Supporting Information for

Metal-Free C8–H Functionalization of Quinoline *N*-Oxides with Ynamides

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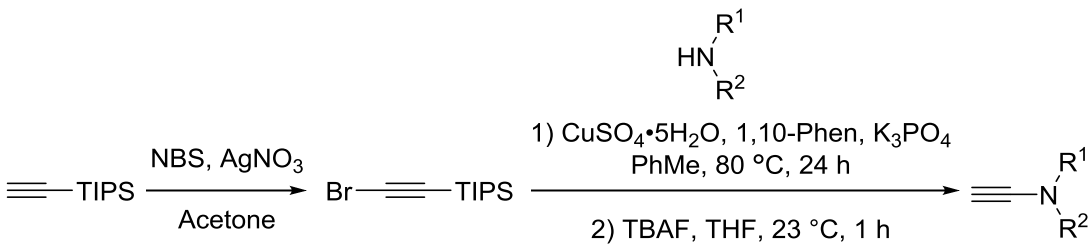
1. General Methods.

All reactions were carried out in solvents dried using a Solvent Purification System (SPS). Thin layer chromatography was carried out using TLC aluminum sheets coated with 0.2 mm of silica gel (Merck Gf234). Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm). NMR spectra were recorded at 23 °C on Bruker Avance 400 Ultrashield apparatus (400 MHz, $CDCl_3$ as solvent). Mass spectra were recorded on a Waters LCT Premier Spectrometer (ESI). Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer and are reported in reciprocal centimeter (cm^{-1}). Melting points were determined using a Büchi melting point apparatus.

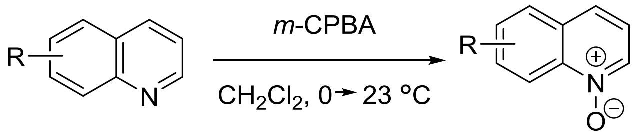
2. Procedures for the preparation of terminal ynamides 1a-l.



Representative procedures—preparation of 1a: To a solution of triisopropylsilylacetylene **S1** (5 mL, 22.3 mmol) in acetone (20 mL) was added *N*-bromosuccinimide (4.36 g, 24.5 mmol) and silver nitrate (373.7 mg, 2.2 mmol) at 23 °C and the mixture was stirred at this temperature for 1 h. The precipitate was removed by filtration and the solvent was evaporated. The residue was dissolved in Et_2O (30 mL) and washed sequentially with water (3×30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (100% hexane) to give **S2** (5.24 g, 90%).

To a solution of **S2** (2.0 g, 7.65 mmol) in toluene (20 mL) was added copper sulfate pentahydrate (191 mg, 0.77 mmol), 1,10-phenanthroline (276 mg, 1.53 mmol) and potassium phosphate (3.25 g, 15.3 mmol) under argon and the mixture was stirred at 80 °C for 24 h before it was diluted with EtOAc (30 mL). The mixture was washed sequentially with water (3×50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc=10/1) to give TIPS protected ynamide (2.38 g, 85%), which was dissolved in THF (30 mL) and tetrabutylammonium fluoride (7.8 mL, 1.0 M in THF, 7.8 mmol) was added dropwise at 0 °C. The reaction mixture was then stirred at 23 °C for 1 h before it was quenched with saturated aqueous NH_4Cl (15 mL). The aqueous layer was extracted with EtOAc (50 mL) and the combined organic layer was washed sequentially with water (2×80 mL) and brine (80 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc=10/1) to give **1a** (1.09 g, 80%). Substrates **1a-l** were synthesized using the same procedures, whose physical data have been reported in previous publications.[1]

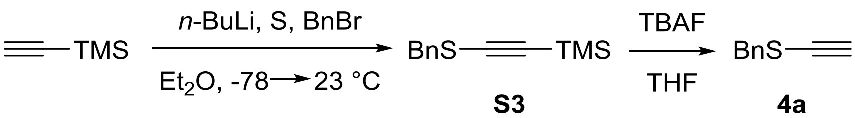
3. Procedures for the preparation of quinoline *N*-oxides 2b-k.



2b-k

Representative procedures—preparation of 2b: To a stirred solution of 3-methylquinoline (1.43 g, 10 mmol) in dichloromethane (30 mL) was added 3-chloroperoxybenzoic acid (3.68 g, 75 wt%, 16 mmol) in portions over a period of 20 minutes at 0 ℃ and the reaction mixture was allowed to stir at 23 ℃ overnight. The reaction mixture was washed sequentially with saturated $NaHCO_3$ (5×30 mL) water (30 mL) and brine (30 mL). The organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/MeOH=10/1) to give **2b** (1.24 g, 78%). Quinoline *N*-oxides **2b-k** were synthesized using the same procedures, whose physical data have been reported in previous publications.[2]

4. Procedures for the preparation of 4a.

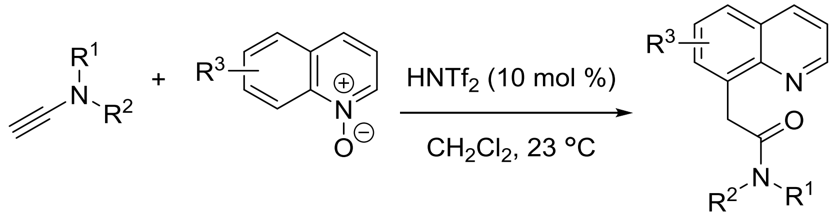


S3 **4a**

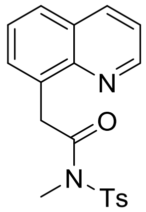
To a solution of trimethylsilylacetylene (7.0 g, 71 mmol) in Et_2O (100 mL) was added *n*-BuLi (28.3 mL, 2.5 M in hexanes, 71 mmol) dropwise at -78 °C and the reaction was allowed to warm up to -20 °C during 2 h before it was re-cooled to -78 °C. Then powered sulfur (2.3 g, 72 mmol) was added in portions and the solution was warmed to 0 °C and treated with benzyl bromide (8.5 mL, 72 mmol), which was stirred at 23 ℃ overnight. The reaction was quenched with saturated aqueous NH_4Cl (100 mL). The aqueous layer was extracted with Et_2O (100 mL) and the combined organic layer was washed sequentially with water (200 mL) and brine (200 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc=40/1) to give **S3** (10.95 g, 70%).

The resulting **S3** was dissolved in THF (200 mL) and tetrabutylammonium fluoride (59.6 mL, 1.0 M in THF, 59.6 mmol) was added dropwise at 0 ℃. The reaction mixture was then stirred at 23 ℃ for 1 h before it was quenched with saturated aqueous NH_4Cl (200 mL). The aqueous layer was extracted with Et_2O (200 mL) and the combined organic layer was washed sequentially with water (2×400 mL) and brine (400 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc=40/1) to give **4a** (5.60 g, 76%), whose physical data have been reported in previous publication.[3]

5. Procedures for the C8-H functionalization of quinoline *N*-oxides.



Representative procedures—preparation of 3aa: To a solution of ynamide **1a** (167.4 mg, 0.8 mmol) and quinoline *N*-oxide **2a** (185.6 mg, 1.28 mmol) in CH_2Cl_2 (4 mL) was added $HNTf_2$ (22.5 mg, 0.08 mmol) and the mixture was stirred at 23 °C for 2 h. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc=5/1) to give **3aa** (263.7 mg, 93%). Other 8-substituted quinolines were synthesized using the same procedures. Note: 0.16 mmol of $HNTf_2$ was used for the preparation of **5aa**.



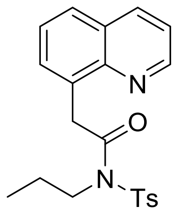
3aa 93%

Colorless crystal, m. p. 151-152 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, J = 4.4, 1.7 Hz, 1H), 8.10 (dd, J = 8.3, 1.7 Hz, 1H), 7.97 (d, J = 8.1 Hz, 2H), 7.75 – 7.70 (m, 1H), 7.51 (d, J = 6.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.38 – 7.31 (m, 3H), 4.63 (s, 2H), 3.37 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.20, 149.33, 146.40, 144.57, 136.27, 136.19, 133.48, 130.35, 129.66, 128.27, 127.83, 127.44, 126.26, 121.10, 39.31, 33.34, 21.62.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}N_2O_3S$ 355.1114; Found 355.1119.



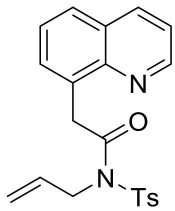
3ba 86%

White solid, m. p. 152-154 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.71 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.28 (m, 3H), 4.56 (s, 2H), 3.87 – 3.75 (m, 2H), 2.42 (s, 3H), 1.79 (h, *J* = 7.5 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.04, 149.30, 146.38, 144.37, 137.01, 136.18, 133.60, 130.32, 129.55, 128.30, 127.93, 127.43, 126.28, 121.14, 48.84, 39.23, 23.30, 21.64, 11.19.

HRMS (ESI) m/z: $[M + H]^+$ $C_{21}H_{23}N_2O_3S$ 383.1424; Found 383.1429.



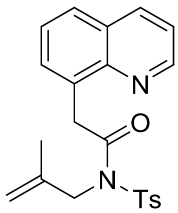
3ca 91%

White solid, m. p. 151-153 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.72 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.35 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.96 (ddt, *J* = 16.0, 10.6, 5.4 Hz, 1H), 5.37 (d, *J* = 17.1 Hz, 1H), 5.25 (d, *J* = 10.3 Hz, 1H), 4.60 (d, *J* = 5.4 Hz, 2H), 4.50 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.96, 149.29, 146.36, 144.47, 136.74, 136.19, 133.41, 133.09, 130.37, 129.45, 128.31, 127.46, 126.30, 121.13, 118.08, 48.96, 39.00, 21.64.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_3S$ 381.1271; Found 381.1268.



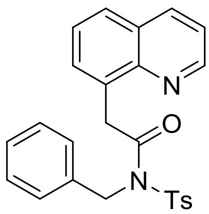
3da 90%

White solid, m. p. 156-158 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.71 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.06 (s, 1H), 5.00 (d, *J* = 2.1 Hz, 1H), 4.57 (s, 2H), 4.43 (s, 2H), 2.42 (s, 3H), 1.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.22, 149.30, 146.31, 144.42, 140.54, 136.64, 136.19, 133.28, 130.28, 129.28, 128.56, 128.33, 127.46, 126.30, 121.14, 111.89, 51.74, 38.64, 21.64, 20.27.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_3S$ 395.1436; Found 395.1422.



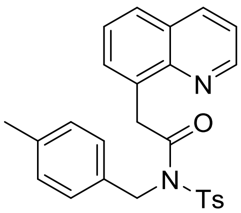
3ea 89%

Off-white solid, m. p. 160-161 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.08 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 – 7.38 (m, 4H), 7.35 – 7.26 (m, 4H), 7.26 – 7.21 (m, 2H), 5.23 (s, 2H), 4.47 (s, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.32, 149.13, 146.32, 144.44, 136.93, 136.70, 136.15, 133.55, 130.50, 129.41, 128.52, 128.27, 128.22, 127.95, 127.56, 127.47, 126.29, 121.10, 49.81, 39.52, 21.64.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_3S$ 431.1426; Found 431.1427.



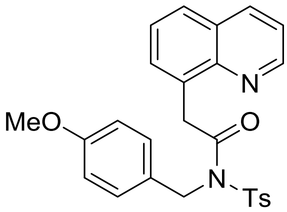
3fa 85%

Off-white solid, m. p. 159-161 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.69 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.32 (dd, *J* = 8.0, 5.1 Hz, 3H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.19 (s, 2H), 4.46 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.32, 149.15, 146.37, 144.36, 137.22, 136.81, 136.12, 133.94, 133.58, 130.46, 129.38, 129.18, 128.27, 128.22, 127.93, 127.42, 126.27, 121.09, 49.64, 39.46, 21.62, 21.16.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}N_2O_3S$ 445.1583; Found 445.1589.



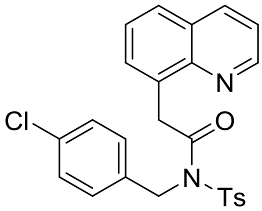
3ga 83%

Off-white solid, m. p. 162-164 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.08 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.70 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.33 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.26 – 7.21 (m, 3H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 2H), 4.47 (s, 2H), 3.80 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.32, 159.08, 149.12, 146.35, 144.36, 136.84, 136.14, 133.62, 130.47, 129.67, 129.42, 129.08, 128.26, 128.13, 127.44, 126.29, 121.09, 113.82, 55.34, 49.26, 39.57, 21.63.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}N_2O_4S$ 461.1533; Found 461.1537.



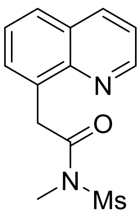
3ha 90%

White solid, m. p. 166-167 °C

¹H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.5, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.71 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.48 (d, *J* = 6.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.29 – 7.23 (m, 4H), 5.14 (s, 2H), 4.50 (s, 2H), 2.41 (s, 3H).

¹³C NMR (101 MHz, $CDCl_3$) δ 172.25, 149.09, 146.32, 144.67, 136.64, 136.18, 135.42, 133.48, 133.38, 130.52, 129.55, 128.55, 128.28, 128.08, 127.52, 126.29, 121.13, 49.12, 39.67, 21.64.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}ClN_2O_3S$ 465.1041; Found 465.1044.



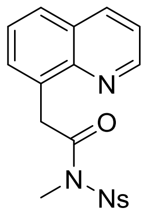
3ia 91%

White solid, m. p. 132-133 °C

¹H NMR (400 MHz, $CDCl_3$) δ 8.85 – 8.77 (m, 1H), 8.16 (dt, *J* = 8.2, 1.3 Hz, 1H), 7.79 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.53 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.41 (ddd, *J* = 8.3, 4.2, 0.9 Hz, 1H), 4.54 (s, 2H), 3.46 (d, *J* = 1.0 Hz, 3H), 3.40 (d, *J* = 0.9 Hz, 3H).

¹³C NMR (101 MHz, $CDCl_3$) δ 172.92, 149.43, 146.31, 136.49, 133.33, 130.87, 128.42, 127.68, 126.48, 121.30, 41.24, 39.20, 32.87.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}N_2O_3S$ 279.0805; Found 279.0808.



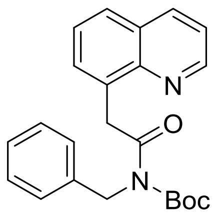
3ja 87%

Off-white solid, m. p. 160-162 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.44 – 8.36 (m, 1H), 8.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.64 (tt, *J* = 9.1, 6.6 Hz, 2H), 7.55 (d, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.35 (dd, J = 8.3, 4.2 Hz, 1H), 4.44 (s, 2H), 3.61 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.40, 149.65, 147.84, 146.20, 136.27, 134.40, 134.31, 133.16, 132.44, 132.10, 130.33, 128.35, 127.78, 126.32, 124.42, 121.36, 38.44, 34.04.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}N_3O_5S$ 386.0815; Found 386.0811.



3ka 85%

Off-white solid, m. p. 153-155 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 – 8.82 (m, 1H), 8.12 (dt, *J* = 8.2, 1.2 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.35 (dd, *J* = 12.6, 8.0 Hz, 3H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.20 (m, 1H), 4.93 (s, 2H), 4.83 (s, 2H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.79, 153.41, 149.43, 146.90, 138.49, 136.16, 135.03, 130.54, 128.33, 128.21, 127.78, 127.21, 126.98, 126.23, 121.02, 83.21, 47.71, 41.46, 27.97.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{25}N_2O_3$ 377.1866; Found 377.1862.

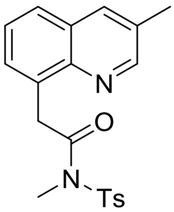
3la 82%

Off-white solid, m. p. 154-156 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.70 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.54 – 7.45 (m, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.29 – 7.17 (m, 5H), 5.04 (s, 2H), 4.32 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.51, 174.54, 149.45, 146.46, 137.51, 136.19, 136.15, 134.24, 132.19, 130.82, 128.66, 128.58, 128.41, 128.30, 127.94, 127.41, 127.27, 126.27, 121.15, 49.69, 41.23.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O_2$ 381.1605; Found 381.1601.



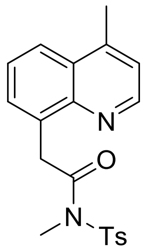
3ab 79%

Off-white solid, m. p. 150-151 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.1 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.90 – 7.84 (m, 1H), 7.65 (dd, *J* = 6.3, 3.3 Hz, 1H), 7.42 (d, *J* = 6.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.61 (s, 2H), 3.36 (s, 2H), 2.48 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.28, 151.41, 144.73, 144.55, 136.31, 134.84, 133.21, 130.49, 129.68, 129.30, 128.14, 127.88, 126.85, 126.32, 39.37, 33.36, 21.66, 18.67.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}N_2O_3S$ 369.1279; Found 369.1272.



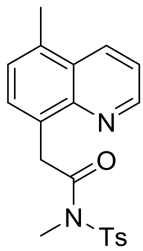
3ac 83%

Off-white solid, m. p. 149-151 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.3 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.92 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 4.3 Hz, 1H), 4.62 (s, 2H), 3.36 (s, 3H), 2.67 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.36, 148.99, 146.15, 144.52, 144.44, 136.34, 133.99, 130.08, 129.65, 128.30, 127.88, 125.93, 123.49, 121.93, 39.73, 33.35, 21.65, 18.83.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}N_2O_3S$ 369.1279; Found 369.1274.



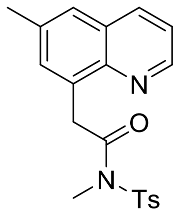
3ad 88%

Off-white solid, m. p. 153-155 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.28 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 4.58 (s, 2H), 3.36 (s, 3H), 2.65 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.46, 148.80, 146.60, 144.51, 136.36, 134.22, 132.63, 131.49, 130.01, 129.65, 127.88, 127.70, 126.68, 120.66, 39.38, 33.36, 21.65, 18.55.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}N_2O_3S$ 369.1279; Found 369.1272.



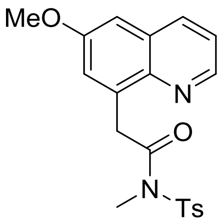
3ae 80%

Off-white solid, m. p. 155-156 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.01 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.49 (s, 1H), 7.37 – 7.28 (m, 4H), 4.59 (s, 2H), 3.36 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.31, 148.50, 145.05, 144.55, 136.31, 136.07, 135.49, 133.03, 132.57, 129.66, 128.39, 127.89, 126.26, 121.12, 39.19, 33.38, 21.64, 21.56.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}N_2O_3S$ 369.1279; Found 369.1274.



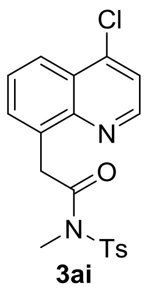
3ah 86%

Off-white solid, m. p. 159-161 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.54 (m, 1H), 7.98 (t, *J* = 7.5 Hz, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.18 (d, *J* = 2.7 Hz, 1H), 6.98 (d, *J* = 2.7 Hz, 1H), 4.58 (s, 2H), 3.89 (s, 3H), 3.36 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.91, 157.24, 146.84, 144.57, 142.73, 136.27, 135.13, 134.88, 129.70, 129.40, 127.83, 123.22, 121.43, 104.64, 55.45, 39.27, 33.33, 21.64.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}N_2O_4S$ 385.1223; Found 385.1226.



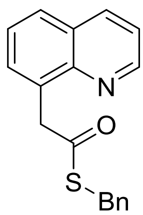
3ai 64%

Off-white solid, m. p. 161-162 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.7 Hz, 1H), 8.17 (dd, *J* = 7.4, 2.6 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.44 (d, *J* = 4.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.64 (s, 2H), 3.36 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.95, 148.70, 147.39, 144.69, 142.84, 136.22, 134.14, 131.49, 129.74, 127.80, 127.29, 126.58, 123.82, 121.28, 39.75, 33.34, 21.69.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}ClN_2O_3S$ 389.0725; Found 389.0723.



5aa 62%

Off-white solid, m. p. 118-120 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.29 – 7.16 (m, 5H), 4.56 (s, 2H), 4.10 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.46, 149.88, 146.76, 137.63, 136.23, 132.79, 130.91, 128.91, 128.53, 128.43, 127.86, 127.14, 126.24, 121.30, 45.71, 33.50.

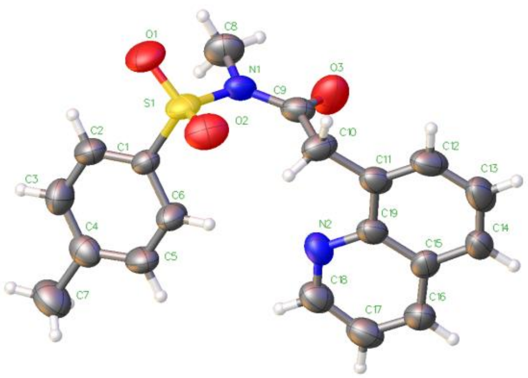
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}NOS$ 294.0955; Found 294.0949.

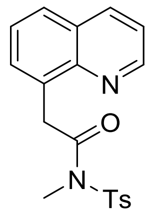
6. References

(1) For compounds **1a-b**, see: (a) Tu, Y.; Zeng, X.; Wang, H.; Zhao, J. *Org. Lett.* **2018**, *20*, 280. For compound **1c**, see: (b) Zhang, X.; Hsung, R. P.; Li, H. *Chem. Commun.* **2007**, 2420. For compound **1d**, see: (c) Hoffmann, R. W.; Brückner, D. *New. J. Chem.* **2001**, *25*, 369. For compounds **1e-g** see: (d) Wezeman, T.; Zhong, S.; Nieger, M.; Bräse, S. *Angew. Chem., Int. Ed.* **2016**, *55*, 3823. For compound **1i**, see: (e) Hu, L.; Xu, S.; Zhao, Z.; Yang, Y.; Peng, Z.; Yang, M.; Wang, C.; Zhao, J. *J. Am.*

Chem. Soc. **2016**, *138*, 13135. For compound **1j**, see: (f) Zimin, D. P.; Dar'in, D. V.; Kukushkin, V. Y.; Dubovtsev, A. Y. *J. Org. Chem.* **2021**, *86*, 1748. For compound **1k**, see: (g) Clavier, H.; Lepronier, A.; Bengobesse-Mintsa, N.; Gatineau, D.; Pellissier, H.; Giordano, L.; Tenaglia, A.; Buono, G. *Adv. Synth. Catal.* **2013**, *355*, 403. For compound **1l**, see: (h) Cassé, M.; Nisole, C.; Dossmann, H.; Gimbert, Y.; Fourquez, J.; Haberkorn, L.; Ollivier, C.; Fensterbank, L. *Sci. China Chem.* **2019**, *62*, 1542.
(2) For compounds **2b-c**, **2e-f**, **2h** and **2j-k** see: (a) Zhang, Y.; Zhang, S.; Xu, G.; Li, M.; Tang, C.; Fan, W. *Org. Biomol. Chem.* **2019**, *17*, 309. For compounds **2d** and **2g**, see: (b) Tröster, A.; Alonso, R.; Bauer, A.; Bach, T. *J. Am. Chem. Soc.* **2016**, *138*, 7808. For compound **2i**, see: (c) Kim, D.; Ghosh, P.; Kwon, N. Y.; Han, S. H.; Han, S.; Mishra, N. K.; Kim, S.; Kim, I. S. *J. Org. Chem.* **2020**, *85*, 2476.
(3) Zhang, Y.-Q.; Zhu, X.-Q.; Chen, Y.-B.; Tan, T.-D.; Yang, M.-Y.; Ye, L.-W. *Org. Lett.* **2018**, *20*, 7721.

7. X-Ray crystal data of 3aa (CCDC 2061599)





3aa

Table 1 Crystal data and structure refinement for exp_7989.

Identification code	exp_7989
Empirical formula	$C_{19}H_{18}N_2O_3S$
Formula weight	354.432
Temperature/K	293
Crystal system	monoclinic
Space group	I2/a
a/Å	27.124(3)
b/Å	7.6958(15)
c/Å	16.5624(16)
α/°	90
β/°	92.951(11)
γ/°	90
Volume/Å^3	3452.7(9)
Z	8
ρ_{calc}g/cm^3	1.364
μ/mm^{-1}	0.208
F(000)	1489.7
Crystal size/mm^3	0.23 × 0.21 × 0.11
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.92 to 50
Index ranges	$-22 \le h \le 36$, $-10 \le k \le 9$, $-21 \le l \le 22$
Reflections collected	9517
Independent reflections	2910 [R_{int} = 0.0761, R_{sigma} = 0.0958]
Data/restraints/parameters	2910/0/228
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.1076, wR_2 = 0.2587
Final R indexes [all data]	R_1 = 0.1497, wR_2 = 0.2998
Largest diff. peak/hole / e $Å^{-3}$	1.55/-0.53

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for exp_7989. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	5947.6(5)	8046.7(18)	5348.3(7)	57.6(6)
O2	6335.9(16)	9234(5)	5569(2)	75.5(12)
O1	5662.4(17)	8294(6)	4614(2)	78.2(13)
N1	6190.1(15)	6046(6)	5312(2)	57.5(12)
N2	6759.2(15)	5610(6)	7622(3)	58.4(12)
O3	6703.4(17)	3895(6)	5651(3)	88.9(14)
C4	4886(2)	7808(7)	7395(3)	57.0(14)
C1	5533.7(18)	7907(6)	6139(3)	44.6(12)
C5	5391(2)	7637(8)	7544(3)	62.8(15)
C9	6630(2)	5446(7)	5689(3)	54.6(14)
C19	7227.4(19)	5288(7)	7418(3)	54.9(14)
C15	7584.8(19)	4499(7)	7969(3)	53.6(14)
C6	5715(2)	7731(8)	6926(3)	60.3(15)
C10	7003(2)	6702(8)	6075(3)	61.6(15)
C2	5043(2)	8076(8)	5970(3)	66.5(17)
C11	7371.7(18)	5790(8)	6646(3)	56.8(14)
C18	6638(2)	5185(8)	8349(4)	65.6(16)
C14	8064.8(19)	4217(9)	7728(4)	66.1(17)
C3	4720(2)	8050(8)	6605(4)	68.6(16)
C16	7430(2)	4075(8)	8748(3)	67.0(16)
C8	5862(2)	4737(9)	4924(4)	76.5(18)
C12	7842(2)	5484(9)	6434(3)	72.4(18)
C17	6958(2)	4440(9)	8935(4)	71.9(17)
C13	8188(2)	4698(10)	6969(4)	79(2)
C7	4533(2)	7784(10)	8066(4)	87(2)

Table 3 Anisotropic Displacement Parameters (Å^2 × 10^3) for exp_7989. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	68.7(10)	72.6(10)	31.1(7)	-2.7(7)	-0.4(6)	7.2(6)
O2	92(3)	67(3)	67(3)	-27(2)	4(2)	10(2)
O1	91(3)	100(3)	43(2)	3(2)	-3(2)	17(2)
N1	51(2)	81(3)	41(2)	-2(2)	-0.8(19)	-19(2)
N2	42(2)	69(3)	64(3)	3(2)	8(2)	-11(2)
O3	91(3)	74(3)	99(4)	6(3)	-27(3)	-24(2)
C4	66(4)	47(3)	58(3)	6(3)	13(3)	1(2)
C1	48(3)	50(3)	35(2)	3(2)	-6(2)	-3(2)
C5	75(4)	75(4)	38(3)	13(3)	0(3)	1(3)
C9	64(3)	60(3)	39(3)	-3(3)	2(2)	-13(2)
C19	50(3)	71(4)	44(3)	-1(3)	0(2)	-19(3)
C15	48(3)	59(3)	52(3)	2(2)	-11(2)	-19(3)
C6	51(3)	90(4)	39(3)	6(3)	0(2)	6(3)
C10	55(3)	87(4)	41(3)	-12(3)	-3(2)	-4(3)
C2	70(4)	86(4)	42(3)	17(3)	-8(3)	-9(3)
C11	48(3)	74(4)	49(3)	-7(3)	3(2)	-21(3)
C18	53(3)	84(4)	61(4)	-6(3)	13(3)	-13(3)
C14	48(3)	89(4)	60(4)	16(3)	-8(3)	-27(3)
C3	44(3)	88(4)	74(4)	7(3)	-3(3)	0(3)
C16	70(4)	81(4)	50(3)	19(3)	-6(3)	-18(3)
C8	84(4)	76(4)	69(4)	-10(3)	-10(3)	-23(3)
C12	60(4)	111(5)	46(3)	-9(3)	12(3)	-20(3)
C17	74(4)	84(4)	59(4)	-1(3)	14(3)	-18(3)
C13	41(3)	112(5)	84(5)	8(3)	1(3)	-36(4)
C7	82(4)	102(5)	80(5)	10(4)	29(4)	1(4)

Table 4 Bond Lengths for exp_7989.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.427(4)	C5	C6	1.385(7)
S1	O1	1.420(4)	C9	C10	1.517(7)
S1	N1	1.677(5)	C19	C15	1.431(8)
S1	C1	1.771(5)	C19	C11	1.411(7)
N1	C9	1.396(7)	C15	C14	1.398(7)
N1	C8	1.469(7)	C15	C16	1.416(8)
N2	C19	1.354(6)	C10	C11	1.513(7)
N2	C18	1.306(7)	C2	C3	1.402(8)
O3	C9	1.212(7)	C11	C12	1.360(7)
C4	C5	1.385(8)	C18	C17	1.391(9)
C4	C3	1.375(8)	C14	C13	1.368(9)
C4	C7	1.503(8)	C16	C17	1.362(8)
C1	C6	1.376(7)	C12	C13	1.395(9)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_7989. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	C2	1.353(8)				

Table 5 Bond Angles for exp_7989.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	119.7(3)	C15	C19	N2	122.1(5)
N1	S1	O2	108.1(2)	C11	C19	N2	118.9(5)
N1	S1	O1	106.8(2)	C11	C19	C15	118.9(5)
C1	S1	O2	109.7(2)	C14	C15	C19	119.6(5)
C1	S1	O1	107.7(3)	C16	C15	C19	117.1(5)
C1	S1	N1	103.6(2)	C16	C15	C14	123.2(5)
C9	N1	S1	128.0(4)	C5	C6	C1	119.7(5)
C8	N1	S1	114.6(4)	C11	C10	C9	111.9(5)
C8	N1	C9	116.9(5)	C3	C2	C1	119.3(5)
C18	N2	C19	117.9(5)	C10	C11	C19	119.2(4)
C3	C4	C5	117.0(5)	C12	C11	C19	119.6(5)
C7	C4	C5	121.9(5)	C12	C11	C10	121.2(5)
C7	C4	C3	121.1(6)	C17	C18	N2	124.7(5)
C6	C1	S1	119.8(4)	C13	C14	C15	119.6(6)
C2	C1	S1	119.7(4)	C2	C3	C4	122.0(5)
C2	C1	C6	120.3(5)	C17	C16	C15	119.1(6)
C6	C5	C4	121.6(5)	C13	C12	C11	121.3(6)
O3	C9	N1	116.3(5)	C16	C17	C18	119.1(6)
C10	C9	N1	120.9(5)	C12	C13	C14	120.9(5)
C10	C9	O3	122.7(5)				

Table 6 Torsion Angles for exp_7989.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N1	C9	O3	171.9(5)	C4	C5	C6	C1	-3.5(7)
S1	N1	C9	C10	-11.7(5)	C4	C3	C2	C1	-1.9(7)
S1	C1	C6	C5	179.5(4)	C9	C10	C11	C19	-76.9(5)
S1	C1	C2	C3	-176.8(4)	C9	C10	C11	C12	104.7(5)
N1	C9	C10	C11	163.5(5)	C19	C15	C14	C13	-0.0(6)
N2	C19	C15	C14	-179.2(5)	C19	C15	C16	C17	-0.4(6)
N2	C19	C15	C16	-0.6(6)	C19	C11	C12	C13	-0.7(7)
N2	C19	C11	C10	1.2(6)	C15	C14	C13	C12	0.7(7)
N2	C19	C11	C12	179.6(5)	C15	C16	C17	C18	1.4(7)
N2	C18	C17	C16	-1.7(7)	C10	C11	C12	C13	177.7(5)

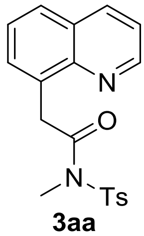
Table 6 Torsion Angles for exp_7989.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C9	C10	C11	-20.2(6)	C11	C12	C13	C14	-0.3(8)

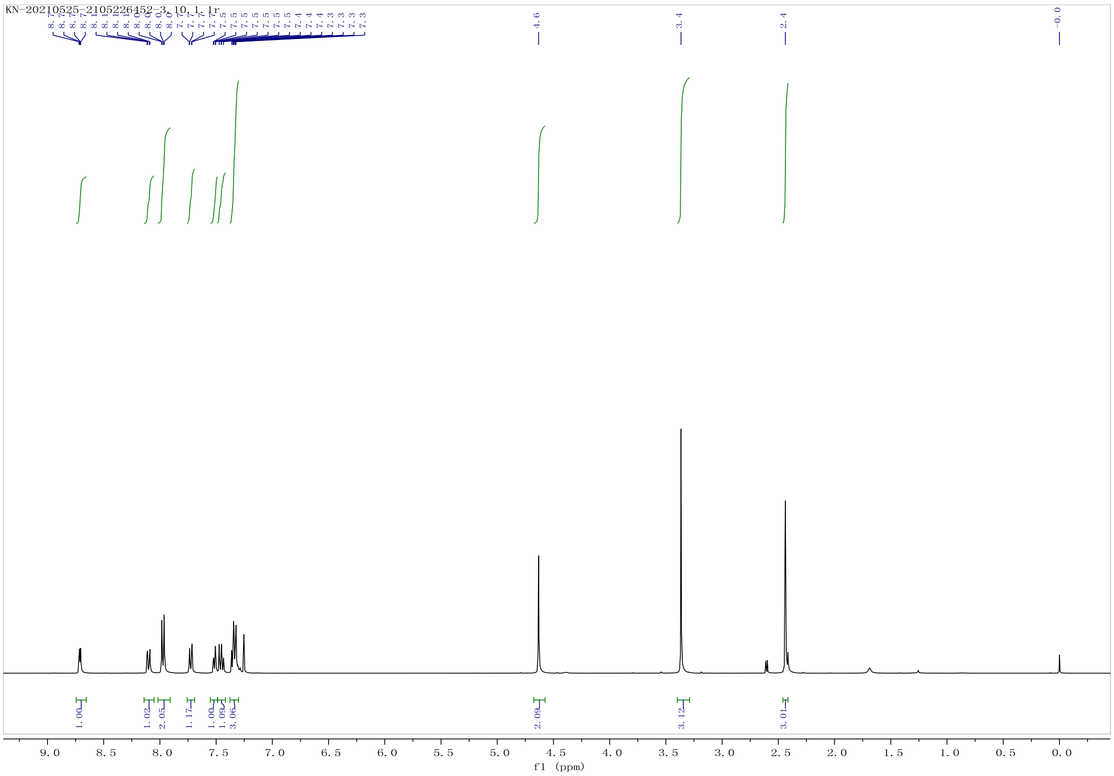
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_7989.

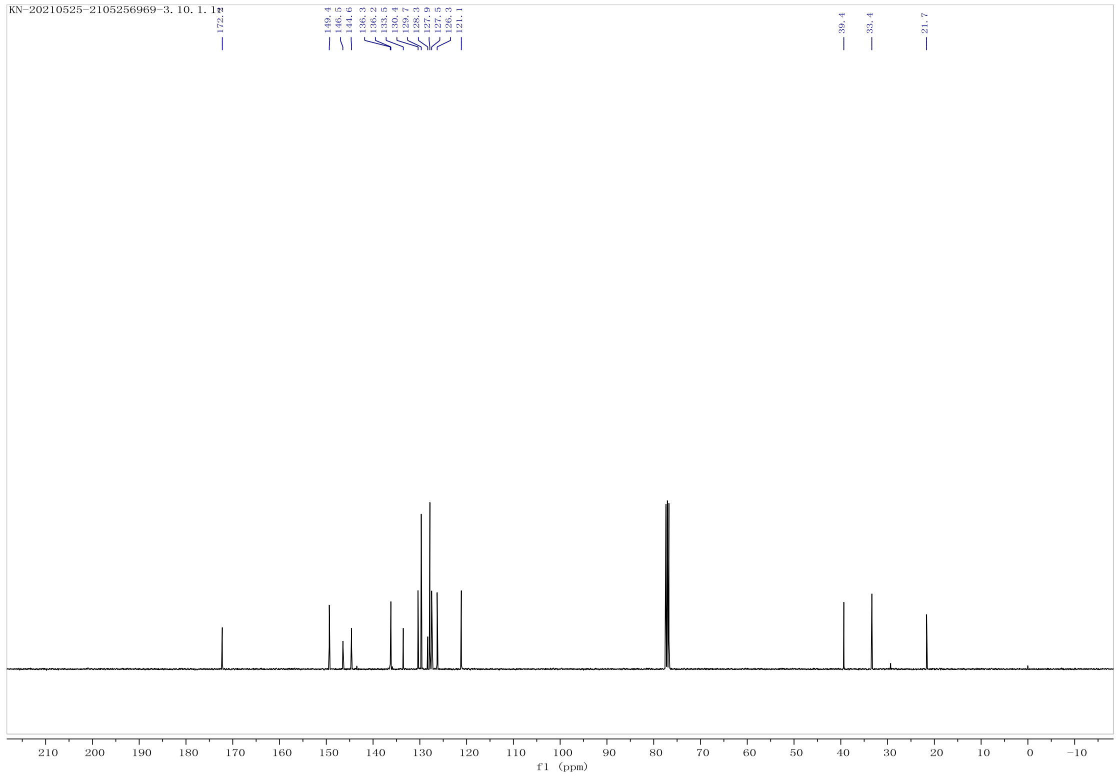
Atom	*x*	*y*	*z*	U(eq)
H5	5515(2)	7454(8)	8071(3)	75.4(18)
H6	6054(2)	7675(8)	7043(3)	72.3(18)
H10a	7177(2)	7280(8)	5655(3)	73.9(18)
H10b	6830(2)	7582(8)	6371(3)	73.9(18)
H2	4921(2)	8208(8)	5439(3)	80(2)
H18	6315(2)	5395(8)	8485(4)	78.7(19)
H14	8299.3(19)	3705(9)	8082(4)	79(2)
H3	4384(2)	8202(8)	6487(4)	82.3(19)
H16	7648(2)	3554(8)	9127(3)	80(2)
H8a	5585(9)	4540(50)	5251(15)	115(3)
H8b	5747(14)	5140(30)	4400(12)	115(3)
H8c	6040(6)	3670(20)	4870(30)	115(3)
H12	7935(2)	5805(9)	5922(3)	87(2)
H17	6851(2)	4194(9)	9447(4)	86(2)
H13	8506(2)	4499(10)	6808(4)	95(2)
H7a	4502(15)	6618(15)	8260(20)	131(3)
H7b	4657(10)	8520(50)	8499(14)	131(3)
H7c	4216(6)	8200(70)	7866(9)	131(3)

8. ^{1}H NMR and ^{13}C NMR Spectra



3aa




KN-20210525-2105256969-3.10.1.1r
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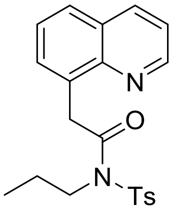
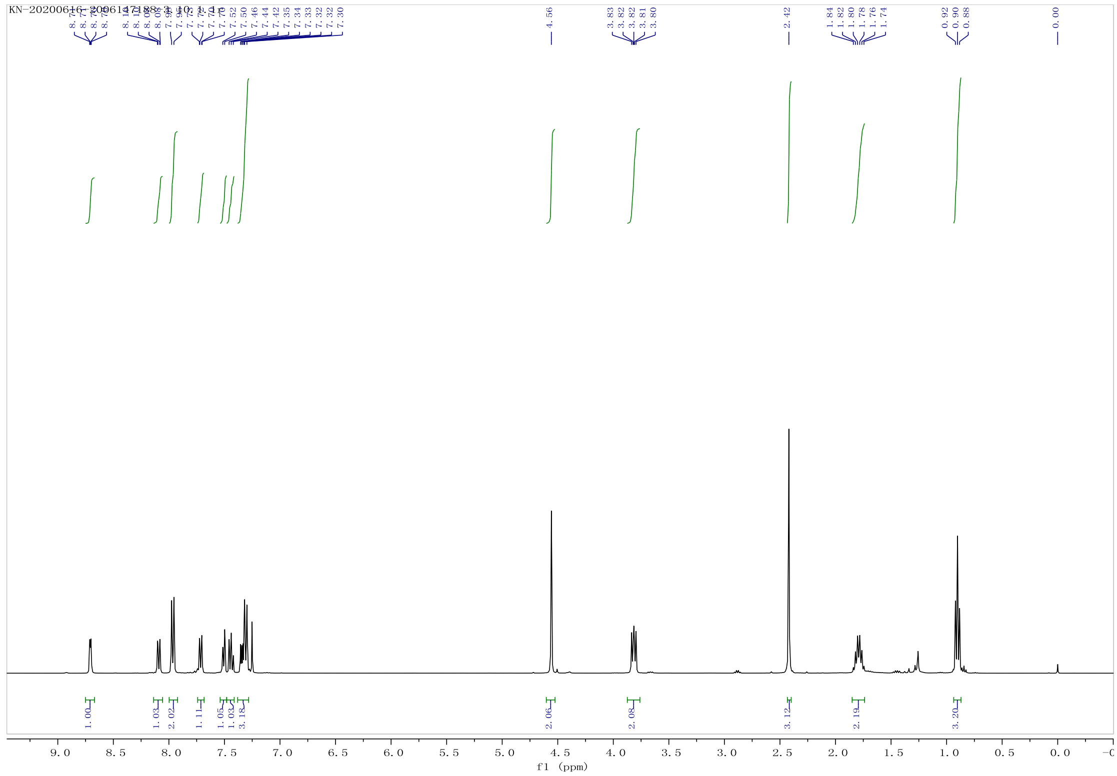
128.3
127.9
127.5
126.3
121.1
39.4
33.4
21.7
f1 (ppm)


N
O
N
Ts

3ba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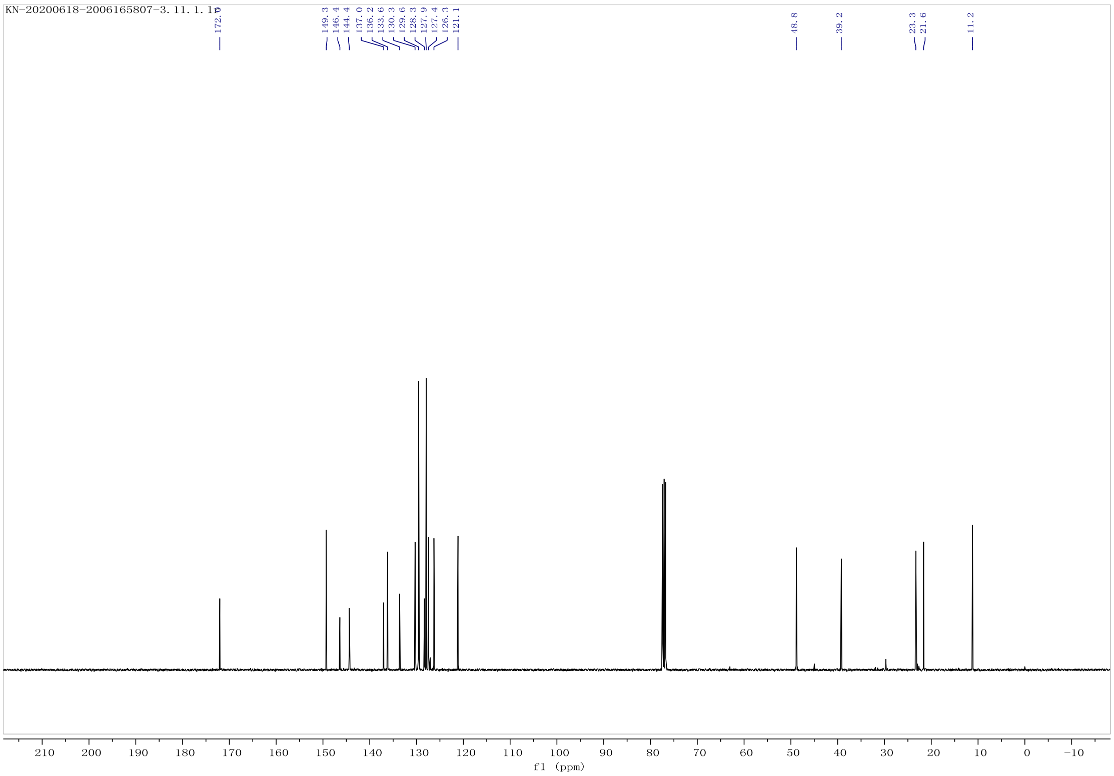
1.84
1.82
1.80
1.78
1.76
1.74
0.92
0.90
0.88
0.00
1.00
1.03
2.02
1.11
1.05
1.02
3.18
2.06
2.08
3.12
2.10
3.20
f1 (ppm)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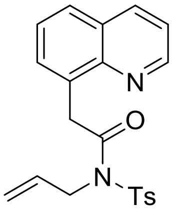
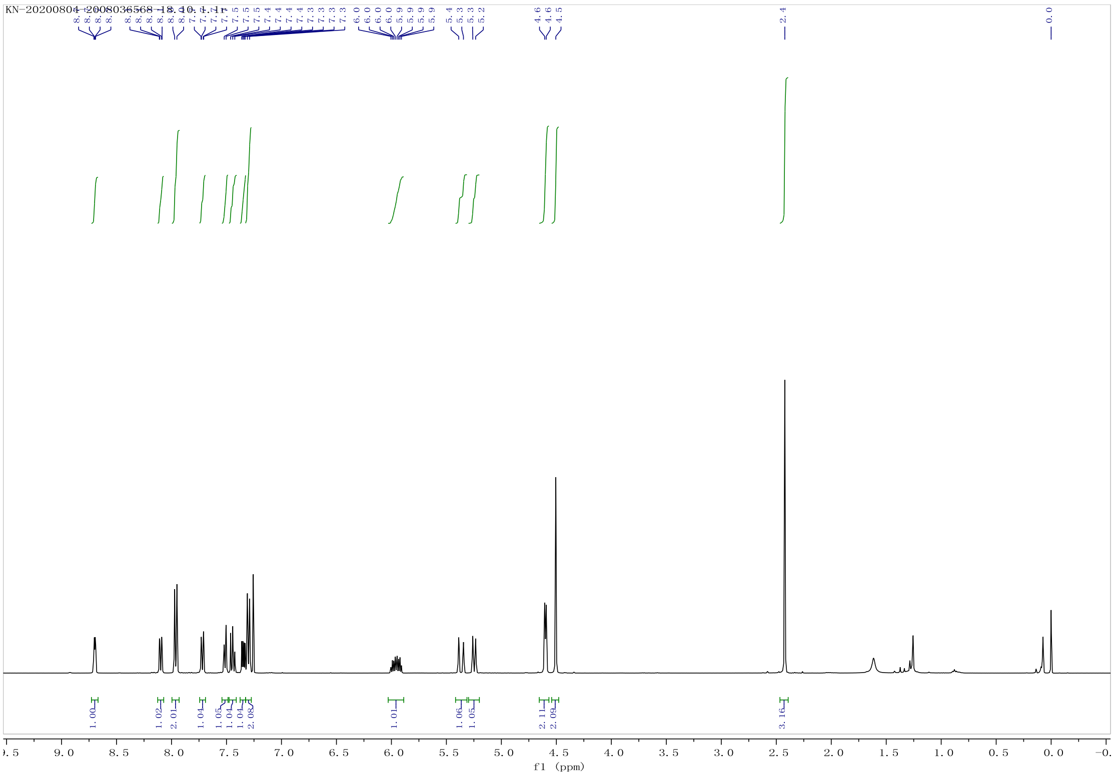
136.2
133.6
130.3
129.6
128.3
127.9
127.4
126.3
121.1
48.8
39.2
23.3
21.6
11.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


N
O
N
Ts

3ca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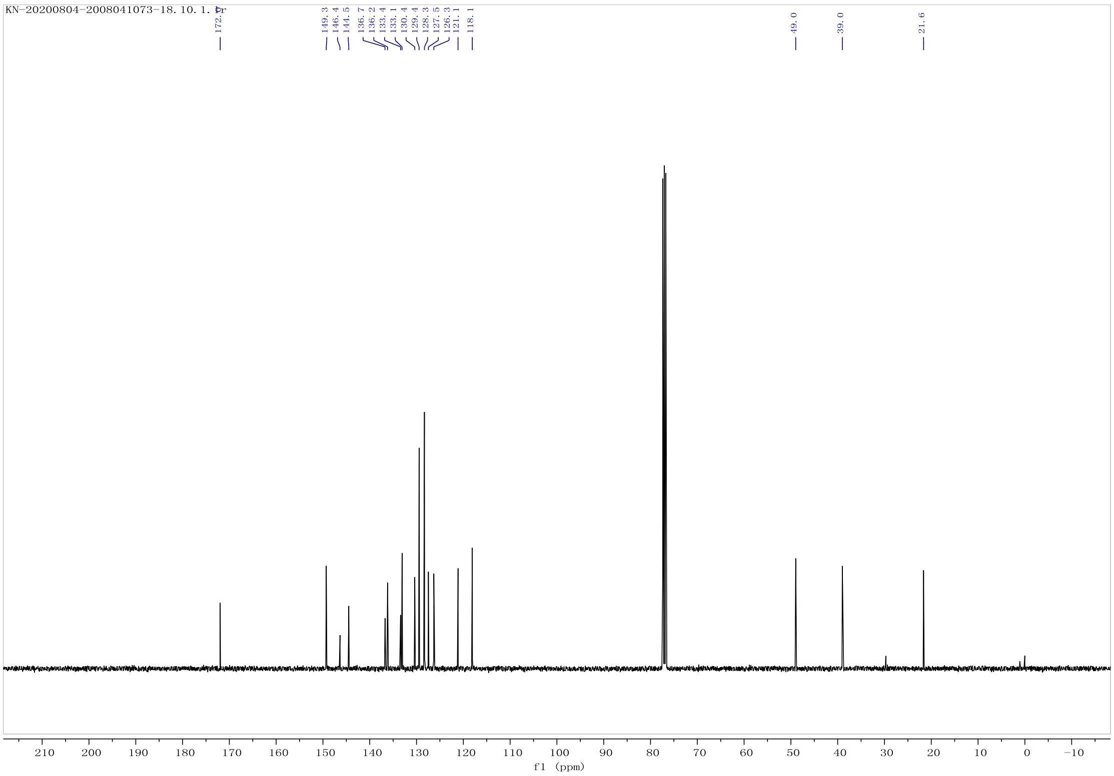
2.01
1.04
1.05
1.04
1.04
2.08
1.01
1.06
1.05
2.11
2.00
3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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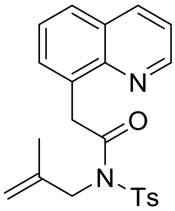
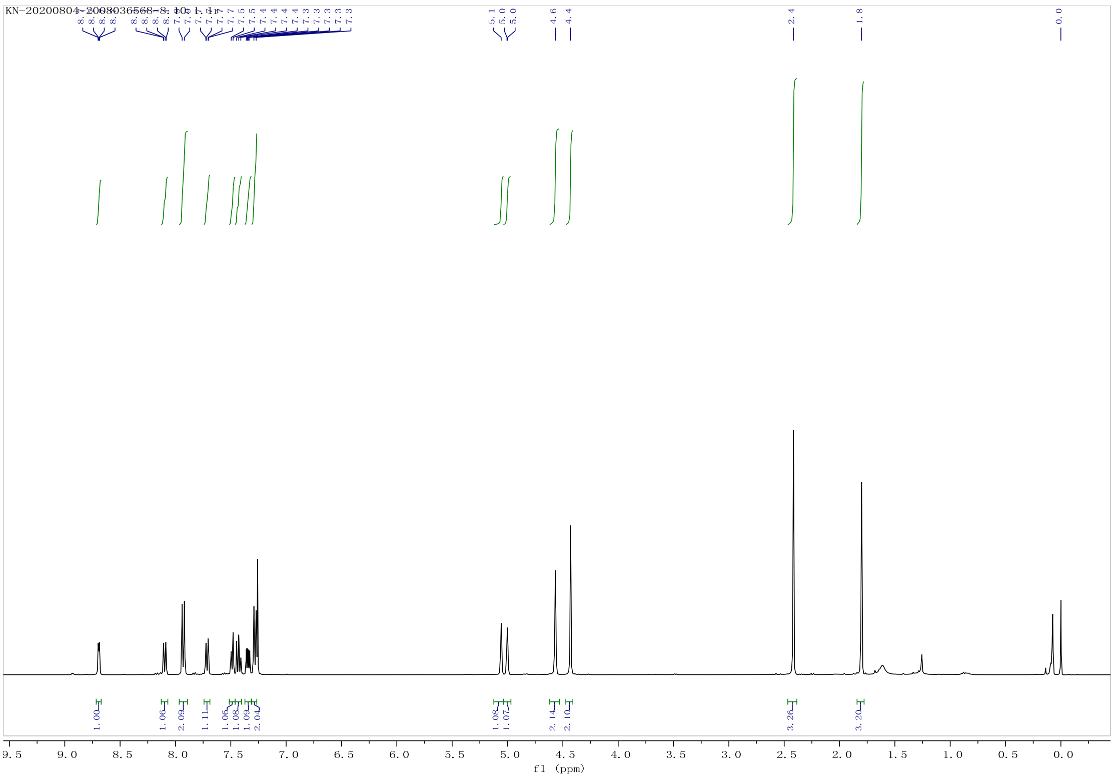
146.4
144.5
136.7
136.2
133.4
133.1
130.4
129.4
128.3
127.5
126.3
121.1
118.1
49.0
39.0
21.6
f1 (ppm)


N
O
N
Ts

3da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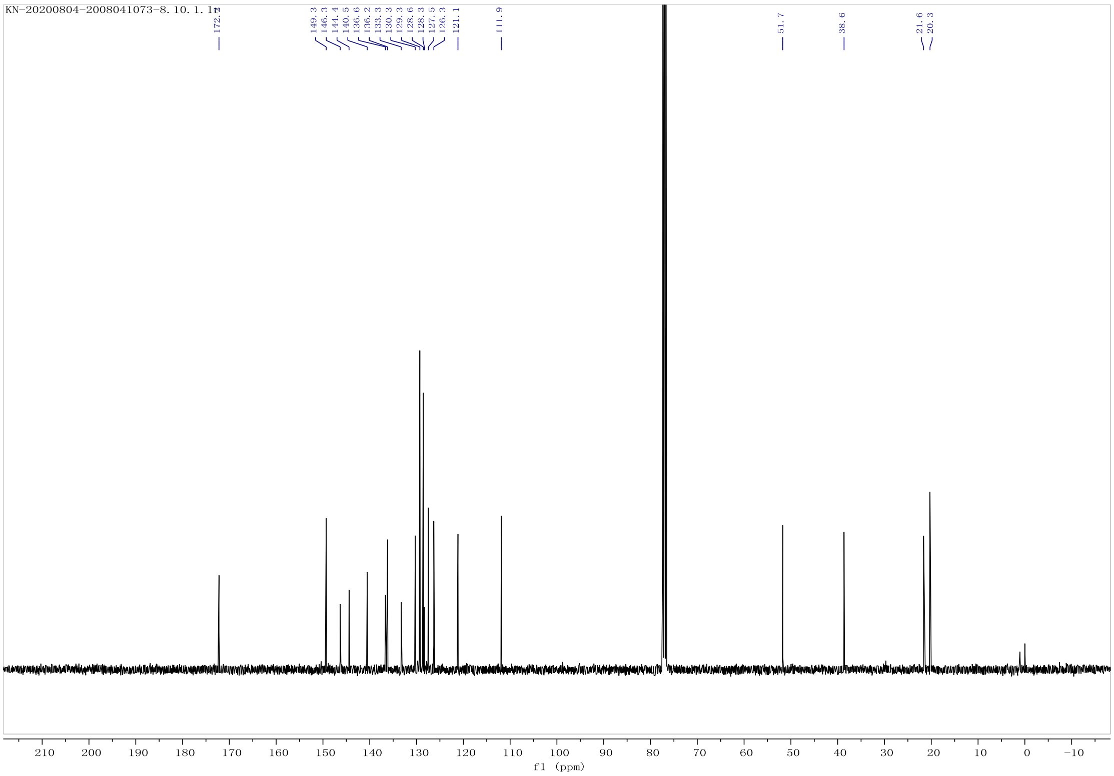
5.0
5.0
4.6
4.4
2.4
1.8
0.0
f1 (ppm)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144.4
140.5
136.6
136.2
133.3
130.3
129.3
128.6
128.3
127.5
126.3
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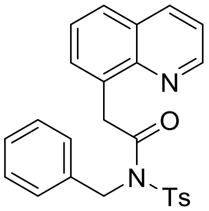
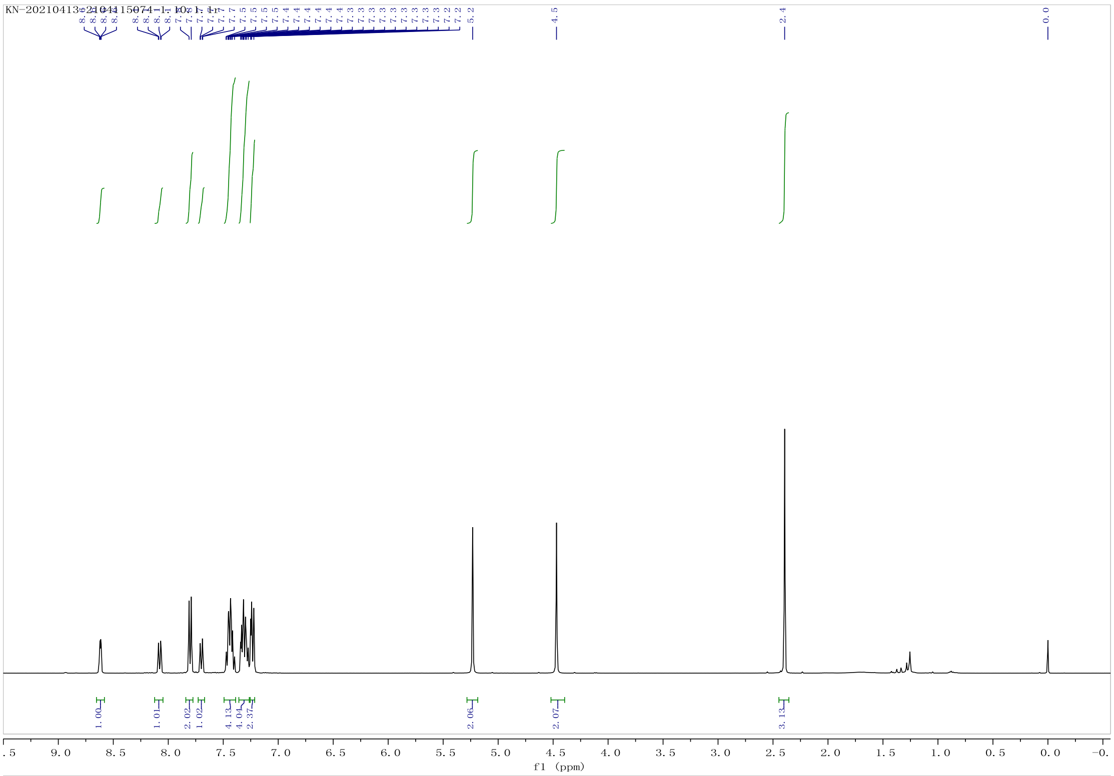
21.6
20.3
f1 (ppm)


N
O
N
Ts

3ea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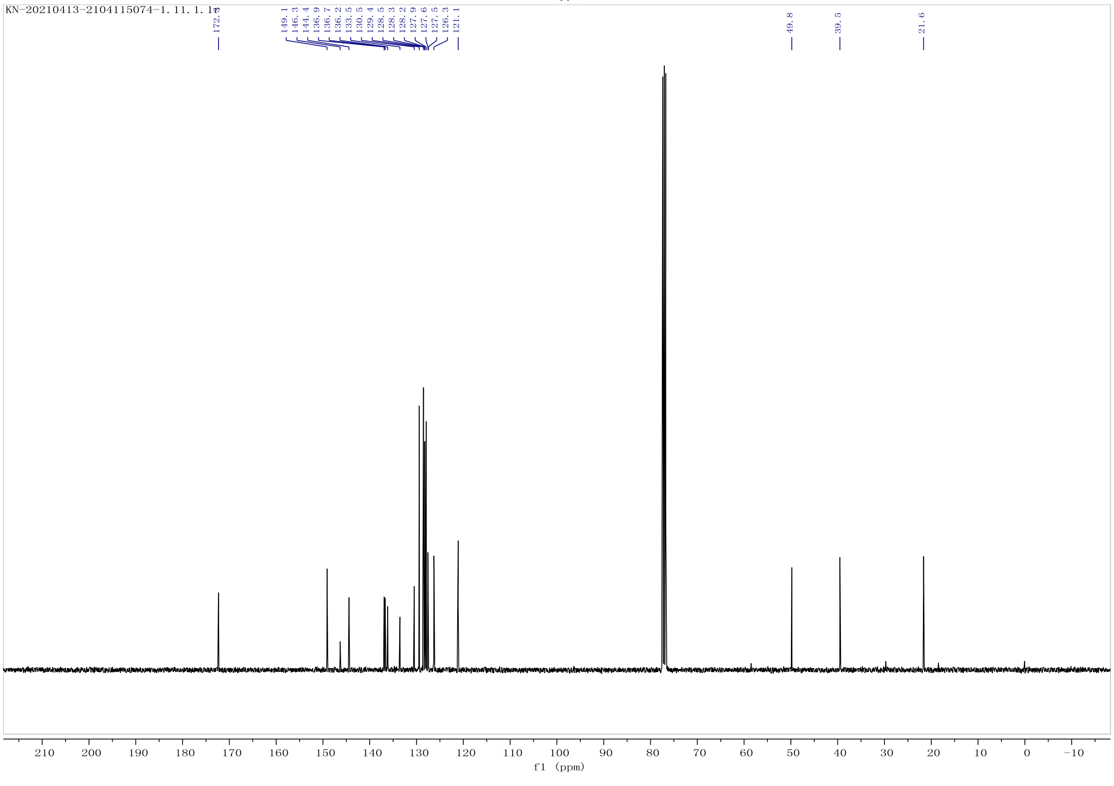
f1 (ppm)


KN-20210413-2104115074-1.11.1.1r
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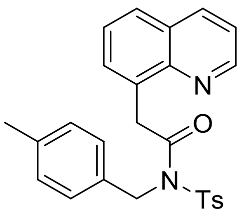
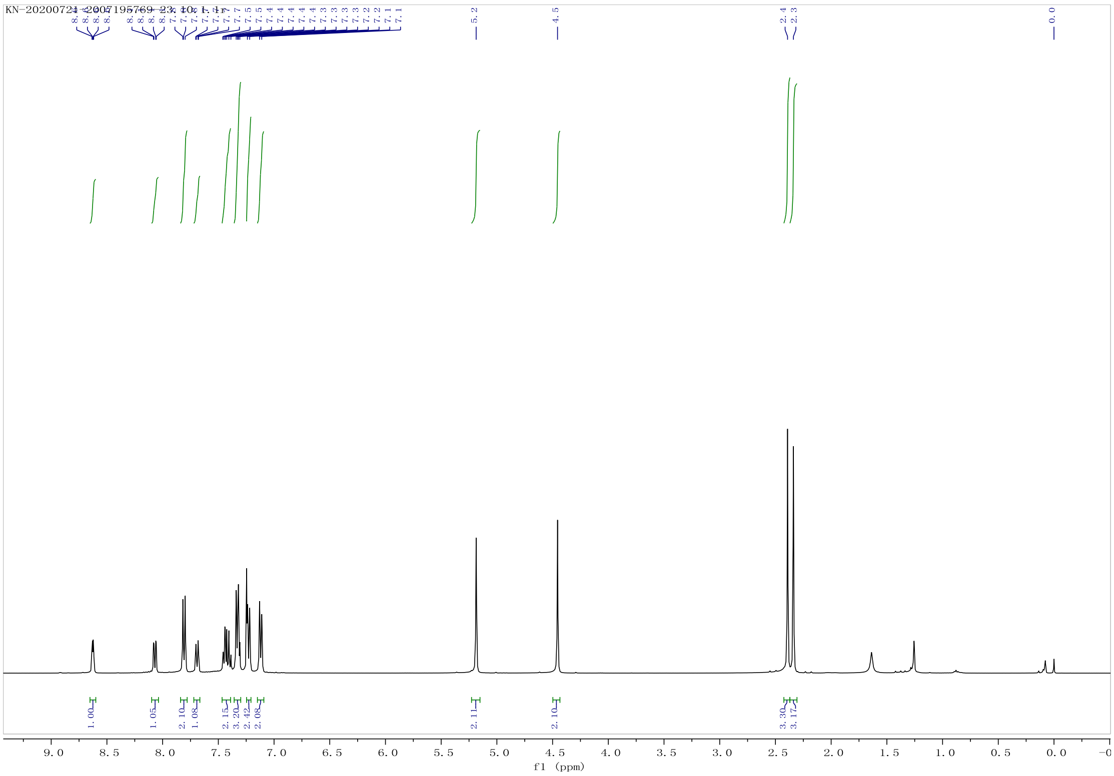
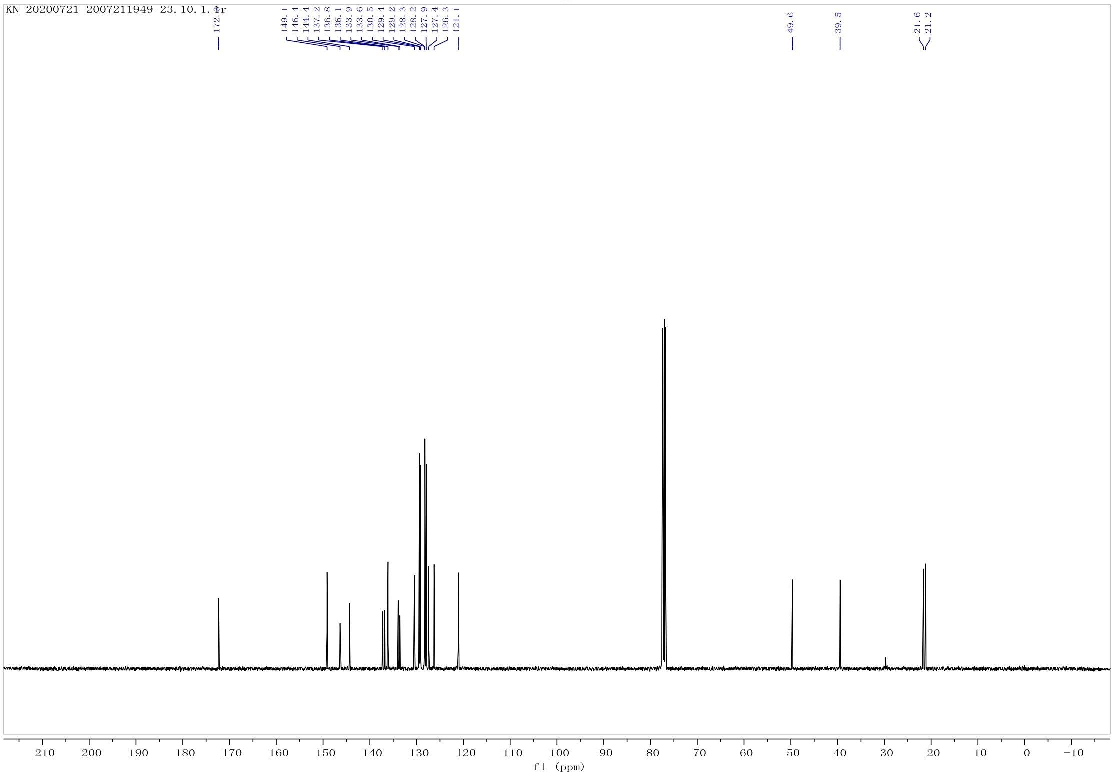
146.3
144.4
136.9
136.7
136.2
133.5
130.5
129.4
128.5
128.3
128.2
127.9
127.6
127.5
126.3
121.1
49.8
39.5
21.6
f1 (ppm)


N
O
N
Ts

3fa


KN-20200721-2007195769-23.10.1.1r
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
f1 (ppm)


KN-20200721-2007211949-23.10.1.1r
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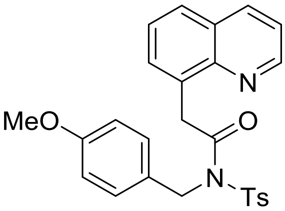
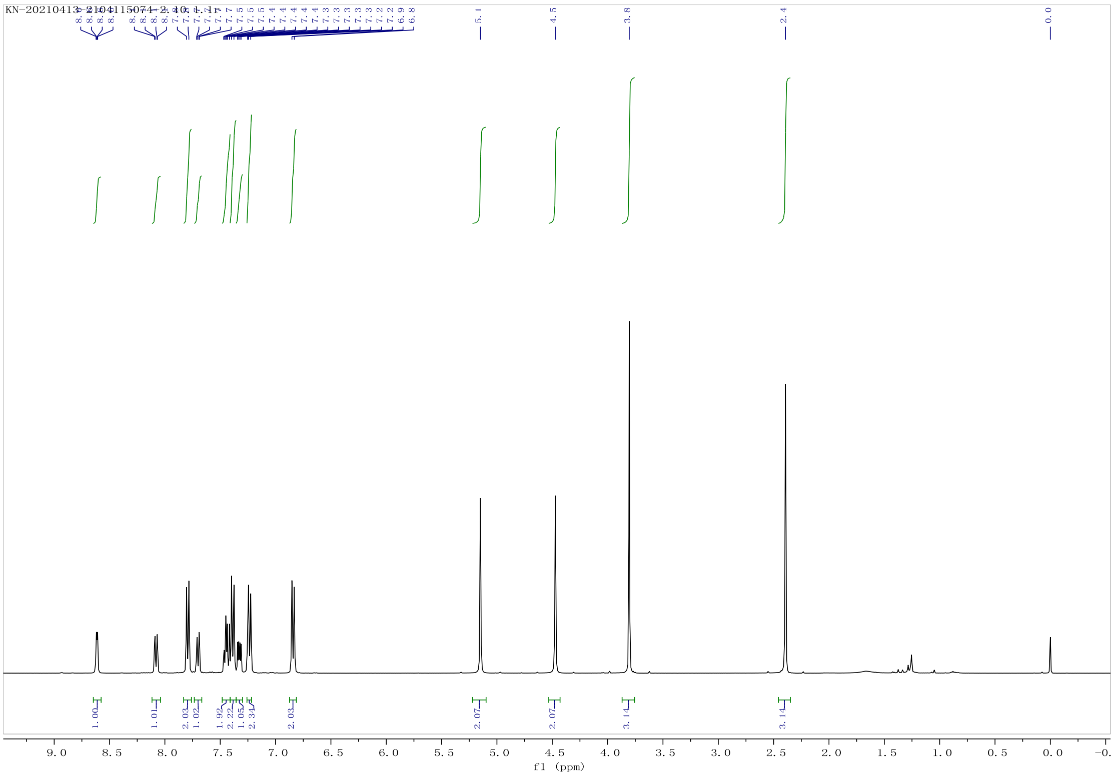
f1 (ppm)



3ga


KN-20210413-2104115074-2.10.1.1r
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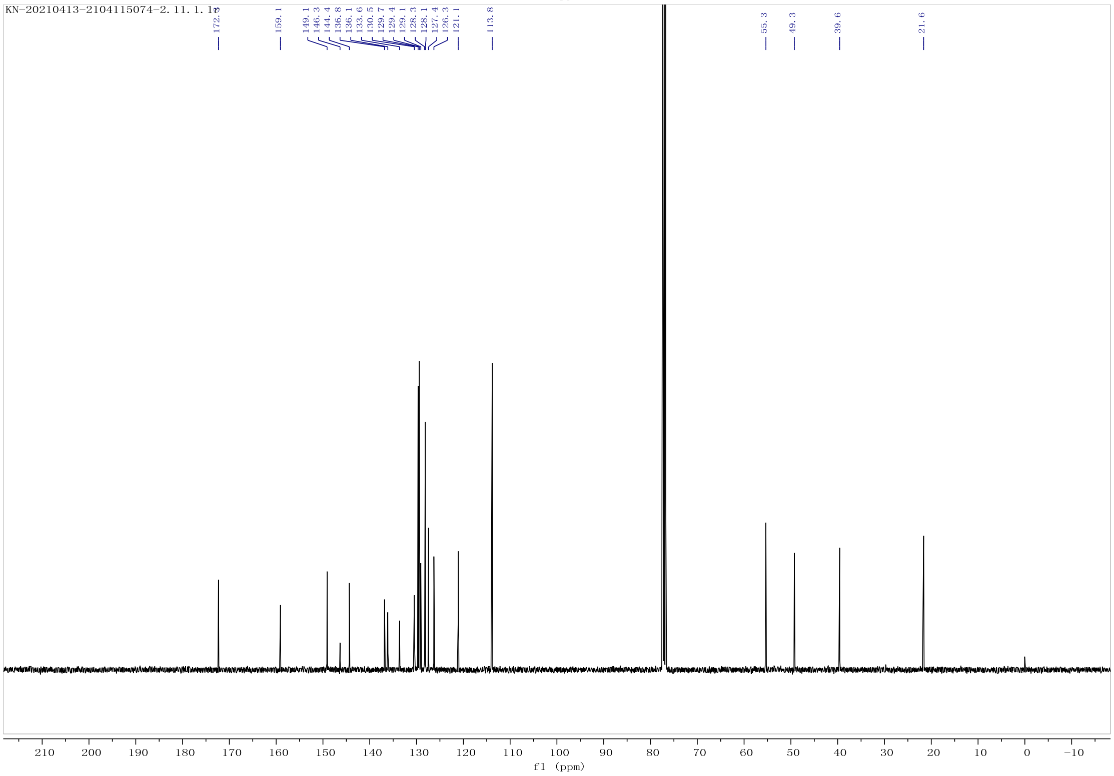
4.5
3.8
2.4
0.0
1.00
1.01
2.03
1.02
1.92
2.22
1.05
2.34
2.03
2.07
2.07
3.14
3.14
f1 (ppm)


KN-20210413-2104115074-2.11.1.1r
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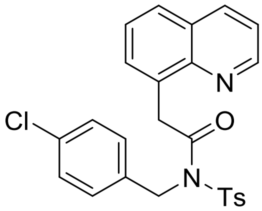
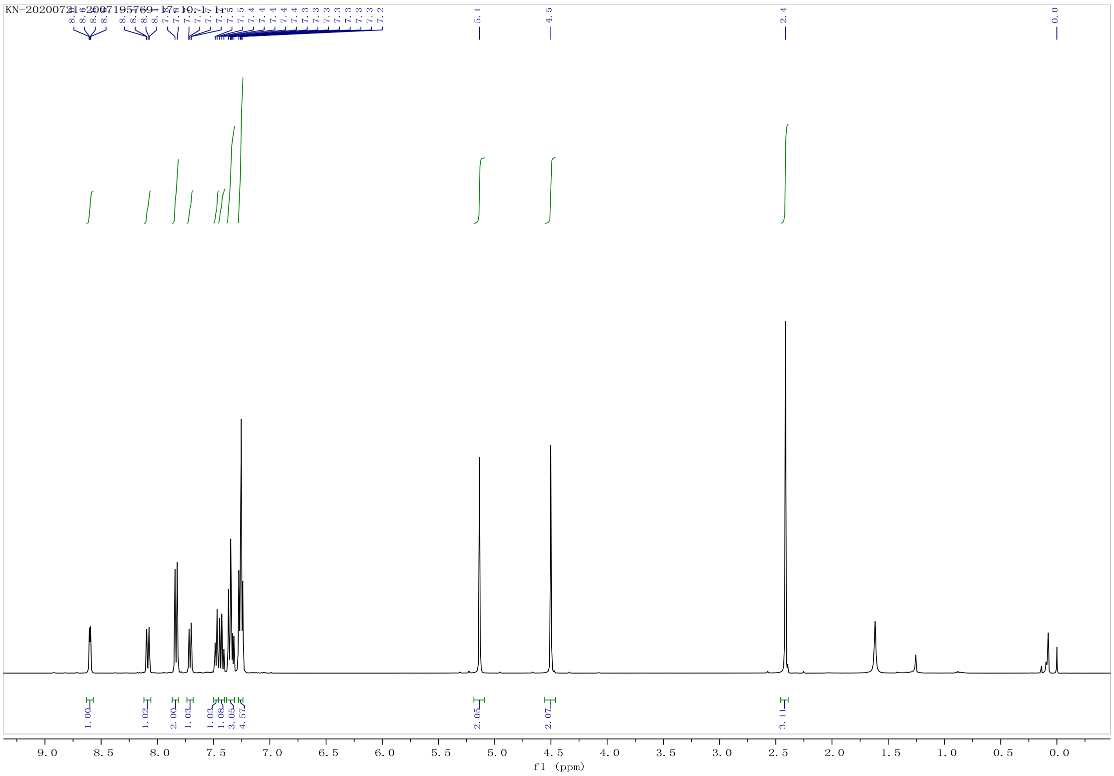
146.3
144.4
136.8
136.1
133.6
130.5
129.7
129.4
129.1
128.3
128.1
127.4
126.3
121.1
113.8
55.3
49.3
39.6
21.6
f1 (ppm)

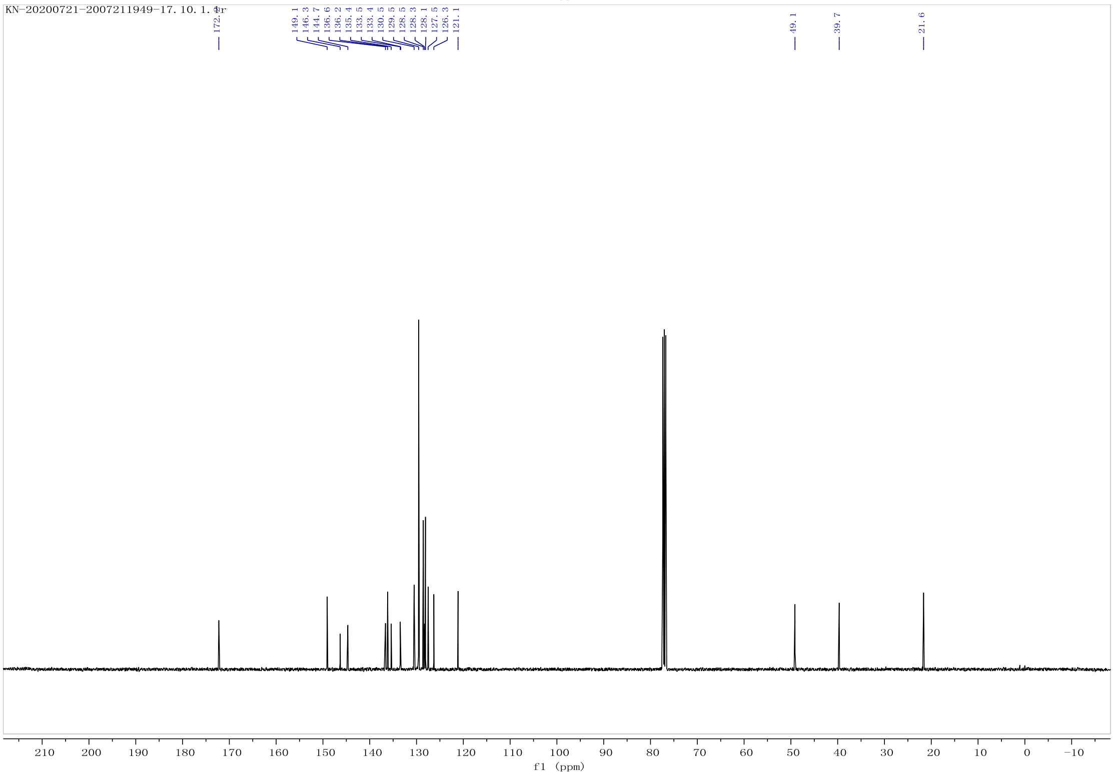


Cl
N
O
N
Ts

3ha



KN-20200721-2007195769-17.10.1.1r
f1 (ppm)



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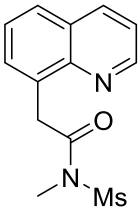
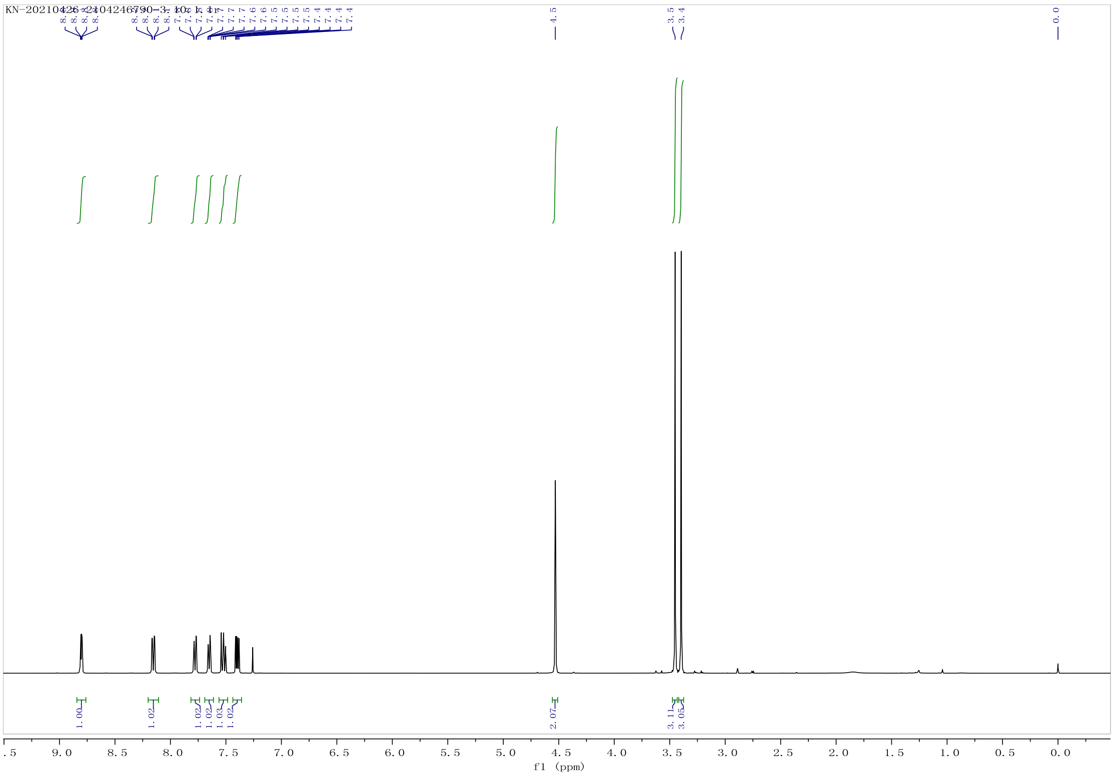
144.7
136.6
136.2
135.4
133.5
133.4
130.5
129.5
128.5
128.3
128.1
127.5
126.3
121.1
49.1
39.7
21.6
f1 (ppm)


N
O
N
Ms

3ia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3.4
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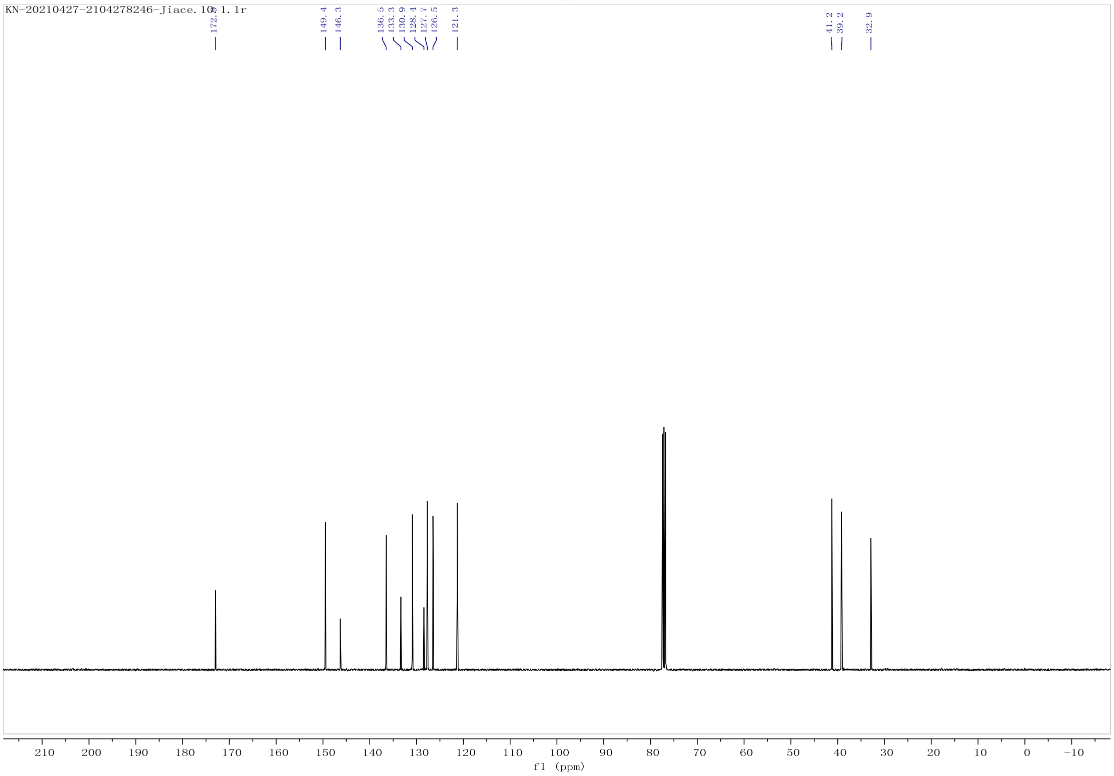
1.02
1.02
1.02
1.03
1.02
2.07
3.11
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


KN-20210427-2104278246-Jiace.10.1.1r
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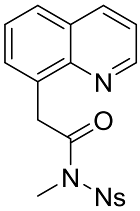
133.3
130.9
128.4
127.7
126.5
121.3
41.2
39.2
32.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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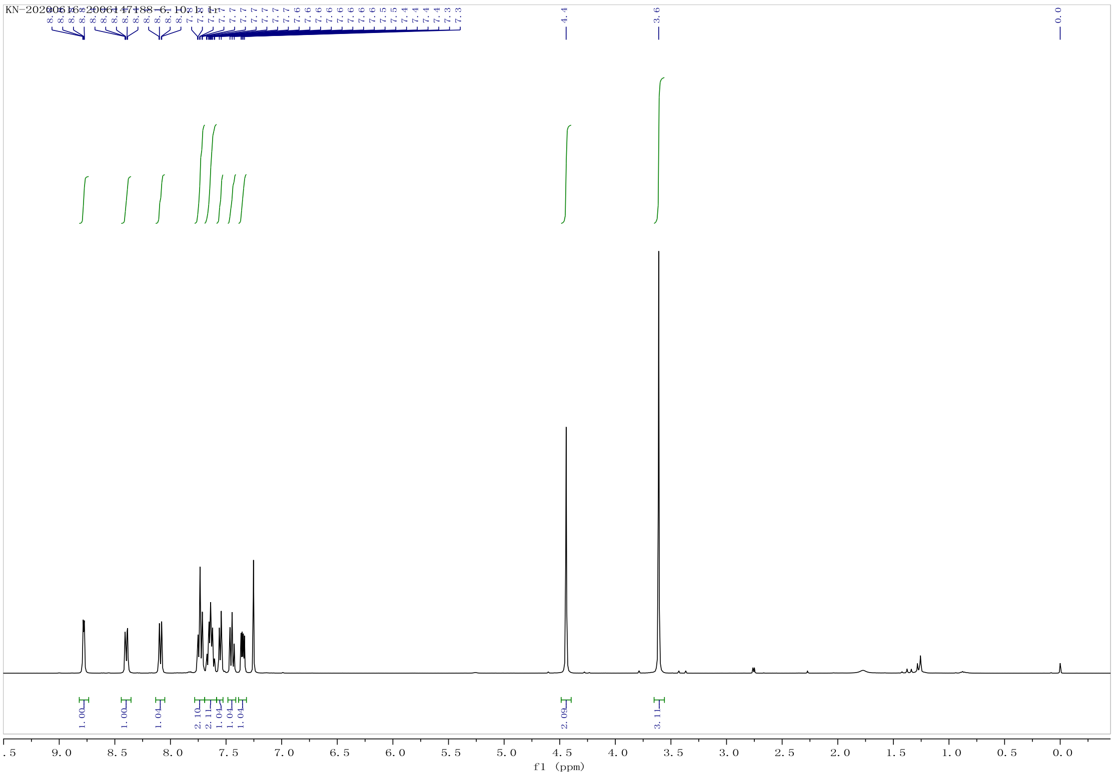
O
N
Ns

3ja



4.4
3.6
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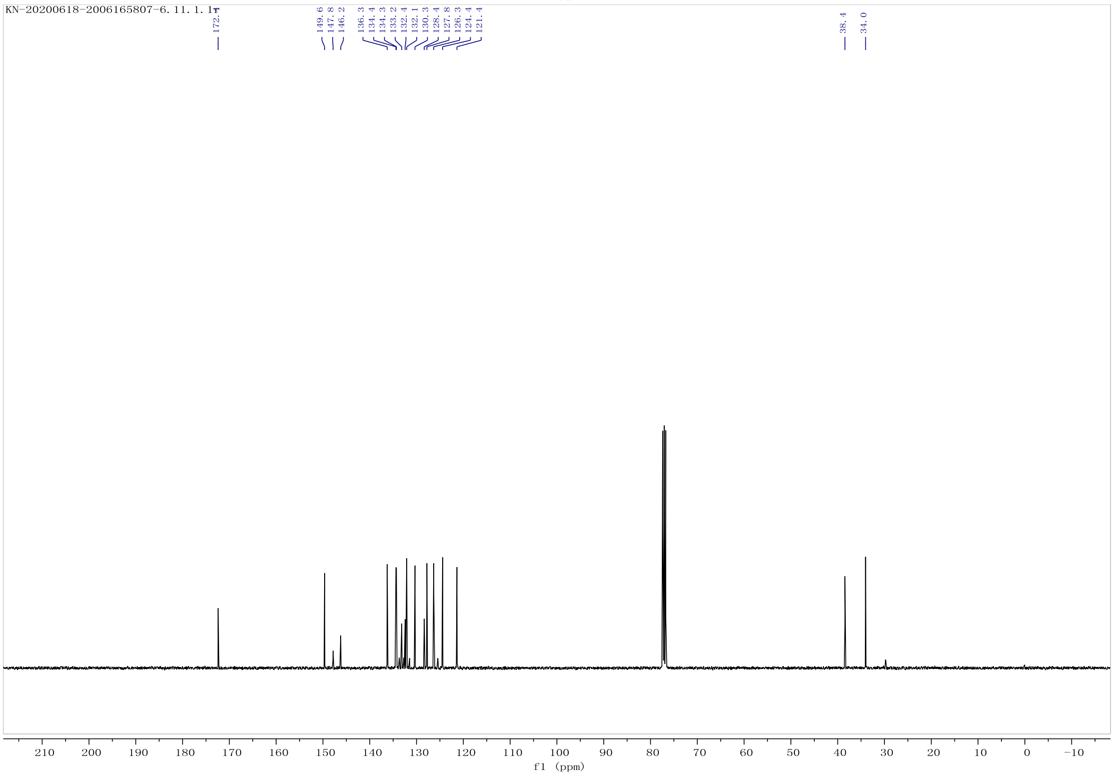
1.00
1.04
2.10
2.11
1.04
1.04
1.04
2.09
3.11
f1 (ppm)



KN-20200618-2006165807-6.11.1.1r
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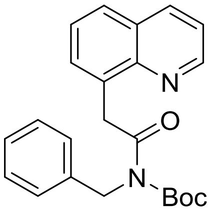
146.2
136.3
134.4
134.3
133.2
132.4
132.1
130.3
128.4
127.8
126.3
124.4
121.4
38.4
34.0
f1 (ppm)



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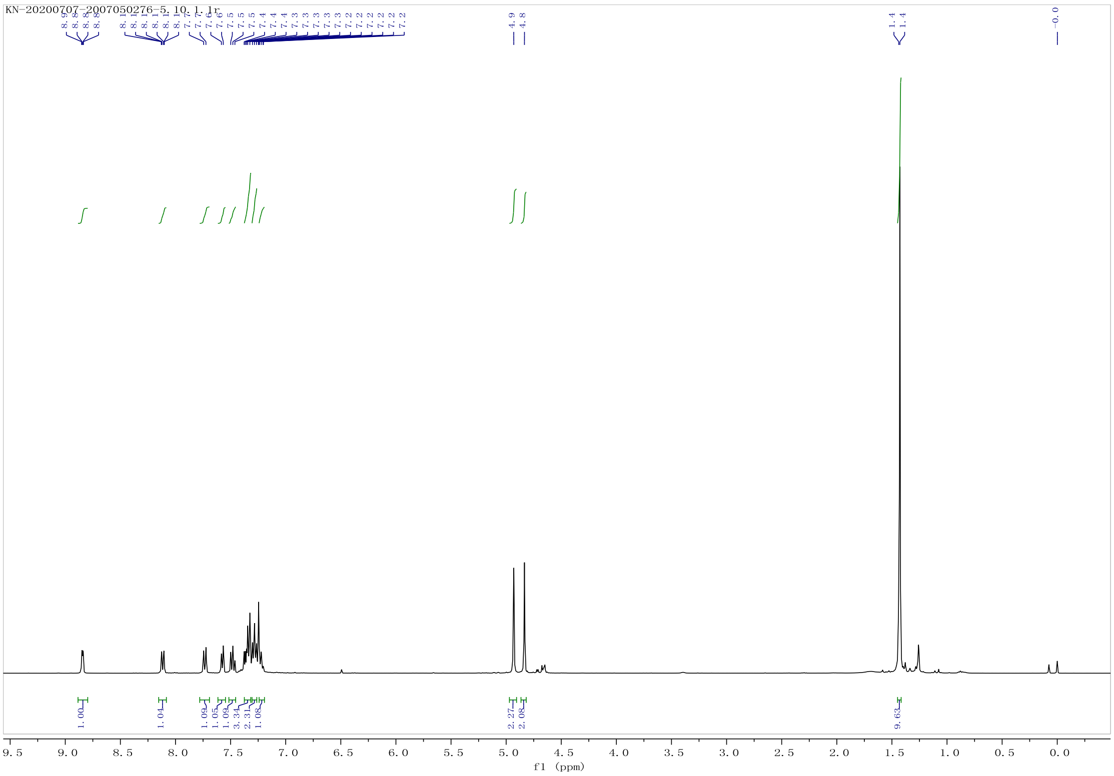

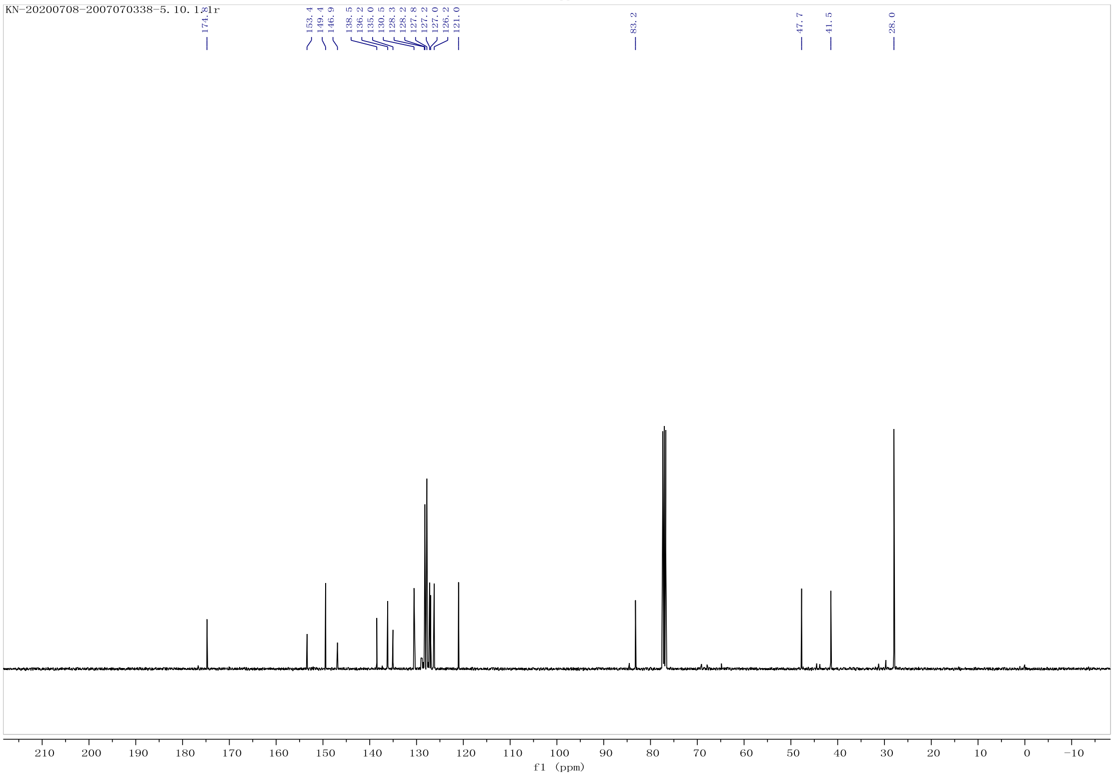

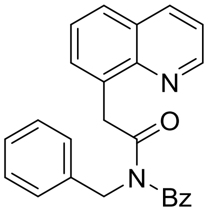

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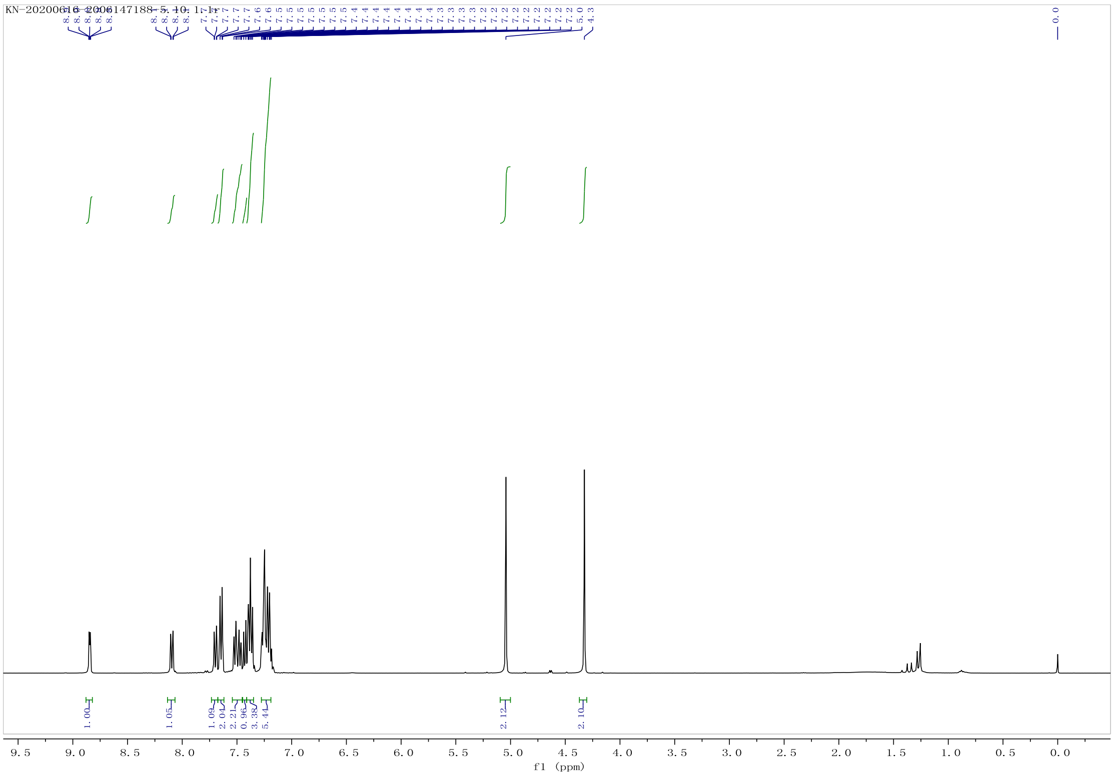
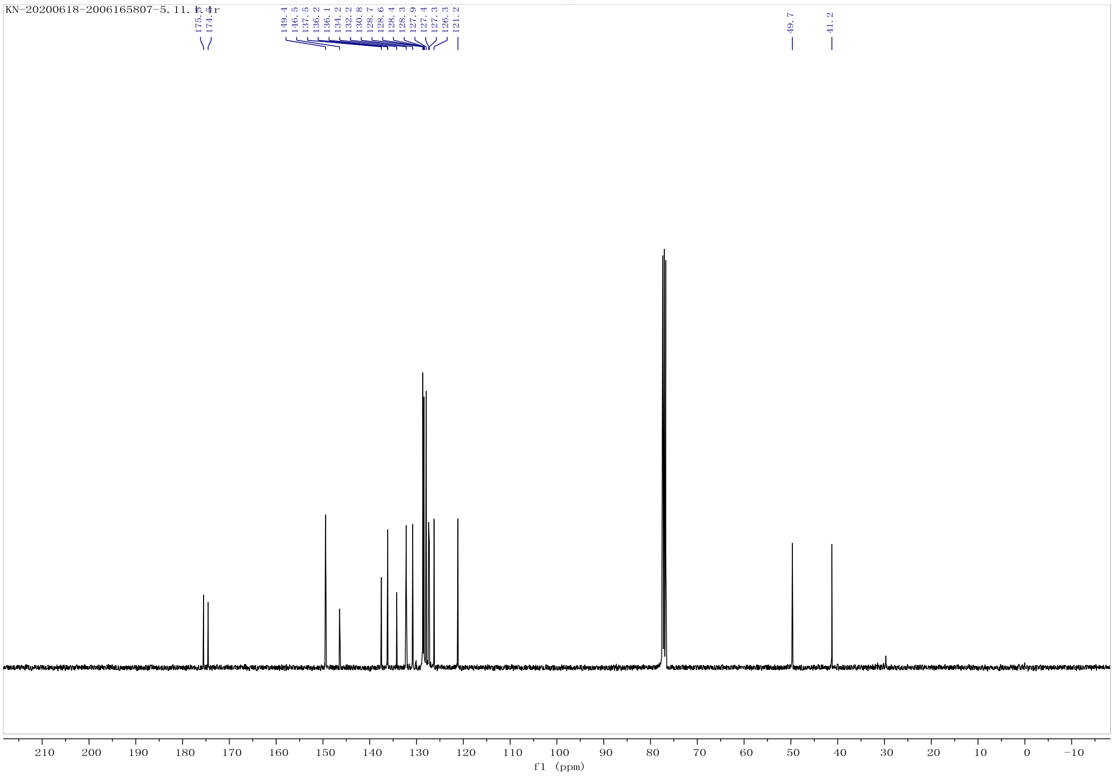
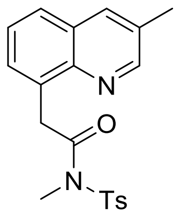
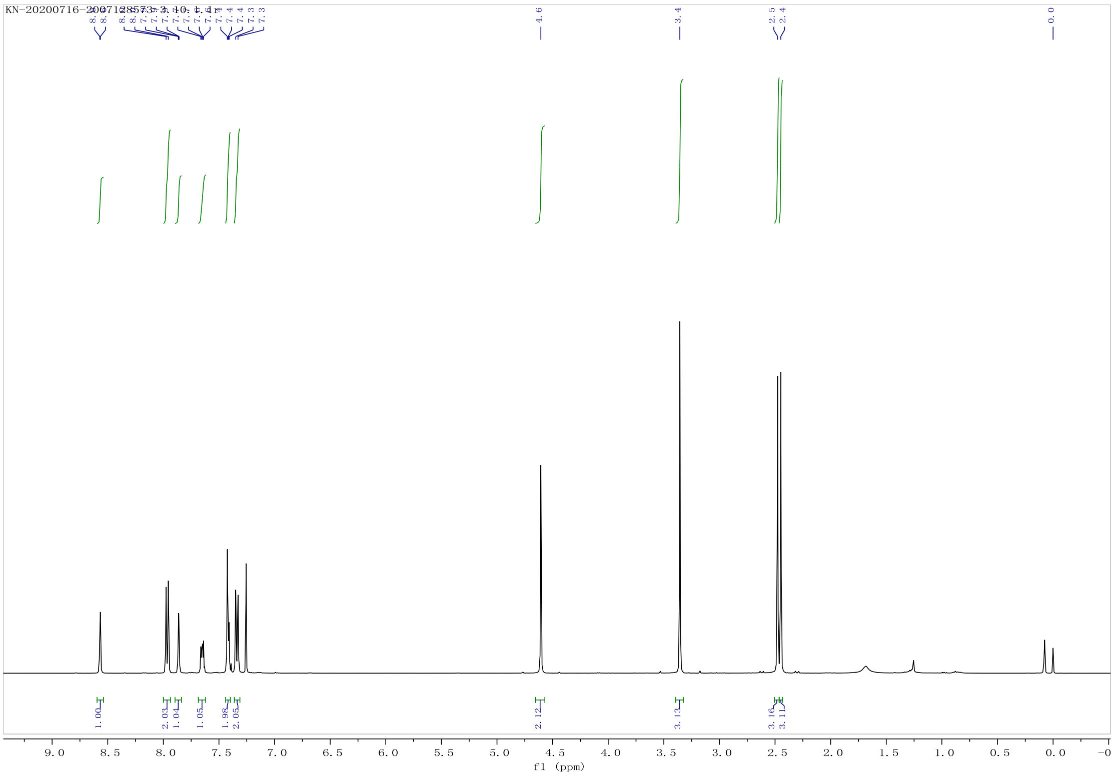





N
O
N
Ts

3ab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2.5
2.4
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1.00
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1.04
1.05
1.98
2.05
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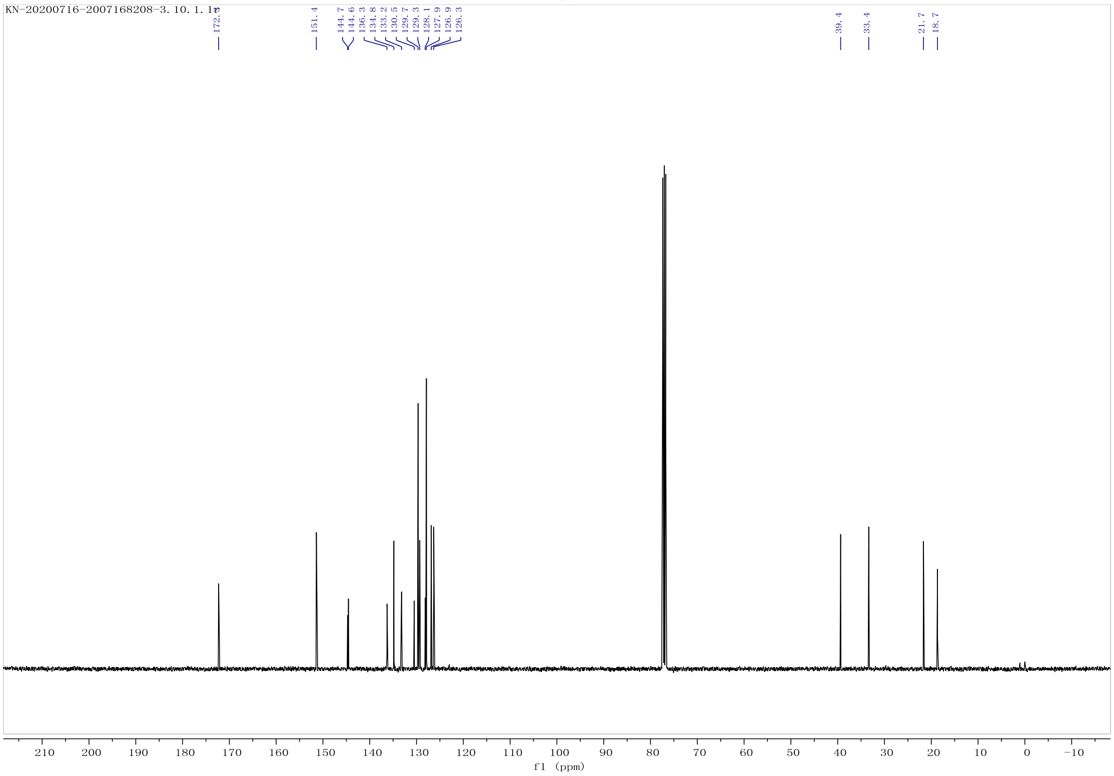
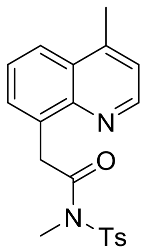
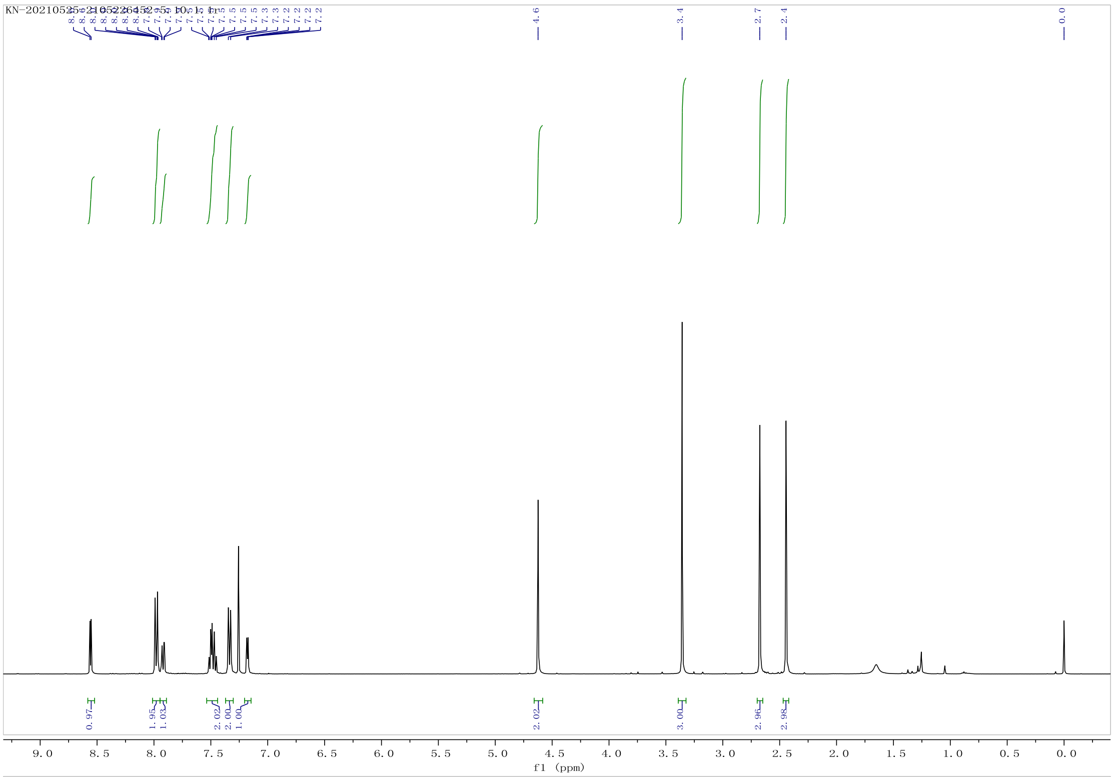
3.13
3.16
3.11
f1 (ppm)


151.4
144.7
144.6
136.3
134.8
133.2
130.5
129.7
129.3
128.1
127.9
126.9
126.3
39.4
33.4
21.7
18.7
f1 (ppm)


N
O
N
Ts

3ac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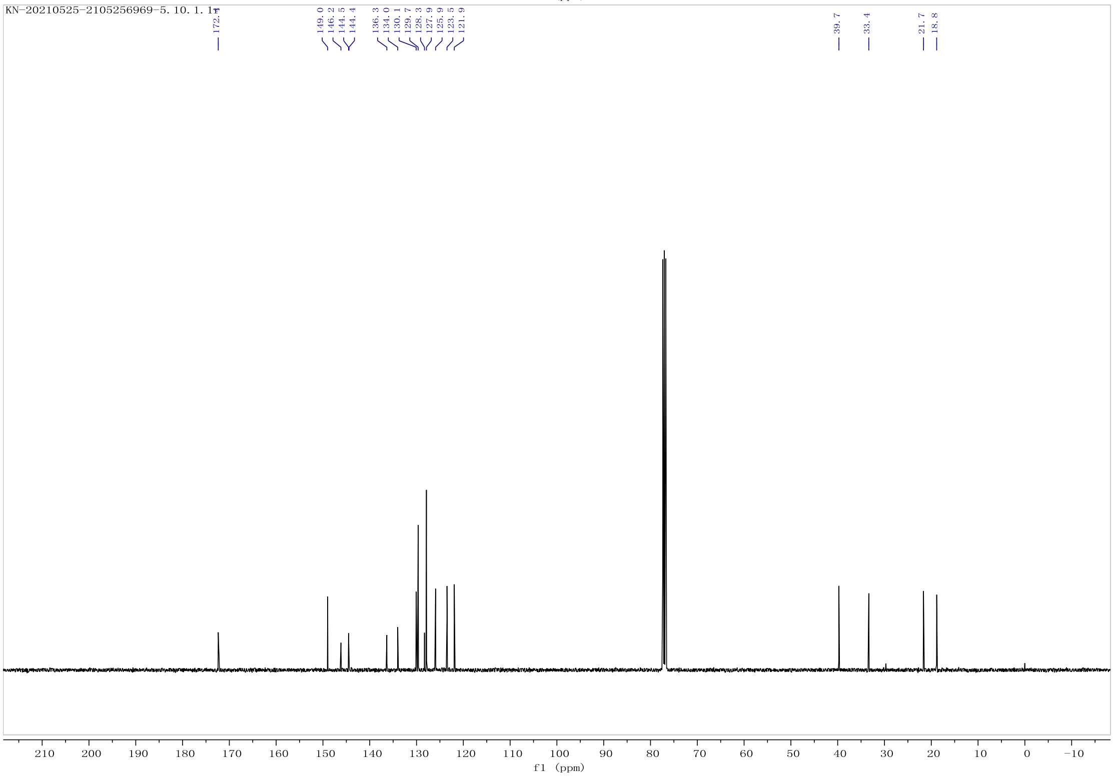
1.95
1.03
2.02
2.00
1.00
2.02
3.00
2.96
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


KN-20210525-2105256969-5.10.1.1r
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144.4
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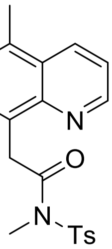
134.0
130.1
129.7
129.3
127.9
125.9
123.5
121.9
39.7
33.4
21.7
18.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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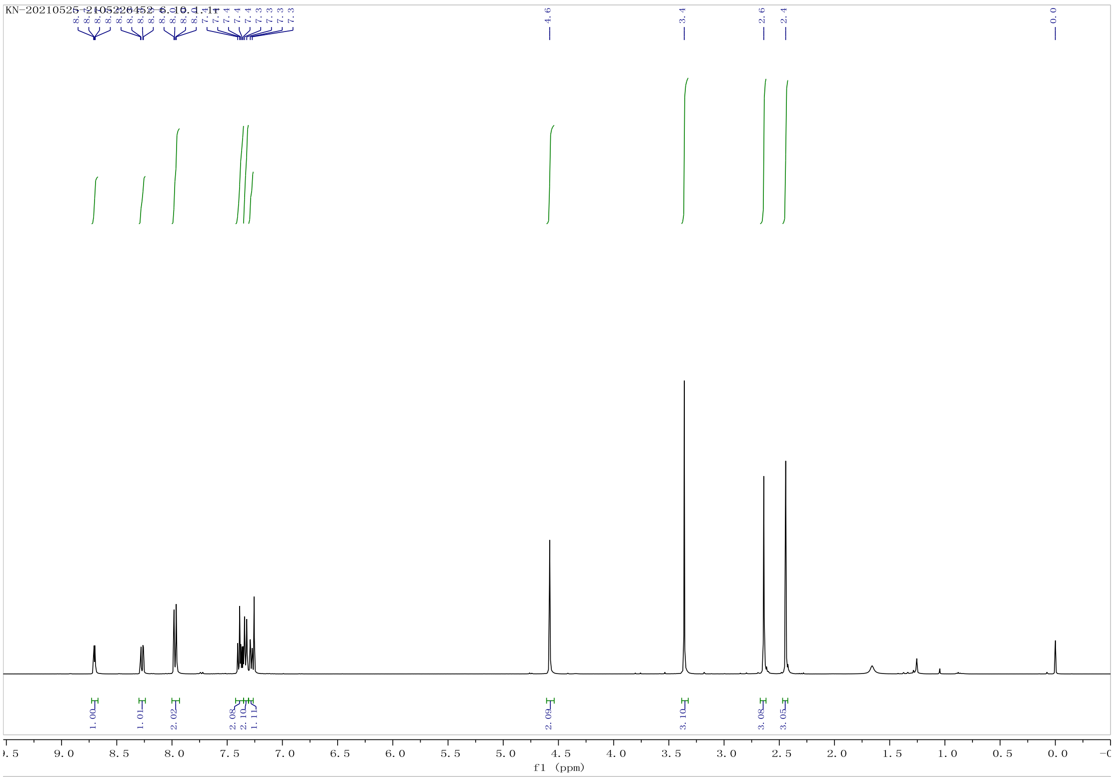

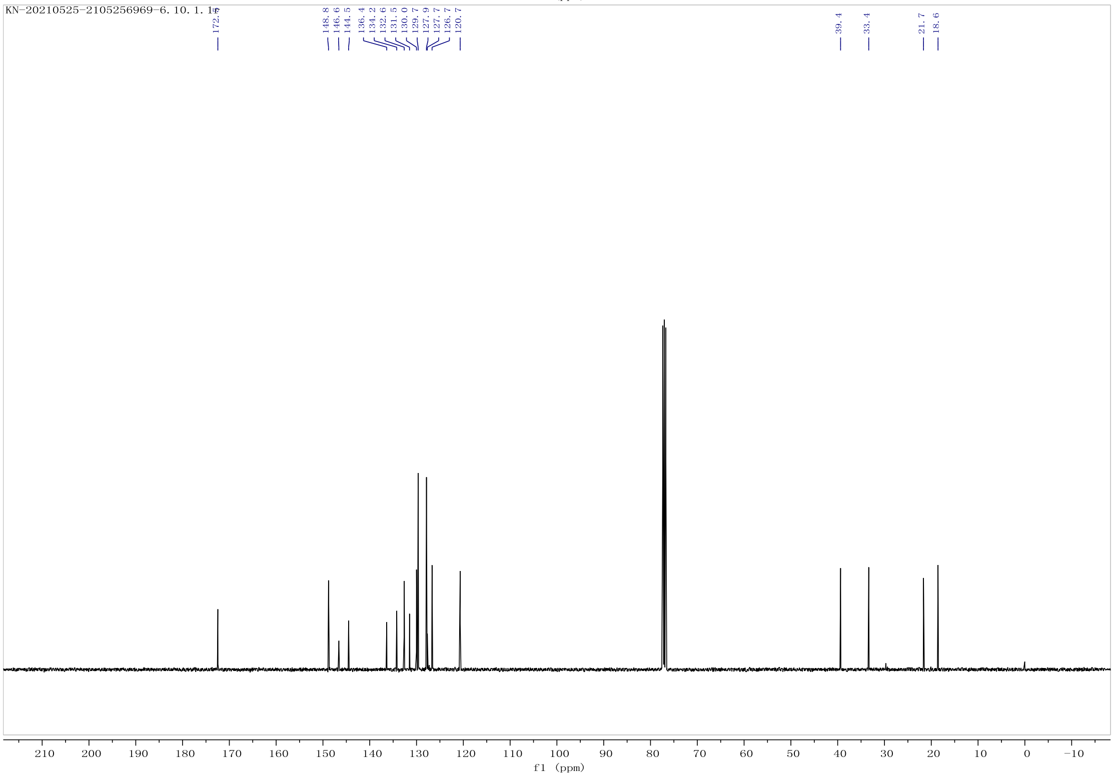

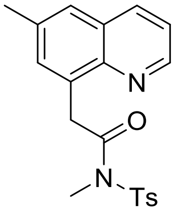

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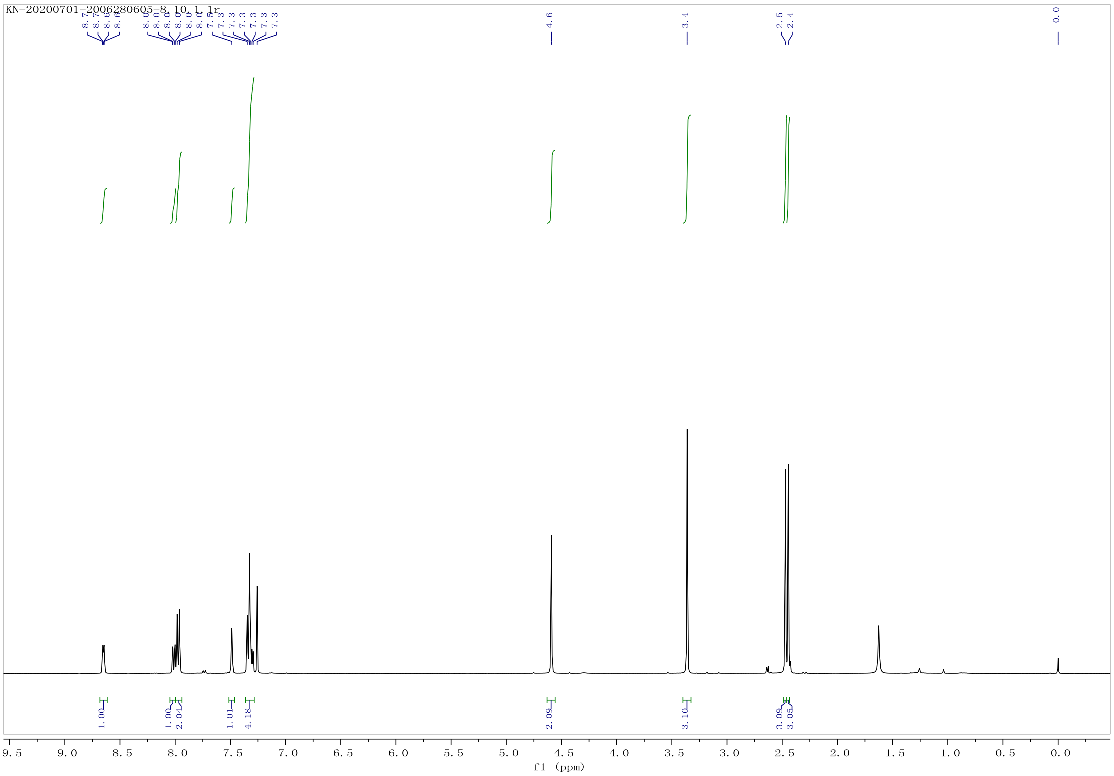
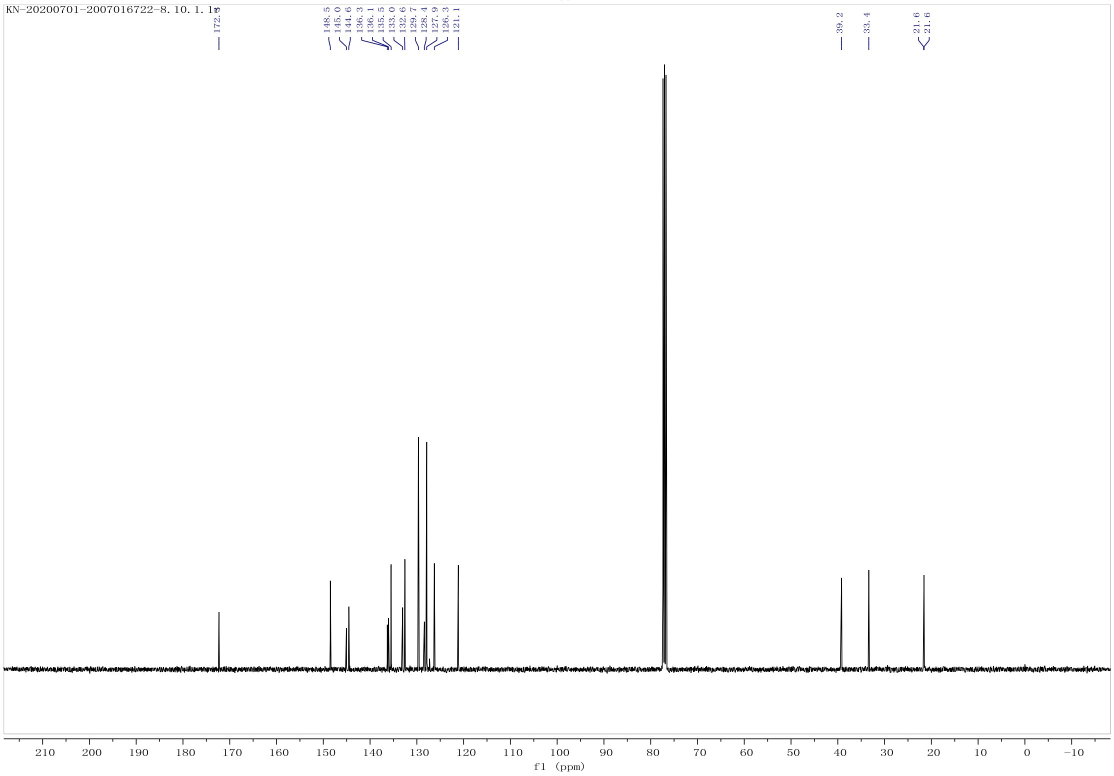
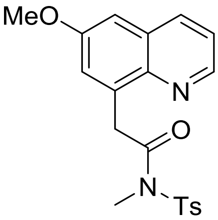
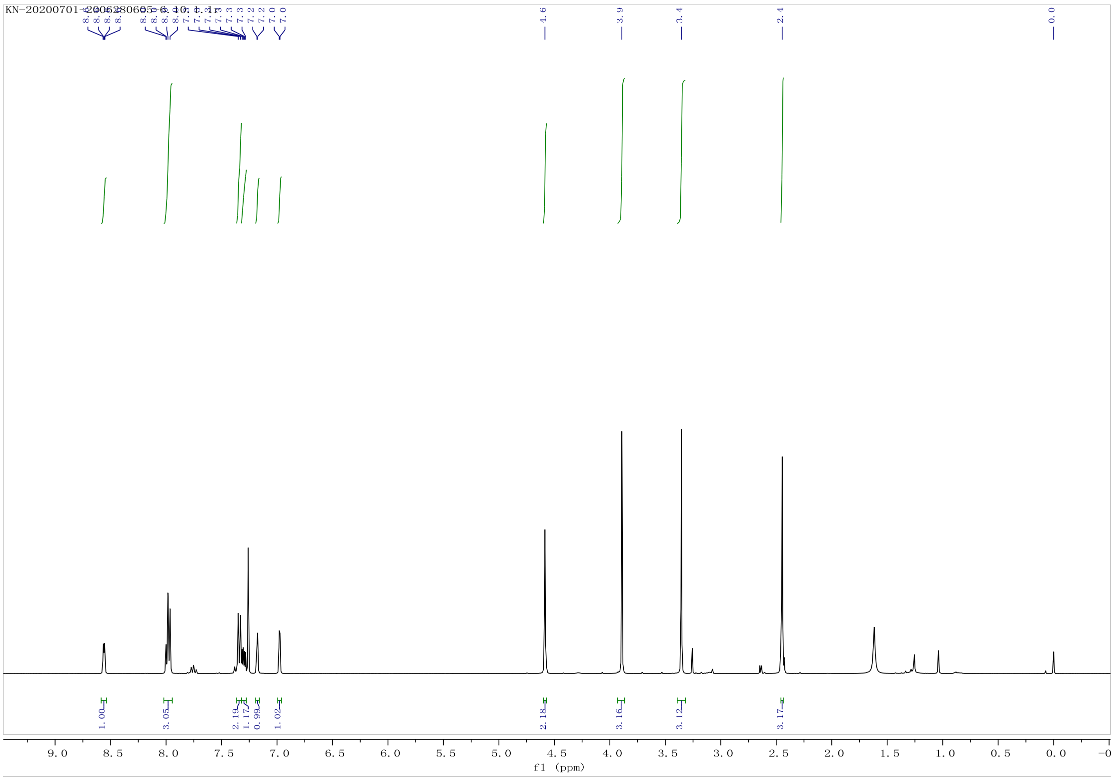
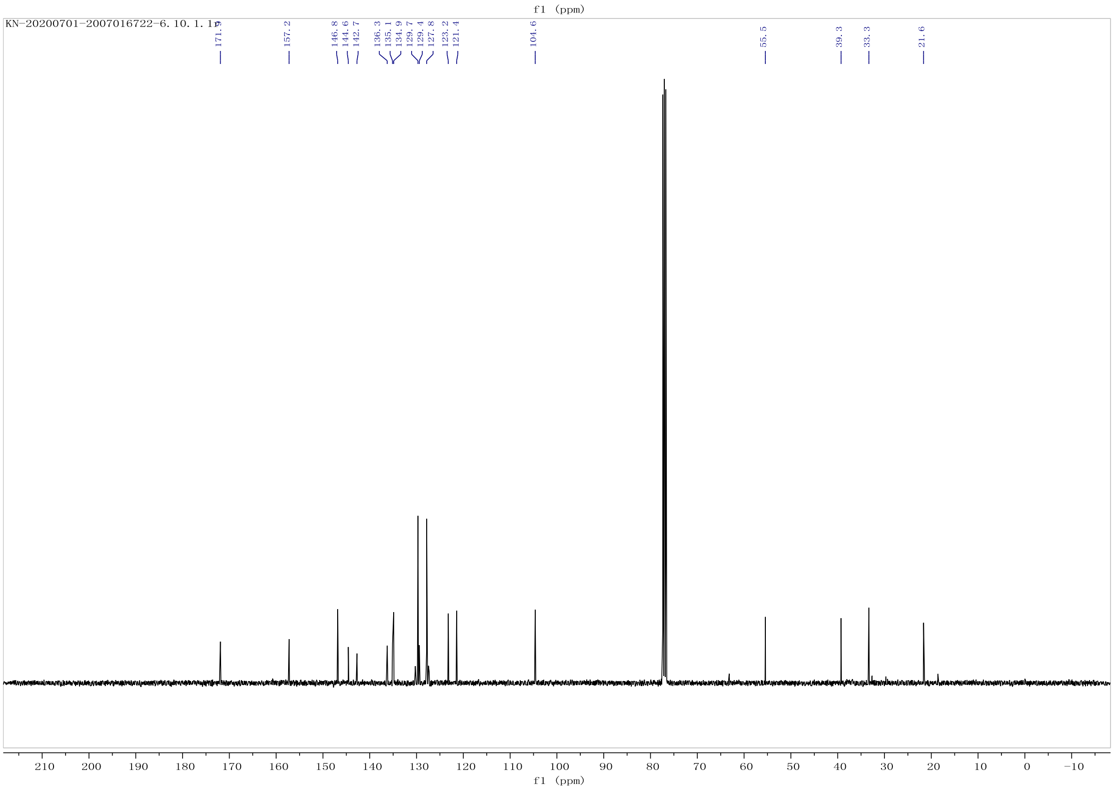


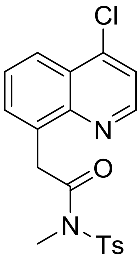




3ah







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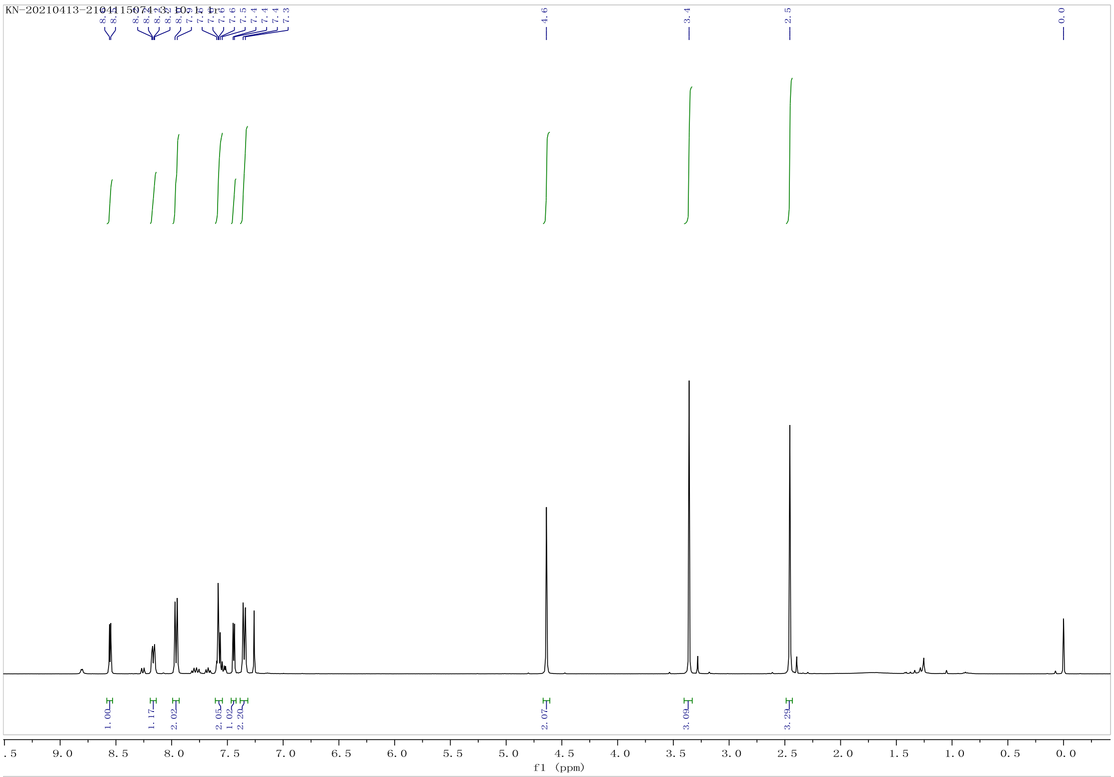

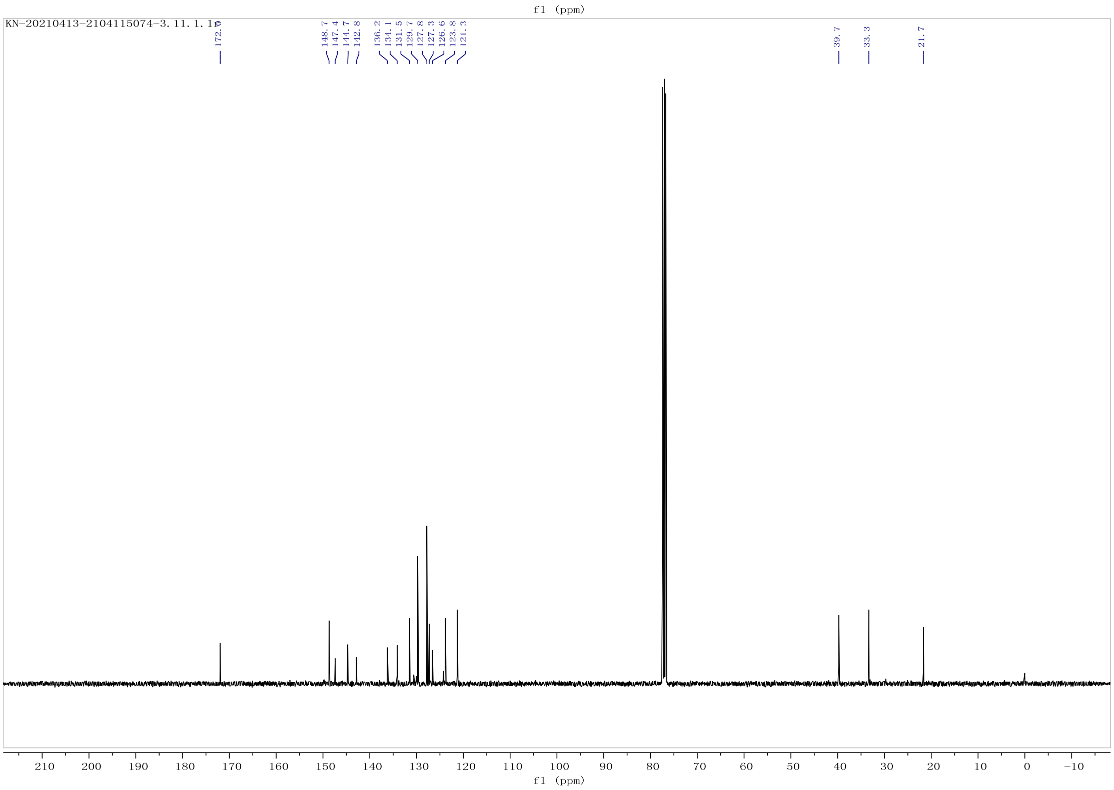

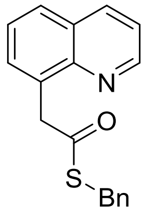
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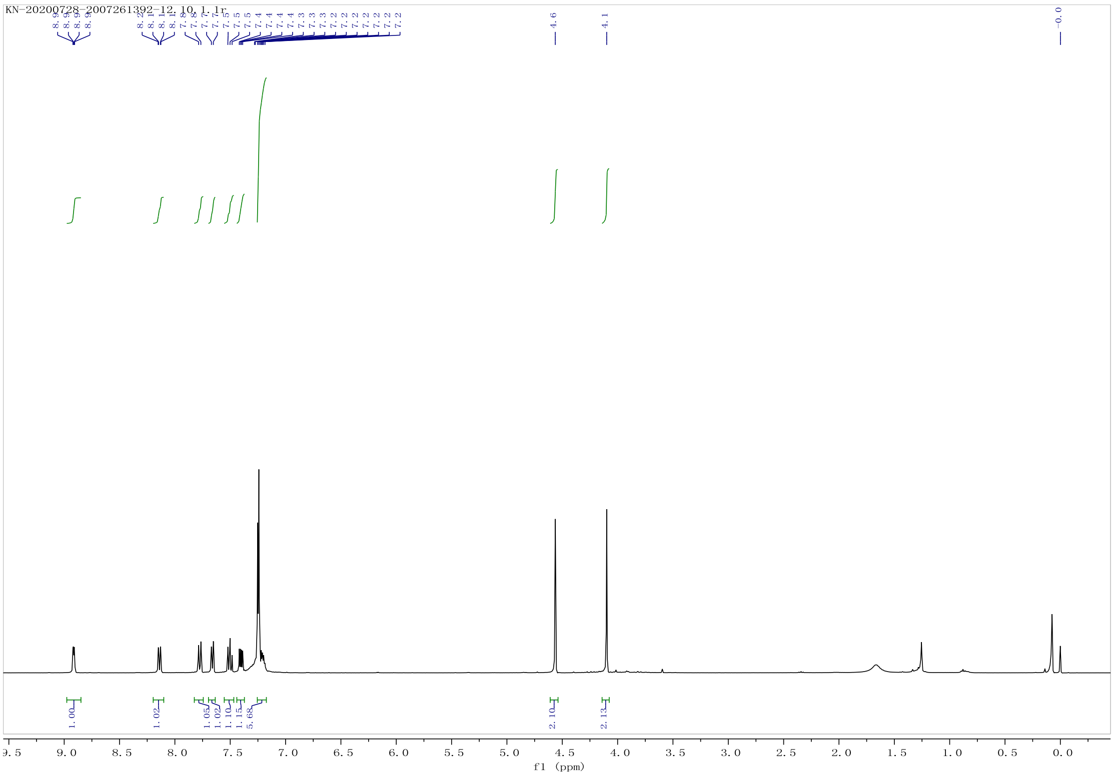
5aa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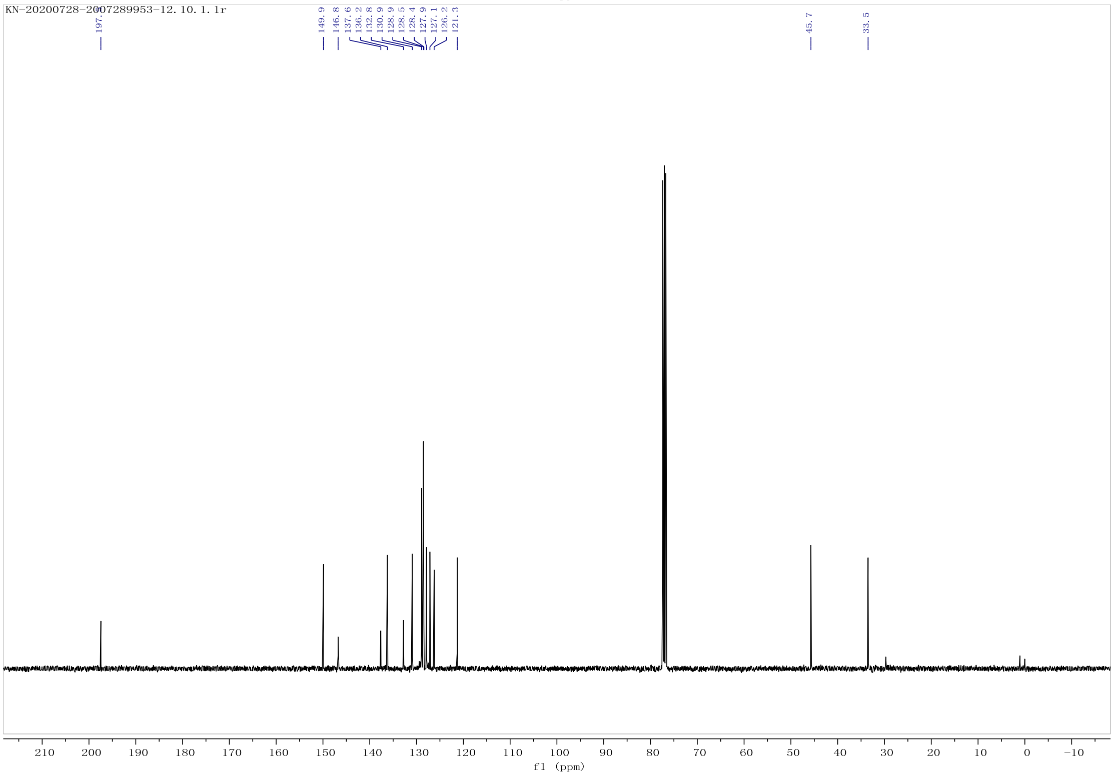
4.6
4.1
-0.0
1.00
1.02
1.05
1.02
1.10
1.15
5.68
2.10
2.13
f1 (ppm)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146.8
137.6
136.2
132.8
130.9
128.9
128.5
128.4
127.9
127.1
126.2
121.3
45.7
33.5
f1 (ppm)