Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Additive Free, N-Heterocyclic Nitrenium Catalyzed Photoreduction of Cycloketone Oxime Esters

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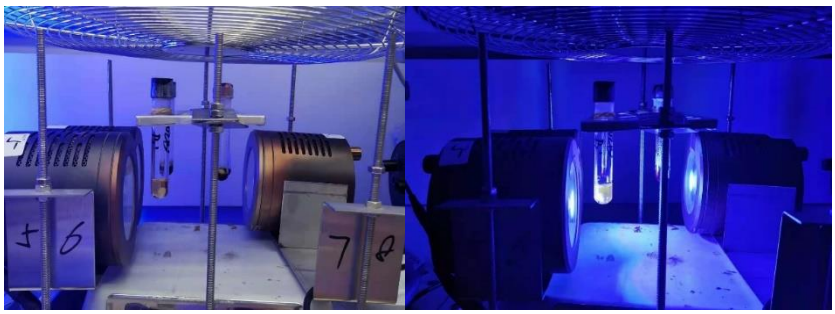
Contents

1. General Experimental Details.

- Chemicals were purchased from Heowns, Innochem and Bidepharm. They were used without further purification unless otherwise noted. The starting materials were readily prepared according to the related literatures.[1-6] Solvents were purified using a solvent-purification system (VSPS-8, Vigor) that contained activated alumina and molecular sieves.
- Chromatographic purification of the products was performed on Mietek 200-300 mesh silica gel.
- IR spectra were taken on a Vertex 70 spectrophotometer and reported as wave numbers (cm^{-1}).
- UV-vis absorption spectra were acquired on UV-2900 spectrophotometer (Shimadzu, Japan).
- The SGW X-4 was used to measure the melting point of solids.
- ^{1}H, ^{19}F and ^{13}C- NMR spectra were recorded at ambient temperature on a JEOL JNM-LA400 Spectrometer and JEOL JNM-ECZ500R Spectrometer. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as the internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, dd= doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (*J*) are reported in Hertz (Hz).
- Photochemical experiments were performed magnetically stirred in 10 mL glass tubes, sealed with a rubber septum. The tubes were irradiated with blue light (450 nm,) using a LED lamp with a power output of 100 W. The distance from the light source to the irradiation vessel is 2 cm, and a fan was used to keep the reaction temperature at 45±5 °C. （The purchase link for LED lamp is https://item.jd.com/52714507033.html）



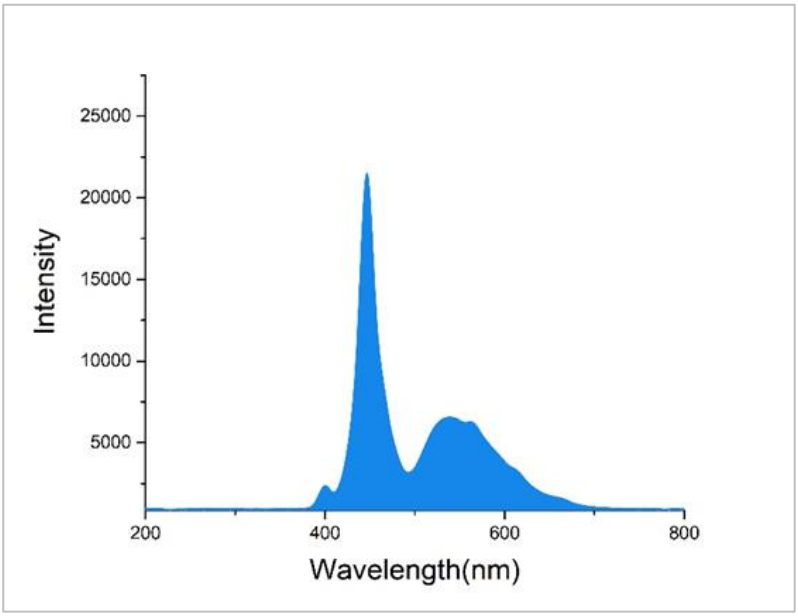
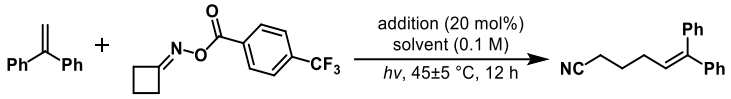


Fig. S1 The spectrum of blue LEDs employed in the reaction

- HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. The mass analysis mode of the HRMS was orbitrap.

2. Detailed Optimization of Reaction Conditions.

Scheme S1 Optimization of the reaction conditions.

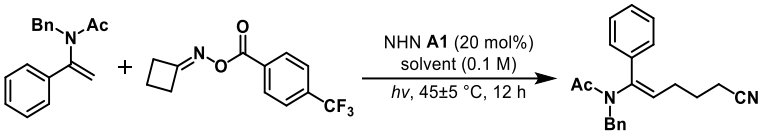


1 2 3

Entry[a]	addition	**1a**:**2a**	Solvent	Yield/%[b]
1	NHN **A1**	1:1.5	Acetone	73
2	NHN **A2**	1:1.5	Acetone	63
3	NHN **B1**	1:1.5	Acetone	24
4	NHN **B2**	1:1.5	Acetone	NR
5	NHN **A1**	1:1.5	DMA	46
6	NHN **A1**	1:1.5	DMSO	55
7	NHN **A1**	1:1.5	THF	40
8	NHN **A1**	1:1.5	MeCN	27
9	NHN **A1**	1:1.5	DMF	70
10	NHN **A1**	1:1.5	Toluene	19
11	NHN **A1**	1:1.0	Acetone	43
12	NHN **A1**	1:1.2	Acetone	57
13	NHN **A1**	1:1.5	Acetone	73
14	NHN **A1**	1:2.0	Acetone	67
15	/	1:1.5	Acetone	NR
16[c]	NHN **A1**	1:1.5	Acetone	NR
17	NaI	1:1.5	Acetone	NR
18	TBAI	1:1.5	Acetone	trace

[a]**1** (27 mg, 0.15 mmol), **2** (58 mg, 0.225 mmol) and addition (20 mol%) in solvent (1.5 mL) under irradiation with blue LED (100W); [b]Yield of isolated products after chromatography; [c]No light, reaction temperature is 60 °C.

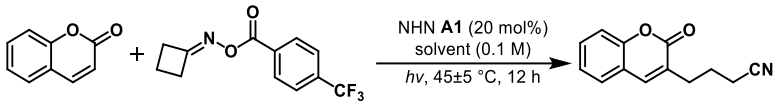
Scheme S2 The screen of the solvent.



Entry[a]	Solvent	Yield/%[b]	*E*/*Z*[d]
1	DMF	65	4:1
2	DMA	30	4:1
3	DMSO	88	4:1
4	THF	72	4:1
5	MeCN	trace	/
6	Acetone	80	4:1
7	Toluene	77	5:1
8[c]	Toluene	NR	/

[a]Enamide (38 mg, 0.15 mmol), **2** (58 mg, 0.225 mmol) and NHN **A1** (9 mg, 20 mol%) in solvent (1.5 mL) under irradiation with blue LED (100W); [b]Yield of isolated products after chromatography; [c]No light, reaction temperature is 60 °C; [d]E/Z ratios were determined by ^{1}H NMR analysis.

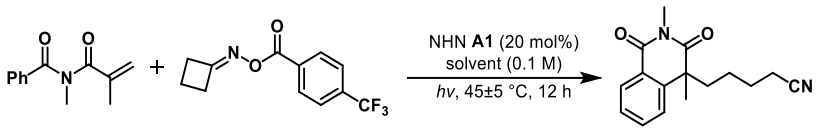
Scheme S3 The screen of the solvent.



Entry[a]	Solvent	Yield/%[b]
1	DMF	24
2	DMA	28
3	DMSO	77
4	THF	38
5	MeCN	trace
6	Acetone	50
7	Toluene	31
8[c]	DMSO	NR

[a]Coumarin (22 mg, 0.15 mmol), **2** (58 mg, 0.225 mmol) and NHN **A1** (9 mg, 20 mol%) in solvent (1.5 mL) under irradiation with blue LED (100 W); [b]Yield of isolated products after chromatography; [c]No light, reaction temperature is 60 °C.

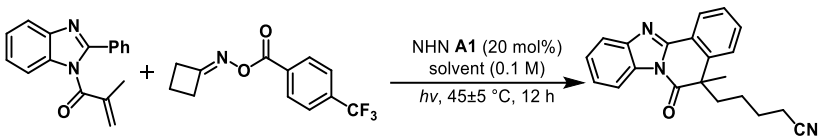
Scheme S4 The screen of the solvent.



Entry[a]	Solvent	Yield/%[b]
1	DMF	30
2	DMA	8
3	DMSO	29
4	THF	57
5	MeCN	trace
6	Acetone	81
7	Toluene	25
8	DCE	22
9[c]	Acetone	NR

[a]*N*-alkyl-*N*-methacryloylbenzamide (30.5 mg, 0.15 mmol), **2** (58 mg, 0.225 mmol) and NHN **A1** (9 mg, 20 mol%) in solvent (1.5 mL) under irradiation with blue LED (100 W); [b]Yield of isolated products after chromatography; [c]No light, reaction temperature is 60 °C.

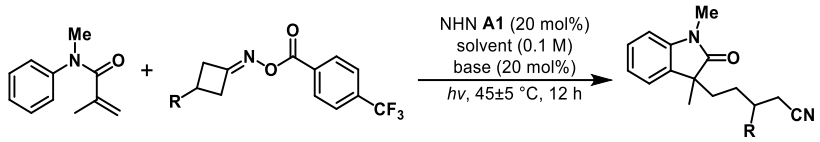
Scheme S5 The screen of the solvent.



Entry[a]	Solvent	Yield/%[b]
1	DMF	53
2	DMA	58
3	DMSO	20
4	THF	68
5	Acetone	40
6	Toluene	30
7[c]	THF	NR

[a]2-methyl-1-(2-phenyl-1*H*-indol-1-yl)prop-2-en-1-one (39.3 mg, 0.15 mmol), **2** (58 mg, 0.225 mmol) and NHN **A1** (9 mg, 20 mol%) in solvent (1.5 mL) under irradiation with blue LED (100 W); [b]Yield of isolated products after chromatography; [c]No light, reaction temperature is 60 °C.

Scheme S6 Optimization of the reaction conditions.

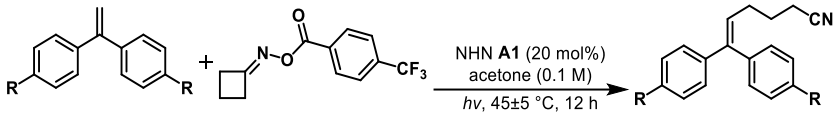


Entry[a]	Base	Solvent	*dr*[b]	Yield/%[c]
1	/	DMF	1:1	56
2	/	DMA	1:1	40
3	/	DMSO	1:1	66
4	/	THF	1:1	47
5	/	Acetone	1:1	58
6	/	Toluene	1:1	56
7	/	MeCN	1:1	NR
8	DMAP	DMSO	1:1	66
9	TMEDA	DMSO	1:1	50
10	Et_3N	DMSO	1:1	70
11	DIPEA	DMSO	1:1	56
12	DBU	DMSO	1:1	trace
13	DABCO	DMSO	1:1	77
14	pyridine	DMSO	1:1	62
15	quinoline	DMSO	1:1	47
16	PMDTA	DMSO	1:1	36
17[d]	DABCO	DMSO	1:1	70
18[e]	DABCO	DMSO	/	NR

[a]*N*-methyl-*N*-phenylmethacrylamide (35 mg, 0.2mmol), **2** (100 mg, 0.3 mmol), base (20 mol%) and NHN **A1** (12 mg, 20 mol%) in solvent (2.0 mL) under irradiation with blue LED (100 W); [b]Detected by ^{1}H NMR; [c]Yield of isolated products after chromatography; [d]Used 2.0 eq. base; [e]No light, reaction temperature is 60 °C.

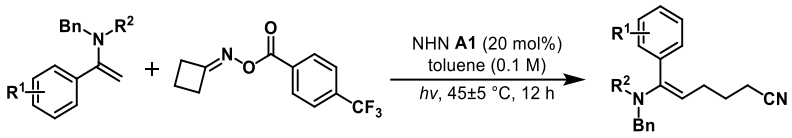
3. General Procedures and Spectral Data of Products.

3.1 General Procedure A for the Synthesis of **3**-**9**.



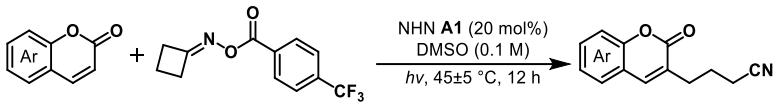
In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged sequentially with ethene-1,1-diyldibenzene[1] (0.20 mmol), **2**[2] (0.30 mmol), NHN **A1** (0.04 mmol) and acetone (2.0 mL). The tube was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 12 hours. Upon completion, the solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired products **3-9**.

3.2 General Procedure B for the Synthesis of **10**-**15**.



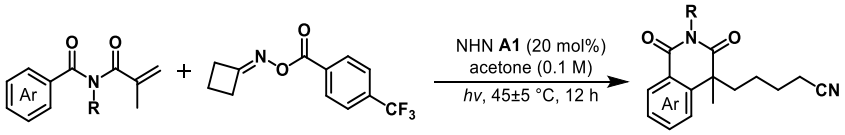
In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged sequentially with enamide[3] (0.20 mmol), **2** (0.30 mmol), NHN **A1** (0.04 mmol) and toluene (2.0 mL). The tube was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 12 hours. Upon completion, the solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired products **10-15**.

3.3 General Procedure C for the Synthesis of **16**-**21**.



In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged sequentially with coumarin (0.20 mmol), **2** (0.30 mmol), NHN **A1** (0.04 mmol) and DMSO (2.0 mL). The tube was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 12 hours. Upon completion, the solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired products **16-21**.

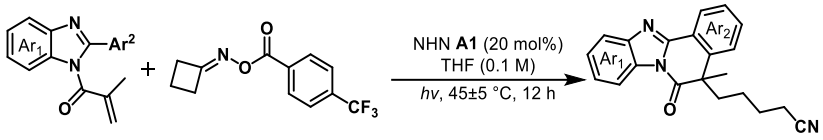
3.4 General Procedure D for the Synthesis of **22**-**25**.



In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged

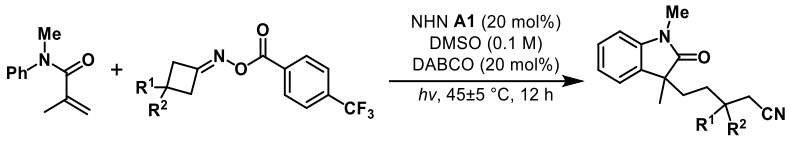
sequentially with *N*-alkyl-*N*-methacryloylbenzamides[4] (0.20 mmol), **2** (0.30 mmol), NHN **A1** (0.04 mmol) and acetone (2.0 mL). The tube was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 12 hours. Upon completion, the solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired products **22-25**.

3.5 General Procedure E for the Synthesis of **26**-**31**.



In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged sequentially with 2-methyl-1-(2-phenyl-1*H*-indol-1-yl)prop-2-en-1-one[5] (0.20 mmol), **2** (0.30 mmol), NHN **A1** (0.04 mmol) and THF (2.0 mL). The tube was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 12 hours. Upon completion, the solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired products **26-31**.

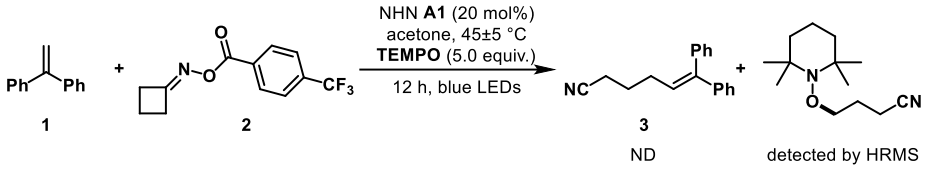
3.6 General Procedure F for the Synthesis of **32**-**39**.



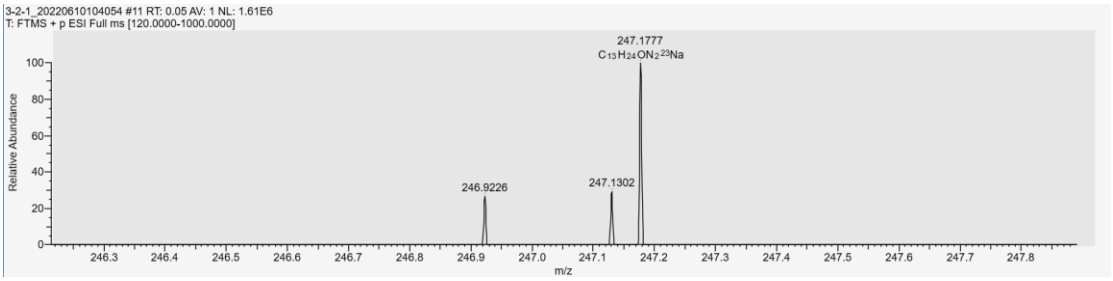
In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged sequentially with *N*-methyl-*N*-phenylmethacrylamide[6] (0.20 mmol), cycloketone ester[2] (0.30 mmol), NHN **A1** (0.04 mmol) and DMSO (2.0 mL). The tube was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 12 hours. Upon completion, the solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired products **32-39**.

4. The Mechanism Studies.

4.1 TEMPO Trapping Experiment.



In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged sequentially with **1** (0.20 mmol), **2** (0.30 mmol), NHN **A1** (0.04 mmol), TEMPO (1.0 mmol) and acetone (2.0 mL). The tube was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 12 hours. The adduct of TEMPO and alkyl radical from decarboxylation of cycloketone ester **2** was detected by HRMS. **HRMS** (ESI): *m/z* [M+Na]$^+$ calcd for $C_{13}H_{24}N_2ONa^+$: 247.1781; found: 247.1777, unfortunately, we could not isolate it.



4.2 UV/vis Absorption Spectrometry.

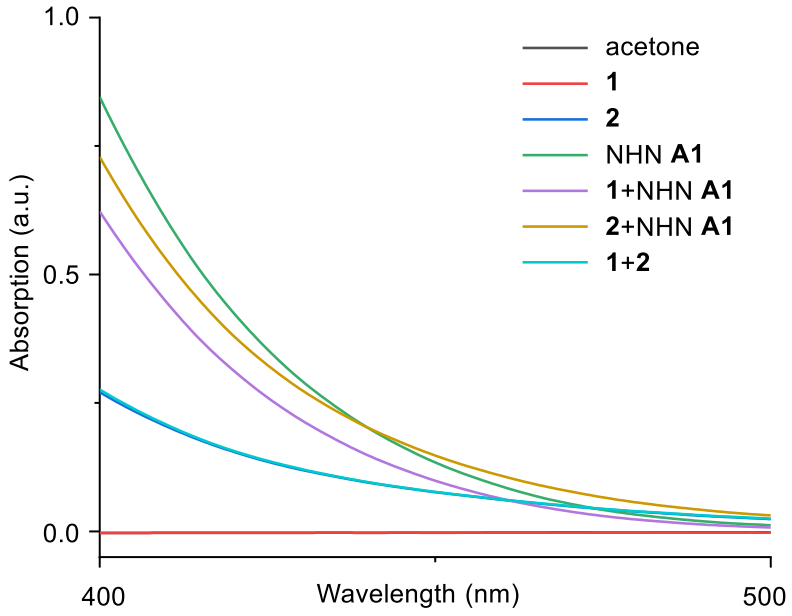


Fig. S2 Absorption spectra of NHN **A1** (0.005 M in acetone), **1** (0.025 M in acetone), **2** (0.025 M in acetone) and their mixtures.

4.3 Cyclic Voltammetry Analysis.

Voltammetric experiments were conducted with a computer-controlled Shanghai Chen Hua CHI440E containing glassy carbon electrode serving as the working electrode, saturated Ag/AgCl reference electrode, Pt wire auxiliary electrode. All solutions used for the voltammetric experiments were deoxygenated by purging with high purity nitrogen and measurements were performed in a Faraday cage at room temperature (25 ± 2 °C).

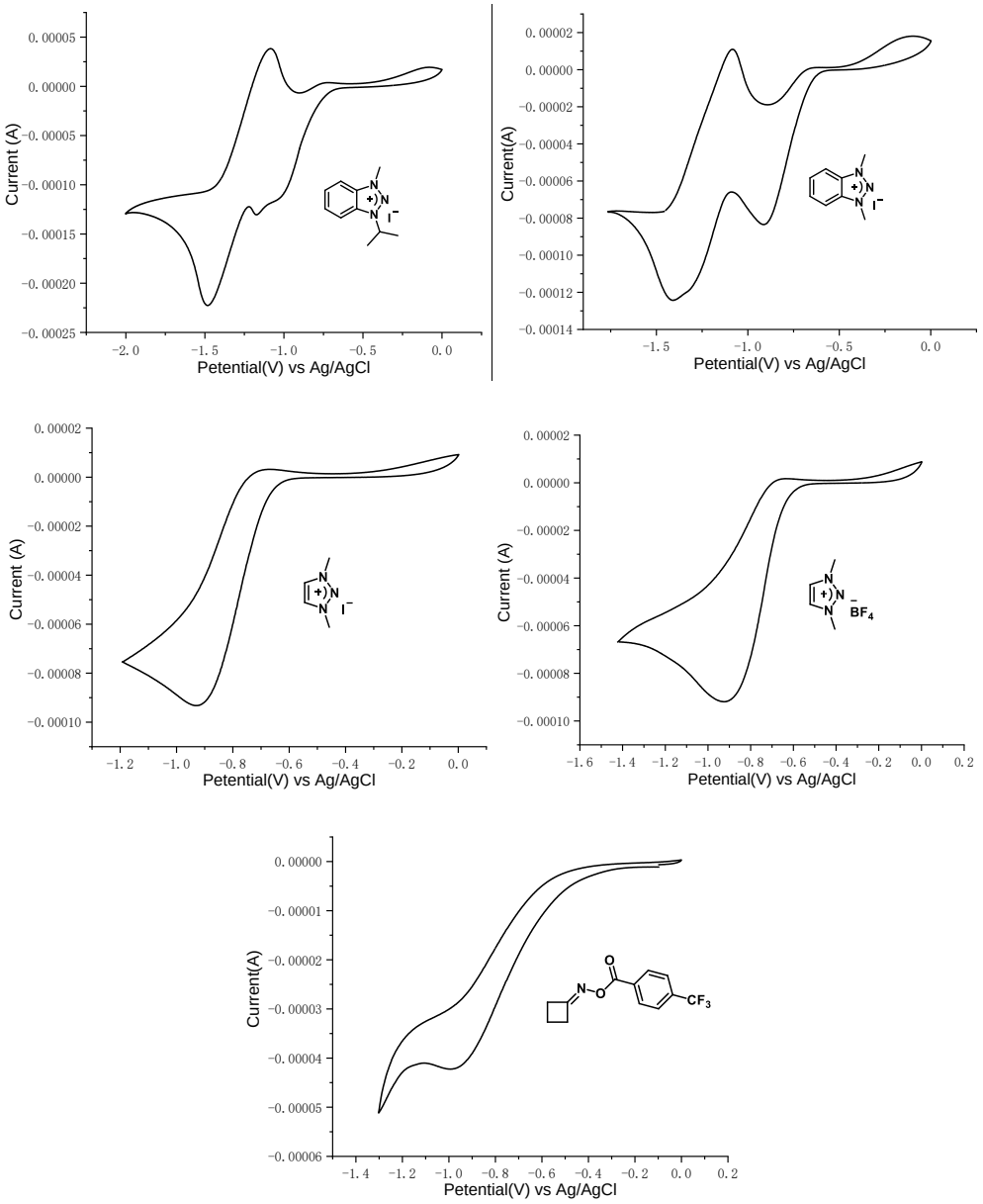


Fig. S3 Cyclic voltammograms of NHN **A1**, NHN **A2**, NHN **B1** and NHN **B2**, in Acetone (0.00625 M), **2** in Acetone (0.0469 M) containing $TBAPF_6$ (0.0625M). Scan rate: 0.04 V/s. E_{red} (NHN **A1**) = -1.48 V, E_{red} (NHN **A2**) = -1.41 V, E_{red} (NHN **B1**) = -0.92 V, E_{red} (NHN **B2**) = -0.92 V, E_{red} (**2**) = -0.95 V.

4.4 Quantum yield determination.

According to the procedure of Xu[7]: To an oven-dried 10 mL glass tubes sealed with rubber septum, the **1** (0.2 mmol), **2** (0.3 mmol), and NHN **A** (0.04 mmol) were combined in acetone (2 mL) under N_2 atmosphere. The reaction mixture was stirred and irradiated (λ = 465 nm, PLS-LED100C) for 2.0 h. After irradiation, the solution was measured the unit area photon

flux (MQ-500 photosynthetic active radiation meter). And the yield of product formed was determined by ^{1}H NMR using 1-(3,4,5-Trimethoxyphenyl)ethanone as an internal standard. The quantum yield is calculated using the following equation：

$$\phi = \frac{mol\ product}{flux \cdot S \cdot t}$$

Where, Φ is quantum yield, S (m^2) is the irradiation area and t (s) is the photoreaction time.

Experiment: the unit photon flux was 391 μmol·s^{-1}·m^{-2} (average of three experiments), the irradiation area was 2.85×10^{-4} m^2, and the product yield was 24% after 2.0 h (7200 s).

Quantum yield calculation:

$$\phi = \frac{mol\ product}{flux \cdot S \cdot t} = \frac{0.24\ \times 0.2\ \times 10^3}{391\ \times 2.85\ \times 10^{-4}\ \times 7200} = 0.060$$

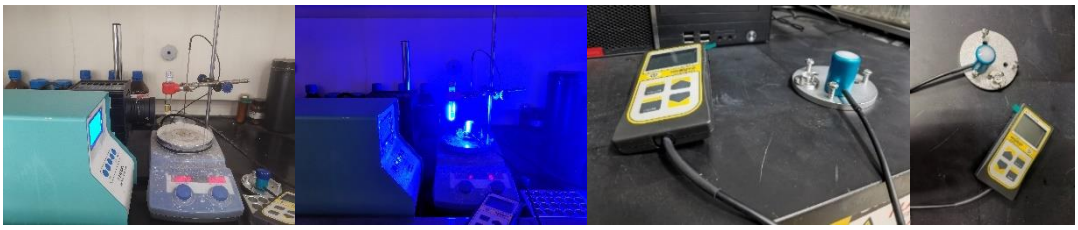
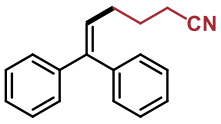


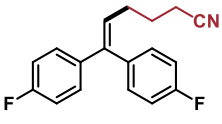
Fig. S4 Placement of PLS-LED100C and MQ-500 photosynthetic active radiation meter.

5. Compound Characterization Data.

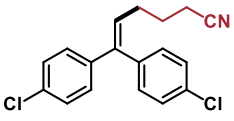


6,6-diphenylhex-5-enenitrile (3): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (36.1 mg, 0.146 mmol, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.31 (m, 1H), 7.29 – 7.18 (m, 5H), 7.18 – 7.12 (m, 2H), 6.01 (t, *J* = 7.4 Hz, 1H), 2.31 – 2.23 (m, 4H), 1.83 – 1.75 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 142.2, 139.7, 129.8, 128.5, 128.3, 127.3, 127.3, 126.7, 119.7, 28.8, 25.8, 16.8. These data are in agreement with those reported previously in the literature.[8]

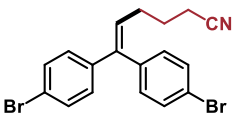
The large-scale reaction general procedure A: In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged sequentially with ethene-1,1-diyldibenzene (**1**, 1.0 mmol, 176 μL), **2** (1.5 mmol, 385.5 mg), and acetone (10.0 mL). The vial was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 12 hours. Upon completion, the solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired product **3** (158 mg, 0.64 mmol, 64%).



6,6-bis(4-fluorophenyl)hex-5-enenitrile (4): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (42.3 mg, 0.150 mmol, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 – 7.14 (m, 2H), 7.13 – 7.04 (m, 4H), 6.98 – 6.94 (m, 2H), 5.95 (t, *J* = 7.4 Hz, 1H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.28 – 2.24 (m, 2H), 1.83 – 1.77 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 248.2 Hz), 162.2 (d, *J* = 248.2 Hz), 142.0, 138.3 (d, *J* = 3.4 Hz), 135.4 (d, *J* = 3.4 Hz), 131.4 (d, *J* = 7.9 Hz), 128.9 (d, *J* = 7.9 Hz), 127.0, 119.5, 115.6 (d, *J* = 21.3 Hz), 115.2 (d, *J* = 21.3 Hz), 28.8, 25.8, 16.9. These data are in agreement with those reported previously in the literature.[9]

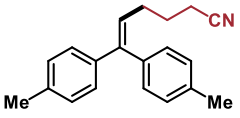


6,6-bis(4-chlorophenyl)hex-5-enenitrile (5): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (40.1 mg, 0.128 mmol, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H), 7.27 – 7.21 (m, 2H), 7.15 – 7.05 (m, 4H), 6.01 (t, *J* = 7.4 Hz, 1H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.29 – 2.23 (m, 2H)., 1.84 – 1.77 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 140.3, 137.6, 133.6, 133.5, 131.2, 128.9, 128.58, 128.55, 127.9, 119.5, 28.9, 25.7, 16.9. These data are in agreement with those reported previously in the literature.[10]

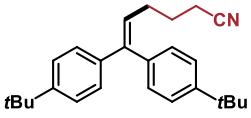


6,6-bis(4-bromophenyl)hex-5-enenitrile (6): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (56.2 mg, 0.138 mmol, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.06 – 7.01 (m, 4H), 6.02 (t, *J* = 7.4 Hz, 1H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.28 – 2.23 (m, 2H), 1.84 – 1.77 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 140.7, 138.1, 131.9, 131.53, 131.49, 128.9, 127.9, 121.8, 121.7, 119.5, 28.9, 25.7, 16.9. **IR (ATR)**: 2931, 2246, 1729, 1486, 1069,

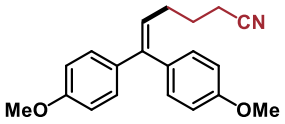
1008, 816 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{18}H_{15}Br_2NNa^+$ 423.9443, found 423.9441



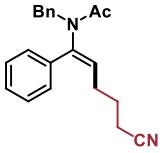
6,6-di-*p*-tolylhex-5-enenitrile (7): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (38.1 mg, 0.138 mmol, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.6 Hz, 2H), 7.14 – 7.00 (m, 6H), 5.94 (t, *J* = 7.4 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 2.30 – 2.21 (m, 4H), 1.82 – 1.75 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 139.7, 137.1, 136.92, 136.87, 129.7, 129.1, 129.0, 127.2, 125.7, 119.8, 28.8, 25.9, 21.4, 21.2, 16.8. These data are in agreement with those reported previously in the literature.[9,10]



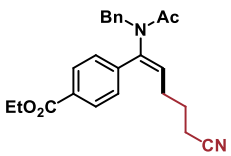
6,6-bis(4-(*tert*-butyl)phenyl)hex-5-enenitrile (8): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (49.6 mg, 0.138 mmol, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 5.96 (t, *J* = 7.4 Hz, 1H), 2.31 – 2.24 (m, 4H), 1.81 – 1.75 (m, 2H), 1.35 (s 9H), 1.30 (s 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3, 150.1, 143.5, 139.6, 136.7, 129.4, 126.9, 125.9, 125.3, 125.2, 119.8, 34.7, 34.6, 31.5, 31.4, 28.8, 26.0, 16.8. **IR (ATR)**: 2960, 2246, 1657, 1268, 1108, 829, 619 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{26}H_{33}NONa^+$ 398.2454, found 398.2451.



6,6-bis(4-methoxyphenyl)hex-5-enenitrile (9): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (46.8 mg, 0.152 mmol, 76%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 2H), 7.10 – 7.03 (m, 2H), 6.94 – 6.87 (m, 2H), 6.83 – 6.77 (m, 2H), 5.87 (t, *J* = 7.4 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.30 (t, *J* = 7.3 Hz, 2H), 2.28 – 2.23 (m, 2H), 1.81 – 1.75 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.1, 158.8, 142.9, 135.4, 132.3, 131.0, 128.5, 124.8, 119.8, 113.8, 113.6, 55.40, 55.36, 28.8, 26.0, 16.8. **IR (ATR)**: 2934, 2246, 1604, 1508, 1241, 1170, 1028, 832 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{20}H_{21}NO_2Na^+$ 330.1465, found 330.1461.

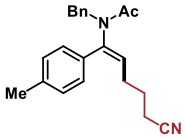


(*E*)-*N*-benzyl-*N*-(5-cyano-1-phenylpent-1-en-1-yl)acetamide (10): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (49.3 mg, 0.154 mmol, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 3H), 7.31 – 7.27 (m, 2H), 7.24 – 7.21 (m, 3H), 7.20 – 7.16 (m, 2H), 5.19 (t, *J* = 7.6 Hz, 1H), 4.50 (s, 2H), 2.34 – 2.28 (m, 2H), 2.21 (s, 3H), 2.15 (t, *J* = 7.2 Hz, 2H), 1.67 – 1.59 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 140.2, 137.6, 134.6, 129.8, 129.1, 128.9, 128.6, 128.4, 127.5, 119.1, 49.0, 27.4, 25.3, 22.4, 16.6. **IR (ATR)**: 2932, 2246, 1641, 1390, 1286, 1126, 777 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{21}H_{22}N_2ONa^+$ 341.1624, found 341.1621.

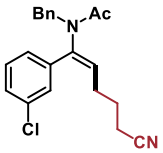


ethyl (*E*)-4-(1-(*N*-benzylacetamido)-5-cyanopent-1-en-1-yl)benzoate (11): Following the general procedure B, the title product

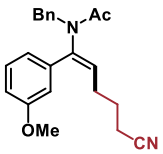
was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (49.2 mg, 0.120 mmol, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.23 (m, 5H), 7.20 – 7.13 (m, 2H), 5.31 (d, *J* = 7.2 Hz, 1H), 4.51 (s, 2H), 4.44 – 4.38 (m, 2H), 2.35 – 2.29 (m, 2H), 2.21 (s, 3H), 2.17 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.5, 166.0, 139.5, 139.1, 137.3, 131.3, 131.0, 130.2, 129.1, 128.6, 128.5, 127.6, 119.0, 61.4, 49.2, 27.5, 25.2, 22.4, 16.7, 14.4. **IR (ATR)**: 2932, 2245, 1712, 1643, 1388, 1271, 1103, 868 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{24}H_{26}N_2O_3Na^+$ 413.1836, found 413.1826.



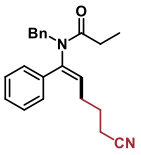
(*E*)-*N*-benzyl-*N*-(5-cyano-1-(p-tolyl)pent-1-en-1-yl)acetamide (12): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (50.4 mg, 0.154 mmol, 76%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.16 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.14 (t, *J* = 7.6 Hz, 1H), 4.50 (s, 2H), 2.40 (s, 3H), 2.33 – 2.29 (m, 2H), 2.21 (s, 3H), 2.15 (t, *J* = 7.1 Hz, 2H), 1.66 – 1.60 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.6, 140.2, 139.2, 137.7, 131.6, 129.6, 129.23, 129.15, 128.6, 128.4, 127.5, 119.2, 48.9, 27.5, 25.4, 22.4, 21.4, 16.7. **IR (ATR)**: 2927, 2246, 1640, 1390, 1167, 819 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{24}N_2ONa^+$ 355.1781, found 355.1776.



(*E*)-*N*-benzyl-*N*-(1-(3-chlorophenyl)-5-cyanopent-1-en-1-yl)acetamide (13): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (43.1 mg, 0.122 mmol, 61%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.27 (m, 3H), 7.20 – 7.16 (m, 3H), 7.14 – 7.10 (m, 1H), 5.25 (t, *J* = 7.6 Hz, 1H), 4.51 (s, 2H), 2.33 – 2.28 (m, 2H), 2.20 (s, 3H), 2.18 (t, *J* = 7.1 Hz, 2H), 1.67 – 1.61 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.4, 139.1, 137.4, 136.6, 135.1, 130.9, 130.2, 129.3, 129.1, 128.6, 128.5, 127.6, 126.9, 119.0, 49.2, 27.4, 25.2, 22.4, 16.7. **IR (ATR)**: 2931, 2246, 1644, 1386, 1128, 794 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{21}H_{21}ClN_2ONa^+$ 375.1235, found 375.1232.

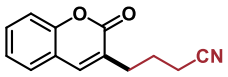


(*E*)-*N*-benzyl-*N*-(5-cyano-1-(3-methoxyphenyl)pent-1-en-1-yl)acetamide (14): Following the general procedure, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (43.0 mg, 0.124 mmol, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.21 – 7.19 (m, 2H), 6.94 – 6.91 (m, 1H), 6.85 – 6.82 (m, 1H), 6.74 – 6.73 (m, 1H), 5.20 (t, *J* = 7.6 Hz, 1H), 4.52 (s, 2H), 3.81 (s, 3H), 2.37 – 2.32 (m, 2H), 2.21 (s, 3H), 2.16 (t, *J* = 7.2 Hz, 2H), 1.68 – 1.60 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.5, 160.0, 140.1, 137.7, 136.1, 130.0, 129.9, 129.2, 128.5, 127.5, 121.1, 119.2, 114.6, 114.1, 55.5, 49.1, 27.5, 25.3, 22.4, 16.7. **IR (ATR)**: 2934, 2247, 1645, 1389, 1247, 1128, 779 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{24}N_2O_2Na^+$ 371.1730, found 371.1725.

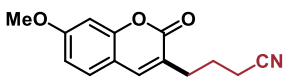


(*E*)-*N*-benzyl-*N*-(5-cyano-1-phenylpent-1-en-1-yl)propionamide (15): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil

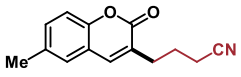
(44.2 mg, 0.132 mmol, 66%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 3H), 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 5H), 5.18 (t, *J* = 7.6 Hz, 1H), 4.52 (s, 2H), 2.51 – 2.46 (m, 2H), 2.35 – 2.30 (m, 2H), 2.16 (t, *J* = 7.1 Hz, 2H), 1.66 – 1.61 (m, 2H), 1.20 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.1, 139.7, 137.9, 134.8, 129.6, 129.2, 129.1, 128.9, 128.6, 128.5, 127.5, 119.2, 49.3, 27.5, 27.4, 25.4, 16.7, 10.4. **IR (ATR)**: 2936, 2246, 1683, 1408, 1164, 757 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{24}N_2ONa^+$ 355.1781, found 355.1779.



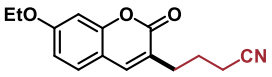
4-(2-oxo-2*H*-chromen-3-yl)butanenitrile (16): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (32.8 mg, 0.154 mmol, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.56 – 7.44 (m, 2H), 7.37 – 7.27 (m, 2H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.10 – 2.02 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6, 153.5, 140.3, 131.3, 127.6, 127.3, 124.7, 119.30, 119.28, 116.7, 30.4, 23.8, 16.9. These data are in agreement with those reported previously in the literature.[11]



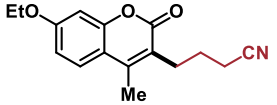
4-(7-methoxy-2-oxo-2*H*-chromen-3-yl)butanenitrile (17): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (27.5 mg, 0.114 mmol, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 6.87 – 6.84 (m, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 3.87 (s, 3H), 2.70 (t, *J* = 7.0 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.07 – 2.02 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 161.9, 155.2, 140.5, 128.5, 123.5, 119.4, 112.9, 112.8, 100.6, 55.9, 30.2, 23.9, 16.8. These data are in agreement with those reported previously in the literature.[11]



4-(6-methyl-2-oxo-2*H*-chromen-3-yl)butanenitrile (18): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (30.0 mg, 0.132 mmol, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.32 – 7.30 (m, 1H), 7.28 – 7.20 (m, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.47 – 2.39 (m, 5H), 2.09 – 2.01 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8, 151.6, 140.3, 134.3, 132.3, 127.4, 127.1, 119.4, 119.0, 116.3, 30.4, 23.8, 20.9, 16.8. These data are in agreement with those reported previously in the literature.[11]

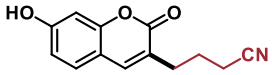


4-(7-ethoxy-2-oxo-2*H*-chromen-3-yl)butanenitrile (19): Following the general procedure, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (31.0 mg, 0.112 mmol, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 6.88 – 6.78 (m, 2H), 4.11 – 4.06 (m, 2H), 2.75 – 2.66 (m, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.07 – 2.00 (m, 2H), 1.46 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0, 161.9, 155.2, 140.5, 128.4, 123.4, 119.4, 113.2, 112.8, 101.1, 64.3, 30.3, 23.9, 16.8, 14.7. These data are in agreement with those reported previously in the literature.[11]

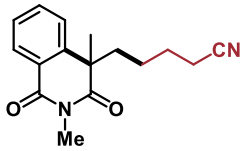


4-(7-ethoxy-4-methyl-2-oxo-2*H*-chromen-3-yl)butanenitrile (20): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA =

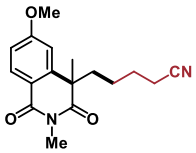
10:1 – 4:1) as a white solid (27.3 mg, 0.100 mmol, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.9 Hz, 1H), 6.90 – 6.83 (m, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 4.12 – 4.06 (m, 2H), 2.84 – 2.76 (m, 2H), 2.46 – 2.43 (m, 5H), 1.97 – 1.90 (m, 2H), 1.46 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 161.6, 154.0, 147.8, 125.8, 121.0, 119.7, 113.8, 112.9, 101.1, 64.2, 26.6, 24.5, 17.1, 15.1, 14.7. **IR (ATR)**: 2921, 2244, 1708, 1614, 1289, 1152, 1082, 866, 776 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{16}H_{17}NO_3Na^+$ 294.1101, found 294.1094.



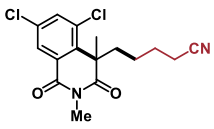
4-(7-hydroxy-2-oxo-2*H*-chromen-3-yl)butanenitrile (21): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (24.3 mg, 0.106 mmol, 53%). **^{1}H NMR** (400 MHz, CD_3CN) δ 7.75 (s, 1H), 7.61 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 6.82 – 6.72 (m, 2H), 2.61 – 2.53 (m, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.94 – 1.86 (m, 2H). **^{13}C NMR** (126 MHz, CD_3CN) δ 162.5, 160.6, 155.8, 140.9, 129.8, 124.3, 121.0, 113.6, 113.5, 103.0, 30.4, 24.5, 16.9. These data are in agreement with those reported previously in the literature.[12]



5-(2,4-dimethyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)pentanenitrile (22): Following the general procedure D, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (43.7 mg, 0.162 mmol, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.3 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.49 – 7.38 (m, 2H), 3.38 (s, 3H), 2.41 – 2.27 (m, 1H), 2.25 – 2.12 (m, 2H), 1.94 – 1.87 (m, 1H), 1.61 (s, 3H), 1.58 – 1.44 (m, 2H), 1.11 – 0.86 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.5, 164.4, 143.1, 134.4, 129.2, 127.7, 125.2, 125.0, 119.3, 47.7, 41.8, 29.8, 27.3, 25.4, 24.6, 16.9. These data are in agreement with those reported previously in the literature.[13]

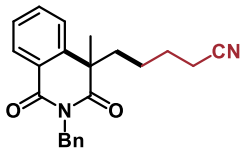


5-(6-methoxy-2,4-dimethyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)pentanenitrile (23): Following the general procedure D, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (40.9 mg, 0.136 mmol, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 1H), 6.98 – 6.96 (m, 1H), 6.85 (s, 1H), 3.91 (s, 3H), 3.37 (s, 3H), 2.38 – 2.27 (m, 1H), 2.24 – 2.14 (m, 2H), 1.90 – 1.84 (m, 1H), 1.60 (s, 3H), 1.59 – 1.46 (m, 2H), 1.11 – 0.90 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.6, 164.5, 164.0, 145.4, 131.5, 119.4, 118.0, 113.3, 110.5, 55.7, 47.9, 41.9, 29.9, 27.2, 25.4, 24.5, 16.9. These data are in agreement with those reported previously in the literature.[13]

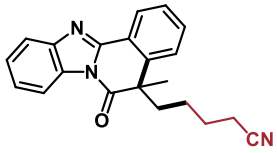


5-(5,7-dichloro-2,4-dimethyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)pentanenitrile (24): Following the general procedure D, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a yellow oil (34.6 mg, 0.102 mmol, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.67 (s, 1H), 3.41 (s, 3H), 2.93 – 2.81 (m, 1H), 2.35 – 2.21 (m, 3H), 1.82 (s, 3H), 1.64 – 1.47 (m, 2H), 1.05 – 0.77 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.2, 162.2, 137.3, 137.0, 134.6, 133.3, 128.7, 119.3, 49.2, 36.8, 28.0, 25.7, 25.3, 25.0, 16.9. **IR (ATR)**: 2940, 2246, 1715, 1665, 1324, 1271, 1117, 775 cm^{-1}.

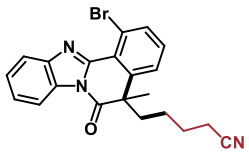
HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{16}H_{16}Cl_2N_2O_2Na^+$ 361.0481, found 361.0479.



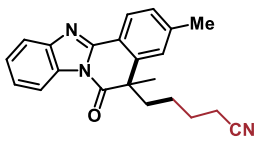
5-(2-benzyl-4-methyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)pentanenitrile (25): Following the general procedure D, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (55.0 mg, 0.160 mmol, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.49 – 7.37 (m, 4H), 7.33 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 5.26 (d, *J* = 13.4 Hz, 1H), 5.15 (d, *J* = 13.4 Hz, 1H), 2.32 – 2.20 (m, 1H), 2.12 – 1.97 (m, 2H), 1.93 – 1.81 (m, 1H), 1.60 (s, 3H), 1.48 – 1.35 (m, 2H), 0.93 – 0.76 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.1, 164.1, 143.2, 137.2, 134.4, 129.3, 128.9, 128.5, 127.7, 127.6, 125.1, 125.0, 119.3, 47.6, 43.6, 42.1, 29.3, 25.3, 24.3, 16.8. These data are in agreement with those reported previously in the literature.[13]



5-(5-methyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinolin-5-yl)pentanenitrile (26): Following the general procedure E, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (45.5 mg, 0.136 mmol, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 – 8.46 (m, 1H), 7.88 – 7.78 (m, 1H), 7.65 – 7.56 (m, 1H), 7.53 – 7.50 (m, 1H), 7.48 (d, *J* = 3.7 Hz, 1H), 7.47 – 7.41 (m, 3H), 2.51 – 2.43 (m, 1H), 2.25 – 2.10 (m, 2H), 2.10 – 2.00 (m, 1H), 1.73 (s, 3H), 1.61 – 1.48 (m, 2H), 1.16 – 0.94 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 149.8, 144.2, 141.2, 132.3, 131.4, 128.1, 126.21, 126.17, 126.0, 125.8, 123.1, 120.0, 119.3, 115.8, 49.4, 41.6, 29.5, 25.5, 24.7, 16.9. **IR (ATR)**: 2931, 2245, 1712, 1613, 1583, 1450, 1352, 1166, 962, 742 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{21}H_{19}N_3ONa^+$ 352.1420, found 352.1417.

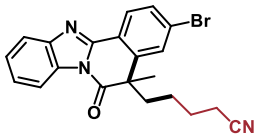


5-(1-bromo-5-methyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinolin-5-yl)pentanenitrile (27): Following the general procedure E, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (47.2 mg, 0.116 mmol, 58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 – 8.34 (m, 1H), 7.95 – 7.92 (m, 1H), 7.85 – 7.82 (m, 1H), 7.49 – 7.45 (m, 3H), 7.40 – 7.36 (m, 1H), 2.51 – 2.39 (m, 1H), 2.27 – 2.08 (m, 2H), 2.08 – 1.96 (m, 1H), 1.73 (s, 3H), 1.63 – 1.44 (m, 2H), 1.05 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.1, 147.2, 144.2, 143.7, 135.5, 131.6, 130.7, 126.6, 126.2, 125.5, 122.5, 121.7, 121.0, 119.3, 115.8, 49.7, 41.9, 29.6, 25.4, 24.5, 16.9. **IR (ATR)**: 2925, 2245, 1704, 1562, 1447, 1329, 1125, 966, 749 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{21}H_{18}BrN_3ONa^+$ 430.0526, found 430.0519.

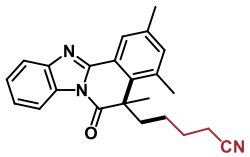


5-(3,5-dimethyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinolin-5-yl)pentanenitrile (28): Following the general procedure E, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (33.0 mg, 0.096 mmol, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 – 8.27 (m, 2H), 7.84 – 7.77 (m, 1H), 7.49 – 7.35 (m, 2H), 7.35 – 7.29 (m, 1H), 7.25 (s, 1H), 2.49 (s, 3H), 2.47 – 2.37 (m, 1H), 2.28 – 2.10 (m, 2H), 2.07 – 1.99 (m, 1H), 1.72 (s, 3H), 1.60 – 1.45 (m, 2H), 1.15 – 0.94 (m, 2H). **^{13}C**

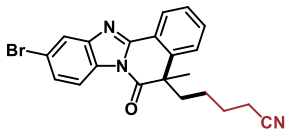
NMR (126 MHz, $CDCl_3$) δ 173.3, 150.1, 144.3, 142.9, 141.3, 131.4, 129.2, 126.4, 126.2, 126.1, 125.6, 120.5, 119.8, 119.3, 115.8, 49.3, 41.7, 29.5, 25.5, 24.6, 22.2, 16.9. **IR (ATR)**: 2919, 2245, 1700, 1612, 1556, 1450, 1354, 1155, 958, 769 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{21}N_3ONa^+$ 366.1577, found 366.1571.



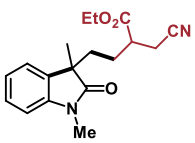
5-(3-bromo-5-methyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinolin-5-yl)pentanenitrile (29): Following the general procedure E, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (55.5 mg, 0.136 mmol, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 2H), 7.85 – 7.78 (m, 1H), 7.66 – 7.63 (m, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.39 (m, 2H), 2.50 – 2.42 (m, 1H), 2.23 – 2.14 (m, 2H), 2.05 – 1.93 (m, 1H), 1.73 (s, 3H), 1.63 – 1.50 (m, 2H), 1.14 – 0.97 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 148.9, 144.1, 143.1, 131.6, 131.3, 129.2, 127.6, 126.9, 126.4, 126.1, 122.1, 120.1, 119.2, 115.8, 49.4, 41.7, 29.3, 25.4, 24.6, 16.9. **IR (ATR)**: 2934, 2241, 1719, 1578, 1413, 1324, 1273, 1113, 862, 768 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{21}H_{18}BrN_3ONa^+$ 430.0526, found 430.0526.



5-(2,4,5-trimethyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-a]isoquinolin-5-yl)pentanenitrile (30): Following the general procedure E, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (53.3 mg, 0.150 mmol, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 – 8.30 (m, 2H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.21 (s, 1H), 2.60 (s, 3H), 2.50 – 2.46 (m, 2H), 2.42 (s, 3H), 2.25 – 2.08 (m, 2H), 1.81 (s, 3H), 1.64 – 1.46 (m, 2H), 1.09 – 0.94 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.3, 150.6, 144.4, 138.1, 137.9, 136.0, 135.5, 131.4, 126.2, 125.5, 125.4, 123.7, 119.8, 119.3, 115.9, 50.6, 38.0, 26.7, 25.6, 25.2, 23.0, 20.7, 16.9. **IR (ATR)**: 2922, 2245, 1722, 1540, 1450, 1364, 1324, 1121, 863, 772 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{23}H_{23}N_3ONa^+$ 380.1733, found 380.1728.

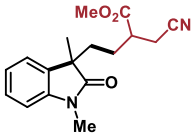


5-(10-bromo-5-methyl-6-oxo-5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinolin-5-yl)pentanenitrile (31): Following the general procedure E, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (45.0 mg, 0.110 mmol, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 – 8.45 (m, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 1.8 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.55 – 7.49 (m, 2H), 7.48 – 7.47 (m, 1H), 2.48 – 2.42 (m, 1H), 2.25 – 2.10 (m, 2H), 2.08 – 2.02 (m, 1H), 1.73 (s, 3H), 1.64 – 1.45 (m, 2H), 1.13 – 0.95 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.0, 150.8, 145.6, 141.4, 132.6, 130.4, 128.7, 128.2, 126.4, 126.0, 123.0, 122.7, 119.2, 116.9, 49.5, 41.6, 29.5, 25.4, 24.6, 16.9. **IR (ATR)**: 2926, 2242, 1705, 1604, 1578, 1445, 1347, 1325, 1157, 969, 776 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{21}H_{18}BrN_3ONa^+$ 430.0526, found 430.0522.

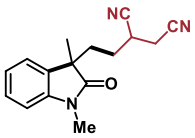


ethyl 2-(cyanomethyl)-4-(1,3-dimethyl-2-oxoindolin-3-yl)butanoate (32): Following the general procedure F, the title product was obtained

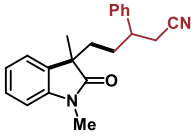
after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (isolated as an inseparable mixture, dr = 1:1, 55.9 mg, 0.178 mmol, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.16 (d, *J* = 7.3 Hz, 2H), 7.10 – 7.07 (m, 2H), 6.86 (d, *J* = 7.8 Hz, 2H), 4.20 – 4.14 (m, 4H), 3.22 (d, *J* = 1.2 Hz, 6H), 2.66 – 2.40 (m, 6H), 1.99 – 1.85 (m, 2H), 1.85 – 1.70 (m, 2H), 1.51 – 1.42 (m, 1H), 1.36 (d, *J* = 2.6 Hz, 6H), 1.34 – 1.24 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.07, 180.02, 172.3, 172.2, 143.4, 143.3, 133.21, 133.15, 128.27, 128.25, 122.94, 122.91, 122.60, 122.58, 117.7, 117.6, 108.4, 61.6, 48.1, 48.0, 41.6, 41.5, 35.0, 34.8, 26.5, 26.4, 26.3, 24.02, 23.92, 19.5, 19.1, 14.3. **IR (ATR)**: 2928, 2247, 1700, 1612, 1471, 1421, 1376, 1181, 1125, 935, 755 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{18}H_{22}N_2O_3Na^+$ 337.1523, found 337.1517.



4-methyl 2-(cyanomethyl)-4-(1,3-dimethyl-2-oxoindolin-3-yl)butanoate (33): Following the general procedure F, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (isolated as an inseparable mixture, dr = 1:1, 52.0 mg, 0.174 mmol, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.18 – 7.16 (m, 2H), 7.11 – 7.08 (m, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 3.71 (d, *J* = 6.1 Hz, 6H), 3.23 (s, 6H), 2.85 – 2.27 (m, 6H), 2.00 – 1.69 (m, 6H), 1.36 (d, *J* = 2.3 Hz, 6H), 1.33 – 1.25 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.0, 172.8, 172.7, 143.3, 133.1, 128.3, 123.0, 122.6, 117.63, 117.55, 108.4, 52.6, 48.03, 47.96, 41.4, 41.3, 34.9, 34.8, 26.44, 26.35, 26.2, 24.0, 23.9, 19.4, 19.1. **IR (ATR)**: 2928, 2249, 1701, 1611, 1493, 1453, 1375, 1243, 1172, 735 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{17}H_{20}N_2O_3Na^+$ 323.1366, found 323.1359.

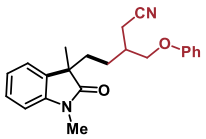


2-(2-(1,3-dimethyl-2-oxoindolin-3-yl)ethyl)succinonitrile (34): Following the general procedure F, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (isolated as an inseparable mixture, dr = 1:1, 32.1 mg, 0.120 mmol, 60%). **^{1}H NMR** (400 MHz, CD_3Cl) 7.33 – 7.30 (m, 2H), 7.23 – 7.18 (m, 2H), 7.15 – 7.08 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 3.23 (d, *J* = 0.9 Hz, 6H), 2.86 – 2.80 (m, 1H), 2.73 – 2.68 (m, 1H), 2.65 – 2.57 (m, 4H), 2.18 – 2.10 (m, 1H), 2.07 – 2.03 (m, 2H), 1.91 – 1.85 (m, 1H), 1.55 – 1.47 (m, 2H), 1.40 (d, *J* = 1.6 Hz, 6H), 1.39 – 1.24 (m, 2H). **^{13}C NMR** (101 MHz, CD_3Cl) δ 179.7, 179.6, 143.1, 132.8, 132.5, 128.6, 128.5, 123.3, 123.2, 122.6, 118.6, 118.5, 115.5, 115.4, 108.6, 47.9, 47.6, 35.2, 34.6, 28.7, 28.4, 27.0, 26.6, 26.4, 24.2, 23.7, 21.1, 20.8. **IR (ATR)**: 2930, 2246, 1697, 1611, 1493, 1454, 1349, 1125, 1075, 751 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{16}H_{17}N_3ONa^+$ 290.1264, found 290.1259.

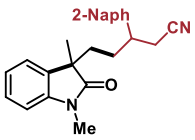


5-(1,3-dimethyl-2-oxoindolin-3-yl)-3-phenylpentanenitrile (35): Following the general procedure F, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (isolated as an inseparable mixture, dr = 1:1, 49.2 mg, 0.154 mmol, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 8H), 7.18 – 7.02 (m, 7H), 6.97 – 6.96 (m, 1H), 6.88 – 6.85 (m, 2H), 3.22 (d, *J* = 6.5 Hz, 6H), 2.87 – 2.68 (m, 2H), 2.50 – 2.42 (m, 4H), 1.91 – 1.60 (m, 4H), 1.57 – 1.33 (m, 4H), 1.28 (d, *J* = 11.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.4, 180.2, 143.3, 143.2, 141.0, 140.8, 133.6, 133.4, 129.03, 129.01, 128.1, 127.64,

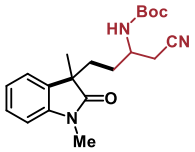
127.59, 127.3, 127.2, 122.8, 122.7, 122.5, 122.4, 118.3, 108.2, 48.12, 48.06, 42.3, 42.2, 35.8, 35.7, 29.5, 29.3, 25.5, 25.1, 24.1, 23.9. **IR (ATR)**: 2925, 2245, 1702, 1611, 1492, 1453, 1348, 1066, 753 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{21}H_{22}N_2ONa^+$ 341.1624, found 341.1618.



5-(1,3-dimethyl-2-oxoindolin-3-yl)-3-(phenoxymethyl)pentanenitrile (36): Following the general procedure F, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (isolated as an inseparable mixture, dr = 1:1, 52.2 mg, 0.150 mmol, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 5H), 7.25 – 7.24 (m, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.17 – 7.04 (m, 3H), 6.99 – 6.92 (m, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.85 – 6.80 (m, 4H), 3.94 – 3.90 (m, 2H), 3.81 – 3.78 (m, 1H), 3.76 – 3.69 (m, 1H), 3.23 (d, *J* = 4.7 Hz, 6H), 2.50 – 2.47 (m, 4H), 2.11 – 1.94 (m, 4H), 1.91 – 1.79 (m, 2H), 1.37 (d, *J* = 5.6 Hz, 6H), 1.28 – 1.06 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.34, 180.32, 158.5, 158.4, 143.4, 143.3, 133.4, 133.3, 129.7, 128.22, 128.19, 123.0, 122.9, 122.7, 122.6, 121.4, 118.3, 118.1, 114.68, 114.65, 108.4, 68.8, 68.2, 48.25, 48.22, 35.9, 35.8, 35.4, 26.4, 25.6, 25.5, 24.2, 24.0, 19.8, 19.4. **IR (ATR)**: 2926, 2245, 1702, 1611, 1492, 1469, 1238, 1124, 1018, 749 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{24}N_2O_2Na^+$ 371.1730, found 371.1723.

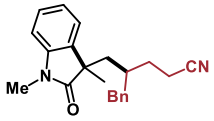


5-(1,3-dimethyl-2-oxoindolin-3-yl)-3-(naphthalen-2-yl)pentanenitrile (37): Following the general procedure F, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a colorless oil (isolated as an inseparable mixture, dr = 1:1, 53.0 mg, 0.144 mmol, 72%). **^{1}H NMR** (400 MHz, CD_3Cl) δ 7.87 – 7.76 (m, 6H), 7.58 (s, 1H), 7.55 – 7.42 (m, 5H), 7.33 – 7.28 (m, 2H), 7.25 – 7.22 (m, 1H), 7.16 – 7.04 (m, 4H), 6.95 – 6.83 (m, 3H), 3.23 (d, *J* = 9.8 Hz, 6H), 3.06 – 2.86 (m, 2H), 2.60 – 2.46 (m, 4H), 1.92 – 1.85 (m, 1H), 1.82 – 1.74 (m, 1H), 1.70 – 1.63 (m, 3H), 1.55 – 1.47 (m, 3H), 1.26 (d, *J* = 16.2 Hz, 6H). **^{13}C NMR** (126 MHz, CD_3Cl) δ 180.4, 180.3, 143.4, 143.3, 138.4, 138.2, 133.7, 133.5, 133.4, 132.93, 132.89, 129.1, 129.0, 128.1, 128.0, 127.9, 127.8, 126.7, 126.53, 126.46, 126.2, 126.1, 124.8, 124.7, 122.83, 122.78, 122.6, 122.5, 118.4, 118.3, 108.3, 48.2, 48.1, 42.5, 35.9, 35.8, 29.6, 29.4, 26.4, 25.7, 25.2, 24.1, 23.9. **IR (ATR)**: 2924, 2244, 1701, 1611, 1469, 1453, 1375, 1251, 1124, 1017, 748 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{25}H_{24}N_2ONa^+$ 391.1781, found 391.1773.



***tert*-butyl (1-cyano-4-(1,3-dimethyl-2-oxoindolin-3-yl)butan-2-yl)carbamate (38)**: Following the general procedure F, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (isolated as an inseparable mixture, dr = 1:1, 54.3 mg, 0.152 mmol, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$) 7.31 – 7.27 (m, 2H), 7.18 – 7.16 (m, 2H), 7.12 – 7.06 (m, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 4.68 (d, *J* = 8.3 Hz, 1H), 4.55 (d, *J* = 8.3 Hz, 1H), 3.66 (s, 2H), 3.23 (d, *J* = 2.5 Hz, 6H), 2.71 – 2.52 (m, 2H), 2.47 – 2.32 (m, 2H), 2.13 – 2.00 (m, 1H), 1.96 – 1.90 (m, 1H), 1.83 – 1.74 (m, 2H), 1.44 (s, 18H), 1.37 (s, 6H), 1.32 – 1.10 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.3, 180.2, 155.2, 155.1, 143.3, 133.3, 133.2, 128.31, 128.29,

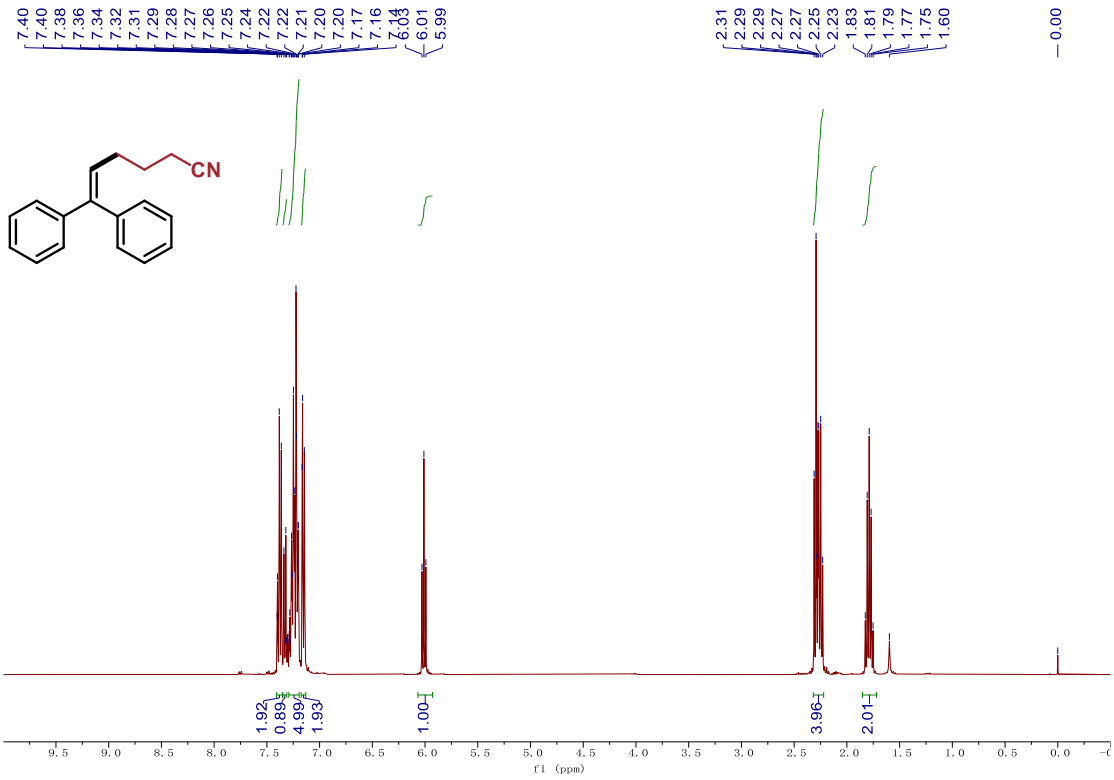
123.1, 123.0, 122.56, 122.52, 117.1, 108.4, 80.3, 48.1, 47.9, 47.5, 34.6, 34.5, 28.7, 28.6, 28.4, 26.4, 24.3, 24.1, 23.9. **IR (ATR)**: 2927, 2247, 1688, 1612, 1525, 1449, 1364, 1254, 1164, 1017, 745 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{20}H_{27}N_3O_3Na^+$ 380.1945, found 380.1938.



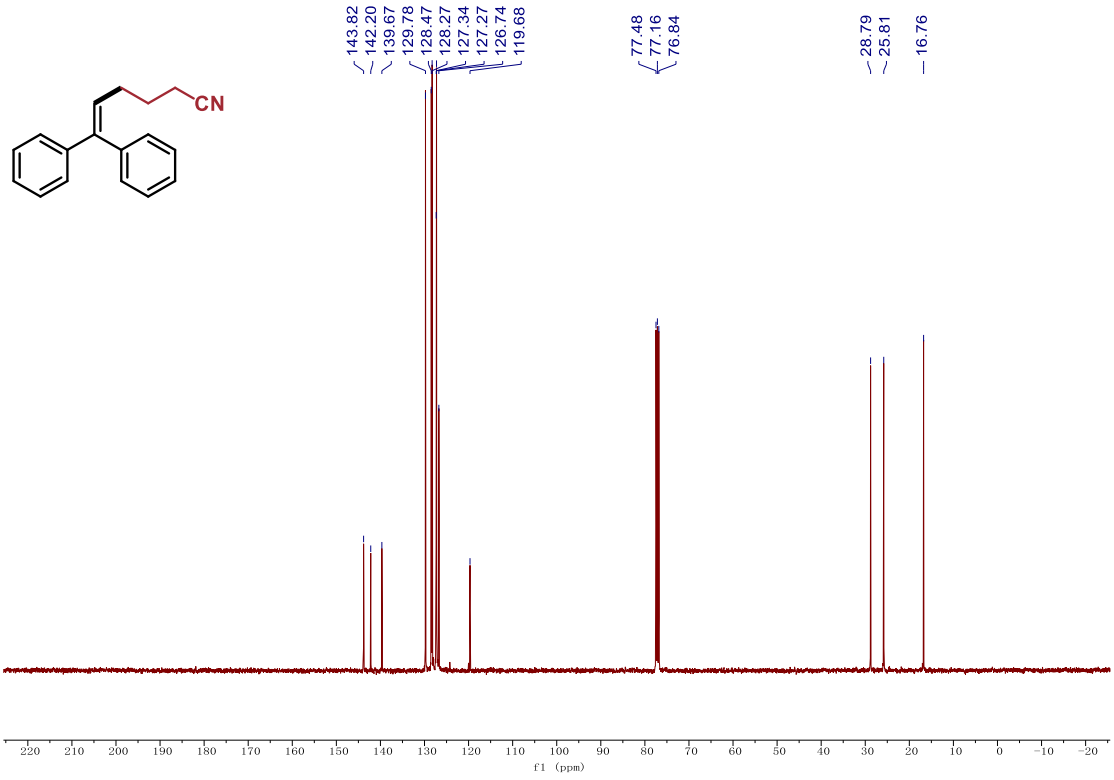
4-benzyl-5-(1,3-dimethyl-2-oxoindolin-3-yl)pentanenitrile (39): Following the general procedure F, the title product was obtained after purification by column chromatography (PE/EA = 10:1 – 4:1) as a white solid (isolated as an inseparable mixture, dr = 1.3:1, 33.9 mg, 0.102 mmol, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) 7.36 – 7.32 (m, 1H), 7.31 – 7.27 (m, 1H), 7.23 – 7.11 (m, 8H), 7.01 – 6.97 (m, 1H), 6.93 – 6.90 (m, 2H), 6.87 – 6.78 (m, 3H), 6.77 – 6.73 (m, 2H), 3.25 (d, J = 7.5 Hz, 6H), 2.49 (dd, J = 13.9, 4.1 Hz, 1H), 2.33 – 1.91 (m, 9H), 1.89 – 1.80 (m, 2H), 1.73 – 1.59 (m, 1H), 1.53 – 1.40 (m, 3H), 1.38 (s, 3H), 1.31 (s, 3H), 1.28 – 1.21 (m, 1H), 1.17 – 1.07 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.73, 180.68, 143.4, 143.3, 139.7, 139.6, 133.4, 133.0, 129.1, 129.0, 128.6, 128.5, 128.4, 128.2, 126.3, 123.1, 123.0, 122.8, 119.8, 119.5, 108.54, 108.45, 48.2, 47.8, 41.8, 41.7, 41.0, 40.3, 36.3, 36.2, 29.5, 29.4, 26.49, 26.45, 25.8, 25.2, 14.6, 14.5. **IR (ATR)**: 2927, 2247, 1688, 1612, 1525, 1449, 1364, 1254, 1164, 1017, 745 cm^{-1}. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{24}N_2ONa^+$ 355.1781, found 355.1775.

6. NMR Spectra.

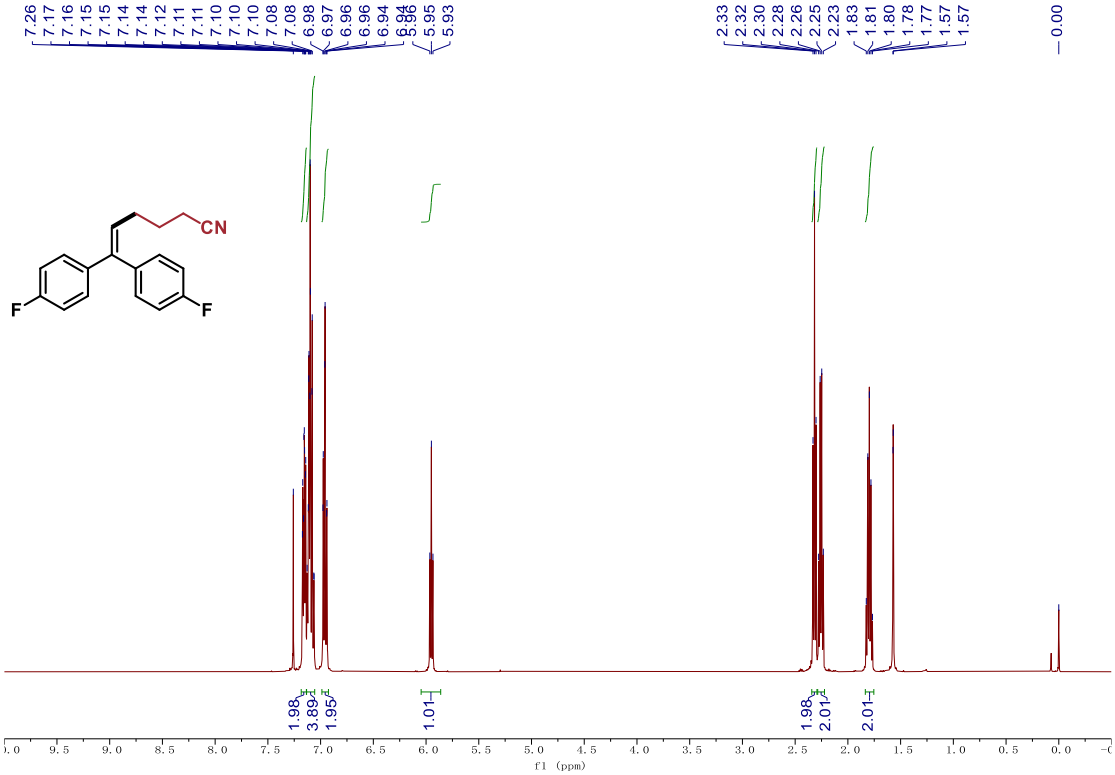
^{1}H NMR of compound **3** (400 MHz in $CDCl_3$)



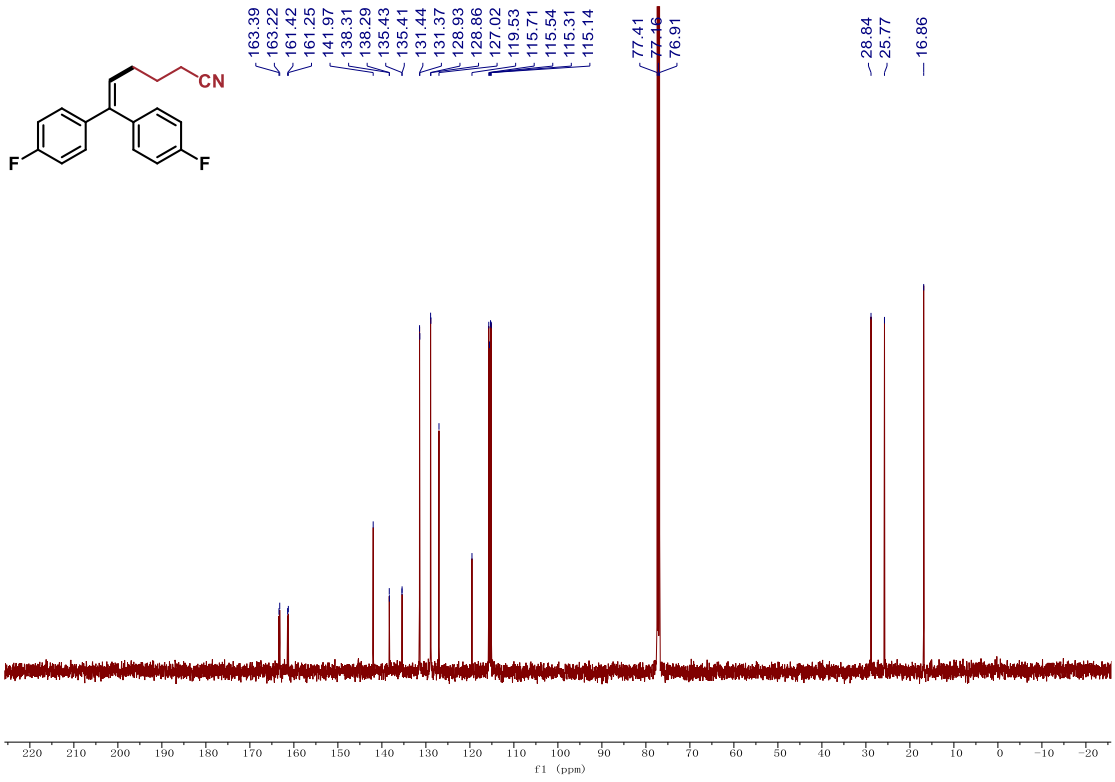
^{13}C NMR of compound **3** (101 MHz in $CDCl_3$)



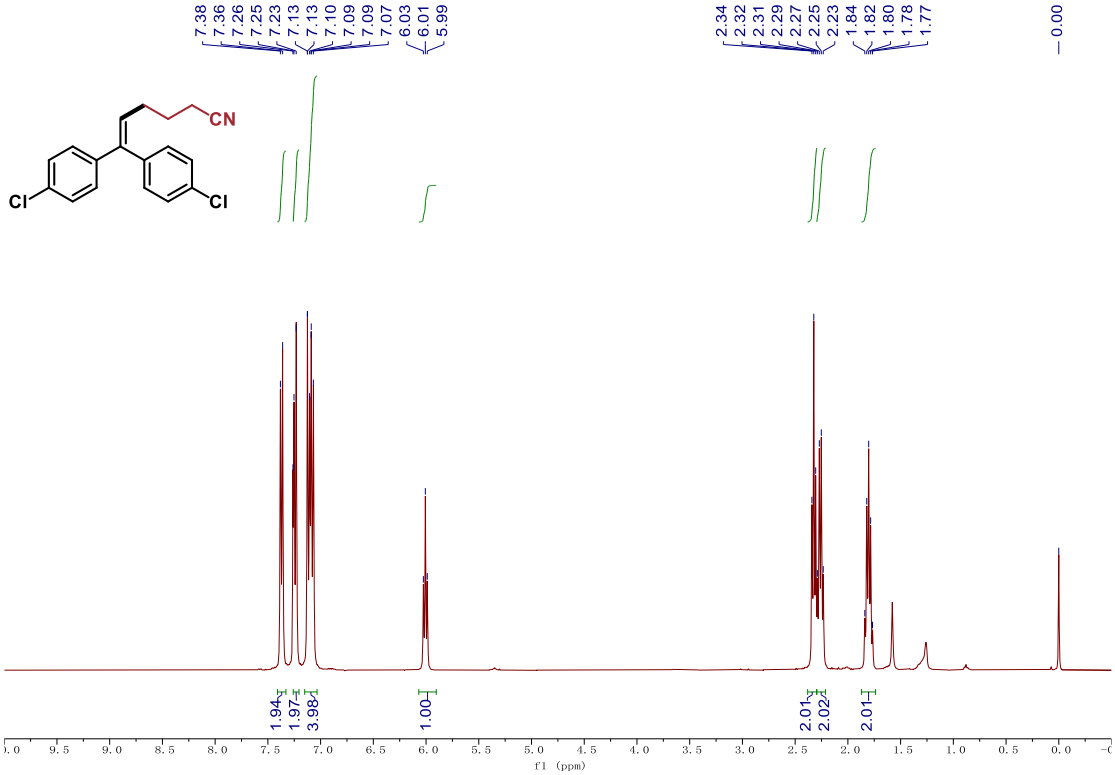
^{1}H NMR of compound **4** (500 MHz in $CDCl_3$)



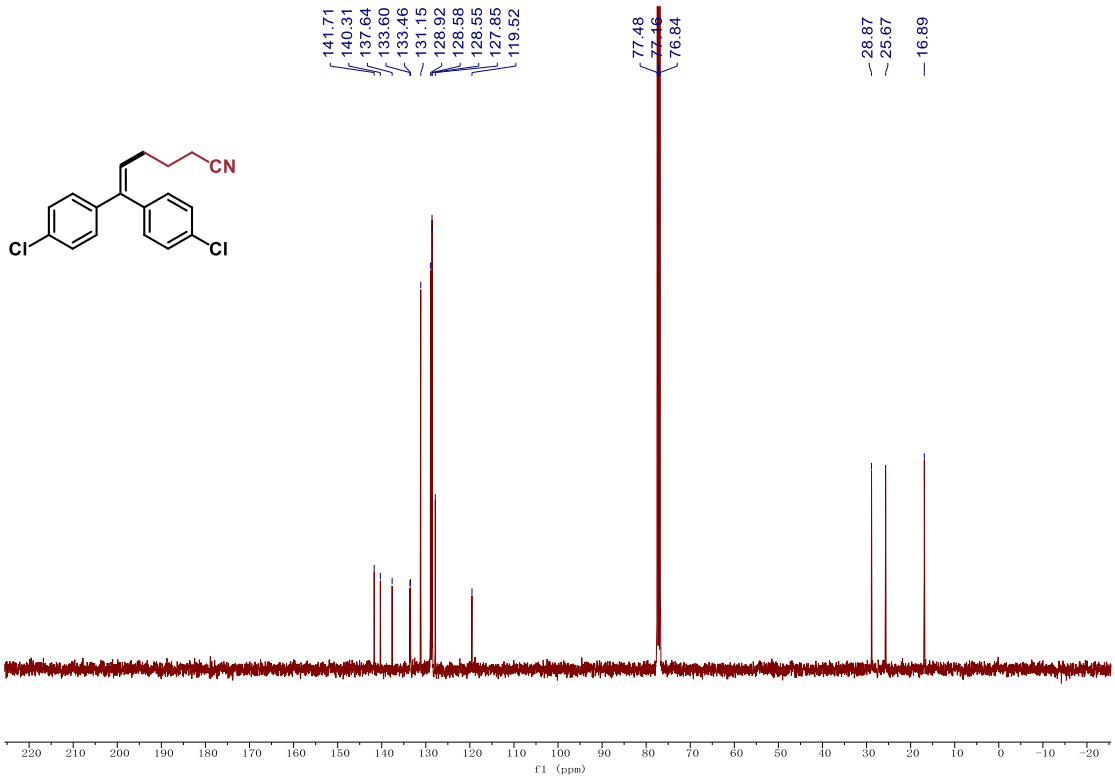
^{13}C NMR of compound **4** (126 MHz in $CDCl_3$)



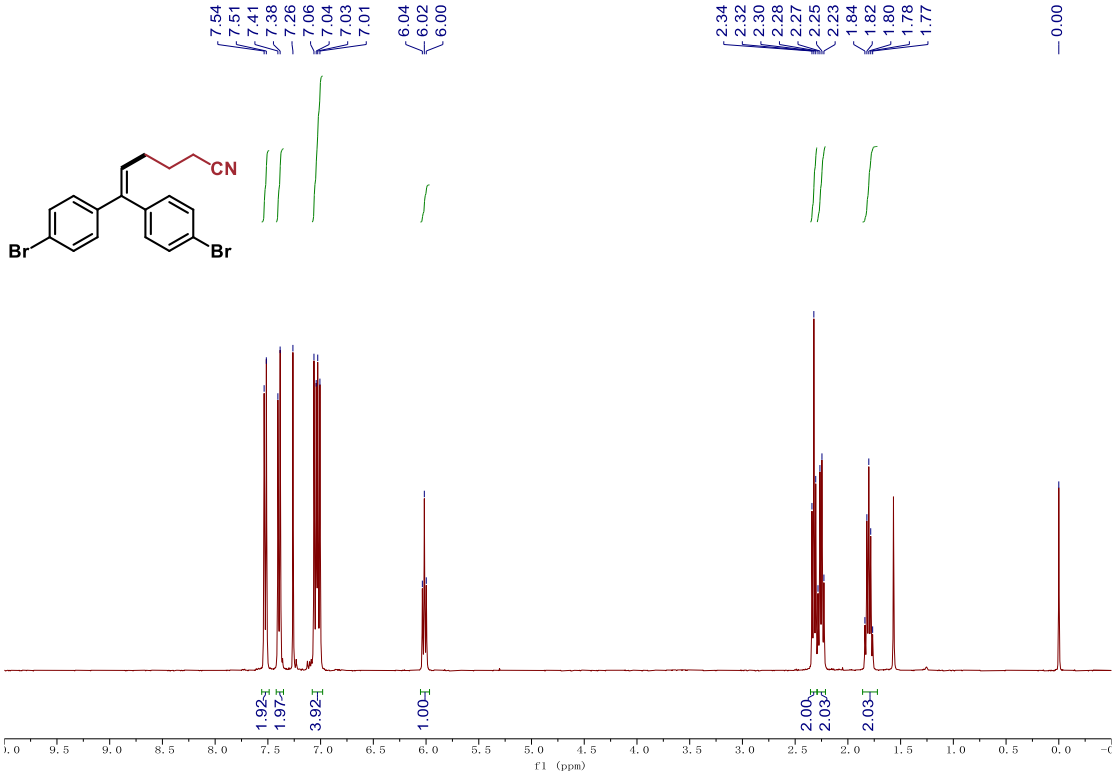
^{1}H NMR of compound **5** (400 MHz in $CDCl_3$)



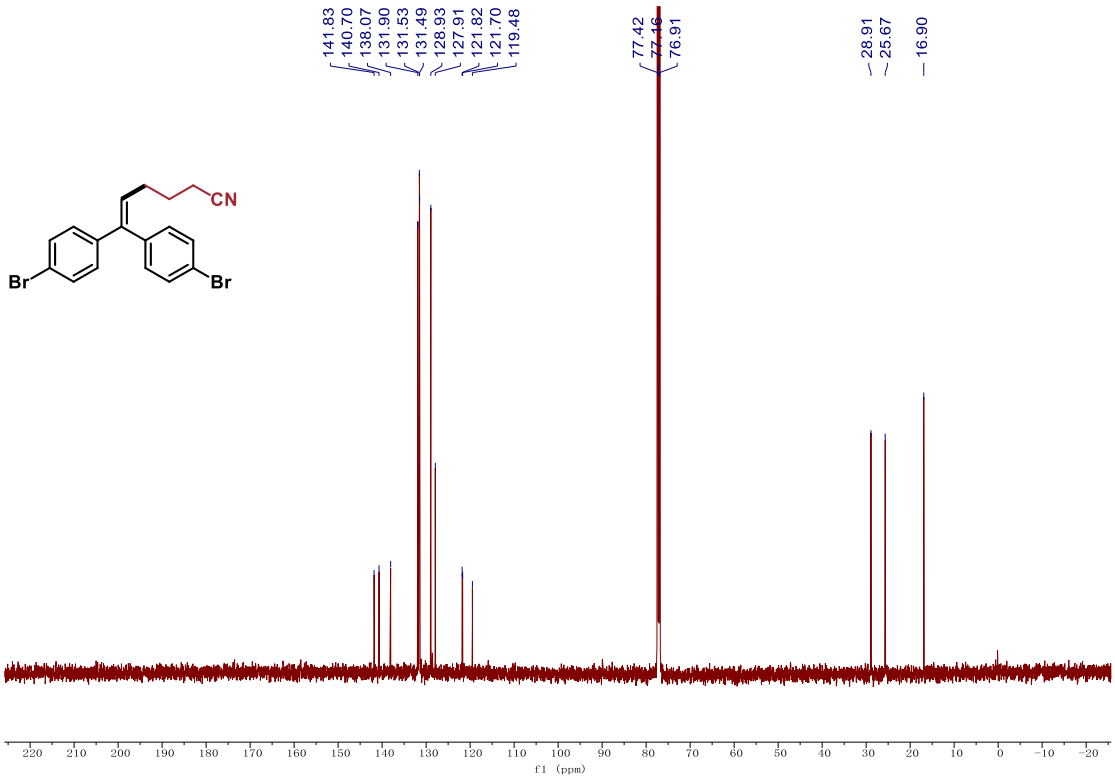
^{13}C NMR of compound **5** (101 MHz in $CDCl_3$)



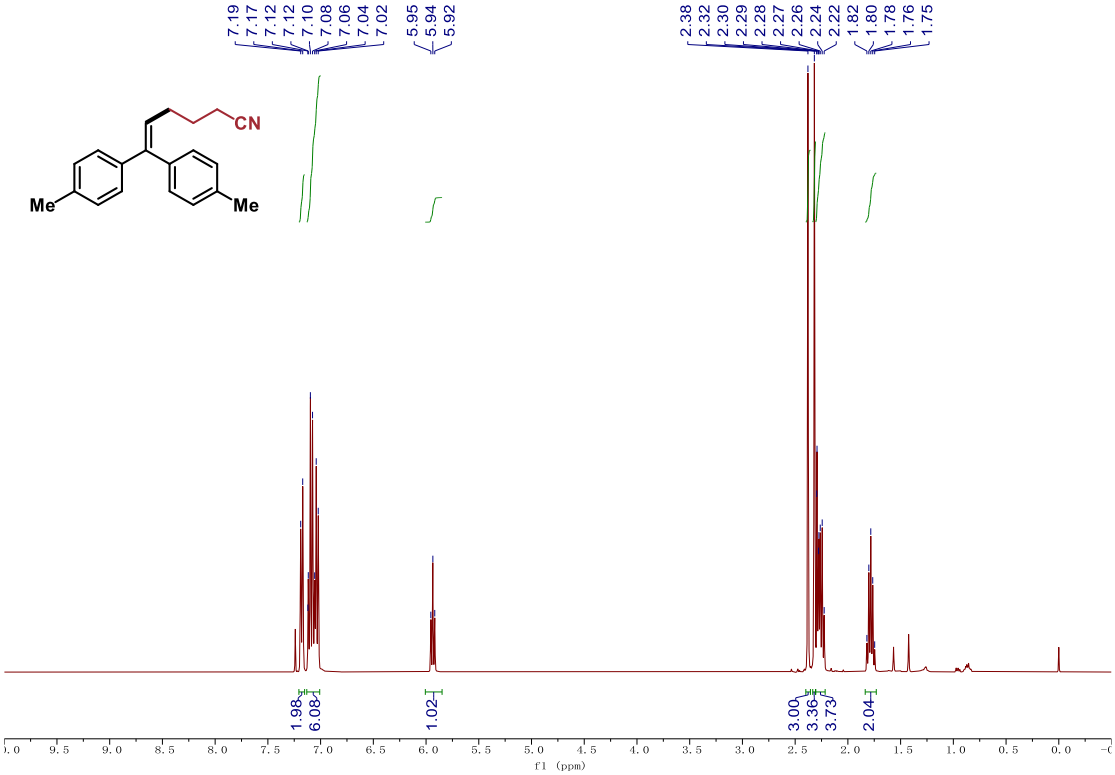
^{1}H NMR of compound **6** (400 MHz in $CDCl_3$)



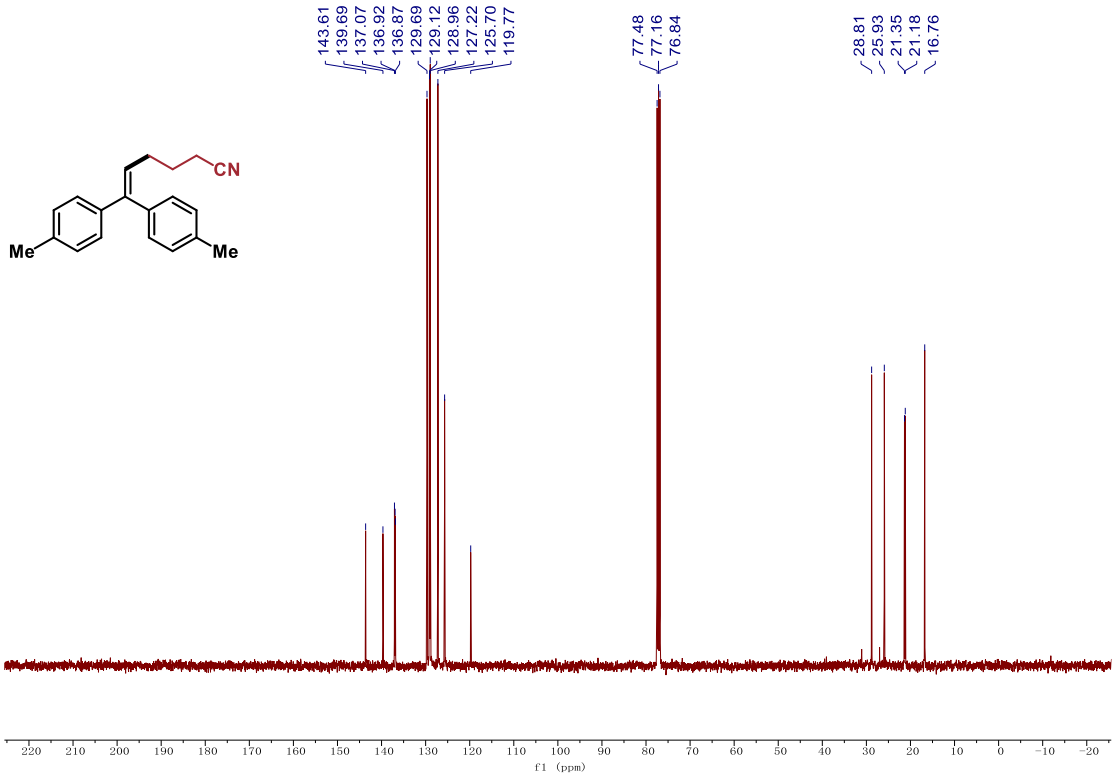
^{13}C NMR of compound **6** (126 MHz in $CDCl_3$)



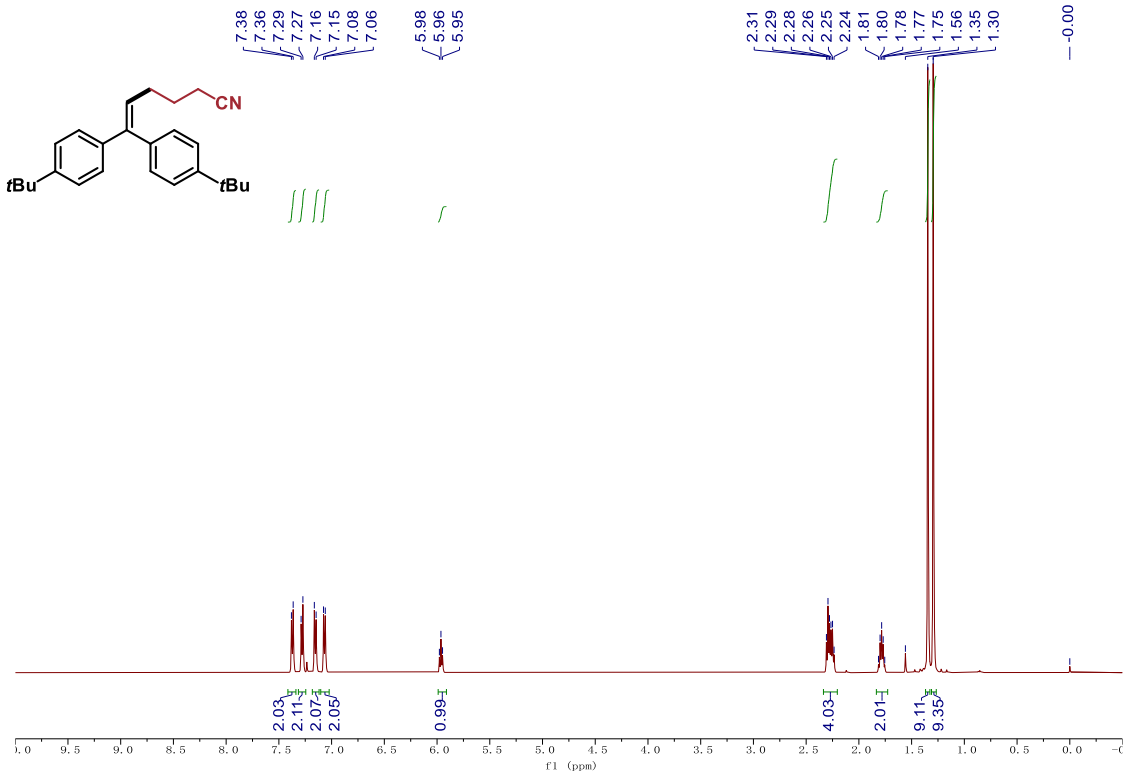
^{1}H NMR of compound **7** (400 MHz in $CDCl_3$)



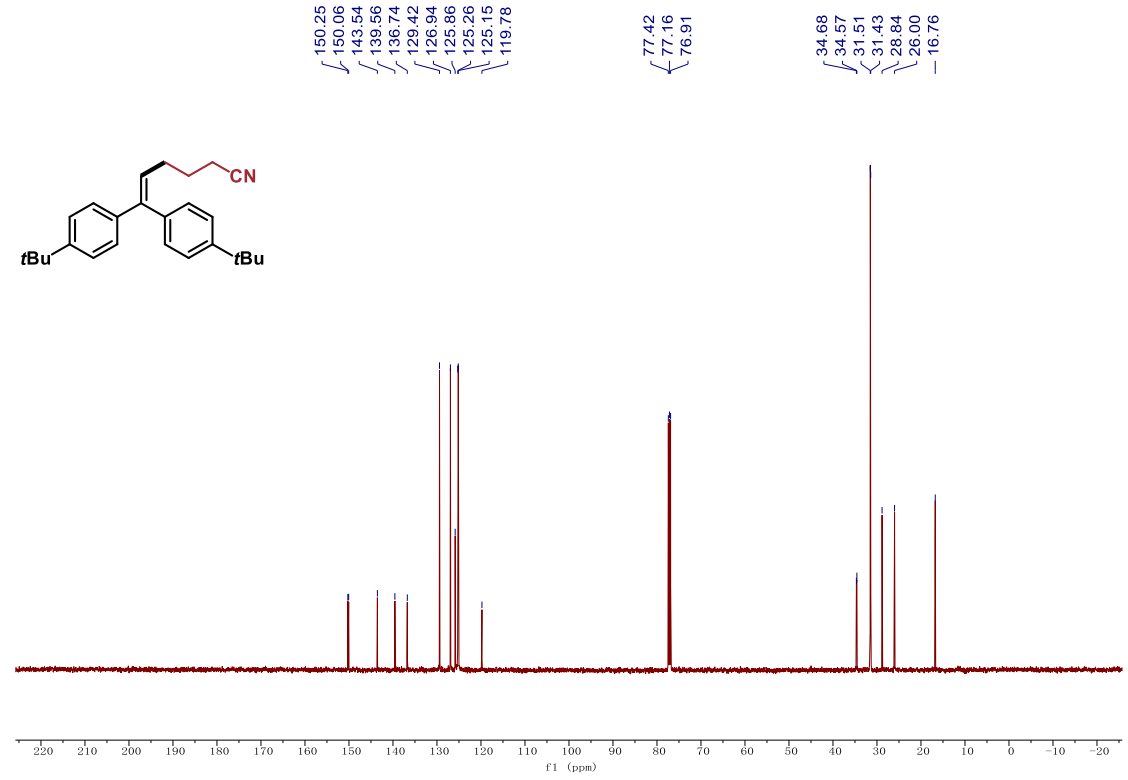
^{13}C NMR of compound **7** (101 MHz in $CDCl_3$)



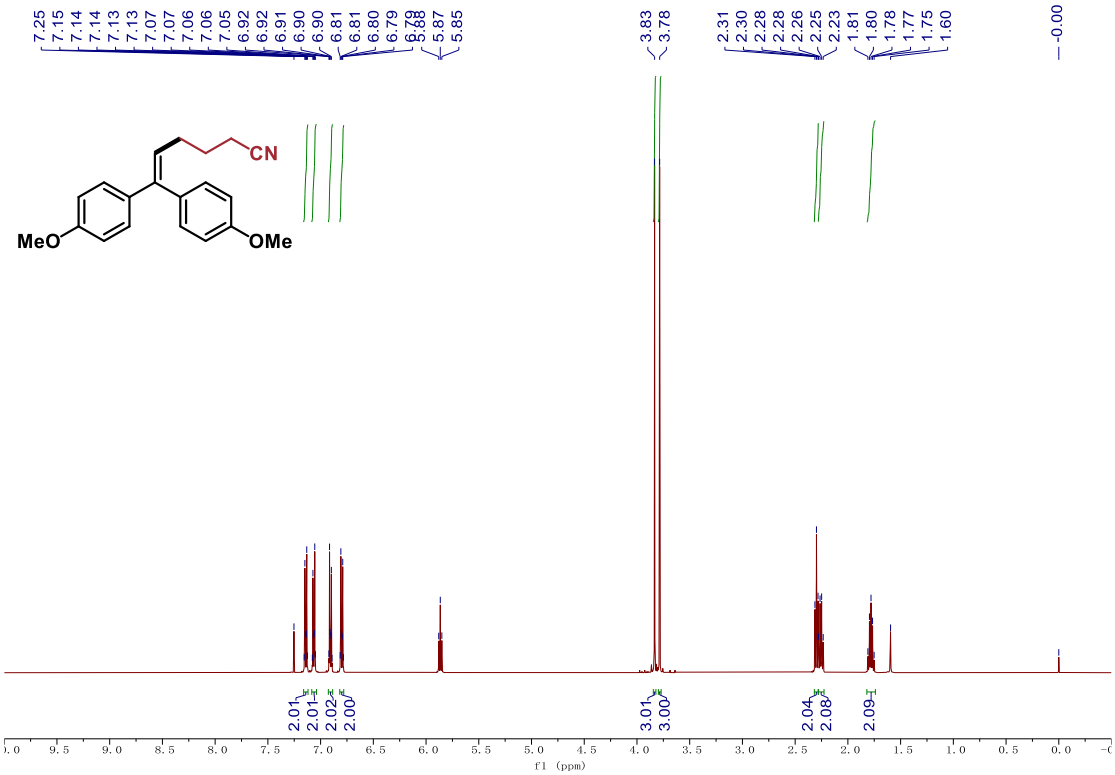
^{1}H NMR of compound **8** (400 MHz in $CDCl_3$)



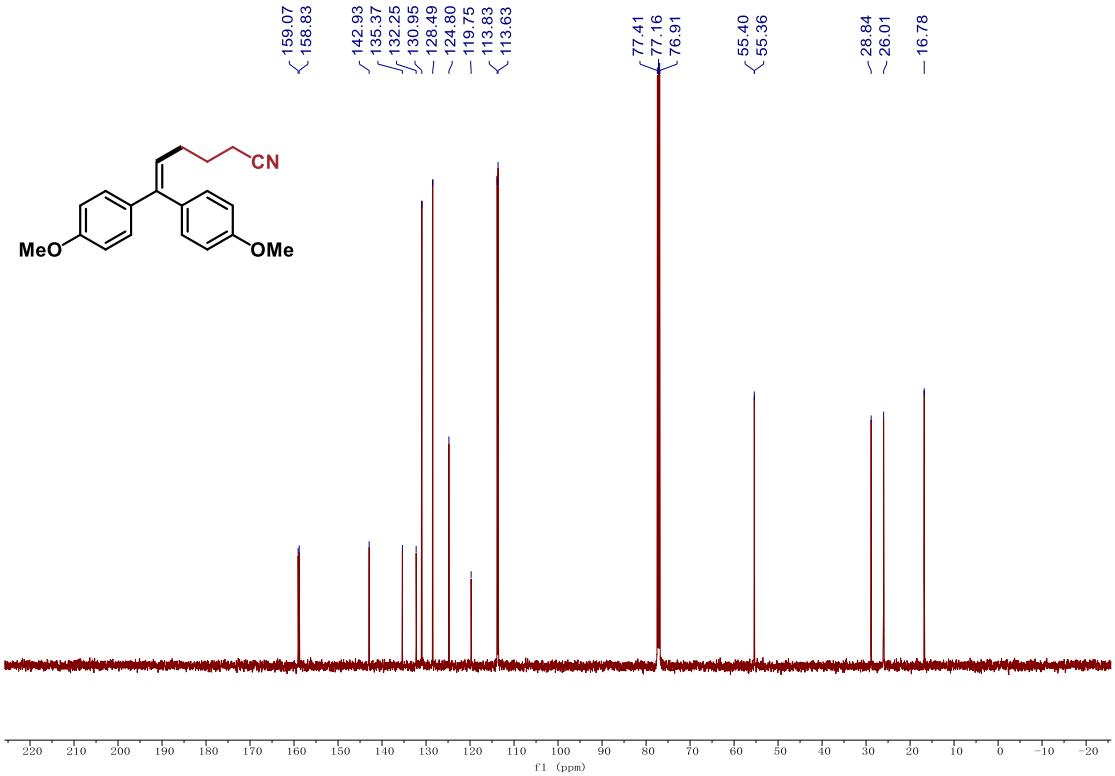
^{13}C NMR of compound **8** (101 MHz in $CDCl_3$)



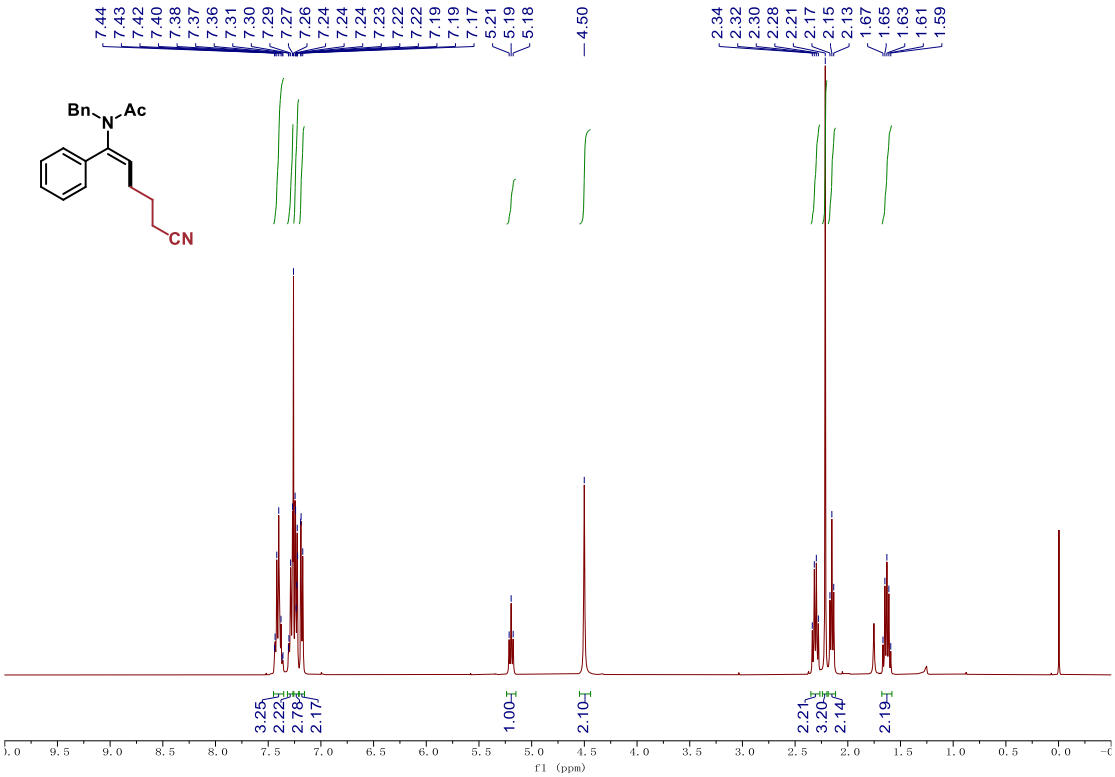
^{1}H NMR of compound **9** (500 MHz in $CDCl_3$)



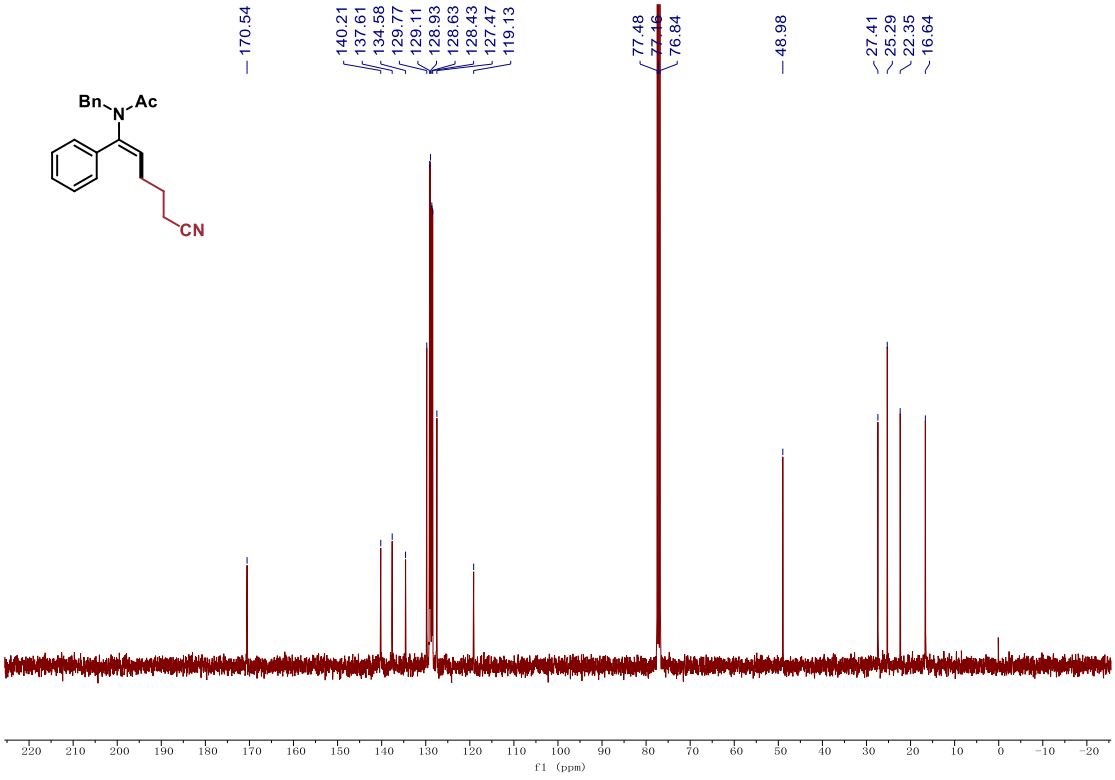
^{13}C NMR of compound **9** (126 MHz in $CDCl_3$)



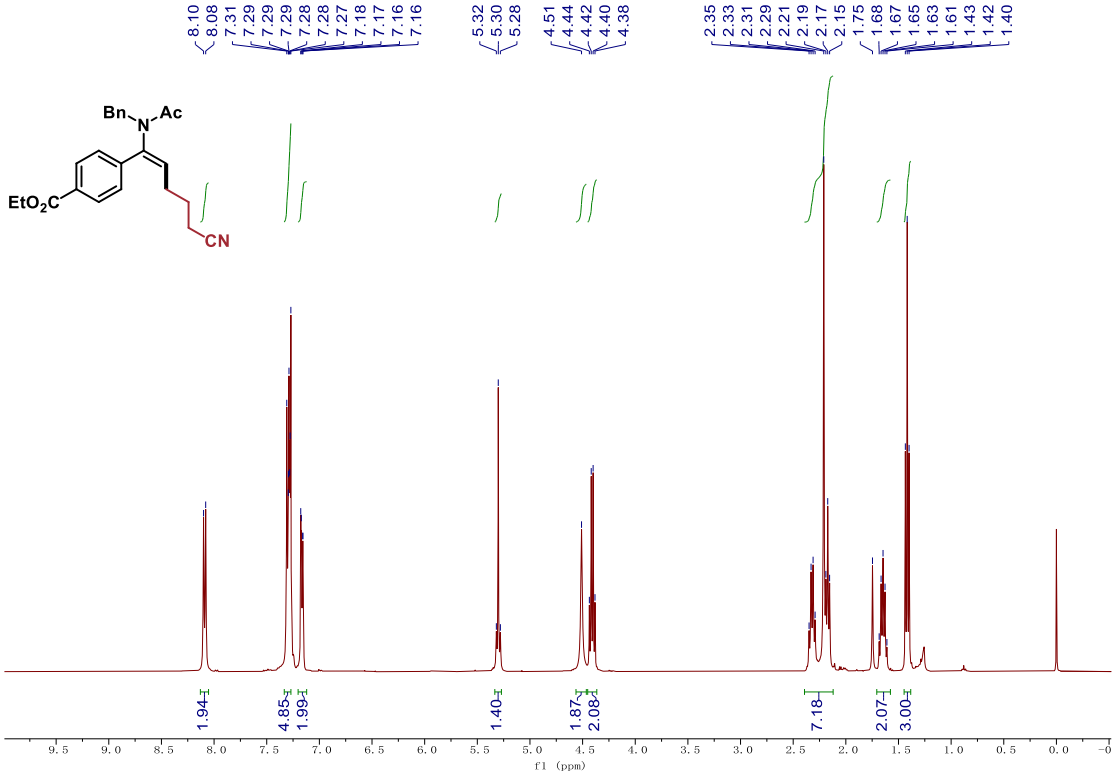
^{1}H NMR of compound **10** (400 MHz in $CDCl_3$)



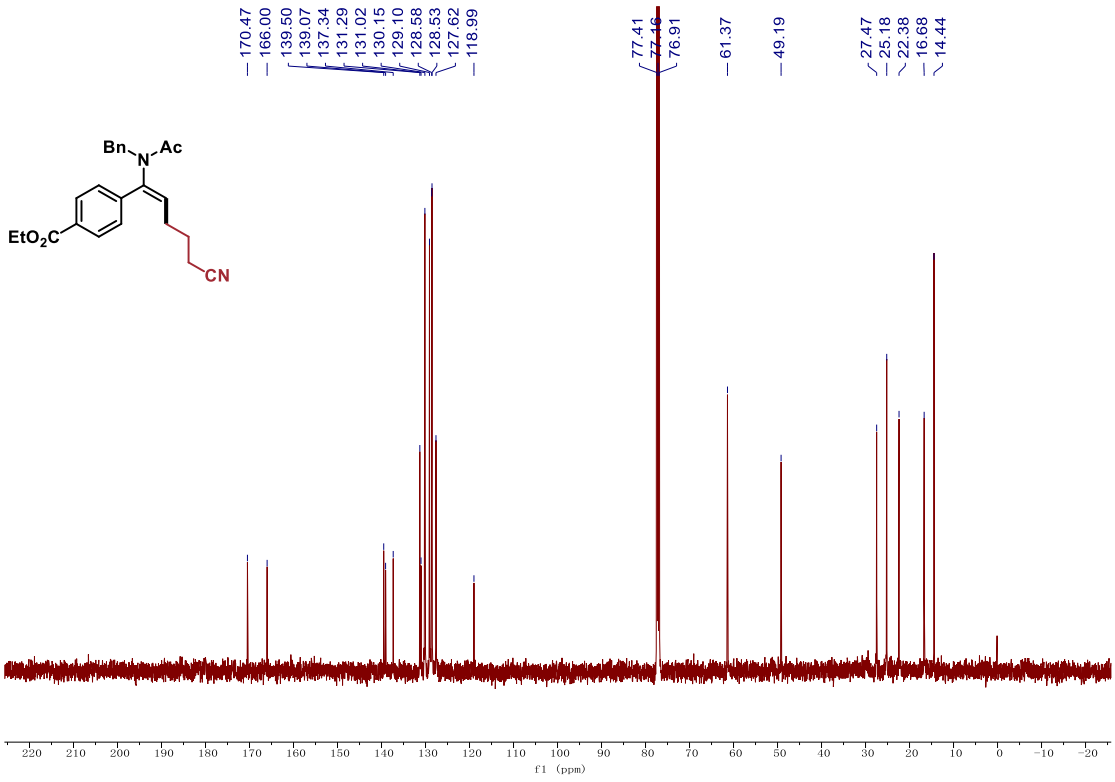
^{13}C NMR of compound **10** (101 MHz in $CDCl_3$)



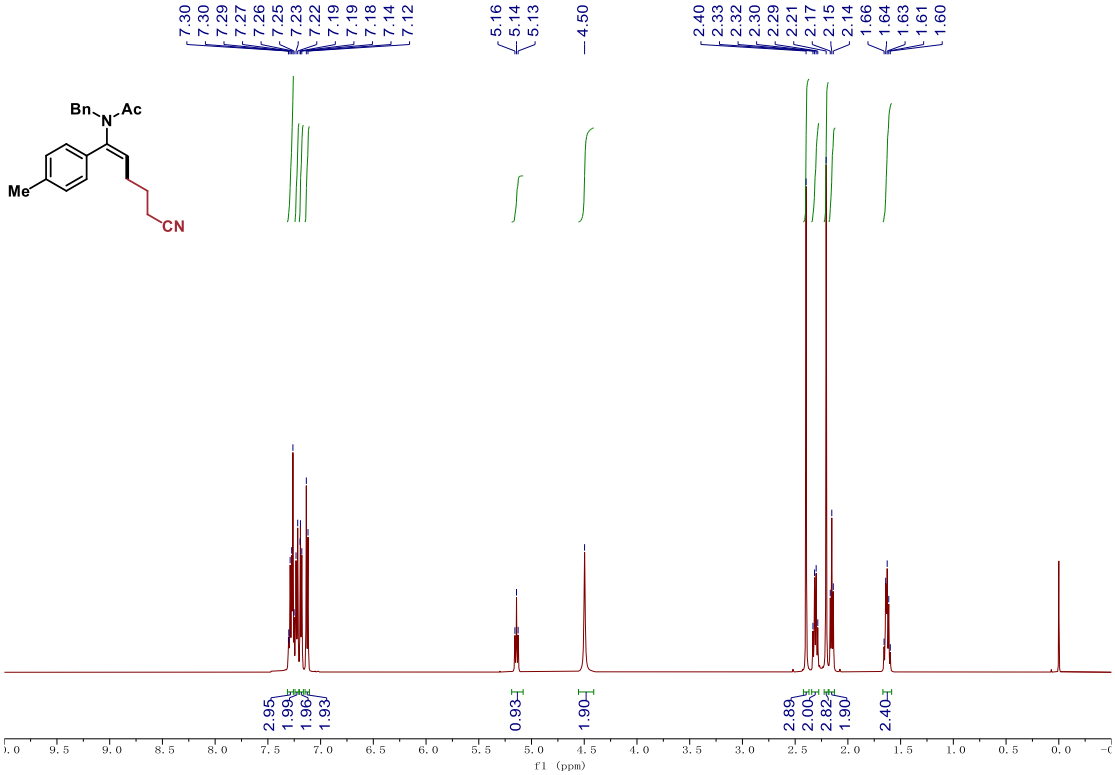
^{1}H NMR of compound **11** (400 MHz in $CDCl_3$)



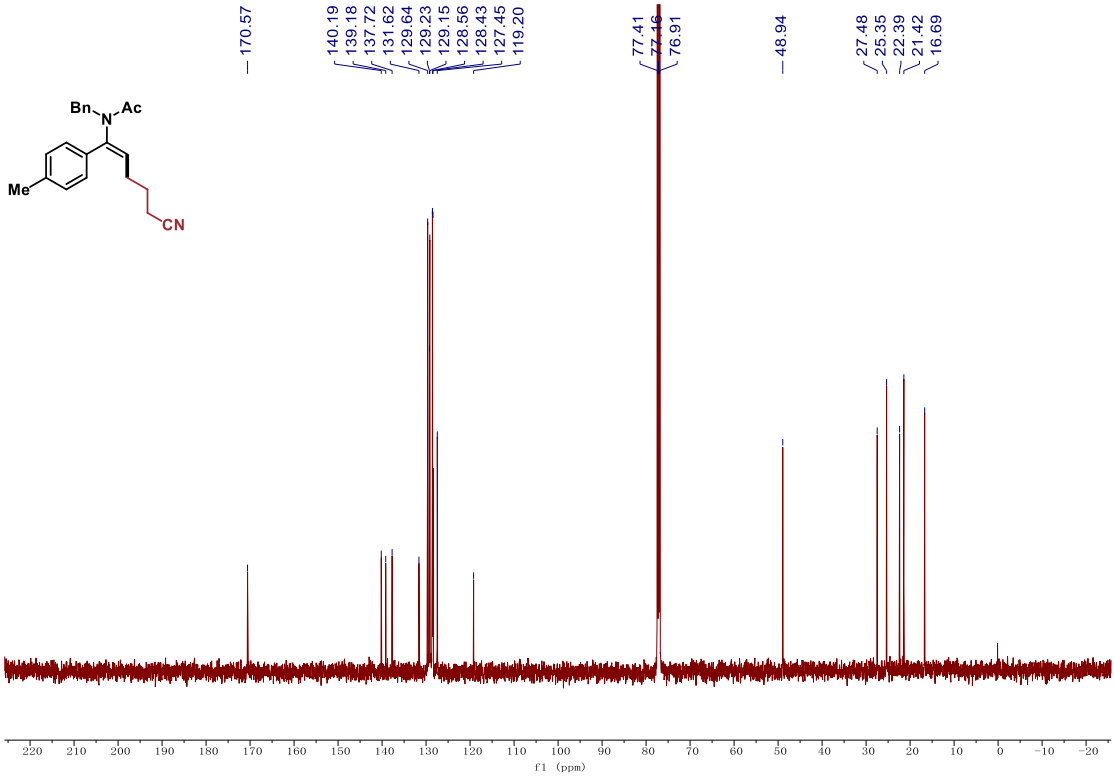
^{13}C NMR of compound **11** (126 MHz in $CDCl_3$)



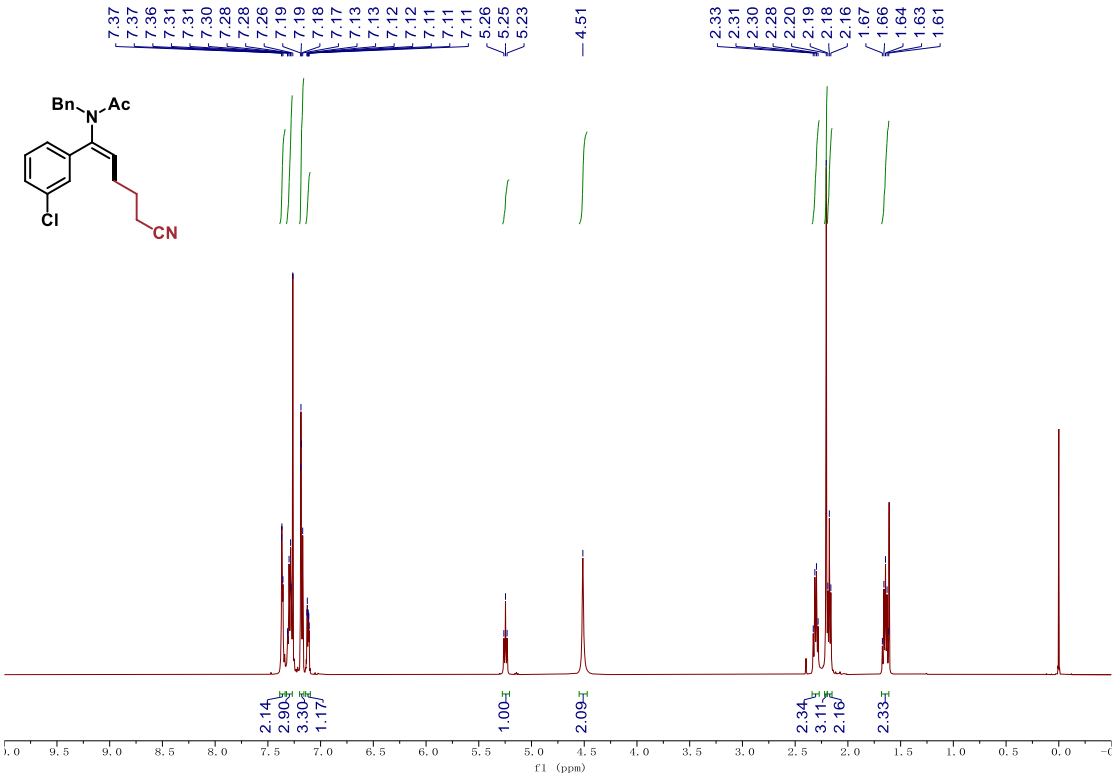
^{1}H NMR of compound **12** (500 MHz in $CDCl_3$)



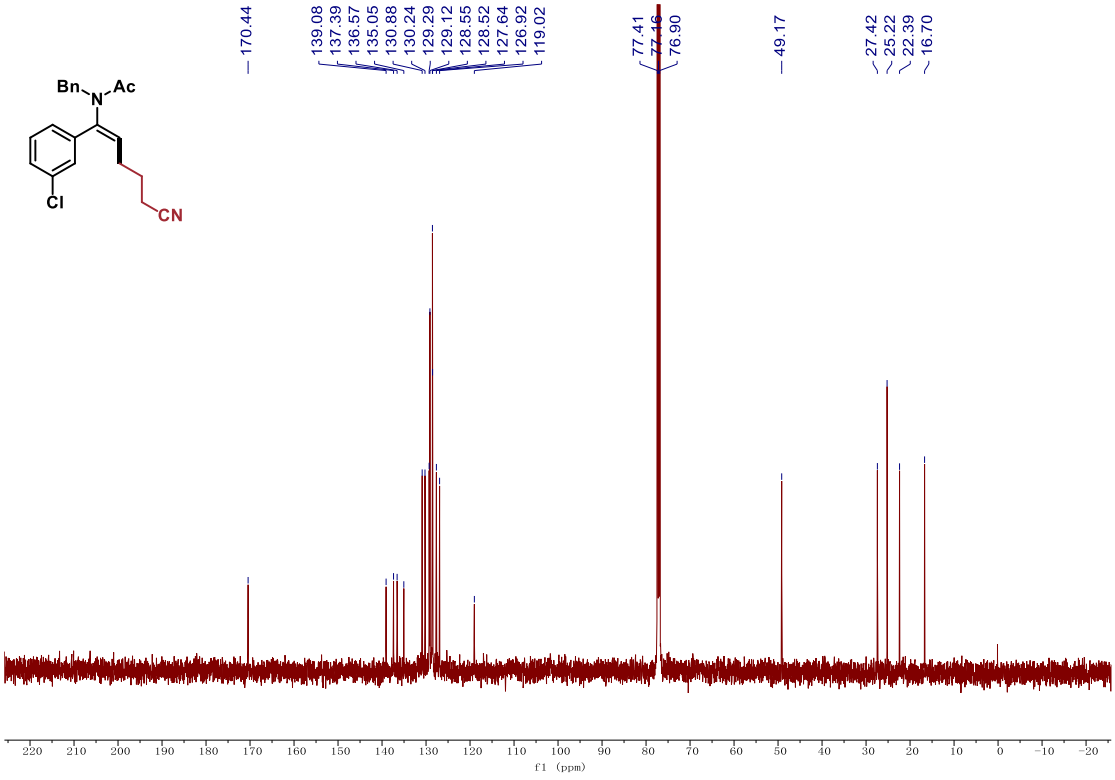
^{13}C NMR of compound **12** (126 MHz in $CDCl_3$)



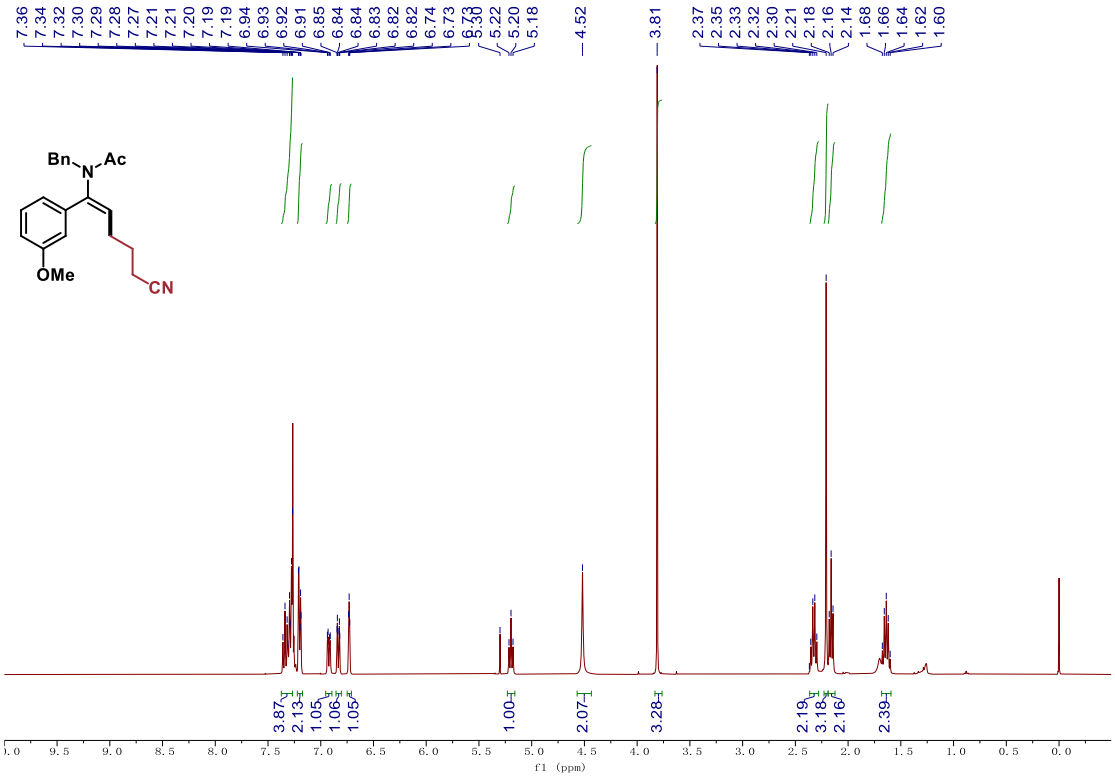
^{1}H NMR of compound **13** (500 MHz in $CDCl_3$)



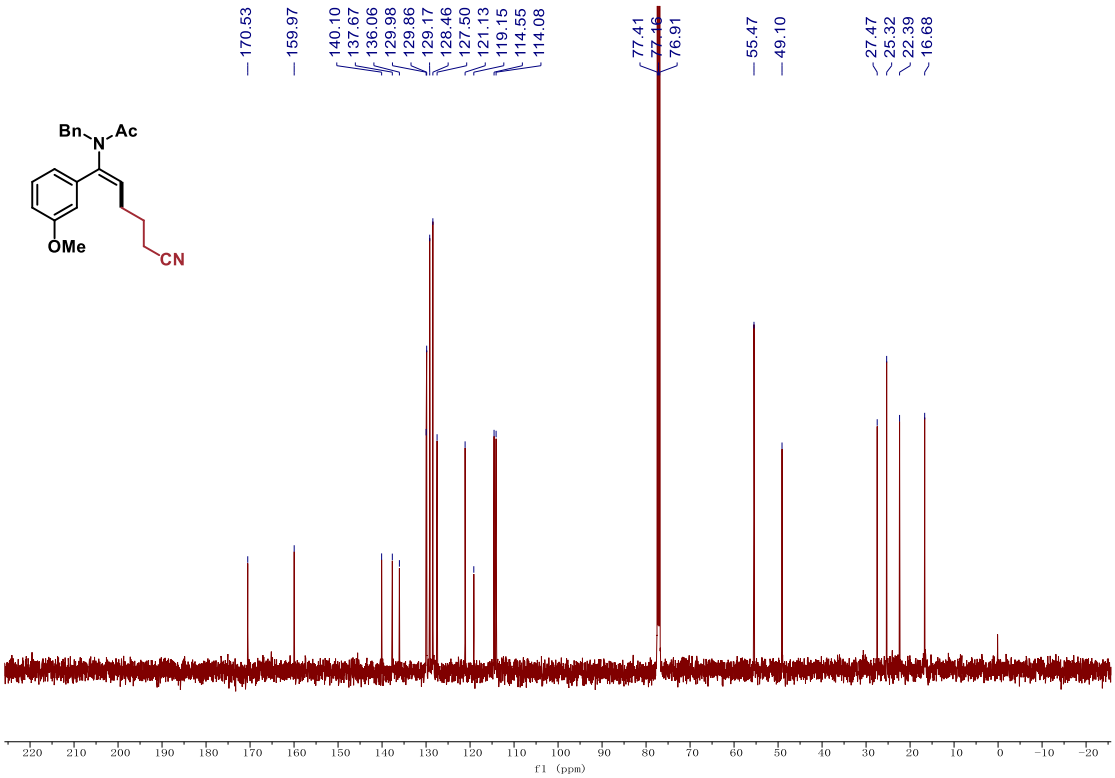
^{13}C NMR of compound **13** (126 MHz in $CDCl_3$)



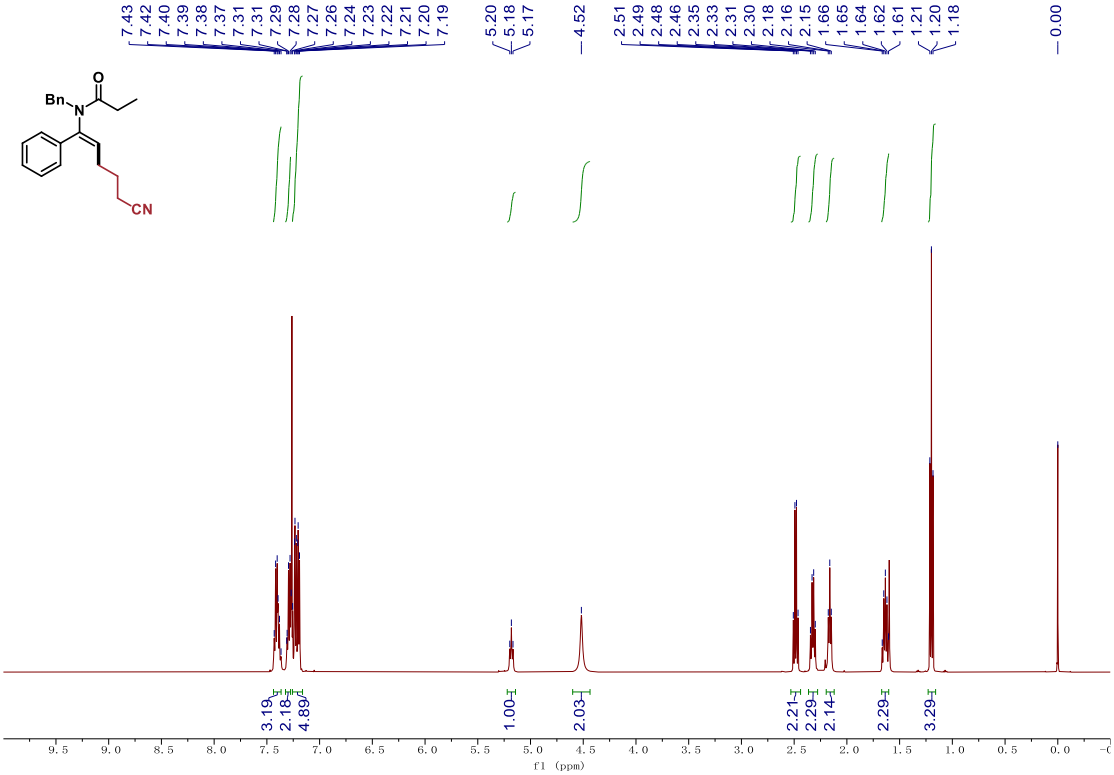
^{1}H NMR of compound **14** (400 MHz in $CDCl_3$)



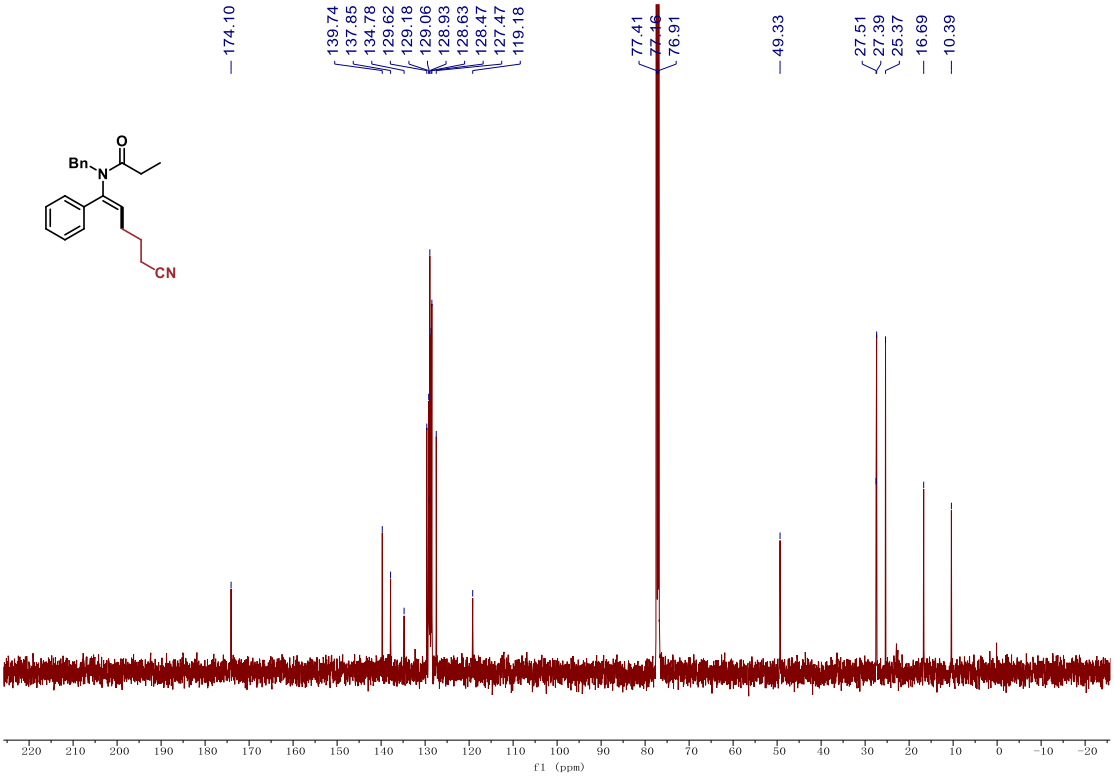
^{13}C NMR of compound **14** (126 MHz in $CDCl_3$)



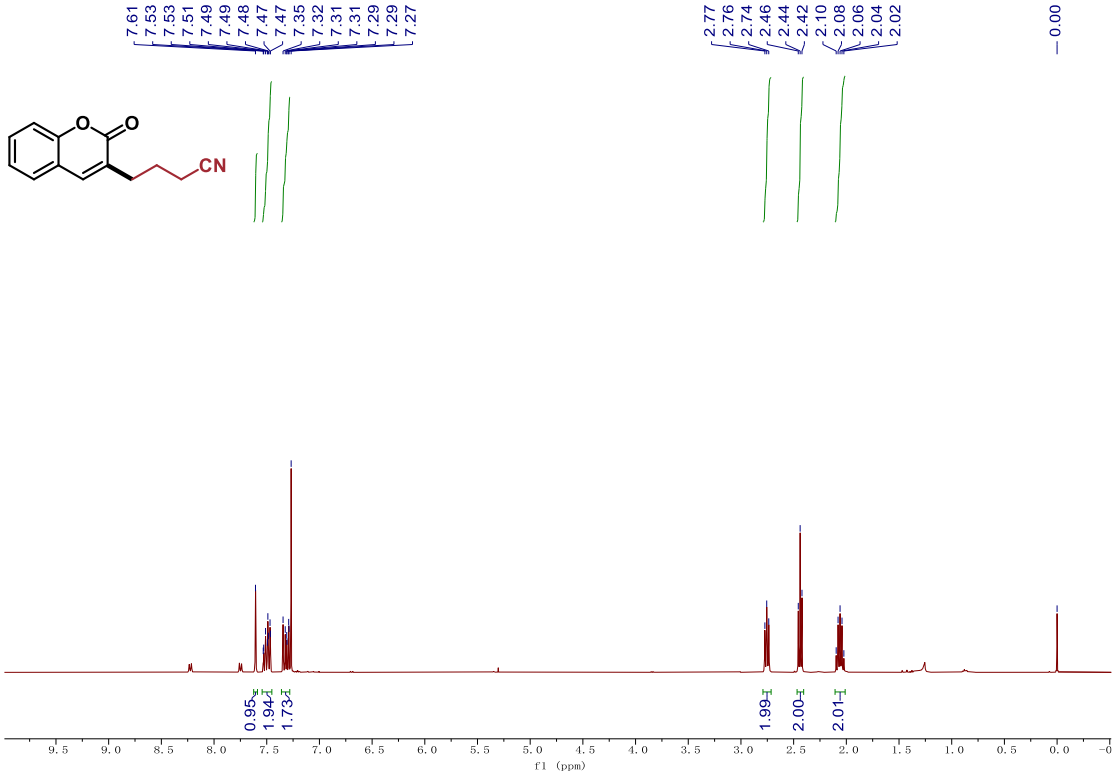
^{1}H NMR of compound **15** (500 MHz in $CDCl_3$)



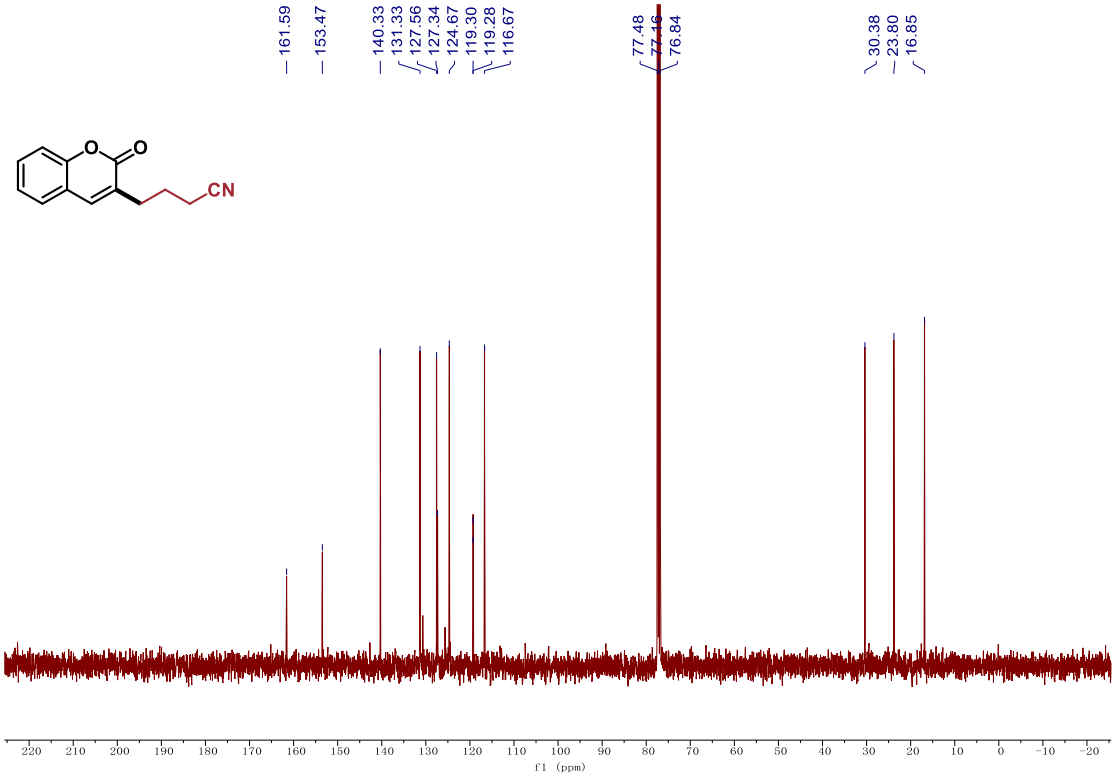
^{13}C NMR of compound **15** (126 MHz in $CDCl_3$)



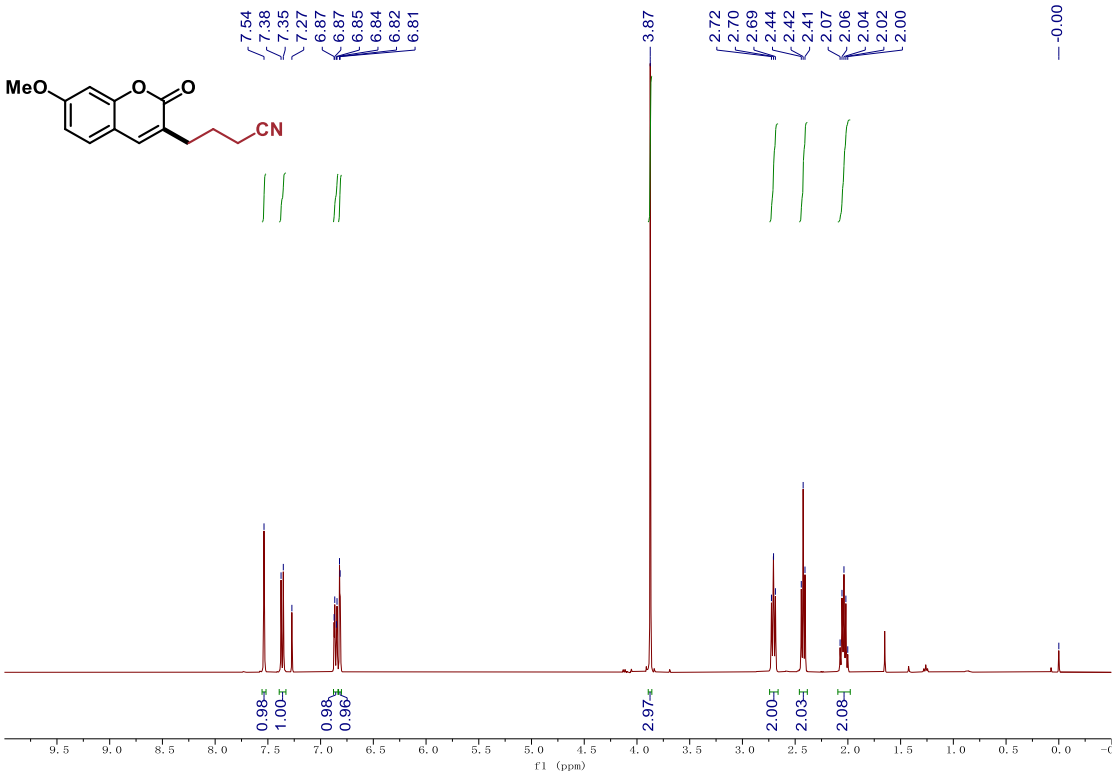
^{1}H NMR of compound **16** (400 MHz in $CDCl_3$)



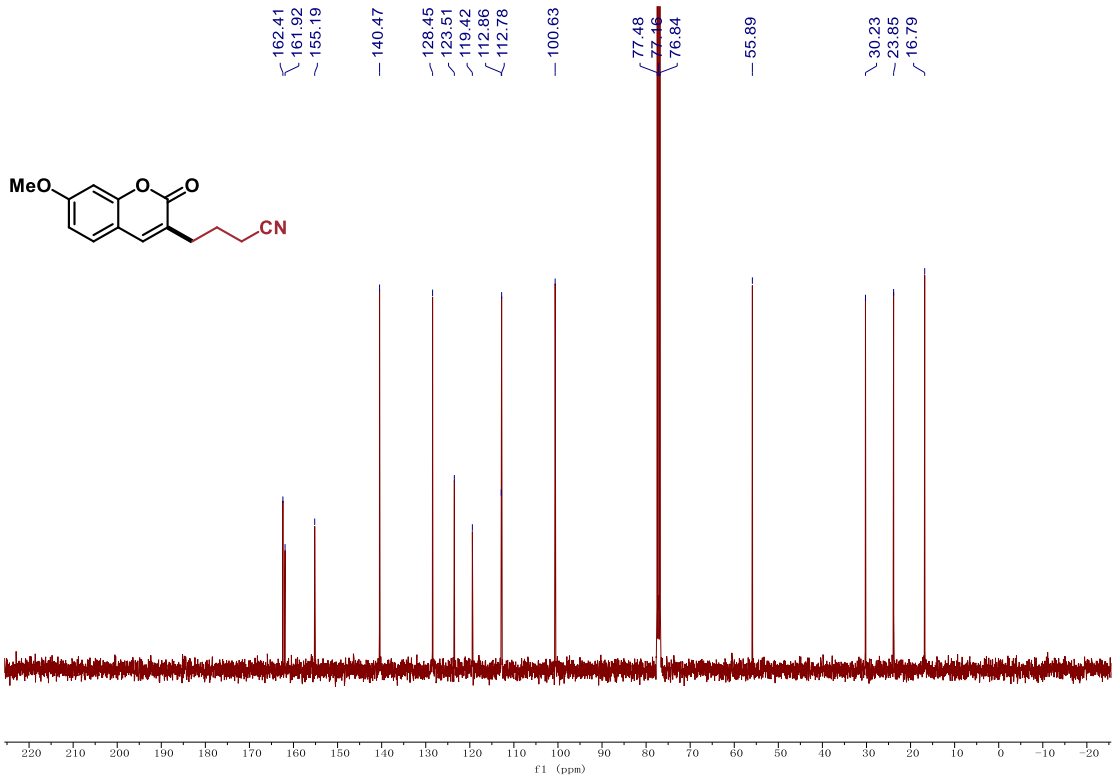
^{13}C NMR of compound **16** (101 MHz in $CDCl_3$)



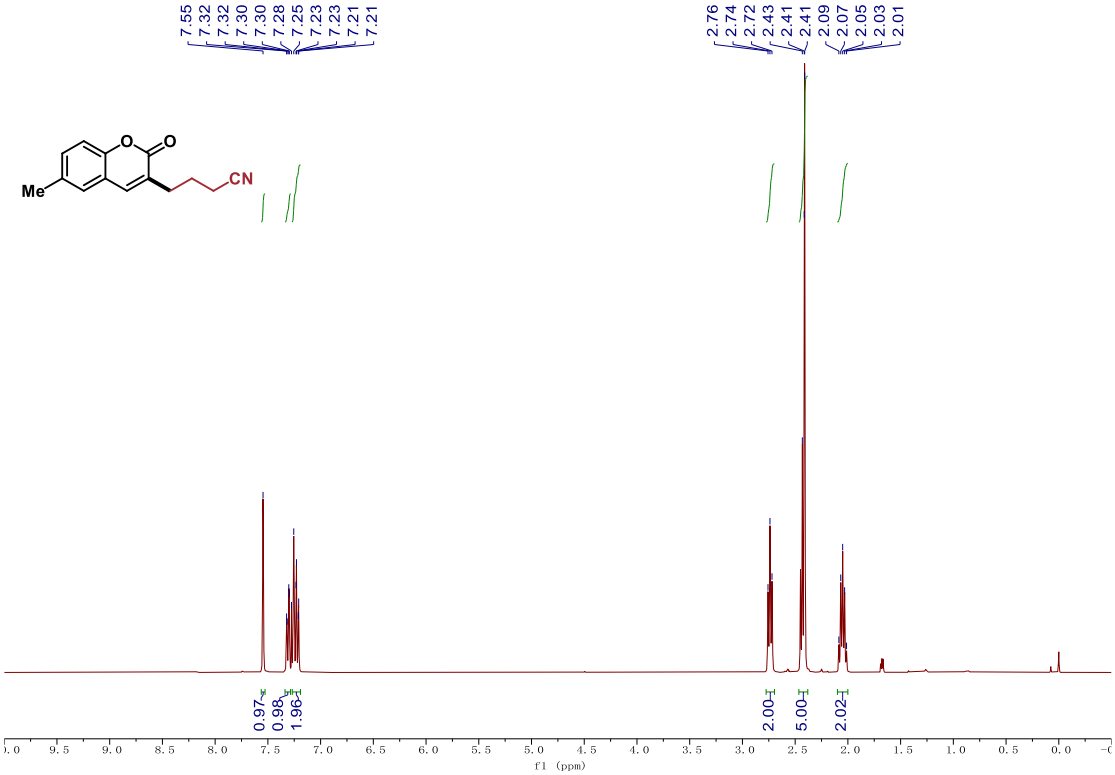
^{1}H NMR of compound **17** (400 MHz in $CDCl_3$)



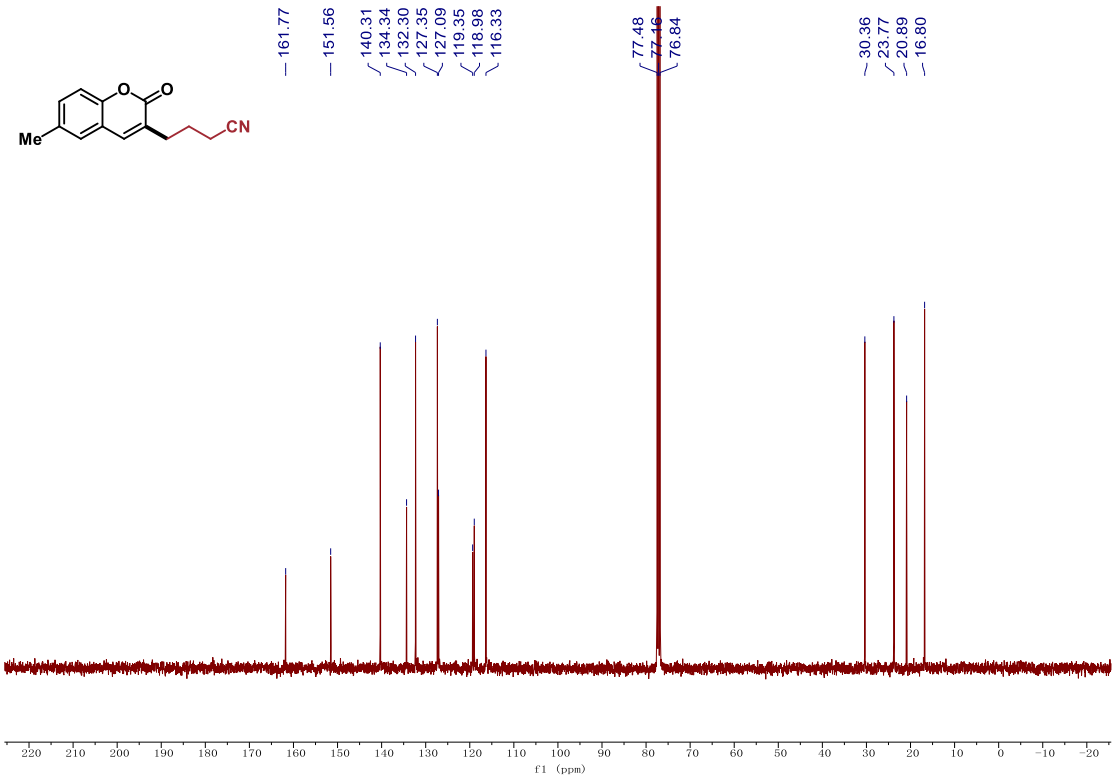
^{13}C NMR of compound **17** (101 MHz in $CDCl_3$)



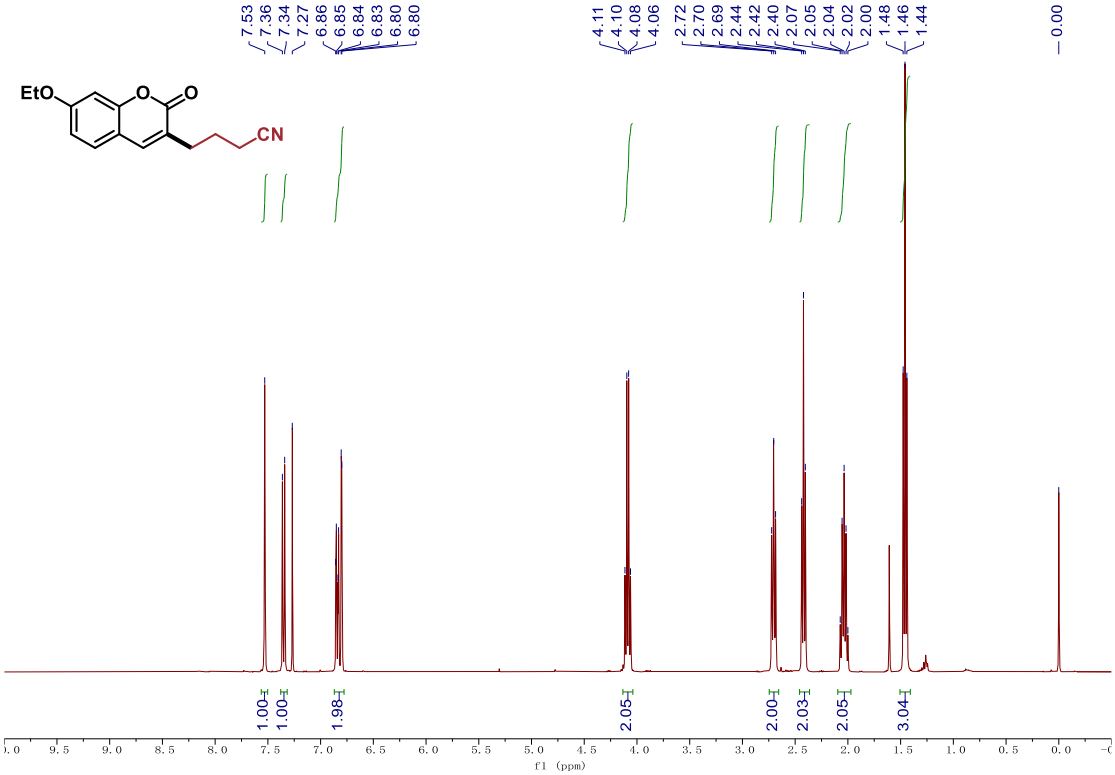
^{1}H NMR of compound **18** (400 MHz in $CDCl_3$)



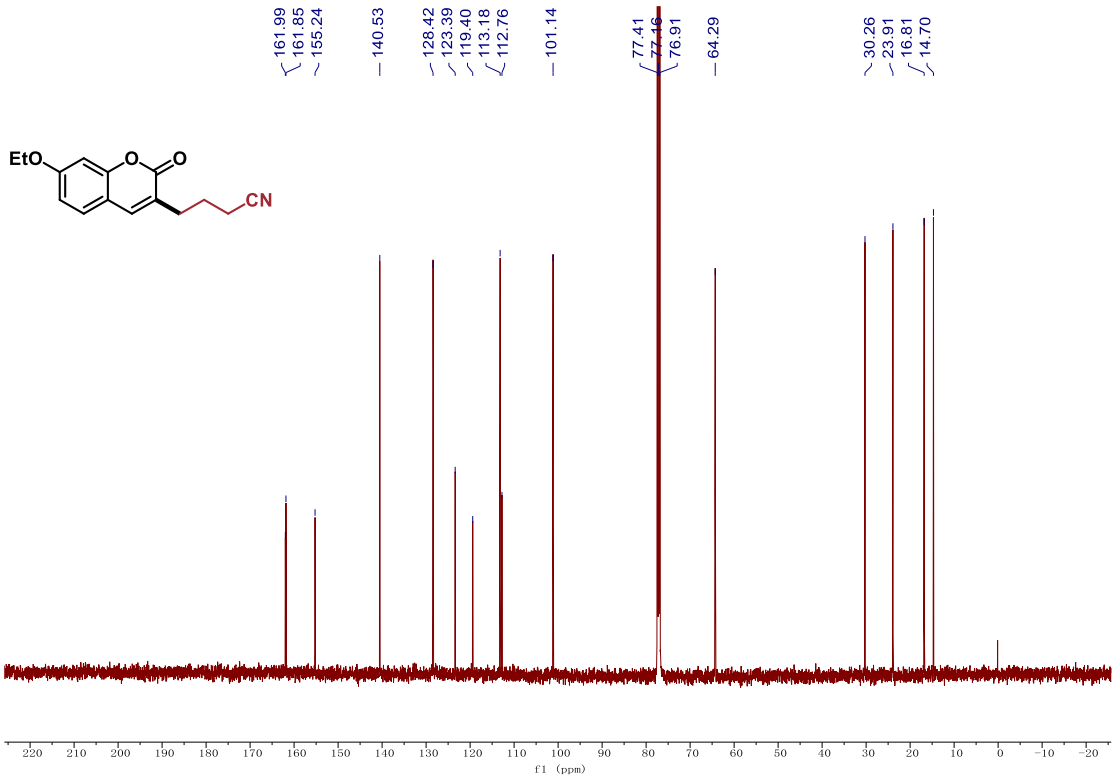
^{13}C NMR of compound **18** (101 MHz in $CDCl_3$)



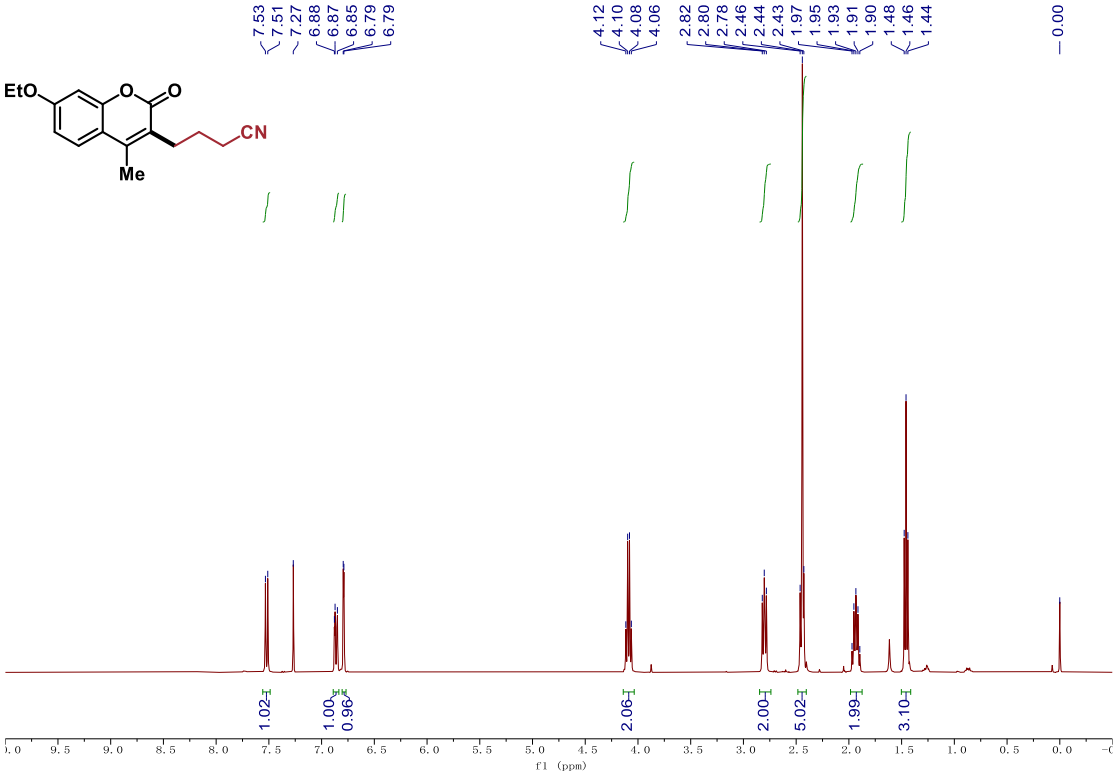
^{1}H NMR of compound **19** (400 MHz in $CDCl_3$)



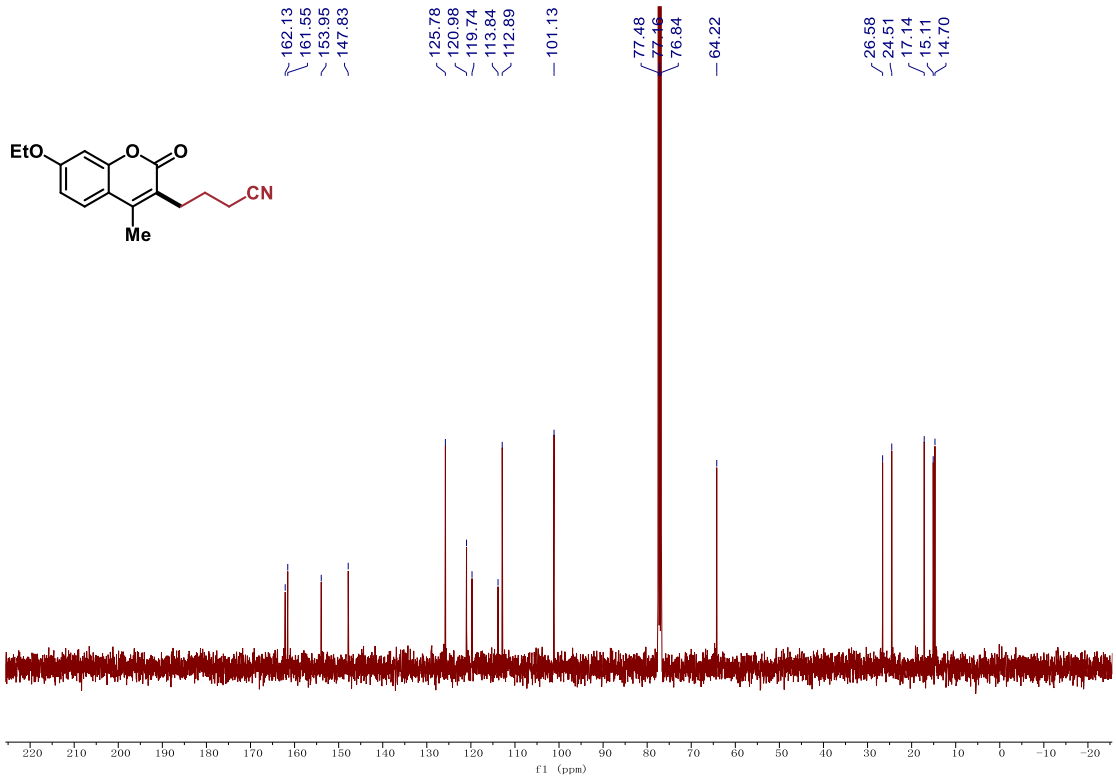
^{13}C NMR of compound **19** (126 MHz in $CDCl_3$)



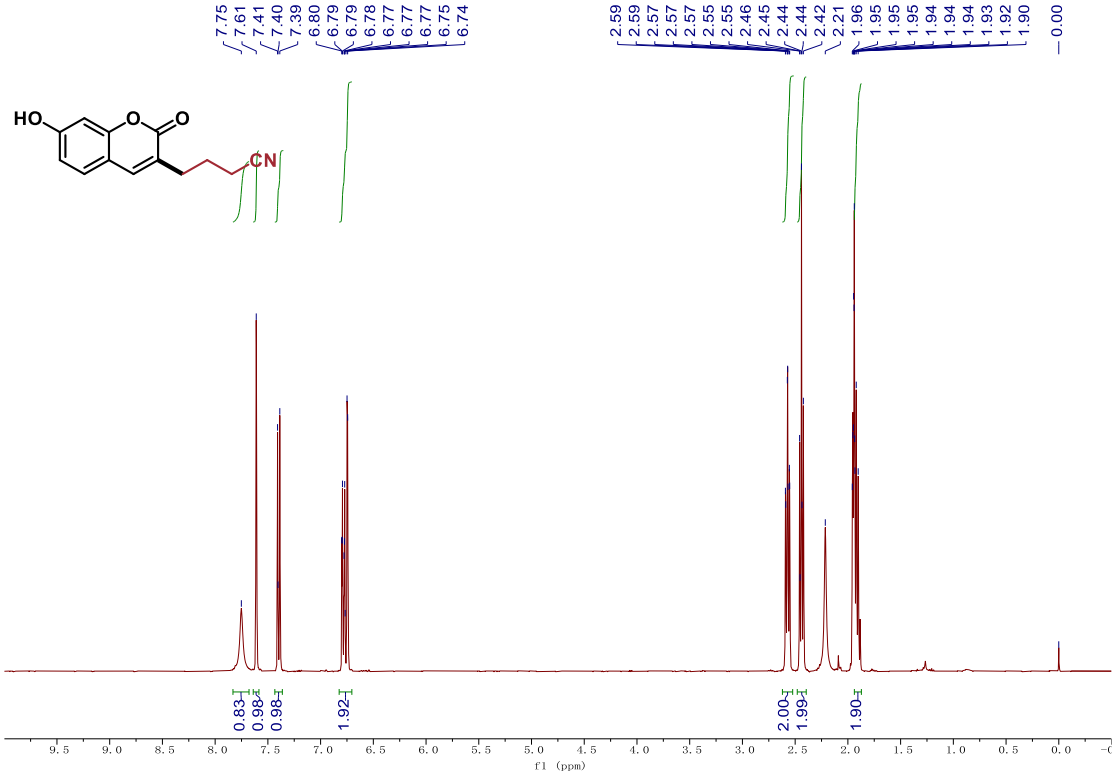
^{1}H NMR of compound **20** (400 MHz in $CDCl_3$)



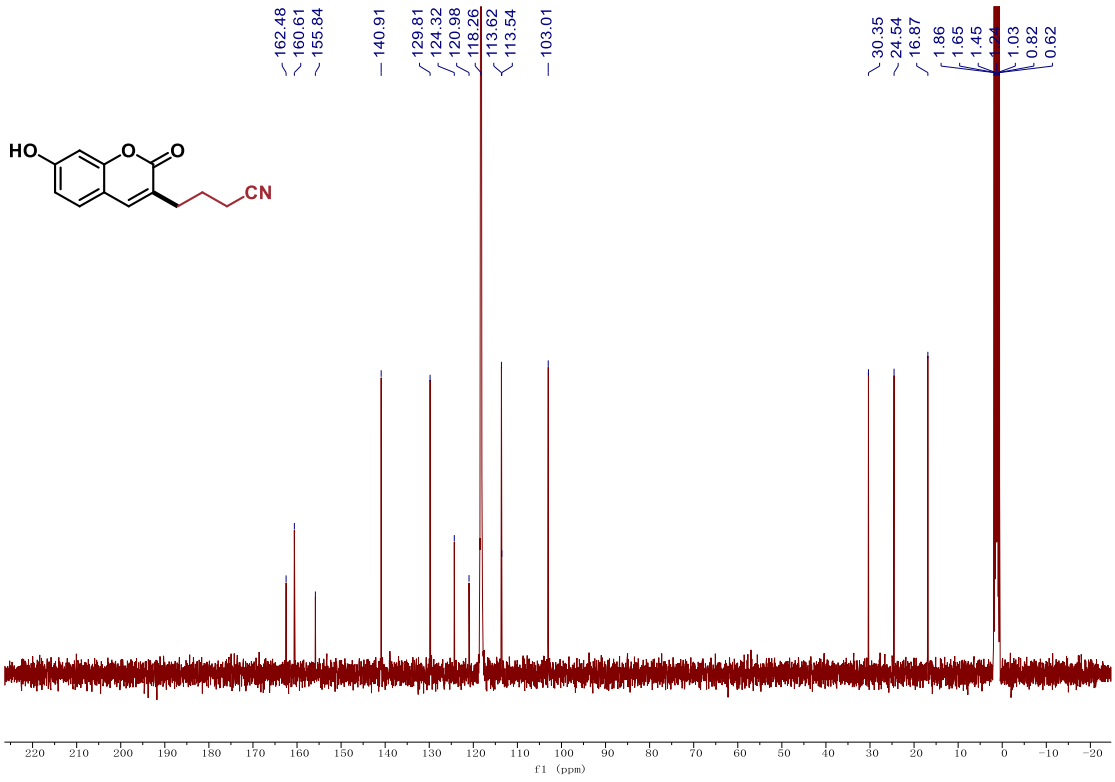
^{13}C NMR of compound **20** (101 MHz in $CDCl_3$)



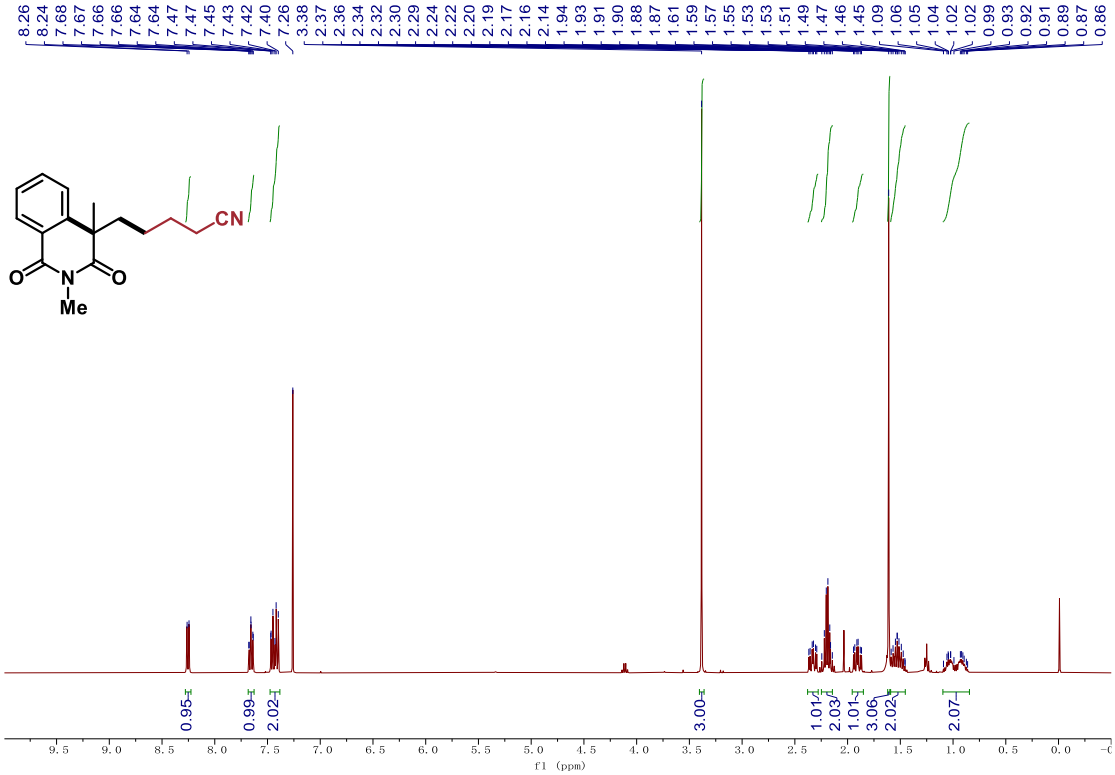
^{1}H NMR of compound **21** (400 MHz in CD_3CN)



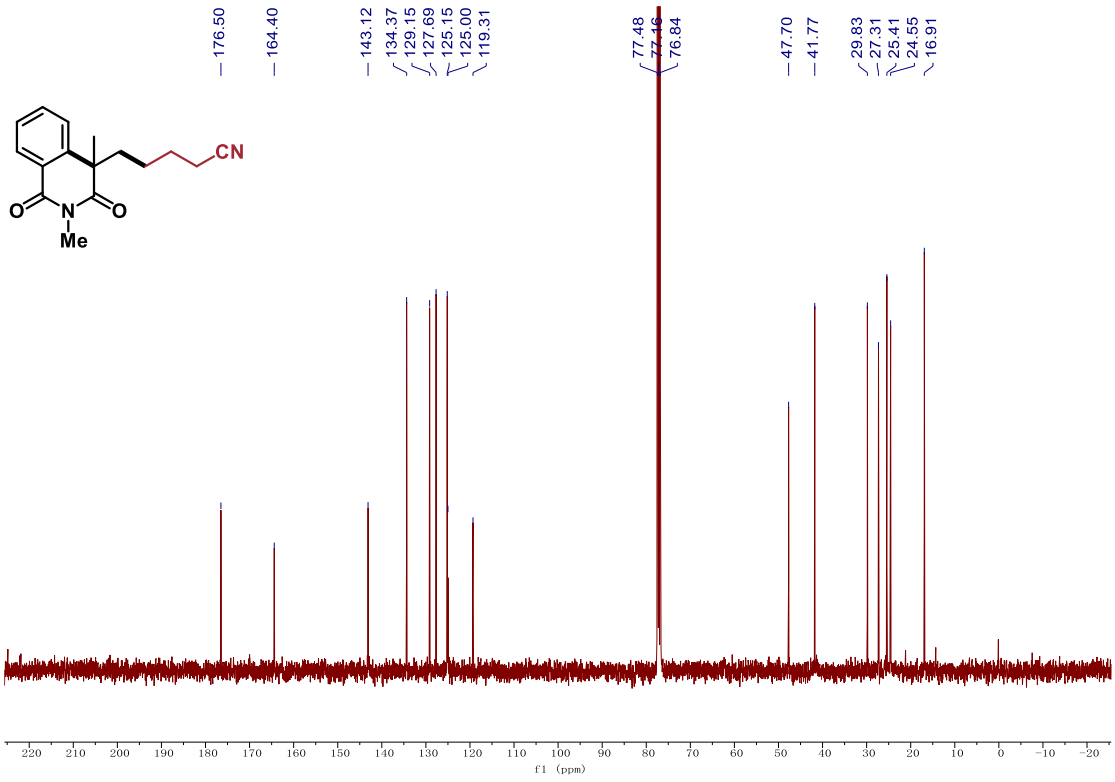
^{13}C NMR of compound **21** (126 MHz in CD_3CN)



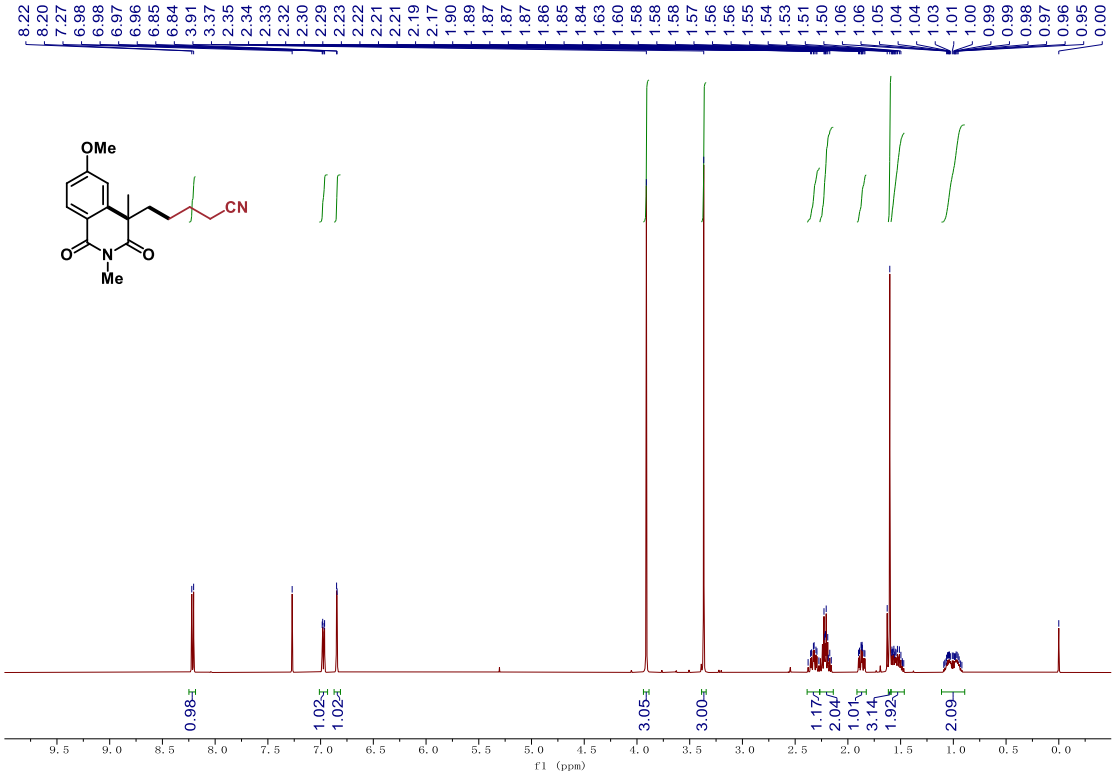
^{1}H NMR of compound **22** (400 MHz in $CDCl_3$)



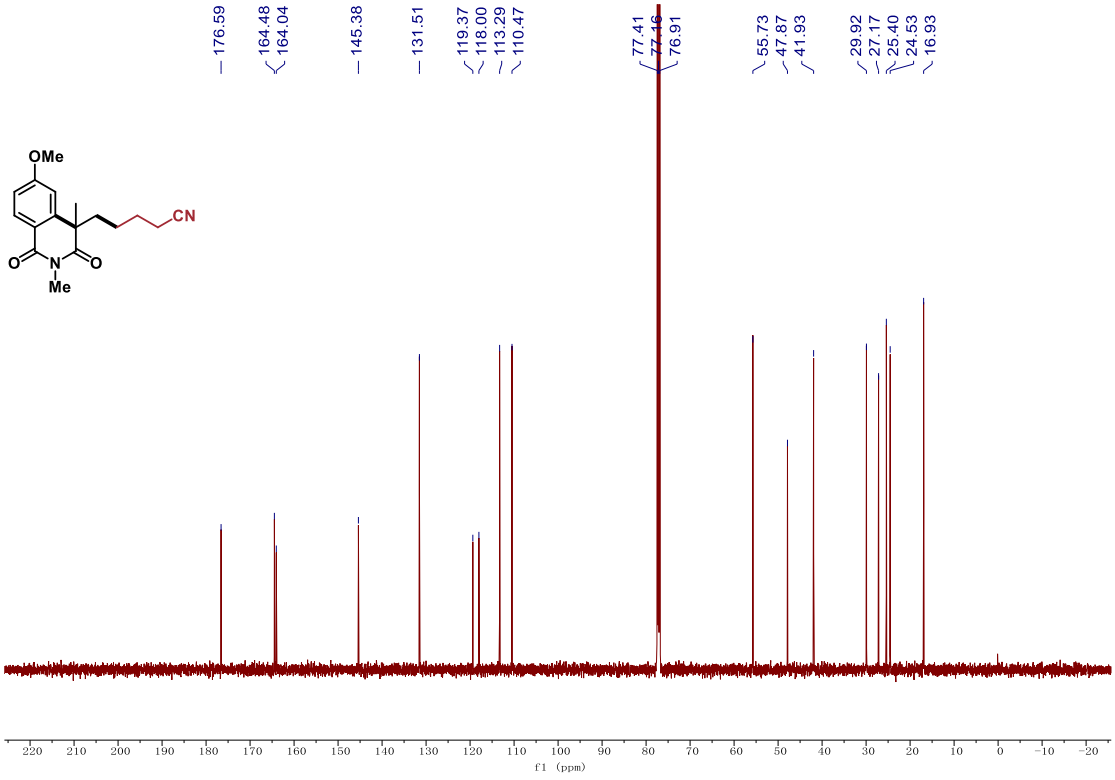
^{13}C NMR of compound **22** (101 MHz in $CDCl_3$)



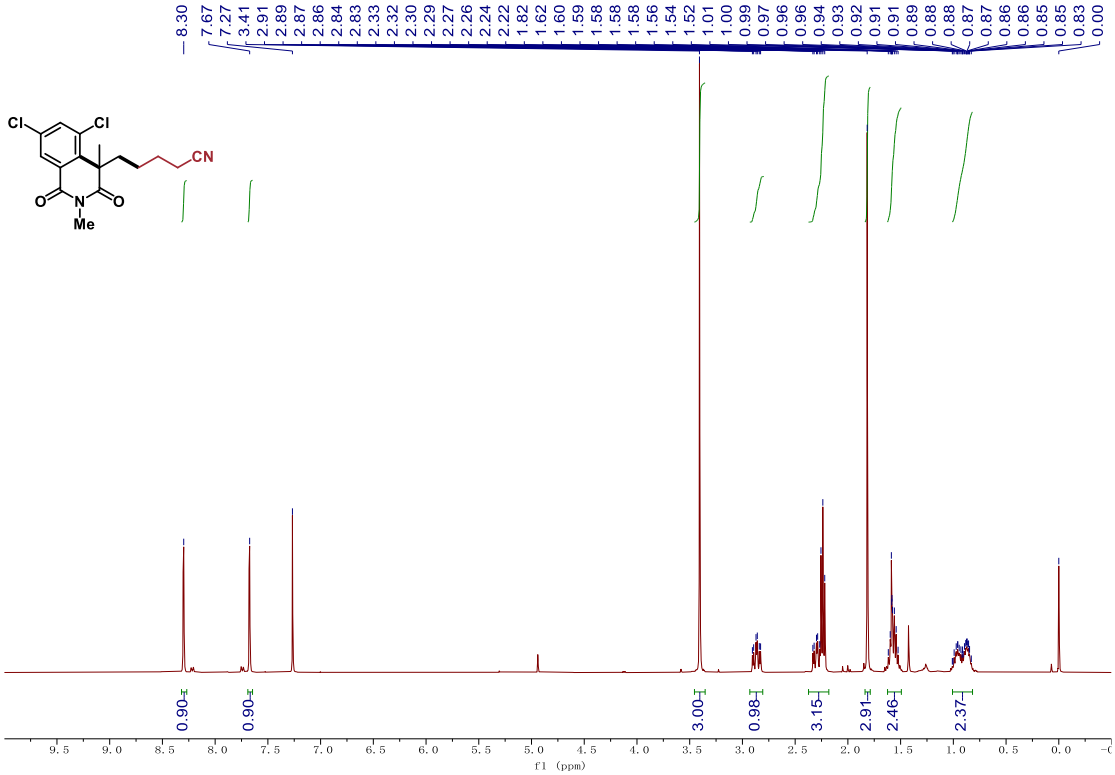
^{1}H NMR of compound **23** (500 MHz in $CDCl_3$)



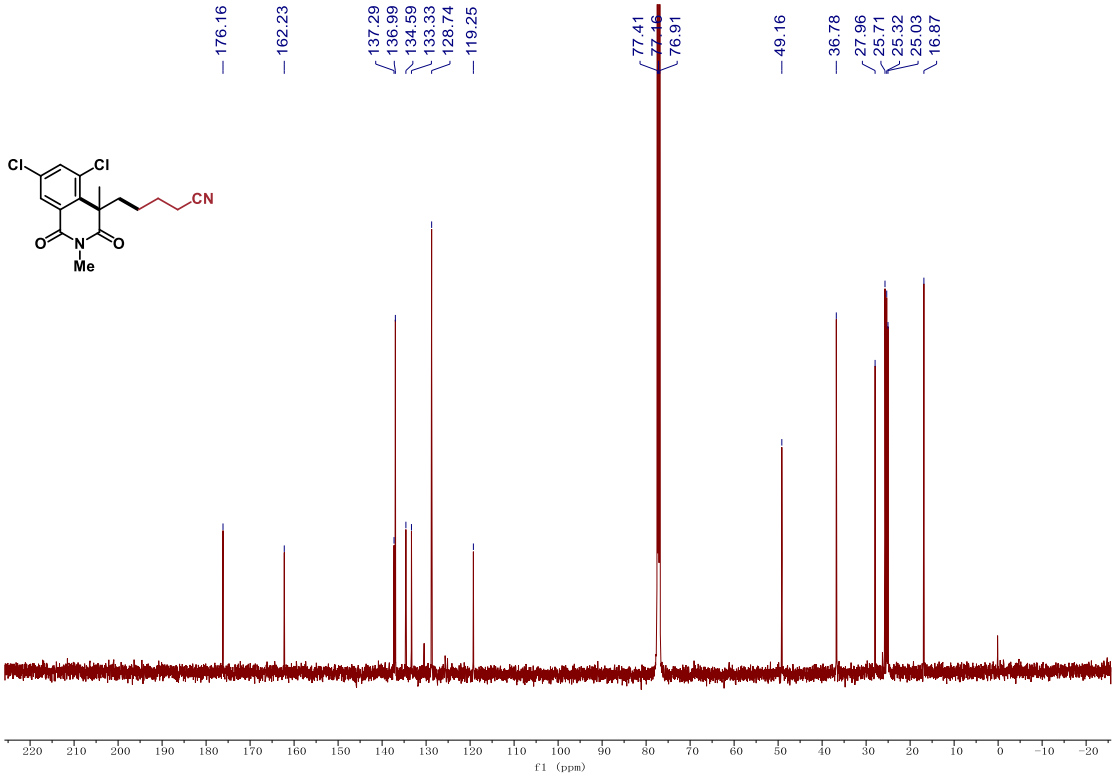
^{13}C NMR of compound **23** (126 MHz in $CDCl_3$)



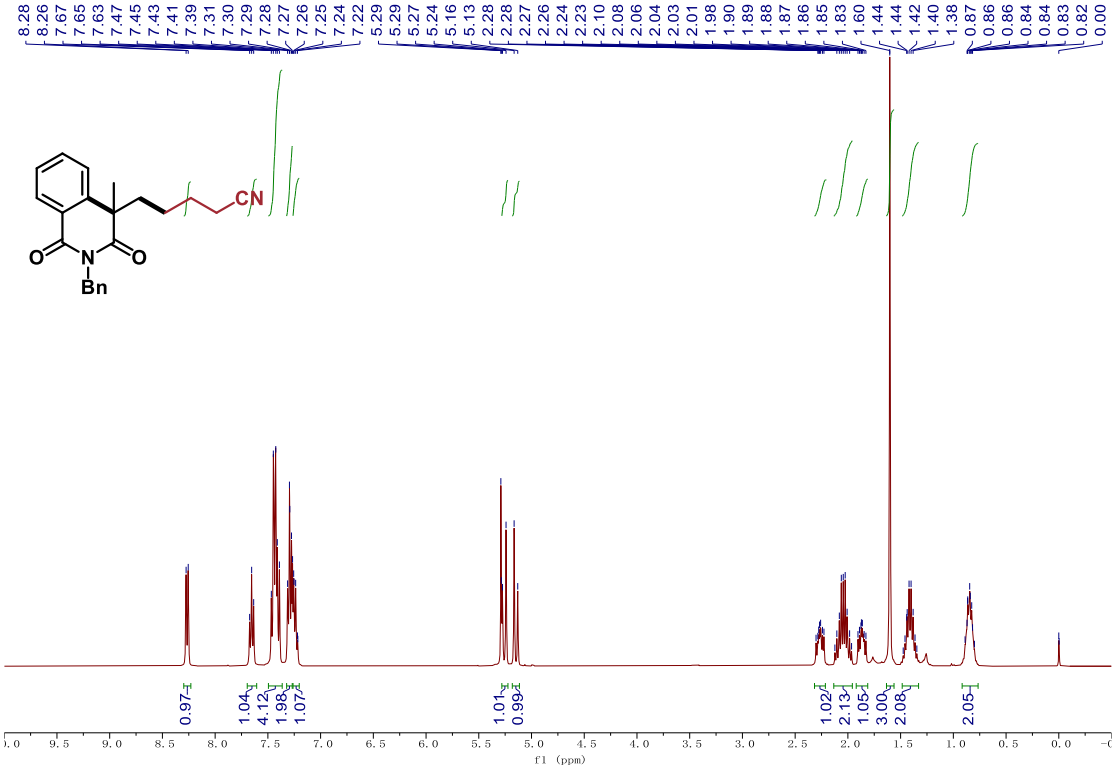
^{1}H NMR of compound **24** (400 MHz in $CDCl_3$)



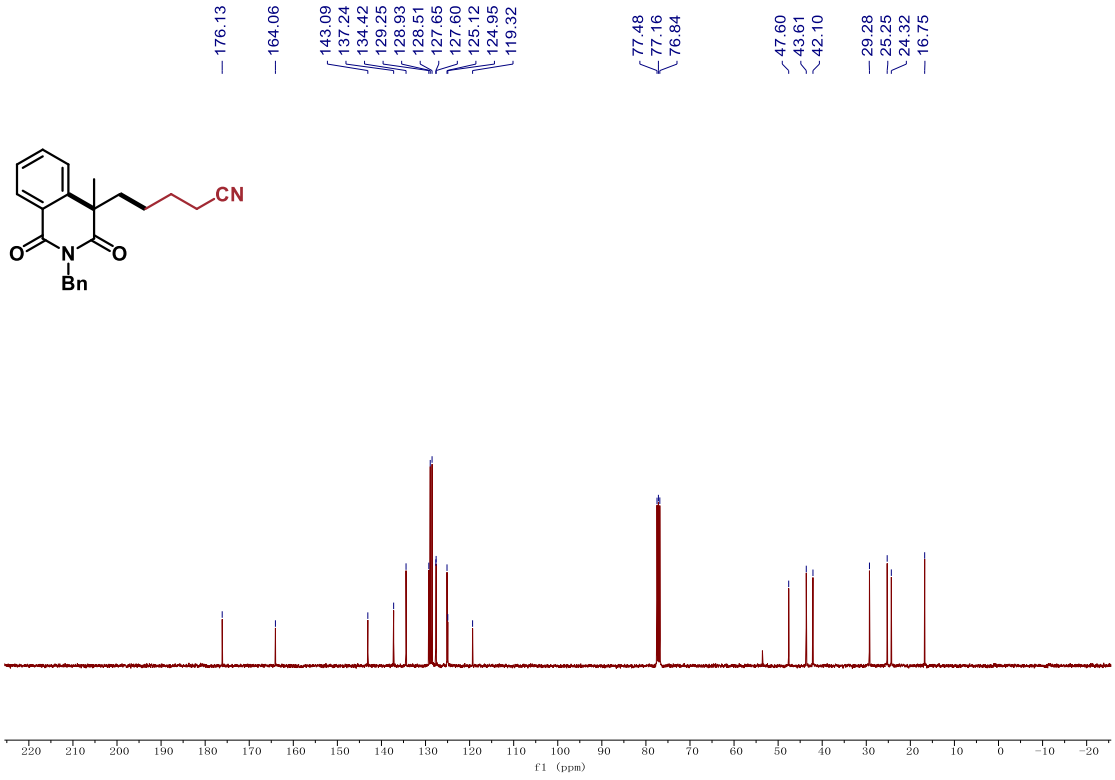
^{13}C NMR of compound **24** (126 MHz in $CDCl_3$)



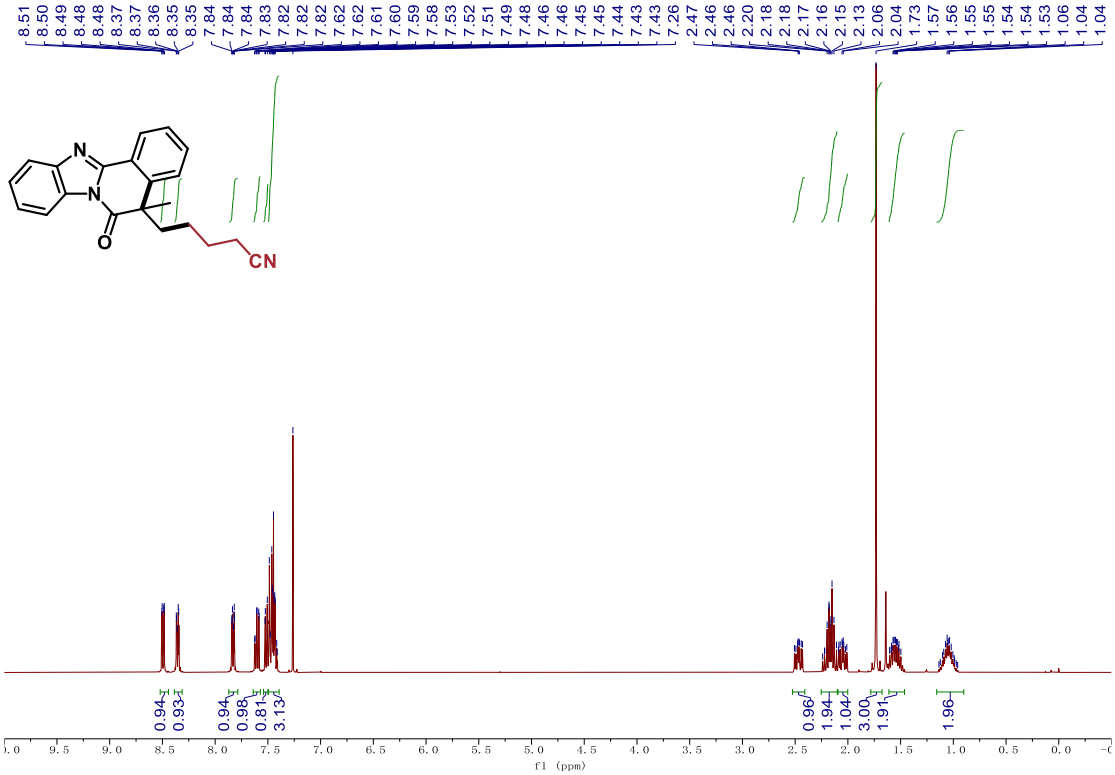
^{1}H NMR of compound **25** (400 MHz in $CDCl_3$)



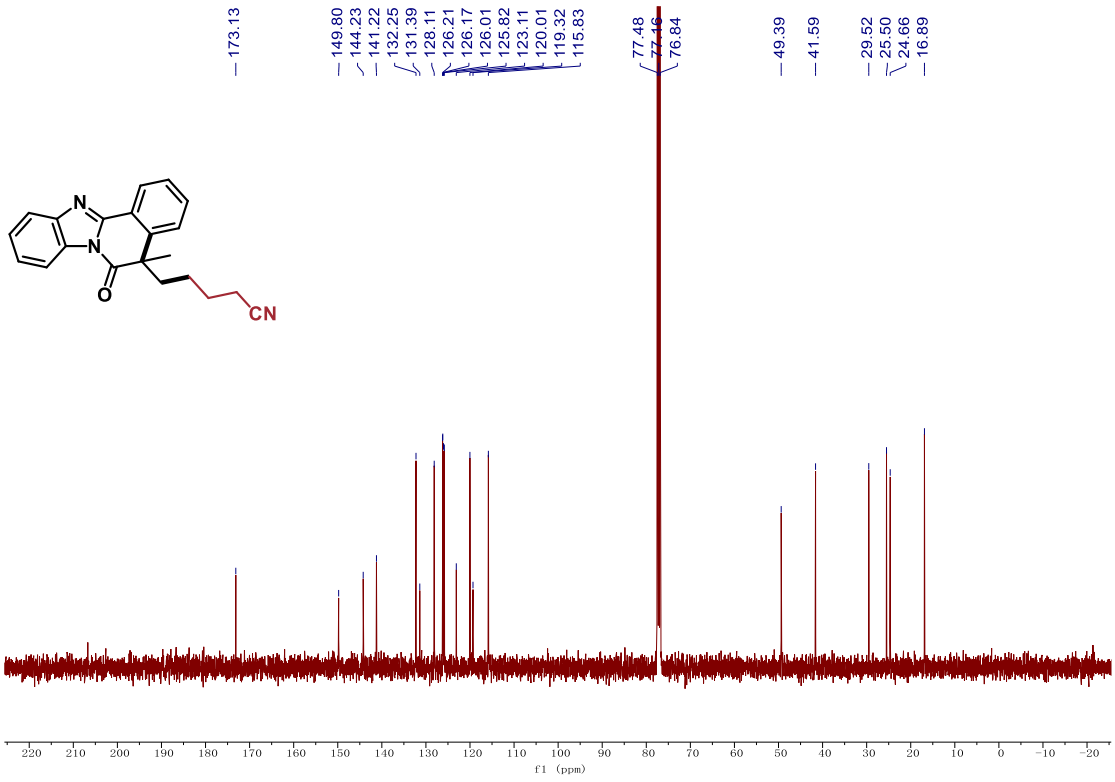
^{13}C NMR of compound **25** (101 MHz in $CDCl_3$)



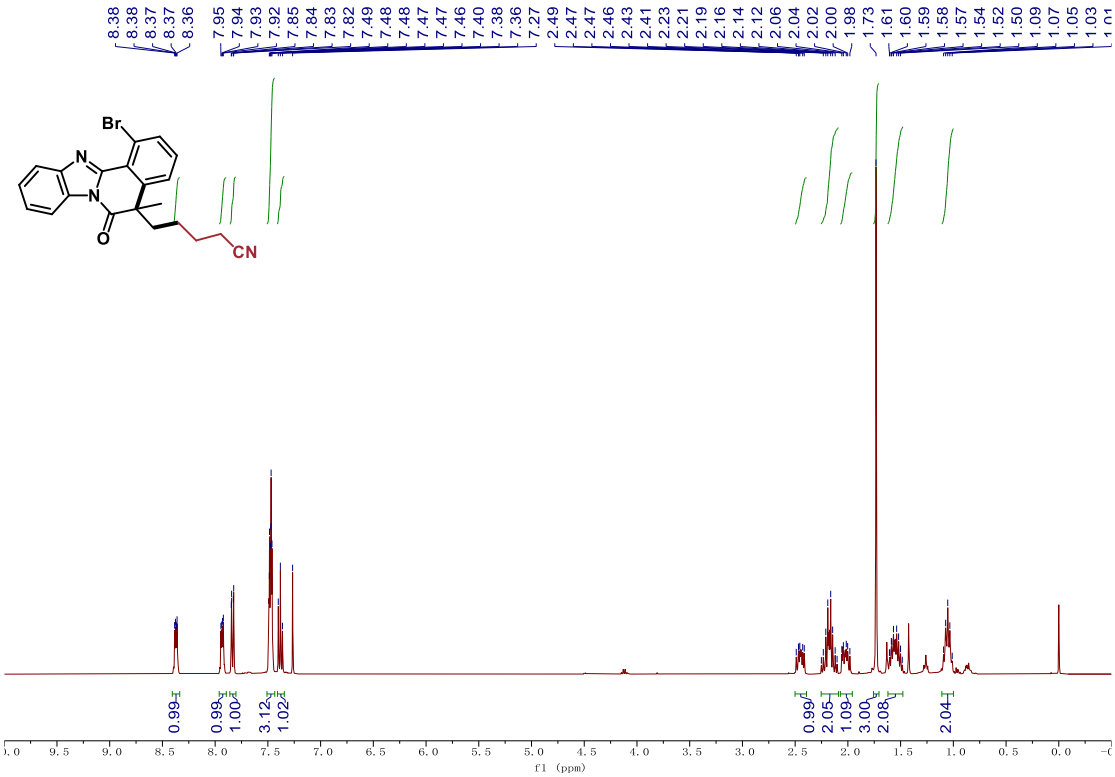
^{1}H NMR of compound **26** (400 MHz in $CDCl_3$)



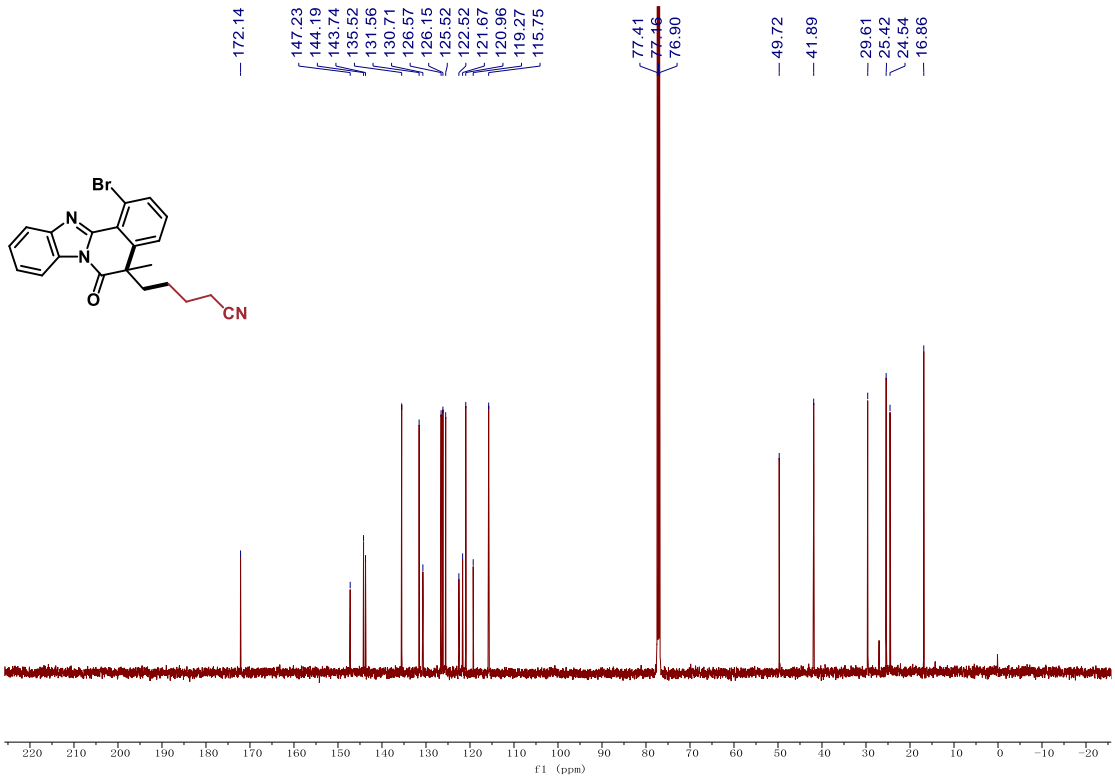
^{13}C NMR of compound **26** (101 MHz in $CDCl_3$)



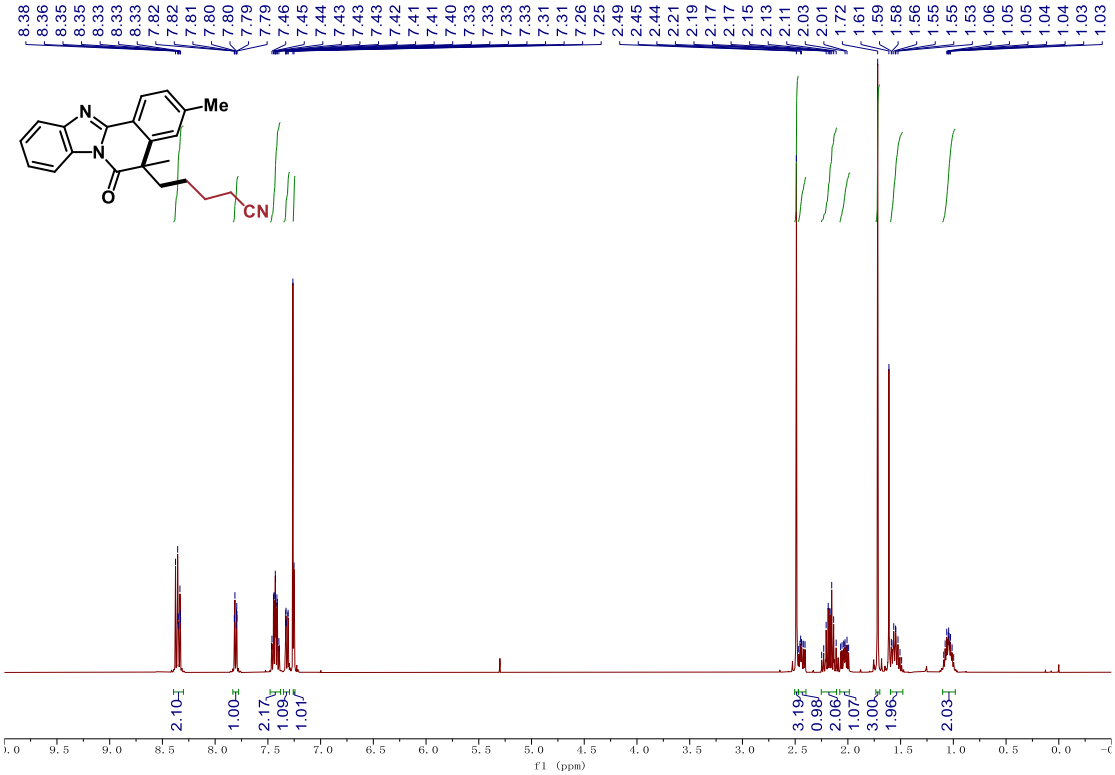
^{1}H NMR of compound **27** (400 MHz in $CDCl_3$)



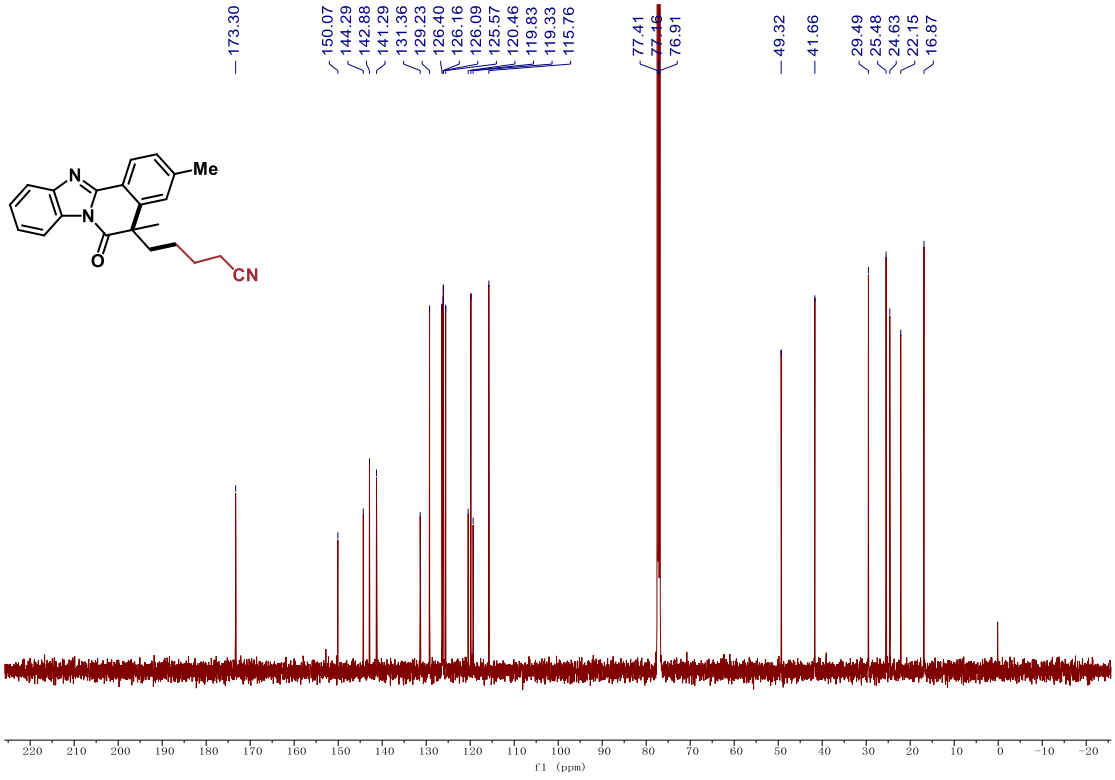
^{13}C NMR of compound **27** (126 MHz in $CDCl_3$)



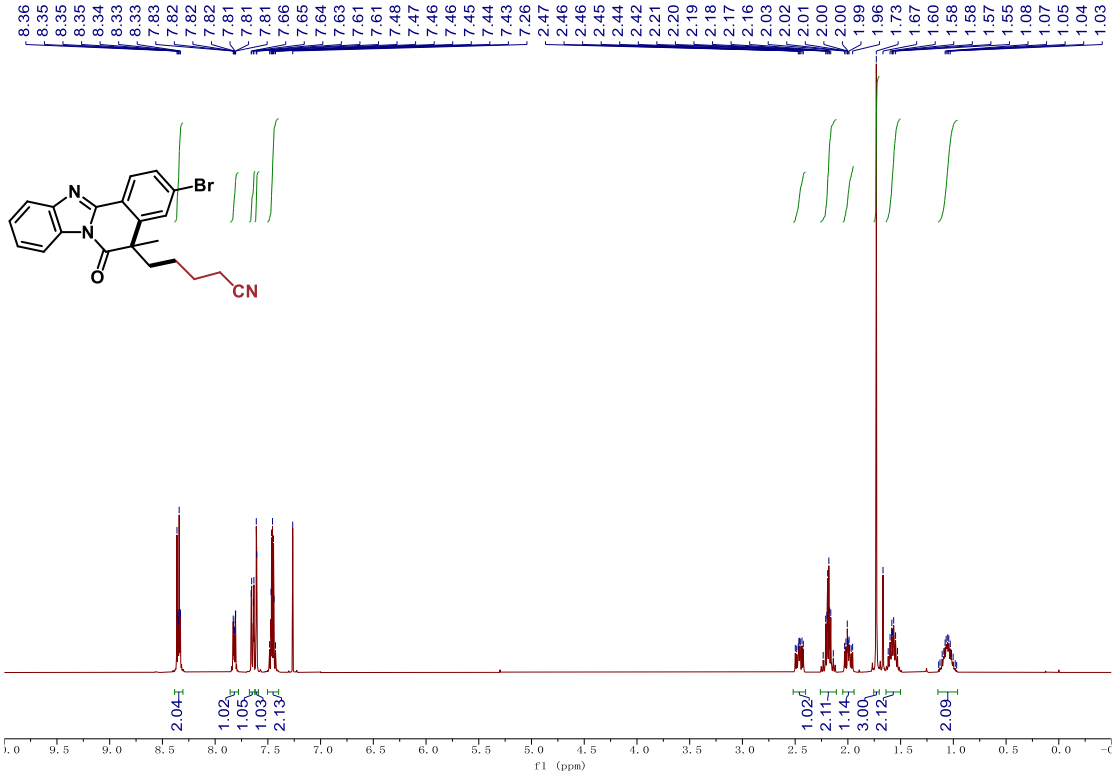
^{1}H NMR of compound **28** (400 MHz in $CDCl_3$)



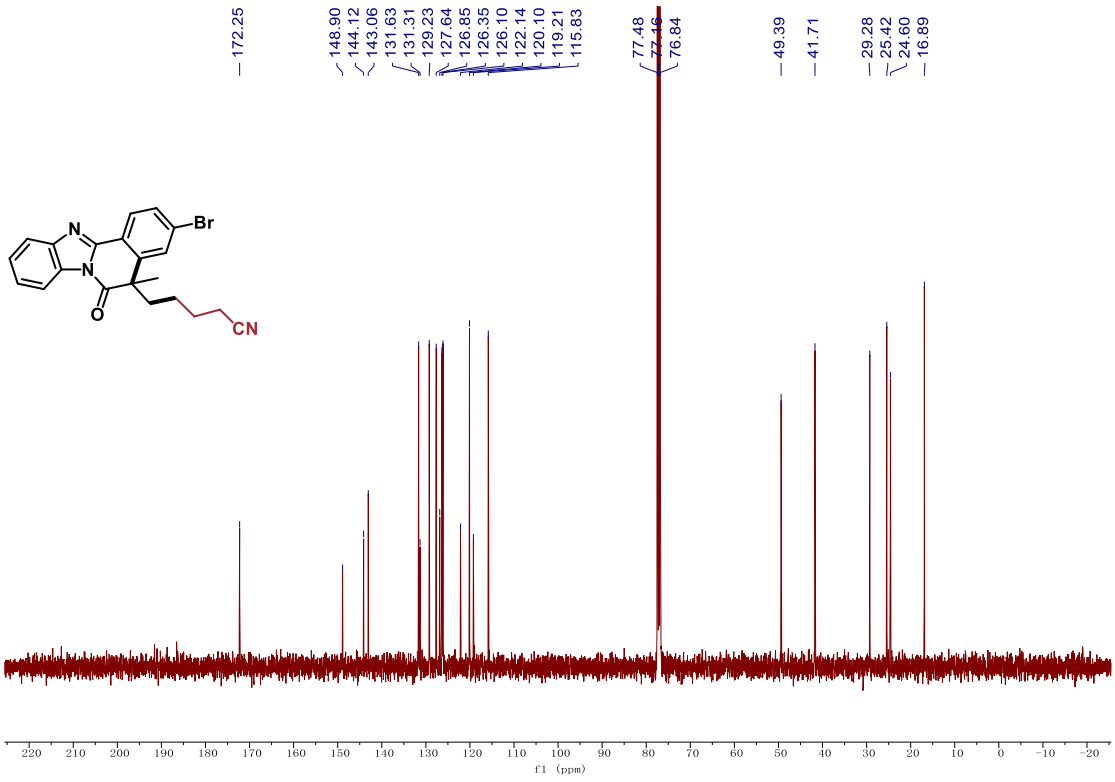
^{13}C NMR of compound **28** (126 MHz in $CDCl_3$)



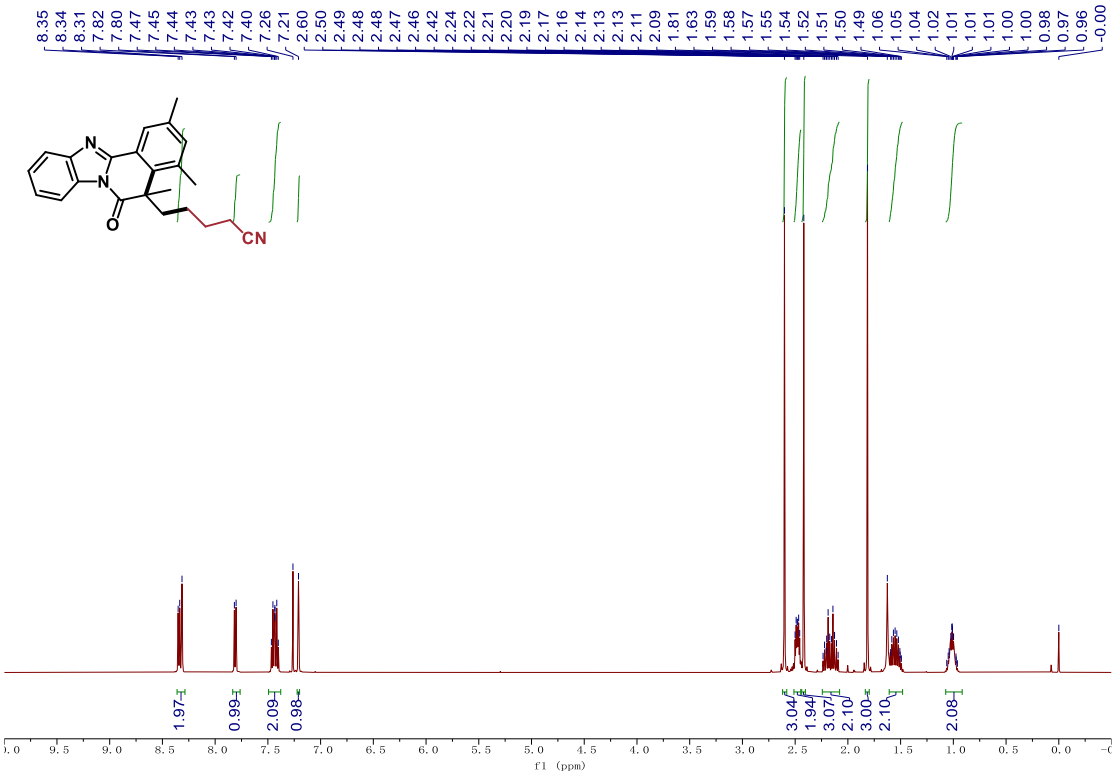
^{1}H NMR of compound **29** (400 MHz in $CDCl_3$)



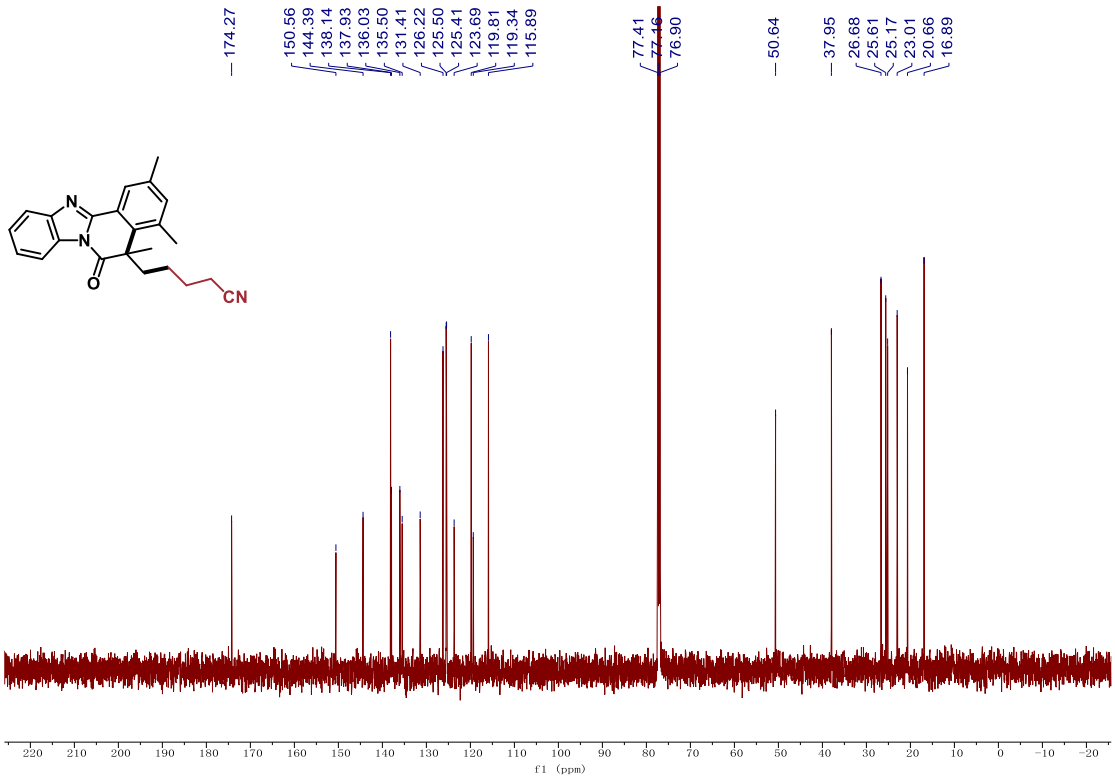
^{13}C NMR of compound **29** (101 MHz in $CDCl_3$)



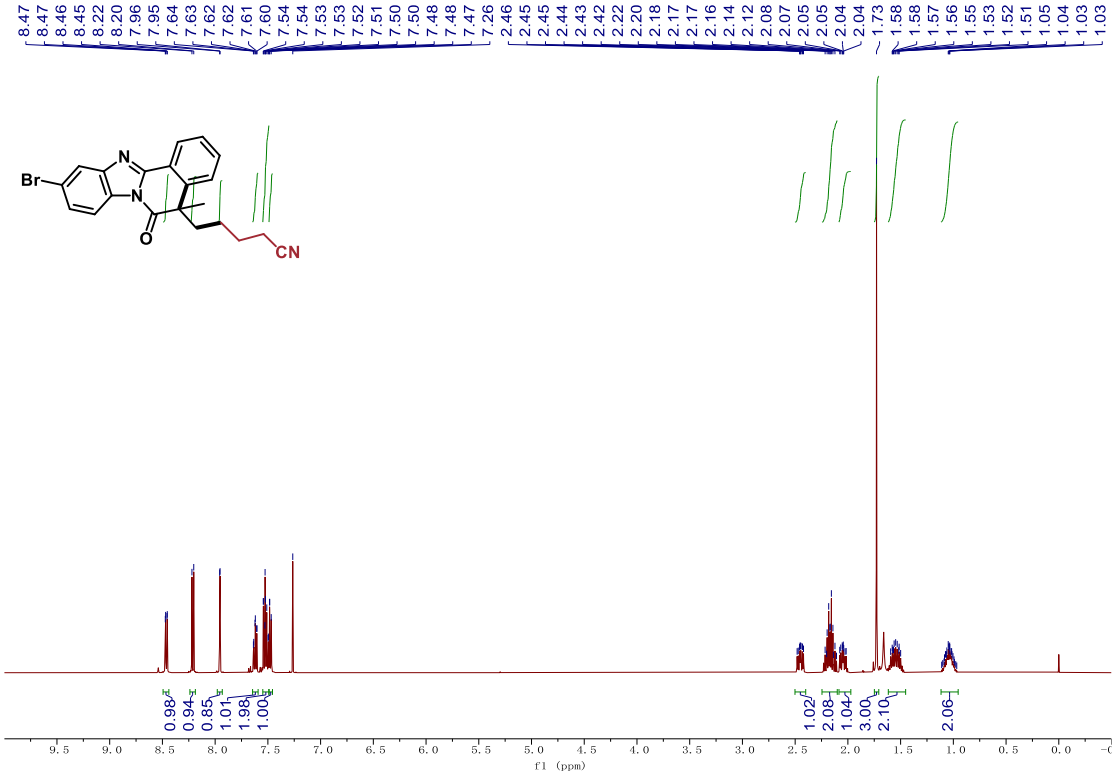
^{1}H NMR of compound **30** (400 MHz in $CDCl_3$)



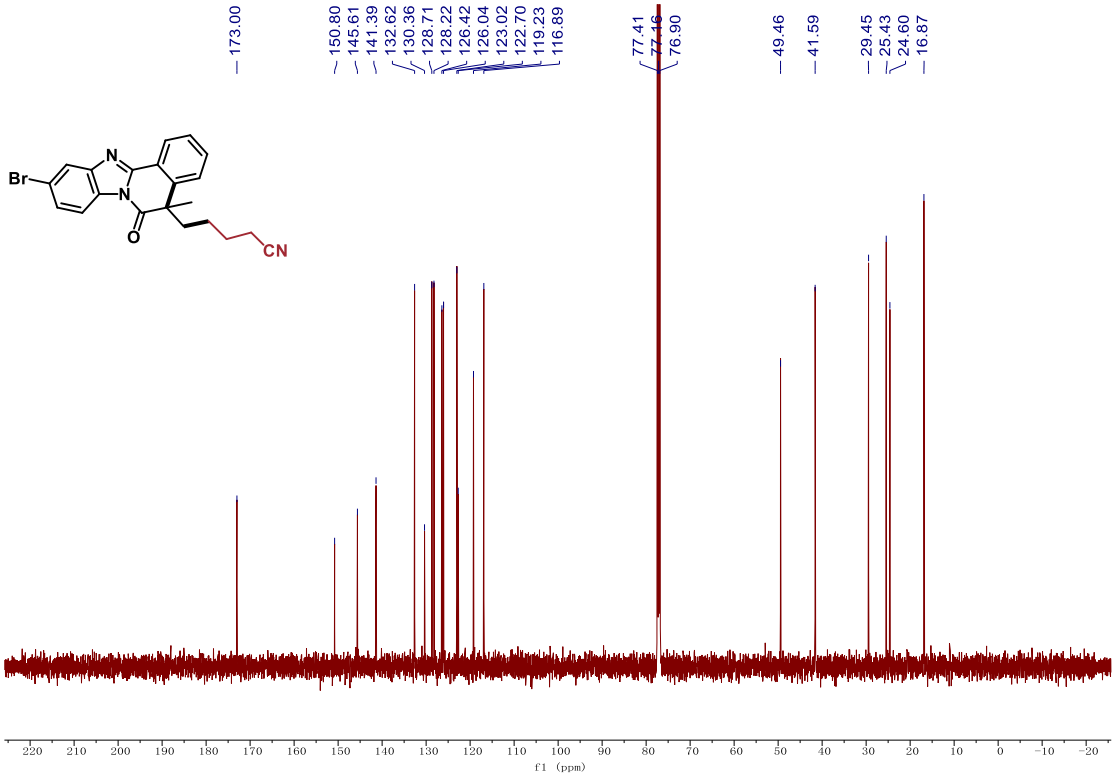
^{13}C NMR of compound **30** (126 MHz in $CDCl_3$)



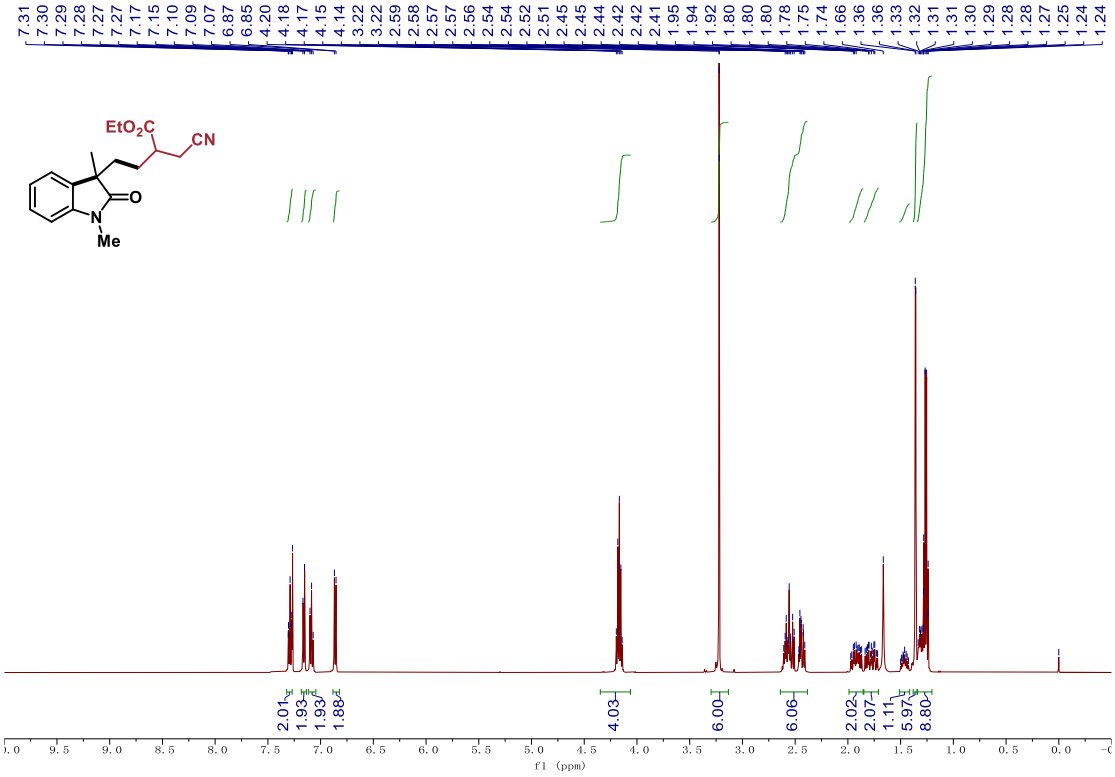
^{1}H NMR of compound **31** (400 MHz in $CDCl_3$)



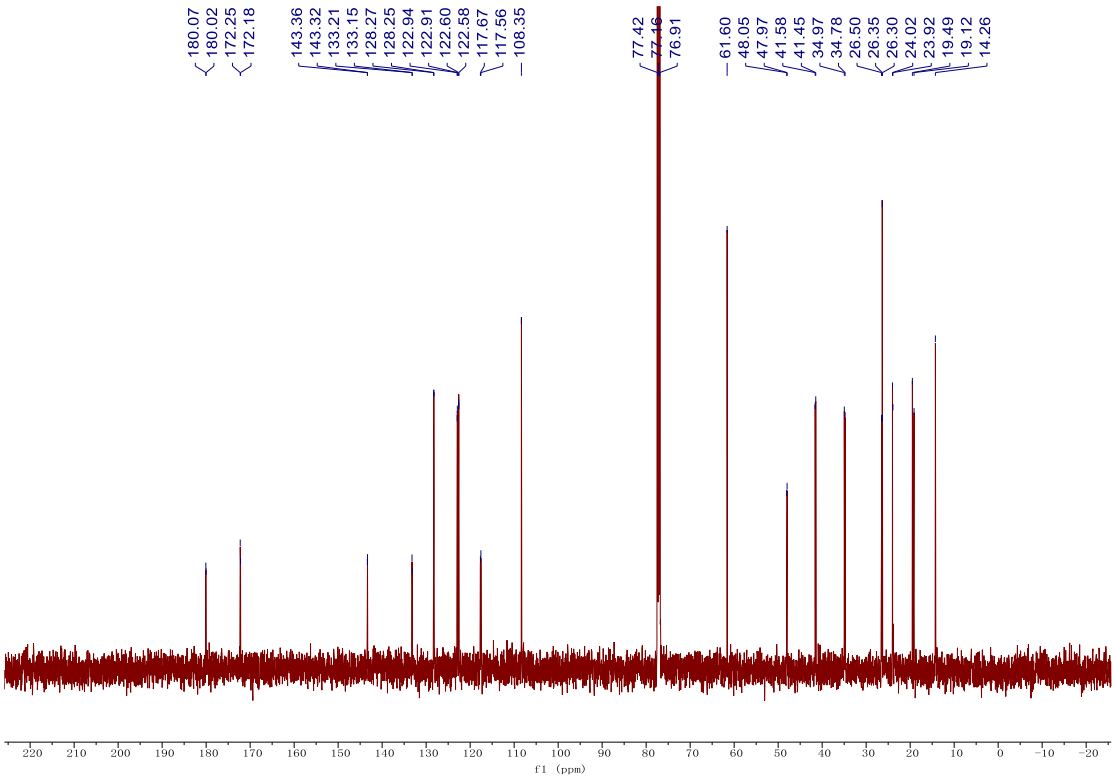
^{13}C NMR of compound **31** (126 MHz in $CDCl_3$)



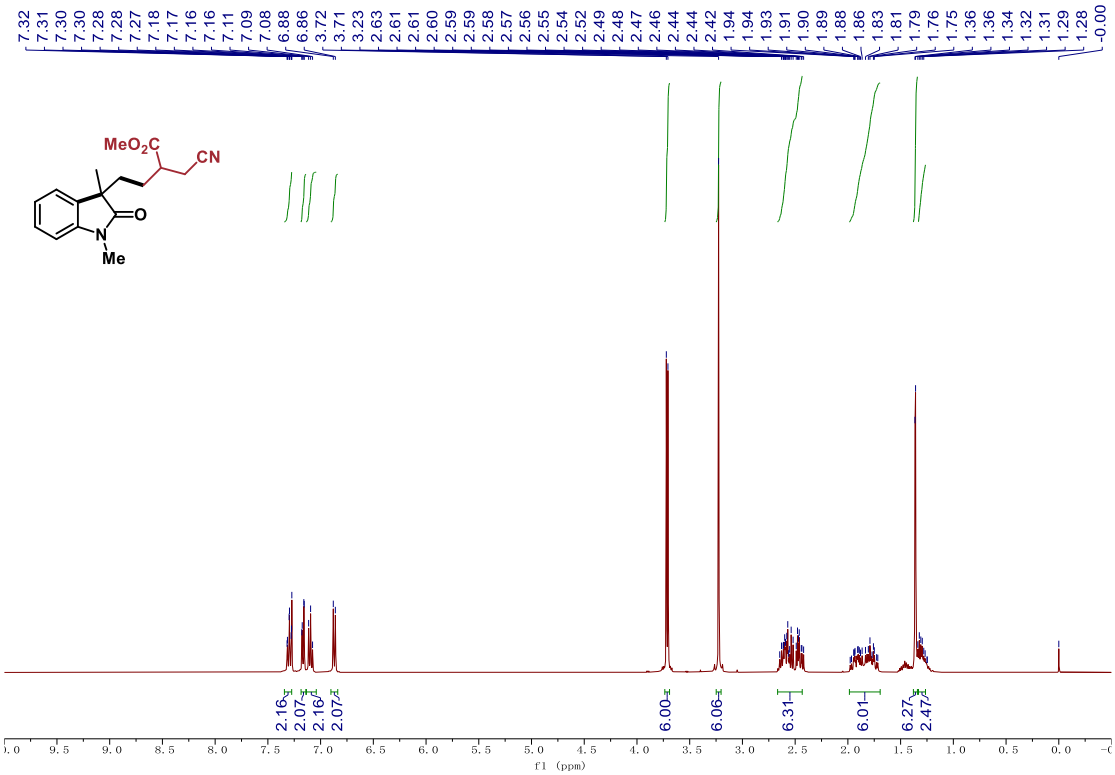
^{1}H NMR of compound **32** (400 MHz in $CDCl_3$)



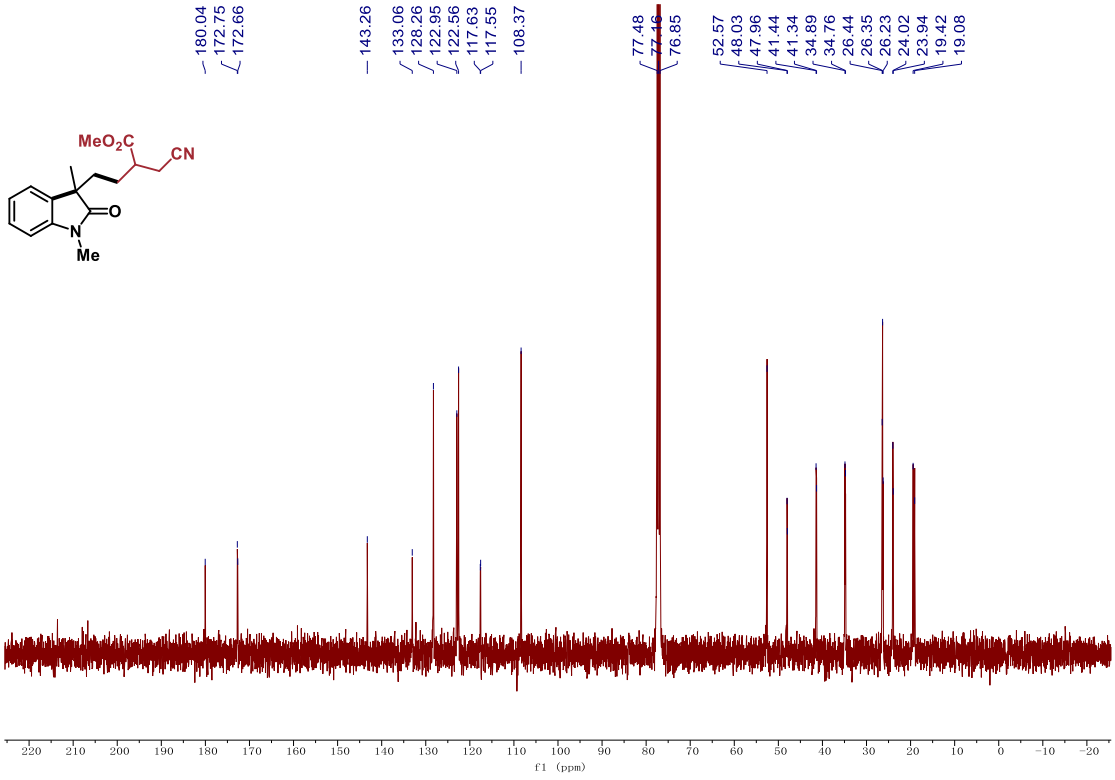
^{13}C NMR of compound **32** (126 MHz in $CDCl_3$)



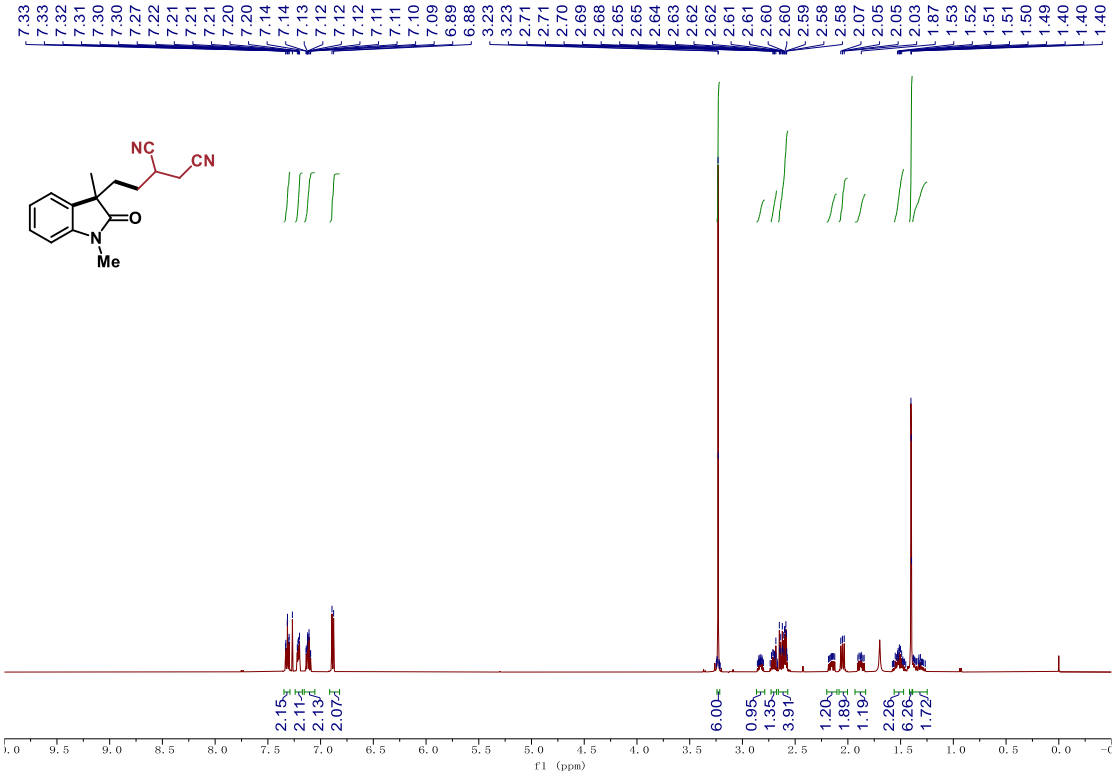
^{1}H NMR of compound **33** (400 MHz in $CDCl_3$)



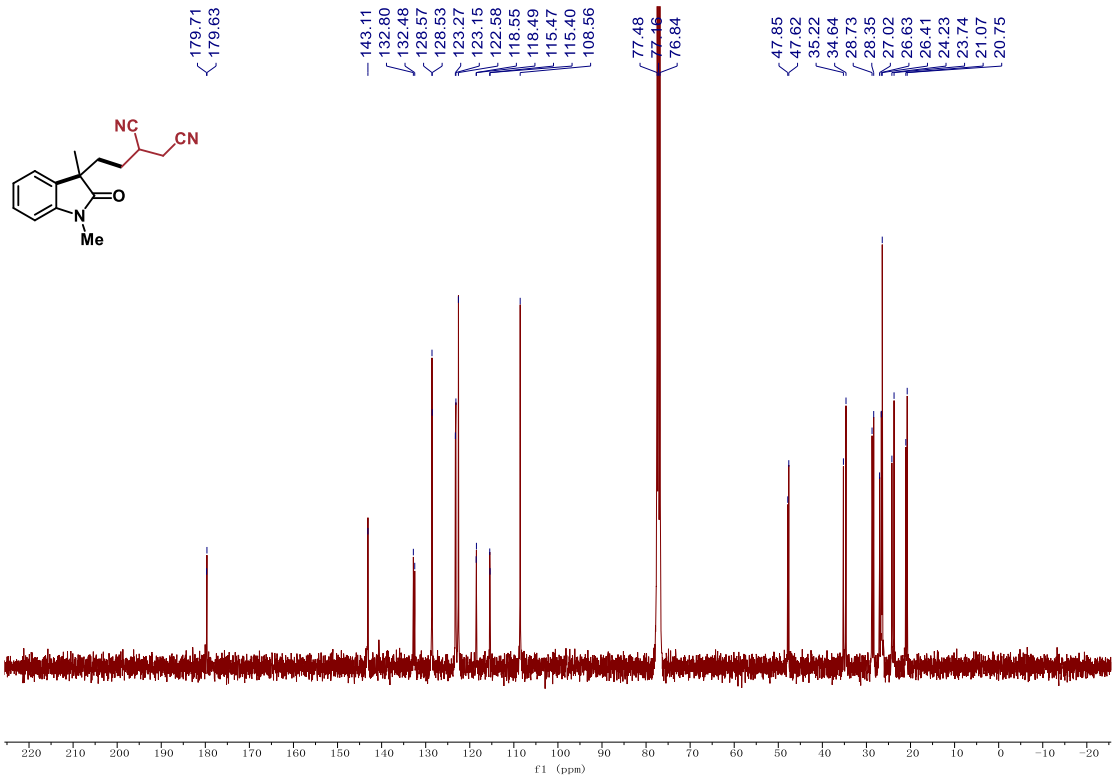
^{13}C NMR of compound **33** (126 MHz in $CDCl_3$)



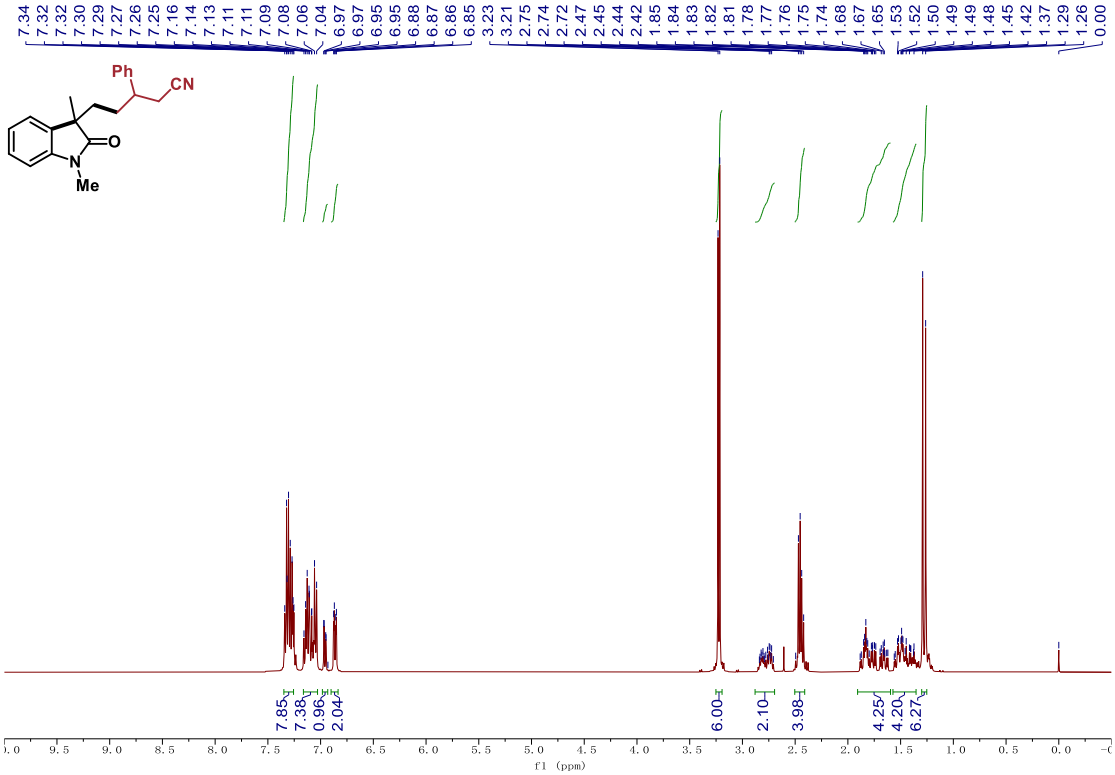
^{1}H NMR of compound **34** (400 MHz in $CDCl_3$)



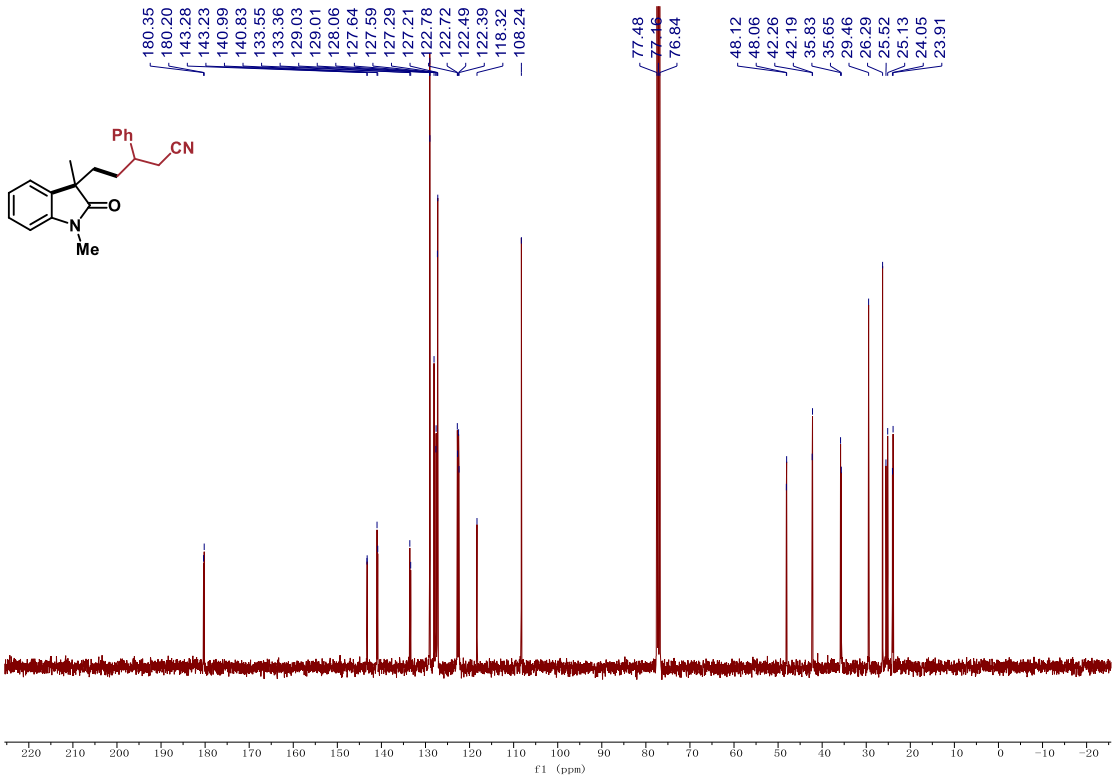
^{13}C NMR of compound **34** (101 MHz in $CDCl_3$)



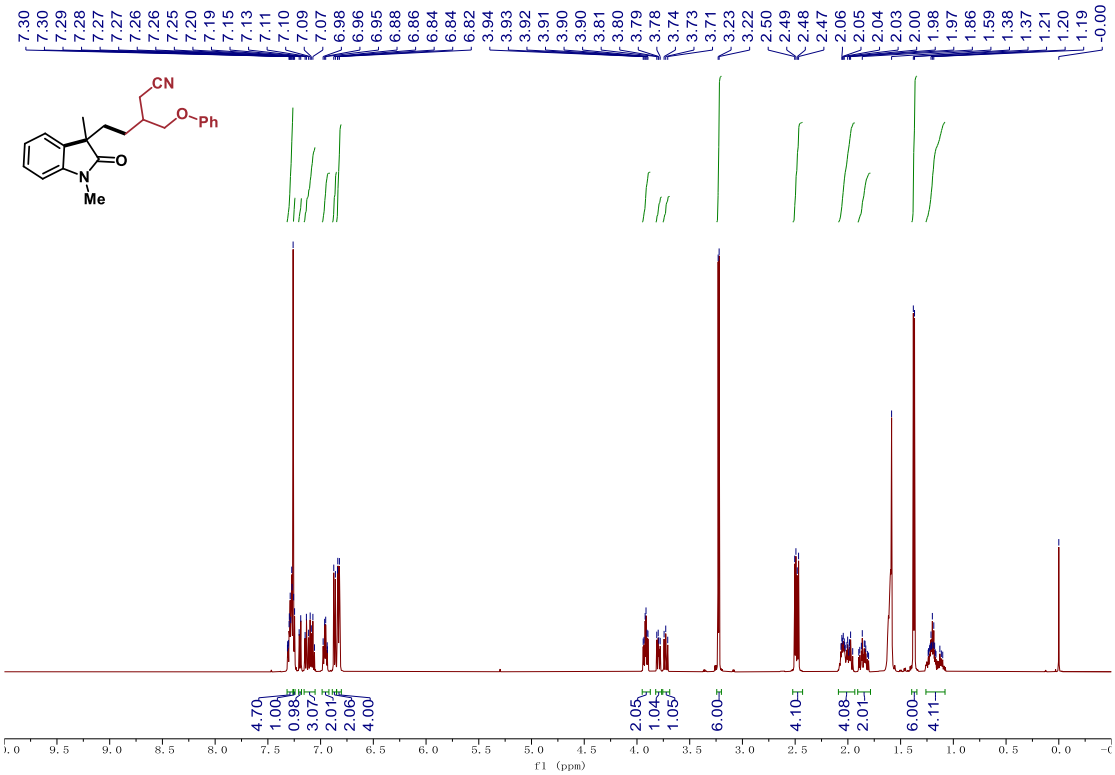
^{1}H NMR of compound **35** (400 MHz in $CDCl_3$)



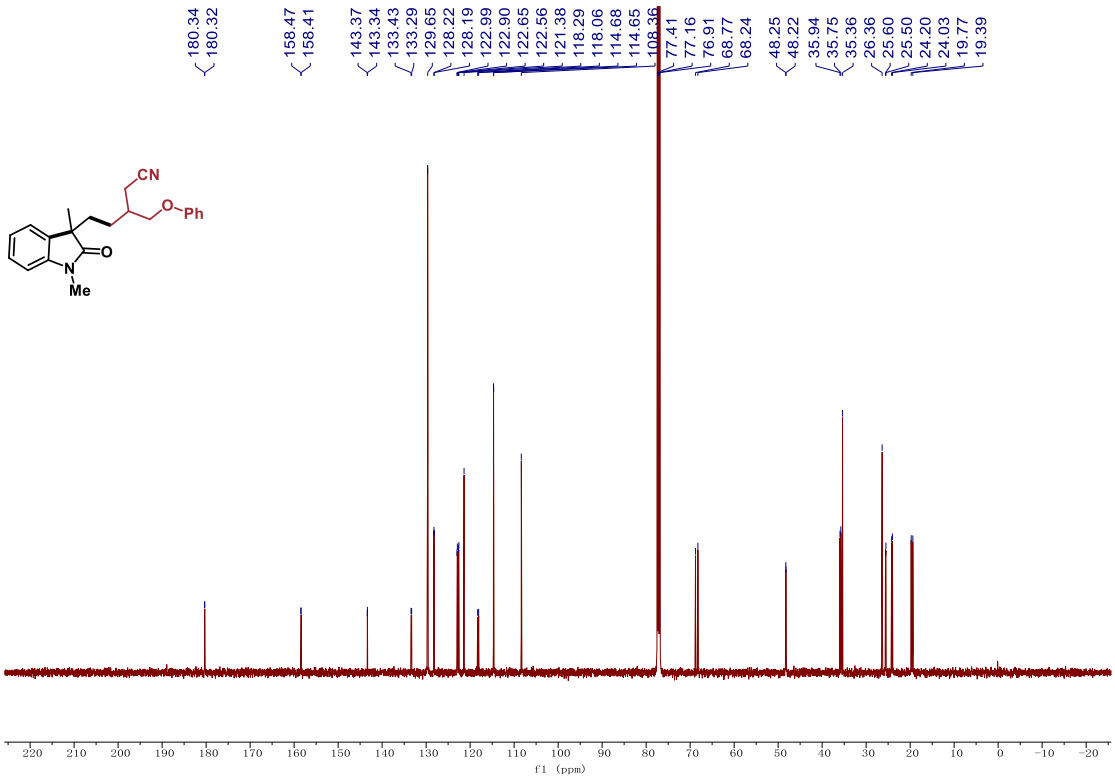
^{13}C NMR of compound **35** (126 MHz in $CDCl_3$)



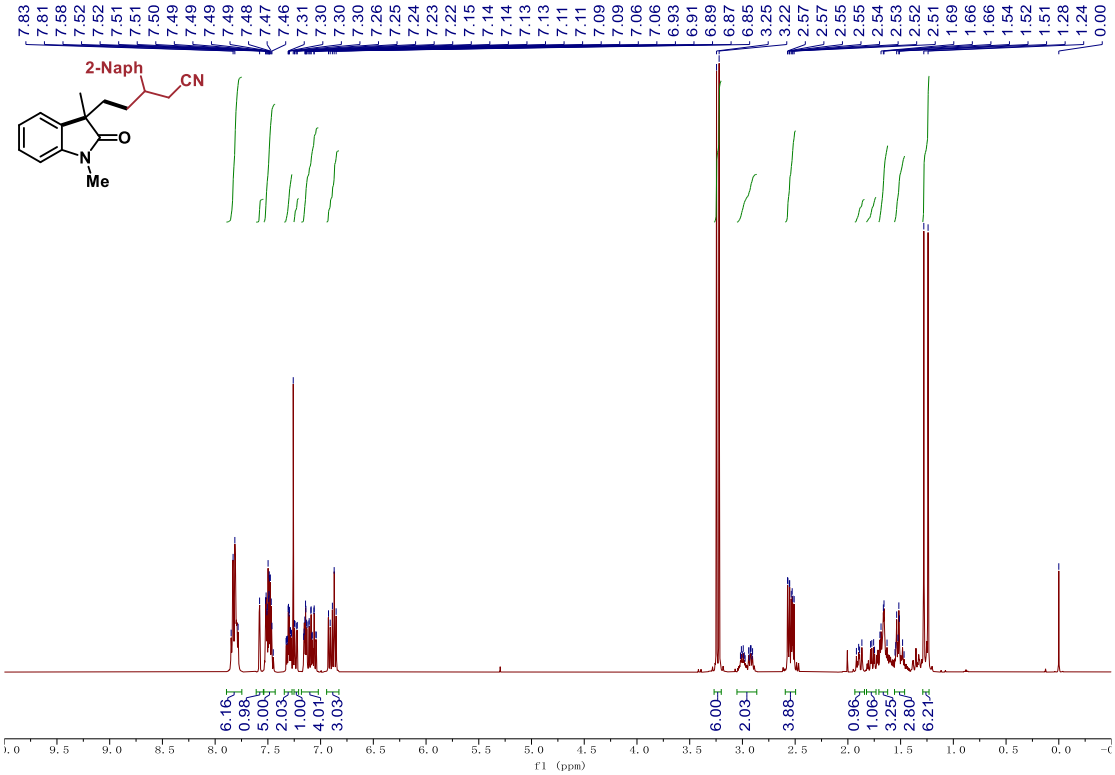
^{1}H NMR of compound **36** (400 MHz in $CDCl_3$)



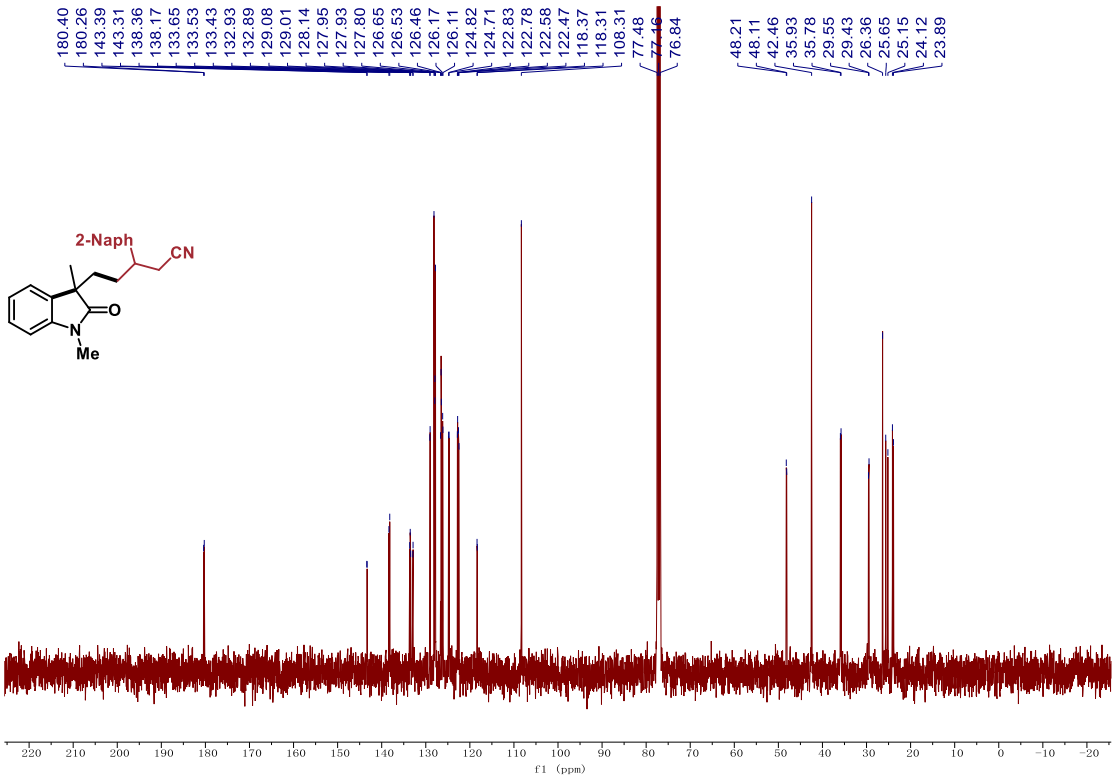
^{13}C NMR of compound **36** (126 MHz in $CDCl_3$)



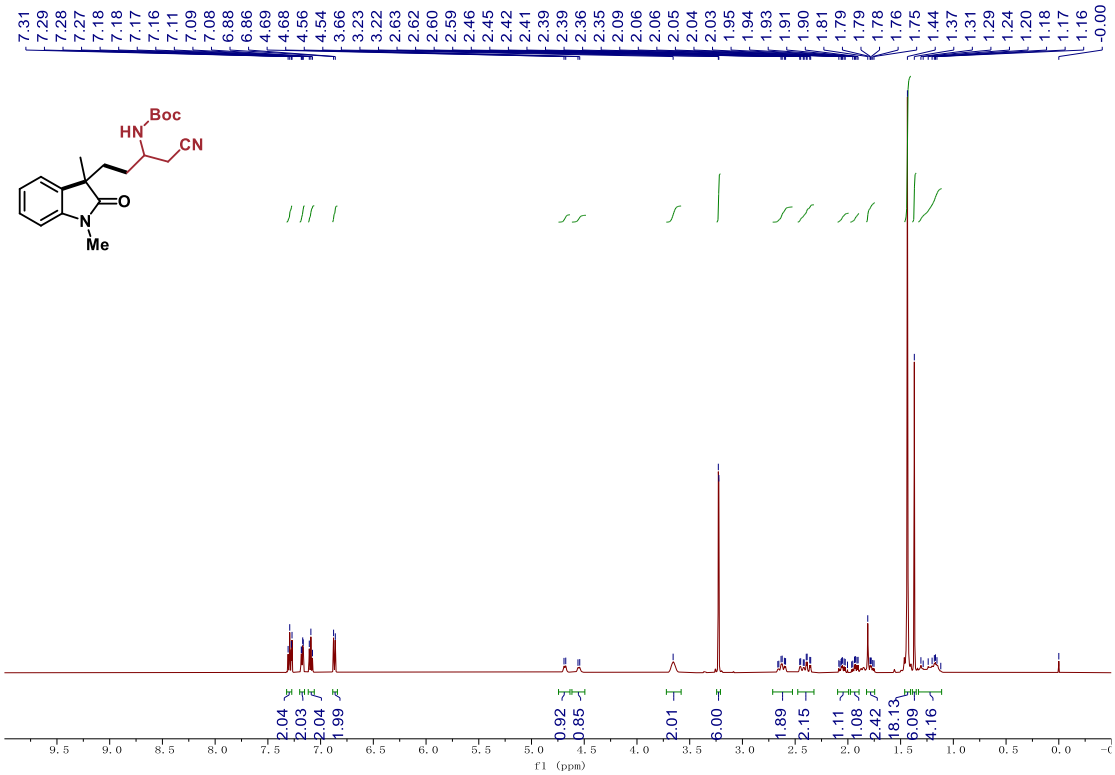
^{1}H NMR of compound **37** (400 MHz in $CDCl_3$)



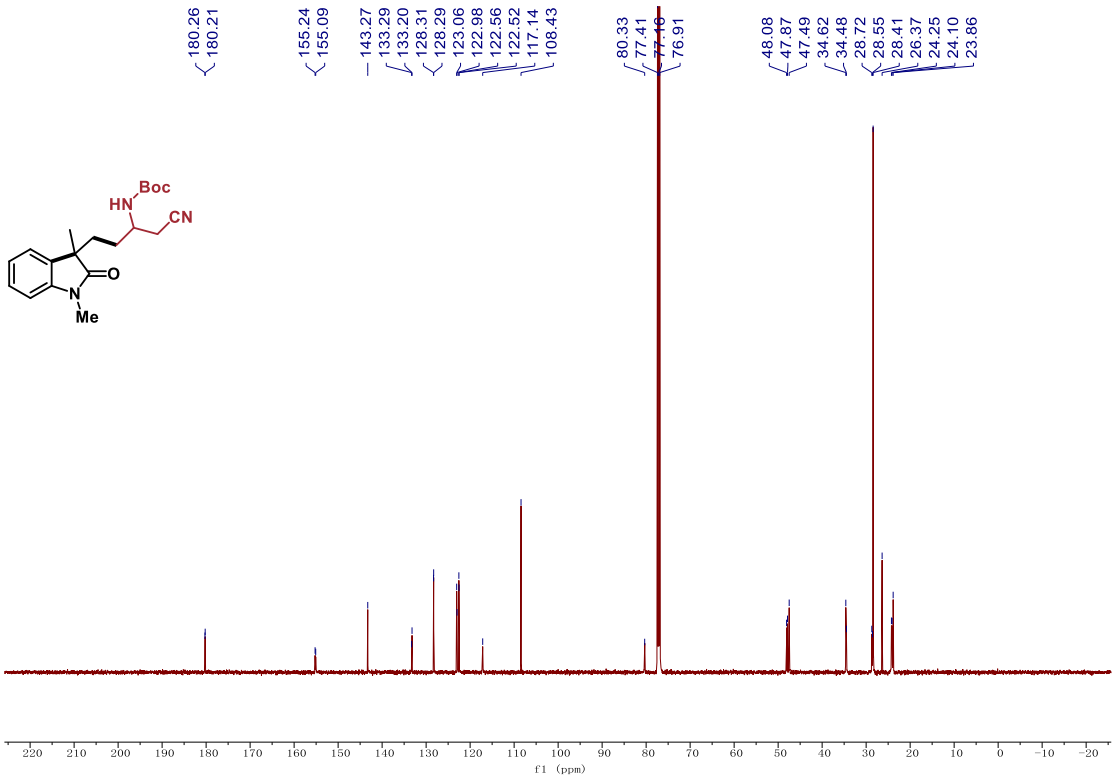
^{13}C NMR of compound **37** (126 MHz in $CDCl_3$)



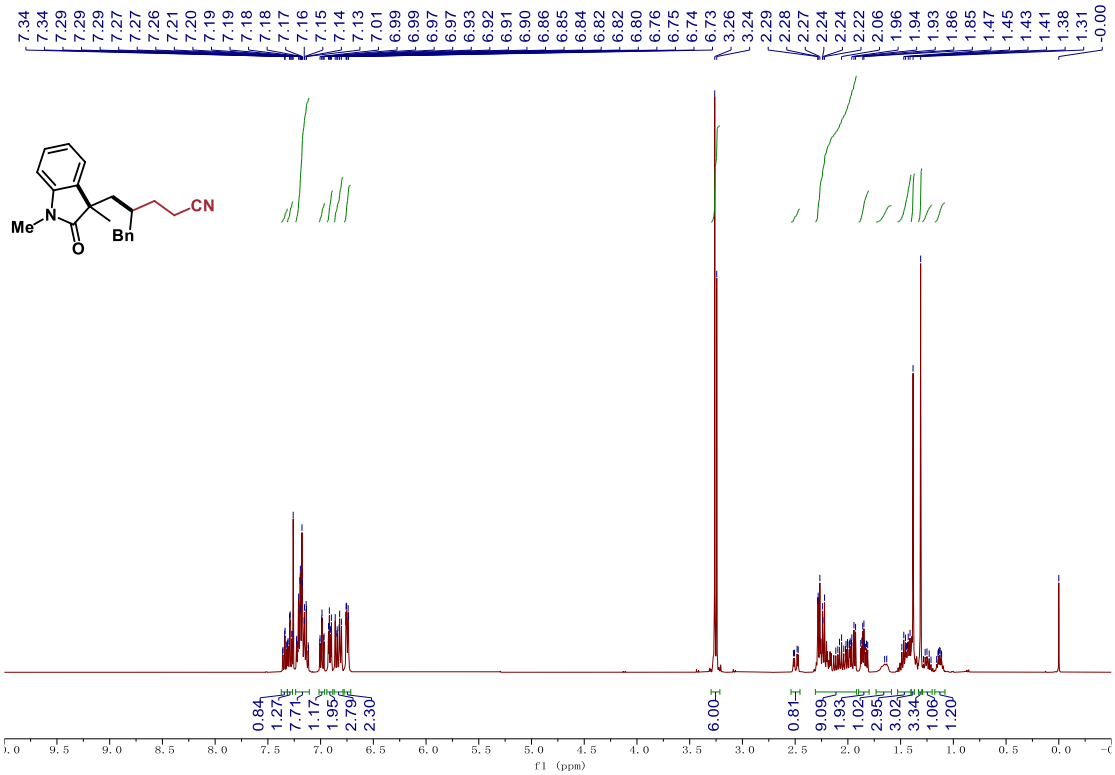
^{1}H NMR of compound **38** (400 MHz in $CDCl_3$)



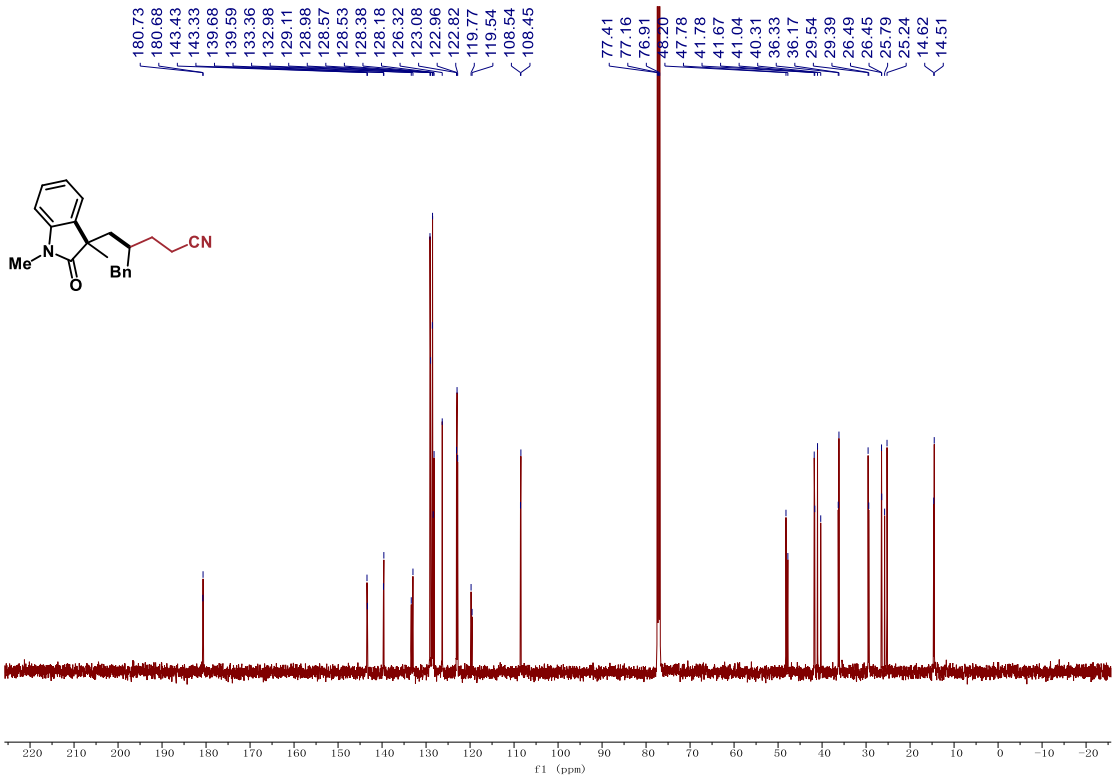
^{13}C NMR of compound **38** (126 MHz in $CDCl_3$)



^{1}H NMR of compound **39** (400 MHz in $CDCl_3$)



^{13}C NMR of compound **39** (126 MHz in $CDCl_3$)



7. Reference.

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