Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Nickel-Catalyzed Asymmetric Reductive Arylcyanation of Alkenes with Acetonitrile as the Cyano Source

Zhenbang Chen, and Zengming Shen*

Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China.

shenzengming@sjtu.edu.cn

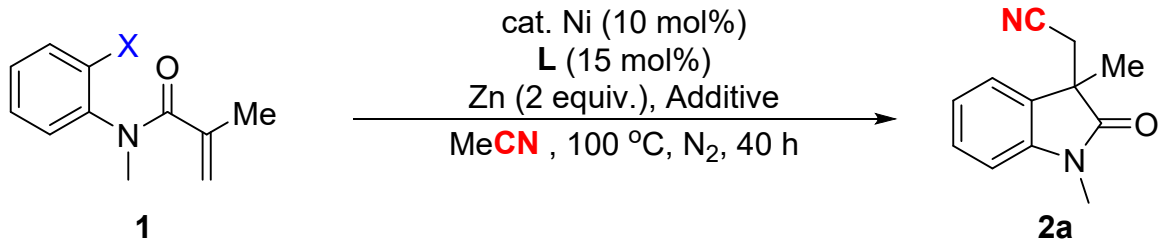
Table of Contents

1、General information

All reactions were set up with glovebox and carried out using Schlenk tubes. Anhydrous CH_3CN were purchased from damas-beta (99.9%, with molecular sieves, water ≤ 50 ppm) and used as received. Commercially available chemicals were obtained from Adamas, Acros Organics, Aldrich Chemical Co., Alfa Aesarand TCI, Energy Chemical and used as received unless otherwise stated. $Zn(OTf)_2$ was dried before use according to the standard methods. Zinc powder was activated with 1 M HCl aqueous solution, filtered and washed thoroughly with water, acetone and diethyl ether and dried under vacuum for 4 h.[1]

Analytical thin layer chromatography (TLC) was performed on percolated silica gel 60 F254 plates. Visualization on TLC was achieved with UV light (254 nm) and potassium permanganate as visualization methods. ^1H NMR spectra were recorded on Bruker-400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. Data for ^1H NMR spectra are reported as follows: chemical shift (δ shift), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublet, ddd = double of dd, dt = double of triplet, td = triple of doublet), integration, coupling constant (Hz), and assignment. ^{13}C NMR spectra were also recorded on Bruker-400 (100 MHz). Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of chloroform-d. High resolution mass spectra were obtained with ACQUITYTM UPLC & Q-TOF MS Premier Spectrometer. Gas chromatograph-mass spectra analysis was performed on LECO Pegasus 4D GC×GC-TOFMS.

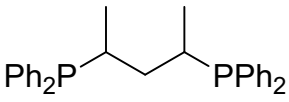
2、Optimization of the racemic reaction conditions:



1 **2a**

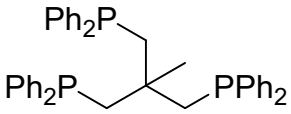
Entry	X	Catalyst	Ligand	Additive	*c* (**1**, y M)	Yield of **2a**
1	Cl	$Ni(OTf)_2$	dppp	$ZnCl_2$（30 mol%）	0.3	Trace
2	Cl	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（30 mol%）	0.3	58 %
3	Cl	$Ni(OTf)_2$	dppp	$Zn(OAc)_2$（30 mol%）	0.3	Trace
4	Cl	$Ni(OTf)_2$	dppp	$Zn(acac)_2$（30 mol%）	0.3	Trace
5	Cl	$Ni(OTf)_2$	dppp	CoPC（10 mol%）	0.3	27 %
6	Cl	$Ni(OTf)_2$	dppb	$Zn(OTf)_2$（30 mol%）	0.3	Trace
7	Cl	$Ni(OTf)_2$	dppf	$Zn(OTf)_2$（30 mol%）	0.3	Trace
8	Cl	$Ni(OTf)_2$	PPh_3	$Zn(OTf)_2$（30 mol%）	0.3	Trace
9	Cl	$Ni(OTf)_2$	XantPhos	$Zn(OTf)_2$（30 mol%）	0.3	NP
10	Cl	$Ni(OTf)_2$	S-Phos	$Zn(OTf)_2$（30 mol%）	0.3	NP
11	Cl	$Ni(OTf)_2$	L1	$Zn(OTf)_2$（30 mol%）	0.3	40%
12	Cl	$Ni(OTf)_2$	L2	$Zn(OTf)_2$（30 mol%）	0.3	NP
13	Cl	$Ni(OTf)_2$	L3	$Zn(OTf)_2$（30 mol%）	0.3	NP
14	Cl	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（50 mol%）	0.3	14 %
15	Cl	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（100 mol%）	0.3	Trace
16	Cl	$Ni(OTf)_2$	dppp	-	0.3	18 %

17	Cl	$NiCl_2$	dppp	$Zn(OTf)_2$（30mol%	0.3	25%
18	Cl	$NiBr_2$	dppp	$Zn(OTf)_2$（30 mol%	0.3	27%
19	Cl	$Ni(OAc)_2$	dppp	$Zn(OTf)_2$（30 mol%	0.3	32%
20	Cl	$Ni(acac)_2$	dppp	$Zn(OTf)_2$（30 mol%	0.3	38%
21	Cl	$Ni(cod)_2$	dppp	$Zn(OTf)_2$（30 mol%	0.3	< 10%
22	Br	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（30 mol%）	0.3	45 %
23	OTf	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（30 mol%）	0.3	56 %
23	OTf	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（50 mol%）	0.3	59 %
25	OTf	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（100 mol%）	0.3	64 %
26	OTf	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（150 mol%）	0.3	46 %
27	OTf	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（200 mol%）	0.3	50 %
28	OTf	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（100 mol%）	0.2	73%
29	OTf	$Ni(OTf)_2$	dppp	$Zn(OTf)_2$（100 mol%）	0.1	85 %



L1

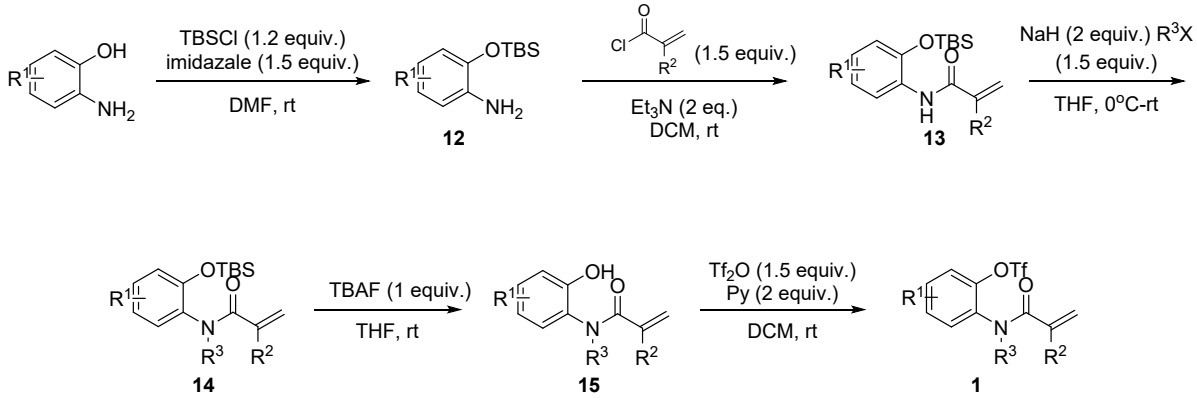
L2



L3

3、Synthesis and characterization data of aryl triflates 1

General procedure for the synthesis of aryl triflates 1:[2]



To a solution of 2-aminophenol derivative (1 equiv) and imidazole (1.5 equiv) in DMF (30 mL) was added a solution of TBSCl (1.2 equiv), the mixture was stirred at room temperature. After the reaction was completed (monitored by TLC), the mixture was quenched with saturated NH_4Cl solution (50 mL) and extracted with EtOAc (50 mL × 3). The combined organic layers were washed with brine (100 mL), dried over anhydrous Na_2SO_4 and filtrated. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **12** as red oil.

To a solution of **12** and triethylamine (2 equiv) in DCM (50 mL) at 0 °C was added dropwise acryloyl chloride under N_2 atmosphere. The mixture was warmed to room temperature and stirred until the amine was consumed completely (monitored by TLC). The mixture was poured into water (50 mL) and extracted by DCM (3 × 50 mL). The combined organic layer was washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue (red oil) **13** was used for the next step without further purification.

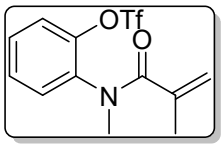
To a stirred mixture of amide **13** in dry THF (50 mL) was added NaH (60% dispersion in mineral oil) (2 equiv) at 0 °C under N_2. After being stirred at rt for 30 min, the reaction was cooled to 0 °C and R^3X (1.5 equiv) was added dropwise. The mixture was then stirred at room temperature overnight. After the reaction was finished (monitored by TLC), the mixture was quenched with saturated aqueous NH_4Cl at 0 °C and extracted with EtOAc (50 mL × 3). The combined extracts were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue **14** was used for the next step without further purification.

To a solution of **14** in THF (50 mL) was added tetrabutylammonium fluoride (1 equiv). The mixture was stirred at rt until the TBS-protected substrate was consumed completely (monitored by TLC). The reaction was poured into water (50 mL) and extracted by EtOAc (3 × 50 mL). The combined organic layer was washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield compound **15** as a yellow solid.

To a solution of phenol **15** and pyridine (2 equiv) in DCM (50 mL) at 0 °C was added dropwise Tf_2O (1.5 equiv) under N_2 atmosphere, the mixture was warmed to room temperature and stirred for 2 h. After completion of the reaction as indicated by TLC, the mixture was poured into water (50 mL) and extracted by DCM (3 × 50 mL). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified on a silica gel column using petroleum ether/EtOAc to afford the aryl triflate **1**.

Characterization data of aryl triflates 1:

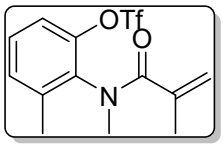
2-(***N*-Methylmethacrylamido)phenyl trifluoromethanesulfonate (1a)**[2]



According to general procedure, **1a** was obtained in 32% yield (2.4 g, over five steps) as a white solid. Melting point: 59.5 - 62.1 °C.

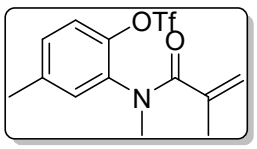
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.27 (m, 4H), 5.04 (s, 1H), 4.77 (s, 1H), 3.34 (s, 3H), 1.87 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.5, 144.5, 139.7, 137.8, 129.4, 129.2, 128.9, 122.6, 119.8, 118.6 (q, *J* = 320.2 Hz), 37.4, 19.9. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.82 (s).

3-Methyl-2-(*N*-methylmethacrylamido)phenyl trifluoromethanesulfonate (1b)[2]



According to general procedure, **1b** was obtained in 24% yield (3.2 g, over five steps) as a brown oil. Two rotamers were observed in 3:1 ratio, NMR data of the major rotamer were reported. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30 – 7.26 (m, 2H), 7.16 (m, 1H), 4.96 (s, 1H), 4.71 (s, 1H), 3.21 (s, 3H), 2.34 (s, 3H), 1.80 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.6, 145.2, 139.7, 138.7, 136.5, 131.1, 128.9, 119.9, 118.5 (q, *J* = 320.0 Hz), 118.5, 36.6, 19.8 18.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.89 (s).

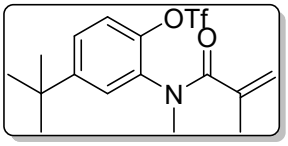
4-Methyl-2-(*N*-methylmethacrylamido)phenyl trifluoromethanesulfonate (1c)[2]



According to general procedure, **1c** was obtained in 29% yield (2.4 g, over five steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 – 7.09 (m, 3H), 5.03 (s, 1H), 4.77 (s, 1H), 3.32 (s, 3H), 2.36 (s, 3H), 1.86 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.2, 142.1, 139.8, 139.6, 137.2, 129.2 (d, *J* = 4.9 Hz), 121.9, 119.4, δ 118.4 (q, *J* = 320.1 Hz), 37.2, 20.7, 19.6. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -74.07 (s).

4-(*tert*-Butyl)-2-(*N*-methylmethacrylamido)phenyl trifluoromethanesulfonate (1d)

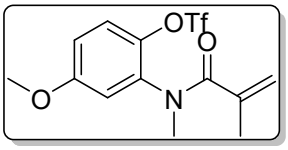


According to general procedure, **1d** was obtained in 16% yield (1.8 g, over five steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 4.99 (s, 1H), 4.78 (s, 1H), 3.31 (s, 3H), 1.81 (s, 3H), 1.29 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.5, 153.0, 141.9, 139.9, 136.9, 126.5, 125.79, 121.8, 119.3, δ 118.5 (q, *J* = 320.1 Hz), 37.3, 34.8, 31.1, 19.9. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -74.00 (s).

HRMS (ESI): m/z Calcd for $C_{16}H_{20}F_3NO_4SNa$ $[M+Na]^+$ 402.0963; found: m/z 402.0983.

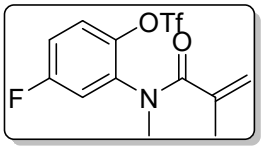
4-Methoxy-2-(*N*-methylmethacrylamido)phenyl trifluoromethanesulfonate (1e)[3]



According to general procedure, **1e** was obtained in 39% yield (4.9 g, over five steps) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 9.4 Hz, 1H), 6.83 – 6.77 (m, 2H), 5.04 (s, 1H), 4.81 (s, 1H), 3.77 (s, 3H), 3.29 (s, 3H), 1.85 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.3, 159.6, 139.7, 138.6, 137.9, 123.2, 119.5, δ 118.5 (q, *J* = 320.2 Hz), 114.2, 113.5, 6.85, 37.4, 19.7. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.74 (s).

4-Fluoro-2-(*N*-methylmethacrylamido)phenyl trifluoromethanesulfonate (1f)

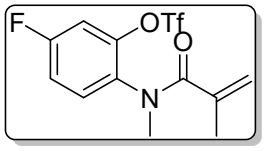


According to general procedure, **1f** was obtained in 23% yield (3.0 g, over five steps) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dd, *J* = 9.1, 5.0 Hz, 1H), 7.14 – 7.03 (m, 2H), 5.16 (s, 1H), 4.92 (s, 1H), 3.35 (s, 3H), 1.93 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.1, 162.7, 160.2, 140.5, 139.4, 139.1, 123.7 (d, *J* = 9.8 Hz), 119.6, δ 118.4 (q, *J* = 320.2 Hz), 116.0, 115.7 (dd, *J* = 39.6, 24.1 Hz), 37.4, 19.5. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.73 (s), -109.69 (s).

HRMS (ESI): m/z Calcd for $C_{12}H_{12}F_4NO_4S$ $[M+H]^+$ 342.0423; found: m/z 342.0434.

5-Fluoro-2-(*N*-methylmethacrylamido)phenyl trifluoromethanesulfonate (1g)

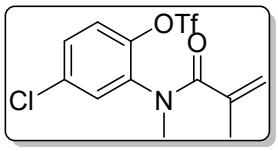


According to general procedure, **1g** was obtained in 27% yield (2.7 g, over five steps) as a white solid. Melting point: 41.3 - 42.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 1H), 7.20 – 7.11 (m, 1H), 7.08 (dd, *J* = 7.9, 2.5 Hz, 1H), 5.08 (s, 1H), 4.78 (s, 1H), 3.32 (s, 3H), 1.88 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.5, 164.9, 147.7, 139.6, 131.4, 130.4, 130.0, 122.8, 120.3, δ 118.6 (q, *J* = 320.3 Hz), 52.9, 19.9. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.71 (d, *J* = 60.1 Hz), -73.82 – -73.86 (m), -108.72 (s).

HRMS (ESI): m/z Calcd for $C_{12}H_{12}F_4NO_4S$ $[M+H]^+$ 342.0423; found: m/z 342.0423.

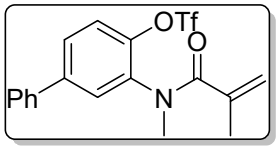
4-Chloro-2-(*N*-methylmethacrylamido)phenyl trifluoromethanesulfonate (1h)[2]



According to general procedure, **1h** was obtained in 30% yield (3.7 g, over five steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 2.4 Hz, 1H), 7.30 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 5.14 (s, 1H), 4.89 (s, 1H), 3.32 (s, 3H), 1.90 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.2, 143.0, 139.4, 138.8, 134.6, 129.0, 128.8, 123.6, 119.8, 118.4 (q, *J* = 320.4 Hz), 37.7, 19.7. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.70 (s).

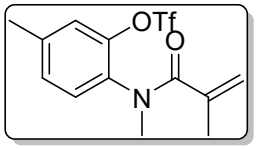
3-(*N*-Methylmethacrylamido)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (1i)[4]



According to general procedure, **1i** was obtained in 31% yield (2.5 g, over five steps) as a brown solid. Melting point: 64.5 - 66.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (td, *J* = 5.3, 2.7 Hz, 4H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7.1 Hz, 1H), 7.40 – 7.36 (m, 1H), 5.13 (s, 1H), 4.91 (s, 1H), 3.42 (s, 3H), 1.94 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.4, 143.6, 142.8, 139.7, 138.4, 129.1, 128.5, 127.5, 127.2, 127.1, 122.8, 119.8, 118.5 (q, *J* = 320.3 Hz), 37.5, 29.7, 19.9. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.69 (s).

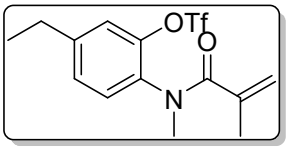
5-Methyl-2-(*N*-methylmethacrylamido)phenyl trifluoromethanesulfonate (1j)[2]



According to general procedure, **1j** was obtained in 29% yield (3.9 g, over five steps) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.13 (m, 2H), 7.06 (s, 1H), 4.99 (s, 1H), 4.75 (s, 1H), 3.27 (s, 3H), 2.41 – 2.28 (m, 3H), 1.81 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.5, 143.9, 139.7, 134.9, 130.0, 128.7, 122.8, 119.4, 118.5 (q, *J* = 320.1 Hz), 37.3, 21.0, 19.8. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -74.02 (s).

5-Ethyl-2-(*N*-methylmethacrylamido)phenyl trifluoromethanesulfonate (1k)



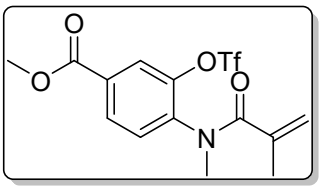
According to general procedure, **1k** was obtained in 6% yield (0.56 g, over five steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 11.0 Hz, 2H), 7.12 (s, 1H), 5.04 (s, 1H), 4.79 (s, 1H), 3.33 (s, 3H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.86 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 146.0, 144.2, 139.9, 135.2, 128.8 (d, *J* = 12.6 Hz), 121.8, 119.6, 118.6 (q, *J* = 320.3 Hz), 37.4, 28.4, 20.0, 15.0. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.83 (s).

HRMS (ESI): m/z Calcd for $C_{14}H_{16}F_3NO_4SNa$ $[M+Na]^+$ 374.0650; found: m/z 474.0654.

Methyl 4-(*N*-methylmethacrylamido)-3-(((trifluoromethyl)sulfonyl)oxy)benzoate (1l)

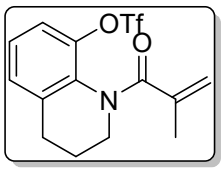


According to general procedure, **1l** was obtained in 39% yield (5.9 g, over five steps) as a yellow solid. Melting point: 41.3 - 44.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 – 7.97 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 4.94 (d, *J* = 135.2 Hz, 2H), 3.94 (s, 3H), 3.38 (s, 3H), 1.92 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.4, 164.9, 147.6, 139.6, 138.1, 131.4, 130.4, 130.0, 122.7, 120.4, 118.6 (q, *J* = 320.4 Hz), 52.9, 37.5, 19.9. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.55 (s).

HRMS (ESI): m/z Calcd for $C_{14}H_{14}F_3NO_6SNa$ $[M+Na]^+$ 404.0392; found: m/z 404.0405.

1-Methacryloyl-1,2,3,4-tetrahydroquinolin-8-yl trifluoromethanesulfonate (1m)

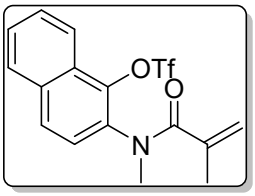


According to general procedure, **1m** was obtained in 45% yield (2.2 g, over four steps) as a white solid. Melting point: 52.5 - 55.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.14 (m, 2H), 7.10 (dd, *J* = 7.0, 2.6 Hz, 1H), 5.19 (s, 1H), 4.76 (s, 1H), 4.20 (s, 1H), 3.45 (s, 1H), 2.89 – 2.64 (m, 2H), 2.17 (s, 1H), 2.01 (s, 3H), 1.85 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.5, 143.2, 140.0, 136.5, 133.0, 128.2, 126.3, 120.1, 119.2, 118.7 (q, *J* = 320.8 Hz), 43.6, 26.5, 24.5, 19.4. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.49 (s).

HRMS (ESI): m/z Calcd for $C_{14}H_{14}F_3NO_4SNa$ $[M+Na]^+$ 372.0493; found: m/z 372.0494.

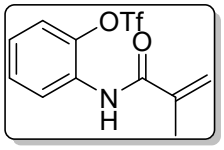
2-(*N*-Methylmethacrylamido)naphthalen-1-yl trifluoromethanesulfonate (1n)[4]



According to general procedure, **1n** was obtained in 16% yield (1.5 g, over five steps) as a brown solid. Melting point: 64.6 - 66.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.64 (dt, *J* = 14.9, 7.1 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 1H), 4.96 (s, 1H), 4.74 (s, 1H), 3.45 (s, 3H), 1.87 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.5, 139.5, 134.9, 133.5, 129.7, 128.7, 128.2, 127.8, 127.4, 125.4, 121.6, 119.8, 118.7 (q, *J* = 320.4 Hz), 100.1, 37.1, 19.9. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.24 (s).

2-Methacrylamidophenyl trifluoromethanesulfonate (1o)

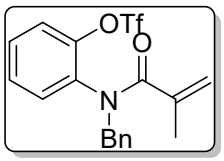


According to general procedure, **1o** was obtained in 41% yield (0.78 g, over four steps) as a white solid. Melting point: 50.7 - 51.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 – 8.26 (m, 1H), 7.87 (s, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.28 (dd, *J* = 9.9, 2.6 Hz, 1H), 7.21 – 7.12 (m, 1H), 5.89 (s, 1H), 5.52 (s, 1H), 2.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.3, 139.9, 139.4, 130.7, 129.2, 125.4, 124.0, 121.7, 121.5, 118.6 (q, *J* = 320.3 Hz), 18.5. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.59 (s).

HRMS (ESI): m/z Calcd for $C_{11}H_{10}F_3NO_4SNa$ $[M+Na]^+$ 332.0180; found: m/z 332.0175.

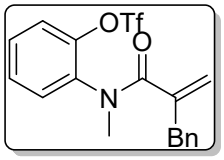
2-(*N*-Benzylmethacrylamido)phenyl trifluoromethanesulfonate (1p)[2]



According to general procedure, **1p** was obtained in 18% yield (3.6 g, over five steps) as a yellow solid. Melting point: 55.6 - 56.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 7H), 7.24 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 5.80 (s, 1H), 5.12 (s, 1H), 4.90 (s, 1H), 4.15 (s, 1H), 1.94 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.5, 144.6, 139.9, 137.5, 136.5, 130.1, 129.1, 128.9, 128.8, 128.5, 127.8, 122.4, 120.0, 118.6 (q, *J* = 320.2 Hz), 52.7, 19.9. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.75 (s).

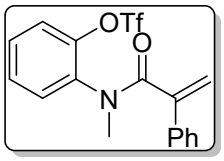
2-(2-Benzyl-*N*-methylacrylamido)phenyl trifluoromethanesulfonate (1q)[2]



According to general procedure, **1q** was obtained in 43% yield (2.3 g, over five steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 6.75 (m, 9H), 5.05 (t, *J* = 103.0 Hz, 2H), 3.89 – 2.98 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.0, 144.4, 143.6, 137.7, 137.4, 129.5, 129.2, 129.0, 128.5, 126.6, 122.3, 119.4, 118.5 (q, *J* = 320.2 Hz), 39.5, 37.3. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.83 (s).

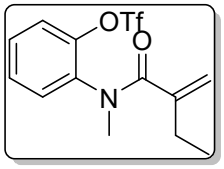
2-(*N*-Methyl-2-phenylacrylamido)phenyl trifluoromethanesulfonate (1r)[2]



According to general procedure, **1r** was obtained in 47% yield (4.0 g, over five steps) as a yellow oil. Two rotamers were observed in 3:1 ratio.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 6.5 Hz, 0.67H), 7.45 – 7.33 (m, 2.44H), 7.24 – 7.14 (m, 5H), 7.05 (d, *J* = 7.2 Hz, 3H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.87 (s, 0.3H), 5.64 (s, 0.3H), 5.51 (s, 1H), 5.43 (s, 1H), 3.36 (s, 3H), 3.25 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.5, 145.4, 144.6, 136.5, 136.2, 130.6, 129.4, 129.1, 128.9, 128.7, 128.4, 128.1, 125.9, 122.3, 121.9, 118.9, 118.5 (q, *J* = 320.0 Hz), 115.5, 39.5, 37.2. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.68 (s), -73.99 (s).

2-(*N*-Methyl-2-methylenebutanamido)phenyl trifluoromethanesulfonate (1s)

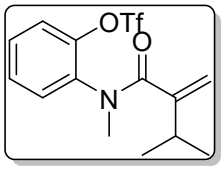


According to general procedure, **1s** was obtained in 36% yield (1.5 g, over five steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.30 (m, 4H), 5.05 (s, 1H), 4.90 (s, 1H), 3.36 (s, 3H), 2.26 (s, 2H), 1.02 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.9, 145.6, 144.5, 137.7, 129.4, 129.3, 129.1, 122.5, 117.4, 118.6 (q, J = 320.1 Hz), 37.6, 25.9, 11.8. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -73.85 (s).

HRMS (ESI): m/z Calcd for $C_{13}H_{14}F_3NO_4SNa$ $[M+Na]^+$ 360.0493; found: m/z 360.0500.

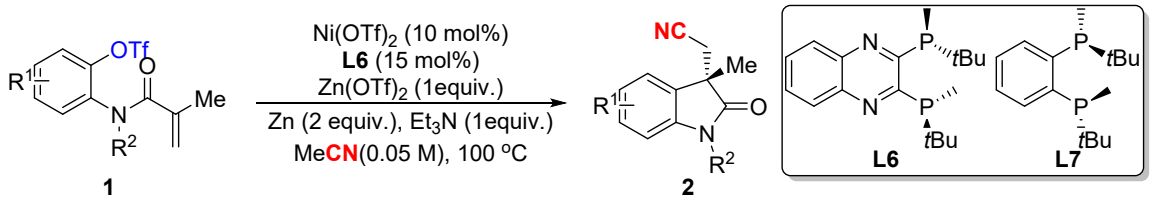
2-(*N*,3-Dimethyl-2-methylenebutanamido)phenyl trifluoromethanesulfonate (1t)[2]



According to general procedure, **1t** was obtained in 41% yield (1.8 g, over five steps) as a white solid. Melting point: 57.4 - 60.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.28 (m, 4H), 5.34 (s, 1H), 5.07 (s, 1H), 3.36 (s, 3H), 2.62 (m, 1H), 1.24 – 0.88 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 172.1, 150.3, 144.8, 137.4, 130.1, 129.2, 122.4, 118.6 (q, J = 320.1 Hz), 116.4, 113.4, 39.6, 37.6, 31.1, 22.2, 21.3. **^{19}F NMR (376 MHz, $CDCl_3$):** -73.86 (s).

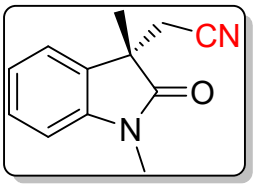
4、General procedure for the synthesis of chiral 3-cyanomethyl oxindoles



To a 25 mL of Schlenk tube equipped with a magnetic stirring bar were added $Ni(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%) and **L6** or **L7** (0.015 mmol, 15 mol%) in a N_2-filled glovebox. Then the tube was sealed with a septum and taken out of the N_2-filled glovebox. The Schlenk tube was evacuated and backfilled with N_2 for three times, MeCN (1 mL) was added and the mixture was stirred at r.t. for 30 min. Then Zn powder (13 mg, 2 equiv) was added and the mixture was stirred for additional 10 min. Reaction color would change from brownish to greenish. Aryl triflate **1** (0.1 mmol, 1 equiv), $Zn(OTf)_2$ (36.6 mg, 0.1 mmol, 100 mol%), base (75 mg, 0.6 mmol, 2 equiv) and MeCN (1 mL) were added into the continuous stirring greenish solution and the mixture was heated at 100 °C. After completion of the reaction monitored by TLC, the residue was purified on a silica gel column using petroleum ether/ EtOAc as the eluent to give the pure target product.

5、Characterizationdata and spectra copies of products

(*S*)-2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetonitrile (2a)[5]



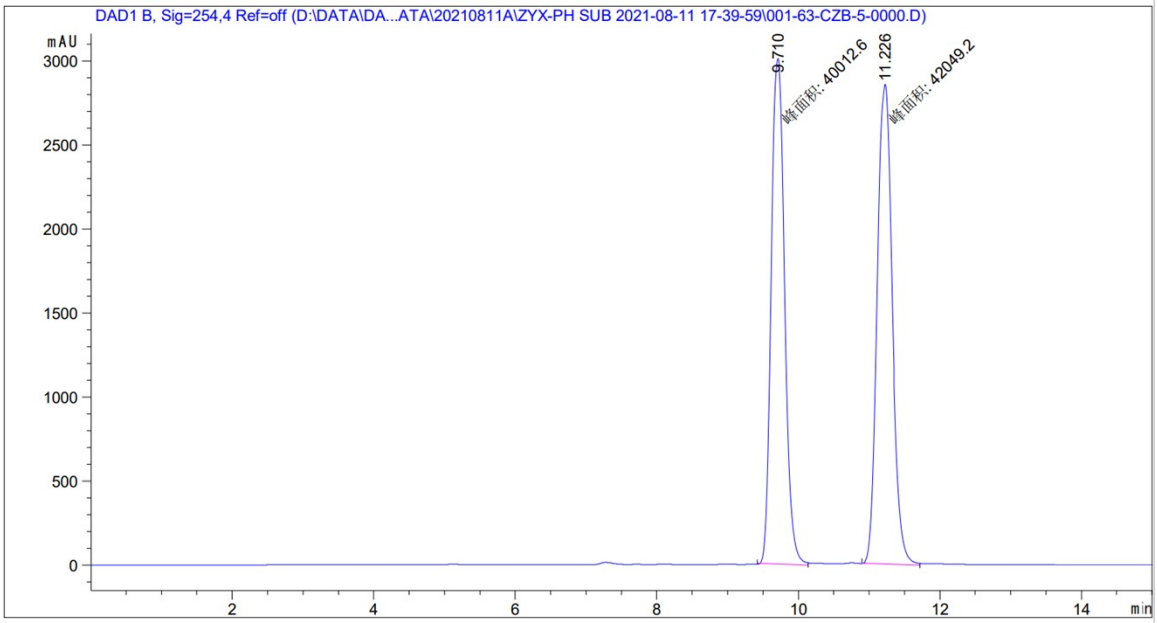
Yellow oil (16.2 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.4 Hz, 1H), 7.36 (td, *J* = 7.8, 1.1 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.24 (s, 3H), 2.85 (d, *J* = 16.6 Hz, 1H), 2.56 (d, *J* = 16.6 Hz, 1H), 1.53 (s, 3H).

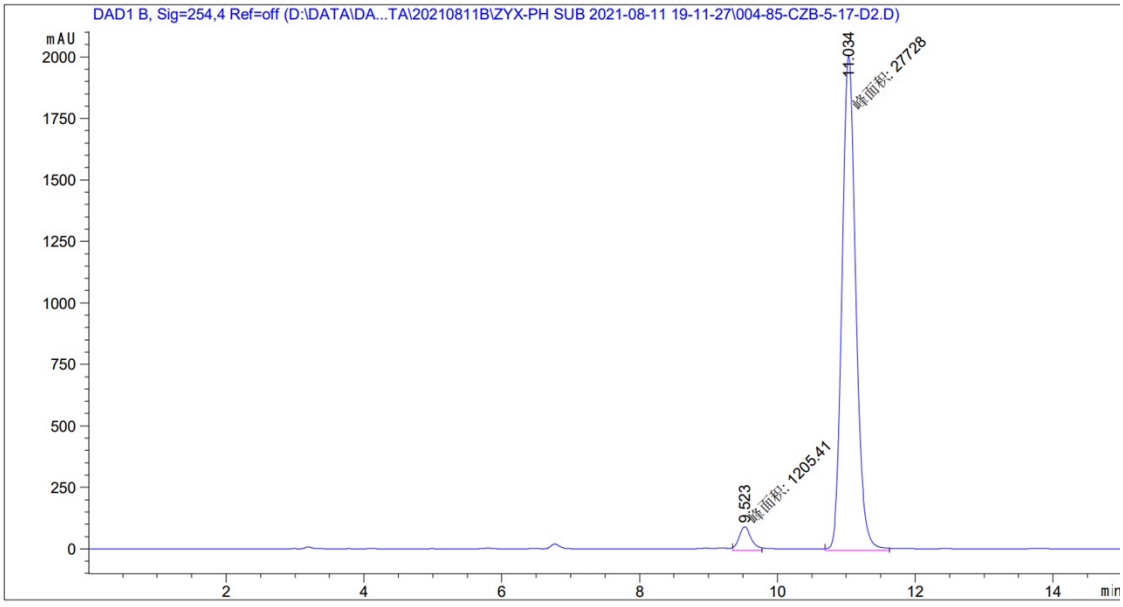
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 142.8, 131.1, 129.3, 123.3 (d, *J* = 13.5 Hz), 116.7, 108.8, 45.0, 26.6, 26.4, 22.3.

Optical Rotation: $[\alpha]_D^{25}$= 85.3 (*c* = 0.36, $CHCl_3$)

92% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm): t_R= 11.0 min (major), t_R= 9.5 min (minor).

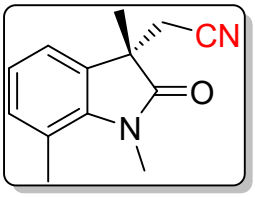


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.710	MM	0.2217	4.00126e4	3007.48291	48.7591
2	11.226	MM	0.2455	4.20492e4	2855.19971	51.2409



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.523	MM	0.2088	1205.40845	96.20621	4.1661
2	11.034	MM	0.2296	2.77280e4	2012.55627	95.8339

(*S*)-2-(1,3,7-Trimethyl-2-oxoindolin-3-yl)acetonitrile (2b)



Yellow oil (16.1 mg, 75% yield).

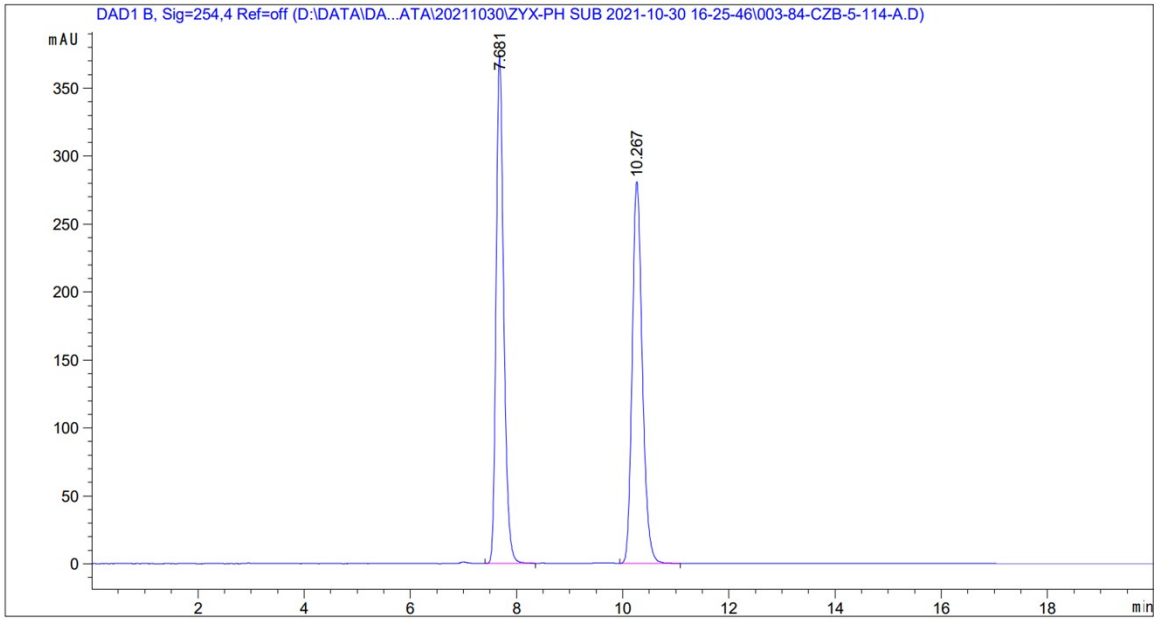
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 3.52 (s, 3H), 2.81 (d, *J* = 16.6 Hz, 1H), 2.61 – 2.52 (m, 4H), 1.49 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 140.5, 132.9, 131.7, 123.2, 121.0, 120.5, 116.7, 44.4, 29.9, 26.7, 22.6, 19.1.

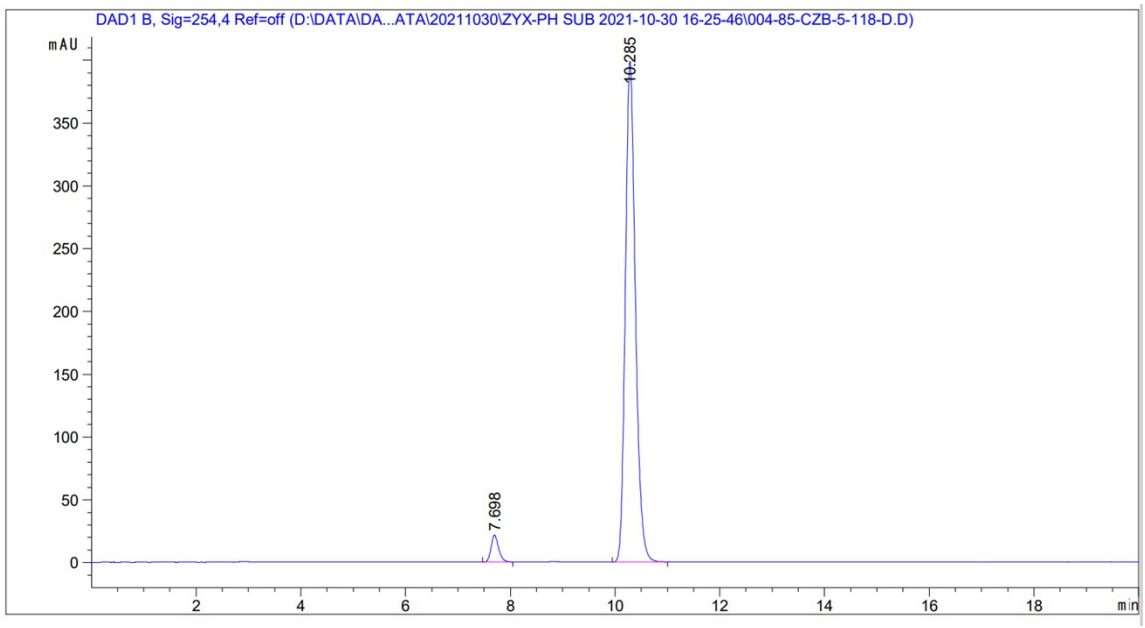
HRMS (ESI): m/z Calcd for $C_{13}H_{14}N_2ONa$ $[M+Na]^+$ 237.1004; found: m/z 237.1015.

Optical Rotation: $[\alpha]_D^{25}$ = 63.7 (*c* = 0.62, $CHCl_3$)

92% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm): t_R= 10.3 min (major), t_R= 7.7 min (minor).

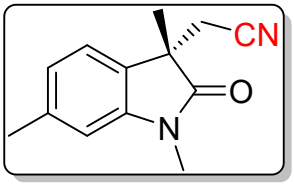


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.681	BB	0.1524	3720.18701	372.74234	49.9680
2	10.267	BB	0.2028	3724.95288	280.76001	50.0320



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.698	BB	0.1499	213.97362	21.53368	3.8733
2	10.285	BB	0.2034	5310.34668	398.69888	96.1267

(*S*)-2-(1,3,6-Trimethyl-2-oxoindolin-3-yl)acetonitrile (2c)[5]



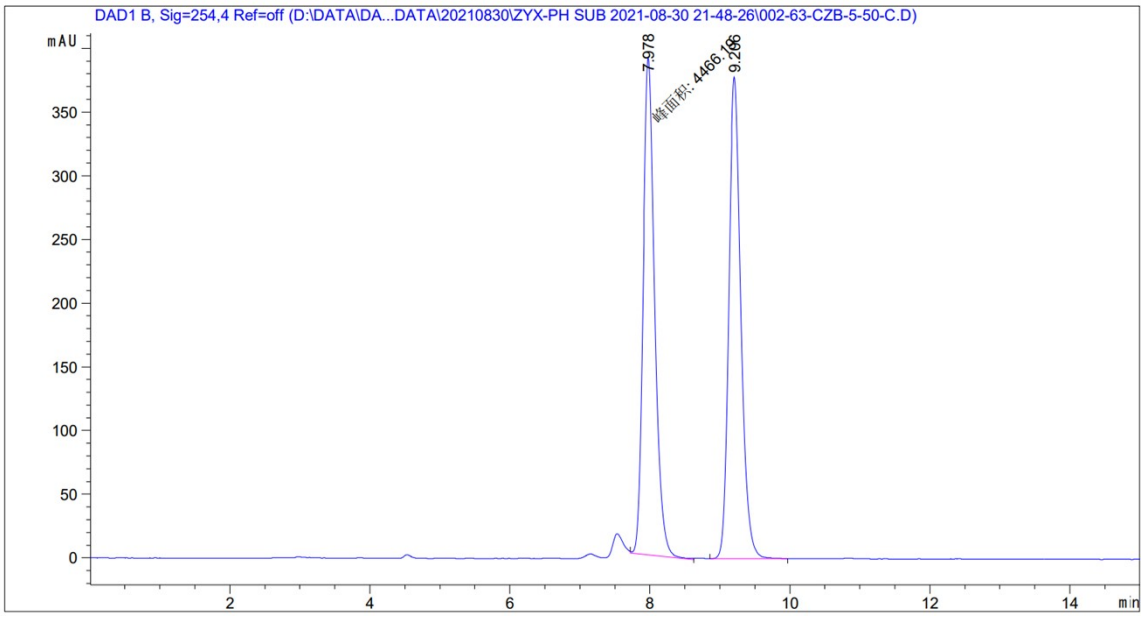
Colorless oil (14.6 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 3.22 (s, 3H), 2.83 (d, *J* = 16.6 Hz, 1H), 2.54 (d, *J* = 16.6 Hz, 1H), 2.40 (s, 3H), 1.50 (s, 3H).

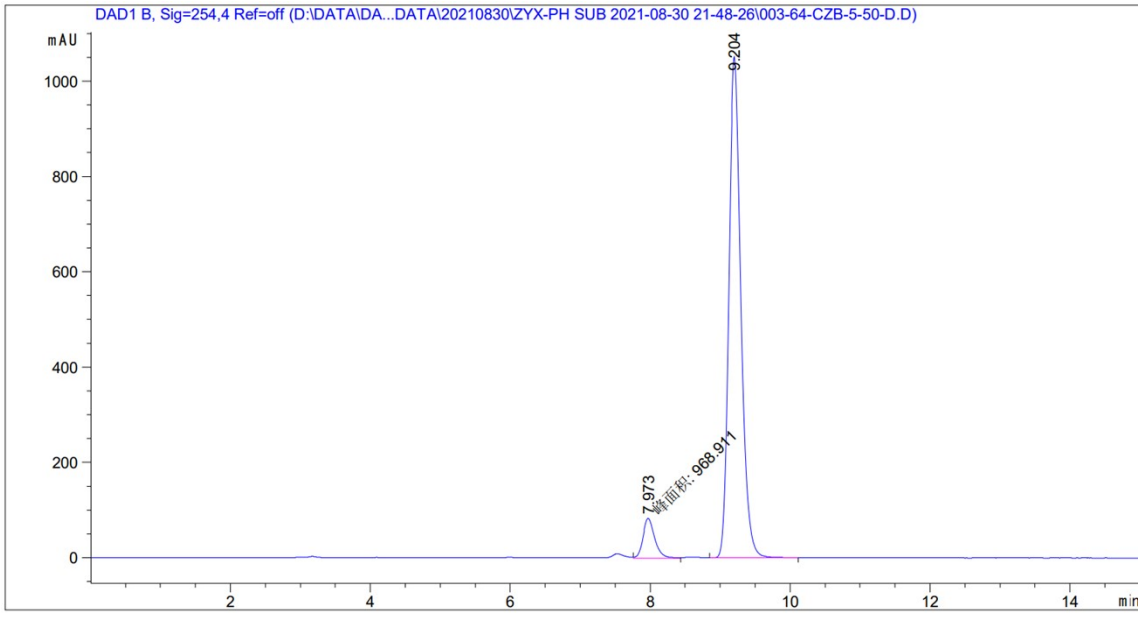
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 142.9, 139.6, 128.2, 123.9, 123.0, 116.8, 109.7, 44.8, 26.6 (d, *J* = 4.9 Hz), 22.4, 22.0.

Optical Rotation: $[\alpha]_D^{25}$ = 53.0 (*c* = 0.54, $CHCl_3$)

86% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm): t_R= 9.2 min (major), t_R= 8.0 min (minor).

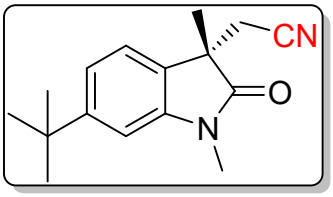


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.978	MM	0.1909	4466.19336	389.97540	49.5161
2	9.206	BB	0.1825	4553.48682	378.21356	50.4839



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.973	MM	0.1945	968.91071	83.04130	7.1467
2	9.204	BB	0.1838	1.25885e4	1050.73560	92.8533

(*S*)-2-(6-(*tert*-Butyl)-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (2d)



White solid (19.3 mg, 75% yield). Melting point: 98.3 - 103.0 °C.

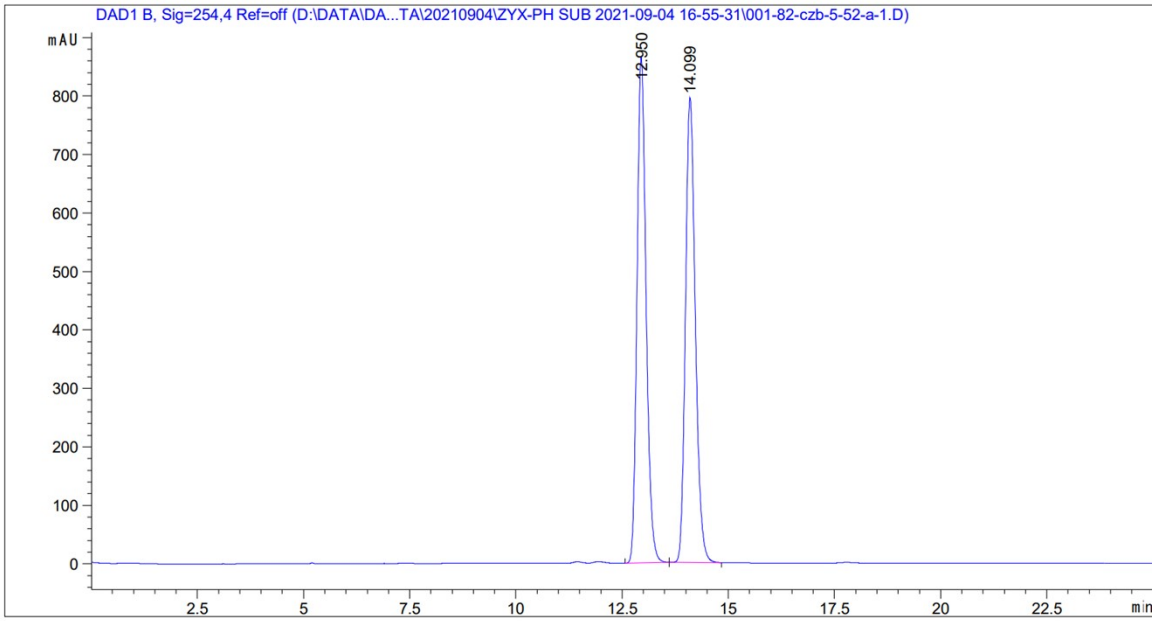
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.90 (s, 1H), 3.25 (s, 3H), 2.84 (d, *J* = 16.6 Hz, 1H), 2.53 (d, *J* = 16.6 Hz, 1H), 1.51 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 153.1, 142.7, 128.2, 122.8, 120.2, 116.9, 106.1, 44.7, 35.3, 31.5, 26.6 (d, *J* = 11.5 Hz), 22.3.

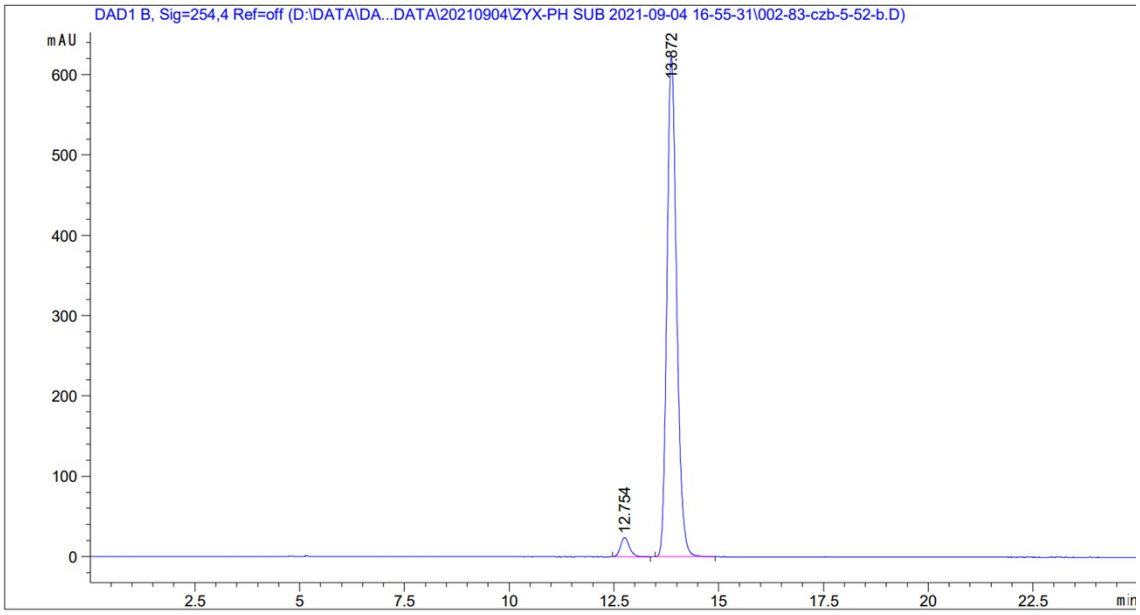
HRMS (ESI): m/z Calcd for $C_{16}H_{20}N_2ONa$ $[M+Na]^+$ 279.1437; found: m/z 279.1485.

Optical Rotation: $[\alpha]_D^{25}$ = 41.4 (*c* = 0.70, $CHCl_3$)

93% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 95:5, flow rate 0.5 mL/min, λ = 254 nm): t_R= 13.9 min (major), t_R= 12.8 min (minor).

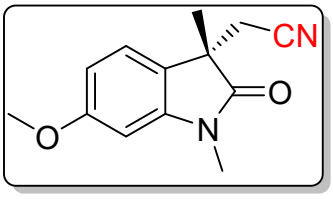


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.950	BB	0.2289	1.28105e4	864.47070	49.9834
2	14.099	BB	0.2483	1.28190e4	794.23975	50.0166



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.754	BB	0.2247	353.57962	23.88886	3.4008
2	13.872	BB	0.2483	1.00435e4	622.18378	96.5992

(*S*)-2-(6-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (2e)[5]



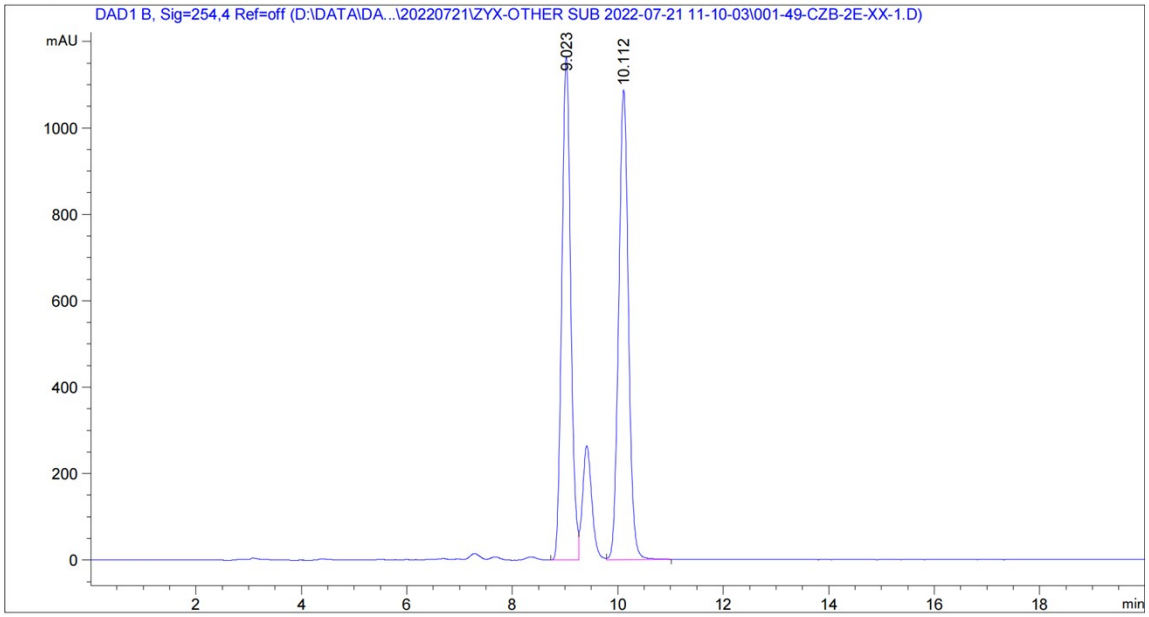
Colorless oil (17.3 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.2 Hz, 1H), 6.61 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.47 (d, *J* = 2.2 Hz, 1H), 3.83 (s, 3H), 3.21 (s, 3H), 2.81 (d, *J* = 16.6 Hz, 1H), 2.53 (d, *J* = 16.6 Hz, 1H), 1.49 (s, 3H).

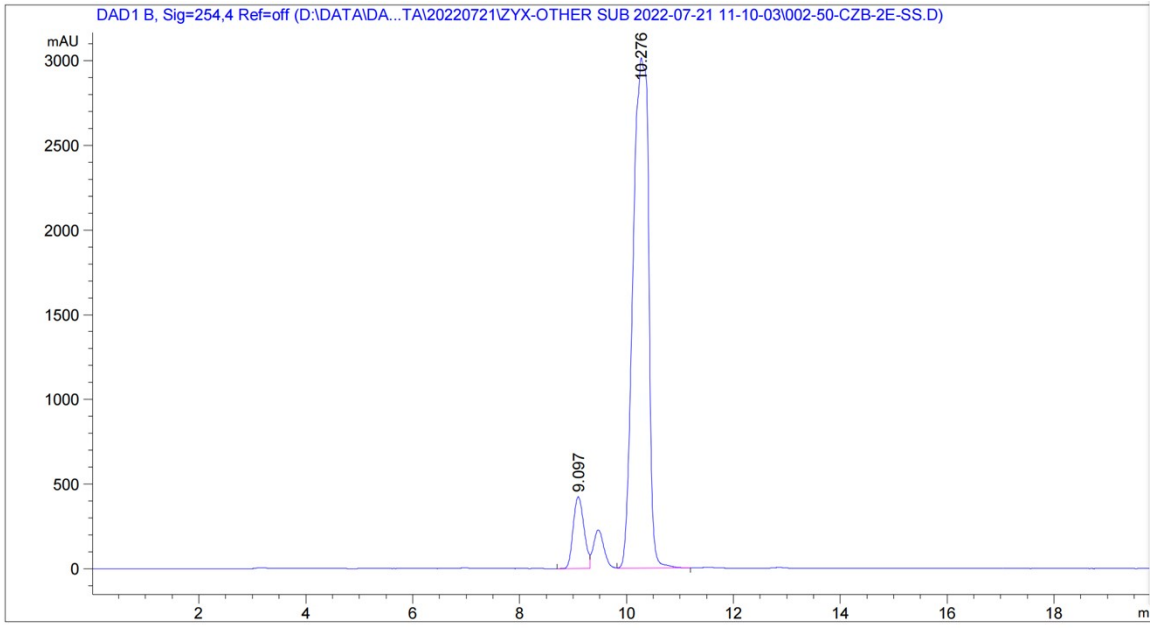
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 161.0, 144.1, 123.9, 123.0, 116.9, 106.9, 96.9, 55.7, 44.6, 26.7 (d, *J* = 6.1 Hz), 22.5.

Optical Rotation: $[\alpha]_D^{25} = 48.7$ ($c = 0.74$, $CHCl_3$)

82 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, $\lambda = 254$ nm): $t_R = 10.3$ min (major), $t_R = 9.1$ min (minor).

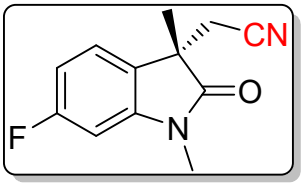


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.023	BV	0.1836	1.37278e4	1164.22400	49.5414
2	10.112	VB	0.1980	1.39819e4	1087.25867	50.4586



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.097	BV	0.2221	5967.75732	424.37466	8.9135
2	10.276	VB	0.2539	6.09838e4	3015.58887	91.0865

(*S*)-2-(6-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (2f)[5]



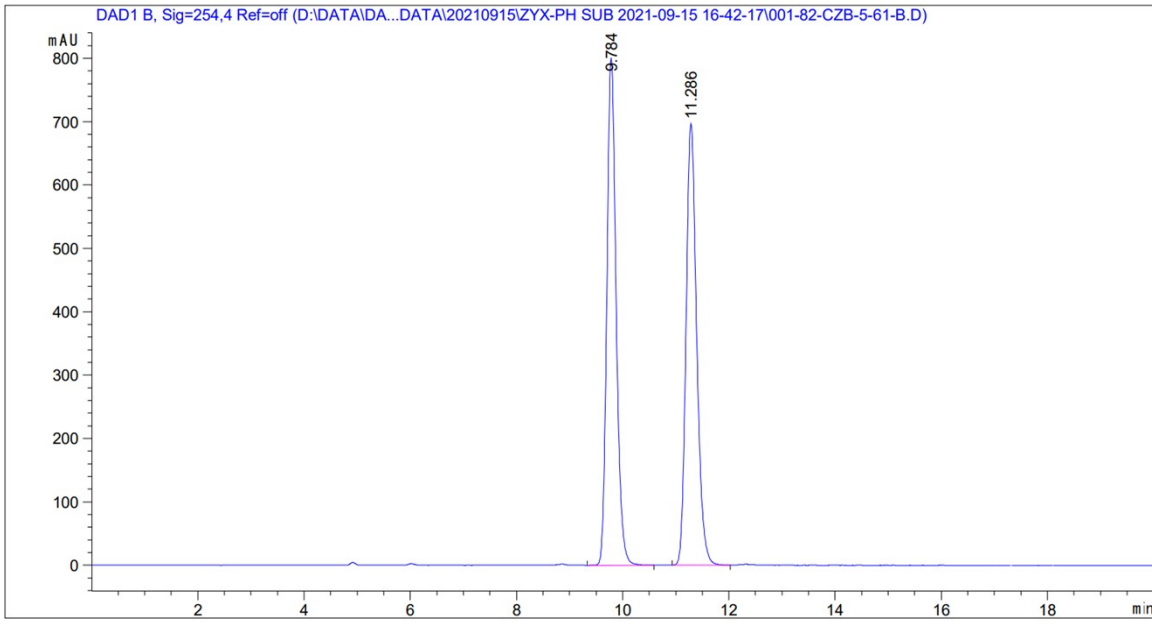
Brown oil (16.4 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 8.2, 5.2 Hz, 1H), 6.88 – 6.74 (m, 1H), 6.64 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.22 (s, 3H), 2.83 (d, *J* = 16.6 Hz, 1H), 2.55 (d, *J* = 16.6 Hz, 1H), 1.50 (s, 3H).

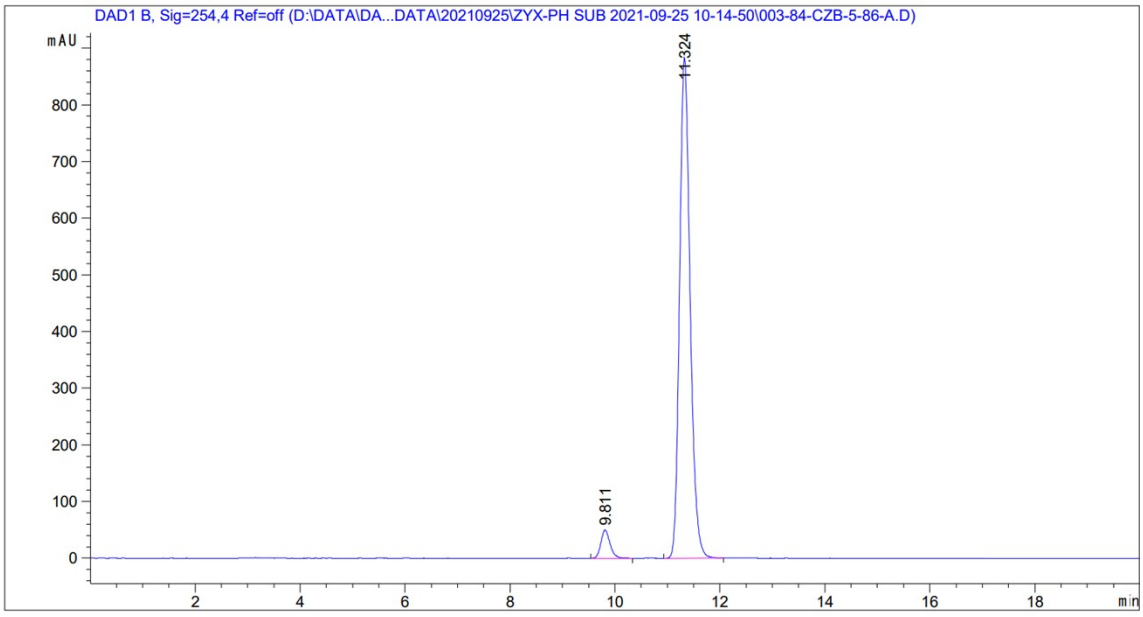
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 164.9, 162.5, 144.4 (d, *J* = 11.6 Hz), 126.4, 124.4 (d, *J* = 9.9 Hz), 116.6, 109.6, 109.3, 97.9, 97.6, 44.7, 26.8, 26.5, 22.4.

Optical Rotation: $[\alpha]_D^{25} = 50.1$ (*c* = 0.80, $CHCl_3$)

91% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 11.3 min (major), t_R= 9.8 min (minor).

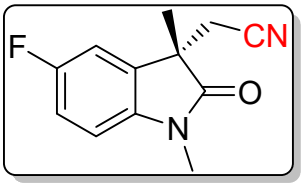


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.784	BB	0.1851	9686.79492	801.14459	50.0551
2	11.286	BB	0.2138	9665.47852	696.89404	49.9449



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.811	BB	0.1852	601.83832	49.73352	4.6522
2	11.324	BB	0.2129	1.23348e4	883.16040	95.3478

(*S*)-2-(5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (2g)



Colorless oil (17.7 mg, 81% yield).

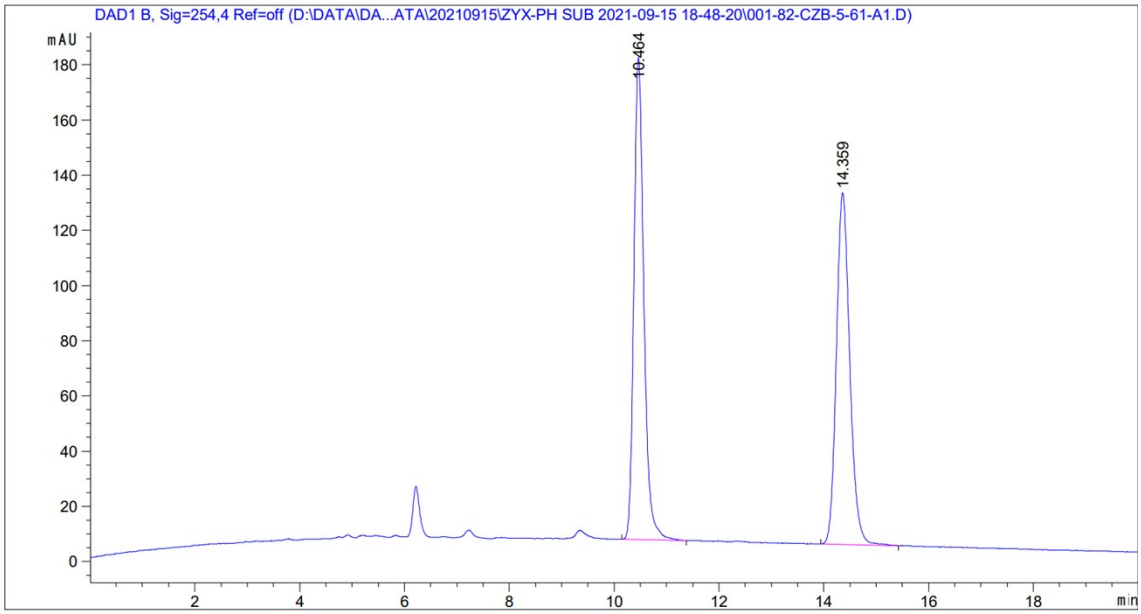
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 7.7, 2.5 Hz, 1H), 7.06 (td, *J* = 8.8, 2.5 Hz, 1H), 6.83 (dd, *J* = 8.5, 4.1 Hz, 1H), 3.24 (s, 3H), 2.85 (d, *J* = 16.7 Hz, 1H), 2.58 (d, *J* = 16.7 Hz, 1H), 1.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 160.9, 138.8 (d, *J* = 2.0 Hz), 132.6 (d, *J* = 8.0 Hz), 116.4, 115.8, 115.5, 111.8, 111.5, 109.4 (d, *J* = 8.1 Hz), 45.4, 26.8, 26.3, 22.3.

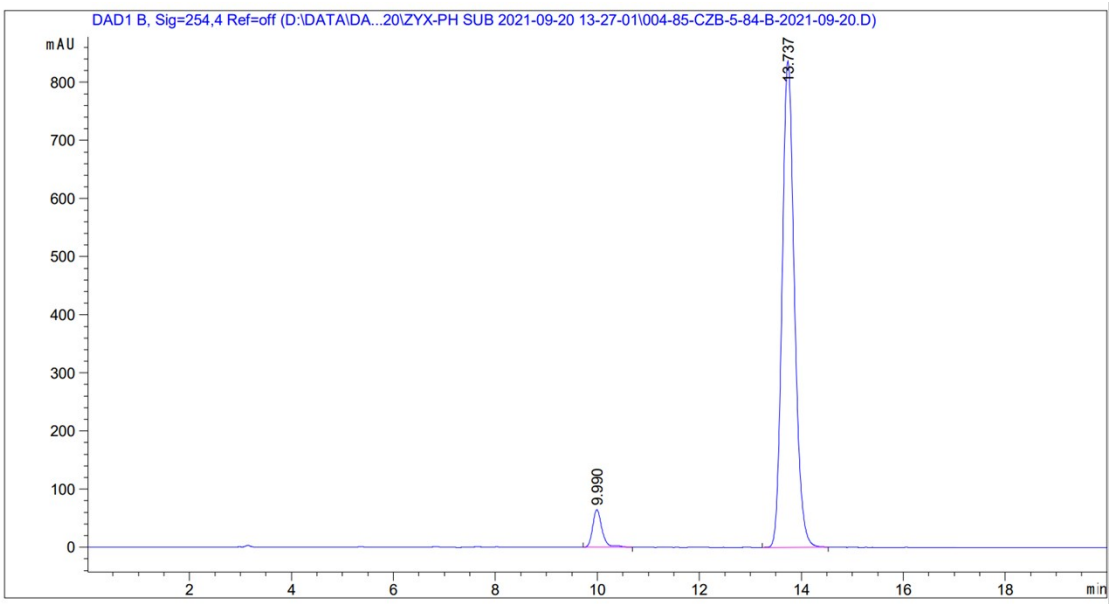
HRMS (ESI): m/z Calcd for $C_{12}H_{11}FN_2ONa$ $[M+Na]^+$ 241.0753; found: m/z 241.0764.

Optical Rotation: $[\alpha]_D^{25}$= 32.5 (*c* = 0.45, $CHCl_3$)

89% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 13.7 min (major), t_R= 10.0 min (minor).

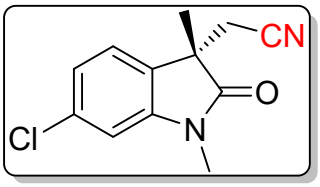


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.464	BB	0.2015	2301.31226	174.89610	50.4972
2	14.359	BB	0.2706	2255.99536	127.39877	49.5028



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.990	BV R	0.1888	830.45184	64.47003	5.5889
2	13.737	BB	0.2596	1.40284e4	836.83716	94.4111

(*S*)-2-(6-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (2h)[5]



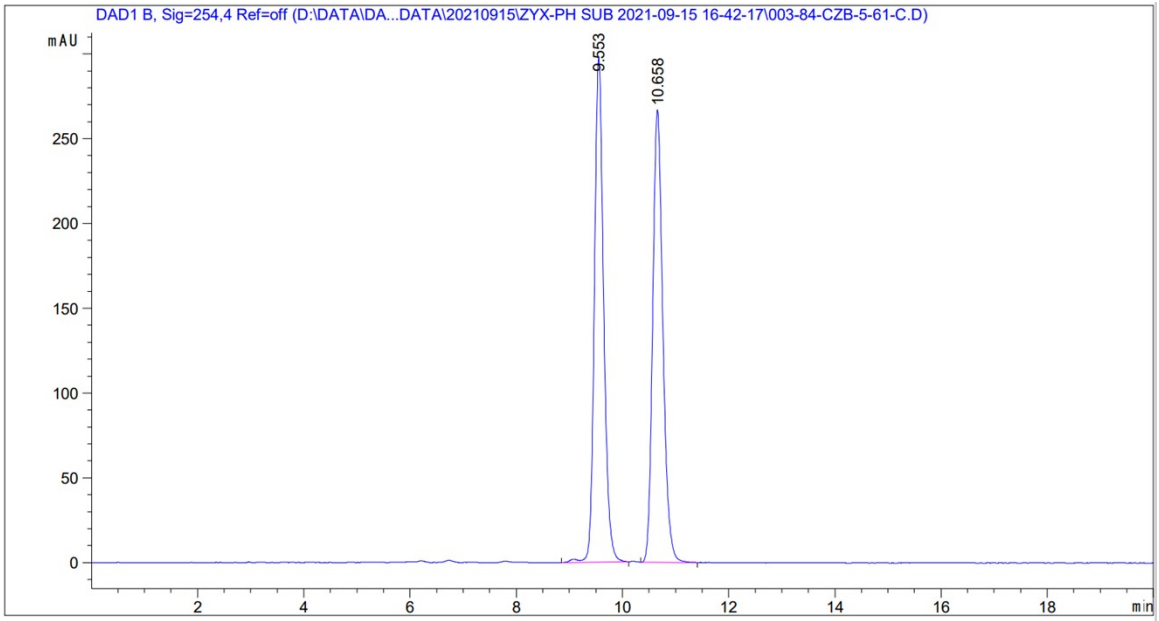
Colorless oil (17.1 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.91 (s, 1H), 3.23 (s, 3H), 2.84 (d, *J* = 16.6 Hz, 1H), 2.55 (d, *J* = 16.6 Hz, 1H), 1.51 (s, 3H).

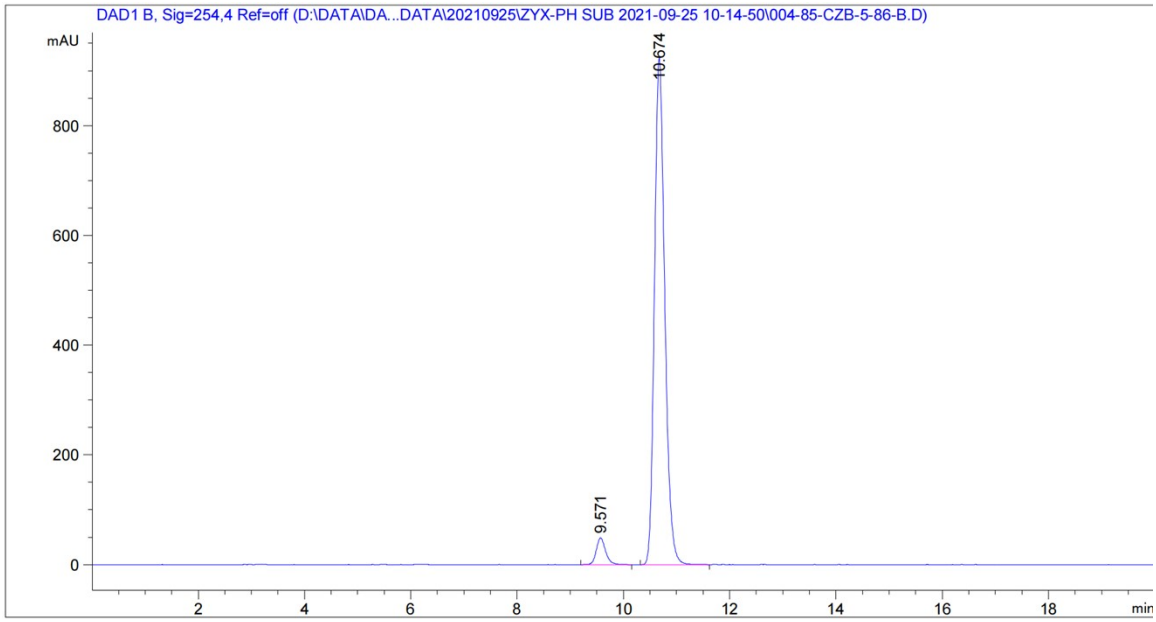
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.5, 144.1, 135.3, 129.4, 124.3, 123.3, 116.5, 109.7, 44.8, 26.8, 26.4, 22.3.

Optical Rotation: $[\alpha]_D^{25} = 58.6$ (*c* = 0.76, $CHCl_3$)

91 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 10.7 min (major), t_R= 9.6 min (minor).

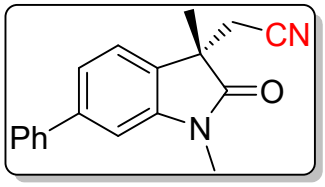


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.553	VB R	0.1846	3610.25073	297.45169	50.4673
2	10.658	BB	0.2029	3543.39551	266.84677	49.5327



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.571	BB	0.1852	599.55005	48.84973	4.6031
2	10.674	BB	0.2049	1.24253e4	924.16919	95.3969

(*S*)-2-(1,3-Dimethyl-2-oxo-6-phenylindolin-3-yl)acetonitrile (2i)[6]



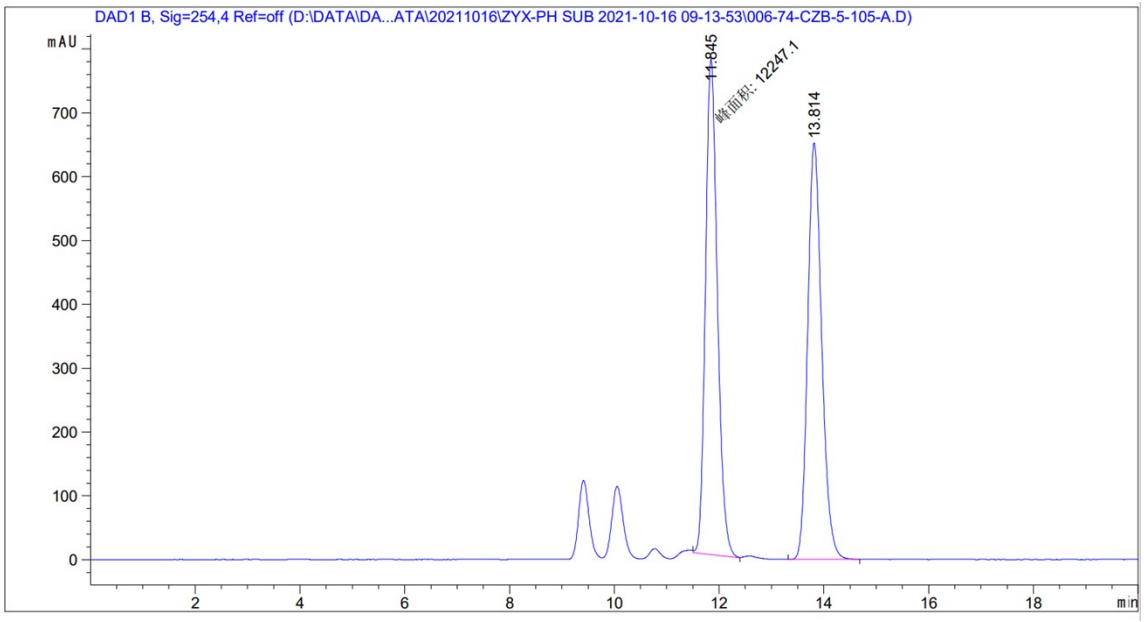
Yellow oil (12.1 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.57 (m, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 6.6 Hz, 2H), 7.37 (ddd, *J* = 10.7, 9.2, 4.4 Hz, 2H), 7.09 (d, *J* = 1.3 Hz, 1H), 3.30 (s, 3H), 2.89 (d, *J* = 16.6 Hz, 1H), 2.60 (d, *J* = 16.6 Hz, 1H), 1.57 (s, 3H).

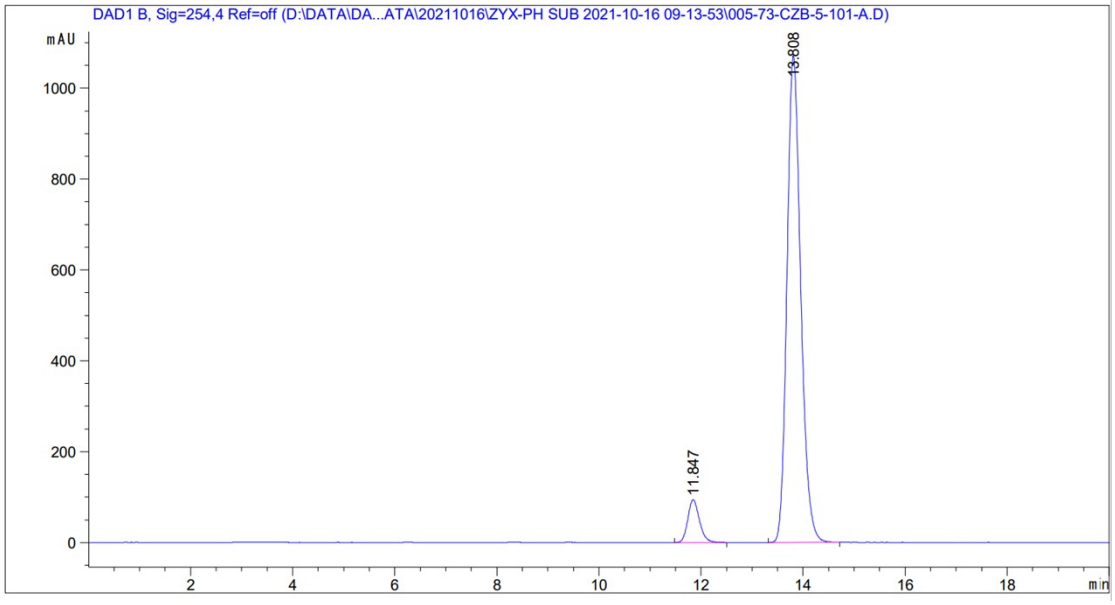
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.8, 143.4, 143.0, 140.8, 130.0, 129.0, 128.0, 127.4, 123.5, 122.4, 116.8, 107.8, 44.9, 26.7, 26.5, 22.4.

Optical Rotation: $[\alpha]_D^{25}$ = 55.1 (*c* = 0.38, $CHCl_3$)

86% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 13.8 min (major), t_R= 11.8 min (minor).

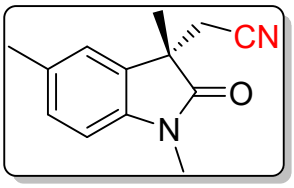


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.845	MM	0.2627	1.22471e4	777.10443	50.1808
2	13.814	BB	0.2873	1.21588e4	652.92773	49.8192



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.847	BB	0.2421	1487.71765	94.29406	6.9173
2	13.808	BB	0.2881	2.00195e4	1070.84741	93.0827

(*S*)-2-(1,3,5-Trimethyl-2-oxoindolin-3-yl)acetonitrile (2j)[5]



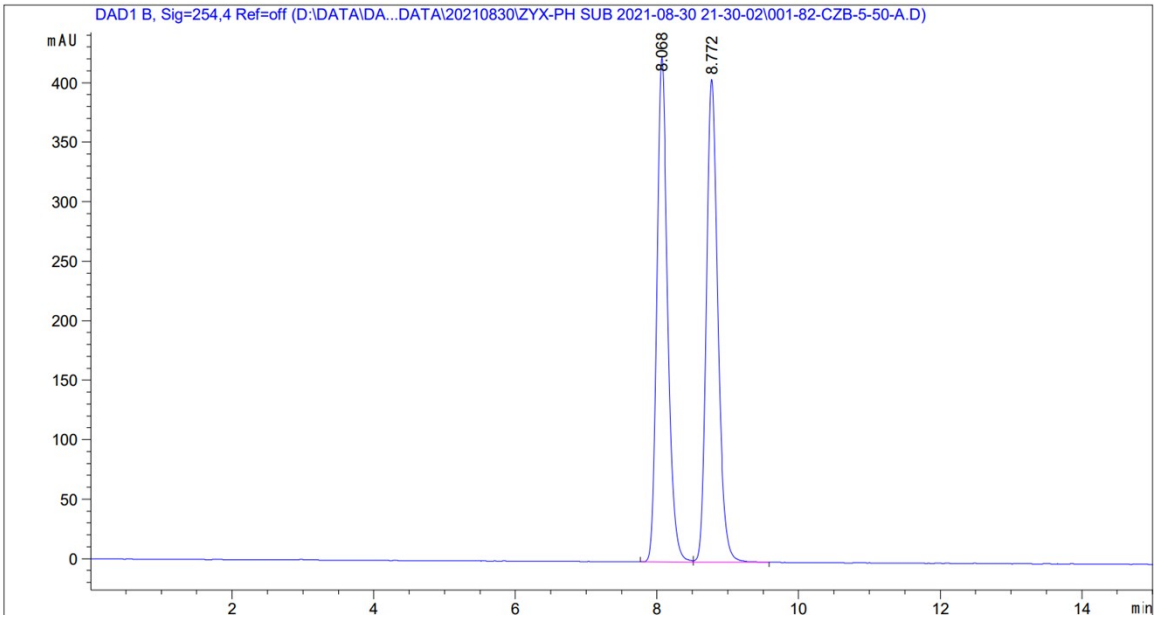
Colorless oil (15.8 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 3.22 (s, 3H), 2.84 (d, *J* = 16.6 Hz, 1H), 2.55 (d, *J* = 16.6 Hz, 1H), 2.37 (s, 3H), 1.51 (s, 3H).

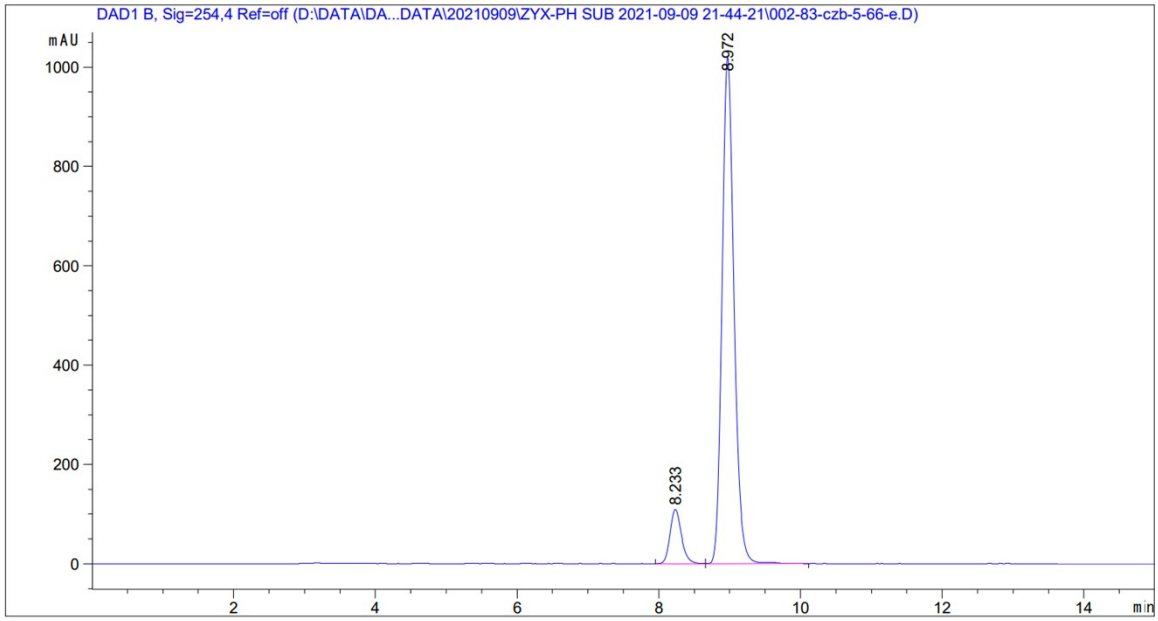
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 140.4, 133.1, 131.2, 129.5, 124.1, 116.8, 108.5, 45.0, 26.7, 26.4, 22.3, 21.3.

Optical Rotation: $[\alpha]_D^{25} = 34.7$ (c = 0.72, $CHCl_3$)

81% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 8.9 min (major), t_R= 8.2 min (minor).

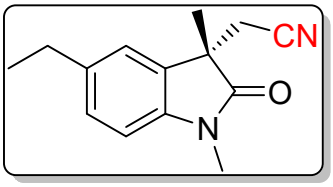


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.068	BV	0.1626	4525.44336	423.87772	49.9152
2	8.772	VB	0.1706	4540.82471	405.74219	50.0848



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.233	BV	0.1706	1223.07471	109.23093	9.4034
2	8.972	VV R	0.1763	1.17836e4	1019.60614	90.5966

(*S*)-2-(5-Ethyl-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (2k)



Colorless oil (17.1 mg, 75% yield).

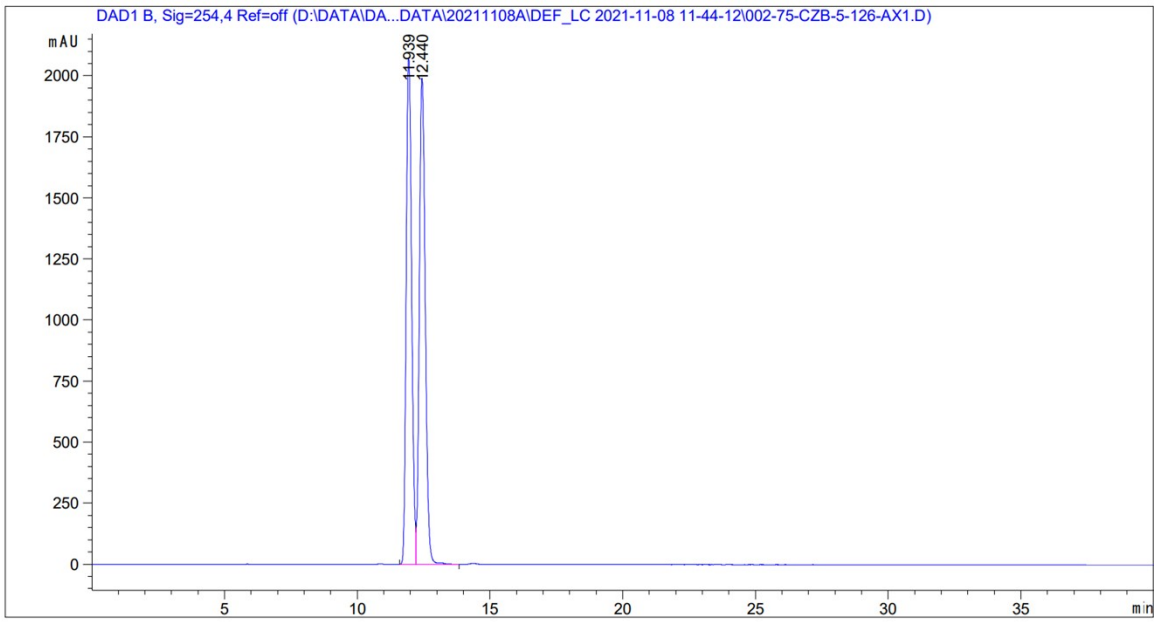
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 1H), 7.17 (d, *J* = 9.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.22 (s, 3H), 2.84 (d, *J* = 16.6 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.55 (d, *J* = 16.6 Hz, 1H), 1.52 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 140.6, 139.7, 131.2, 128.4, 122.9, 116.8, 108.6, 45.0, 28.7, 26.6 (d, *J* = 19.7 Hz), 22.3, 16.1.

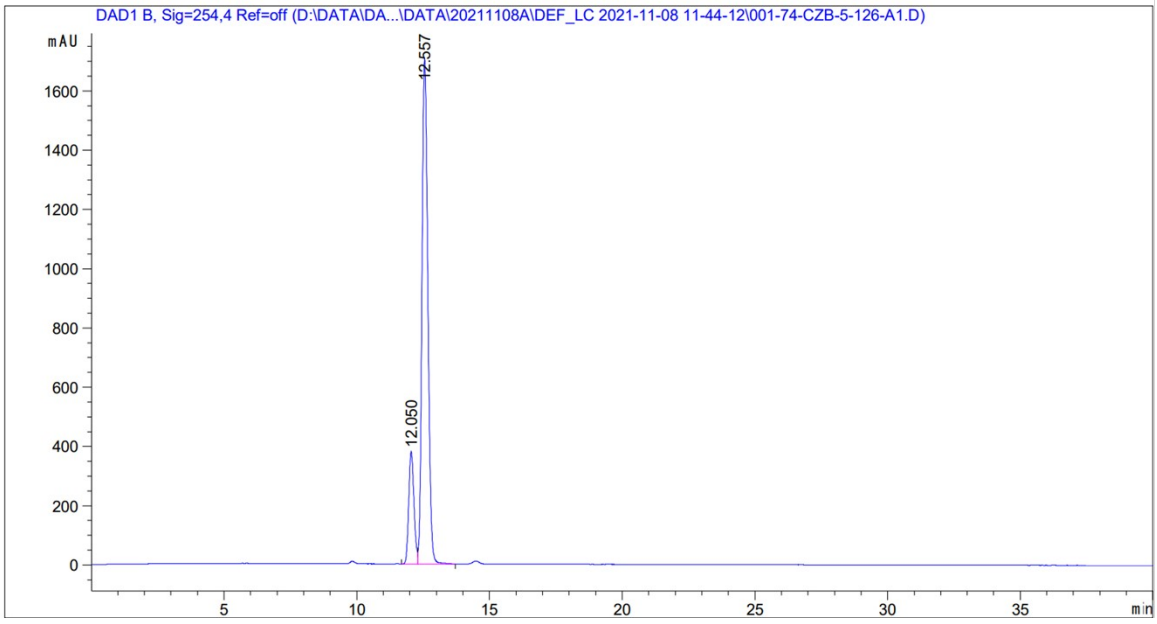
HRMS (ESI): m/z Calcd for $C_{14}H_{16}N_2ONa$ $[M+Na]^+$ 251.1160; found: m/z 251.1167.

Optical Rotation: $[\alpha]_D^{25}$ = 30.4 (*c* = 0.85, $CHCl_3$)

67% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 0.5 mL/min, λ = 254 nm): t_R= 12.6 min (major), t_R= 12.0 min (minor).

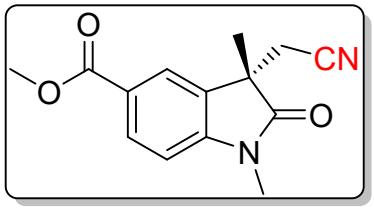


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.939	BV	0.2250	2.96327e4	2070.03662	48.8739
2	12.440	VV R	0.2432	3.09982e4	1989.98438	51.1261



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.050	BV	0.2110	5165.07471	378.95963	16.4504
2	12.557	VB	0.2414	2.62329e4	1706.34558	83.5496

Methyl-(*S*)-3-(cyanomethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (2l)



White solid (8.5 mg, 33% yield). Melting point: 139.6 - 142.1 °C.

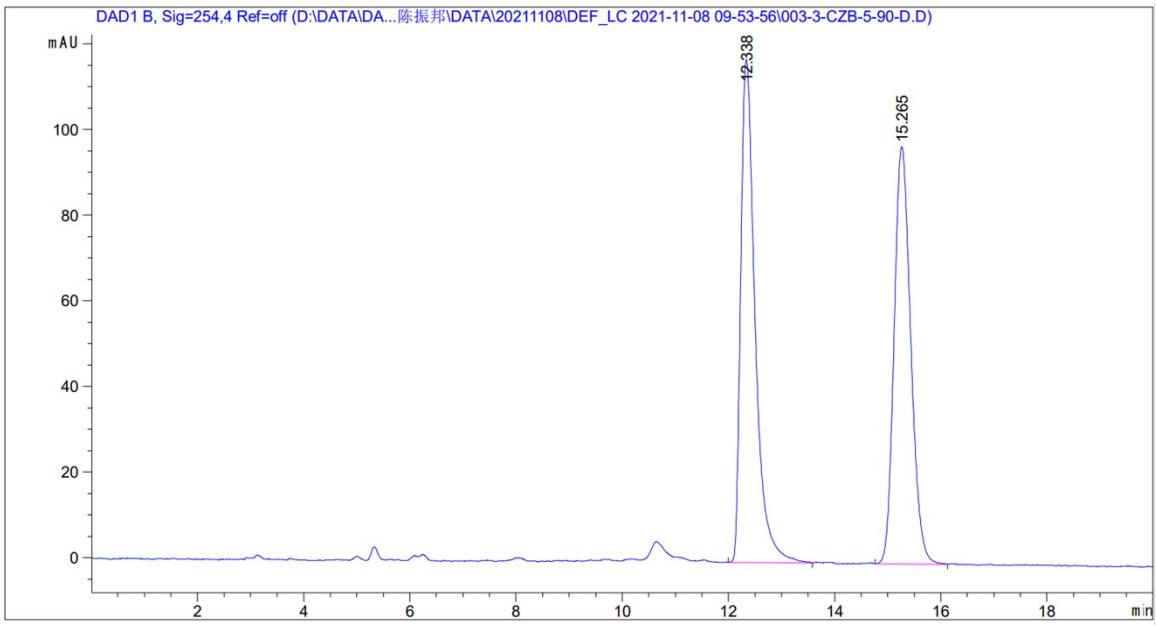
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 3.95 (s, 3H), 3.29 (s, 3H), 2.88 (d, *J* = 16.7 Hz, 1H), 2.59 (d, *J* = 16.6 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 166.5, 143.2, 136.0, 131.4, 125.1, 123.1, 116.4, 109.5, 52.5, 45.1, 26.8, 26.1, 22.1.

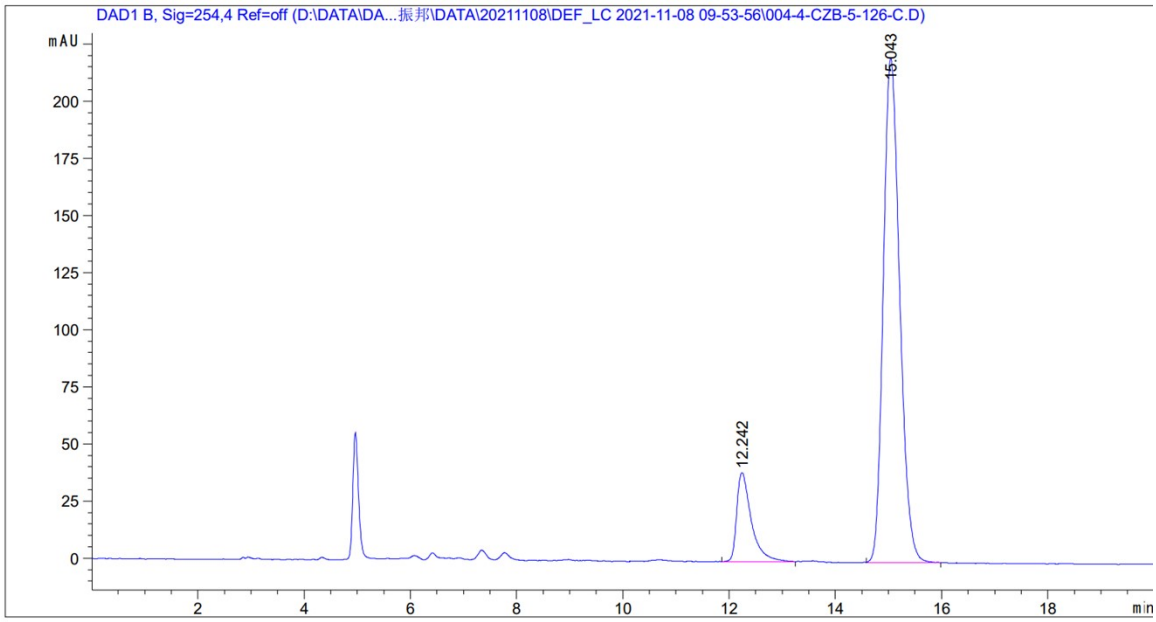
HRMS (ESI): m/z Calcd for $C_{14}H_{14}N_2O_3Na$ $[M+Na]^+$ 281.0902; found: m/z 281.0911.

Optical Rotation: $[\alpha]_D^{25}$ = 3.6 (*c* = 0.11, $CHCl_3$)

73% ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 15.0 min (major), t_R= 12.2 min (minor).

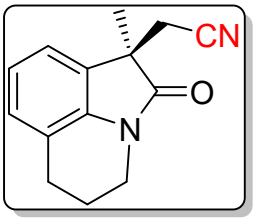


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.338	BB	0.2873	2206.98950	117.41142	51.0276
2	15.265	BB	0.3356	2118.10229	97.43942	48.9724



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.242	BB	0.2843	742.07623	38.94530	13.5675
2	15.043	BB	0.3338	4727.41895	220.74994	86.4325

(*R*)-2-(1-Methyl-2-oxo-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-ij]quinolin-1-yl)acetonitrile (2m)[7]



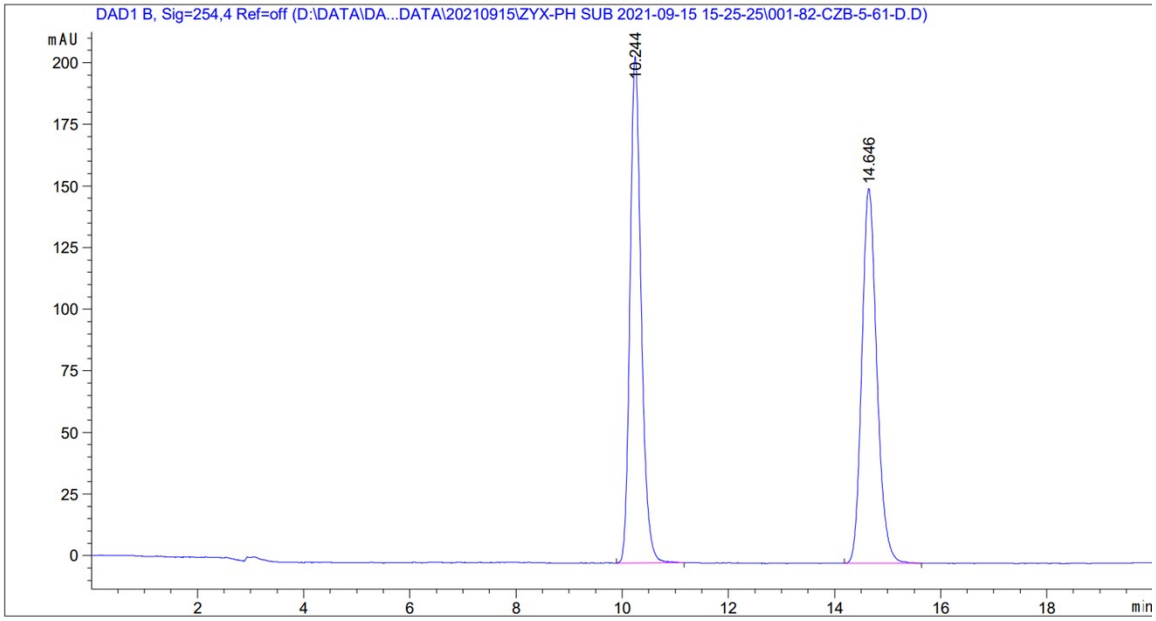
Colorless oil (18.9 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 3.73 (td, *J* = 5.4, 2.5 Hz, 2H), 2.82 (dd, *J* = 18.3, 11.4 Hz, 3H), 2.56 (d, *J* = 16.6 Hz, 1H), 2.07 – 1.99 (m, 2H), 1.53 (s, 3H).

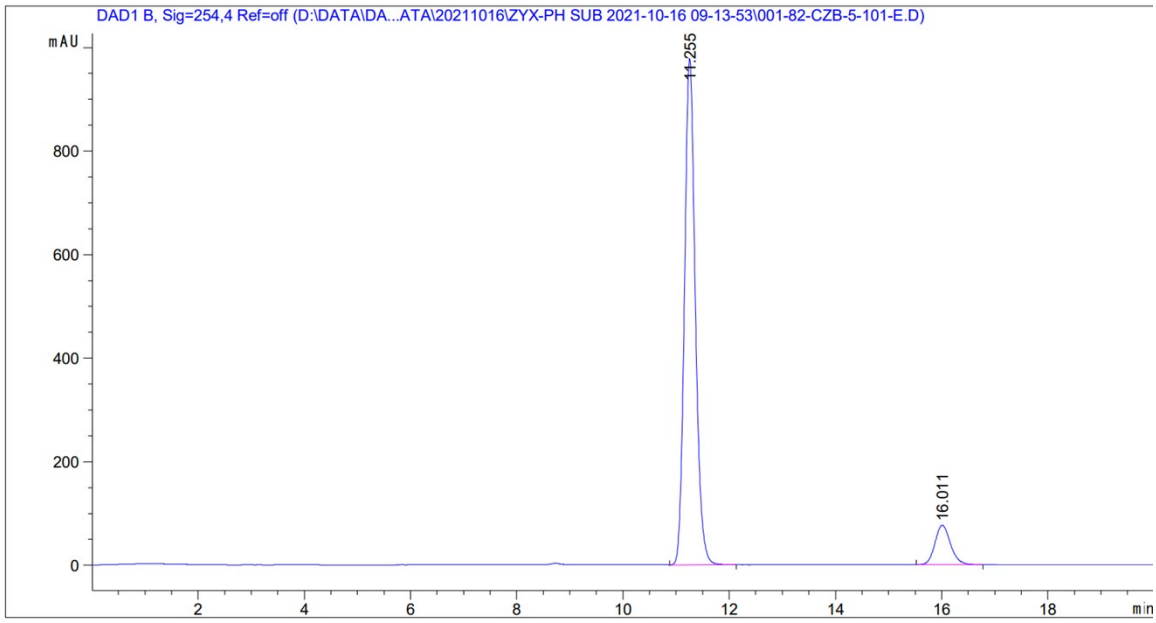
^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 138.6, 129.8, 128.1, 122.8, 121.0 (d, *J* = 18.2 Hz), 116.9, 46.2, 39.2, 26.3, 24.6, 22.1, 21.2.

Optical Rotation: $[\alpha]_D^{25}$ = -49.8 (*c* = 0.52, $CHCl_3$)

80 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 11.3 min (major), t_R= 16.0 min (minor).

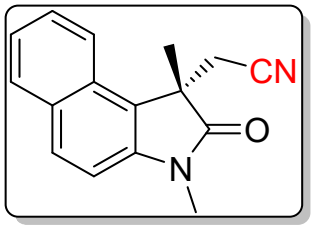


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.244	BB	0.2223	2997.92529	205.39369	50.0822
2	14.646	BB	0.3033	2988.08374	152.05110	49.9178



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.255	BB	0.2174	1.38702e4	978.58972	89.9854
2	16.011	BB	0.3142	1543.63245	76.25620	10.0146

(*S*)-2-(1,3-Dimethyl-2-oxo-2,3-dihydro-1*H*-benzo[e]indol-1-yl)acetonitrile (2n)



White solid (12.7 mg, 51% yield). Melting point:129.1 - 131.3 °C.

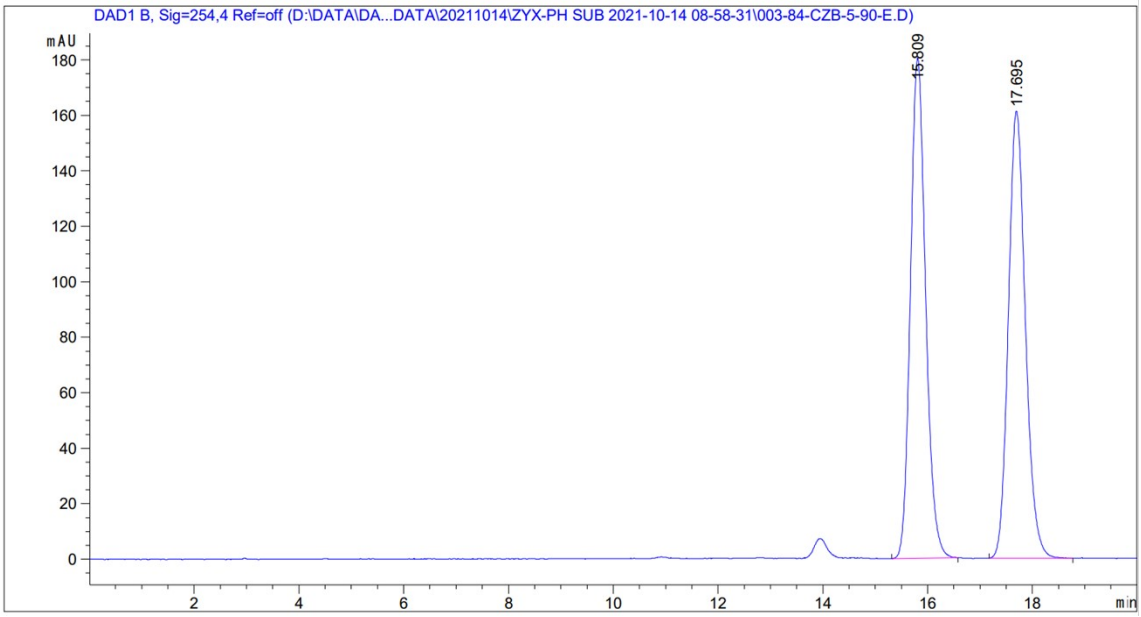
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (t, *J* = 9.2 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.26 (m, 1H), 3.41 (s, 3H), 3.19 (d, *J* = 16.6 Hz, 1H), 3.13 (d, *J* = 16.7 Hz, 1H), 1.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.8, 141.2, 130.9 (d, *J* = 6.0 Hz), 130.3, 129.2, 128.0, 124.1, 1221, 121.2, 116.2, 109.9, 47.4, 26.9, 26.2, 22.5.

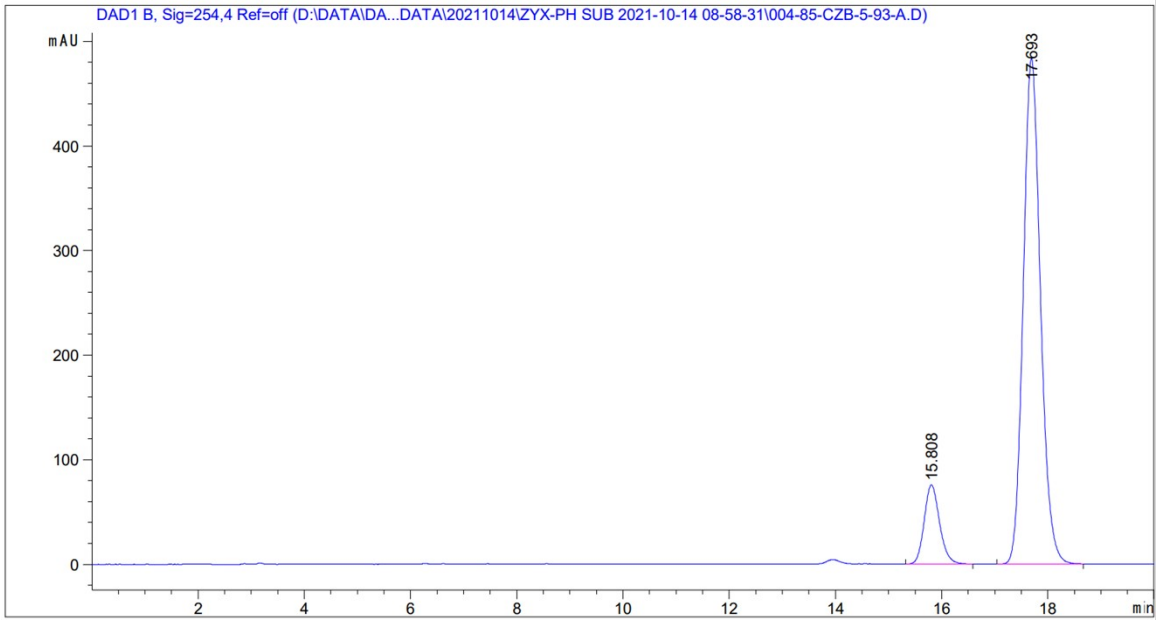
HRMS (ESI): m/z Calcd for $C_{16}H_{14}N_2ONa$ $[M+Na]^+$ 273.1004; found: m/z 273.1009.

Optical Rotation: $[\alpha]_D^{25}$ = -2.4 (*c* = 0.65, $CHCl_3$)

76 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 17.7 min (major), t_R= 15.8 min (minor).

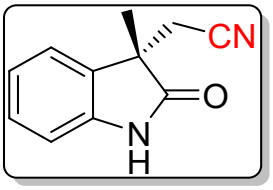


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.809	BB	0.3089	3630.50269	180.34590	49.9688
2	17.695	BB	0.3471	3635.03735	161.16617	50.0312



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.808	BB	0.3086	1523.17004	75.74116	12.2541
2	17.693	BB	0.3469	1.09068e4	483.92142	87.7459

(*S*)-2-(3-Methyl-2-oxoindolin-3-yl)acetonitrile (2o)[8]



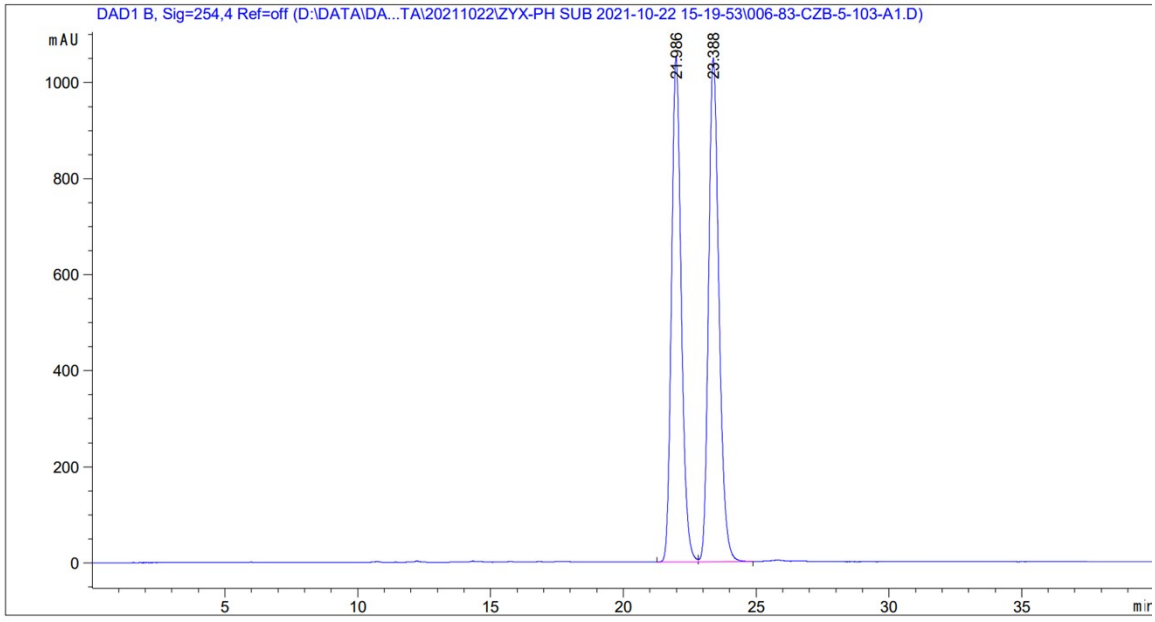
Colorless oil (11.1 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.29 (td, *J* = 7.7, 1.1 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 2.85 (d, *J* = 16.6 Hz, 1H), 2.63 (d, *J* = 16.6 Hz, 1H), 1.56 (s, 3H).

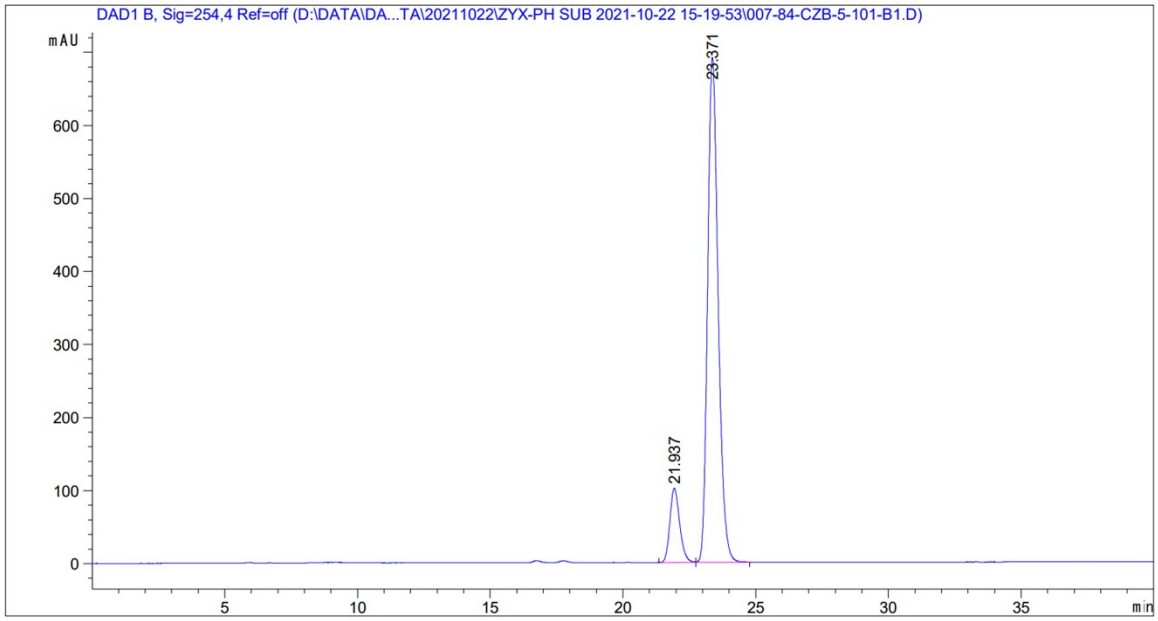
^{13}C NMR (100 MHz, $CDCl_3$): δ 179.9, 139.9, 131.6, 129.3, 123.5 (d, *J* = 17.9 Hz), 116.6, 110.60, 45.4, 26.4, 22.3.

Optical Rotation: $[\alpha]_D^{25}$ = 34.9 (*c* = 0.38, $CHCl_3$)

76 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 0.5 mL/min, λ = 254 nm): t_R= 23.4 min (major), t_R= 21.9 min (minor).

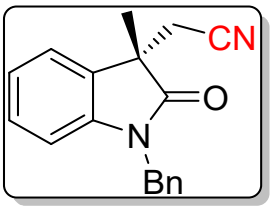


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.986	BV	0.3907	2.67330e4	1051.24841	48.2745
2	23.388	VB	0.4185	2.86440e4	1049.38733	51.7255



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.937	BV	0.3928	2601.55322	101.58399	12.0298
2	23.371	VB	0.4232	1.90244e4	691.05615	87.9702

(*R*)-2-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)acetonitrile (2p)[9]



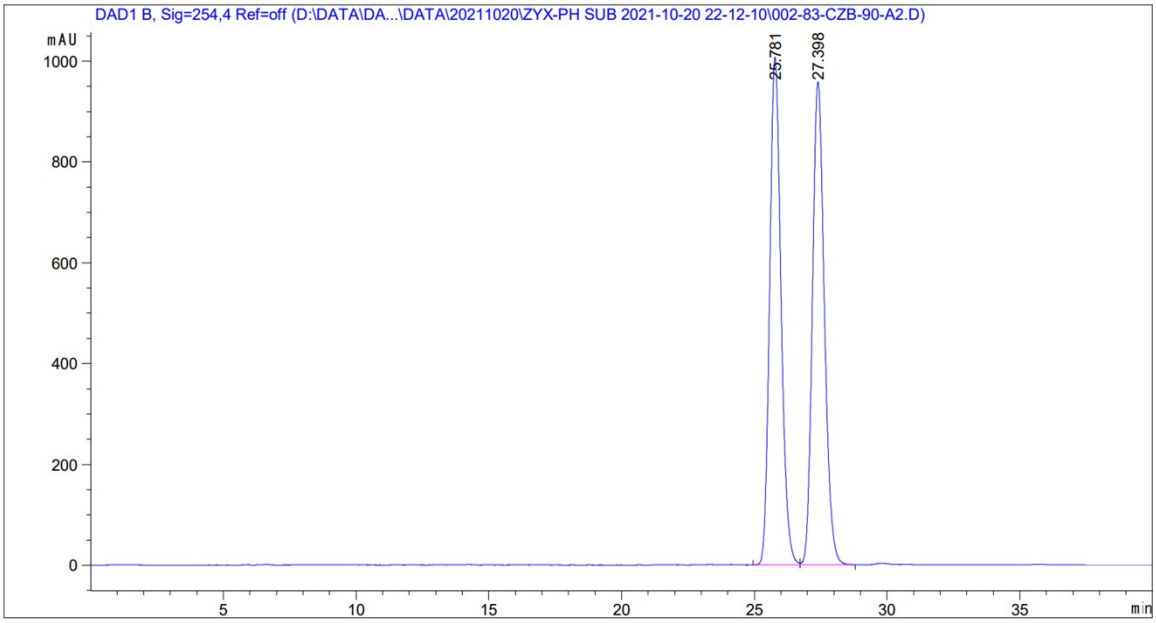
Colorless oil (19.3 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.21 (m, 6H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 4.94 (s, 2H), 2.91 (d, *J* = 16.6 Hz, 1H), 2.65 (d, *J* = 16.6 Hz, 1H), 1.59 (s, 3H).

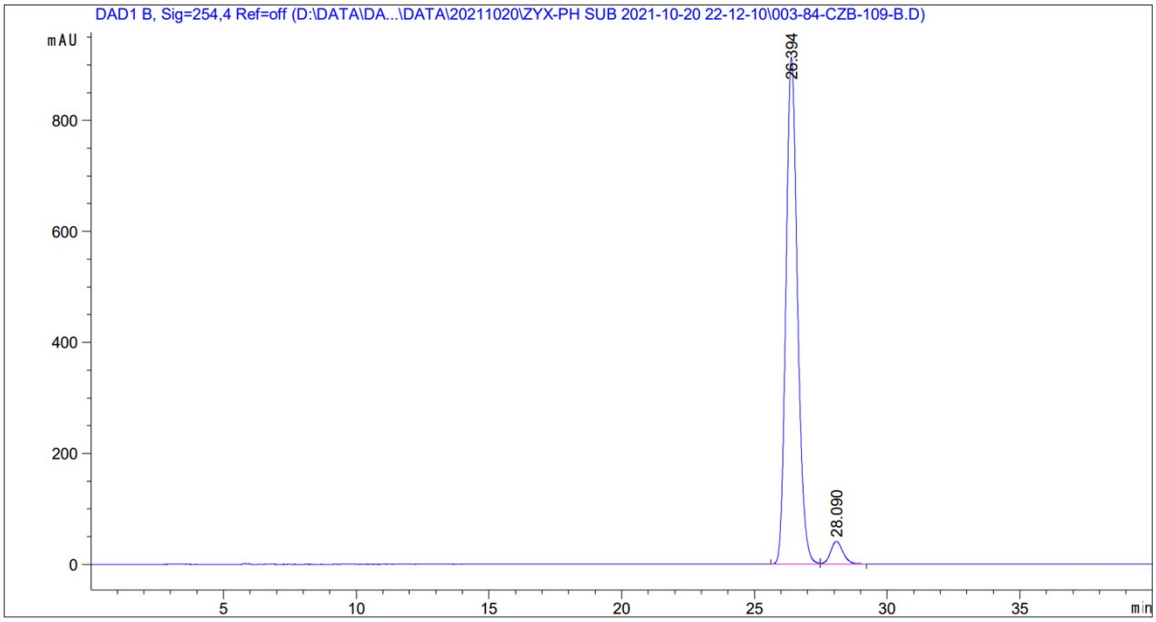
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.8, 141.9, 135.4, 131.1, 129.1 (d, *J* = 20.0 Hz), 128.0, 127.3, 123.4 (d, *J* = 11.1 Hz), 116.7, 109.9, 45.1, 44.1, 26.5, 22.7.

Optical Rotation: $[\alpha]_D^{25}$ = -46.2 (*c* = 0.61, $CHCl_3$). Absolute stereochemistry was determined by comparing the optical rotation value $[\alpha]_D^{26}$ = 26.9 (*c* = 0.90, $CHCl_3$), (*S*)-2-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)acetonitrile (81% ee) in the literature.[9]

90 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 0.5 mL/min, λ = 254 nm): t_R= 26.4 min (major), t_R= 28.1 min (minor).

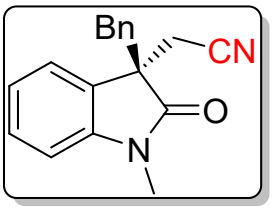


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.781	BV	0.4582	2.98693e4	1006.58704	49.9195
2	27.398	VB	0.4830	2.99656e4	957.87238	50.0805



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	26.394	BV	0.4662	2.75557e4	912.75043	95.4242
2	28.090	VB	0.4848	1321.34692	40.91438	4.5758

(*S*)-2-(3-Benzyl-1-methyl-2-oxoindolin-3-yl)acetonitrile (2q)[5]



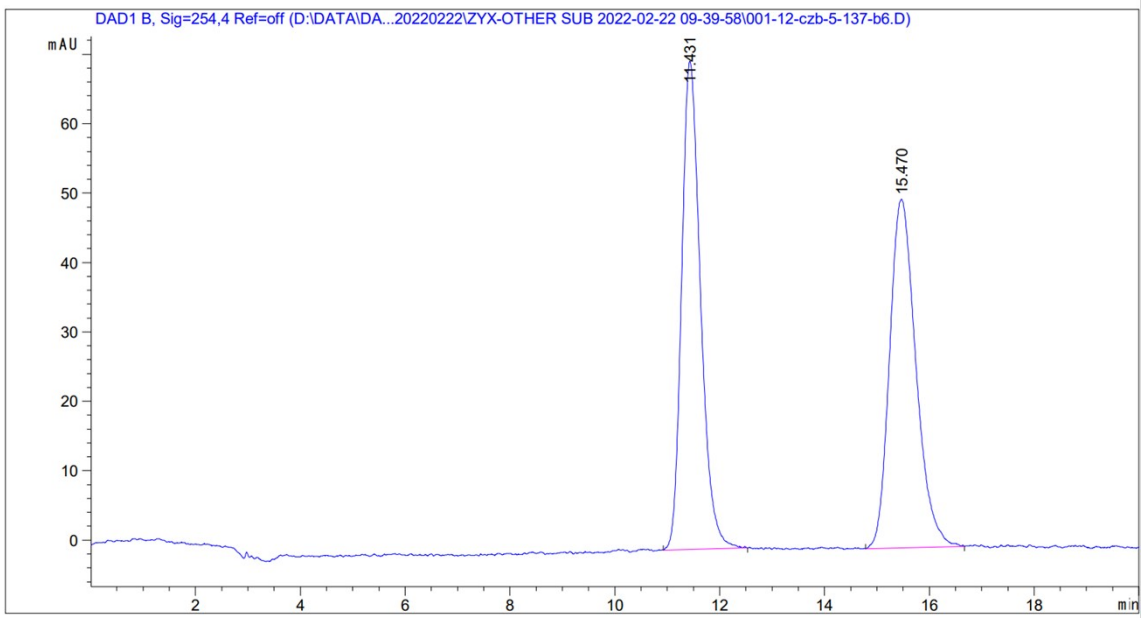
White solid (14.0 mg, 51% yield). Melting point: 85.2 - 86.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 6.7 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.15 – 7.02 (m, 4H), 6.83 (dd, *J* = 7.9, 1.5 Hz, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 3.22 (q, *J* = 12.9 Hz, 2H), 3.01 – 2.94 (m, 4H), 2.74 (d, *J* = 16.7 Hz, 1H).

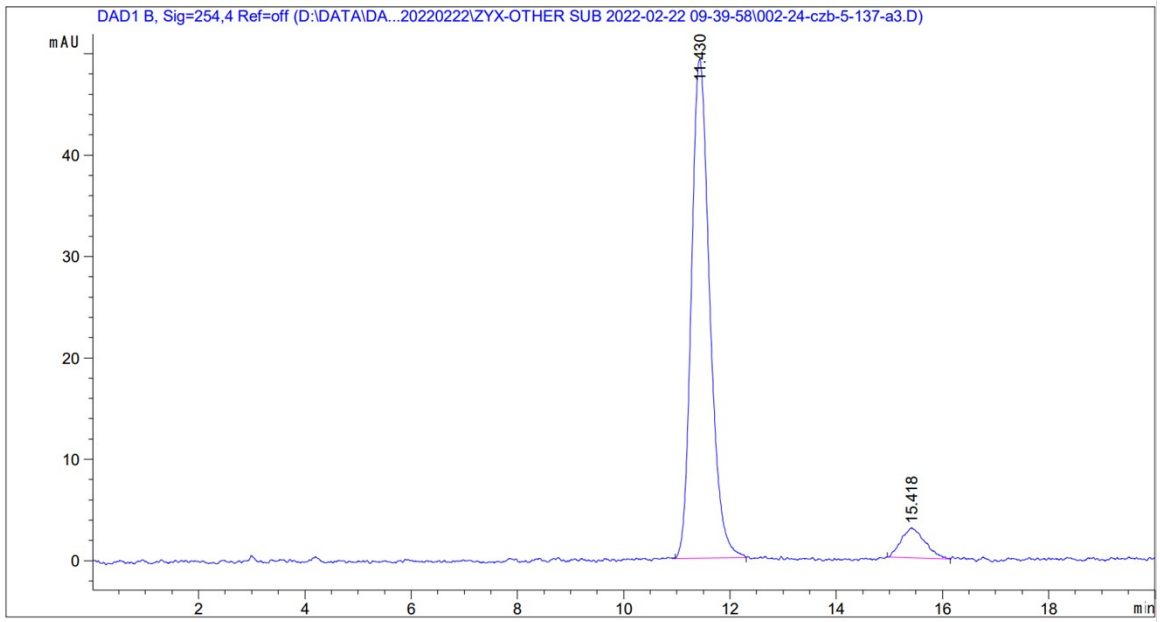
^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 143.4, 134.3, 129.9, 129.4, 128.5, 127.9, 127.2, 124.0, 123.0, 116.7, 108.5, 50.6, 42.5, 26.2, 25.2.

Optical Rotation: $[\alpha]_D^{25}$ = 71.7 (*c* = 0.62, $CHCl_3$)

86 % ee. Determined by HPLC (Daicel Chiralpak AS-H Column, *n*-Hexane: *i*-PrOH = 85:15, flow rate 1 mL/min, λ = 254 nm): t_R= 11.4 min (major), t_R= 15.4 min (minor).

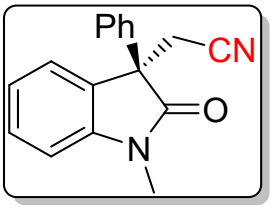


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.431	BV R	0.3778	1759.45776	70.35056	50.1338
2	15.470	BV R	0.5246	1750.06396	50.21130	49.8662



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.430	BB	0.3632	1177.63440	49.21714	92.8351
2	15.418	BB	0.3850	90.88804	2.93749	7.1649

(*S*)-2-(1-Methyl-2-oxo-3-phenylindolin-3-yl)acetonitrile (2r)[5]



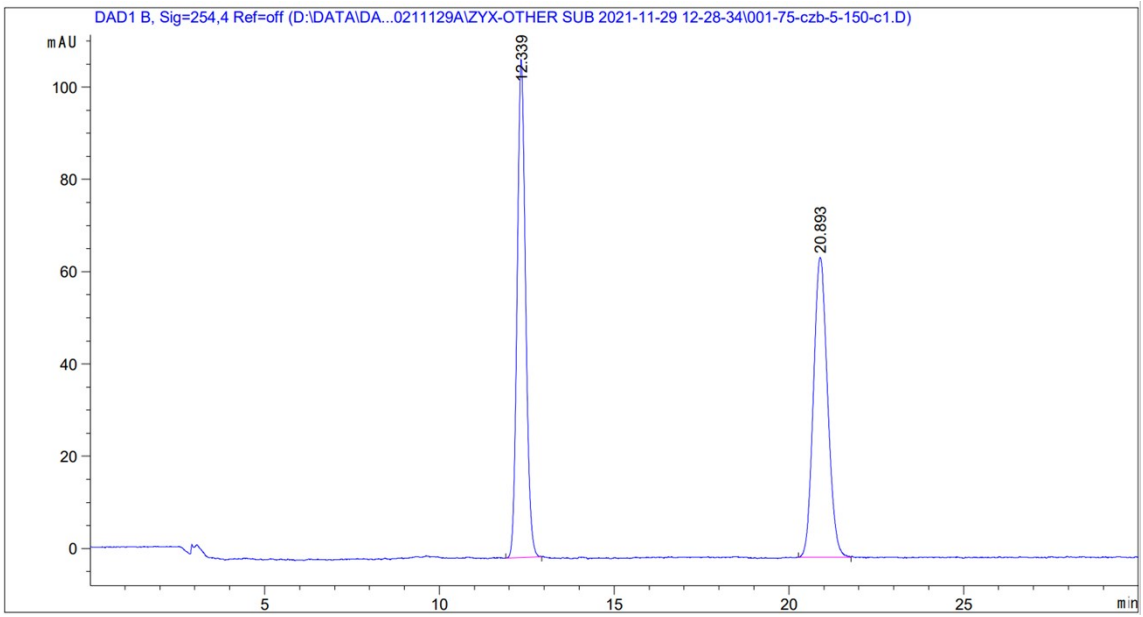
Colorless oil (13.6 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.31 (m, 5H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 3.39 (d, *J* = 16.6 Hz, 1H), 3.24 (s, 3H), 3.05 (d, *J* = 16.6 Hz, 1H).

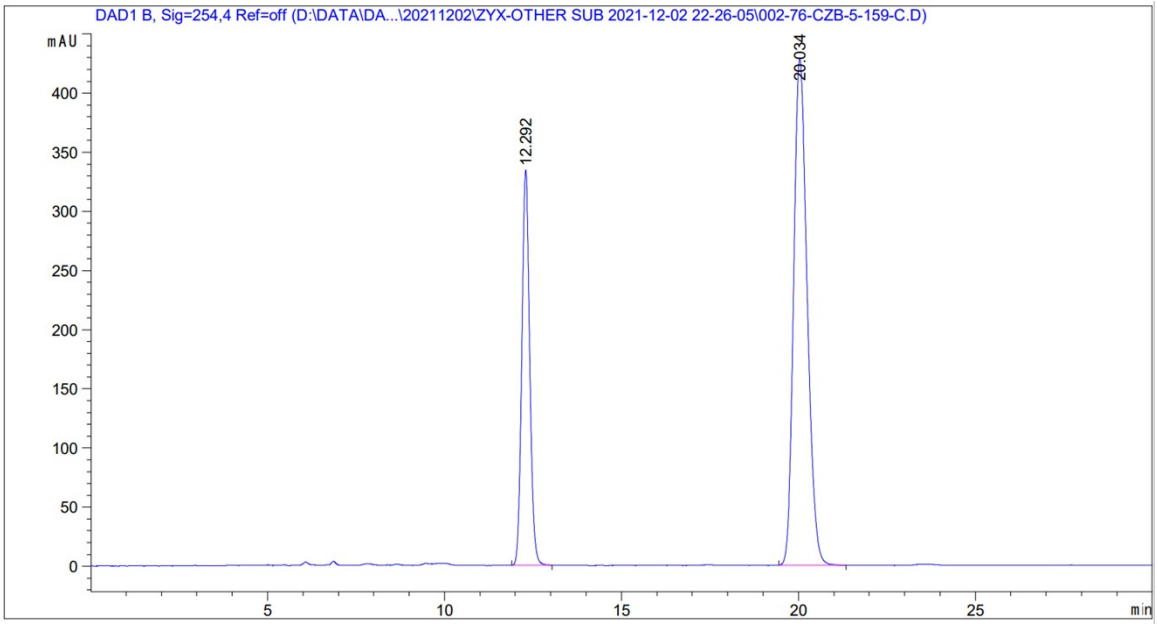
^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 143.7, 136.6, 129.8, 129.5, 129.1, 128.5, 126.9, 125.4, 123.5, 116.6, 109.1, 52.8, 26.9, 26.5.

Optical Rotation: $[\alpha]_D^{25} = 53.0$ (c = 0.65, $CHCl_3$)

37 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 20.0 min (major), t_R= 12.3 min (minor).

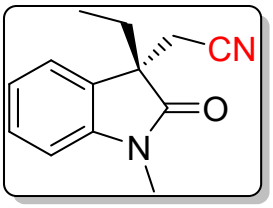


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.339	BB	0.2610	1822.18066	107.90031	49.9566
2	20.893	BB	0.4316	1825.34521	64.99825	50.0434



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.292	BB	0.2420	5214.84619	334.33200	31.4748
2	20.034	BB	0.4132	1.13535e4	428.42776	68.5252

(*S*)-2-(3-Ethyl-1-methyl-2-oxoindolin-3-yl)acetonitrile (2s)[10]



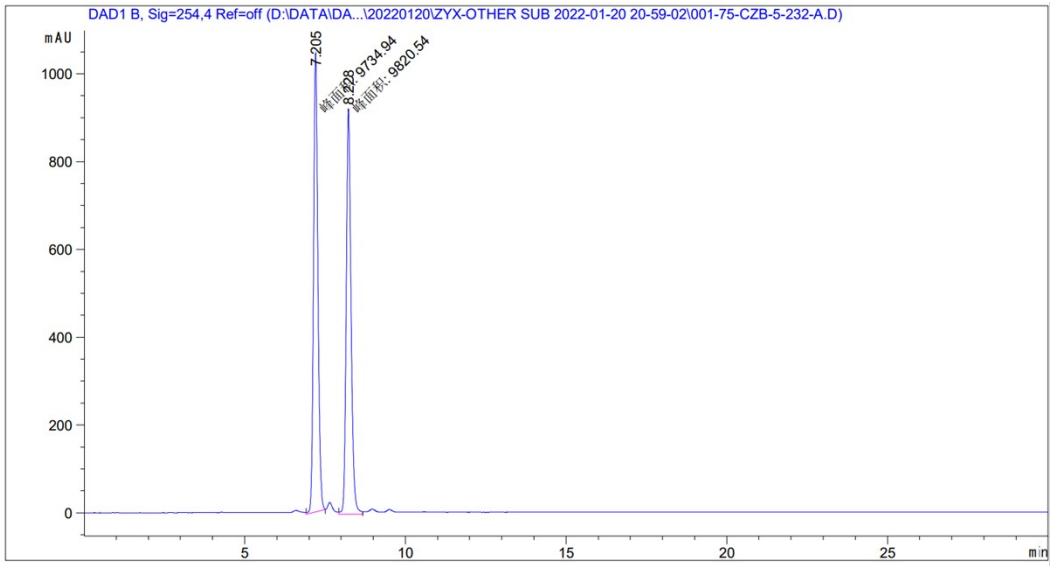
Colorless oil (15.2 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.36 (td, *J* = 7.8, 1.2 Hz, 1H), 7.15 (td, *J* = 7.6, 0.9 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.24 (s, 3H), 2.84 (d, *J* = 16.6 Hz, 1H), 2.59 (d, *J* = 16.6 Hz, 1H), 2.02 (q, *J* = 7.4 Hz, 2H), 0.61 (t, *J* = 7.4 Hz, 3H).

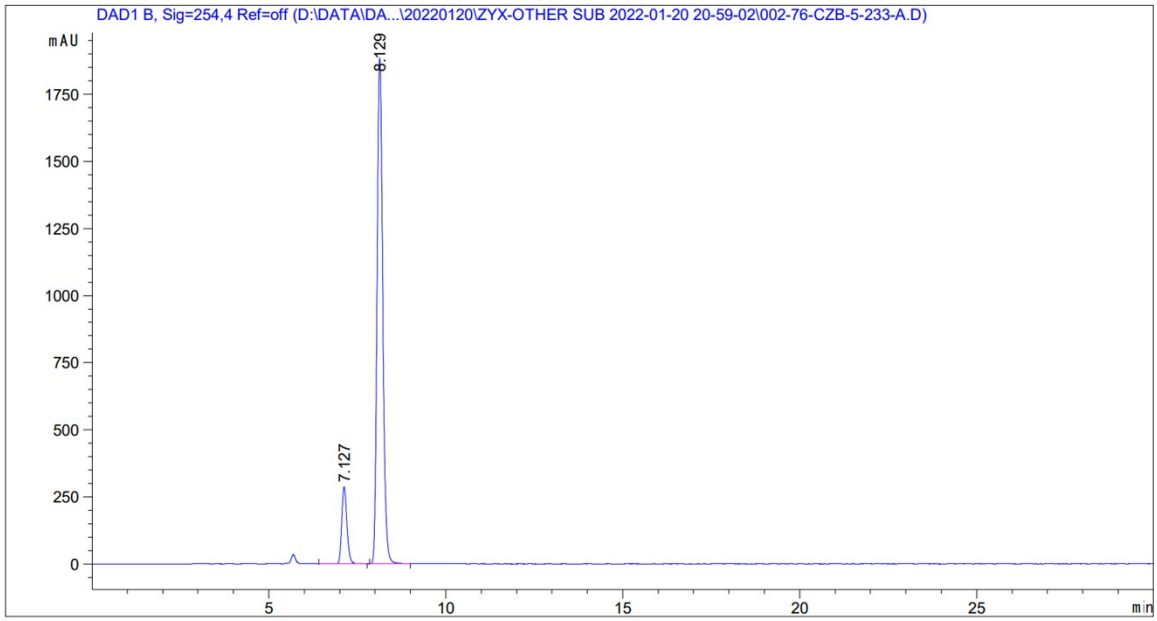
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 143.7, 129.2 (d, *J* = 18.7 Hz), 123.4 (d, *J* = 1.5 Hz), 116.7, 108.6, 49.7, 29.5, 26.5, 25.8, 8.5.

Optical Rotation: $[\alpha]_D^{25} = 7.6$ (*c* = 0.11, $CHCl_3$)

76 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 8.1 min (major), t_R= 7.1 min (minor).

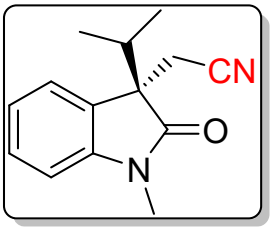


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.205	MM	0.1552	9734.93945	1045.14209	49.7811
2	8.228	MM	0.1771	9820.54297	924.11456	50.2189



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.127	VB R	0.1524	2895.21973	287.80273	12.0953
2	8.129	BB	0.1741	2.10416e4	1886.67126	87.9047

2-(3-Isopropyl-1-methyl-2-oxoindolin-3-yl)acetonitrile (2t)[6]

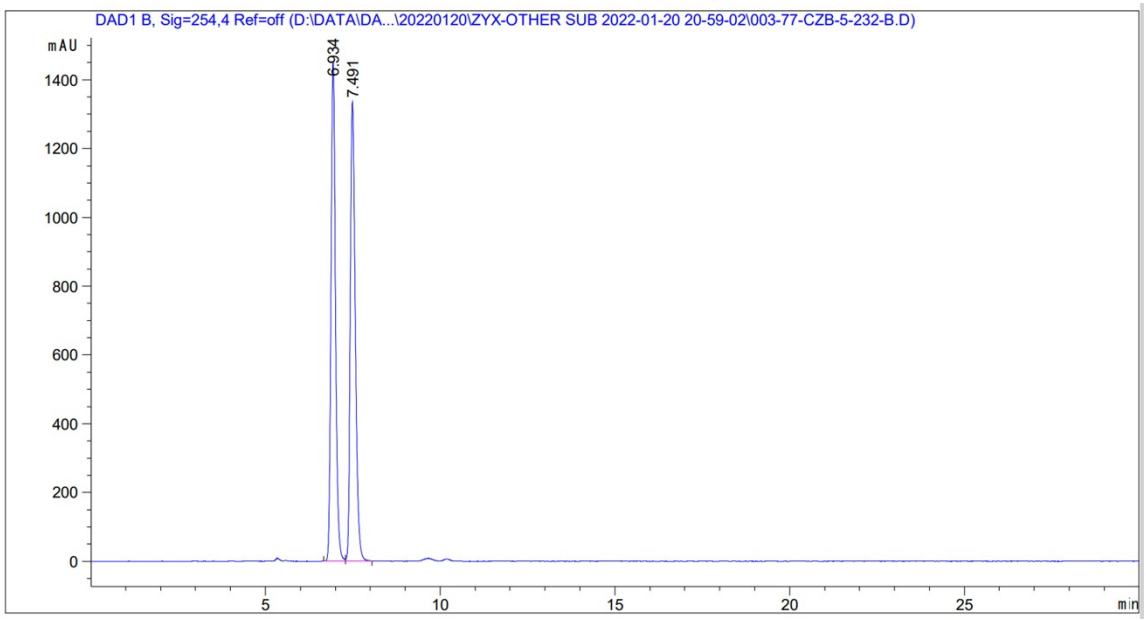


Colorless oil (10.0 mg, 44% yield).

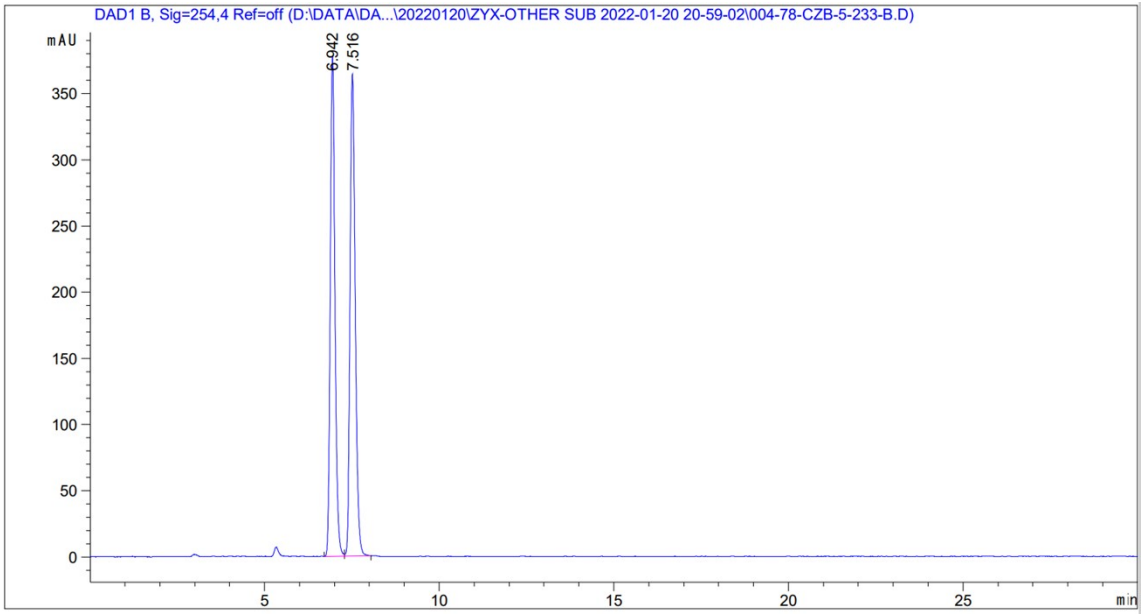
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (ddd, *J* = 8.8, 5.6, 1.7 Hz, 2H), 7.12 (td, *J* = 7.7, 0.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 2.94 (d, *J* = 16.6 Hz, 1H), 2.68 (d, *J* = 16.6 Hz, 1H), 2.40 – 2.27 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 143.9, 129.1 (d, *J* = 16.1 Hz), 123.6, 123.1, 116.8, 108.5, 52.3, 34.5, 26.4, 24.0, 17.2, 17.0.

2 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, λ = 254 nm): t_R= 7.5 min (major), t_R= 6.9 min (minor).



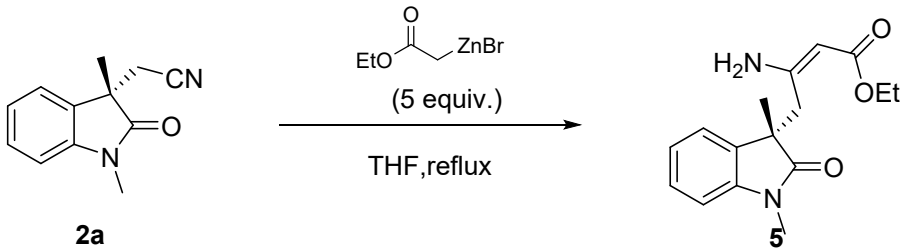
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.934	BV	0.1402	1.32053e4	1450.17297	49.8958
2	7.491	VB	0.1540	1.32605e4	1333.68420	50.1042



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.942	BV	0.1472	3595.28125	377.36691	48.9742
2	7.516	VB	0.1580	3745.89282	364.13153	51.0258

6、Experimental Procedures and Characterization Data for Derivatization Studies

Ethyl (*S*, *E*)-3-amino-4-(1,3-dimethyl-2-oxoindolin-3-yl)but-2-enoate (5)



2a
91% ee

5
59% yield, 87% ee

To a suspension of activated zinc powder (50 mg, 0.75 mmol, 5.0 equiv) in THF (0.5 mL) at reflux (70 °C), 2 drops of ethyl 2-bromoacetate was added. After the observation of a pale green colour, **2a** (30 mg, 0.15 mmol, 1.0 equiv) dissolved in THF(0.5 mL) was added in one portion into the above mixture. The remaining ethyl 2-bromoacetate (125 μL, 0.75 mmol, 5.0 equiv) was added dropwise over 30 minutes and the mixture was stirred at 70 °C for 3 hours. After the reaction finished (monitored by TLC), the mixture was diluted with 2 mL of THF and quenched with 50% aqueous K_2CO_3. The resulting biphasic mixture was stirred overnight to allow separation. The resulting organic phase was transferred to a separate container. The remaining yellow residue was thoroughly rinsed with additional THF (3 x 2 mL) and the combined organic layers were sequentially dried over $MgSO_4$, filtered and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield product **5** as a yellow oil (24.4 mg, yield: 59%).

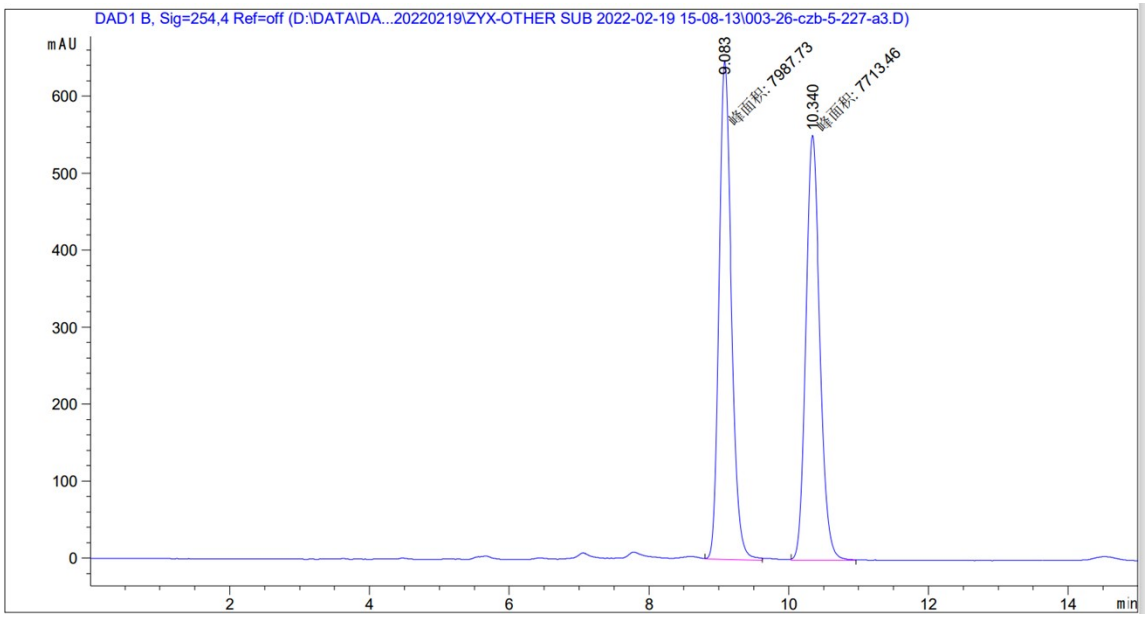
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.20 (s, 1H), 4.34 (s, 1H), 4.08 – 3.93 (m, 2H), 3.22 (s, 3H), 2.66 (d, *J* = 13.8 Hz, 1H), 2.56 (d, *J* = 13.8 Hz, 1H), 1.43 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.5, 170.1, 158.7, 143.0, 132.9, 128.4, 123.0, 122.8, 108.6, 86.1, 58.6, 48.1, 43.6, 26.5, 24.0, 14.6.

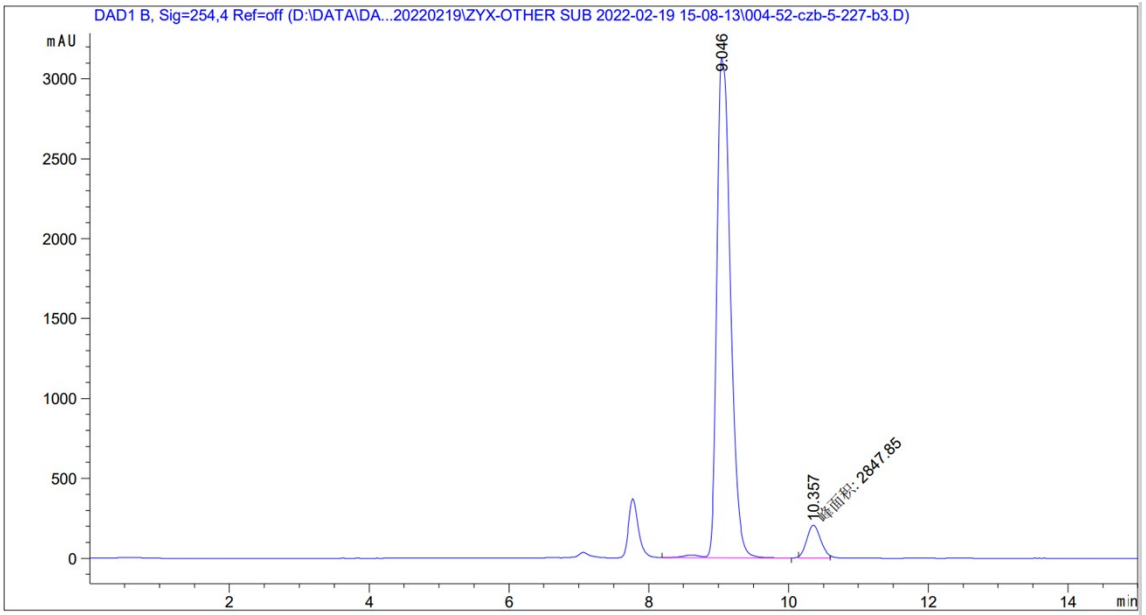
HRMS (ESI): m/z Calcd for $C_{16}H_{20}N_2NaO_3$ [M+Na^+]: 311.1366; found 311.1368.

Optical Rotation: $[\alpha]_D^{25}$ = 34.1 (*c* = 0.27, $CHCl_3$)

87 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 80:20, flow rate 0.8 mL/min, λ = 254 nm): t_R= 9.0 min (major), t_R= 10.4 min (minor)

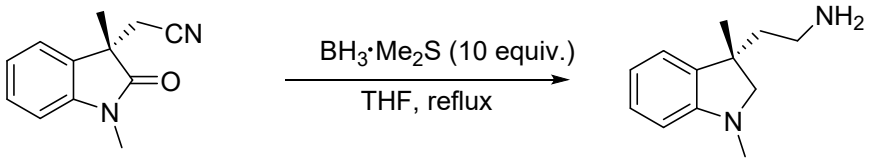


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.083	MM	0.2055	7987.73096	647.72748	50.8734
2	10.340	MM	0.2326	7713.45996	552.69556	49.1266



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.046	VB R	0.1783	4.21633e4	3127.20288	93.6730
2	10.357	MM	0.2297	2847.84692	206.60307	6.3270

(*S*)-2-(1,3-Dimethylindolin-3-yl)ethan-1-amine (6)



2a
92% ee

6
84% yield

The mixture of **2a** (30 mg, 0.15 mmol, 1.0 equiv) and $BH_3 \cdot Me_2S$ (1.5 mL, 1.0 M, 1.5 mmol, 10 equiv) in THF (1 mL) was heated at 70 °C for 12 hours. After the reaction was completed (monitored by TLC), the mixture was quenched with MeOH, and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (DCM/MeOH) to yield product **6** as a yellow oil (24 mg, yield: 84%).

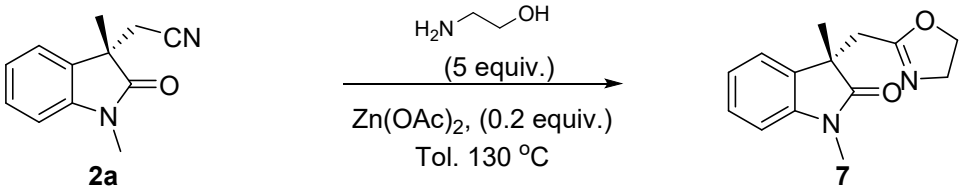
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 3.23 (d, *J* = 8.7 Hz, 1H), 2.98 (d, *J* = 8.7 Hz, 1H), 2.79 – 2.69 (m, 4H), 2.68 – 2.57 (m, 1H), 1.87 – 1.79 (m, 1H), 1.75 – 1.67 (m, 3H), 1.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 137.6, 127.8, 122.3, 117.9, 107.5, 68.5, 44.7, 43.0, 38.6, 36.1, 25.9.

HRMS (ESI): m/z Calcd for $C_{12}H_{19}N_2$ [M+H]:191.1543; found 191.1543.

Optical Rotation:$[\alpha]_D^{25}$ = 19.0 (*c* = 0.31, $CHCl_3$)

(*S*)-3-((4,5-*D*ihydrooxazol-2-yl)methyl)-1,3-dimethylindolin-2-one (7)



2a
92% ee

7
59% yield, 92% ee

The mixture of **2a** (30 mg, 0.15 mmol, 1.0 equiv), 2-aminoethan-1-ol (45.8 mg, 0.75 mmol, 5.0 equiv), and $Zn(OAc)_2$ (6 mg, 0.03 mmol, 20 mol%) in Tol. (1 mL) was heated at 130 °C for 48 hours. After the reaction was completed (monitored by TLC), the mixture was concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield product **7** as a yellow oil (21.6 mg, yield: 59%).

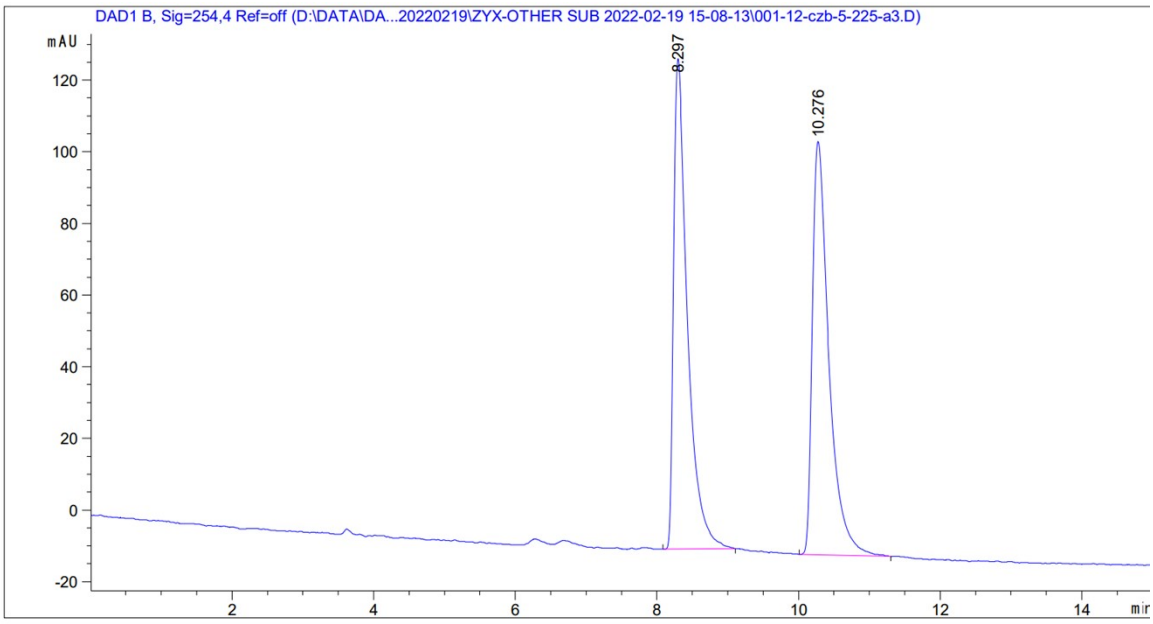
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.21 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.04 (dd, *J* = 18.0, 8.4 Hz, 1H), 3.82 (dd, *J* = 18.7, 8.6 Hz, 1H), 3.57 (td, *J* = 9.4, 4.9 Hz, 2H), 3.24 (s, 3H), 2.86 (q, *J* = 14.8 Hz, 2H), 1.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.0, 164.5, 143.4, 132.6, 128.1, 123.1, 122.4, 108.0, 67.4, 54.3, 46.4, 35.8, 26.5, 24.2.

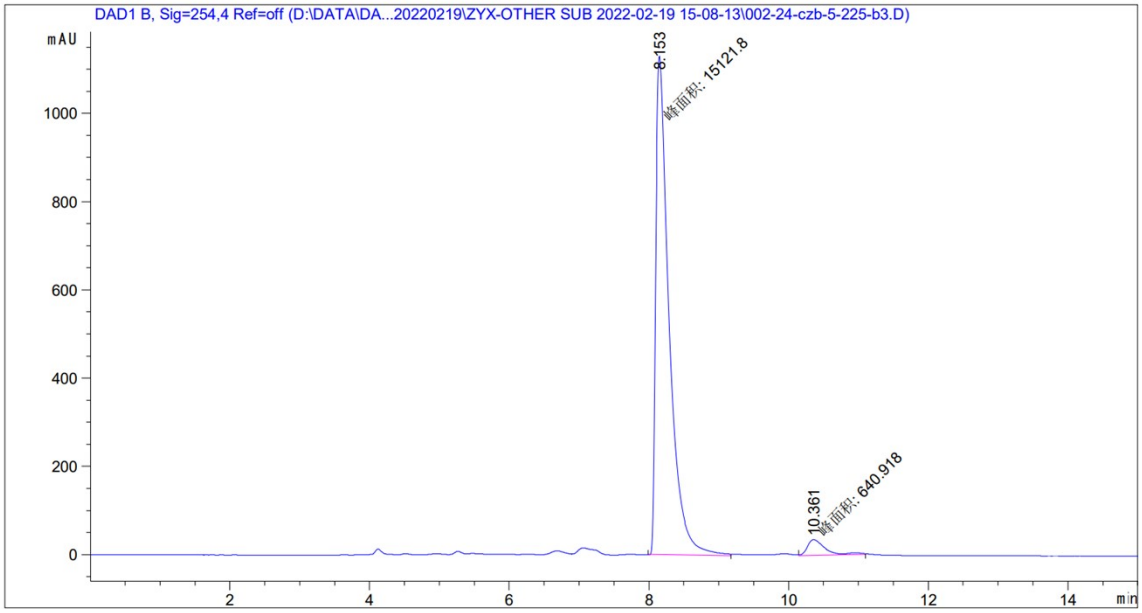
HRMS (ESI): m/z Calcd for $C_{16}H_{19}N_3O_2$ $[M+CH_3CN]^+$ 285.1477; found: m/z 285.1430.

Optical Rotation: $[\alpha]_D^{25}$ = 1.5 (*c* = 0.41, $CHCl_3$)

92 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 80:20, flow rate 0.8 mL/min, λ = 254 nm): t_R= 8.2 min (major), t_R= 10.4 min (minor).

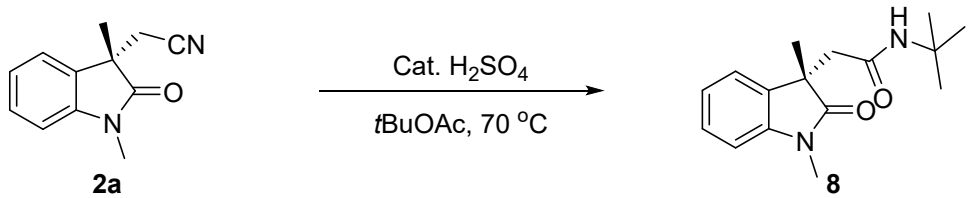


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.297	BB	0.2016	1873.49438	136.97008	50.0634
2	10.276	BB	0.2409	1868.74683	115.42234	49.9366



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.153	MM	0.2232	1.51218e4	1129.22595	95.9340
2	10.361	MM	0.2972	640.91760	35.93908	4.0660

(*S*)-*N*-(*tert*-Butyl)-2-(1,3-dimethyl-2-oxoindolin-3-yl)acetamide (8)[11]



2a
92% ee

8
99% yield, 89% ee

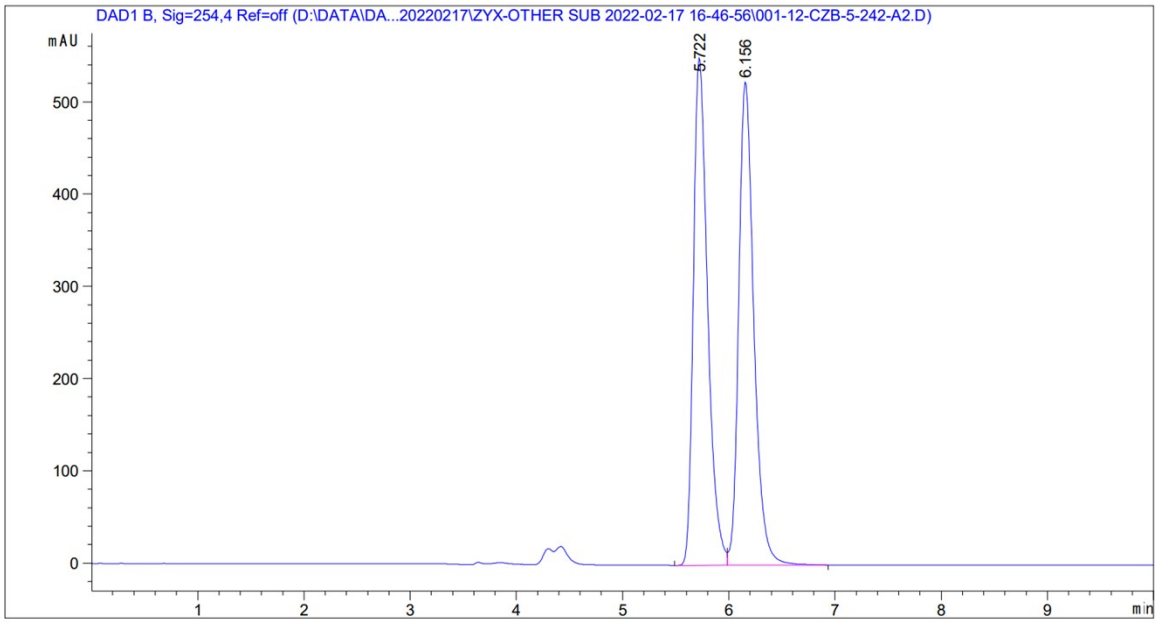
The mixture of **2a** (25 mg, 0.125 mmol, 1.0 equiv) and H_2SO_4 (4 drops) in *t*-BuOAc (1 mL) was heated at 70 °C for 3 hours. After the reaction was completed (monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ solution (20 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4 and filtrated, the filter was concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield product **8** as a white solid (33.9 mg, yield: 99%). Melting point: 137.4 - 139.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.25 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 5.99 (s, 1H), 3.24 (s, 3H), 2.69 (d, *J* = 14.1 Hz, 1H), 2.56 (d, *J* = 14.1 Hz, 1H), 1.43 (s, 3H), 1.17 (s, 9H).

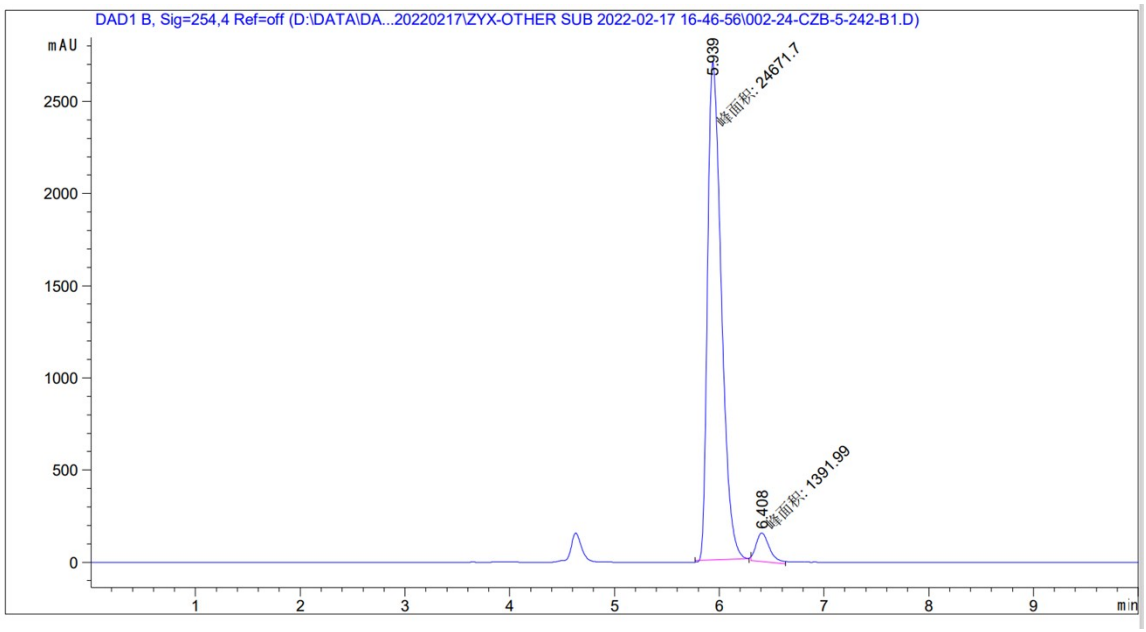
^{13}C NMR (100 MHz, $CDCl_3$):) δ 180.6, 168.2, 142.9, 133.2, 128.2, 123.1, 122.8, 108.2, 51.0, 46.7, 45.3, 28.5, 26.4, 23.6.

Optical Rotation: $[\alpha]_D^{25}$ = -17.3 (*c* = 0.50, $CHCl_3$)

89 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 85:15, flow rate 0.8 mL/min, λ = 254 nm): t_R= 5.9 min (major), t_R= 6.4 min (minor).

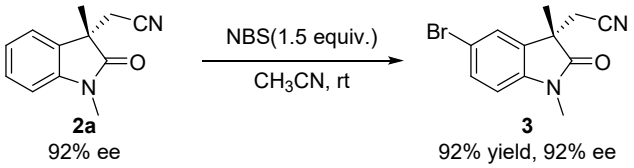


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.722	BV	0.1428	5123.72510	549.66577	49.7856
2	6.156	VV R	0.1491	5167.85596	523.62158	50.2144



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.939	MM	0.1520	2.46717e4	2704.35620	94.6593
2	6.408	MM	0.1499	1391.98889	154.79451	5.3407

(*S*)-2-(5-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (3)[12]



2a
92% ee

3
92% yield, 92% ee

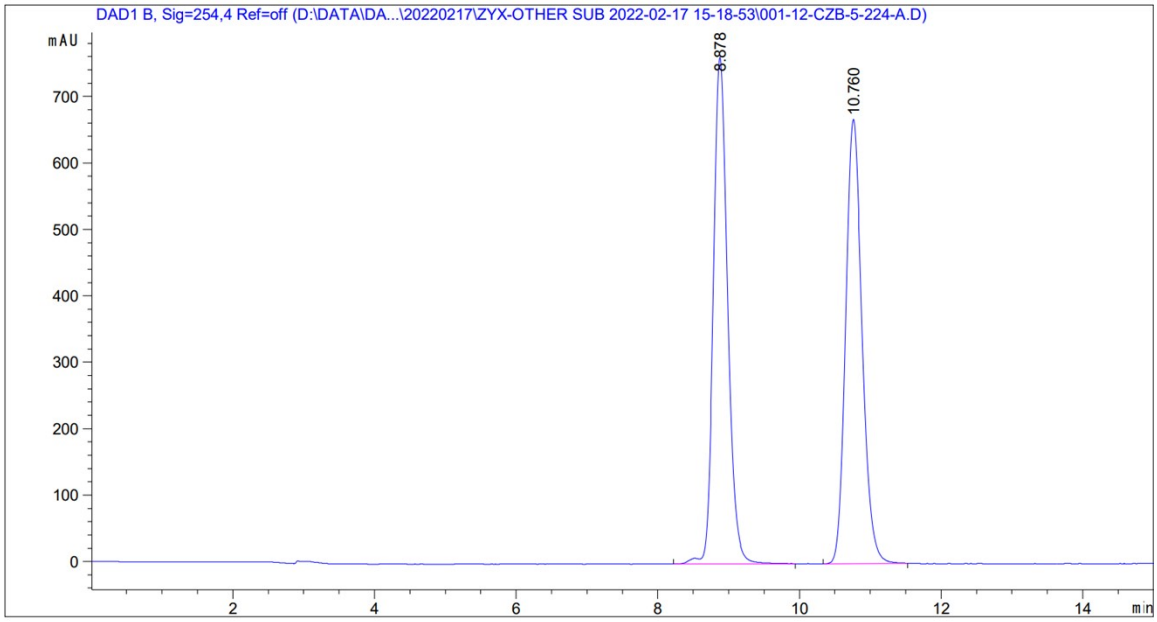
The mixture of **2a** (40 mg, 0.2 mmol, 1.0 equiv) and NBS(53.4 mg, 0.3 mmol, 1.5 equiv) in MeCN (1 mL) was stirred at r.t. for 12 hours. After the reaction was finished (monitored by TLC), the mixture was concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield product **3** as a yellow oil (51.4 mg, yield: 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 1.9 Hz, 1H), 7.47 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 3.22 (s, 3H), 2.83 (d, *J* = 16.7 Hz, 1H), 2.59 (d, *J* = 16.7 Hz, 1H), 1.51 (s, 3H).

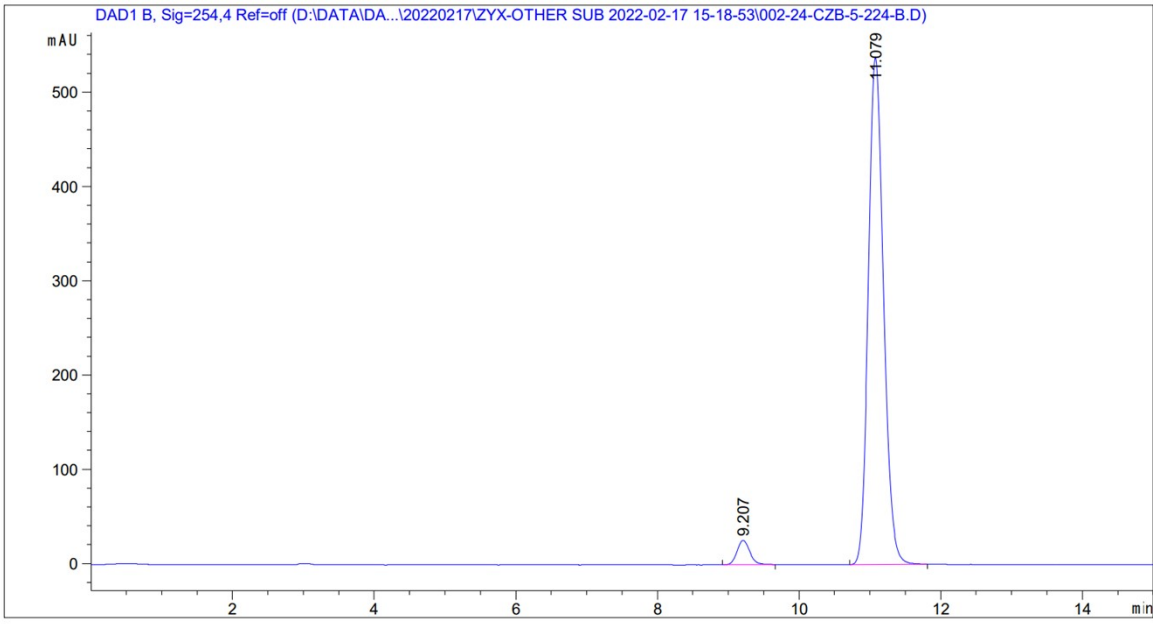
^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 141.8, 132.9, 132.1, 126.4, 116.2, 115.9, 110.2, 45.1, 26.7, 26.2, 22.2.

Optical Rotation: $[\alpha]_D^{25} = 17.9$ ($c = 0.69$, $CHCl_3$)

92 % ee. Determined by HPLC (Daicel Chiralpak AD-H Column, *n*-Hexane: *i*-PrOH = 90:10, flow rate 1 mL/min, $\lambda = 254$ nm): $t_R = 11.1$ min (major), $t_R = 9.2$ min (minor).

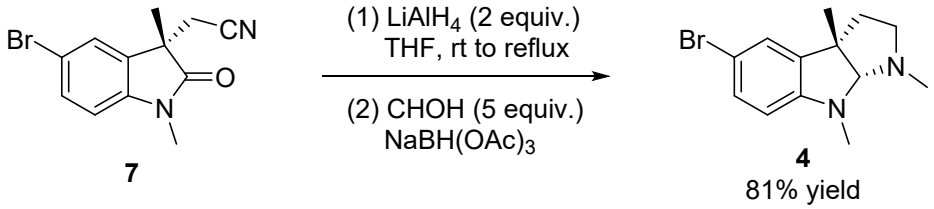


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.878	VB R	0.2136	1.06441e4	762.22589	49.7416
2	10.760	BB	0.2497	1.07547e4	668.62000	50.2584



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.207	BB	0.1918	322.02426	25.76472	3.8865
2	11.079	BB	0.2288	7963.64746	537.74072	96.1135

(3a *S*, 8a *R*)-5-Bromo-1,3a,8-trimethyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole (4)[12]



To a suspension of $LiAlH_4$ (11 mg, 0.28 mmol, 2.0 equiv) in THF (200 μL) at room temperature, **2a** (40 mg, 0.14 mmol, 1.0 equiv) was added dropwise as a solution in THF (300 μL). After the addition of **2a** was completed, the reaction was stirred for 1 hour under N_2 before being brought to reflux (70 °C) to stir for 1h. After the heating period had elapsed, the reaction was cooled to room temperature and complete consumption of **2a** was observed as indicated by TLC. The mixture was diluted with 2 mL of THF and carefully quenched with water (11 mg), 15% NaOH solution (11 mg) and water (33 mg), and the resulting mixture was stirred for 5 min. Then the mixture was allowed to separate and the remaining residue was washed with DCM (10 mL x 5). The combined organic layers were sequentially dried over MgSO4, filtered and concentrated in vacuo. The crude product was used for the next step without further purification.

To a stirring mixture of hexahydropyrrolo crude product (1.0 equiv) and paraformaldehyde (21 mg, 0.7 mmol, 5 equiv) in MeOH (3 mL) for 3 hours was added carefully $NaBH_4$ (25.9 mg, 0.7 mmol, 5 equiv), the reaction was stirred for additional 2 hours. After the reaction was completed (monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ solution (10 mL) and extracted with DCM (20 mL × 3). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4 and filtrated, the filter was concentrated in vacuo. The remaining residue was purified by

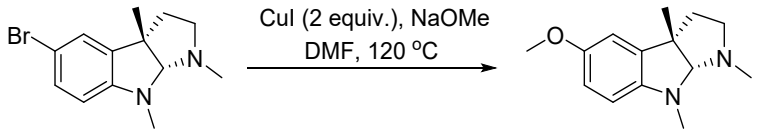
column chromatography on silica gel (DCM/MeOH) to yield product **4** as a colorless oil (31.7 mg, yield: 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.26 (d, *J* = 8.3 Hz, 1H), 4.11 (s, 1H), 2.91 (s, 3H), 2.76 – 2.68 (m, 1H), 2.62 (dd, *J* = 15.8, 8.1 Hz, 1H), 2.54 (s, 3H), 1.95 (dd, *J* = 9.4, 5.0 Hz, 2H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 139.0, 130.4, 125.5, 109.1, 108.0, 97.6, 53.3, 52.8, 40.7, 38.6, 36.4, 27.3.

Optical Rotation: $[\alpha]_D^{25}$ = -68.9 (*c* = 10.0, $CHCl_3$)

(3a *S*, 8a *R*)-5-Methoxy-1,3a,8-trimethyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b] indole ((-)-Esermethole)[12]



8 **(-)-Esermethole** 74% yield

The mixture of **8**, CuI and NaOMe in DMF (1 mL) was stirred at 120 °C for 12 hours. After the reaction was completed (monitored by TLC), the mixture was diluted with water (10 mL) and extracted with DCM (10 mL × 3). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4 and filtrated, the filter was concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (DCM/MeOH) to yield product (-)-**Esermethole** as a colorless oil (31.7 mg, yield: 74%).

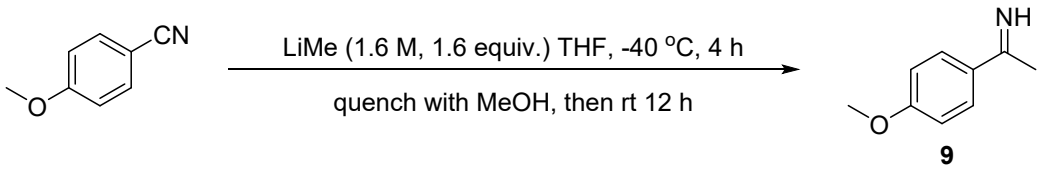
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 – 6.63 (m, 2H), 6.37 (d, *J* = 8.3 Hz, 1H), 4.15 (s, 1H), 3.75 (s, 3H), 2.90 (s, 3H), 2.80 (m, 1H), 2.61 (dd, *J* = 16.0, 8.8 Hz, 1H), 2.53 (s, 3H), 2.00 – 1.94 (m, 2H), 1.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 146.2, 137.7, 112.6, 109.7, 108.0, 97.2, 56.0, 53.1, 52.8, 40.3, 38.3, 36.9, 27.2.

Optical Rotation: $[\alpha]_D^{25}$ = -76.3 (*c* = 2.50, $CHCl_3$)

Absolute stereochemistry was determined by comparing the optical rotation value $[\alpha]_D^{22}$ = 98.0, *c* = 0.4, $CHCl_3$, (+)-**Esermethole** in the literature.[13]

Synthesis of 1-(4-methoxyphenyl)ethan-1-imine (9)[14]



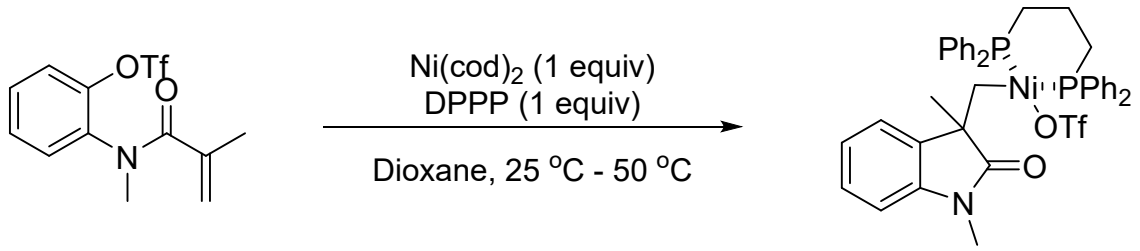
9

A round-bottom flask was charged with nitrile (5 g, 40.0 mmol) and THF (40 mL). The mixture was cooled to −40 °C and MeLi (40.0 mL, 1.6 equiv, 1.6 M in diethyl ether) was added dropwise over 30 min. Next, the resulting mixture was stirred for 4 houes at −40 °C. The mixture was quenched with anhydrous MeOH (10 mL). The cooling bath was removed, and the reaction mixture was allowed to warm to r.t. overnight. The resulting white slurry was filtered through a 2 cm pad of Celite on a medium porosity stone frit filter, and the filtrate was concentrated on a rotary evaporator. The resulting turbid oil was dissolved in MTBE (40 mL) and filtered through a 2 cm pad of Celite on a medium porosity stone frit filter, and the filtrate was concentrated on a rotary evaporator to furnish a yellow solid **9** (3.4 g, yield: 57%).

^{1}H NMR (400 MHz, THF-d_8): δ 9.52 (s, 1H), 7.81 (d, *J* = 6.0 Hz, 2H), 6.91 – 6.86 (m, 2H), 3.78 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, THF-d_8): δ 172.5, 162.5, 132.6, 129.1, 114.2, 55.7, 26.0.

Synthesis of σ-alkyl-Ni(II) complex11:[15]

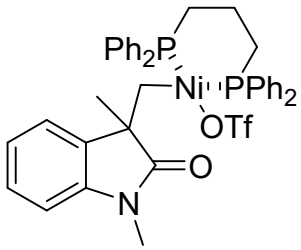


1a **11**

In a nitrogen filled glove box, a 50 mL round bottom flask containing a PTFE-coated stirring bar was charged with $Ni(COD)_2$ (0.5 mmol, 135 mg), dppp (0.5 mmol, 206 mg) and dry dioxane (5 mL), the mixture was stirred at r.t. overnight. **1a** (0.5 mmol, 161 mg) was added to the above orange mixture and stirred at 50 °C for 24 hours. Dry n-hexane (20 mL) was added to the brown mixture and filtered. The resulting participate was

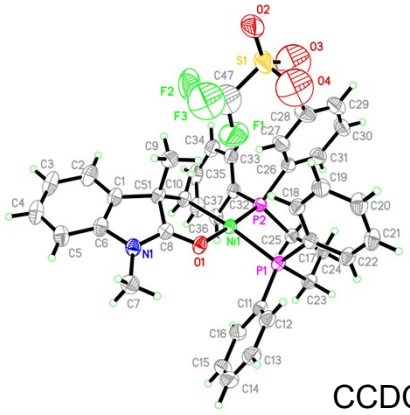
washed with *n*-hexane (5 x 10 mL) to remove residual cyclooctadiene and **1a** was dried under vacuum to give the complex **11** as a orange-yellow solid (240 mg, 61%). **HRMS (ESI)**: m/z Calcd for $C_{39}H_{39}F_3NNiO_4P_2S$ $[M+H]^+$ 794.1381; found: m/z 794.1379.

Crystallographic data for compounds **11**:



11

≡



CCDC 2192547

7、References

[1] D. A. Everson, B. A. Jones, D. J. Weix, *J.Am.Chem.Soc.*, 2012, **134**, 6146−6159.

[2] W. Kong, Q. Wang, J. Zhu, *J. Am. Chem. Soc.* 2015, **137**, 16028 −16031.

[3] W. Kong, Q. Wang, J. Zhu, *Angew. Chem. Int. Ed.* 2017, **56**, 3987-3991.

[4] Y. Li, K. Wang, Y. Ping, Y.Wang, W. Kong, *Org.Lett.* 2018, **20**, 921−924.

[5] Y. Feng, S. Zhao, G. Du, S. Zhang, D. Zhang, H. Liu, X. Li, Y. Dong, F.-G. Sun, *Org. Chem. Fron.* 2021, **8**, 1149-1154.

[6] H. Li, J. Chen, J. Dong, W. Kong, *Org. Lett.* 2021, **23**, 6466-6470.

[7] Z. Ni, X. Huang, J. Wang, Y. Pan, *RSC. Adv.*, 2016, **6**, 522–526.

[8] Y. Kobayashi, H. Kamisaki, H. Takeda, Y. Yasui, R. Yanada, Y. Takemoto, *Tetrahedron*, 2007, **63**, 2978–2989.

[9] Y. Yasui, H. Kamisaki, Y. Takemoto, *Org. Lett.* 2008, **10**, 3303-3306.

[10] G. Wang, C. Shen, X. Ren, K. Dong, *Chem. Commun.* 2022, **58**, 1135-1138.

[11] W. Kong, Q. Wang, J. Zhu, *Angew. Chem. Int. Ed.* 2016, **55**, 9714 –9718.

[12] J. Xu, L. Liang, H. Zheng, Y. R. Chi, R. Tong, *Nat.Commun.*, 2019, **10**, 4754.

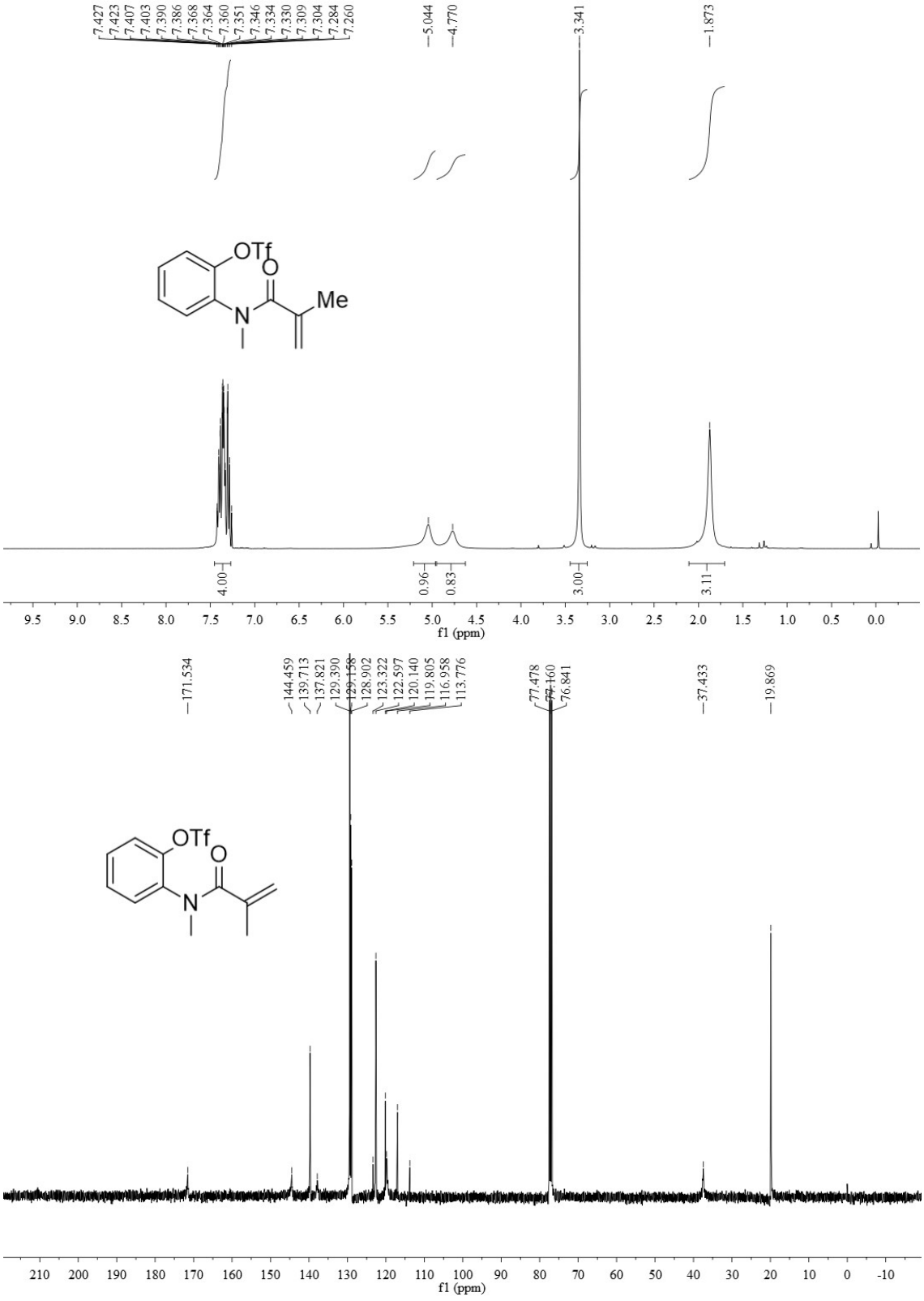
[13] Chen, M.; Wang, X.: Yang, P.; Kou, X.; Ren, Z.; Guan, Z. Chem., *Angew. Chem. Int. Ed.* 2020, **59**, 12199-12205.

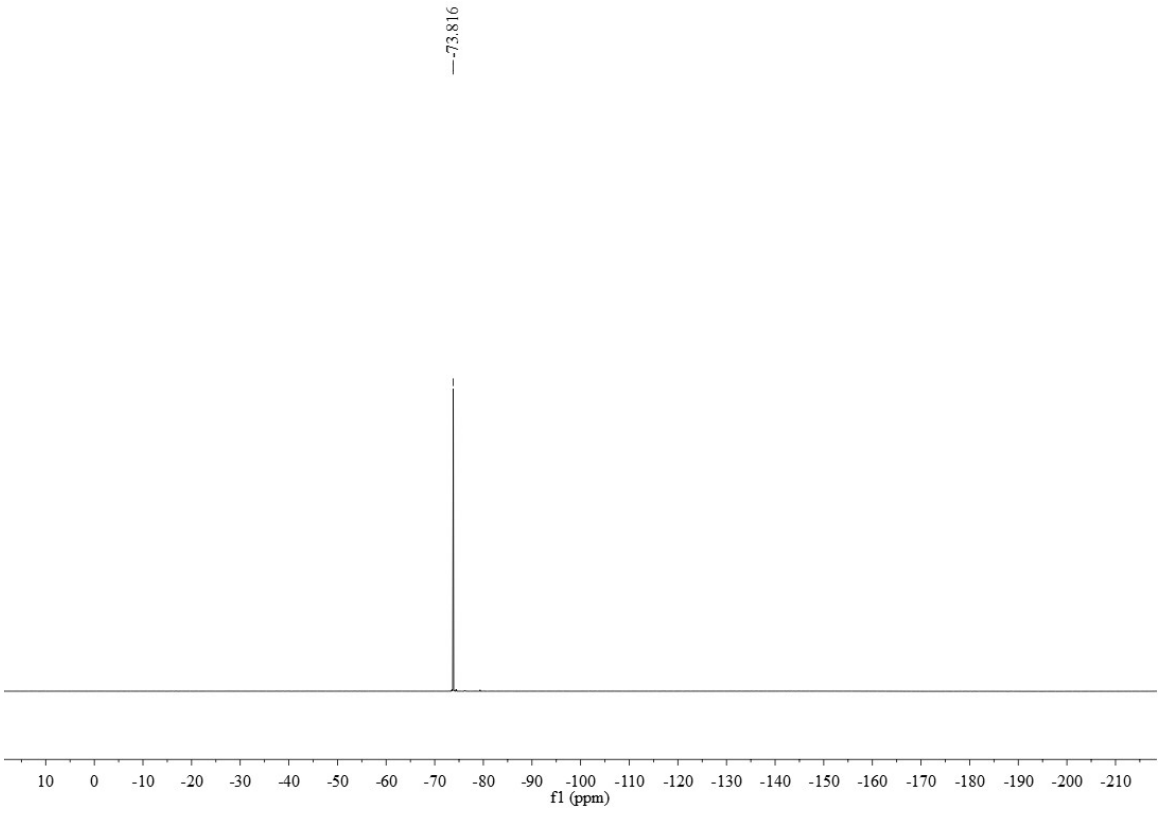
[14] V. N. Wakchaure, B. List, *Angew. Chem. Int. Ed.*, 2016, **55**, 15775 –15778.

[15] K. Wang, Z. Ding, Z. Zhou, W. Kong, *J. Am.Chem.Soc.*, 2018, **140**, 12364−12368.

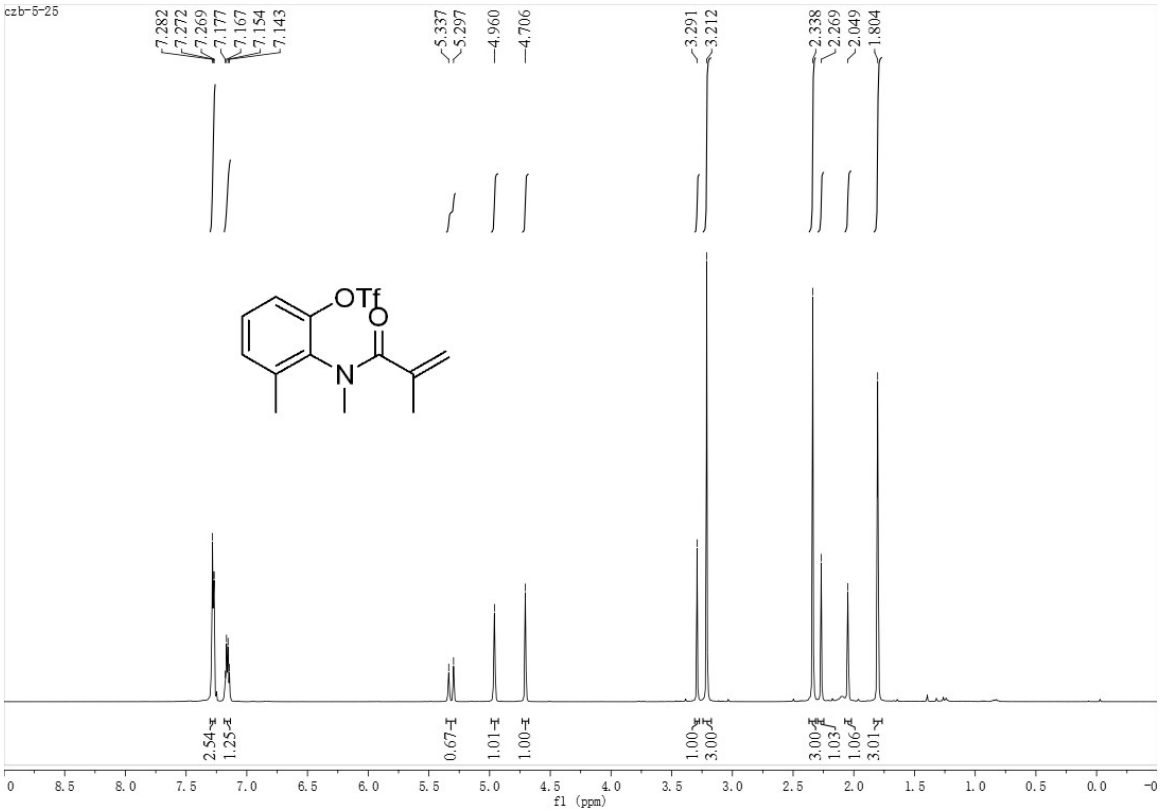
8、The copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

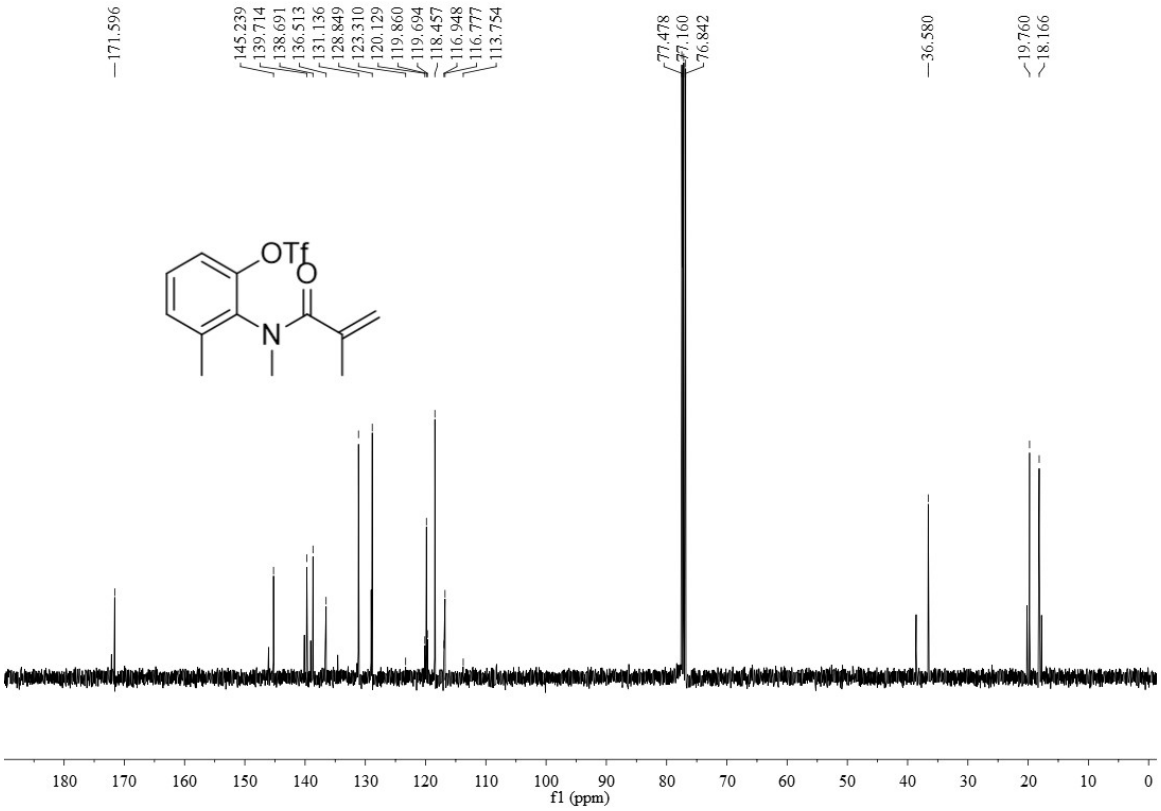
1a

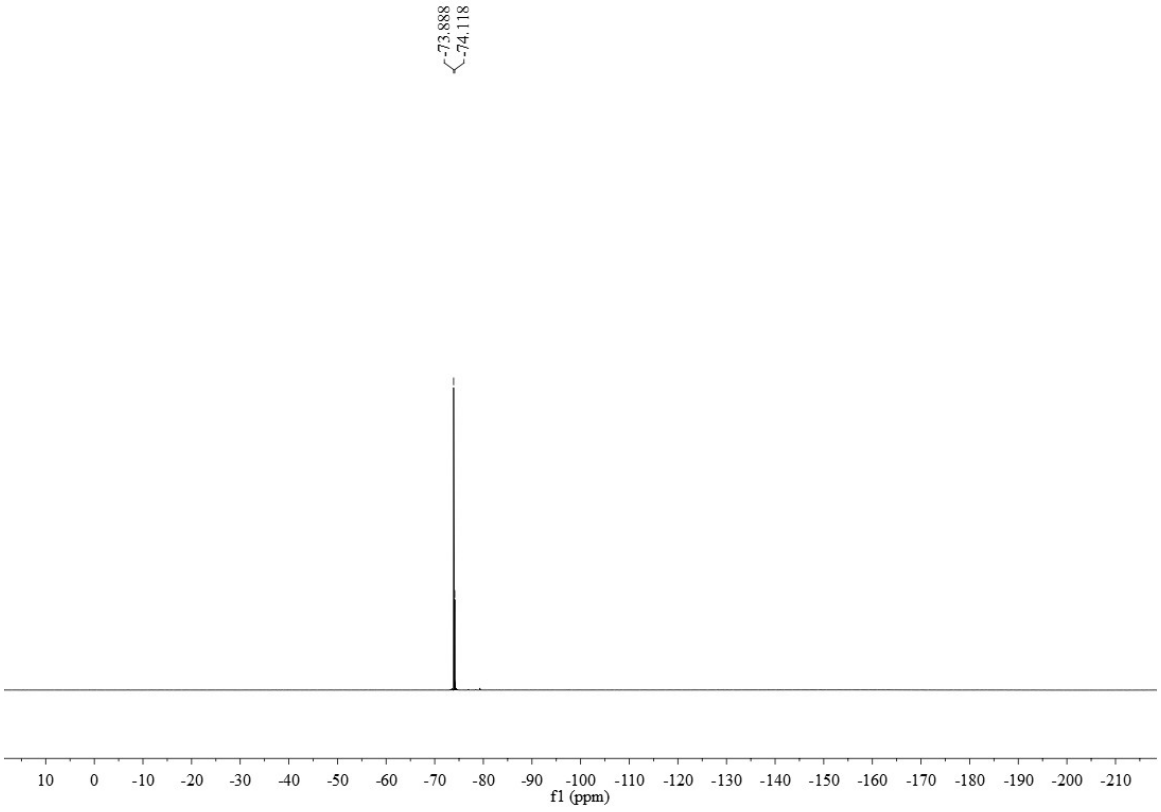

7.427
7.423
7.407
7.403
7.390
7.386
7.368
7.364
7.360
7.351
7.346
7.334
7.330
7.309
7.304
7.284
7.260
5.044
4.770
3.341
1.873
OTf
O
N
Me
4.00
0.96
0.83
3.00
3.11
f1 (ppm)
171.534
144.459
139.713
137.821
129.390
128.902
123.322
122.597
120.140
119.805
116.958
113.776
77.478
77.160
76.841
37.433
19.869
f1 (ppm)


-73.816
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

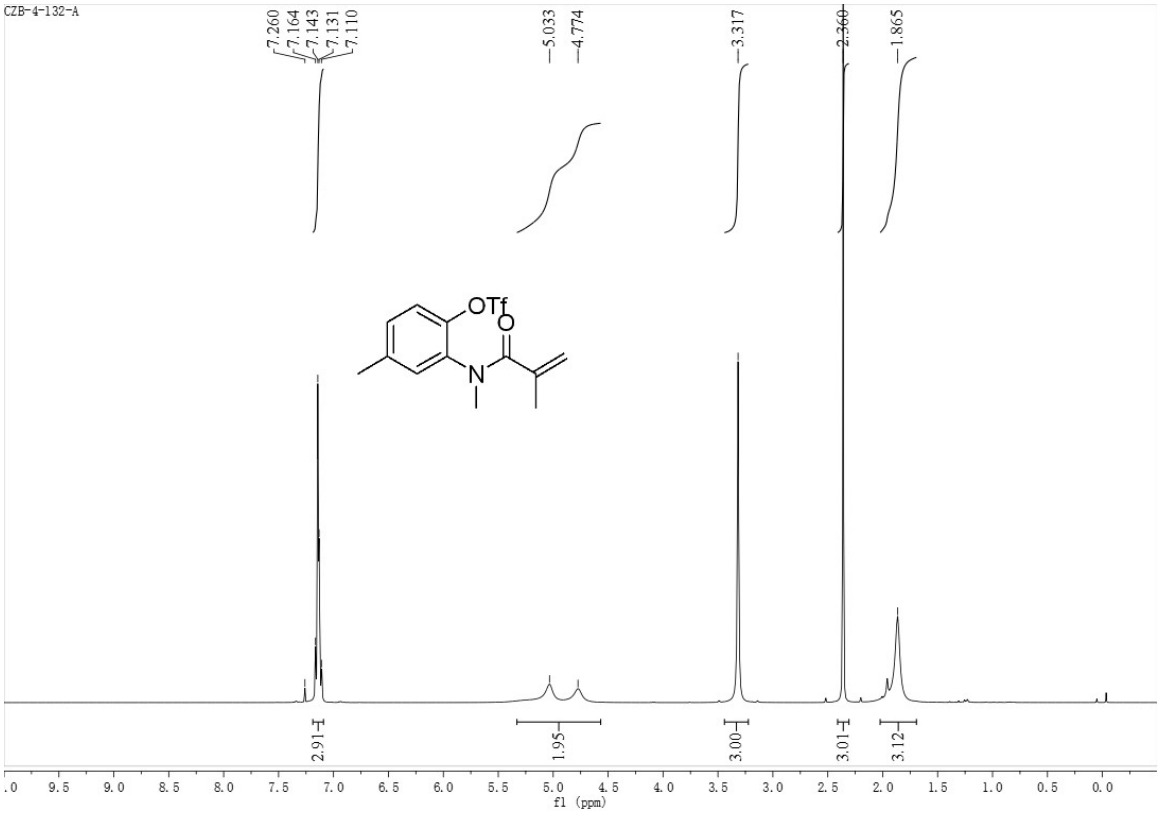
1b

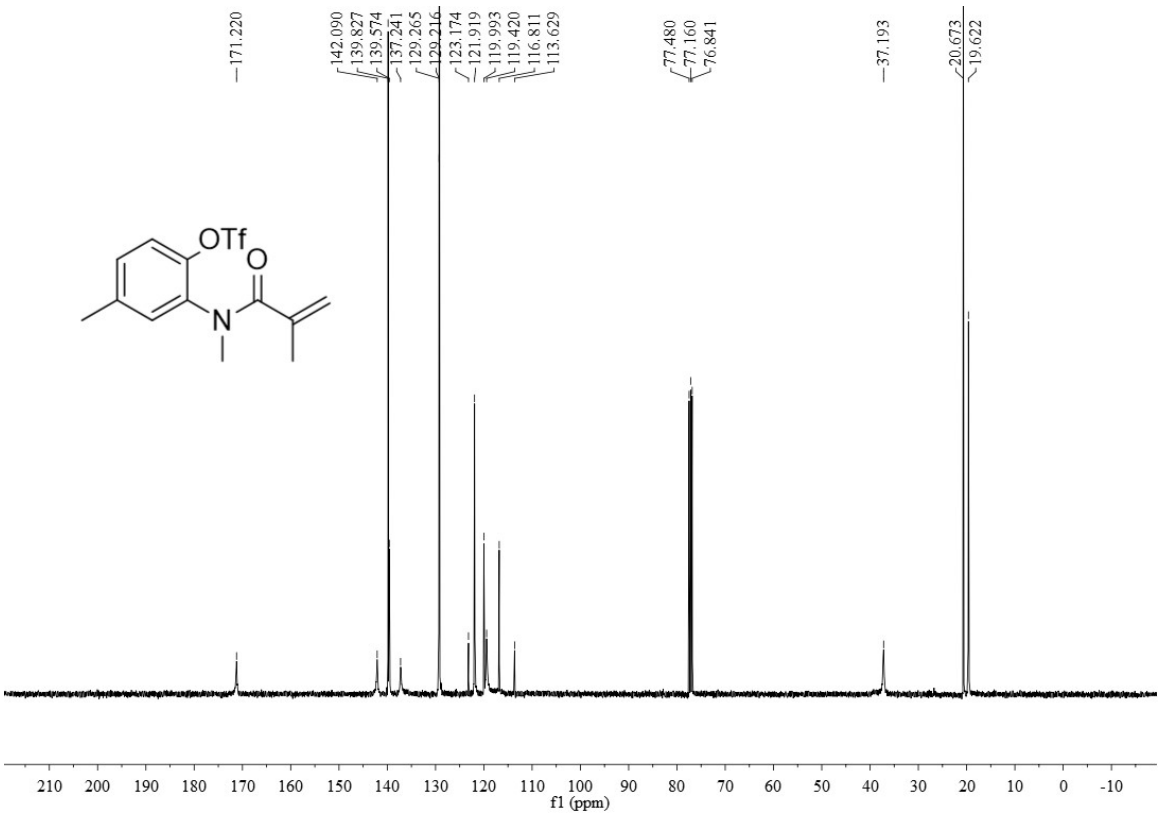

czb-5-25
7.282
7.272
7.269
7.177
7.167
7.154
7.143
5.337
5.297
4.960
4.706
3.291
3.212
2.338
2.269
2.049
1.804
OTf
O
N
2.54
1.25
0.67
1.01
1.00
1.00
3.00
3.00
1.03
1.06
3.01
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

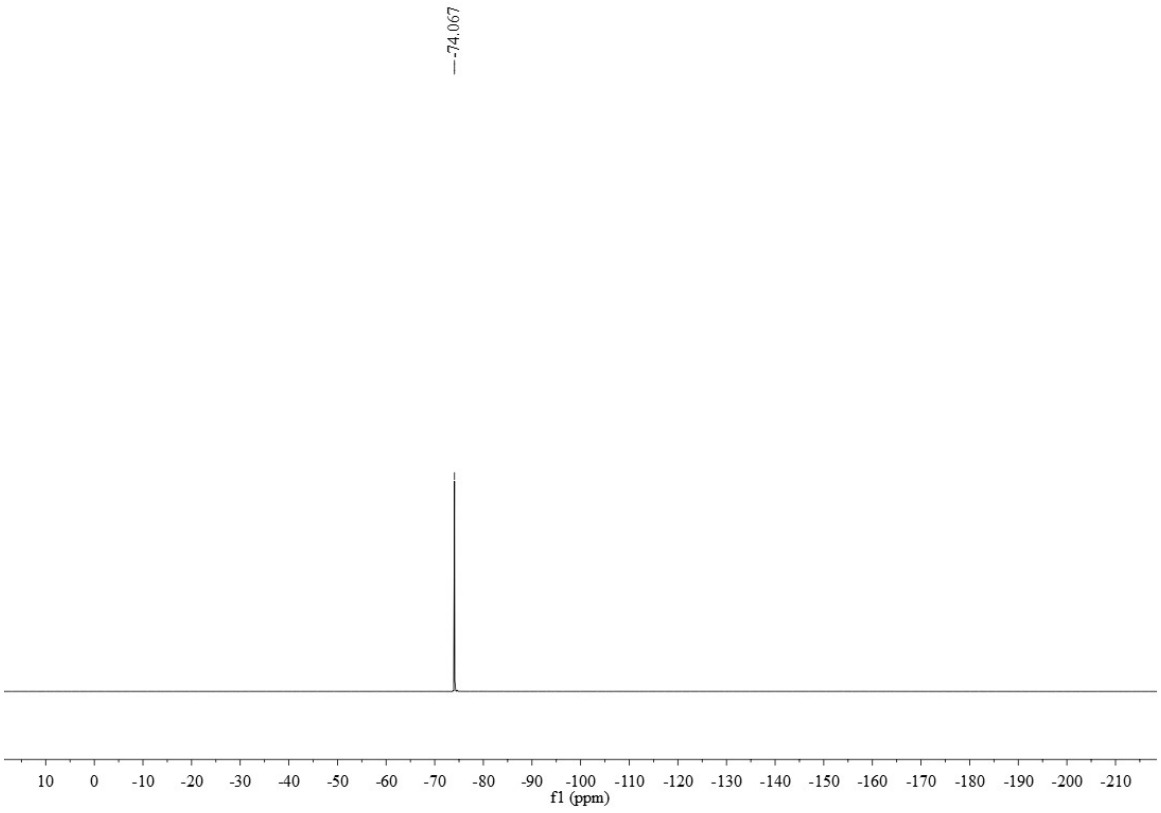

171.596
145.239
139.714
138.691
136.513
131.136
128.849
123.310
120.129
119.860
119.694
118.457
116.948
116.777
113.754
77.478
77.160
76.842
36.580
19.760
18.166
OTf
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-73.888
-74.118
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

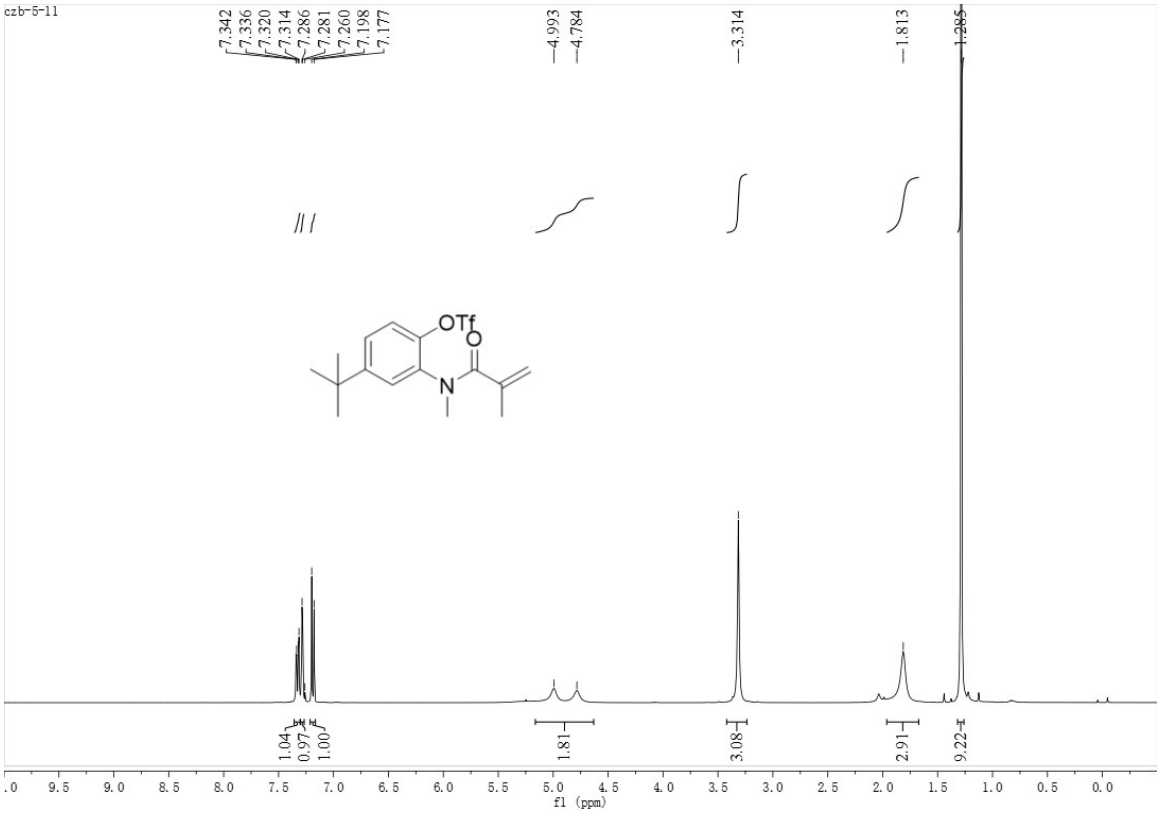
1c

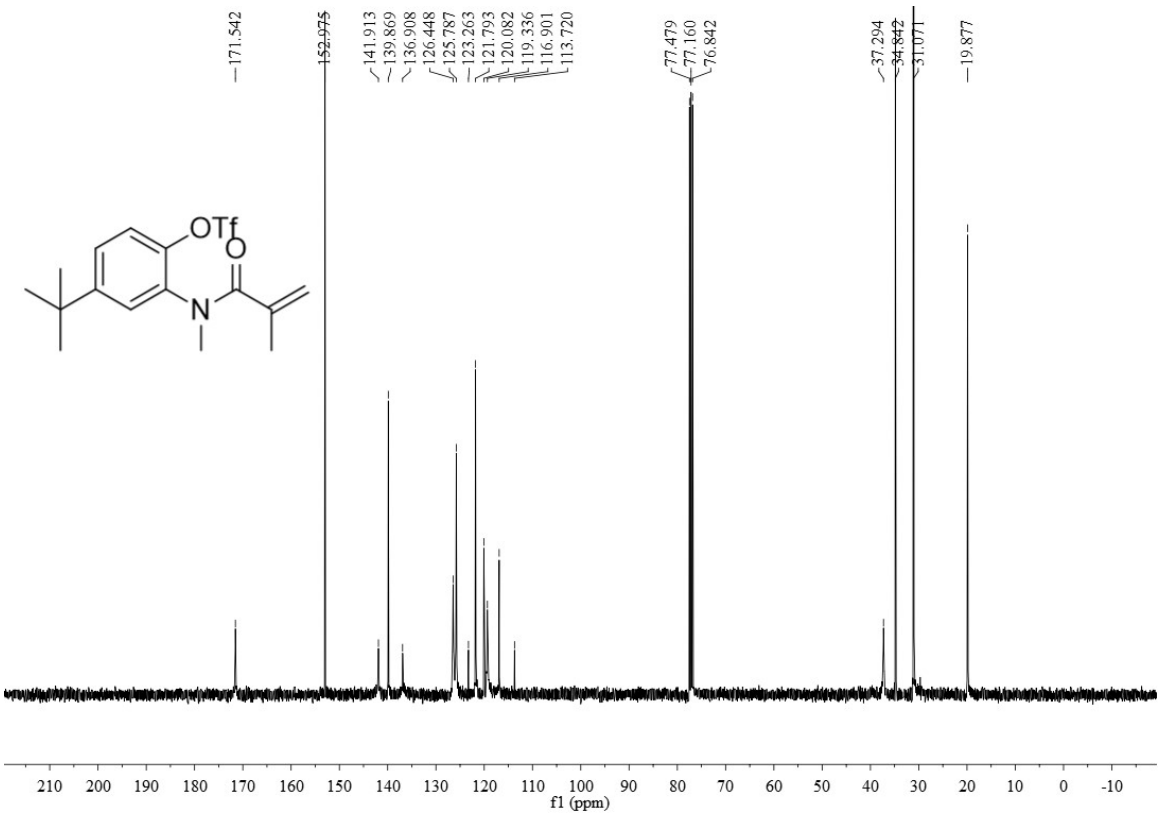

CZB-4-132-A
7.260
7.164
7.143
7.131
7.110
5.033
4.774
3.317
2.360
1.865
OTf
O
N
2.91
1.95
3.00
3.01
3.12
f1 (ppm)

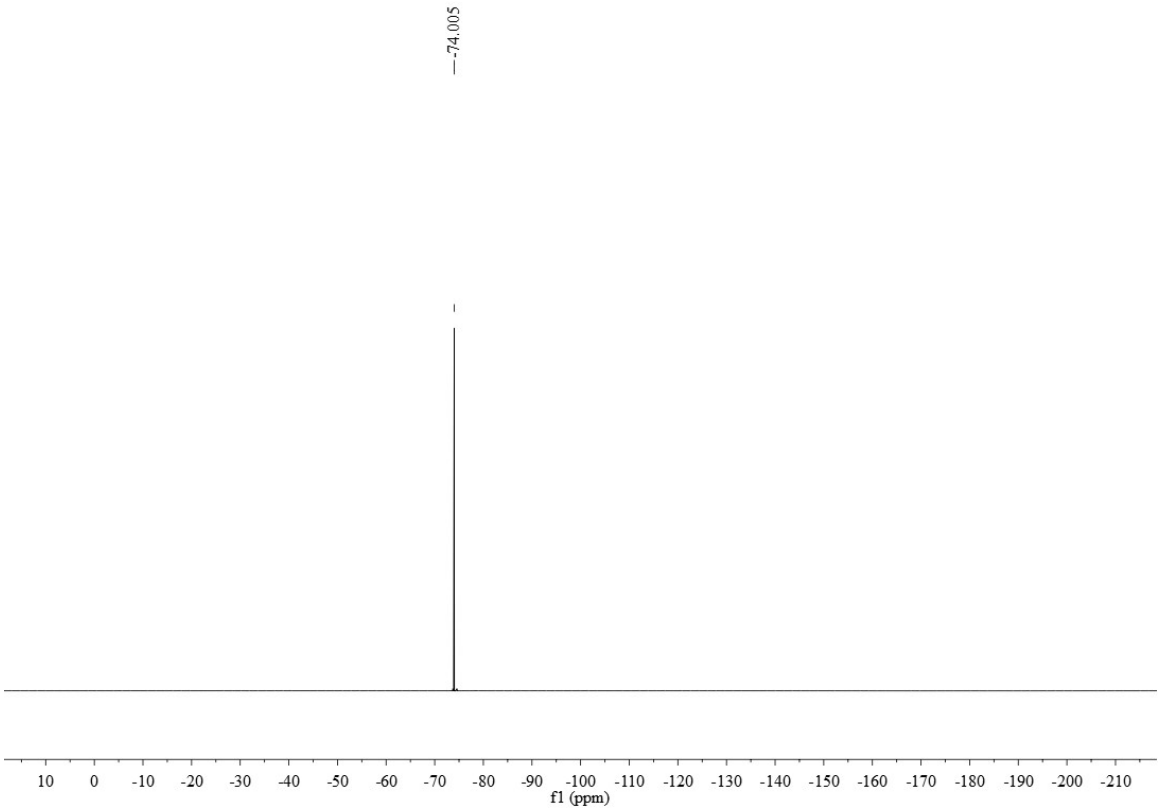

171.220
142.090
139.827
139.574
137.241
129.265
129.216
123.174
121.919
119.993
119.420
116.811
113.629
77.480
77.160
76.841
37.193
20.673
19.622
OTf
O
N
f1 (ppm)


-74.067
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

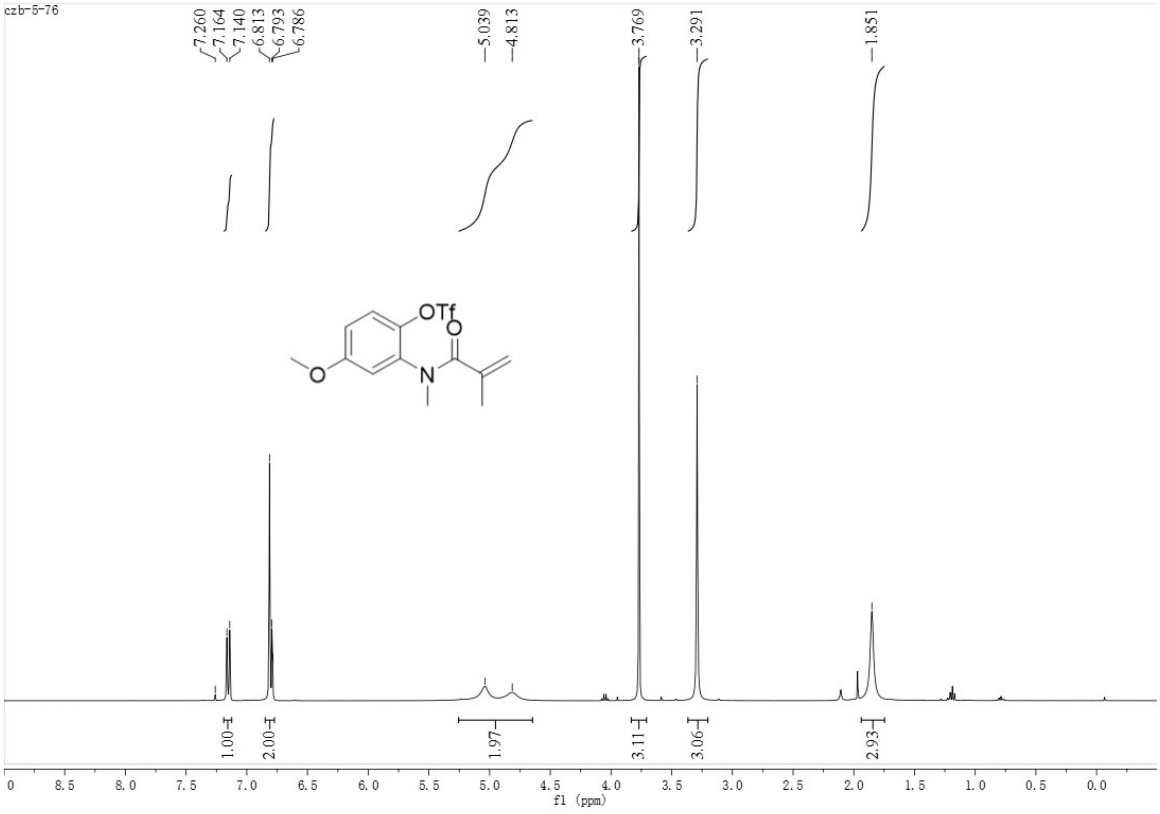
1d

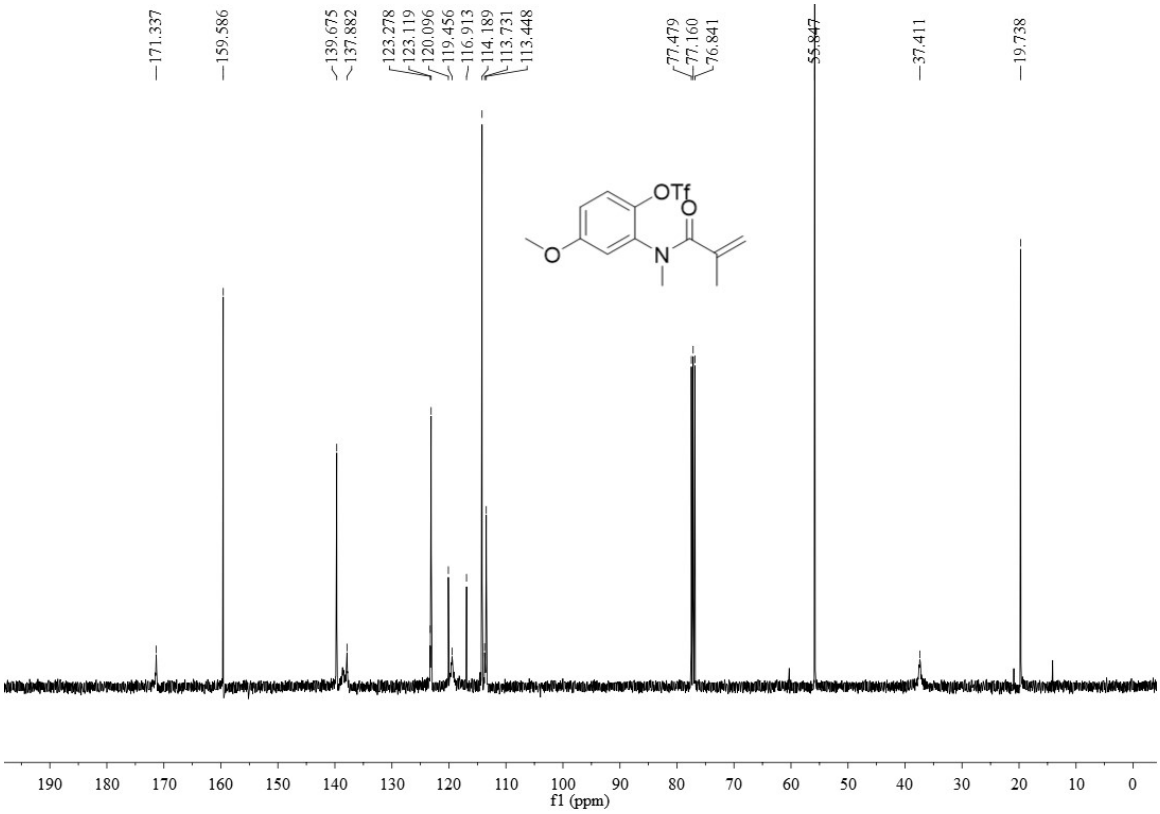

czb-5-11
7.342
7.336
7.320
7.314
7.286
7.281
7.260
7.198
7.177
4.993
4.784
3.314
1.813
1.285
OTf
O
N
1.04
0.97
1.00
1.81
3.08
2.91
9.22
f1 (ppm)

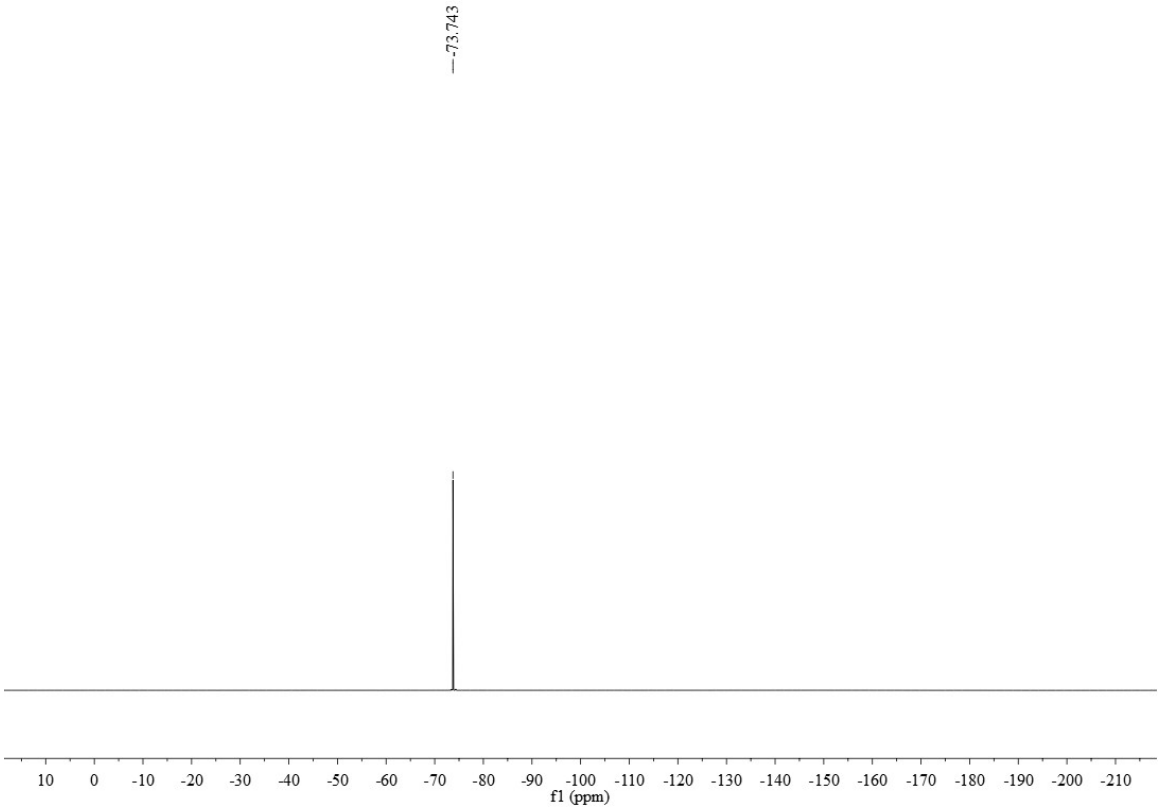

171.542
152.975
141.913
139.869
136.908
126.448
125.787
123.263
121.793
120.082
119.336
116.901
113.720
77.479
77.160
76.842
37.294
34.842
31.071
19.877
OTf
O
N
f1 (ppm)


-74.005
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

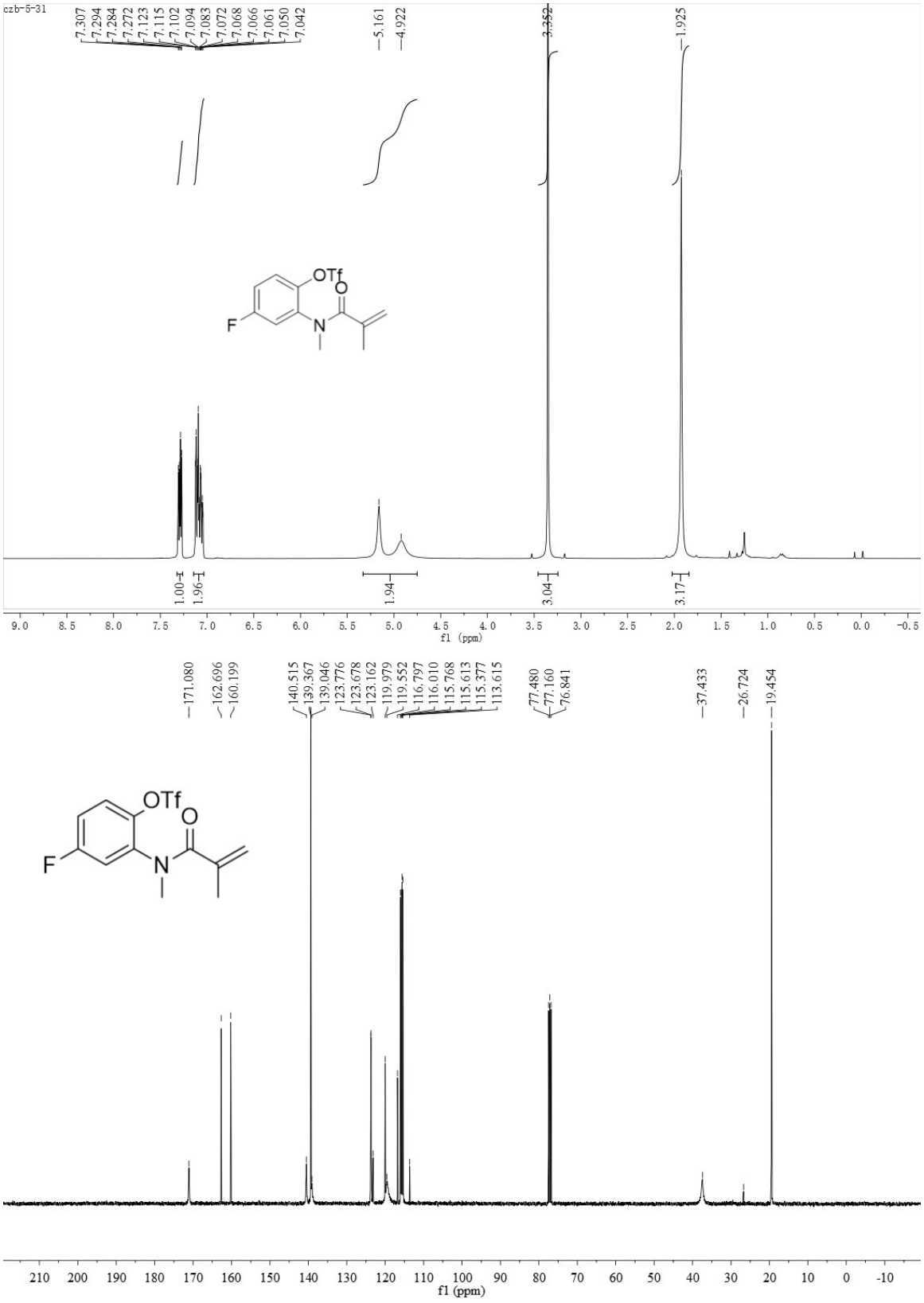
1e

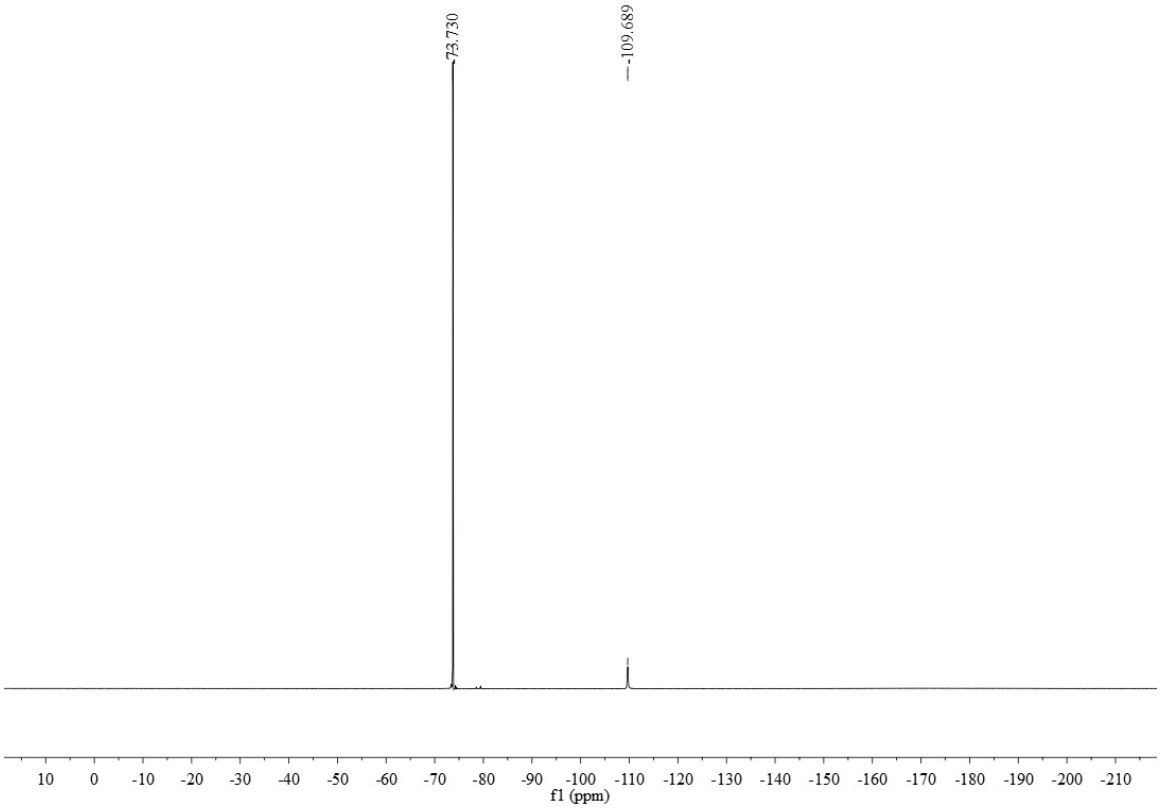

czb-5-76
7.260
7.164
7.140
6.813
6.793
6.786
5.039
4.813
3.769
3.291
1.851
OTf
O
O
N
1.00
2.00
1.97
3.11
3.06
2.93
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.337
159.586
139.675
137.882
123.278
123.119
120.096
119.456
116.913
114.189
113.731
113.448
77.479
77.160
76.841
55.847
37.411
19.738
OTf
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

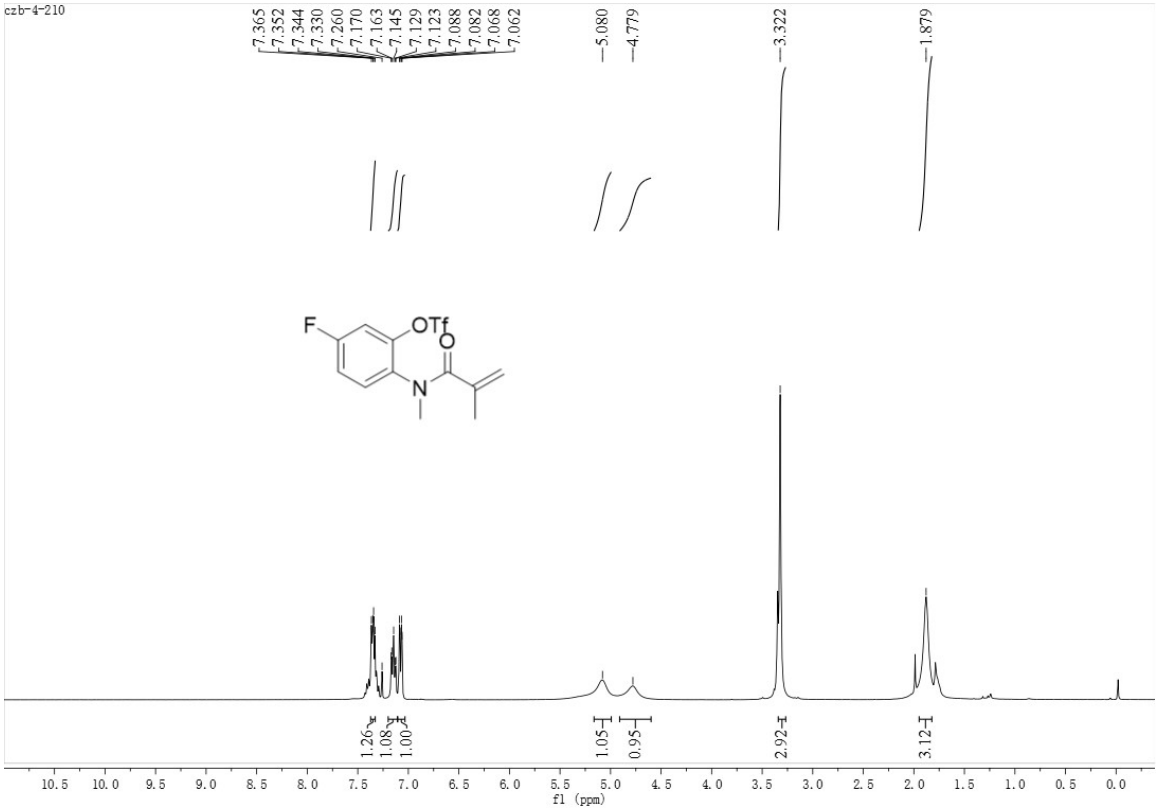

-73.743
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

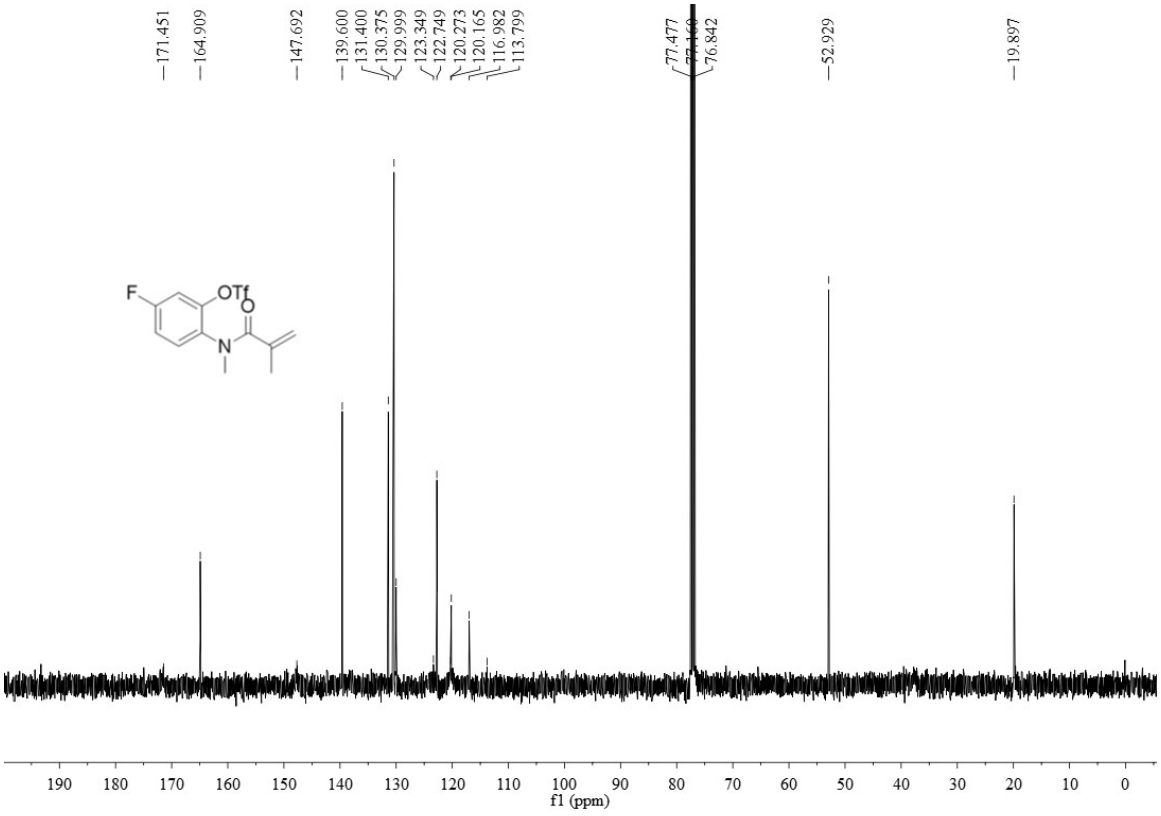
1f

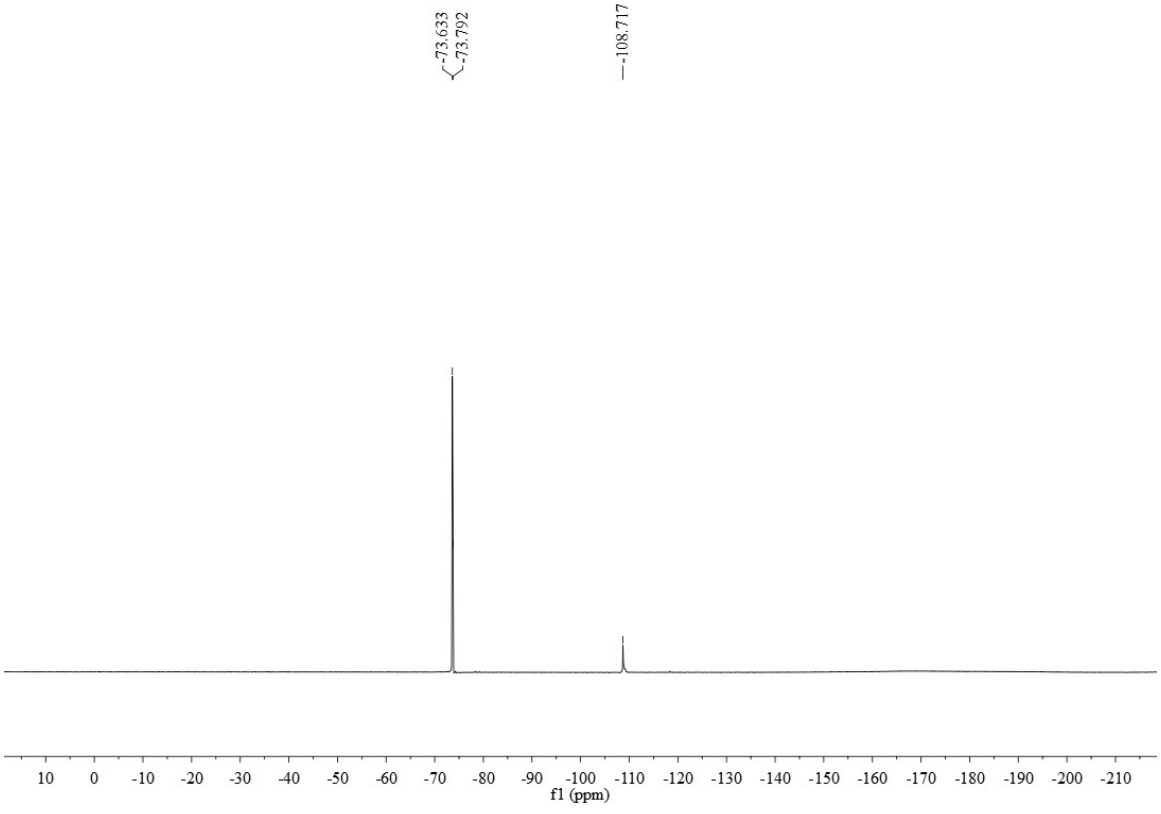

czb-5-31
7.307
7.294
7.284
7.272
7.123
7.115
7.102
7.094
7.083
7.072
7.068
7.066
7.061
7.050
7.042
5.161
4.922
3.352
1.925
OTf
O
F
N
1.00
1.96
1.94
3.04
3.17
f1 (ppm)
171.080
162.696
160.199
140.515
139.367
139.046
123.776
123.678
123.162
119.979
119.552
116.797
116.010
115.768
115.613
115.377
113.615
77.480
77.160
76.841
37.433
26.724
19.454
f1 (ppm)


-73.730
-109.689
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

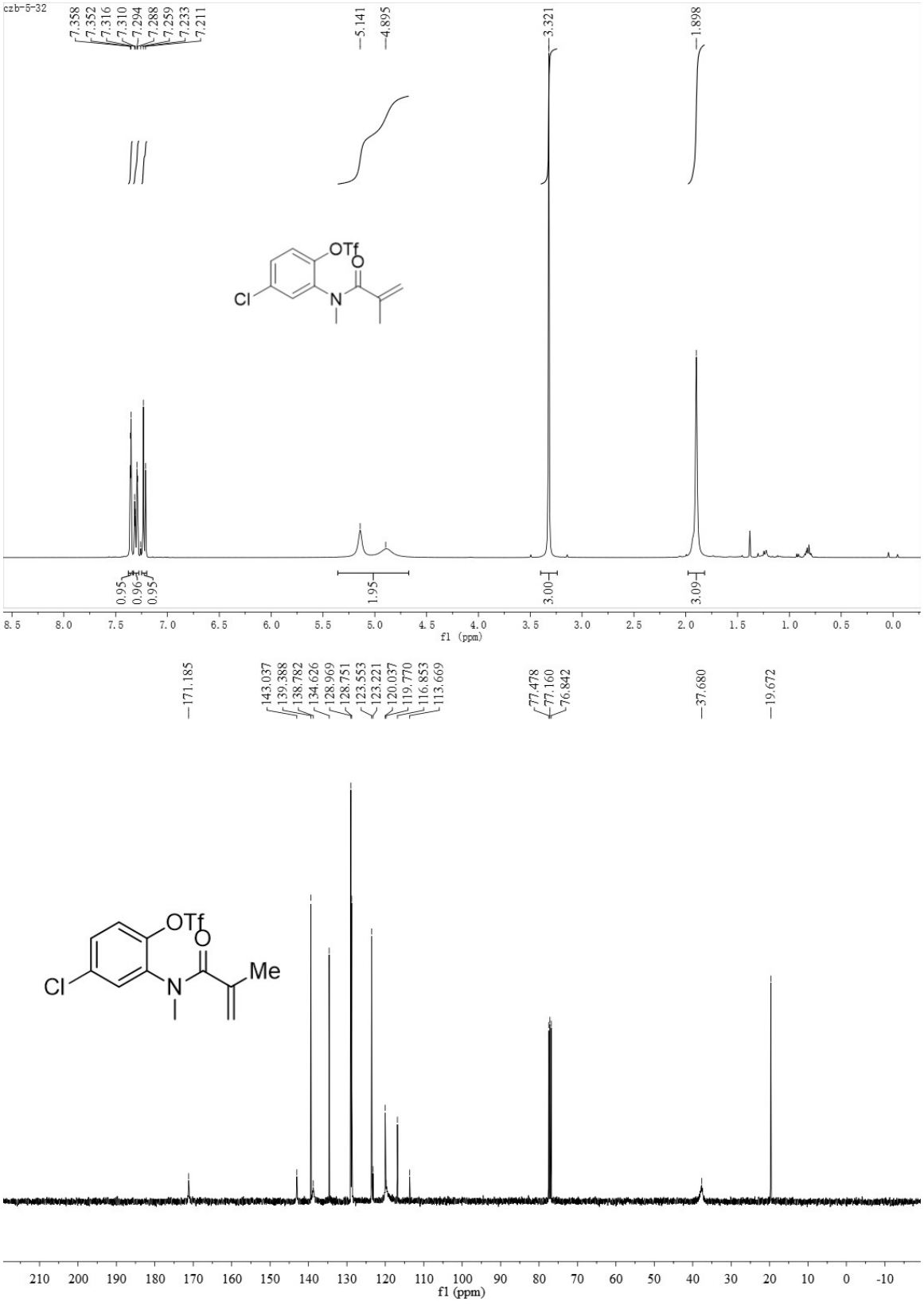
1g

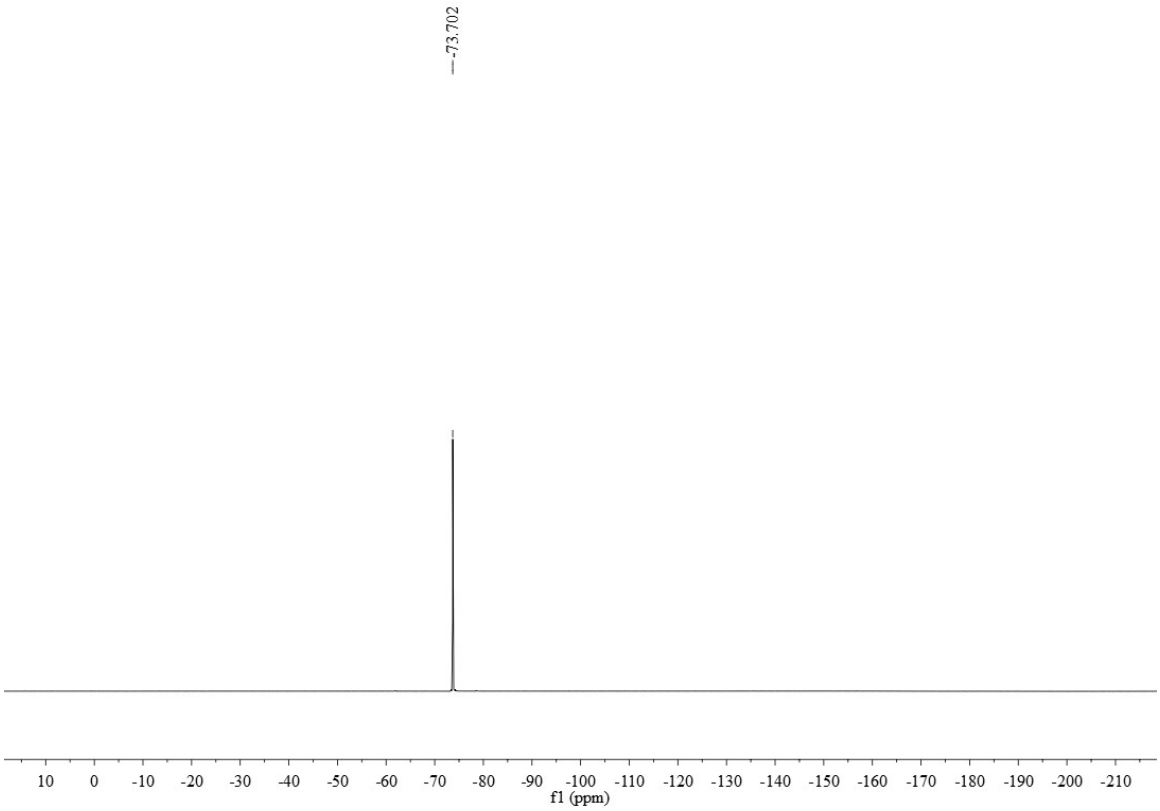

czb-4-210
7.365
7.352
7.344
7.330
7.260
7.170
7.163
7.145
7.129
7.123
7.088
7.082
7.068
7.062
5.080
4.779
3.322
1.879
F
OTf
O
N
1.26
1.08
1.00
1.05
0.95
2.92
3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.451
164.909
147.692
139.600
131.400
130.375
129.999
123.349
122.749
120.273
120.165
116.982
113.799
77.477
77.160
76.842
52.929
19.897
F
OTf
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

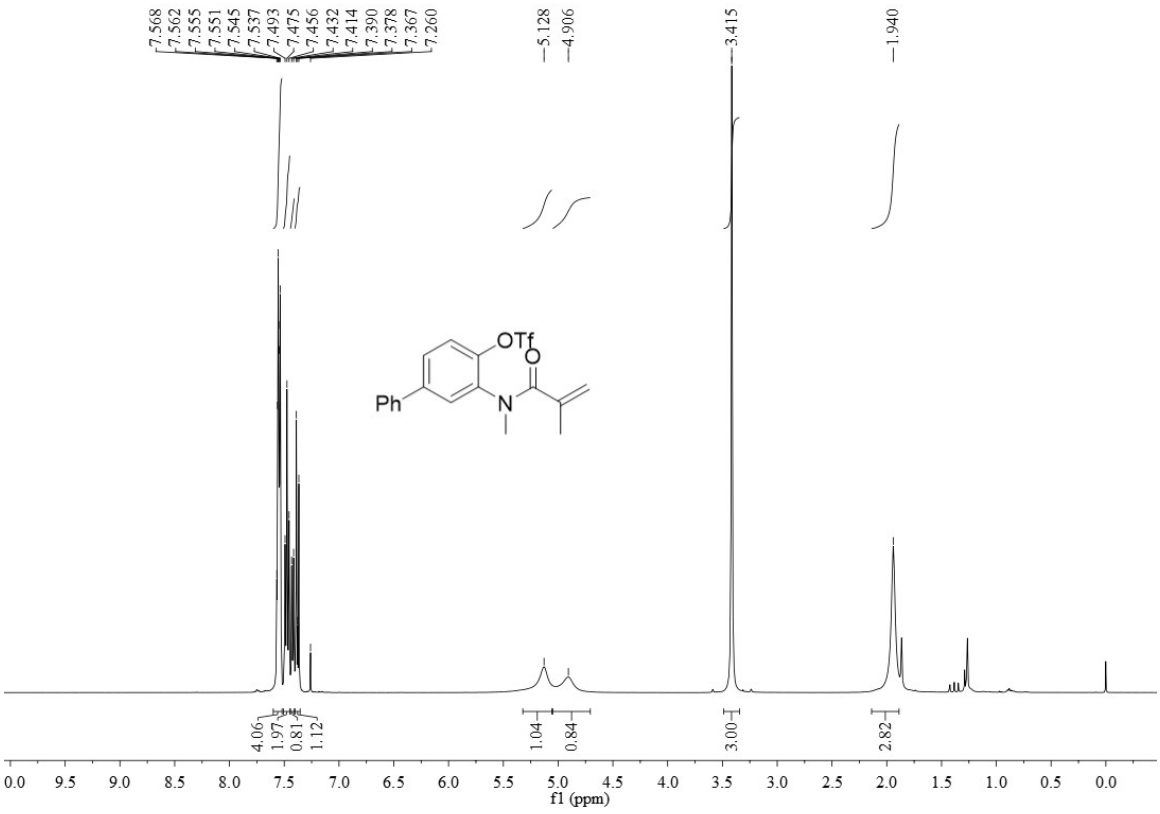

-73.633
-73.792
-108.717
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

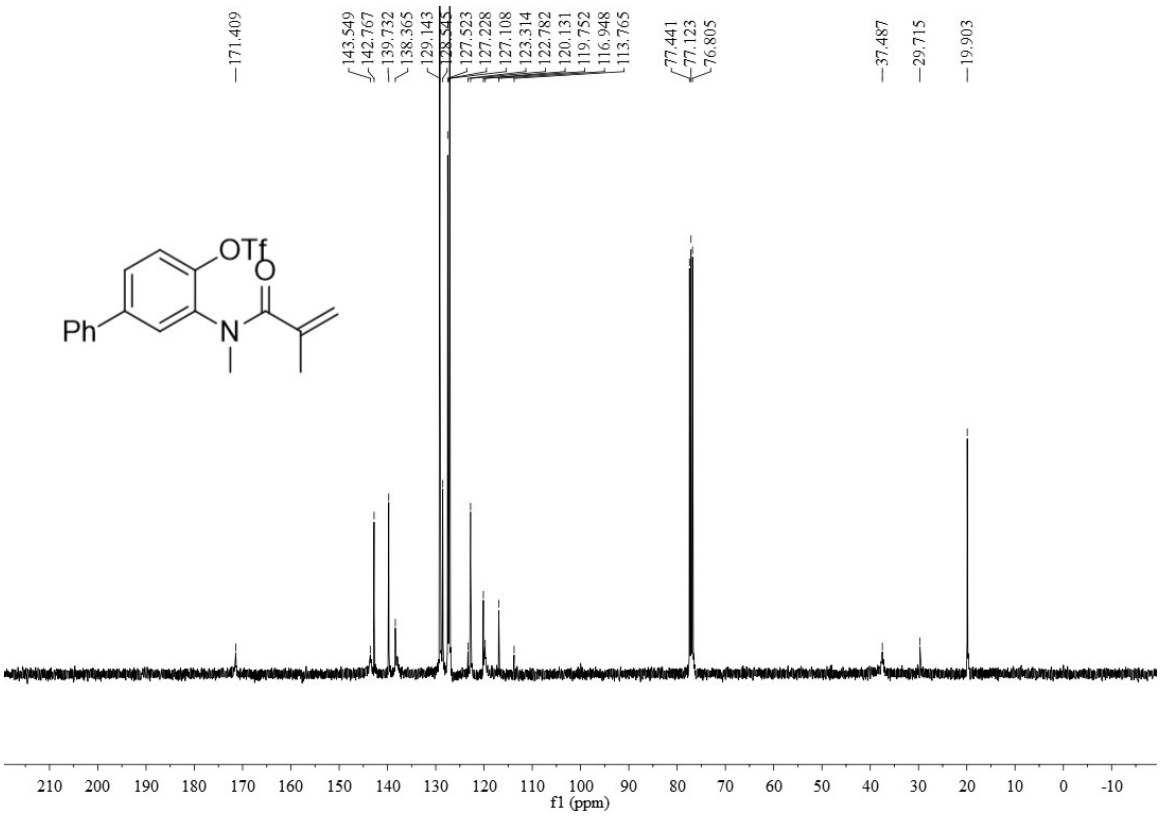
1h

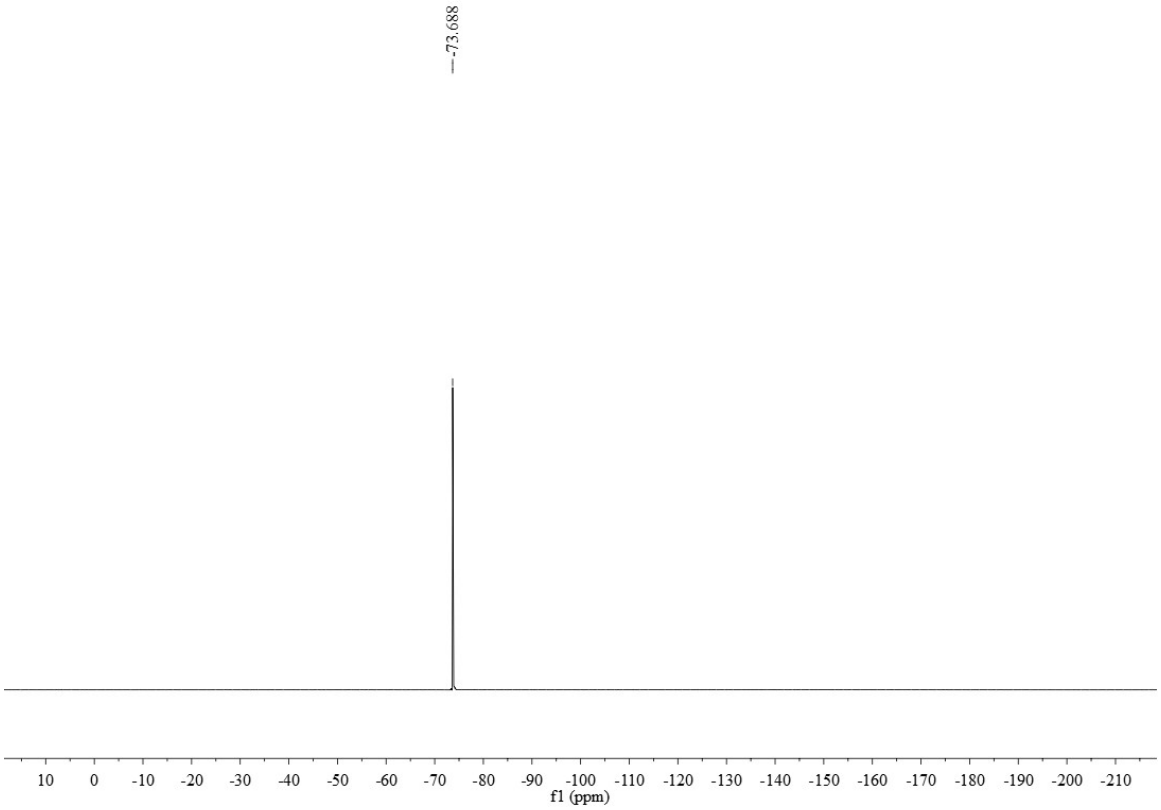

czb-5-32
7.358
7.352
7.316
7.310
7.294
7.288
7.259
7.233
7.211
5.141
4.895
3.321
1.898
OTf
O
Cl
N
0.95
0.96
0.95
1.95
3.00
3.09
f1 (ppm)
171.185
143.037
139.388
138.782
134.626
128.969
128.751
123.553
123.221
120.037
119.770
116.853
113.669
77.478
77.160
76.842
37.680
19.672
OTf
O
Cl
N
Me
f1 (ppm)


-73.702
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

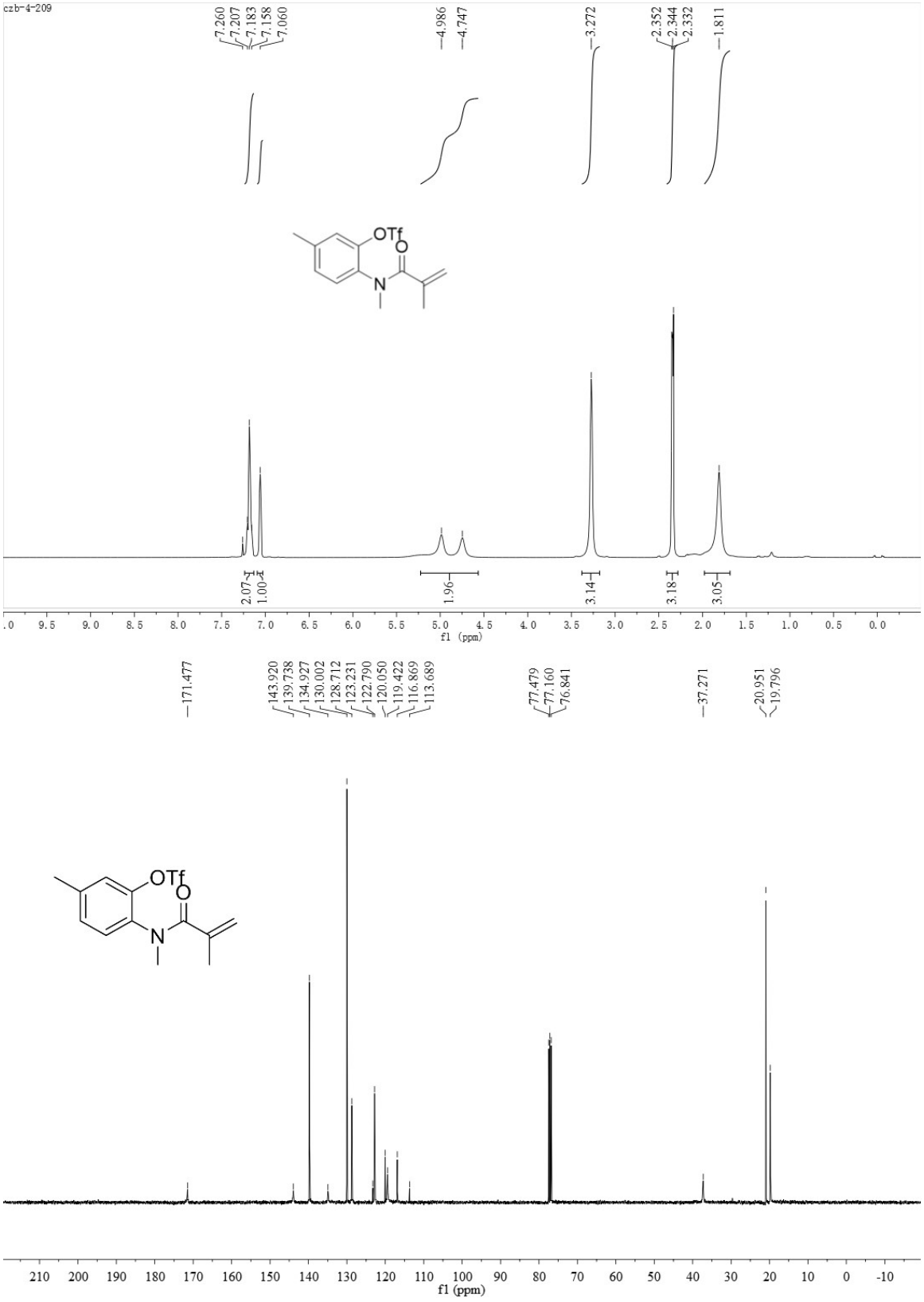
1i

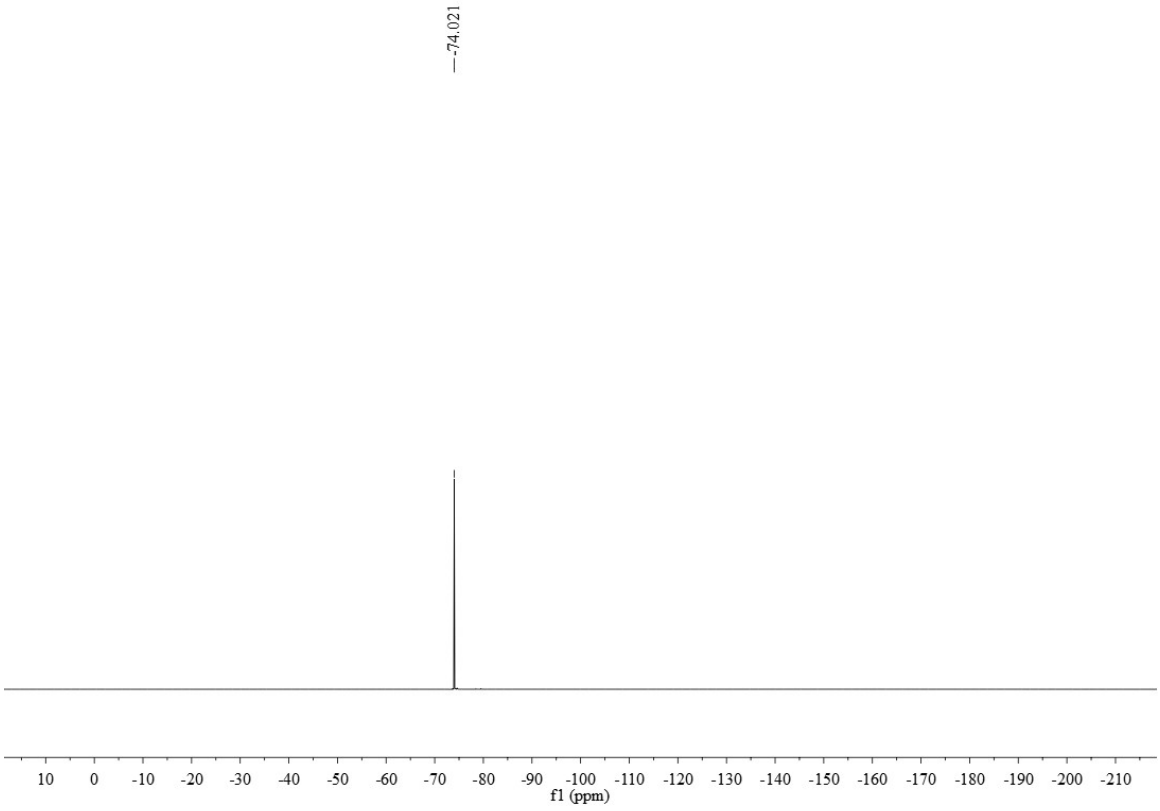

7.568
7.562
7.555
7.551
7.545
7.537
7.493
7.475
7.456
7.432
7.414
7.390
7.378
7.367
7.260
5.128
4.906
3.415
1.940
OTf
O
Ph
N
4.06
1.97
0.81
1.12
1.04
0.84
3.00
2.82
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.409
143.549
142.767
139.732
138.365
129.143
128.545
127.523
127.228
127.108
123.314
122.782
120.131
119.752
116.948
113.765
77.441
77.123
76.805
37.487
29.715
19.903
OTf
O
Ph
N
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)

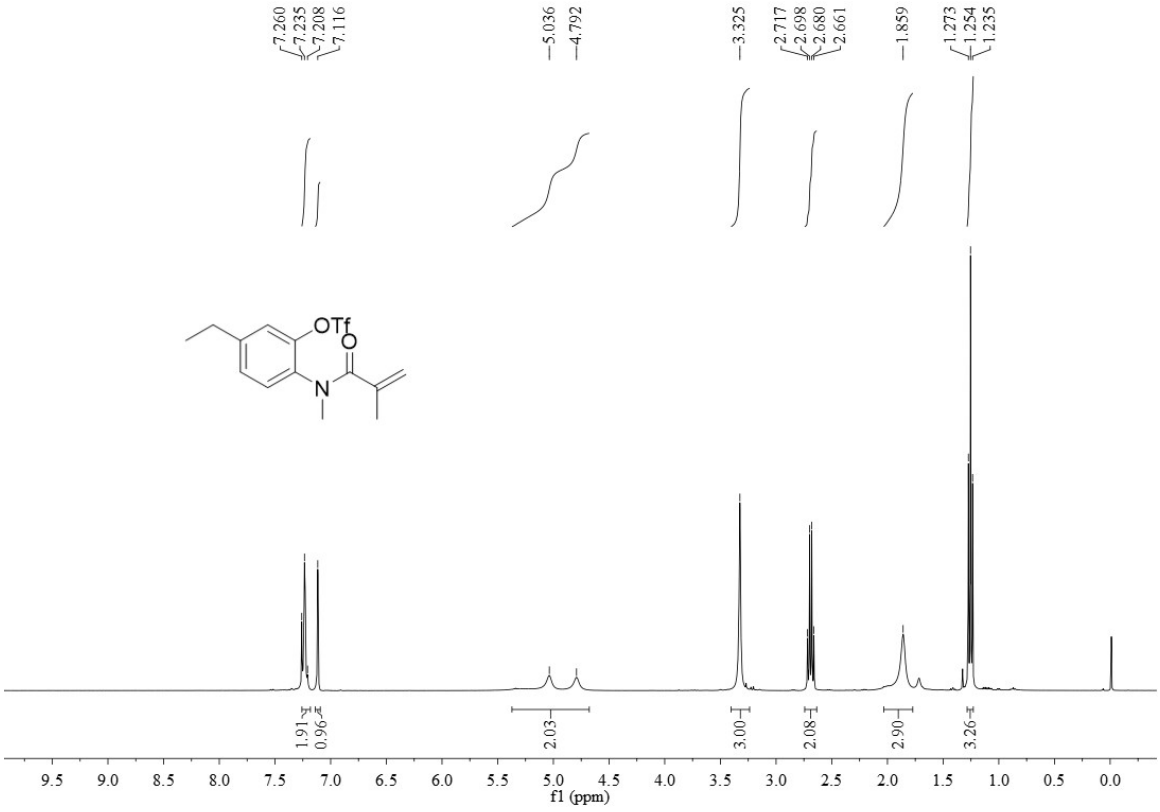

-73.688
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

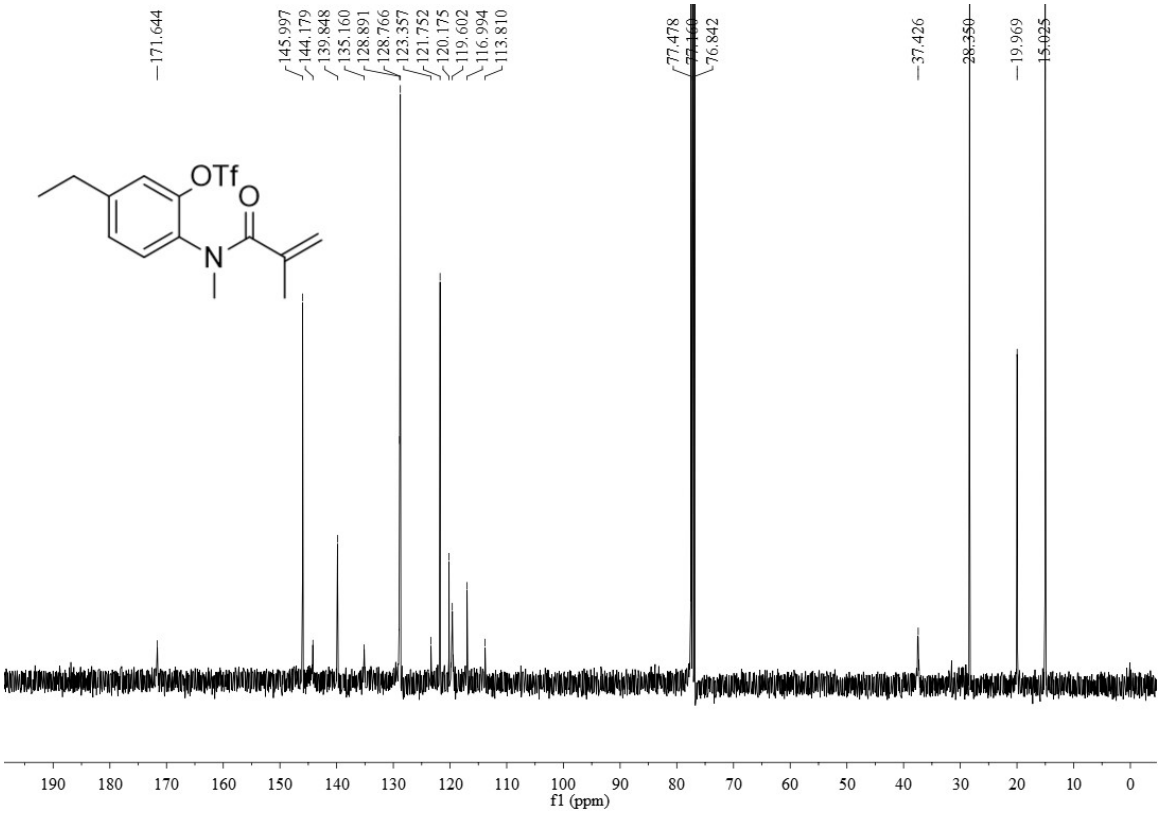
1j

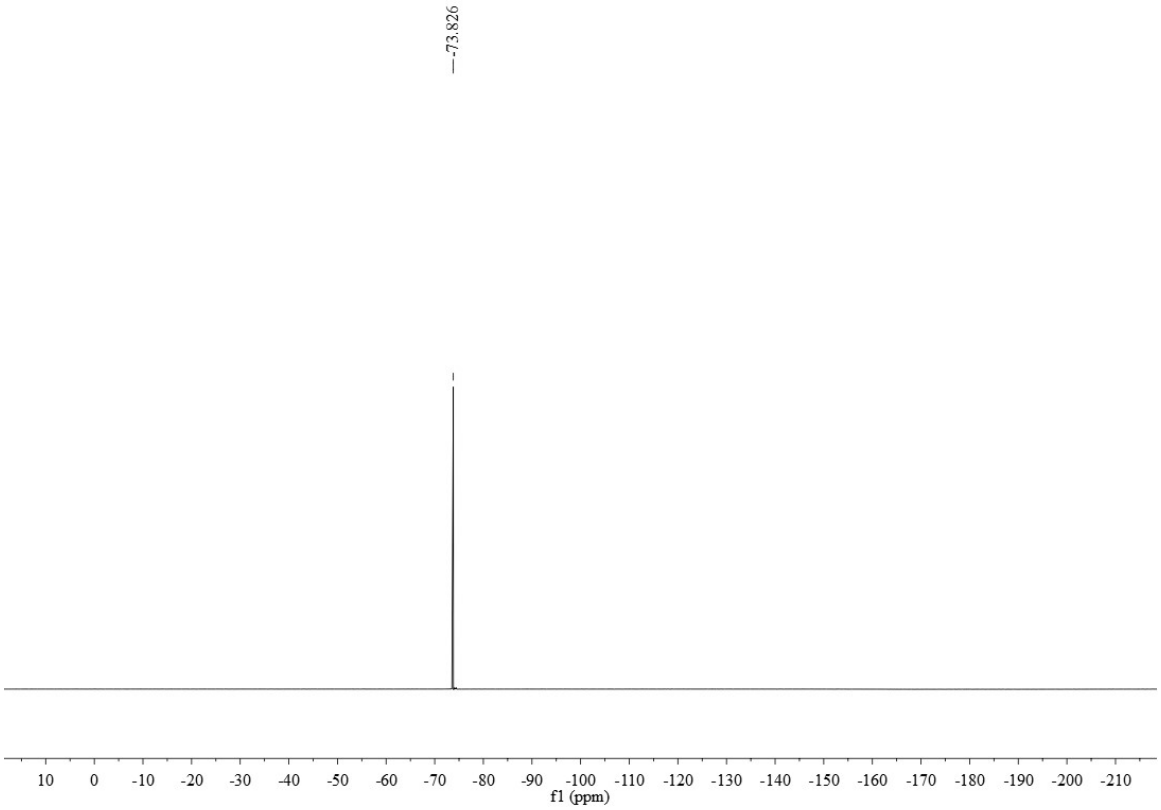

czb-4-209
7.260
7.207
7.183
7.158
7.060
4.986
4.747
3.272
2.352
2.344
2.332
1.811
OTf
O
N
2.07
1.00
1.96
3.14
3.18
3.05
f1 (ppm)
171.477
143.920
139.738
134.927
130.002
128.712
123.231
122.790
120.050
119.422
116.869
113.689
77.479
77.160
76.841
37.271
20.951
19.796
OTf
O
N
f1 (ppm)


-74.021
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

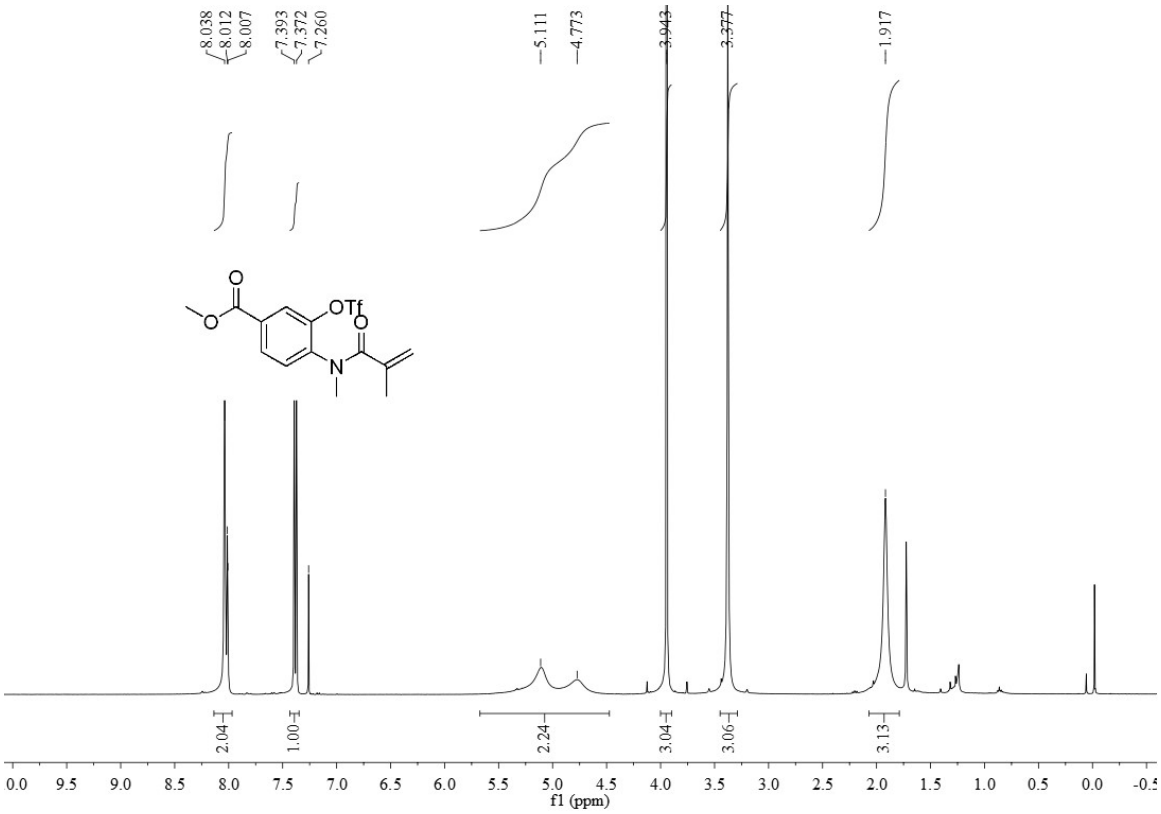
1k

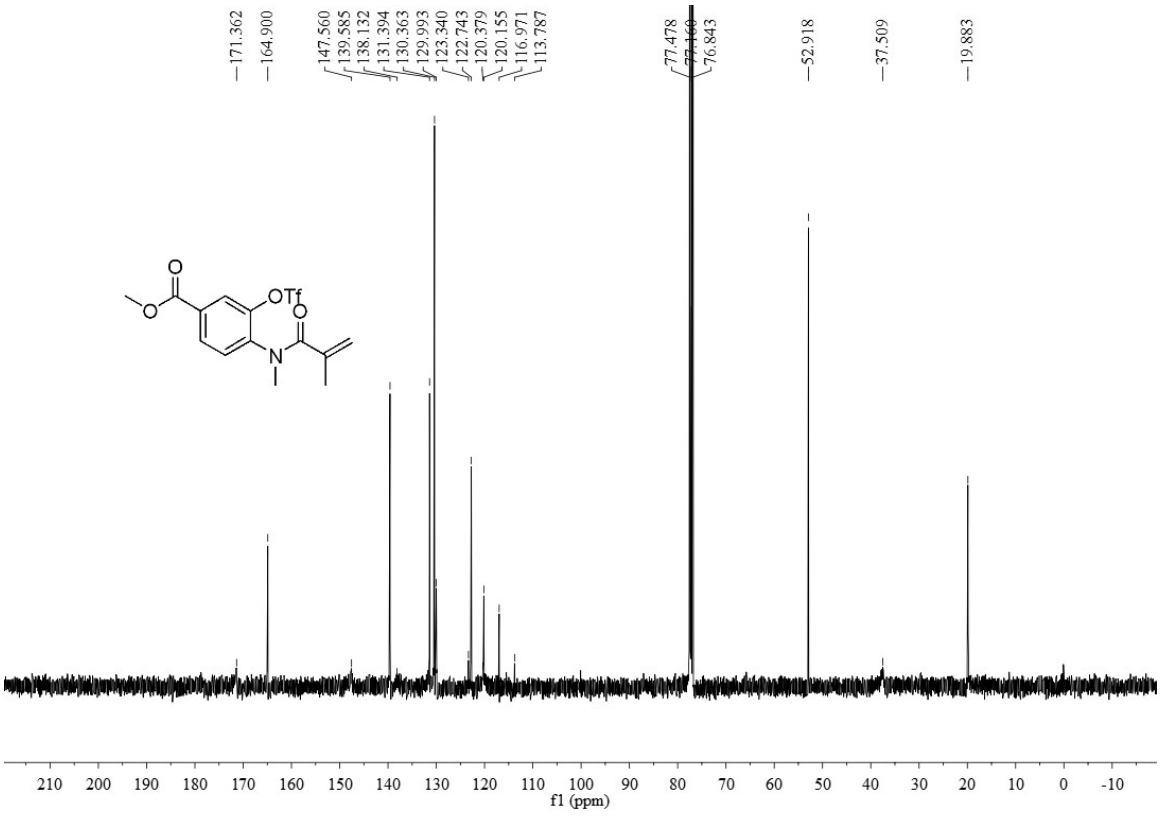

7.260
7.235
7.208
7.116
5.036
4.792
3.325
2.717
2.698
2.680
2.661
1.859
1.273
1.254
1.235
OTf
O
N
1.91
0.96
2.03
3.00
2.08
2.90
3.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

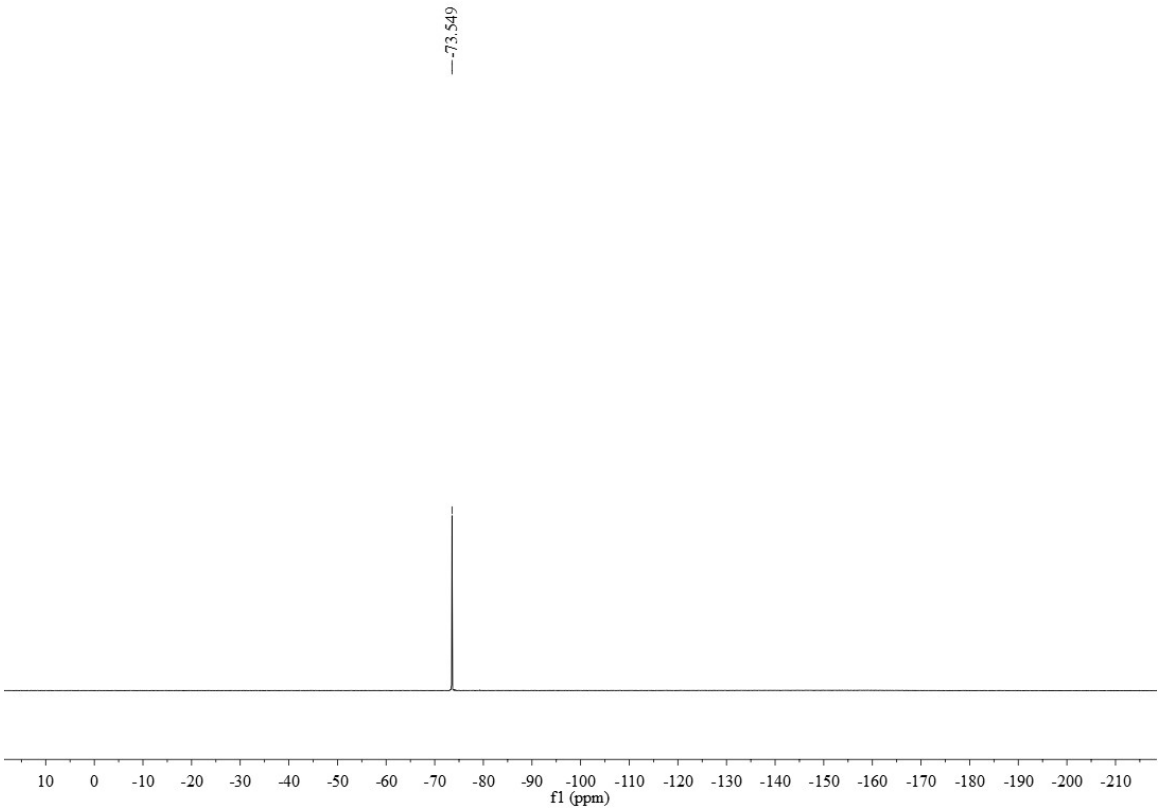

171.644
145.997
144.179
139.848
135.160
128.891
128.766
123.357
121.752
120.175
119.602
116.994
113.810
77.478
77.160
76.842
37.426
28.350
19.969
15.025
OTf
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-73.826
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

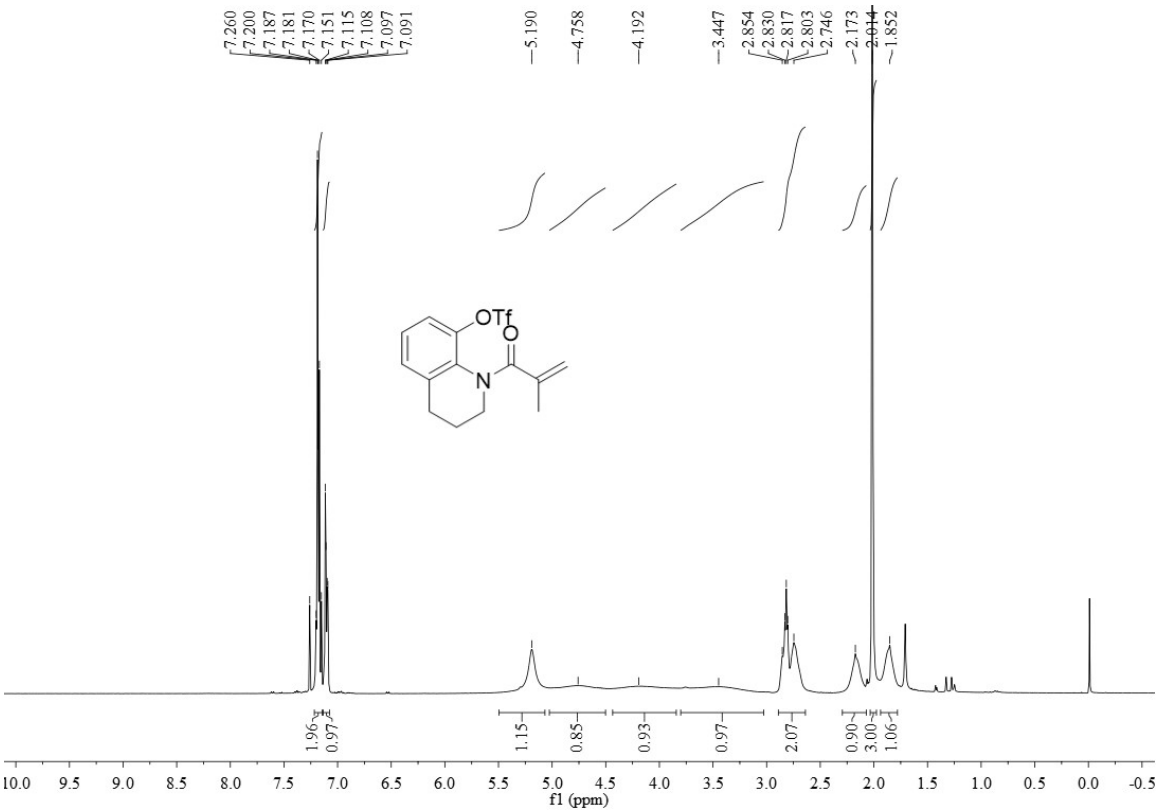
1l

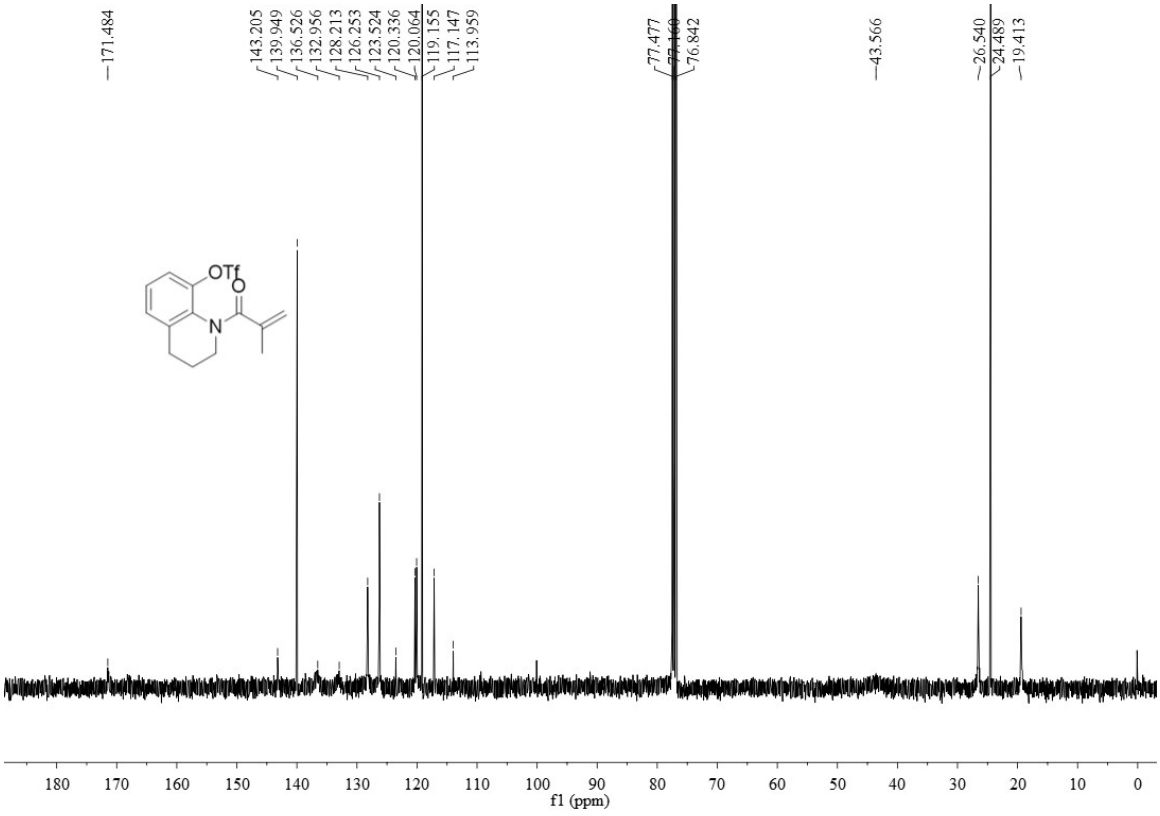

8.038
8.012
8.007
7.393
7.372
7.260
5.111
4.773
3.043
3.377
1.917
2.04
1.00
2.24
3.04
3.06
3.13
f1 (ppm)

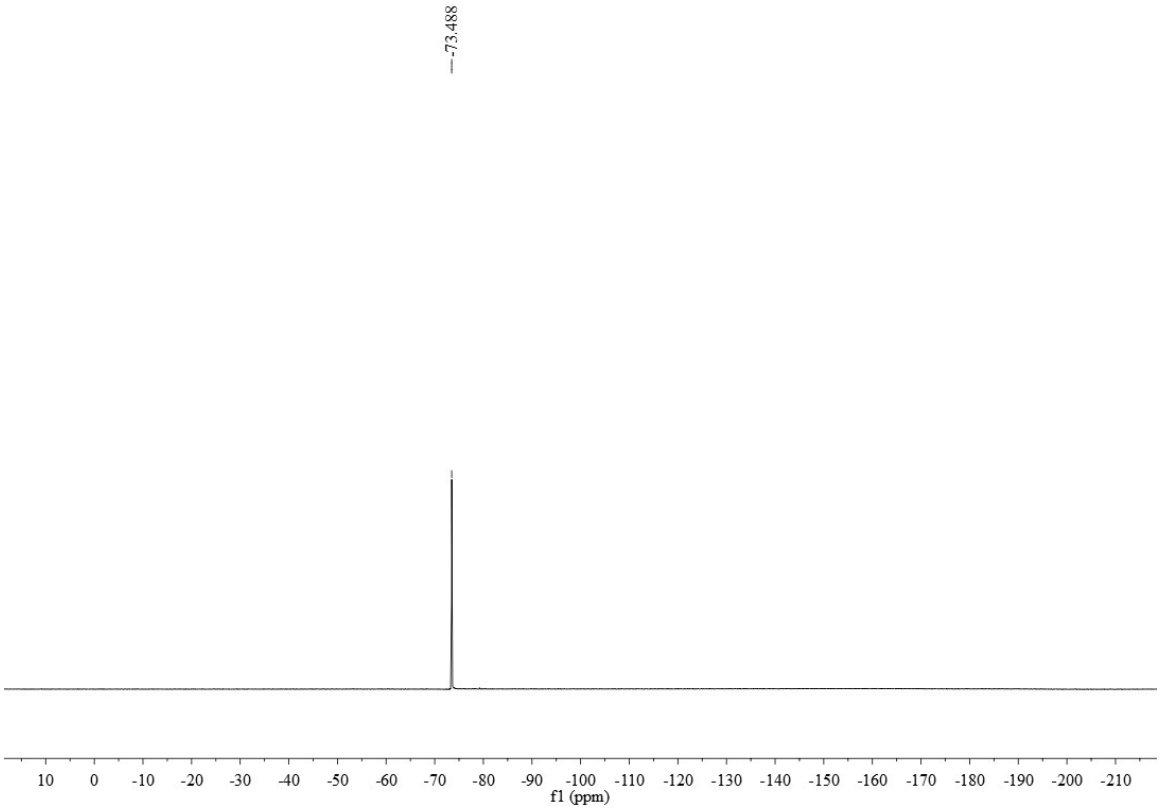

171.362
164.900
147.560
139.585
138.132
131.394
130.363
129.993
123.340
122.743
120.379
120.155
116.971
113.787
77.478
76.843
52.918
37.509
19.883
f1 (ppm)


-73.549
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

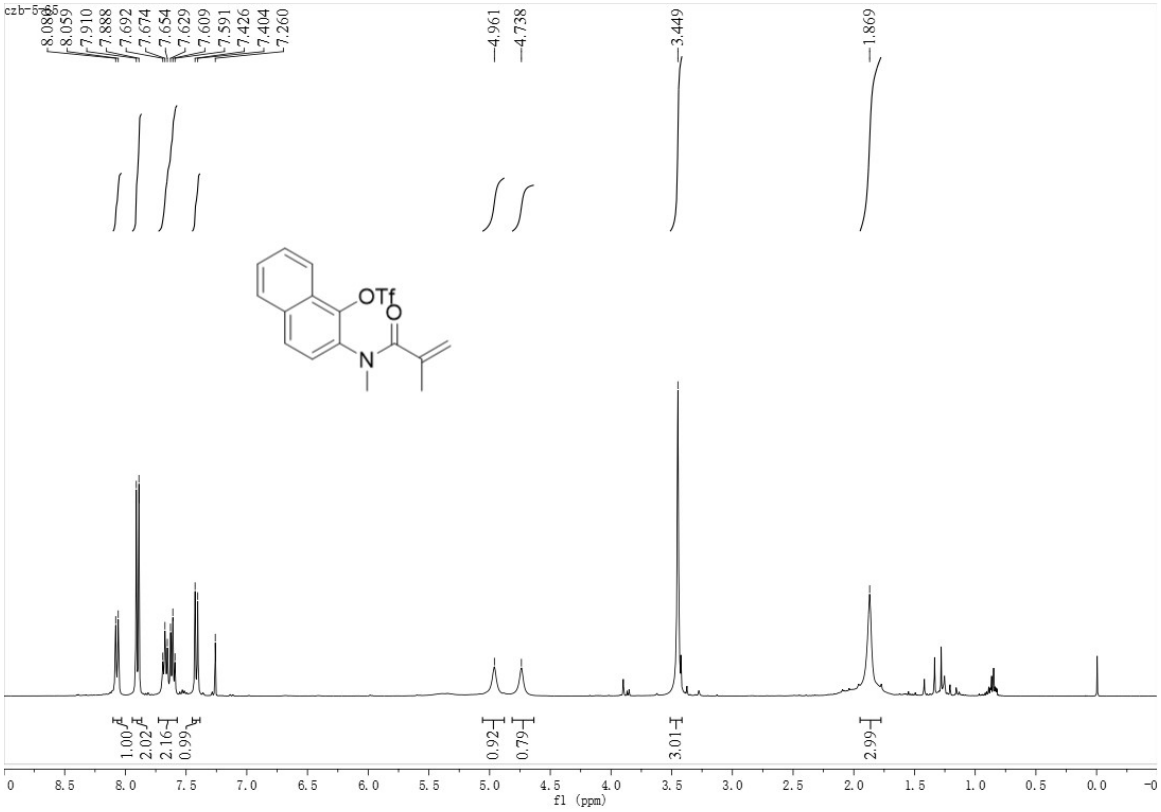
1m

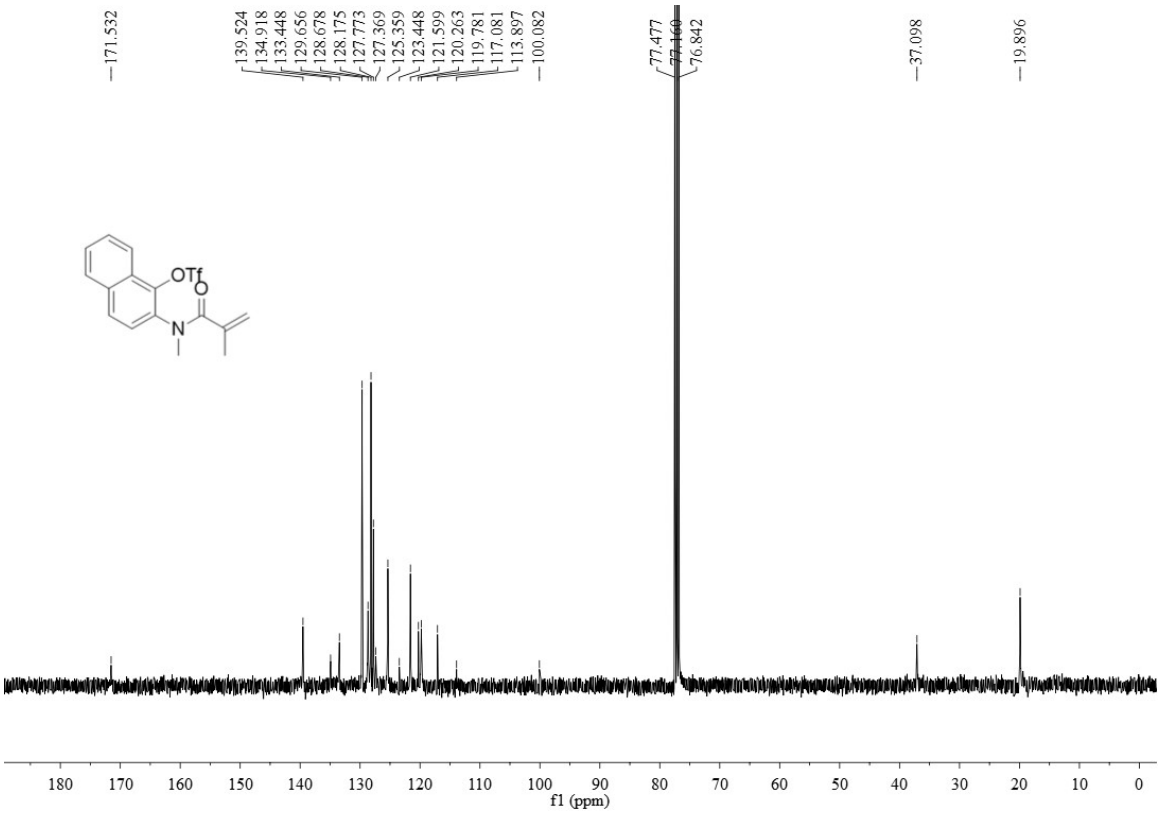

7.260
7.200
7.187
7.181
7.170
7.151
7.115
7.108
7.097
7.091
5.190
4.758
4.192
3.447
2.854
2.830
2.817
2.803
2.746
2.173
2.014
1.852
OTf
O
N
1.96
0.97
1.15
0.85
0.93
0.97
2.07
0.90
3.00
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

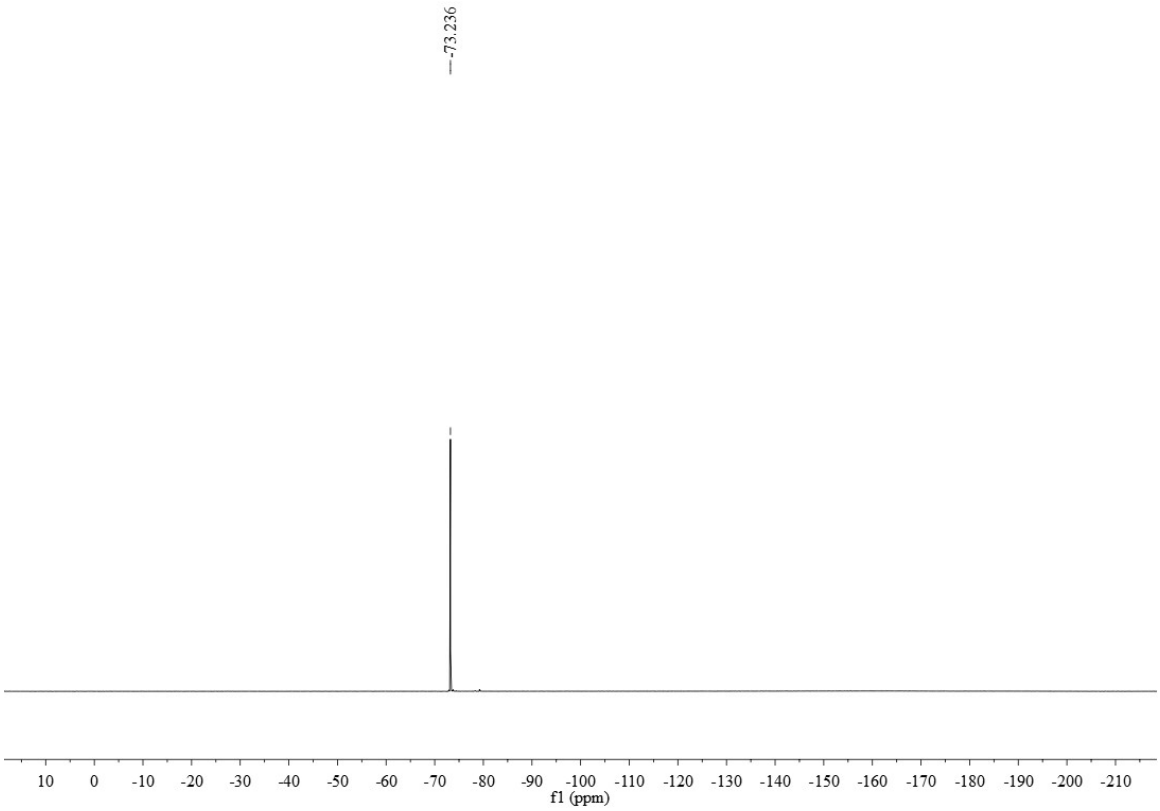

171.484
143.205
139.949
136.526
132.956
128.213
126.253
123.524
120.336
120.064
119.155
117.147
113.959
77.477
77.160
76.842
43.566
26.540
24.489
19.413
OTf
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-73.488
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

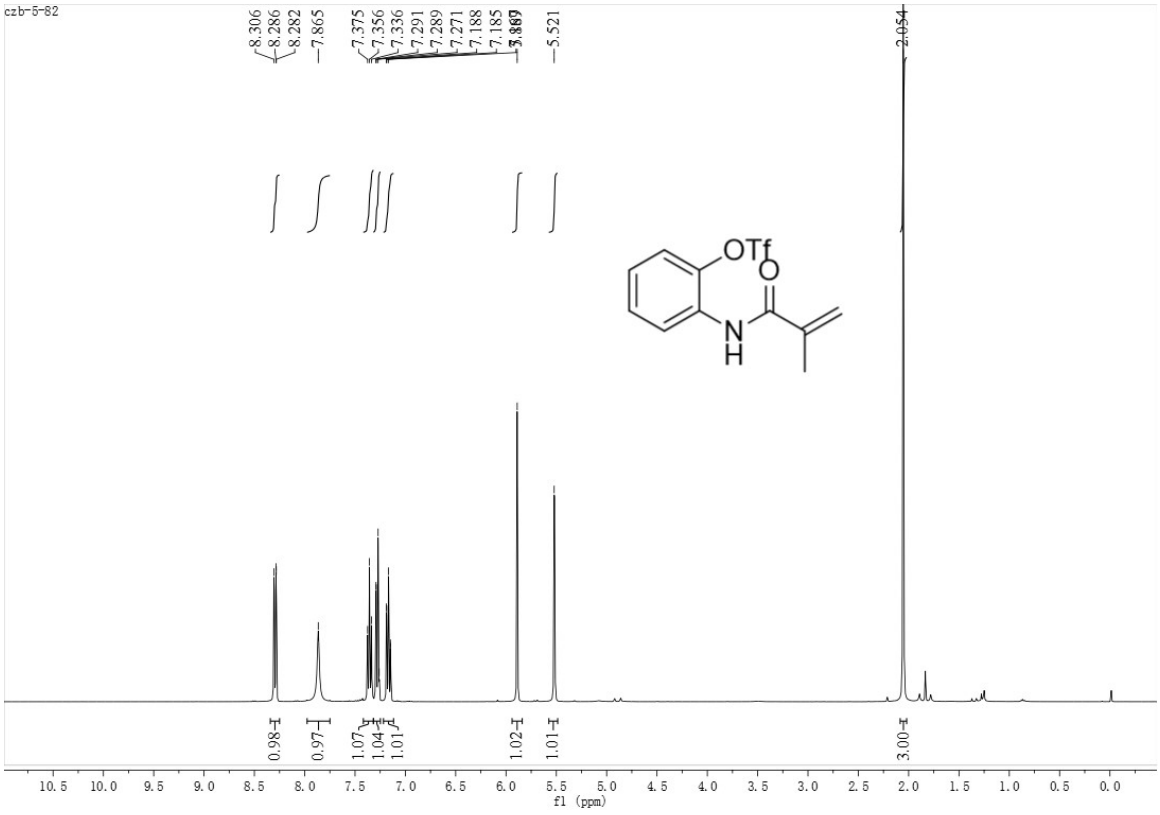
1n

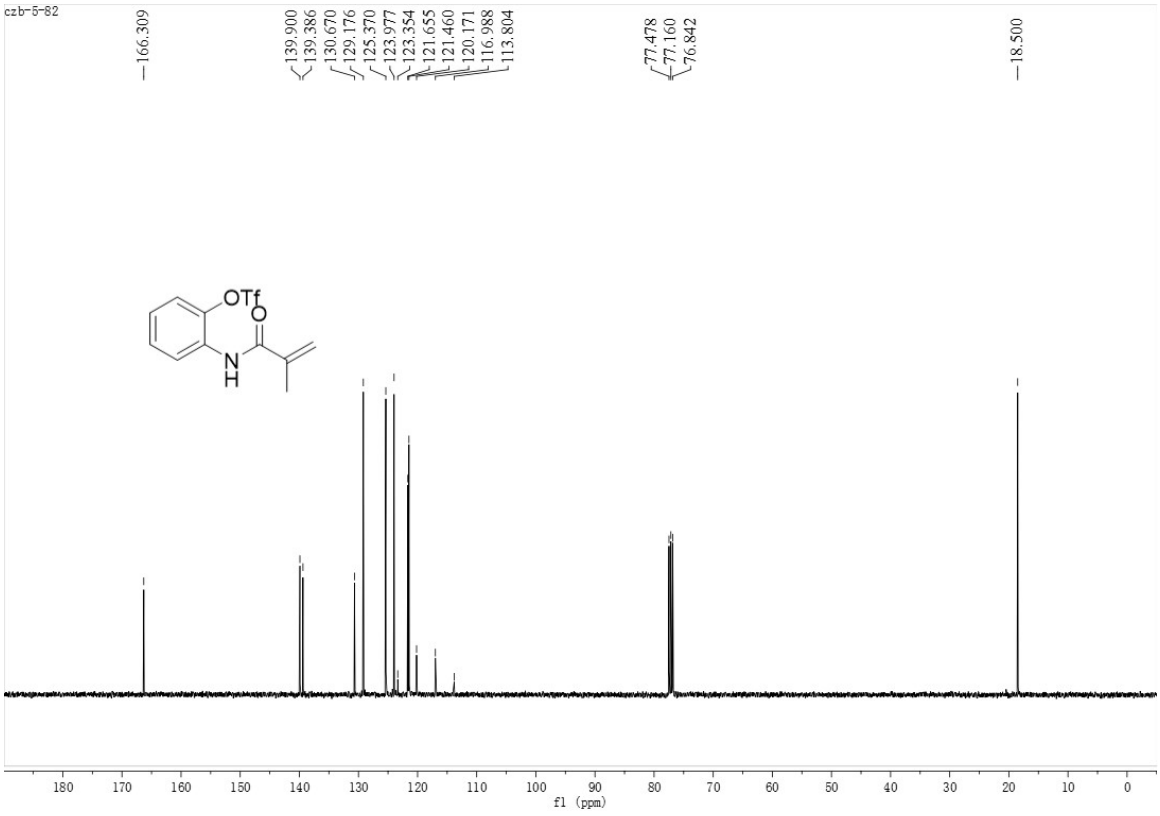

8.088
8.059
7.910
7.888
7.692
7.674
7.654
7.629
7.609
7.591
7.426
7.404
7.260
4.961
4.738
3.449
1.869
OTf
O
N
1.00
2.02
2.16
0.99
0.92
0.79
3.01
2.99
f1 (ppm)

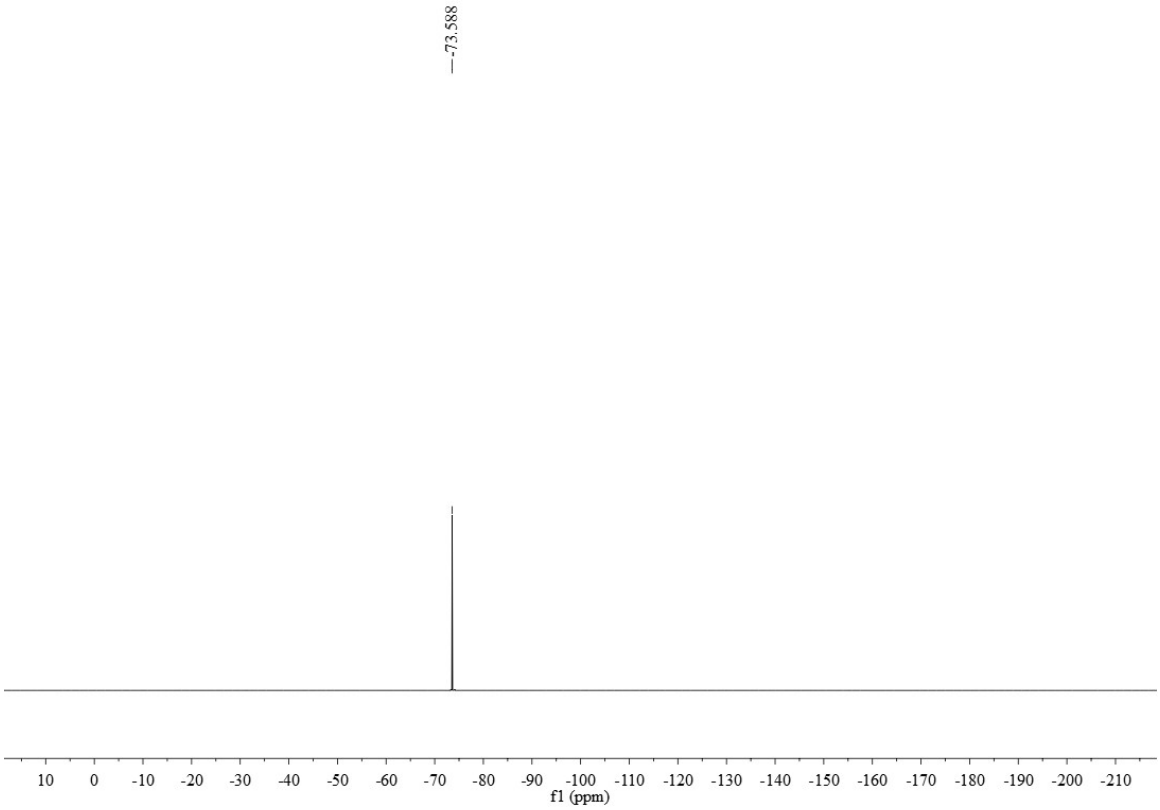

171.532
139.524
134.918
133.448
129.656
128.678
128.175
127.773
127.369
125.359
123.448
121.599
120.263
119.781
117.081
113.897
100.082
77.477
77.160
76.842
37.098
19.896
OTf
O
N
f1 (ppm)


-73.236
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

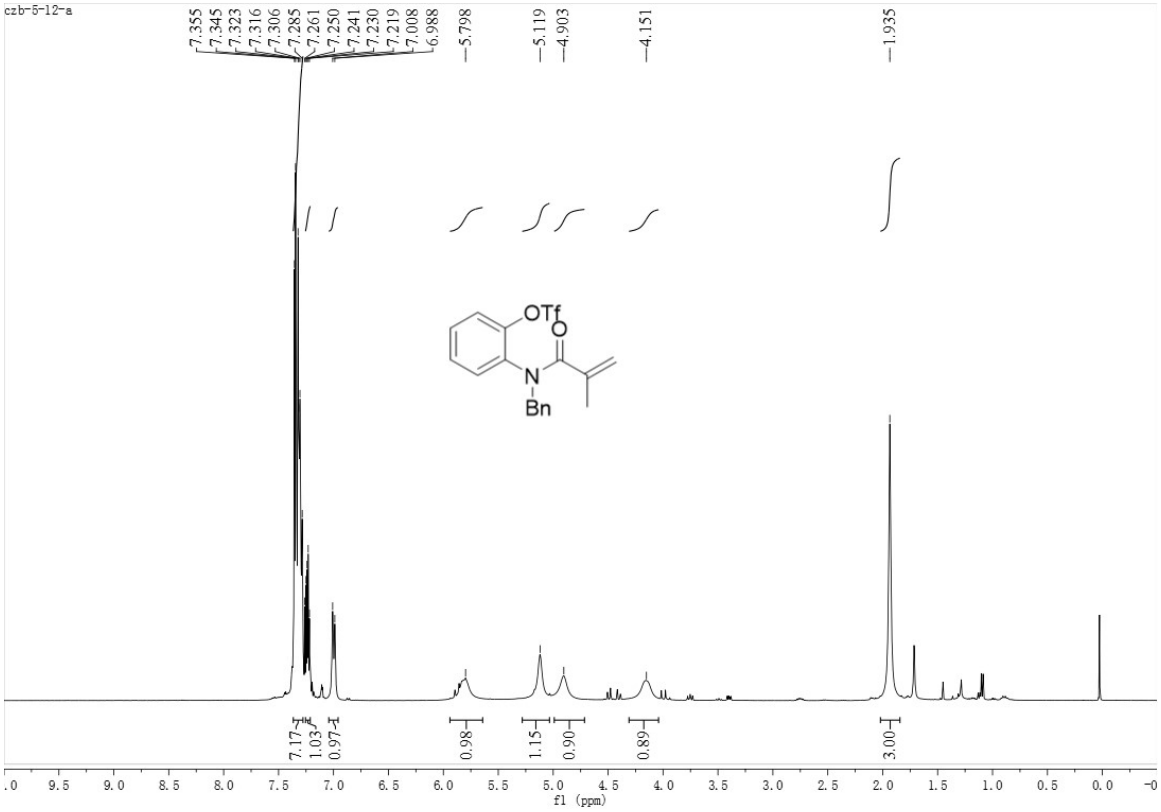
1o

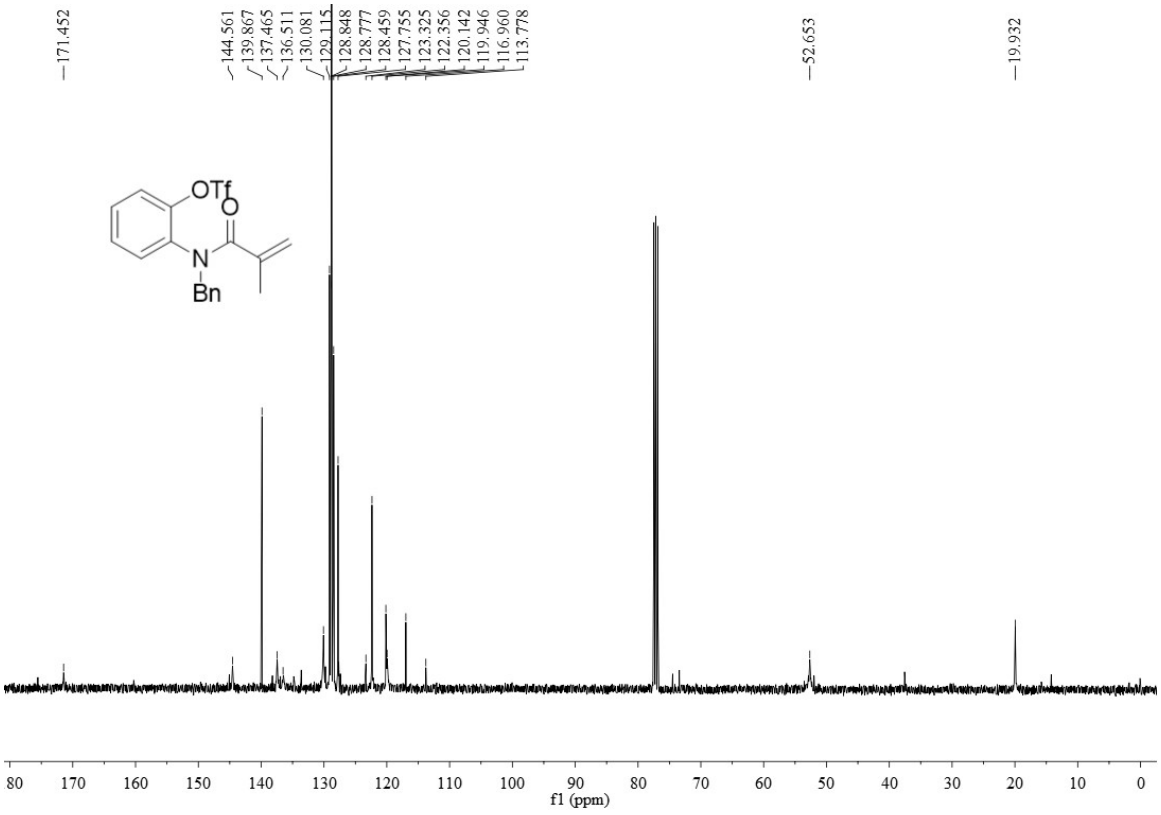

czb-5-82
8.306
8.286
8.282
7.865
7.375
7.356
7.336
7.291
7.289
7.271
7.188
7.185
5.521
2.054
OTf
O
N
H
0.98
0.97
1.07
1.04
1.01
1.02
1.01
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

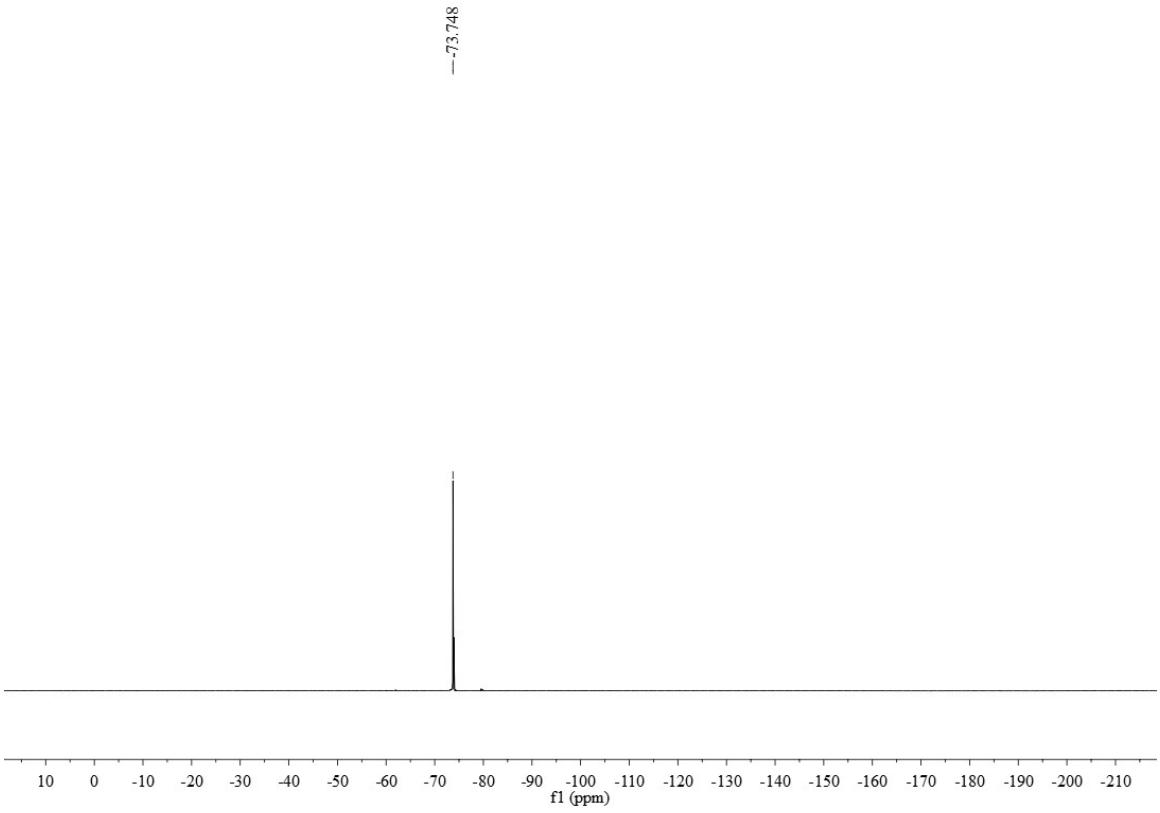

czb-5-82
166.309
139.900
139.386
130.670
129.176
125.370
123.977
123.354
121.655
121.460
120.171
116.988
113.804
77.478
77.160
76.842
18.500
OTf
O
N
H
f1 (ppm)


-73.588
f1 (ppm)

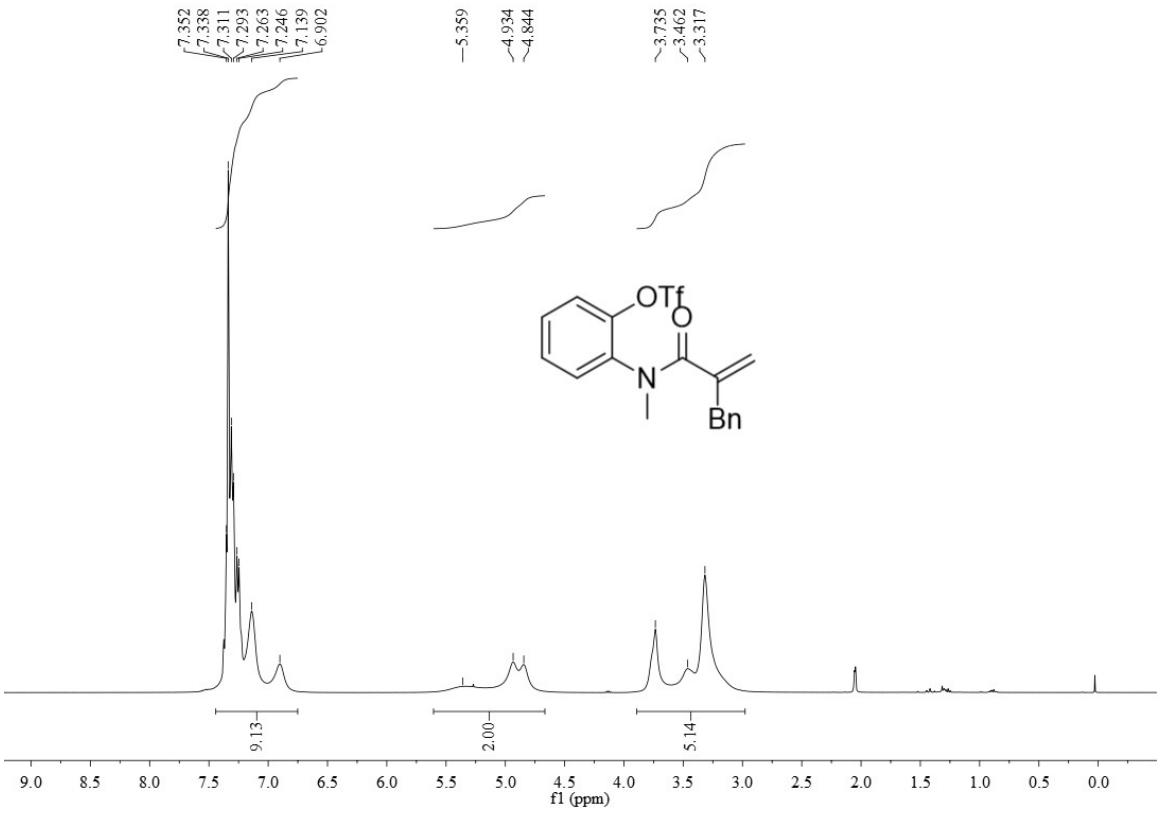
1p

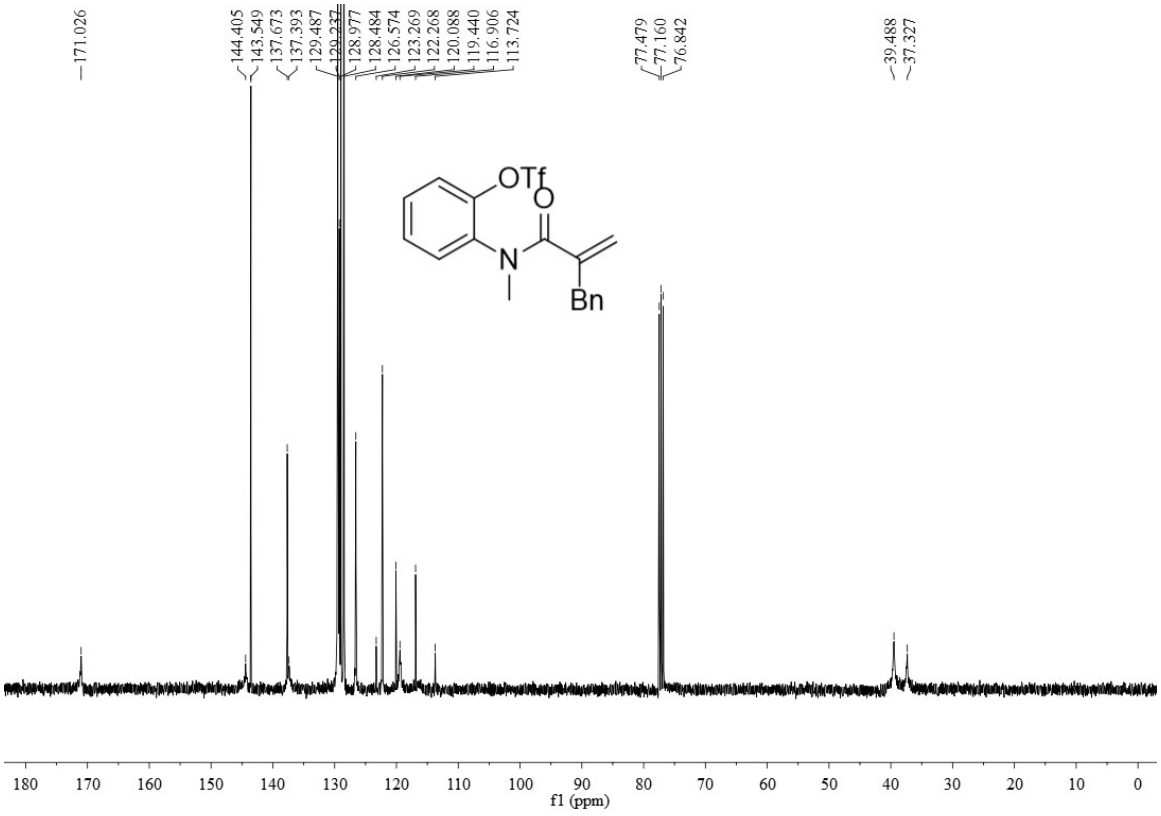

czb-5-12-a
7.355
7.345
7.323
7.316
7.306
7.285
7.261
7.250
7.241
7.230
7.219
7.008
6.988
5.798
5.119
4.903
4.151
1.935
OTf
O
N
Bn
7.17
1.03
0.97
0.98
1.15
0.90
0.89
3.00
f1 (ppm)

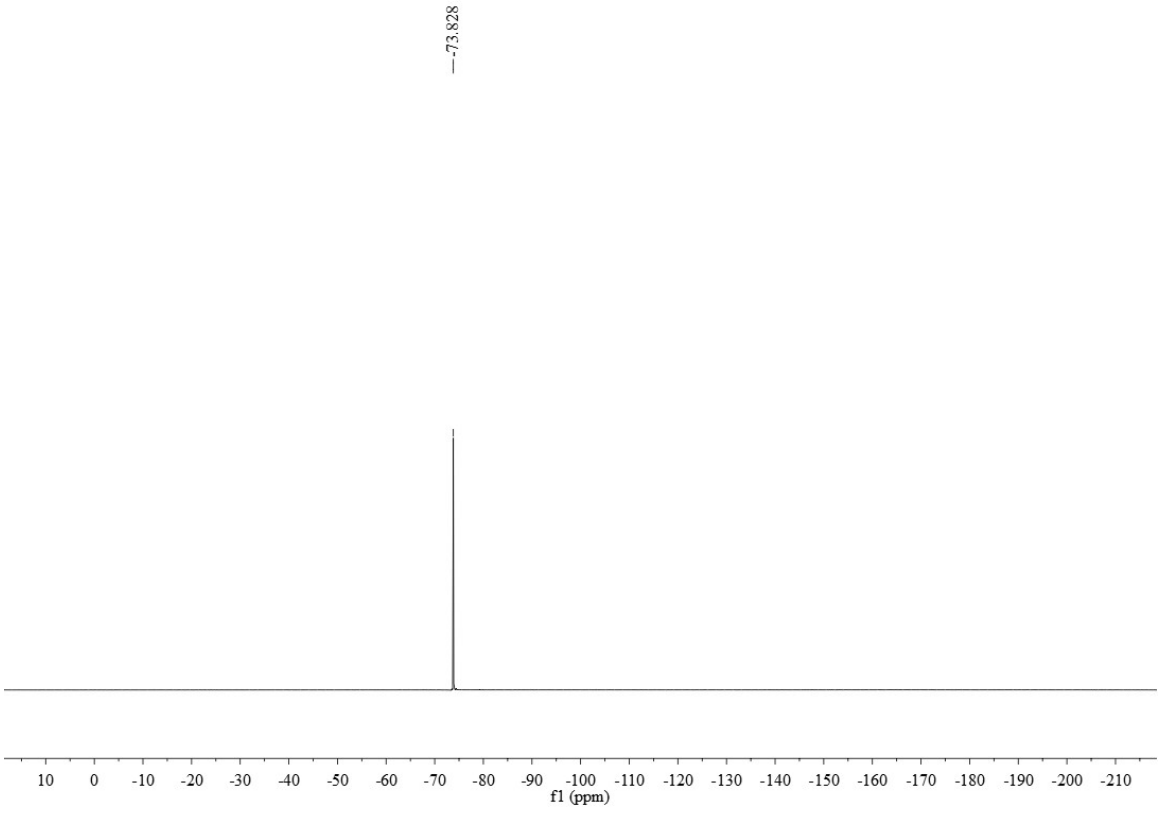

171.452
144.561
139.867
137.465
136.511
130.081
129.115
128.848
128.777
128.459
127.755
123.325
122.356
120.142
119.946
116.960
113.778
52.653
19.932
OTf
O
N
Bn
f1 (ppm)


-73.748
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

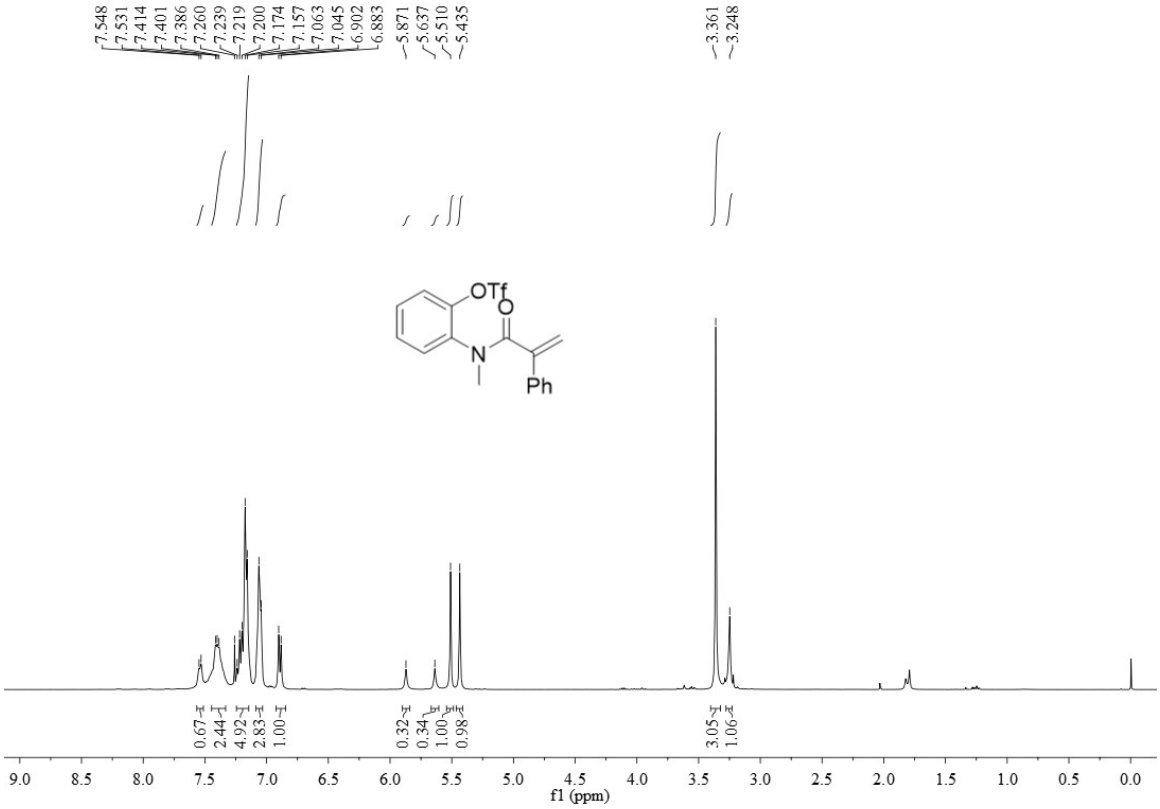
1q

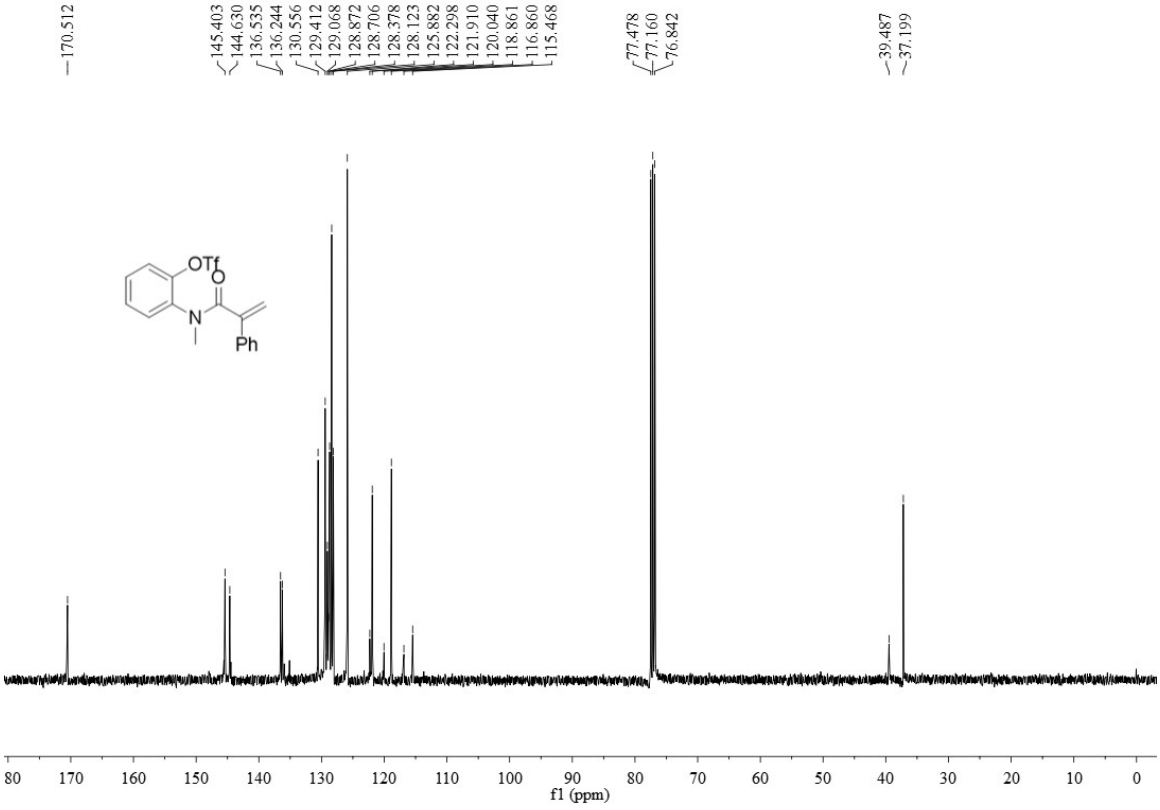

7.352
7.338
7.311
7.293
7.263
7.246
7.139
6.902
5.359
4.934
4.844
3.735
3.462
3.317
OTf
O
N
Bn
9.13
2.00
5.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

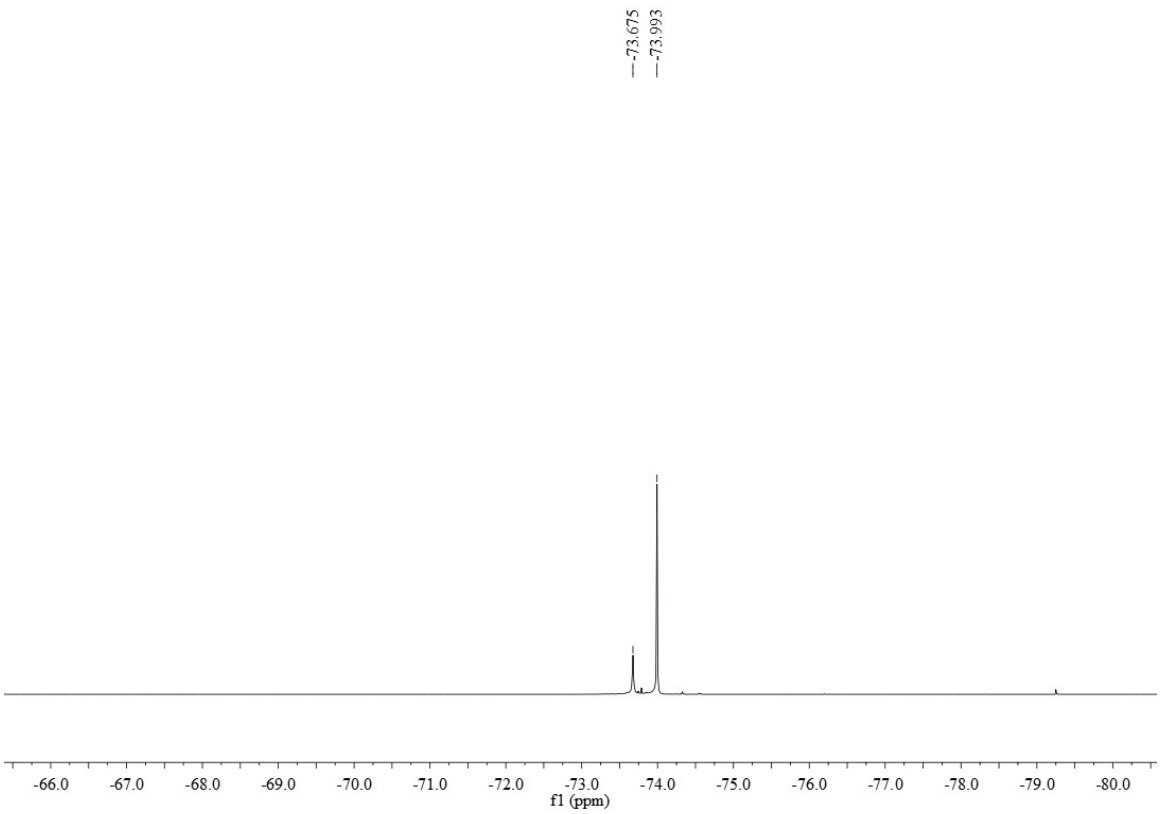

171.026
144.405
143.549
137.673
137.393
129.487
129.232
128.977
128.484
126.574
123.269
122.268
120.088
119.440
116.906
113.724
77.479
77.160
76.842
39.488
37.327
OTf
O
N
Bn
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-73.828
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

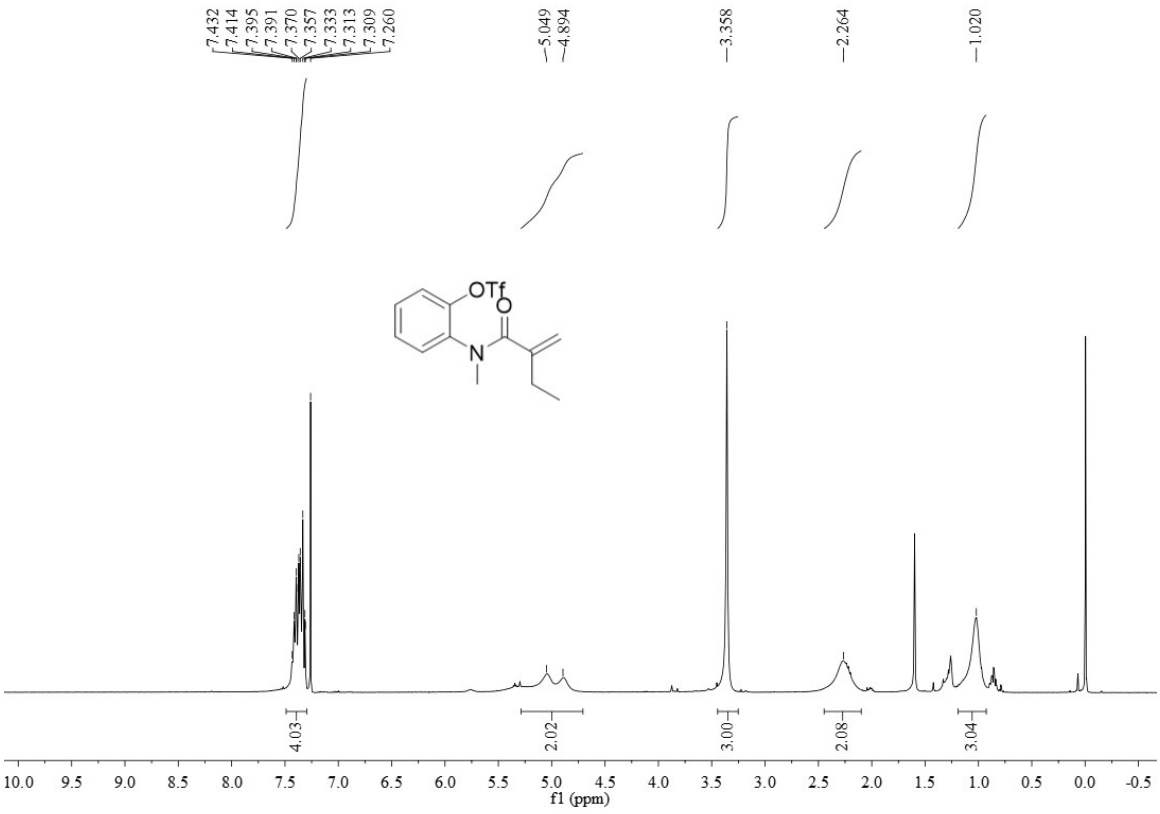
1r

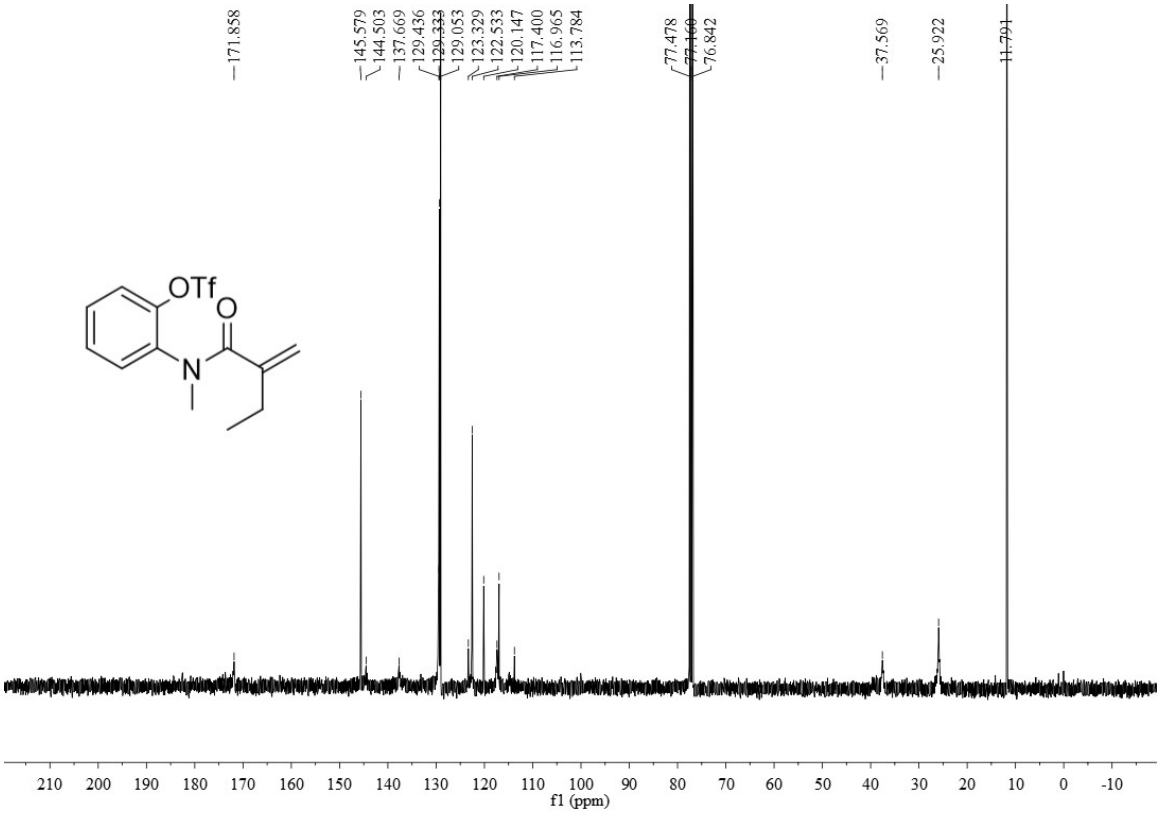

7.548
7.531
7.414
7.401
7.386
7.260
7.239
7.219
7.200
7.174
7.157
7.063
7.045
6.902
6.883
5.871
5.637
5.510
5.435
3.361
3.248
OTf
O
N
Ph
0.67
2.44
4.92
2.83
1.00
0.32
0.34
1.00
0.98
3.05
1.06
f1 (ppm)

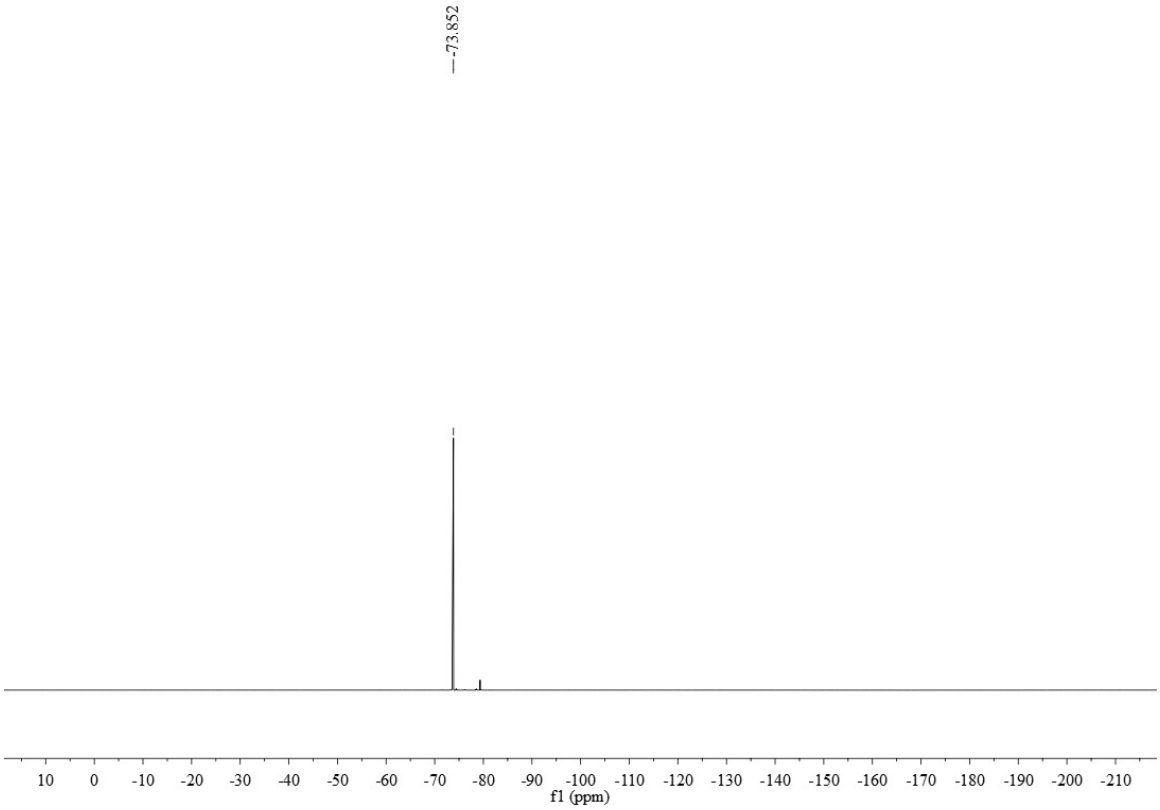

170.512
145.403
144.630
136.535
136.244
130.556
129.412
129.068
128.872
128.706
128.378
128.123
125.882
122.298
121.910
120.040
118.861
116.860
115.468
77.478
77.160
76.842
39.487
37.199
OTf
O
N
Ph
f1 (ppm)


-73.675
-73.993
-66.0
-67.0
-68.0
-69.0
-70.0
-71.0
-72.0
-73.0
-74.0
-75.0
-76.0
-77.0
-78.0
-79.0
-80.0
f1 (ppm)

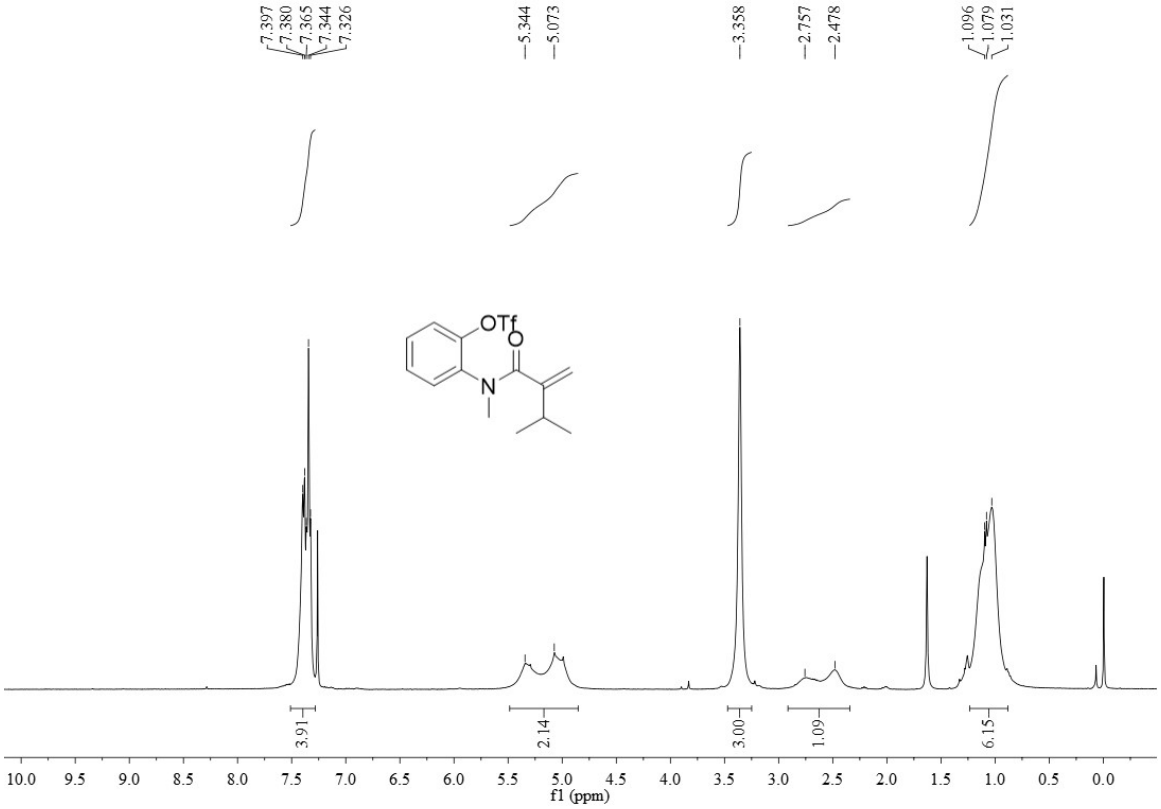
1s

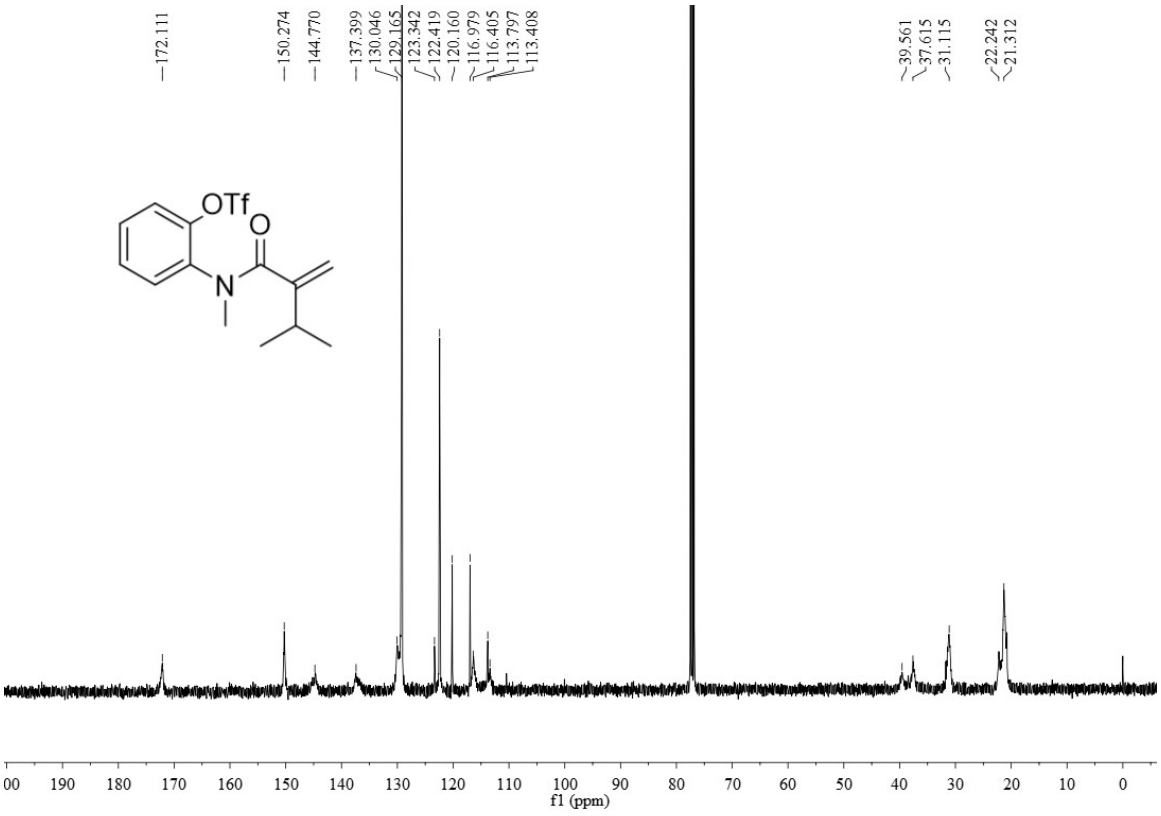

7.432
7.414
7.395
7.391
7.370
7.357
7.333
7.313
7.309
7.260
5.049
4.894
3.358
2.264
1.020
OTf
O
N
4.03
2.02
3.00
2.08
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

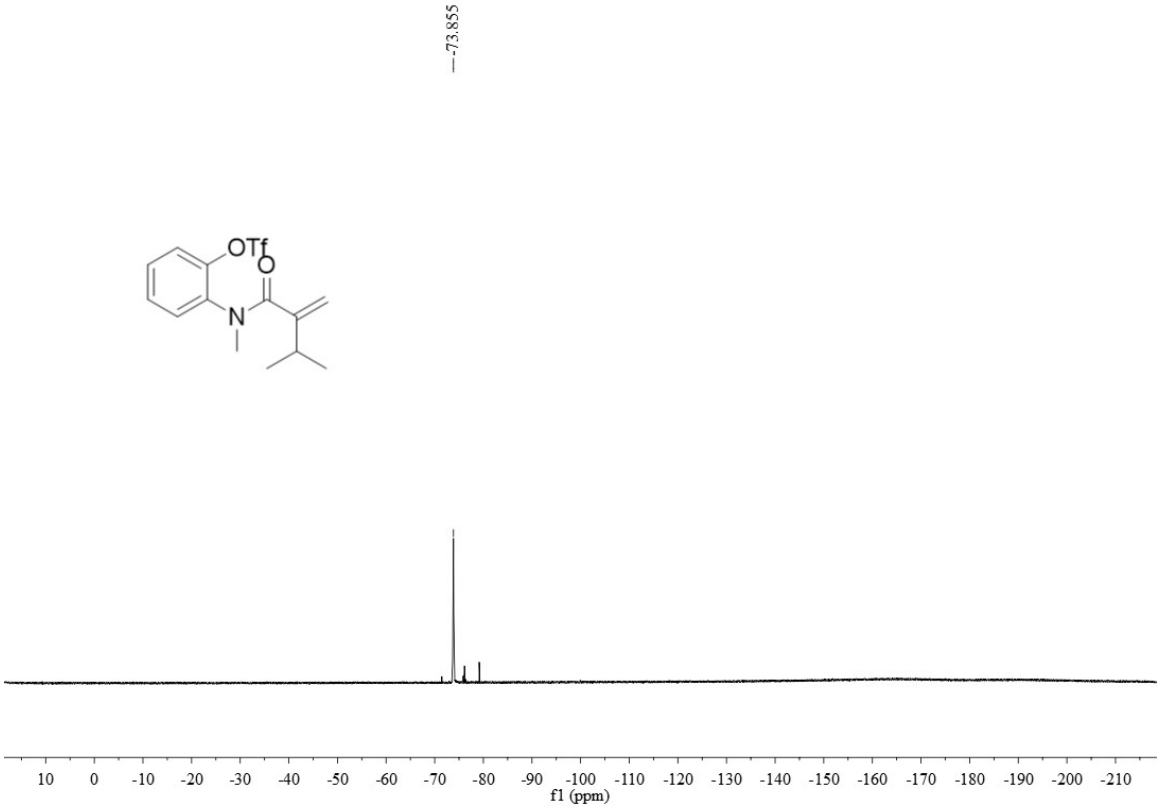

171.858
145.579
144.503
137.669
129.436
129.333
129.053
123.329
122.533
120.147
117.400
116.965
113.784
77.478
77.160
76.842
37.569
25.922
11.791
OTf
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-73.852
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

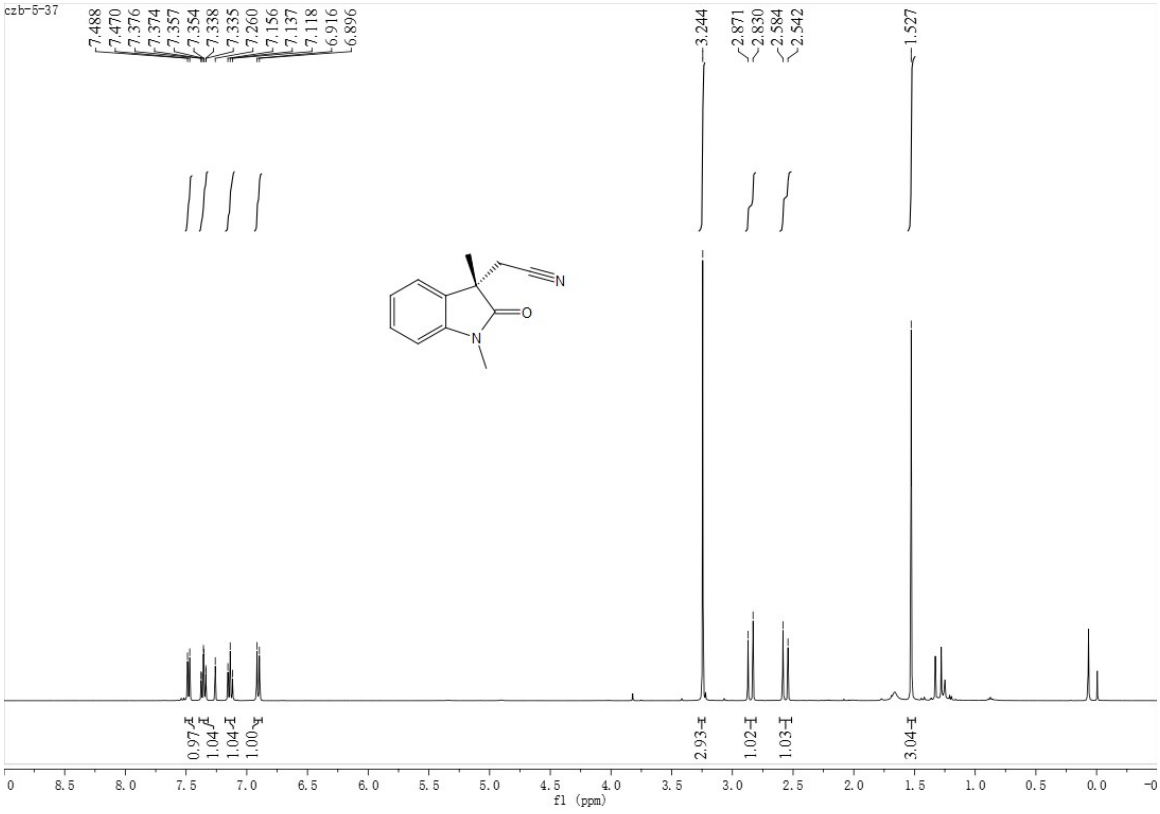
1t

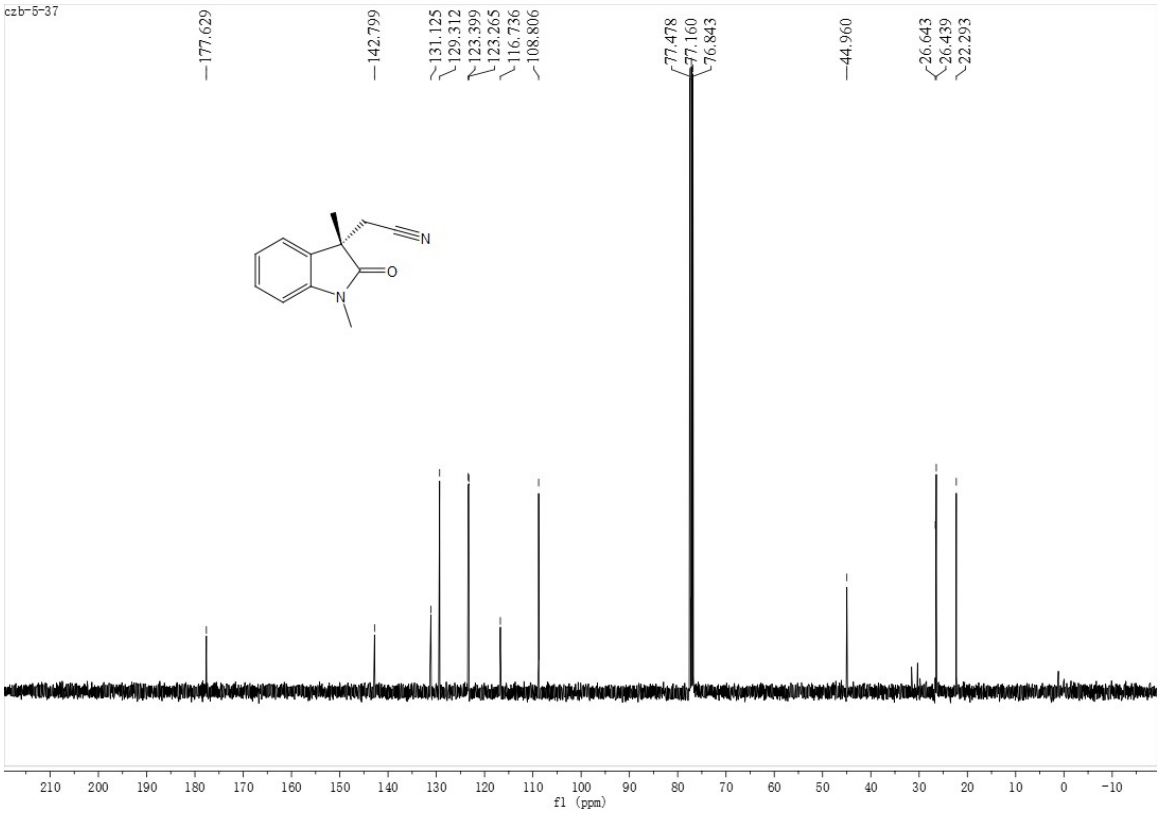

7.397
7.380
7.365
7.344
7.326
5.344
5.073
3.358
2.757
2.478
1.096
1.079
1.031
OTf
O
N
3.91
2.14
3.00
1.09
6.15
f1 (ppm)


172.111
150.274
144.770
137.399
130.046
129.165
123.342
122.419
120.160
116.979
116.405
113.797
113.408
39.561
37.615
31.115
22.242
21.312
OTf
O
N
f1 (ppm)

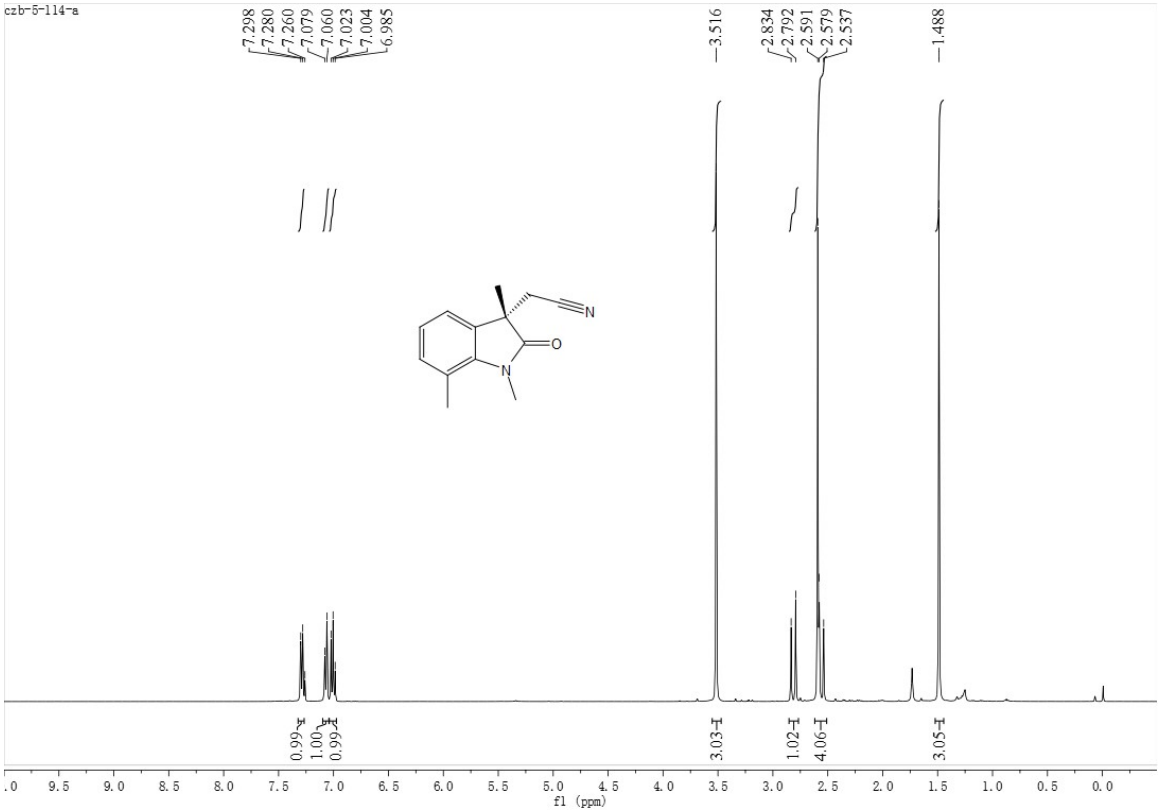

-73.855
OTf
O
N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

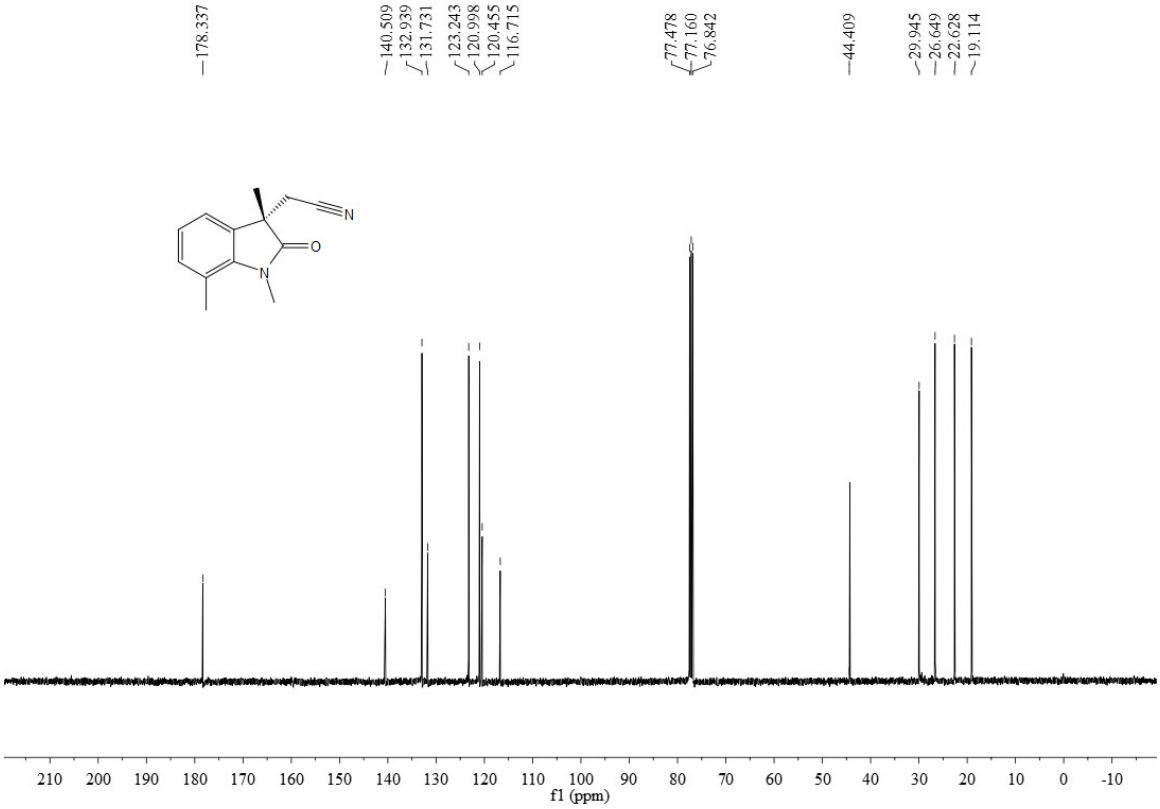
2a


czb-5-37
7.488
7.470
7.376
7.374
7.357
7.354
7.338
7.335
7.260
7.156
7.137
7.118
6.916
6.896
3.244
2.871
2.830
2.584
2.542
1.527
N
O
N
0.97
1.04
1.04
1.00
2.93
1.02
1.03
3.04
f1 (ppm)

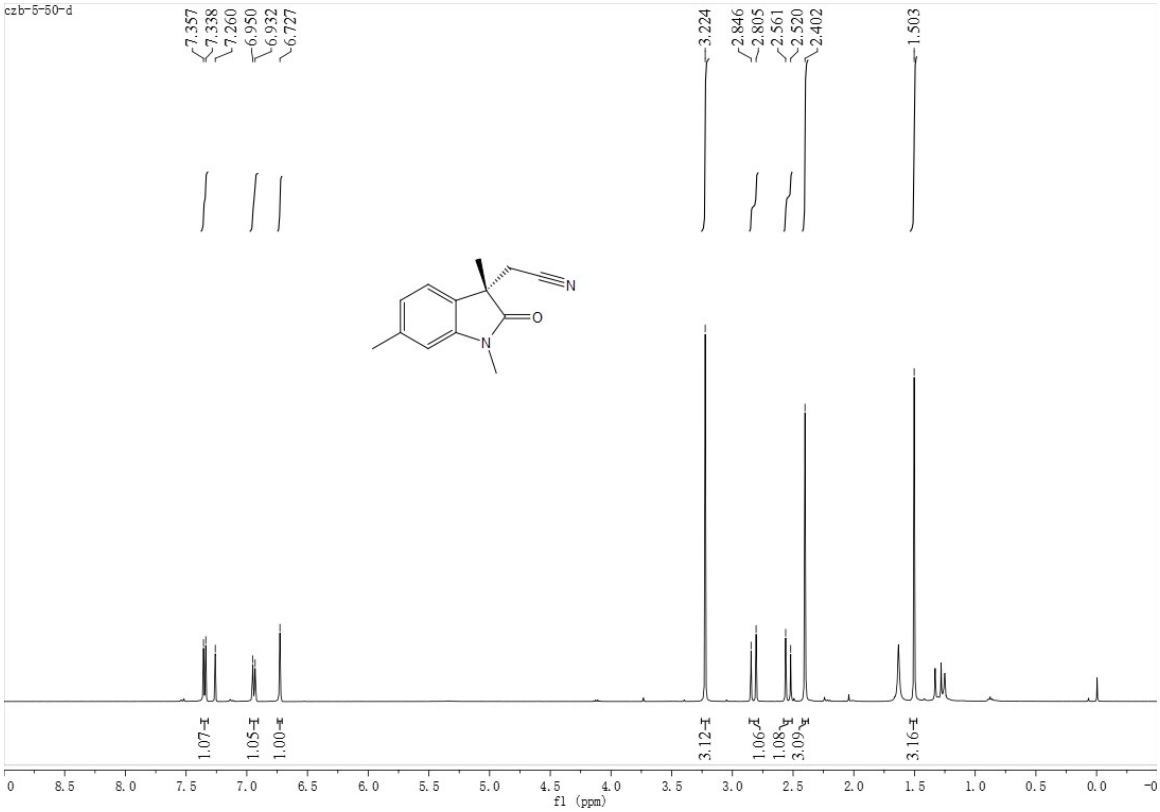

czb-5-37
177.629
142.799
131.125
129.312
123.399
123.265
116.736
108.806
77.478
77.160
76.843
44.960
26.643
26.439
22.293
N
O
N
f1 (ppm)

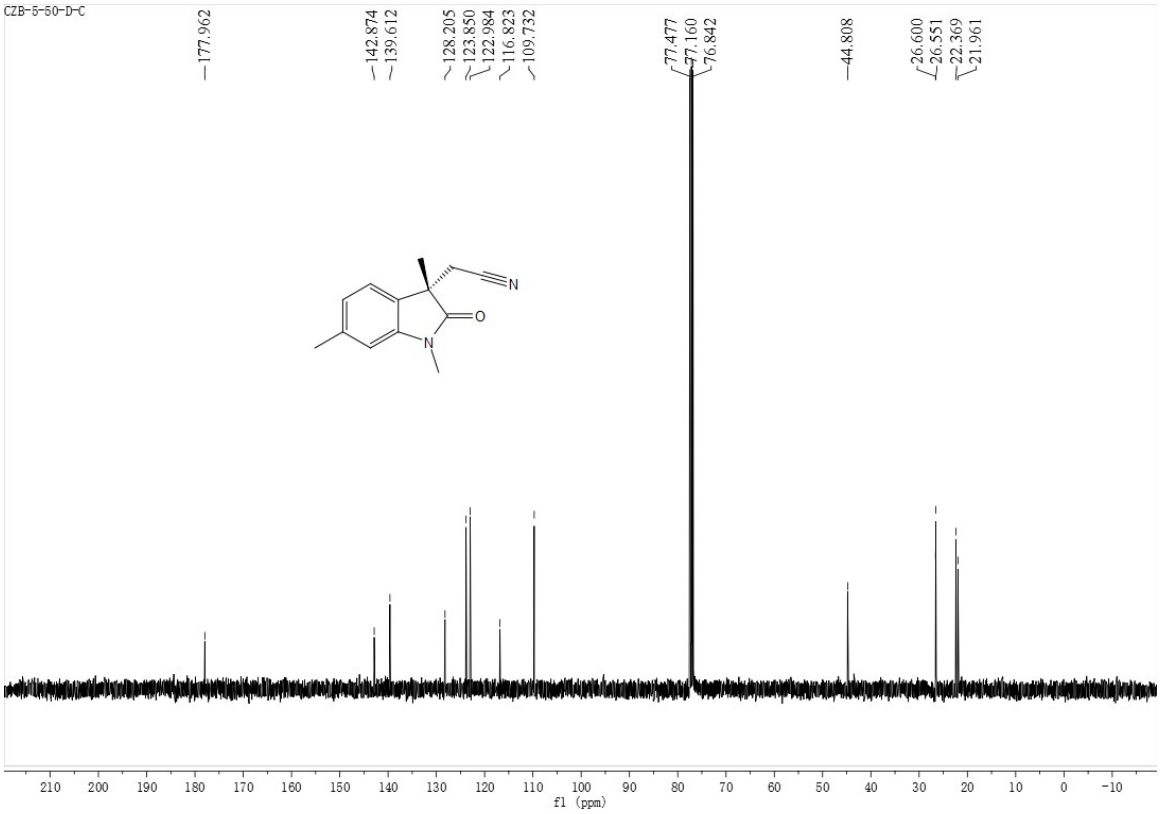
2b


czb-5-114-a
7.298
7.280
7.260
7.079
7.060
7.023
7.004
6.985
3.516
2.834
2.792
2.591
2.579
2.537
1.488
0.99
1.00
0.99
3.03
1.02
4.06
3.05
N
O
N
f1 (ppm)

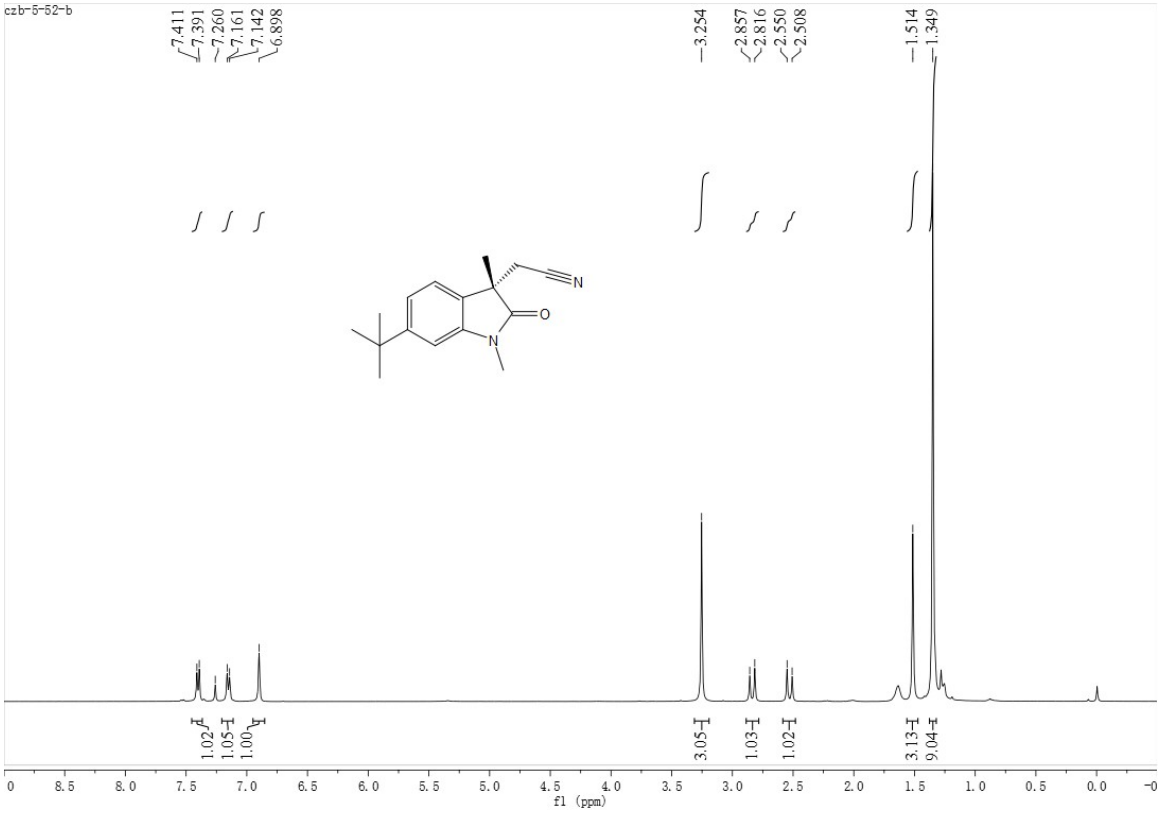

178.337
140.509
132.939
131.731
123.243
120.998
120.455
116.715
77.478
77.160
76.842
44.409
29.945
26.649
22.628
19.114
N
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

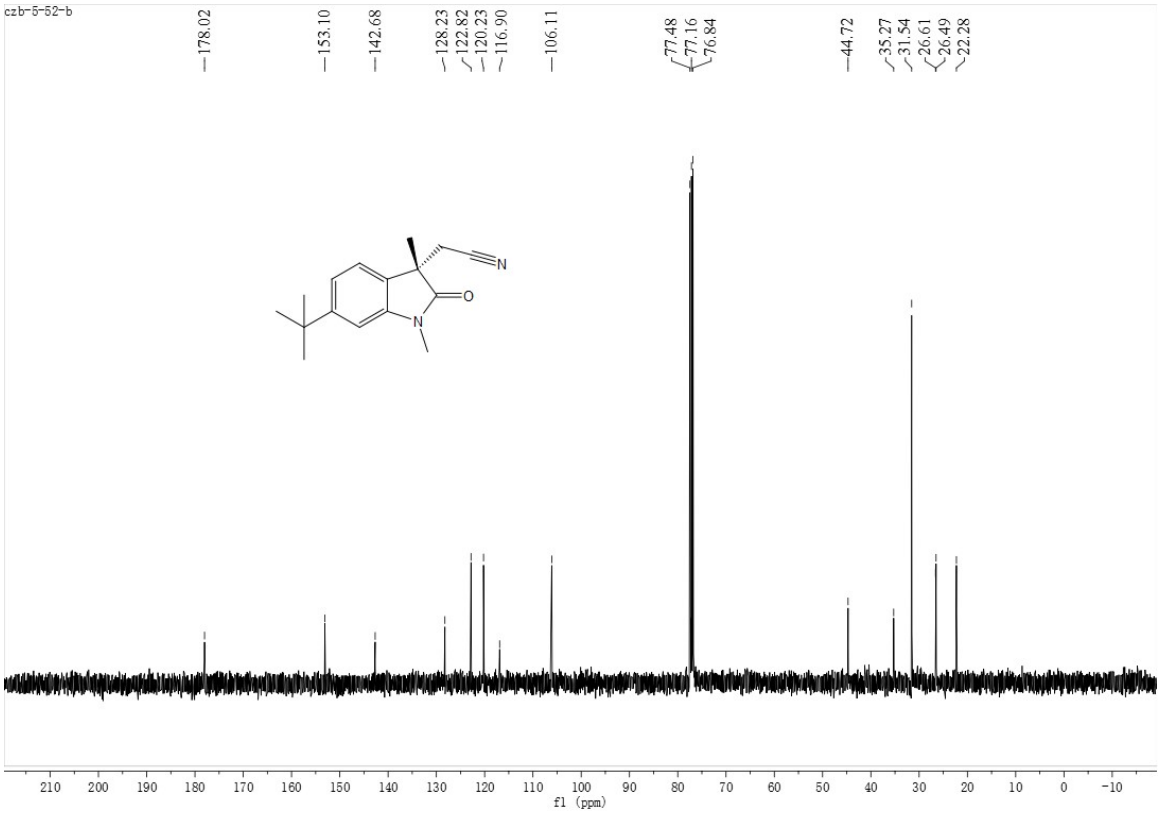
2c


czb-5-50-d
7.357
7.338
7.260
6.950
6.932
6.727
3.224
2.846
2.805
2.561
2.520
2.402
1.503
N
O
N
1.07
1.05
1.00
3.12
1.06
1.08
3.09
3.16
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)

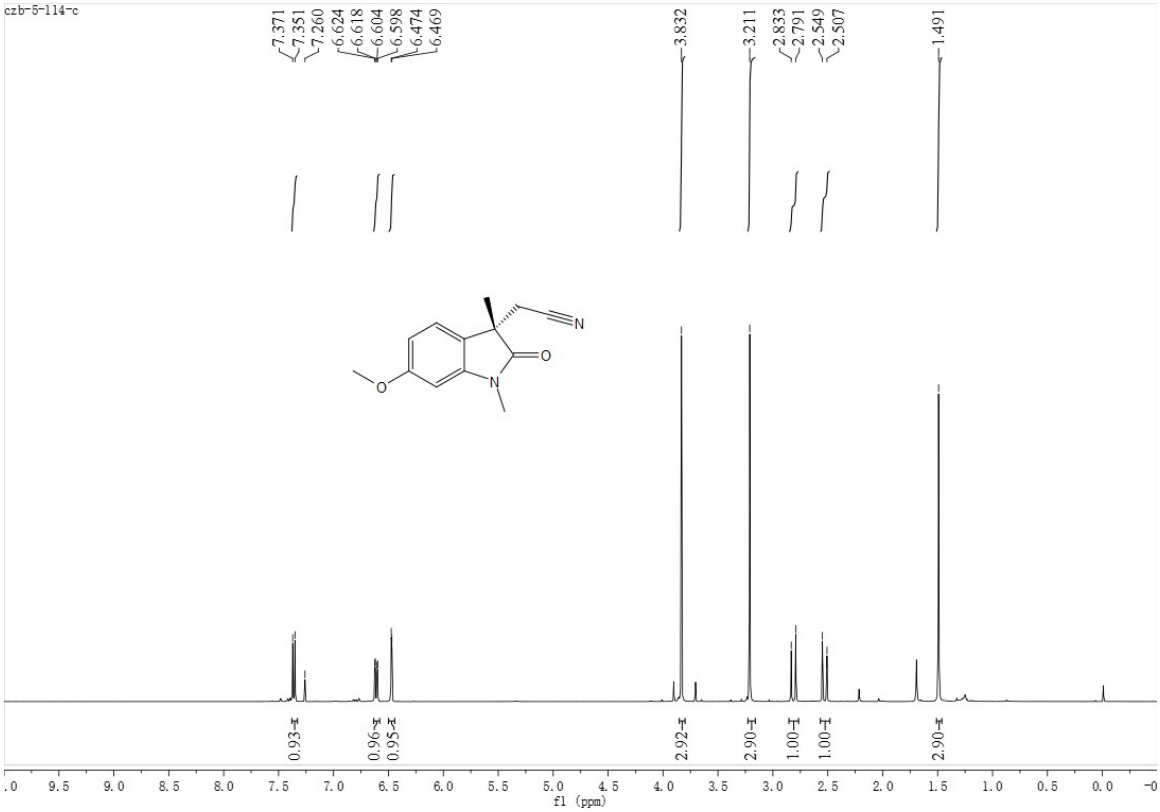

CZB-5-50-D-C
177.962
142.874
139.612
128.205
123.850
122.984
116.823
109.732
77.477
77.160
76.842
44.808
26.600
26.551
22.369
21.961
N
O
N
f1 (ppm)

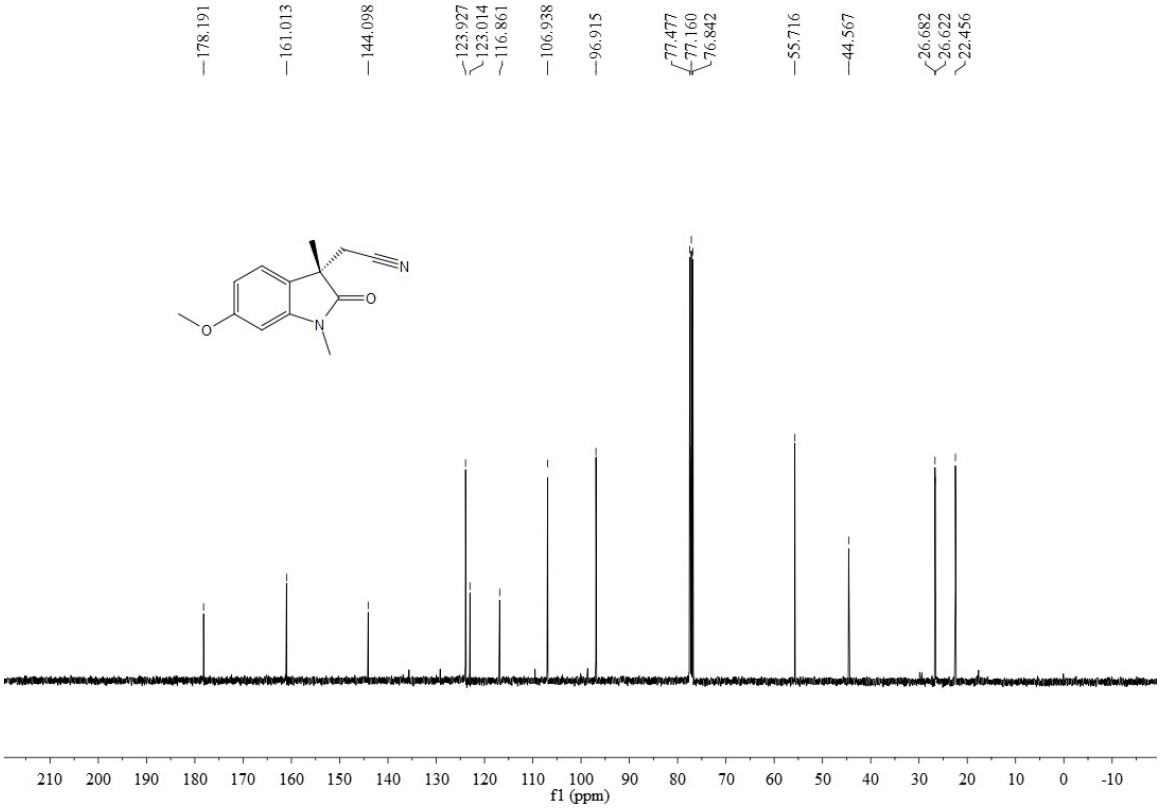
2d


czb-5-52-b
7.411
7.391
7.260
7.161
7.142
6.898
3.254
2.857
2.816
2.550
2.508
1.514
1.349
1.02
1.05
1.00
3.05
1.03
1.02
3.13
9.04
N
O
N
f1 (ppm)

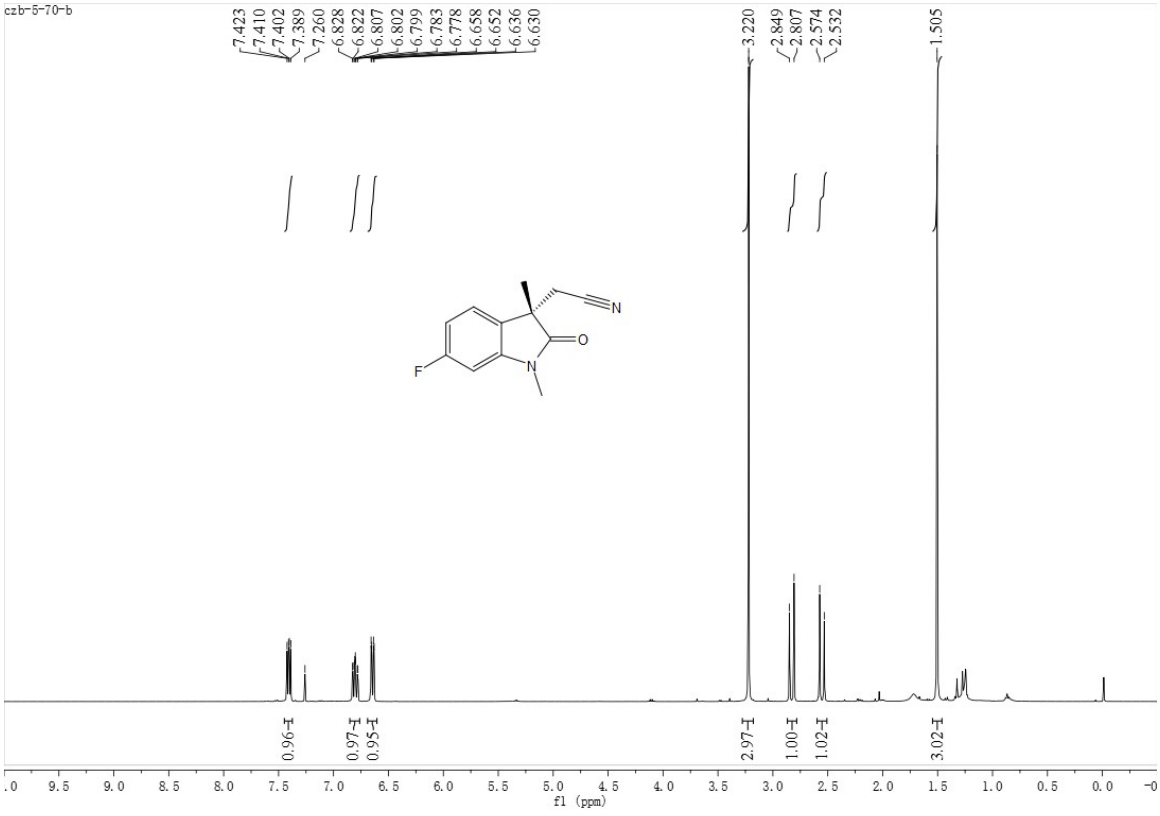

czb-5-52-b
178.02
153.10
142.68
128.23
122.82
120.23
116.90
106.11
77.48
77.16
76.84
44.72
35.27
31.54
26.61
26.49
22.28
f1 (ppm)

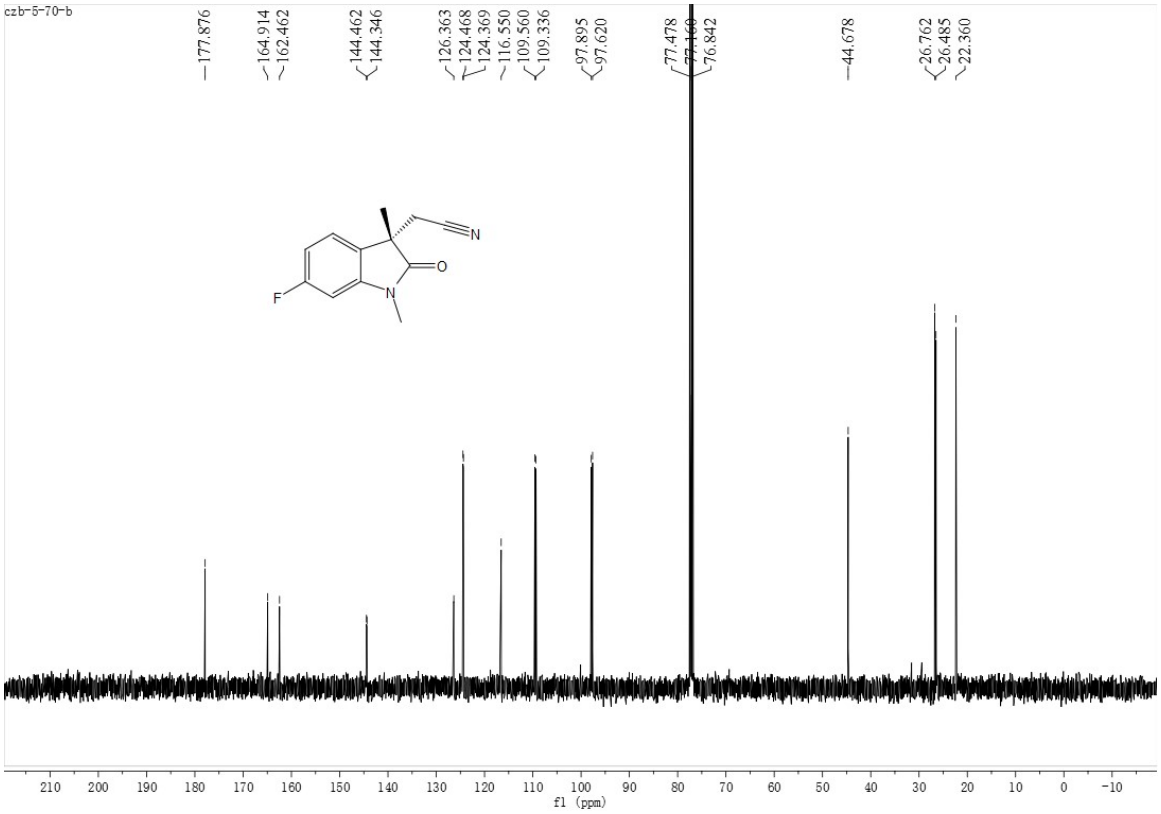
2e


czb-5-114-c
7.371
7.351
7.260
6.624
6.618
6.604
6.598
6.474
6.469
3.832
3.211
2.833
2.791
2.549
2.507
1.491
0.93
0.96
0.95
2.92
2.90
1.00
1.00
2.90
f1 (ppm)

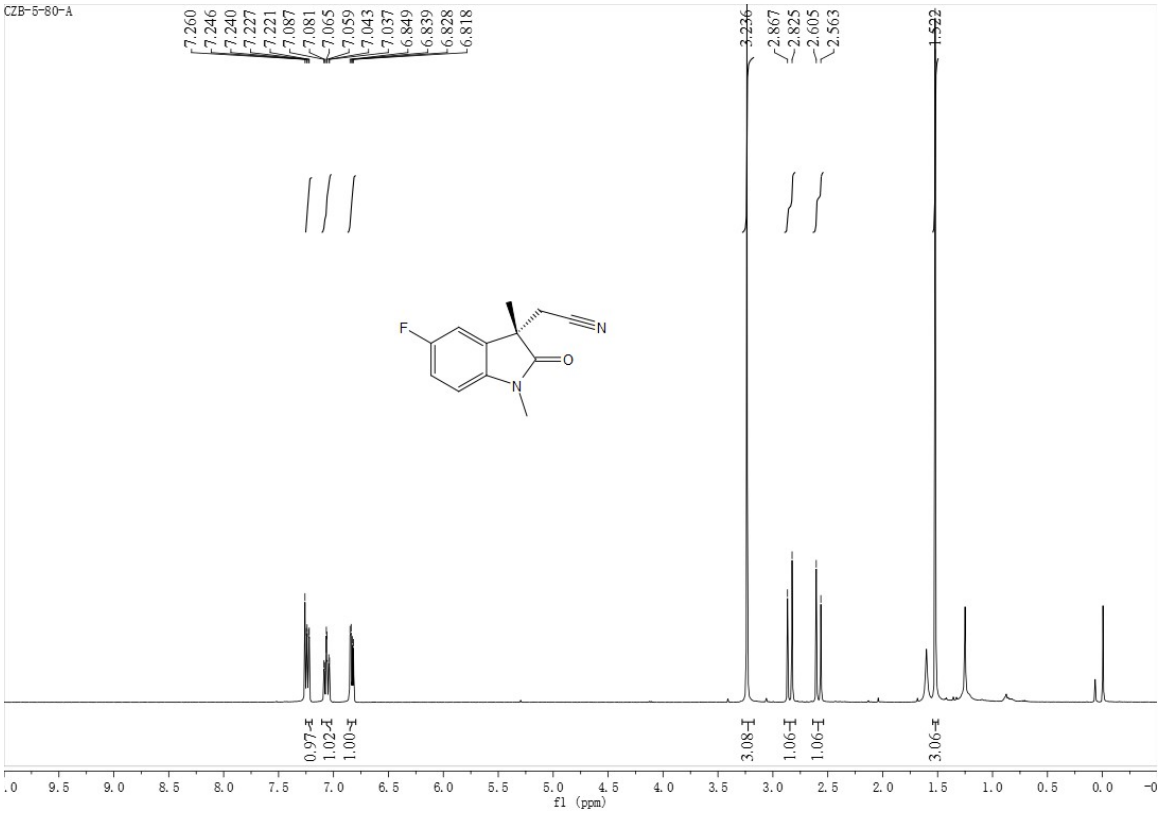

178.191
161.013
144.098
123.927
123.014
116.861
106.938
96.915
77.477
77.160
76.842
55.716
44.567
26.682
26.622
22.456
N
O
O
N
f1 (ppm)

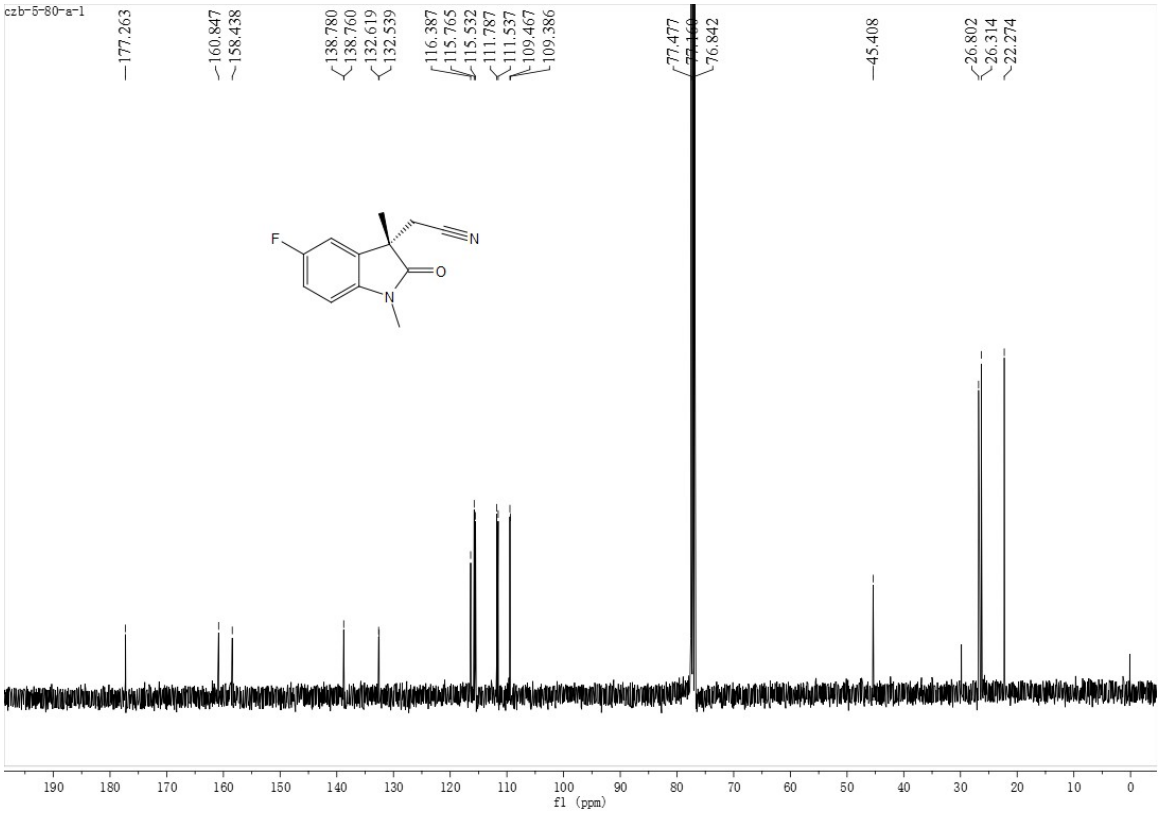
2f


czb-5-70-b
7.423
7.410
7.402
7.389
7.260
6.828
6.822
6.807
6.802
6.799
6.783
6.778
6.658
6.652
6.636
6.630
3.220
2.849
2.807
2.574
2.532
1.505
F
N
O
N
0.96
0.97
0.95
2.97
1.00
1.02
3.02
f1 (ppm)

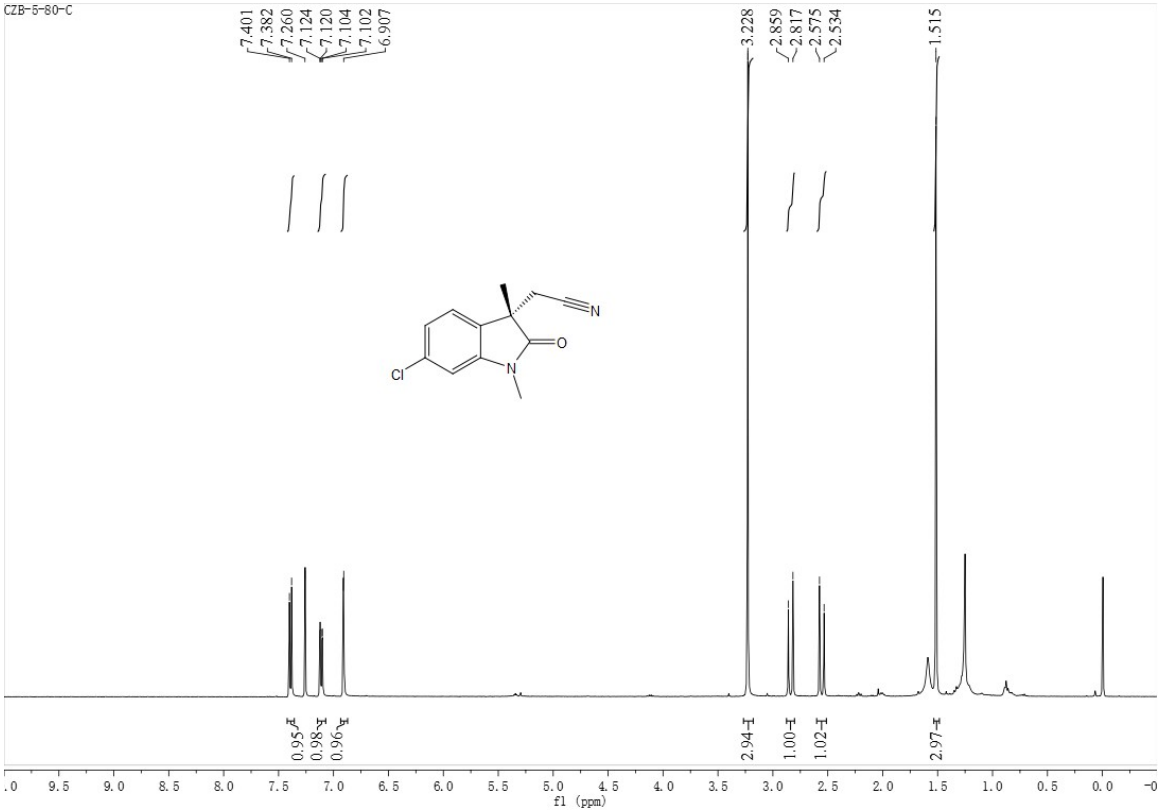

czb-5-70-b
177.876
164.914
162.462
144.462
144.346
126.363
124.468
124.369
116.550
109.560
109.336
97.895
97.620
77.478
76.842
44.678
26.762
26.485
22.360
N
O
F
N
fl (ppm)

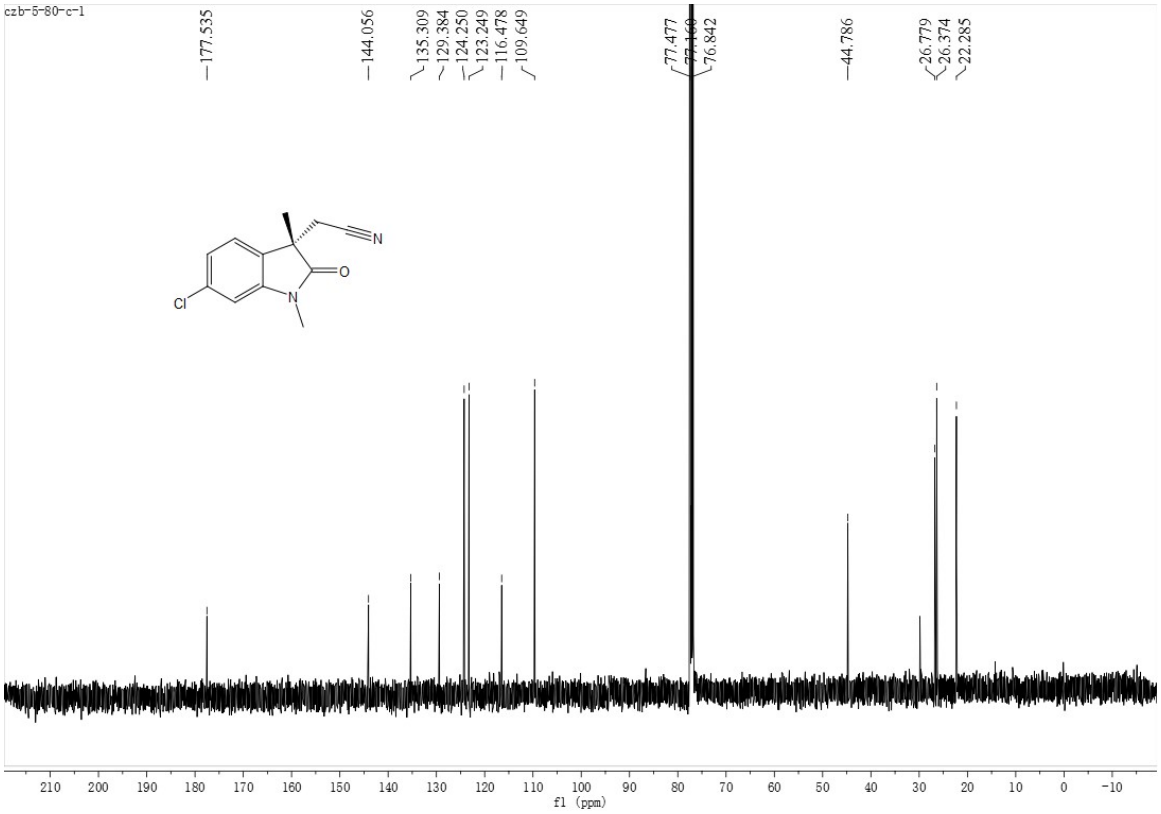
2g


CZB-5-80-A
7.260
7.246
7.240
7.227
7.221
7.087
7.081
7.065
7.059
7.043
7.037
6.849
6.839
6.828
6.818
3.236
2.867
2.825
2.605
2.563
1.522
F
N
O
N
0.97
1.02
1.00
3.08
1.06
1.06
3.06
fl (ppm)

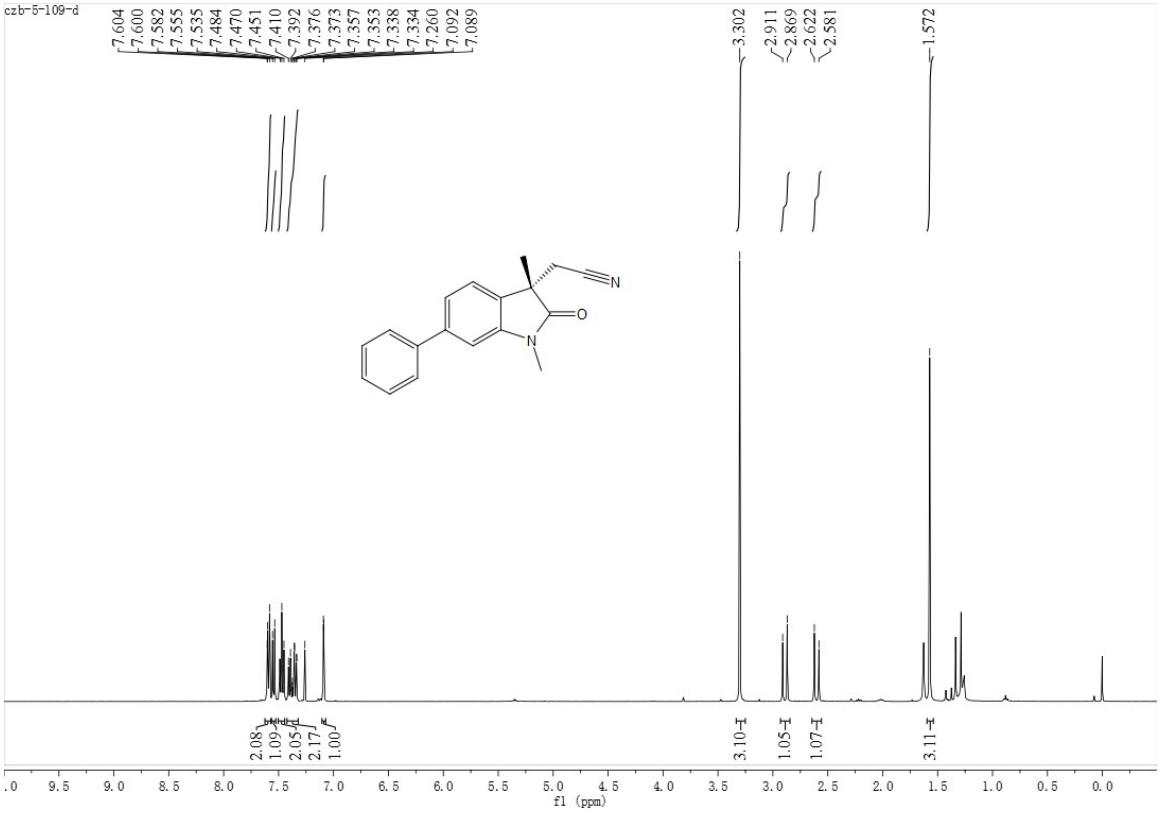

czb-5-80-a-1
177.263
160.847
158.438
138.780
138.760
132.619
132.539
116.387
115.765
115.532
111.787
111.537
109.467
109.386
77.477
76.842
45.408
26.802
26.314
22.274
F
N
O
N
f1 (ppm)

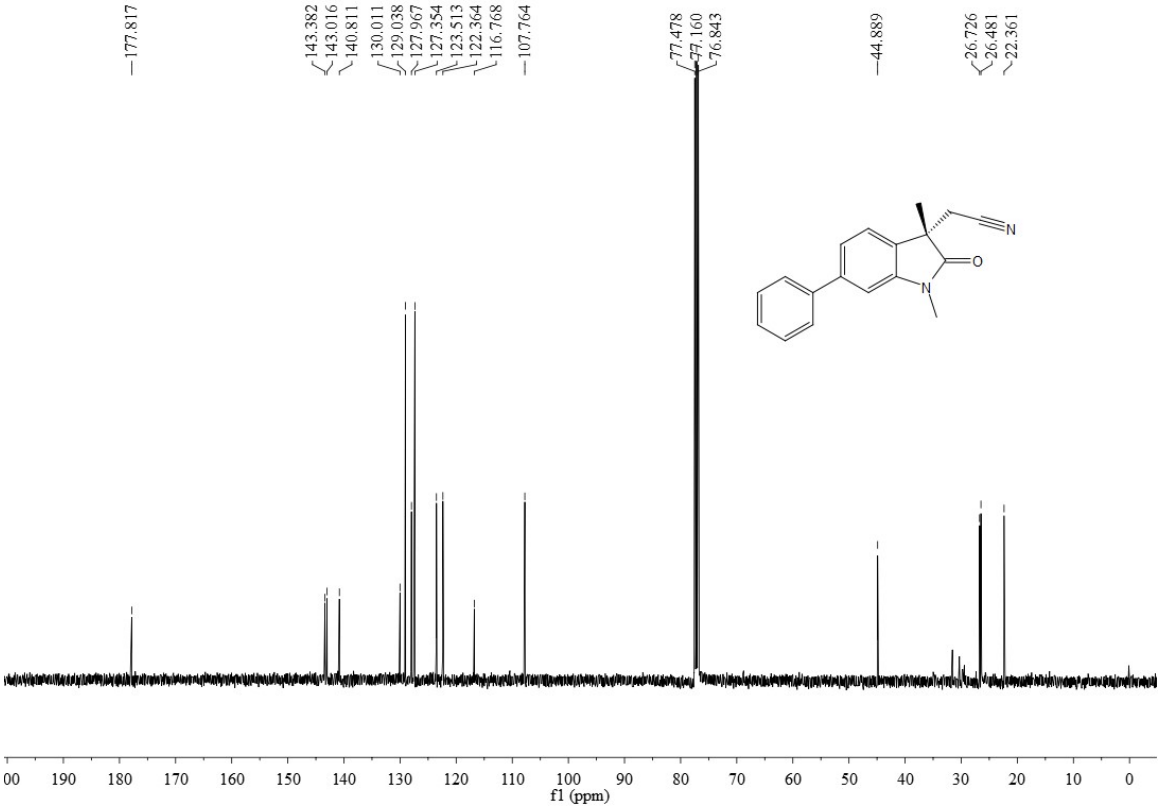
2h


CZB-5-80-C
7.401
7.382
7.260
7.124
7.120
7.104
7.102
6.907
3.228
2.859
2.817
2.575
2.534
1.515
Cl
N
O
N
0.95
0.98
0.96
2.94
1.00
1.02
2.97
f1 (ppm)

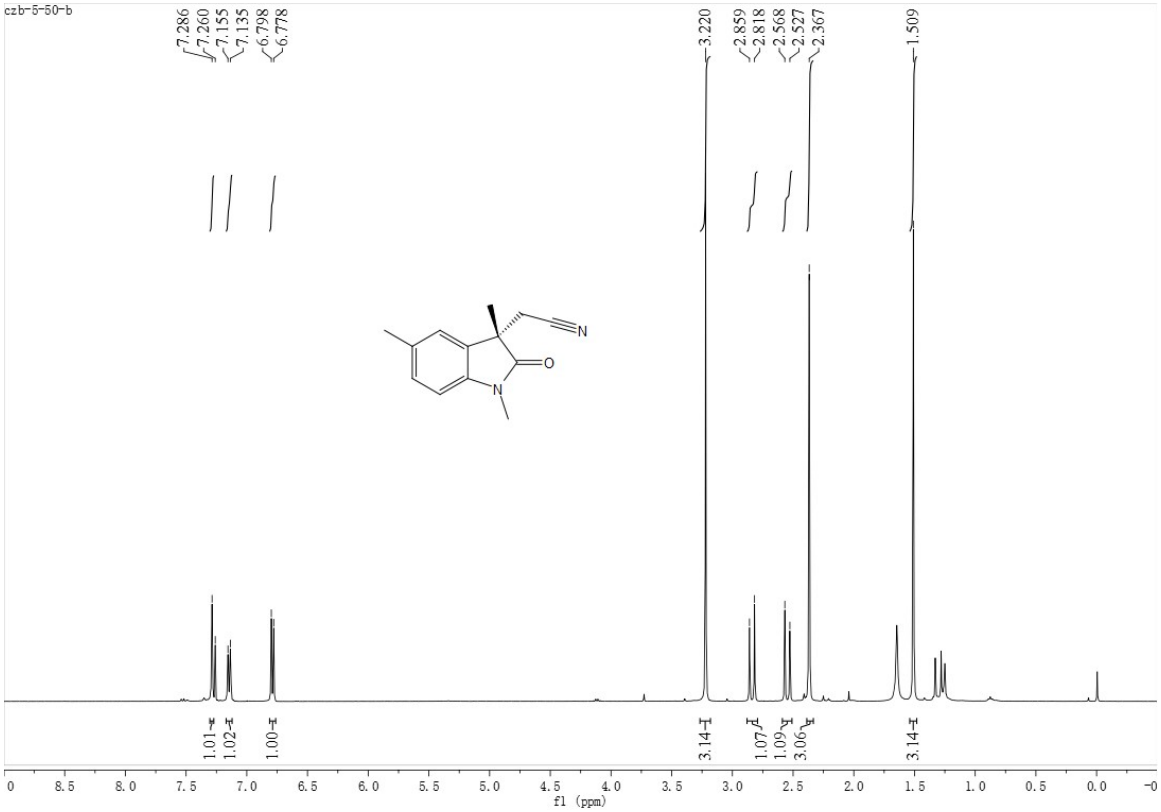

czb-5-80-c-1
177.535
144.056
135.309
129.384
124.250
123.249
116.478
109.649
77.477
76.842
44.786
26.779
26.374
22.285
Cl
N
O
N
f1 (ppm)

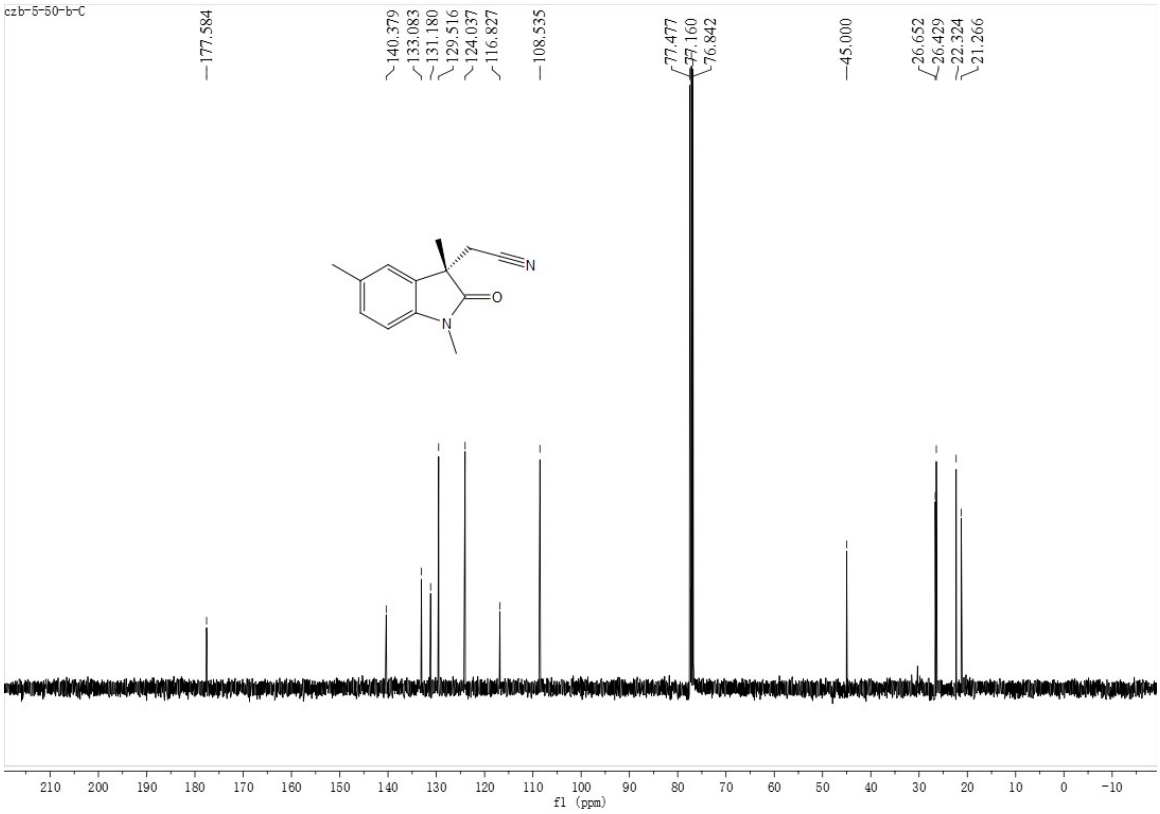
2i


czb-5-109-d
7.604
7.600
7.582
7.555
7.535
7.484
7.470
7.451
7.410
7.392
7.376
7.373
7.357
7.353
7.338
7.334
7.260
7.092
7.089
3.302
2.911
2.869
2.622
2.581
1.572
2.08
1.09
2.05
2.17
1.00
3.10
1.05
1.07
3.11
N
O
N
f1 (ppm)

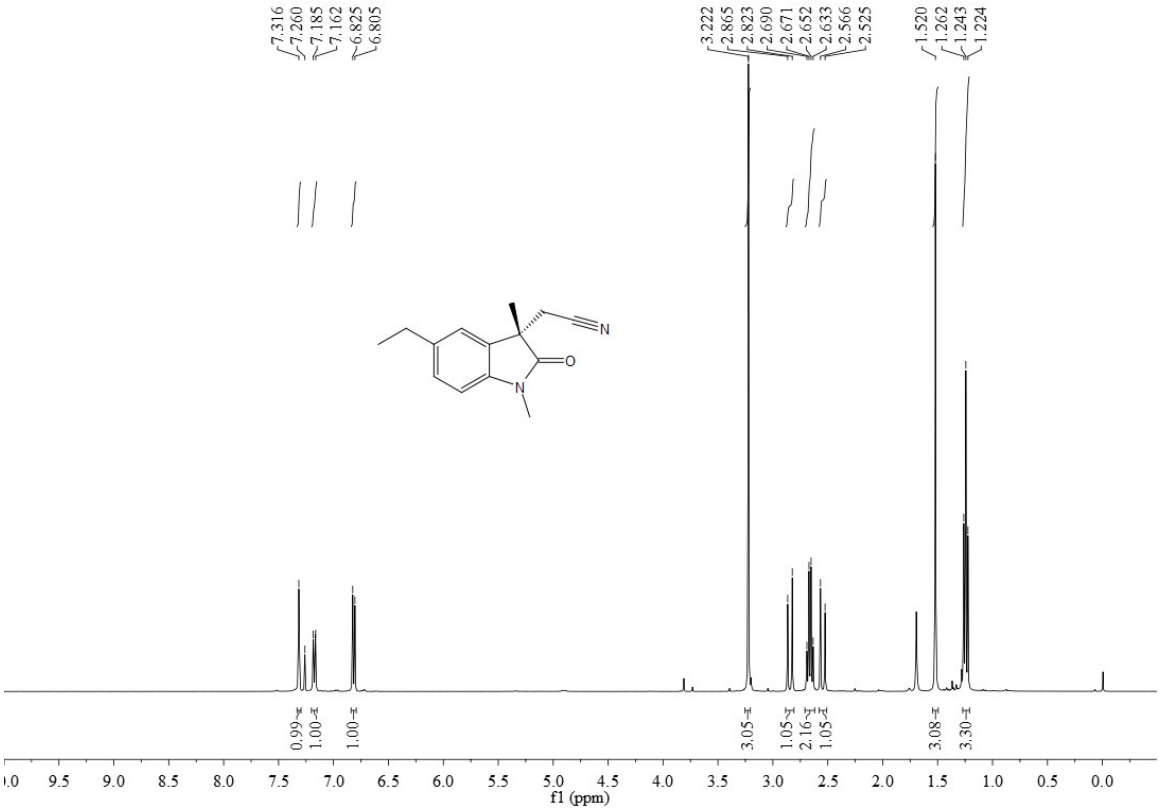

177.817
143.382
143.016
140.811
130.011
129.038
127.967
127.354
123.513
122.364
116.768
107.764
77.478
77.160
76.843
44.889
26.726
26.481
22.361
N
O
N
f1 (ppm)

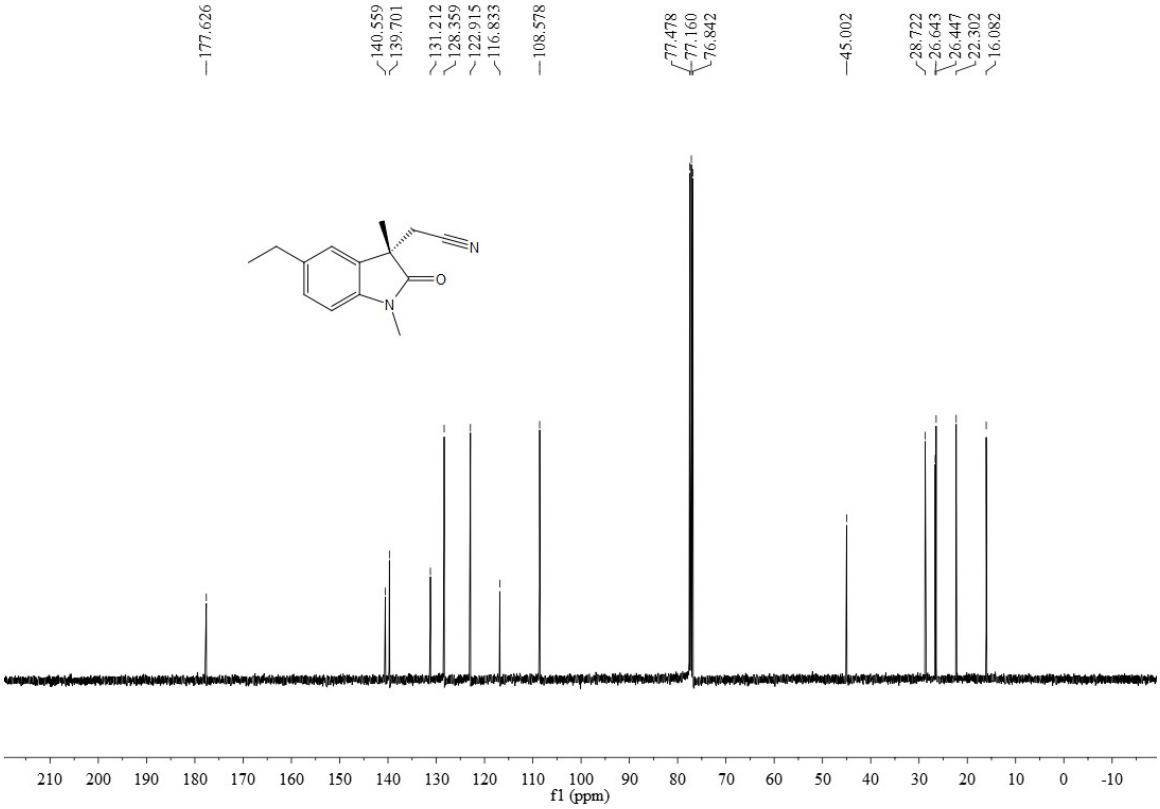
2j


czb-5-50-b
7.286
7.260
7.155
7.135
6.798
6.778
3.220
2.859
2.818
2.568
2.527
2.367
1.509
1.01
1.02
1.00
3.14
1.07
1.09
3.06
3.14
N
O
N
f1 (ppm)

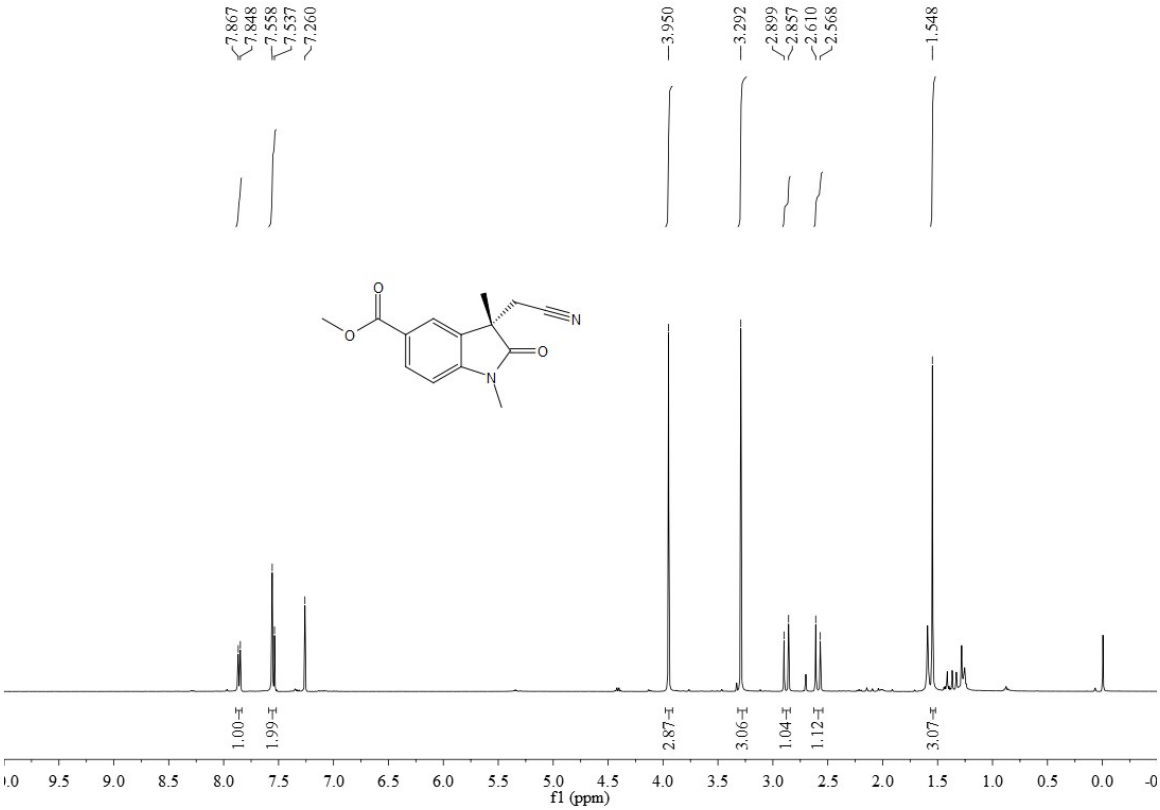

czb-5-50-b-C
177.584
140.379
133.083
131.180
129.516
124.037
116.827
108.535
77.477
77.160
76.842
45.000
26.652
26.429
22.324
21.266
N
O
N
f1 (ppm)

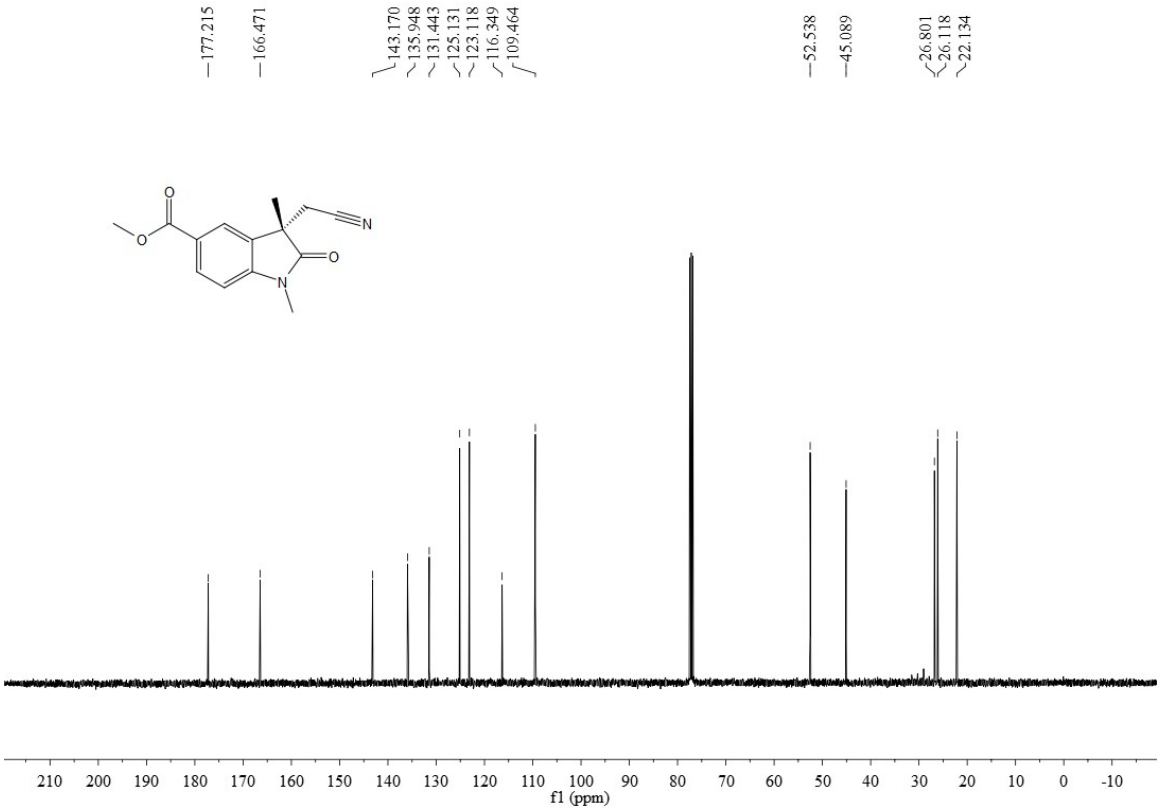
2k


7.316
7.260
7.185
7.162
6.825
6.805
3.222
2.865
2.823
2.690
2.671
2.652
2.633
2.566
2.525
1.520
1.262
1.243
1.224
0.99
1.00
1.00
3.05
1.05
2.16
1.05
3.08
3.30
N
O
N
f1 (ppm)

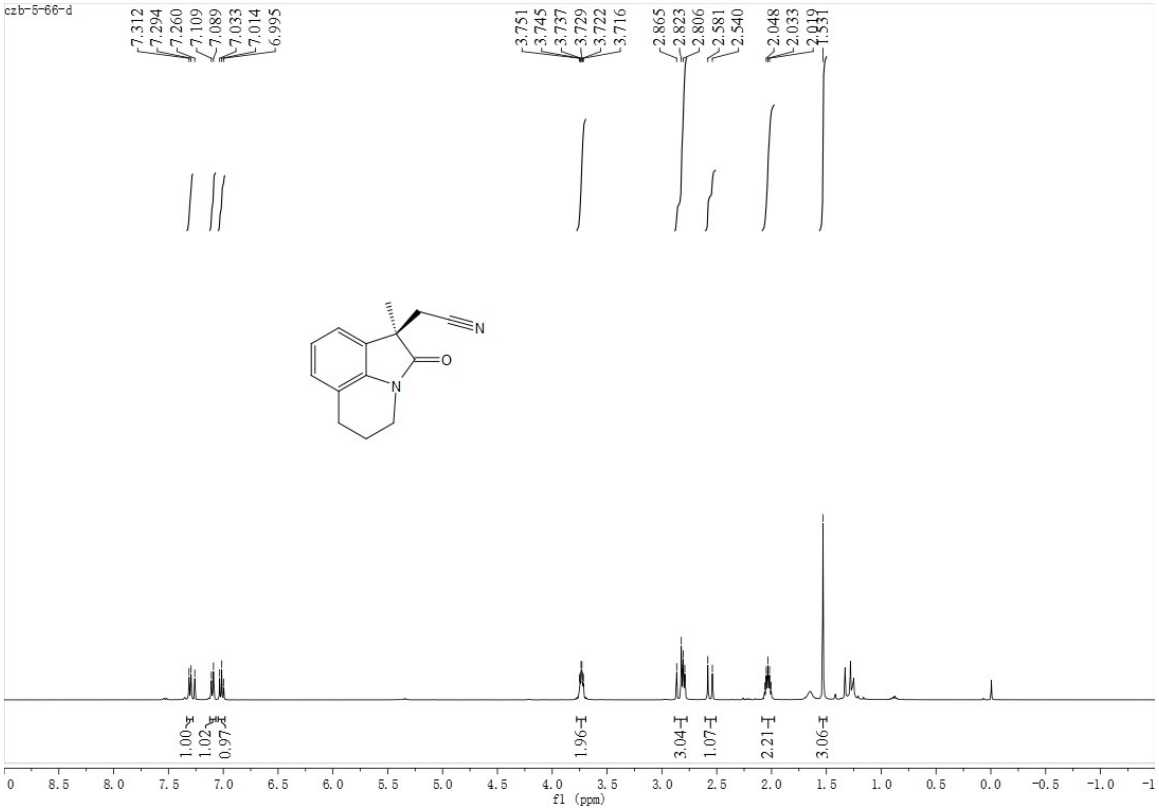

177.626
140.559
139.701
131.212
128.359
122.915
116.833
108.578
77.478
77.160
76.842
45.002
28.722
26.643
26.447
22.302
16.082
N
O
N
f1 (ppm)

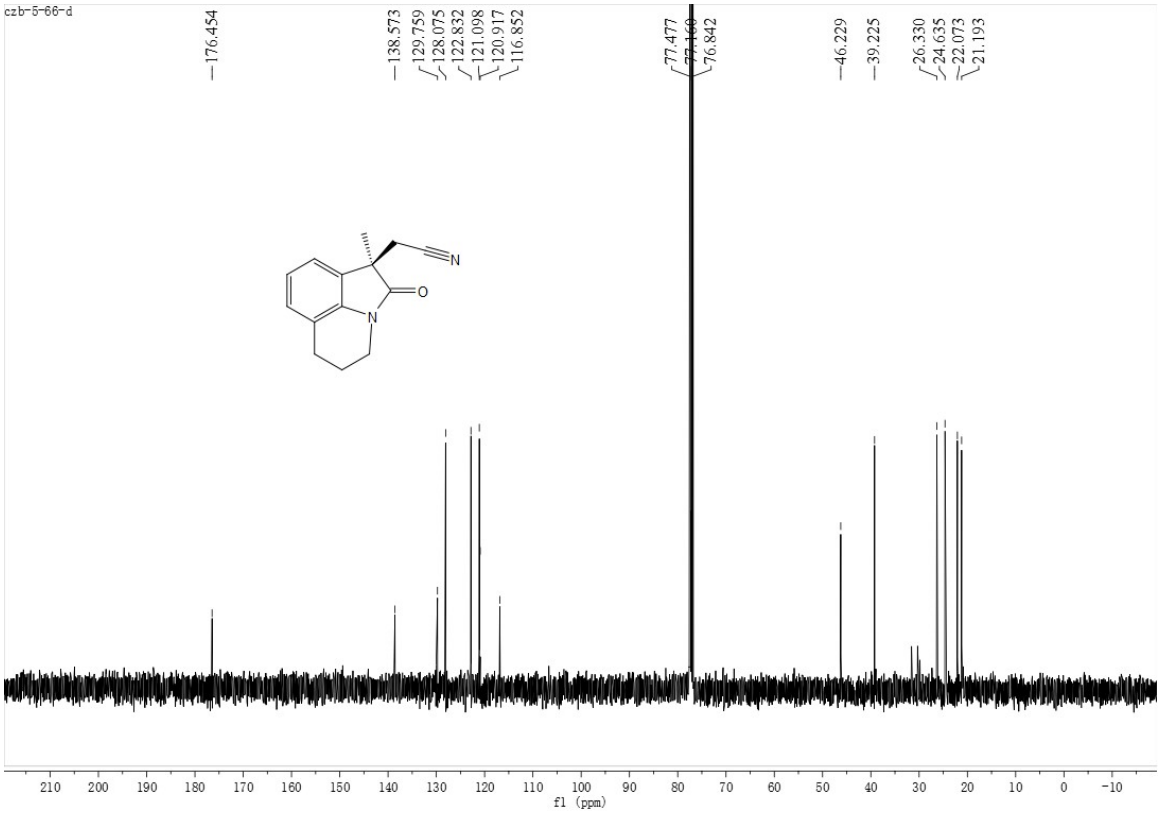
2l


7.867
7.848
7.558
7.537
7.260
3.950
3.292
2.899
2.857
2.610
2.568
1.548
O
O
N
1.00
1.99
2.87
3.06
1.04
1.12
3.07
f1 (ppm)

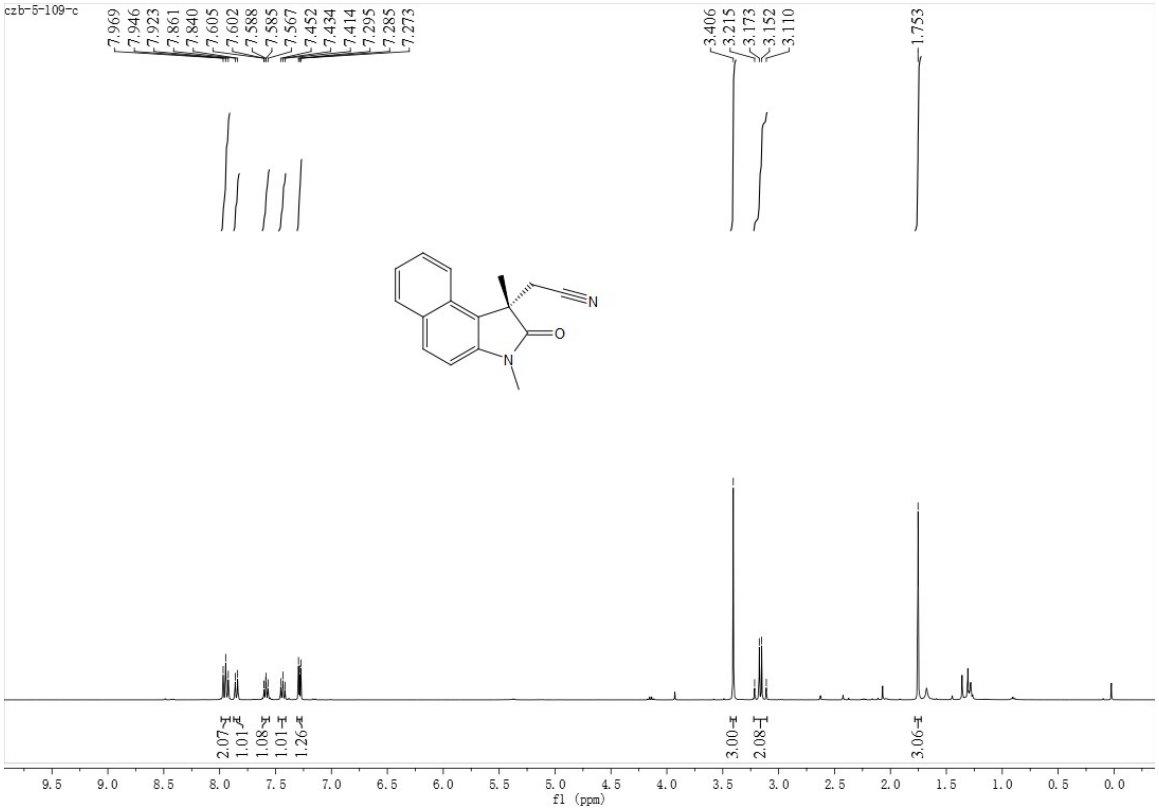

177.215
166.471
143.170
135.948
131.443
125.131
123.118
116.349
109.464
52.538
45.089
26.801
26.118
22.134
O
O
N
O
N
f1 (ppm)

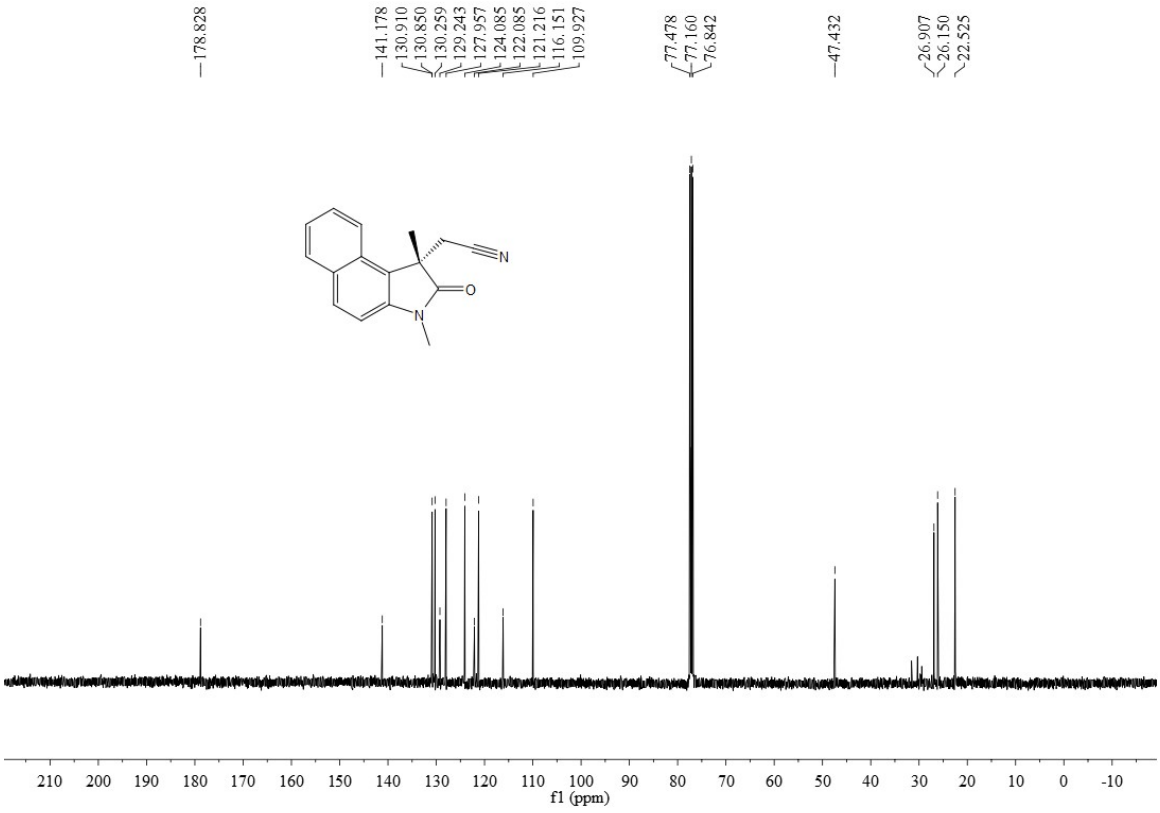
2m


czb-5-66-d
7.312
7.294
7.260
7.109
7.089
7.033
7.014
6.995
3.751
3.745
3.737
3.729
3.722
3.716
2.865
2.823
2.806
2.581
2.540
2.048
2.033
2.019
1.531
N
O
1.00
1.02
0.97
1.96
3.04
1.07
2.21
3.06
f1 (ppm)

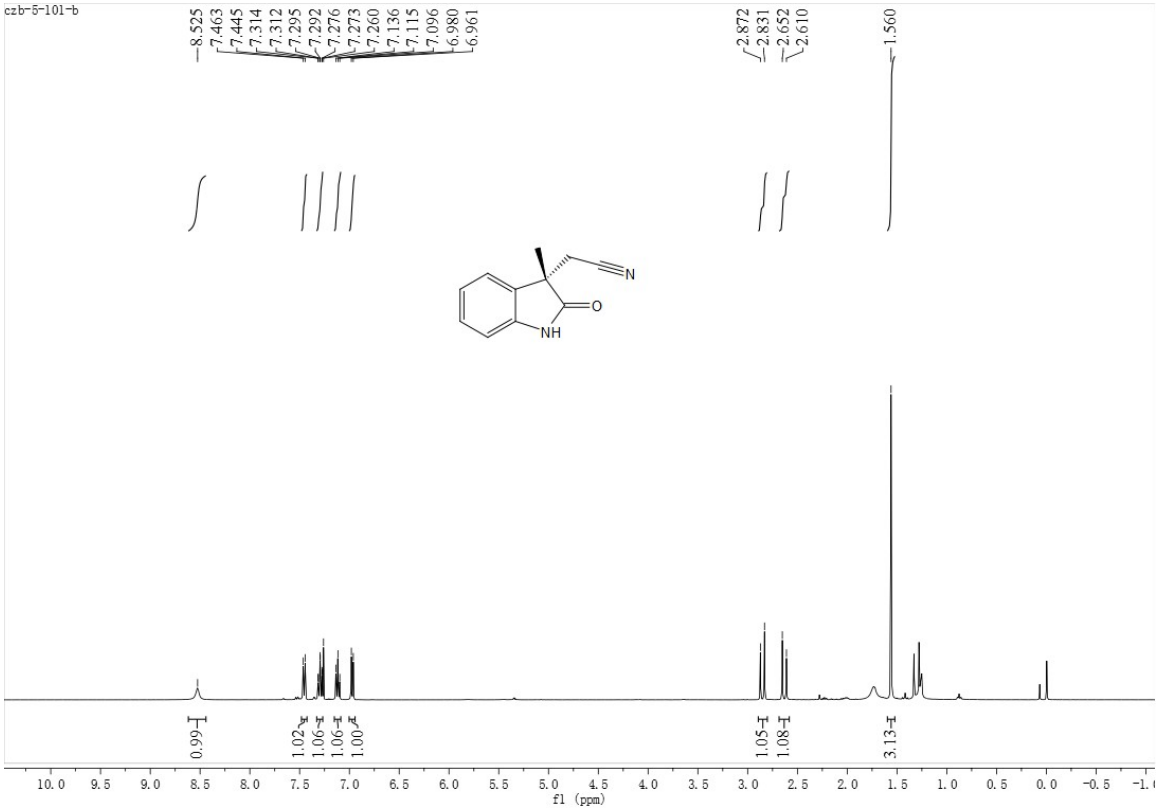

czb-5-66-d
176.454
138.573
129.759
128.075
122.832
121.098
120.917
116.852
77.477
77.160
76.842
46.229
39.225
26.330
24.635
22.073
21.193
N
O
N
f1 (ppm)

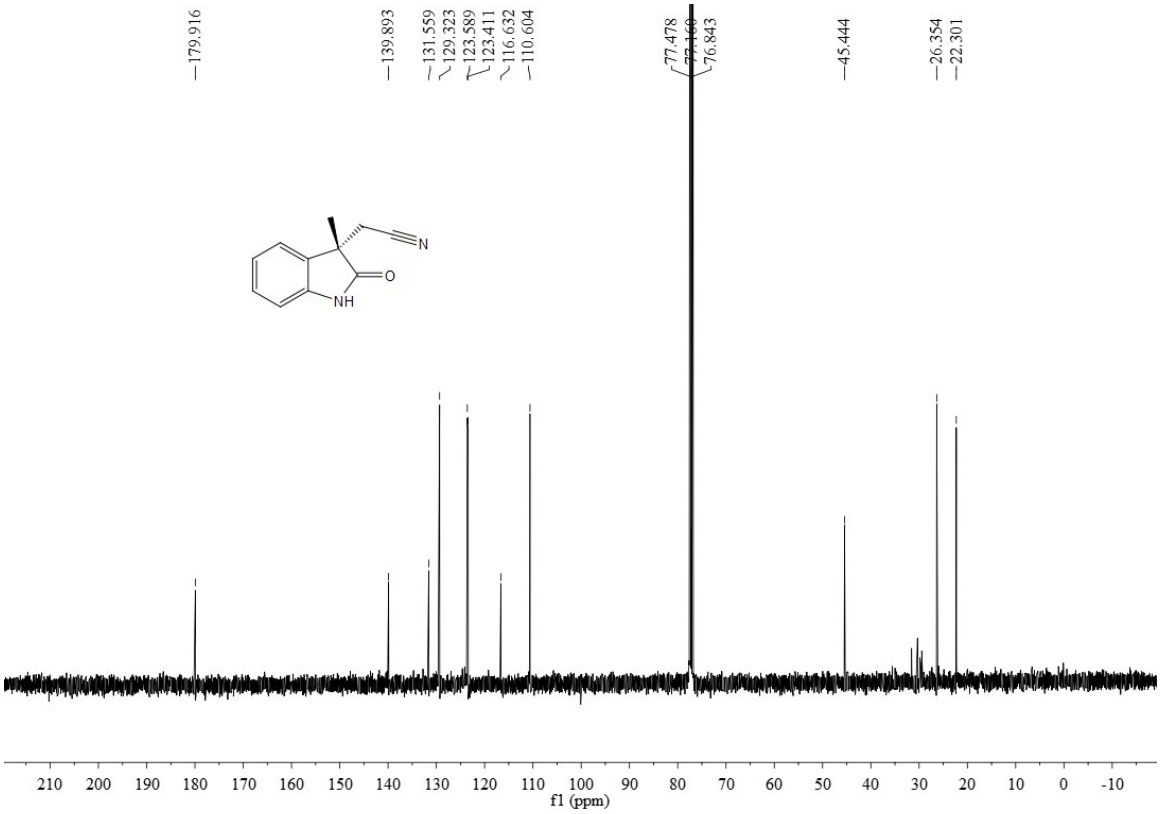
2n


czb-5-109-c
7.969
7.946
7.923
7.861
7.840
7.605
7.602
7.588
7.585
7.567
7.452
7.434
7.414
7.295
7.285
7.273
3.406
3.215
3.173
3.152
3.110
1.753
N
O
N
2.07
1.01
1.08
1.01
1.26
3.00
2.08
3.06
f1 (ppm)

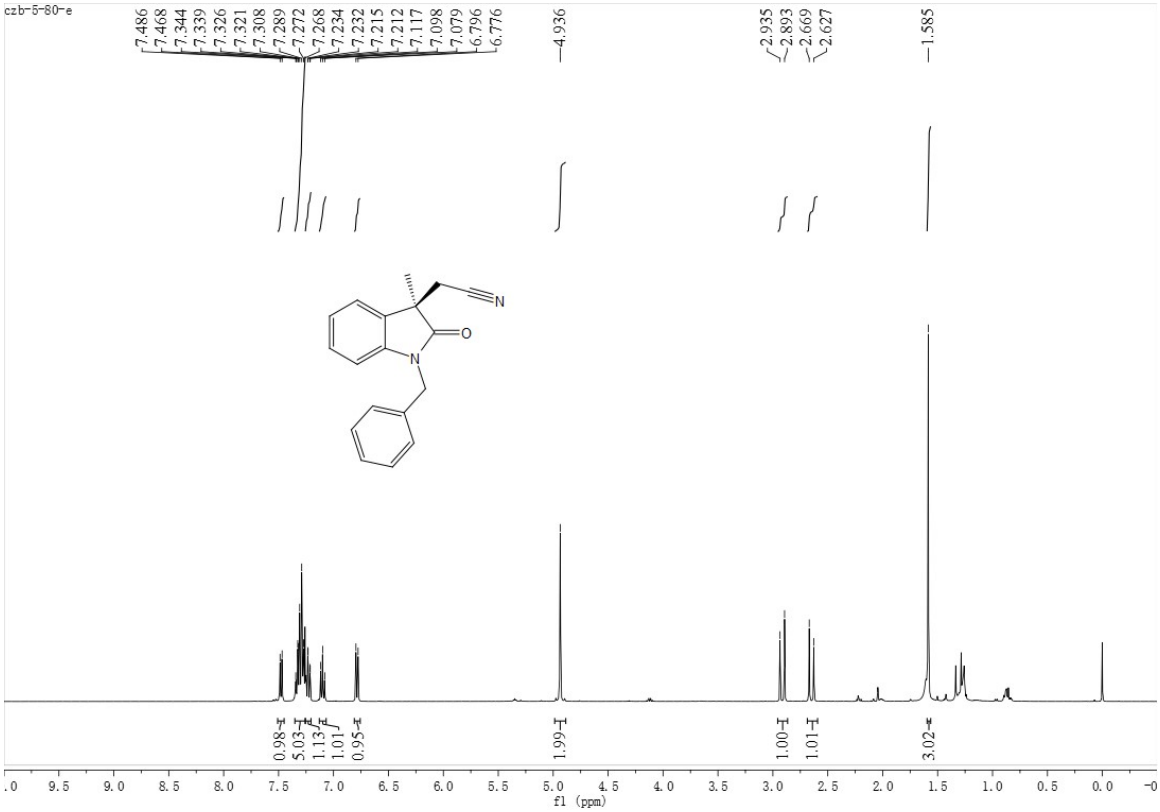

178.828
141.178
130.910
130.850
130.259
129.243
127.957
124.085
122.085
121.216
116.151
109.927
77.478
77.160
76.842
47.432
26.907
26.150
22.525
N
O
N
f1 (ppm)

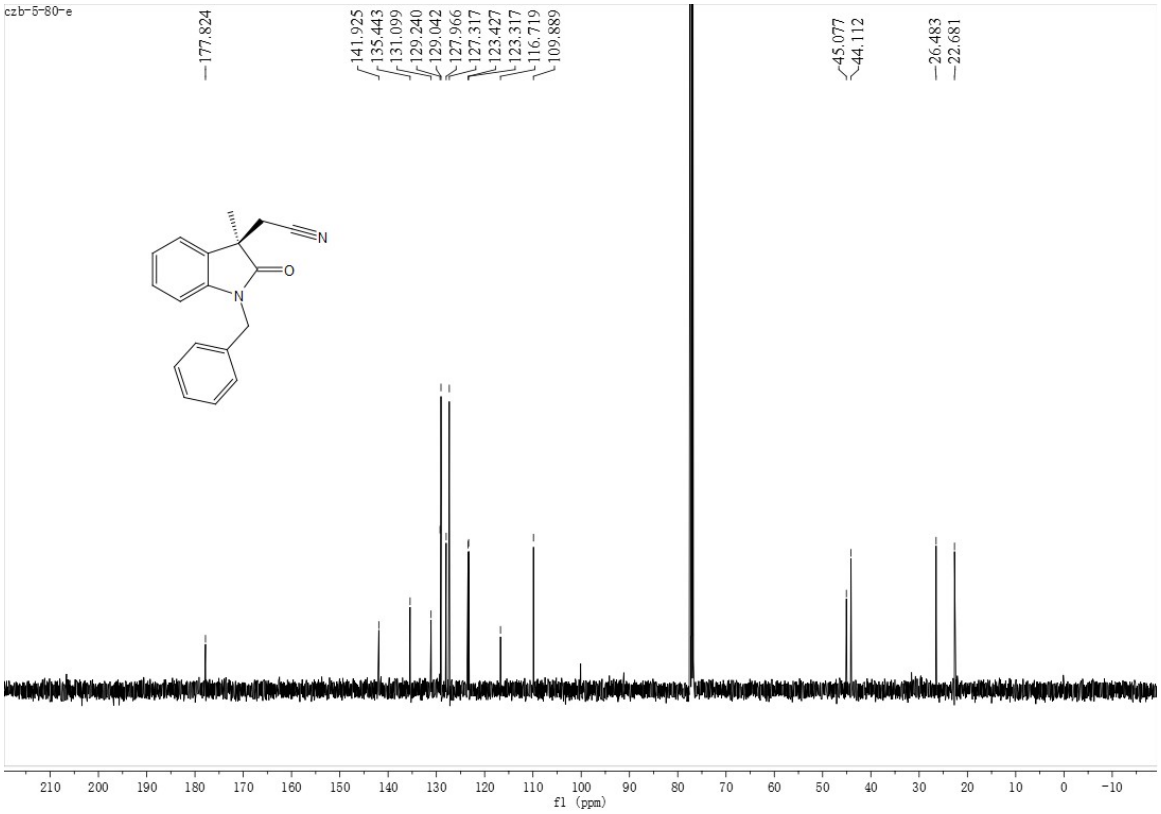
2o


czb-5-101-b
8.525
7.463
7.445
7.314
7.312
7.295
7.292
7.276
7.273
7.260
7.136
7.115
7.096
6.980
6.961
2.872
2.831
2.652
2.610
1.560
N
O
NH
0.99
1.02
1.06
1.06
1.00
1.05
1.08
3.13
f1 (ppm)

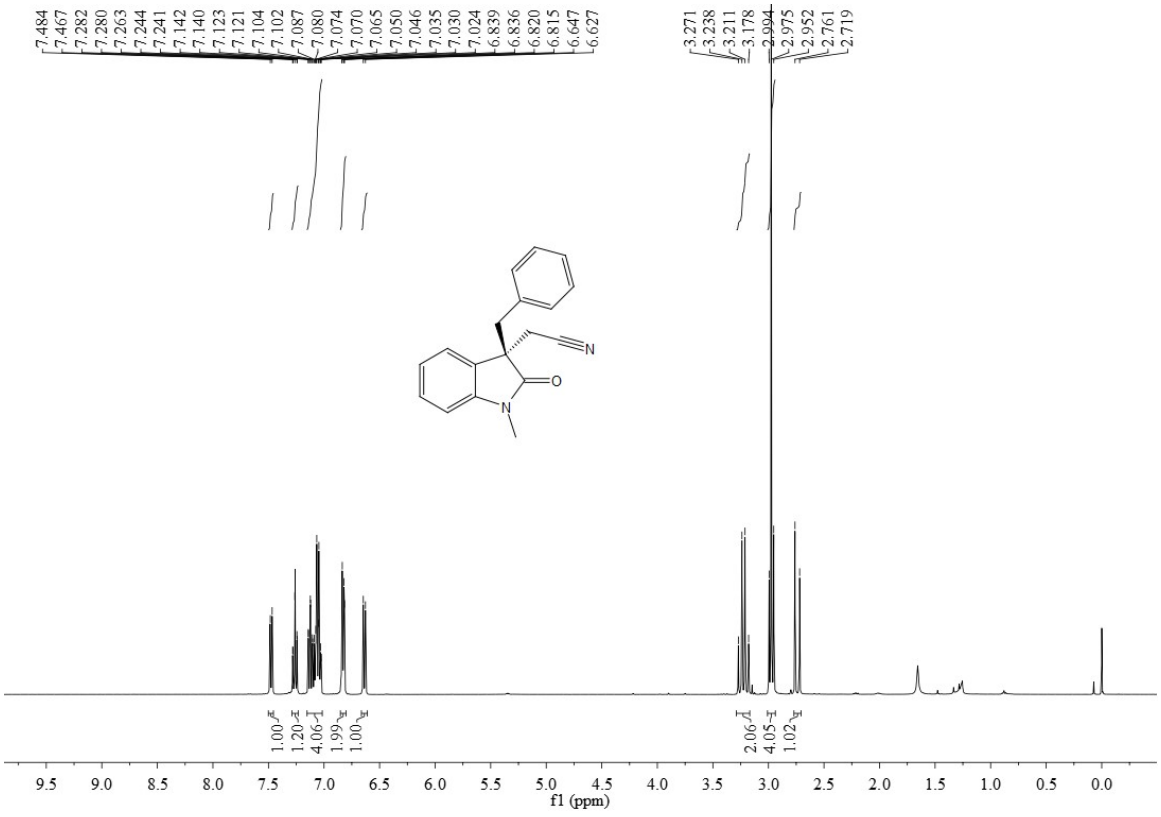

179.916
139.893
131.559
129.323
123.589
123.411
116.632
110.604
77.478
77.160
76.843
45.444
26.354
22.301
N
O
NH
f1 (ppm)

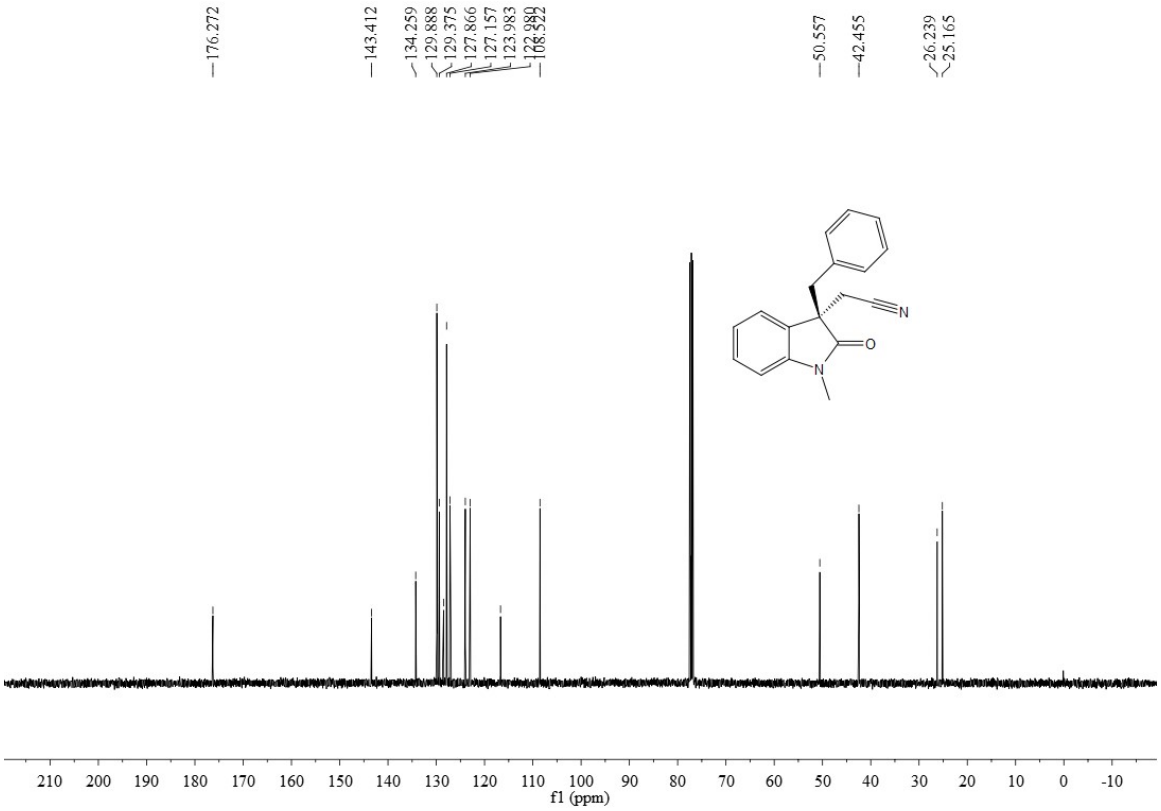
2p


czb-5-80-e
7.486
7.468
7.344
7.339
7.326
7.321
7.308
7.289
7.272
7.268
7.234
7.232
7.215
7.212
7.117
7.098
7.079
6.796
6.776
4.936
2.935
2.893
2.669
2.627
1.585
N
O
N
0.98
5.03
1.13
1.01
0.95
1.99
1.00
1.01
3.02
f1 (ppm)

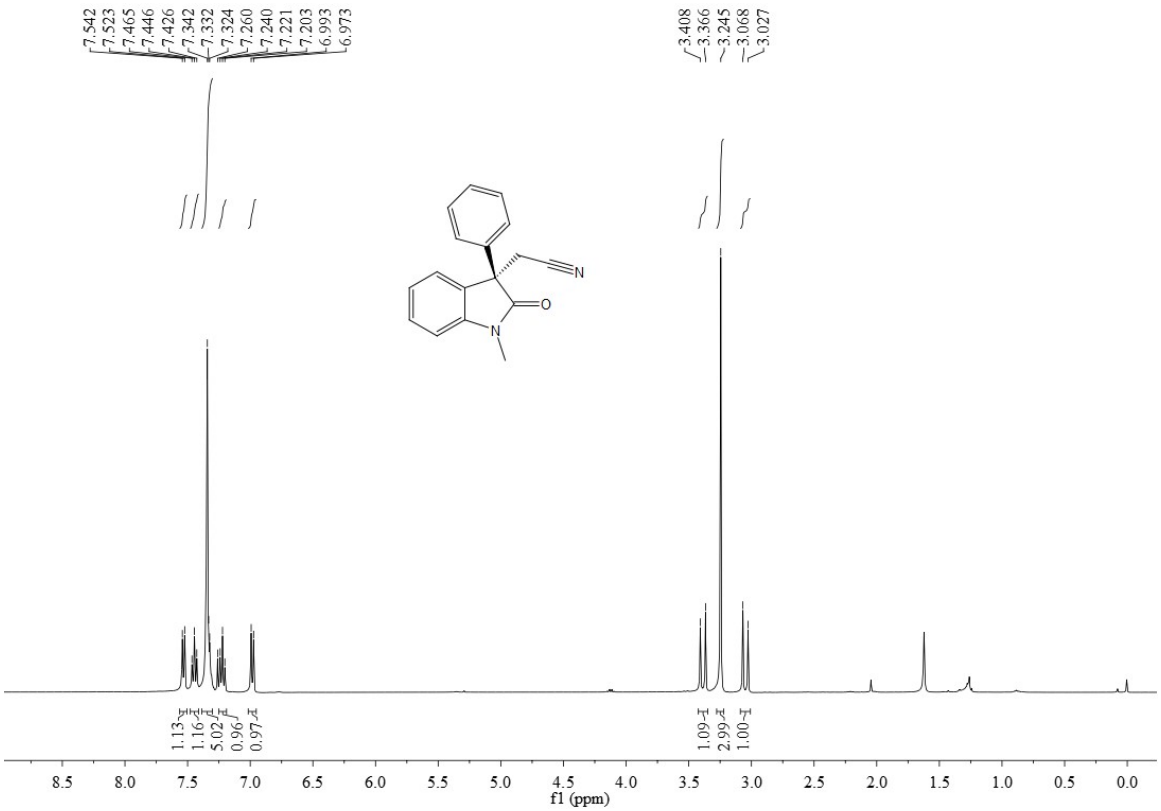

czb-5-80-e
177.824
141.925
135.443
131.099
129.240
129.042
127.966
127.317
123.427
123.317
116.719
109.889
45.077
44.112
26.483
22.681
N
O
N
f1 (ppm)

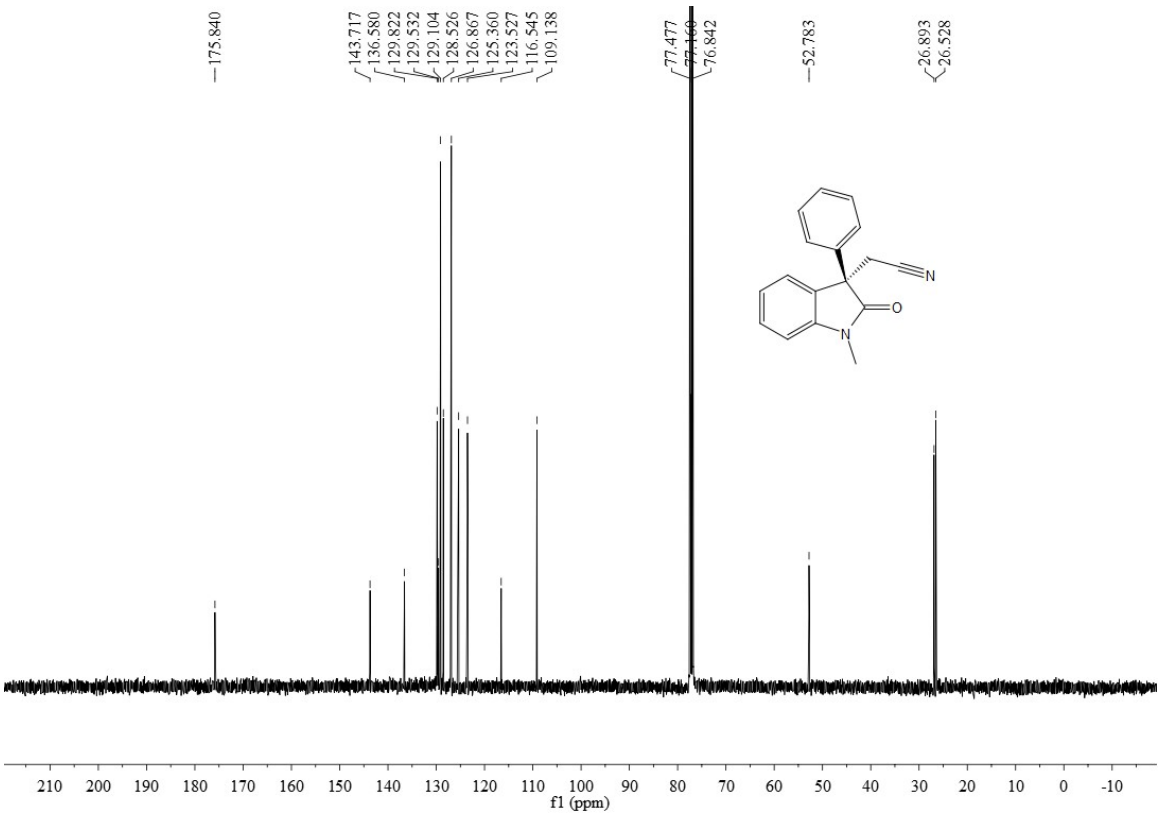
2q


7.484
7.467
7.282
7.280
7.263
7.244
7.241
7.142
7.140
7.123
7.121
7.104
7.102
7.087
7.080
7.074
7.070
7.065
7.050
7.046
7.035
7.030
7.024
6.839
6.836
6.820
6.815
6.647
6.627
3.271
3.238
3.211
3.178
2.994
2.975
2.952
2.761
2.719
1.00
1.20
4.06
1.99
1.00
2.06
4.05
1.02
N
O
N
f1 (ppm)

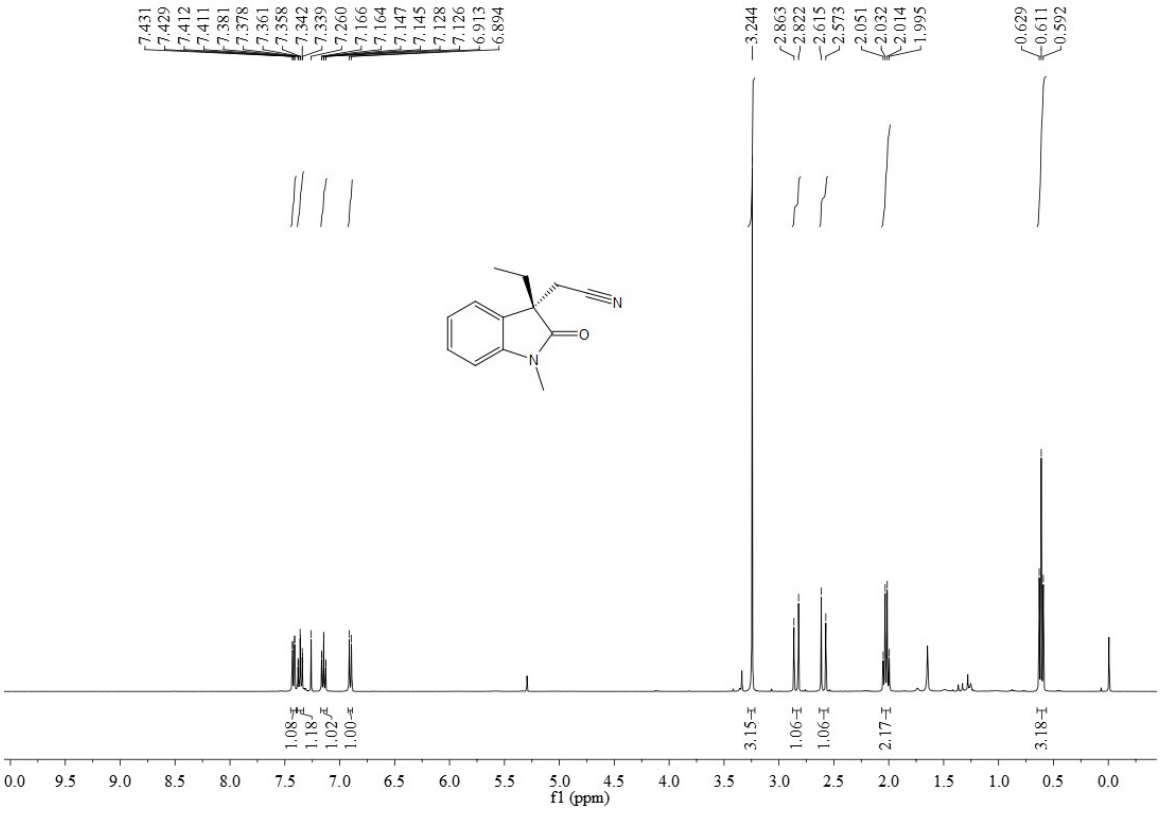

176.272
143.412
134.259
129.888
129.375
127.866
127.157
123.983
122.980
108.522
50.557
42.455
26.239
25.165
N
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

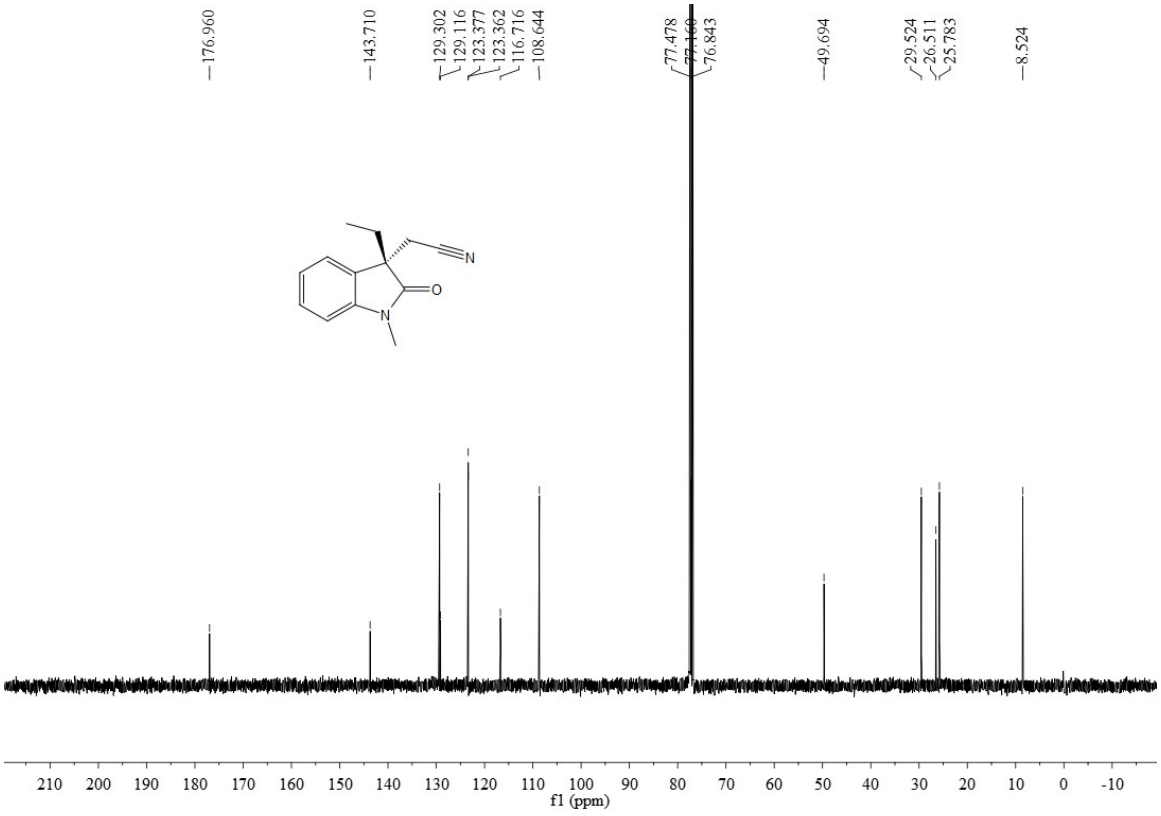
2r


7.542
7.523
7.465
7.446
7.426
7.342
7.332
7.324
7.260
7.240
7.221
7.203
6.993
6.973
3.408
3.366
3.245
3.068
3.027
N
O
N
1.13
1.16
5.02
0.96
0.97
1.09
2.99
1.00
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)

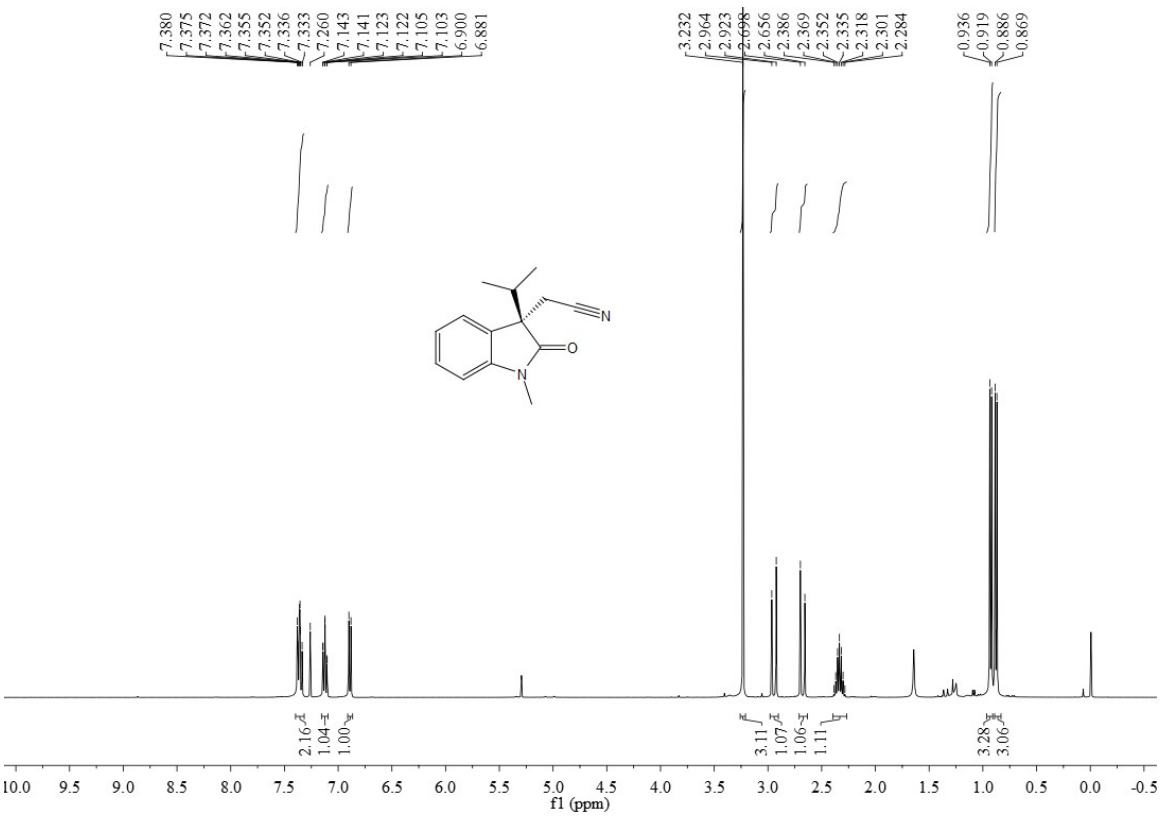

175.840
143.717
136.580
129.822
129.532
129.104
128.526
126.867
125.360
123.527
116.545
109.138
77.477
77.160
76.842
52.783
26.893
26.528
N
O
N
f1 (ppm)

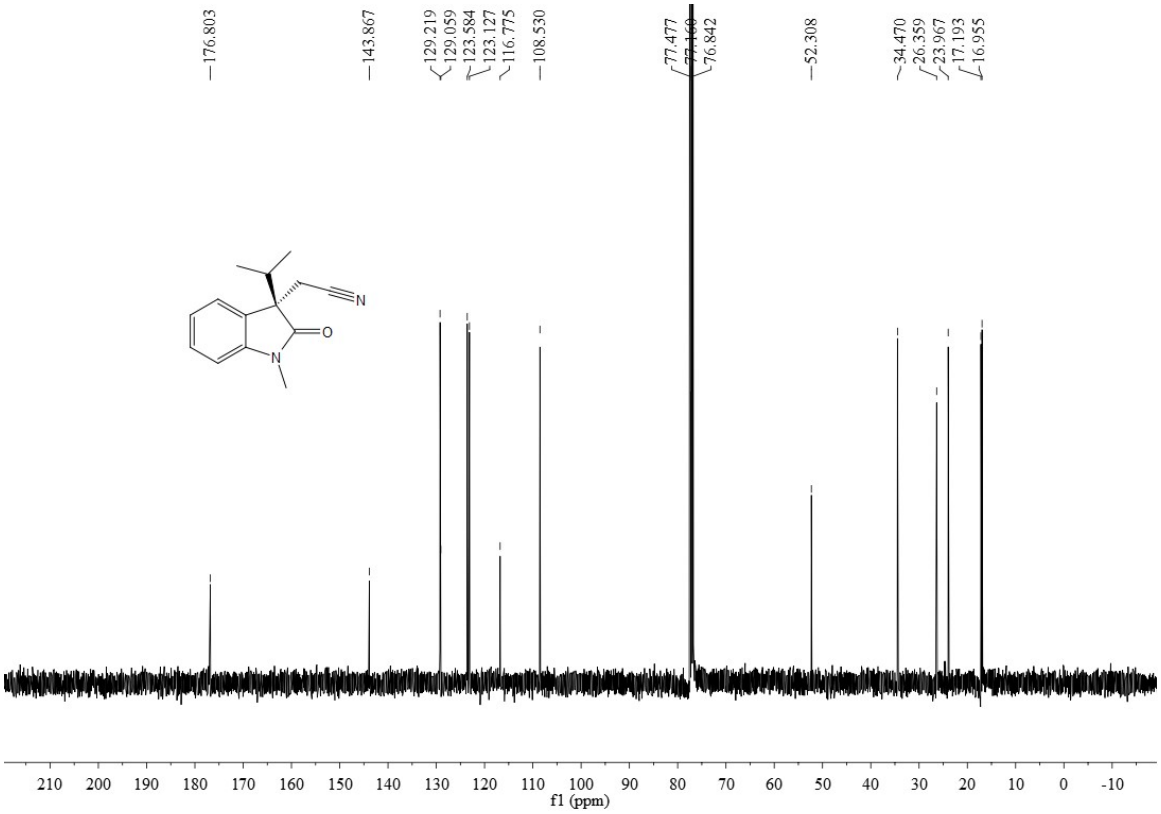
2s


7.431
7.429
7.412
7.411
7.381
7.378
7.361
7.358
7.342
7.339
7.260
7.166
7.164
7.147
7.145
7.128
7.126
6.913
6.894
3.244
2.863
2.822
2.615
2.573
2.051
2.032
2.014
1.995
0.629
0.611
0.592
1.08
1.18
1.02
1.00
3.15
1.06
1.06
2.17
3.18
N
O
N
f1 (ppm)

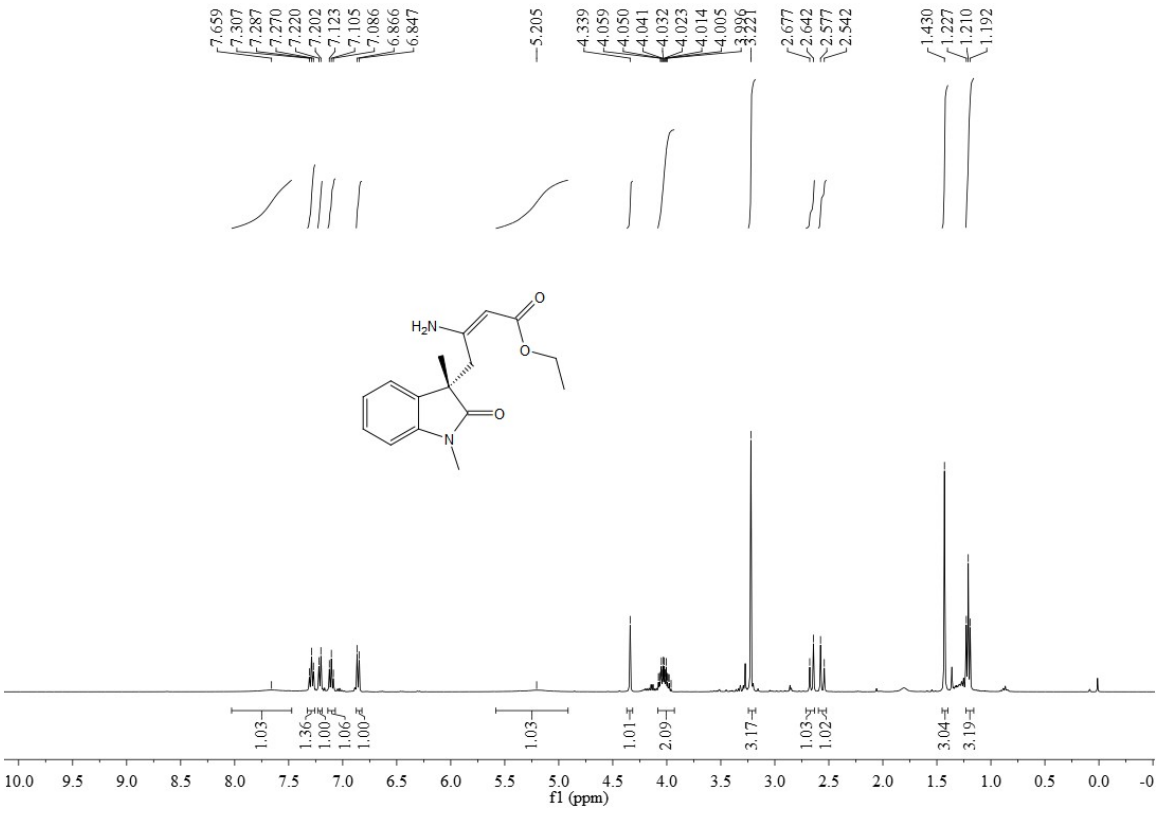

176.960
143.710
129.302
129.116
123.377
123.362
116.716
108.644
77.478
77.160
76.843
49.694
29.524
26.511
25.783
8.524
N
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

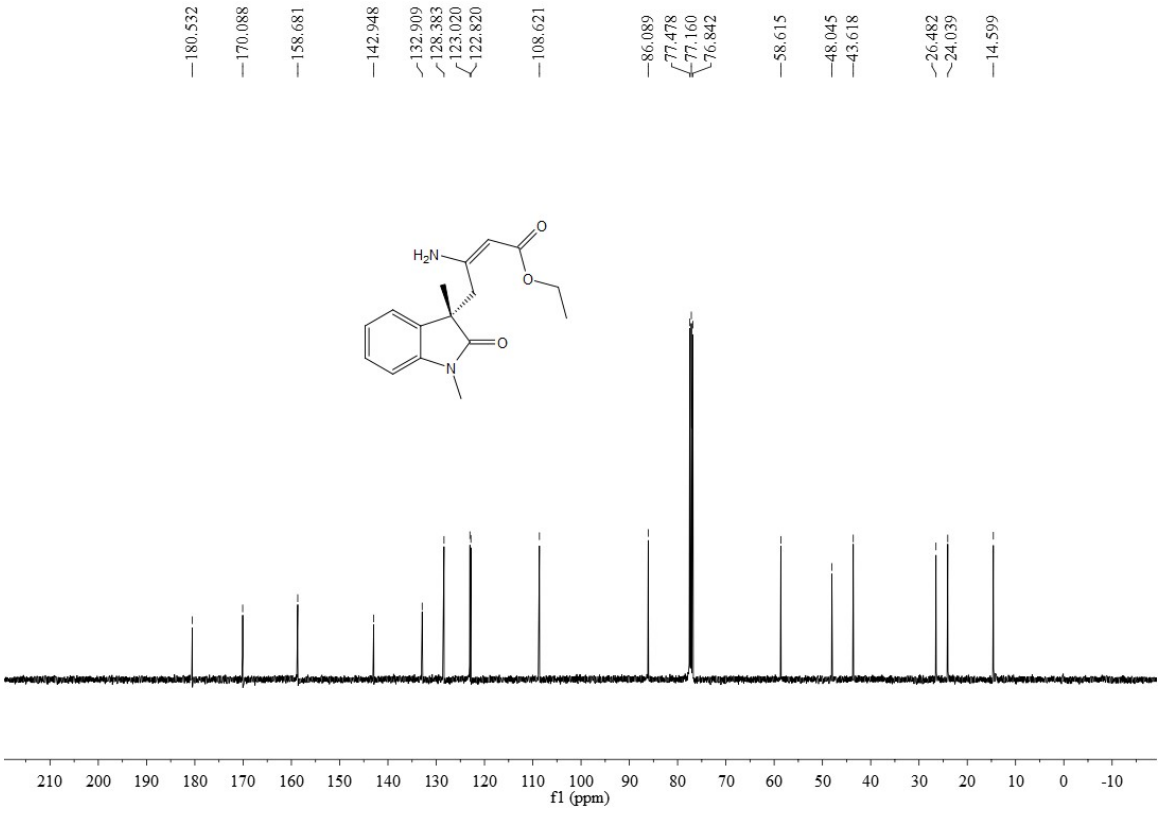
2t


7.380
7.375
7.372
7.362
7.355
7.352
7.336
7.333
7.260
7.143
7.141
7.123
7.122
7.105
7.103
6.900
6.881
3.232
2.964
2.923
2.698
2.656
2.386
2.369
2.352
2.335
2.318
2.301
2.284
0.936
0.919
0.886
0.869
N
O
N
2.16
1.04
1.00
3.11
1.07
1.06
1.11
3.28
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

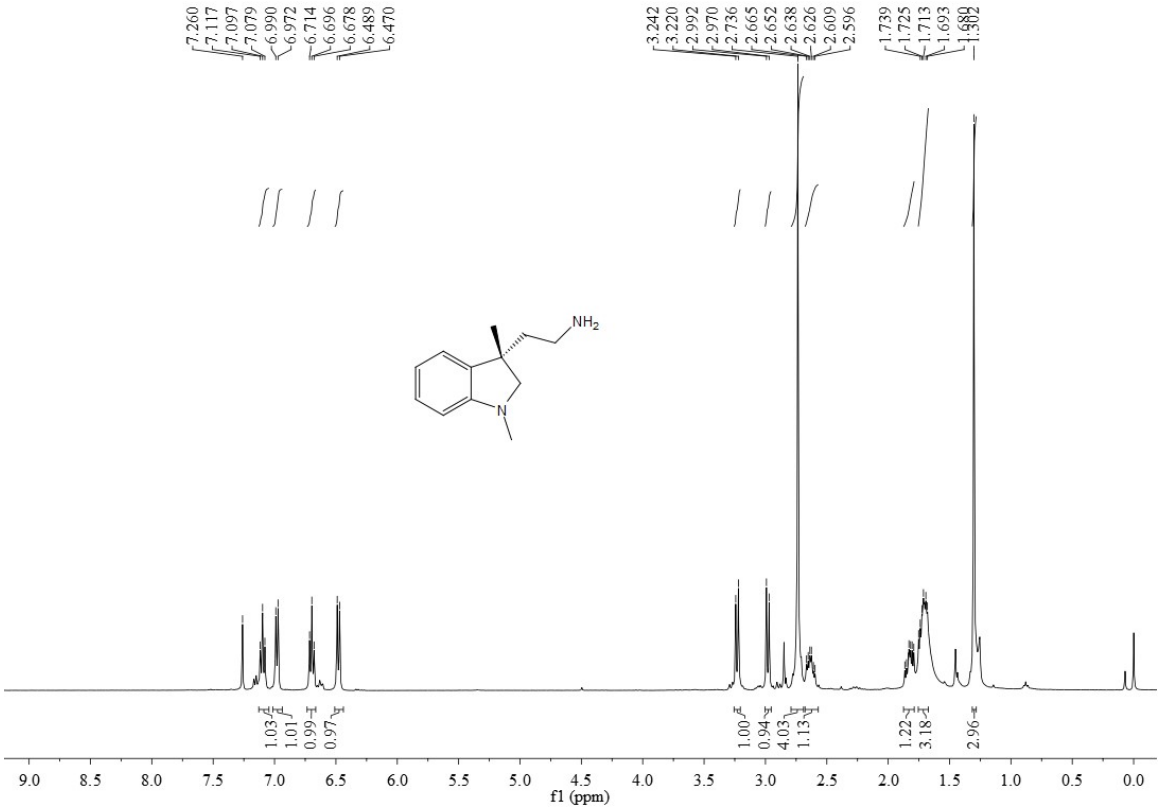

176.803
143.867
129.219
129.059
123.584
123.127
116.775
108.530
77.477
77.160
76.842
52.308
34.470
26.359
23.967
17.193
16.955
N
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

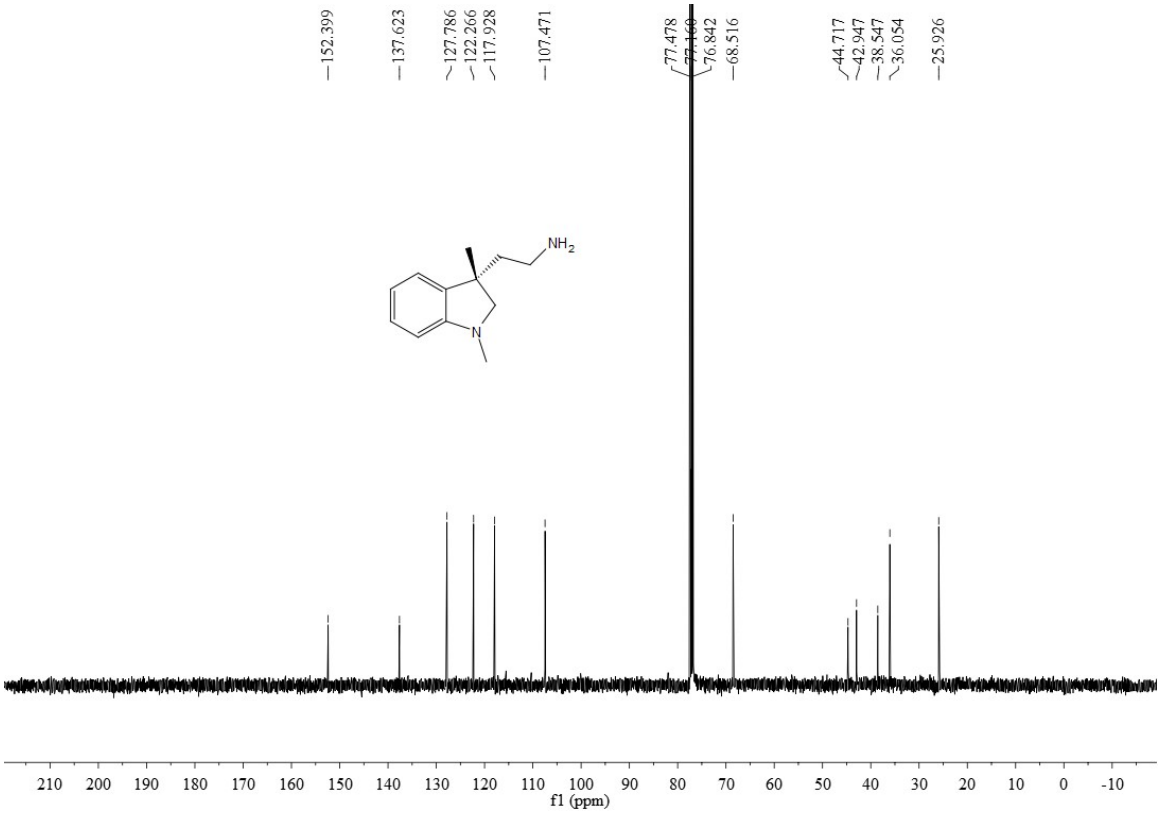
3


7.659
7.307
7.287
7.270
7.220
7.202
7.123
7.105
7.086
6.866
6.847
5.205
4.339
4.059
4.050
4.041
4.032
4.023
4.014
4.005
3.896
3.221
2.677
2.642
2.577
2.542
1.430
1.227
1.210
1.192
H2N
O
O
O
N
1.03
1.36
1.00
1.06
1.00
1.03
1.01
2.09
3.17
1.03
1.02
3.04
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

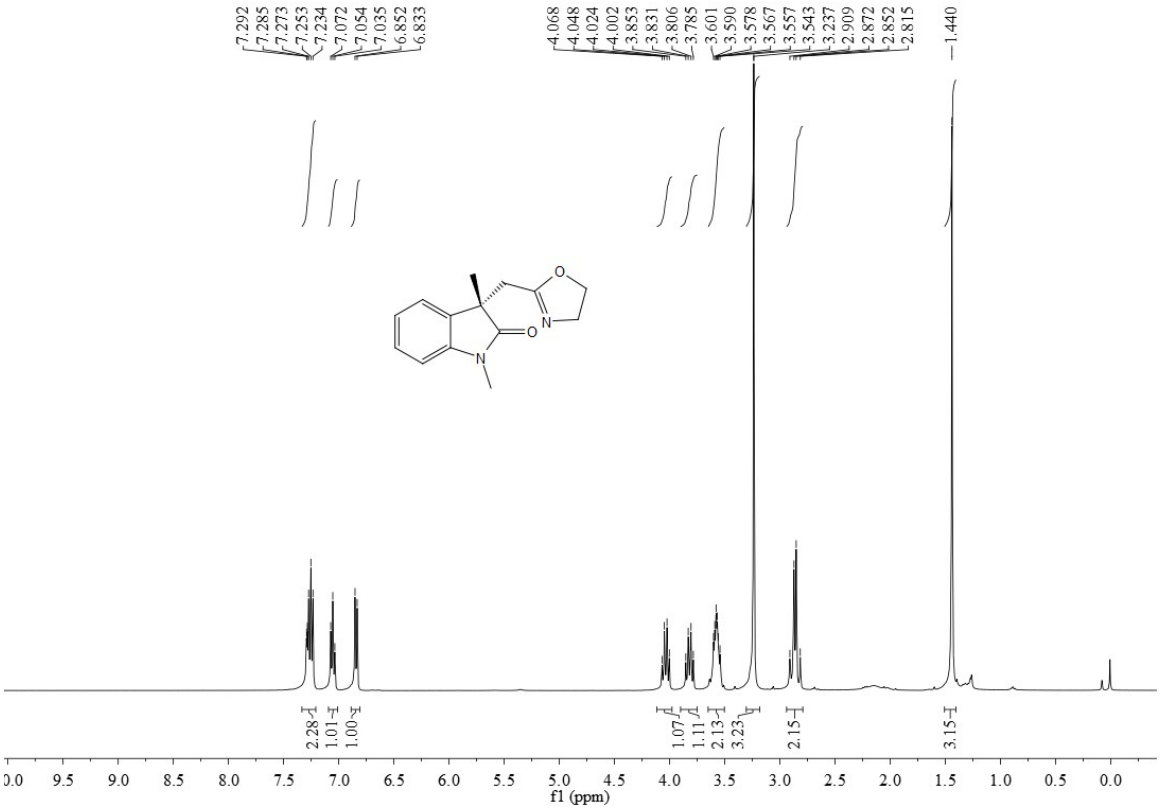

180.532
170.088
158.681
142.948
132.909
128.383
123.020
122.820
108.621
86.089
77.478
77.160
76.842
58.615
48.045
43.618
26.482
24.039
14.599
H2N
O
O
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

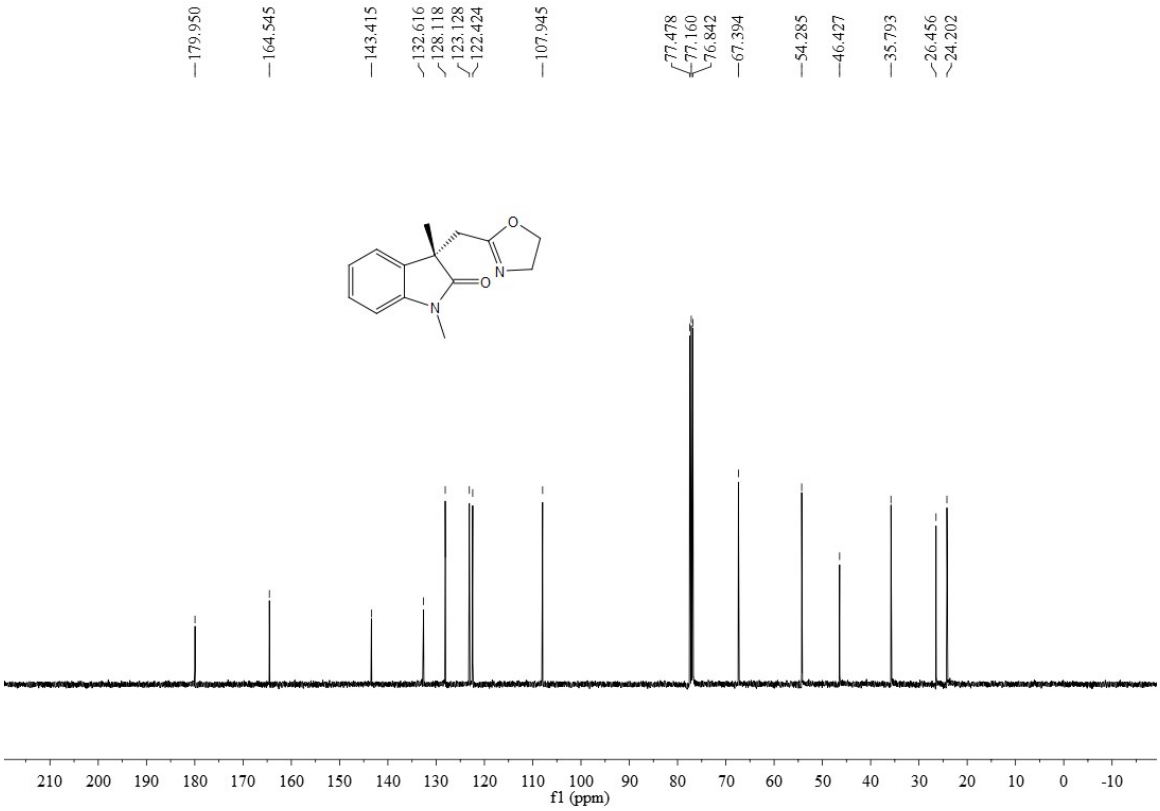
4


7.260
7.117
7.097
7.079
6.990
6.972
6.714
6.696
6.678
6.489
6.470
3.242
3.220
2.992
2.970
2.736
2.665
2.652
2.638
2.626
2.609
2.596
1.739
1.725
1.713
1.693
1.680
1.302
NH2
N
1.03
1.01
0.99
0.97
1.00
0.94
4.03
1.13
1.22
3.18
2.96
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)

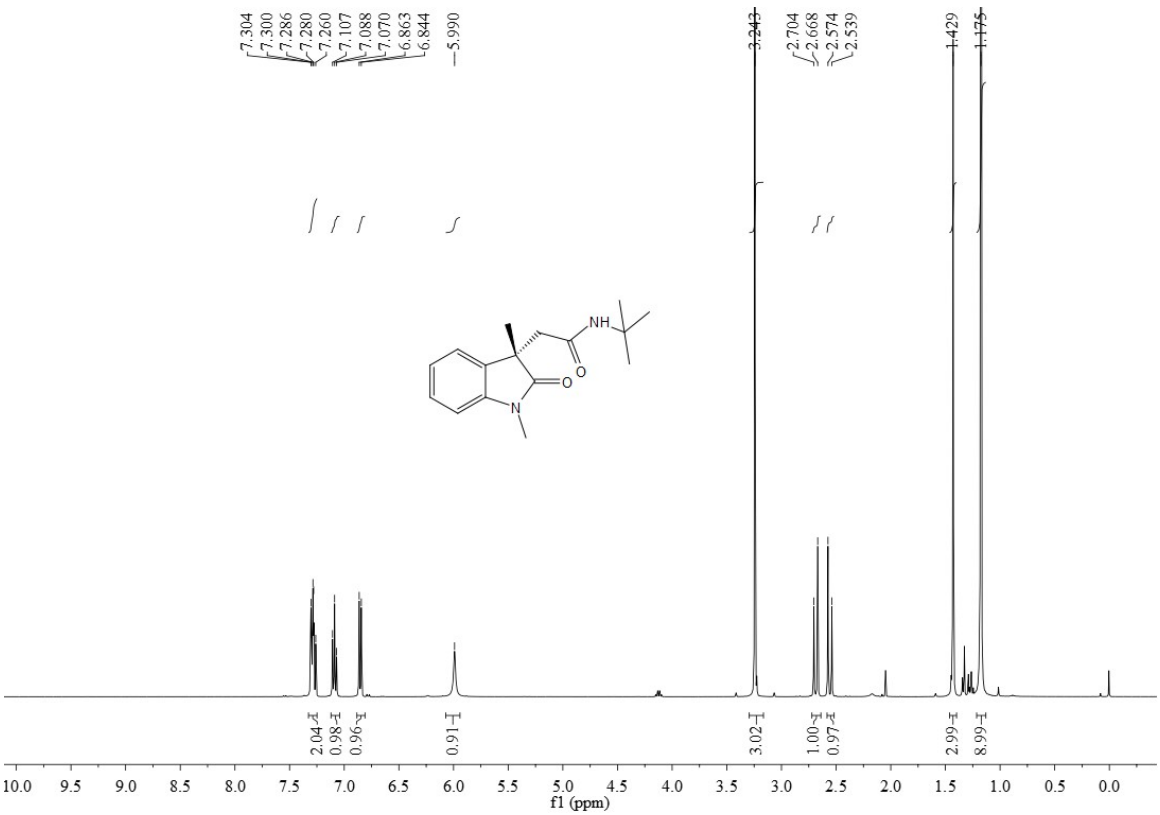

152.399
137.623
127.786
122.266
117.928
107.471
77.478
77.160
76.842
68.516
44.717
42.947
38.547
36.054
25.926
NH2
N
f1 (ppm)

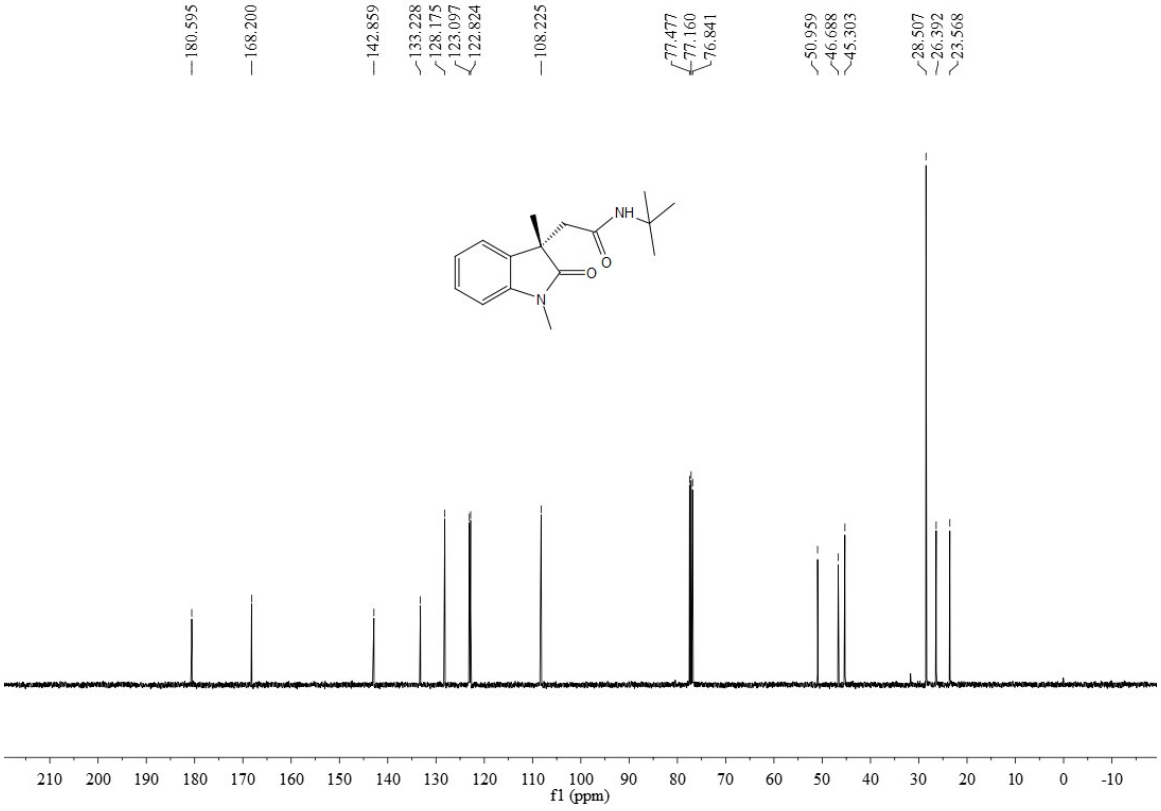
5


7.292
7.285
7.273
7.253
7.234
7.072
7.054
7.035
6.852
6.833
4.068
4.048
4.024
4.002
3.853
3.831
3.806
3.785
3.601
3.590
3.578
3.567
3.557
3.543
3.237
2.909
2.872
2.852
2.815
1.440
O
N
O
N
2.28
1.01
1.00
1.07
1.11
2.13
3.23
2.15
3.15
f1 (ppm)

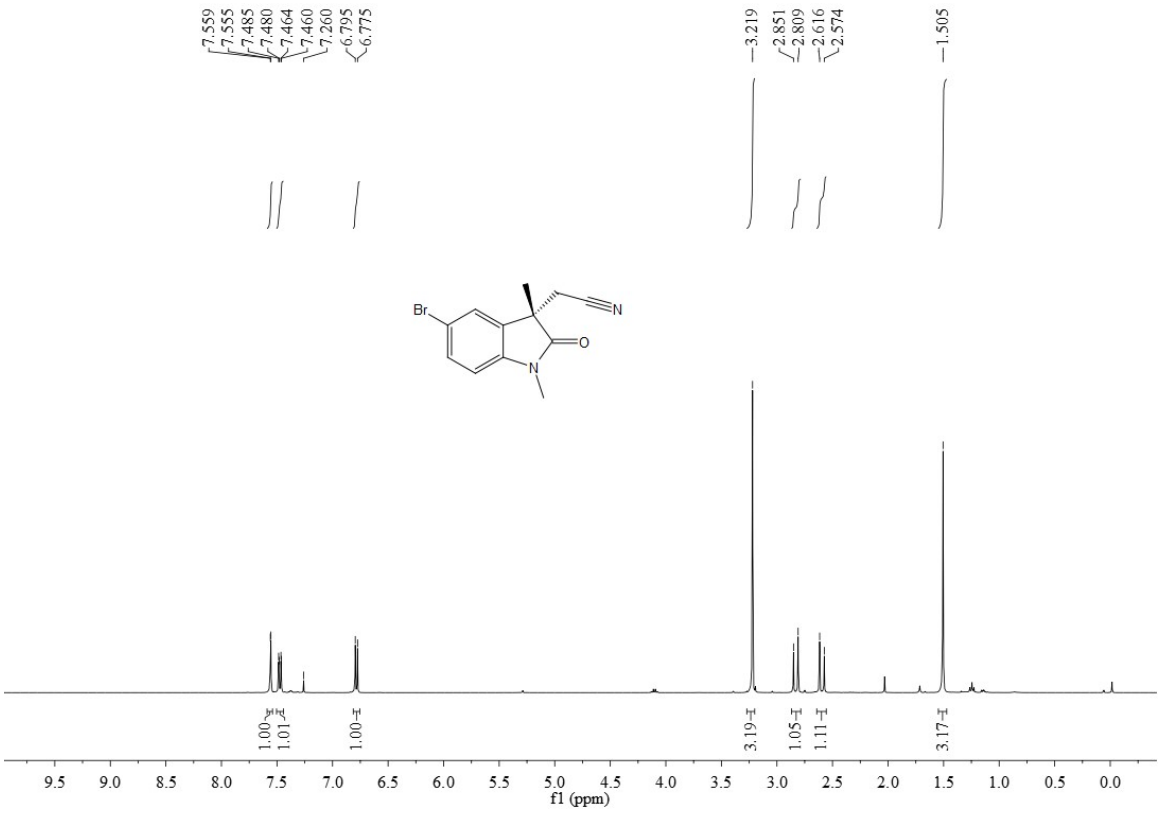

179.950
164.545
143.415
132.616
128.118
123.128
122.424
107.945
77.478
77.160
76.842
67.394
54.285
46.427
35.793
26.456
24.202
O
N
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

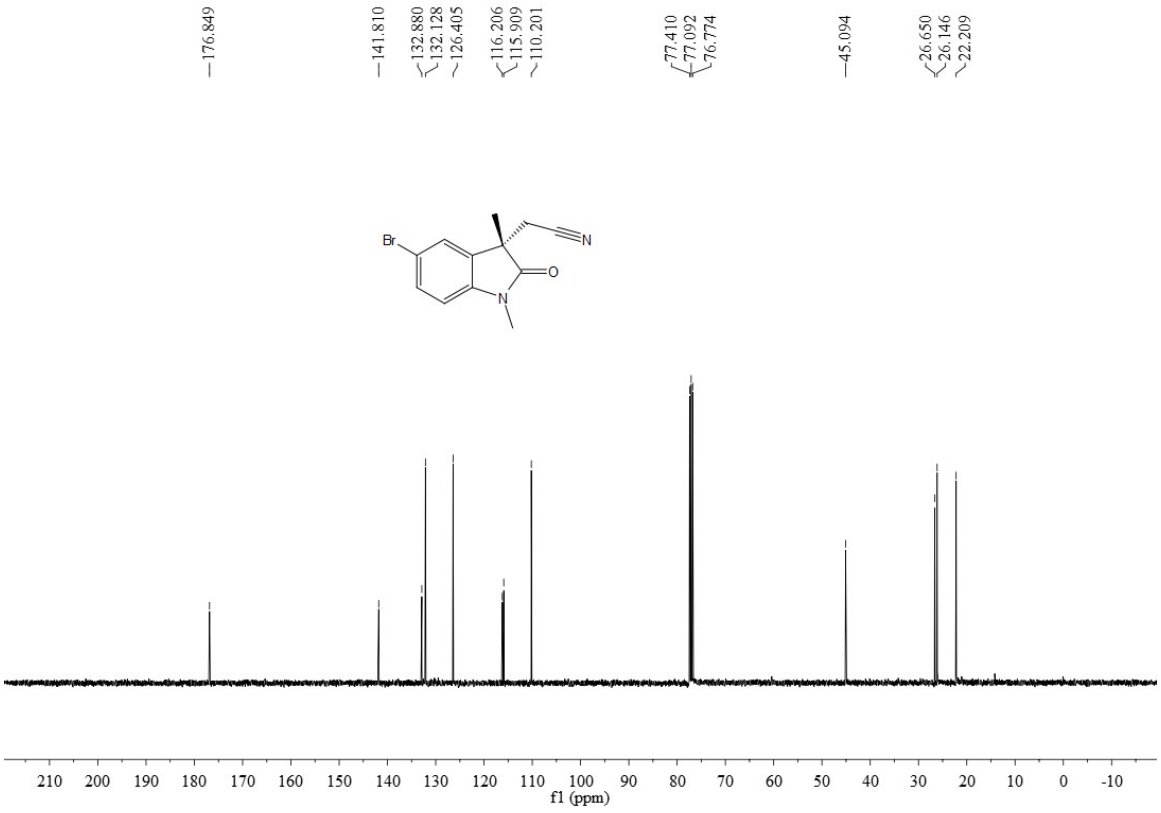
6


7.304
7.300
7.286
7.280
7.260
7.107
7.088
7.070
6.863
6.844
5.990
3.243
2.704
2.668
2.574
2.539
1.429
1.175
NH
O
N
2.04
0.98
0.96
0.91
3.02
1.00
0.97
2.99
8.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

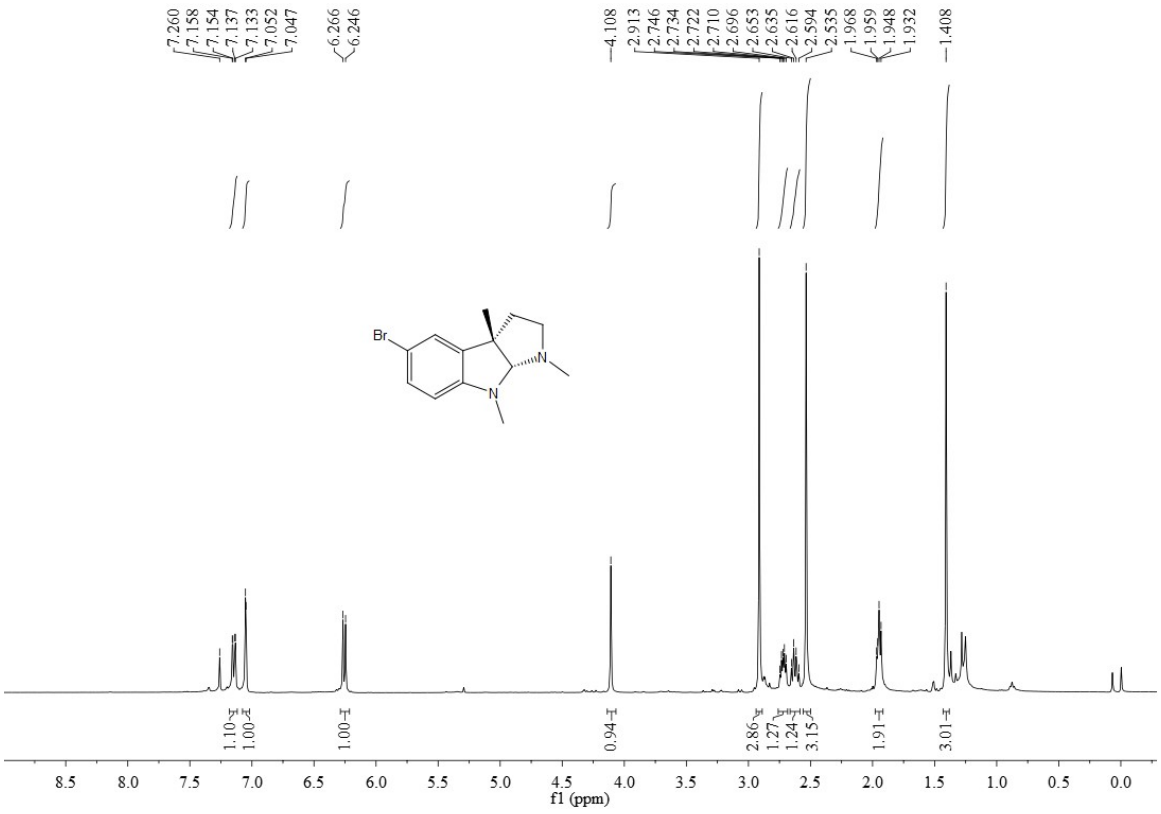

180.595
168.200
142.859
133.228
128.175
123.097
122.824
108.225
77.477
77.160
76.841
50.959
46.688
45.303
28.507
26.392
23.568
NH
O
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

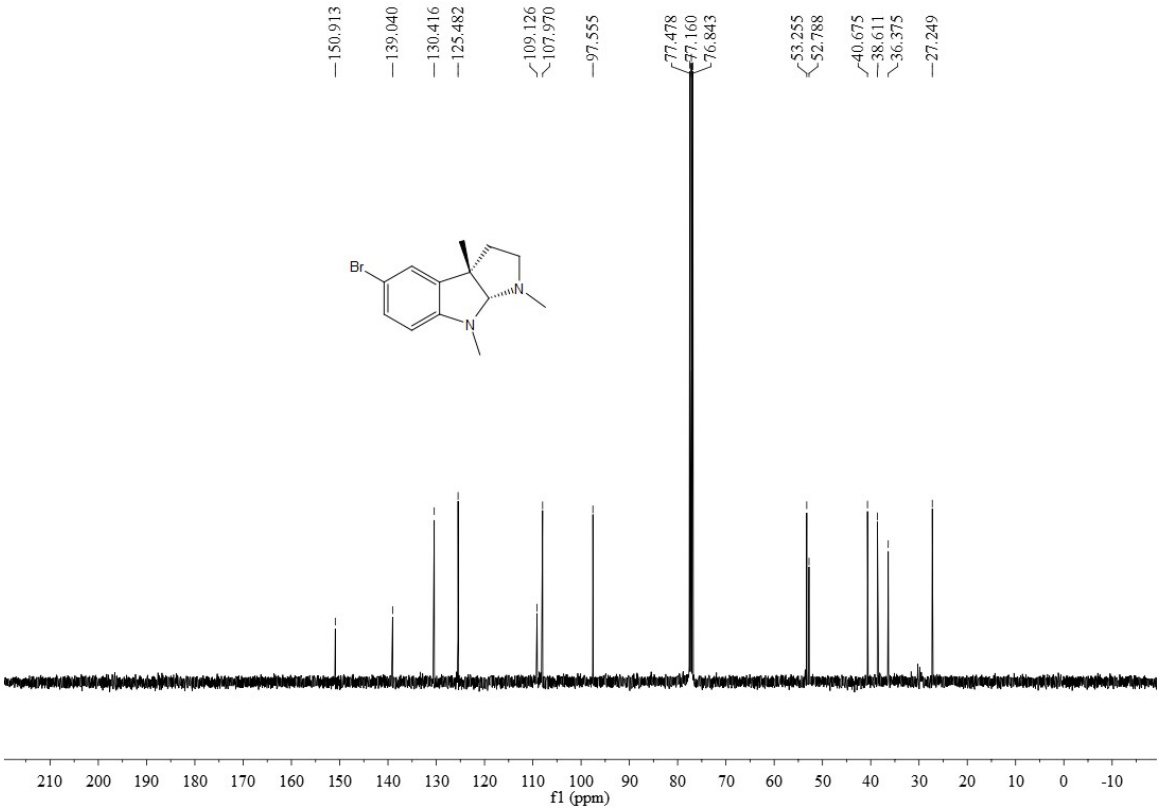
7


7.559
7.555
7.485
7.480
7.464
7.460
7.260
6.795
6.775
3.219
2.851
2.809
2.616
2.574
1.505
Br
N
O
N
1.00
1.01
1.00
3.19
1.05
1.11
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

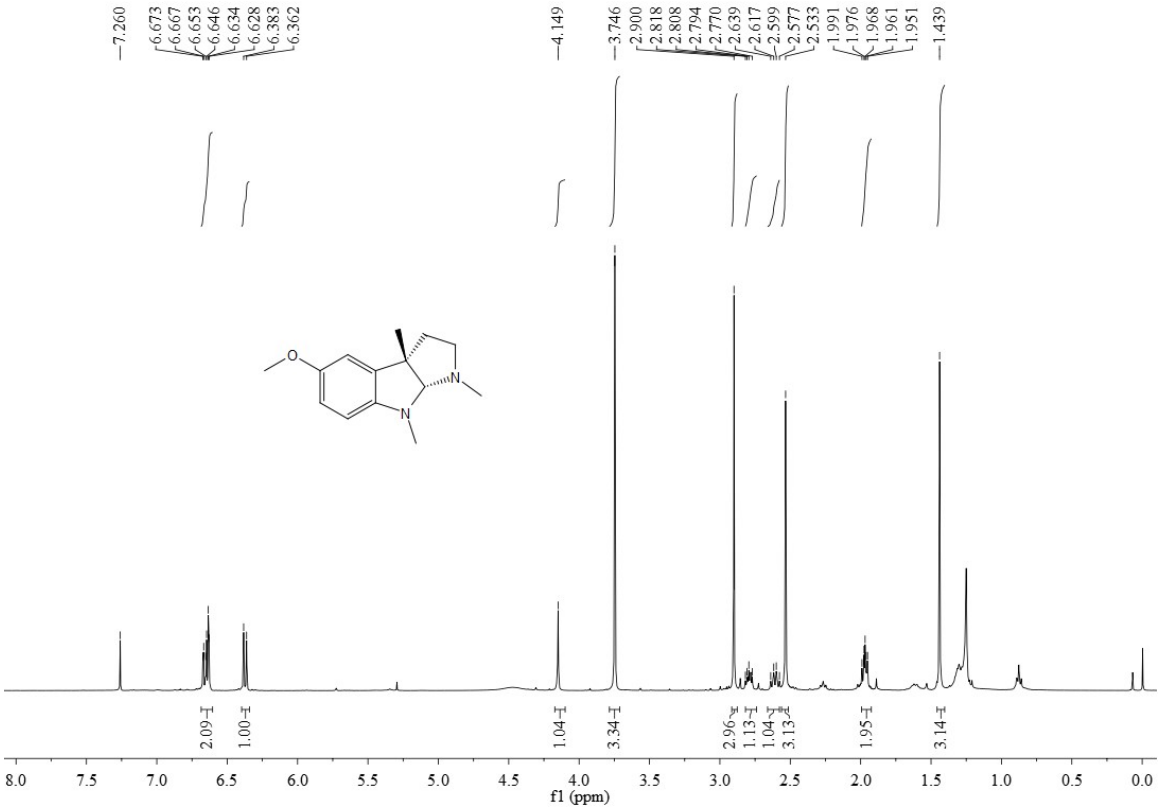

176.849
141.810
132.880
132.128
126.405
116.206
115.909
110.201
77.410
77.092
76.774
45.094
26.650
26.146
22.209
Br
N
O
N
f1 (ppm)

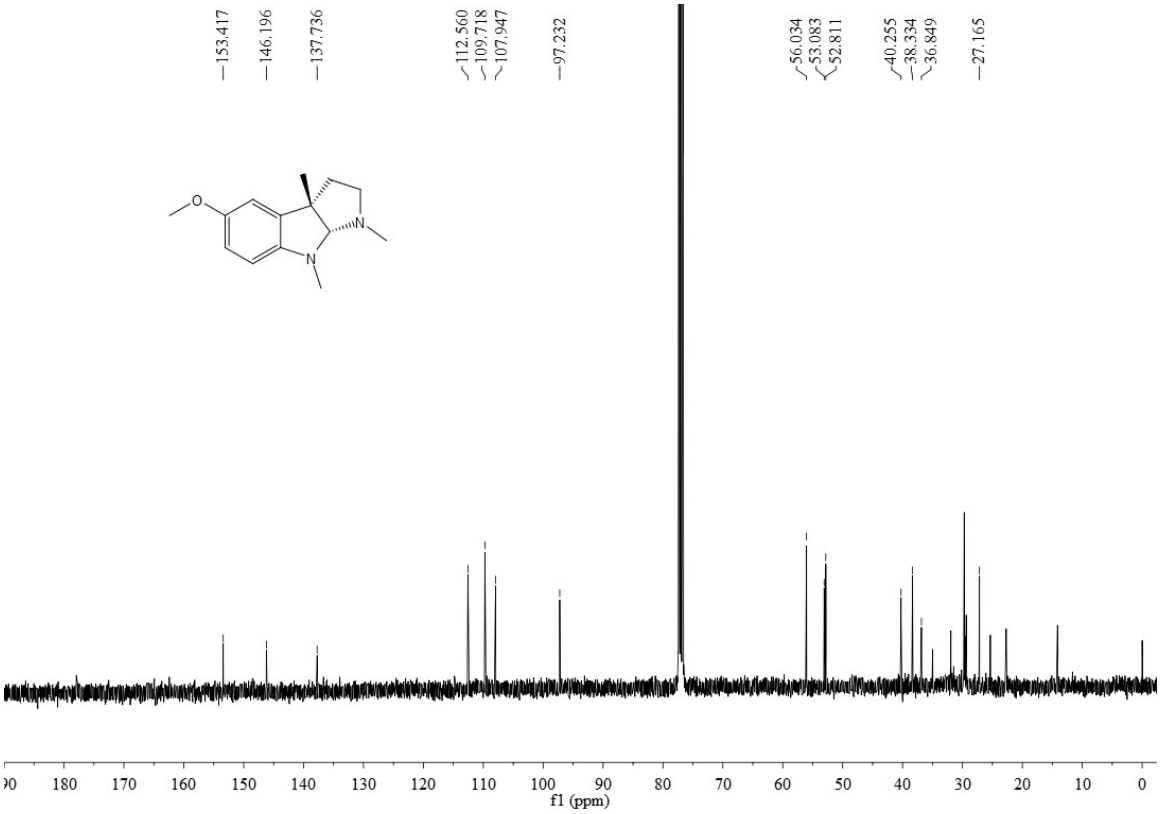
8


7.260
7.158
7.154
7.137
7.133
7.052
7.047
6.266
6.246
4.108
2.913
2.746
2.734
2.722
2.710
2.696
2.653
2.635
2.616
2.594
2.535
1.968
1.959
1.948
1.932
1.408
Br
N
N
1.10
1.00
1.00
0.94
2.86
1.27
1.24
3.15
1.91
3.01
f1 (ppm)

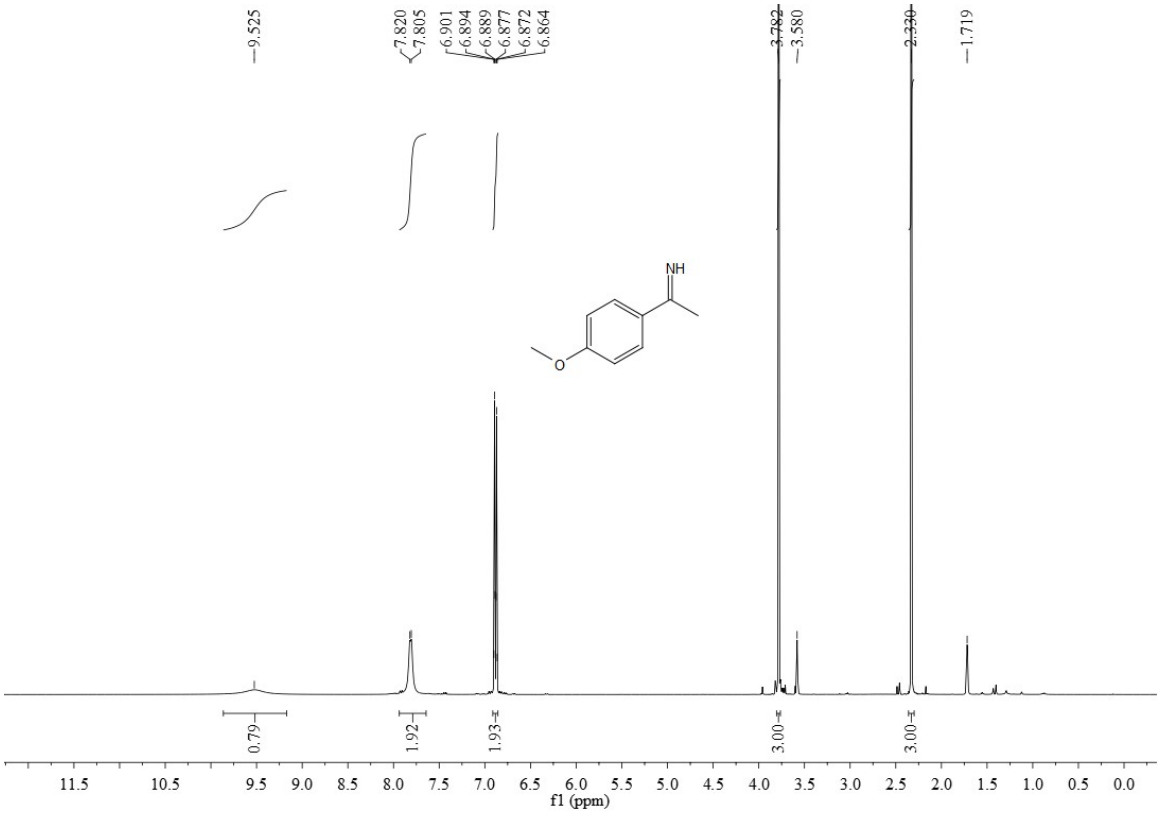


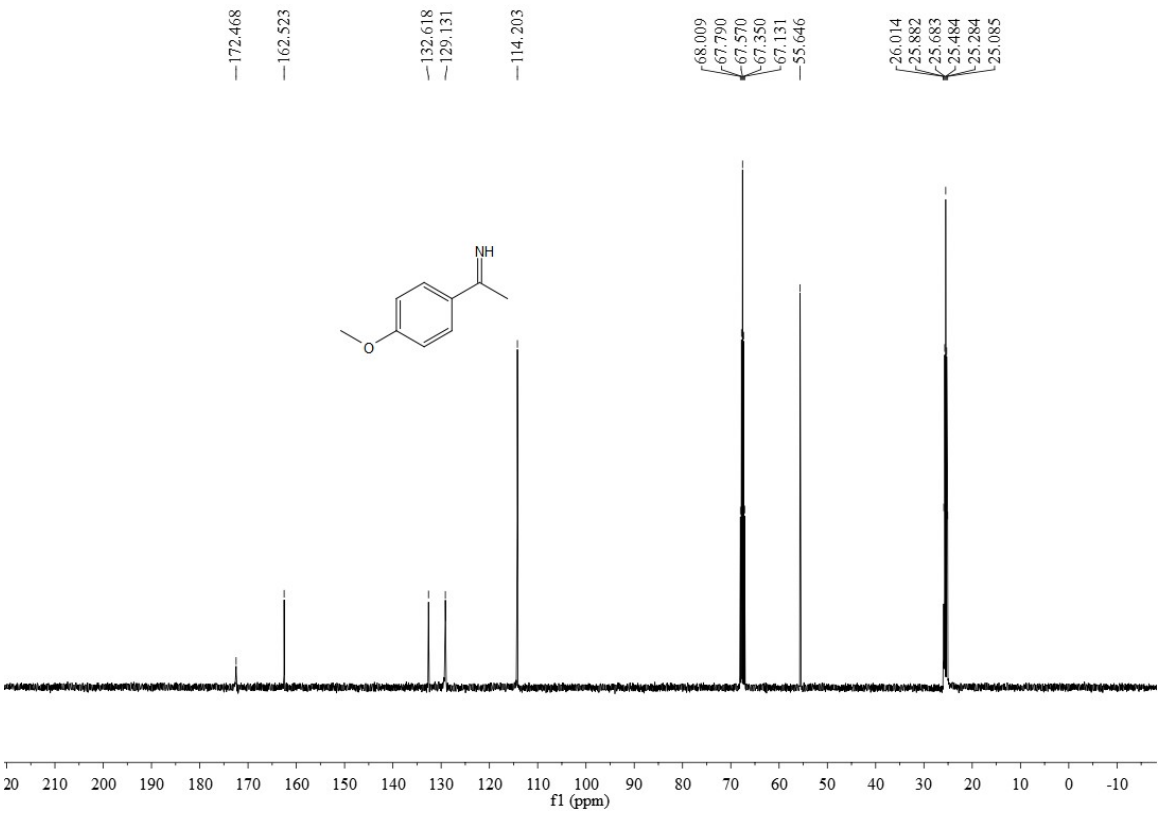
Esermethole



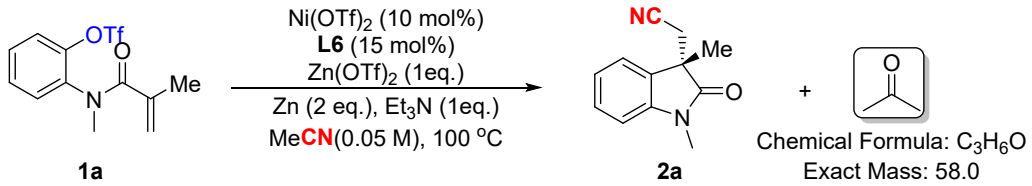

153.417
146.196
137.736
112.560
109.718
107.947
97.232
56.034
53.083
52.811
40.255
38.334
36.849
27.165
O
N
N
f1 (ppm)

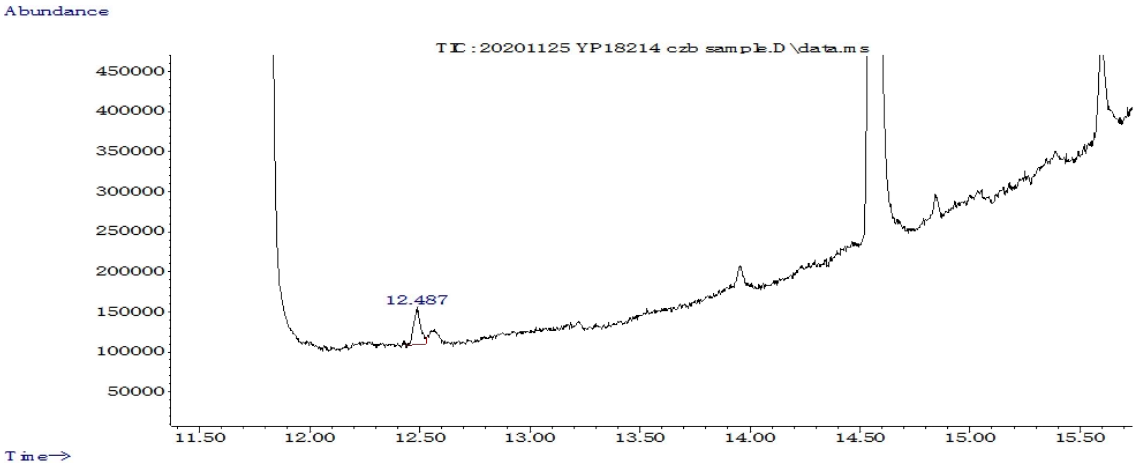
9

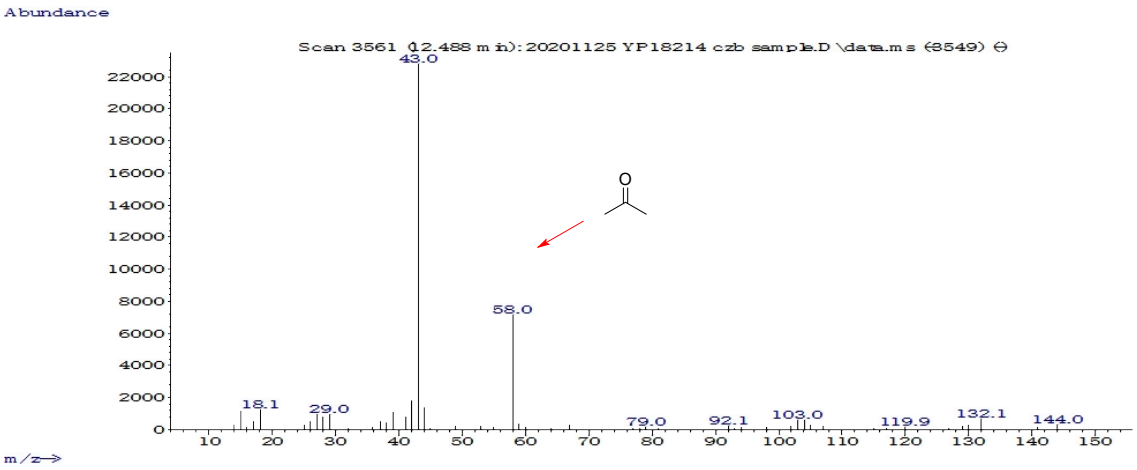

9.525
7.820
7.805
6.901
6.894
6.889
6.877
6.872
6.864
3.782
3.580
2.330
1.719
NH
O
0.79
1.92
1.93
3.00
3.00
f1 (ppm)



9、The GC-MS date







10、X-Ray crystallographic data

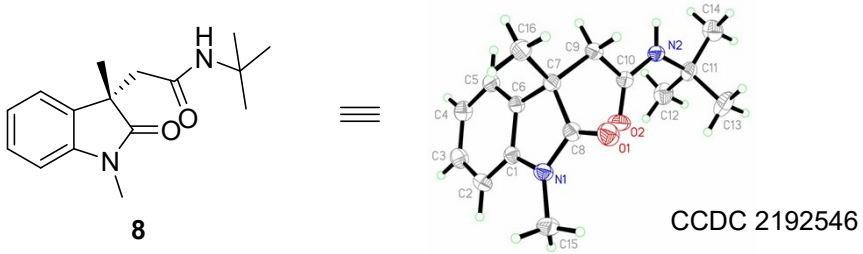


Table 1-8. Crystal data and structure refinement for **8**.

Identification code	**8**
Empirical formula	C16 H22 N2 O2
Formula weight	274.35
Temperature	173(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 8.7602(4) A alpha = 90 deg.
	b = 9.7822(4) A beta = 114.580(2) deg.
	c = 10.3505(4) A gamma = 90 deg.
Volume	806.60(6) A^3
Z, Calculated density	2, 1.130 Mg/m^3
Absorption coefficient	0.597 mm^-1
F(000)	296
Crystal size	0.180 x 0.160 x 0.140 mm

Theta range for data collection	4.698 to 68.353 deg.
Limiting indices	-10<=h<=10, -11<=k<=11, -12<=l<=12
Reflections collected / unique	11696 / 2932 [R(int) = 0.0636]
Completeness to theta = 67.679	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.5876
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2932 / 1 / 186
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0904
R indices (all data)	R1 = 0.0455, wR2 = 0.0959
Absolute structure parameter	0.21(18)
Extinction coefficient	n/a
Largest diff. peak and hole	0.125 and -0.199 e.A^-3

Table 2-8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **8**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	10175(2)	4216(2)	6664(2)	42(1)
C(1)	6364(3)	4915(2)	6780(2)	28(1)
N(1)	7694(3)	4032(2)	6916(2)	31(1)
O(2)	6777(3)	5172(2)	3827(2)	48(1)
C(2)	4869(3)	4589(3)	6857(3)	34(1)
N(2)	7607(2)	6836(2)	2726(2)	31(1)
C(5)	5600(3)	7279(3)	6334(3)	34(1)
C(4)	4084(3)	6964(3)	6411(3)	39(1)
C(3)	3730(3)	5645(3)	6660(3)	39(1)
C(6)	6737(3)	6240(3)	6513(2)	28(1)
C(8)	8901(3)	4725(3)	6683(3)	31(1)
C(7)	8486(3)	6245(3)	6555(3)	30(1)

C(9)	8652(3)	6897(3)	5278(3)	32(1)
C(10)	7584(3)	6215(3)	3874(3)	32(1)
C(11)	6784(3)	6340(3)	1247(3)	35(1)
C(12)	4892(4)	6217(4)	775(3)	50(1)
C(13)	7530(5)	4976(4)	1106(4)	58(1)
C(14)	7122(4)	7412(4)	331(3)	50(1)
C(15)	7746(3)	2578(3)	7220(3)	39(1)
C(16)	9731(3)	6924(3)	7931(3)	39(1)

Table 3-8. Bond lengths [A] and angles [deg] for **8**.

O(1)-C(8)	1.229(3)
C(1)-C(2)	1.382(3)
C(1)-C(6)	1.392(4)
C(1)-N(1)	1.409(3)
N(1)-C(8)	1.360(3)
N(1)-C(15)	1.453(3)
O(2)-C(10)	1.231(3)
C(2)-C(3)	1.392(4)
N(2)-C(10)	1.343(3)
N(2)-C(11)	1.477(3)
C(5)-C(6)	1.381(4)
C(5)-C(4)	1.398(4)
C(4)-C(3)	1.376(4)
C(6)-C(7)	1.515(3)
C(8)-C(7)	1.524(4)
C(7)-C(9)	1.528(3)
C(7)-C(16)	1.539(3)
C(9)-C(10)	1.517(4)
C(11)-C(13)	1.519(4)
C(11)-C(14)	1.523(4)
C(11)-C(12)	1.525(4)
C(2)-C(1)-C(6)	122.1(2)

C(2)-C(1)-N(1)	128.0(2)
C(6)-C(1)-N(1)	109.8(2)
C(8)-N(1)-C(1)	110.37(19)
C(8)-N(1)-C(15)	124.7(2)
C(1)-N(1)-C(15)	124.9(2)
C(1)-C(2)-C(3)	117.4(2)
C(10)-N(2)-C(11)	126.0(2)
C(6)-C(5)-C(4)	118.7(2)
C(3)-C(4)-C(5)	120.7(3)
C(4)-C(3)-C(2)	121.3(2)
C(5)-C(6)-C(1)	119.8(2)
C(5)-C(6)-C(7)	131.8(2)
C(1)-C(6)-C(7)	108.4(2)
O(1)-C(8)-N(1)	125.4(2)
O(1)-C(8)-C(7)	125.4(2)
N(1)-C(8)-C(7)	109.1(2)
C(6)-C(7)-C(8)	101.6(2)
C(6)-C(7)-C(9)	115.9(2)
C(8)-C(7)-C(9)	112.2(2)
C(6)-C(7)-C(16)	110.3(2)
C(8)-C(7)-C(16)	106.8(2)
C(9)-C(7)-C(16)	109.5(2)
C(10)-C(9)-C(7)	113.7(2)
O(2)-C(10)-N(2)	124.1(2)
O(2)-C(10)-C(9)	121.2(2)
N(2)-C(10)-C(9)	114.7(2)
N(2)-C(11)-C(13)	110.1(2)
N(2)-C(11)-C(14)	106.3(2)
C(13)-C(11)-C(14)	110.0(2)
N(2)-C(11)-C(12)	110.8(2)
C(13)-C(11)-C(12)	110.7(3)
C(14)-C(11)-C(12)	108.7(2)

Symmetry transformations used to generate equivalent atoms:

Table 4-8. Anisotropic displacement parameters (A^2 x 10^3) for **8**.

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	38(1)	41(1)	52(1)	6(1)	25(1)	6(1)
C(1)	29(1)	31(1)	22(1)	0(1)	10(1)	0(1)
N(1)	33(1)	27(1)	34(1)	4(1)	15(1)	1(1)
O(2)	70(1)	36(1)	38(1)	-3(1)	22(1)	-20(1)
C(2)	33(1)	36(2)	35(1)	4(1)	15(1)	-4(1)
N(2)	38(1)	26(1)	29(1)	0(1)	15(1)	-2(1)
C(5)	40(1)	31(1)	31(1)	1(1)	15(1)	0(1)
C(4)	35(1)	42(2)	39(2)	2(1)	15(1)	7(1)
C(3)	32(1)	48(2)	39(2)	3(1)	16(1)	2(1)
C(6)	32(1)	29(1)	24(1)	0(1)	12(1)	-2(1)
C(8)	32(1)	32(1)	30(1)	1(1)	14(1)	0(1)
C(7)	30(1)	31(1)	29(1)	-1(1)	13(1)	-3(1)
C(9)	36(1)	30(1)	32(1)	1(1)	16(1)	-4(1)
C(10)	36(1)	28(1)	32(1)	0(1)	16(1)	-1(1)
C(11)	40(1)	37(1)	28(1)	-3(1)	13(1)	4(1)
C(12)	45(2)	62(2)	40(2)	-10(2)	13(1)	-4(2)
C(13)	78(2)	49(2)	46(2)	-8(1)	25(2)	18(2)
C(14)	60(2)	57(2)	32(2)	5(1)	17(1)	-3(2)
C(15)	41(2)	30(1)	44(2)	7(1)	16(1)	2(1)
C(16)	38(1)	44(2)	32(1)	-6(1)	12(1)	-10(1)

Table 5-8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **8**.

	x	y	z	U(eq)

H(2)	4629	3680	7037	41
H(2A)	8164	7611	2868	37
H(5)	5843	8190	6161	41
H(4)	3290	7669	6291	46
H(3)	2686	5452	6698	47
H(9A)	8329	7872	5225	38
H(9B)	9843	6858	5428	38
H(12A)	4375	5867	-201	76
H(12B)	4425	7118	813	76
H(12C)	4662	5587	1408	76
H(13A)	7029	4686	109	87
H(13B)	7296	4290	1690	87
H(13C)	8747	5073	1428	87
H(14A)	6627	7114	-663	75
H(14B)	8336	7527	652	75
H(14C)	6620	8284	415	75
H(15A)	6673	2159	6603	58
H(15B)	7946	2446	8217	58
H(15C)	8655	2150	7046	58
H(16A)	10873	6837	7992	58
H(16B)	9663	6474	8752	58
H(16C)	9448	7894	7927	58

Table 6-8. Torsion angles [deg] for **8**.

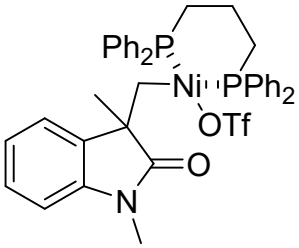
C(2)-C(1)-N(1)-C(8)	176.0(2)
C(6)-C(1)-N(1)-C(8)	-2.8(3)
C(2)-C(1)-N(1)-C(15)	-2.3(4)
C(6)-C(1)-N(1)-C(15)	179.0(2)
C(6)-C(1)-C(2)-C(3)	-0.2(4)
N(1)-C(1)-C(2)-C(3)	-178.8(2)
C(6)-C(5)-C(4)-C(3)	-0.1(4)

C(5)-C(4)-C(3)-C(2)	0.7(4)
C(1)-C(2)-C(3)-C(4)	-0.6(4)
C(4)-C(5)-C(6)-C(1)	-0.7(4)
C(4)-C(5)-C(6)-C(7)	-177.0(2)
C(2)-C(1)-C(6)-C(5)	0.8(4)
N(1)-C(1)-C(6)-C(5)	179.6(2)
C(2)-C(1)-C(6)-C(7)	177.9(2)
N(1)-C(1)-C(6)-C(7)	-3.2(3)
C(1)-N(1)-C(8)-O(1)	-176.5(2)
C(15)-N(1)-C(8)-O(1)	1.8(4)
C(1)-N(1)-C(8)-C(7)	7.5(3)
C(15)-N(1)-C(8)-C(7)	-174.2(2)
C(5)-C(6)-C(7)-C(8)	-176.2(3)
C(1)-C(6)-C(7)-C(8)	7.1(2)
C(5)-C(6)-C(7)-C(9)	-54.3(4)
C(1)-C(6)-C(7)-C(9)	129.0(2)
C(5)-C(6)-C(7)-C(16)	70.8(3)
C(1)-C(6)-C(7)-C(16)	-105.9(2)
O(1)-C(8)-C(7)-C(6)	175.2(2)
N(1)-C(8)-C(7)-C(6)	-8.8(2)
O(1)-C(8)-C(7)-C(9)	50.8(3)
N(1)-C(8)-C(7)-C(9)	-133.2(2)
O(1)-C(8)-C(7)-C(16)	-69.2(3)
N(1)-C(8)-C(7)-C(16)	106.7(2)
C(6)-C(7)-C(9)-C(10)	-59.6(3)
C(8)-C(7)-C(9)-C(10)	56.5(3)
C(16)-C(7)-C(9)-C(10)	174.9(2)
C(11)-N(2)-C(10)-O(2)	-4.4(4)
C(11)-N(2)-C(10)-C(9)	175.4(2)
C(7)-C(9)-C(10)-O(2)	-5.2(3)
C(7)-C(9)-C(10)-N(2)	175.0(2)
C(10)-N(2)-C(11)-C(13)	-62.6(3)
C(10)-N(2)-C(11)-C(14)	178.2(2)
C(10)-N(2)-C(11)-C(12)	60.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 7-8. Hydrogen bonds for **8** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)



11

≡

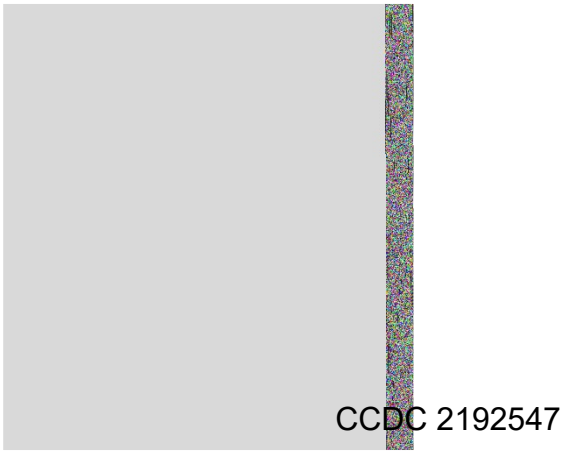


Table 1-11. Crystal data and structure refinement for **11**.

Identification code	**11**
Empirical formula	C54 H53 F3 N Ni O4 P2 S
Formula weight	989.68
Temperature	173(2) K
Wavelength	1.54178 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 12.3940(7) A alpha = 79.158(2) deg.
	b = 13.4581(7) A beta = 69.71 deg.
	c = 17.8731(13) A gamma = 62.58 deg.
Volume	2480.8(3) A^3
Z, Calculated density	2, 1.325 Mg/m^3
Absorption coefficient	2.037 mm^-1
F(000)	1034
Crystal size	0.180 x 0.160 x 0.140 mm
Theta range for data collection	4.210 to 66.574 deg.

Limiting indices	-14<=h<=14, -16<=k<=16, -21<=l<=21
Reflections collected / unique	34415 / 8609 [R(int) = 0.0774]
Completeness to theta = 66.574	98.5 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8609 / 1 / 562
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.1044, wR2 = 0.2880
R indices (all data)	R1 = 0.1372, wR2 = 0.3237
Extinction coefficient	n/a
Largest diff. peak and hole	1.899 and -1.144 e.A^-3

Table 2-11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **11**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
P(1)	7886(1)	1674(1)	1216(1)	43(1)
F(1)	2824(7)	3054(8)	1558(7)	187(5)
O(1)	5987(4)	3967(3)	1153(2)	51(1)
N(1)	4982(5)	5873(4)	958(3)	51(1)
C(1)	3747(6)	6386(5)	2248(4)	52(1)
C(5)	3750(8)	7924(6)	1267(5)	66(2)
C(6)	4130(6)	6795(5)	1477(4)	56(2)
C(7)	5660(8)	5973(6)	122(4)	66(2)
C(52)	11768(19)	3276(18)	4822(11)	186(9)
C(8)	5162(6)	4933(5)	1389(4)	48(1)
C(9)	3239(7)	4772(6)	2324(5)	63(2)
C(10)	5161(6)	4336(5)	2745(4)	47(1)
C(11)	8549(5)	2289(5)	276(4)	50(1)
C(12)	8401(7)	2196(5)	-445(4)	58(2)
C(13)	8917(8)	2687(6)	-1139(4)	71(2)
C(14)	9565(8)	3277(7)	-1137(5)	80(2)

Ni(1)	6420(1)	3016(1)	2073(1)	41(1)
S(1)	1188(2)	2244(2)	2113(2)	99(1)
C(15)	9706(8)	3386(7)	-441(6)	79(2)
C(16)	9197(7)	2899(6)	278(5)	62(2)
C(17)	7246(6)	861(5)	955(4)	46(1)
C(18)	5937(6)	1271(5)	1118(4)	54(2)
C(19)	5409(7)	710(6)	900(5)	63(2)
C(20)	6190(8)	-257(6)	487(5)	71(2)
C(21)	7503(7)	-677(6)	303(5)	67(2)
C(22)	8026(7)	-131(5)	545(4)	58(2)
C(23)	9309(6)	656(5)	1482(4)	50(1)
C(24)	9012(6)	124(5)	2318(4)	51(1)
C(25)	8448(6)	969(5)	2973(4)	48(1)
C(26)	5903(6)	1140(5)	3425(4)	50(1)
C(27)	4828(7)	1445(6)	3183(5)	64(2)
C(28)	4201(8)	764(8)	3369(5)	79(2)
C(29)	4636(9)	-231(7)	3801(6)	83(2)
C(30)	5671(8)	-531(7)	4038(6)	80(2)
C(31)	6301(8)	162(6)	3852(5)	68(2)
C(32)	6446(6)	2703(5)	3985(4)	48(1)
C(33)	5479(7)	2742(5)	4678(4)	58(2)
C(34)	5264(8)	3285(6)	5337(4)	72(2)
C(35)	6026(9)	3817(6)	5297(5)	77(2)
C(36)	6968(8)	3793(6)	4606(5)	69(2)
C(37)	7196(7)	3246(5)	3943(4)	54(2)
C(38)	8782(8)	825(7)	5123(5)	73(2)
C(39)	9771(7)	972(6)	4525(5)	68(2)
C(40)	10993(7)	148(6)	4399(5)	64(2)
C(41)	-2443(10)	5800(8)	1291(8)	97(3)
C(42)	-2089(9)	5194(8)	1954(7)	92(3)
C(43)	-2305(13)	5752(11)	2613(8)	123(4)
C(44)	-2946(15)	6918(10)	2619(8)	136(6)
C(45)	-3331(11)	7496(9)	1929(9)	114(4)
C(46)	-3040(12)	6943(9)	1283(9)	110(4)
C(48)	10364(16)	2806(14)	6321(10)	138(5)
C(47)	1660(20)	3268(17)	1687(12)	159(6)

C(49)	10680(20)	3683(18)	6269(14)	184(7)
C(50)	11230(30)	4090(30)	5421(18)	271(14)
C(51)	4308(6)	5116(5)	2228(4)	47(1)
C(01J)	11361(16)	2487(14)	4982(10)	144(6)
C(01M)	10600(14)	2314(12)	5722(9)	129(4)
P(2)	6786(1)	1997(1)	3101(1)	42(1)
F(2)	905(8)	4234(6)	2156(8)	190(5)
O(2)	-70(7)	2589(6)	2111(6)	122(3)
C(2)	2931(8)	7139(6)	2831(5)	72(2)
O(3)	1803(17)	1377(15)	2562(10)	227(6)
F(3)	1129(14)	3851(13)	1090(9)	231(5)
C(3)	2541(9)	8281(6)	2638(6)	82(3)
O(4)	2017(18)	1522(16)	1392(11)	241(7)
C(4)	2920(9)	8665(6)	1872(6)	78(2)

Table 3-11. Bond lengths [A] and angles [deg] for **11**.

P(1)-C(17)	1.815(6)
P(1)-C(23)	1.823(6)
P(1)-C(11)	1.824(6)
P(1)-Ni(1)	2.2358(16)
F(1)-C(47)	1.28(2)
O(1)-C(8)	1.264(7)
O(1)-Ni(1)	1.954(4)
N(1)-C(8)	1.318(8)
N(1)-C(6)	1.435(8)
N(1)-C(7)	1.454(9)
C(1)-C(2)	1.363(10)
C(1)-C(6)	1.390(10)
C(1)-C(51)	1.522(8)
C(5)-C(4)	1.383(12)
C(5)-C(6)	1.386(10)
C(52)-C(01J)	1.32(2)
C(52)-C(50)	1.432(17)
C(8)-C(51)	1.493(8)

C(9)-C(51)	1.542(9)
C(10)-C(51)	1.537(8)
C(10)-Ni(1)	1.996(5)
C(11)-C(16)	1.389(9)
C(11)-C(12)	1.399(9)
C(12)-C(13)	1.385(10)
C(13)-C(14)	1.366(13)
C(14)-C(15)	1.358(13)
Ni(1)-P(2)	2.1256(16)
S(1)-O(3)	1.356(18)
S(1)-O(2)	1.408(7)
S(1)-O(4)	1.514(18)
S(1)-C(47)	1.69(2)
C(15)-C(16)	1.407(11)
C(17)-C(18)	1.390(9)
C(17)-C(22)	1.394(9)
C(18)-C(19)	1.375(9)
C(19)-C(20)	1.372(11)
C(20)-C(21)	1.389(11)
C(21)-C(22)	1.377(9)
C(23)-C(24)	1.529(9)
C(24)-C(25)	1.534(8)
C(25)-P(2)	1.838(6)
C(26)-C(31)	1.358(9)
C(26)-C(27)	1.399(10)
C(26)-P(2)	1.826(6)
C(27)-C(28)	1.385(10)
C(28)-C(29)	1.383(12)
C(29)-C(30)	1.351(13)
C(30)-C(31)	1.402(11)
C(32)-C(33)	1.383(9)
C(32)-C(37)	1.399(9)
C(32)-P(2)	1.820(6)
C(33)-C(34)	1.384(10)
C(34)-C(35)	1.402(13)
C(35)-C(36)	1.367(12)

C(36)-C(37)	1.390(10)
C(38)-C(39)	1.385(12)
C(38)-C(40)#1	1.390(11)
C(39)-C(40)	1.372(11)
C(41)-C(46)	1.366(14)
C(41)-C(42)	1.389(15)
C(42)-C(43)	1.397(17)
C(43)-C(44)	1.394(17)
C(44)-C(45)	1.435(19)
C(45)-C(46)	1.343(17)
C(48)-C(01M)	1.240(19)
C(48)-C(49)	1.38(2)
C(47)-F(3)	1.37(2)
C(47)-F(2)	1.42(2)
C(49)-C(50)	1.54(3)
C(01J)-C(01M)	1.383(19)
C(2)-C(3)	1.395(12)
C(3)-C(4)	1.370(13)

C(17)-P(1)-C(23)	105.8(3)
C(17)-P(1)-C(11)	105.6(3)
C(23)-P(1)-C(11)	102.4(3)
C(17)-P(1)-Ni(1)	113.1(2)
C(23)-P(1)-Ni(1)	118.3(2)
C(11)-P(1)-Ni(1)	110.36(19)
C(8)-O(1)-Ni(1)	108.9(4)
C(8)-N(1)-C(6)	108.5(5)
C(8)-N(1)-C(7)	126.0(5)
C(6)-N(1)-C(7)	125.1(5)
C(2)-C(1)-C(6)	118.1(6)
C(2)-C(1)-C(51)	133.6(7)
C(6)-C(1)-C(51)	108.1(5)
C(4)-C(5)-C(6)	116.5(8)
C(5)-C(6)-C(1)	123.9(7)
C(5)-C(6)-N(1)	126.7(7)
C(1)-C(6)-N(1)	109.4(5)

C(01J)-C(52)-C(50)	117(2)
O(1)-C(8)-N(1)	125.7(6)
O(1)-C(8)-C(51)	121.5(5)
N(1)-C(8)-C(51)	112.8(5)
C(51)-C(10)-Ni(1)	104.6(4)
C(16)-C(11)-C(12)	118.6(6)
C(16)-C(11)-P(1)	118.9(5)
C(12)-C(11)-P(1)	122.5(5)
C(13)-C(12)-C(11)	120.0(7)
C(14)-C(13)-C(12)	121.3(8)
C(15)-C(14)-C(13)	119.4(7)
O(1)-Ni(1)-C(10)	87.3(2)
O(1)-Ni(1)-P(2)	176.90(15)
C(10)-Ni(1)-P(2)	91.12(18)
O(1)-Ni(1)-P(1)	87.50(12)
C(10)-Ni(1)-P(1)	173.49(19)
P(2)-Ni(1)-P(1)	94.27(6)
O(3)-S(1)-O(2)	125.0(8)
O(3)-S(1)-O(4)	88.0(10)
O(2)-S(1)-O(4)	104.9(8)
O(3)-S(1)-C(47)	123.5(10)
O(2)-S(1)-C(47)	109.4(8)
O(4)-S(1)-C(47)	92.1(9)
C(14)-C(15)-C(16)	121.1(8)
C(11)-C(16)-C(15)	119.6(8)
C(18)-C(17)-C(22)	118.2(6)
C(18)-C(17)-P(1)	119.4(4)
C(22)-C(17)-P(1)	122.3(5)
C(19)-C(18)-C(17)	121.6(6)
C(18)-C(19)-C(20)	119.5(7)
C(19)-C(20)-C(21)	120.2(6)
C(22)-C(21)-C(20)	120.1(6)
C(21)-C(22)-C(17)	120.4(6)
C(24)-C(23)-P(1)	113.2(4)
C(23)-C(24)-C(25)	112.0(5)
C(24)-C(25)-P(2)	115.6(4)

C(31)-C(26)-C(27)	117.9(6)
C(31)-C(26)-P(2)	122.2(5)
C(27)-C(26)-P(2)	119.8(5)
C(28)-C(27)-C(26)	120.9(7)
C(27)-C(28)-C(29)	119.9(8)
C(30)-C(29)-C(28)	119.7(7)
C(29)-C(30)-C(31)	120.3(7)
C(26)-C(31)-C(30)	121.4(7)
C(33)-C(32)-C(37)	119.4(6)
C(33)-C(32)-P(2)	123.2(5)
C(37)-C(32)-P(2)	117.4(5)
C(34)-C(33)-C(32)	120.9(7)
C(33)-C(34)-C(35)	119.6(7)
C(36)-C(35)-C(34)	119.4(7)
C(35)-C(36)-C(37)	121.5(8)
C(36)-C(37)-C(32)	119.2(7)
C(39)-C(38)-C(40)#1	120.9(7)
C(40)-C(39)-C(38)	119.9(7)
C(39)-C(40)-C(38)#1	119.2(8)
C(46)-C(41)-C(42)	120.7(11)
C(41)-C(42)-C(43)	120.1(10)
C(44)-C(43)-C(42)	119.5(13)
C(43)-C(44)-C(45)	117.8(12)
C(46)-C(45)-C(44)	121.5(10)
C(45)-C(46)-C(41)	120.2(12)
C(01M)-C(48)-C(49)	121.9(19)
F(1)-C(47)-F(3)	116.4(18)
F(1)-C(47)-F(2)	107.3(14)
F(3)-C(47)-F(2)	89.2(15)
F(1)-C(47)-S(1)	118.1(15)
F(3)-C(47)-S(1)	112.0(15)
F(2)-C(47)-S(1)	109.7(13)
C(48)-C(49)-C(50)	116(2)
C(49)-C(50)-C(52)	114(2)
C(8)-C(51)-C(1)	100.4(5)
C(8)-C(51)-C(10)	105.1(5)

C(1)-C(51)-C(10)	122.2(5)
C(8)-C(51)-C(9)	108.9(5)
C(1)-C(51)-C(9)	109.0(5)
C(10)-C(51)-C(9)	110.2(5)
C(52)-C(01J)-C(01M)	123.8(15)
C(48)-C(01M)-C(01J)	122.2(17)
C(32)-P(2)-C(26)	105.7(3)
C(32)-P(2)-C(25)	101.4(3)
C(26)-P(2)-C(25)	103.6(3)
C(32)-P(2)-Ni(1)	117.32(19)
C(26)-P(2)-Ni(1)	111.8(2)
C(25)-P(2)-Ni(1)	115.4(2)
C(1)-C(2)-C(3)	119.3(8)
C(4)-C(3)-C(2)	121.6(7)
C(3)-C(4)-C(5)	120.6(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+1

Table 4-11. Anisotropic displacement parameters (A^2 x 10^3) for **11**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
P(1)	38(1)	42(1)	44(1)	-4(1)	-13(1)	-12(1)
F(1)	84(5)	168(7)	328(13)	-85(8)	-14(6)	-76(5)
O(1)	54(2)	42(2)	44(2)	-1(2)	-22(2)	-7(2)
N(1)	57(3)	46(3)	49(3)	2(2)	-22(2)	-17(2)
C(1)	53(4)	46(3)	58(4)	-7(3)	-31(3)	-10(3)
C(5)	74(5)	51(3)	81(5)	3(3)	-41(4)	-23(3)
C(6)	55(4)	48(3)	68(4)	-6(3)	-32(3)	-12(3)
C(7)	75(5)	66(4)	54(4)	8(3)	-24(3)	-26(4)

C(52)	176(17)	205(19)	159(15)	-69(14)	46(13)	-113(16)
C(8)	48(3)	52(3)	46(3)	-4(2)	-20(3)	-18(3)
C(9)	52(4)	62(4)	74(4)	3(3)	-27(3)	-20(3)
C(10)	46(3)	42(3)	50(3)	-8(2)	-21(3)	-10(2)
C(11)	35(3)	44(3)	57(4)	-5(3)	-11(3)	-7(2)
C(12)	53(4)	50(3)	54(4)	0(3)	-15(3)	-9(3)
C(13)	68(5)	65(4)	53(4)	6(3)	-10(3)	-14(4)
C(14)	70(5)	63(4)	68(5)	13(4)	0(4)	-18(4)
Ni(1)	39(1)	39(1)	43(1)	-2(1)	-15(1)	-12(1)
S(1)	72(1)	62(1)	171(3)	27(1)	-60(2)	-31(1)
C(15)	58(4)	60(4)	101(7)	11(4)	-7(4)	-27(4)
C(16)	51(4)	57(4)	76(5)	-2(3)	-17(3)	-24(3)
C(17)	44(3)	42(3)	50(3)	0(2)	-18(3)	-13(2)
C(18)	47(3)	50(3)	63(4)	-7(3)	-16(3)	-17(3)
C(19)	53(4)	62(4)	83(5)	-3(3)	-29(4)	-24(3)
C(20)	73(5)	56(4)	100(6)	-6(4)	-48(4)	-25(4)
C(21)	69(5)	52(3)	84(5)	-16(3)	-34(4)	-17(3)
C(22)	48(3)	52(3)	70(4)	-10(3)	-22(3)	-13(3)
C(23)	41(3)	53(3)	56(3)	-6(3)	-17(3)	-14(3)
C(24)	44(3)	44(3)	60(4)	-1(3)	-23(3)	-9(2)
C(25)	46(3)	47(3)	47(3)	2(2)	-18(3)	-16(3)
C(26)	47(3)	47(3)	54(3)	-4(3)	-15(3)	-19(3)
C(27)	64(4)	62(4)	72(4)	9(3)	-23(4)	-32(3)
C(28)	72(5)	97(6)	94(6)	15(5)	-36(5)	-56(5)
C(29)	81(6)	75(5)	105(7)	5(5)	-24(5)	-50(5)
C(30)	75(5)	55(4)	110(7)	20(4)	-29(5)	-34(4)
C(31)	62(4)	60(4)	82(5)	12(4)	-28(4)	-25(3)
C(32)	52(3)	41(3)	47(3)	1(2)	-22(3)	-13(2)
C(33)	66(4)	49(3)	47(3)	-1(3)	-14(3)	-18(3)
C(34)	80(5)	58(4)	49(4)	0(3)	-14(3)	-12(4)
C(35)	100(6)	55(4)	63(5)	-6(3)	-44(5)	-9(4)
C(36)	86(5)	56(4)	79(5)	-5(3)	-50(5)	-22(4)
C(37)	60(4)	48(3)	59(4)	1(3)	-31(3)	-19(3)
C(38)	56(4)	65(4)	86(5)	-9(4)	-31(4)	-6(3)
C(39)	60(4)	63(4)	77(5)	8(3)	-32(4)	-20(3)
C(40)	59(4)	66(4)	66(4)	-6(3)	-23(3)	-22(3)

C(41)	92(7)	67(5)	154(10)	0(6)	-62(7)	-37(5)
C(42)	76(6)	65(5)	120(8)	-4(5)	-14(5)	-29(4)
C(43)	135(11)	105(8)	97(8)	23(7)	-7(7)	-56(8)
C(44)	167(13)	89(7)	103(8)	-23(7)	36(8)	-61(8)
C(45)	90(7)	66(5)	150(11)	6(7)	-12(7)	-24(5)
C(46)	110(8)	84(7)	161(11)	11(7)	-68(8)	-48(6)
C(51)	41(3)	44(3)	52(3)	-9(2)	-18(3)	-9(2)
C(01J)	146(13)	142(12)	142(12)	-48(10)	4(10)	-79(11)
C(01M)	114(10)	115(9)	131(11)	-24(8)	-23(8)	-29(8)
P(2)	41(1)	41(1)	44(1)	0(1)	-15(1)	-16(1)
F(2)	122(6)	87(4)	382(16)	-53(7)	-81(8)	-41(4)
O(2)	77(4)	88(4)	221(9)	4(5)	-57(5)	-46(4)
C(2)	72(5)	64(4)	72(5)	-14(3)	-36(4)	-8(4)
C(3)	83(6)	57(4)	93(6)	-25(4)	-47(5)	4(4)
C(4)	86(6)	46(3)	105(7)	-10(4)	-56(5)	-9(4)

Table 5-11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **11**.

	x	y	z	U(eq)
H(5)	4044	8175	735	79
H(7A)	6312	5232	-70	100
H(7B)	6066	6471	64	100
H(7C)	5058	6285	-192	100
H(52)	12388	3305	4334	223
H(9A)	3612	3974	2221	94
H(9B)	2766	5212	1944	94
H(9C)	2658	4911	2869	94
H(10A)	4654	4107	3248	56
H(10B)	5596	4710	2875	56
H(12)	7946	1795	-458	69
H(13)	8818	2613	-1627	85

H(14)	9914	3609	-1619	96
H(15)	10155	3797	-439	95
H(16)	9296	2987	762	74
H(18)	5393	1955	1386	65
H(19)	4510	991	1034	76
H(20)	5831	-642	327	85
H(21)	8042	-1341	10	80
H(22)	8924	-433	431	69
H(23A)	9802	58	1088	61
H(23B)	9848	1031	1452	61
H(24A)	9804	-505	2392	62
H(24B)	8401	-183	2369	62
H(25A)	8980	1381	2852	57
H(25B)	8506	549	3486	57
H(27)	4524	2129	2888	77
H(28)	3473	980	3201	95
H(29)	4208	-700	3930	99
H(30)	5974	-1216	4332	96
H(31)	7022	-56	4028	82
H(33)	4954	2391	4703	69
H(34)	4604	3298	5812	86
H(35)	5889	4190	5745	92
H(36)	7479	4159	4579	83
H(37)	7852	3240	3467	65
H(38)	7938	1397	5206	88
H(39)	9604	1642	4204	81
H(40)	11676	242	3989	77
H(41)	-2269	5415	839	116
H(42)	-1698	4398	1960	110
H(43)	-2018	5341	3054	147
H(44)	-3122	7316	3065	163
H(45)	-3802	8287	1929	137
H(46)	-3250	7349	819	132
H(48)	9955	2572	6830	165
H(49)	10558	4020	6730	221
H(50)	11213	4810	5304	325

H(01J)	11605	2010	4566	173
H(01M)	10246	1802	5773	154
H(2)	2631	6890	3362	86
H(3)	1999	8805	3049	99
H(4)	2610	9449	1755	94

Table 6-11. Torsion angles [deg] for **11**.

C(4)-C(5)-C(6)-C(1)	-1.4(11)
C(4)-C(5)-C(6)-N(1)	-179.8(7)
C(2)-C(1)-C(6)-C(5)	1.3(10)
C(51)-C(1)-C(6)-C(5)	177.2(6)
C(2)-C(1)-C(6)-N(1)	180.0(6)
C(51)-C(1)-C(6)-N(1)	-4.2(7)
C(8)-N(1)-C(6)-C(5)	176.5(7)
C(7)-N(1)-C(6)-C(5)	4.0(11)
C(8)-N(1)-C(6)-C(1)	-2.2(7)
C(7)-N(1)-C(6)-C(1)	-174.6(6)
Ni(1)-O(1)-C(8)-N(1)	153.3(5)
Ni(1)-O(1)-C(8)-C(51)	-23.9(7)
C(6)-N(1)-C(8)-O(1)	-169.5(6)
C(7)-N(1)-C(8)-O(1)	2.8(10)
C(6)-N(1)-C(8)-C(51)	7.9(7)
C(7)-N(1)-C(8)-C(51)	-179.8(6)
C(17)-P(1)-C(11)-C(16)	-175.3(5)
C(23)-P(1)-C(11)-C(16)	-64.7(5)
Ni(1)-P(1)-C(11)-C(16)	62.1(5)
C(17)-P(1)-C(11)-C(12)	6.4(6)
C(23)-P(1)-C(11)-C(12)	117.0(5)
Ni(1)-P(1)-C(11)-C(12)	-116.2(5)
C(16)-C(11)-C(12)-C(13)	1.3(9)
P(1)-C(11)-C(12)-C(13)	179.5(5)
C(11)-C(12)-C(13)-C(14)	-0.6(11)
C(12)-C(13)-C(14)-C(15)	-0.1(12)
C(13)-C(14)-C(15)-C(16)	0.1(12)

C(12)-C(11)-C(16)-C(15)	-1.2(9)
P(1)-C(11)-C(16)-C(15)	-179.5(5)
C(14)-C(15)-C(16)-C(11)	0.5(11)
C(23)-P(1)-C(17)-C(18)	147.0(5)
C(11)-P(1)-C(17)-C(18)	-104.8(5)
Ni(1)-P(1)-C(17)-C(18)	16.0(6)
C(23)-P(1)-C(17)-C(22)	-37.4(6)
C(11)-P(1)-C(17)-C(22)	70.7(6)
Ni(1)-P(1)-C(17)-C(22)	-168.5(5)
C(22)-C(17)-C(18)-C(19)	1.4(10)
P(1)-C(17)-C(18)-C(19)	177.1(6)
C(17)-C(18)-C(19)-C(20)	-2.3(11)
C(18)-C(19)-C(20)-C(21)	1.1(12)
C(19)-C(20)-C(21)-C(22)	1.0(12)
C(20)-C(21)-C(22)-C(17)	-1.9(12)
C(18)-C(17)-C(22)-C(21)	0.7(10)
P(1)-C(17)-C(22)-C(21)	-174.9(6)
C(17)-P(1)-C(23)-C(24)	-77.6(5)
C(11)-P(1)-C(23)-C(24)	172.0(4)
Ni(1)-P(1)-C(23)-C(24)	50.5(5)
P(1)-C(23)-C(24)-C(25)	-68.3(6)
C(23)-C(24)-C(25)-P(2)	74.2(6)
C(31)-C(26)-C(27)-C(28)	-0.6(11)
P(2)-C(26)-C(27)-C(28)	175.0(6)
C(26)-C(27)-C(28)-C(29)	0.2(13)
C(27)-C(28)-C(29)-C(30)	0.0(15)
C(28)-C(29)-C(30)-C(31)	0.3(15)
C(27)-C(26)-C(31)-C(30)	0.9(11)
P(2)-C(26)-C(31)-C(30)	-174.6(7)
C(29)-C(30)-C(31)-C(26)	-0.7(14)
C(37)-C(32)-C(33)-C(34)	-1.6(10)
P(2)-C(32)-C(33)-C(34)	179.6(5)
C(32)-C(33)-C(34)-C(35)	0.9(10)
C(33)-C(34)-C(35)-C(36)	0.2(11)
C(34)-C(35)-C(36)-C(37)	-0.5(11)
C(35)-C(36)-C(37)-C(32)	-0.3(10)

C(33)-C(32)-C(37)-C(36)	1.3(9)
P(2)-C(32)-C(37)-C(36)	-179.9(5)
C(40)#1-C(38)-C(39)-C(40)	0.2(13)
C(38)-C(39)-C(40)-C(38)#1	-0.2(13)
C(46)-C(41)-C(42)-C(43)	-2.0(16)
C(41)-C(42)-C(43)-C(44)	3.8(18)
C(42)-C(43)-C(44)-C(45)	-1(2)
C(43)-C(44)-C(45)-C(46)	-3(2)
C(44)-C(45)-C(46)-C(41)	4.6(19)
C(42)-C(41)-C(46)-C(45)	-2.3(18)
O(3)-S(1)-C(47)-F(1)	23(2)
O(2)-S(1)-C(47)-F(1)	-172.6(14)
O(4)-S(1)-C(47)-F(1)	-65.9(17)
O(3)-S(1)-C(47)-F(3)	162.4(14)
O(2)-S(1)-C(47)-F(3)	-33.2(17)
O(4)-S(1)-C(47)-F(3)	73.5(16)
O(3)-S(1)-C(47)-F(2)	-100.2(16)
O(2)-S(1)-C(47)-F(2)	64.2(15)
O(4)-S(1)-C(47)-F(2)	170.8(14)
C(01M)-C(48)-C(49)-C(50)	5(3)
C(48)-C(49)-C(50)-C(52)	-21(4)
C(01J)-C(52)-C(50)-C(49)	23(4)
O(1)-C(8)-C(51)-C(1)	167.7(5)
N(1)-C(8)-C(51)-C(1)	-9.8(7)
O(1)-C(8)-C(51)-C(10)	40.1(7)
N(1)-C(8)-C(51)-C(10)	-137.4(5)
O(1)-C(8)-C(51)-C(9)	-77.9(7)
N(1)-C(8)-C(51)-C(9)	104.6(6)
C(2)-C(1)-C(51)-C(8)	-177.0(7)
C(6)-C(1)-C(51)-C(8)	8.0(6)
C(2)-C(1)-C(51)-C(10)	-61.7(10)
C(6)-C(1)-C(51)-C(10)	123.3(6)
C(2)-C(1)-C(51)-C(9)	68.7(9)
C(6)-C(1)-C(51)-C(9)	-106.3(6)
Ni(1)-C(10)-C(51)-C(8)	-32.5(5)
Ni(1)-C(10)-C(51)-C(1)	-145.5(5)

Ni(1)-C(10)-C(51)-C(9)	84.7(5)
C(50)-C(52)-C(01J)-C(01M)	-9(4)
C(49)-C(48)-C(01M)-C(01J)	10(3)
C(52)-C(01J)-C(01M)-C(48)	-9(3)
C(33)-C(32)-P(2)-C(26)	-13.4(6)
C(37)-C(32)-P(2)-C(26)	167.9(5)
C(33)-C(32)-P(2)-C(25)	-121.2(5)
C(37)-C(32)-P(2)-C(25)	60.0(5)
C(33)-C(32)-P(2)-Ni(1)	112.1(5)
C(37)-C(32)-P(2)-Ni(1)	-66.7(5)
C(31)-C(26)-P(2)-C(32)	-76.2(6)
C(27)-C(26)-P(2)-C(32)	108.4(6)
C(31)-C(26)-P(2)-C(25)	30.1(7)
C(27)-C(26)-P(2)-C(25)	-145.3(5)
C(31)-C(26)-P(2)-Ni(1)	155.0(6)
C(27)-C(26)-P(2)-Ni(1)	-20.4(6)
C(24)-C(25)-P(2)-C(32)	173.6(5)
C(24)-C(25)-P(2)-C(26)	64.1(5)
C(24)-C(25)-P(2)-Ni(1)	-58.5(5)
C(6)-C(1)-C(2)-C(3)	-1.7(11)
C(51)-C(1)-C(2)-C(3)	-176.3(7)
C(1)-C(2)-C(3)-C(4)	2.5(13)
C(2)-C(3)-C(4)-C(5)	-2.7(13)
C(6)-C(5)-C(4)-C(3)	2.0(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+1

Table 7-11. Hydrogen bonds for **11** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)