Supplementary Information for:

Emission behaviors of unsymmetrical 1,3-diaryl-β-diketones: A model perfectly disclosing the effect of molecular conformation on luminescence of organic solids

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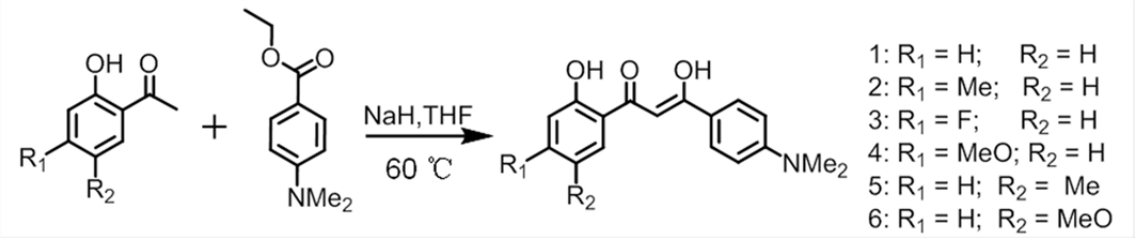

Figure S1. Synthetic procedure of complexes **1**–**6**.

3-Hydroxy-3-(4-dimethylaminophenyl)-1-(2-hydroxy-4-methylphenyl)-propenone, ***2***:

Yield: 60%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): enol tautomer (~66%) 15.94 (s, 1H), 12.29 (s, 1H), 7.92 (d, *J* = 9.5 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 2H), 6.79 (s, 1H), 6.71 (m, 3H), 6.68 (s, 1H), 3.08 (s, 6H), 2.35 (s, 3H); diketone tautomer (~34%) 12.08 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 6.77 (s, 1H), 6.71 (m, 1H), 6.66 (m, 2H), 4.50 (s, 2H), 3.07 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 200.25, 193.32, 190.91, 178.35, 162.92, 162.19, 153.85, 153.23, 148.51, 146.27, 131.25, 131.18, 128.71, 128.03, 120.52, 120.14, 118.73, 118.42, 116.94, 111.21, 110.76, 89.51, 50.04, 40.06, 40.01, 21.99, 21.78. MS m/z: $[M]^+$ calcd for $C_{18}H_{19}NO_3$: 297.14; found: 296.95. Anal. calcd (%) for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71; found: C, 73.00; H, 6.37; N, 4.63.

3-Hydroxy-3-(4-dimethylaminophenyl)-1-(2-hydroxy-4-fluorophenyl)-propenone, ***3***:

Yield: 62%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): enol tautomer (~72%) 15.80 (s, 1H), 12.69 (d, *J* = 1.5 Hz, 1H), 7.18 (s, 1H), 7.88 (m, 2H), 7.74 (dd, *J* = 9.0, 6.5 Hz, 1H), 6.66 (m, 5H), 3.08 (s, 6H); diketone tautomer (~28%) 12.40 (d, *J* = 1.5 Hz, 1H), 7.88 (m, 2H), 6.66 (m, 5H), 4.49 (s, 2H), 3.08 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 199.81, 192.41, 190.43, 178.70, 167.69, 165.67, 164.48, 164.38, 153.94, 153.29, 134.00, 133.91, 131.29, 130.21, 130.12, 128.84, 116.20, 116.18, 111.32, 110.79,

107.00, 106.82, 105.20, 105.01, 89.41, 50.26, 40.11, 40.02. MS *m/z*: $[M]^+$ calcd for $C_{17}H_{16}FNO_3$: 301.18; found: 301.11. Anal. calcd (%) for $C_{17}H_{16}FNO_3$: C, 67.76; H, 5.35; N, 4.65; found: C, 68.00; H, 5.25; N, 4.60.

3-Hydroxy-3-(4-dimethylaminophenyl)-1-(2-hydroxy-4-methoxylphenyl)-propenone, ***4***: Yield: 64%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): enol tautomer (~59%) 15.76 (s, 1H), 12.76 (s, 1H), 7.84 (d, *J* = 8.5Hz, 2H), 7.67 (d, *J* = 8.5Hz, 1H), 7.73 (dd, *J* = 7.5Hz, 2H), 6.60 (s, 1H), 6.45 (m, 2H), 3.84 (s, 3H), 3.07 (s, 6H); diketone tautomer (~41%) 12.55 (s, 1H), 7.93 (d, *J* = 9.0Hz, 2H), 7.78 (d, *J* = 9.0Hz, 1H), 6.45 (m, 1H), 6.40 (m, 1H), 3.82 (s, 3H), 3.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 198.74, 192.81, 190.98, 177.37, 166.43, 165.73, 165.22, 164.80, 153.82, 133.03, 131.30, 129.70, 128.56, 124.21, 111.42, 110.77, 107.95, 107.55, 101.32, 100.90, 89.29, 55.60, 55.49, 50.05, 40.19, 40.03. MS *m/z*: $[M]^+$ calcd for $C_{18}H_{19}FNO_4$: 313.13; found: 313.26. Anal. calcd (%) for $C_{18}H_{19}FNO_4$: C, 69.00; H, 6.11; N, 4.47; found: C, 69.39; H, 5.96; N, 4.40.

3-Hydroxy-3-(4-dimethylaminophenyl)-1-(2-hydroxy-5-methoxylphenyl)-propenone, ***6***: Yield: 52%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): enol tautomer (~59%) 15.76 (s, 1H), 12.76 (s, 1H), 7.85 (d, *J* = 2.0Hz, 2H), 7.67 (d, *J* = 8.5Hz, 1H), 7.74 (dd, *J* = 9.0Hz, 2H), 6.60 (s, 1H), 6.44 (m, 2H), 3.84 (s, 3H), 3.08 (s, 6H); diketone tautomer (~41%) 12.55 (s, 1H), 7.93 (d, *J* = 9.5Hz, 2H), 7.83 (d, *J* = 2.0Hz, 1H), 6.66(d, *J* = 9.0Hz, 2H), 6.44 (m, 1H), 6.40 (d, *J* = 2.5Hz, 1H), 3.82 (s, 3H), 3.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 198.77, 192.77, 190.99, 177.41, 166.42, 165.72, 165.20, 164.79, 153.82, 153.03, 133.03, 131.28, 129.70, 128.56, 124.18, 120.37, 113.95, 112.86, 111.31,

110.75, 107.94, 107.52, 101.33, 100.91, 89.24, 55.60, 55.94, 50.00, 40.12, 40.01. MS *m/z*: $[M]^+$ calcd for $C_{18}H_{19}FNO_4$: 313.13; found: 313.31. Anal. calcd (%) for $C_{18}H_{19}FNO_4$: C, 69.00; H, 6.11; N, 4.47; found: C, 69.41; H, 5.94; N, 4.41.

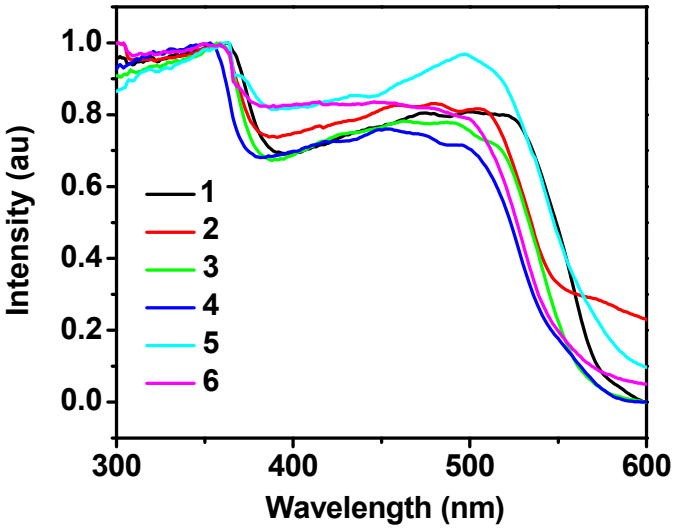

Figure S2. Absorption spectra of crystals for compounds **1**–**6**.

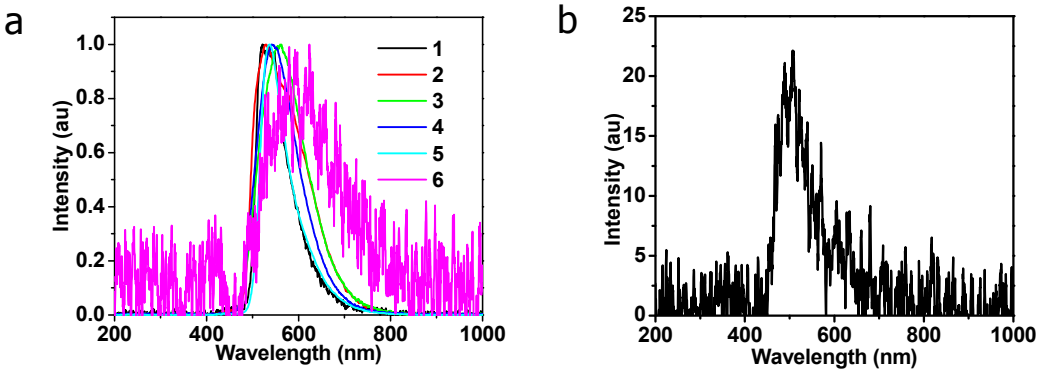

Figure S3. (a) Photoluminescent spectra of thin films for compounds **1**–**6**; (b) Photoluminescent spectra of thin film for compound **1** in PMMA.

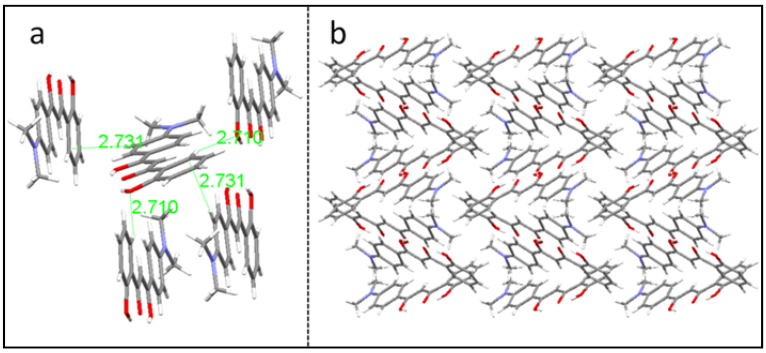

Figure S4. (a) Two types of intermolecular interaction between the adjacent molecules (/Å); (b) cross-shape network structures of crystal **1**.

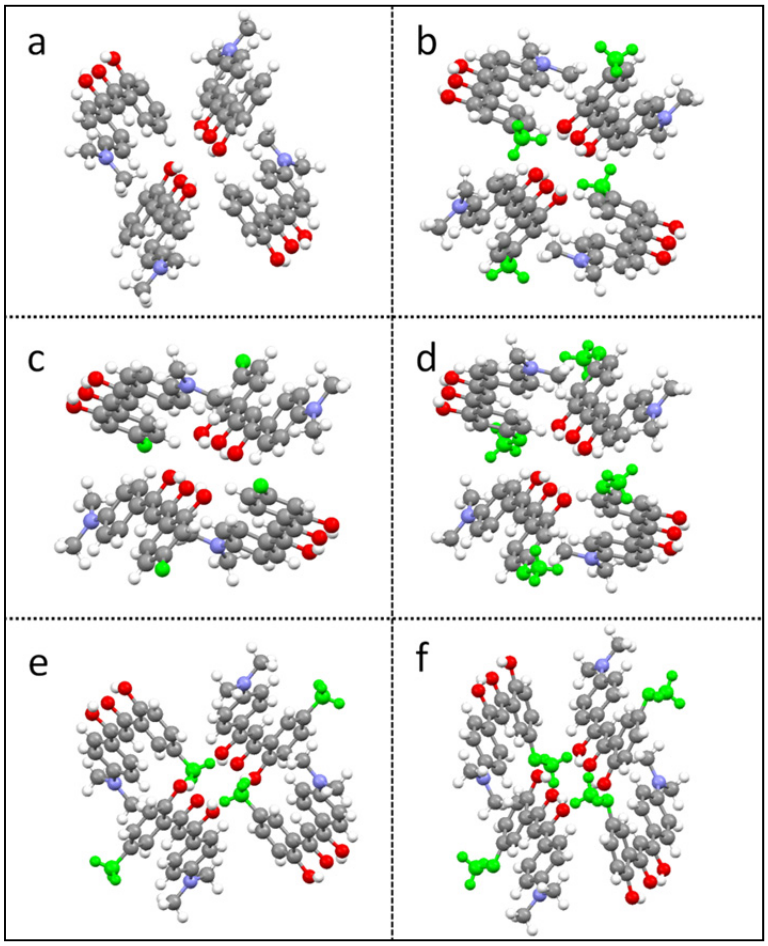

Figure S5. Molecular packing structures of crystals **1–6** (a–f) with different substituents (marked in green color).

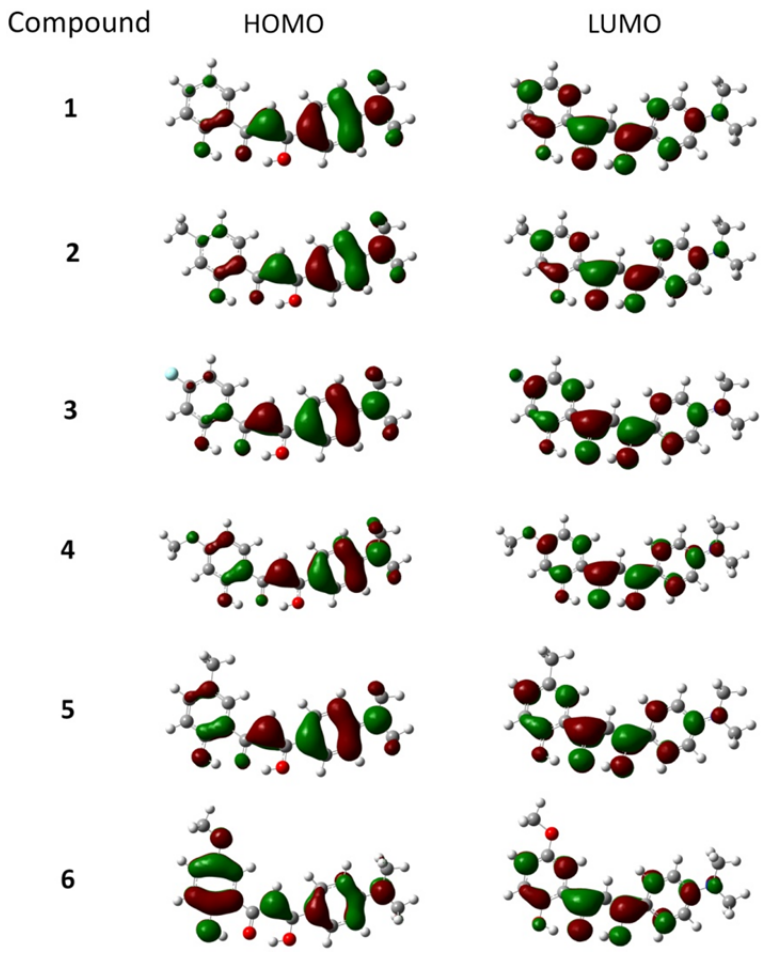

Figure S6. Theoretical calculations of HOMO, LUMO distributions on the ground state for compounds **1–6**.

Table S1. HOMO and LUMO values calculated for **1–6**.

	1	**2**	**3**	**4**	**5**	**6**
HOMO, eV	–6.66	–6.59	–6.70	–6.53	–6.60	–6.52
LUMO, eV	–0.65	–0.58	–0.71	–0.49	–0.62	–0.64
Eg, eV	6.01	6.01	5.99	6.04	5.98	5.98

Table S2. Threshold of ASE for different organic crystals

Compound	**1**	**2**	**3**	**4**	**5**	**AC5** (Ref 45)	**BP1T** (Ref 45)	**BP3T** (Ref 46)	**BOXD-4** (Ref 47)
Threshold value (kW/cm^2)	39	71	38	109	46	84	54	< 260	20

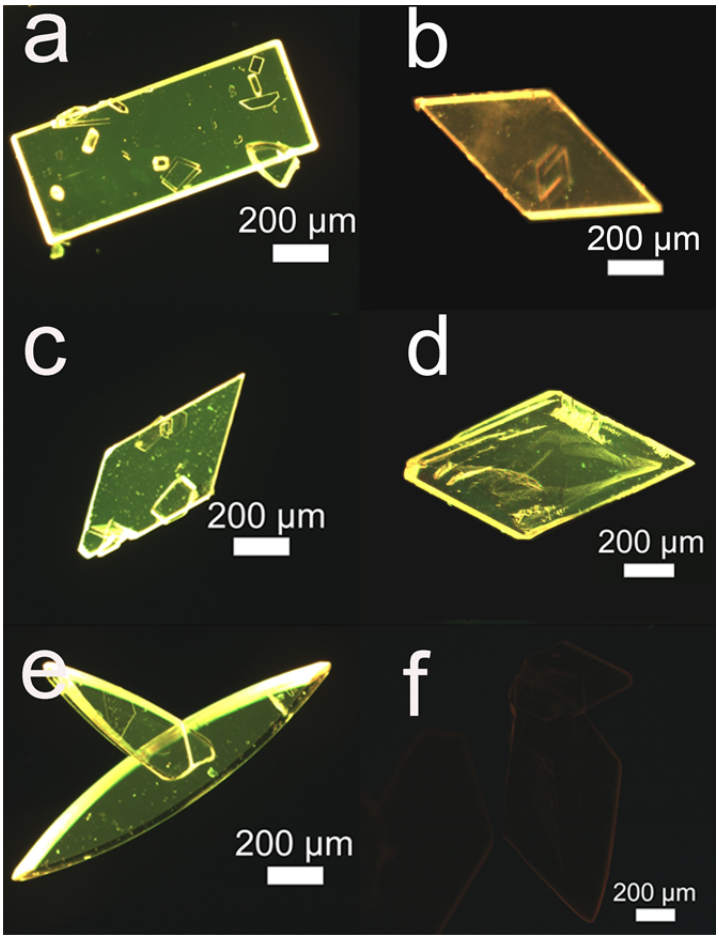

Figure S7. Fluorescent microphotograph of crystals for compounds **1–6**.

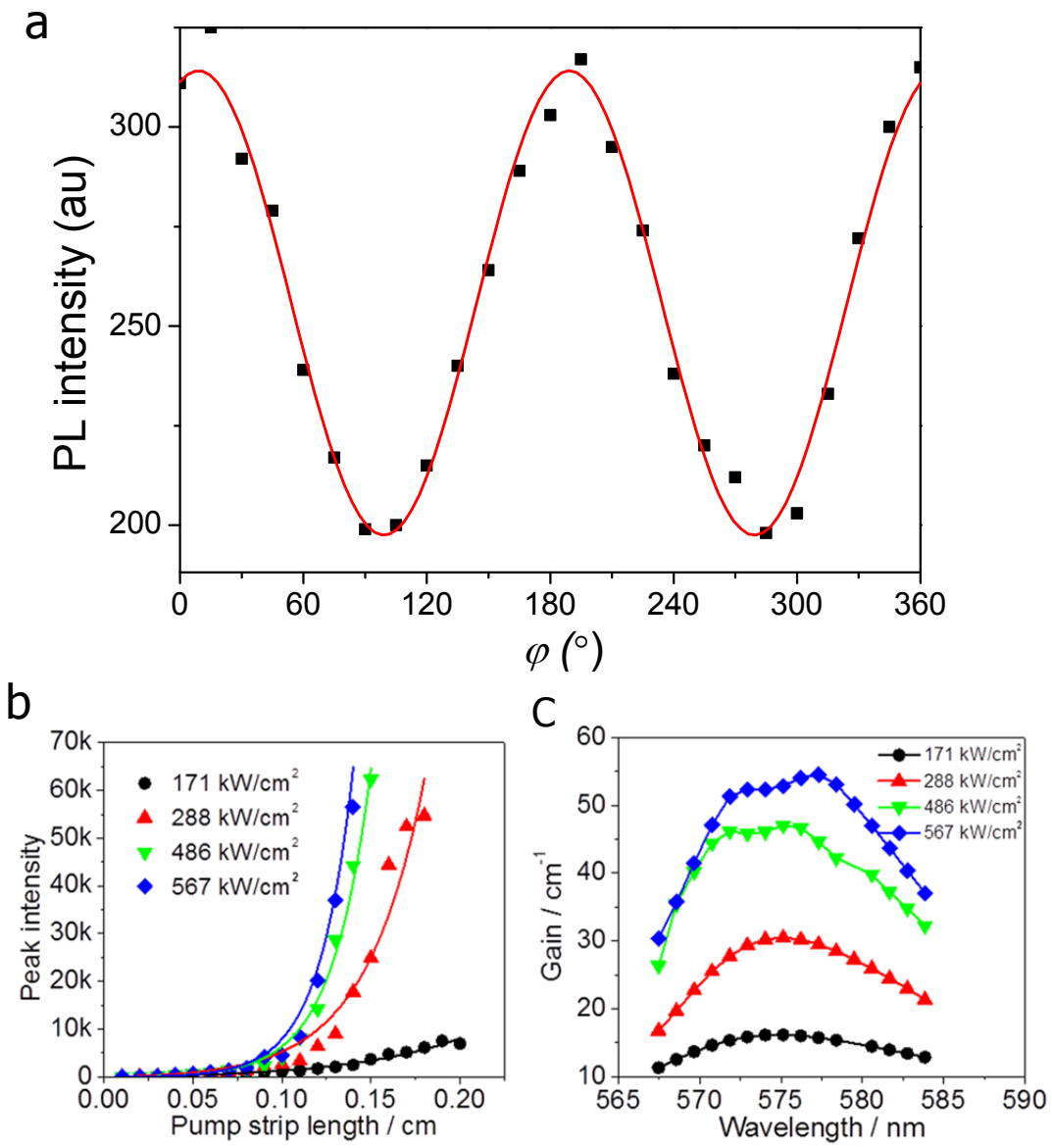

Figure S8. (a) Dependence of the intensity of porlarized light from crystal **1** on the relative porlarization angle φ at the energy of pumping laser about 200 μJ·pulse^{-1}·cm^{-2}; (b) The peak intensity of PL spectra as a function of the pump stripe length at different pump energies; (c) The net gain coefficient as a function of wavelength at different pump intensities.

Table S3. Crystal data and structure refinement for **1–6**.

Table S3-1. Crystal data and structure refinement for **1**, **2** and **3**.			
Identification code	**1**	**2**	**3**
Empirical formula	C_{17} H_{17} N O_3	C_{18} H_{19} N O_3	C_{17} H_{16} F N O_3
Formula weight	283.32	297.34	301.31
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, P2(1)/c	Monoclinic, P2(1)/n	Monoclinic, P2(1)/n
Unit cell dimensions	a = 11.877(2) Å	a = 11.795(2) Å	a = 11.957(2) Å
	b = 10.491(2) Å	b = 12.023(2) Å	b = 10.726(2) Å
	c = 12.835(3) Å	c = 12.097(2) Å	c = 12.789(3) Å
	alpha = 90 deg.	alpha = 90 deg.	alpha = 90 deg.
	beta = 117.51(3) deg.	beta = 115.79(3) deg.	beta = 117.80(3) deg.
	gamma = 90 deg.	gamma = 90 deg.	gamma = 90 deg.
Volume ($Å^3$)	1418.5(5)	1544.6(5)	1450.9(5)
Z, Calculated density (mg/m^3)	4, 1.327	4, 1.279	4, 1.379
Absorption coefficient (mm^{-1})	0.091	0.087	0.103
F(000)	600	632	632
Crystal size, mm	0.49 × 0.41 × 0.31	0.41 × 0.37 × 0.35	0.50 × 0.33 × 0.12
Theta range for data collection	3.19 to 27.48 deg.	3.21 to 27.48 deg.	3.19 to 27.48 deg.
Limiting indices	-15<=h<=14, -13<=k<=13, -15<=l<=16	-14<=h<=15, -15<=k<=15, -14<=l<=15	-15<=h<=15, -13<=k<=13, -16<=l<=16
Reflections collected / unique	13518 / 3249 [*R*(int) = 0.0370]	14815 / 3526 [*R*(int) = 0.0396]	13714 / 3302 [*R*(int) = 0.0601]
Completeness to theta = 27.48	99.60%	99.20%	99.40%
Max. and min. transmission	0.9726 and 0.9564	0.9702 and 0.9648	0.9882 and 0.9504
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	3249 / 0 / 195	3526 / 0 / 204	3302 / 0 / 263
Goodness-of-fit on F^2	1.063	1.038	0.778
Final R indices [*I* > 2sigma(*I*)]	R1 = 0.0470, wR2 = 0.1287	R1 = 0.0487, wR2 = 0.1314	R1 = 0.0402, wR2 = 0.0918
R indices (all data)	R1 = 0.0647, wR2 = 0.1389	R1 = 0.0797, wR2 = 0.1453	R1 = 0.0960, wR2 = 0.1238
Largest diff. peak and hole	0.194 and -0.232 e.$Å^{-3}$	0.262 and -0.152 e. $Å^{-3}$	0.268 and -0.214 e. $Å^{-3}$

Table S3-2. Crystal data and structure refinement for **4**, **5** and **6**.			
Identification code	**4**	**5**	**6**
Empirical formula	C_{18} H_{19} N O_4	C_{18} H_{19} N O_3	C_{18} H_{19} N O_4
Formula weight	313.34	297.34	313.34
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, P2(1)/c	Monoclinic, P2(1)/n	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.263(2) Å	a = 10.858(2) Å	a = 11.793(2) Å
	b = 12.388(3) Å	b = 13.738(3) Å	b = 11.504(2) Å
	c = 12.571(3) Å	c = 10.878(2) Å	c = 13.028(3) Å
	alpha = 90 deg.	alpha = 90 deg.	alpha = 90 deg.
	beta = 115.73(3) deg.	beta = 106.98(3) deg.	beta = 114.25(3) deg.
	gamma = 90 deg.	gamma = 90 deg.	gamma = 90 deg.
Volume ($Å^3$)	1580.1(6)	1552.0(5)	1611.7(6)
Z, Calculated density (mg/m^3)	4, 1.317	4, 1.273	4, 1.291
Absorption coefficient (mm^{-1})	0.093	0.087	0.091
F(000)	664	632	664
Crystal size, mm	0.40 × 0.35 × 0.32	0.61 × 0.22 × 0.20	0.45 × 0.34 × 0.11
Theta range for data collection	3.27 to 27.47 deg.	3.15 to 27.47 deg.	3.16 to 27.48 deg.
Limiting indices	-14<=h<=14, -16<=k<=16, -16<=l<=15	-13<=h<=14, -17<=k<=17, -14<=l<=13	-15<=h<=15, -13<=k<=14, -16<=l<=16
Reflections collected / unique	15209 / 3593 [*R*(int) = 0.0391]	14464 / 3520 [*R*(int) = 0.0732]	14918 / 3673 [*R*(int) = 0.0565]
Completeness to theta = 27.48	99.20%	99.10%	99.50%
Max. and min. transmission	0.9707 and 0.9641	0.9826 and 0.9488	0.9901 and 0.9603
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	3593 / 0 / 213	3520 / 0 / 231	3673 / 0 / 208
Goodness-of-fit on F^2	1.054	1.025	1.064
Final R indices [*I* > 2sigma(*I*)]	R1 = 0.0470, wR2 = 0.1271	R1 = 0.0670, wR2 = 0.1429	R1 = 0.0614, wR2 = 0.1734
R indices (all data)	R1 = 0.0739, wR2 = 0.1391	R1 = 0.1489, wR2 = 0.1756	R1 = 0.1107, wR2 = 0.1981
Largest diff. peak and hole	0.194 and -0.179 $e.Å^{-3}$	0.154 and -0.167 $e.Å^{-3}$	0.271 and -0.243 $e.Å^{-3}$

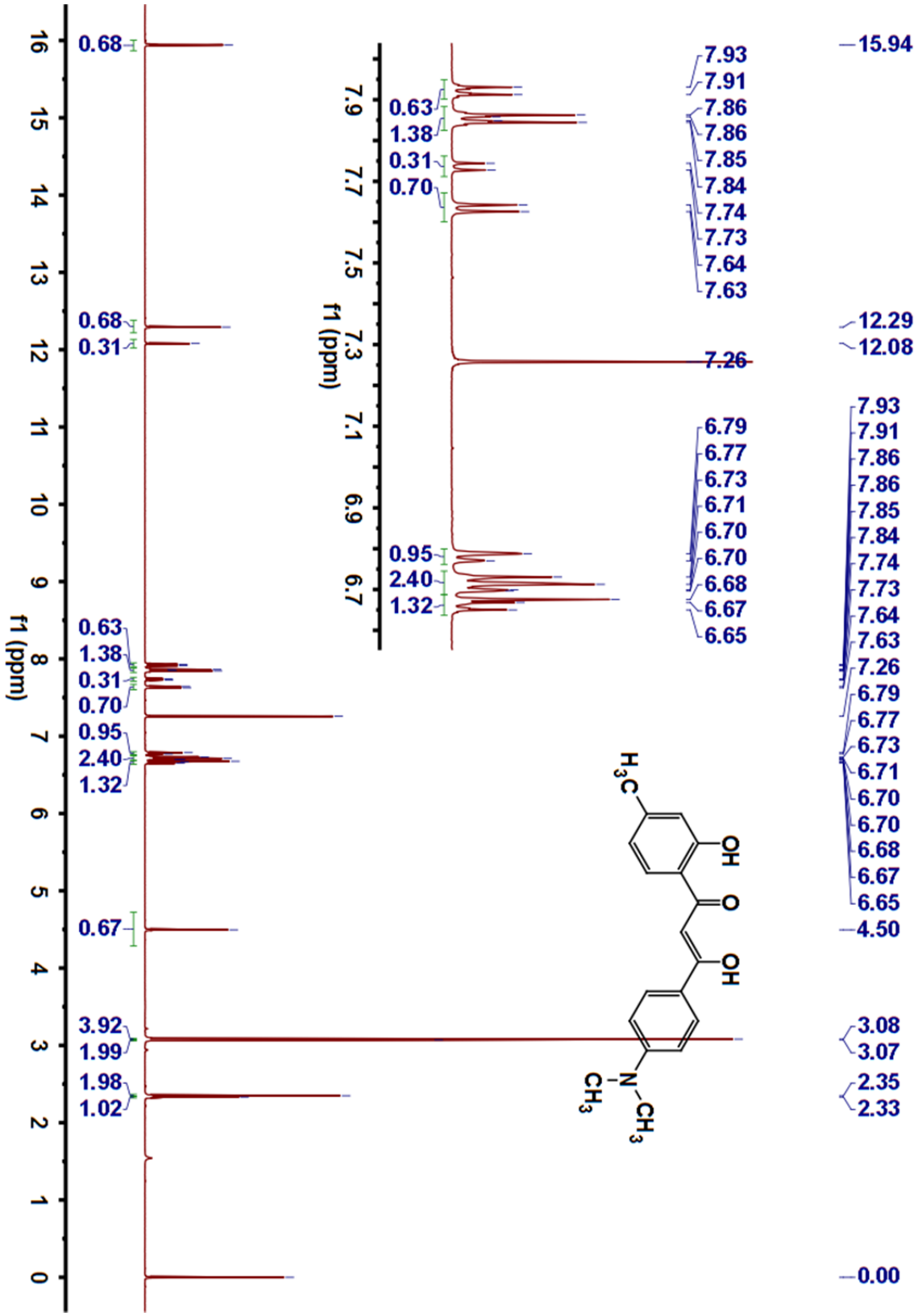

Figure S8. ^{1}H spectra of **2** recorded in $CDCl_3$ (500 MHz).

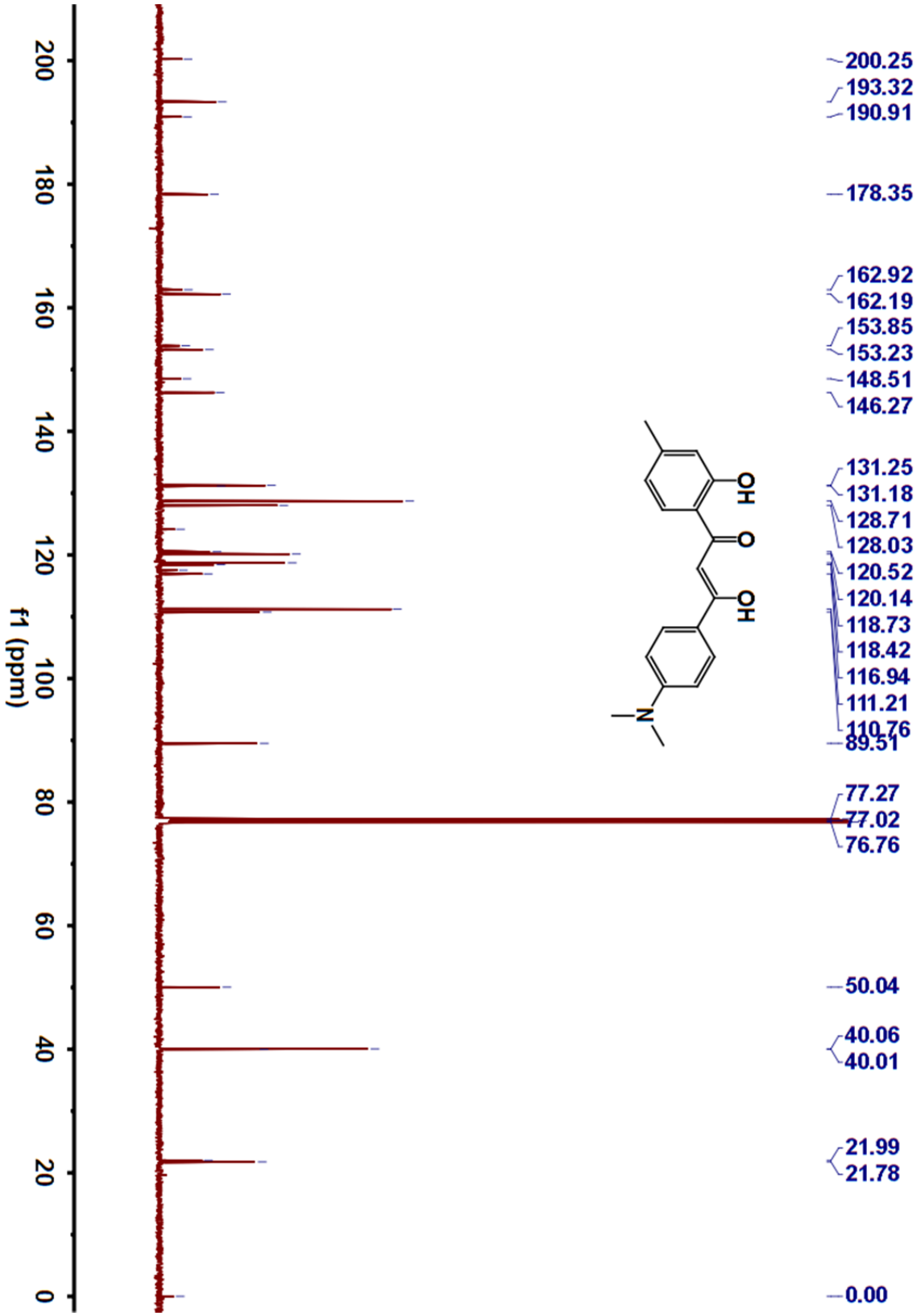

Figure S9. ^{13}C spectra of **2** recorded in $CDCl_3$ (125 MHz).

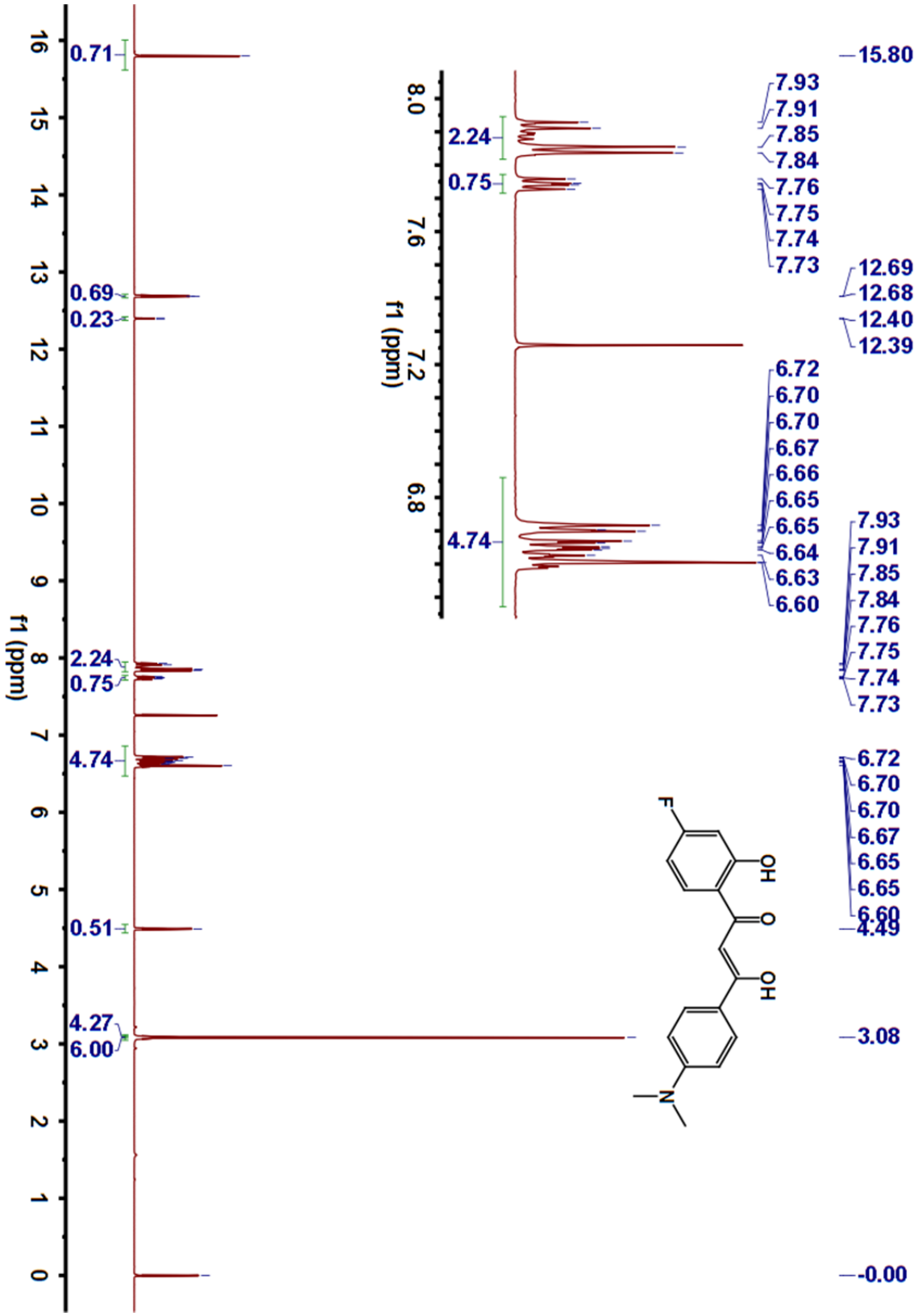

Figure S10. ^{1}H spectra of **3** recorded in $CDCl_3$ (500 MHz).

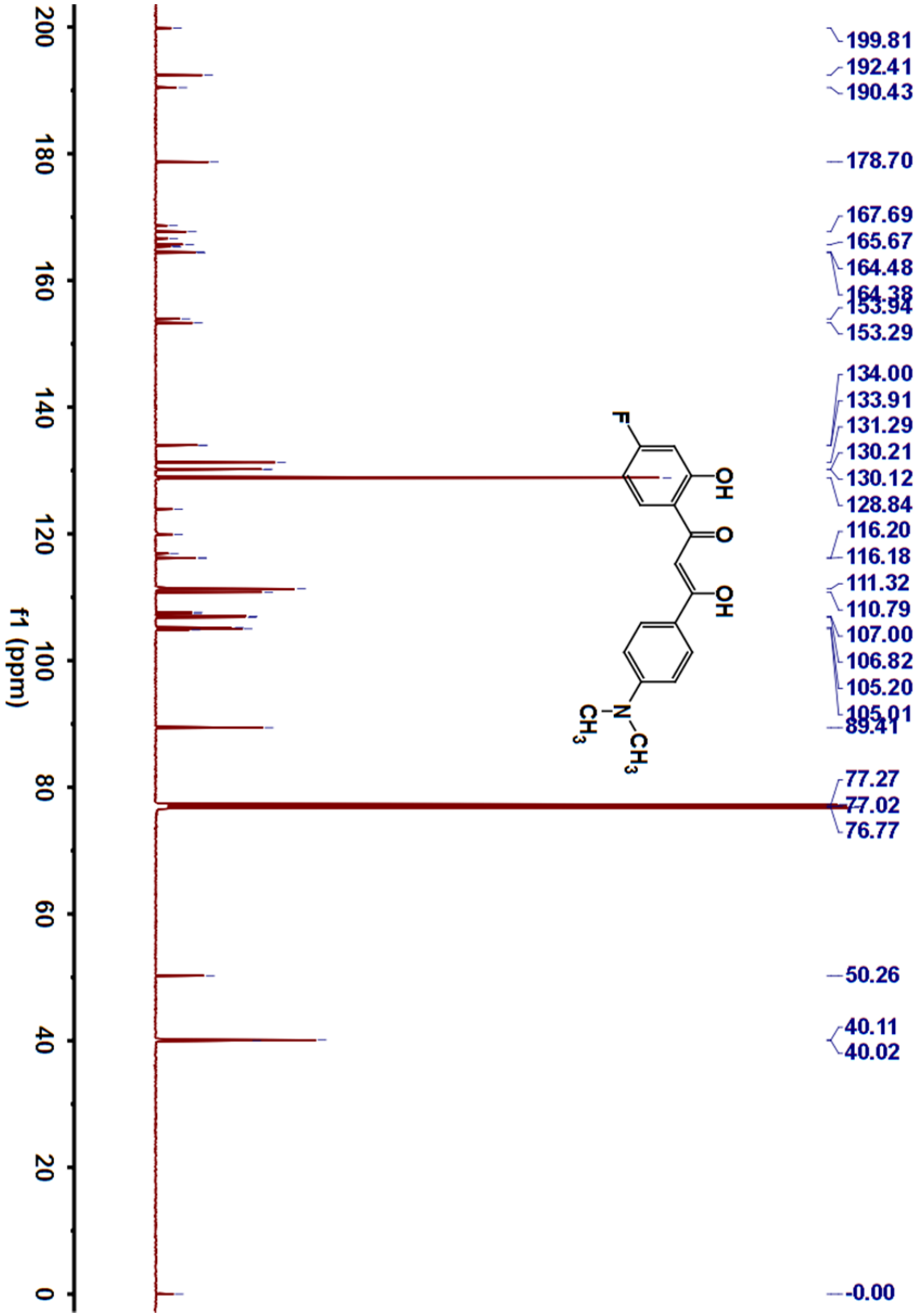

Figure S11. ^{13}C spectra of **3** recorded in $CDCl_3$ (125 MHz).

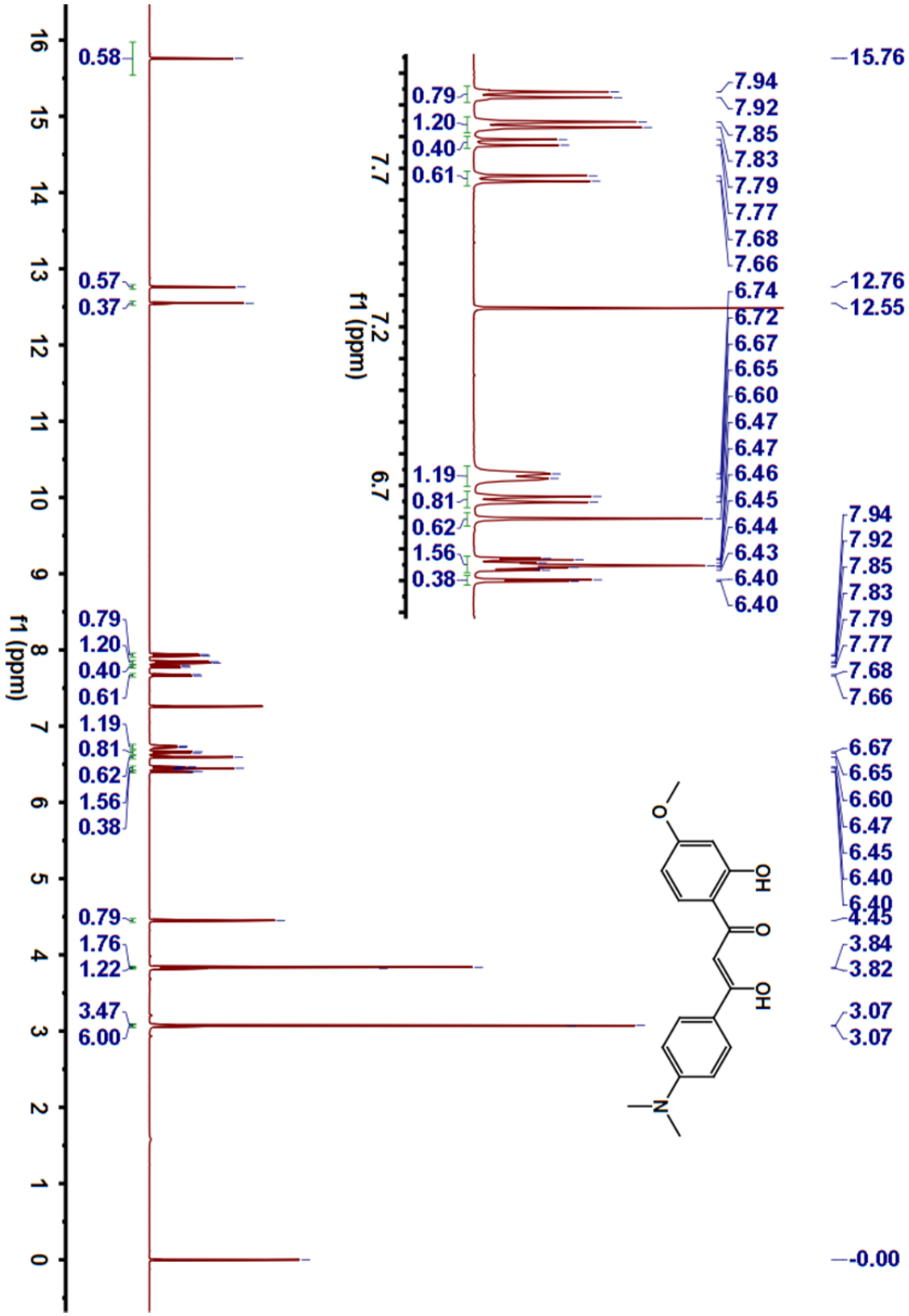

Figure S12. ^{1}H spectra of **4** recorded in $CDCl_3$ (500 MHz).

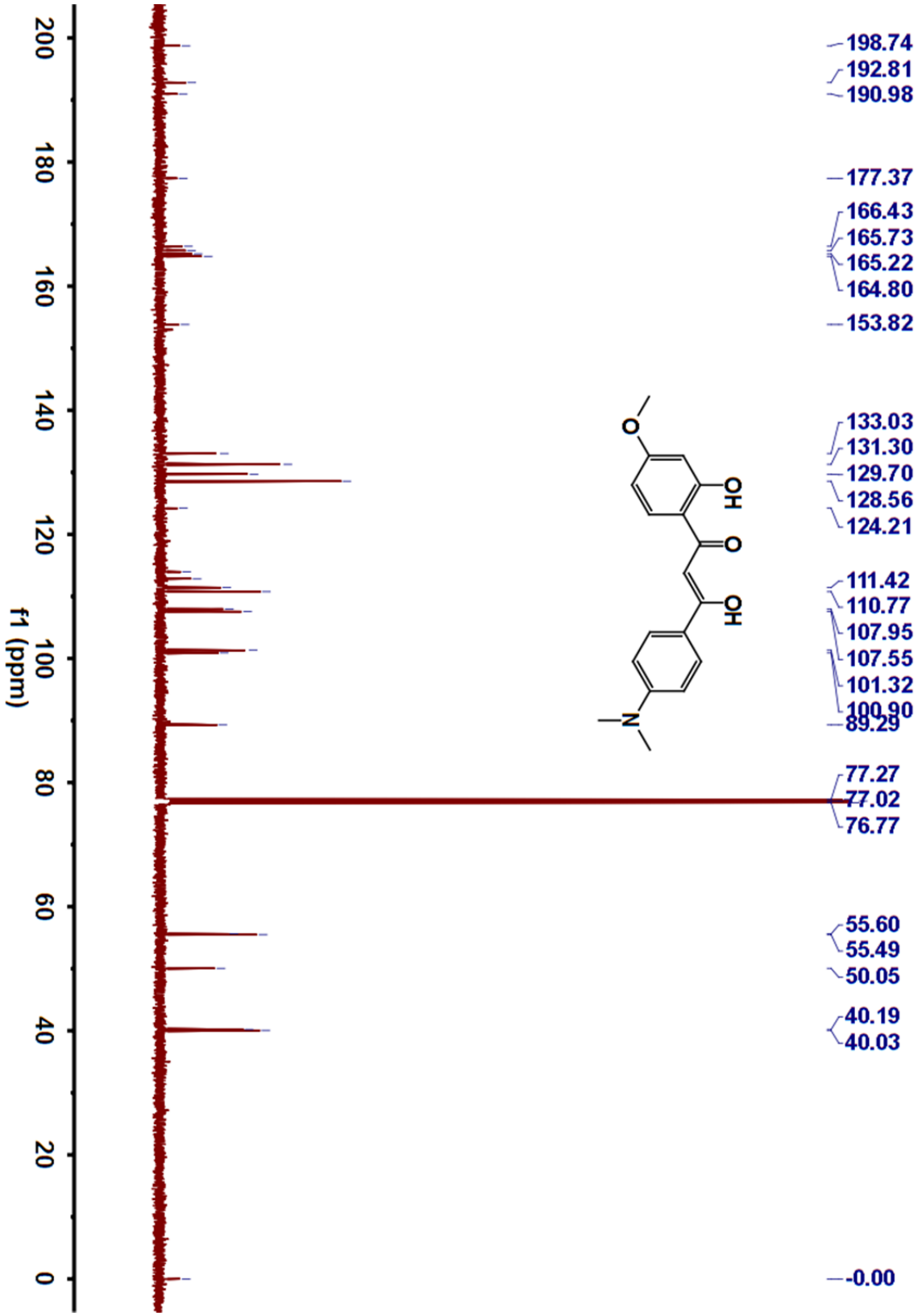

Figure S13. ^{13}C spectra of **4** recorded in $CDCl_3$ (125 MHz).

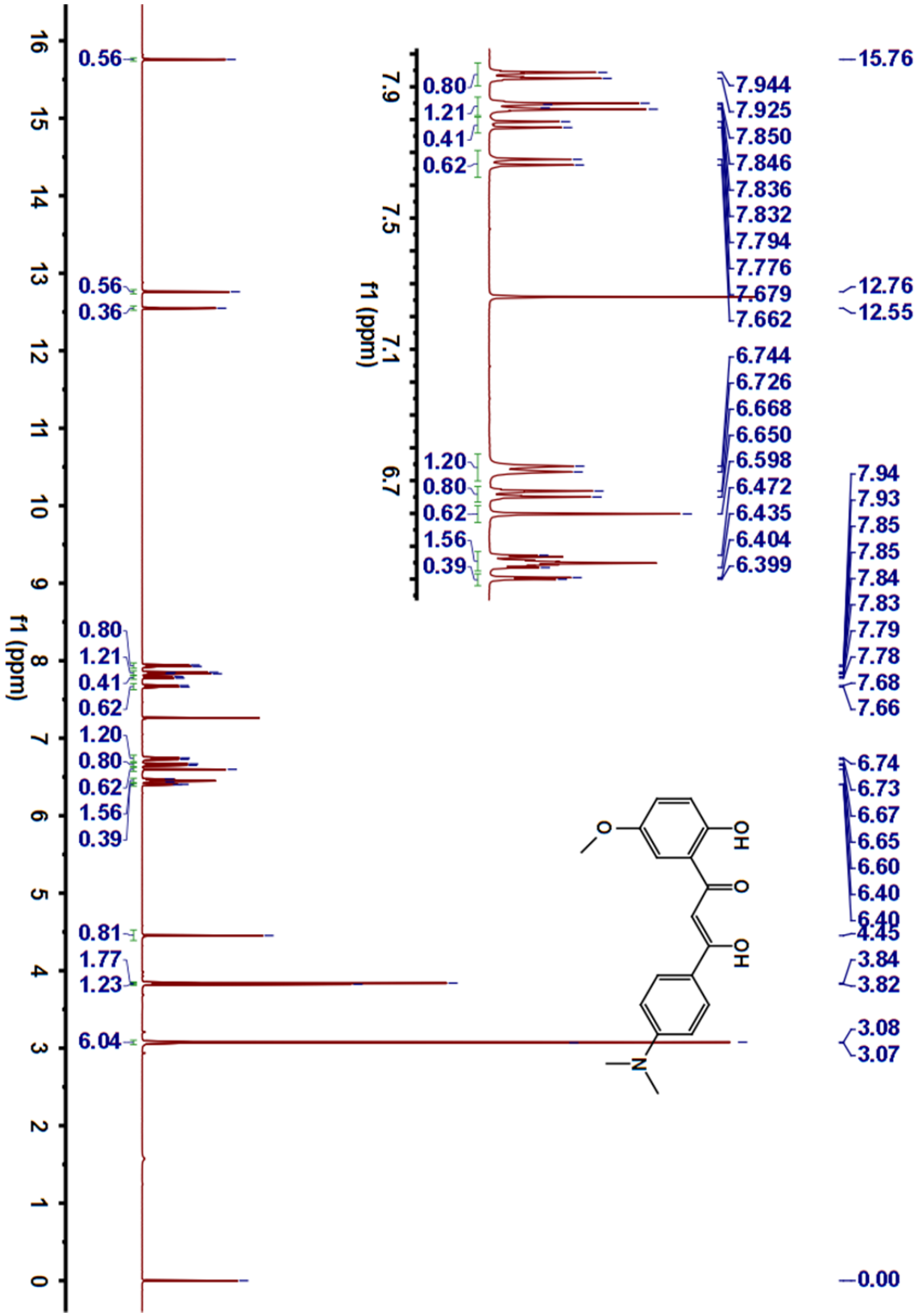

Figure S14. ^{1}H spectra of **6** recorded in $CDCl_3$ (500 MHz).

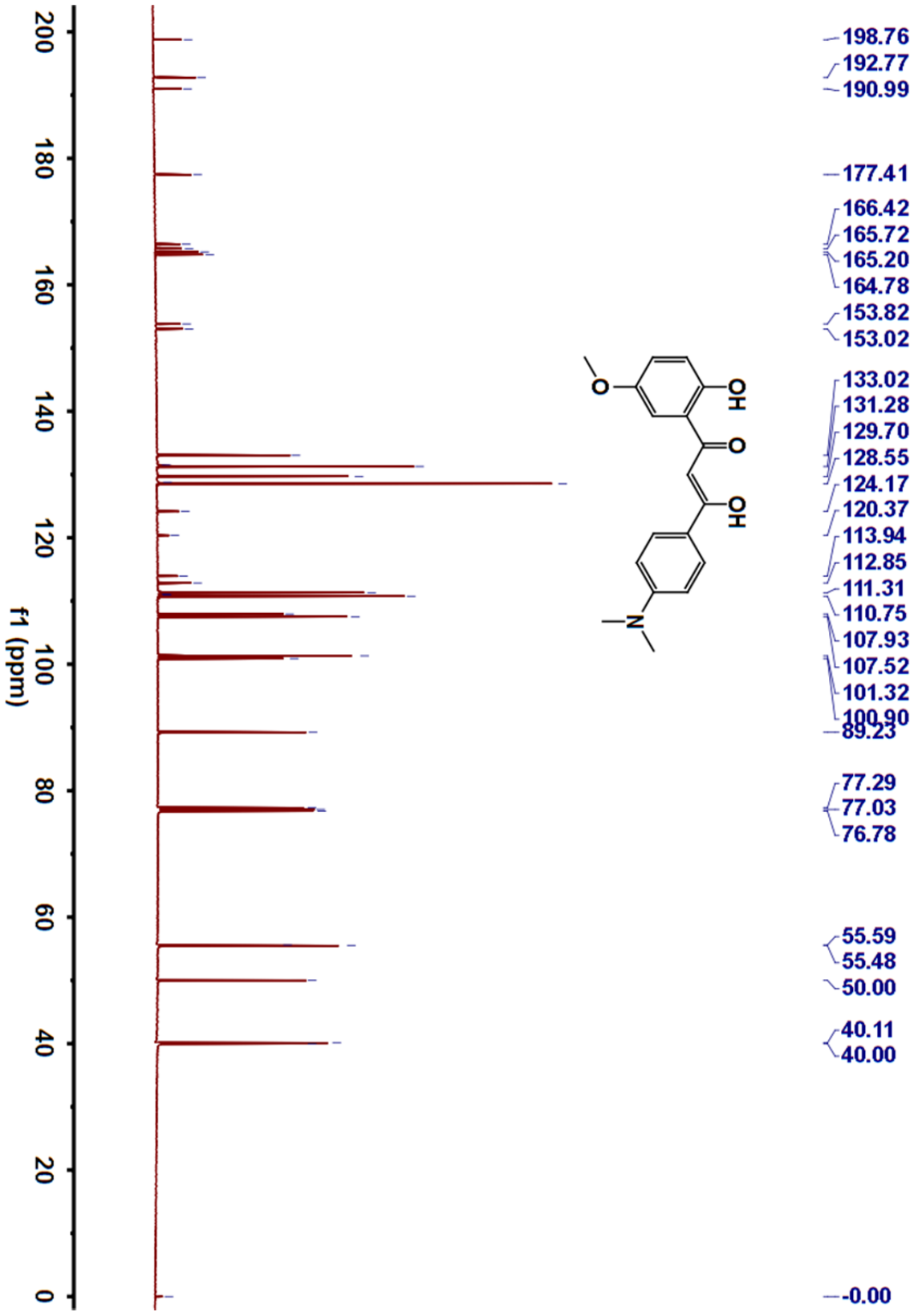

Figure S15. ^{13}C spectra of **6** recorded in $CDCl_3$ (125 MHz).