Supporting Information

Arylacetylenes as Two-carbon Synthons: Synthesis of Eight-membered Rings via C≡C Bond Cleavage

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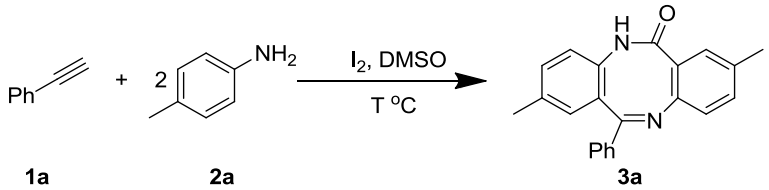
1. General

All other substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ^{1}H spectra were recorded in $CDCl_3$/DMSO on 600/400MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$/ DMSO on 150/100 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. The X-ray crystal-structure determinations of **3a, 3k** were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

2. General procedure for the synthesis of 3 (3a as an example)

A mixture of phenylacetylene **1a** (1.2 mmol), **2a** (2.0 mmol), H_2O (2.0 mmol) and Iron(III) trifluoromethanesulfonate (1.0 mmol), iodine (1.0 mmol) in DMSO (4 mL), the mixture was stirred at 130 ℃, untill almost completed conversion of the substrates by TLC analysis, the mixture was quenched with saturation $Na_2S_2O_3$ solution (50 mL), extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 3:1) to afford the product **3a**.

3. Optimization of the bicyclization reaction[a] (Table S1)



1a **2a** **3a**

Entry	I_2 (mmol)	Temp (^{o}C)	Additive	Yield (%)[b]
1	1.6	120	-	40
2	1.6	80	-	trace
3	1.6	100	-	15
4	1.6	110	-	23
5	1.6	130	-	45
6	1.6	140	-	32
7	1.0	130	-	55
8	0.8	130	-	38
9	0.5	130	-	20
10	2.0	130	-	37

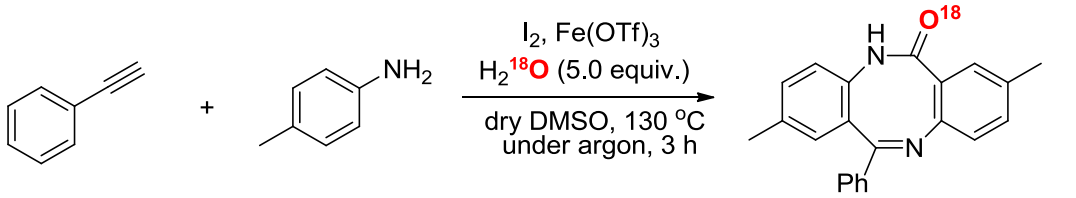
11	-	130	-	ND
12	1.0	130	TFA	60
13	1.0	130	TfOH	46
14	1.0	130	HCl	35
15	1.0	130	$Cu(OTf)_2$	38
16	1.0	130	$Fe(OTf)_3$	62
17	1.0	130	$Fe(OTf)_3$	65[c](60)[d](57)[e]

[a]Reaction conditions: **1a** (1.2 mmol), **2a** (2.0 mmol), I_2 (mmol), additive (1.0 mmol), indicated temperature, DMSO 4 mL, 3 h, unless otherwise noted. [b]Isolated yields. [c]2.0 mmol of water was added. [d]4.0 mmol of water was added. [e]6.0 mmol of water was added.

4. Mechanistic studies

4.1 Spectra for ^{18}O-labling experiment

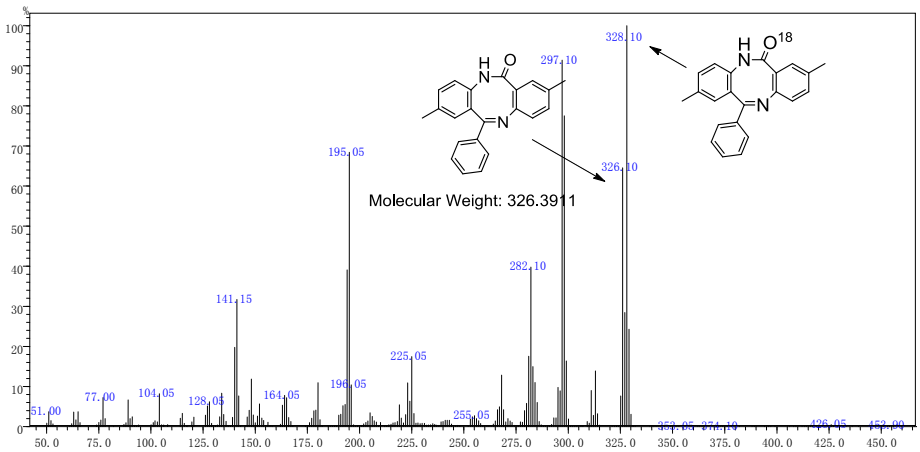
We have conducted ^{18}O-labling to investigate the source of oxygen in eight-membered N-Heterocycles ring. ring, as determined by GC-MS. Moreover, an oxygen atom exchange experiment have excluded the oxygen atom exchange between ^{16}O-labeled product 3a and $H_2{}^{18}O$ under the reaction conditions. The ^{18}O-labeling experiment suggests that $H_2{}^{18}O$ participated in this bicyclization/ring-opening process to provide the oxygen atom in the eight-membered N-Heterocycles ring.

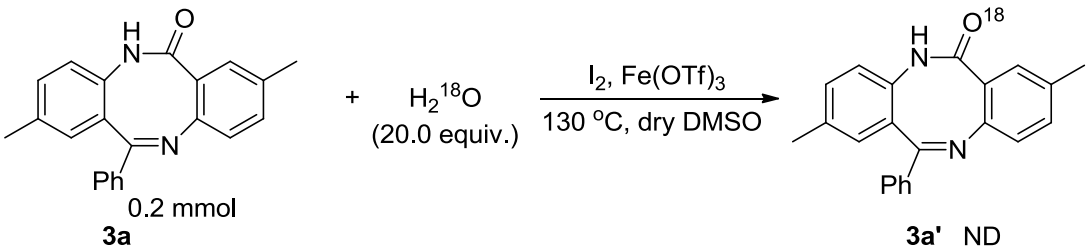


1a **2a** **3a'**, 58%

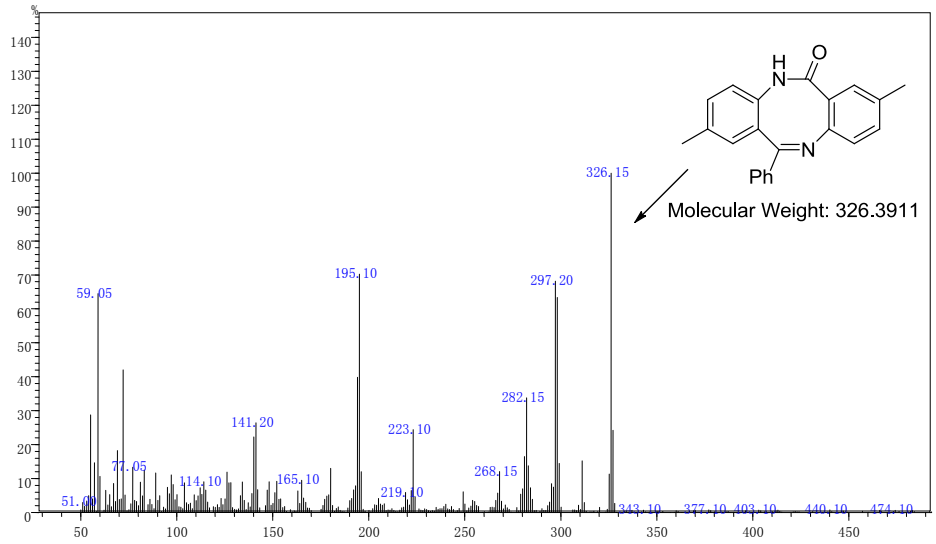
3a'-^{16}O : 3a'-^{18}O = 1: 1.5

The MS-spectrums of ^{18}O-labling experiment



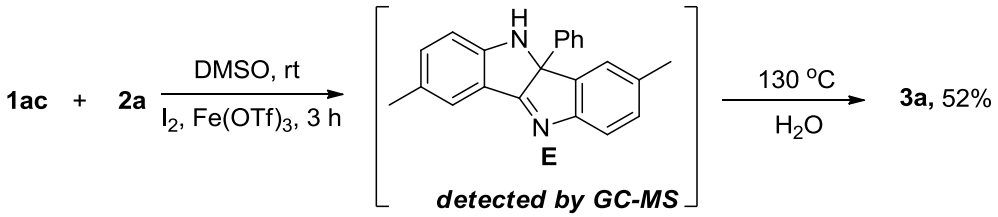


The MS-spectrums of oxygen atom exchange experiment

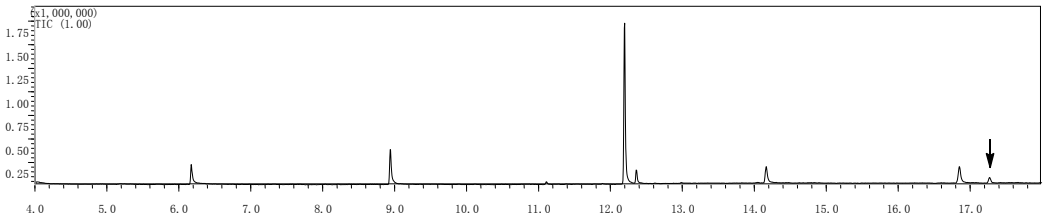


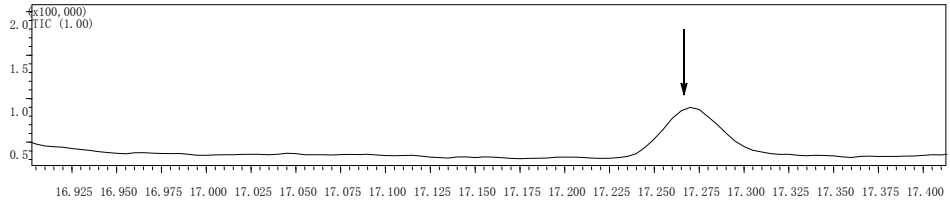
4.2 Research on intermediates

1ac reacted with *p*-toluidine **2a** with adding Iron(III) trifluoromethanesulfonate in DMSO at room temperature for 3 h, affording bicyclization structure **E** (detected by GC-MS), which was further transformed into eight-membered ring **3a** at 130 °C.

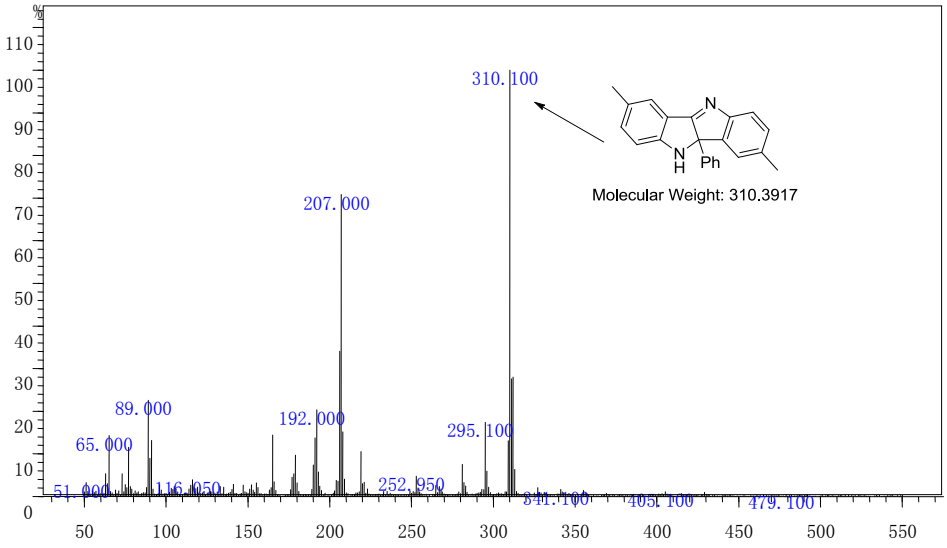


The GC-spectrums see below

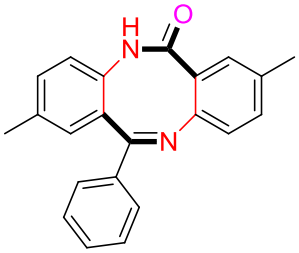




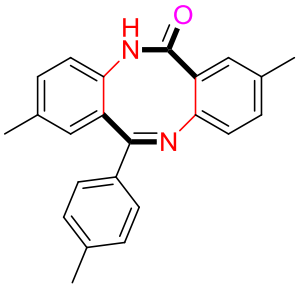
The MS-spectrums see below: Retention time: [17.265]



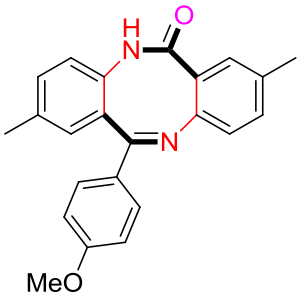
5. Characterization data for compounds 3, 4 and 9a



(Z)-2,8-dimethyl-12-phenyldibenzo[b,f][1,5]diazocin-6(5H)-one (3a):
Yield 65%; 211.9 mg; yellow solid; mp > 300 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.89 (s, 1H), 7.64 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.19 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 7.03 (s, 1H), 6.90 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 2.20 (s, 6H). ^{13}C NMR (150 MHz, DMSO-d$_6$) δ (ppm) 170.7, 167.1, 145.7, 137.5, 136.2, 134.7, 133.3, 133.0, 131.5, 131.0, 130.9, 128.70, 128.68, 128.0, 127.7, 125.8, 125.7, 120.4, 20.4, 20.2 HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{24}H_{18}NO_2$: 327.1492, found: 327.1496.

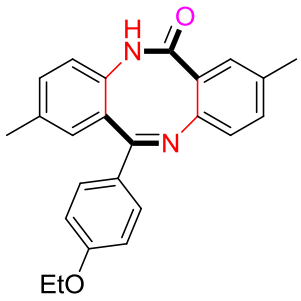


(Z)-2,8-dimethyl-12-(p-tolyl)dibenzo[b,f][1,5]diazocin-6(5H)-one (3b):
Yield 68%; 231.2 mg; yellow solid; mp 250-252 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.94 (s, 1H), 7.66 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.18 (s, 1H), 7.10-7.07 (m, 3H), 6.87 (s, 1H), 6.83 (d, J = 7.8 Hz, 1H), 2.41 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 173.2, 166.8, 146.4, 141.5, 136.7, 135.4, 134.0, 133.6, 133.4, 131.4, 130.7, 129.2, 129.0, 128.5, 128.3, 125.5, 124.5, 121.0, 21.4, 20.9, 20.6; HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2O^+$ (M+H)$^+$ 341.1648, found 341.1649.

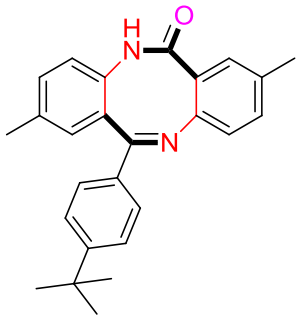


(Z)-12-(4-methoxyphenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3c):
Yield 53%; 189.2 mg; yellow solid; mp 228-230 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.87 (s, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 7.8 Hz, 1H), 7.08 (d, J =

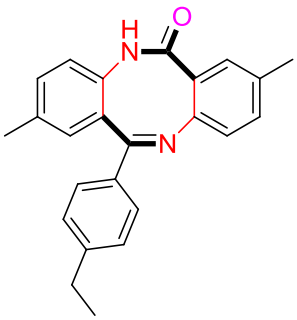
7.8 Hz, 2H), 7.06-6.98 (m, 3H), 6.89 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 3.80 (s, 3H), 2.18 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 170.8, 166.2, 161.9, 146.0, 136.0, 134.7, 133.2, 132.8, 130.8, 130.6, 130.5, 130.1, 127.9, 127.8, 126.0, 125.6, 120.5, 113.9, 55.4, 20.3, 20.1; HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2O_2^+$ $(M+H)^+$ 357.1598, found 357.1599.



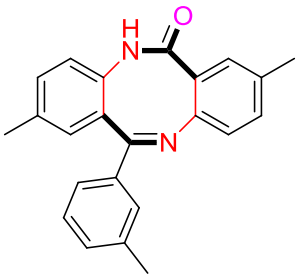
(Z)-12-(4-ethoxyphenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3d): Yield 52%; 192.4 mg; yellow solid; mp 237-239 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.84 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.03-6.97 (m, 3H), 6.89 (s, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 4.07 (q, *J* = 6.6 Hz, 2H), 2.20 (s, 3H), 2.18 (s, 3H), 1.34 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 170.7, 166.1, 161.1, 146.0, 136.0, 134.7, 133.1, 132.8, 130.8, 130.6, 130.4, 129.9, 127.9, 127.7, 126.0, 125.5, 120.5, 114.3, 63.4, 20.3, 20.1, 14.5; HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2O_2^+$ $(M+H)^+$ 371.1754, found 371.1758.



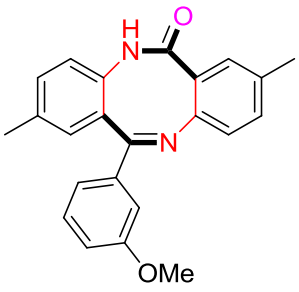
(Z)-12-(4-(tert-butyl)phenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3e): Yield 62%; 236.8 mg; yellow solid; mp 286-288 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.92 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.17 (s, 1H), 7.10-7.07 (m, 3H), 6.89 (s, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 2.24 (d, *J* = 9.6 Hz, 6H), 1.35 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 173.2, 166.8, 154.7, 146.3, 136.7, 135.2, 134.0, 133.5, 131.5, 130.7, 129.1, 128.5, 128.3, 125.5, 125.3, 124.4, 121.0, 34.9, 31.1, 20.9, 20.6. HRMS (ESI) m/z calcd for $C_{32}H_{23}N_2O^+$ $(M+H)^+$ 383.2118, found 383.2129.



(Z)-12-(4-ethylphenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3f):
Yield 65%; 230.1 mg; yellow solid; mp 256-258 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.63 (s, 1H), 7.66 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 7.16 (s, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 1H), 6.87 (s, 1H), 6.81 (d, J = 8.4 Hz, 1H), 2.69 (q, J = 7.8 Hz, 2H), 2.23 (d, J = 8.4 Hz, 6H), 1.25 (t, J = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 173.0, 166.8, 147.9, 146.3, 136.8, 135.5, 133.9, 133.7, 133.5, 131.5, 130.8, 129.3, 128.5, 128.3, 127.8, 125.5, 124.4, 121.0, 103.8, 28.8, 20.9, 20.6, 15.3. HRMS (ESI) m/z calcd for $C_{24}H_{22}N_2ONa^+$ $(M+Na)^+$ 377.1624, found 377.1629.

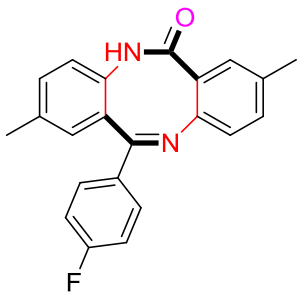


(Z)-2,8-dimethyl-12-(m-tolyl)dibenzo[b,f][1,5]diazocin-6(5H)-one (3g):
Yield 59%; 200.6 mg; yellow solid; mp 220–222 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) ^{1}H 8.98 (s, 1H), 7.67 (s, 1H), 7.43 (d, J = 6.0 Hz, 1H), 7.28 (d, J = 7.2 Hz, 2H), 7.17 (s, 1H), 7.11-7.08 (m, 3H), 6.87-6.79 (m, 2H), 2.38 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 173.2, 167.3, 146.2, 138.1, 137.9, 136.8, 134.0, 133.6, 132.0, 131.5, 130.8, 129.4, 128.5, 128.2, 128.1, 126.8, 125.5, 124.4, 120.9, 21.3, 20.9, 20.6; HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2O^+$ $(M+H)^+$ 341.1648, found 341.1649.

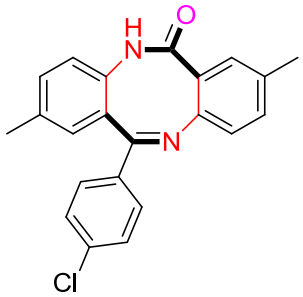


(Z)-12-(3-methoxyphenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3h):
Yield 61%; 217.4 mg; yellow solid; mp 220–222 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.69 (s, 1H), 7.48 (s, 1H), 7.28 (d, J = 7.8 Hz, 1H), 7.19-7.13 (m, 2H),

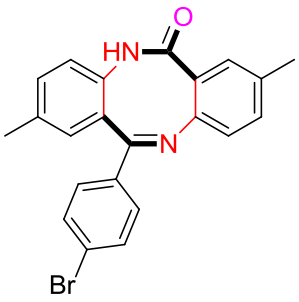
7.13-7.08 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.87 (s, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.84 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 173.0, 166.7, 159.6, 146.2, 139.3, 136.8, 133.9, 133.6, 133.5, 131.5, 130.8, 129.2, 128.6, 128.3, 125.5, 124.3, 122.4, 120.9, 117.5, 113.2, 55.4, 20.9, 20.6; HRMS (ESI) m/z calcd for $C_{23}H_{21}N_2O_2^+$(M+H)$^+$ 357.1597, found 357.1598.



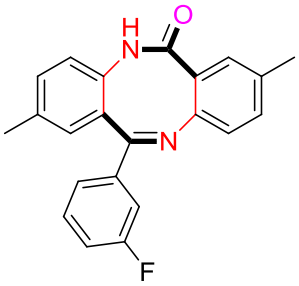
(Z)-12-(4-fluorophenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3i): Yield 66%; 227.2 mg; yellow solid; mp 250-252 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.92 (s, 1H), 7.73-7.71 (m, 2H), 7.31 (t, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.14-7.08 (m, 2H), 7.06 (s, 1H), 6.91 (s, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 2.18 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 170.6, 165.9, 164.9, 163.2, 145.6, 136.2, 134.7, 134.1, 133.3, 132.7, 131.2, 131.1, 130.9, 128.0, 127.6, 125.8, 125.7, 120.4, 115.7, 115.6, 20.3, 20.1.; HRMS (ESI) m/z calcd for $C_{22}H_{18}FN_2O^+$ (M+H)$^+$ 345.1398, found 345.1402.



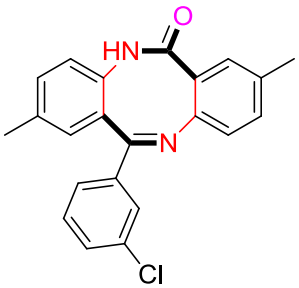
(Z)-12-(4-chlorophenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3j): Yield 64%; 230.4 mg; yellow solid; mp 242-244 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.86 (s, 1H), 7.18-7.13 (m, 4H), 7.08 (s, 2H), 7.04 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.90 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 2.18 (s, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 170.6, 166.0, 145.4, 136.4, 136.3, 136.2, 134.8, 133.3, 132.5, 130.95, 130.91, 130.3, 128.7, 128.0, 127.6, 125.8, 125.7, 120.4, 20.3, 20.1; HRMS (ESI) m/z calcd for $C_{22}H_{18}ClN_2O^+$ (M+H)$^+$ 361.1102, found 361.1107.



(Z)-12-(4-bromophenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3k): Yield 60%; 243.6 mg; yellow solid; mp 268-270 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.34 (s, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.16 (s, 1H), 7.09 (s, 3H), 6.81 (d, J = 10.2 Hz, 2H), 2.22 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 173.3, 166.1, 145.9, 136.9, 134.2, 134.1, 133.8, 132.8, 131.5, 131.4, 131.0, 130.6, 128.5, 128.0, 125.9, 125.6, 124.3, 120.8, 20.9, 20.6.; HRMS (ESI) m/z calcd for $C_{22}H_{18}BrN_2O^+$ $(M+H)^+$ 407.0597, found 407.0602.

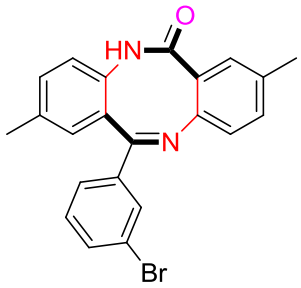


(Z)-12-(3-fluorophenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3l): Yield 56%; 192.6 mg; yellow solid; mp 270-272℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.96 (s, 1H), 7.53-7.49 (m, 2H), 7.41-7.37 (m, 2H), 7.18 (d, J = 8.4 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 7.08 (s, 1H), 6.93 (s, 1H), 6.81 (d, J = 7.8 Hz, 1H), 2.17 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.6, 166.0, 163.1, 161.4, 145.3, 140.04, 140.00, 136.3, 134.8, 133.6, 132.5, 131.1, 131.0, 130.8, 128.0, 127.7, 125.8, 125.2, 120.4, 118.5, 118.3, 114.7, 114.5, 20.3, 20.1; HRMS (ESI) m/z calcd for $C_{22}H_{18}FN_2O^+$ $(M+H)^+$ 345.1398, found 345.1402.

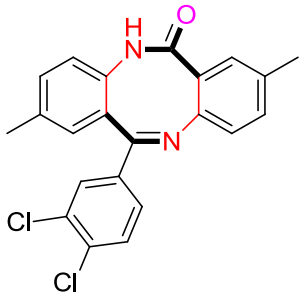


(Z)-12-(3-chlorophenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3m): Yield 65 %; 234.5 mg; yellow solid; mp 252-254 ℃;^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.95 (s, 1H), 7.72 (s, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.54–7.46 (m, 2H), 7.18 (d, J = 7.8 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 7.07 (s, 1H), 6.92 (s, 1H), 6.81 (d, J =

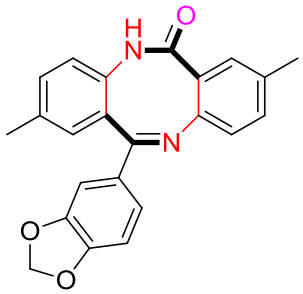
7.8 Hz, 1H), 2.17 (d, *J* = 5.4 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.6, 165.9, 145.3, 139.7, 136.4, 134.8, 133.7, 133.6, 132.4, 131.22, 131.18, 131.0, 130.7, 128.0, 127.9, 127.6, 127.5, 125.81, 125.76, 120.4, 20.3, 20.2. HRMS (ESI) m/z calcd for $C_{22}H_{18}ClN_2O^+$ $(M+H)^+$ 361.1102, found 361.1096.



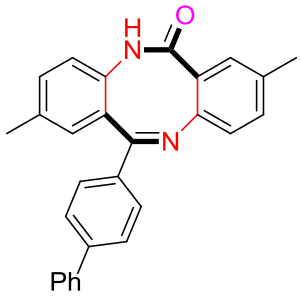
(Z)-12-(3-bromophenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3n): Yield 52%; 211.1 mg; yellow solid; mp 258-260 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) *δ* (ppm) 9.96 (s, 1H), 7.92 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.43-7.38 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.09 (s, 2H), 6.92 (s, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 2.16 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) *δ* (ppm) 170.5, 165.8, 145.3, 139.8, 136.3, 134.8, 134.0, 133.5, 132.3, 131.1, 130.9, 130.8, 128.0, 127.9, 127.5, 125.8, 125.7, 122.1, 120.4, 20.3, 20.1; HRMS (ESI) m/z calcd for $C_{22}H_{18}BrN_2O^+$ $(M+H)^+$ 407.0579, found 407.0585.



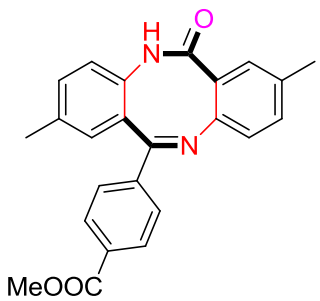
(Z)-12-(3,4-dichlorophenyl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3o): Yield 49%; 193.0 mg; yellow solid; mp 290-292 ℃; ^{1}H NMR (600 MHz, DMSO-d_6 + $CDCl_3$) *δ* (ppm) 9.78 (s, 1H), 7.84 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.05 (s, 1H), 6.90 (s, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 2.21 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6 + $CDCl_3$) *δ* (ppm) 170.3, 164.9, 145.0, 137.9, 136.3, 134.8, 134.3, 133.5, 131.8, 131.7, 131.1, 130.85, 130.81, 129.7, 128.6, 127.9, 127.5, 125.7, 125.6, 120.3, 20.3, 20.1; HRMS (ESI) m/z calcd for $C_{22}H_{17}Cl_2N_2O^+$ $(M+H)^+$ 395.0712, found 395.0718.



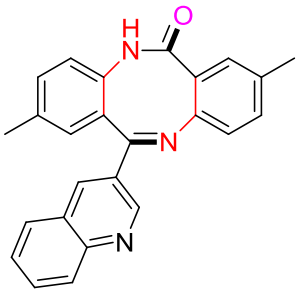
(Z)-12-(benzo[d][1,3]dioxol-5-yl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3p): Yield 47%; 173.9 mg; yellow solid; mp 265-267 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.39 (s, 1H), 7.58 (s, 1H), 7.18 (s, 2H), 7.12 (d, J = 7.8 Hz, 1H), 6.96 (s, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.08 (d, J = 6.6 Hz, 2H), 2.33 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 173.3, 166.0, 150.2, 147.9, 146.3, 136.6, 134.0, 133.4, 133.3, 132.5, 131.4, 130.7, 128.4, 128.2, 125.5, 125.2, 124.5, 120.9, 108.3, 107.5, 101.5, 20.8, 20.5; HRMS (ESI) m/z calcd for $C_{23}H_{19}N_2O_3^+$(M+H)$^+$ 371.1390, found 371.1395.



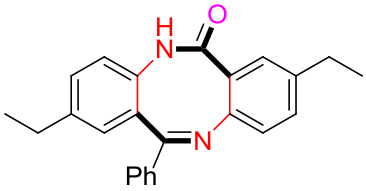
(Z)-12-([1,1'-biphenyl]-4-yl)-2,8-dimethyldibenzo[b,f][1,5]diazocin-6(5H)-one (3q): Yield 38%; 152.7 mg; yellow solid; mp 264-266 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.99 (s, 1H), 7.78 (t, J = 5.4 Hz, 4H), 7.72 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.10 (d, J = 6.6 Hz, 2H), 6.93 (s, 1H), 6.83 (d, J = 7.8 Hz, 1H), 2.18 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 170.7, 166.7, 145.8, 142.9, 139.1, 136.5, 136.1, 134.8, 133.1, 132.9, 130.9, 130.8, 129.3, 129.0, 128.1, 128.0, 127.7, 126.81, 126.77, 125.9, 125.6, 120.5, 20.3, 20.1; HRMS (ESI) m/z calcd for $C_{28}H_{23}N_2O^+$ (M+H)$^+$ 403.1805, found 403.1811.



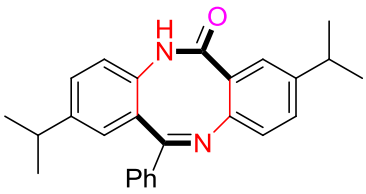
(Z)-methyl4-(2,8-dimethyl-12-oxo-11,12-dihydrodibenzo[b,f][1,5]diazocin-6-yl)benzoate (3r): Yield 53%; 203.5 mg; yellow solid; mp 230-232 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.06 (d, J = 8.4 Hz, 3H), 7.81 (d, J = 8.4 Hz, 2H), 7.19 (s, 1H), 7.15 (t, J = 6.6 Hz, 2H), 7.09 (d, J = 8.4 Hz, 1H), 6.87–6.81 (m, 2H), 3.94 (s, 3H), 2.26 (d, J = 6.6 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 172.5, 166.5, 166.2, 145.8, 141.7, 137.3, 134.2, 133.8, 133.2, 132.2, 131.7, 131.2, 129.5, 129.1, 128.7, 128.2, 125.7, 124.0, 120.9, 52.4, 21.0, 20.7. HRMS (ESI) m/z calcd for $C_{24}H_{22}N_2O_3^+$ $(M+H)^+$ 385.1547, found 385.1551.



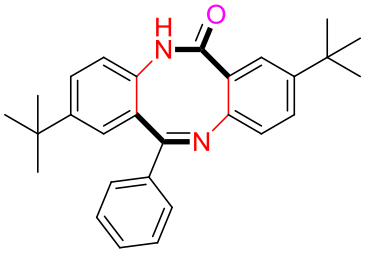
(E)-2,8-dimethyl-12-(quinolin-3-yl)dibenzo[b,f][1,5]diazocin-6(5H)-one (3s): Yield 55%; 207.4 mg; yellow solid; mp 295-297 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.93 (s, 1H), 9.38 (d, J = 1.8 Hz, 1H), 8.28 (s, 1H), 8.10 (t, J = 9.0 Hz, 2H), 7.87 (t, J = 7.8 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 7.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 10.8 Hz, 2H), 6.87 (d, J = 7.8 Hz, 1H), 2.23 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 170.5, 165.7, 149.3, 148.3, 145.2, 137.2, 136.6, 134.8, 133.7, 132.1, 131.5, 131.3, 131.1, 130.2, 129.4, 128.8, 128.0, 127.8, 127.6, 126.6, 125.9, 125.8, 120.5, 20.4, 20.2; HRMS (ESI) m/z calcd for $C_{25}H_{20}N_3O^+$ $(M+H)^+$ 378.1601, found 378.1606.



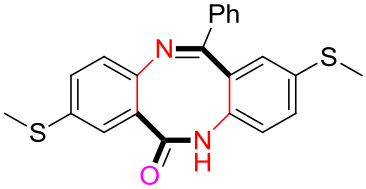
(Z)-2,8-diethyl-12-phenyldibenzo[b,f][1,5]diazocin-6(5H)-one (4a): Yield 66%; 234.3 mg; yellow solid; mp 226-226 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 9.83 (s, 1H), 7.57 (d, J = 7.2 Hz, 2H), 7.46 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.16 (d, J = 7.2 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.06–6.99 (m, 2H), 6.85 (s, 1H), 6.75 (d, J = 8.0 Hz, 1H), 2.47-2.41 (m, 4H), 1.04 (t, J = 7.6 Hz, 3H), 1.00 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 170.7, 166.9, 145.9, 142.2, 139.3, 137.6, 134.9, 132.9, 131.4, 129.8, 129.5, 128.64, 128.60, 126.8, 126.7, 125.71, 125.67, 120.5, 27.3, 27.2, 15.1, 15.0; HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2O^+$ $(M+H)^+$ 355.1805, found 355.1810.



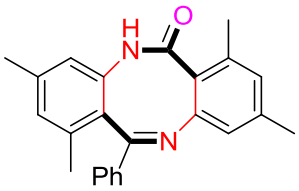
(2-benzoyl-6-methylquinolin-3-yl)(4-chlorophenyl)methanone (4b):
Yield 53%; 202.5 mg; orange solid; mp 224-226 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.93 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.54–7.49 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.27 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 7.2 Hz, 2H), 6.94 (s, 1H), 6.85–6.82 (m, 1H), 1.14–1.09 (m, 6H), 1.08-1.06 (m, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 170.7, 166.7, 146.6, 145.9, 143.9, 137.7, 135.1, 132.7, 131.4, 128.7, 128.6, 128.5, 128.1, 125.8, 125.7, 125.6, 125.5, 120.7, 32.6, 32.5, 23.8, 23.7, 23.5, 23.3; HRMS (ESI) m/z calcd for $C_{26}H_{27}N_2O^+$ $(M+H)^+$ 383.2118, found 383.2122.



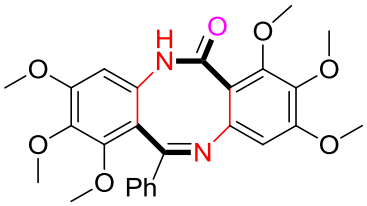
(Z)-2,8-di-tert-butyl-12-phenyldibenzo[b,f][1,5]diazocin-6(5H)-one (4c):
Yield 55%; 225.5 mg; yellow solid; mp 244-266 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.81 (s, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.48 (d, J = 7.2 Hz, 1H), 7.42-7.39 (m, 3H), 7.38 – 7.34 (m, 2H), 7.14 – 7.08 (m, 2H), 6.86 (d, J = 8.3 Hz, 1H), 1.26 (s, 9H), 1.24 (s, 9H). ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 170.8, 166.6, 148.9, 146.2, 145.6, 137.7, 134.8, 132.3, 131.4, 128.7, 128.6, 127.7, 127.2, 125.5, 125.4, 125.0, 124.6, 124.5, 120.7, 113.8, 34.3, 34.1, 31.0, 30.9. HRMS (ESI) m/z calcd for $C_{28}H_{31}N_2O^+$ $(M+H)^+$ 411.2431, found 411.2430.



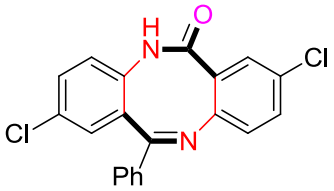
(Z)-2,8-bis(methylthio)-12-phenyldibenzo[b,f][1,5]diazocin-6(5H)-one (4d):
Yield 58%; 226.2 mg; yellow soild; mp 219-221℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 9.99 (s, 1H), 7.66 (d, J = 7.8 Hz, 2H), 7.59-7.54 (m, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.28 (d, J = 7.2 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.07 (s, 1H), 6.96 (s, 1H), 6.87 (d, J = 8.4 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 169.8, 166.8, 145.2, 137.2, 137.0, 133.8, 133.54, 133.52, 131.7, 128.72, 128.67, 128.1, 127.2, 126.54, 126.46, 124.8, 123.9, 121.3, 14.8, 14.4; HRMS (ESI) m/z calcd for $C_{22}H_{19}N_2OS_2^+$ $(M+H)^+$ 391.0933, found 391.0940**.**



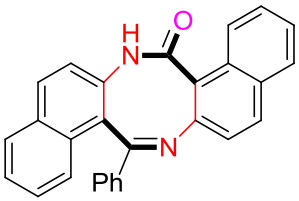
(Z)-1,3,7,9-tetramethyl-12-phenyldibenzo[b,f][1,5]diazocin-6(5H)-one (4e):
Yield 52%; 184.1 mg; yellow solid; mp 254-256 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 10.02 (s, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.54-7.51 (m, 1H), 7.46 (t, J = 7.2 Hz, 2H), 6.86 (s, 1H), 6.83 (s, 1H), 6.64 (s, 1H), 6.54 (s, 1H), 2.21 (s, 3H), 2.16 (s, 3H), 2.15 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 169.8, 167.7, 149.1, 139.2, 138.6, 137.1, 137.0, 134.8, 131.4, 130.1, 129.1, 128.8, 127.7, 126.4, 123.1, 122.7, 116.6, 20.7, 20.5, 19.4, 18.9; HRMS (ESI) m/z calcd for $C_{24}H_{23}N_2O^+$(M+H)$^+$ 355.1805, found 355.1809.



(Z)-1,2,3,7,8,9-hexamethoxy-12-phenyldibenzo[b,f][1,5]diazocin-6(5H)-one (4f):
Yield 60%; 286.8 mg; yellow solid; mp 229-231℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 9.49 (s, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.6 Hz, 2H), 6.47 (s, 1H), 6.26 (s, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.72 (s, 6H), 3.71 (s, 3H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 169.2, 166.2, 154.43, 154.41, 150.7, 150.0, 145.6, 140.5, 138.3, 138.2, 132.5, 130.7, 128.03, 128.02, 120.1, 112.5, 104.1, 99.3, 61.4, 60.7, 60.6, 60.5, 55.9, 55.8; HRMS (ESI) m/z calcd for $C_{26}H_{27}N_2O_7^+$ (M+H)$^+$ 479.1813, found 479.1820.

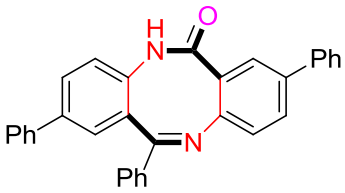


(Z)-2,8-dichloro-12-phenyldibenzo[b,f][1,5]diazocin-6(5H)-one (4g):
Yield 43%; 157.4 mg; yellow solid; mp 257-259 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.20 (s, 1H), 7.65 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.8 Hz, 3H), 7.41 (d, J = 8.4 Hz, 1H), 7.30 (s, 2H), 7.26 (d, J = 8.4 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.7, 166.4, 146.7, 136.4, 135.8, 134.4, 132.0, 131.3, 130.5, 130.4, 128.8, 128.7, 128.4, 127.9, 127.6, 127.29, 127.26, 122.5; HRMS (ESI) m/z calcd for C_{20} $H_{13}Cl_2N_2O^+$ (M+H)$^+$ 367.0399, found 367.0404.



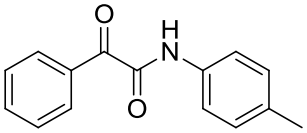
(Z)-16-phenyldinaphtho[2,1-b:2',1'-f][1,5]diazocin-8(7H)-one (4h):

Yield 64%; 254.7 mg; yellow solid; mp > 300℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) 10.64 (s, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.77 (t, J = 9.0 Hz, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.54-7.50 (m, 2H), 7.47-7.43 (m, 2H), 7.43-7.36 (m, 4H), 7.33 (d, J = 9.0 Hz, 1H), 7.14 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 169.0, 167.2, 146.8, 137.2, 135.6, 131.8, 131.3, 130.5, 130.3, 130.0, 129.7, 129.6, 128.9, 128.34, 128.32, 128.1, 128.0, 127.6, 127.4, 126.2, 125.05, 124.99, 124.4, 123.4, 119.5; HRMS (ESI) m/z calcd for $C_{28}H_{19}N_2O^+$ $(M+H)^+$ 399.1492, found 399.1497.



(Z)-2,8,12-triphenyldibenzo[b,f][1,5]diazocin-6(5H)-one (4i):

Yield 58%; 261.3 mg; yellow solid; mp 264-266 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 10.18 (s, 1H), 7.77–7.73 (m, 2H), 7.71-7.69 (m, 1H), 7.64-7.62 (m, 1H), 7.58 (s, 1H), 7.58-7.55 (m, 3H), 7.53-7.49 (m, 4H), 7.42 (d, J = 2.4 Hz, 1H), 7.40 (s, 1H), 7.38 (s, 1H), 7.36 (s, 1H), 7.34 (s, 1H), 7.33-7.29 (m, 3H), 7.04 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 170.3, 167.0, 147.5, 138.6, 138.2, 138.1, 137.2, 136.4, 135.9, 133.5, 131.7, 128.9, 128.8, 128.7, 128.6, 128.4, 127.9, 127.4, 126.6, 126.5, 126.4, 126.2, 125.8, 125.5, 121.3; HRMS (ESI) m/z calcd for $C_{32}H_{23}N_2O^+$ $(M+H)^+$ 451.1805, found 451.1810.



2-oxo-2-phenyl-N-(p-tolyl)acetamide (9a):

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.02 (s, 1H), 8.39 (d, J = 7.2 Hz, 2H), 7.66–7.57 (m, 3H), 7.48 (t, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 187.5, 158.8, 134.8, 134.4, 134.0, 133.0, 131.3, 129.6, 128.4, 119.8, 20.9.

6. Crystallographic data and molecular structure of 3a, 3k

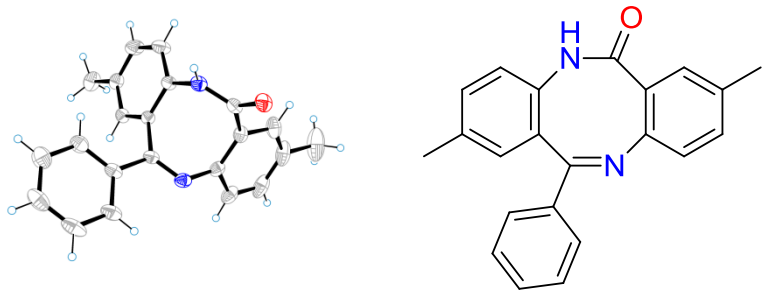


Figure S1. X-ray crystal structure of **3a**

Crystal Data for Compound **3a**: CCDC 2021412 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

```
Bond precision:  C-C = 0.0027 A          Wavelength=0.71073

Cell:            a=13.602(3)     b=13.685(3)         c=19.401(4)
                 alpha=90        beta=99.361(3)      gamma=90
Temperature:     293 K

                Calculated               Reported
Volume          3563.3(13)               3563.2(12)
Space group     C 2/c                    C 1 2/c 1
Hall group      -C 2yc                   -C 2yc
Moiety formula  C22 H18 N2 O             C22 H18 N2 O
Sum formula     C22 H18 N2 O             C22 H18 N2 O
Mr              326.38                   326.38
Dx,g cm-3       1.217                    1.217
Z               8                        8
Mu (mm-1)       0.075                    0.075
F000            1376.0                   1376.0
F000'           1376.52
h,k,lmax        16,16,23                 16,16,23
Nref            3328                     3323
Tmin,Tmax       0.985,0.989              0.669,0.746
Tmin'           0.985

Correction method= # Reported T Limits: Tmin=0.669 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 25.500

R(reflections)= 0.0486( 2732)     wR2(reflections)= 0.1557( 3323)

S = 1.057                 Npar= 229
```

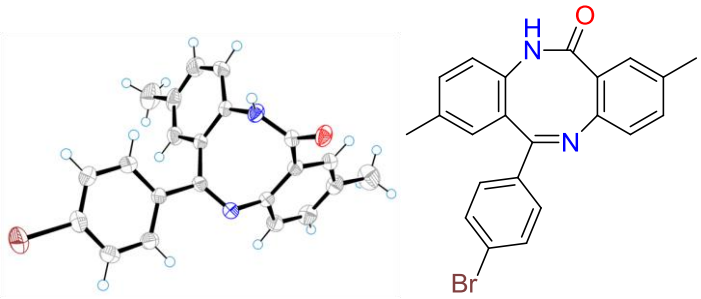


Figure S2. X-ray crystal structure of **3k**

Crystal Data for Compound **3k**: CCDC 2021411 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

```
Bond precision:  C-C = 0.0057 A          Wavelength=0.71073

Cell:          a=8.4050(19)       b=10.003(2)       c=15.623(4)
               alpha=71.488(4)    beta=78.914(5)    gamma=66.772(3)
Temperature:   273 K

                Calculated                Reported
Volume          1141.2(5)                 1141.2(5)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C22 H17 Br N2 O, C H Cl3  C22 H17 Br N2 O, C H Cl3
Sum formula     C23 H18 Br Cl3 N2 O       C23 H18 Br Cl3 N2 O
Mr              524.64                    524.65
Dx,g cm-3       1.527                     1.527
Z               2                         2
Mu (mm-1)       2.170                     2.170
F000            528.0                     528.0
F000'           528.47
h,k,lmax        10,12,18                  10,12,18
Nref            4233                      4184
Tmin,Tmax       0.771,0.805               0.315,0.746
Tmin'           0.771

Correction method= # Reported T Limits: Tmin=0.315 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.988          Theta(max)= 25.500

R(reflections)= 0.0606( 3381)     wR2(reflections)= 0.1799( 4184)

S = 1.082                 Npar= 273
```

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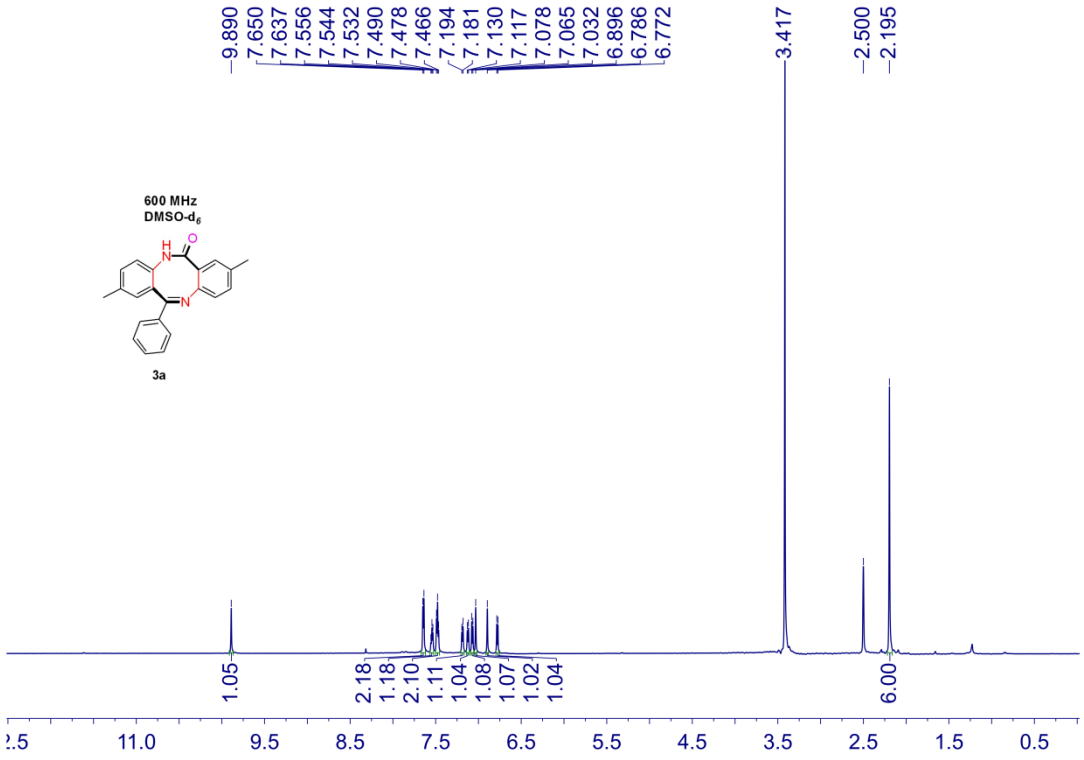
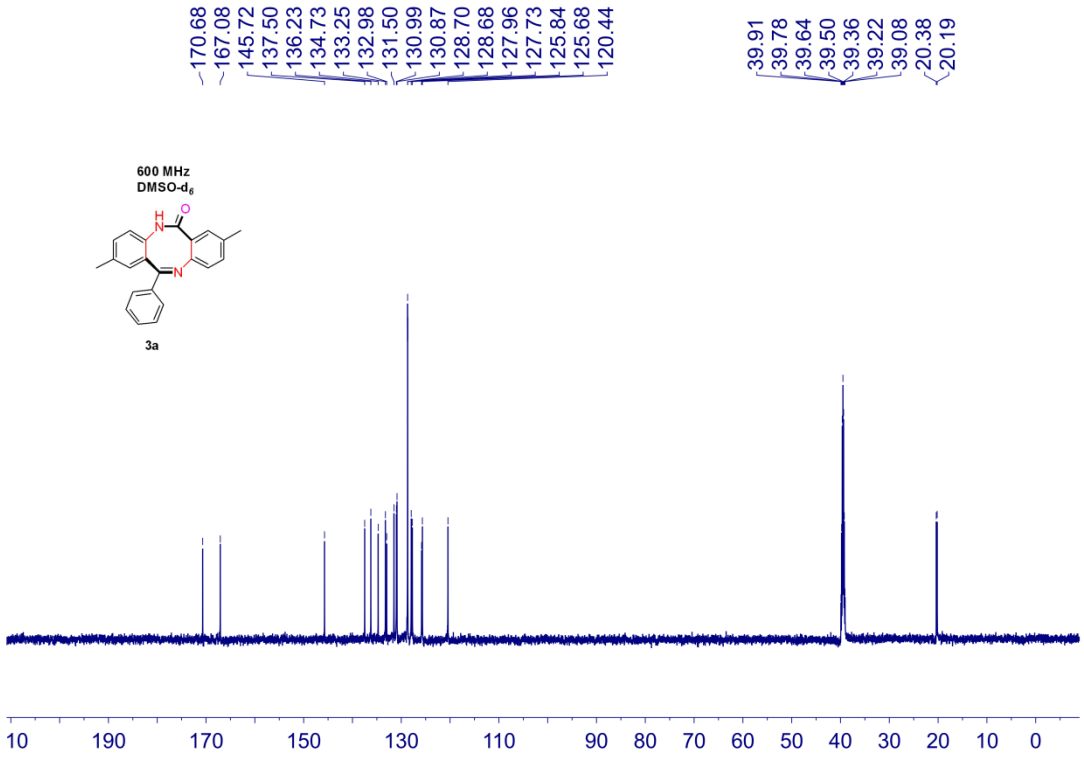
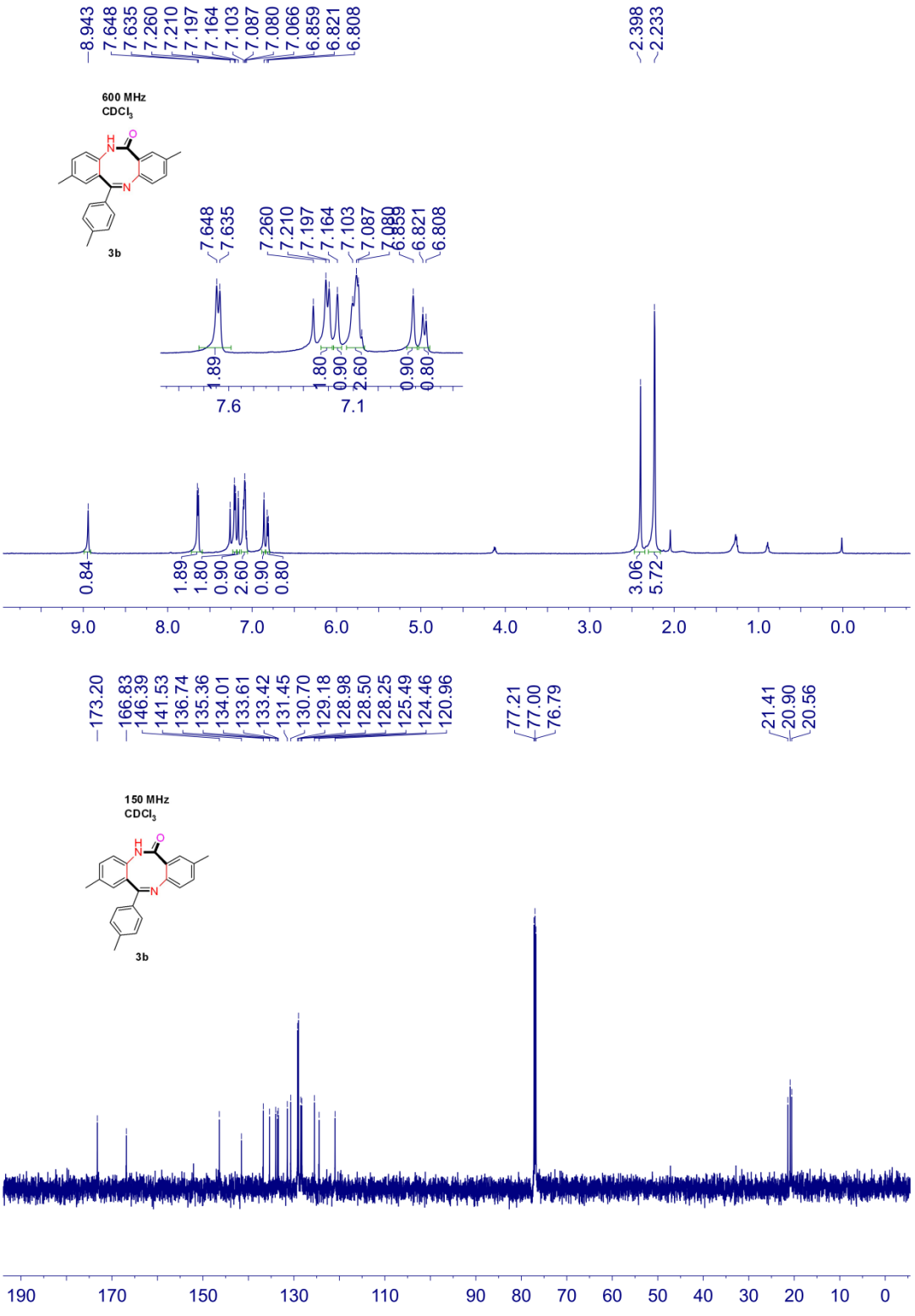
7. ^{1}H and ^{13}C NMR spectra of compounds 3, 4, 9a



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7.103
7.087
7.080
7.066
6.859
6.821
6.808
2.398
2.233
1.89
1.80
0.90
2.60
0.90
0.80
7.6
7.1
0.84
1.89
1.80
0.90
2.60
0.90
0.80
3.06
5.72
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
150 MHz
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134.01
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130.70
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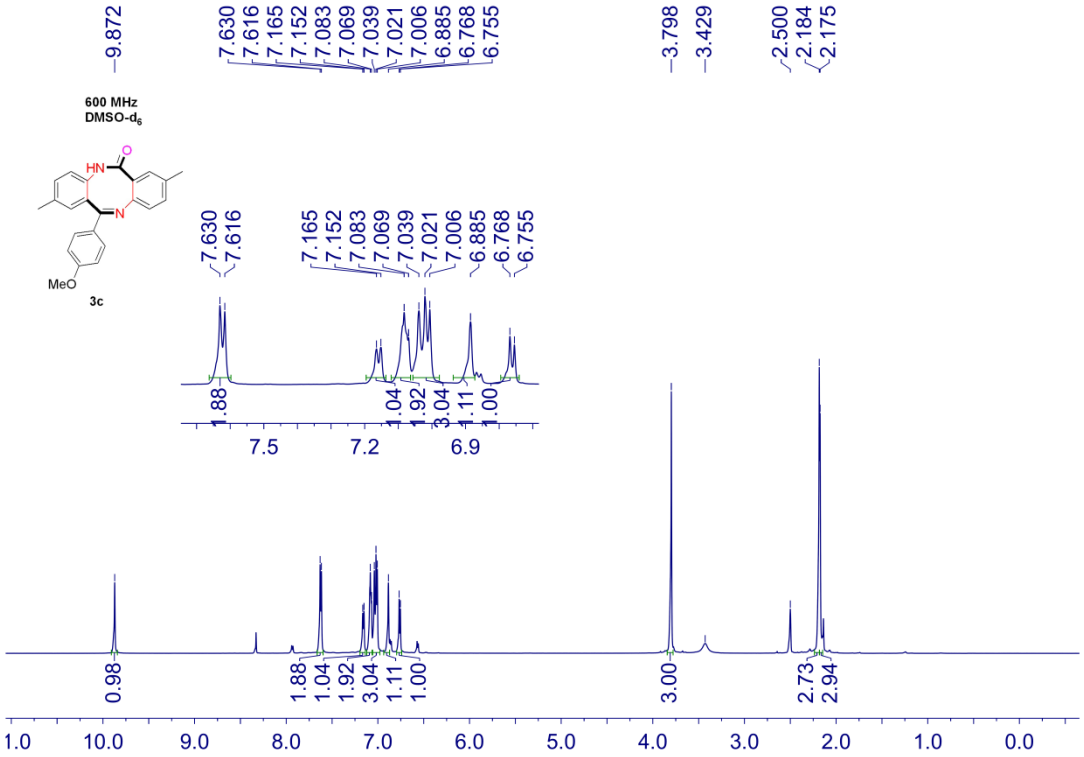
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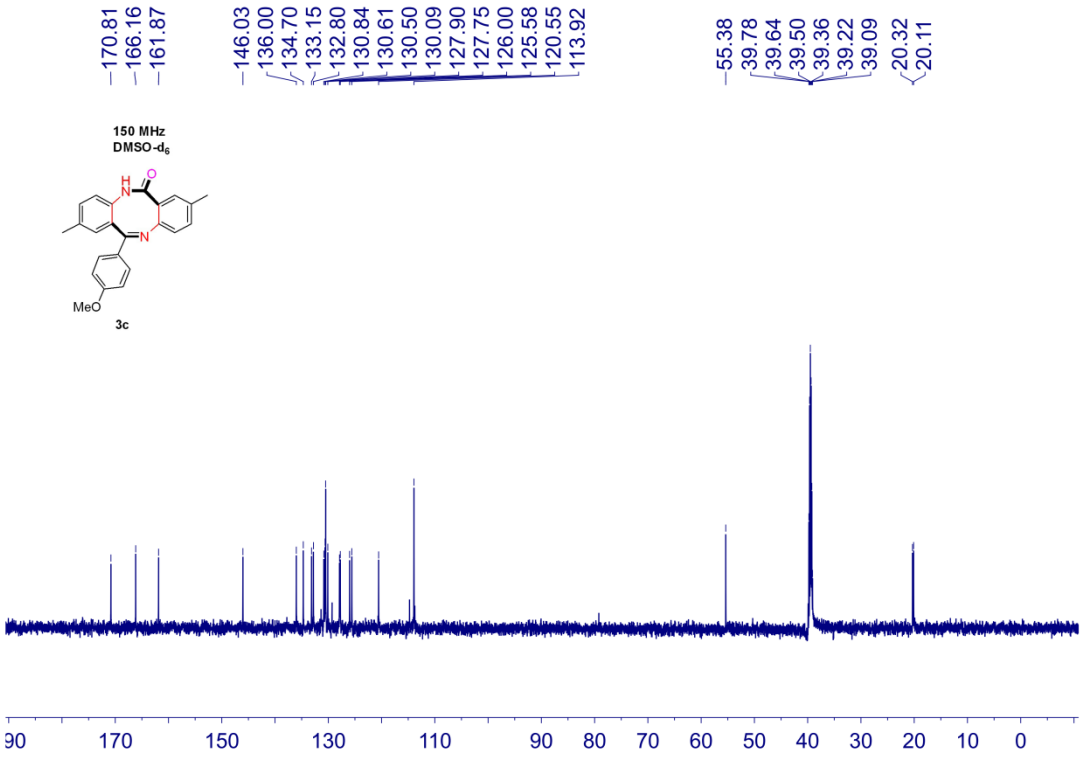
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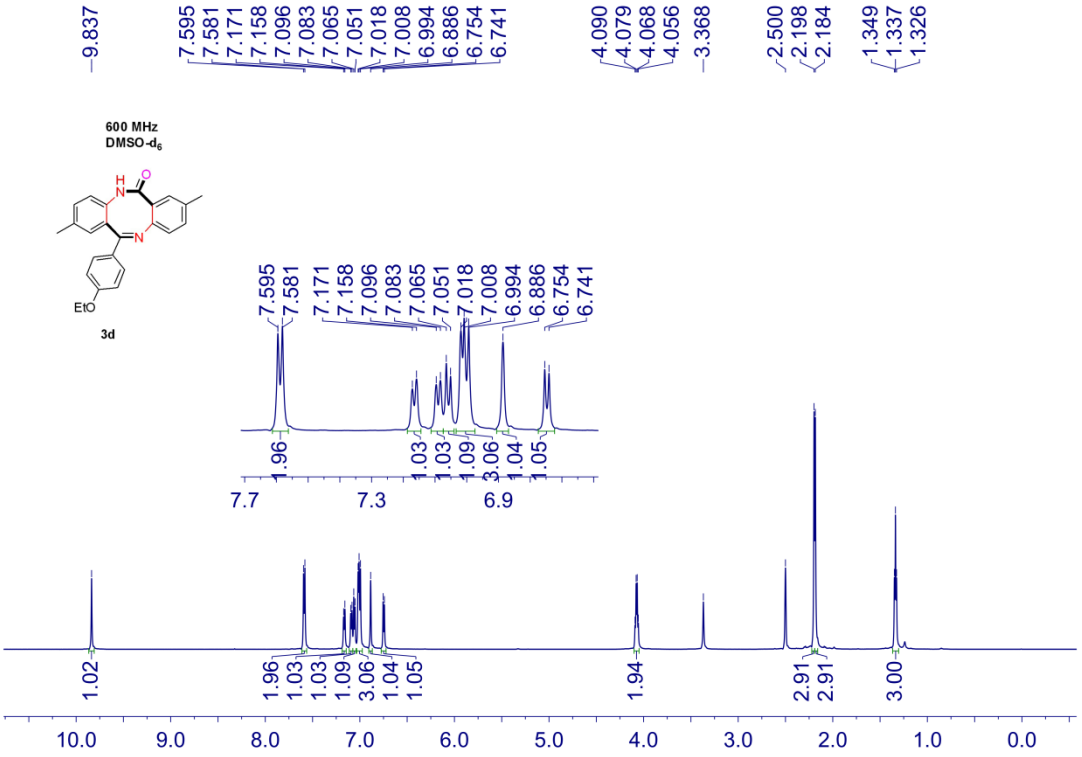
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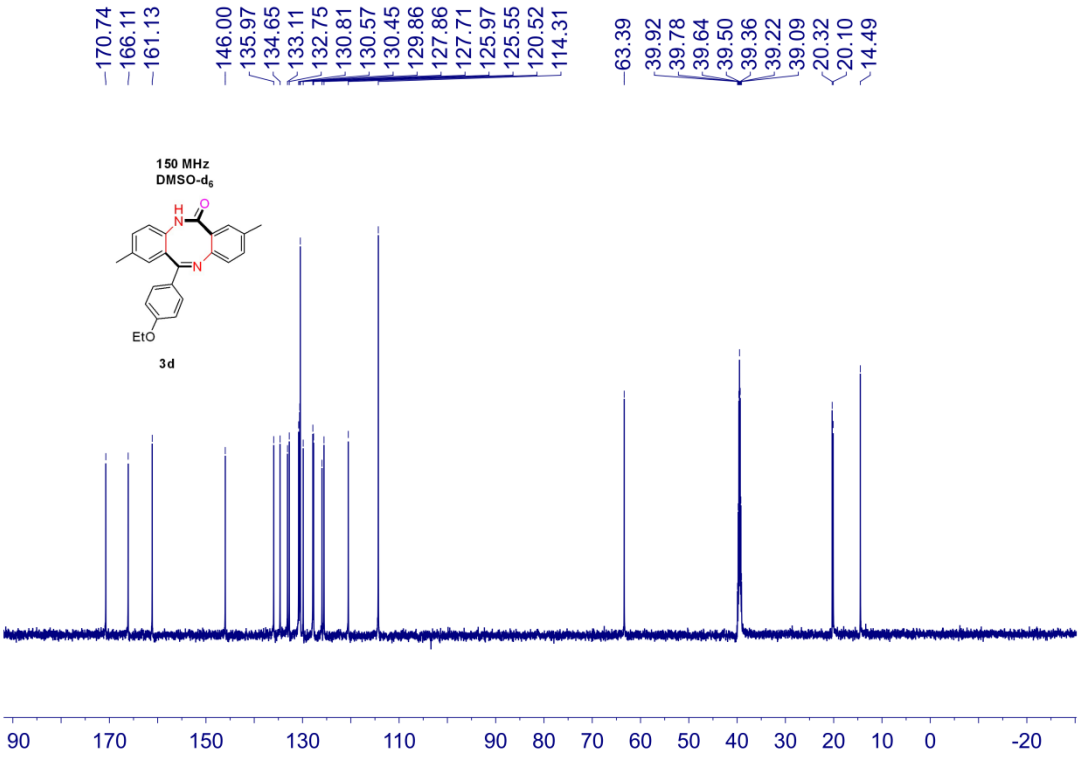
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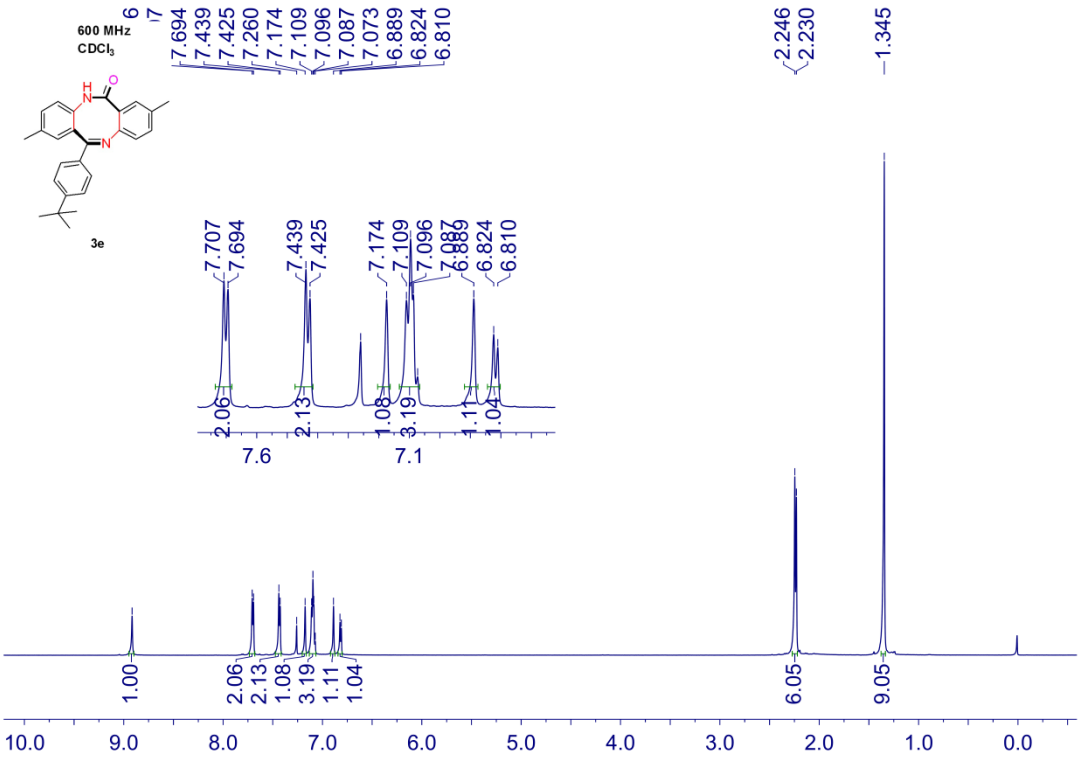
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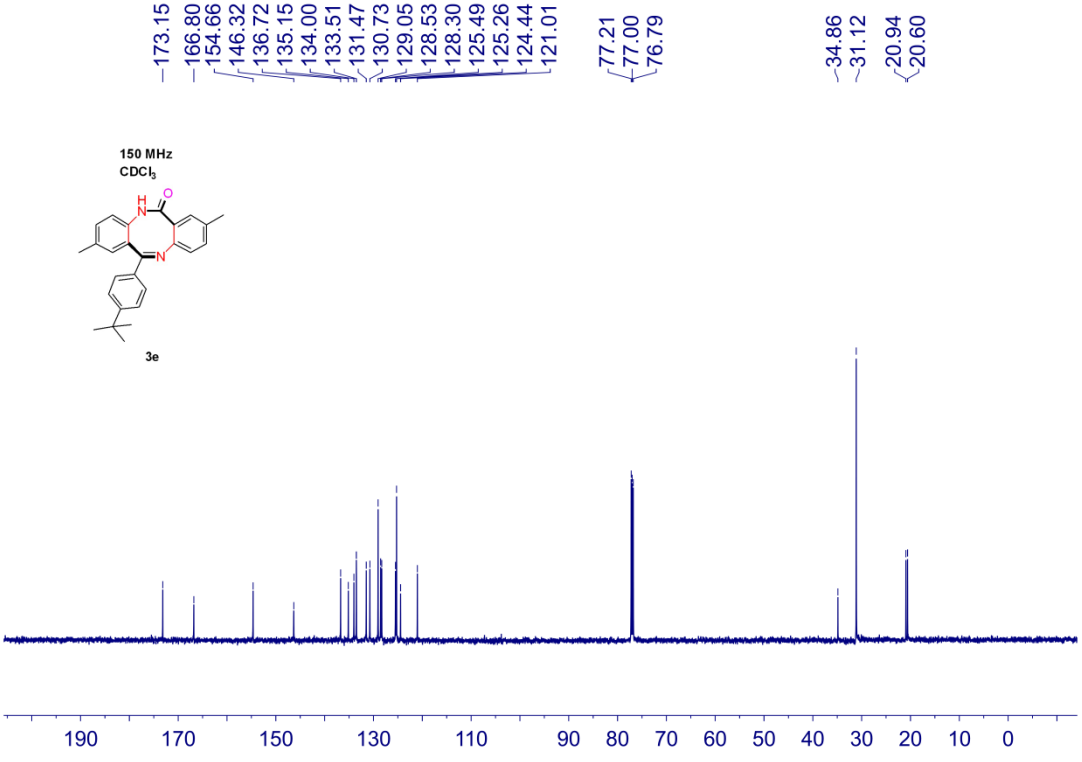
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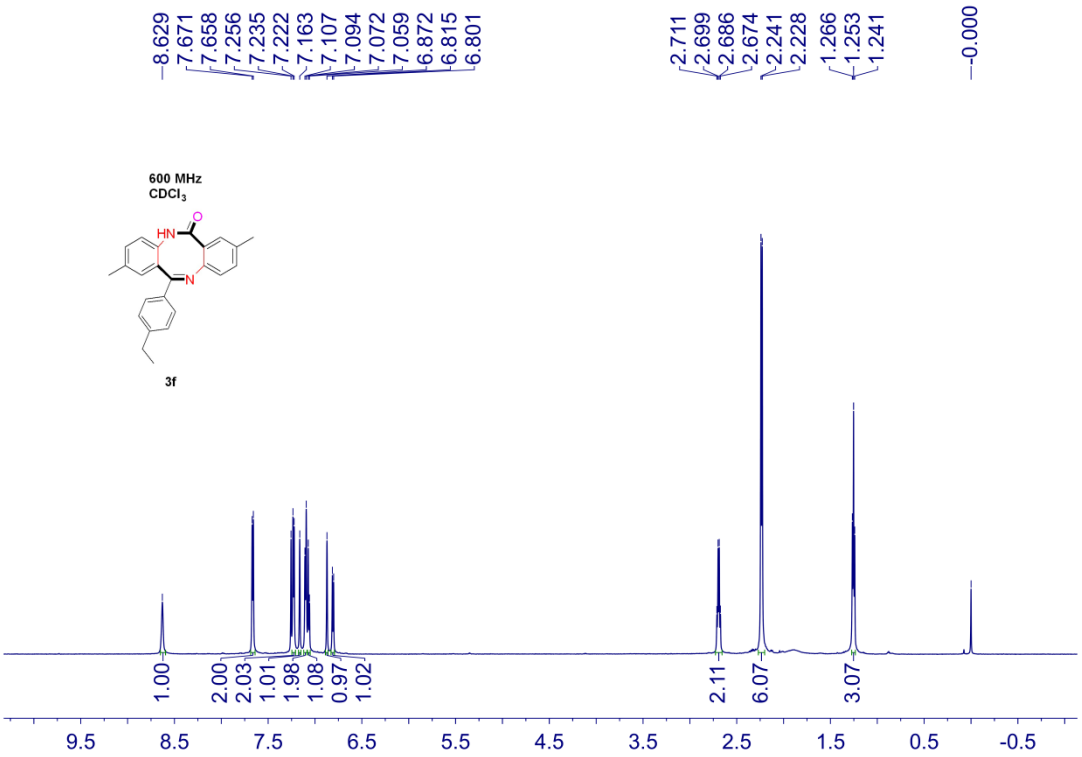
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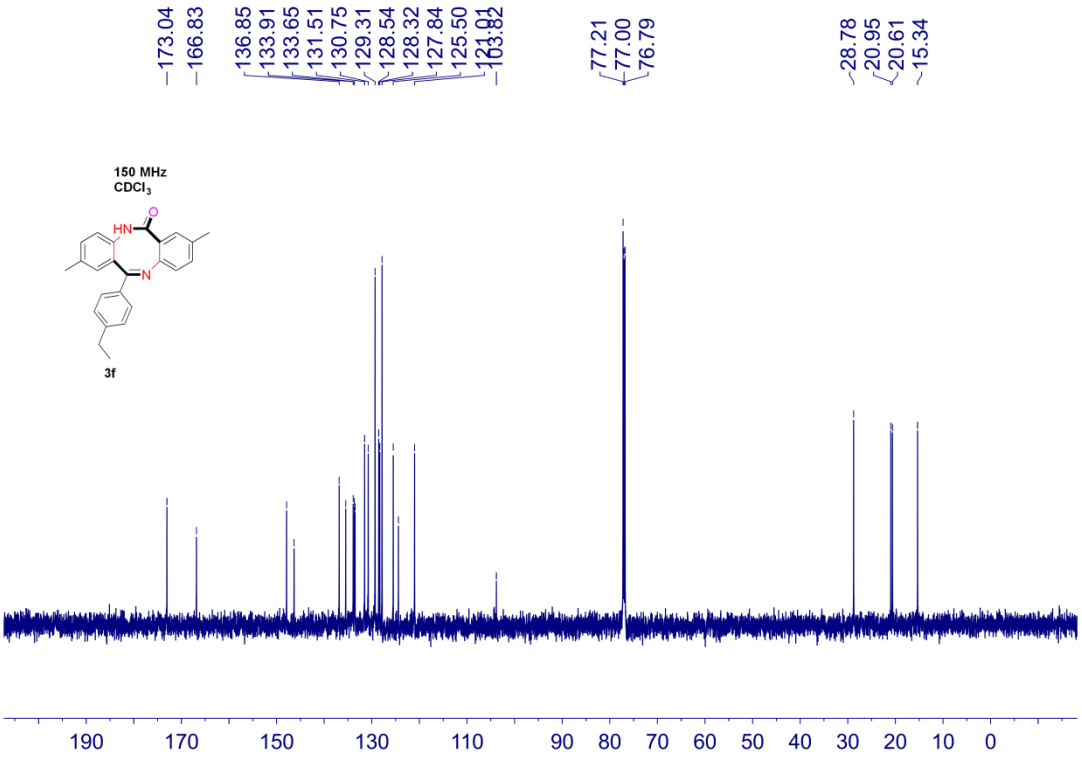
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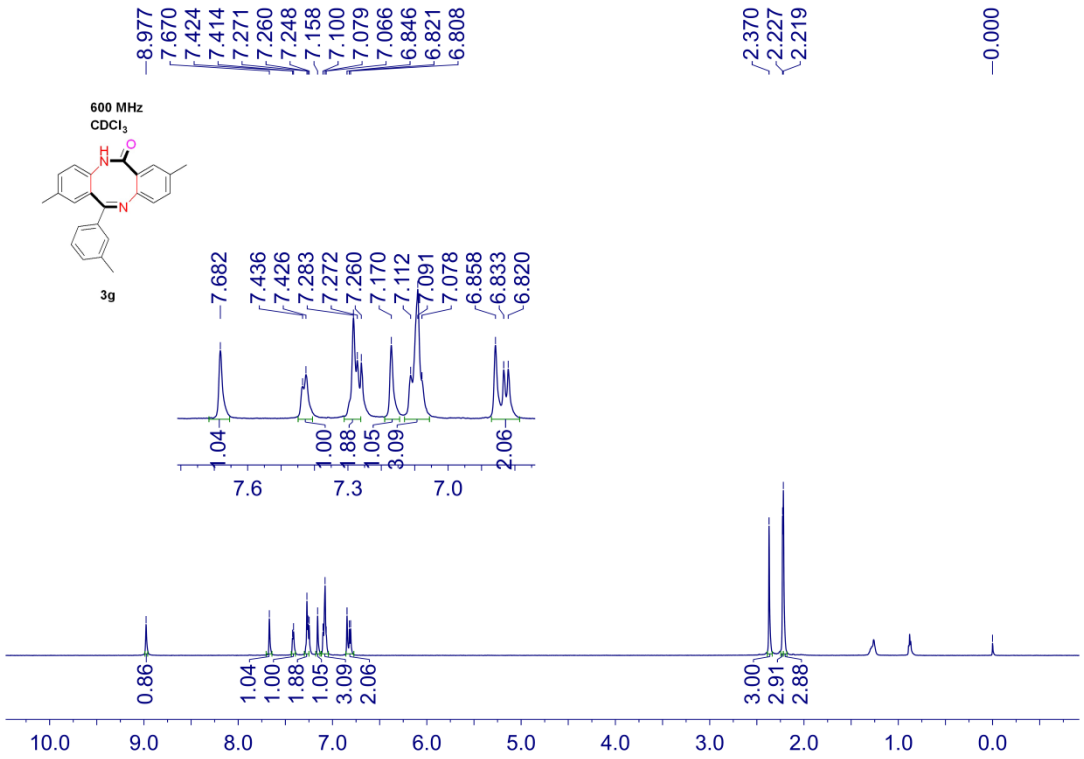
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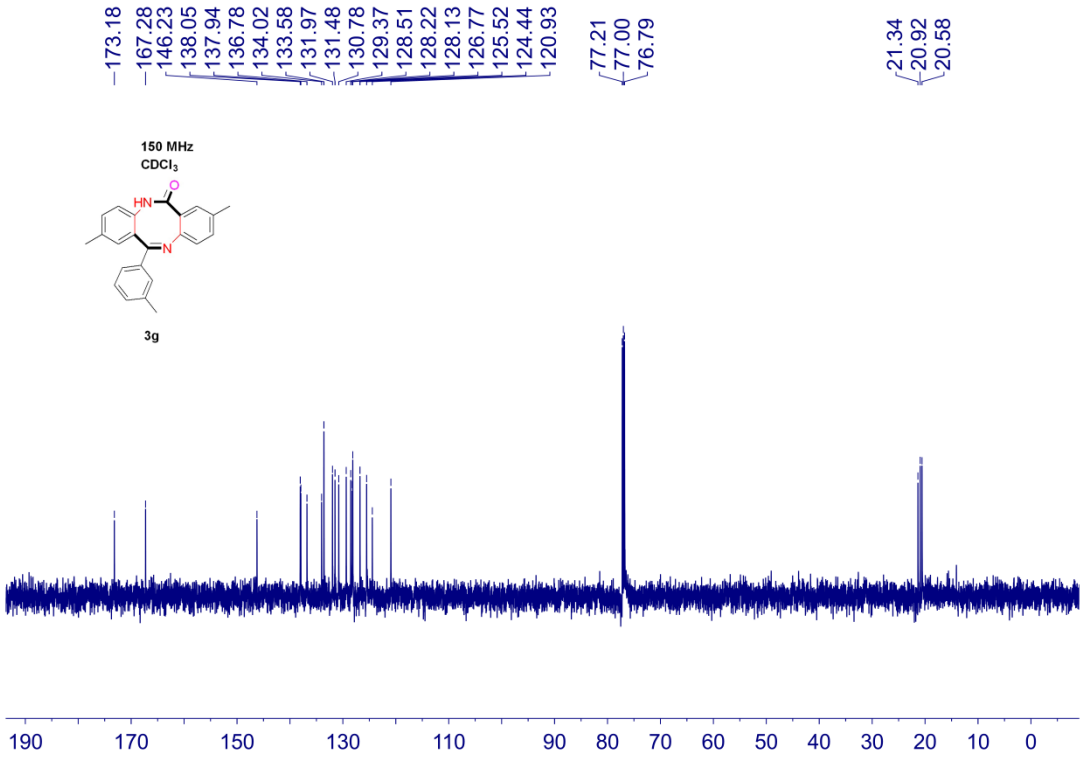
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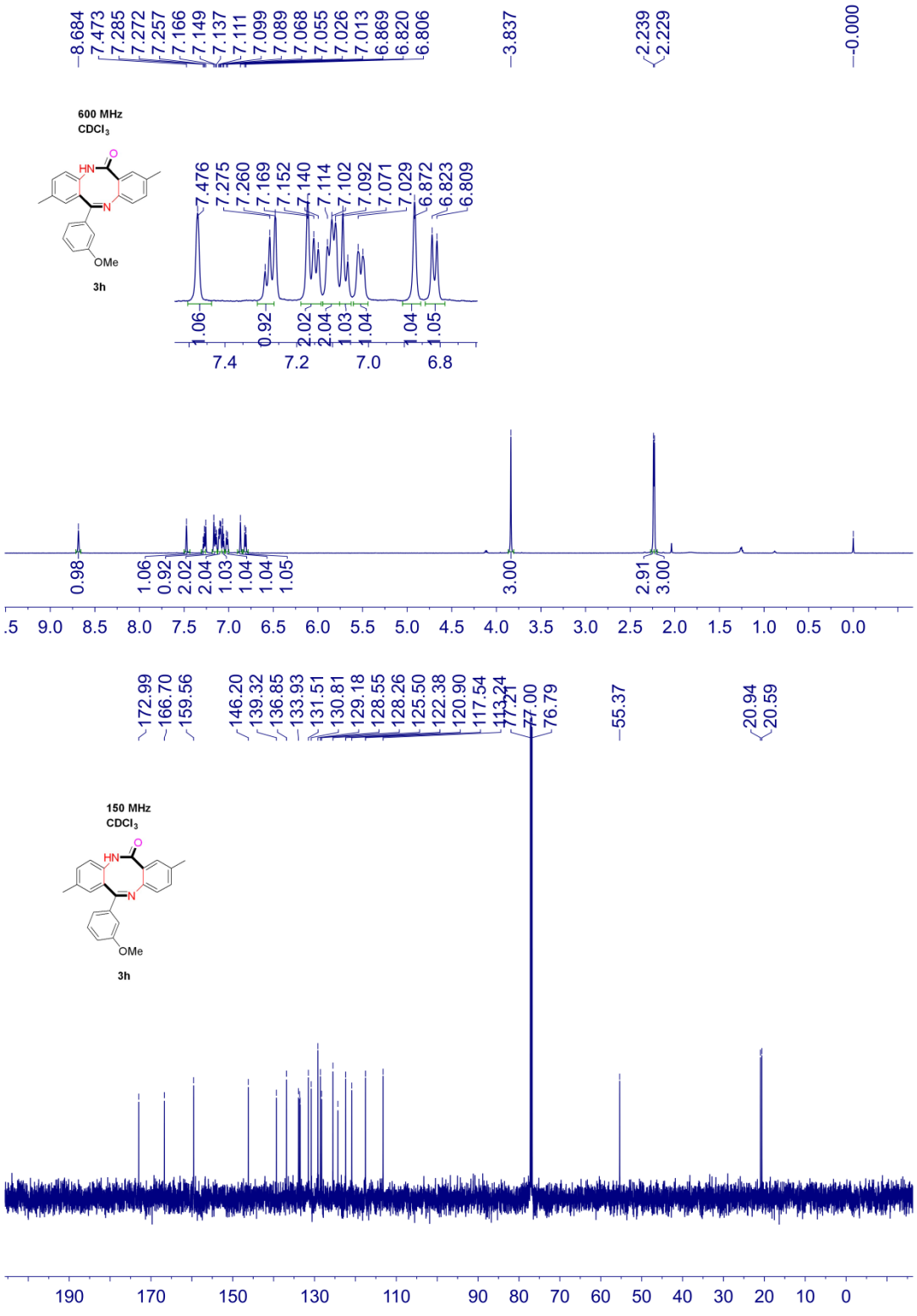
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1.04
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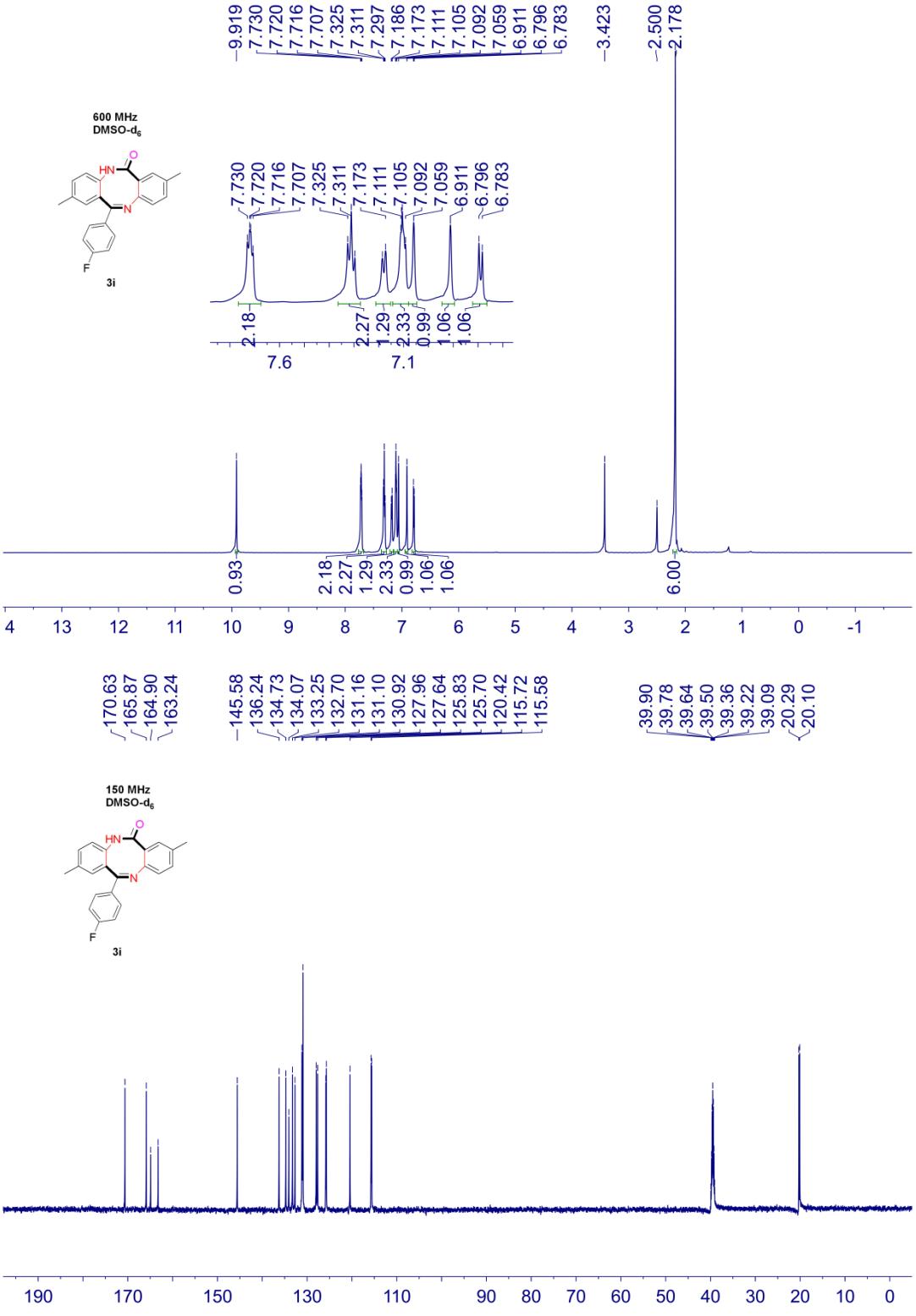
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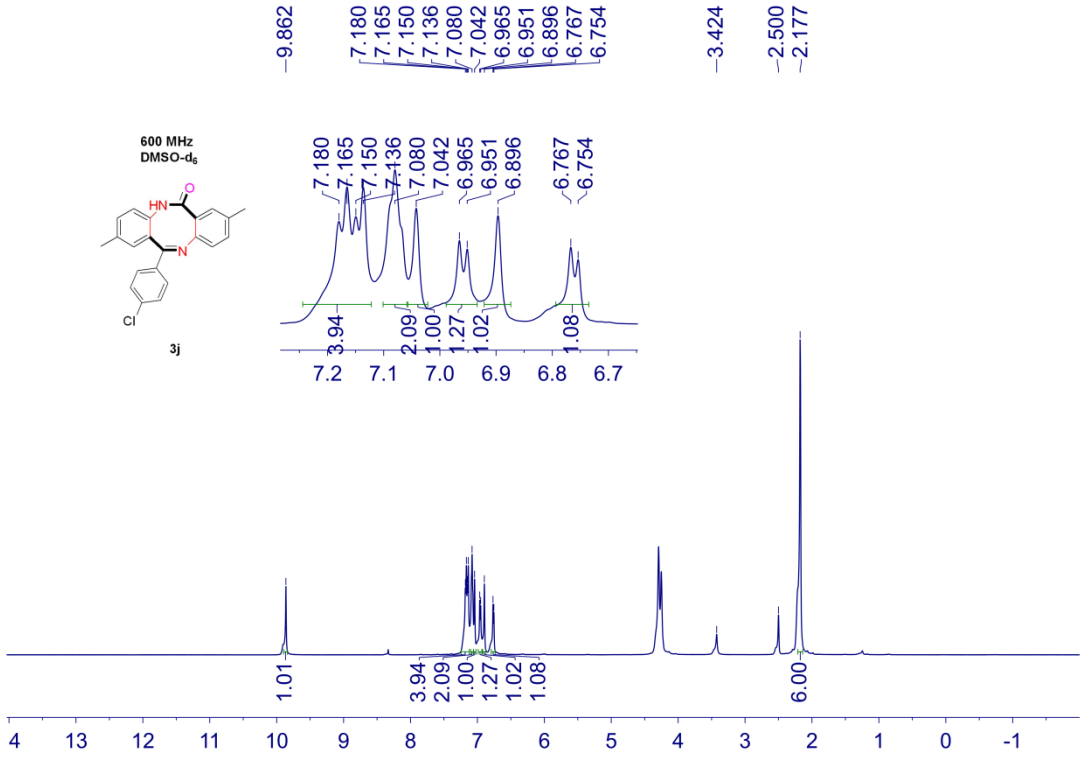
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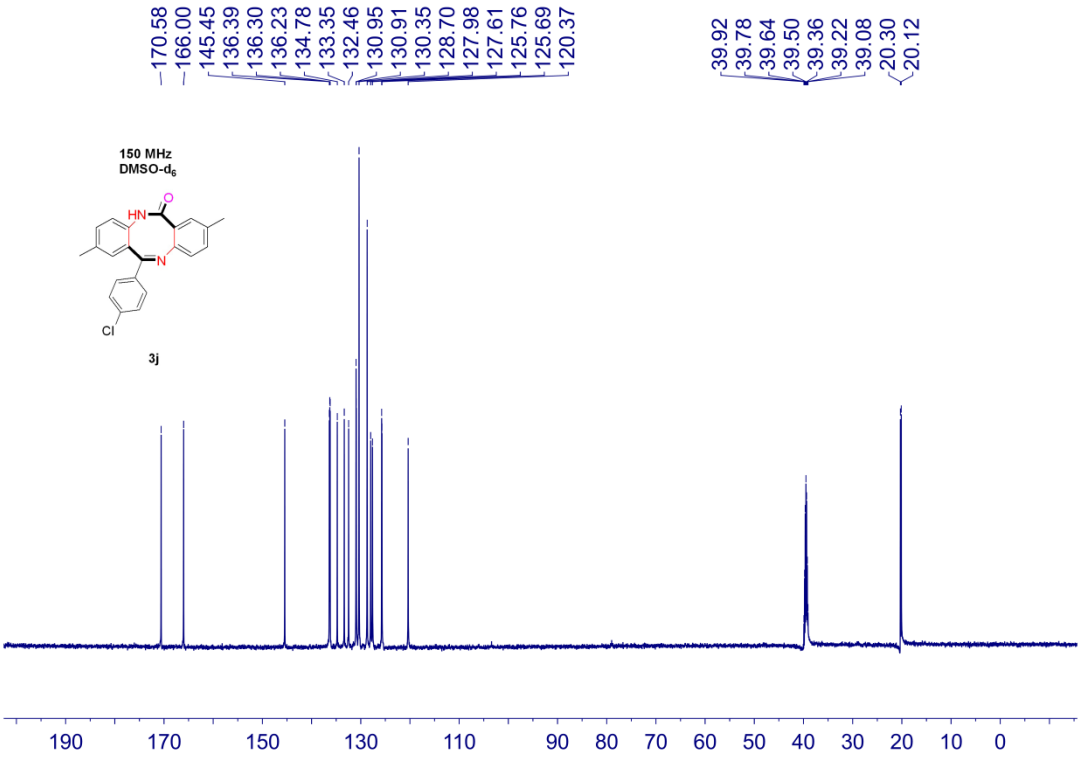
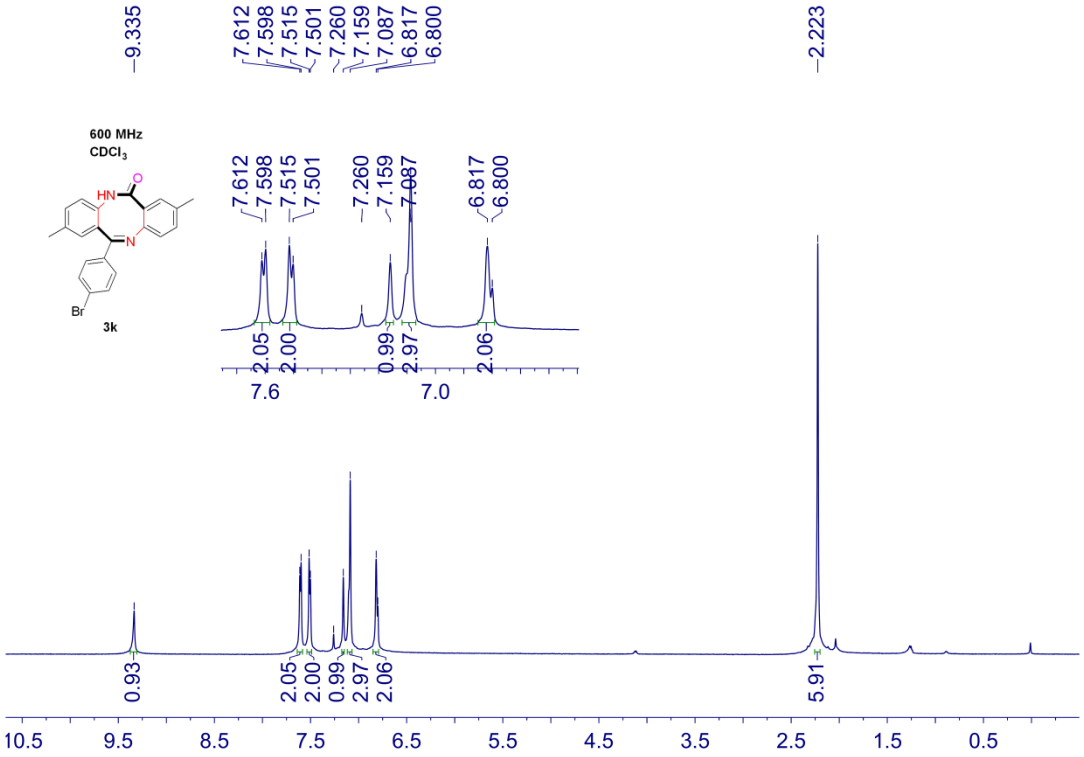
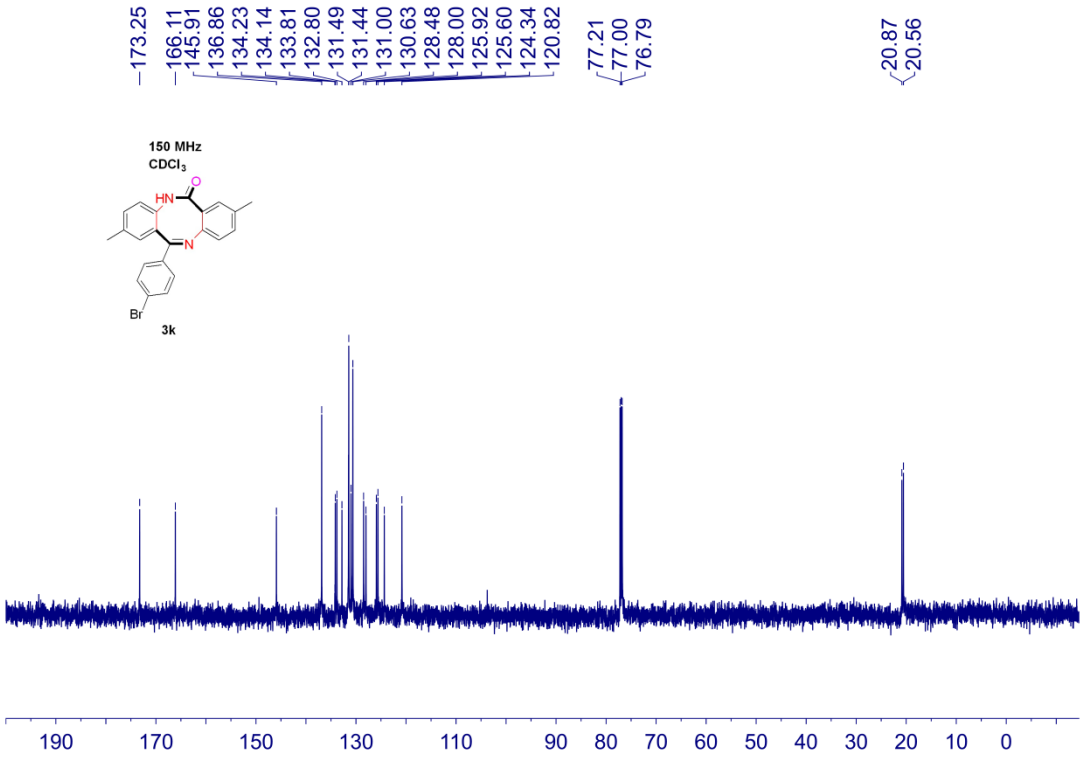
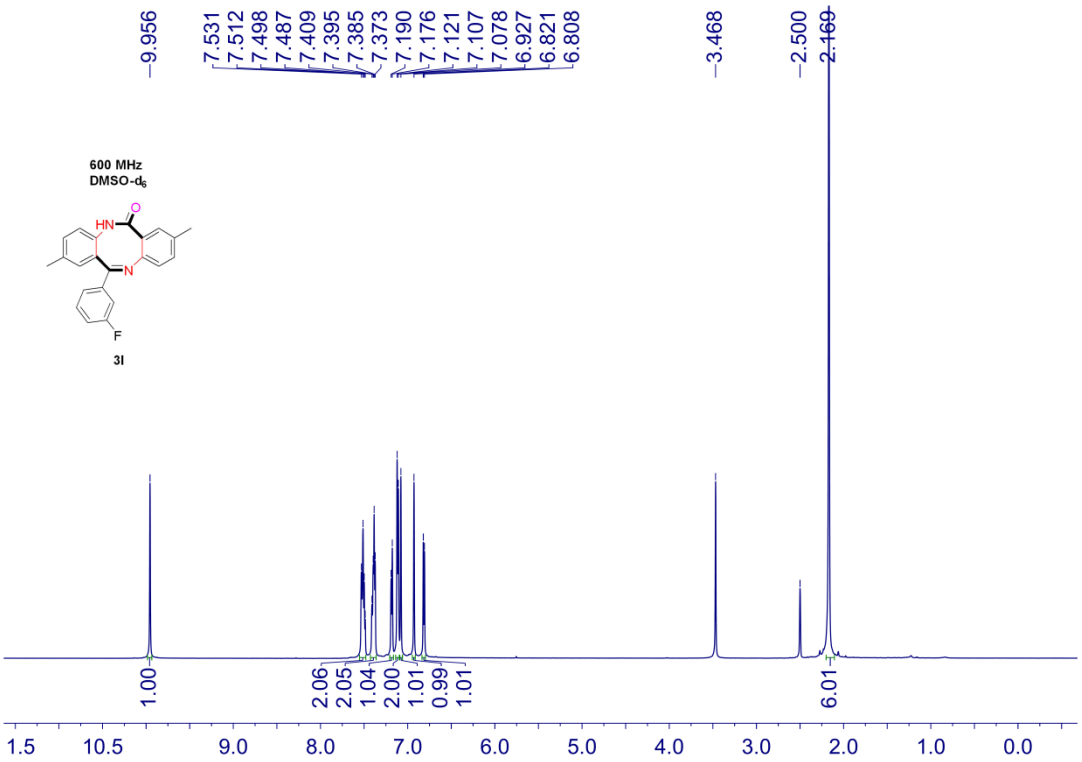
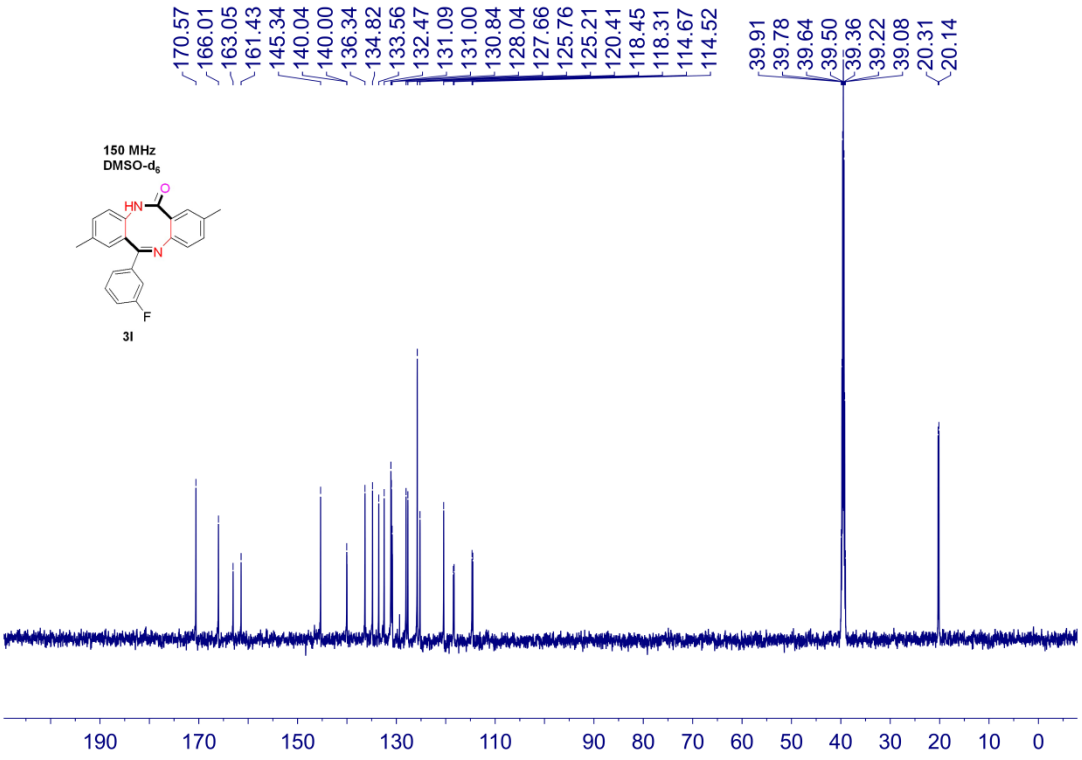
7.165
7.150
7.136
7.080
7.042
6.965
6.951
6.896
6.767
6.754
3.424
2.500
2.177
600 MHz
DMSO-d6
HN
O
N
Cl
3j
3.94
2.09
1.00
1.27
1.02
1.08
7.2
7.1
7.0
6.9
6.8
6.7
1.01
6.00
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

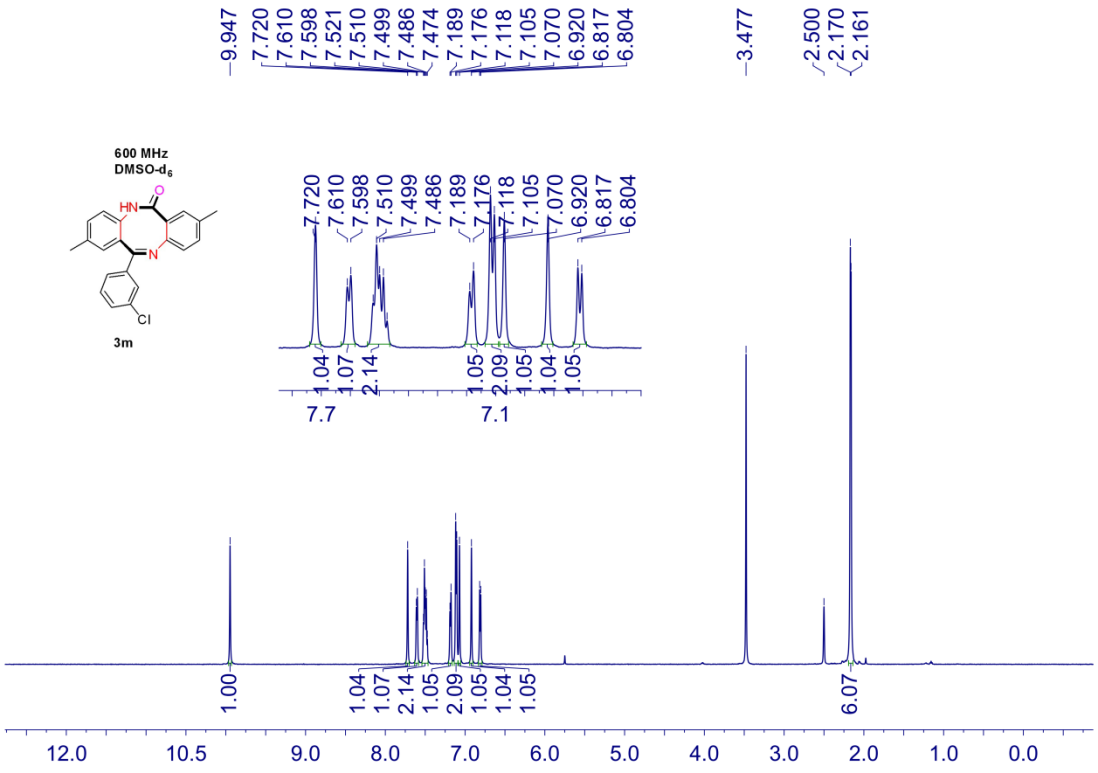

170.58
166.00
145.45
136.39
136.30
136.23
134.78
133.35
132.46
130.95
130.91
130.35
128.70
127.98
127.61
125.76
125.69
120.37
39.92
39.78
39.64
39.50
39.36
39.22
39.08
20.30
20.12
150 MHz
DMSO-d6
HN
O
N
Cl
3j
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

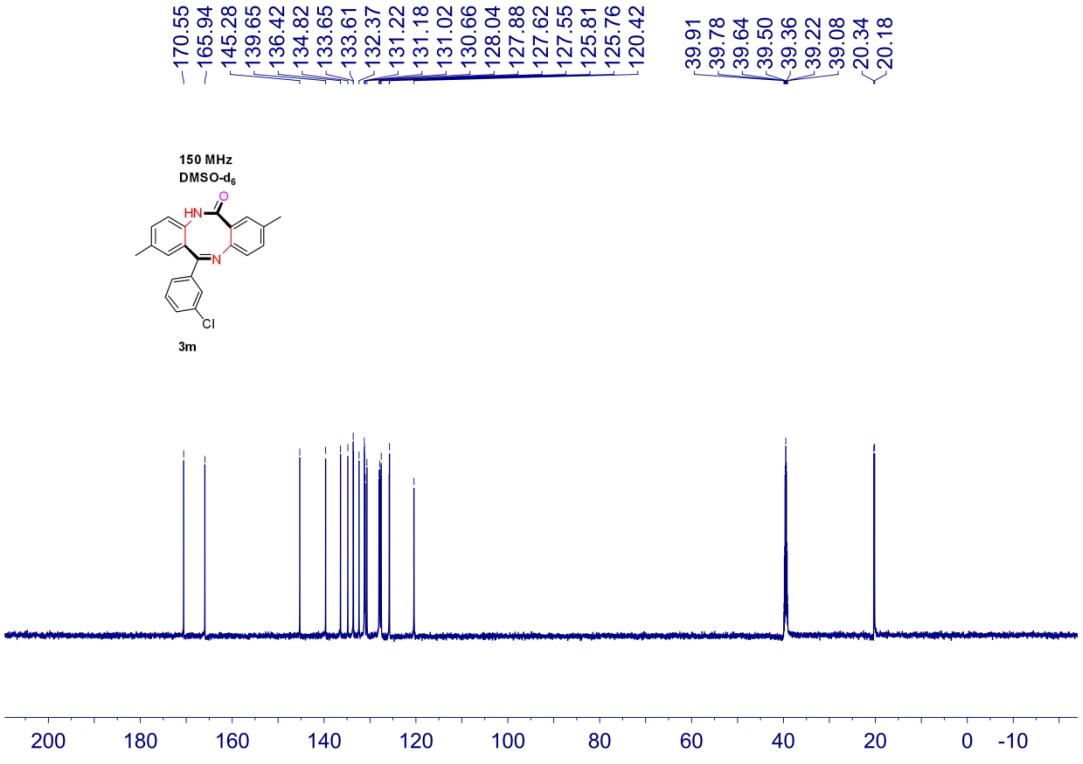

9.335
7.612
7.598
7.515
7.501
7.260
7.159
7.087
6.817
6.800
2.223
600 MHz
CDCl3
HN
O
N
Br
3k
2.05
2.00
0.99
2.97
2.06
7.6
7.0
0.93
5.91
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

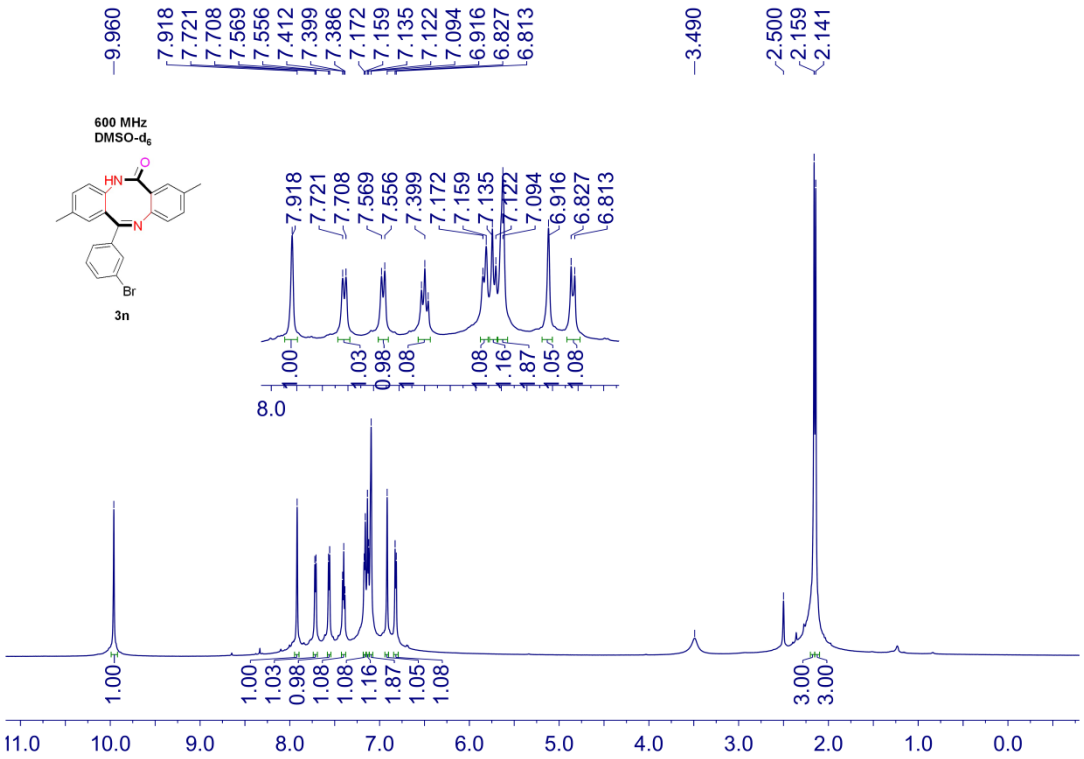

173.25
166.11
145.91
136.86
134.23
134.14
133.81
132.80
131.49
131.44
131.00
130.63
128.48
128.00
125.92
125.60
124.34
120.82
77.21
77.00
76.79
20.87
20.56
150 MHz
CDCl3
HN
O
N
Br
3k
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

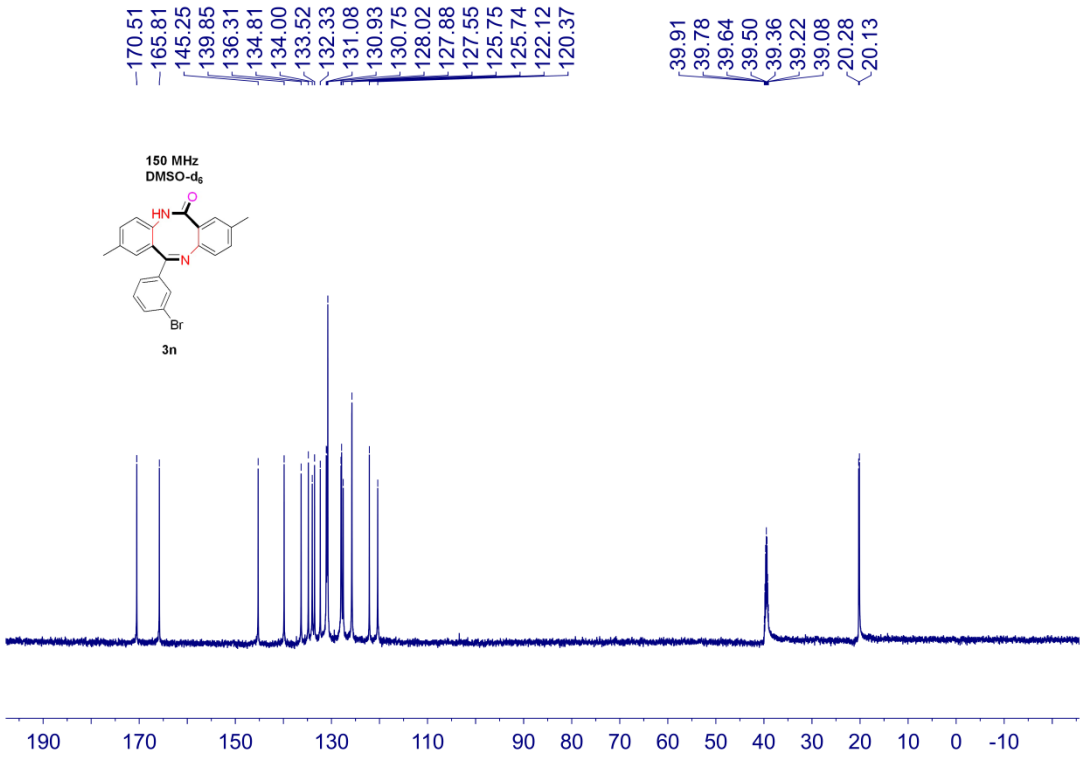

9.956
7.531
7.512
7.498
7.487
7.409
7.395
7.385
7.373
7.190
7.176
7.121
7.107
7.078
6.927
6.821
6.808
3.468
2.500
2.160
600 MHz
DMSO-d6
HN
O
N
F
3l
1.00
2.06
2.05
1.04
2.00
1.01
0.99
1.01
6.01
1.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

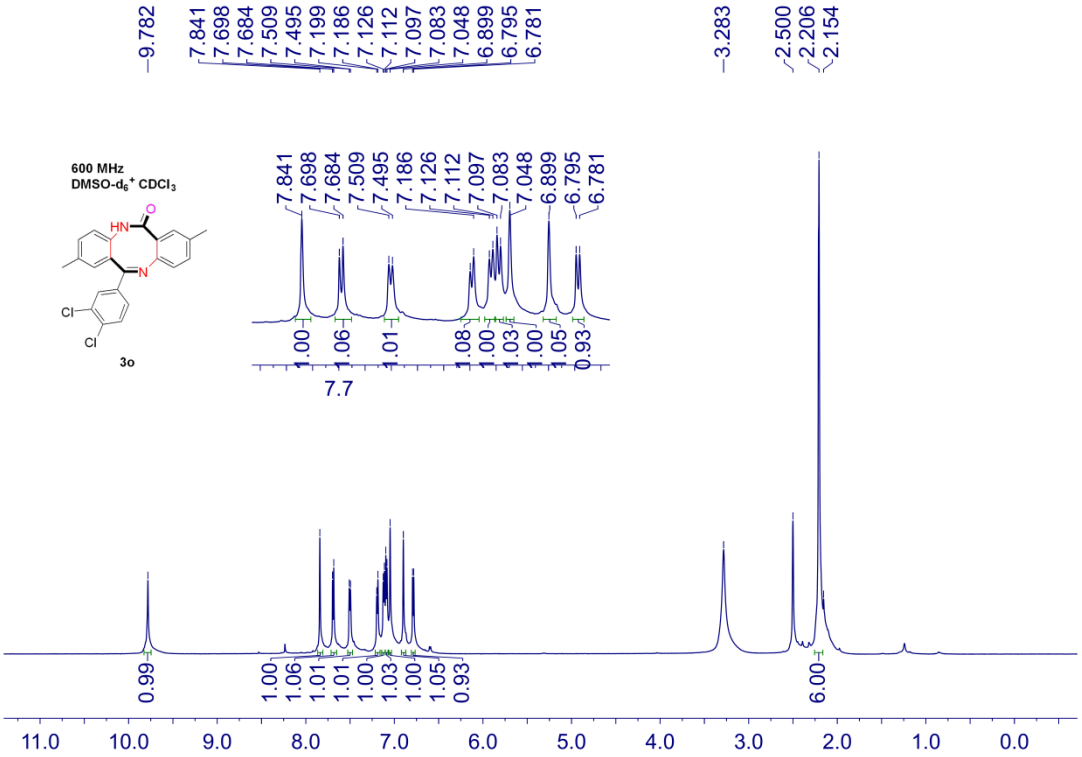

170.57
166.01
163.05
161.43
145.34
140.04
140.00
136.34
134.82
133.56
132.47
131.09
131.00
130.84
128.04
127.66
125.76
125.21
120.41
118.45
118.31
114.67
114.52
39.91
39.78
39.64
39.50
39.36
39.22
39.08
20.31
20.14
150 MHz
DMSO-d6
HN
O
N
F
3l
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

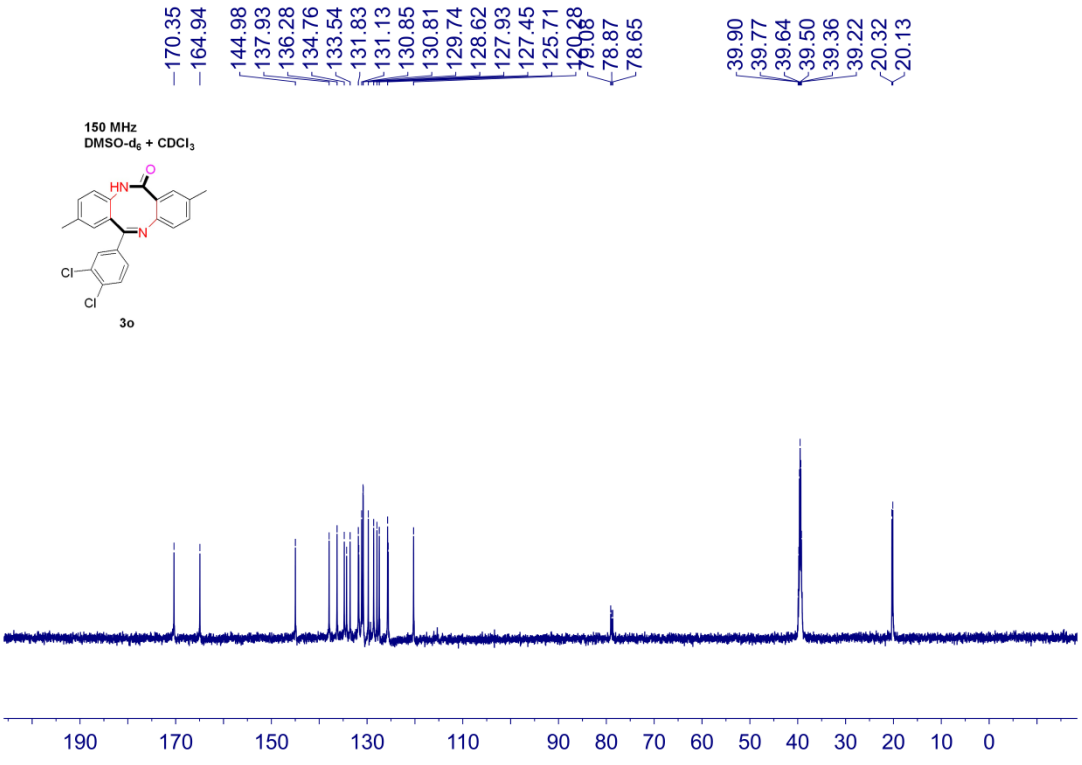

9.947
7.720
7.610
7.598
7.521
7.510
7.499
7.486
7.474
7.189
7.176
7.118
7.105
7.070
6.920
6.817
6.804
3.477
2.500
2.170
2.161
600 MHz
DMSO-d6
HN
O
N
Cl
3m
1.04
1.07
2.14
1.05
2.09
1.05
1.04
1.05
7.7
7.1
1.00
6.07
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

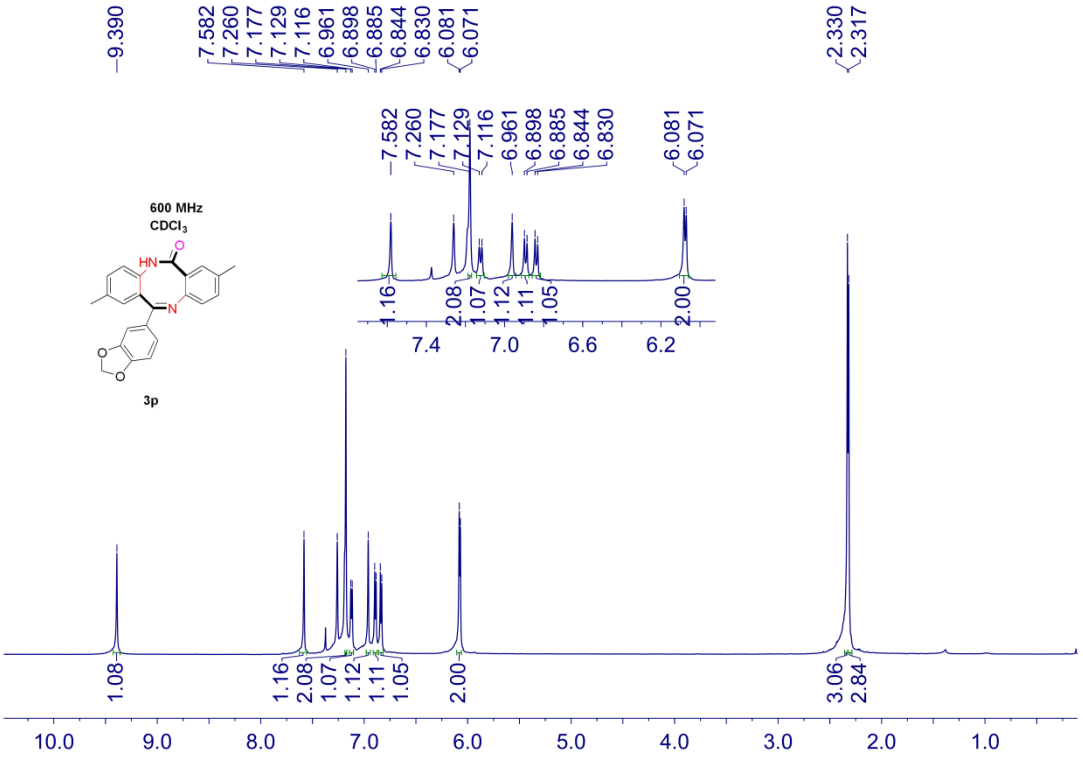

170.55
165.94
145.28
139.65
136.42
134.82
133.65
133.61
132.37
131.22
131.18
131.02
130.66
128.04
127.88
127.62
127.55
125.81
125.76
120.42
39.91
39.78
39.64
39.50
39.36
39.22
39.08
20.34
20.18
150 MHz
DMSO-d6
HN
O
N
Cl
3m
200
180
160
140
120
100
80
60
40
20
0
-10

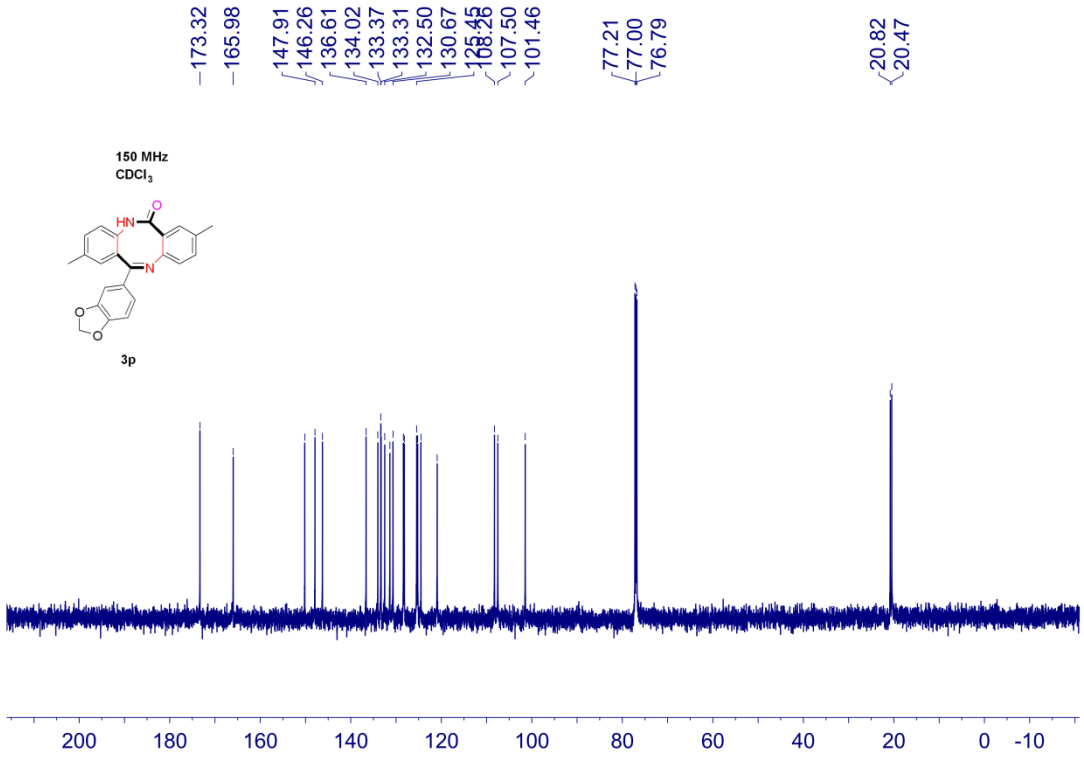

9.960
7.918
7.721
7.708
7.569
7.556
7.412
7.399
7.386
7.172
7.159
7.135
7.122
7.094
6.916
6.827
6.813
3.490
2.500
2.159
2.141
600 MHz
DMSO-d6
HN
O
N
Br
3n
8.0
1.00
1.03
0.98
1.08
1.08
1.16
1.87
1.05
1.08
3.00
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

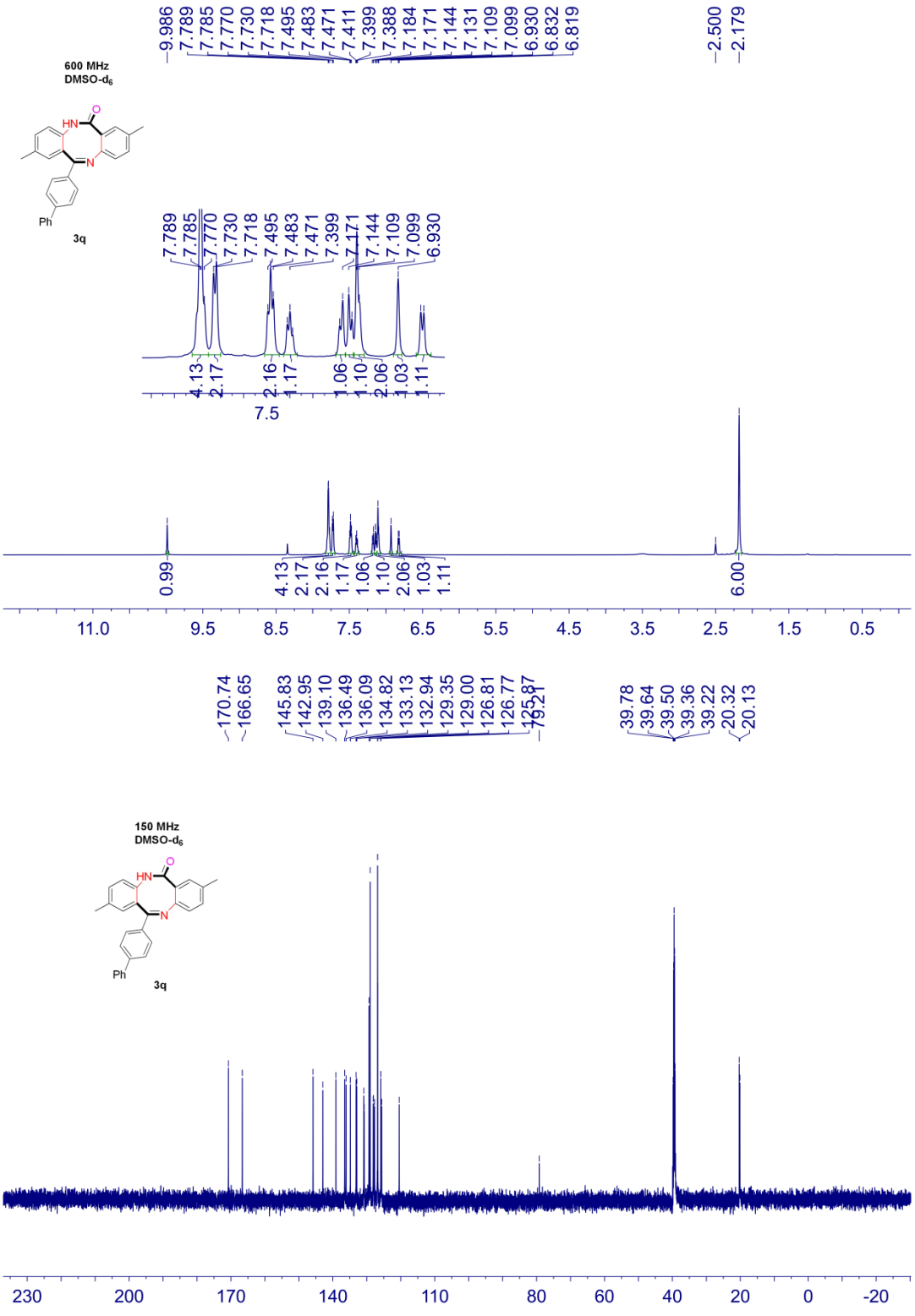

170.51
165.81
145.25
139.85
136.31
134.81
134.00
133.52
132.33
131.08
130.93
130.75
128.02
127.88
127.55
125.75
125.74
122.12
120.37
39.91
39.78
39.64
39.50
39.36
39.22
39.08
20.28
20.13
150 MHz
DMSO-d6
HN
O
N
Br
3n
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10

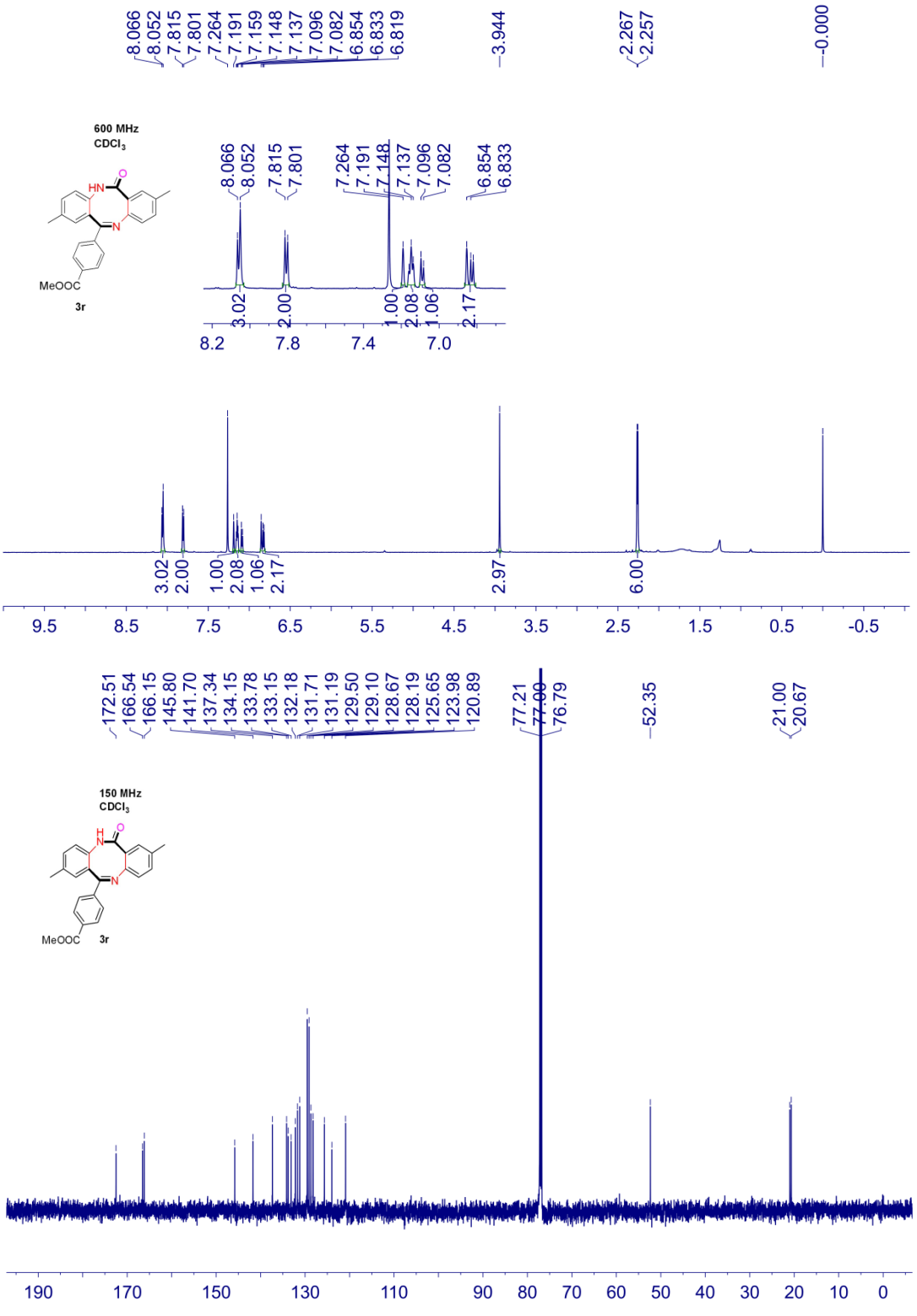

9.782
7.841
7.698
7.684
7.509
7.495
7.199
7.186
7.126
7.112
7.097
7.083
7.048
6.899
6.795
6.781
3.283
2.500
2.206
2.154
600 MHz
DMSO-d6 + CDCl3
HN
O
N
Cl
Cl
3o
7.7
0.99
1.00
1.06
1.01
1.01
1.00
1.03
1.00
1.05
0.93
6.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

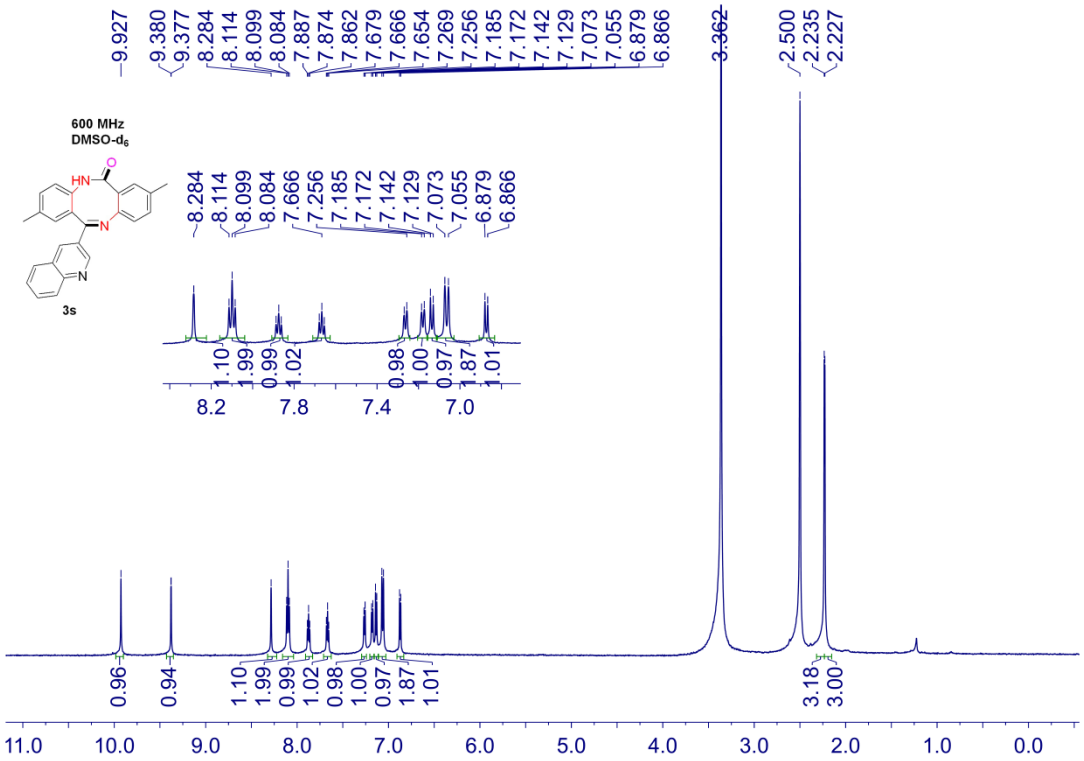

170.35
164.94
144.98
137.93
136.28
134.76
133.54
131.83
131.13
130.85
130.81
129.74
128.62
127.93
127.45
125.71
120.28
79.08
78.87
78.65
39.90
39.77
39.64
39.50
39.36
39.22
20.32
20.13
150 MHz
DMSO-d6 + CDCl3
HN
O
N
Cl
Cl
3o
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

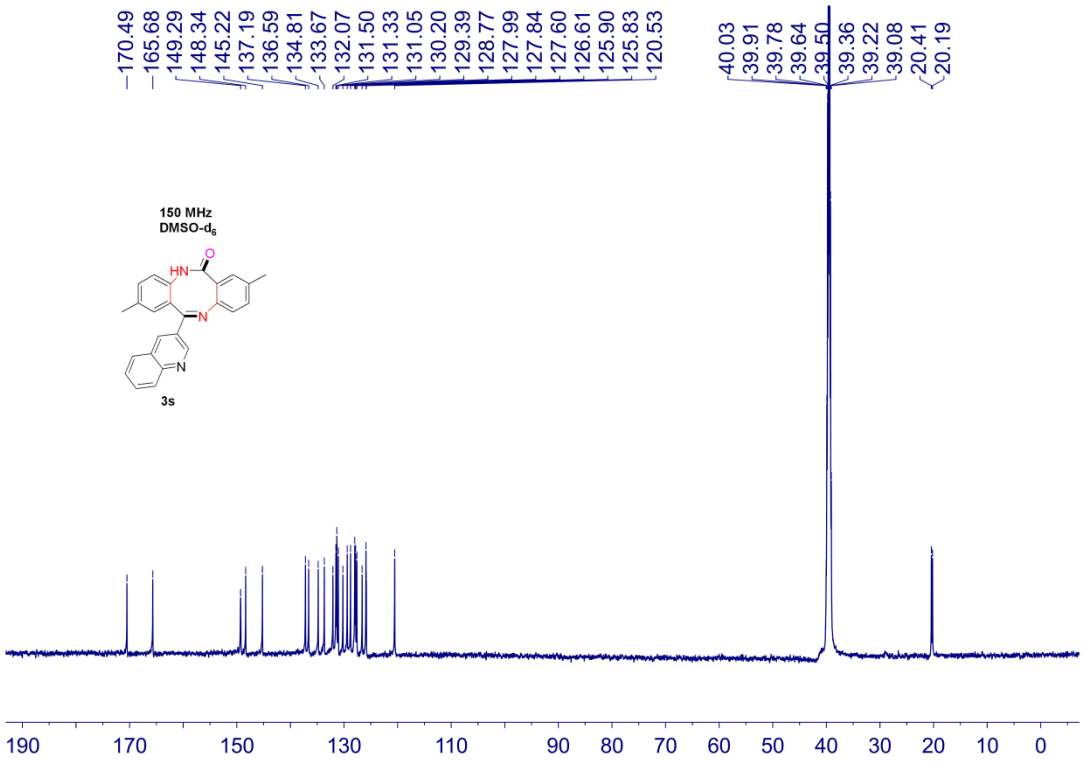

9.390
7.582
7.260
7.177
7.129
7.116
6.961
6.898
6.885
6.844
6.830
6.081
6.071
2.330
2.317
600 MHz
CDCl3
3p
1.08
1.16
2.08
1.07
1.12
1.11
1.05
2.00
3.06
2.84
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.4
7.0
6.6
6.2

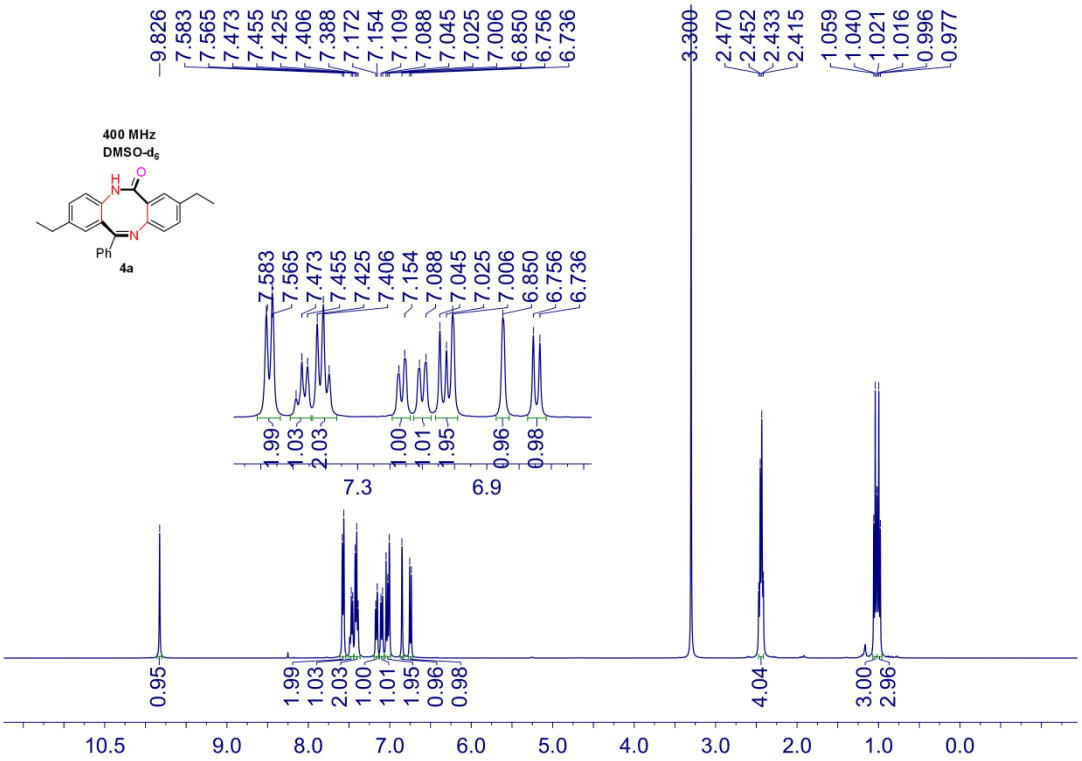

173.32
165.98
147.91
146.26
136.61
134.02
133.37
133.31
132.50
130.67
125.45
108.26
107.50
101.46
77.21
77.00
76.79
20.82
20.47
150 MHz
CDCl3
3p
200
180
160
140
120
100
80
60
40
20
0
-10

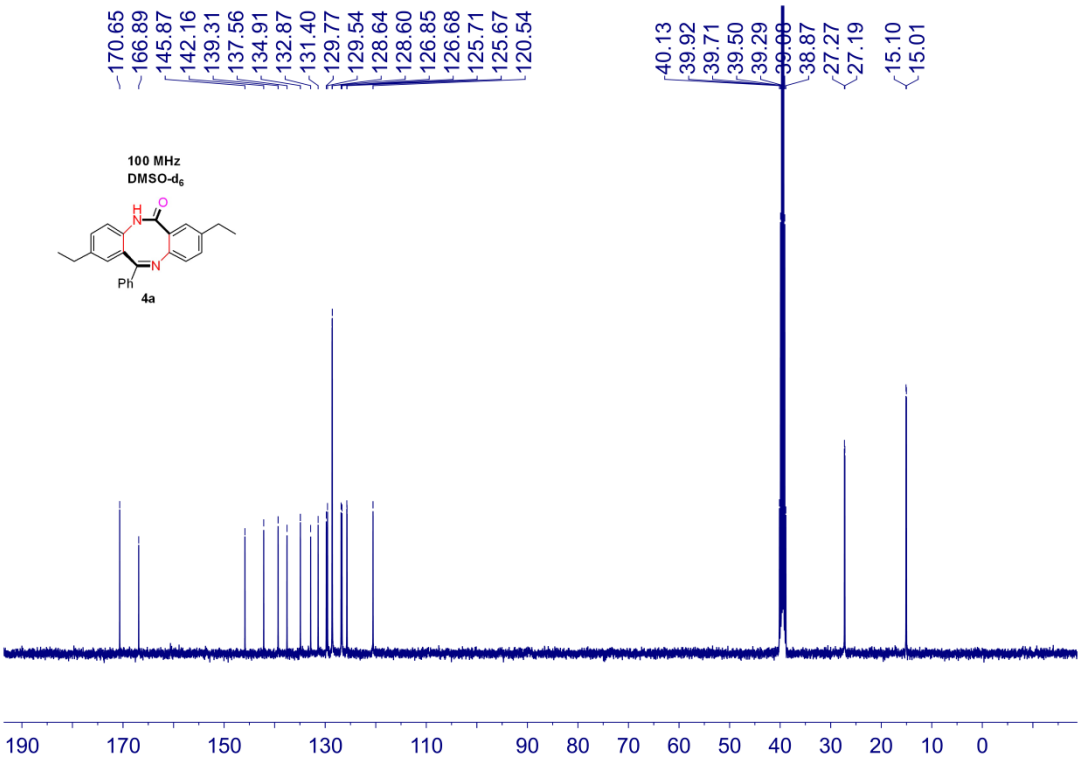

600 MHz
DMSO-d6
3q
9.986
7.789
7.785
7.770
7.730
7.718
7.495
7.483
7.471
7.411
7.399
7.388
7.184
7.171
7.144
7.131
7.109
7.099
6.930
6.832
6.819
2.500
2.179
4.13
2.17
2.16
1.17
1.06
1.10
2.06
1.03
1.11
0.99
6.00
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
170.74
166.65
145.83
142.95
139.10
136.49
136.09
134.82
133.13
132.94
129.35
129.00
126.81
126.77
125.87
79.21
39.78
39.64
39.50
39.36
39.22
20.32
20.13
150 MHz
DMSO-d6
3q
230
200
170
140
110
80
60
40
20
0
-20

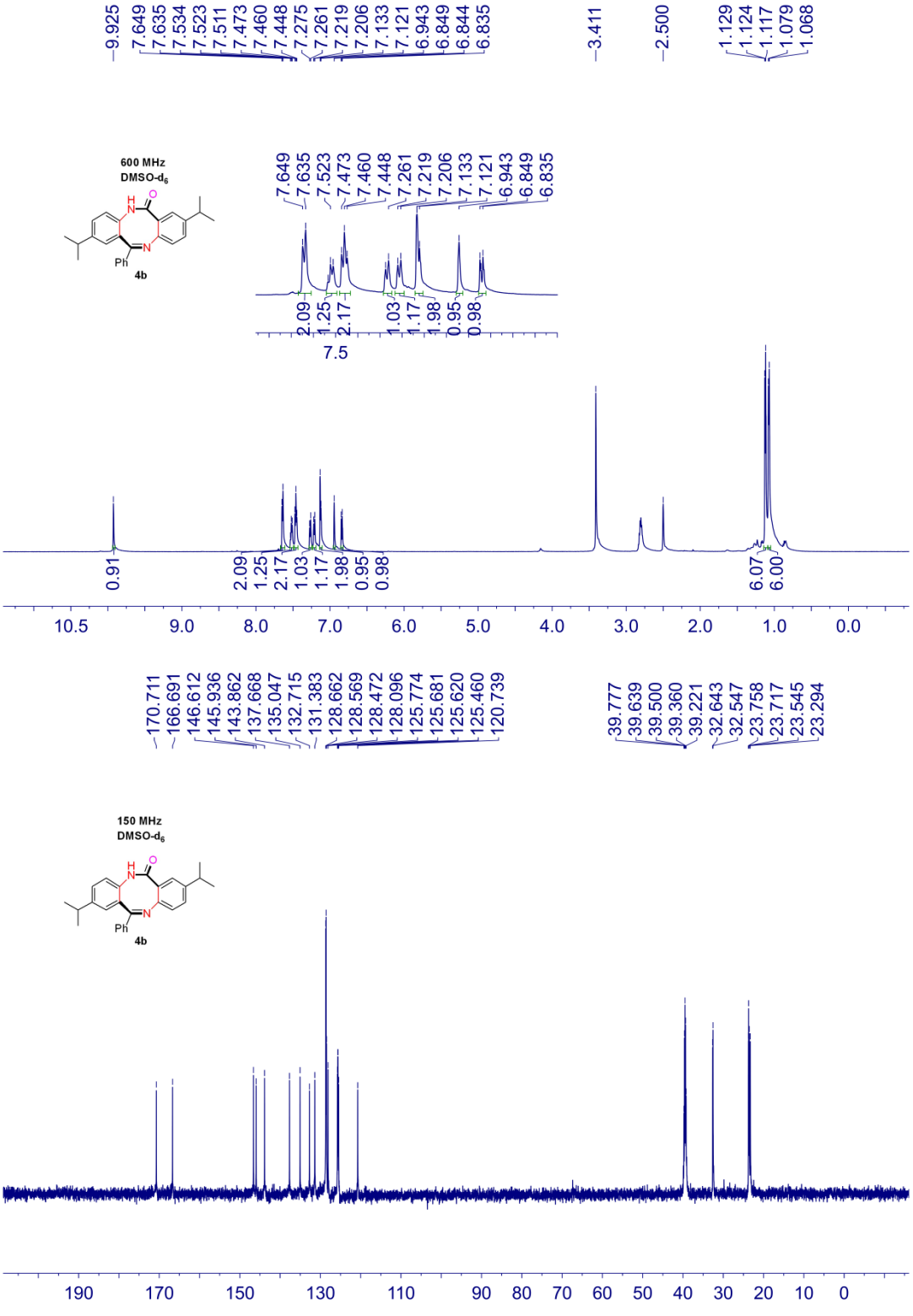

8.066
8.052
7.815
7.801
7.264
7.191
7.159
7.148
7.137
7.096
7.082
6.854
6.833
6.819
3.944
2.267
2.257
0.000
600 MHz
CDCl3
HN
O
N
MeOOC
3r
3.02
2.00
1.00
2.08
1.06
2.17
2.97
6.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
8.2
7.8
7.4
7.0
172.51
166.54
166.15
145.80
141.70
137.34
134.15
133.78
133.15
132.18
131.71
131.19
129.50
129.10
128.67
128.19
125.65
123.98
120.89
77.21
77.00
76.79
52.35
21.00
20.67
150 MHz
CDCl3
H
N
O
N
MeOOC
3r
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

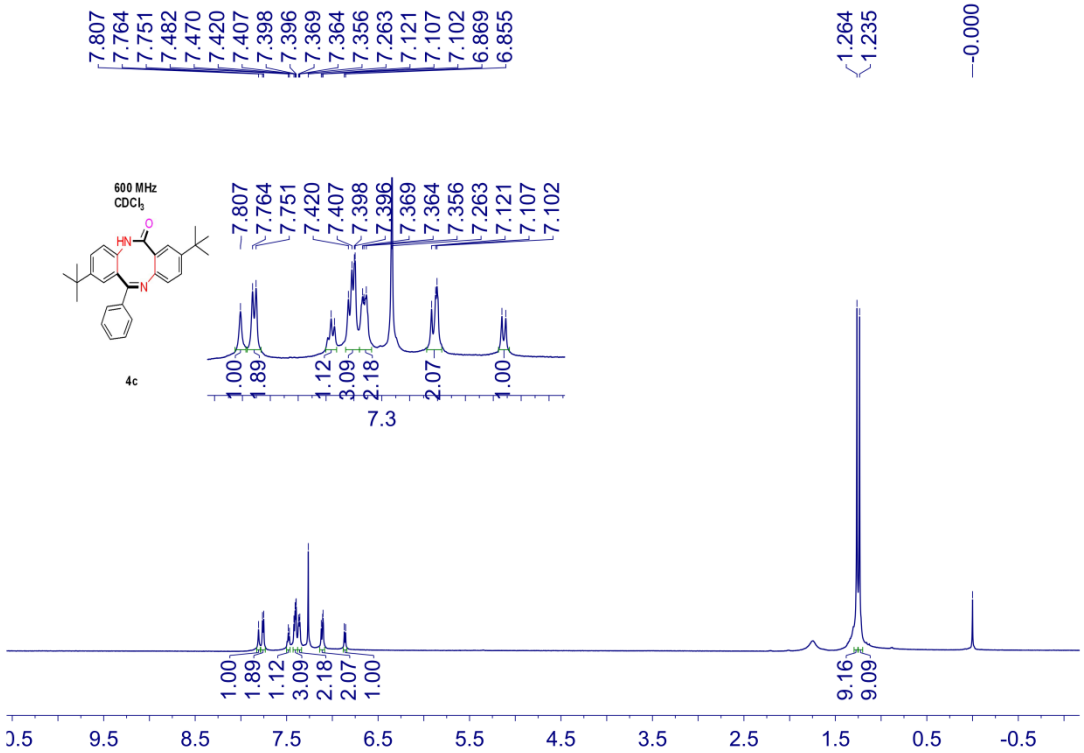

600 MHz
DMSO-d6
3s

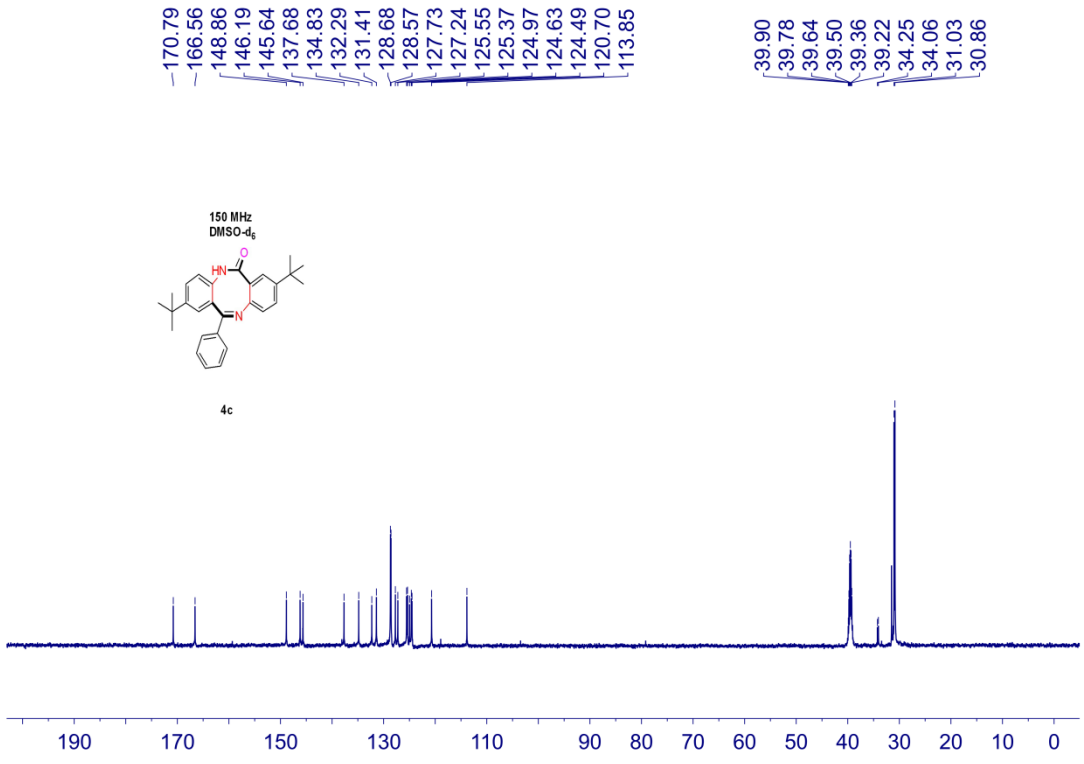

150 MHz
DMSO-d6
3s

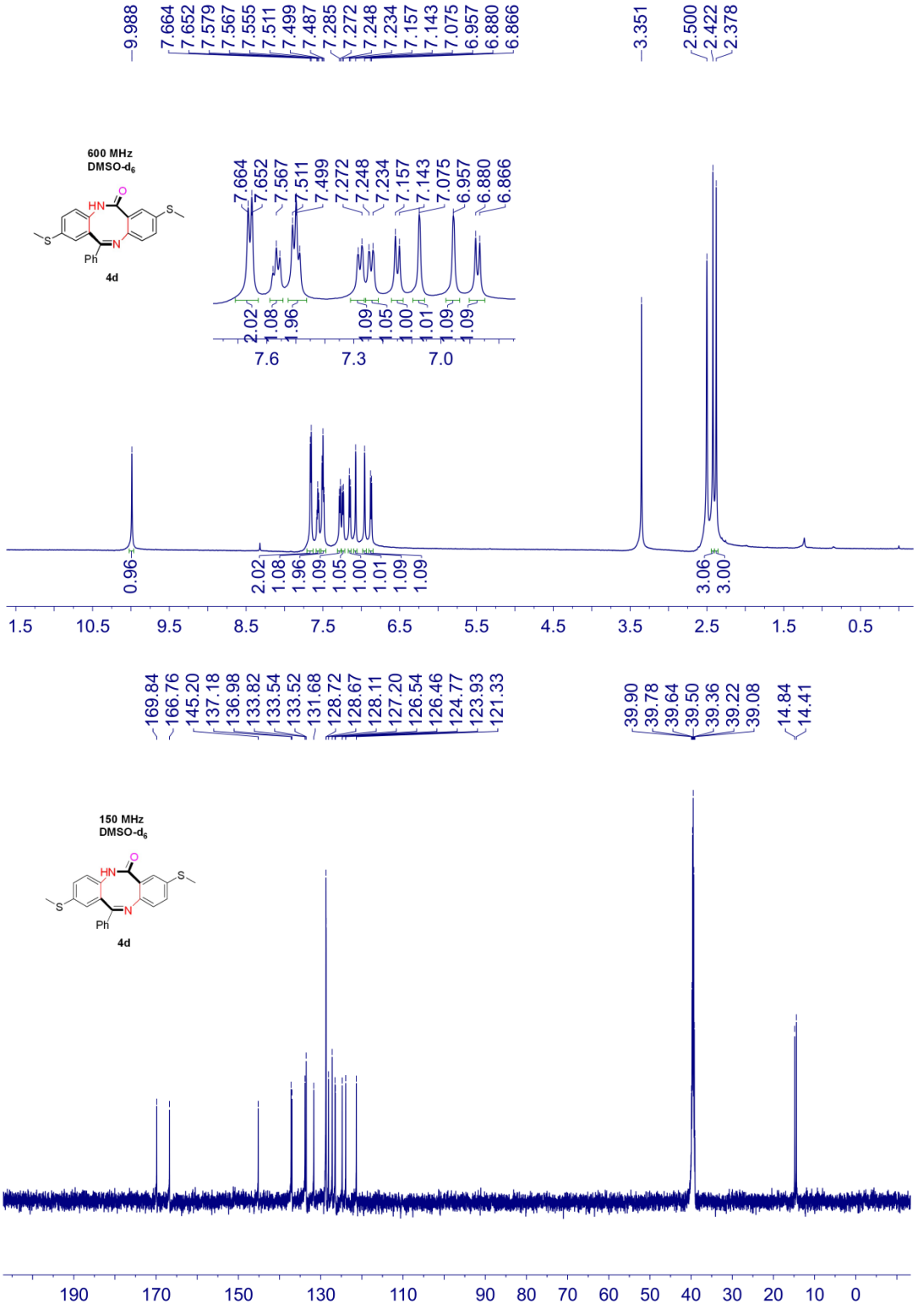

9.826
7.583
7.565
7.473
7.455
7.425
7.406
7.388
7.172
7.154
7.109
7.088
7.045
7.025
7.006
6.850
6.756
6.736
3.300
2.470
2.452
2.433
2.415
1.059
1.040
1.021
1.016
0.996
0.977
400 MHz
DMSO-d6
4a
0.95
1.99
1.03
2.03
1.00
1.01
1.95
0.96
0.98
4.04
3.00
2.96
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

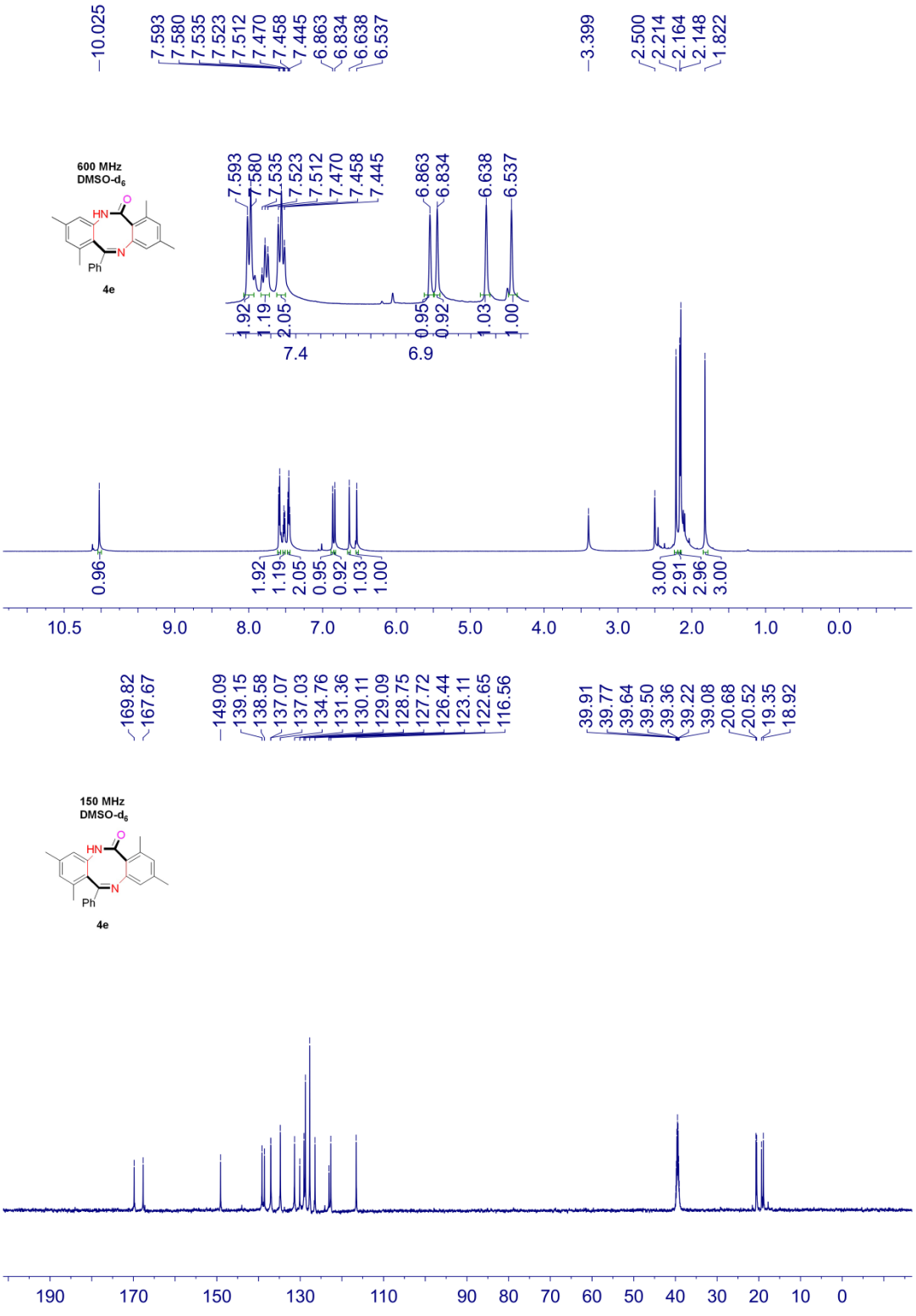

170.65
166.89
145.87
142.16
139.31
137.56
134.91
132.87
131.40
129.77
129.54
128.64
128.60
126.85
126.68
125.71
125.67
120.54
40.13
39.92
39.71
39.50
39.29
39.08
38.87
27.27
27.19
15.10
15.01
100 MHz
DMSO-d6
4a
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

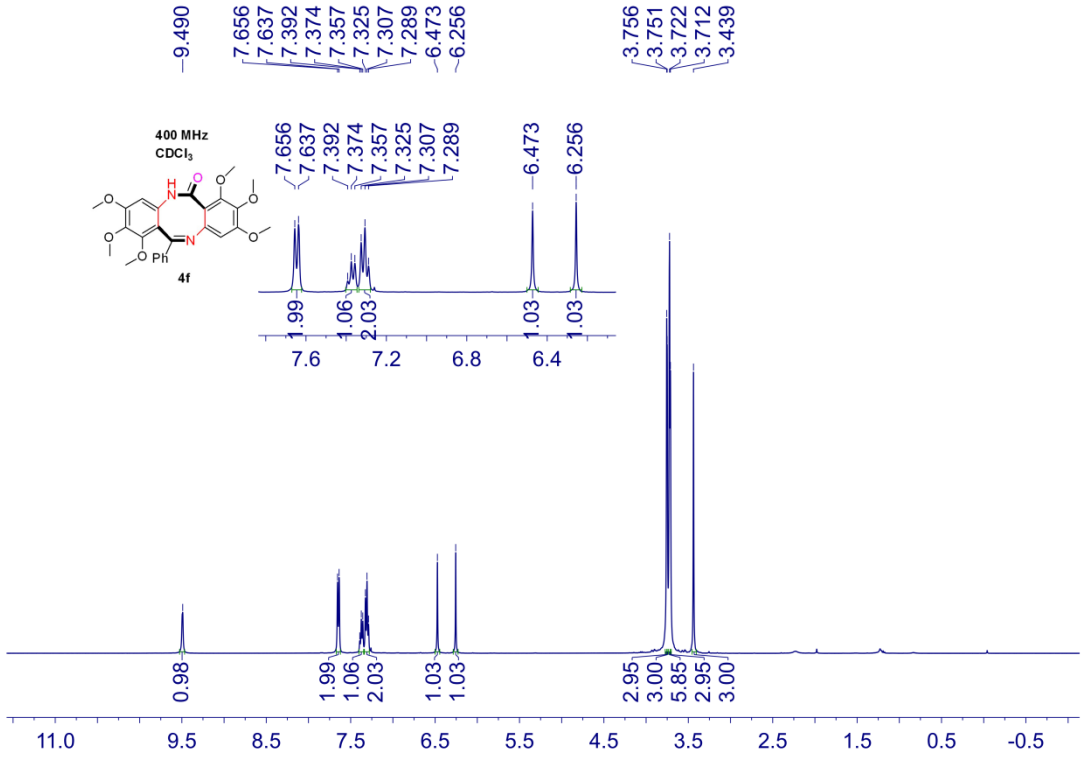

9.925
7.649
7.635
7.534
7.523
7.511
7.473
7.460
7.448
7.275
7.261
7.219
7.206
7.133
7.121
6.943
6.849
6.844
6.835
3.411
2.500
1.129
1.124
1.117
1.079
1.068
600 MHz
DMSO-d6
4b
2.09
1.25
2.17
1.03
1.17
1.98
0.95
0.98
7.5
0.91
6.07
6.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
170.711
166.691
146.612
145.936
143.862
137.668
135.047
132.715
131.383
128.662
128.569
128.472
128.096
125.774
125.681
125.620
125.460
120.739
39.777
39.639
39.500
39.360
39.221
32.643
32.547
23.758
23.717
23.545
23.294
150 MHz
DMSO-d6
4b
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

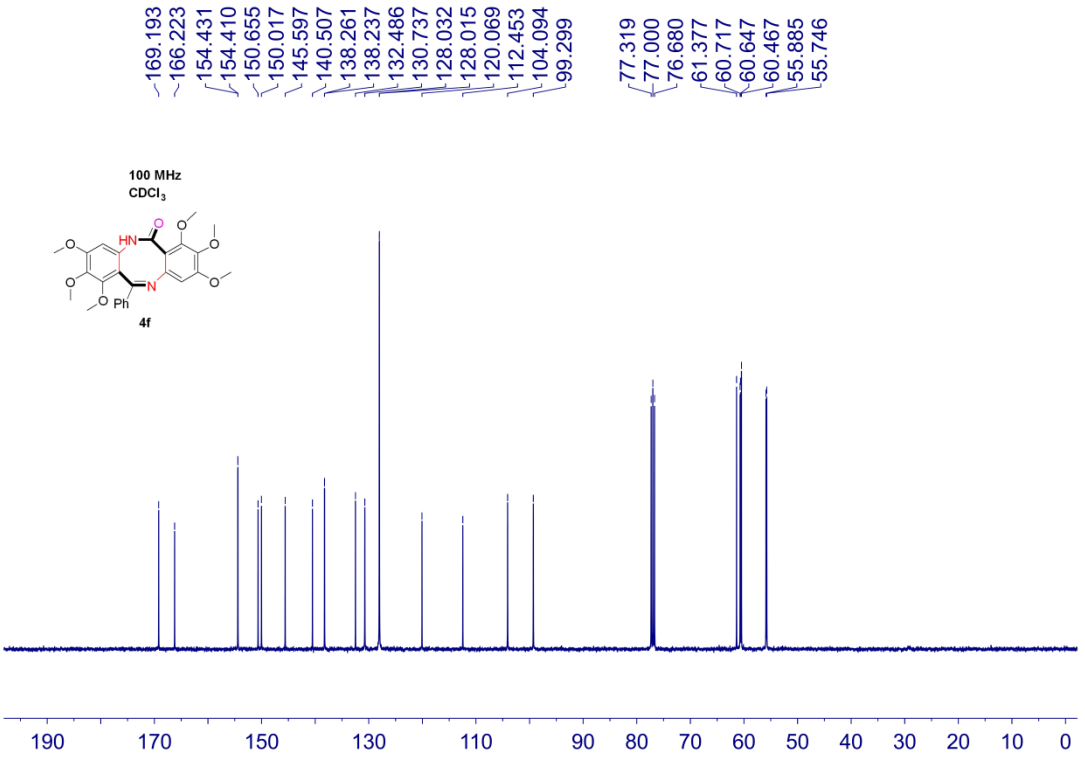

7.807
7.764
7.751
7.482
7.470
7.420
7.407
7.398
7.396
7.369
7.364
7.356
7.263
7.121
7.107
7.102
6.869
6.855
1.264
1.235
-0.000
600 MHz
CDCl3
4c
1.00
1.89
1.12
3.09
2.18
2.07
1.00
9.16
9.09
7.3
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


170.79
166.56
148.86
146.19
145.64
137.68
134.83
132.29
131.41
128.68
128.57
127.73
127.24
125.55
125.37
124.97
124.63
124.49
120.70
113.85
39.90
39.78
39.64
39.50
39.36
39.22
34.25
34.06
31.03
30.86
150 MHz
DMSO-d6
4c
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

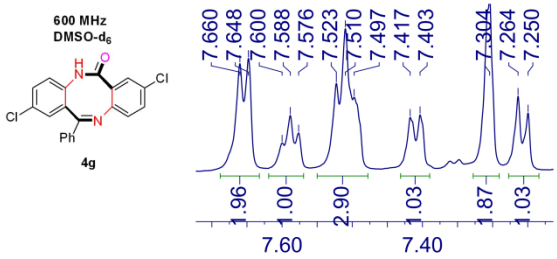

9.988
7.664
7.652
7.579
7.567
7.555
7.511
7.499
7.487
7.285
7.272
7.248
7.234
7.157
7.143
7.075
6.957
6.880
6.866
3.351
2.500
2.422
2.378
600 MHz
DMSO-d6
4d
0.96
2.02
1.08
1.96
1.09
1.05
1.00
1.01
1.09
1.09
3.06
3.00
1.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
169.84
166.76
145.20
137.18
136.98
133.82
133.54
133.52
131.68
128.72
128.67
128.11
127.20
126.54
126.46
124.77
123.93
121.33
39.90
39.78
39.64
39.50
39.36
39.22
39.08
14.84
14.41
150 MHz
DMSO-d6
4d
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

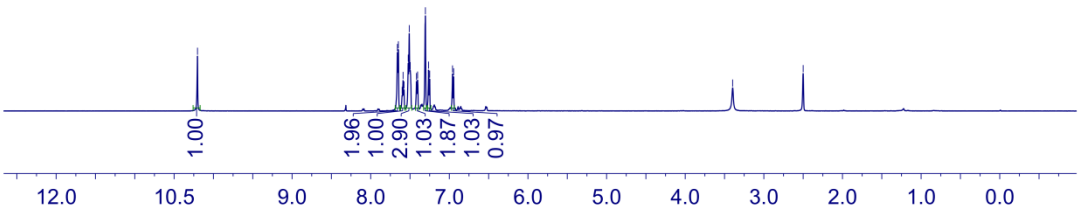

10.025
7.593
7.580
7.535
7.523
7.512
7.470
7.458
7.445
6.863
6.834
6.638
6.537
3.399
2.500
2.214
2.164
2.148
1.822
600 MHz
DMSO-d6
HN
O
N
Ph
4e
1.92
1.19
2.05
0.95
0.92
1.03
1.00
7.4
6.9
0.96
3.00
2.91
2.96
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
169.82
167.67
149.09
139.15
138.58
137.07
137.03
134.76
131.36
130.11
129.09
128.75
127.72
126.44
123.11
122.65
116.56
39.91
39.77
39.64
39.50
39.36
39.22
39.08
20.68
20.52
19.35
18.92
150 MHz
DMSO-d6
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

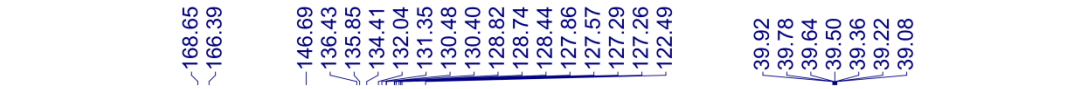

9.490
7.656
7.637
7.392
7.374
7.357
7.325
7.307
7.289
6.473
6.256
3.756
3.751
3.722
3.712
3.439
400 MHz
CDCl3
4f
0.98
1.99
1.06
2.03
1.03
1.03
2.95
3.00
5.85
2.95
3.00

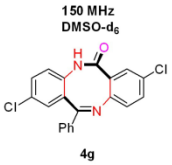

169.193
166.223
154.431
154.410
150.655
150.017
145.597
140.507
138.261
138.237
132.486
130.737
128.032
128.015
120.069
112.453
104.094
99.299
77.319
77.000
76.680
61.377
60.717
60.647
60.467
55.885
55.746
100 MHz
CDCl3
4f

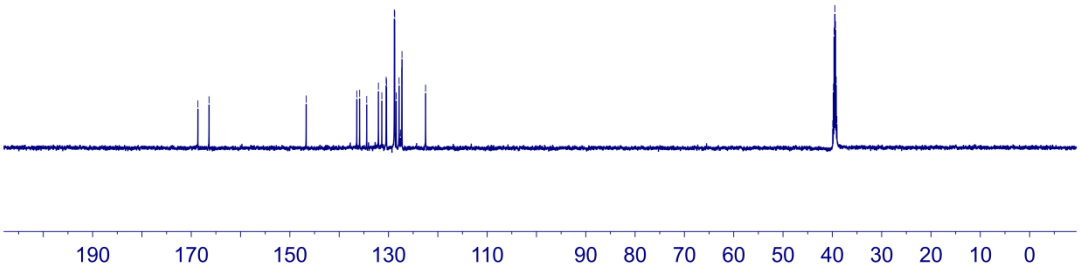

10.203
7.660
7.648
7.600
7.588
7.576
7.523
7.510
7.497
7.417
7.403
7.304
7.264
7.250
6.959
6.945
3.396
2.500

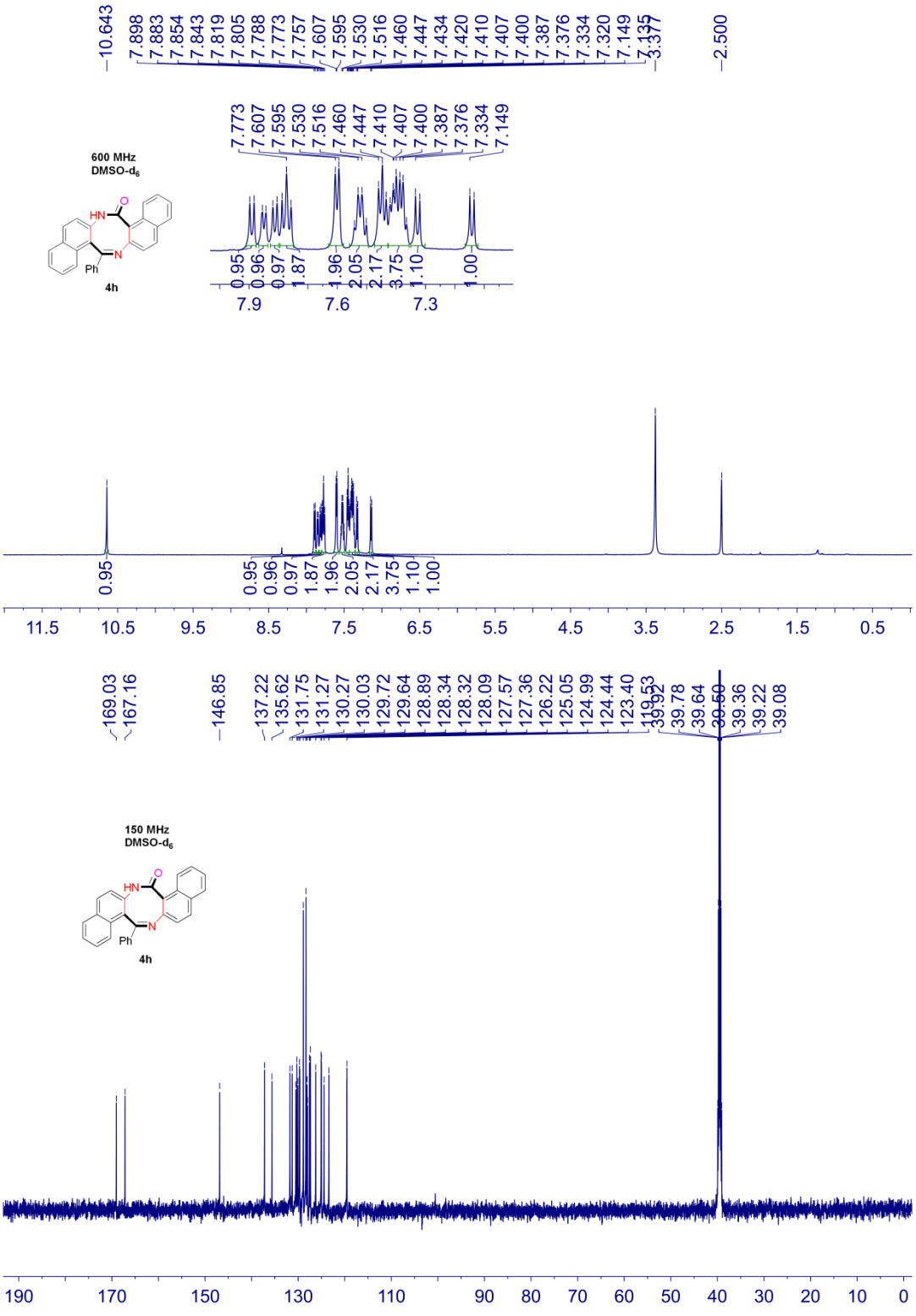

600 MHz
DMSO-d6
4g
7.660
7.648
7.600
7.588
7.576
7.523
7.510
7.497
7.417
7.403
7.304
7.264
7.250
1.96
1.00
2.90
1.03
1.87
1.03
7.60
7.40

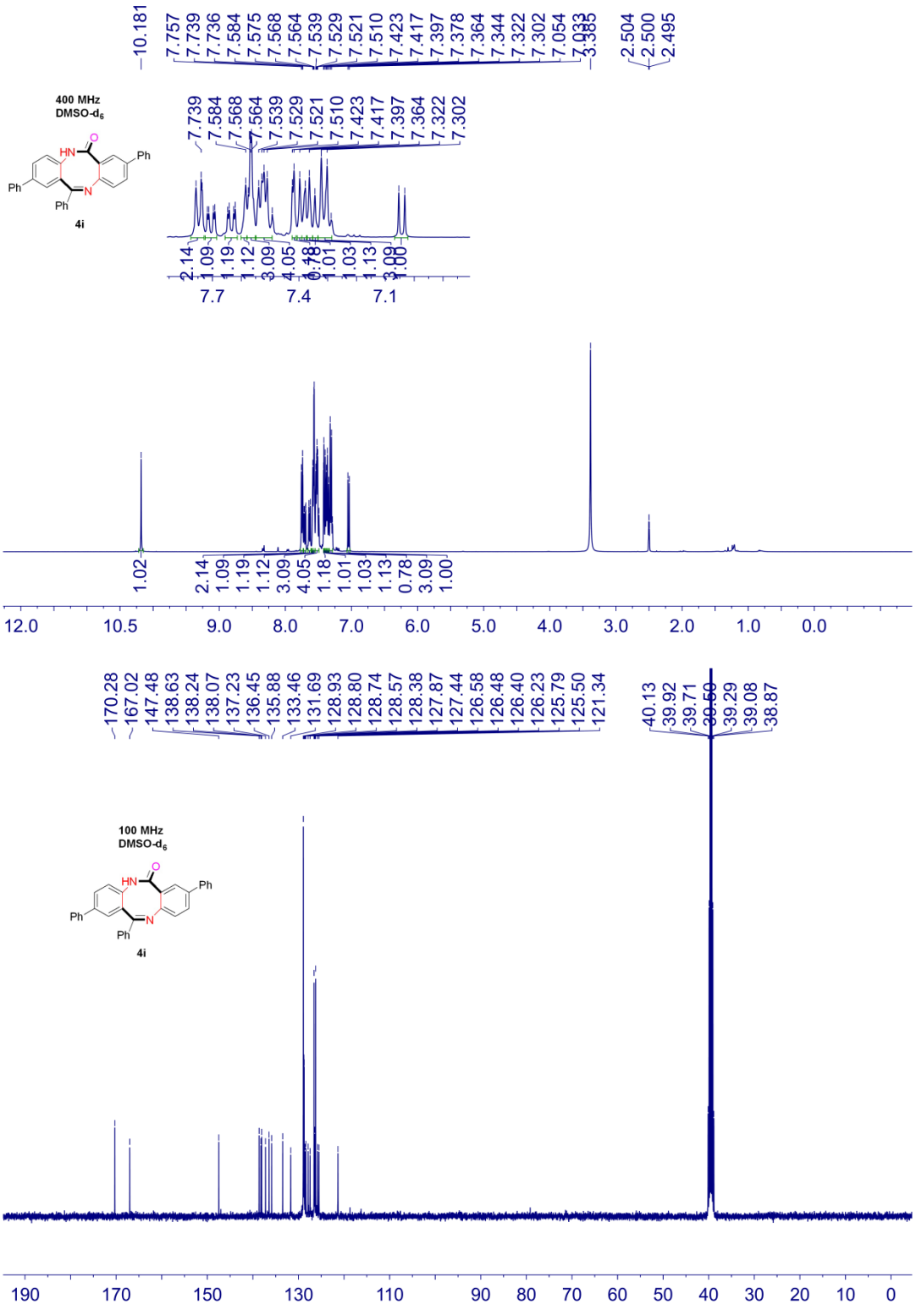

1.00
1.96
1.00
2.90
1.03
1.87
1.03
0.97
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

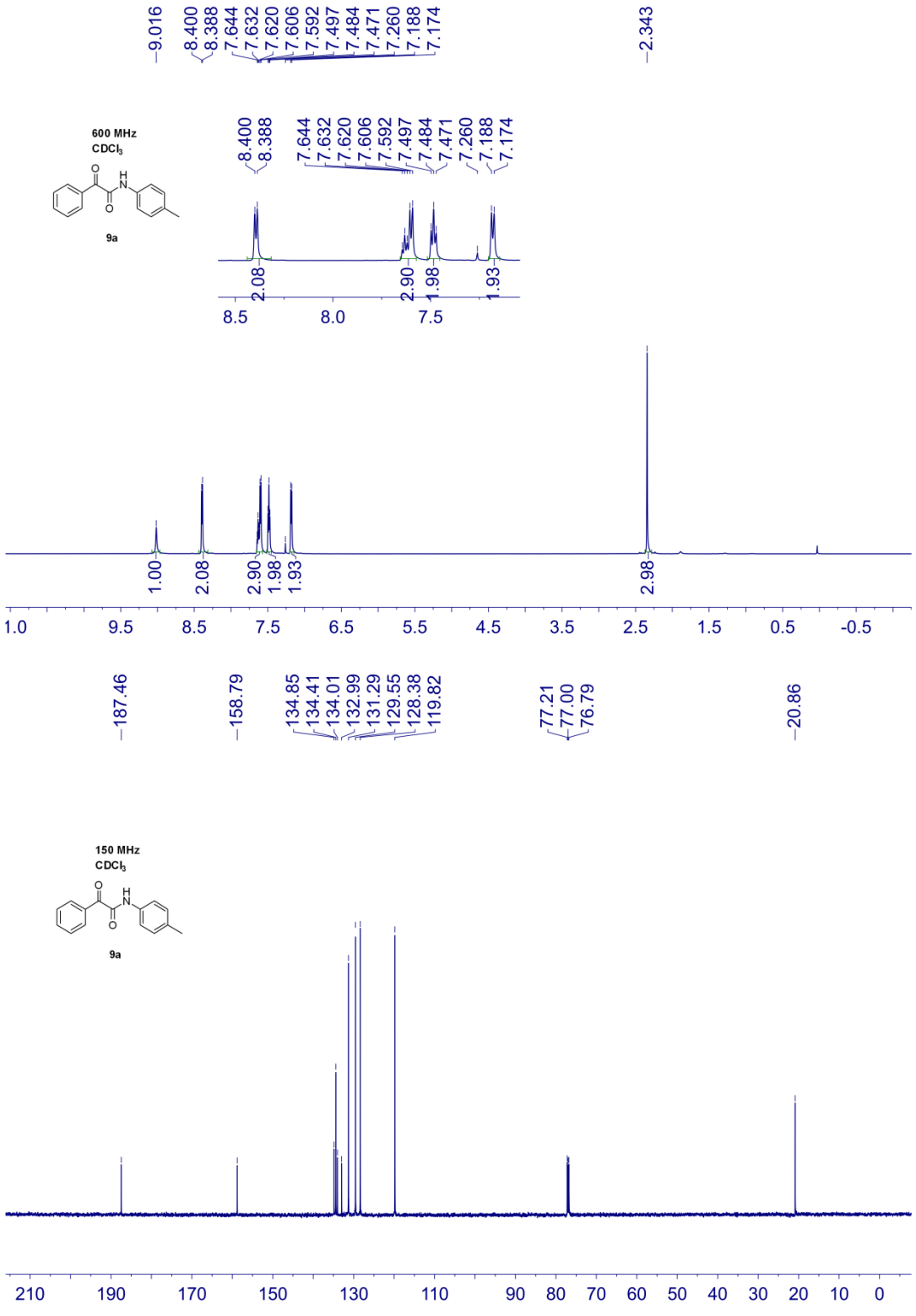

168.65
166.39
146.69
136.43
135.85
134.41
132.04
131.35
130.48
130.40
128.82
128.74
128.44
127.86
127.57
127.29
127.26
122.49
39.92
39.78
39.64
39.50
39.36
39.22
39.08


150 MHz
DMSO-d6
4g


190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


600 MHz
DMSO-d6
4h
150 MHz
DMSO-d6
4h


400 MHz
DMSO-d6
4i
100 MHz
DMSO-d6
4i


9.016
8.400
8.388
7.644
7.632
7.620
7.606
7.592
7.497
7.484
7.471
7.260
7.188
7.174
2.343
600 MHz
CDCl3
9a
2.08
2.90
1.98
1.93
8.5
8.0
7.5
1.00
2.08
2.90
1.98
1.93
2.98
1.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
187.46
158.79
134.85
134.41
134.01
132.99
131.29
129.55
128.38
119.82
77.21
77.00
76.79
20.86
150 MHz
CDCl3
9a
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0