Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Transition-Metal-Free Synthesis of 5-Amino-1,2,3-triazoles via Nucleophilic Addition/Cyclization of Carbodiimides with Diazo Compounds

Shilong Wang, Yuanyuan Zhang, Guixin Liu, Hui Xu, Lijuan Song, Jinchun Chen, Jiazhu Li, and Zhen Zhang*

College of Chemistry and Chemical Engineering, Yantai University, Yantai, 264005, P. R. China.

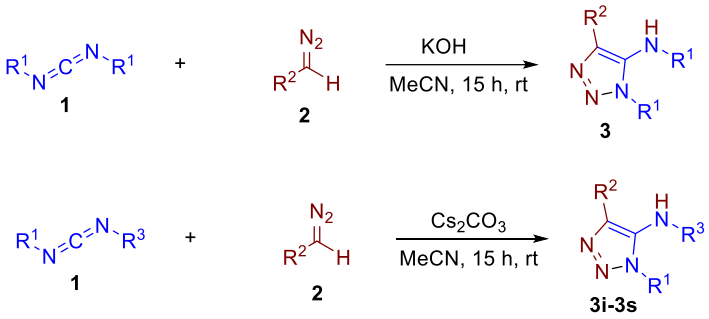
E-mail: zhangz@ytu.edu.cn

Table of Contents

1. General

All reactions were performed in a glass vial under nitrogen atmosphere. The boiling point of petroleum ether is between 60 °C and 90 °C. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Ascend 400, Bruker Biospin GmbH 500 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ (^{1}H, TMS δ 0; ^{13}C, δ 77.16), DMSO-d_6 (^{1}H, δ 2.50; ^{13}C, δ 39.52). HMRS were obtained on a Bruker SolanX 70 FT-MS or Waters Xevo G2-XS QT spectrometer. All reagents and solvents were obtained from commercial sources and used as supplied unless otherwise noted. All carbodiimides[1] and diazo compounds[2] were prepared according to literature methods, respectively.

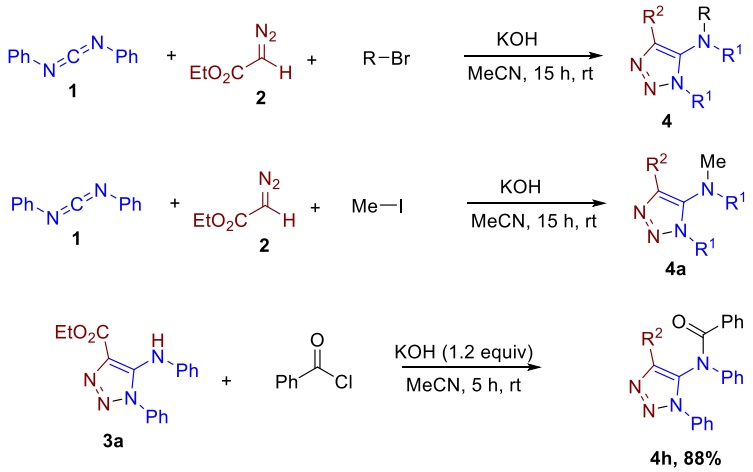
2. General procedure for the synthesis of 5-amino-1,2,3-triazole



To a 20 mL dry thick walled tube equipped with a magnetic stir bar, was added KOH (0.45 mmol, 25.2 mg, flaky KOH needs to be crushed), MeCN (5 mL) and Ethyl diazoacetate **2a** (0.36 mmol, 41.1 mg, added slowly), the mixture was stirred for 5 min. Then, and carbodiimide **1a** (0.3 mmol, 58.2 mg) was added. The flask was sealed and the reaction mixture was stirred at rt for 15 h. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography (petroleum ether/ethyl acetate = 7:1-5:1) on silica gel to afford the desired product **3a** (75 mg, 81%). *Note*: *the purity of the carbodiimide will affect its reactivity.*

For unsymmetric carbodiimides, Cs_2CO_3 was used as base instead of KOH.

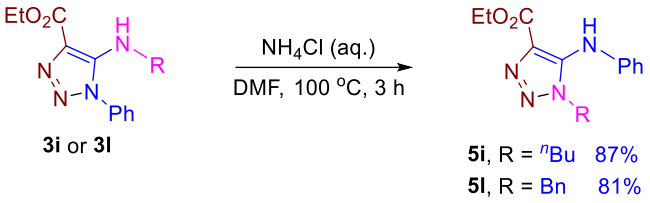
3. General procedure for the synthesis of fully substituted 5-amino-1,2,3-triazoles



To a 20 mL dry thick walled tube equipped with a magnetic stir bar, was added KOH (0.3 mmol, 25.2 mg, flaky KOH needs to be crushed), MeCN (4 mL) and ethyl diazoacetate **2a** (0.36 mmol,

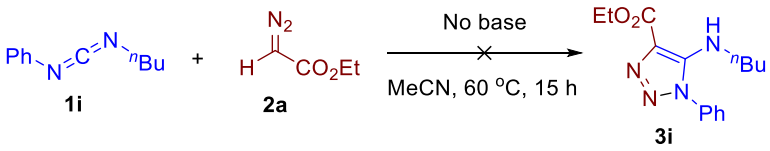
41.1 mg, added slowly). The mixture was stirred for 5 mins. Then, and carbodiimide **1a** (0.3 mmol, 58.2 mg) and bromide (0.45 mmol) was added. The flask was sealed and the reaction mixture was stirred at rt for 15 h. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography (petroleum ether/ethyl acetate = 6:1 to 4:1) on silica gel to afford the desired product **4**. For **4a**, MeI was used as halides. For **4h**, the product was synthesized from the reaction of isolated **3a** with benzoyl chloride.

4. Procedure for the isomerization of 5-amino-1,2,3-triazoles

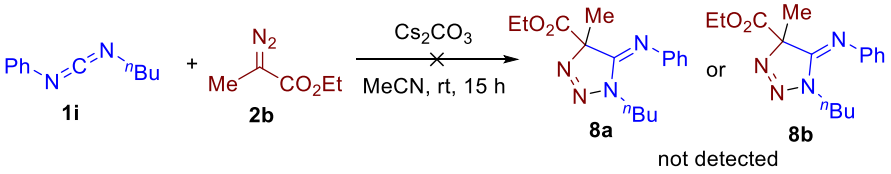


To a 20 mL dry thick walled tube equipped with a magnetic stir bar, was added **3** (0.2 mmol), DMF (2 mL) and saturated NH_4Cl aqueous solution 0.5 mL. The mixture was stirred at 100 °C for 3 h. Upon the reaction completed, 15 mL H_2O was added to mixture and extracted with dichloromethane (15 mL x 3). The combined organic layer was dried (anhydrous Na_2SO_4), filtered, and evaporated followed by a silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford desired product **5**.

5. Control experiments

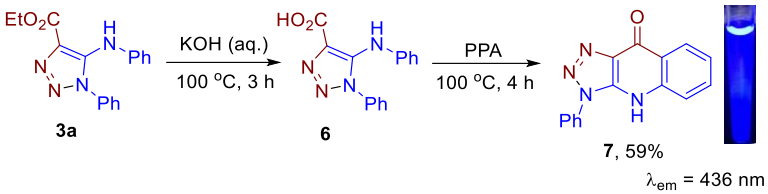


To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added MeCN (2 mL) and Ethyl diazoacetate **2a** (0.18 mmol, 20.5 mg) and carbodiimide **1i** (0.15 mmol, 26.1 mg) was added. The flask was sealed and the reaction mixture was stirred at 60 °C for 15 h.



To a 10 mL dry thick walled tube equipped with a magnetic stir bar, was added MeCN (2 mL) Cs_2CO_3 (0.225 mmol, 73.3 mg) and diazo **2b** (0.18 mmol, 23.0 mg, added slowly), the mixture was stirred for 5 min. Then carbodiimide **1i** (0.15 mmol, 26.1 mg) was added. The flask was sealed and the reaction mixture was stirred at rt for 15 h.

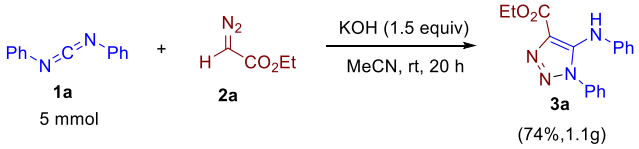
6. Procedure for the synthesis of triazolo[4,5-b]quinolin-9-one 7



To a 10 mL thick walled tubes equipped with a magnetic stir bar, were added **3** (0.2 mmol, 61.6 mg), KOH aqueous solution (1N, 2 mL). The tube were sealed and the reaction mixture was stirred at 100 ℃ for 3 h. Upon the reaction completed, the reaction mixture was quenched with HCl solution (1 N, 3 mL) and extracted with dichloromethane (5 mL x 3). The combined organic layer was dried (anhydrous Na_2SO_4), filtered, and evaporated to give crude **6**, which was used in the following step without further purifications.

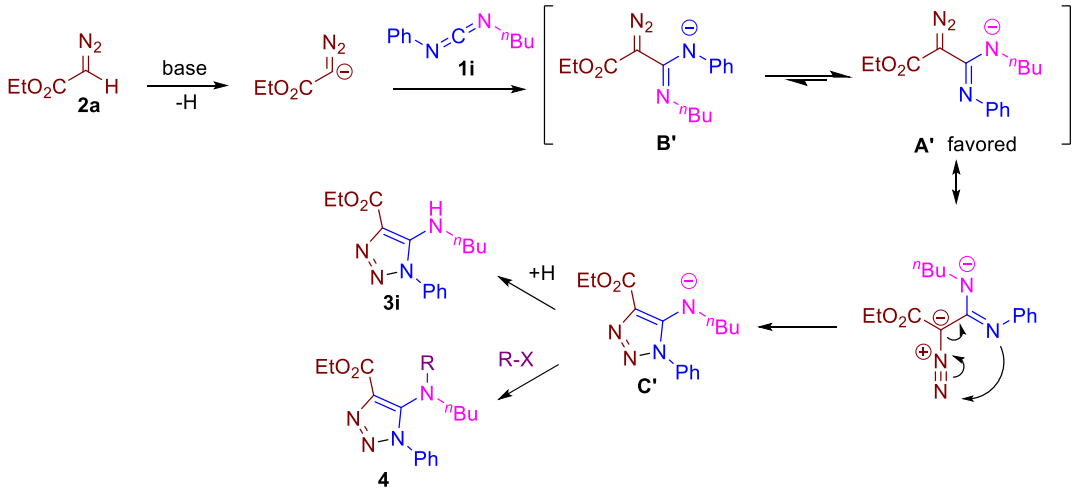
To a 10 mL thick walled tubes equipped with a magnetic stir bar, were added the above obtained crude **6** and 1 mL PPA (polyphosphoric acid). The tube were sealed and the reaction mixture was stirred at 100 ℃ for 4 h. Upon the reaction completed, the reaction mixture was poured slowly into ice water (50 mL). The mixture was extracted with EtOAc (20 mL x 3). The combined organic layer was dried (anhydrous Na_2SO_4), filtered, and evaporated followed by a silica gel column chromatography (petroleum ether/ethyl acetate = 1:1) to afford desired product **7**.

7. Procedure for gram-scale synthesis of product 3a



To a 250 mL dry thick walled tube equipped with a magnetic stir bar, was added KOH (7.5 mmol, 420 mg, flaky KOH needs to be crushed), MeCN (80 mL). Ethyl diazoacetate **2a** (6 mmol, 684 mg) were added dropwise and the mixture was stirred for 25 min. Then carbodiimide **1a** (5 mmol, 58.2 mg) was added under 0 °C. The flask was sealed and was slowly warmed to room temperature. The reaction mixture continued to be stirred for 15 h. Upon the reaction completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography (petroleum ether/ethyl acetate = 7:1-5:1) on silica gel to afford the desired product **3a**.

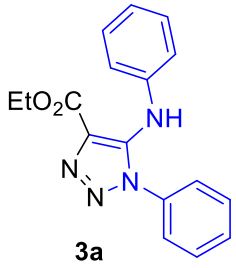
8. Another possible mechanism



For another plausible process, first, **2a** is deprotonated in base condition, and then undergoes a nucleophilic addition to carbodiimide **1i**, giving anionic intermediate **A'** and **B'**. The favored isomer **A'** is more prone to undergo a cascade intramolecular cyclization, giving desired anionic intermediate **C'**. Subsequently, hydrogen capture or participation of halides render the generation triazole **3i** and **4** respectively.

9. Characteristic Data of 5-amino-1,2,3-triazoles

ethyl 1-phenyl-5-(phenylamino)-1H-1,2,3-triazole-4-carboxylate (3a)



3a

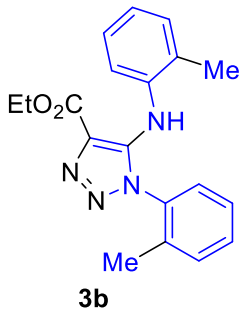
White solid; yield 81% (75 mg); mp 124−125 ℃;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.37 (dd, *J* = 7.7, 2.1 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.00 (dd, *J* = 8.5, 7.3 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.15, 143.29, 138.29, 135.97, 129.04, 128.94, 128.91, 124.56, 124.27, 123.54, 120.88, 61.24, 14.55.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{17}N_4O_2^+$, 309.1346; found, 309.1348

ethyl 1-(o-tolyl)-5-(o-tolylamino)-1H-1, 2, 3-triazole-4-carboxylate (3b)



3b

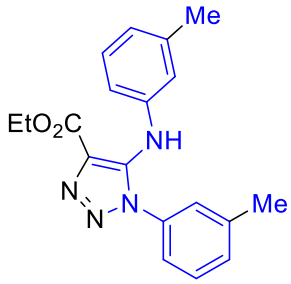
White solid; yield 73% (73mg); mp 85−86 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.13 – 7.09 (m, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.01 – 6.93 (m, 3H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 2.21 (s, 3H), 2.09 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.52, 145.85, 136.15, 134.85, 134.71, 132.49, 130.85, 130.51, 129.87, 127.89, 126.65, 126.40, 125.98, 124.22, 122.40, 61.11, 17.92, 17.78, 14.61.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{21}N_4O_2^+$, 337.1659; found, 337.1658

ethyl 1-(m-tolyl)-5-(m-tolylamino)-1H-1, 2, 3-triazole-4-carboxylate (3c)



3c

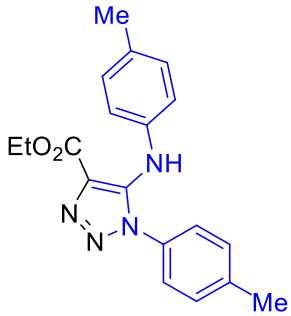
White solid; yield 82% (83 mg); mp 106−107 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.18 – 7.08 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 1H), 6.47 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.21 (s, 3H), 2.06 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.21, 143.47, 139.11, 138.75, 137.96, 135.95, 129.58, 128.74, 128.67, 125.09, 124.28, 124.13, 121.92, 120.68, 118.30, 61.17, 21.13, 21.09, 14.57.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{21}N_4O_2^+$, 337.1659; found, 337.1657

ethyl 1-(p-tolyl)-5-(p-tolylamino)-1H-1,2,3-triazole-4-carboxylate (3d)



3d

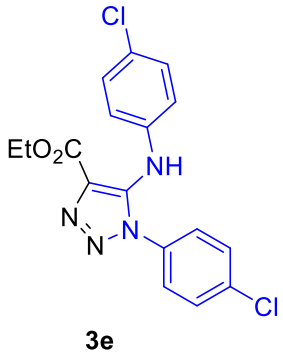
White solid; yield 77% (78 mg); mp 67−68 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.52 (d, *J* = 8.2 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 2.09 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.23, 143.66, 138.97, 135.87, 133.95, 133.56, 129.54, 129.41, 124.24, 123.47, 121.10, 61.16, 21.22, 20.78, 14.58.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{21}N_4O_2^+$, 337.1659; found, 337.1657

ethyl 1-(4-chlorophenyl)-5-((4-chlorophenyl)amino)-1H-1,2,3-triazole-4-carboxylate (3e)



3e

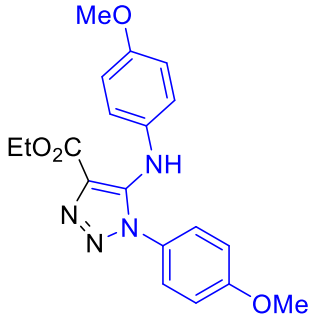
White solid; yield 68% (77 mg); mp 139−140 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.39 – 7.32 (m, 2H), 7.30 – 7.24 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.99, 142.90, 137.08, 135.25, 134.24, 129.84, 129.52, 129.24, 125.15, 124.54, 121.80, 61.49, 14.51.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{15}Cl_2N_4O_2^+$, 377.0567; found, 377.0561

ethyl 1-(4-methoxyphenyl)-5-((4-methoxyphenyl)amino)-1H-1,2,3-triazole-4-carboxylate (3f)



3f

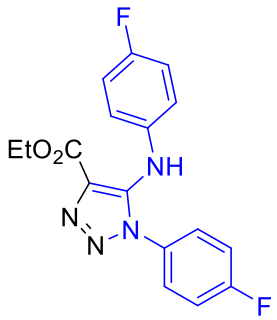
White solid; yield 69% (76 mg); mp 81−82 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.21 – 7.13 (m, 2H), 6.74 – 6.64 (m, 4H), 6.58 – 6.50 (m, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.67 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.35, 159.76, 156.94, 144.50, 131.03, 128.86, 125.61, 124.05, 123.23, 114.10, 114.03, 61.07, 55.61, 55.55, 14.59.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{21}N_4O_4^+$, 369.1557; found, 369.1553

ethyl 1-(4-fluorophenyl)-5-((4-fluorophenyl)amino)-1H-1,2,3-triazole-4-carboxylate (3g)



3g

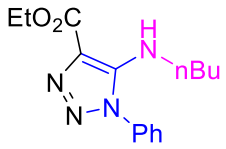
White solid; yield 85% (88 mg); mp 115−116 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.34 – 7.28 (m, 2H), 6.99 – 6.91 (m, 2H), 6.78 – 6.66 (m, 4H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.20, 162.48 (d, *J* = 250.9 Hz), 159.85 (d, *J* = 245.2 Hz), 143.92 , 134.16 (d, *J* = 2.9 Hz), 131.87 (d, *J* = 3.3 Hz), 125.88 (d, *J* = 9.1 Hz), 124.09 , 123.62 (d, *J* = 8.6 Hz), 116.17 (d, *J* = 23.1 Hz), 115.89 (d, *J* = 22.9 Hz), 61.36, 14.55.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{15}F_2N_4O_2^+$, 345.1163; found, 345.1167

ethyl 5-(butylamino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3i)



3i

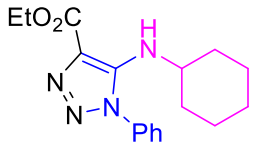
Colorless liquid; yield 80% (69 mg);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.47 (m, 5H), 6.08 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.81 (t, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.36 (p, *J* = 7.2 Hz, 2H), 1.18 (h, *J* = 7.4 Hz, 2H), 0.77 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.50, 148.30, 136.41, 129.91, 129.52, 125.81, 121.43, 60.79, 44.68, 32.29, 19.62, 14.61, 13.60.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{21}N_4O_2^+$, 289.1660; found, 289.1665

ethyl 5-(cyclohexylamino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3j)



3j

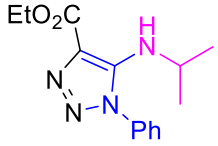
White solid; yield 77% (73 mg); mp 155−156 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 5H), 5.98 (d, *J* = 10.1 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.87 – 2.77 (m, 1H), 1.66 (dd, *J* = 8.9, 3.7 Hz, 2H), 1.57 (dt, *J* = 13.3, 3.9 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.43 – 1.38 (m, 1H), 1.18 – 1.08 (m, 3H), 0.92 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.31, 147.37, 136.42, 129.83, 129.48, 125.37, 122.11, 60.68, 52.70, 33.51, 25.19, 24.15, 14.52.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{23}N_4O_2^+$, 315.1816; found, 315.1817

ethyl 5-(isopropylamino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3k)



3k

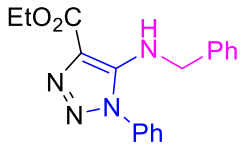
White solid; yield 71% (58 mg); mp 126−127 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (ddd, *J* = 17.8, 10.5, 7.4 Hz, 5H), 5.77 (d, *J* = 10.5 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.26 – 3.14 (m, 1H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.35, 147.55, 136.46, 129.81, 129.63, 125.07, 122.60, 60.79, 46.40, 23.49, 14.55.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{22}N_4O_2^+$, 275.1503; found, 275.1507

ethyl 5-(benzylamino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3l)



3l

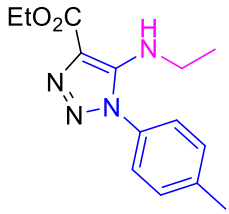
Colorless liquid; yield 81% (78 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 3H), 7.46 – 7.40 (m, 2H), 7.22 (dd, *J* = 5.0, 1.8 Hz, 3H), 6.95 (dd, *J* = 6.5, 3.1 Hz, 2H), 6.56 (t, *J* = 6.7 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.05 (d, *J* = 6.8 Hz, 2H), 1.43 (d, *J* = 14.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.40, 147.68, 137.40, 136.09, 130.00, 129.48, 128.82, 127.87, 127.00, 125.91, 122.02, 60.89, 48.67, 14.56.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{19}N_4O_2^+$, 323.1503; found, 323.1502

ethyl 5-(ethylamino)-1-(p-tolyl)-1H-1,2,3-triazole-4-carboxylate (3m)



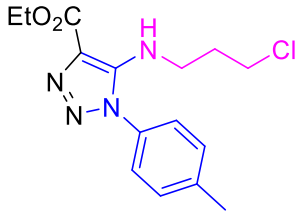
3m

White solid; yield 74% (61 mg); mp 97−98 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 5.96 (t, *J* = 5.8 Hz, 1H), 4.43 (q, *J* = 7.0 Hz, 2H), 2.86 (p, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.09 – 1.01 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.54, 148.10, 140.19, 133.86, 130.08, 125.65, 121.39, 60.77, 39.82, 21.43, 15.70, 14.62.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{14}H_{18}N_4O_2Na^+$, 297.1322; found, 297.1322



3n

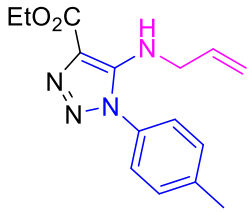
Colorless liquid; yield 74% (61 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.06 (t, *J* = 6.4 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.44 (t, *J* = 6.2 Hz, 2H), 3.05 (q, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 1.81 (p, *J* = 6.5 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.43, 147.83, 140.38, 133.53, 130.22, 125.47, 121.78, 77.48, 77.16, 76.84, 60.85, 41.73, 41.45, 32.67, 21.38, 14.55.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{20}N_4O_2Cl^+$, 323.1269; found, 323.1270

ethyl 5-(allylamino)-1-(p-tolyl)-1H-1,2,3-triazole-4-carboxylate (3o)



3o

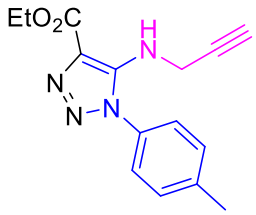
Colorless liquid; yield 77% (66 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.19 (t, *J* = 5.9 Hz, 1H), 5.70 – 5.58 (m, 1H), 5.11 – 4.99 (m, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.51 – 3.43 (m, 2H), 2.44 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.37, 147.72, 140.23, 133.86, 133.64, 130.06, 125.50, 121.75, 117.02, 60.76, 46.80, 21.36, 14.54.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{19}N_4O_2^+$, 287.1503; found, 287.1503

ethyl 5-(prop-2-yn-1-ylamino)-1-(p-tolyl)-1H-1,2,3-triazole-4-carboxylate (3p)



3p

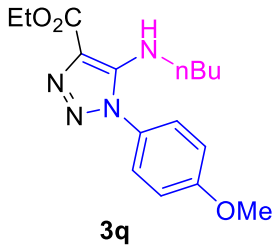
Colorless liquid; yield 43% (37 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.16 (t, *J* = 6.9 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.63 (dd, *J* = 7.1, 2.5 Hz, 2H), 2.45 (s, 3H), 2.18 (t, *J* = 2.5 Hz, 1H), 1.45 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.19, 146.97, 140.62, 133.17, 130.33, 125.48, 123.33, 79.15, 73.15, 61.04, 34.43, 21.45, 14.55.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{17}N_4O_2^+$, 285.1346; found, 285.1347

ethyl 5-(butylamino)-1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-carboxylate (3q)



3q

Colorless liquid; yield 81% (77 mg);

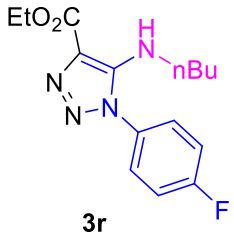
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.04 – 6.98 (m, 2H), 6.05 (t, *J* = 6.0 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 2.81 (q, *J* = 6.9 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.39 – 1.32 (m, 2H), 1.25 – 1.16 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.50, 160.62, 148.31, 129.14, 127.37, 121.18, 114.59, 60.72, 55.74,

44.36, 32.33, 19.65, 14.60, 13.64.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{23}N_4O_3^+$, 319.1770; found, 319.1771

ethyl 5-(butylamino)-1-(4-fluorophenyl)-1H-1,2,3-triazole-4-carboxylate (3r)



3r

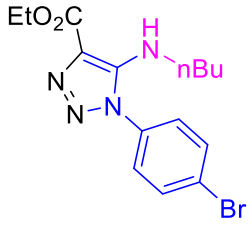
Colorless liquid; yield 51% (47 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 2H), 7.26 – 7.19 (m, 2H), 6.09 (t, *J* = 5.8 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.80 (q, *J* = 6.8 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.42 – 1.33 (m, 2H), 1.21 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.80 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.45, 163.15 (d, *J* = 251.0 Hz), 148.40, 132.51 (d, *J* = 3.3 Hz), 127.84 (d, *J* = 9.0 Hz), 121.50, 116.65 (d, *J* = 23.1 Hz), 60.89, 44.77, 32.31, 19.68, 14.62, 13.65.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{15}H_{19}FN_4O_2Na^+$, 329.1384; found, 329.1385

ethyl 1-(4-bromophenyl)-5-(butylamino)-1H-1,2,3-triazole-4-carboxylate (3s)



3s

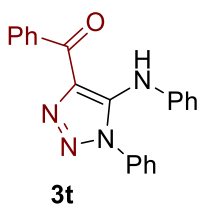
Colorless liquid; yield 65% (71 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H), 7.46 – 7.39 (m, 2H), 6.06 (t, *J* = 5.7 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.81 (q, *J* = 6.7 Hz, 2H), 1.40 (dt, *J* = 19.4, 7.5 Hz, 5H), 1.20 (dq, *J* = 14.4, 7.2, 6.7 Hz, 2H), 0.79 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.38, 148.34, 135.41, 132.79, 123.87, 121.72, 60.92, 32.30, 19.67, 14.60, 13.66.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{15}H_{19}BrN_4O_2Na^+$, 389.0584; found, 389.0582

phenyl(1-phenyl-5-(phenylamino)-1H-1,2,3-triazol-4-yl)methanone (3t)



3t

White solid; yield 87% (86 mg); mp 134−135 ℃;

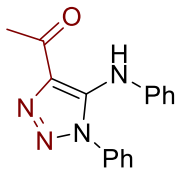
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.60 – 8.53 (m, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.21 (dd, *J* = 4.4, 2.3 Hz, 3H), 6.99 (t, *J* = 7.7 Hz, 2H), 6.89 (t, *J* =

7.3 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 187.03, 144.82, 137.43, 137.14, 135.96, 132.95, 131.63, 130.52, 128.98, 128.88, 128.82, 128.46, 124.71, 123.80, 121.88.

HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{17}N_4O^+$, 341.1397; found, 341.1399

1-(1-phenyl-5-(phenylamino)-1H-1,2,3-triazol-4-yl)ethan-1-one (3u)[3]



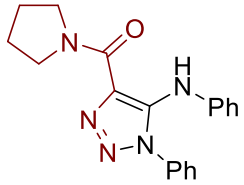
3u

White solid; yield 67% (56 mg); mp 114−115 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.28 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.24 – 7.17 (m, 3H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 2H), 2.73 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.59, 142.51, 137.33, 135.90, 132.10, 128.96, 128.88, 128.81, 124.79, 123.73, 121.91, 26.63.

(1-phenyl-5-(phenylamino)-1H-1,2,3-triazol-4-yl)(pyrrolidin-1-yl)methanone (3v)



3v

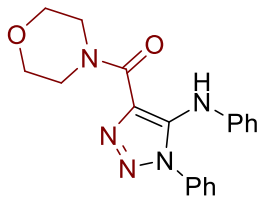
White solid; yield 69% (69 mg); mp 132−133 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.51 – 7.42 (m, 2H), 7.27 – 7.20 (m, 3H), 6.96 (t, *J* = 7.9 Hz, 2H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 2H), 4.24 (t, *J* = 6.8 Hz, 2H), 3.68 (t, *J* = 6.9 Hz, 2H), 2.06 (p, *J* = 6.7 Hz, 2H), 1.94 (p, *J* = 6.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.86, 143.08, 139.25, 136.46, 129.06, 128.75, 128.64, 128.04, 123.30, 123.09, 120.08, 49.08, 46.77, 26.73, 23.93.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{20}N_5O^+$, 334.1662; found, 334.1664

morpholino(1-phenyl-5-(phenylamino)-1H-1,2,3-triazol-4-yl)methanone (3w)



3w

White solid; yield 82% (86 mg); mp 158−159 ℃;

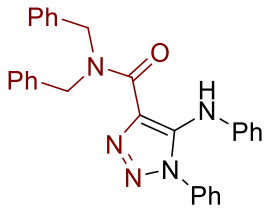
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.48 – 7.40 (m, 2H), 7.27 – 7.20 (m, 3H), 6.97 (td, *J* = 8.9, 8.3, 1.9 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.72 – 6.62 (m, 2H), 4.60 (s, 2H), 3.91 – 3.72 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.77, 143.50, 139.03, 136.23, 129.05, 128.77, 127.43, 123.39, 123.16,

120.01, 67.33, 67.07, 47.56, 42.76.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{20}N_5O_2^+$, 350.1612; found, 350.1612

N,N-dibenzyl-1-phenyl-5-(phenylamino)-1H-1,2,3-triazole-4-carboxamide (3x)



3x

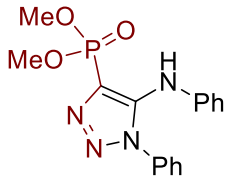
White solid; yield 79% (109 mg); mp 146−147 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.44 (t, *J* = 8.6 Hz, 2H), 7.39 – 7.21 (m, 13H), 7.04 – 6.94 (m, 2H), 6.84 (q, *J* = 6.8 Hz, 1H), 6.71 (t, *J* = 8.9 Hz, 2H), 5.53 (s, 2H), 4.71 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.58, 143.87, 139.14, 139.10, 137.51, 137.14, 136.39, 129.08, 129.06, 128.84, 128.82, 128.75, 128.25, 127.96, 127.58, 127.39, 123.49, 123.25, 120.34, 51.18, 48.27.

HRMS (ESI): $[M+H]^+$ calcd for $C_{29}H_{26}N_5O^+$, 460.2132; found, 460.2130

dimethyl (1-phenyl-5-(phenylamino)-1H-1,2,3-triazol-4-yl)phosphonate (3y)



3y

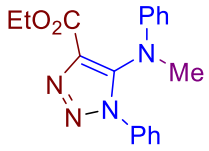
White solid; yield 59% (61 mg); mp 162−164 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.26 (q, *J* = 7.3, 6.3 Hz, 3H), 7.00 (t, *J* = 7.8 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 2H), 3.88 (d, *J* = 11.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.46, 146.20, 139.43, 136.01, 129.15, 128.97, 128.94, 123.65, 123.32, 121.57, 120.00, 119.66, 53.73, 53.68.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{18}N_4O_3P^+$, 345.1111; found, 345.1116

ethyl 5-(methyl(phenyl)amino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (4a)



4a

White solid; yield 79% (76 mg); mp 137−138 ℃;

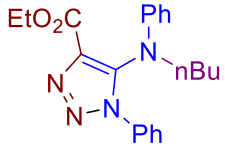
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.43 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.19 (dd, *J* = 8.9, 7.3 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.62 (dd, *J* = 8.9, 1.1 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.17 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.14, 146.45, 144.29, 135.26, 132.96, 129.84, 129.68, 129.37, 123.64,

120.36, 114.12, 61.2SS1, 38.53, 14.18.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{19}N_4O_2^+$, 323.1503; found, 323.1510

ethyl 5-(butyl(phenyl)amino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (4b)



4b

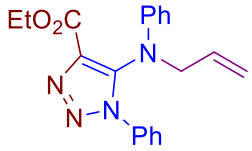
White solid; yield 63% (69 mg); mp 113−115 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.45 (dd, *J* = 5.2, 2.1 Hz, 3H), 7.23 (dd, *J* = 8.9, 7.3 Hz, 2H), 6.92 – 6.86 (m, 1H), 6.70 – 6.64 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.42 – 3.35 (m, 2H), 1.46 – 1.36 (m, 2H), 1.16 (h, *J* = 7.1 Hz, 5H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.13, 146.73, 143.48, 135.39, 133.61, 129.92, 129.69, 129.51, 124.02, 120.32, 114.68, 61.15, 51.59, 29.79, 20.15, 14.12, 13.82.

HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{25}N_4O_2^+$, 365.1972; found, 365.1979

ethyl 5-(allyl(phenyl)amino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (4c)



4c

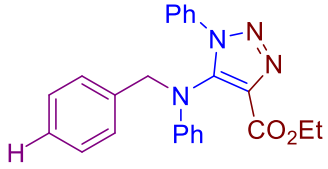
White solid; yield 65% (68 mg); mp 111−112 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 5H), 7.22 (dd, *J* = 8.9, 7.3 Hz, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 2H), 5.74 – 5.62 (m, 1H), 5.15 – 5.03 (m, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.07 (d, *J* = 5.9 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.14, 146.56, 143.45, 135.30, 133.52, 132.88, 129.99, 129.65, 129.41, 124.28, 120.71, 118.68, 115.12, 61.21, 54.64, 14.16.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{20}H_{20}N_4O_2Na^+$, 371.1478; found, 371.1477

ethyl 5-(benzyl(phenyl)amino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (4d)



4d

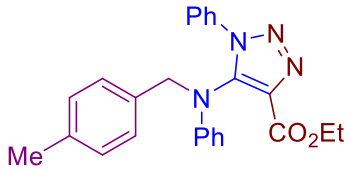
White solid; yield 77% (92 mg); mp 121−123 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 1H), 7.39 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.23 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.17 – 7.07 (m, 3H), 6.93 (dd, *J* = 14.1, 7.0 Hz, 3H), 6.74 (dd, *J* = 8.7, 0.9 Hz, 2H), 4.66 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.21, 147.32, 143.75, 136.00, 135.20, 133.70, 129.93, 129.49, 129.48, 128.52, 127.85, 127.66, 124.54, 120.94, 115.34, 61.30, 56.06, 14.18.

HRMS (ESI): $[M+H]^+$ calcd for $C_{24}H_{23}N_4O_2^+$, 399.1816; found, 399.1813

ethyl 5-((4-methylbenzyl)(phenyl)amino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (4e)



4e

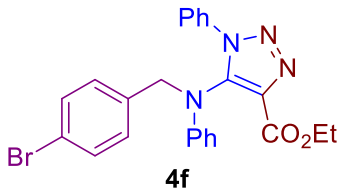
White solid; yield 71% (88 mg); mp 115−116 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 6.91 (dd, *J* = 14.1, 7.5 Hz, 3H), 6.82 (d, *J* = 7.9 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 2H), 4.62 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.24, 147.41, 143.74, 137.39, 135.27, 133.77, 132.85, 129.87, 129.47, 129.43, 129.19, 127.93, 124.51, 120.87, 115.37, 61.28, 55.73, 21.15, 14.20.

HRMS (ESI): $[M+H]^+$ calcd for $C_{25}H_{25}N_4O_2^+$, 413.1972; found, 413.1974

ethyl 5-((4-bromobenzyl)(phenyl)amino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (4f)



4f

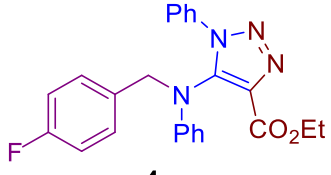
White solid; yield 65% (93 mg); mp 155−157 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 1H), 7.34 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.19 – 7.12 (m, 4H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 7.9 Hz, 2H), 4.54 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.20, 147.05, 143.79, 135.17, 135.13, 133.67, 131.63, 130.11, 129.59, 129.45, 124.60, 121.64, 121.19, 115.33, 61.43, 55.62, 14.23.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{21}BrN_4O_2Na^+$, 479.0906; found, 479.0915

ethyl 5-((4-fluorobenzyl)(phenyl)amino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (4g)



4g

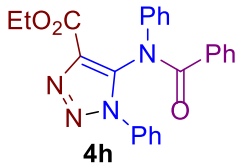
White solid; yield 69% (86 mg); mp 121−123 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 8.1 Hz, 2H), 6.99 – 6.88 (m, 3H), 6.80 – 6.69 (m, 4H), 4.64 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.25 (d, *J* = 246.4 Hz), 160.23, 147.17, 143.70, 135.18, 133.80, 131.69 (d, *J* = 3.3 Hz), 130.02, 129.64 (d, *J* = 8.3 Hz), 129.58, 129.55, 124.51, 121.11, 115.41 (d, *J* = 21.0 Hz), 115.33, 61.39, 55.30, 14.23.

HRMS (ESI): $[M+H]^+$ calcd for $C_{24}H_{22}FN_4O_2^+$, 417.1721; found, 417.1725

ethyl 1-phenyl-5-(N-phenylbenzamido)-1H-1,2,3-triazole-4-carboxylate (4h)



4h

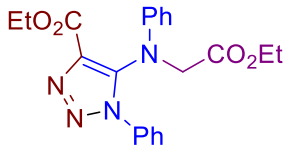
White solid; yield 88% (61 mg); mp 119−120 ℃;

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 – 7.49 (m, 3H), 7.46 – 7.28 (m, 7H), 7.11 (s, 3H), 6.79 (s, 2H), 4.30 (d, *J* = 5.3 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 159.22, 139.97, 139.75, 133.74, 133.19, 131.53, 130.67, 129.84, 129.02, 128.59, 128.18, 127.00, 125.88, 124.59, 61.01, 14.02.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{20}N_4O_3Na^+$, 435.1428; found, 435.1426

ethyl 5-((2-ethoxy-2-oxoethyl)(phenyl)amino)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (4i)



4i

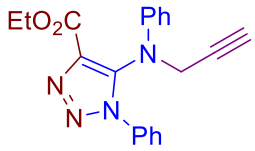
White solid; yield 57% (67 mg); mp 118−119 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 2H), 7.33 (dd, *J* = 5.2, 2.2 Hz, 3H), 7.10 (dd, *J* = 8.7, 7.3 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.62 – 6.55 (m, 2H), 4.55 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.02, 160.71, 145.69, 143.75, 135.62, 131.64, 129.55, 129.28, 129.16, 124.60, 122.22, 116.99, 61.57, 61.41, 54.98, 14.30, 14.21.

HRMS (ESI): $[M+ Na]^+$ calcd for $C_{21}H_{22}N_4O_4Na^+$, 417.1533; found, 417.1531

ethyl 1-phenyl-5-(phenyl(prop-2-yn-1-yl)amino)-1H-1,2,3-triazole-4-carboxylate (4j)



4j

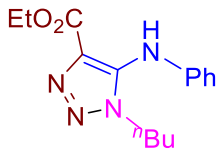
White solid; yield 56% (58 mg); mp 142−144 ℃;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.15 (dd, *J* = 8.8, 7.4 Hz, 2H), 6.89 – 6.83 (m, 1H), 6.72 – 6.66 (m, 2H), 4.47 (d, *J* = 2.6 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 2.31 (t, *J* = 2.5 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.43, 145.23, 142.90, 135.21, 133.16, 129.86, 129.41, 129.38, 124.35, 121.47, 115.58, 78.48, 74.44, 61.41, 41.96, 14.28.

HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{19}N_4O_2^+$, 347.1508; found, 347.1511

ethyl 1-benzyl-5-(phenylamino)-1H-1,2,3-triazole-4-carboxylate (5i)



5i

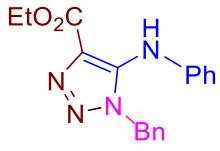
Colorless liquid; yield 87% (50 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.25 (s, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.00 – 3.94 (m, 2H), 1.73 – 1.65 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.14 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.78 (t, *J* = 7.4 Hz, 3H).

^{1}H NMR (101 MHz, $CDCl_3$) δ 162.91, 143.30, 140.29, 129.76, 126.13, 124.67, 120.82, 61.13, 48.75, 30.52, 19.58, 14.50, 13.39.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{21}N_4O_2^+$, 289.1660; found, 289.1664

ethyl 1-butyl-5-(phenylamino)-1H-1,2,3-triazole-4-carboxylate (5l)



5l

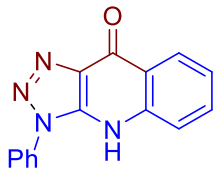
Colorless liquid; yield 81% (52 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.12 (m, 5H), 6.89 – 6.78 (m, 4H), 5.21 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.85, 143.35, 139.61, 133.97, 129.69, 128.71, 128.35, 127.67, 125.95, 124.94, 121.52, 61.17, 52.64, 14.51.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{19}N_4O_2^+$, 323.1508; found, 323.1516

3-phenyl-3,4-dihydro-9*H*-[1,2,3]triazolo[4,5-*b*]quinolin-9-one (7)



7

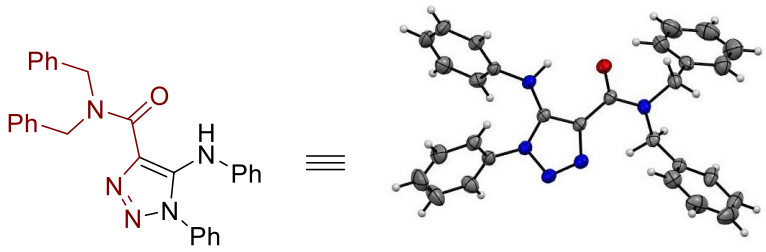
White solid; yield 59% (31 mg); >263 ℃ (decomposition);

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.34 (s, 1H), 8.34 – 8.30 (m, 1H), 7.85 – 7.80 (m, 2H), 7.76 – 7.71 (m, 4H), 7.70 – 7.65 (m, 1H), 7.36 (ddd, *J* = 8.1, 5.5, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 170.43, 140.65, 139.95, 134.45, 133.20, 130.38, 130.07, 130.03, 126.16, 125.02, 123.78, 122.41, 118.68.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{11}N_4^+$, 263.0927; found, 263.0930

10. Crystal data and structure refinement for 3x



3x **CCDC 2032795**

Table 1. Crystal data and structure refinement for 20200106ZH_KHAZ0863_0m_a.

Identification code	20200106ZH_KHAZ0863_0m_a	
Empirical formula	C29 H25 N5 O	
Formula weight	459.54	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 27.8270(12) Å	α= 90 °.
	b = 7.9969(4) Å	β= 119.399(2) °.
	c = 24.2837(11) Å	γ = 90 °.
Volume	4707.9(4) $Å^3$	
Z	8	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	1936	
Crystal size	0.120 x 0.110 x 0.080 mm^3	
Theta range for data collection	2.682 to 28.306 °.	
Index ranges	-36<=h<=36, -8<=k<=10, -32<=l<=32	
Reflections collected	22877	
Independent reflections	5836 [R(int) = 0.0476]	
Completeness to theta = 25.242 °	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5836 / 0 / 316	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1050	
R indices (all data)	R1 = 0.0686, wR2 = 0.1188	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.211 and -0.208 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for 20200106ZH_KHAZ0863_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7266(1)	4007(2)	4311(1)	53(1)
C(2)	7624(1)	5006(3)	4211(1)	65(1)
C(3)	7556(1)	6699(3)	4169(1)	63(1)
C(4)	7134(1)	7420(3)	4228(1)	63(1)
C(5)	6780(1)	6431(2)	4334(1)	50(1)
C(6)	6841(1)	4708(2)	4374(1)	38(1)
C(7)	6447(1)	3623(2)	4476(1)	37(1)
C(8)	5446(1)	471(2)	3418(1)	42(1)
C(9)	5454(1)	-1224(2)	3313(1)	58(1)
C(10)	5758(1)	-1845(2)	3051(1)	65(1)
C(11)	6059(1)	-773(2)	2897(1)	58(1)
C(12)	6053(1)	926(2)	2999(1)	42(1)
C(13)	5748(1)	1561(2)	3263(1)	30(1)
C(14)	5737(1)	3422(2)	3352(1)	29(1)
C(15)	5532(1)	4696(2)	4162(1)	28(1)
C(16)	4934(1)	4817(2)	3723(1)	28(1)
C(17)	4576(1)	5754(2)	3846(1)	27(1)
C(18)	4436(1)	8300(2)	4325(1)	28(1)
C(19)	4414(1)	8848(2)	4854(1)	34(1)
C(20)	4195(1)	10410(2)	4848(1)	41(1)
C(21)	3995(1)	11408(2)	4319(1)	45(1)
C(22)	4014(1)	10854(2)	3791(1)	45(1)
C(23)	4238(1)	9301(2)	3794(1)	37(1)
C(24)	3411(1)	5814(2)	3725(1)	35(1)
C(25)	2875(1)	6155(2)	3588(1)	49(1)
C(26)	2474(1)	6539(3)	2983(1)	63(1)
C(27)	2597(1)	6568(3)	2497(1)	60(1)
C(28)	3127(1)	6215(2)	2619(1)	42(1)
C(29)	3527(1)	5861(2)	3231(1)	31(1)
N(1)	5870(1)	3895(2)	3996(1)	31(1)
N(2)	4629(1)	4003(2)	3161(1)	33(1)
N(3)	4112(1)	4369(2)	2928(1)	34(1)
N(4)	4070(1)	5445(1)	3348(1)	29(1)

N(5)	4687(1)	6722(1)	4358(1)	32(1)
O(1)	5709(1)	5316(1)	4697(1)	36(1)

Table 3. Bond lengths [Å] and angles [°] for 20200106ZH_KHAZ0863_0m_a.

C(1)-C(6)	1.383(2)
C(1)-C(2)	1.389(3)
C(1)-H(1)	0.9500
C(2)-C(3)	1.364(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.376(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.381(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.386(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.510(2)
C(7)-N(1)	1.4649(17)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.381(2)
C(8)-C(13)	1.384(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.377(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.372(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.383(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.3871(18)
C(12)-H(12)	0.9500
C(13)-C(14)	1.5061(19)
C(14)-N(1)	1.4682(16)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-O(1)	1.2448(16)
C(15)-N(1)	1.3533(16)

C(15)-C(16)	1.4725(19)
C(16)-N(2)	1.3669(17)
C(16)-C(17)	1.3925(17)
C(17)-N(4)	1.3557(17)
C(17)-N(5)	1.3641(16)
C(18)-C(23)	1.381(2)
C(18)-C(19)	1.3876(18)
C(18)-N(5)	1.4251(17)
C(19)-C(20)	1.387(2)
C(19)-H(19)	0.9500
C(20)-C(21)	1.376(2)
C(20)-H(20)	0.9500
C(21)-C(22)	1.382(2)
C(21)-H(21)	0.9500
C(22)-C(23)	1.387(2)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
C(24)-C(25)	1.385(2)
C(24)-C(29)	1.3877(18)
C(24)-H(24)	0.9500
C(25)-C(26)	1.375(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.380(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.383(2)
C(27)-H(27)	0.9500
C(28)-C(29)	1.380(2)
C(28)-H(28)	0.9500
C(29)-N(4)	1.4316(16)
N(2)-N(3)	1.2940(16)
N(3)-N(4)	1.3837(15)
N(5)-H(5A)	0.9495

C(6)-C(1)-C(2)	120.84(18)
C(6)-C(1)-H(1)	119.6
C(2)-C(1)-H(1)	119.6
C(3)-C(2)-C(1)	119.85(18)
C(3)-C(2)-H(2)	120.1

C(1)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	120.16(19)
C(2)-C(3)-H(3)	119.9
C(4)-C(3)-H(3)	119.9
C(3)-C(4)-C(5)	120.1(2)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(4)-C(5)-C(6)	120.60(17)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(1)-C(6)-C(5)	118.43(16)
C(1)-C(6)-C(7)	120.90(15)
C(5)-C(6)-C(7)	120.66(14)
N(1)-C(7)-C(6)	112.62(12)
N(1)-C(7)-H(7A)	109.1
C(6)-C(7)-H(7A)	109.1
N(1)-C(7)-H(7B)	109.1
C(6)-C(7)-H(7B)	109.1
H(7A)-C(7)-H(7B)	107.8
C(9)-C(8)-C(13)	120.14(16)
C(9)-C(8)-H(8)	119.9
C(13)-C(8)-H(8)	119.9
C(10)-C(9)-C(8)	120.46(18)
C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	119.80(17)
C(11)-C(10)-H(10)	120.1
C(9)-C(10)-H(10)	120.1
C(10)-C(11)-C(12)	120.15(17)
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-C(13)	120.41(16)
C(11)-C(12)-H(12)	119.8
C(13)-C(12)-H(12)	119.8
C(8)-C(13)-C(12)	119.04(14)
C(8)-C(13)-C(14)	121.74(12)
C(12)-C(13)-C(14)	119.19(13)
N(1)-C(14)-C(13)	113.27(11)

N(1)-C(14)-H(14A)	108.9
C(13)-C(14)-H(14A)	108.9
N(1)-C(14)-H(14B)	108.9
C(13)-C(14)-H(14B)	108.9
H(14A)-C(14)-H(14B)	107.7
O(1)-C(15)-N(1)	121.46(13)
O(1)-C(15)-C(16)	117.29(11)
N(1)-C(15)-C(16)	121.22(12)
N(2)-C(16)-C(17)	108.08(12)
N(2)-C(16)-C(15)	128.30(11)
C(17)-C(16)-C(15)	123.52(12)
N(4)-C(17)-N(5)	125.93(11)
N(4)-C(17)-C(16)	104.50(11)
N(5)-C(17)-C(16)	129.51(12)
C(23)-C(18)-C(19)	120.11(13)
C(23)-C(18)-N(5)	121.79(12)
C(19)-C(18)-N(5)	118.05(12)
C(20)-C(19)-C(18)	119.56(14)
C(20)-C(19)-H(19)	120.2
C(18)-C(19)-H(19)	120.2
C(21)-C(20)-C(19)	120.45(14)
C(21)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
C(20)-C(21)-C(22)	119.88(14)
C(20)-C(21)-H(21)	120.1
C(22)-C(21)-H(21)	120.1
C(21)-C(22)-C(23)	120.17(15)
C(21)-C(22)-H(22)	119.9
C(23)-C(22)-H(22)	119.9
C(18)-C(23)-C(22)	119.82(14)
C(18)-C(23)-H(23)	120.1
C(22)-C(23)-H(23)	120.1
C(25)-C(24)-C(29)	117.89(15)
C(25)-C(24)-H(24)	121.1
C(29)-C(24)-H(24)	121.1
C(26)-C(25)-C(24)	120.89(15)
C(26)-C(25)-H(25)	119.6
C(24)-C(25)-H(25)	119.6

C(25)-C(26)-C(27)	120.38(15)
C(25)-C(26)-H(26)	119.8
C(27)-C(26)-H(26)	119.8
C(26)-C(27)-C(28)	119.95(17)
C(26)-C(27)-H(27)	120.0
C(28)-C(27)-H(27)	120.0
C(29)-C(28)-C(27)	118.98(15)
C(29)-C(28)-H(28)	120.5
C(27)-C(28)-H(28)	120.5
C(28)-C(29)-C(24)	121.90(13)
C(28)-C(29)-N(4)	118.44(12)
C(24)-C(29)-N(4)	119.58(13)
C(15)-N(1)-C(7)	118.93(11)
C(15)-N(1)-C(14)	126.22(11)
C(7)-N(1)-C(14)	114.44(10)
N(3)-N(2)-C(16)	110.07(11)
N(2)-N(3)-N(4)	107.23(11)
C(17)-N(4)-N(3)	110.12(10)
C(17)-N(4)-C(29)	131.90(11)
N(3)-N(4)-C(29)	117.50(11)
C(17)-N(5)-C(18)	124.43(12)
C(17)-N(5)-H(5A)	111.9
C(18)-N(5)-H(5A)	114.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 20200106ZH_KHAZ0863_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	47(1)	57(1)	65(1)	-9(1)	34(1)	2(1)
C(2)	54(1)	77(1)	80(2)	-18(1)	45(1)	-10(1)
C(3)	51(1)	81(2)	53(1)	-6(1)	23(1)	-21(1)
C(4)	47(1)	53(1)	66(1)	1(1)	12(1)	-8(1)
C(5)	35(1)	51(1)	53(1)	-4(1)	13(1)	4(1)
C(6)	29(1)	49(1)	29(1)	-4(1)	10(1)	3(1)

C(7)	32(1)	49(1)	30(1)	3(1)	15(1)	10(1)
C(8)	45(1)	41(1)	43(1)	5(1)	23(1)	-1(1)
C(9)	65(1)	38(1)	57(1)	8(1)	18(1)	-6(1)
C(10)	88(2)	32(1)	47(1)	-2(1)	12(1)	14(1)
C(11)	81(1)	51(1)	40(1)	2(1)	28(1)	32(1)
C(12)	50(1)	44(1)	37(1)	6(1)	26(1)	17(1)
C(13)	33(1)	32(1)	25(1)	3(1)	14(1)	6(1)
C(14)	32(1)	33(1)	27(1)	2(1)	18(1)	4(1)
C(15)	33(1)	27(1)	28(1)	1(1)	18(1)	3(1)
C(16)	32(1)	28(1)	28(1)	-2(1)	18(1)	1(1)
C(17)	30(1)	27(1)	27(1)	0(1)	16(1)	-1(1)
C(18)	27(1)	27(1)	33(1)	-4(1)	17(1)	-2(1)
C(19)	40(1)	31(1)	37(1)	-4(1)	24(1)	-1(1)
C(20)	45(1)	36(1)	50(1)	-12(1)	30(1)	-2(1)
C(21)	42(1)	29(1)	62(1)	-6(1)	24(1)	3(1)
C(22)	47(1)	34(1)	47(1)	6(1)	17(1)	0(1)
C(23)	42(1)	36(1)	34(1)	-2(1)	20(1)	-3(1)
C(24)	38(1)	34(1)	41(1)	-4(1)	24(1)	-1(1)
C(25)	42(1)	59(1)	58(1)	-9(1)	35(1)	-3(1)
C(26)	32(1)	91(2)	72(1)	-6(1)	29(1)	4(1)
C(27)	31(1)	88(2)	52(1)	6(1)	14(1)	6(1)
C(28)	33(1)	54(1)	40(1)	2(1)	18(1)	-2(1)
C(29)	28(1)	28(1)	39(1)	-3(1)	19(1)	-2(1)
N(1)	29(1)	38(1)	26(1)	0(1)	14(1)	6(1)
N(2)	32(1)	37(1)	32(1)	-7(1)	17(1)	0(1)
N(3)	33(1)	38(1)	34(1)	-10(1)	18(1)	-2(1)
N(4)	29(1)	31(1)	30(1)	-5(1)	17(1)	-1(1)
N(5)	33(1)	34(1)	28(1)	-5(1)	15(1)	4(1)
O(1)	37(1)	41(1)	27(1)	-5(1)	14(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 20200106ZH_KHAZ0863_0m_a.

	x	y	z	U(eq)
H(1)	7313	2828	4337	64
H(2)	7916	4510	4171	78

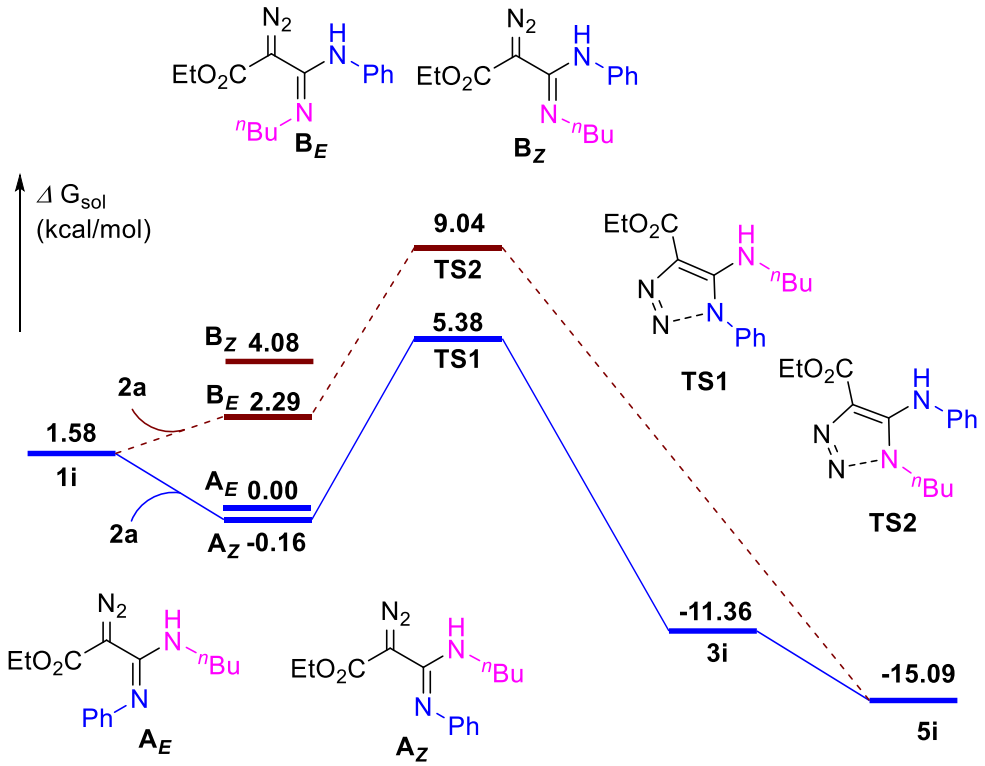
H(3)	7800	7383	4100	75
H(4)	7085	8598	4195	75
H(5)	6493	6937	4379	60
H(7A)	6542	2434	4468	44
H(7B)	6491	3862	4898	44
H(8)	5234	889	3596	51
H(9)	5247	-1967	3422	70
H(10)	5759	-3011	2977	78
H(11)	6271	-1200	2719	70
H(12)	6260	1663	2889	50
H(14A)	6005	3961	3251	35
H(14B)	5366	3853	3050	35
H(19)	4549	8158	5219	40
H(20)	4182	10793	5211	49
H(21)	3845	12476	4317	54
H(22)	3873	11538	3424	55
H(23)	4254	8928	3432	44
H(24)	3689	5557	4143	42
H(25)	2784	6124	3917	58
H(26)	2110	6785	2898	76
H(27)	2318	6831	2080	72
H(28)	3214	6215	2287	51
H(5A)	5063	6653	4675	38

---

11. Computational details

All the DFT calculations were performed using Gaussian09 (Revision D.01).[4] Geometry optimizations were carried out with B3LYP[5] level of theory. Lanl2dz[6] basis set was used for Pd, I and K atom and 6-31G(d, p)[7] basis set for other atoms. Gibbs free energy was corrected by frequency calculations using the optimized structures. Single point energies of the optimized geometries were calculated at the level of M06[8] denoting the basis set combination of SDD[9] for Pd and 6-311+G(d, p) for all other atoms. Single point solvation energy corrections in MeCN computed by the IEFPCM[10] method were added to the gas-phase free energy.

1). Free-energy profile of nucleophilic addition/cyclization of carbodiimide 1i with diazo 2a.

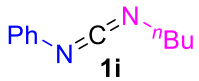


2). B3LYP and M06 absolute calculation energies and free energies

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$G_{(corr\text{-}B3LYP)}$[2]	$E_{(sol\text{-}M06)}$[3]
1i	-536.921751	0.186546	-536.8150427
2a	-415.880903	0.07108	-415.81540289
A_E	-952.800677	0.284033	-952.659364321
A_Z	-952.748385	0.284028	-952.3755922
B_E	-952.797989	0.284042	-952.655717914
B_Z	-952.737900	0.28311	-952.3688254
TS1	-952.799674	0.285429	-952.652192851
TS2	-952.794202	0.286088	-952.647016352
3i	-952.825138	0.28978	-952.683220483
4i	-952.829718	0.289968	-952.689347028

1. The electronic and thermal energy calculated by B3LYP in gas phase. 2. The thermal correction to Gibbs free energy calculated 3. The electronic and thermal energy calculated by M06 in MeCN.

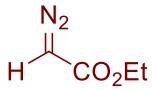
3). B3LYP optimized Cartesian coordinates.



Charge: 0 Multiplicity: 1

C	-2.11934200	-0.48478300	-0.01702200
C	-3.39867500	-0.89604400	0.37857600
C	-1.90088000	0.86023000	-0.35625300

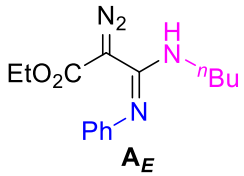
C	-4.44264200	0.02507800	0.43824600
H	-3.55298000	-1.93905000	0.63408300
C	-2.95000600	1.77378400	-0.29460200
H	-0.91066600	1.17903300	-0.66975700
C	-4.22467500	1.36269200	0.10323300
H	-5.43039600	-0.30473000	0.74681400
H	-2.77108600	2.81191400	-0.55985900
H	-5.03949000	2.07863500	0.14997000
N	-1.10749900	-1.46133100	-0.06195500
C	0.09153900	-1.31829800	-0.30512900
N	1.25869700	-1.33888100	-0.65691400
C	3.20997600	0.11477600	-0.23741200
H	3.37798300	0.12265200	-1.32132500
H	2.55928000	0.97085200	-0.01642900
C	2.47565200	-1.17678200	0.13500500
H	3.12048700	-2.03708900	-0.07879200
H	2.25387200	-1.19287900	1.21012200
C	4.54365300	0.26979000	0.50336600
H	5.18637800	-0.59181500	0.27782900
H	4.36599500	0.24168500	1.58699000
C	5.27863200	1.56367900	0.14099600
H	6.22602500	1.64835700	0.68246300
H	5.50220300	1.60500100	-0.93074600
H	4.67461600	2.44419600	0.38669200



2a

Charge: 0 Multiplicity: 1

C	-1.68354200	0.62985200	-0.00006900
H	-2.44105900	1.39916700	0.00002200
N	-2.08646000	-0.61297700	-0.00003800
N	-2.42556000	-1.69950000	0.00026000
C	-0.26228300	0.96149900	-0.00006400
O	0.15756600	2.10188900	-0.00001000
O	0.51722700	-0.14777700	-0.00005800
C	1.94381800	0.09371000	-0.00001900
H	2.20151000	0.68724300	-0.88261700
H	2.20146400	0.68722700	0.88260300
C	2.63283500	-1.25672300	-0.00001300
H	3.71826900	-1.11766900	0.00001600
H	2.36030200	-1.83578100	0.88684500
H	2.36034600	-1.83576600	-0.88689400

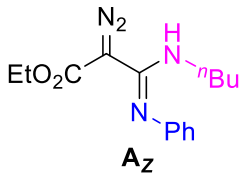


$\mathbf{A}_{E}$

Charge: 0 Multiplicity: 1

C	-0.09069600	-0.22186300	-0.48188700
C	0.72413000	-1.22400700	0.21784100
O	1.53996200	-0.96555000	1.08174300
O	0.45024000	-2.47685400	-0.21838000
C	1.18759100	-3.54325900	0.42711000
H	1.00461400	-3.49546300	1.50467600
H	2.25749400	-3.37862300	0.26597200
C	0.71313500	-4.85059000	-0.17607500
H	1.24814700	-5.68562800	0.28637700
H	-0.35801100	-4.99274100	-0.00825500
H	0.90017600	-4.87654900	-1.25324300
N	-0.96221600	-0.66715400	-1.36349300
N	-1.69939600	-1.05352700	-2.13337700
C	-0.13727000	1.24280100	-0.17111300
N	-1.21859300	1.93394500	-0.01577500
N	1.06427200	1.88435600	-0.06114600
H	0.94205800	2.85100000	0.21460200
C	2.33466900	1.54148200	-0.68725600
H	2.50878900	2.19406200	-1.55706200
H	2.26676800	0.52174500	-1.07005400
C	3.50435700	1.65415200	0.29469000
H	3.53273200	2.67368400	0.70560000
H	3.31010600	0.97724000	1.13282800
C	4.85497100	1.33031800	-0.35402200
H	5.02164900	1.99694500	-1.21145300
H	4.82420300	0.31094000	-0.76234300
C	6.02931900	1.45074700	0.62178900
H	6.97946200	1.20639500	0.13608800
H	6.11112700	2.46859900	1.01951400
H	5.90488000	0.77289100	1.47325800
C	-2.47772500	1.36240500	0.20932000
C	-3.57154400	1.81958400	-0.54771100
C	-2.71531200	0.42082700	1.22930400
C	-4.85266300	1.32569000	-0.31541800
H	-3.39212200	2.56451000	-1.31684600
C	-4.00223600	-0.06285700	1.46043600

H	-1.88738700	0.09521200	1.85215600
C	-5.07723200	0.37934500	0.68753600
H	-5.68201800	1.68656500	-0.91761400
H	-4.16552900	-0.78476400	2.25624100
H	-6.07818200	0.00123100	0.87192600

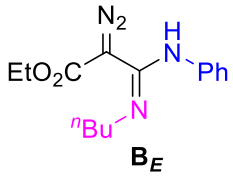


A*Z*

Charge: 0 Multiplicity: 1

C	0.88634300	-1.11968500	-0.26782300
C	2.16809900	-0.65893000	0.27995300
O	2.34024500	0.39389100	0.86476800
O	3.15258800	-1.56179300	0.04749000
C	4.45969200	-1.21450800	0.56361900
H	4.38345200	-1.06599300	1.64494900
H	4.77232100	-0.26383300	0.12075200
C	5.40201000	-2.34754400	0.20768400
H	6.40555300	-2.12393900	0.58223900
H	5.06952700	-3.28843000	0.65486200
H	5.46139100	-2.48241700	-0.87595100
N	0.87604100	-2.33205900	-0.79711900
N	0.88331800	-3.35921200	-1.27120300
C	-0.46414300	-0.53230800	-0.06213600
N	-1.42875900	-1.38247600	0.09728300
N	-0.58185200	0.83053300	0.00081600
H	-1.52708100	1.12373600	0.21617000
C	0.21107600	1.82785900	-0.71634600
H	-0.32186400	2.13237300	-1.63108800
H	1.14892000	1.37002400	-1.02885200
C	0.49954100	3.05180500	0.15457400
H	-0.45068500	3.47651900	0.50990200
H	1.05141100	2.71529800	1.03791100
C	1.29206500	4.13245200	-0.58994200
H	0.74536800	4.43309000	-1.49456100
H	2.24353900	3.70637900	-0.93545300
C	1.57088500	5.36811400	0.27075200
H	2.14426600	6.11905500	-0.28223700
H	0.63846900	5.83921800	0.60181700
H	2.14335700	5.10387800	1.16656800
C	-2.76881300	-0.95677900	0.13441000
C	-3.39643800	-0.35670900	-0.97529400

C	-3.54118700	-1.21680300	1.27996900
C	-4.75035400	-0.02498700	-0.93137800
H	-2.81805500	-0.17923100	-1.87774000
C	-4.89143100	-0.87531400	1.31882700
H	-3.06190800	-1.69348800	2.12921700
C	-5.50497200	-0.27718100	0.21558200
H	-5.21770400	0.42833000	-1.80148000
H	-5.46930400	-1.08279100	2.21529200
H	-6.55910200	-0.01895400	0.24646900

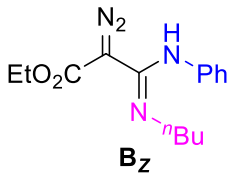


B*E*

Charge: 0 Multiplicity: 1

C	-1.29085100	-0.76106800	0.30065600
C	-2.43413600	-0.30273900	-0.49889300
O	-2.34841700	0.49692200	-1.40914200
O	-3.58724800	-0.89129100	-0.10063300
C	-4.77177700	-0.51714700	-0.84585500
H	-4.62168000	-0.77591000	-1.89850300
H	-4.89541700	0.56830600	-0.78679000
C	-5.94379700	-1.26042300	-0.23596500
H	-6.86206000	-1.00546600	-0.77365700
H	-5.79778900	-2.34242300	-0.29874400
H	-6.07468500	-0.99015600	0.81556900
N	-1.49918500	-1.68191300	1.21376300
N	-1.66042800	-2.47621000	2.01251600
C	0.11588900	-0.24615300	0.12225200
N	0.46870100	0.97655500	0.18111900
N	1.01233500	-1.28500900	-0.10249500
H	0.58421100	-2.15808600	-0.37104000
C	2.41606200	-1.28184200	-0.18693400
C	3.03398100	-2.50567700	-0.50215800
C	3.21596000	-0.15223800	0.04604600
C	4.41888200	-2.60123500	-0.57955300
H	2.42039000	-3.38597300	-0.68328000
C	4.60441800	-0.26744400	-0.02993600
H	2.74111100	0.79156900	0.26931700
C	5.21747500	-1.48045000	-0.34154200
H	5.21186300	0.61462000	0.15268500
H	6.29882200	-1.55280500	-0.40241300

C	-0.46803500	2.02942400	0.53781800
H	-0.95937600	2.38409100	-0.37624900
H	-1.27128300	1.65910000	1.19426500
C	0.25412900	3.18896800	1.23749600
H	-0.50694000	3.89926000	1.58957600
H	0.75157200	2.79580700	2.13308300
C	1.28191500	3.93215700	0.36939500
H	1.83696500	4.62935300	1.01002000
H	2.01475100	3.21161300	-0.01157500
C	0.67303700	4.70835600	-0.80371000
H	-0.06531300	5.44068100	-0.45564900
H	1.44525700	5.25394100	-1.35600500
H	0.17227800	4.04495200	-1.51599200
H	4.87377300	-3.55641500	-0.82545400

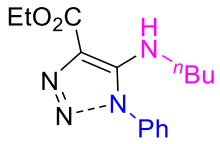


B$_Z$

Charge: 0 Multiplicity: 1

C	-1.59102000	-0.62116600	-0.02250600
C	-2.73716000	0.29747700	-0.17468800
O	-2.65745300	1.45803400	-0.50786800
O	-3.90503100	-0.34765100	0.07965400
C	-5.10341000	0.44554300	-0.08784000
H	-5.14383400	0.81211800	-1.11841200
H	-5.04233200	1.31799800	0.56958100
C	-6.28589400	-0.44154600	0.24913100
H	-7.21591700	0.12390900	0.13589900
H	-6.32811900	-1.30918300	-0.41547600
H	-6.22476000	-0.79998100	1.28050600
N	-1.85502100	-1.89219700	0.18940500
N	-2.06909500	-2.99641000	0.36137700
C	-0.16466100	-0.19972300	-0.06323400
N	0.14622000	0.91923300	0.46152700
N	0.67348600	-1.11350300	-0.72773500
H	0.25917600	-1.61643100	-1.50011300
C	1.95366600	-1.54691500	-0.33664700
C	2.76693300	-2.19088600	-1.28265300
C	2.41656400	-1.40719400	0.98106100
C	4.01723400	-2.68215700	-0.91711600
H	2.41511700	-2.29831700	-2.30567200

C	3.67677700	-1.89057300	1.33003200
H	1.78353200	-0.93853300	1.72629900
C	4.48516500	-2.53030000	0.38971800
H	4.02091800	-1.77474200	2.35376100
H	5.46336900	-2.90698900	0.67068700
H	4.63118800	-3.17972800	-1.66225400
C	1.43461000	1.54554000	0.22420500
H	2.12428700	1.28930300	1.04246500
H	1.90962800	1.18046500	-0.69953800
C	1.26347800	3.06765900	0.16703100
H	0.54797000	3.31132000	-0.62822700
H	0.80277500	3.40324900	1.10423400
C	2.58441000	3.80856700	-0.06826800
H	3.29550800	3.55003200	0.72872900
H	3.03969100	3.45657500	-1.00419500
C	2.41488200	5.32973100	-0.12564400
H	1.99448500	5.71608800	0.80964700
H	3.37192400	5.83434100	-0.29429000
H	1.73669700	5.62123700	-0.93543700

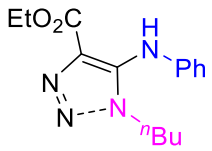


TS1

Charge: 0 Multiplicity: 1

C	0.22421800	-0.46152000	-0.01633100
C	1.69029400	-0.74450500	-0.08312000
N	-0.55173100	-1.44578200	-0.34483600
N	1.29562500	-2.97129200	-0.66463800
N	1.89004000	-2.01682200	-0.41838600
N	-0.09360100	0.81231700	0.33680000
H	0.71254300	1.41028000	0.50913000
C	-1.91094700	-1.60506300	-0.07981400
C	-2.74674500	-2.10987300	-1.09277900
C	-2.45966600	-1.38714900	1.19980300
C	-4.09443400	-2.35302900	-0.84280900
H	-2.31538200	-2.30411900	-2.06955700
C	-3.80903000	-1.63845400	1.44163300
H	-1.81364400	-1.03696000	1.99924100
C	-4.63617600	-2.11686900	0.42358100
H	-4.72524200	-2.73529700	-1.64058600

H	-4.21392900	-1.46500700	2.43499900
H	-5.68639500	-2.31302900	0.61665400
C	2.78063300	0.17146500	0.16135400
O	2.63323600	1.34861200	0.48403100
O	3.99232000	-0.40409900	0.00134700
C	5.13352200	0.45274700	0.24122500
H	5.08871700	0.82222600	1.27044200
H	5.07142900	1.31970700	-0.42351500
C	6.37892400	-0.37338500	-0.01402400
H	7.26952800	0.23903800	0.15705700
H	6.42070700	-1.23669300	0.65593100
H	6.40314600	-0.73600000	-1.04541600
C	-1.37563400	1.46311100	0.07765300
H	-1.81187500	1.05087600	-0.83934400
H	-2.08910600	1.25072400	0.88392500
C	-1.18202600	2.97445800	-0.06270800
H	-0.71720700	3.36539100	0.85316200
H	-0.47676000	3.17488400	-0.88003200
C	-2.49951600	3.71521700	-0.32136300
H	-3.20316200	3.50001000	0.49358700
H	-2.96278900	3.32077700	-1.23536600
C	-2.31607800	5.22981000	-0.45310100
H	-3.27082500	5.73097600	-0.64070600
H	-1.88875800	5.65853100	0.46022800
H	-1.64179900	5.47685500	-1.28063300

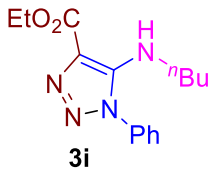


TS2

Charge: 0 Multiplicity: 1

C	-0.20278600	-0.25887700	0.00575400
C	-1.63668200	-0.65338200	0.14384200
N	0.66393800	-1.13750600	0.36390400
N	-1.01151900	-2.76839000	0.89791700
N	-1.70930500	-1.90434700	0.59239300
N	-0.00437200	0.99636900	-0.53754400
H	-0.86657900	1.42187200	-0.88017100
C	-2.80807200	0.11527200	-0.21082700
O	-2.76922000	1.22888000	-0.73055300
O	-3.96116200	-0.52444900	0.07947300
C	-5.17716300	0.17389900	-0.27986300
H	-5.16115100	0.38395100	-1.35371000

H	-5.20073900	1.13425600	0.24405900
C	-6.34010600	-0.71715200	0.11025700
H	-7.28371600	-0.22484200	-0.14409900
H	-6.29625000	-1.67265000	-0.41982300
H	-6.33544200	-0.91854300	1.18507700
C	2.07934200	-1.08030100	0.06257900
H	2.26833500	-0.47975500	-0.84011000
H	2.62202000	-0.58408500	0.88043100
C	2.63596200	-2.49643300	-0.12350300
H	2.41740700	-3.07860600	0.78039400
H	2.09319300	-2.98565300	-0.94242600
C	4.14134800	-2.51310700	-0.41039800
H	4.67449500	-2.01530300	0.41119400
H	4.34933600	-1.91779600	-1.30996400
C	4.69876300	-3.92758700	-0.59591200
H	4.21204900	-4.43796700	-1.43462700
H	5.77501900	-3.91083900	-0.79593400
H	4.53533800	-4.53732700	0.29975500
C	1.00917100	1.91338000	-0.16164200
C	1.34675400	2.92883300	-1.06805400
C	1.62541000	1.88381100	1.09723900
C	2.29089100	3.89260100	-0.72242000
H	0.86760400	2.94910500	-2.04251900
C	2.58317000	2.84302300	1.42635600
H	1.33869000	1.12535900	1.81749500
C	2.92125900	3.85114600	0.52316100
H	2.54070100	4.67384200	-1.43439100
H	3.05444600	2.80810500	2.40441600
H	3.66354000	4.59777600	0.78747300

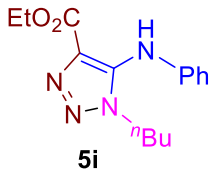


3i

Charge: 0 Multiplicity: 1

C	0.38514000	-0.25811600	0.12531700
C	1.72977500	-0.63706000	0.02837900
N	-0.29657200	-1.41866200	-0.08614600
N	0.60759300	-2.46252600	-0.31795400
N	1.79370700	-1.97728800	-0.24071000
N	-0.13621800	0.97998700	0.40645900
H	0.64873300	1.61746900	0.54625400
C	-1.67986800	-1.73382100	0.02734700

C	-2.23939200	-2.64341600	-0.87437600
C	-2.44819200	-1.18414700	1.05886600
C	-3.58124200	-2.99600000	-0.74346200
H	-1.61718700	-3.06909700	-1.65271400
C	-3.79355400	-1.53448200	1.16830100
H	-1.99130700	-0.49575700	1.76150200
C	-4.36288500	-2.43993100	0.27119100
H	-4.01729600	-3.70447600	-1.44101400
H	-4.39283700	-1.10710200	1.96645300
H	-5.40928900	-2.71356100	0.36462200
C	2.85498900	0.27856000	0.16939500
O	2.70923600	1.46938100	0.43890600
O	4.05048300	-0.29637300	-0.02620500
C	5.19985600	0.57092500	0.10965200
H	5.19974400	1.00370300	1.11508200
H	5.10701300	1.39628900	-0.60327200
C	6.43306000	-0.27191100	-0.14972900
H	7.33106400	0.34653000	-0.05508400
H	6.50170900	-1.09398300	0.56793500
H	6.41018800	-0.69696300	-1.15689700
C	-1.19831900	1.57087800	-0.42731900
H	-0.86424600	1.66925500	-1.47218400
H	-2.06508800	0.90550800	-0.42792400
C	-1.59886600	2.93844400	0.12440500
H	-1.93607800	2.81819800	1.16173300
H	-0.71363200	3.58917000	0.15968000
C	-2.69382500	3.61504400	-0.70885300
H	-3.57684900	2.96304700	-0.74514700
H	-2.34945800	3.71902700	-1.74641900
C	-3.09489700	4.98897000	-0.16410500
H	-3.87739600	5.44675700	-0.77721600
H	-3.47570900	4.91351300	0.86048500
H	-2.24008200	5.67420600	-0.14907700



5i

Charge: 0 Multiplicity: 1

C	-0.36935500	-0.24986800	0.16656100
C	-1.72970400	-0.55299800	0.29227300
N	0.25474800	-1.22952400	0.86841700
N	-0.68667200	-2.09286100	1.40526800

N	-1.85694100	-1.68061100	1.05526300
N	0.20674000	0.74966800	-0.57849300
H	-0.50762300	1.20771900	-1.14477400
C	-2.79804200	0.21322500	-0.33706500
O	-2.57143300	1.14560300	-1.10698400
O	-4.03074200	-0.19082100	-0.00295200
C	-5.12373500	0.52932100	-0.61945400
H	-5.03401500	0.44445400	-1.70710000
H	-5.03728000	1.59000600	-0.36389600
C	-6.41216000	-0.08018900	-0.10288200
H	-7.26955000	0.43516300	-0.54683100
H	-6.47330300	-1.14066200	-0.36197100
H	-6.47844500	0.01177600	0.98465000
C	1.66337000	-1.60843000	0.94484200
H	2.25373300	-0.73665800	1.23827500
H	1.71427400	-2.34384400	1.75161700
C	2.18768100	-2.20262600	-0.36779600
H	1.56536900	-3.06534500	-0.63533900
H	2.07305600	-1.46533400	-1.17163100
C	3.65741000	-2.62675400	-0.25873000
H	3.76645300	-3.35471600	0.55639900
H	4.26671300	-1.75769900	0.02340300
C	4.19883200	-3.22970800	-1.55818000
H	4.13412300	-2.51279400	-2.38412500
H	5.24805100	-3.52268900	-1.45295500
H	3.63124700	-4.12081300	-1.84788000
C	1.28641900	1.57596800	-0.17273700
C	1.97401600	2.29004900	-1.16451100
C	1.65789600	1.73260400	1.17009300
C	3.01734600	3.14401300	-0.81650500
H	1.68479600	2.16399700	-2.20370900
C	2.71944300	2.57412400	1.50571700
H	1.10064400	1.22123200	1.94852500
C	3.40304600	3.28423200	0.51880600
H	3.53844500	3.69380400	-1.59471900
H	2.99744800	2.68697800	2.54954800
H	4.22335200	3.94269600	0.78622500

References:

[1] A. R. Ali, H. Ghosh, B. K. Patel, *Tetrahedron Lett.* **2010**, *51*, 1019-1021. Tateno, K.; Ogawa, R.; Sakamoto, R.; Tsuchiya, M.; Kutsumura, N.; Otani, T.; Ono, K.; Kawai, H.; Saito, T. *J. Org. Chem*. **2018**, *83*, 690.

[2] Liu, Q.; Li, M.; Xiong, R.; Mo, F. *Org. Lett.* **2017**, *19*, 6756.

[3] Dorokhov, V. A.; Komkov, A. V. *Russ.Chem.Bull., Int.Ed.* **2004**, *53*, 676.

[4] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, **2013**.

[5] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

[6] a) P. J. Hay, *J. Chem. Phys.* **1977**, *66*, 4377-4384; b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.

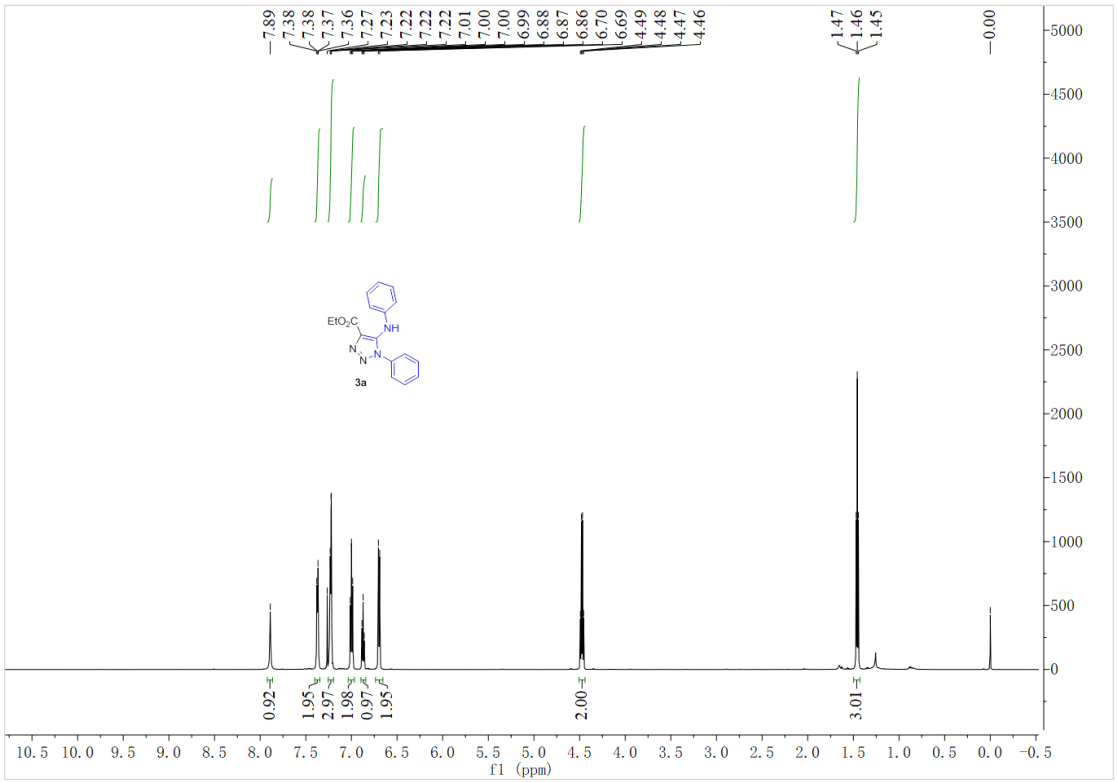
[7] A. J. H. Wachters, *J. Chem. Phys.* **1970**, *52*, 1033-1036.

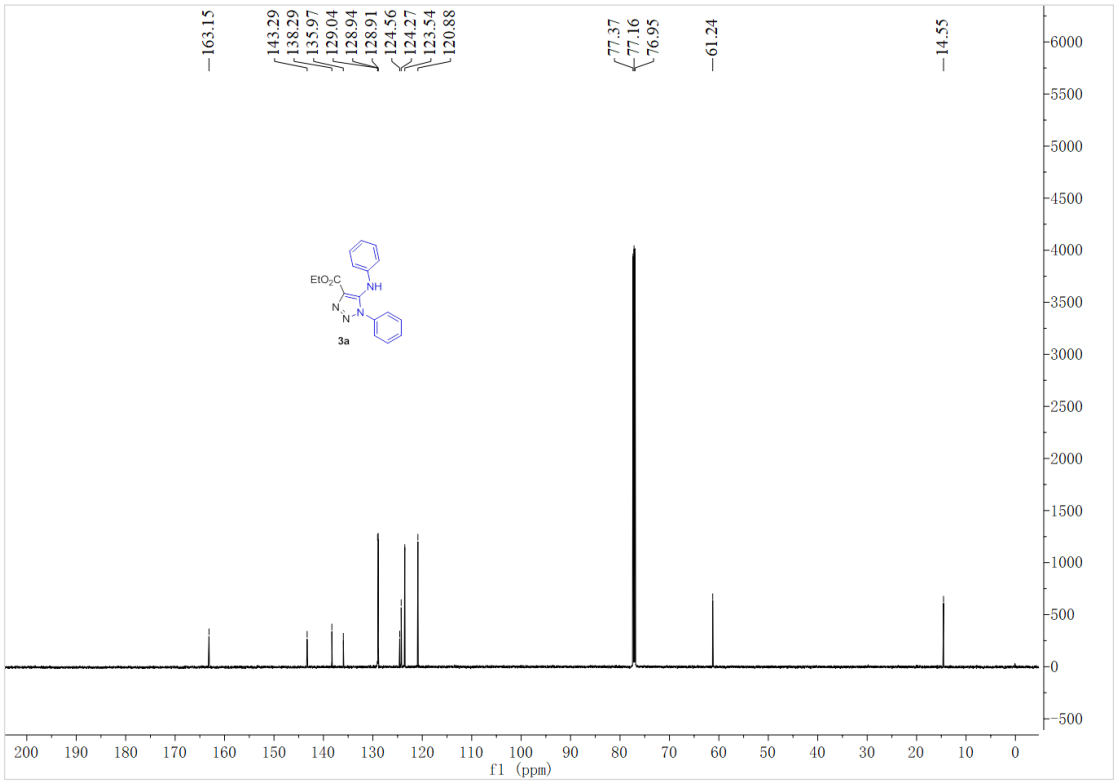
[8] a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241; b) Y. Zhao, D. G. Truhlar, *J. Chem. Theory Comput.* **2009**, *5*, 324-333.

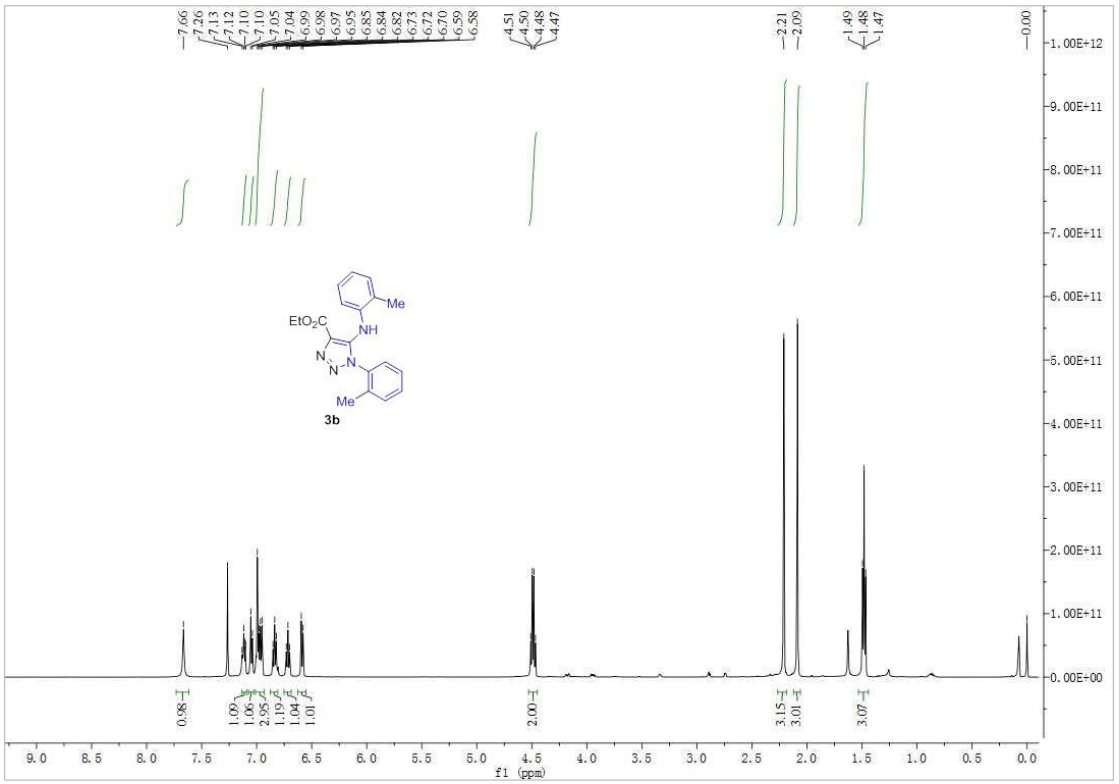
[9] a) M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* **1987**, *86*, 866-872; b) D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theoretica Chimica Acta* **1990**, *77*, 123-141.

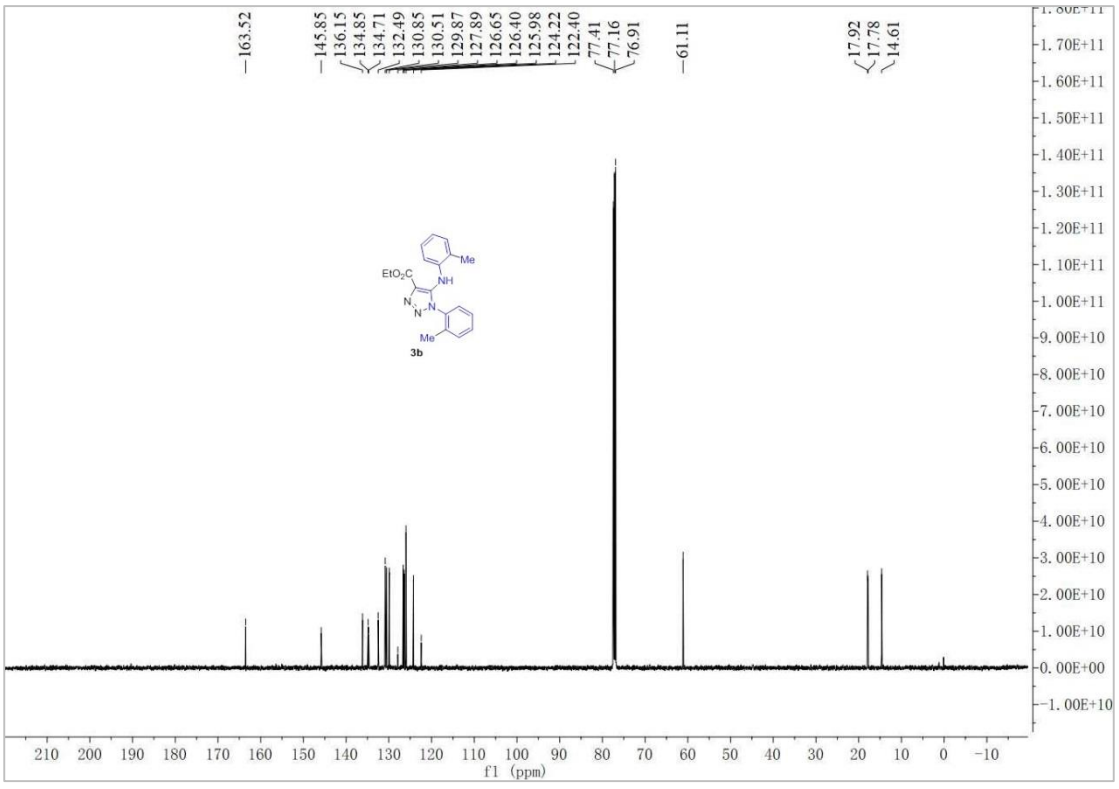
[10] a) E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032-3041; b) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chem. Phys. Lett.* **1998**, *286*, 253-260.

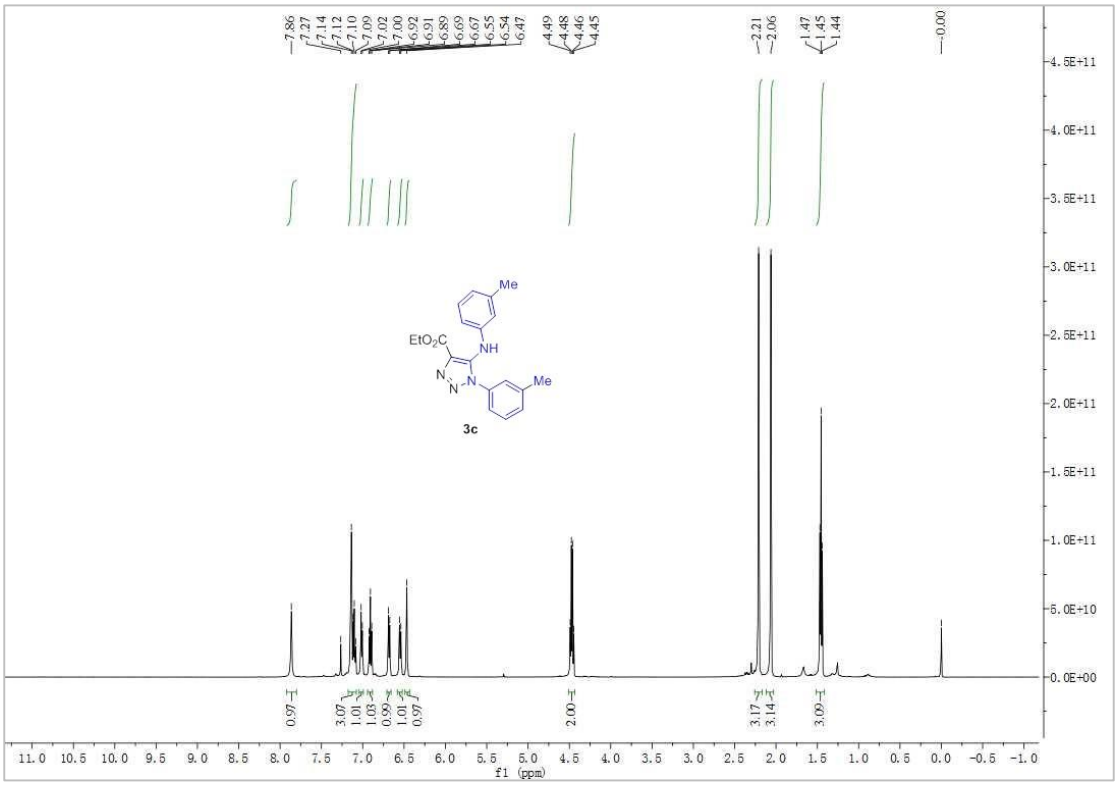
12. Copy of ^{1}H and ^{13}C NMR for new Compounds

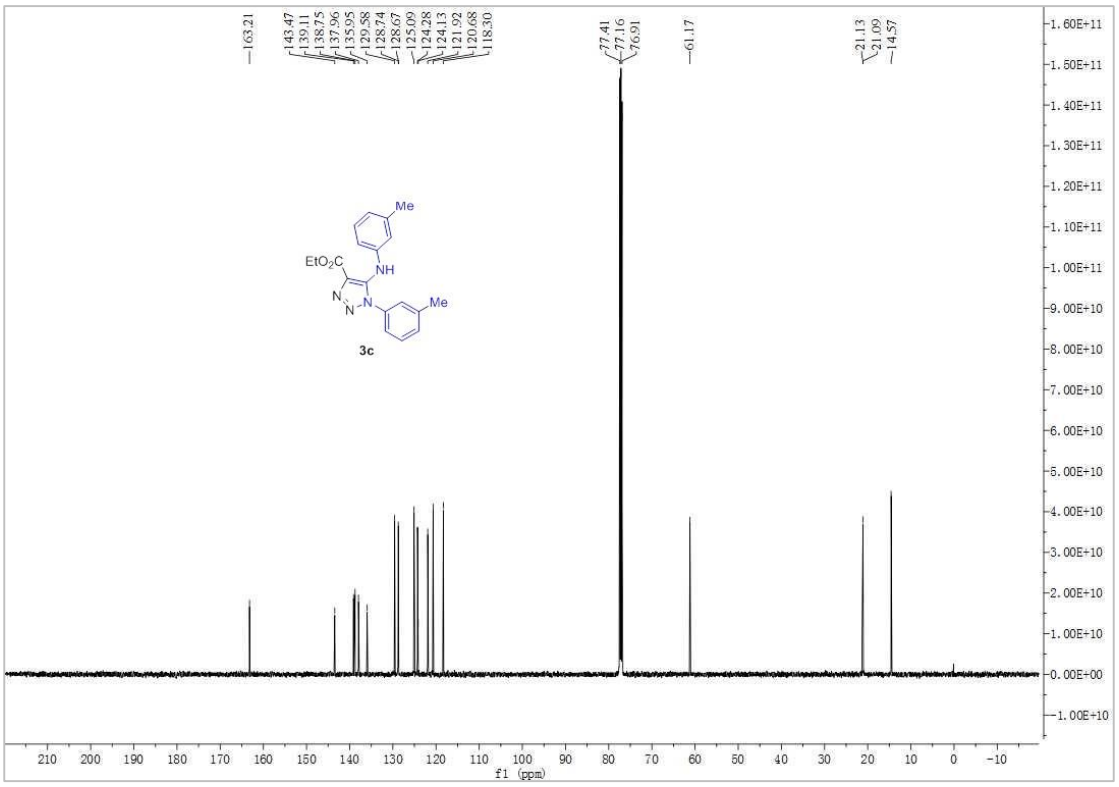


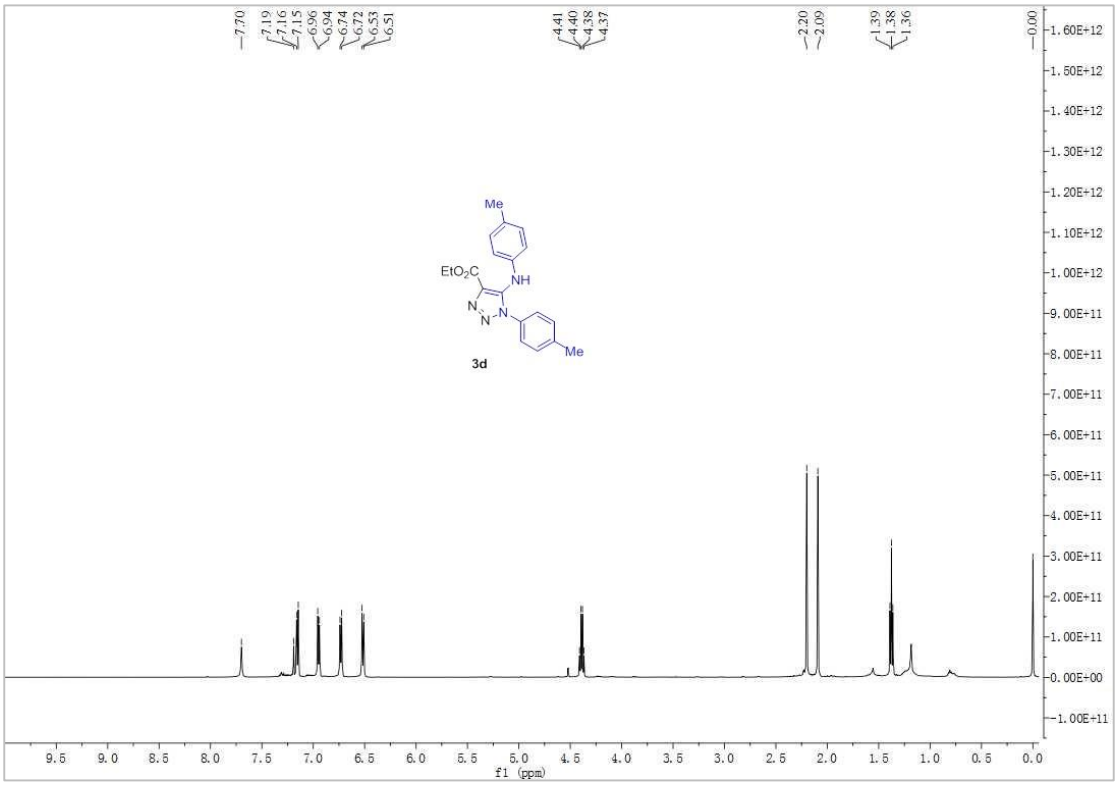


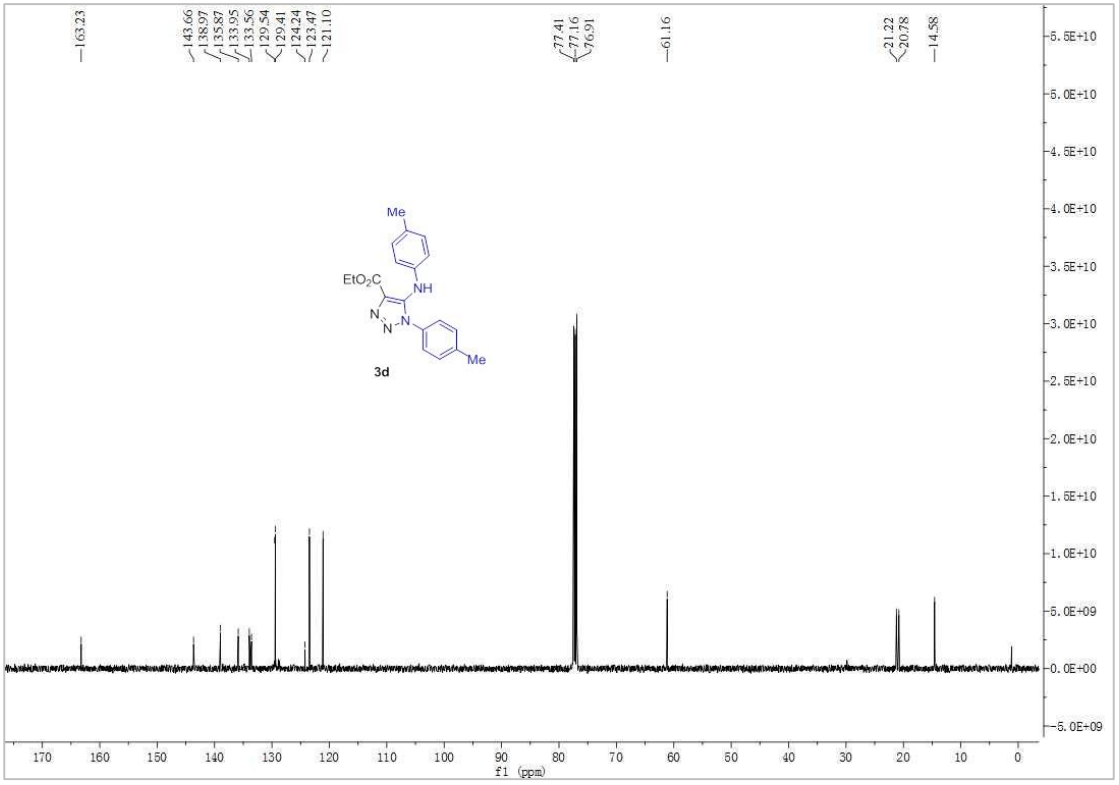

7.66
7.26
7.13
7.12
7.10
7.10
7.05
7.04
6.99
6.98
6.97
6.95
6.85
6.84
6.82
6.73
6.72
6.70
6.59
6.58
4.51
4.50
4.48
4.47
2.21
2.09
1.49
1.48
1.47
0.00
Me
EtO2C
NH
N
N
N
Me
3b
0.98
1.09
1.06
2.95
1.19
1.04
1.01
2.00
3.15
3.01
3.07
f1 (ppm)

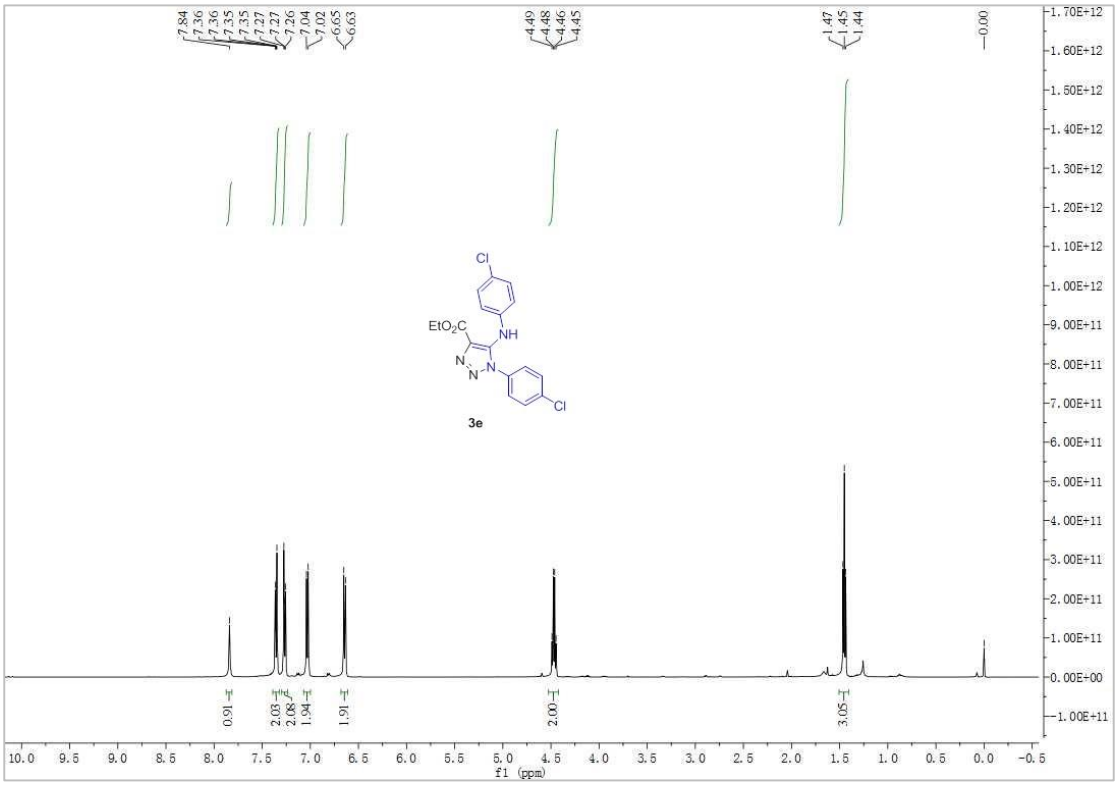

163.52
145.85
136.15
134.85
134.71
132.49
130.85
130.51
129.87
127.89
126.65
126.40
125.98
124.22
122.40
77.41
77.16
76.91
61.11
17.92
17.78
14.61
Me
EtO2C
NH
N
N
N
Me
3b
f1 (ppm)

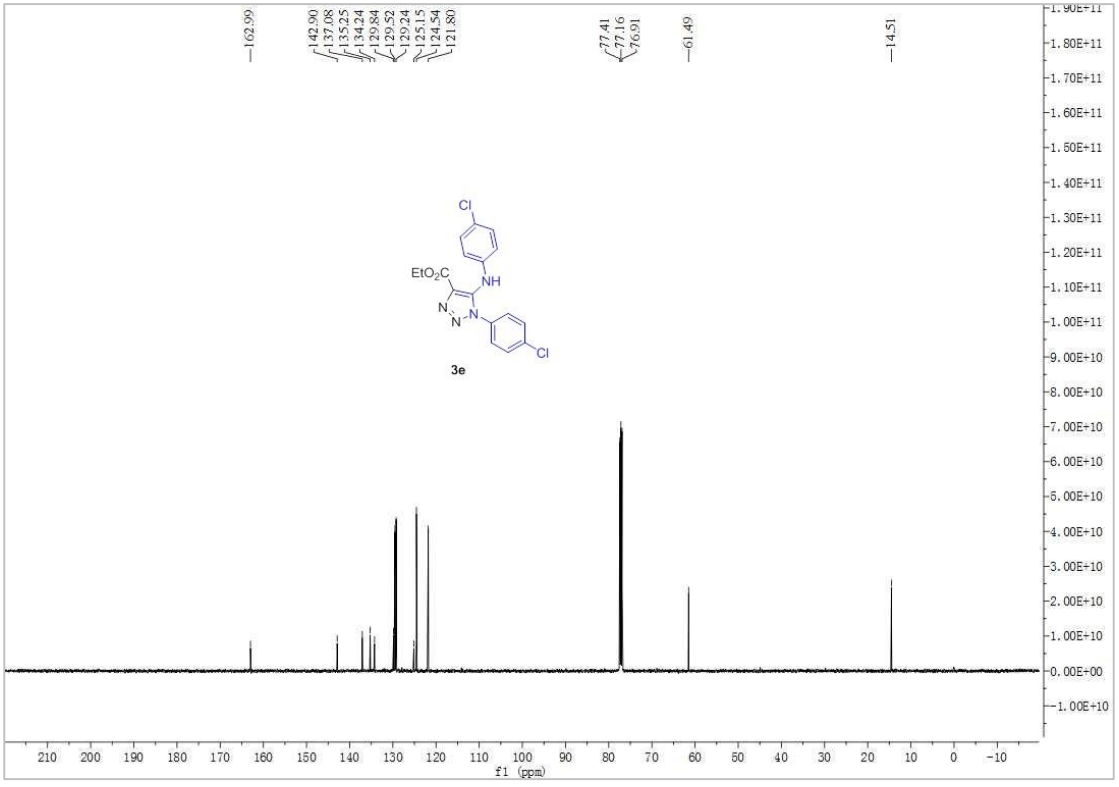

7.86
7.27
7.14
7.12
7.10
7.09
7.02
7.00
6.92
6.91
6.89
6.69
6.67
6.55
6.54
6.47
4.49
4.48
4.46
4.45
2.21
2.06
1.47
1.45
1.44
0.00
Me
EtO2C
NH
N
N
N
Me
3c
0.97
3.07
1.01
1.03
0.99
1.01
0.97
2.00
3.17
3.14
3.09
f1 (ppm)

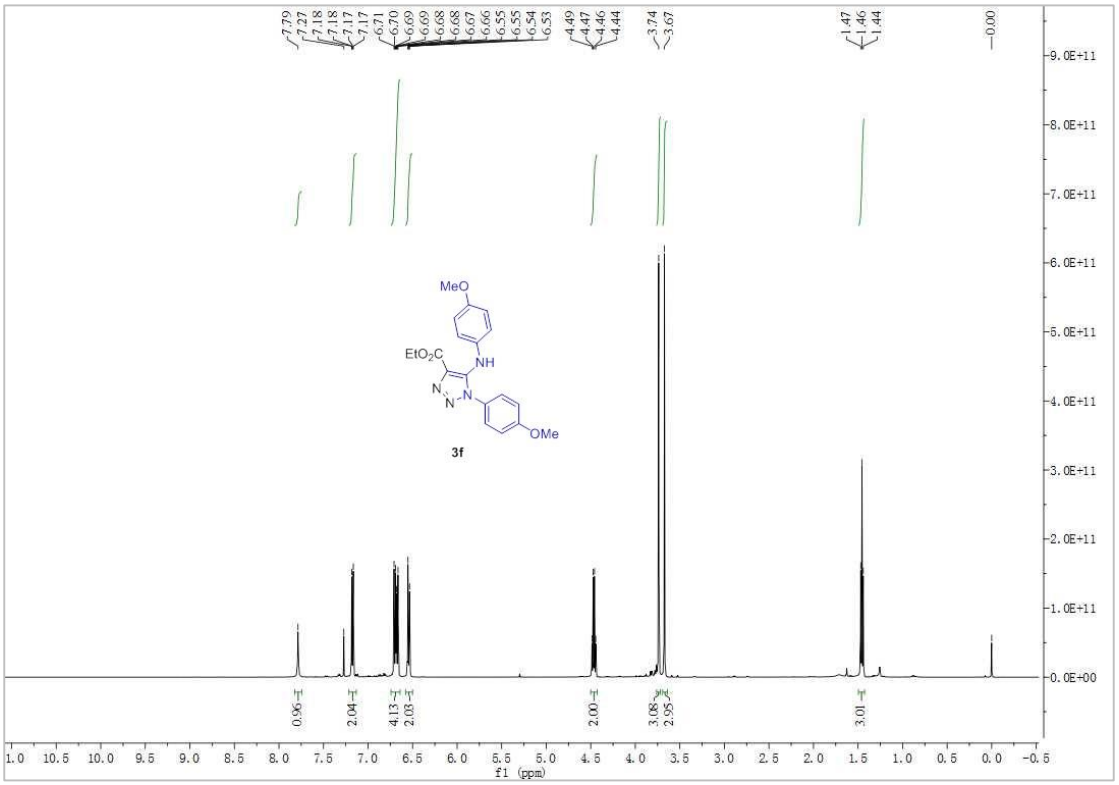

163.21
143.47
139.11
138.75
137.96
135.95
129.58
128.74
128.67
125.09
124.28
124.13
121.92
120.68
118.30
77.41
77.16
76.91
61.17
21.13
21.09
14.57
Me
EtO2C
NH
N
N
N
Me
3c
f1 (ppm)

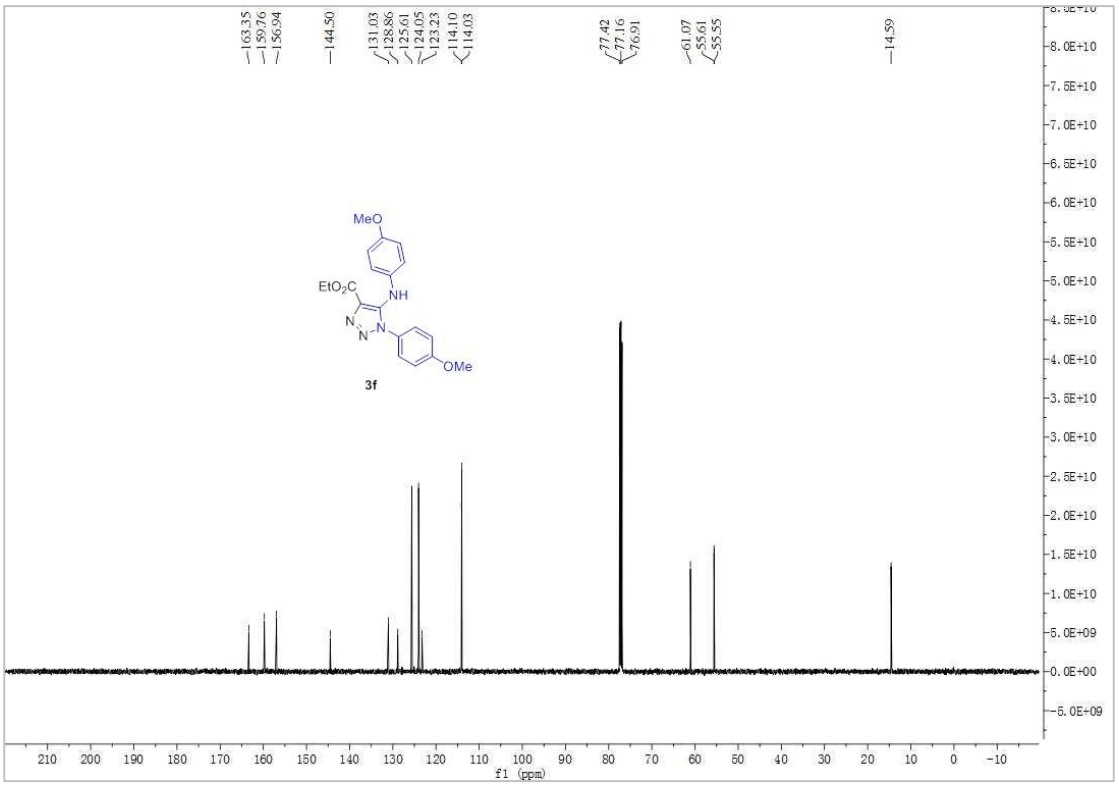

7.70
7.19
7.16
7.15
6.96
6.94
6.74
6.72
6.53
6.51
4.41
4.40
4.38
4.37
2.20
2.09
1.39
1.38
1.36
0.00
Me
EtO2C
NH
N
N
N
Me
3d
f1 (ppm)

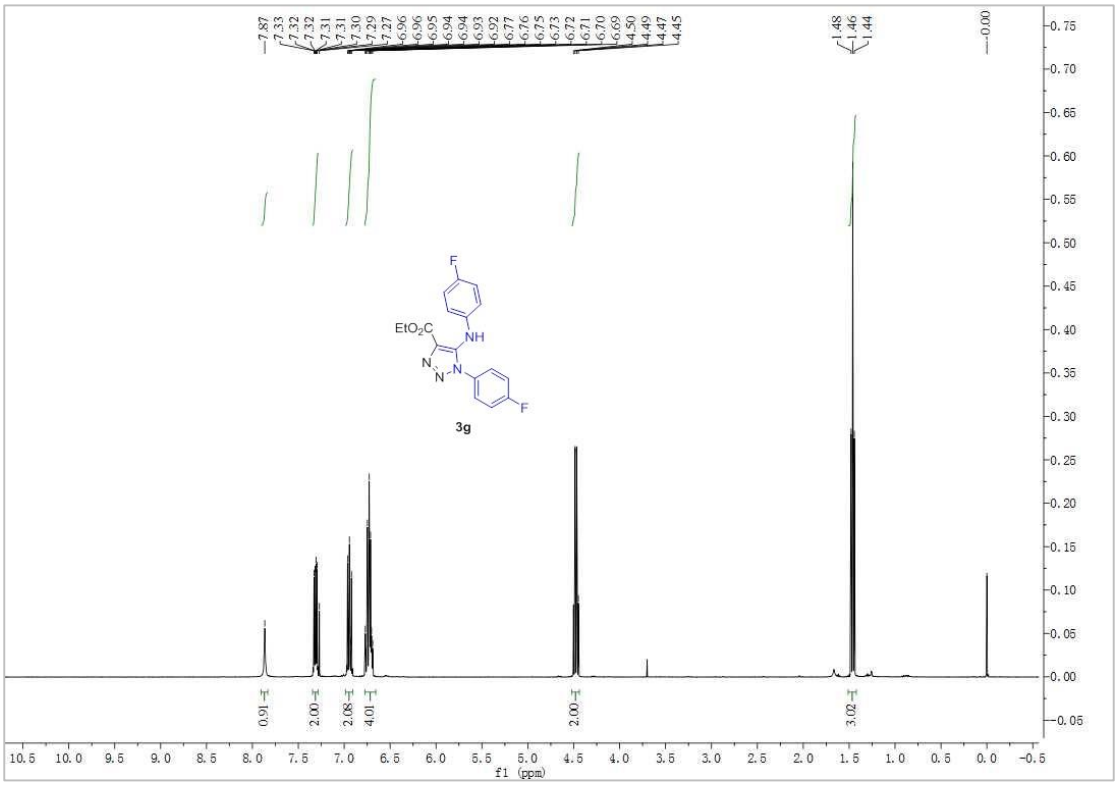

163.23
143.66
138.97
135.87
133.95
133.56
129.54
129.41
124.24
123.47
121.10
77.41
77.16
76.91
61.16
21.22
20.78
14.58
Me
EtO2C
NH
N
N
N
Me
3d
f1 (ppm)

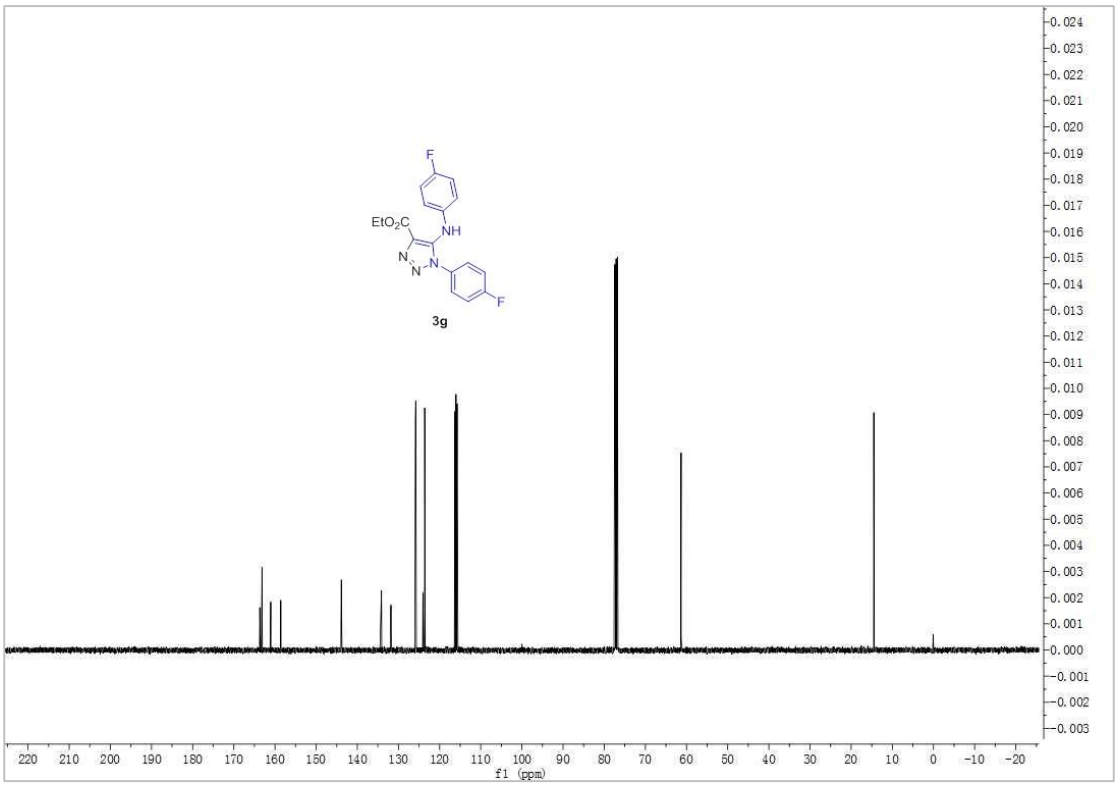

7.84
7.36
7.36
7.35
7.35
7.27
7.27
7.26
7.04
7.02
6.65
6.63
4.49
4.48
4.46
4.45
1.47
1.45
1.44
0.00
Cl
EtO2C
NH
N
N
N
Cl
3e
0.91
2.03
2.08
1.94
1.91
2.00
3.05
f1 (ppm)

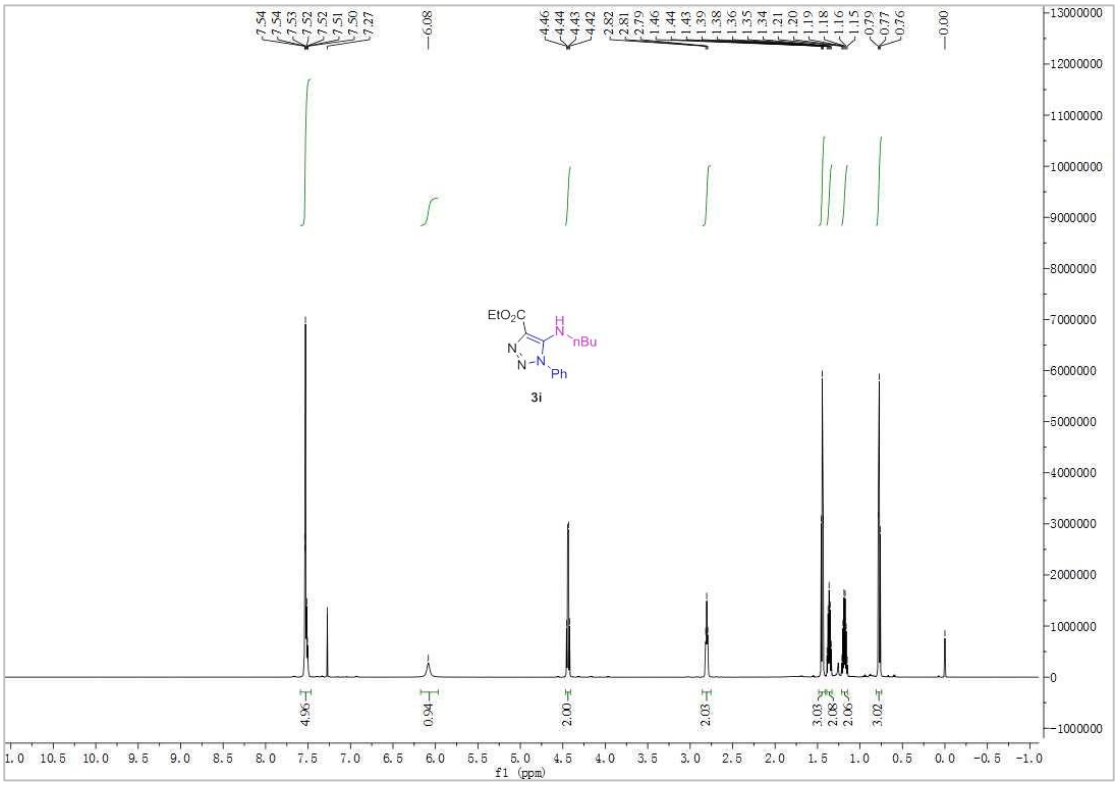

162.99
142.90
137.08
135.25
134.24
129.84
129.52
129.24
125.15
124.54
121.80
77.41
77.16
76.91
61.49
14.51
Cl
EtO2C
NH
N
N
N
Cl
3e
f1 (ppm)

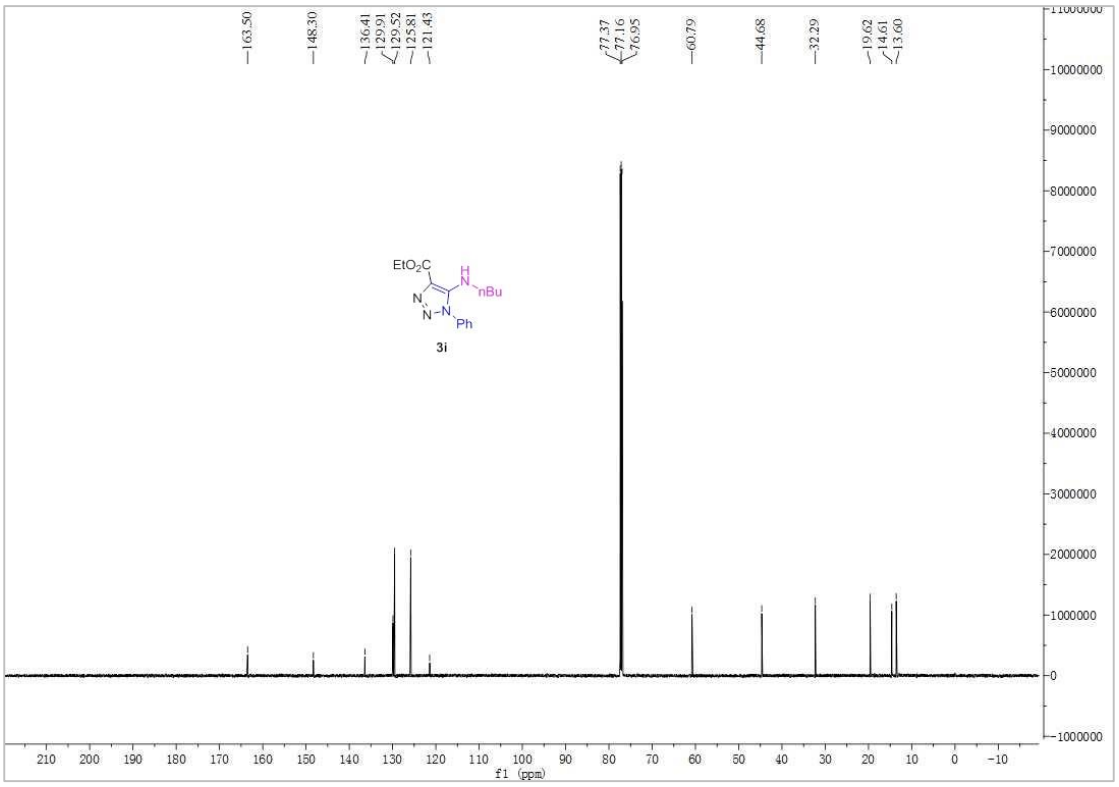

MeO
EtO2C
NH
N
N
N
OMe
3f
f1 (ppm)

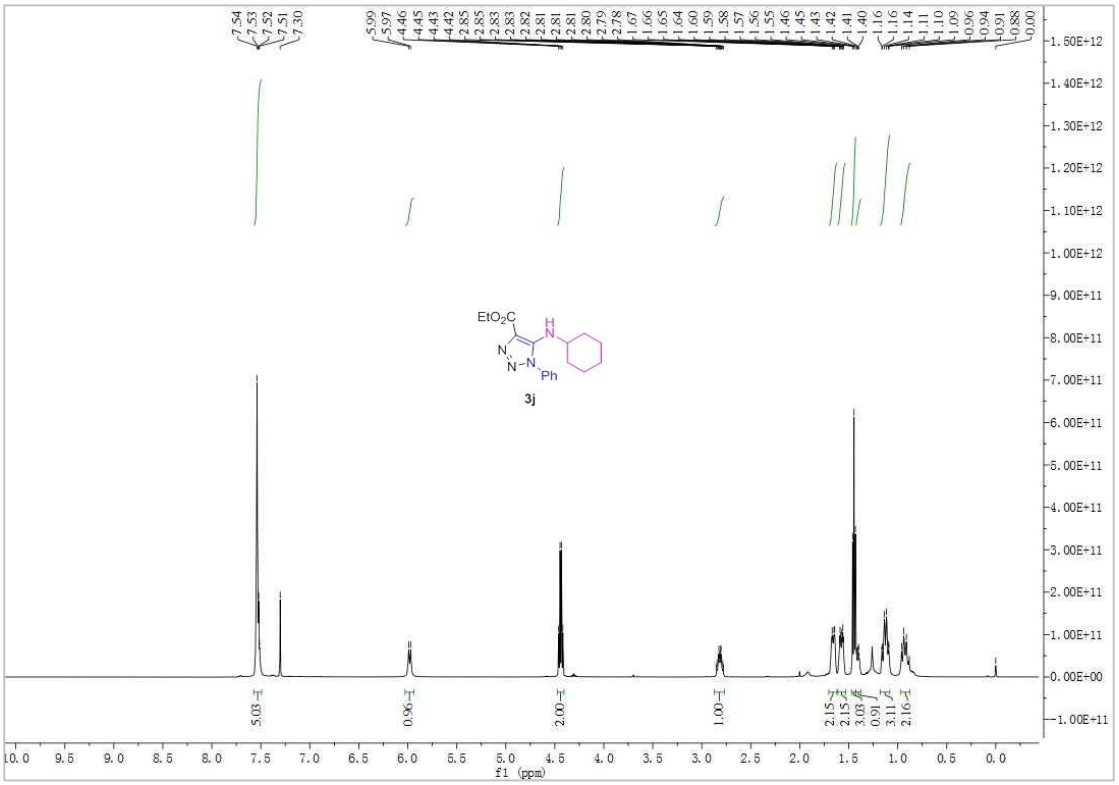

MeO
EtO2C
NH
N
N
N
OMe
3f
f1 (ppm)

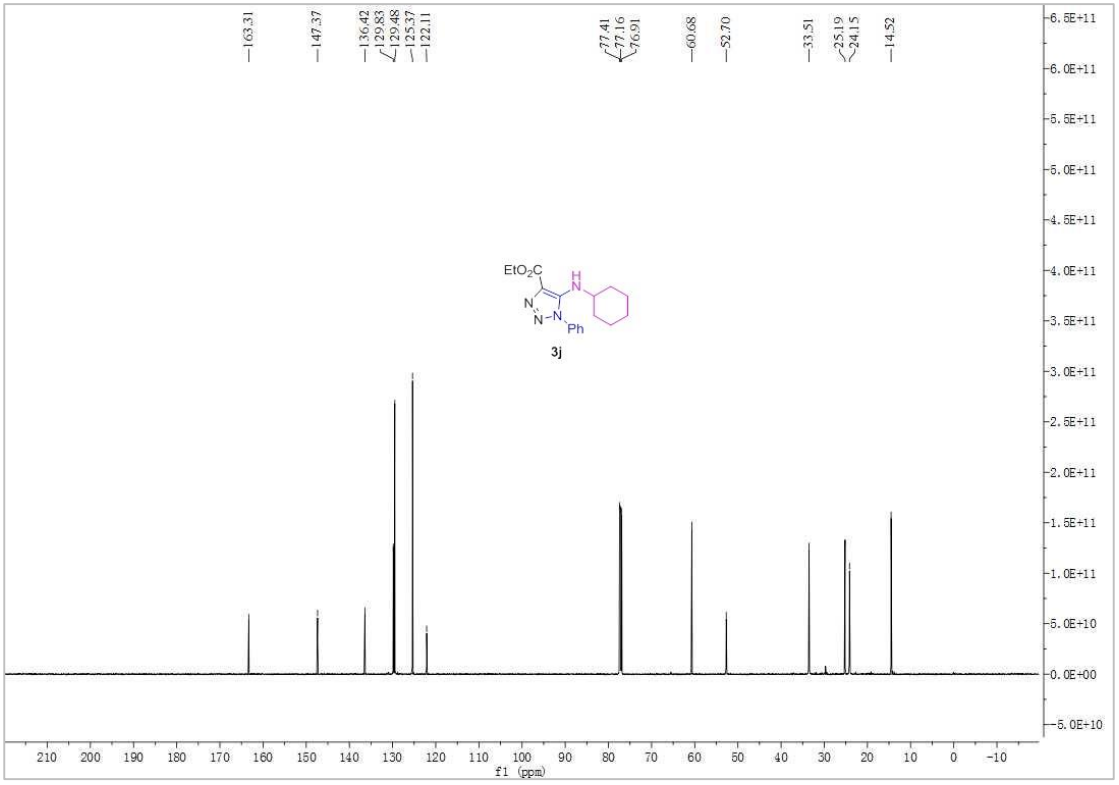

7.87
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.27
6.96
6.96
6.95
6.94
6.94
6.93
6.92
6.77
6.76
6.75
6.73
6.72
6.71
6.70
6.69
4.50
4.49
4.47
4.45
1.48
1.46
1.44
0.00
F
EtO2C
NH
N
N
N
F
3g
0.91
2.00
2.08
4.01
2.00
3.02
f1 (ppm)

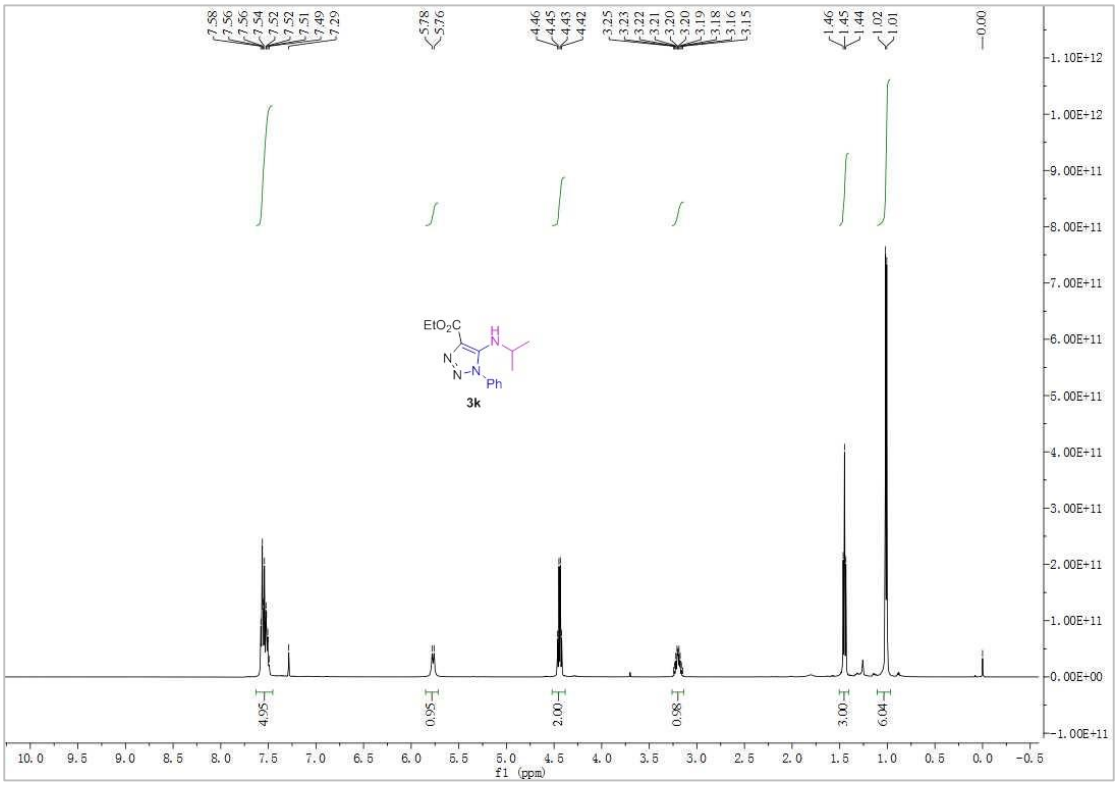

F
EtO2C
NH
N
N
N
F
3g
f1 (ppm)

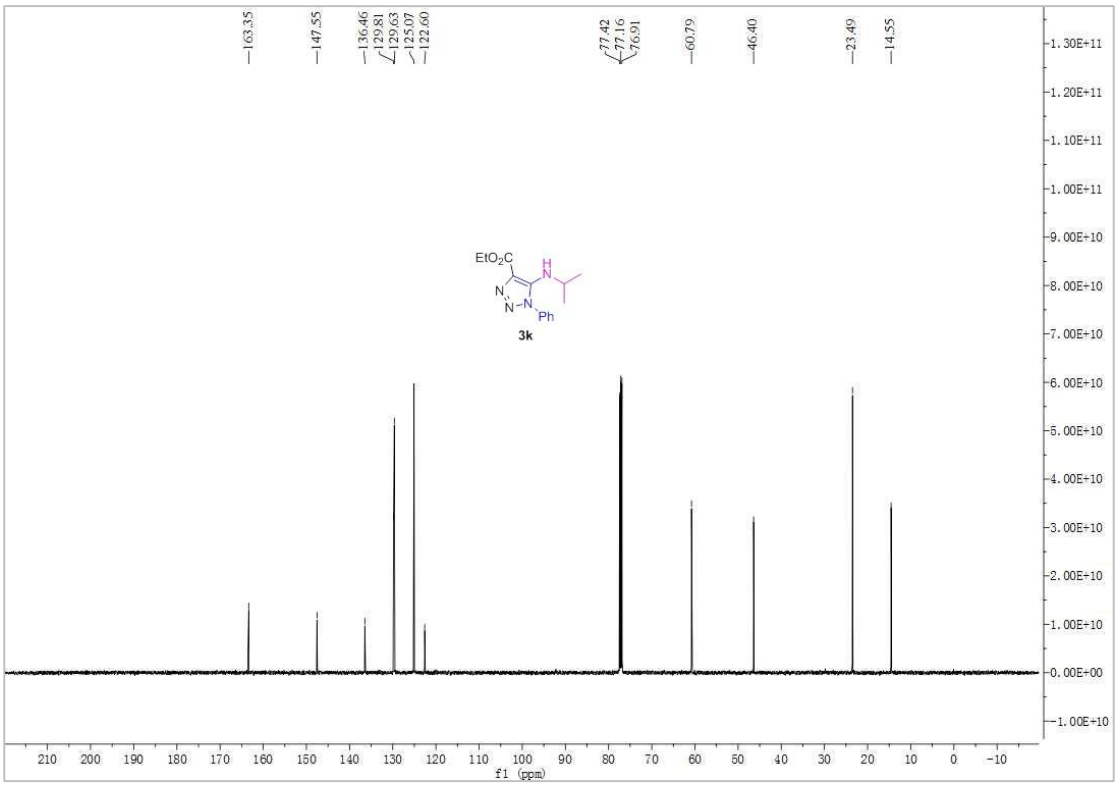

7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.27
6.08
4.46
4.44
4.43
4.42
2.82
2.81
2.79
1.46
1.44
1.43
1.39
1.38
1.36
1.35
1.34
1.21
1.20
1.19
1.18
1.16
1.15
0.79
0.77
0.76
0.00
EtO2C
N
H
nBu
N
N
Ph
3i
4.96
0.94
2.00
2.03
3.03
2.08
2.06
3.02
f1 (ppm)

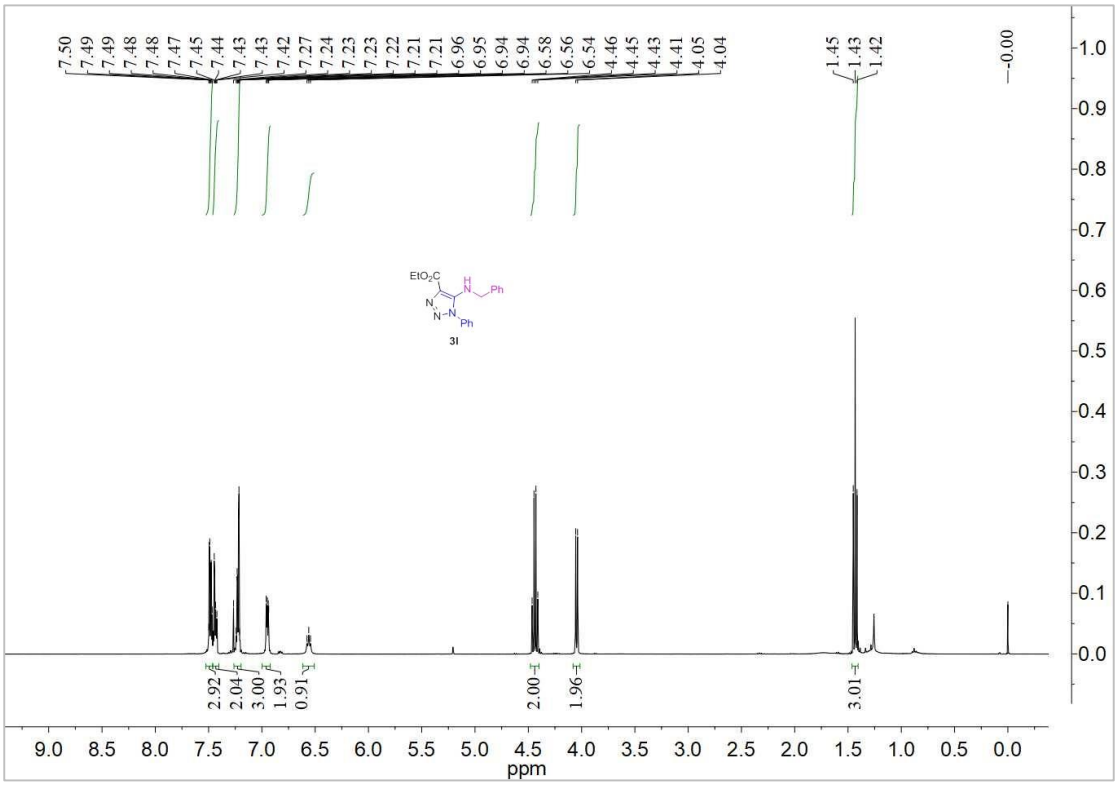

163.50
148.30
136.41
129.91
129.52
125.81
121.43
77.37
77.16
76.95
60.79
44.68
32.29
19.62
14.61
13.60
EtO2C
N
H
nBu
N
N
Ph
3i
f1 (ppm)

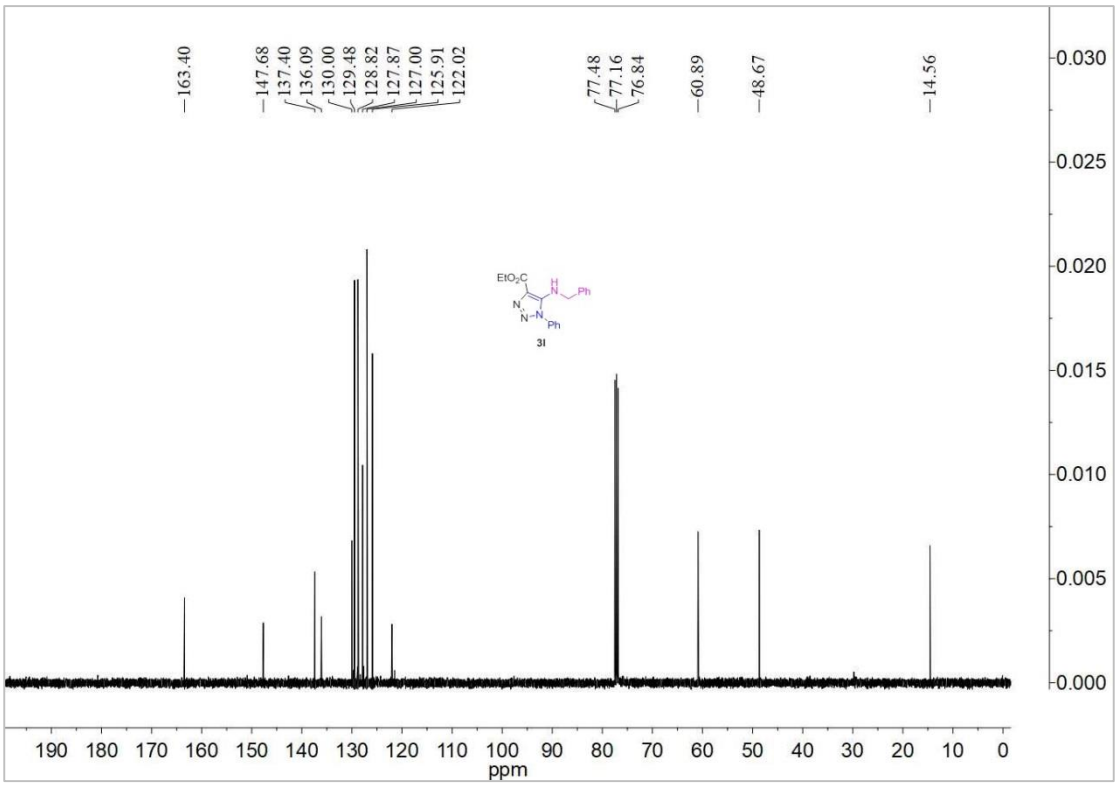

7.54
7.53
7.52
7.51
7.30
5.99
5.97
4.46
4.45
4.43
4.42
2.85
2.83
2.82
2.81
2.80
2.79
2.78
1.67
1.66
1.65
1.64
1.60
1.59
1.58
1.57
1.56
1.55
1.46
1.45
1.43
1.42
1.41
1.40
1.16
1.14
1.11
1.10
1.09
0.96
0.94
0.91
0.88
0.00
EtO2C
N
N
N
H
Ph
3j
5.03
0.96
2.00
1.00
2.15
2.15
3.03
0.91
3.11
2.16
f1 (ppm)

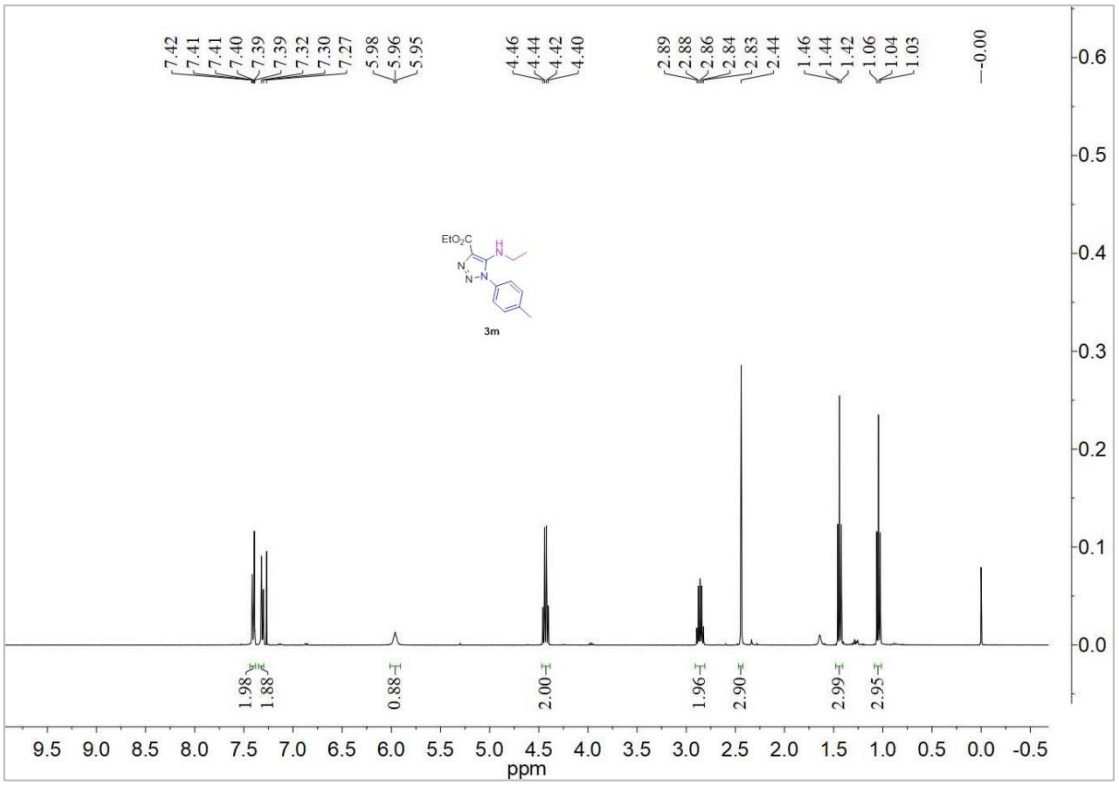

163.31
147.37
136.42
129.83
129.48
125.37
122.11
77.41
77.16
76.91
60.68
52.70
33.51
25.19
24.15
14.52
EtO2C
N
N
N
H
Ph
3j
f1 (ppm)

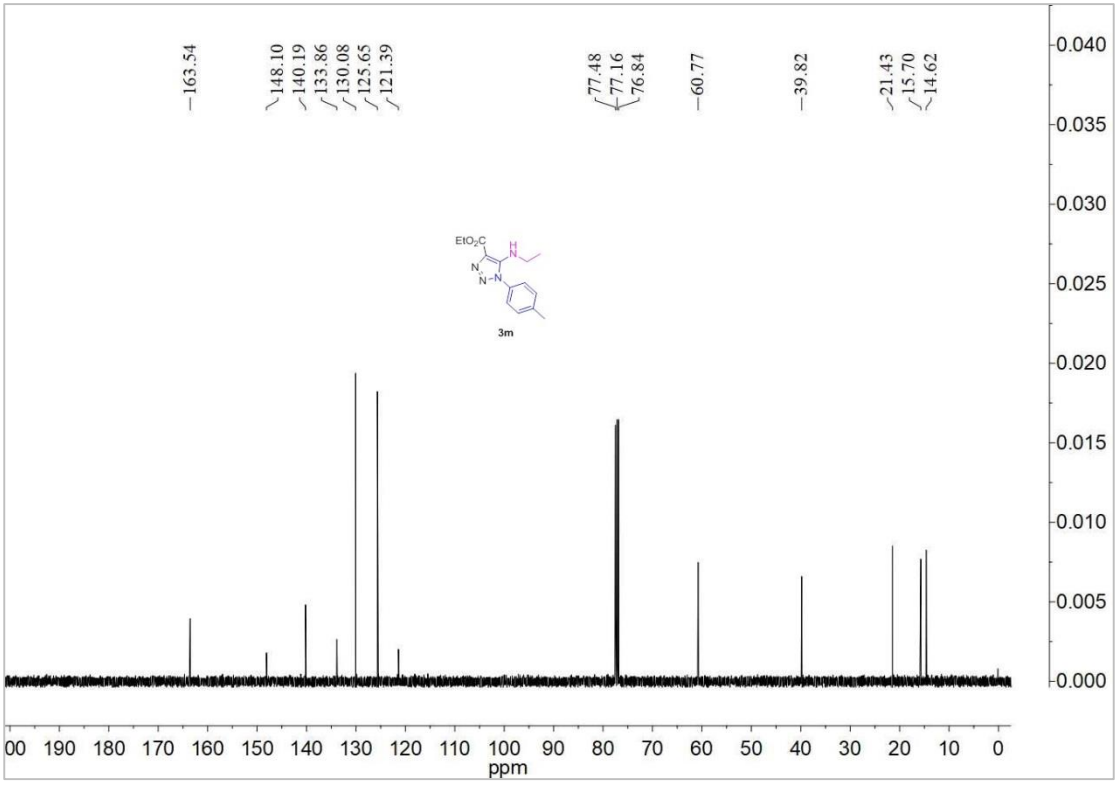

7.58
7.56
7.56
7.54
7.52
7.52
7.51
7.49
7.29
5.78
5.76
4.46
4.45
4.43
4.42
3.25
3.23
3.22
3.21
3.20
3.20
3.19
3.18
3.16
3.15
1.46
1.45
1.44
1.02
1.01
0.00
EtO2C
N
N
N
Ph
H
3k
4.95
0.95
2.00
0.98
3.00
6.04
f1 (ppm)

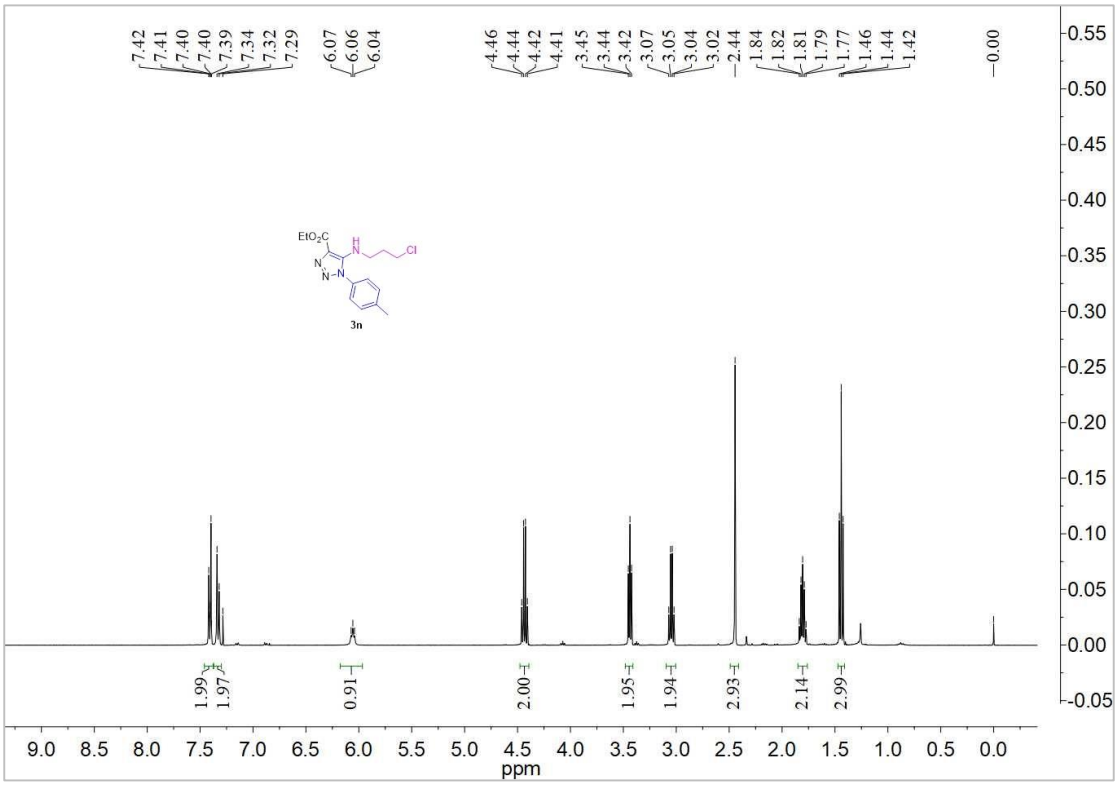

163.35
147.55
136.46
129.81
129.63
125.07
122.60
77.42
77.16
76.91
60.79
46.40
23.49
14.55
EtO2C
N
N
N
Ph
H
3k
f1 (ppm)

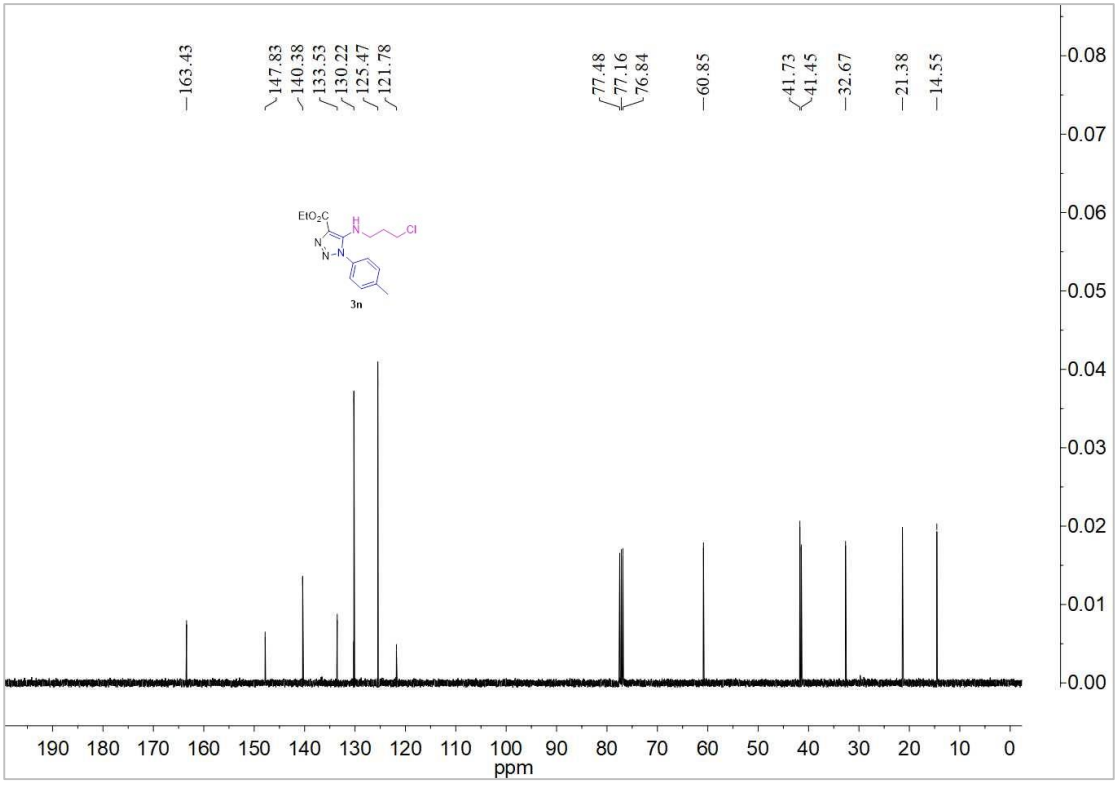

7.50
7.49
7.49
7.48
7.48
7.47
7.45
7.44
7.43
7.43
7.42
7.27
7.24
7.23
7.23
7.22
7.21
7.21
6.96
6.95
6.94
6.94
6.58
6.56
6.54
4.46
4.45
4.43
4.41
4.05
4.04
1.45
1.43
1.42
0.00
EtO2C
N
N
N
H
Ph
Ph
3l
2.92
2.04
3.00
1.93
0.91
2.00
1.96
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

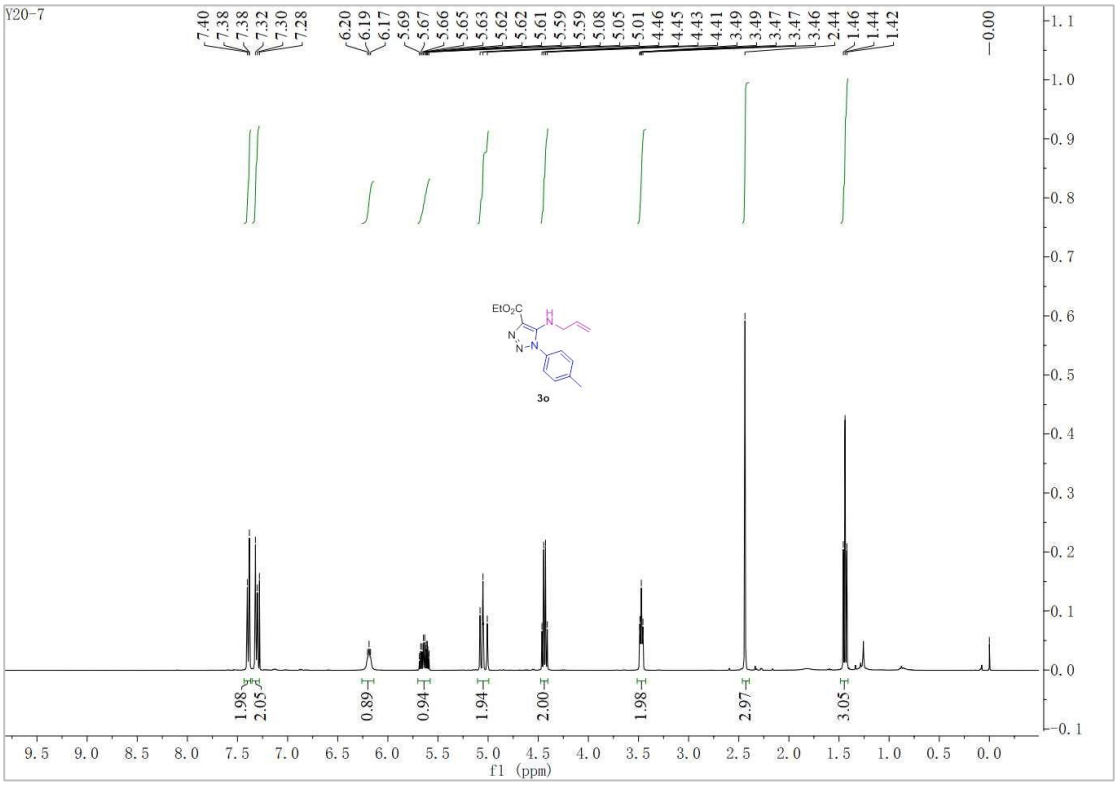

163.40
147.68
137.40
136.09
130.00
129.48
128.82
127.87
127.00
125.91
122.02
77.48
77.16
76.84
60.89
48.67
14.56
EtO2C
N
N
N
H
Ph
Ph
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
0.030
0.025
0.020
0.015
0.010
0.005
0.000

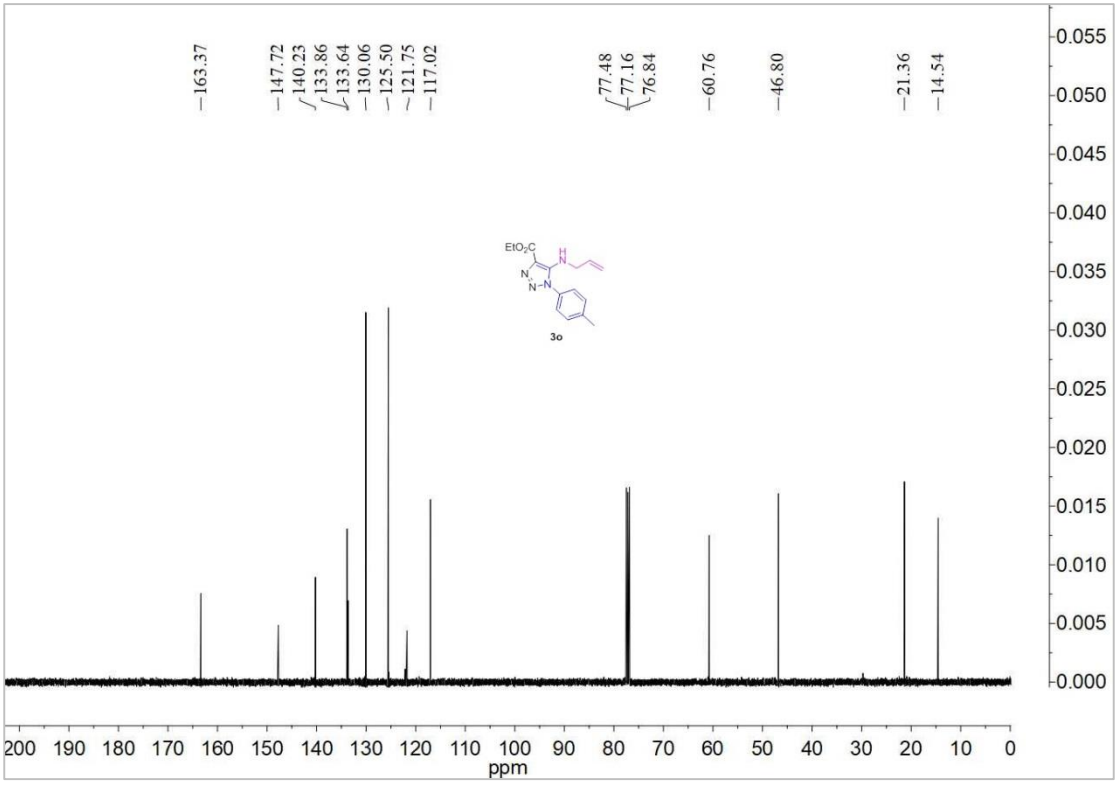

7.42
7.41
7.41
7.40
7.39
7.39
7.32
7.30
7.27
5.98
5.96
5.95
4.46
4.44
4.42
4.40
2.89
2.88
2.86
2.84
2.83
2.44
1.46
1.44
1.42
1.06
1.04
1.03
0.00
3m
1.98
1.88
0.88
2.00
1.96
2.90
2.99
2.95
ppm

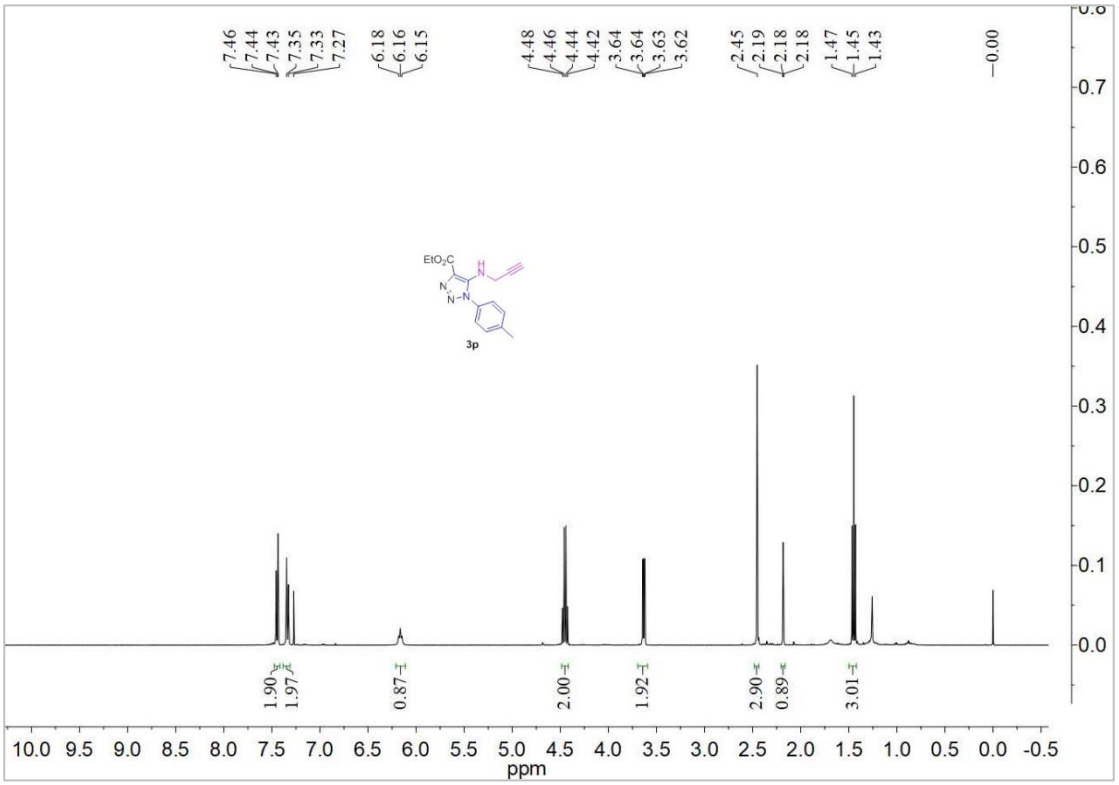

163.54
148.10
140.19
133.86
130.08
125.65
121.39
77.48
77.16
76.84
60.77
39.82
21.43
15.70
14.62
3m
ppm

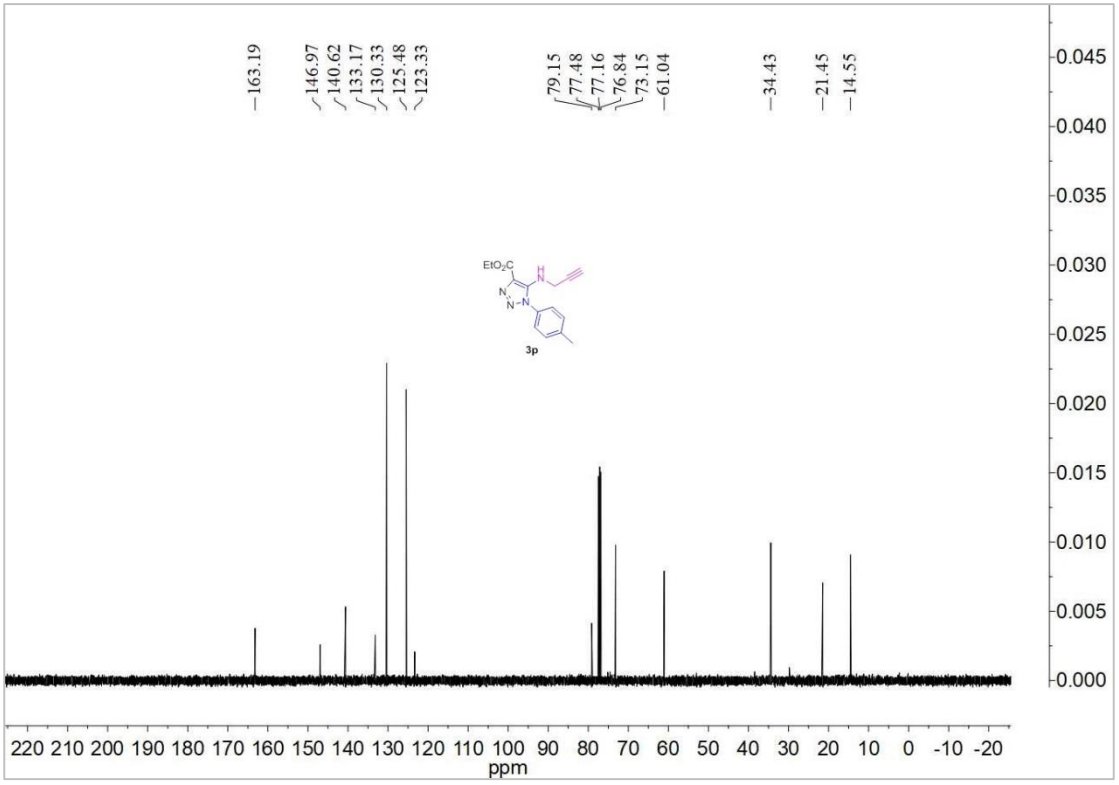

7.42
7.41
7.40
7.40
7.39
7.34
7.32
7.29
6.07
6.06
6.04
4.46
4.44
4.42
4.41
3.45
3.44
3.42
3.07
3.05
3.04
3.02
2.44
1.84
1.82
1.81
1.79
1.77
1.46
1.44
1.42
0.00
EtO2C
N
N
N
H
Cl
3n
1.99
1.97
0.91
2.00
1.95
1.94
2.93
2.14
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05

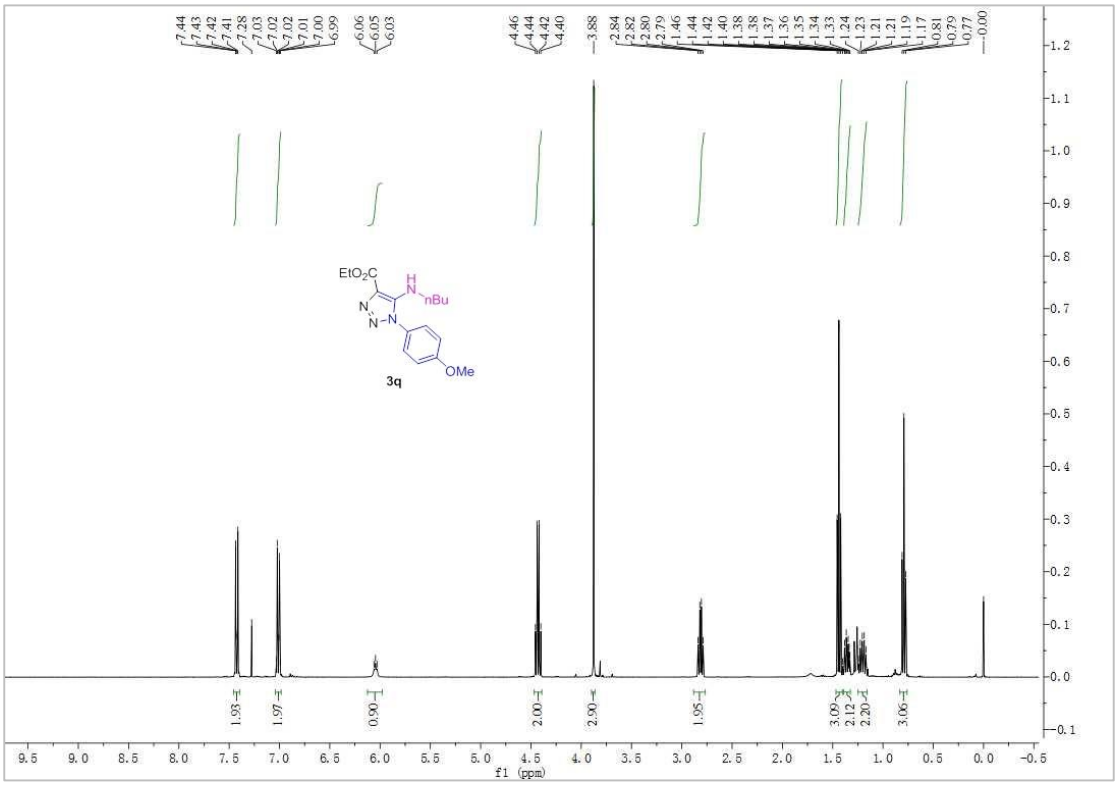

163.43
147.83
140.38
133.53
130.22
125.47
121.78
77.48
77.16
76.84
60.85
41.73
41.45
32.67
21.38
14.55
EtO2C
N
N
N
H
Cl
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00

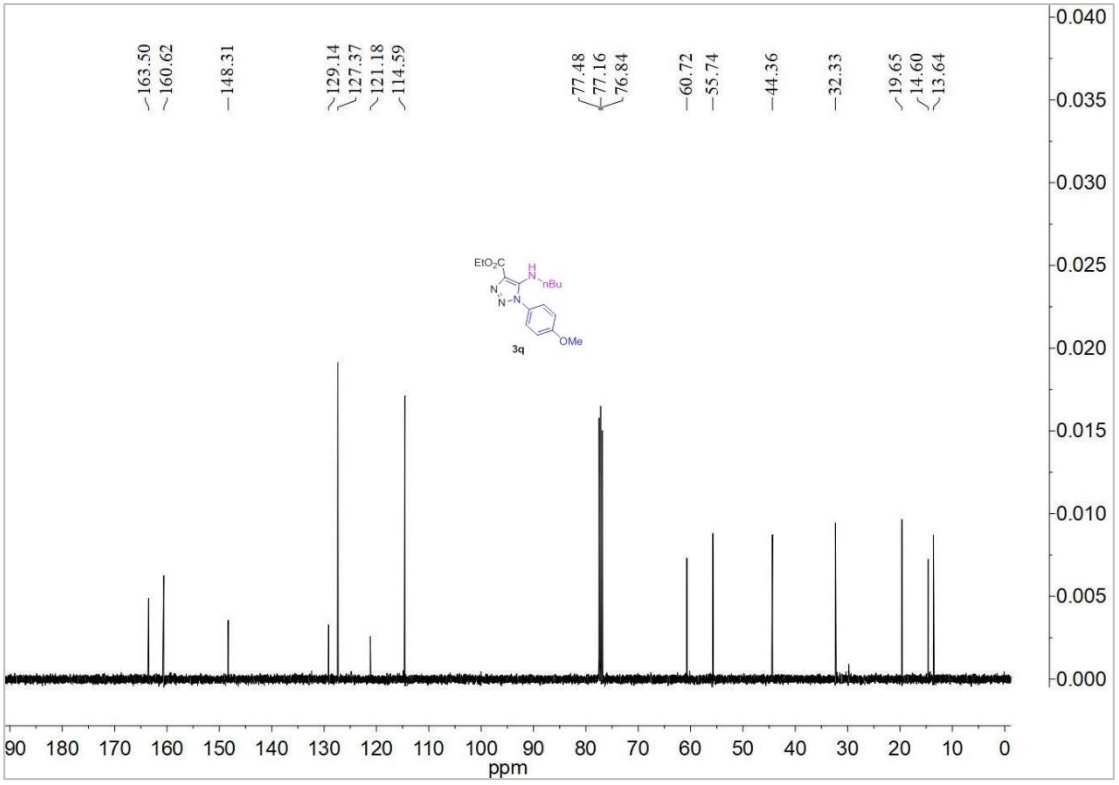

Y20-7
7.40
7.38
7.38
7.32
7.30
7.28
6.20
6.19
6.17
5.69
5.67
5.66
5.65
5.63
5.62
5.62
5.61
5.59
5.59
5.08
5.05
5.01
4.46
4.45
4.43
4.41
3.49
3.49
3.47
3.47
3.46
2.44
1.46
1.44
1.42
0.00
1.98
2.05
0.89
0.94
1.94
2.00
1.98
2.97
3.05
f1 (ppm)
3o

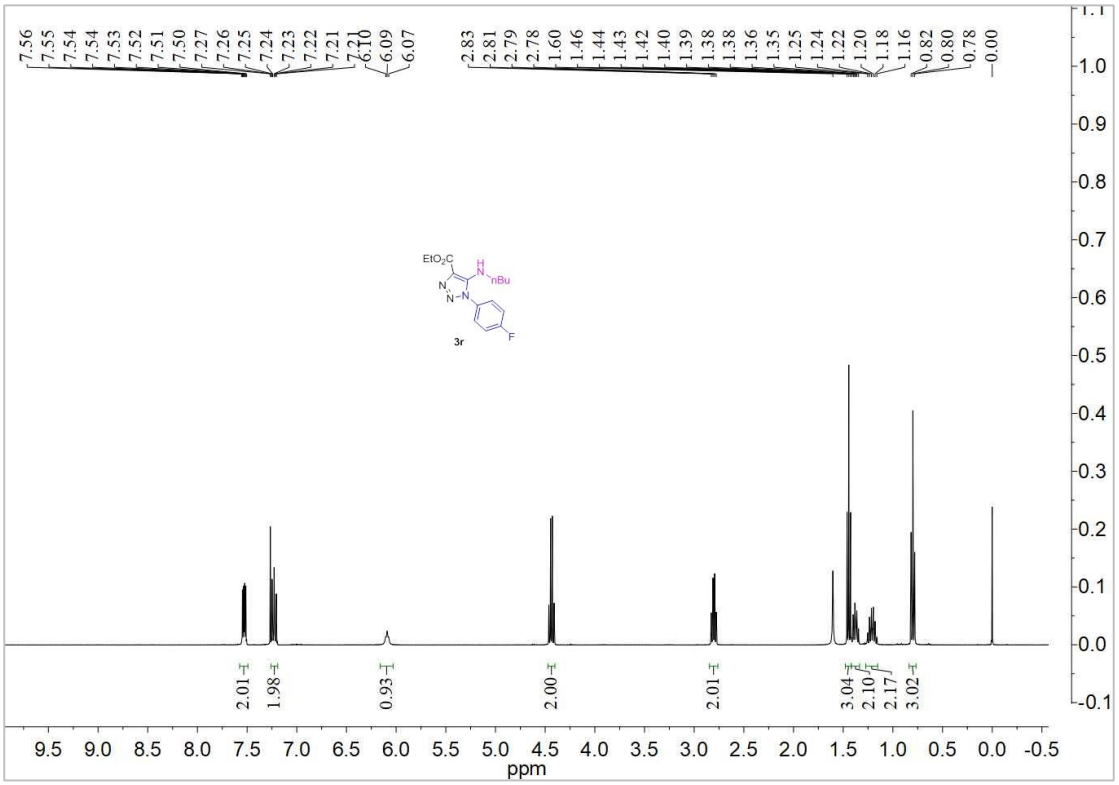

163.37
147.72
140.23
133.86
133.64
130.06
125.50
121.75
117.02
77.48
77.16
76.84
60.76
46.80
21.36
14.54
ppm
3o

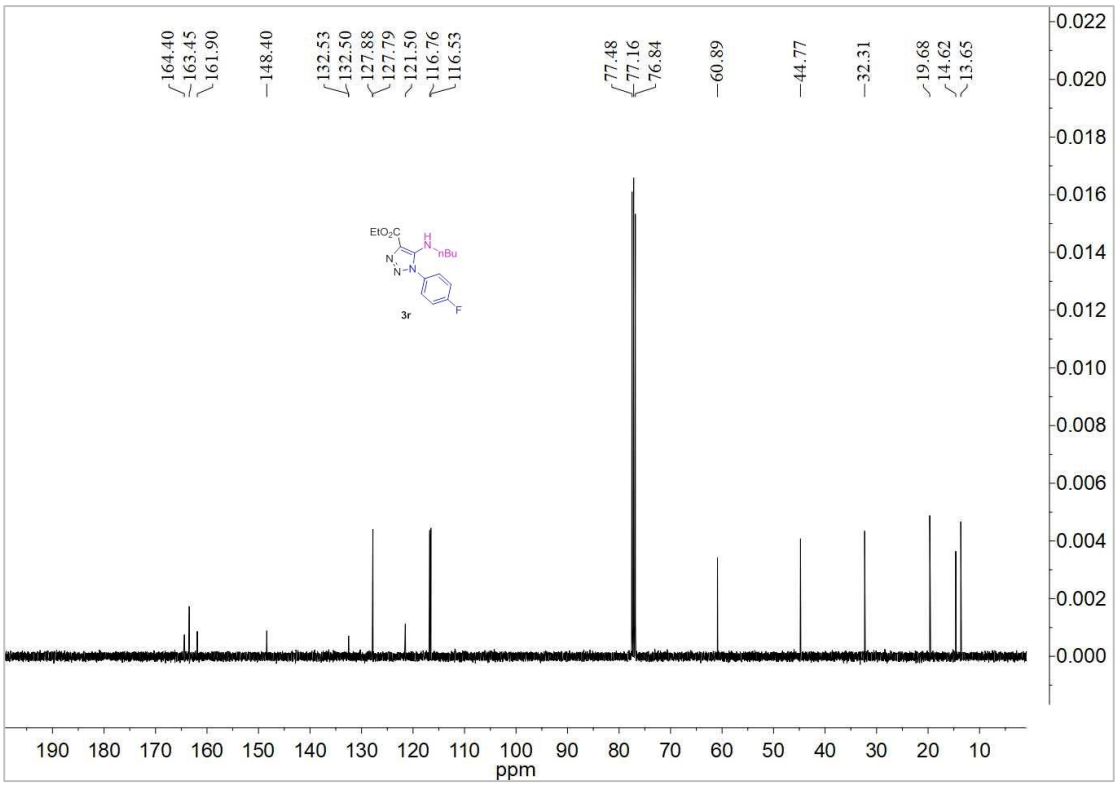

7.46
7.44
7.43
7.35
7.33
7.27
6.18
6.16
6.15
4.48
4.46
4.44
4.42
3.64
3.64
3.63
3.62
2.45
2.19
2.18
2.18
1.47
1.45
1.43
0.00
3p
1.90
1.97
0.87
2.00
1.92
2.90
0.89
3.01
ppm

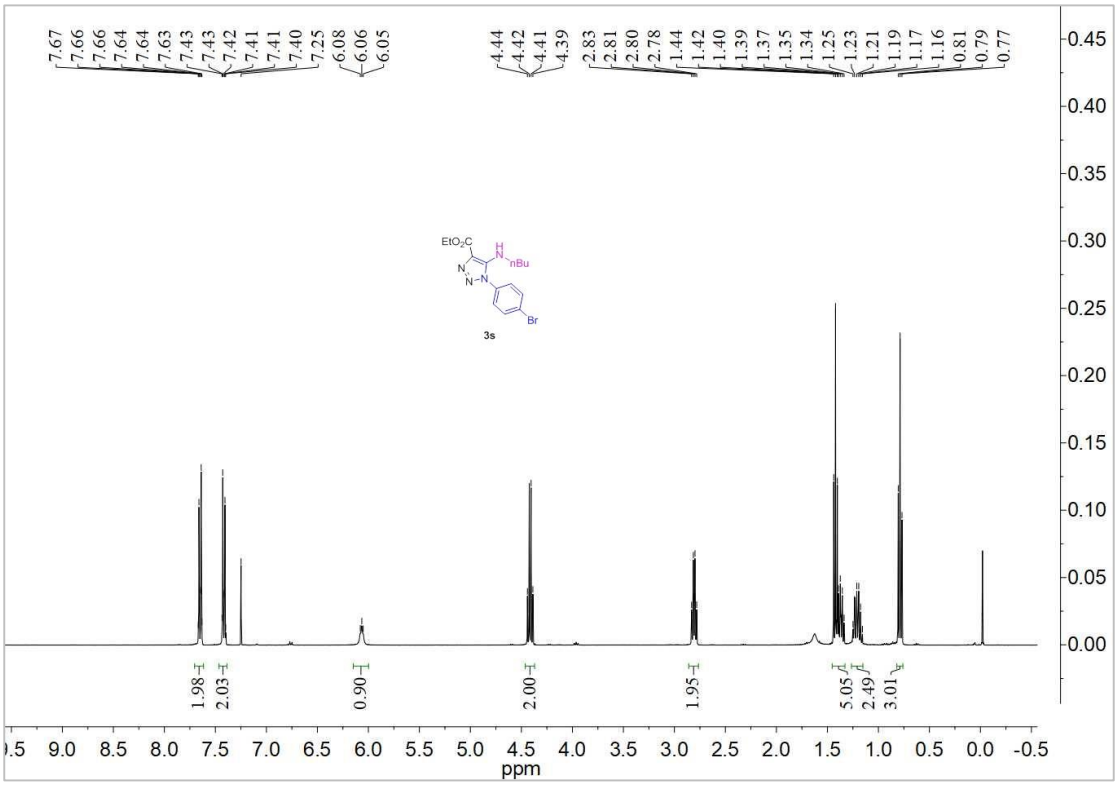

163.19
146.97
140.62
133.17
130.33
125.48
123.33
79.15
77.48
77.16
76.84
73.15
61.04
34.43
21.45
14.55
3p
ppm

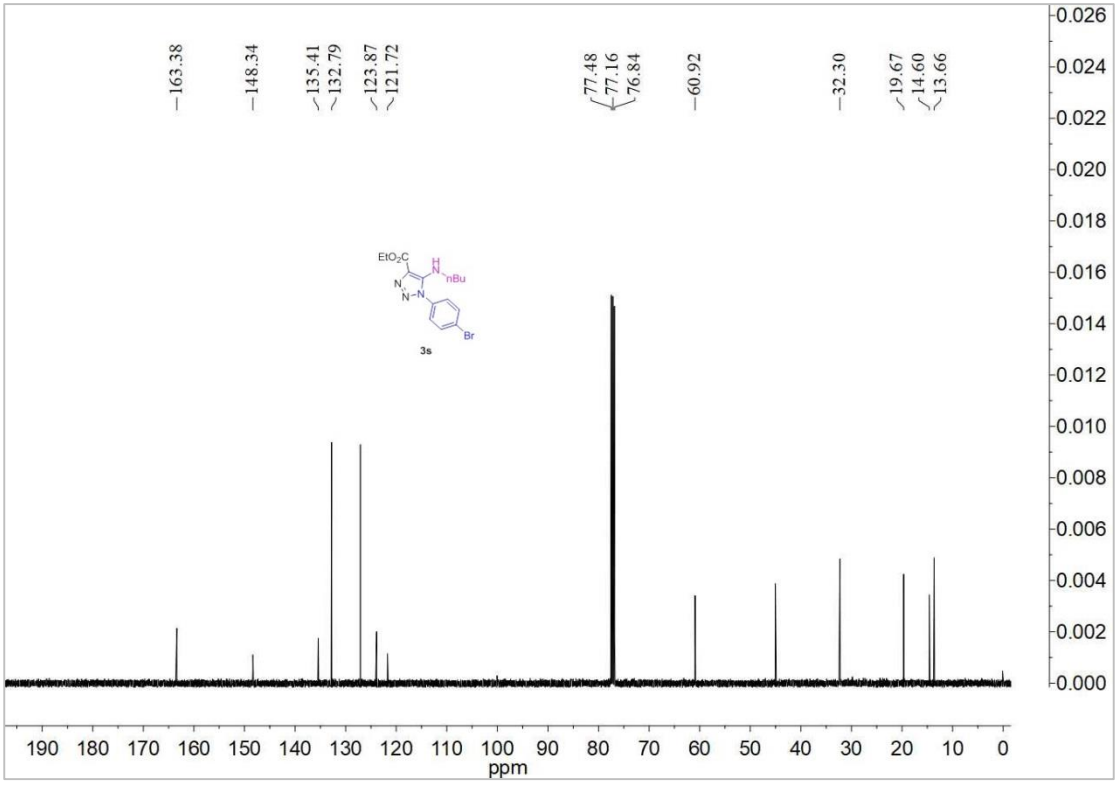

7.44
7.43
7.42
7.41
7.28
7.03
7.02
7.02
7.01
7.00
6.99
6.06
6.05
6.03
4.46
4.44
4.42
4.40
3.88
2.84
2.82
2.80
2.79
1.46
1.44
1.42
1.40
1.38
1.38
1.37
1.36
1.35
1.34
1.33
1.24
1.23
1.21
1.21
1.19
1.17
0.81
0.79
0.77
0.00
EtO2C
H
N
nBu
N
N
OMe
3q
1.93
1.97
0.90
2.00
2.50
1.95
3.09
2.12
2.20
3.06
f1 (ppm)

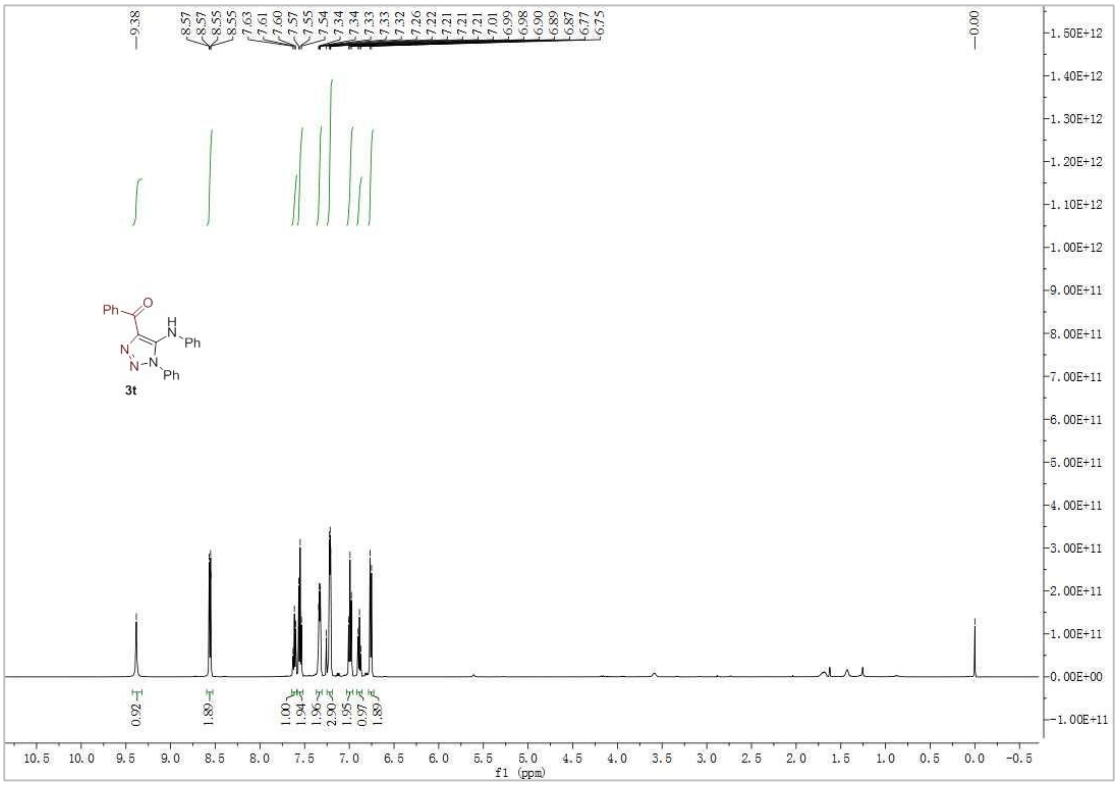

163.50
160.62
148.31
129.14
127.37
121.18
114.59
77.48
77.16
76.84
60.72
55.74
44.36
32.33
19.65
14.60
13.64
EtO2C
H
N
nBu
N
N
OMe
3q
ppm

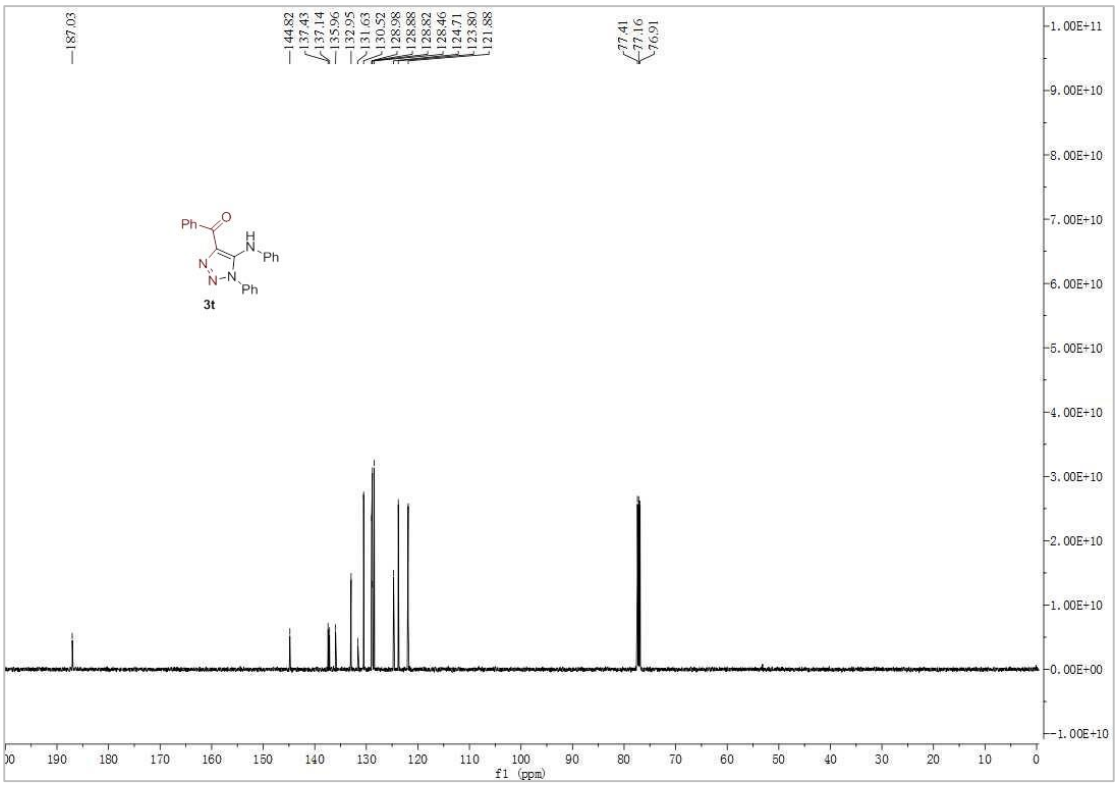

7.56
7.55
7.54
7.54
7.53
7.52
7.51
7.50
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.10
6.09
6.07
2.83
2.81
2.79
2.78
1.60
1.46
1.44
1.43
1.42
1.40
1.39
1.38
1.38
1.36
1.35
1.25
1.24
1.22
1.20
1.18
1.16
0.82
0.80
0.78
0.00
EtO2C
nBu
3r
2.01
1.98
0.93
2.00
2.01
3.04
2.10
2.17
3.02
ppm

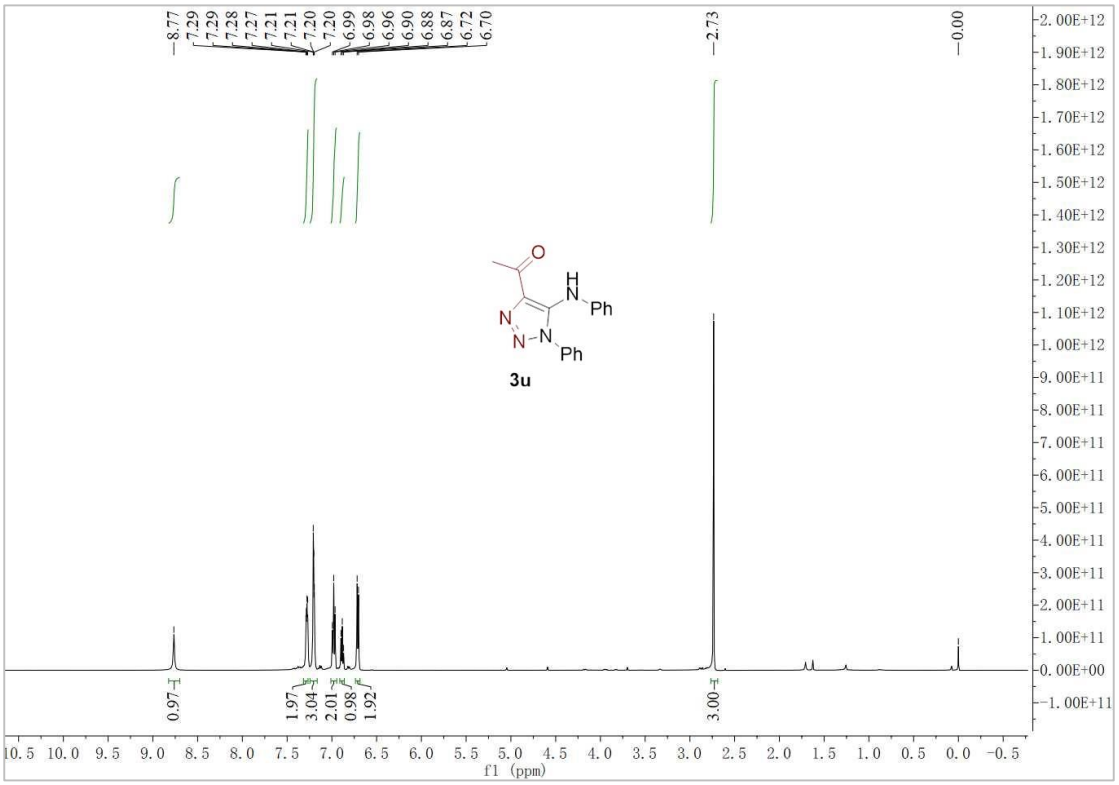

164.40
163.45
161.90
148.40
132.53
132.50
127.88
127.79
121.50
116.76
116.53
77.48
77.16
76.84
60.89
44.77
32.31
19.68
14.62
13.65
EtO2C
nBu
3r
ppm

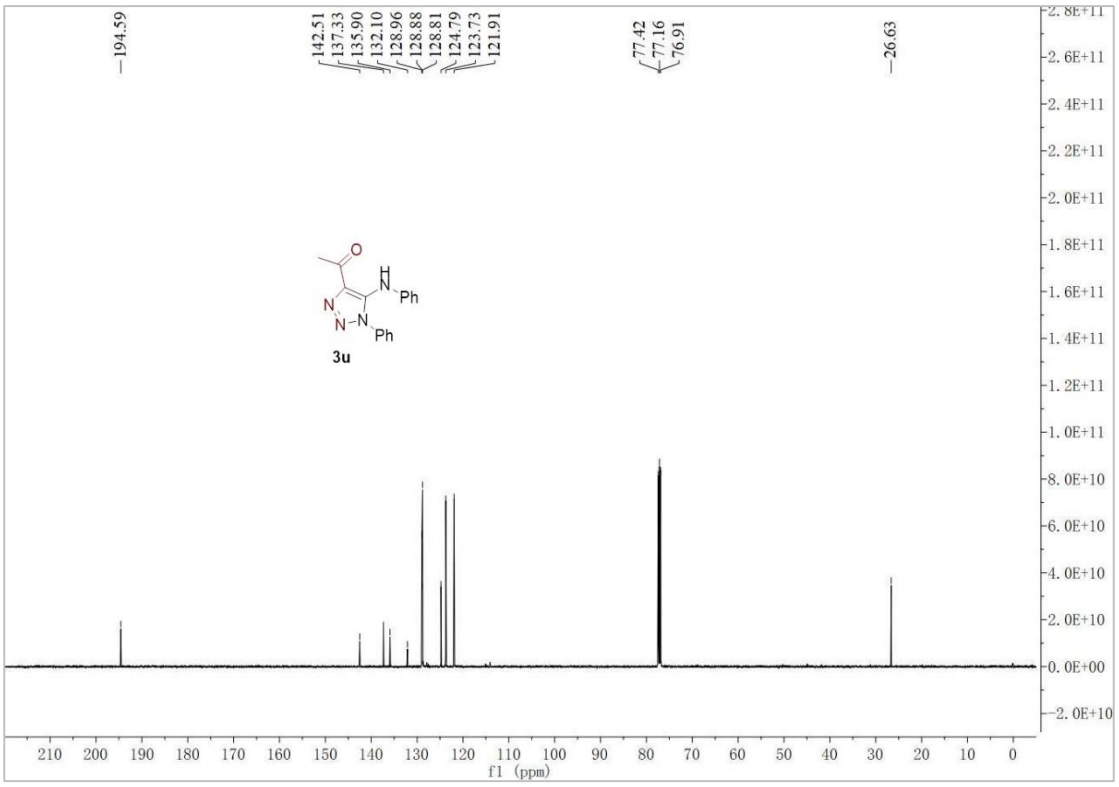

7.67
7.66
7.66
7.64
7.64
7.63
7.43
7.43
7.42
7.41
7.41
7.40
7.25
6.08
6.06
6.05
4.44
4.42
4.41
4.39
2.83
2.81
2.80
2.78
1.44
1.42
1.40
1.39
1.37
1.35
1.34
1.25
1.23
1.21
1.19
1.17
1.16
0.81
0.79
0.77
EtO2C
nBu
Br
3s
1.98
2.03
0.90
2.00
1.95
5.05
2.49
3.01
ppm

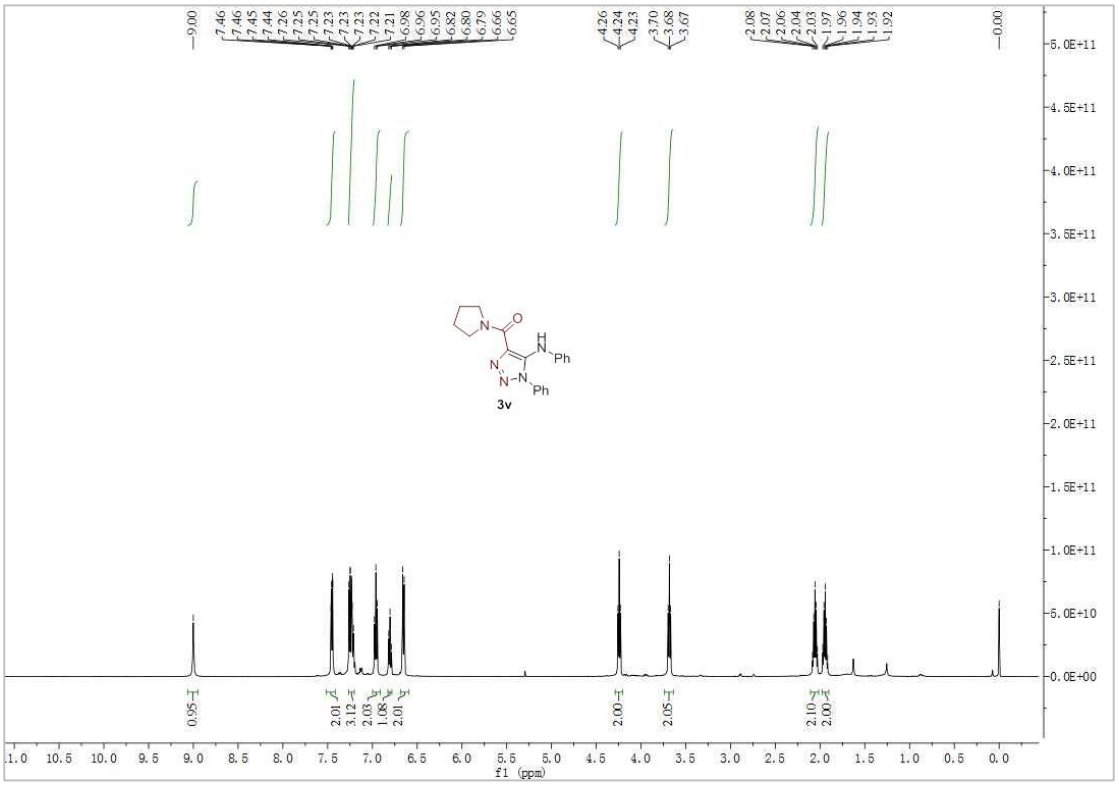

163.38
148.34
135.41
132.79
123.87
121.72
77.48
77.16
76.84
60.92
32.30
19.67
14.60
13.66
EtO2C
nBu
Br
3s
ppm

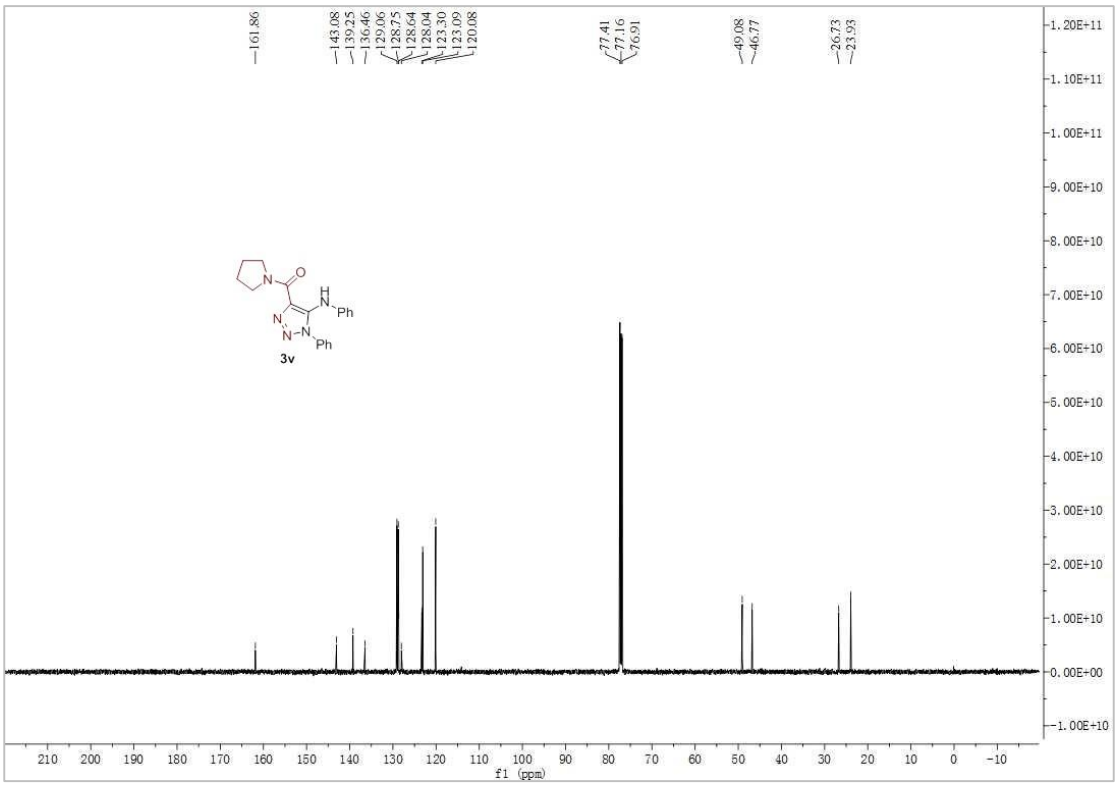

9.38
8.57
8.57
8.55
8.55
7.63
7.61
7.60
7.57
7.55
7.54
7.34
7.34
7.33
7.33
7.32
7.26
7.22
7.21
7.21
7.01
6.99
6.98
6.90
6.89
6.87
6.77
6.75
0.00
Ph
O
N
H
Ph
N
N
Ph
3t
0.92
1.89
1.00
1.94
1.96
2.00
1.95
0.97
1.89
f1 (ppm)

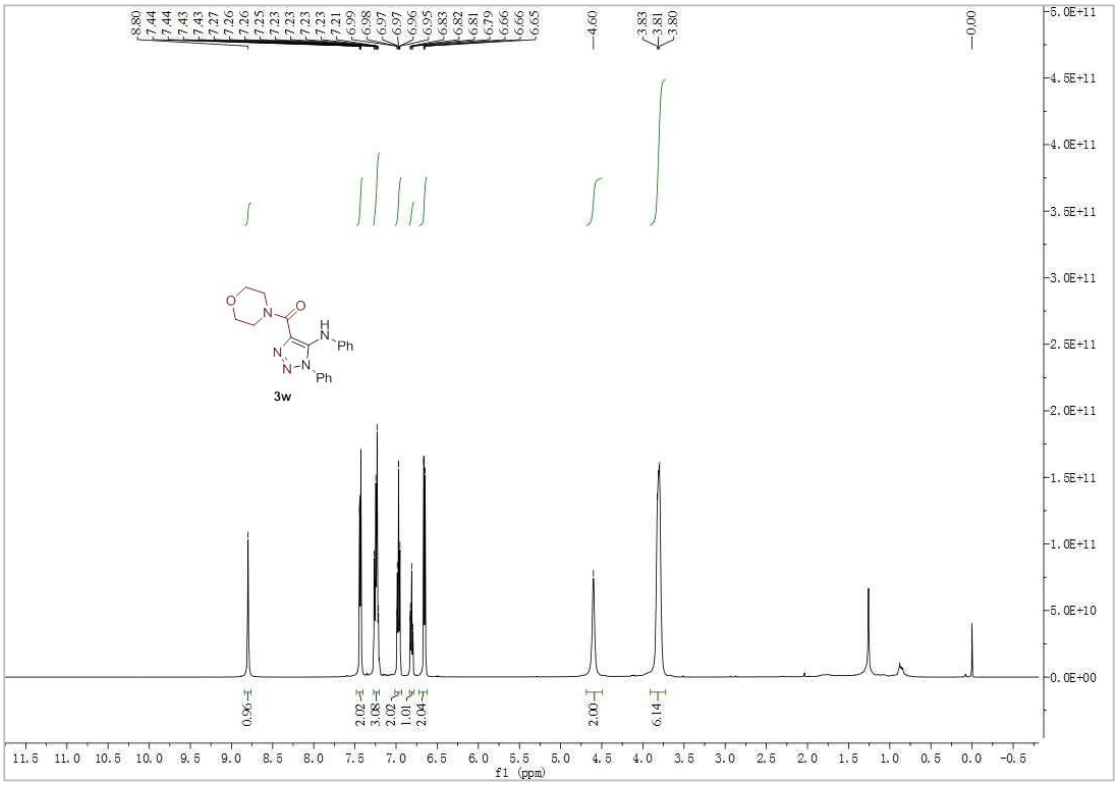

187.03
144.82
137.43
137.14
135.96
132.95
131.63
130.52
128.98
128.88
128.82
128.46
124.71
123.80
121.88
77.41
77.16
76.91
Ph
O
N
H
Ph
N
N
Ph
3t
f1 (ppm)

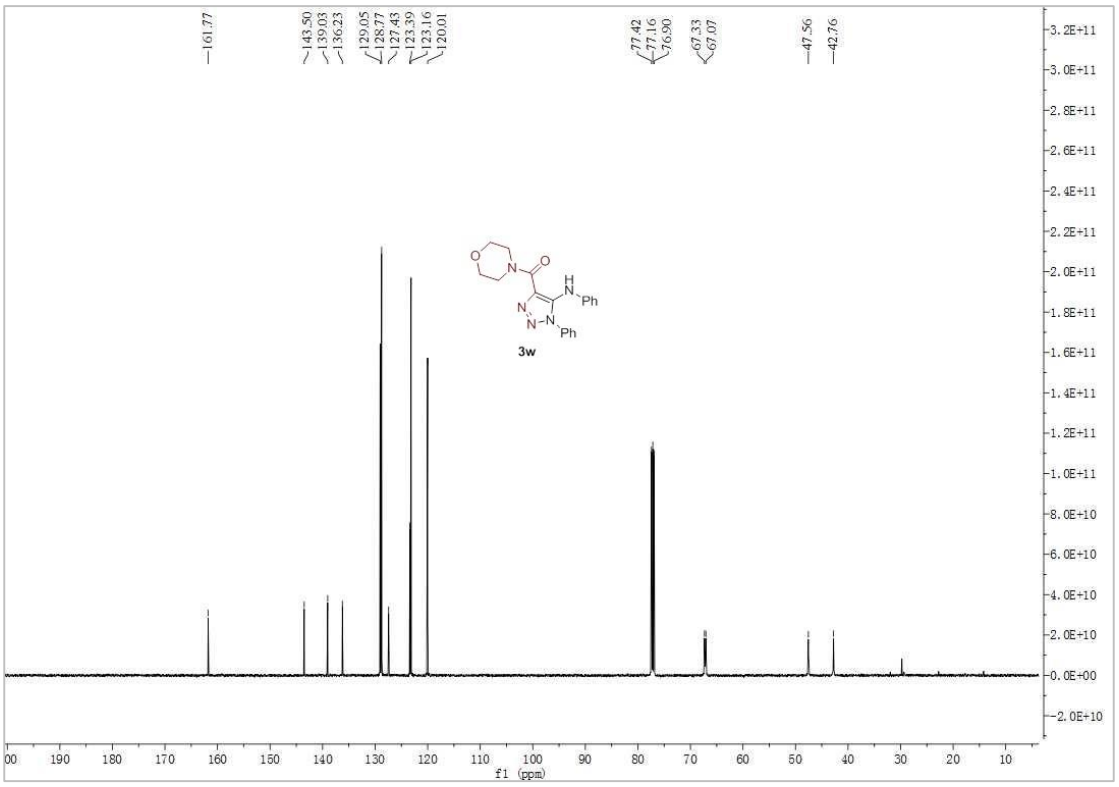

8.77
7.29
7.29
7.28
7.27
7.21
7.21
7.20
7.20
6.99
6.98
6.96
6.90
6.88
6.87
6.72
6.70
2.73
0.00
0.97
1.97
3.04
2.01
0.98
1.92
3.00
3u
f1 (ppm)

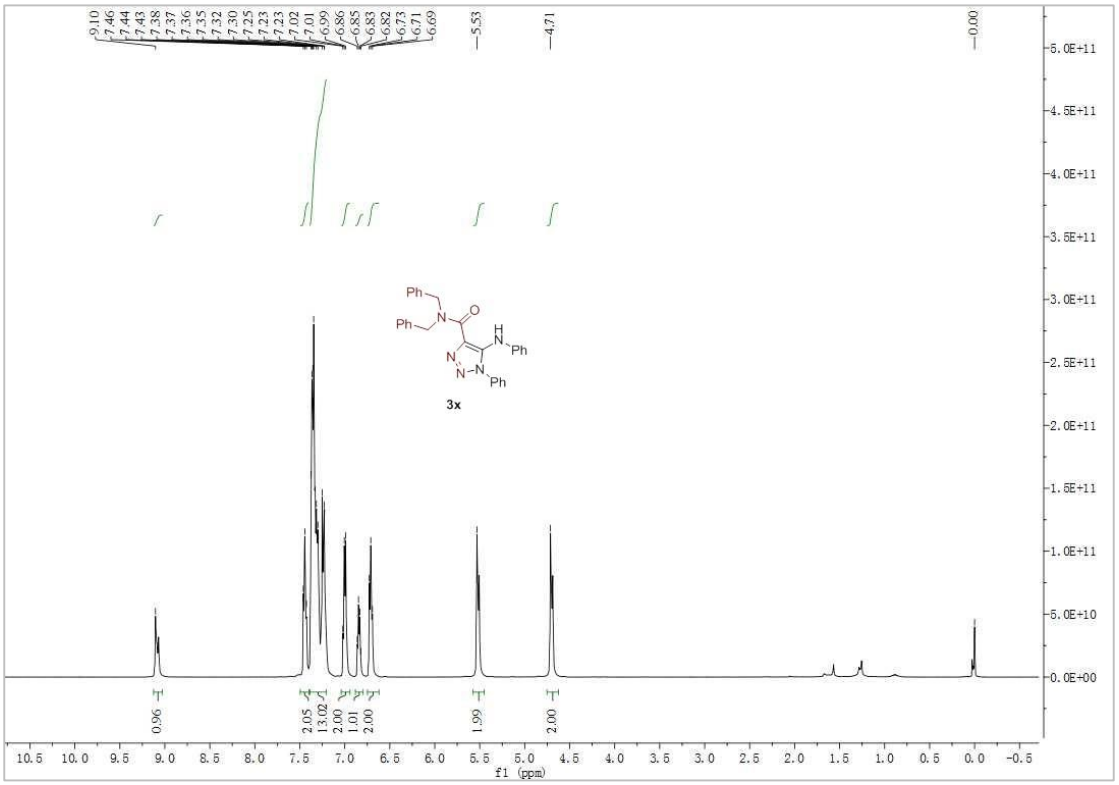

194.59
142.51
137.33
135.90
132.10
128.96
128.88
128.81
124.79
123.73
121.91
77.42
77.16
76.91
26.63
3u
f1 (ppm)

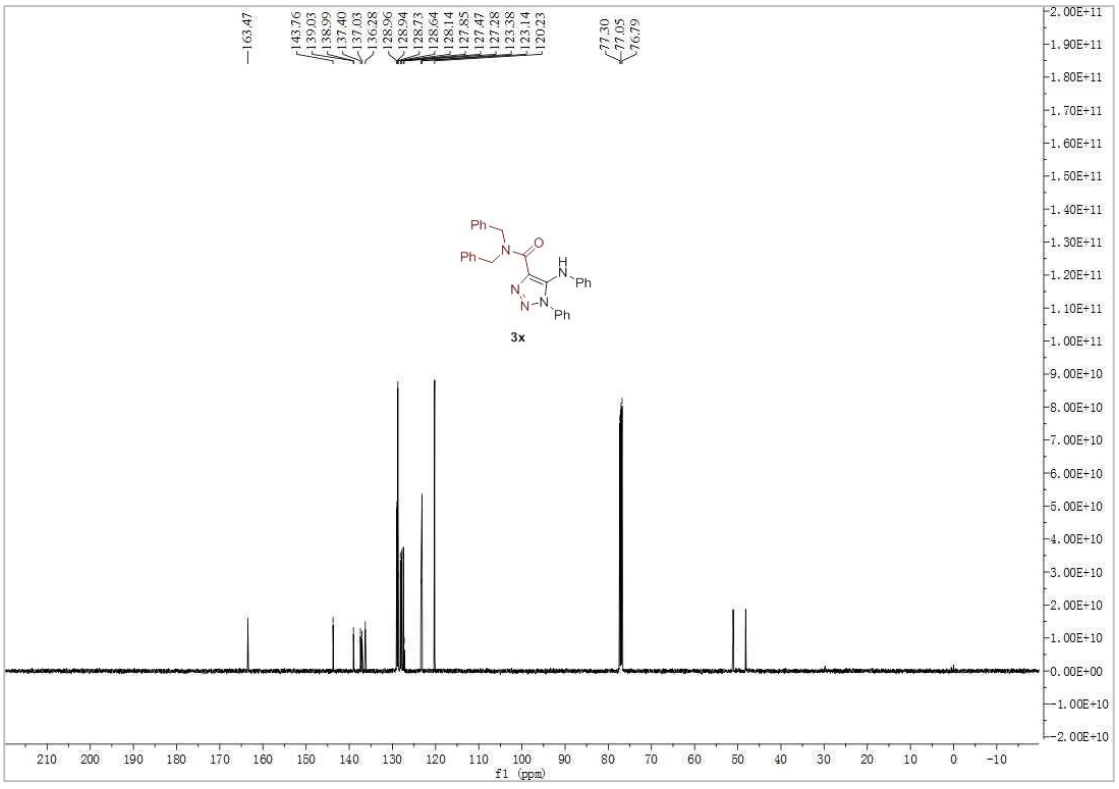

9.00
7.46
7.45
7.44
7.26
7.25
7.23
7.22
7.21
6.98
6.96
6.95
6.82
6.80
6.79
6.66
6.65
4.26
4.24
4.23
3.70
3.68
3.67
2.08
2.07
2.06
2.04
2.03
1.97
1.96
1.94
1.93
1.92
0.00
3v
0.95
2.01
3.12
2.03
1.08
2.01
2.00
2.05
2.10
2.00
f1 (ppm)

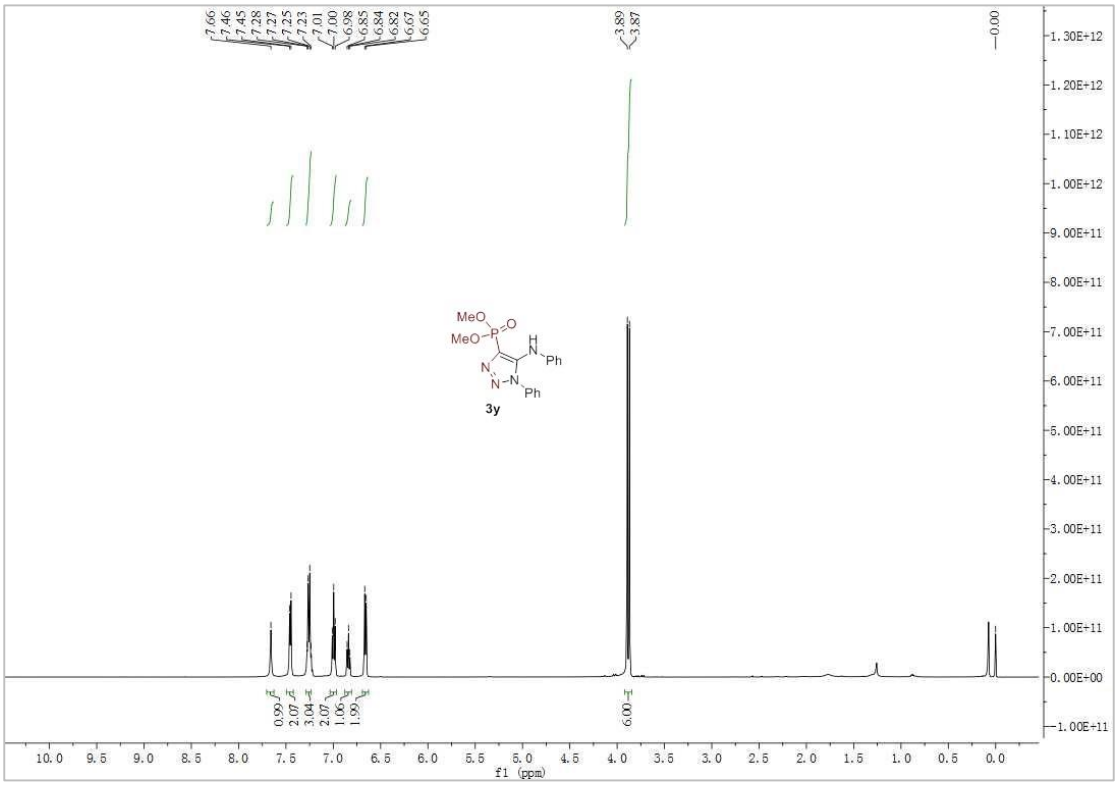

161.86
143.08
139.25
136.46
129.06
128.75
128.64
128.04
123.30
123.09
120.08
77.41
77.16
76.91
49.08
46.77
26.73
23.93
3v
f1 (ppm)

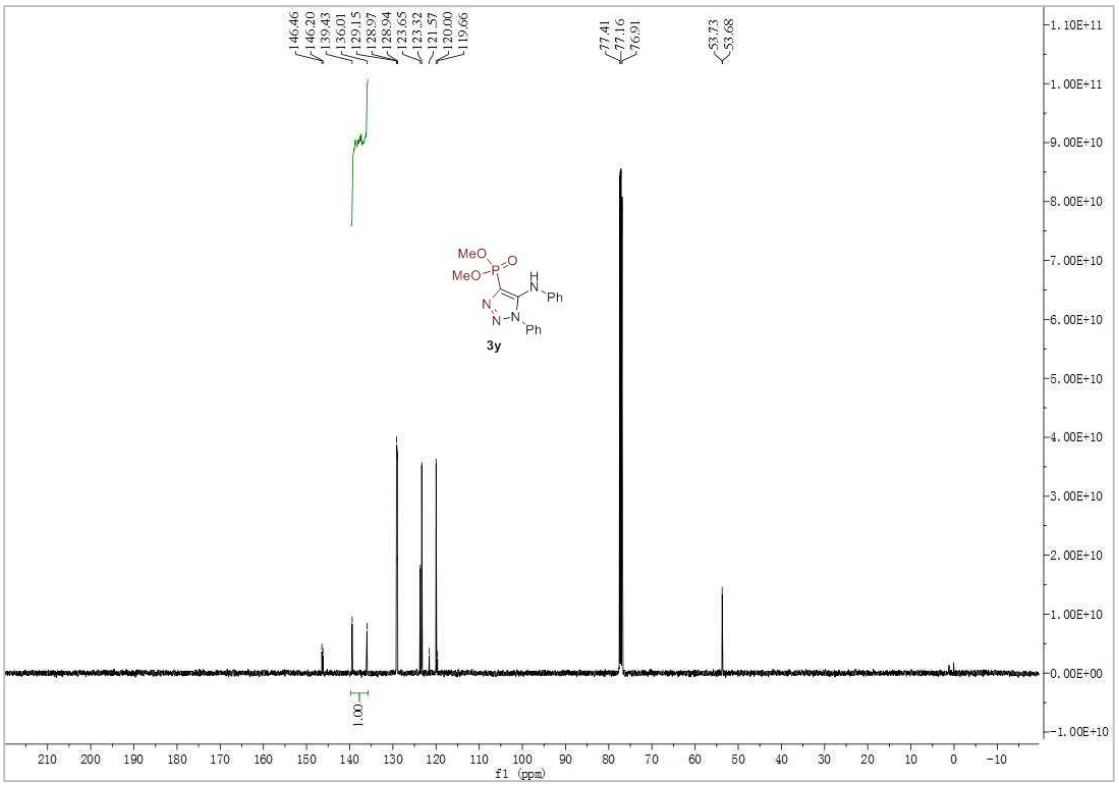

8.80
7.44
7.44
7.43
7.43
7.27
7.26
7.26
7.25
7.23
7.23
7.23
7.21
6.99
6.98
6.97
6.97
6.96
6.95
6.83
6.82
6.81
6.79
6.66
6.65
4.60
3.83
3.81
3.80
0.00
3w
0.96
2.02
3.08
2.02
1.01
2.04
2.00
6.14
f1 (ppm)

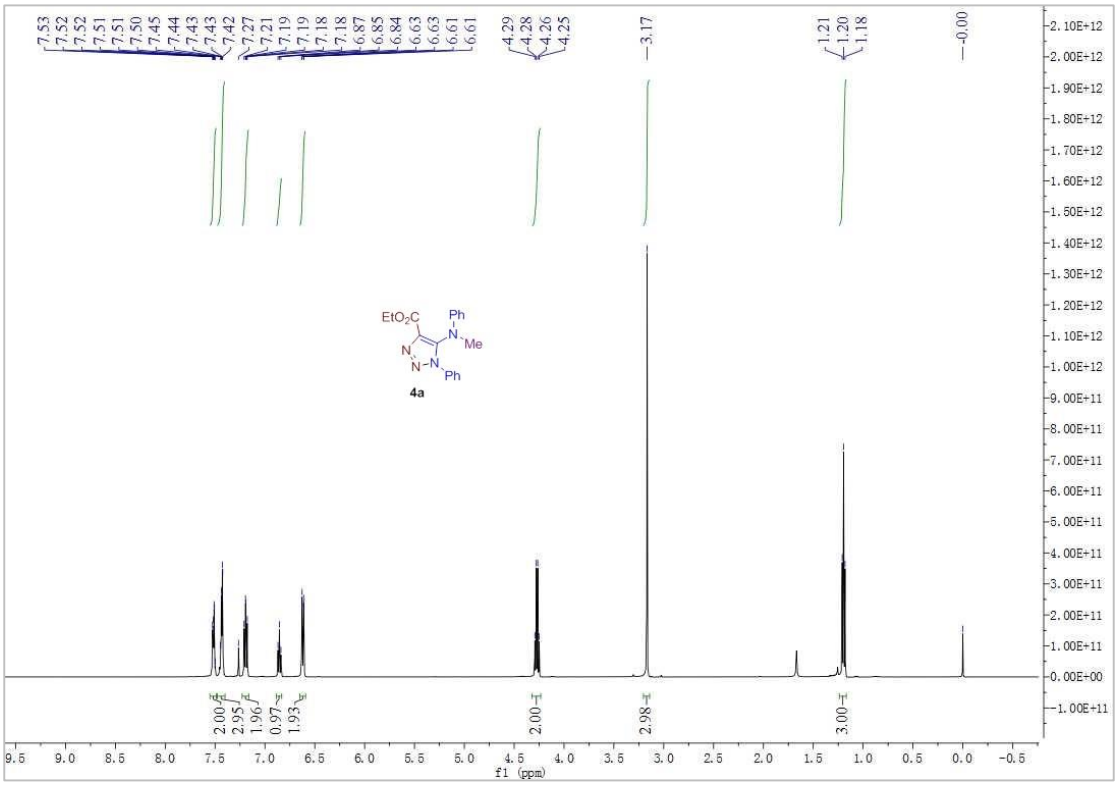

161.77
143.50
139.03
136.23
129.05
128.77
127.43
123.39
123.16
120.01
77.42
77.16
76.90
67.33
67.07
47.56
42.76
3w
f1 (ppm)

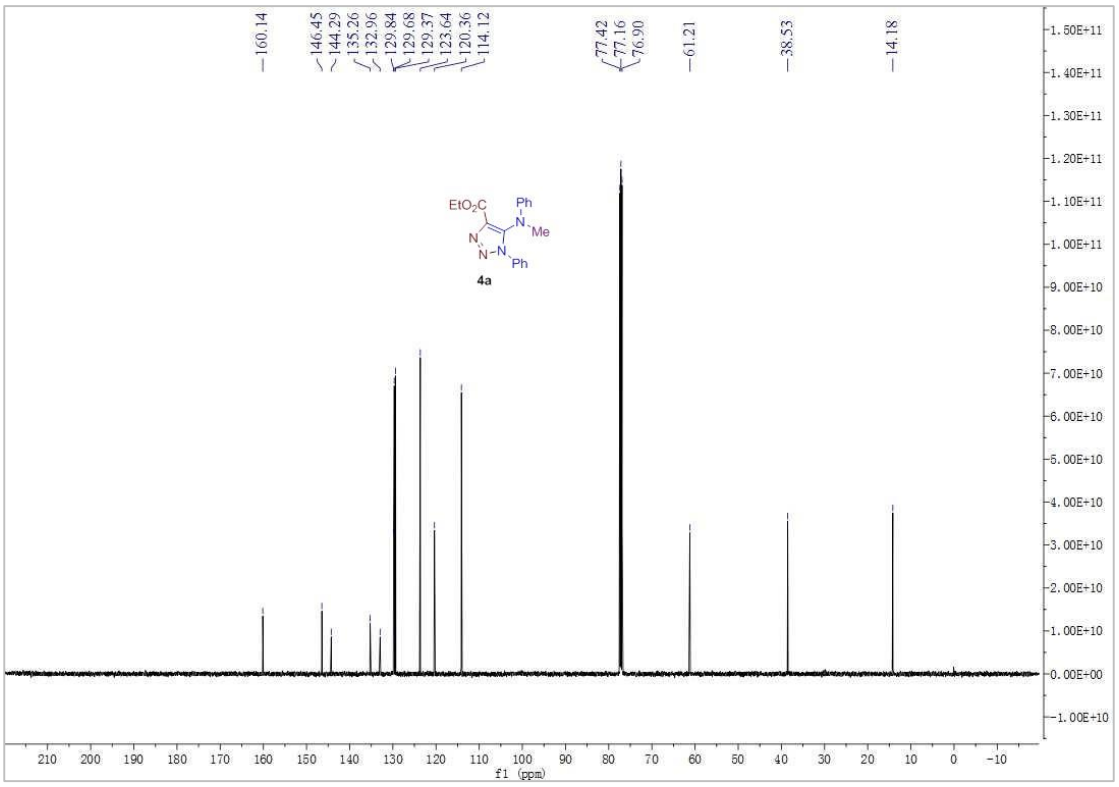

9.10
7.46
7.44
7.43
7.38
7.37
7.36
7.35
7.32
7.30
7.25
7.23
7.23
7.02
7.01
6.99
6.86
6.85
6.83
6.82
6.73
6.71
6.69
5.53
4.71
0.00
Ph
Ph
N
O
H
N
Ph
N
N
N
Ph
3x
0.96
2.05
13.02
2.00
1.01
2.00
1.99
2.00
f1 (ppm)

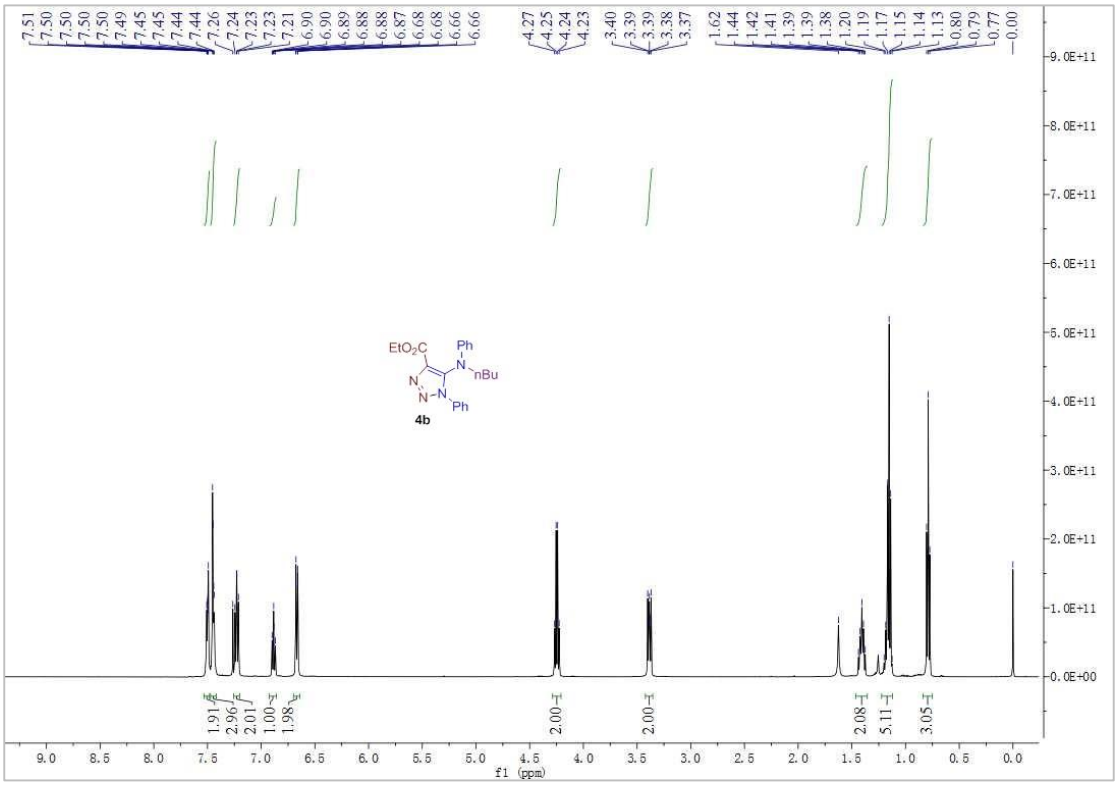

163.47
143.76
139.03
138.99
137.40
137.03
136.28
128.96
128.94
128.73
128.64
128.14
127.85
127.47
127.28
123.38
123.14
120.23
77.30
77.05
76.79
Ph
Ph
N
O
H
N
Ph
N
N
N
Ph
3x
f1 (ppm)

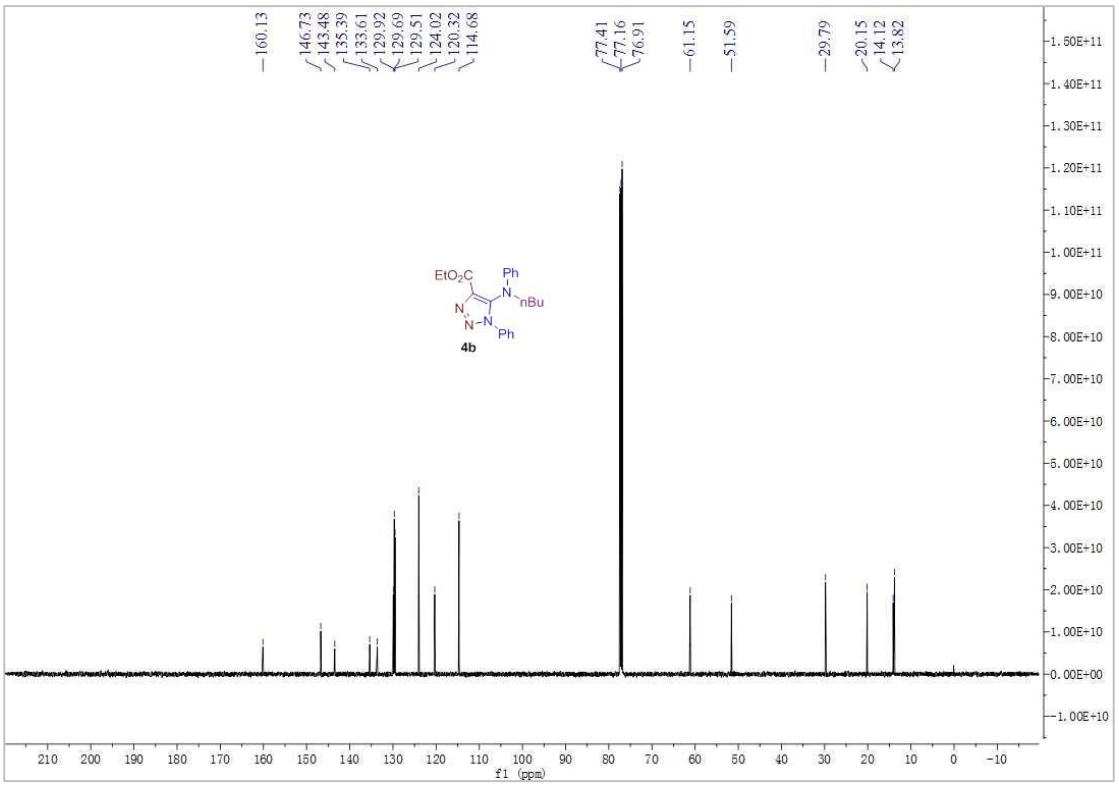

7.66
7.46
7.45
7.28
7.27
7.25
7.23
7.01
7.00
6.98
6.85
6.84
6.82
6.67
6.65
3.89
3.87
0.00
MeO
MeO
P
O
N
N
N
H
Ph
Ph
3y
0.99
2.07
3.04
2.07
1.06
1.99
6.00
f1 (ppm)

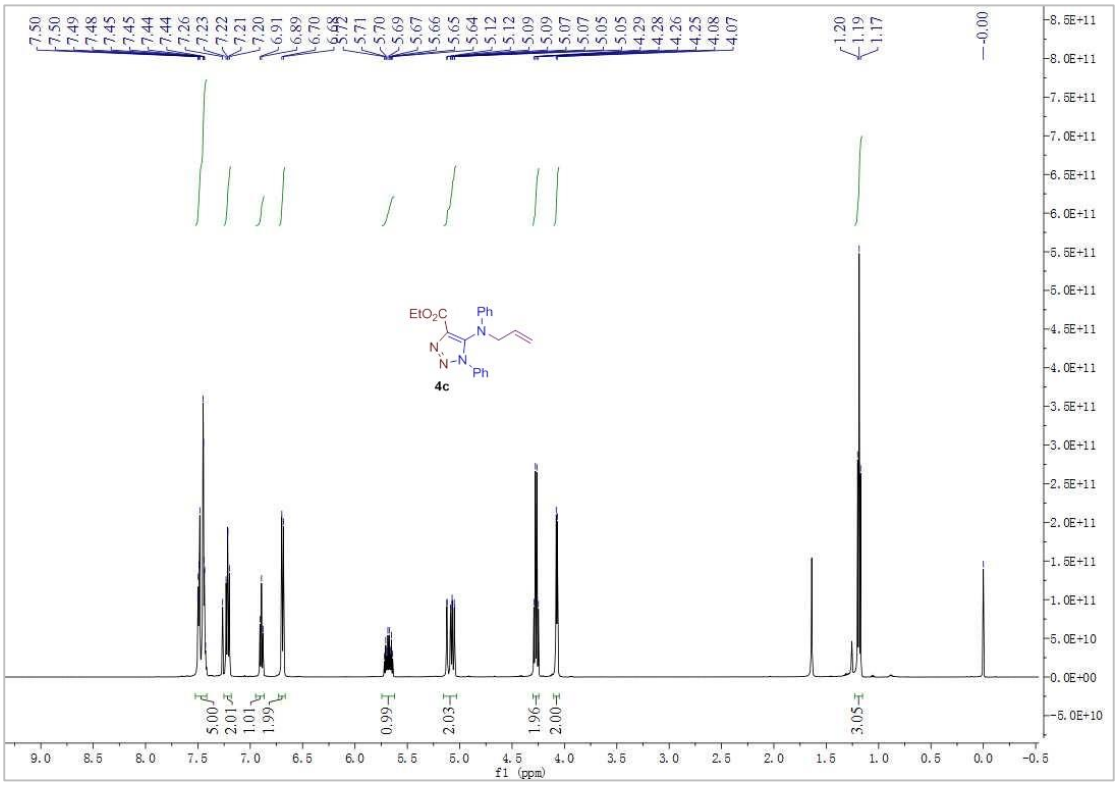

146.46
146.20
139.43
136.01
129.15
128.97
128.94
123.65
123.32
121.57
120.00
119.66
77.41
77.16
76.91
53.73
53.68
MeO
MeO
P
O
N
N
N
H
Ph
Ph
3y
1.00
f1 (ppm)

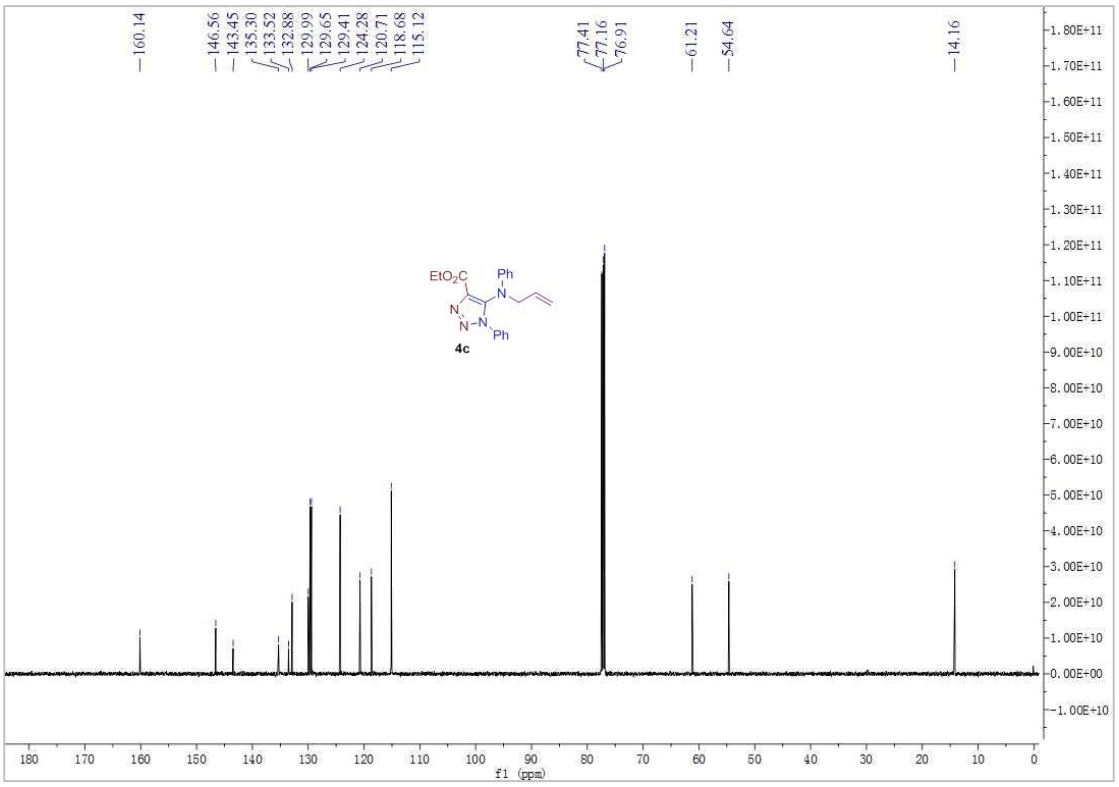

7.53
7.52
7.52
7.51
7.51
7.50
7.45
7.44
7.43
7.43
7.42
7.27
7.21
7.19
7.19
7.18
7.18
6.87
6.85
6.84
6.63
6.63
6.61
6.61
4.29
4.28
4.26
4.25
3.17
1.21
1.20
1.18
0.00
EtO2C
Ph
N
Me
N
N
Ph
4a
2.00
2.95
1.96
0.97
1.93
2.00
2.98
3.00
f1 (ppm)

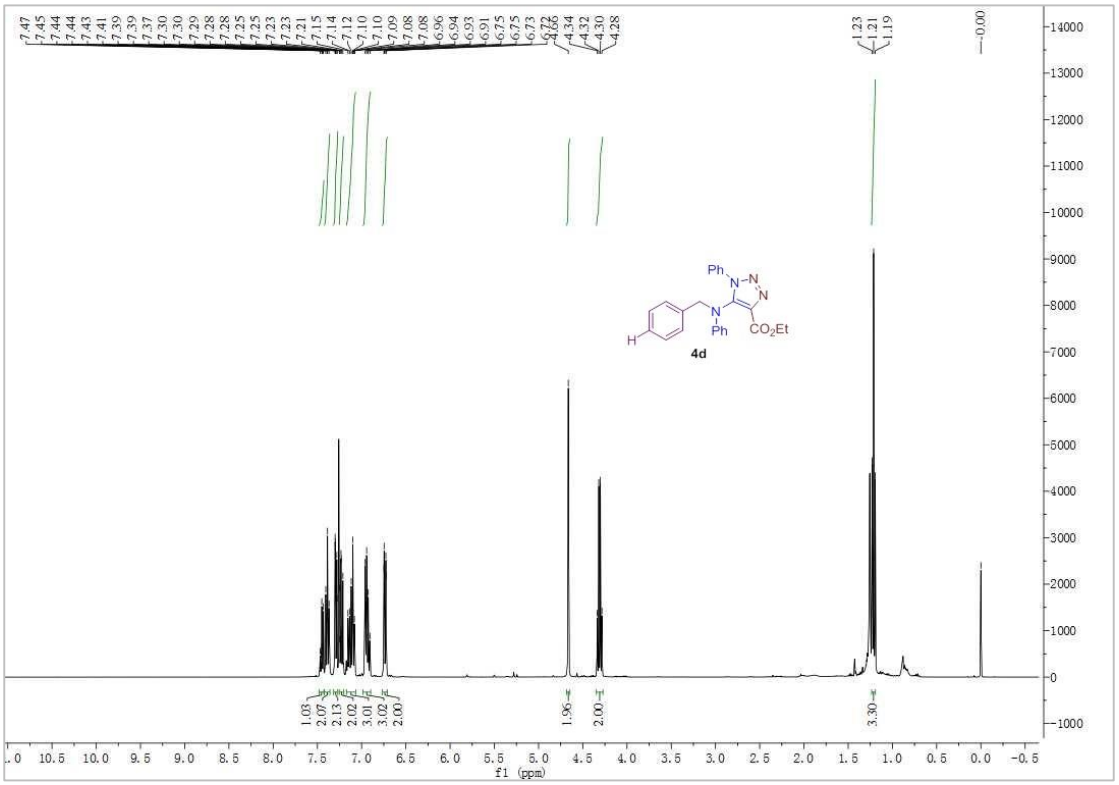

160.14
146.45
144.29
135.26
132.96
129.84
129.68
129.37
123.64
120.36
114.12
77.42
77.16
76.90
61.21
38.53
14.18
EtO2C
Ph
N
Me
N
N
Ph
4a
f1 (ppm)

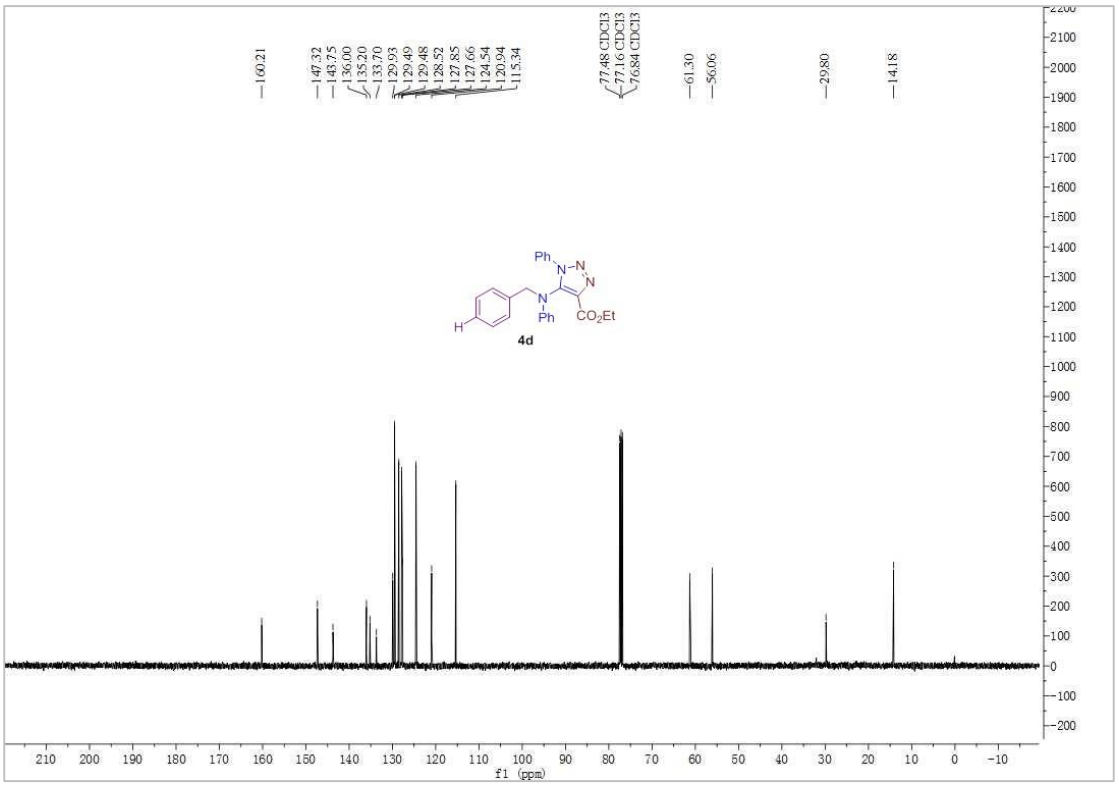

7.51 7.50 7.50 7.50 7.50 7.49 7.45 7.45 7.44 7.44 7.26 7.24 7.23 7.23 7.21 6.90 6.90 6.89 6.88 6.88 6.87 6.68 6.68 6.66 6.66
4.27 4.25 4.24 4.23
3.40 3.39 3.39 3.38 3.37
1.62 1.44 1.42 1.41 1.39 1.39 1.38 1.20 1.19 1.17 1.15 1.14 1.13 0.80 0.79 0.77 0.00
EtO2C
Ph
N
nBu
N
N
N
Ph
4b
1.91 2.96 2.01 1.00 1.98 2.00 2.00 2.08 5.11 3.05
f1 (ppm)

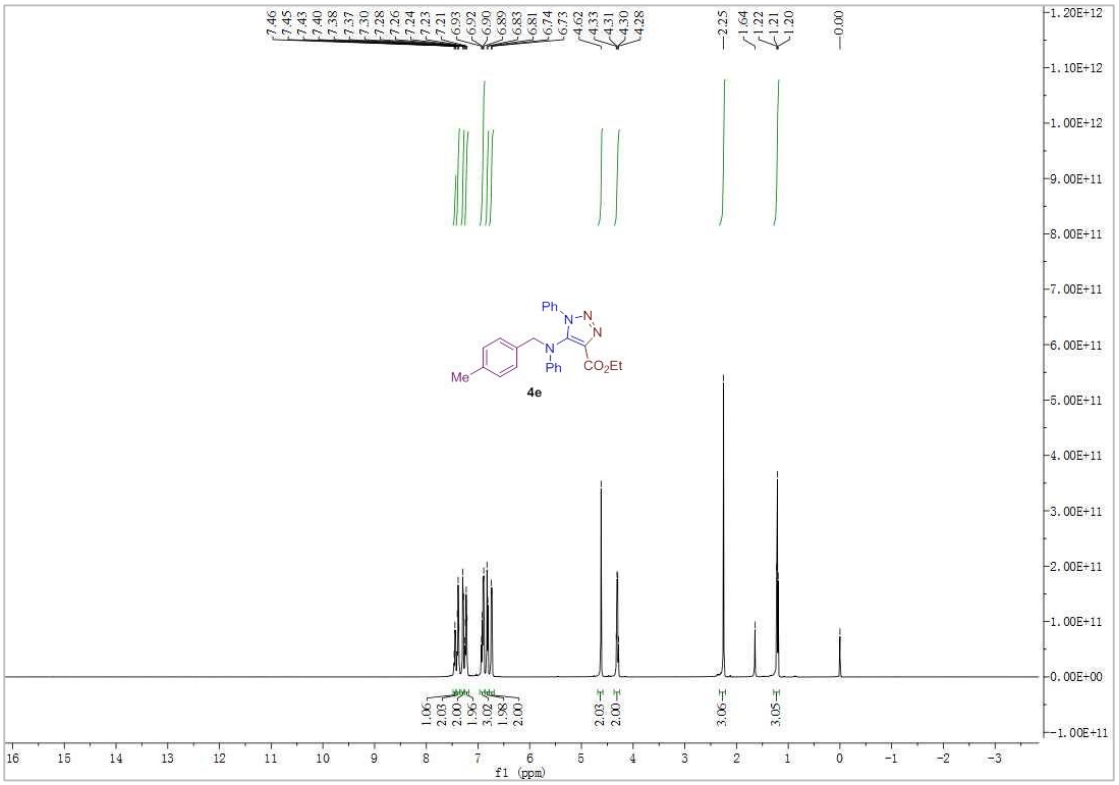

160.13
146.73
143.48
135.39
133.61
129.92
129.69
129.51
124.02
120.32
114.68
77.41
77.16
76.91
61.15
51.59
29.79
20.15
14.12
13.82
EtO2C
Ph
N
nBu
N
N
N
Ph
4b
f1 (ppm)

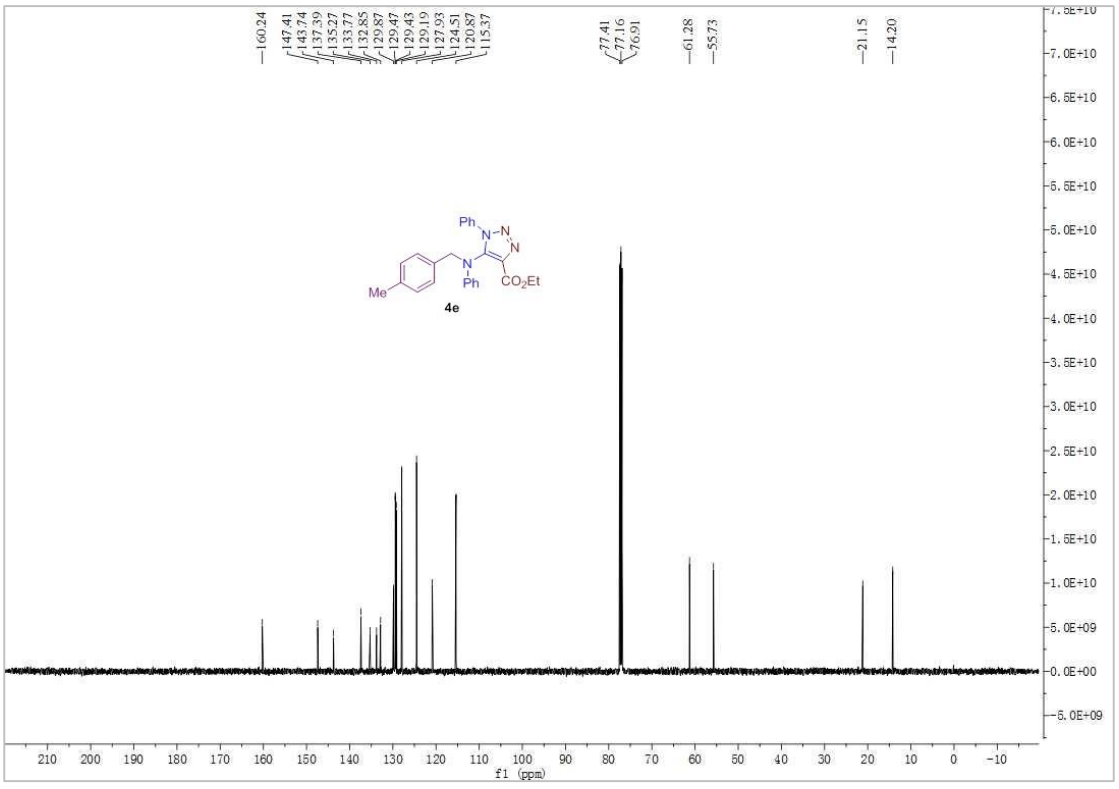

7.50
7.50
7.49
7.48
7.45
7.45
7.44
7.44
7.26
7.23
7.22
7.21
7.20
6.91
6.89
6.70
6.68
5.72
5.71
5.70
5.69
5.67
5.66
5.65
5.64
5.12
5.12
5.09
5.09
5.07
5.07
5.05
5.05
4.29
4.28
4.26
4.25
4.08
4.07
1.20
1.19
1.17
-0.00
EtO2C
Ph
N
N
N
Ph
4c
5.00
2.01
1.01
1.99
0.99
2.03
1.96
2.00
3.05
f1 (ppm)

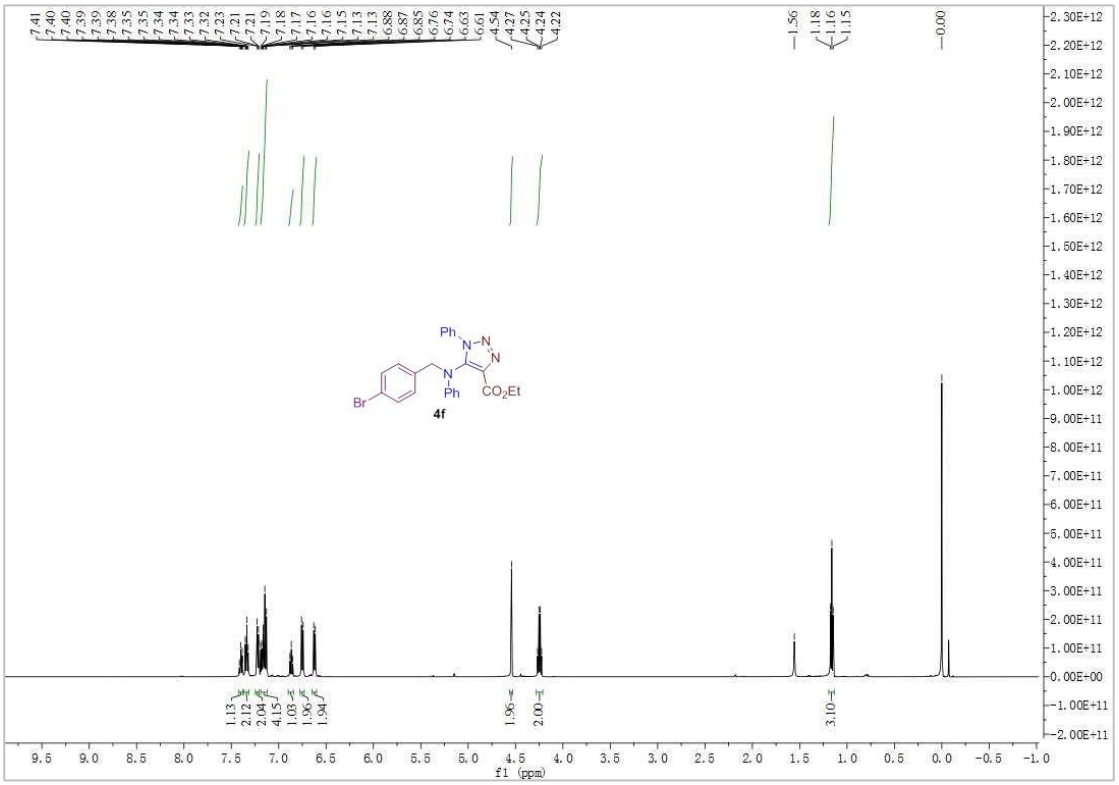

160.14
146.56
143.45
135.30
133.52
132.88
129.99
129.65
129.41
124.28
120.71
118.68
115.12
77.41
77.16
76.91
61.21
54.64
14.16
EtO2C
Ph
N
N
N
Ph
4c
f1 (ppm)

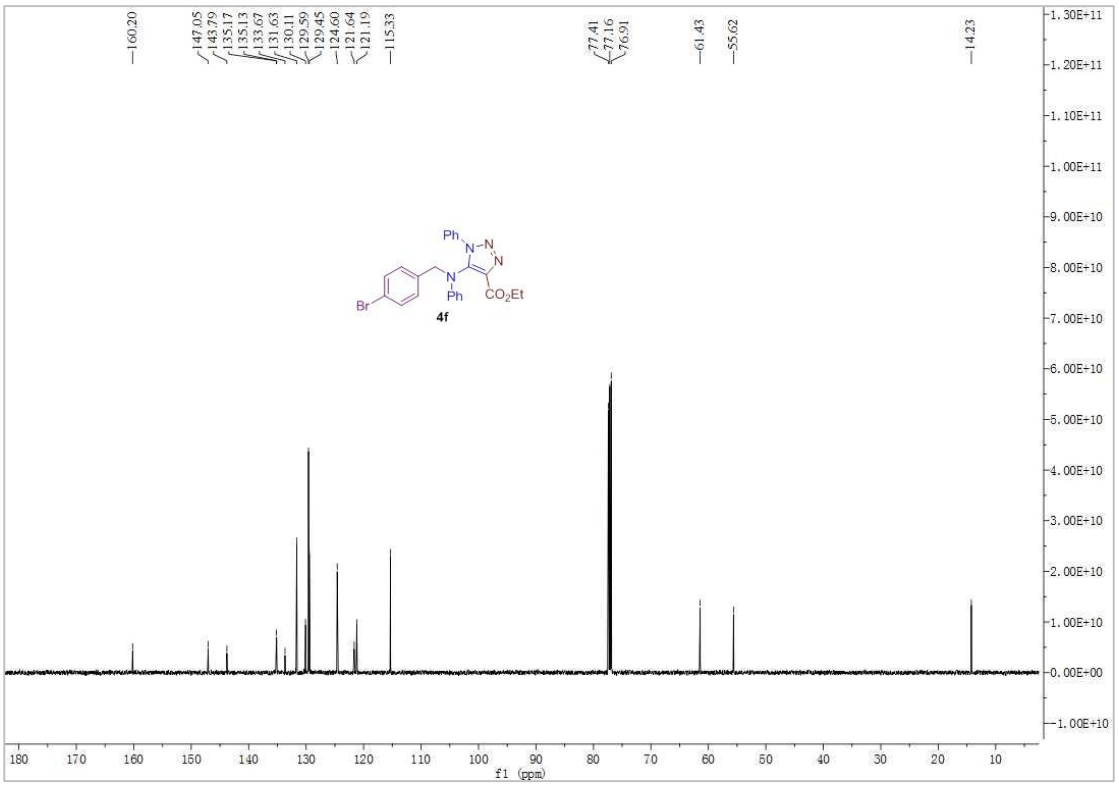

7.47
7.45
7.44
7.44
7.43
7.41
7.39
7.39
7.37
7.30
7.30
7.29
7.28
7.28
7.25
7.25
7.23
7.23
7.21
7.15
7.14
7.12
7.10
7.10
7.09
7.08
7.08
6.96
6.94
6.93
6.91
6.75
6.75
6.73
6.72
4.34
4.32
4.30
4.28
1.23
1.21
1.19
0.00
Ph
N
N
N
N
Ph
CO2Et
H
4d
1.03
2.07
2.13
2.02
3.01
3.02
2.00
1.96
2.00
3.30
f1 (ppm)

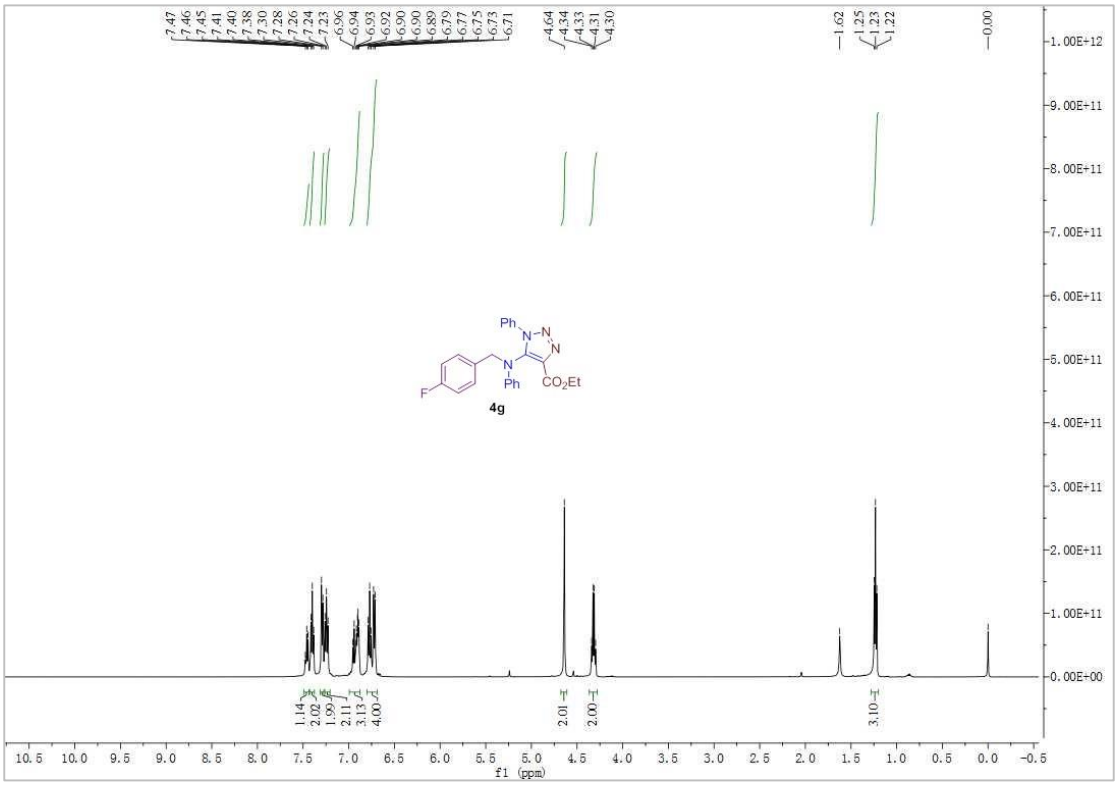

160.21
147.32
143.75
136.00
135.20
133.70
129.93
129.49
129.48
128.52
127.85
127.66
124.54
120.94
115.34
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.30
56.06
29.80
14.18
Ph
N
N
N
N
Ph
CO2Et
H
4d
f1 (ppm)

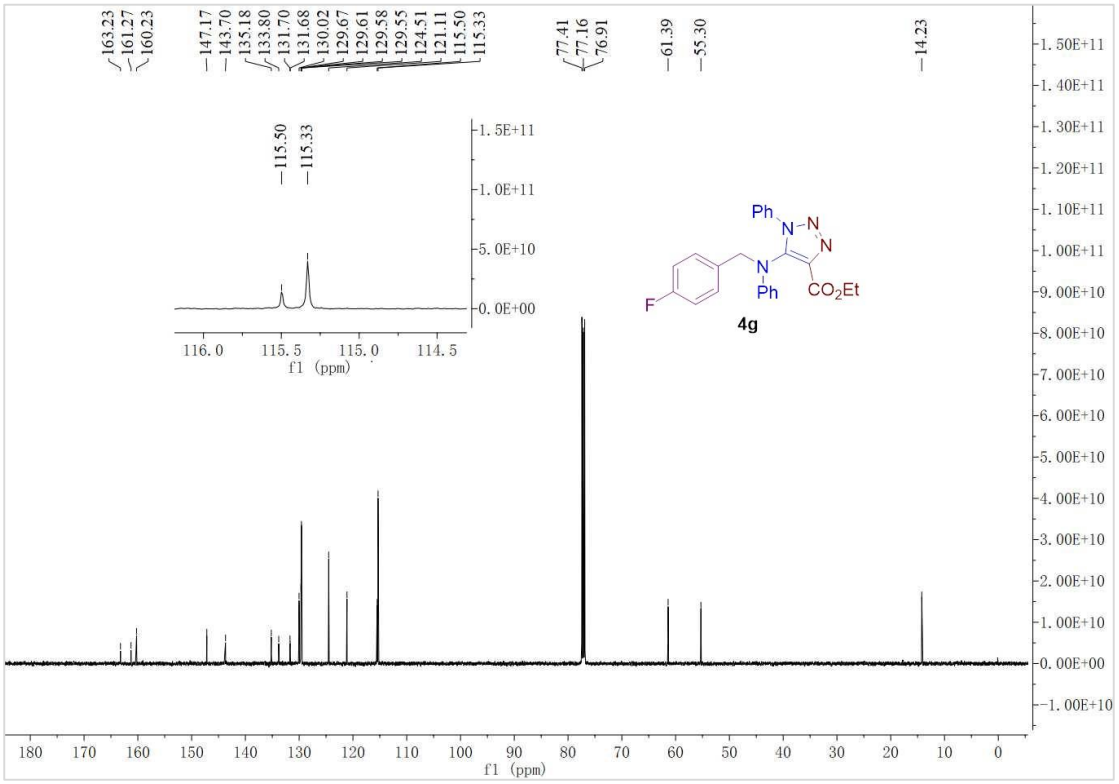

7.46
7.45
7.43
7.40
7.38
7.37
7.30
7.28
7.26
7.24
7.23
7.21
6.93
6.92
6.90
6.89
6.83
6.81
6.74
6.73
4.62
4.33
4.31
4.30
4.28
2.25
1.64
1.22
1.21
1.20
0.00
Ph
N
N
N
N
Ph
CO2Et
Me
4e
1.06
2.03
2.00
1.96
3.02
1.98
2.00
2.03
2.00
3.06
3.05
f1 (ppm)

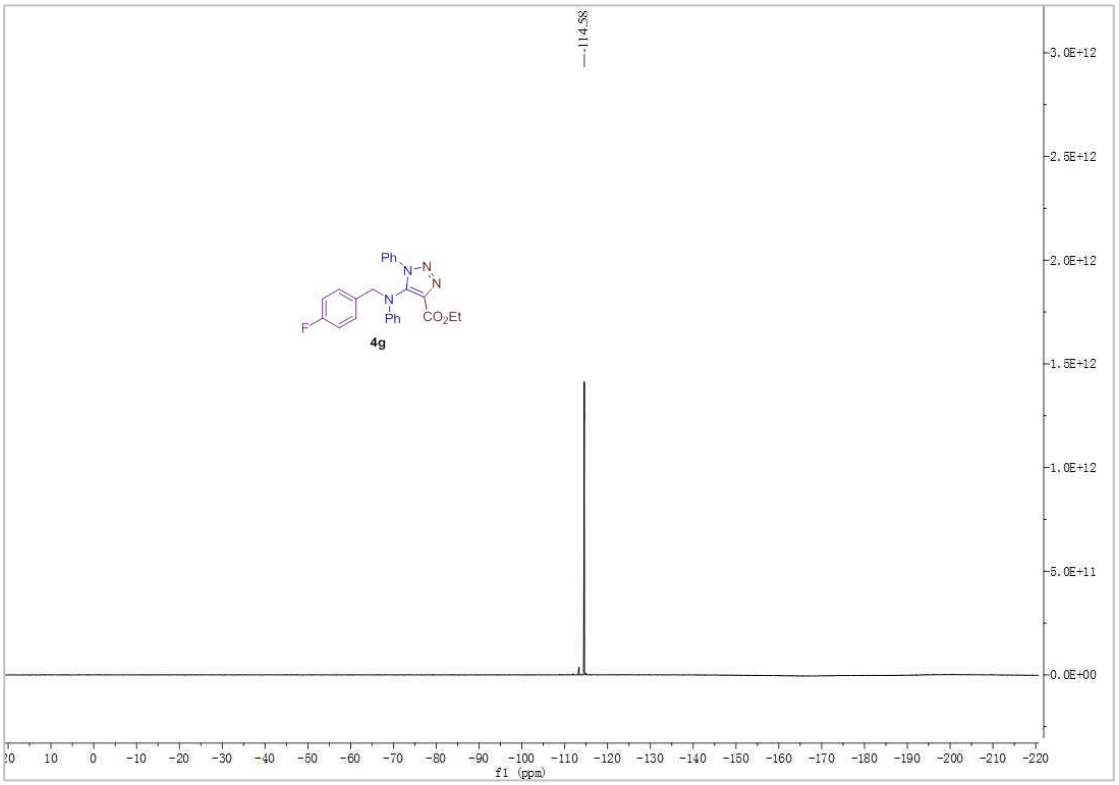

160.24
147.41
143.74
137.39
135.27
133.77
132.85
129.87
129.47
129.43
129.19
127.93
124.51
120.87
115.37
77.41
77.16
76.91
61.28
55.73
21.15
14.20
Ph
N
N
N
N
Ph
CO2Et
Me
4e
f1 (ppm)

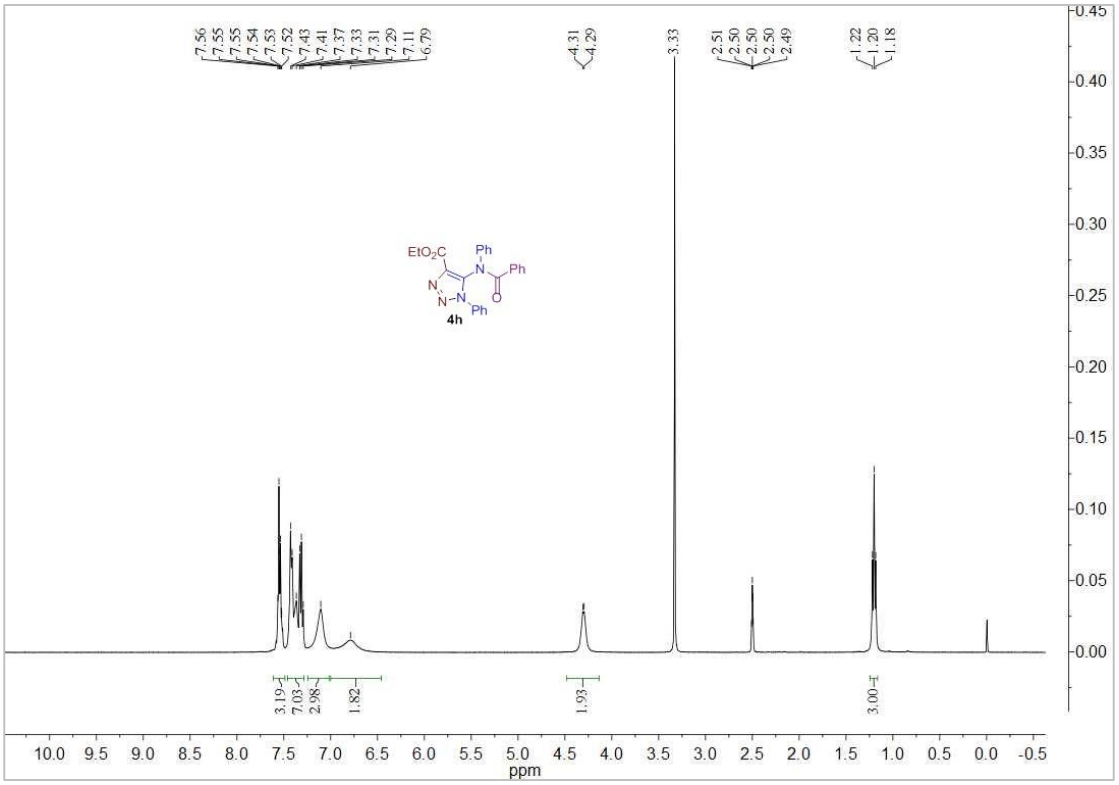

7.41
7.40
7.40
7.39
7.39
7.38
7.35
7.35
7.34
7.34
7.33
7.32
7.23
7.21
7.21
7.19
7.18
7.17
7.16
7.16
7.15
7.13
7.13
6.88
6.87
6.85
6.76
6.74
6.63
6.61
4.54
4.27
4.25
4.24
4.22
1.56
1.18
1.16
1.15
0.00
Ph
N
N
N
Br
N
Ph
CO2Et
4f
1.13
2.12
2.04
4.15
1.03
1.06
1.94
1.96
2.00
3.10
f1 (ppm)

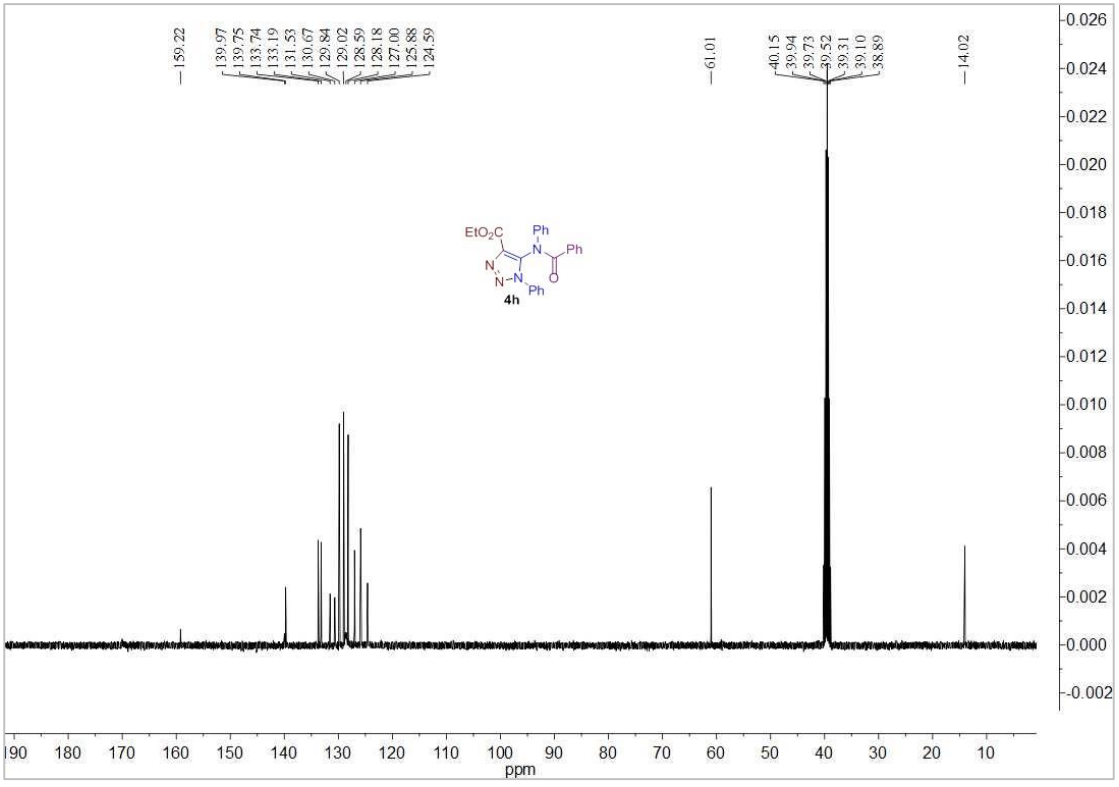

160.20
147.05
143.79
135.17
135.13
133.67
131.63
130.11
129.59
129.45
124.60
121.64
121.19
115.33
77.41
77.16
76.91
61.43
55.62
14.23
Ph
N
N
N
Br
N
Ph
CO2Et
4f
f1 (ppm)

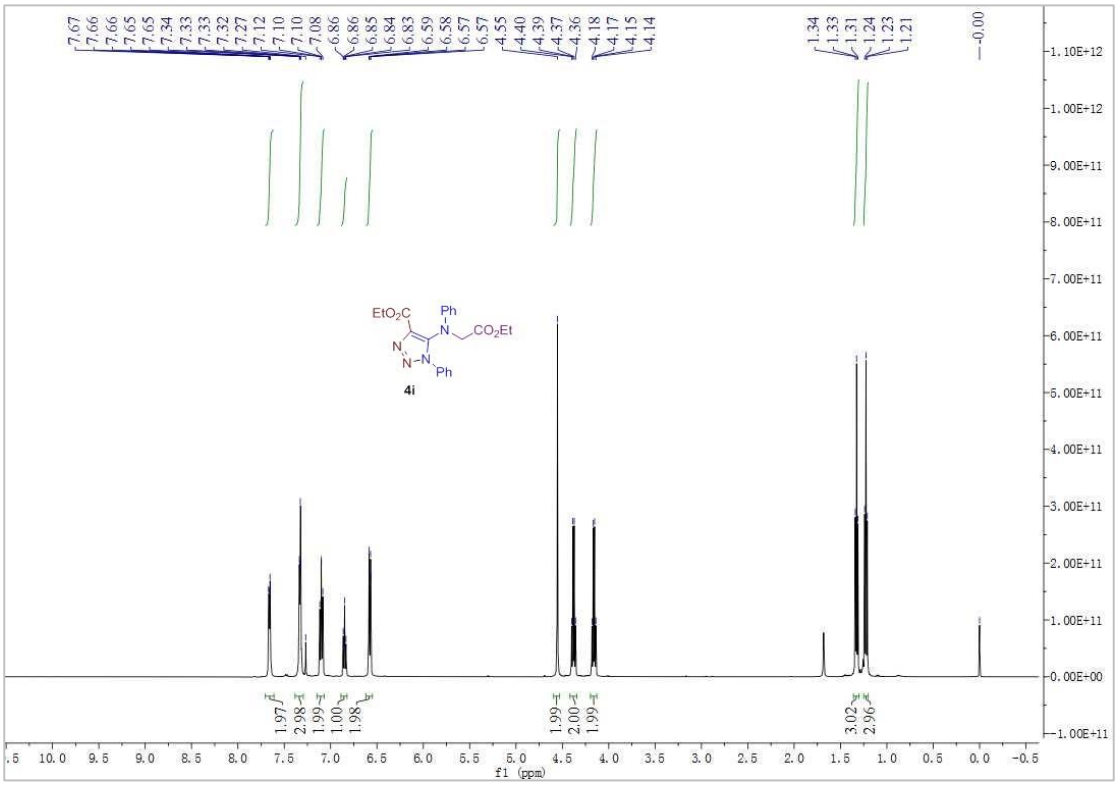

7.47
7.46
7.45
7.41
7.40
7.38
7.30
7.28
7.26
7.24
7.23
6.96
6.94
6.93
6.92
6.90
6.90
6.89
6.79
6.77
6.75
6.73
6.71
4.64
4.34
4.33
4.31
4.30
1.62
1.25
1.23
1.22
0.00
Ph
N
N
N
Ph
CO2Et
F
4g
1.14
2.02
1.99
2.11
3.13
4.00
2.01
2.00
3.10
f1 (ppm)

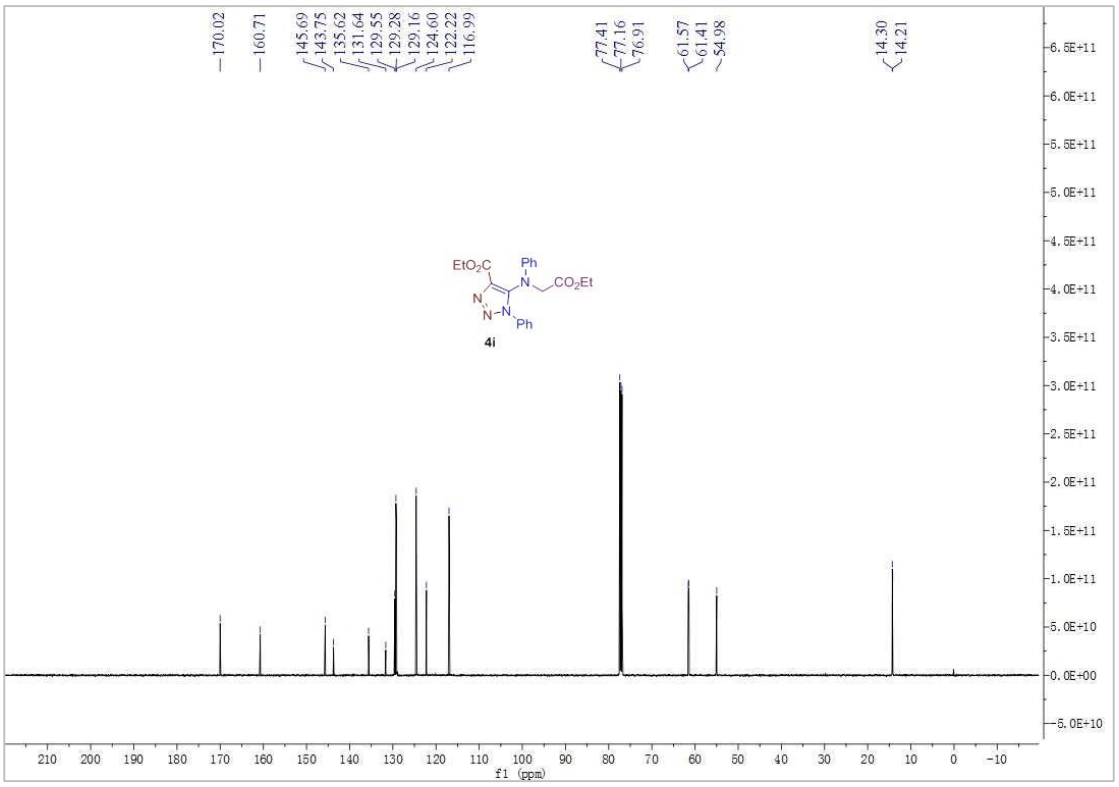

163.23
161.27
160.23
147.17
143.70
135.18
133.80
131.70
131.68
130.02
129.67
129.61
129.58
129.55
124.51
121.11
115.50
115.33
77.41
77.16
76.91
61.39
55.30
14.23
115.50
115.33
f1 (ppm)
Ph
N
N
N
Ph
CO2Et
F
4g
f1 (ppm)

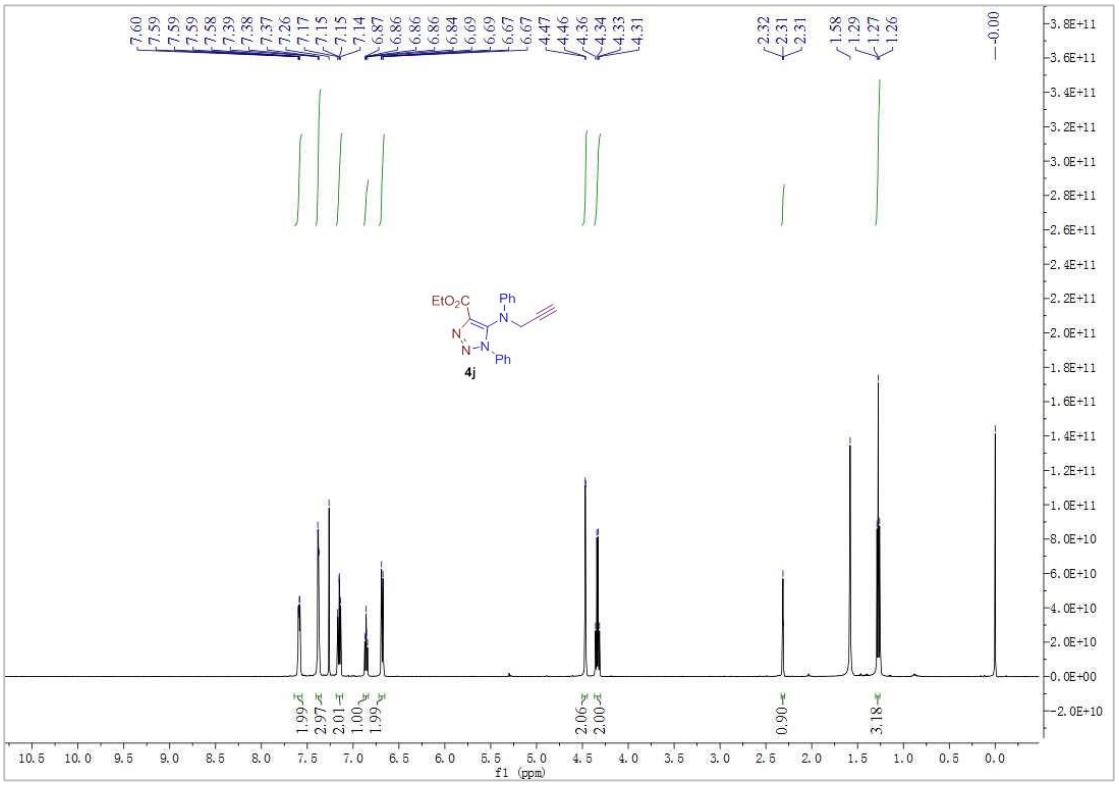

-114.58
3.0E+12
2.5E+12
2.0E+12
1.5E+12
1.0E+12
5.0E+11
0.0E+00
Ph
N
N
N
Ph
CO2Et
F
4g
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

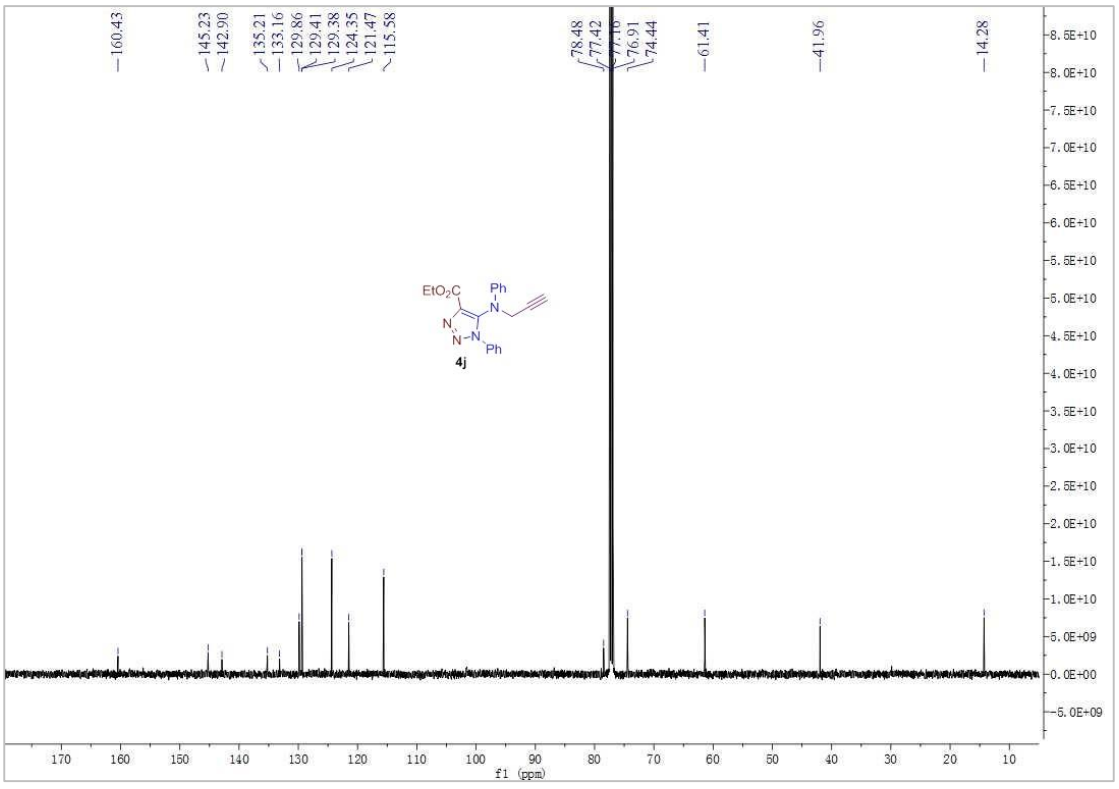

7.56
7.55
7.55
7.55
7.54
7.53
7.52
7.43
7.41
7.37
7.33
7.31
7.29
7.11
6.79
4.31
4.29
3.33
2.51
2.50
2.50
2.50
2.49
1.22
1.20
1.18
EtO2C
Ph
N
Ph
N
N
N
Ph
O
Ph
4h
3.19
7.03
2.98
1.82
1.93
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00

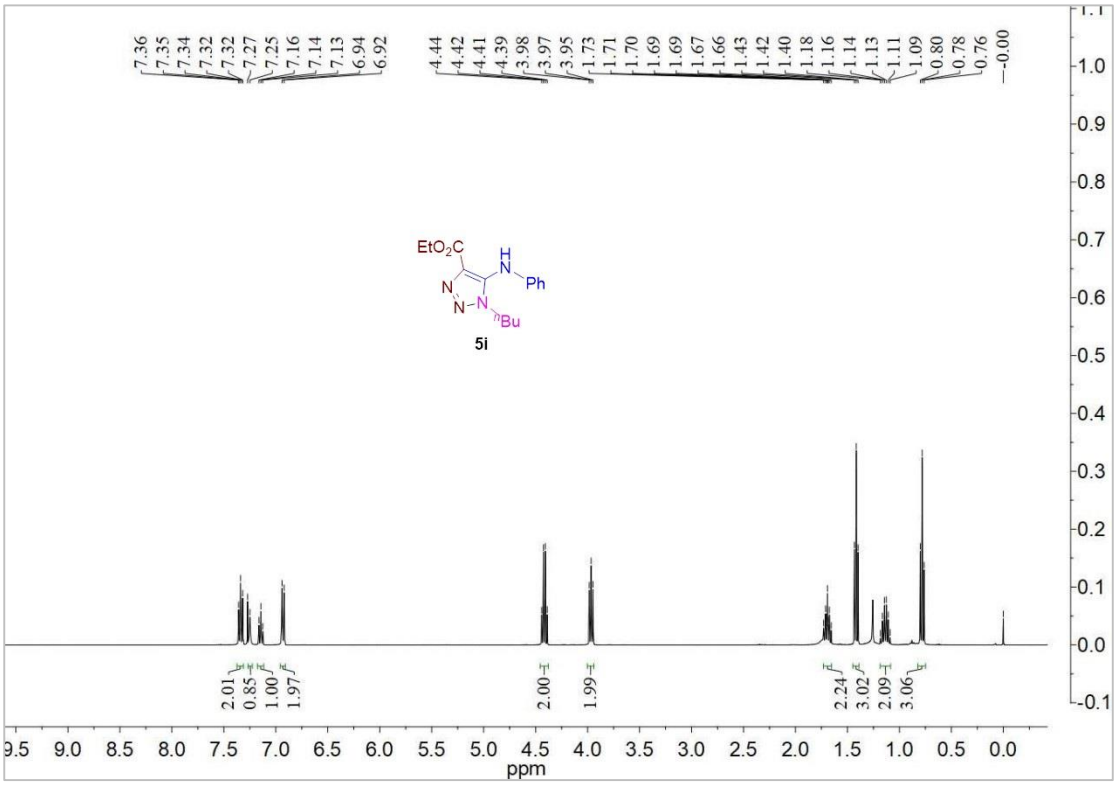

159.22
139.97
139.75
133.74
133.19
131.53
130.67
129.84
129.02
128.59
128.18
127.00
125.88
124.59
61.01
40.15
39.94
39.73
39.52
39.31
39.10
38.89
14.02
EtO2C
Ph
N
Ph
N
N
N
Ph
O
Ph
4h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
-0.002

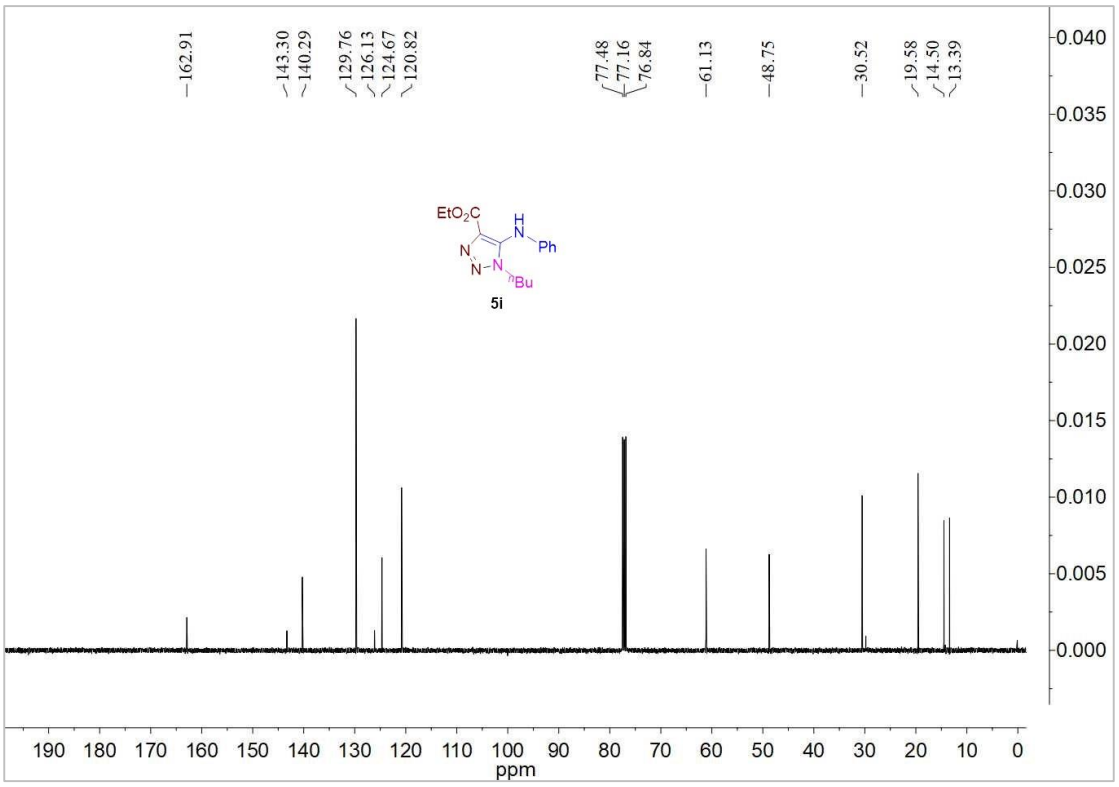

7.67
7.66
7.66
7.65
7.65
7.34
7.33
7.33
7.32
7.27
7.12
7.10
7.10
7.08
6.86
6.86
6.85
6.84
6.83
6.59
6.58
6.57
6.57
4.55
4.40
4.39
4.37
4.36
4.18
4.17
4.15
4.14
1.34
1.33
1.31
1.24
1.23
1.21
0.00
EtO2C
Ph
N
CO2Et
N
N
Ph
4i
1.97
2.98
1.99
1.00
1.98
1.99
2.00
1.99
3.02
2.96
f1 (ppm)

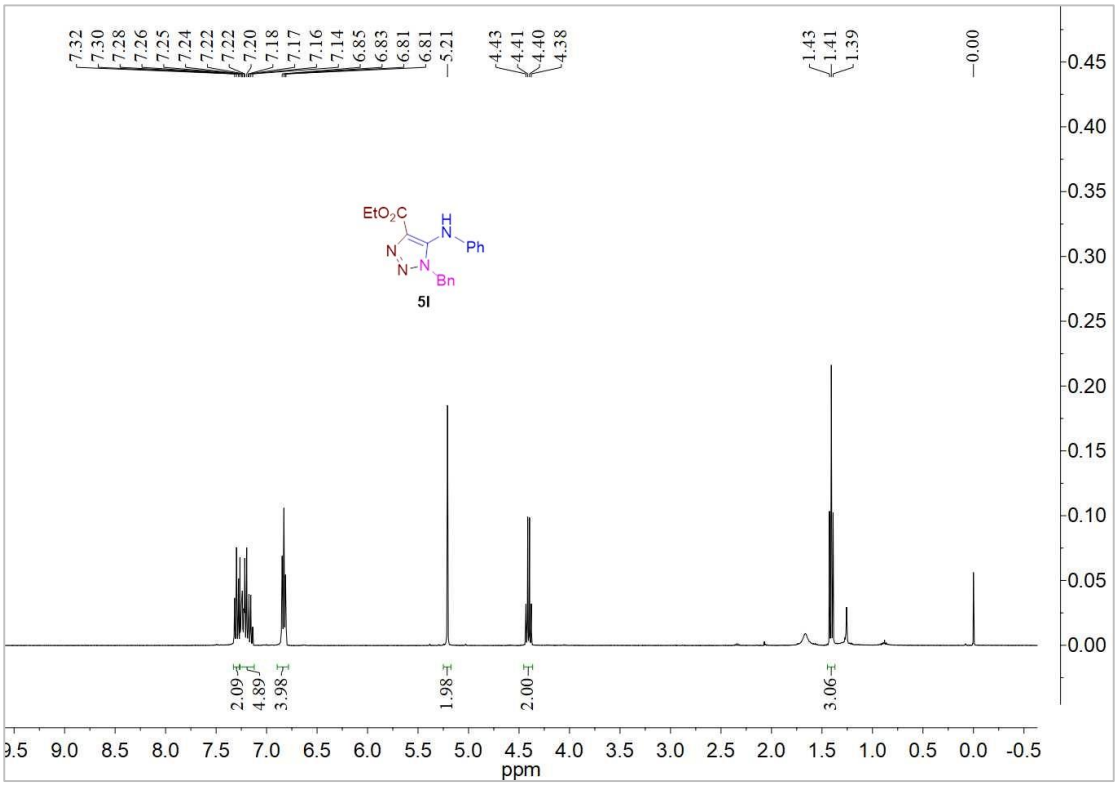

170.02
160.71
145.69
143.75
135.62
131.64
129.55
129.28
129.16
124.60
122.22
116.99
77.41
77.16
76.91
61.57
61.41
54.98
14.30
14.21
EtO2C
Ph
N
CO2Et
N
N
Ph
4i
f1 (ppm)

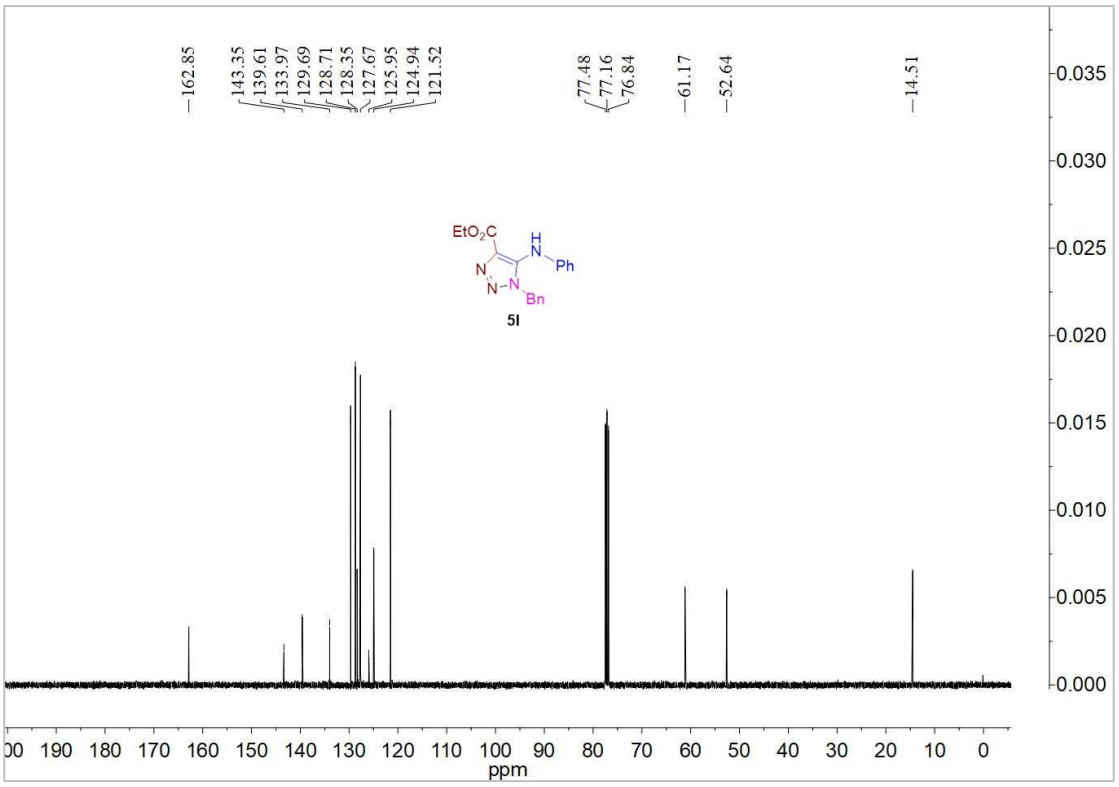

7.60
7.59
7.59
7.59
7.58
7.39
7.38
7.37
7.26
7.17
7.15
7.15
7.14
6.87
6.86
6.86
6.86
6.84
6.69
6.69
6.67
6.67
4.47
4.46
4.36
4.34
4.33
4.31
2.32
2.31
2.31
1.58
1.29
1.27
1.26
0.00
EtO2C
Ph
N
N
N
Ph
4j
1.99
2.97
2.01
1.00
1.99
2.06
2.00
0.90
3.18
f1 (ppm)

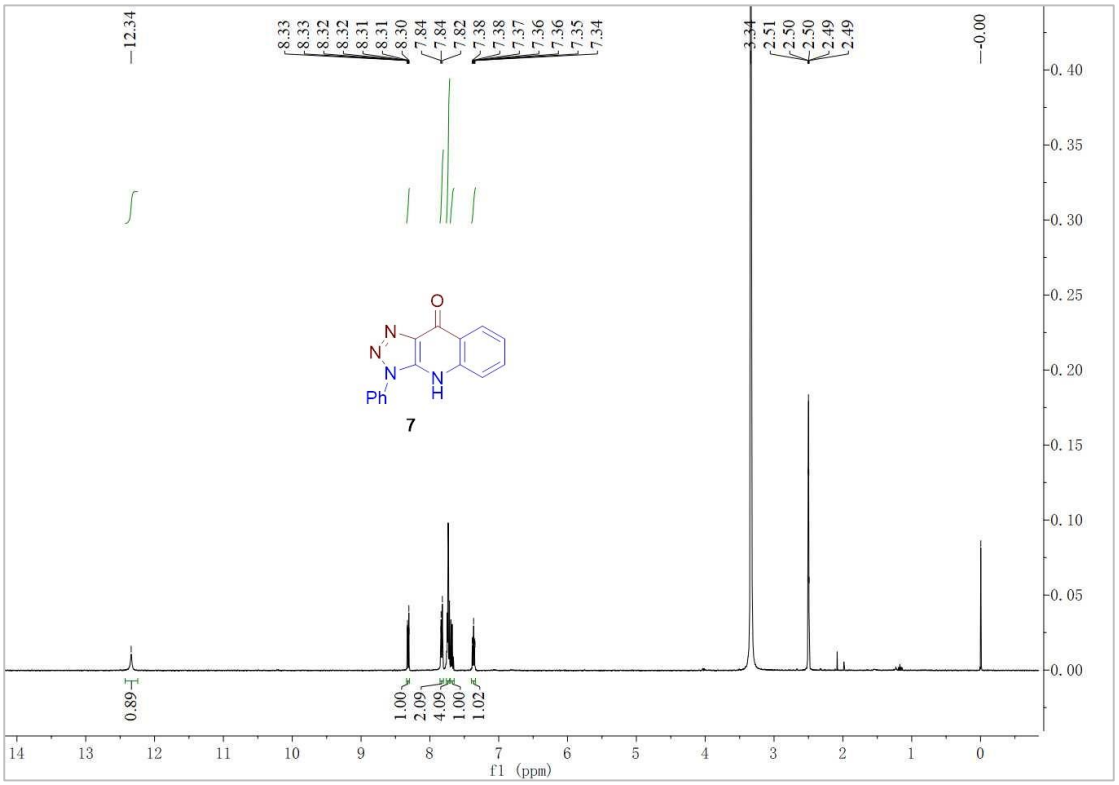

160.43
145.23
142.90
135.21
133.16
129.86
129.41
129.38
124.35
121.47
115.58
78.48
77.42
76.91
74.44
61.41
41.96
14.28
EtO2C
Ph
N
N
N
Ph
4j
f1 (ppm)

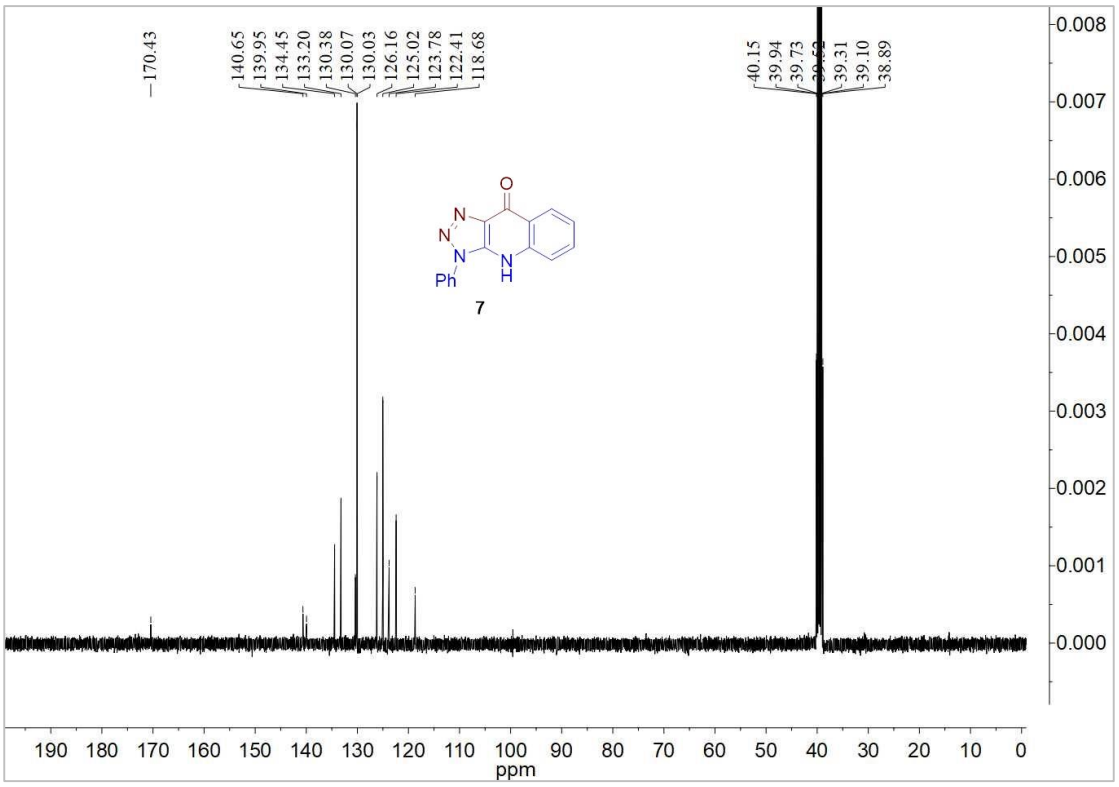

7.36
7.35
7.34
7.32
7.32
7.27
7.25
7.16
7.14
7.13
6.94
6.92
4.44
4.42
4.41
4.39
3.98
3.97
3.95
1.73
1.71
1.70
1.69
1.69
1.67
1.66
1.43
1.42
1.40
1.18
1.16
1.14
1.13
1.11
1.09
0.80
0.78
0.76
0.00
EtO2C
N
N
N
H
Ph
nBu
5i
2.01
0.85
1.00
1.97
2.00
1.99
2.24
3.02
2.09
3.06
ppm


162.91
143.30
140.29
129.76
126.13
124.67
120.82
77.48
77.16
76.84
61.13
48.75
30.52
19.58
14.50
13.39
EtO2C
N
N
N
H
Ph
nBu
5i
ppm


7.32
7.30
7.28
7.26
7.25
7.24
7.22
7.22
7.20
7.18
7.17
7.16
7.14
6.85
6.83
6.81
6.81
5.21
4.43
4.41
4.40
4.38
1.43
1.41
1.39
0.00
EtO2C
H
N
Ph
N
N
N
Bn
5l
2.09
4.89
3.98
1.98
2.00
3.06
ppm


162.85
143.35
139.61
133.97
129.69
128.71
128.35
127.67
125.95
124.94
121.52
77.48
77.16
76.84
61.17
52.64
14.51
EtO2C
H
N
Ph
N
N
N
Bn
5l
ppm


12.34
8.33
8.33
8.32
8.32
8.31
8.31
8.30
7.84
7.84
7.82
7.38
7.38
7.37
7.36
7.36
7.35
7.34
3.34
2.51
2.50
2.50
2.49
2.49
0.00
0.89
1.00
2.09
4.09
1.00
1.02
f1 (ppm)
7


170.43
140.65
139.95
134.45
133.20
130.38
130.07
130.03
126.16
125.02
123.78
122.41
118.68
40.15
39.94
39.73
39.52
39.31
39.10
38.89
ppm
7