Electronic Supporting Information

Lewis acid-switched regiodivergent N^1/N^2-alkylation of benzotriazoles with α-hydroxyl diazo compounds

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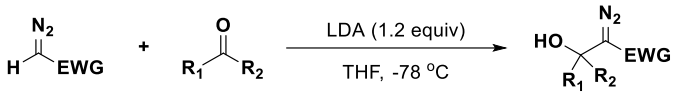
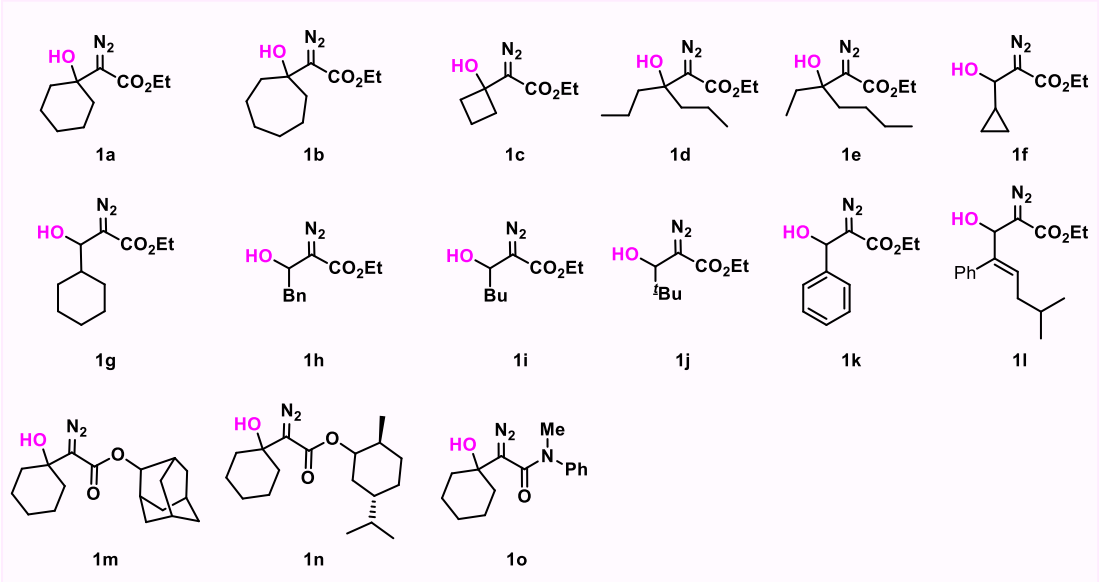
General Information:

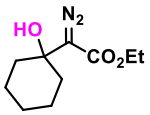
All reagents purchased from commercial sources were used as received. The silica gel for column chromatography was supplied as 200–300 meshes. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III (400 Hz) spectrometer and are referenced to the residual solvent signals (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C in $CDCl_3$). The HRMS spectra were recorded on a Bruker MicroTOF Q II spectrometer.

General Procedure for the Synthesis of α-Hydroxyl Diazo Compounds



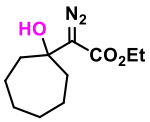
α-Hydroxyl diazo compounds **1a**−**1q** were prepared by the below mentioned method. [1] Diisopropyl aminolithium (12 mmol, 1.2 equiv) was slowly added to a stirred solution of ethyl diazoacetate (10 mmol, 1 equiv) and ketones (10 mmol, 1 equiv) in THF (20 mL) at -78 °C under argon protection and stirred for 12 h. Saturated $NaHCO_3$ solution was added to quench the reaction and then this was extracted with EtOAc three times. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, and evaporated to give the crude diazoacetate. The crude diazoacetate was then purified by flash column chromatography (PE/EtOAc = 20/1) to give the α-hydroxyl diazo compounds.





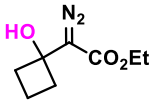
1a

***Ethyl 2-diazo-2-(1-hydroxycyclohexyl)acetate* (1a),** known compound.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, *J* = 7.1 Hz, 2 H), 3.45 (s, 1 H), 1.93 – 1.85 (m, 3 H), 1.76 – 1.67 (m, 4 H), 1.47 – 1.38 (m, 3 H), 1.27 (t, *J* = 7.1 Hz, 3 H).



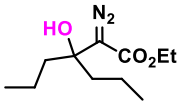
1b

***Ethyl 2-diazo-2-(1-hydroxycycloheptyl)acetate* (1b)**, known compound.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, *J* = 7.1 Hz, 2 H), 3.75 (s, 1 H), 2.12 – 1.85 (m, 4 H), 1.74 – 1.45 (m, 8 H), 1.28 (t, *J* = 7.1 Hz, 3 H).



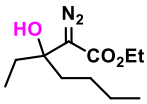
1c

Ethyl 2-diazo-2-(1-hydroxycyclobutyl)acetate (**1c**), known compound.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (q, *J* = 7.1 Hz, 2 H), 3.36 (s, 1 H), 2.45 – 2.22 (m, 4 H), 1.99 – 1.89 (m, 1 H), 1.75 – 1.61 (m, 1 H), 1.29 (t, *J* = 7.1 Hz, 3 H).



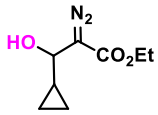
1d

Ethyl 2-diazo-3-hydroxy-3-propylhexanoate (**1d**), known compound.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (t, *J* = 7.1 Hz, 2 H), 3.86 (s, 1 H), 1.75 – 1.62 (m, 3 H), 1.47 – 1.34 (m, 5 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 0.93 (t, *J* = 7.3 Hz, 6 H).



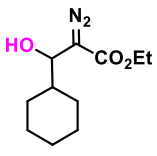
1e

Ethyl 2-diazo-3-ethyl-3-hydroxyheptanoate (**1e**), new compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, *J* = 7.2 Hz, 2 H), 3.85 (s, 1 H), 1.90 – 1.63 (m, 5 H), 1.41 – 1.16 (m, 6 H), 1.04 – 0.65 (m, 6 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.7, 73.6, 60.8, 38.3, 31.9, 25.8, 22.9, 14.4, 14.0, 8.0. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{20}N_2NaO_3$ 251.1366, found 251.1371.



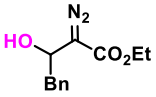
1f

Ethyl 3-cyclopropyl-2-diazo-3-hydroxypropanoate (**1f**), known compound.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (q, 2 H), 2.70 (s, 1 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.23 – 1.19 (m, 1 H), 1.12 – 0.99 (m, 1 H), 0.71 – 0.49 (m, 3 H), 0.43 – 0.32 (m, 1 H).



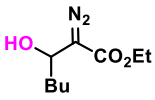
1g

Ethyl 3-cyclohexyl-2-diazo-3-hydroxypropanoate (**1g**), known compound.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 – 4.27 (m, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 2.50 (s, 1 H), 2.08 – 1.99 (m, 1 H), 1.82 – 1.49 (m, 5 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 1.23 – 0.95 (m, 5 H).



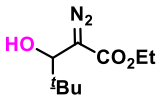
1h

Ethyl 2-diazo-3-hydroxy-4-phenylbutanoate (**1h**), known compound.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.01 (m, 5 H), 4.99 – 4.83 (m, 1 H), 4.25 (q, *J* = 6.9 Hz, 2 H), 3.17 – 2.96 (m, 2 H), 1.29 (t, *J* = 7.1 Hz, 3 H).



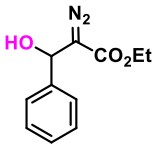
1i

Ethyl 2-diazo-3-hydroxyheptanoate (**1i**), known compound.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (m, 1 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 2.63 (s, 1 H), 1.79 – 1.66 (m, 1 H), 1.66 – 1.54 (m, 1 H), 1.49 – 1.31 (m, 4 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 0.91 (t, *J* = 7.0 Hz, 3 H).



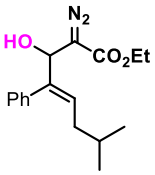
1j

Ethyl 2-diazo-3-hydroxy-4,4-dimethylpentanoate (**1j**), known compound.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 – 3.95 (m, 3 H), 2.75 (s, 1 H), 1.27 (t, *J* = 7.1 Hz, 3 H), 0.97 (s, 9 H).



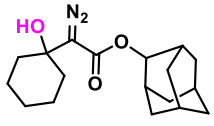
1k

Ethyl 2-diazo-3-hydroxy-3-phenylpropanoate (**1k**), known compound.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.30 (m, 5 H), 5.91 (m, 1 H), 4.28 (q, *J* = 7.1 Hz, 2 H), 3.06 (s, 1 H), 1.30 (t, *J* = 7.1 Hz, 3 H).



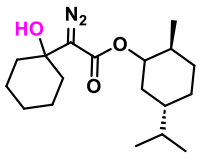
1l

Ethyl (Z)-2-diazo-3-hydroxy-7-methyl-5-phenyloct-4-enoate (**1l**), new compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 3 H), 7.17 – 7.05 (m, 2 H), 6.09 – 5.94 (m, 1 H), 5.47 (m, 1 H), 4.33 – 4.02 (m, 2 H), 2.00 – 1.82 (m, 2 H), 1.76 – 1.55 (m, 2 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 0.97 – 0.70 (m, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 137.5, 128.9, 128.7, 128.3, 127.4, 70.3, 60.9, 37.3, 28.7, 22.4, 22.2, 14.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{22}N_2NaO_3$ 325.1523, found 325.1519.



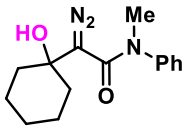
1m

(1r,5R,7S)-Adamantan-2-yl 2-diazo-2-(1-hydroxycyclohexyl)acetate (**1m**), new compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 – 4.87 (m, 1 H), 3.55 (s, 1 H), 2.05 – 1.96 (m, 2 H), 1.95 – 1.68 (m, 16 H), 1.61 – 1.38 (m, 5 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.7, 70.2, 37.3, 36.4, 36.3, 32.0, 31.7, 27.2, 26.9, 25.3, 22.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{27}N_2O_3$ 319.2016, found 319.2011.



1n

(2S,5S)-5-isopropyl-2-methylcyclohexyl 2-diazo-2-(1-hydroxycyclohexyl)acetate (**1n**), new compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 – 4.49 (m, 1 H), 3.55 (s, 1 H), 1.93 – 1.82 (m, 3 H), 1.77 – 1.58 (m, 7 H), 1.55 – 1.42 (m, 6 H), 1.20 – 0.97 (m, 2 H), 0.96 – 0.82 (m, 6 H), 0.76 (d, *J* = 7.0 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.0, 74.9, 70.2, 47.1, 41.3, 36.5, 36.4, 34.2, 31.4, 26.5, 25.3, 23.7, 21.99, 21.96, 20.7, 16.5. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{30}N_2NaO_3$ 345.2149, found 345.2144.



1o

Diazo-2-(1-hydroxycyclohexyl)-N-methyl-N-phenylacetamide (**1o**), new compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 2 H), 7.33 – 7.27 (m, 1 H), 7.21 – 7.10 (m, 2 H), 5.08 (s, 1 H), 3.33 (s, 3 H), 1.88 – 1.54 (m, 6 H), 1.53 – 1.21 (m, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.4, 143.4, 130.0, 127.3, 125.9, 77.3, 77.0, 76.7, 71.5, 38.2, 36.4, 25.3, 22.2. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{20}N_2NaO_2$ 295.1417, found 295.1419.

References

[1] J. Fang, E. Howard and M. Brewer, *Angew. Chem. Int. Ed.,* 2020, ***59***, 12827−12831.

[2] X. Wang, J. Gao, K. Ji and Z. Chen, *Chem. Commun*., 2020, ***56***, 782−785.

[3] X. Chen, Y. Gao and L. Zhou, *Org. Lett*., 2025, ***27***, 2515−2520.

[4] M. Peck and M. Brewer, *Org. Lett*., 2023, ***25,*** 2647−2651.

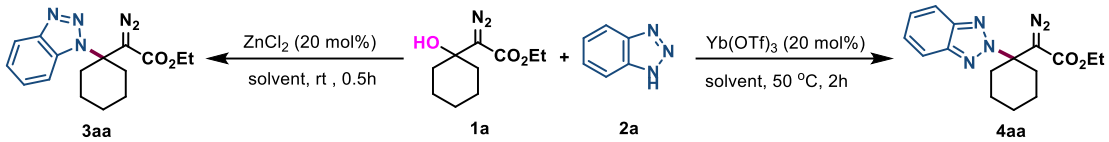
[5] B. Trost, S. Malhotra and P. Koschker, *J. Am. Chem. Soc*., 2012, ***134***, 2075−2084.

[6] F. Shi, P. Xiao and B. Wang, *J. Org. Chem*., 2005, ***70***, 4318-4322.

[7] W. Qi, X. Xie, T. Zhong and X. Zhang, *Chin. Chem. Lett.,* 2018, ***29***, 194−196.

Optimization of Reaction Conditions

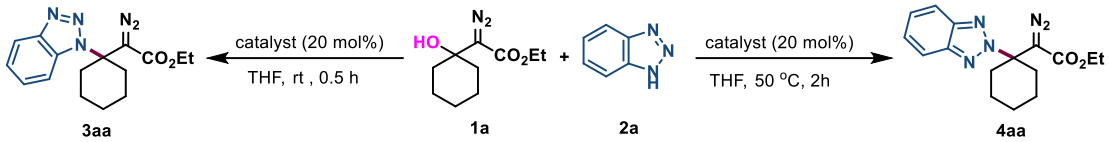
Table S1. Solvent Screening[a]



entry	solvent	yield of **3aa** (%)	yield of **4aa** (%)
1	**THF**	**87**	< **5**
2	1,4-dioxane	50	< 5
3	DCM	< 20	trace
4	EtOAc	< 20	trace
5	MeCN	< 20	trace
6	MeOH	< 5	trace
7	DCE	< 5	trace
8[b]	**THF**	< **5**	**75**
9[b]	1,4-dioxane	< 20	43
10[b]	DCM	32	< 20
11[b]	EtOAc	< 20	< 20
12[b]	MeCN	25	< 20
13[b]	MeOH	< 5	N.D.
14[b]	DCE	31	< 5

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), $ZnCl_2$ (0.06 mmol), solvent (2 mL), rt, 0.5 h. [b]$Yb(OTf)_3$ (0.06 mmol), 50 °C. Isolated yield after column chromatography. N.D. indicates “not detected”.

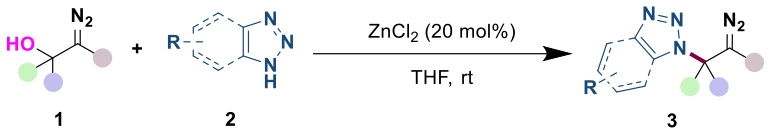
Table S2. Catalyst Screening



entry	Catalyst	yield of **3aa** (%)	yield of **4aa** (%)
1	**$ZnCl_2$**	**87**	< **5**
2	$ZnBr_2$	55	< 5
3	ZnI_2	< 5	0
4	$Zn(OAc)_2$	< 5	0
5	$Zn(OTf)_2$	< 15	60
6	$FeCl_2$	12	42
7	$CuCl_2$	45	< 5
8	AgOTf	< 5	20
9	$Ni(OTf)_2$	< 5	25
10	$Sc(OTf)_3$	< 5	18
11	$Ga(OTf)_3$	< 5	< 10
12	$In(OTf)_3$	< 5	35
13	$Y(OTf)_3$	20	38
14	$Yb(OTf)_2$	15	65
15	no $ZnCl_2$	0	0
16[b]	$ZnCl_2$	< 5	61
17[b]	$ZnBr_2$	< 5	43
18[b]	ZnI_2	< 5	< 5
19[b]	$Zn(OAc)_2$	< 5	< 5
20[b]	$Zn(OTf)_2$	< 5	< 5
21[b]	$FeCl_2$	< 5	22
22[b]	$CuCl_2$	32	< 5
23[b]	AgOTf	< 5	< 5
24[b]	$Ni(OTf)_2$	< 5	< 5
25[b]	$Sc(OTf)_3$	< 5	< 5
26[b]	$Ga(OTf)_3$	< 5	< 5
27[b]	$In(OTf)_3$	< 5	< 5
28[b]	$Y(OTf)_3$	17	56
29[b]	**$Yb(OTf)_3$**	**< 5**	**75**
30[b]	no $Yb(OTf)_3$	0	0

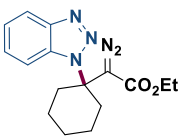
[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), Catalyst (0.06 mmol), THF (2 mL), rt, 0.5 h. [b]50 °C. Isolated yield after column chromatography.

Typical Experimental Procedure A and Data of Compounds 3



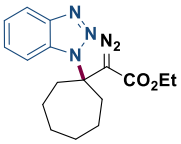
1 2 3

To a 5 mL tube with a stir bar was added α-hydroxyl diazo compounds **1** (0.3 mmol, 1 equiv), benzotriazole **2** (0.36 mmol, 1.2 equiv) and THF (2 mL), followed by $ZnCl_2$ (20 mol%). Then tube was tightly screw capped. The mixture was stirred at room temperature for 0.5 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 10/1), affording the desired *N*[1]-product **3**.



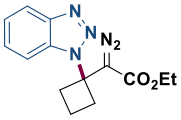
3aa

***Ethyl 2-(1-(1H-benzo[d][1,2,3]triazol-1-yl)cyclohexyl)-2-diazoacetate* (3aa)**, new compound: 81.7 mg of **3aa** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 87% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 54.7 – 56.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 1 H), 7.70 (d, *J* = 8.5 Hz, 1 H), 7.50 – 7.39 (m, 1 H), 7.37 – 7.31 (m, 1 H), 4.08 (q, *J* = 7.1 Hz, 2 H), 2.83 – 2.59 (m, 4 H), 1.84 – 1.42 (m, 6 H), 1.13 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 146.6, 131.9, 127.1, 123.6, 120.2, 111.6, 64.1, 60.9, 34.8, 24.8, 22.4, 14.2. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{19}N_5NaO_2$ 336.1431, found 336.1430.



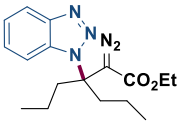
3ba

***Ethyl 2-(1-(1H-benzo[d][1,2,3]triazol-1-yl)cycloheptyl)-2-diazoacetate* (3ba)**, new compound: 56.9 mg of **3ba** was obtained from **1b** (67.8 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 58% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H), 7.47 – 7.38 (m, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 4.03 (q, *J* = 7.1 Hz, 2 H), 3.01 – 2.82 (m, 2 H), 2.75 – 2.54 (m, 2 H), 1.87 – 1.56 (m, 8 H), 1.04 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.7, 146.7, 131.7, 127.1, 123.6, 120.3, 110.9, 67.4, 61.0 37.8, 29.0, 22.5, 14.1. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{21}N_5NaO_2$ 350.1587, found 350.1586.



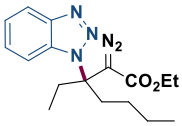
3ca

***Ethyl 2-(1-(1H-benzo[d][1,2,3]triazol-1-yl)cyclobutyl)-2-diazoacetate* (3ca)**, new compound: 71.0 mg of **3ca** was obtained from **1c** (55.2 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 83% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 7.98 (m, 1 H), 7.74 (d, *J* = 8.4 Hz, 1 H), 7.52 – 7.40 (m, 1 H), 7.40 – 7.29 (m, 1 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 3.35 – 3.12 (m, 2 H), 3.10 – 2.92 (m, 2 H), 2.39 – 1.95 (m, 2 H), 1.20 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.6, 146.2, 131.6, 127.2, 123.8, 119.9, 111.5, 61.0, 60.5, 32.3, 16.3, 14.3. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{16}N_5O_2$ 286.1299, found 286.1303.



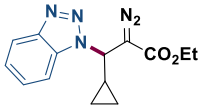
3da

***Ethyl 3-(1H-benzo[d][1,2,3]triazol-1-yl)-2-diazo-3-propylhexanoate* (3da)**, new compound: 60.2 mg of **3da** was obtained from **1d** (68.4 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 61% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 1 H), 7.54 (d, *J* = 8.4 Hz, 1 H), 7.47 – 7.39 (m, 1 H), 7.37 – 7.29 (m, 1 H), 3.99 (d, *J* = 7.1 Hz, 2 H), 2.77 – 2.26 (m, 4 H), 1.47 – 1.32 (m, 2 H), 1.11 – 1.02 (m, 2 H), 0.98 (t, *J* = 7.0 Hz, 3 H), 0.94 – 0.89 (m, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 146.4, 132.0, 127.1, 123.6, 120.3, 110.6, 65.8, 60.9, 36.5, 16.6, 13.94, 13.86. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{23}N_5NaO_2$ 352.1744, found 352.1751.



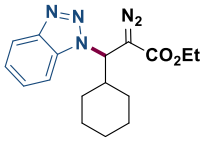
3ea

***Ethyl 3-(1H-benzo[d][1,2,3]triazol-1-yl)-2-diazo-3-propylhexanoate* (3ea)**, new compound: 75.0 mg of **3ea** was obtained from **1e** (68.4 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 76% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H), 7.43 (t, *J* = 7.7 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 3.99 (q, *J* = 7.1 Hz, 2 H), 2.69 – 2.37 (m, 4 H), 1.40 – 1.18 (m, 4 H), 0.98 (t, *J* = 7.0 Hz, 3 H), 0.95 – 0.76 (m, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.6, 146.5, 132.1, 127.1, 123.7, 120.4, 110.7, 66.2, 61.0, 33.3, 27.3, 25.3, 22.5, 14.0, 13.7, 7.7. HRMS (ESI) *m/z*: [M + K]$^+$ Calcd for $C_{17}H_{23}N_5KO_2$ 368.1483, found 368.1471.



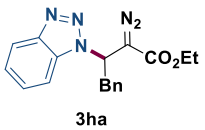
3fa

***Ethyl 3-(1H-benzo[d][1,2,3]triazol-1-yl)-3-cyclopropyl-2-diazopropanoate* (3fa)**, new compound: 65.8 mg of **3fa** was obtained from **1f** (55.2 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 77% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.97 (m, 1 H), 7.58 (d, *J* = 8.4 Hz, 1 H), 7.53 – 7.42 (m, 1 H), 7.41 – 7.31 (m, 1 H), 5.07 (d, *J* = 9.6 Hz, 1 H), 4.25 – 4.01 (m, 2 H), 1.99 – 1.71 (m, 1 H), 1.19 – 1.17 (m, 3 H), 0.92 – 0.75 (m, 1 H), 0.74 – 0.60 (m, 1 H), 0.58 – 0.46 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.1, 145.4, 132.4, 127.4, 123.8, 119.7, 109.4, 61.2, 58.4, 14.1, 13.7, 4.9, 3.9. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{15}N_5NaO_2$ 308.1118, found 308.1107.



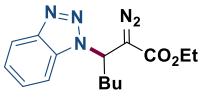
3ga

***Ethyl 3-(1H-benzo[d][1,2,3]triazol-1-yl)-3-cyclohexyl-2-diazopropanoate* (3ga)**, new compound: 92.2 mg of **3ga** was obtained from **1g** (67.8 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 94% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 70.2 – 72.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.56 – 7.45 (m, 1 H), 7.42 – 7.32 (m, 1 H), 5.35 (d, *J* = 11.2 Hz, 1 H), 4.22 – 4.13 (m, 2 H), 2.51 – 2.32 (m, 1 H), 2.12 – 1.95 (m, 1 H), 1.91 – 1.81 (m, 1 H), 1.76 – 1.61 (m, 1 H), 1.64 – 1.53 (m, 1 H), 1.40 – 1.11 (m, 7 H), 1.06 – 1.02 (m, 1 H), 0.97 – 0.80 (m, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 145.3, 133.4, 127.6, 124.0, 119.9, 109.6, 61.4, 59.0, 39.8, 30.3, 29.7, 25.9, 25.6, 25.1, 14.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{21}N_5NaO_2$ 350.1587, found 350.1582.



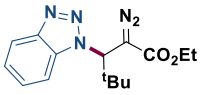
3ha

***Ethyl 3-(1H-benzo[d][1,2,3]triazol-1-yl)-2-diazo-4-phenylbutanoate* (3ha)**, new compound: 79.4 mg of **3ha** was obtained from **1h** (70.2 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 79% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1 H), 7.45 – 7.36 (m, 1 H), 7.34 – 7.28 (m, 1 H), 7.22 – 7.13 (m, 2 H), 7.12 – 7.07 (m, 2 H), 6.00 – 5.81 (m, 1 H), 4.23 – 4.05 (m, 2 H), 3.79 – 3.49 (m, 2 H), 1.58 (s, 2 H), 1.19 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.3, 145.4, 135.3, 132.9, 128.74, 128.67, 127.5, 127.4, 124.0, 119.7, 109.4, 61.5, 55.1, 38.8, 14.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{17}N_5NaO_2$ 358.1274, found 358.1266.



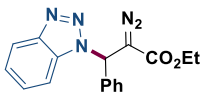
3ia

2-(1H-benzo[d][1,2,3]triazol-1-yl)-1-diazohexyl propionate **(3ia)**, new compound: 75.9 mg of **3ia** was obtained from **1i** (60.0 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 84% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.96 (m, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.52 – 7.43 (m, 1 H), 7.41 – 7.30 (m, 1 H), 5.77 – 5.60 (m, 1 H), 4.28 – 4.09 (m, 2 H), 2.53 – 2.35 (m, 1 H), 2.34 – 2.20 (m, 1 H), 1.46 – 1.28 (m, 3 H), 1.21 (t, *J* = 7.1 Hz, 4 H), 0.87 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 145.6, 132.8, 127.5, 124.0, 119.9, 109.7, 61.3, 53.8, 32.0, 28.1, 21.9, 14.3, 13.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{20}N_5O_2$ 302.1612, found 302.1620.



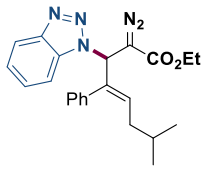
3ja

Ethyl 3-(1H-benzo[d][1,2,3]triazol-1-yl)-2-diazo-4,4-dimethylpentanoate **(3ja)**, new compound: 81.3 mg of **3ja** was obtained from **1j** (60.0 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 90% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 45.1 – 47.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.36 (t, *J* = 7.6 Hz, 1 H), 5.41 (s, 1 H), 4.26 – 4.11 (m, 2 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 1.12 (s, 9 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 144.7, 133.9, 127.6, 124.0, 119.8, 109.6, 61.4, 61.0, 39.1, 27.2, 14.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{19}N_5NaO_2$ 324.1431, found 324.1425.



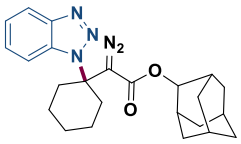
3ka

Ethyl (R)-3-(1H-benzo[d][1,2,3]triazol-1-yl)-2-diazo-3-phenylpropanoate **(3ka)**, new compound: 65.5 mg of **3ka** was obtained from **1k** (60.0 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 68% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 105.4 – 106.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1 H), 7.47 – 7.30 (m, 6 H), 7.16 – 7.11 (m, 2 H), 6.98 (s, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 1.26 (t, *J* = 7.9 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.1, 146.1, 135.0, 132.7, 129.3, 129.0, 127.7, 126.3, 124.2, 120.1, 109.5, 61.6, 58.1, 14.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{15}N_5NaO_2$ 344.1118, found 344.1114.



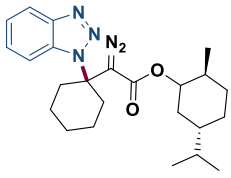
3la

Ethyl (E)-3-(1H-benzo[d][1,2,3]triazol-1-yl)-2-diazo-7-methyl-4-phenyl oct-4-enoate **(3la)**, new compound: 82.2 mg of **3la** was obtained from **1l** (90.6 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 68% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 1 H), 7.50 (d, *J* = 8.3 Hz, 1 H), 7.46 – 7.37 (m, 1 H), 7.37 – 7.29 (m, 1 H), 7.22 – 7.07 (m, 3 H), 6.72 (d, *J* = 7.2 Hz, 2 H), 6.21 (s, 1 H), 5.82 – 5.59 (m, 1 H), 4.31 – 4.14 (m, 2 H), 2.60 – 2.36 (m, 1 H), 2.21 – 1.98 (m, 1 H), 1.53 – 1.33 (m, 1 H), 1.31 – 1.19 (m, 3 H), 0.99 – 0.84 (m, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.6, 146.0, 135.2, 133.0, 132.5, 128.9, 128.2, 128.0, 126.9, 123.6, 119.9, 113.2, 109.9, 64.1, 61.2, 40.4, 24.6, 22.7, 21.7, 14.2. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{23}H_{25}N_5NaO_2$ 426.1900, found 426.1897.



3ma

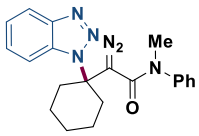
(1r,5R,7S)-Adamantan-2-yl 2-(1-(1H-benzo[d][1,2,3]triazol-1-yl) cyclohexyl)-2-diazo acetate **(3ma)**, new compound: 90.5 mg of **3ma** was obtained from **1m** (95.4 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 72% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 98.3 – 98.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 5.02 – 4.66 (m, 1 H), 3.16 – 2.46 (m, 4 H), 2.11 – 1.32 (m, 20 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.3, 146.6, 131.9, 127.1, 123.6, 120.2, 111.3, 78.0, 64.0, 37.2, 36.1, 34.9, 31.8, 31.5, 26.9, 26.8, 24.9, 22.5. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{24}H_{29}N_5NaO_2$ 442.2213, found 442.2218.



3na

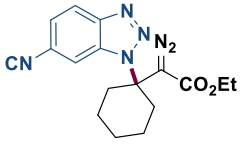
(2S,5S)-5-Isopropyl-2-methylcyclohexyl 2-(1-(1H-benzo[d][1,2,3]tri azol-1-yl)cyclohexyl)-2-diazoacetate **(3na)**, new compound: 88.8 mg of **3na** was obtained from **1n** (96.6 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 70% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 87.5 – 88.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 1 H), 7.60 (d, *J* = 8.4 Hz, 1 H), 7.53 – 7.38 (m, 1 H), 7.36 – 7.23 (m, 1 H), 4.75 – 4.45 (m, 1 H), 2.74 – 2.54 (m, 4 H), 1.89 – 1.45 (m, 8 H), 1.39 – 1.07 (m, 4 H), 0.97 – 0.72 (m, 6 H), 0.67 (d, *J* = 7.0 Hz, 3 H), 0.48 (d, *J* = 6.9 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 146.5, 131.8, 127.0, 123.5, 120.2, 111.1, 75.0, 63.7, 46.8, 40.8, 35.0, 34.9, 33.9, 31.2, 26.0, 24.8, 23.2,

22.4, 21.8, 20.5, 15.9. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{24}H_{33}N_5NaO_2$ 446.2526, found 446.2531.



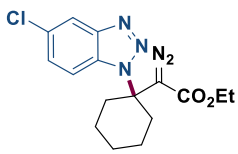
3oa

E-(1-(1H-benzo[d][1,2,3]triazol-1-yl)cyclohexyl)-2-diazo-N-methyl-N-phenylacetamide **(3oa)**, new compound: 67.3 mg of **3oa** was obtained from **1o** (81.9 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 60% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 75.4 – 76.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1 H), 7.80 (d, *J* = 8.5 Hz, 1 H), 7.55 – 7.20 (m, 5 H), 7.15 – 6.97 (m, 2 H), 3.20 (s, 3 H), δ 2.76 – 2.56 (m, 4H), 1.90 – 1.45 (m, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.2, 146.4, 143.8, 132.3, 130.0, 127.2, 127.0, 125.8, 123.4, 120.1, 112.3, 65.4, 62.7, 38.6, 34.7, 24.9, 22.5. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{22}N_6NaO$ 397.1747, found 397.1736.



3ab(N^1 or N^3= 2.4:1)

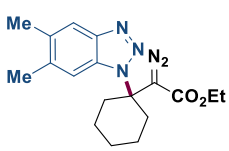
Ethyl 2-(1-(7-cyano-1H-benzo[d][1,2,3]triazol-1-yl)cyclohexyl)-2-diazoacetate **(3ab)**, new compound: 87.2 mg of **3ab** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2b** (51.8 mg, 0.36 mmol) in 86% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 67.8 – 68.5 ºC. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (m, 2 H), 8.14 – 8.06 (m, 2 H), 7.81 (d, *J* = 8.8 Hz, 2 H), 7.60 (d, *J* = 8.7 Hz, 2 H), 7.51 (d, *J* = 8.6 Hz, 1 H), 4.02 (q, *J* = 7.5 Hz, 6 H), 2.83 – 2.51 (m, 13 H), 1.80 – 1.38 (m, 20 H), 1.19 – 1.01 (m, 10 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.4, 145.6, 133.7, 129.2, 126.0, 117.8, 113.3, 107.3, 65.1, 61.0, 34.7, 24.6, 22.3, 14.1. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{18}N_6NaO_2$ 361.1383, found 361.1384.



3ac,(N^1 or N^3= 1.1:1)

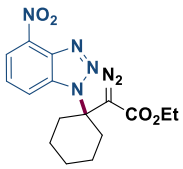
Ethyl 2-(1-(5-chloro-1H-benzo[d][1,2,3]triazol-1-yl)cyclohexyl)-2-diazoacetate **(3ac)**, new compound: 81.2 mg of **3ac** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2c** (55.3 mg, 0.36 mmol) in 78% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.93 (m, 1 H), 7.74 – 7.63 (m, 1 H), 7.46 – 7.28 (m, 1 H), 4.10 (q, *J* = 7.2 Hz, 2 H), 2.91 – 2.54 (m, 4 H), 1.87 – 1.40 (m, 6 H), 1.15 (t, *J* = 7.3 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.6, 147.2, 145.0, 133.5, 132.4, 130.7, 129.4, 128.0, 124.8,

121.0, 119.4, 112.6, 111.5, 64.5, 64.5, 62.9, 61.0, 60.9, 34.7, 24.7, 22.5, 22.4, 22.3, 14.1. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{18}ClN_5NaO_2$ 370.1041, found 370.1033.



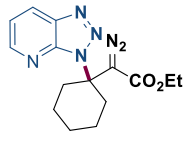
3ad

***Ethyl 2-diazo-2-(1-(5,6-dimethyl-1H-benzo[d][1,2,3]triazol-1-yl) cyclohexyl)acetate* (3ad)**, new compound: 79.8 mg of **3ad** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2d** (52.3 mg, 0.36 mmol) in 78% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 89.7 – 91.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1 H), 7.42 (s, 1 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 2.98 – 2.49 (m, 4 H), 2.41 (s, 3 H), 2.37 (s, 3 H), 1.82 – 1.41 (m, 6 H), 1.14 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 145.8, 137.2, 133.3, 130.9, 119.2, 111.0, 63.7, 60.8, 34.7, 24.8, 22.4, 21.1, 20.2, 14.2. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{23}N_5NaO_2$ 364.1744, found 364.1746.



3ae

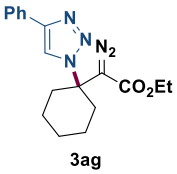
***Ethyl 2-diazo-2-(1-(7-nitro-1H-benzo[d][1,2,3]triazol-1-yl)cyclohexyl) acetate* (3ae)**, new compound: 93.4 mg of **3ae** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2e** (59.0 mg, 0.36 mmol) in 87% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 67.9 – 68.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.32 (m, 1 H), 8.30 – 8.17 (m, 1 H), 7.63 – 7.38 (m, 1 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 2.90 – 2.50 (m, 4 H), 2.00 – 1.66 (m, 3 H), 1.65 – 1.41 (m, 3 H), 1.23 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.7, 145.9, 138.2, 136.9, 126.4, 124.6, 124.2, 70.7, 60.9, 35.2, 24.7, 22.8, 14.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{18}N_6NaO_4$ 381.1282, found 381.1271.



3af

***Ethyl 2-(1-(3H-[1,2,3]triazolo[4,5-b]pyridin-3-yl)cyclohexyl)-2-diazo acetate* (3af)**, new compound: 66.9 mg of **3af** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2f** (43.2 mg, 0.36 mmol) in 71% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow solid. mp 68.2 – 69.6 ºC. **Major isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.45 (m, 1 H), 8.45 – 8.22 (m, 1 H), 7.39 – 7.30 (m, 1 H), 4.05 (q, *J* = 7.1 Hz, 2 H), 3.14 – 2.38 (m, 4 H), 1.94 – 1.37 (m, 6 H), 1.12 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.0, 149.3, 145.8, 137.6, 128.4, 119.4, 64.4, 60.6, 34.1, 24.9, 22.5, 14.1. **Minor isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.66 (m, 1 H),

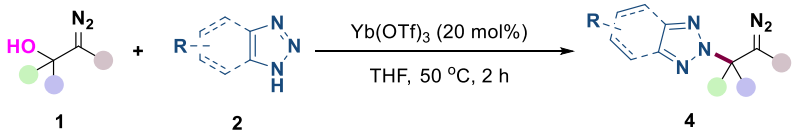
8.29 – 8.05 (m, 1 H), 7.37 – 7.28 (m, 1 H), 4.18 – 4.05 (m, 2 H), 2.79 – 2.48 (m, 4 H), 1.93 – 1.67 (m, 2 H), 1.65 – 1.35 (m, 3 H), 1.19 (t, *J* = 7.1, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.5, 155.2, 151.6, 135.8, 127.3, 121.8, 70.0, 60.6, 34.9, 24.7, 22.7, 14.1. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{18}N_6NaO_2$ 337.1383, found 337.1379.



3ag

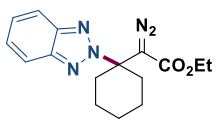
***Ethyl 2-diazo-2-(1-(4-phenyl-1H-1,2,3-triazol-1-yl)cyclohexyl)acetate* (3ag)**, new compound: 83.4 mg of **3ag** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2g** (52.2 mg, 0.36 mmol) in 82% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1 H), 7.96 – 7.79 (m, 2 H), 7.41 (t, *J* = 7.7 Hz, 2 H), 7.36 – 7.31 (m, 1 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 2.85 – 2.59 (m, 2 H), 2.51 – 2.31 (m, 2 H), 1.90 – 1.38 (m, 6 H), 1.23 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.7, 146.8, 130.7, 128.7, 127.9, 125.6, 118.2, 62.5, 60.8, 34.6, 24.7, 22.2, 14.2. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{21}N_5NaO_2$ 362.1587, found 362.1584.

Typical Experimental Procedure B and Data of Compounds 4



1 2 4

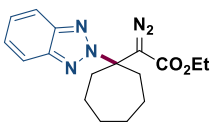
To a 5 mL tube with a stir bar was added α-hydroxyl diazo compounds **1** (0.3 mmol, 1 equiv), benzotriazole **2** (0.36 mmol, 1.2 equiv) and THF (2 mL), followed by $Yb(OTf)_3$ (20 mol%). Then tube was tightly screw capped. The mixture was stirred at 50 °C for 2 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired N^2-product **4**.



4aa

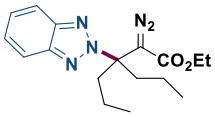
***Ethyl 2-(1-(2H-benzo[d][1,2,3]triazol-2-yl)cyclohexyl)-2-diazoace tate* (4aa)**, new compound: 70.4 mg of **4aa** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 75% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2 H), 7.40 – 7.31 (m, 2 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 2.80 – 2.48 (m, 4 H), 1.85 – 1.40 (m, 6 H), 1.20 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.8,

143.8, 126.1, 118.3, 68.8, 60.7, 35.1, 24.8, 22.8, 14.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{19}N_5NaO_2$ 336.1431, found 336.1430.



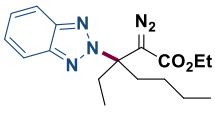
4ba

***Ethyl 2-(1-(2H-benzo[d][1,2,3]triazol-2-yl)cycloheptyl)-2-diazoace tate* (4ba)**, new compound: 69.7 mg of **4ba** was obtained from **1b** (67.8 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 71% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.67 (m, 2 H), 7.29 – 7.18 (m, 2 H), 4.03 (q, *J* = 7.1 Hz, 2 H), 2.73 – 2.60 (m, 2 H), 2.56 – 2.35 (m, 2 H), 1.88 – 1.66 (m, 2 H), 1.64 – 1.47 (m, 6 H), 1.08 (t, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.1, 143.9, 126.1, 118.3, 72.7, 60.8, 38.5, 28.8, 22.7, 14.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{21}N_5NaO_2$ 350.1587, found 350.1586.



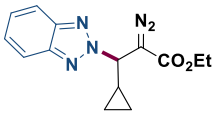
4da

***Ethyl 3-(2H-benzo[d][1,2,3]triazol-2-yl)-2-diazo-3-propylhexanoate* (4da)**, new compound: 79.0 mg of **4da** was obtained from **1d** (68.4 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 80% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 2 H), 7.39 – 7.30 (m, 2 H), 4.07 (q, *J* = 7.1 Hz, 2 H), 2.54 – 2.40 (m, 4 H), 1.45 – 1.20 (m, 4 H), 1.11 (t, *J* = 7.1 Hz, 3 H), 0.94 (t, *J* = 7.1 Hz, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 143.6, 126.1, 118.3, 70.7, 60.7, 37.1, 16.9, 14.2, 14.0. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{23}N_5NaO_2$ 352.1744, found 352.1751.



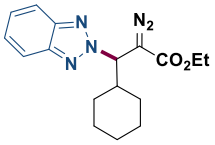
4ea

***Ethyl 3-(2H-benzo[d][1,2,3]triazol-2-yl)-2-diazo-3-ethylheptanoate* (4ea)**, new compound: 65.1 mg of **4ea** was obtained from **1e** (68.4 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 66% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.75 (m, 2 H), 7.42 – 7.27 (m, 2 H), 4.22 – 3.94 (m, 2 H), 2.77 – 2.18 (m, 4 H), 1.50 – 1.23 (m, 4 H), 1.23 – 1.02 (m, 3 H), 0.91 – 0.68 (m, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 143.7, 126.1, 118.3, 71.2, 60.7, 34.0, 28.3, 25.6, 22.6, 14.2, 13.9, 7.9. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{17}H_{23}N_5KO_2$ 368.1483, found 368.1471.



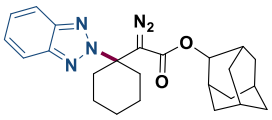
4fa

***Ethyl (R)-3-(2H-benzo[d][1,2,3]triazol-2-yl)-3-cyclopropyl-2-diazopropanoate* (4fa)**, new compound: 42.8 mg of **4fa** was obtained from **1f** (55.2 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 50% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 7.63 (m, 2 H), 7.49 – 7.12 (m, 2 H), 5.20 (d, *J* = 9.7 Hz, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 1.74 – 1.56 (m, 1 H), 1.23 (t, *J* = 7.0 Hz, 3 H), 0.90 – 0.61 (m, 3 H), 0.60 – 0.47 (m, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.1, 126.3, 118.2, 66.0, 61.3, 14.4, 14.3, 4.7, 4.0. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{15}N_5NaO_2$ 308.1118, found 308.1107.



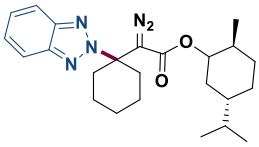
4ga

***Ethyl 3-(2H-benzo[d][1,2,3]triazol-2-yl)-3-cyclohexyl-2-diazopropanoate* (4ga)**, new compound: 44.1 mg of **4ga** was obtained from **1g** (67.8 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 45% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow solid. mp 57.2 – 58.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.79 (m, 2 H), 7.49 – 7.32 (m, 2 H), 5.55 (d, *J* = 11.1 Hz, 1 H), 4.21 (d, *J* = 7.1 Hz, 2 H), 2.29 – 2.13 (m, 1 H), 1.95 – 1.92 (m, 1 H), 1.88 – 1.79 (m, 1 H), 1.72 – 1.56 (m, 3 H), 1.38 – 0.99 (m, 7 H), 0.83 – 0.80 (m, 1 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.0, 126.3, 118.2, 66.7, 61.3, 40.7, 29.9, 29.3, 25.9, 25.6, 25.1, 14.4. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{21}N_5NaO_2$ 350.1587, found 350.1582.



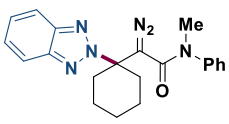
4ma

***(1r,5R,7S)-Adamantan-2-yl 2-(1-(2H-benzo[d][1,2,3]triazol-2-yl)cyclohexyl)-2-diazoacetate* (4ma)**, new compound: 95.5 mg of **4ma** was obtained from **1m** (95.4 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 76% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow solid. mp 110.7 – 111.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.64 (m, 2 H), 7.43 – 7.32 (m, 2 H), 4.94 – 4.92 (m, 1 H), 2.92 – 2.42 (m, 4 H), 2.06 – 0.83 (m, 20 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 143.8, 126.0, 118.2, 77.8, 68.7, 37.2, 36.1, 35.2, 31.8, 31.5, 27.0, 26.8, 24.8, 22.8. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{29}N_5NaO_2$ 442.2213, found 442.2218.



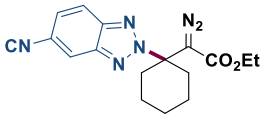
4na

(2S,5S)-5-Isopropyl-2-methylcyclohexyl 2-(1-(2H-benzo[d][1,2,3]triazol-2-yl)cyclohexyl)-2-diazoacetate **(4na)**, new compound: 90.1 mg of **4na** was obtained from **1n** (96.6 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 71% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow solid. mp 106.4 – 107.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.75 (m, 2 H), 7.54 – 7.32 (m, 2 H), 4.78 – 4.48 (m, 1 H), 2.74 – 2.41 (m, 4 H), 1.93 – 1.34 (m, 12 H), 1.01 – 0.75 (m, 6 H), 0.71 (d, *J* = 7.0 Hz, 3 H), 0.60 (d, *J* = 6.9 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.8, 126.1, 118.2, 74.9, 69.0, 47.1, 41.1, 35.6, 35.2, 34.1, 31.3, 26.1, 24.9, 23.4, 22.8, 22.8, 21.9, 20.6, 16.2. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{24}H_{33}N_5NaO_2$ 446.2526, found 446.2531.



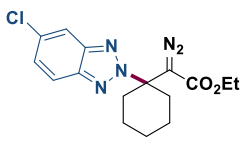
4oa

2-(1-(2H-benzo[d][1,2,3]triazol-2-yl)cyclohexyl)-2-diazo-N-methyl-N-phenylacetamide **(4oa)**, new compound: 78.5 mg of **4oa** was obtained from **1o** (81.9 mg, 0.3 mmol) and **2a** (42.8 mg, 0.36 mmol) in 70% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow solid. mp 118.8 – 119.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 2 H), 7.41 – 7.31 (m, 5 H), 7.18 – 7.03 (m, 2 H), 3.24 (s, 3 H), 2.71 – 2.45 (m, 4 H), 1.80 – 1.35 (m, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.2, 143.9, 143.8, 129.9, 126.9, 125.9, 125.6, 118.3, 69.7, 62.7, 38.4, 34.9, 25.0, 22.9. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{21}H_{22}N_6ONa$ 397.1747, found 397.1736.



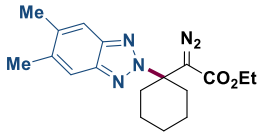
4ab

Ethyl 2-(1-(4-cyano-2H-benzo[d][1,2,3]triazol-2-yl)cyclohexyl) -2-diazoacetate **(4ab)**, new compound: 75.0 mg of **4ab** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2b** (51.8 mg, 0.36 mmol) in 74% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow solid. mp 97.7 – 98.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1 H), 8.07 – 7.86 (m, 1 H), 7.69 – 7.45 (m, 1 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 2.82 – 2.42 (m, 4 H), 1.93 – 1.66 (m, 2 H), 1.64 – 1.42 (m, 4 H), 1.21 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 144.9, 142.6, 127.1, 125.6, 120.1, 118.9, 109.6, 70.3, 60.9, 35.1, 24.7, 22.7, 14.2. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{17}H_{18}N_6NaO_2$ 361.1383, found 361.1384.



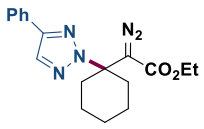
4ac

Ethyl 2-(1-(5-chloro-2H-benzo[d][1,2,3]triazol-2-yl)cyclohexyl) -2-diazoacetate **(4ac)**, new compound: 95.8 mg of **4ac** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2c** (55.3 mg, 0.36 mmol) in 92% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.76 (m, 2 H), 7.37 – 7.28 (m, 1 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 2.81 – 2.31 (m, 4 H), 2.02 – 1.67 (m, 2 H), 1.66 – 1.39 (m, 4 H), 1.20 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.7, 144.2, 142.3, 131.9, 127.6, 119.5, 117.4, 69.2, 60.8, 35.1, 24.8, 22.7, 14.3. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{16}H_{18}ClN_5NaO_2$ 370.1041, found 370.1033.



4ad

Ethyl 2-diazo-2-(1-(5,6-dimethyl-2H-benzo[d][1,2,3]triazol-2-yl) cyclohexyl)acetate **(4ad)**, new compound: 51.2 mg of **4ad** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2d** (52.3 mg, 0.36 mmol) in 50% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 2.92 – 2.49 (m, 4 H), 2.37 (s, 6 H), 1.89 – 1.42 (m, 6 H), 1.19 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.7, 143.2, 136.4, 116.7, 68.1, 60.6, 35.0, 24.8, 22.7, 20.8, 14.2. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{18}H_{23}N_5NaO_2$ 364.1744, found 364.1746.



4ag

Ethyl 2-diazo-2-(1-(4-phenyl-2H-1,2,3-triazol-2-yl)cyclohexyl)acetate **(4ag)**, new compound: 62.0 mg of **4ag** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2g** (52.2 mg, 0.36 mmol) in 61% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1 H), 7.82 – 7.78 (m, 2 H), 7.45 – 7.39 (m, 2 H), 7.37 – 7.31 (m, 1 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 2.65 – 2.30 (m, 4 H), 1.81 – 1.35 (m, 6 H), 1.23 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 147.2, 130.6, 130.5, 128.7, 128.2, 125.8, 66.6, 60.6, 34.5, 24.8, 22.6, 14.3. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{18}H_{21}N_5NaO_2$ 362.1587, found 362.1584.

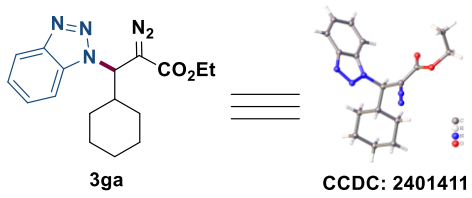
Crystallographic Data for Compound 3ga

Crystallization of **3ga** (30 mg) was dissolved in 1 mL of $CHCl_3$. Then **3ga** were sealed in a 6.5 cm glass ampule with 5 mL of PE, the $CHCl_3$/PE = 1 : 5 (volume ratio). The ampule was placed in a refrigerator at 25 °C and kept at that temperature for 48 hours. Yellow block was crystals deposited in the glass ampule. The data were collected on a Bruker D8 Venture CCD diffractometer.

A good-quality single-crystal of **3ga** was respectively picked carefully and their diffraction intensity data were collected on a Bruker Apex II diffractometer equipped with CCD two-dimensional detector using monochromated Mo Kα radiation (λ = 0.71073 Å) at 150.0 K.

Routine Lorentz and polarization corrections were applied and a multi-scan absorption correction was utilized with the SADABS program. Direct methods were used to solve the structures, refined on F^2 by full-matrix least-squares method, using the SHELXTL-97 program. All H atoms connected to C atoms were generated geometrically and refined isotropically as a riding model using the default Olex2 parameters.

The ellipsoid contour 30% probability levels in the caption for the image of the structure.



Single crystal structure of **3ga**

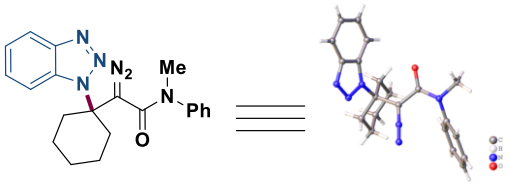
Crystallographic Data for Compound 3oa

Crystallization of **3oa** (30 mg) was dissolved in 1 mL of acetone. Then **3oa** were sealed in a 6.5 cm glass ampule with 5 mL of PE, the acetone/PE = 1 : 5 (volume ratio). The ampule was placed in a refrigerator at 25 °C and kept at that temperature for 48 hours. Yellow block was crystals deposited in the glass ampule. The data were collected on a Bruker D8 Venture CCD diffractometer.

A good-quality single-crystal of **3oa** was respectively picked carefully and their diffraction intensity data were collected on a Bruker Apex II diffractometer equipped with CCD two-

dimensional detector using monochromated Mo Kα radiation (λ = 0.71073 Å) at 150.0 K. Routine Lorentz and polarization corrections were applied and a multi-scan absorption correction was utilized with the SADABS program. Direct methods were used to solve the structures, refined on F^2 by full-matrix least-squares method, using the SHELXTL-97 program. All H atoms connected to C atoms were generated geometrically and refined isotropically as a riding model using the default Olex2 parameters.

The ellipsoid contour 30% probability levels in the caption for the image of the structure.

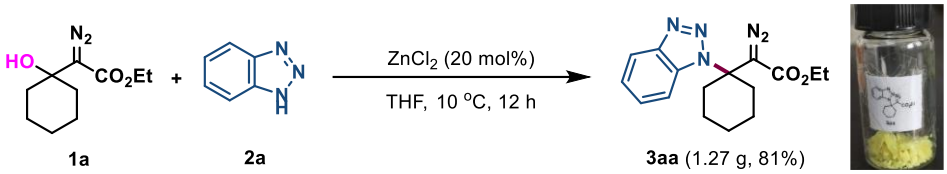


3oa

CCDC: 2467096

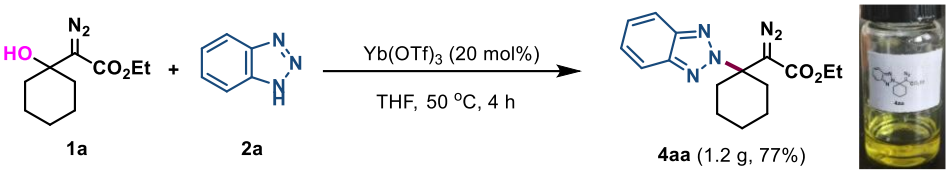
Single crystal structure of **3oa**

Gram-Scale Synthesis of 3aa and 4aa



1a **2a** **3aa** (1.27 g, 81%)

To a 100 mL tube with a stir bar was added ethyl 2-diazo-2-(1-hydroxycyclohexyl)acetate **1a** (5 mmol, 1 equiv, 1.06 g), benzotriazole **2a** (6 mmol, 1.2 equiv, 0.714 g) and THF (15 mL), followed by $ZnCl_2$ (1 mmol, 20 mol%, 0.14 g). Then tube was tightly screw capped. The mixture was stirred at 10 °C under the for 12 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 10/1), affording the desired product **3aa** (1.27 g, 81% yield).

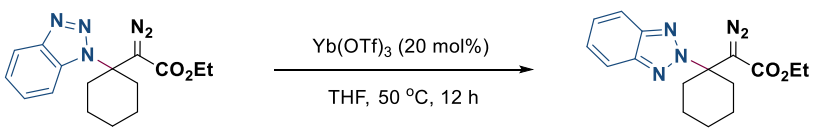


1a **2a** **4aa** (1.2 g, 77%)

To a 100 mL tube with a stir bar was added ethyl 2-diazo-2-(1-hydroxycyclohexyl)acetate **1a** (5 mmol, 1 equiv, 1.06 g), benzotriazole **2a** (6 mmol, 1.2 equiv, 0.714 g) and THF (15 mL), followed by $Yb(OTf)_3$ (1 mmol, 20 mol%, 0.62 g). Then tube was tightly screw capped. The mixture was stirred at 50°C under the for 4 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired product 4aa (1.2 g, 77% yield).

Control Experiments

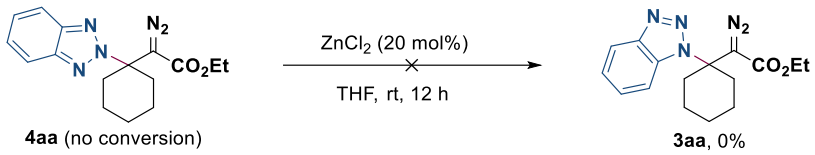
(a) Transformation of 3aa and 4aa



3aa (conv. 95%) **4aa**, 95%

To a 5 mL tube equipped with a stir bar were added ethyl 2-(1-(1H-benzo[d][1,2,3]triazol-1-yl)cyclohexyl)-2-diazoacetate **3aa** (0.3 mmol, 1 equiv) and THF (2 mL), followed by $Yb(OTf)_3$ (20 mol%). The mixture was stirred at 50 °C for 12 h, yielding ethyl 2-(1-(2H-

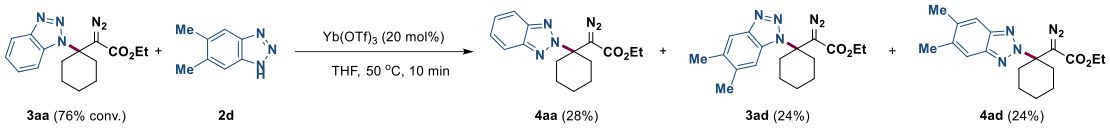
benzo[d][1,2,3]triazol-2-yl)cyclohexyl)-2-diazoacetate **4aa** (89.2 mg, 95% yield) as the *N*2-product. The product was purified by column chromatography (PE/EtOAc = 10/1) to give a slightly yellow oil.



4aa (no conversion) **3aa**, 0%

To a 5 mL tube equipped with a stir bar were added ethyl 2-(1-(2H-benzo[d][1,2,3]triazol-2-yl)cyclohexyl)-2-diazoacetate **4aa** (0.3 mmol, 1 equiv) and THF (2 mL), followed by $ZnCl_2$ (20 mol%). The mixture was stirred at room temperature for 12 h. No reaction was observed by TLC analysis, as the starting material **4aa** remained unchanged.

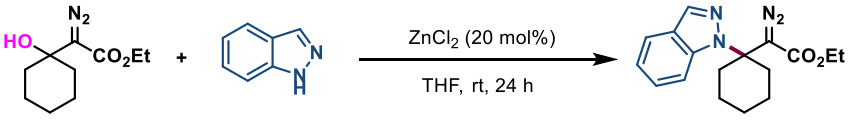
(b) Crossover experiments: intramolecular and intermolecular



3aa (76% conv.) **2d** **4aa** (28%) **3ad** (24%) **4ad** (24%)

To a 5 mL tube equipped with a stir bar were added ethyl 2-(1-(1H-benzo[d][1,2,3]triazol-1-yl)cyclohexyl)-2-diazoacetate **3aa** (0.3 mmol, 1 equiv), 5,6-dimethyl-1H-benzo[d][1,2,3]triazole **2d** and THF (2 mL), followed by $Yb(OTf)_3$ (20 mol%). The reaction mixture was stirred at 50 °C for 10 min, yielding a mixture of three products: ethyl 2-(1-(2H-benzo[d][1,2,3]triazol-2-yl)cyclohexyl)-2-diazoacetate (**4aa**, 28%), ethyl 2-diazo-2-(1-(5,6-dimethyl-1H-benzo[d][1,2,3]triazol-1-yl)cyclohexyl)acetate (**3ad**, 24%), and ethyl 2-diazo-2-(1-(5,6-dimethyl-2H-benzo[d][1,2,3]triazol-2-yl)cyclohexyl)acetate (**4ad**, 24%).

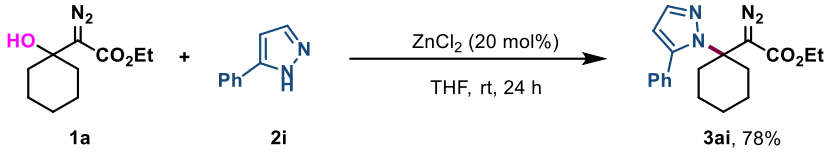
(c) Diazoles Instead of Triazoles



1a **2h** **3ah**, 40%

To a 5 mL tube with a stir bar was added ethyl 2-diazo-2-(1-hydroxycyclohexyl)acetate **1a** (0.3 mmol, 1 equiv), 1*H*-indazole **2h** (0.36 mmol, 1.2 equiv) and THF (2 mL), followed by $ZnCl_2$ (20 mol%). Then tube was tightly screw capped. The mixture was stirred at room temperature

for 24 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 10/1), affording the desired N^1-product **3ah** (37.4 mg, 40% yield). ***Ethyl 2-(1-(1H-indazol-1-yl)cyclohexyl)-2-diazoacetate*** (**3ah**), new compound: 37.4 mg of **3ah** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2h** (42.3 mg, 0.36 mmol) in 40% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.0 Hz, 1 H), 8.02 – 7.57 (m, 2 H), 7.34 – 7.19 (m, 1 H), 7.12 – 6.89 (m, 1 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.09 – 2.64 (m, 2 H), 2.64 – 2.34 (m, 2 H), 1.81 – 1.44 (m, 6 H), 1.20 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.0, 148.3, 125.9, 121.3, 121.0 (2C, overlap), 120.5, 117.5, 63.5, 60.6, 34.8, 24.9, 22.5, 14.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}N_4O_2$ 313.1659, found 313.1663.

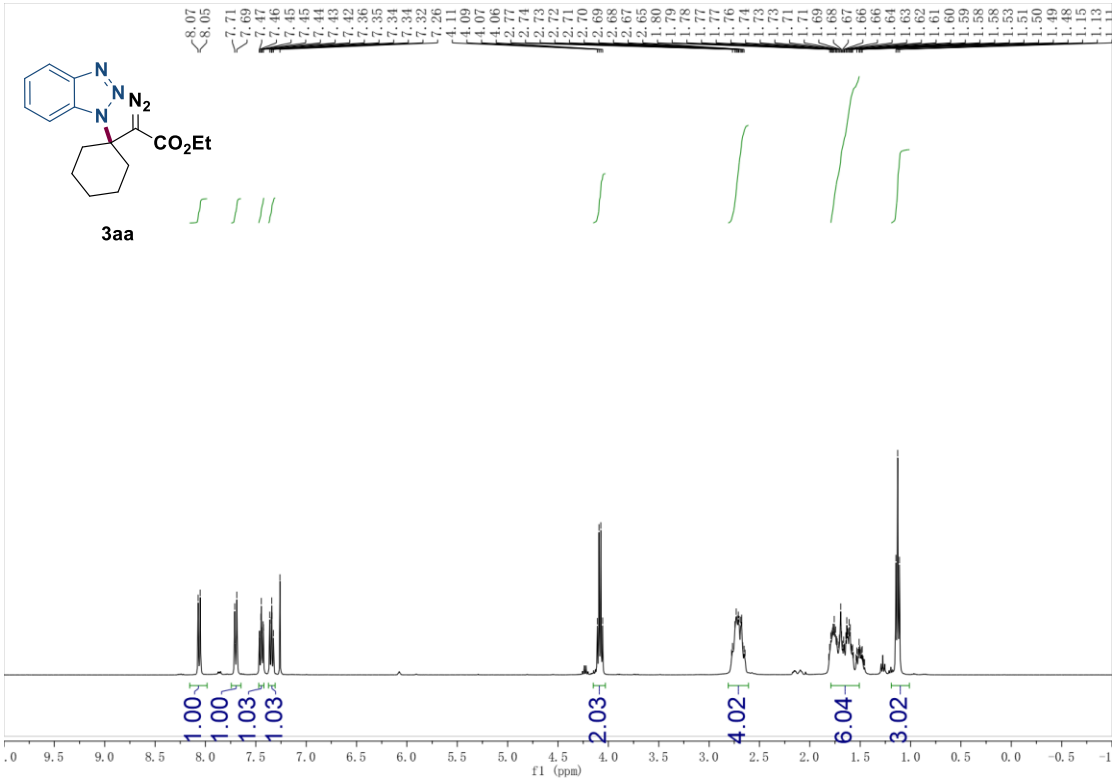


1a **2i** **3ai**, 78%

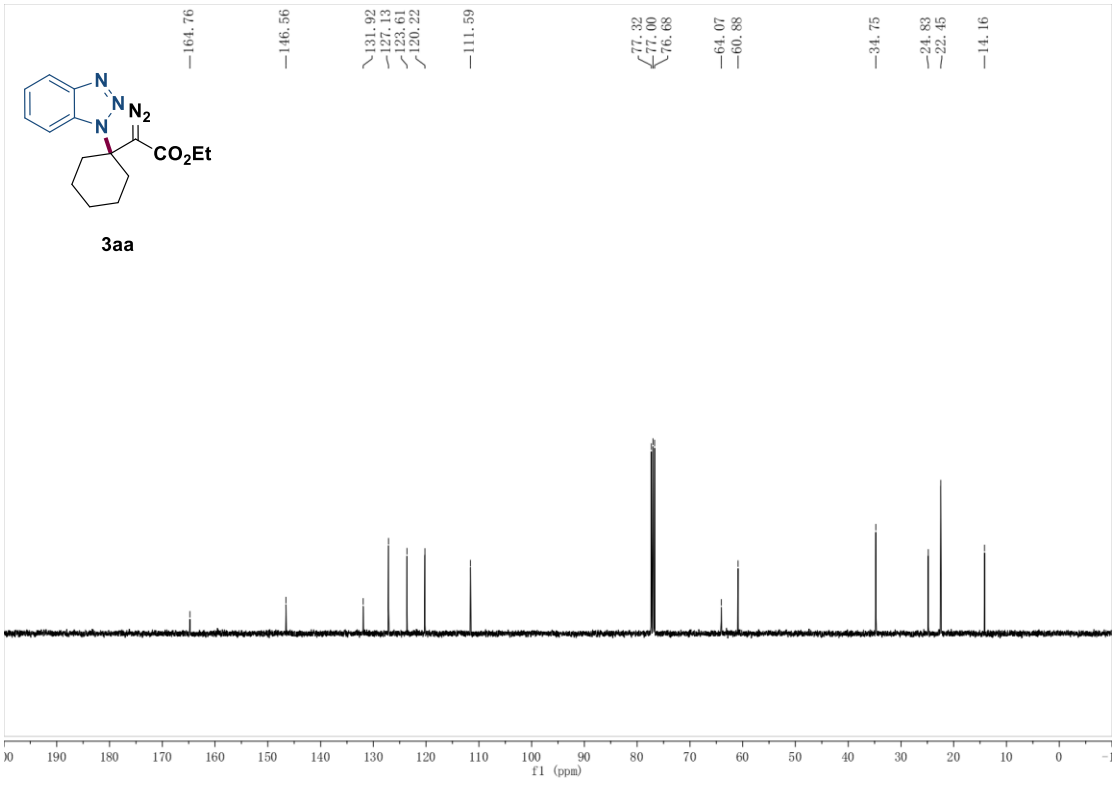
To a 5 mL tube with a stir bar was added ethyl 2-diazo-2-(1-hydroxycyclohexyl)acetate **1a** (0.3 mmol, 1 equiv), 5-phenyl-1*H*-pyrazole **2i** (0.36 mmol, 1.2 equiv) and THF (2 mL), followed by $ZnCl_2$ (20 mol%). Then tube was tightly screw capped. The mixture was stirred at room temperature for 24 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 10/1), affording the desired N^1-product ***3ai*** (79.1 mg, 78% yield). ***Ethyl 2-diazo-2-(1-(5-phenyl-1H-pyrazol-1-yl)cyclohexyl)acetate*** (**3ai**), new compound: 79.1 mg of **3ai** was obtained from **1a** (63.6 mg, 0.3 mmol) and **2i** (51.8 mg, 0.36 mmol) in 78% yield. Purified by column chromatography (PE/EtOAc = 10/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 2 H), 7.55 (d, *J* = 2.4 Hz, 1 H), 7.34 – 7.20 (m, 2 H), 7.22 – 7.07 (m, 1 H), 6.57 – 6.23 (m, 1 H), 4.02 (q, *J* = 7.1 Hz, 2 H), 2.63 – 2.40 (m, 2 H), 2.34 – 2.14 (m, 2 H), 1.71 – 1.27 (m, 6 H), 1.10 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2, 150.8, 133.8, 128.4, 127.4, 125.5, 101.9, 61.7, 60.4, 34.4, 24.9, 22.4, 14.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{23}N_4O_2$ 339.1816, found 339.1822.

Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of All the Products

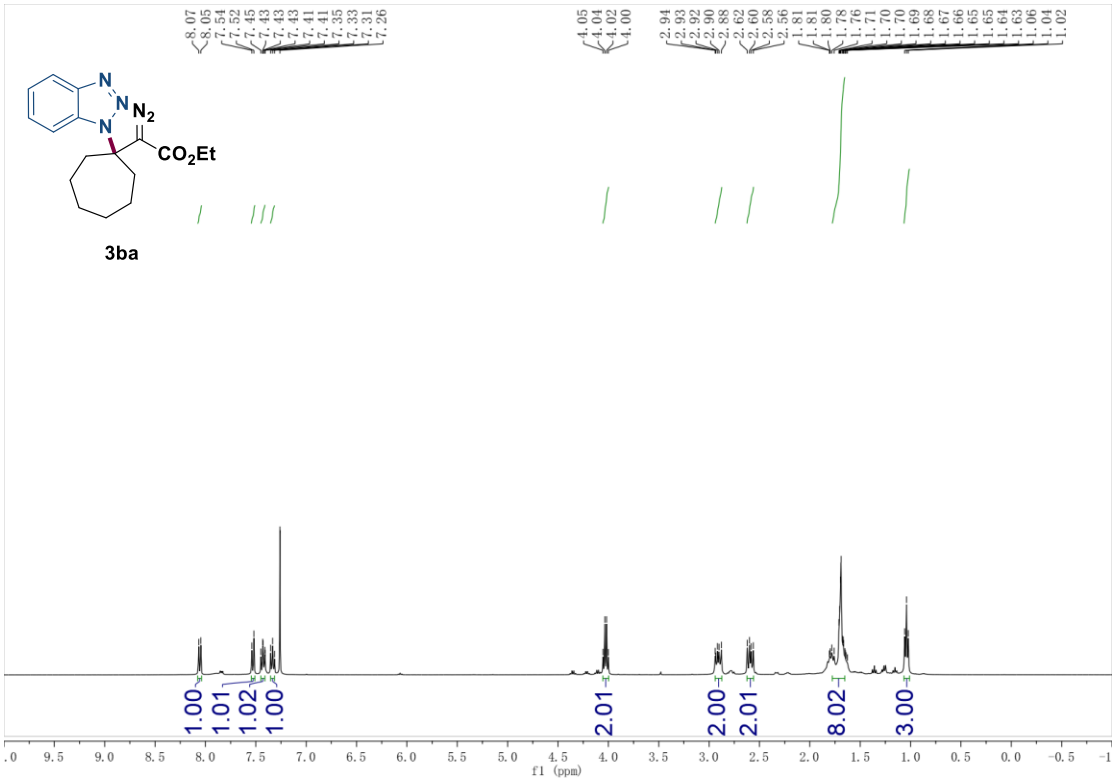
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3aa**



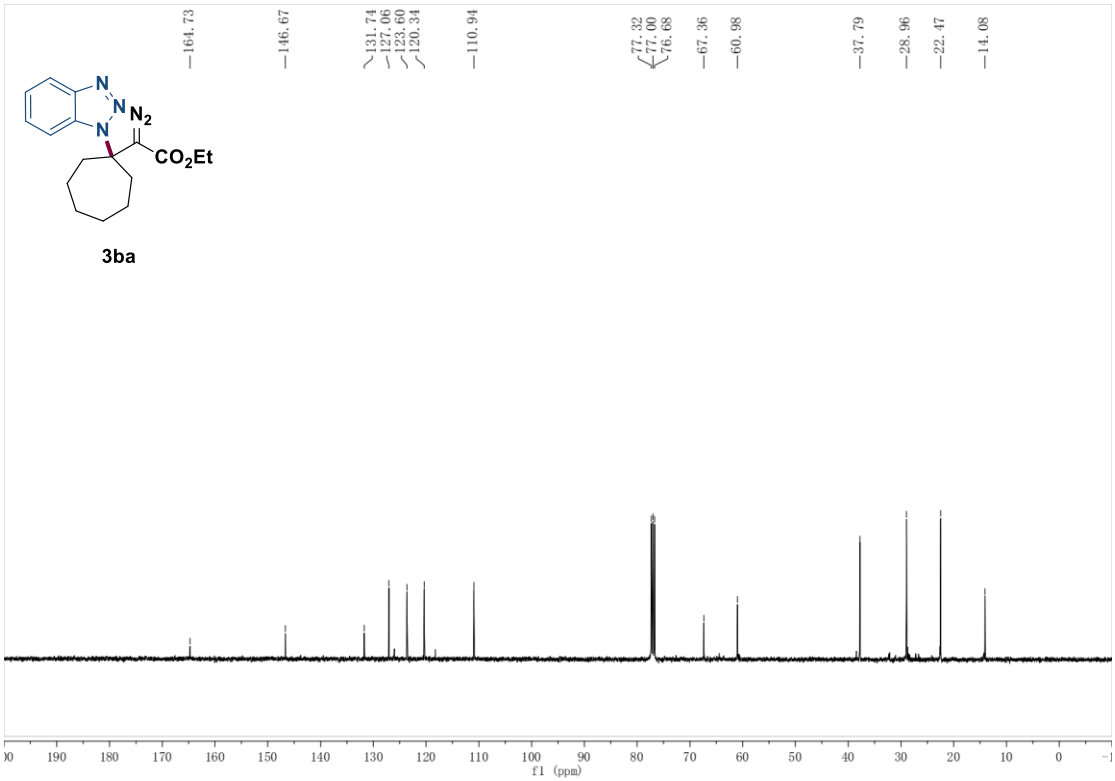
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) Spectrum of **3aa**



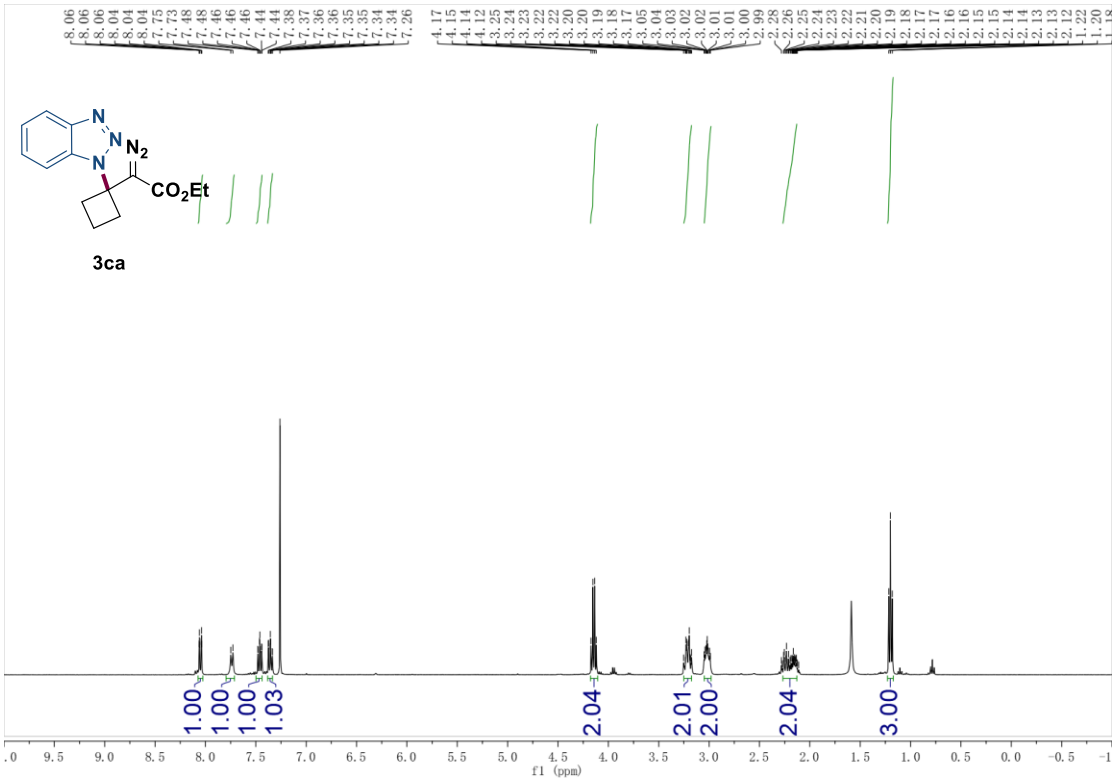
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ba**



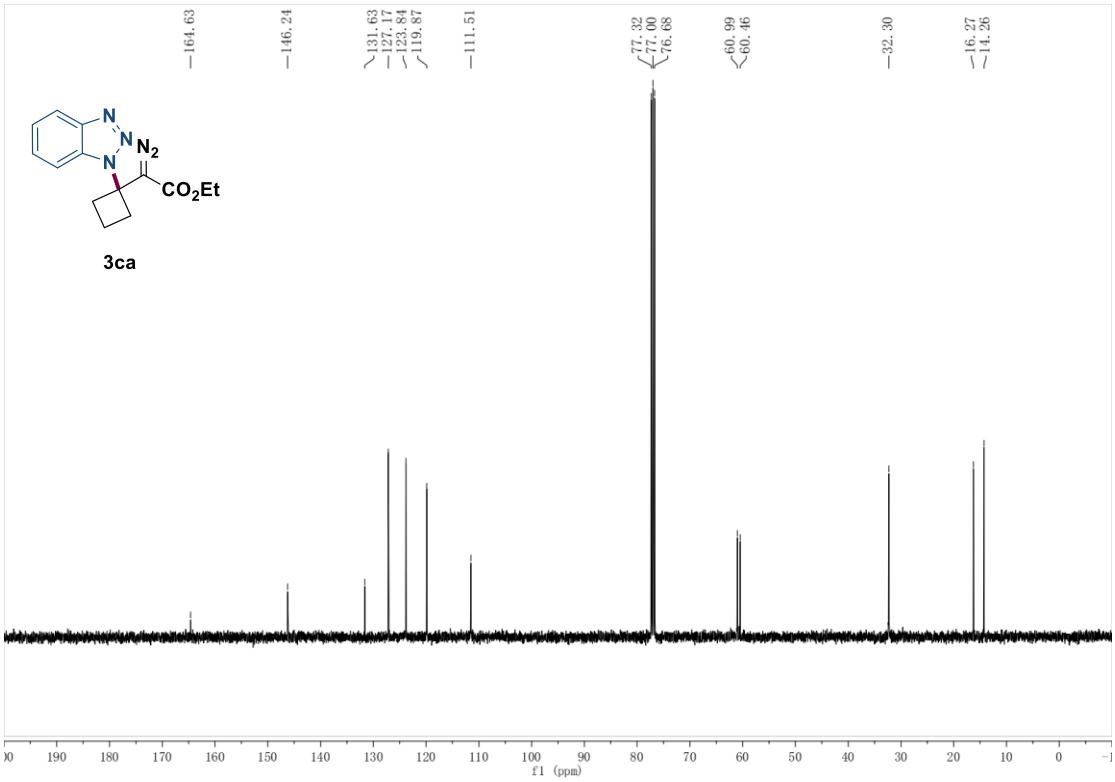
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ba**



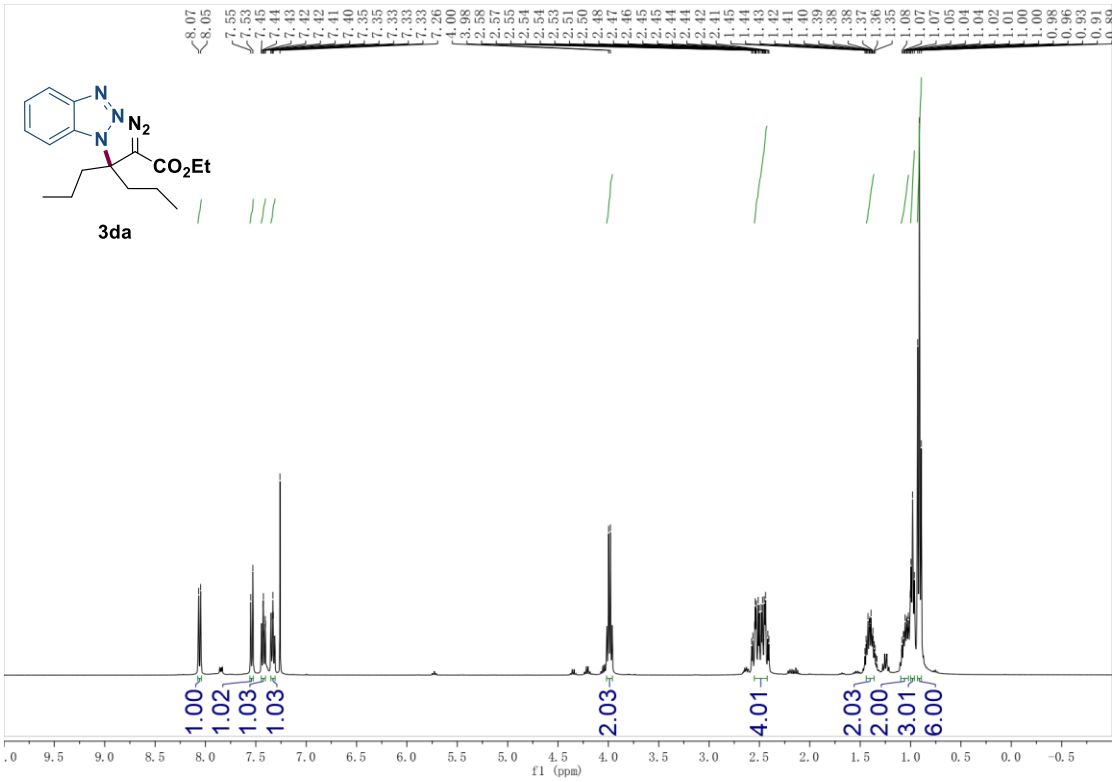
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ca**



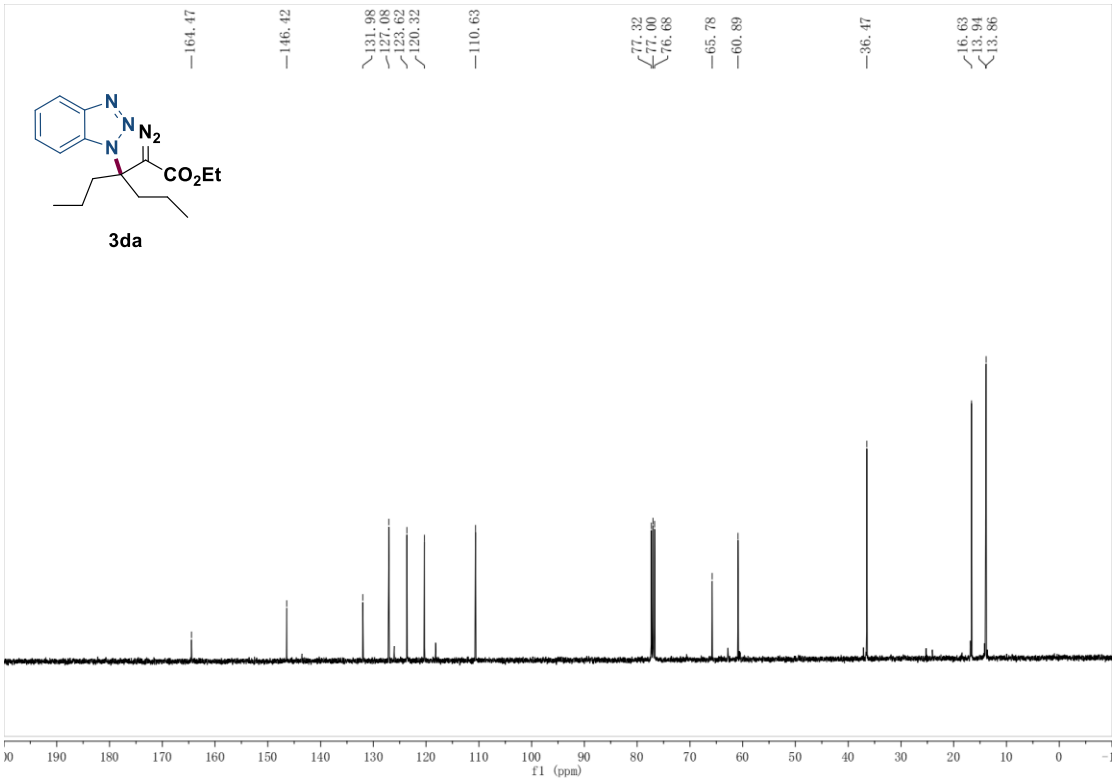
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ca**



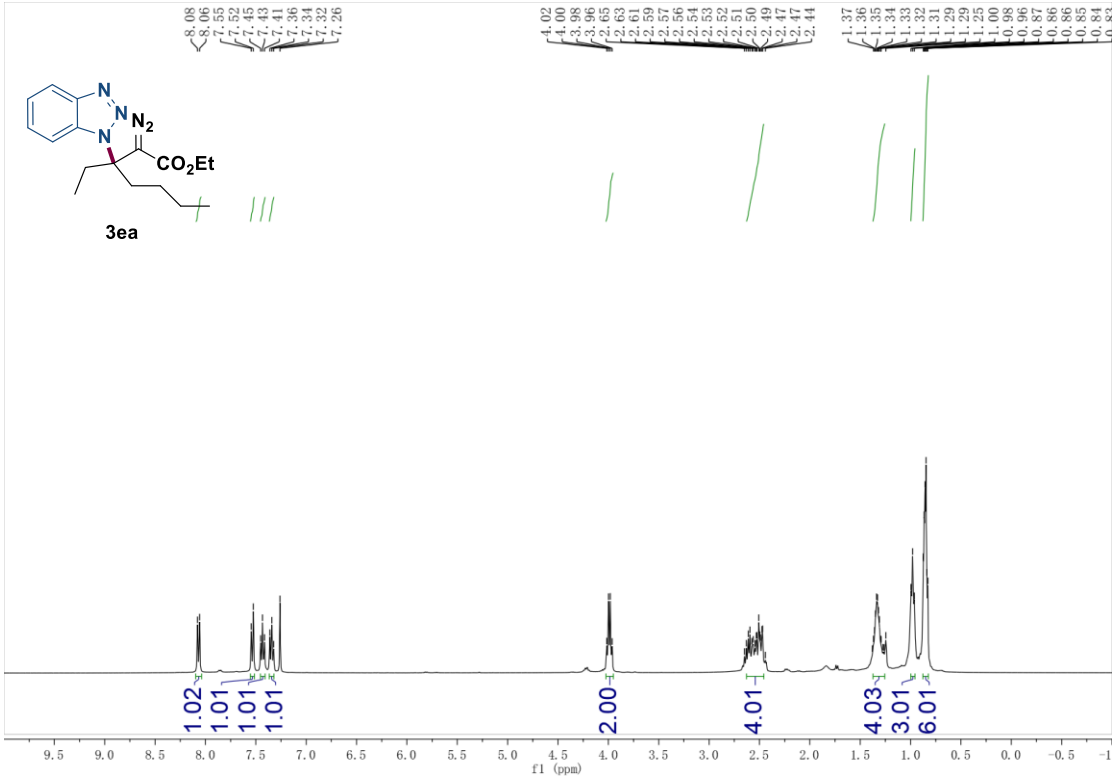
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3da**



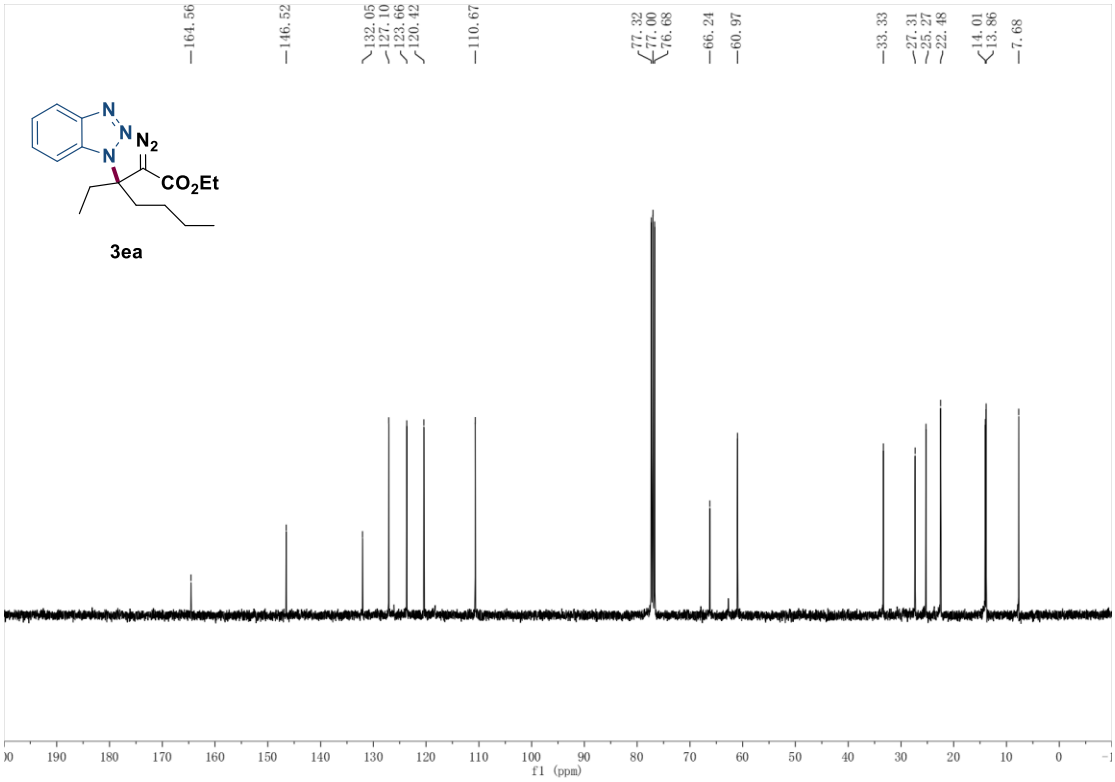
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3da**



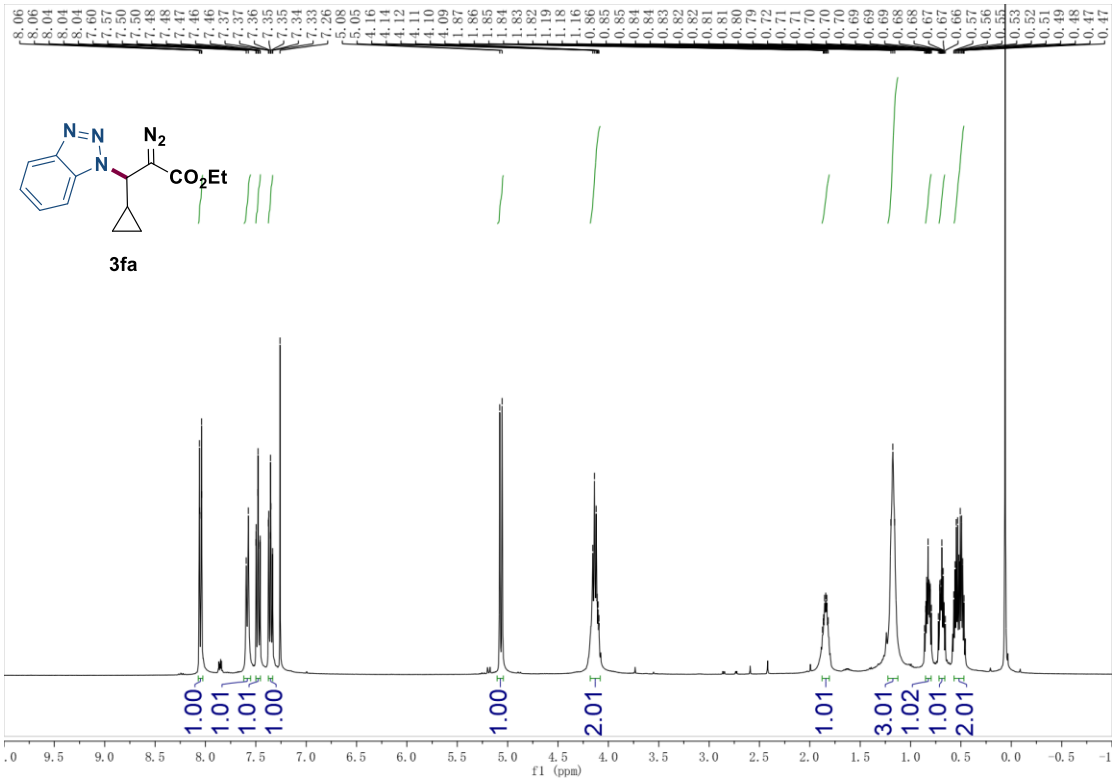
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ea**



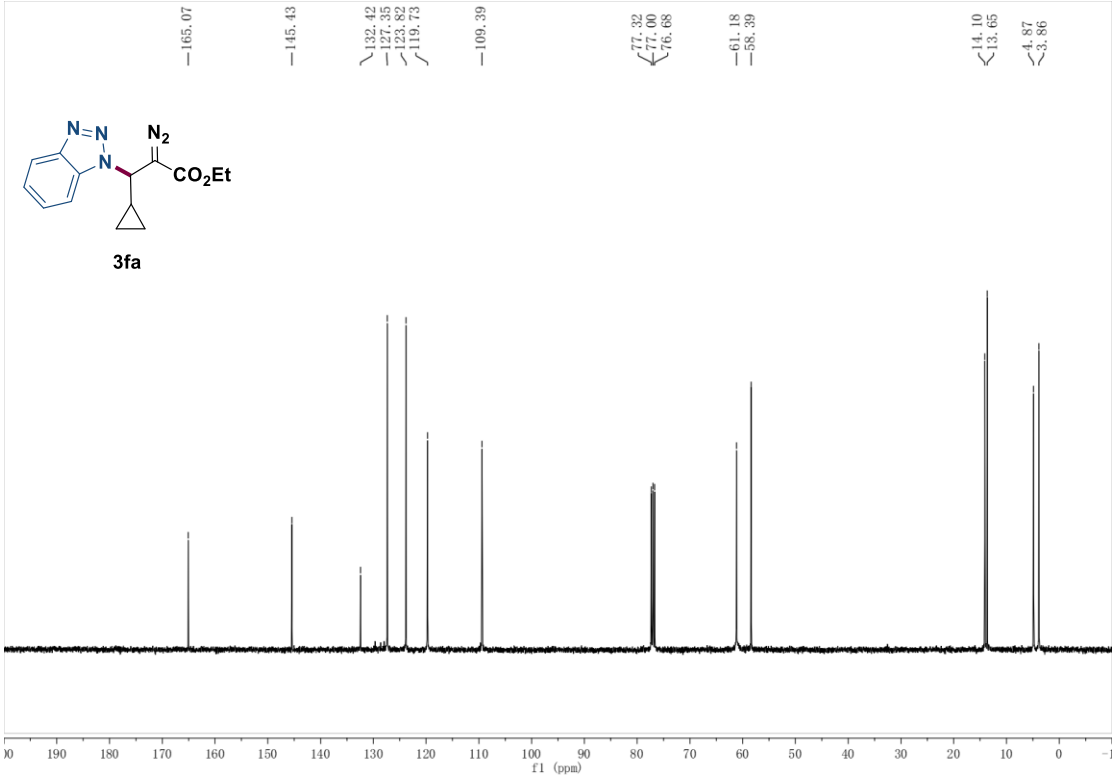
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ea**



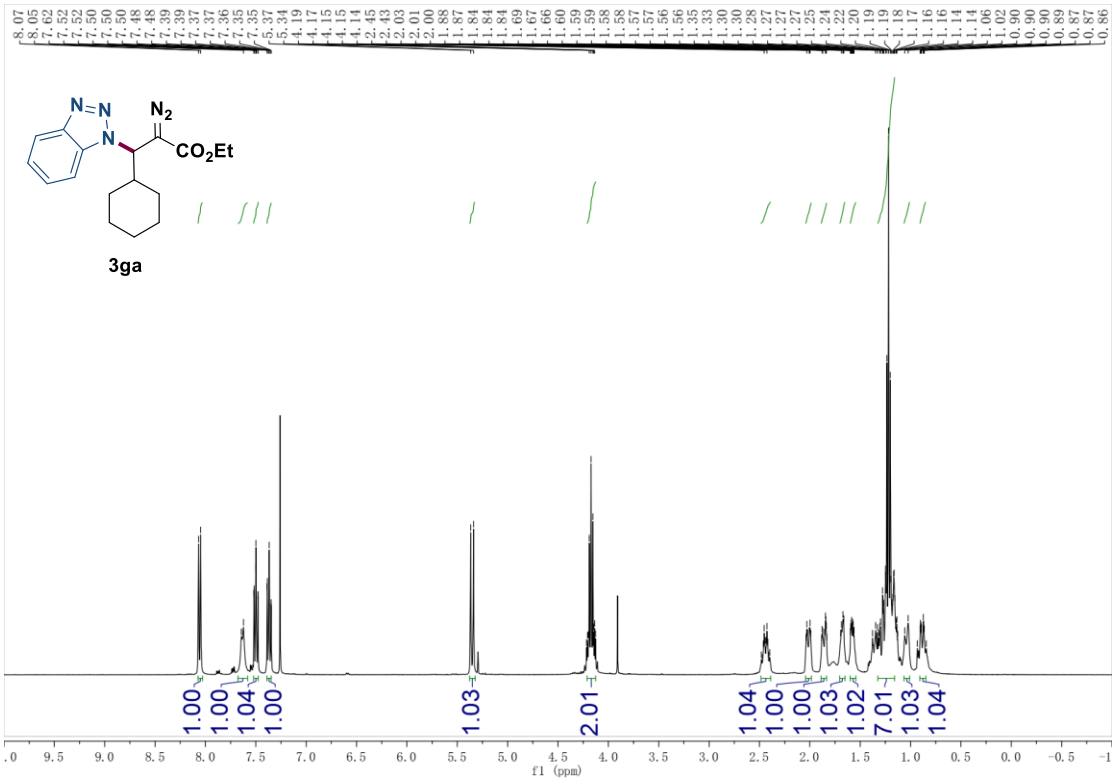
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3fa**



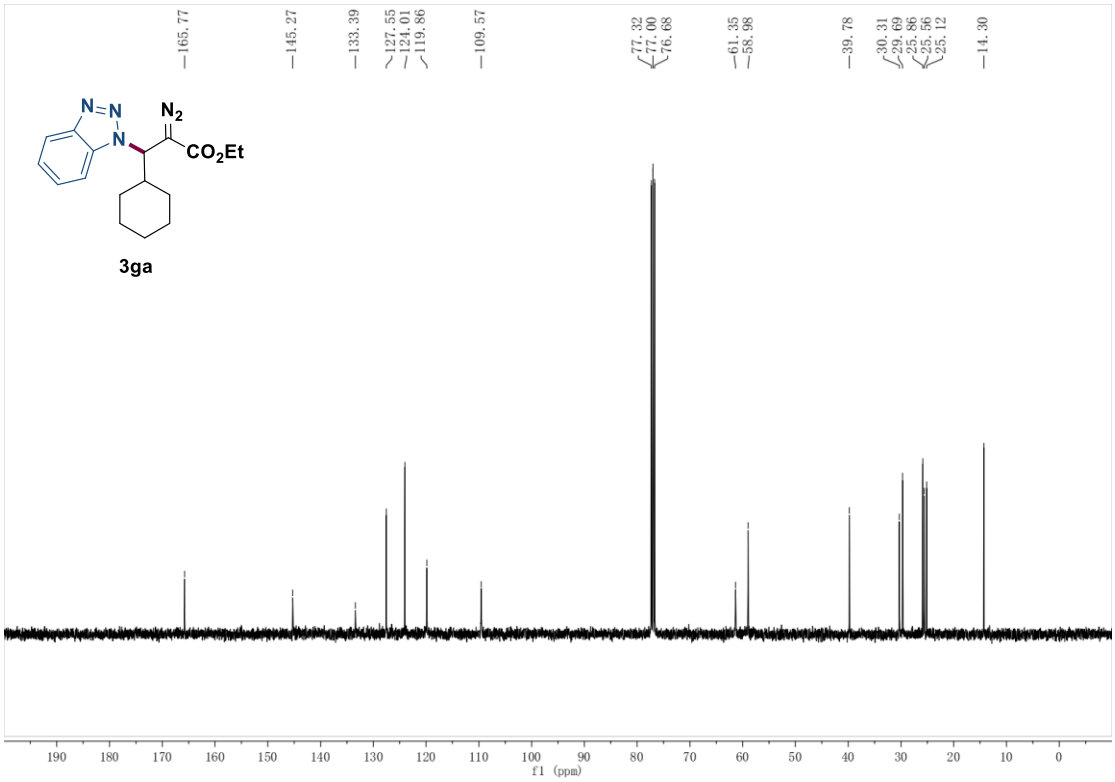
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3fa**



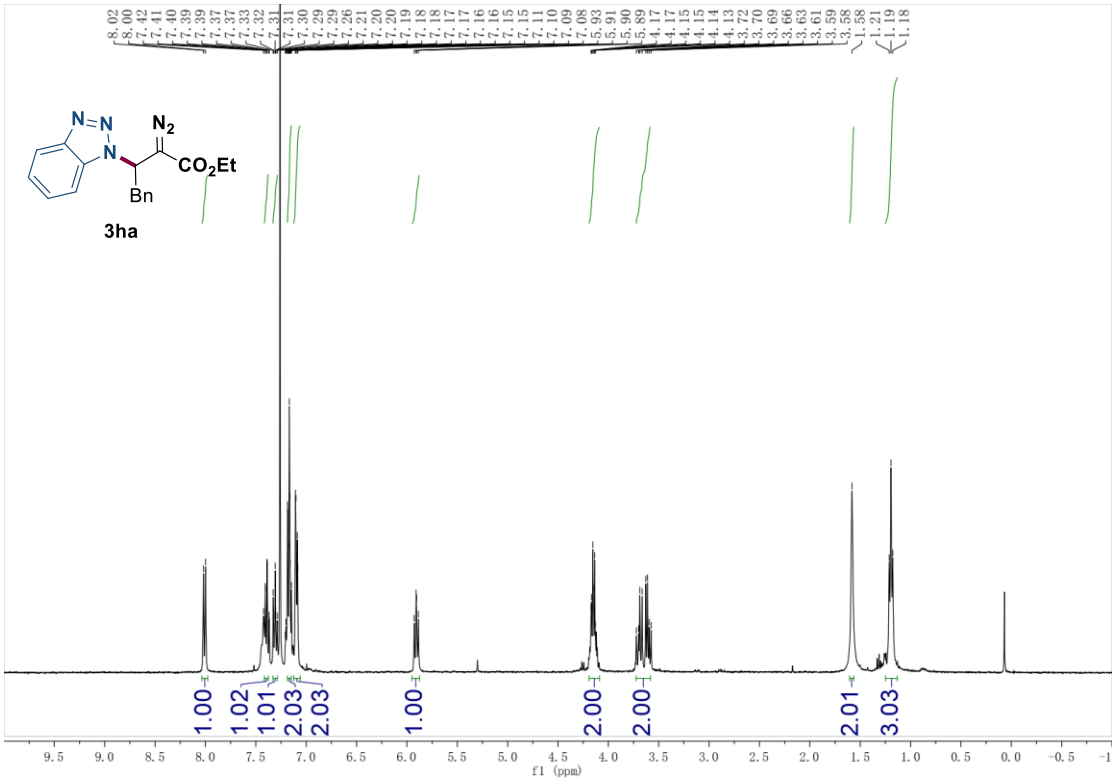
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ga**



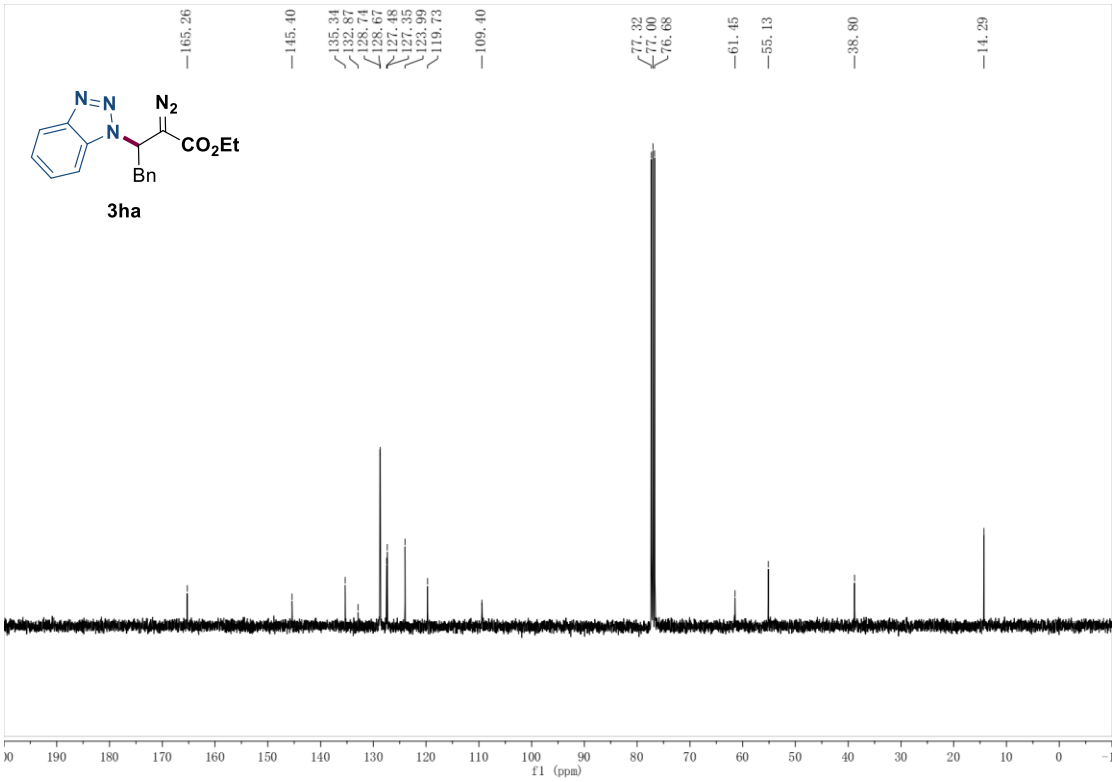
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ga**



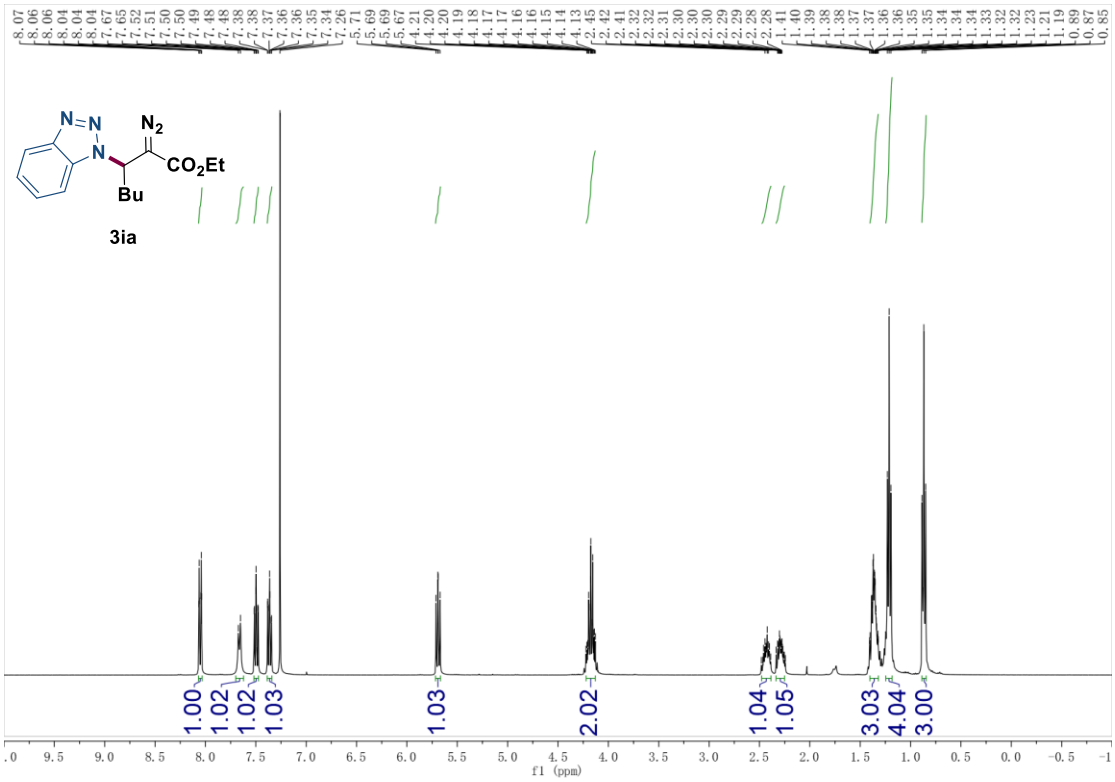
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ha**



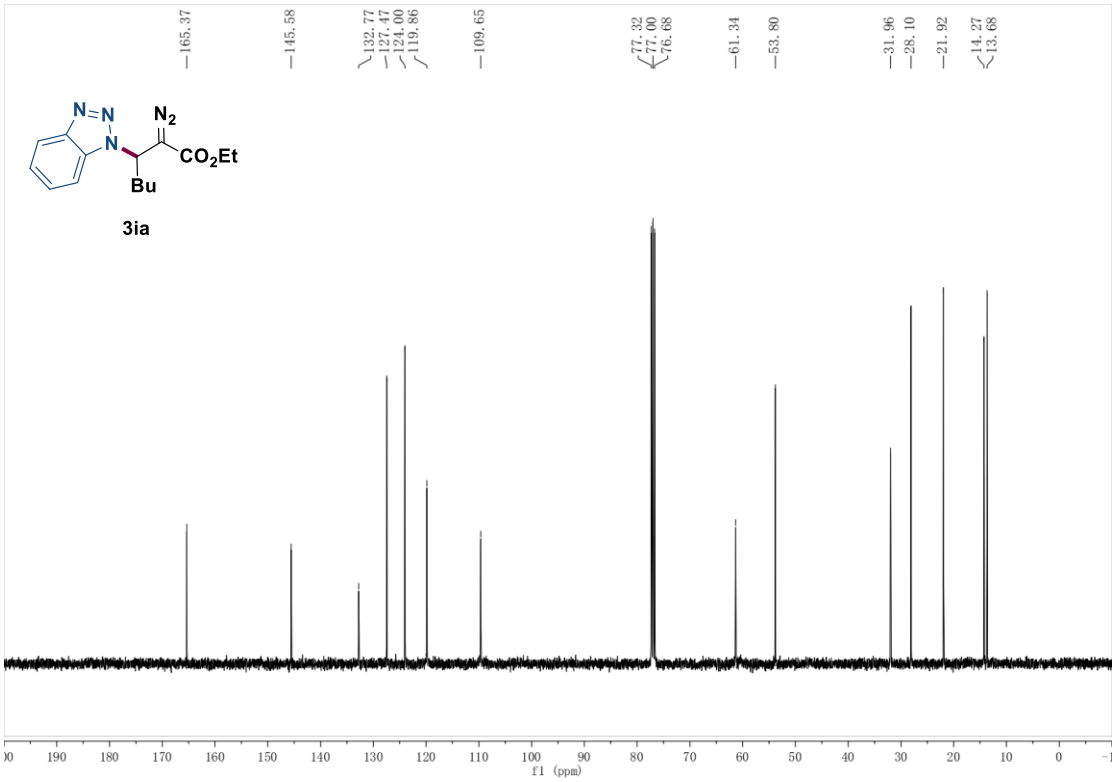
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ha**



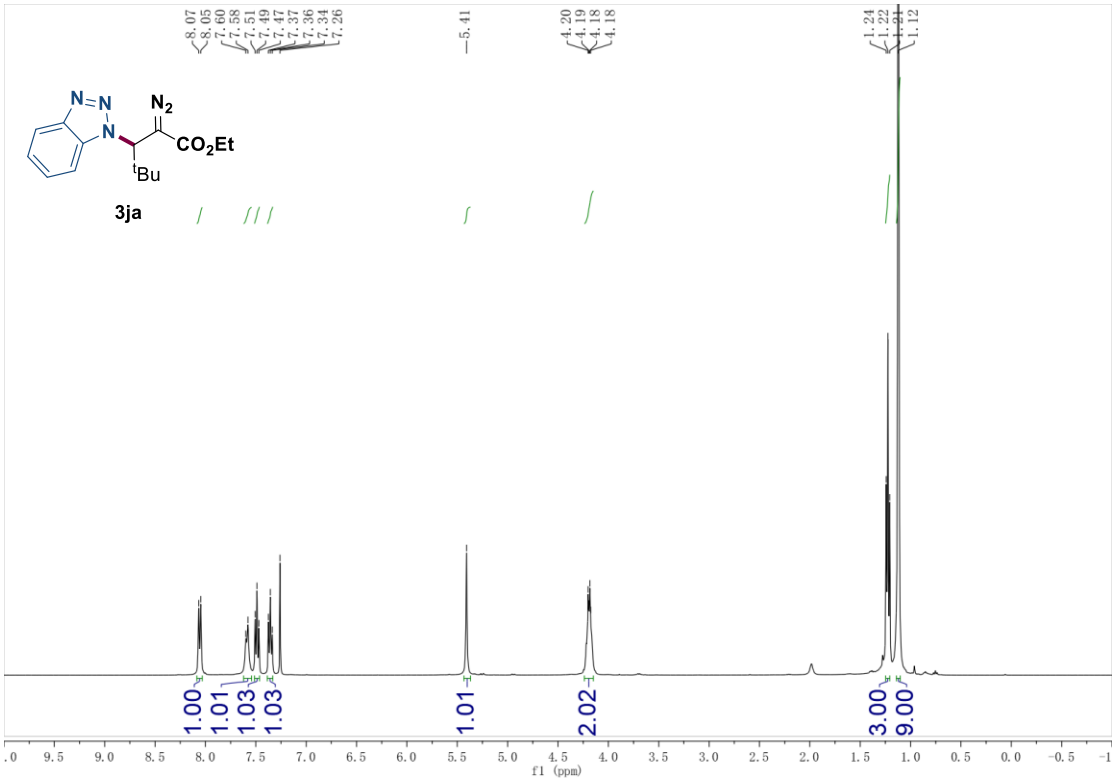
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ia**



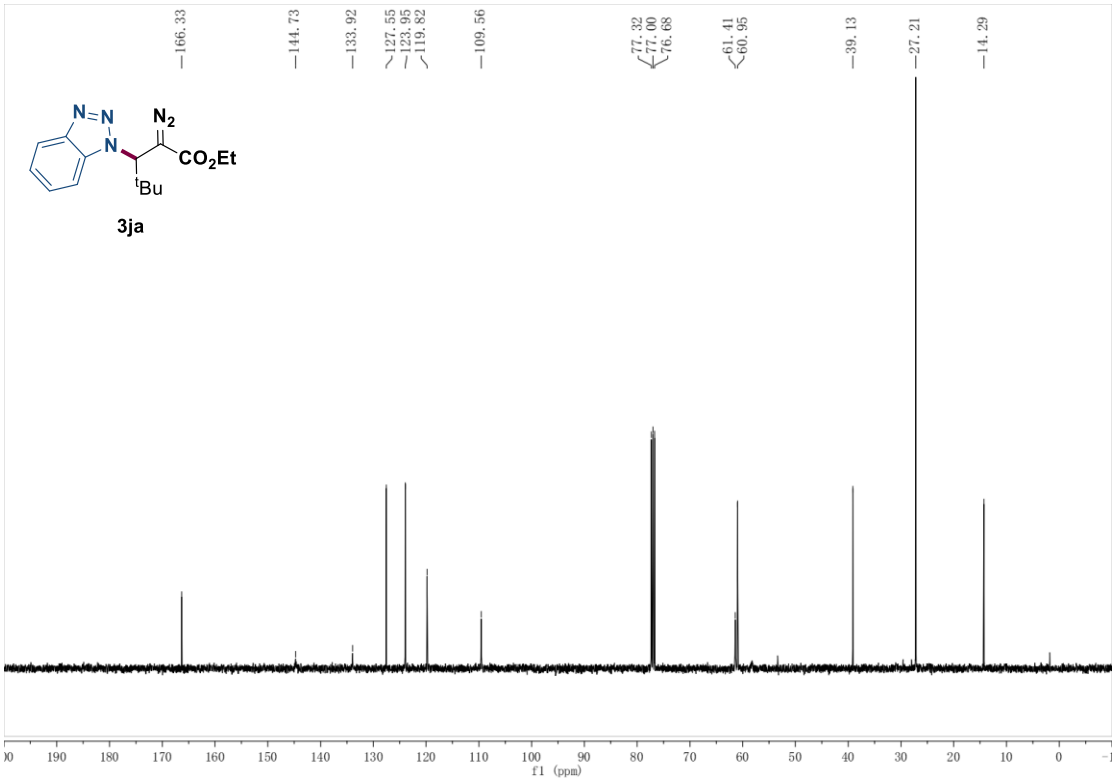
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ia**



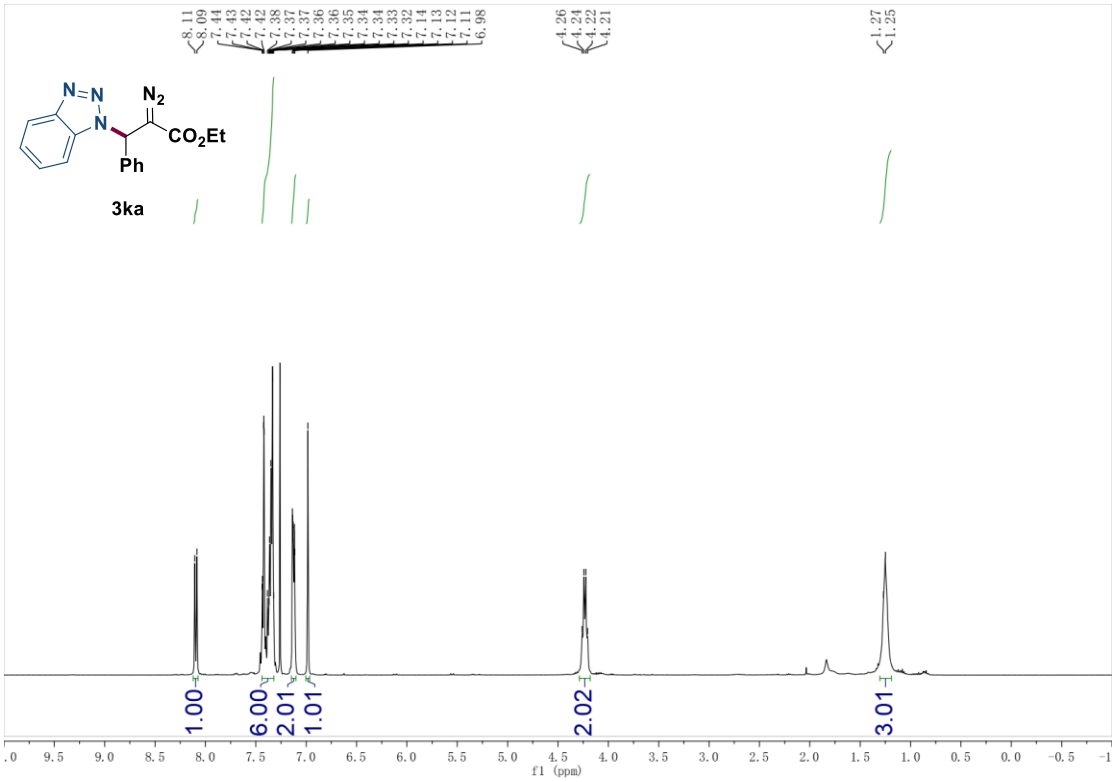
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ja**



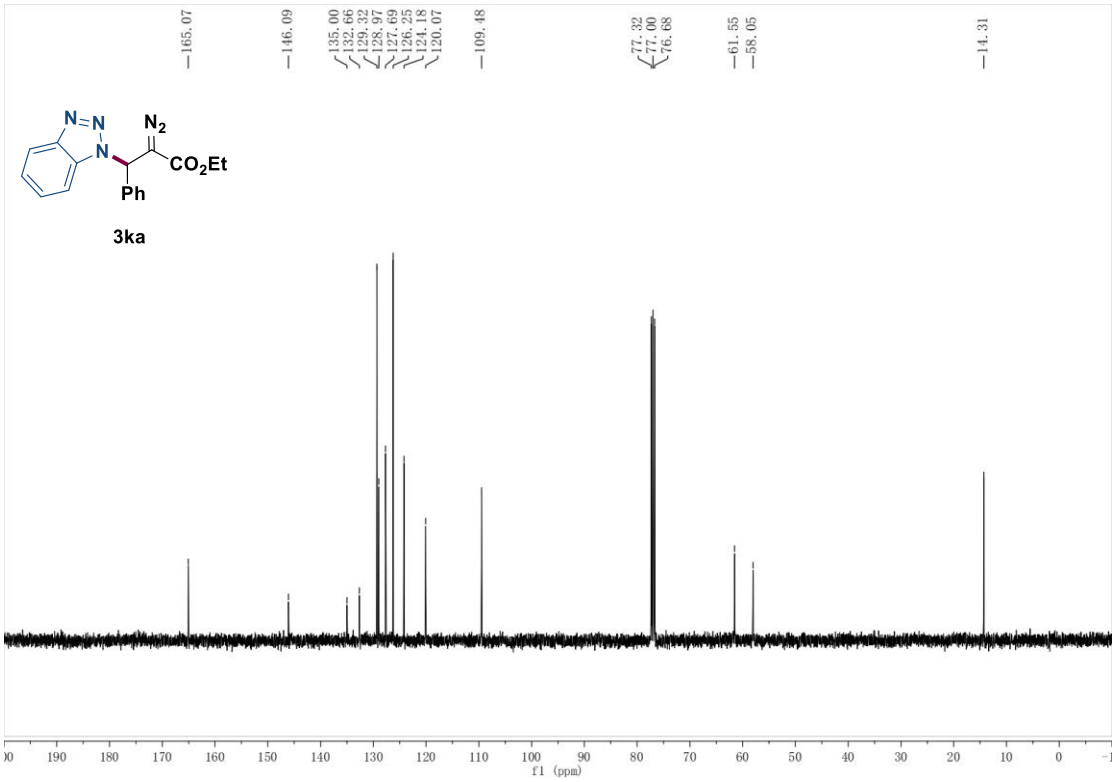
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ja**



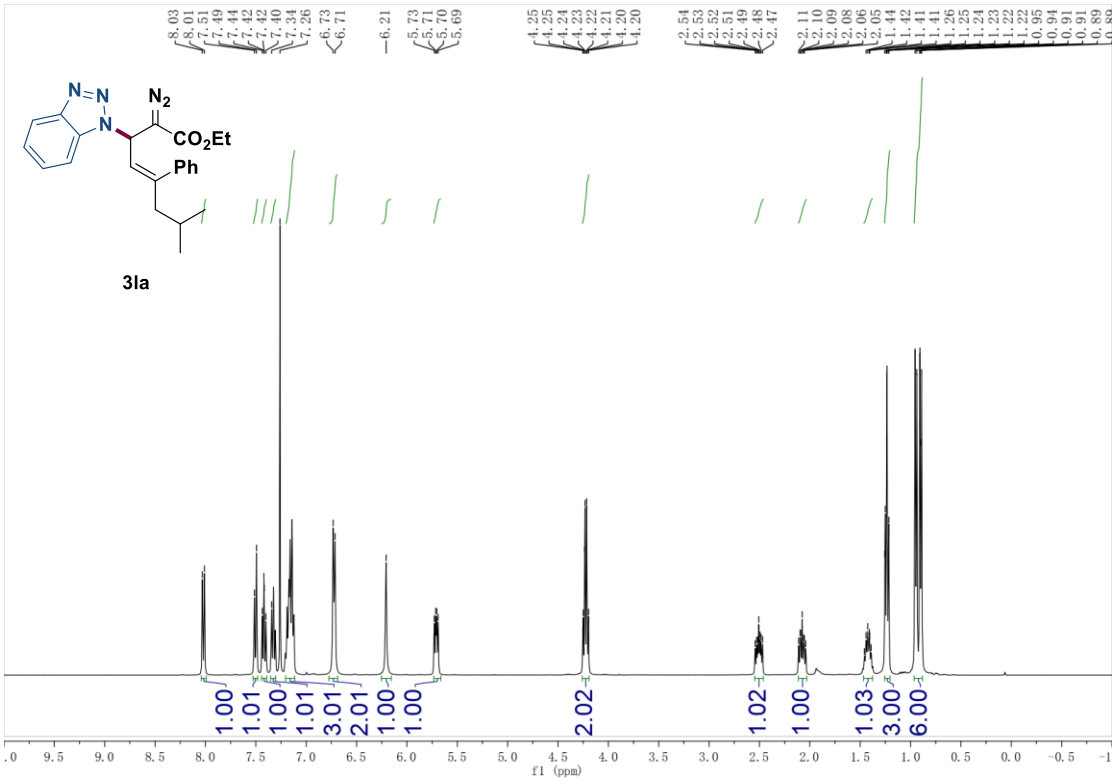
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ka**



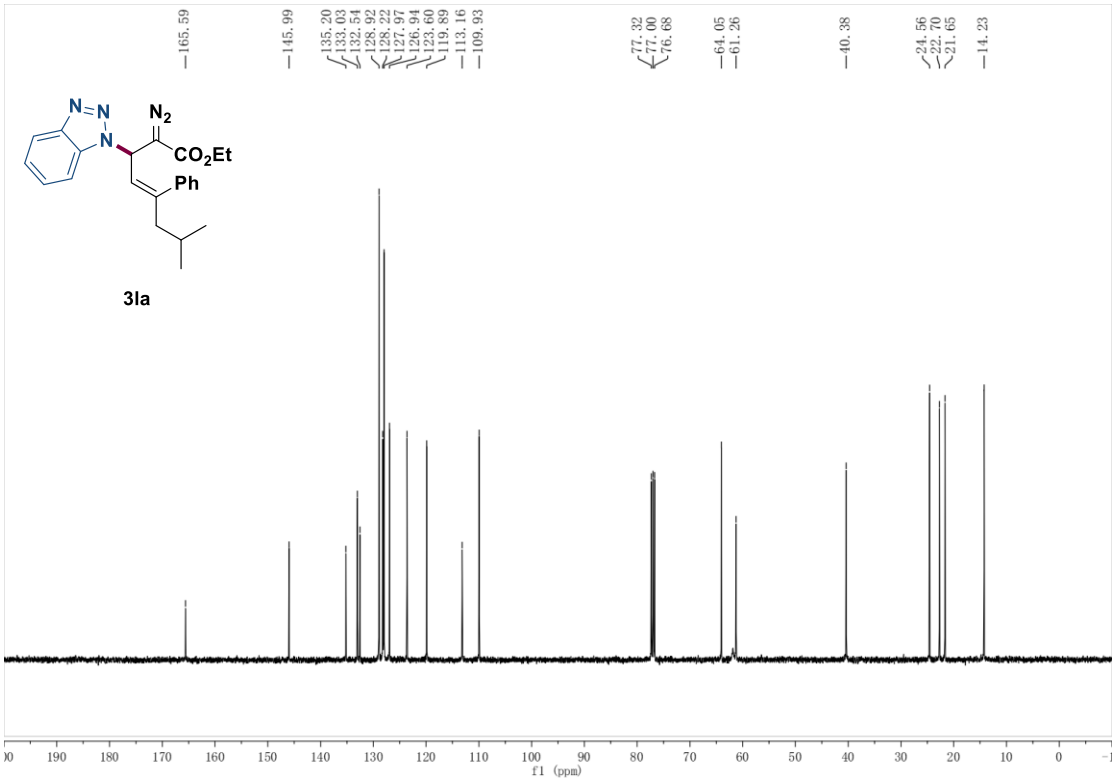
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ka**



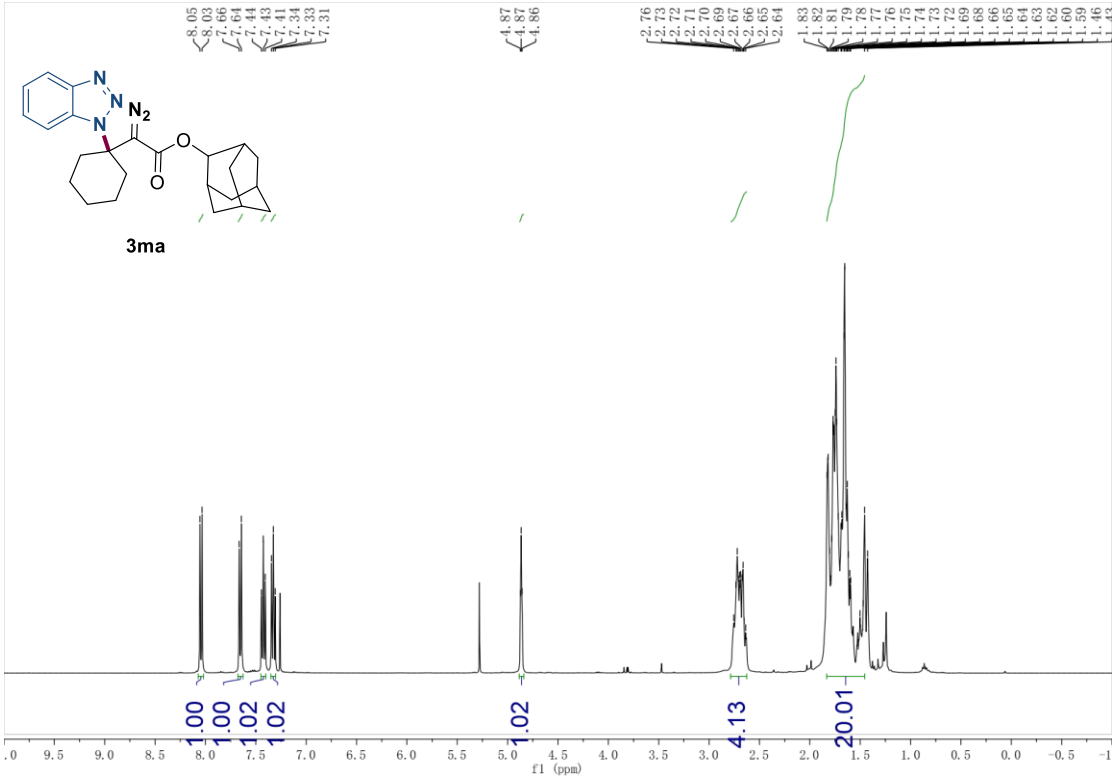
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3la**



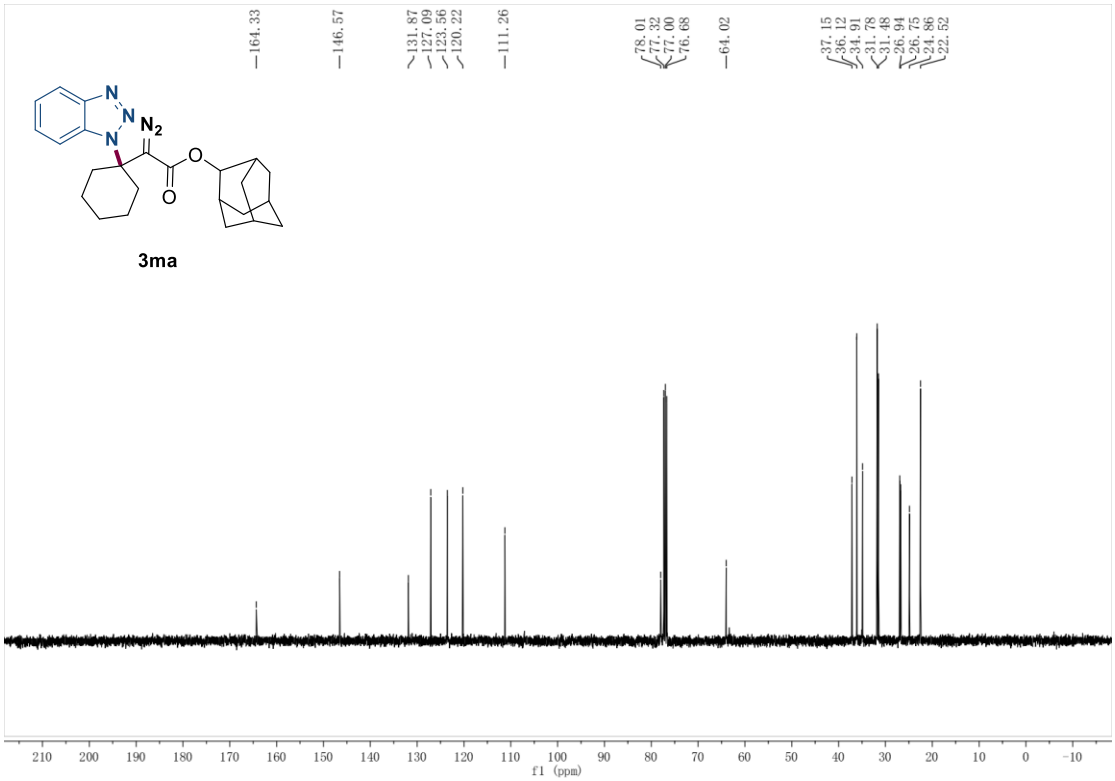
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3la**



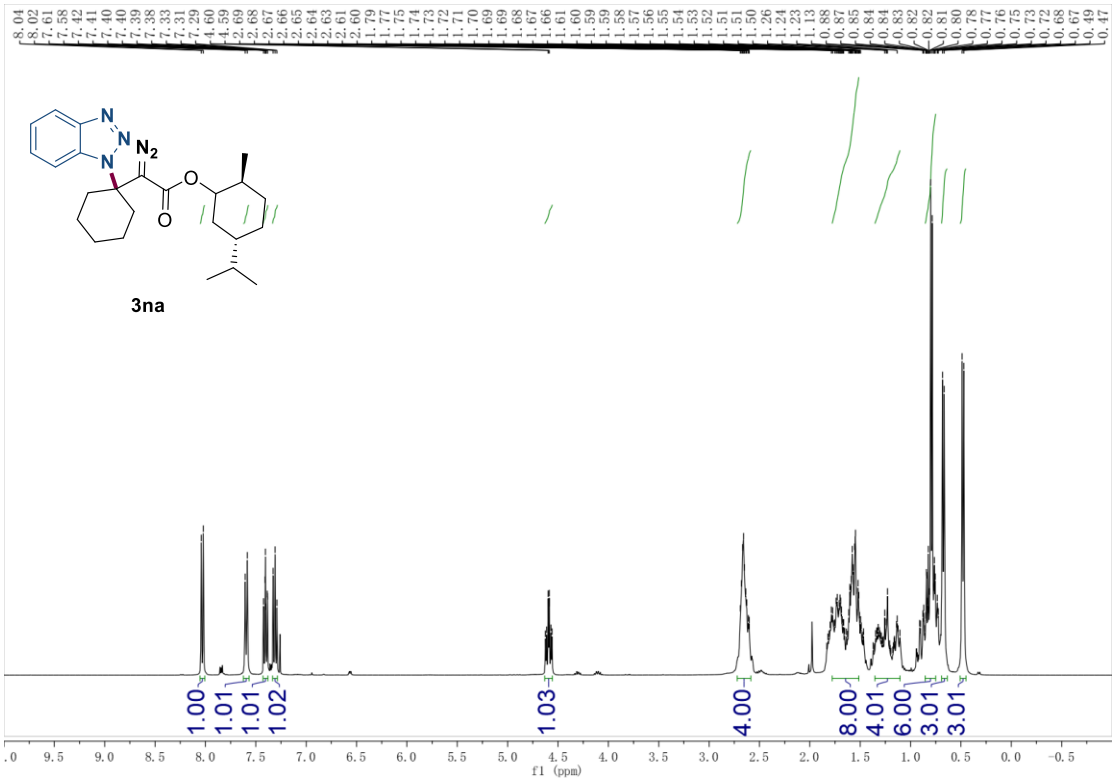
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ma**



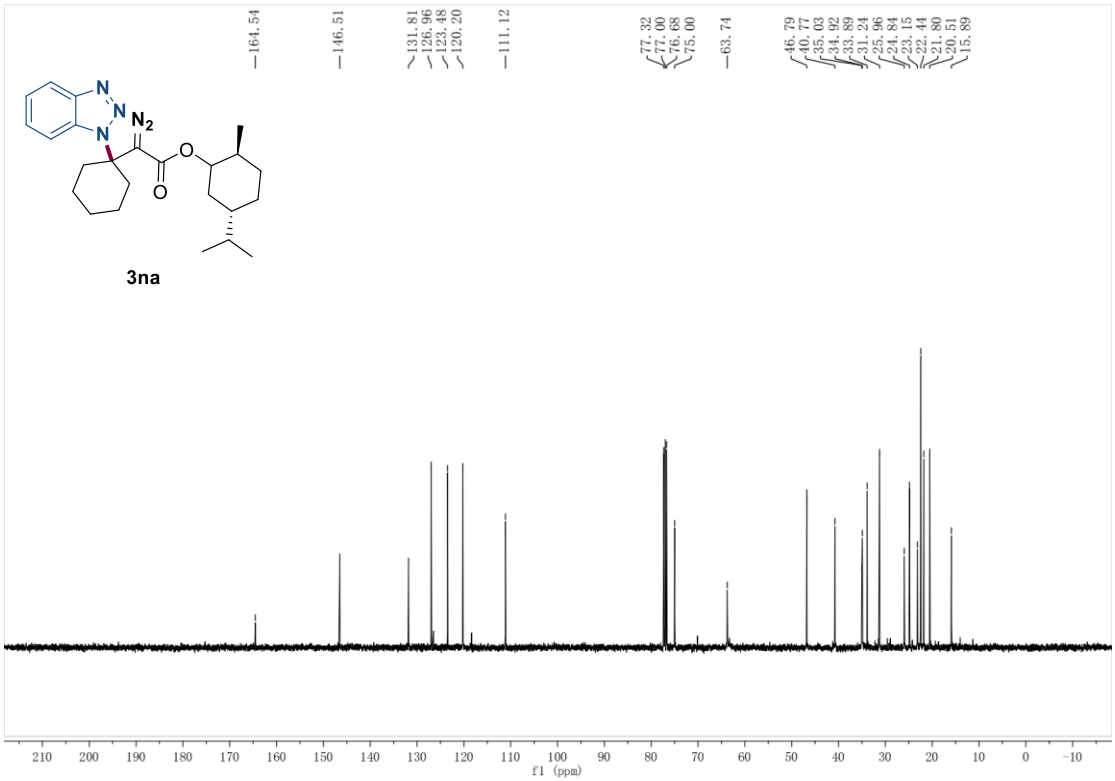
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ma**



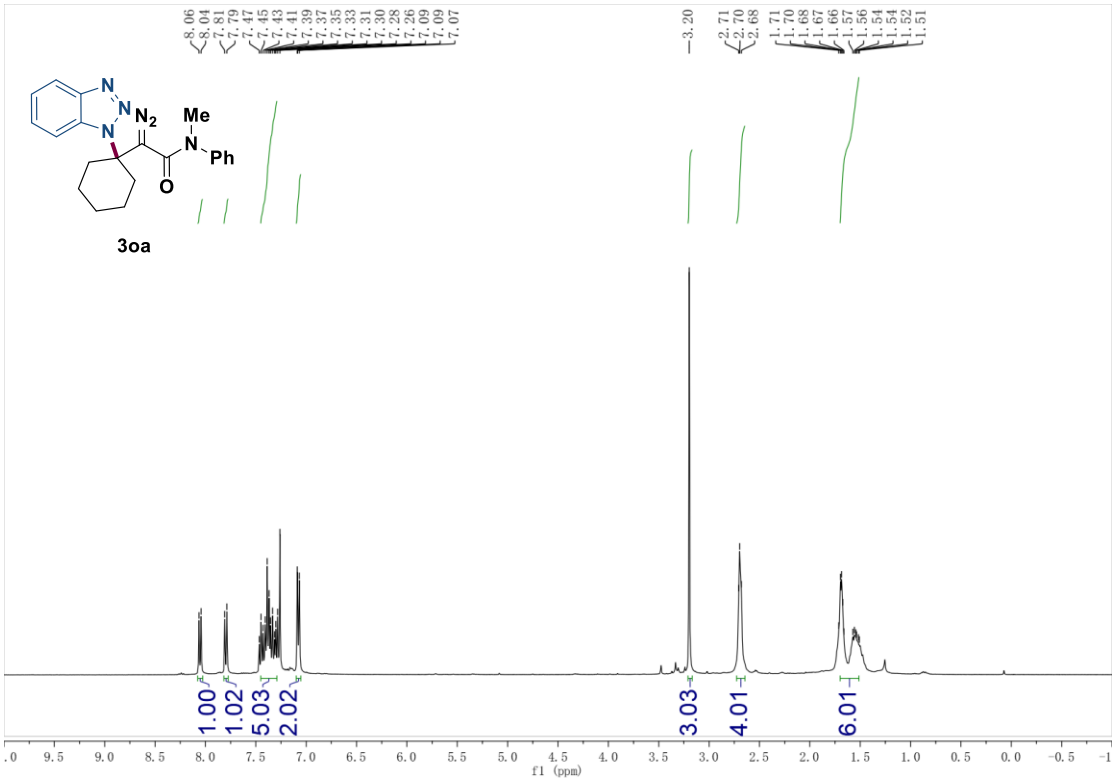
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3na**



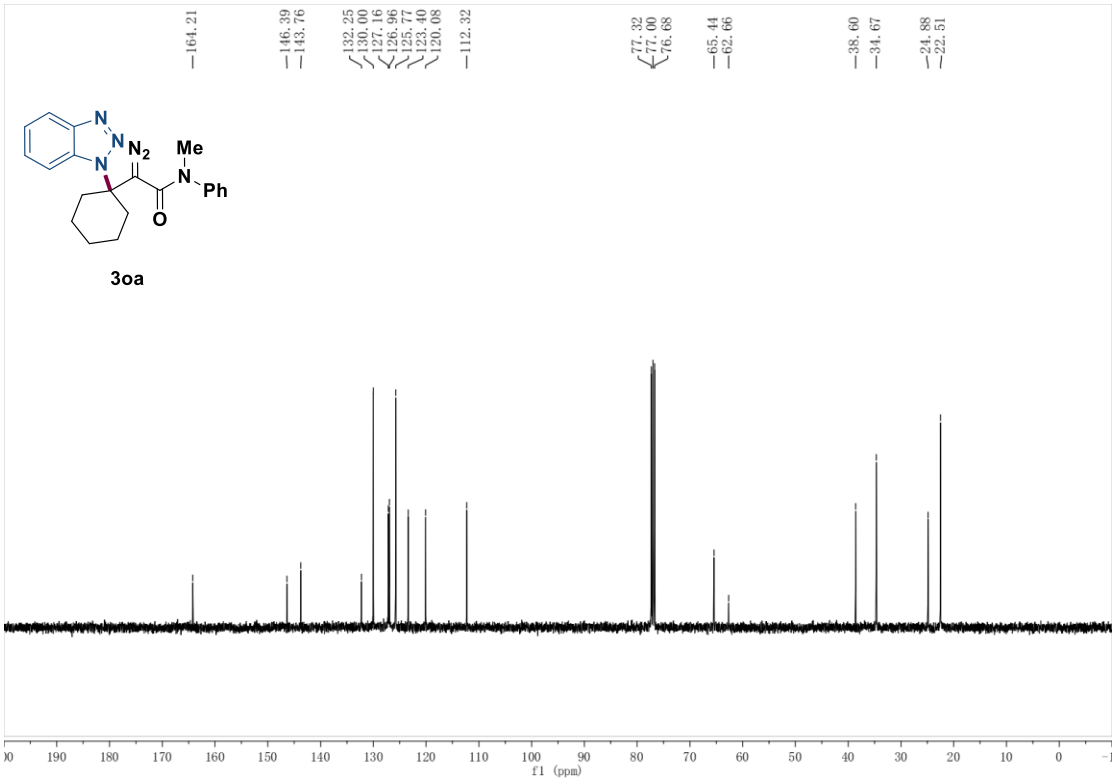
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3na**



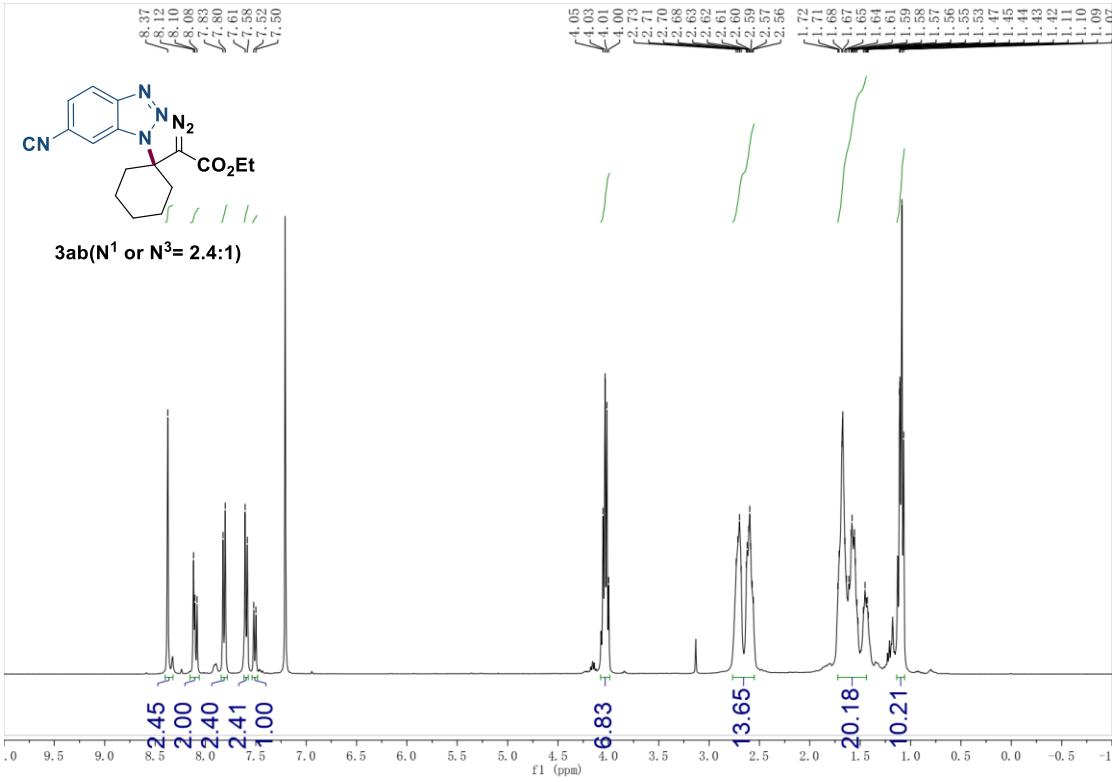
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3oa**



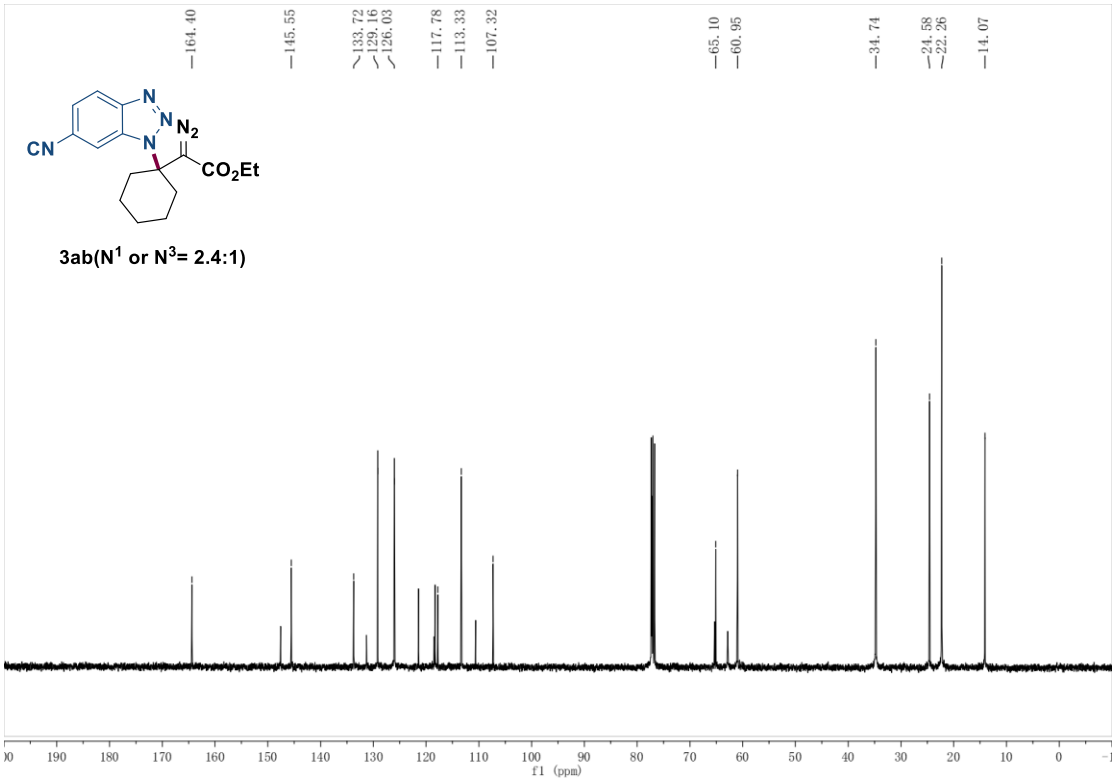
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3oa**



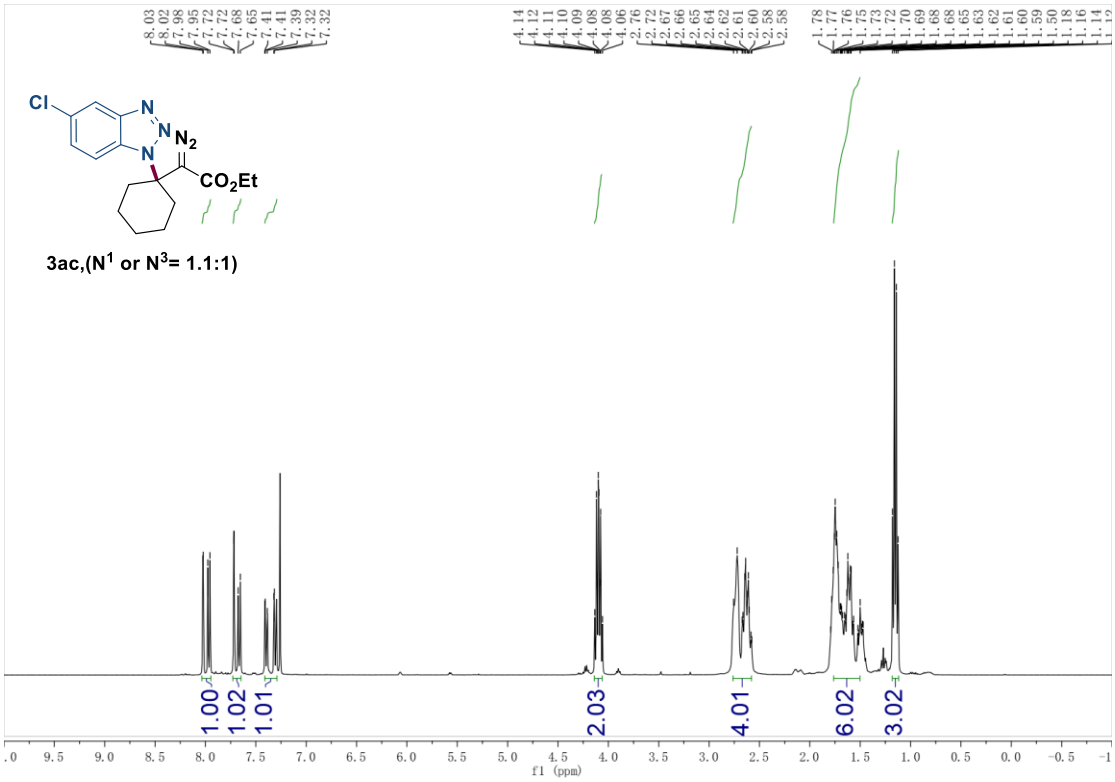
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ab**



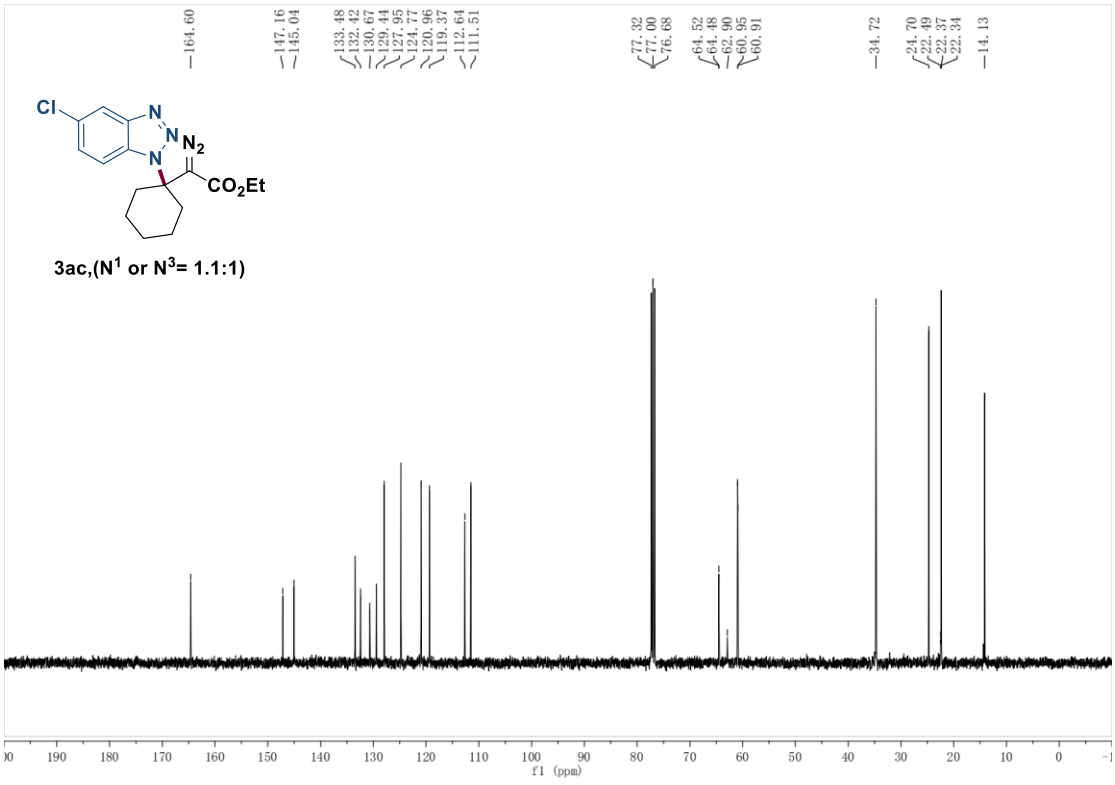
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ab**



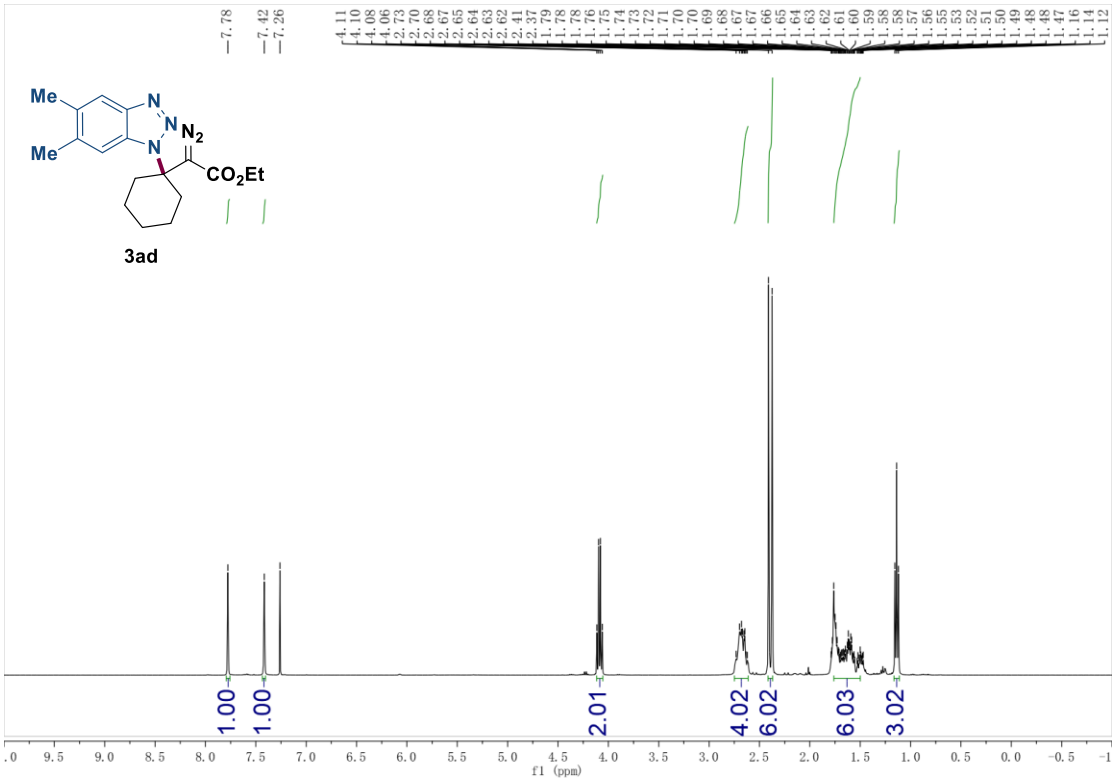
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ac**



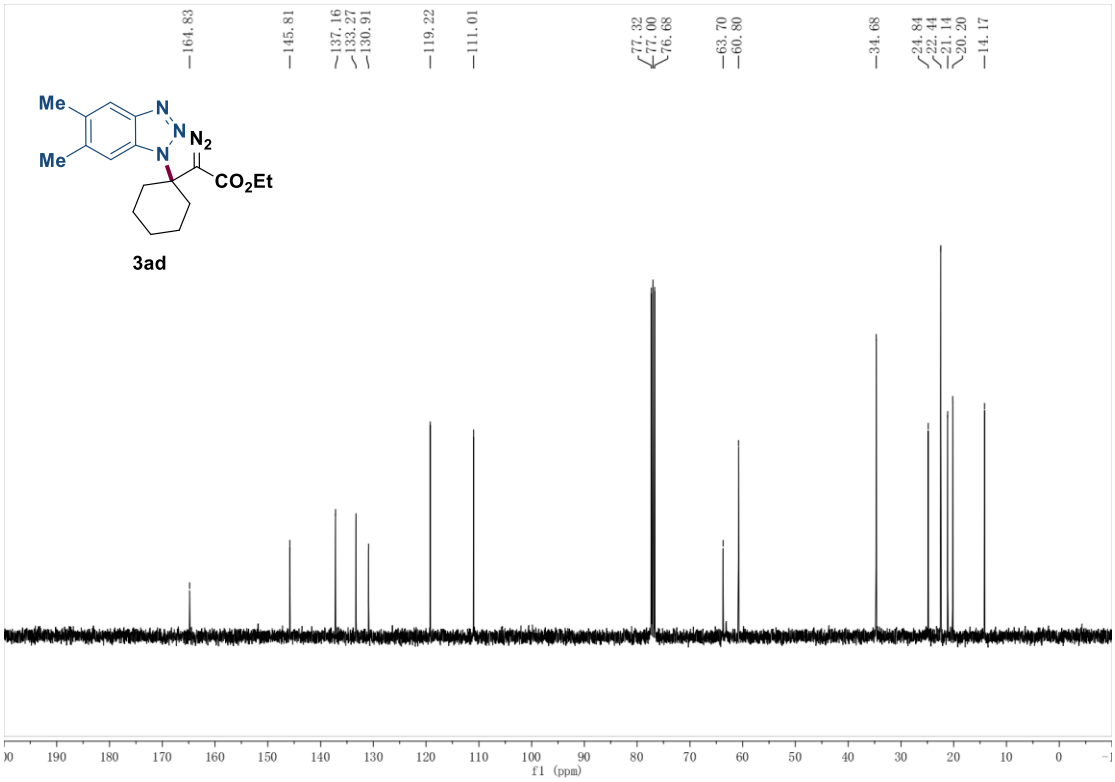
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ac**



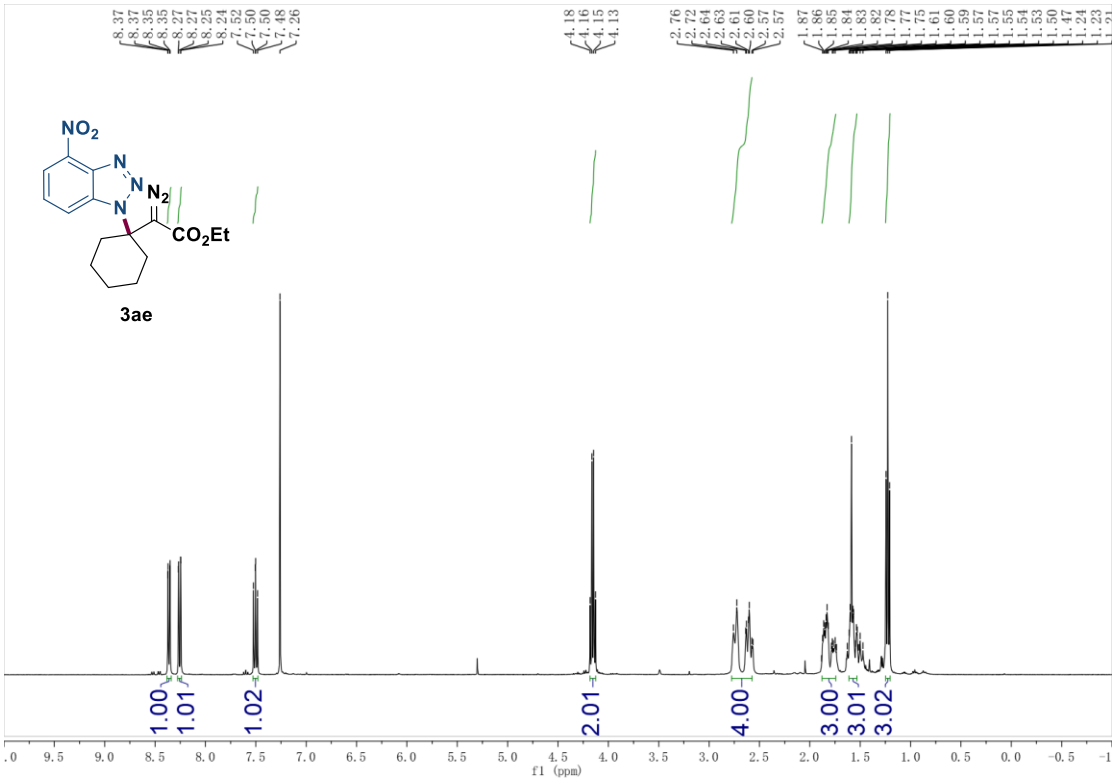
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ad**



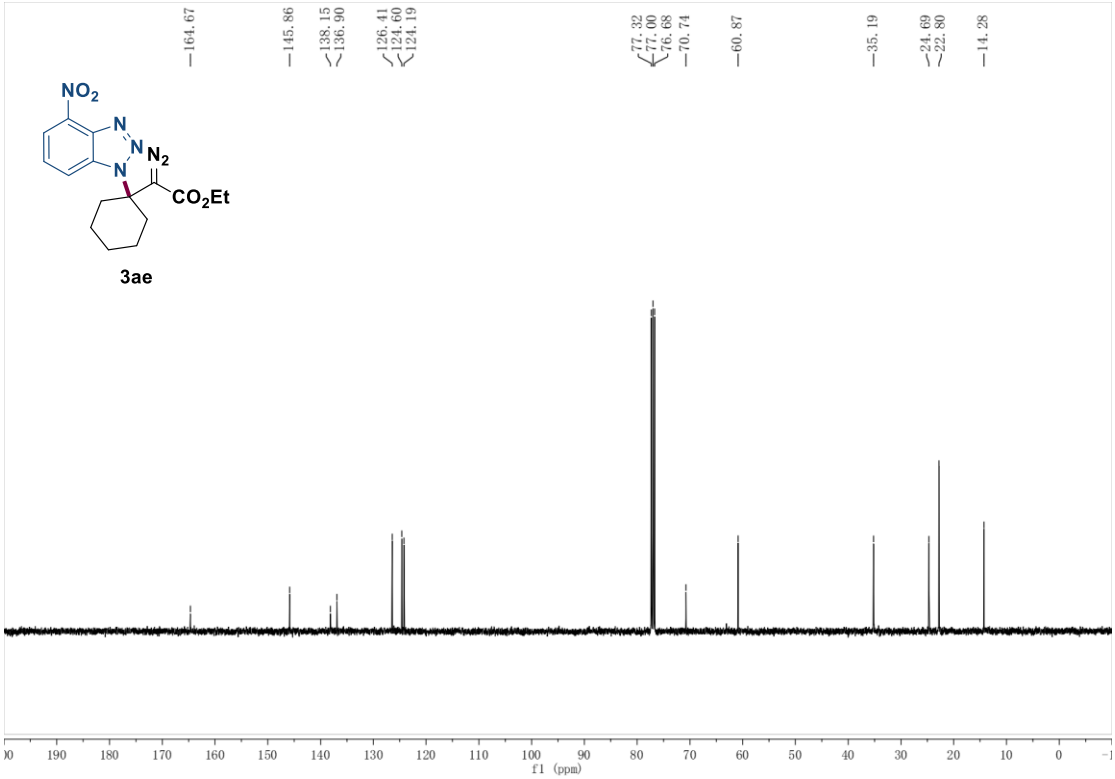
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ad**



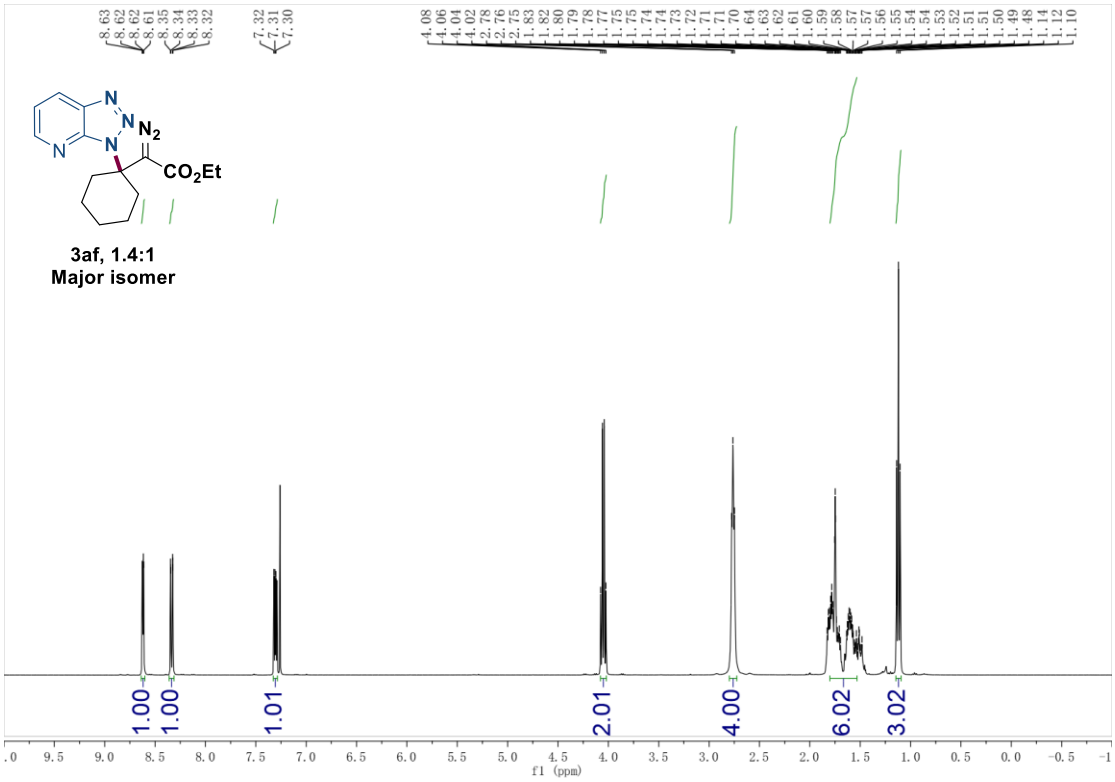
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ae**



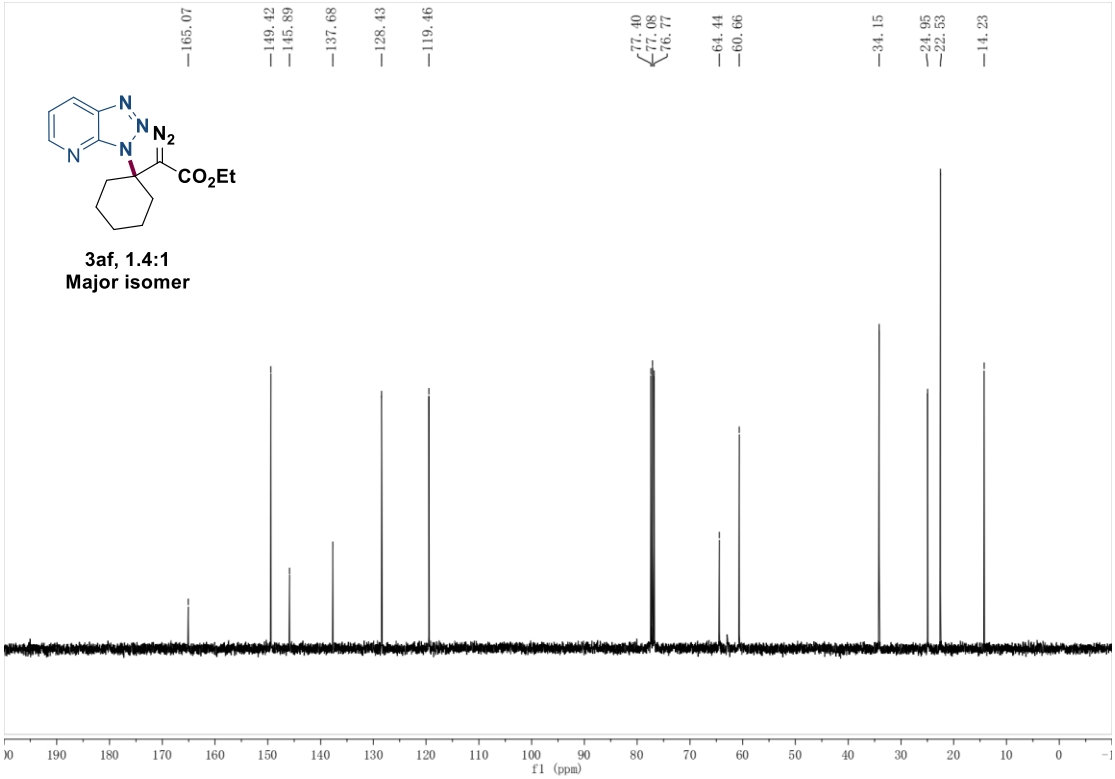
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ae**



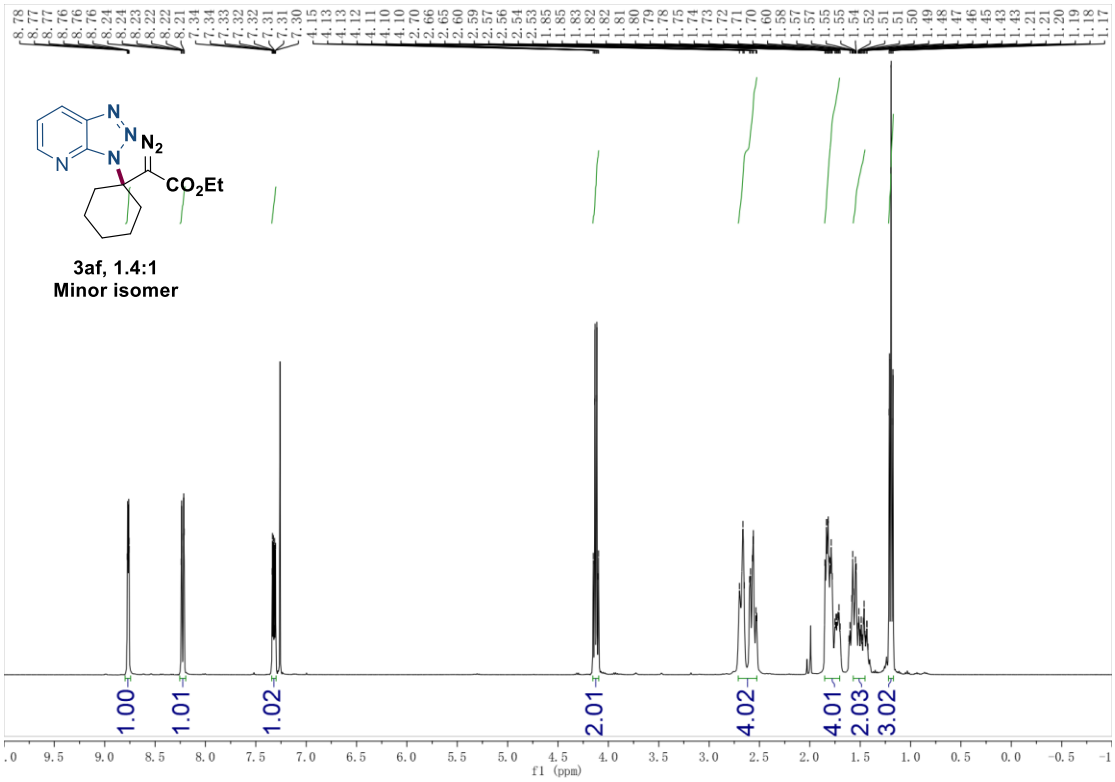
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3af**



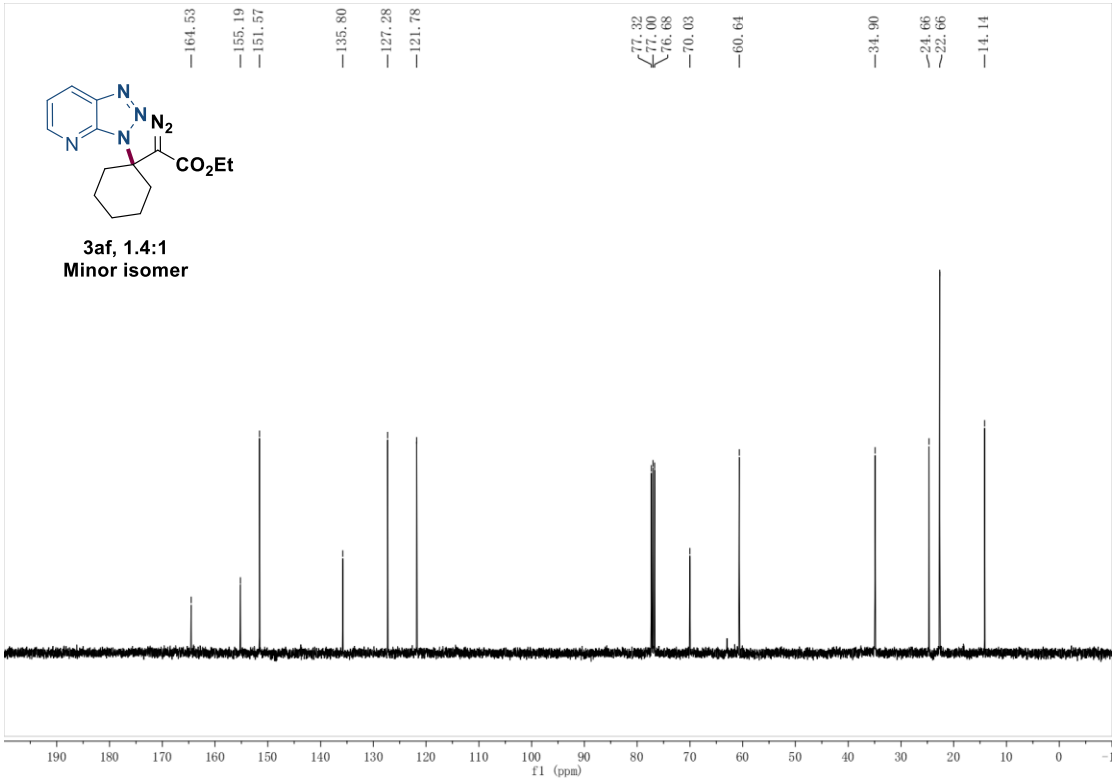
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3af**



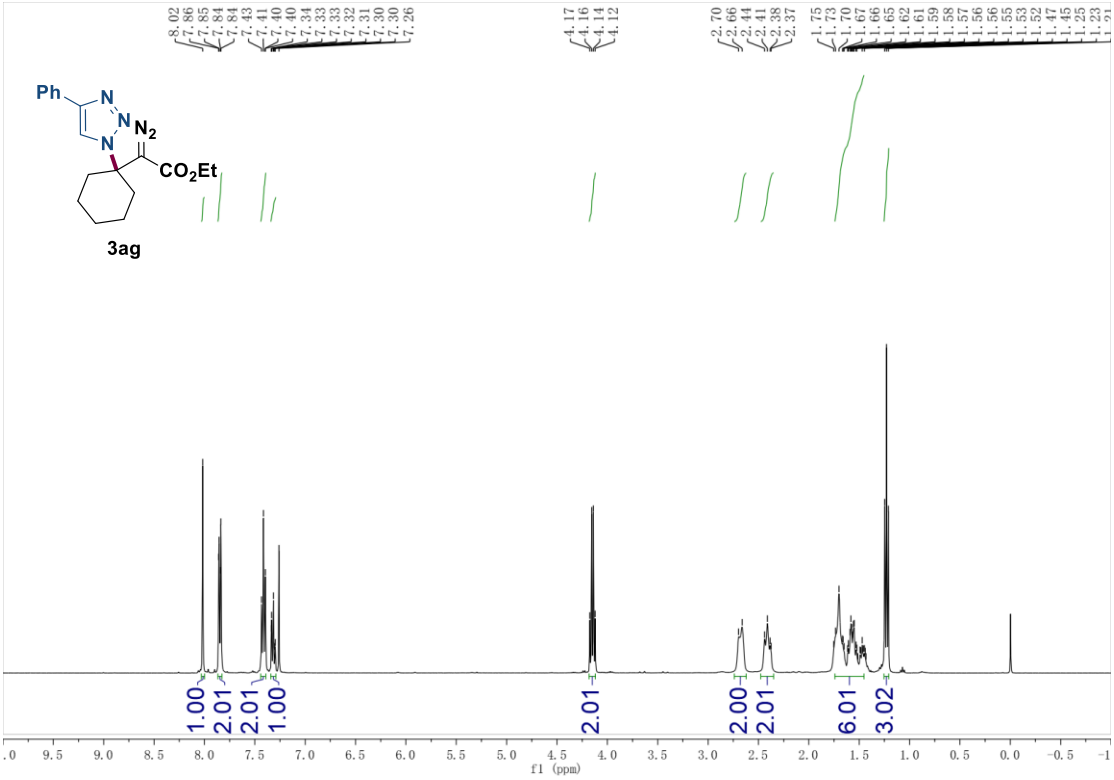
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3af**



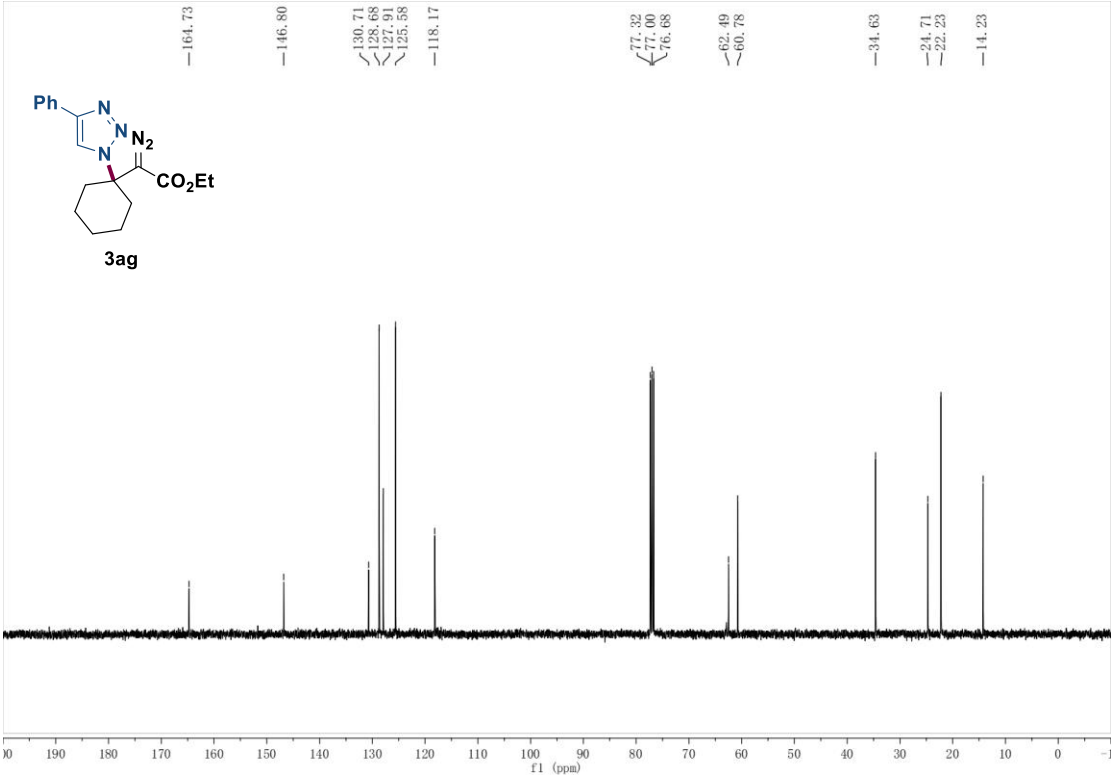
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3af**



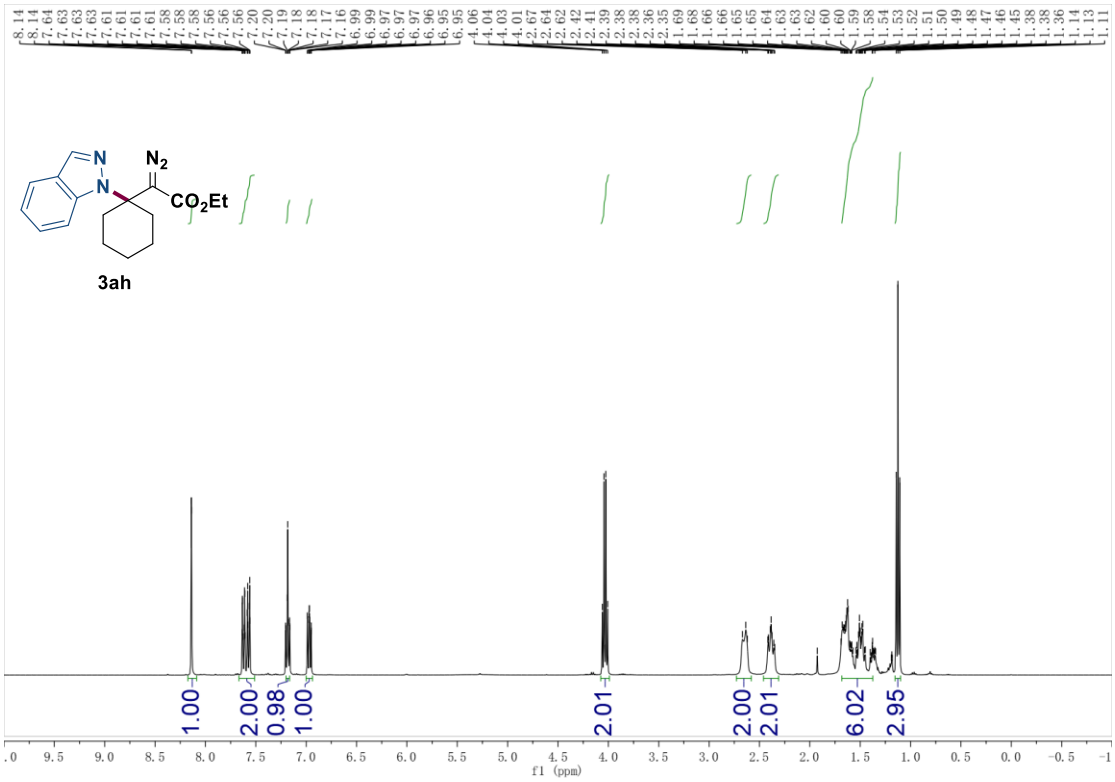
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ag**



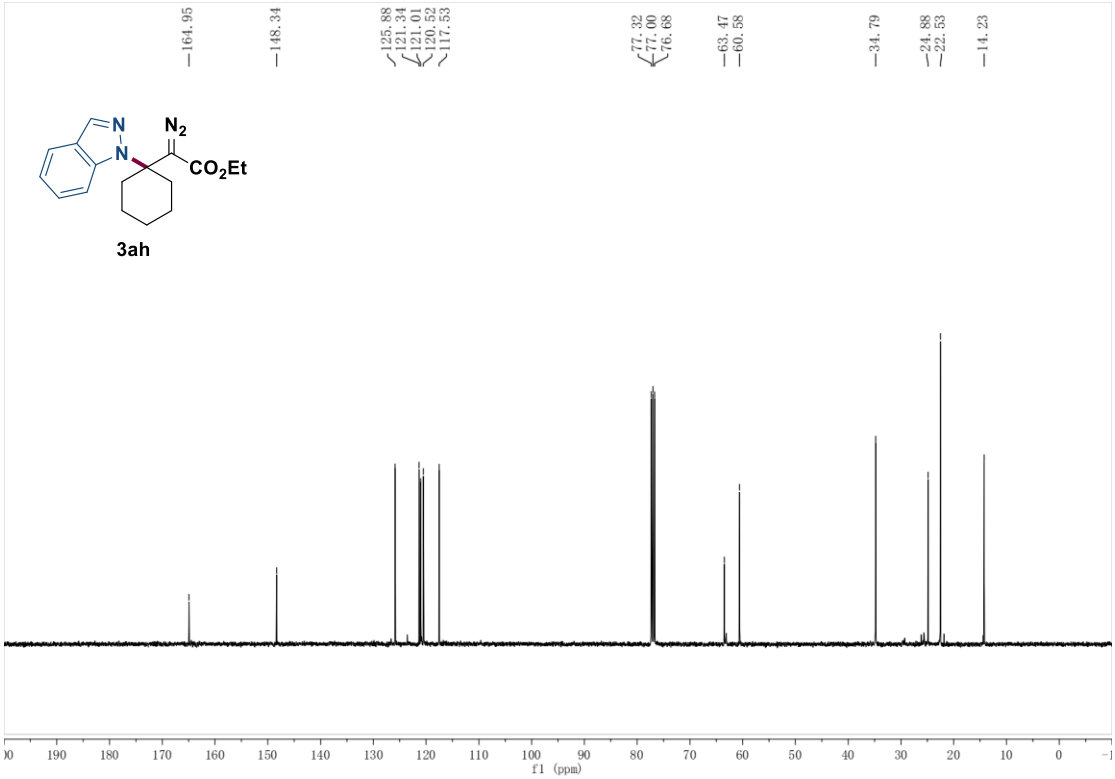
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ag**



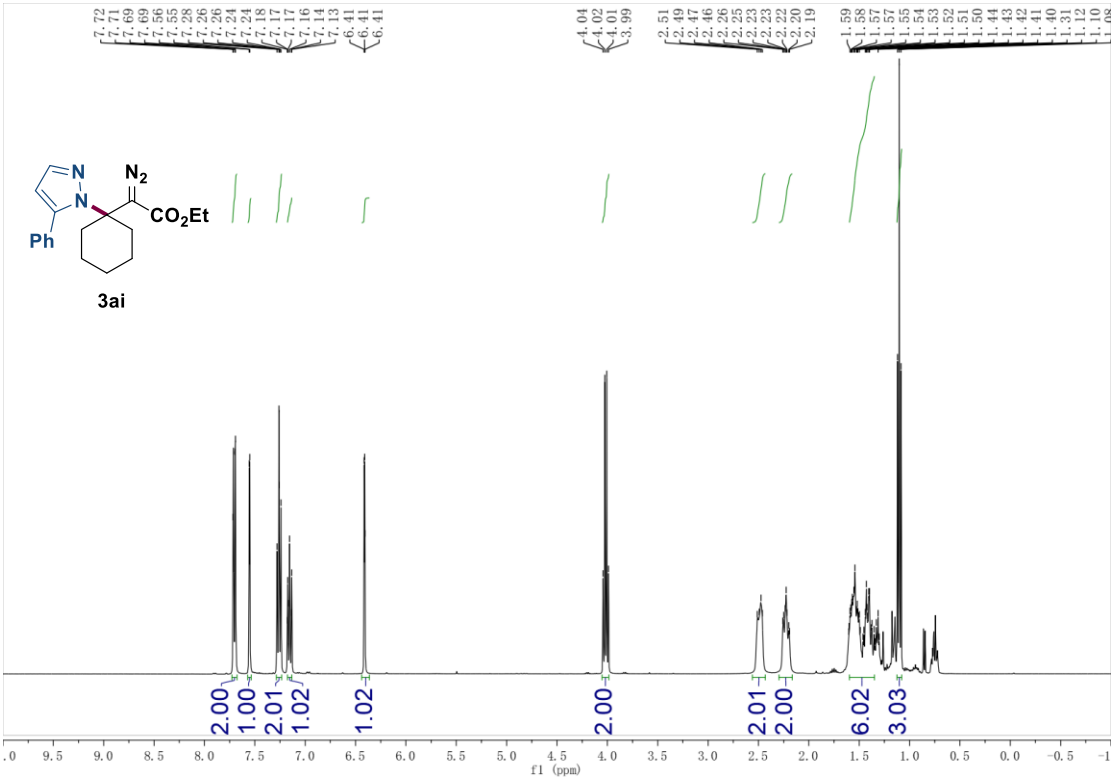
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ah**



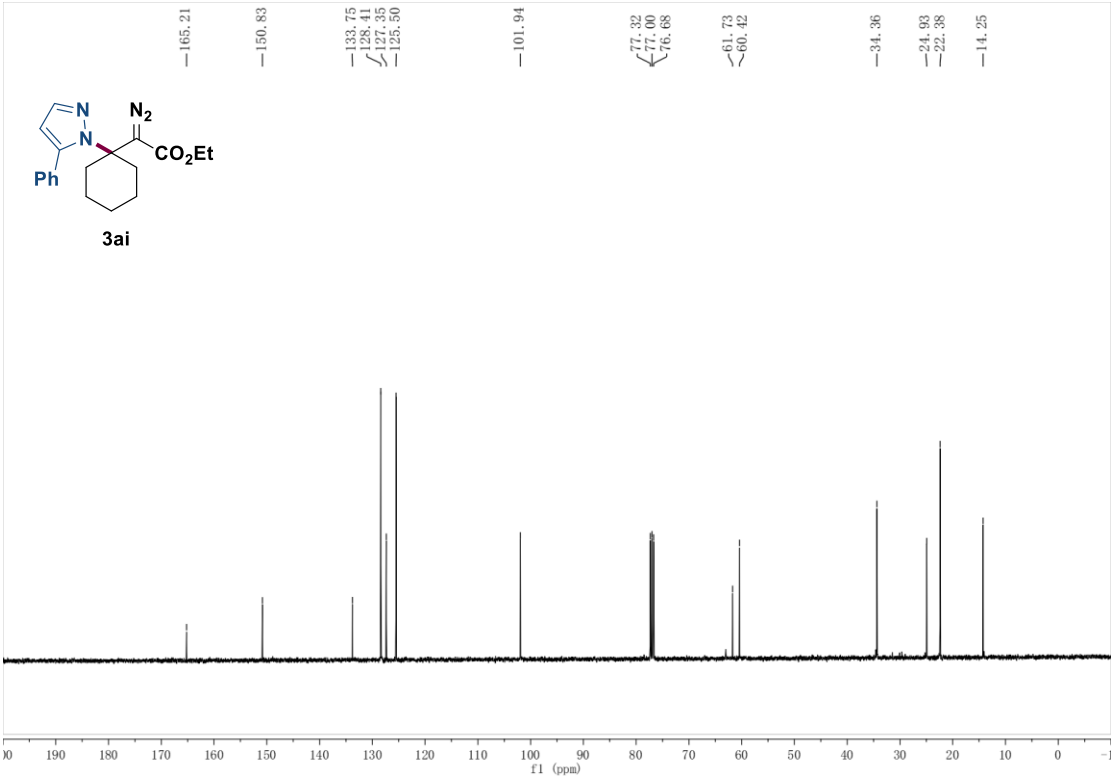
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ah**



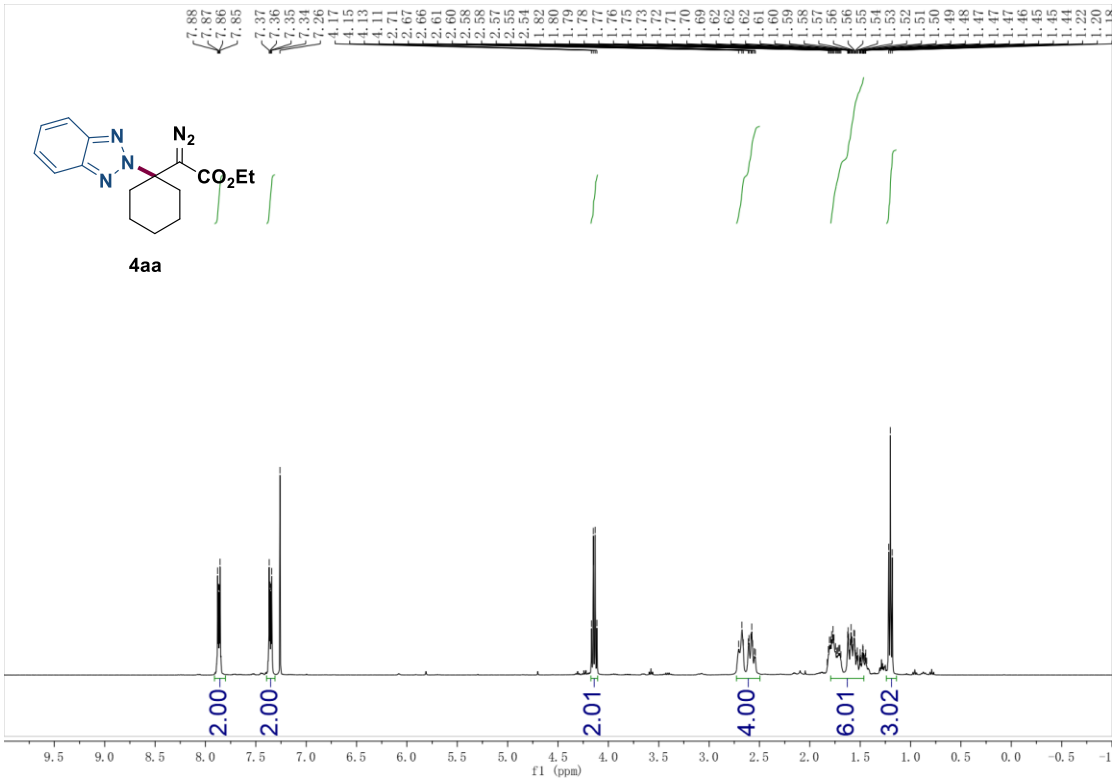
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ai**



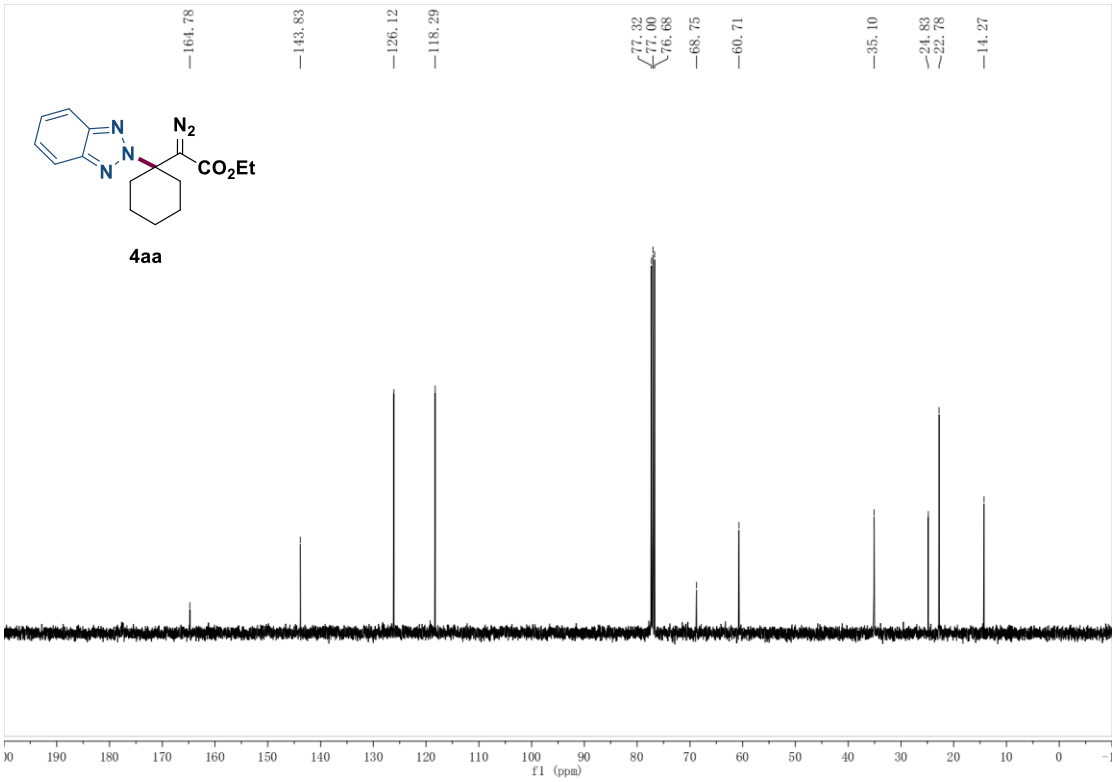
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ai**



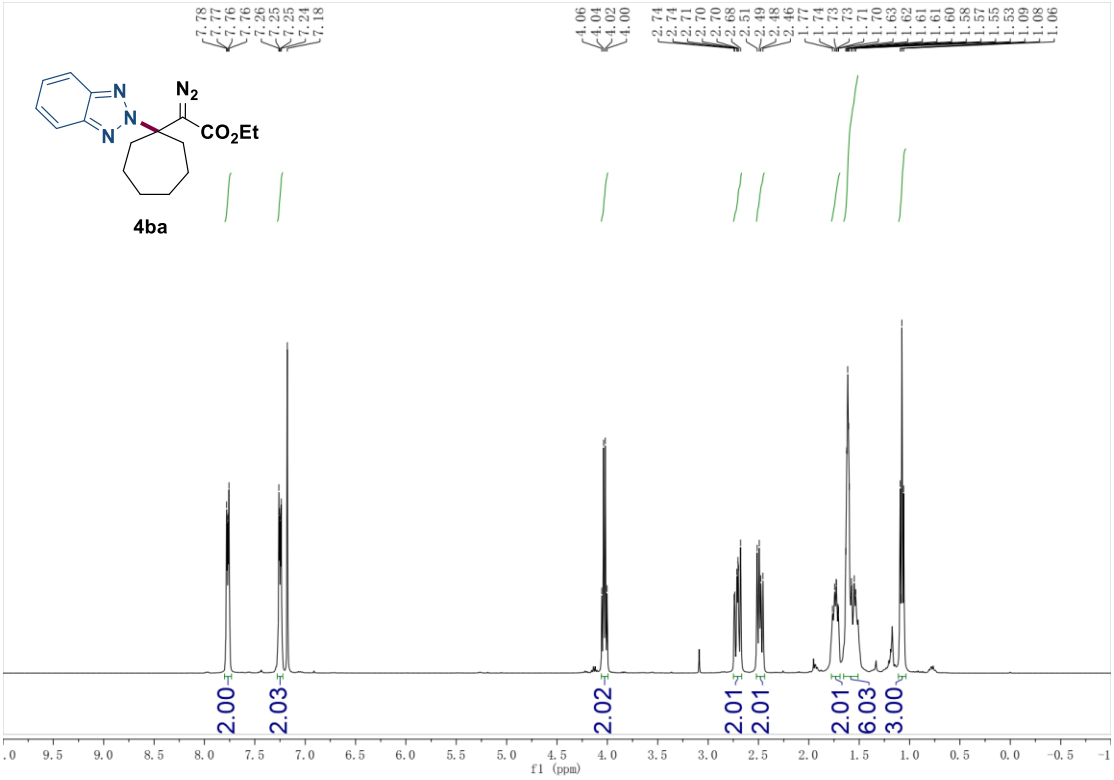
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4aa**



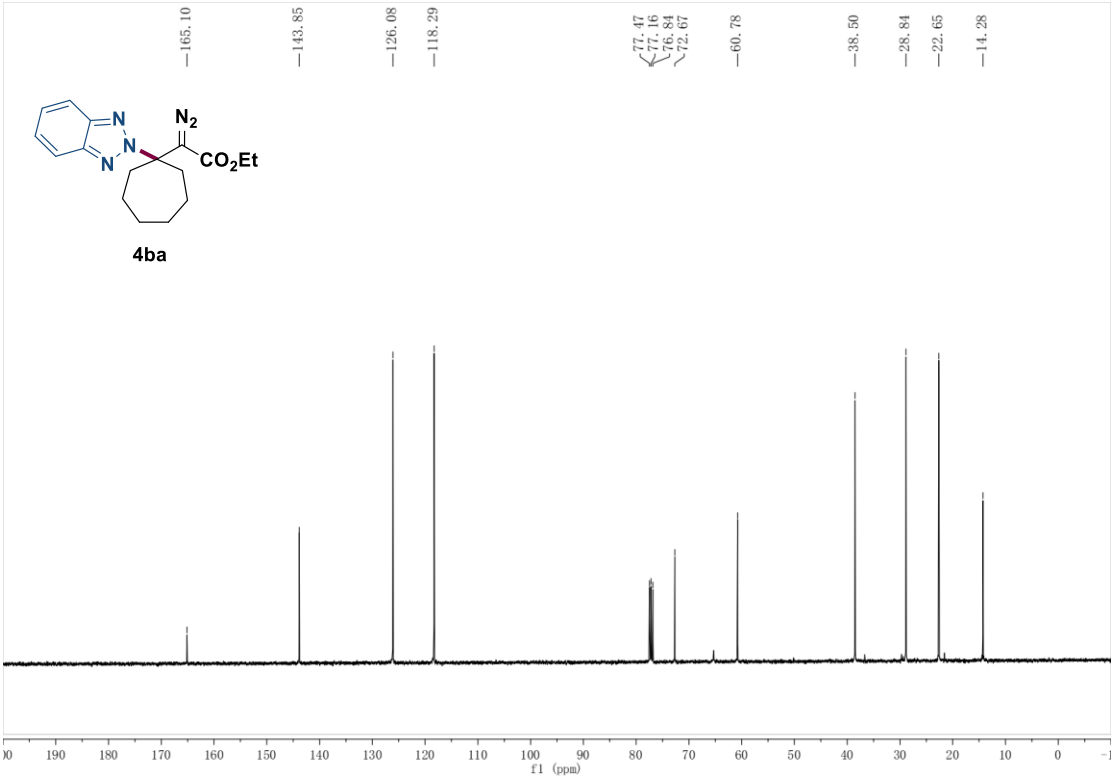
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 4**aa**



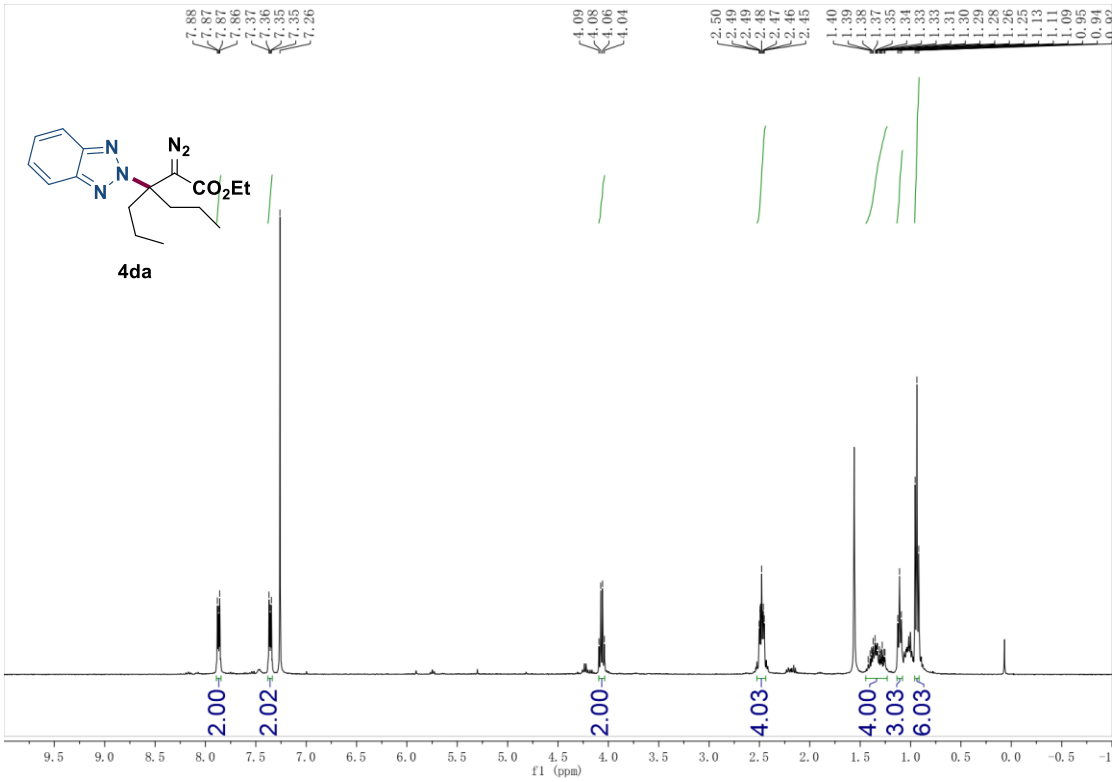
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ba**



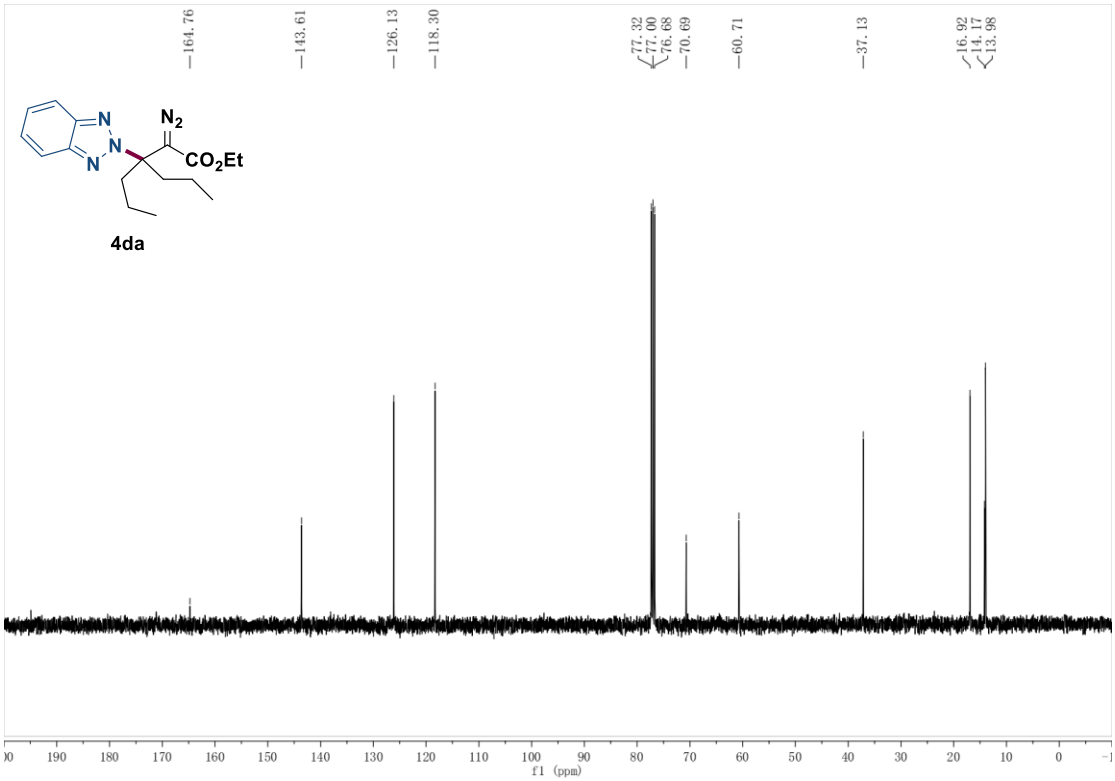
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ba**



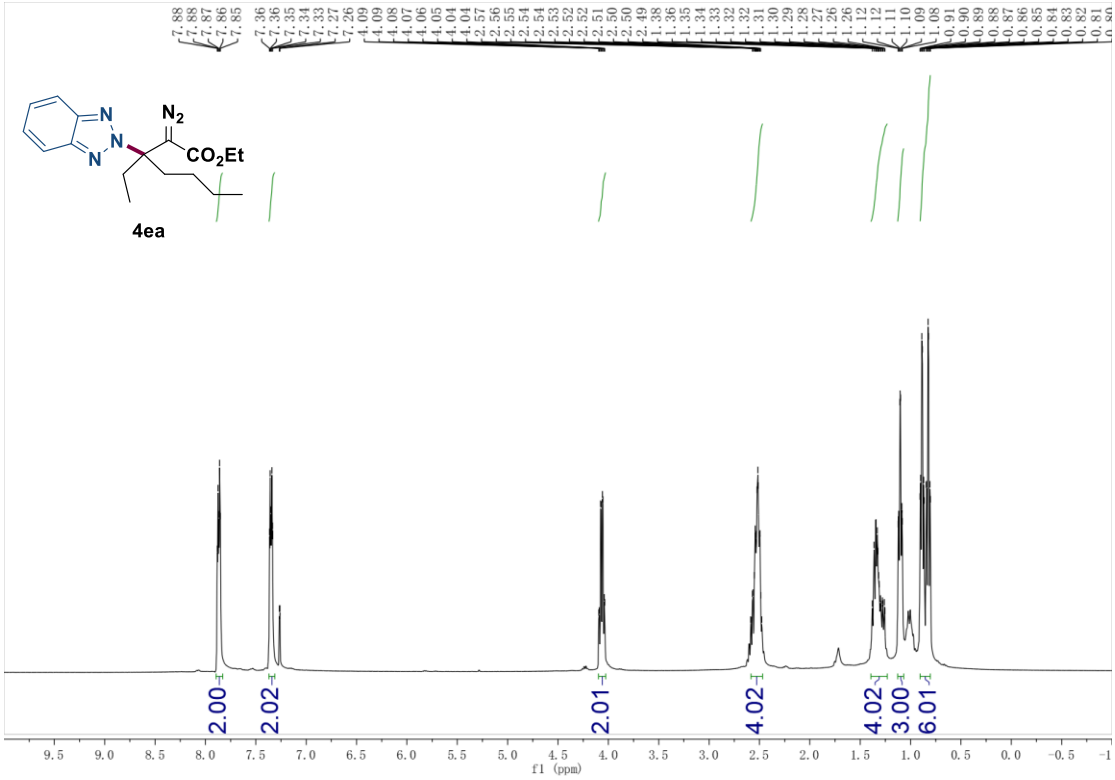
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4da**



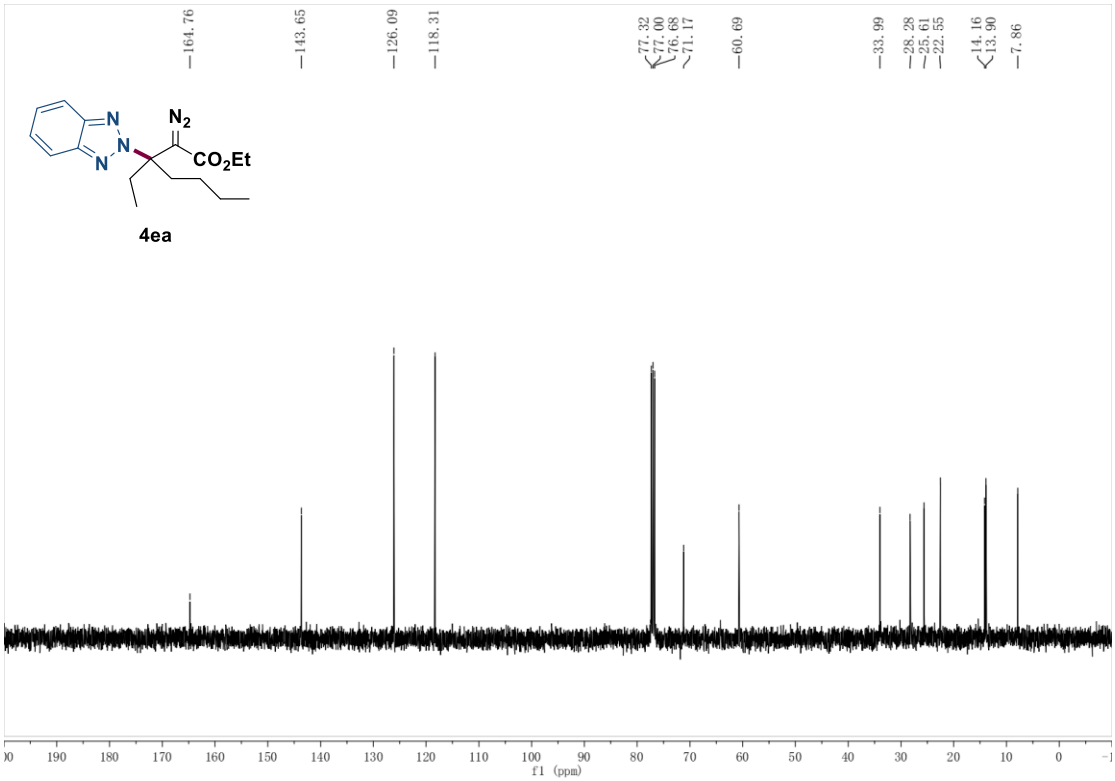
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4da**



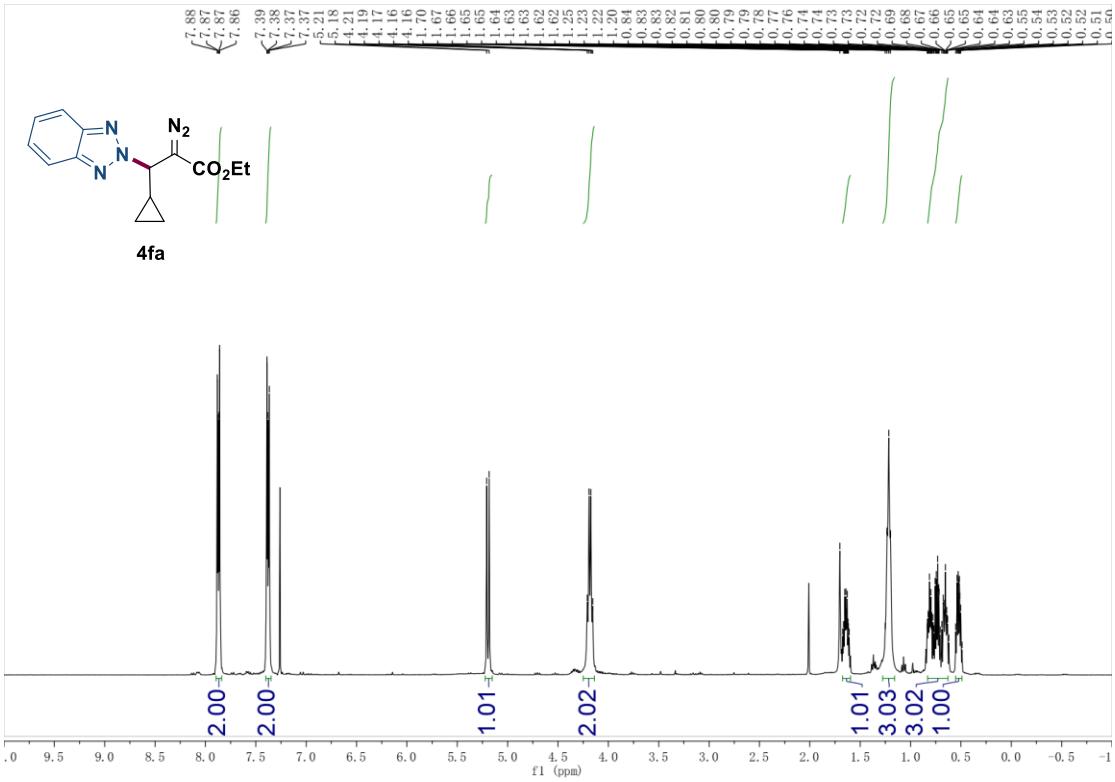
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ea**



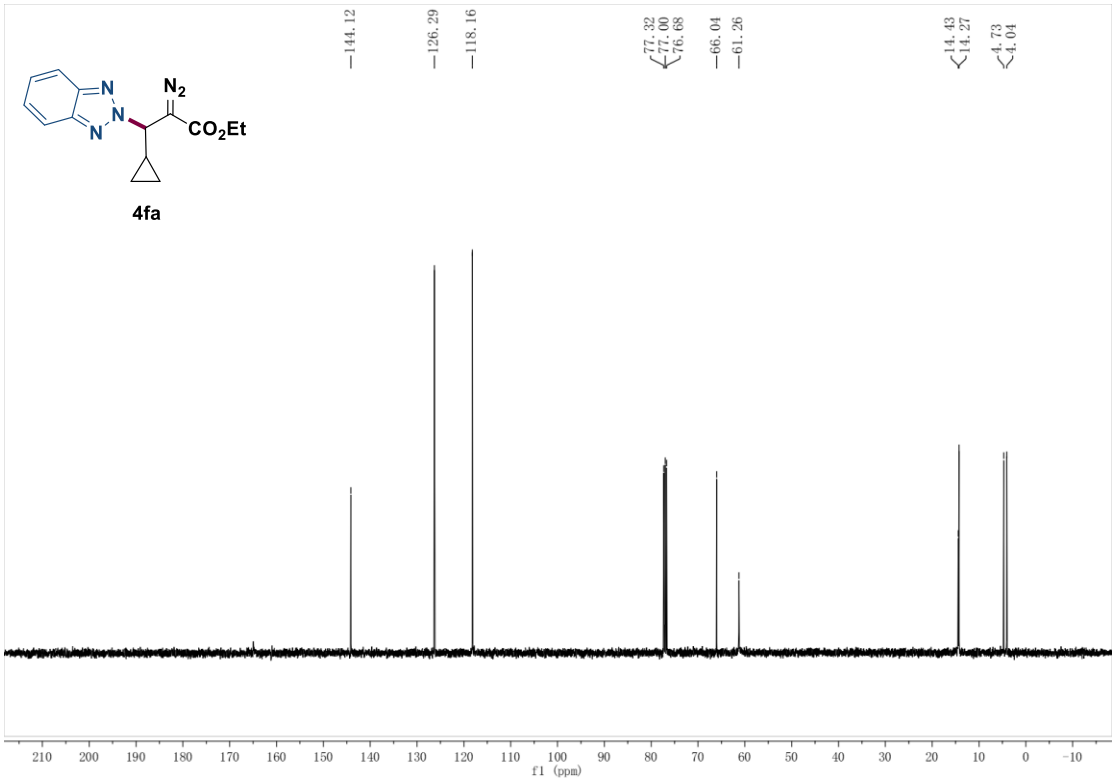
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ea**



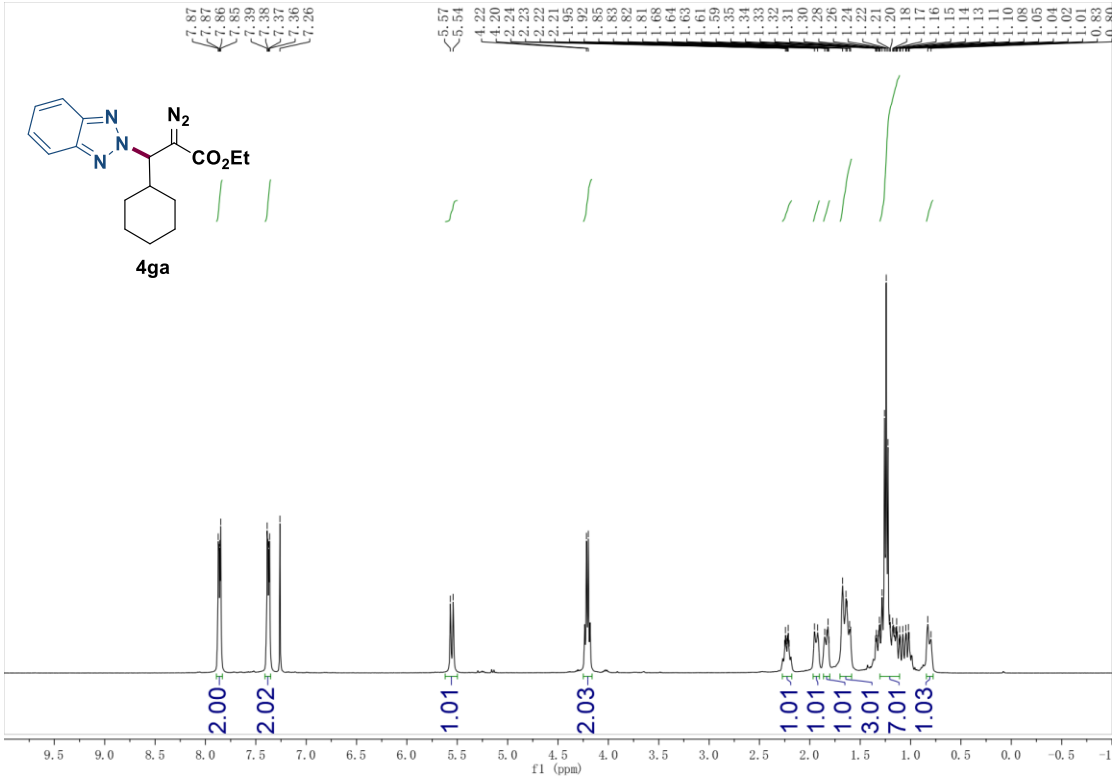
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4fa**



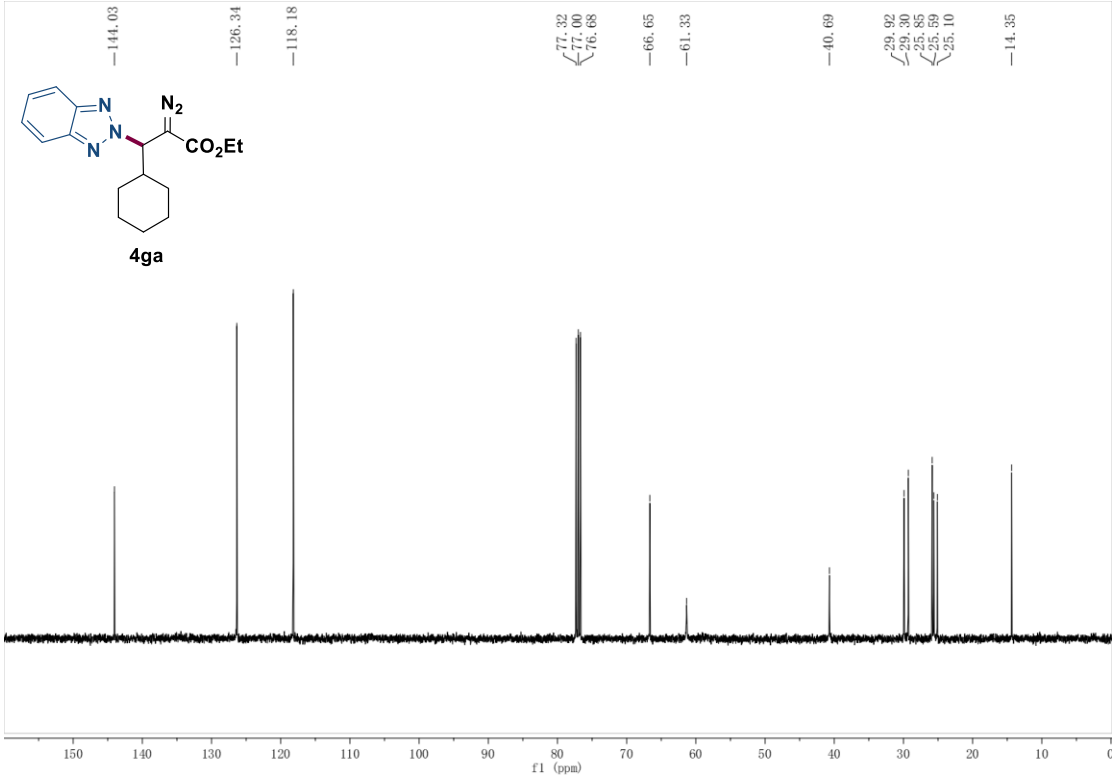
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4fa**



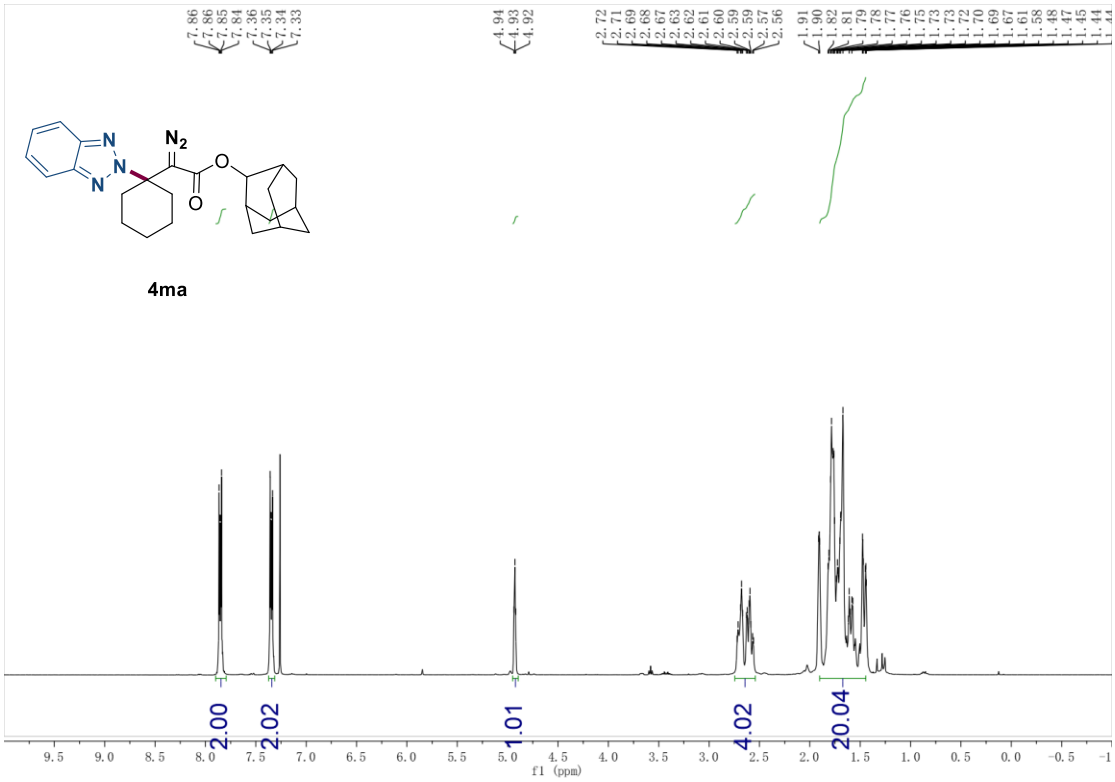
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ga**



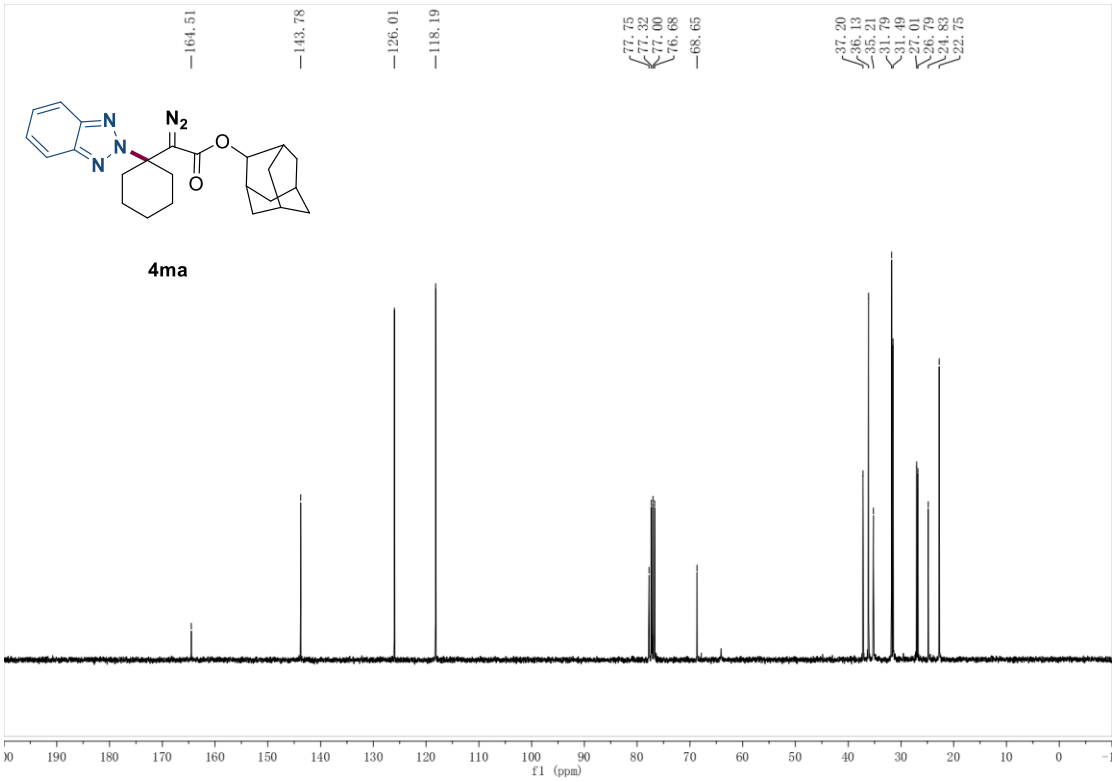
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ga**



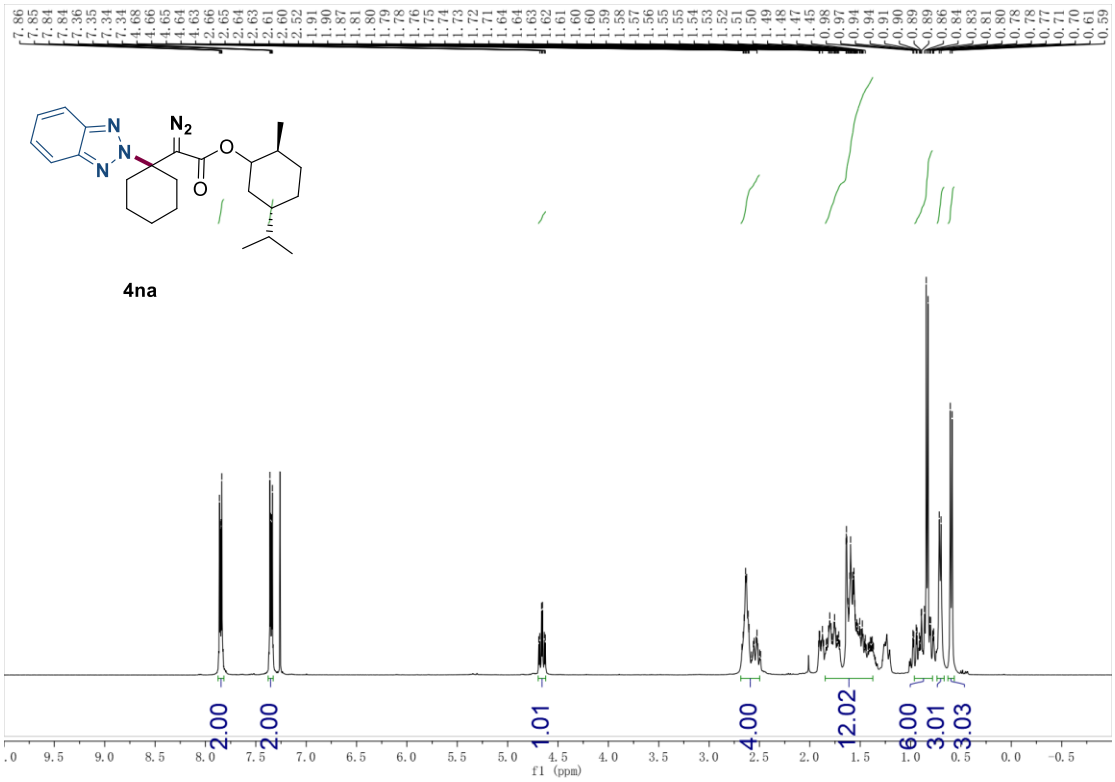
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ma**



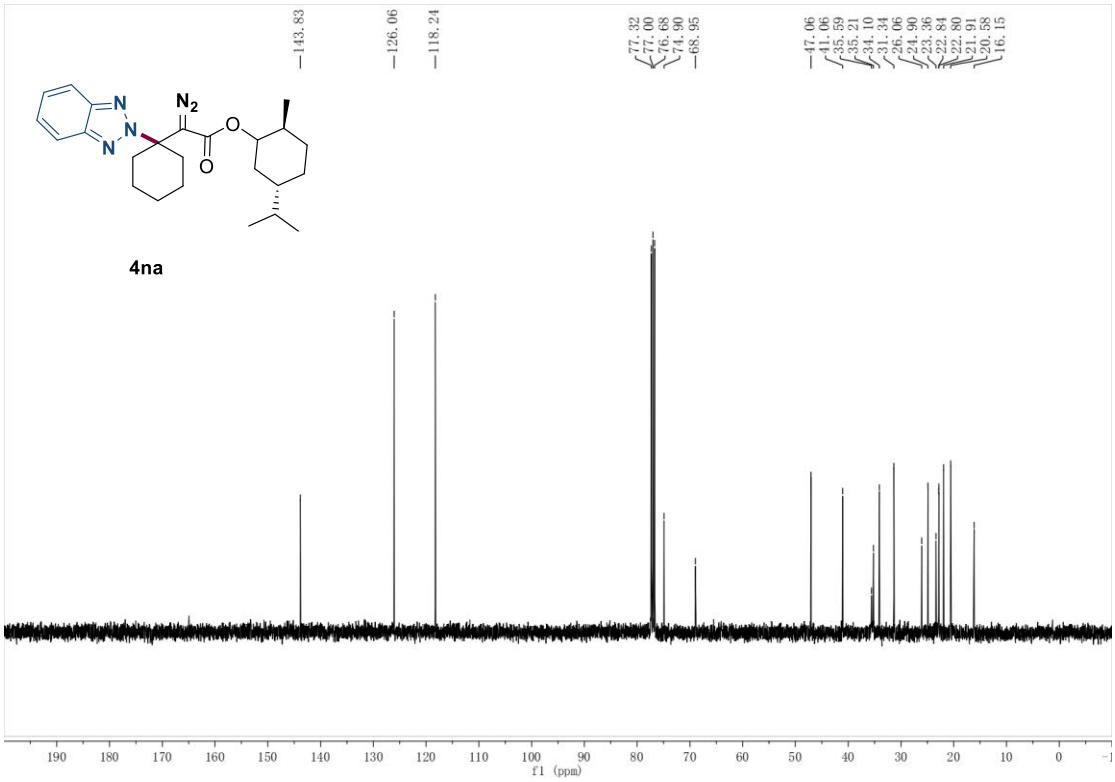
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ma**



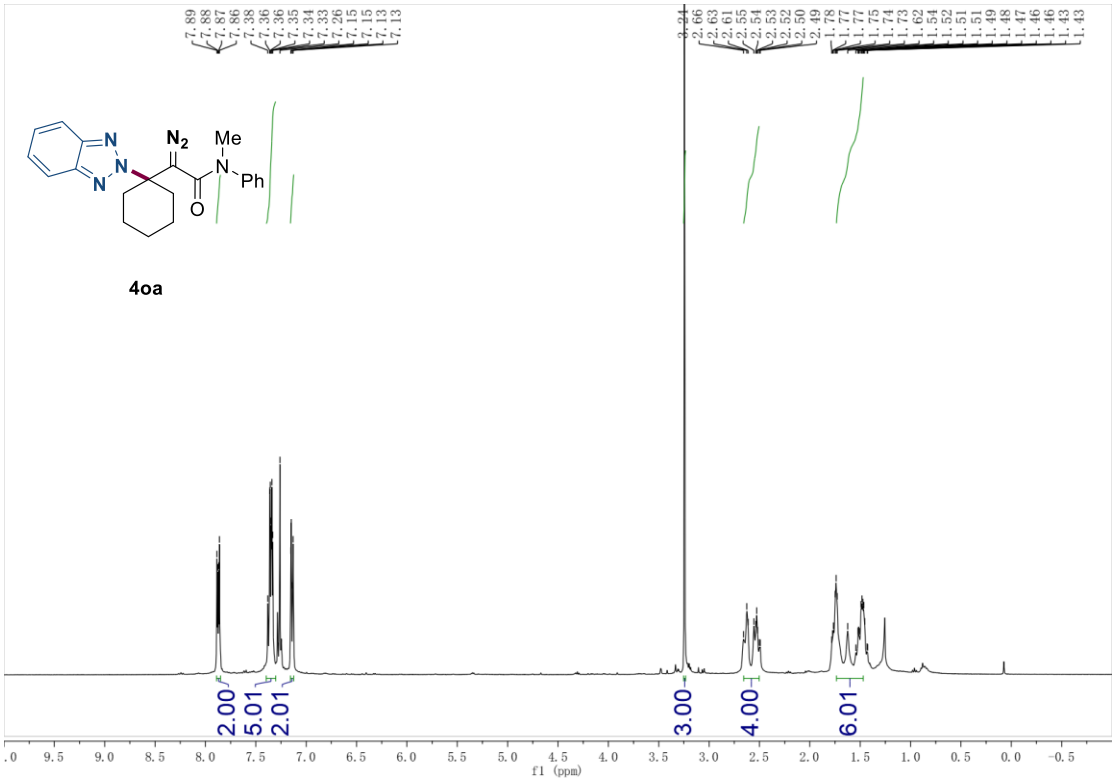
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4na**



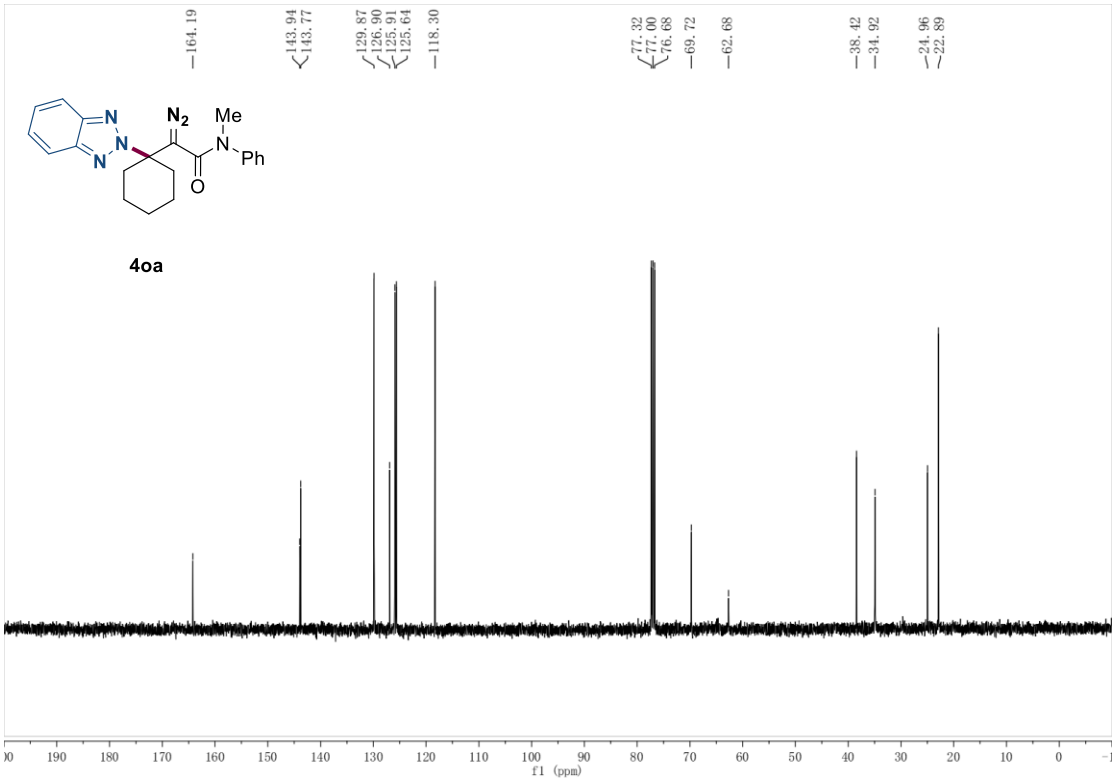
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4na**



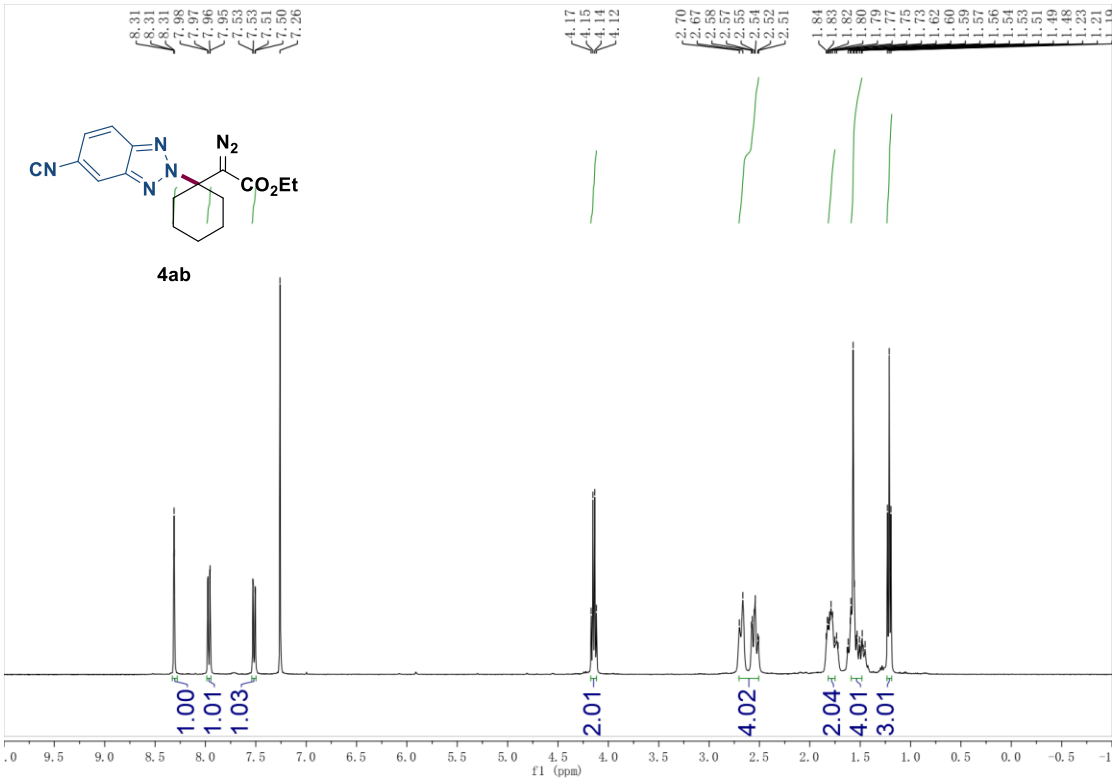
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4oa**



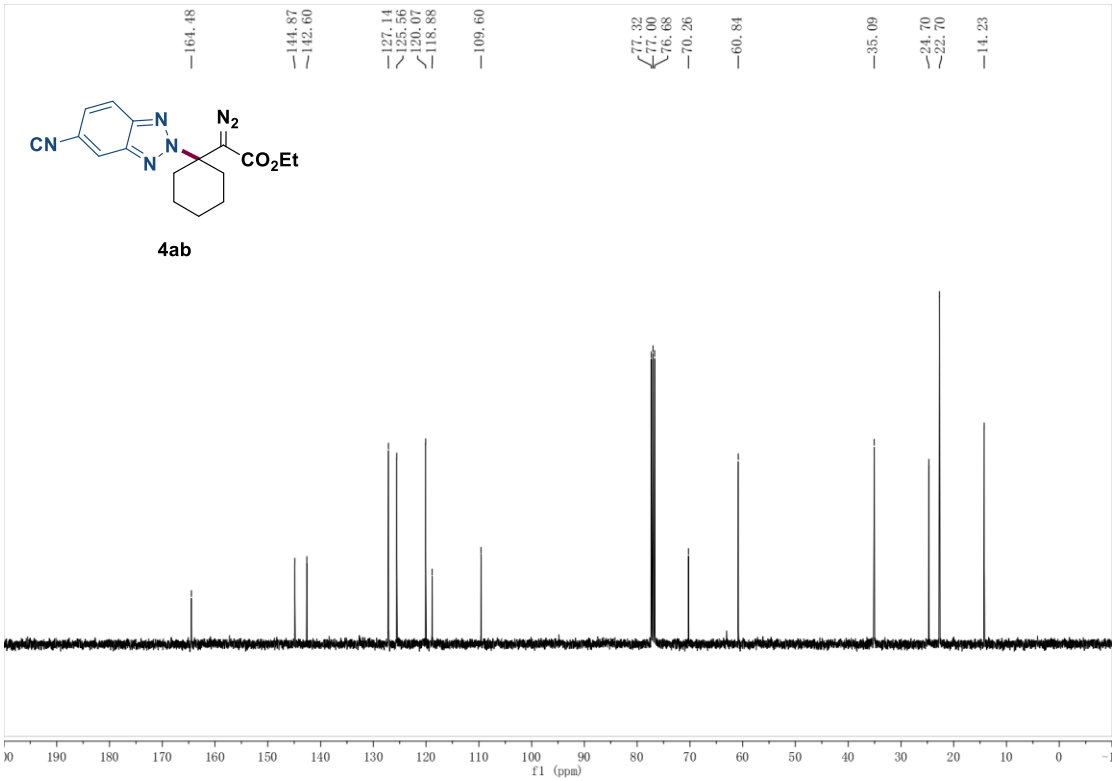
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4oa**



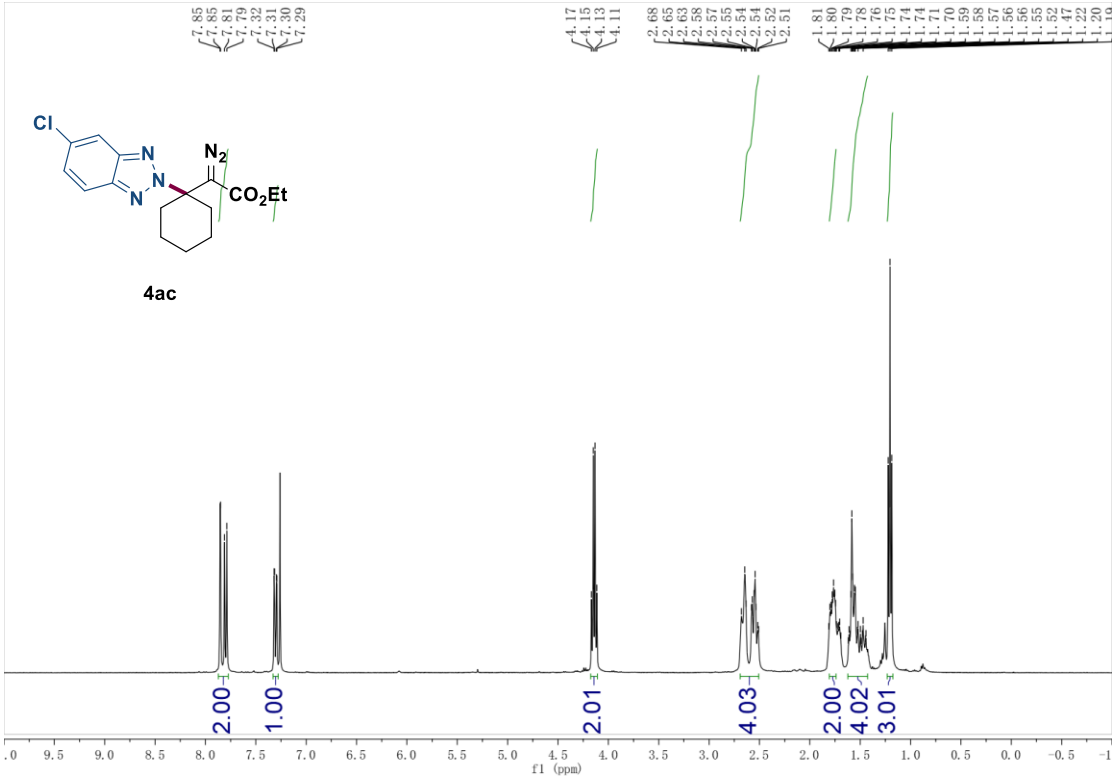
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ab**



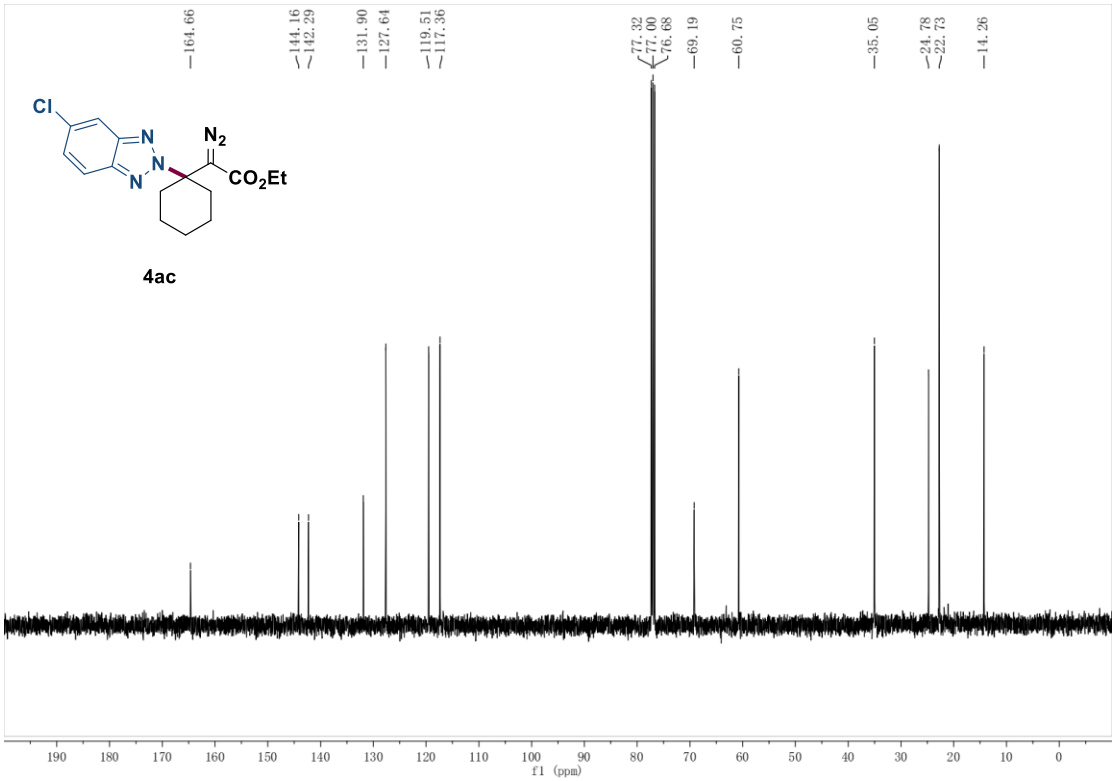
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ab**



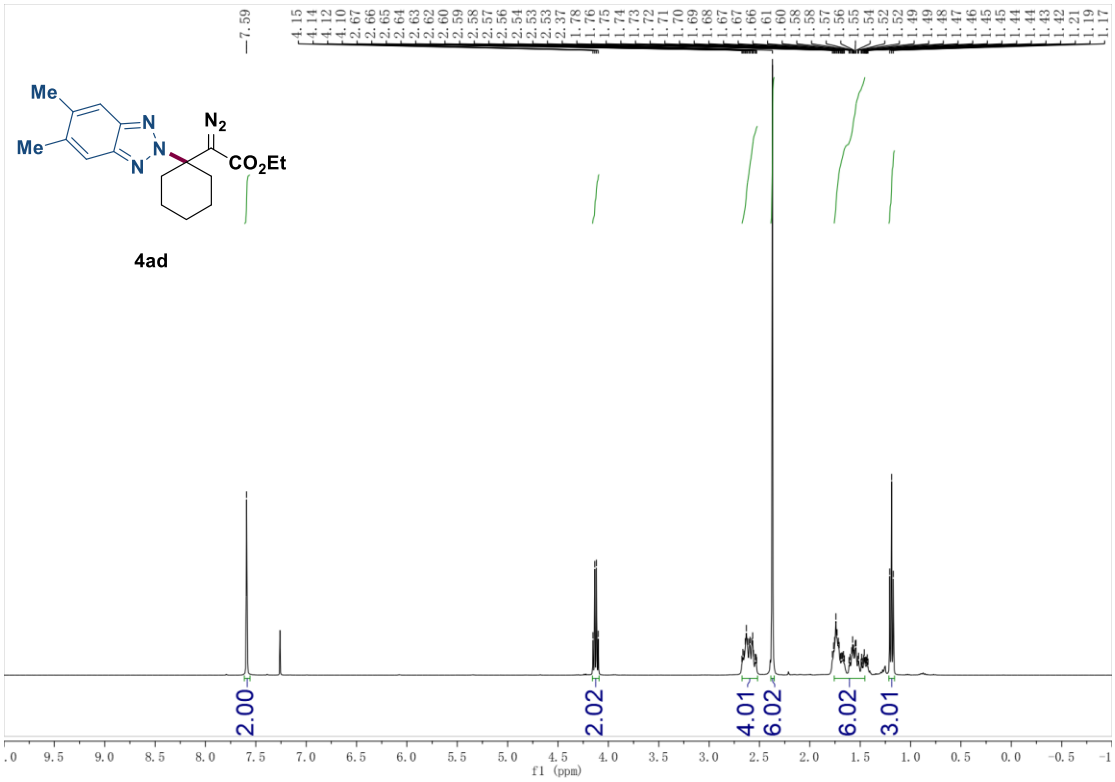
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ac**



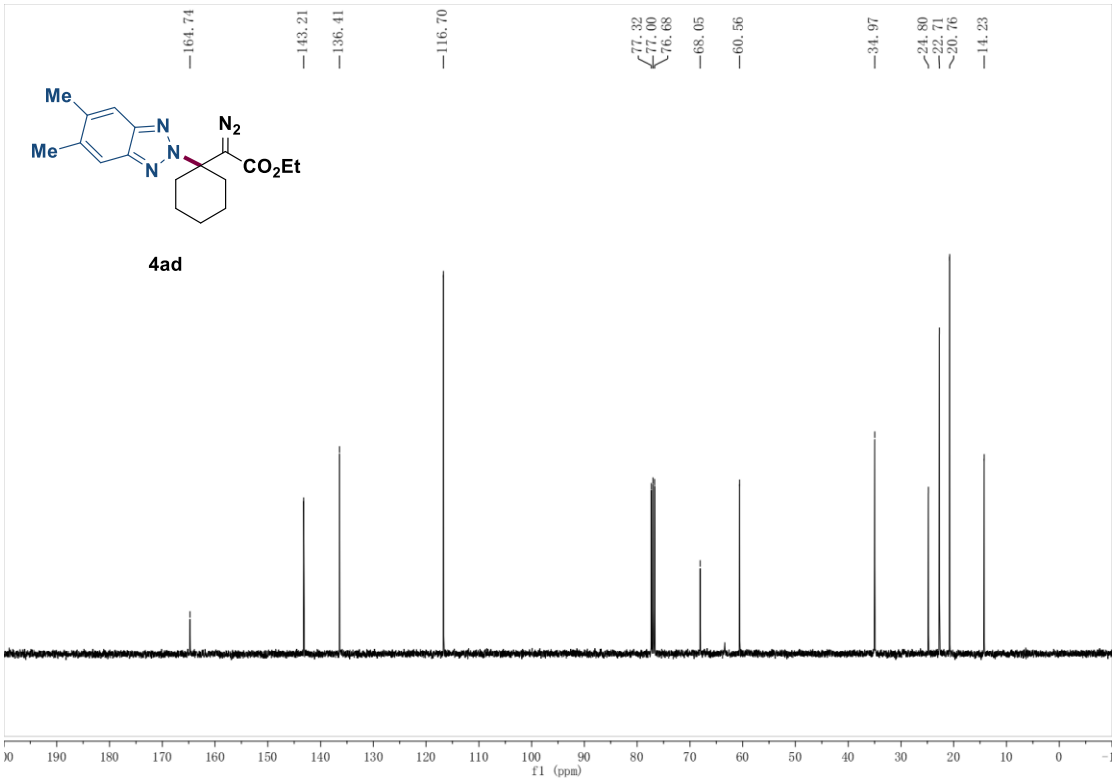
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ac**



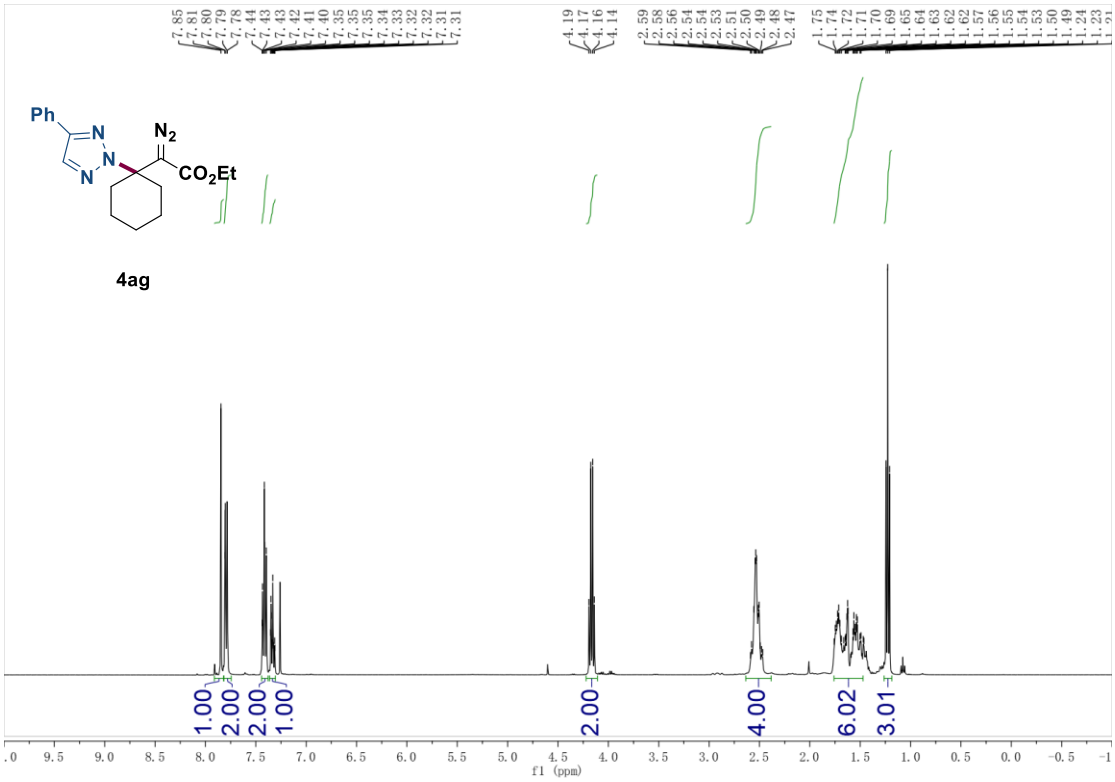
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ad**



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ad**



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ag**



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ag**