Supporting Information available

Transition-metal-free, base-promoted annulation/ring-cleavage/ring-reconstruction cascades: a facile access to *N*-protection free indole-indenones

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1. General

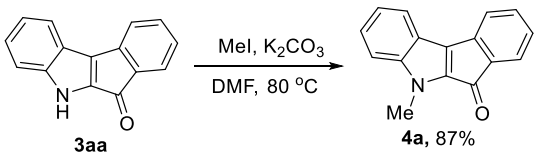
All indolin-2-ones (**2a**-**2j**) and other reagents were obtained from commercial suppliers and used without further purification. 2-halogenated arylglyoxals (**1a**-**1h)** were obtained from commercial suppliers or prepared by oxidation of the corresponding *o*-haloacetophenone.[1] Compound **5** is synthesized from isatin and *o*-bromoacetophenone though two-step addition and dehydration.[2] TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a Varian Mercury 300, 400 or 600 MHz spectrometer. Chemical shifts are reported in ppm, relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on a Thermo Scientific LTQ Orbitrap XL equipped with an electrospray source. Melting points were determined using XT-4 apparatus and not corrected.

2. Experimental procedures

General procedure for preparation of 3 (3aa as an example)

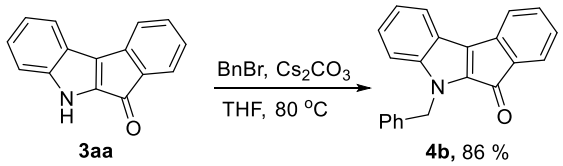
A sealed tube was charged with 2-bromophenylglyoxal **1a** (92 mg, 0.4 mmol), indolin-2-one **2a** (85 mg, 0.64 mmol), and Cs_2CO_3 (391 mg, 1.2 mmol) at room temperature, and then degassed DMSO (4 mL) was added. The resulting mixture was stirred at 120 ℃ in a sealed vessel under nitrogen atmosphere, after disappearance of the reactant (monitored by TLC), then added 50 mL water to the mixture, extracted with EtOAc three times (3 × 50 mL). The extract was washed with 30% NaCl solution (V/V), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Petroleum ether / ethyl acetate = 10:1) to yield the desired product **3aa** as a dark red solid (63 mg, 72% yield).

General procedure for preparation of 4a-4e

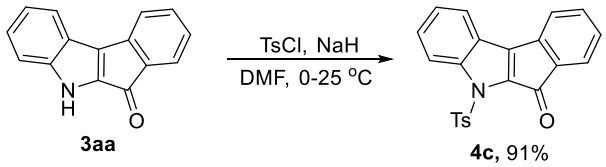


A sealed tube was charged with **3aa** (44 mg, 0.2 mmol), MeI (57 mg, 0.4 mmol), and K_2CO_3 (55 mg, 0.4 mmol) at room temperature, and then 3 mL DMF was added. The

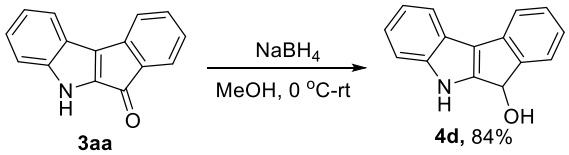
resulting mixture was stirred for about 2 h at 80 °C in a sealed vessel, after disappearance of the reactant (monitored by TLC), then added 30 mL water to the mixture, extracted with EtOAc three times (3 × 30 mL). The extract was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Petroleum ether / ethyl acetate = 50:1) to yield the desired product **4a** as a dark red solid (87%, 40 mg).



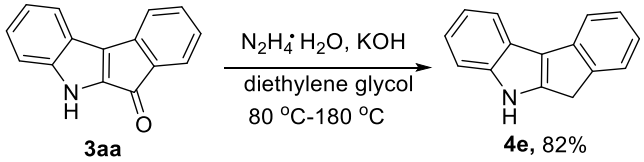
3aa (44 mg, 0.2 mmol) and Cs_2CO_3 (130 mg, 0.4 mmol) were dissolved in THF (2 mL). Benzyl bromide (41 mg, 0.24 mmol) was added into the above solution and reacted for 30 min. The resulting reaction mixture was monitored by TLC. The solution was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated and purified on silica gel chromatography using petroleum ether/EtOAc (3:1) to give the product (dark red solid, 53 mg, 86%).



3aa (44 mg, 0.2 mmol) was weighed directly into a Schlenk tube, then dry DMF (2 mL) was added and stirred. NaH (60% dispersion in mineral oil, 16 mg, 0.4 mmol) was slowly added at 0 °C. After stirring for 30 min, *p*-toluenesulfonyl chloride (38 mg, 0.2 mmol) was added. The solution was allowed to reach room temperature and it was stirred overnight. The mixture was diluted with ethyl acetate and washed with a saturated aqueous solution of ammonium chloride. The aqueous phase was then extracted three times with ethyl acetate. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ethe/EtOAc 20:1) affording product **4c** (68 mg, dark orange solid, 91%).

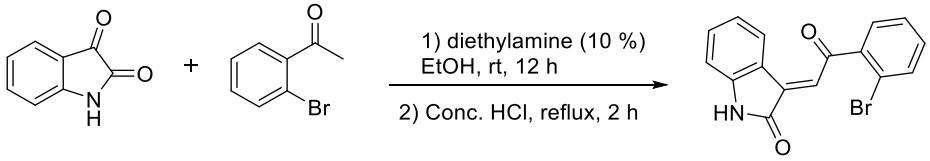


To a 15 mL round bottom flask, **3aa** (44 mg, 0.2 mmol) and ethanol (3 mL) was taken at 0 °C. Next $NaBH_4$ (11.3 mg, 0.3 mmol) was added to the reaction mixture in portions with stirring. The mixture was then allowed to rt for 12 h. The resulting mixture was quenched with sat. NaCl (aq), extracted with EtOAc, dried over Na_2SO_4, concentrated and purified on silica gel chromatography using petroleum ether/EtOAc (10:1) to give the product (37 mg, white solid, 84%).



A mixture of **3aa (**44 mg ,0.2 mmol) and 0.5 ml of hydrazine monohydraye in 10 mL of diethylene glycol was stirred at 80 °C for 1 h and then heated for 1 h at 180 °C. The resulting mixture was cooled to room temperature, treated with a solution of 0.6 g (11 mmol) of KOH in 2.5 mL of water, and was stirred at 180 °C for 2 h. The resulting mixture was quenched with sat. NaCl (aq), extracted with EtOAc, dried over Na_2SO_4, concentrated and purified on silica gel chromatography using petroleum ether/EtOAc (10:1) to give the product (34 mg, white solid, 82%).

General procedure for preparation of 5



A mixture of isatin (7.35 g, 50 mmol) and 2-bromoacetophenone (10 g, 50 mmol) was dissolved in ethanol (50 mL) and diethylamine (365 mg, 5 mmol) was added. The mixture was allowed to stand overnight at room temperature. The resulting reaction mixture was monitored by TLC. The white solid (16.39 g, 95%) was obtained after filtration, The above-mentioned white solid (6.92 g, 20 mmol), ethanol (50 mL) and dilute HCl solution (25%, 100 mL) were taken and the reaction mixture was refluxed

for 2 h. After completion, the reaction mixture was filtered to yield red solid (4.33 g, 66 %).

3. X-ray crystal data of compound 4e

The purified compound 4e is dissolved in a mixed solvent of dichloromethane and petroleum ether, and placed in a dark cabinet to slowly evaporate. After two days, colourless particles crystal ware obtained. Single Crystal X-ray diffraction data were collected using a Bruker-AXS D8 Quest diffractometer (Mo Kα, λ= 0.71073 Å).

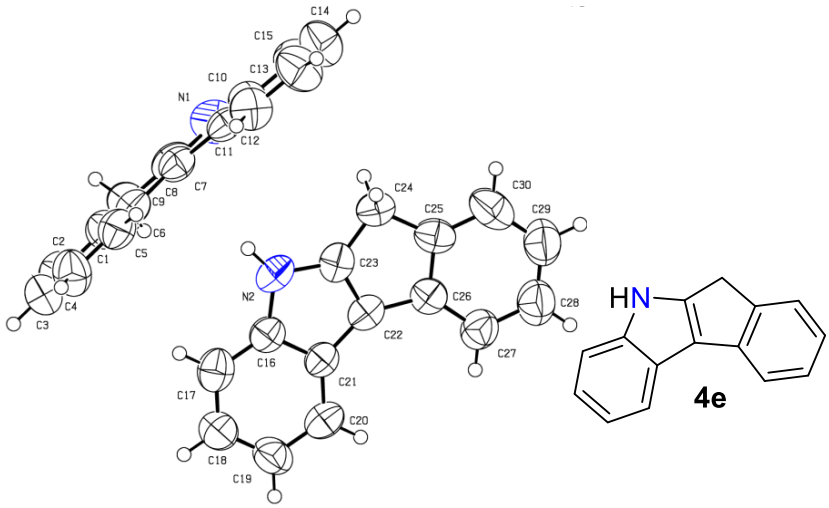


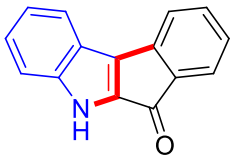
Figure S1 X-ray crystal structure of **4e** (CCDC: 2102218).

Table S1. Crystal data and structure refinement for **4e**

CCDC Number	2102218	
Identification code	4e	
Empirical formula	C15 H11 N	
Formula weight	205.25	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 17.526 Å	α= 90°.
	b = 22.025 Å	β= 90°.
	c = 5.561 Å	γ = 90°.
Volume	2146.7 $Å^3$	
Z	8	

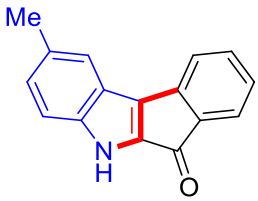
Density (calculated)	1.270 Mg/m^3
Absorption coefficient	0.074 mm^{-1}
F(000)	864
Crystal size	0.200 x 0.200 x 0.200 mm^3
Theta range for data collection	1.485 to 24.994°.
Index ranges	-20<=h<=20, -25<=k<=26, -6<=l<=6
Reflections collected	56737
Independent reflections	3779 [R(int) = 0.1516]
Completeness to theta = 24.994°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3779 / 15 / 241
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0996, wR2 = 0.2158
R indices (all data)	R1 = 0.2063, wR2 = 0.2647
Absolute structure parameter	1.8(10)
Extinction coefficient	n/a
Largest diff. peak and hole	0.158 and -0.210 $e.Å^{-3}$

4. Spectral data of compound 3aa-3ah,3ba-3he, 4a-4e, 5 and 7.



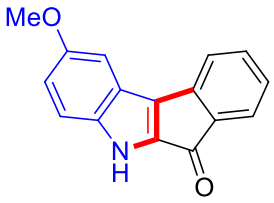
indeno[2,1-*b*]indol-6(5*H*)-one (3aa)[3]:

Yield 72% (63 mg); dark red solid, mp 261-262 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.10 (s, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.37-7.26 (m, 3H), 7.24 (d, J = 7.2 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H) , 7.04 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ =183.6, 143.0, 140.1, 136.5, 136.4, 134.2, 133.9, 126.7, 126.2, 123.1, 121.8, 121.4, 120.7, 119.4, 114.3. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{15}H_{10}NO^+$: 220.0757; found: 220.0756.



2-methylindeno[2,1-*b*]indol-6(5*H*)-one (3ab):

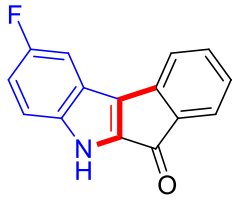
Yield 73% (68 mg); dark red solid, mp 212-213 ℃； ^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.95 (s, 1H), 7.61 (s, 1H), 7.35-7.25 (m, 3H), 7.21 (d, J = 7.2 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ =183.5, 141.5, 140.2, 136.5, 136.4, 134.1, 133.3, 130.8, 128.1, 126.5, 123.0, 120.9, 120.5, 119.2, 113.9, 21.1; HRMS (ESI): m/z calcd for $C_{16}H_{12}NO^+$ $(M+H)^+$: 234.0913; found: 234.0914.



2-methoxyindeno[2,1-*b*]indol-6(5*H*)-one (3ac):

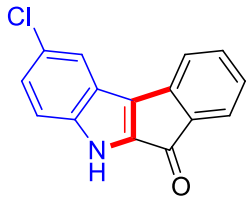
Yield 68% (68 mg); dark red solid, mp 236-237 ℃； ^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.96 (s, 1H), 7.42 (d, J = 7.2 Hz, 1H), 7.32-7.25 (m, 3H), 7.21 (d, J = 7.2 Hz, 1H),

7.01 (t, J = 7.8 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ =183.3, 155.2, 140.2, 138.4, 136.7, 136.4, 134.1, 133.2, 126.4, 123.0, 121.0, 119.4, 117.8, 115.1, 101.2, 55.5; HRMS (ESI): m/z calcd for $C_{16}H_{11}NO_2Na^+$ $(M+Na)^+$: 272.0682; found: 272.0678.



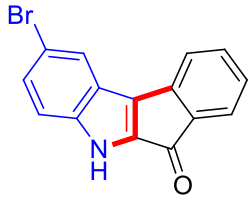
2-fluoroindeno[2,1-*b*]indol-6(5*H*)-one (3ad):

Yield 47% (45 mg); dark red solid. mp 293-294℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.10 (s, 1H), 7.51 (d, J = 9.6 Hz, 1H), 7.33-7.30 (m, 1H), 7.26-7.17 (m, 2H), 7.14 (d, J = 7.2 Hz, 1H), 7.04 (t, J = 9.0 Hz, 1H), 6.94 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ =183.6, 158.2 (d, J = 235.0 Hz), 139.9, 139.6, 138.2, 136.0, 134.2, 133.4 (d, J = 5.4 Hz), 126.5, 123.1, 120.5 (d, J = 10.7 Hz), 119.4, 115.5 (d, J = 9.8 Hz), 114.7 (d, J = 26.9 Hz), 105.5 (d, J = 23.5 Hz); HRMS (ESI): m/z calcd for $C_{15}H_8FNONa^+$ $(M+Na)^+$: 260.0482; found: 260.0484.



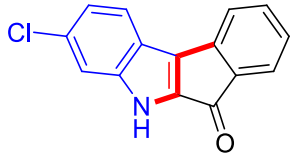
2-chloroindeno[2,1-*b*]indol-6(5*H*)-one (3ae):

Yield 62% (63 mg); brown solid, mp 287-288 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.21 (s, 1H), 7.86 (s, 1H), 7.39-7.29 (m, 2H), 7.25 (t, J = 7.2 Hz, 1H), 7.18 (t, J = 7.8 Hz, 2H), 6.99 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ =183.6, 141.2, 139.6, 137.8, 135.9, 134.3, 132.9, 126.7, 126.4, 125.9, 123.2, 121.3, 120.3, 119.7, 115.8; HRMS (ESI): m/z calcd for $C_{15}H_9ClNO^+$ $(M+H)^+$; 254.0367; found: 254.0368.



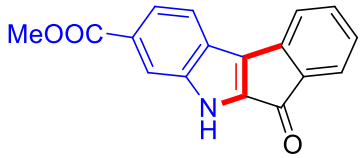
2-bromoindeno[2,1-*b*]indol-6(5*H*)-one (3af):

Yield 65% (77 mg); dark red solid, mp 294-295 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.19 (s, 1H), 7.97 (s, 1H), 7.40-7.25 (m, 3H), 7.23 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 7.2 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ =183.5,141.3, 139.6, 137.6, 135.9, 134.2, 132.7, 128.3, 126.7, 123.4, 123.1, 121.9, 119.6, 116.1, 114.4; HRMS (ESI): m/z calcd for $C_{15}H_9BrNO^+$ $(M+H)^+$: 297.9862; found: 297.9862.



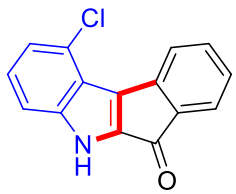
3-chloroindeno[2,1-*b*]indol-6(5*H*)-one (3ag):

Yield 54% (55 mg); brown solid, mp 292-293 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.07 (s, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.27 (s, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 6.0 Hz, 2H), 7.01 (d, J = 8.4 Hz, 1H), 6.94 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 183.2, 142.9, 139.5, 137.3, 136.1, 134.0, 133.6, 130.3, 126.7, 123.0, 122.5, 122.2, 119.3, 119.2, 113.5; HRMS (ESI): m/z calcd for $C_{15}H_9ClNO^+$ $(M+H)^+$: 254.0367; found : 254.0367.



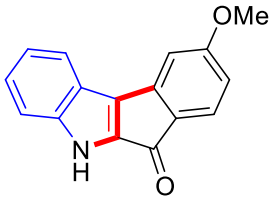
methyl 6-oxo-5,6-dihydroindeno[2,1-*b*]indole-3-carboxylate (3ah):

Yield 64% (71 mg); dark red solid, mp 281-282℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.35 (s, 1H), 7.85 (s, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.33-7.21 (m, 2H), 7.18 (d, J = 6.6 Hz, 1H), 6.99 (t, J = 7.2 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ =183.7, 166.3, 141.9, 139.7, 139.4, 135.9, 134.5, 132.7, 126.8, 126.2, 123.4, 123.3, 121.6, 121.1, 119.6, 116.1, 52.1; HRMS (ESI): m/z calcd for $C_{17}H_{12}NO_3^+$ $(M+H)^+$: 278.0812; found: 278.0812.



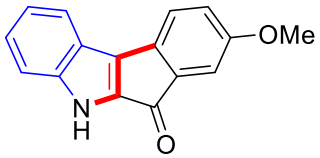
1-chloroindeno[2,1-*b*]indol-6(5*H*)-one (3aj):

Yield 9% (9 mg); dark red solid, mp: >300℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.44 (s, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.34-7.26 (m, 2H), 7.25-7.14 (m, 3H), 7.03 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ =183.5, 143.6, 139.3, 137.5, 135.8, 134.6, 131.9, 126.8, 126.6, 125.2, 123.4, 121.8, 121.2, 120.3, 113.4; HRMS (ESI): m/z calcd for $C_{15}H_9ClNO^+$ $(M+H)^+$: 254.0367; found: 254.0368.



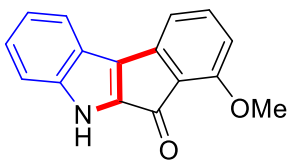
9-methoxyindeno[2,1-*b*]indol-6(5*H*)-one (3ba)

Yield 51% (51 mg); dark red solid, mp 260-261 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.05 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.97 (s, 1H), 6.46-6.41 (m,1H), 3.82(s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) : δ = 182.9, 164.7, 142.6, 142.5, 137.9, 131.4, 128.7, 125.6, 125.1, 121.7, 121.3, 120.7, 114.1, 108.6, 107.8, 55.7; HRMS (ESI): m/z calcd for $C_{16}H_{12}NO_2^+$ $(M+H)^+$: 250.0863; found: 250.0864.



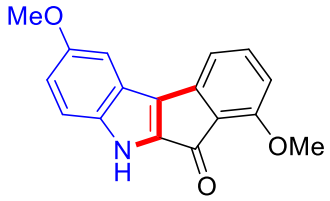
8-methoxyindeno[2,1-*b*]indol-6(5*H*)-one (3ca)

Yield 73% (73 mg); dark red solid, mp 279-280℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.95 (s, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.29–7.21 (m, 2H), 7.12 (t, J = 7.2 Hz, 1H), 6.83 (s, 1H), 6.79–6.71 (m, 1H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 182.9, 158.7, 143.0, 138.6, 136.0, 135.1, 131.7, 126.3, 121.6, 121.5, 120.3, 120.0, 115.6, 114.2, 112.0, 55.5; HRMS (ESI): m/z calcd for $C_{16}H_{12}NO_2^+$ $(M+H)^+$: 250.0863; found: 250.0864.



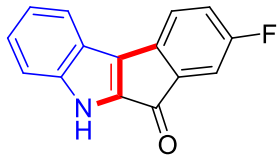
7-methoxyindeno[2,1-*b*]indol-6(5*H*)-one (3da)[4]

Yield 65% (65 mg); brown solid, mp: 250-251℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.97 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.31-7.25 (m, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 6.8 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 182.3, 157.0, 142.4, 142.0, 137.0, 136.8, 131.0, 125.4, 121.7, 121.0, 120.8, 119.7, 114.2, 113.2, 112.9, 55.5; HRMS (ESI): m/z calcd for $C_{16}H_{12}NO_2^+$ $(M+H)^+$: 250.0863; found: 250.0864.



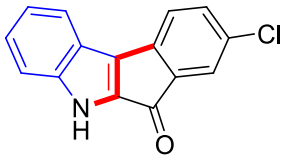
2,7-dimethoxyindeno[2,1-*b*]indol-6(5*H*)-one (3dc)

Yield 67% (75 mg); brown solid, mp: 264℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.81 (s, 1H), 7.31-7.20 (m, 3H), 7.03 (d, J = 6.8 Hz, 1H), 6.88 (dd, J = 2.4, 9.2 Hz, 1H), 6.76 (d, J = 8.8 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 182.0, 157.0, 155.1, 142.2, 137.7, 137.2, 136.5, 130.3, 121.1, 119.8, 116.7, 114.9, 112.9, 112.8, 101.2, 55.43, 55.39; HRMS (ESI): m/z calcd for $C_{17}H_{14}NO_3^+$ $(M+H)^+$: 280.0968; found: 280.0969.



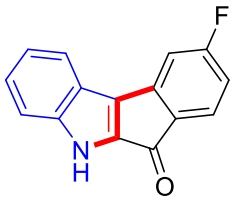
8-fluoroindeno[2,1-*b*]indol-6(5*H*)-one (3ea)

Yield 53% (50 mg); dark red solid, mp: 261-262℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.10 (s, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.35-7.30 (m, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.11-7.00 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 181.7, 161.5 (d, J = 243.2 Hz), 143.1, 139.0 (d, J = 6.1 Hz), 136.4, 136.0, 133.9, 126.5, 121.9, 121.5, 120.4, 120.2 (d, J = 6.9 Hz), 118.7 (d, J = 22.0 Hz), 114.2, 112.0 (d, J = 24.7 Hz); HRMS (ESI): m/z calcd for $C_{15}H_9FNO^+$ $(M+H)^+$: 238.0663; found: 238.0664.



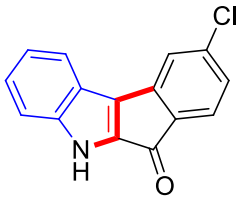
8-chloroindeno[2,1-*b*]indol-6(5*H*)-one (3fa):

Yield 62% (63 mg); dark red solid, mp: 292-293℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.14 (s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.33-7.19 (m, 3H), 7.14 (t, J = 7.8 Hz, 1H), 7.11 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ =181.8, 143.1, 138.5, 138.4, 136.4, 133.5, 133.0, 130.9, 126.5, 123.2, 122.0, 121.4, 120.5, 120.3,114.3; HRMS (ESI): m/z calcd for $C_{15}H_9ClNO^+$ $(M+H)^+$: 254.0367; found: 254.0368.



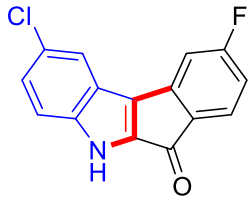
9-fluoroindeno[2,1-*b*]indol-6(5*H*)-one（3ga）

Yield 71% (67 mg); Gray solid, mp: 273-274℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.19 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.34-7.20 (m, 3H), 7.17 (t, J = 7.8 Hz, 1H), 6.76 (t, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 182.2, 166.5 (d, J = 249.2 Hz), 143.4 (d, J = 10.7 Hz) , 142.8, 137.4, 132.4, 131.6, 126.2, 125.0 (d, J = 10.2 Hz), 122.0, 121.4, 120.6, 114.2, 111.4 (d, J = 22.9 Hz) , 108.4 (d, J = 26.1 Hz); HRMS (ESI): m/z calcd for $C_{15}H_9FNO^+$ $(M+H)^+$: 238.0663; found: 238.0663.



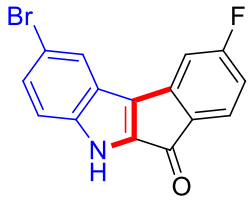
9-chloroindeno[2,1-*b*]indol-6(5*H*)-one （3ha）

Yield 67% (68 mg); dark red solid, mp: >300℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.21 (s, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.50-7.36 (m, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.22-7.12 (m, 2H), 7.05 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ =182.2, 142.9, 142.2, 139.0, 137.0, 134.9, 132.4, 126.4, 125.9, 124.2, 122.1, 121.6, 120.6, 119.7, 114.3; HRMS (ESI) m/z: calcd for $C_{15}H_9ClNO^+$ $(M+H)^+$: 254.0367; found: 254.0368.



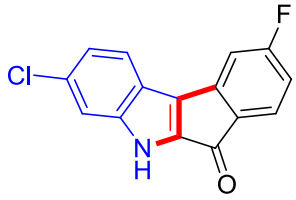
2-chloro-9-fluoroindeno[2,1-*b*]indol-6(5*H*)-one （3ge）

Yield 60% (65 mg); dark red solid, mp: >300℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.13 (s, 1H), 7.76 (s, 1H), 7.20 (d, J = 7.2 Hz, 1H), 7.10-7.04 (m, 3H), 6.57 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 182.0, 167.3 (d, J = 249.8 Hz), 142.8 (d, J = 10.3 Hz), 141.0, 138.5, 131.9, 130.5, 126.6, 125.8, 124.9 (d, J = 9.2 Hz) , 121.1, 120.3, 115.6, 111.4 (d, J = 22.6 Hz) , 108.6 (d, J = 26.0 Hz); HRMS (ESI): m/z calcd for $C_{15}H_8FClNO^+$ $(M+H)^+$: 272.0273; found: 272.0275.



2-bromo-9-fluoroindeno[2,1-*b*]indol-6(5*H*)-one （3gf）

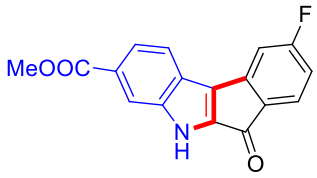
Yield 58% (73 mg); dark red solid, mp: >300℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.37 (s, 1H), 8.21 (s, 1H), 7.44-7.24 (m, 4H), 6.77 (t, J = 7.6 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 182.1, 166.5 (d, J = 249.5 Hz), 142.9 (d, J = 10.8 Hz), 141.2, 138.4, 131.9, 130.4, 128.4, 125.1 (d, J = 10.1 Hz), 123.5, 121.8, 116.1, 114.7, 111.5 (d, J = 22.9 Hz), 108.8 (d, J = 26.1 Hz); HRMS (ESI): m/z calcd for $C_{15}H_8FBrNO^+$ $(M+H)^+$: 315.9768; found: 315.9768.



3-chloro-9-fluoroindeno[2,1-*b*]indol-6(5*H*)-one （3gg）

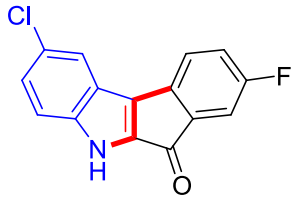
Yield 55% (60 mg); dark red solid, mp: >300℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.27 (s, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.36 (s, 1H), 7.28-7.20 (m, 2H), 7.14 (d, J = 8.8 Hz, 1H), 6.76 (t, J = 8.0 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 181.9, 167.3 (d, J = 249.3 Hz), 142.9, 142.8, 138.2, 132.0, 131.4, 130.4, 125.1 (d, J = 8.8 Hz), 122.7,

122.5, 119.2, 113.6, 111.7 (d, J = 22.4 Hz), 108.7 (d, J = 26.1 Hz); HRMS (ESI): m/z calcd for $C_{15}H_8FClNO^+$ $(M+H)^+$: 272.0273; found: 272.0274.



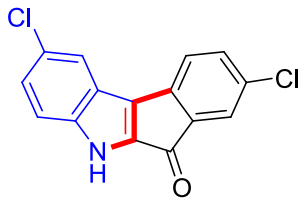
methyl 9-fluoro-6-oxo-5,6-dihydroindeno[2,1-*b*]indole-3-carboxylate（3gh）

Yield 61% (72 mg); dark red solid, mp: >300℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.50 (s, 1H), 7.92 (t, J = 8.4 Hz, 2H), 7.63 (d, J = 8.8 Hz, 1H), 7.30-7.24 (m, 2H), 6.78 (t, J = 8.8 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 182.2, 166.6 (d, J = 250.1 Hz), 166.2, 143.0 (d, J = 10.4 Hz), 141.7, 140.1, 131.9, 130.4, 126.2, 125.4 (d, J = 10.4 Hz), 123.2, 121.7, 121.1, 116.0, 111.7 (d, J = 22.4 Hz), 108.7 (d, J = 25.8 Hz), 52.1; HRMS (ESI): m/z calcd for $C_{17}H_{11}FNO_3^+$ $(M+H)^+$: 296.0718; found: 296.0718.



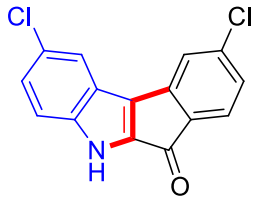
2-chloro-8-fluoroindeno[2,1-*b*]indol-6(5*H*)-one （3ee）

Yield 42% (45 mg); dark red solid, mp: >300℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.25 (s, 1H), 7.92 (s, 1H), 7.44-7.30 (m, 2H), 7.24 (d, J = 8.8 Hz, 1H), 7.08 (t, J = 8.8 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 181.7, 161.6 (d, J = 243.4 Hz), 141.2, 138.4 (d, J = 6.3 Hz), 137.7, 135.5, 132.9, 126.4 (d, J = 30.7 Hz), 121.0, 120.7 (d, J = 6.6 Hz), 120.5, 119.0, 118.9, 115.8, 112.0 (d, J = 24.5 Hz); HRMS (ESI): m/z calcd for $C_{15}H_8FClNO^+$ $(M+H)^+$: 272.0273; found: 272.0271.



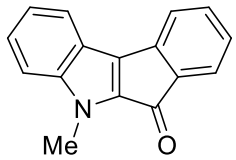
2,8-dichloroindeno[2,1-*b*]indol-6(5*H*)-one （3fe）

Yield 45% (52 mg); dark red solid, mp: >300℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.33 (s, 1H), 7.96 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.39-7.33 (m, 2H), 7.25 (d, J = 8.8 Hz, 1H), 7.16 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 181.9, 141.3, 138.1, 137.9, 137.7, 133.3, 132.5, 131.1, 126.7, 126.4, 123.4, 121.1, 120.9, 120.6, 115.9; HRMS (ESI): m/z calcd for $C_{15}H_8Cl_2NO^+$ $(M+H)^+$: 287.9978; found: 287.9980.



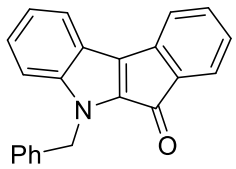
2,9-dichloroindeno[2,1-*b*]indol-6(5*H*)-one （3he）

Yield 64% (73 mg); dark red solid, mp: >300℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.31 (s, 1H), 7.98 (s, 1H), 7.47 (s, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.21 (d, J = 6.6 Hz, 1H), 7.12 (d, J = 6.0 Hz, 1H), 7.01-6.99 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 182.1, 141.6, 141.1, 139.1, 138.2, 134.3, 131.3, 126.7, 126.1, 125.8, 124.2, 121.2, 120.6, 120.0, 115.7; HRMS (ESI): m/z calcd for $C_{15}H_8Cl_2NO^+$ $(M+H)^+$: 287.9978; found: 287.9977.



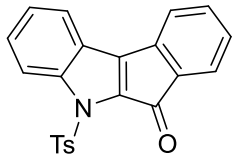
5-methylindeno[2,1-*b*]indol-6(5*H*)-one (4a)[3a]

Dark red solid; mp: 146-147 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 6.4 Hz, 2H), 7.17–7.12 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 184.3, 143.6, 140.1, 136.9, 136.5, 133.6, 133.1, 126.1, 125.6, 123.1, 121.6, 121.3, 120.9, 118.7, 111.1, 30.2. HRMS (ESI): m/z calcd for $C_{16}H_{11}NONa^+$ $(M+Na)^+$: 256.0733; found: 256.0732.



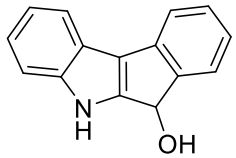
5-benzylindeno[2,1-*b*]indol-6(5*H*)-one (4b)

Dark red solid; mp:137-138 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.84 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.36–7.22 (m, 9H), 7.17 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 5.47 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 183.7, 143.0, 139.4, 137.1, 136.3, 135.8, 134.4, 133.4, 128.7, 127.7, 127.2, 126.9, 126.4, 123.3, 122.3, 121.8, 120.7, 119.6, 112.8, 47.1; HRMS (ESI): m/z calcd for $C_{22}H_{16}NO^+$ $(M+H)^+$: 310.1226; found: 310.1225.



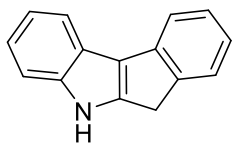
5-tosylindeno[2,1-*b*]indol-6(5*H*)-one (4c)[3b]

Dark orange solid; mp:216-217℃; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.40–7.21 (m, 6H), 7.13 (t, J = 7.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.3, 145.6, 142.6, 142.4, 136.9, 135.7, 135.3, 134.6, 133.6, 129.9, 128.8, 128.4, 127.3, 124.7, 124.0, 122.5, 121.7, 120.0, 115.6, 21.6.



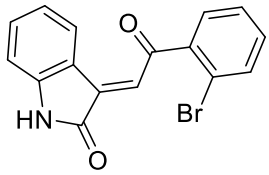
5,6-dihydroindeno[2,1-*b*]indol-6-ol (4d)

White solid; mp: 203-204℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.71 (s, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 7.6 Hz, 1H), 7.17-7.09 (m, 2H), 7.05 (t, J = 7.2 Hz, 1H), 5.89 (d, J = 8.4 Hz, 1H), 5.45 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 149.6, 147.9, 140.8, 138.5, 128.2, 124.4, 123.0, 121.3, 121.2, 119.9, 119.2, 118.6, 117.8, 112.7, 68.5; HRMS (ESI): m/z calcd for $C_{15}H_{12}NO^+$ $(M+H)^+$: 222.0913; found: 222.0913.



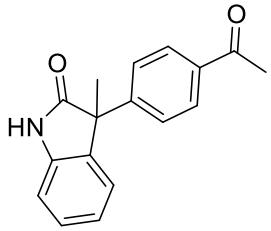
5,6-dihydroindeno[2,1-*b*]indole (4e)[5]

White solid; mp: 206-207 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.57 (s, 1H), 7.87-7.83 (m, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.47-7.42 (m, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.14-7.11 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 3.82 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.4, 142.6, 140.7, 139.8, 126.7, 124.8, 122.0, 121.4, 120.7, 120.0, 119.5, 118.7, 117.8, 112.2, 30.7.



(*E*)-3-(2-(2-bromophenyl)-2-oxoethylidene)indolin-2-one (5)[6]

Red solid; mp: 157-158℃; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.84 (s, 1H), 8.36 (d, J = 7.8 Hz, 1H), 7.82-7.68 (m, 2H), 7.60-7.46 (m, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.34 (s, 1H), 7.01 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 192.8, 168.2, 145.5, 140.5, 136.8, 133.8, 133.6, 133.1, 130.1, 128.2, 127.5, 126.4, 121.9, 119.9, 118.9, 110.5.



3-(4-acetylphenyl)-3-methylindolin-2-one (7)

White solid; mp: 206-207 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.61 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.25-7.20 (m, 1H), 7.12-7.01 (m, 2H), 6.99 (d, J = 8.0 Hz, 1H), 2.56 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 181.8, 145.8, 140.4, 135.9, 134.8, 128.6, 128.3, 126.9, 124.1, 122.9, 110.5, 52.9, 26.6, 23.2; HRMS (ESI): m/z calcd for $C_{17}H_{16}NO_2^+$ $(M+H)^+$: 266.1176; found: 266.1175.

5. Reference:

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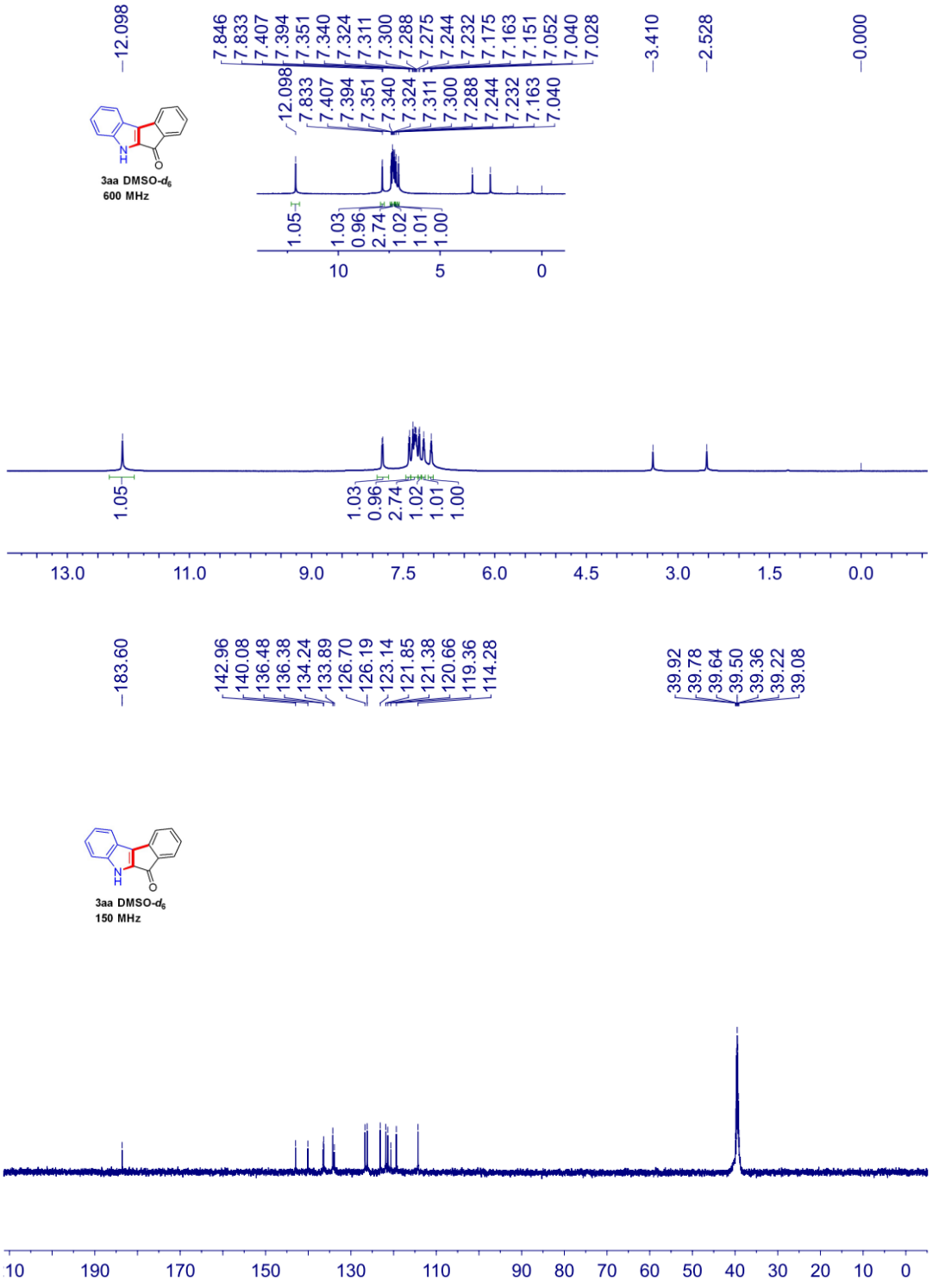
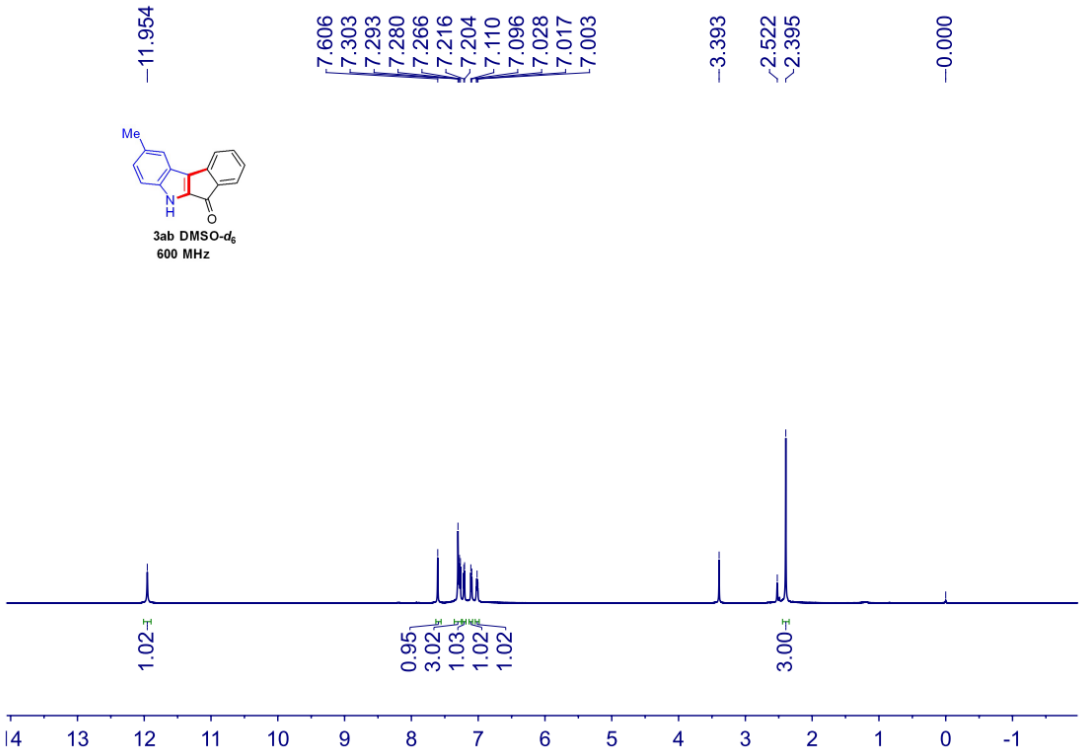
5. S. M. Barolo, A. E. Lukach and R. A. Rossi, Syntheses of 2-Substituted Indoles and Fused Indoles by Photostimulated Reactions Of *o*-Iodoanilines with Carbanions by the $S_{RN}1$ Mechanism. *J. Org. Chem.*, 2003, **68**, 2807−2811.

6. J. Wang, D. Yun, J. Yao, W. Fu, F. Huang, L. Chen, T. Wei, C. Yu, H. Xu, X. Zhou, Y. Huang, J. Wu, P. Qiu and W. Li, Design, Synthesis and QSAR Study of Novel Isatin Analogues Inspired Michael Acceptor as Potential Anticancer Compounds. *Eur. J. Med. Chem.*, 2018, **144**, 493−503.

6. Spectral copies of ^{1}H NMR, and ^{13}C NMR

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7.003
3.393
2.522
2.395
0.000
Me
N
H
O
3ab DMSO-d_6
600 MHz
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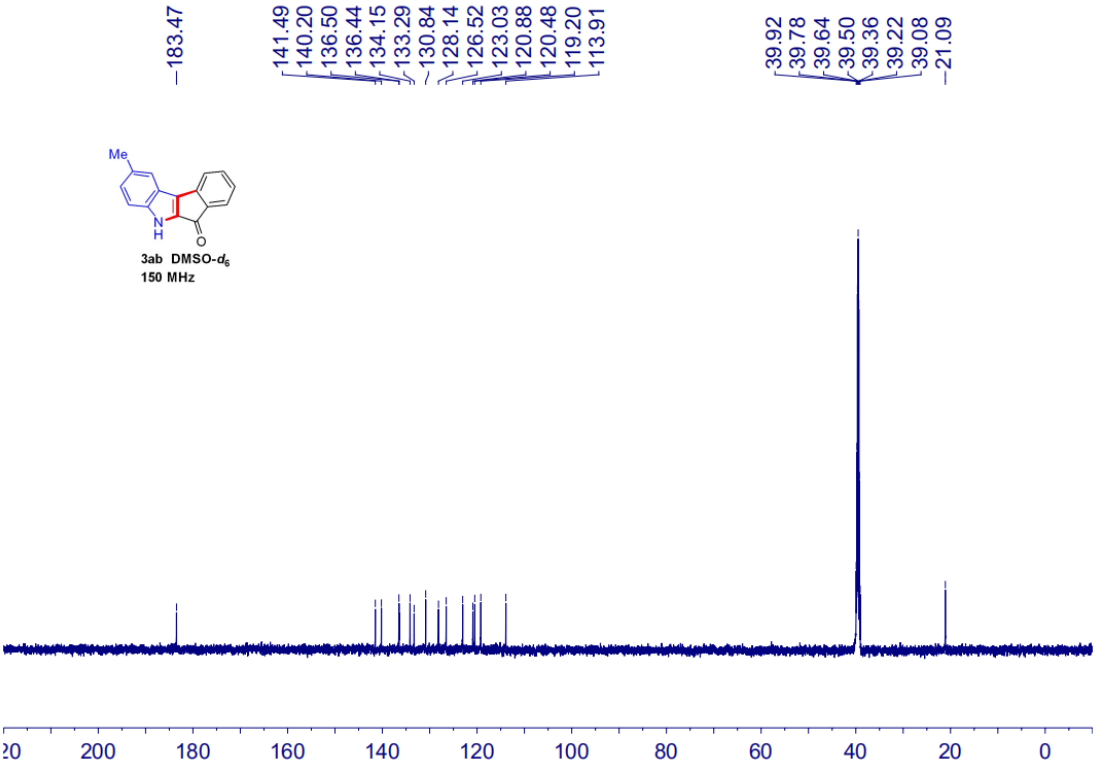
0.95
3.02
1.03
1.02
1.02
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1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140.20
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134.15
133.29
130.84
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126.52
123.03
120.88
120.48
119.20
113.91
39.92
39.78
39.64
39.50
39.36
39.22
39.08
21.09
Me
N
H
O
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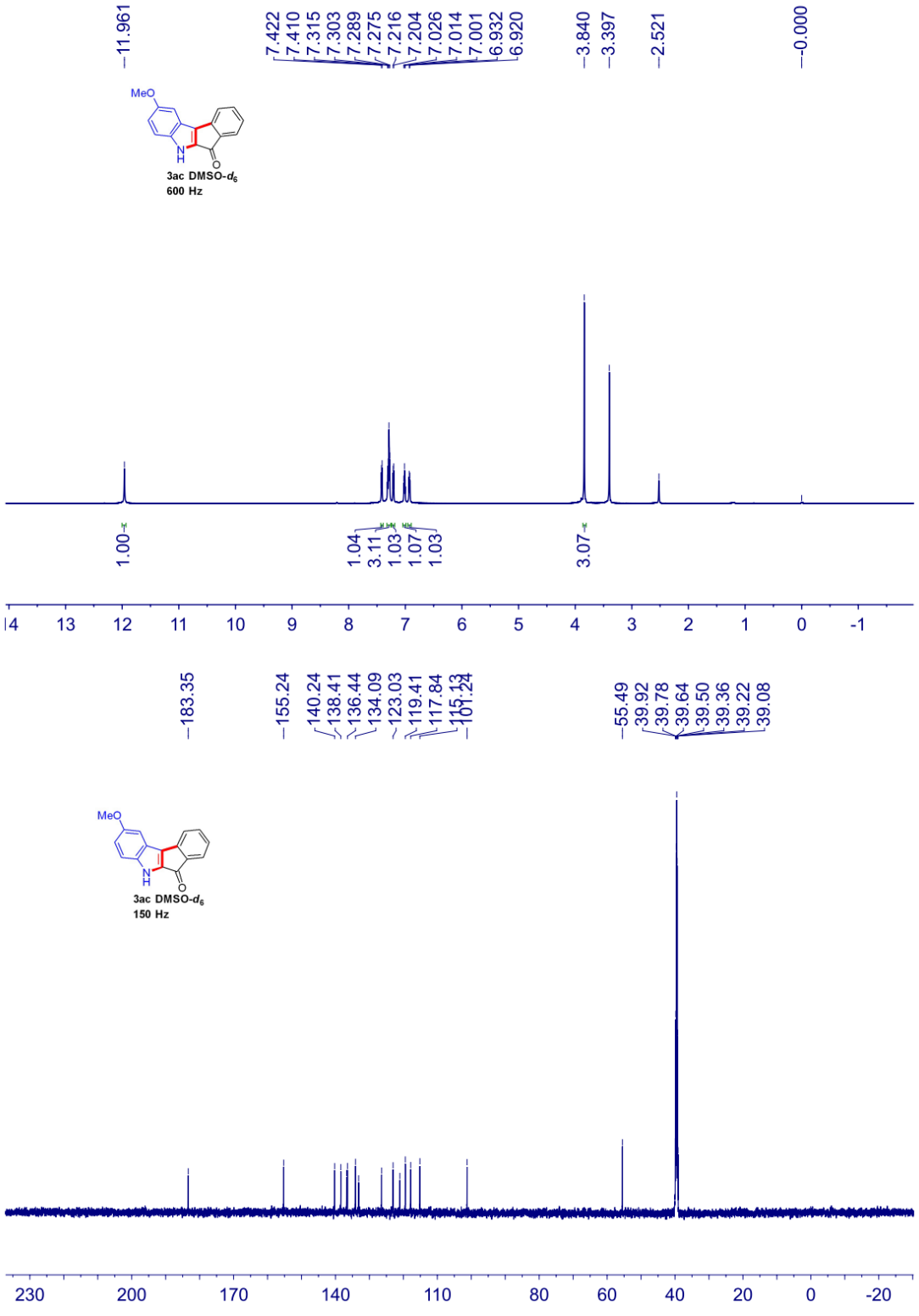
220 200 180 160 140 120 100 80 60 40 20 0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6.932
6.920
3.840
3.397
2.521
0.000
MeO
3ac DMSO-d_6
600 Hz
1.00
1.04
3.11
1.03
1.07
1.03
3.07
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183.35
155.24
140.24
138.41
136.44
134.09
123.03
119.41
117.84
115.13
101.24
55.49
39.92
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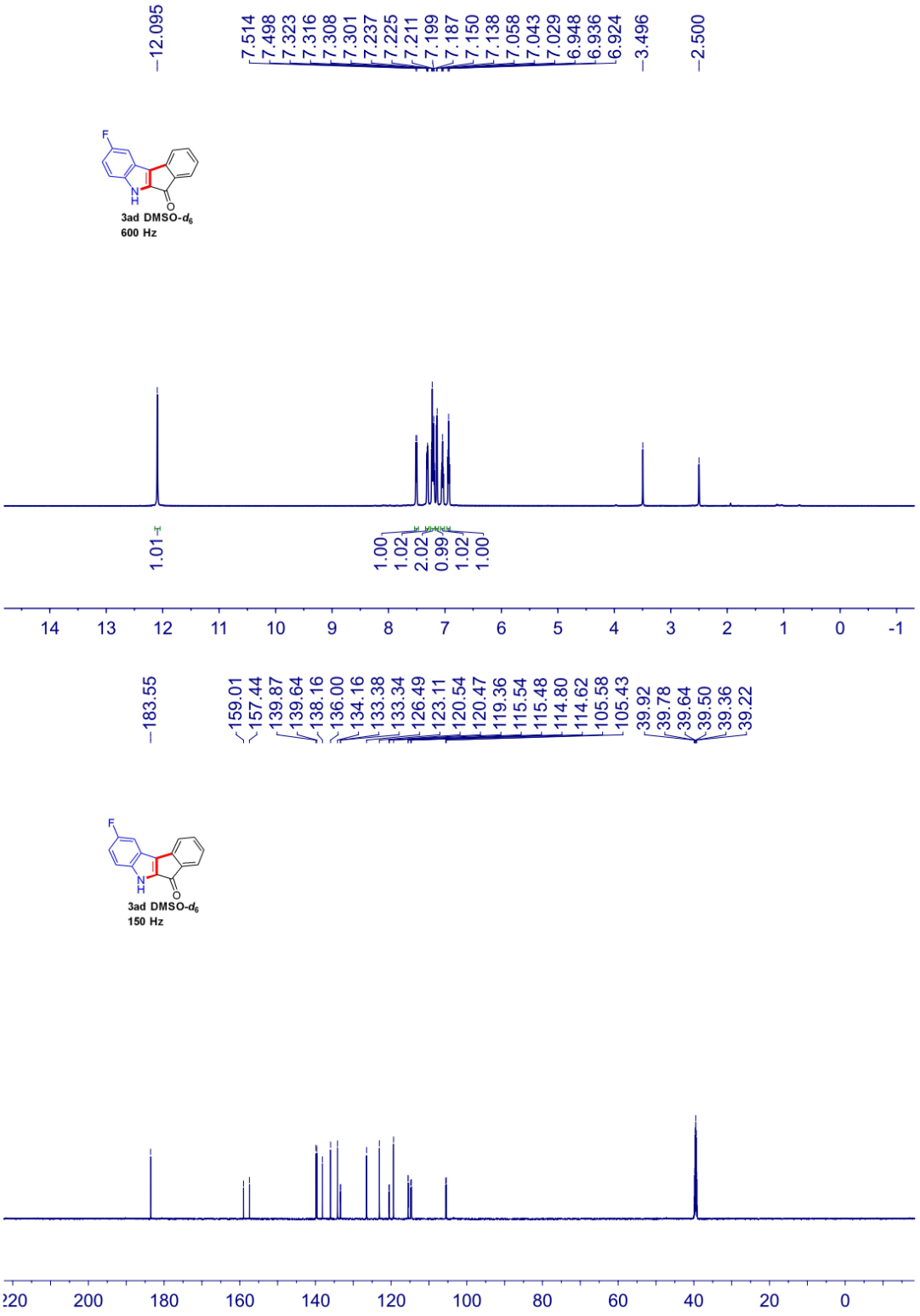
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7.138
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7.043
7.029
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6.924
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600 Hz
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1.00
1.02
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1.00
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159.01
157.44
139.87
139.64
138.16
136.00
134.16
133.38
133.34
126.49
123.11
120.54
120.47
119.36
115.54
115.48
114.80
114.62
105.58
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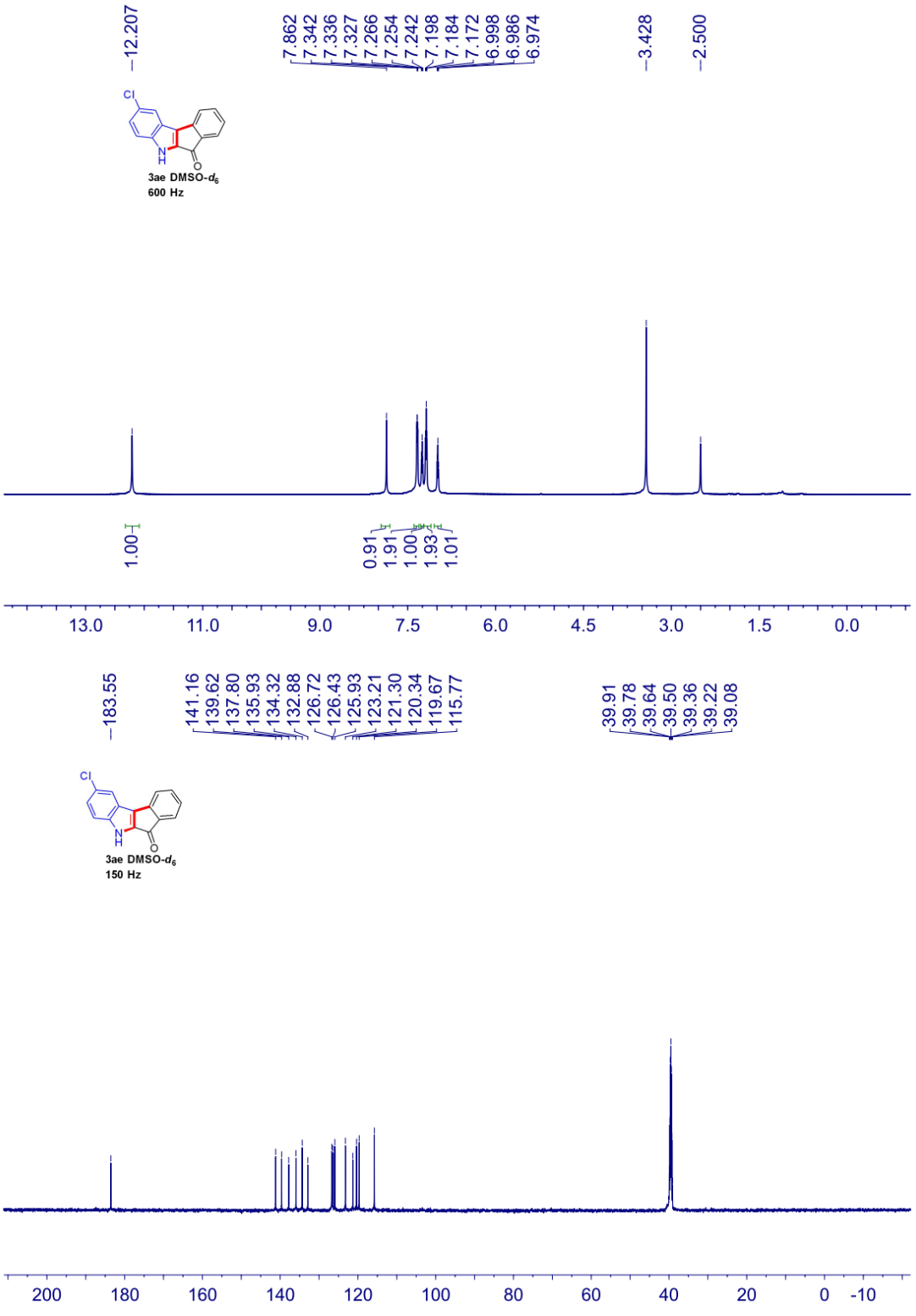
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6.974
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N
H
O
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600 Hz
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0.91
1.91
1.00
1.93
1.01
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11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
183.55
141.16
139.62
137.80
135.93
134.32
132.88
126.72
126.43
125.93
123.21
121.30
120.34
119.67
115.77
39.91
39.78
39.64
39.50
39.36
39.22
39.08
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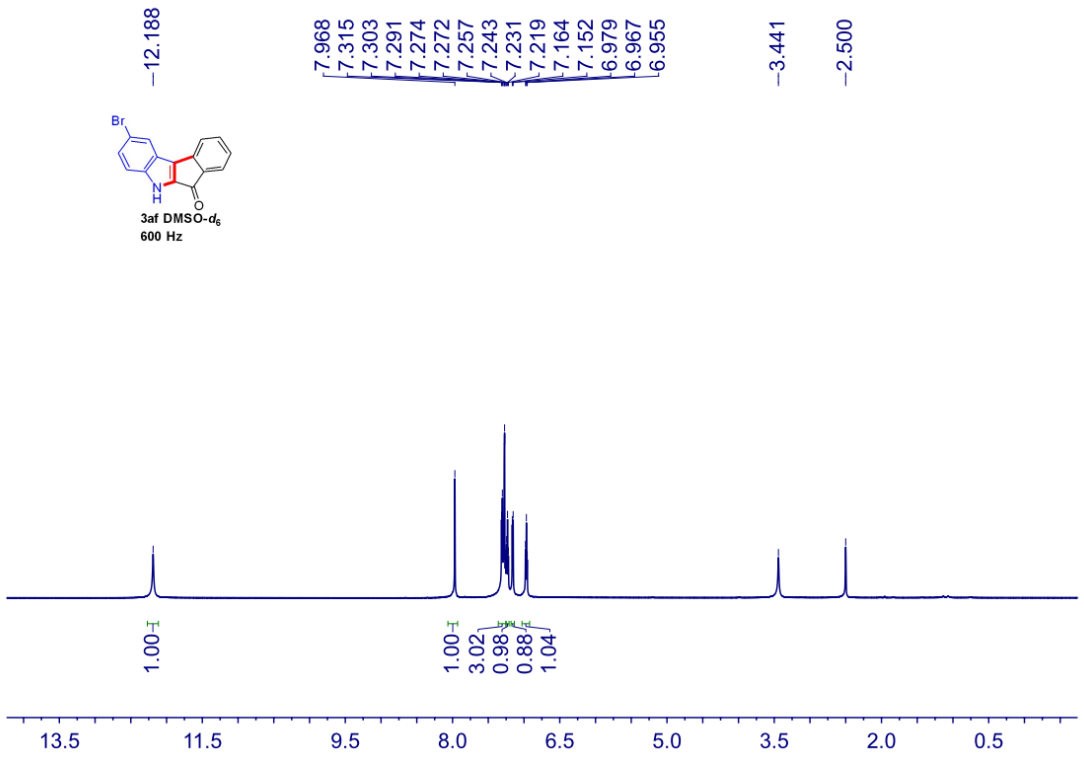
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6.967
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1.00
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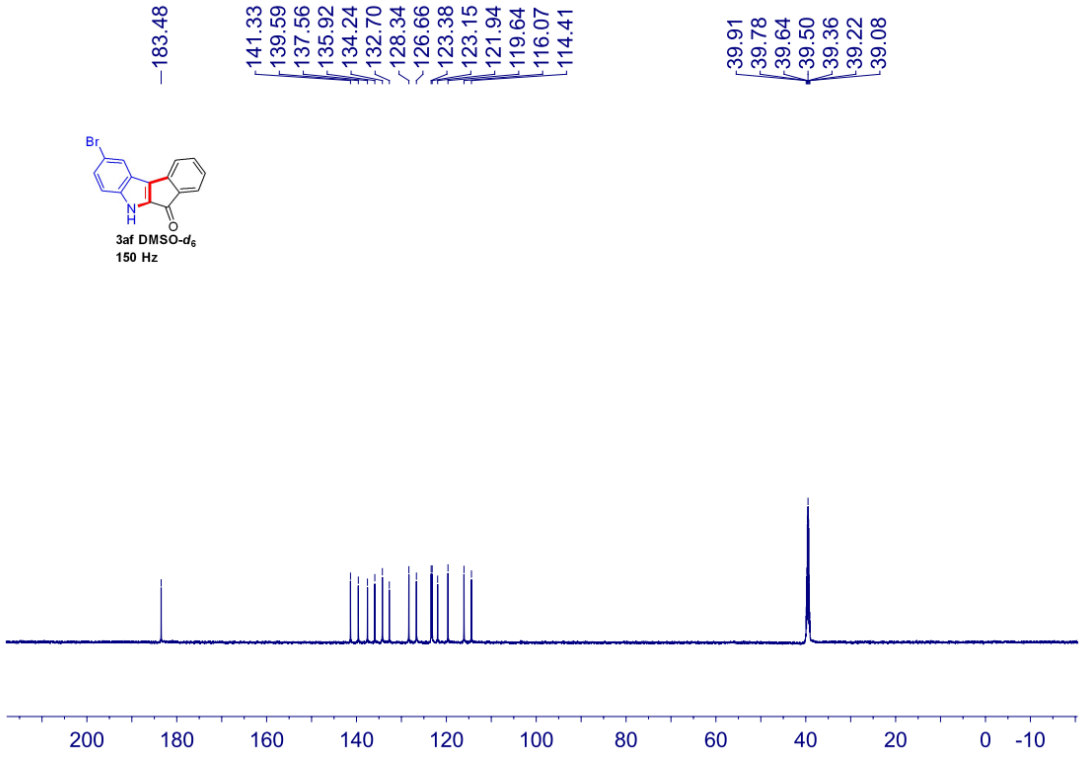
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114.41
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39.78
39.64
39.50
39.36
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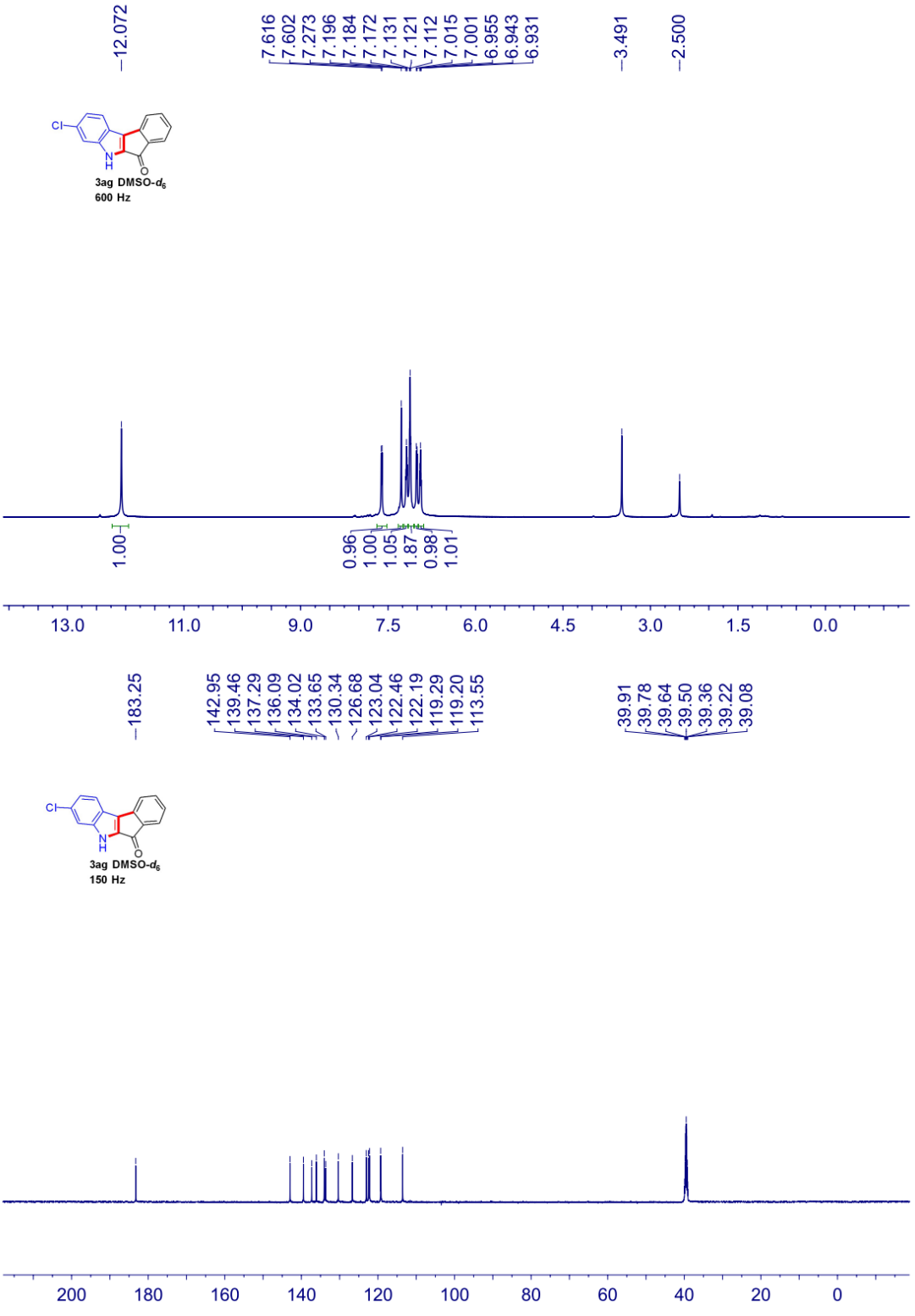
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113.55
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39.78
39.64
39.50
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60
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20
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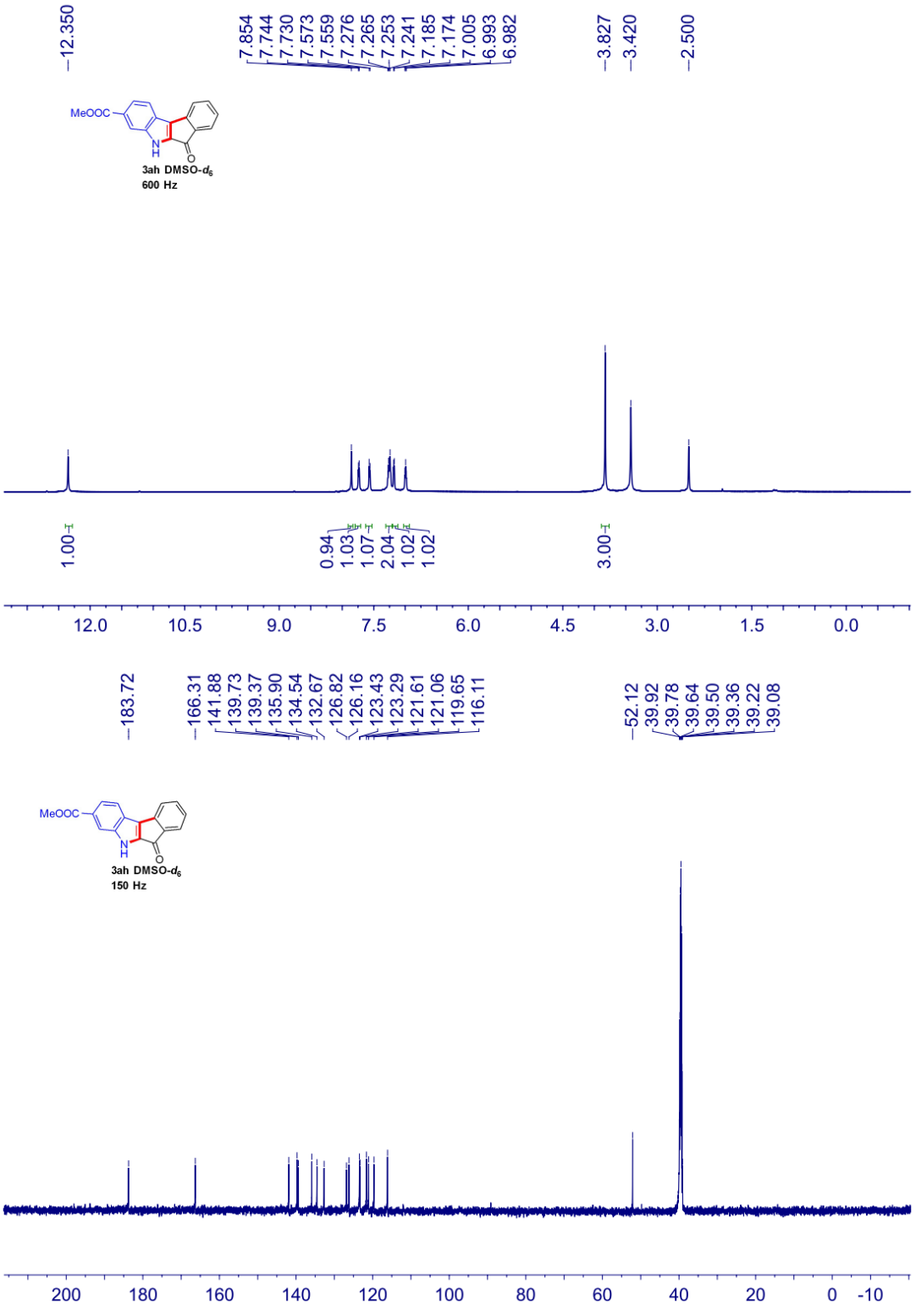
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N
H
O
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2.04
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39.50
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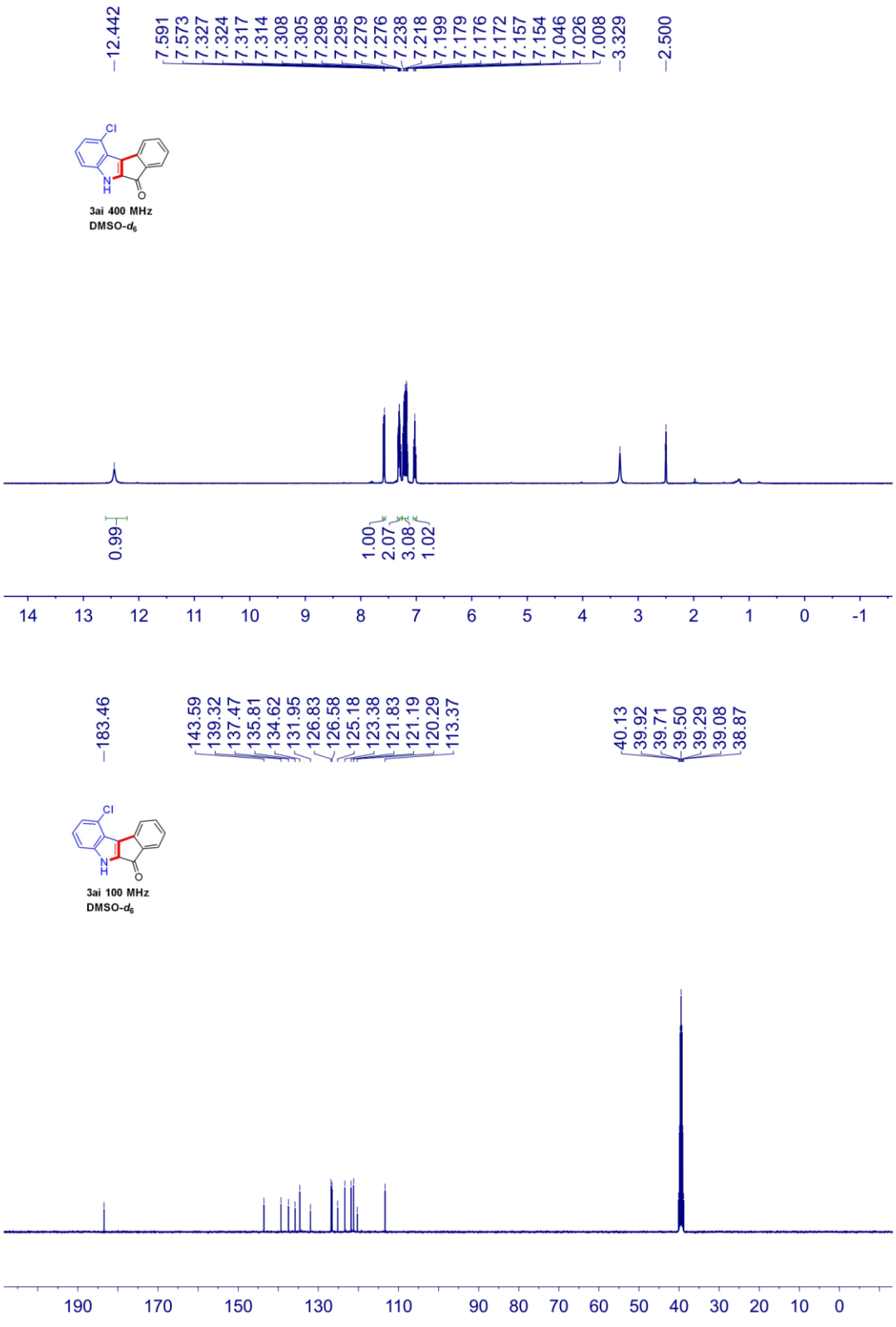
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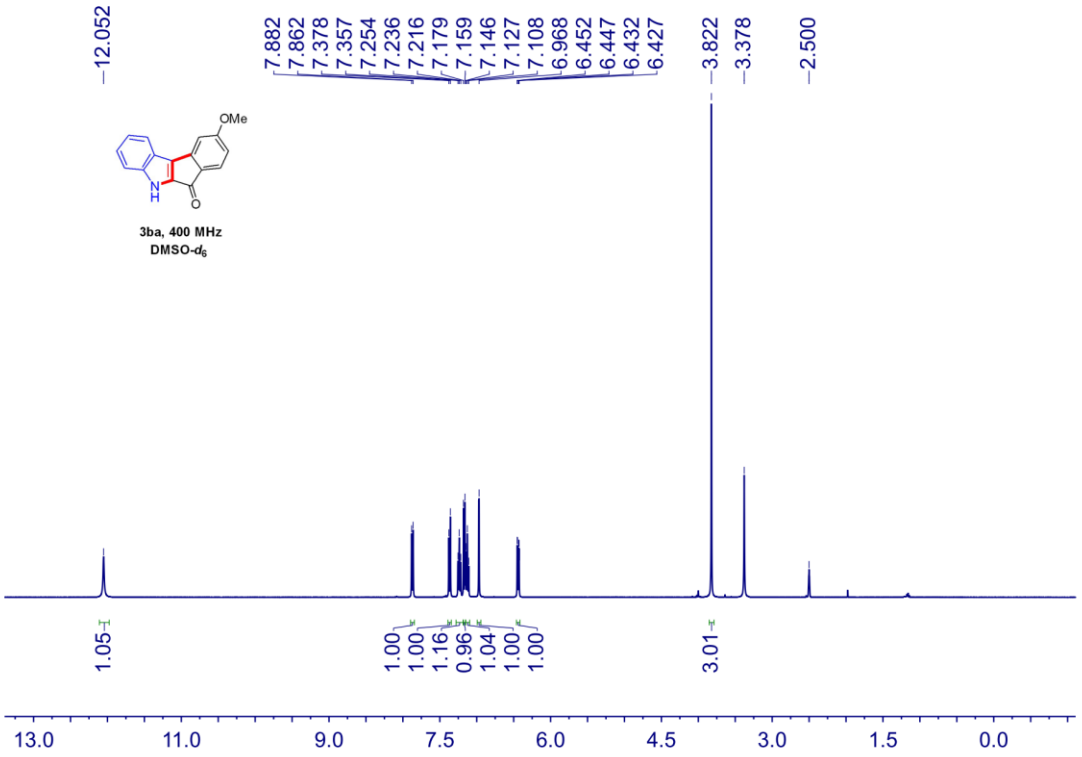
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6.447
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OMe
3ba, 400 MHz
DMSO-d6
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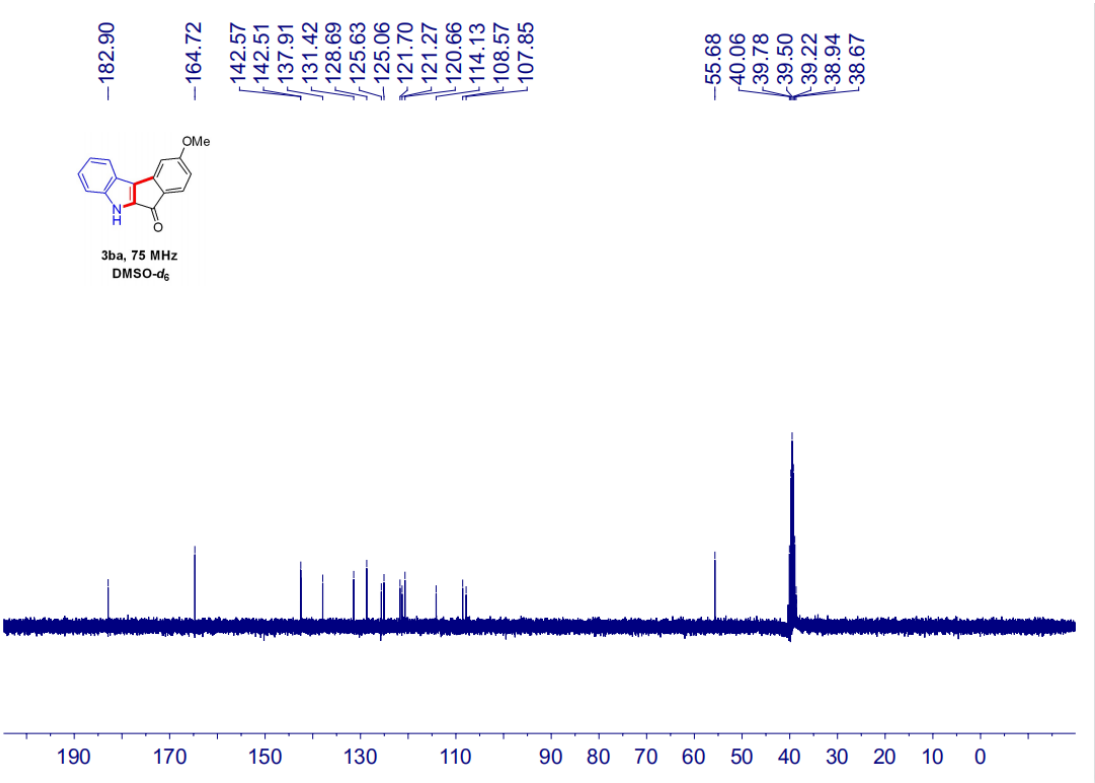
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39.22
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38.67
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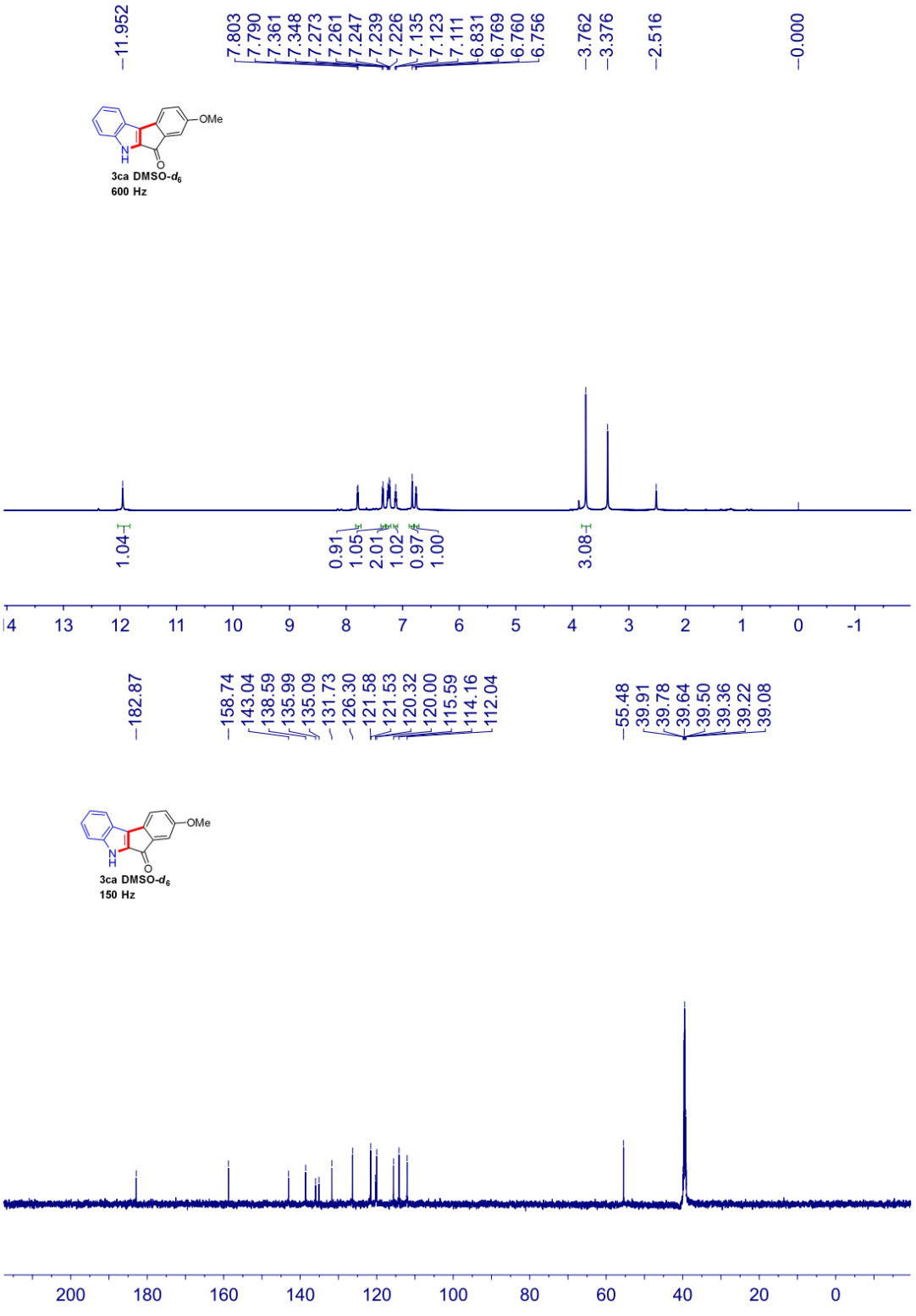
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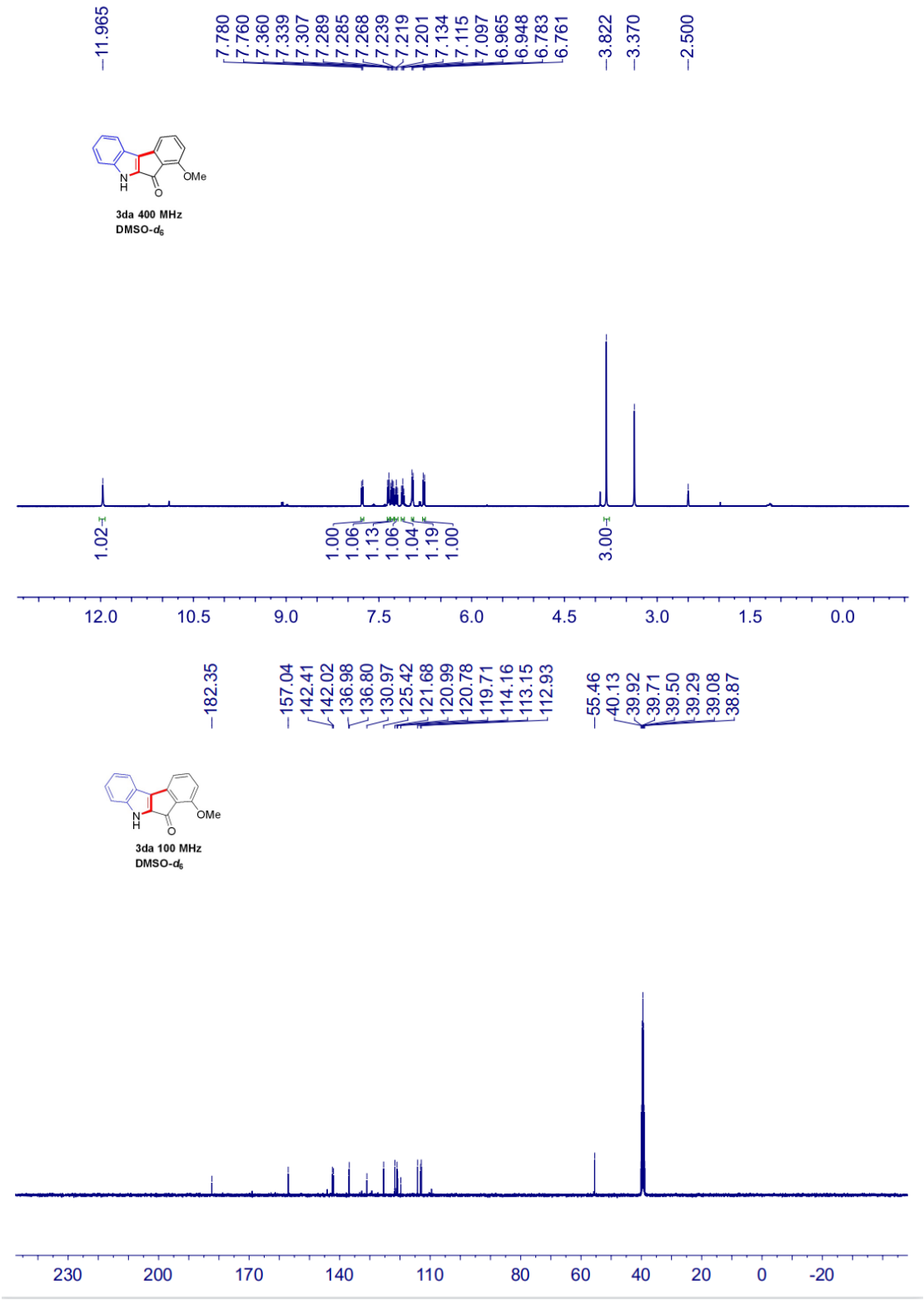
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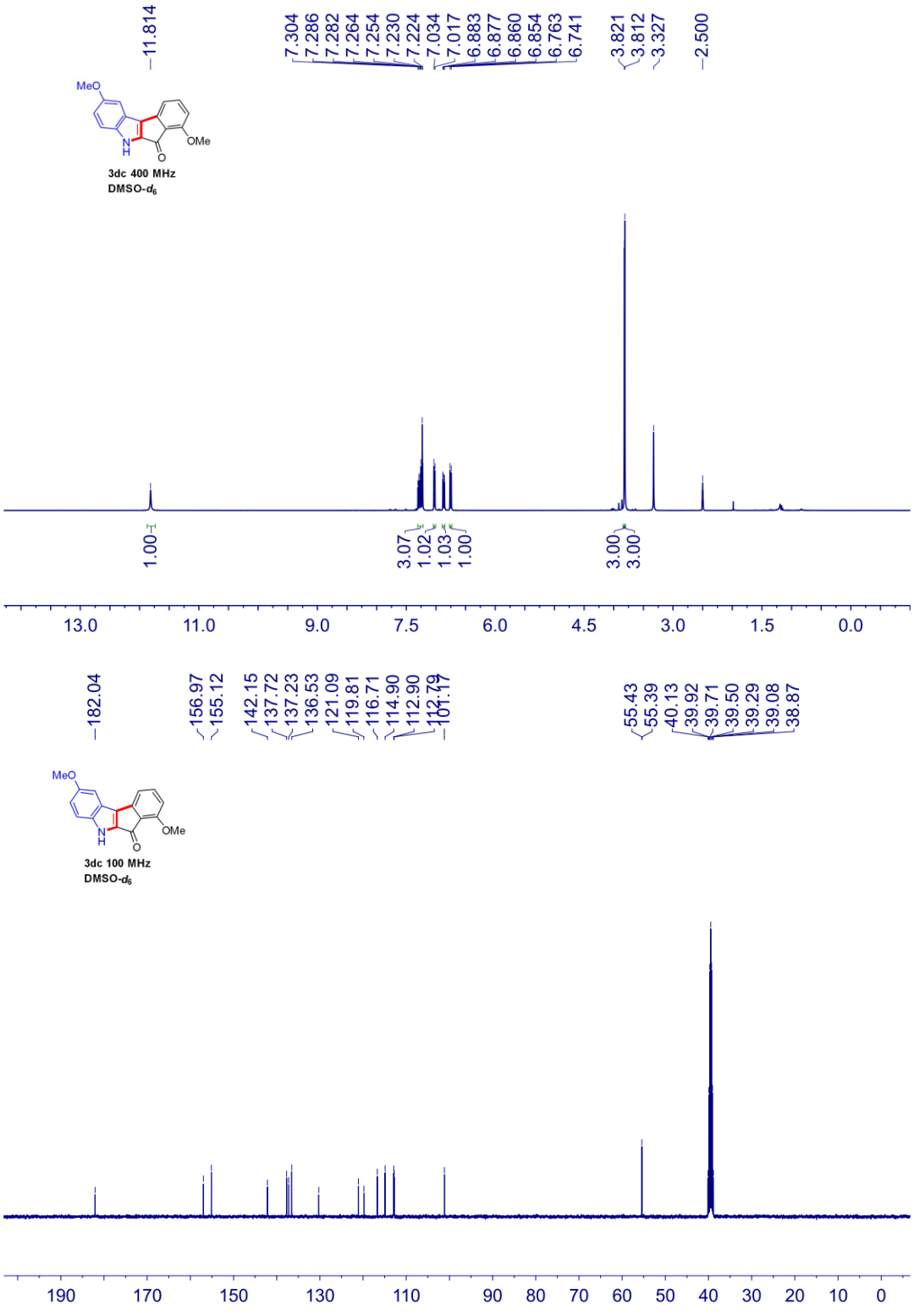
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OMe
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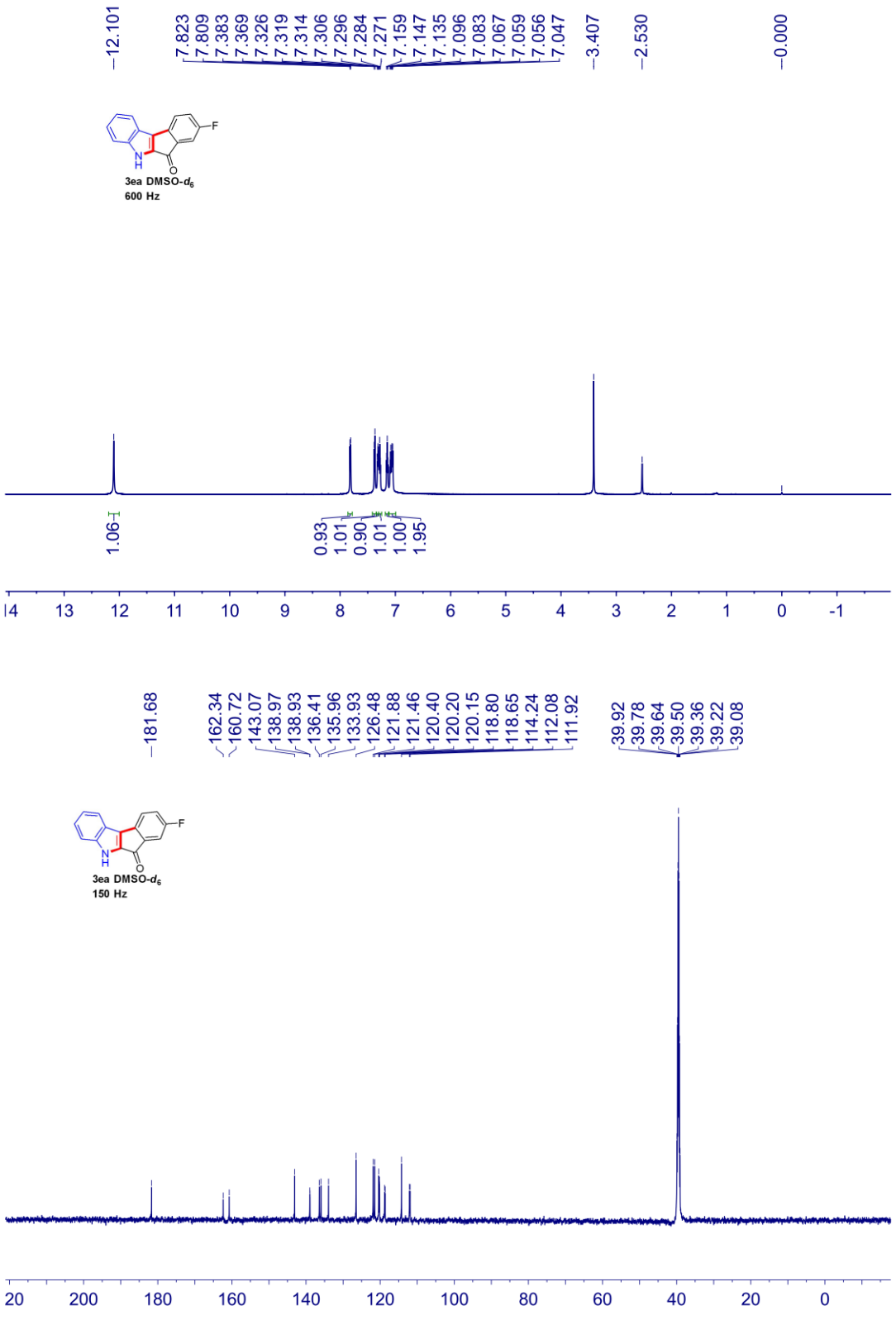
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F
N
H
O
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600 Hz
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0.90
1.01
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1.95
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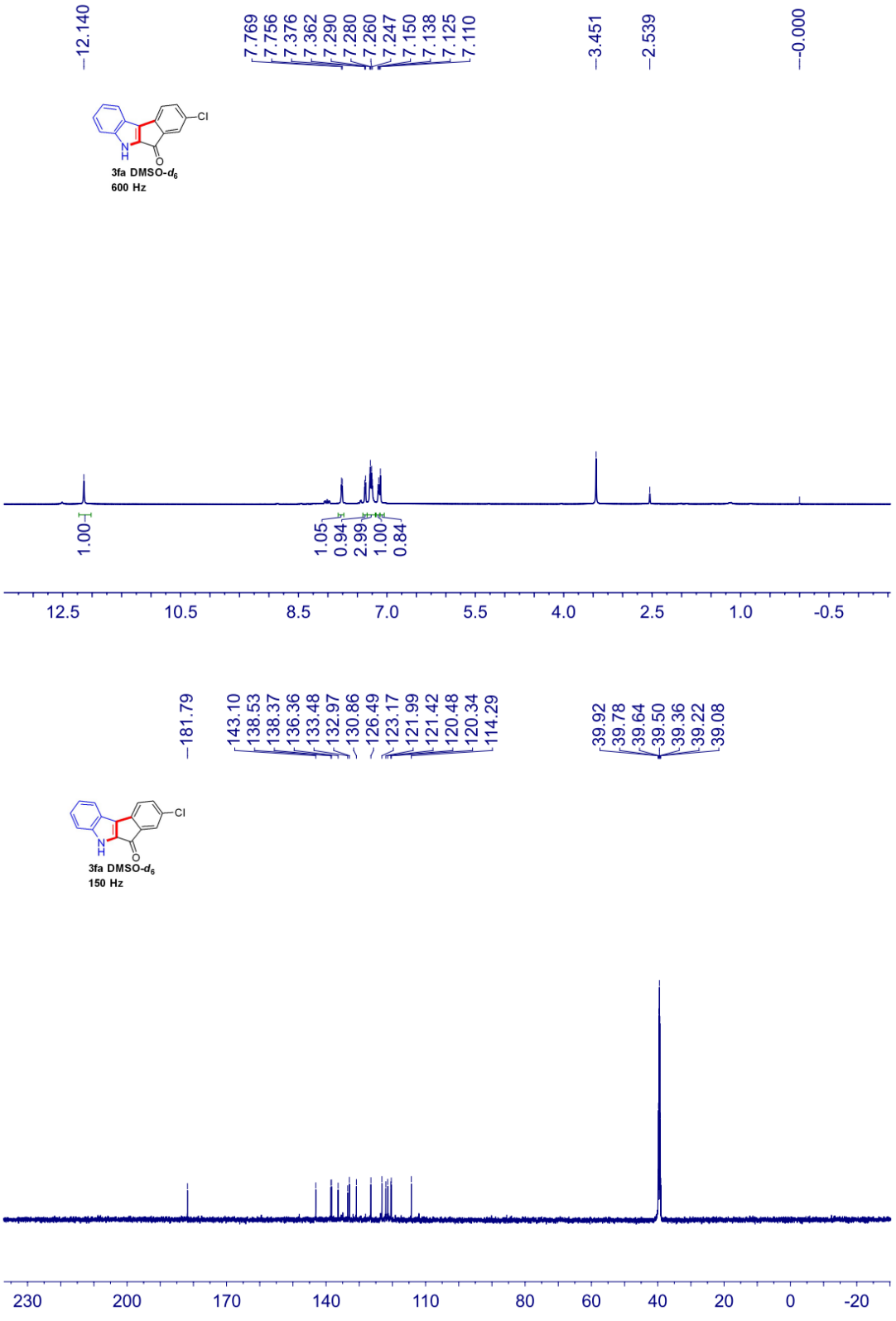
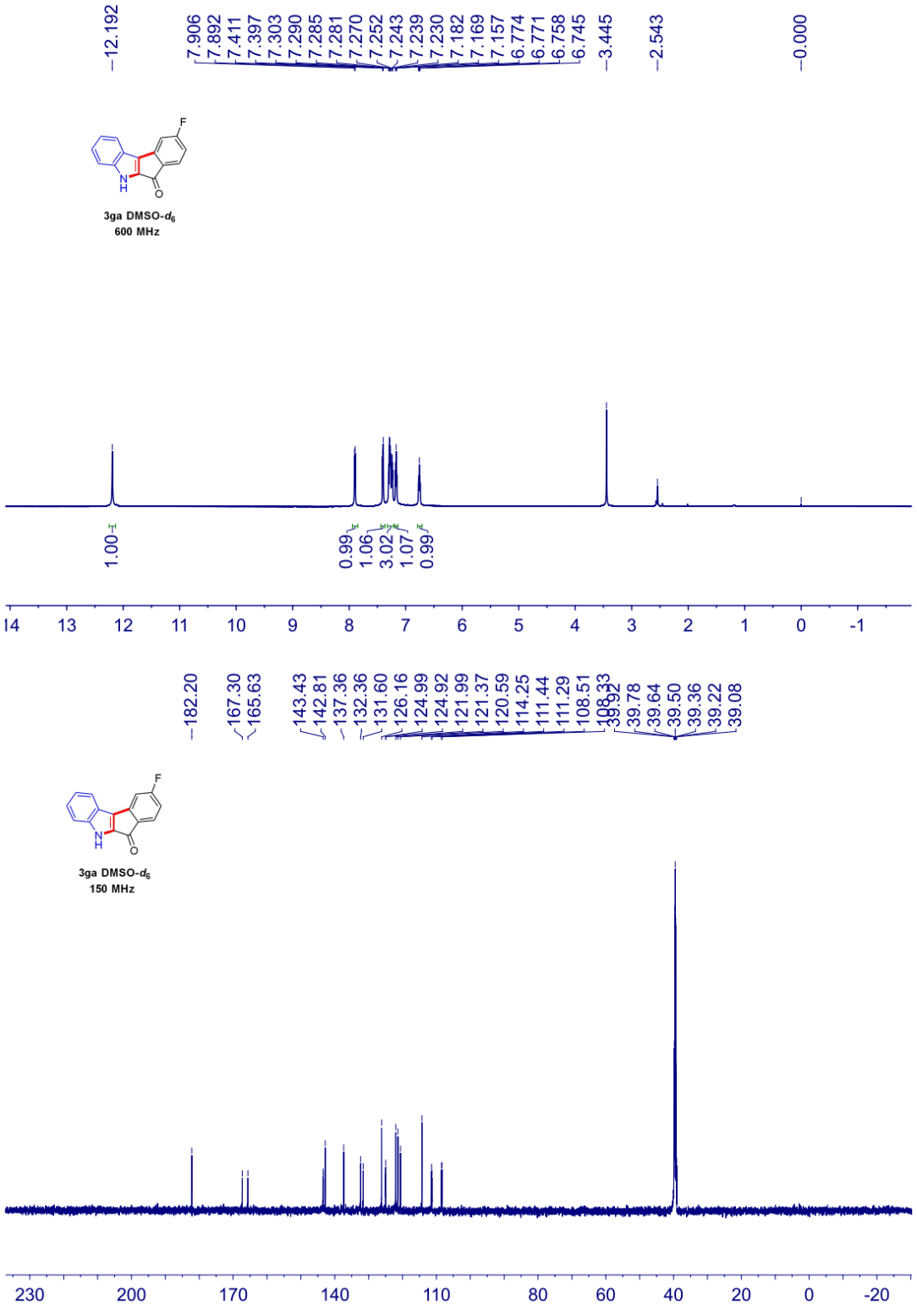
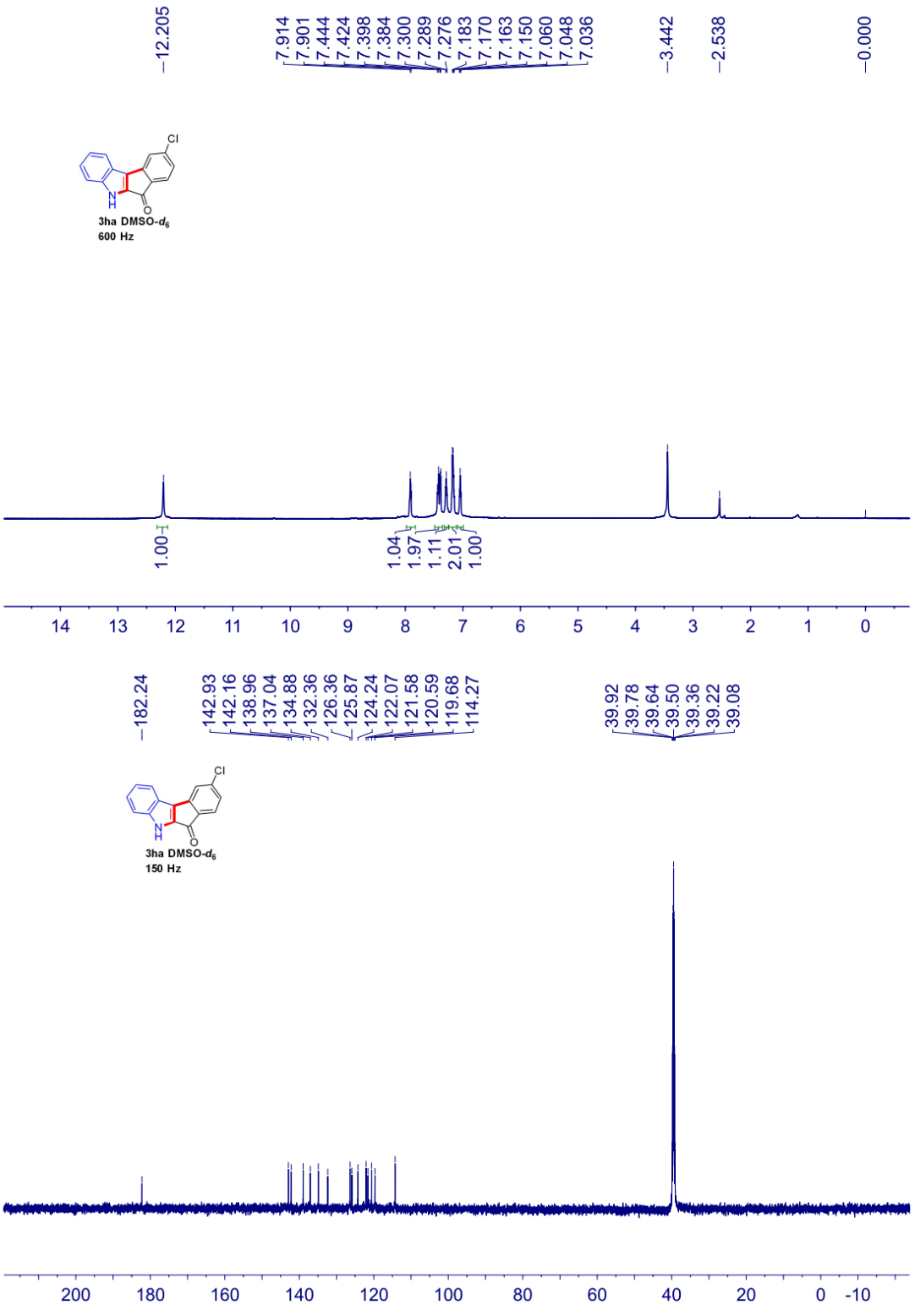
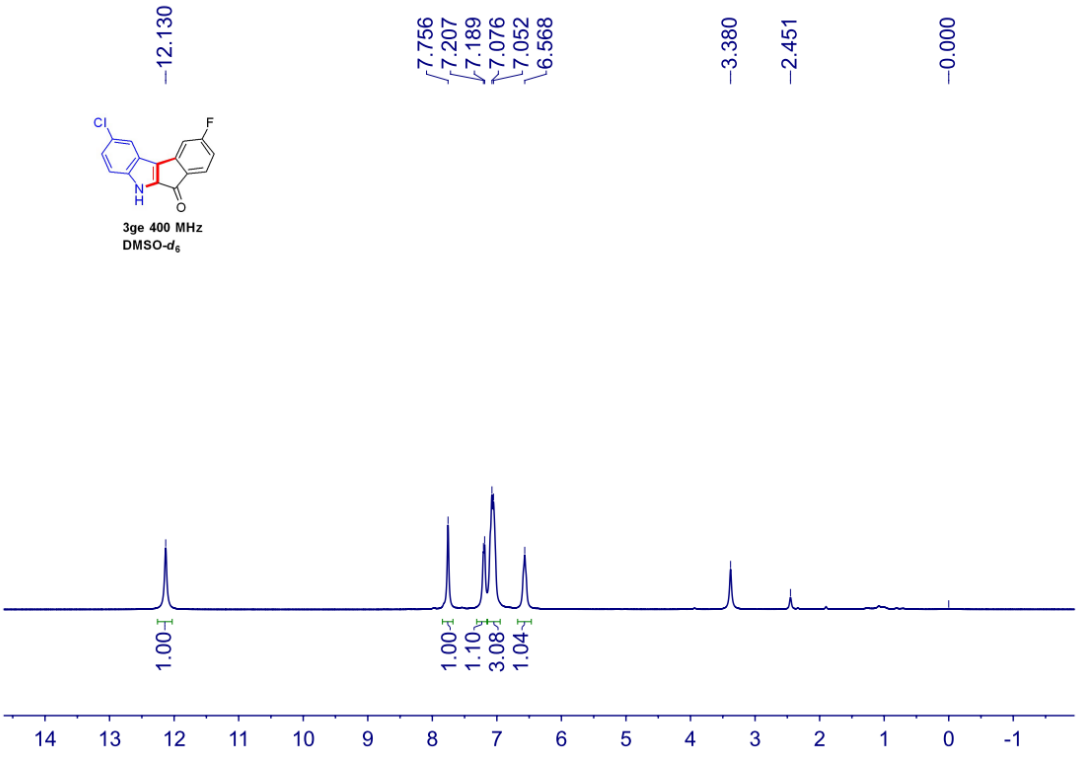
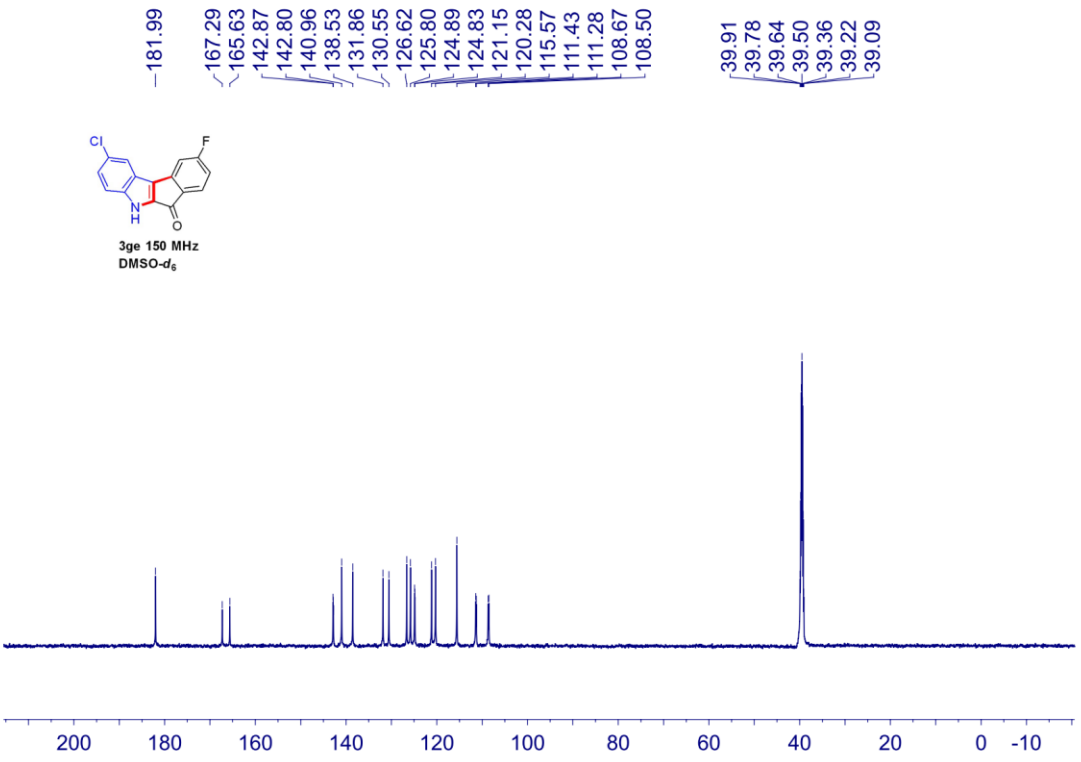
118.80
118.65
114.24
112.08
111.92
39.92
39.78
39.64
39.50
39.36
39.22
39.08
F
N
H
O
3ea DMSO-d6
150 Hz
220 200 180 160 140 120 100 80 60 40 20 0

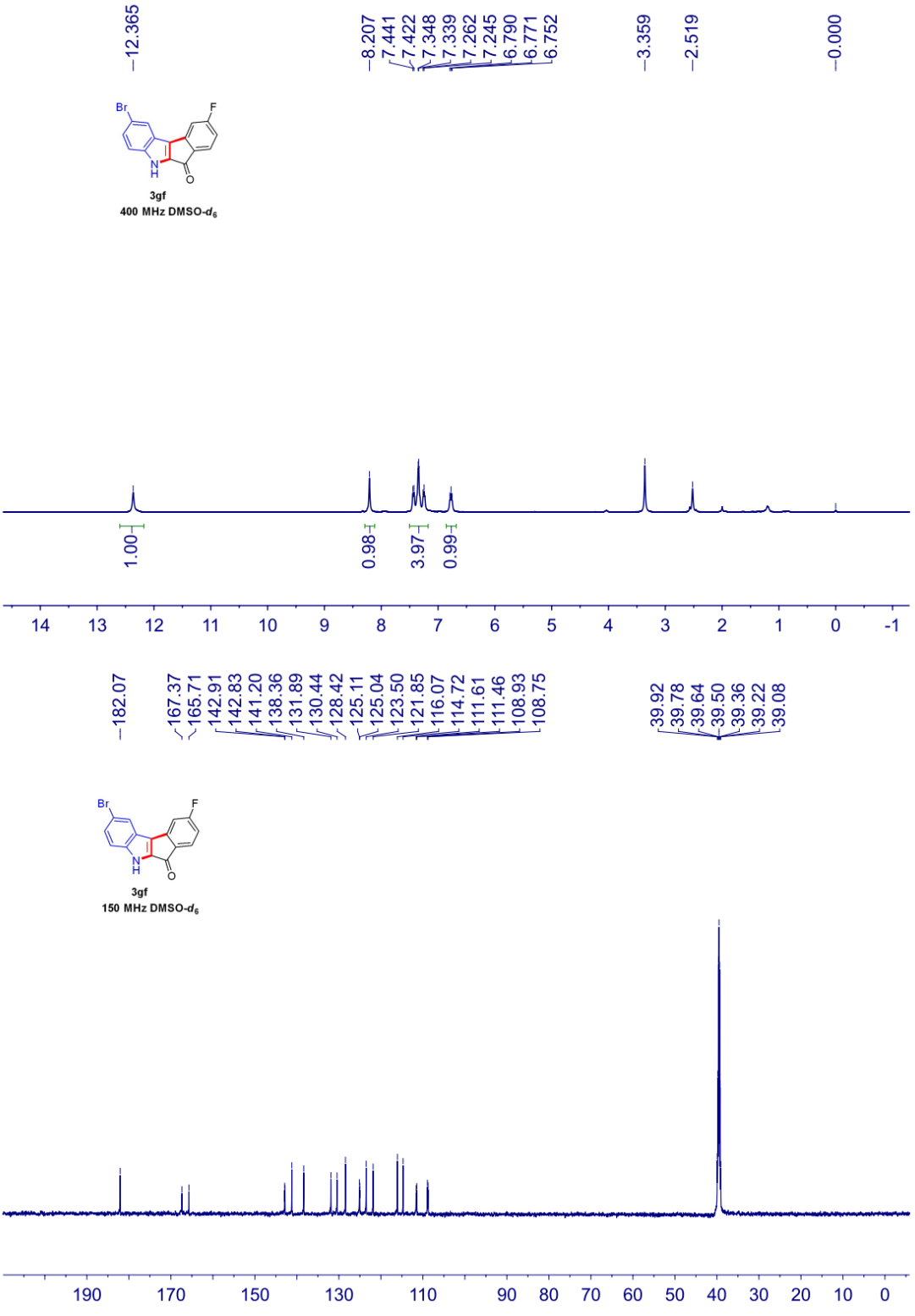

12.140
7.769
7.756
7.376
7.362
7.290
7.280
7.260
7.247
7.150
7.138
7.125
7.110
3.451
2.539
0.000
Cl
O
N
H
3fa DMSO-d6
600 Hz
1.00
1.05
0.94
2.99
1.00
0.84
12.5
10.5
8.5
7.0
5.5
4.0
2.5
1.0
-0.5
181.79
143.10
138.53
138.37
136.36
133.48
132.97
130.86
126.49
123.17
121.99
121.42
120.48
120.34
114.29
39.92
39.78
39.64
39.50
39.36
39.22
39.08
Cl
O
N
H
3fa DMSO-d6
150 Hz
230
200
170
140
110
80
60
40
20
0
-20

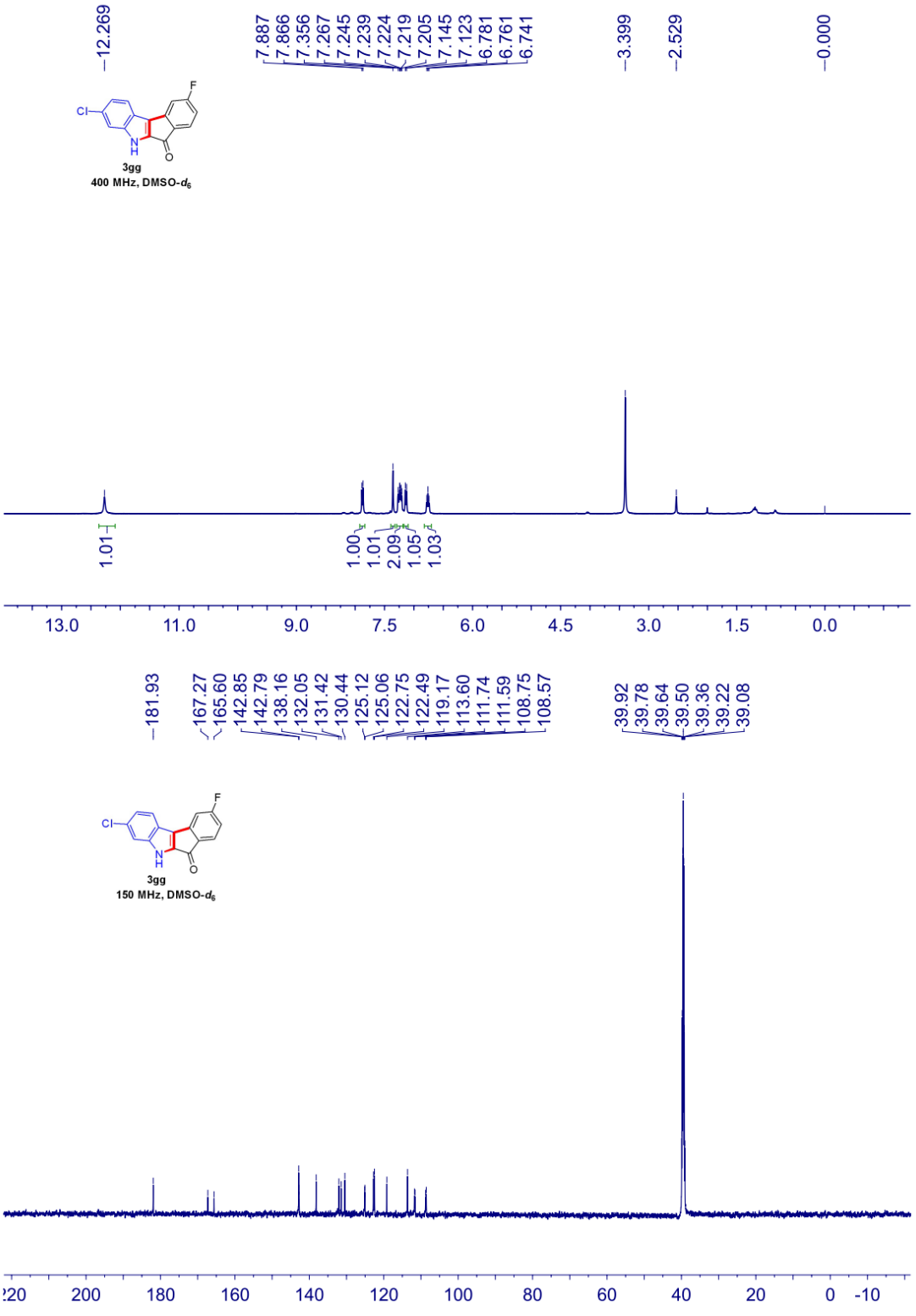

12.192
7.906
7.892
7.411
7.397
7.303
7.290
7.285
7.281
7.270
7.252
7.243
7.239
7.230
7.182
7.169
7.157
6.774
6.771
6.758
6.745
3.445
2.543
0.000
3ga DMSO-d_6
600 MHz
1.00
0.99
1.06
3.02
1.07
0.99
182.20
167.30
165.63
143.43
142.81
137.36
132.36
131.60
126.16
124.99
124.92
121.99
121.37
120.59
114.25
111.44
111.29
108.51
108.33
39.92
39.78
39.64
39.50
39.36
39.22
39.08
3ga DMSO-d_6
150 MHz

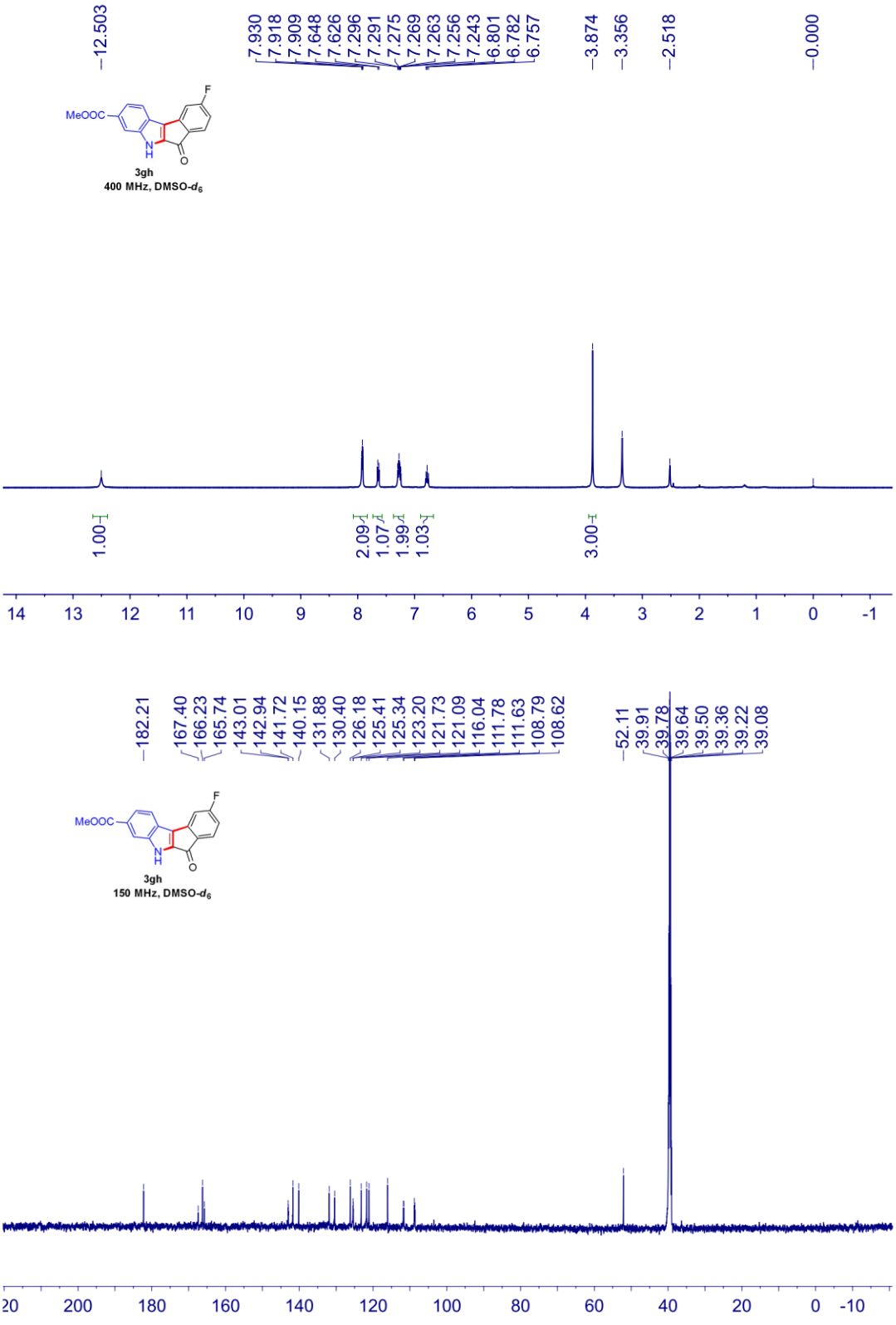

12.205
7.914
7.901
7.444
7.424
7.398
7.384
7.300
7.289
7.276
7.183
7.170
7.163
7.150
7.060
7.048
7.036
3.442
2.538
0.000
Cl
O
3ha DMSO-d_6
600 Hz
1.00
1.04
1.97
1.11
2.01
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
182.24
142.93
142.16
138.96
137.04
134.88
132.36
126.36
125.87
124.24
122.07
121.58
120.59
119.68
114.27
39.92
39.78
39.64
39.50
39.36
39.22
39.08
Cl
O
3ha DMSO-d_6
150 Hz
200 180 160 140 120 100 80 60 40 20 0 -10


12.130
7.756
7.207
7.189
7.076
7.052
6.568
3.380
2.451
0.000
Cl
F
N
H
O
3ge 400 MHz
DMSO-d_6
1.00
1.00
1.10
3.08
1.04
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1

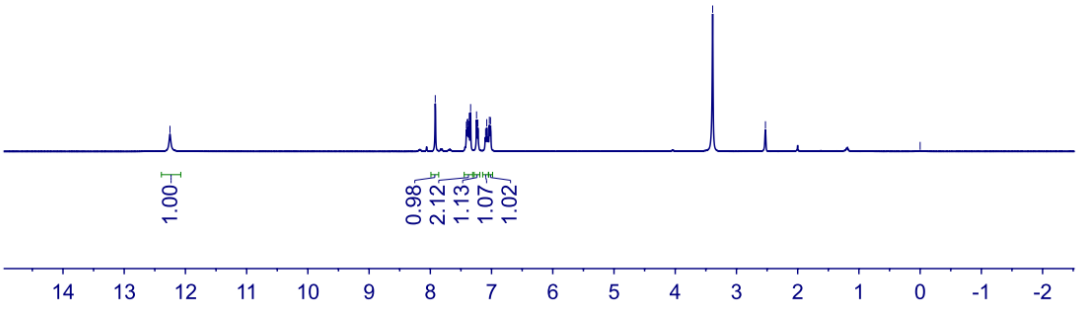

181.99
167.29
165.63
142.87
142.80
140.96
138.53
131.86
130.55
126.62
125.80
124.89
124.83
121.15
120.28
115.57
111.43
111.28
108.67
108.50
39.91
39.78
39.64
39.50
39.36
39.22
39.09
Cl
F
N
H
O
3ge 150 MHz
DMSO-d_6
200 180 160 140 120 100 80 60 40 20 0 -10

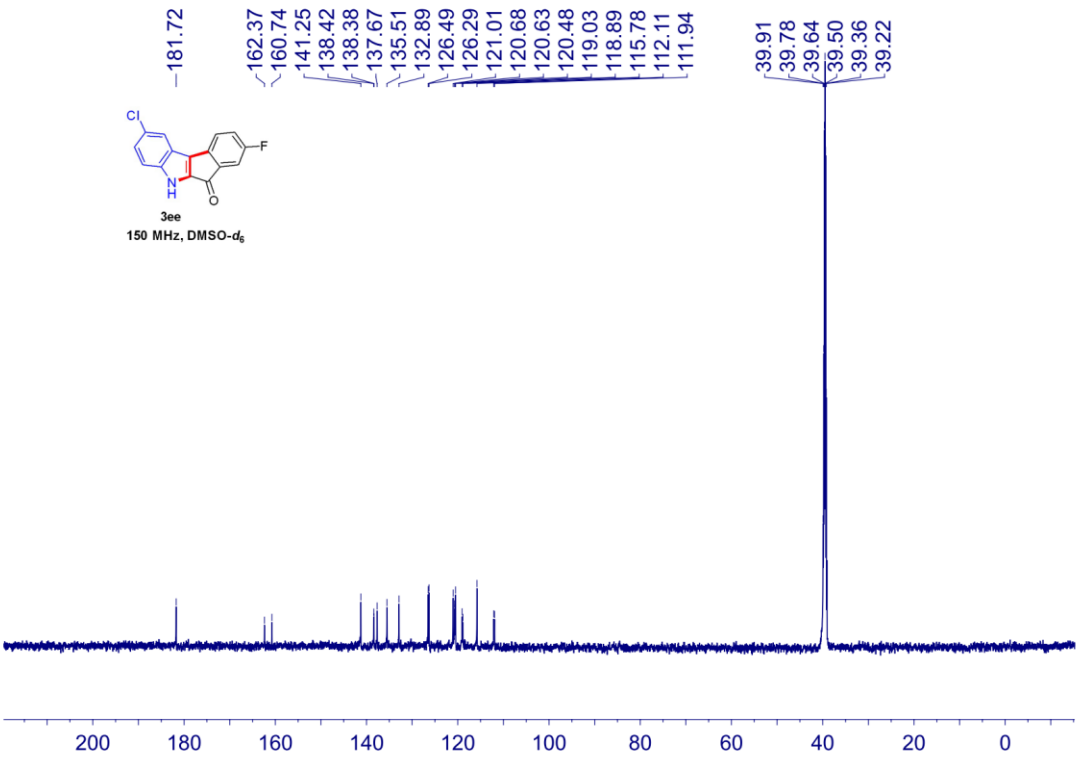

12.365
8.207
7.441
7.422
7.348
7.339
7.262
7.245
6.790
6.771
6.752
3.359
2.519
0.000
Br
F
N
H
O
3gf
400 MHz DMSO-d_6
1.00
0.98
3.97
0.99
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
182.07
167.37
165.71
142.91
142.83
141.20
138.36
131.89
130.44
128.42
125.11
125.04
123.50
121.85
116.07
114.72
111.61
111.46
108.93
108.75
39.92
39.78
39.64
39.50
39.36
39.22
39.08
3gf
150 MHz DMSO-d_6
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

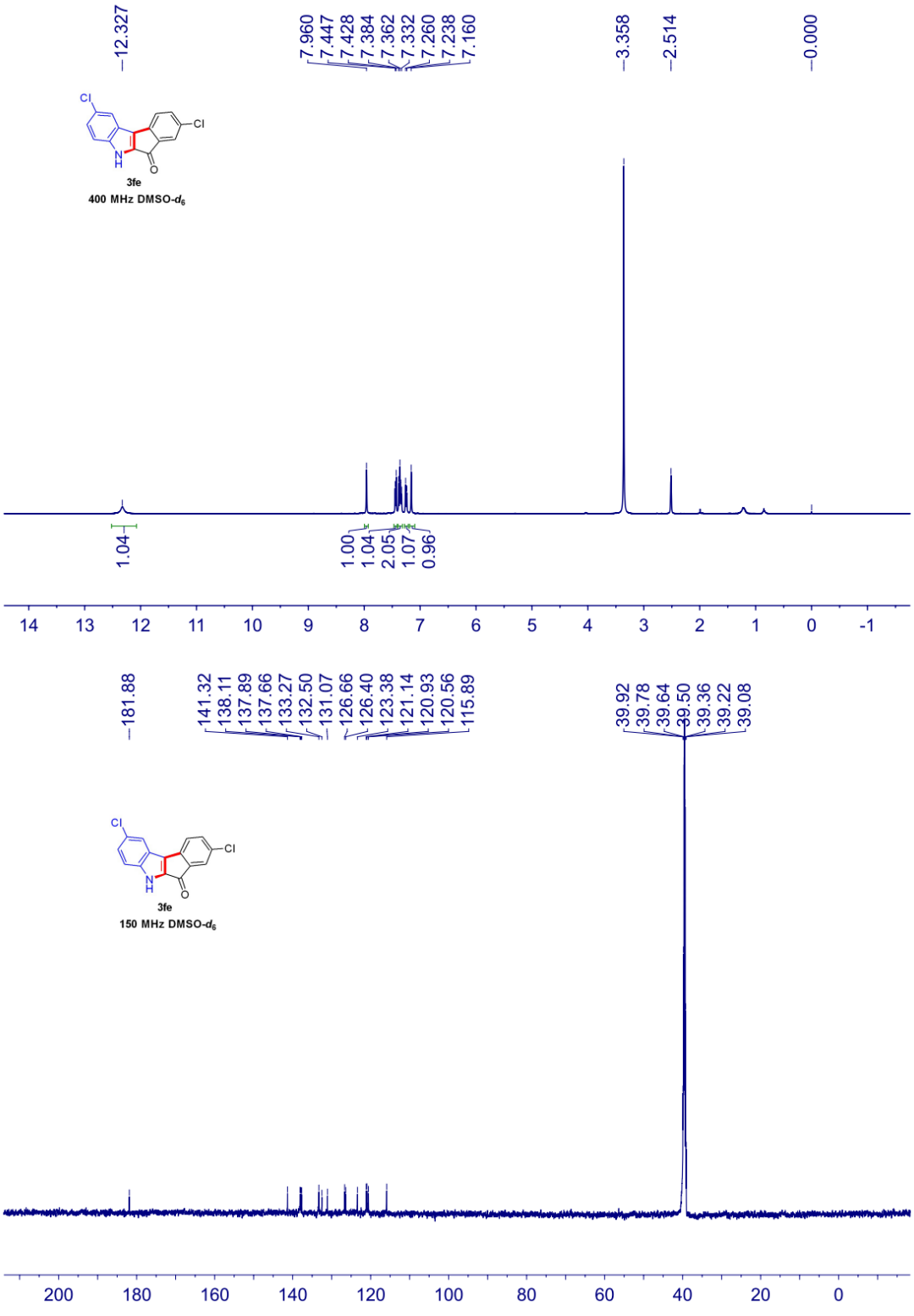

12.269
7.887
7.866
7.356
7.267
7.245
7.239
7.224
7.219
7.205
7.145
7.123
6.781
6.761
6.741
3.399
2.529
0.000
Cl
F
N
H
O
3gg
400 MHz, DMSO-d_6
1.01
1.00
1.01
2.09
1.05
1.03
13.0
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
181.93
167.27
165.60
142.85
142.79
138.16
132.05
131.42
130.44
125.12
125.06
122.75
122.49
119.17
113.60
111.74
111.59
108.75
108.57
39.92
39.78
39.64
39.50
39.36
39.22
39.08
3gg
150 MHz, DMSO-d_6
220
200
180
160
140
120
100
80
60
40
20
0
-10

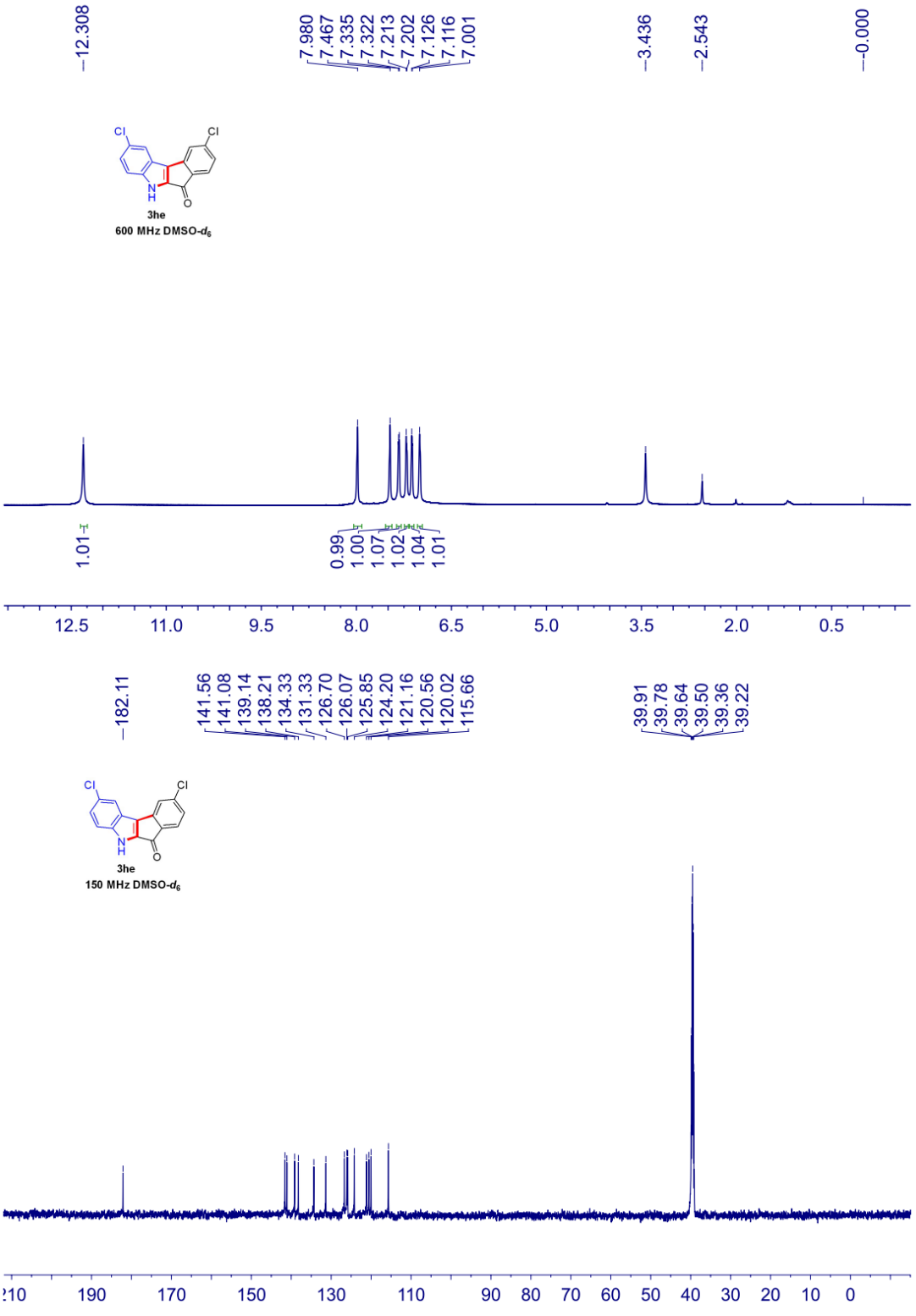

12.503
7.930
7.918
7.909
7.648
7.626
7.296
7.291
7.275
7.269
7.263
7.256
7.243
6.801
6.782
6.757
3.874
3.356
2.518
0.000
MeOOC
F
O
H
N
3gh
400 MHz, DMSO-d6
1.00
2.09
1.07
1.99
1.03
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
182.21
167.40
166.23
165.74
143.01
142.94
141.72
140.15
131.88
130.40
126.18
125.41
125.34
123.20
121.73
121.09
116.04
111.78
111.63
108.79
108.62
52.11
39.91
39.78
39.64
39.50
39.36
39.22
39.08
3gh
150 MHz, DMSO-d6
220 200 180 160 140 120 100 80 60 40 20 0 -10

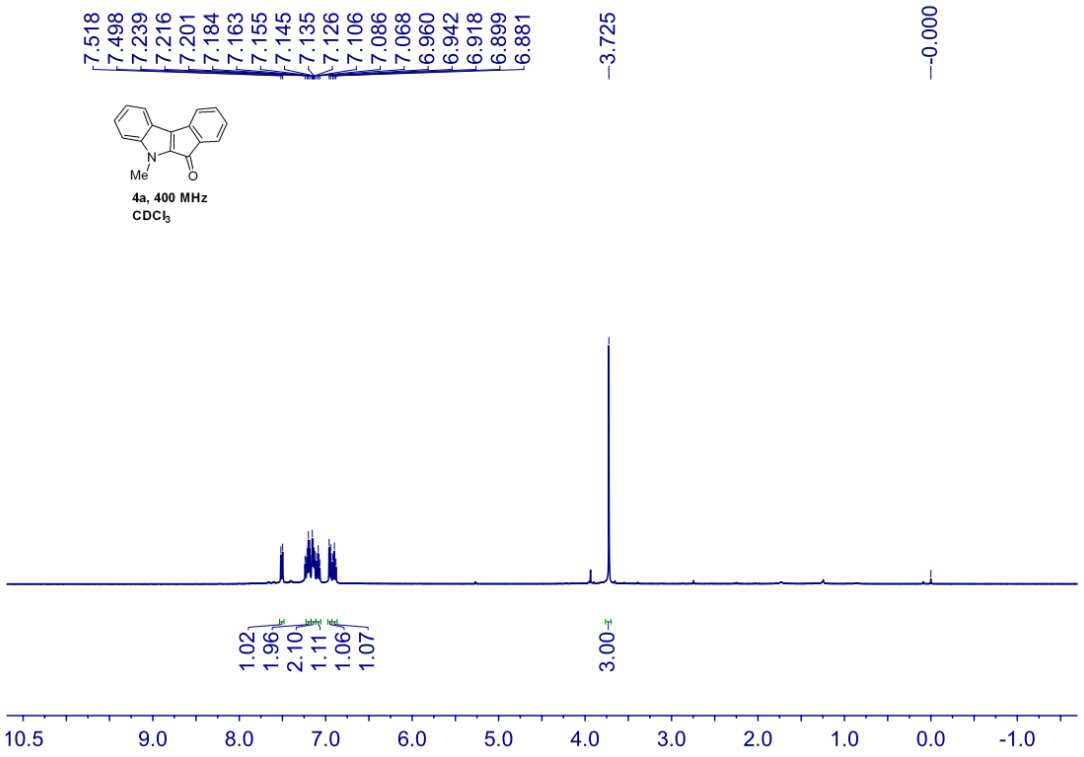

12.252
7.919
7.411
7.399
7.391
7.379
7.364
7.342
7.245
7.223
7.098
7.079
7.054
7.036
7.017
3.389
2.527
0.000
Cl
F
N
H
O
3ee
400 MHz, DMSO-d_6

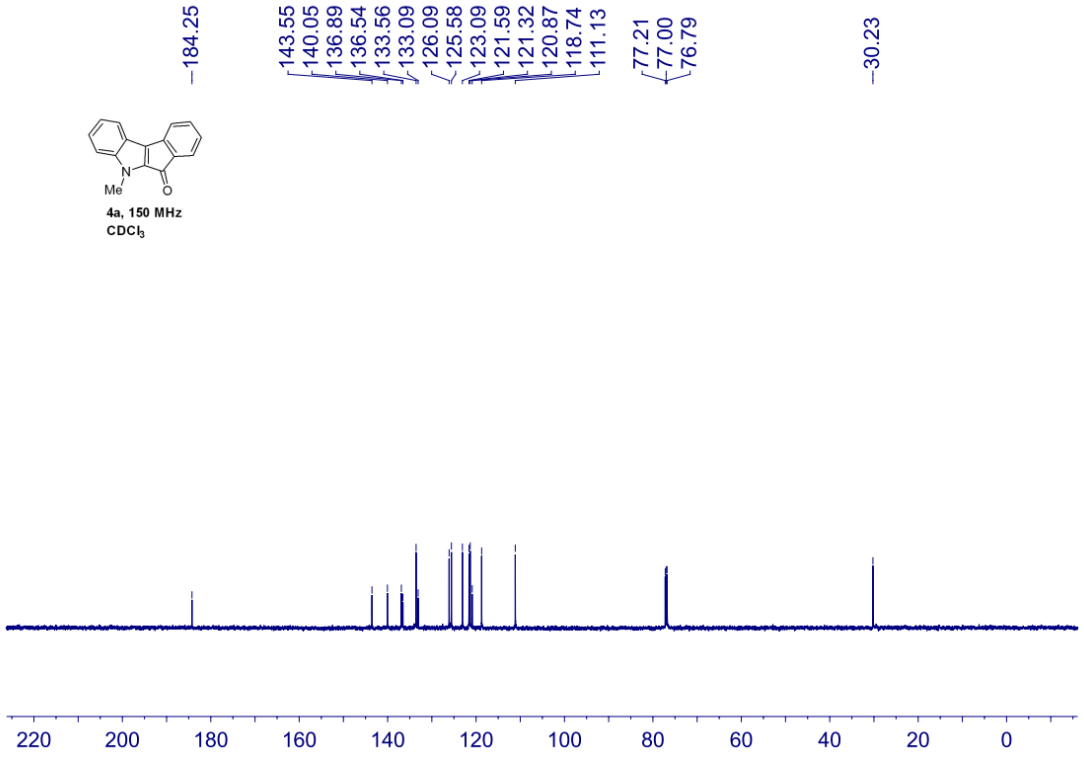

1.00
0.98
2.12
1.13
1.07
1.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2

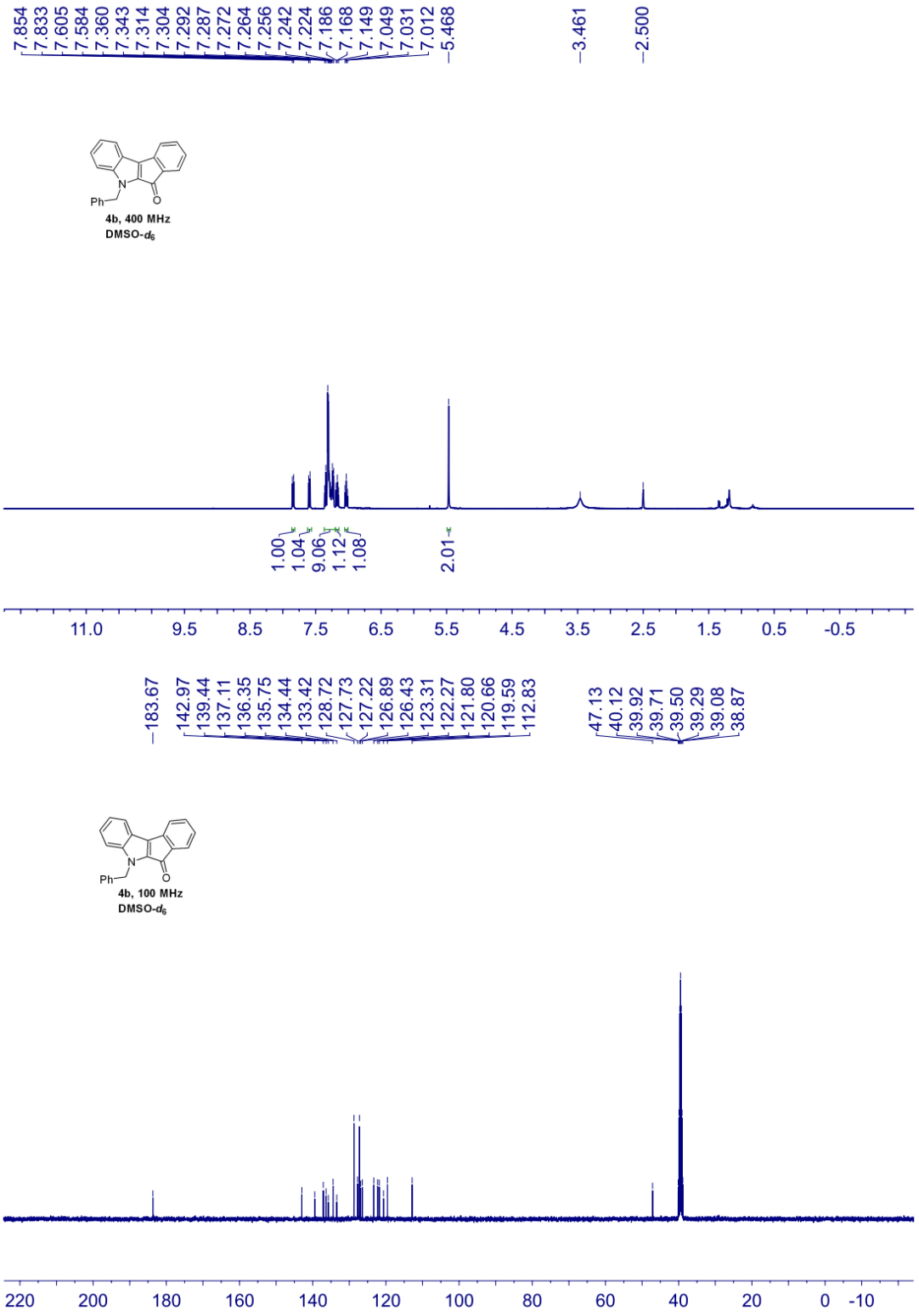

181.72
162.37
160.74
141.25
138.42
138.38
137.67
135.51
132.89
126.49
126.29
121.01
120.68
120.63
120.48
119.03
118.89
115.78
112.11
111.94
39.91
39.78
39.64
39.50
39.36
39.22
Cl
F
N
H
O
3ee
150 MHz, DMSO-d_6
200
180
160
140
120
100
80
60
40
20
0

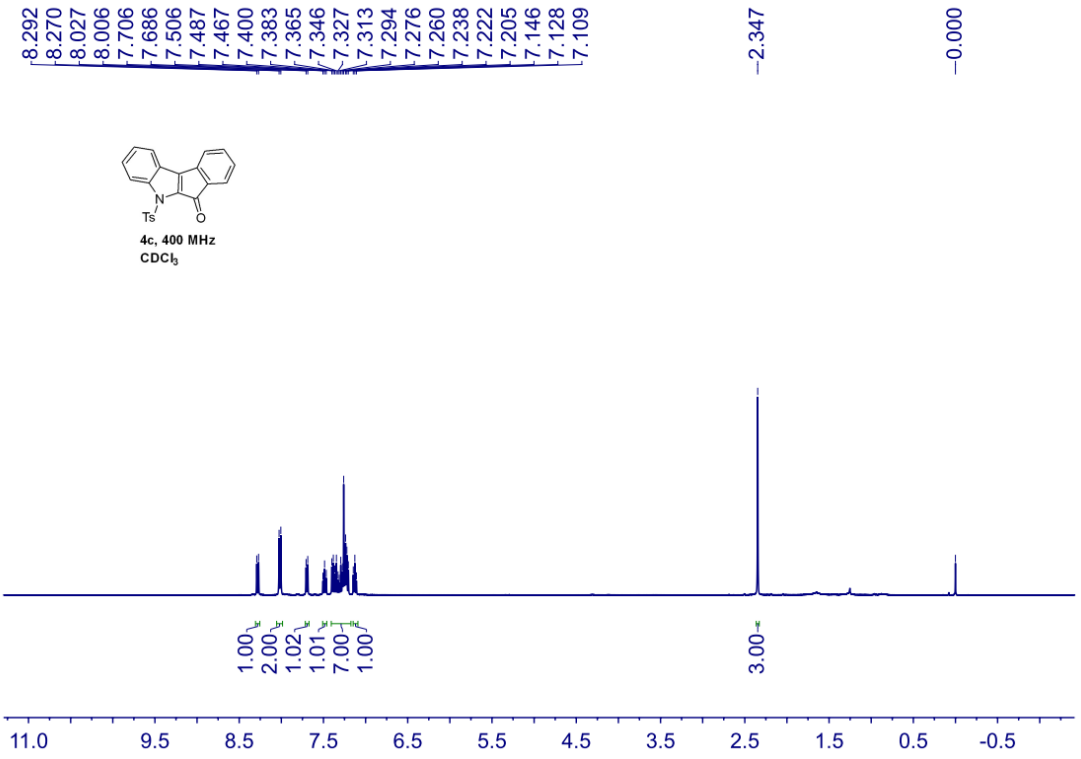

12.327
7.960
7.447
7.428
7.384
7.362
7.332
7.260
7.238
7.160
3.358
2.514
0.000
Cl
Cl
N
H
O
3fe
400 MHz DMSO-d_6
1.04
1.00
1.04
2.05
1.07
0.96
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
181.88
141.32
138.11
137.89
137.66
133.27
132.50
131.07
126.66
126.40
123.38
121.14
120.93
120.56
115.89
39.92
39.78
39.64
39.50
39.36
39.22
39.08
Cl
Cl
N
H
O
3fe
150 MHz DMSO-d_6
200 180 160 140 120 100 80 60 40 20 0

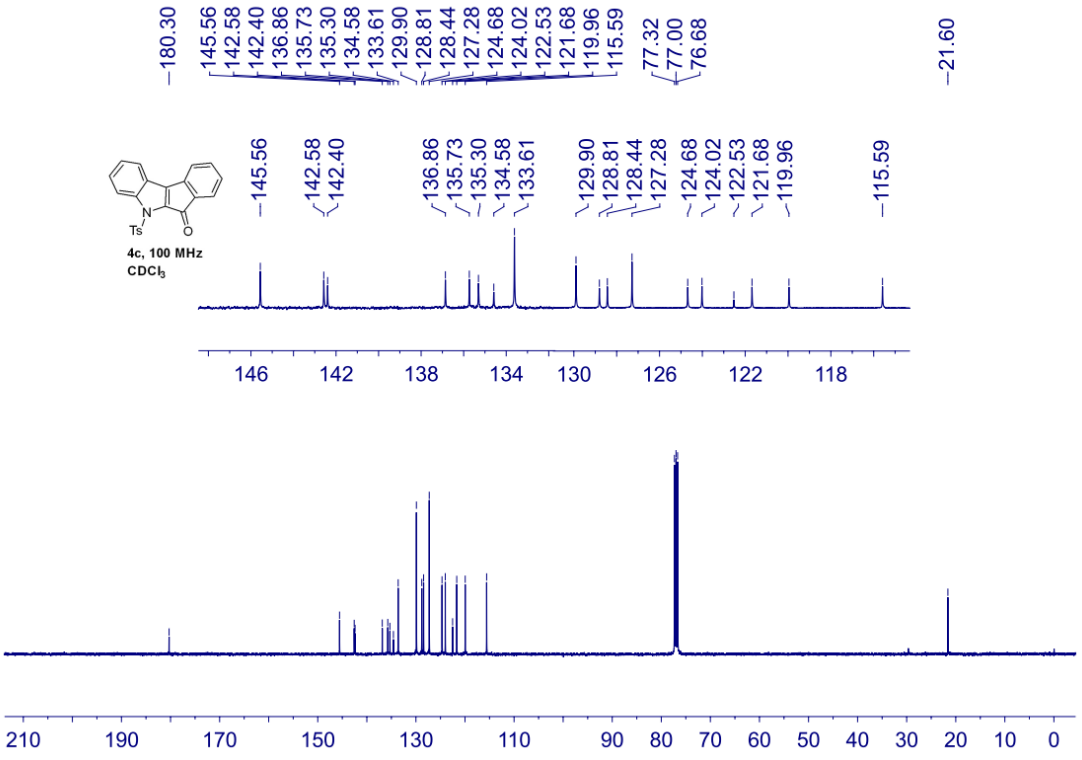

12.308
7.980
7.467
7.335
7.322
7.213
7.202
7.126
7.116
7.001
3.436
2.543
0.000
Cl
Cl
N
H
O
3he
600 MHz DMSO-d_6
1.01
0.99
1.00
1.07
1.02
1.04
1.01
12.5
11.0
9.5
8.0
6.5
5.0
3.5
2.0
0.5
182.11
141.56
141.08
139.14
138.21
134.33
131.33
126.70
126.07
125.85
124.20
121.16
120.56
120.02
115.66
39.91
39.78
39.64
39.50
39.36
39.22
3he
150 MHz DMSO-d_6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

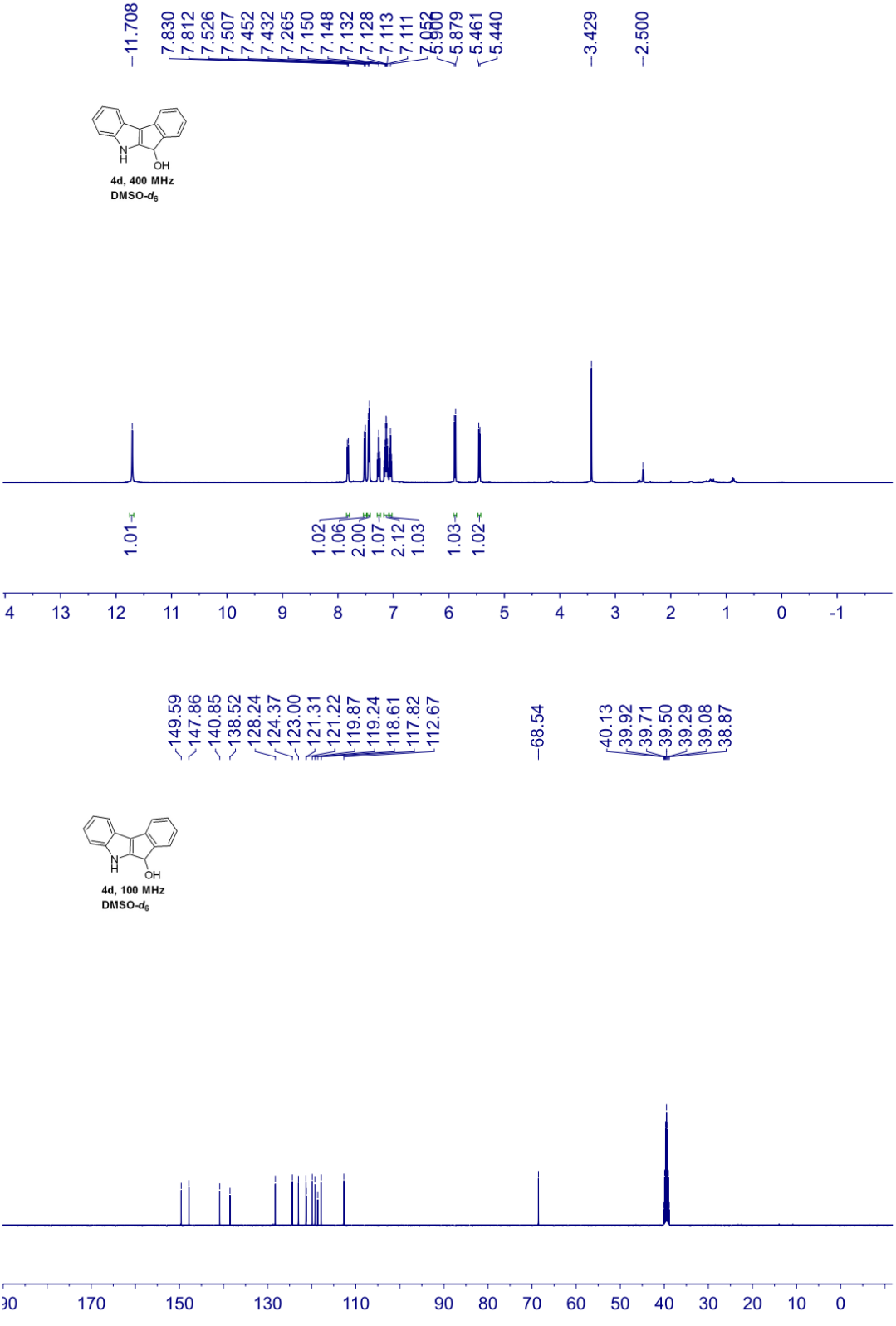

7.518
7.498
7.239
7.216
7.201
7.184
7.163
7.155
7.145
7.135
7.126
7.106
7.086
7.068
6.960
6.942
6.918
6.899
6.881
3.725
0.000
Me
O
4a, 400 MHz
CDCl3
1.02
1.96
2.10
1.11
1.06
1.07
3.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

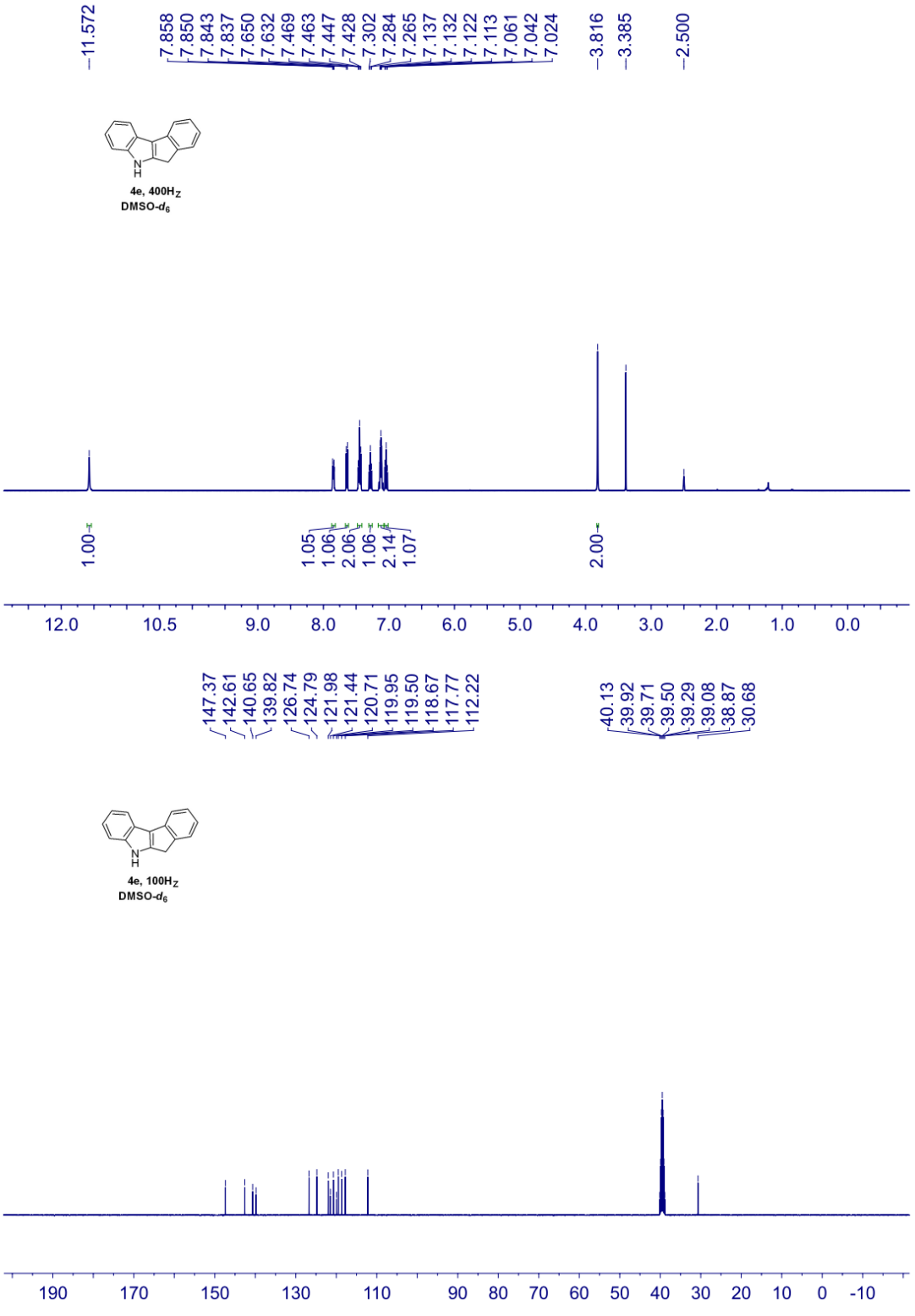

184.25
143.55
140.05
136.89
136.54
133.56
133.09
126.09
125.58
123.09
121.59
121.32
120.87
118.74
111.13
77.21
77.00
76.79
30.23
Me
O
4a, 150 MHz
CDCl3
220
200
180
160
140
120
100
80
60
40
20
0

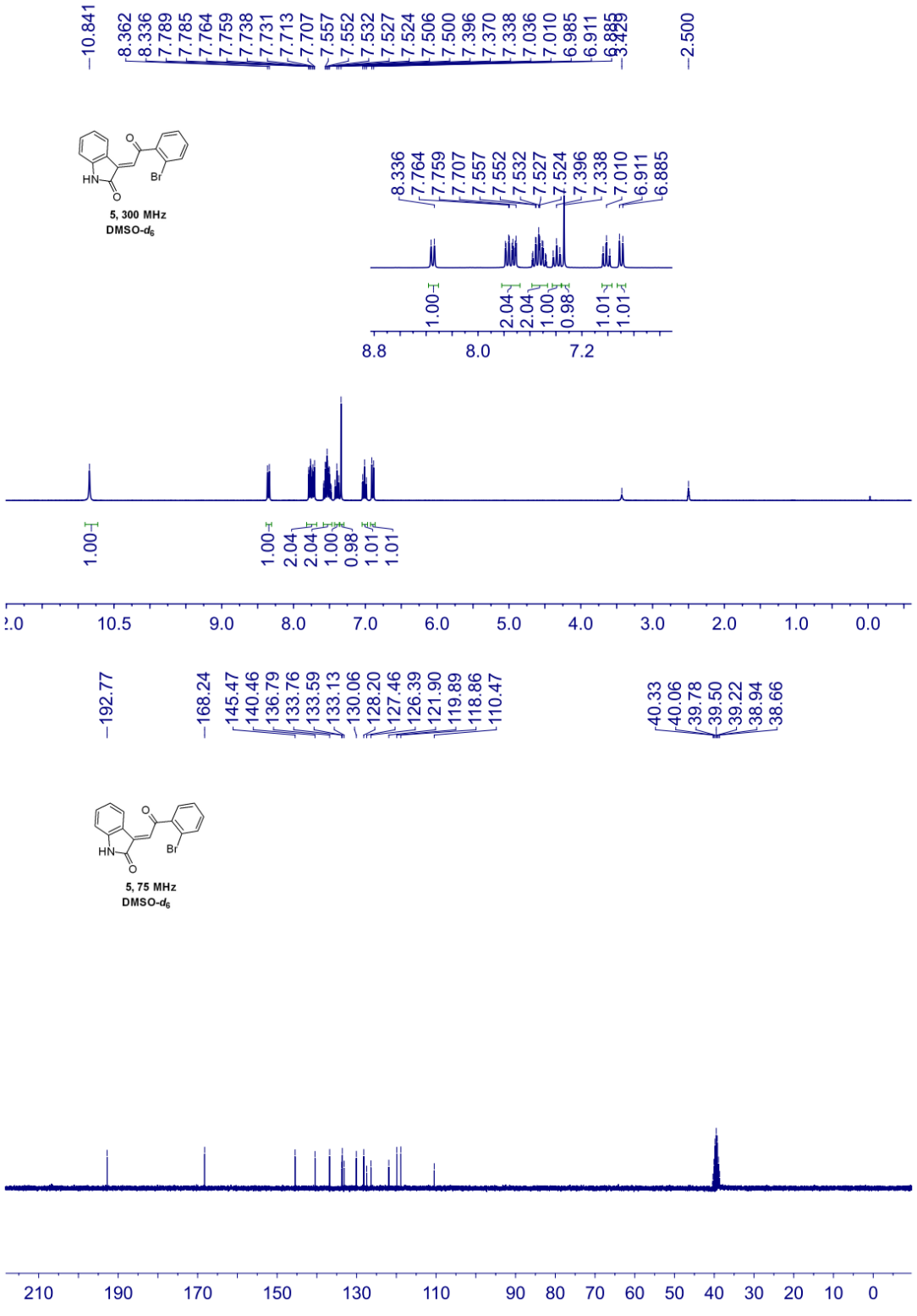

7.854
7.833
7.605
7.584
7.360
7.343
7.314
7.304
7.292
7.287
7.272
7.264
7.256
7.242
7.224
7.186
7.168
7.149
7.049
7.031
7.012
5.468
3.461
2.500
Ph
N
O
4b, 400 MHz
DMSO-d6
1.00
1.04
9.06
1.12
1.08
2.01
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
183.67
142.97
139.44
137.11
136.35
135.75
134.44
133.42
128.72
127.73
127.22
126.89
126.43
123.31
122.27
121.80
120.66
119.59
112.83
47.13
40.12
39.92
39.71
39.50
39.29
39.08
38.87
Ph
N
O
4b, 100 MHz
DMSO-d6
220
200
180
160
140
120
100
80
60
40
20
0
-10

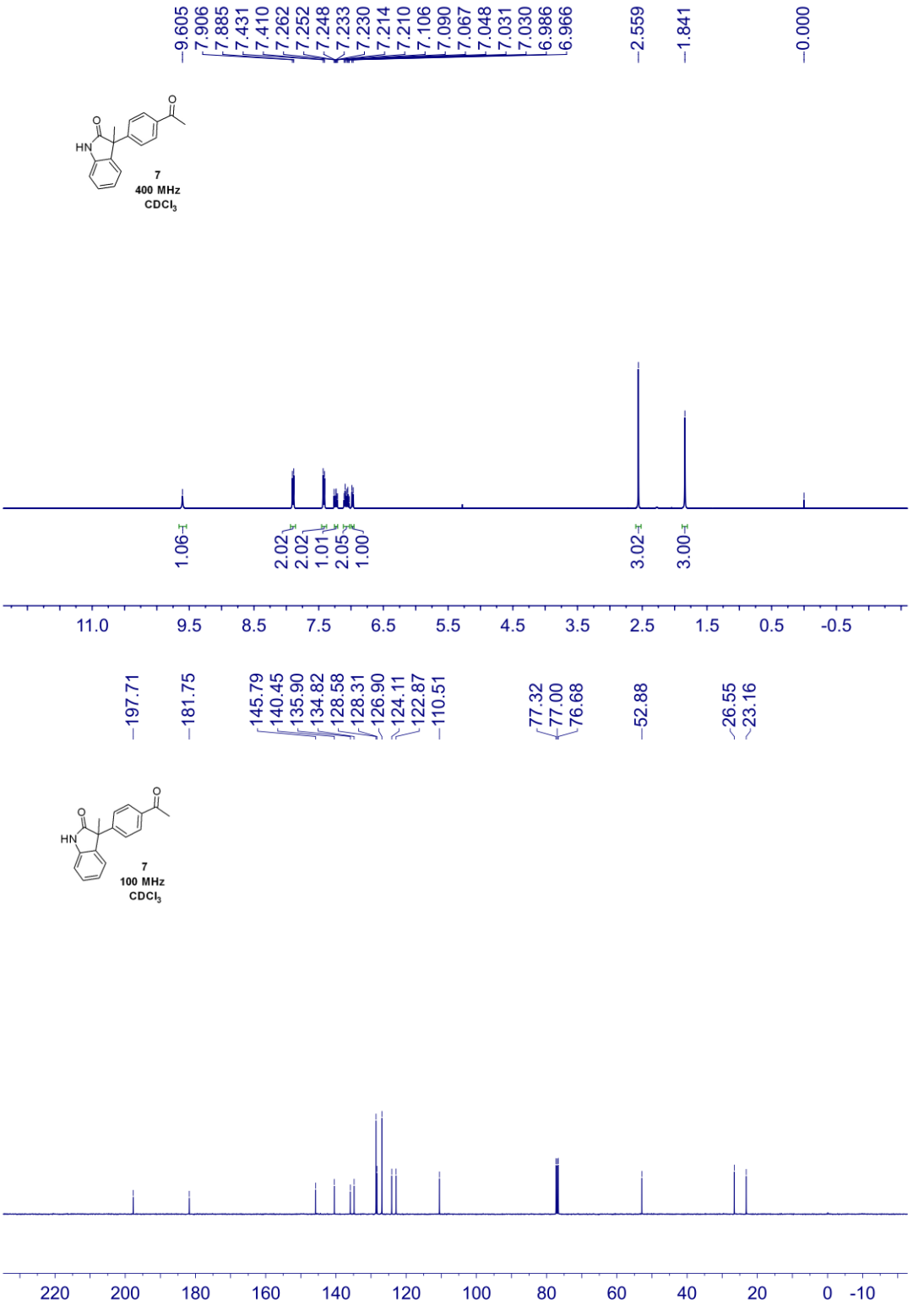

8.292
8.270
8.027
8.006
7.706
7.686
7.506
7.487
7.467
7.400
7.383
7.365
7.346
7.327
7.313
7.294
7.276
7.260
7.238
7.222
7.205
7.146
7.128
7.109
2.347
0.000
Ts
O
4c, 400 MHz
CDCl3
1.00
2.00
1.02
1.01
7.00
1.00
3.00
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


180.30
145.56
142.58
142.40
136.86
135.73
135.30
134.58
133.61
129.90
128.81
128.44
127.28
124.68
124.02
122.53
121.68
119.96
115.59
77.32
77.00
76.68
21.60
Ts
O
4c, 100 MHz
CDCl3
146
142
138
134
130
126
122
118
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


11.708
7.830
7.812
7.526
7.507
7.452
7.432
7.265
7.150
7.148
7.132
7.128
7.113
7.111
7.052
5.879
5.461
5.440
3.429
2.500
4d, 400 MHz
DMSO-d6
1.01
1.02
1.06
2.00
1.07
2.12
1.03
1.03
1.02
149.59
147.86
140.85
138.52
128.24
124.37
123.00
121.31
121.22
119.87
119.24
118.61
117.82
112.67
68.54
40.13
39.92
39.71
39.50
39.29
39.08
38.87
4d, 100 MHz
DMSO-d6


11.572
7.858
7.850
7.843
7.837
7.650
7.632
7.469
7.463
7.447
7.428
7.302
7.284
7.265
7.137
7.132
7.122
7.113
7.061
7.042
7.024
3.816
3.385
2.500
4e, 400H$_Z$
DMSO-d_6
1.00
1.05
1.06
2.06
1.06
2.14
1.07
2.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
147.37
142.61
140.65
139.82
126.74
124.79
121.98
121.44
120.71
119.95
119.50
118.67
117.77
112.22
40.13
39.92
39.71
39.50
39.29
39.08
38.87
30.68
4e, 100H$_Z$
DMSO-d_6
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10


10.841
8.362
8.336
7.789
7.785
7.764
7.759
7.738
7.731
7.713
7.707
7.557
7.552
7.532
7.527
7.524
7.506
7.500
7.396
7.370
7.338
7.036
7.010
6.985
6.911
6.885
3.429
2.500
HN
O
Br
5, 300 MHz
DMSO-d6
1.00
2.04
2.04
1.00
0.98
1.01
1.01
8.8
8.0
7.2
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
192.77
168.24
145.47
140.46
136.79
133.76
133.59
133.13
130.06
128.20
127.46
126.39
121.90
119.89
118.86
110.47
40.33
40.06
39.78
39.50
39.22
38.94
38.66
5, 75 MHz
DMSO-d6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


9.605
7.906
7.885
7.431
7.410
7.262
7.252
7.248
7.233
7.230
7.214
7.210
7.106
7.090
7.067
7.048
7.031
7.030
6.986
6.966
2.559
1.841
0.000
HN
O
O
7
400 MHz
CDCl3
1.06
2.02
2.02
1.01
2.05
1.00
3.02
3.00
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
197.71
181.75
145.79
140.45
135.90
134.82
128.58
128.31
126.90
124.11
122.87
110.51
77.32
77.00
76.68
52.88
26.55
23.16
HN
O
O
7
100 MHz
CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
-10