Supplementary Information for

Electrochemical oxidative regio- and stereo-selective thio(seleno)cyanation of enamides and mechanistic insights

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List

1. General information……....S1

2. Preparation and characterizations of compounds 3aa-w, 5aa-i, 6-11……S1-19

3. Current efficiency of reaction with representative substrates……S19

4. Procedure for cyclic voltammetry (CV)…….....S20

5. Gram-Scale synthesis of 3aa…….....S20

6. X-ray Crystallographic Data of 11…….....S21-26

7. References……..…….....S26

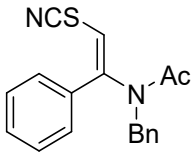
8. ^{1}H NMR and ^{13}C NMR spectra of compounds……S27-67

1. General information

All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$. TMS was used as an internal reference and *J* values are given in Hz. HR-MS were obtained on a Bruker micrOTOF-Q II spectrometer. PE is petroleum ether (60-90 ^{o}C). All enamides (**1a-y, 10**) are known compounds, they were prepared according to the reported procedures.[1] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

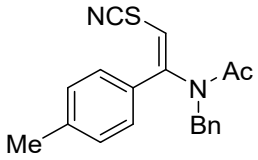
2. Preparation and characterizations of compounds 3aa-w, 5aa-i, 6-11

In 15 mL three-necked round bottom flask, with carbon plate anode (10 mm × 10 mm × 0.3 mm), iron plate cathode (10 mm × 10 mm × 0.3 mm), a mixture of enamides (**1a-y**, 0.4 mmol), NH_4SCN or KSeCN (**2a** or **4a**, 1.6 mmol, 4 equiv.), $LiBF_4$ (113 mg, 3 equiv.) in CH_3CN/HOAc (6 mL, 3:1) was stirred with constant current of 20 mA at room temperature for 3 h (monitored by TLC). After it was cooled down to room temperature, the mixture was poured into water (15 mL) and was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (2 x 15 mL) and dried over $MgSO_4$. The solvent was removed by vacuum and the residue was purified by column chromatography (20% EtOAc in PE) to give the corresponding products **3aa-w, 5aa-i**.

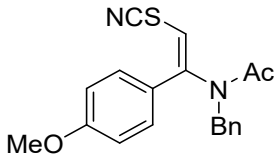


(*E*)-*N*-benzyl-*N*-(1-phenyl-2-thiocyanatovinyl)acetamide (3aa). 108.1 mg (88%); White solid; mp 80-82 °C (lit.[2] 77-79 ^{o}C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.49-7.46 (m, 3H), 7.34-7.28 (m, 3H), 7.24-7.22 (m, 2H), 7.17-7.15 (m, 2H), 5.92 (s, 1H), 4.57 (s, 2H), 2.21 (s, 3H).**^{13}C NMR (100 MHz,**

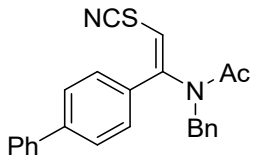
$CDCl_3$) δ 170.1, 145.5, 136.4, 132.2, 130.7, 129.3, 128.6, 128.5, 128.2, 127.8, 112.2, 109.4, 49.8, 22.4.



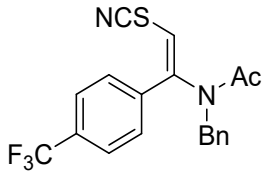
(*E*)-*N*-benzyl-*N*-(2-thiocyanato-1-(*p*-tolyl)vinyl)acetamide (3ab). 110.6 mg (86%); White solid; mp 96-98 °C (lit.[2] 98-100 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.31-7.26 (m, 5H), 7.17-7.15 (m, 2H), 7.13-7.11 (m, 2H), 5.85 (s, 1H), 4.56 (s, 2H), 2.42 (s, 3H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.2, 145.7, 141.3, 136.5, 123.0, 129.3, 128.7, 128.6, 128.2, 127.8, 111.3, 109.6, 49.8, 22.4, 21.4.



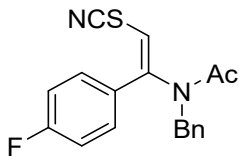
(*E*)-*N*-benzyl-*N*-(1-(4-methoxyphenyl)-2-thiocyanatovinyl)acetamide (3ac). 117.8 mg (87%); White solid; mp 84-86 °C (lit.[2] 85-87 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.34-7.27 (m, 3H), 7.18-7.15 (m, 4H), 6.98-6.96 (m, 2H), 5.80 (s, 1H), 4.56 (s, 2H), 3.86 (s, 3H), 2.19 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.1, 161.2, 145.7, 136.5, 129.8, 128.6, 128.5, 127.7, 124.2, 114.6, 110.0, 109.6, 55.4, 49.8, 22.4.



(*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)-2-thiocyanatovinyl)-*N*-benzylacetamide (3ad). 125.2 mg (82%); White solid; mp 120-122 ℃ (lit.[2] 119-121 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.63-7.61 (m, 2H), 7.50-7.46 (m, 2H), 7.43-7.38 (m, 1H), 7.33-7.29 (m, 5H), 7.21-7.18 (m, 2H), 5.94 (s, 1H), 4.62 (s, 2H), 2.23 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.2, 145.3, 143.6, 139.4, 136.5, 131.0, 129.0, 128.7 (2C), 128.6, 128.2, 127.9, 127.8, 127.1, 112.1, 109.4, 50.0, 22.4.

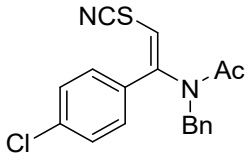


(***E*)-*N*-benzyl-*N*-(2-thiocyanato-1-(4-(trifluoromethyl)phenyl)vinyl)acetamide (3ae)**[2]**.** 84.2 mg (56%); Yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.37-7.30 (m, 5H), 7.16-7.13 (m, 2H), 6.07 (s, 1H), 4.59 (s, 2H), 2.22 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 144.3, 136.1, 136.0, 132.5 (q, *J* = 32.9 Hz), 128.8, 128.7, 128.6, 128.1, 126.3 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 271.3 Hz), 114.2, 108.8, 50.2, 22.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.99.

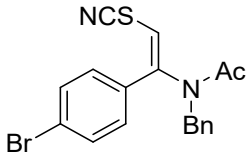


(*E*)-*N*-benzyl-*N*-(1-(4-fluorophenyl)-2-thiocyanatovinyl)acetamide (3af). 99.1 mg (76%); White solid; mp 48-50 ℃ (lit.[2] 46-48 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.34-7.28 (m, 3H), 7.25-7.21 (m, 2H), 7.18-7.13 (m,

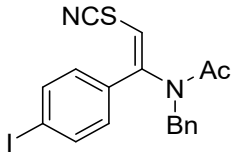
4H), 5.93 (s, 1H), 4.56 (s, 2H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 164.6 (d, *J* = 251.5 Hz), 144.9, 136.3, 130.4 (d, *J* = 8.6 Hz), 128.6, 128.5, 128.3 (d, *J* = 3.3 Hz), 127.9, 116.6 (d, *J* = 21.9 Hz), 112.0, 109.1, 49.9, 22.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -107.85.



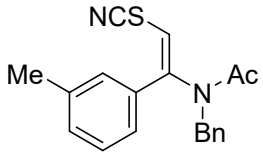
(*E*)-*N*-benzyl-*N*-(1-(4-chlorophenyl)-2-thiocyanatovinyl)acetamide (3ag). 102.9 mg (75%); Yellow solid; mp 90-92 °C (lit.[2] 90-92 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.34-7.29 (m, 3H), 7.18-7.13 (m, 4H), 5.95 (s, 1H), 4.57 (s, 2H), 2.19 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 144.7, 136.8, 136.2, 130.7, 129.6, 129.5, 128.7, 128.6, 127.9, 112.6, 109.0, 50.0, 22.4.



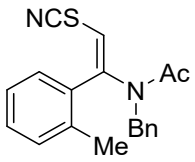
(*E*)-*N*-benzyl-*N*-(1-(4-bromophenyl)-2-thiocyanatovinyl)acetamide (3ah). 105.7 mg (68%); Yellow solid; mp 89-91 °C (lit.[2] 91-93 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.33-7.29 (m, 3H), 7.14 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.11-7.08 (m, 2H), 5.96 (s, 1H), 4.57 (s, 2H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 144.7, 136.2, 132.6, 131.2, 129.7, 128.7, 128.6, 127.9, 125.1, 112.7, 109.0, 50.0, 22.4.



(*E*)-*N*-benzyl-*N*-(1-(4-iodophenyl)-2-thiocyanatovinyl)acetamide (3ai). 106.4 mg (61%); Yellow solid; mp 96-98 °C (lit.[2] 98-100 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.33-7.28 (m, 3H), 7.15-7.13 (m, 2H), 6.96-6.94 (m, 2H), 5.95 (s, 1H), 4.56 (s, 2H), 2.19 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 144.8, 138.5, 136.2, 131.8, 129.7, 128.7, 128.6, 127.9, 112.7, 109.0, 97.1, 50.0, 22.4.

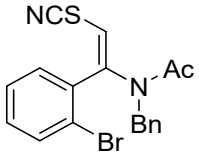


(*E*)-*N*-benzyl-*N*-(2-thiocyanato-1-(m-tolyl)vinyl)acetamide (3aj). 115.2 mg (89%); White solid; mp 94-96 °C (lit.[2] 93-95 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.37-7.27 (m, 5H), 7.18-7.16 (m, 2H), 7.04-6.99 (m, 2H), 5.90 (s, 1H), 4.57 (s, 2H), 2.39 (s, 3H), 2.21 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.3, 145.6, 139.4, 136.5, 132.2, 131.6, 129.1, 128.7, 128.6, 128.5, 127.8, 125.5, 112.1, 109.6, 49.9, 22.4, 21.4.

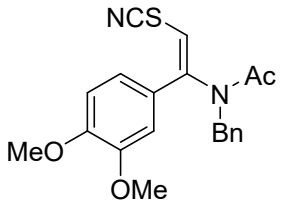


(*E*)-*N*-benzyl-*N*-(2-thiocyanato-1-(*o*-tolyl)vinyl)acetamide (3ak). 103.0 mg (80%); White solid; mp 92-94 °C (lit.[2] 93-95 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.39-7.34 (m, 1H), 7.32-7.22 (m, 5H), 7.09-7.07 (m, 2H), 7.03

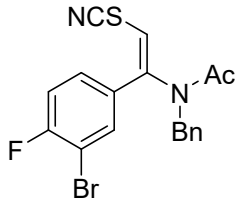
(d, *J* = 3 Hz, 1H), 6.13 (s, 1H), 4.50 (s, 2H), 2.35 (s, 3H), 2.18 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.3, 146.0, 137.0, 136.6, 131.4, 131.4, 130.5, 129.6, 128.6, 127.6, 127.5, 126.5, 110.7, 109.8, 49.5, 22.8, 19.4.



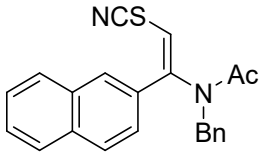
(*E*)-*N*-benzyl-*N*-(1-(2-bromophenyl)-2-thiocyanatovinyl)acetamide (3al)[2]**.** 131.8 mg (85%); Yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.67-7.65 (m, 1H), 7.38-7.31 (m, 2H), 7.32-7.26 (m, 3H), 7.14-7.09 (m, 3H), 6.17 (s, 1H), 4.56 (s, 2H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.6, 146.2, 136.5, 134.0, 132.9, 131.8, 131.7, 128.6, 127.8, 127.7, 127.5, 122.9, 111.6, 109.5, 50.1, 22.9.



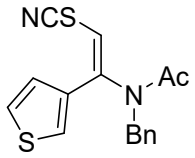
(*E*)-*N*-benzyl-*N*-(1-(3,4-dimethoxyphenyl)-2-thiocyanatovinyl)acetamide (3am). 93.6 mg (64%); Yellow solid; mp 128-130 ℃ (lit.[2] 129-131 ℃); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.34-7.28 (m, 3H), 7.20-7.18 (m, 2H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.81 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.58 (d, *J* = 2.1 Hz, 1H), 5.90 (s, 1H), 4.63 (s, 2H), 3.93 (s, 3H), 3.80 (s, 3H), 2.18 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.3, 150.9, 149.5, 145.7, 136.6, 128.7, 128.6, 127.8, 124.7, 121.8, 111.1, 110.3 (2C), 109.7, 56.0, 55.9, 50.3, 22.5.



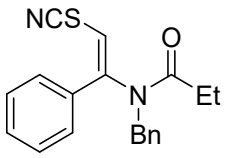
(*E*)-*N*-benzyl-*N*-(1-(3-bromo-4-fluorophenyl)-2-thiocyanatovinyl)acetamide (3an). 95.3 mg (59%); White solid; mp 144-146 °C (lit.[2] 144-146 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.39 (dd, *J* = 6.3, 2.2 Hz, 1H), 7.36-7.30 (m, 3H), 7.23-7.19 (m, 1H), 7.19-7.16 (m, 1H), 7.16-7.13 (m, 2H), 5.99 (s, 1H), 4.58 (s, 2H), 2.21 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 160.1 (d, *J* = 252.3 Hz), 143.6, 136.1, 133.4, 129.9 (d, *J* = 3.7 Hz), 129.3 (d, *J* = 8.2 Hz), 128.8, 128.6, 128.1, 117.4 (d, *J* = 22.9 Hz), 113.3, 110.6 (d, *J* = 21.6 Hz), 108.7, 50.2, 22.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -101.94.



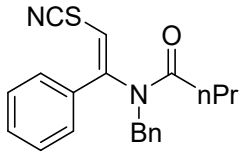
(*E*)-*N*-benzyl-*N*-(1-(naphthalen-2-yl)-2-thiocyanatovinyl)acetamide (3ao)[2]**.** 93.3 mg (65%); Yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.6 Hz, 1H), 7.90-7.84 (m, 2H), 7.67 (s, 1H), 7.62-7.56 (m, 2H), 7.32-7.29 (m, 4H), 7.19-7.17 (m, 2H), 6.01 (s, 1H), 4.62 (s, 2H), 2.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.3, 145.6, 136.5, 133.9, 132.8, 129.6, 129.4, 128.8, 128.7, 128.6, 128.4, 127.9, 127.8 (2C), 127.3, 124.2, 112.4, 109.5, 50.0, 22.5.



(*E*)-*N*-benzyl-*N*-(2-thiocyanato-1-(thiophen-3-yl)vinyl)acetamide (3ap). 95.1 mg (76%); White solid; mp 60-62 ℃ (lit.[2] 60-62 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.44 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.37-7.36 (m, 1H), 7.34-7.29 (m, 3H), 7.21-7.19 (m, 2H), 7.07 (dd, *J* = 5.1, 1.4 Hz, 1H), 5.84 (s, 1H), 4.64 (s, 2H), 2.12 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.9, 140.4, 136.5, 134.1, 128.8, 128.6, 127.9, 127.8, 127.7, 126.3, 112.0, 109.1, 50.3, 22.2.

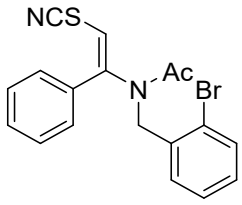


(*E*)-*N*-benzyl-*N*-(1-phenyl-2-thiocyanatovinyl)propionamide (3aq)[2]. 97.7 mg (76%); Yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.48-7.45 (m, 3H), 7.34-7.28 (m, 3H), 7.23-7.20 (m, 2H), 7.19-7.16 (m, 2H), 5.91 (s, 1H), 4.58 (s, 2H), 2.44 (q, *J* = 7.4 Hz, 2H), 1.20 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.7, 145.2, 136.6, 132.4, 130.6, 129.3, 128.7, 128.6, 128.2, 127.7, 112.0, 109.5, 50.1, 27.6, 9.9.

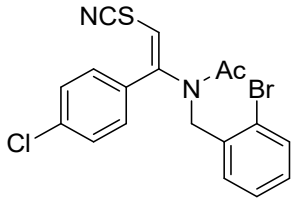


(*E*)-*N*-benzyl-*N*-(1-phenyl-2-thiocyanatovinyl)butyramide (3ar)[2]. 101.7 mg (76%); Yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.49-7.45 (m,

3H), 7.34-7.28 (m, 3H), 7.24-7.21 (m, 2H), 7.18-7.16 (m, 2H), 5.88 (s, 1H), 4.58 (s, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.74 (h, *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.9, 145.3, 136.7, 132.5, 130.7, 129.3, 128.7, 128.6, 128.2, 127.8, 111.9, 109.5, 50.0, 36.1, 19.1, 13.8.

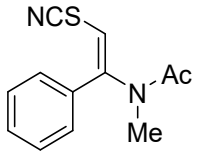


(*E*)-*N*-(2-bromobenzyl)-*N*-(1-phenyl-2-thiocyanatovinyl)acetamide (3as). 109.8 mg (71%); Yellow solid; mp 142-144 °C (lit.[2] 140-142 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.52 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.47-7.44 (m, 3H), 7.27 (td, *J* = 7.5, 1.3 Hz, 1H), 7.21-7.18 (m, 3H), 7.17-7.13 (m, 1H), 6.09 (s, 1H), 4.77 (s, 2H), 2.22 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.4, 145.2, 135.5, 133.0, 132.2, 130.8, 130.7, 129.4, 129.2, 128.2, 127.7, 123.9, 112.8, 109.5, 49.8, 22.4.

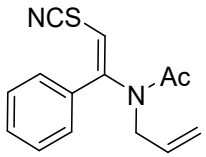


(*E*)-*N*-(2-bromobenzyl)-*N*-(1-(4-chlorophenyl)-2-thiocyanatovinyl)acetamide (3at). 98.7 mg (58%); White solid; mp 140-142 °C (lit.[2] 141-143 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.53 (d, *J* = 8, 1H), 7.44-7.42 (m, 2H), 7.29-7.25 (m, 1H), 7.22-7.13 (m, 4H), 6.11 (s, 1H), 4.76 (s, 2H), 2.21 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.2, 144.2,

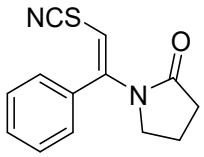
136.8, 135.3, 133.0, 130.8, 130.6, 129.6(2C), 129.5, 127.8, 123.9, 113.3, 109.0, 49.8, 22.4.



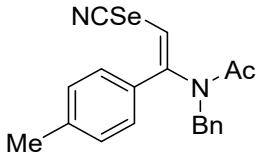
(*E*)-*N*-methyl-*N*-(1-phenyl-2-thiocyanatovinyl)acetamide (3au). 83.7 mg (90%); Brown solid; mp 100-102 °C (lit.[2] 102-104 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.49-7.47 (m, 3H), 7.31-7.28 (m, 2H), 6.27 (s, 1H), 3.03 (s, 3H), 2.13 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.5, 147.6, 132.5, 130.6, 129.3, 128.0, 110.5, 109.6, 35.6, 22.2.



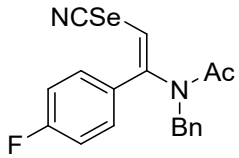
(*E*)-*N*-allyl-*N*-(1-phenyl-2-thiocyanatovinyl)acetamide (3av). 68.0 mg (66%); White solid; mp 60-62 °C (lit.[2] 59-61 °C); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.49-7.46 (m, 3H), 7.30-7.27 (m, 2H), 6.24 (s, 1H), 5.84-5.74 (m, 1H), 5.18 (dq, *J* = 10.2, 1.2 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.4 Hz, 1H), 4.02 (dt, *J* = 6.4, 1.3 Hz, 2H), 2.15 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.9, 145.9, 132.6, 132.2, 130.6, 129.2, 128.1, 118.8, 111.6, 109.6, 49.7, 22.4.



(*E*)-1-(1-phenyl-2-thiocyanatovinyl)pyrrolidin-2-one (3aw). 73.2 mg (75%); Yellow solid; mp 52-54 ℃; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.47-7.44 (m, 3H), 7.25-7.23 (m, 2H), 6.88 (s, 1H), 3.35 (t, *J* = 7.1 Hz, 2H), 2.56 (t, *J* = 8.1 Hz, 2H), 2.01 (p, *J* = 7.6 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.6, 143.8, 132.8, 129.7, 128.9, 128.3, 111.1, 101.7, 49.2, 32.1, 18.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{13}H_{13}N_2OS^+$ 245.0743; Found 245.0745.

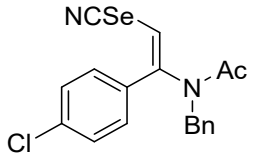


(*E*)-*N*-benzyl-*N*-(2-selenocyanato-1-(*p*-tolyl)vinyl)acetamide (5aa). 102.7 mg (70%); White solid; mp. 108-110 ℃ **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.33-7.26 (m, 5H), 7.18-7.15 (m, 2H), 7.05-7.03 (m, 2H), 6.20 (s, 1H), 4.57 (s, 2H), 2.41 (s, 3H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.3, 145.4, 141.3, 136.6, 130.7, 130.2, 128.6, 128.5, 127.7, 127.4, 110.2, 100.4, 49.8, 22.4, 21.4. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2OSe^+$ 371.0657; Found 371.0657.

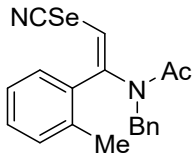


(*E*)-*N*-benzyl-*N*-(1-(4-fluorophenyl)-2-selenocyanatovinyl)acetamide (5ab). 95.9 mg (64%); Yellow solid; mp 53-55 ℃; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.33-7.28 (m, 3H), 7.17-7.13 (m, 6H), 6.27 (s, 1H), 4.57 (s, 2H), 2.21 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.2, 163.7 (d, *J* = 251.5

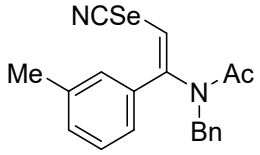
Hz), 144.7, 136.3, 129.8 (d, J = 8.6Hz), 128.7, 128.6, 127.8, 116.8 (d, J = 22.0 Hz), 110.8, 99.9, 93.0, 49.9, 22.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -107.73. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{18}H_{16}FN_2OSe^+$ 375.0406; Found 375.0407.



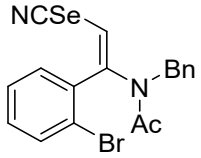
(*E*)-*N*-benzyl-*N*-(1-(4-chlorophenyl)-2-selenocyanatovinyl)acetamide (5ac). 65.4 mg (42%)**;** Yellow solid; mp 103-105 ℃; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.46-7.44 (m, 2H), 7.34-7.29 (m, 3H), 7.16-7.13 (m, 2H), 7.11-7.08 (m, 2H), 6.29 (s, 1H), 4.58 (s, 2H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.1, 144.7, 137.0, 136.3, 132.2, 129.9, 129.0, 128.7, 128.6, 127.9, 111.3, 99.8, 50.0, 22.5. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{18}H_{16}ClN_2OSe^+$ 391.0111; Found 391.0115.



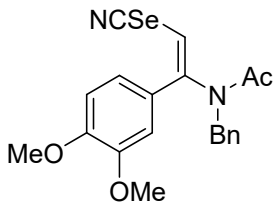
(*E*)-*N*-benzyl-*N*-(2-selenocyanato-1-(*o*-tolyl)vinyl)acetamide (5ad). 140.5 mg (95%); White solid; mp 85-87 ℃;**^{1}H NMR (400MHz, $CDCl_3$)** δ 7.39-7.35 (m, 1H), 7.32-7.21 (m, 5H), 7.09-7.07 (m, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.43 (s, 1H), 4.51 (s, 2H), 2.36 (s, 3H), 2.21 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.4, 145.5, 136.7, 136.6, 132.6, 131.8, 130.7, 129.5, 128.6, 127.5, 127.4, 126.6, 109.5, 100.4, 49.5, 22.8, 19.4. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2OSe^+$ 371.0657; Found 371.0653.



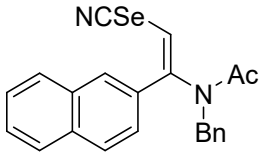
(*E*)-*N*-benzyl-*N*-(2-selenocyanato-1-(*m*-tolyl)vinyl)acetamide (5ae). 111.0 mg (75%); White solid; mp 80-82 ℃; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.38-7.28 (m, 5H), 7.19-7.16 (m, 2H), 6.94-6.92 (m, 2H), 6.25 (s, 1H), 4.58 (s, 2H), 2.39 (s, 3H), 2.21 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.2, 145.4, 139.7, 136.6, 133.7, 131.6, 129.4, 128.6, 128.5, 127.8, 127.7, 124.7, 111.0, 100.4, 49.9, 22.4, 21.4. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2OSe^+$ 371.0657; Found 371.0655.



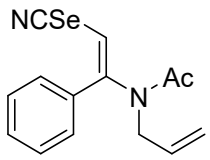
(*E*)-*N*-benzyl-*N*-(1-(2-bromophenyl)-2-selenocyanatovinyl)acetamide (5af). 160.5 mg (92%); yellow solid; mp 106-108 ℃; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.66 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.38-7.32 (m, 2H), 7.31-7.26 (m, 3H), 7.15-7.13 (m, 2H), 7.11 (dd, *J* = 7.3, 2.1 Hz, 1H), 6.49 (s, 1H), 4.57 (s, 2H), 2.35 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.6, 146.3, 136.5, 134.2, 134.0, 131.9, 131.2, 128.5, 128.0, 127.8, 127.5, 122.8, 110.4, 100.3, 50.2, 22.8. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{18}H_{16}BrN_2OSe^+$ 434.9606; Found 434.9608.



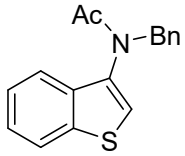
(*E*)-*N*-benzyl-*N*-(1-(3,4-dimethoxyphenyl)-2-(selenocyanatovinyl)acetamide (5ag). 154.9 mg (93%); Yellow solid; mp 140-142 ℃; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.34-7.29 (m, 3H), 7.21-7.19 (m, 2H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.50 (d, *J* = 2.1 Hz, 1H), 6.23 (s, 1H), 4.64 (s, 2H), 3.93 (s, 3H), 3.79 (s, 3H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.4, 151.0, 149.9, 145.4, 136.7, 128.8, 128.6, 127.8, 126.5, 120.9, 111.2, 109.6, 109.5, 100.6, 56.0, 56.0, 50.4, 22.6. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{20}H_{21}N_2O_3Se^+$ 417.0712; Found 417.0716.



(*E*)-*N*-benzyl-*N*-(1-(naphthalen-2-yl)-2-selenocyanatovinyl)acetamide (5ah).78.7 mg (49%); Yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.6 Hz, 1H), 7.92-7.89 (m, 1H), 7.86-7.84 (m, 1H), 7.62-7.59 (m, 2H), 7.57 (s, 1H), 7.33-7.30 (m, 3H), 7.26-7.23 (m, 1H), 7.20-7.17 (m, 2H), 6.36 (s, 1H), 4.63 (s, 2H), 2.27 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.4, 145.4, 136.6, 134.0, 132.9, 131.2, 129.9, 128.7, 128.3, 128.0 (2C), 127.9, 127.8, 127.4, 123.6, 111.5, 100.3, 92.0, 50.1, 22.6. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{22}H_{19}N_2OSe^+$ 407.0657; Found 407.0655.



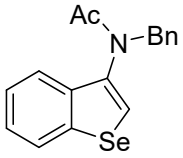
(*E*)-*N*-allyl-*N*-(1-phenyl-2-selenocyanatovinyl)acetamide (5ai). 37.0 mg (30%); Yellow solid; mp 52-54 ℃; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.49-7.48 (m, 3H), 7.23-7.20 (m, 2H), 6.56 (s, 1H), 5.85-5.75 (m, 1H), 5.18 (dd, *J* = 10.1, 1.5 Hz, 1H), 5.05 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.03 (dt, *J* = 6.3, 1.2 Hz, 2H), 2.16 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 145.7, 134.1, 132.4, 130.7, 129.5, 127.5, 118.7, 110.4, 100.4, 49.7, 22.4. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{14}H_{15}N_2OSe^+$ 307.0344; Found 307.0347.



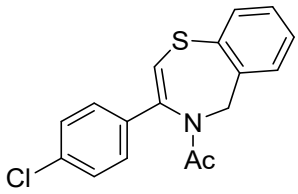
Preparation of product 6 from 3al: To a mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), PPh_3 (13.1 mg, 0.05 mmol, 10 mol%), and Cs_2CO_3 (325.8 mg, 1 mmol, 2 equiv.) was added a solution of **3al** (193.6 mg, 0.5 mmol) in 2 mL DMF under nitrogen atmosphere. After stirring at 100 °C overnight, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography over silica gel (petroleum ether/EtOAc, 10:1). The product of **6** was isolated as yellow oil in 50% (70.9 mg) yield.

***N*-(benzo[*b*]thiophen-3-yl)-*N*-benzylacetamide (6)**[2]**. ^{1}H NMR (400MHz, $CDCl_3$)** δ 7.86-7.82 (m, 1H), 7.53-7.49 (m, 1H), 7.42-7.38 (m, 2H), 7.26-7.20 (m, 5H), 6.93 (s, 1H), 5.51 (d, *J* = 14.1 Hz, 1H), 4.27 (d, *J* = 14.1 Hz, 1H), 1.89 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1, 138.6,

137.6, 135.1, 134.8, 128.9, 128.3, 127.5, 125.2, 124.9, 124.2, 123.3, 120.7, 51.4, 22.0.



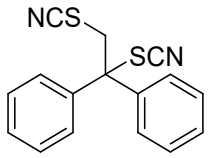
***N*-(benzo[*b*]selenophen-3-yl)-*N*-benzylacetamide (7).** Following the procedure described above for the preparation of **6** from **3al**, product **7** was obtained as brown oil in 46% (75.7 mg) yield; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.43-7.34 (m, 3H), 7.26-7.20 (m, 5H), 5.55 (d, *J* = 14.1 Hz, 1H), 4.17 (d, *J* = 14.1 Hz, 1H), 1.88 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.0, 139.4, 137.7, 137.4, 136.6, 129.0, 128.3, 127.4, 127.2, 126.3, 125.5, 125.1, 122.7, 51.0, 21.9**. HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{17}H_{16}NOSe^+$ 330.0392; Found 330.0396.



Preparation of product 8 from 3at: To a mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), PPh_3 (13.1 mg, 0.05 mmol, 10 mol%), and Cs_2CO_3 (325.8 mg, 1 mmol, 2 equiv.) was added a solution of **3at** (209.5 mg, 0.5 mmol) in 2 mL DMF under nitrogen atmosphere. After stirring at 100 °C overnight, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine. The combined organic layers were dried over

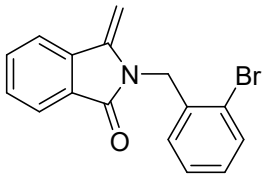
anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography over silica gel (petroleum ether/EtOAc, 10:1). The product **8** was isolated as yellow solid in 35% yield (55.1 mg);

1-(3-(4-chlorophenyl)benzo[*f*][1,4]thiazepin-4(5*H*)-yl)ethan-1-one (8)[2]**. ^{1}H NMR (400MHz, $CDCl_3$)** δ 7.48-7.46 (m, 1H), 7.35-7.32 (m, 2H), 7.29-7.26 (m, 3H), 7.21-7.17 (m, 2H), 6.06 (s, 1H), 4.82 (s, 2H), 1.63 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.7, 140.3, 138.4, 137.6, 133.7, 132.3, 131.4, 129.3, 127.8, 127.7, 126.2, 125.7, 114.5, 53.1, 23.9.

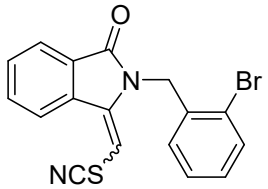


In 15 mL three-necked round bottom flask with carbon plate anode (10 mm × 10 mm × 0.3 mm), iron plate cathode (10 mm × 10 mm × 0.3 mm), a mixture of enamides (**1a**, 100 mg, 0.4 mmol), NH_4SCN (**2a**, 122 mg, 1.6 mmol, 4 equiv.), $LiBF_4$ (113 mg, 3 equiv.), DPE (216 mg, 1.2 mmol, 3 equiv.) in CH_3CN/HOAc (6 mL, 3:1) was stirred with constant current of 20 mA at room temperature for 3 h (monitored by TLC). Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under vacuo. The residue was purified by column chromatography over silica gel (petroleum ether/EtOAc, 3:1). The adduct product **9** of DPE and SCN radical was isolated as yellow oil in 35% yield. Trace amount of corresponding **3aa** was detected.

(1,2-dithiocyanatoethane-1,1-diyl)dibenzene (9)[3]**. ^{1}H NMR (400MHz, $CDCl_3$)** δ 7.43-7.35 (m, 6H), 7.33-7.30 (m, 4H), 4.00 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.9, 129.0, 129.0, 126.0, 111.1, 72.0, 46.4.

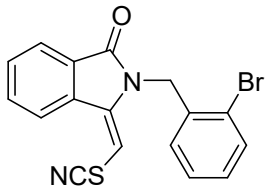


2-(2-bromobenzyl)-3-methyleneisoindolin-1-one (10). White solid; mp 106-108 ℃ (lit.[4] 110 ℃); **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.90 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.63-7.60 (m, 1H), 7.58-7.52 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.1 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.17 (d, *J* = 2.5 Hz, 1H), 5.07 (s, 2H), 4.72 (d, *J* = 2.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.2, 141.2, 136.2, 135.3, 132.7, 132.2, 129.6, 129.0, 128.7, 127.6, 127.5, 123.4, 122.3, 120.0, 90.3, 43.1.



2-(2-bromobenzyl)-3-(thiocyanatomethylene)isoindolin-1-one (11). 51.5mg (35%, *E*:*Z*=10:1); White solid; mp 140-142 ℃; **^{1}H NMR (400MHz, $CDCl_3$)** δ 8.39 (d, *J* = 7.8 Hz, 1H$_{(E)}$), 7.99-7.97 (m, 1H$_{(E)}$), 7.93 (d, *J* = 7.5 Hz, 0.14H$_{(Z)}$), 7.76-7.72 (m, 1H$_{(E)}$), 7.69-7.65 (m, 1.28 H $_{(E+Z)}$), 7.63-7.60 (m, 1.14 H$_{(E+Z)}$), 7.25-7.21 (m, 1.28 H$_{(E+Z)}$), 7.18-7.14 (m, 1.14 H$_{(E+Z)}$), 6.94-6.92 (m, 1H$_{(E)}$), 6.75 (d, *J* = 2 Hz, 0.14H$_{(Z)}$), 6.05 (s, 0.14H$_{(Z)}$), 5.70 (s, 1H$_{(E)}$), 5.32 (s, 0.28H$_{(Z)}$), 5.08 (s, 2H$_{(E)}$). **^{13}C NMR (100 MHz,**

$CDCl_3$) δ ***E* isomer:** 166.3, 144.0, 133.9, 133.6, 133.2, 133.0, 131.2, 129.7, 129.3, 128.0, 127.4, 125.2, 124.3, 122.2, 109.6, 88.1, 43.3; ***Z* isomer:** 167.6, 141.2, 135.9, 134.9, 133.1, 130.8, 129.2, 127.1, 125.9, 124.0, 122.1, 120.0, 85.7, 45.0. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{17}H_{12}BrN_2OS^+$ 370.9848; Found 370.9847.



(*E*)-2-(2-bromobenzyl)-3-(thiocyanatomethylene)isoindolin-1-one (*E* isomer of 11). White solid; mp 140-142 °C;**^{1}H NMR (400MHz, $CDCl_3$)** δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.99-7.97 (m, 1H), 7.77-7.72 (m, 1H), 7.69-7.65 (m, 1H), 7.62-7.59 (m, 1H), 7.25-7.14 (m, 2H), 6.93 (dd, *J* = 7.6, 1.8 Hz, 1H), 5.70 (s, 1H), 5.08 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.3, 144.0, 133.9, 133.6, 133.2, 133.0, 131.2, 129.7, 129.3, 128.0, 127.4, 125.2, 124.3, 122.2, 109.6, 88.1, 43.3. **HRMS (ESI) m/z**: $[M+H]^+$ Calcd for $C_{17}H_{12}BrN_2OS^+$ 370.9848; Found 370.9847.

3. Current efficiency of reaction with representative substrates

Current efficiency (c.e.) is the percentage value that specifies the ratio of Coulombs consumed in forming the chemical products to the total number of Coulombs passed through the cell. It is calculated in the following formula:

$$c.e. = \frac{z * N_p * F}{I * t} \times 100\%$$

z: the number of electrons added to or removed from one product molecule [−]; N_p: number of mols of the product [mol]; *F:* Faraday constant [96485 s·A·mol^{-1}]; I: the current [A]; t: the time [s].

For product **3aa** in Table 2,

$$c.e. = \frac{2 * 3.5 \times 10^{-4}\, mol * 96485\, s \cdot A \cdot mol^{-1}}{2 \times 10^{-2}\, A * 10800\, s} \times 100\% = 31\%$$

For product **5ai** in Table 3,

$$c.e. = \frac{2 * 1.2 \times 10^{-4}\, mol * 96485\, s \cdot A \cdot mol^{-1}}{2 \times 10^{-2}\, A * 10800\, s} \times 100\% = 11\%$$

4. Procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon disk electrode while the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 0.1 M $LiBF_4$ and related compounds (0.01 M) in MeCN was poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 0.10 V/s, ranging from 0 V to 3 V.

5. Gram-Scale synthesis of 3aa

Following the general procedure described, the reaction was carried out at gram-scale in an oven-dried round-bottom flask (250 mL) equipped with carbon plate (3 cm × 3 cm × 0.3 mm) as the anode, iron plate (3 cm × 3 cm × 0.3 mm) as the cathode. A mixture of enamides (**1a**, 5 mmol, 1.26 g), NH_4SCN (**2a** 1.52 g, 4 equiv.), $LiBF_4$ (1.41 g, 3 equiv.) in CH_3CN/HOAc

(80 mL, 3:1) was stirred with constant current of 40 mA at room temperature for 24 h (monitored by TLC). After it was cooled down to room temperature, the mixture was poured into water (100 mL) and was extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine (2 x 50 mL) and dried over $MgSO_4$. The solvent was removed by vacuum and the residue was purified by column chromatography (20% EtOAc in PE) to give the corresponding products **3aa** in 76% yield.

6. X-ray Crystallographic Data of *E*-isomer of 11

Sample preparation: Single crystals of ***E*-isomer of 11** for X-ray diffraction experiment was obtained by slow evaporation of DCM/n-hexane (1:10, v/v) solution containing ***E*-isomer of 11**. CCDC 2167617 contain the supplementary crystallographic data for this paper, these data can be obtained free of charge from the Cambridge Crystallographic Data Center.

Figure S1. ORTEP Structure of *E*-isomer of 11 (CCDC 2167617)

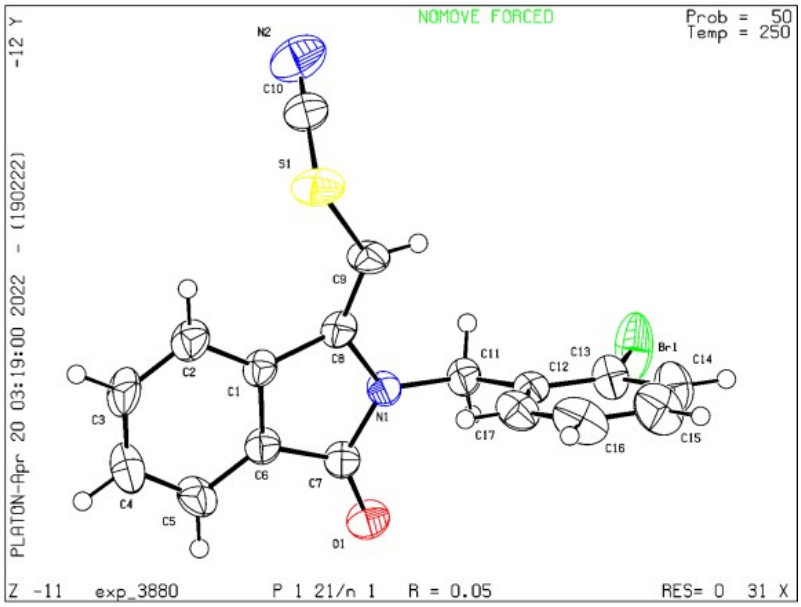


Table S1 Crystal data and structure refinement for *E*-isomer of 11 (CCDC 2167617).

Identification code	exp_3880
Empirical formula	$C_{17}H_{11}BrN_2OS$
Formula weight	371.25
Temperature/K	249.97(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.8390(12)
b/Å	9.1349(11)
c/Å	13.4055(16)
α/°	90
β/°	99.269(11)
γ/°	90
Volume/Å^3	1551.7(3)
Z	4
ρ_{calc}g/cm^3	1.589
μ/mm^{-1}	2.786
F(000)	744.0
Crystal size/mm^3	0.15 × 0.11 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.796 to 49.998
Index ranges	-15 ≤ h ≤ 15, -10 ≤ k ≤ 8, -11 ≤ l ≤ 15
Reflections collected	6587
Independent reflections	2726 [R_{int} = 0.0524, R_{sigma} = 0.0766]
Data/restraints/parameters	2726/0/200
Goodness-of-fit on F^2	0.991
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.1072
Final R indexes [all data]	R_1 = 0.0876, wR_2 = 0.1260
Largest diff. peak/hole / e Å^{-3}	0.52/-0.69

Crystal structure determination of *E*-isomer of 11 (CCDC 2167617).

Crystal Data for $C_{17}H_{11}BrN_2OS$ (*M* =371.25 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 12.8390(12) Å, *b* = 9.1349(11) Å, *c* = 13.4055(16) Å, *β* = 99.269(11)°, *V* = 1551.7(3) Å^3, *Z* = 4, *T* = 249.97(10) K, μ(Mo Kα) = 2.786 mm^{-1}, *Dcalc* = 1.589 g/cm^3, 6587 reflections measured (4.796° ≤ 2Θ ≤ 49.998°), 2726 unique (R_{int} = 0.0524, R_{sigma} = 0.0766) which were used in all calculations. The final R_1 was 0.0524 (I > 2σ(I)) and wR_2 was 0.1260 (all data).

Refinement model description

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for *E*-isomer of 11 (CCDC 2167617). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	10139.8(4)	5883.3(6)	2308.2(5)	74.0(3)
S1	6497.2(11)	7810.1(14)	5385.1(9)	56.4(4)

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for *E*-isomer of 11 (CCDC 2167617). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	6114(2)	4074(3)	1485(2)	50.8(8)
N2	6809(4)	10826(5)	5089(4)	73.8(14)
N1	6734(2)	5556(4)	2842(3)	36.3(8)
C1	5186(3)	5946(4)	3457(3)	34.8(10)
C2	4368(3)	6381(5)	3948(3)	46.8(11)
C3	3346(4)	5915(5)	3554(4)	52.9(13)
C4	3153(3)	5045(6)	2714(4)	55.8(13)
C5	3963(3)	4600(5)	2223(3)	47.4(12)
C6	4976(3)	5061(5)	2601(3)	37.2(10)
C7	5964(3)	4792(5)	2210(3)	37.1(10)
C8	6335(3)	6286(4)	3627(3)	33.7(10)
C9	6946(3)	7065(5)	4325(3)	43.2(11)
C10	6677(4)	9599(6)	5181(3)	48.2(12)
C11	7817(3)	5638(4)	2656(3)	36.5(10)
C12	8566(3)	4588(4)	3288(3)	31.4(9)
C13	9627(3)	4554(5)	3214(3)	41.0(11)
C14	10338(4)	3622(6)	3757(4)	59.1(14)
C15	9986(4)	2650(6)	4417(4)	64.6(15)
C16	8934(4)	2636(5)	4514(4)	61.4(14)
C17	8235(4)	3590(5)	3953(3)	45.8(11)

Table S3 Anisotropic Displacement Parameters (Å^2×10^3) for *E*-isomer of 11 (CCDC 2167617). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	48.2(4)	93.0(5)	90.1(6)	41.5(3)	39.1(3)	14.2(3)
S1	80.0(9)	62.2(8)	31.9(8)	-16.0(6)	23.6(6)	-13.4(7)
O1	54.6(18)	71(2)	29(2)	-18.9(15)	11.7(15)	3.0(16)
N2	98(4)	70(3)	60(4)	-13(2)	32(3)	6(3)
N1	32.3(18)	54(2)	24(2)	-11.8(16)	7.1(15)	-0.8(17)
C1	36(2)	43(2)	28(3)	-1.5(19)	10.5(19)	3.9(19)
C2	46(3)	58(3)	39(3)	-6(2)	15(2)	5(2)
C3	38(3)	75(4)	51(4)	-3(3)	24(2)	11(2)
C4	32(2)	81(4)	53(4)	4(3)	4(2)	2(2)
C5	42(2)	69(3)	29(3)	-8(2)	-3(2)	-3(2)
C6	38(2)	49(3)	25(3)	-5(2)	6.5(19)	4(2)
C7	38(2)	51(3)	22(3)	-5(2)	3.7(19)	4(2)
C8	40(2)	44(2)	20(3)	-1.1(19)	14.8(19)	2(2)
C9	49(2)	54(3)	29(3)	-16(2)	13(2)	-10(2)
C10	58(3)	60(3)	28(3)	-12(2)	11(2)	1(3)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for *E*-isomer of 11 (CCDC 2167617). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	33(2)	52(3)	26(3)	-4(2)	9.5(19)	2(2)
C12	37(2)	42(2)	15(2)	-4.4(18)	6.1(18)	-2(2)
C13	37(2)	58(3)	29(3)	9(2)	8(2)	0(2)
C14	44(3)	74(3)	54(4)	10(3)	-9(2)	9(3)
C15	68(3)	72(4)	45(4)	21(3)	-17(3)	4(3)
C16	80(4)	68(3)	32(3)	16(2)	-3(3)	-16(3)
C17	49(3)	60(3)	27(3)	-1(2)	4(2)	-9(2)

Table S4 Bond Lengths for *E*-isomer of 11 (CCDC 2167617).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C13	1.908(4)	C3	C4	1.368(7)
S1	C9	1.754(4)	C4	C5	1.378(6)
S1	C10	1.679(6)	C5	C6	1.383(5)
O1	C7	1.214(5)	C6	C7	1.470(5)
N2	C10	1.143(5)	C8	C9	1.327(5)
N1	C7	1.383(5)	C11	C12	1.517(5)
N1	C8	1.409(5)	C12	C13	1.382(5)
N1	C11	1.454(5)	C12	C17	1.389(6)
C1	C2	1.384(5)	C13	C14	1.369(6)
C1	C6	1.394(6)	C14	C15	1.379(7)
C1	C8	1.489(5)	C15	C16	1.378(7)
C2	C3	1.400(6)	C16	C17	1.383(6)

Table S5 Bond Angles for *E*-isomer of 11 (CCDC 2167617).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	S1	C9	100.0(2)	N1	C8	C1	104.9(3)
C7	N1	C8	112.8(3)	C9	C8	N1	122.4(4)
C7	N1	C11	121.9(3)	C9	C8	C1	132.7(4)
C8	N1	C11	125.2(3)	C8	C9	S1	123.1(3)
C2	C1	C6	119.8(4)	N2	C10	S1	176.8(5)
C2	C1	C8	132.6(4)	N1	C11	C12	114.2(3)
C6	C1	C8	107.6(3)	C13	C12	C11	121.2(3)
C1	C2	C3	118.1(4)	C13	C12	C17	116.0(4)
C4	C3	C2	121.5(4)	C17	C12	C11	122.8(4)
C3	C4	C5	120.9(4)	C12	C13	Br1	118.5(3)
C4	C5	C6	118.2(4)	C14	C13	Br1	117.8(3)
C1	C6	C7	109.1(3)	C14	C13	C12	123.8(4)
C5	C6	C1	121.6(4)	C13	C14	C15	118.9(4)

Table S5 Bond Angles for *E*-isomer of 11 (CCDC 2167617).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	C6	C7	129.3(4)	C16	C15	C14	119.6(5)
O1	C7	N1	125.1(4)	C15	C16	C17	120.2(5)
O1	C7	C6	129.3(4)	C16	C17	C12	121.6(4)
N1	C7	C6	105.7(3)				

Table S6 Torsion Angles for *E*-isomer of 11 (CCDC 2167617).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C13	C14	C15	180.0(4)	C7	N1	C11	C12	-99.9(5)
N1	C8	C9	S1	-172.7(3)	C8	N1	C7	O1	-179.7(4)
N1	C11	C12	C13	-178.7(4)	C8	N1	C7	C6	1.0(5)
N1	C11	C12	C17	2.8(6)	C8	N1	C11	C12	83.8(5)
C1	C2	C3	C4	0.4(7)	C8	C1	C2	C3	176.5(4)
C1	C6	C7	O1	179.6(5)	C8	C1	C6	C5	-177.6(4)
C1	C6	C7	N1	-1.1(5)	C8	C1	C6	C7	0.8(5)
C1	C8	C9	S1	6.7(7)	C10	S1	C9	C8	-118.4(4)
C2	C1	C6	C5	0.0(7)	C11	N1	C7	O1	3.6(7)
C2	C1	C6	C7	178.4(4)	C11	N1	C7	C6	-175.7(4)
C2	C1	C8	N1	-177.4(5)	C11	N1	C8	C1	176.1(4)
C2	C1	C8	C9	3.1(8)	C11	N1	C8	C9	-4.4(6)
C2	C3	C4	C5	-0.1(8)	C11	C12	C13	Br1	1.0(5)
C3	C4	C5	C6	-0.3(7)	C11	C12	C13	C14	-179.3(4)
C4	C5	C6	C1	0.3(7)	C11	C12	C17	C16	179.4(4)
C4	C5	C6	C7	-177.7(5)	C12	C13	C14	C15	0.3(8)
C5	C6	C7	O1	-2.1(8)	C13	C12	C17	C16	0.9(7)
C5	C6	C7	N1	177.2(4)	C13	C14	C15	C16	0.1(8)
C6	C1	C2	C3	-0.4(6)	C14	C15	C16	C17	0.0(8)
C6	C1	C8	N1	-0.2(4)	C15	C16	C17	C12	-0.6(8)
C6	C1	C8	C9	-179.7(5)	C17	C12	C13	Br1	179.5(3)
C7	N1	C8	C1	-0.5(5)	C17	C12	C13	C14	-0.8(7)
C7	N1	C8	C9	179.0(4)					

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *E*-isomer of 11 (CCDC 2167617).

Atom	*x*	*y*	*z*	U(eq)
H2	4494.16	6966.84	4522.28	56
H3	2785.91	6201.82	3871.13	63
H4	2465.74	4750.69	2470.27	67
H5	3831.99	4006.16	1653.6	57
H9	7644.05	7223.05	4249.25	52
H11A	8073.21	6629	2790.08	44

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *E*-isomer of 11 (CCDC 2167617).

Atom	*x*	*y*	*z*	U(eq)
H11B	7825.77	5435.48	1946.84	44
H14	11045.17	3642.94	3682.28	71
H15	10456.62	2008.83	4793.94	78
H16	8693.34	1983.72	4958.51	74
H17	7526.34	3561.35	4022.29	55

7. Reference

[1]. (a) M. Van den Berg, R. M. Haak, A. J. Minnaard, A. H. M. de Vries, J. G. de Vries and B. L. Feringa, *Adv. Synth. Catal.* **2002**, *344*, 1003-1007; (b) S. Pankajakshan, Y.-H. Xu, J. K. Cheng, M. T. Low and T.-P. Loh, *Angew. Chem. Int. Ed.* **2012**, *51*, 5701-5705; (c) Z.- Y. Shen, J.-K. Cheng, C. Wang, C. Yuan, T.-P. Loh and X.-H. Hu, *ACS Catal.* **2019**, *9*, 8128–8135; (d) X.-J. Dai, M. Liu, J.-Y. Zhang, X.-Y. Xu, W.-C. Yuan and X.-M. Zhang, *Chemistryselect.* **2019**, *4*, 4458–4461;

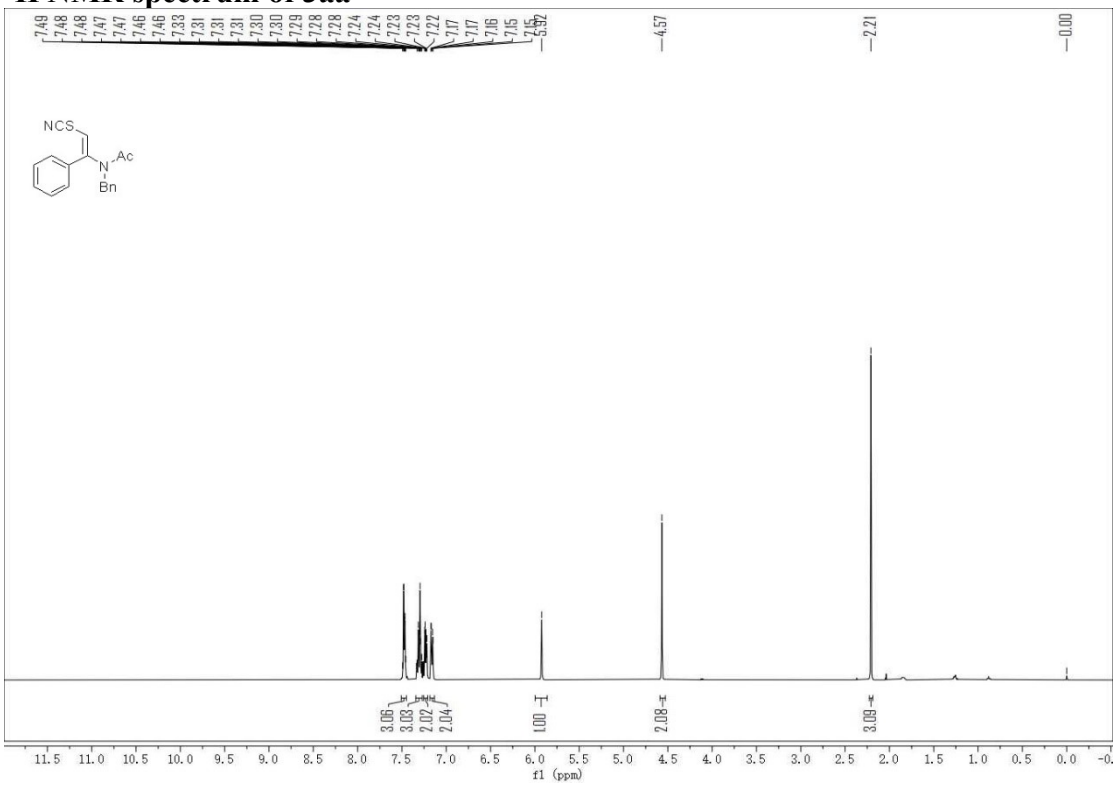
[2]. Q. Gu, Q. Wang, W. Dai, X. Wang, Y. Ban, T. Liu, Y. Zhao, Y. Zhang, Y. Ling and X. Zeng, $K_2S_2O_8$-mediated regio- and stereo-selective thiocyanation of enamides with NH_4SCN. *Org. Biomol. Chem.* **2021**, *19*, 2512-2516.

[3]. D. Amrita and H. Alakananda, Potassium Persulfate-Mediated Thiocyanation of *2H*-Indazole under Iron-Catalysis. *Adv. Synth. Catal.* **2019**, *361*, 842-849.

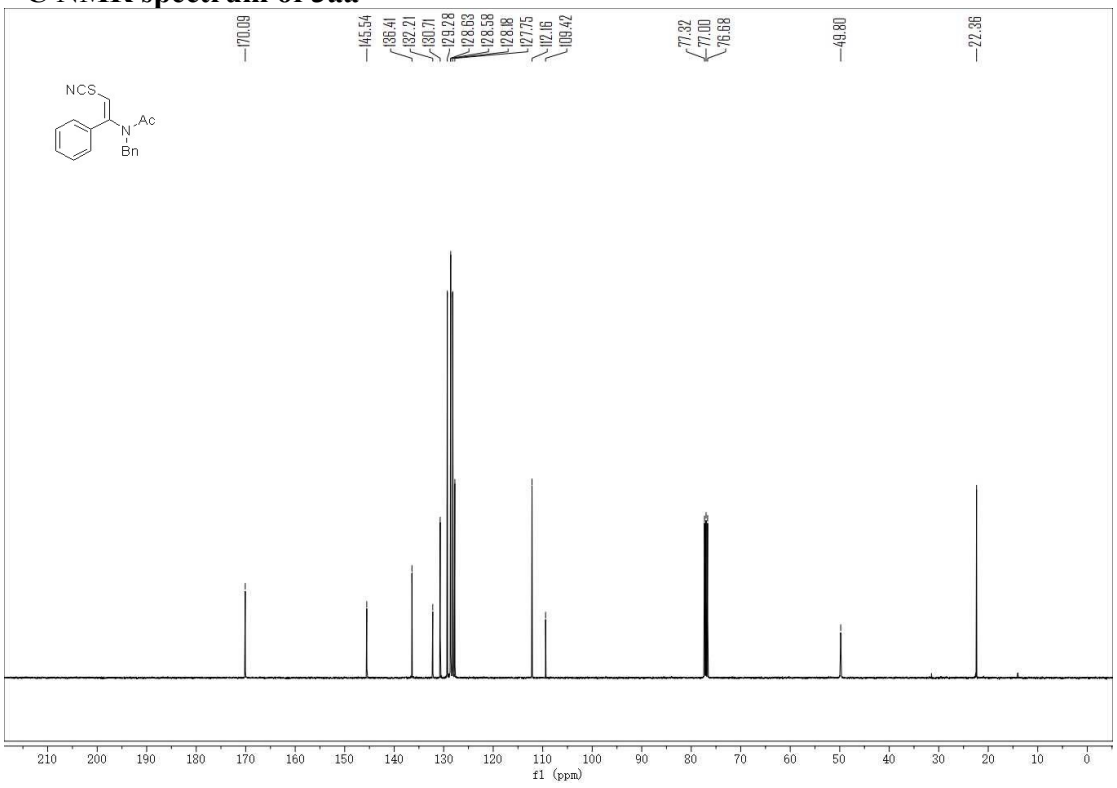
[4] C. Sylvain, L. Benoît, M. Christophe and C. Janine. Heck−Suzuki−Miyaura Domino Reactions Involving Ynamides. An Efficient Access to 3-(Arylmethylene)isoindolinones. *Org. Lett.* **2004**, *6*, 2511–2514.

8. ^{1}H NMR and ^{13}C NMR spectra of compounds 3aa-w, 5aa-i, 6-11

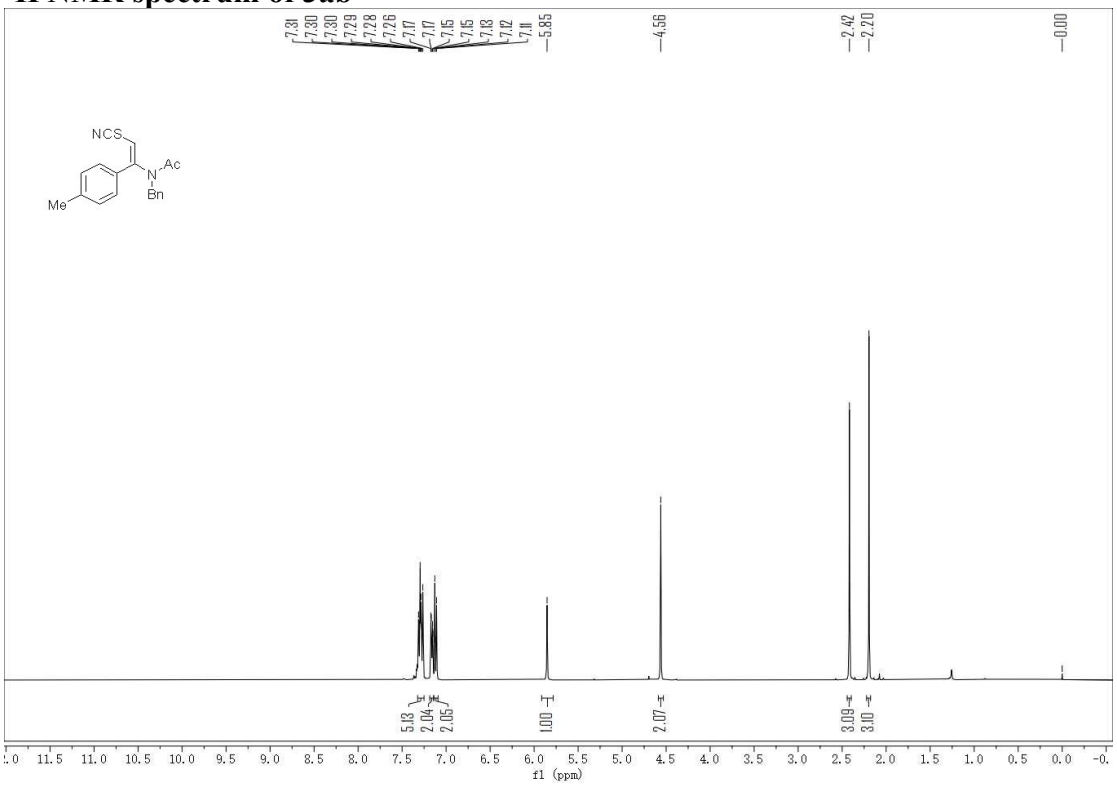
^{1}H NMR spectrum of 3aa



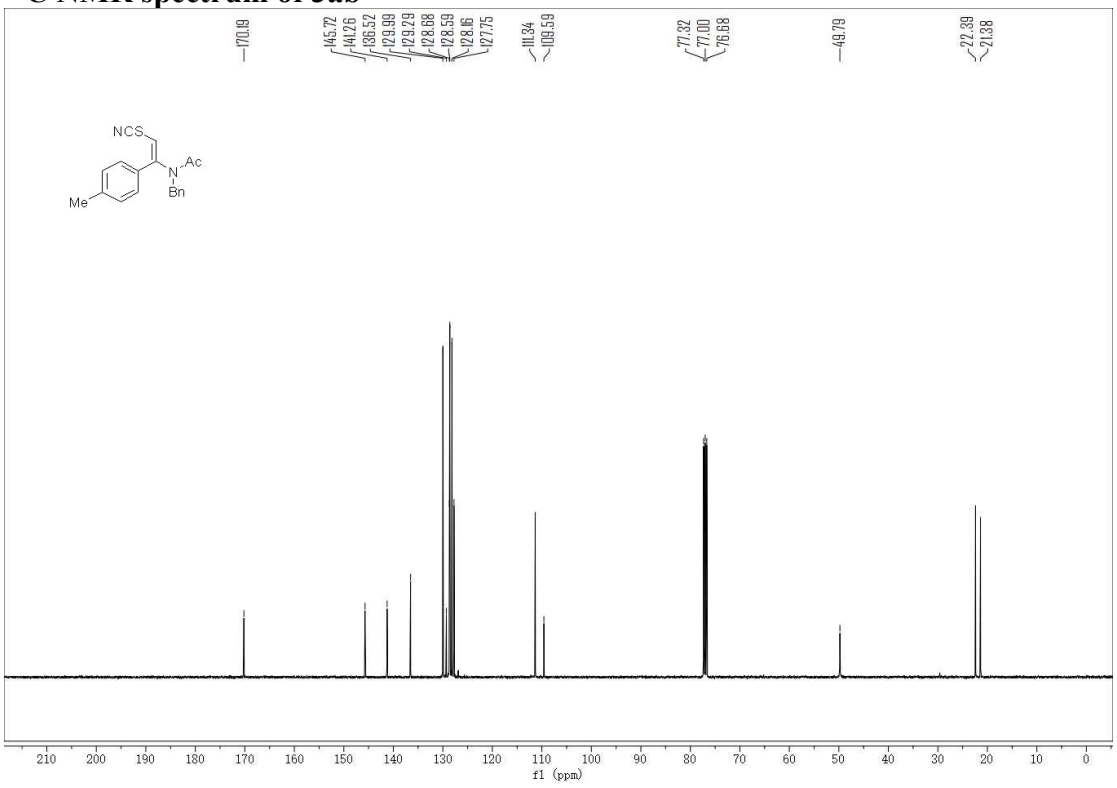
^{13}C NMR spectrum of 3aa



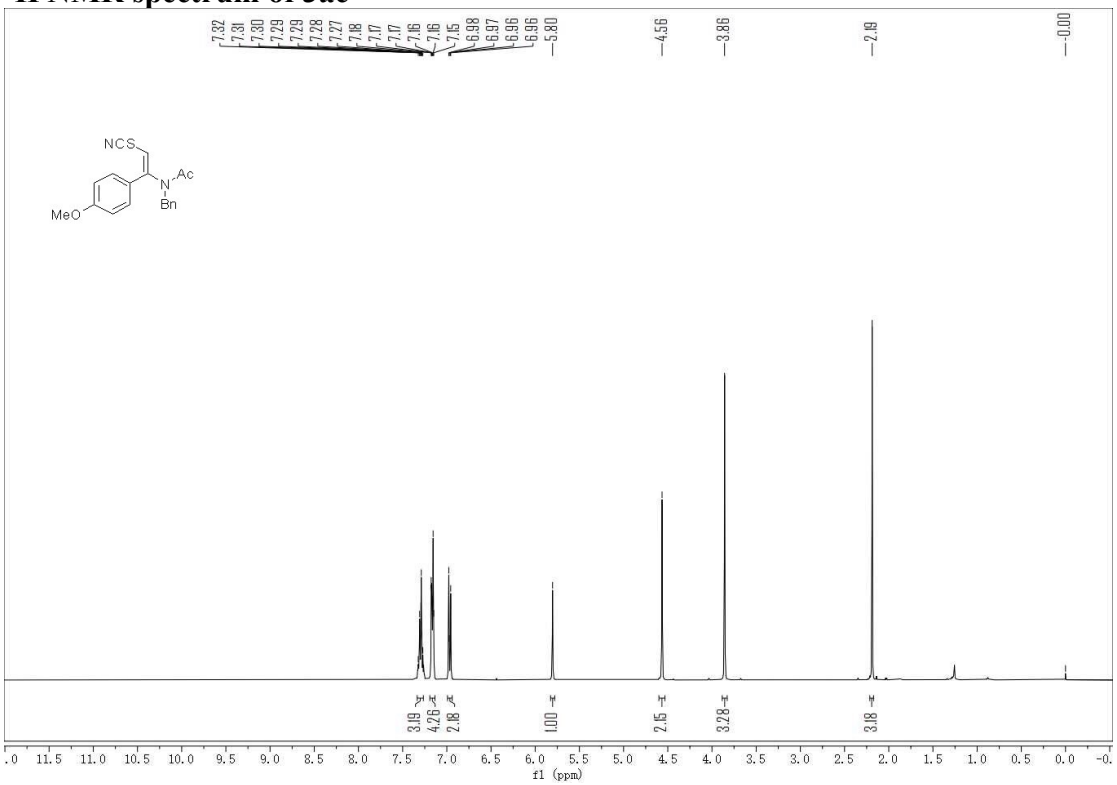
^{1}H NMR spectrum of 3ab



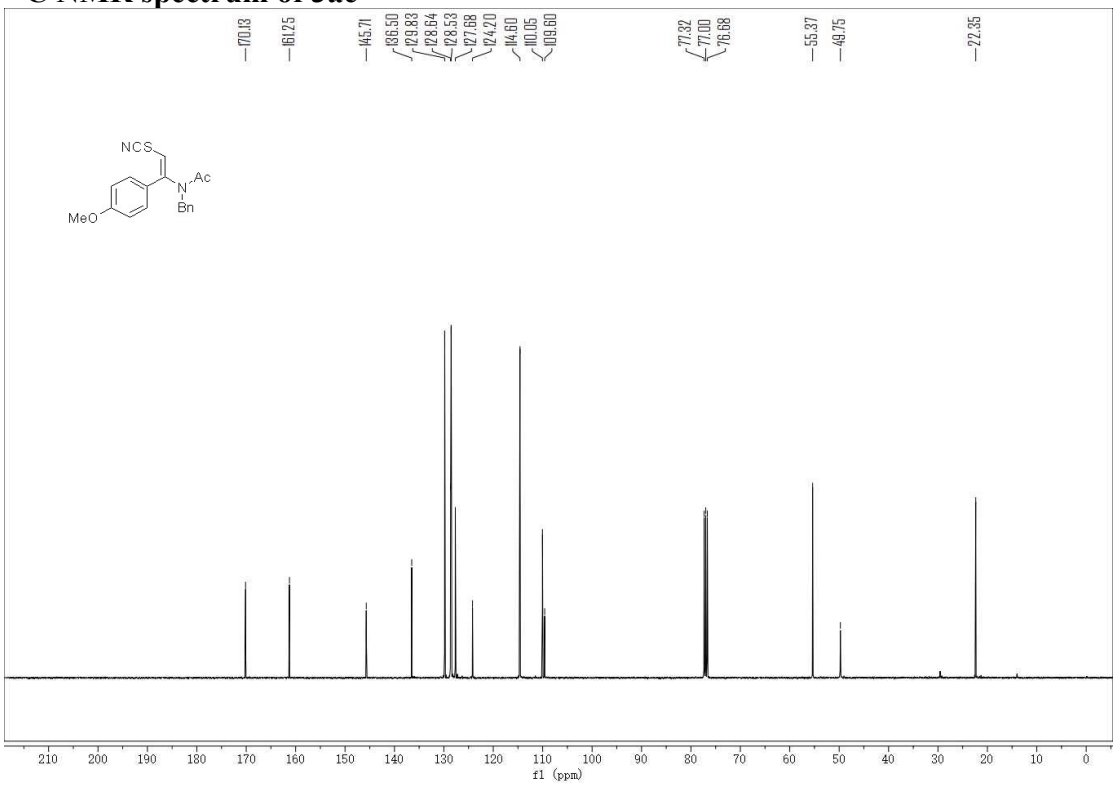
^{13}C NMR spectrum of 3ab



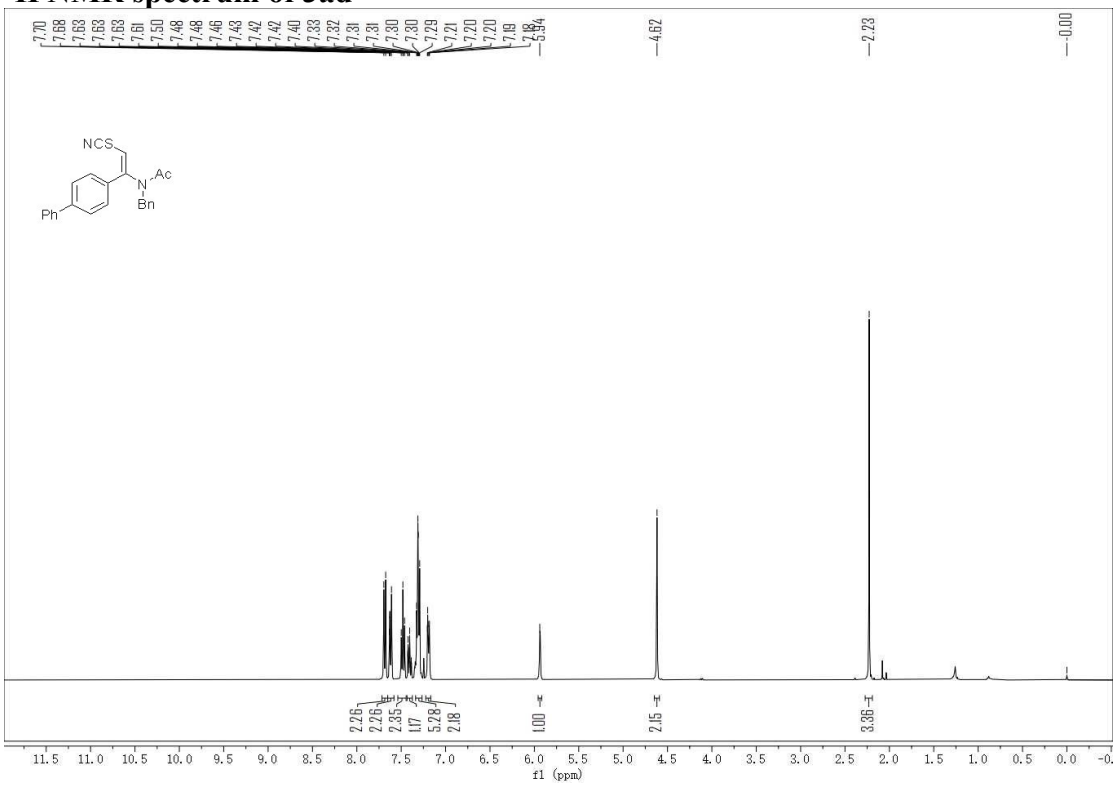
^{1}H NMR spectrum of 3ac



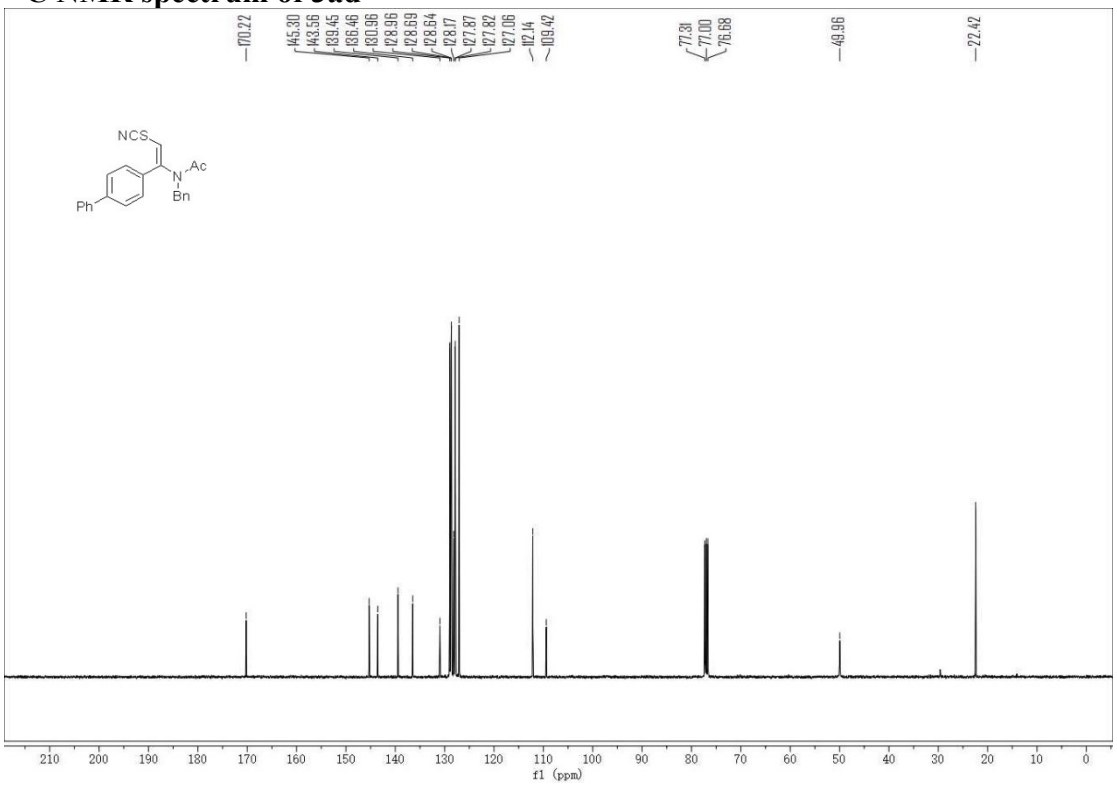
^{13}C NMR spectrum of 3ac



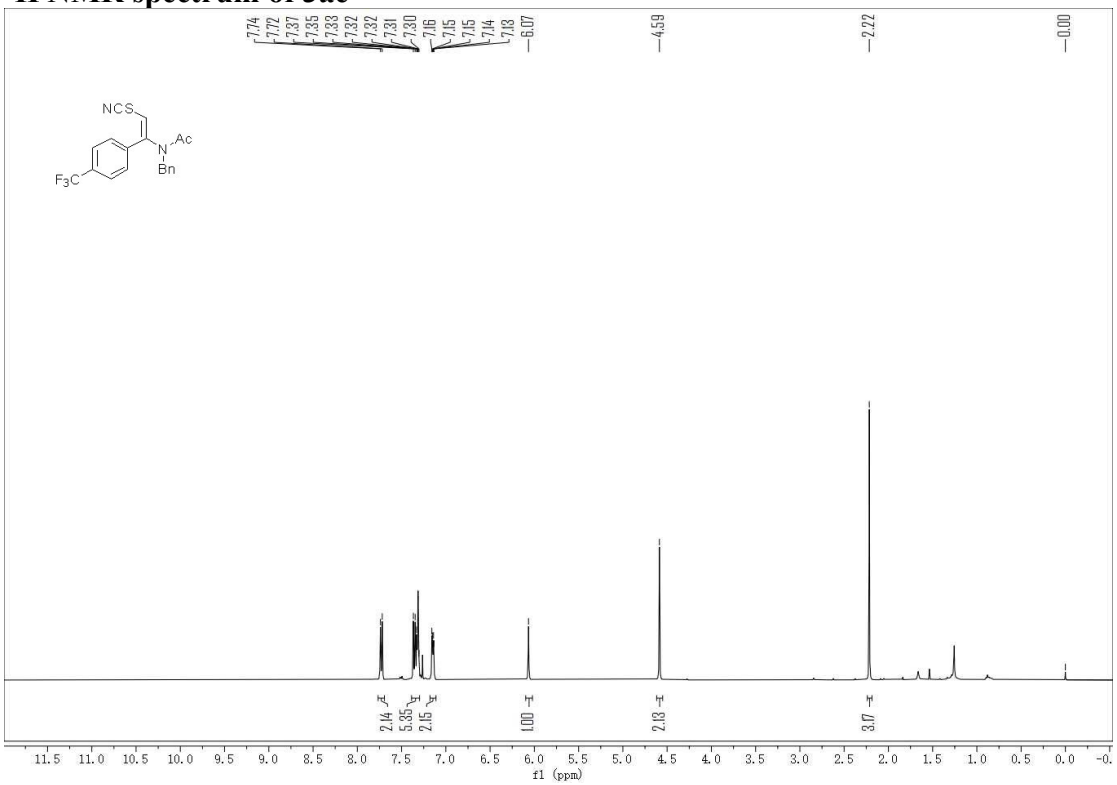
^{1}H NMR spectrum of 3ad



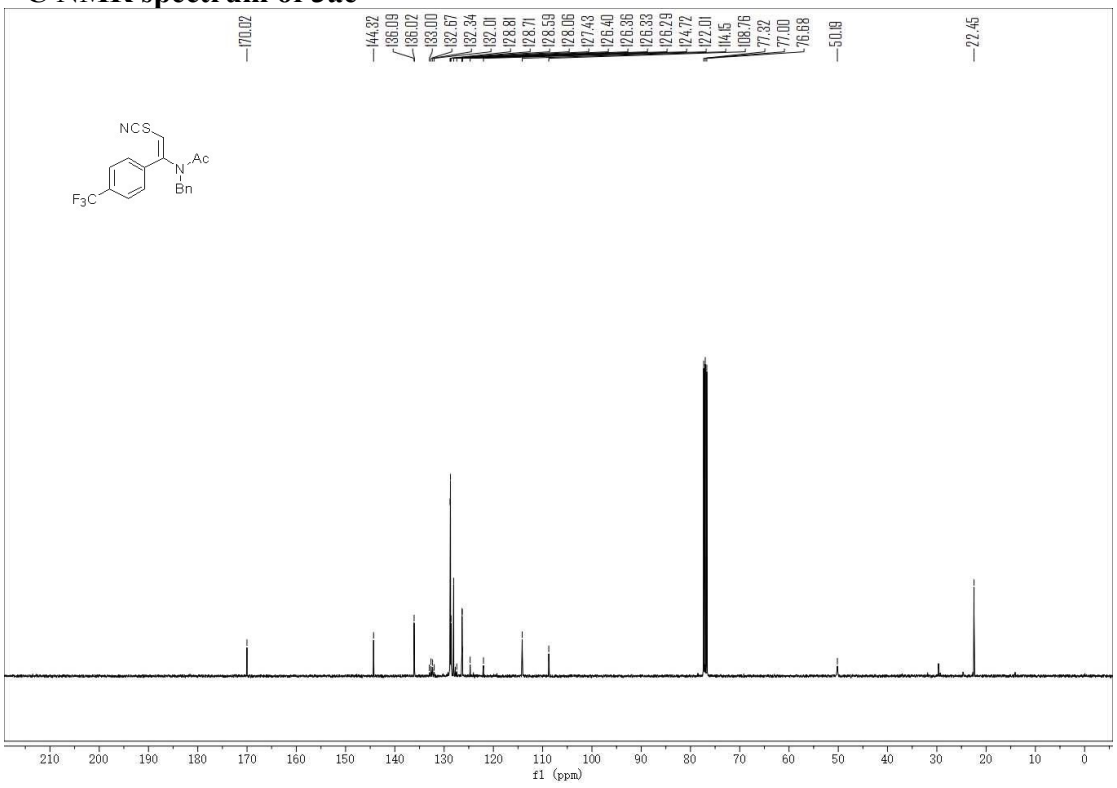
^{13}C NMR spectrum of 3ad



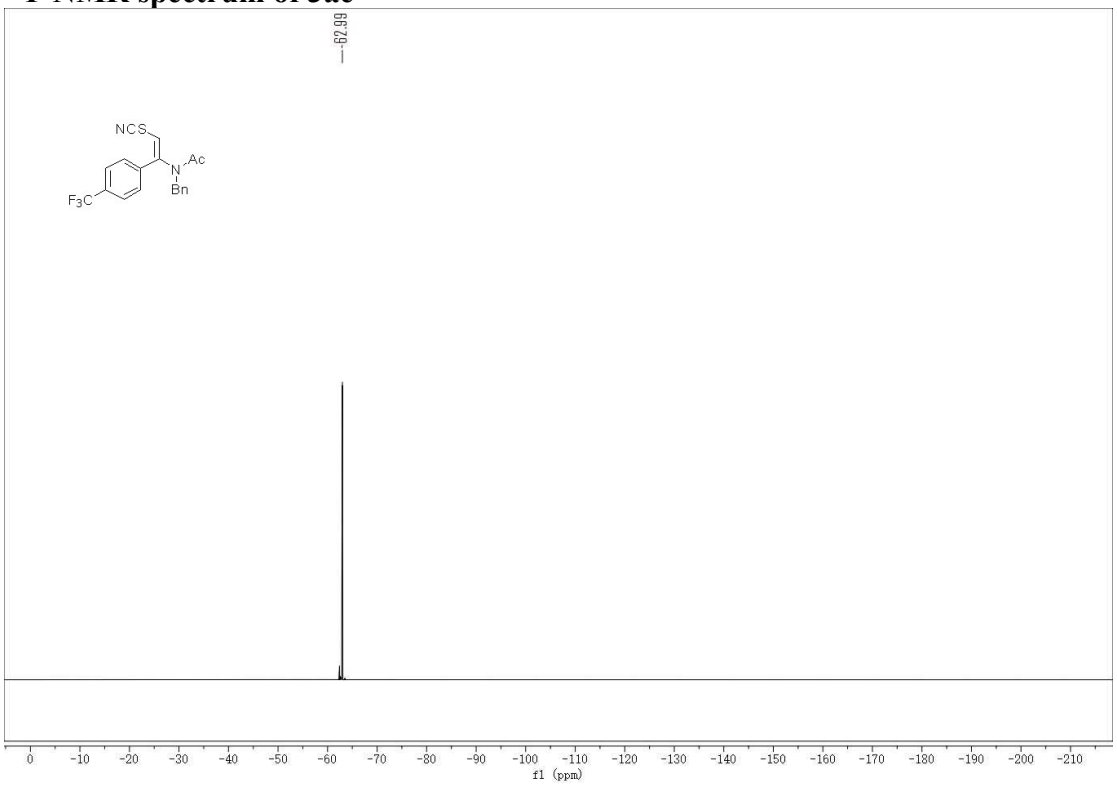
^{1}H NMR spectrum of 3ae



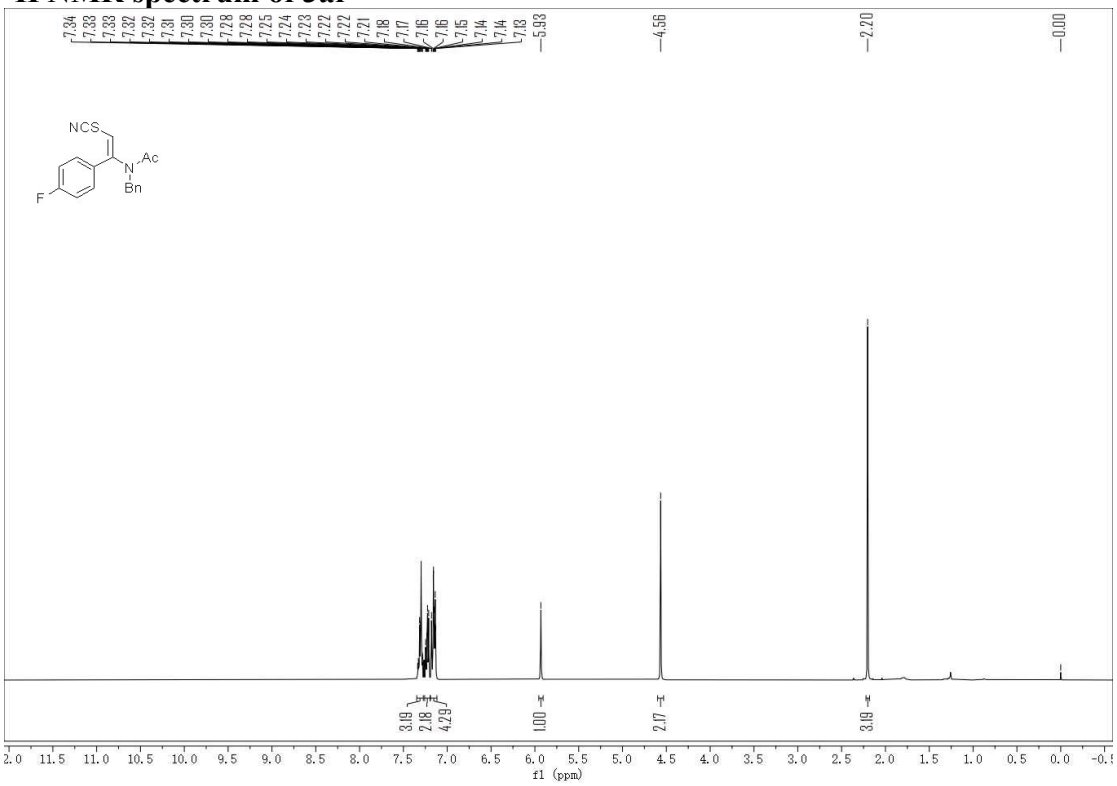
^{13}C NMR spectrum of 3ae



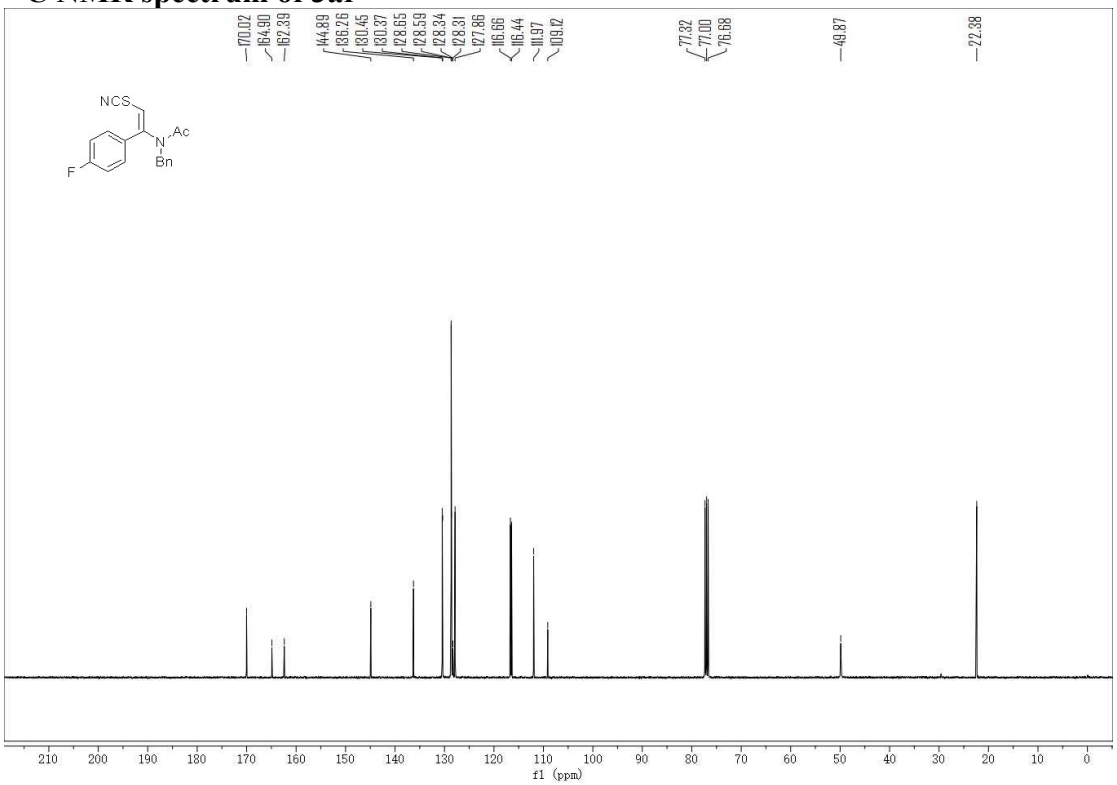
^{19}F NMR spectrum of 3ae



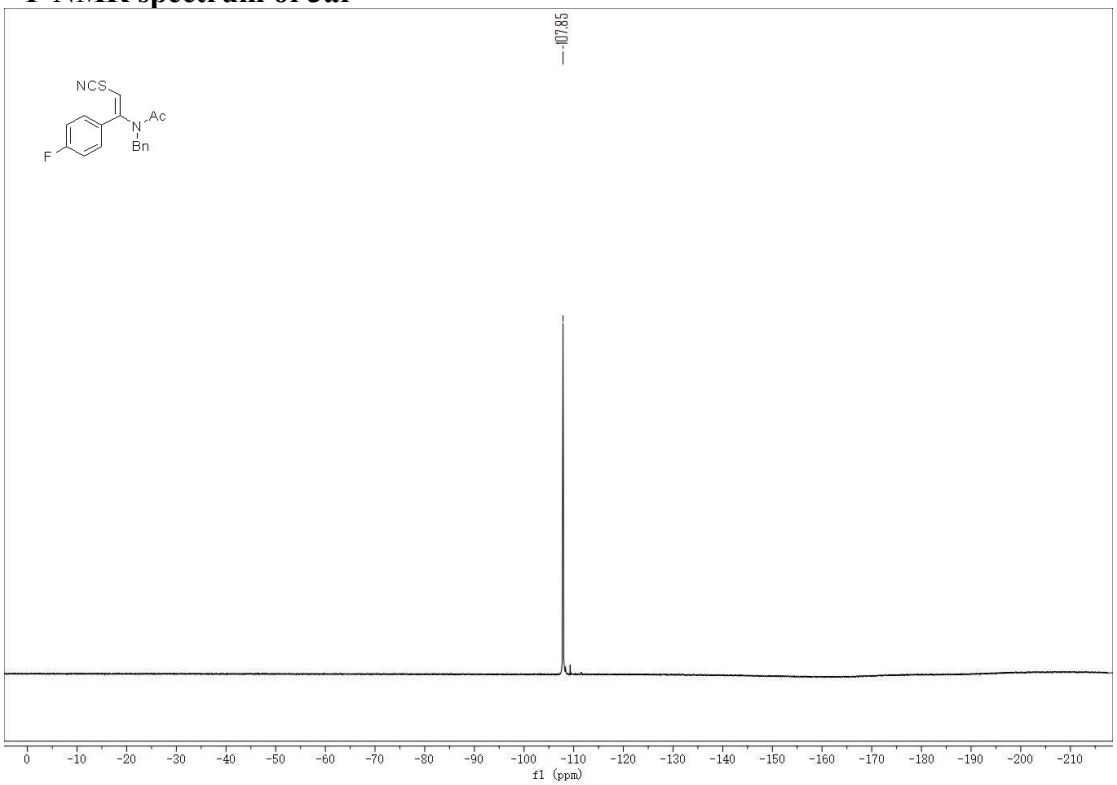
^{1}H NMR spectrum of 3af



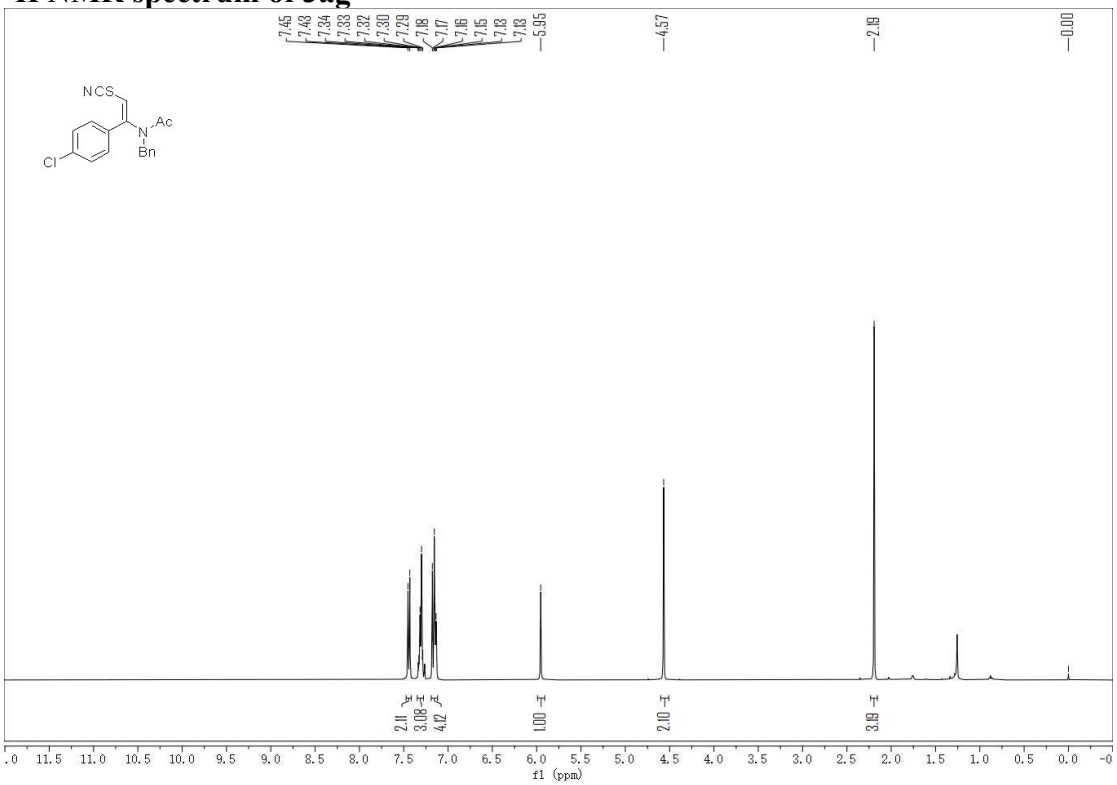
^{13}C NMR spectrum of 3af



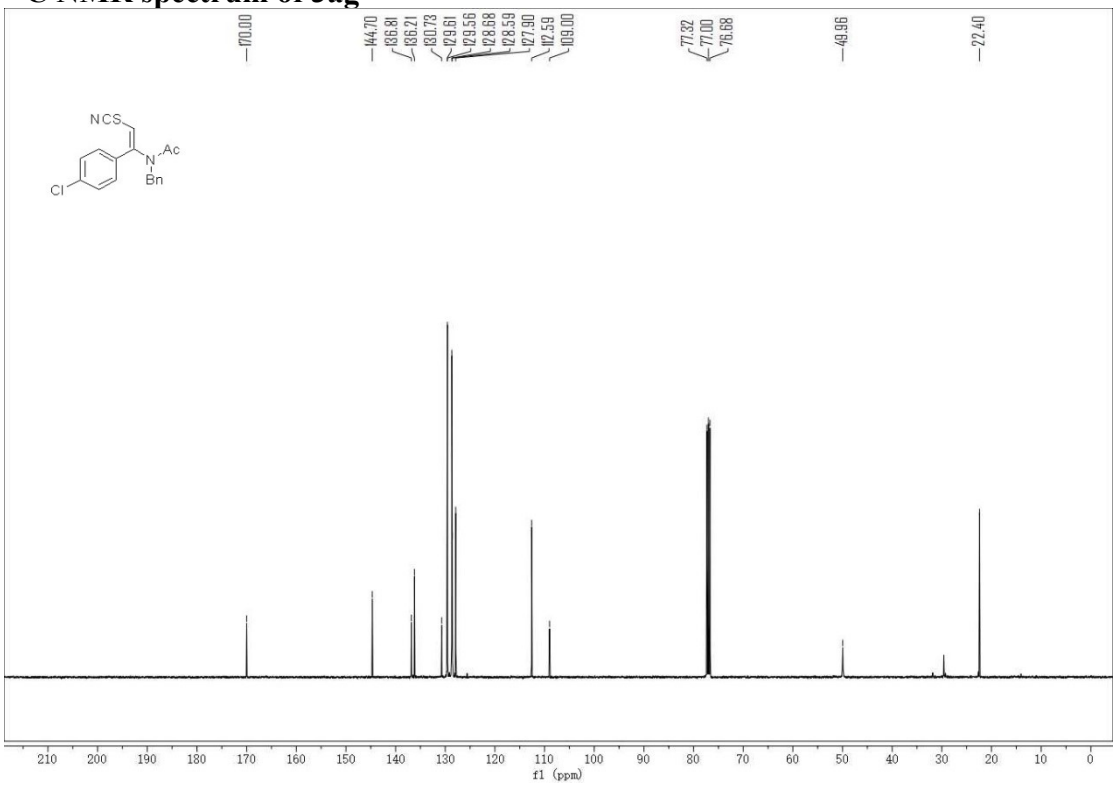
^{19}F NMR spectrum of 3af



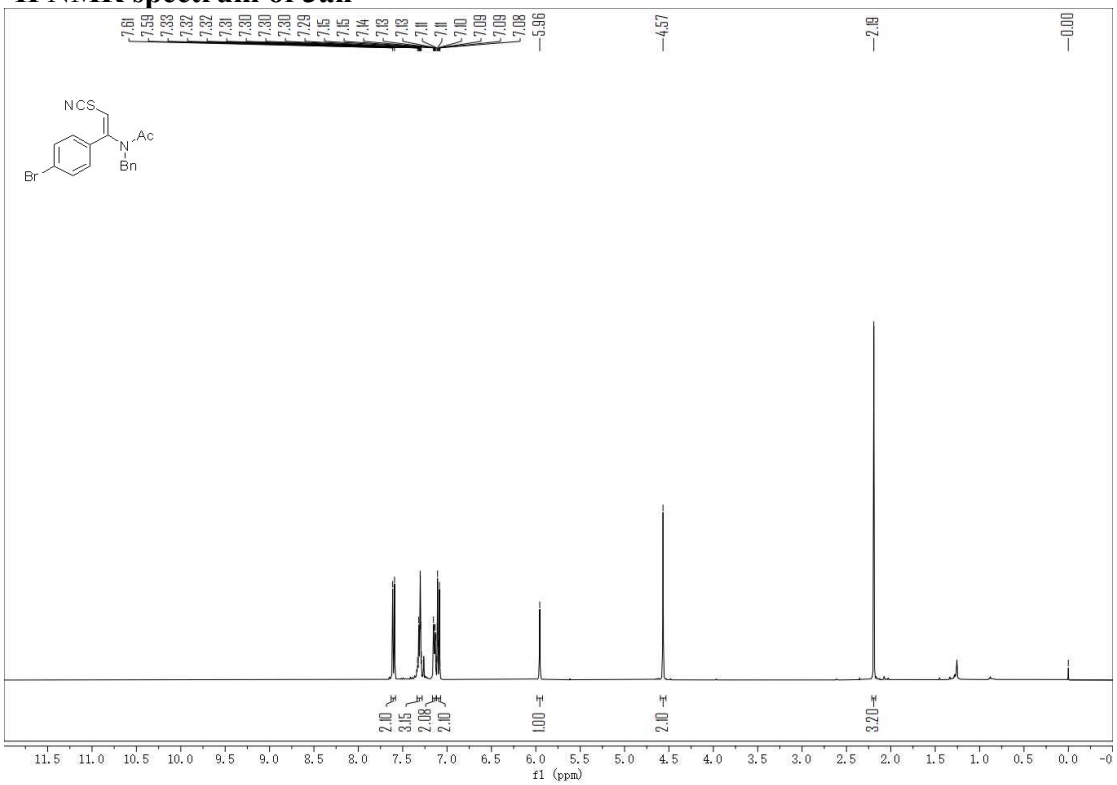
^{1}H NMR spectrum of 3ag



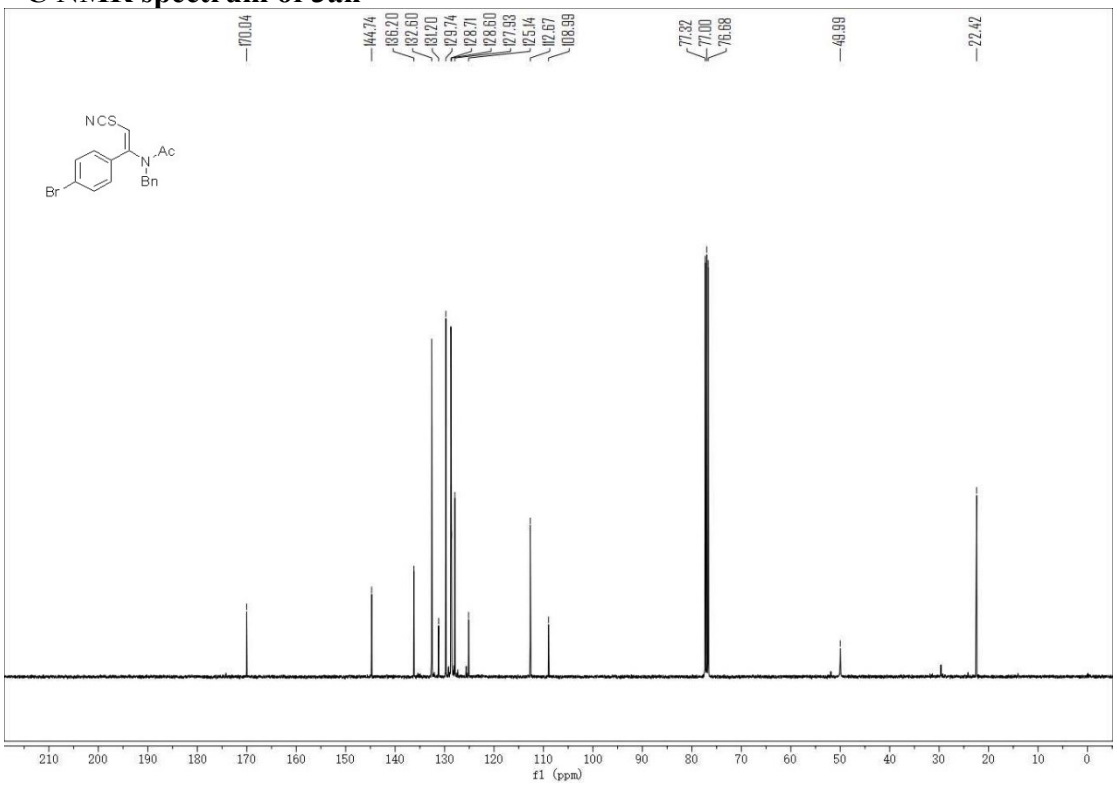
^{13}C NMR spectrum of 3ag



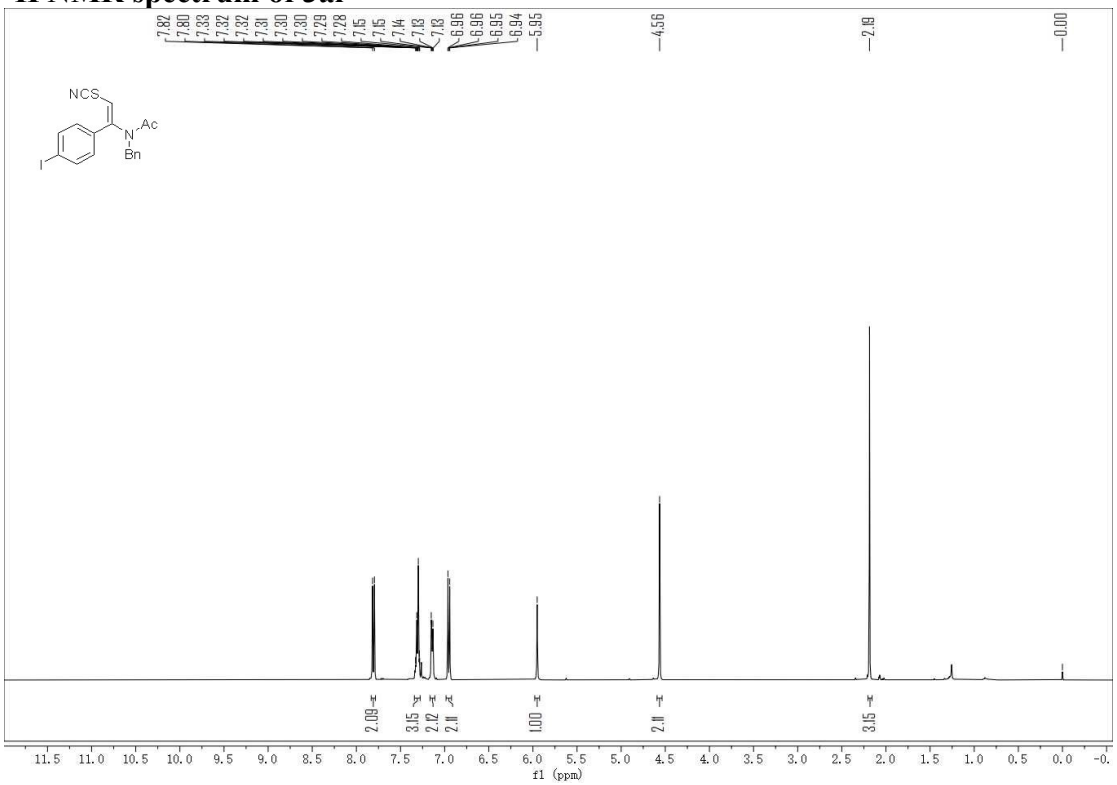
^{1}H NMR spectrum of 3ah



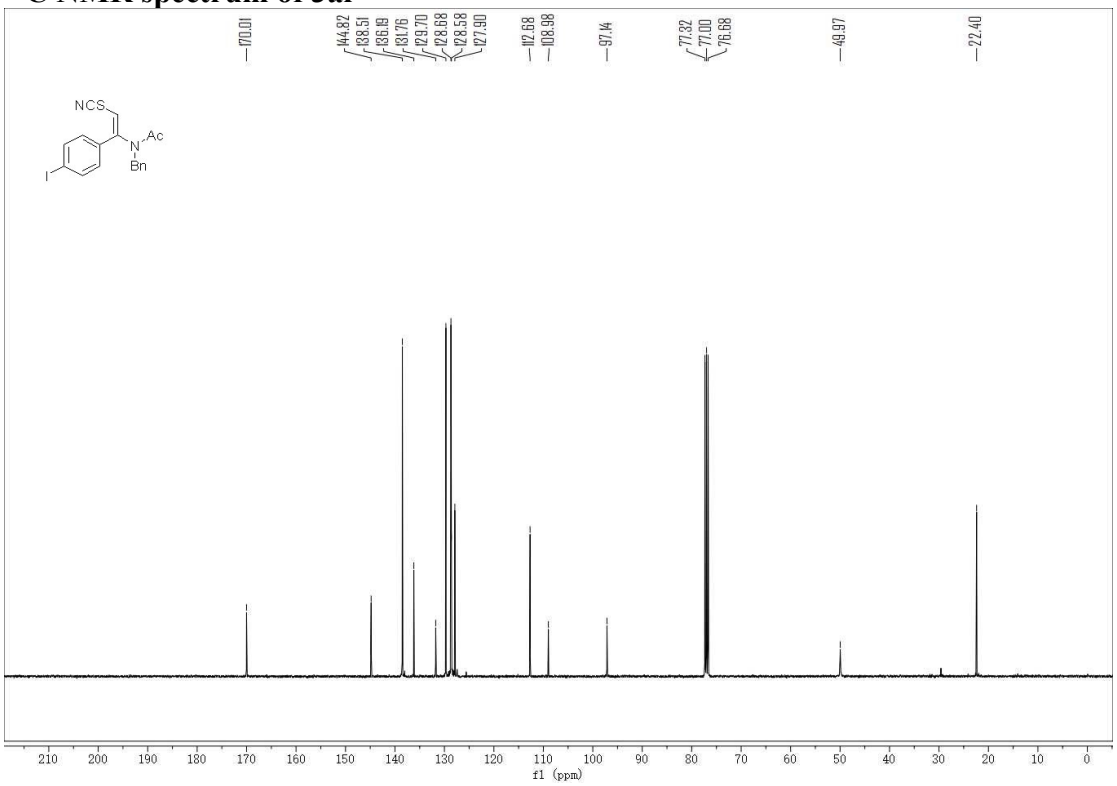
^{13}C NMR spectrum of 3ah



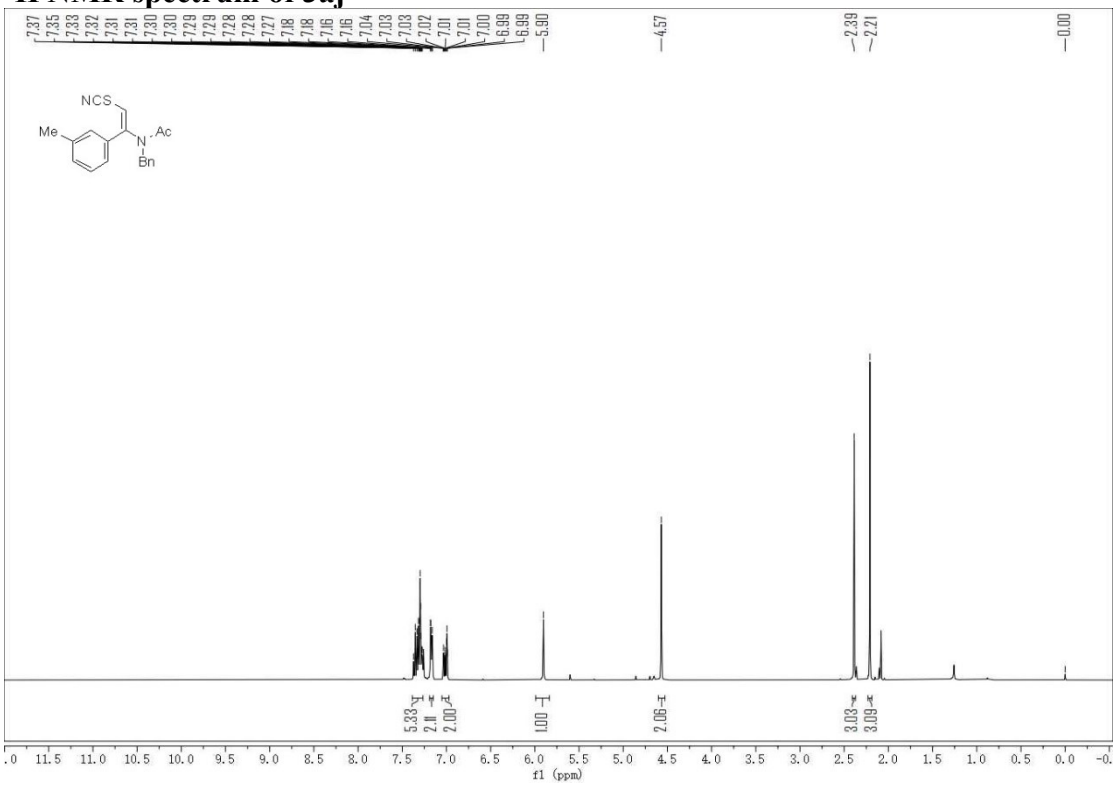
^{1}H NMR spectrum of 3ai



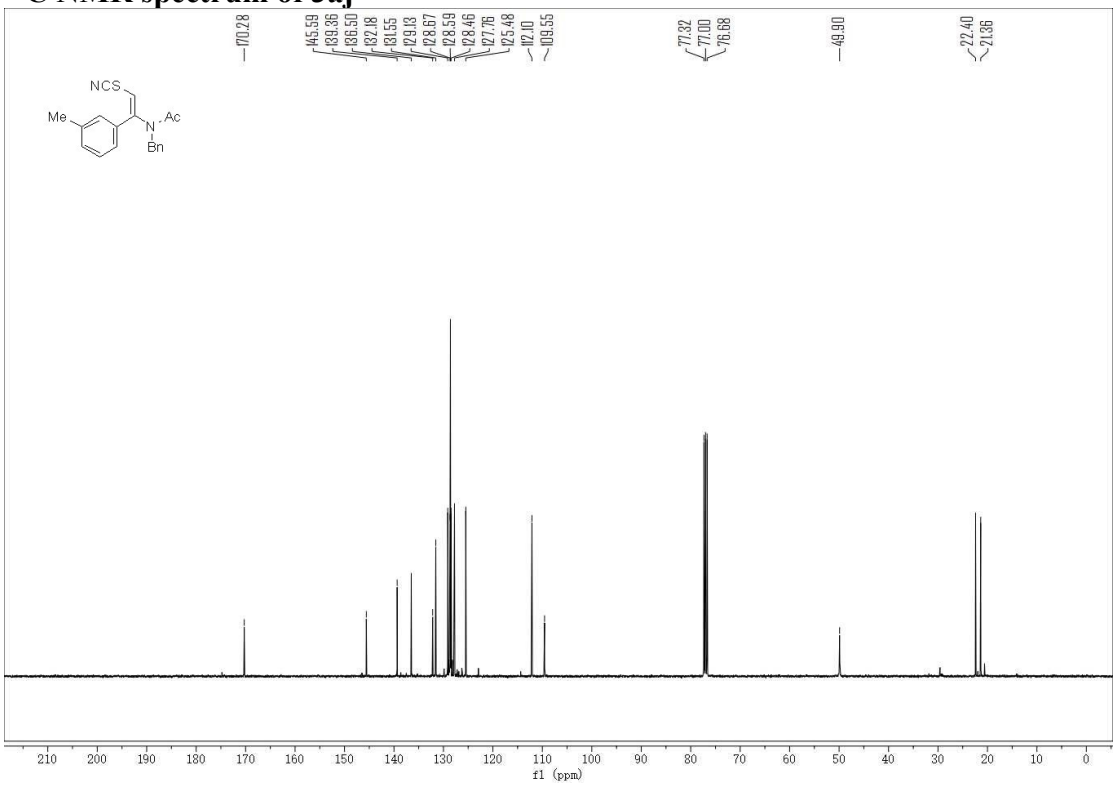
^{13}C NMR spectrum of 3ai



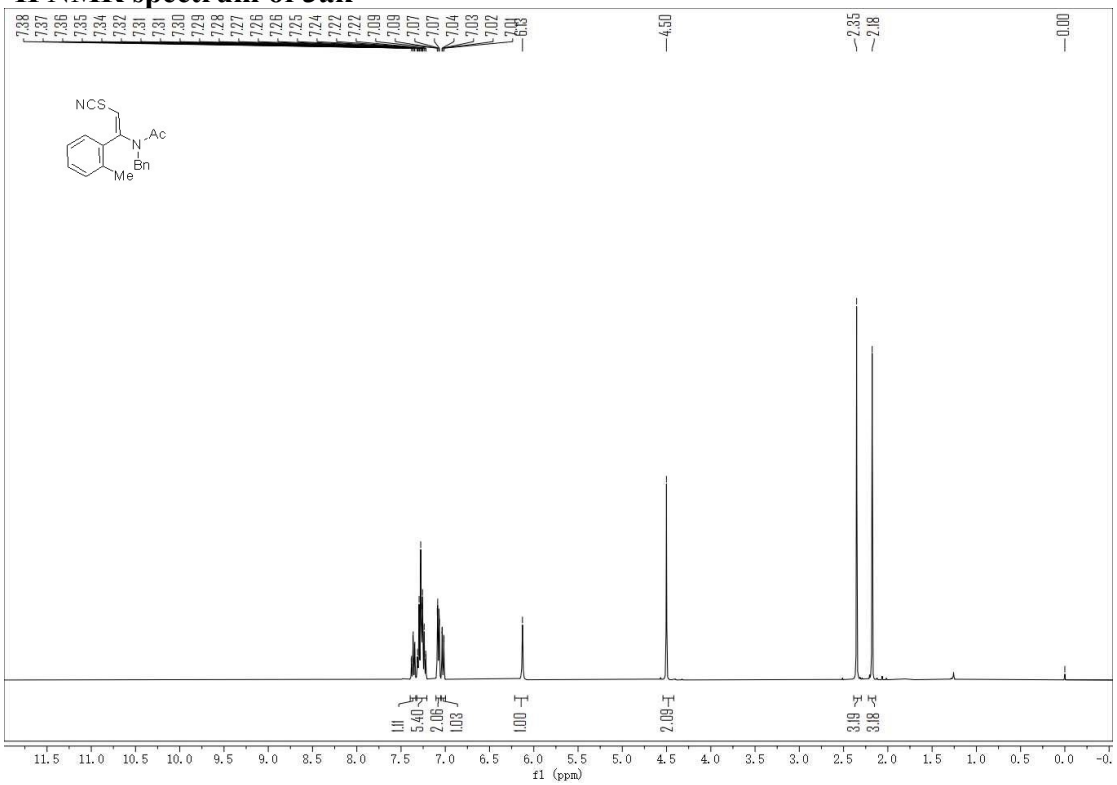
^{1}H NMR spectrum of 3aj



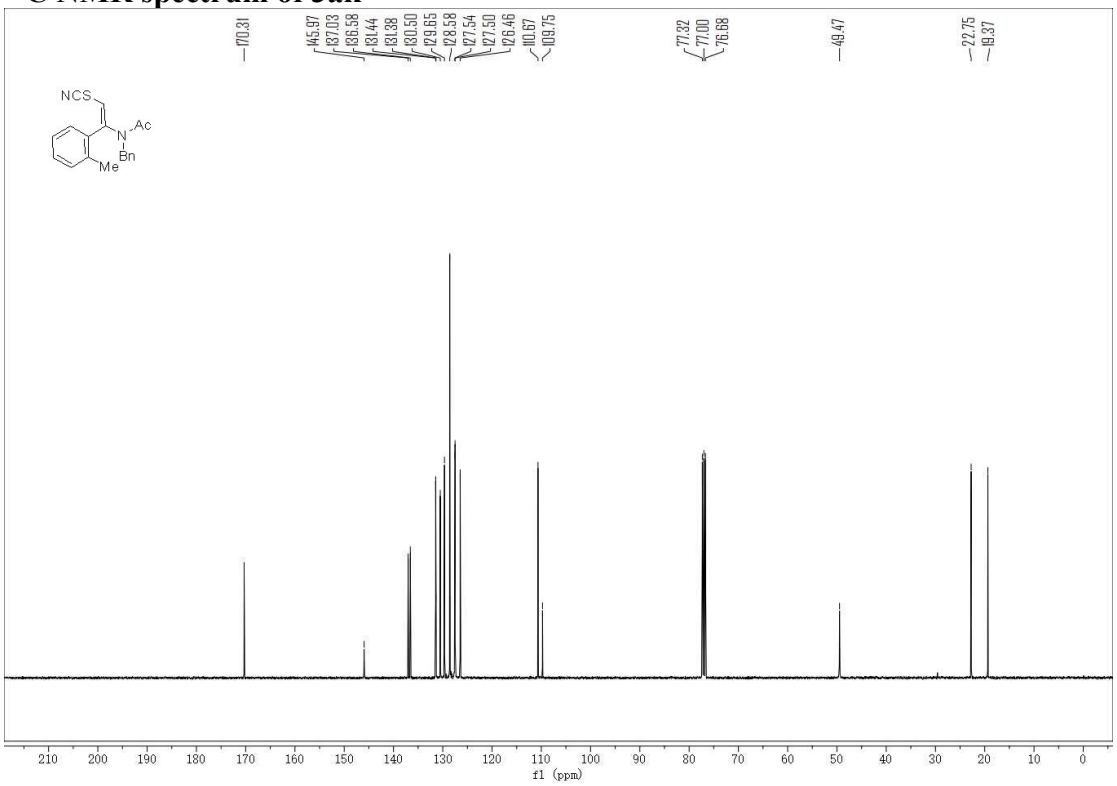
^{13}C NMR spectrum of 3aj



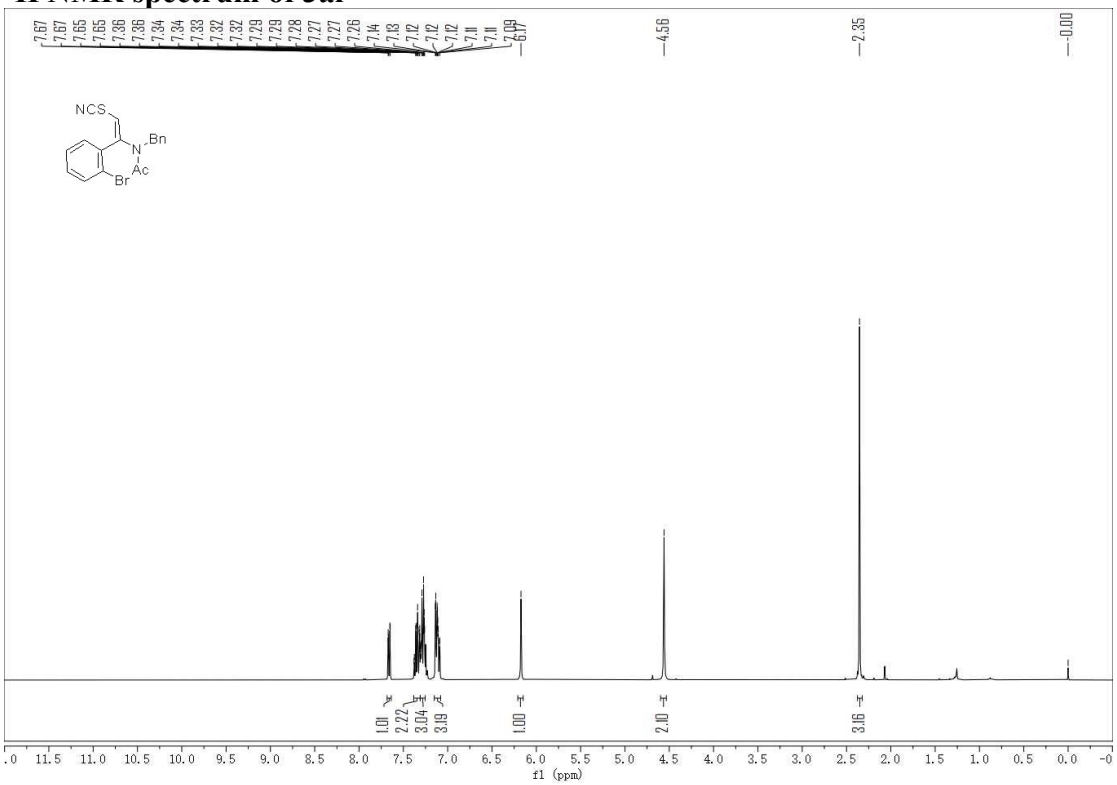
^{1}H NMR spectrum of 3ak



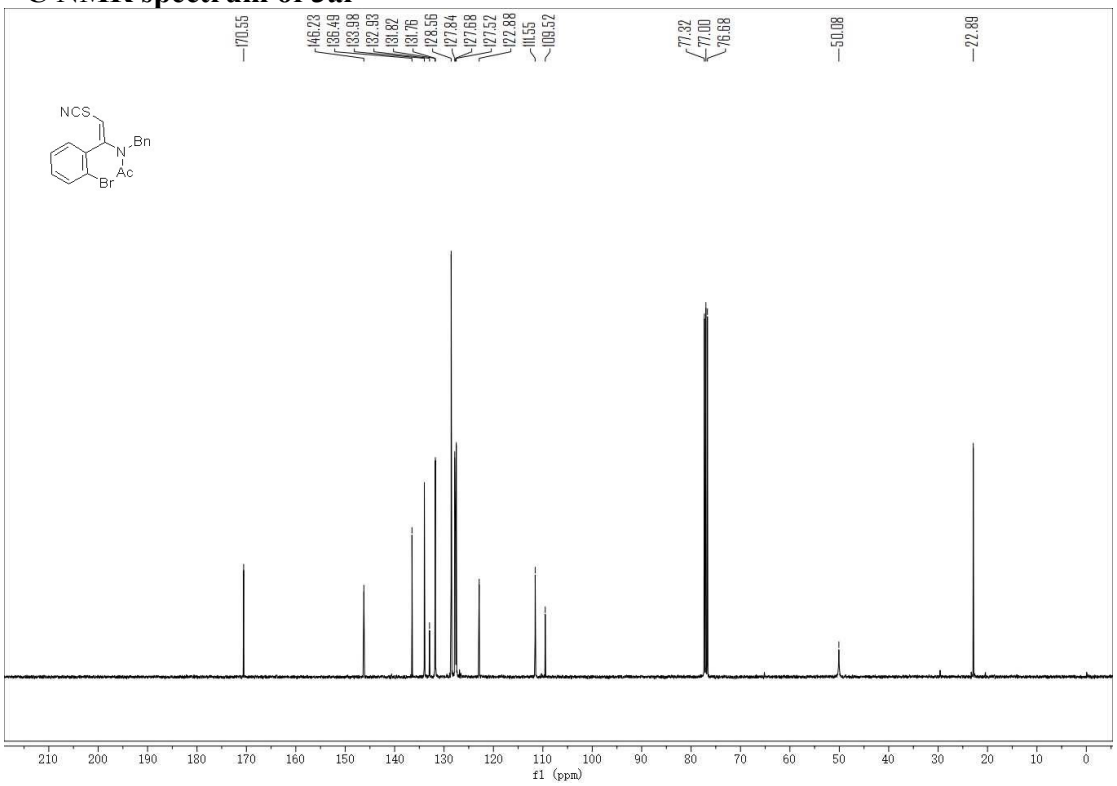
^{13}C NMR spectrum of 3ak



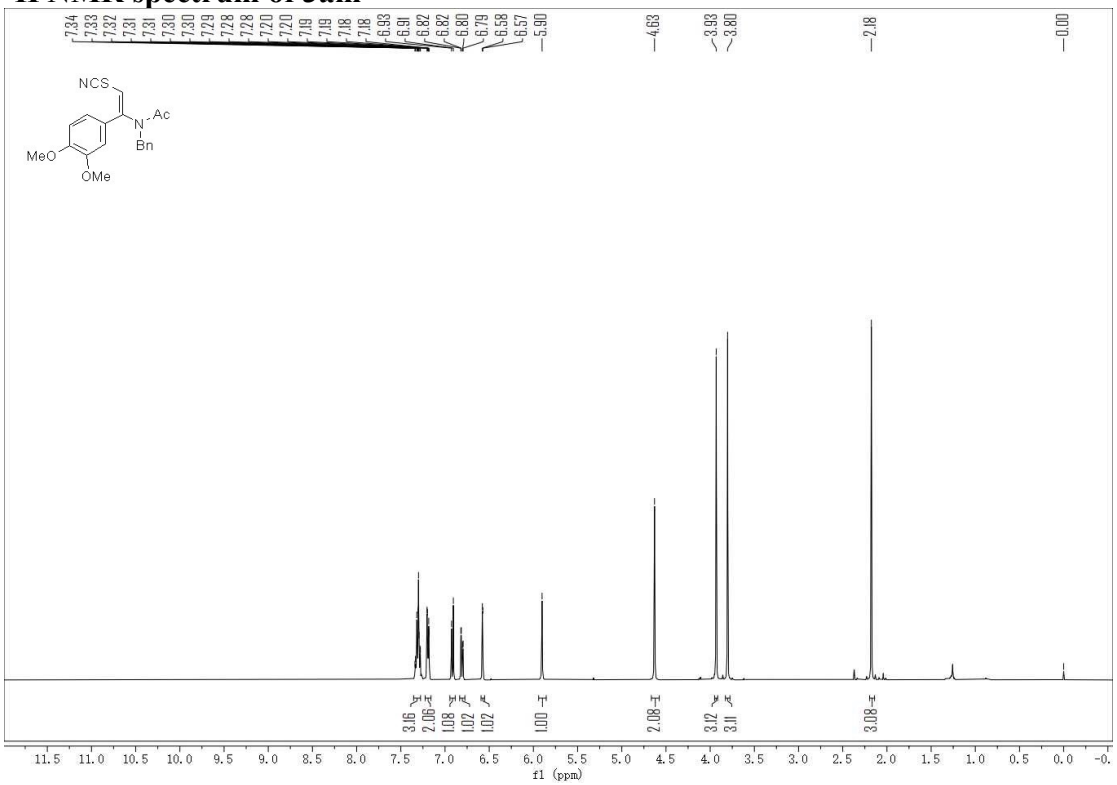
^{1}H NMR spectrum of 3al



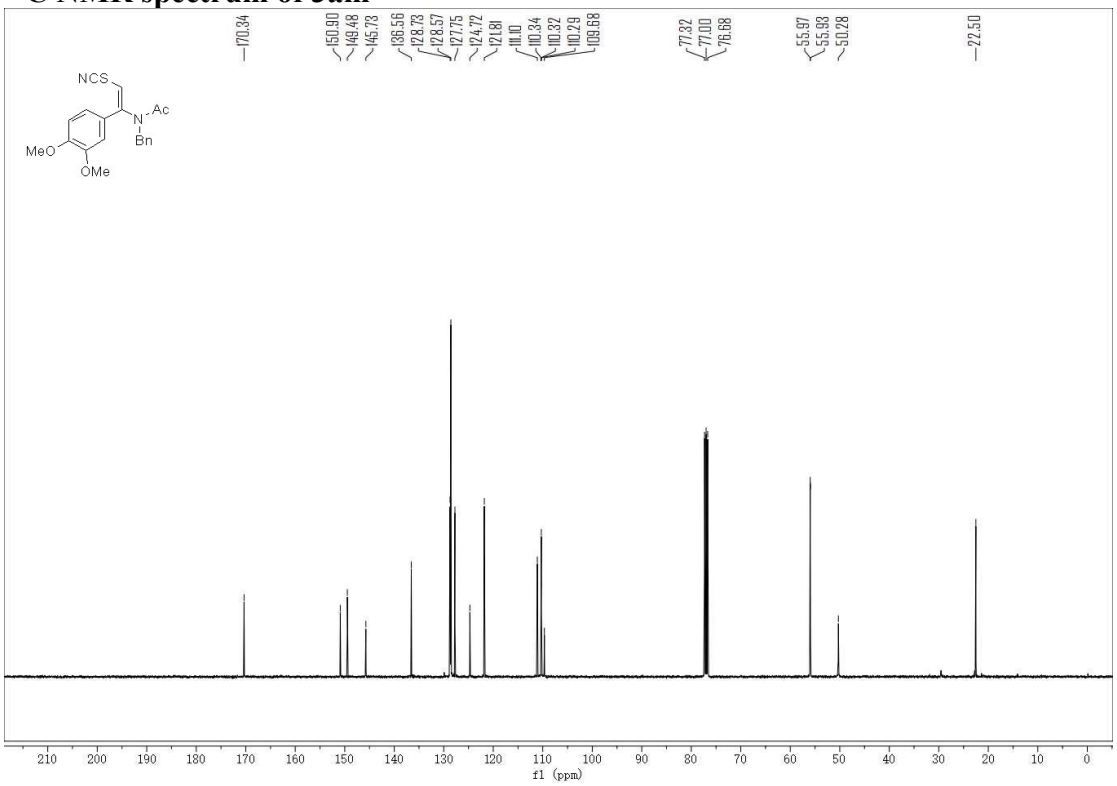
^{13}C NMR spectrum of 3al



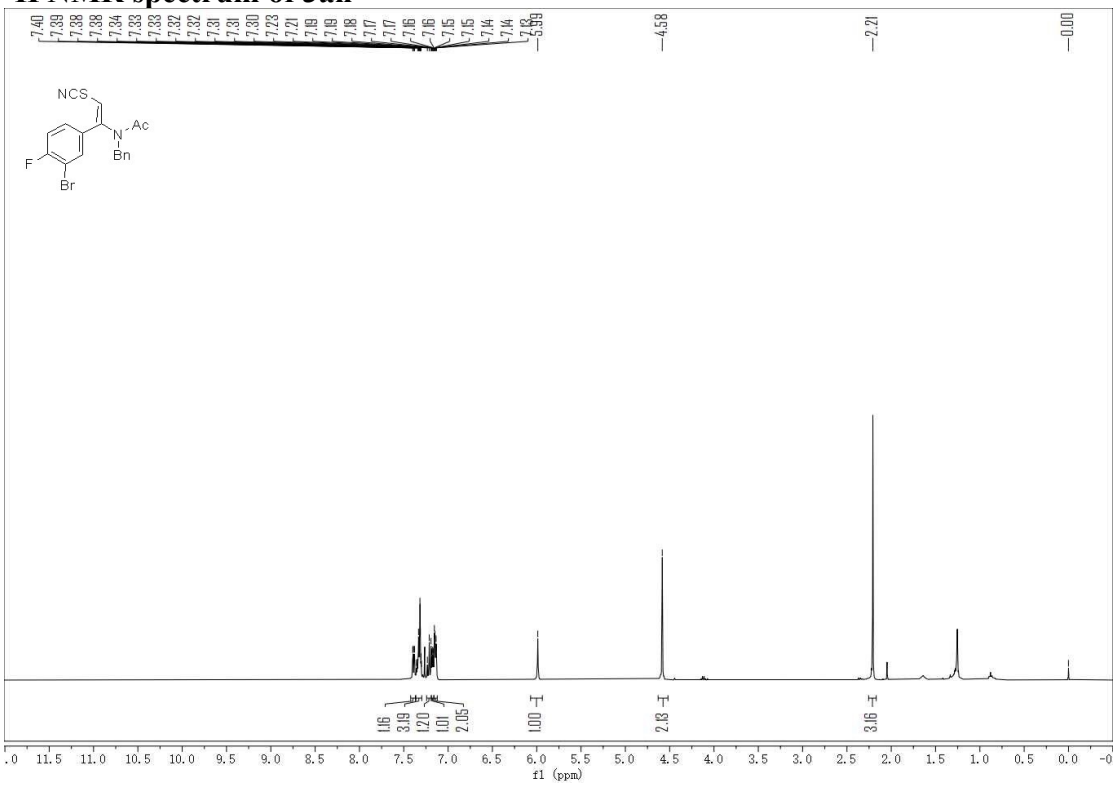
^{1}H NMR spectrum of 3am



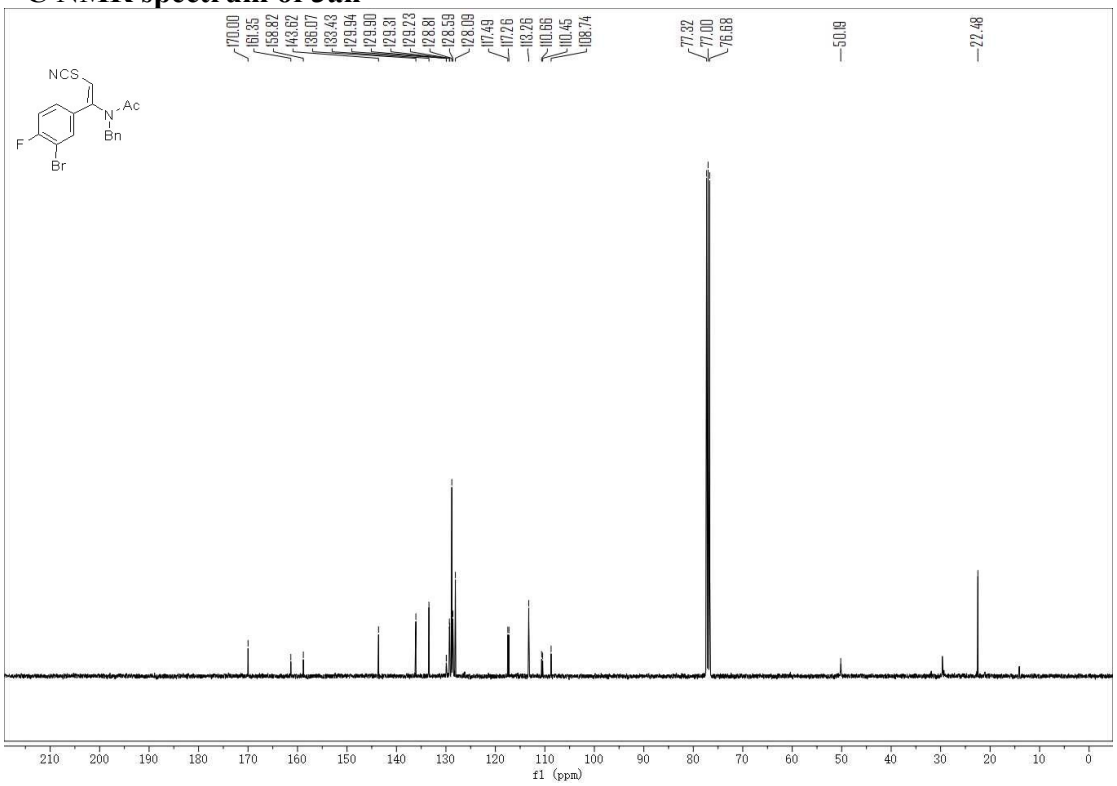
^{13}C NMR spectrum of 3am



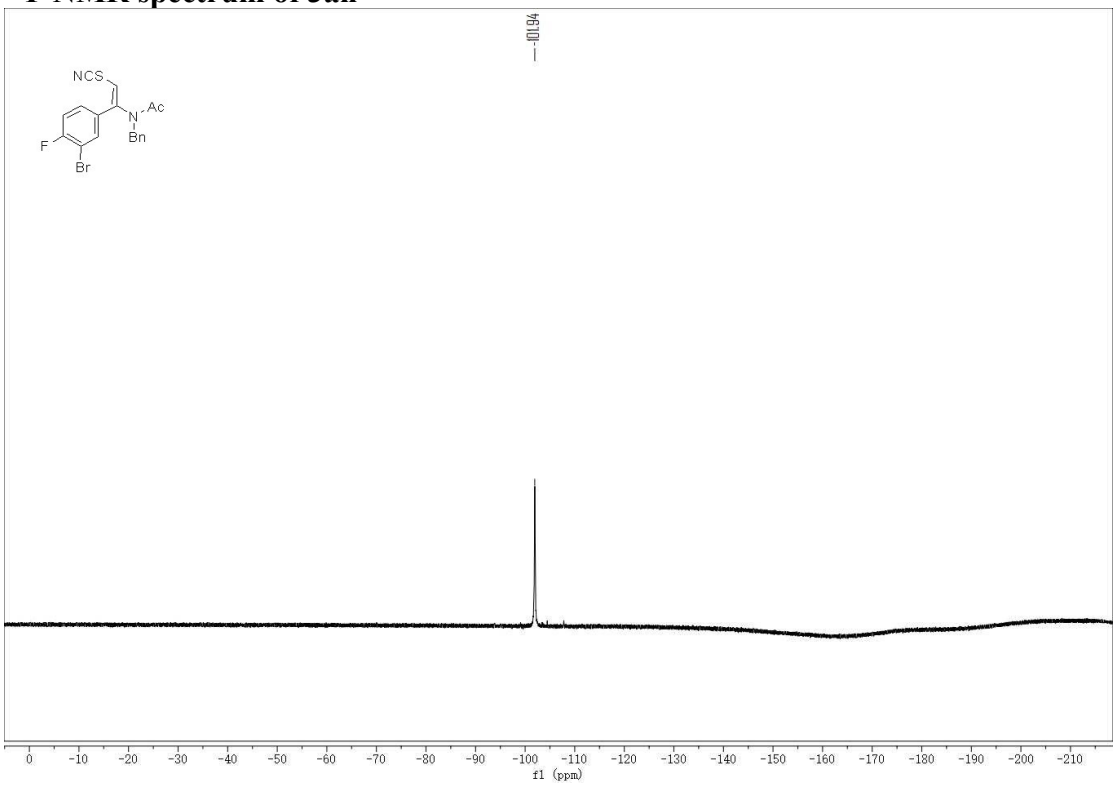
^{1}H NMR spectrum of 3an



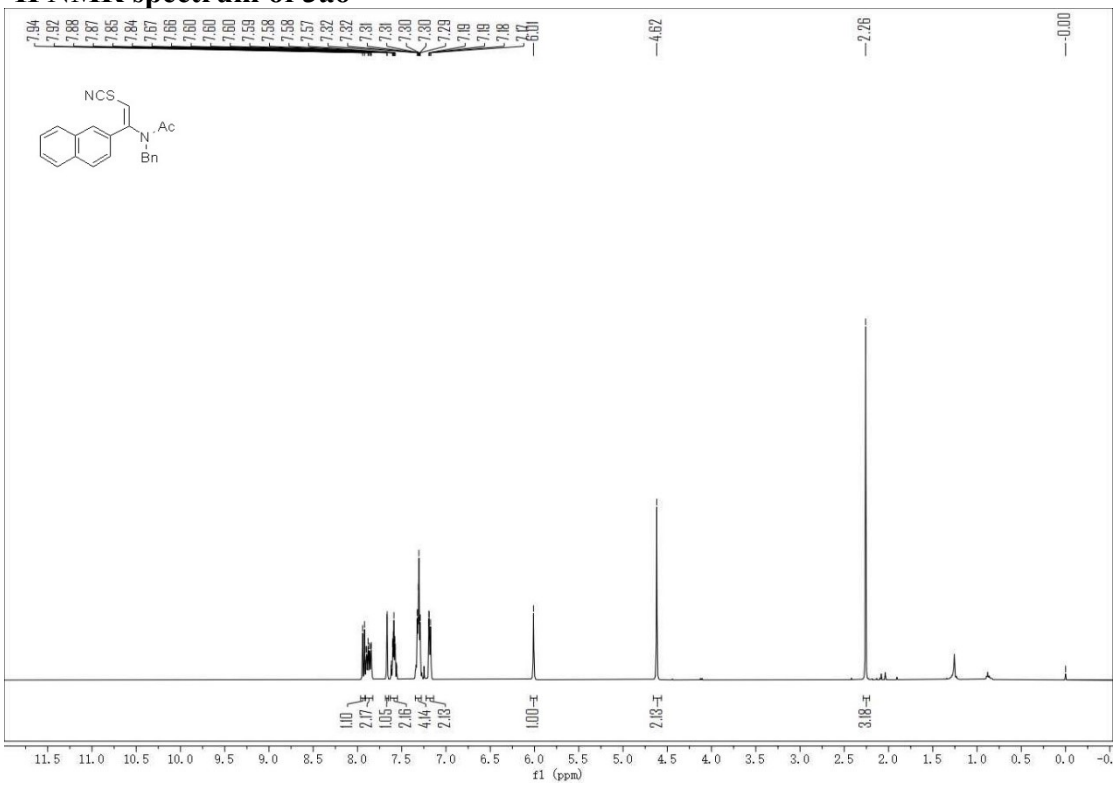
^{13}C NMR spectrum of 3an



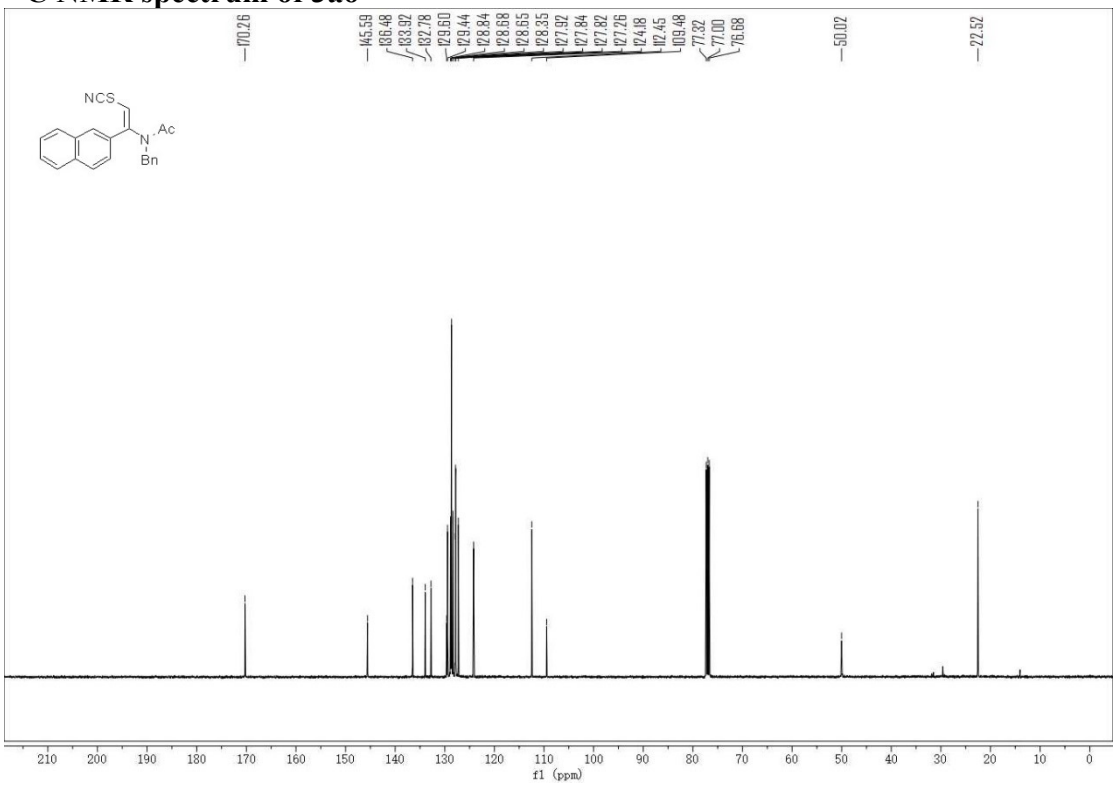
^{19}F NMR spectrum of 3an



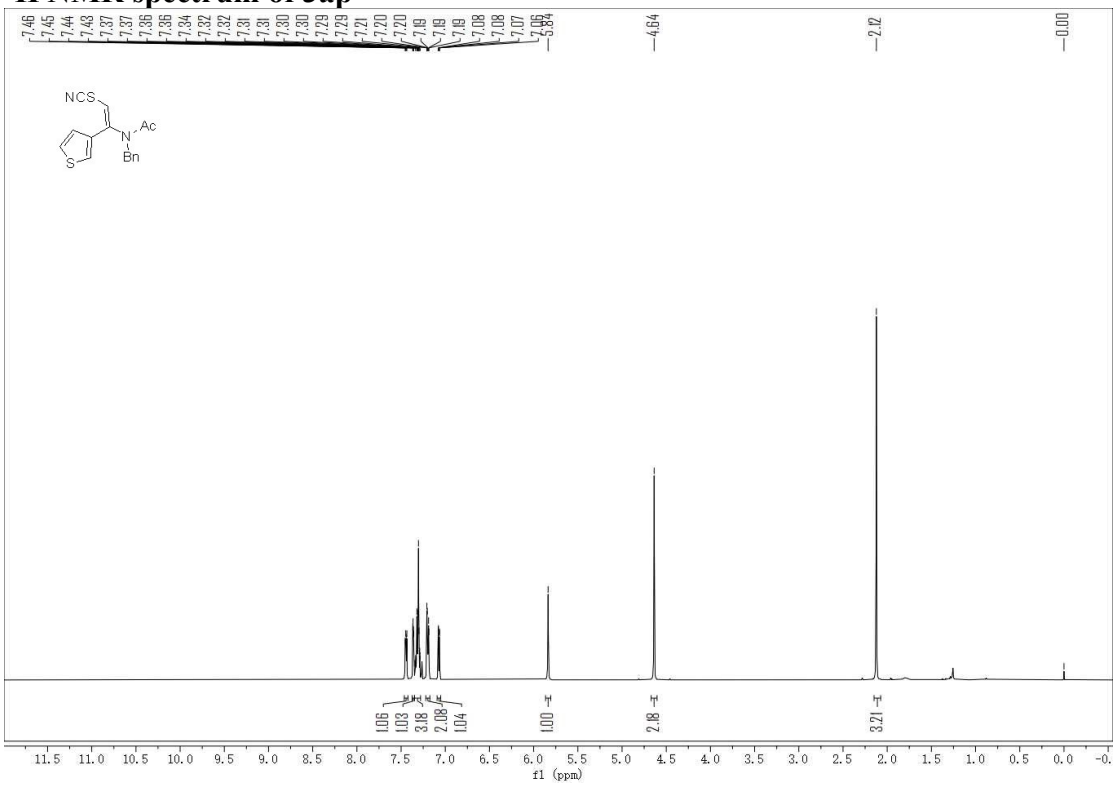
^{1}H NMR spectrum of 3ao



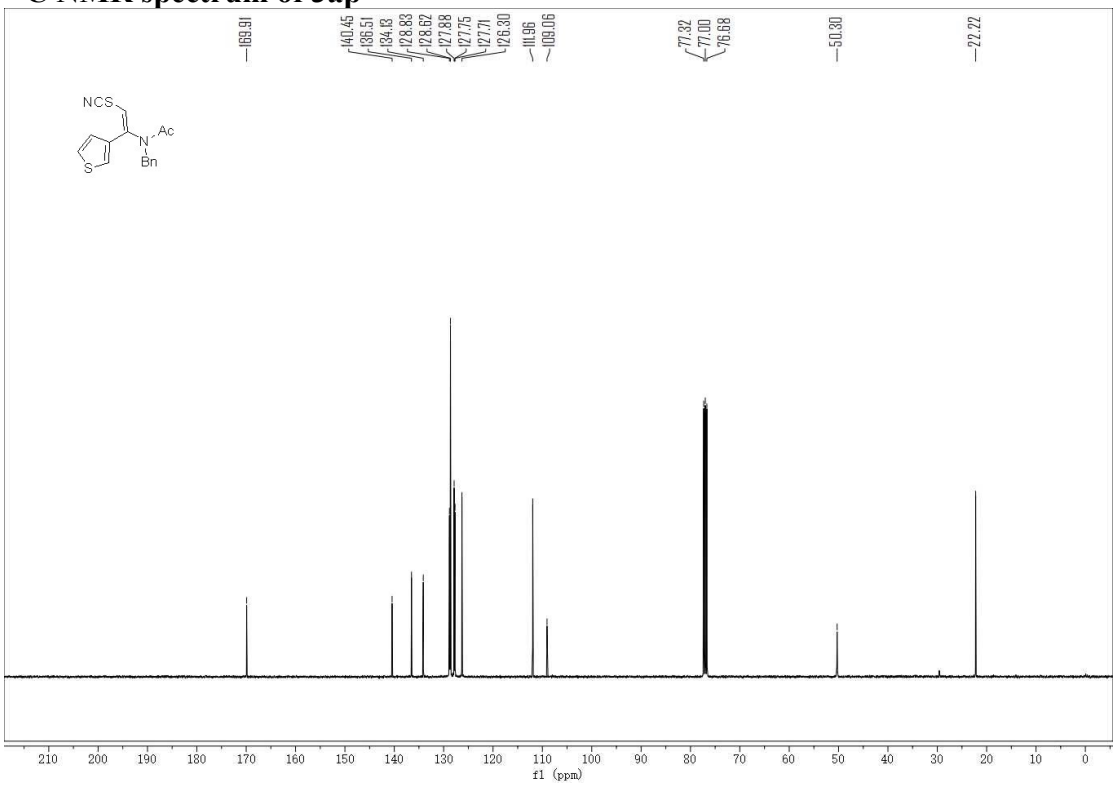
^{13}C NMR spectrum of 3ao



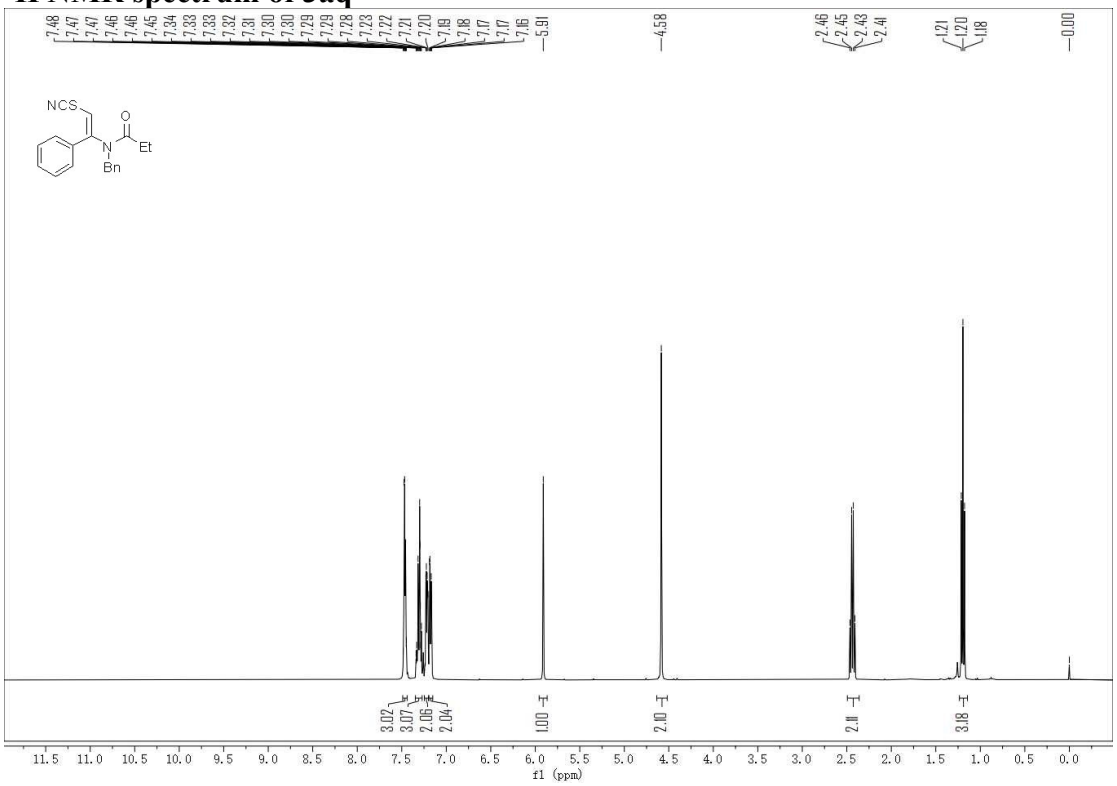
^{1}H NMR spectrum of 3ap



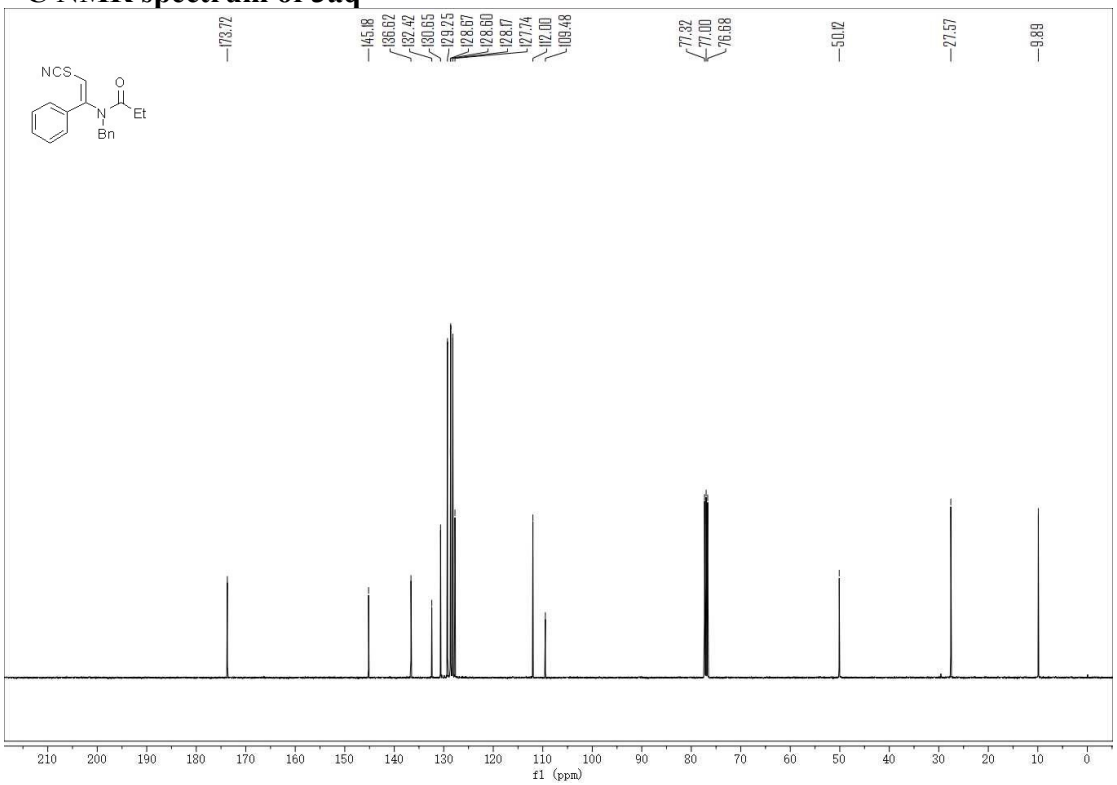
^{13}C NMR spectrum of 3ap



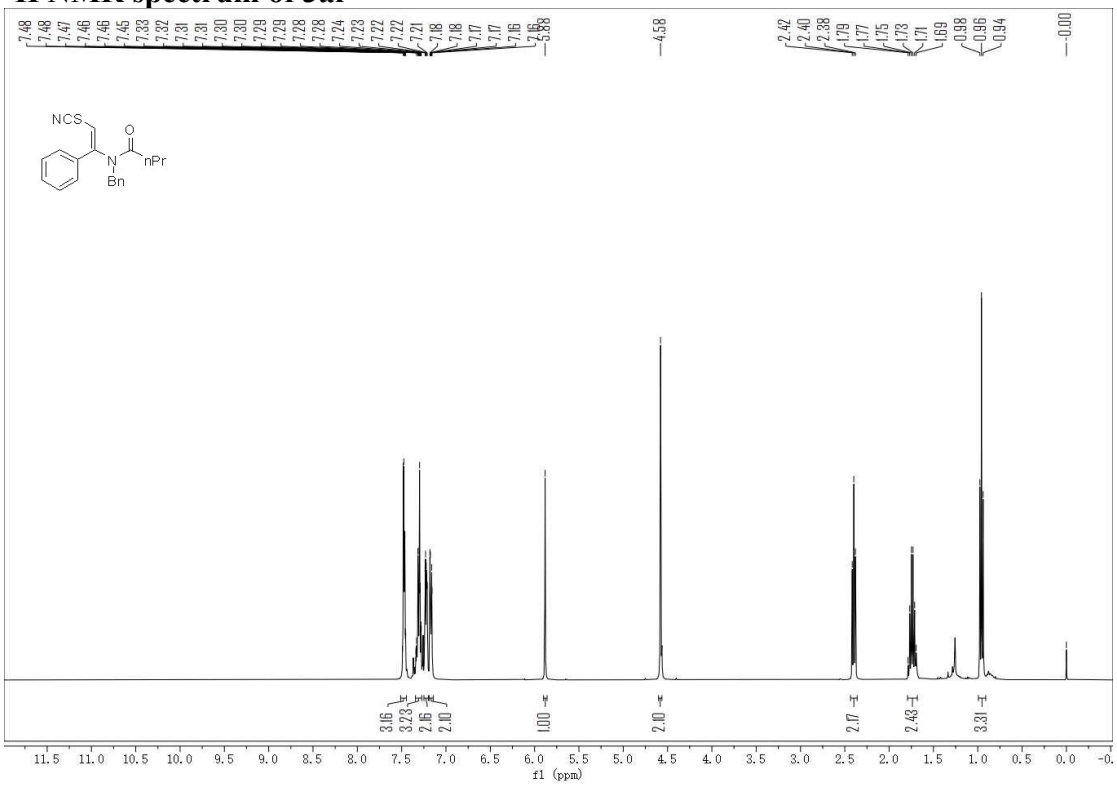
^{1}H NMR spectrum of 3aq



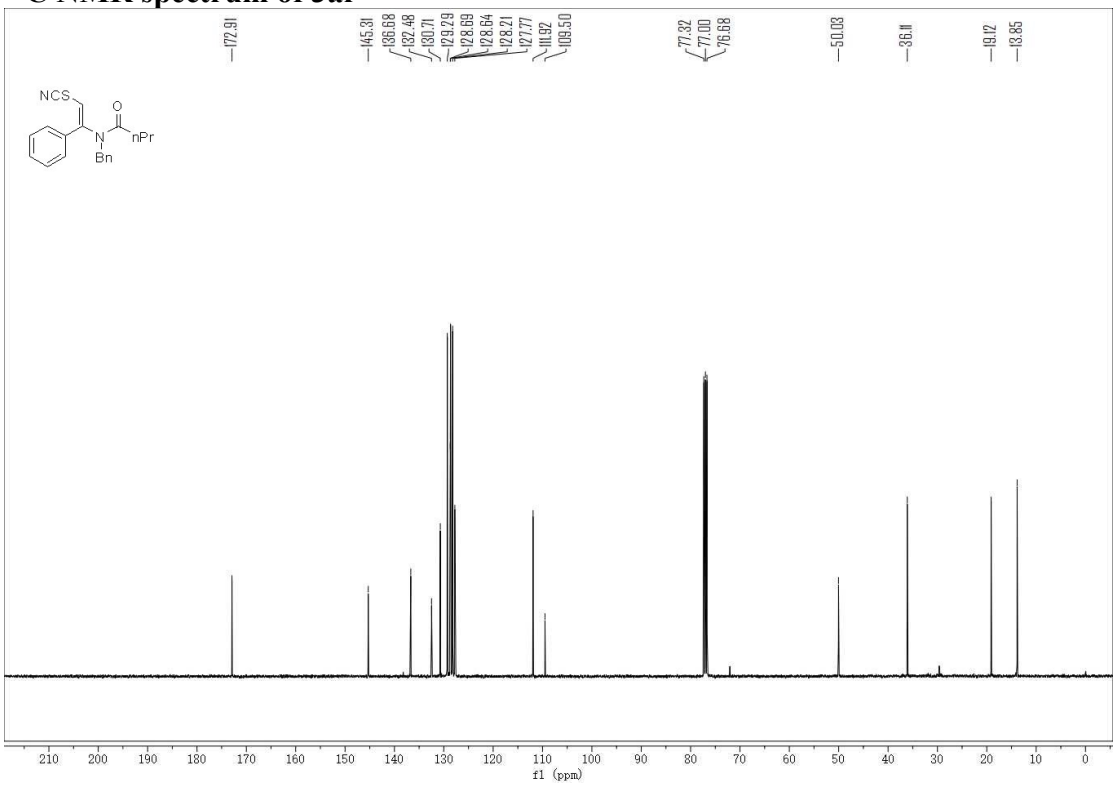
^{13}C NMR spectrum of 3aq



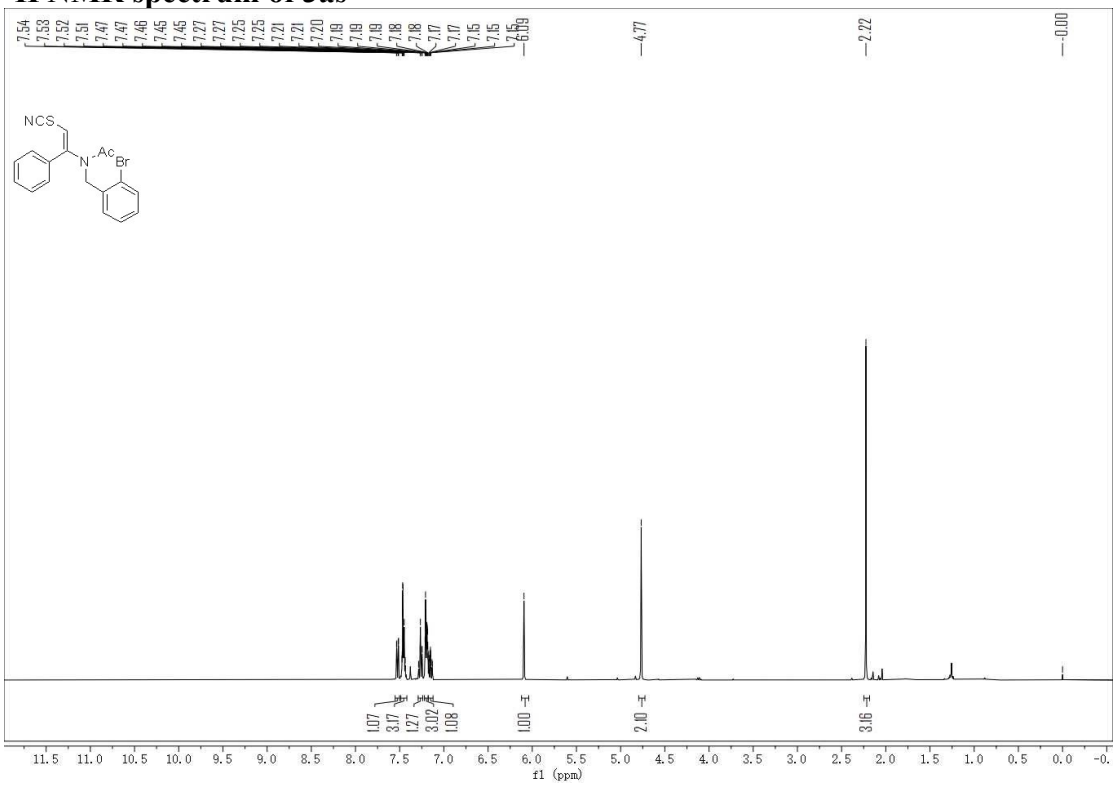
^{1}H NMR spectrum of 3ar



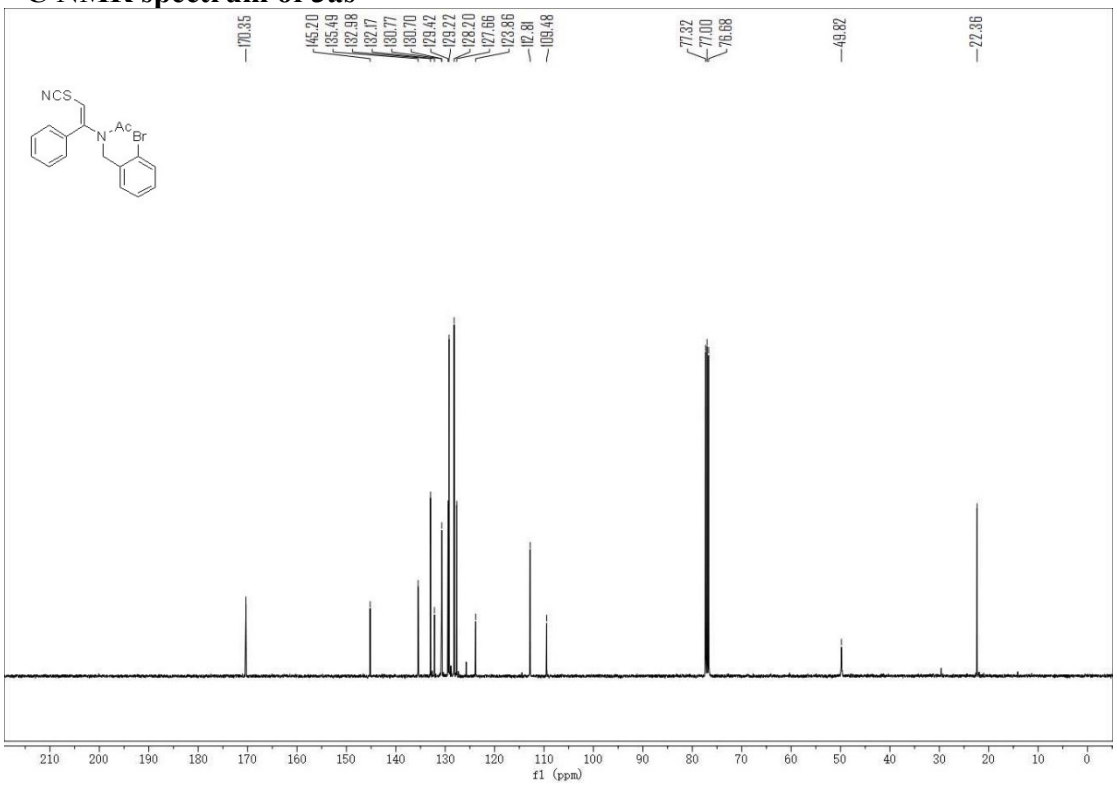
^{13}C NMR spectrum of 3ar



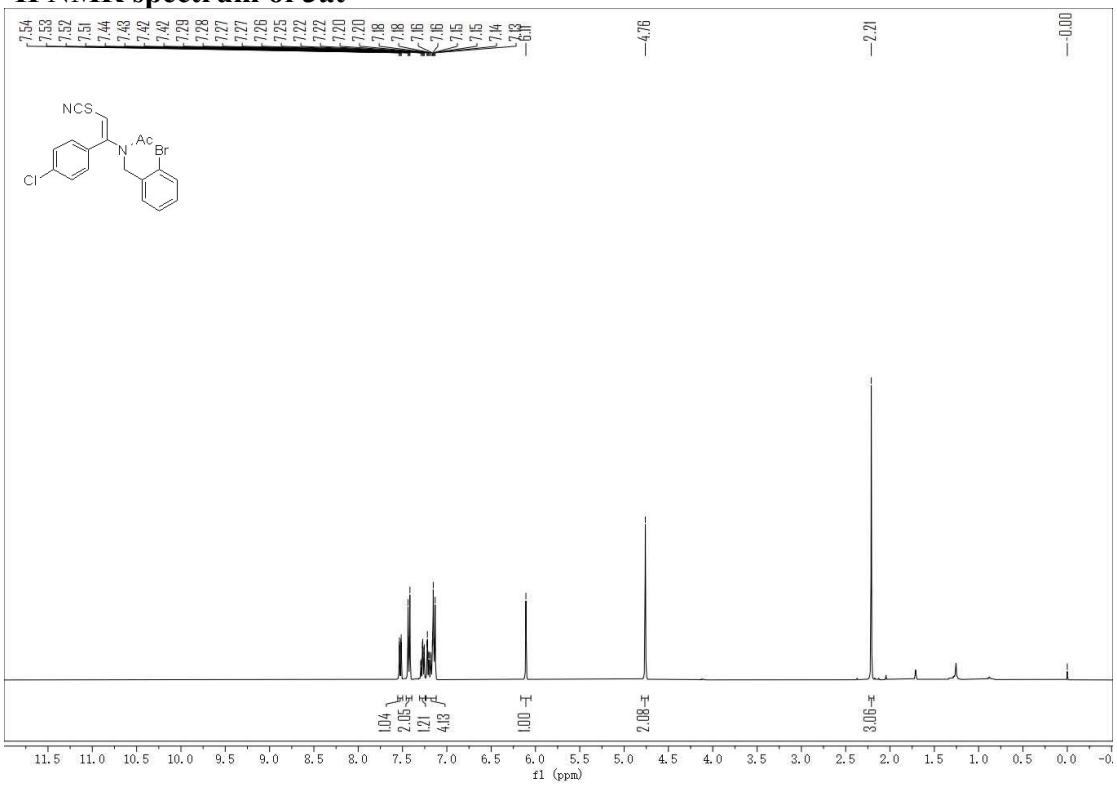
^{1}H NMR spectrum of 3as



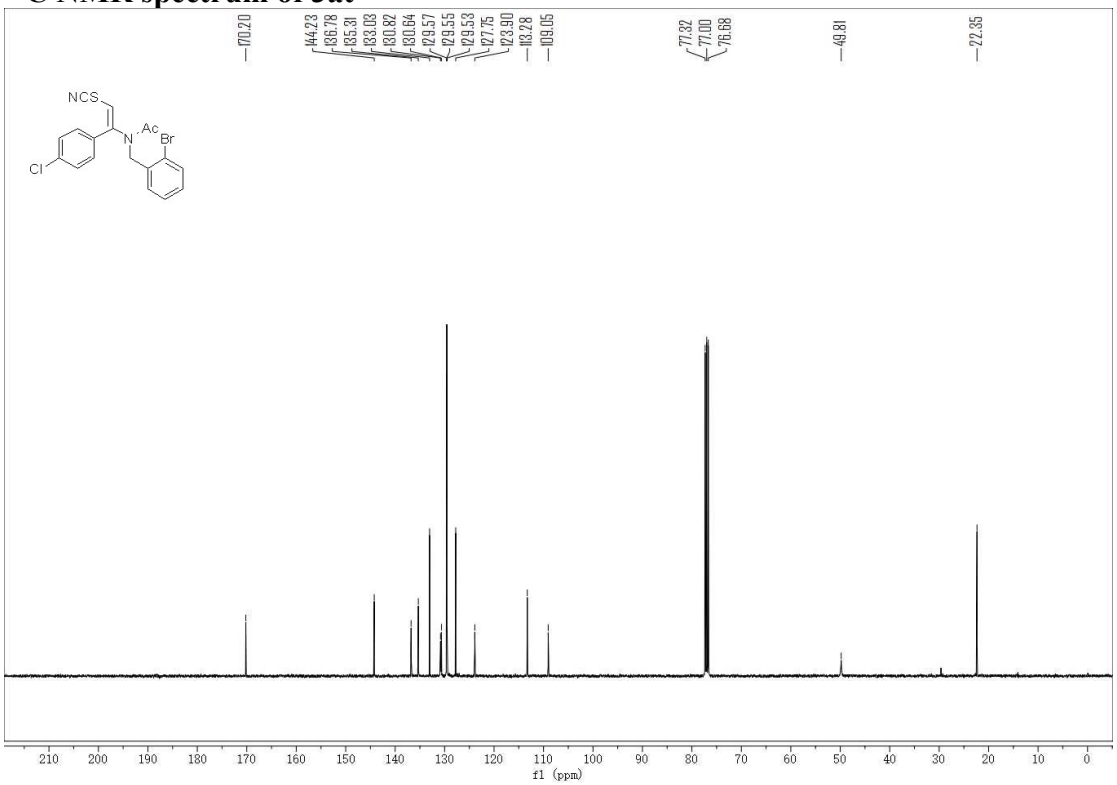
^{13}C NMR spectrum of 3as



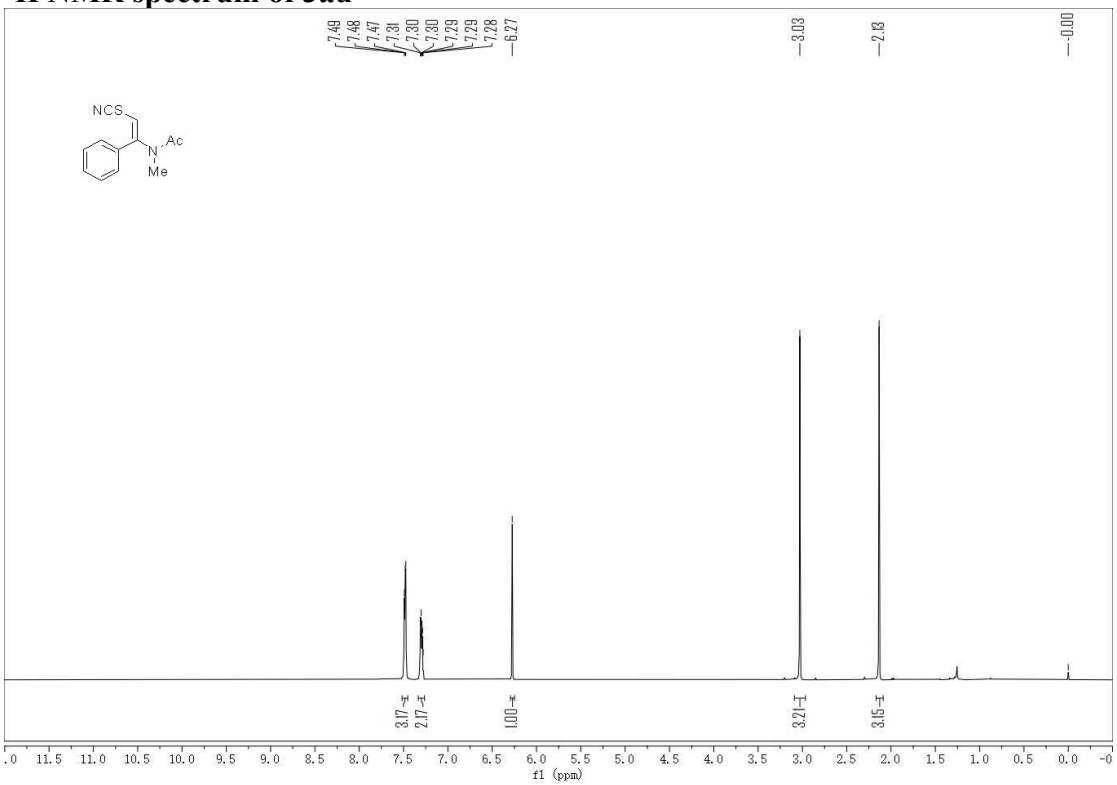
^{1}H NMR spectrum of 3at



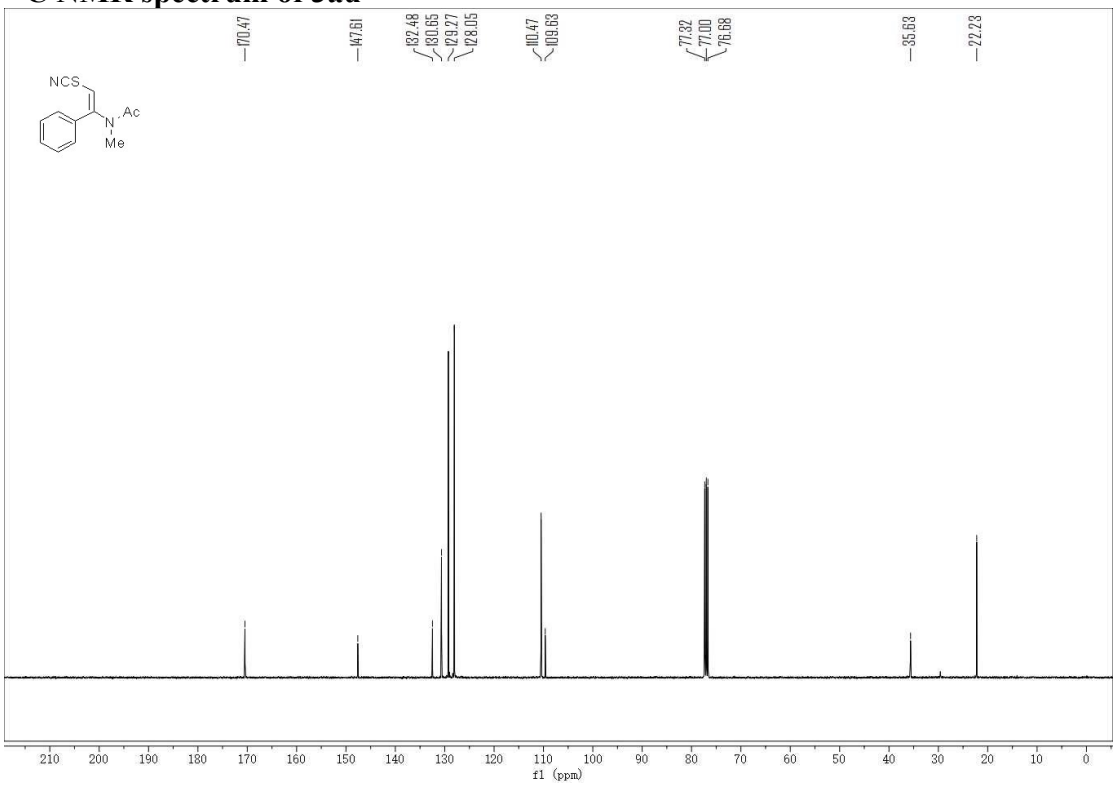
^{13}C NMR spectrum of 3at



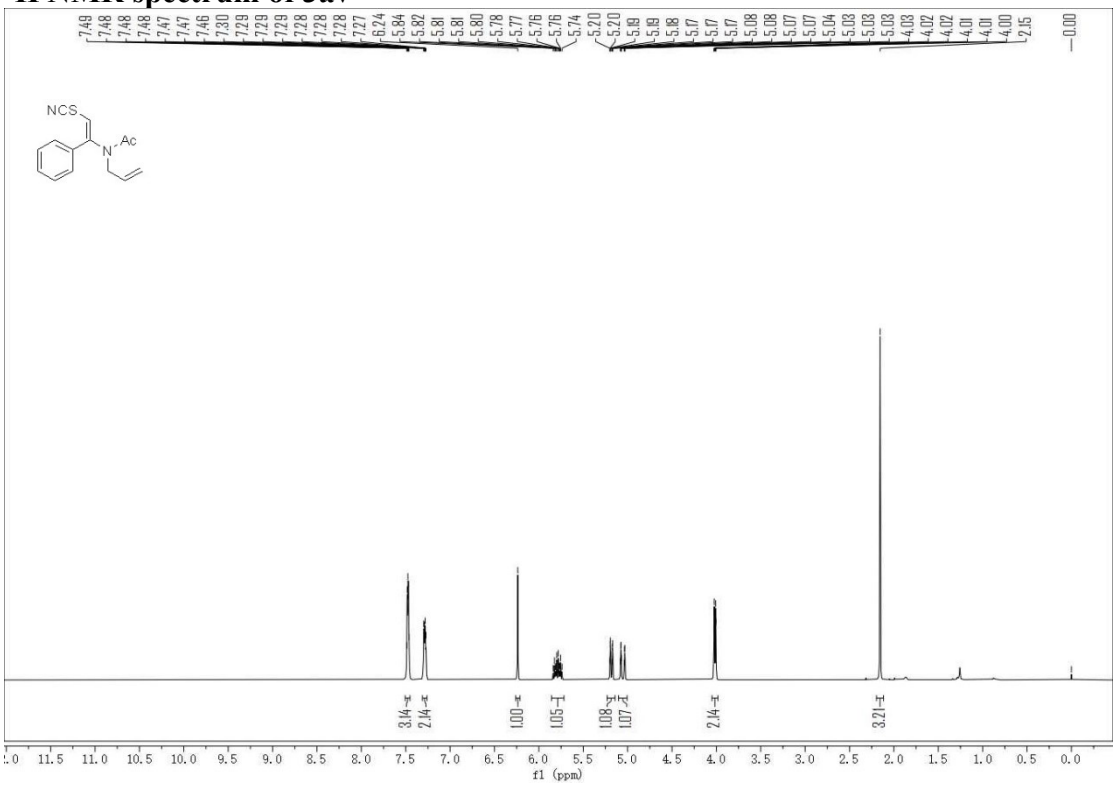
^{1}H NMR spectrum of 3au



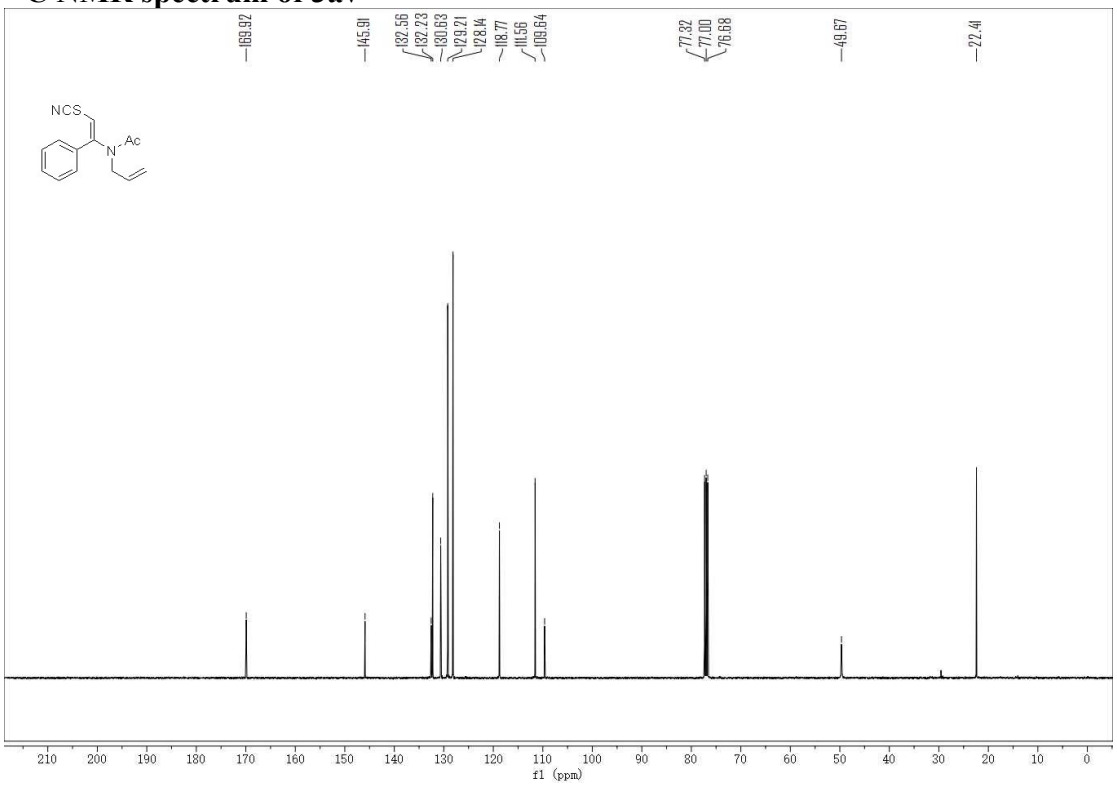
^{13}C NMR spectrum of 3au



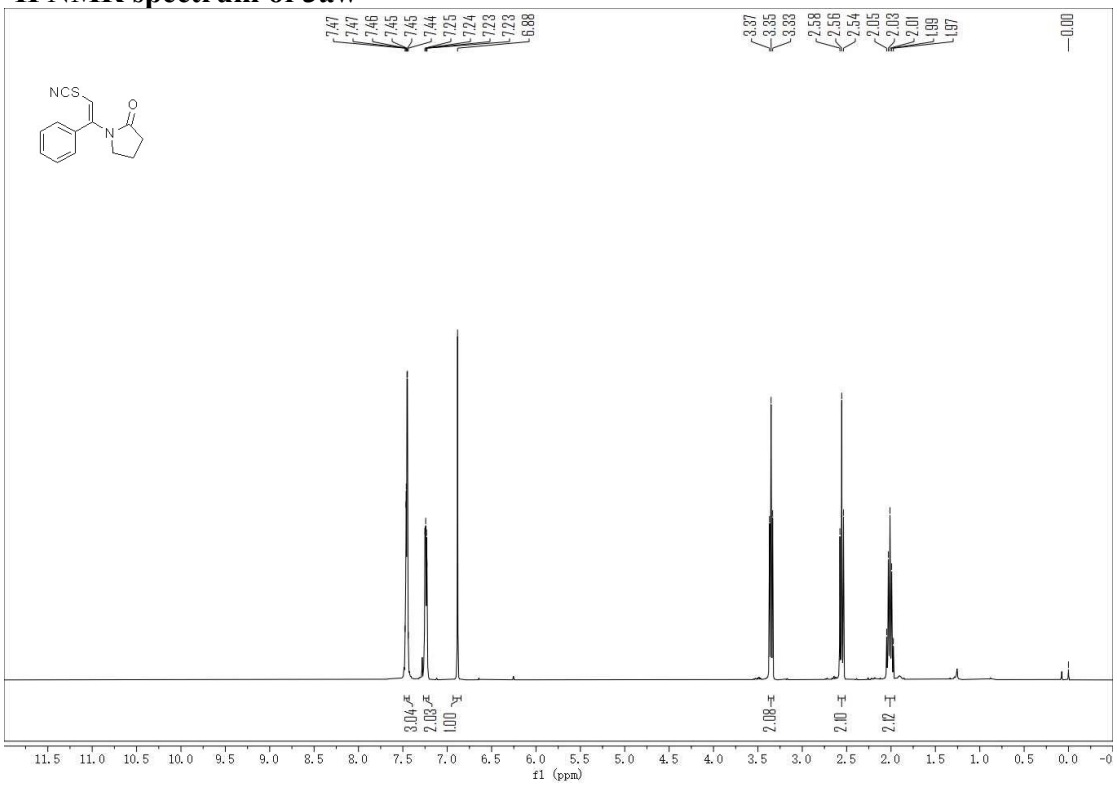
^{1}H NMR spectrum of 3av



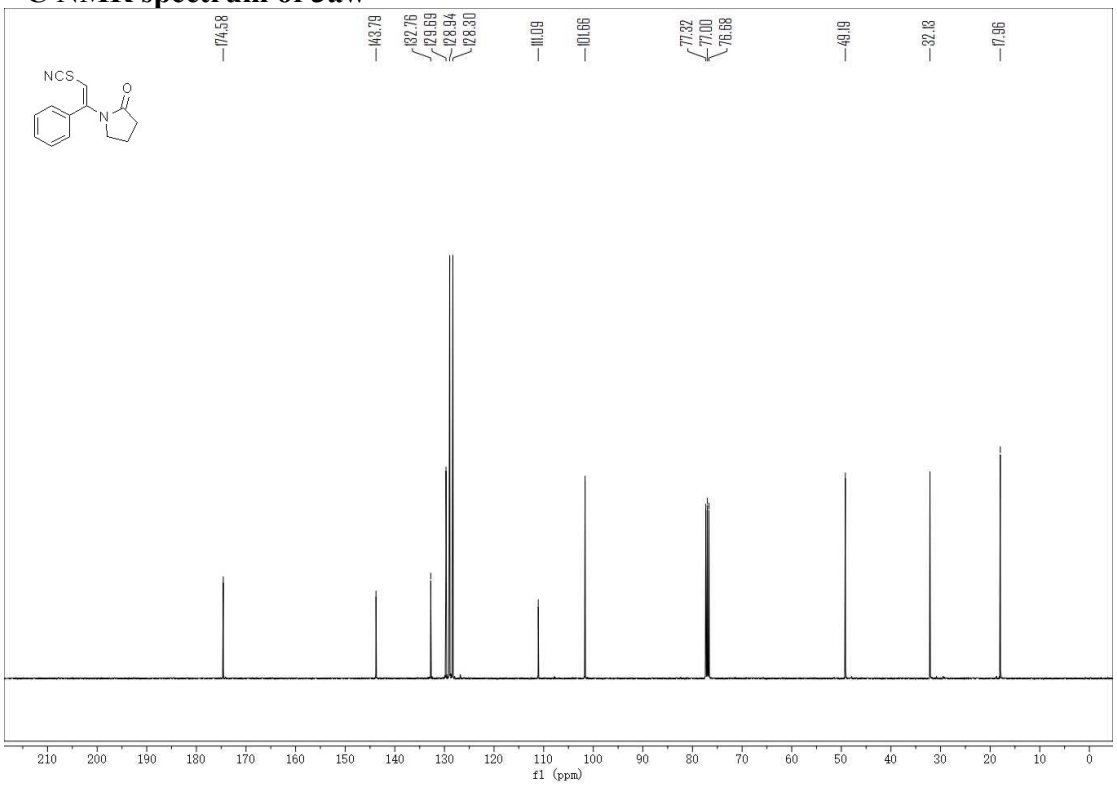
^{13}C NMR spectrum of 3av



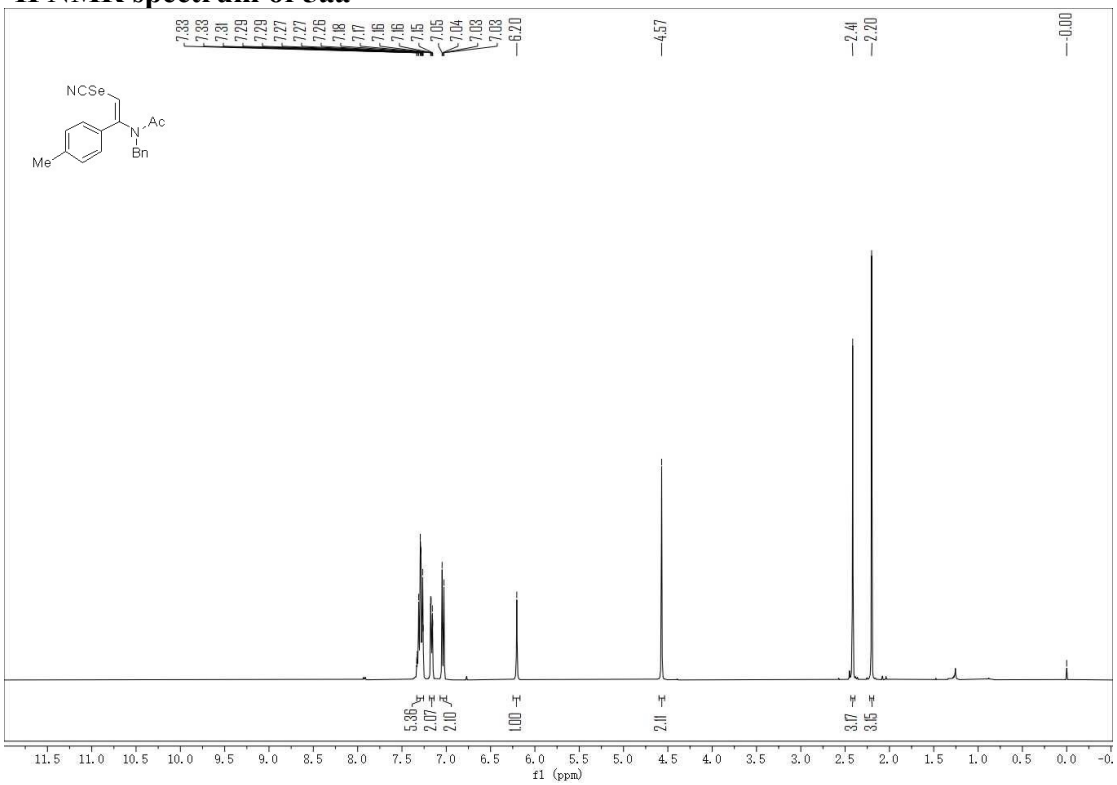
^{1}H NMR spectrum of 3aw



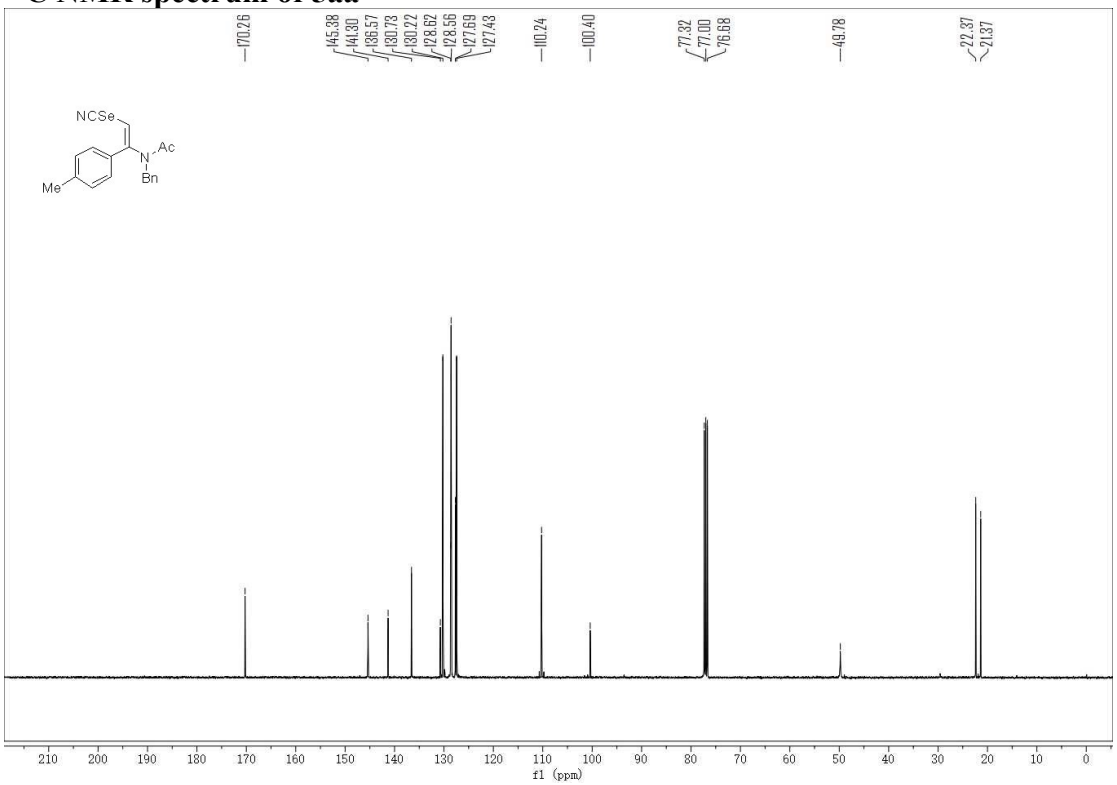
^{13}C NMR spectrum of 3aw



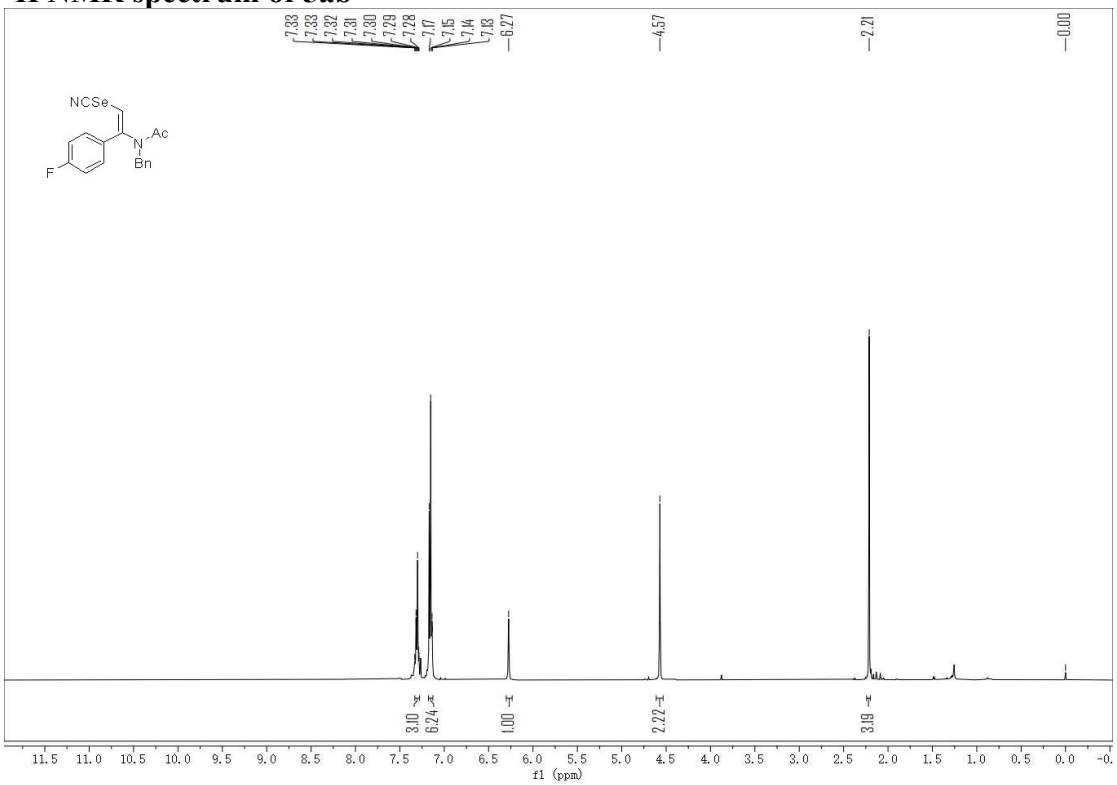
^{1}H NMR spectrum of 5aa



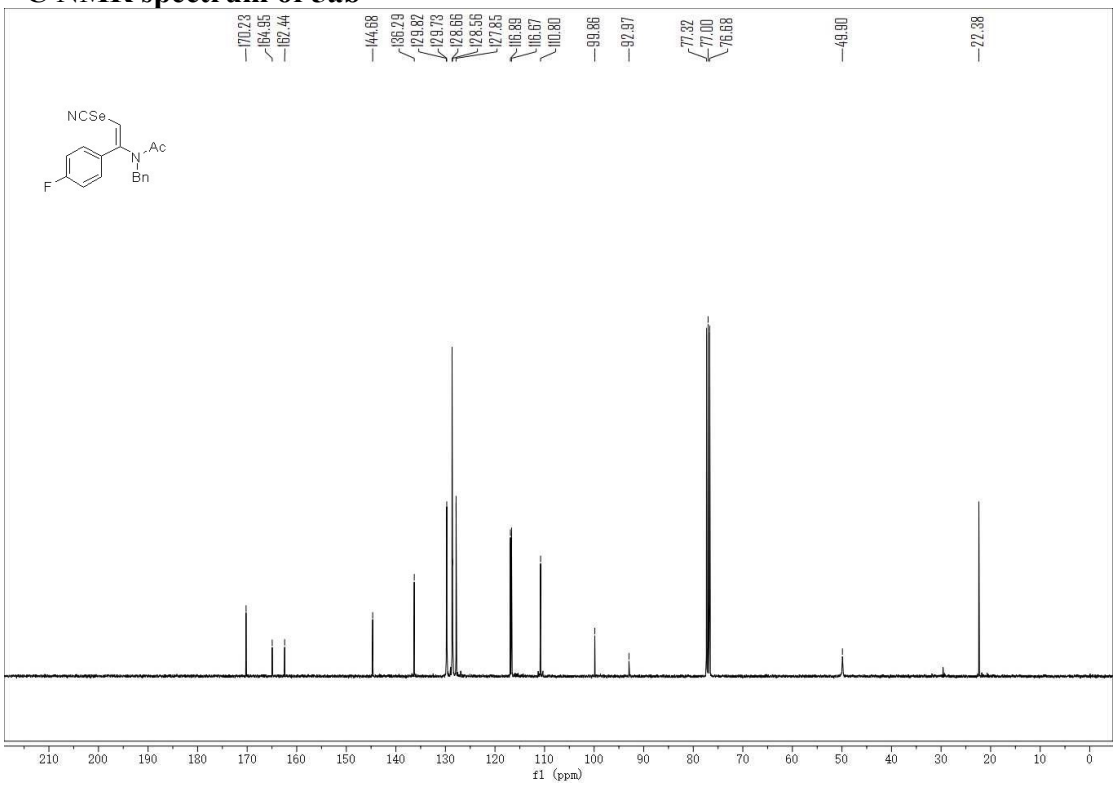
^{13}C NMR spectrum of 5aa



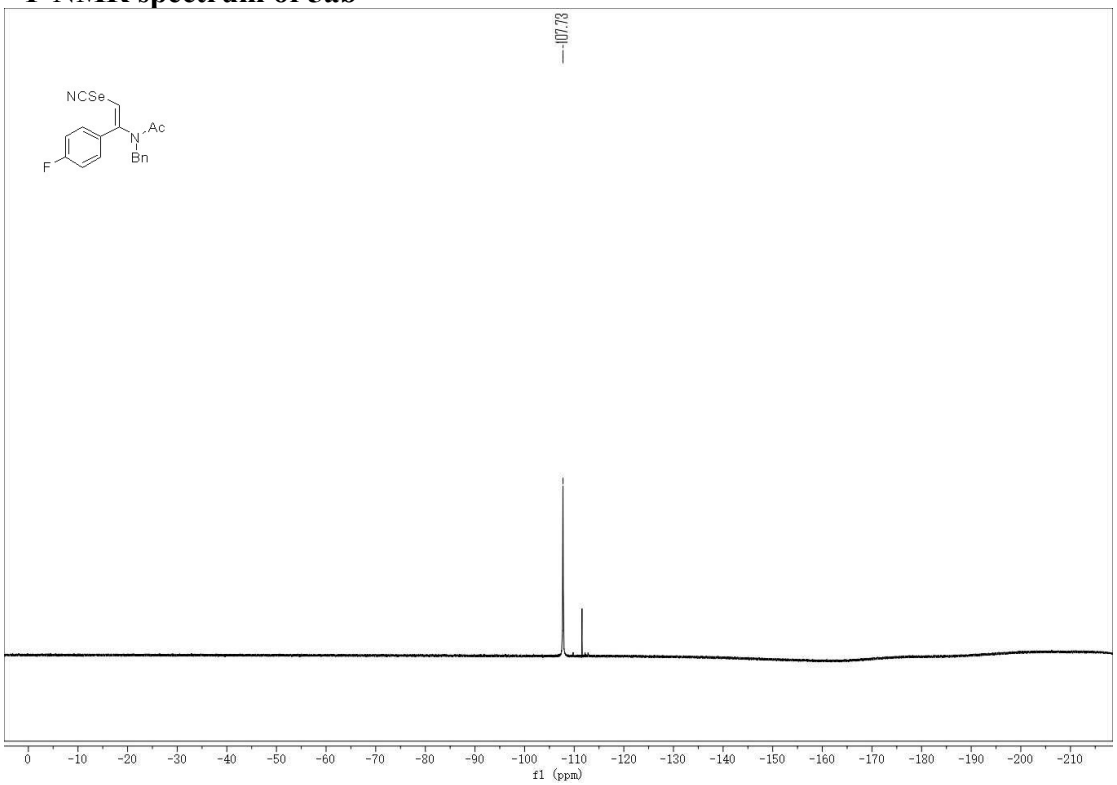
^{1}H NMR spectrum of 5ab



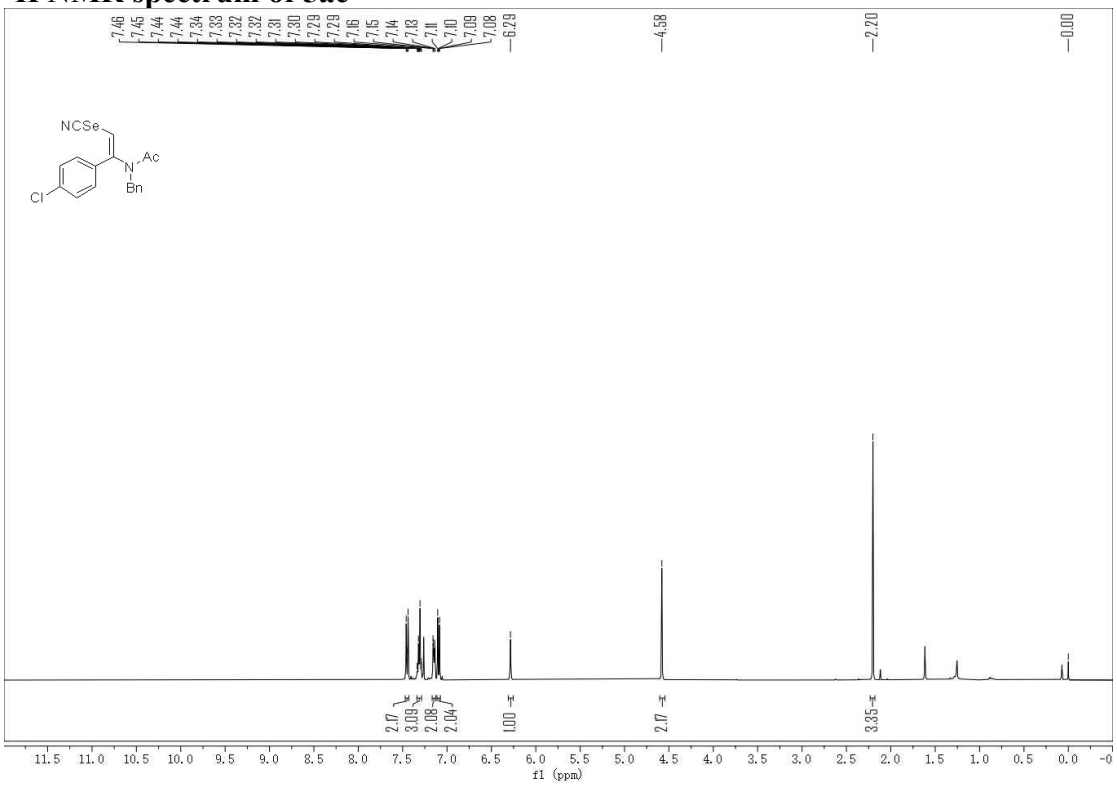
^{13}C NMR spectrum of 5ab



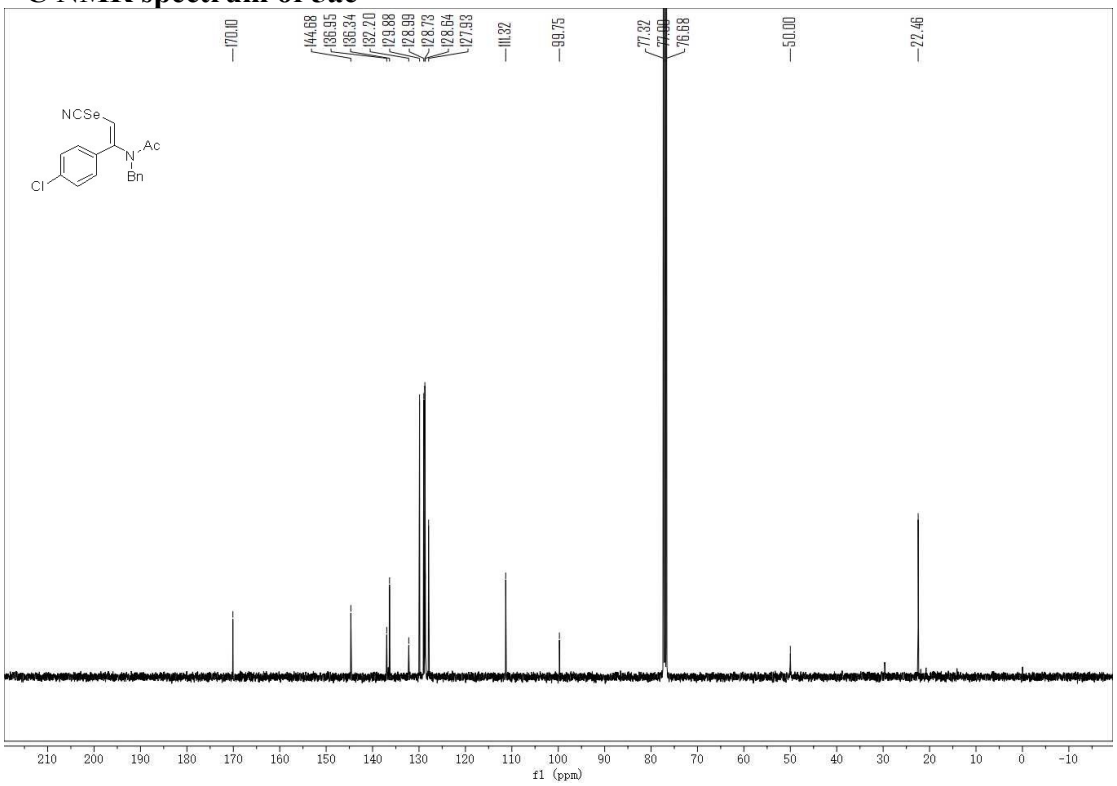
^{19}F NMR spectrum of 5ab



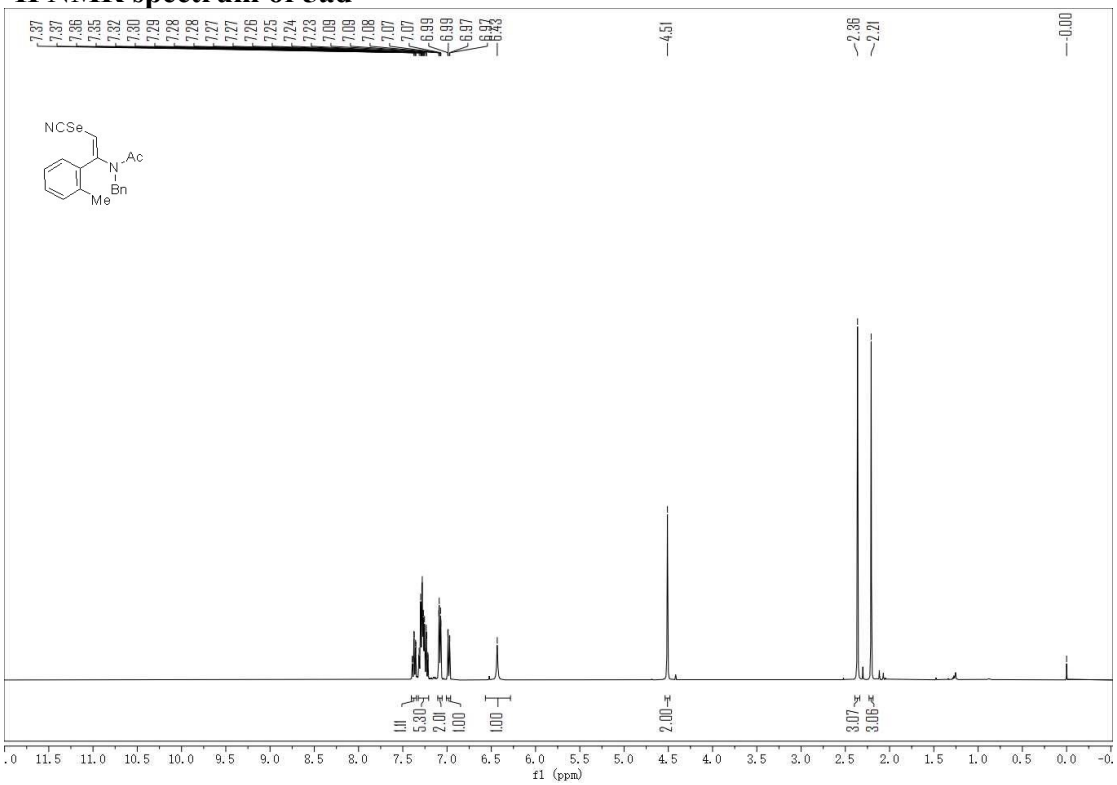
^{1}H NMR spectrum of 5ac



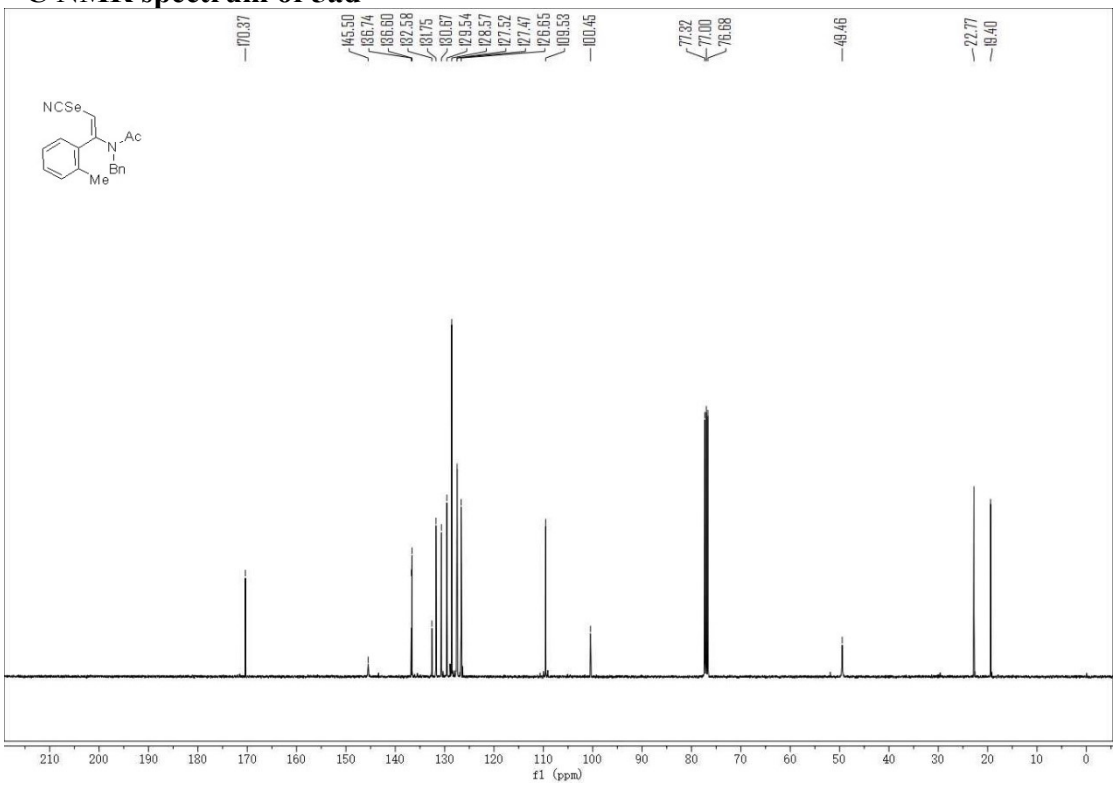
^{13}C NMR spectrum of 5ac



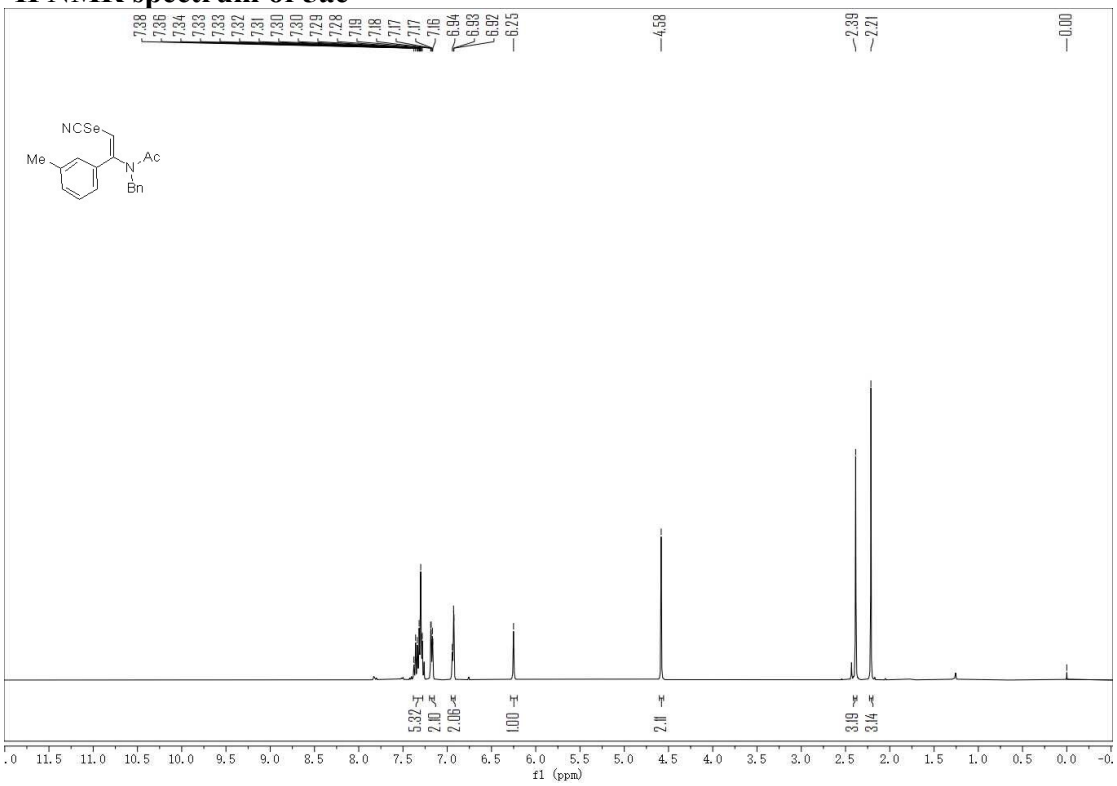
^{1}H NMR spectrum of 5ad



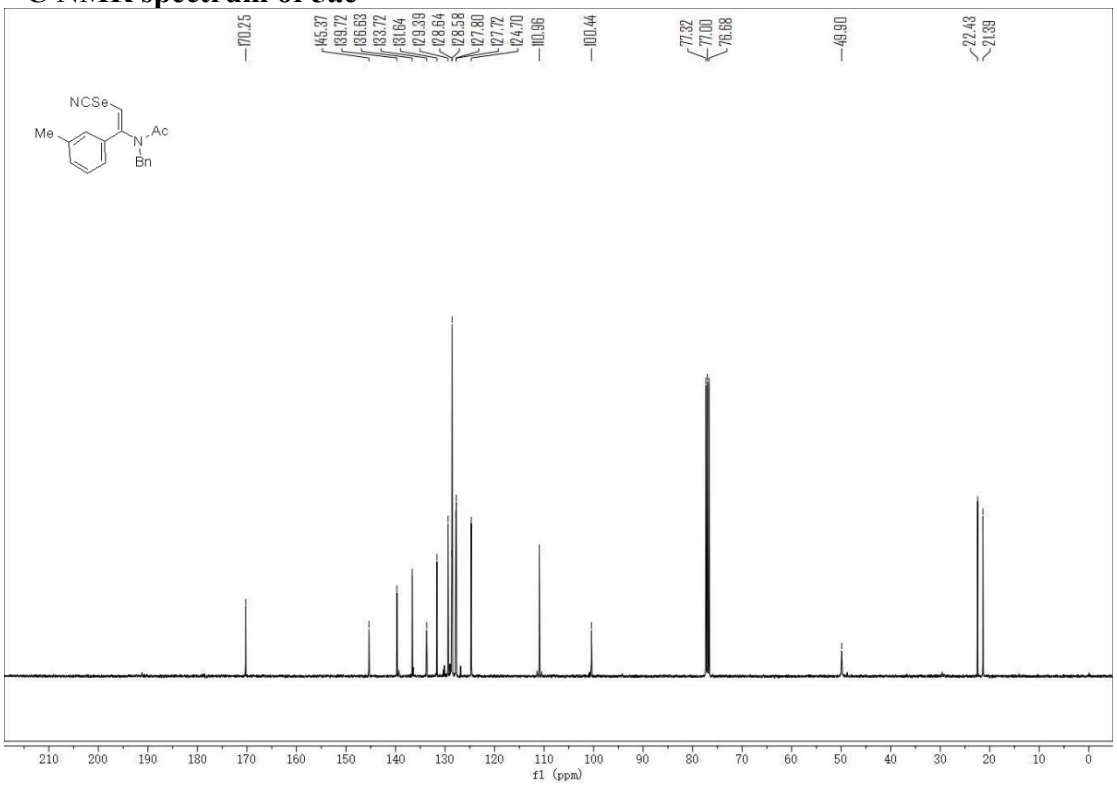
^{13}C NMR spectrum of 5ad



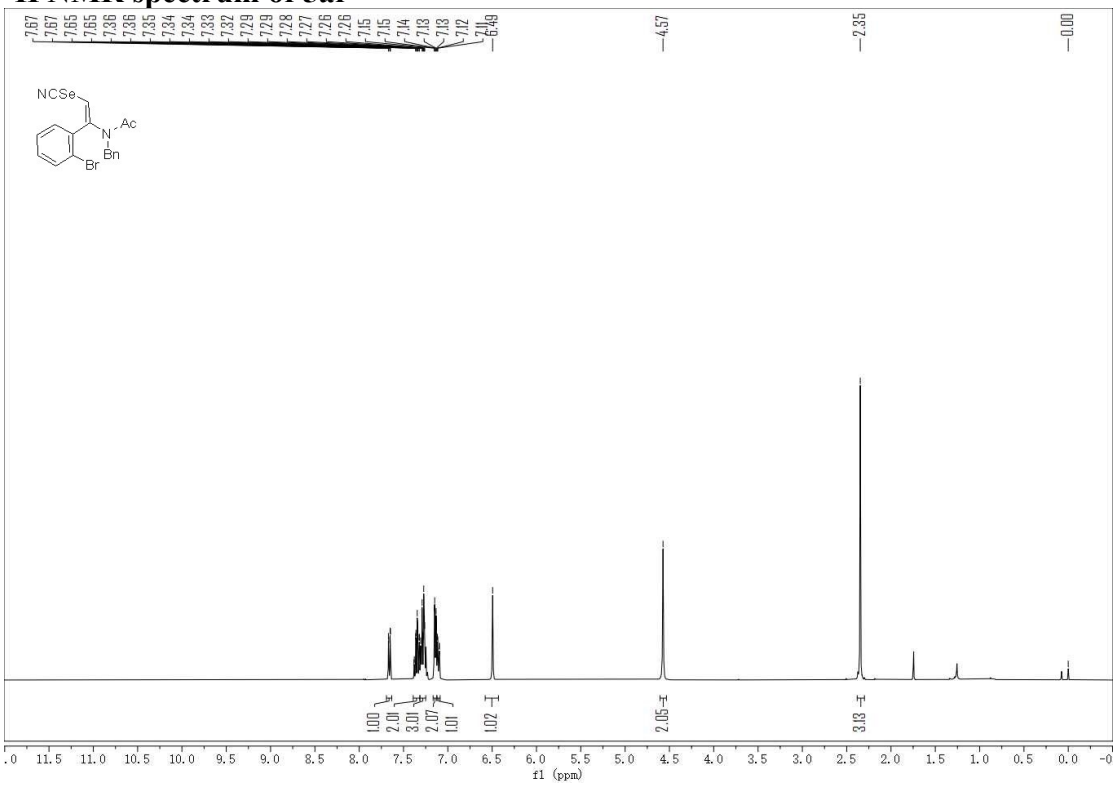
^{1}H NMR spectrum of 5ae



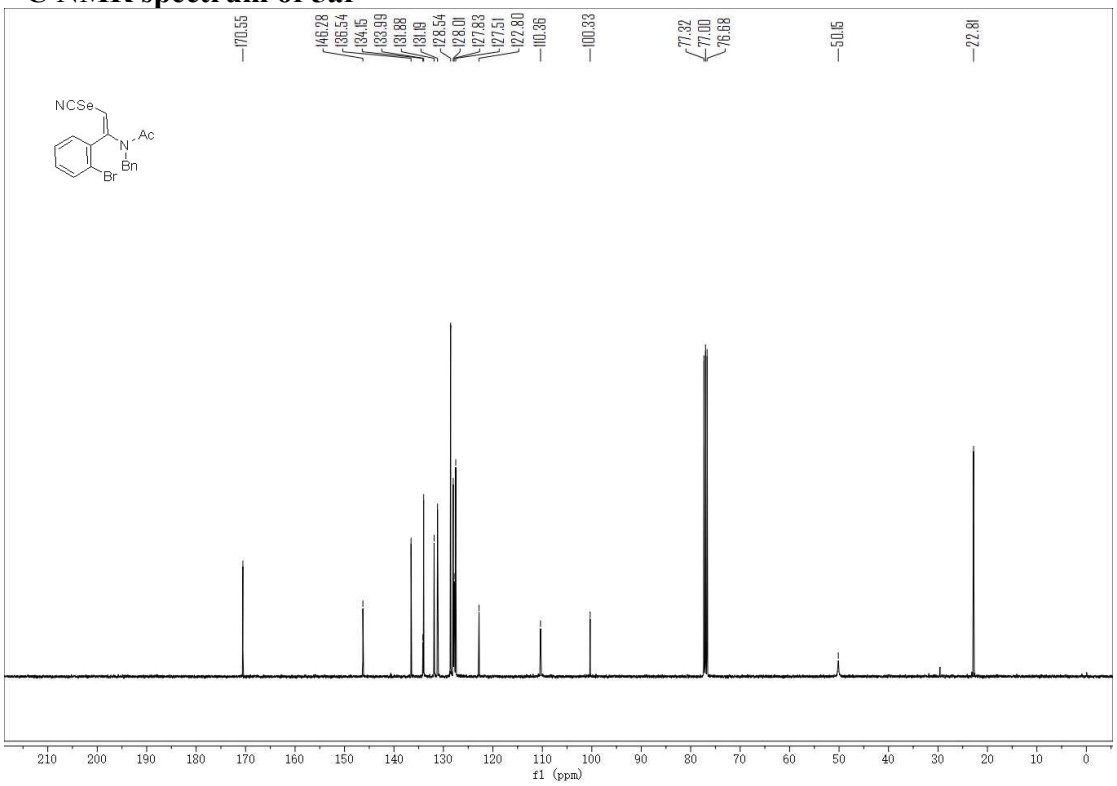
^{13}C NMR spectrum of 5ae



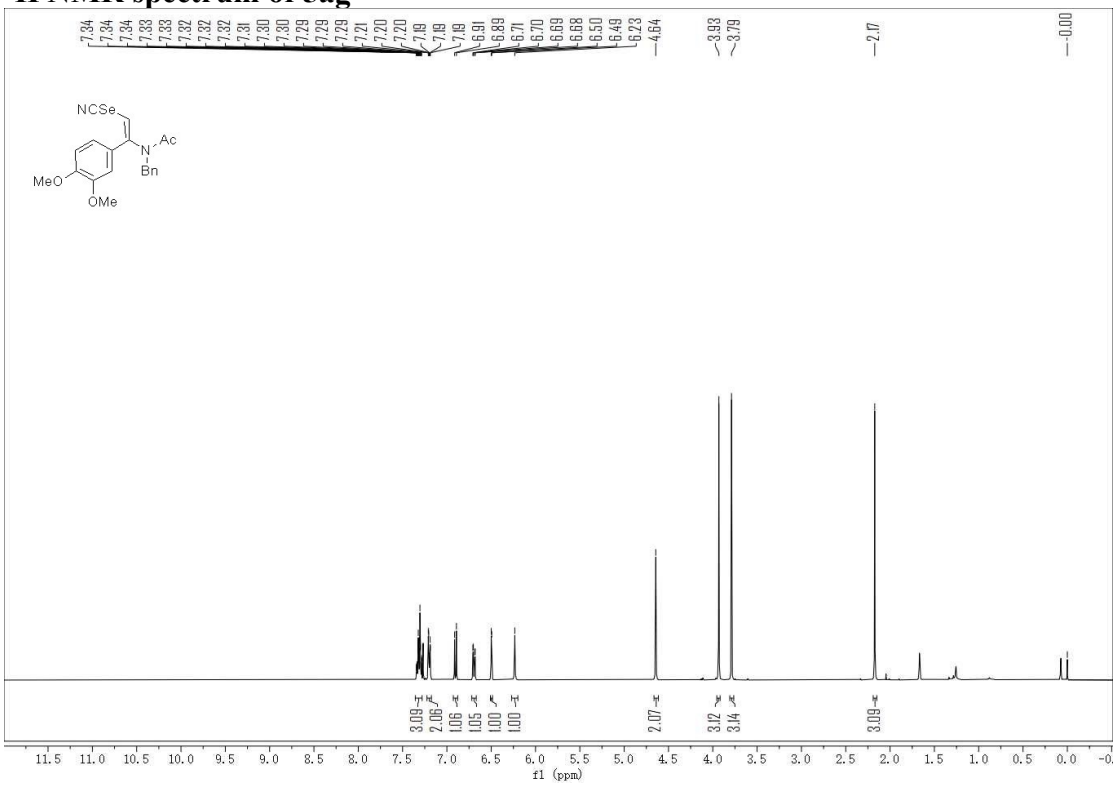
^{1}H NMR spectrum of 5af



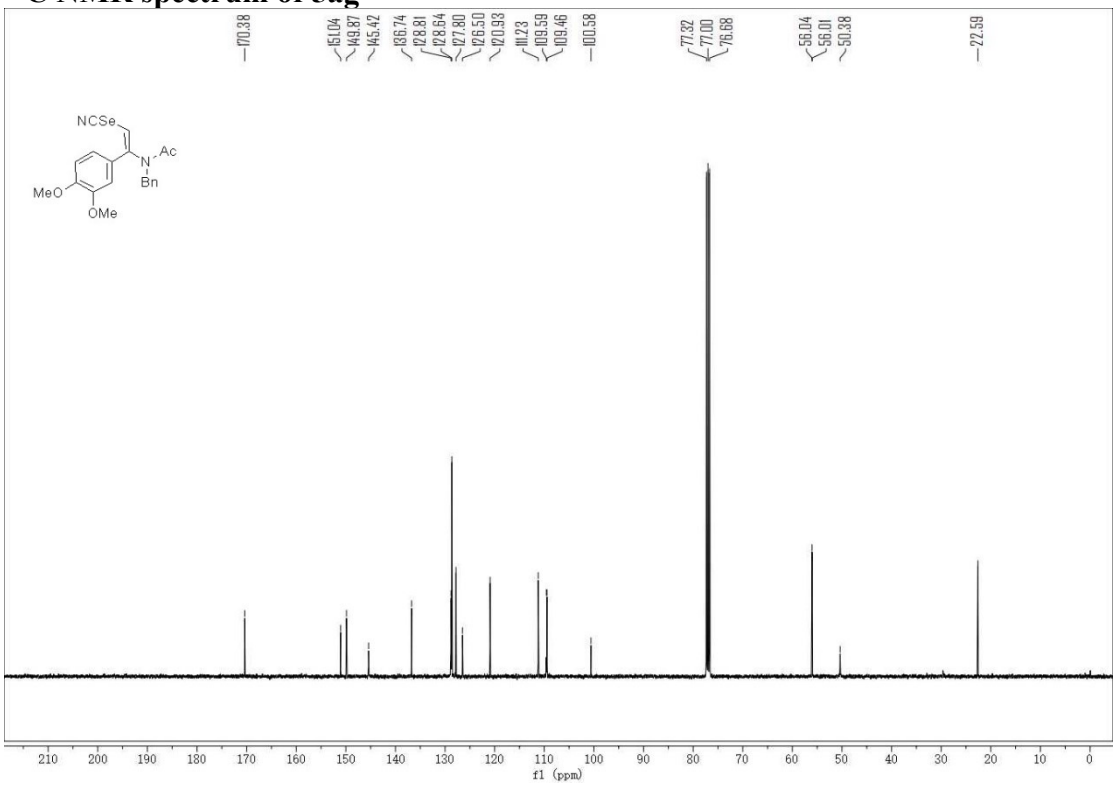
^{13}C NMR spectrum of 5af



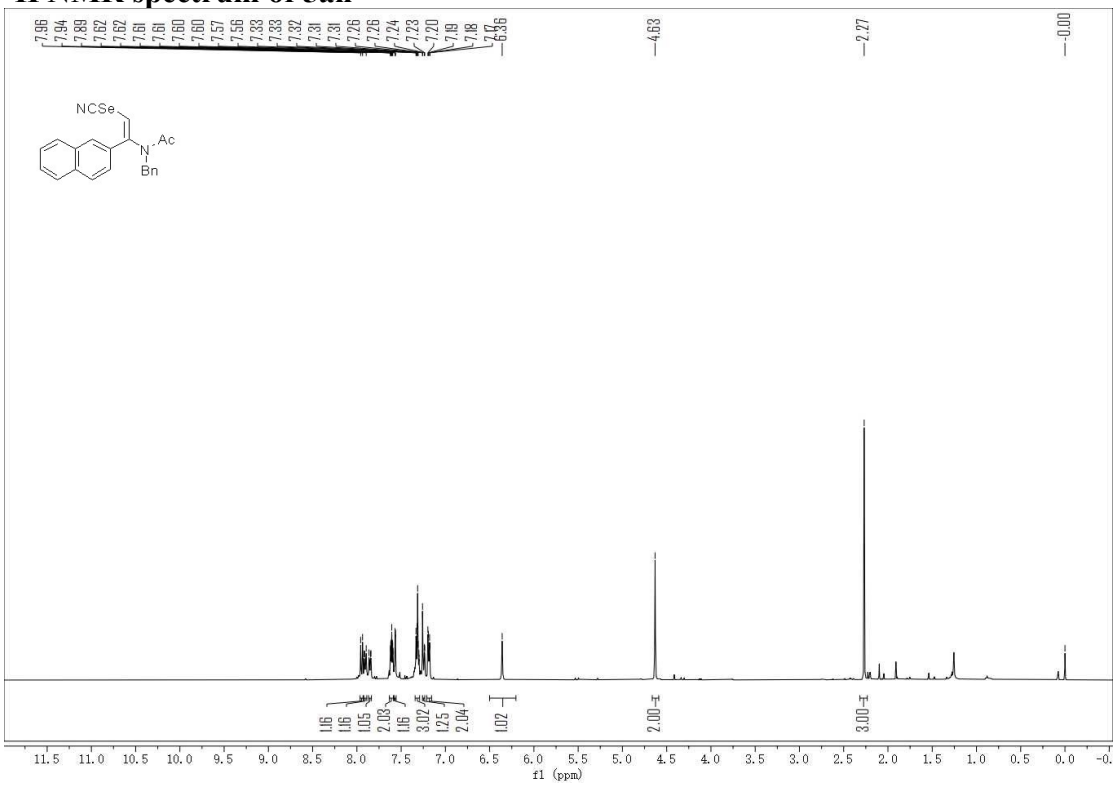
^{1}H NMR spectrum of 5ag



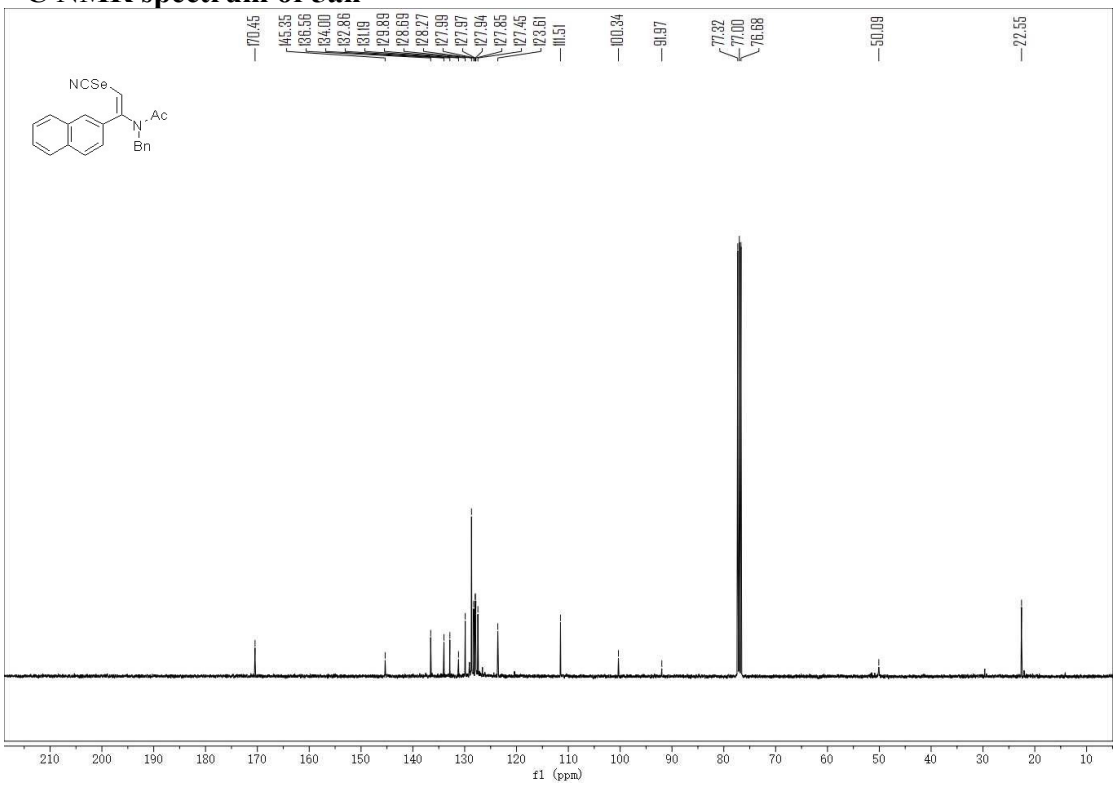
^{13}C NMR spectrum of 5ag



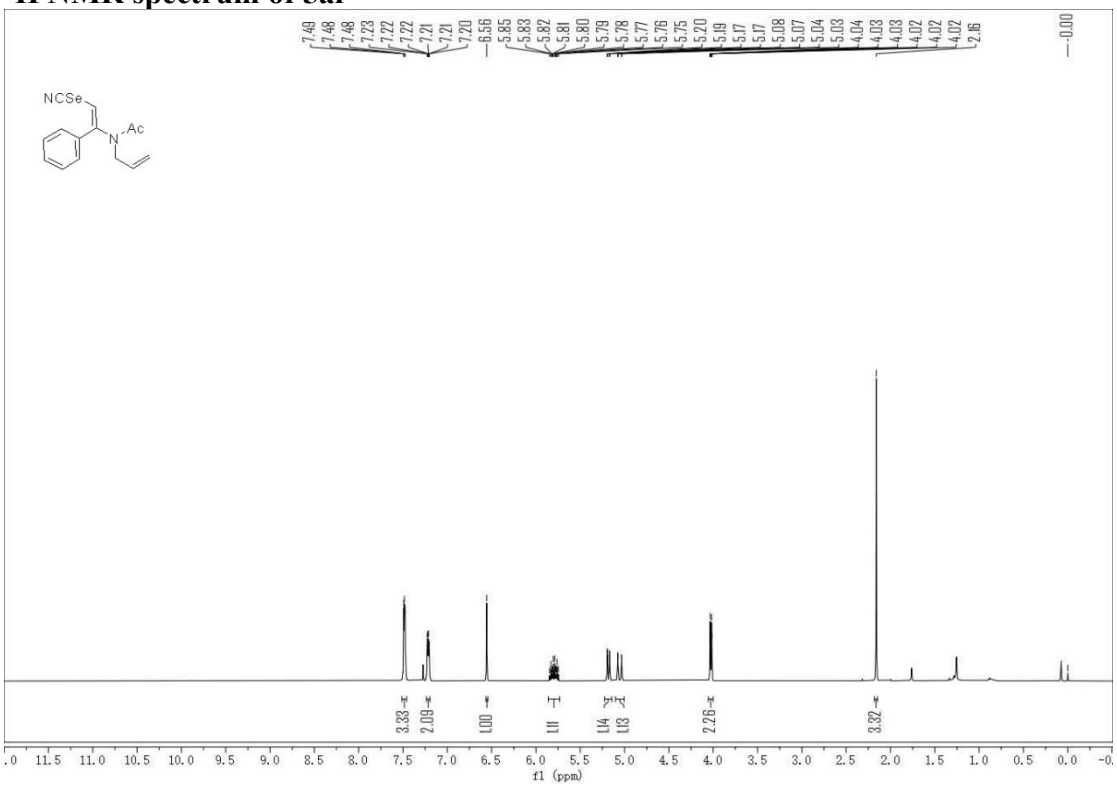
^{1}H NMR spectrum of 5ah



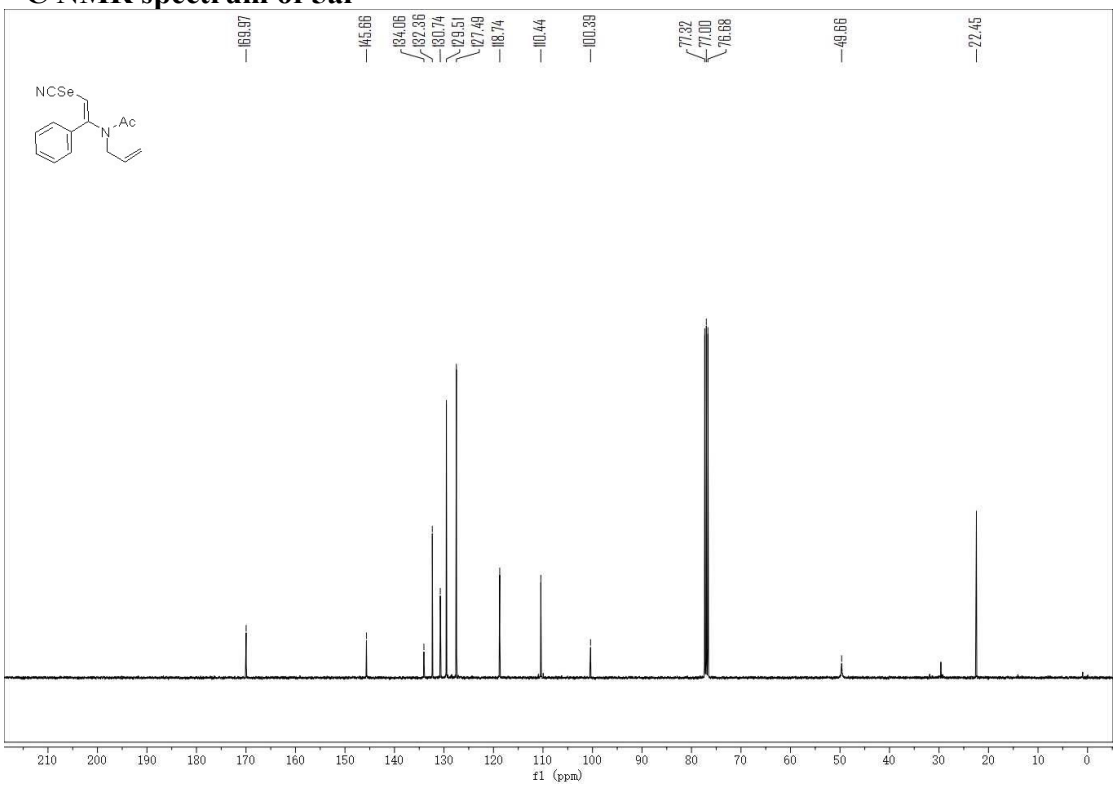
^{13}C NMR spectrum of 5ah



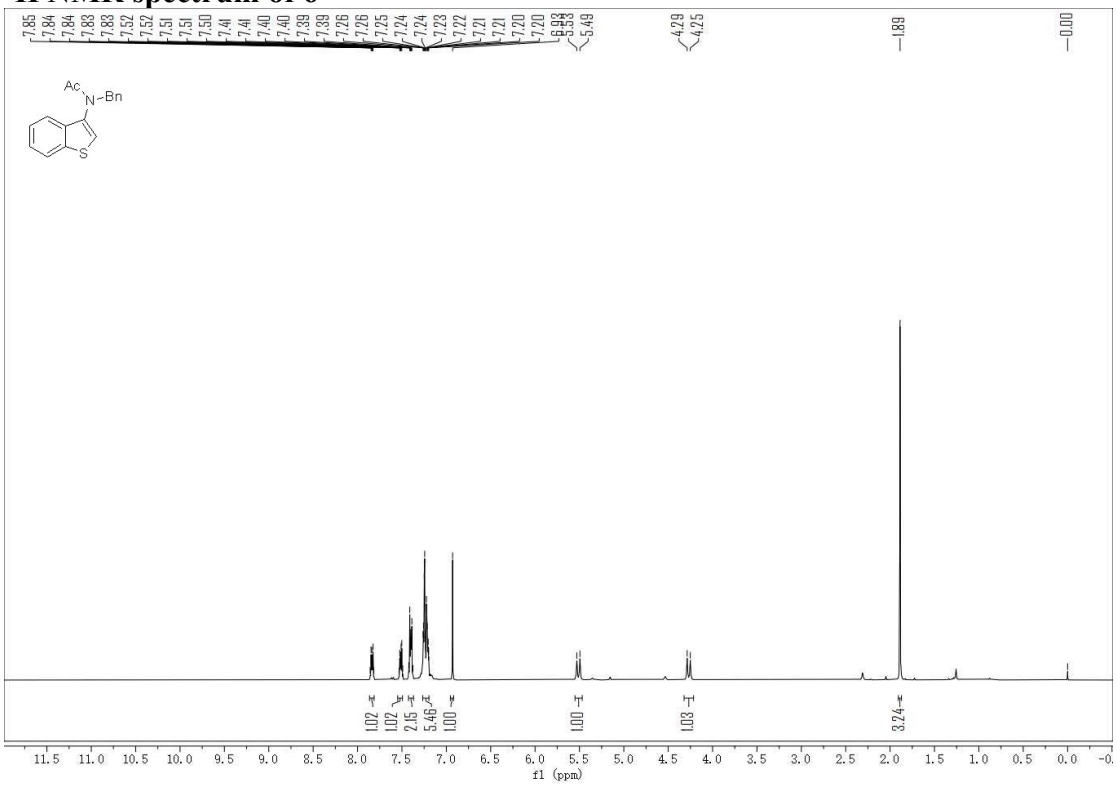
^{1}H NMR spectrum of 5ai



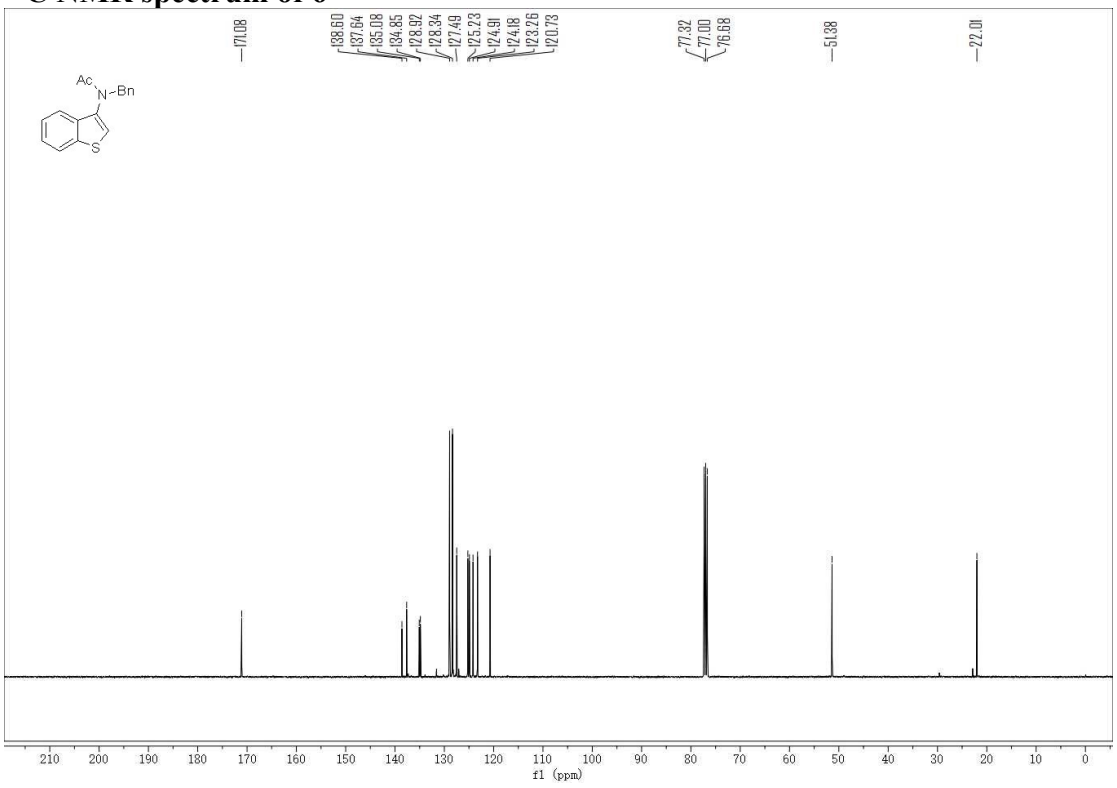
^{13}C NMR spectrum of 5ai



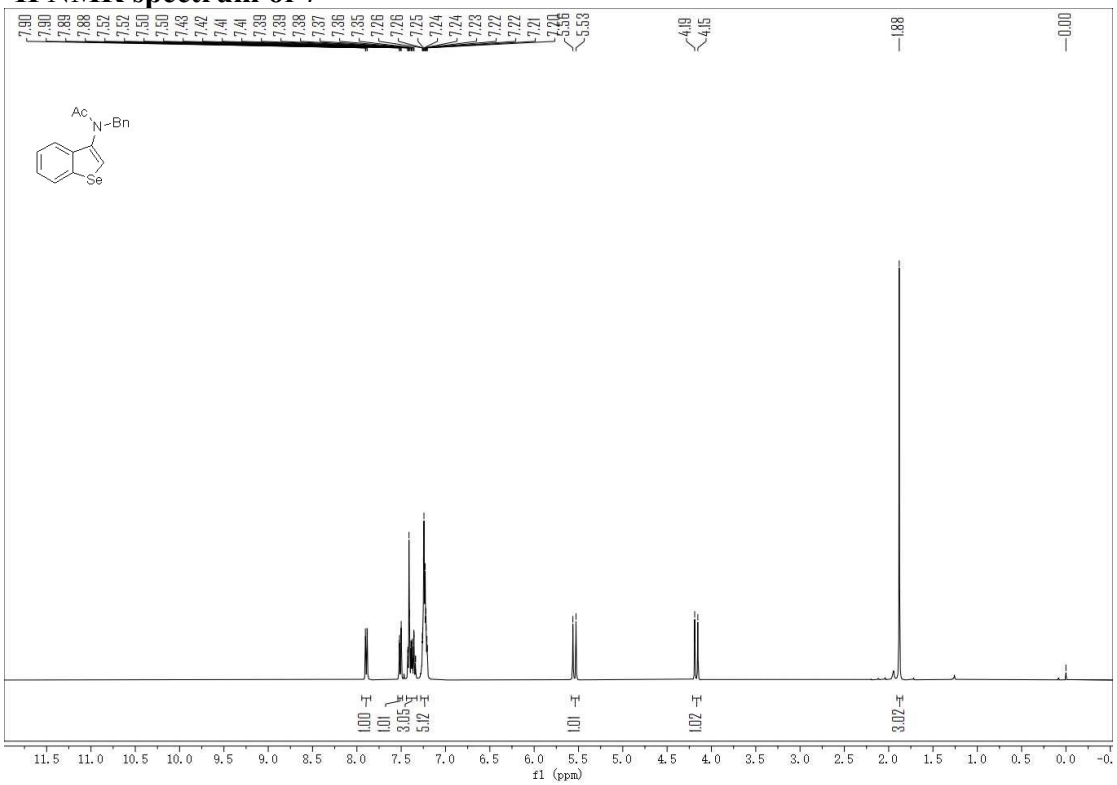
^{1}H NMR spectrum of 6



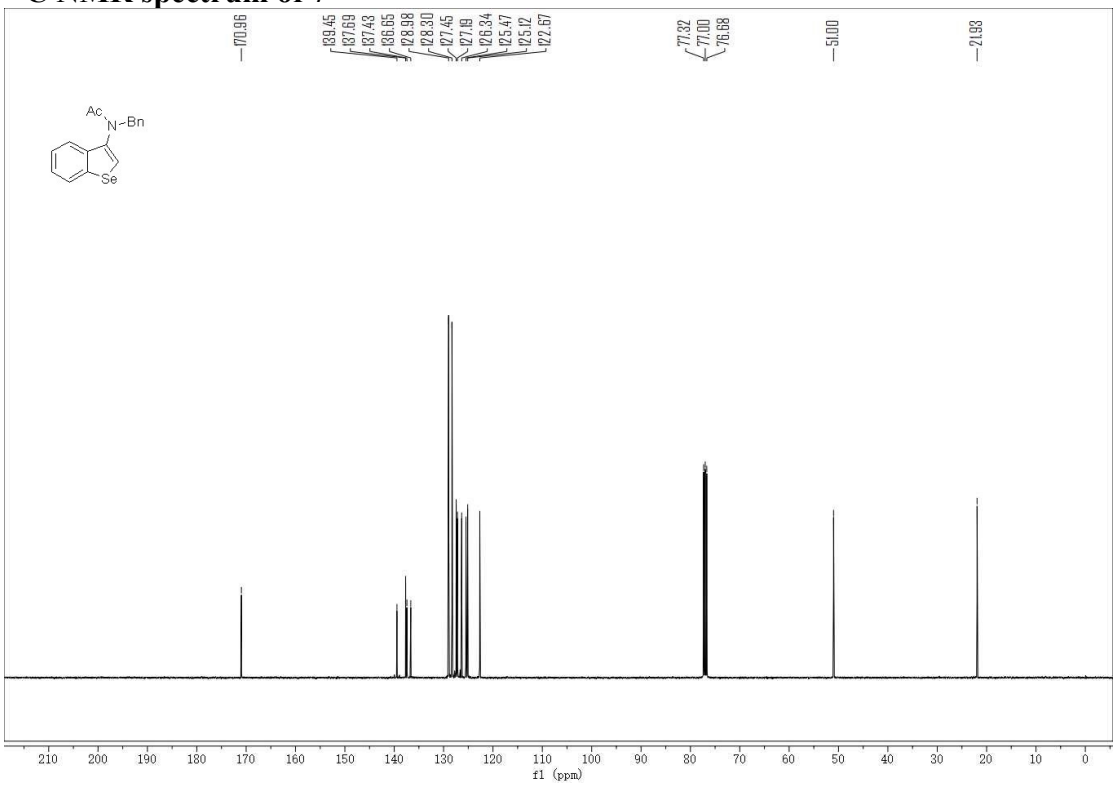
^{13}C NMR spectrum of 6



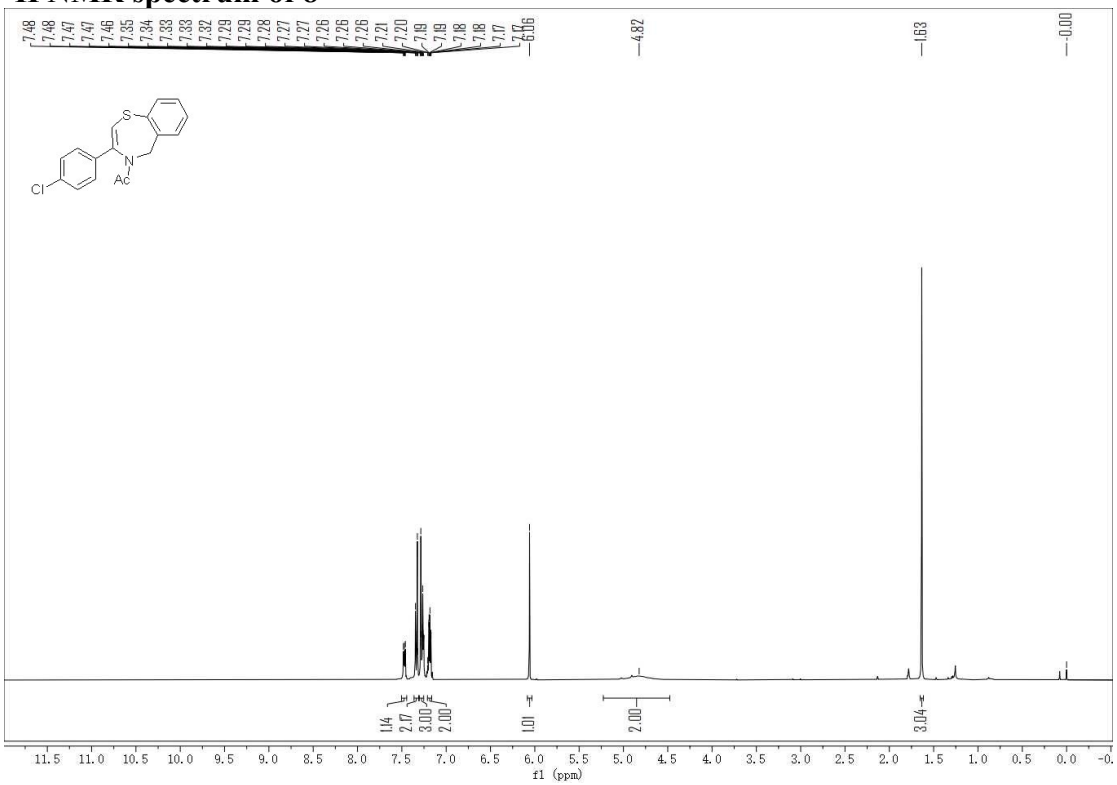
^{1}H NMR spectrum of 7



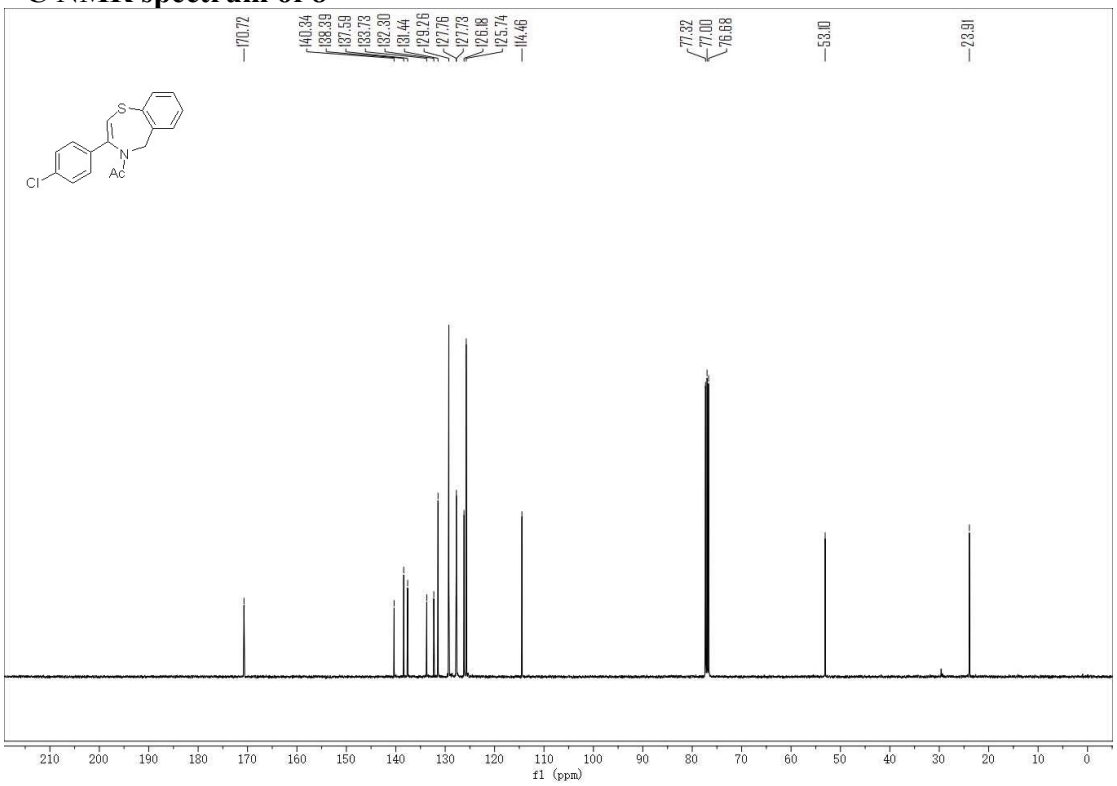
^{13}C NMR spectrum of 7



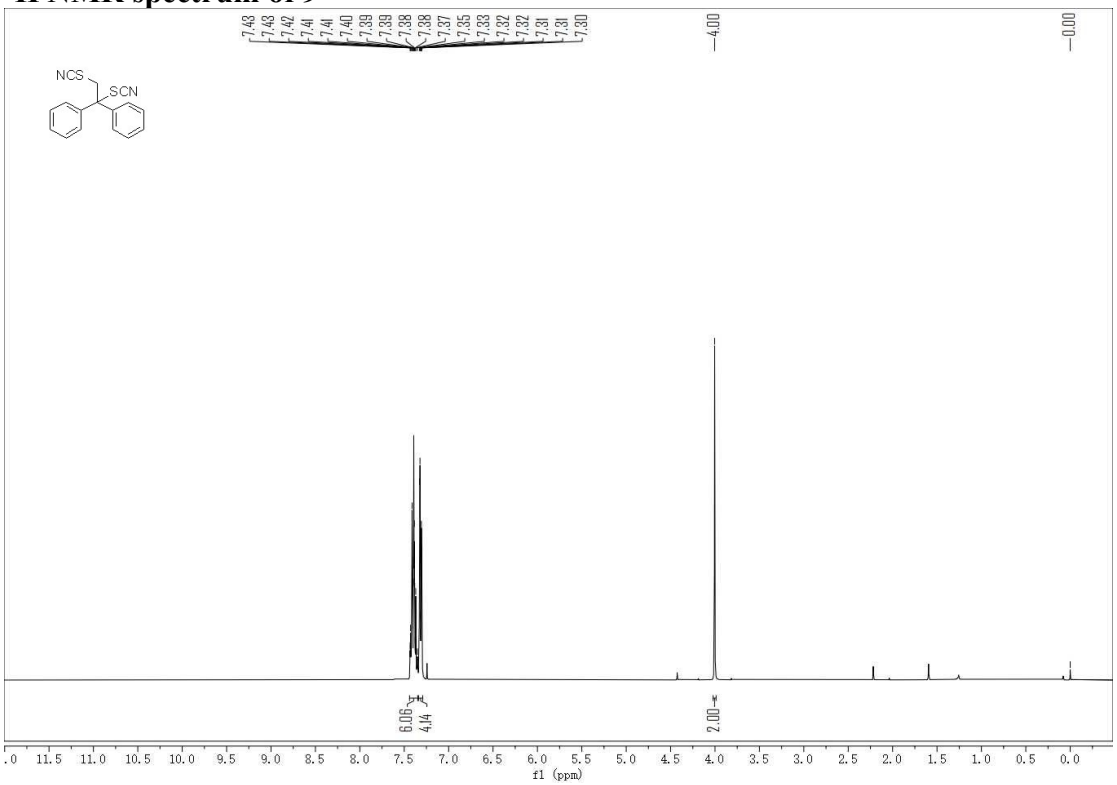
^{1}H NMR spectrum of 8



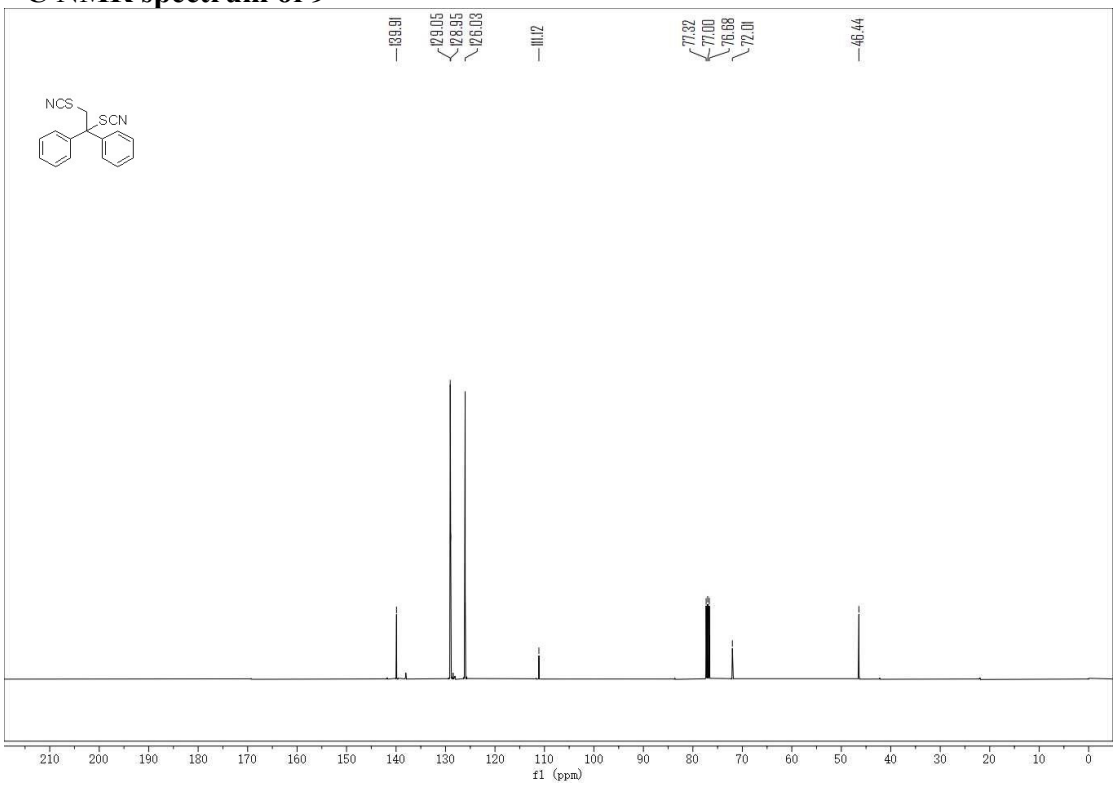
^{13}C NMR spectrum of 8



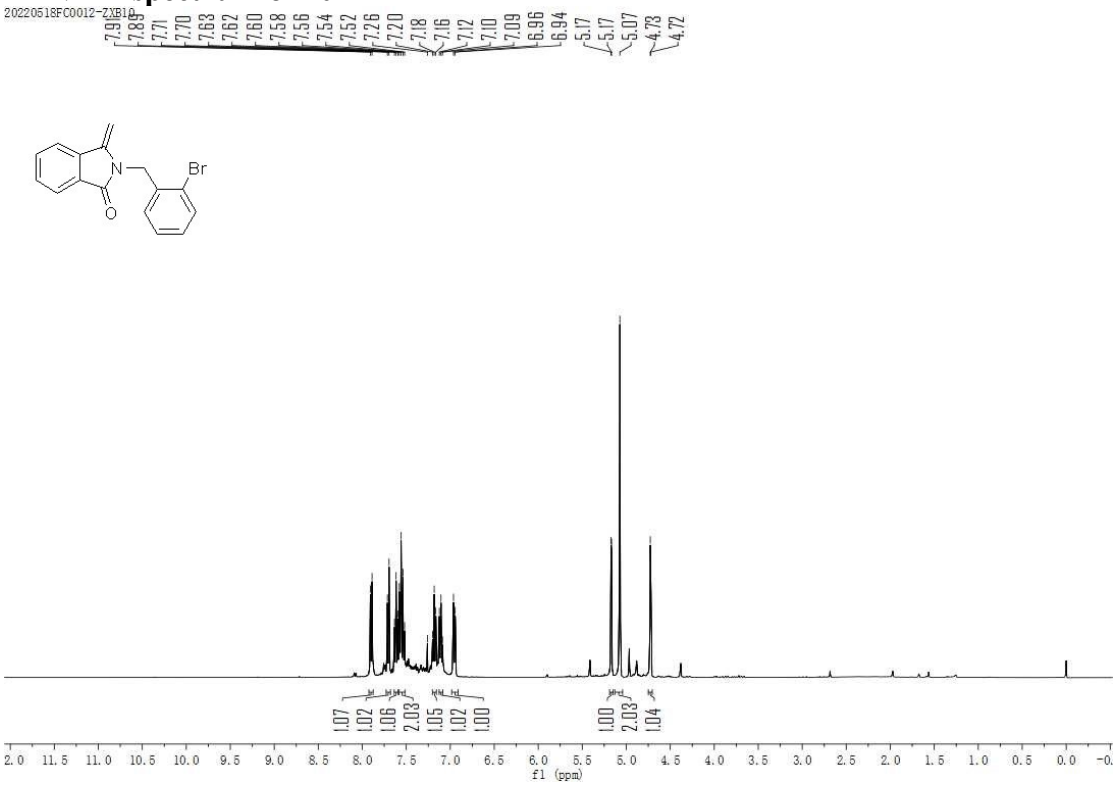
^{1}H NMR spectrum of 9



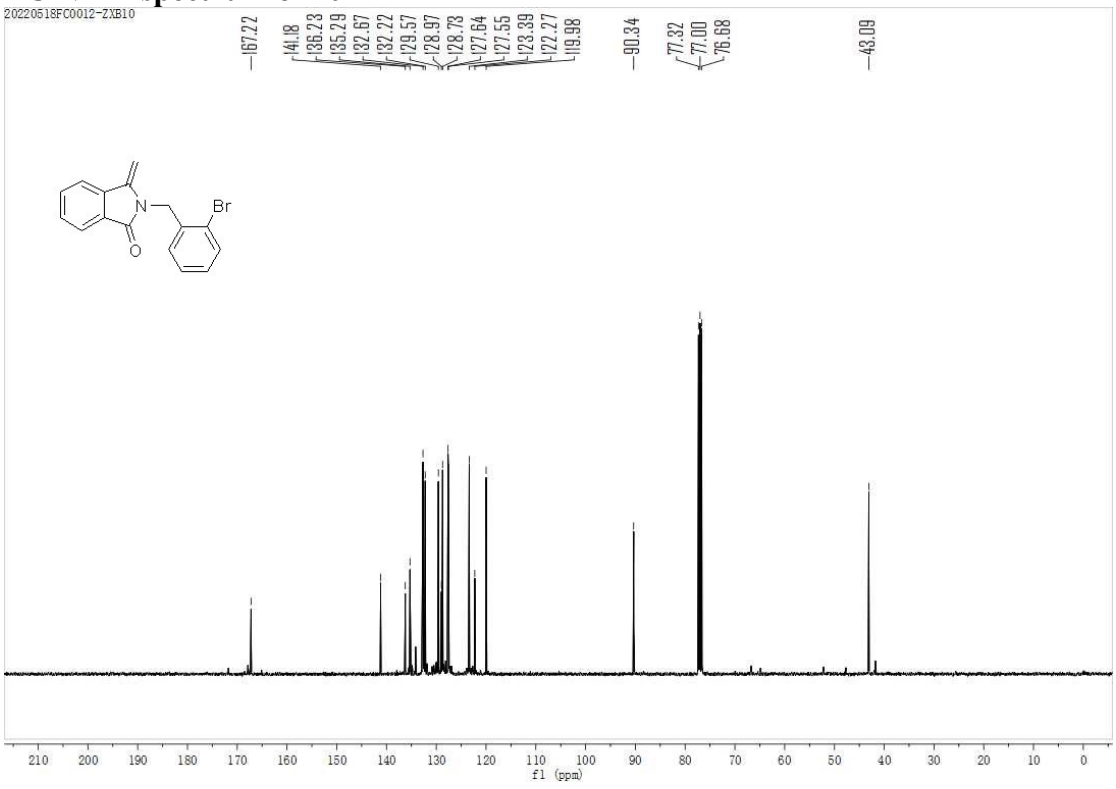
^{13}C NMR spectrum of 9



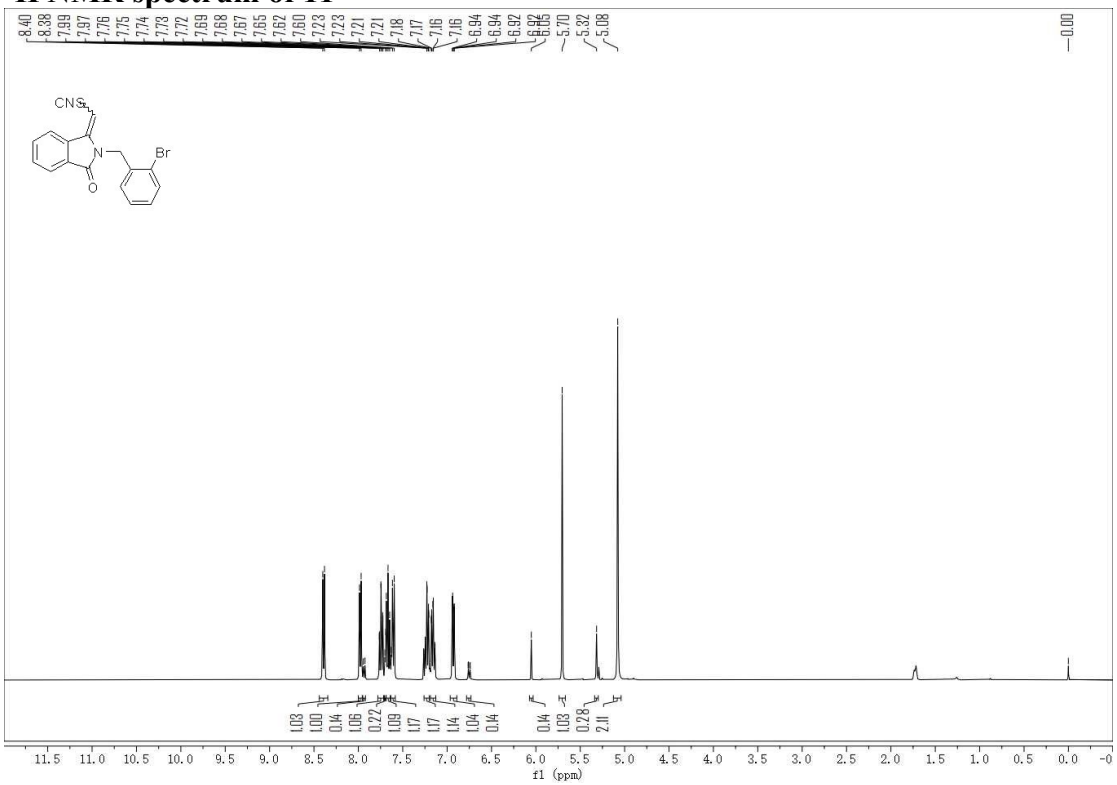
^{1}H NMR spectrum of 10



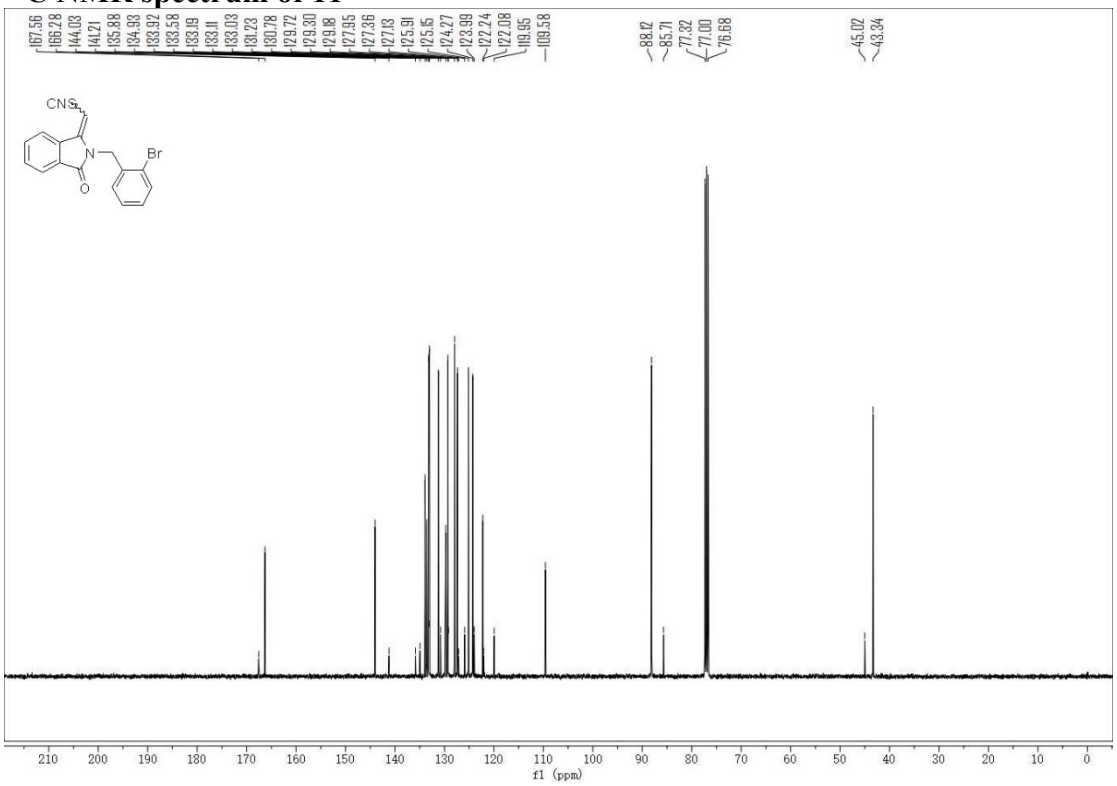
^{13}C NMR spectrum of 10



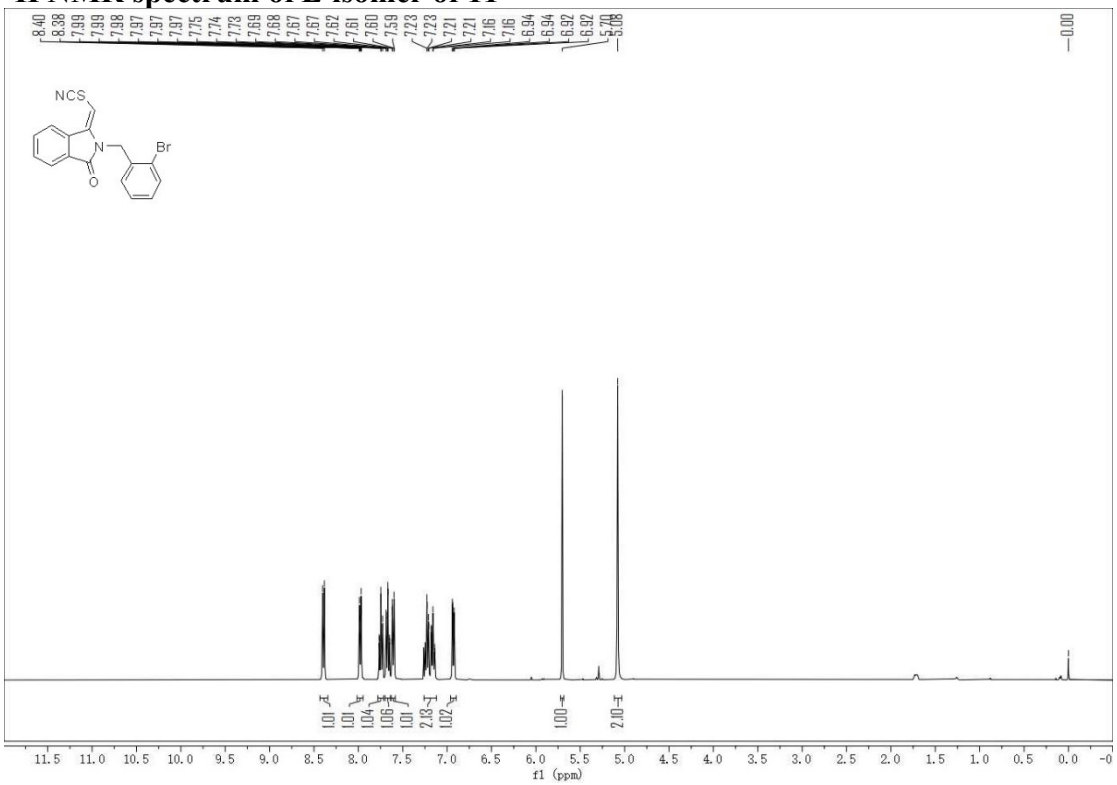
^{1}H NMR spectrum of 11



^{13}C NMR spectrum of 11



^{1}H NMR spectrum of *E* isomer of 11



^{13}C NMR spectrum of *E* isomer of 11