

Supporting Information

Transition-metal-free [3+2] cycloaddition of *C,N*-cycloazomethylimines with *in situ* formed isocyanates from dioxazolones: a facile synthesis of triazolinones

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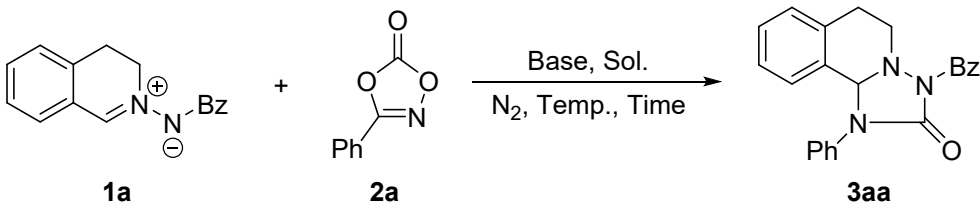
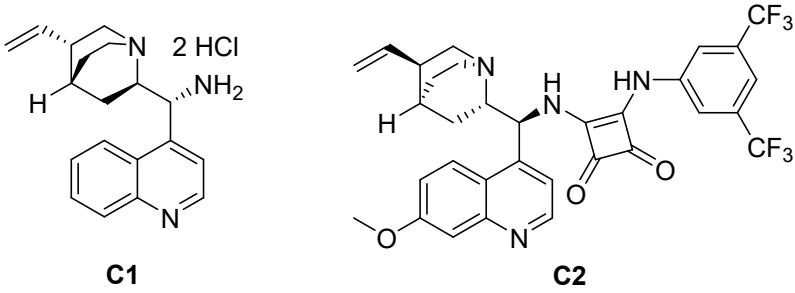
1. General information

All reactions were performed under a nitrogen atmosphere and solvents were dried according to established procedures. Melting points were determined by a micro-melting point apparatus (SGW X-4A, Shanghai, China). Unless noted, ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AVANCE-400 (400 MHz, 100 MHz and 376 MHz) spectrometer in CDCl_3 using tetramethylsilane (TMS) as internal standard. ^1H NMR spectra are referred to the TMS signal ($\delta = 0$ ppm) and ^{13}C NMR spectra are referred to the residual solvent signal ($\delta = 77.0$ ppm). Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, coupling constant (s) in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ , ppm). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources.

Materials: *C,N*-cycloazomethylamines were synthesized according to the procedures.^[1-2] dioxazolones were synthesized according to the procedures.^[3-4]

2. Details for condition optimization

Table S1 Optimization of reaction conditions^a

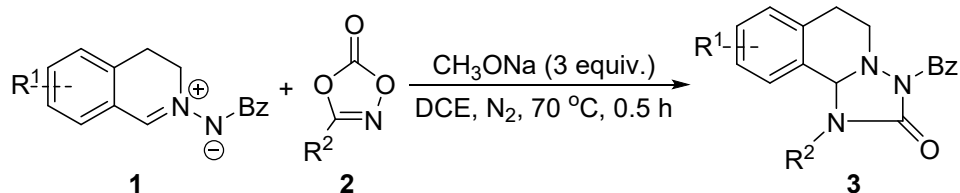
					
					
Entry	Temp.	Time (h)	Base	Solvent	Yield ^b
1	50	0.5	KOH	DCE	18
2	60	0.5	KOH	DCE	22
3	70	0.5	KOH	DCE	51

4	80	0.5	KOH	DCE	46
5	70	0.5	/	DCE	N.D.
6	70	0.17	KOH	DCE	28
7	70	1	KOH	DCE	51
8	70	4	KOH	DCE	18
9	70	8	KOH	DCE	2
10	70	0.5	LiOH	DCE	30
11	70	0.5	Cs ₂ CO ₃	DCE	31
12	70	0.5	CH₃ONa	DCE	86 (84^c)
13	70	0.5	<i>t</i> -BuONa	DCE	68
14	70	0.5	CH ₃ ONa/LiOH	DCE	64
15	70	0.5	DIPEA	DCE	N.D.
16	70	0.5	DABCO	DCE	N.D.
17	70	0.5	Et ₃ N	DCE	36
18	70	0.5	CH ₃ ONa	CHCl ₃	61
19	70	0.5	CH ₃ ONa	PhCl	56
20	70	0.5	CH ₃ ONa	THF	39
21	70	0.5	CH ₃ ONa	EA	56
22	70	0.5	CH ₃ ONa	DMF	8
23	70	0.5	CH ₃ ONa	CH ₃ OH	N.D.
24	70	0.5	CH ₃ ONa	DMSO	N.D.
25 ^d	70	0.5	CH ₃ ONa	DCE	N.D.
26 ^e	70	0.5	CH ₃ ONa	DCE	39
27 ^f	70	0.5	CH ₃ ONa	DCE	21
28 ^g	70	0.5	CH ₃ ONa	DCE	46
29 ^h	70	0.5	CH ₃ ONa	DCE	38
30 ⁱ	70	0.5	CH ₃ ONa	DCE	31

^a All reactions were carried out by using **1a** (0.10 mmol), **2a** (0.30 mmol), base (0.30 mmol), and solvent (1.0 mL) under nitrogen and stirred at specified temperature for 0.5 h, except as noted; ^b Yields were determined by ¹H NMR using mesitylene as an internal standard. N.D. = not detected; ^c Isolated yield; ^d Reaction was performed under aerobic conditions; ^e Using **C1** (20 mol%) as catalyst; ^f Using **C2** (20 mol%) as catalyst; ^g Using 18-crown-6 (20 mol%) as catalyst, Base amount: CH₃ONa (3.0 equiv.); ^h Using 18-crown-6 (20 mol%) as catalyst, Base amount: CH₃ONa (2.0 equiv.); ⁱ Using 18-crown-6 (20 mol%) as catalyst, Base amount: CH₃ONa (1.0 equiv.).

3. General procedure and spectral data of products

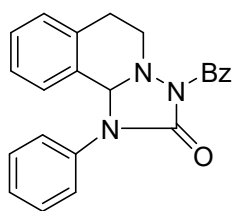
3.1 General procedure for the [3+2] cycloaddition of *C,N*-cycloazomethylimines with dioxazolones



CH₃ONa (0.6 mmol, 3.0 equiv) was added to a solution of *C,N*-cycloazomethylimine **1** (0.2 mmol, 1.0 equiv) and dioxazolone **2** (0.6 mmol, 3.0 equiv) in DCE (2.0 mL) under nitrogen atmosphere. The resulting suspension was stirred for 0.5 h at 70 °C. After the reaction was completed by TLC monitoring, the mixture was quenched with 1N NH₄Cl and extracted with CH₂Cl₂ 3 times. The combined organic layer was dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EtOAc = 5:1, add 1% Et₃N) to afford product **3** which were summarized below.

3.2 Characterization Data of Products

3-benzoyl-1-phenyl-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (**3aa**)

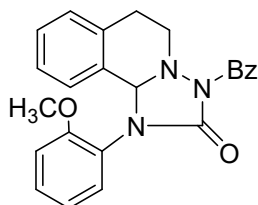


3aa

White solid (93 mg, 84%). m.p. 171–176 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.53–7.47 (m, 1H), 7.45–7.39 (m, 2H), 7.35–7.29 (m, 3H), 7.25 (dt, *J* = 13.5, 6.1 Hz, 2H), 7.01–6.91 (m, 3H), 6.48 (d, *J* = 7.7 Hz, 1H), 6.03 (s, 1H), 3.73 (ddd, *J* = 10.6, 4.7, 3.7 Hz, 1H), 3.47 (td, *J* = 11.0, 3.5 Hz, 1H), 3.25 (ddd, *J* = 16.3, 11.3, 4.8 Hz, 1H), 3.00 (dt, *J* = 16.6, 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 152.5, 135.1, 134.6, 133.8, 131.6, 130.0, 129.4, 129.3 (2C), 128.9 (2C), 128.8 (2C), 128.5, 128.4, 127.8, 127.7 (2C), 125.8, 75.8, 47.7, 27.7. HRMS (ESI-TOF) *m/z*: Calcd for C₂₃H₁₉O₂N₃ [M+H]⁺ 370.1511; Found: 370.1550.

3-benzoyl-1-(2-methoxyphenyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one

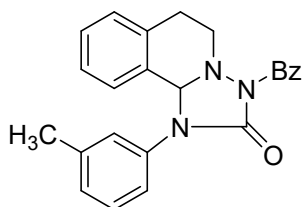
(3ab)



3ab

White solid (63 mg, 79%). m.p. 167-168 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.51–7.46 (m, 1H), 7.43–7.38 (m, 2H), 7.34–7.29 (m, 1H), 7.23–7.17 (m, 2H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.93–6.88 (m, 1H), 6.81 (dd, *J* = 16.8, 9.4 Hz, 2H), 6.39 (d, *J* = 7.8 Hz, 1H), 6.10 (s, 1H), 3.88 (s, 3H), 3.81–3.75 (m, 1H), 3.52–3.44 (m, 1H), 3.29 (ddd, *J* = 16.9, 12.2, 4.9 Hz, 1H), 2.95 (dt, *J* = 16.6, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 156.2, 152.8, 134.8, 133.8, 131.9, 131.5, 130.3, 129.0, 128.9, 128.8 (2C), 128.3, 128.0, 127.6 (2C), 125.6, 123.2, 120.9, 111.7, 73.8, 55.7, 47.1, 27.9. HRMS (ESI-TOF) *m/z*: Calcd for C₂₄H₂₁O₃N₃ [M+H]⁺ 400.1656; Found: 400.1664.

3-benzoyl-1-(*m*-tolyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3ac)

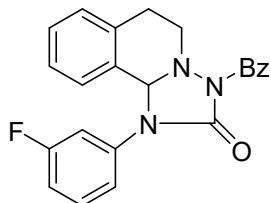


3ac

White solid (76 mg, 92%). m.p. 135-139 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.50 (ddd, *J* = 6.6, 3.9, 1.3 Hz, 1H), 7.41 (dd, *J* = 10.3, 4.6 Hz, 2H), 7.30–7.21 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.97 (dd, *J* = 10.8, 4.1 Hz, 1H), 6.81 (s, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.50 (d, *J* = 7.7 Hz, 1H), 6.01 (s, 1H), 3.72 (ddd, *J* = 10.5, 4.7, 3.7 Hz, 1H), 3.46 (td, *J* = 11.0, 3.5 Hz, 1H), 3.25 (ddd, *J* = 16.3, 11.4, 4.8 Hz, 1H), 3.00 (dt, *J* = 16.6, 3.4 Hz, 1H), 2.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 152.5, 139.2, 135.0, 134.4, 133.8, 131.5, 129.9, 129.3, 129.2, 129.1, 128.9, 128.8 (2C), 128.4, 127.8, 127.6 (2C), 125.7, 125.6, 75.6, 47.6, 27.6, 21.1. HRMS (ESI-TOF) *m/z*: Calcd for C₂₄H₂₁O₂N₃ [M+H]⁺ 384.1706; Found: 384.1691.

3-benzoyl-1-(3-fluorophenyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one

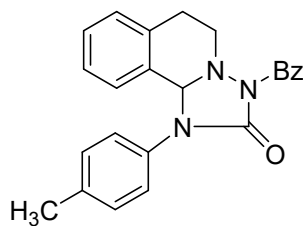
(3ad)



3ad

White solid (62 mg, 80%). m.p. 159-160 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.70 (m, 2H), 7.54–7.49 (m, 1H), 7.42 (dd, *J* = 10.3, 4.6 Hz, 2H), 7.32–7.22 (m, 3H), 7.04–6.98 (m, 2H), 6.78 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.71 (dt, *J* = 9.4, 2.2 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 1H), 6.02 (s, 1H), 3.74–3.68 (m, 1H), 3.44 (td, *J* = 10.9, 3.5 Hz, 1H), 3.23 (ddd, *J* = 16.1, 11.1, 4.8 Hz, 1H), 3.00 (dt, *J* = 16.6, 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 166.31, 163.83, 161.36, 152.32, 136.18, 136.08, 135.08, 133.59, 131.75, 130.27, 130.18, 129.82, 129.54, 128.79, 128.57, 127.73, 127.43, 125.88, 124.37, 124.34, 116.25, 116.02, 115.53, 115.32, 75.79, 47.78, 27.56. ¹⁹F NMR (377 MHz, CDCl₃) δ -111.1 (s). HRMS (ESI-TOF) *m/z*: Calcd for C₂₃H₁₈FO₂N₃ [M+H]⁺ 388.1456; Found: 388.1459.

3-benzoyl-1-(*p*-tolyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3ae)

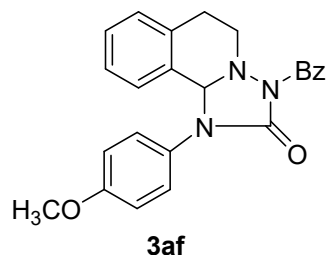


3ae

White solid (65 mg, 85%). m.p. 178-182 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.69 (m, 2H), 7.53–7.47 (m, 1H), 7.44–7.38 (m, 2H), 7.29–7.21 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.98 (dd, *J* = 10.8, 4.0 Hz, 1H), 6.88–6.81 (m, 2H), 6.50 (d, *J* = 7.7 Hz, 1H), 5.99 (s, 1H), 3.72 (ddd, *J* = 10.5, 4.8, 3.5 Hz, 1H), 3.45 (td, *J* = 11.0, 3.4 Hz, 1H), 3.25 (ddd, *J* = 16.4, 11.5, 4.8 Hz, 1H), 2.99 (dt, *J* = 16.6, 3.4 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 152.6, 138.4, 135.0, 133.8, 131.9, 131.6, 129.9, 129.8 (2C), 129.2, 128.8 (2C), 128.6 (2C), 128.4, 127.8, 127.7 (2C), 125.8, 75.7, 47.6, 27.7, 21.2. HRMS (ESI-TOF) *m/z*: Calcd for C₂₄H₂₁O₂N₃ [M+H]⁺ 384.1706; Found: 384.1697.

3-benzoyl-1-(4-methoxyphenyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one

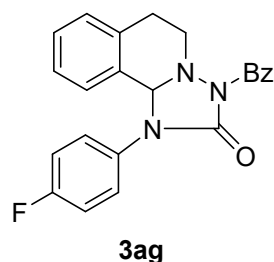
(3af)



White solid (55 mg, 69%). m.p. 188-191 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.74–7.70 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.25 (dt, *J* = 18.7, 7.4 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.89–6.80 (m, 4H), 6.47 (d, *J* = 7.7 Hz, 1H), 5.94 (s, 1H), 3.76 (s, 3H), 3.74–3.68 (m, 1H), 3.42 (td, *J* = 11.1, 3.4 Hz, 1H), 3.24 (ddd, *J* = 16.4, 11.6, 4.8 Hz, 1H), 2.97 (dt, *J* = 16.5, 3.1 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 159.3, 152.6, 134.9, 133.7, 131.5, 130.1 (2C), 129.9, 129.2, 128.8 (2C), 128.4, 127.7, 127.6 (2C), 127.1, 125.7, 114.4 (2C), 75.6, 55.3, 47.5, 27.7. HRMS (ESI-TOF) *m/z*: Calcd for C₂₄H₂₁O₃N₃ [M+H]⁺ 400.1656; Found: 400.1656.

3-benzoyl-1-(4-fluorophenyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one

(3ag)

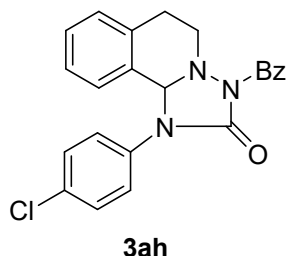


White solid (56 mg, 72%). m.p. 157-159 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.69 (m, 2H), 7.54–7.48 (m, 1H), 7.45–7.39 (m, 2H), 7.29 (td, *J* = 7.5, 1.1 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.04–6.97 (m, 3H), 6.96–6.90 (m, 2H), 6.46 (d, *J* = 7.7 Hz, 1H), 5.97 (s, 1H), 3.72 (ddd, *J* = 10.5, 4.8, 3.5 Hz, 1H), 3.43 (td, *J* = 11.0, 3.4 Hz, 1H), 3.25 (ddd, *J* = 16.4, 11.5, 4.8 Hz, 1H), 2.99 (dt, *J* = 16.6, 3.3 Hz, 1H). ¹³C NMR (100MHz, CDCl₃) δ 166.3, 163.4, 161.0, 152.6, 135.0, 133.6, 131.7, 130.8, 130.7, 129.8, 129.5, 128.8 (2C), 128.6, 127.7 (2C), 127.5, 125.8, 116.3, 116.1, 75.8, 47.7, 27.7. ¹⁹F NMR (377 MHz, CDCl₃) δ -112.3 (s). HRMS (ESI-TOF) *m/z*: Calcd for C₂₃H₁₈FO₂N₃ [M+H]⁺ 388.1456; Found:

388.1439.

3-benzoyl-1-(4-chlorophenyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one

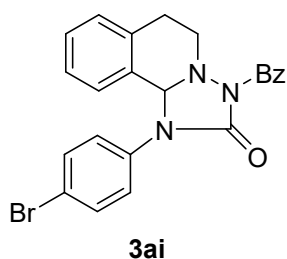
(3ah)



White solid (57 mg, 72%). m.p. 157-159 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.70 (m, 2H), 7.54–7.48 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.32–7.27 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.93–6.86 (m, 2H), 6.51 (d, *J* = 7.7 Hz, 1H), 5.99 (s, 1H), 3.71 (ddd, *J* = 10.5, 4.7, 3.7 Hz, 1H), 3.43 (td, *J* = 11.0, 3.5 Hz, 1H), 3.23 (ddd, *J* = 16.3, 11.3, 4.8 Hz, 1H), 2.99 (dt, *J* = 16.6, 3.4 Hz, 1H). ¹³C NMR (100MHz, CDCl₃) δ 166.3, 152.4, 135.0, 134.2, 133.6, 133.1, 131.7, 130.1 (2C), 129.9, 129.5, 129.4 (2C), 128.8 (2C), 128.6, 127.7 (2C), 127.4, 125.9, 75.8, 47.7, 27.6. HRMS (ESI-TOF) *m/z*: Calcd for C₂₃H₁₈ClO₂N₃ [M+H]⁺ 404.1160; Found: 404.1161.

3-benzoyl-1-(4-bromophenyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one

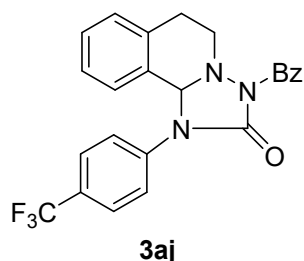
(3ai)



White solid (75 mg, 84%). m.p. 163-165 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.69 (m, 2H), 7.51 (dd, *J* = 8.4, 6.5 Hz, 1H), 7.46–7.39 (m, 4H), 7.33–7.28 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.87–6.79 (m, 2H), 6.52 (d, *J* = 7.7 Hz, 1H), 5.99 (s, 1H), 3.71 (dt, *J* = 8.4, 4.6 Hz, 1H), 3.43 (td, *J* = 11.0, 3.5 Hz, 1H), 3.24 (ddd, *J* = 16.2, 11.3, 4.8 Hz, 1H), 3.00 (dt, *J* = 16.6, 3.4 Hz, 1H). ¹³C NMR (100MHz, CDCl₃) δ 166.3, 152.3, 135.0, 133.7, 133.6, 132.4 (2C), 131.8, 130.3 (2C), 129.9, 129.5, 128.8 (2C), 128.6, 127.7 (2C), 127.4, 125.9, 122.2, 75.8, 47.7, 27.6. HRMS (ESI-TOF) *m/z*:

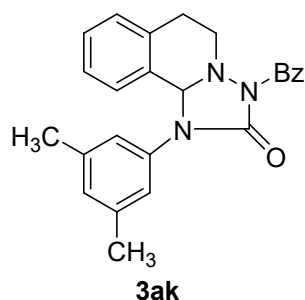
Calcd for C₂₃H₁₈BrO₂N₃ [M+H]⁺ 448,0655; Found: 448.0656.

3-benzoyl-1-(4-(trifluoromethyl)phenyl)-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one (3aj)



White solid (56 mg, 64%). m.p. 140-141 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.55–7.50 (m, 1H), 7.43 (dd, *J* = 10.4, 4.6 Hz, 2H), 7.32 (td, *J* = 7.6, 1.0 Hz, 1H), 7.28–7.24 (m, 1H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 1H), 6.08 (s, 1H), 3.71 (dt, *J* = 10.8, 4.5 Hz, 1H), 3.47 (td, *J* = 10.9, 3.6 Hz, 1H), 3.22 (ddd, *J* = 16.0, 10.9, 4.8 Hz, 1H), 3.02 (dt, *J* = 16.7, 3.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 152.3, 138.0, 135.2, 133.5, 131.9, 129.9, 129.7, 128.8, 128.8, 128.7, 127.8, 127.4, 126.2, 126.2, 126.0, 75.9, 47.9, 27.5. ¹⁹F NMR (377 MHz, CDCl₃) δ -62.6 (s). HRMS (ESI-TOF) *m/z*: Calcd for C₂₄H₁₈FO₂N₃ [M+H]⁺ 438.1424; Found: 438.1427.

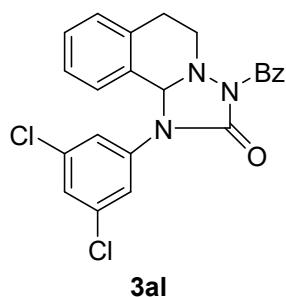
3-benzoyl-1-(3,5-dimethylphenyl)-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one (3ak)



White solid (94.7 mg, 82 %). m.p. 150-155 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.74–7.70 (m, 2H), 7.49 (ddd, *J* = 6.6, 3.9, 1.3 Hz, 1H), 7.43–7.39 (m, 2H), 7.29–7.20 (m, 2H), 6.99–6.94 (m, 1H), 6.92 (s, 1H), 6.57 (s, 2H), 6.50 (d, *J* = 7.7 Hz, 1H), 5.99 (s, 1H), 3.71 (ddd, *J* = 10.5, 4.7, 3.6 Hz, 1H), 3.44 (td, *J* = 11.0, 3.4 Hz, 1H), 3.25 (ddd, *J* = 16.3, 11.4, 4.8 Hz, 1H), 2.99 (dt, *J* = 16.6, 3.4 Hz, 1H), 2.22 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 152.5, 138.9 (2C), 135.0, 134.3, 133.8, 131.5, 130.1, 130.0,

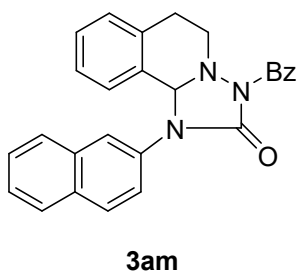
129.2, 128.8 (2C), 128.4, 127.9, 127.7 (2C), 126.3 (2C), 125.6, 75.6, 47.6, 27.7, 21.1 (2C). HRMS (ESI-TOF) m/z : Calcd for $C_{25}H_{23}O_2N_3$ $[M+H]^+$ 398.1863; Found: 398.1853.

3-benzoyl-1-(3,5-dichlorophenyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3al)



White solid (46 mg, 52 %). m.p. 145-147 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, $J = 5.2, 3.4$ Hz, 2H), 7.56–7.51 (m, 1H), 7.44 (dd, $J = 10.5, 4.6$ Hz, 2H), 7.34 (td, $J = 7.5, 1.0$ Hz, 1H), 7.30–7.25 (m, 2H), 7.09 (t, $J = 7.4$ Hz, 1H), 6.87 (d, $J = 1.8$ Hz, 2H), 6.61 (d, $J = 7.7$ Hz, 1H), 6.00 (s, 1H), 3.70 (dt, $J = 8.6, 4.5$ Hz, 1H), 3.41 (td, $J = 10.9, 3.6$ Hz, 1H), 3.23 (ddd, $J = 16.1, 11.1, 4.8$ Hz, 1H), 3.01 (dt, $J = 16.6, 3.6$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 152.1, 136.6, 135.1 (2C), 133.4, 131.9, 129.9, 129.9, 128.8 (2C), 128.8, 128.4, 127.8 (2C), 127.1 (4C), 126.0, 75.9, 47.9, 27.5. HRMS (ESI-TOF) m/z : Calcd for $C_{23}H_{17}Cl_2O_2N_3$ $[M+H]^+$ 438.0771; Found: 438.0772.

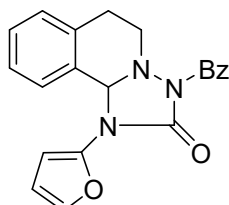
3-benzoyl-1-(naphthalen-1-yl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3am)



White solid (58 mg, 69%). m.p. 184-186 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.80 (m, 1H), 7.80–7.75 (m, 3H), 7.73–7.69 (m, 1H), 7.54–7.46 (m, 4H), 7.44 (t, $J = 7.4$ Hz, 2H), 7.26 (d, $J = 3.3$ Hz, 2H), 7.05 (dd, $J = 8.7, 2.0$ Hz, 1H), 6.87 (td, $J = 8.3, 3.8$ Hz, 1H), 6.49 (d, $J = 7.7$ Hz, 1H), 6.13 (s, 1H), 3.77 (dt, $J = 8.4, 4.5$ Hz, 1H), 3.54 (td, $J = 11.0, 3.5$ Hz, 1H), 3.28 (ddd, $J = 16.3, 11.3, 4.9$ Hz, 1H), 3.05

(dt, $J = 16.6, 3.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 152.6, 135.0, 133.8, 133.2, 132.6, 132.0, 131.6, 129.9, 129.3, 129.1, 128.8 (2C), 128.5, 127.9, 127.8, 127.7, 127.7 (2C), 127.6, 126.7, 126.5, 126.0, 125.8, 75.8, 47.7, 27.7. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{27}\text{H}_{21}\text{O}_2\text{N}_3$ $[\text{M}+\text{H}]^+$ 420.1706; Found: 420.1709.

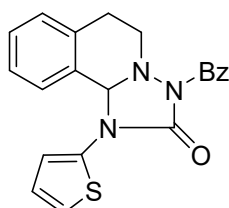
3-benzoyl-1-(furan-2-yl)-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one (3an)



3an

White solid (65 mg, 91%). m.p. 165-166 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (dd, $J = 5.2, 3.3$ Hz, 2H), 7.51 (ddd, $J = 6.7, 3.9, 1.2$ Hz, 1H), 7.42 (dd, $J = 10.4, 4.6$ Hz, 2H), 7.31 (td, $J = 7.6, 1.0$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 7.21 (dd, $J = 5.6, 1.3$ Hz, 1H), 7.04 (t, $J = 7.5$ Hz, 1H), 6.87 (dd, $J = 5.6, 3.7$ Hz, 1H), 6.66 (d, $J = 7.7$ Hz, 1H), 6.57 (dd, $J = 3.7, 1.3$ Hz, 1H), 5.91 (s, 1H), 3.71 (ddd, $J = 10.2, 4.7, 3.3$ Hz, 1H), 3.42–3.33 (m, 1H), 3.24 (ddd, $J = 16.5, 11.7, 4.7$ Hz, 1H), 2.97 (dt, $J = 16.5, 3.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 152.4, 135.9, 135.0, 133.4, 131.8, 129.6, 129.5, 128.9 (2C), 128.4, 127.7 (2C), 127.2, 127.1, 125.9, 125.7, 125.7, 76.4, 47.8, 27.7. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{21}\text{H}_{17}\text{O}_3\text{N}_3$ $[\text{M}+\text{H}]^+$ 376.1114; Found: 376.1116.

3-benzoyl-1-(thiophen-2-yl)-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one (3ao)

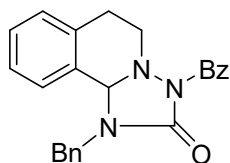


3ao

White solid (63 mg, 83%). m.p. 163-164 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (dd, $J = 5.2, 3.4$ Hz, 2H), 7.51 (ddd, $J = 6.7, 3.9, 1.2$ Hz, 1H), 7.42 (dd, $J = 10.5, 4.6$ Hz, 2H), 7.31 (td, $J = 7.6, 0.9$ Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 7.21 (dd, $J = 5.6, 1.3$ Hz, 1H), 7.04 (t, $J = 7.5$ Hz, 1H), 6.87 (dd, $J = 5.6, 3.7$ Hz, 1H), 6.66 (d, $J = 7.7$ Hz, 1H), 6.58 (dd, $J = 3.7, 1.3$ Hz, 1H), 5.92 (s, 1H), 3.71 (ddd, $J = 10.2, 4.7,$

3.3 Hz, 1H), 3.42–3.33 (m, 1H), 3.25 (ddd, $J = 16.5, 11.7, 4.7$ Hz, 1H), 2.98 (dt, $J = 16.5, 3.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 152.4, 135.8, 135.0, 133.4, 131.8, 129.6, 129.5, 128.9 (2C), 128.4, 127.7 (2C), 127.2, 127.1, 125.9, 125.7, 125.7, 76.4, 47.8, 27.7. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ 376.1114; Found: 376.1114.

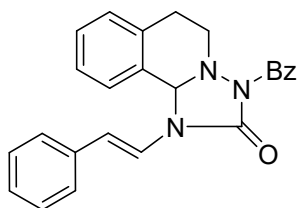
3-benzoyl-1-benzyl-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3ap)



3ap

White solid (40 mg, 52%). m.p. 138–140 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.75–7.70 (m, 2H), 7.56–7.50 (m, 1H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.36–7.18 (m, 6H), 7.08 (d, $J = 6.8$ Hz, 2H), 7.04 (d, $J = 7.5$ Hz, 1H), 5.79 (s, 1H), 4.69 (d, $J = 15.9$ Hz, 1H), 4.08 (d, $J = 15.9$ Hz, 1H), 3.56 (dt, $J = 10.7, 4.5$ Hz, 1H), 3.20 (td, $J = 10.6, 3.5$ Hz, 1H), 3.08 (ddd, $J = 15.1, 10.3, 4.4$ Hz, 1H), 2.87 (dt, $J = 16.4, 3.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 153.1, 135.9, 135.9, 133.8, 131.6, 129.5, 129.4, 128.8 (4C), 128.7 (2C), 127.7 (2C), 127.6, 127.4 (2C), 126.2, 72.4, 47.9, 44.6, 27.2. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{24}\text{H}_{21}\text{O}_2\text{N}_3$ $[\text{M}+\text{H}]^+$ 384.1706; Found: 384.1703.

3-benzoyl-1-styryl-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one(3aq)



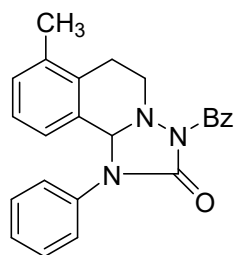
3aq

White solid (74 mg, 94%). m.p. 130–135 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.74–7.69 (m, 2H), 7.58–7.52 (m, 1H), 7.48–7.36 (m, 5H), 7.30 (d, $J = 7.5$ Hz, 1H), 7.26–7.21 (m, 2H), 7.18–7.13 (m, 3H), 6.94 (d, $J = 14.8$ Hz, 1H), 6.61 (d, $J = 14.7$ Hz, 1H), 5.98 (s, 1H), 3.72–3.64 (m, 1H), 3.30 (td, $J = 10.6, 3.8$ Hz, 1H), 3.15 (ddd, $J = 15.1, 10.2, 4.7$ Hz, 1H), 2.99 (dt, $J = 16.6, 4.1$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 150.8, 136.1, 136.1, 133.6, 131.9, 130.0, 130.0, 129.0, 128.8 (2C), 128.6 (2C), 127.8

(2C), 127.1, 127.0, 126.4, 125.5 (2C), 121.1, 118.5, 74.2, 47.8, 27.2. HRMS (ESI-TOF) m/z : Calcd for $C_{25}H_{21}O_2N_3$ $[M+H]^+$ 396.1706; Found: 396.1708.

3-benzoyl-7-methyl-1-phenyl-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one

(3ba)

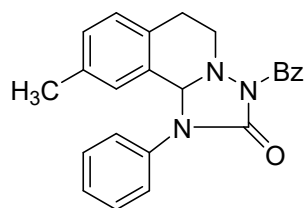


3ba

White solid (51 mg, 66%). m.p. 155-157 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, $J = 5.2, 3.3$ Hz, 2H), 7.52–7.47 (m, 1H), 7.41 (dd, $J = 10.3, 4.6$ Hz, 2H), 7.33–7.27 (m, 3H), 7.13 (d, $J = 7.5$ Hz, 1H), 7.01–6.96 (m, 2H), 6.86 (t, $J = 7.6$ Hz, 1H), 6.31 (d, $J = 7.7$ Hz, 1H), 5.99 (s, 1H), 3.77 (ddd, $J = 10.5, 5.1, 3.1$ Hz, 1H), 3.44 (td, $J = 11.0, 4.0$ Hz, 1H), 3.05 (ddd, $J = 16.6, 11.4, 5.1$ Hz, 1H), 2.93 (dt, $J = 17.0, 3.5$ Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 152.5, 136.1, 134.7, 133.7, 133.4, 131.6, 130.6, 129.1 (2C), 128.9 (2C), 128.8 (2C), 128.3, 127.8, 127.7 (2C), 127.4, 125.4, 76.1, 47.1, 25.2, 19.2. HRMS (ESI-TOF) m/z : Calcd for $C_{24}H_{21}O_2N_3$ $[M+H]^+$ 384.1706; Found: 384.1713.

3-benzoyl-9-methyl-1-phenyl-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one

(3ca)

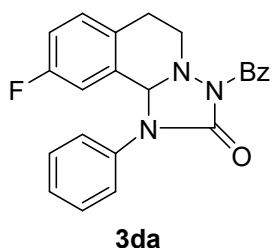


3ca

White solid (95 mg, 82%). m.p. 160-164 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, $J = 5.2, 3.3$ Hz, 2H), 7.52–7.47 (m, 1H), 7.41 (dd, $J = 10.3, 4.6$ Hz, 2H), 7.34–7.29 (m, 3H), 7.08 (dt, $J = 7.9, 4.4$ Hz, 2H), 6.98–6.93 (m, 2H), 6.22 (s, 1H), 5.95 (s, 1H), 3.70 (ddd, $J = 10.5, 4.7, 3.6$ Hz, 1H), 3.43 (td, $J = 11.0, 3.5$ Hz, 1H), 3.19 (ddd, $J = 16.3, 11.5, 4.7$ Hz, 1H), 2.94 (dt, $J = 16.5, 3.4$ Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.3, 152.4, 135.2, 134.6, 133.8, 131.8, 131.5, 130.4, 130.0, 129.0

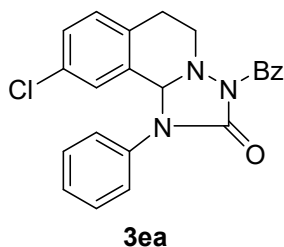
(2C), 128.9 (2C), 128.8 (2C), 128.3, 128.1, 127.6 (2C), 127.4, 75.8, 47.8, 27.2, 20.7. HRMS (ESI-TOF) m/z : Calcd for $C_{24}H_{21}O_2N_3$ $[M+H]^+$ 384.1706; Found: 384.1705.

3-benzoyl-9-fluoro-1-phenyl-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one
(3da)



White solid (59 mg, 76%). m.p. 163-165 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.69 (m, 2H), 7.53–7.48 (m, 1H), 7.44–7.39 (m, 2H), 7.38–7.32 (m, 3H), 7.21 (dd, $J = 8.5, 5.5$ Hz, 1H), 7.03–6.95 (m, 3H), 6.17 (dd, $J = 9.2, 2.6$ Hz, 1H), 5.97 (s, 1H), 3.73 (ddd, $J = 10.6, 4.7, 3.7$ Hz, 1H), 3.45 (td, $J = 11.0, 3.5$ Hz, 1H), 3.20 (ddd, $J = 16.1, 11.3, 4.7$ Hz, 1H), 2.97 (dt, $J = 16.5, 3.4$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 160.3 (d, $J = 245.5$ Hz), 152.4, 134.3, 133.6, 131.7, 130.7, 130.0, 129.5, 129.4 (2C), 128.8 (2C), 128.7, 128.7 (2C), 127.7 (2C), 116.6 (d, $J = 21.4$ Hz), 116.3 (d, $J = 22.9$ Hz), 75.2, 47.6, 27.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.5. HRMS (ESI-TOF) m/z : Calcd for $C_{23}H_{18}O_2N_3F$ $[M+H]^+$ 388.1456; Found: 388.1458.

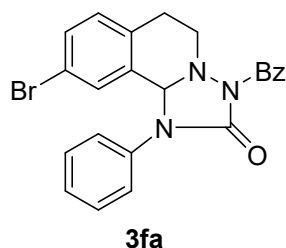
3-benzoyl-9-chloro-1-phenyl-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one
(3ea)



White solid (48 mg, 60%). m.p. 178-180 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, $J = 5.2, 3.3$ Hz, 2H), 7.53–7.47 (m, 1H), 7.41 (dd, $J = 10.3, 4.6$ Hz, 2H), 7.39–7.33 (m, 3H), 7.26–7.22 (m, 1H), 7.17 (d, $J = 8.2$ Hz, 1H), 7.01–6.96 (m, 2H), 6.41 (d, $J = 2.0$ Hz, 1H), 5.94 (s, 1H), 3.73 (ddd, $J = 10.6, 4.7, 3.6$ Hz, 1H), 3.43 (td, $J = 11.0, 3.5$ Hz, 1H), 3.20 (ddd, $J = 16.3, 11.3, 4.8$ Hz, 1H), 2.96 (dt, $J = 16.7,$

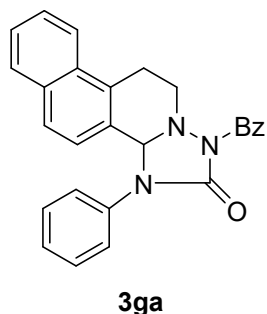
3.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 152.3, 134.2, 133.5, 133.5, 131.7, 131.4, 129.8, 129.7, 129.5, 129.5, 129.4 (2C), 128.8 (2C), 128.7, 128.7 (2C), 127.7 (2C), 75.1, 47.4, 27.2. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_3\text{Cl}$ $[\text{M}+\text{H}]^+$ 404.1160; Found: 404.1164.

3-benzoyl-9-bromo-1-phenyl-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one
(3fa)



White solid (57 mg, 63%). m.p. 176-178 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.8$ Hz, 2H), 7.54–7.48 (m, 1H), 7.45–7.34 (m, 6H), 7.11 (d, $J = 8.2$ Hz, 1H), 6.98 (dd, $J = 7.1, 1.7$ Hz, 2H), 6.55 (d, $J = 1.6$ Hz, 1H), 5.93 (s, 1H), 3.73 (dt, $J = 10.4, 4.1$ Hz, 1H), 3.43 (td, $J = 11.0, 3.4$ Hz, 1H), 3.18 (ddd, $J = 16.3, 11.4, 4.8$ Hz, 1H), 2.95 (dt, $J = 16.7, 3.3$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 152.3, 134.2, 134.0, 133.5, 132.6, 132.3, 131.7, 130.1, 129.9, 129.4 (2C), 128.8 (2C), 128.8, 128.7 (2C), 127.7 (2C), 119.1, 75.0, 47.4, 27.2. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_3\text{Br}$ $[\text{M}+\text{H}]^+$ 448.0655; Found: 448.0655.

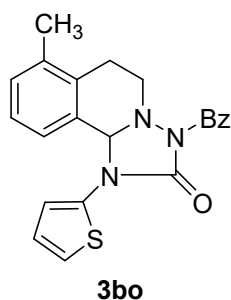
1-benzoyl-3-phenyl-3,3*a*,10,11-tetrahydrobenzo[*f*][1,2,4]triazolo[5,1-*a*]isoquinolin-2(1*H*)-one
(3ga)



White solid (43 mg, 51%). m.p. 182-183 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.3$ Hz, 1H), 7.80–7.74 (m, 3H), 7.62–7.48 (m, 3H), 7.45–7.40 (m, 3H), 7.33–7.29 (m, 3H), 7.05–7.00 (m, 2H), 6.49 (d, $J = 8.6$ Hz, 1H), 6.12 (s, 1H), 3.96 (ddd, $J = 9.8, 4.7, 2.8$ Hz, 1H), 3.62–3.46 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 152.4, 134.7, 133.7, 133.3, 131.7, 131.6, 131.0, 129.3 (2C), 129.0

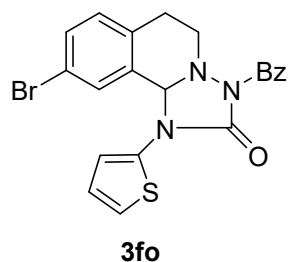
(2C), 128.8 (2C), 128.5, 128.5, 127.7 (2C), 126.9, 126.8, 126.5, 126.2, 124.9, 123.5, 76.0, 46.7, 24.6.
HRMS (ESI-TOF) *m/z*: Calcd for C₂₇H₂₁O₂N₃ [M+H]⁺ 420.1706; Found: 420.1711.

3-benzoyl-7-methyl-1-(thiophen-2-yl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3bo)



White solid (66 mg, 84%). m.p. 167-169 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.71 (m, 2H), 7.54–7.48 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.21–7.15 (m, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.86 (dd, *J* = 5.6, 3.7 Hz, 1H), 6.59 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.50 (d, *J* = 7.7 Hz, 1H), 5.89 (s, 1H), 3.75 (ddd, *J* = 10.4, 5.1, 2.9 Hz, 1H), 3.35 (td, *J* = 11.1, 4.0 Hz, 1H), 3.02 (td, *J* = 11.7, 5.8 Hz, 1H), 2.92 (dt, *J* = 17.0, 3.4 Hz, 1H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 152.4, 136.0, 136.0, 133.4, 133.4, 131.8, 130.8, 128.9 (3C), 127.7 (2C), 127.5, 127.1, 126.9, 125.7, 125.6 (2C), 47.3, 25.3, 19.2. HRMS (ESI-TOF) *m/z*: Calcd for C₂₂H₁₉O₂N₃S [M+H]⁺ 390.1271; Found: 390.1273.

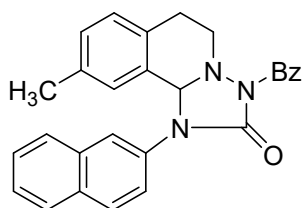
3-benzoyl-9-bromo-1-(thiophen-2-yl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3fo)



White solid (52 mg, 57%). m.p. 152-153 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73–7.70 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (ddd, *J* = 7.3, 4.6, 2.4 Hz, 3H), 7.28–7.25 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.93 (dd, *J* = 5.6, 3.7 Hz, 1H), 6.73 (d, *J* = 1.9 Hz, 1H), 6.61 (dd, *J* = 3.7, 1.2 Hz, 1H), 5.82 (s, 1H), 3.72 (ddd, *J* = 10.3, 4.6, 3.3 Hz, 1H), 3.34 (td, *J* = 11.1, 3.4 Hz, 1H), 3.17 (ddd, *J* = 16.5, 11.7, 4.7 Hz, 1H),

2.92 (dt, $J = 16.7, 3.1$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 152.2, 135.4, 133.9, 133.2, 132.5, 132.3, 131.9, 130.0, 129.3, 128.9 (2C), 127.8 (2C), 127.4, 126.1, 125.9, 119.3, 75.7, 47.5, 27.3. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$ 454.0219; Found: 454.0221.

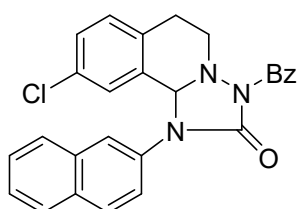
3-benzoyl-9-methyl-1-(naphthalen-1-yl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3cm)



3cm

White solid (57 mg, 65%). m.p. 162-163 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.83–7.79 (m, 1H), 7.78–7.74 (m, 3H), 7.72–7.69 (m, 1H), 7.53–7.40 (m, 6H), 7.13 (d, $J = 7.8$ Hz, 1H), 7.06 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.02 (dd, $J = 8.7, 2.1$ Hz, 1H), 6.25 (s, 1H), 6.05 (s, 1H), 3.73 (ddd, $J = 10.6, 4.7, 3.8$ Hz, 1H), 3.50 (td, $J = 11.0, 3.5$ Hz, 1H), 3.21 (ddd, $J = 16.1, 11.3, 4.7$ Hz, 1H), 2.99 (dt, $J = 16.5, 3.4$ Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 152.6, 135.4, 133.8, 133.2, 132.6, 132.0, 131.9, 131.6, 130.6, 130.1, 128.8 (2C), 128.8, 128.2, 127.8, 127.8, 127.7 (2C), 127.6, 127.5, 126.6, 126.4, 126.0, 76.0, 48.0, 27.3, 20.7. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{28}\text{H}_{23}\text{O}_2\text{N}_3$ $[\text{M}+\text{H}]^+$ 434.1863; Found: 434.1866.

3-benzoyl-9-chloro-1-(naphthalen-1-yl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3em)

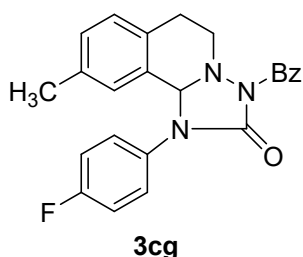


3em

White solid (50 mg, 55%). m.p. 160-162 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.84–7.79 (m, 2H), 7.77–7.72 (m, 3H), 7.54–7.47 (m, 4H), 7.46–7.40 (m, 2H), 7.21 (dt, $J = 18.1, 5.1$ Hz, 2H), 7.01 (dd, $J = 8.7, 2.1$ Hz, 1H), 6.47 (d, $J = 1.9$ Hz, 1H), 6.05 (s, 1H), 3.75 (dt, $J = 8.6, 4.6$ Hz, 1H), 3.51 (td, $J = 11.0, 3.5$

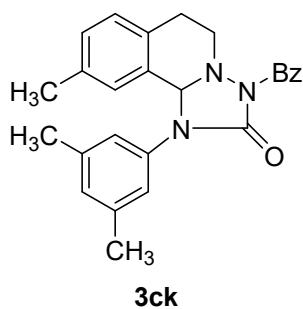
Hz, 1H), 3.21 (ddd, $J = 16.2, 11.1, 4.8$ Hz, 1H), 3.01 (dt, $J = 16.7, 3.5$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 152.5, 133.6, 133.3, 132.7, 131.8, 131.6, 131.5, 129.8, 129.7, 129.6, 129.5, 129.3, 128.9 (2C), 127.9, 127.7 (3C), 127.7, 127.7, 126.8, 126.7, 125.6, 75.2, 47.6, 27.2. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{27}\text{H}_{20}\text{O}_2\text{N}_3\text{Cl}$ $[\text{M}+\text{H}]^+$ 454.1317; Found: 454.1318.

3-benzoyl-1-(4-fluorophenyl)-9-methyl-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3cg)



White solid (67 mg, 83%). m.p. 156-158 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (dd, $J = 5.2, 3.3$ Hz, 2H), 7.50 (ddd, $J = 6.6, 3.9, 1.2$ Hz, 1H), 7.41 (dd, $J = 10.4, 4.6$ Hz, 2H), 7.14–7.07 (m, 2H), 7.03–6.97 (m, 2H), 6.91 (ddd, $J = 9.6, 4.9, 2.4$ Hz, 2H), 6.22 (s, 1H), 5.90 (s, 1H), 3.70 (ddd, $J = 10.4, 4.7, 3.5$ Hz, 1H), 3.40 (td, $J = 11.0, 3.5$ Hz, 1H), 3.19 (ddd, $J = 16.3, 11.5, 4.7$ Hz, 1H), 2.93 (dt, $J = 16.5, 3.3$ Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 162.11 (d, $J = 248.6$ Hz), 152.5, 135.6, 133.7, 131.8, 131.7, 130.8, 130.7, 130.5, 130.4, 130.2, 128.8 (2C), 128.3, 127.7 (2C), 127.3, 116.1, 115.9, 75.9, 47.8, 27.2, 20.8. ^{19}F NMR (377 MHz, CDCl_3) δ -112.5 (s). HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{24}\text{H}_{20}\text{O}_2\text{N}_3\text{F}$ $[\text{M}+\text{H}]^+$ 402.1612; Found: 402.1616.

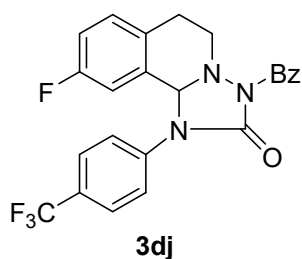
3-benzoyl-1-(3,5-dimethylphenyl)-9-methyl-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3ck)



White solid (71 mg, 87%). m.p. 178-180 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.74–7.70 (m, 2H), 7.52–

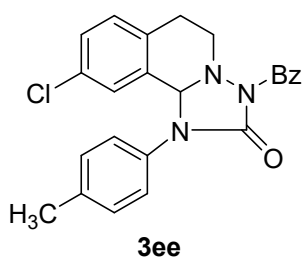
7.46 (m, 1H), 7.41 (t, $J = 7.4$ Hz, 2H), 7.12–7.05 (m, 2H), 6.92 (s, 1H), 6.55 (s, 2H), 6.26 (s, 1H), 5.91 (s, 1H), 3.72–3.66 (m, 1H), 3.41 (td, $J = 11.0, 3.4$ Hz, 1H), 3.19 (ddd, $J = 16.2, 11.5, 4.7$ Hz, 1H), 2.93 (dt, $J = 16.4, 3.3$ Hz, 1H), 2.22 (s, 6H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 152.5, 138.7 (2C), 135.0, 134.3, 133.9, 131.8, 131.5, 130.6, 129.9, 129.9, 128.8 (2C), 128.1, 127.6 (3C), 126.3 (2C), 75.8, 47.8, 27.3, 21.0 (2C), 20.7. HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{26}\text{H}_{25}\text{O}_2\text{N}_3$ $[\text{M}+\text{H}]^+$ 412.2019; Found: 412.2016.

3-benzoyl-9-fluoro-1-(4-(trifluoromethyl)phenyl)-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one (3dj)



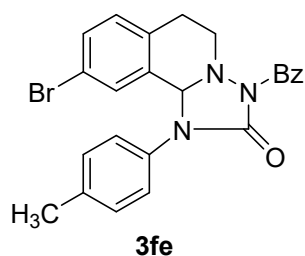
White solid (69 mg, 76%). m.p. 168-169 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.74–7.71 (m, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.55–7.50 (m, 1H), 7.43 (dd, $J = 10.5, 4.6$ Hz, 2H), 7.27–7.21 (m, 1H), 7.14 (d, $J = 8.3$ Hz, 2H), 7.03 (td, $J = 8.4, 2.6$ Hz, 1H), 6.27 (dd, $J = 8.9, 2.6$ Hz, 1H), 6.04 (s, 1H), 3.71 (dt, $J = 10.9, 4.4$ Hz, 1H), 3.46 (td, $J = 10.9, 3.7$ Hz, 1H), 3.17 (ddd, $J = 15.6, 10.7, 4.6$ Hz, 1H), 3.00 (dt, $J = 16.5, 3.7$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3 (d, $J = 246.5$ Hz), 160.4, 152.2, 137.8, 133.3, 132.0, 130.9, 130.4, 129.2, 128.9 (2C), 128.6 (2C), 127.8 (2C), 126.5, 123.5 (d, $J = 272.3$ Hz), 117.1, 116.9, 116.5, 116.2, 75.3, 47.9, 26.8. ^{19}F NMR (377 MHz, CDCl_3) δ -62.7 (s), -114.8 (s). HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{24}\text{H}_{17}\text{O}_2\text{N}_3\text{F}_4$ $[\text{M}+\text{H}]^+$ 456.1330; Found: 456.1329.

3-benzoyl-9-chloro-1-(p-tolyl)-1,5,6,10b-tetrahydro-[1,2,4]triazolo[5,1-a]isoquinolin-2(3H)-one (3ee)



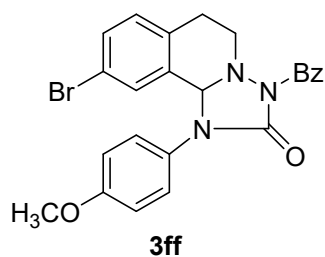
White solid (50 mg, 61%). m.p. 178-180 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73–7.69 (m, 2H), 7.50 (ddd, *J* = 6.6, 3.8, 1.2 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.26–7.22 (m, 1H), 7.16 (dd, *J* = 8.2, 3.7 Hz, 3H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.44 (d, *J* = 2.0 Hz, 1H), 5.91 (s, 1H), 3.71 (ddd, *J* = 10.6, 4.6, 3.7 Hz, 1H), 3.42 (td, *J* = 11.0, 3.4 Hz, 1H), 3.19 (ddd, *J* = 16.3, 11.3, 4.8 Hz, 1H), 2.95 (dt, *J* = 16.7, 3.4 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 152.4, 138.8, 133.6, 133.5, 131.7, 131.5, 131.4, 130.0 (2C), 129.8, 129.7, 129.6, 129.4, 128.8 (2C), 128.4 (2C), 127.7 (2C), 75.0, 47.4, 27.2, 21.1. HRMS (ESI-TOF) *m/z*: Calcd for C₂₄H₂₀O₂N₃Cl [M+H]⁺ 420.1706; Found: 420.1711.

3-benzoyl-9-bromo-1-(*p*-tolyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3fe)



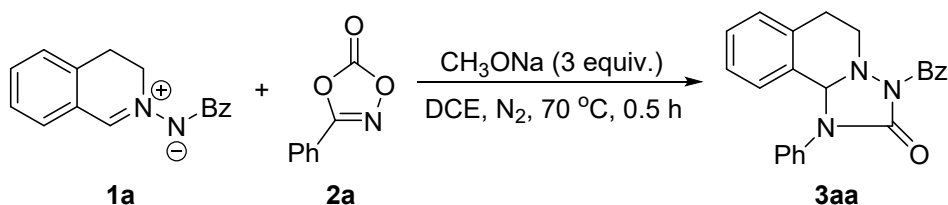
White solid (54 mg, 58%). m.p. 176-177 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73–7.69 (m, 2H), 7.50 (ddd, *J* = 6.7, 3.9, 1.2 Hz, 1H), 7.44–7.37 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 1.9 Hz, 1H), 5.90 (s, 1H), 3.71 (ddd, *J* = 10.6, 4.7, 3.7 Hz, 1H), 3.41 (td, *J* = 11.0, 3.4 Hz, 1H), 3.17 (ddd, *J* = 16.3, 11.4, 4.7 Hz, 1H), 2.93 (dt, *J* = 16.7, 3.4 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 152.4, 138.8, 134.0, 133.6, 132.7, 132.3, 131.7, 131.5, 130.0, 130.0 (2C), 130.0, 128.8 (2C), 128.4 (2C), 127.7 (2C), 119.1, 74.9, 47.3, 27.3, 21.1. HRMS (ESI-TOF) *m/z*: Calcd for C₂₄H₂₀O₂N₃Br [M+H]⁺ 462.0812; Found: 462.0814.

3-benzoyl-9-bromo-1-(4-methoxyphenyl)-1,5,6,10*b*-tetrahydro-[1,2,4]triazolo[5,1-*a*]isoquinolin-2(3*H*)-one (3ff)



White solid (45 mg, 47%). m.p. 160-162 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.53–7.48 (m, 1H), 7.44–7.37 (m, 3H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.87 (s, 4H), 6.56 (d, *J* = 1.9 Hz, 1H), 5.86 (s, 1H), 3.79 (s, 3H), 3.71 (ddd, *J* = 8.1, 4.4, 3.1 Hz, 1H), 3.39 (td, *J* = 11.1, 3.4 Hz, 1H), 3.18 (ddd, *J* = 16.4, 11.5, 4.8 Hz, 1H), 2.93 (dt, *J* = 16.7, 3.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 159.6, 152.5, 134.0, 133.7, 132.7, 132.3, 131.7, 130.0, 130.0 (2C), 129.9, 128.8 (2C), 127.7 (2C), 126.7, 119.1, 114.7 (2C), 75.0, 55.5, 47.3, 27.3. HRMS (ESI-TOF) *m/z*: Calcd for C₂₄H₂₀O₃N₃Br [M+H]⁺ 478.0760; Found: 478.0765.

4. Scale-up experiment

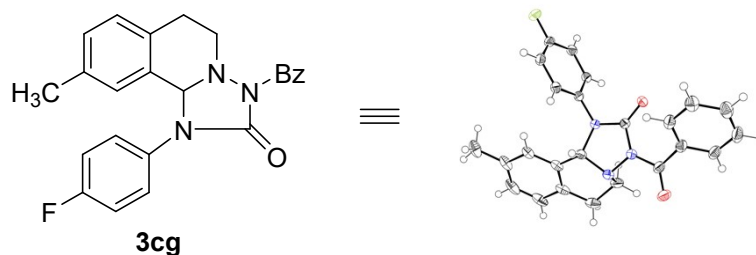


The scale-up reaction of *C,N*-cycloazomethylimine **1a** and dioxazolone **2a** was performed. Reaction of 4.0 mmol of **1a** and 12.0 mmol of **2a** proceeded well under the standard reaction conditions, affording the desired product **3aa** in 82% yield (1.21 g).

5. References

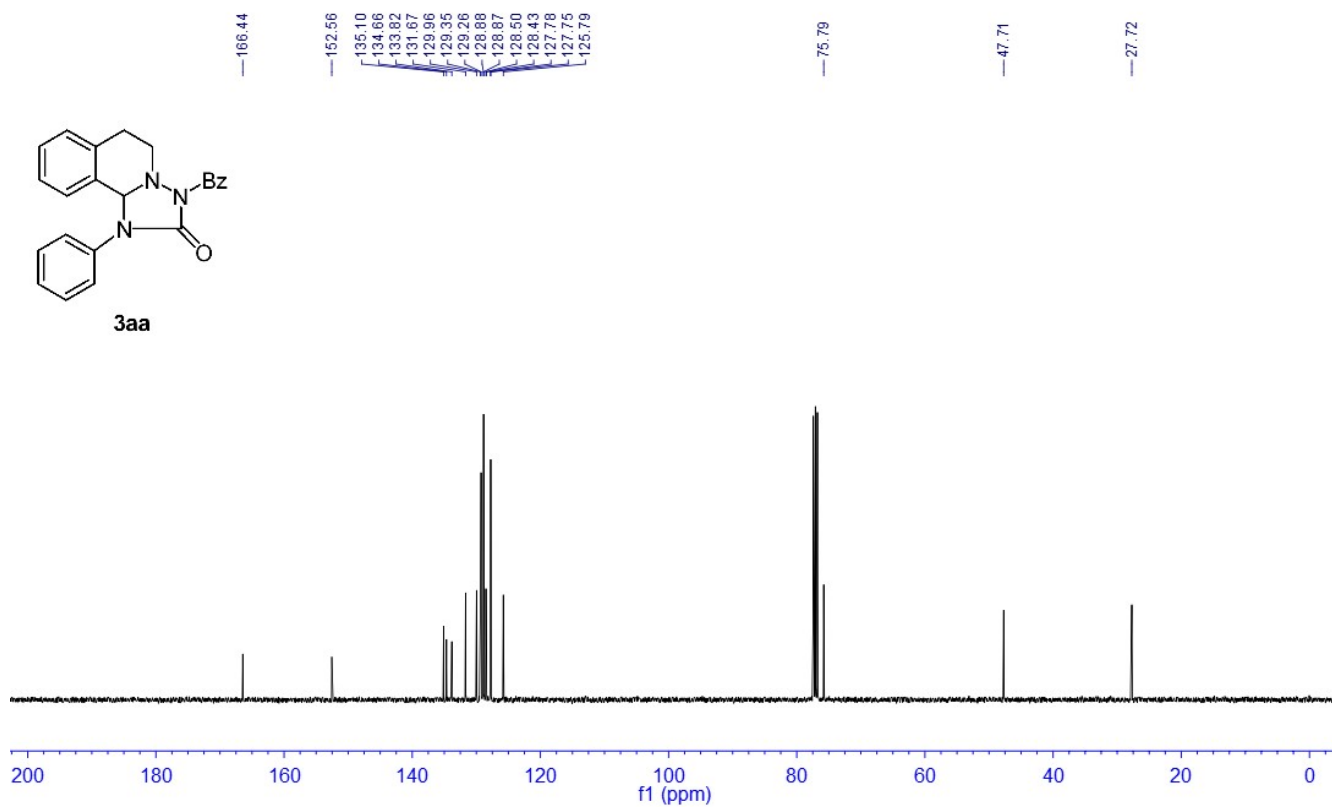
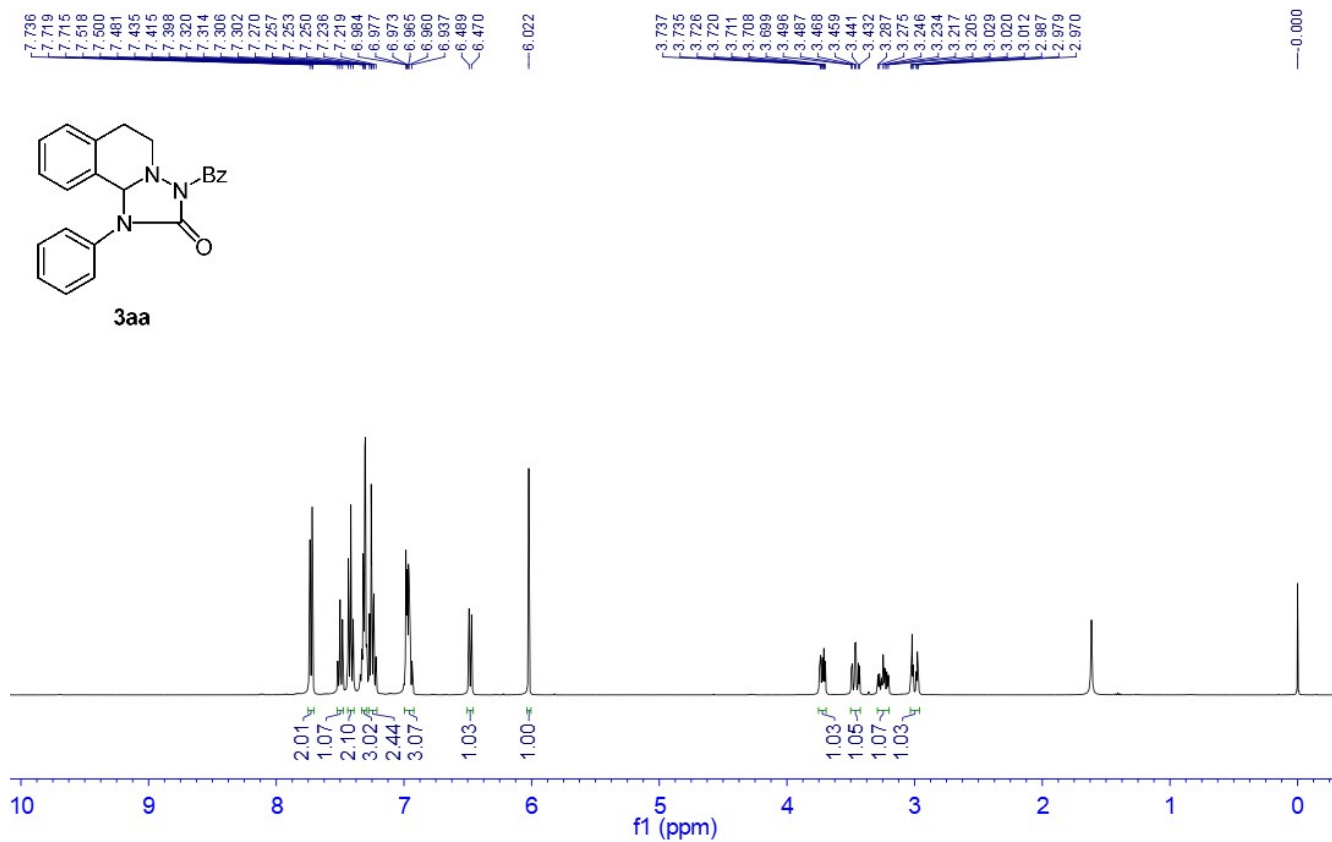
- [1] Y. Wang, L. Zhu, M. Wang, J. Xiong, N. Chen, X. Feng, Z. Xu, and X. Jiang, *Org. Lett.*, 2018, **20**, 6506-6510.
- [2] D. Wang, X. Liu, M. J. Ajitha, Z. Liu, Y. Hu, and K.-W. Huang, *Org. Lett.*, 2023, **25**, 3249-3253.
- [3] Y. Park, K. T. Park, J. G. Kim, and S. Chang, *J. Am. Chem. Soc.*, 2015, **137**, 4534-4542.
- [4] Q. Wang, F. Wang, X. Yang, X. Zhou, and X. Li, *Org. Lett.*, 2016, **18**, 6144-6147.

6. X-ray crystallographic data of 3cg



CCDC number	2308902
Empirical formula	C ₂₄ H ₂₀ FN ₃ O ₂
Formula weight	401.43
Temperature/K	100
Crystal system	Monoclinic
Space group	P ₁ 2 ₁ /n ₁
Hall group	-P 2yn
a/Å	9.5606 (2)
b/Å	22.0542 (2)
c/Å	9.7194 (2)
α/Å	90
β/°	108.419 (2)
γ/Å	90
Volume/Å ³	1944.36 (7)
Z	4
ρ _{calc} /g/cm ³	1.371
μ/mm ⁻¹	0.781
F(000)	840.0
Crystal size/mm ³	0.25 × 0.2 × 0.15
Radiation type	Cu Kα (λ = 1.54184)
2θ range for data collection/°	3.9760 to 75.7380
Index ranges	-11 ≤ h ≤ 11, -27 ≤ k ≤ 21, -12 ≤ l ≤ 12
Reflections collected	8871
Independent reflections	3860 [R _{int} = 0.0403, R _{sigma} = 0.629]
Data/restraints/parameters	3860/0/273
Goodness-of-fit on F ²	1.061
Final R indexes [I > 2σ (I)]	R1 = 0.0403, wR2 = 0.1077
Final R indexes [all data]	R1 = 0.0455, wR2 = 0.1118
Largest diff. peak/hole e Å ⁻³	0.23/-0.24

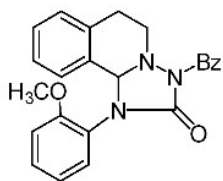
7. NMR spectra of products



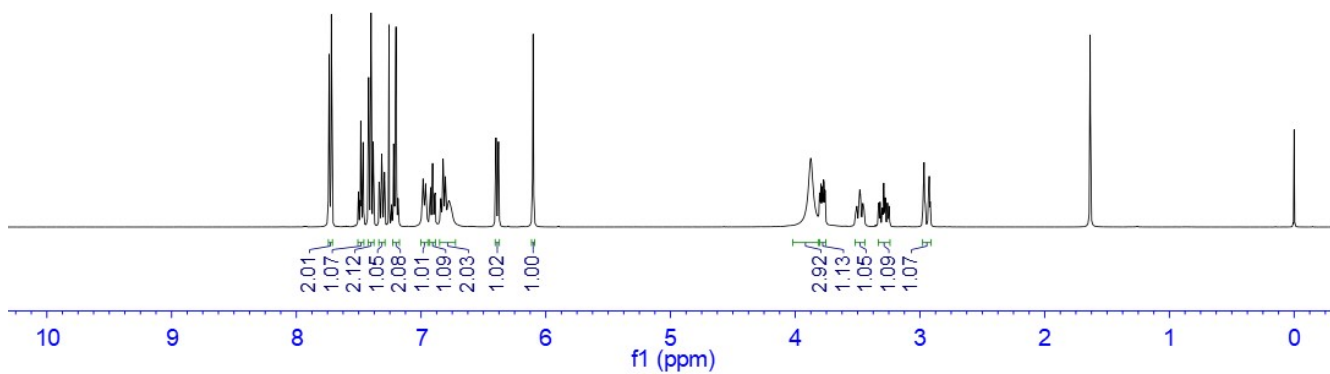
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7.715
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7.420
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7.401
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7.337
7.316
7.314
7.298
7.293
7.266
7.220
7.217
7.203
7.201
6.984
6.964
6.908
6.824
6.805
6.399
6.379
6.102

3.876
3.798
3.793
3.786
3.780
3.773
3.768
3.761
3.514
3.506
3.483
3.458
3.451
3.332
3.320
3.302
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2.960
2.933
2.926
2.918

0.000



3ab



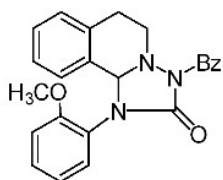
166.3
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129.0
128.9
128.8
128.3
128.0
127.6
125.6
123.1
120.9
111.7

77.0
73.8

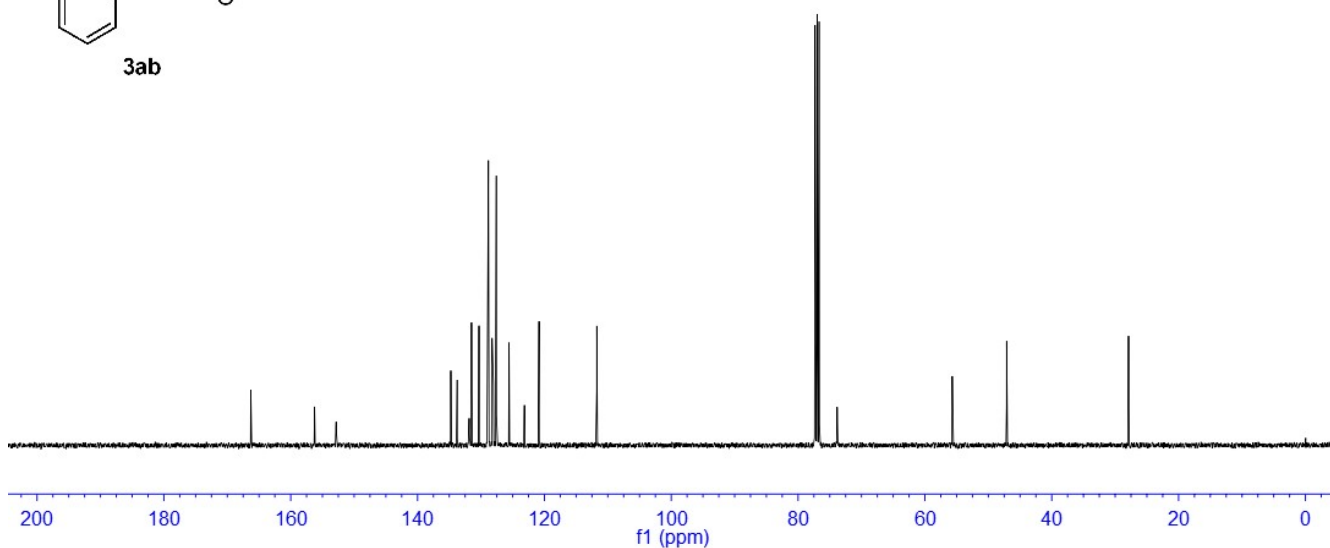
56.7

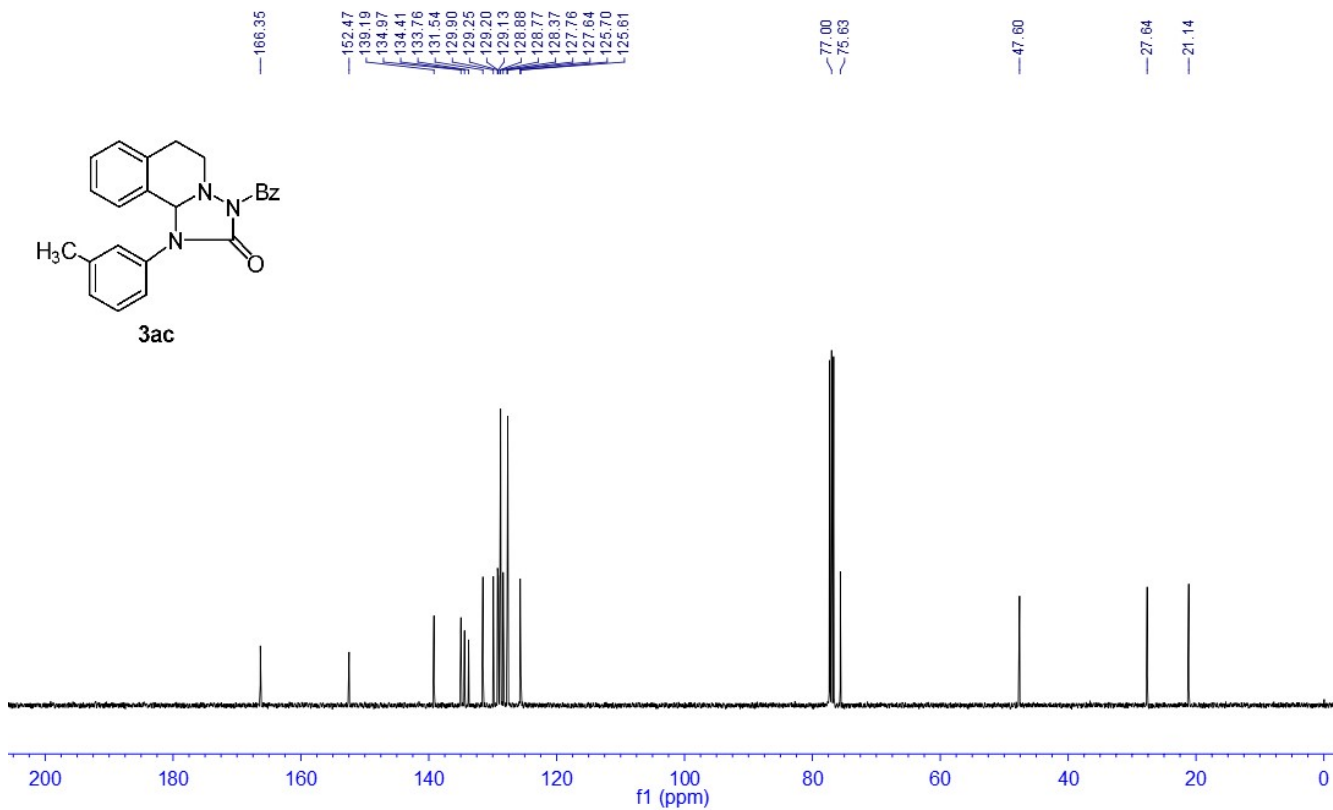
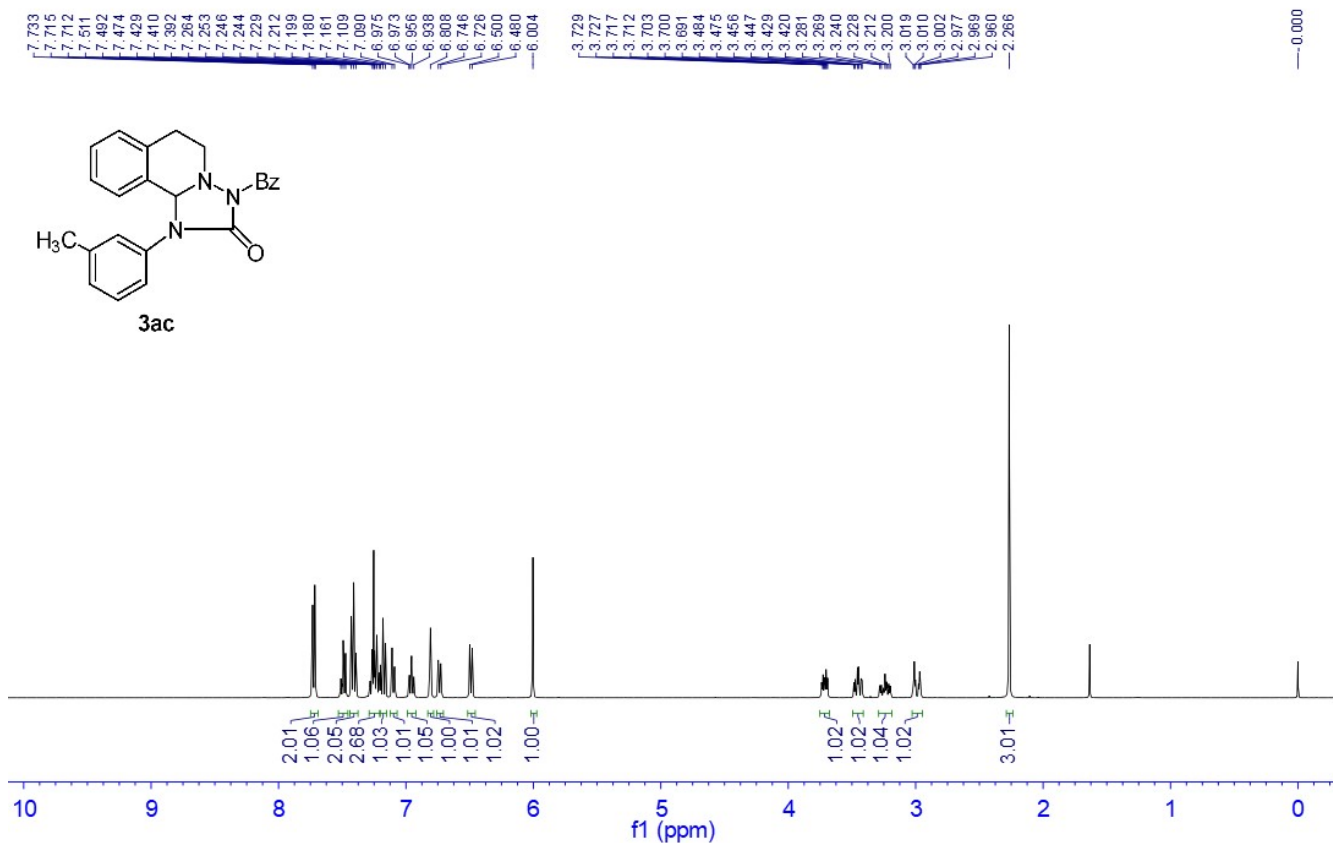
47.1

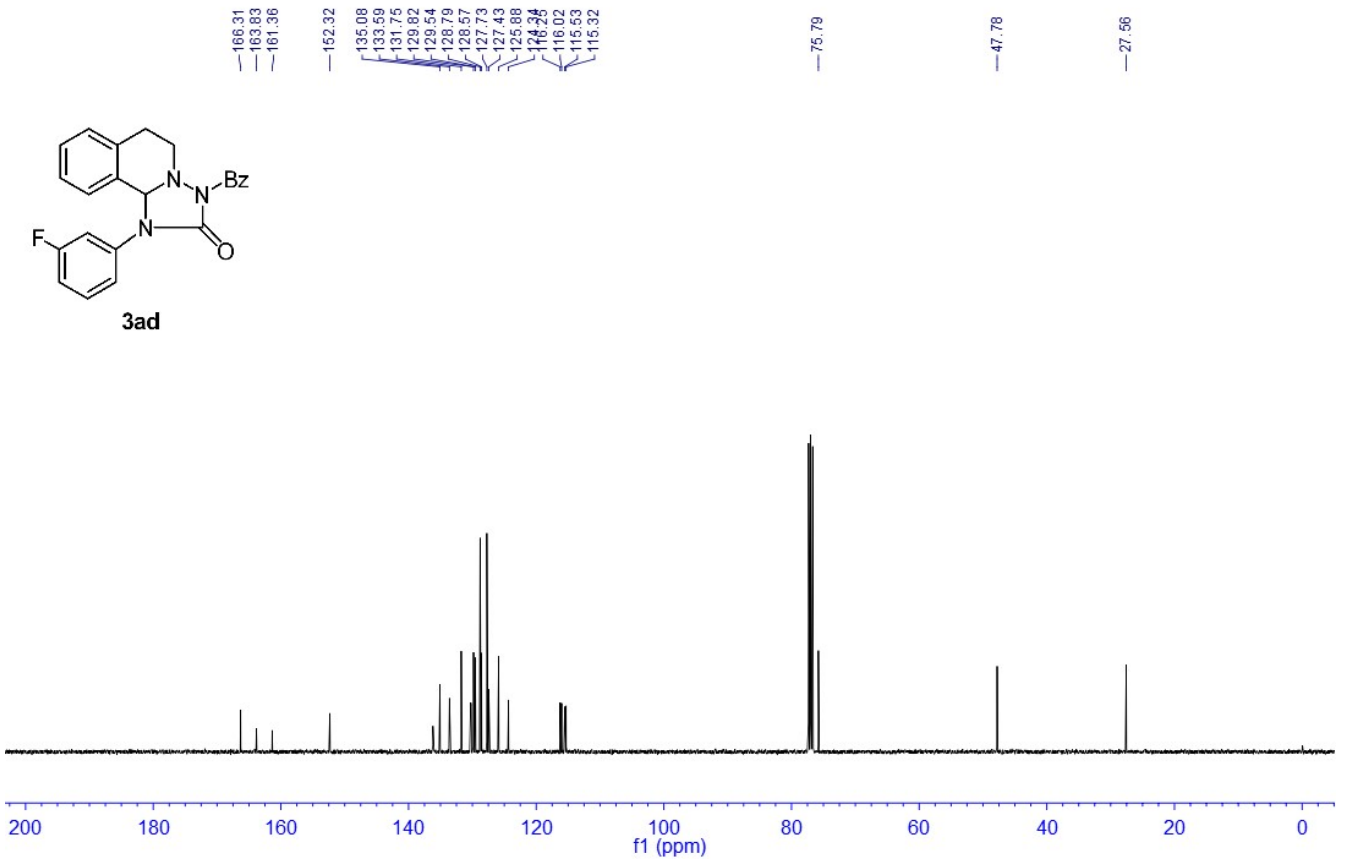
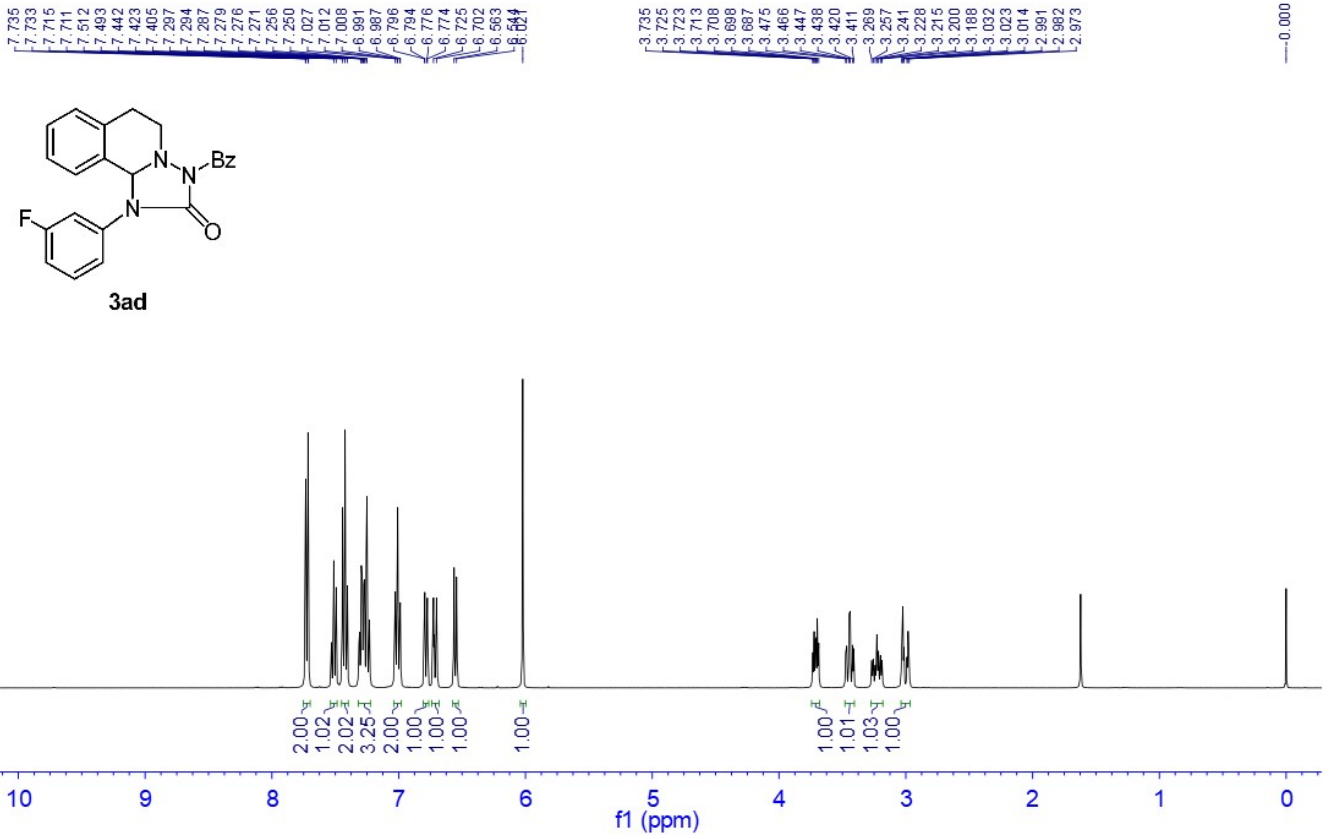
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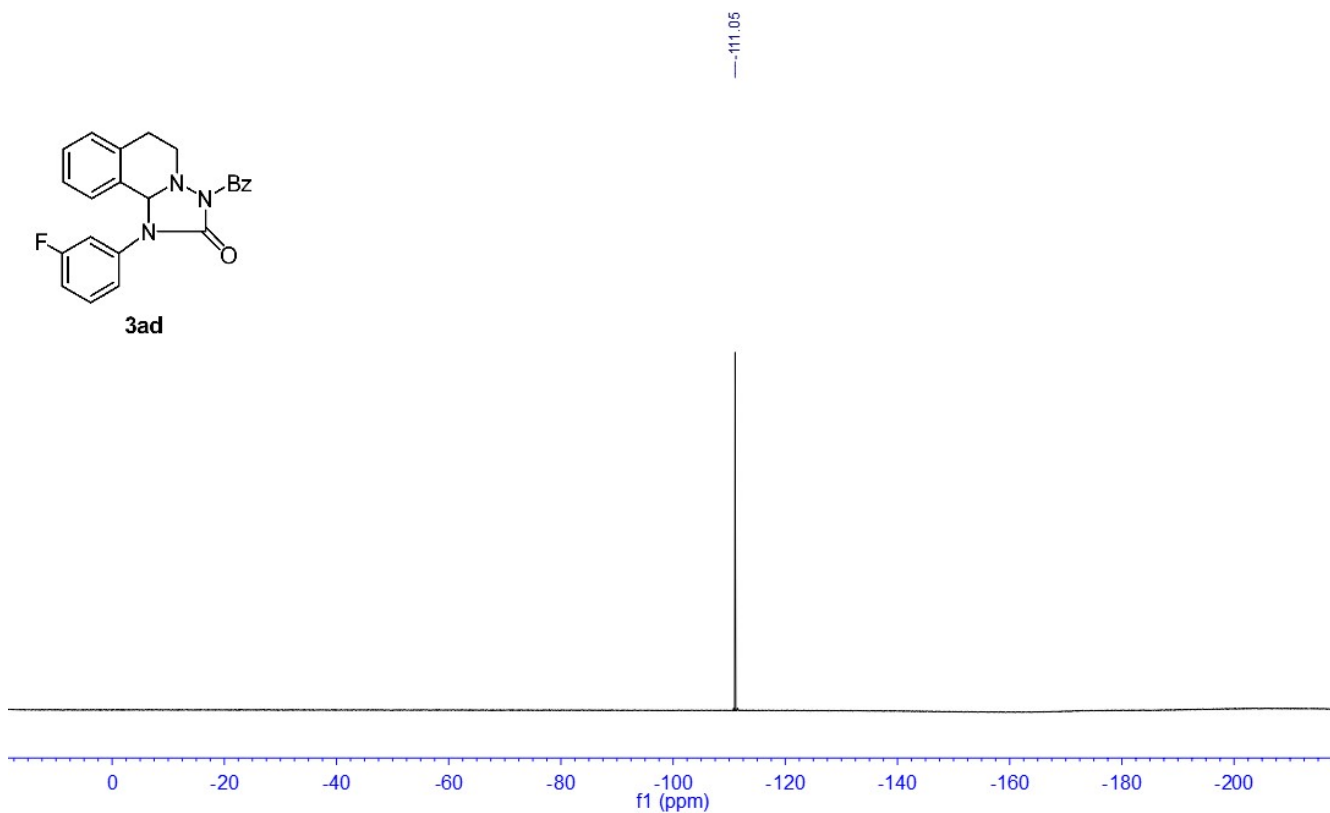
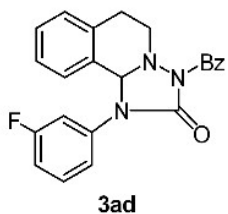


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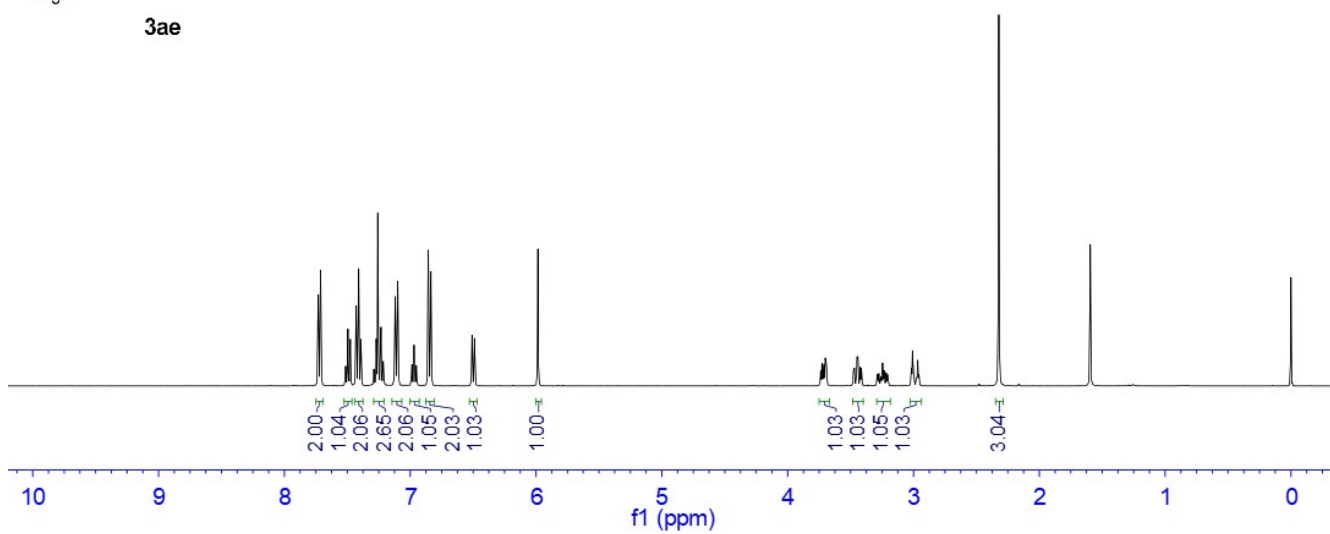
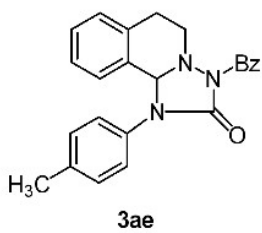


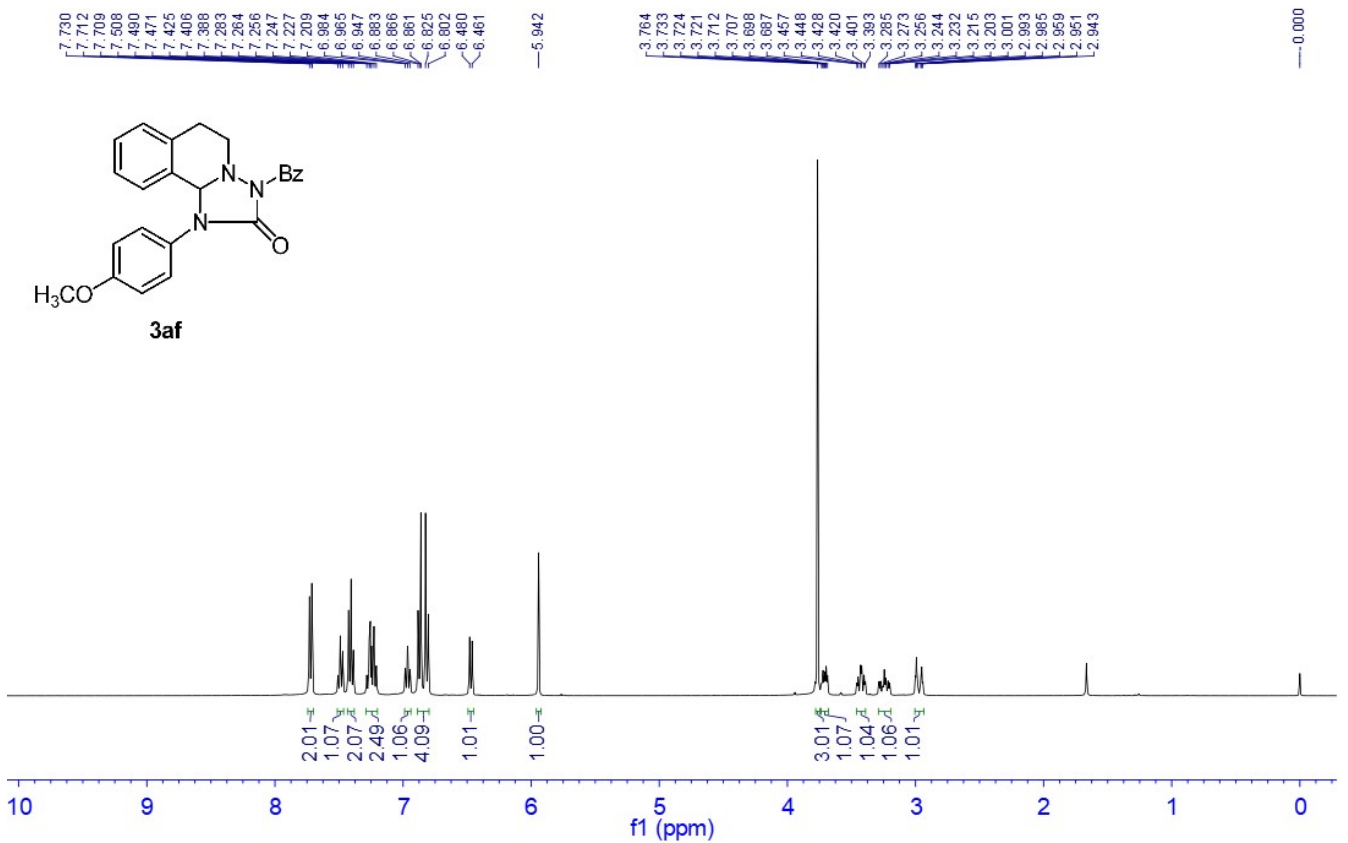
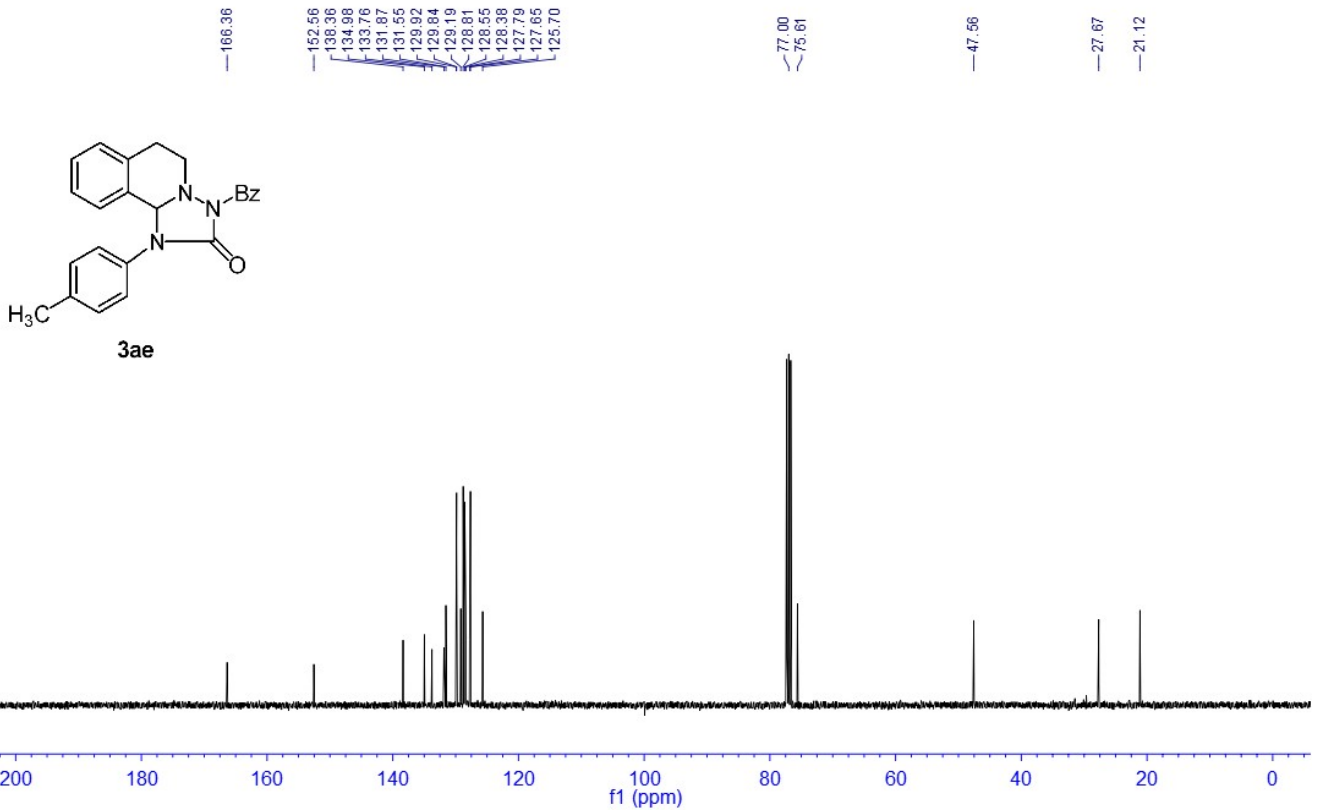


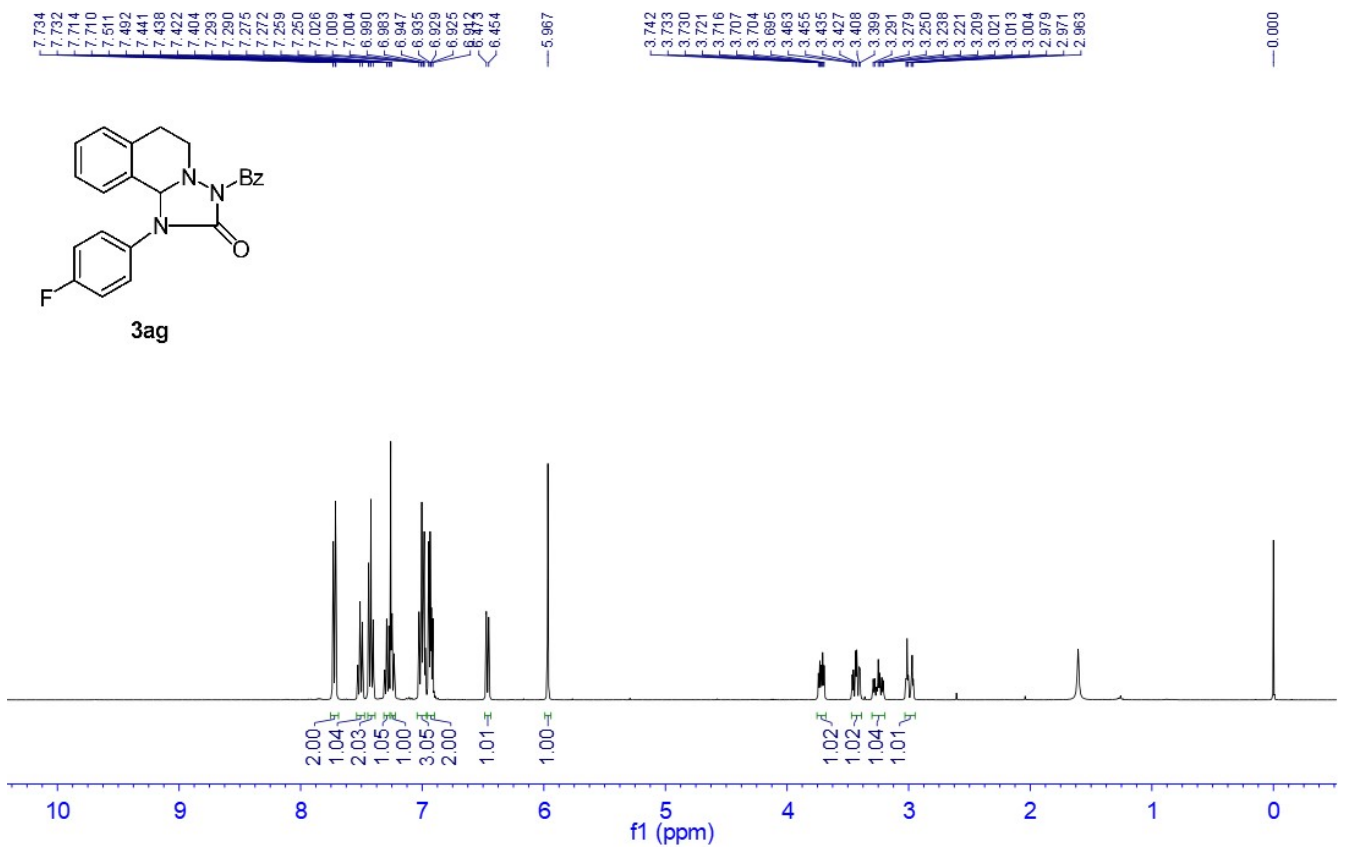
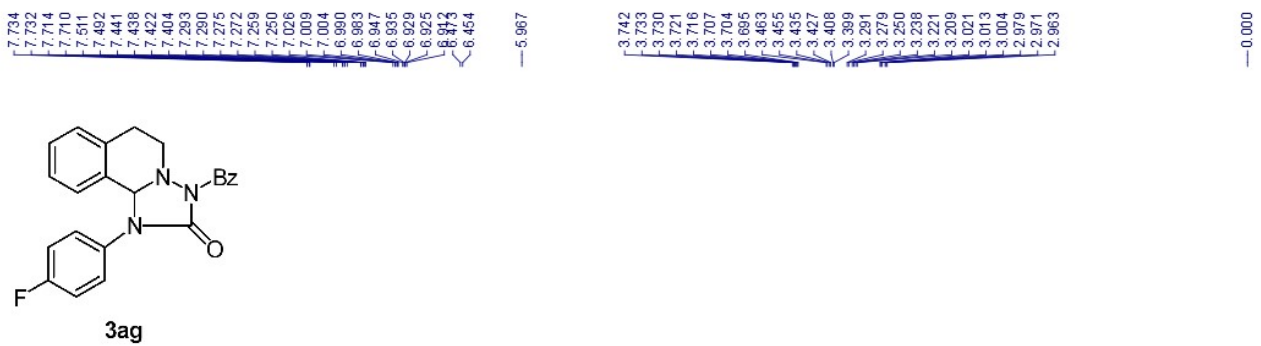
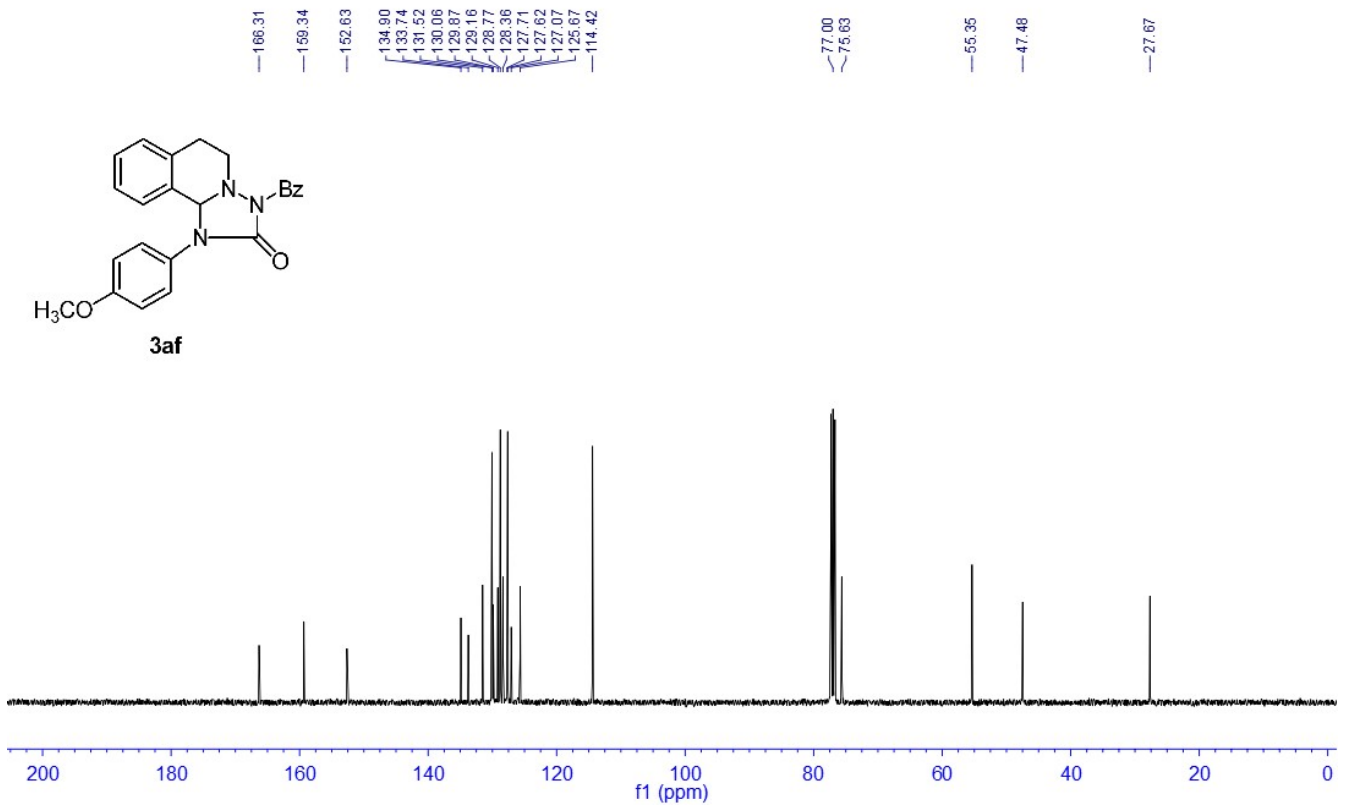
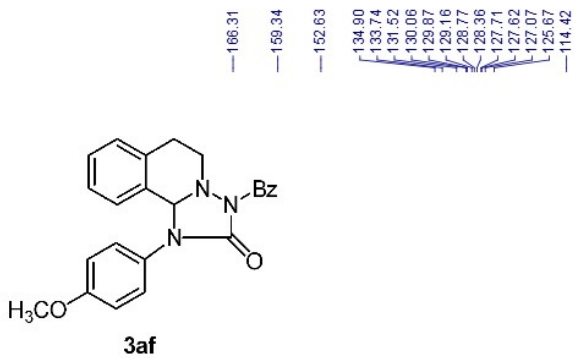


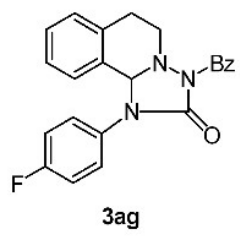
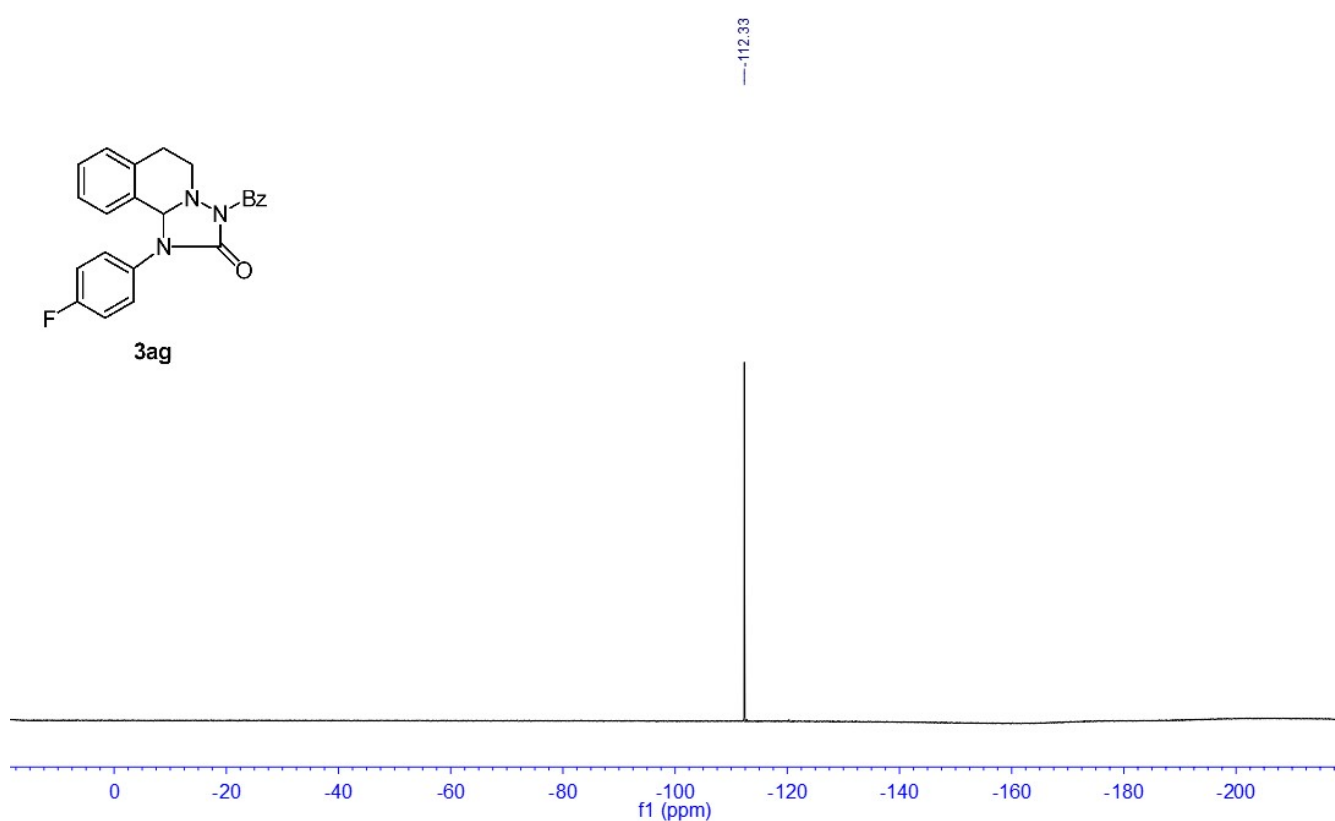
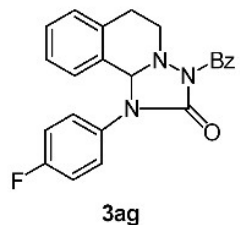
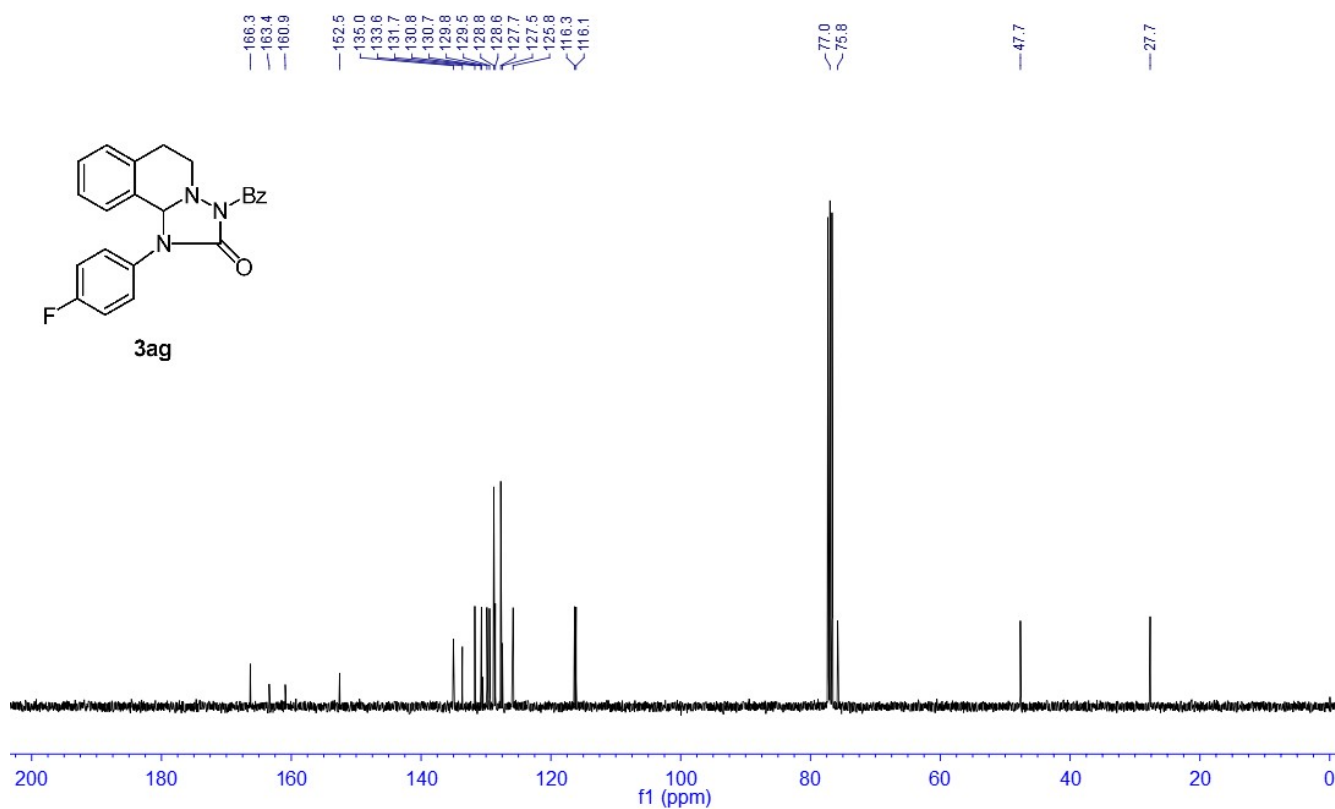


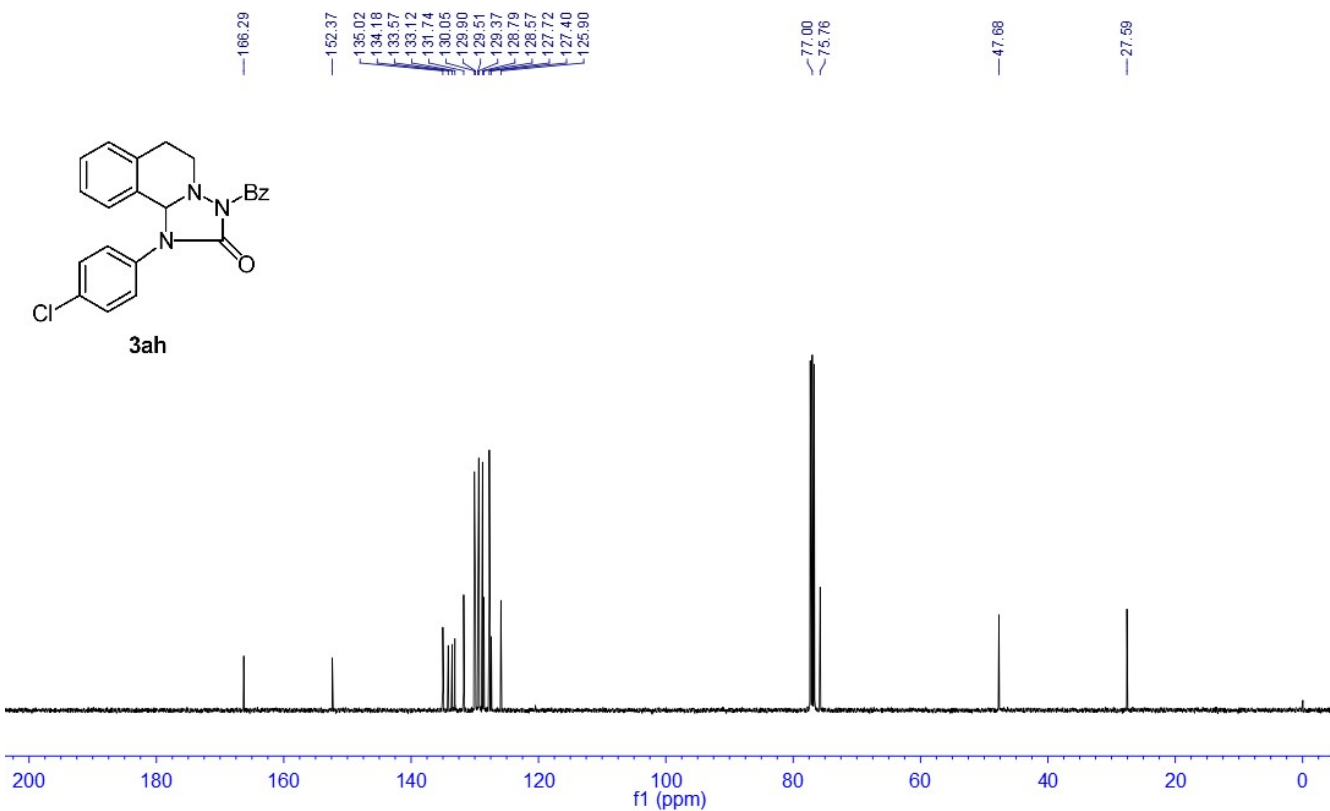
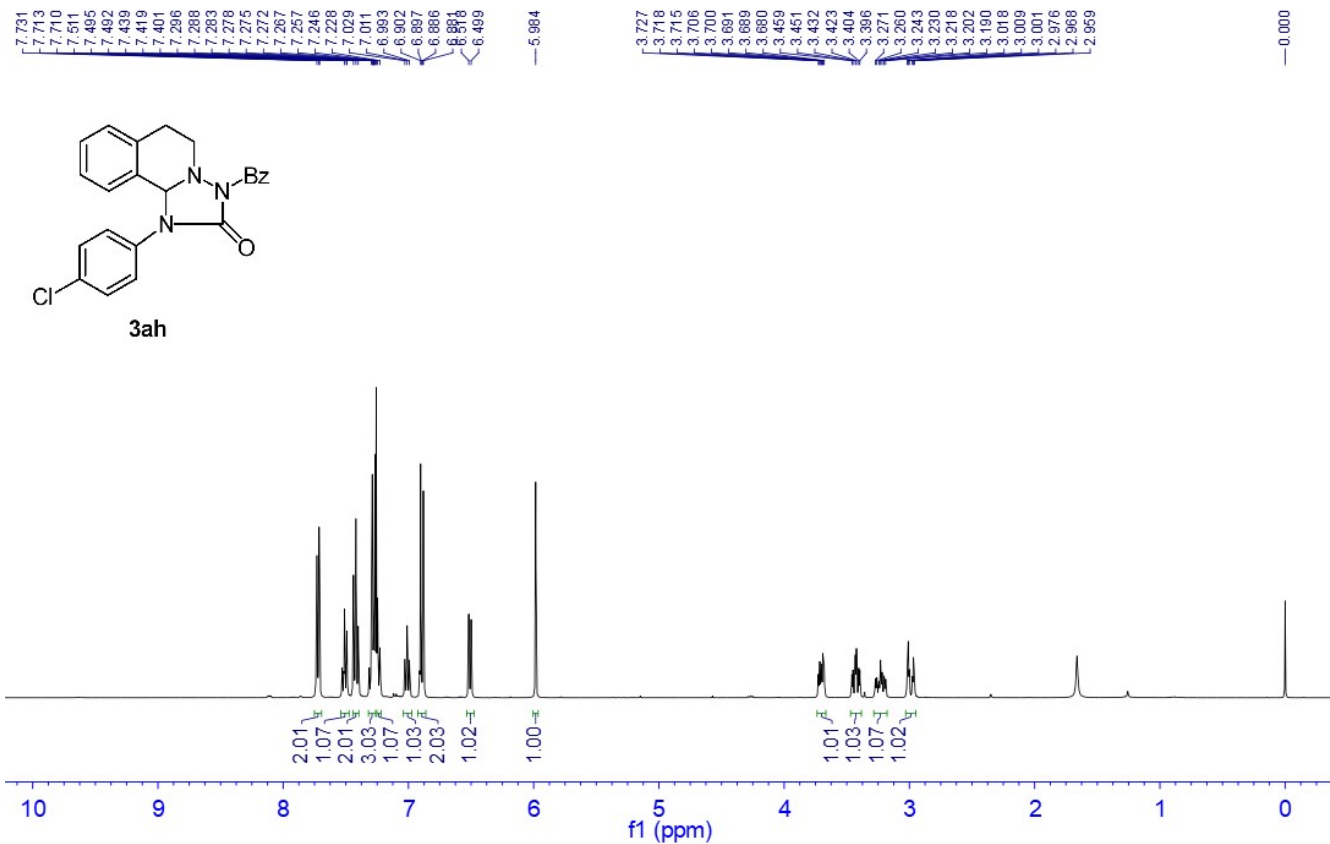
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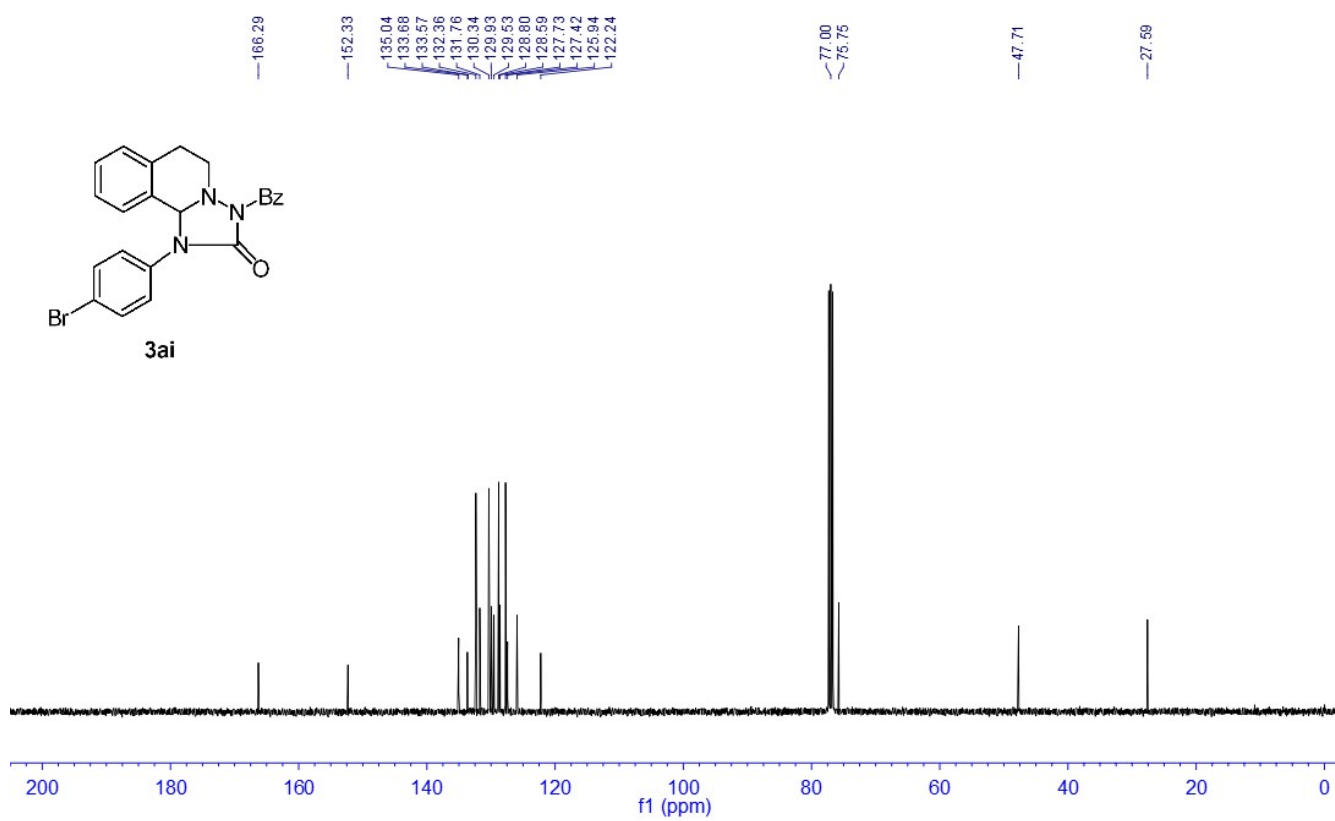
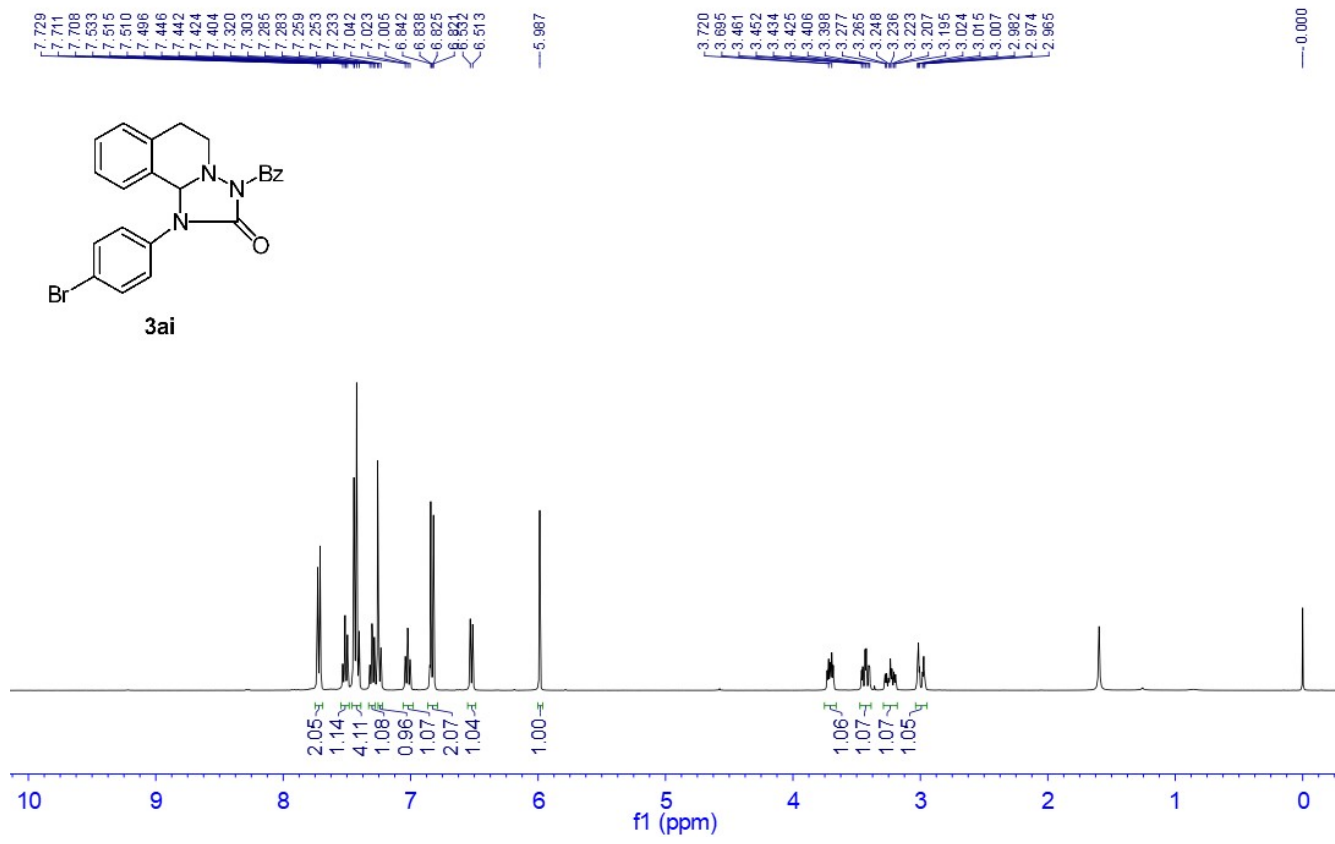


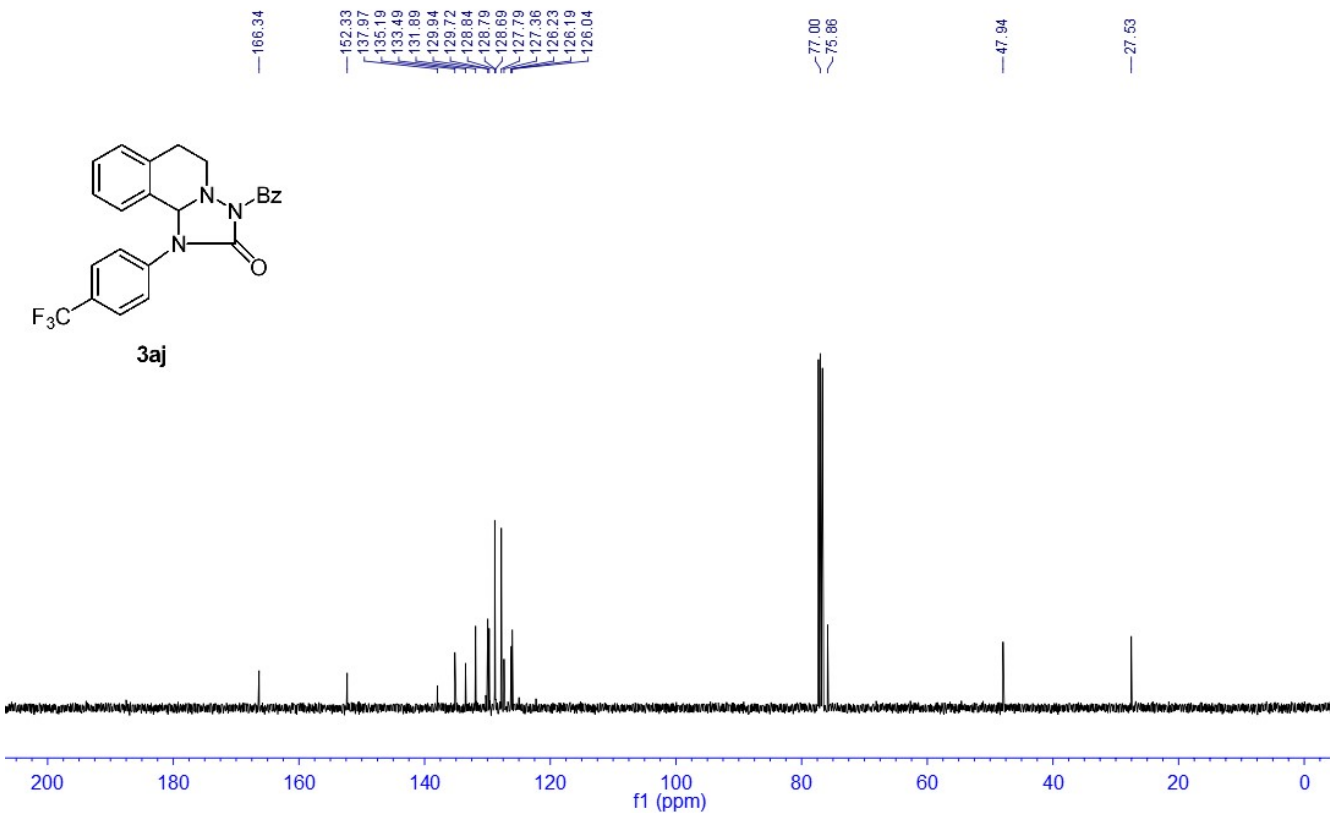
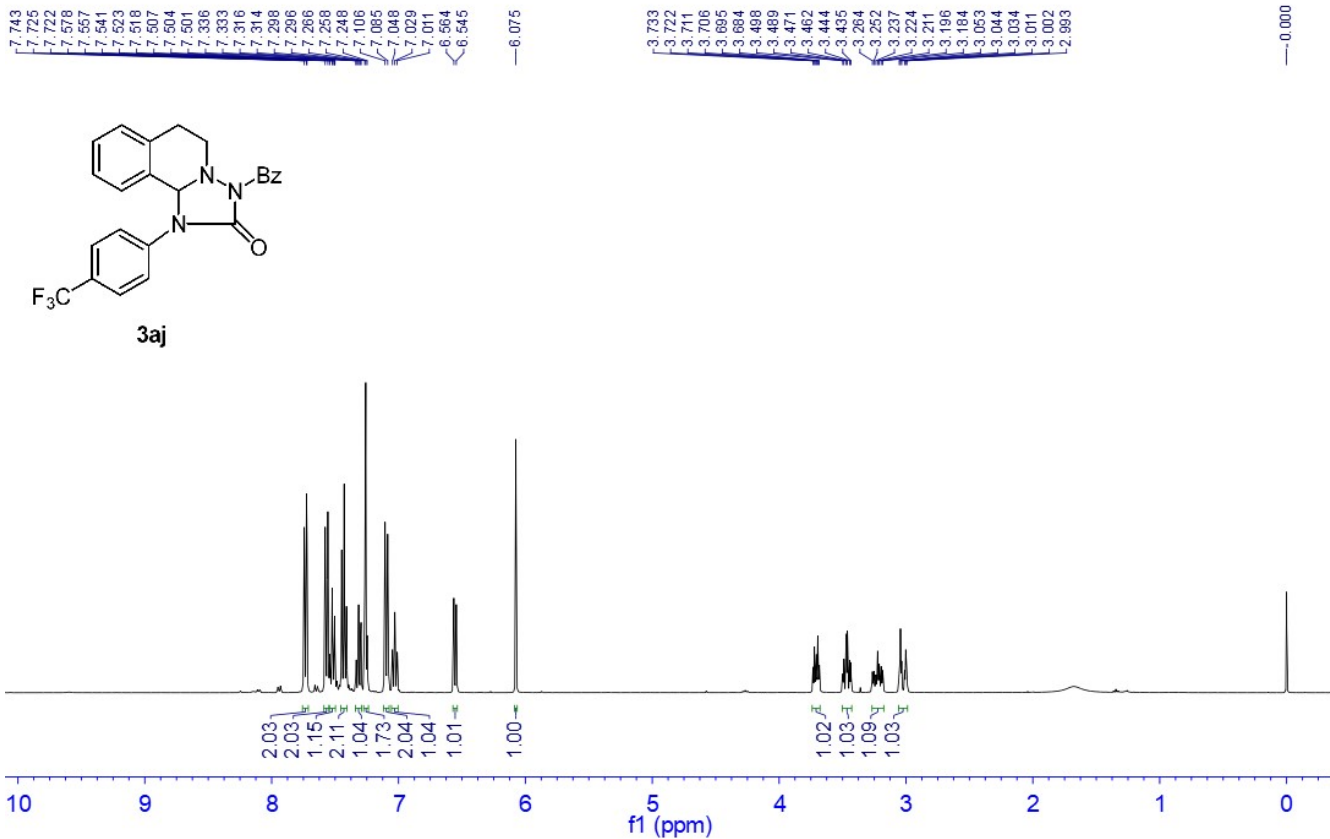


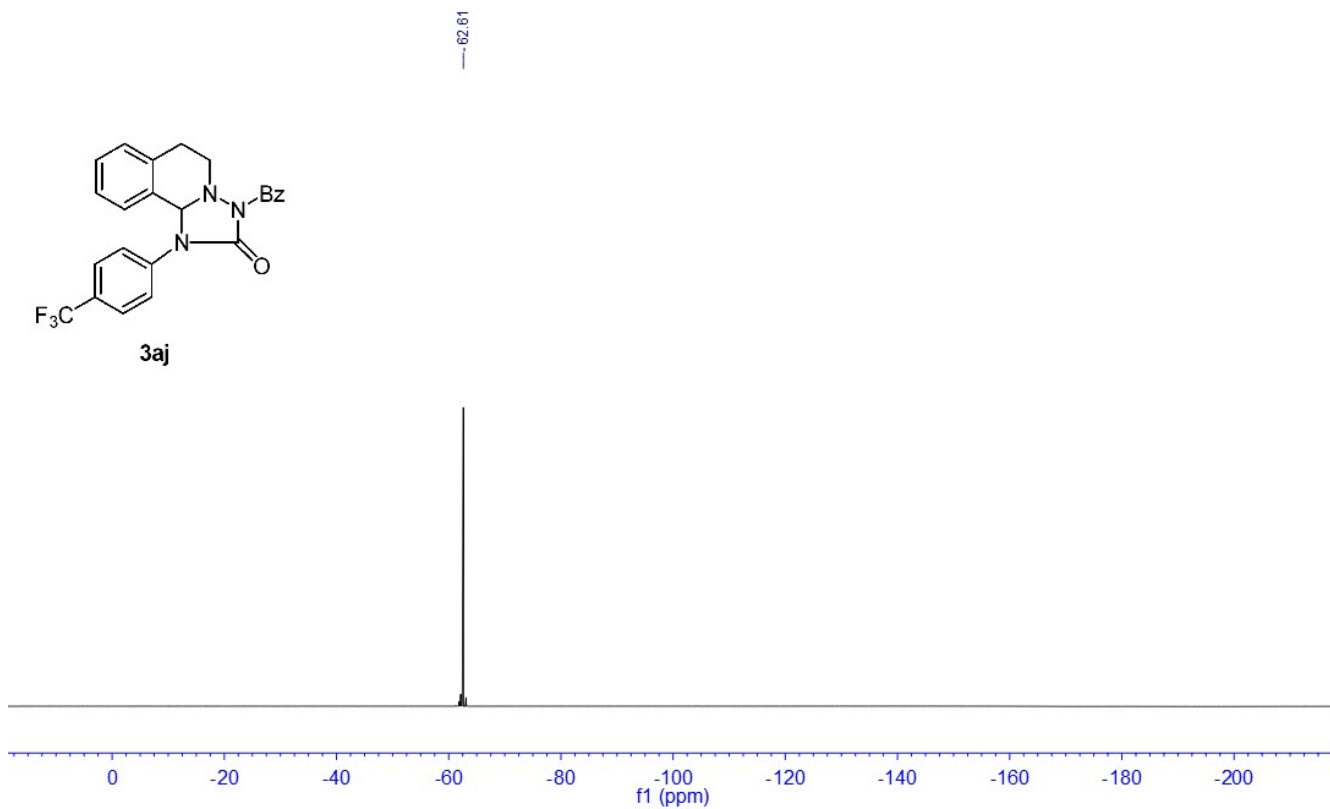
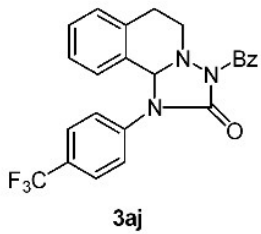










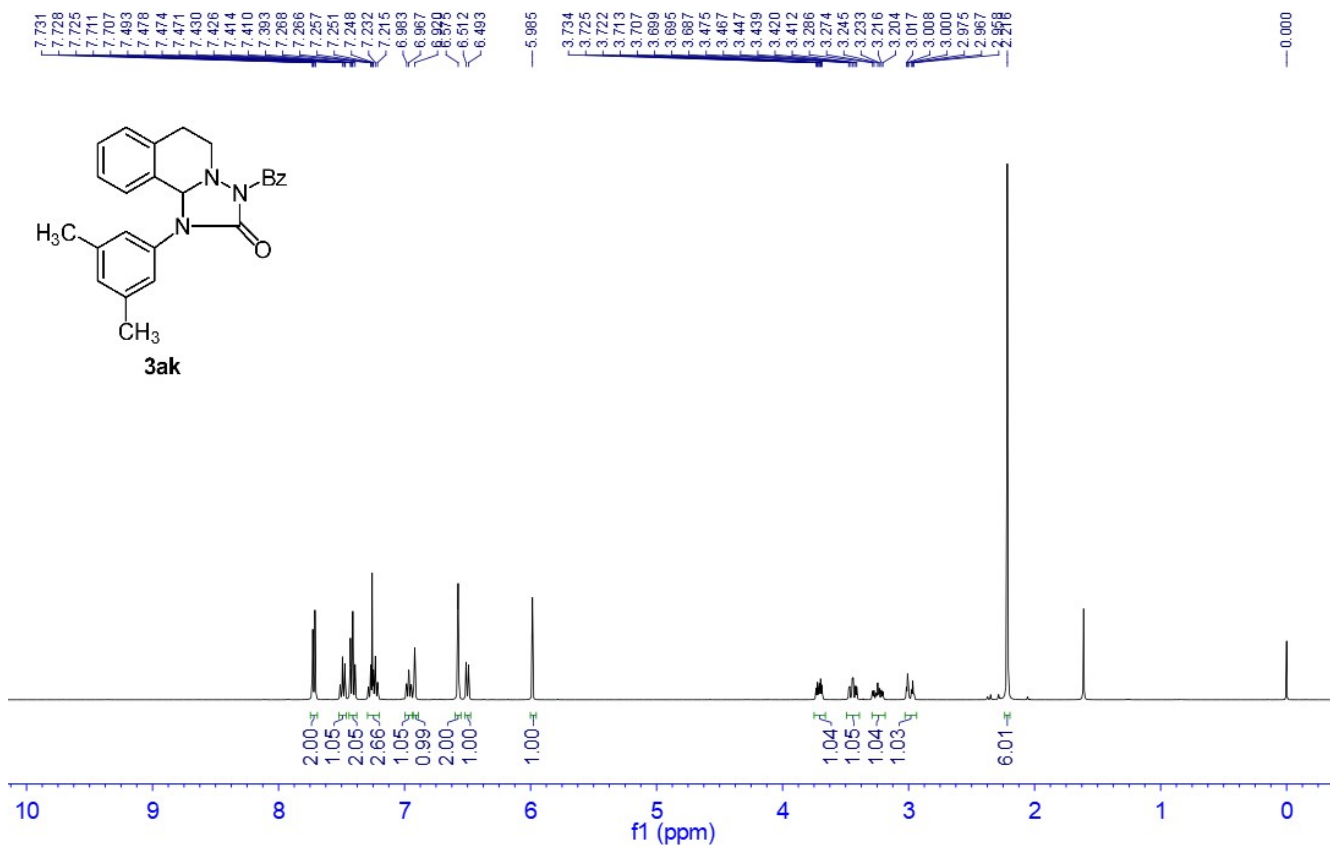
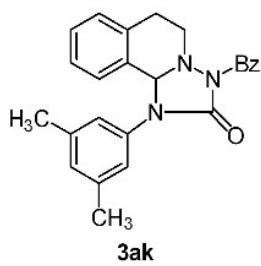


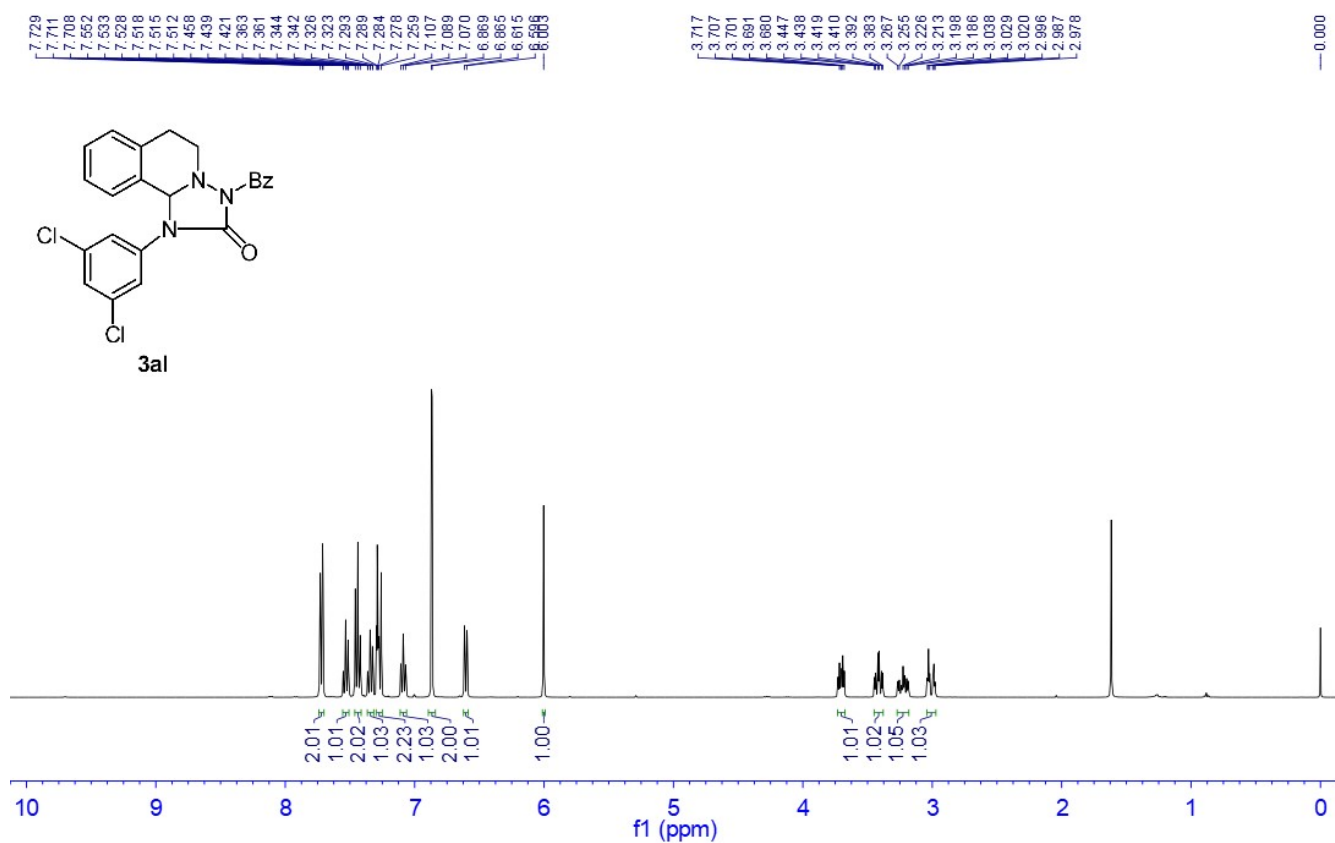
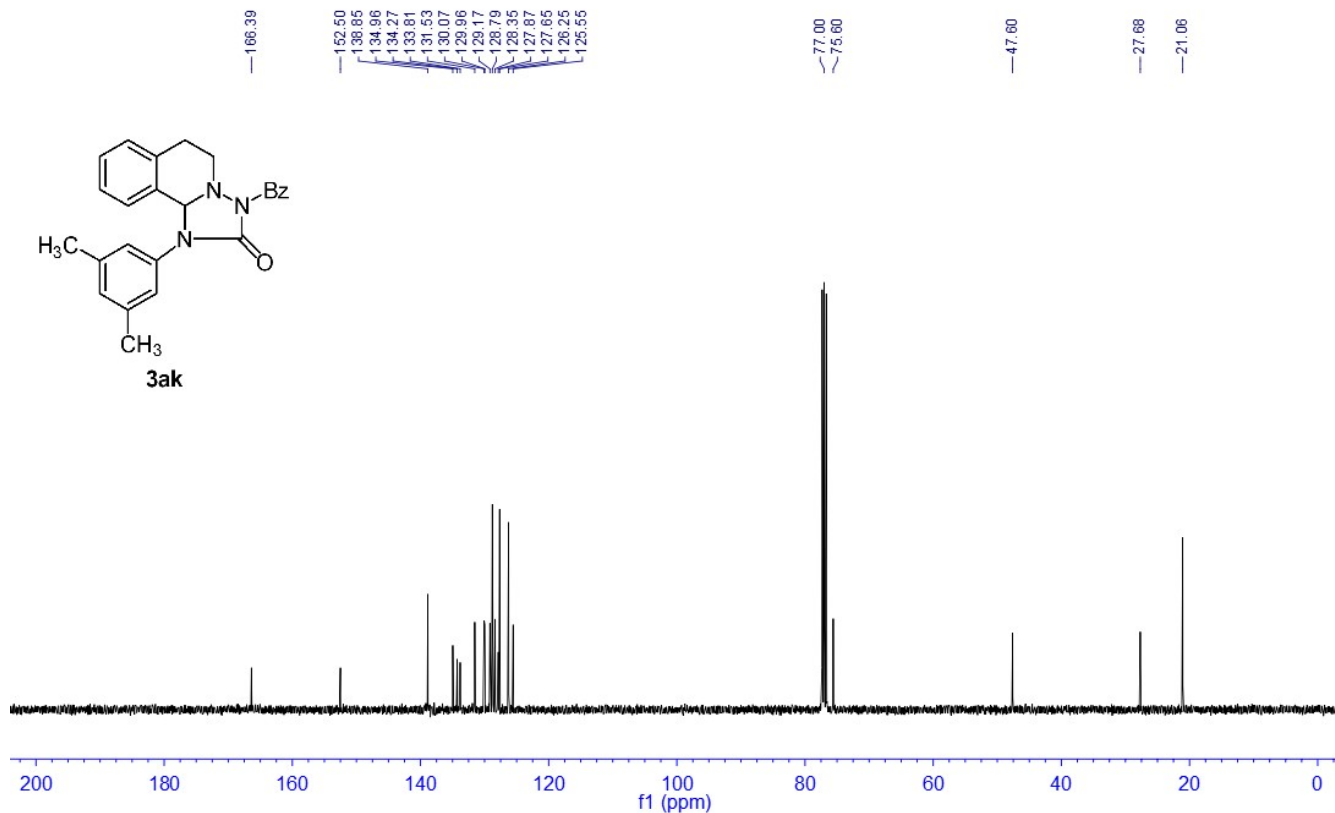
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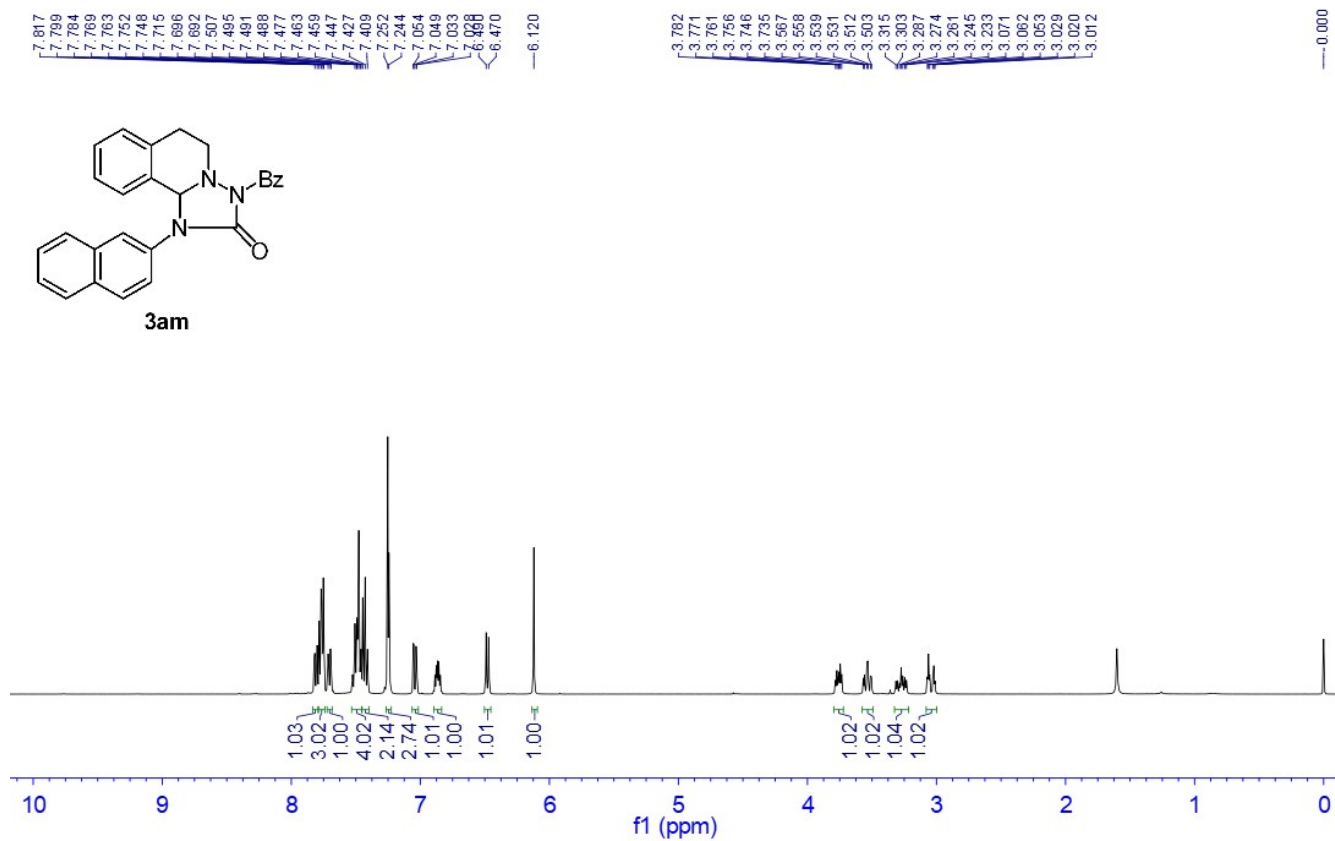
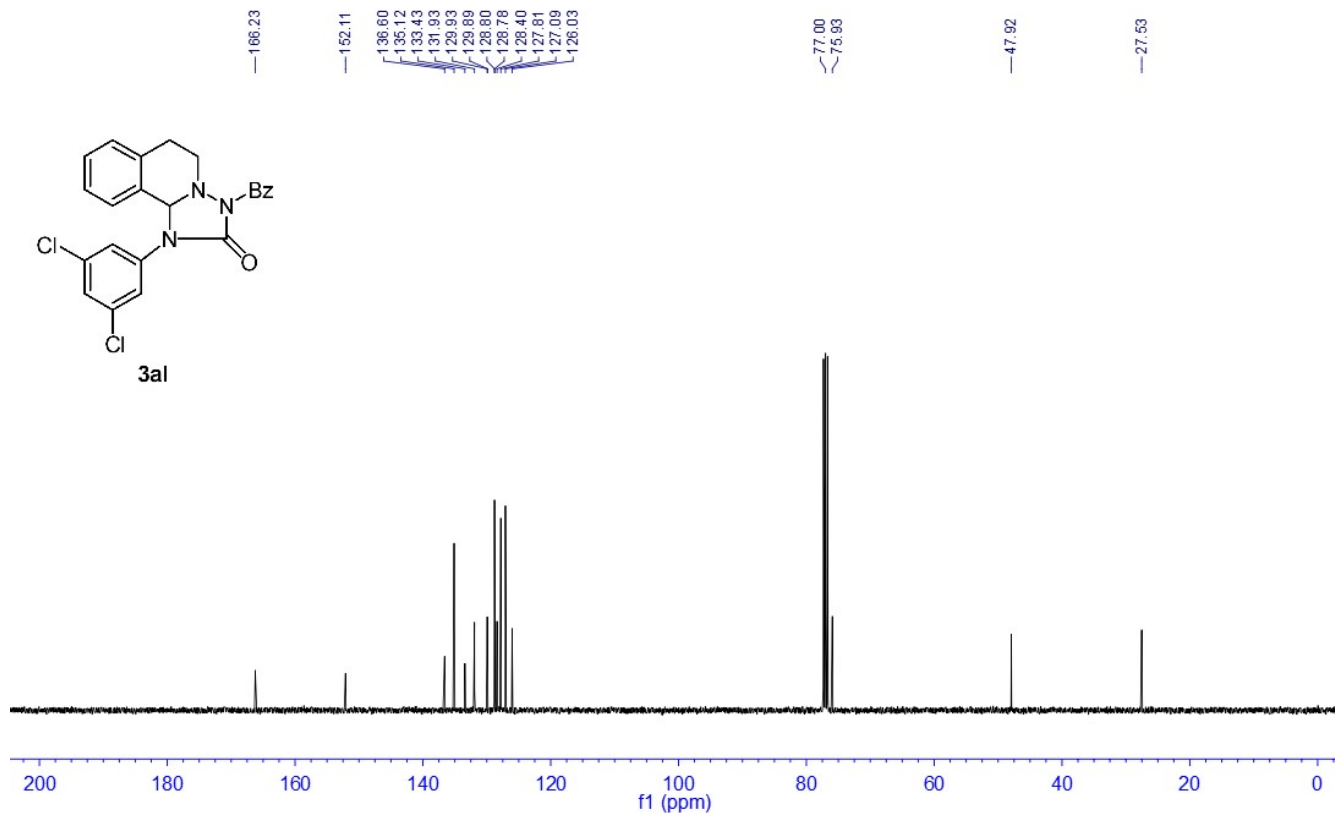
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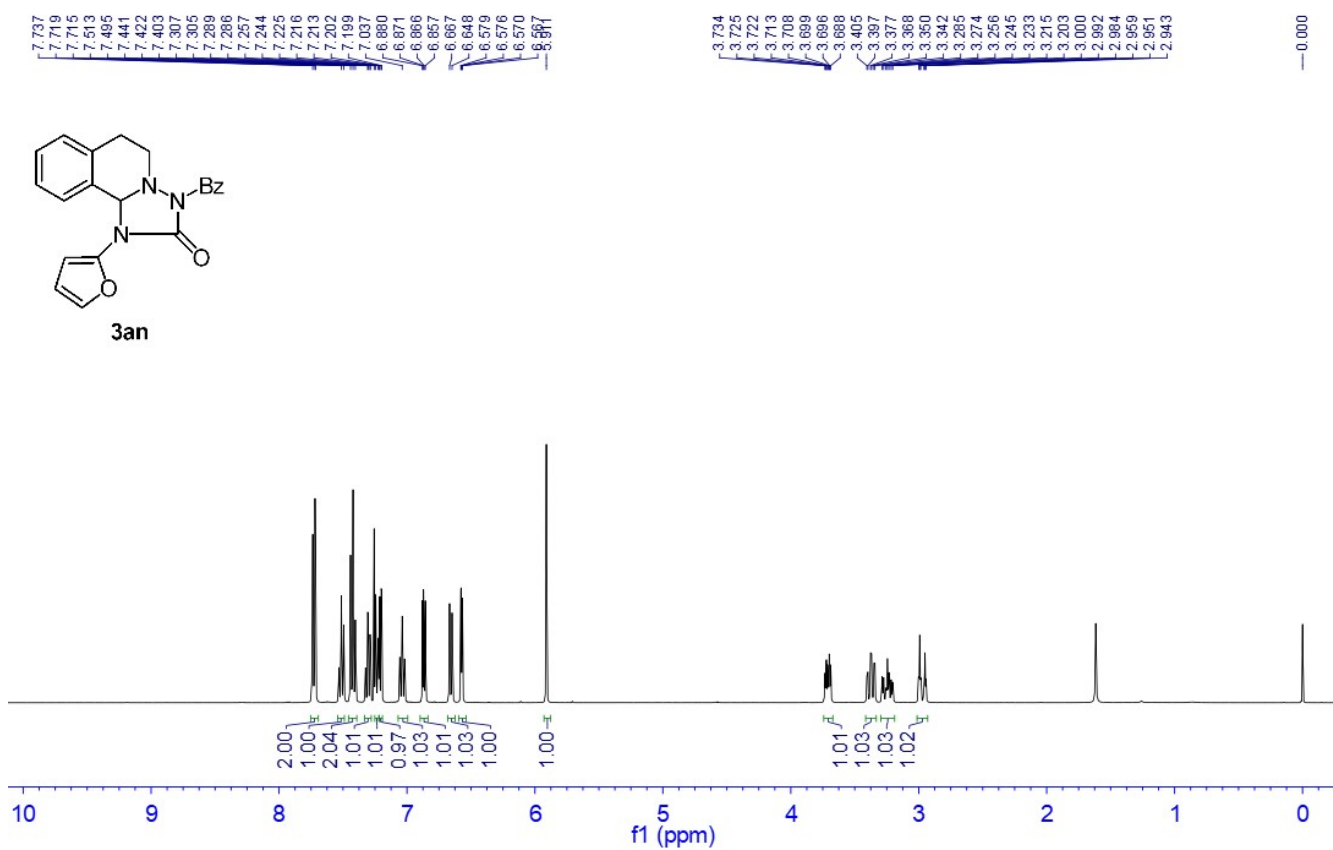
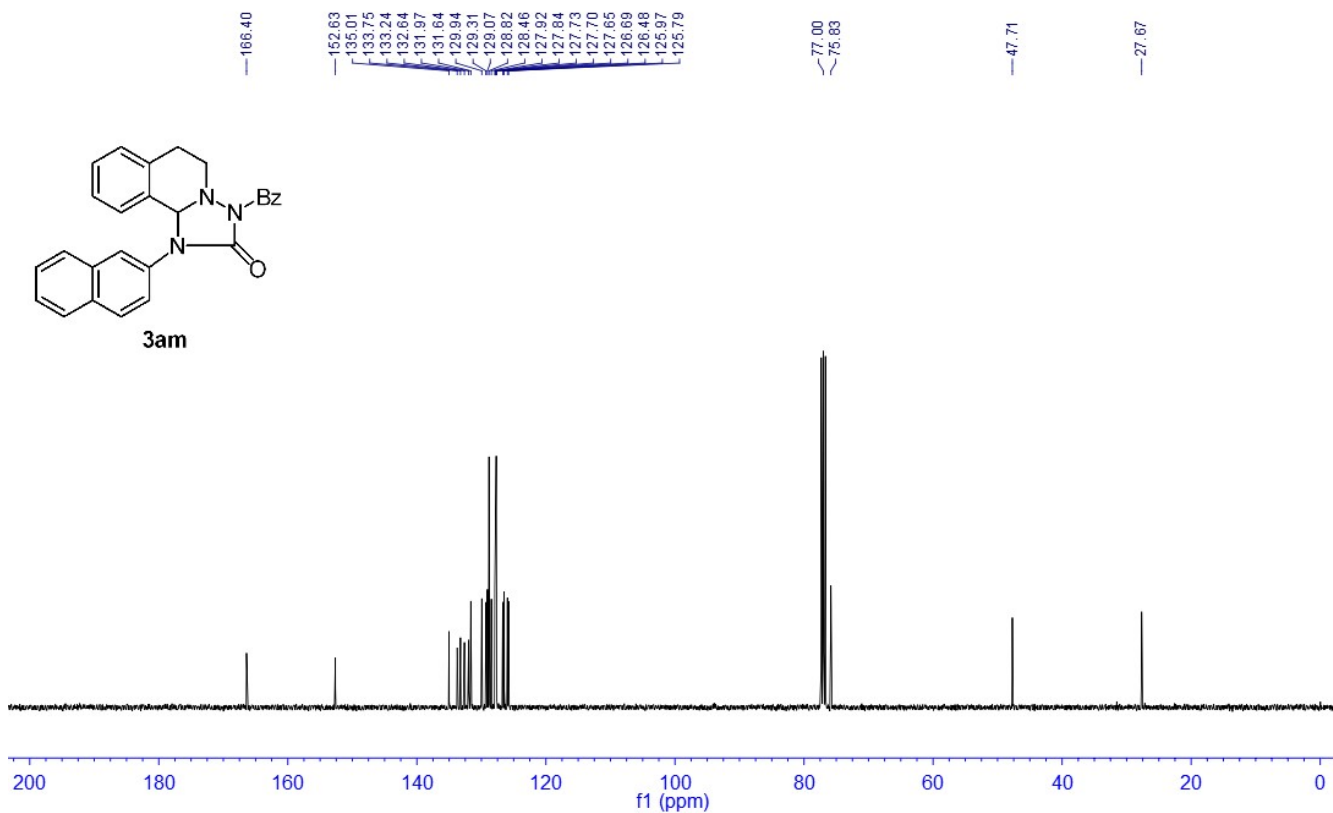
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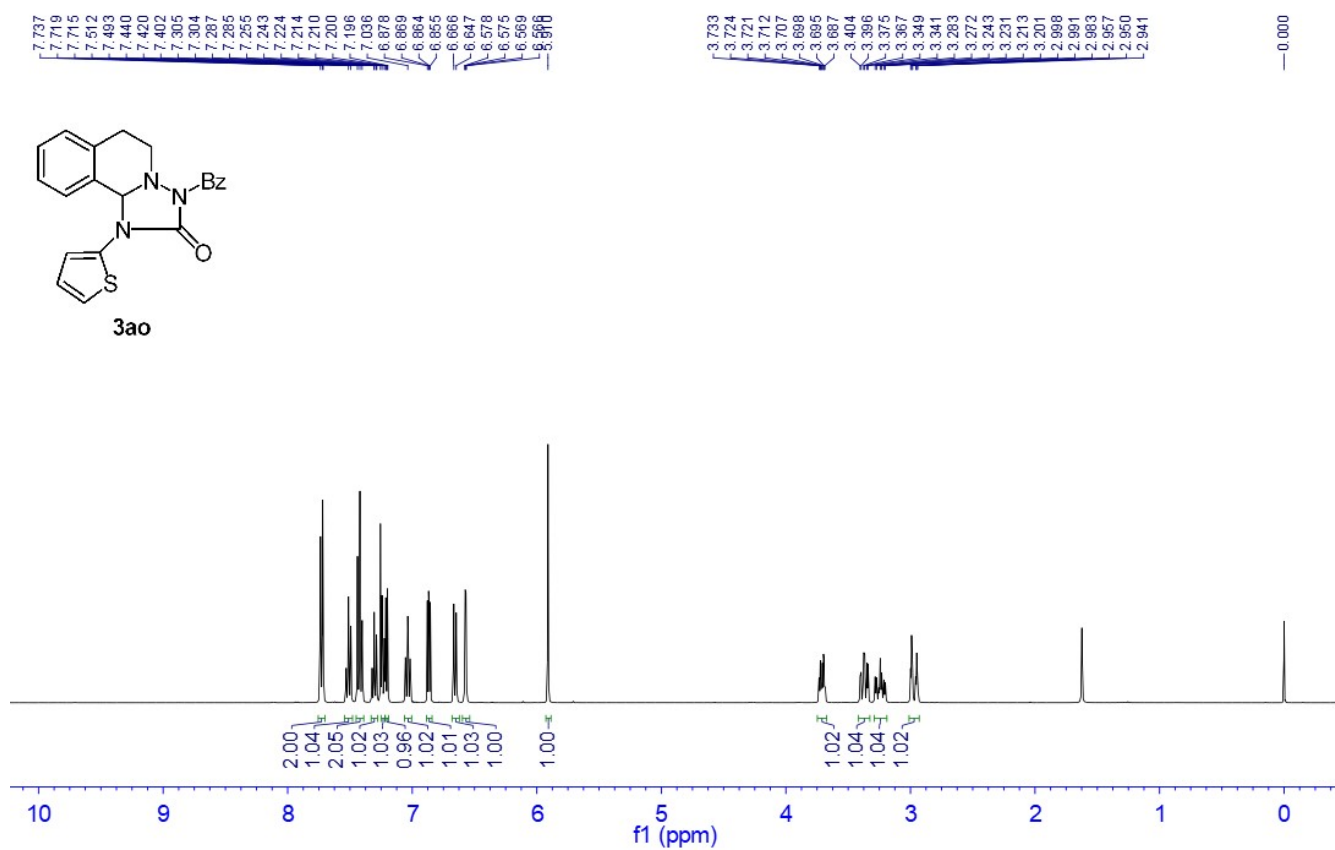
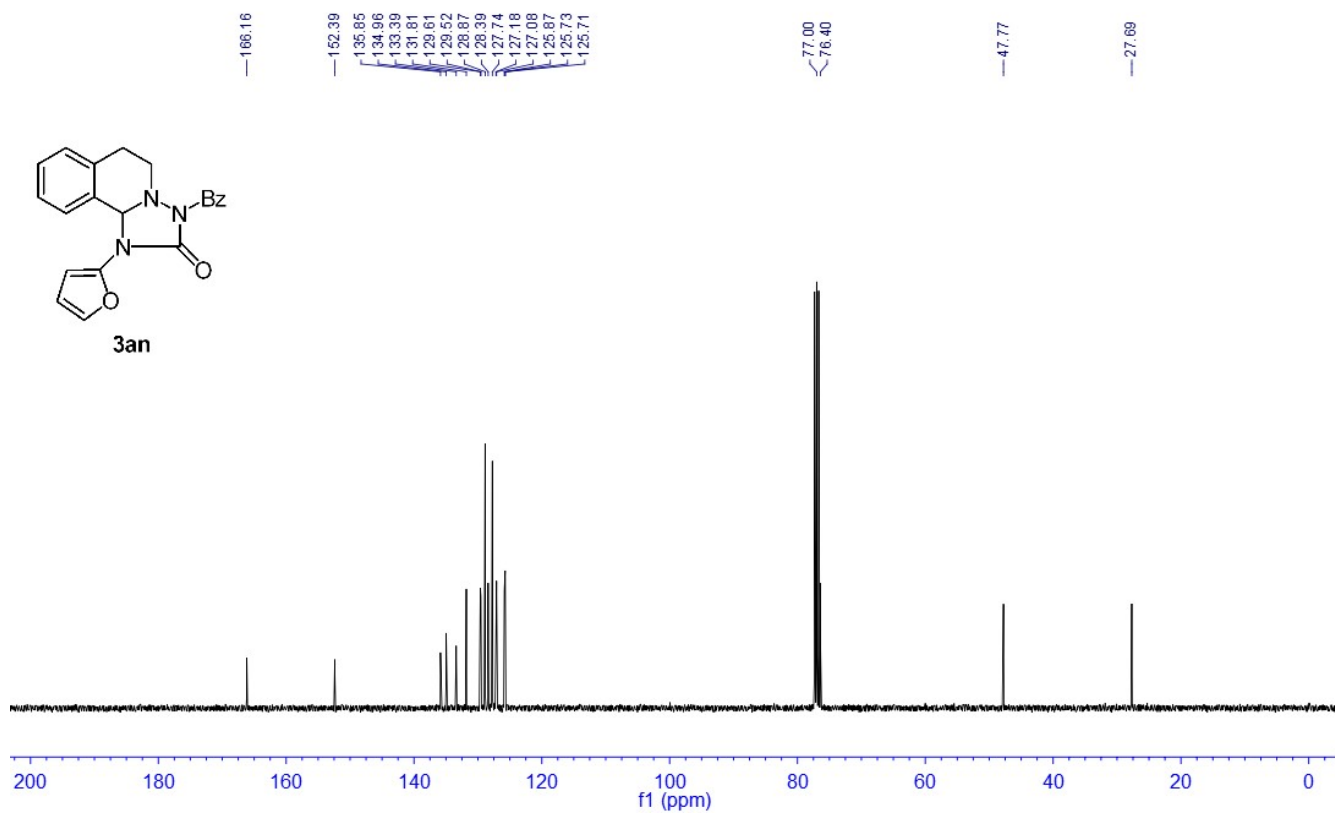
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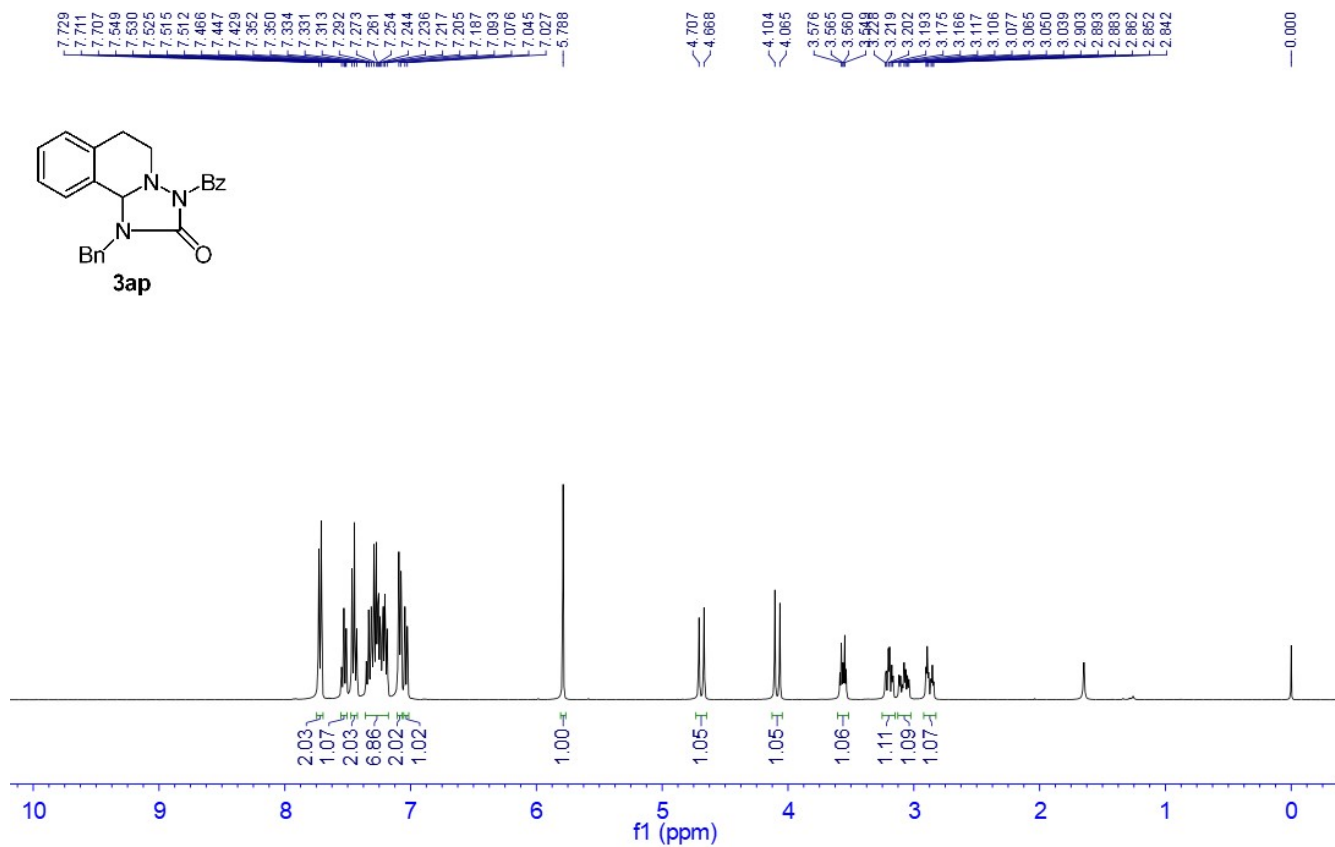
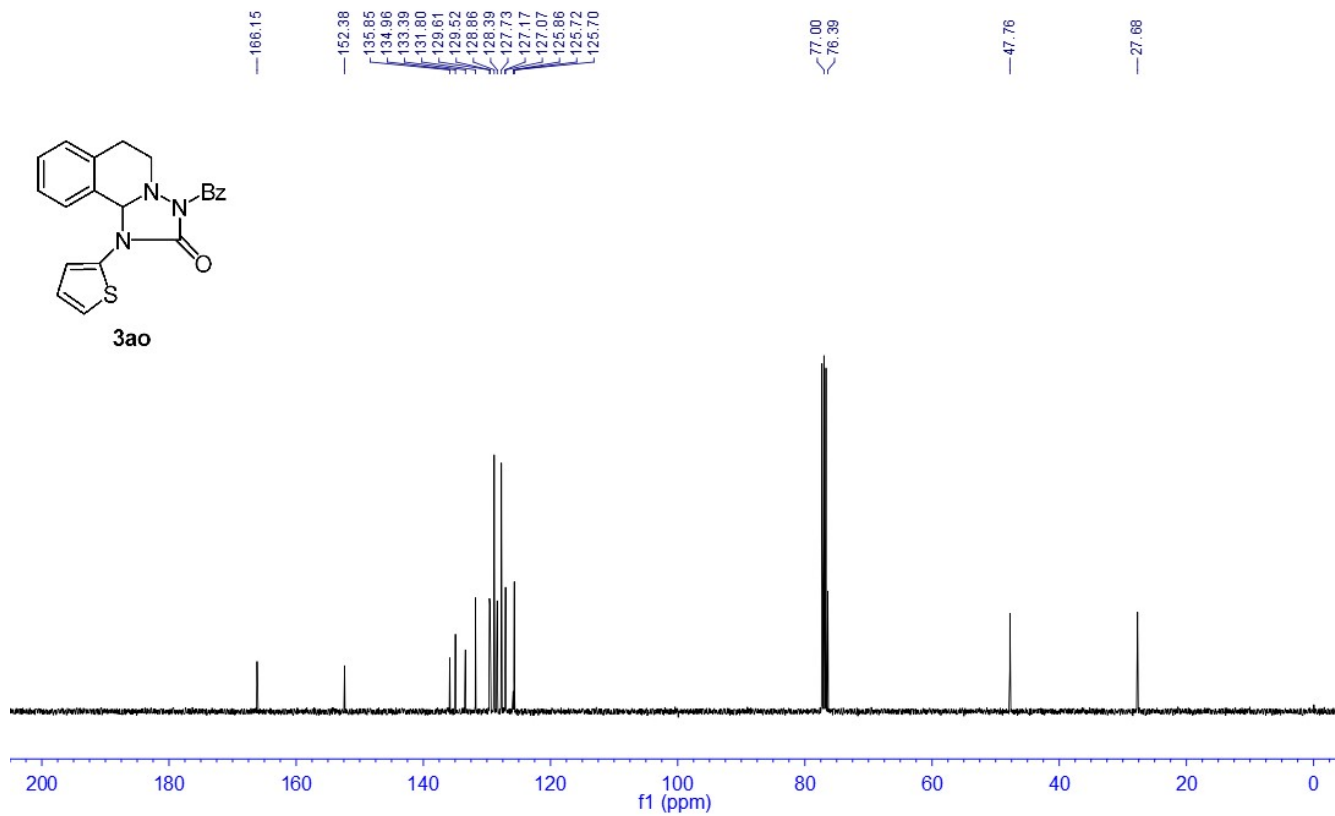


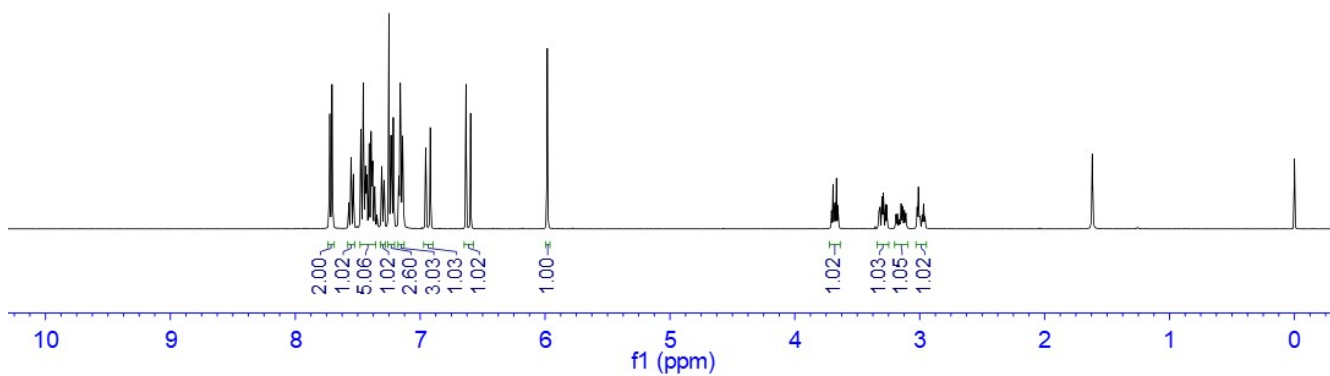
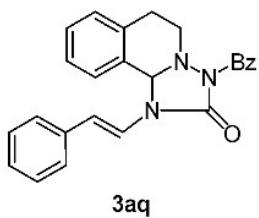
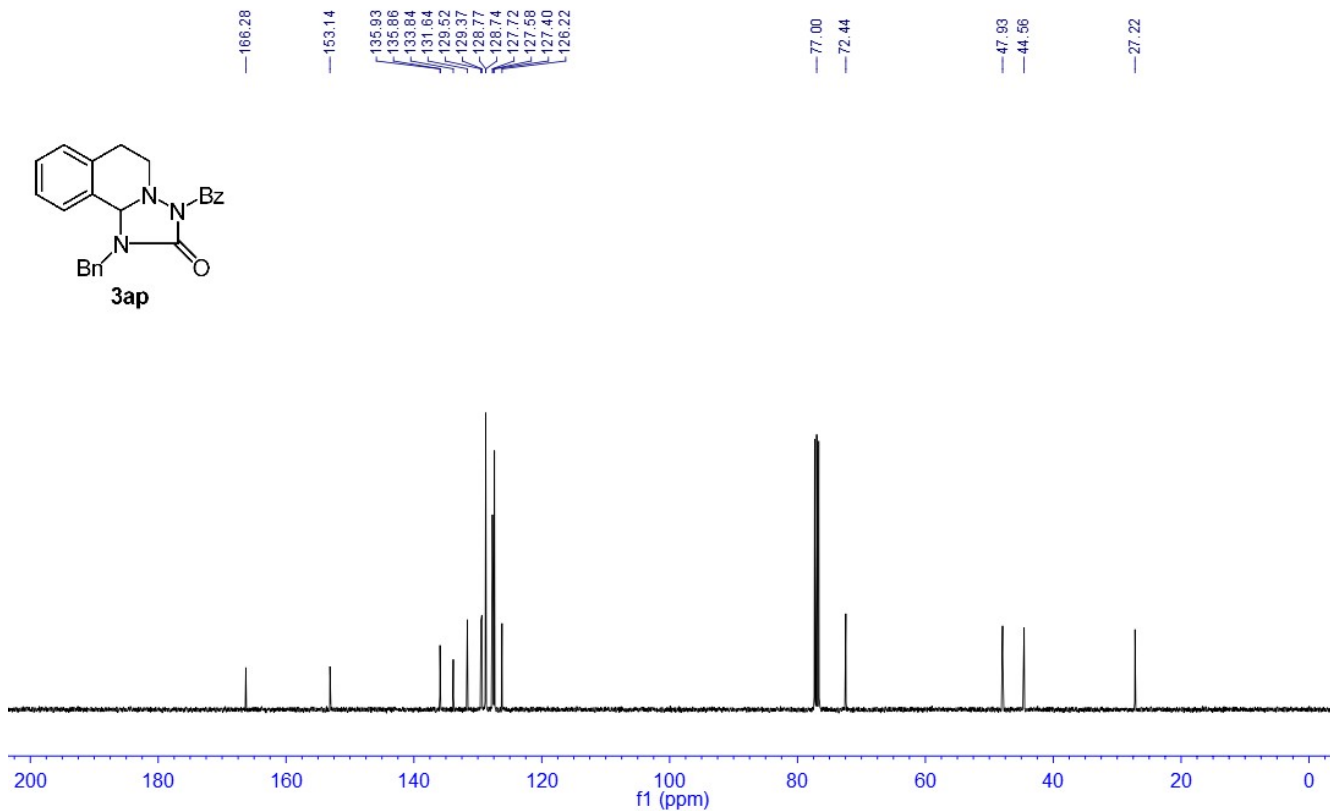


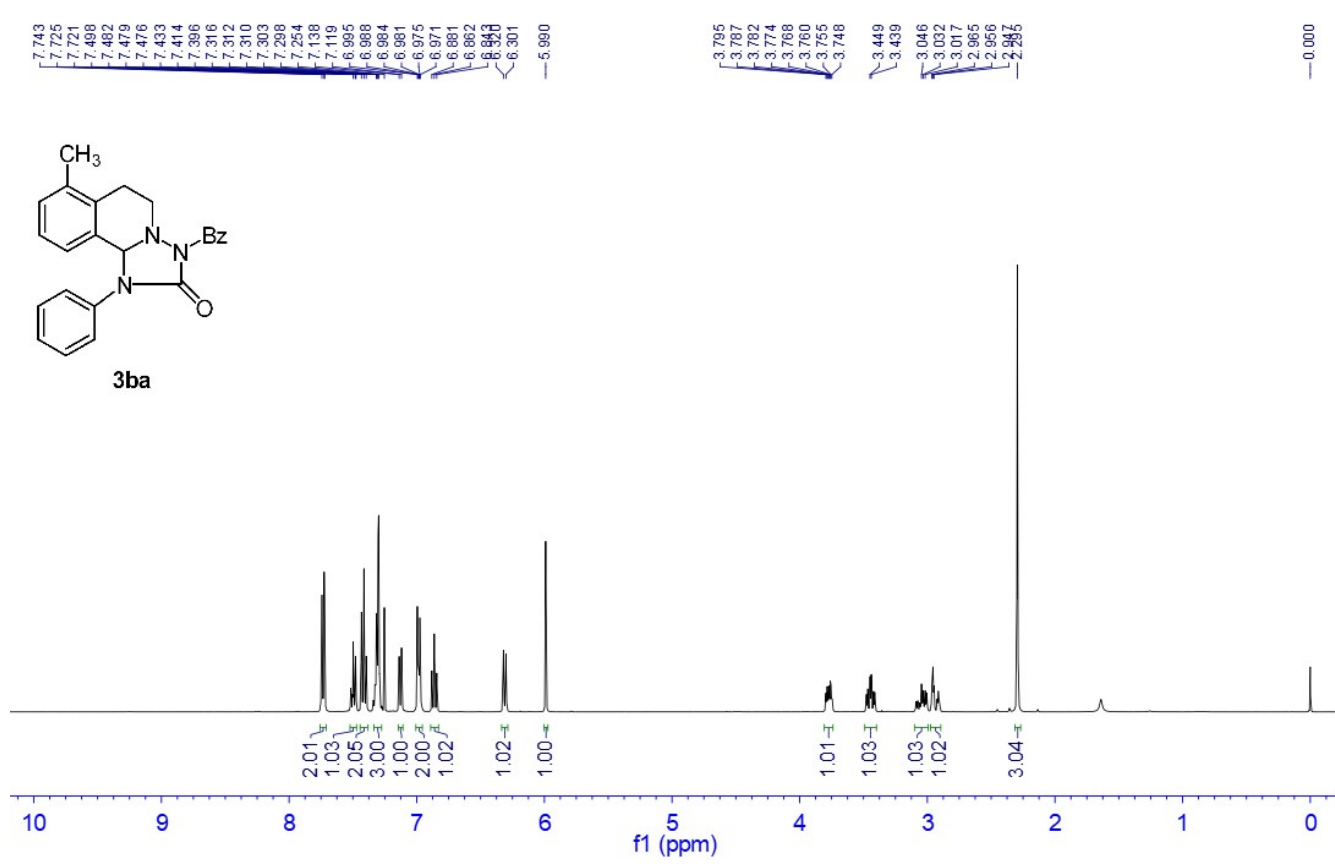
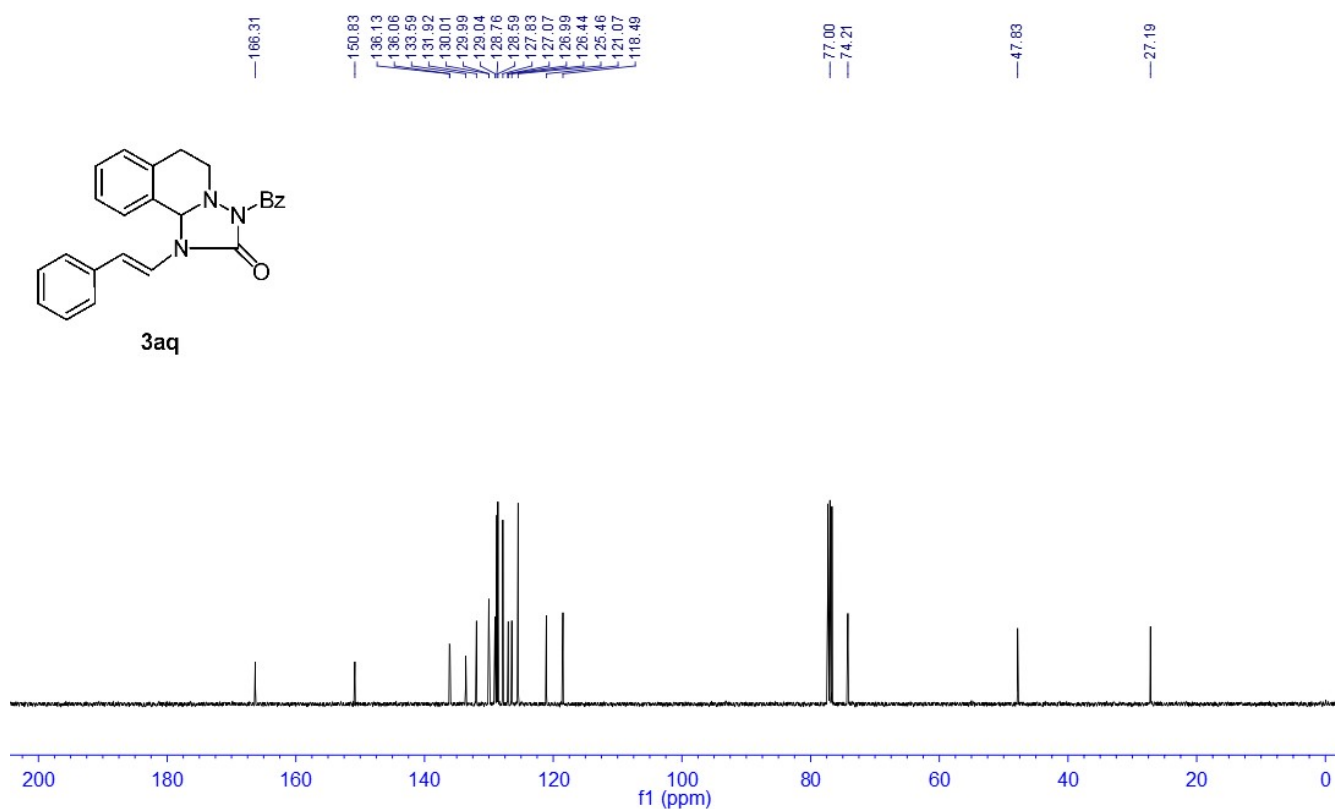


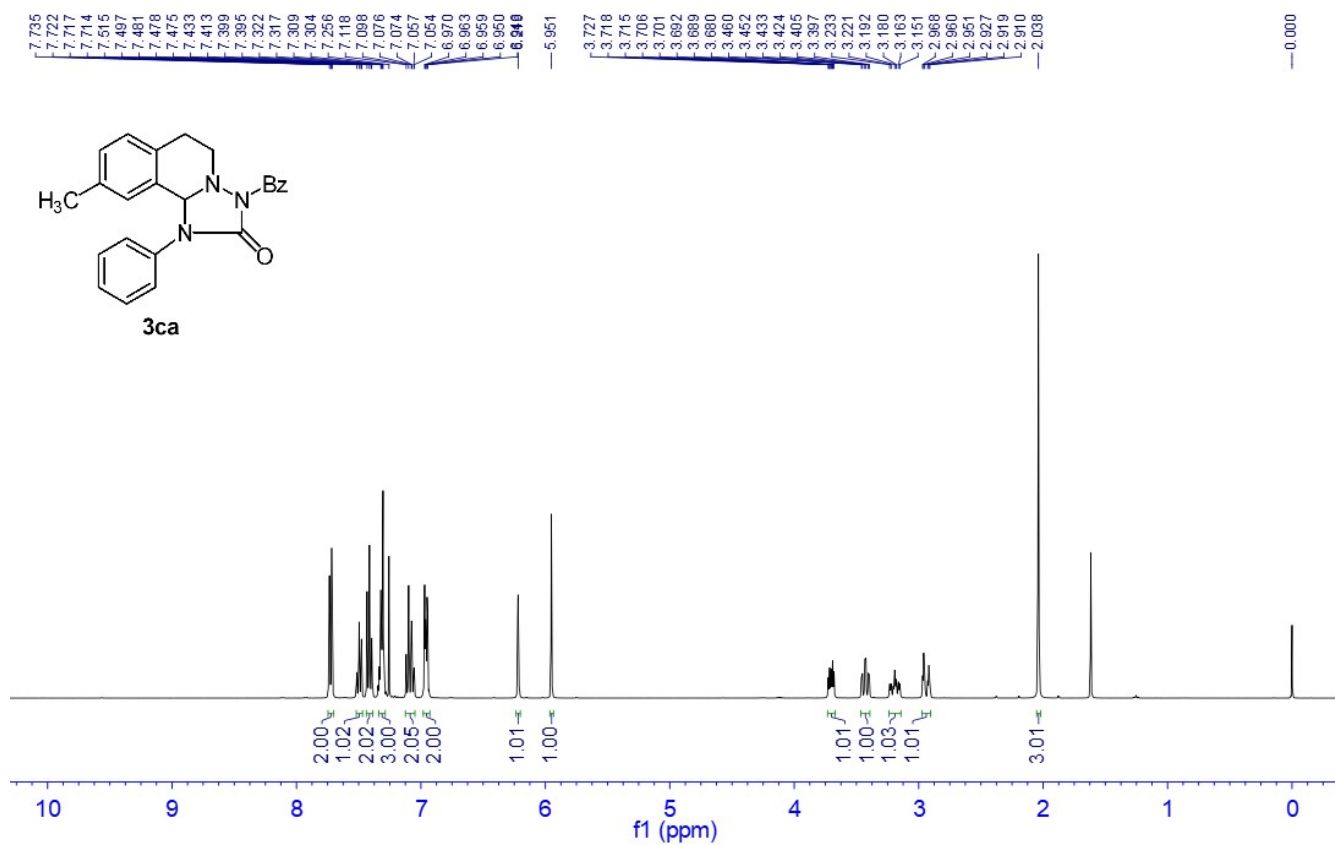
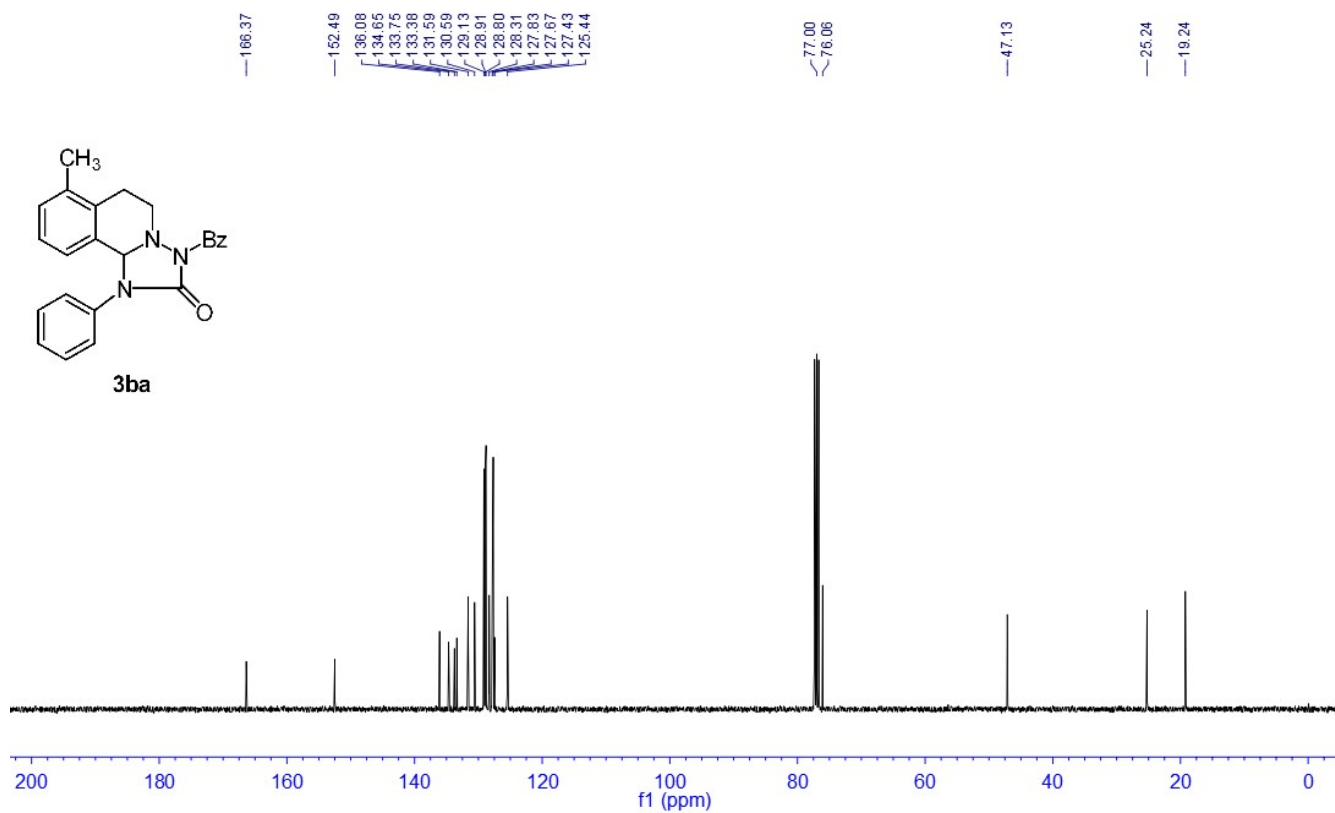


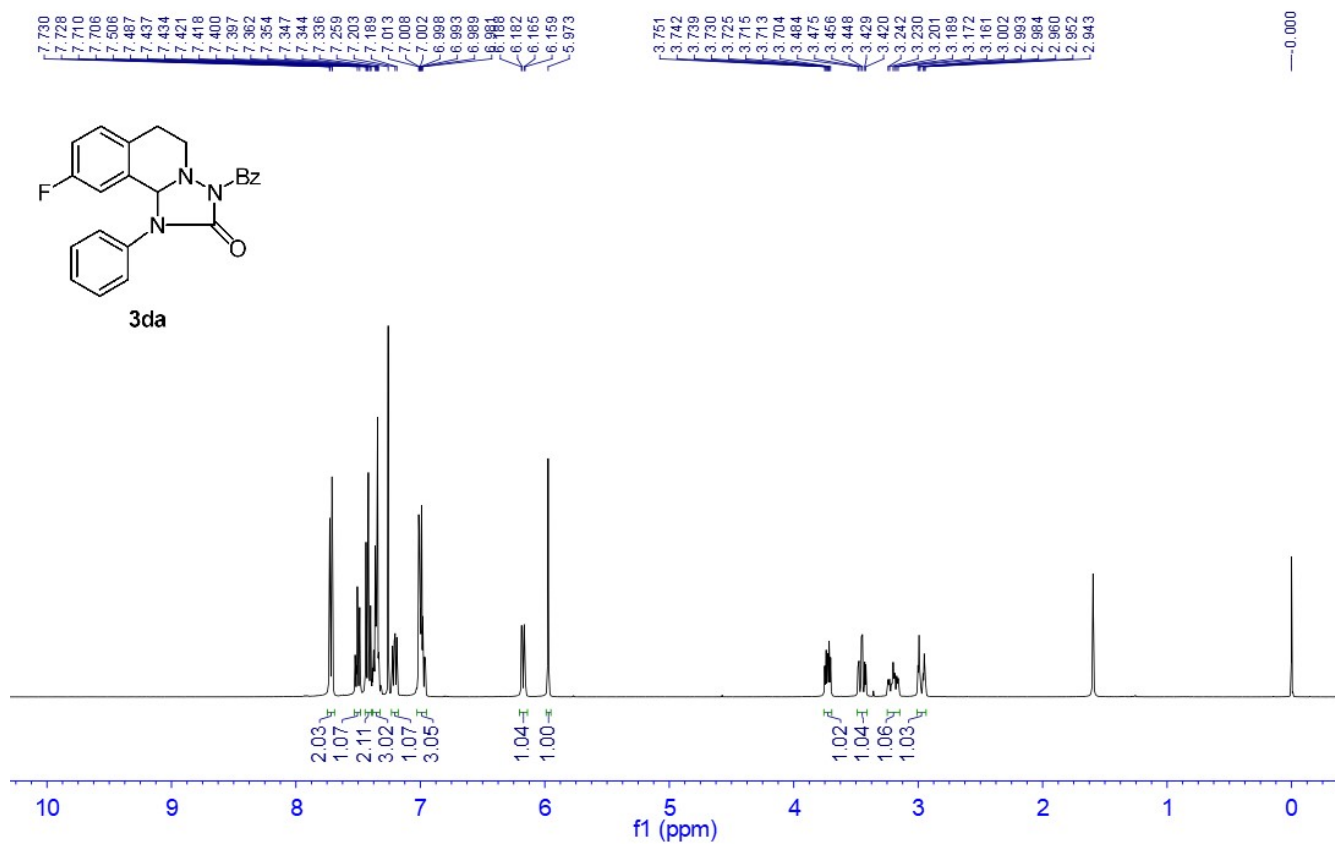
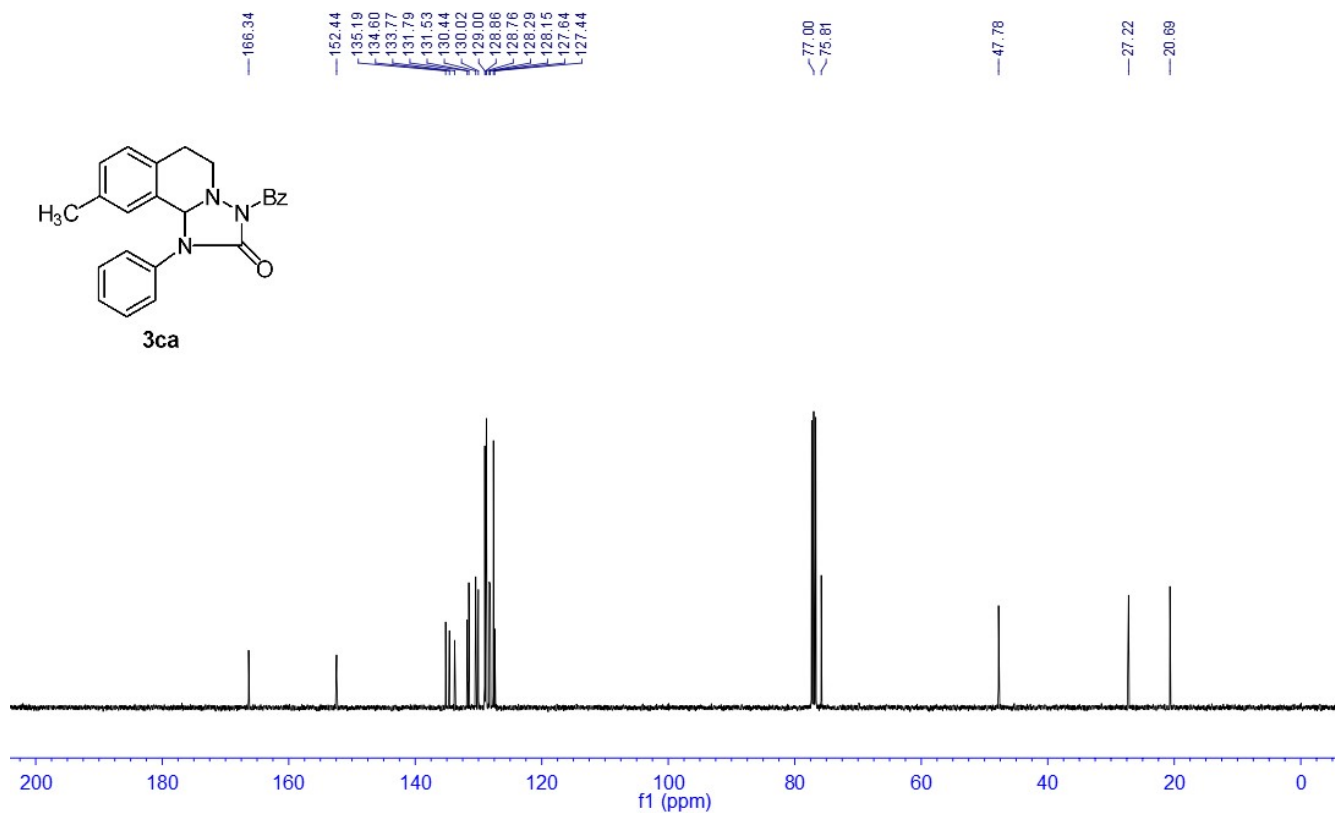


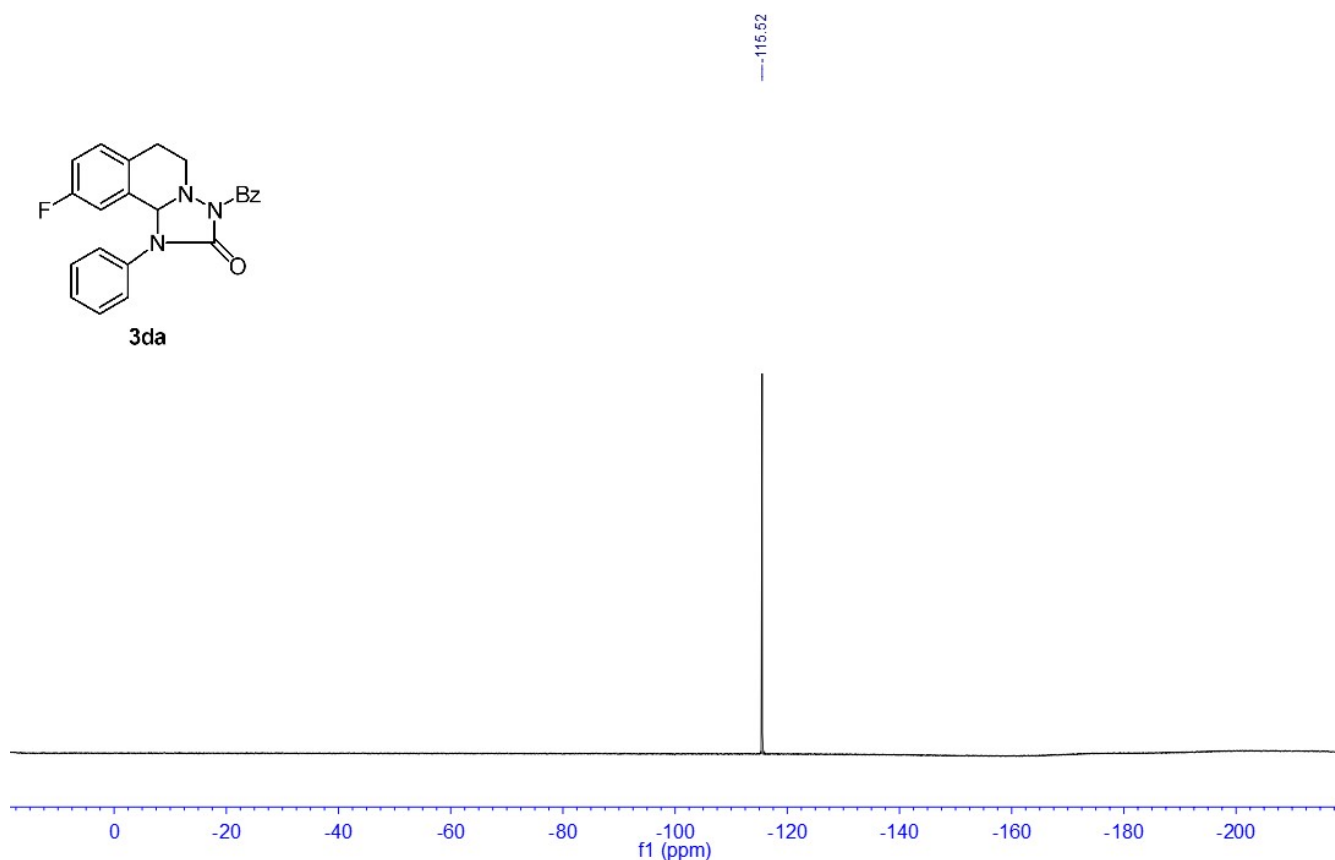
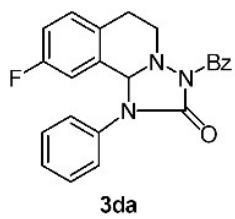
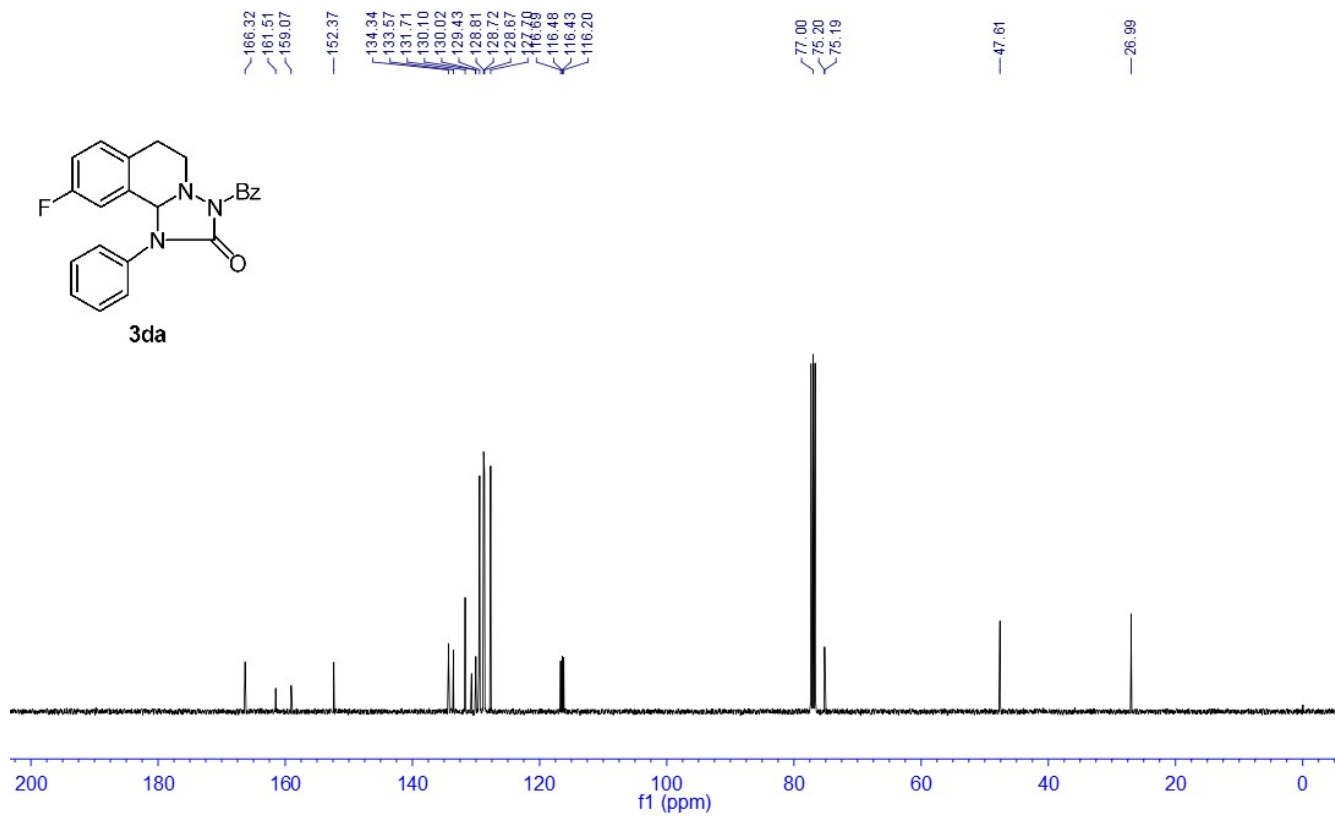
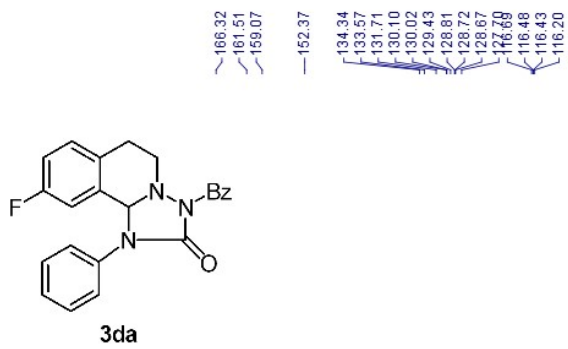


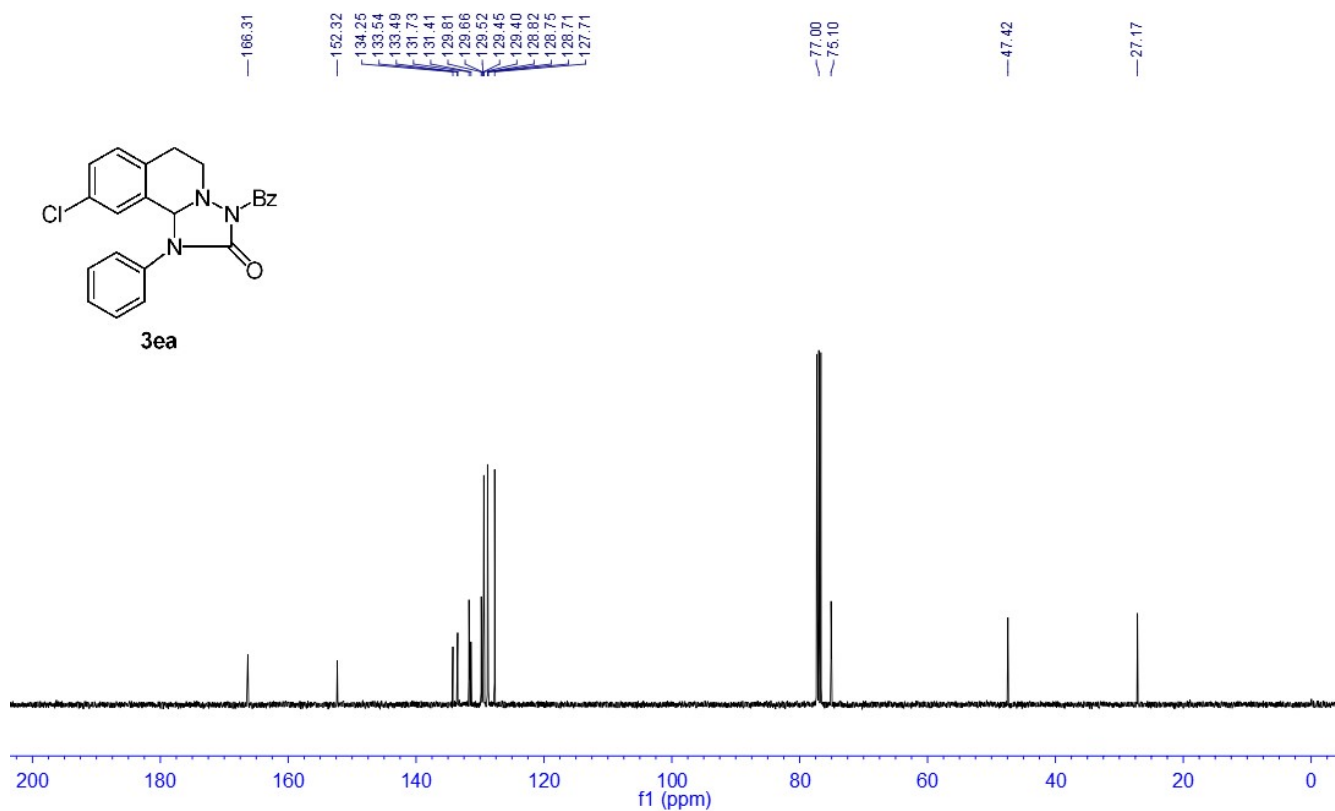
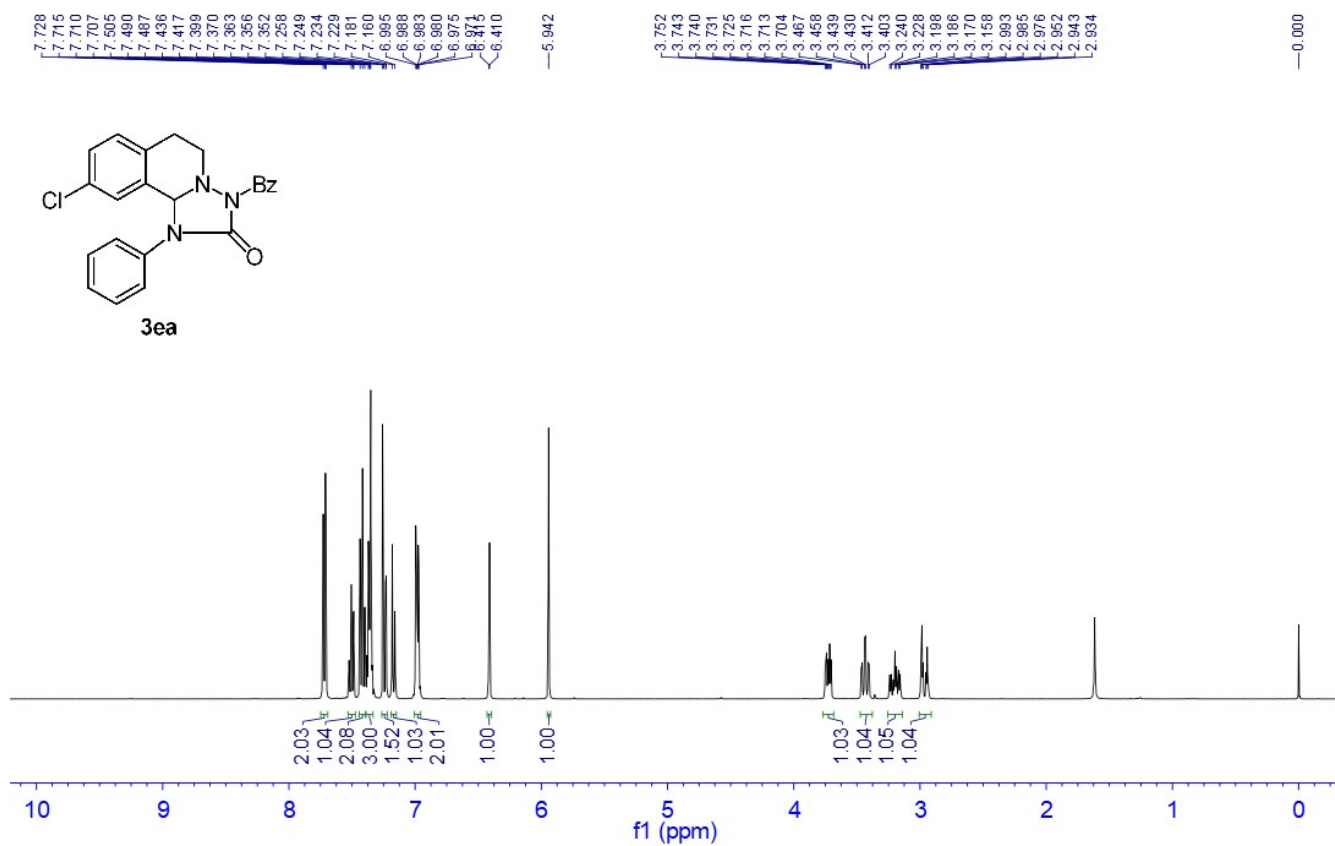


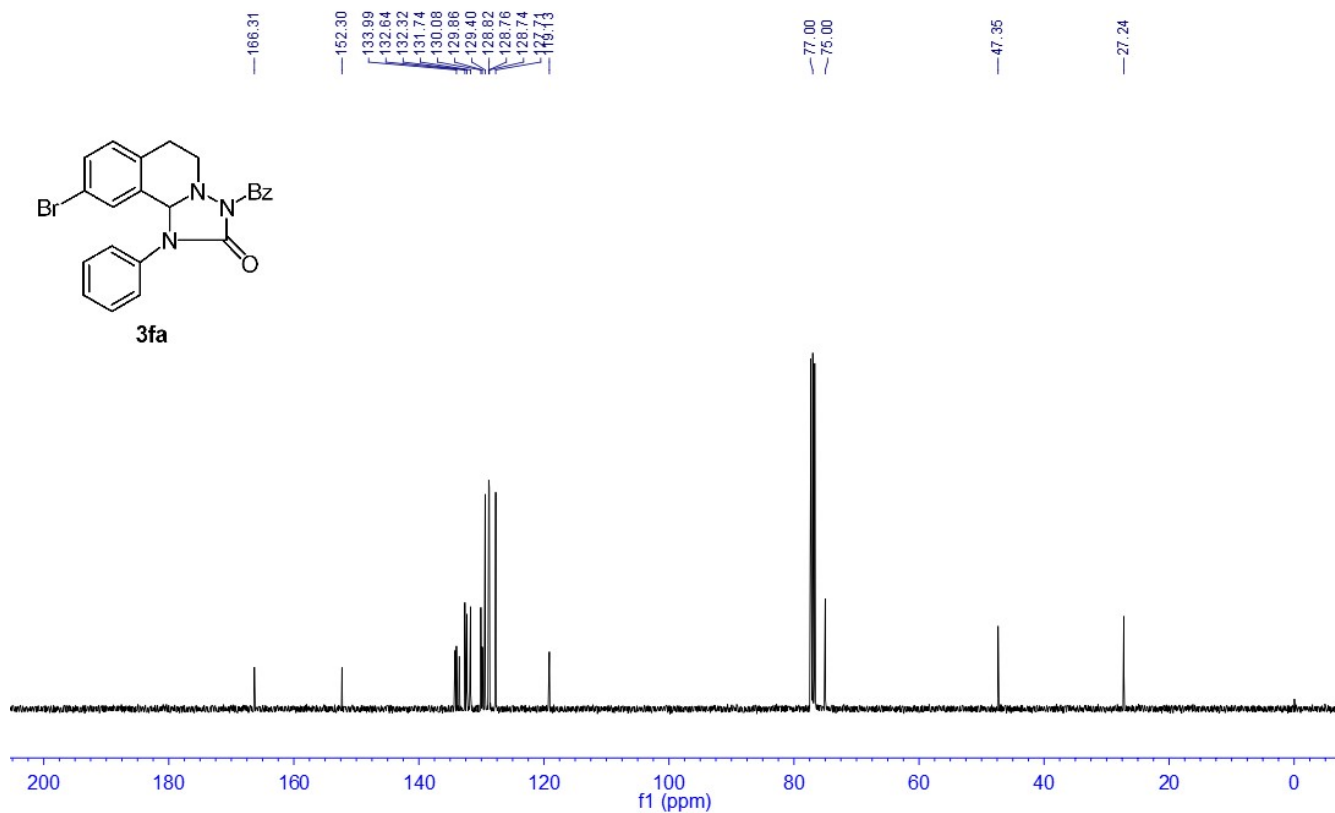
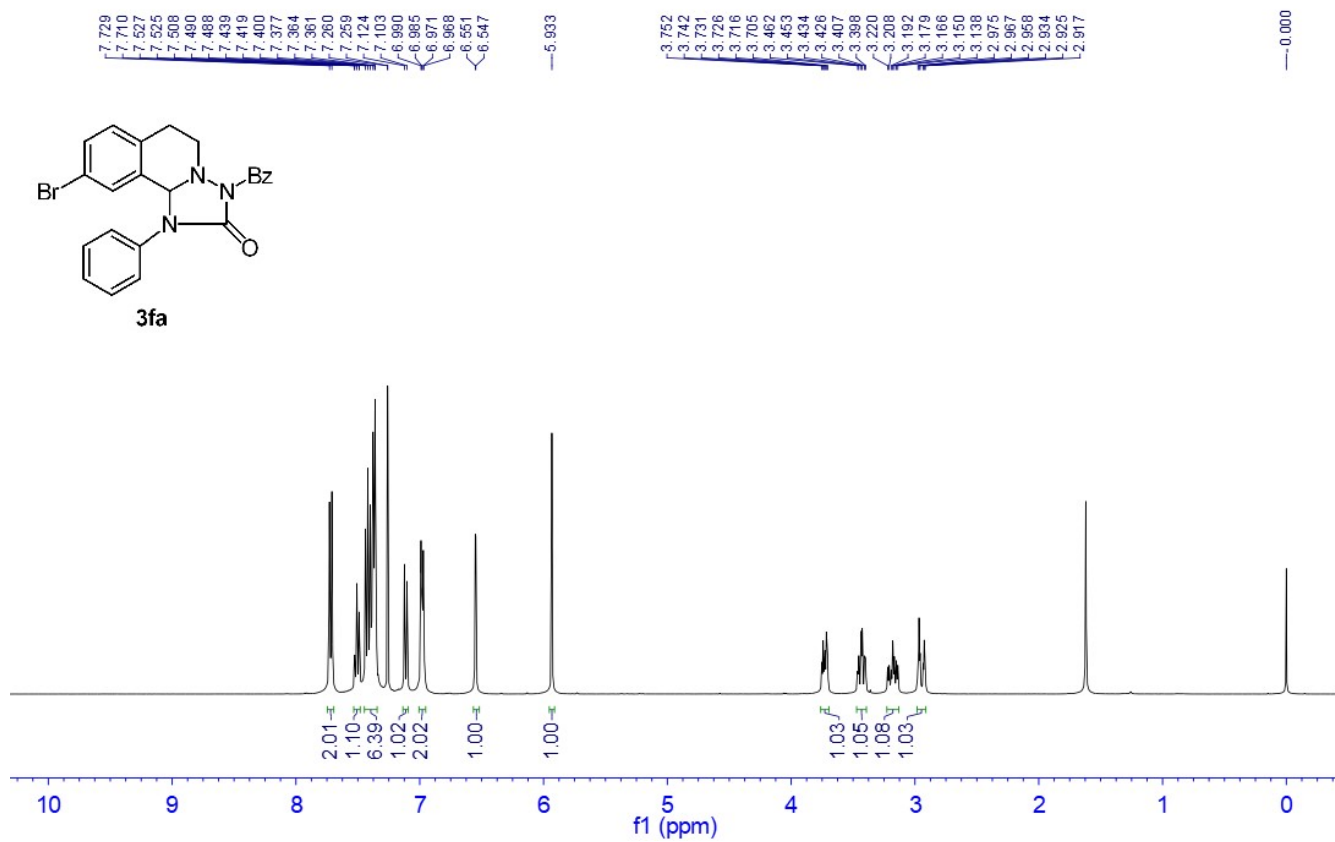


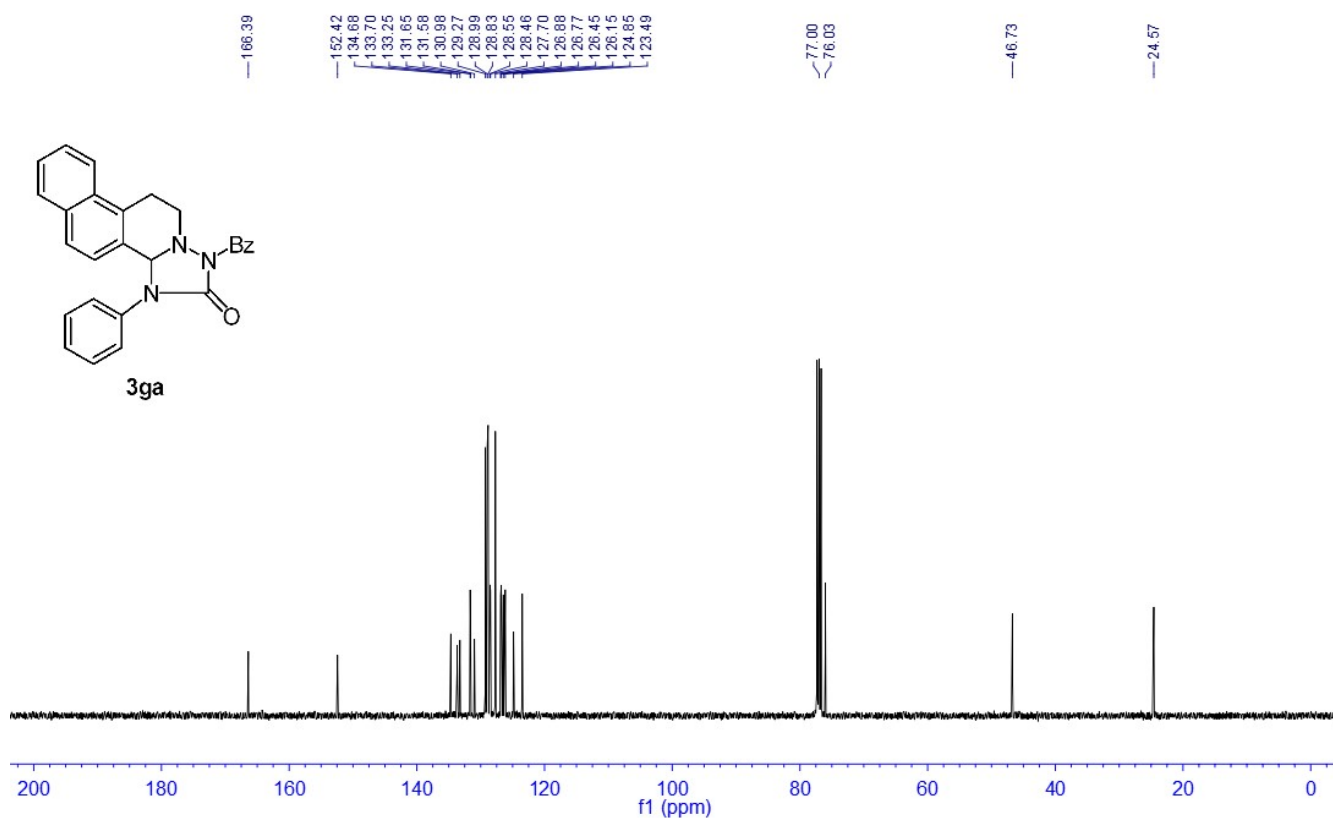
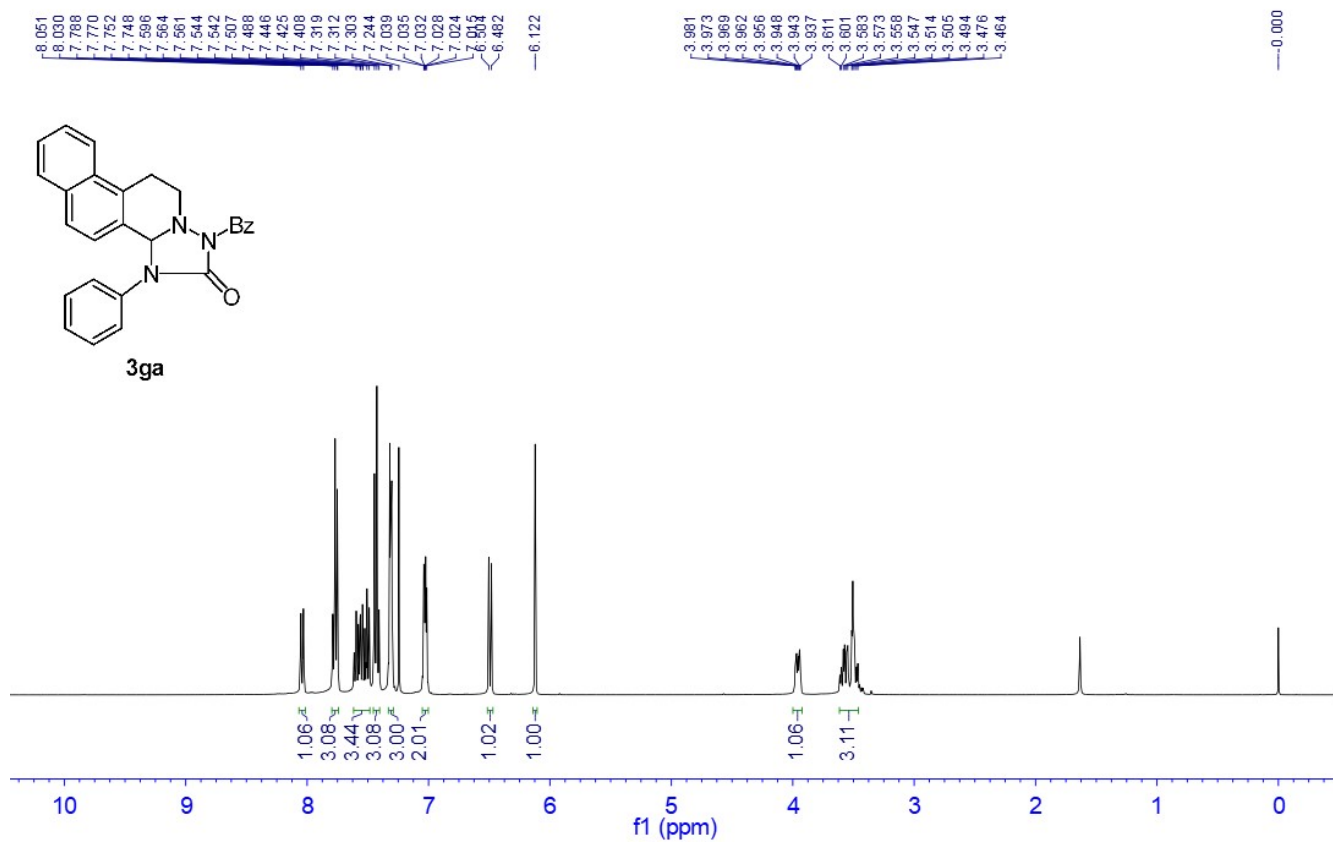


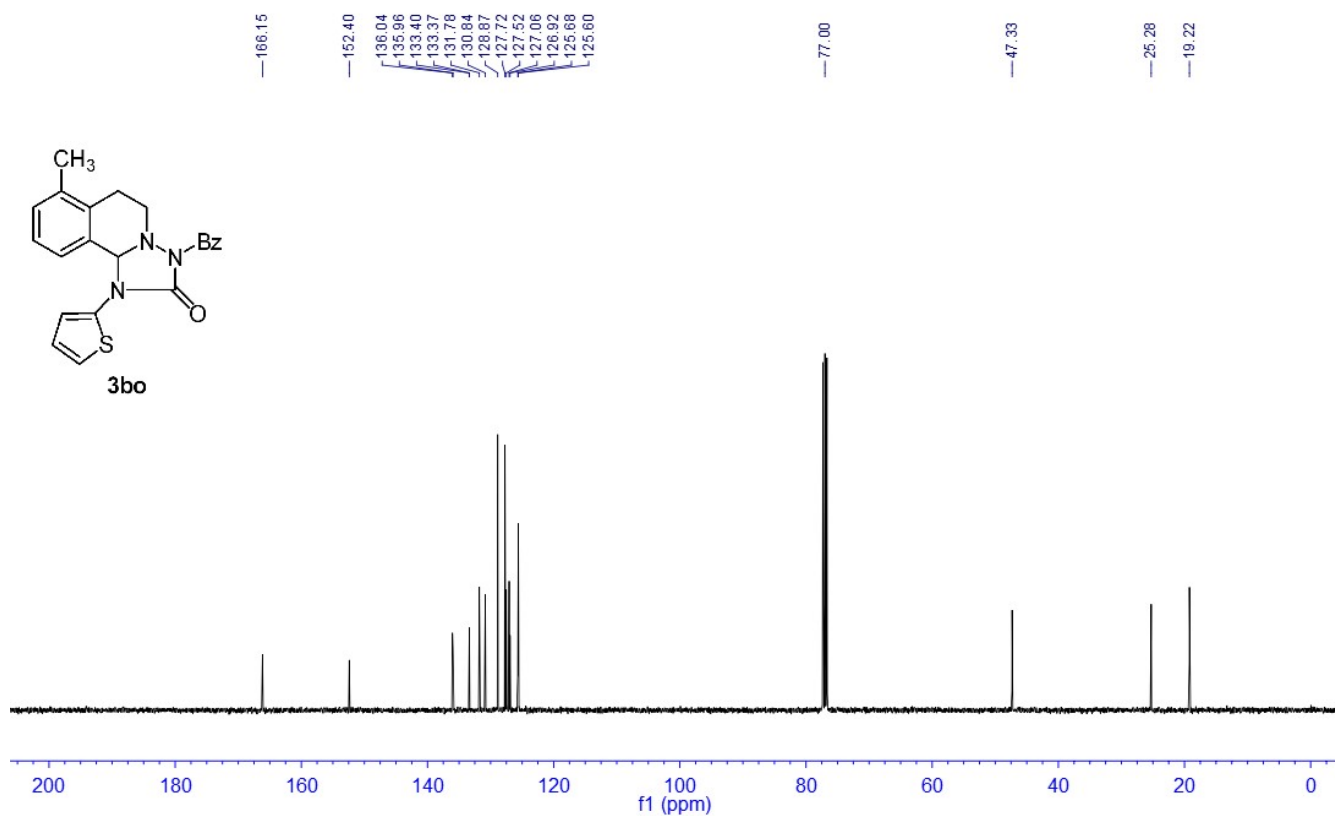
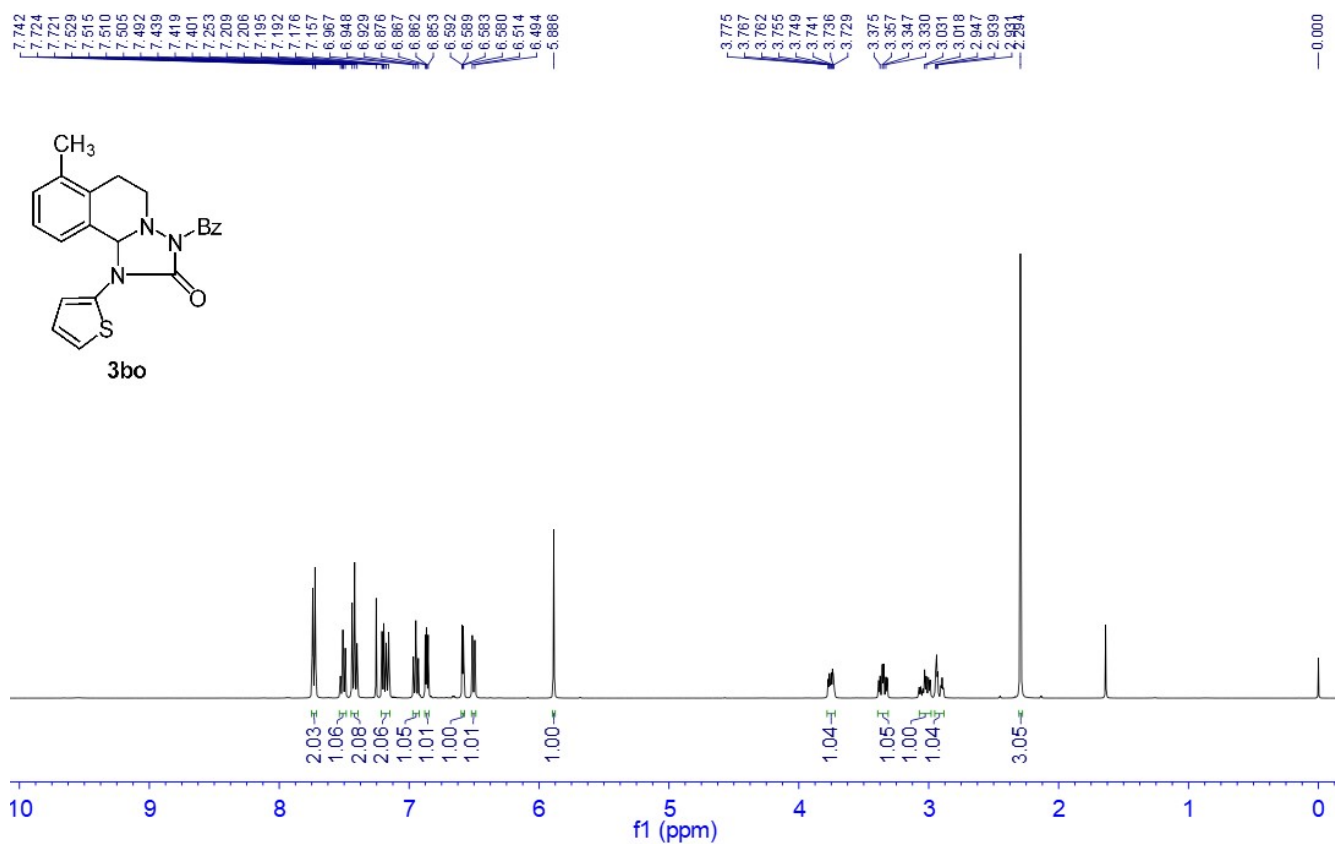


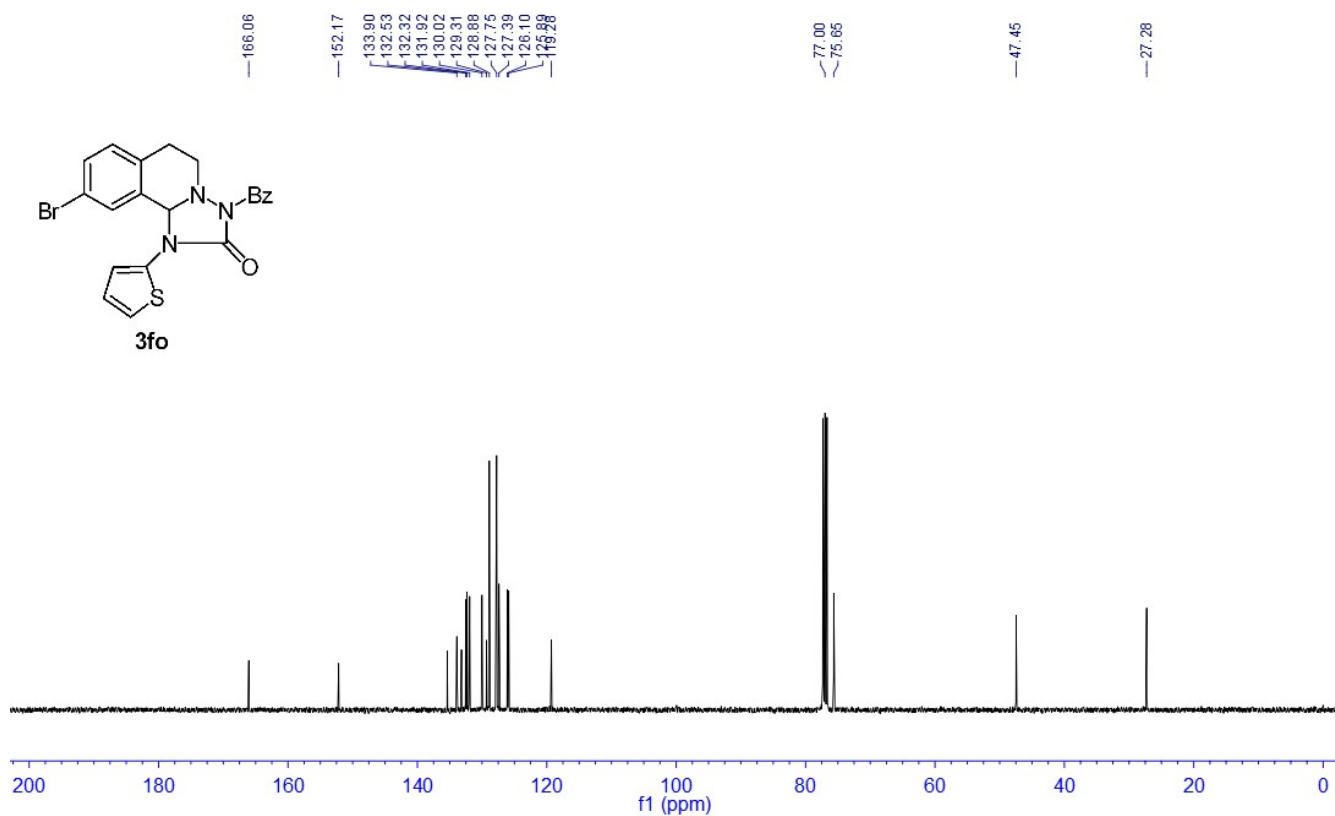
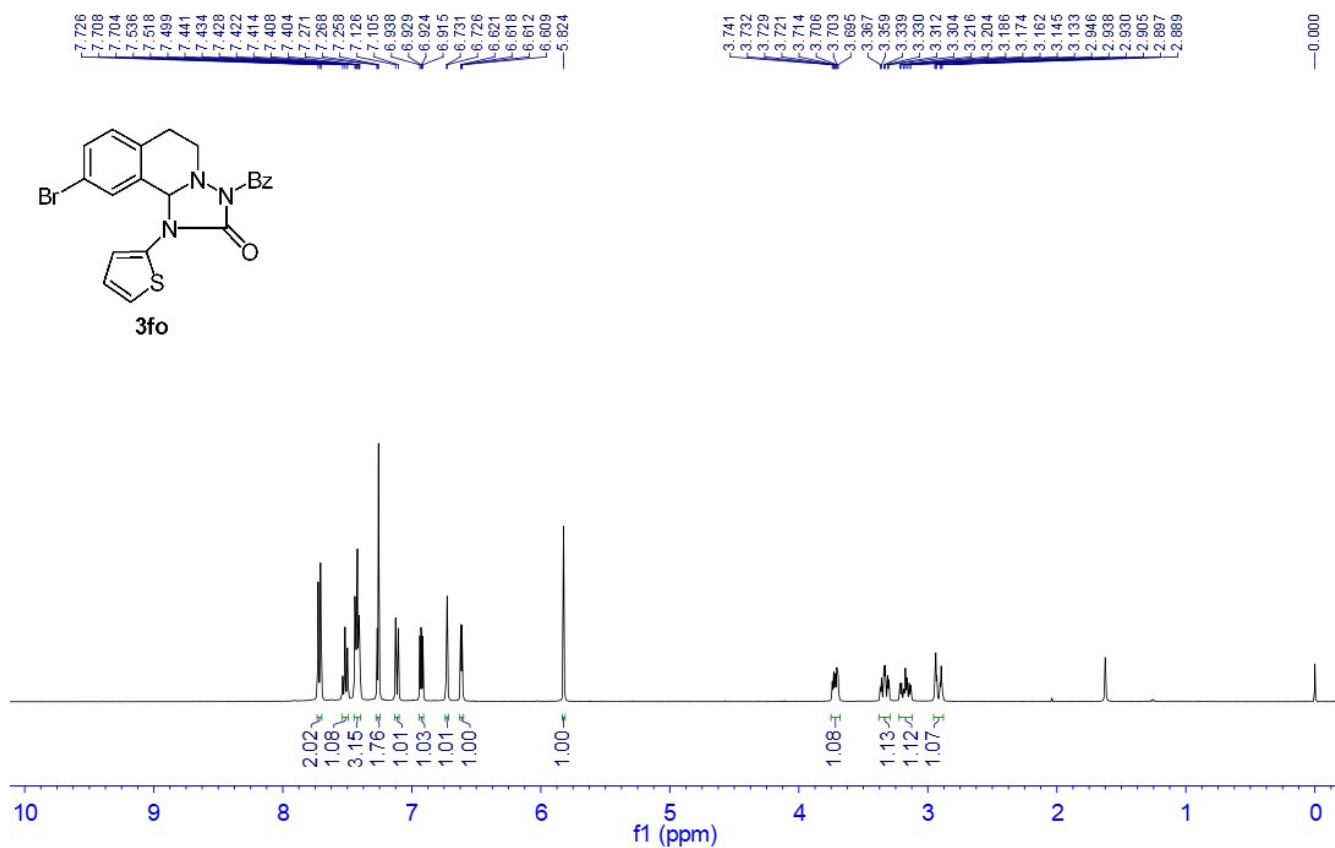


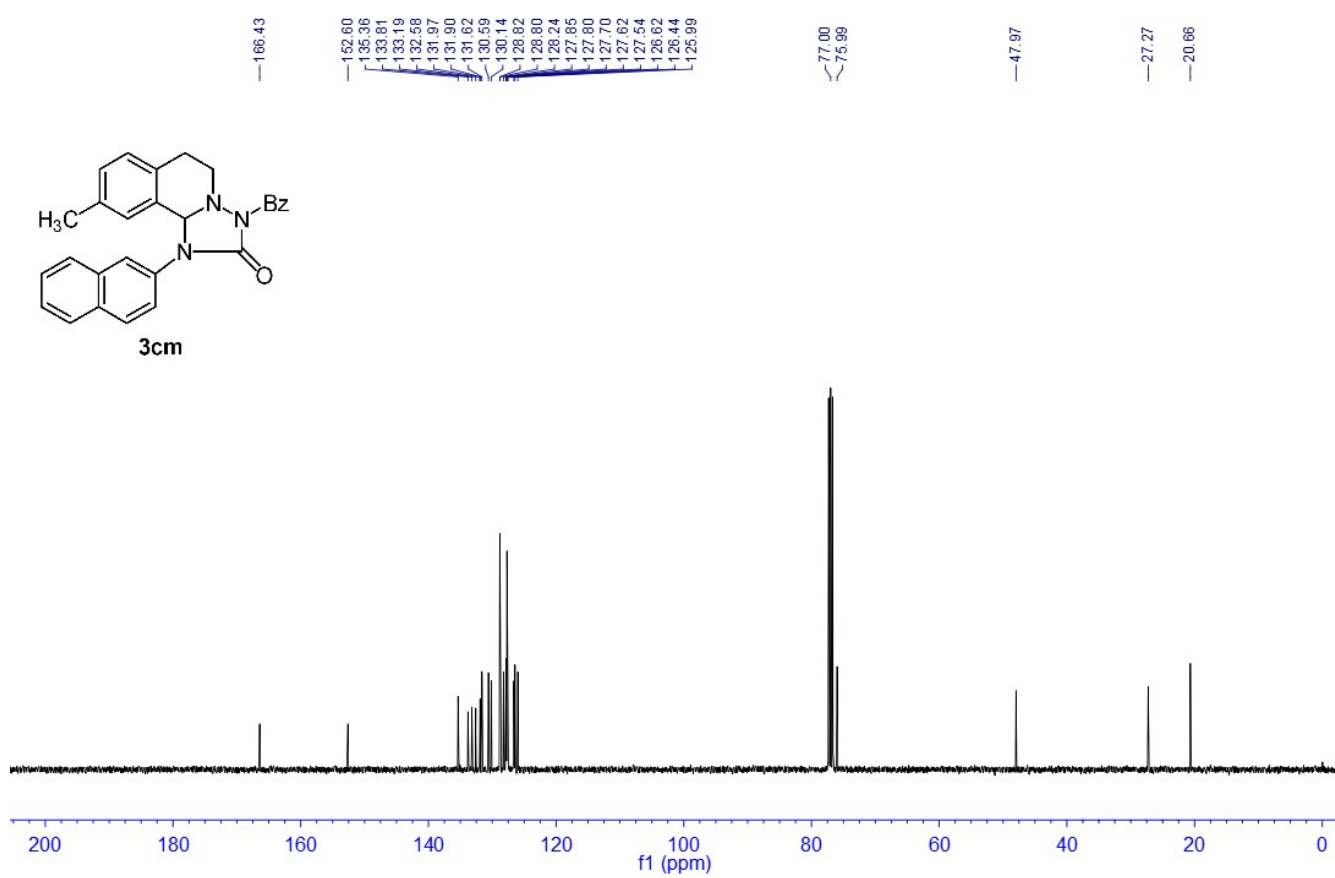
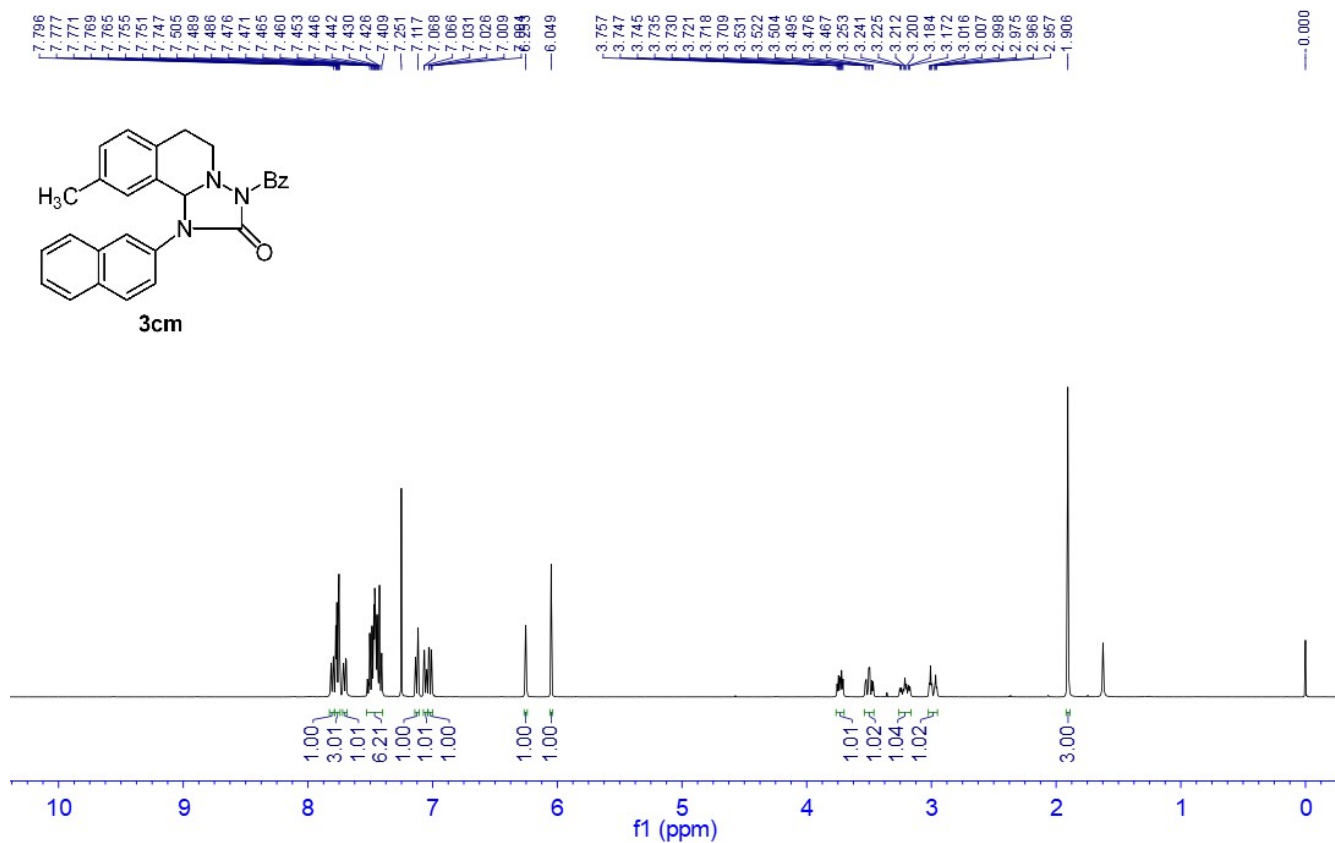


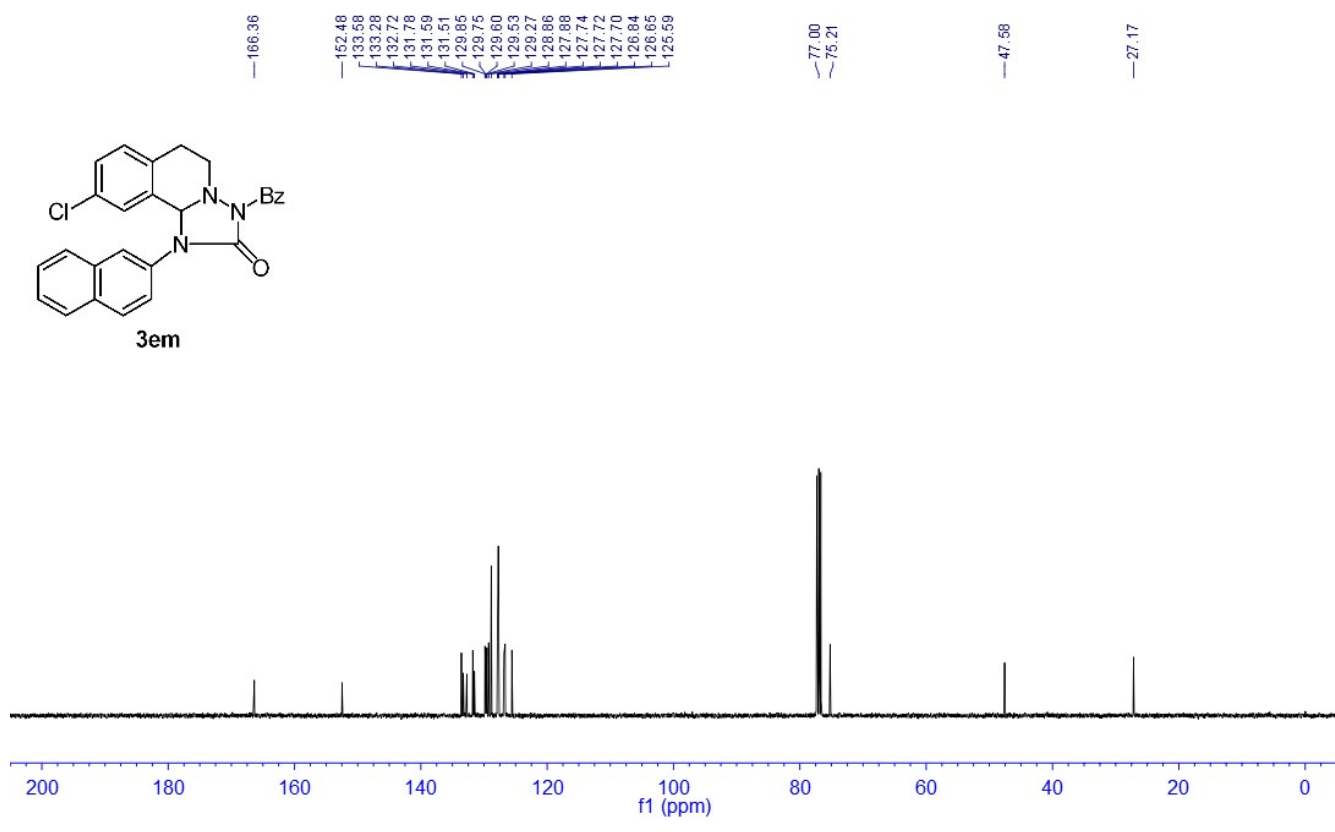
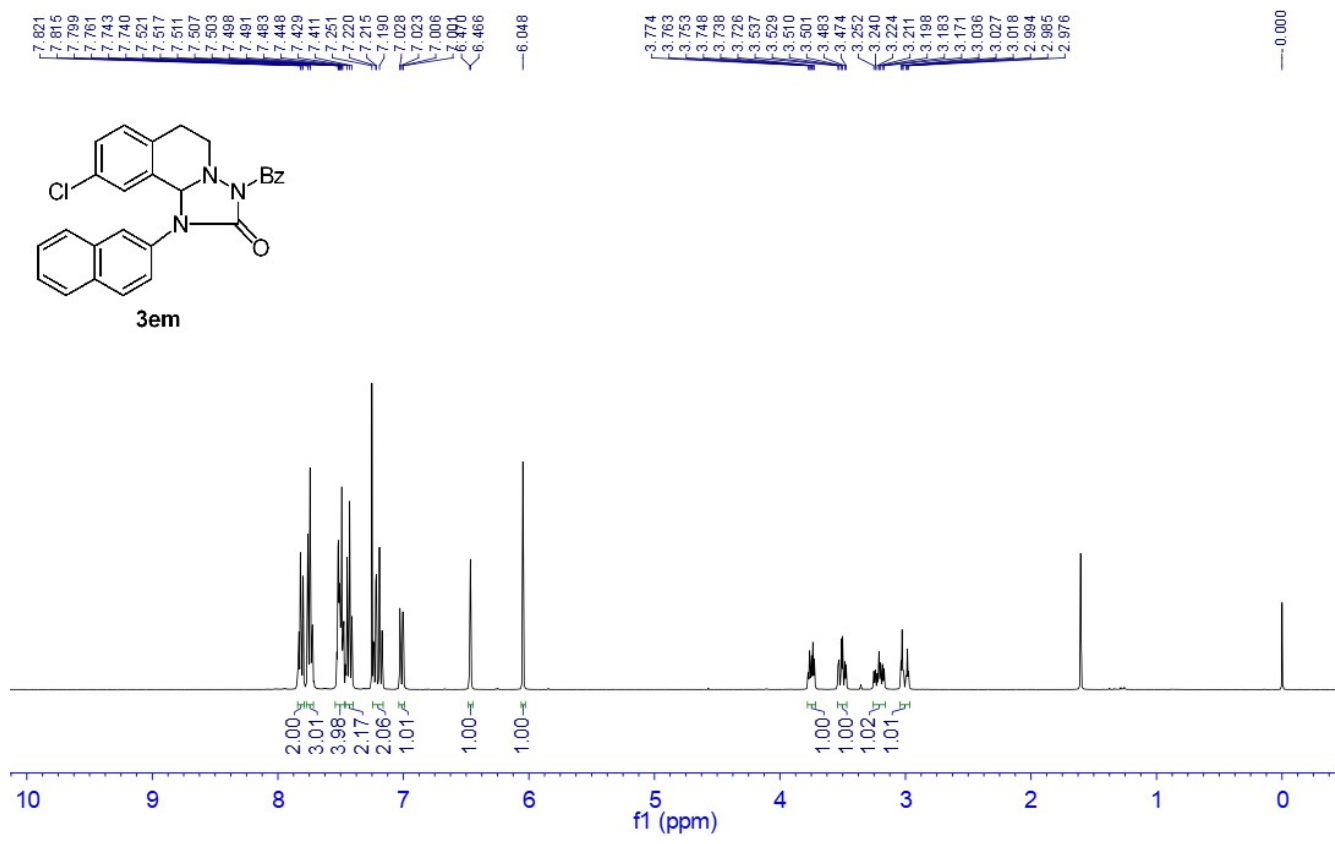


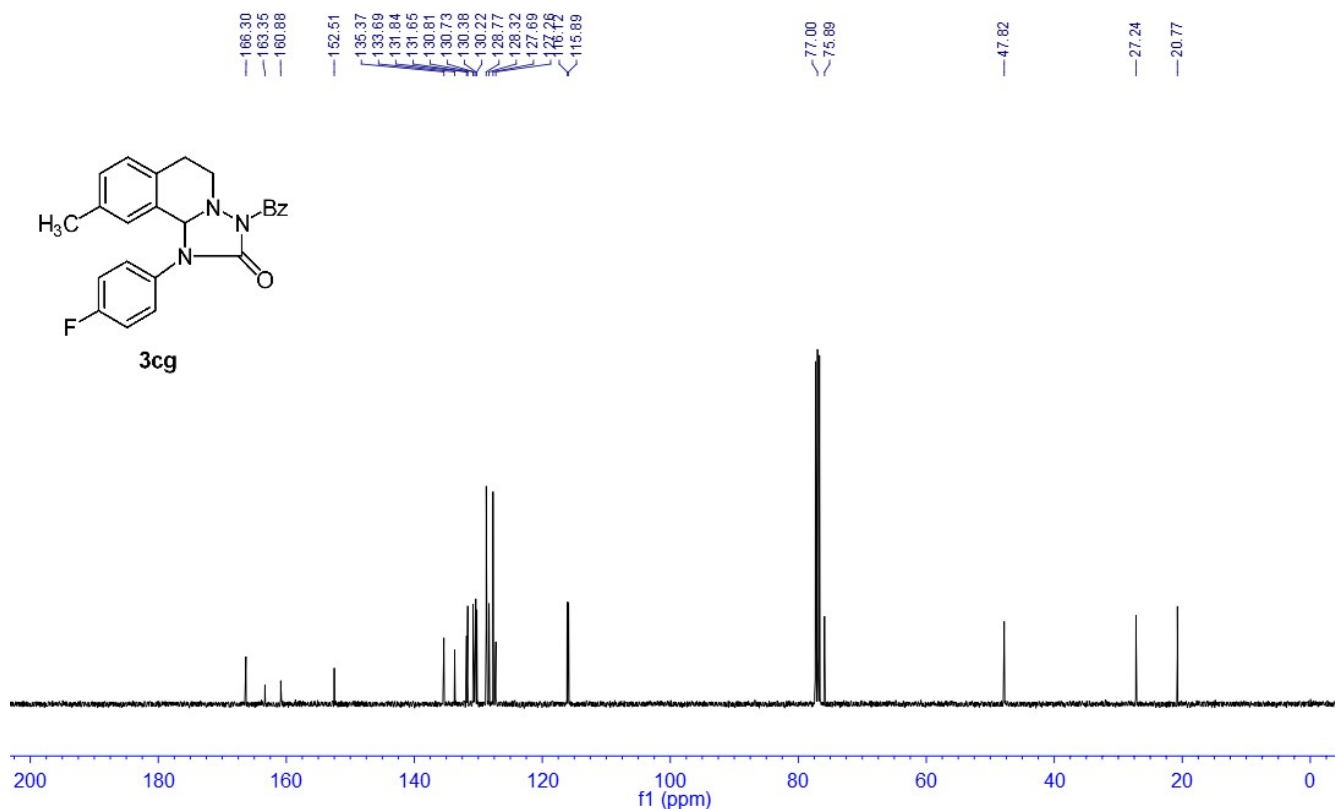
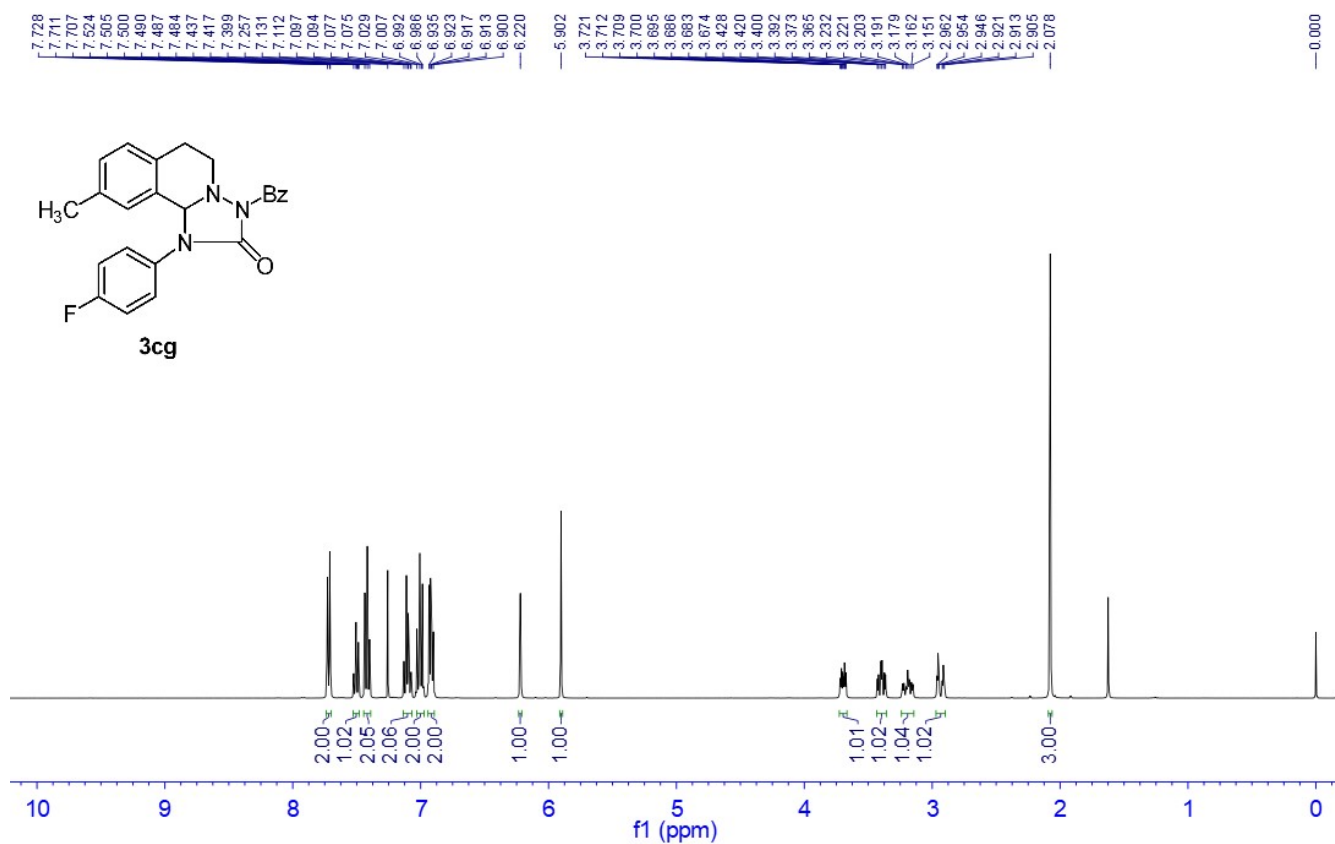


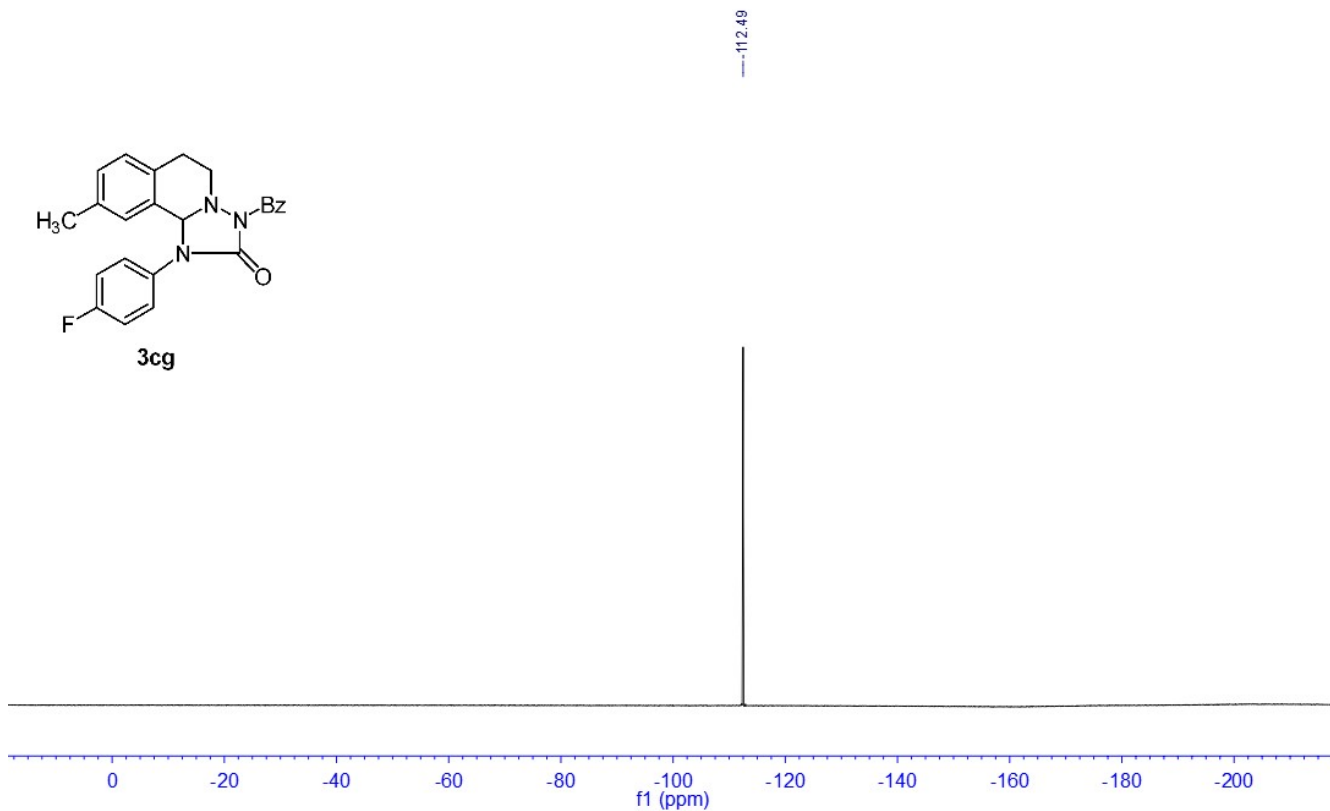
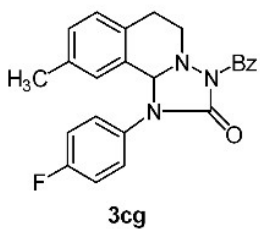












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