

Supporting Information

Copper-Catalyzed Construction of Eight-Membered Rings via Oxidative Ring Expansion and Intermolecular Cyclization Sequence of Indoles with Amidines: Efficient Synthesis of Benzo[1,3,5]triazocin-6(5*H*)-ones

Wen-Bin Cao,^a Xue-Qiang Chu,^a Yu Zhou,^a Ling Yin,^{a,b} Xiao-Ping Xu,^{*,a} and Shun-Jun Ji^{*,a}

^a*Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, P. R. China*

^b*Department of Chemistry and Chemical Engineering, Jining University, Qufu 273155, P. R. China*

Fax : (+86)-512-65880307; phone: (+86)- 512-65880307; E-mail: xuxp@suda.edu.cn; shunjun@suda.edu.cn

Table of Contents

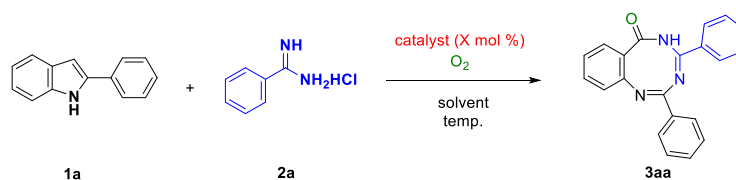
General information.....	page S2
General procedure for assembly of benzo[1,3,5]triazocin-6(5 <i>H</i>)-ones.....	page S2
Optimization of the reaction conditions.....	page S3
Analytical and spectral data for compounds.....	page S5
The ¹ H, ¹³ C and ¹⁹ F spectra of compounds.....	page S16
X-ray structure of 3aa and 3ta	page S50

Experimental Section:

General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under an atmosphere of oxygen and using undistilled solvent unless otherwise noted. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^1H , ^{13}C , ^{19}F NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ on 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for ^1H NMR and ^{13}C NMR. High resolution mass spectra were obtained using a commercial apparatus (ESI or EI Source).

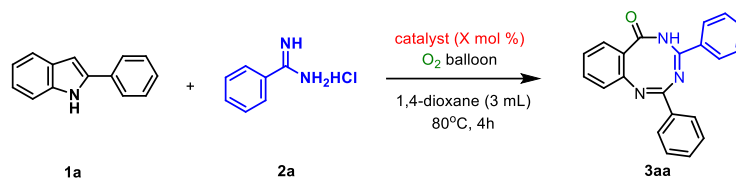
General procedure for assembly of benzo[1,3,5]triazocin-6(5*H*)-ones



2-phenyl-1*H*-indole **1a** (0.4 mmol), benzimidamide hydrochloride **2a** (0.3 mmol), catalyst (X mol %) in solvent (3 mL) was stirred at 80 °C under oxygen for 4h. After cooling to room temperature, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4 . Purification by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent delivered the desired product **3aa**.

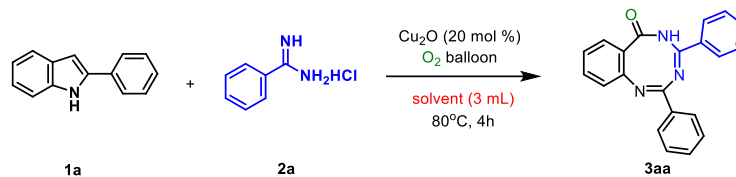
Optimization of the reaction conditions^a

Table S1. Catalyst



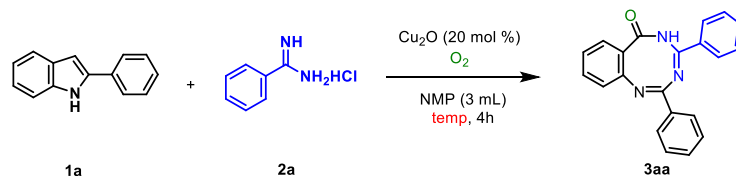
entry	catalyst (X)	LC yield (%)
1	--	trace
2	CuCl ₂ (15)	40 (38 ^b)
3	CuSO ₄ (15)	11
4	Cu(NO ₃) ₂ (15)	15
5	CuBr ₂ (15)	45
6	Cu(OAc) ₂ (15)	33
7	Cu(OTf) ₂ (15)	15
8	CuO (15)	18
9	Cu(acac) ₂ (15)	8
10	Cu(TFA) ₂ (15)	27
11	CuI (15)	46
12	CuCl (15)	46
13	CuBr (15)	43
14	Cu ₂ O (15)	65 (58 ^b)
15	CuOAc (15)	29
16	CuCN (15)	20
17	Cu (15)	30
18	NiO (15)	trace
19	Fe ₂ O ₃ (15)	trace
20	Co ₃ O ₄ (15)	trace
21	MnO ₂ (15)	trace
22	Mn ₃ O ₄ (15)	trace
23	Ag ₂ O (15)	18
24	Cu ₂ O (5)	6
25	Cu ₂ O (10)	45
26	Cu₂O (20)	67 (65^b)
27	Cu ₂ O (25)	67

Table S2. Solvent



entry	solvent (3 mL)	LC yield (%)
28	DCM	31
29	DCE	47
30	MeCN	70 (67 ^b)
31	THF	N.R.
32	toluene	45
33	DMF	60 (57 ^b)
34	DMSO	52
35	DME	43
36	EA	17
37	MeOH	48
38	EtOH	59
39	H ₂ O	trace
40	NMP	82 (79^b)

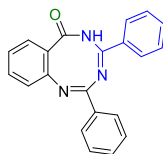
Table S3. Temperature and Atmosphere



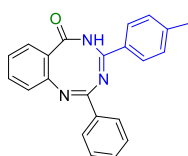
entry	Temperature (°C)	Atmosphere	LC yield (%)
41	r.t.	O ₂ balloon	51
42	40	O ₂ balloon	69
43	60	O ₂ balloon	69
44	100	O ₂ balloon	76 (72 ^b)
45	80	air	48
46	80	O ₂ (sealed tube)	68

^aReaction conditions: **1a** (0.4 mmol), **2a** (0.3 mmol), catalyst (X mol %), O₂ balloon, solvent (3 mL), temperature, 4 h. The yields were determined by LC analysis using biphenyl as the internal standard. ^bIsolated yield.

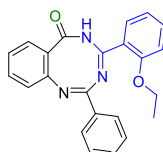
Analytical and spectral data of products:



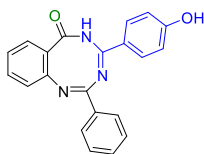
(1Z,3Z)-2,4-diphenylbenzo[f][1,3,5]triazocin-6(5H)-one (3aa): Yield = 79% (77 mg). Light yellow solid. M.p. 197.5-198.4 °C. IR (KBr) ν = 3194, 3065, 2923, 1675, 1615, 1595, 1446, 1217, 754, 685 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.61 (s, 1H), 8.07 (d, J = 7.4 Hz, 2H), 7.98 (d, J = 7.6 Hz, 2H), 7.60 – 7.38 (m, 8H), 7.10 (t, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.8, 161.1, 151.9, 146.7, 133.9, 132.7, 132.2, 131.6, 131.2, 128.6, 128.6, 128.3, 128.1, 127.6, 124.1, 124.0, 122.9 ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 326.1293, found: 326.1280.



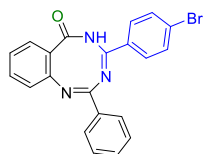
(1Z,3Z)-2-phenyl-4-(p-tolyl)benzo[f][1,3,5]triazocin-6(5H)-one (3ab): Yield = 81% (82 mg). Light yellow solid. M.p. 197.6-198.5 °C. IR (KBr) ν = 3191, 3068, 2904, 1673, 1630, 1574, 1338, 1265, 758, 688 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.57 (s, 1H), 8.06 (d, J = 7.2 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.47 (m, 5H), 7.30 – 7.22 (m, 2H), 7.09 (t, J = 7.7 Hz, 2H), 2.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.5, 161.2, 151.6, 146.8, 143.7, 134.1, 131.6, 131.1, 129.4, 129.4, 128.7, 128.3, 128.0, 127.6, 124.1, 123.9, 122.8, 21.1 ppm. HRMS m/z : calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 340.1450, found: 340.1440.



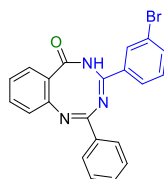
(1Z,3Z)-4-(2-ethoxyphenyl)-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ac): Yield = 56% (62 mg). Light yellow solid. M.p. 197.1-198.7 °C. IR (KBr) ν = 3082, 2936, 1682, 1596, 1312, 1247, 746, 712, 689 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.42 (s, 1H), 8.06 (d, J = 7.2 Hz, 2H), 7.91 (d, J = 6.4 Hz, 1H), 7.48 (m, 6H), 7.13 (t, J = 7.7 Hz, 2H), 7.03 – 6.91 (m, 2H), 4.12 (m, 2H), 1.47 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.1, 161.0, 157.6, 152.4, 146.7, 134.3, 133.4, 131.4, 131.3, 130.9, 129.1, 127.9, 127.7, 124.4, 123.8, 122.7, 121.0, 120.5, 112.2, 64.1, 14.3 ppm. HRMS m/z : calcd for $\text{C}_{23}\text{H}_{20}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 370.1556, found: 370.1560.



(1Z,3Z)-4-(4-hydroxyphenyl)-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ad): Yield = 72% (74 mg). Light yellow solid. M.p. 203.8-204.7 °C. IR (KBr) ν = 3070, 2922, 1681, 1643, 1580, 1264, 1222, 1174, 758, 707 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6) δ = 10.78 (s, 1H), 10.44 (s, 1H), 8.02 (d, J = 7.3 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.60 (dt, J = 14.4, 6.9 Hz, 3H), 7.48 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.19 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.9 Hz, 1H), 6.93 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO- d_6) δ = 170.1, 162.1, 161.7, 153.5, 146.6, 134.2, 131.7, 131.2, 128.7, 128.5, 127.6, 126.6, 124.2, 123.1, 122.4, 115.7 ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{16}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 342.1243, found: 342.1254.

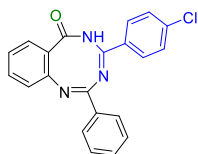


(1Z,3Z)-4-(4-bromophenyl)-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ae): Yield = 80% (97 mg). Light yellow solid. M.p. 212.4-213.1 °C. IR (KBr) ν = 3229, 3058, 1670, 1638, 1592, 1334, 1255, 757, 717 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 9.14 (s, 1H), 8.04 (d, J = 7.4 Hz, 2H), 7.83 (d, J = 8.5 Hz, 2H), 7.55 (dd, J = 20.3, 7.8 Hz, 3H), 7.51 – 7.39 (m, 3H), 7.36 (d, J = 7.6 Hz, 1H), 7.09 (t, J = 7.8 Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.8, 160.8, 151.1, 146.6, 133.7, 131.9, 131.7, 131.3, 131.0, 129.7, 128.5, 128.1, 127.9, 127.6, 124.0, 123.8, 122.9 ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{15}\text{BrN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 404.0398, found: 404.0403.

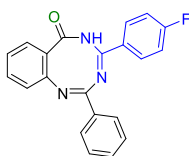


(1Z,3Z)-4-(3-bromophenyl)-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3af): Yield = 61% (74 mg). Light yellow solid. M.p. 200.4-200.7 °C. IR (KBr) ν = 3174, 3064, 2908, 1678, 1629, 1618, 1596, 1251, 732, 721 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 9.08 (s, 1H), 8.16 (s, 1H), 8.03 (d, J = 7.3 Hz, 2H), 7.88 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.50 – 7.38 (m, 4H), 7.34 (t, J = 7.9 Hz, 1H), 7.11 (t, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3)

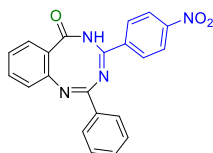
δ = 171.7, 160.6, 150.6, 146.5, 135.6, 134.2, 133.6, 131.8, 131.3, 131.2, 130.1, 128.7, 128.1, 127.6, 126.8, 124.1, 123.7, 122.9, 122.8 ppm. HRMS m/z : calcd for $C_{21}H_{15}BrN_3O$ $[M+H]^+$ 404.0398, found: 404.0405.



(1Z,3Z)-4-(4-chlorophenyl)-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ag): Yield = 78% (84 mg). Light yellow solid. M.p. 204.1-204.9 °C. IR (KBr) ν = 3223, 3067, 1669, 1624, 1577, 1255, 758, 720, 684 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ = 8.91 (s, 1H), 8.04 (d, J = 7.2 Hz, 2H), 7.91 (d, J = 8.6 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.51 – 7.39 (m, 5H), 7.38 (dd, J = 8.0, 1.1 Hz, 1H), 7.10 (t, J = 7.1 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.6, 160.8, 150.8, 146.6, 139.3, 133.8, 131.7, 131.2, 130.6, 129.6, 128.9, 128.6, 128.1, 127.6, 124.0, 123.8, 122.9 ppm. HRMS m/z : calcd for $C_{21}H_{15}ClN_3O$ $[M+H]^+$ 360.0904, found: 360.0900.

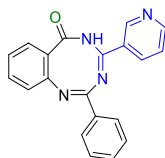


(1Z,3Z)-4-(4-fluorophenyl)-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ah): Yield = 78% (80 mg). Light yellow solid. M.p. 190.5-191.4 °C. IR (KBr) ν = 3177, 3067, 2904, 1669, 1630, 1595, 1266, 1160, 759, 690 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ = 9.08 (s, 1H), 8.05 (d, J = 7.3 Hz, 2H), 7.98 (dd, J = 8.7, 5.2 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.36 (d, J = 7.5 Hz, 1H), 7.17 – 7.06 (m, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.8, 166.7, 164.2, 160.9, 150.8, 146.6, 133.8, 131.7, 131.2, 130.8, 130.7, 128.6, 128.4, 128.3, 128.1, 127.6, 124.0, 123.9, 122.9, 116.0, 115.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.92. HRMS m/z : calcd for $C_{21}H_{15}FN_3O$ $[M+H]^+$ 344.1199, found: 344.1190.

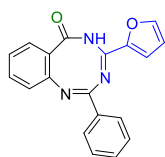


(1Z,3Z)-4-(4-nitrophenyl)-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ai): Yield = 40% (44 mg). Light yellow solid. M.p. 130.4-131.8 °C. IR (KBr) ν = 3180, 3068, 2903, 1675, 1634, 1577, 1491, 1346, 758, 706 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ = 9.11 (s, 1H), 8.29 (d, J = 8.8 Hz, 2H),

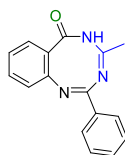
8.16 (d, J = 8.8 Hz, 2H), 8.04 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.39 (d, J = 8.1 Hz, 1H), 7.16 – 7.08 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.6, 160.2, 150.1, 150.0, 146.3, 137.7, 133.3, 132.0, 131.5, 129.3, 128.5, 128.2, 127.6, 124.2, 123.7, 123.4, 123.0. ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{15}\text{N}_4\text{O}_3$ $[\text{M}+\text{H}]^+$ 371.1144, found: 371.1139.



(1Z,3Z)-2-phenyl-4-(pyridin-3-yl)benzo[f][1,3,5]triazocin-6(5H)-one (3aj): Yield = 61% (60 mg). Light yellow solid. M.p. 192.1-193.8 °C. IR (KBr) ν = 3182, 1684, 1620, 1270, 756, 695, 670 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 9.26 (d, J = 33.6 Hz, 2H), 8.76 (d, J = 3.4 Hz, 1H), 8.26 (d, J = 7.9 Hz, 1H), 8.04 (d, J = 7.4 Hz, 2H), 7.48 (m, 6H), 7.18 – 7.04 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.6, 160.4, 152.9, 150.2, 149.4, 146.4, 135.8, 133.6, 131.8, 131.3, 128.7, 128.1, 127.6, 124.1, 123.7, 123.3, 122.9 ppm. HRMS m/z : calcd for $\text{C}_{20}\text{H}_{15}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$ 327.1246, found: 327.1242.

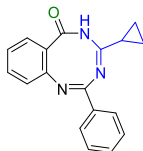


(1Z,3Z)-4-(furan-2-yl)-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ak): Yield = 54% (51 mg). Light yellow solid. M.p. 216.4-217.6 °C. IR (KBr) ν = 3177, 3068, 2900, 1668, 1637, 1616, 1480, 1281, 1017, 827, 754 cm^{-1} . ^1H NMR (400 MHz, DMSO-d_6) δ = 10.92 (s, 1H), 8.07 (s, 1H), 8.00 (d, J = 7.4 Hz, 2H), 7.66 – 7.49 (m, 4H), 7.38 (dd, J = 12.3, 5.4 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 7.9 Hz, 1H), 6.77 (s, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ = 170.0, 160.7, 148.5, 146.5, 146.2, 144.5, 133.8, 131.8, 131.4, 128.8, 128.6, 127.6, 126.0, 124.4, 122.5, 119.1, 113.0 ppm. HRMS m/z : calcd for $\text{C}_{19}\text{H}_{14}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 316.1086, found: 316.1083.

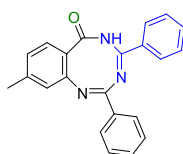


(1Z,3Z)-4-methyl-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3al): Yield = 53% (42 mg). Light yellow solid. M.p. 113.6-115.1 °C. IR (KBr) ν = 3208, 2927, 1693, 1640, 1616, 1212, 762, 694, 630 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.45 (s, 1H), 7.97 (d, J = 7.4 Hz, 2H), 7.47 (m,

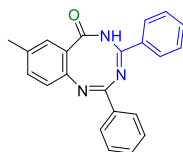
5H), 7.17 (t, $J = 7.5$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 2.24 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 170.9, 153.5, 146.5, 133.7, 131.7, 131.1, 128.8, 127.9, 127.6, 124.0, 123.9, 122.9, 26.4, 23.8$ ppm. HRMS m/z : calcd for $\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 264.1137, found: 264.1133.



(1Z,3Z)-4-cyclopropyl-2-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3am): Yield = 72% (62 mg). Light yellow solid. M.p. 171.8-173.2 °C. IR (KBr) $\nu = 3049, 2908, 1681, 1618, 1577, 1351, 1197, 962, 753, 669$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3) $\delta = 8.90$ (s, 1H), 7.93 (d, $J = 7.1$ Hz, 2H), 7.53 – 7.33 (m, 5H), 7.15 (t, $J = 7.2$ Hz, 1H), 7.07 (d, $J = 7.7$ Hz, 1H), 1.69 (s, 1H), 1.11 (d, $J = 3.8$ Hz, 1H), 1.04 – 0.85 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 171.5, 160.7, 158.6, 146.5, 134.1, 131.5, 130.9, 128.6, 127.9, 127.5, 124.4, 123.8, 122.9, 16.0, 9.8, 7.7$ ppm. HRMS m/z : calcd for $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 290.1293, found: 290.1286.

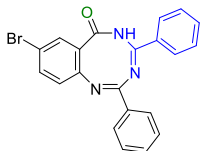


(1Z,3Z)-9-methyl-2,4-diphenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ba): Yield = 77% (78 mg). Light yellow solid. M.p. 204.9-205.8 °C. IR (KBr) $\nu = 3165, 3052, 2893, 1666, 1627, 1605, 1257, 790, 780, 700, 687$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3) $\delta = 8.41$ (s, 1H), 8.06 (d, $J = 7.3$ Hz, 2H), 7.98 (d, $J = 7.5$ Hz, 2H), 7.51 (m, 6H), 7.34 (d, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 2H), 2.32 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 170.2, 161.4, 151.6, 145.8, 134.6, 133.6, 133.0, 131.8, 131.4, 131.2, 128.7, 128.3, 128.1, 127.7, 125.8, 124.9, 116.9, 26.4$ ppm. HRMS m/z : calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 340.1450, found: 340.1446.

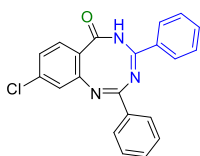


(1Z,3Z)-8-methyl-2,4-diphenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ca): Yield = 46% (47 mg). Light yellow solid. M.p. 208.3-209.6 °C. IR (KBr) $\nu = 3159, 3060, 2888, 1663, 1630, 1262, 813, 774, 712, 686, 639$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3) $\delta = 8.87$ (s, 1H), 8.07 (d, $J = 7.1$ Hz, 2H), 7.99 (d, $J = 7.4$ Hz, 2H), 7.51 (m, 6H), 7.22 (d, $J = 10.4$ Hz, 2H), 7.00 (d, $J = 8.0$ Hz, 1H), 2.26 (s,

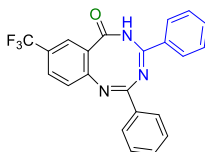
3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.9, 160.9, 151.7, 144.2, 134.1, 133.7, 132.6, 132.6, 132.3, 131.0, 128.8, 128.6, 128.3, 128.0, 127.6, 123.8, 122.9, 20.2 ppm. HRMS m/z : calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 340.1450, found: 340.1456.



(1Z,3Z)-8-bromo-2,4-diphenylbenzo[f][1,3,5]triazocin-6(5H)-one (3da): Yield = 79% (96 mg). Light yellow solid. M.p. 148.9-150.8°C. IR (KBr) ν = 3162, 3062, 2901, 1673, 1632, 1612, 1256, 711, 686, 676 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.91 (s, 1H), 7.98 (dd, J = 11.0, 8.3 Hz, 4H), 7.57 (t, J = 7.3 Hz, 1H), 7.52 – 7.33 (m, 6H), 7.10 (t, J = 8.1 Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.6, 160.8, 150.8, 146.6, 139.3, 133.8, 131.7, 131.2, 130.6, 129.6, 128.9, 128.6, 128.1, 127.6, 124.0, 123.8, 122.9 ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{15}\text{BrN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 404.0398, found: 404.0402.

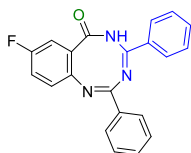


(1Z,3Z)-9-chloro-2,4-diphenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ea): Yield = 76% (82 mg). Light yellow solid. M.p. 200.3-201.9°C. IR (KBr) ν = 3161, 3061, 2901, 1671, 1632, 1618, 1263, 710, 687 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 9.17 (s, 1H), 8.05 (d, J = 7.5 Hz, 2H), 7.96 (d, J = 7.6 Hz, 2H), 7.55 (dd, J = 16.0, 7.5 Hz, 2H), 7.46 (t, J = 7.3 Hz, 4H), 7.27 (d, J = 8.3 Hz, 1H), 7.10 (s, 1H), 7.03 (d, J = 8.3 Hz, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.0, 161.8, 151.9, 148.0, 137.5, 133.5, 132.9, 131.9, 131.5, 129.9, 128.7, 128.3, 128.1, 127.7, 124.2, 123.0, 122.6 ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{15}\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 360.0904, found: 360.0906.

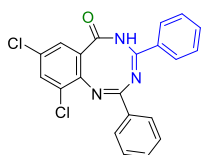


(1Z,3Z)-2,4-diphenyl-8-(trifluoromethyl)benzo[f][1,3,5]triazocin-6(5H)-one (3fa): Yield = 73% (86 mg). Light yellow solid. M.p. 178.3-179.5°C. IR (KBr) ν = 3167, 3063, 2884, 1667, 1633, 1608, 1307, 1226, 713 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 9.14 (s, 1H), 8.07 (d, J = 7.3 Hz, 2H), 8.00 (d, J = 7.5 Hz, 2H), 7.71 – 7.63 (m, 2H), 7.58 (dt, J = 14.5, 7.3 Hz, 2H), 7.49 (m, 4H),

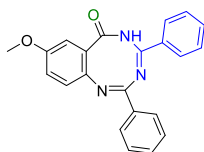
7.22 (d, $J = 8.3$ Hz, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 170.4, 161.8, 151.7, 149.9, 133.4, 133.1, 131.7, 131.6, 128.8, 128.4, 128.4, 128.2, 127.8, 126.4, 126.2, 126.2, 126.0, 124.4, 123.8, 121.9$ ppm. ^{19}F NMR (376 MHz, CDCl_3) $\delta = -62.13$ ppm. HRMS m/z : calcd for $\text{C}_{22}\text{H}_{15}\text{F}_3\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 394.1167, found: 394.1162.



(1Z,3Z)-8-fluoro-2,4-diphenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ga): Yield = 81% (83 mg). Light yellow solid. M.p. 182.1-183.9°C. IR (KBr) $\nu = 3156, 3065, 2892, 1674, 1633, 1608, 1614, 1281, 768, 690$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3) $\delta = 8.97$ (s, 1H), 8.05 (d, $J = 7.2$ Hz, 2H), 7.97 (d, $J = 7.4$ Hz, 2H), 7.62 – 7.42 (m, 6H), 7.19 – 7.02 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 170.4, 161.4, 160.2, 157.8, 151.6, 142.8, 142.8, 133.7, 132.9, 131.9, 131.3, 128.7, 128.3, 128.1, 127.6, 125.2, 125.1, 124.9, 124.8, 119.0, 118.8, 115.0$ ppm. ^{19}F NMR (376 MHz, CDCl_3) $\delta = -118.49$ ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{15}\text{FN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 344.1199, found: 344.1195.

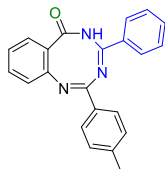


(1Z,3Z)-8,10-dichloro-2,4-diphenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ha): Yield = 65% (77 mg). Light yellow solid. M.p. >250°C. IR (KBr) $\nu = 3161, 3066, 2883, 1679, 1635, 1608, 1266, 760, 711, 686$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3) $\delta = 8.71$ (s, 1H), 8.09 (d, $J = 7.3$ Hz, 2H), 7.97 (d, $J = 7.4$ Hz, 2H), 7.64 – 7.45 (m, 7H), 7.30 (d, $J = 2.2$ Hz, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 169.0, 161.8, 151.4, 142.6, 133.2, 131.9, 131.7, 131.6, 129.6, 128.8, 128.7, 128.4, 128.2, 127.9, 127.0, 126.4$ ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{14}\text{Cl}_2\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 394.0514, found: 394.0522.

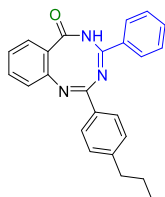


(1Z,3Z)-8-methoxy-2,4-diphenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ia): Yield = 62% (66 mg). Light yellow solid. M.p. 206.1-207.0°C. IR (KBr) $\nu = 3177, 3060, 1671, 1633, 1606, 1263, 760, 685$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3) $\delta = 8.96$ (s, 1H), 8.06 (d, $J = 7.2$ Hz, 2H), 7.99 (d, $J = 7.5$ Hz, 2H), 7.51 (m, 6H), 7.00 (dt, $J = 8.8, 5.7$ Hz, 2H), 6.92 (d, $J = 2.5$ Hz, 1H), 3.74 (s, 3H)

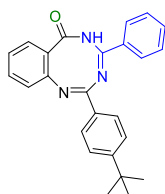
ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.5, 160.8, 156.0, 151.6, 139.8, 134.2, 132.7, 132.2, 131.0, 128.6, 128.3, 128.0, 127.5, 124.6, 124.5, 118.6, 112.5, 55.1 ppm. HRMS m/z : calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 356.1399, found: 356.1394.



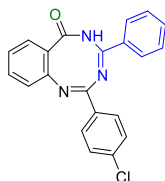
(1Z,3Z)-4-phenyl-2-(p-tolyl)benzo[f][1,3,5]triazocin-6(5H)-one (3ja): Yield = 80% (81 mg). Light yellow solid. M.p. 216.7-217.9°C. IR (KBr) ν = 3156, 3061, 2878, 1672, 1631, 1595, 1319, 784, 755, 694 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.55 (s, 1H), 7.96 (t, J = 7.3 Hz, 4H), 7.56 (t, J = 7.4 Hz, 1H), 7.50 – 7.38 (m, 4H), 7.27 (d, J = 9.2 Hz, 2H), 7.14 – 7.05 (m, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.2, 161.0, 151.4, 146.8, 141.6, 132.7, 132.3, 131.6, 131.2, 128.8, 128.7, 128.6, 128.2, 127.6, 124.0, 123.8, 122.9, 21.1 ppm. HRMS m/z : calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 340.1450, found: 340.1439.



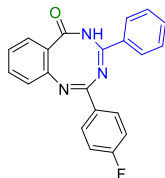
(1Z,3Z)-4-phenyl-2-(4-propylphenyl)benzo[f][1,3,5]triazocin-6(5H)-one (3ka): Yield = 76% (84 mg). Light yellow solid. M.p. 176.4-177.8°C. IR (KBr) ν = 3188, 2868, 1672, 1629, 1595, 799, 754, 684 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.99 (s, 1H), 7.98 (m, 4H), 7.54 (t, J = 7.3 Hz, 1H), 7.50 – 7.34 (m, 4H), 7.26 (t, J = 7.6 Hz, 2H), 7.08 (dd, J = 14.9, 7.7 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 1.73 – 1.65 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.8, 161.1, 151.7, 146.9, 146.4, 132.6, 132.2, 131.6, 131.4, 128.6, 128.6, 128.3, 128.2, 127.6, 124.2, 123.8, 122.9, 37.6, 23.9, 13.3 ppm. HRMS m/z : calcd for $\text{C}_{24}\text{H}_{22}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 368.1763, found: 368.1756.



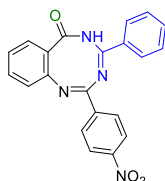
(1Z,3Z)-2-(4-(tert-butyl)phenyl)-4-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3la): Yield = 79% (90 mg). Light yellow solid. M.p. 215.3-216.6°C. IR (KBr) ν = 3196, 2963, 1670, 1619, 1597, 1339, 788, 683 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.86 (s, 1H), 7.99 (m, 4H), 7.57 – 7.39 (m, 7H), 7.12 – 7.03 (m, 2H), 1.36 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.7, 161.0, 154.7, 151.6, 146.9, 132.6, 132.2, 131.6, 131.2, 128.7, 128.6, 128.3, 127.5, 125.0, 124.1, 123.8, 122.9, 34.5, 30.7 ppm. HRMS m/z : calcd for $\text{C}_{25}\text{H}_{24}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 382.1919, found: 382.1934.



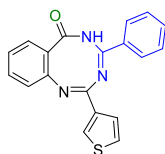
(1Z,3Z)-2-(4-chlorophenyl)-4-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ma): Yield = 73% (79 mg). Light yellow solid. M.p. >250 °C. IR (KBr) ν = 3174, 3063, 2898, 1674, 1630, 1614, 759, 697, 681 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.91 (s, 1H), 7.98 (dd, J = 11.0, 8.3 Hz, 4H), 7.57 (t, J = 7.3 Hz, 1H), 7.52 – 7.34 (m, 6H), 7.10 (t, J = 8.1 Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.6, 160.0, 152.2, 146.4, 137.4, 132.9, 132.4, 132.0, 131.7, 128.9, 128.7, 128.3, 128.3, 124.1, 123.9, 122.8 ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{15}\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 360.0904, found: 360.0904.



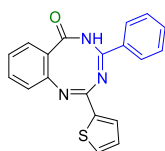
(1Z,3Z)-2-(4-fluorophenyl)-4-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3na): Yield = 72% (75 mg). Light yellow solid. M.p. >250 °C. IR (KBr) ν = 3172, 3063, 2901, 1671, 1630, 1614, 757, 692, 682 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 9.08 (s, 1H), 8.06 (m, 2H), 7.97 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.52 – 7.34 (m, 4H), 7.10 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.8, 165.8, 163.2, 160.0, 152.1, 146.5, 132.8, 132.0, 131.7, 130.1, 130.1, 129.9, 129.8, 128.6, 128.3, 124.0, 122.9, 115.2, 115.0 ppm. ^{19}F NMR (376 MHz, CDCl_3) δ = -108.0. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{15}\text{FN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 344.1199, found: 344.1196.



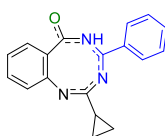
(1Z,3Z)-2-(4-nitrophenyl)-4-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3oa): Yield = 61% (68 mg). Light yellow solid. M.p. 239.3-240.9 °C. IR (KBr) ν = 3179, 3059, 2899, 1671, 1630, 1615, 757, 692, 680 cm^{-1} . ^1H NMR (400 MHz, DMSO-d_6) δ = 11.10 (s, 1H), 8.42 (d, J = 8.7 Hz, 2H), 8.31 (d, J = 8.7 Hz, 2H), 8.04 (d, J = 7.5 Hz, 2H), 7.71 (t, J = 7.2 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.52 (dd, J = 16.7, 7.9 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 169.8, 160.0, 155.3, 149.4, 145.6, 139.4, 133.5, 132.1, 131.5, 129.2, 129.0, 128.6, 126.0, 125.0, 124.0, 122.4 ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{15}\text{N}_4\text{O}_3$ $[\text{M}+\text{H}]^+$ 371.1144, found: 371.1152.



(1Z,3Z)-4-phenyl-2-(thiophen-3-yl)benzo[f][1,3,5]triazocin-6(5H)-one (3qa): Yield = 83% (82 mg). Light yellow solid. M.p. 202.5-204.1 °C. IR (KBr) ν = 3182, 3052, 2894, 1671, 1630, 1615, 757, 692, 680, 656 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 9.03 (s, 1H), 8.03 – 7.93 (m, 2H), 7.89 (dd, J = 2.9, 1.1 Hz, 1H), 7.70 (dd, J = 5.1, 1.0 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.49 – 7.36 (m, 5H), 7.12 – 7.05 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.8, 157.5, 152.2, 146.3, 137.2, 132.7, 132.1, 131.6, 128.6, 128.6, 128.4, 128.3, 126.6, 125.8, 124.1, 124.0, 122.8 ppm. HRMS m/z : calcd for $\text{C}_{19}\text{H}_{14}\text{N}_3\text{OS}$ $[\text{M}+\text{H}]^+$ 332.0858, found: 332.0859.



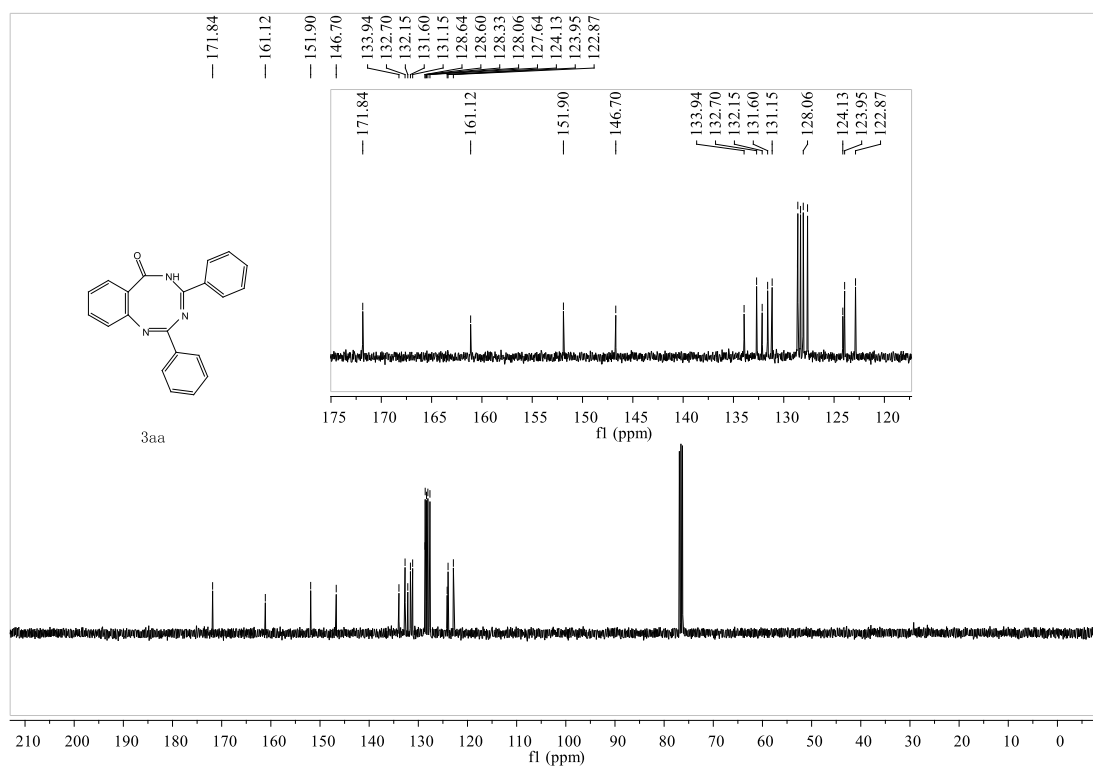
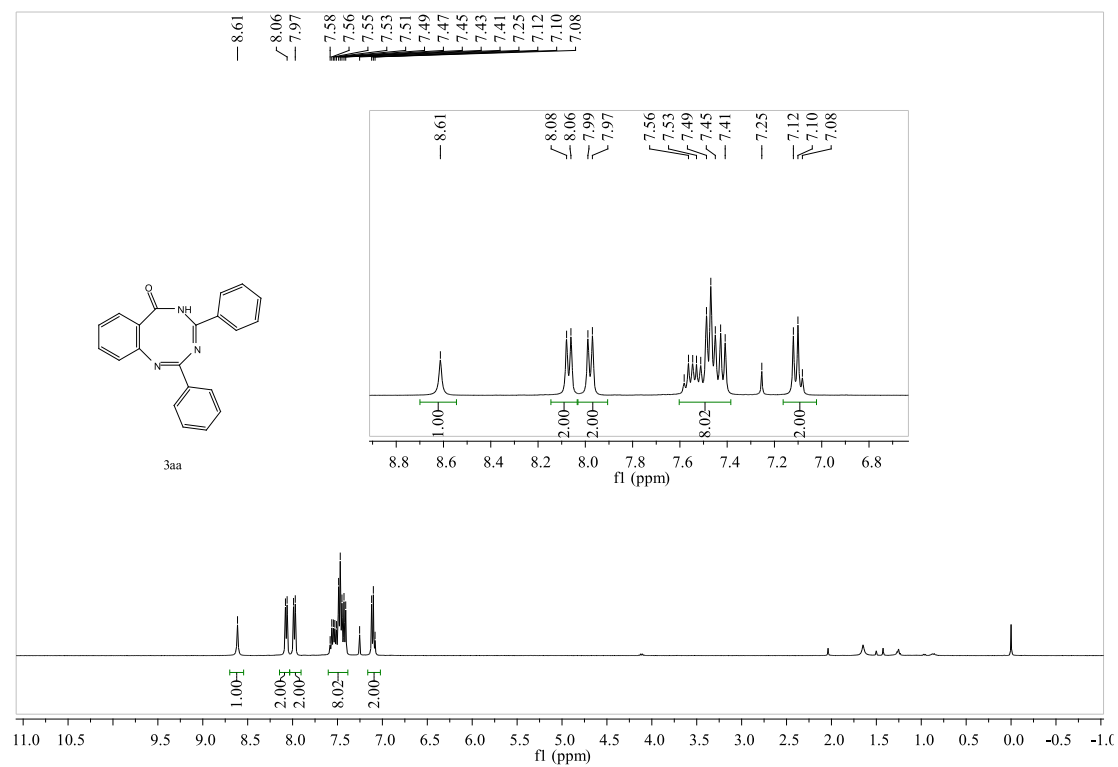
(1Z,3Z)-4-phenyl-2-(thiophen-2-yl)benzo[f][1,3,5]triazocin-6(5H)-one (3ra): Yield = 70% (69 mg). Light yellow solid. M.p. 207.3-208.9 °C. IR (KBr) ν = 3182, 3055, 2898, 1671, 1630, 1620, 754, 699, 680, 655 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 8.69 (s, 1H), 7.97 (d, J = 7.5 Hz, 2H), 7.63 – 7.53 (m, 3H), 7.51 – 7.39 (m, 4H), 7.17 – 7.06 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 171.4, 156.9, 153.0, 145.9, 138.7, 132.9, 132.1, 131.7, 130.3, 129.5, 128.8, 128.7, 128.4, 127.3, 124.2, 124.1, 123.1 ppm. HRMS m/z : calcd for $\text{C}_{19}\text{H}_{14}\text{N}_3\text{OS}$ $[\text{M}+\text{H}]^+$ 332.0858, found: 332.0855.



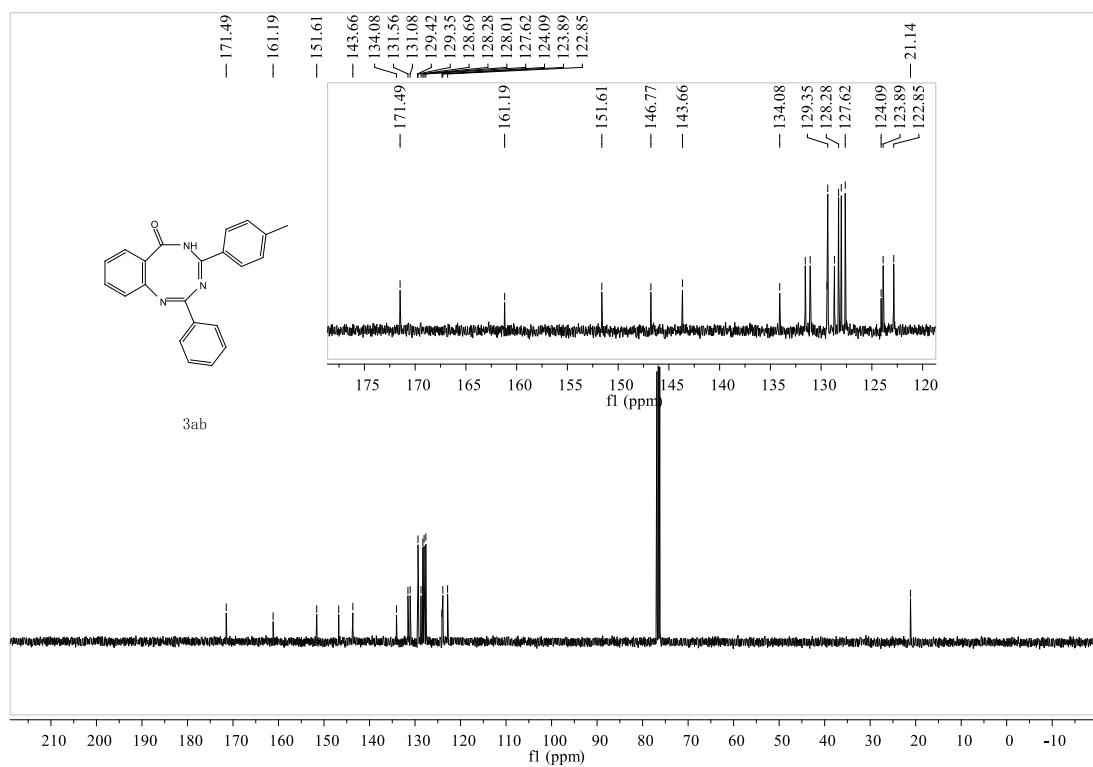
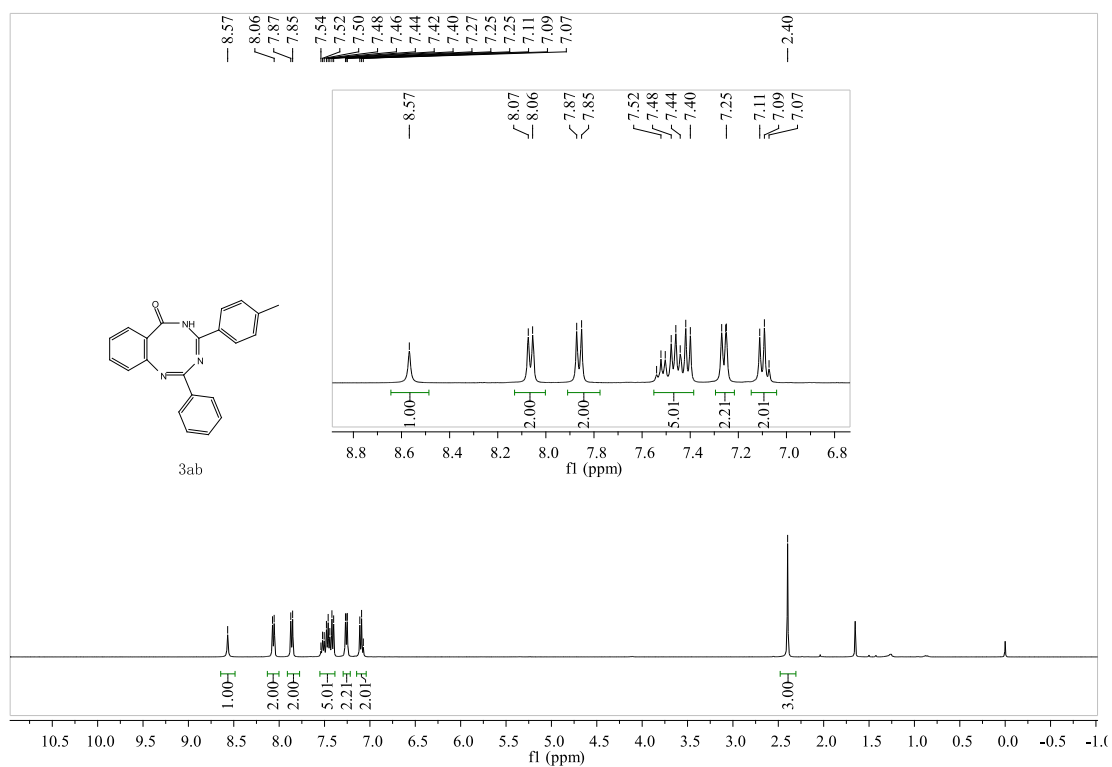
(1Z,3Z)-2-cyclopropyl-4-phenylbenzo[f][1,3,5]triazocin-6(5H)-one (3ta): Yield = 71% (62 mg). Yellow solid. M.p. 165.1-166.9 °C. IR (KBr) ν = 3172, 3603, 2901, 1671, 1630, 1592, 1397, 1347, 773, 692 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ = 11.67-9.10 (d, 1H), 8.15-7.83 (m, 2H), 7.70 and 7.06 (m, 1H), 7.59 and 6.99 (m, 1H), 7.53 (t, J = 7.3 Hz, 1H), 7.40 (m, 4H), 2.04-1.92 (m, 1H), 1.33-0.90 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 172.0, 168.0, 151.1, 146.5, 132.6, 132.1, 131.5, 128.5, 128.5, 128.2, 126.5, 125.8, 125.1, 124.5, 123.6, 122.6, 16.5, 14.2, 9.2, 7.8, 7.0 ppm. HRMS m/z : calcd for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_1$ $[\text{M}+\text{H}]^+$ 290.1293, found: 290.1295.

The ^1H , ^{13}C and ^{19}F spectra of compounds:

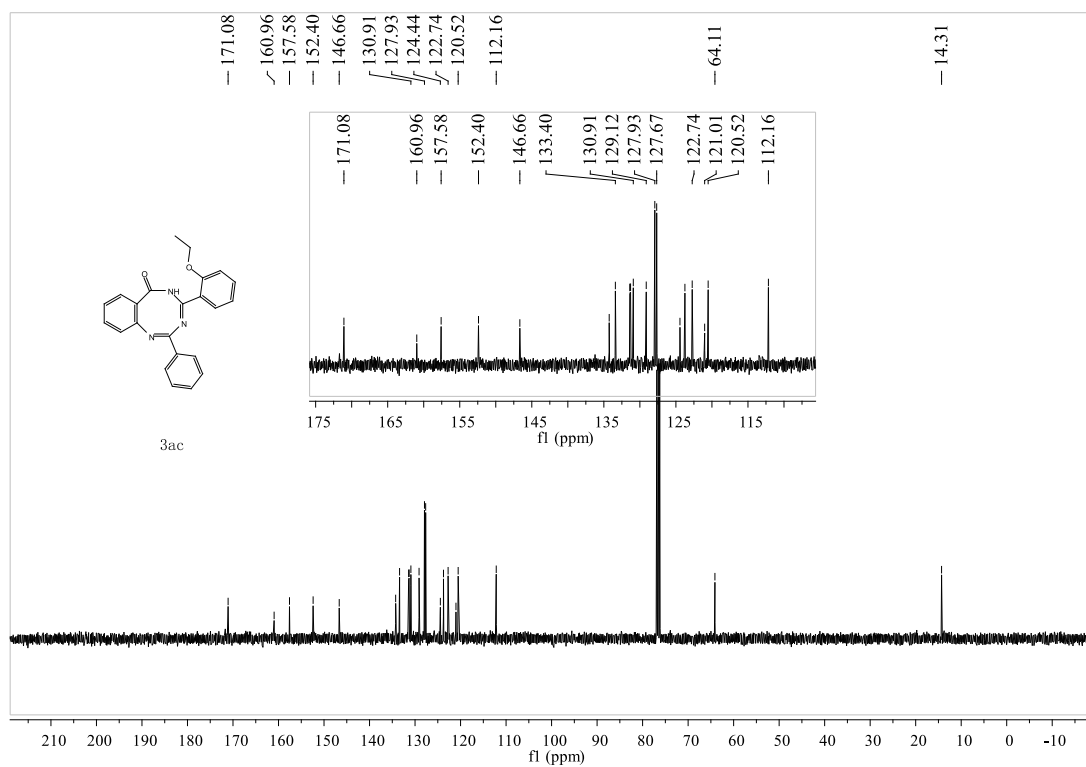
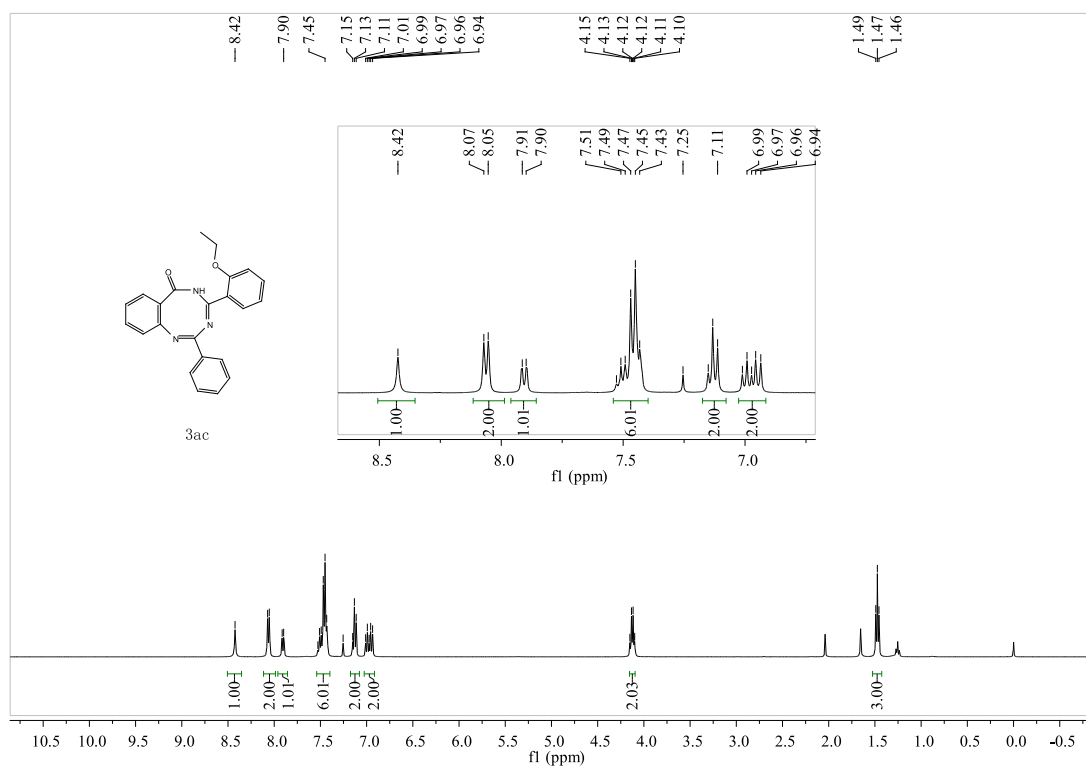
3aa



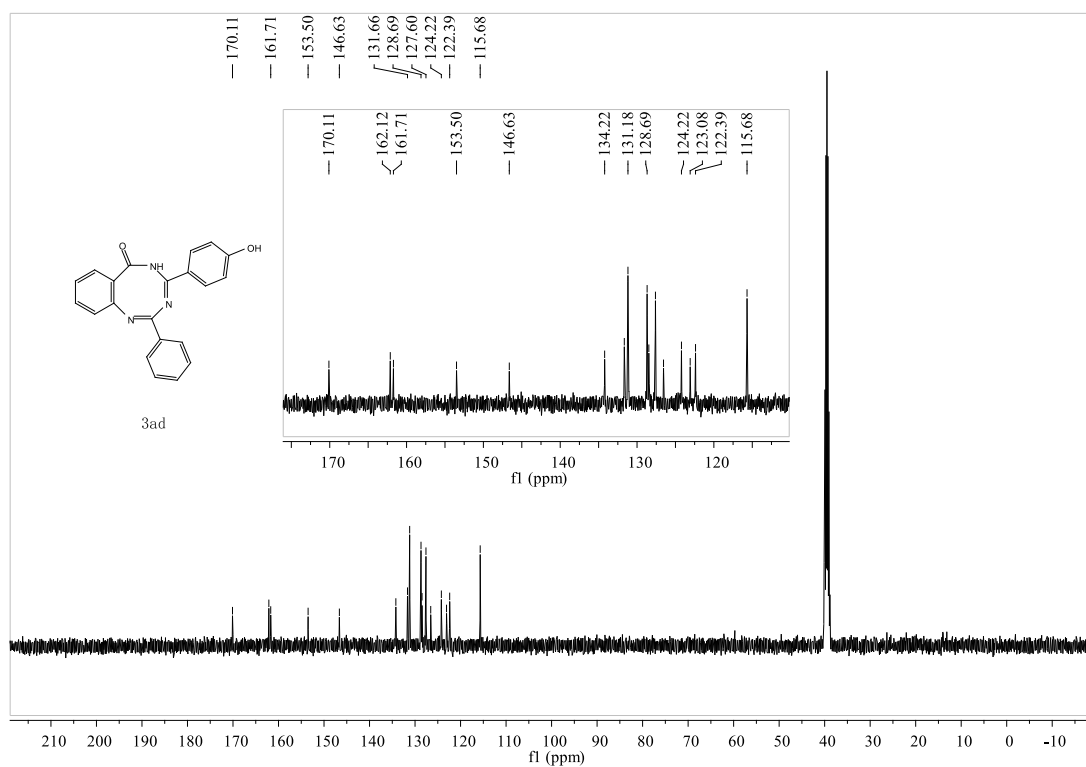
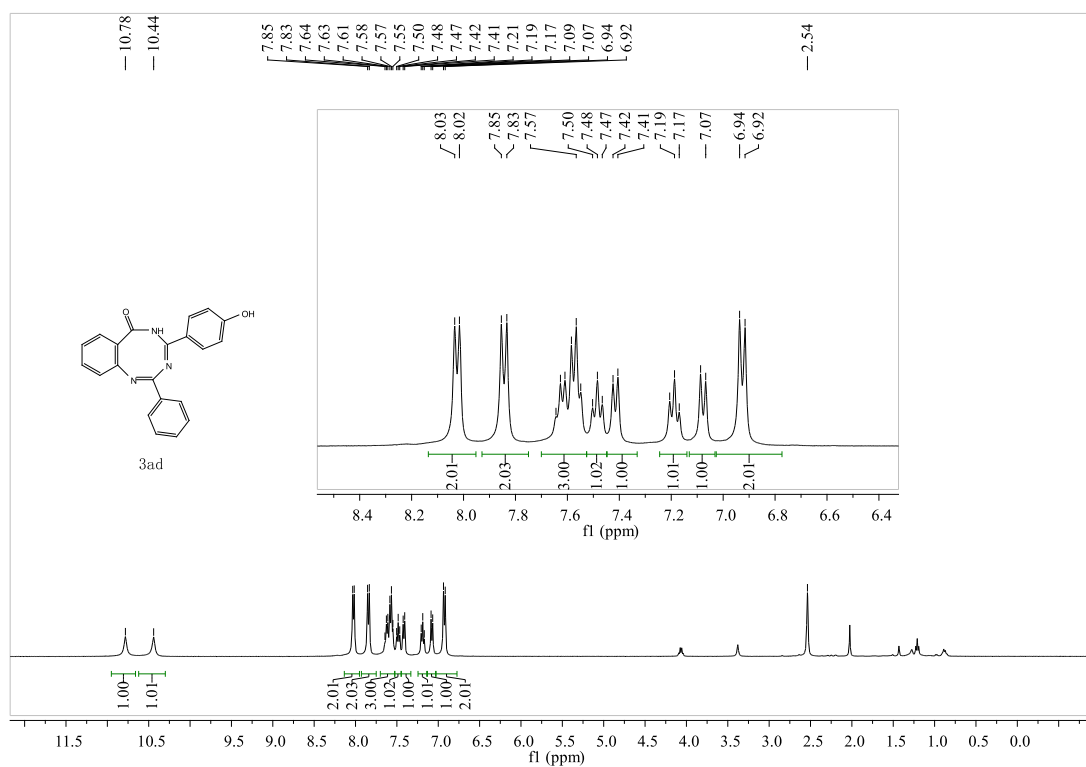
3ab



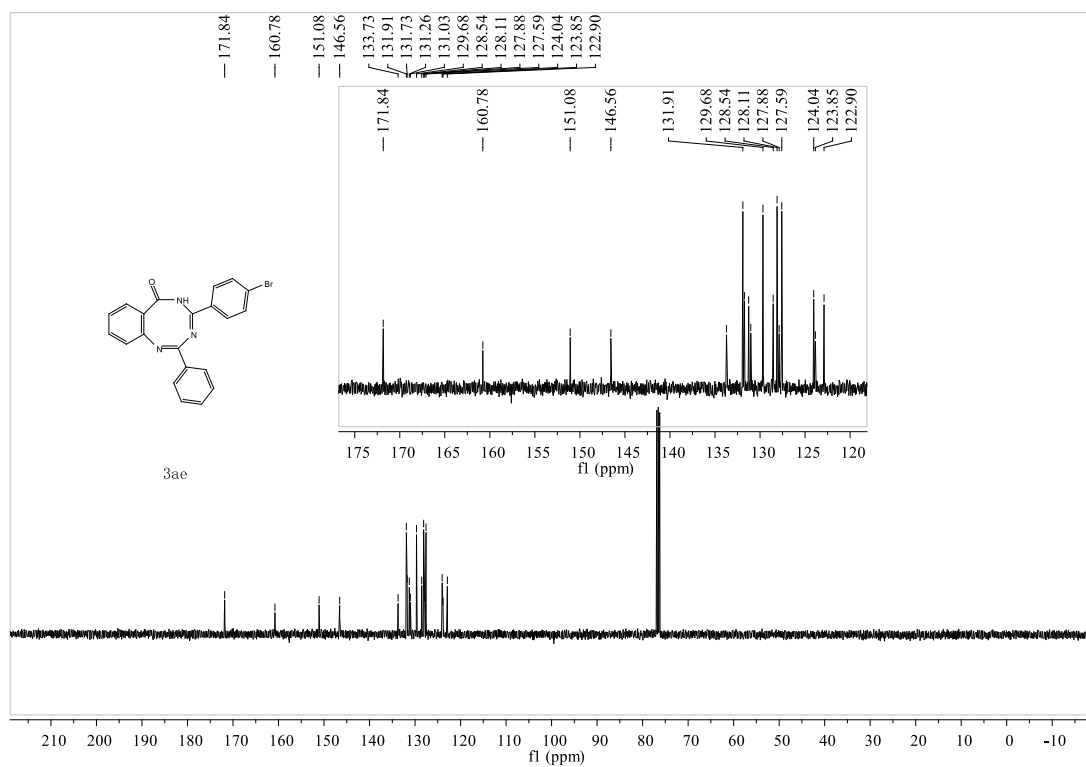
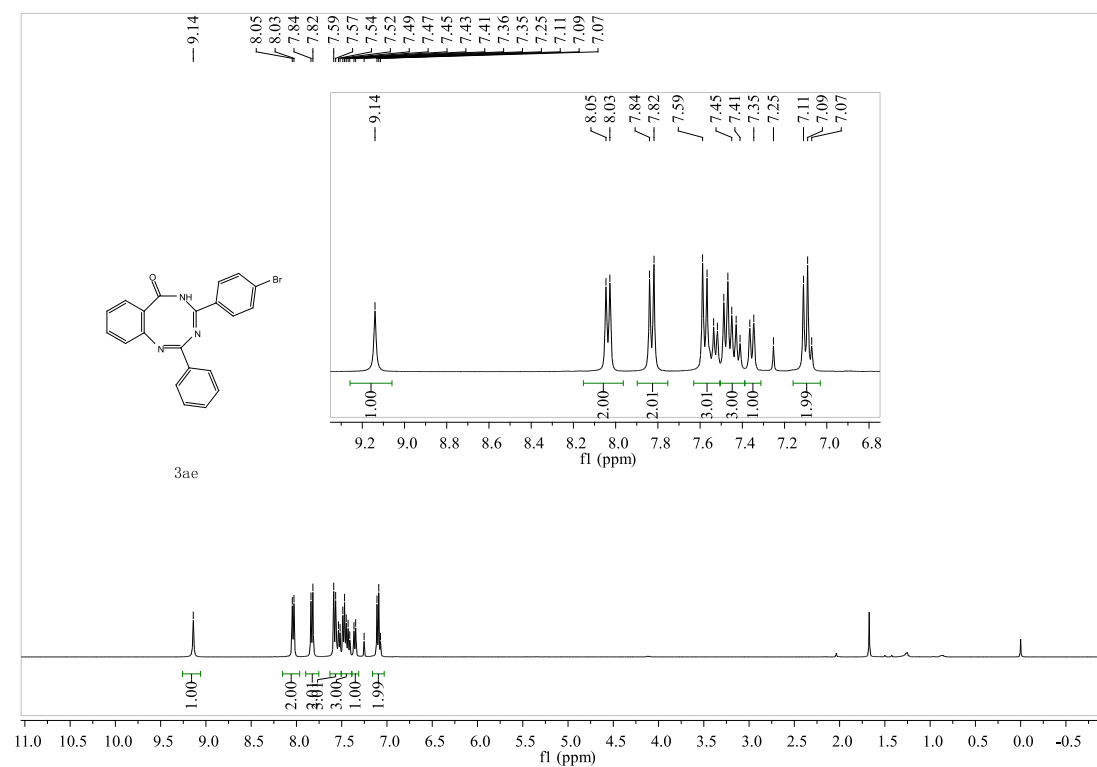
3ac



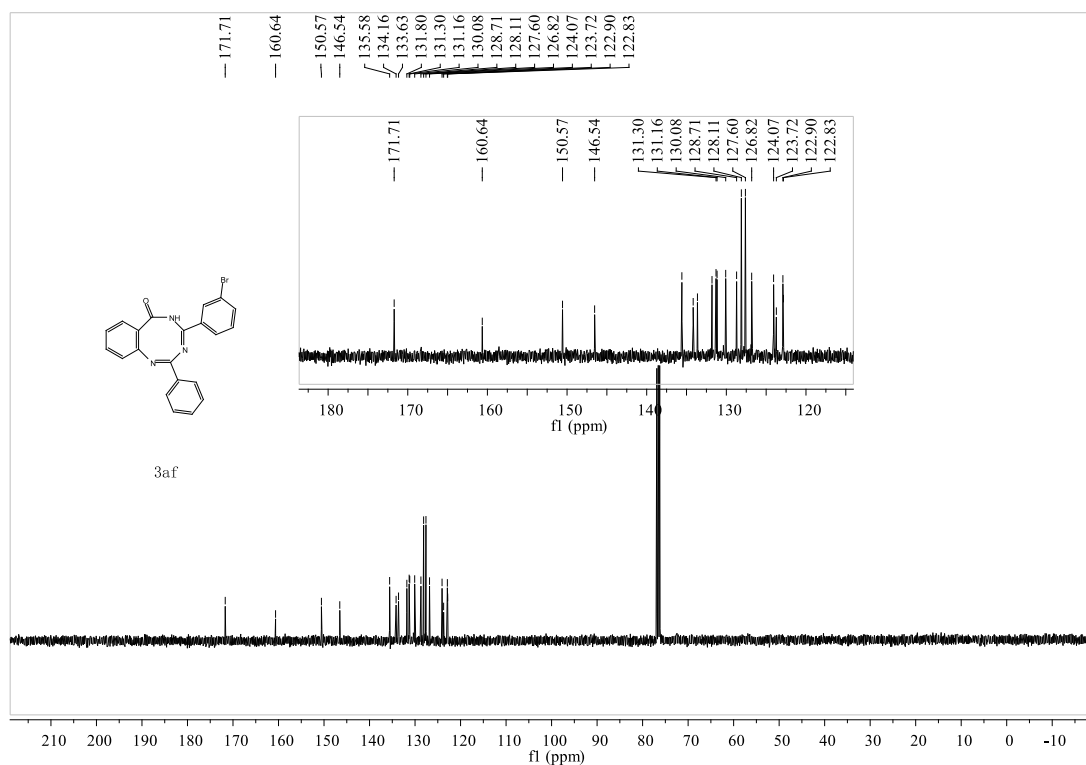
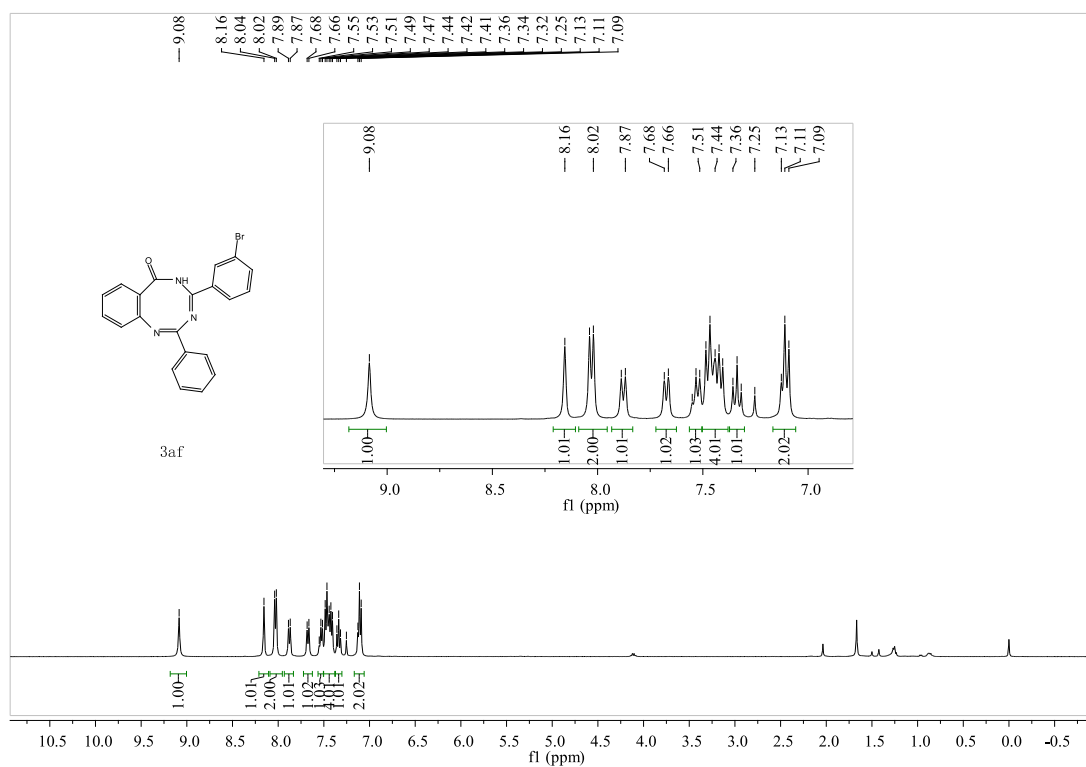
3ad



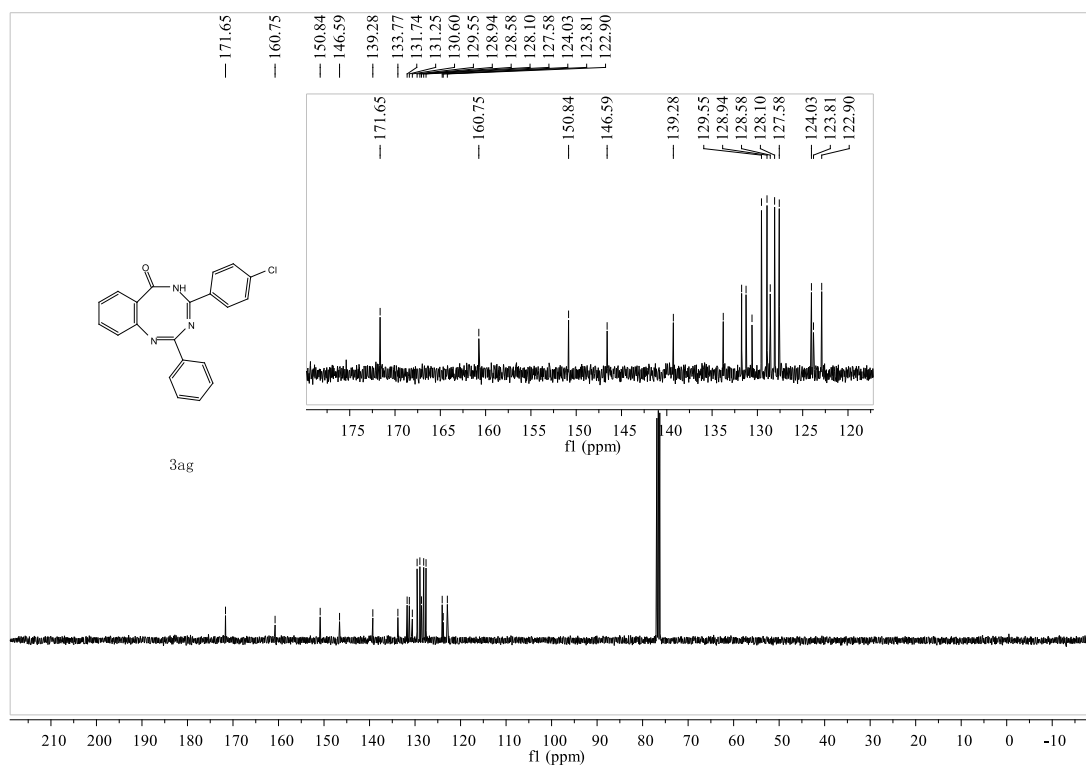
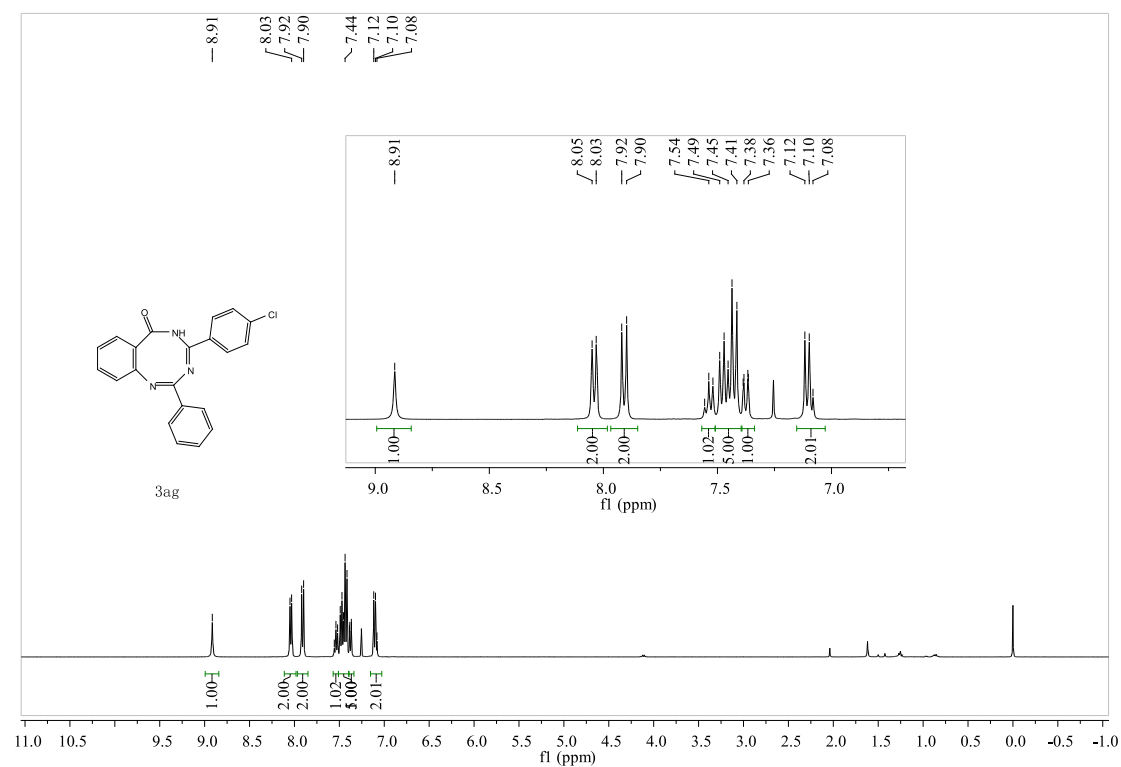
3ae



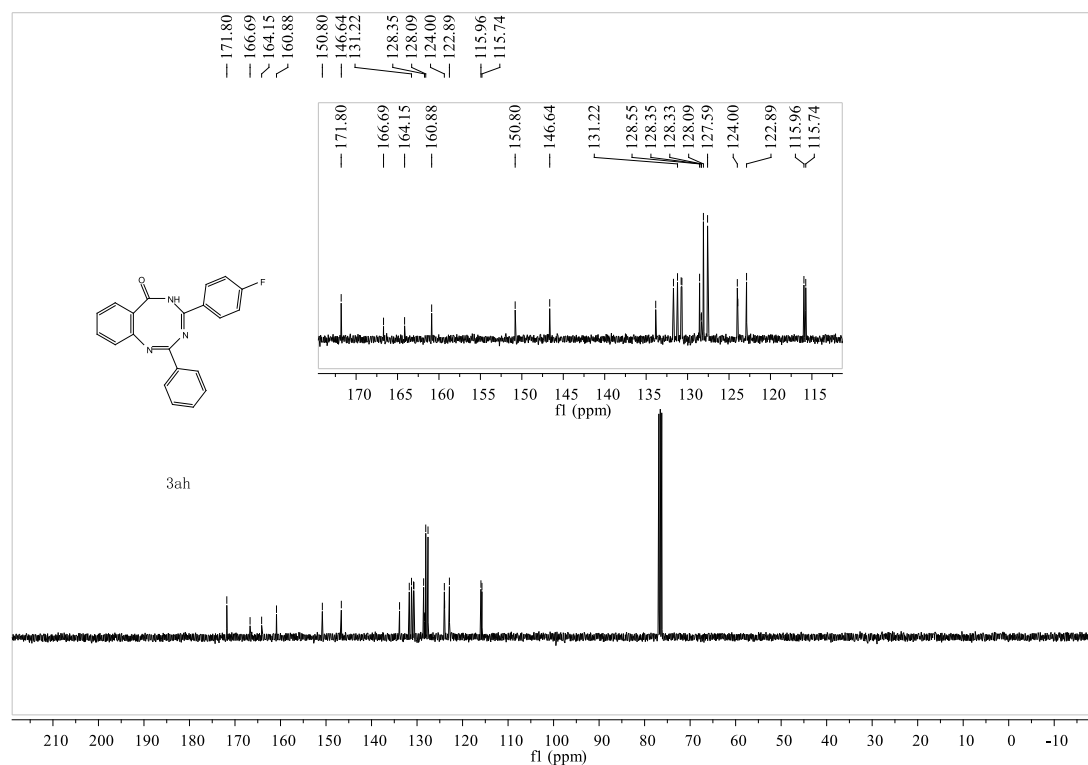
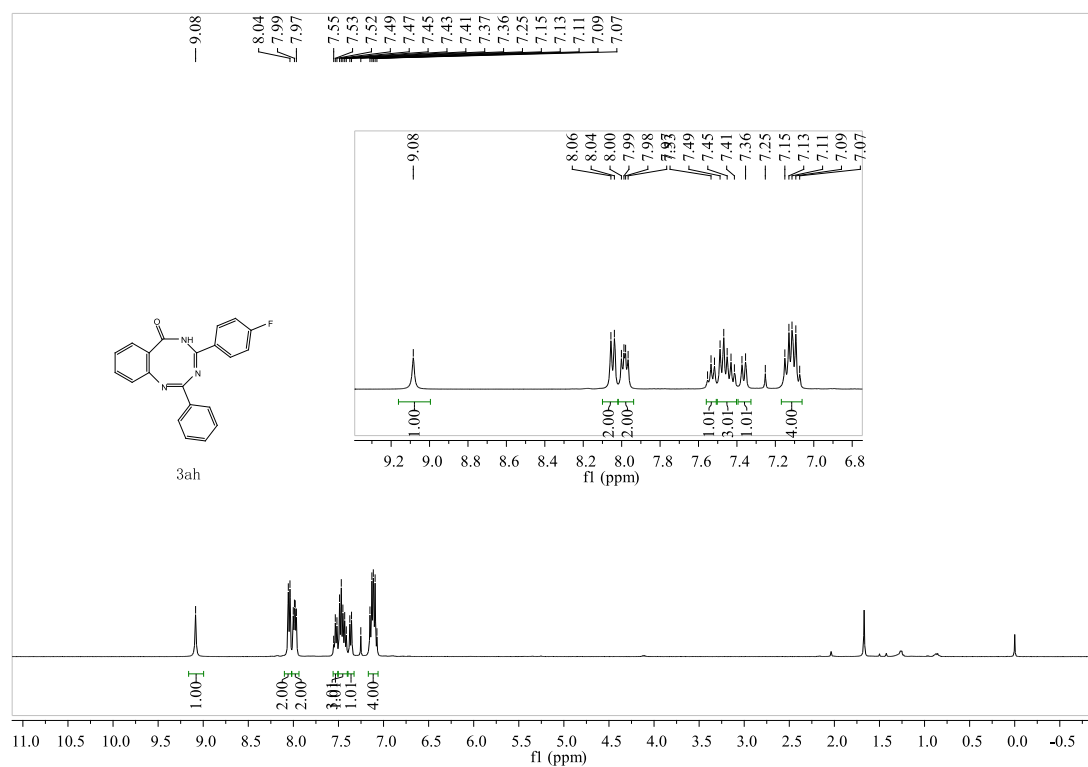
3af

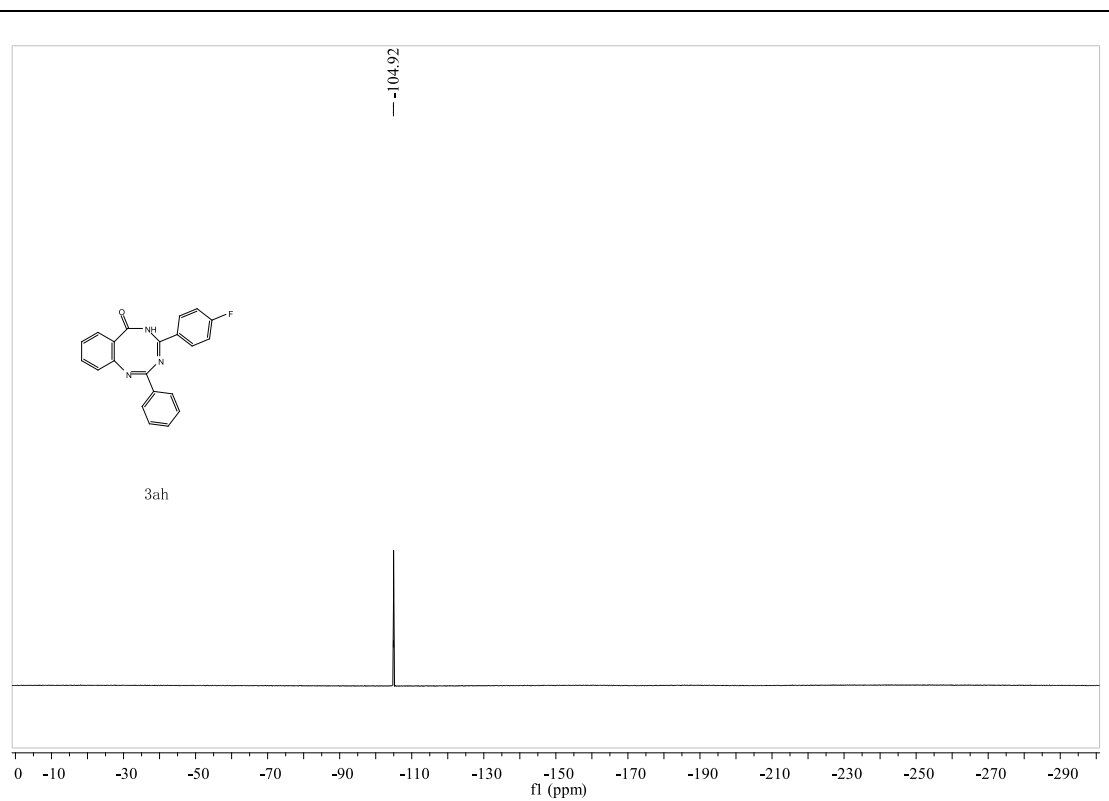


3ag

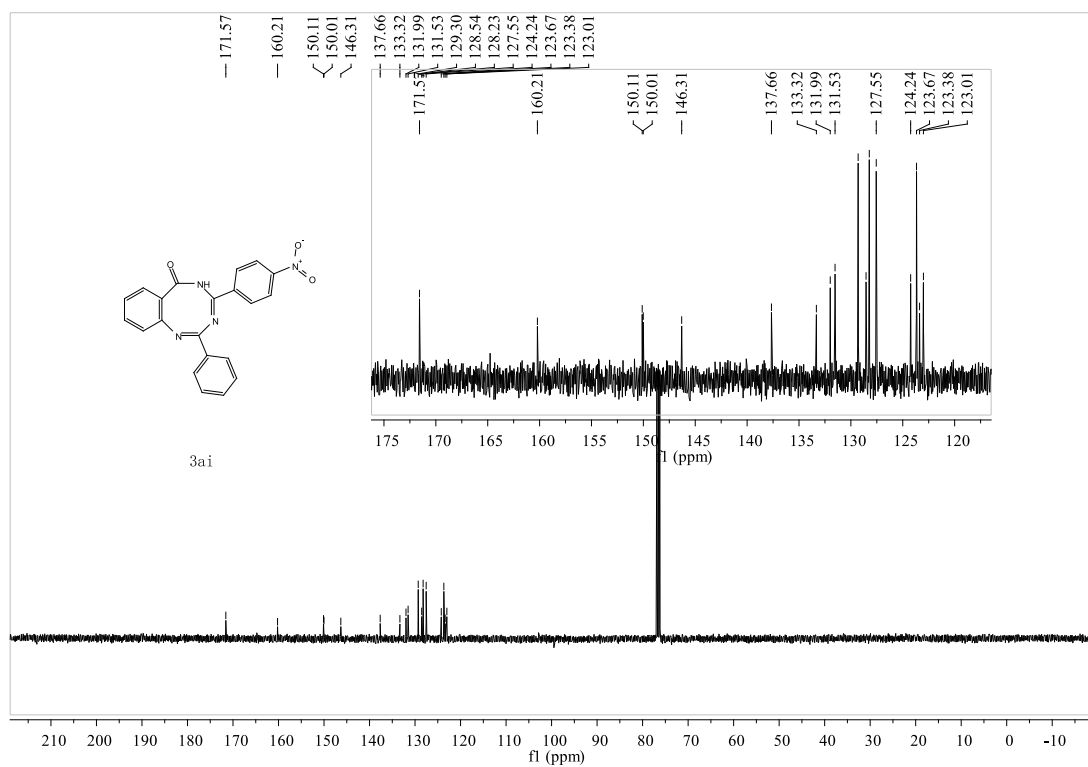
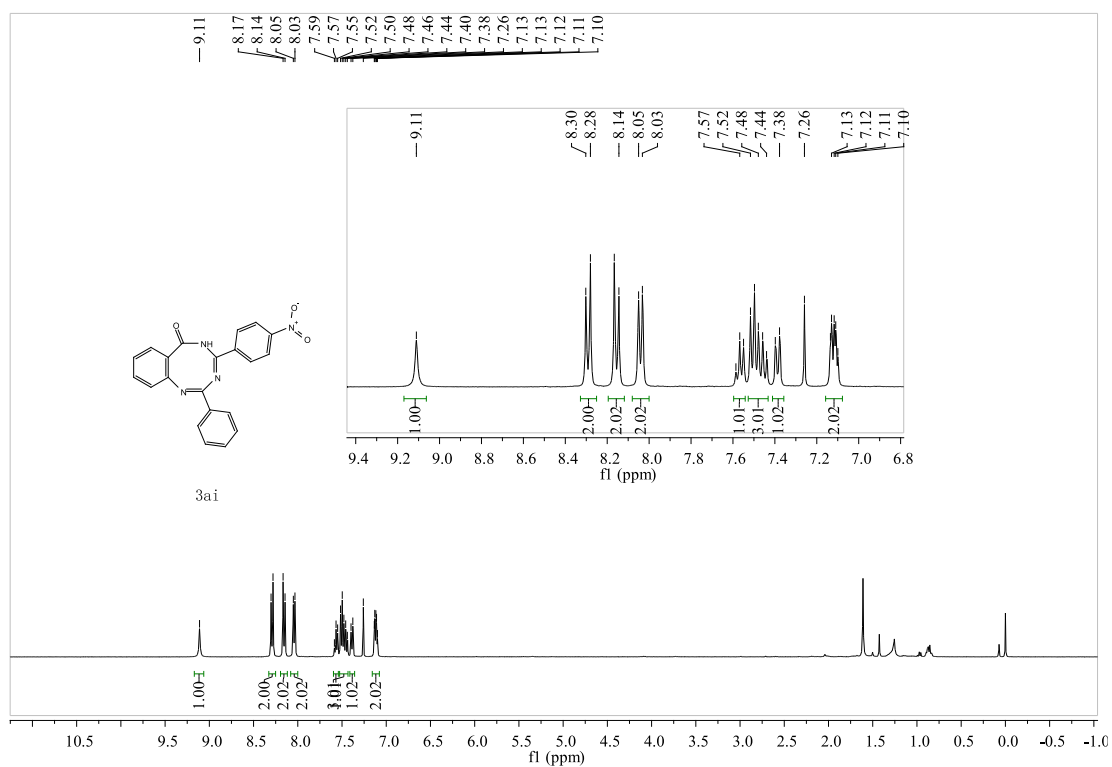


3ah

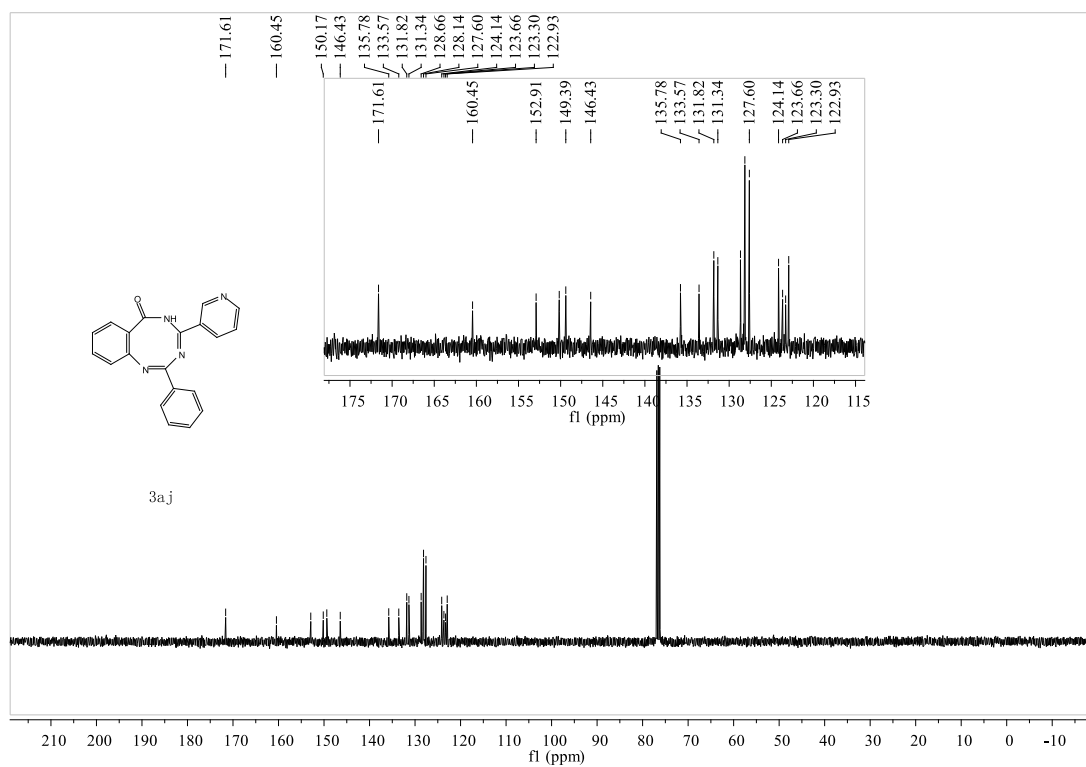
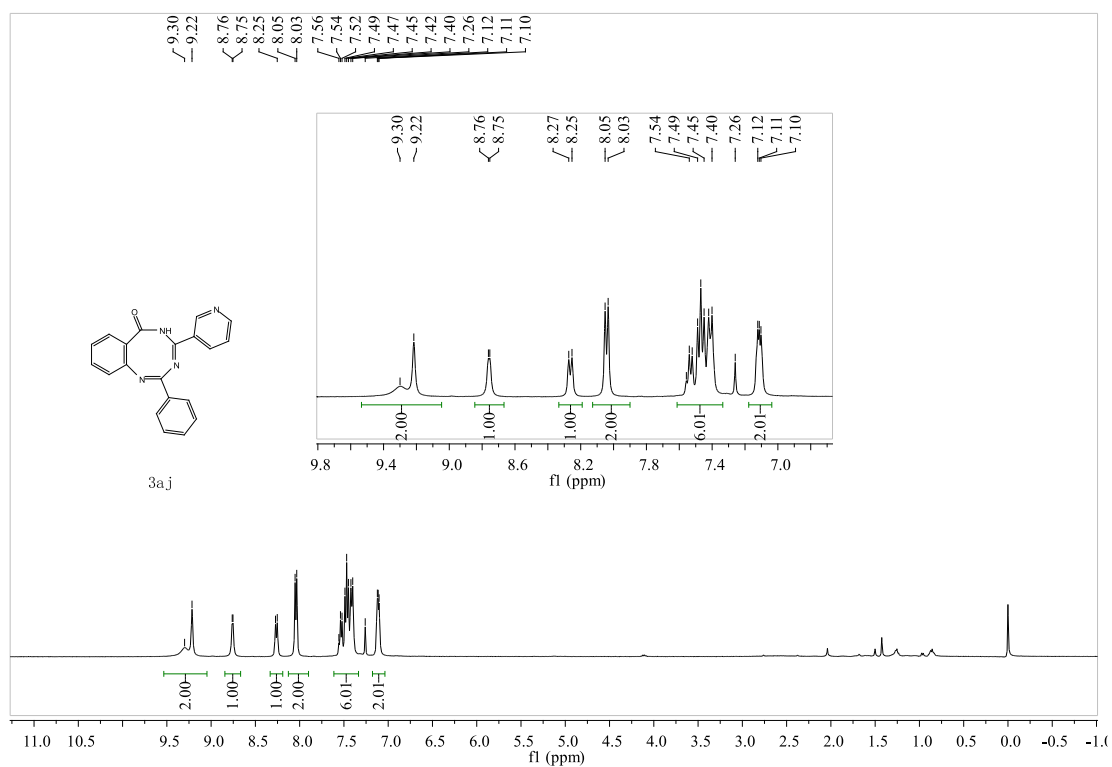




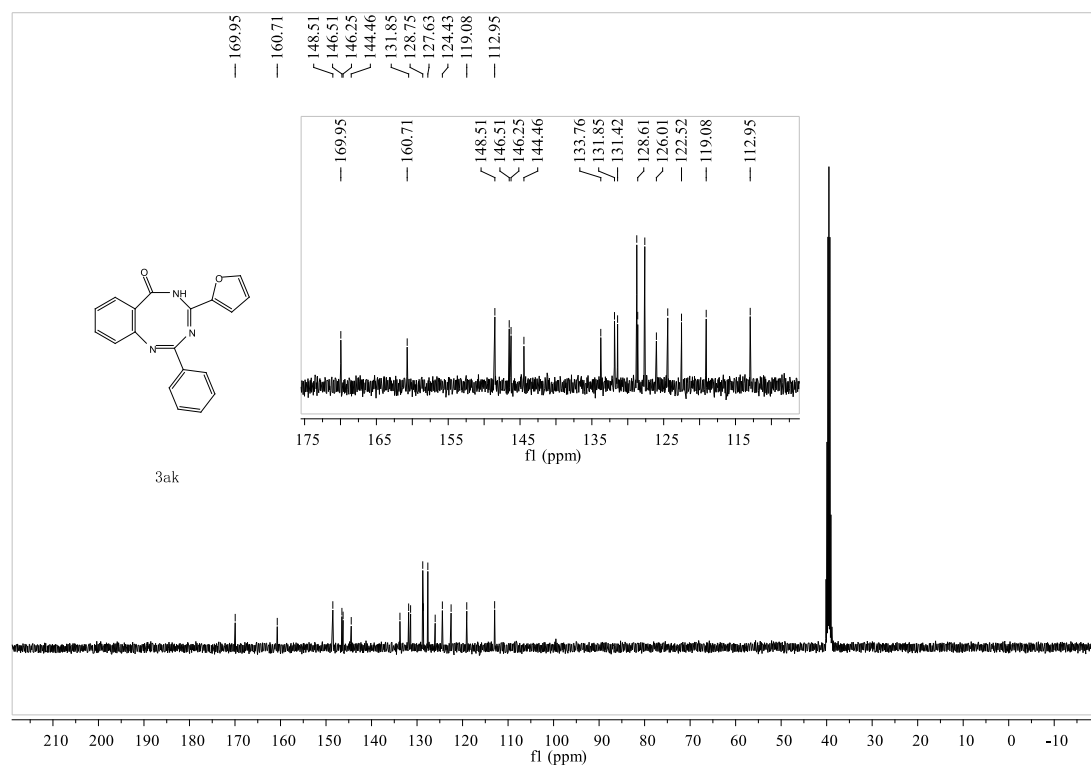
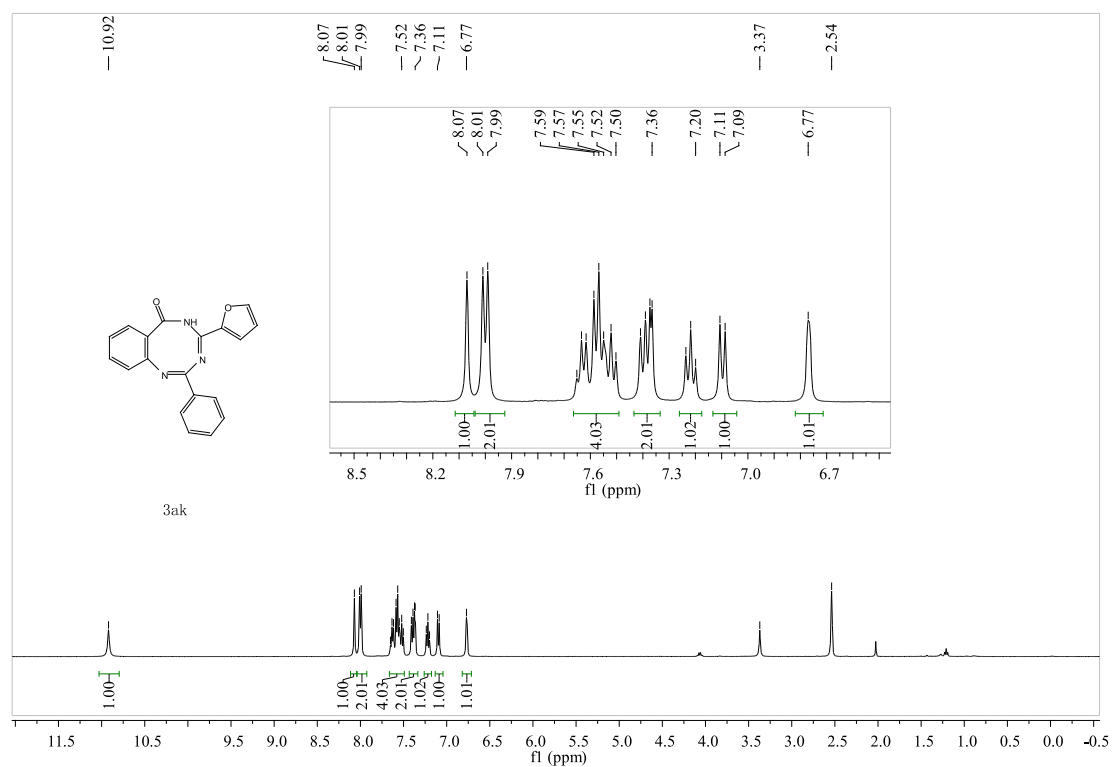
3ai



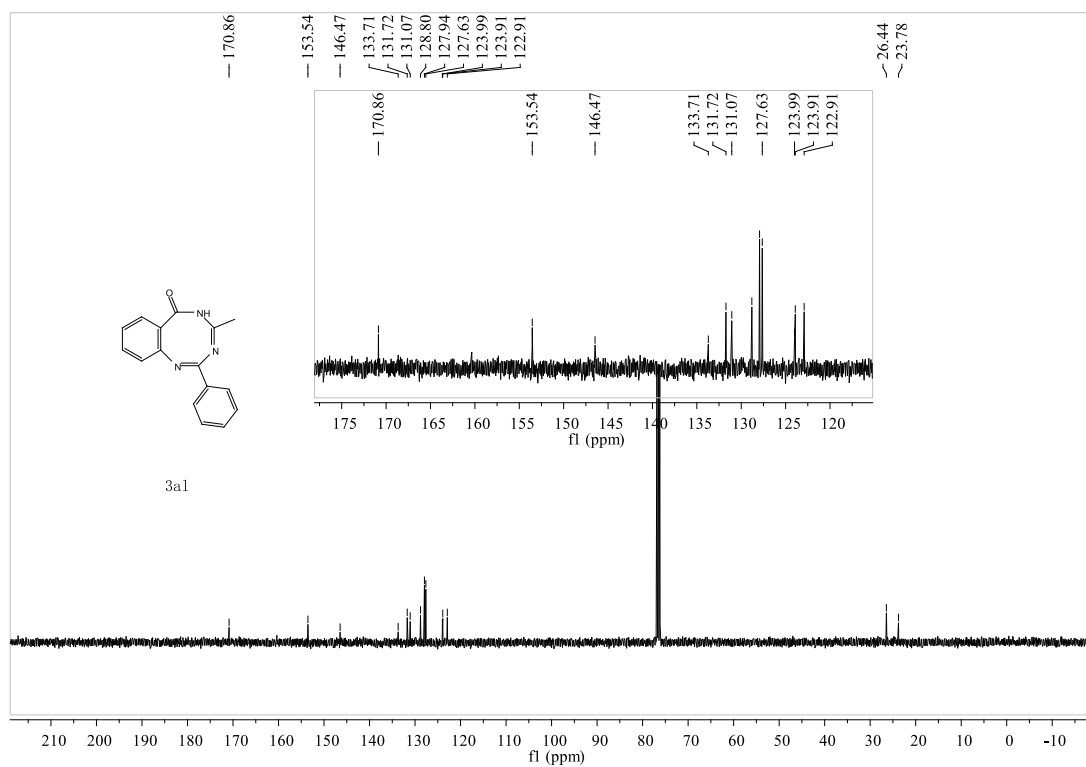
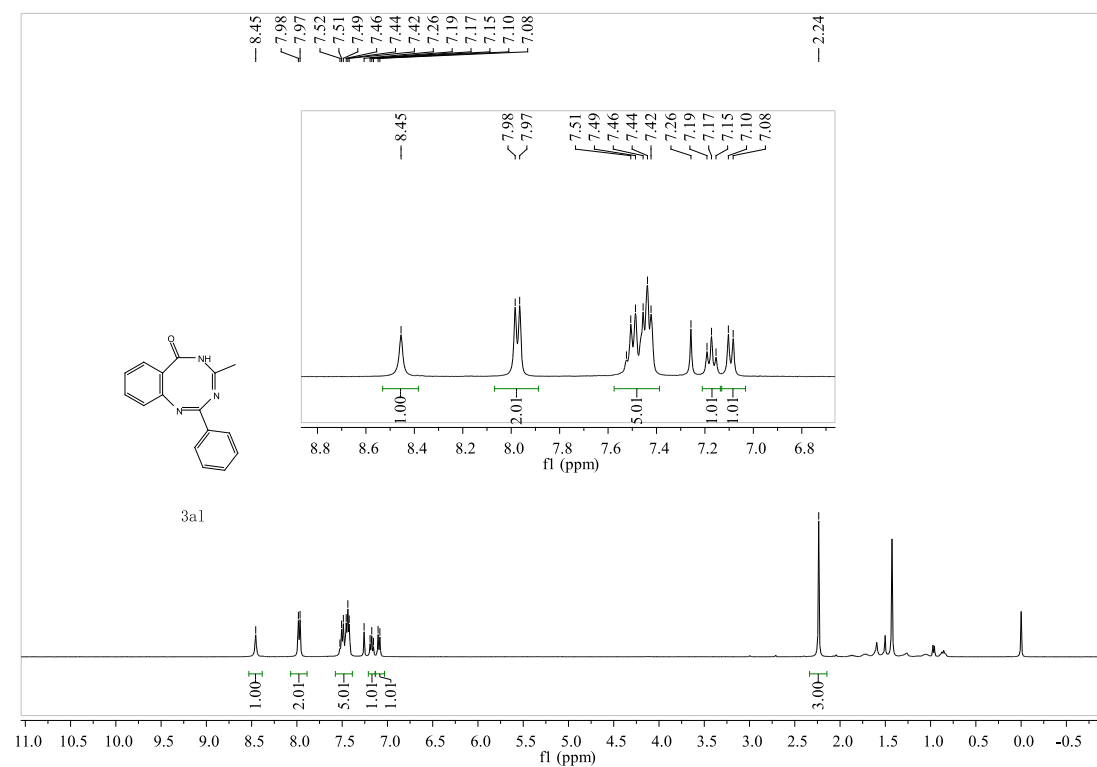
3aj



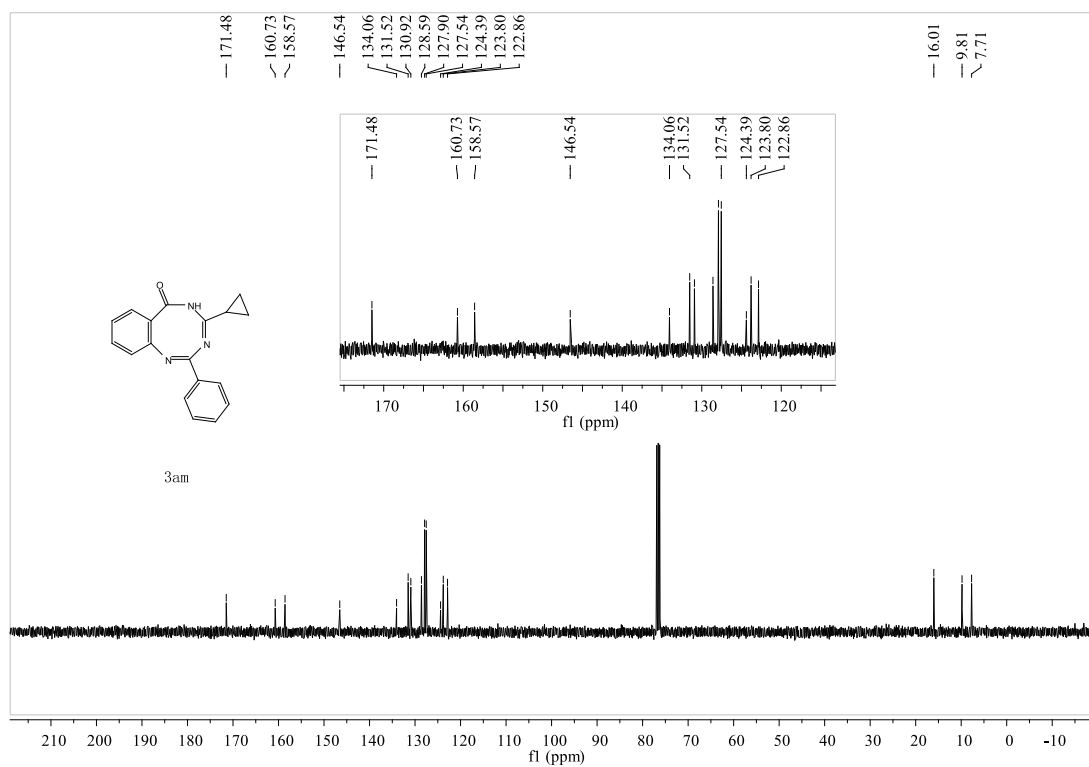
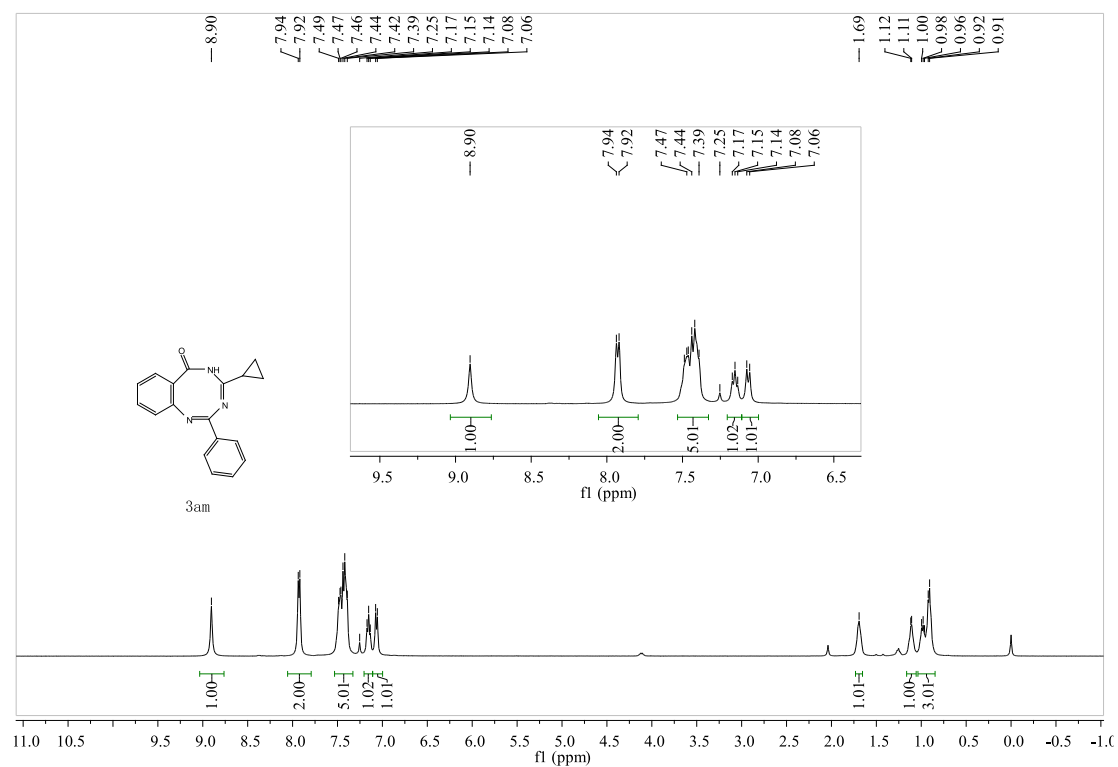
3ak



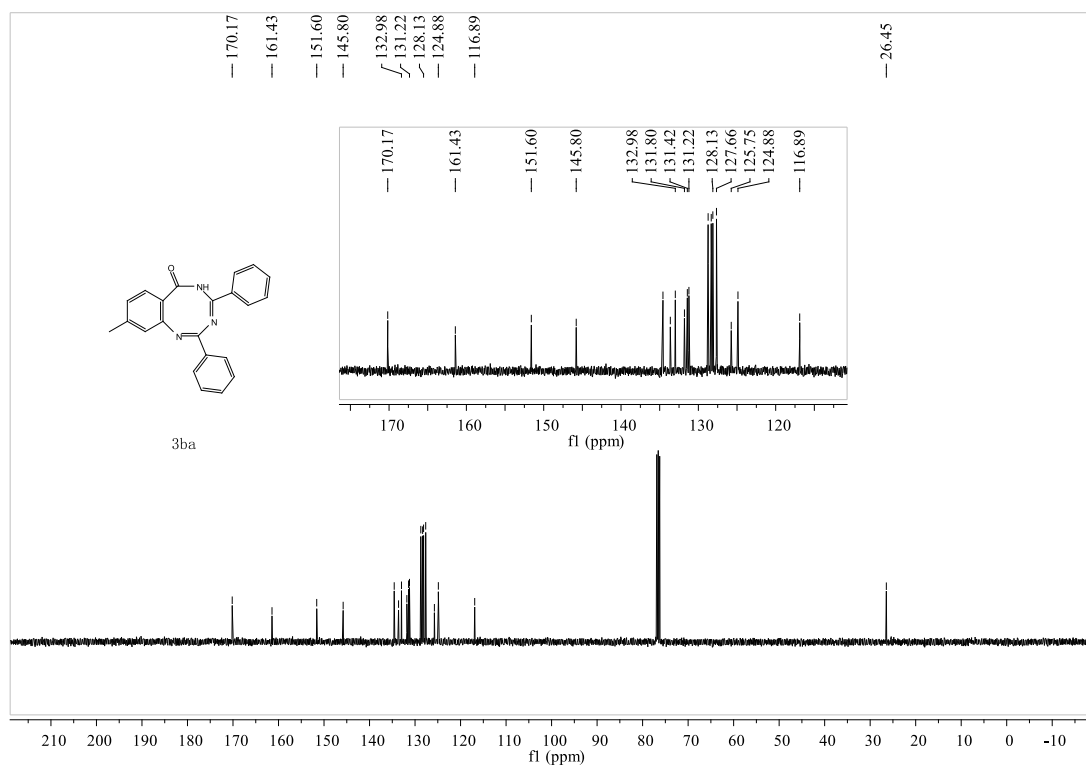
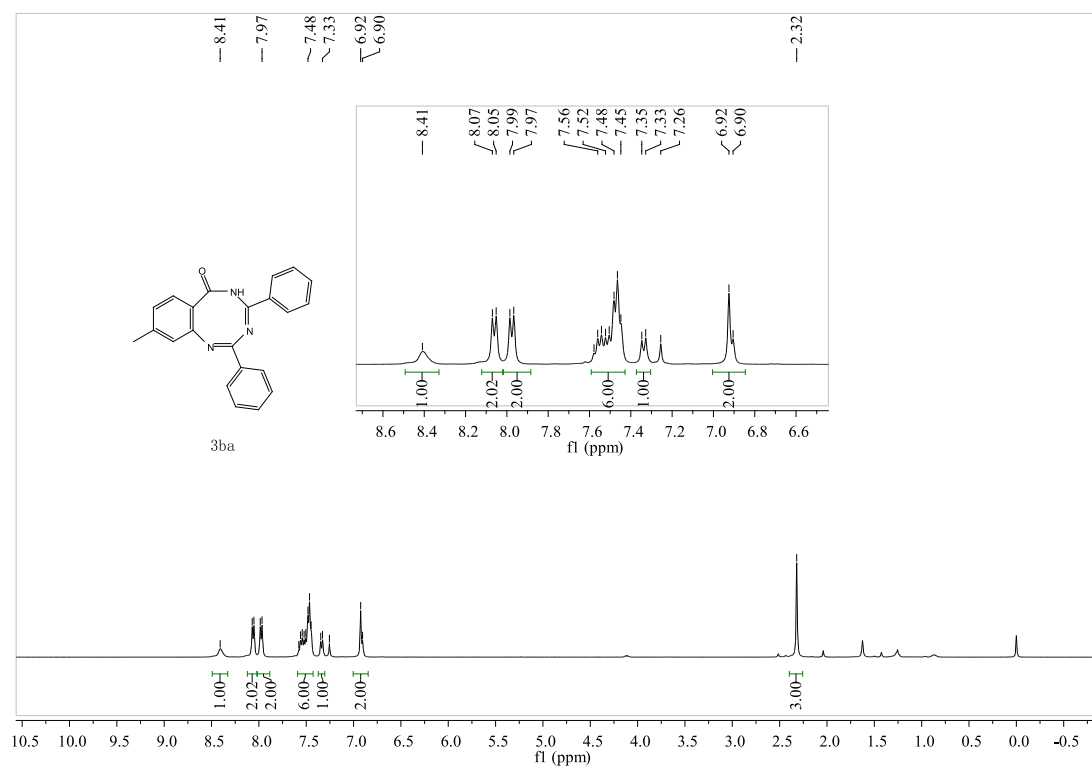
3al



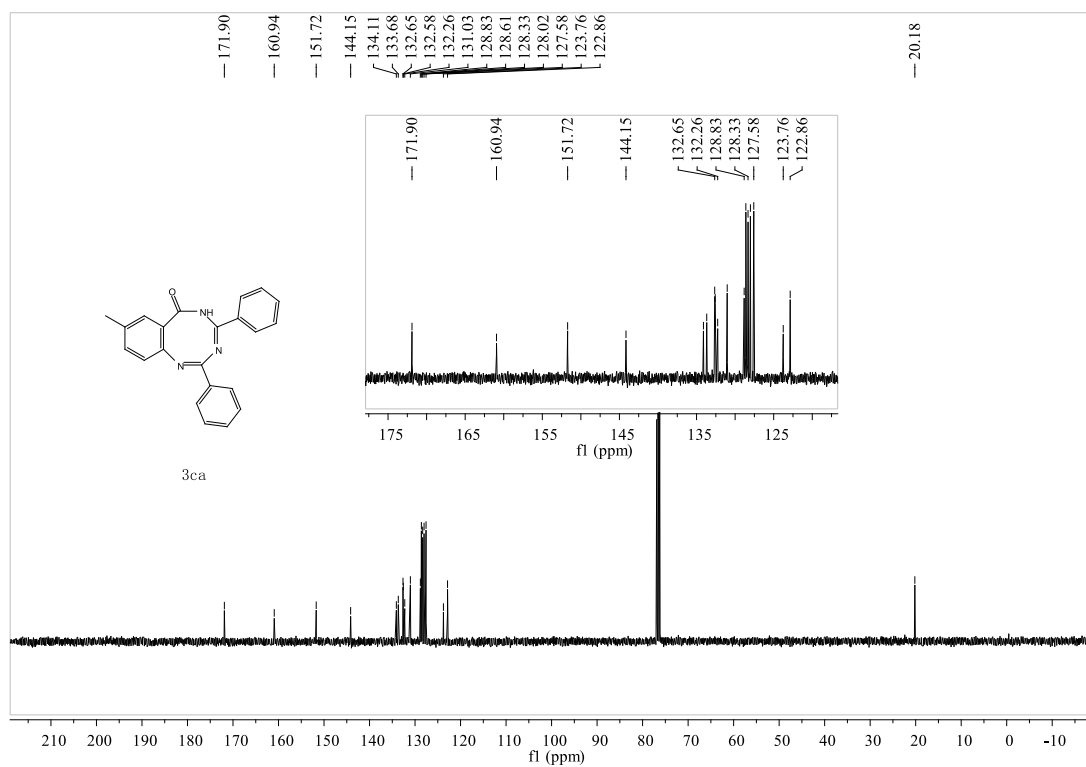
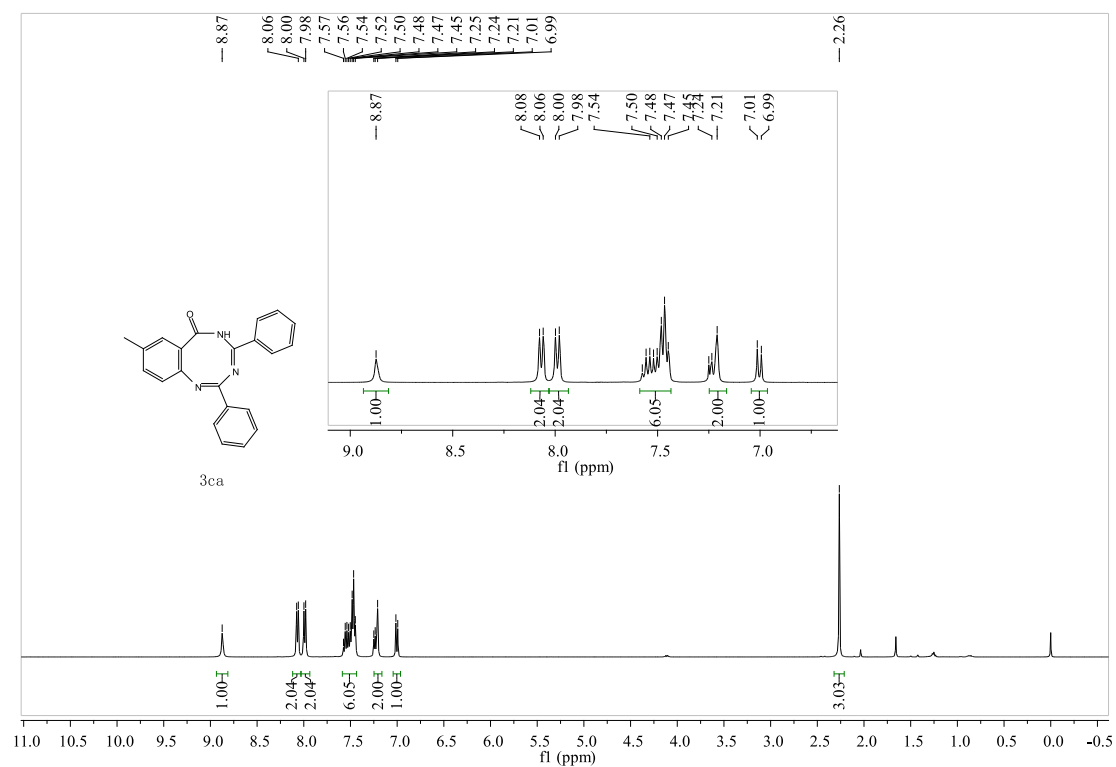
3am



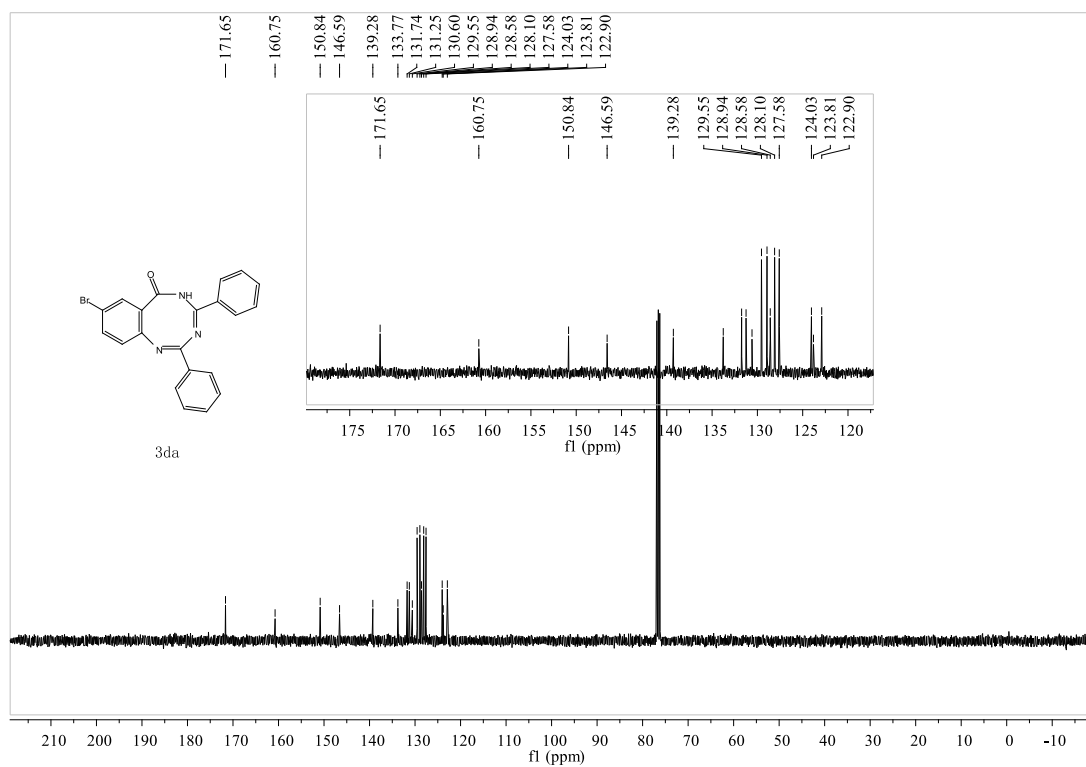
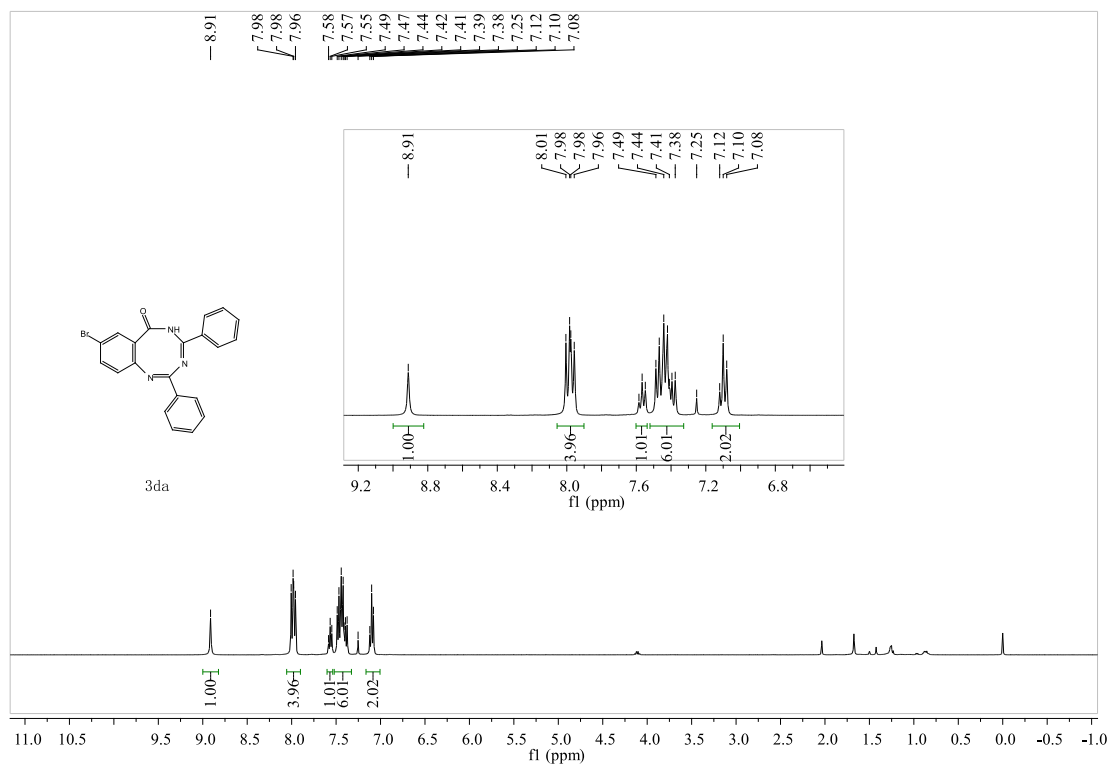
3ba



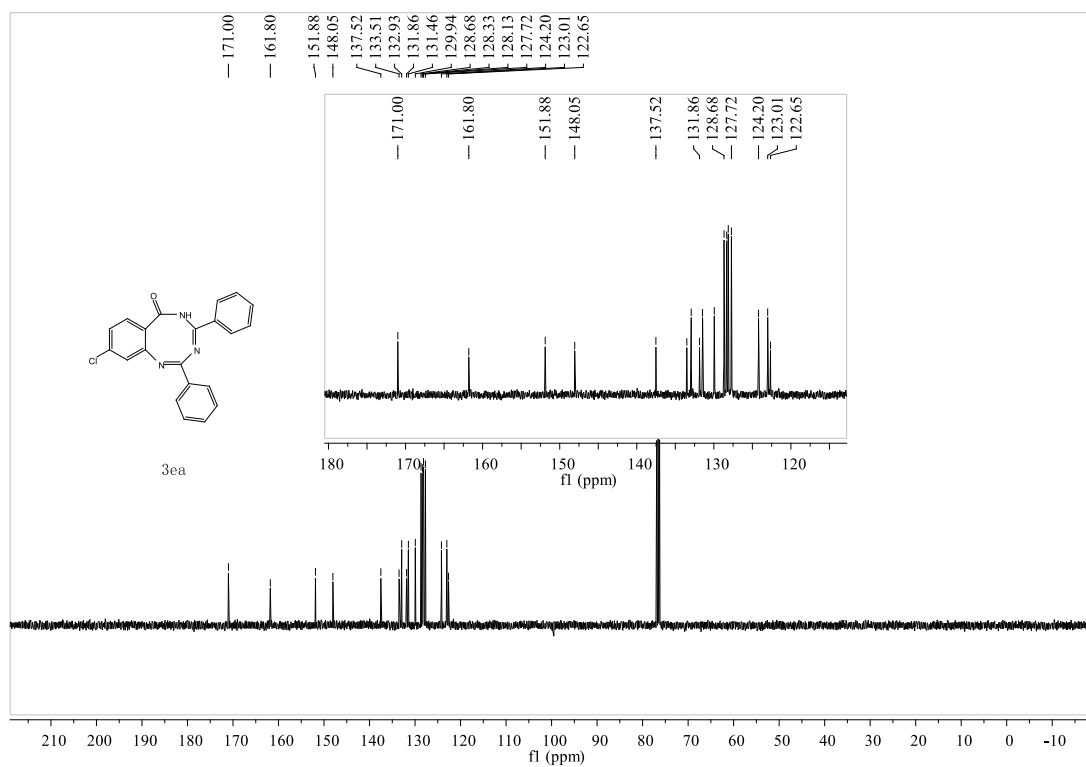
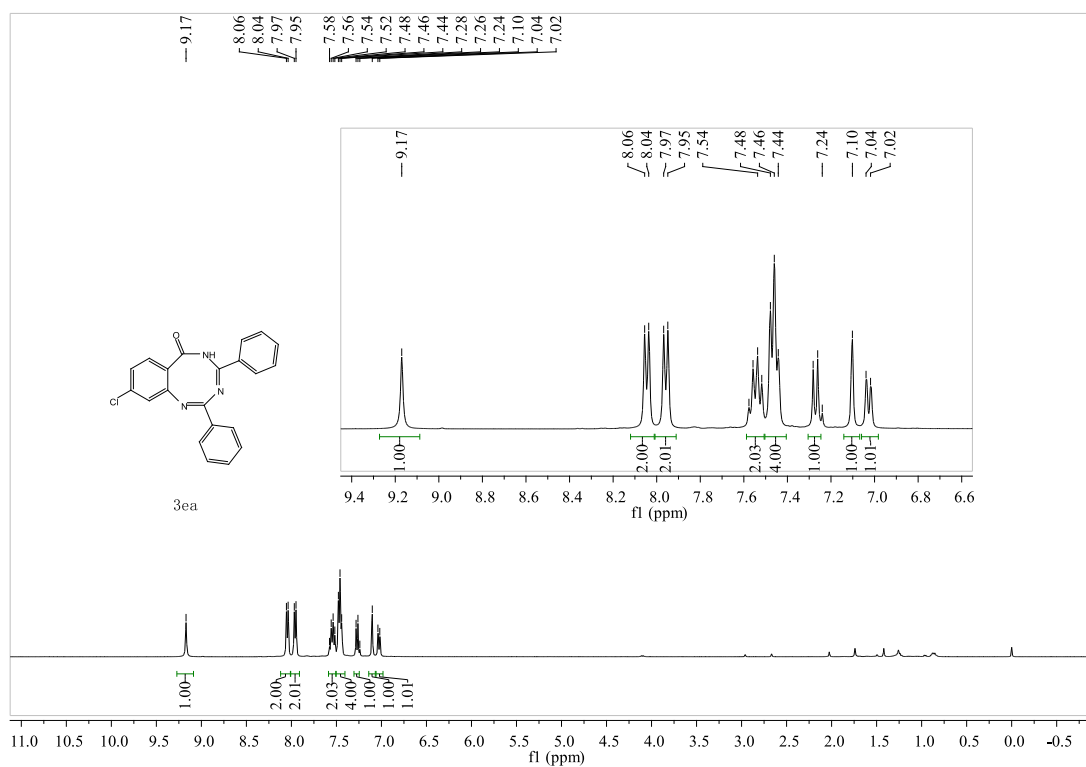
3ca



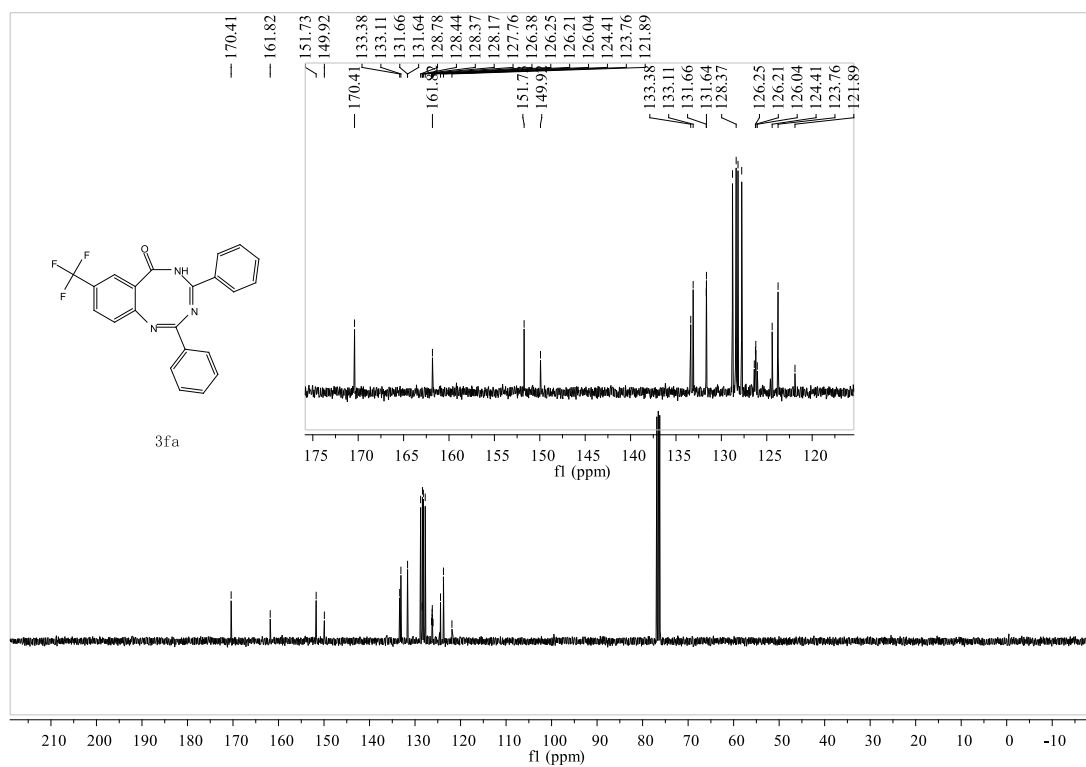
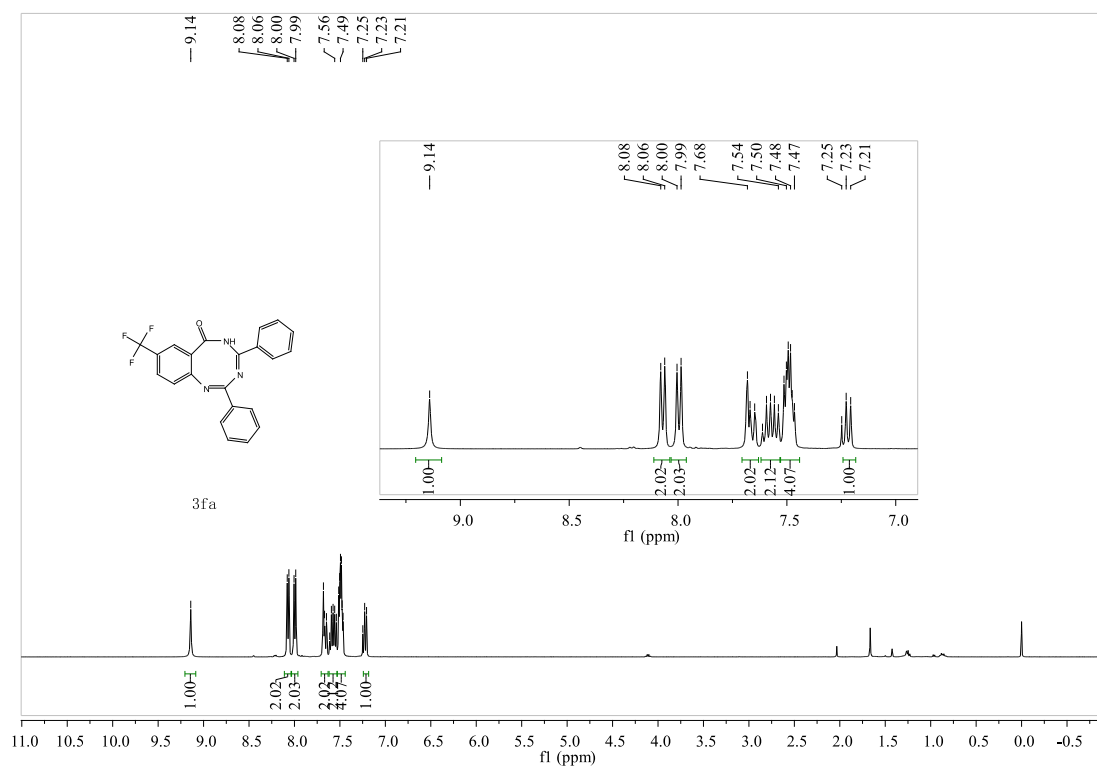
3da

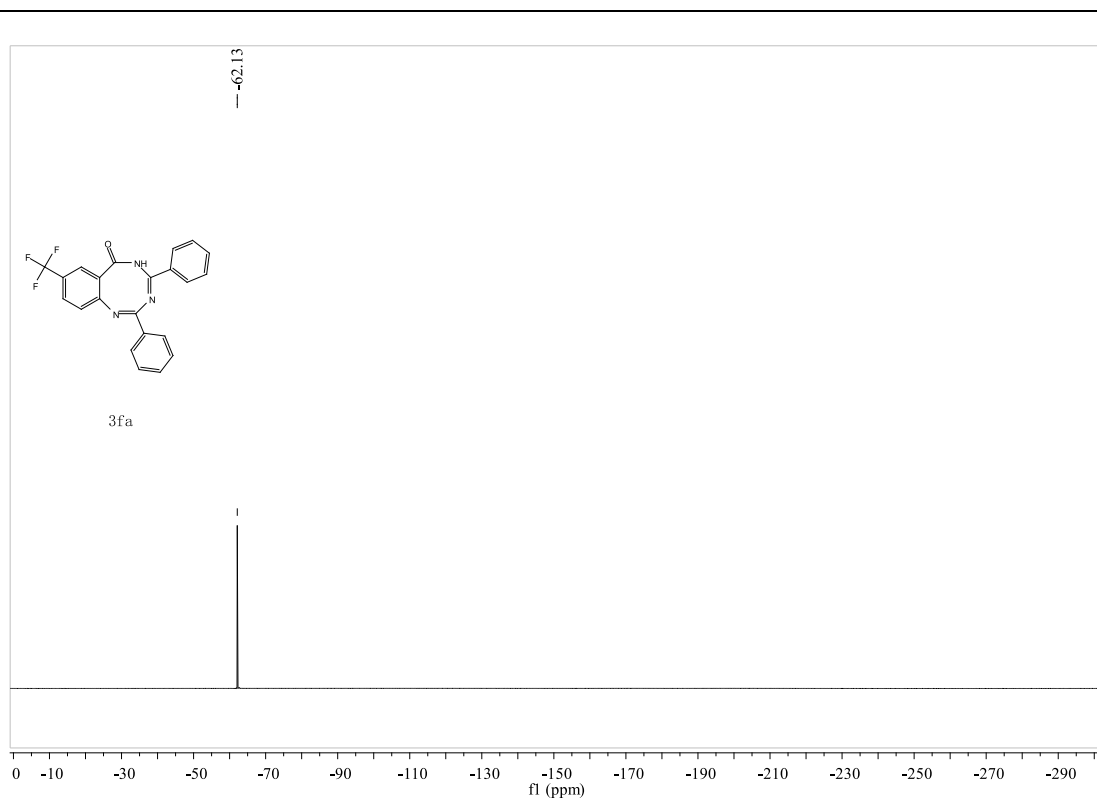


3ea

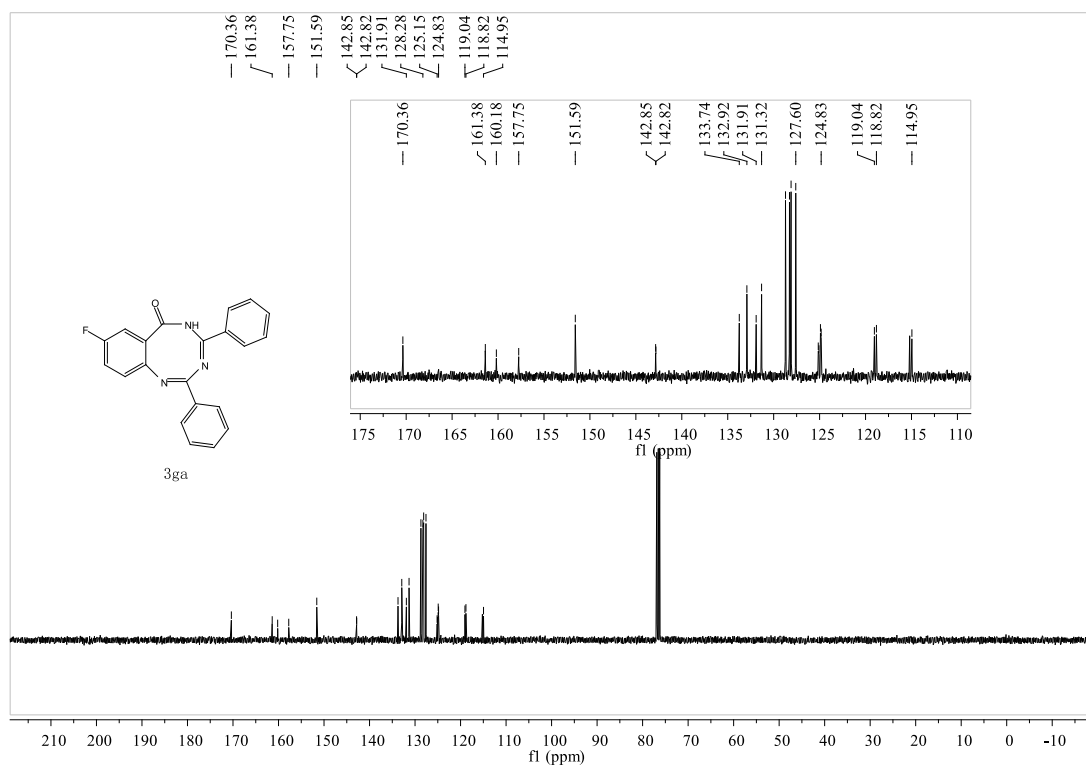
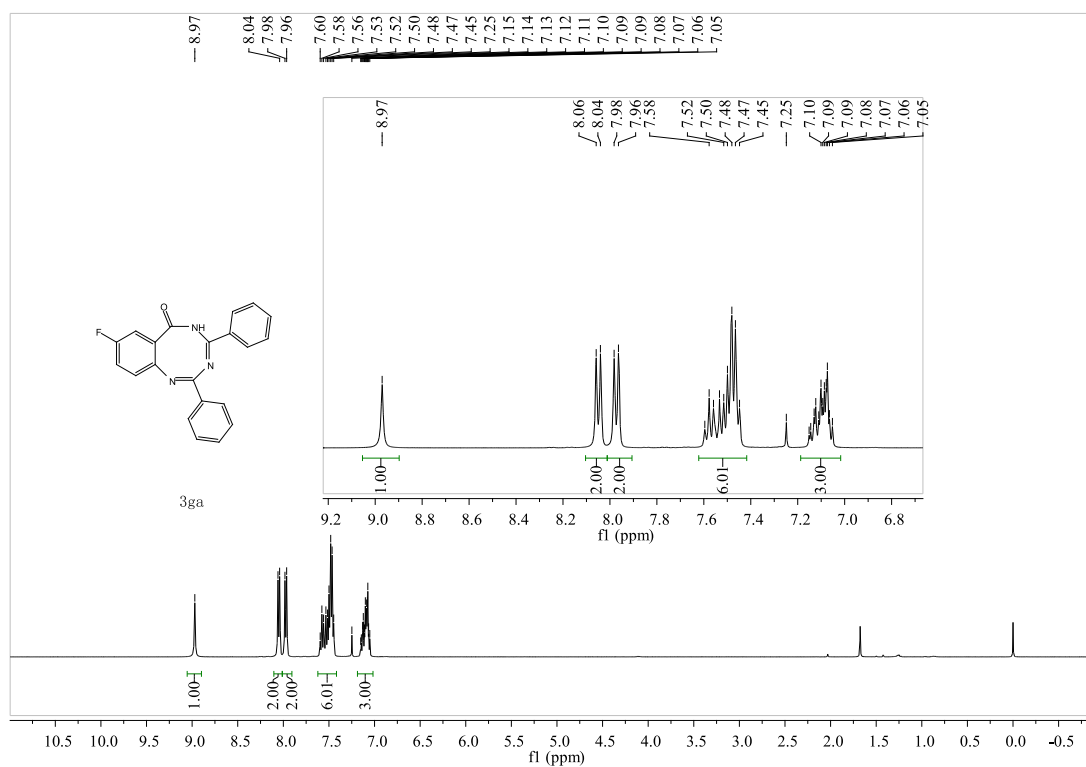


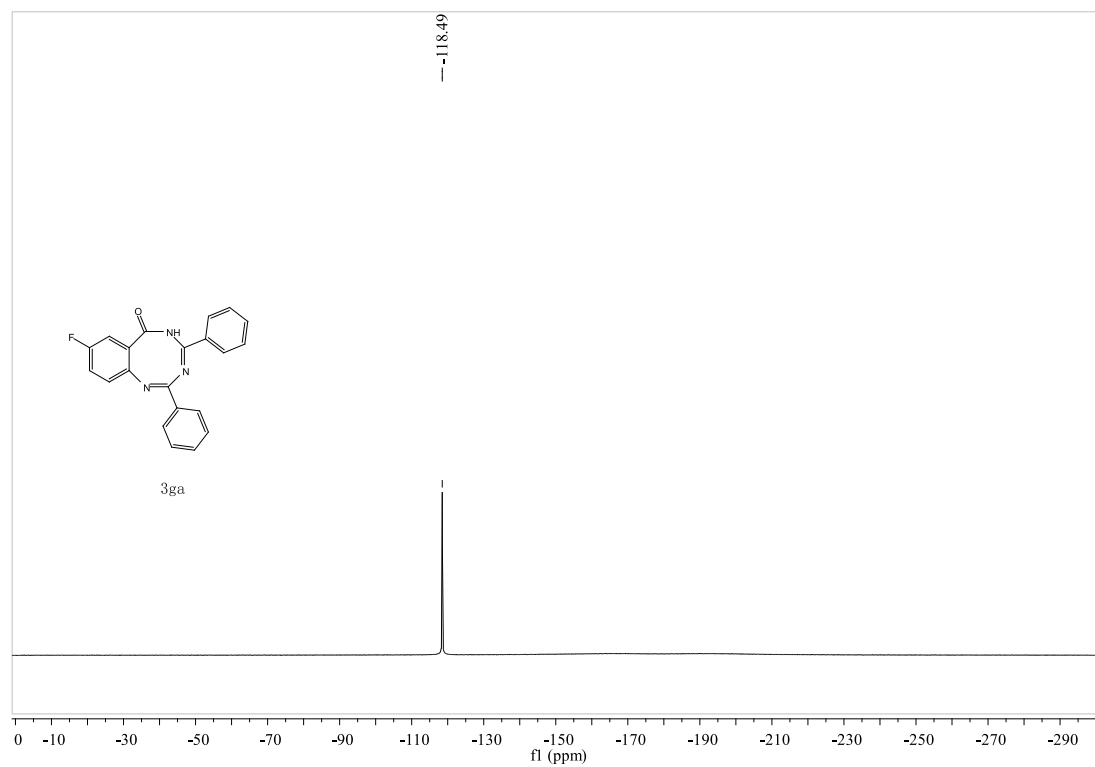
3fa



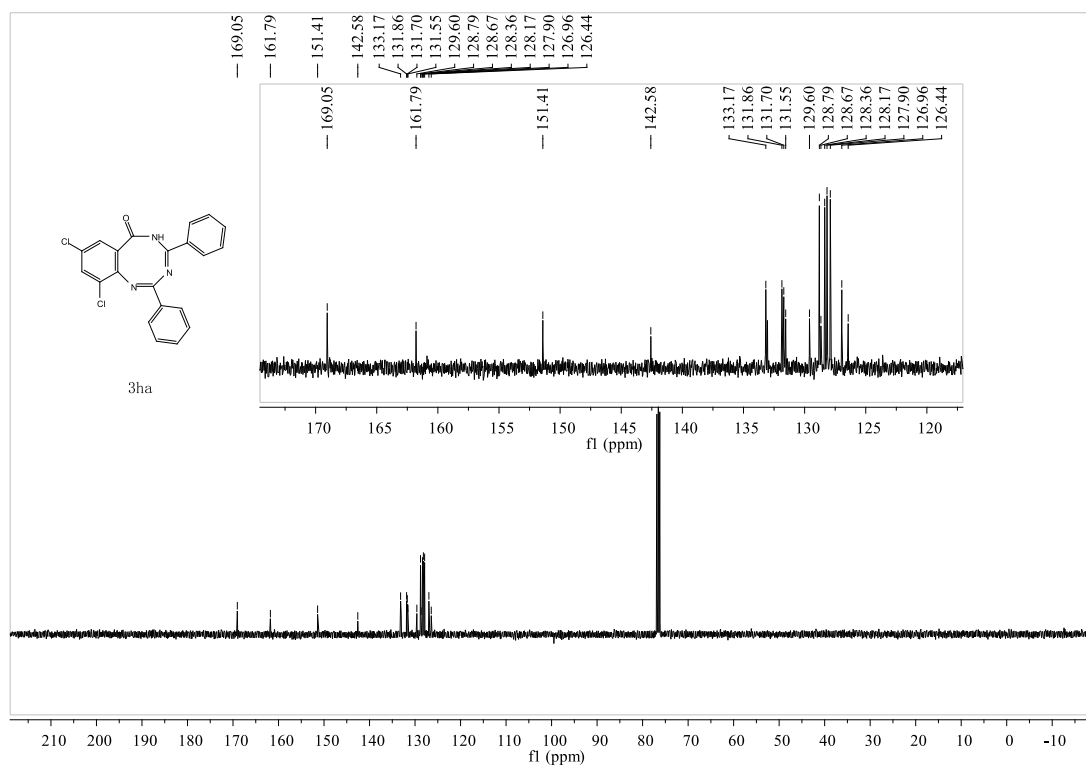
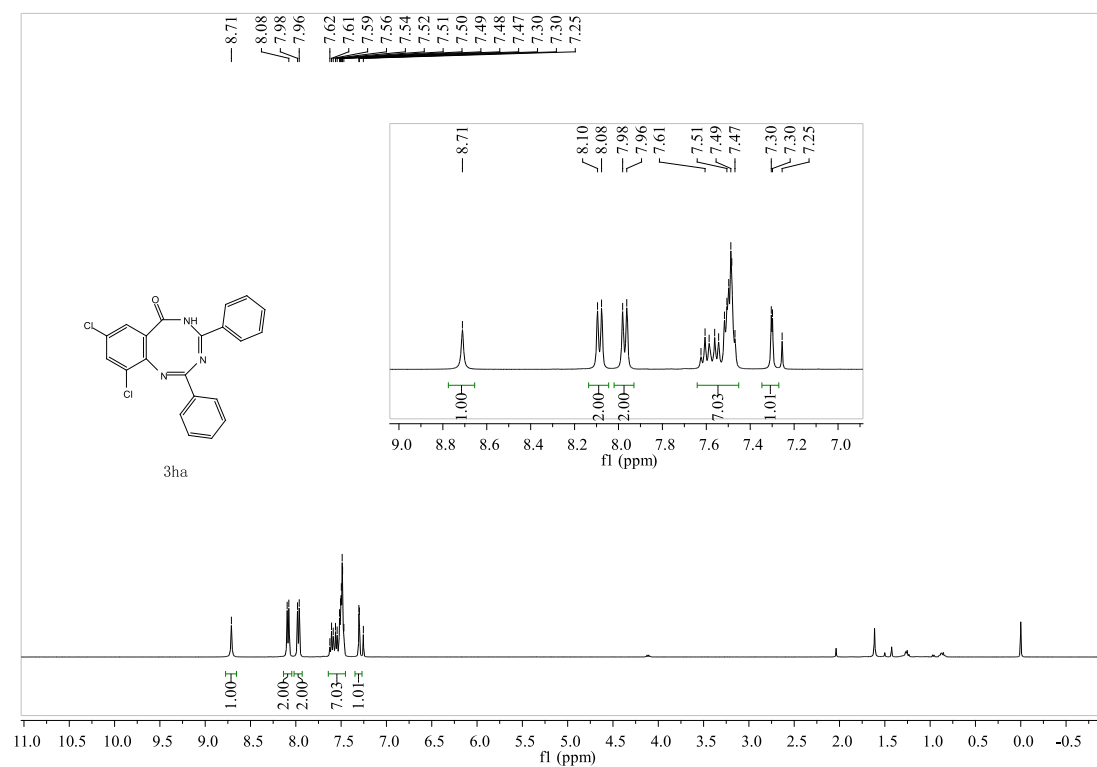


3ga

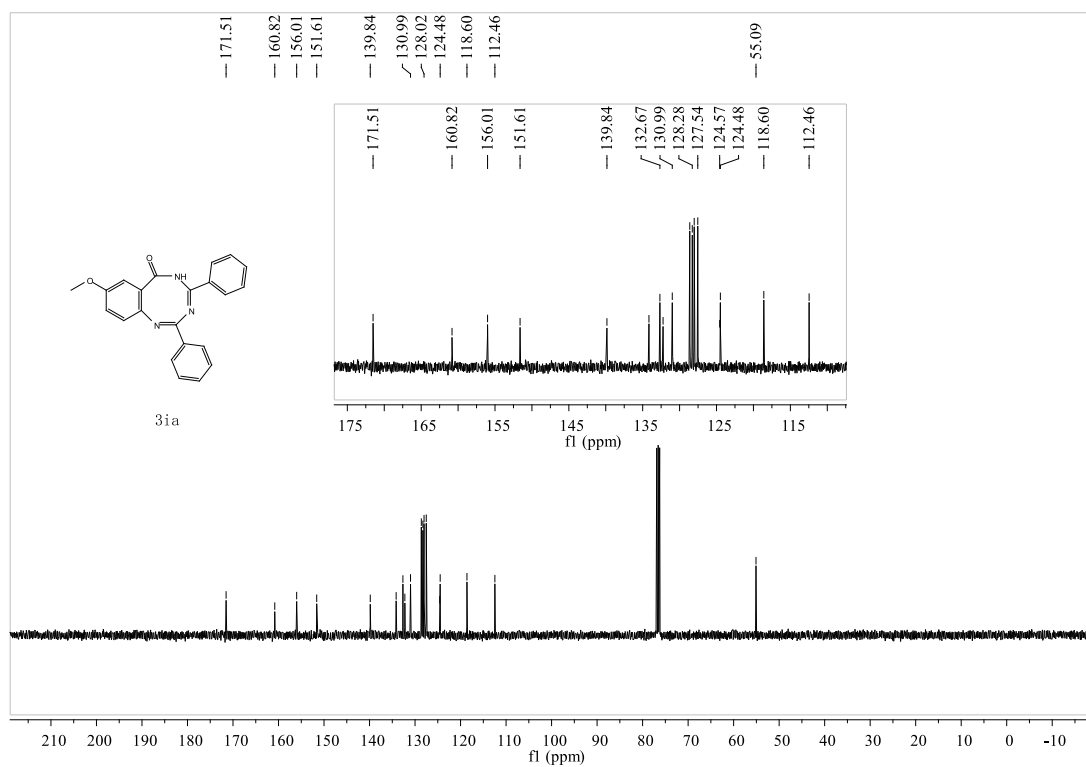
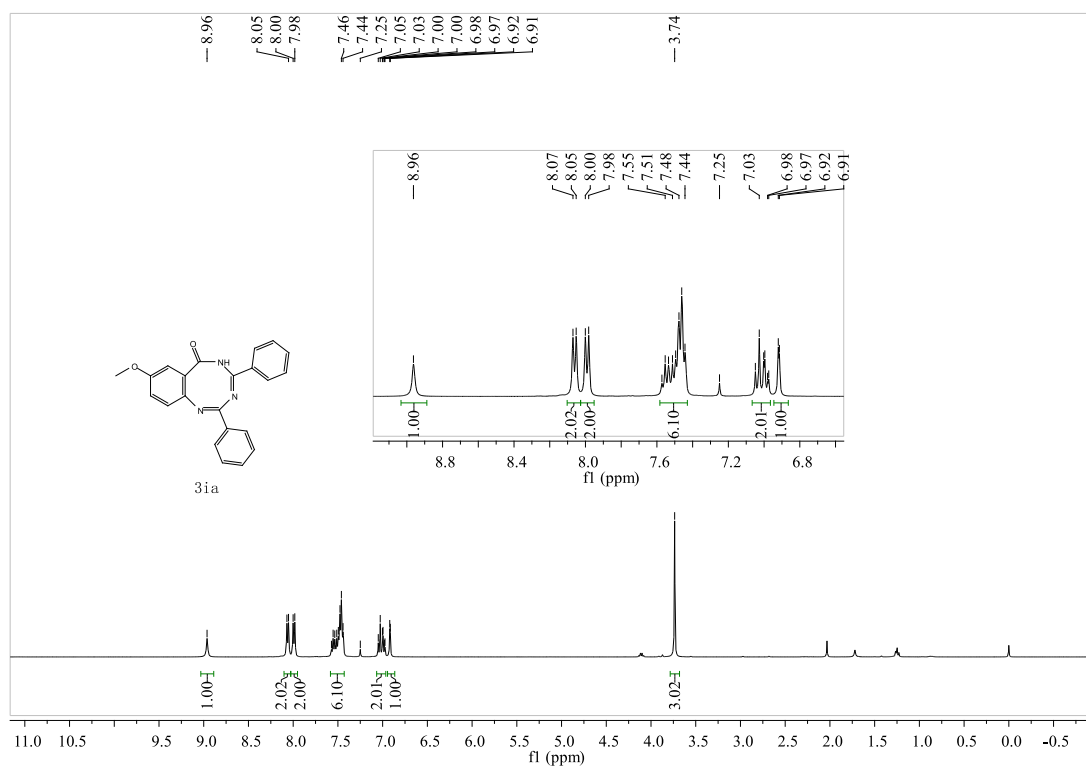




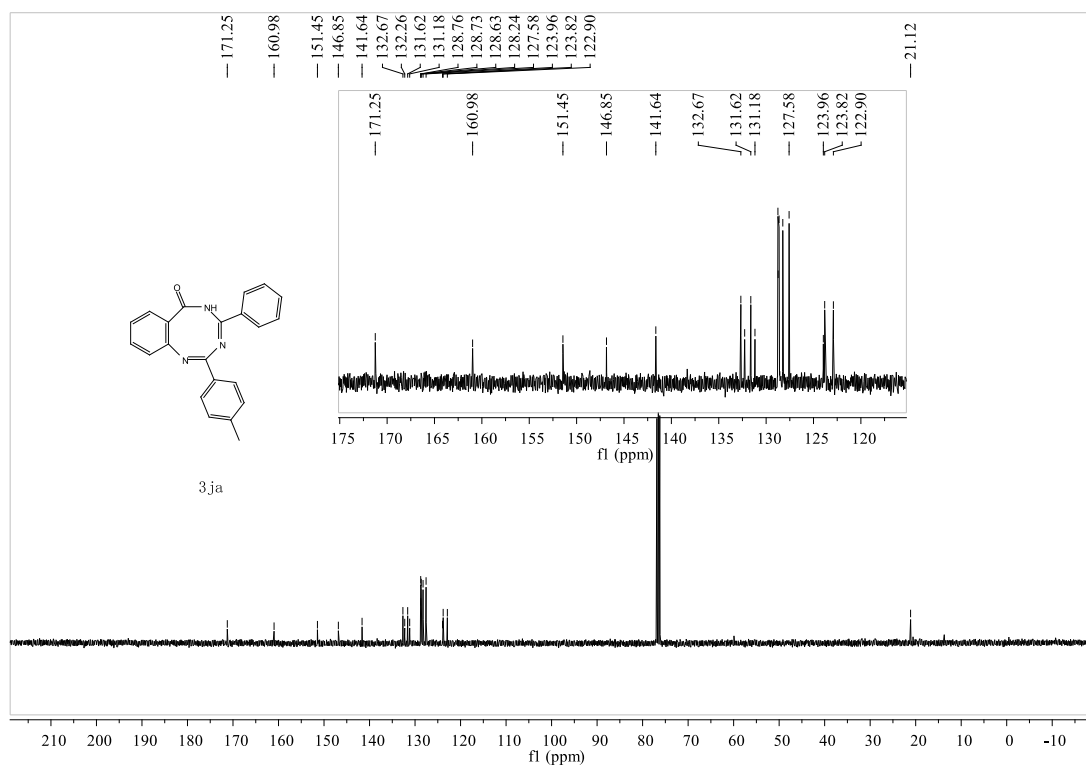
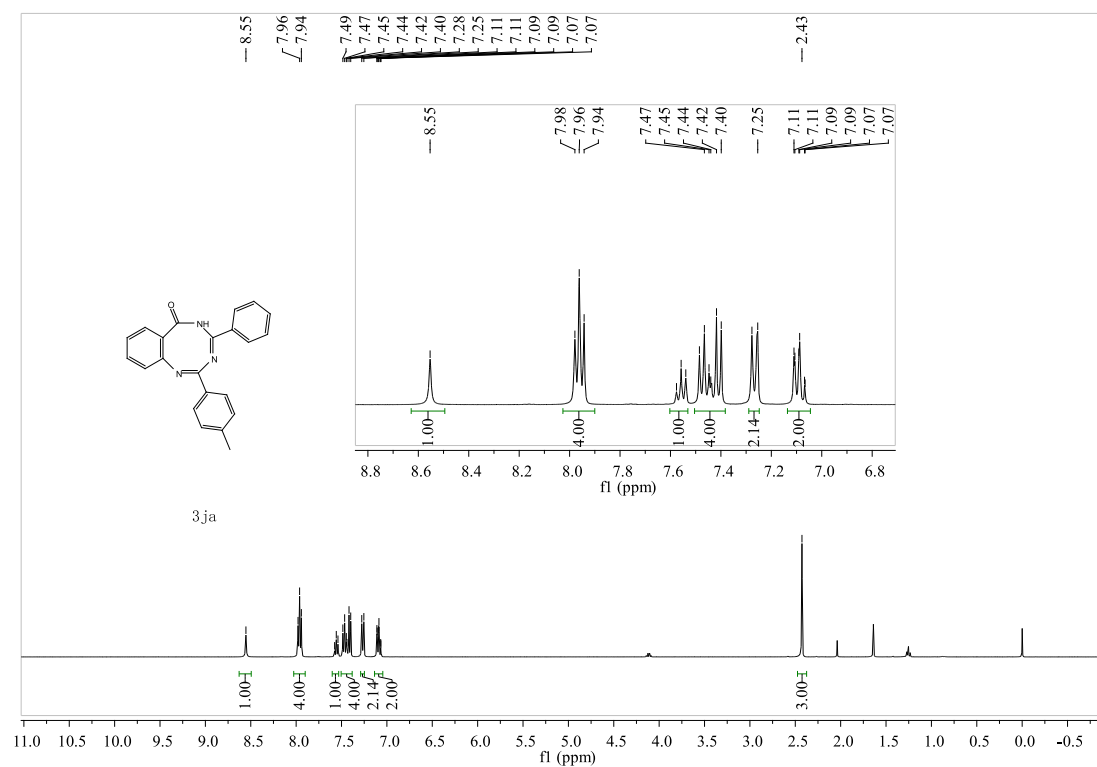
3ha



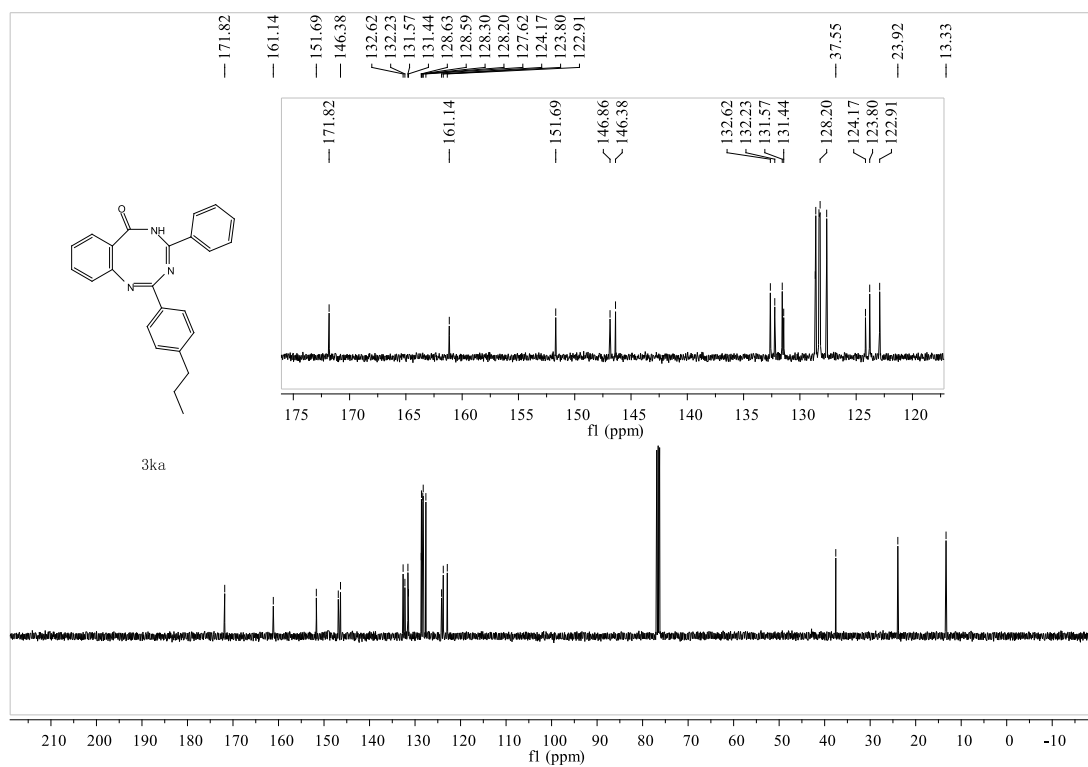
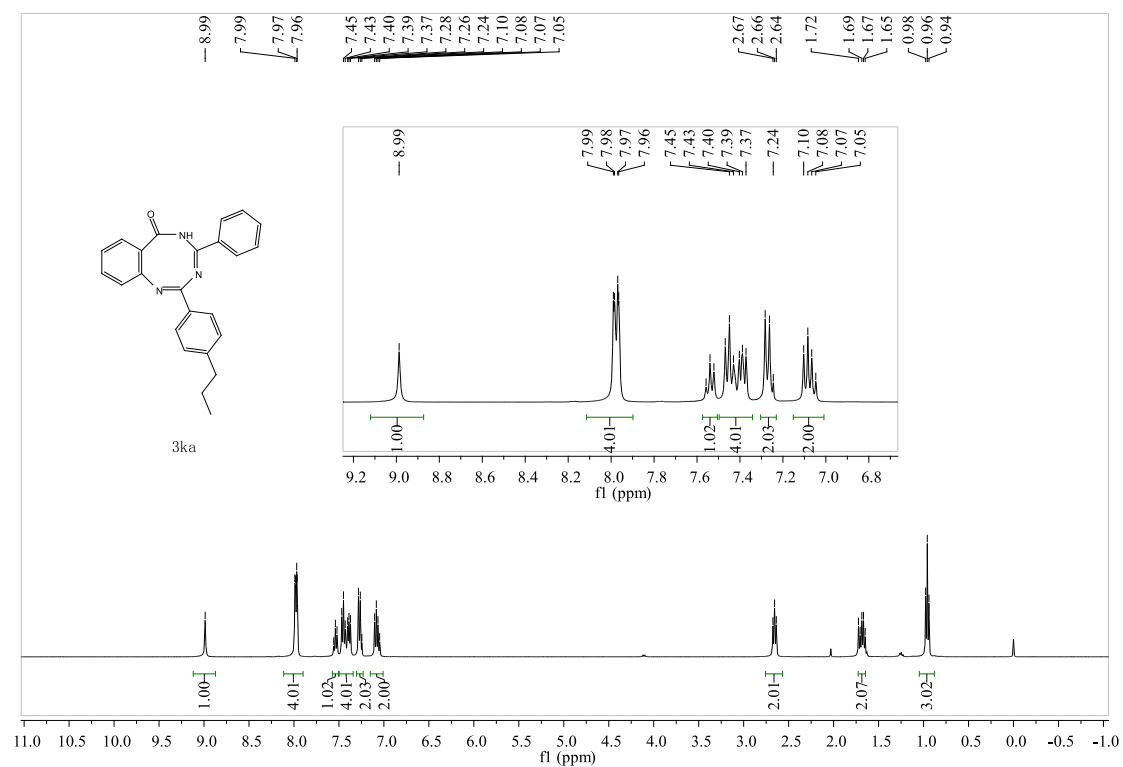
3ia



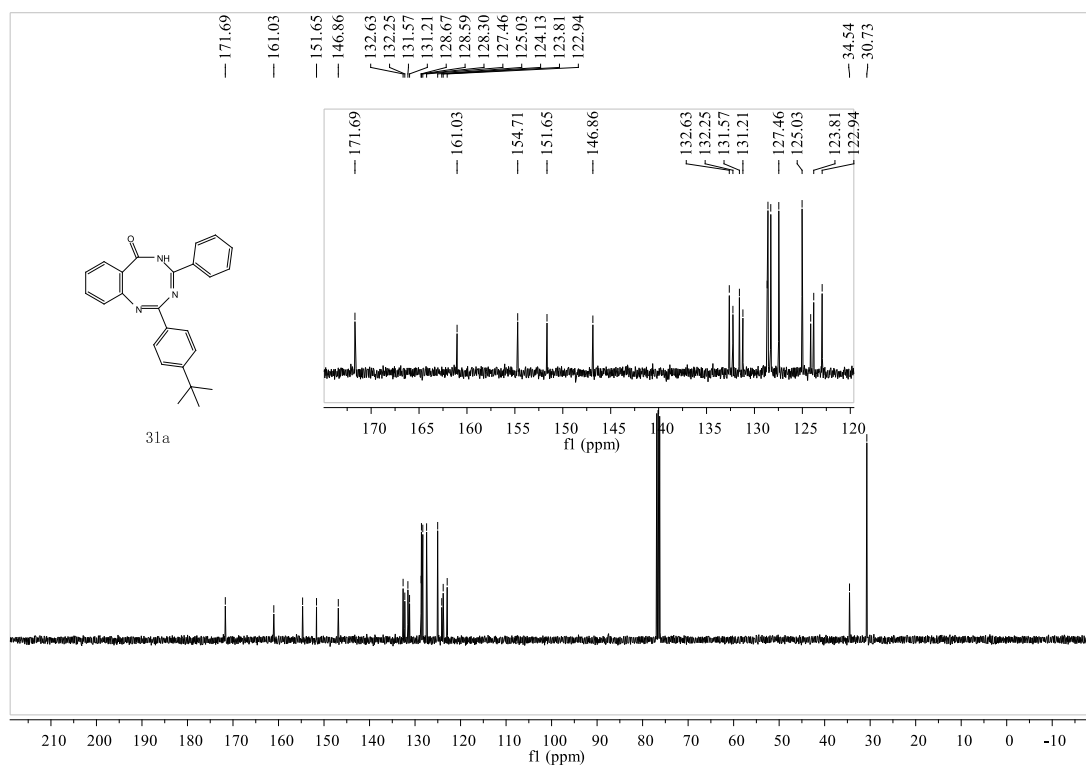
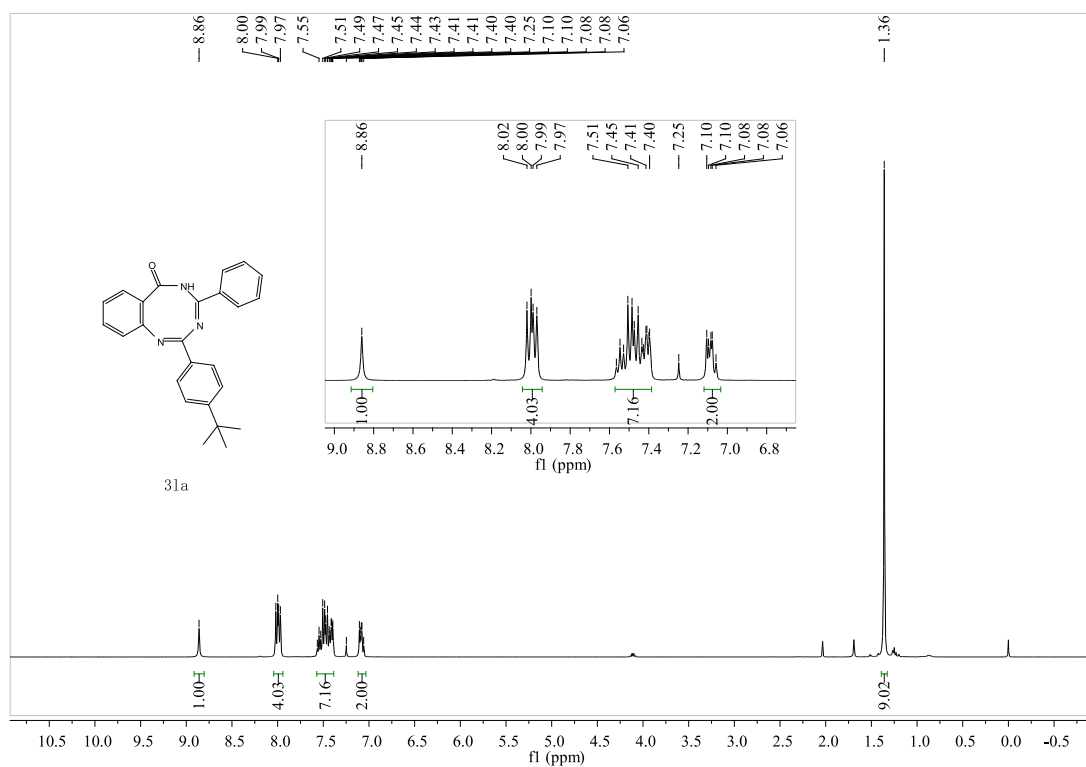
3ja



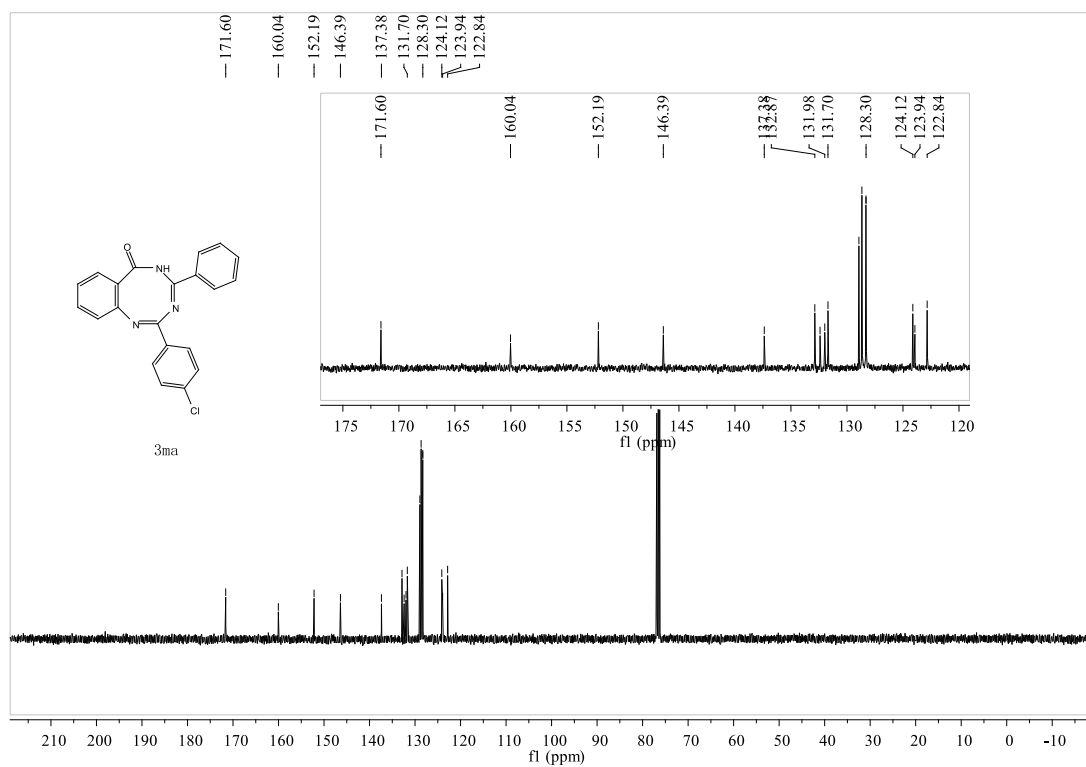
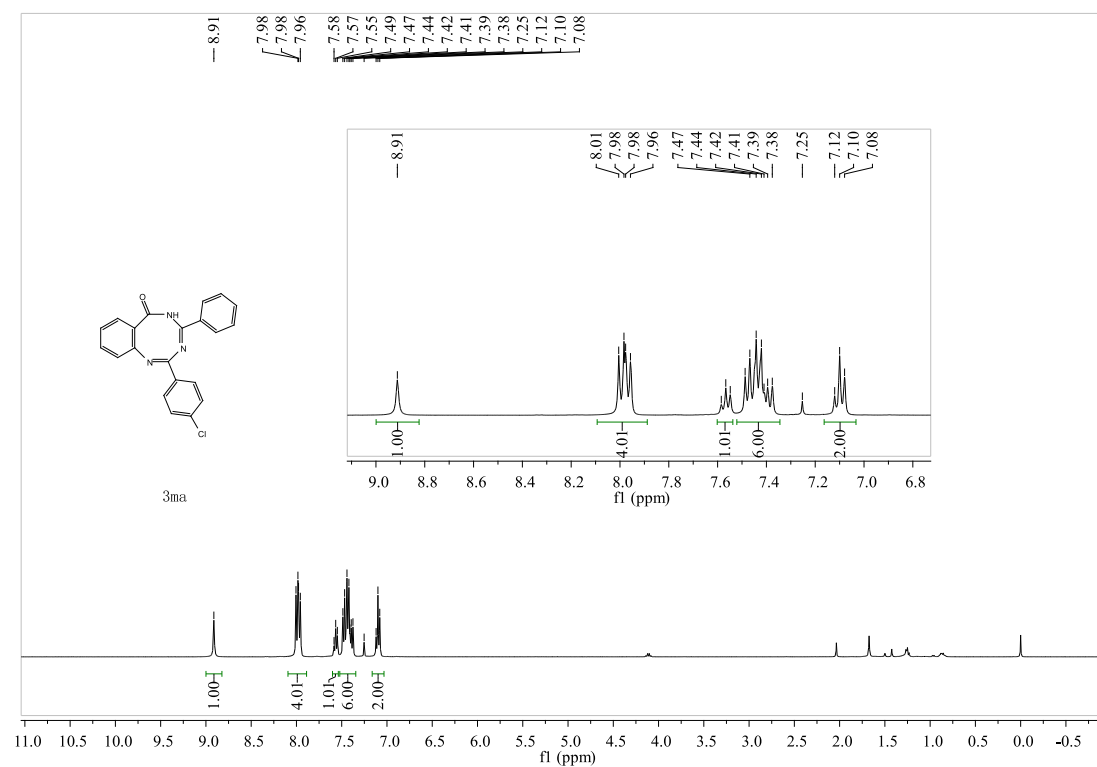
3ka



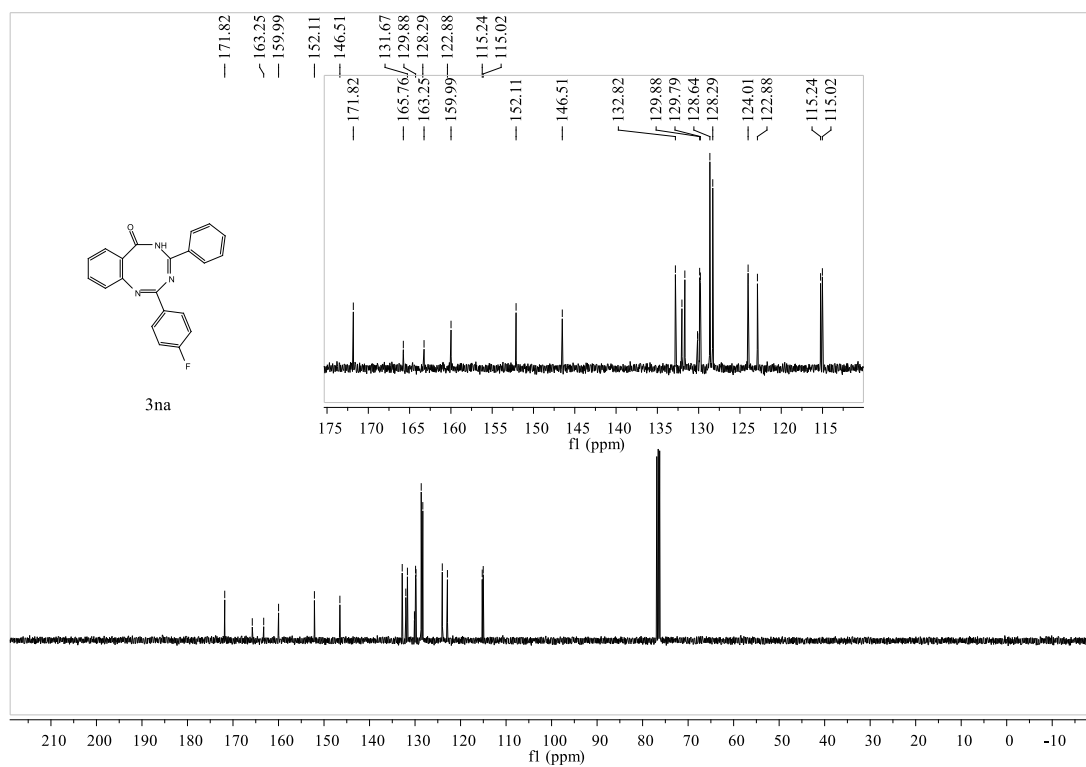
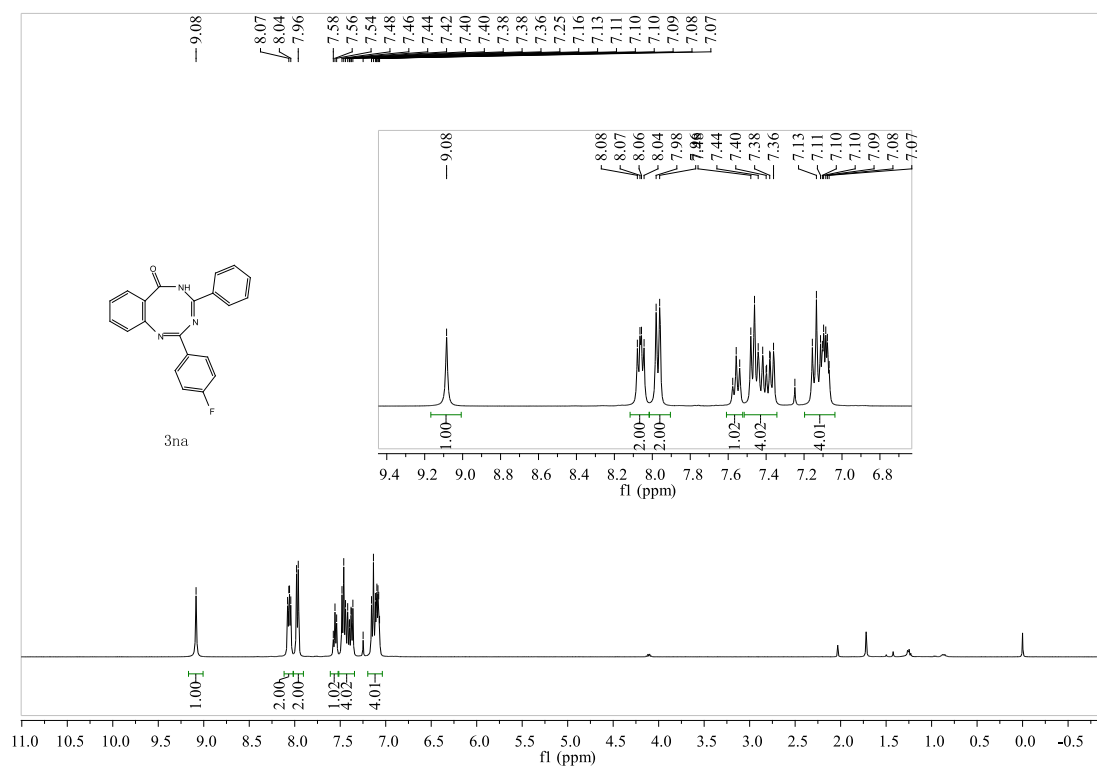
3la

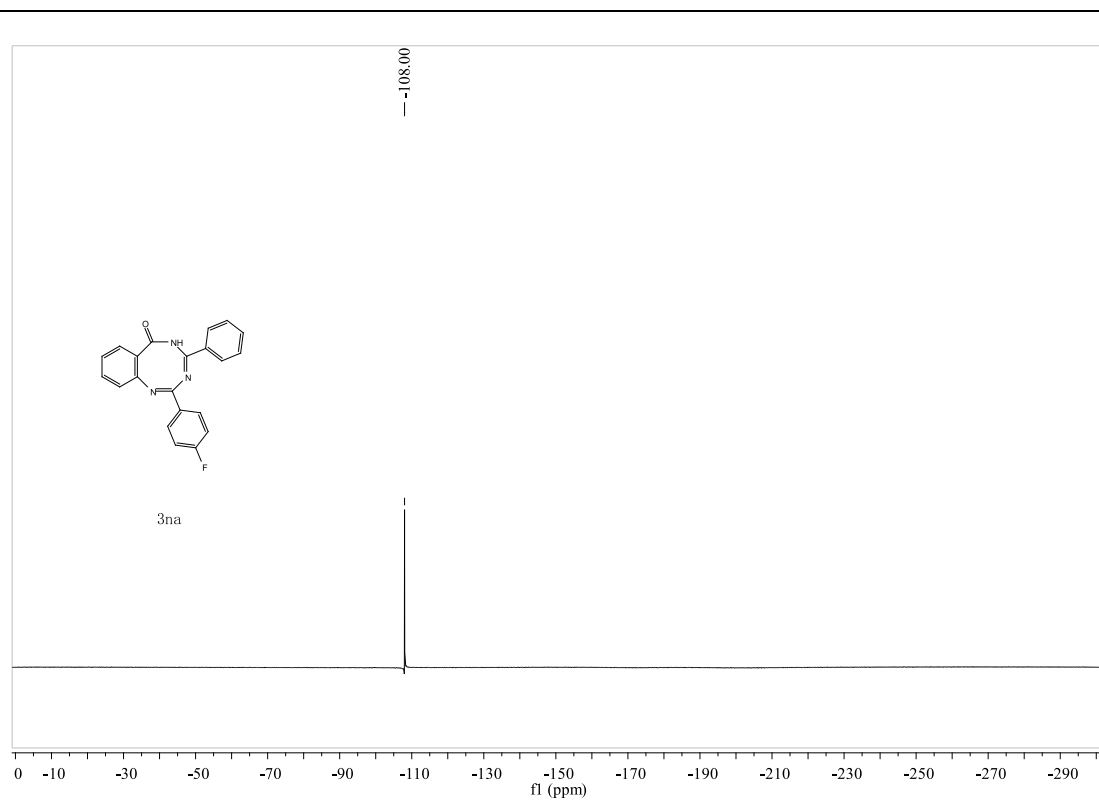


3ma

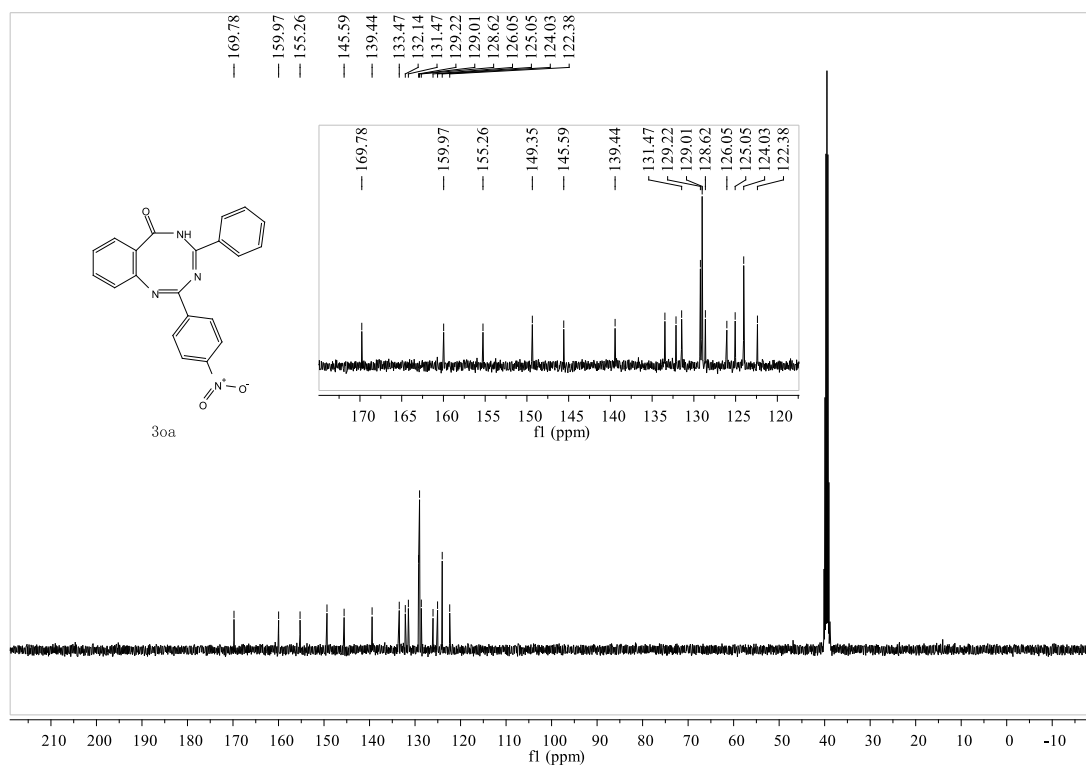
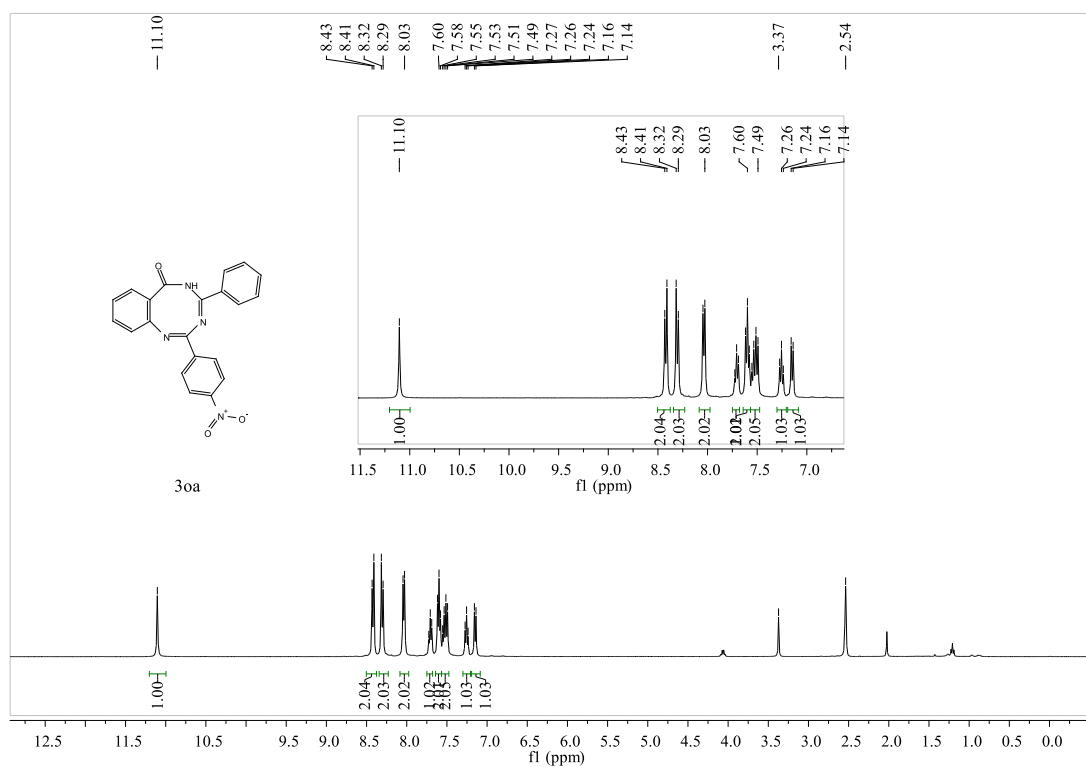


3na

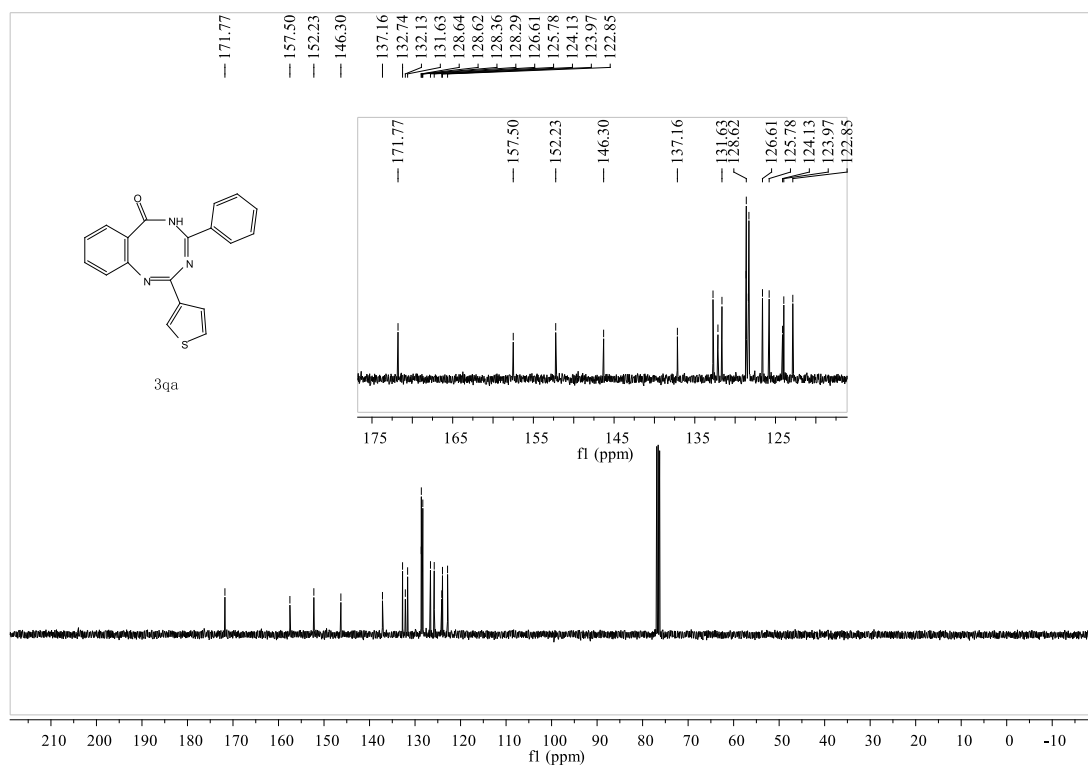
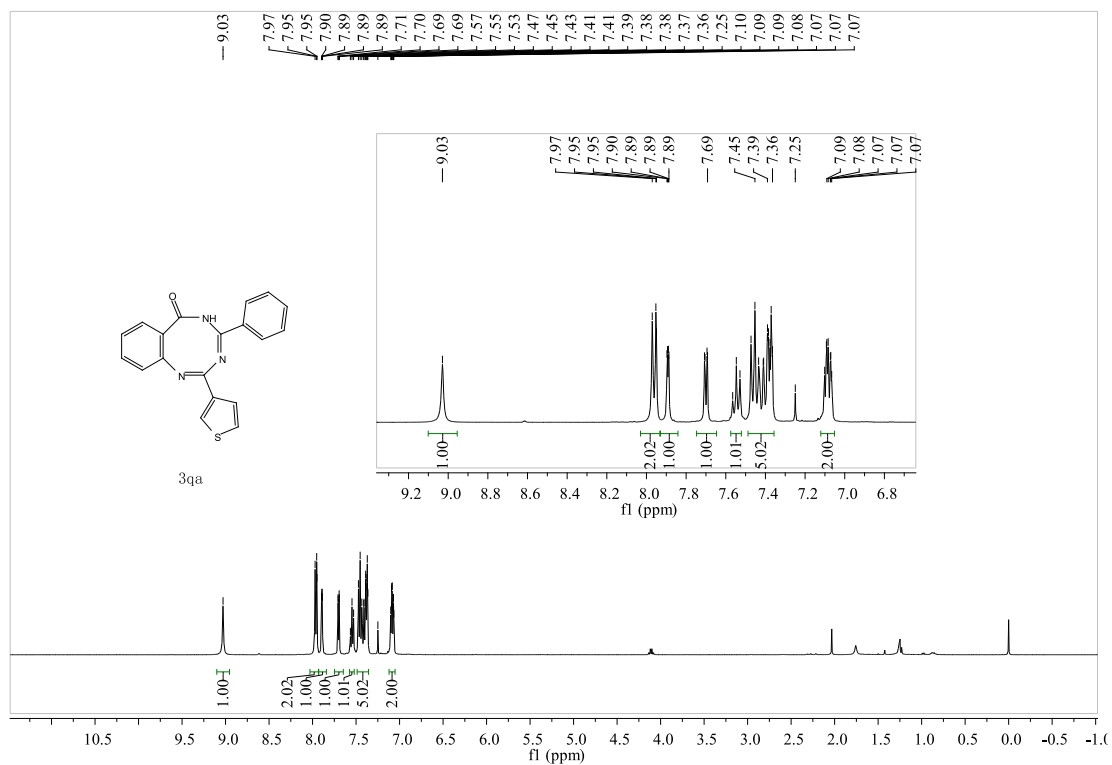




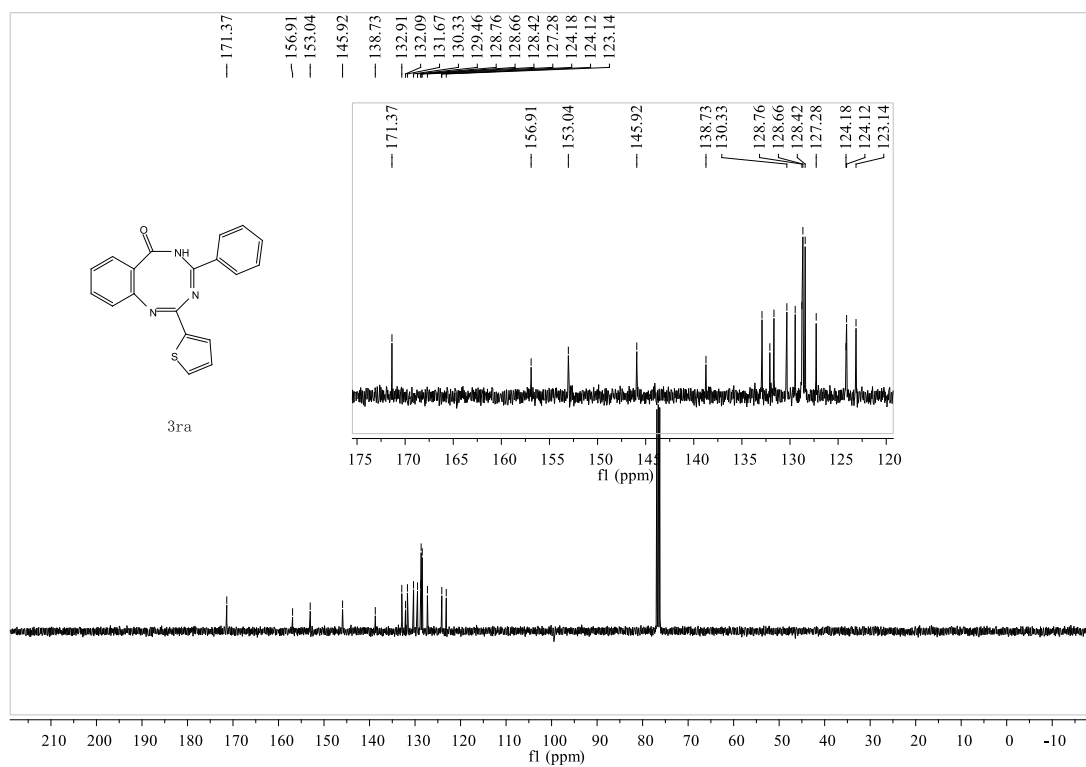
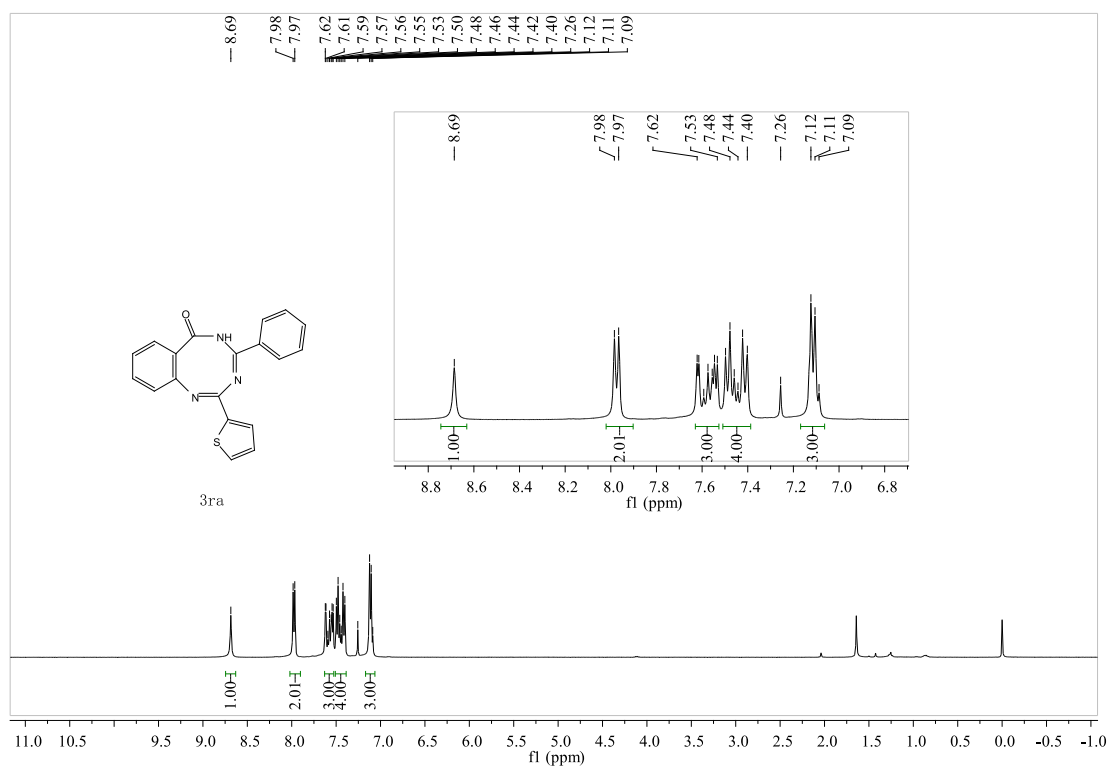
30a



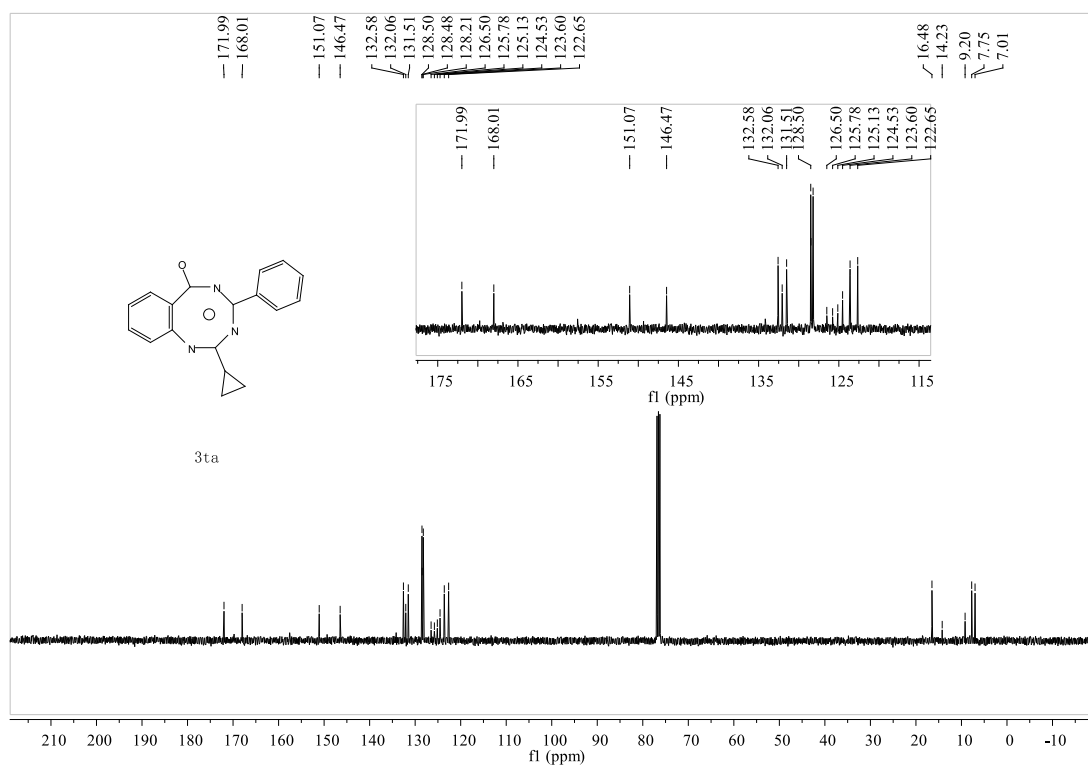
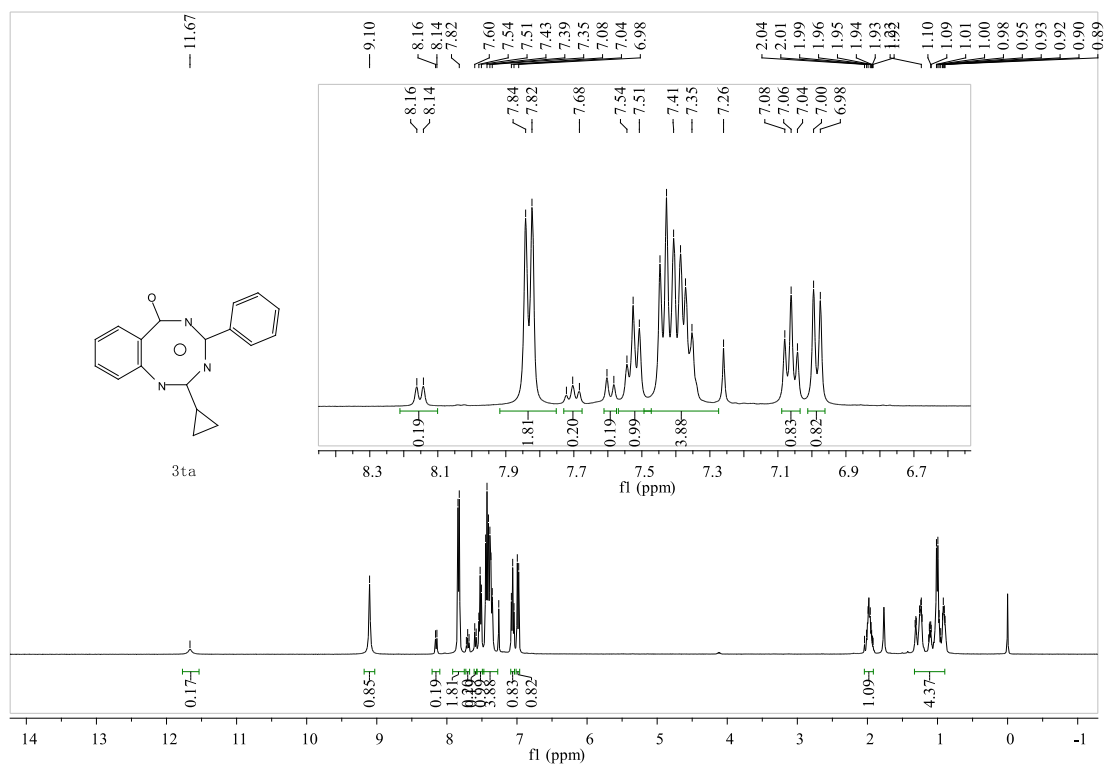
3qa



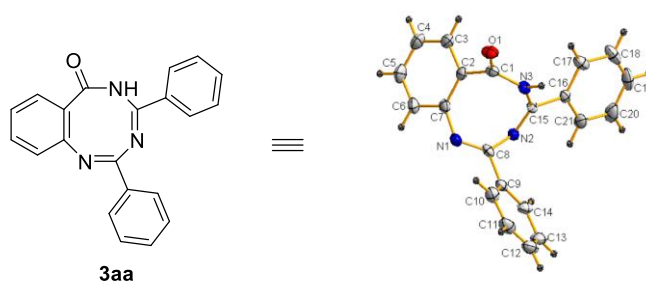
3ra



3ta



X-ray Structure of 3aa and 3ta



Crystal Number: CCDC 1526678

Empirical formula: C₂₁H₁₅N₃O₁

Formula weight: 325.36

Unit cell parameters: $a = 10.6190 (6) \text{ \AA}$, $b = 13.1044 (9) \text{ \AA}$, $c = 13.2310 (7) \text{ \AA}$,
 $\alpha = 95.734 (5)$, $\beta = 98.239 (4)$, $\gamma = 112.608 (6)$

Temperature: 213 (2) K

Wavelength: 0.71073 $\text{\AA}$

Crystal system: Triclinic

Volume: 1657.68 (17) $\text{\AA}^3$

Calculated density: 1.304 Mg/m³

Absorption coefficient: 0.083 mm⁻¹

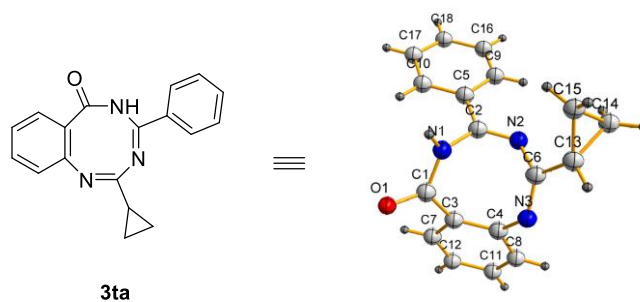
F (000): 680

Crystal size: 0.55×0.4×0.3 mm³

Correction-type: multi-scan

h, k, l max: 13, 16, 16

Tmin, Tmax: 0.81561/1.00000



Crystal Number: CCDC 1541660

Empirical formula: C₂₀H₁₇N₃O₁

Formula weight: 289.12

Unit cell parameters: $a = 8.6108 (4) \text{ \AA}$, $b = 9.2715 (3) \text{ \AA}$, $c = 19.9066 (10) \text{ \AA}$,
 $\alpha = 82.497 (4)$, $\beta = 88.246 (4)$, $\gamma = 74.495 (4)$

Temperature: 293 (2) K

Wavelength: 0.71073 $\text{\AA}$

Crystal system: Triclinic

Volume: 1518.28 (17) $\text{\AA}^3$

Calculated density: 1.265 Mg/m³

Absorption coefficient: 0.080 mm⁻¹
F (000): 660
Correction-type: phi and omega scans
h, k, l max: 10, 11, 20