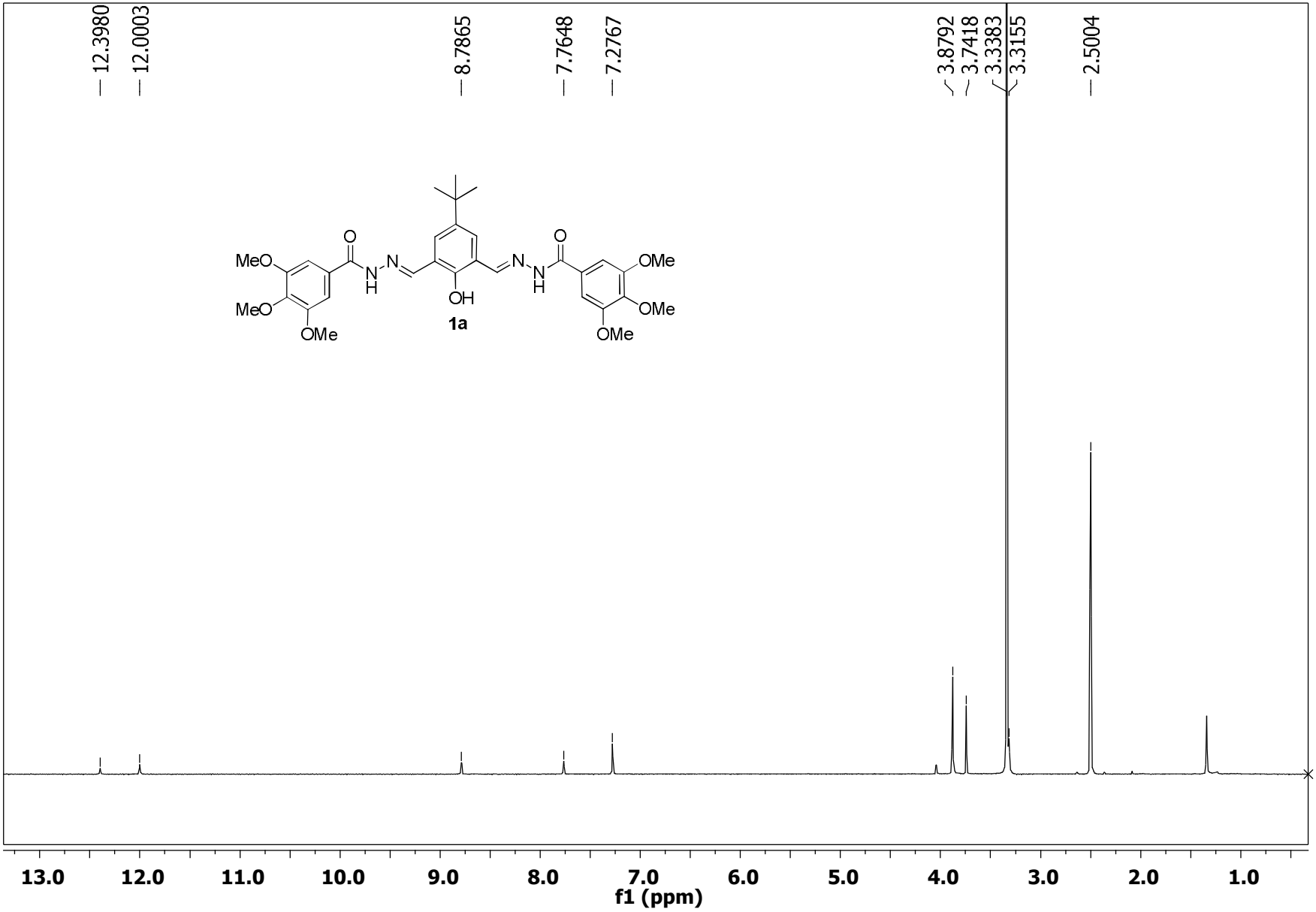

Figure S21 ^{13}C NMR spectrum of compound 1a

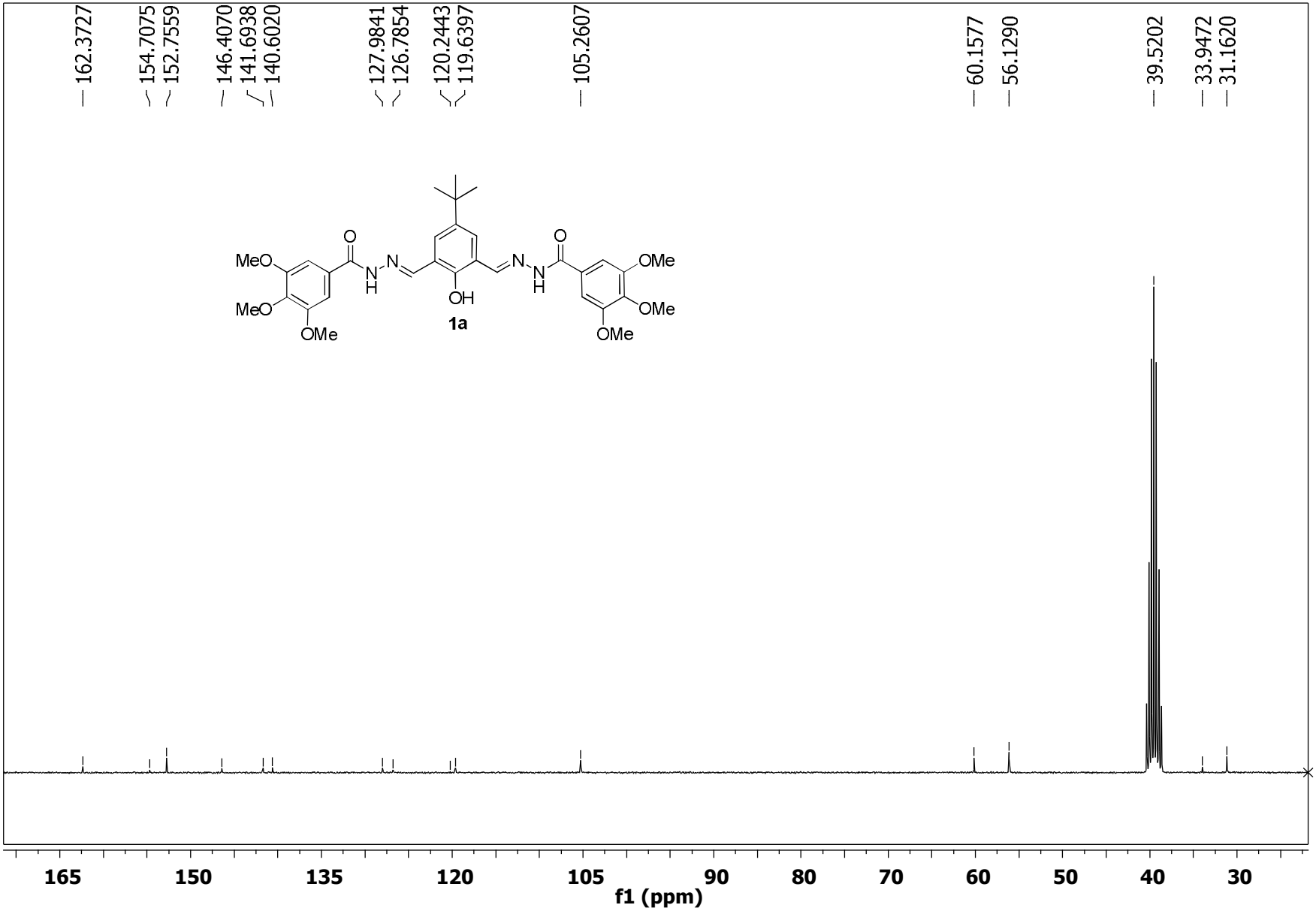

Figure S22 2D NOESY spectrum of compound 1a

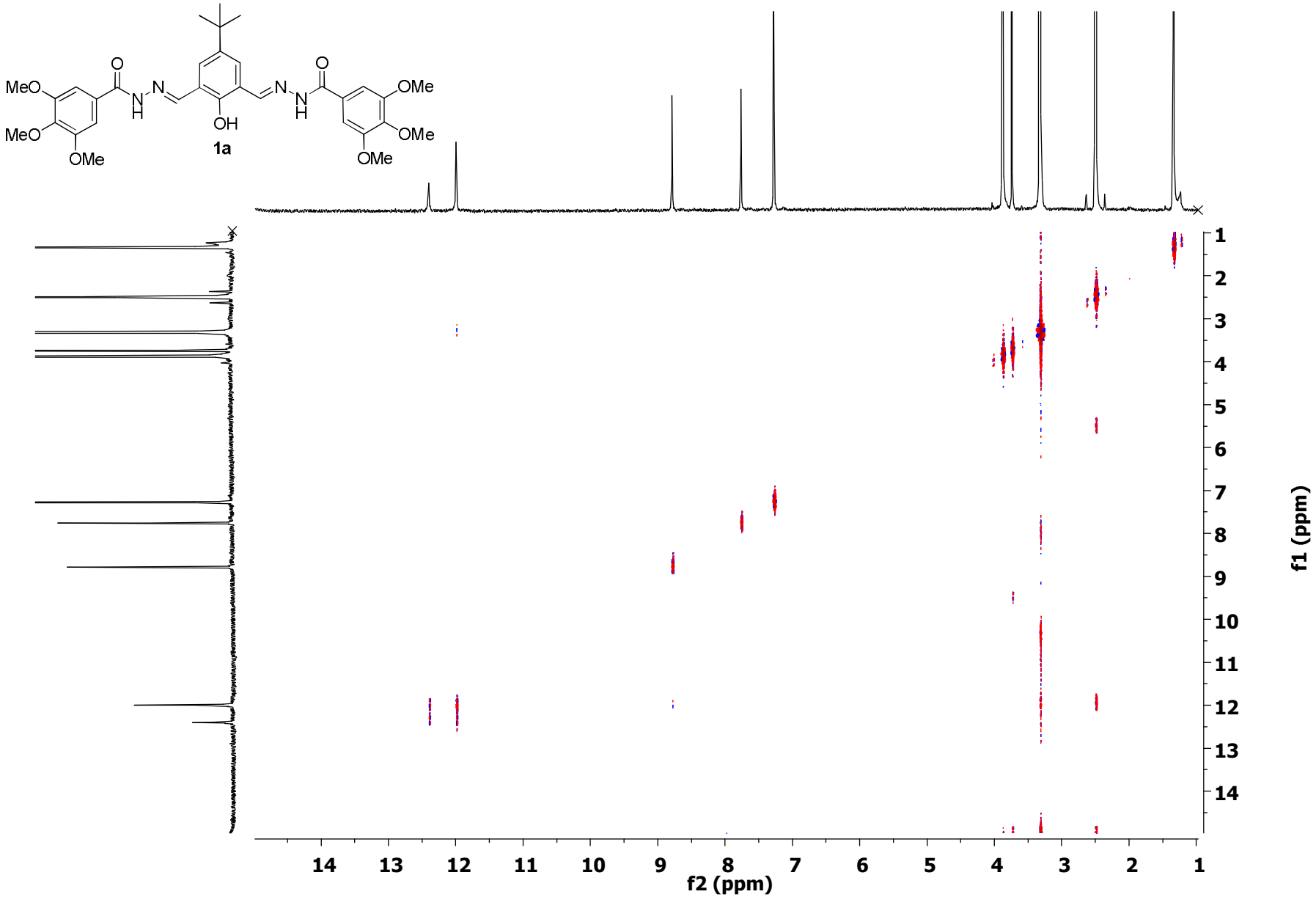

Figure S23 ^{1}H NMR spectrum of compound 1a

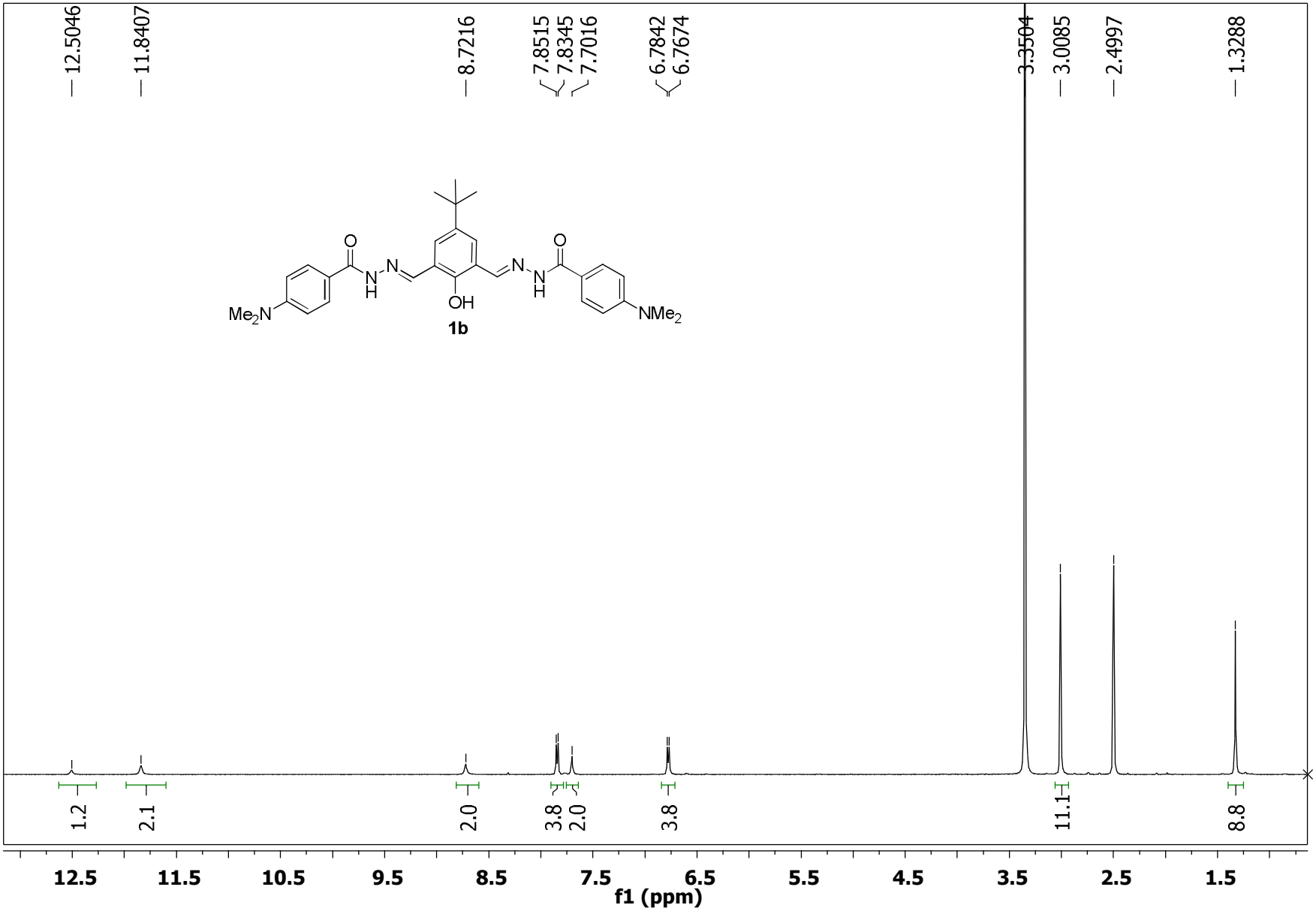

Figure S24 ^{13}C NMR spectrum of compound 1b

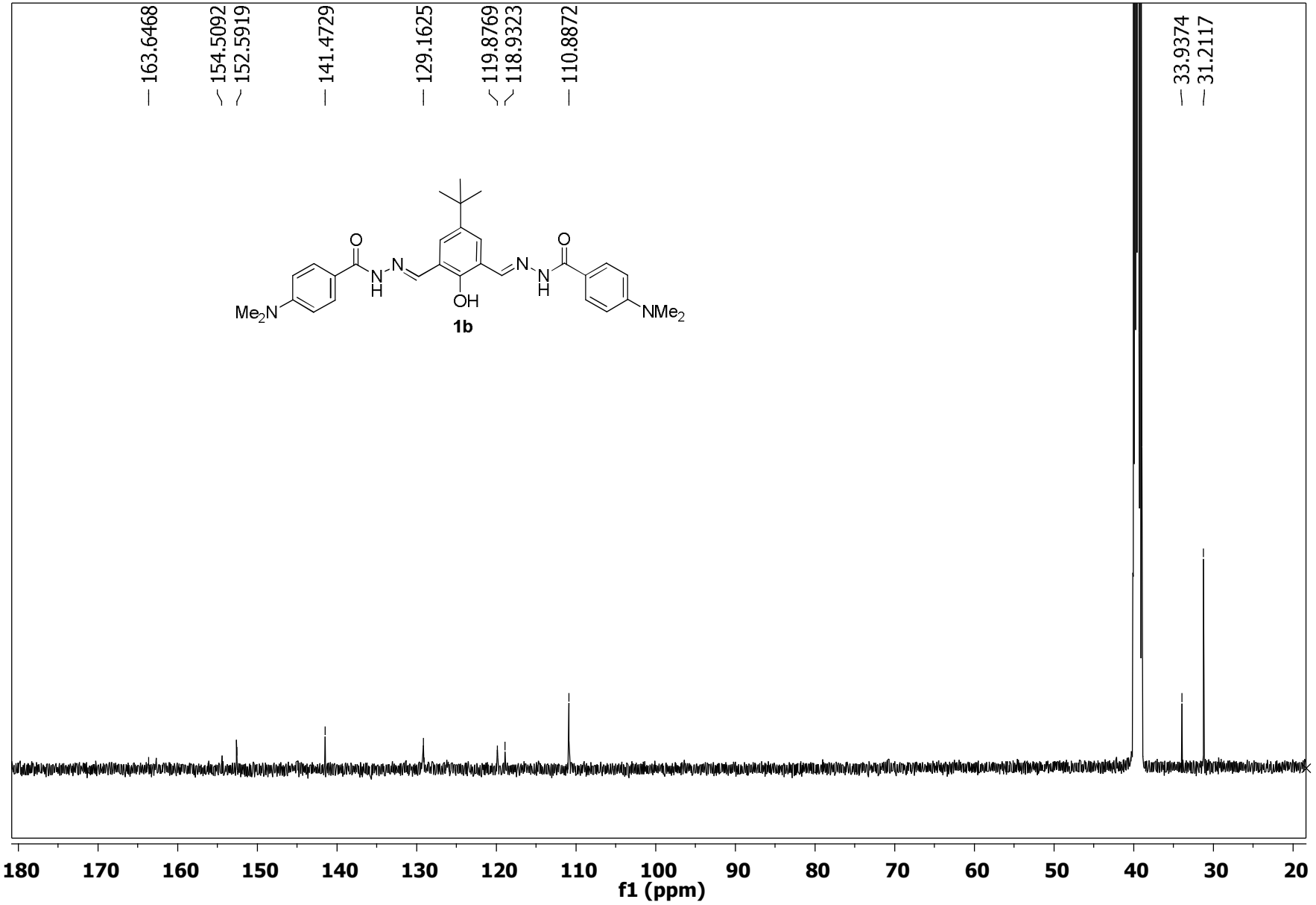

Figure S25 ^{13}C NMR spectrum of compound 1b

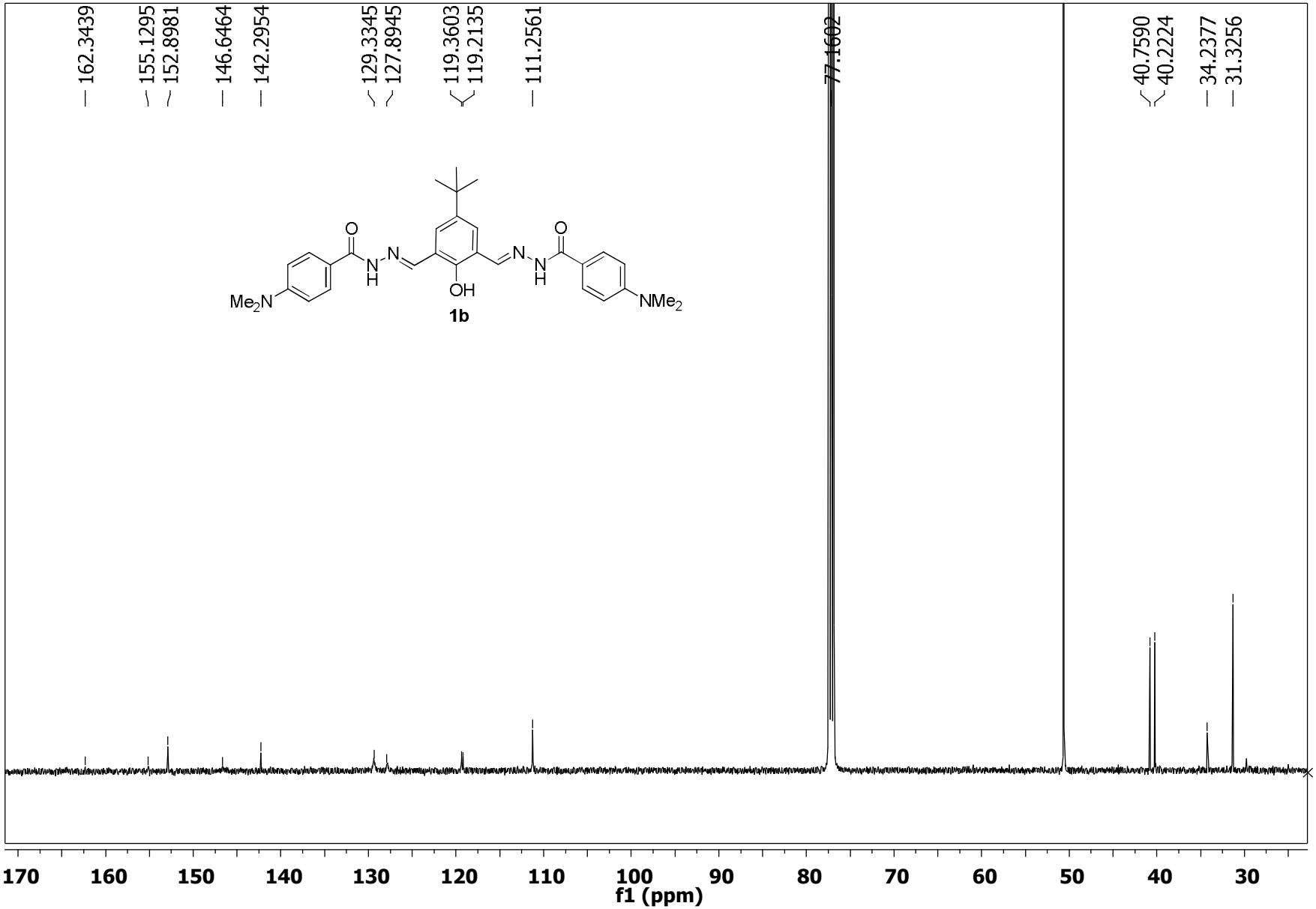

Figure S26 2D NOESY spectrum of compound 1b

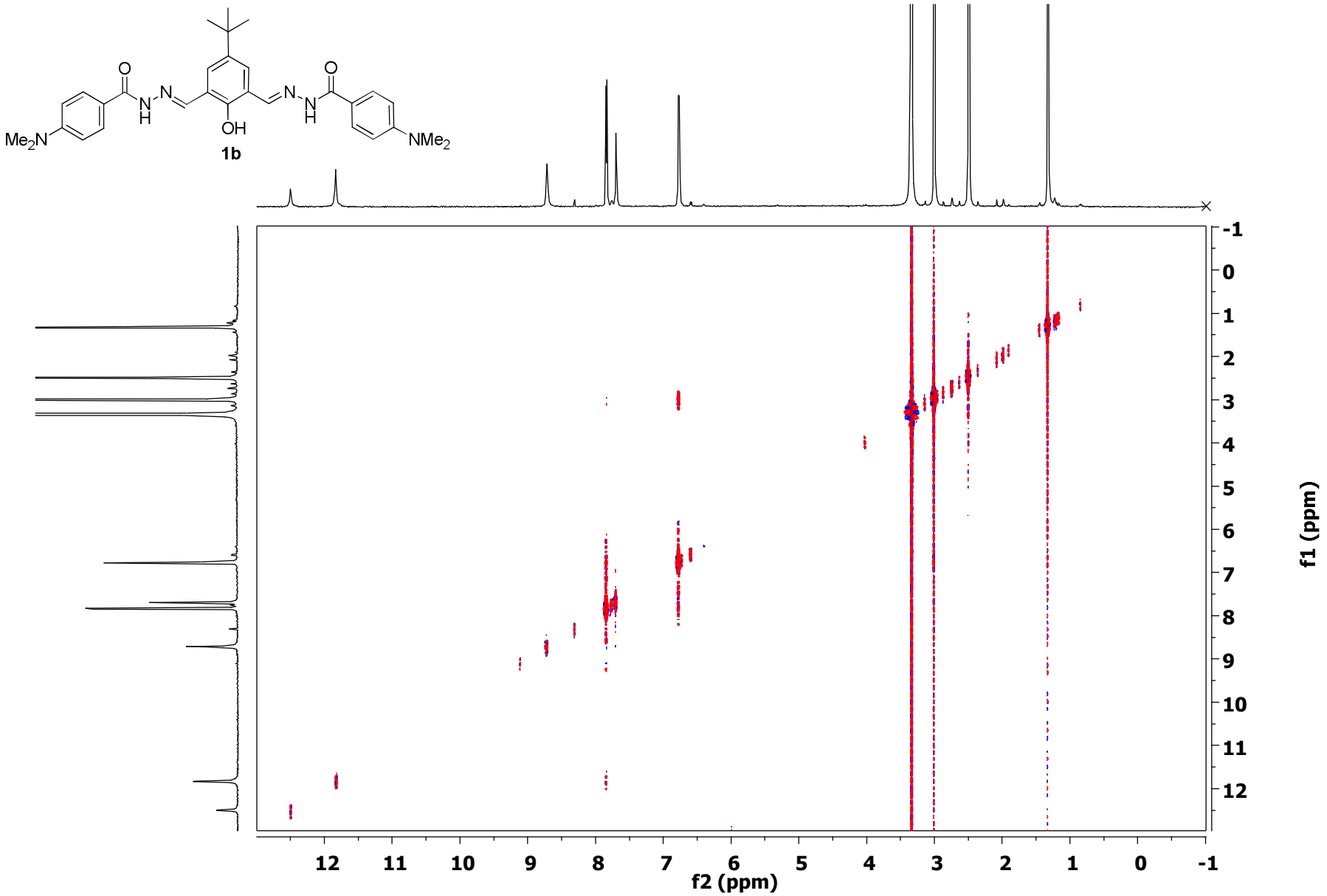

Figure S27 ^{1}H NMR spectrum of compound 1c

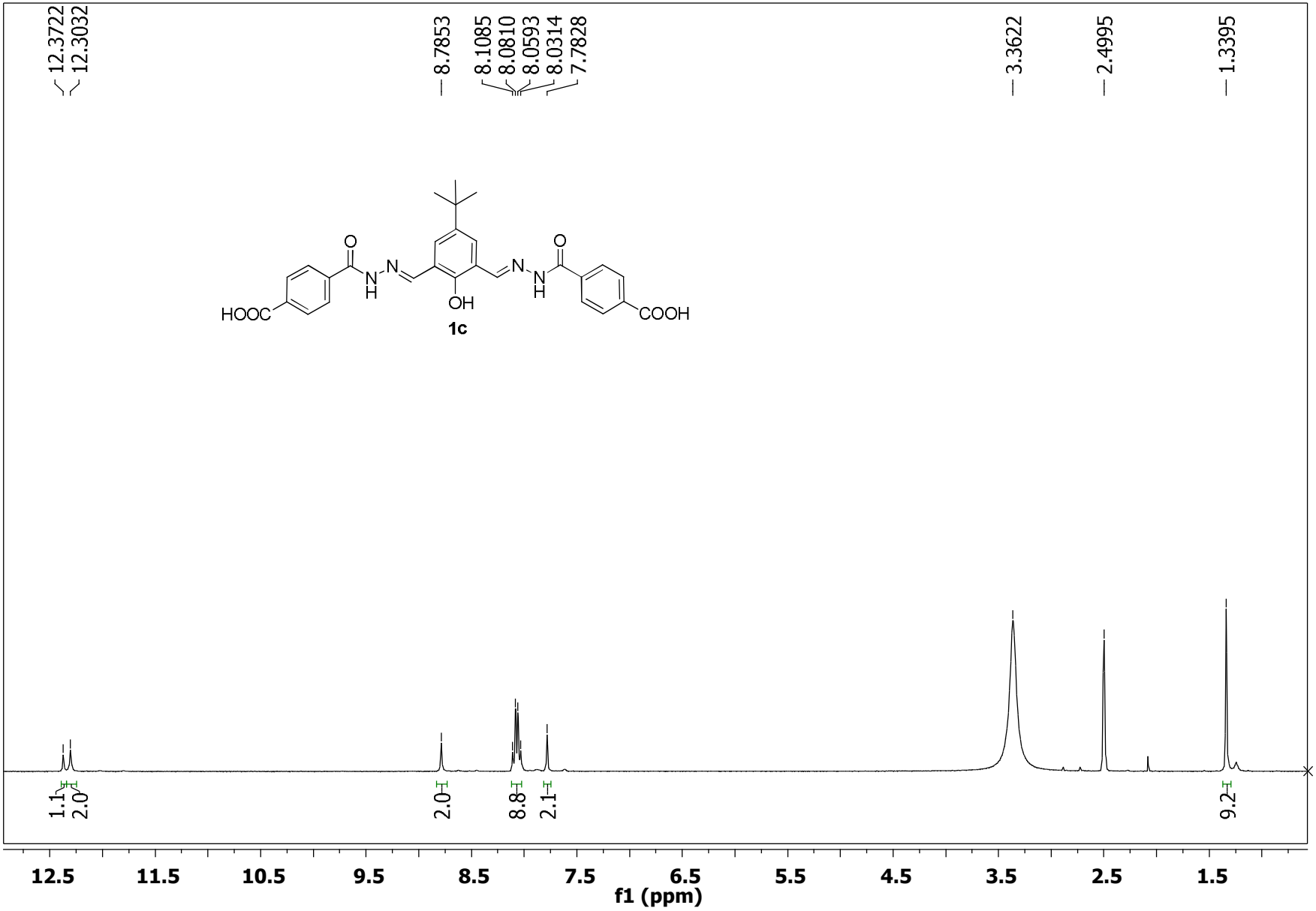

Figure S28 ^{13}C NMR spectrum of compound 1c

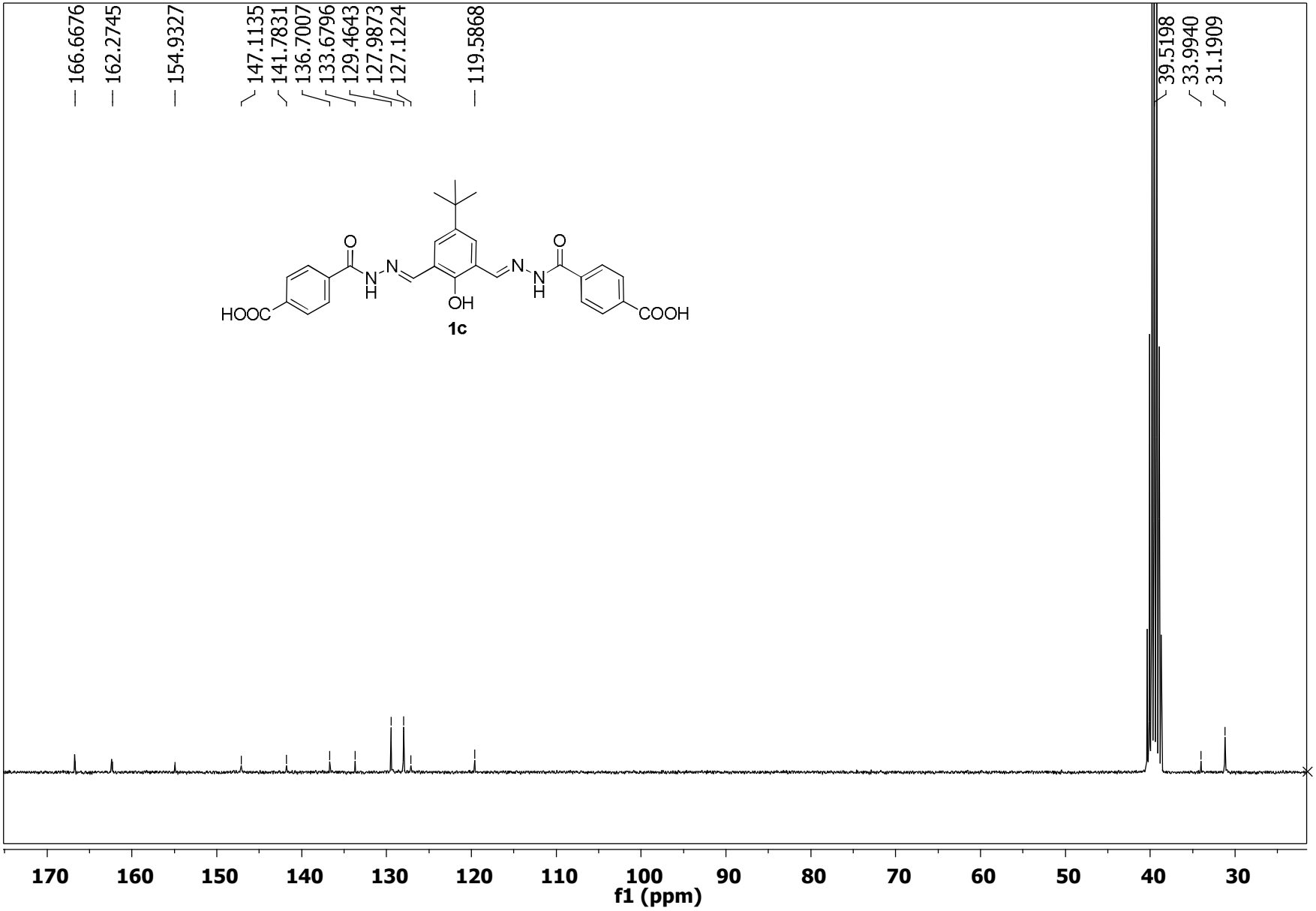

Figure S29 ^{1}H NMR spectrum of compound 1d

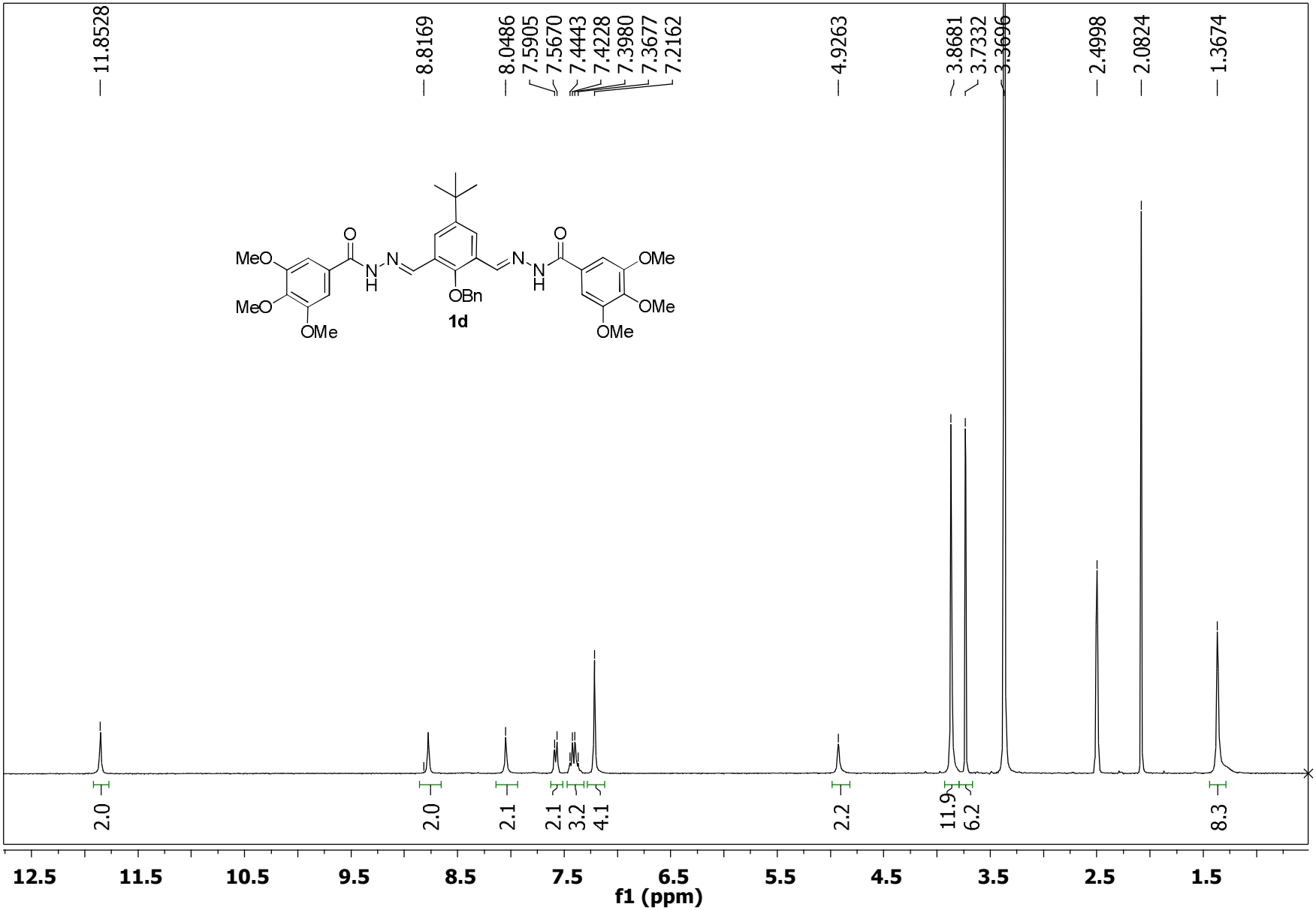

Figure S30 ^{13}C NMR spectrum of compound 1d

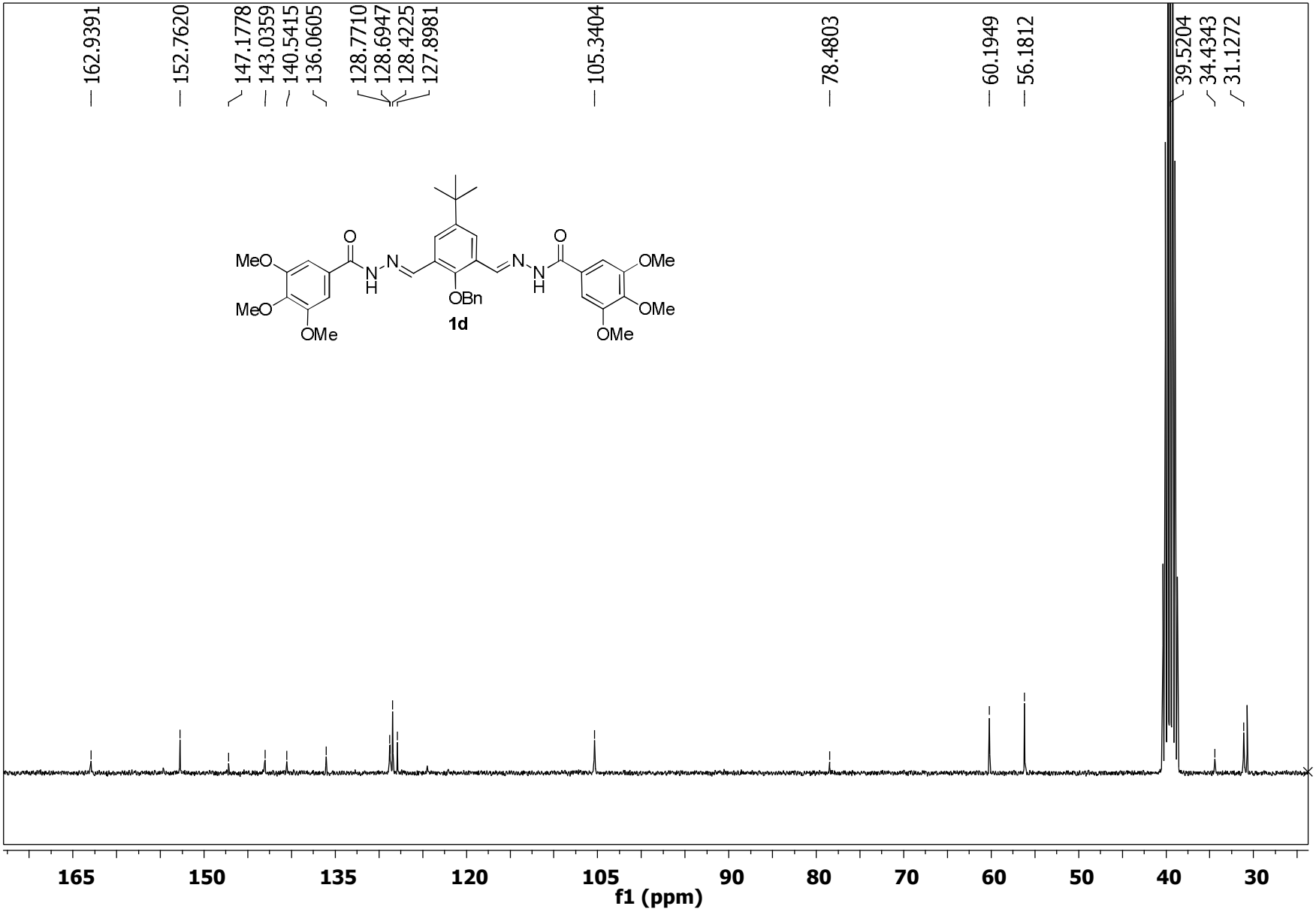

Figure S31 ^{1}H NMR spectrum of compound 2a

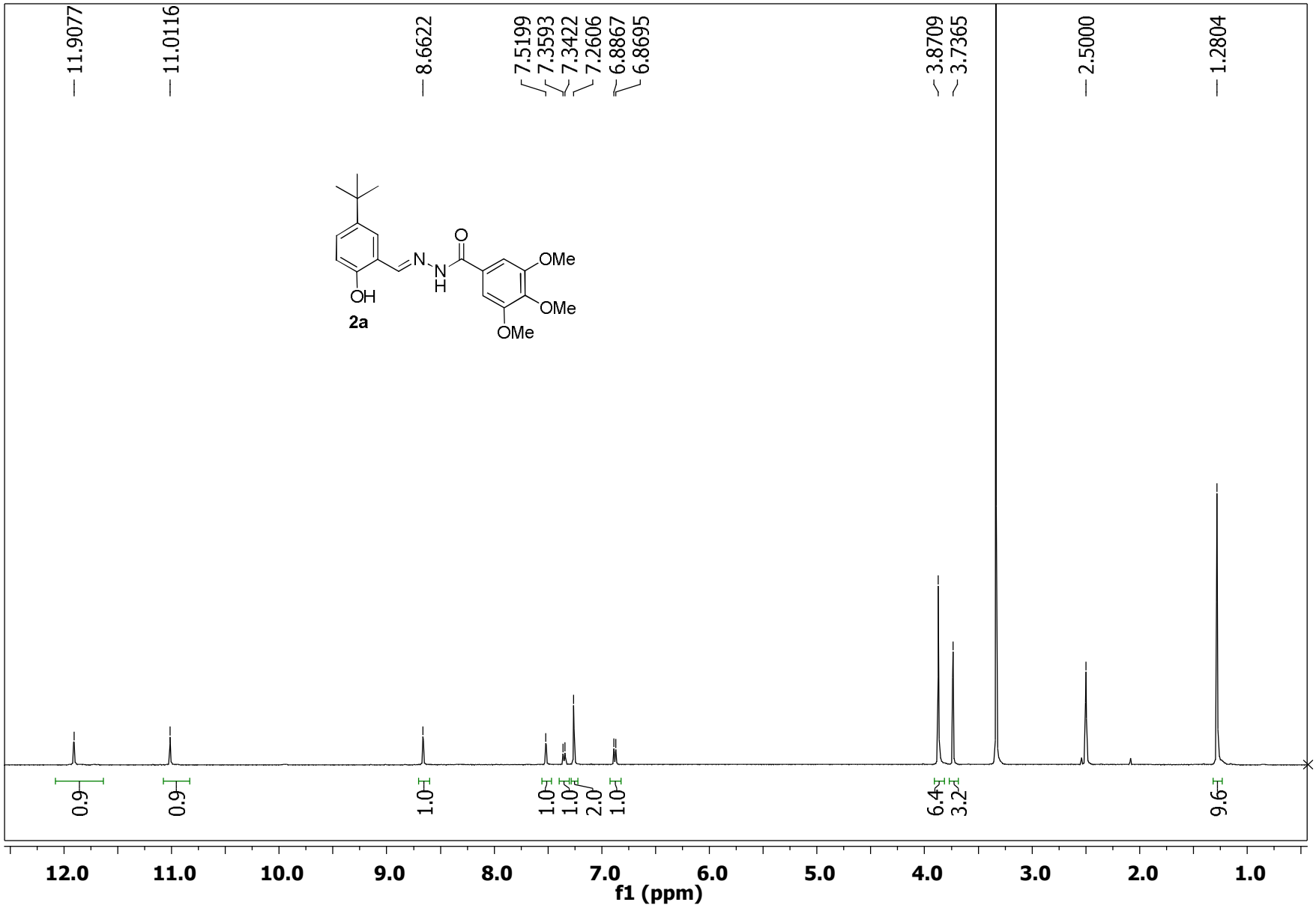

Figure S32 ^{13}C NMR spectrum of compound 2a

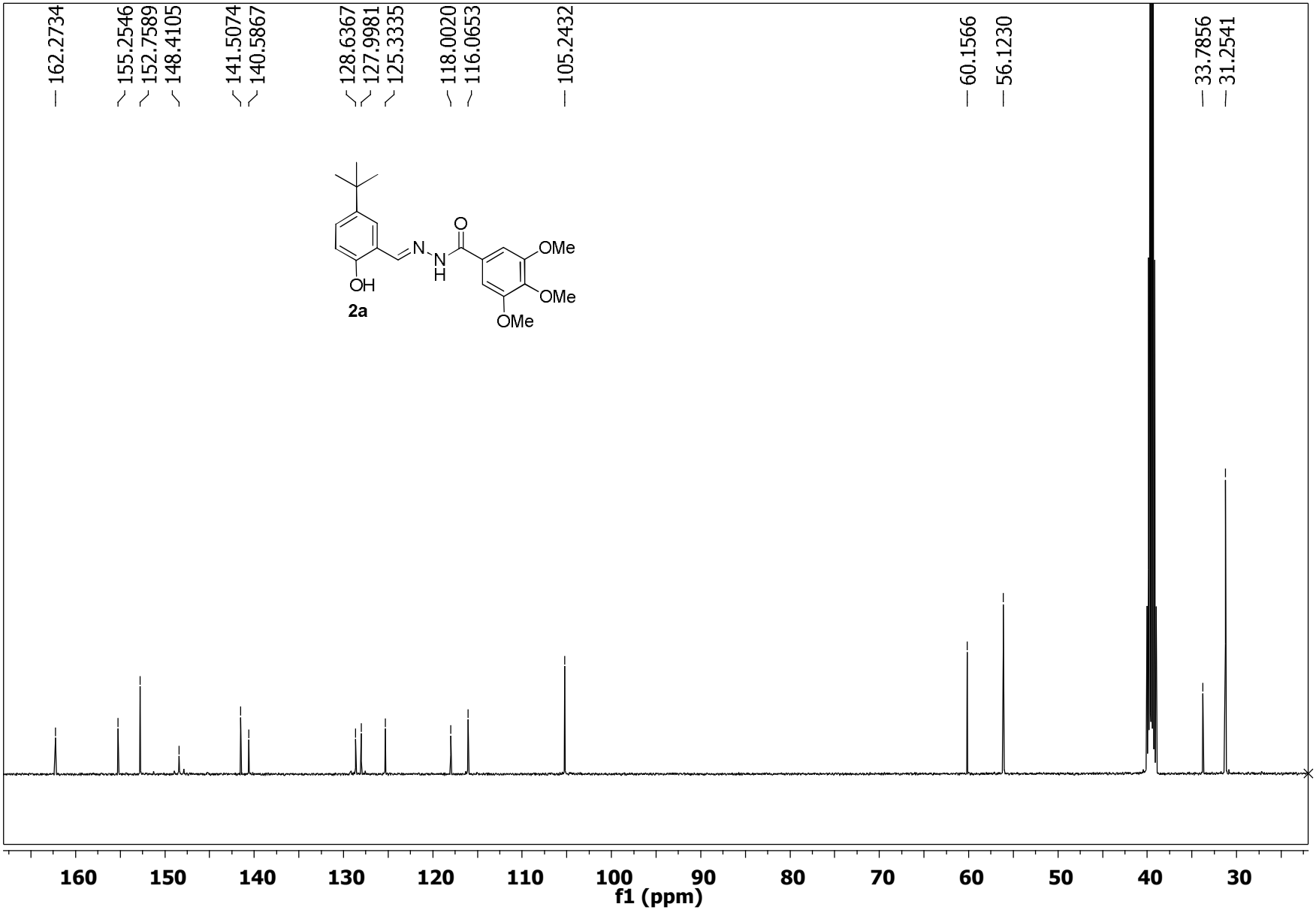

Figure S33 ^{1}H NMR spectrum of compound 2b

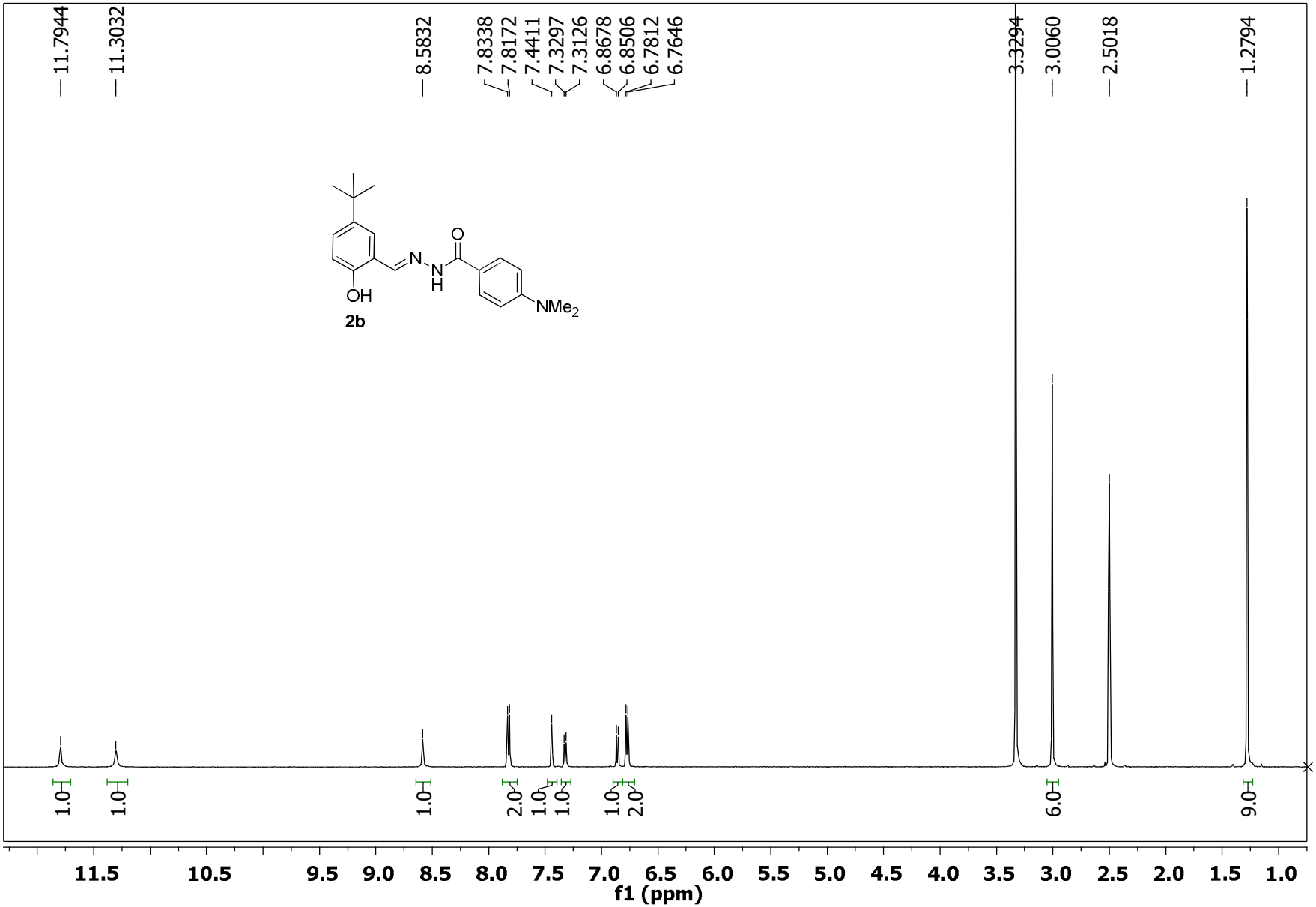

Figure S34 ^{13}C NMR spectrum of compound 2b