Supporting Information

A Facile Synthesis of [1,2,3]Triazolo[1,5-*a*]quinazolines via Copper-Catalyzed Tandem Reaction and Its Denitrogenative Transformation to 2-Acyl-quinazolines

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1. General information

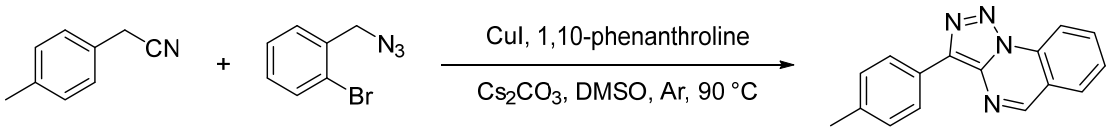
All reactions are basically carried out under air atmosphere. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. Column chromatography was generally performed on silica gel (300−400 mesh), and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) data were recorded on 400 M spectrometers using $CDCl_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz.^{1}H NMR spectra were recorded with $CDCl_3$ (δ = 7.26 ppm) as internal reference, and ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference.

2. Experimental section

2.1. General procedure for the synthesis of azid

To the solution of Sodium azide (390 mg, 6.0 mmol) and 1-bromo-2-(bromomethyl)benzene (1.00g, 4.0 mmol) in DMF (20 mL) and stirred at room temperature overnight. After complete the reaction, the mixture was diluted with EtOAc, then washed with water and extracted with EtOAc. The combined organic layer was washed with brine then dried with anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure to give 1-(azidomethyl)-2-bromobenzene (yield: 815 mg, 96 %) and the product was used without further purification by column chromatography.

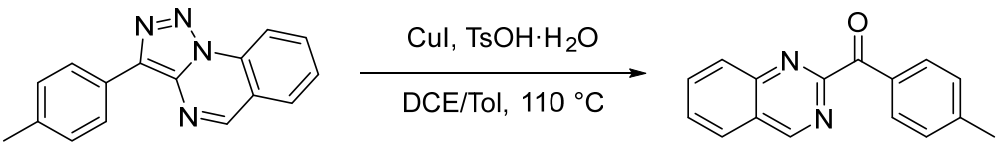
2.2. General procedure for the synthesis of 3-(p-tolyl)-[1,2,3]triazolo[1,5-a]quinazoline(4a)



1a **2a** **4a**

In a typical procedure of 4a, 2-(p-tolyl)acetonitrile (65.5 mg, 0.5 mmol) and CuI (9.5 mg, 0.05 mmol), Cs_2CO_3 (195.5mg, 0.6 mmol), 1,10-phenanthroline (13.5 mg, 0.075 mmol) was added to a pear-shaped Schlenk tube charged with a magnetic stirrer. The tube was evacuated and backfilled with argon, then DMSO (2.5 mL) and 1-(azidomethyl)-2-bromobenzene (0.6 mmol) were added to the tube under a stream of argon. The tube was sealed and the mixture was stirred at 90 ℃ under an argon atmosphere. The reaction was monitored by TLC (thin layer chromatography), after complete the reaction, the mixture was diluted with EtOAc, then washed with water and extracted with EtOAc. The combined organic layer was washed with brine then dried with anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure to give a residue, the residue was purified by flash silica gel column chromatographic purification (petroleum/ethyl acetate = 3:1) to afforded product 4a.

2.3. General procedure for the synthesis of quinazolin-2-yl(p-tolyl)methanone(5a)



4a **5a**

In a typical procedure of 5a, 3-(p-tolyl)-[1,2,3]triazolo[1,5-*a*]quinazoline (130.5 mg, 0.5 mmol) and CuI (14.3 mg, 0.075 mmol), $TsOH·H_2O$ (114.1 mg, 0.6 mmol),was added to a Round-bottom flask charged with a magnetic stirrer. Then DCE/Tol (V/V = 2:1, 3 ml) was added to the flask. The mixture was stirred at 110 ℃. The reaction was monitored by TLC (thin layer chromatography), after complete the reaction, the solvent was removed under reduced pressure to give a residue, the mixture was diluted with EtOAc, then washed with water and extracted with EtOAc. The combined organic layer was washed with brine then dried with anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure to give a residue, the residue was purified by flash silica gel column chromatographic purification (petroleum/ethyl acetate = 5:1) to afforded product 5a.

3. X-Ray crystallographic data

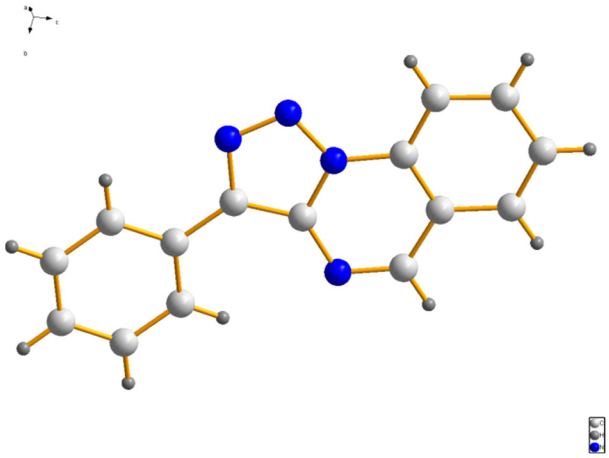


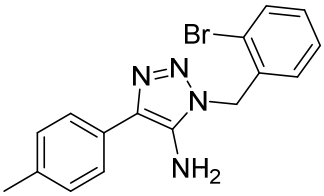
Table 1. X-Ray crystallographic data.

Identification code	**4b**
Empirical formula	$C_{15}H_{10}N_4$
Formula weight	246.27
Temperature	296(2)K
Crystal system	monoclinic
Space group	$P2_1/n$
Cell parameters	*a* =5.732(2) Å *a* = 90° *b* =8.394(3) Å β = 90.848(5)° *c* =23.847(8) Å *g*= 90 °
Volume	1147.26(7) $Å^3$
Z	4
Density (calculated)	1.42572 g/cm^3
Crystal size	0.15 x 0.12 x 0.1 mm^3
Theta range for data collection	1.708 to 32.008°
F000	512
Goodness-of-fit on F^2	1.029
R_1 (I≥2σ(I) / all)	0.0519 / 0.0709
wR_2 (I≥2σ(I) / all)	0.1410 / 0.1602

An X-ray crystallographic measurement was carried out on a Bruker SMART APEX2 area detector diffractometer with Mo-Kα radiation at 296(2)K. Of 11544 reflections measured, 3690 unique (Rint = 0.0525) which were used in all calculations. Using Olex2, the structure of **4b** was solved with the XM (Sheldrick, 2008) solution program using dual methods and by using Olex2 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with XL (Sheldrick, 2008) using full matrix least squares minimisation on $|F|^2$.

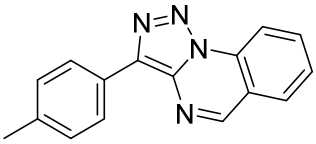
4. NMR spectra data

1-(2-bromobenzyl)-4-(p-tolyl)-1H-1,2,3-triazol-5-amine(3a)



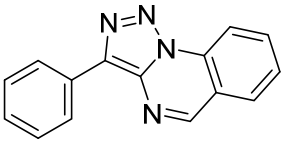
White solid, mp: 127−128 ºC, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.51 (m, 3H), 7.27 – 7.18 (m, 3H), 7.16 (td, *J* = 7.6, 1.6 Hz, 1H), 6.90 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.46 (s, 2H), 3.98 (s, 2H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.3, 136.7, 133.7, 132.8, 130.8, 129.8, 129.5, 128.6, 128.5, 128.2, 125.4, 122.2, 49.9, 21.2.

3-(p-tolyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4a)



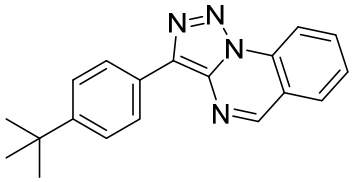
Yellow green solid, mp: 191-193 ºC, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.92 (s, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.96 – 7.91 (m, 1H), 7.74 – 7.63 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.2, 138.1, 138.0, 136.8, 134.6, 133.3, 129.4, 128.5, 127.8, 127.6, 126.3, 118.8, 115.4, 21.4. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{16}H_{12}N_4$: 261.1135; Found: 261.1134.

3-phenyl-[1,2,3]triazolo[1,5-*a*]quinazoline(4b)



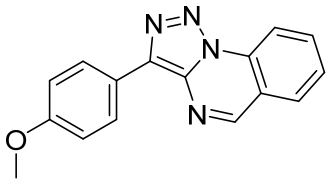
Yellow green solid, mp: 178-180 ºC, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.99 (s, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 2H), 8.06 – 7.96 (m, 2H), 7.76 – 7.67 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.37 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.5, 134.8, 133.4, 130.5, 128.7, 128.6, 128.2, 127.9, 126.5, 118.9, 115.6. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{15}H_{10}N_4$: 247.0978; Found: 247.0977.

3-(4-(tert-butyl)phenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4c)



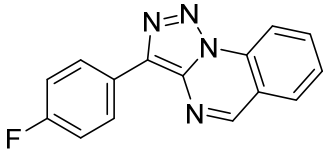
Yellow green solid, mp: 168-170 °C, **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.96 (s, 1H), 8.67 (d, J = 8.4 Hz, 1H), 8.42 – 8.34 (m, 2H), 8.01 (d, J = 8.0 Hz, 1H), 8.01 – 7.93 (m, 1H), 7.75 – 7.66 (m, 1H), 7.58 – 7.54 (m, 2H), 1.39 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 153.3, 151.3, 138.2, 136.9, 134.7, 133.4, 128.5, 127.8, 127.6, 126.3, 125.7, 118.9, 115.5, 34.7, 31.3. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{19}H_{18}N_4$: 303.1604 ; Found: 303.1604.

3-(4-methoxyphenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4d)



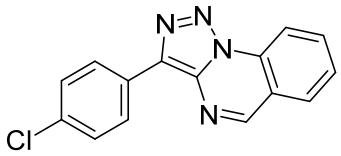
Yellow solid, mp: 190-191 °C, **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.96 (s, 1H), 8.69 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.99 (t, J = 8.0 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 159.7, 153.0, 138.2, 136.6, 134.7, 133.5, 128.5, 127.9, 127.8, 123.3, 118.9, 115.6, 114.2, 55.3. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{16}H_{12}N_4O$: 277.1084; Found: 277.1082.

3-(4-fluorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4e)



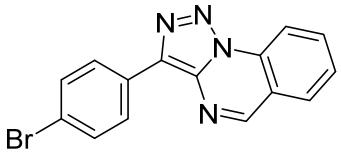
Green solid, mp: 227-229 °C, **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.96 (s, 1H), 8.65 (d, J = 8.4 Hz, 1H), 8.46 – 8.38 (m, 2H), 8.02 (d, J = 8.0 Hz, 1H), 8.01 – 7.96 (m, 1H), 7.75 – 7.69 (m, 1H), 7.21 – 7.15 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 162.7 (d, J = 247.7 Hz), 153.6, 137.2, 136.8, 134.9, 133.3, 128.6, 128.1, 128.1 (d, J = 25.6 Hz), 126.6 (d, J = 3.3 Hz), 118.8, 115.8, 115.5 (d, J = 6.1 Hz). **^{19}F NMR (375 MHz, CDCl$_3$)** δ -113.2. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{15}H_9FN_4$: 265.0884; Found: 265.0882.

3-(4-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4f)



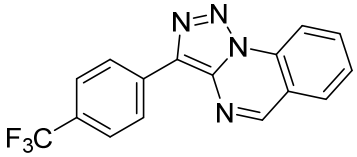
Yellow green solid, mp: 206-208 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.99 (s, 1H), 8.69 (d, J = 8.4 Hz, 1H), 8.43 – 8.39 (m, 2H), 8.05 (d, J = 7.6 Hz, 1H), 8.04 – 7.99 (m, 1H), 7.77 – 7.72 (m, 1H), 7.49 – 7.45 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.8, 135.0, 134.0, 133.4, 129.0, 128.9, 128.6, 128.0, 127.6, 118.9, 118.2, 115.6. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{15}H_9ClN_4$: 281.0589; Found: 281.0586.

3-(4-bromophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4g)



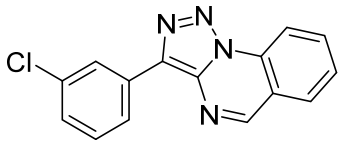
Yellow green solid, mp: 226-228 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.01 (s, 1H), 8.70 (d, J = 8.4 Hz, 1H), 8.40 – 8.33 (m, 2H), 8.07 (d, J = 7.6 Hz, 1H), 8.05 – 8.00 (m, 1H), 7.78 – 7.73 (m, 1H), 7.66 – 7.61 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.8, 135.0, 133.4, 131.9, 129.5, 128.6, 128.1, 127.9, 122.3, 118.9, 115.6. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{15}H_9BrN_4$: 325.0083; Found: 325.0080.

3-(4-(trifluoromethyl)phenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4h)



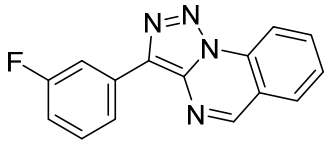
Green solid, mp: 236-237 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.04 (s, 1H), 8.71 (d, J = 8.4 Hz, 1H), 8.61 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 8.0 Hz, 1H), 8.08 – 7.99 (m, 1H), 7.77 (t, J = 8.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.3, 137.6, 136.6, 135.2, 134.0, 133.4, 129.8 (d, J = 32.2 Hz), 128.7, 128.2, 126.5, 125.6 (d, J = 4.1 Hz), 124.4 (d, J = 291.6 Hz), 118.9, 115.7. **^{19}F NMR (375 MHz, $CDCl_3$)** δ -62.5. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{16}H_9F_3N_4$: 315.0852; Found: 315.0849.

3-(3-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4i)



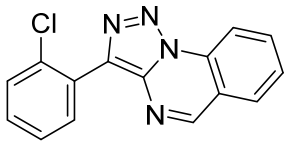
Yellow green solid, mp: 198-200 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.02 (s, 1H), 8.70 (d, J = 8.4 Hz, 1H), 8.50 (s, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.02 (t, J = 8.0 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.37 – 7.32 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.0, 135.0, 134.7, 133.4, 132.3, 130.0, 128.7, 128.1, 128.1, 126.4, 124.4, 118.9, 115.6. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{15}H_9ClN_4$: 281.0589; Found: 281.0586.

3-(3-fluorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4j)



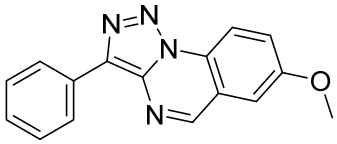
Green solid, mp: 211-212 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.02 (s, 1H), 8.70 (d, J = 8.4 Hz, 1H), 8.27 (dt, J = 8.0, 1.2 Hz, 1H), 8.26 – 8.17 (m, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.04 – 7.99 (m, 1H), 7.79 – 7.71 (m, 1H), 7.53 – 7.42 (m, 1H), 7.07 (tdd, J = 8.4, 2.8, 0.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.1 (d, J = 244.6 Hz), 154.0, 135.0, 133.4, 132.6 (d, J = 8.8 Hz), 130.3 (d, J = 8.4 Hz), 128.7, 128.1, 122.0 (d, J = 2.9 Hz), 118.9, 115.6, 115.0 (d, J = 21.3 Hz), 113.3 (d, J = 23.5 Hz). **^{19}F NMR (375 MHz, $CDCl_3$)** δ -112.7. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{15}H_9FN_4$: 265.0884; Found: 265.0882.

3-(2-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4k)



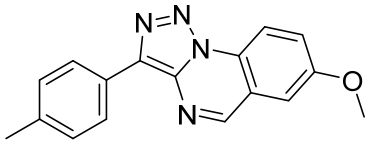
Yellow green solid, mp: 204-206 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.01 (s, 1H), 8.72 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.03 – 7.99 (m, 1H), 7.78 – 7.71 (m, 2H), 7.60 – 7.54 (m, 1H), 7.44 – 7.36 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.1, 138.0, 137.5, 134.9, 133.8, 133.4, 132.2, 130.3, 130.0, 129.0, 128.6, 128.0, 126.8, 118.9, 115.6. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{15}H_9ClN_4$: 281.0589; Found: 281.0586.

7-methoxy-3-phenyl-[1,2,3]triazolo[1,5-*a*]quinazoline(4l)



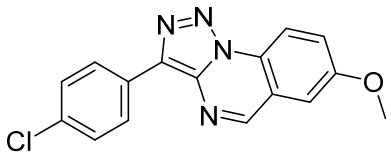
Yellow solid, mp: 197-198 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.93 (s, 1H), 8.61 (d, J = 9.2 Hz, 1H), 8.46 (d, J = 7.2 Hz, 2H), 7.57 (dd, J = 9.2, 2.8 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.43 – 7.34 (m, 2H), 3.98 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.9, 152.9, 138.0, 136.7, 130.7, 128.7, 128.1, 126.5, 124.5, 120.1, 117.2, 108.7, 56.0. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{16}H_{12}N_4O$: 277.1084; Found: 277.1082.

7-methoxy-3-(p-tolyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4m)



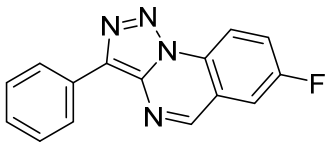
Yellow solid, mp: 209-211 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.88 (s, 1H), 8.57 (d, J = 9.2 Hz, 1H), 8.33 (d, J = 8.0 Hz, 2H), 7.54 (dd, J = 9.2, 2.8 Hz, 1H), 7.33 (d, J = 2.4 Hz, 2H), 7.31 (s, 1H), 3.96 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.8, 152.5, 138.1, 138.0, 136.4, 129.4, 128.1, 127.8, 126.3, 124.3, 120.1, 117.1, 108.6, 55.9, 21.4. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{17}H_{14}N_4O$: 291.1240; Found: 291.1239.

3-(4-chlorophenyl)-7-methoxy-[1,2,3]triazolo[1,5-*a*]quinazoline(4n)



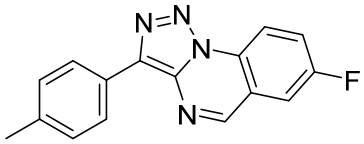
Yellow solid, mp: 214-216 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.93 (s, 1H), 8.61 (d, J = 9.2 Hz, 1H), 8.41 (d, J = 8.8 Hz, 2H), 7.59 (dd, J = 9.2, 2.8 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 2.8 Hz, 1H), 3.99 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.0, 153.1, 136.9, 136.7, 133.9, 129.2, 128.9, 128.1, 127.6, 124.6, 120.1, 117.2, 108.7, 56.0. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{16}H_{11}ClN_4$: 311.0694; Found: 311.0689.

7-fluoro-3-phenyl-[1,2,3]triazolo[1,5-*a*]quinazoline(4o)



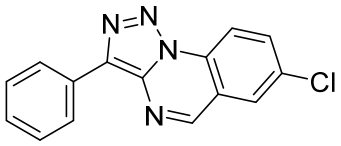
Yellow green solid, mp: 234-235 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.94 (s, 1H), 8.72 (dd, J = 9.2, 4.4 Hz, 1H), 8.44 (d, J = 7.2 Hz, 2H), 7.76 – 7.69 (m, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.45 – 7.36 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.0 (d, J = 250.9 Hz), 152.4 (d, J = 3.2 Hz), 130.3, 128.8, 128.4, 126.5, 123.4 (d, J = 24.9 Hz), 120.0 (d, J = 8.1 Hz), 118.1 (d, J = 8.4 Hz), 113.6, 113.4. **^{19}F NMR (375 MHz, $CDCl_3$)** δ -110.2. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{15}H_9FN_4$: 265.0884; Found: 265.0882.

7-fluoro-3-(p-tolyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4p)



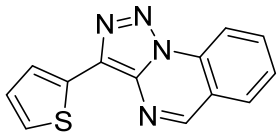
Yellow green solid, mp: 247-248 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.91 (s, 1H), 8.70 (dd, J = 9.2, 4.5 Hz, 1H), 8.32 (d, J = 8.0 Hz, 2H), 7.77 – 7.65 (m, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.0 (d, J = 250.8 Hz), 152.1 (d, J = 3.1 Hz), 138.3, 129.5, 127.4, 126.4, 123.3 (d, J = 24.9 Hz), 120.0 (d, J = 8.2 Hz), 118.1 (d, J = 8.1 Hz), 113.5, 113.3, 21.4. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{16}H_{11}FN_4$: 279.1041; Found: 279.1038.

7-chloro-3-phenyl-[1,2,3]triazolo[1,5-*a*]quinazoline(4q)



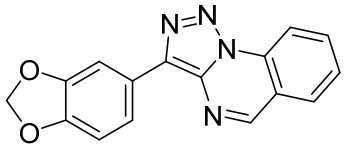
Yellow green solid, mp: 232-233 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.94 (s, 1H), 8.67 (d, J = 8.8 Hz, 1H), 8.45 (d, J = 8.0 Hz, 2H), 8.04 (s, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 7.42 (d, J = 7.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.2, 137.0, 135.2, 133.9, 131.9, 130.2, 128.8, 128.5, 127.8, 126.6, 119.8, 117.4. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{15}H_9ClN_4$: 281.0589; Found: 281.0586.

3-(thiophen-2-yl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4r)



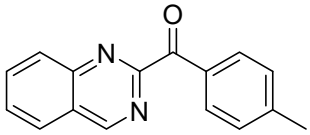
Yellow green solid, mp: 197-198 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.99 (s, 1H), 8.68 (d, J = 8.0 Hz, 1H), 8.05 (d, J 8.0 Hz, 1H), 8.05 – 7.96 (m, 2H), 7.78 – 7.70 (m, 1H), 7.42 (dd, J = 5.2, 1.2 Hz, 1H), 7.20 (dd, J = 5.2, 3.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.6, 135.0, 134.9, 133.3, 132.0, 128.7, 128.1, 127.7, 125.8, 125.4, 119.1, 115.6. **HRMS** (ESI-TOF) (m/z): $[M+H]^+$Calcd for $C_{13}H_8N_4S$: 253.0542; Found: 253.0541.

3-(benzo[d][1,3]dioxol-5-yl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4s)



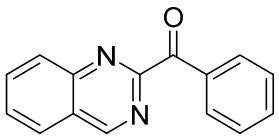
Yellow solid, mp: 201-203 °C, **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.98 (s, 1H), 8.70 (d, J = 8.4Hz, 1H), 8.11 – 7.93 (m, 4H), 7.74 (s, 1H), 6.98 (d, J = 6.6 Hz, 1H), 6.03 (s, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.2, 148.0, 147.7, 138.0, 136.6, 134.8, 133.5, 128.6, 127.9, 124.6, 120.6, 119.0, 115.6, 108.7, 107.1, 101.1. **HRMS** (ESI-TOF) (m/z): [M+H]+Calcd for $C_{16}H_{10}N_4O_2$: 291.0877; Found: 291.0874.

quinazolin-2-yl(p-tolyl)methanone(5a)



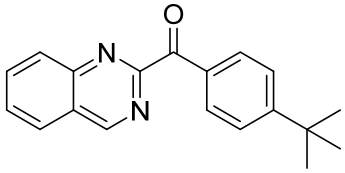
White solid, mp: 107−108 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.58 (s, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.08-7.97 (m, 4H), 7.79 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.4, 160.8, 159.0, 149.6, 144.5, 134.8, 132.9, 131.2, 129.3, 129.3, 129.1, 127.2, 124.7, 21.8.

phenyl(quinazolin-2-yl)methanone(5b)



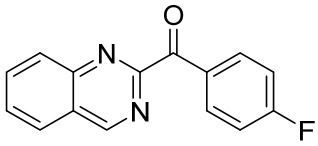
White solid, mp: 106-107 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.57 (s, 1H), 8.17 (dd, J = 8.4, 1.0 Hz, 1H), 8.14 – 8.07 (m, 2H), 8.05 – 8.02 (m, 1H), 7.77 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.52 – 7.44 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.69, 160.80, 158.56, 149.45, 135.37, 134.90, 133.47, 130.97, 129.43, 129.17, 128.25, 127.19, 124.63.

(4-(tert-butyl)phenyl)(quinazolin-2-yl)methanone(5c)



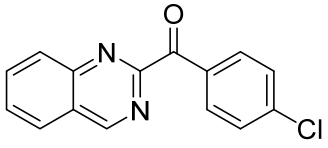
White solid, mp: 102-104 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.58 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.09 – 8.03 (m, 3H), 8.03 – 7.99 (m, 1H), 7.83 – 7.75 (m, 1H), 7.56 – 7.48 (m, 2H), 1.36 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.3, 160.8, 159.0, 157.4, 149.6, 134.9, 132.8, 131.0, 129.3, 129.3, 127.2, 125.4, 124.7, 35.2, 31.0.

(4-fluorophenyl)(quinazolin-2-yl)methanone(5e)



White solid, mp: 134-135 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.58 (s, 1H), 8.25 – 8.15 (m, 3H), 8.08 – 7.98 (m, 2H), 7.80 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 8.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.0, 166.0 (d, J = 255.9 Hz), 160.9, 158.4, 149.5, 135.0, 133.8 (d, J = 9.4 Hz), 131.8 (d, J = 2.9 Hz), 129.6, 129.2, 127.2, 124.7, 115.5 (d, J = 22.0 Hz).

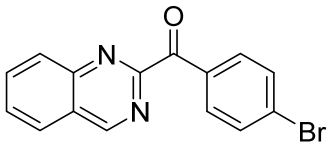
(4-chlorophenyl)(quinazolin-2-yl)methanone(5f)



White solid, mp: 157-158 °C, **^{1}H NMR (700 MHz, $CDCl_3$)** δ 9.59 (s, 1H), 8.19 (dd, J = 8.4, 1.0 Hz, 1H), 8.13 – 8.10 (m, 2H), 8.05 (d, J = 8.4 Hz, 1H), 8.04 - 8.02 (m, 1H), 7.82 – 7.79 (m, 1H), 7.49 – 7.46 (m,

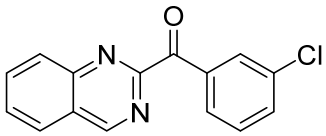
2H). **^{13}C NMR (175 MHz, $CDCl_3$)** δ 190.3, 161.0, 158.1, 149.5, 140.0, 135.0, 133.9, 132.5, 129.7, 129.3, 128.6, 127.3, 124.7.

(4-bromophenyl)(quinazolin-2-yl)methanone(5g)



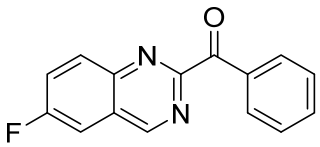
White solid, mp: 147-148 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.59 (s, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.10 – 8.00 (m, 4H), 7.82 (t, J = 7.6 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.6, 161.0, 158.1, 149.6, 135.1, 134.3, 132.6, 131.7, 129.7, 129.4, 128.9, 127.3, 124.8.

(3-chlorophenyl)(quinazolin-2-yl)methanone(5i)



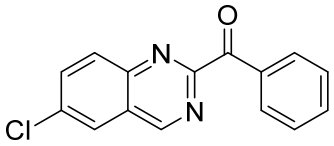
White solid, mp: 145-146 °C, **^{1}H NMR (700 MHz, $CDCl_3$)** δ 9.60 (s, 1H), 8.22 (dd, J = 8.4, 0.7 Hz, 1H), 8.15 (t, J = 2.1 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 8.06 – 8.03 (m, 2H), 7.84 – 7.81 (m, 1H), 7.61 – 7.59 (m, 1H), 7.46 (t, J = 7.7 Hz, 1H). **^{13}C NMR (175 MHz, CDCl3)** δ 190.3, 161.0, 157.9, 149.6, 137.1, 135.1, 134.5, 133.4, 131.0, 129.8, 129.6, 129.4, 129.2, 127.3, 124.8.

(6-fluoroquinazolin-2-yl)(phenyl)methanone(5o)



White solid, mp: 109-110 °C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.55 (s, 1H), 8.21 (dd, J = 9.2, 5.2 Hz, 1H), 8.10 (d, J = 7.2 Hz, 2H), 7.77 (td, J = 8.8, 2.8 Hz, 1H), 7.65 (dd, J = 7.6, 2.8 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.4, 161.6 (d, J = 254.7 Hz), 160.1 (d, J = 5.8 Hz), 158.2 (d, J = 3.0 Hz), 146.7, 135.4, 133.5, 132.2 (d, J = 9.0 Hz), 131.0, 128.3, 125.4 (d, J = 26.3 Hz), 125.4, 110.4 (d, J = 22.1 Hz).

(6-chloroquinazolin-2-yl)(phenyl)methanone(5q)



White solid, mp: 131-132 °C, **^{1}H NMR (700 MHz, $CDCl_3$)** δ 9.52 (s, 1H), 8.15 (d, J = 9.1 Hz, 1H), 8.11 (dd, J = 8.4, 1.3 Hz, 2H), 8.03 (d, J = 2.1 Hz, 1H), 7.94 (dd, J = 9.1, 2.1 Hz, 1H), 7.63 (tt, J = 7.7, 1.4 Hz, 1H), 7.51 – 7.49 (m, 2H). **^{13}C NMR (175 MHz, $CDCl_3$)** δ 191.3, 159.9, 159.9, 158.8, 148.0, 136.0, 135.4, 135.3, 133.6, 131.0, 128.3, 125.9, 125.1.

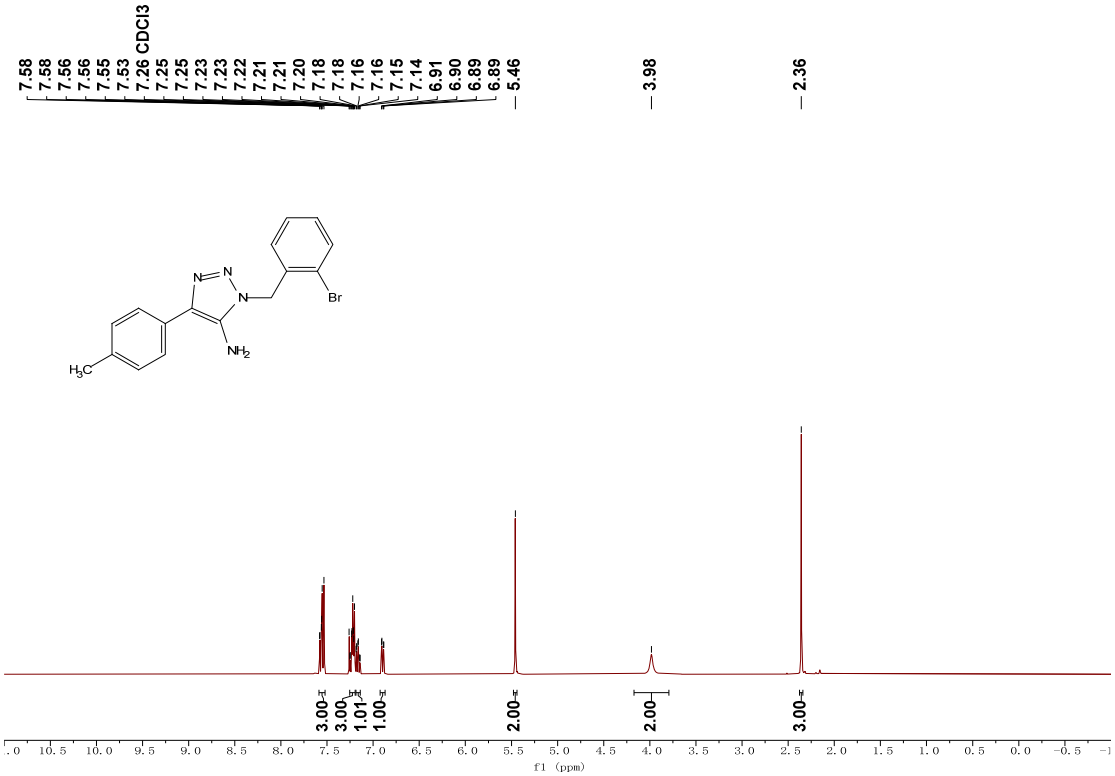
For additional compound data on 2-acyl-quinazolines, reference be made to the following literature:

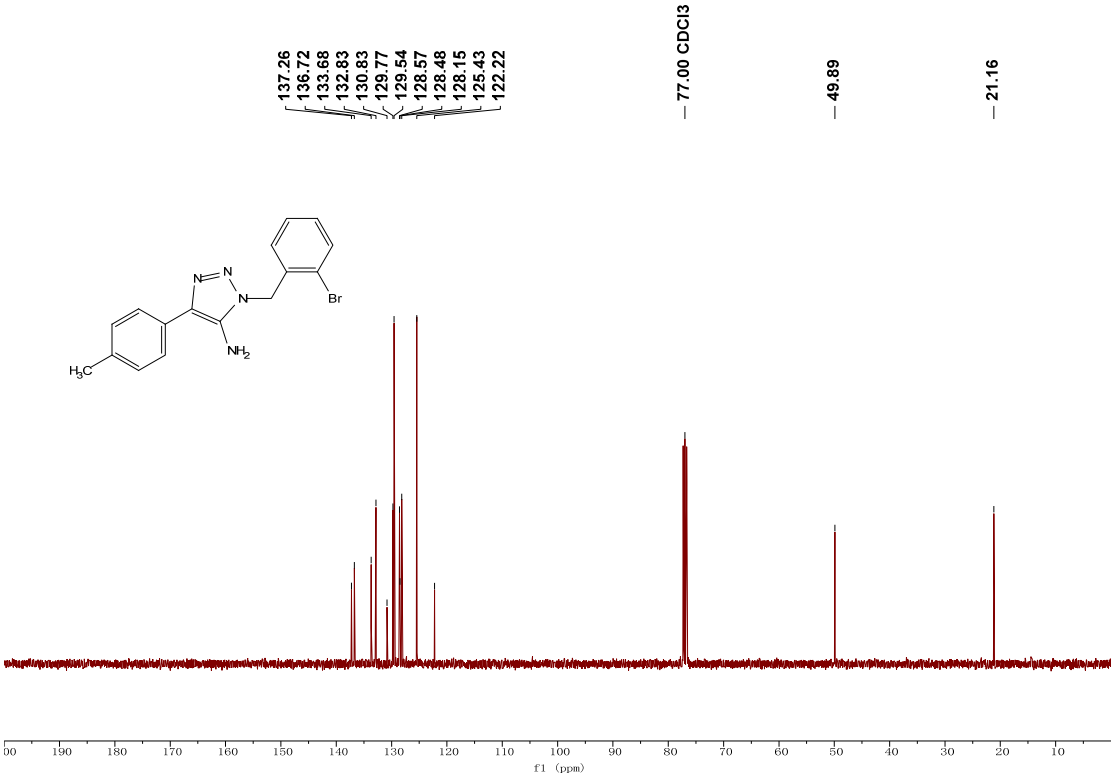
1. Y. Sun, H. Sun, Y. Wang and F. Xie, *Org. Lett*., 2020, 22, 6756-6759.

2. S. Liu, A.-J. Wang, M. Li, J. Zhang, G.-D. Yin, W.-M. Shu and W.-C. Yu, *J. Org. Chem*., 2022, 87, 11253-11260.

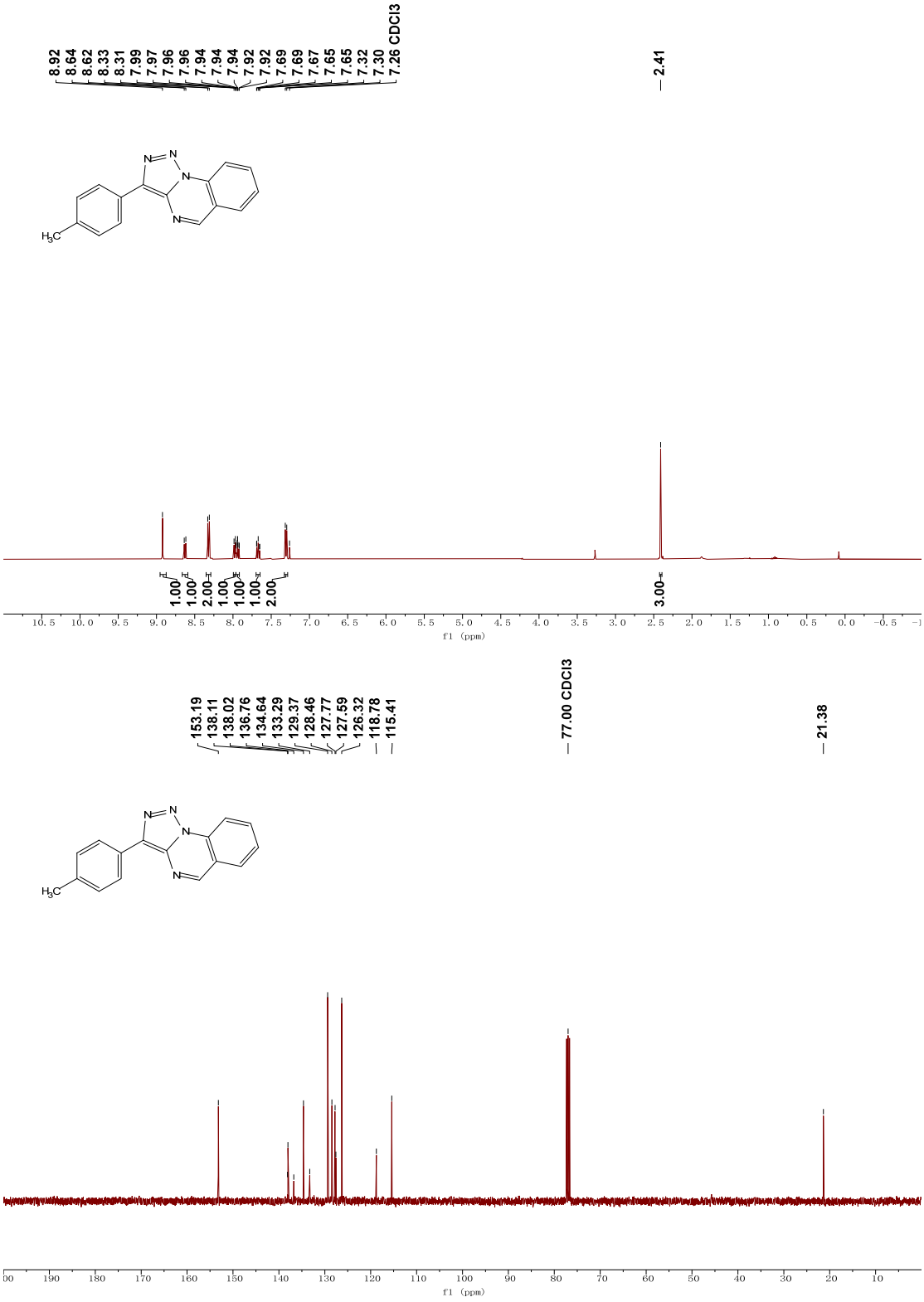
5. NMR spectra

1-(2-bromobenzyl)-4-(p-tolyl)-1H-1,2,3-triazol-5-amine(3a)

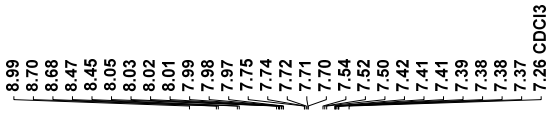


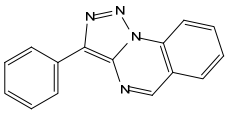


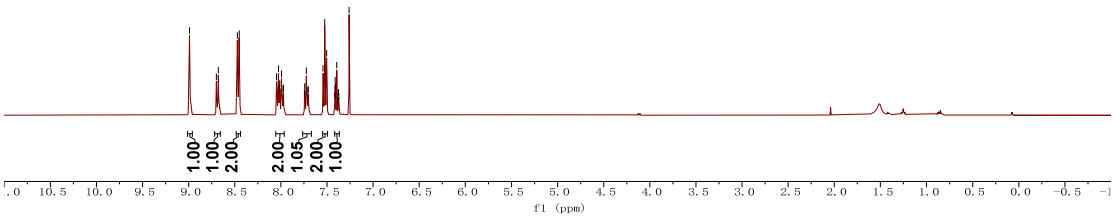
3-(p-tolyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4a)

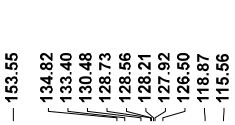


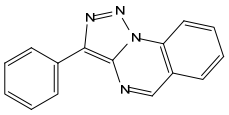
3-phenyl-[1,2,3]triazolo[1,5-*a*]quinazoline(4b)

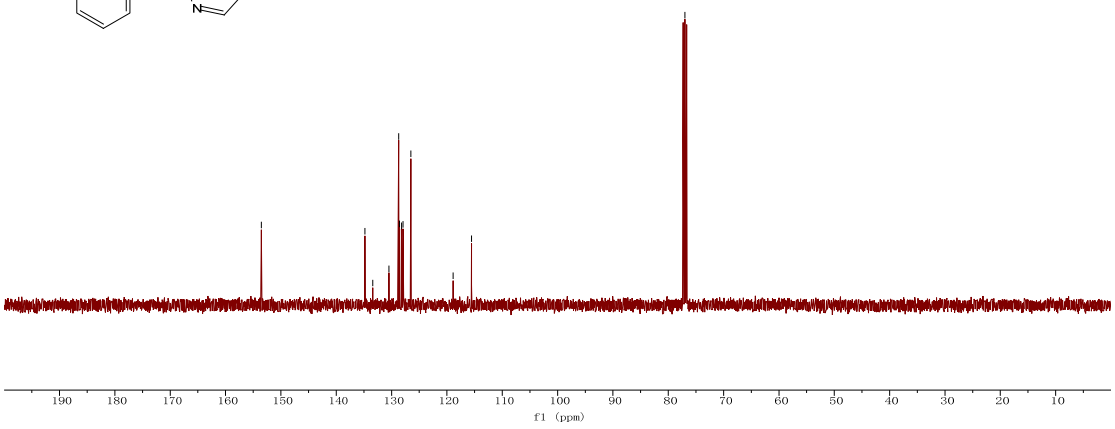




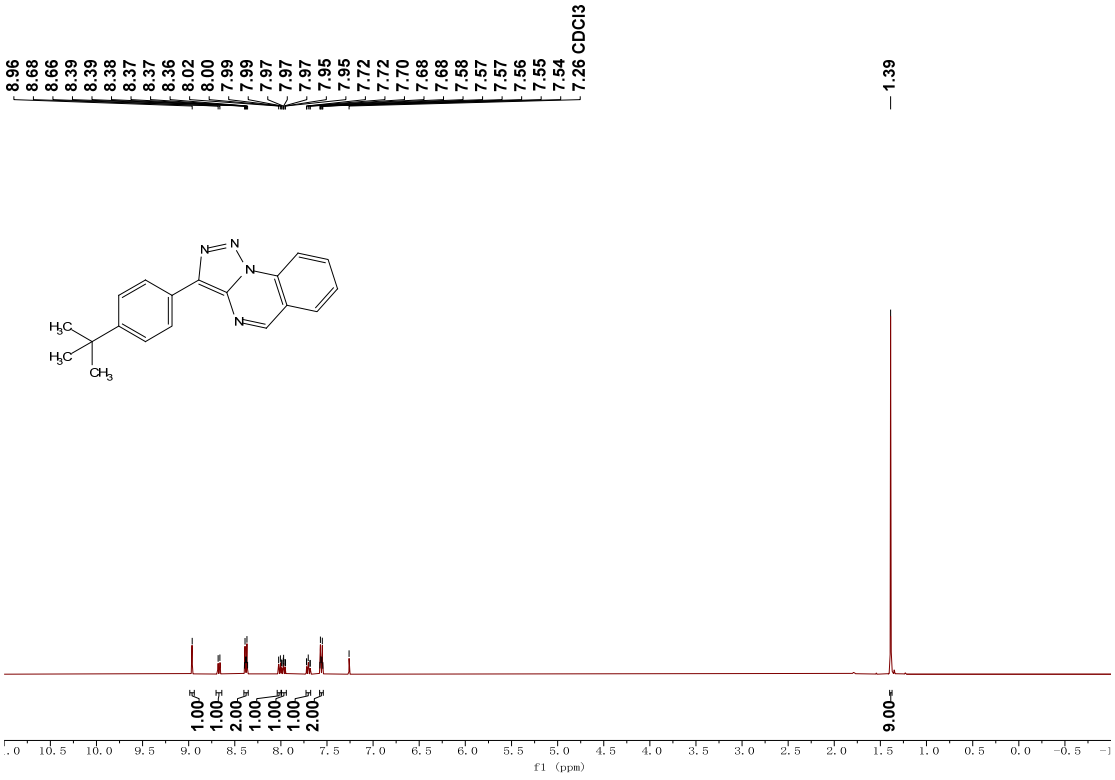


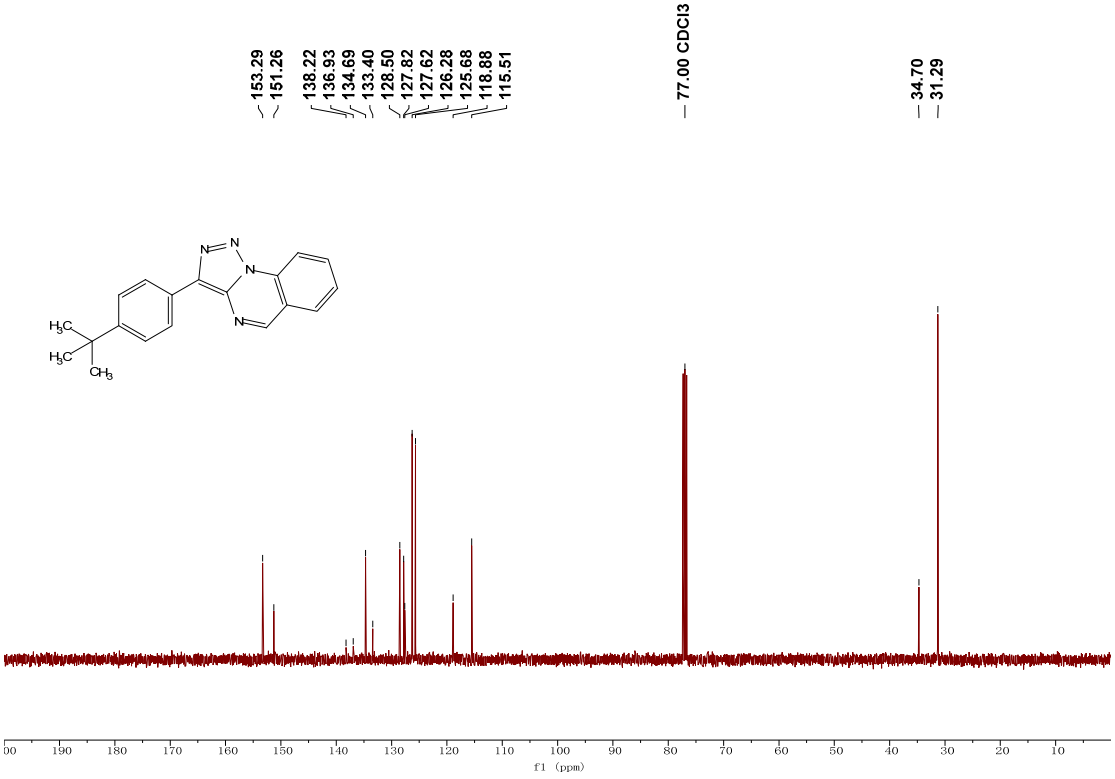




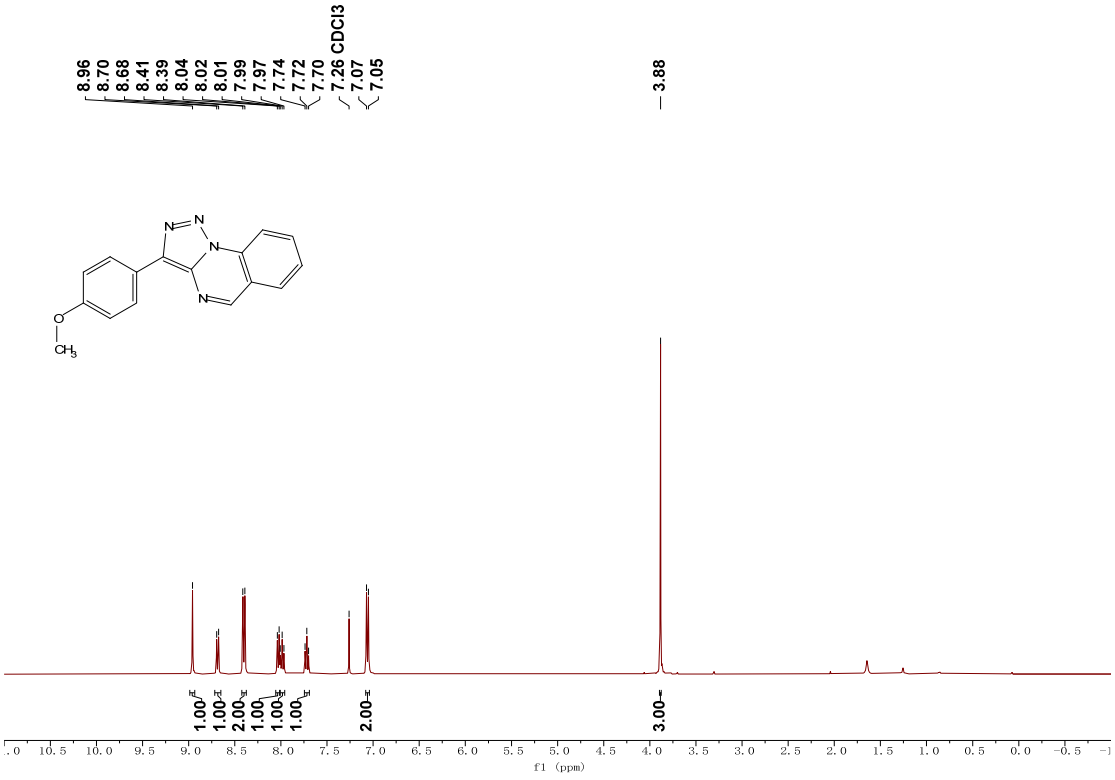


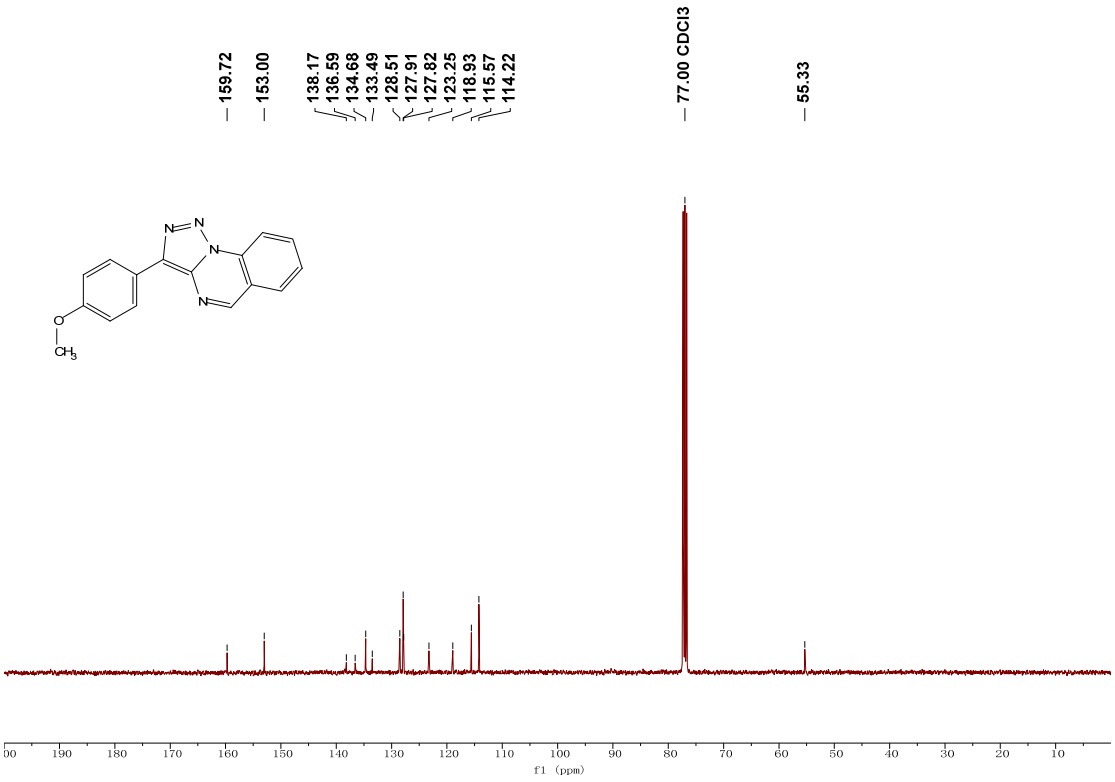
3-(4-(tert-butyl)phenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4c)



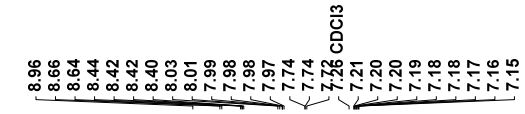


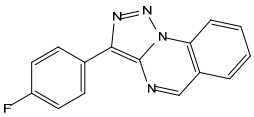
3-(4-methoxyphenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4d)

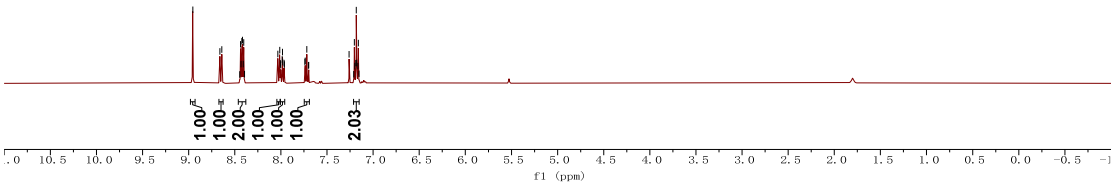


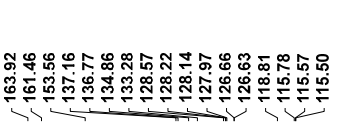


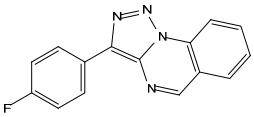
3-(4-fluorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4e)

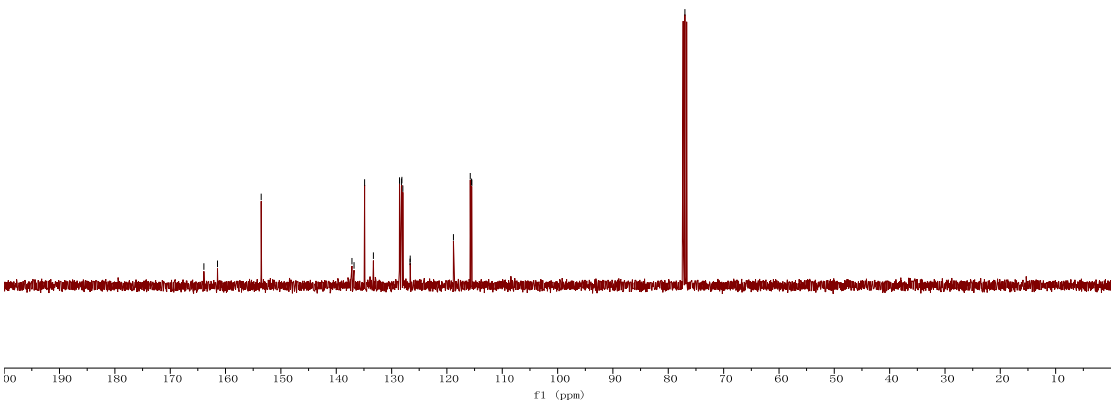


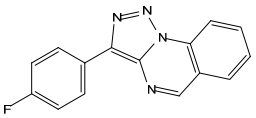








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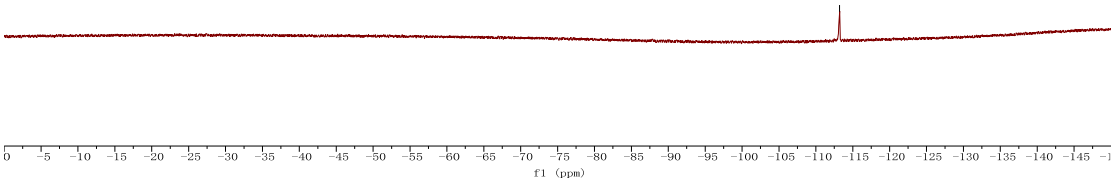
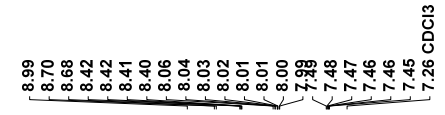
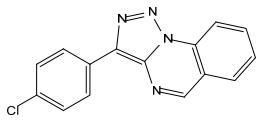
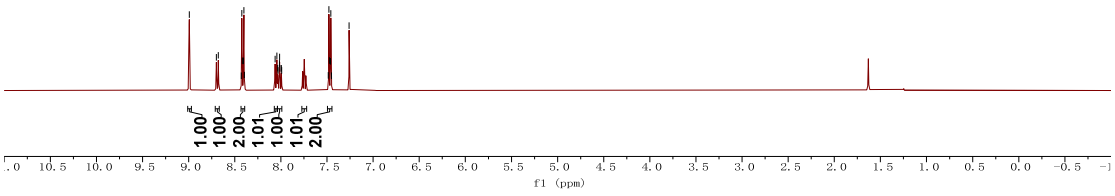
N
F

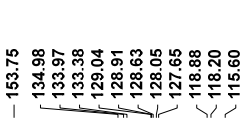

-113.22
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

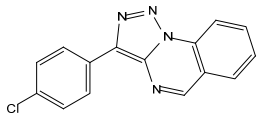
3-(4-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4f)

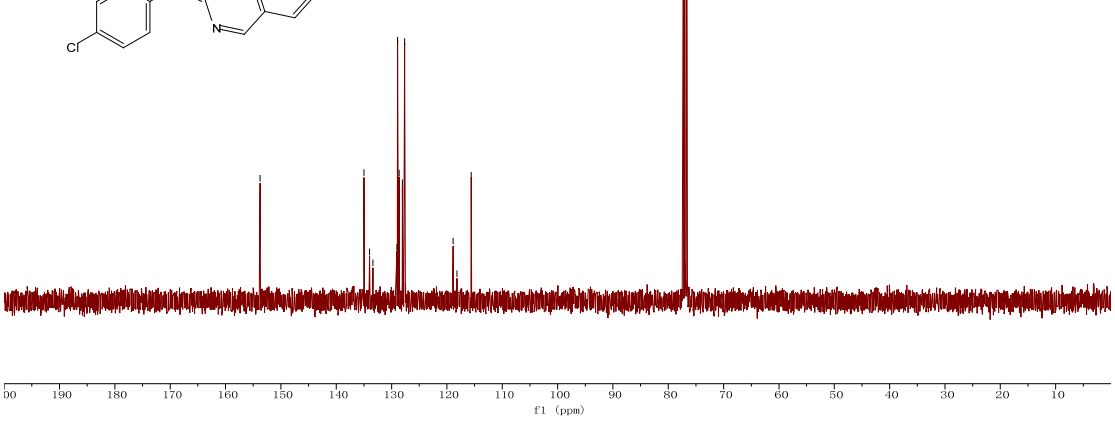




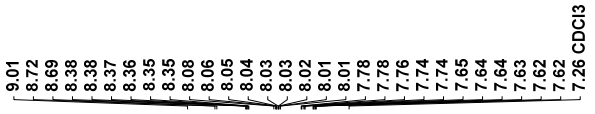


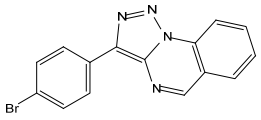


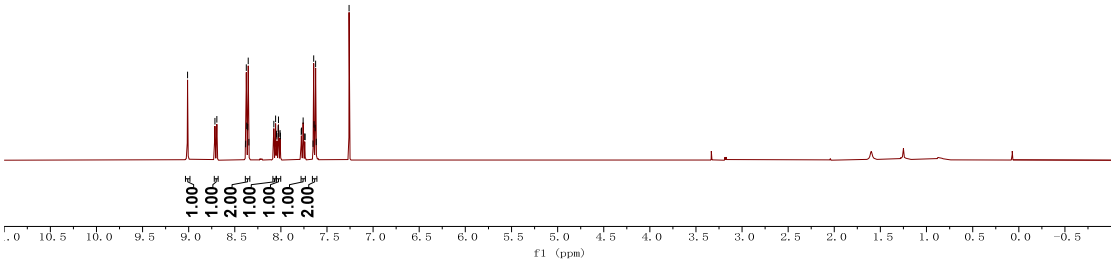


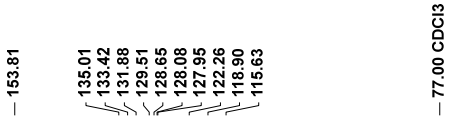


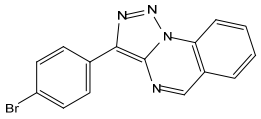
3-(4-bromophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4g)

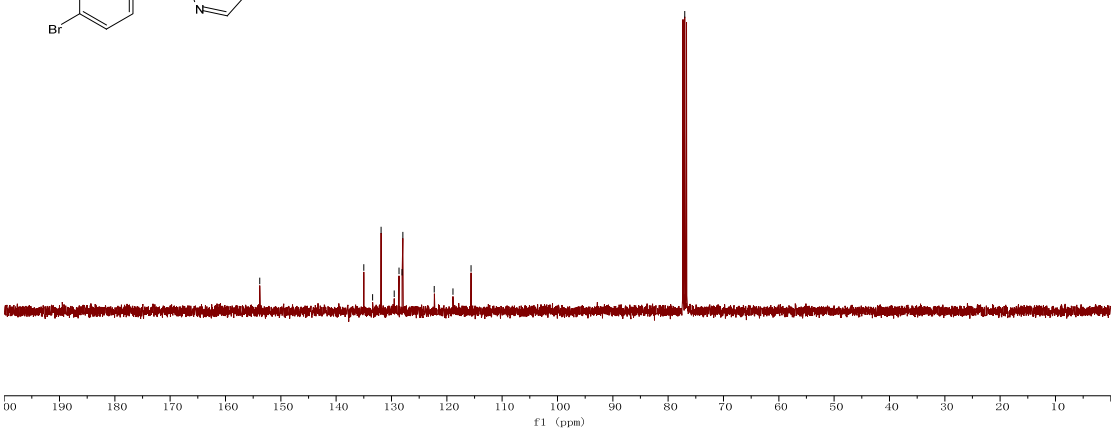




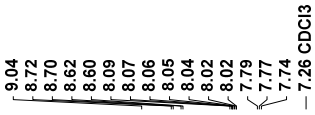


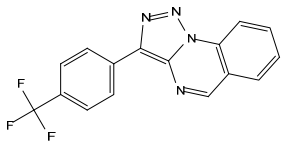


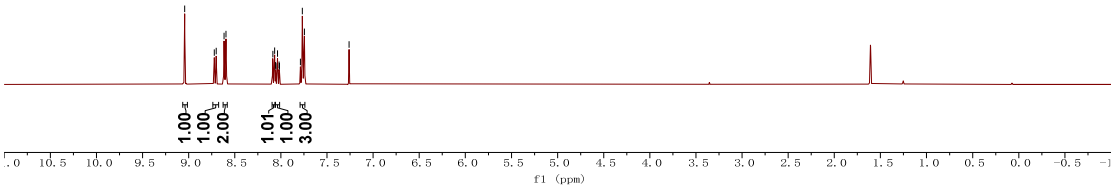


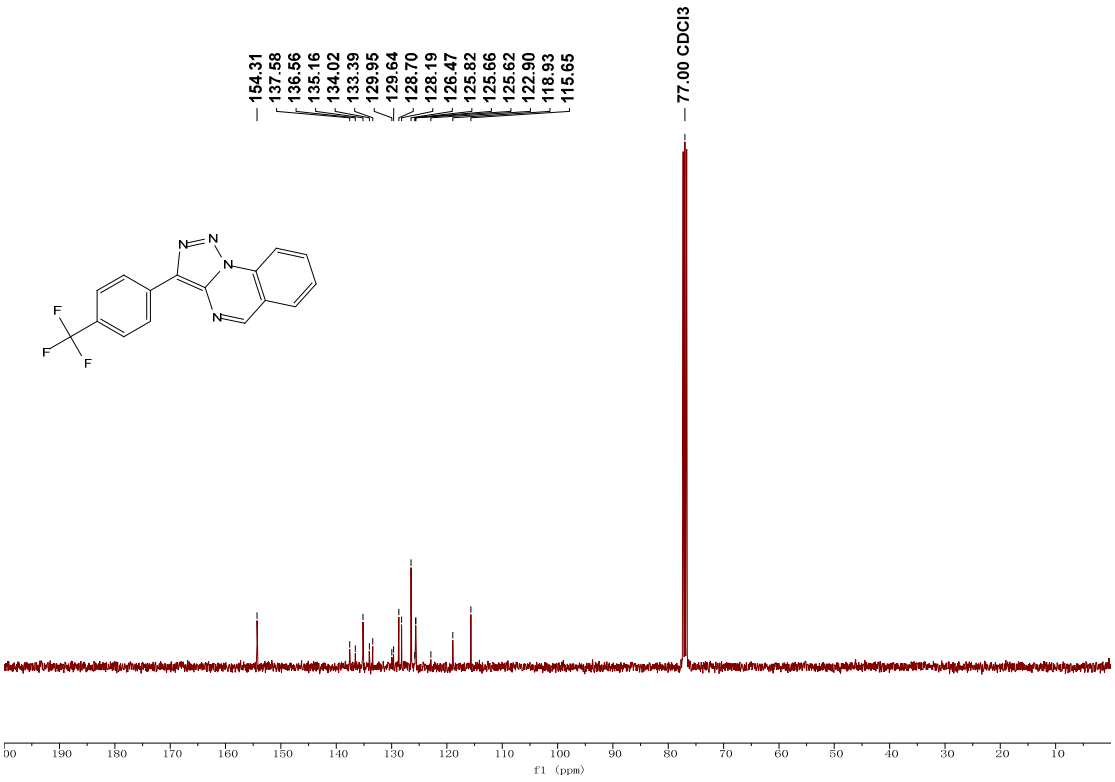


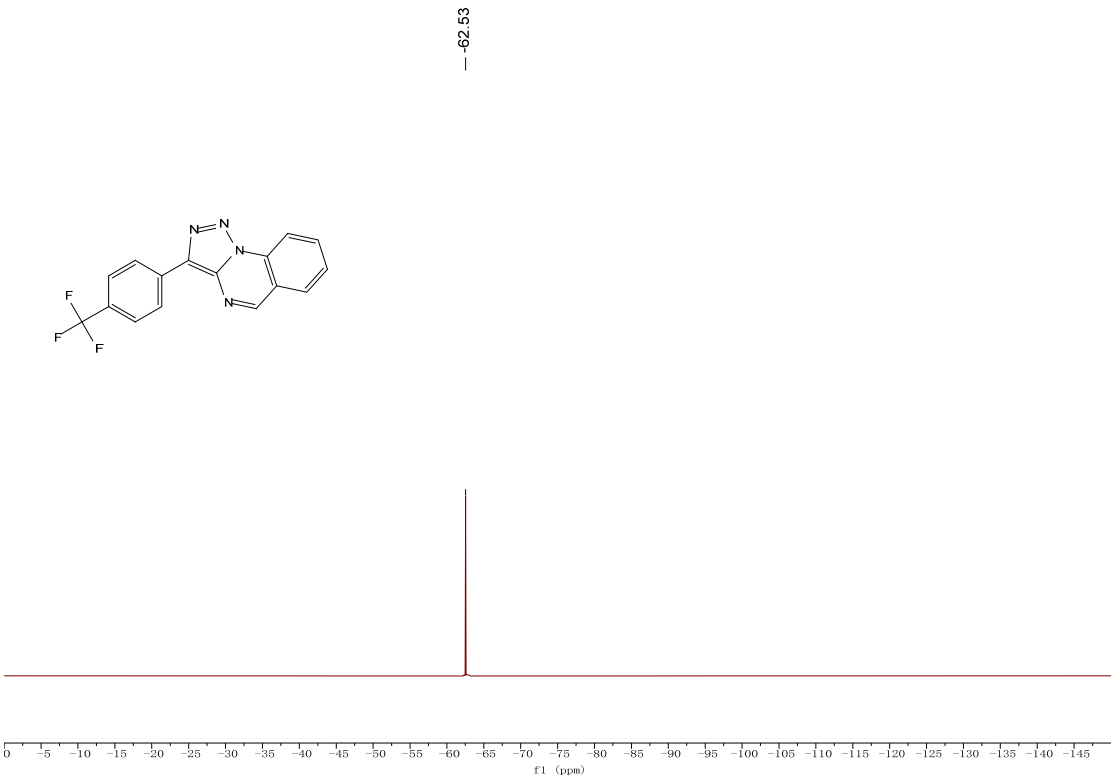
3-(4-(trifluoromethyl)phenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4h)







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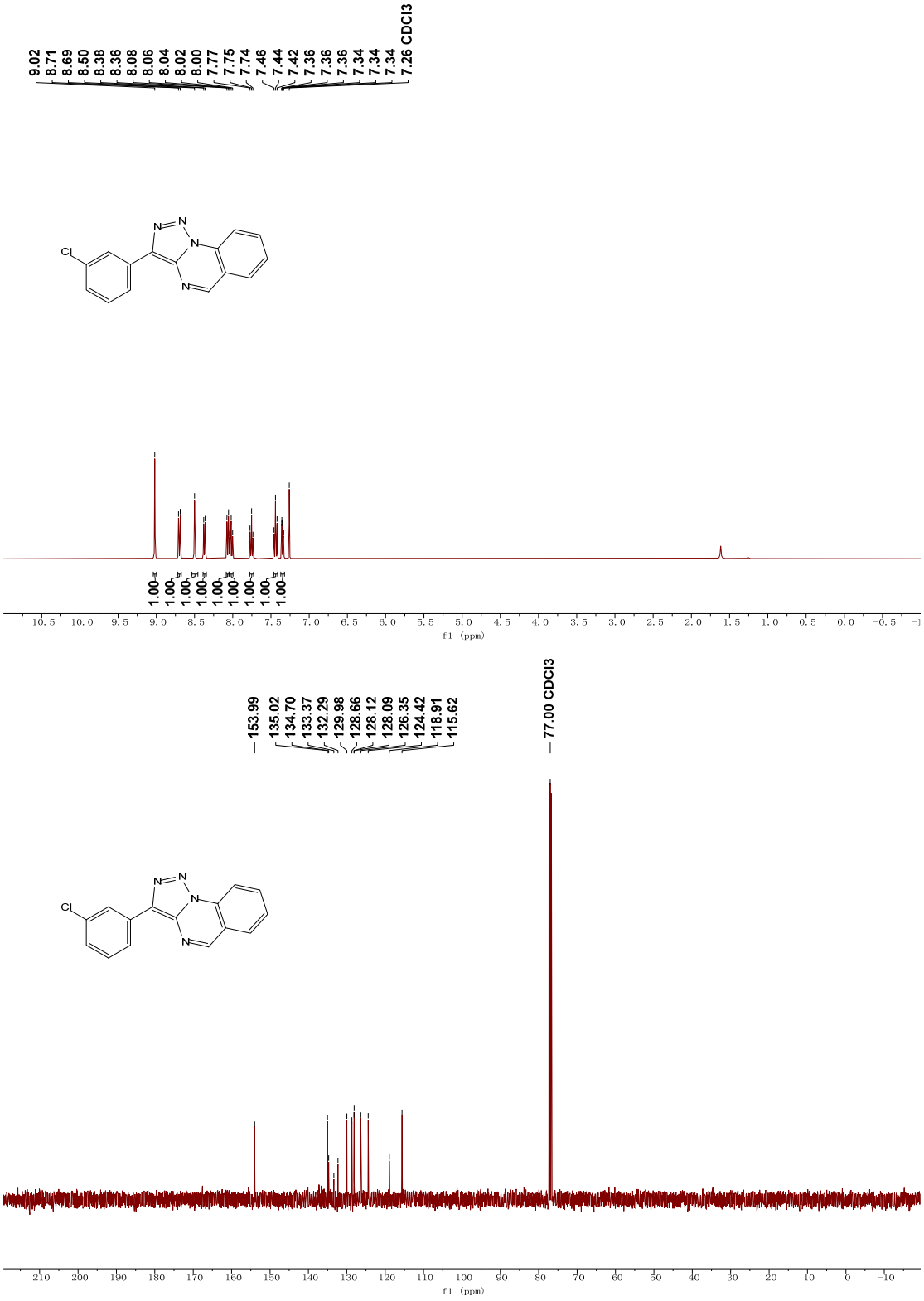
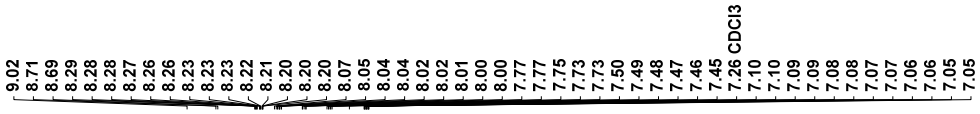
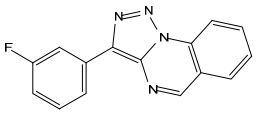
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

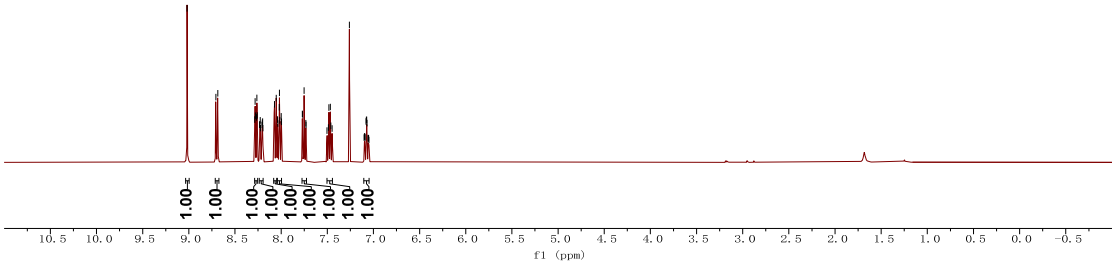
3-(3-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4i)

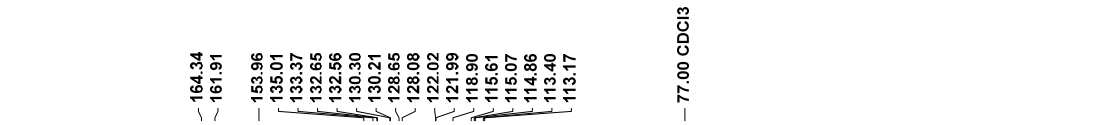


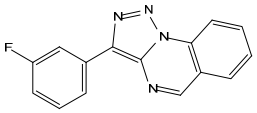
3-(3-fluorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4j)

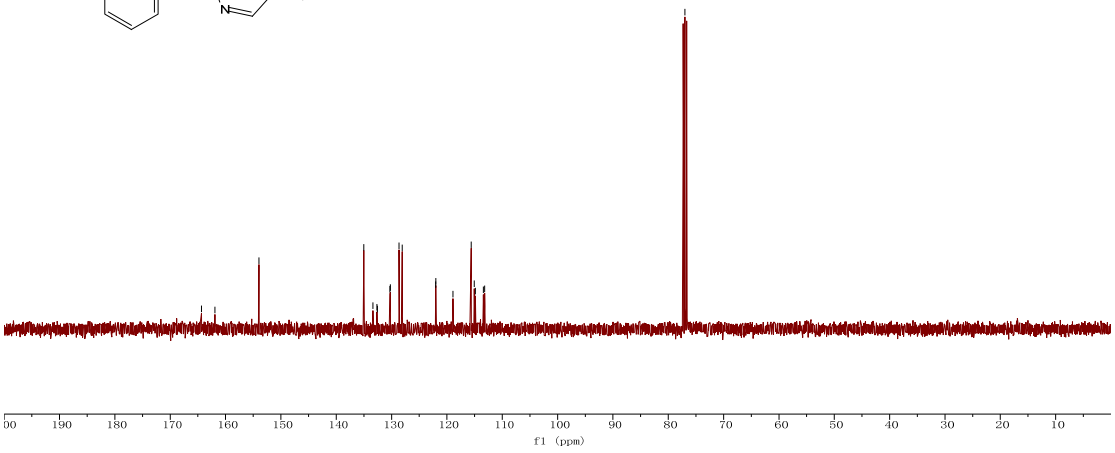


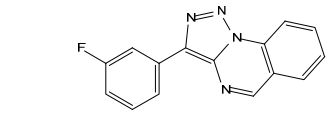








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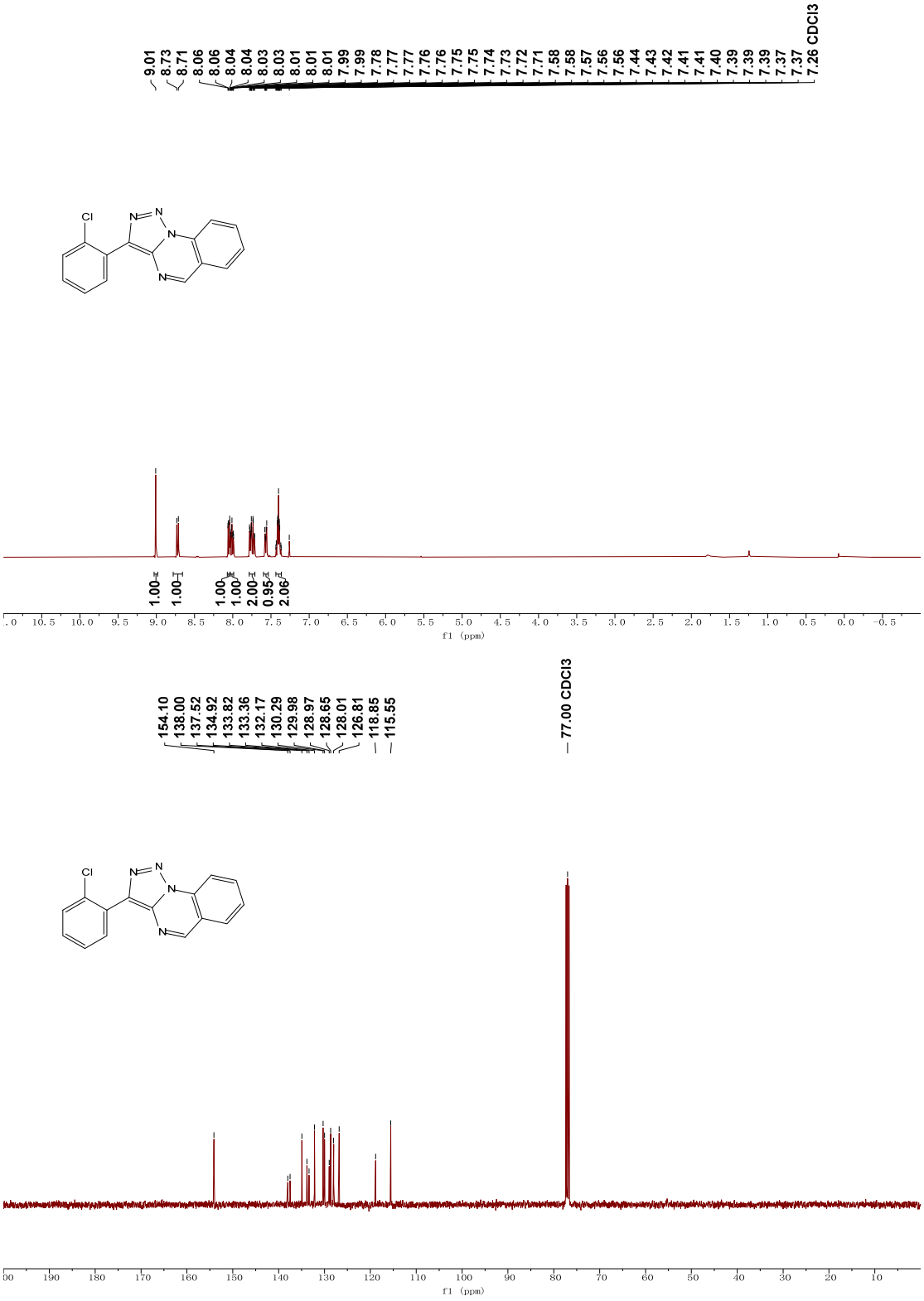
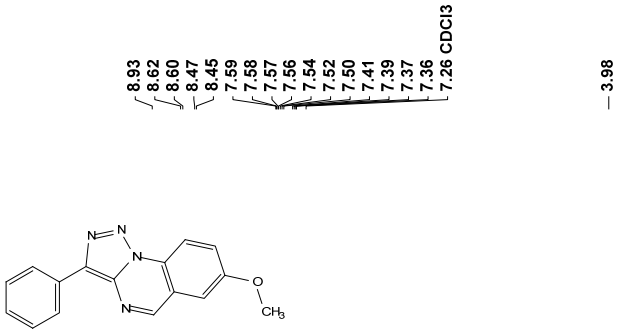
N
N
N

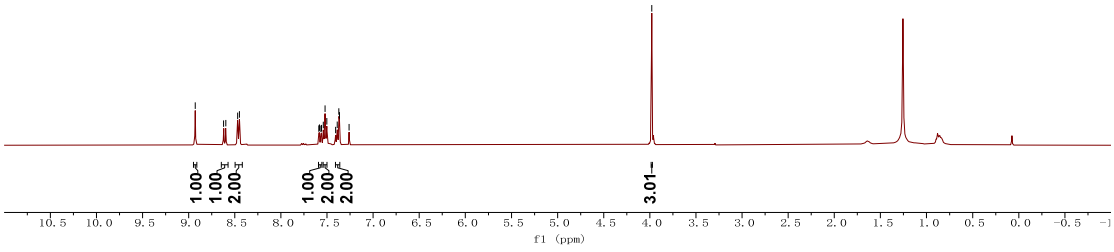
-112.66
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

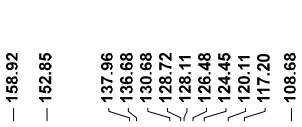
3-(2-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4k)

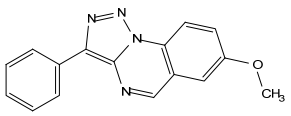


7-methoxy-3-phenyl-[1,2,3]triazolo[1,5-*a*]quinazoline(4l)

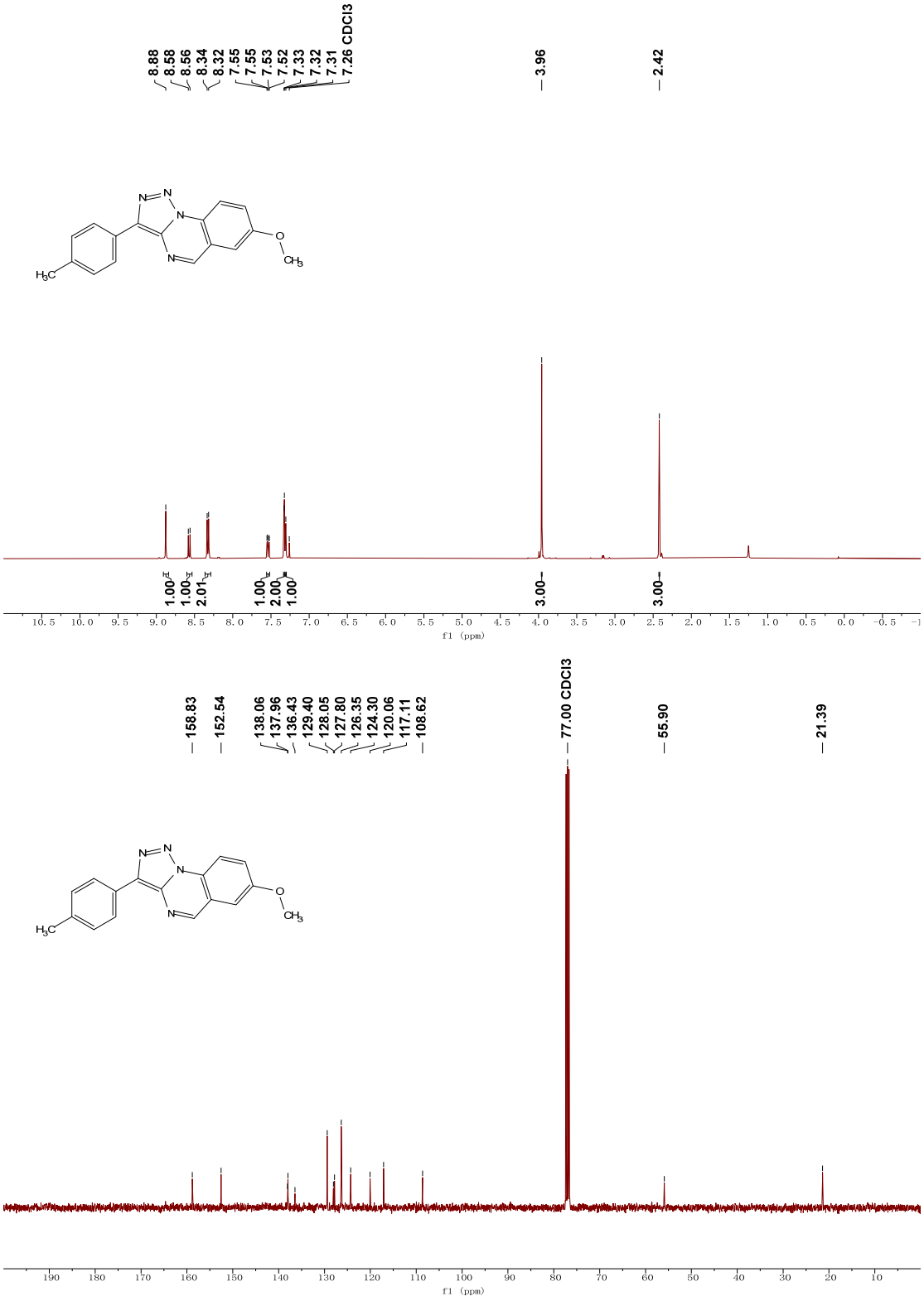




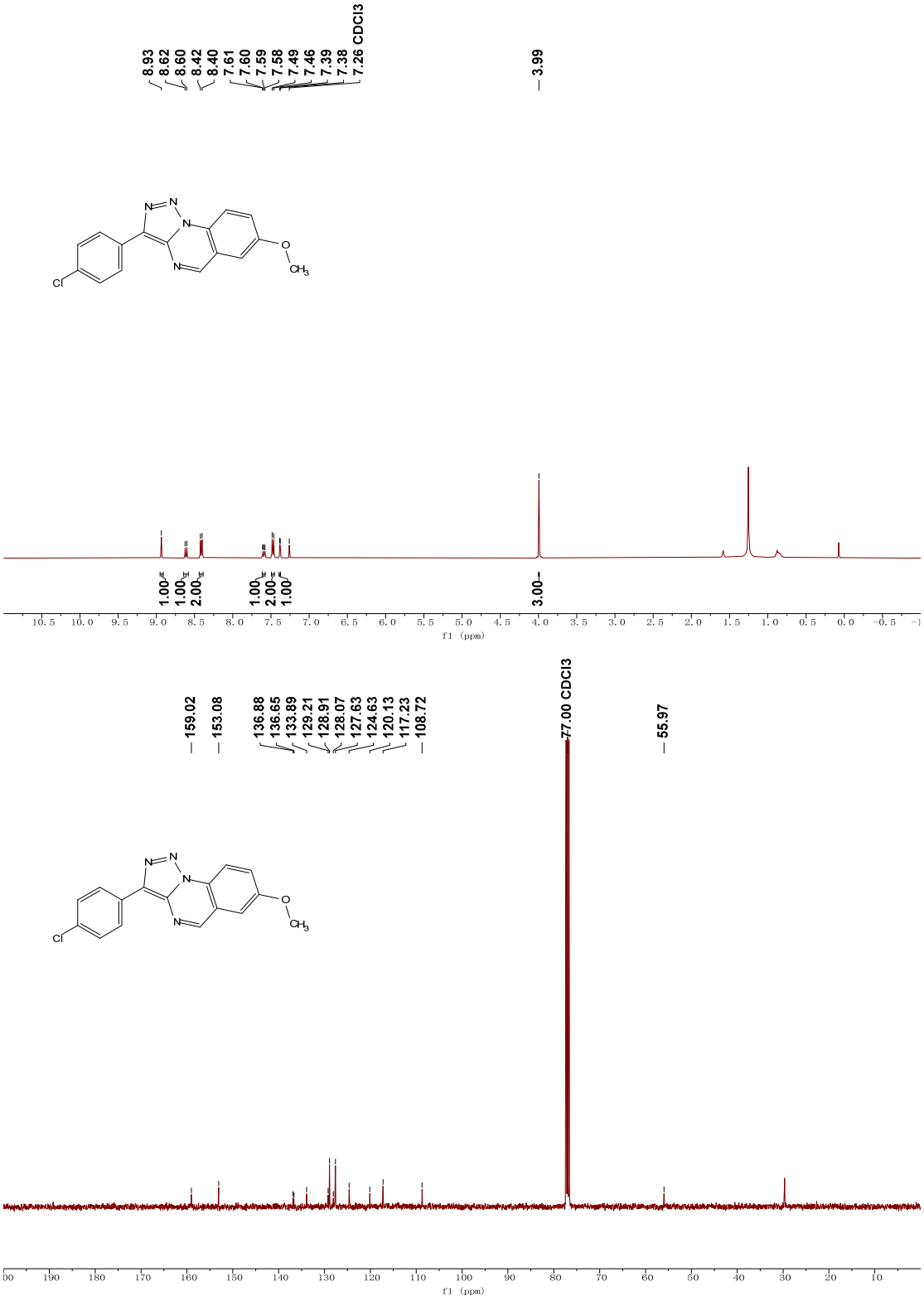




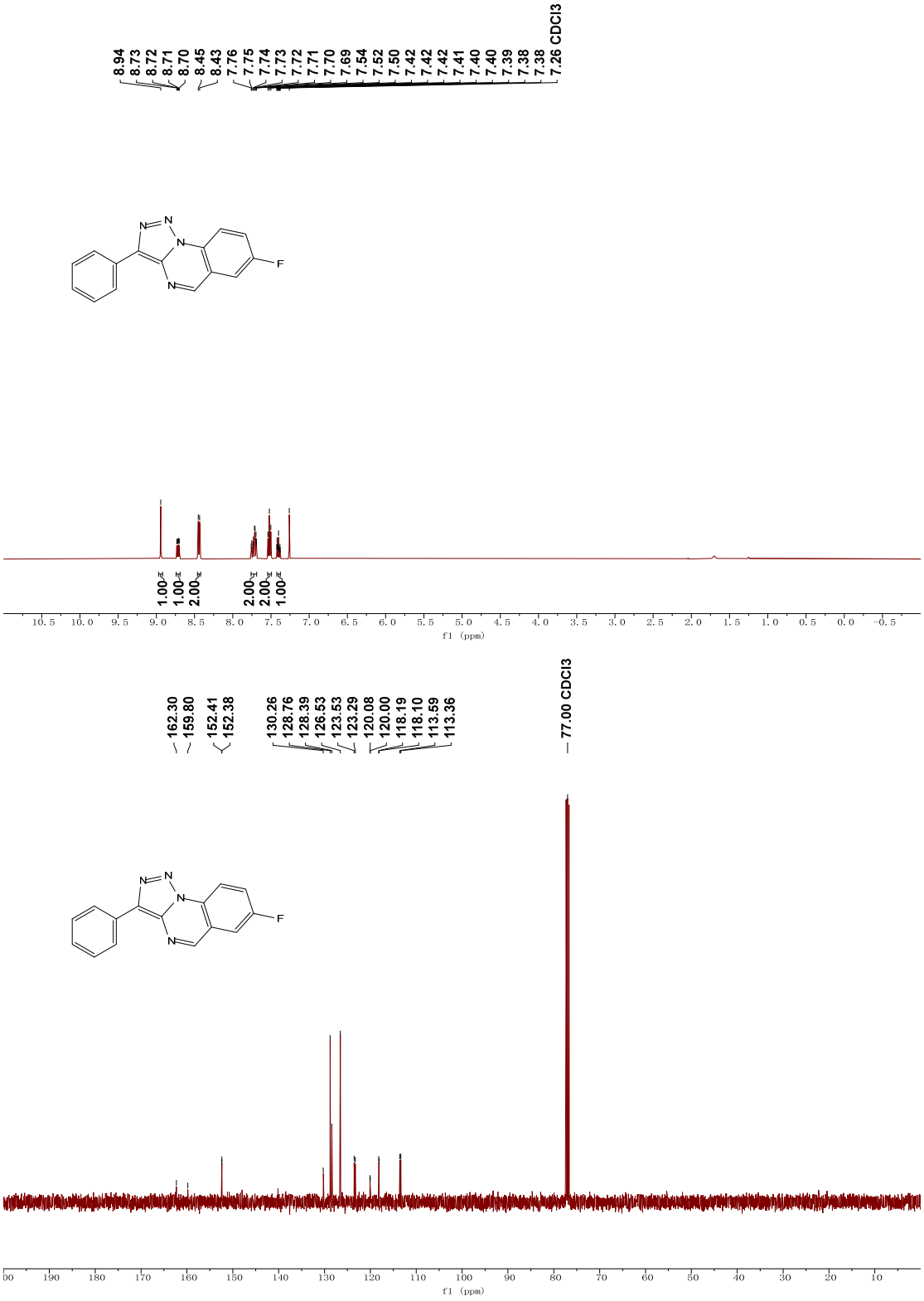
7-methoxy-3-(p-tolyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4m)

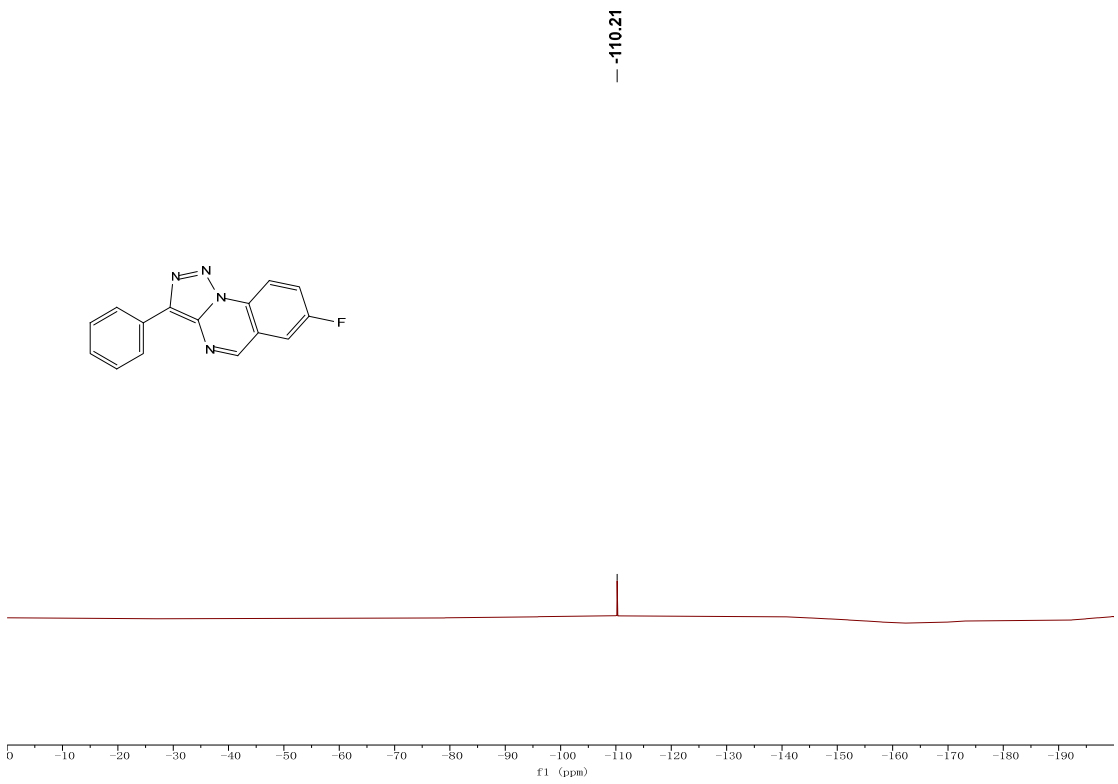


3-(4-chlorophenyl)-7-methoxy-[1,2,3]triazolo[1,5-*a*]quinazoline(4n)



7-fluoro-3-phenyl-[1,2,3]triazolo[1,5-*a*]quinazoline(4o)

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N
N
F
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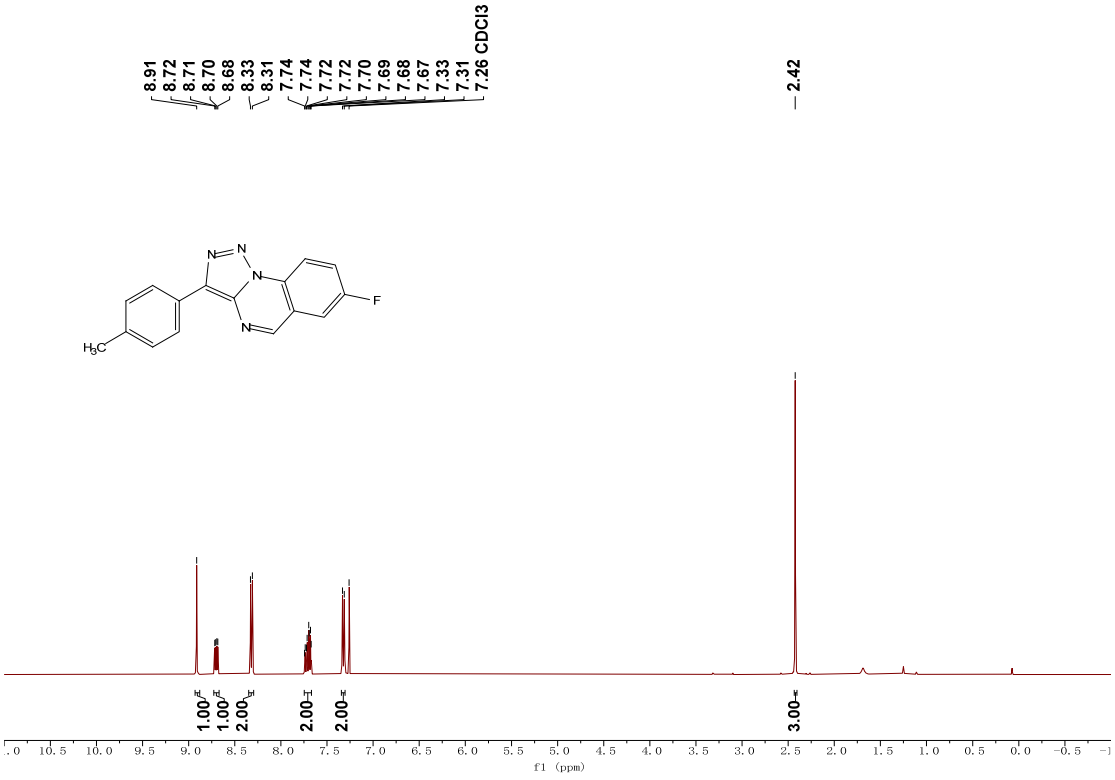
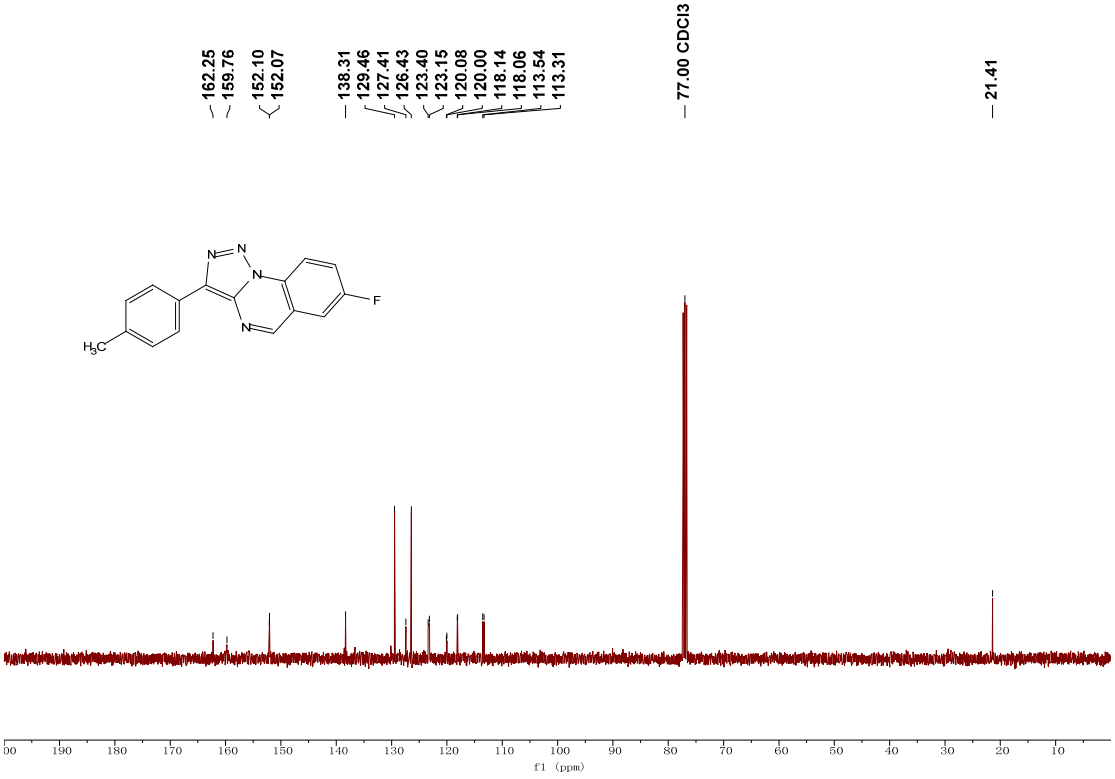
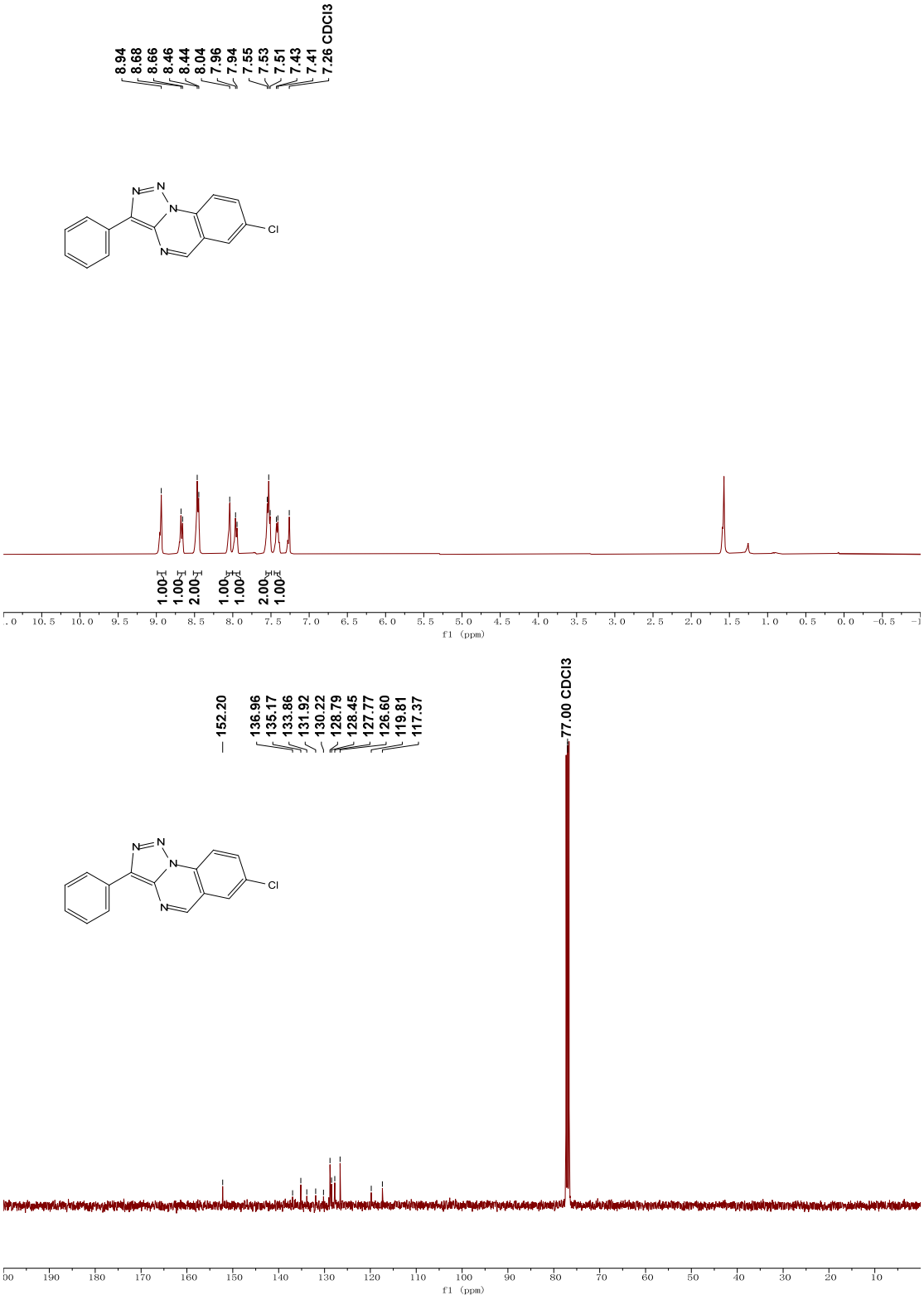
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

7-fluoro-3-(p-tolyl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4p)

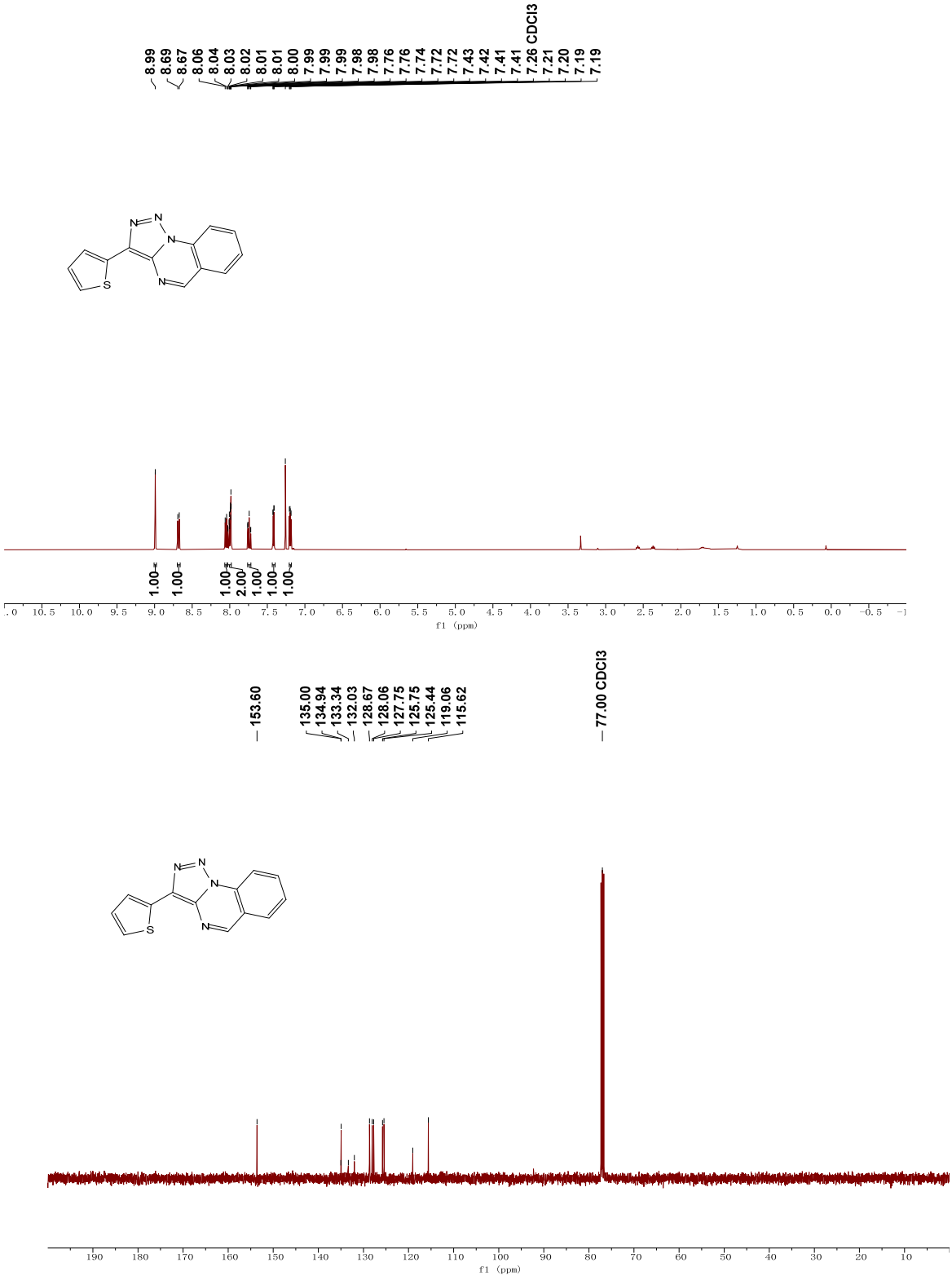




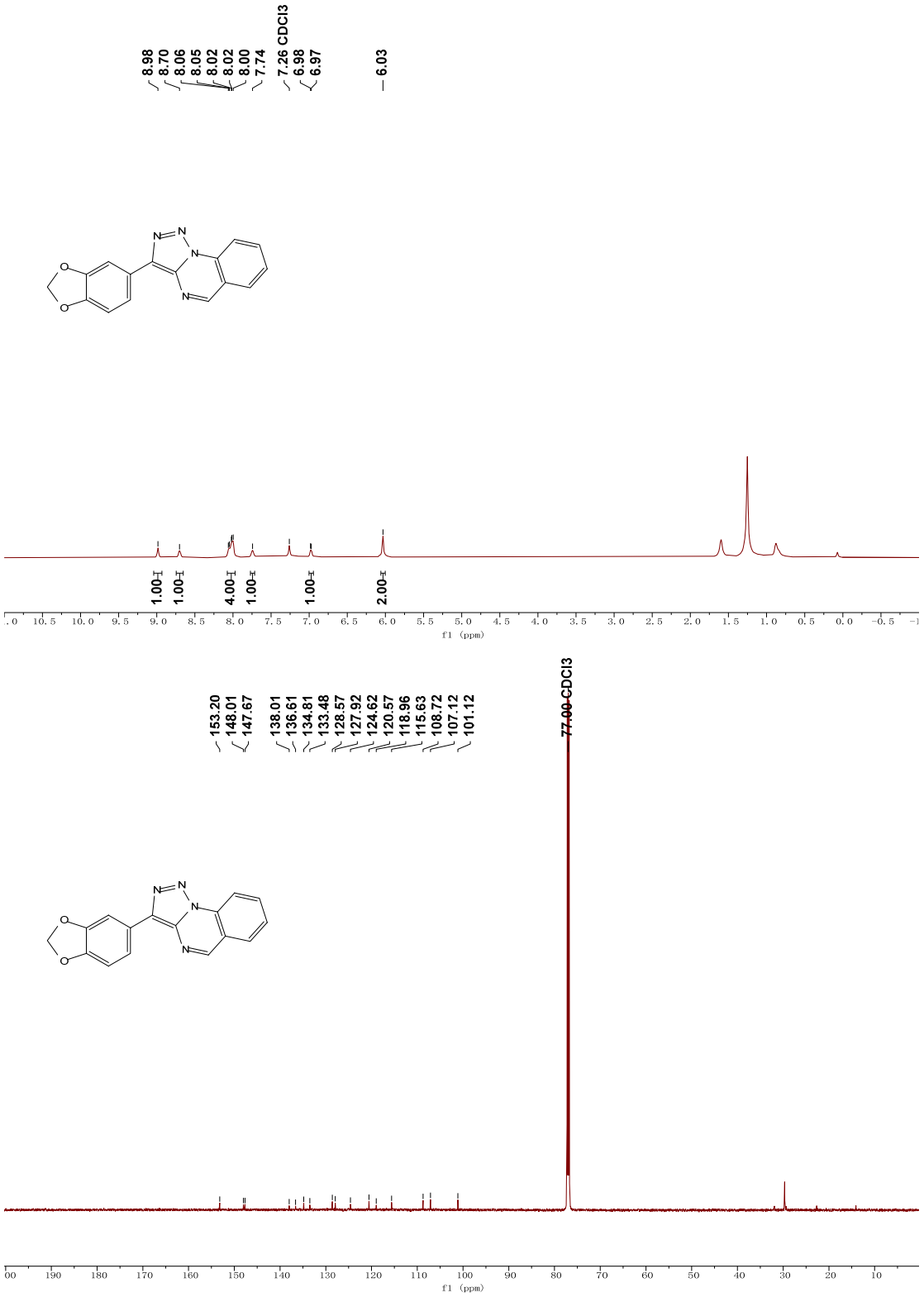
7-chloro-3-phenyl-[1,2,3]triazolo[1,5-*a*]quinazoline(4q)



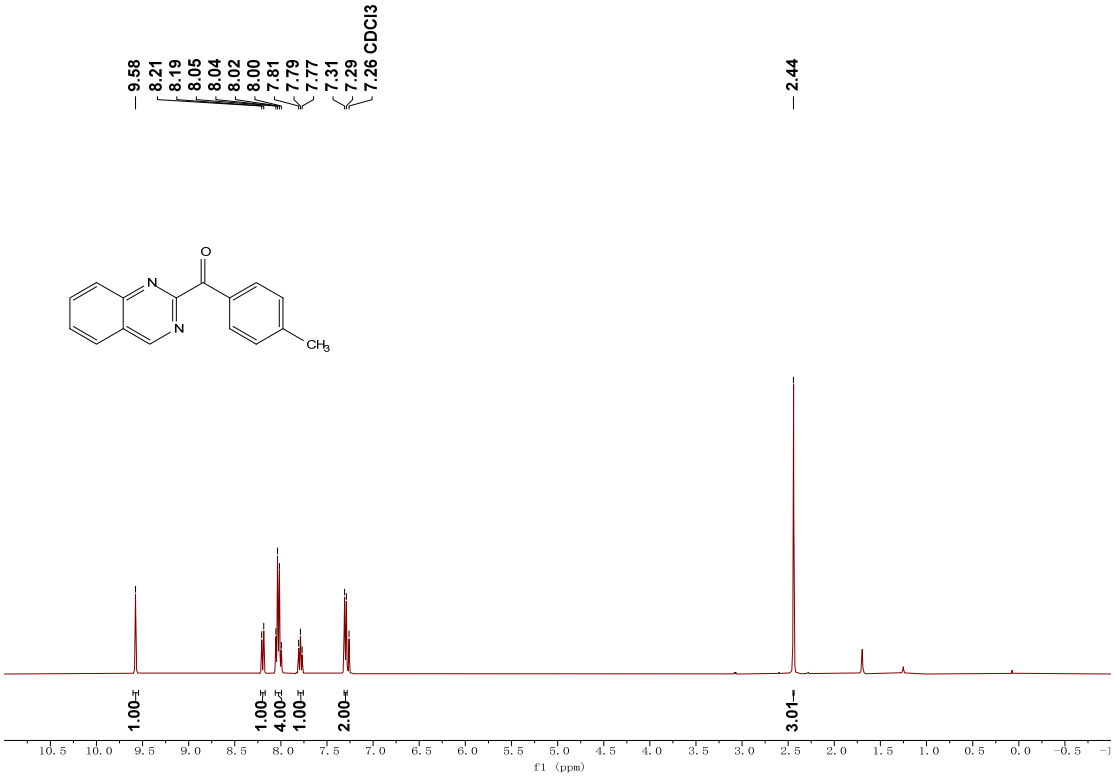
3-(thiophen-2-yl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4r)

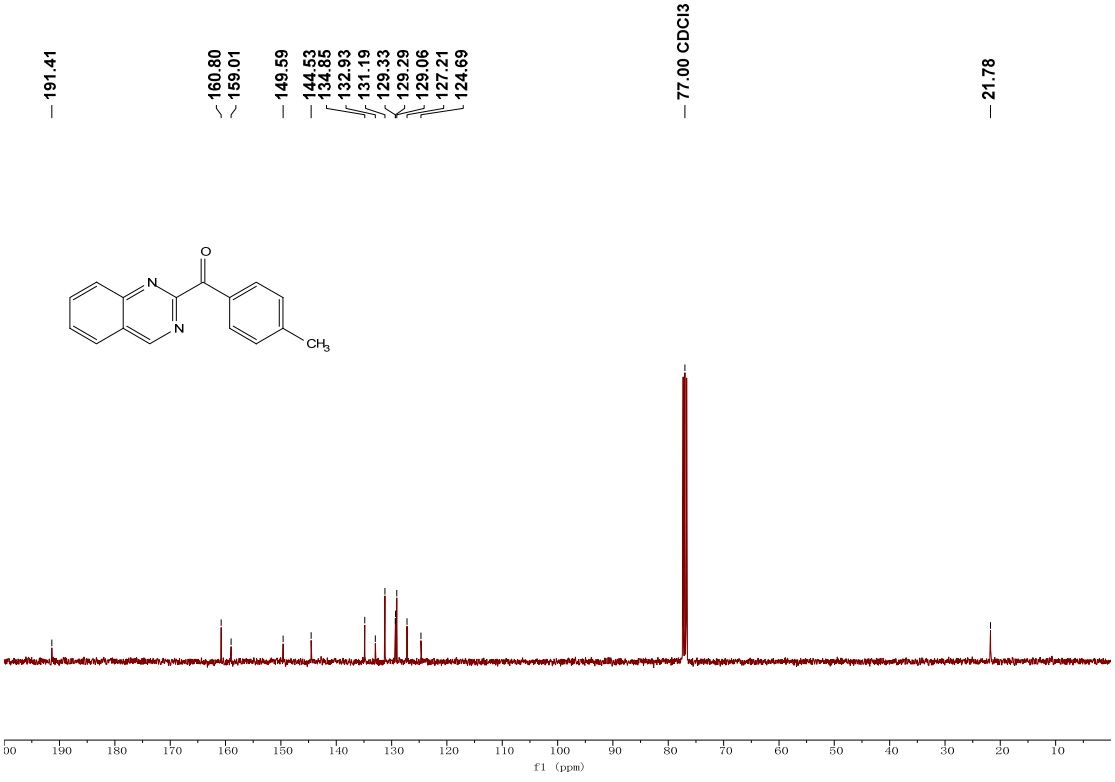


3-(benzo[d][1,3]dioxol-5-yl)-[1,2,3]triazolo[1,5-*a*]quinazoline(4s)

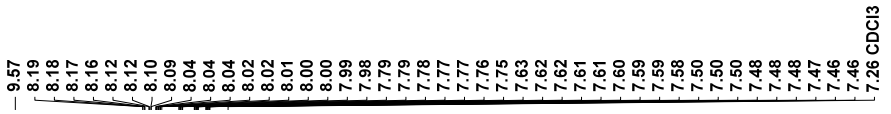


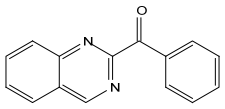
quinazolin-2-yl(p-tolyl)methanone(5a)

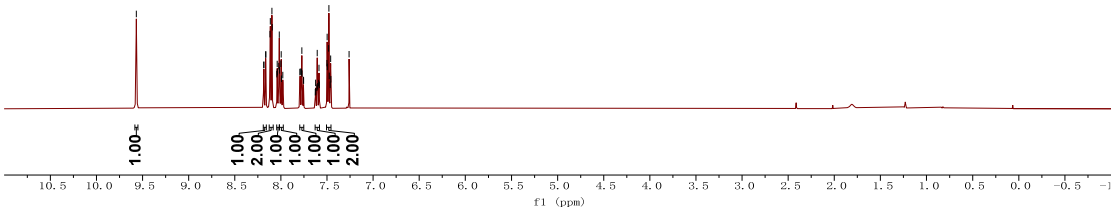


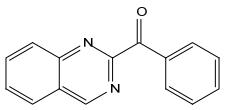


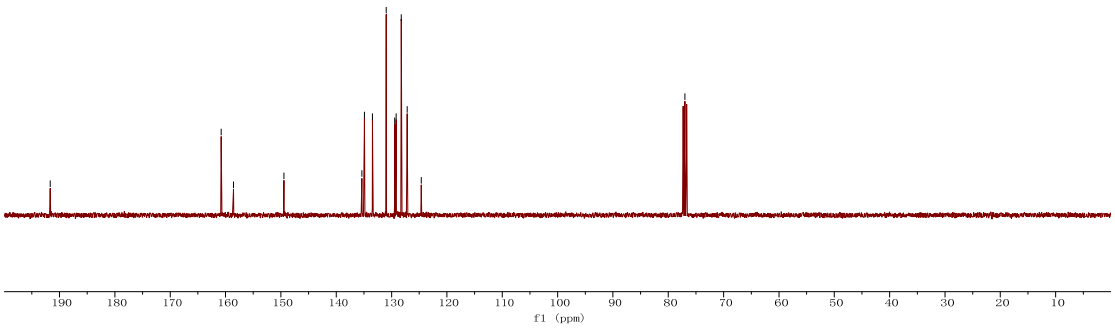
phenyl(quinazolin-2-yl)methanone(5b)



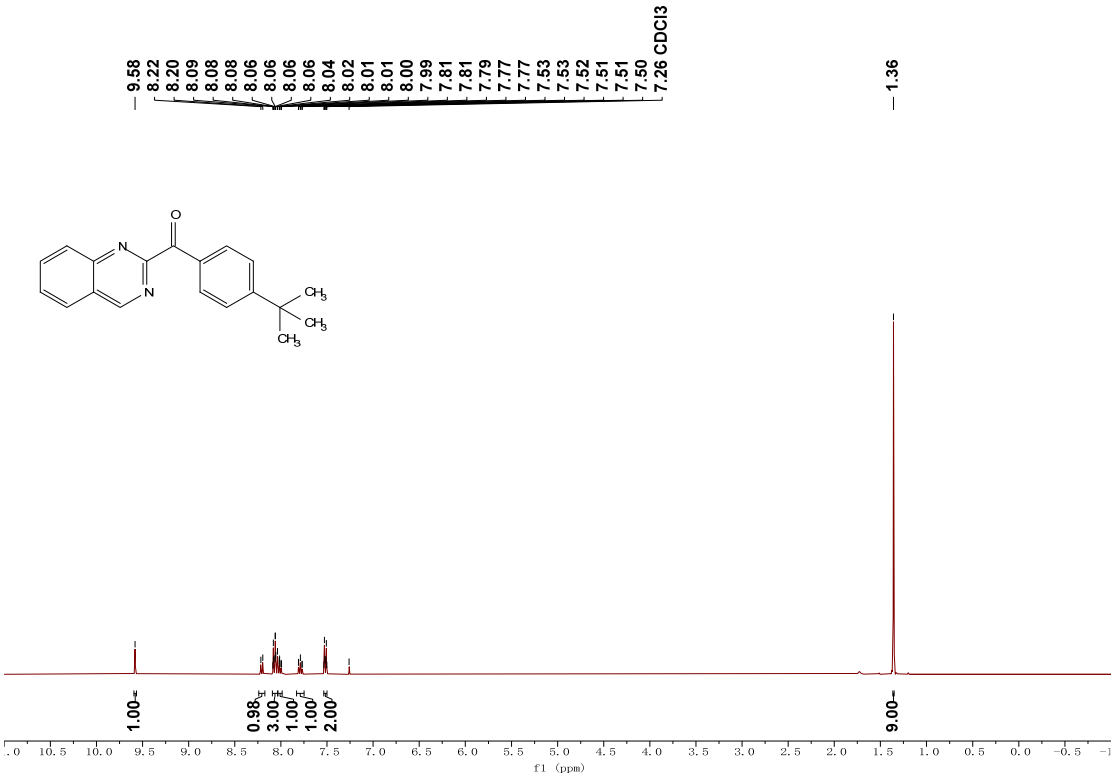


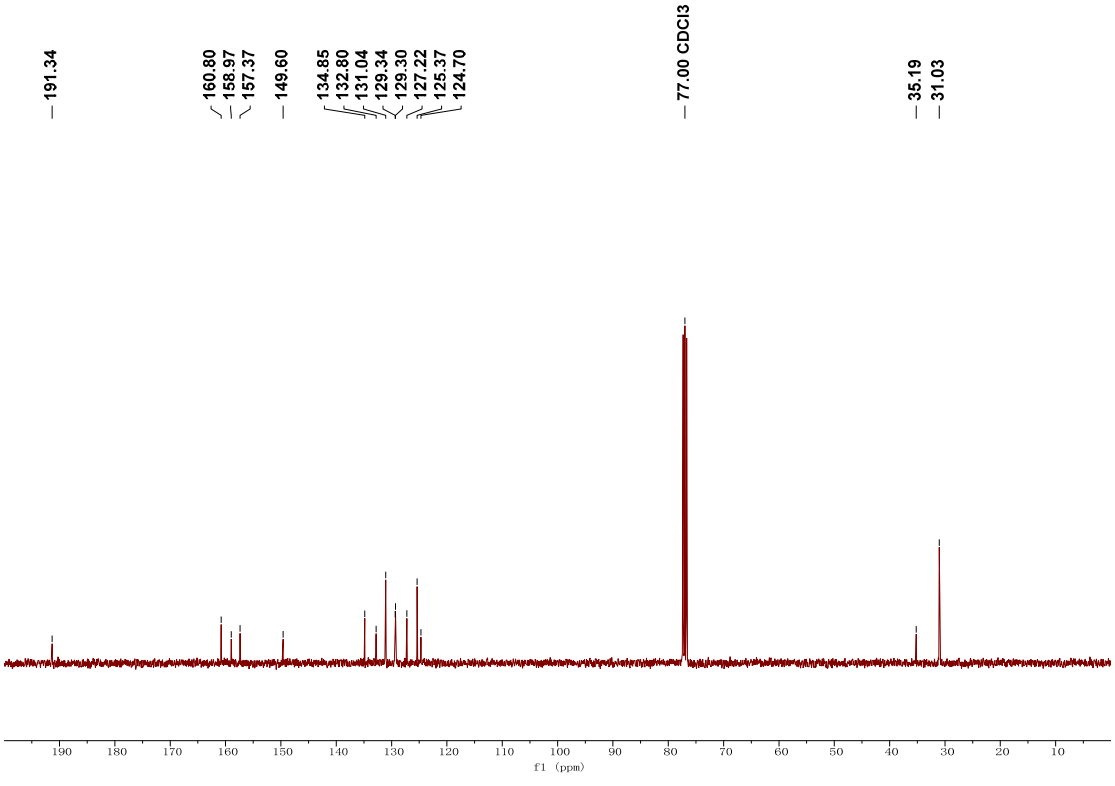




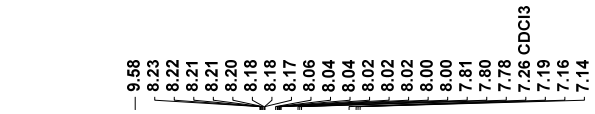


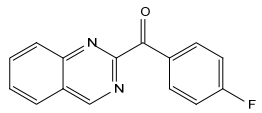
(4-(tert-butyl)phenyl)(quinazolin-2-yl)methanone(5c)

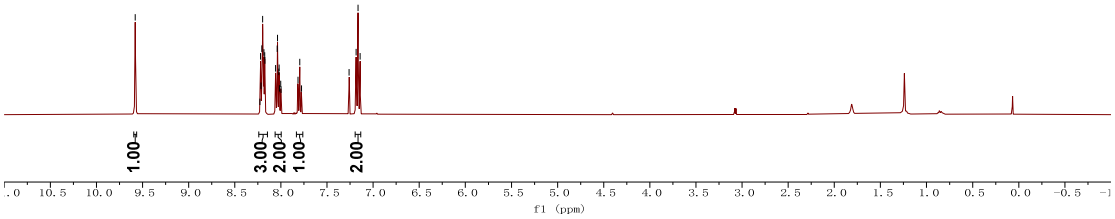


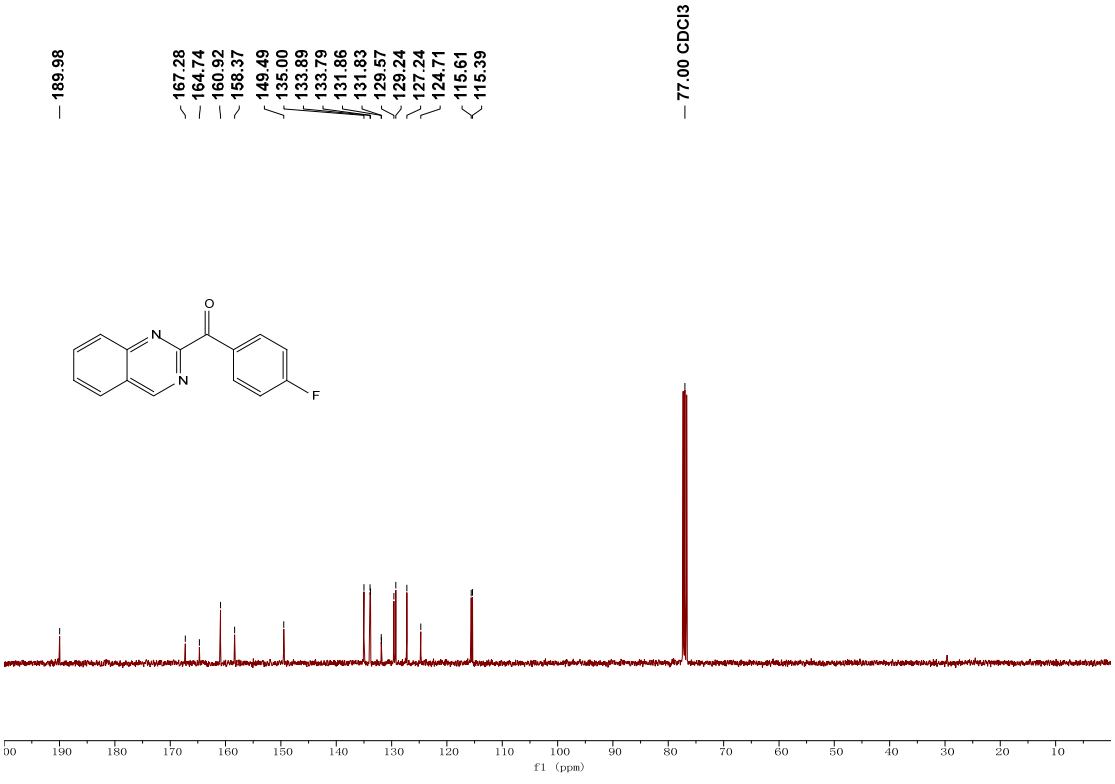


(4-fluorophenyl)(quinazolin-2-yl)methanone(5e)

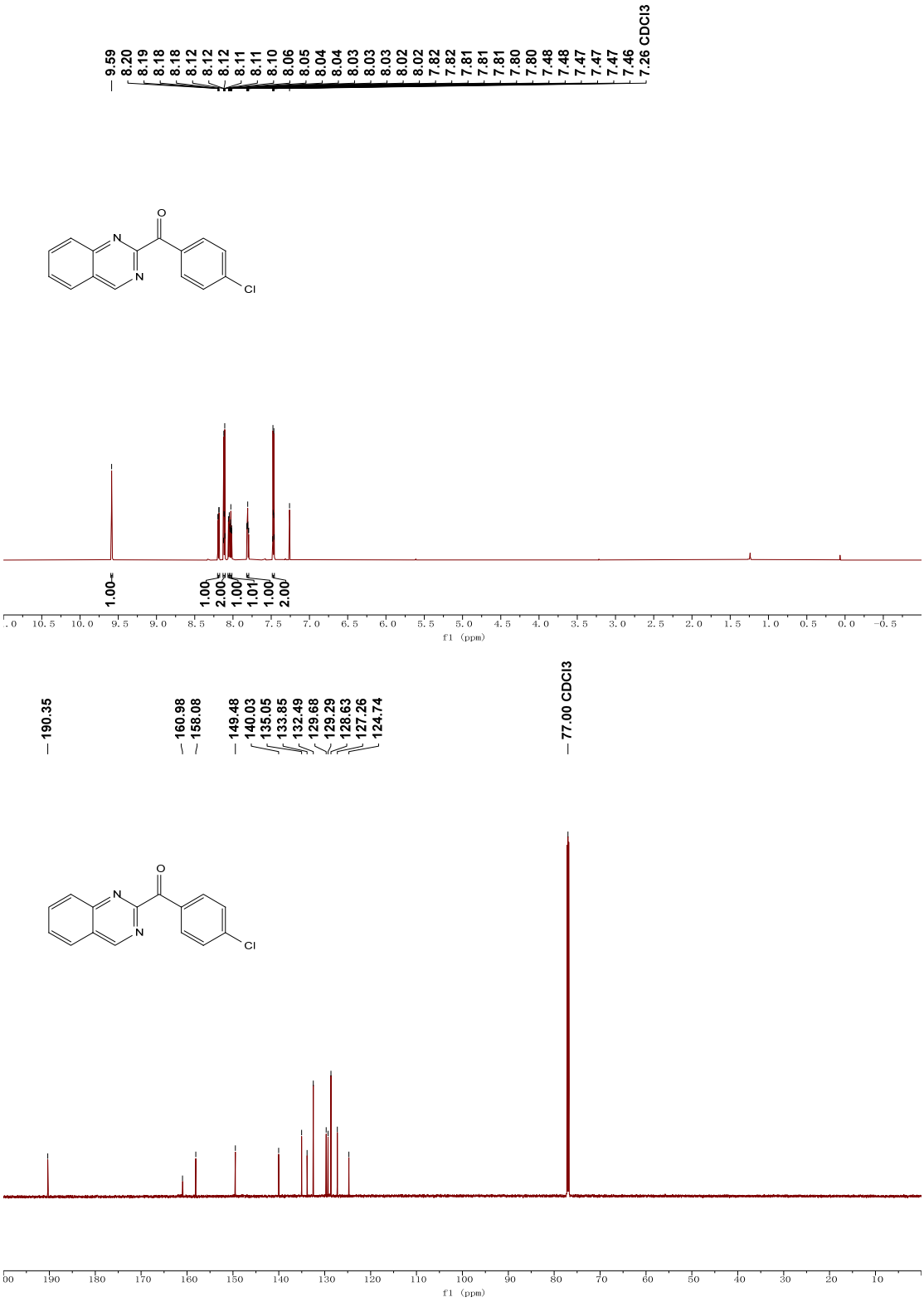




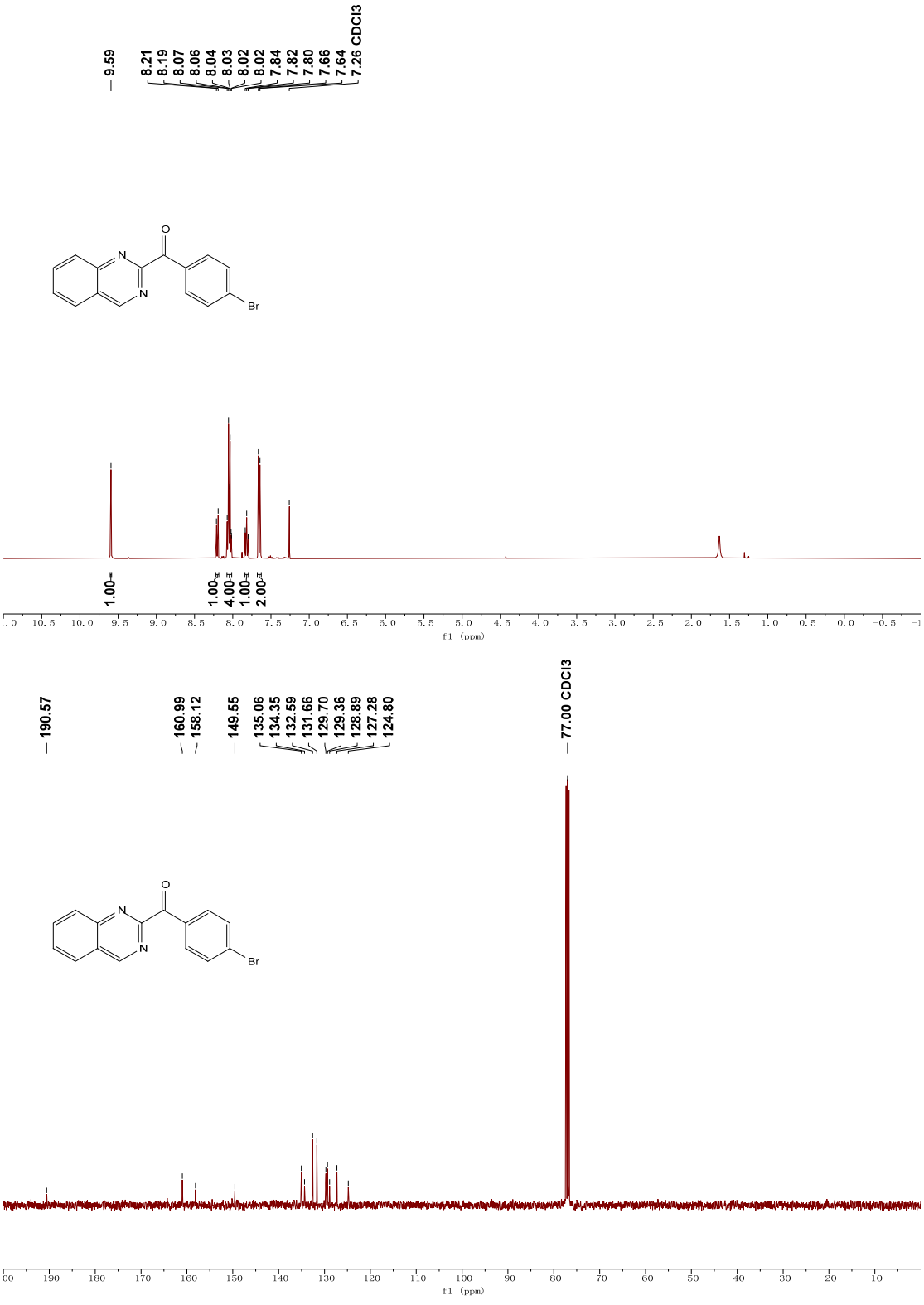




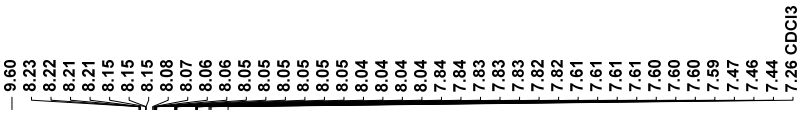
(4-chlorophenyl)(quinazolin-2-yl)methanone(5f)

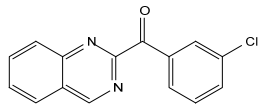


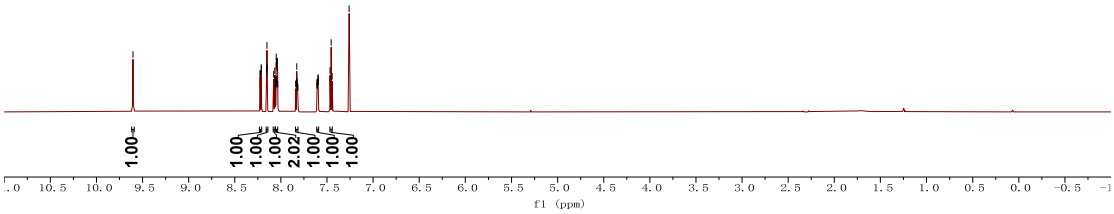
(4-bromophenyl)(quinazolin-2-yl)methanone(5g)

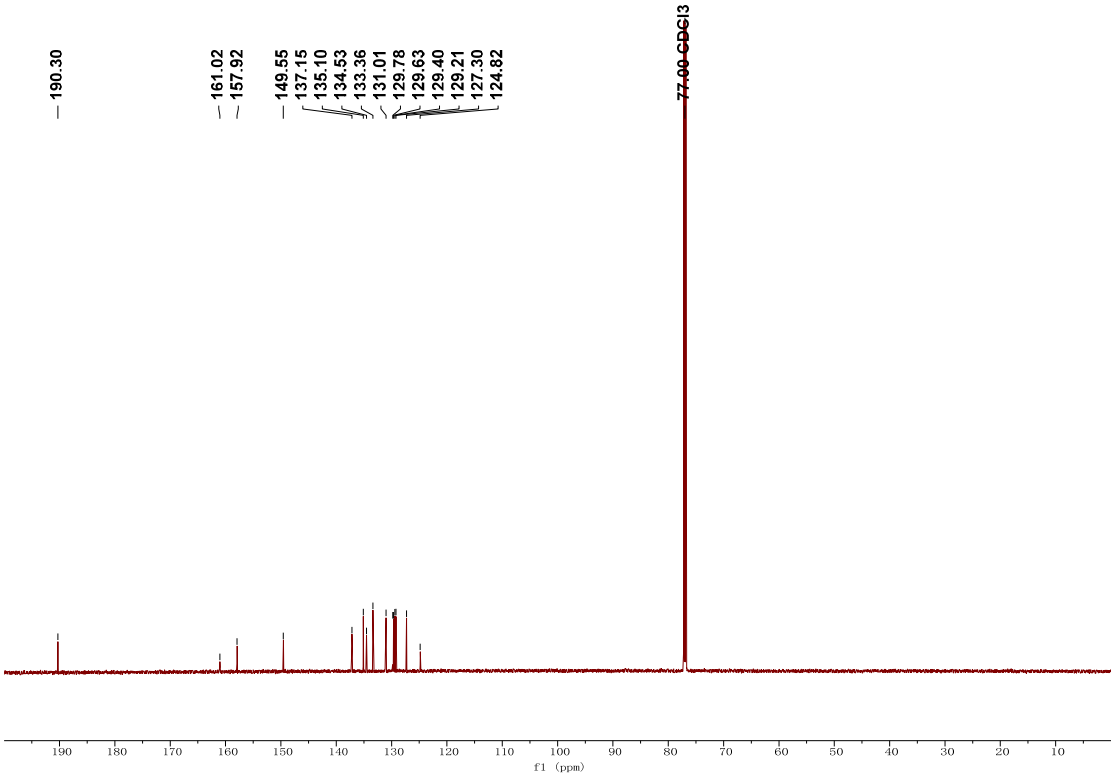


(3-chlorophenyl)(quinazolin-2-yl)methanone(5i)

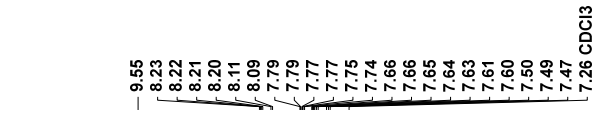


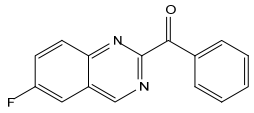


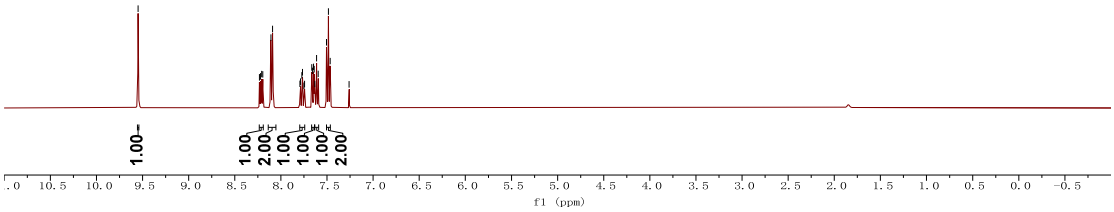


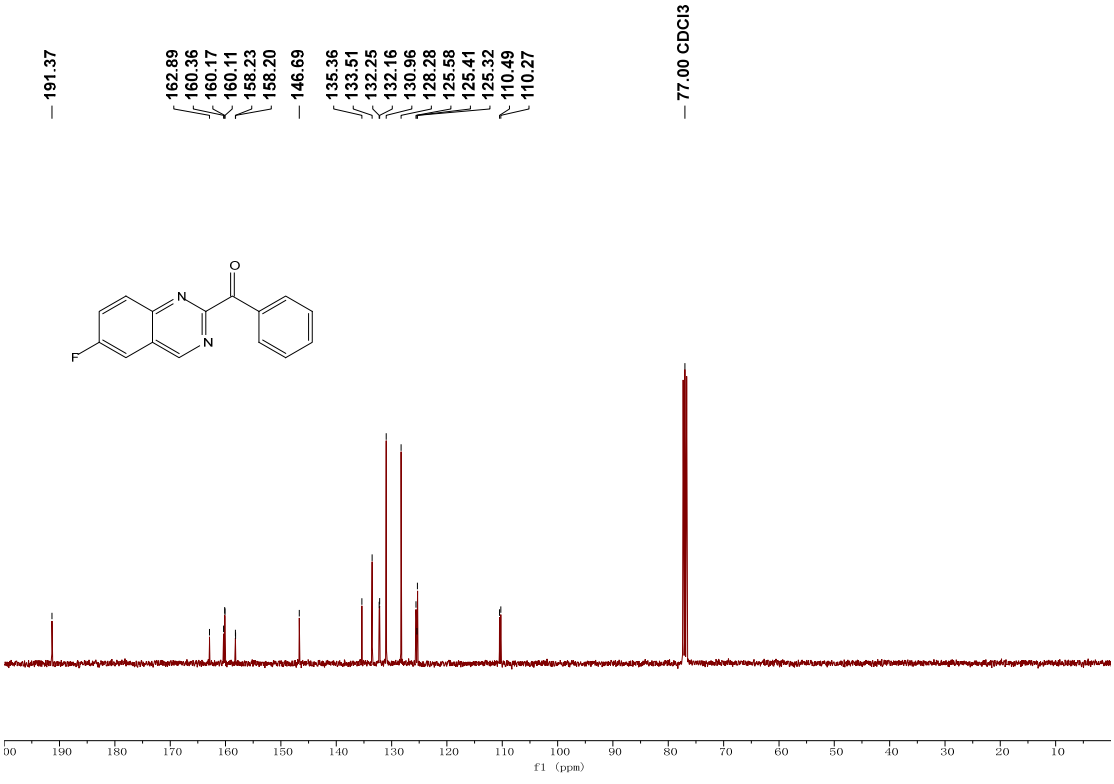


(6-fluoroquinazolin-2-yl)(phenyl)methanone(5o)

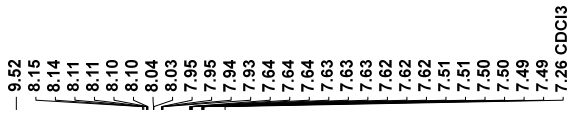








(6-chloroquinazolin-2-yl)(phenyl)methanone(5q)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8.11
8.11
8.10
8.10
8.04
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7.95
7.95
7.94
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7.64
7.64
7.64
7.63
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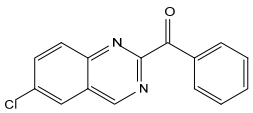
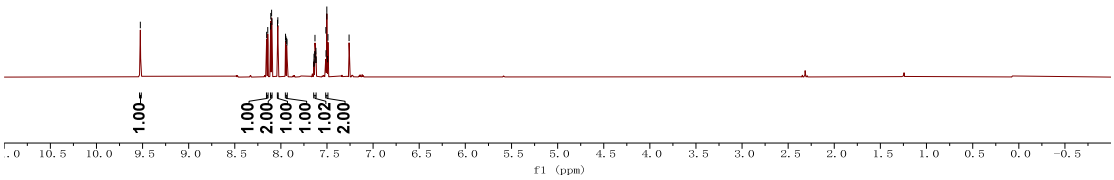
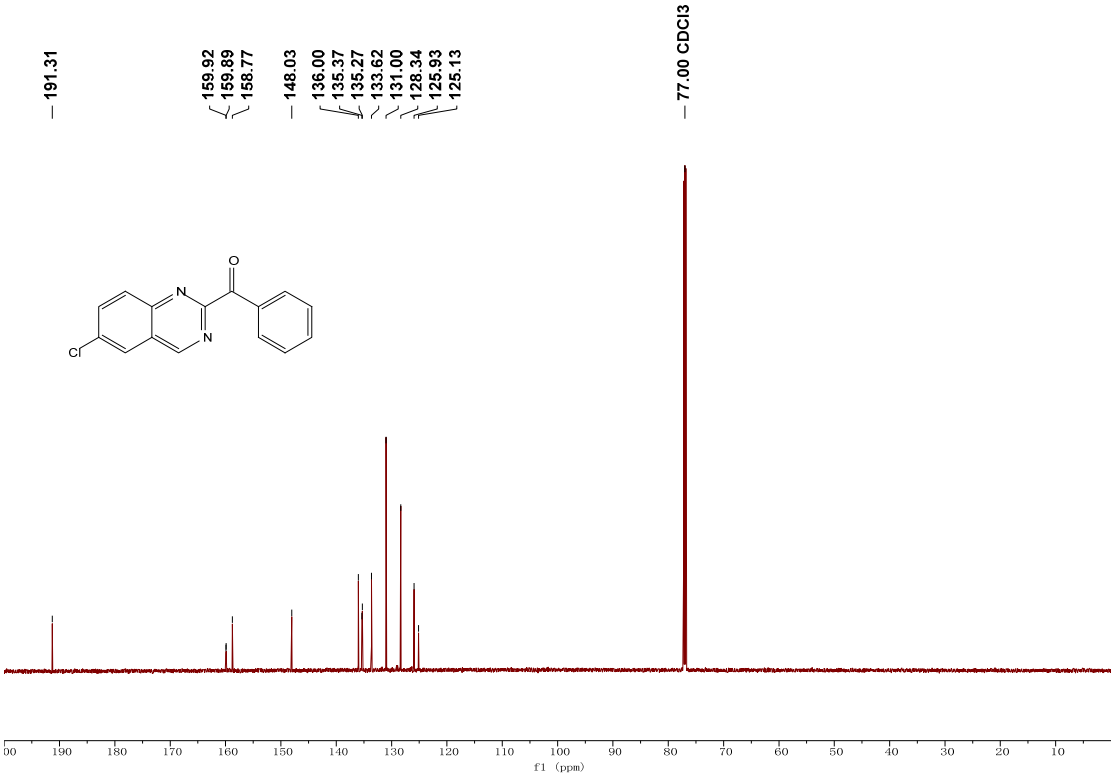
7.50
7.50
7.49
7.49
7.26 CDCl3


O
N
N
Cl


1.00
1.00
2.00
1.00
1.00
1.02
2.00
f1 (ppm)


191.31
159.92
159.89
158.77
148.03
136.00
135.37
135.27
133.62
131.00
128.34
125.93
125.13
77.00 CDCl3
f1 (ppm)

O
N
N
Cl

6. DFT Calculations of Mechanism of Dimroth Rearrangement

All Density Functional Theory (DFT) computations for the reaction mechanism were conducted using the Gaussian 16 software package. The geometric structures of the species involved in the Dimroth rearrangement were optimized with the M062X functional and the 6-311++G(d,p) basis set. To characterize the nature of the optimized structures, frequency calculations were performed at the same theoretical level, confirming minima (no imaginary frequencies) and transition states (one imaginary frequency), and providing thermal corrections to the Gibbs free energy at 298.15 K and 1 atm in the gas phase. The intrinsic reaction coordinate (IRC) method was employed to verify the correct connectivity between each transition state and its corresponding reactants and products.

Table 2. The calculated Gibbs free energy of all species in this study.

Specise	E(a.u.)	G(a.u.)	deltG(kcal/mol)
B	-796.238207	-796.279119	0
TS1	-796.210077	-796.25122	17.51
Int-1	-796.241165	-796.281873	-1.728
TS2	-796.225851	-796.267492	7.296
Int-2	-796.239618	-796.280458	-0.8402
TS3	-796.216374	-796.258686	12.82
4b	-796.256857	-796.297866	-11.76