Supporting Information

Mn-Electrocatalytic Oxidative C(sp^3)-H Azidation of 2-Oxindoles, *β*-Keto Esters and Azidation-Cyclization of Trypamines

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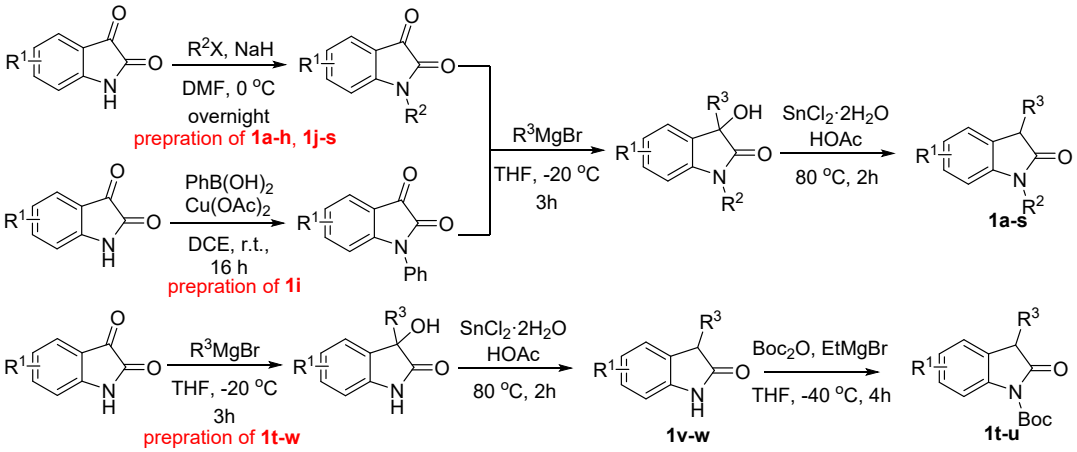
Table of Contents:

1. General considerations

THF were distilled over sodium/benzophenone under N_2 atmosphere. Toluene, Acetonitrile and Dichloromethane were distilled over CaH_2 under N_2 atmosphere. Commercially available materials and other solvents purchased from commercial suppliers were used as received. ^1H and ^{13}C NMR spectra were recorded on Bruker-400 (400 MHz) and JEOL ECZ400R (400MHz) spectrometer. Chemical shifts are recorded as δ in units of parts per million (ppm) relative to $CDCl_3$ (δ: 7.26) for the ^1H NMR and to $CDCl_3$ (δ: 77.00, the middle peak) the ^{13}C NMR measurements. ^{19}F NMR was performed on a JEOL ECZ400R (400MHz) spectrometer. High resolution mass spectra (HRMS) were obtained on the UltiMate 3000 spectrometer. HRMS were reported in units of mass of charge ratio (*m/z*). Enantiomeric excess values were determined by HPLC analysis on Agress P1100. X-ray crystallography analysis was performed on BrukerSmart APEXIICCD instrument Mo-Kα diffractionmeter. Visualization was performed using a UV lamp. Flash chromatography separations were performed on 200-300 mesh silica gel.

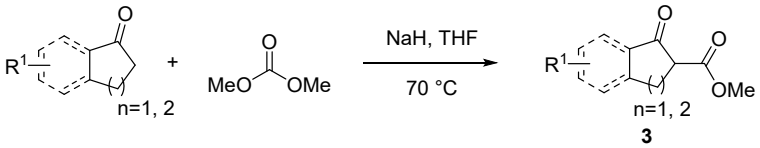
Electrodes cleaning procedure: (1) To clean the Pt electrode, immerse it in concentrated nitric acid (~70%) for 5 minutes, followed by rinsing it with deionized water and then acetone. Afterward, dry it in a vacuum drying oven at 40°C; (2) To clean the C electrode, rinse it with deionized water and then acetone, and subsequently, dry it in a vacuum drying oven at 40°C. After that, sand it with sandpaper for additional cleaning. Due to their inexpensiveness, C electrodes are typically disposed of after being used three or four times.

2. Preparation of substrates



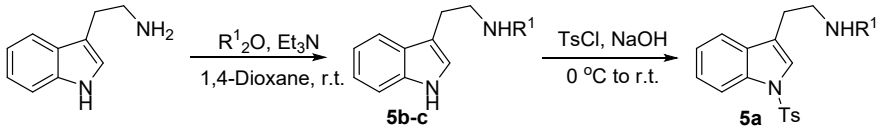
Scheme S1 Synthesis of compounds **1**.

Compounds **1** were synthesized via the synthetic routes in scheme S1, according to the literatures known procedures.[1]



Scheme S2 Synthesis of compounds **3**.

Compounds **3** were synthesized via the synthetic route in scheme S2, according to the literatures known procedures.[2]

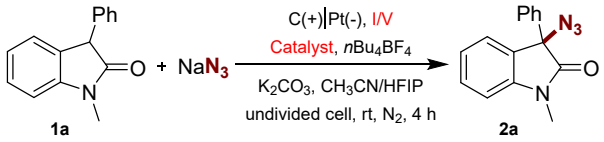


Scheme S3. Synthesis of compounds **5**.

Compounds **5** were synthesized via the synthetic routes in scheme S3, according to the literatures known procedures.[3]

3. Optimization of the racemic reaction conditions

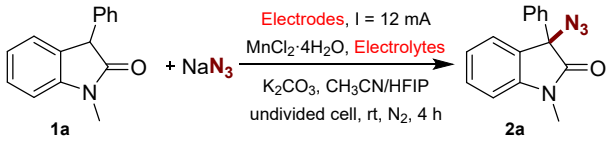
Table S1 Optimization of the catalysts and current or voltage[a]



Entry	Catalyst	Current I/Voltage V	Yield[b]
1	***$MnCl_2·4H_2O$***	***12mA***	***82***
2	$MnCl_2·4H_2O$	5mA	64
3	$MnCl_2·4H_2O$	15mA	72
4	$MnCl_2·4H_2O$	2.3 V	67
5	$MnCl_2·4H_2O$	1.5 V	54
6	$Mn(OAc)_2·4H_2O$	12mA	78
7	$MnBr_2$	12mA	74
8	MnF_2	12mA	72
9	CuI	12mA	25
10	$FeCl_3$	12mA	trace

[a] Standard conditions: graphite plate anode, platinum plate cathode, **1a** (0.2 mmol), NaN_3 (3.0 equiv.), catalyst (5.0 mol%), nBu$_4$BF$_4$ (2.0 equiv.), K_2CO_3 (2.0 equiv.), CH_3CN/HFIP (4.0/0.1 mL), current or voltage, room temperature, N_2, 4h, undivided cell. [b] Isolated yield.

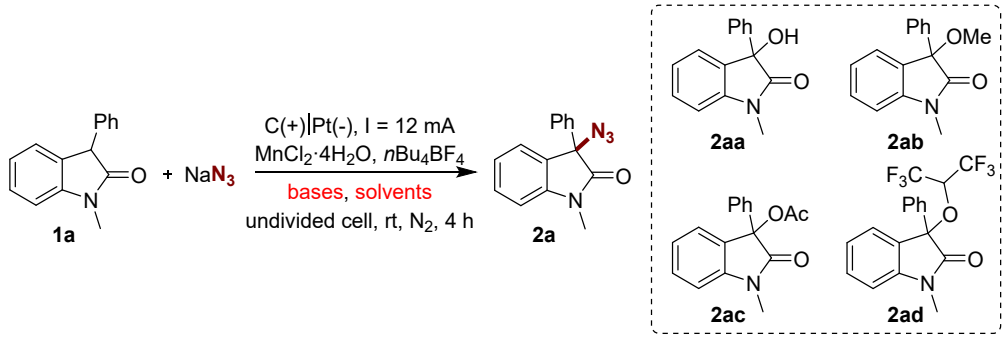
Table S2 Optimization of the electrodes and electrolytes[a]



Entry	Anode	Cathode	Electrolyte	Yield[b]
1	***graphite plate***	***platinum plate***	***nBu$_4$BF$_4$***	***82***
2	graphite rod	platinum plate	*n*Bu$_4$BF$_4$	65
3	graphite cloth	platinum plate	*n*Bu$_4$BF$_4$	64
4	RVC	platinum plate	*n*Bu$_4$BF$_4$	62
5	platinum plate	graphite plate	*n*Bu$_4$BF$_4$	trace
6	graphite plate	graphite plate	*n*Bu$_4$BF$_4$	24
7	platinum plate	platinum plate	*n*Bu$_4$BF$_4$	trace
8	graphite plate	platinum plate	*n*LiClO$_4$	74
9	graphite plate	platinum plate	*n*Bu$_4$NPF$_6$	70
10	graphite plate	platinum plate	*n*Bu$_4$NClO$_4$	65
11	graphite plate	platinum plate	*n*Bu$_4$NBr	15

[a] Standard conditions: electrodes, constant current = 12mA (j = 12 mA cm^{-1}), **1a** (0.2 mmol), NaN_3 (3.0 equiv.), $MnCl_2·4H_2O$ (5.0 mol%), electrolytes (2.0 equiv.), K_2CO_3 (2.0 equiv.), CH_3CN/HFIP (4.0/0.1 mL), room temperature, N_2, 4h, undivided cell. [b] Isolated yield.

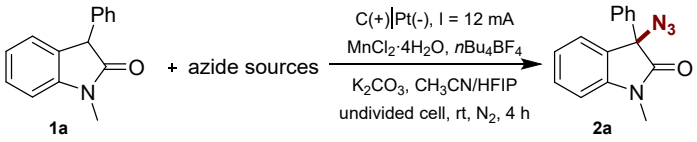
Table S3 Optimization of the bases and solvents[a]



Entry	Bases	Solvent (4 ml)	H^+ source (0.1 ml)	Yield[b]
1	***K_2CO_3***	***CH_3CN***	***HFIP***	***82***
2	K_2CO_3	CH_3CN	HFIP (1ml)	16 (with **2ad** in 32%)
3	K_2CO_3	CH_3CN	H_2O	32 (with **2aa** in 15%)
4	K_2CO_3	CH_3CN	MeOH	21 (with **2ab** in 22%)
5	K_2CO_3	CH_3CN	HOAc	25 (with **2ac** in 42%)
6	K_2CO_3	DMF	HFIP	26
7	K_2CO_3	DMSO	HFIP	trace
8	K_2CO_3	DCE	HFIP	trace
9	Na_2CO_3	CH_3CN	HFIP	68
10	Cs_2CO_3	CH_3CN	HFIP	72
11	$KHCO_3$	CH_3CN	HFIP	75
12	*t*BuOK	CH_3CN	HFIP	64
13	NEt_3	CH_3CN	HFIP	23

[a] Standard conditions: graphite plate anode, platinum plate cathode, constant current = 12mA (j = 12 mA cm^{-1}), **1a** (0.2 mmol), NaN_3 (3.0 equiv.), $MnCl_2·4H_2O$ (5.0 mol%), nBu_4BF_4 (2.0 equiv.), base (2.0 equiv.), solvent/H^+ source (4.0/0.1 mL), room temperature, N_2, 4h, undivided cell. [b] Isolated yield.

Table S4 Optimization of the azide sources[a]

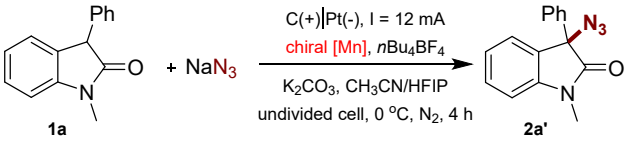


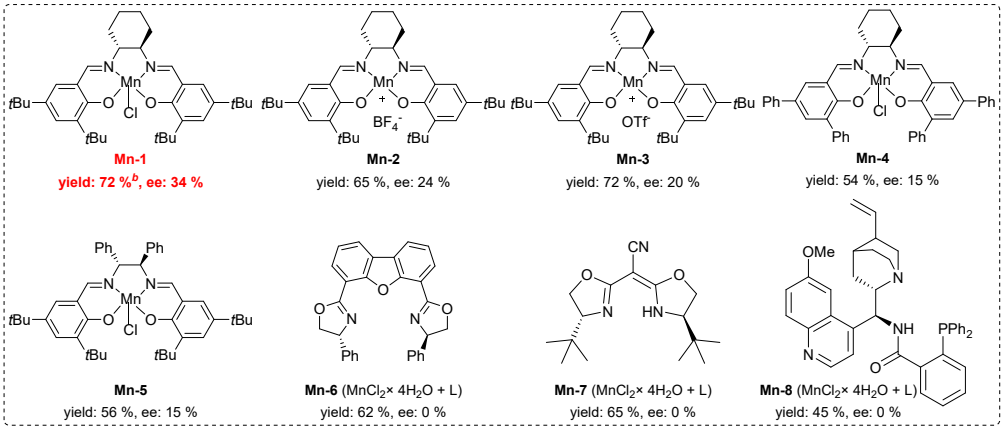
Entry	Azide source	Yield[b]
1	***NaN_3***	***82***
2	$TMSN_3$	72
3	TsN_3	trace
4	Zhdankin reagent	45

[a] Standard conditions: graphite plate anode, platinum plate cathode, constant current = 12mA (j = 12 mA cm^{-1}), **1a** (0.2 mmol), azide source (3.0 equiv.), $MnCl_2·4H_2O$ (5.0 mol%), $n$$Bu_4BF_4$ (2.0 equiv.), K_2CO_3 (2.0 equiv.), CH_3CN/HFIP (4.0/0.1 mL), room temperature, N_2, 4h, undivided cell. [b] Isolated yield.

4. Optimization of the enantioselective reaction conditions

Table S5 Optimization of the enantioselective reaction conditions[a]





[a] Standard conditions: graphite plate anode, platinum plate cathode, constant current = 12mA (j = 12 mA cm^{-1}), **1a** (0.2 mmol), NaN_3 (3.0 equiv.), chiral [Mn] (10.0 mol%), $n$$Bu_4BF_4$ (2.0 equiv.), K_2CO_3 (2.0 equiv.), CH_3CN /HFIP (4.0/0.1 mL), 0 °C, N_2, 4h, undivided cell. [b] Isolated yield.

5. General procedures characterization data

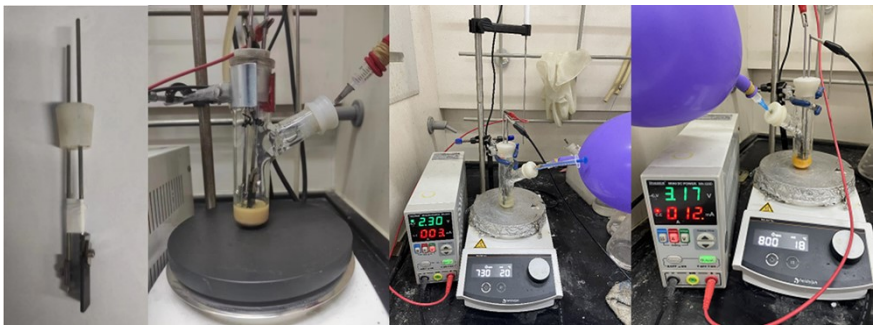
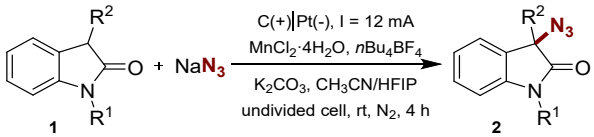


Fig. S1 Reaction device diagram.

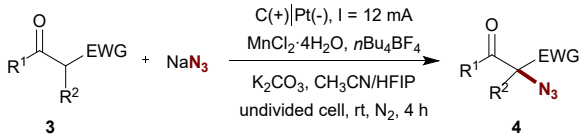
5.1 General procedures of azidation of 2-oxindoles



Inside of an oven-dried 20 mL vial was charged with substrate **1** (0.2 mmol), $MnCl_2$•$4H_2O$ (0.01 mmol, 1.9 mg, 0.05 equiv.), Bu_4NBF_4 (0.4 mmol, 131.7 mg, 2.0 equiv.), K_2CO_3 (0.2 mmol, 27.6 mg, 2.0 equiv.), and NaN_3 (0.6 mmol, 39.0 mg, 3.0 equiv.). CH_3CN (4.0 mL) and HFIP (0.1 mL) were added and stirred with a stir bar to form a homogeneous solution. The vial was equipped with graphite plate (1.0 × 1.0 cm^2) as anode and platinum plate (1.0 × 1.0 cm^2) as cathode with the electric connector under N_2 atmosphere. The vial was stirred and electrolyzed at constant current of 12 mA for 4 hours at room temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by ethyl acetate. The combined organic layer was washed with water (10 mL × 3) and brine, and then dried over with anhydrous Na_2SO_4. After concentrated under *vacuo*, the crude product was purified by silica gel column chromatography to afford the desired compounds **2**.

CAUTION: NaN_3 is a poisonous and explosive compound. After treatment of the reaction, the aqueous phase was treated with NaClO solution to remove the azide.

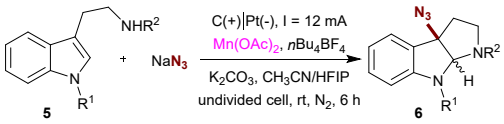
5.2. General procedures of azidation of *β*-keto esters



Inside of an oven-dried 20 mL vial was charged with substrate **3** (0.2 mmol), $MnCl_2$•$4H_2O$ (0.01 mmol, 1.9 mg, 0.05 equiv.), Bu_4NBF_4 (0.4 mmol, 131.7 mg, 2.0 equiv.), K_2CO_3 (0.2 mmol, 27.6 mg, 2.0 equiv.), and NaN_3 (0.6 mmol, 39.0 mg, 3.0 equiv.). CH_3CN (4.0 mL) and HFIP (0.1 mL) were added and stirred with a stir bar to form a homogeneous solution. The vial was equipped with graphite plate (1.0 × 1.0 cm^2) as anode and platinum plate (1.0 × 1.0 cm^2) as cathode with the electric connector under N_2 atmosphere. The vial was stirred and electrolyzed at constant current of 12 mA for 4 hours at room temperature or high temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by ethyl acetate. The combined organic layer was washed with water (10 mL × 3) and brine, and then dried over with anhydrous

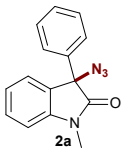
Na_2SO_4. After concentrated under *vacuo*, the crude product was purified by silica gel column chromatography to afford the desired compounds **4**.

5.3 General procedures of azidation-cyclization of trypamines

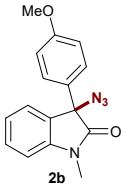


Inside of an oven-dried 20 mL vial was charged with substrate **5** (0.2 mmol), $Mn(OAc)_2$ (0.01 mmol, 1.7 mg, 0.05 equiv.), Bu_4NBF_4 (0.4 mmol, 131.7 mg, 2.0 equiv.), K_2CO_3 (0.2 mmol, 27.6 mg, 2.0 equiv.), and NaN_3 (0.6 mmol, 39.0 mg, 3.0 equiv.). CH_3CN (4.0 mL) and HFIP (0.1 mL) were added and stirred with a stir bar to form a homogeneous solution. The vial was equipped with graphite plate (1.0 × 1.0 cm^2) as anode and platinum plate (1.0 × 1.0 cm^2) as cathode with the electric connector under N_2 atmosphere. The vial was stirred and electrolyzed at constant current of 12 mA for 6 hours at room temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by ethyl acetate. The combined organic layer was washed with water (10 mL × 3) and brine, and then dried over with anhydrous Na_2SO_4. After concentrated under *vacuo*, the crude product was purified by silica gel column chromatography to afford the desired compounds **6**.

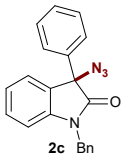
5.4 Characterization data



3-azido-1-methyl-3-phenylindolin-2-one (2a): Purified by column chromatography (hexane/ethyl acetate = 5:1, Rf = 0.40). Colorless oil (43.2 mg, 82 %).^{1}H NMR (400MHz, $CDCl_3$) δ: 7.54 – 7.23 (m, 7H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H), 3.27(s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 143.4, 136.3, 130.3, 128.8 (2×C), 128.8, 128.2, 126.5 (2×C), 125.1, 123.5, 108.9, 69.6, 26.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{12}N_4ONa$ 287.0903; Found 287.0897.

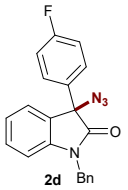


3-azido-3-(4-methoxyphenyl)-1-methylindolin-2-one (2b): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.70). Colorless oil (46.5 mg,78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (t, *J* = 7.9 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.91 – 6.87 (m, 2H), 3.79 (s, 3H), 3.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 143.4, 136.3, 130.3, 128.8 (2×C), 128.8, 128.3, 128.2, 126.5 (2×C), 125.1, 123.5, 108.9, 69.6, 26.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{14}N_4O_2Na$ 317.1009; Found 317.1021.



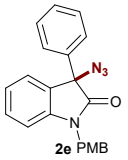
2c

3-azido-1-benzyl-3-phenylindolin-2-one (2c): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf= 0.60). Colorless oil (48.2 mg, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 (q, *J* = 8.2, 7.7 Hz, 3H), 7.36 – 7.26 (m, 7H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.31 – 4.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.7, 142.5, 136.4, 135.0, 130.2, 128.9 (2×C), 128.8 (2×C), 128.8, 128.4, 127.8 (2×C), 127.2, 126.5 (2×C), 125.1, 123.5, 110.0, 69.8, 44.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}N_4ONa$ 363.1216; Found 363.1218.



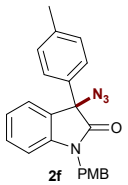
2d

3-azido-1-benzyl-3-(4-fluorophenyl)indolin-2-one (2d): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.80). Yellow oil (54.3 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 – 7.39 (m, 2H), 7.38 – 7.24 (m, 7H), 7.13 (t, *J* = 7.8 Hz, 3H), 7.08 (t, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 5.05 – 4.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 164.2, 161.7, 142.5, 135.0, 132.1(d, J = 3.0 Hz), 130.5, 128.9 (2×C), 128.6 (d, J = 8.2 Hz), 128.0, 127.9, 127.2 (2×C), 125.2, 123.7, 116.0, 115.8, 110.1, 69.3, 44.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.50. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{15}FN_4ONa$ 381.1122; Found 381.1114.



2e

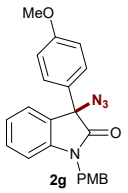
3-azido-1-(4-methoxybenzyl)-3-phenylindolin-2-one (2e): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.70). Colorless oil (50.4 mg, 67 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 – 7.40 (m, 3H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 6.9 Hz, 2H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.84 (t, *J* = 4.0 Hz,1H), 4.92 (dd, *J* = 16.0, 24.0 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.7, 159.2, 142.5, 136.4, 130.2, 128.9 (2×C), 128.8, 128.7 (2×C), 128.5, 127.1, 126.5 (2×C), 125.2, 123.5, 114.2 (2×C), 110.0, 69.8, 55.2, 43.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}N_4O_2Na$ 393.1322; Found 393.1316.



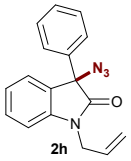
2f

3-azido-1-(4-methoxybenzyl)-3-(p-tolyl)indolin-2-one (2f): Purified by column chromatography (hexane/ethyl acetate = 5:1, Rf = 0.80). Colorless oil (55.8 mg, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 – 7.16 (m, 8H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.89 – 6.81 (m, 3H), 4.96 – 4.81 (m, 2H), 3.78 (s, 3H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.8, 159.2, 142.5, 138.8, 133.4, 130.2, 129.6

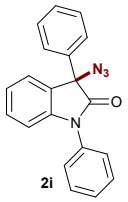
(2×C), 128.7 (2×C), 128.6, 127.1, 126.4 (2×C), 125.1, 123.5, 114.2 (2×C), 110.0, 69.7, 55.2, 43.6, 21.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{21}N_4O_2$ 385.1659; Found 385.1663.



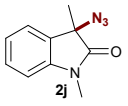
3-azido-1-(4-methoxybenzyl)-3-(4-methoxyphenyl)indolin-2-one (2g): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.60). Colorless oil (67.2 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 – 7.34 (m, 2H), 7.29 (ddd, *J* = 15.7, 7.8, 1.4 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.14–7.06 (m, 1H), 6.94–6.88 (m, 2H), 6.84 (t, *J* = 8.1 Hz, 3H), 4.99–4.80 (m, 2H), 3.80 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.8, 159.9, 159.2, 142.5, 130.2, 128.6 (2×C), 128.5, 128.2, 128.0 (2×C), 127.1, 125.1, 123.4, 114.3 (2×C), 114.2 (2×C), 110.0, 69.4, 55.3, 55.2, 43.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}N_4O_3Na$ 423.1428; Found 423.1436.



1-allyl-3-azido-3-phenylindolin-2-one (2h): Purified by column chromatography (hexane/ethyl acetate = 10:1, Rf = 0.50). Colorless oil (36.4 mg, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 – 7.42 (m, 2H), 7.42 – 7.34 (m, 4H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 5.87 (ddt, *J* = 17.6, 10.3, 5.2 Hz, 1H), 5.31 – 5.17 (m, 2H), 4.50 – 4.32 (m, 2H) .^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.2, 142.5, 136.3, 130.6, 130.2, 128.8 (2×C), 128.7, 128.2, 126.4 (2×C), 125.1, 123.4, 117.9, 109.8, 69.7, 42.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{14}N_4ONa$ 313.1060; Found 313.1065.

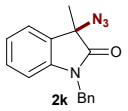


3-azido-1,3-diphenylindolin-2-one (2i): Purified by column chromatography (hexane/ethyl acetate = 5:1, R_f = 0.60). Colorless oil (60 mg, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 7.6 Hz, 4H), 7.50 – 7.37 (m, 7H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.9, 143.3, 136.5, 133.6, 130.2, 129.7 (2×C), 129.0 (2×C), 128.9, 128.5, 128.2, 126.5 (2×C), 126.4 (2×C), 125.4, 124.0, 110.2, 69.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{14}N_4ONa$ 349.1060; Found 349.1053.

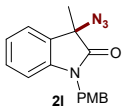


3-azido-1,3-dimethylindolin-2-one (2j): Purified by column chromatography (hexane/ethyl acetate = 10:1, Rf = 0.40). Colorless oil (21.6 mg, 52 %). ^{1}H NMR (400 MHz, CDCl3) δ: 7.39 – 7.30 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 1.68 (s, 3H). ^{13}C

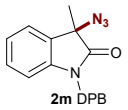
NMR (101 MHz, $CDCl_3$) δ: 174.9, 142.8, 130.1, 128.7, 123.5, 123.3, 108.7, 63.2, 26.4, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{10}N_4ONa$ 225.0747; Found 225.0740.



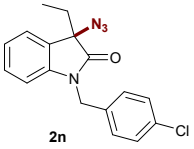
3-azido-1-benzyl-3-methylindolin-2-one (2k): Purified by column chromatography (hexane/ethyl acetate = 10:1, Rf = 0.40). Colorless oil (56.3 mg, 47 %). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37 – 7.30 (m, 3H), 7.28 (d, *J* = 6.9 Hz, 3H), 7.25 (d, *J* = 9.9 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 4.92 (s, 2H), 1.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.1, 141.9, 135.1, 130.0, 128.9 (2×C), 128.8, 127.8, 127.2 (2×C), 123.6, 123.3, 109.8, 63.4, 43.9, 21.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{14}N_4ONa$ 301.1060; Found 301.1066.



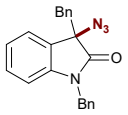
3-azido-1-(4-methoxybenzyl)-3-methylindolin-2-one (2l): Purified by column chromatography (hexane/ethyl acetate = 8:1, Rf = 0.40). Colorless oil (42.3 mg, 68 %). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.16 – 7.06 (m, 2H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 4.92 (d, *J* = 1.9 Hz, 2H), 2.39 (s, 3H), 1.77 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.0, 142.1, 135.7, 132.5, 130.7, 130.0, 128.7, 127.6, 126.3 (2×C), 123.5, 123.3, 110.0, 63.3, 42.1, 21.6, 19.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}N_4O_2Na$ 331.1165; Found 331.1162.



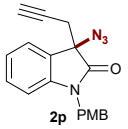
3-azido-1-benzhydryl-3-methylindolin-2-one (2m): Purified by column chromatography (hexane/ethyl acetate = 8:1, Rf = 0.40). Colorless oil (40.1 mg, 57 %). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44 – 7.20 (m, 11H), 7.10 – 7.01 (m, 2H), 6.99 (s, 1H), 6.52 – 6.40 (m, 1H), 1.73 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.2, 141.6, 137.2, 136.9, 129.5, 128.7 (2×C), 128.6 (2×C), 128.3 (2×C), 128.2 (2×C), 127.9 (2×C), 127.1, 123.5, 123.1, 112.5, 63.0, 58.5, 21.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}N_4ONa$ 377.1371; Found 377.1375.



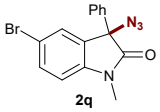
3-azido-1-(4-chlorobenzyl)-3-ethylindolin-2-one (2n): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.50). Colorless oil (40.6 mg, 61 %). 1H NMR (400 MHz, CDCl3) δ:7.31 (dd, *J* = 8.0, 6.1 Hz, 3H), 7.24 (t, *J* = 7.8 Hz, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 4.99 – 4.77 (m, 2H), 2.16 (d, *J* = 14.1, 7.1 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.7, 142.6, 138.0, 133.9, 130.1, 129.2 (2×C), 128.8 (2×C), 127.0, 124.2, 123.6, 109.6, 67.5, 43.5, 28.8, 8.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{15}ClN_4ONa$ 349.0827; Found 349.0830.



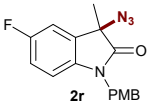
3-azido-1,3-dibenzylindolin-2-one (2o): Purified by column chromatography (hexane/ethyl acetate = 10:1, Rf = 0.60). Colorless oil (47.4 mg, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 7.1 Hz, 1H), 7.24 – 7.05 (m, 8H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.70 (d, *J* = 6.8 Hz, 2H), 6.45 (d, *J* = 7.8 Hz, 1H), 4.75 (m, 2H), 3.43 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ:173.9, 142.7, 134.5, 133.1, 130.5 (2×C), 130.1, 128.7 (2×C), 128.2 (2×C), 127.4, 127.2, 126.6 (2×C), 126.2, 124.5, 123.0, 109.8, 67.7, 43.8, 41.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}N_4ONa$ 377.1371; Found 377.1375.



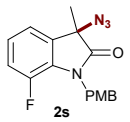
3-azido-1-(4-methoxybenzyl)-3-(prop-2-yn-1-yl)indolin-2-one (2p): Purified by column chromatography (hexane/ethyl acetate = 6:1, Rf = 0.40). Colorless oil (38.3 mg, 57 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.3 Hz, 1H), 7.33 – 7.18 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.06 – 4.67 (m, 2H), 3.77 (s, 3H), 3.14 – 2.70 (m, 2H), 1.95 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.2, 159.2, 142.6, 130.5 (2×C), 128.8 (2×C), 127.0, 126.0, 124.4, 123.3, 114.1 (2×C), 109.8, 72.0, 64.8, 55.2, 43.6, 26.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}N_4O_2Na$ 355.1165; Found 355.1165.



3-azido-1-benzhydryl-3-methylindolin-2-one (2q): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.50). Colorless oil (60.4 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.40 (d, *J* = 2.5 Hz, 6H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.2, 142.3, 135.7, 133.2 (2×C), 130.4, 129.1 (2×C), 128.3, 126.4 (2×C), 116.1, 110.4, 69.4, 26.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{11}N_4OBrNa$ 365.0008; Found 365.0013.

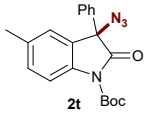


3-azido-5-fluoro-1-(4-methoxybenzyl)-3-methylindolin-2-one (2r): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.80). Colorless oil (44.3 mg, 67 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (d, *J* = 8.7 Hz, 2H), 7.07 (dd, *J* = 7.4, 2.5 Hz, 1H), 6.93 (td, *J* = 8.7, 2.5 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.68 (dd, *J* = 8.6, 4.1 Hz, 1H), 4.83 (dd, *J* = 2.6 Hz, 2H), 3.77 (s, 3H), 1.71 (s, 3mH). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.0, 159.5 (d, *J* = 7.9 Hz), 159.4, 137.9, 130.5 (d, *J* = 7.9 Hz), 128.7 (2×C), 126.9, 116.4 (d, *J* = 23.8 Hz), 114.5 (2×C), 111.9 (d, *J* = 25.0 Hz), 110.7 (d, *J* = 8.0 Hz), 63.4, 55.4, 43.7, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -118.84. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{15}FN_4O_2Na$ 349.1071; Found 349.1066.



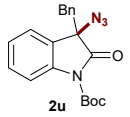
2s

3-azido-7-fluoro-1-(4-methoxybenzyl)-3-methylindolin-2-one (2s): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.80). Brown oil (46.2 mg, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 – 7.22 (m, 2H), 7.14 – 7.08 (m, 1H), 7.06 – 7.00 (m, 2H), 6.84 (dd, *J* = 8.4, 1.6 Hz, 2H), 4.98 (s, 2H), 3.77 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.8, 159.2, 148.7, 146.3, 131.7 (d, *J* = 2.7 Hz), 129.0, 128.5 (2×C), 124.1 (d, *J* = 6.2 Hz), 119.5 (d, *J* = 3.0 Hz), 118.1(d, *J* = 20.0 Hz), 114.0 (2×C), 63.2, 55.2, 45.0, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -132.15. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{15}FN_4O_2Na$ 349.1071; Found 349.1068.



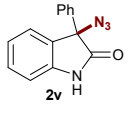
2t

tert-butyl 3-azido-5-methyl-2-oxo-3-phenyl-2,3-dihydro-1H-indene-1-carboxylate (2t): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.40). Yellow oil (63.5 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (dd, *J* = 8.5, 2.8 Hz, 1H), 7.38 (dd, *J* = 7.2, 3.3 Hz, 5H), 7.29 – 7.21 (m, 1H), 7.10 (s, 1H), 2.36 (s, 3H), 1.63 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 148.8, 137.3, 136.4, 135.2, 131.2, 129.0, 128.9 (2×C), 126.9, 126.7 (2×C), 125.5, 115.5, 85.0, 70.0, 28.0 (3×C), 21.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_4O_3Na$ 387.1428; Found 387.1423.



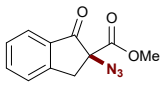
2u

tert-butyl (R)-3-azido-3-benzyl-2-oxoindoline-1-carboxylate (2u): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.60). Yellow colorless oil (39.3 mg, 54 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 8.2 Hz, 1H), 7.31 (td, J = 7.8, 1.6 Hz, 1H), 7.21 – 7.12 (m, 4H), 7.12 – 7.05 (m, 1H), 6.95 – 6.85 (m, 2H), 3.44 – 3.12 (m, 2H), 1.59 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.0, 148.3, 139.5, 132.5, 130.30 (2×C), 130.27, 128.1 (2×C), 127.4, 125.1, 124.6, 124.5, 115.2, 84.77, 67.5, 42.8, 28.0 (3×C). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_4O_3Na$ 387.1428; Found 387.1434.



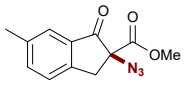
2v

3-azido-3-phenylindolin-2-one (2v): Purified by column chromatography (hexane/ethyl acetate = 2:1, Rf = 0.60). Colorless oil (28.3 mg, 56 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.38 (s, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.36 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.4, 140.7, 136.1, 130.5, 128.9 (2×C), 128.9, 128.8, 126.4 (2×C), 125.3, 123.6, 111.2, 70.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{10}F_4ONa$ 273.0747; Found 273.0751.



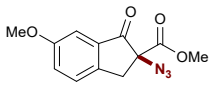
4a

methyl 2-azido-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4a): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.40). Yellow solid (35.3 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.37 (m, 2H), 3.75 (s, 3H), 3.33 (dd, *J* = 258.0, 17.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.2, 168.7, 151.9, 136.4, 132.7, 128.3, 126.3, 125.4, 70.0, 53.3, 38.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{10}O_3Na$ 254.0536; Found 254.0538.



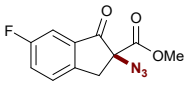
4b

methyl 2-azido-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4b): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.80). Yellow solid (40.3 mg, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 3H), 3.30 (dd, *J* = 252.0, 17.3 Hz, 2H), 2.43 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.4, 169.0, 149.4, 138.6, 137.8, 133.1, 126.1, 125.5, 70.5, 53.5, 38.2, 21.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{11}N_3O_3Na$ 268.0693; Found 268.0700.



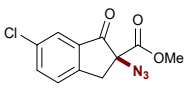
4c

methyl 2-azido-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4c): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.40). White solid (46.4 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 8.5 Hz, 1H), 7.25 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.21 (s, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.26 (dd, *J* = 252.3, 17.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.2, 168.9, 160.0, 144.9, 134.1, 127.1, 125.9, 106.3, 70.8, 55.6, 53.4, 37.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{11}N_3O_4Na$ 284.0642; Found 284.0649.



4d

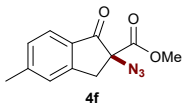
methyl 2-azido-6-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4d): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.50). White solid (24.6 mg, 49 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 – 7.36 (m, 3H), 3.81 (s, 3H), 3.64 (d, *J* = 17.1 Hz, 1H), 3.01 (d, *J* = 17.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.56 (d, *J* = 2.3 Hz), 162.7 (d, *J* = 250.4 Hz), 134.7 (d, *J* = 8.1 Hz), 127.9 (d, *J* = 7.9 Hz), 124.31 (d, *J* = 23.7 Hz), 124.3 (d, *J* = 23.7 Hz), 111.4 (d, *J* = 22.8 Hz), 70.8, 53.6, 38.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.29. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_8FN_3O_3Na$ 272.0442; Found 272.0443.



4e

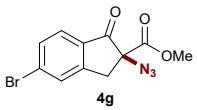
methyl 2-azido-6-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4e): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.80). White solid (32.3 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 7.9, 1.8 Hz,

1H), 3.80 (s, 3H), 3.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.0, 168.5, 153.4, 143.2, 131.3, 129.3, 126.7, 126.6, 70.1, 53.6, 38.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_8ClN_3O_3Na$ 288.0146; Found 288.0152.



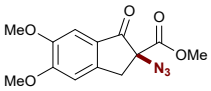
4f

methyl 2-azido-5-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4f): Purified by column chromatography (hexane/ethyl acetate = 8:1, Rf = 0.40). Coloeless oil (38.7 mg, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 3.29 (dd, *J* = 256.9, 17.4 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.6, 169.0, 152.5, 148.2, 130.5, 129.7, 126.7, 125.3, 70.3, 53.4, 38.2, 22.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{11}N_3O_3Na$ 268.0693; Found 268.0688.



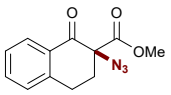
4g

methyl 2-azido-5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4g): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.40). White solid (28.3 mg, 46 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 – 7.65 (m, 2H), 7.60 (dd, *J* = 8.2, 1.5 Hz, 1H), 3.81 (s, 3H), 3.65 (d, *J* = 17.4 Hz, 1H), 3.02 (d, *J* = 17.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.0, 168.5, 153.4, 143.2, 131.3, 129.3, 126.7, 126.6, 70.1, 53.6, 38.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_8BrN_3O_3Na$ 331.9641; Found 331.9635.



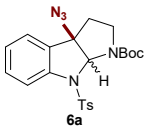
4h

methyl 2-azido-5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4h): Purified by column chromatography (hexane/ethyl acetate = 2:1, Rf = 0.40). White solid (44.7 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (s, 1H), 6.86 (s, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.79 (s, 3H), 3.24 (dd, *J* = 255.3, 17.1 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.5, 169.2, 156.9, 150.1, 147.9, 125.5, 107.1, 105.3, 70.5, 56.4, 56.1, 53.4, 38.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{13}N_3O_5Na$ 314.0747; Found 314.0753.



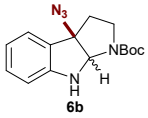
4i

methyl 2-azido-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4i): Purified by column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.40). Coloeless oil (25.6 mg, 52 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.07 (ddd, *J* = 17.4, 9.7, 4.7 Hz, 1H), 2.88 (dt, *J* = 17.1, 5.2 Hz, 1H), 2.56 (ddd, *J* = 14.1, 9.5, 4.6 Hz, 1H), 2.16 (dt, *J* = 13.9, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.1, 168.8, 143.3, 134.4, 129.5, 128.6, 128.2, 127.0, 70.7, 53.0, 31.1, 24.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{11}N_3O_3Na$ 268.0693; Found 268.0694.



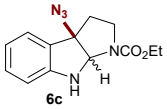
6a

***tert*-butyl 3a-azido-8-tosyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (6a):** Purified by column chromatography (hexane/ethyl acetate = 6:1, Rf = 0.40). White solid (58.3 mg, dr = 1.8:1, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 8.1 Hz, 3.7H), 7.67 (d, *J* = 7.9 Hz, 3.6H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.44 (ddd, *J* = 8.2, 5.6, 2.9 Hz, 2H), 7.39 – 7.32 (m, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 3.7H), 7.18 (s, 3.9H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.55 (s, 1H), 5.39 (s, 1.8H), 3.48 – 3.19 (m, 3.7H), 3.18 – 2.92 (m, 2H), 2.37 (s, 3.7H), 2.33 (s, 5.5H), 2.08 (s, 3H), 2.03 (s, 2H), 1.45 (s, 16.2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.9, 155.8, 145.3, 145.1, 140.0, 139.1, 135.0, 134.4, 131.7, 130.9, 130.2 (2×C), 130.0 (3.6×C), 129.8, 129.7, 127.4 (3.6×C), 127.3 (2×C), 125.3, 125.2, 124.4, 123.8, 116.9, 115.8, 84.4, 83.7, 79.6, 79.5, 72.2, 72.1, 38.7, 36.5, 35.6, 31.9, 28.5, 28.3, 21.7 (3×C), 21.6 (5.4×C). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}N_5O_4S$ 456.1700; Found 456.1708.



6b

***tert*-butyl 3a-azido-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2*H*)-carboxylate (6b):** Purified by columnchromatography (hexane/ethyl acetate = 4:1, Rf = 0.40). Coloeless oil (21.1 mg, dr = 1:1, 35 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (t, *J* = 4.0 Hz, 2H), 7.21 (dd, *J* = 7.9, 2.7 Hz, 2H), 6.85 (q, *J* = 7.8 Hz, 2H), 6.70 (d, *J* = 7.9 Hz, 2H), 5.31 (s, 1H), 5.24 (s, 1H), 5.18 (s, 0.94H), 4.72 (s, 0.80H), 3.71 (dt, *J* = 48.2, 9.3 Hz, 2H), 3.09 (dtd, *J* = 14.7, 10.6, 6.2 Hz, 2H), 2.41 (dt, *J* = 9.3, 4.9 Hz, 2H), 2.37 – 2.28 (m, 2H), 1.53 (s, 9H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.4, 153.4, 150.0, 149.7, 131.1, 131.0, 125.2, 125.1, 124.0, 123.9, 119.8, 119.4, 110.5, 110.4, 80.9, 80.6, 80.5, 77.3, 76.4, 45.8, 45.4, 35.2, 35.0, 28.7 (3×C), 28.5 (3×C). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H1_9N_5O_2Na$ 324.1431; Found 324.1426.

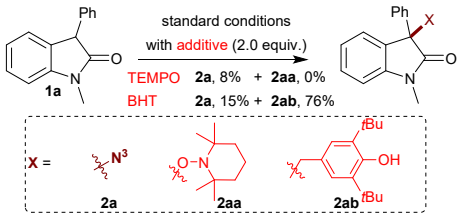


6c

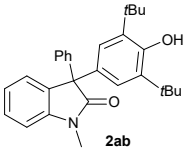
ethyl 3a-azido-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2*H*)-carboxylate (6c): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.40). Colorless oil (21.3 mg, dr = 1.4:1, 39 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, *J* = 4.1 Hz, 2.8H), 7.24 (d, *J* = 9.6 Hz, 2.8H), 6.86 (q, *J* = 6.9 Hz, 2H), 6.70 (d, *J* = 7.9 Hz, 2H), 5.34 (s, 1.3H), 5.31 (s, 1.0H), 5.21 (s, 1.2H), 4.79 (s, 0.8H), 4.22 (dd, *J* = 7.1, 3.8 Hz, 2H), 4.14 (dd, 2.9H), 3.81 (t, *J* = 9.5 Hz, 1.0H), 3.71 (t, *J* = 9.6 Hz, 1.4H), 3.19 – 3.13 (m, 1.0H), 3.11 (dd, *J* = 7.4, 3.3 Hz, 1.4H), 2.43 (q, *J* = 7.5 Hz, 2.8H), 2.40 – 2.26 (m, 2.0H), 1.34 (t, *J* = 7.1 Hz, 3.0H), 1.26 (t, *J* = 5.7 Hz, 4.4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.1, 155.1, 149.8, 131.0, 131.0, 124.9, 123.8, 123.7, 119.7, 119.4, 110.4, 110.3, 80.7, 80.3, 76.2, 61.6, 61.4, 60.4, 45.7, 45.5, 35.1, 35.0, 29.7, 21.0, 14.8, 14.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{15}N_5O_2Na$ 296.1118; Found 296.1122.

6. Mechanism studies

6.1 Radical trapping experiment



Inside of an oven-dried 20 mL vial was charged with substrate **5** (0.2 mmol), $Mn(OAc)_2$ (0.01 mmol, 1.7 mg, 0.05 equiv.), Bu_4NBF_4 (0.4 mmol, 131.7 mg, 2.0 equiv.), K_2CO_3 (0.2 mmol, 27.6 mg, 2.0 equiv.), NaN_3 (0.6 mmol, 39.0 mg, 3.0 equiv.), and TEMPO or BHT (0.4 mmol, 2.0 equiv.). CH_3CN (4.0 mL) and HFIP (0.1 mL) were added and stirred with a stir bar to form a homogeneous solution. The vial was equipped with graphite plate (1.0 × 1.0 cm^2) as anode and platinum plate (1.0 × 1.0 cm^2) as cathode with the electric connector under N_2 atmosphere. The vial was stirred and electrolyzed at constant current of 12 mA for 6 hours at room temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by ethyl acetate. The combined organic layer was washed with water (10 mL × 3) and brine, and then dried over with anhydrous Na_2SO_4. After concentrated under *vacuo*, the crude product was purified by silica gel column chromatography to afford the desired compounds **2a**, or **2ab**.



3-(3,5-di-tert-butyl-4-hydroxybenzyl)-1-methyl-3-phenylindolin-2-one (2ab): Purified by column chromatography (hexane/ethyl acetate = 4:1, Rf = 0.70). Yellow solid (82 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.18 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.61 (s, 2H), 6.58 (d, *J* = 8.1 Hz, 1H), 4.97 (s, 1H), 3.49 (m, 2H), 2.91 (s, 3H), 1.27 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 177.8, 152.3, 143.8, 139.5, 134.6 (2×C), 131.6, 128.4 (2×C), 127.9, 127.4 (2×C), 127.2, 126.7 (2×C), 125.8, 125.5, 121.9, 107.7, 58.7, 44.4, 34.0 (2×C), 30.2 (6×C), 25.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{35}NO_2Na$ 564.2560; Found 564.2560.

6.2 CV experiments

CV experiments was recorded on the CHI 660E instrument. A 3 mm diameter glassy carbon disc electrode was used as the working electrode; a platinum plated electrode was used as the counter electrode; a Ag/AgCl was used as reference electrode. The working temperature was 298 K. All solutions were degassed via freeze-pump-thaw method prior to use and nitrogen was bubbled through the solutions for at least 5 min before the experiment was performed. A CH_3CN solution (5.0 mL) of sample including 10 mM of each sample and 0.1 M of $n$$Bu_4BF_4$ was prepared as an electrochemical solution. The spectra were recorded with the scan rate of 100 mVs^{-1} or 200 mVs^{-1}. For ease of testing, we selected more soluble $Mn(OTf)_2$ and $n$$Bu_4N_3$ as the catalyst and azide source.

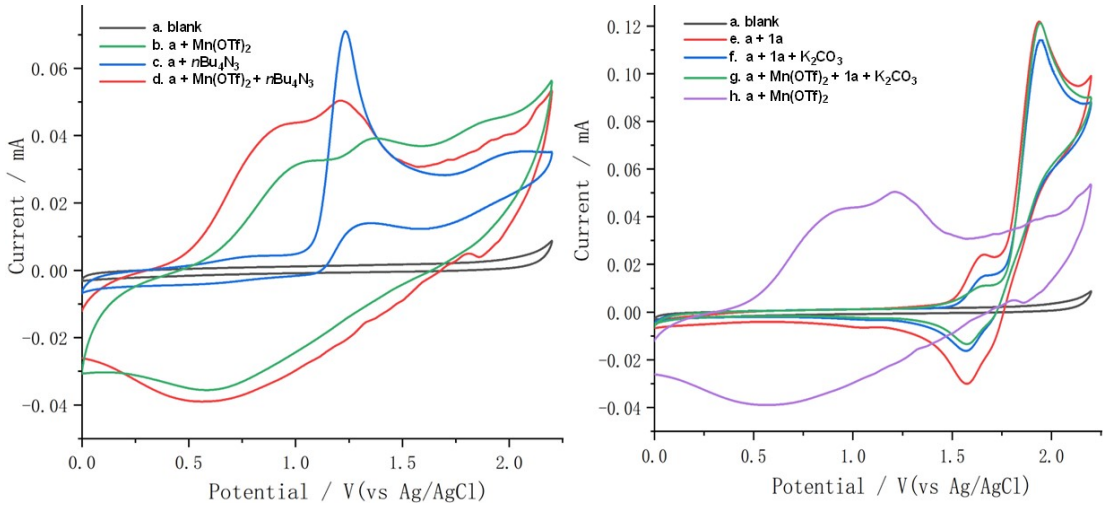


Fig. S2 CV (Cyclic voltammetry) experiments

6.3 Proposed mechanisms of the successful azidation-cyclization of tryptamines and the unsuccessful azidation-cyclization of tryptophols

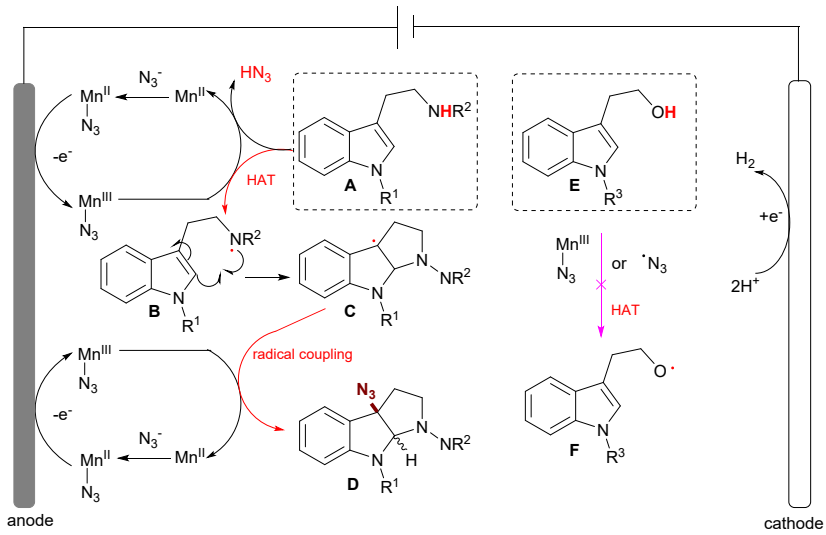


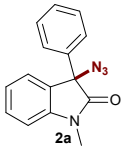
Fig. S3 Proposed mechanisms of azidation-cyclization of tryptamines and tryptophols

We proposed a mechanism, as illustrated in Figure S3, to explain why tryptamines could undergo azidation-cyclization while tryptophols could not. Initially, the Mn(II)-N_3 species was oxidized to Mn(III)-N_3 at the anode, which then underwent a HAT process with substrate **A**, generating N radical **B**. Subsequently, N radical **B** participated in a radical cyclization, forming carbon radical **C**. Following this step, the Mn(III)-N_3 transferred a azidyl radical to **C**, leading to the production of the final product 3a-azido-pyrroloindoline **D**. However, the alkyl OH groups of tryptophols faced challenges in forming O radicals **F** through HAT under our electrocatalytic conditions, leading to side reactions.

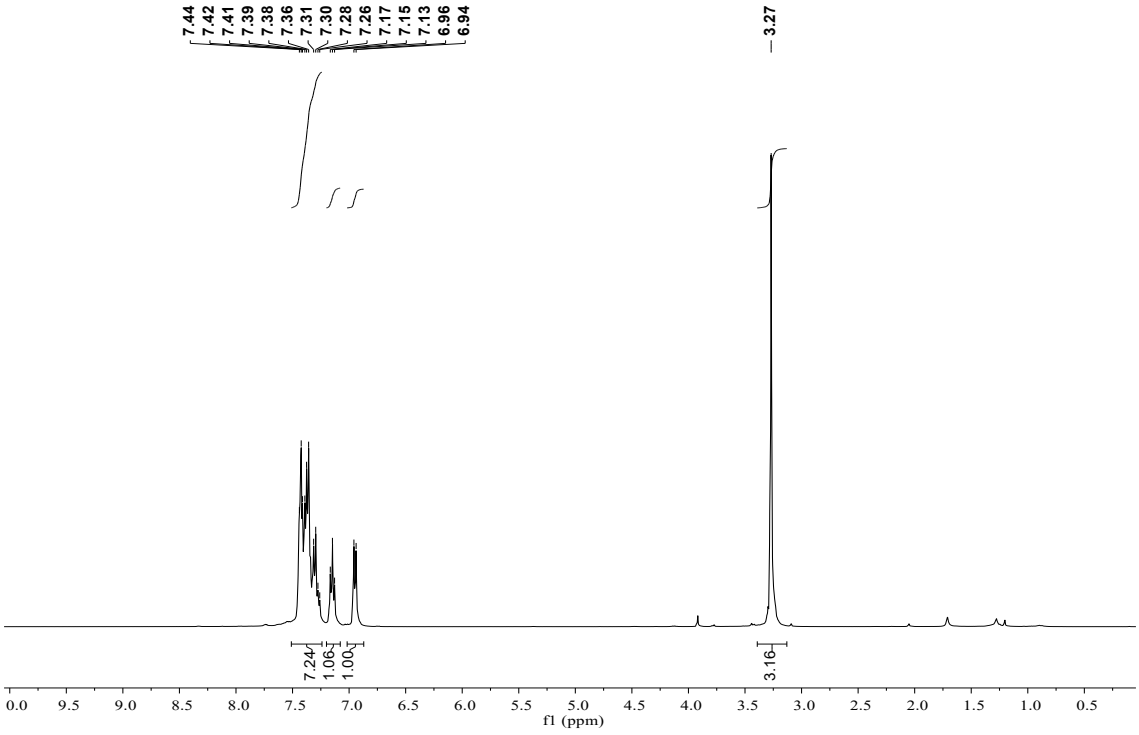
7. References

1. (a) R. He, C. Ding and K. Maruoka, Phosphonium Salts as Chiral Phase-Transfer Catalysts: Asymmetric Michael and Mannich Reactions of 3-Aryloxindoles, *Angew. Chem. Int. Ed.*, 2009, **48**, 4559; (b) L. Zong, S. Du, K. F. Chin, C. Wang and C.-H. Tan, Enantioselective Synthesis of Quaternary Carbon Stereocenters: Addition of 3-Substituted Oxindoles to Vinyl Sulfone Catalyzed by Pentanidiums, *Angew. Chem. Int. Ed.*, 2015, **54**, 9390; (c) S. Liu, K. Maruoka and S. Shirakawa, Chiral Tertiary Sulfonium Salts as Effective Catalysts for Asymmetric Base-Free Neutral Phase-Transfer Reactions, *Angew. Chem. Int. Ed.*, 2017, **56**, 4819.
2. (a) Q.-H. Deng, T. Bleith, H. Wadepohl and L. H. Gade, Enantioselective Iron-Catalyzed Azidation of β-Keto Esters and Oxindoles, *J. Am. Chem. Soc.*, 2013, **135**, 5356; (b) M. V. Vita and J. Waser, Azidation of *β*-Keto Esters and Silyl Enol Ethers with a Benziodoxole Reagent, *Org. Lett.*, 2013, **15**, 3246; (c) A. Yanagisawa, K. Takagi, M. Horiguchi, K. Dezaki, T. Marui, E. Saito, T. Ebihara, G. M. Russell, T. Watanabe and K. Midorikawa, Asymmetric *α*-Azidation Reaction of *β*-Ketoesters Catalyzed by Chiral Tin Alkoxides, *Asian J. Org. Chem.*, 2023, **12**.
3. (a) J. Xu and R. Tong, An Environmentally Friendly Protocol for Oxidative Halocyclization of Tryptamine and Tryptophol Derivatives, *Green Chem.*, 2017, **19**, 2952; (b) J. C. Yi, C. Liu, L. X. Dai and S. L. You, Synthesis of C3-Methyl-Substituted Pyrroloindolines and Furoindolines Via Cascade Dearomatization of Indole Derivatives with Methyl Iodide, *Chem. Asian J.*, 2017, **12**, 2975.

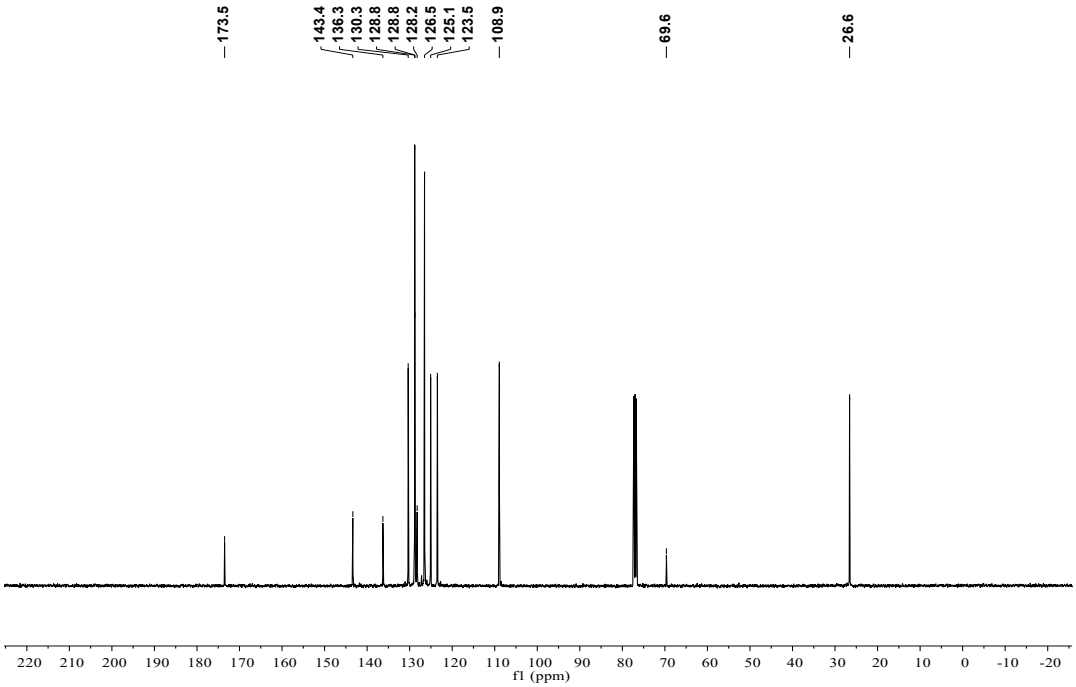
8. NMR spectra

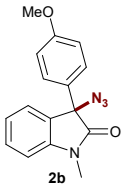


^{1}H NMR (400MHz, $CDCl_3$)



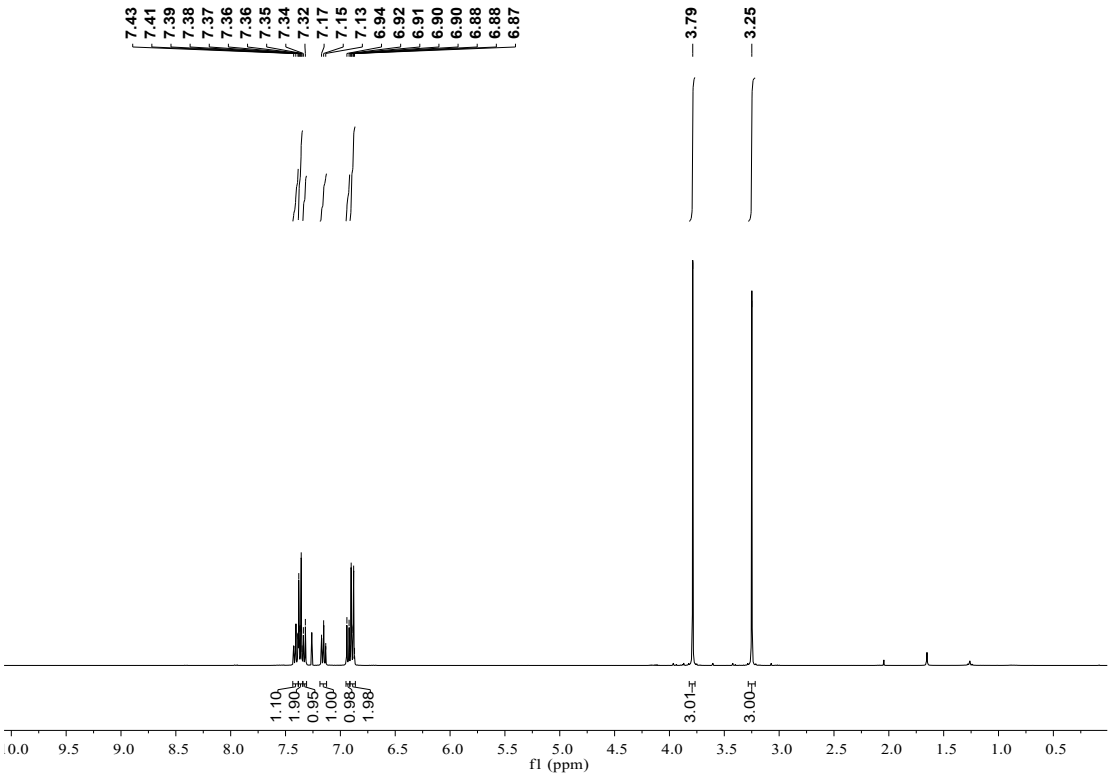
^{13}C NMR (101MHz, $CDCl_3$)



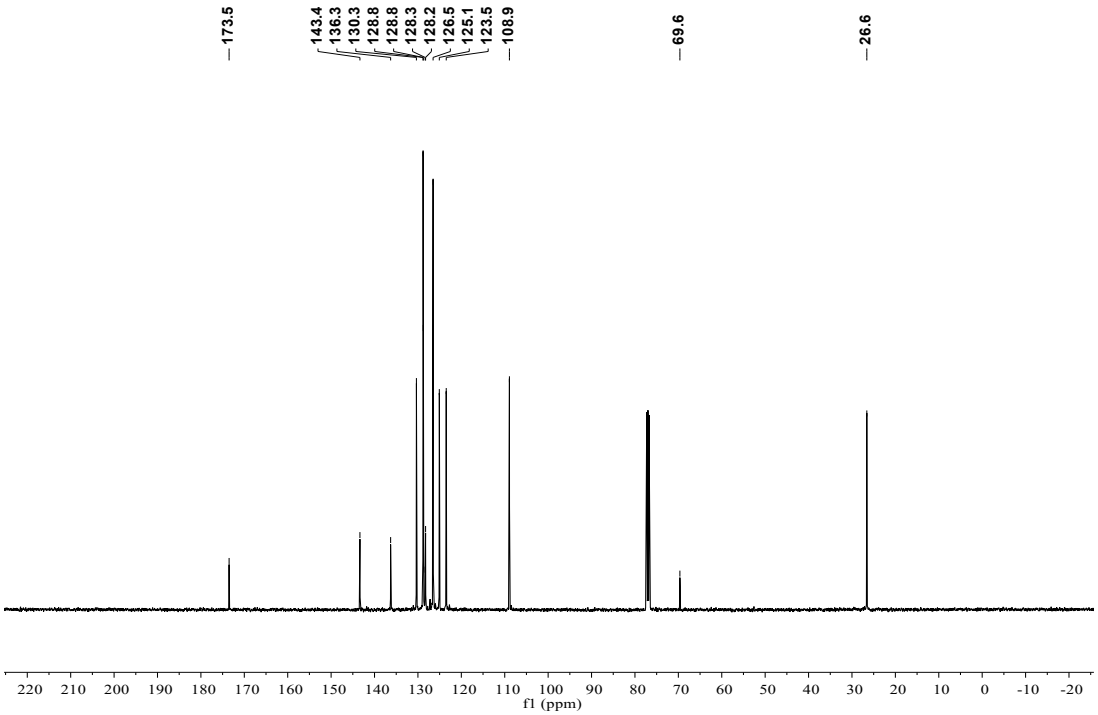


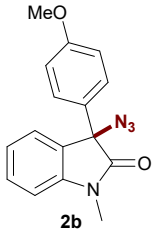
2b

^{1}H NMR (400MHz, $CDCl_3$)



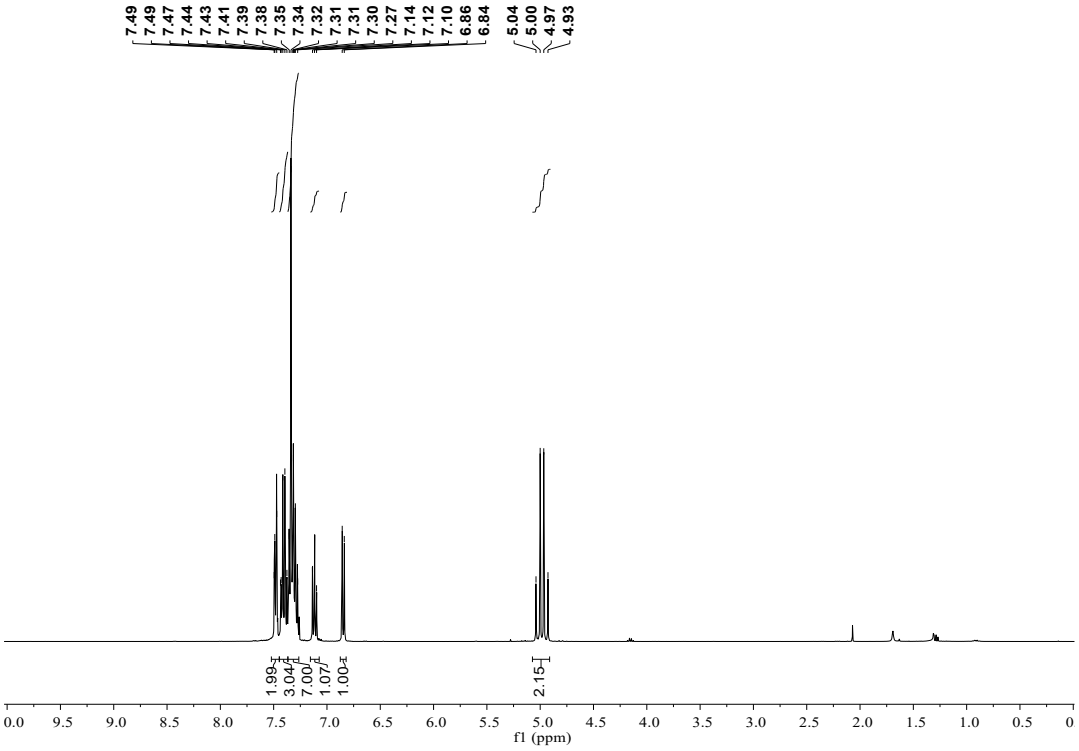
^{13}C NMR (101MHz, $CDCl_3$)



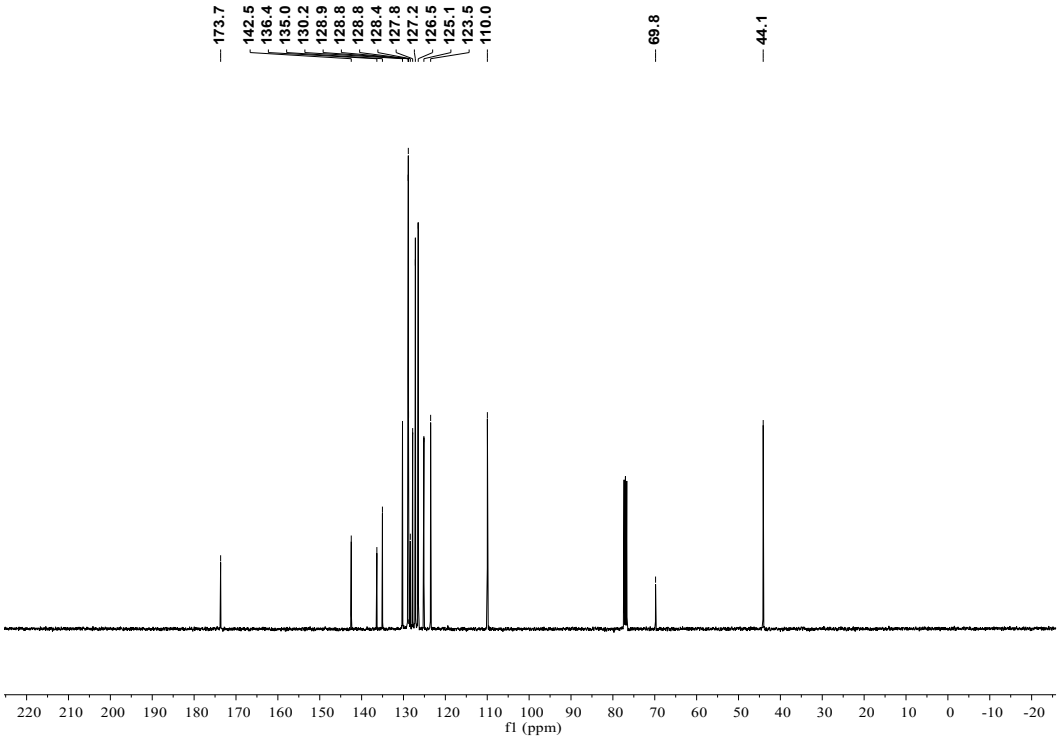


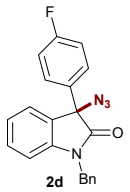
2b

^{1}H NMR (400MHz, $CDCl_3$)



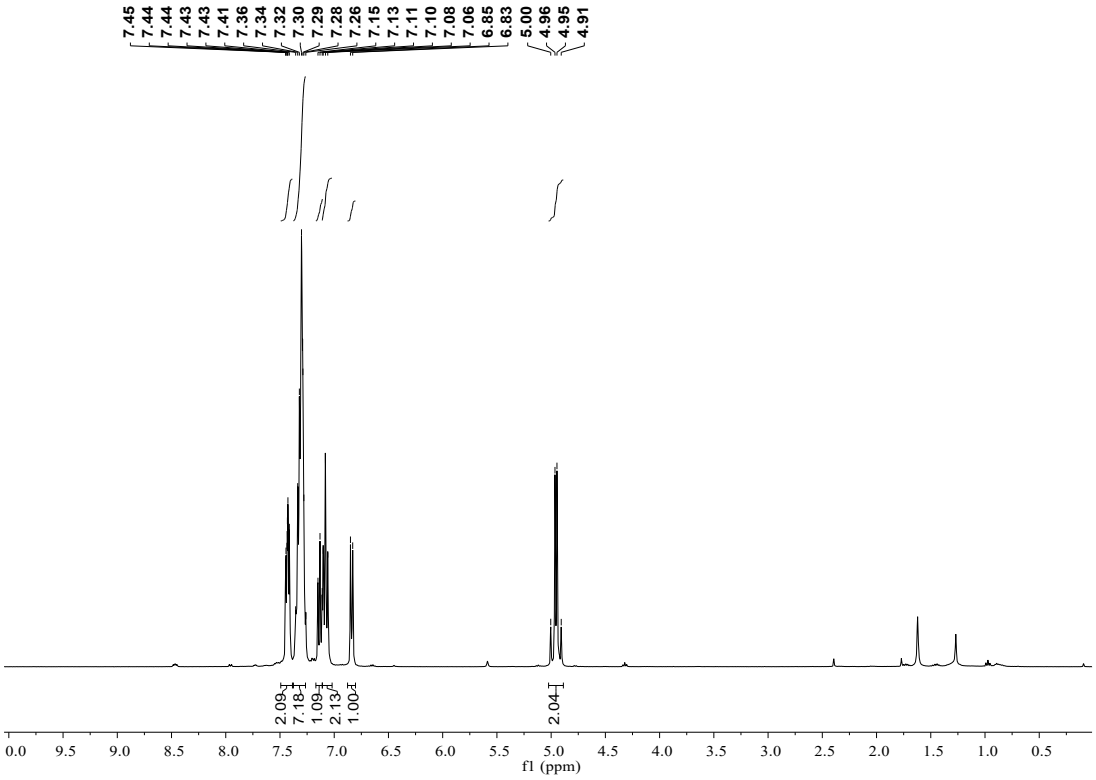
^{13}C NMR (101MHz, $CDCl_3$)



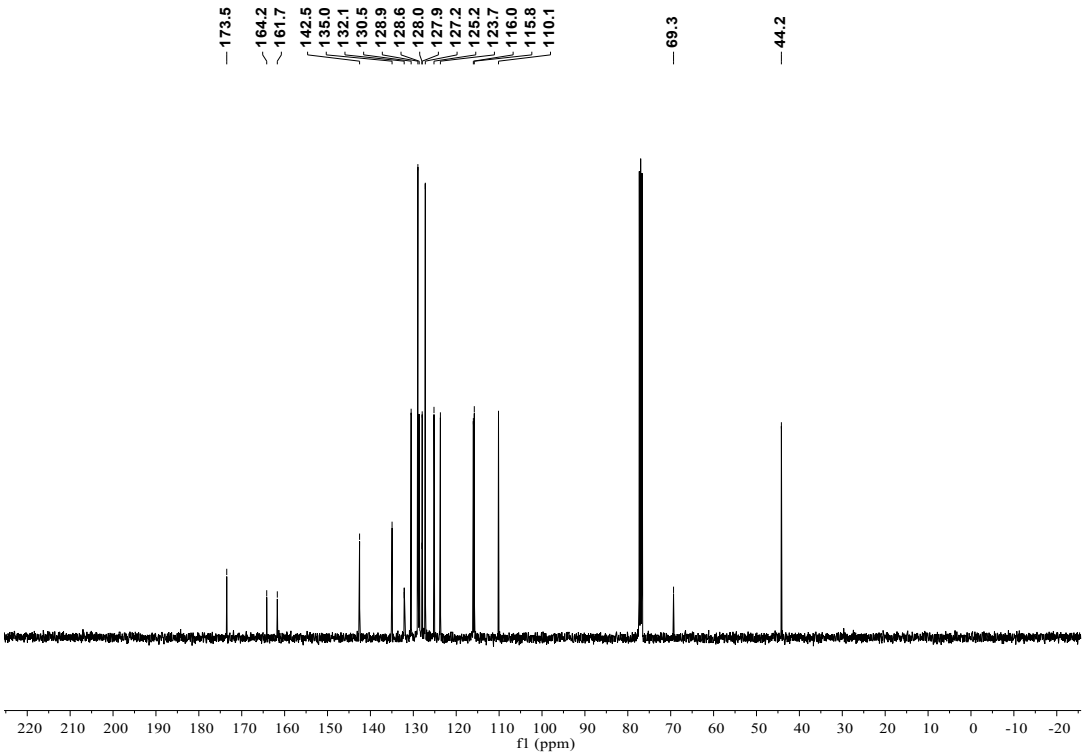


2d

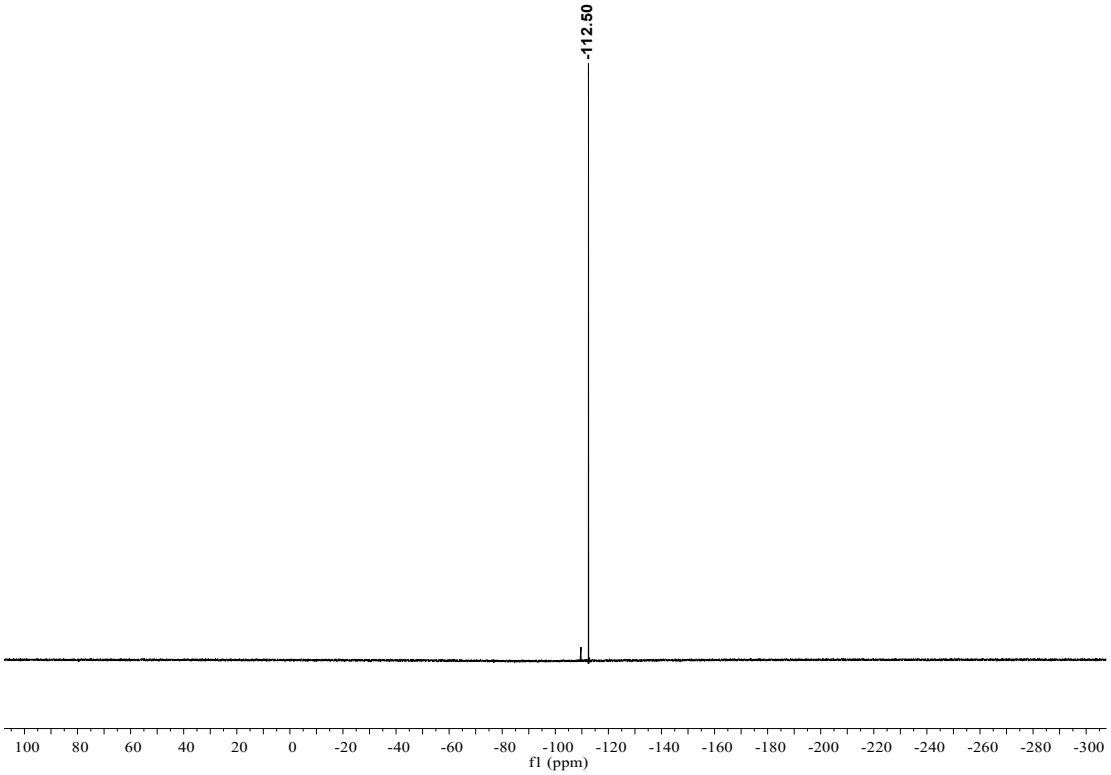
^{1}H NMR (400MHz, $CDCl_3$)

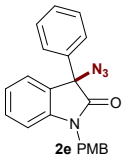


^{13}C NMR (101MHz, $CDCl_3$)

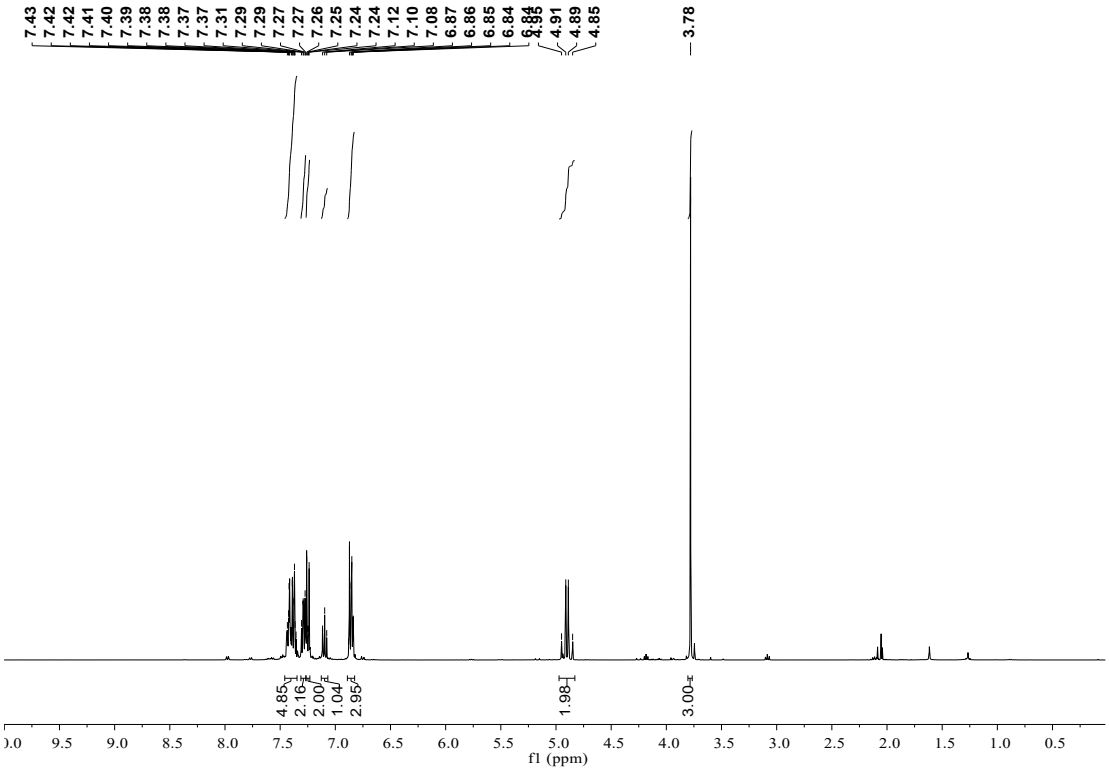


^{19}F NMR（376MHz, $CDCl_3$）

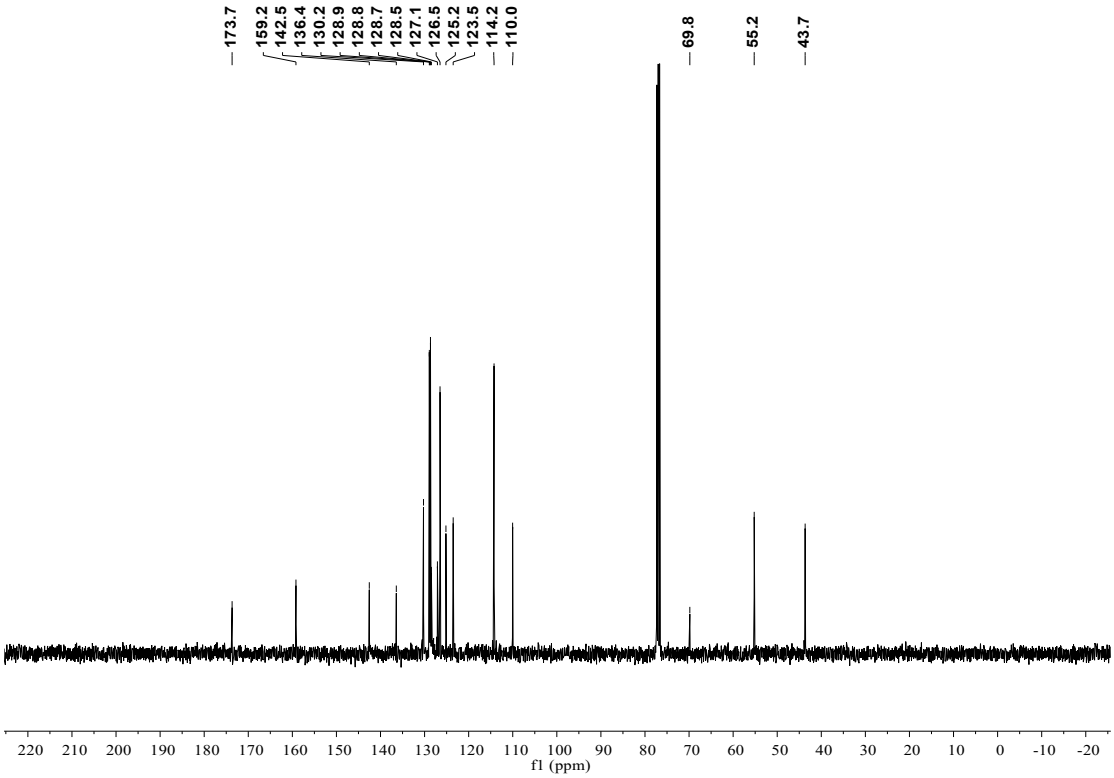


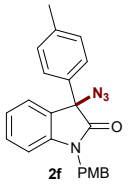


^{1}H NMR (400MHz, $CDCl_3$)

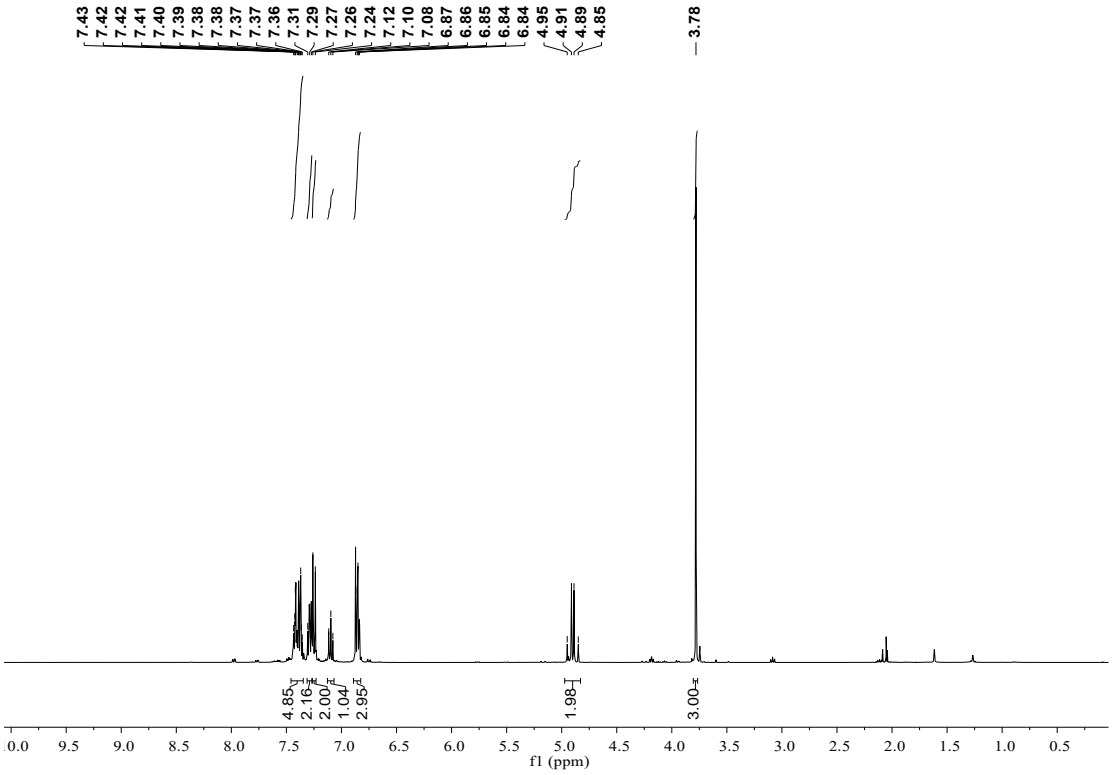


^{13}C NMR (101MHz, $CDCl_3$)

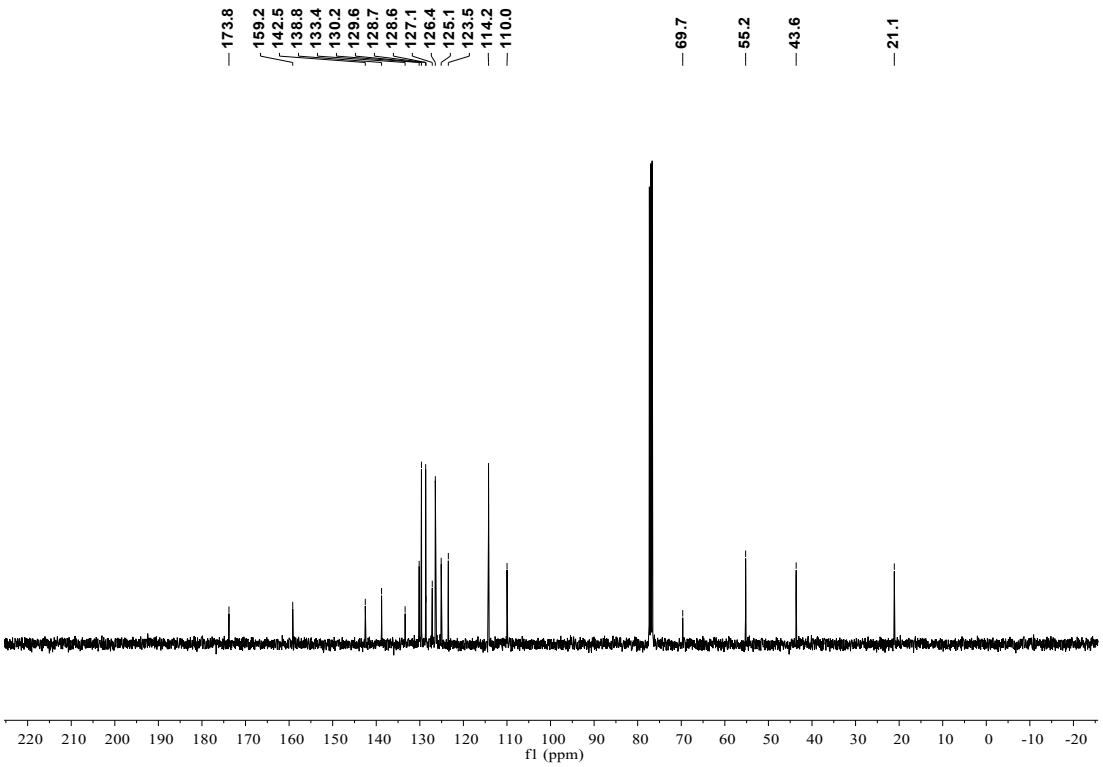


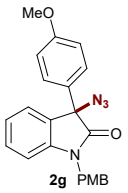


^{1}H NMR (400MHz, $CDCl_3$)

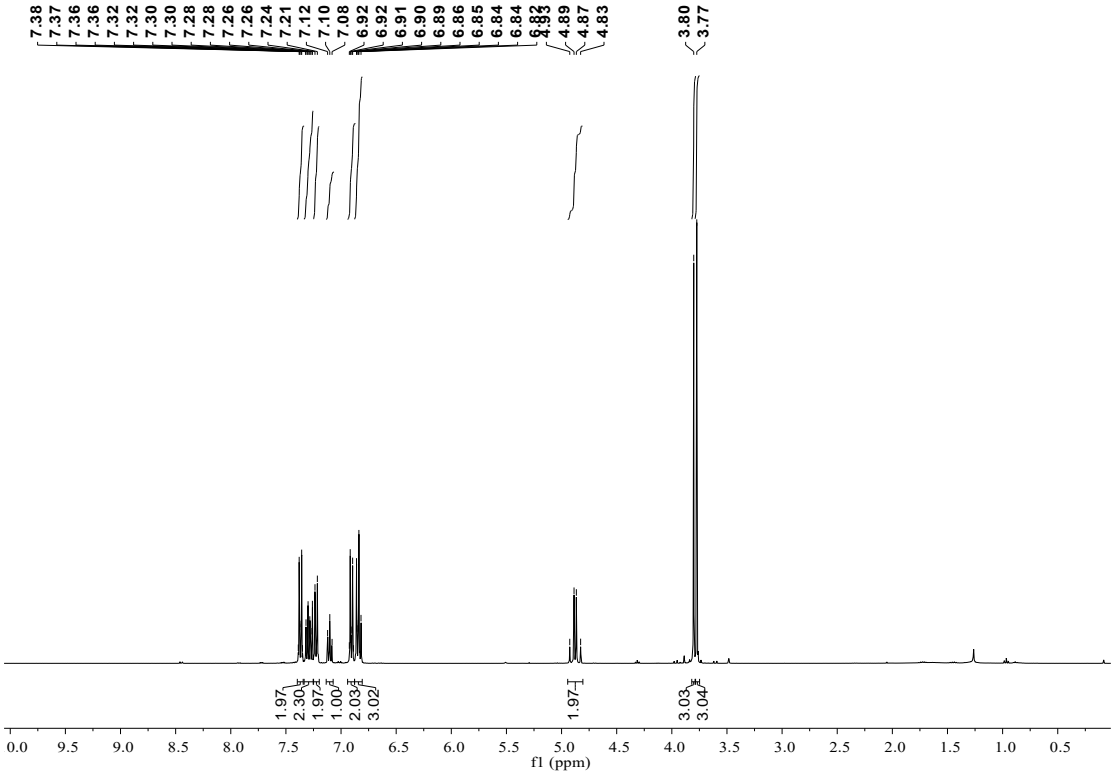


^{13}C NMR (101MHz, $CDCl_3$)

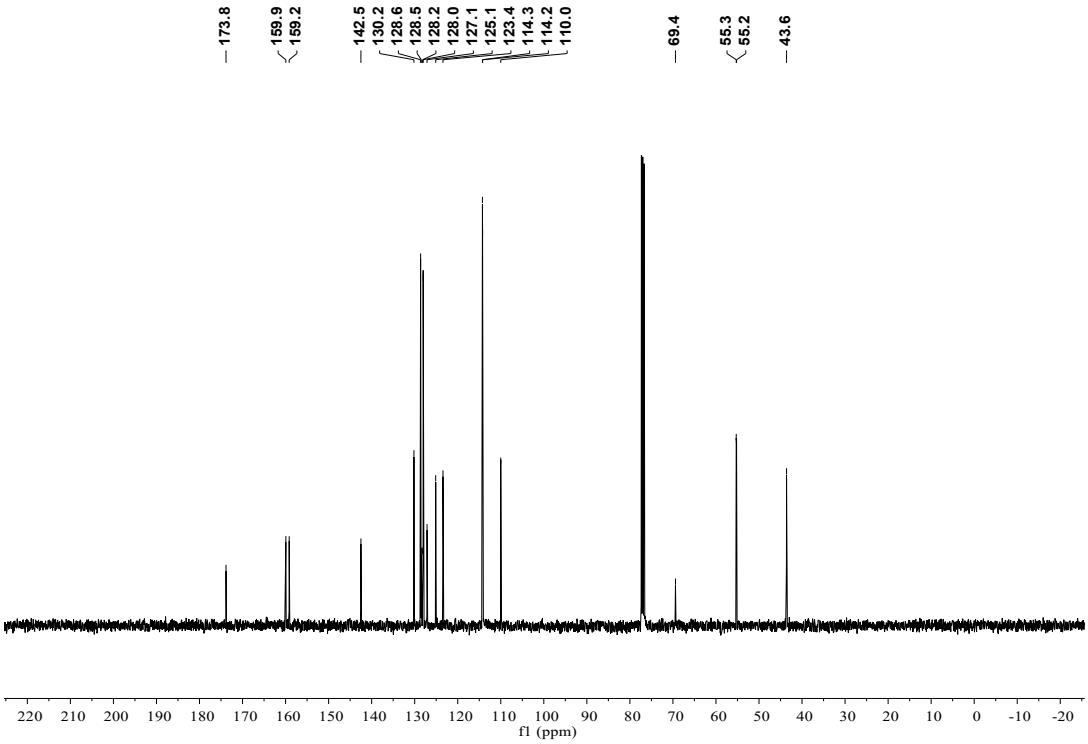


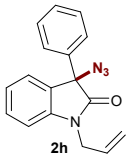


^{1}H NMR (400MHz, $CDCl_3$)



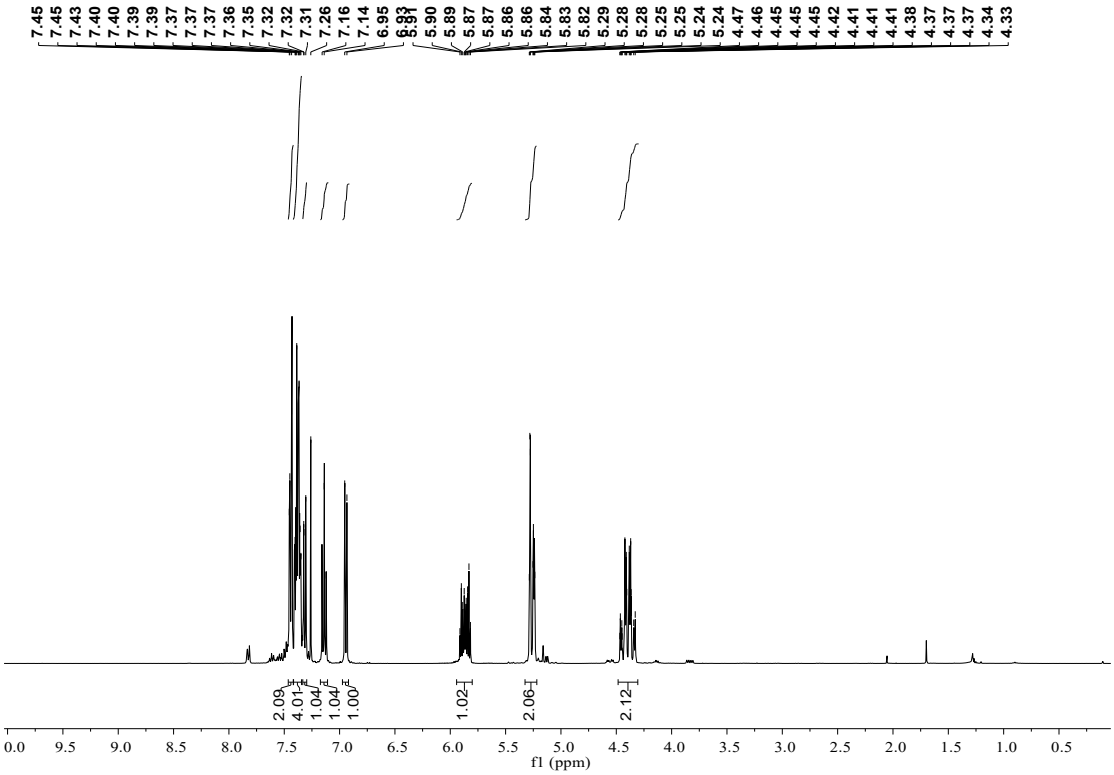
^{13}C NMR (101MHz, $CDCl_3$)



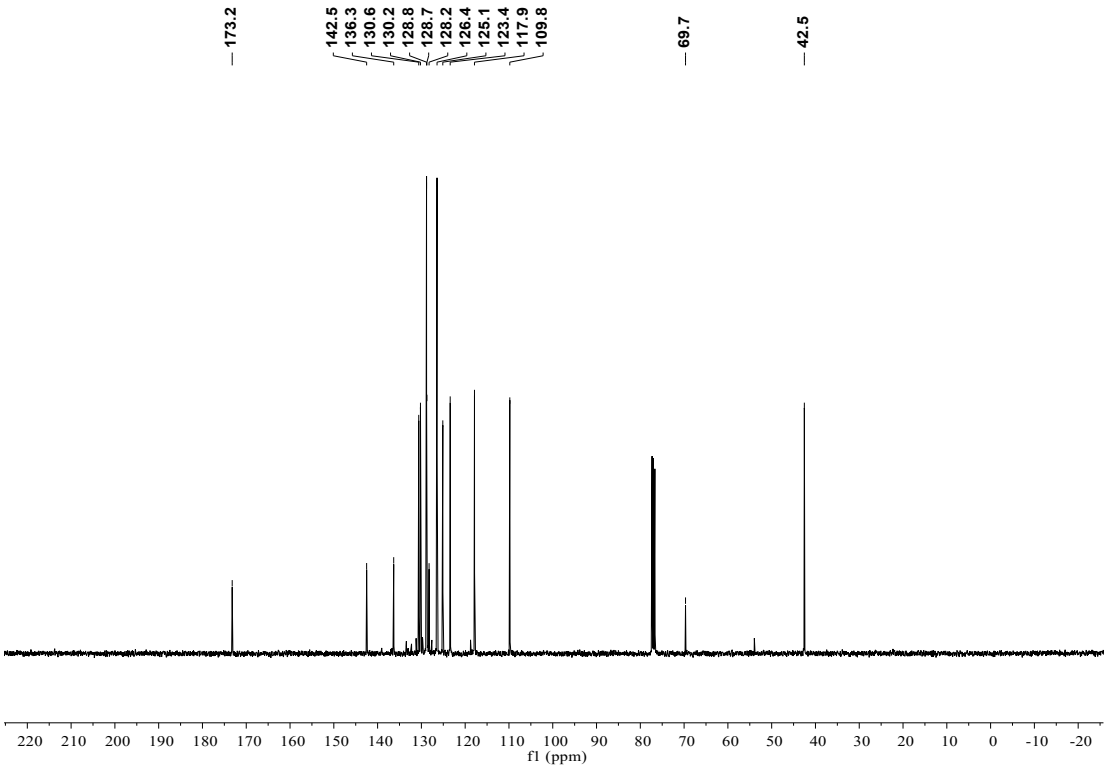


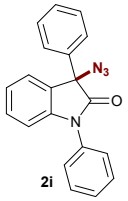
2h

^{1}H NMR (400MHz, $CDCl_3$)



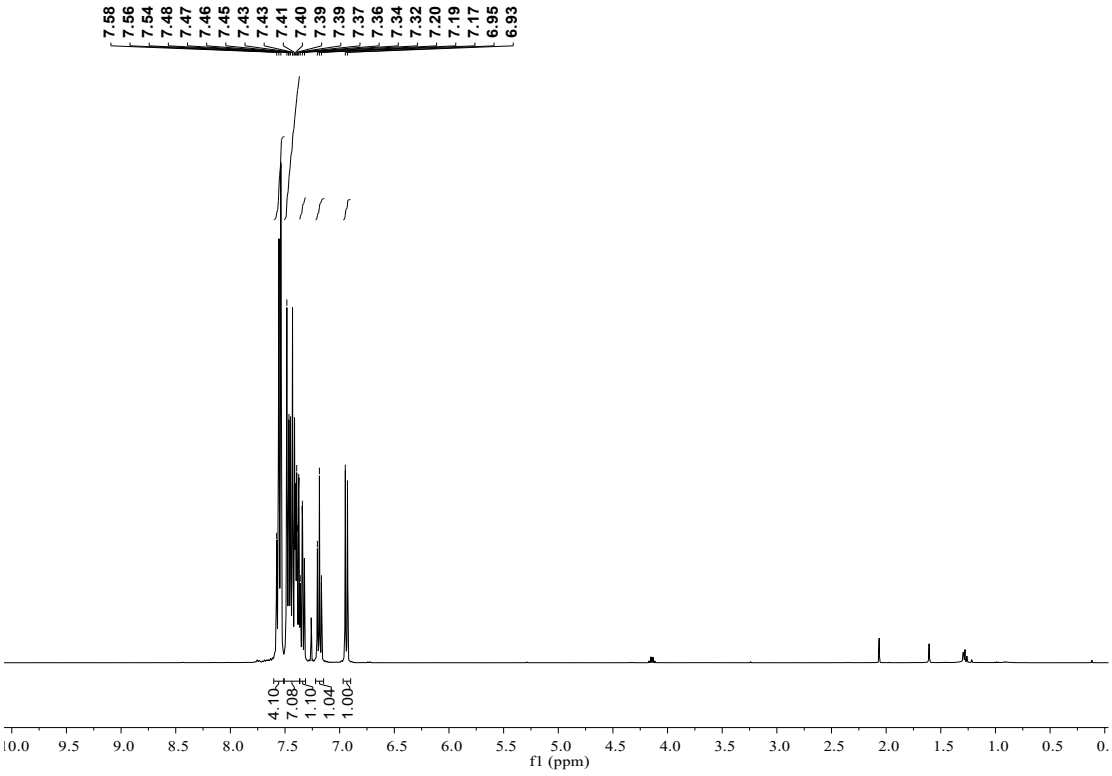
^{13}C NMR (101MHz, $CDCl_3$)



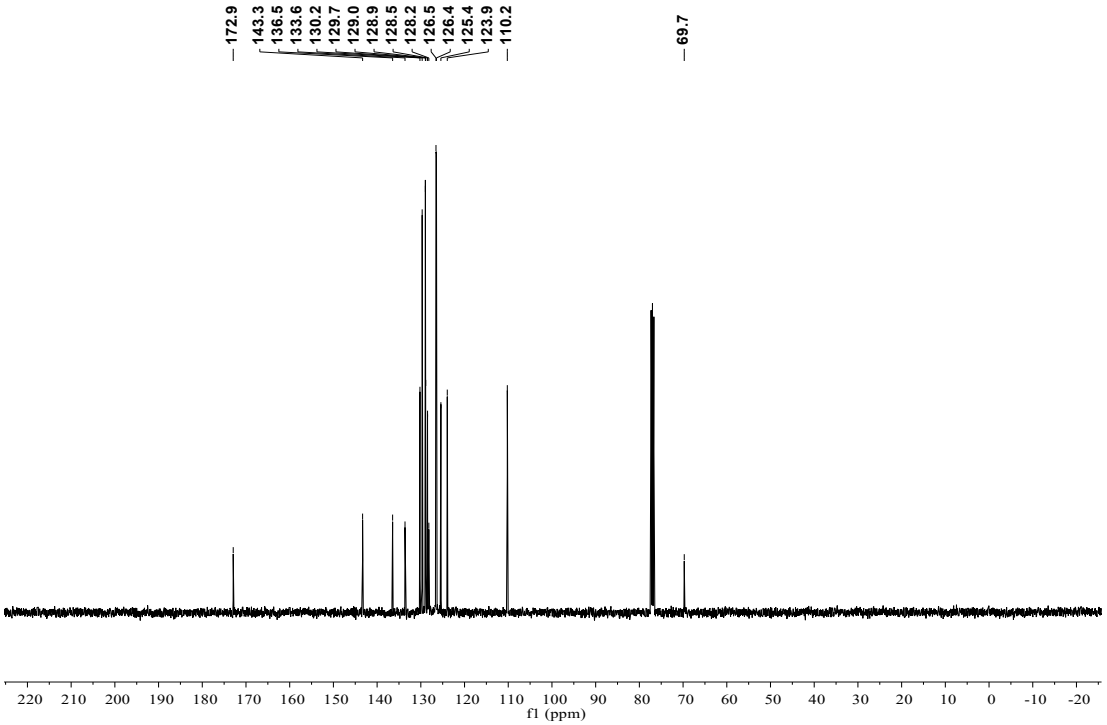


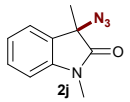
2i

^{1}H NMR (400MHz, $CDCl_3$)



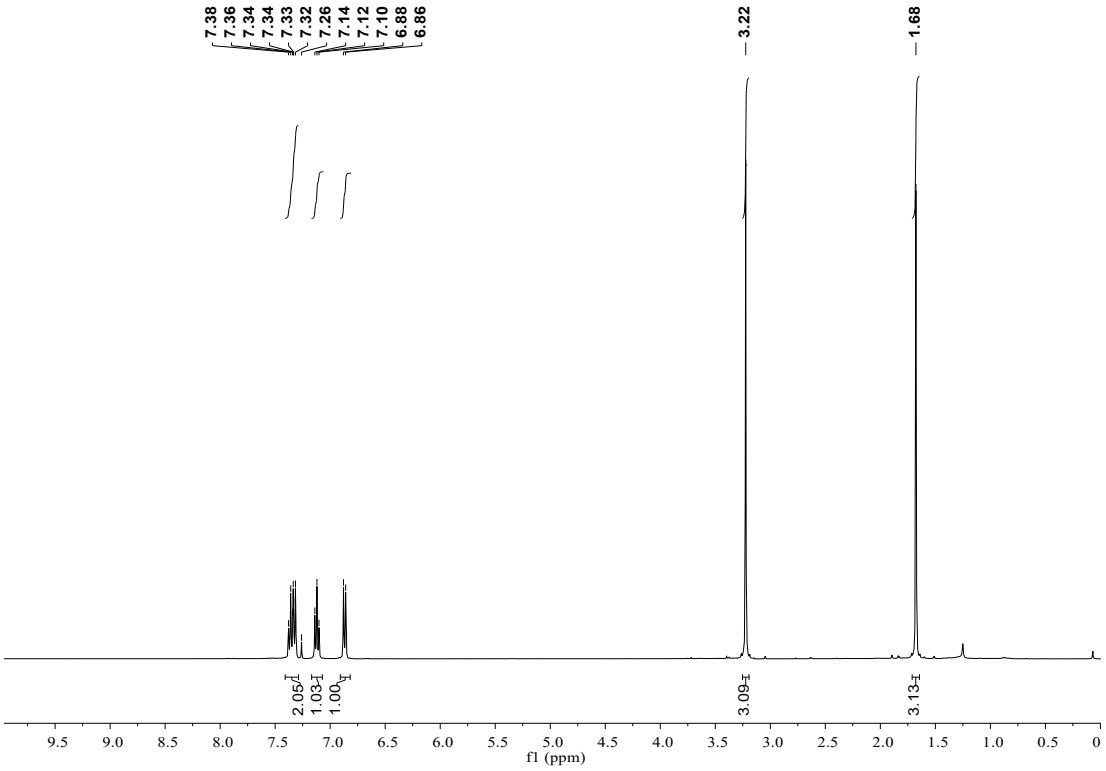
^{13}C NMR (101MHz, $CDCl_3$)



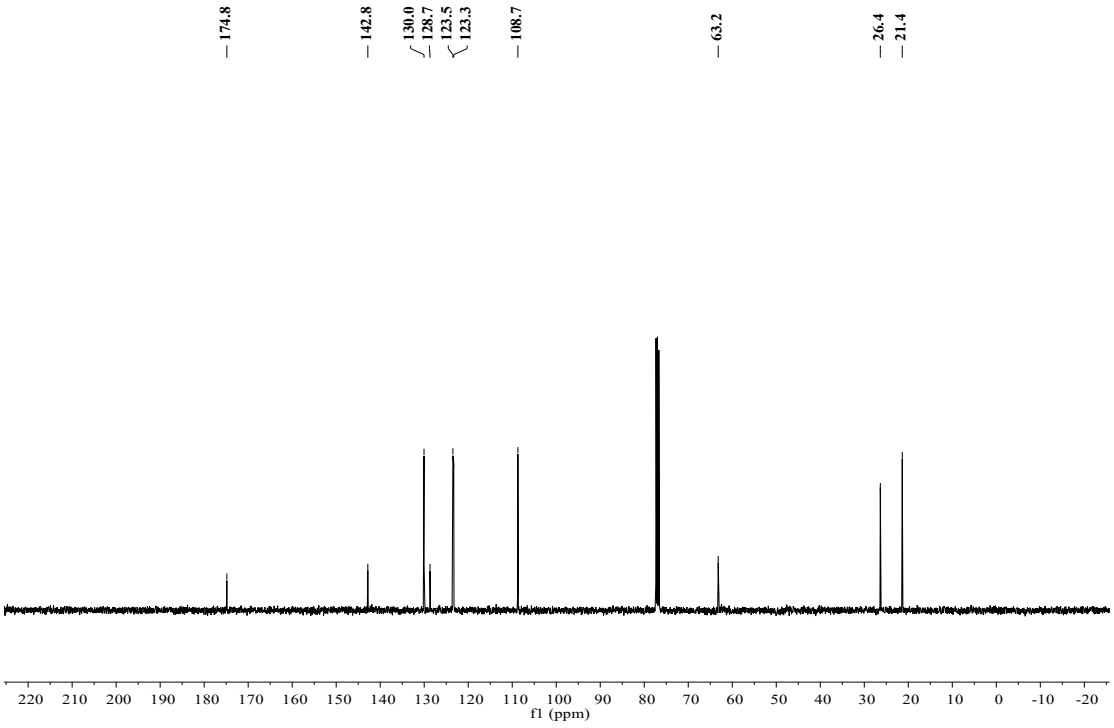


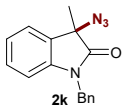
2j

^{1}H NMR (400MHz, $CDCl_3$)



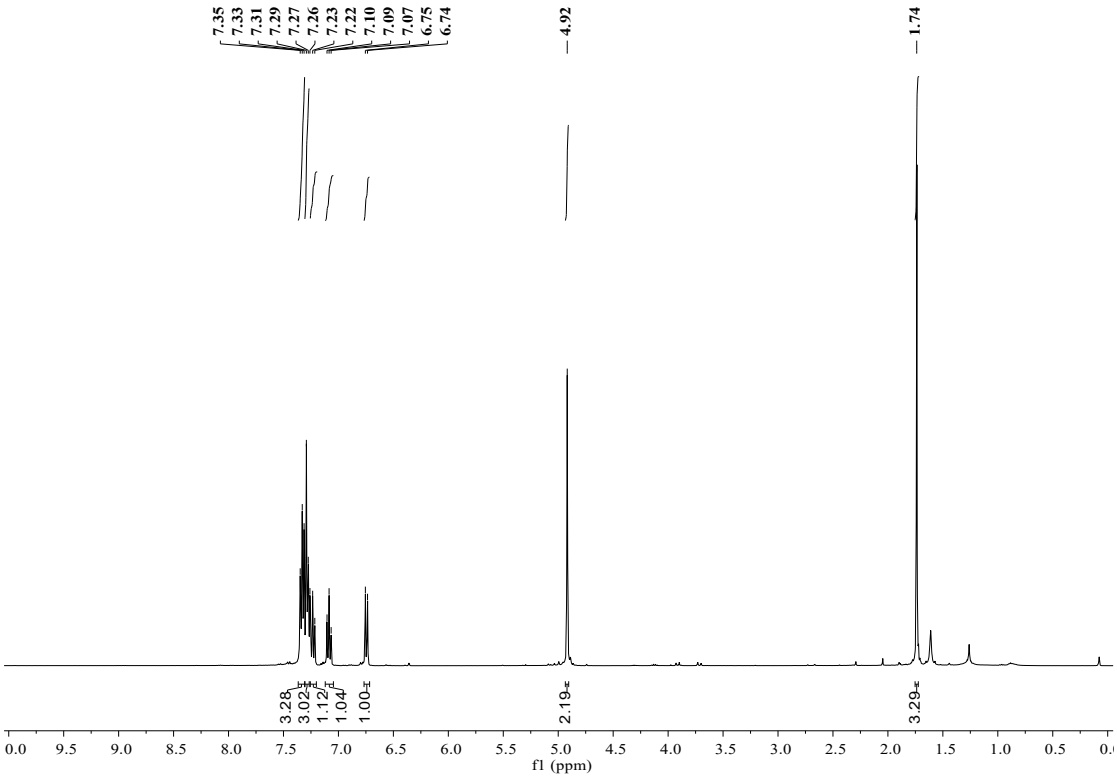
^{13}C NMR (101MHz, $CDCl_3$)



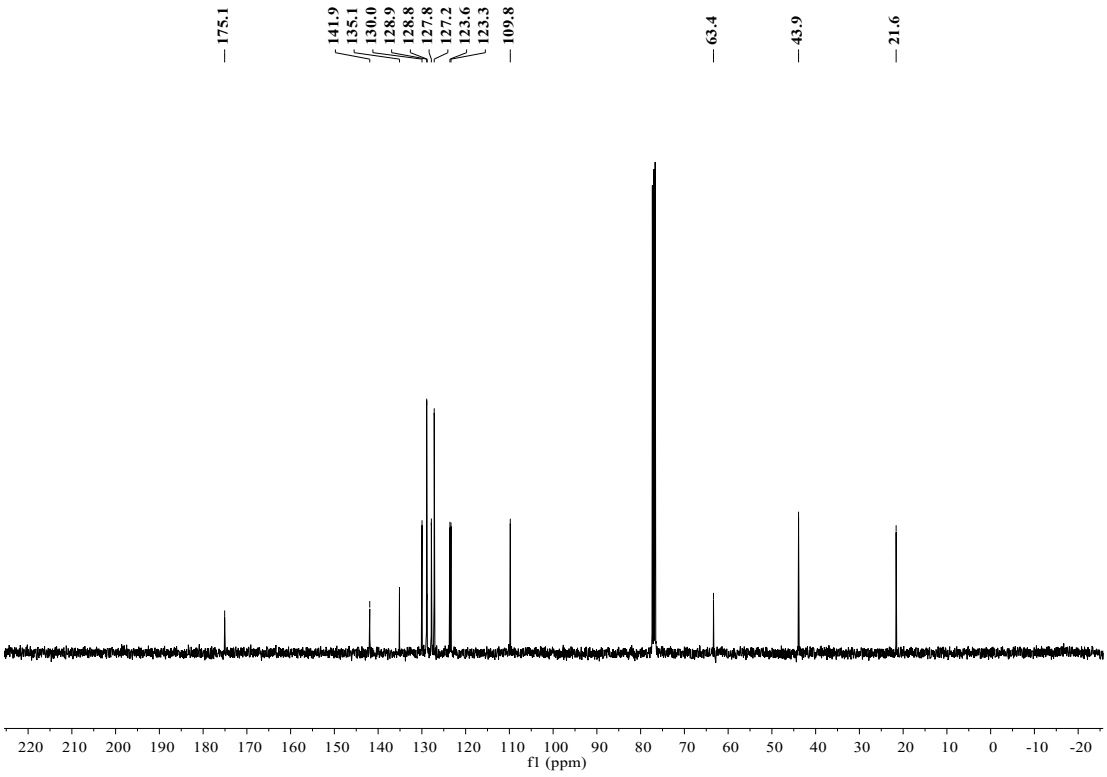


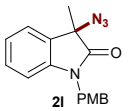
2k

^{1}H NMR (400MHz, $CDCl_3$)



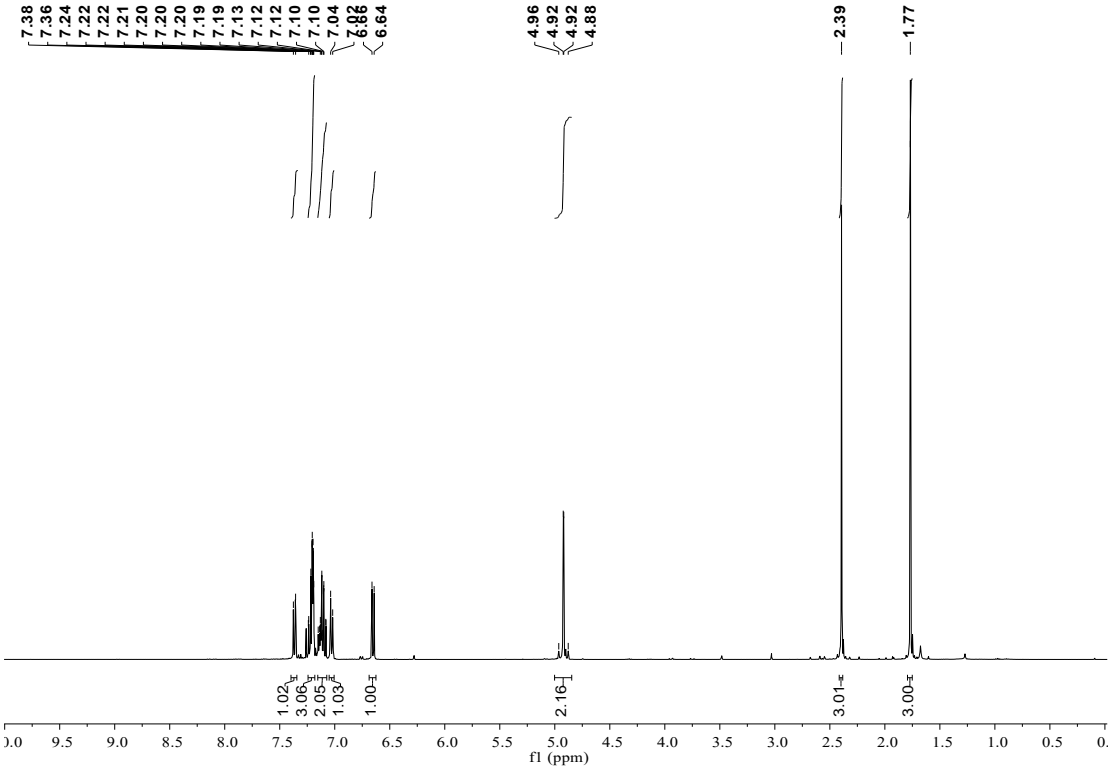
^{13}C NMR (101MHz, $CDCl_3$)



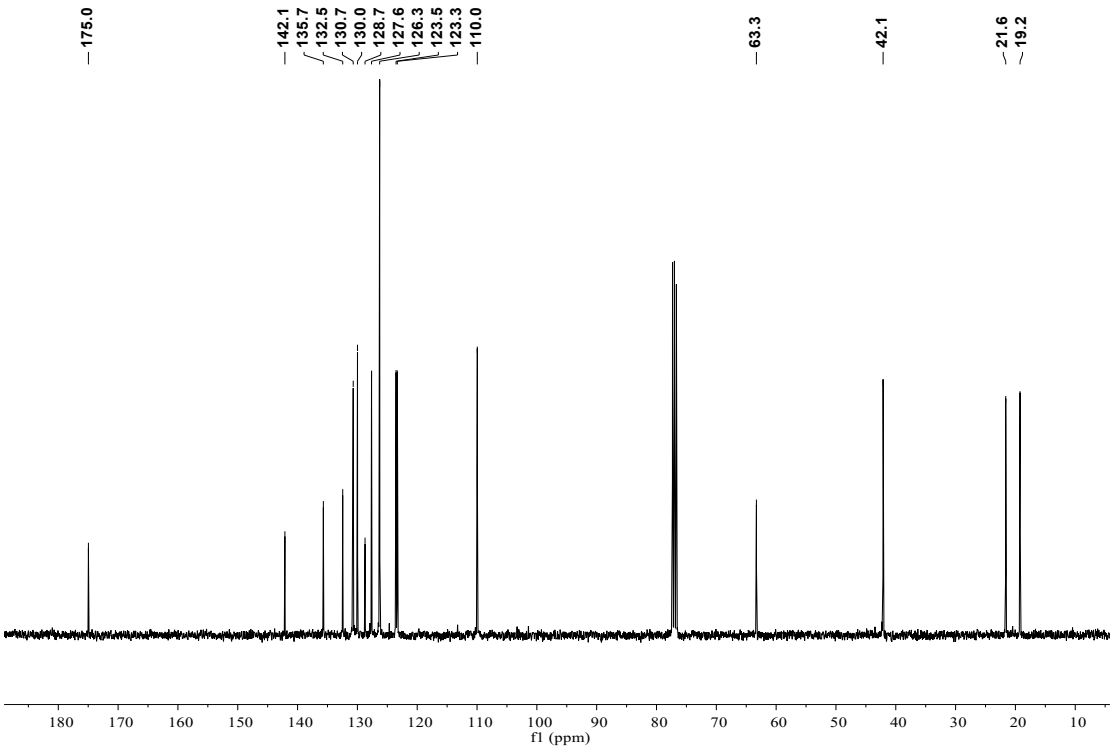


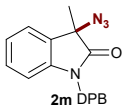
2l

^{1}H NMR (400MHz, $CDCl_3$)



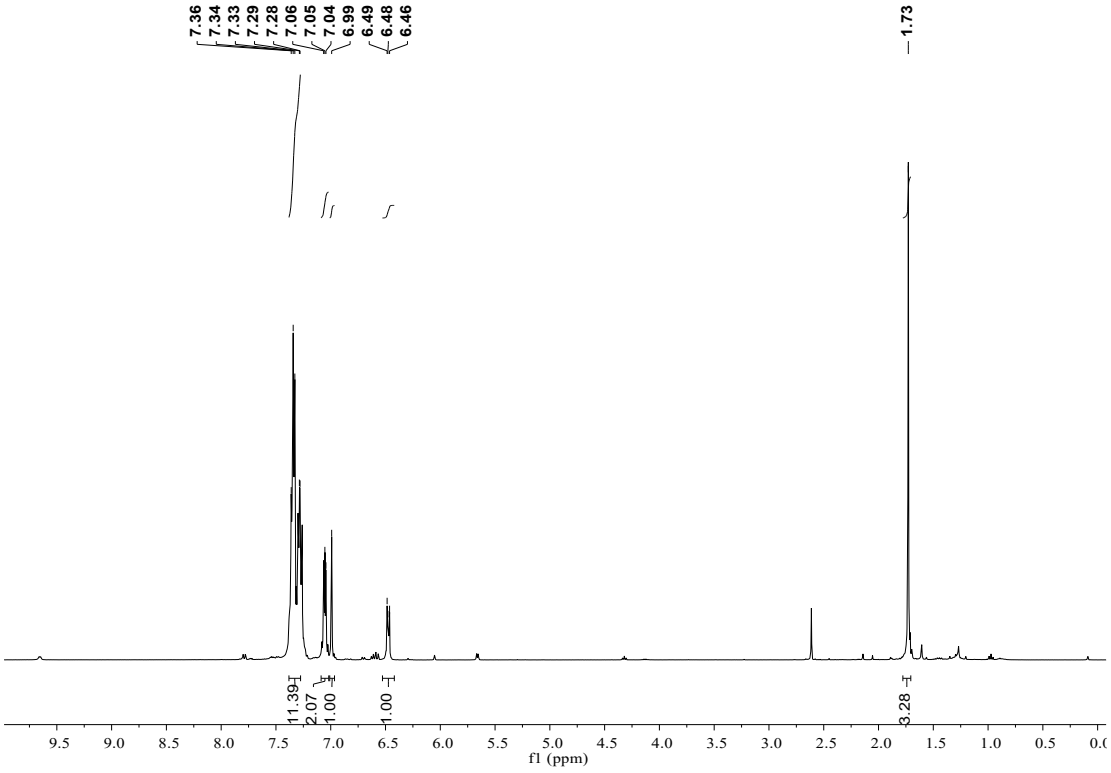
^{13}C NMR (101MHz, $CDCl_3$)



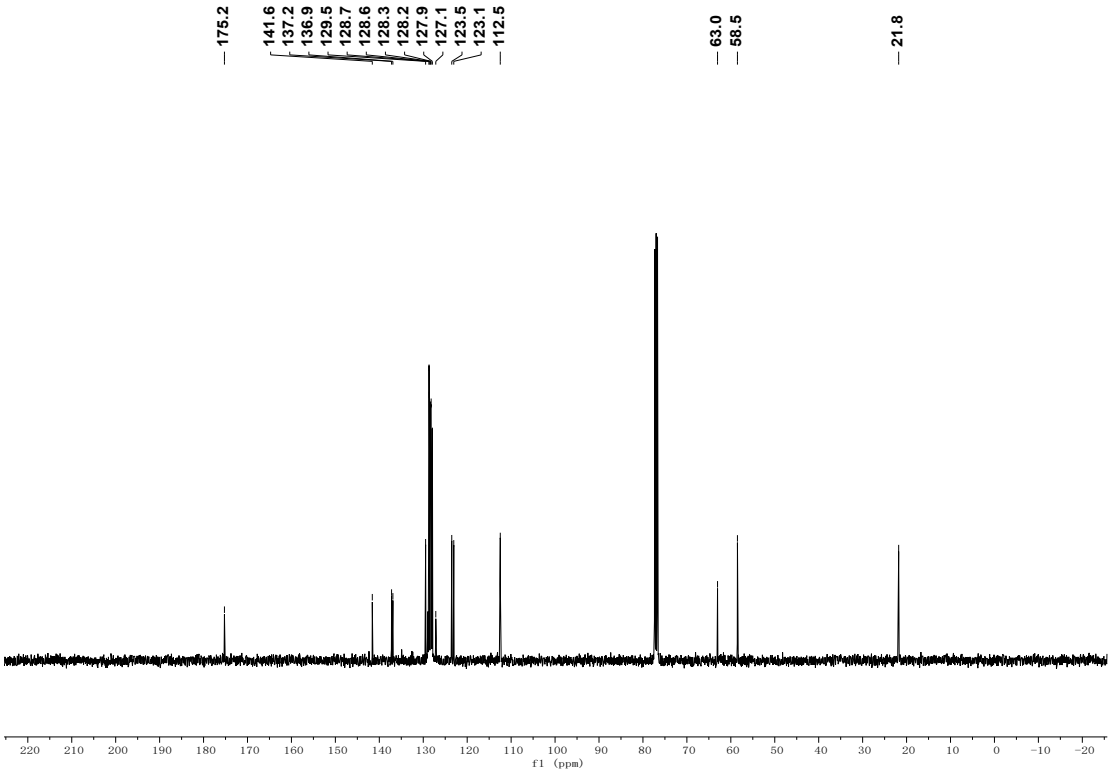


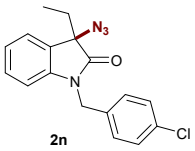
2m DPB

^{1}H NMR (400MHz, $CDCl_3$)



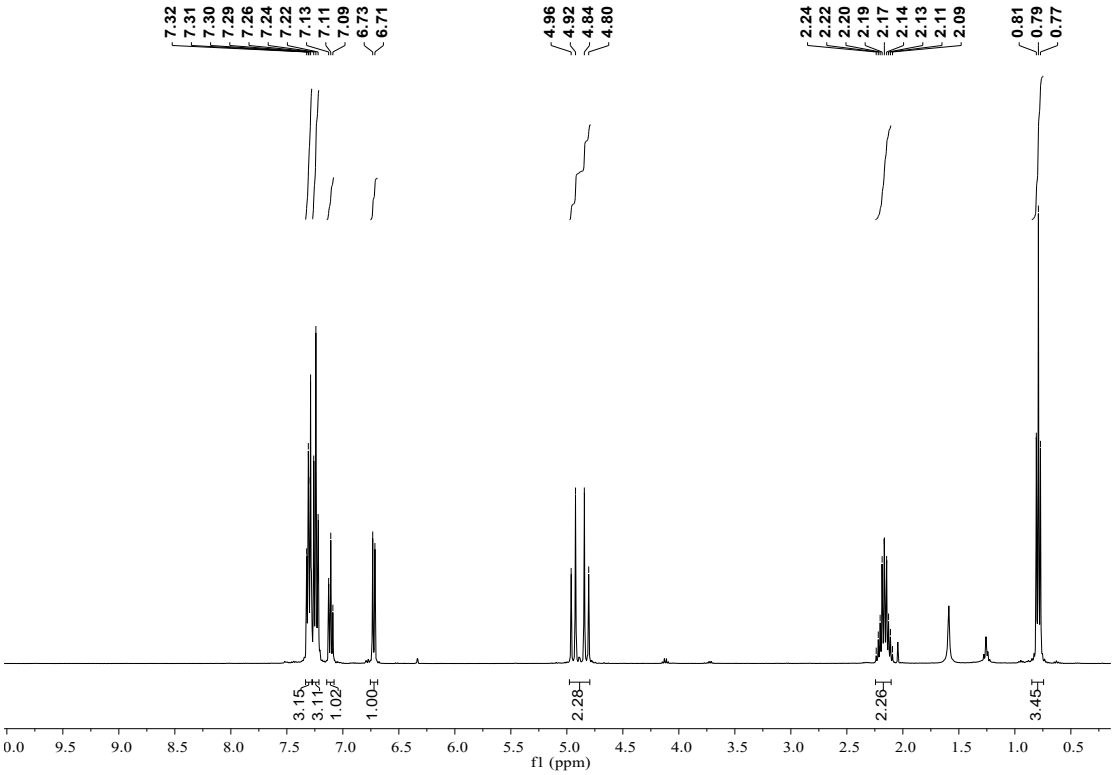
^{13}C NMR (101MHz, $CDCl_3$)



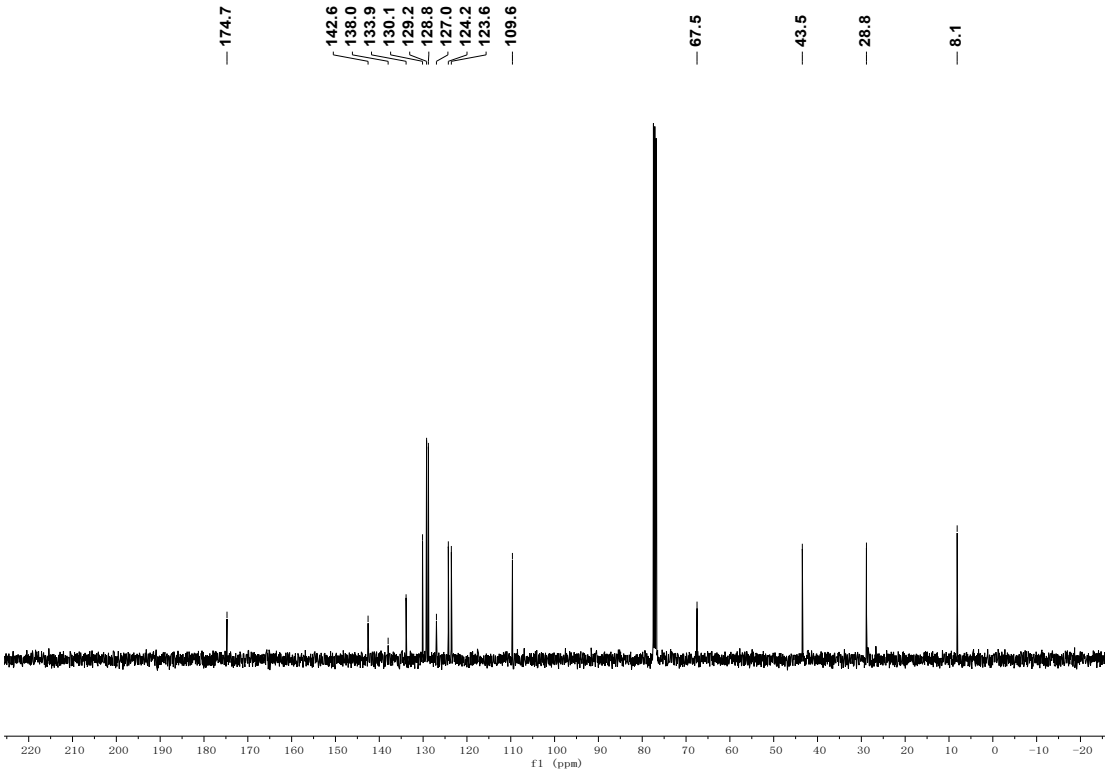


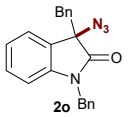
2n

^{1}H NMR (400MHz, $CDCl_3$)



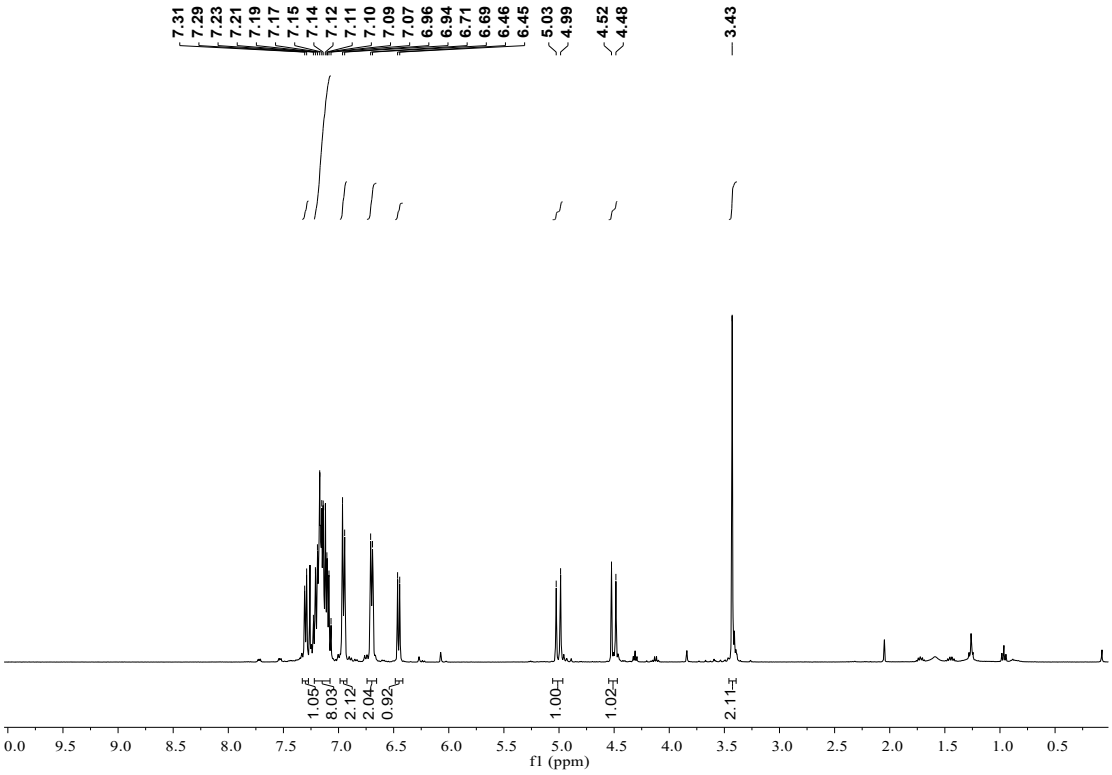
^{13}C NMR (101MHz, $CDCl_3$)



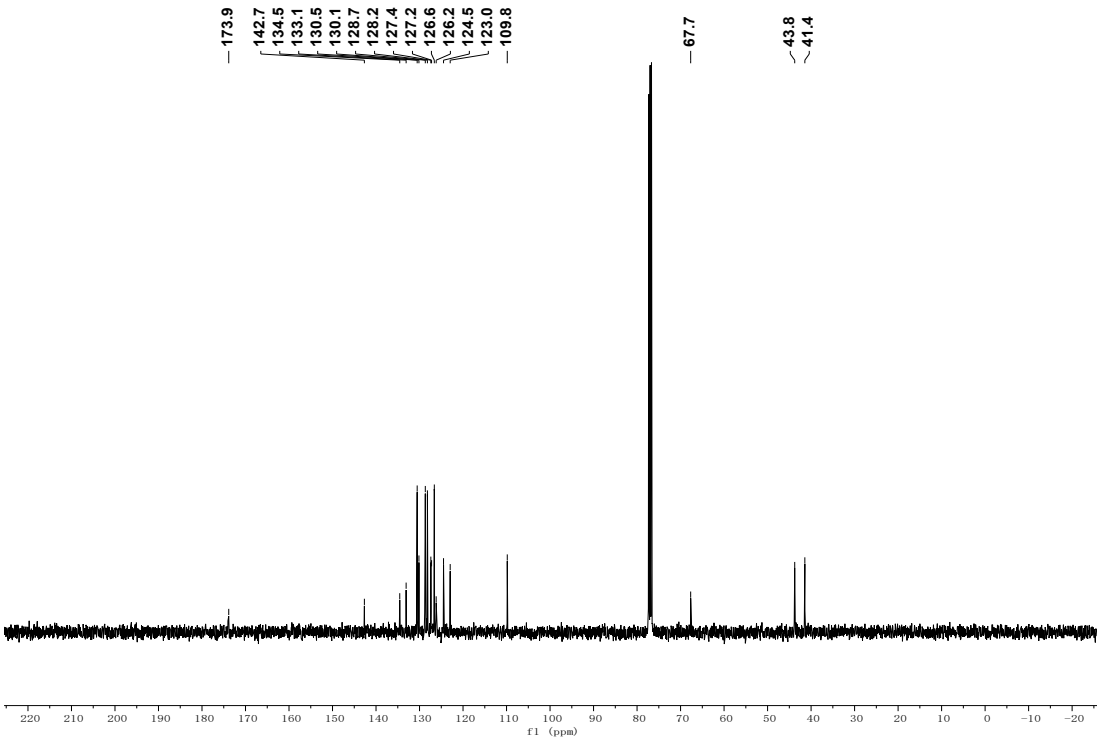


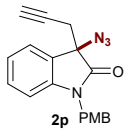
2o

^{1}H NMR (400MHz, $CDCl_3$)



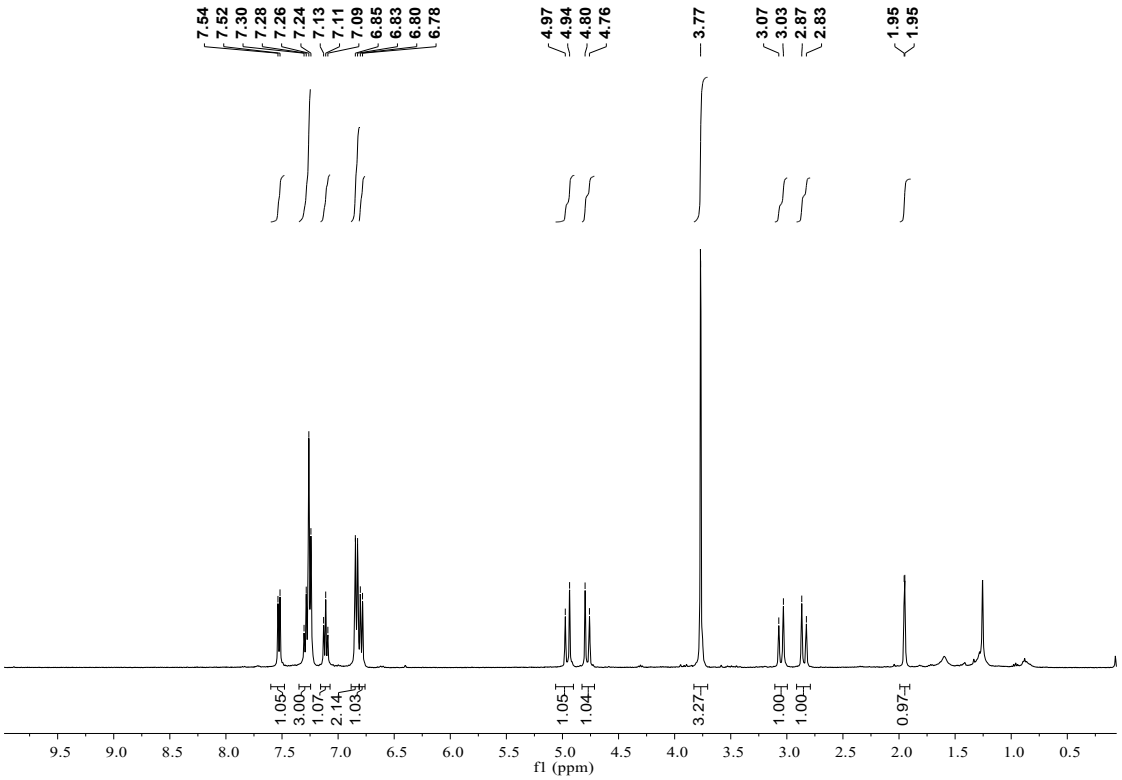
^{13}C NMR (101MHz, $CDCl_3$)



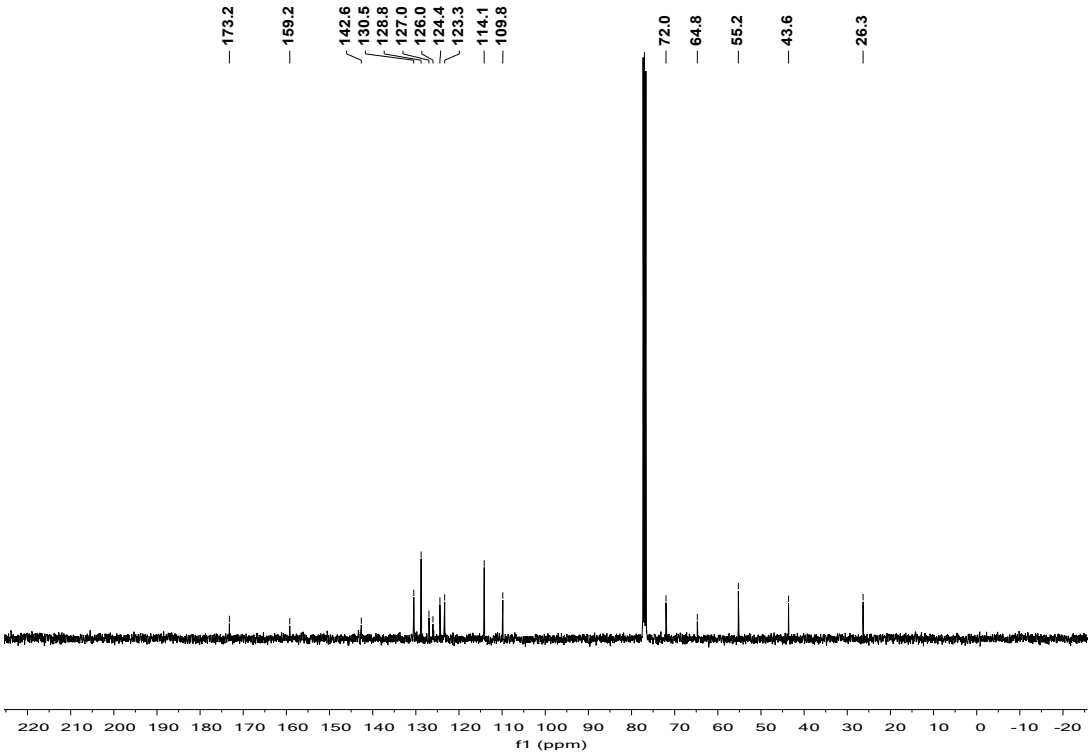


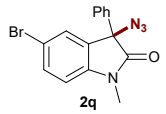
2p

^{1}H NMR (400MHz, $CDCl_3$)



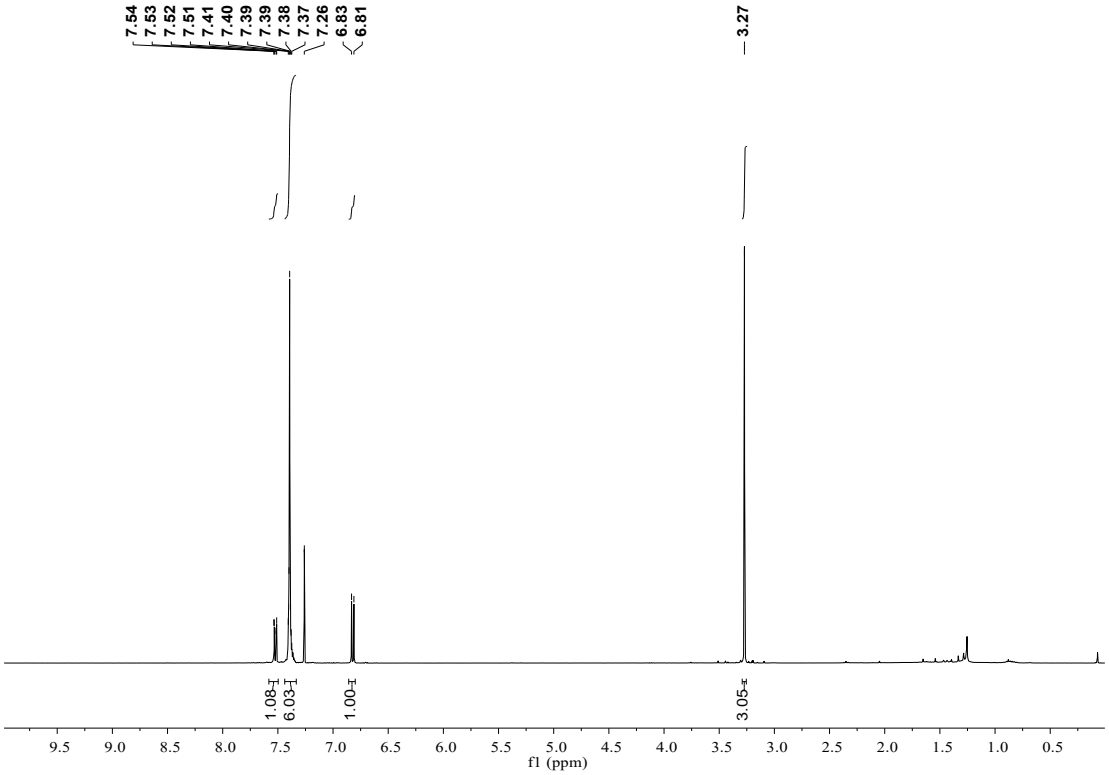
^{13}C NMR (101MHz, $CDCl_3$)



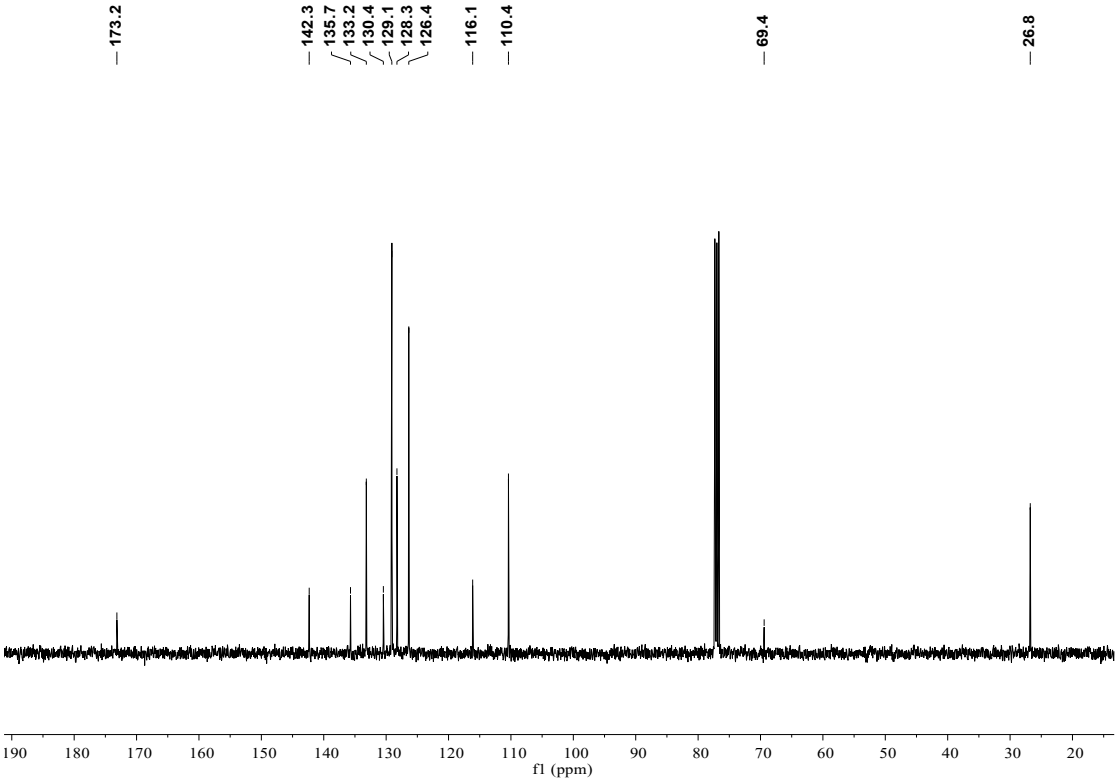


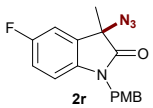
2q

^{1}H NMR (400MHz, $CDCl_3$)



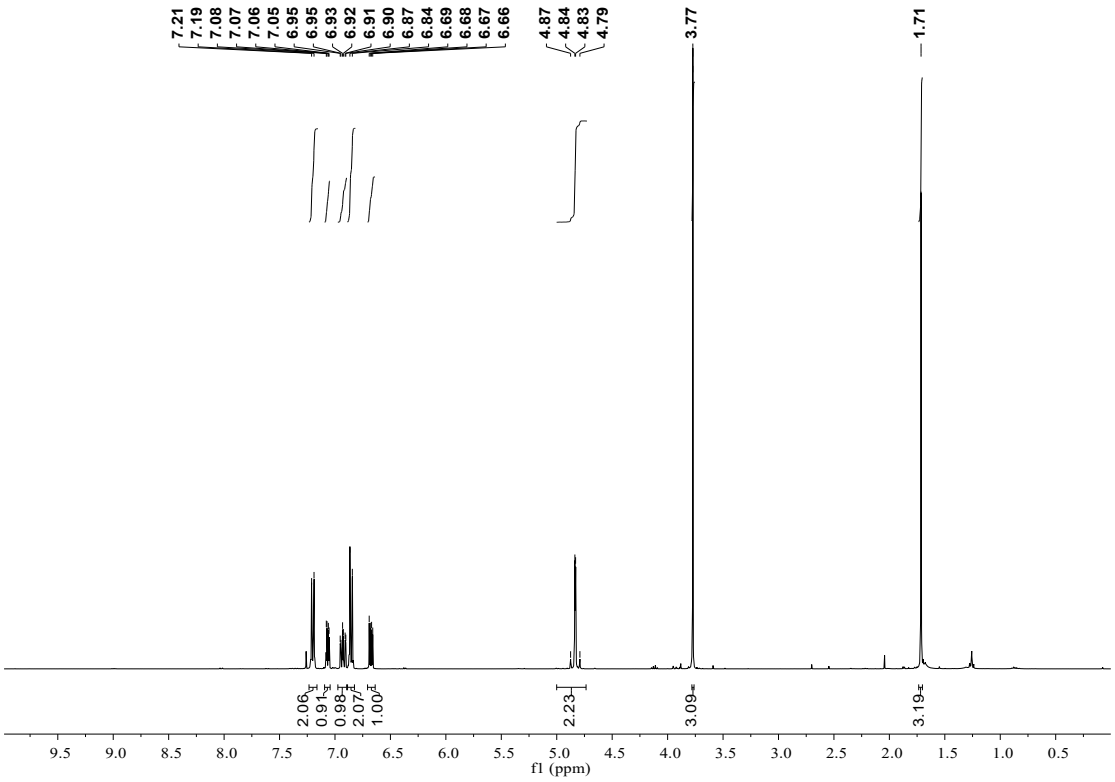
^{13}C NMR (101MHz, $CDCl_3$)



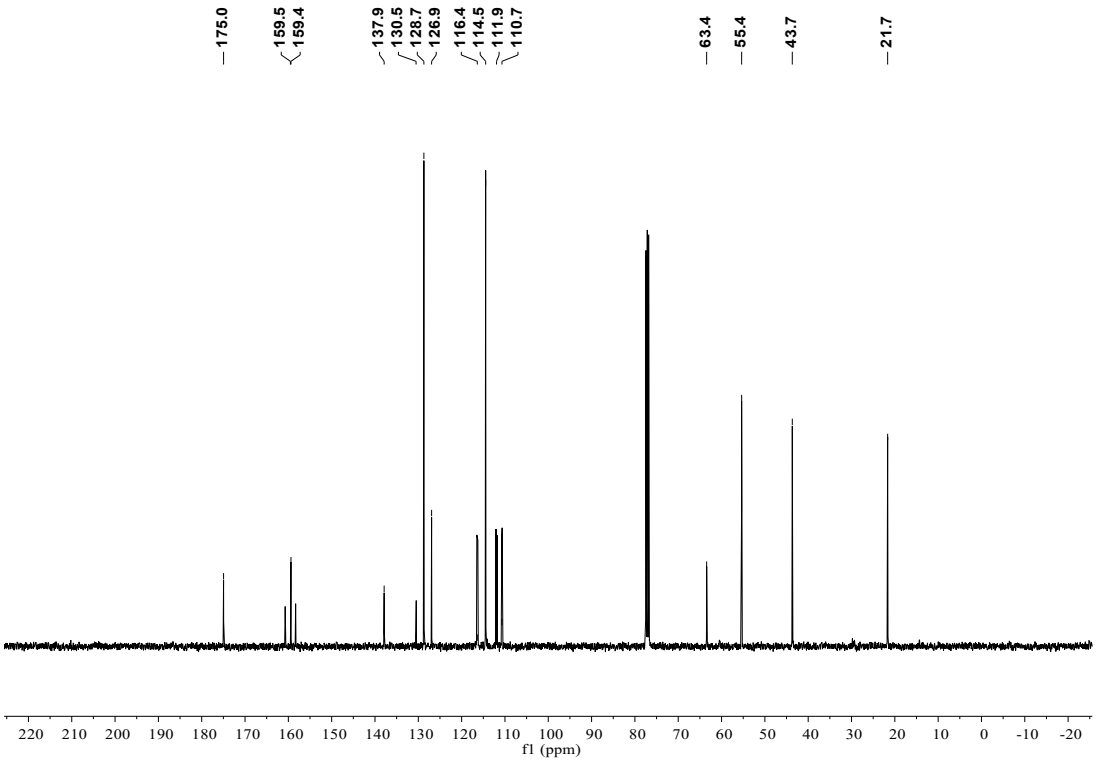


2r

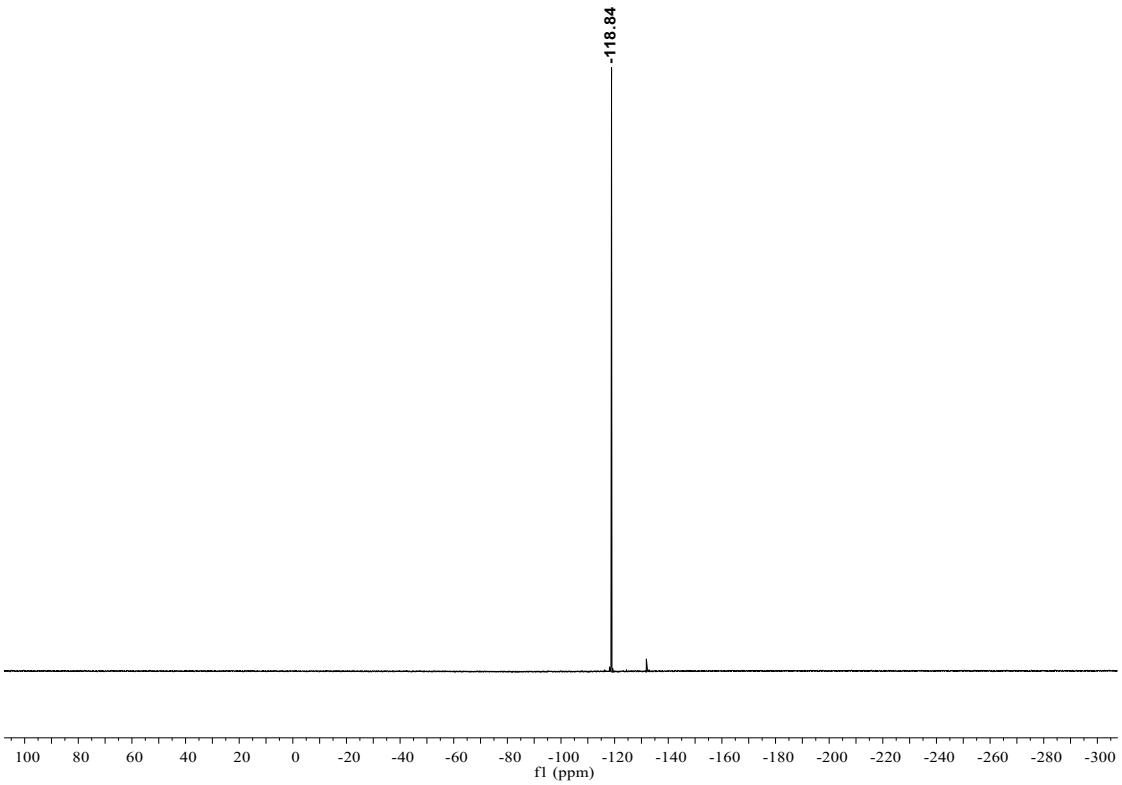
^{1}H NMR (400MHz, $CDCl_3$)

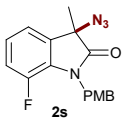


^{13}C NMR (101MHz, $CDCl_3$)



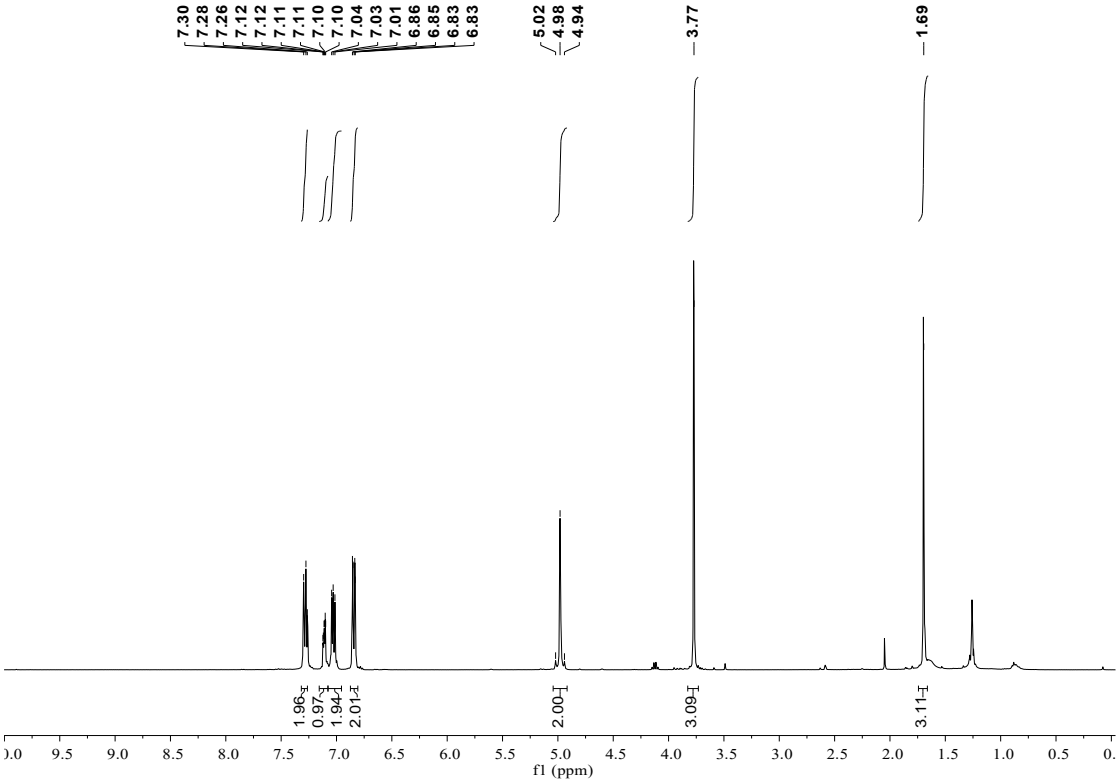
^{19}F NMR（376MHz, $CDCl_3$）



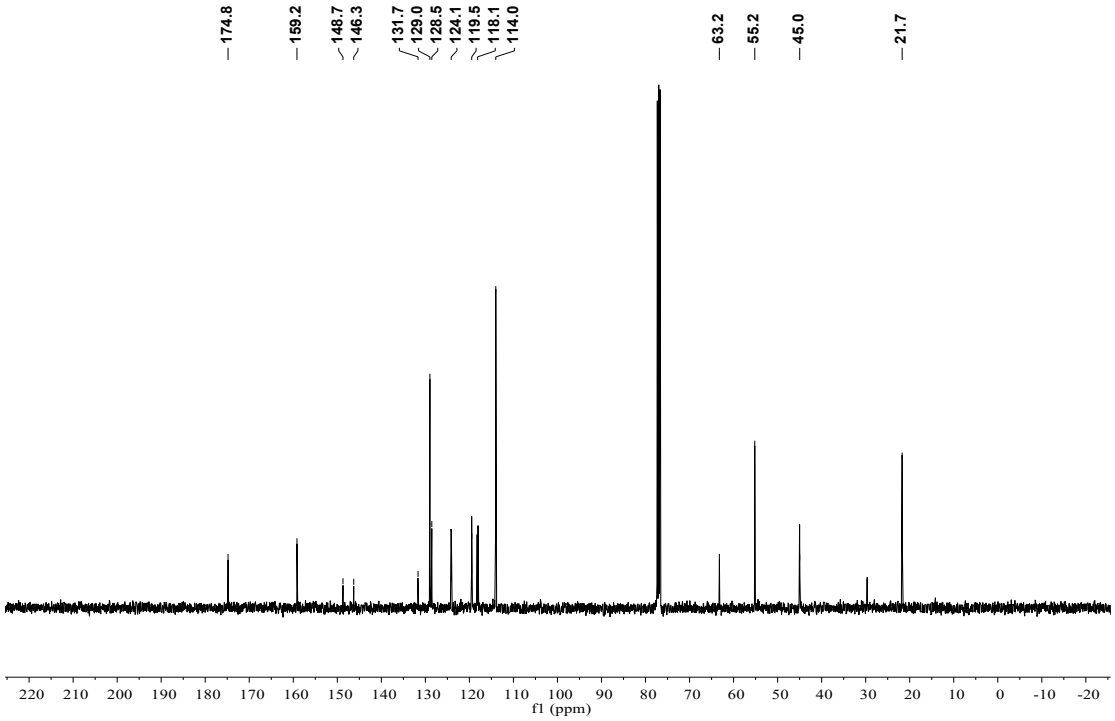


2s

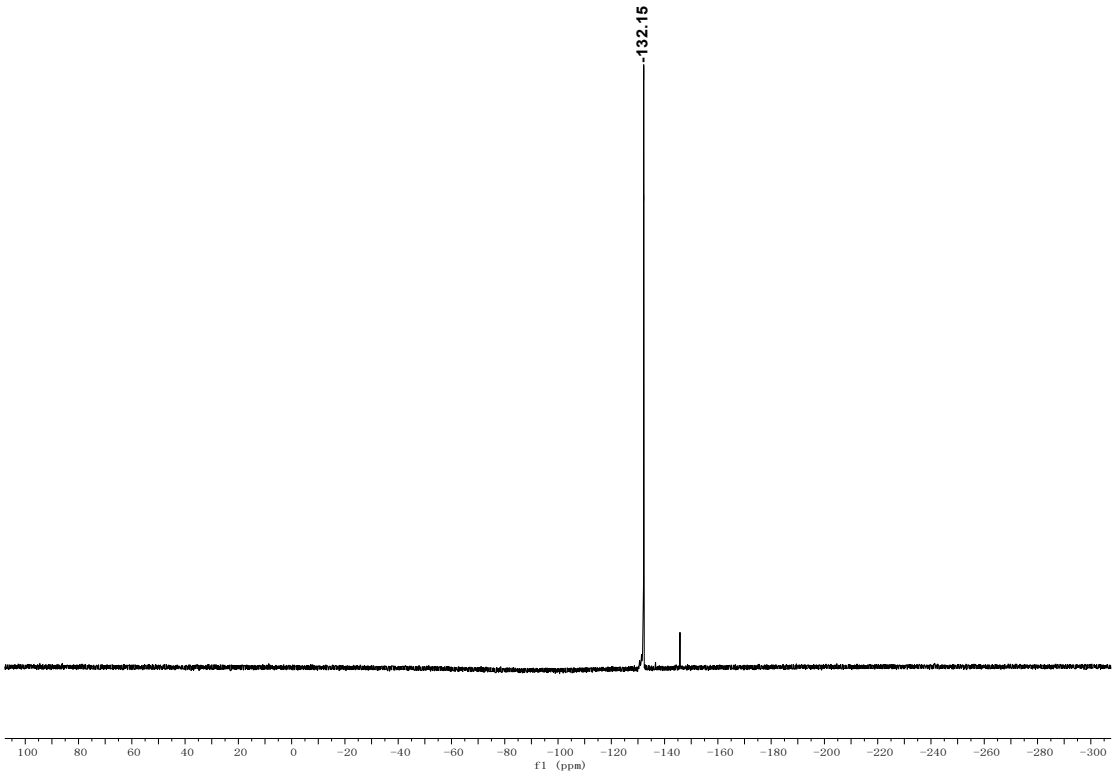
^{1}H NMR (400MHz, $CDCl_3$)

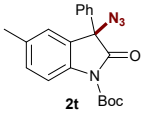


^{13}C NMR (101MHz, $CDCl_3$)



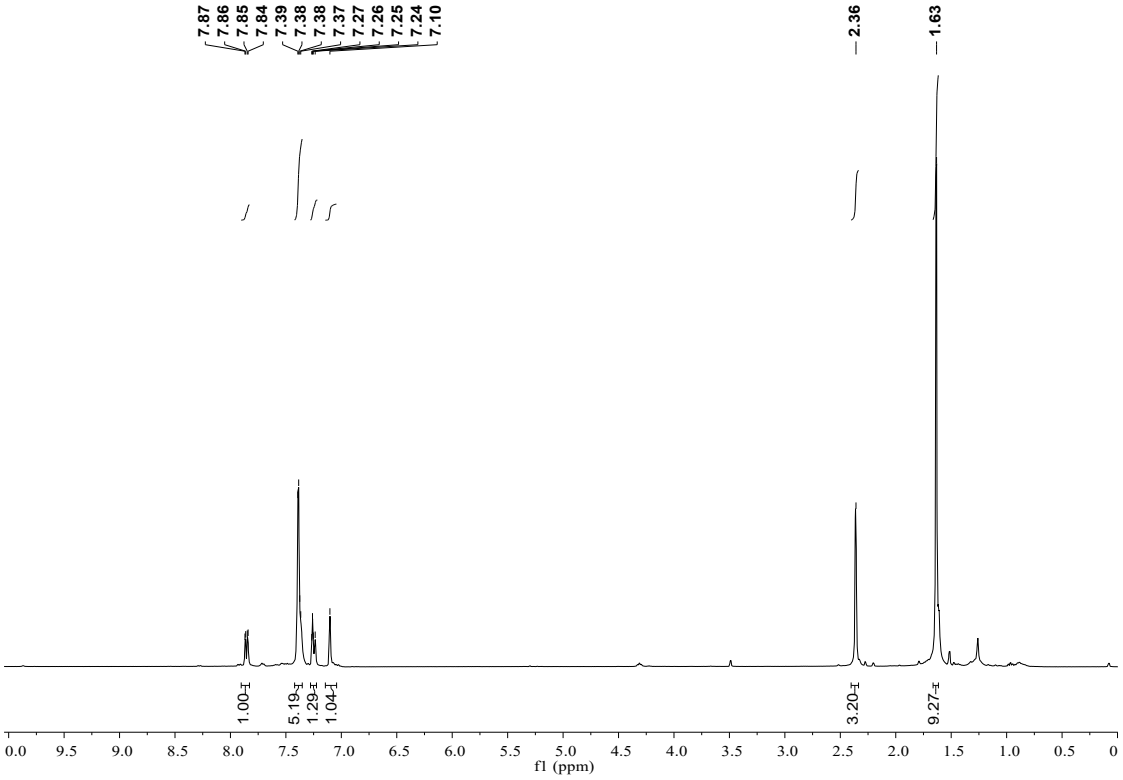
^{19}F NMR（376MHz, $CDCl_3$）



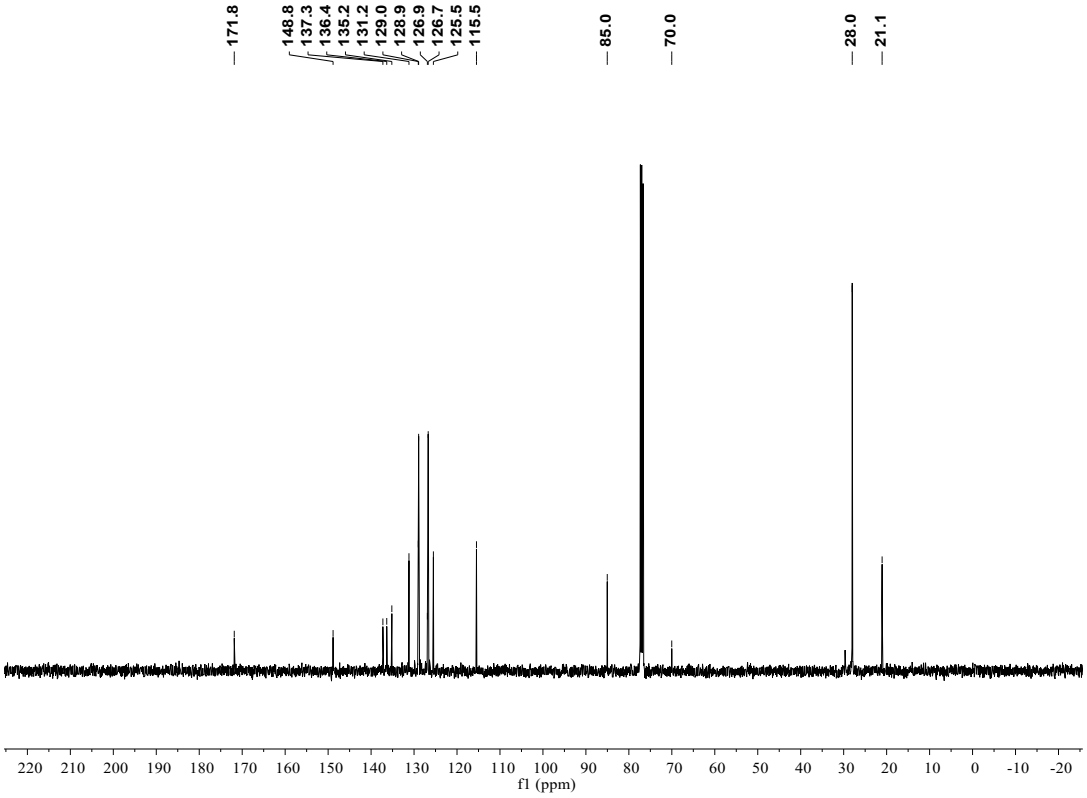


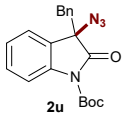
2t

^{1}H NMR (400MHz, $CDCl_3$)



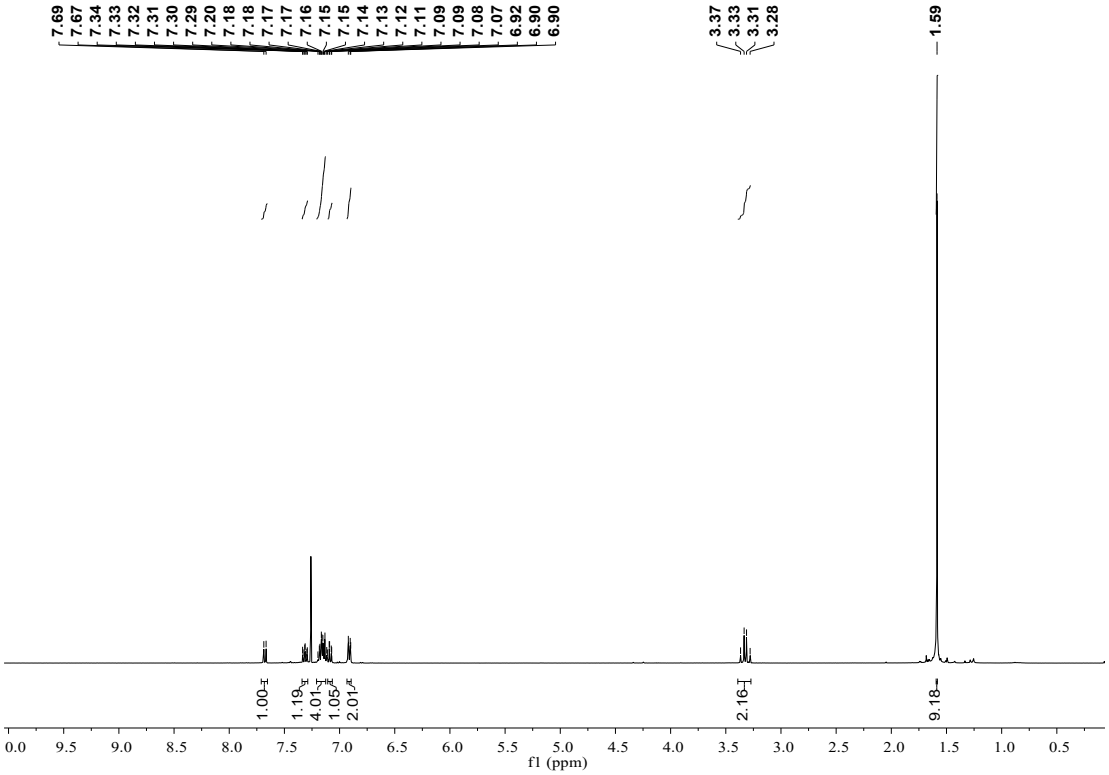
^{13}C NMR (101MHz, $CDCl_3$)



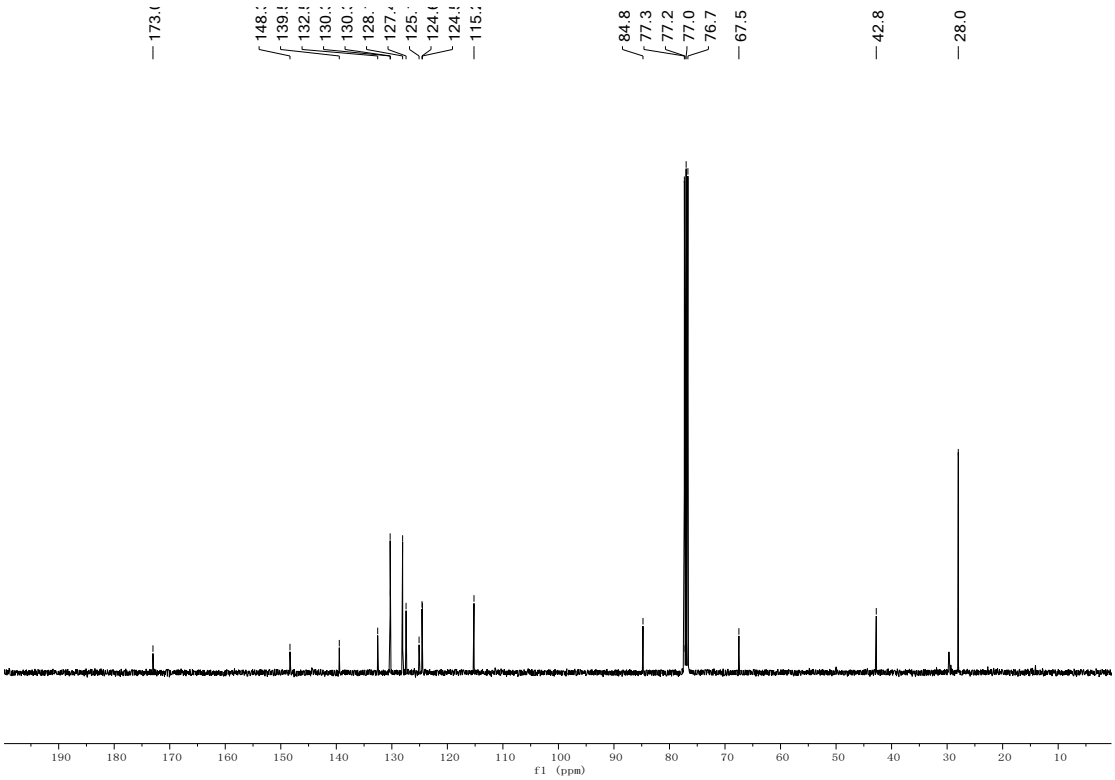


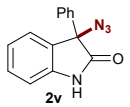
2u

^{1}H NMR (400MHz, $CDCl_3$)



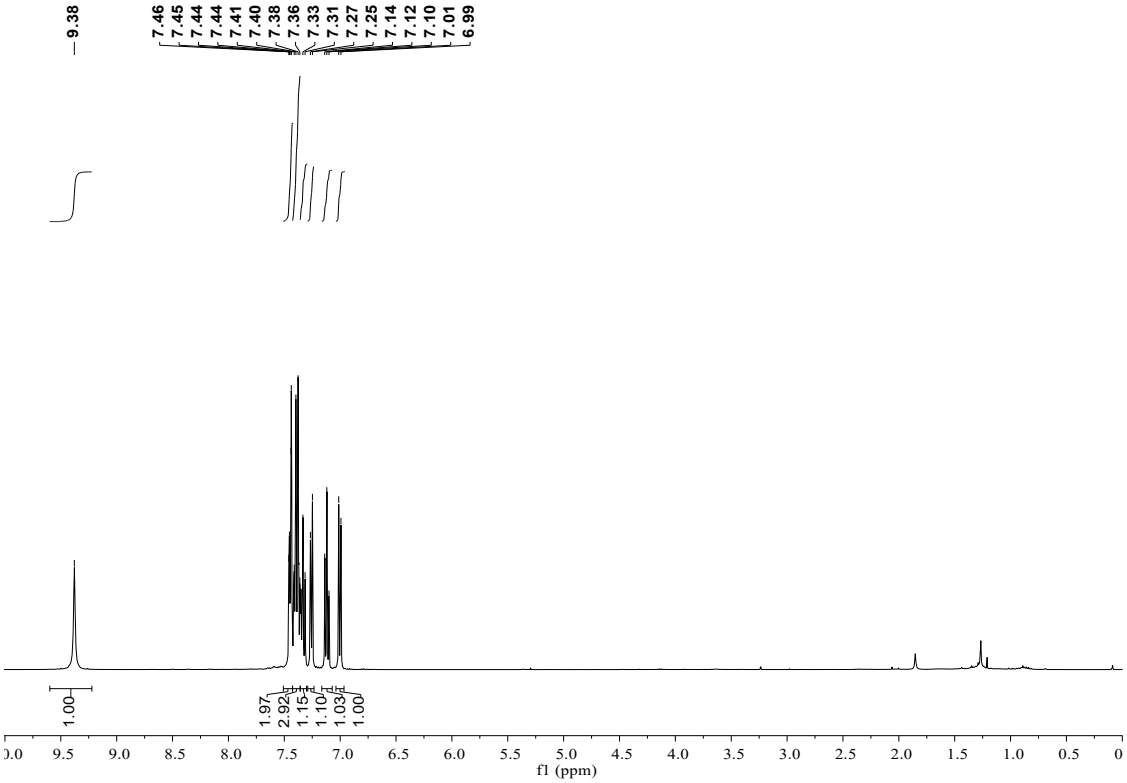
^{13}C NMR (101MHz, $CDCl_3$)



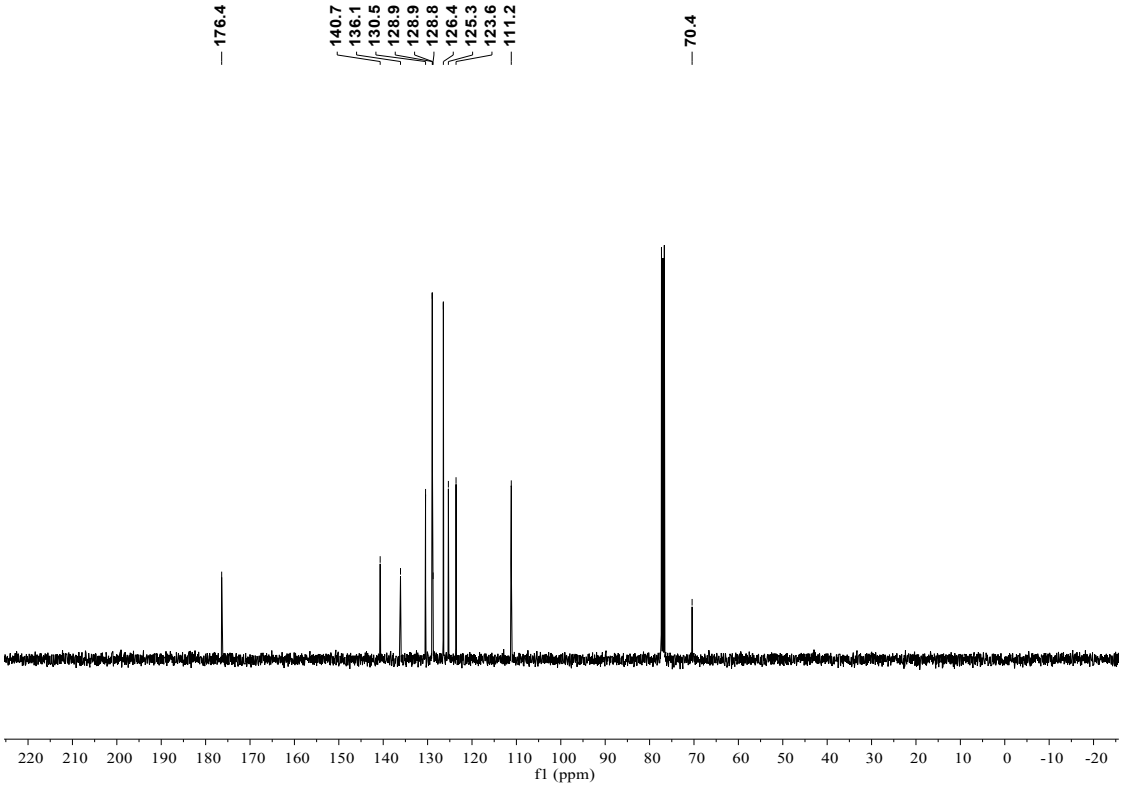


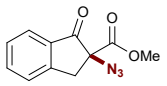
2v

^{1}H NMR (400MHz, $CDCl_3$)



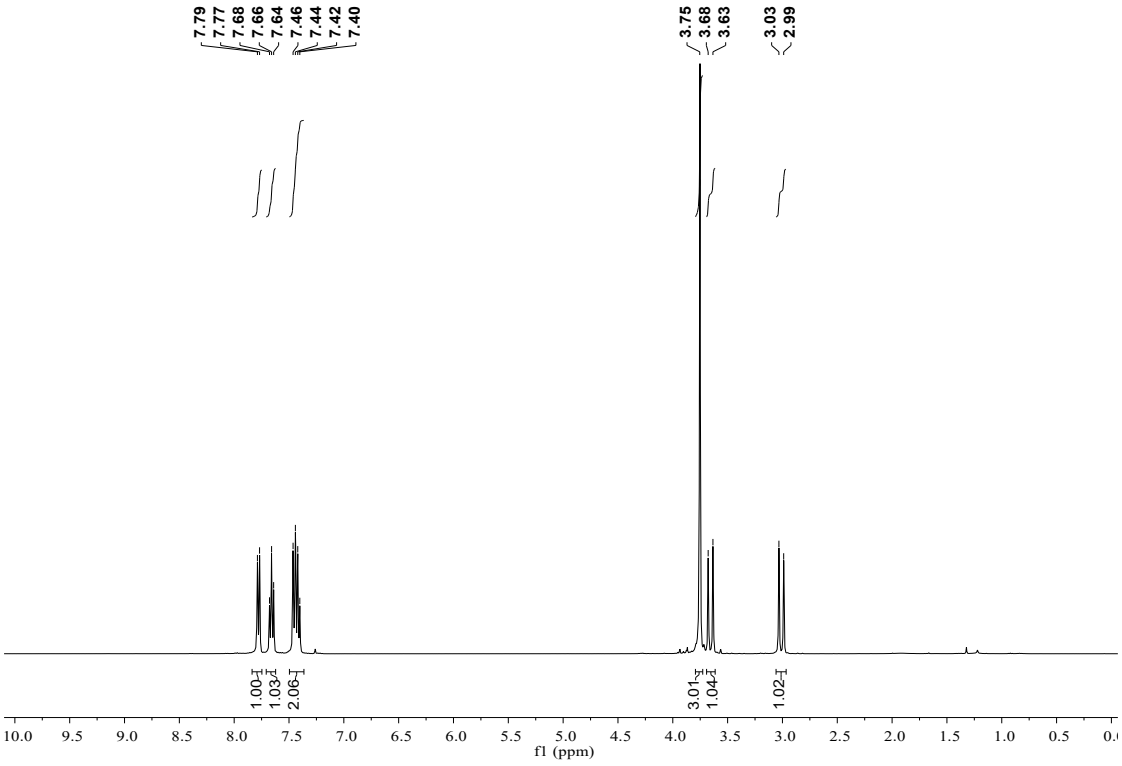
^{13}C NMR (101MHz, $CDCl_3$)



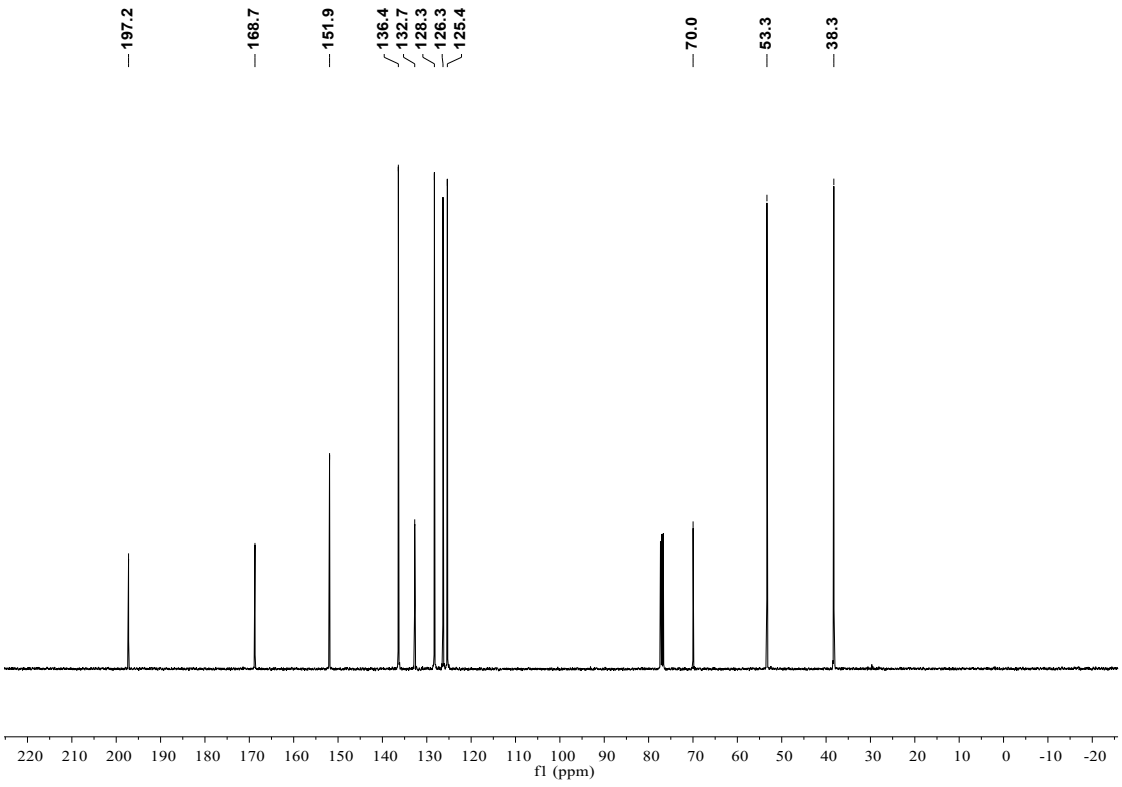


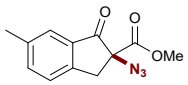
4a

^{1}H NMR (400MHz, $CDCl_3$)



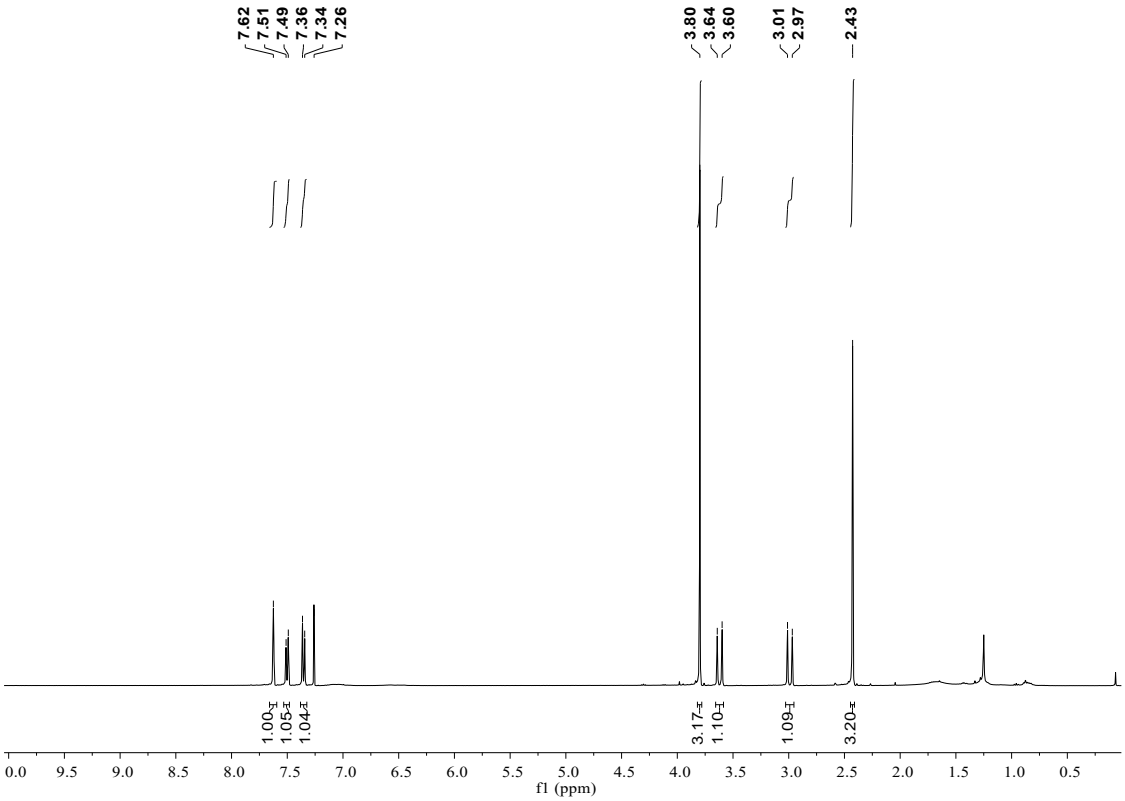
^{13}C NMR (101MHz, $CDCl_3$)



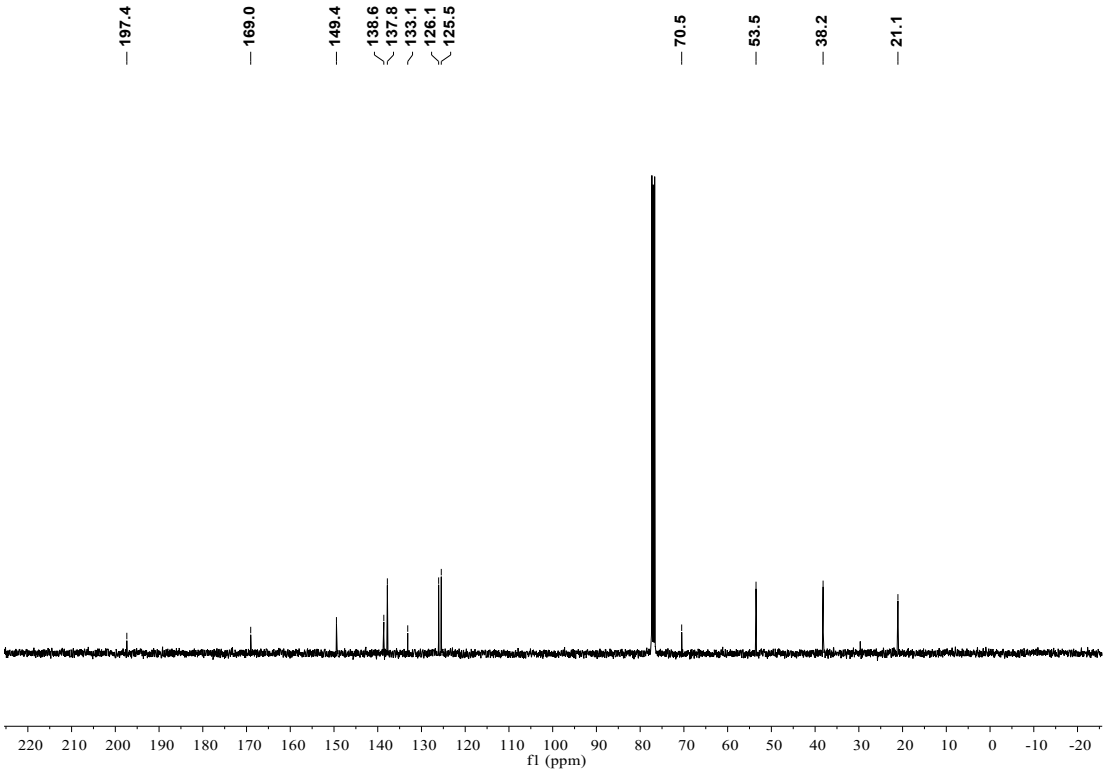


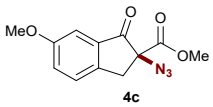
4b

^{1}H NMR (400MHz, $CDCl_3$)



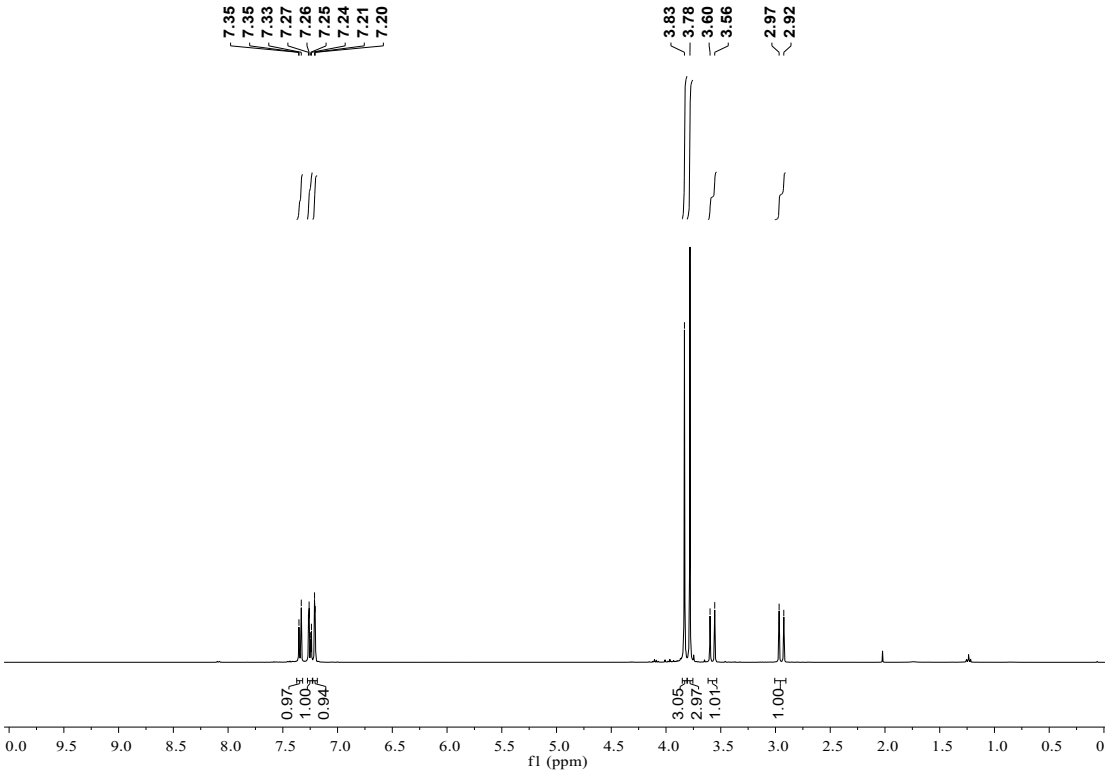
^{13}C NMR (101MHz, $CDCl_3$)



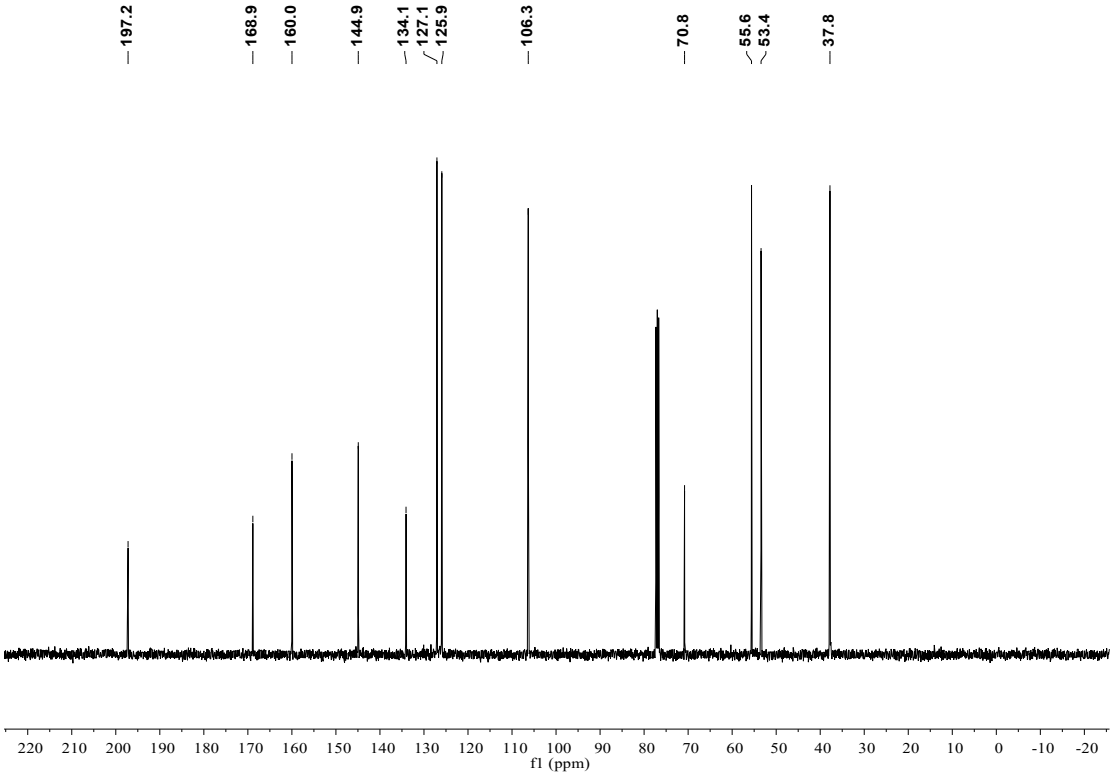


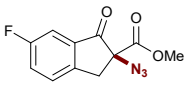
4c

^{1}H NMR (400MHz, $CDCl_3$)



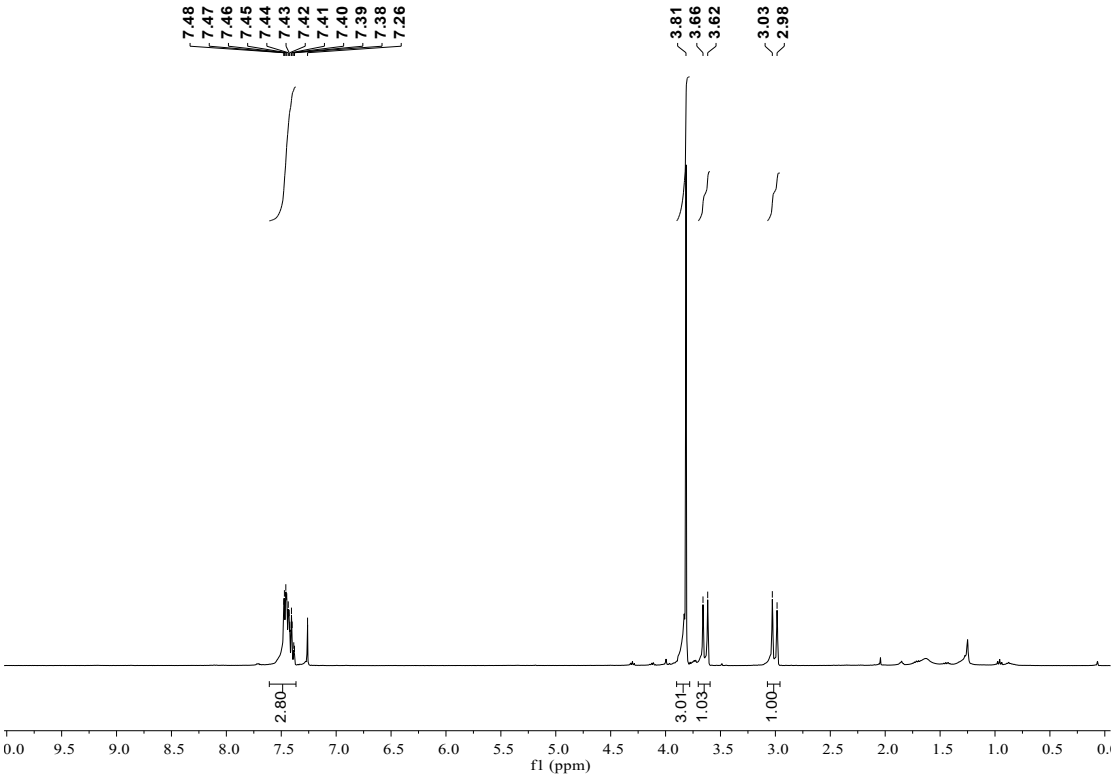
^{13}C NMR (101MHz, $CDCl_3$)



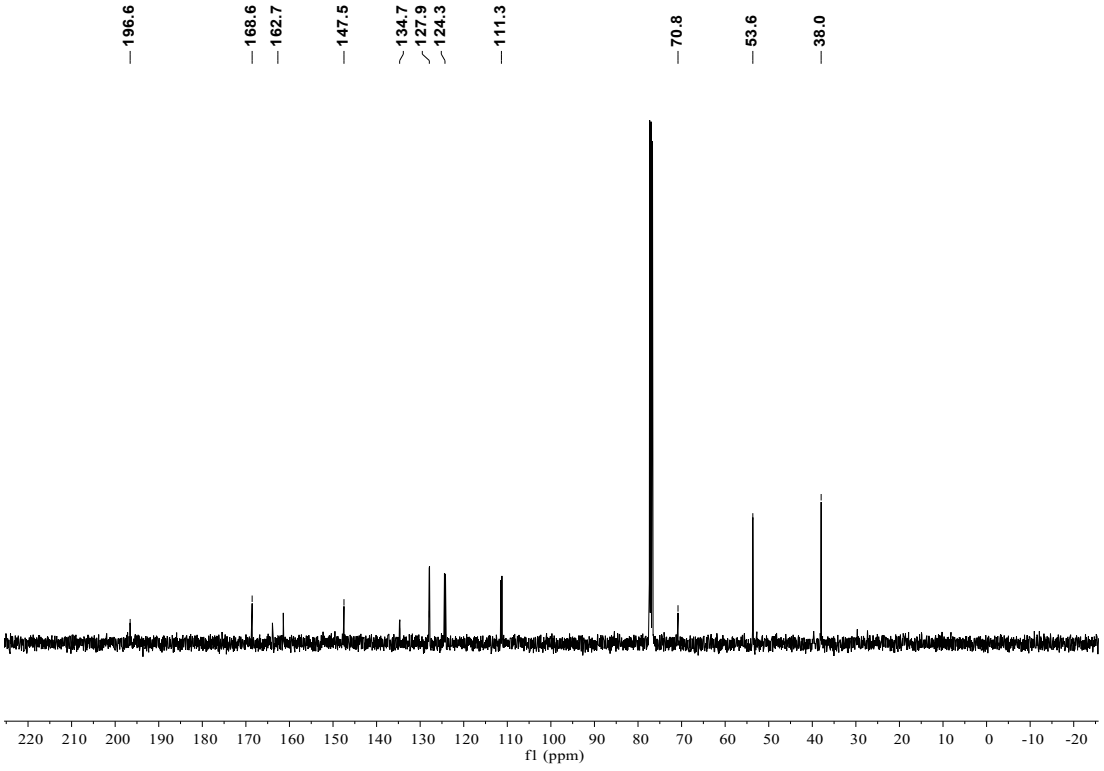


4d

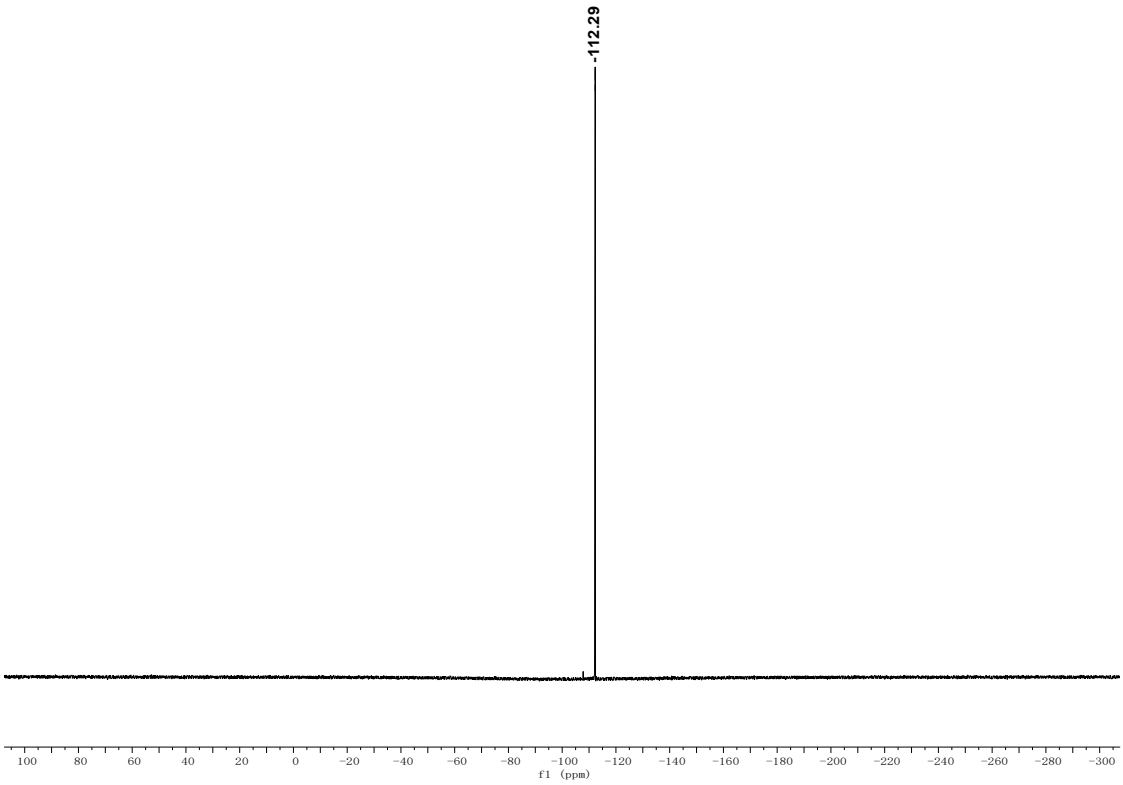
^{1}H NMR (400MHz, $CDCl_3$)

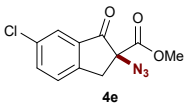


^{13}C NMR (101MHz, $CDCl_3$)



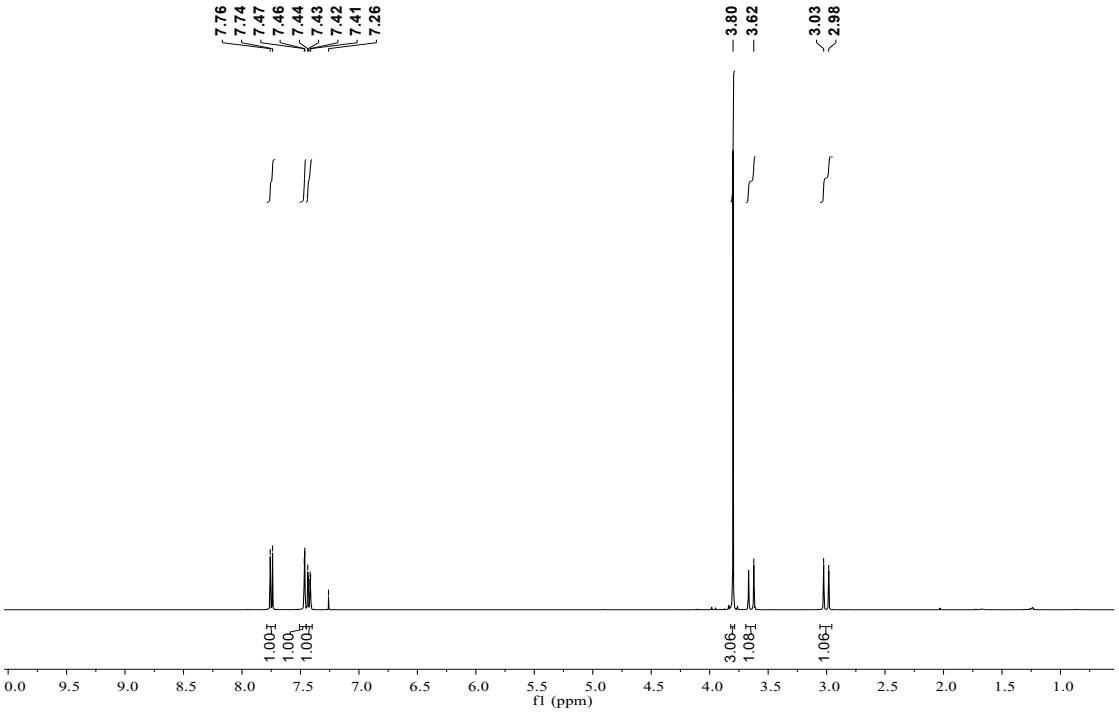
^{19}F NMR（376MHz, $CDCl_3$）



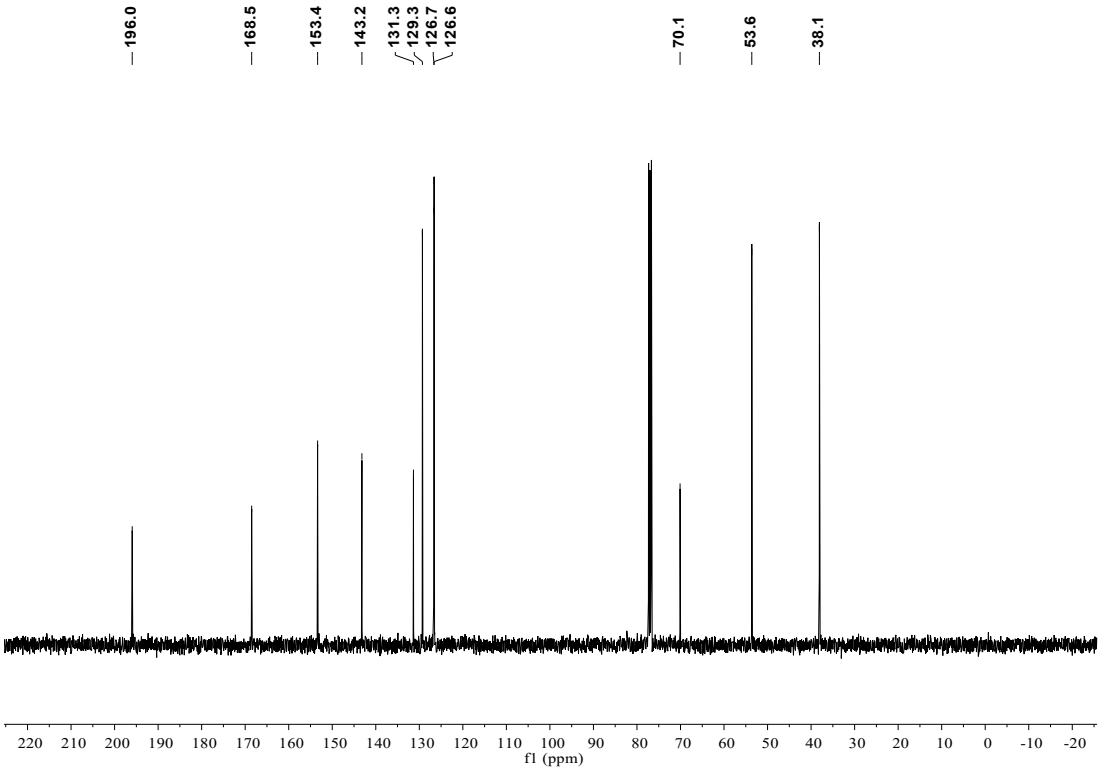


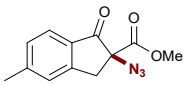
4e

^{1}H NMR (400MHz, $CDCl_3$)



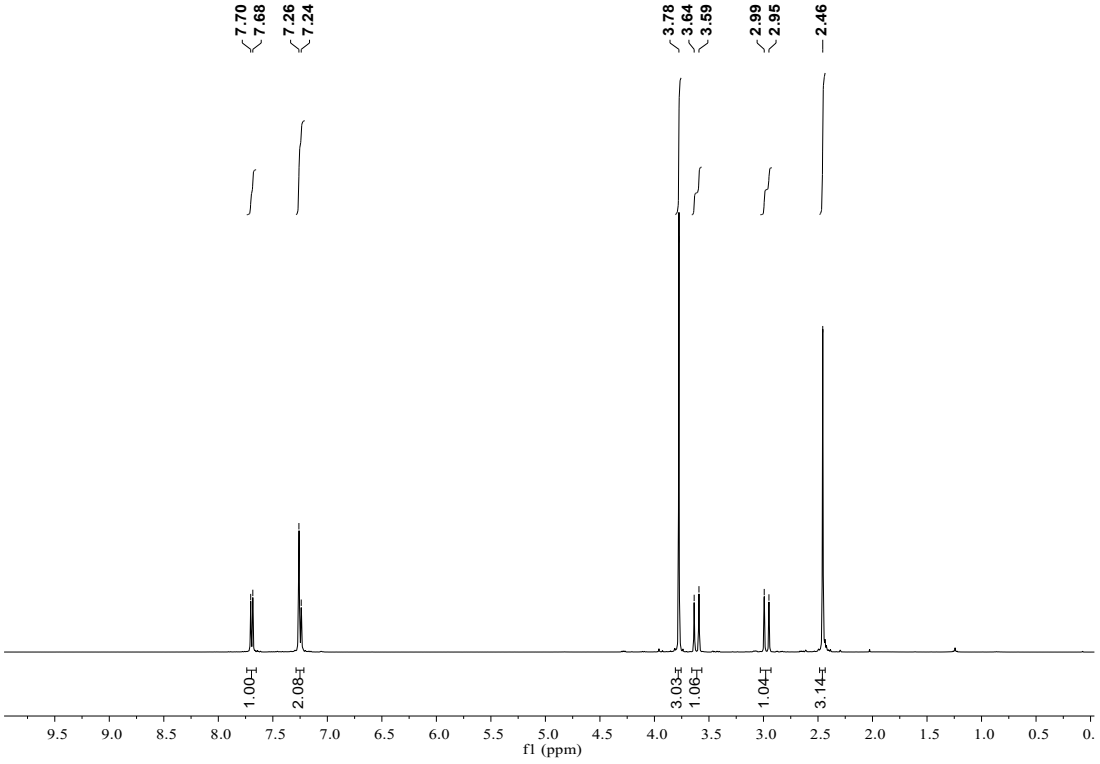
^{13}C NMR (101MHz, $CDCl_3$)



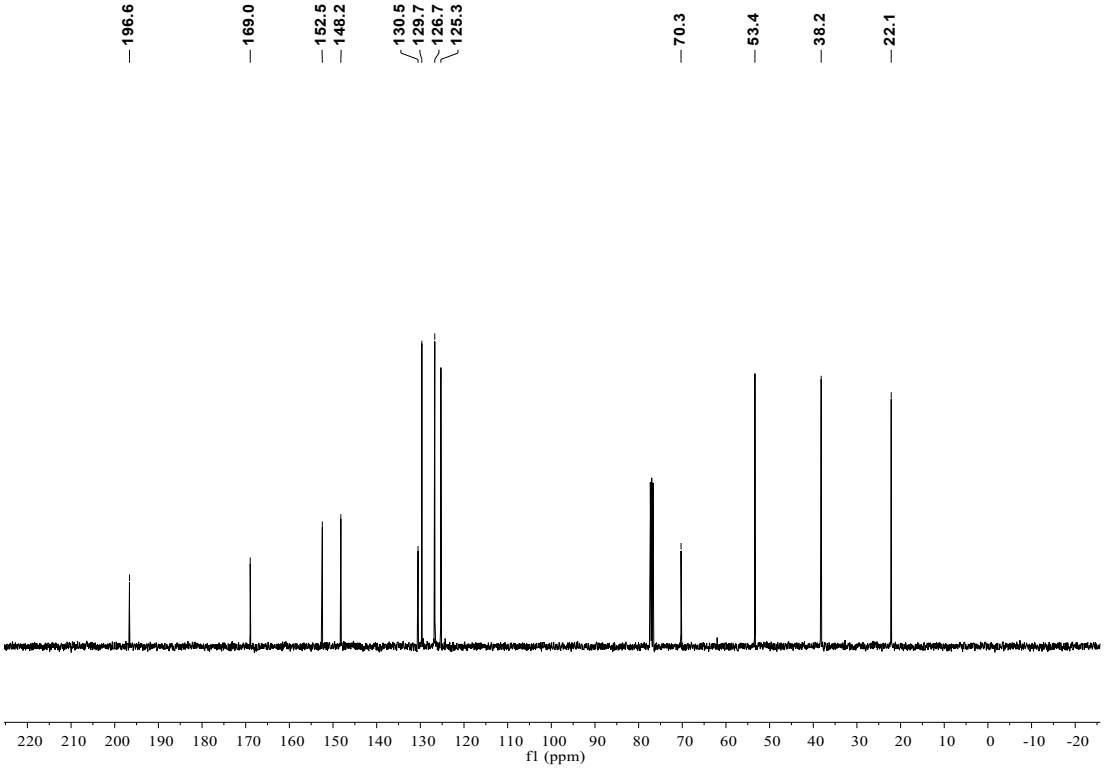


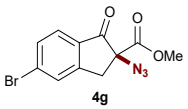
4f

^{1}H NMR (400MHz, $CDCl_3$)



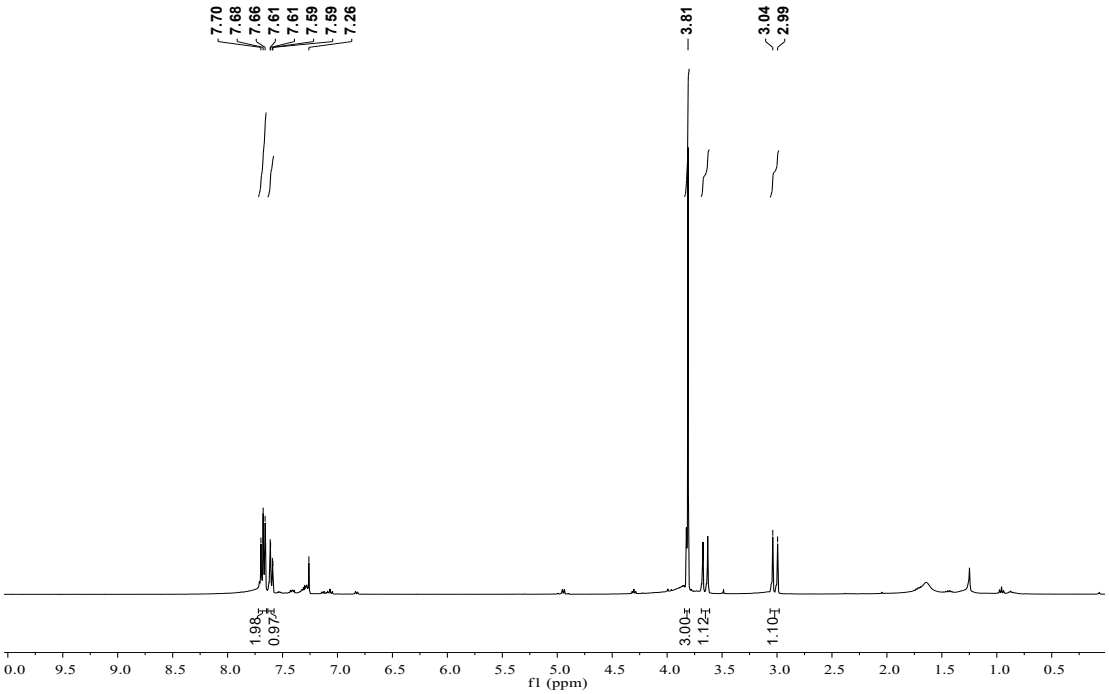
^{13}C NMR (101MHz, $CDCl_3$)



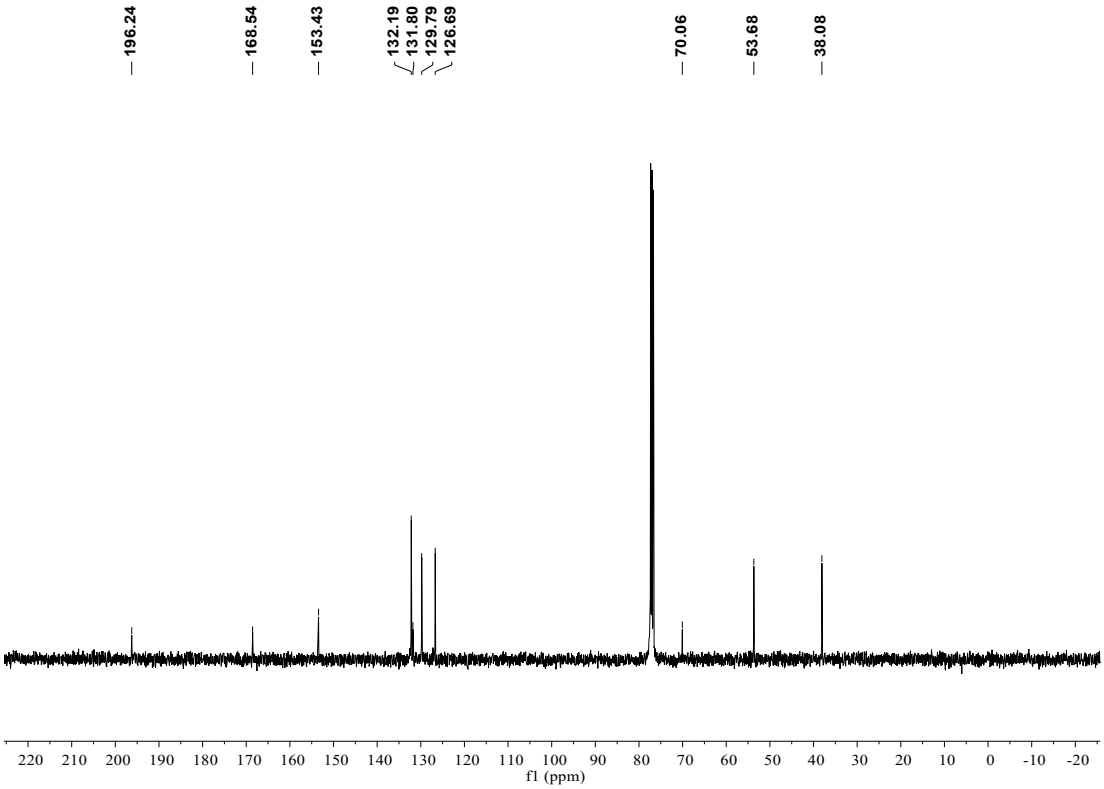


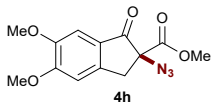
4g

^{1}H NMR (400MHz, $CDCl_3$)



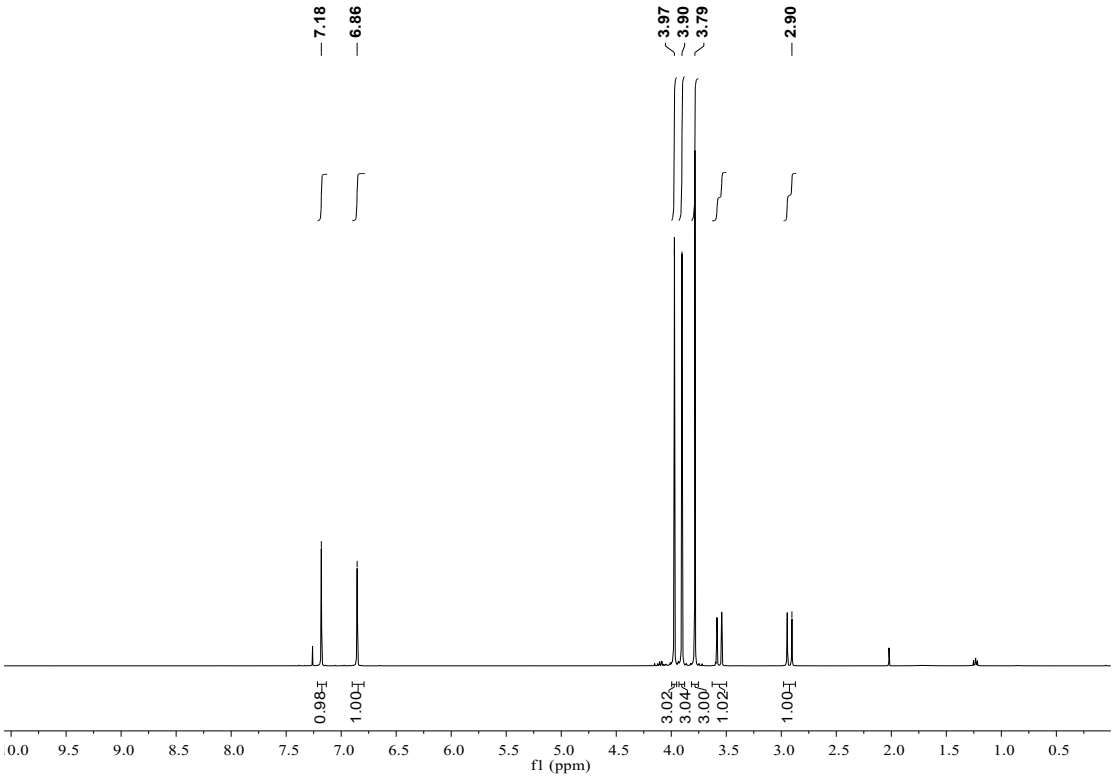
^{13}C NMR (101MHz, $CDCl_3$)



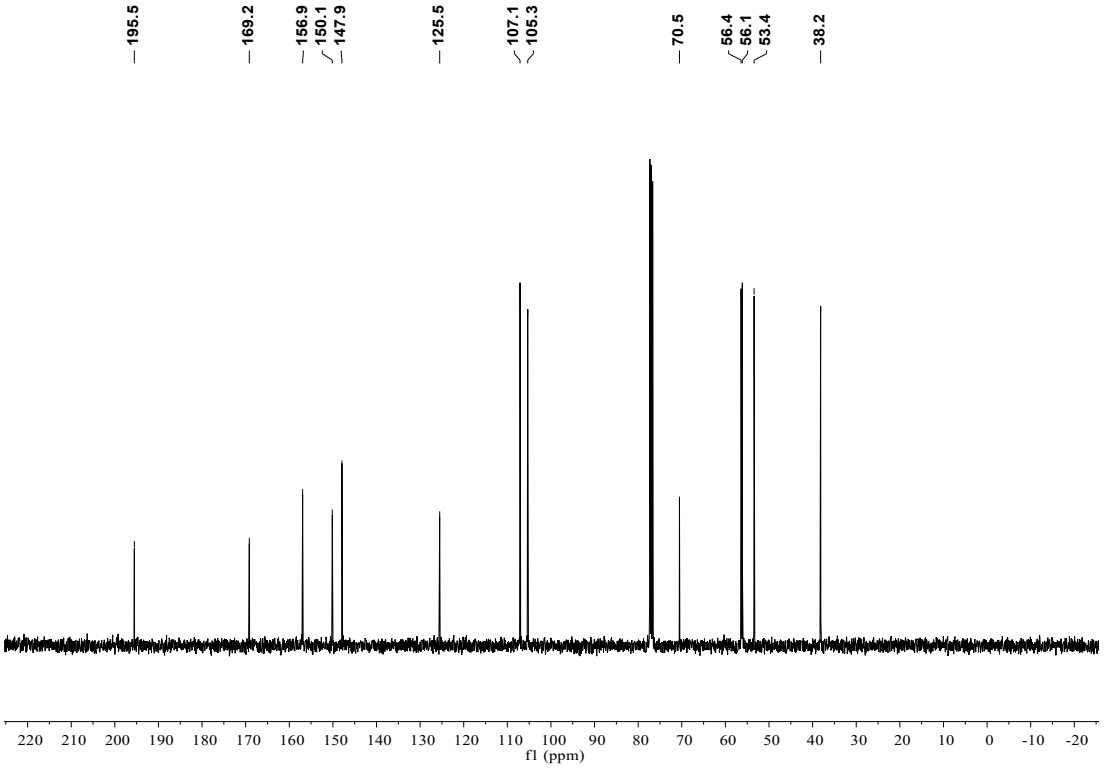


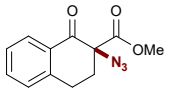
4h

^{1}H NMR (400MHz, $CDCl_3$)



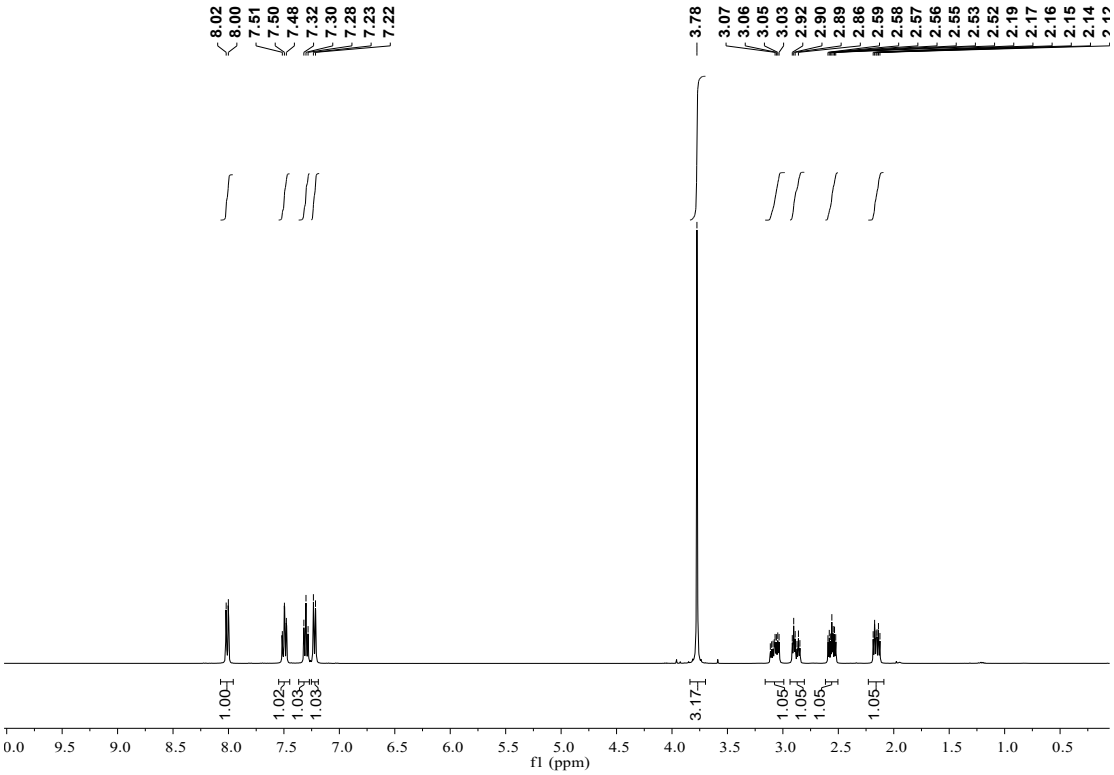
^{13}C NMR (101MHz, $CDCl_3$)



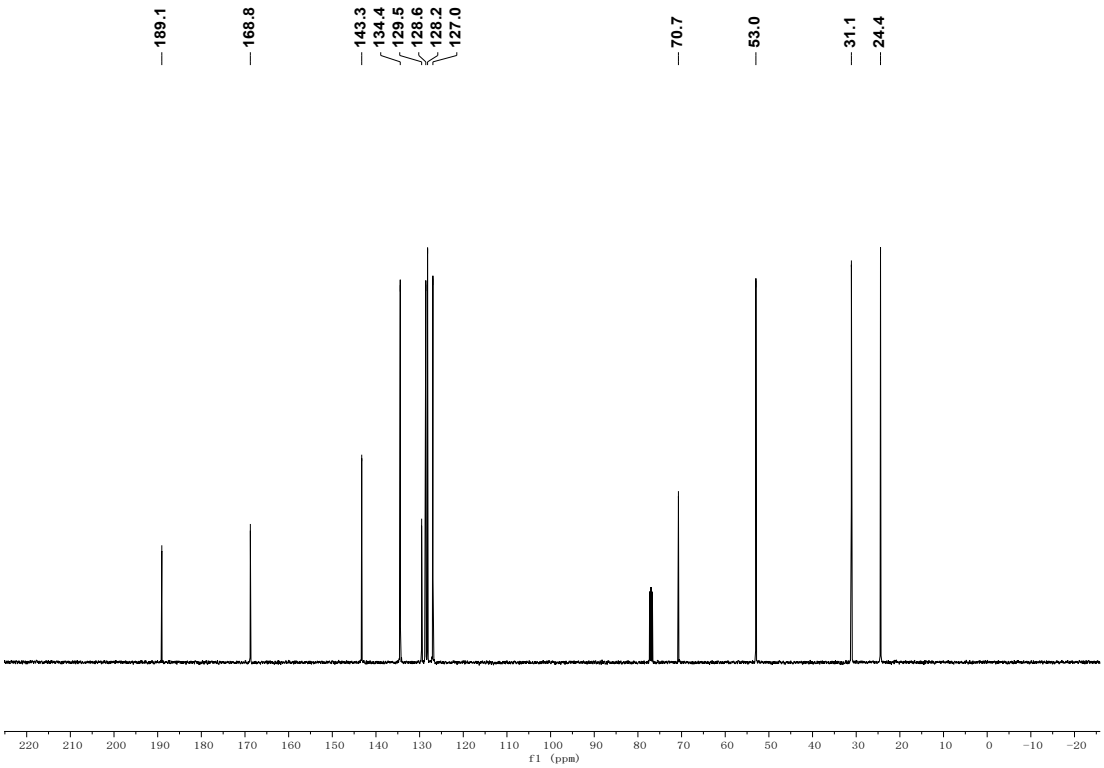


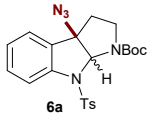
4i

^{1}H NMR (400MHz, $CDCl_3$)



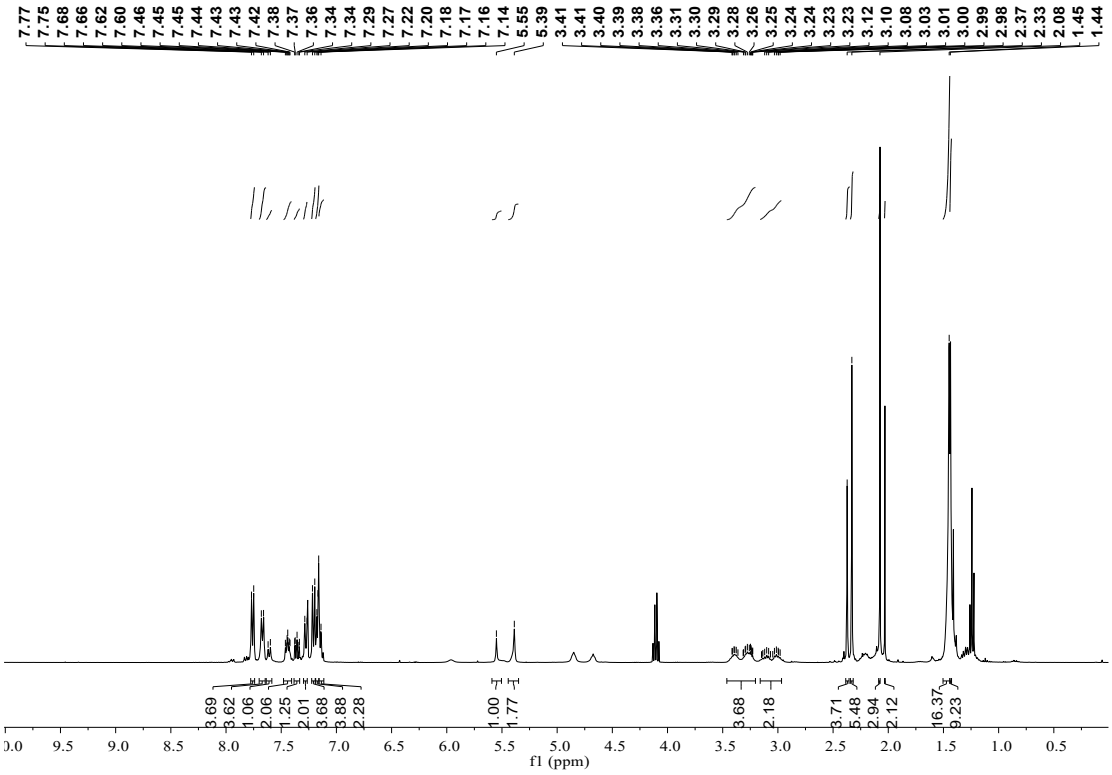
^{13}C NMR (101MHz, $CDCl_3$)



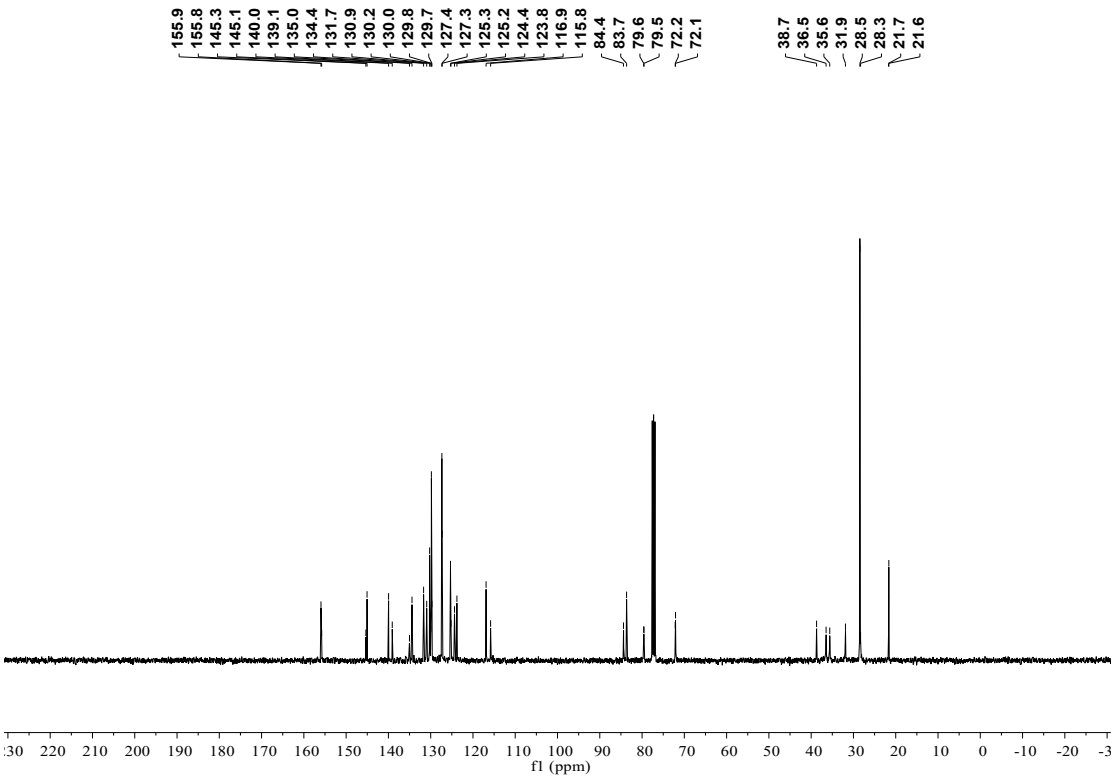


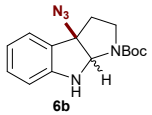
6a

^{1}H NMR (400MHz, $CDCl_3$)



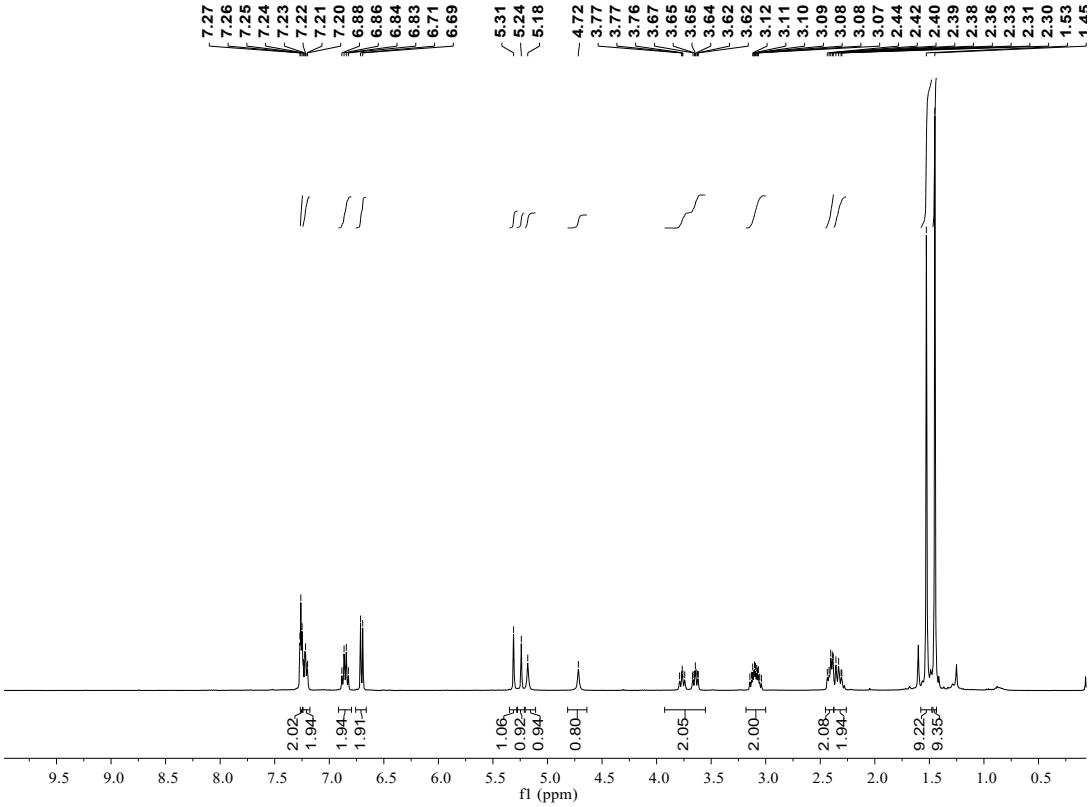
^{13}C NMR (101MHz, $CDCl_3$)



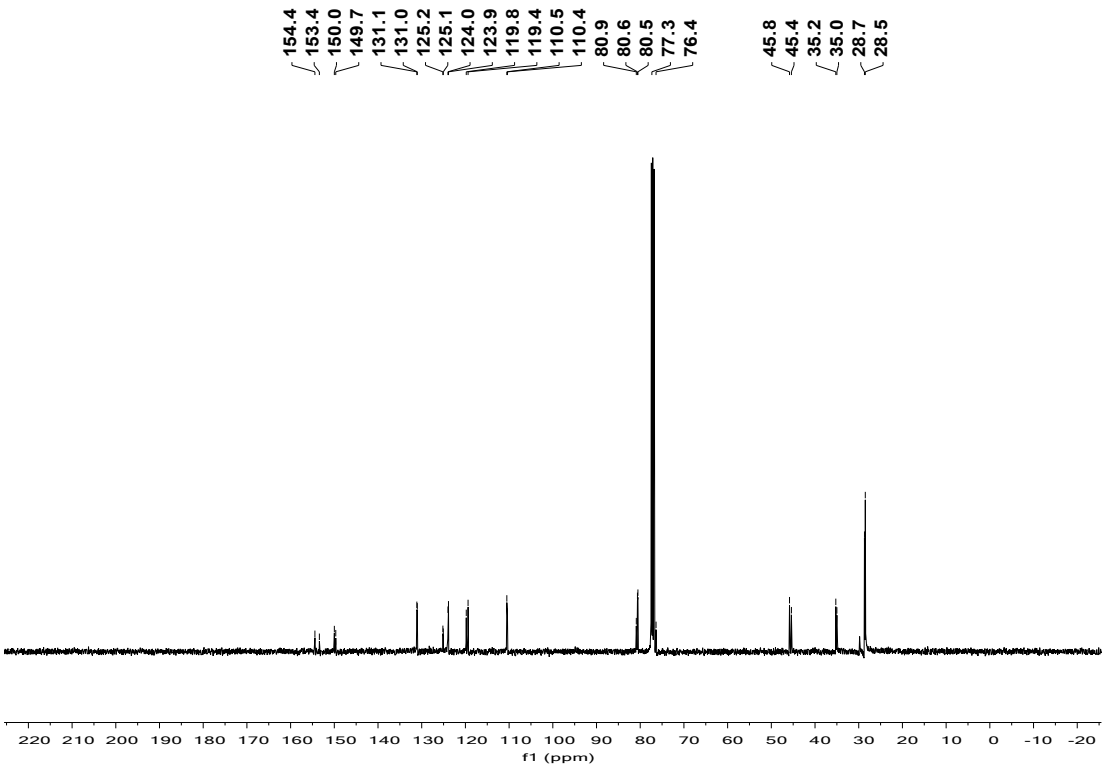


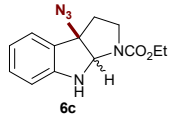
6b

^{1}H NMR (400MHz, $CDCl_3$)



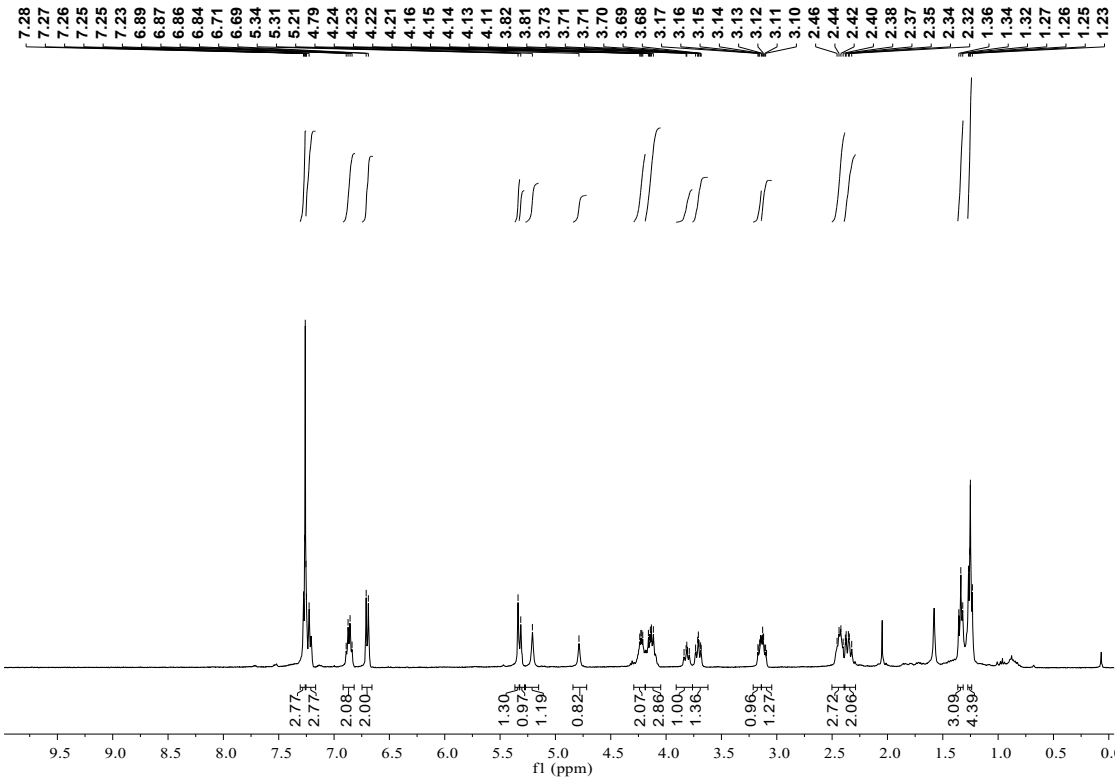
^{13}C NMR (101MHz, $CDCl_3$)



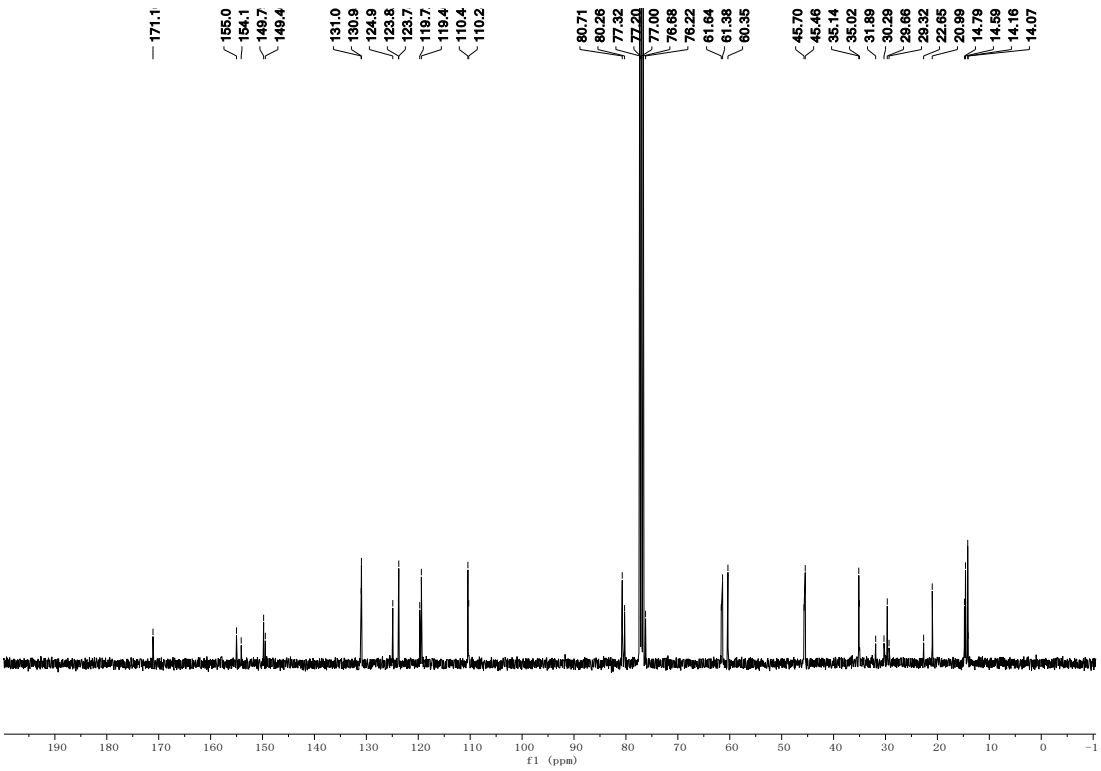


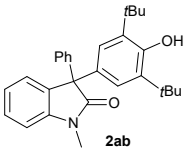
6c

^{1}H NMR (400MHz, $CDCl_3$)



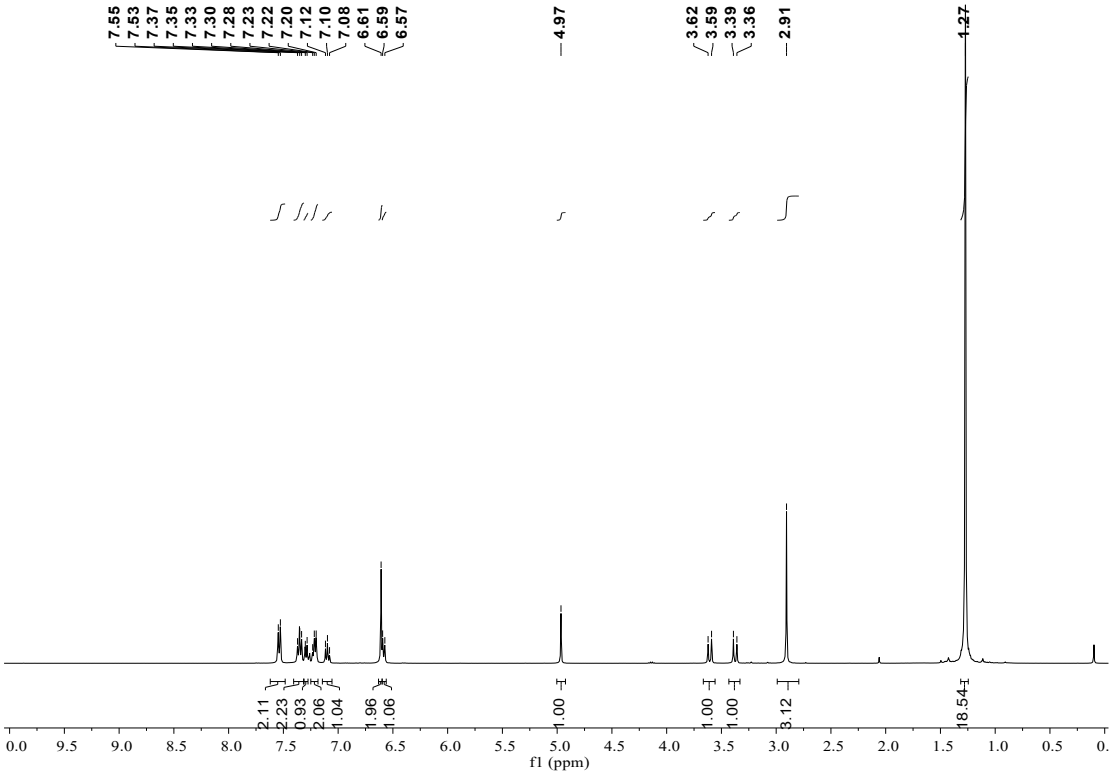
^{13}C NMR (101MHz, $CDCl_3$)



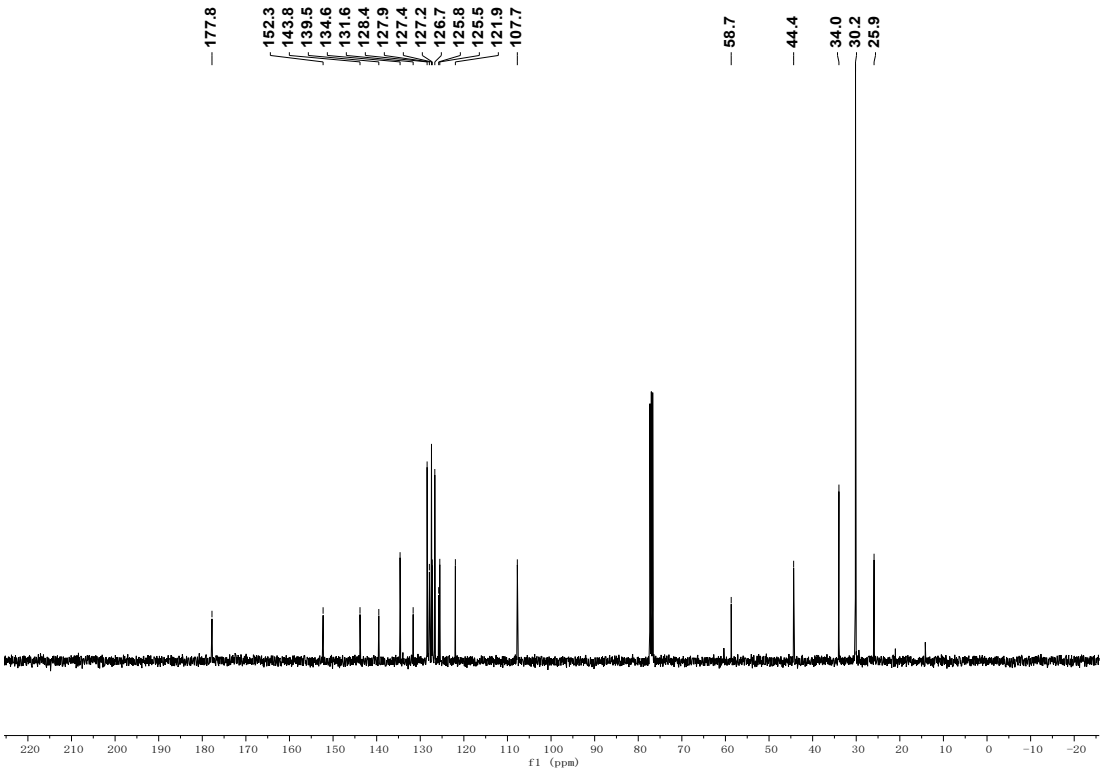


2ab

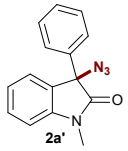
^{1}H NMR (400MHz, $CDCl_3$)



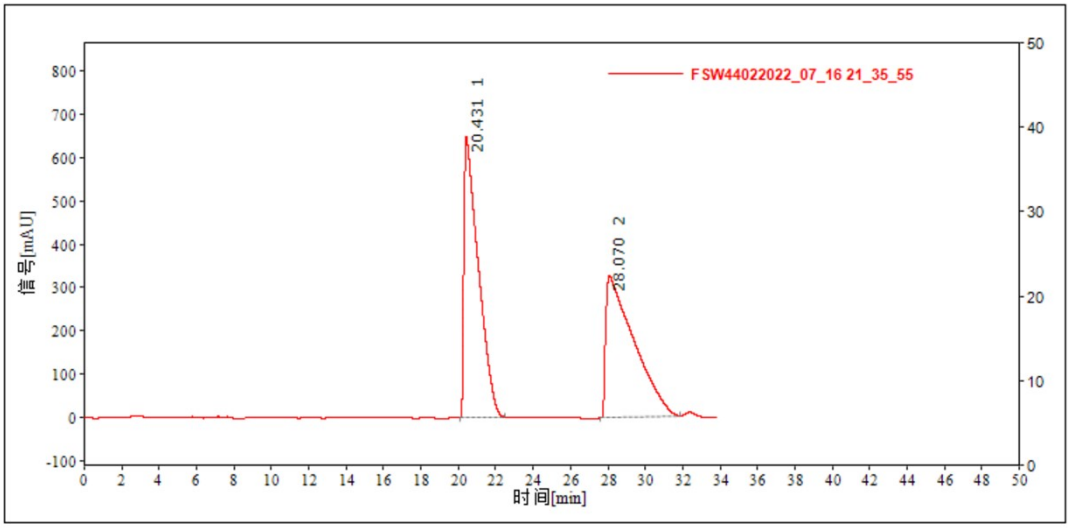
^{13}C NMR (101MHz, $CDCl_3$)



9. Chiral HPLC spectra

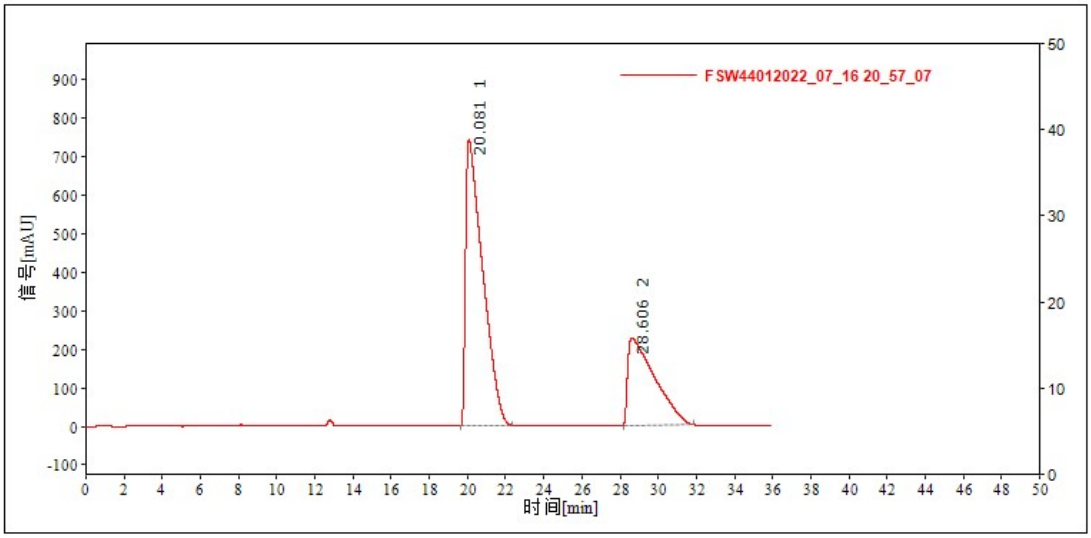


Enantiomeric excess was determined by chiral HPLC: Chiralcel IA (Hex/IPA = 99/1, 1.0 mL/min, 254 nm, 25°C), 20.08 min (major), 28.61 min, 34% *ee*.



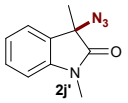
结果表(FSW44022022_07_16 21_35_55)

序号	保留时间[min]	峰高[mAU]	峰高[%]	峰面积[mAU.s]	峰面积[%]	0.05峰高处峰宽[min]	化合物名称
1	20.431	647.073	66.3	34741.121	50.4	1.792	
2	28.070	328.155	33.7	34208.669	49.6	3.494	
合计		975.228	100.0	68949.790	100.0		

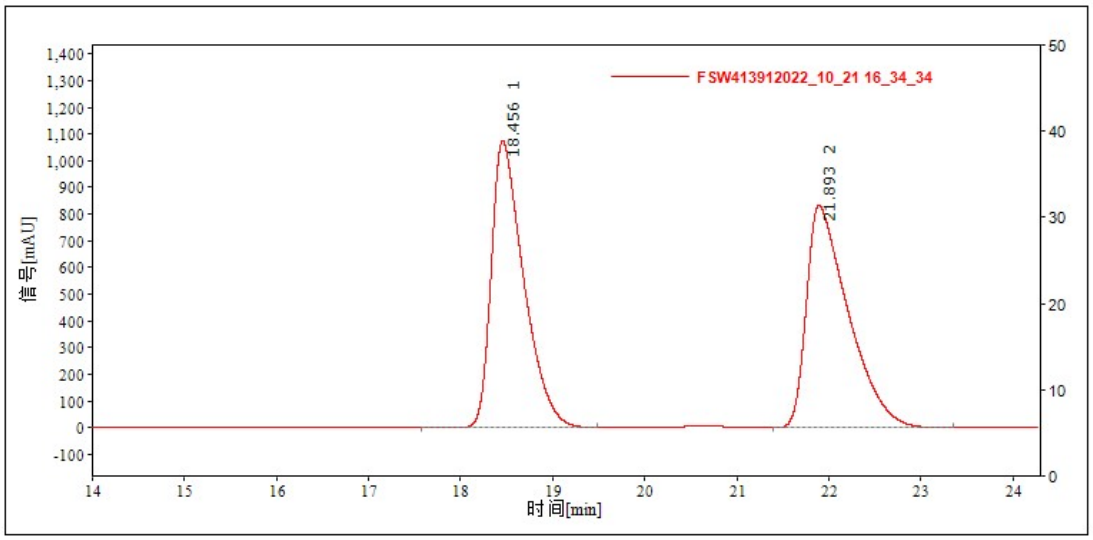


结果表(FSW44012022_07_16 20_57_07)

序号	保留时间[min]	峰高[mAU]	峰高[%]	峰面积[mAU.s]	峰面积[%]	0.05峰高处峰宽[min]	化合物名称
1	20.081	744.079	76.5	46569.131	67.0	2.060	
2	28.606	228.603	23.5	22928.931	33.0	3.247	
合计		972.682	100.0	69498.062	100.0		

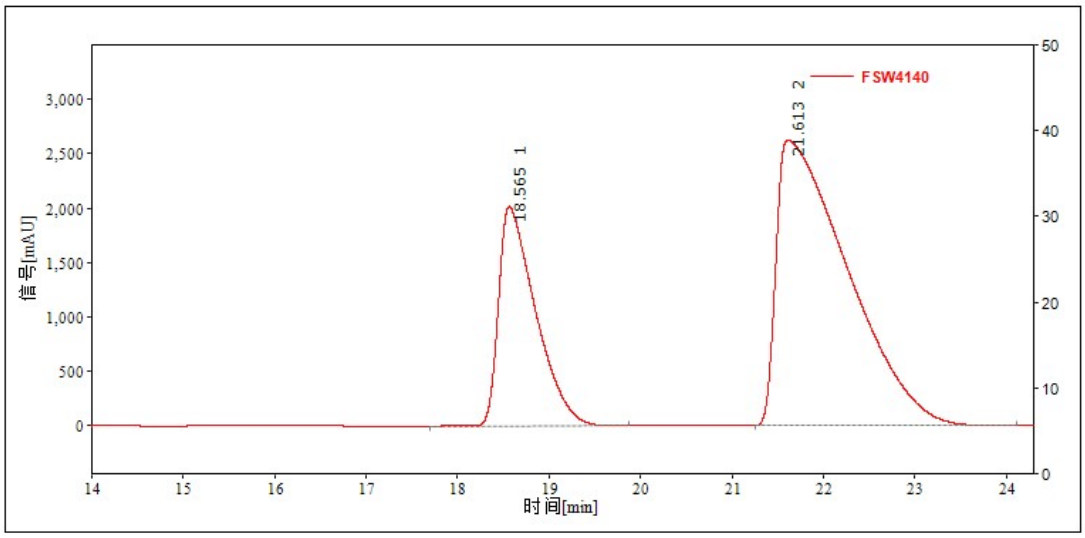


Enantiomeric excess was determined by chiral HPLC: Chiralcel IA (Hex/IPA = 99/1, 1.0 mL/min, 254 nm, 25°C), 18.57 min, 21.61 min (major), 43% *ee*.



结果表(FSW413912022_10_21 16_34_34)

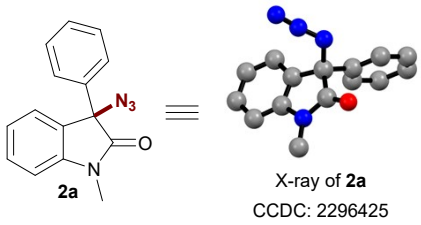
序号	保留时间[min]	峰高[mAU]	峰高[%]	峰面积[mAU.s]	峰面积[%]	0.05峰高处峰宽[min]	化合物名称
1	18.456	1074.291	56.4	26319.115	49.9	0.850	
2	21.893	832.071	43.6	26380.189	50.1	1.104	
合计		1906.362	100.0	52699.304	100.0		



结果表(FSW4140)

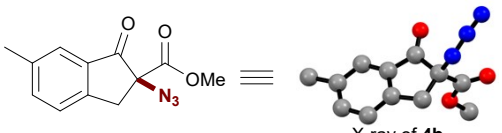
序号	保留时间[min]	峰高[mAU]	峰高[%]	峰面积[mAU.s]	峰面积[%]	0.05峰高处峰宽[min]	化合物名称
1	18.565	2014.851	43.5	56639.203	28.5	0.960	
2	21.613	2621.066	56.5	142307.576	71.5	1.763	
合计		4635.917	100.0	198946.779	100.0		

10. X-ray structure of 2a and 4b.



The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

```
Bond precision:   C-C = 0.0200 A          Wavelength=1.34139

Cell:             a=13.2924(12)     b=43.711(4)         c=9.1248(8)
                  alpha=90          beta=98.601(4)      gamma=90
Temperature:      260 K

                  Calculated                Reported
Volume            5242.1(8)                 5242.1(8)
Space group       C c                       C c
Hall group        C -2yc                    C -2yc
Moiety formula    C15 H12 N4 O              ?
Sum formula       C15 H12 N4 O              C15 H12 N4 O
Mr                264.29                    264.29
Dx,g cm-3         1.339                     1.339
Z                 16                        16
Mu (mm-1)         0.457                     0.457
F000              2208.0                    2208.0
F000'             2212.90
h,k,lmax          15,52,10                  15,52,10
Nref              9330[ 4678]               7549
Tmin,Tmax         0.872,0.892               0.308,0.705
Tmin'             0.872

Correction method= # Reported T Limits: Tmin=0.308 Tmax=0.705
AbsCorr = MULTI-SCAN

Data completeness= 1.61/0.81        Theta(max)= 53.199

R(reflections)= 0.1215( 5027)                wR2(reflections)=
                                             0.3051( 7549)
S = 1.167                  Npar= 720
```



4b

X-ray of **4b**

CCDC: 2296455

The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Bond precision: C-C = 0.0116 A Wavelength=1.34139

Cell: a=7.753(4) b=11.904(6) c=12.899(6)
alpha=87.788(19) beta=81.71(3) gamma=86.87(2)
Temperature: 150 K

	Calculated	Reported
Volume	1175.7(10)	1175.6(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C12 H11 N3 O3	C12 H11 N3 O3
Sum formula	C12 H11 N3 O3	C12 H11 N3 O3
Mr	245.24	245.24
Dx,g cm-3	1.385	1.386
Z	4	4
Mu (mm-1)	0.545	0.549
F000	512.0	512.0
F000'	513.30	
h,k,lmax	9,14,15	0,0,0
Nref	4257	4105
Tmin,Tmax	0.896,0.921	
Tmin'	0.896	

Correction method= Not given

Data completeness= 0.964 Theta(max)= 53.559

R(reflections)= 0.1492(1766) wR2(reflections)= 0.3297(4105)

S = 1.060 Npar= 323
