

Supplementary Information

Article

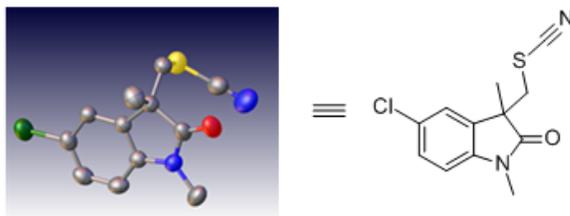
Ag/Pyridine Co-Mediated Oxidative Arylthiocyanation of Activated Alkenes

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1. X-ray crystallography of compound 2g (thermal ellipsoids are shown with 30% probability)



CCDC number: 1849159

Table S1. Crystal data and structure refinement for 2g

Identification code	2g
Empirical formula	C ₁₂ H ₁₁ ClN ₂ O _s
Formula weight	266.74
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P1
a/Å, b/Å, c/Å	7.1852(2), 24.5633(6), 7.5740(2)
α/°, β/°, γ/°	90, 108.676(3), 90
Volume/Å ³	1266.36(7)
Z	4
ρ _{calc} /mm ³	1.399
m/mm ⁻¹	4.089
F(000)	552
Crystal size/mm ³	0.26 × 0.21 × 0.18
Theta range for data collection	3.599 to 66.663°

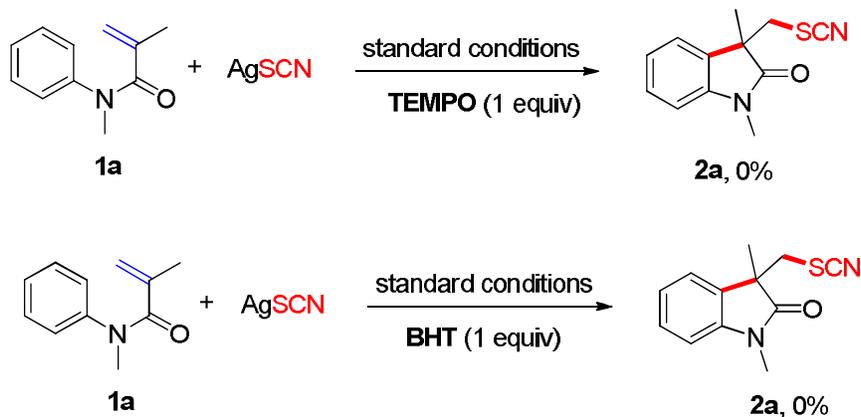
Index ranges	$-7 \leq h \leq 8, -29 \leq k \leq 29, -8 \leq l \leq 8$
Reflections collected	13972
Independent reflections	2231[R(int) = 0.0483]
Data/restraints/parameters	2231/0/157
Goodness-of-fit on F^2	1.055
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0406, wR_2 = 0.1017$
Final R indexes [all data]	$R_1 = 0.0500, wR_2 = 0.1098$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.422/-0.284

Crystal Data. $C_{12}H_{11}ClN_2Os$, $M = 266.74$, Triclinic, $a = 7.1852(2) \text{ \AA}$, $b = 24.5633(6) \text{ \AA}$, $c = 7.5740(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 108.676(3)$, $\gamma = 90^\circ$, $U = 1266.36(7) \text{ \AA}^3$, $T = 293(2)$, space group P1 (no. 1), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 4.089$, 13972 reflections measured, 2231 unique ($R_{\text{int}} = 0.0483$) which were used in all calculations. The final $wR(F_2)$ was 0.1098 (all data).

2. Mechanistic Studies

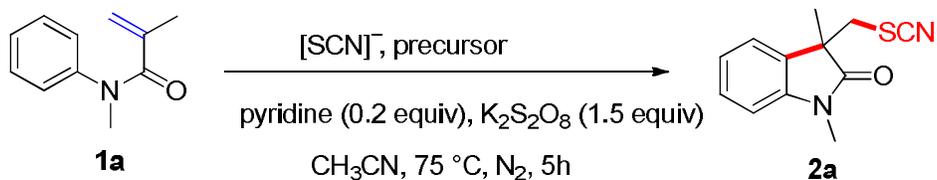
In this section, clarify several mechanistic details are clarified: 1) this transformation proceeded through a unique NCS• radical addition path; 2) pyridine functioned not only as a base but also as a ligand to accelerate the oxidation of Ag(I) to Ag(II); 3) Ag(II) is the likely oxidant responsible for the formation of NCS• radical.

2.1. Radical Verification Experiments



Compound **1a** (0.2 mmol), $K_2S_2O_8$ (81.0 mg, 0.3 mmol), AgSCN (48 mg, 0.3 mmol), TEMPO (31.3 mg, 0.2 mmol) or BHT (44 mg, 0.2 mmol) and were combined in an oven-dried sealed tube. The vessel was evacuated and backfilled with N_2 and CH_3CN (3 mL) and pyridine (3.5 μL , 0.04 mmol) were added via syringe. The tube was then sealed with a Teflon lined cap and placed into a preheated oil bath at 75°C with vigorous stirring. After 8 h, the reaction mixture was cooled to room temperature and filtered through a plug of silica (eluted with EtOAc). Only trace **2a** was detected with 90% **1a** recovered. The result indicates that the radical intermediate probably be involved in the catalytic cycle of the reaction.

2.2 Role of Silver Experiments



CuSCN (1.5 equiv)	2a , 0%
KSCN (1.5 equiv)	2a , 0%
KSCN/AgNO ₃ (1:1, 1.5 equiv)	2a , 15%

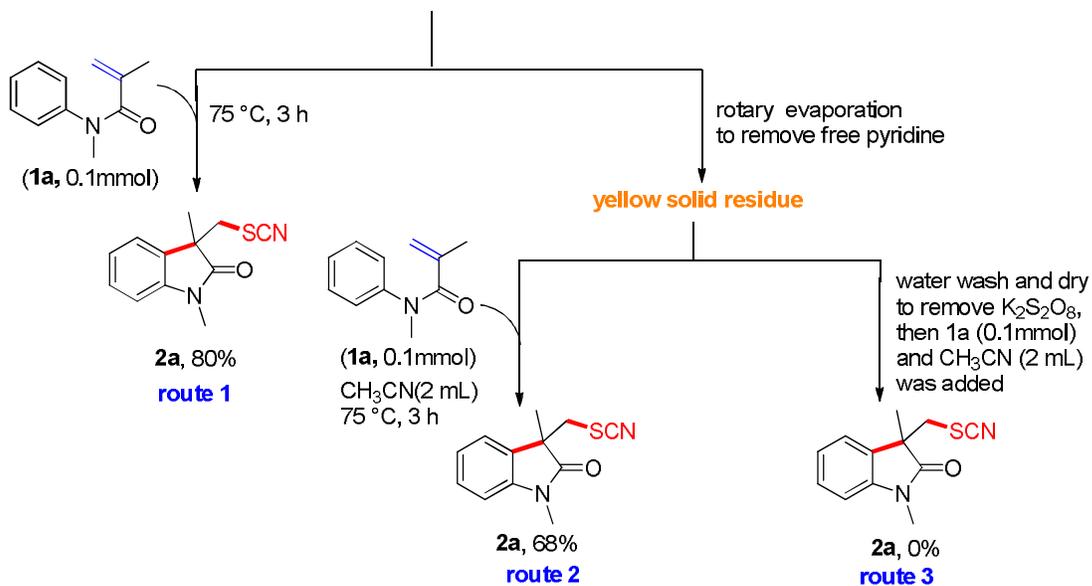
2.3 Role of Pyridine Experiments

AgSCN (0.15 mmol), K₂S₂O₈ (0.15 mmol), pyridine (0.05 mmol)

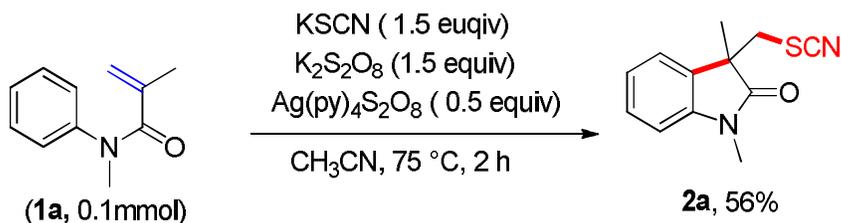
CH₃CN, 75 °C, 1 h



yellow suspension containing catalytic amount of Ag(II)-pyridine complex



In the above experiment, we found that stirring of AgSCN/K₂S₂O₈/pyridine mixture in CH₃CN at 75 °C for 1 h led to the formation of colored Ag(II)–pyridine complexes, which could react with **1a** without free pyridine to give **2a** in 68% yield. However, the desired arylthiocyanation of **1a** with silver–pyridine complexes cannot proceed when K₂S₂O₈ was removed by water wash of yellow solid residue, which indicated the crucial roles of K₂S₂O₈ in oxidizing Ag(I) to Ag(II).

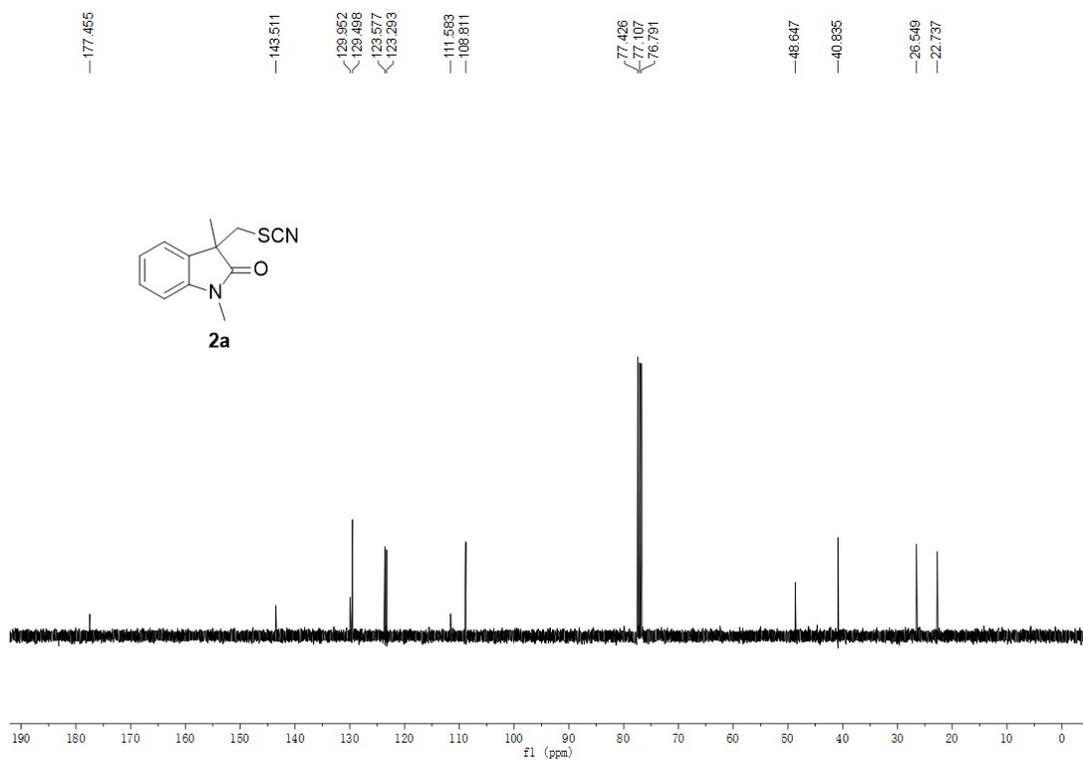
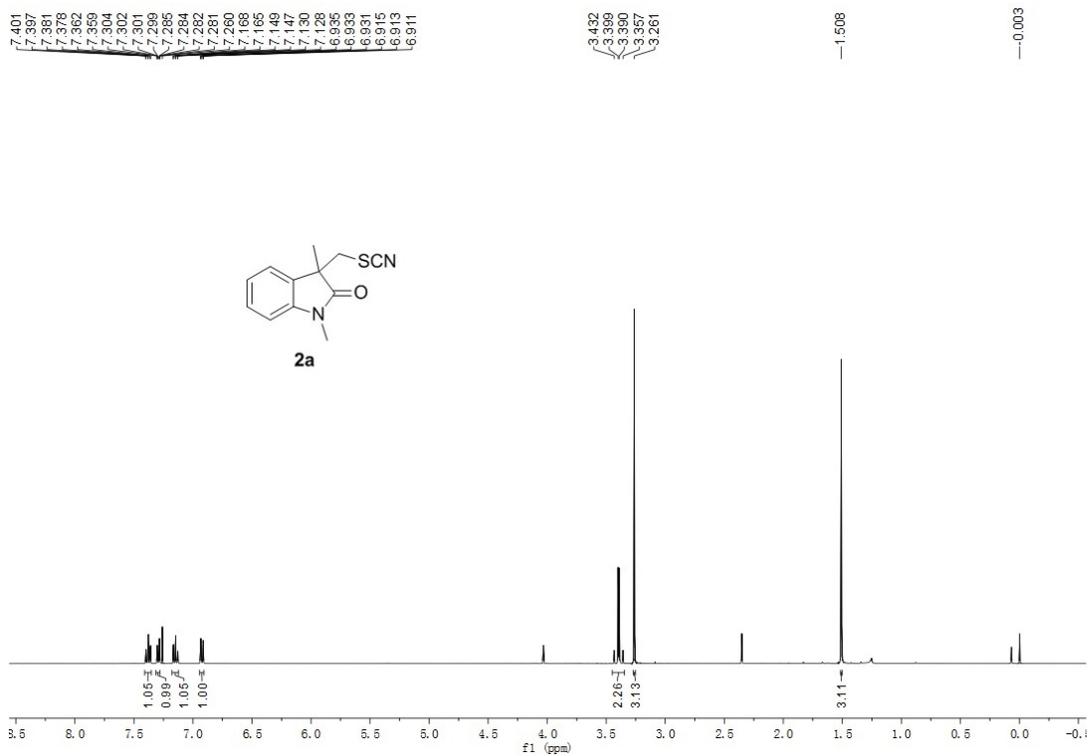


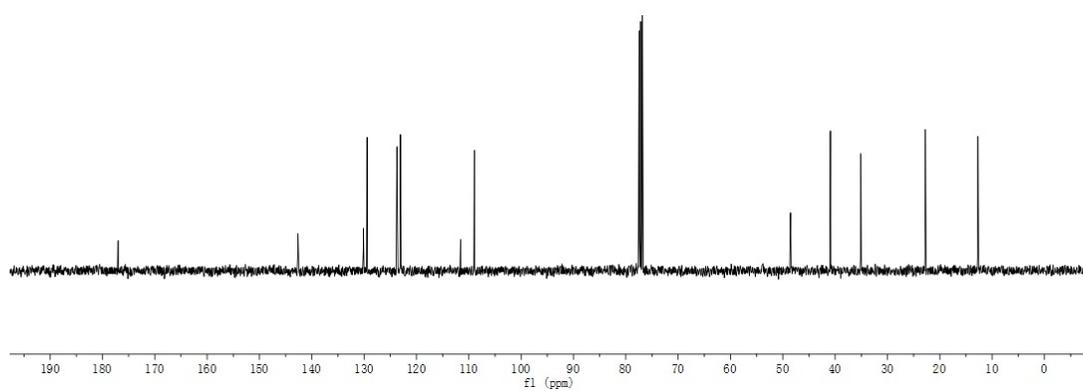
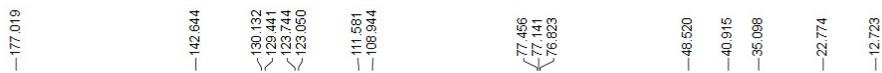
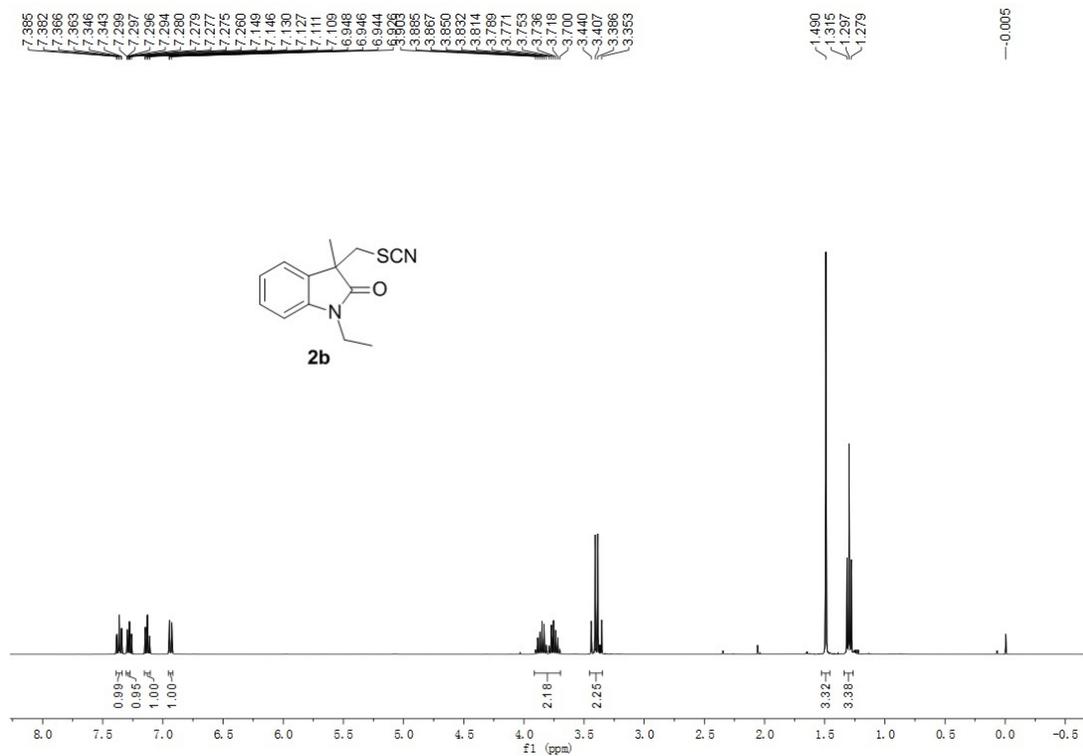
Ag(py)₄S₂O₈, which has been well established in the literature², was considered to be a possible formation of the Ag(II)–pyridine complex. Accordingly, it was prepared as an orange solid.^{2a} Treatment of **1a** with Ag(py)₄S₂O₈ (0.5 equiv), KSCN(1.5 equiv), and K₂S₂O₈ (1.5 equiv) in CH₃CN at 75 °C for 2 h led to the formation of **2a** in 56% isolated yield. In this experiment, a very quick reduction of orange-Ag(II) to colorless-Ag(I) was observed at the beginning of the reaction which suggested that Ag(II) should be the active species to oxidize NCS⁻ to NCS• radical.

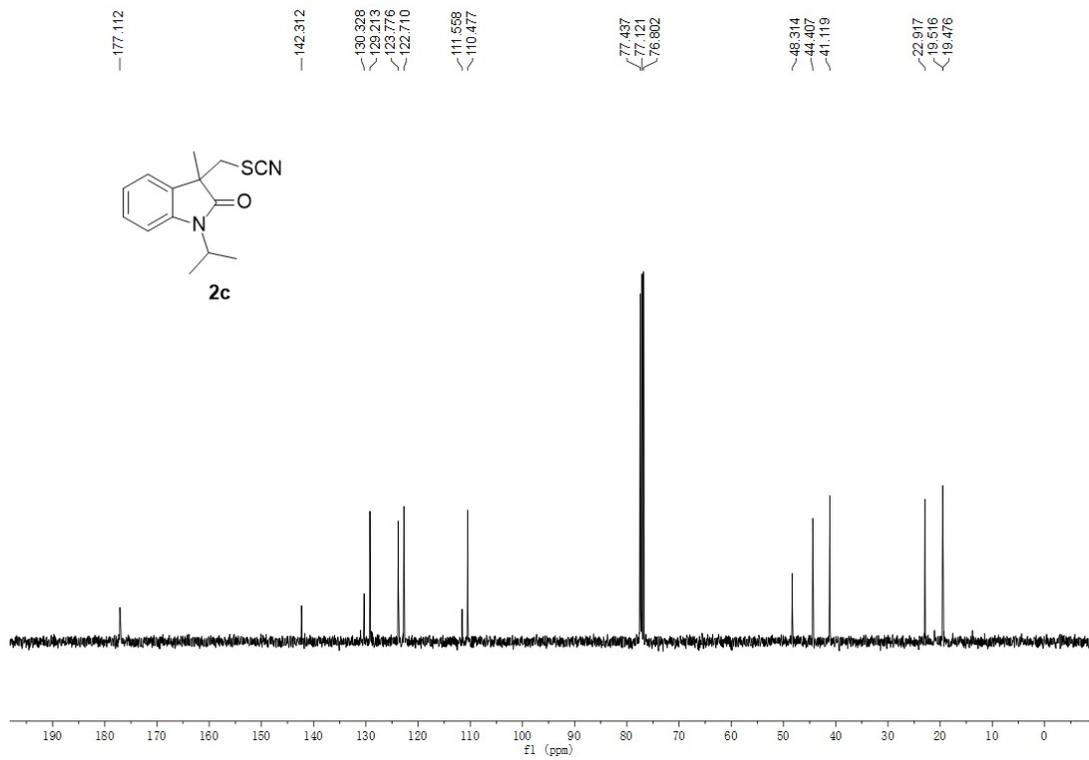
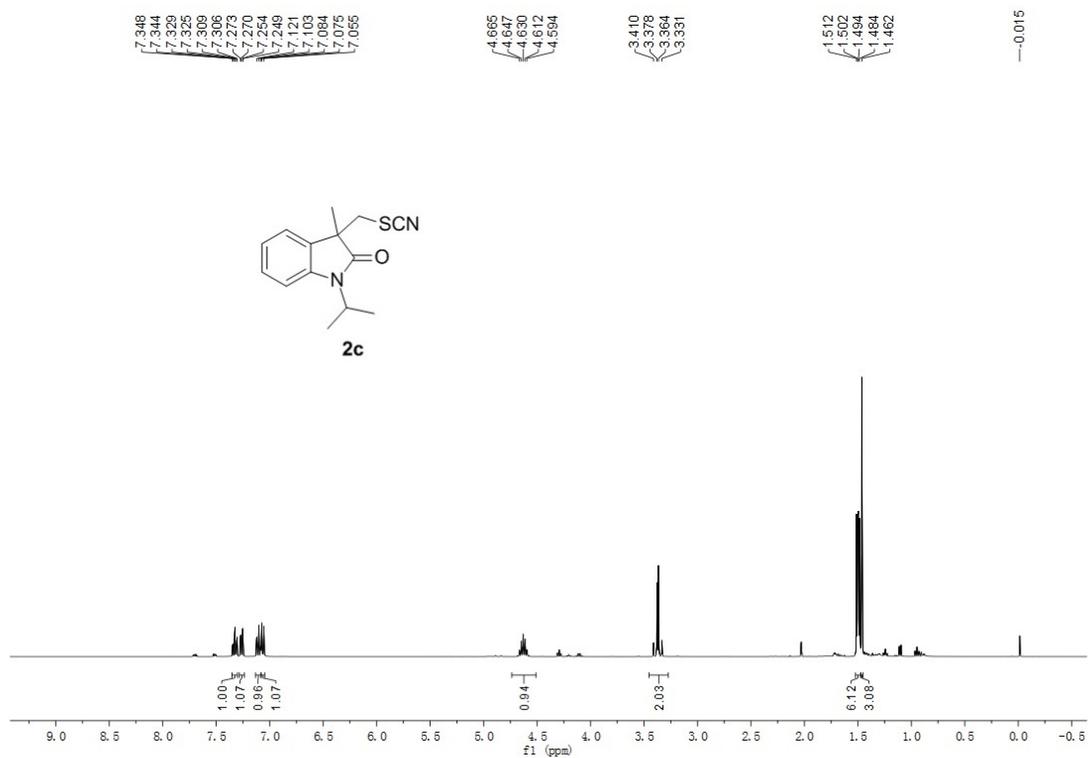
3. References

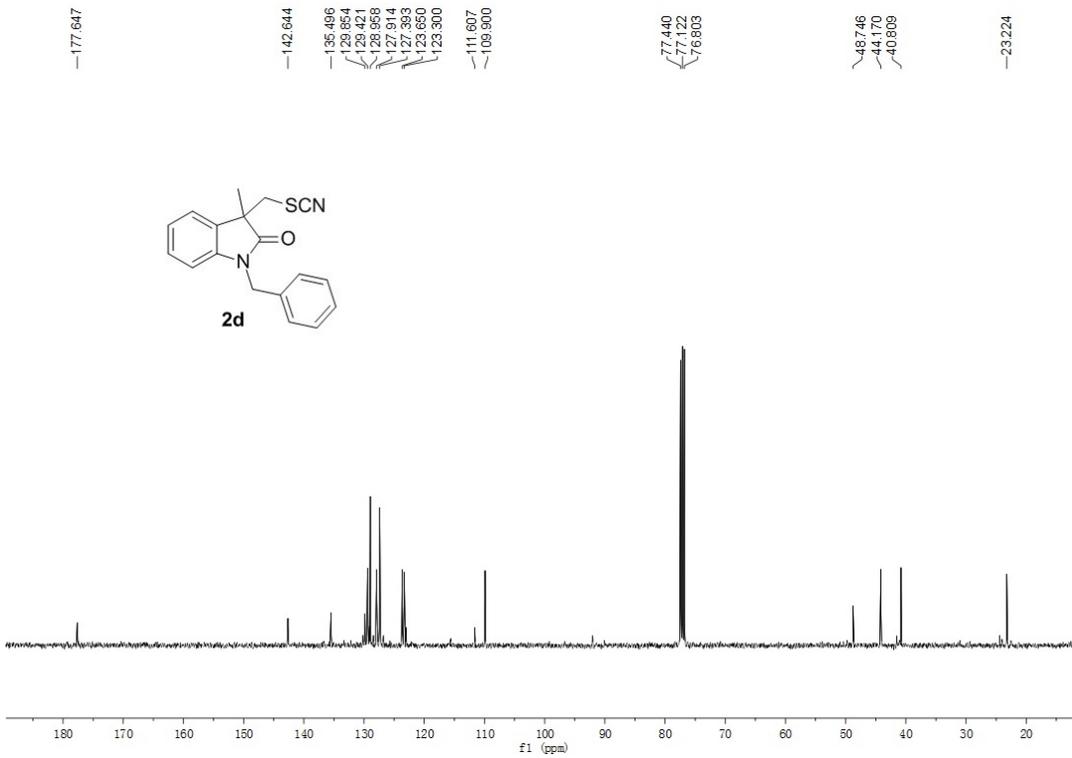
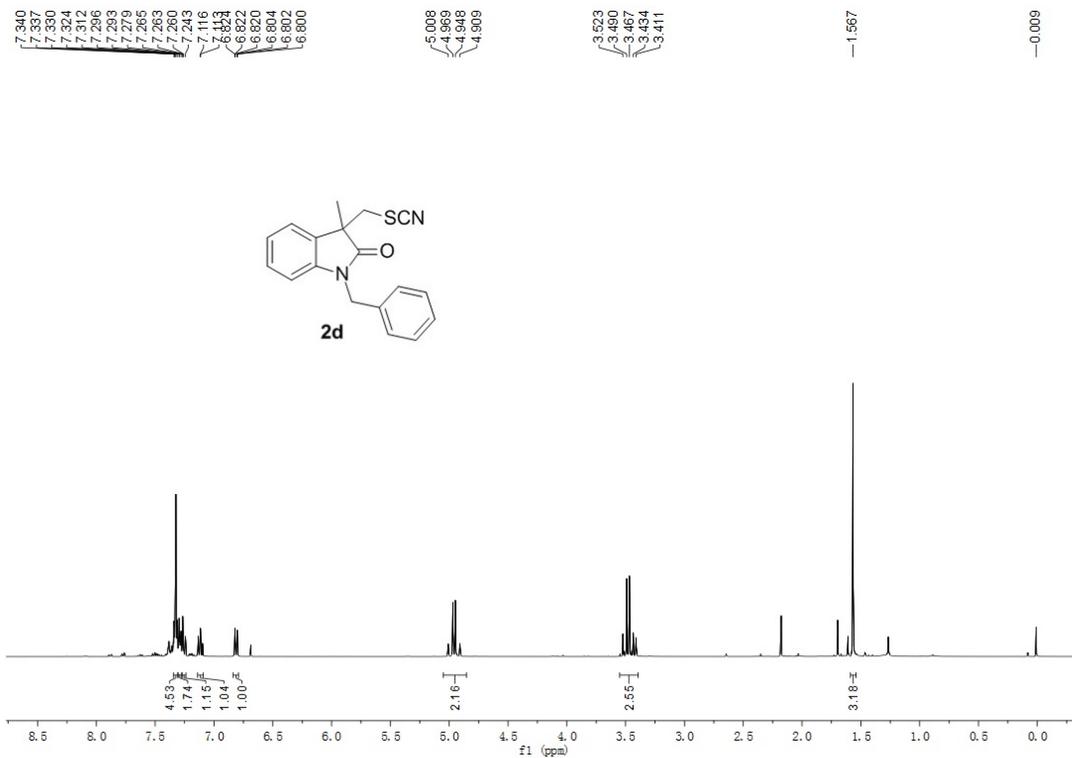
- [1] Mu, X.; Wu, T.; Wang, H. Y.; Guo, Y. L.; Liu, G. *J. Am. Chem. Soc.* **2012**, *134*, 878.
- [2] (a) H. Firouzabadi, P. Salehi, A. R. Sardarian and M. Seddighi, *Synthetic commun.*, 1991, **21**, 1121. (b) H. Firouzabadi, P. Salehi and I. Mohammadpour-Baltork, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2878. (c) A. Nikolaev, C. Y. Legault, M. Zhang and A. Orellana, *Org. Lett.*, 2018, **20**, 796

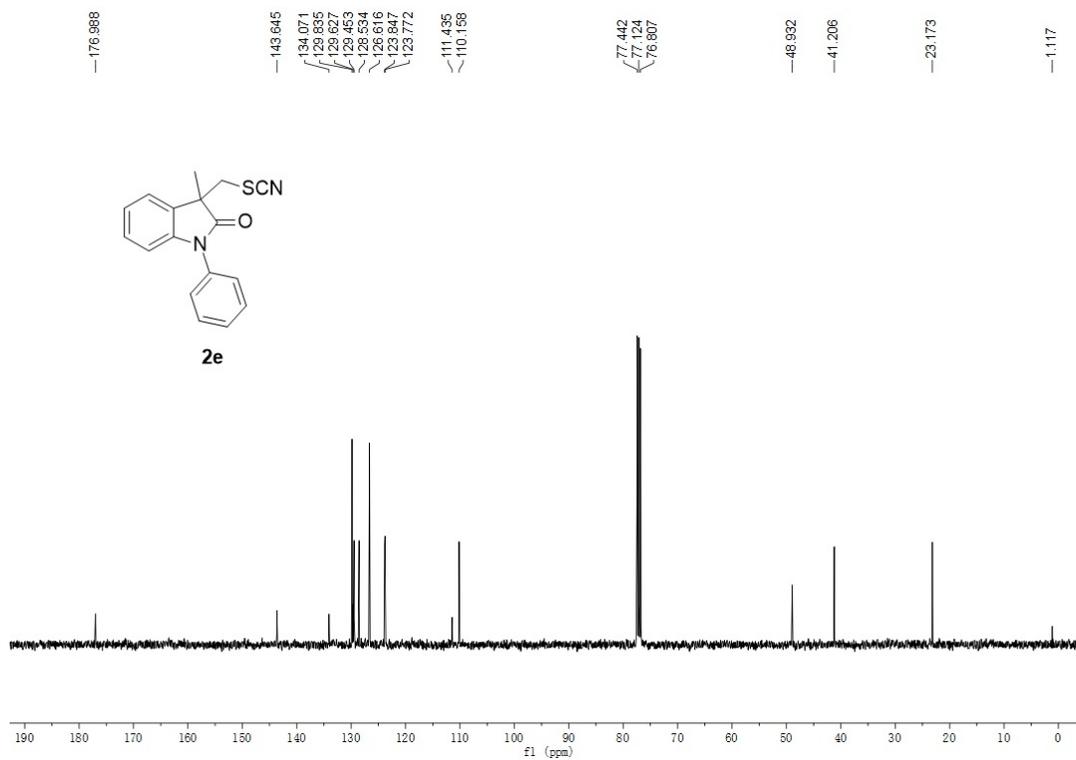
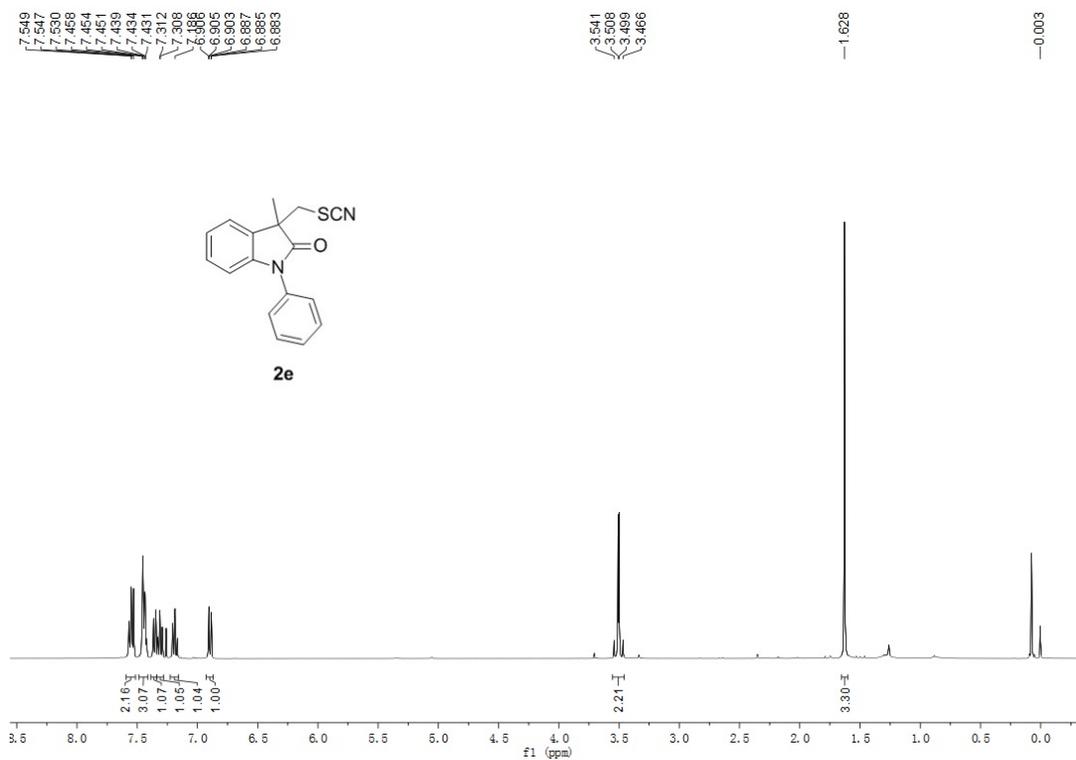
6. Copies of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra

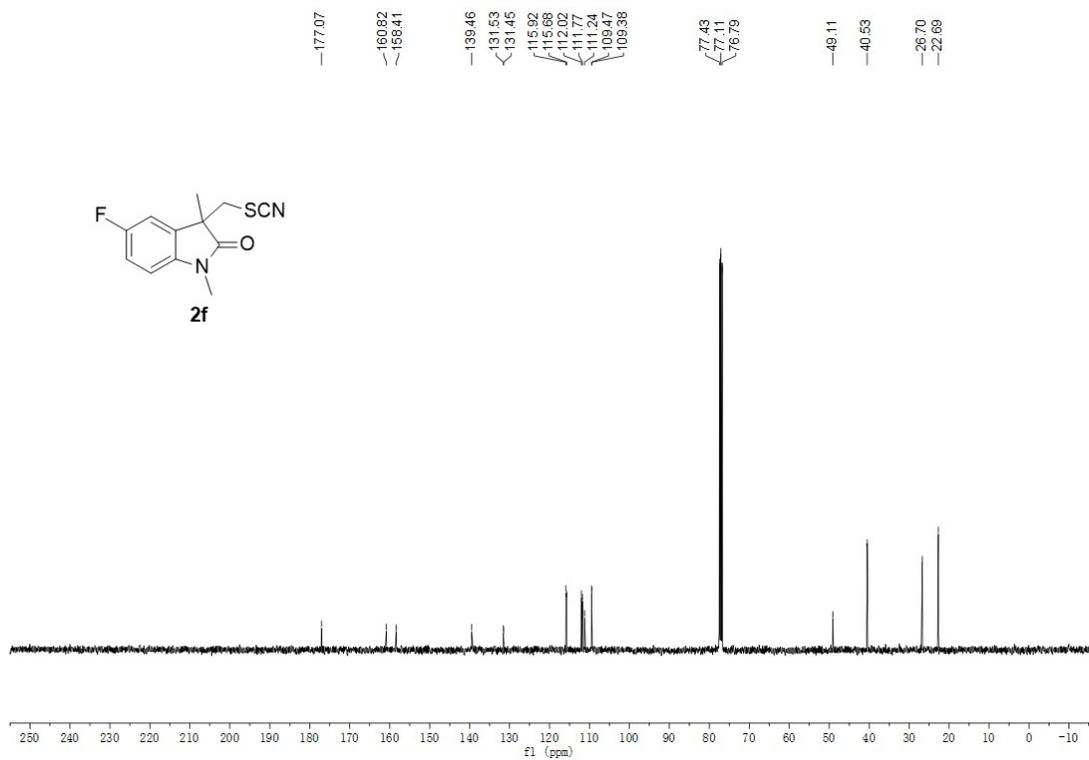
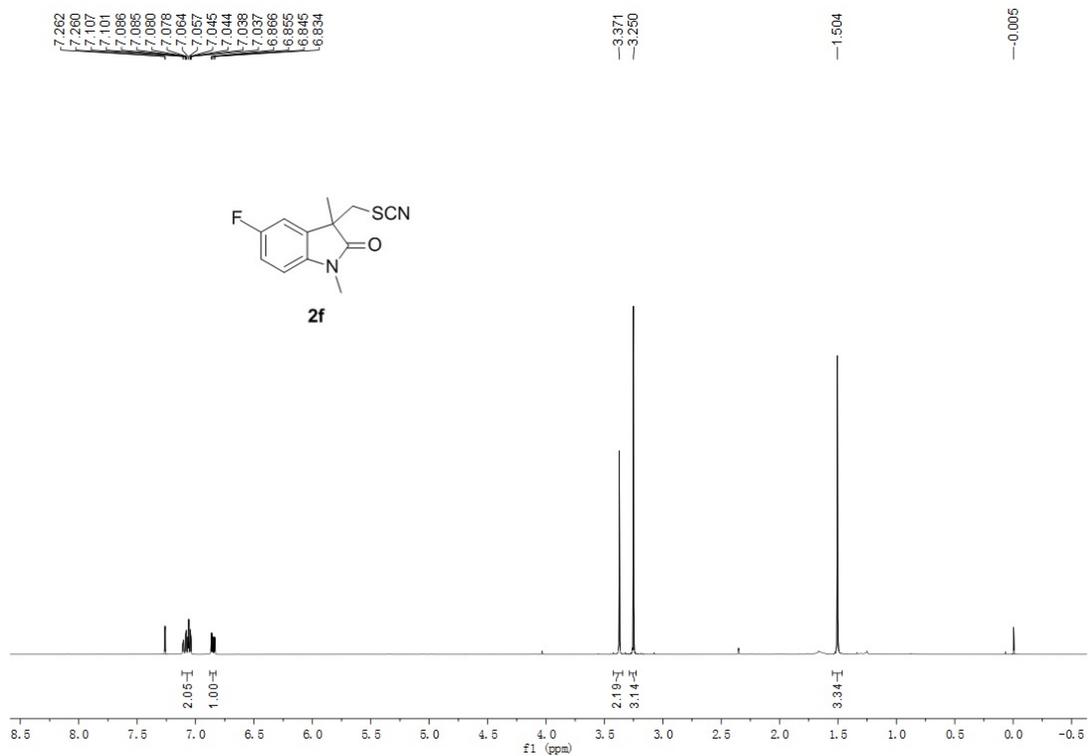


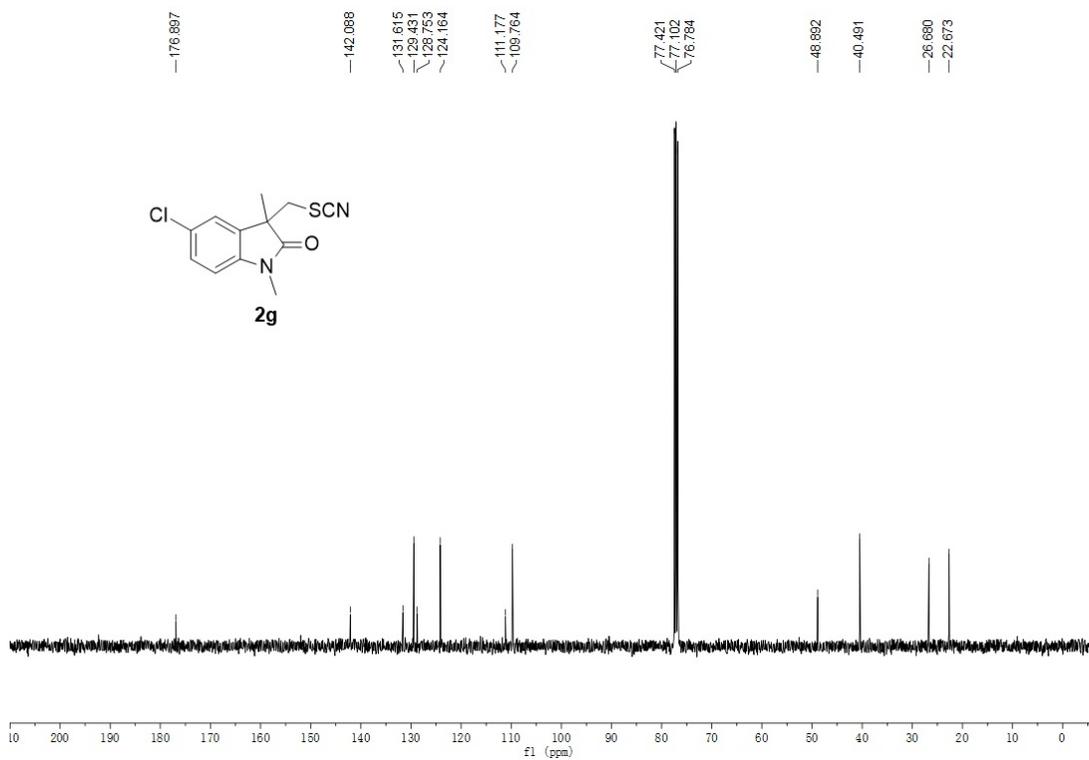


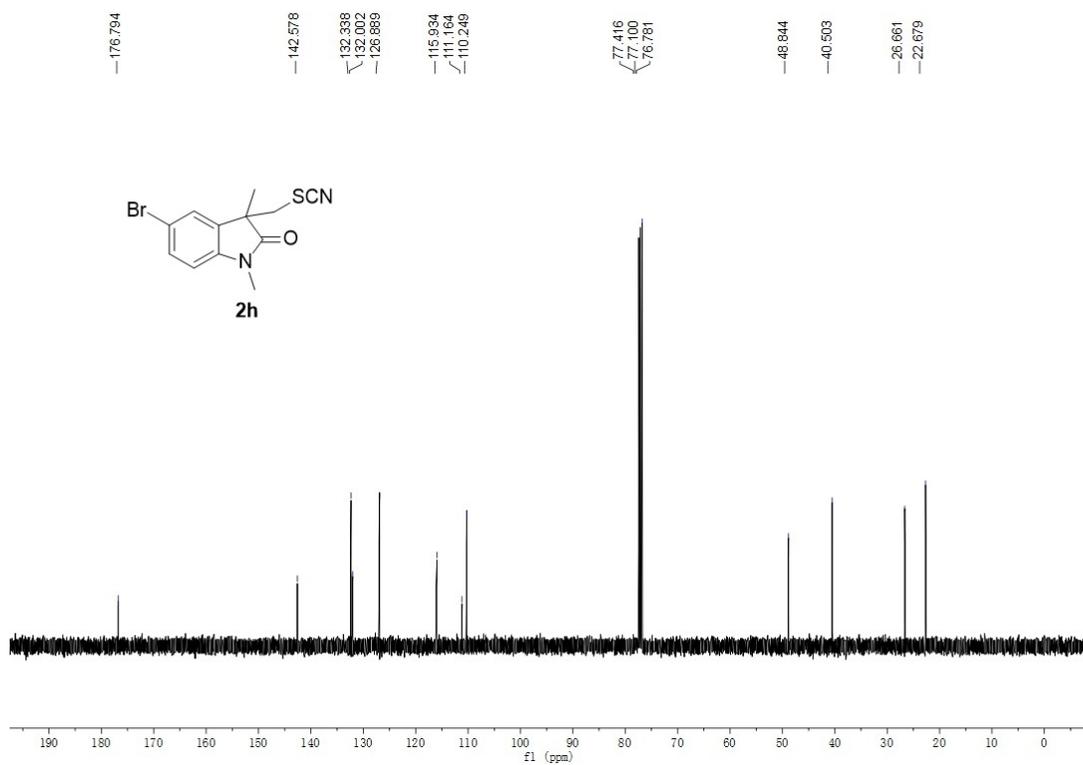
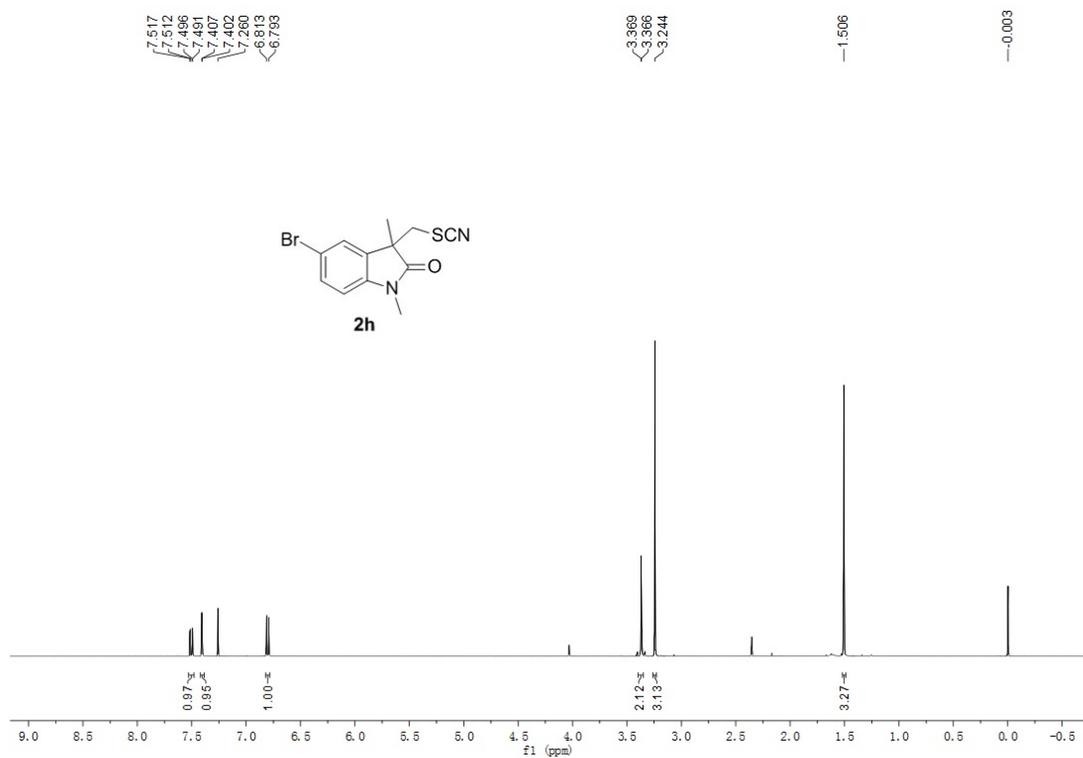


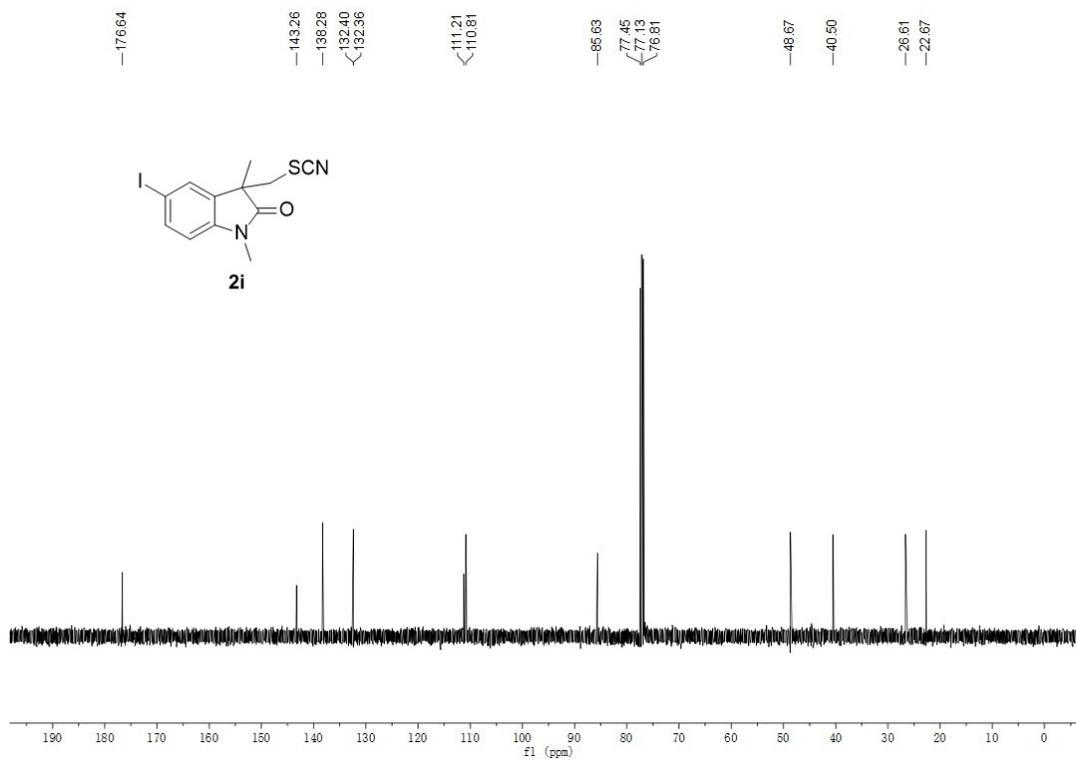
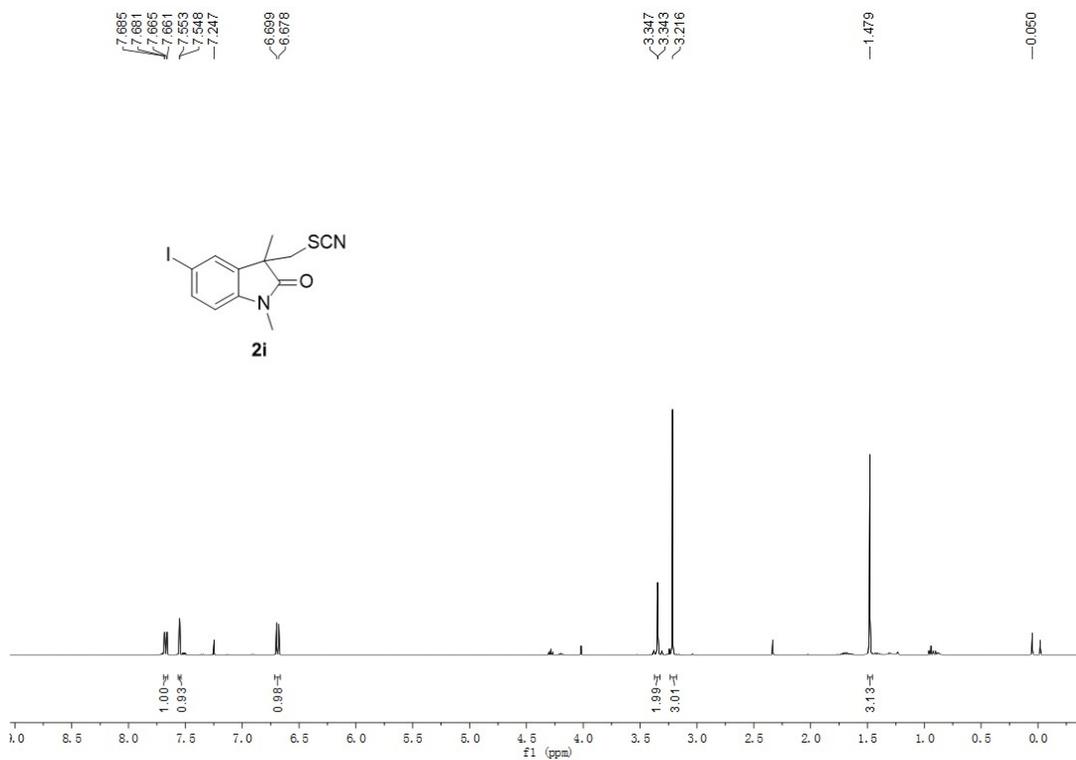








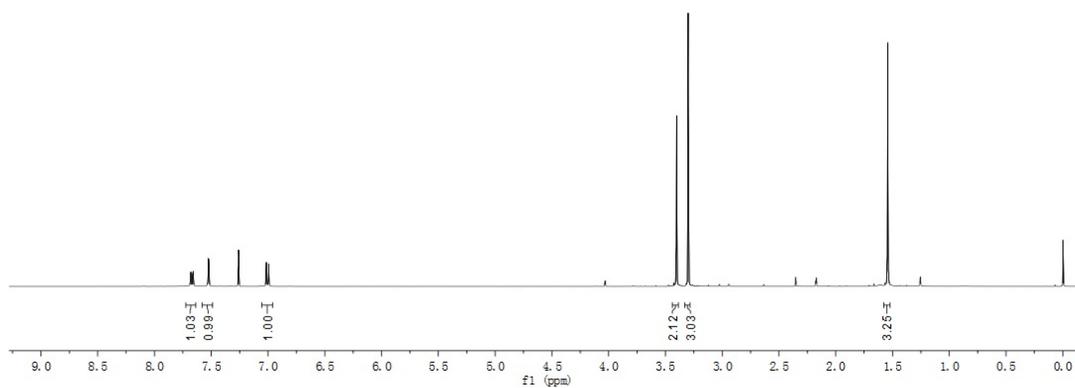
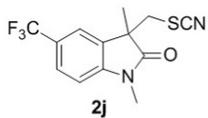




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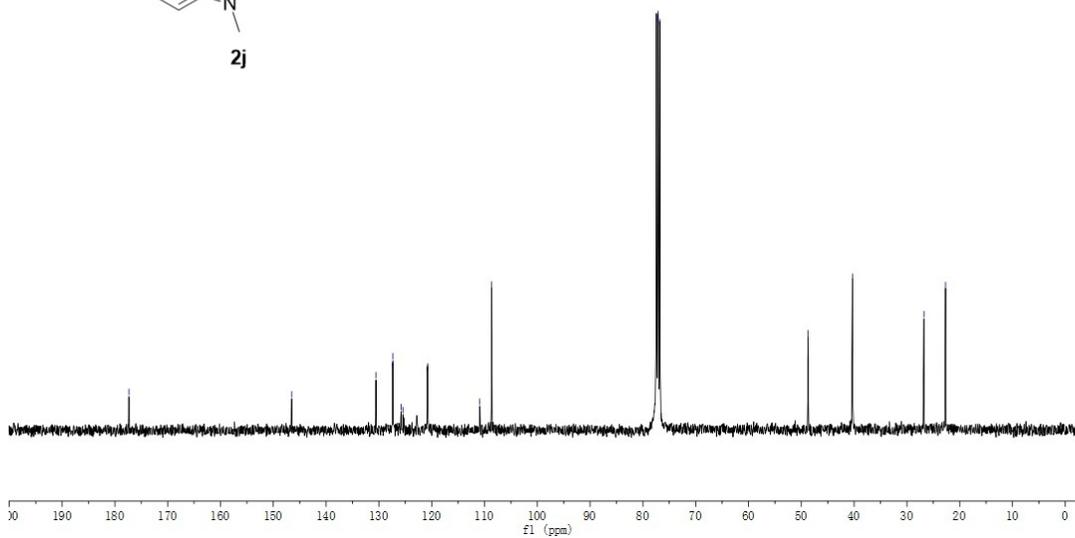
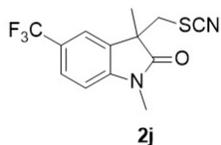
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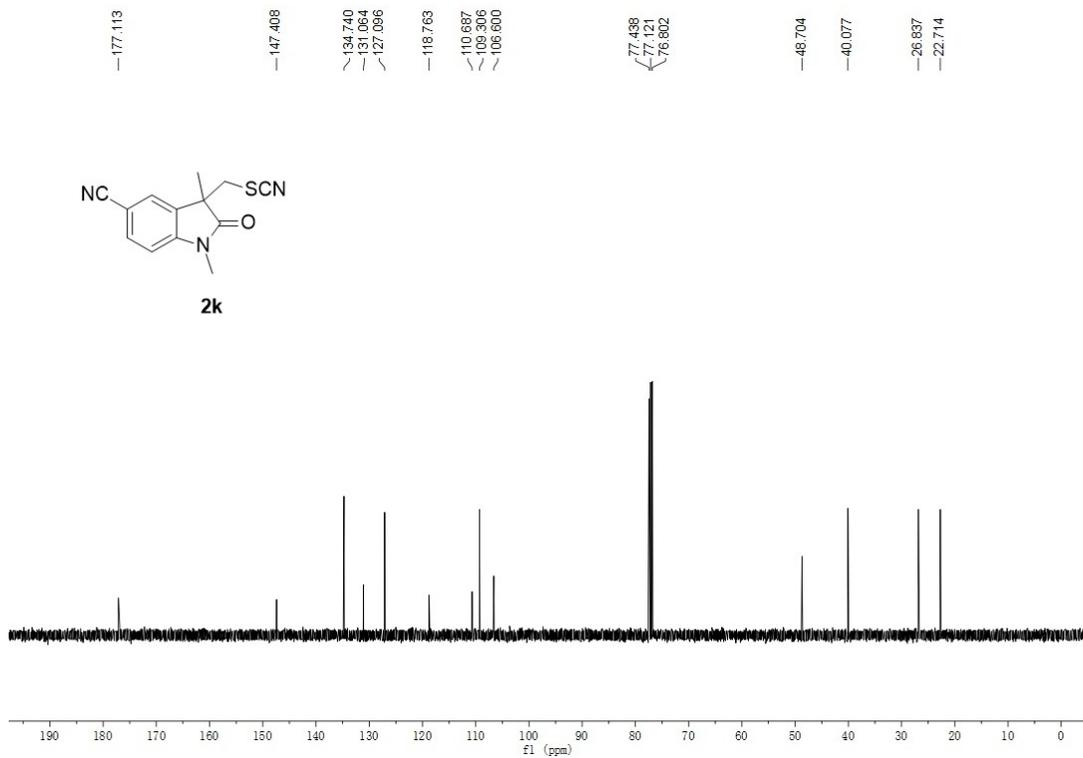
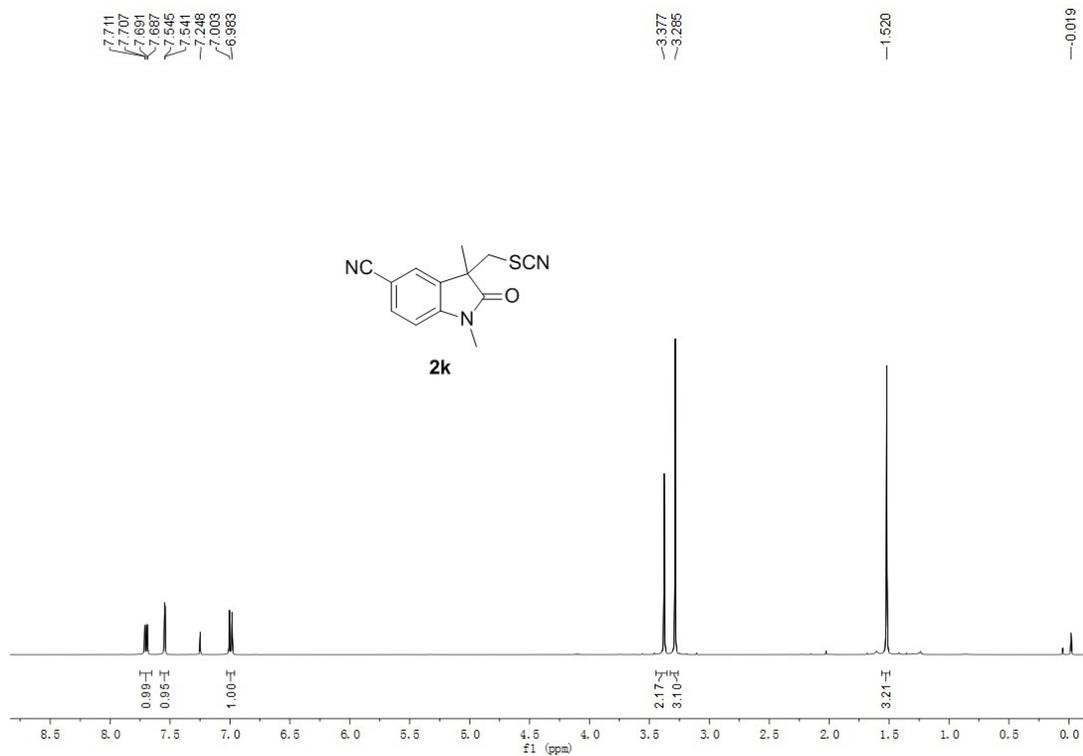
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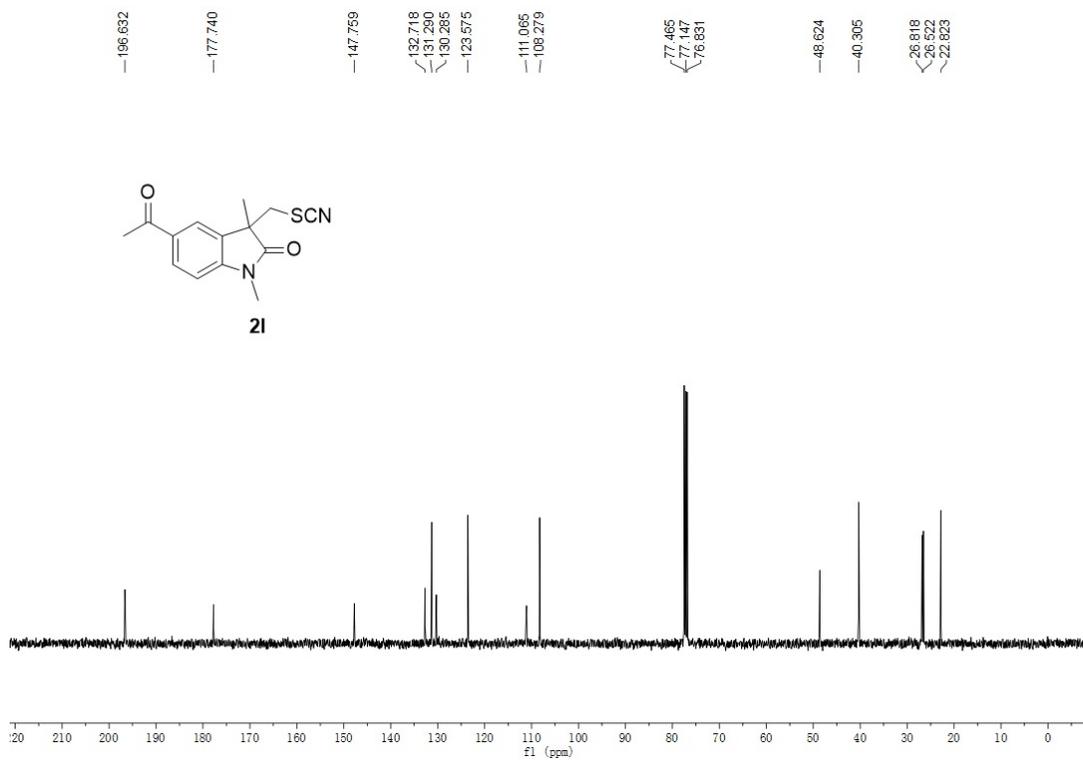
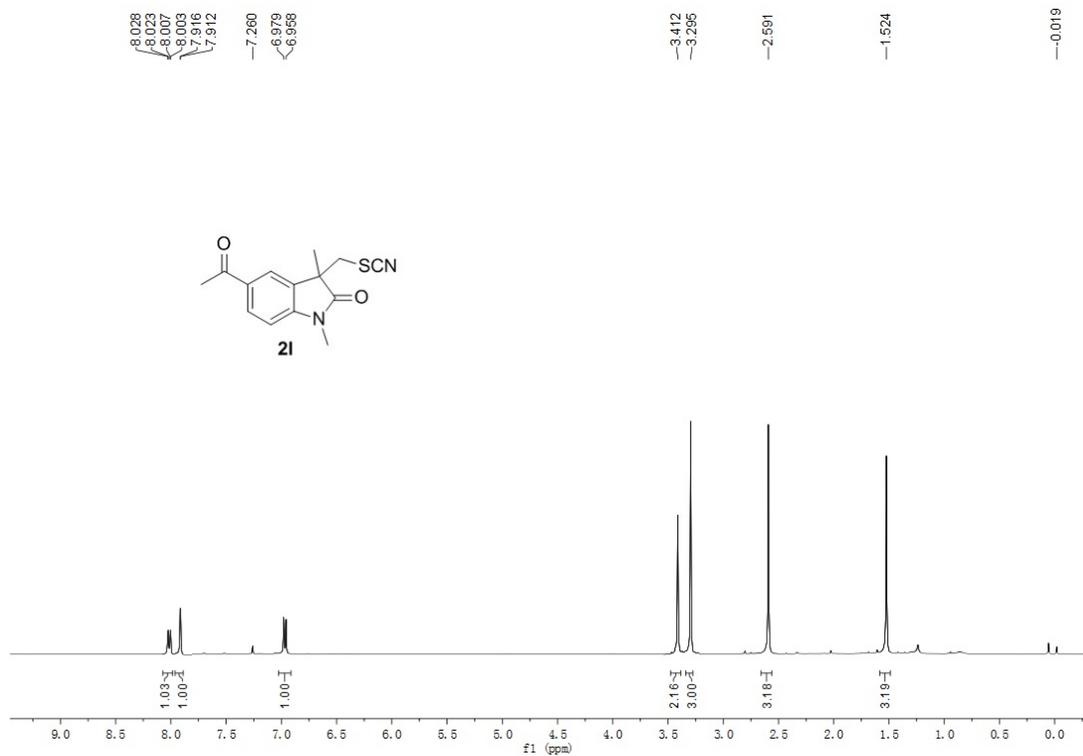
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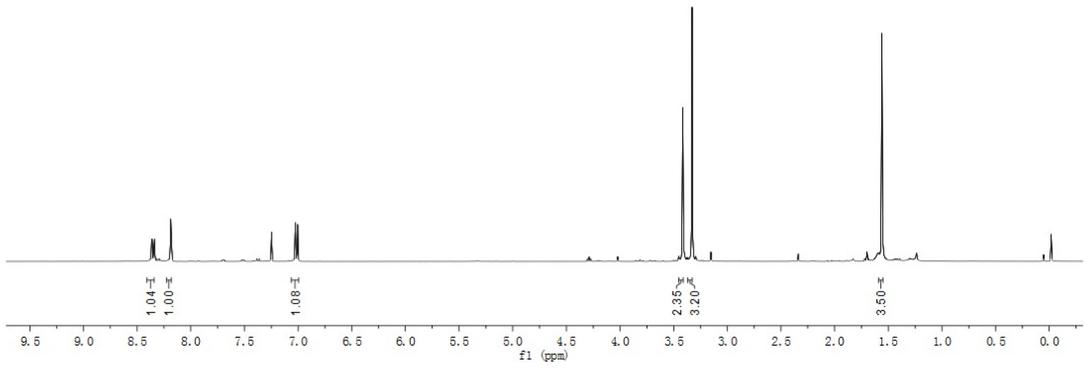
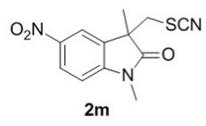
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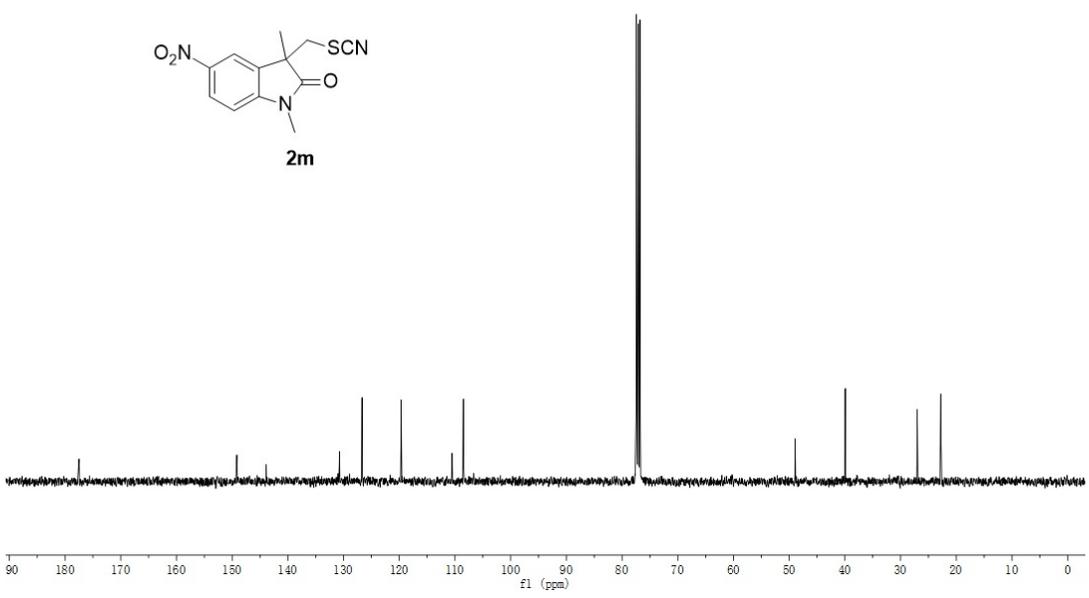
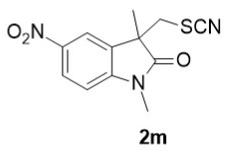
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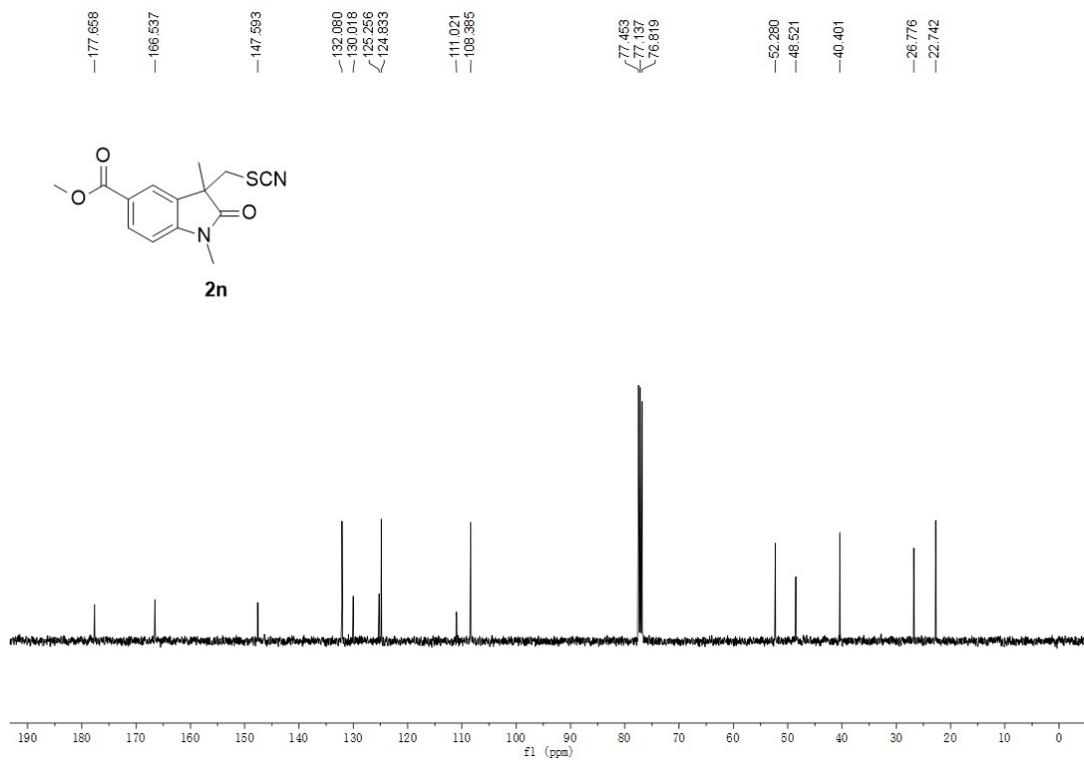
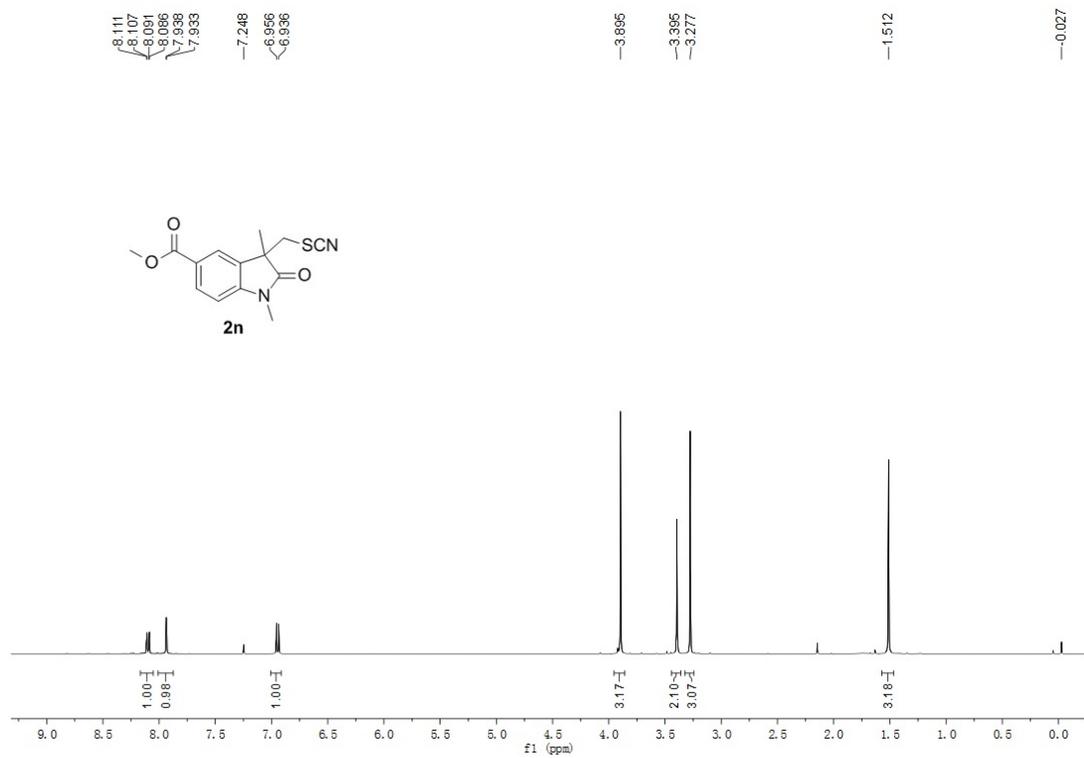
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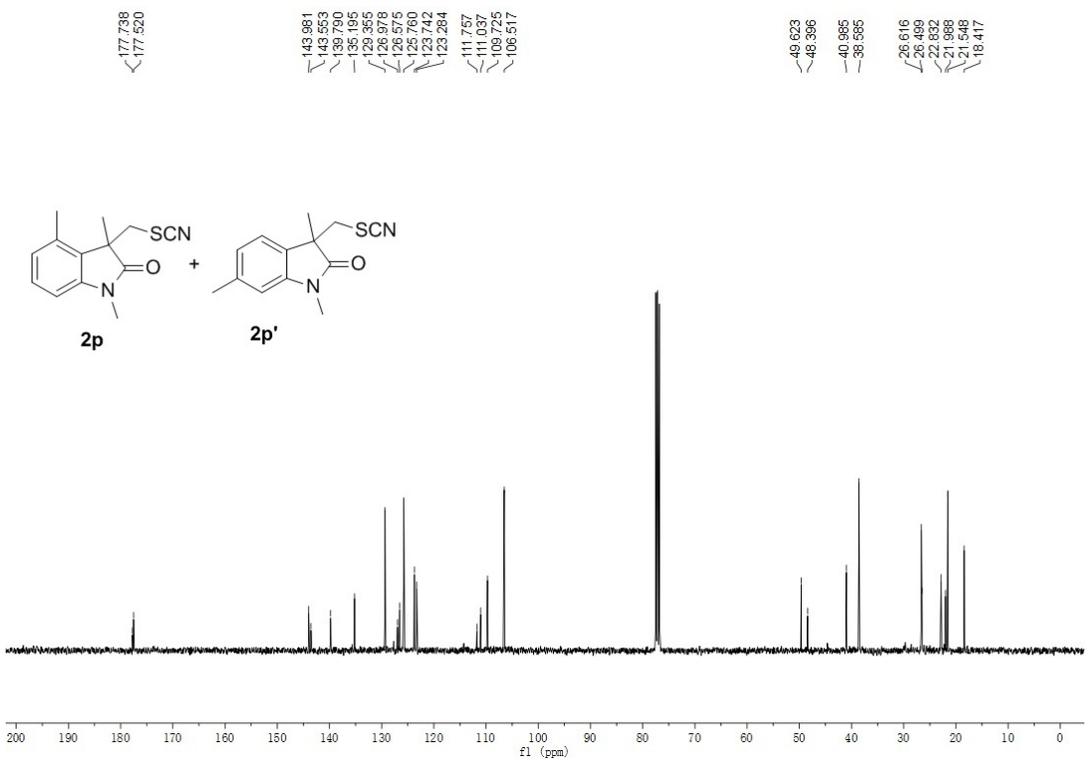
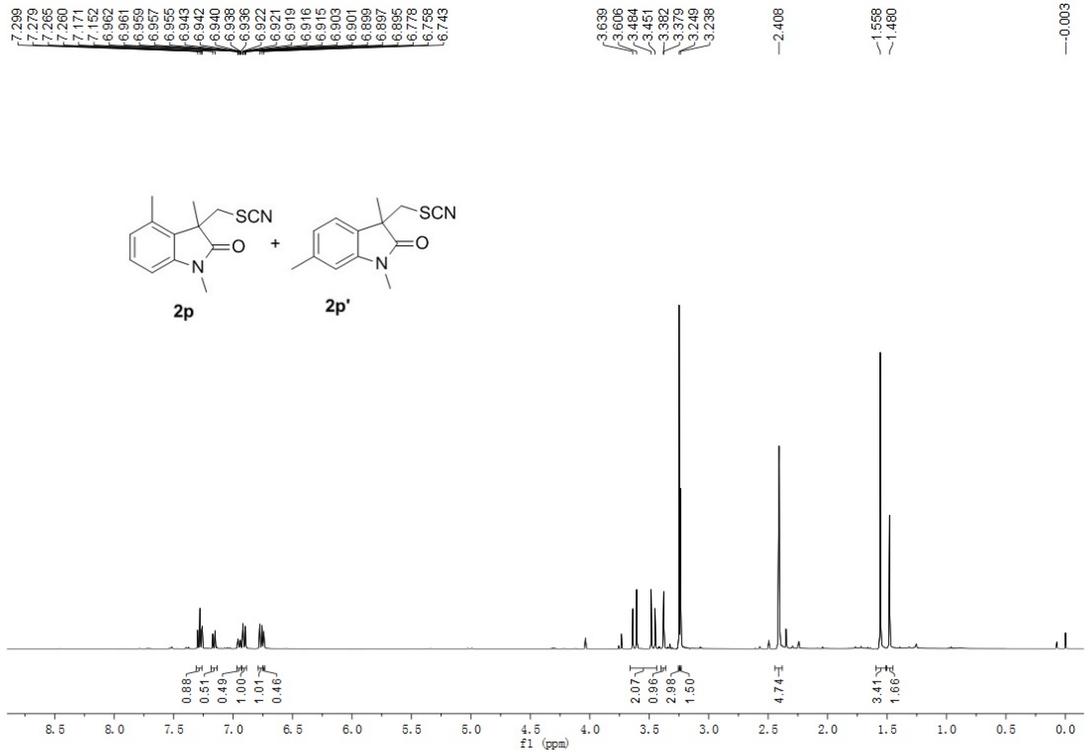
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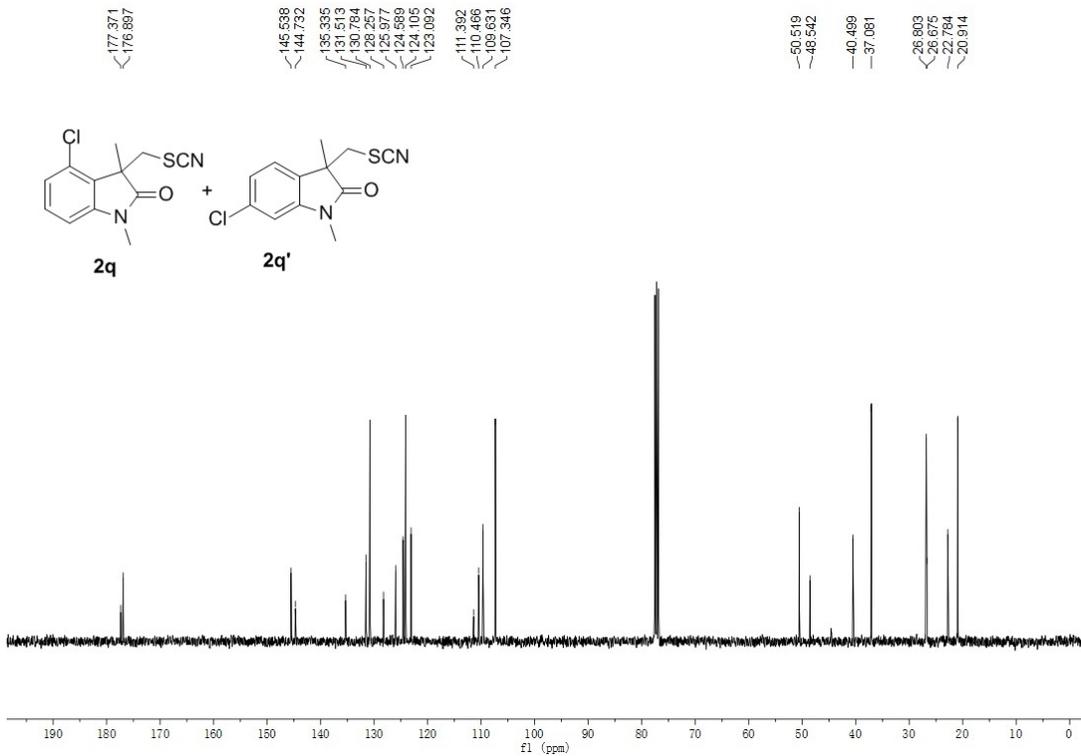
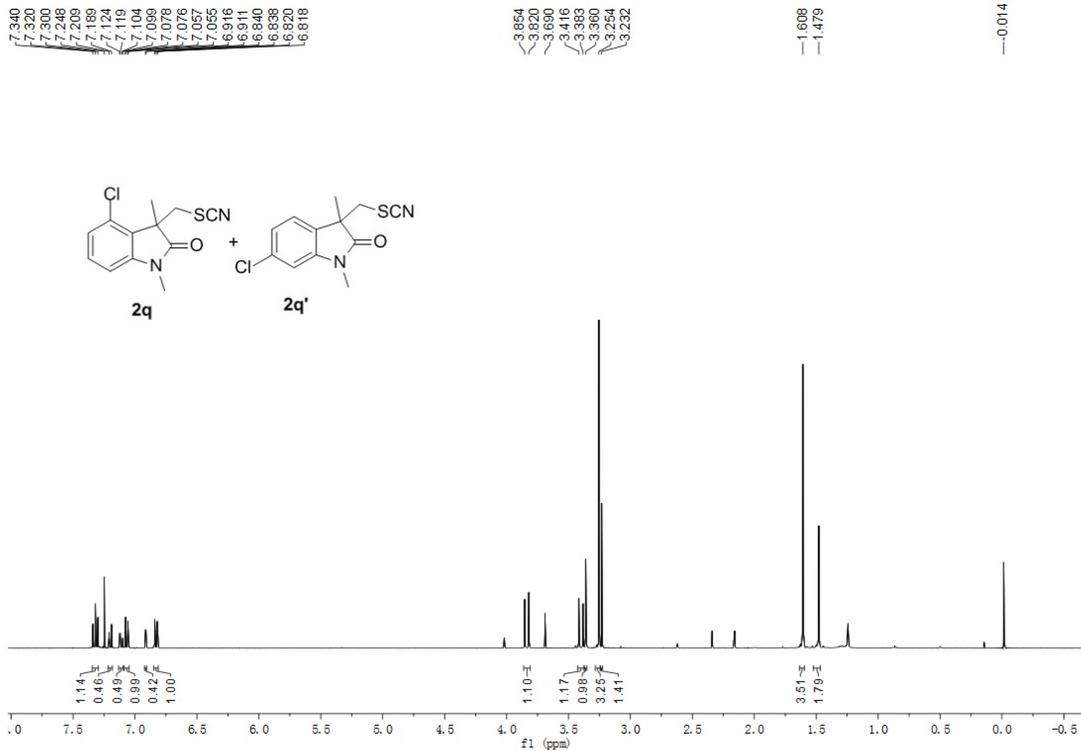
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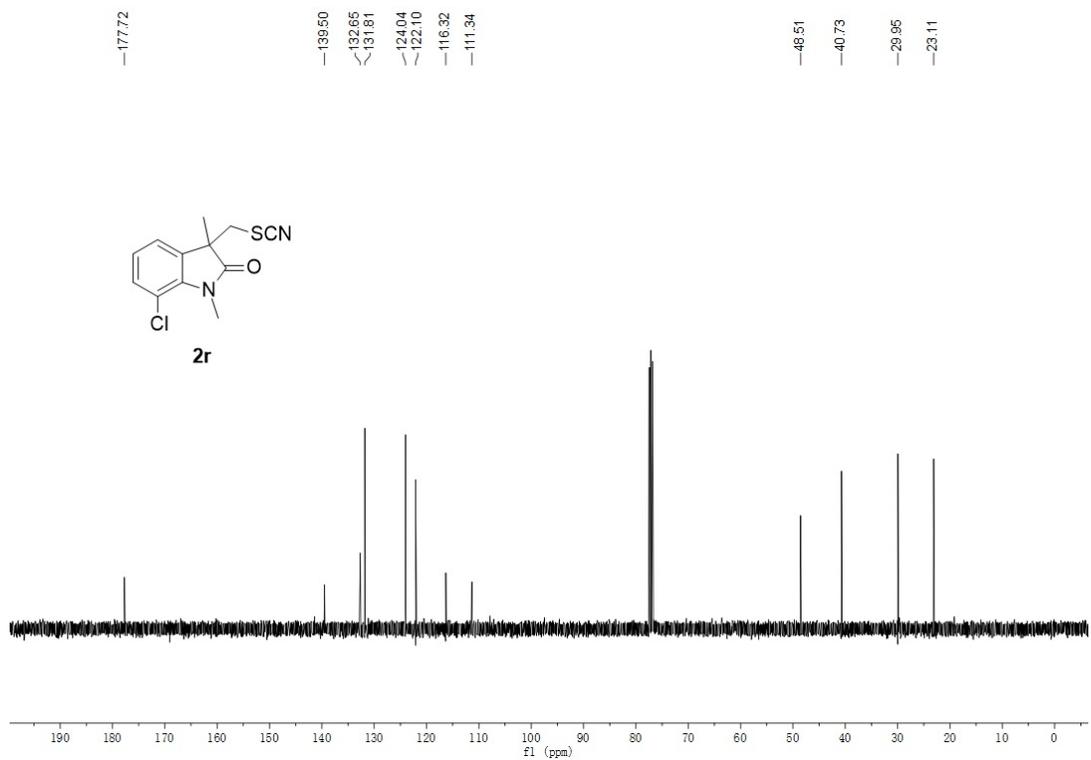
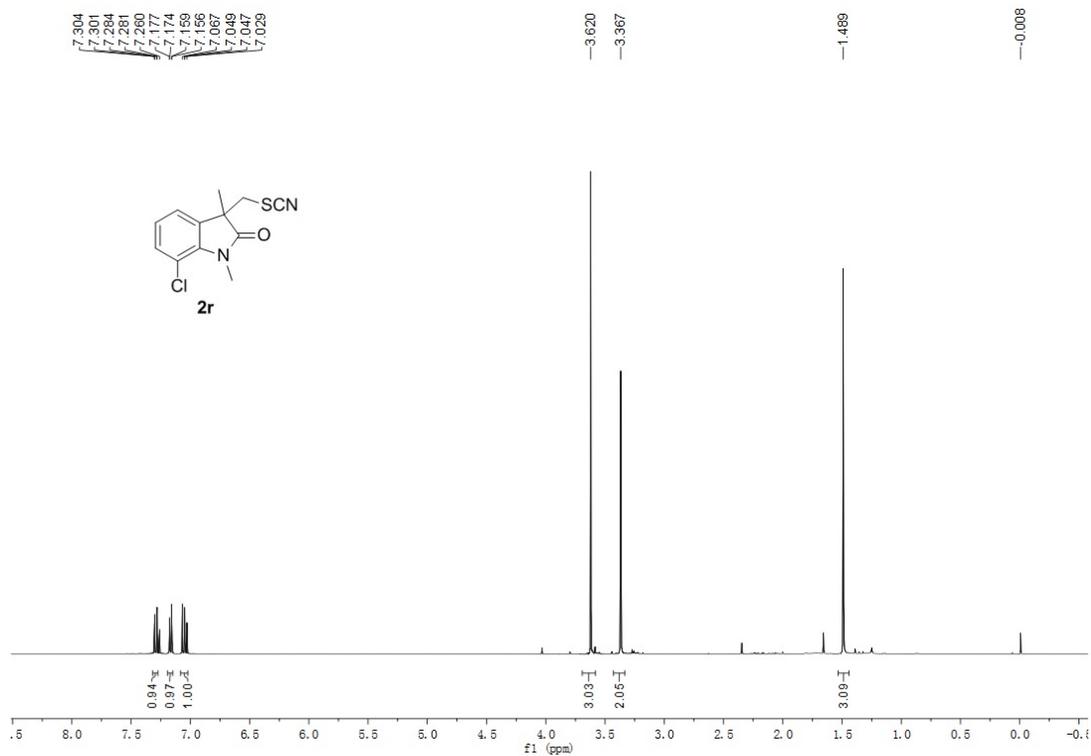
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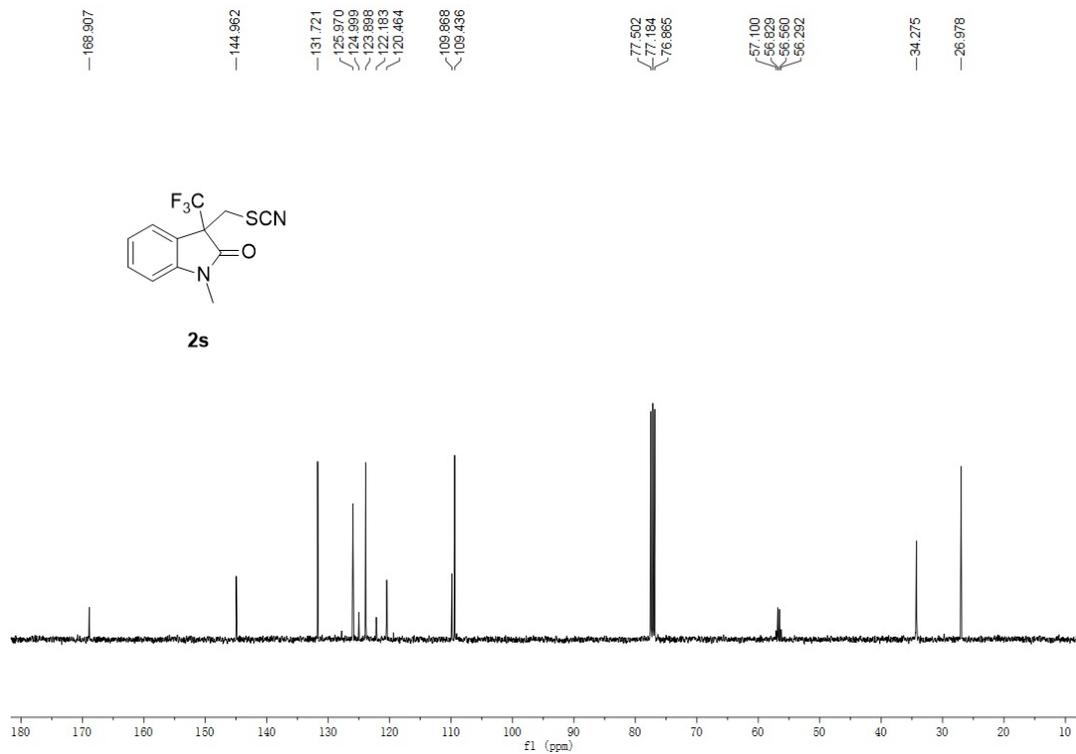
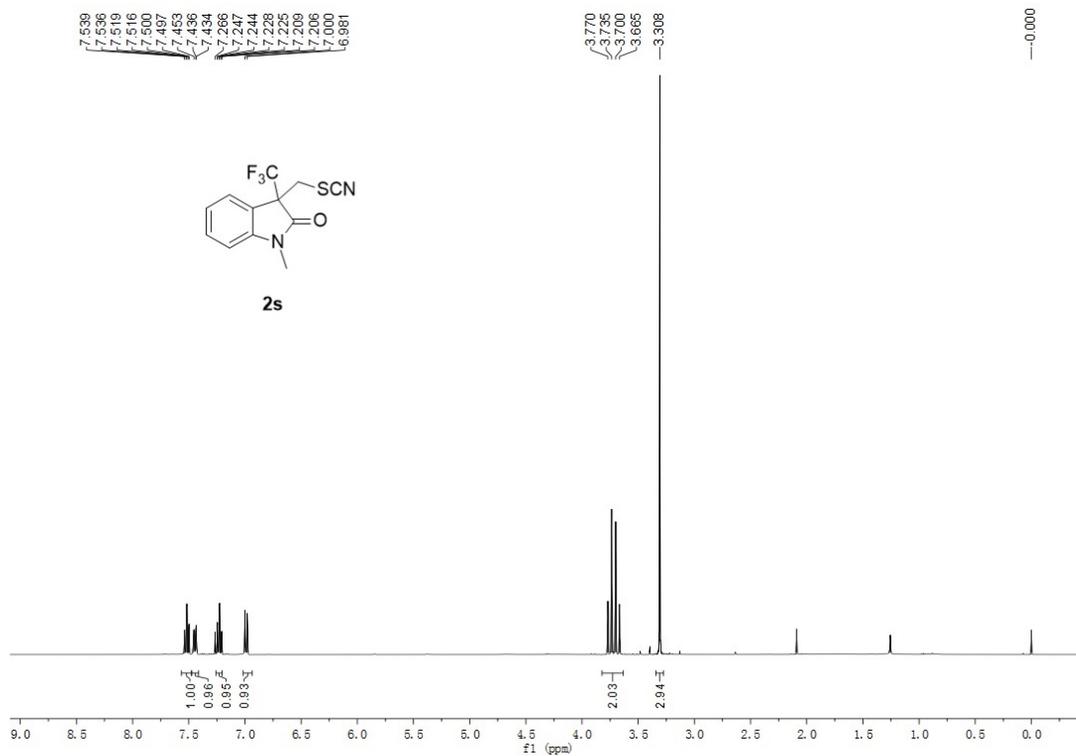






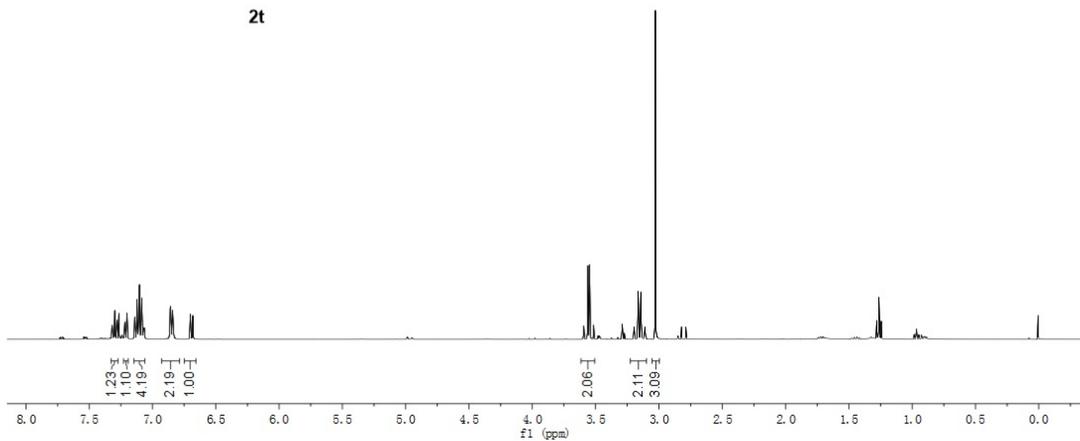
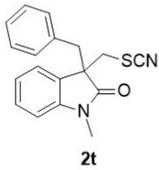




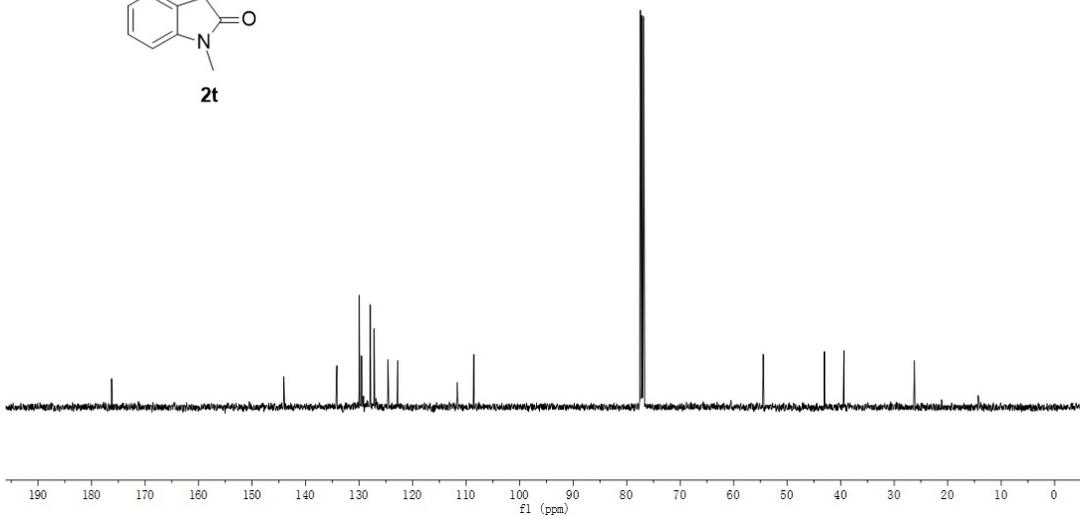
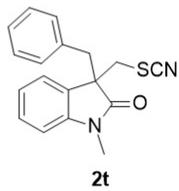


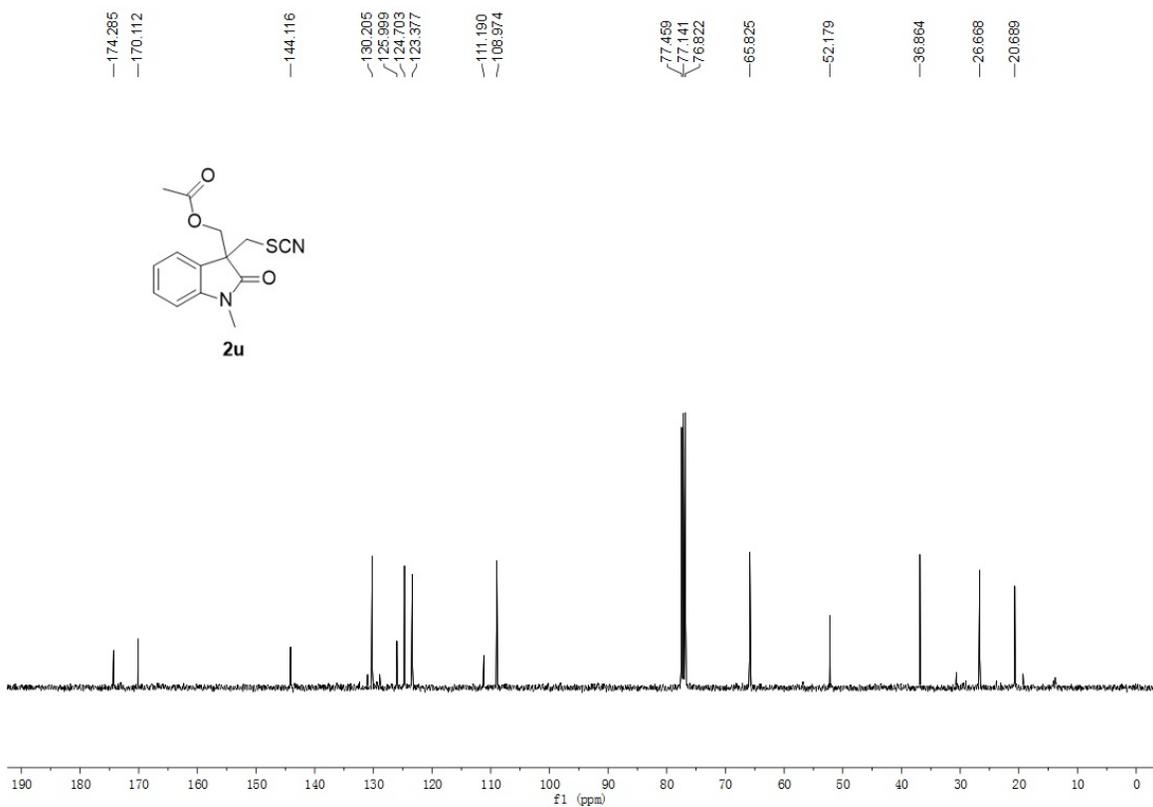
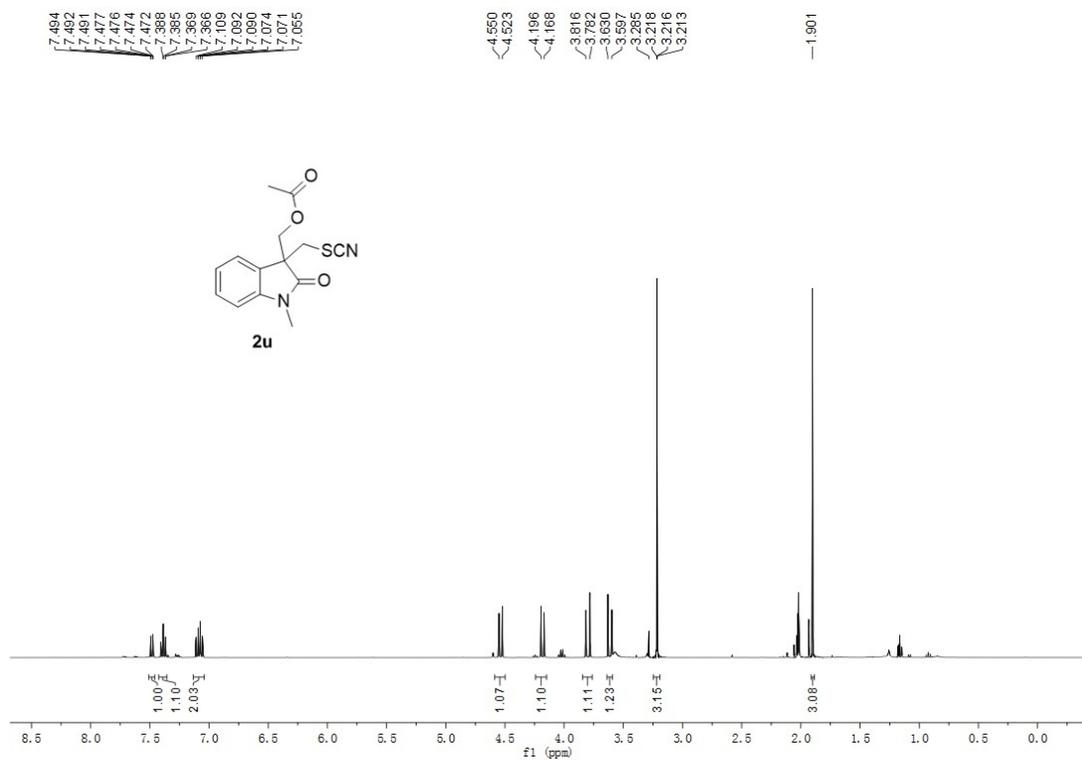
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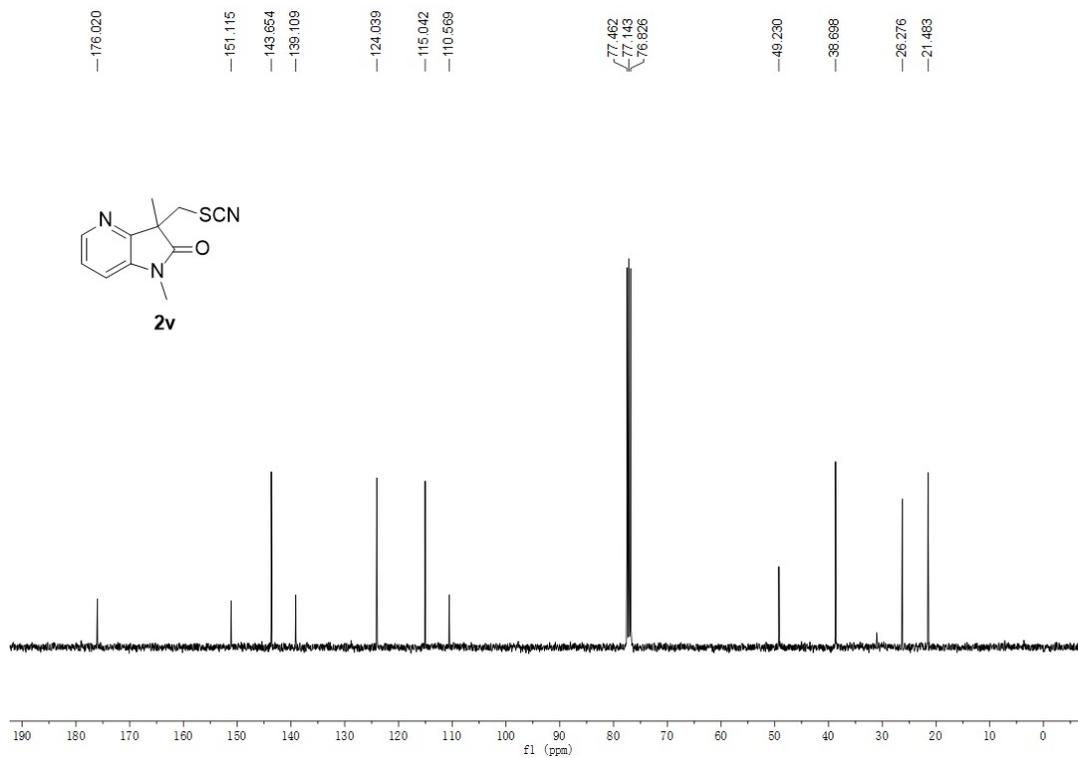
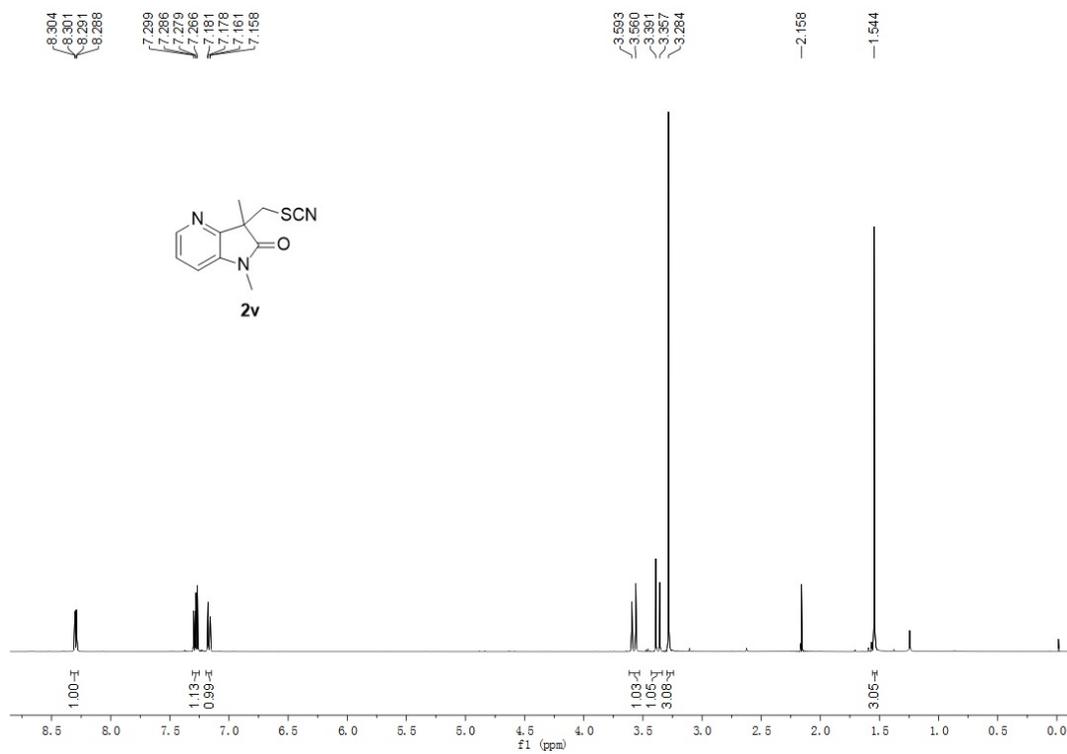
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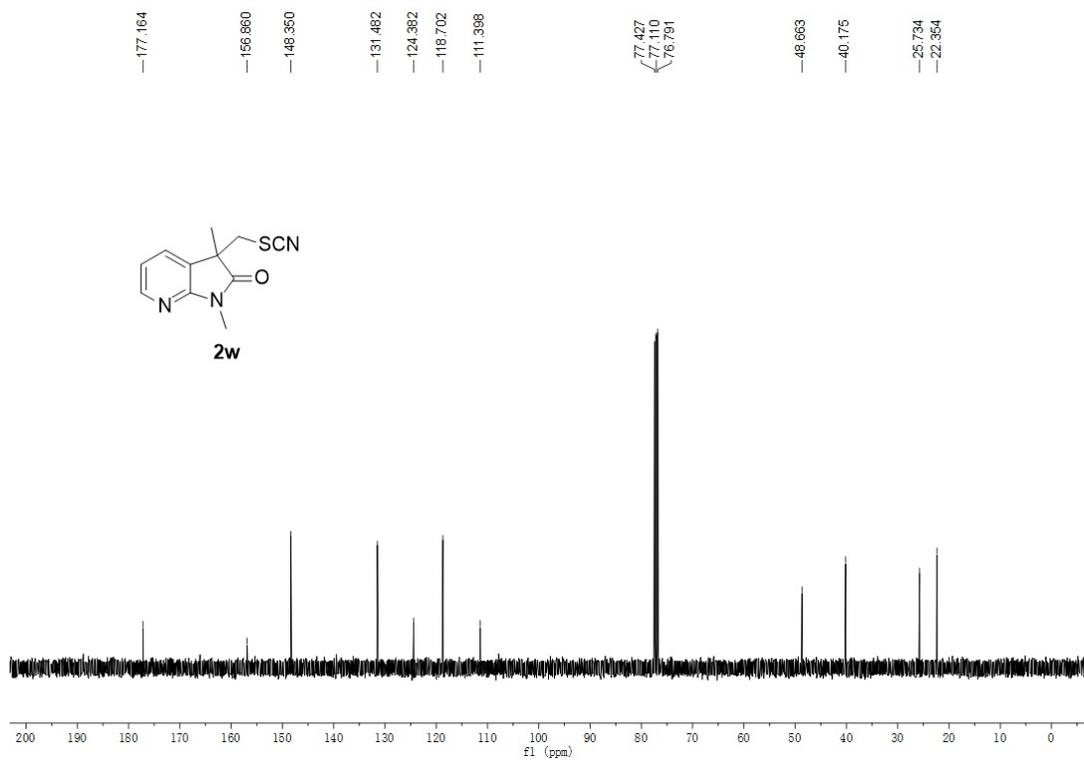
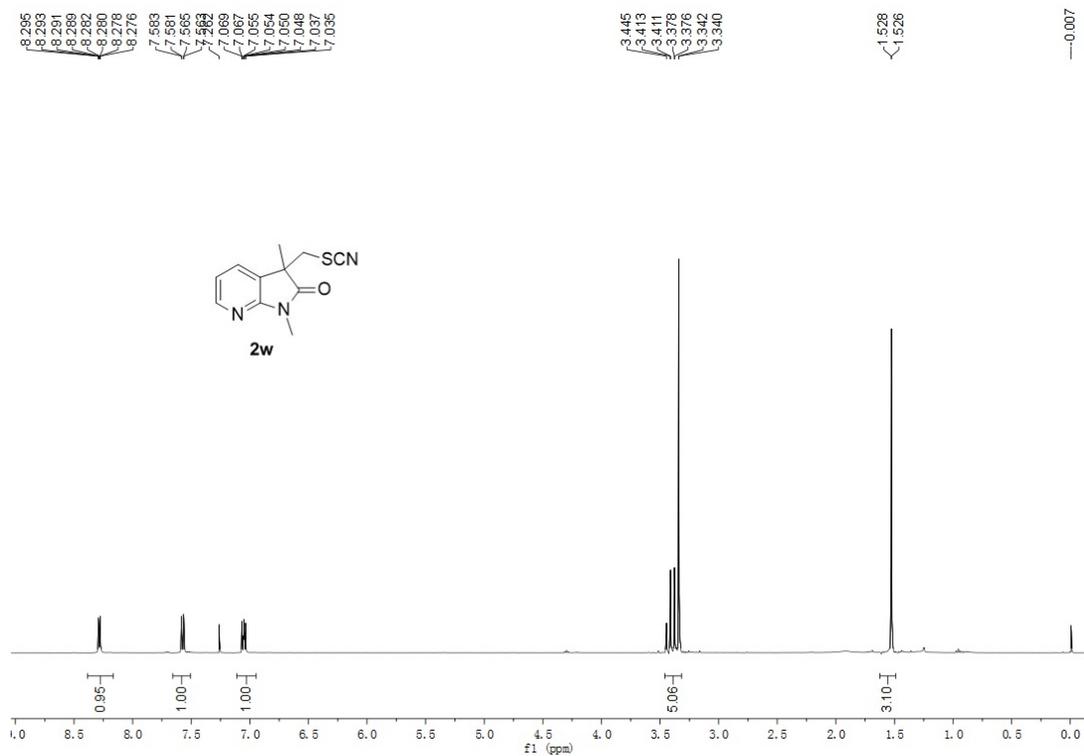


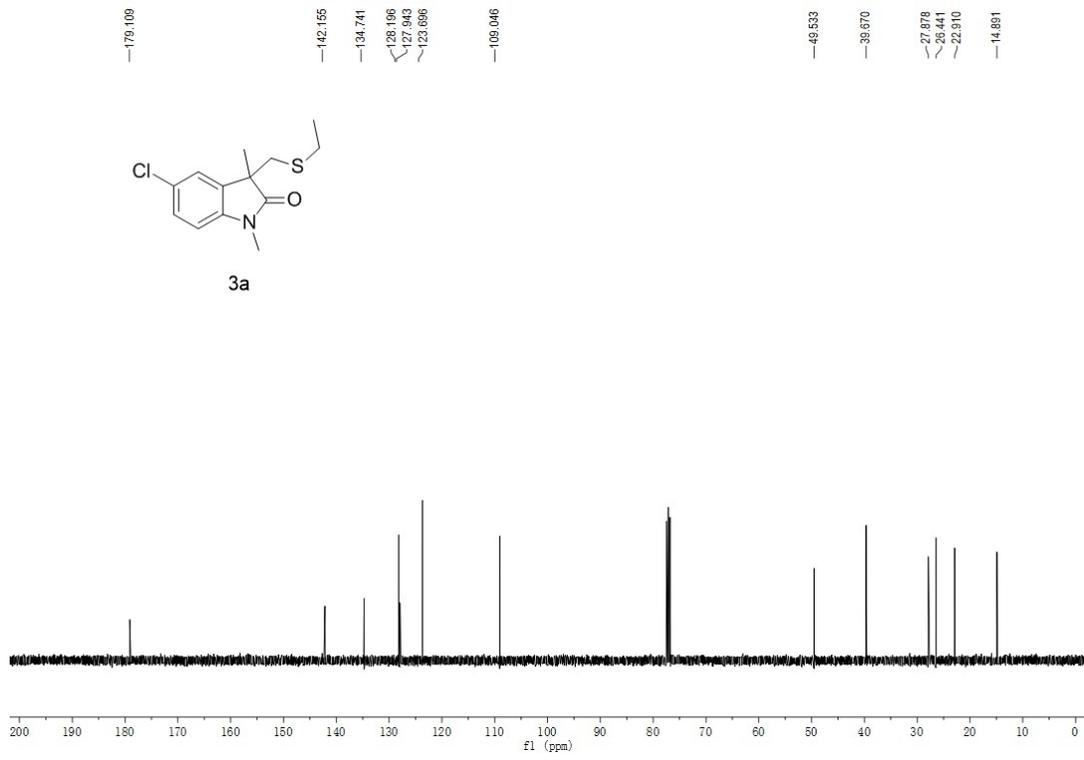
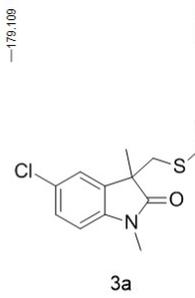
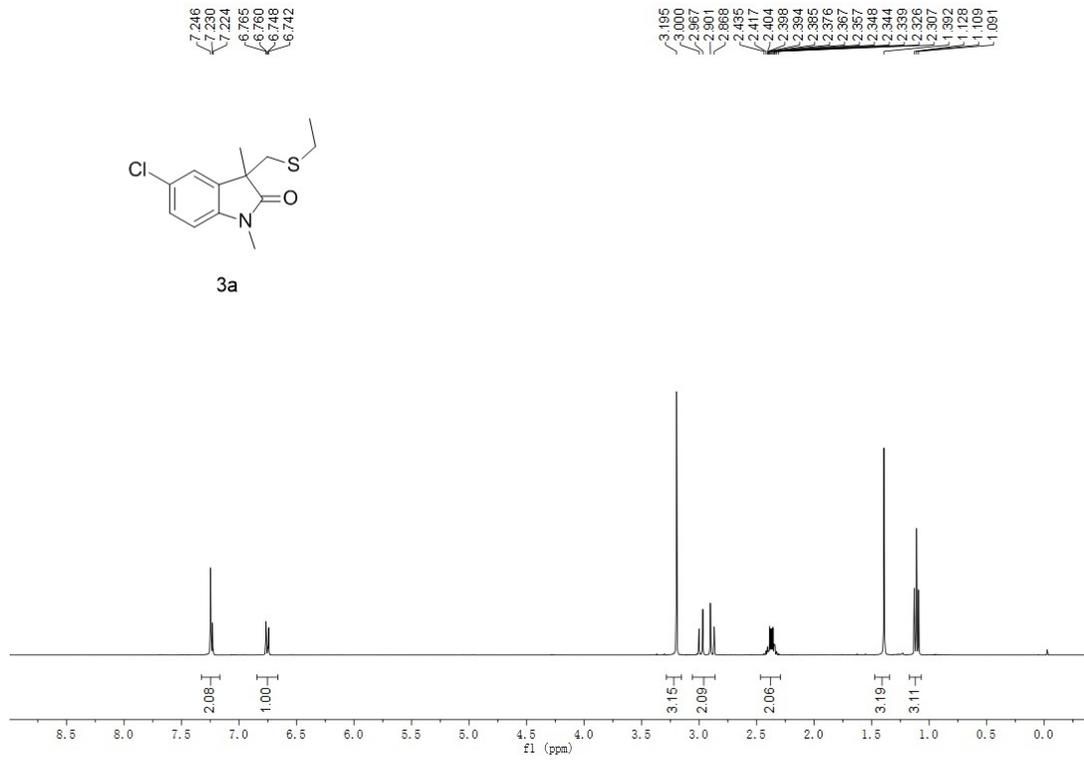
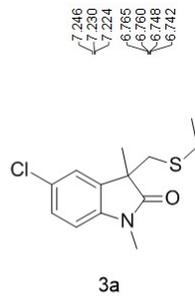
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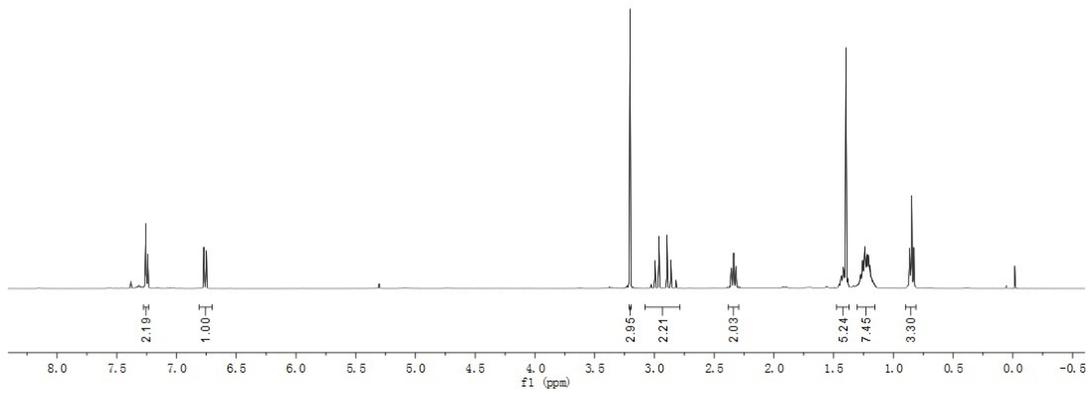
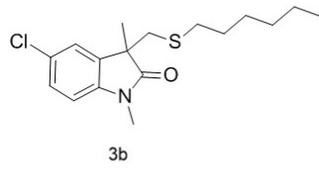
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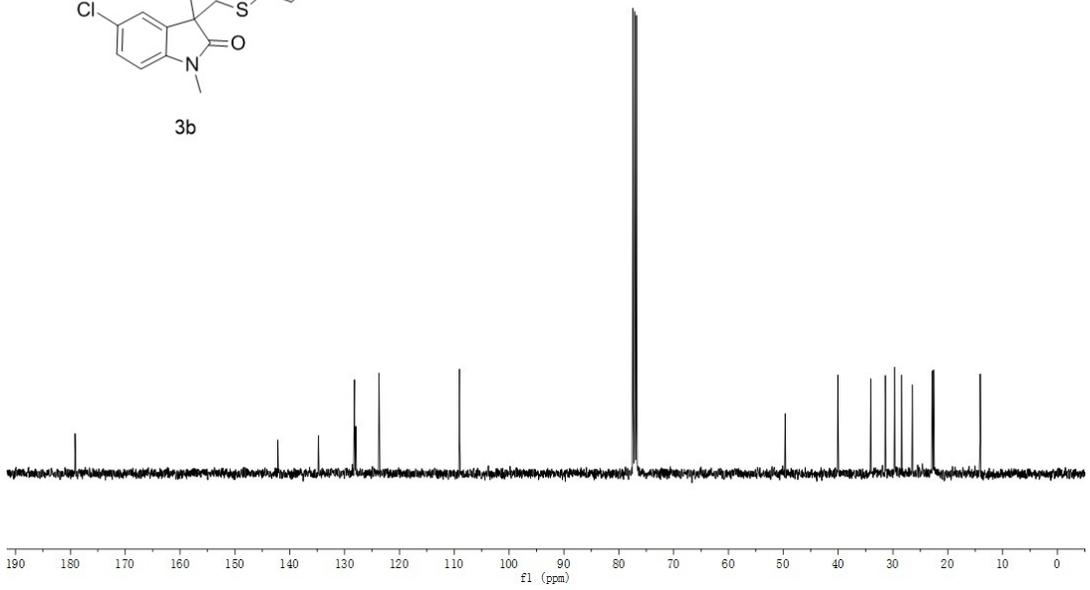
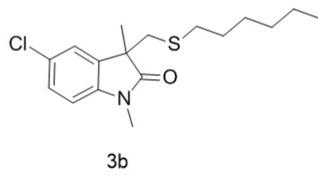
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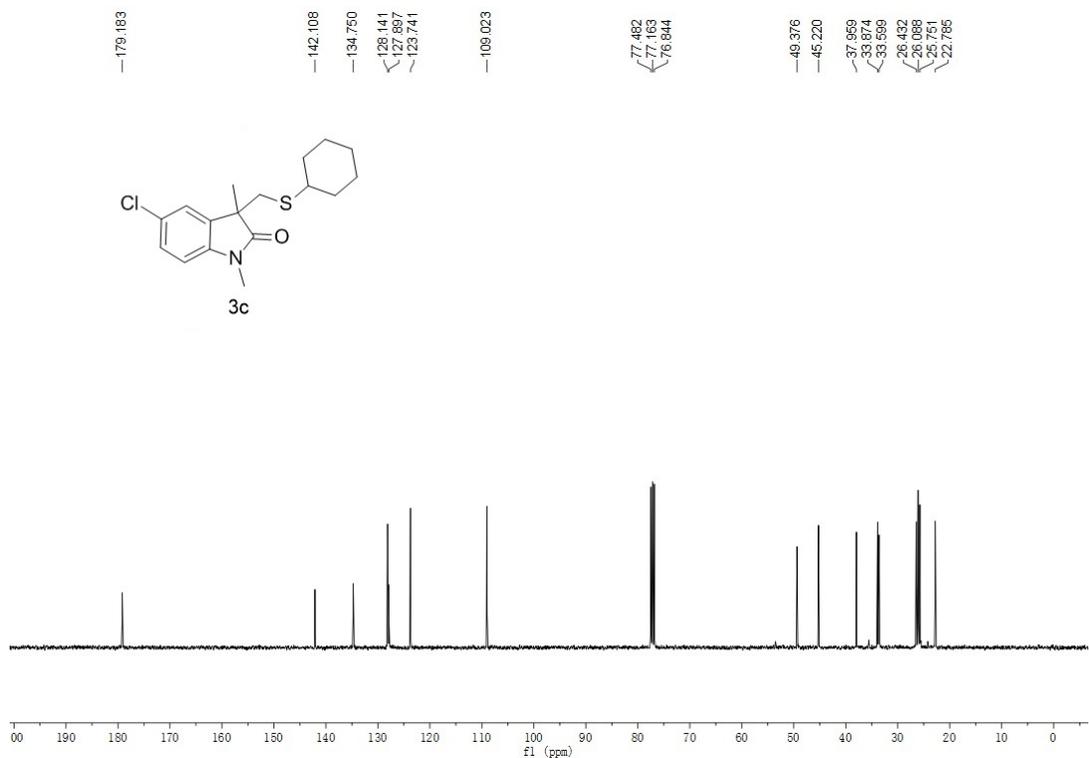
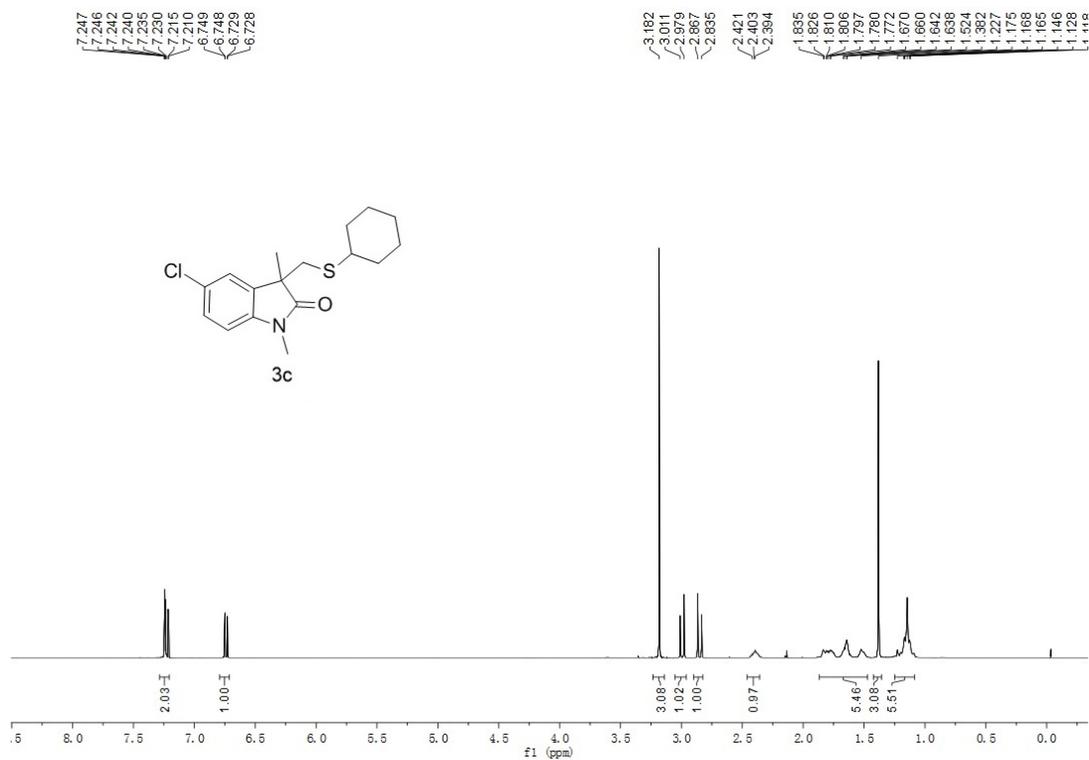
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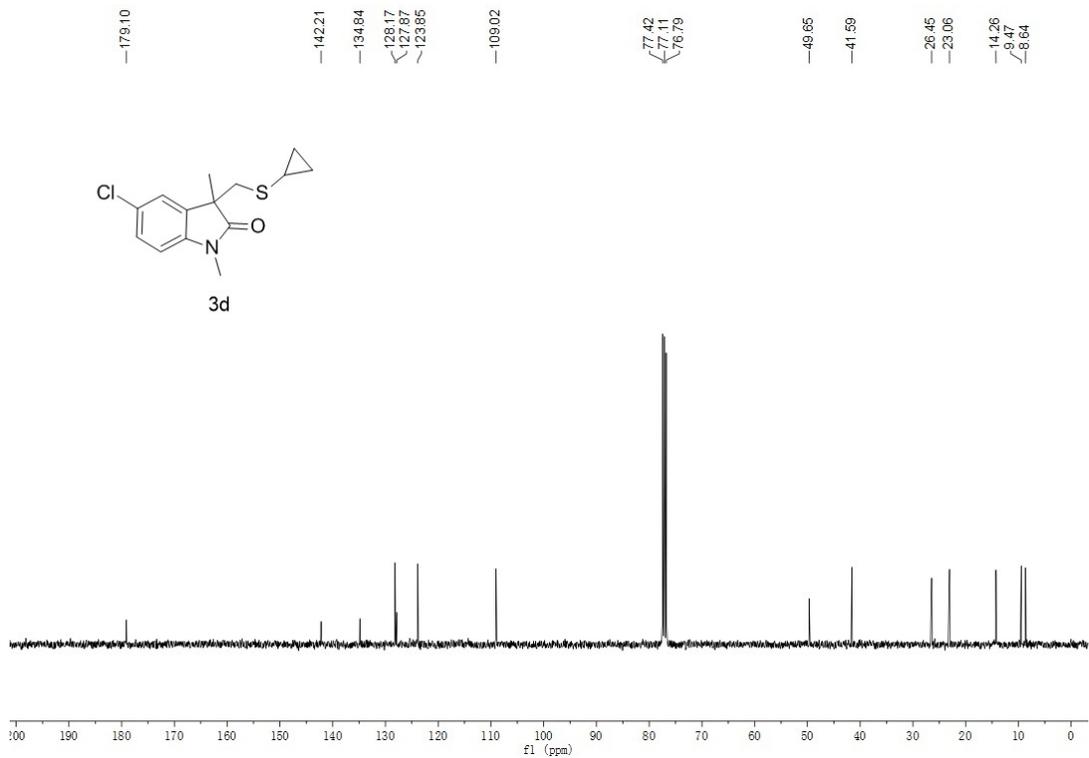
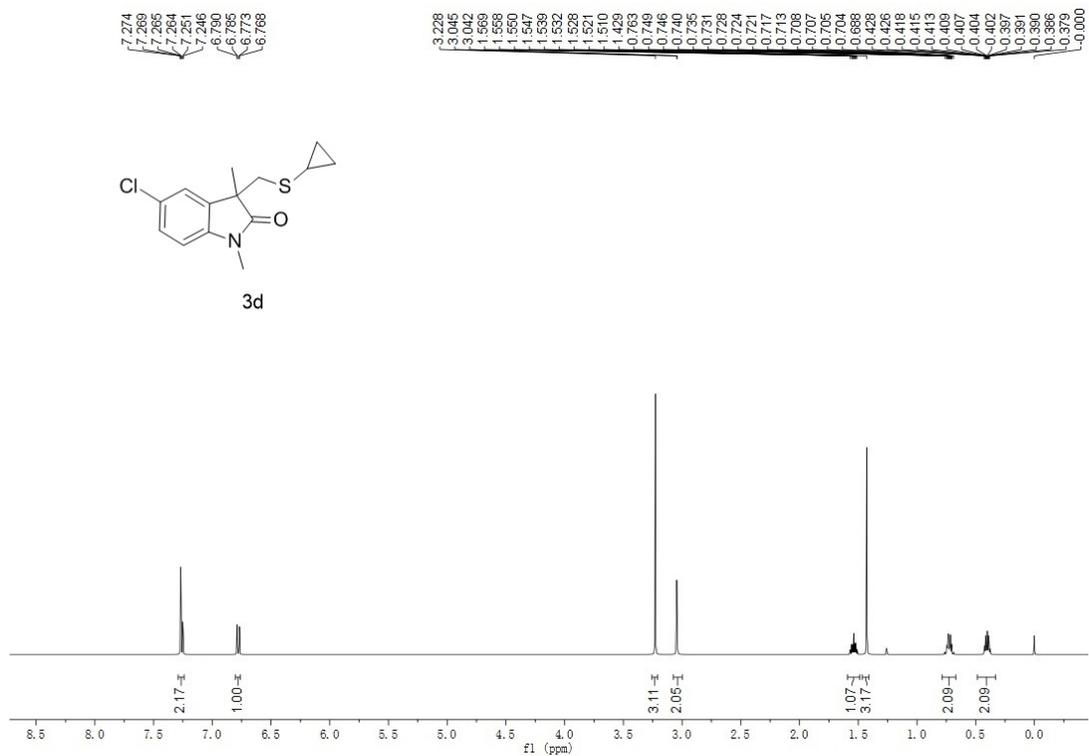
-22.866

-22.598

-14.095



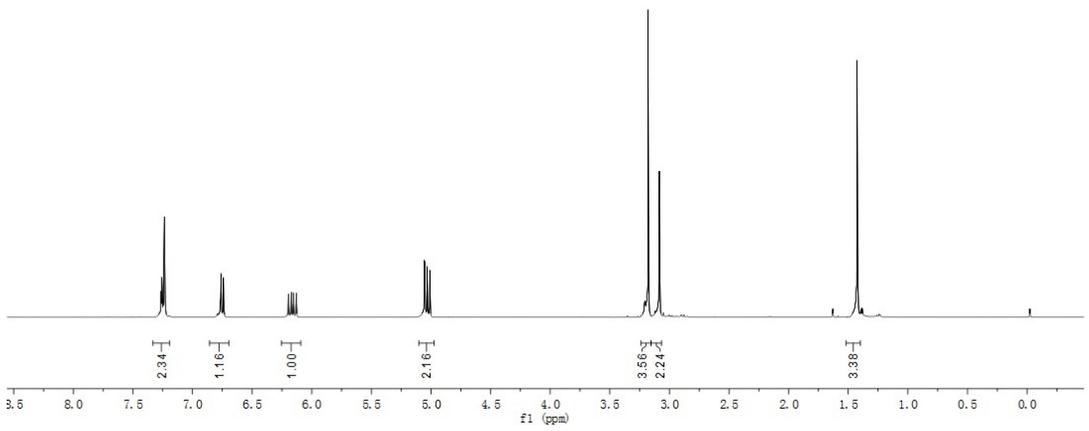
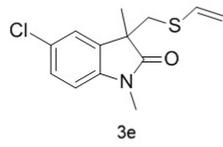




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6.763
6.761
6.743
6.741
6.197
6.172
6.170
6.155
6.153
6.130
6.128
5.064
5.061
5.049
5.036
5.009
5.007

3.179
3.177
3.065

1.425



178.63

142.09

134.16

132.73

128.37

128.06

123.95

112.40

109.12

49.22

40.13

26.49

22.67

