

Supplementary Information for
**K₂S₂O₈-mediated regio- and stereo-selective thiocyanation of
enamides with NH₄SCN**

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List

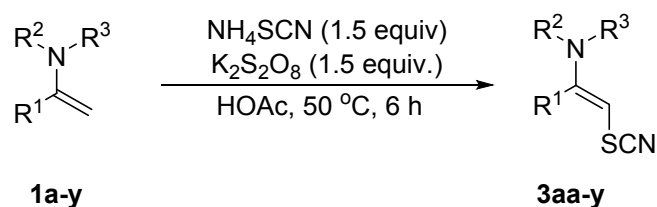
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1. General Information

All ^1H 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 °C). All enamides (**1a-e**)¹ are known compounds. They were purchased directly or were prepared according to the reported procedures. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation and characterizations of compounds 3aa-y, 4-9

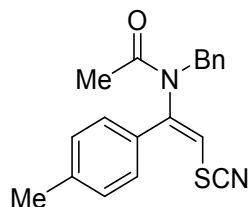
2.1 Preparation and characterizations of compounds 3aa-y



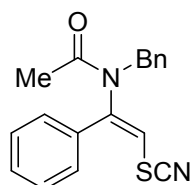
A mixture of enamides (**1a-y**) (0.3 mmol), NH_4SCN (34.2 mg, 0.45 mmol, 1.5 equiv.) and $\text{K}_2\text{S}_2\text{O}_8$ (121.5 mg, 0.45 mmol, 1.5 equiv.) in HOAc (2 mL) was stirred at 50 °C for 6 h (monitored by TLC). After it was cooled down to room temperature, the reaction was quenched by the slow addition of a saturated solution of Na_2CO_3 . 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 (10% EtOAc in PE) to give the corresponding products

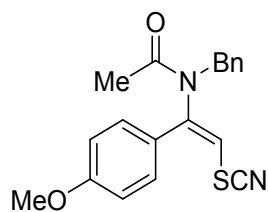
3aa-y.



(E)-N-benzyl-N-(2-thiocyanato-1-(p-tolyl)vinyl)acetamide (3aa). 84.1 mg (87%); Yellow solid; mp 98-100 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.31-7.26 (m, 5H), 7.19-7.10 (m, 4H), 5.85 (s, 1H), 4.56 (s, 2H), 2.42 (s, 3H), 2.19 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.1, 145.7, 141.2, 136.5, 129.9, 129.3, 128.6, 128.5, 128.1, 127.7, 111.3, 109.6, 49.7, 22.4, 21.4. HRMS m/z (ESI) calcd. for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{OS}$ (M + H) $^+$ 323.1213, found 323.1212.

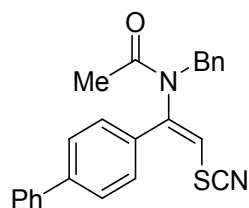


(E)-N-benzyl-N-(1-phenyl-2-thiocyanatovinyl)acetamide (3ab). 78.6 mg (85%); Yellow solid; mp 77-79 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.50-7.44 (m, 3H), 7.34-7.28 (m, 3H), 7.24-7.22 (m, 2H), 7.18-7.13 (m, 2H), 5.92 (s, 1H), 4.57 (s, 2H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.2, 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. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{OS}$ (M + H) $^+$ 309.1056, found 309.1056.



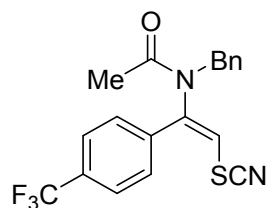
(E)-N-benzyl-N-(1-(4-methoxyphenyl)-2-thiocyanatovinyl)acetamide

(3ac). 82.2 mg (81%); Yellow solid; mp 85-87 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.32-7.29 (m, 3H), 7.18-7.15 (m, 4H), 6.97 (d, $J = 8.8$ Hz, 2H), 5.80 (s, 1H), 4.57 (s, 2H), 3.87 (s, 3H), 2.19 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.2, 161.3, 145.7, 136.5, 129.9, 128.7, 128.6, 127.8, 124.2, 114.7, 110.1, 109.7, 55.4, 49.8, 22.4. HRMS m/z (ESI) calcd. for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$ ($\text{M} + \text{H}$) $^+$ 339.1162, found 339.1161.

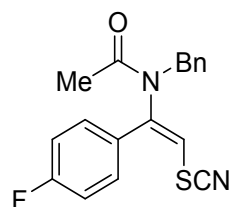


(E)-N-(1-([1,1'-biphenyl]-4-yl)-2-thiocyanatovinyl)-N-

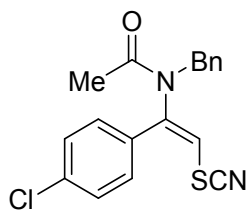
benzylacetamide (3ad). 88.7 mg (77%); Yellow solid; mp 119-121 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.69-7.67 (m, 2H), 7.63-7.61 (m, 2H), 7.50-7.46 (m, 2H), 7.42-7.38 (m, 1H), 7.32-7.26 (m, 5H), 7.20-7.17 (m, 2H), 5.93 (s, 1H), 4.61 (s, 2H), 2.22 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.1, 145.3, 143.5, 139.4, 136.5, 130.9, 128.9, 128.8, 128.7, 128.6, 128.1, 127.8, 127.8, 127.0, 112.1, 109.4, 49.9, 22.4. HRMS m/z (ESI) calcd. for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{OS}$ ($\text{M} + \text{H}$) $^+$ 385.1369, found 385.1369.



(E)-N-benzyl-N-(2-thiocyanato-1-(4-(trifluoromethyl)phenyl)vinyl)acetamide (3ae). 90.3 mg (80%); Yellow oil; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.37-7.30 (m, 5H), 7.16-7.13 (m, 2H), 6.06 (s, 1H), 4.59 (s, 2H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.5, 145.4, 139.1, 137.2, 131.1 (q, $J_{\text{C-F}} = 33$ Hz), 129.0, 128.4, 127.5, 126.1 (2C), 126.0 (q, $J_{\text{C-F}} = 4$ Hz), 123.8 (d, $J_{\text{C-F}} = 271$ Hz), 116.7, 49.9, 22.0. HRMS m/z (ESI) calcd. for $\text{C}_{19}\text{H}_{16}\text{F}_3\text{N}_2\text{OS}$ ($\text{M} + \text{H}$)⁺ 377.0930, found 377.0929.

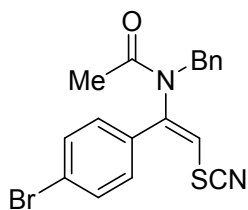


(E)-N-benzyl-N-(1-(4-fluorophenyl)-2-thiocyanatovinyl)acetamide (3af). 81.2 mg (83%); Yellow solid; mp 46-48 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.33-7.28 (m, 3H), 7.25-7.21 (m, 2H), 7.18-7.13 (m, 4H), 5.93 (s, 1H), 4.56 (s, 2H), 2.20 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.0, 163.6 (d, $J_{\text{C-F}} = 251$ Hz), 144.9, 136.3, 130.4 (d, $J_{\text{C-F}} = 8$ Hz), 128.7, 128.6, 128.3 (d, $J_{\text{C-F}} = 4$ Hz), 127.9, 116.6 (d, $J_{\text{C-F}} = 22$ Hz), 112.0, 109.1, 49.9, 22.4. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{FN}_2\text{OS}$ ($\text{M} + \text{H}$)⁺ 327.0962, found 327.0961.



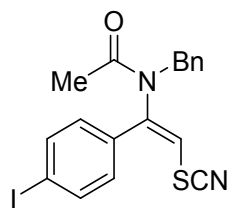
(E)-N-benzyl-N-(1-(4-chlorophenyl)-2-thiocyanatovinyl)acetamide

(3ag). 82.1 mg (80%); Yellow solid; mp 90-92 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.45-7.43 (m, 2H), 7.32-7.29 (m, 3H), 7.18-7.13 (m, 4H), 5.95 (s, 1H), 4.57 (s, 2H), 2.19 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.0, 144.7, 136.8, 136.2, 130.7, 129.6, 129.5, 128.7, 128.6, 127.9, 112.6, 109.0, 49.9, 22.4. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{OS}$ ($\text{M} + \text{H}$) $^+$ 343.0666, found 343.0663.



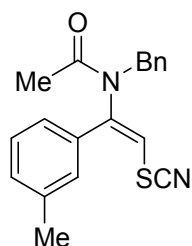
(E)-N-benzyl-N-(1-(4-bromophenyl)-2-thiocyanatovinyl)acetamide

(3ah). 98.4 mg (85%); Yellow solid; mp 91-93 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.60 (d, $J = 8.3$ Hz, 2H), 7.31-7.28 (m, 3H), 7.15 – 7.08 (m, 4H), 5.96 (s, 1H), 4.56 (s, 2H), 2.19 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.0, 144.6, 136.1, 132.5, 131.1, 129.7, 128.6, 128.5, 127.8, 125.0, 112.6, 108.9, 49.9, 22.4. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{BrN}_2\text{OS}$ ($\text{M} + \text{H}$) $^+$ 387.0161, found 387.0161.

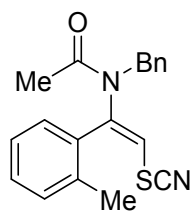


(E)-N-benzyl-N-(1-(4-iodophenyl)-2-thiocyanatovinyl)acetamide (3ai).

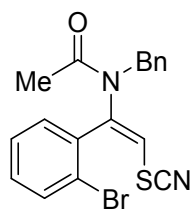
101.6 mg (78%); Yellow solid; mp 98-100 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.80 (d, $J = 8.4$ Hz, 2H), 7.33-7.28 (m, 3H), 7.15-7.13 (m, 2H), 6.96-6.94 (m, 2H), 5.95 (s, 1H), 4.56 (s, 2H), 2.18 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.0, 144.8, 138.5, 136.2, 131.7, 129.7, 128.7, 128.6, 127.9, 112.7, 109.0, 97.1, 49.9, 22.4. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{IN}_2\text{OS}$ ($\text{M} + \text{H}$) $^+$ 435.0023, found 435.0022.



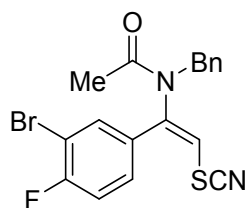
(E)-N-benzyl-N-(2-thiocyanato-1-(*m*-tolyl)vinyl)acetamide (3aj). 82.1 mg (85%); Yellow solid; mp 93-95 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.37-7.27 (m, 5H), 7.18-7.16 (m, 2H), 7.03-6.99 (m, 2H), 5.90 (s, 1H), 4.57 (s, 2H), 2.39 (s, 3H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.2, 145.6, 139.4, 136.5, 132.2, 131.5, 129.1, 128.7, 128.6, 128.5, 127.8, 125.5, 112.0, 109.6, 49.9, 22.4, 21.4. HRMS m/z (ESI) calcd. for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{OS}$ ($\text{M} + \text{H}$) $^+$ 323.1213, found 323.1211.



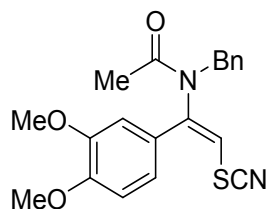
(E)-N-benzyl-N-(2-thiocyanato-1-(o-tolyl)vinyl)acetamide (3ak). 80.2 mg (83%); Yellow solid; mp 93-95 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.36 (t, $J = 7.5$ Hz, 1H), 7.32-7.22 (m, 5H), 7.09-7.02 (m, 3H), 6.13 (s, 1H), 4.50 (s, 2H), 2.35 (s, 3H), 2.18 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.3, 146.0, 137.0, 136.6, 131.4, 131.3, 130.5, 129.6, 128.6, 127.5, 127.4, 126.5, 110.7, 109.8, 49.5, 22.8, 19.4. HRMS m/z (ESI) calcd. for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{OS}$ ($\text{M} + \text{H}$) $^+$ 323.1213, found 323.1216.



(E)-N-benzyl-N-(1-(2-bromophenyl)-2-thiocyanatovinyl)acetamide (3al). 77.8 mg (67%); Yellow oil; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.68-7.65 (m, 1H), 7.37-7.32 (m, 2H), 7.31-7.26 (m, 3H), 7.14-7.09 (m, 3H), 6.17 (s, 1H), 4.56 (s, 2H), 2.36 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.6, 146.2, 136.5, 134.0, 132.9, 131.9, 131.8, 128.6, 127.9, 127.7, 127.5, 122.9, 111.6, 109.6, 50.1, 22.9. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{BrN}_2\text{OS}$ ($\text{M} + \text{H}$) $^+$ 387.0161, found 387.0165.

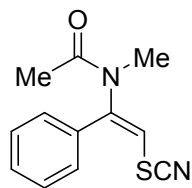


(E)-N-benzyl-N-(1-(3-bromo-4-fluorophenyl)-2-thiocyanatovinyl)acetamide (3am). 94.5 mg (78%); White solid; mp 144-146 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.40–7.30 (m, 4H), 7.23-7.13 (m, 4H), 5.99 (s, 1H), 4.58 (s, 2H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.0, 160.1 (d, $J_{\text{C-F}} = 253$ Hz), 143.6, 136.1, 133.4, 129.9 (d, $J_{\text{C-F}} = 4$ Hz), 129.3 (d, $J_{\text{C-F}} = 8$ Hz), 128.8, 128.6, 128.1, 117.4 (d, $J_{\text{C-F}} = 23$ Hz), 113.2, 110.5 (d, $J_{\text{C-F}} = 21$ Hz), 108.7, 50.2, 22.5. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{15}\text{BrFN}_2\text{OS}$ (M + H) $^+$ 405.0067, found 405.0067.

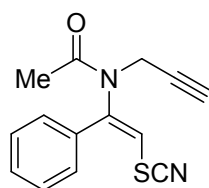


(E)-N-benzyl-N-(1-(3,4-dimethoxyphenyl)-2-thiocyanatovinyl)acetamide (3an). 82.8 mg (75%); Yellow solid; mp 129-131°C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.32-7.27 (m, 3H), 7.20-7.18 (m, 2H), 6.92 (d, $J = 8.3$ Hz, 1H), 6.81 (dd, $J = 8.3, 2.1$ Hz, 1H), 6.57 (d, $J = 2.1$ Hz, 1H), 5.88 (s, 1H), 4.63 (s, 2H), 3.94 (s, 3H), 3.80 (s, 3H), 2.17 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.3, 150.9, 149.5, 145.8, 136.6, 128.8, 128.6 (2C), 127.8, 124.7, 121.8, 111.1, 110.3, 109.7, 56.0 (2C), 50.3, 22.6. HRMS m/z (ESI) calcd. for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_3\text{S}$ (M + H) $^+$ 369.1267,

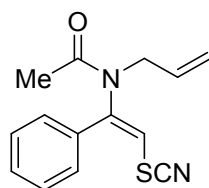
found 369.1267.



(E)-N-methyl-N-(1-phenyl-2-thiocyanatovinyl)acetamide (3ao). 59.2 mg (85%); Brown solid; mp 102-104 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.49-7.48 (m, 3H), 7.31-7.29 (m, 2H), 6.27 (s, 1H), 3.03 (s, 3H), 2.13 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.5, 147.6, 132.5, 130.7, 129.3, 128.1, 110.5, 109.6, 35.6, 22.2. HRMS m/z (ESI) calcd. for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{OS}$ (M + H) $^+$ 233.0743, found 233.0743.

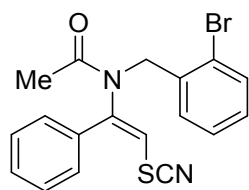


(E)-N-(1-phenyl-2-thiocyanatovinyl)-N-(prop-2-yn-1-yl)acetamide (3ap). 63.8 mg (83%); Yellow oil; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.49-7.47 (m, 3H), 7.34-7.32 (m, 2H), 6.43 (s, 1H), 4.25 (d, $J = 2.4$ Hz, 2H), 2.30 (t, $J = 2.5$ Hz, 1H), 2.14 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.7, 144.7, 132.1, 130.8, 129.3, 128.1, 112.7, 109.5, 77.9, 72.9, 36.4, 22.3. HRMS m/z (ESI) calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{OS}$ (M + H) $^+$ 257.0743, found 257.0743.



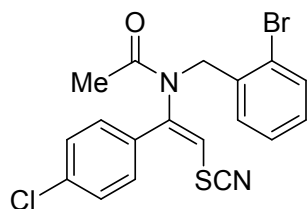
(E)-N-allyl-N-(1-phenyl-2-thiocyanatovinyl)acetamide (3aq). 62.7 mg

(81%); Yellow solid; mp 59-61 °C; ¹H NMR (400MHz, CDCl₃) δ 7.48-7.47 (m, 3H), 7.31-7.26 (m, 2H), 6.24 (s, 1H), 5.79 (ddt, *J* = 16.6, 10.1, 6.3 Hz, 1H), 5.18 (d, *J* = 10.1 Hz, 1H), 5.05 (d, *J* = 17.2 Hz, 1H), 4.02 (d, *J* = 6.2 Hz, 2H), 2.16 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 145.9, 132.5, 132.2, 130.6, 129.2, 128.1, 118.8, 111.6, 109.6, 49.7, 22.4. HRMS *m/z* (ESI) calcd. for C₁₄H₁₅N₂OS (M + H)⁺ 259.0900, found 259.0900.



(E)-N-(2-bromobenzyl)-N-(1-phenyl-2-thiocyanatovinyl)acetamide

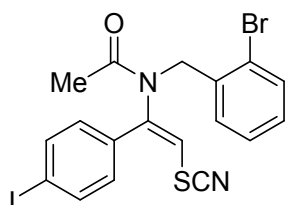
(3ar). 84.5 mg (73%); Yellow solid; mp 140-142 °C; ¹H NMR (400MHz, CDCl₃) δ 7.54-7.44 (m, 4H), 7.27-7.25 (m, 1H), 7.21-7.14 (m, 4H), 6.09 (s, 1H), 4.77 (s, 2H), 2.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 145.2, 135.5, 133.0, 132.2, 130.8, 130.7, 129.5, 129.2, 128.2, 127.7, 123.9, 112.8, 109.5, 49.8, 22.4. HRMS *m/z* (ESI) calcd. for C₁₈H₁₆BrN₂OS (M + H)⁺ 387.0161, found 387.0161.



(E)-N-(2-bromobenzyl)-N-(1-(4-chlorophenyl)-2-

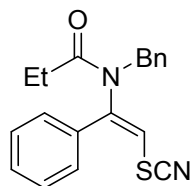
thiocyanatovinyl)acetamide (3as). 84.4 mg (67%); Yellow solid; m.p. 141-143 °C; ¹H NMR (400MHz, CDCl₃) δ 7.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.44-7.41 (m, 2H), 7.27-7.20 (m, 2H), 7.18-7.13 (m, 3H), 6.12 (s, 1H), 4.76

(s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 144.2, 136.7, 135.3, 133.0, 130.8, 130.6, 129.5, 129.5, 127.7, 123.9, 113.3, 109.0, 76.7, 49.8, 22.3. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{15}\text{BrClIN}_2\text{OS}$ ($\text{M} + \text{H}$) $^+$ 420.9772, found 420.9775.



(E)-N-(2-bromobenzyl)-N-(1-(4-iodophenyl)-2-

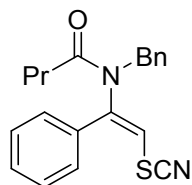
thiocyanatovinyl)acetamide (3at). 106.0 mg (69%); Yellow solid; m.p. 150-152 °C; ^1H NMR (400MHz, CDCl_3) δ 7.81-7.77 (m, 2H), 7.53 (d, J = 7.9 Hz, 1H), 7.29-7.25 (m, 1H), 7.22-7.14 (m, 2H), 6.95-6.91 (m, 2H), 6.11 (s, 1H), 4.76 (s, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 144.3, 138.4, 135.3, 133.0, 131.7, 130.8, 129.7, 129.6, 127.7, 123.9, 113.4, 109.0, 97.1, 49.8, 22.4. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{15}\text{BrIN}_2\text{OS}$ ($\text{M} + \text{H}$) $^+$ 512.9128, found 512.9125.



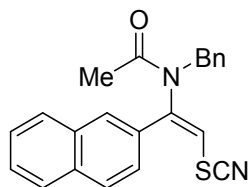
(E)-N-benzyl-N-(1-phenyl-2-thiocyanatovinyl)propionamide (3au).

79.2 mg (82%); Yellow oil; ^1H NMR (400MHz, CDCl_3) δ 7.48-7.46 (m, 3H), 7.32-7.30 (m, 3H), 7.23-7.21 (m, 2H), 7.19-7.17 (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 173.8, 145.3, 136.7, 132.5, 130.8, 129.4, 128.8,

128.7, 128.3, 127.9, 112.1, 109.6, 50.2, 27.7, 10.0. HRMS m/z (ESI) calcd. for $C_{19}H_{19}N_2OS$ ($M + H$)⁺ 323.1213, found 323.1212.

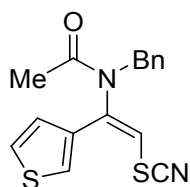


(E)-N-benzyl-N-(1-phenyl-2-thiocyanatovinyl)butyramide (3av). 88.7 (88%); Yellow oil; ¹H NMR (400MHz, CDCl₃) δ 7.48-7.46 (m, 3H), 7.34-7.28 (m, 3H), 7.24-7.21 (m, 2H), 7.18-7.16 (m, 2H), 5.88 (s, 1H), 4.58 (s, 2H), 2.40 (t, $J = 7.4$ Hz, 2H), 1.74 (q, $J = 7.3$ Hz, 2H), 0.96 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 145.3, 136.7, 132.4, 130.7, 129.3, 128.7, 128.6, 128.2, 127.8, 111.9, 109.5, 50.0, 36.1, 19.1, 13.9. HRMS m/z (ESI) calcd. for $C_{20}H_{21}N_2OS$ ($M + H$)⁺ 337.1369, found 337.1369.



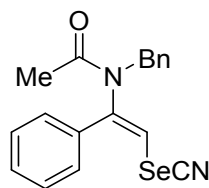
(E)-N-benzyl-N-(1-(naphthalen-2-yl)-2-thiocyanatovinyl)acetamide (3aw). 82.7 mg (77%); Yellow oil; ¹H NMR (400MHz, CDCl₃) δ 7.94 (d, $J = 8.6$ Hz, 1H), 7.91-7.85 (m, 2H), 7.67 (d, $J = 1.8$ Hz, 1H), 7.63-7.58 (m, 2H), 7.34-7.29 (m, 4H), 7.20-7.17 (m, 2H), 6.01 (s, 1H), 4.62 (s, 2H), 2.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 145.6, 136.5, 133.9, 132.8, 129.6, 129.5, 128.6, 128.7 (2C), 128.4, 127.9, 127.8 (2C), 127.3, 124.2, 112.5, 109.5, 50.0, 22.6. HRMS m/z (ESI) calcd. for $C_{22}H_{19}N_2OS$ ($M + H$)⁺

359.1213, found 359.1212.



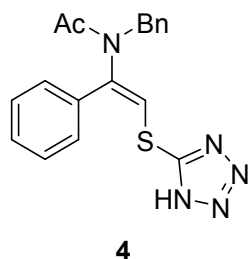
(E)-N-benzyl-N-(2-thiocyanato-1-(thiophen-3-yl)vinyl)acetamide

(3ax). 78.2 mg (83%); Yellow solid; m.p. 60-62 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.45 (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 (d, $J = 5.0$ Hz, 1H), 5.84 (s, 1H), 4.64 (s, 2H), 2.13 (s, 3H). $^{13}\text{C NMR}$ (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. HRMS m/z (ESI) calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{OS}_2$ ($\text{M} + \text{H}$) $^+$ 315.0620, found 315.0620.



(E)-N-benzyl-N-(1-phenyl-2-selenocyanatovinyl)acetamide (3ay). 91.9 mg (86%); Yellow solid; m.p. 68-70 °C; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.50-7.46 (m, 3H), 7.34-7.28 (m, 3H), 7.18-7.14 (m, 4H), 6.26 (s, 1H), 4.58 (s, 2H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.2, 145.4, 136.5, 133.7, 130.8, 129.6, 128.6 (2C), 127.8, 127.5, 111.0, 100.2, 49.9, 22.4. HRMS m/z (ESI) calcd. for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{OSe}$ ($\text{M} + \text{H}$) $^+$ 357.0501, found 357.0500.

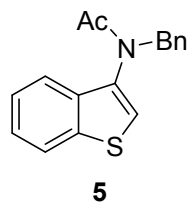
2.2 Preparation and characterizations of compounds 4-9



Preparation of product **4** from **3ab**: Compound **3ab** (154.2 mg, 0.5 mmol), ZnBr₂ (112.6 mg, 0.5 mmol, 1 equiv.) and NaN₃ (81.3 mg, 1.25 mmol, 2.5 equiv.) were combined in a mixed solvent [H₂O/*i*PrOH (1:1, 3 mL)] and refluxed for 12 h. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under vacuo. Column chromatography of the residue (petroleum ether/EtOAc, 1:1) provided tetrazole **4** as yellow solid in 133.4 mg (76%); m.p. 141-143 °C;

***E*-N-(2-((1*H*-tetrazol-5-yl)thio)-1-phenylvinyl)-N-benzylacetamide (4).**

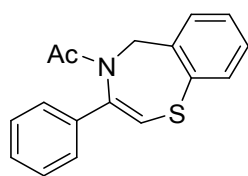
¹H NMR (400MHz, DMSO-*d*₆) δ 7.58-7.54 (m, 2H), 7.49-7.42 (m, 3H), 7.35-7.21 (m, 3H), 7.22-7.21 (m, 2H), 6.83 (s, 1H), 4.51 (s, 2H), 2.21 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 170.5, 154.1, 137.5, 134.6, 134.3, 129.1, 129.0, 128.5, 128.4, 127.8, 127.3, 126.0, 49.2, 22.2. HRMS *m/z* (ESI) calcd. for C₁₈H₁₈N₅OS (M + H)⁺ 352.1227, found 352.1225.



Preparation of product **5** from **3al**: To a mixture of Pd(OAc)₂ (5.6 mg, 0.025 mmol, 5 mol%), PPh₃ (13.1 mg, 0.05 mmol, 10 mol%), and Cs₂CO₃ (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 Na₂SO₄ and evaporated in vacuo. The residue was purified by column chromatography over silica gel (petroleum ether/EtOAc, 10:1). The product of **5** was isolated as yellow oil in 45% yield (63.2 mg);

***N*-(benzo[*b*]thiophen-3-yl)-*N*-benzylacetamide (**5**). ¹H NMR (400MHz, CDCl₃) δ 7.87-7.81 (m, 1H), 7.54-7.48 (m, 1H), 7.43-7.37 (m, 2H), 7.27-7.20 (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). ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 138.6, 137.6, 135.1, 134.9, 128.9, 128.4, 127.5, 125.2, 124.9, 124.2, 123.3, 120.7, 51.4, 22.0. HRMS *m/z* (ESI) calcd. for C₁₇H₁₆NOS (M + H)⁺ 282.0947, found 282.0945.**

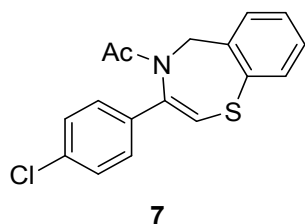


6

Preparation of product **6** from **3ar**: To a mixture of Pd(OAc)₂ (5.6 mg, 0.025 mmol, 5 mol%), PPh₃ (13.1 mg, 0.05 mmol, 10 mol%), and Cs₂CO₃ (325.8 mg, 1 mmol, 2 equiv.) was added a solution of **3ar** (193 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 Na₂SO₄ 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 solid in 36% yield (50.6 mg); m.p. 86-88 °C;

1-(3-phenylbenzo[*f*][1,4]thiazepin-4(5*H*)-yl)ethan-1-one (6). ¹H NMR (400MHz, CDCl₃) δ 7.49-7.46 (m, 1H), 7.39-7.33 (m, 4H), 7.31-7.26 (m, 2H), 7.20-7.15 (m, 2H), 6.07 (s, 1H), 4.84 (s, 2H), 1.64 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 141.6, 139.0, 138.5, 132.6, 131.4, 129.1, 128.0, 127.7 (2C), 126.1, 124.5, 113.8, 53.1, 23.9. HRMS m/z (ESI) calcd. for C₁₇H₁₆NOS (M + H)⁺ 282.0947, found 282.0943.



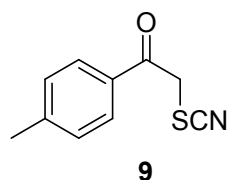
Preparation of product **7** from **3as**: To a mixture of Pd(OAc)₂ (5.6 mg, 0.025 mmol, 5 mol%), PPh₃ (13.1 mg, 0.05 mmol, 10 mol%), and Cs₂CO₃ (325.8 mg, 1 mmol, 2 equiv.) was added a solution of **3as** (210.0 mg, 0.5 mmol) in 2 mL DMF under nitrogen atmosphere. After stirring at 100 °C overnight, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine. The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated in vacuo. The residue was purified by column chromatography over silica gel (petroleum ether/EtOAc, 10:1). The product of **7** was isolated as yellow solid in 33% yield (52.0 mg); m.p.

90-92 °C;

1-(3-(4-chlorophenyl)benzo[*f*][1,4]thiazepin-4(5*H*)-yl)ethan-1-one (7).

¹H NMR (400 MHz, CDCl₃) δ 7.49-7.45 (m, 1H), 7.36-7.31 (m, 2H), 7.30-7.25 (m, 3H), 7.21-7.16 (m, 2H), 6.06 (s, 1H), 4.82 (s, 2H), 1.64 (s, 3H).

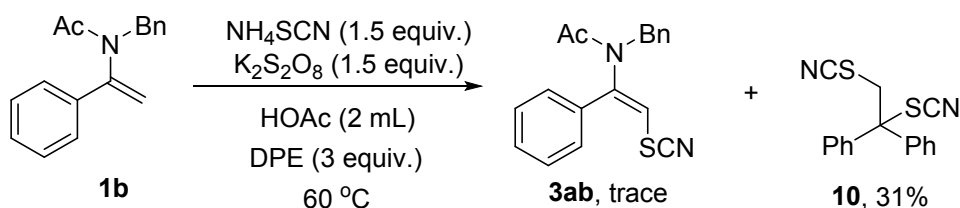
¹³C NMR (100 MHz, CDCl₃) δ 170.7, 140.3, 138.4, 137.6, 133.7, 132.3, 131.4, 129.3, 127.8, 127.7, 126.2, 125.7, 114.5, 53.1, 23.9. HRMS *m/z* (ESI) calcd. for C₁₇H₁₅ClNOS (M + H)⁺ 316.0557, found 316.0554.



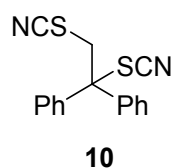
Preparation of product **9** from **3aa**: To a solution of **3aa** (161.0 mg, 0.5 mmol) in a mixed solvent of THF/H₂O (1:1, 2.0 mL) was added concentrated hydrochloric acid (1 mL), and the vial was heated at 50 °C for 24 h. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under vacuo. The residue was purified by column chromatography over silica gel (petroleum ether/EtOAc, 20:1). The product of **9** was isolated as yellow solid in 81% yield (77.4 mg);

2-thiocyanato-1-(*p*-tolyl)ethan-1-one (9).² **¹H NMR (400 MHz, CDCl₃)** δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.73 (s, 2H), 2.45 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 190.4, 146.0, 131.4, 129.8, 128.5, 112.0, 43.0, 21.8.

3. Preliminary Mechanistic Studies

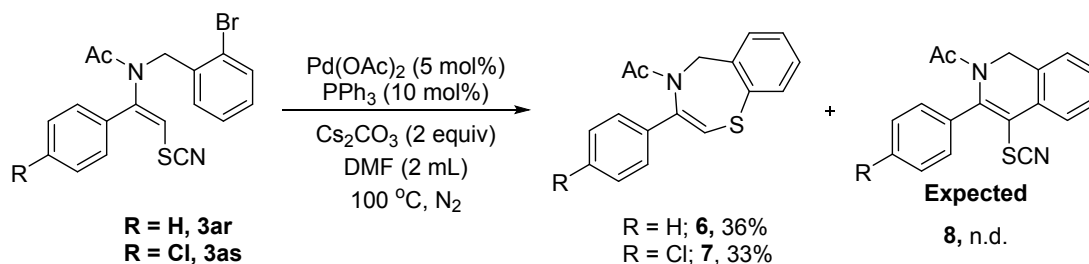


To a solution of enamides **1b** (75.4 mg, 0.30 mmol), NH_4SCN (34.3 mg, 0.45 mmol, 1.5 equiv.), $\text{K}_2\text{S}_2\text{O}_8$ (121.6 mg, 0.45 mmol, 1.5 equiv.) in HOAc (2 mL) was added DPE (162.2 mg, 0.6 mmol, 3 equiv.). The vial was sealed with a septum and allowed to stir at 50 °C for 6 h. Upon 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 **10** of DPE and SCN radical was isolated as yellow oil in 31% yield (55.1 mg). Trace amount of corresponding **3ab** was detected.

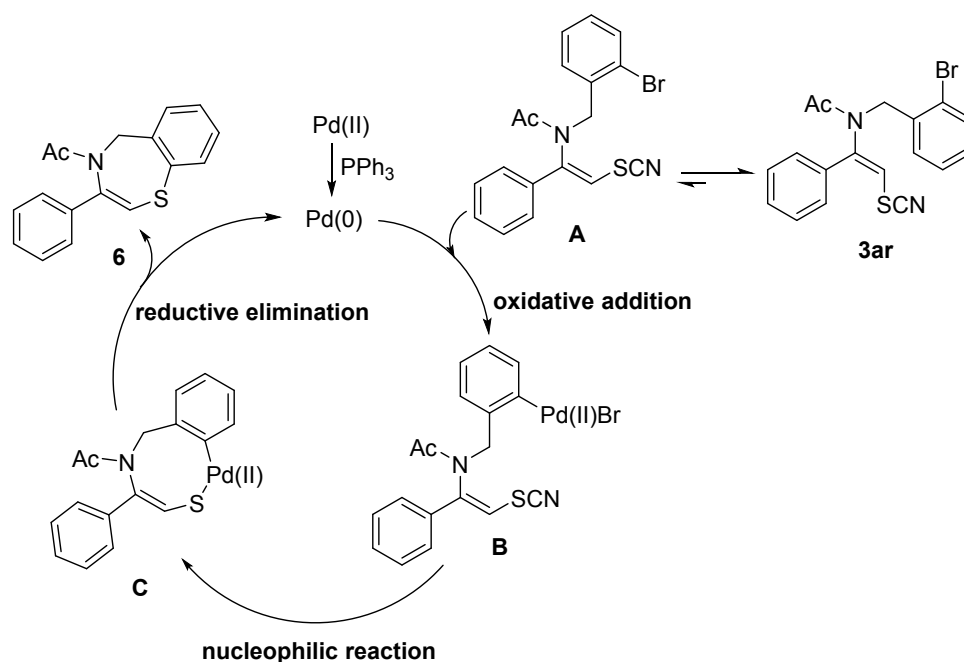


(1,2-dithiocyanatoethane-1,1-diyl)dibenzene(10).³ ^1H NMR (400MHz, CDCl_3) δ 7.44-7.37 (m, 6H), 7.34-7.29 (m, 4H), 4.01 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.9, 129.1, 129.0, 126.1, 111.2, 72.0, 46.5.

4. Plausible mechanism for Scheme 3c



Scheme 3c. Preparation of seven-membered S-containing heterocycles



Based on the results obtained and previous reports,⁴ a plausible reaction mechanism is proposed. Initially, transition-metal catalyst Pd(II) is reduced to Pd(0) species in the presence of PPh_3 . Meanwhile, intermediate **A** is probably generated from **3ar** through isomerization reaction under heating conditions. The active Pd(0) species then undergoes oxidative addition with intermediate **A** to afford intermediates **B**. Intramolecular nucleophilic reaction of thiolate with the metal complex furnishes intermediates **C**, followed by reductive elimination reaction to provide seven-membered

ring product **6** and Pd(0) species.

5. X-ray Crystallographic Data of **3ar**

Sample preparation: Single crystals of **3ar** for X-ray diffraction experiment was obtained by slow evaporation of DCM/*n*-hexane (1:10, *v/v*) solution containing **3ar**. CCDC 2014798 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 **3ar** (CCDC 2014798)

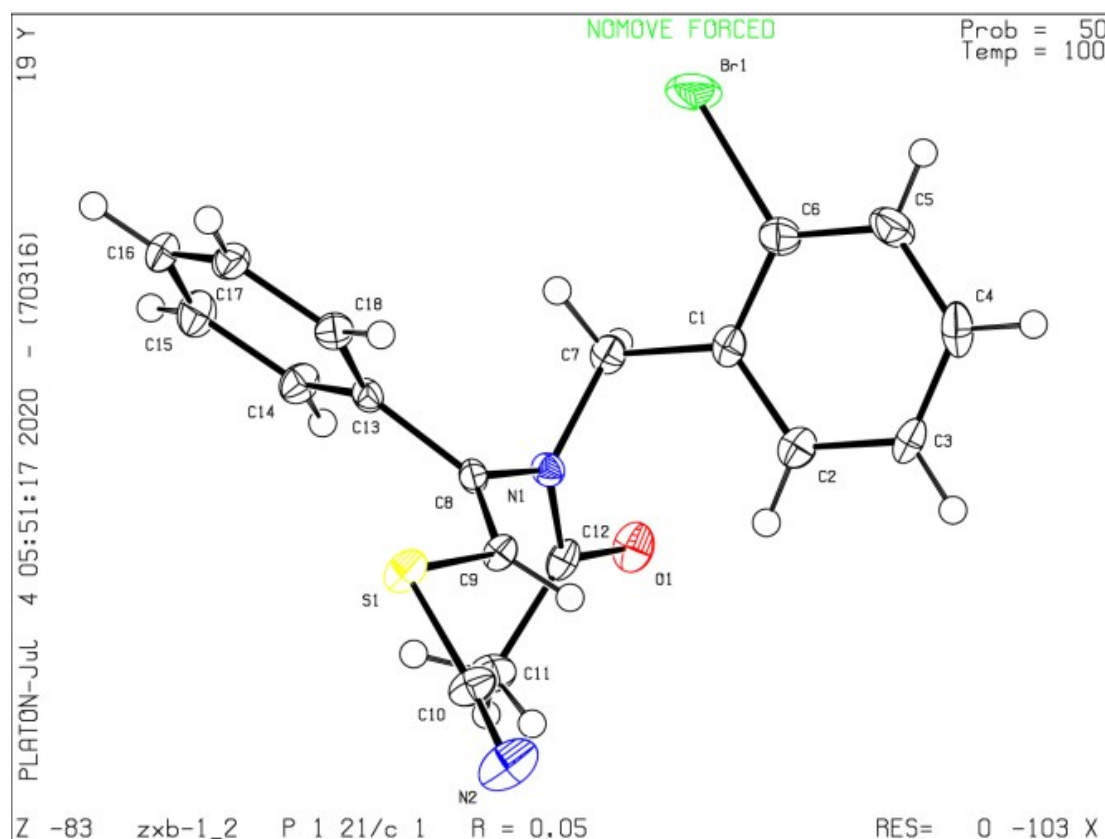


Table S1 Crystal data and structure refinement for 3ar (CCDC 2014798).

Identification code	3ar
Empirical formula	C ₁₈ H ₁₅ BrN ₂ OS
Formula weight	387.29
Temperature/K	99.9(4)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	10.6922(6)
b/Å	8.9341(8)
c/Å	17.5905(13)
α /°	90
β /°	98.505(6)
γ /°	90
Volume/Å ³	1661.9(2)
Z	4
ρ_{calc} /cm ³	1.548
μ /mm ⁻¹	2.604
F(000)	784.0
Crystal size/mm ³	0.13 × 0.12 × 0.1
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/°	3.852 to 49.996
Index ranges	-12 ≤ h ≤ 12, -10 ≤ k ≤ 6, -20 ≤ l ≤ 20
Reflections collected	7414
Independent reflections	2931 [R _{int} = 0.0508, R _{sigma} = 0.0641]
Data/restraints/parameters	2931/0/209
Goodness-of-fit on F ²	1.072
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0482, wR ₂ = 0.1103
Final R indexes [all data]	R ₁ = 0.0607, wR ₂ = 0.1207
Largest diff. peak/hole / e Å ⁻³	1.04/-1.61

Table S2 Bond Lengths for 3ar (CCDC 2014798).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C6	1.905(4)	C3	C4	1.392(5)
S1	C9	1.766(4)	C4	C5	1.373(6)
S1	C10	1.684(4)	C5	C6	1.380(5)
O1	C12	1.223(4)	C8	C9	1.325(5)
N1	C7	1.468(4)	C8	C13	1.486(5)
N1	C8	1.430(5)	C11	C12	1.505(5)
N1	C12	1.370(4)	C13	C14	1.392(5)
N2	C10	1.149(5)	C13	C18	1.391(5)
C1	C2	1.392(5)	C14	C15	1.385(5)
C1	C6	1.400(5)	C15	C16	1.389(6)
C1	C7	1.516(5)	C16	C17	1.375(6)
C2	C3	1.380(5)	C17	C18	1.391(5)

Table S3 Bond Angles for 3ar (CCDC 2014798).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	S1	C9	101.08(18)	C9	C8	N1	119.6(3)
C8	N1	C7	115.6(3)	C9	C8	C13	124.8(3)
C12	N1	C7	119.1(3)	C8	C9	S1	121.2(3)
C12	N1	C8	125.3(3)	N2	C10	S1	172.8(4)
C2	C1	C6	116.2(3)	O1	C12	N1	120.1(3)
C2	C1	C7	121.5(3)	O1	C12	C11	121.8(3)
C6	C1	C7	122.2(3)	N1	C12	C11	118.0(3)
C3	C2	C1	121.9(3)	C14	C13	C8	119.5(3)
C2	C3	C4	120.0(3)	C18	C13	C8	121.8(3)
C5	C4	C3	119.6(4)	C18	C13	C14	118.7(3)
C4	C5	C6	119.5(3)	C15	C14	C13	120.7(4)
C1	C6	Br1	119.6(3)	C16	C15	C14	120.1(4)
C5	C6	Br1	117.7(3)	C17	C16	C15	119.6(4)
C5	C6	C1	122.7(3)	C16	C17	C18	120.6(4)

Table S3 Bond Angles for 3ar (CCDC 2014798).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C7	C1	113.3(3)	C17	C18	C13	120.3(4)
N1	C8	C13	115.6(3)				

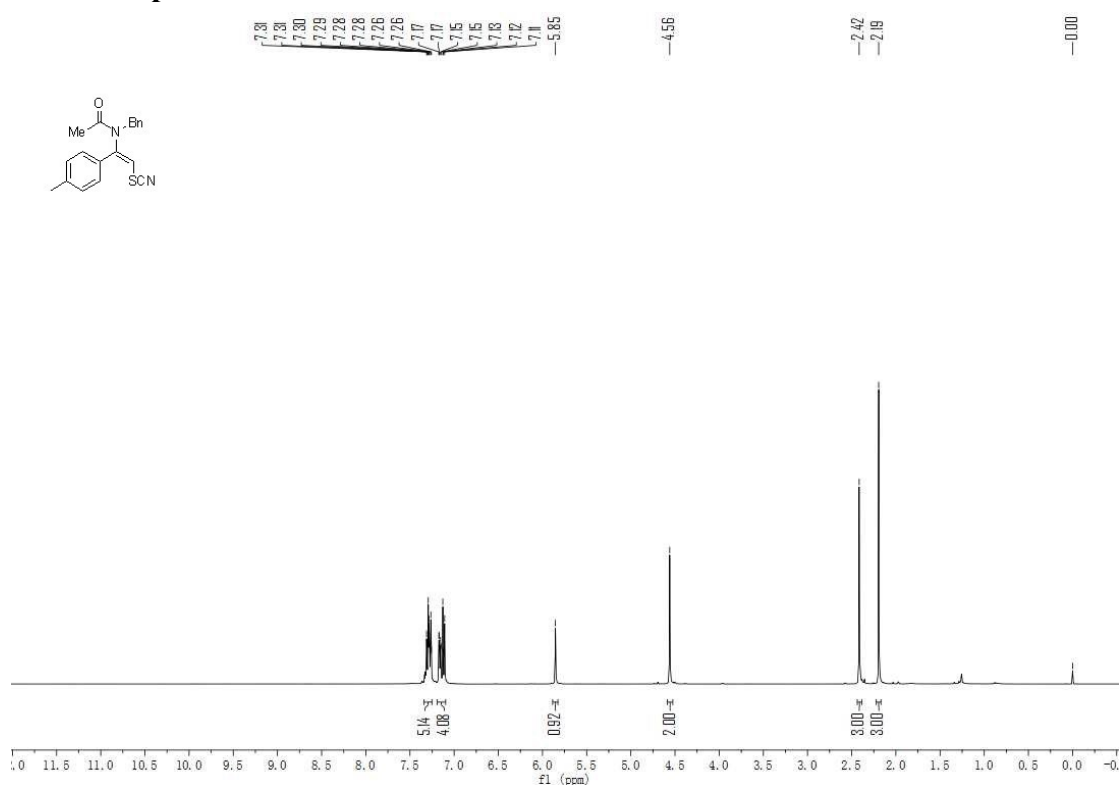
6. Reference

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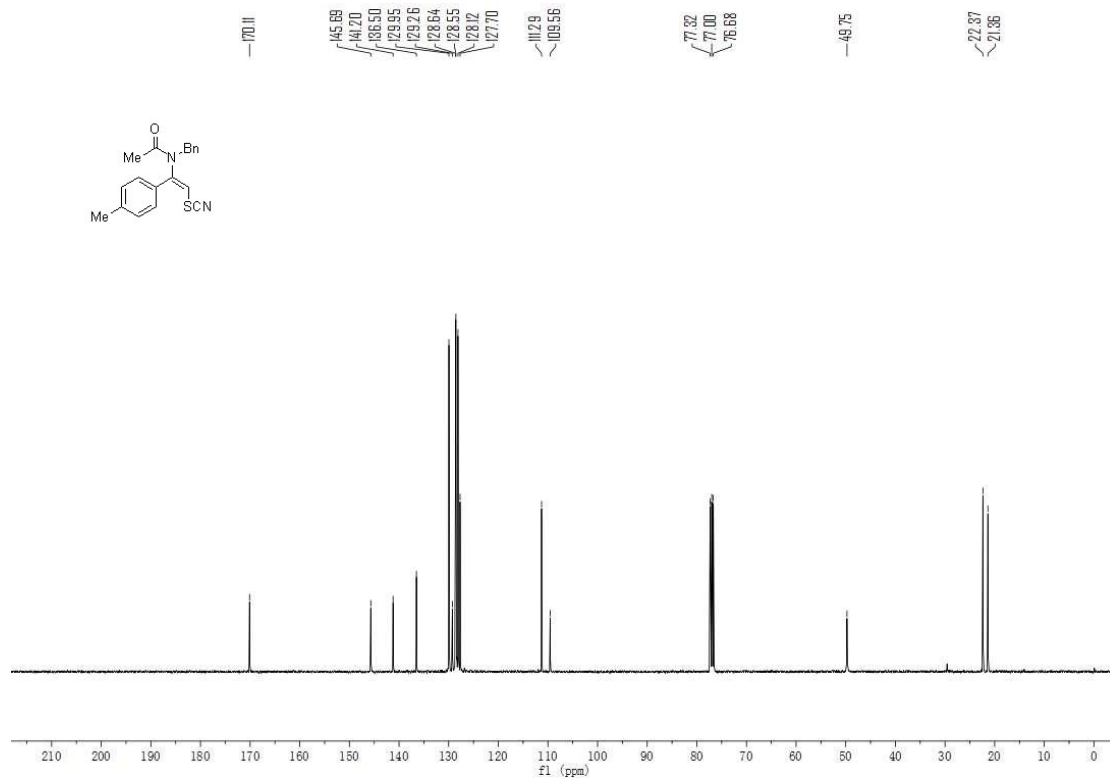
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7. ¹H NMR and ¹³C NMR spectra of compounds 3aa-y, 4-10

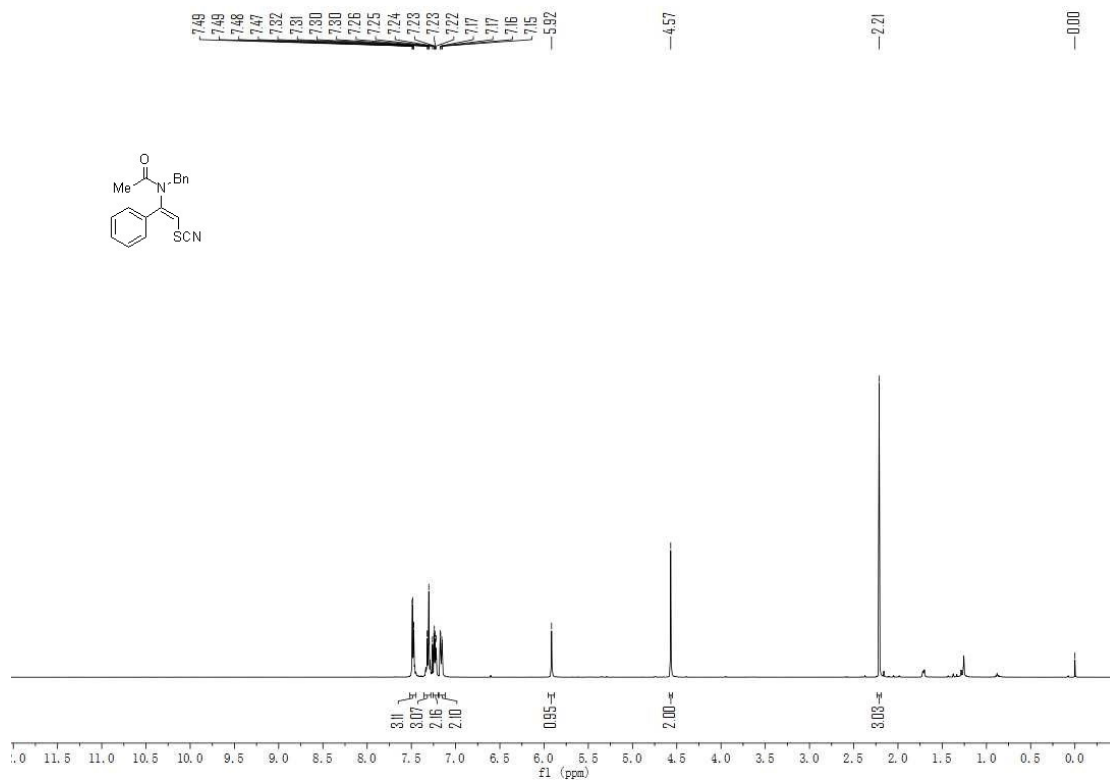
¹H NMR spectrum of 3aa



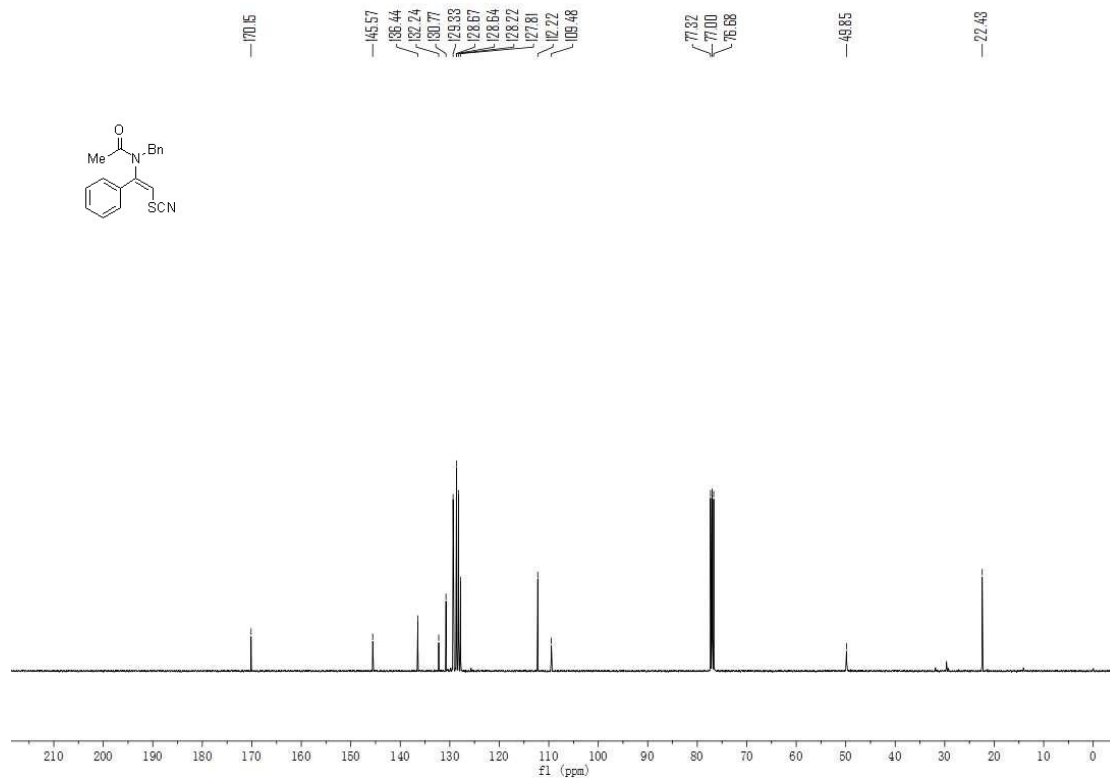
¹³C NMR spectrum of 3aa



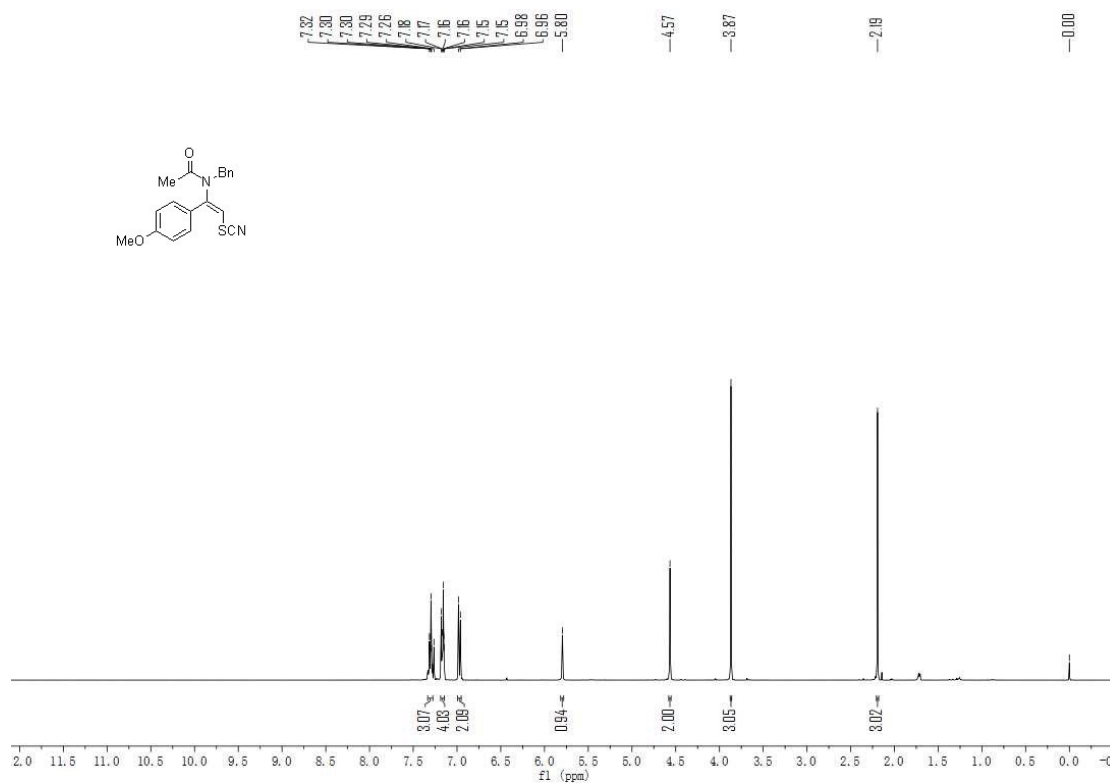
¹H NMR spectrum of 3ab



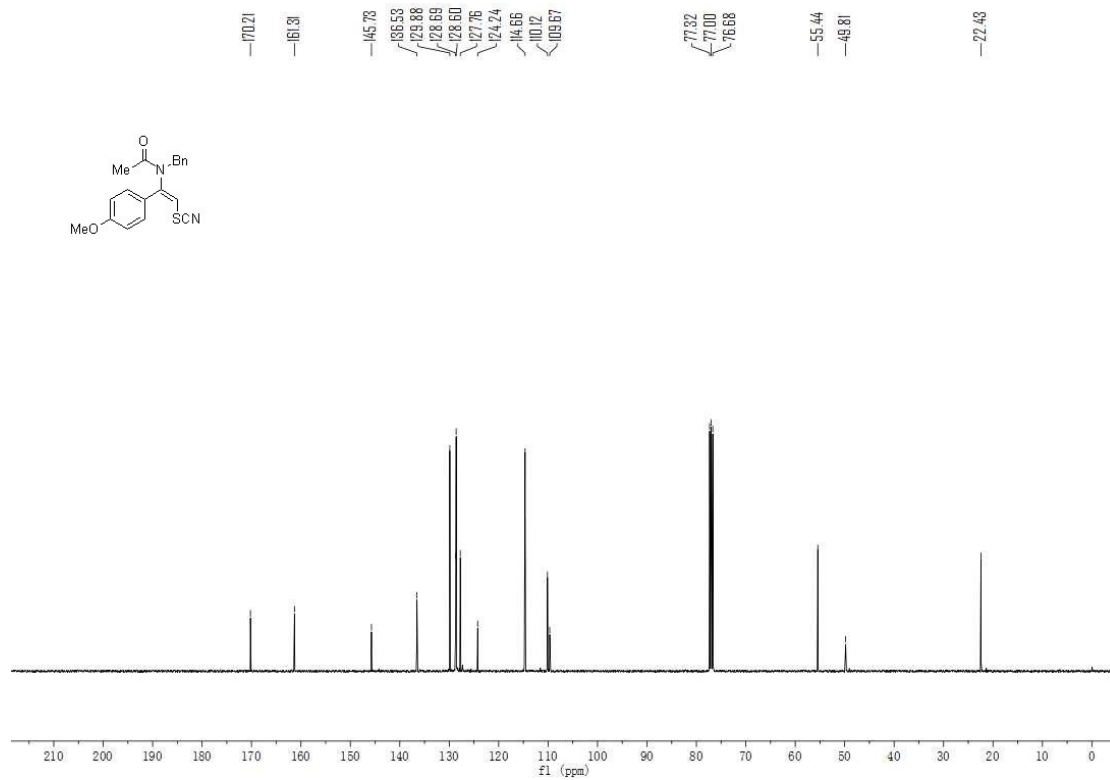
¹³C NMR spectrum of 3ab



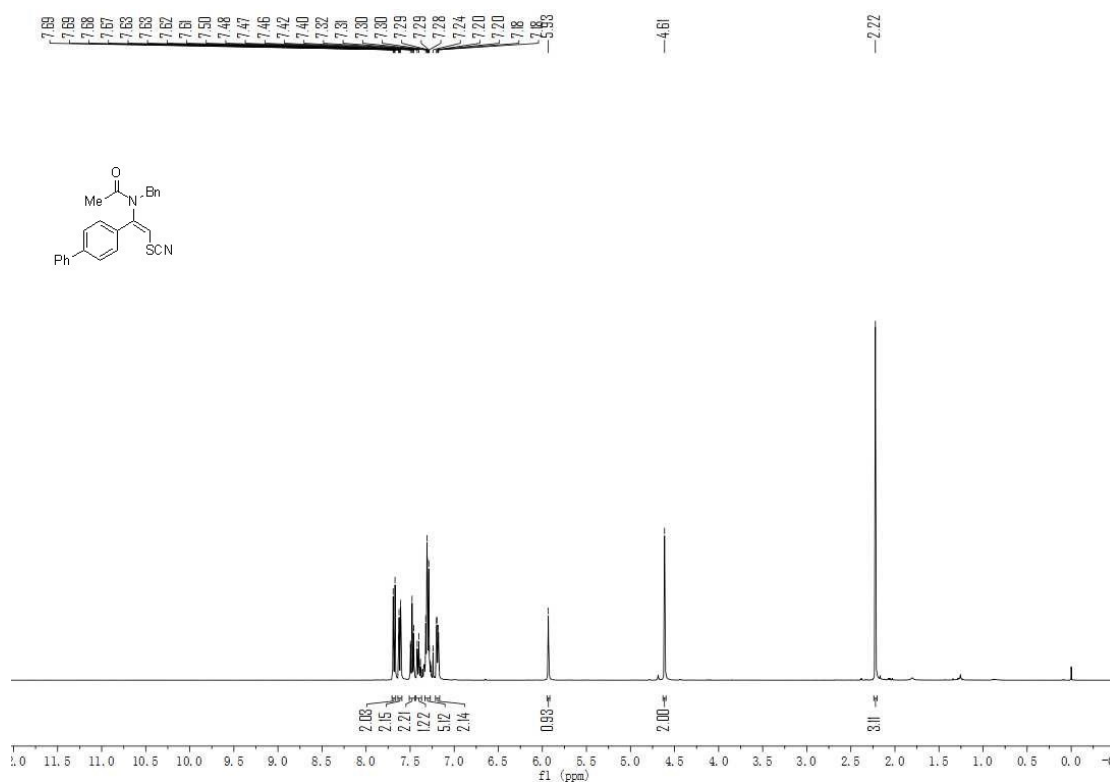
¹H NMR spectrum of 3ac



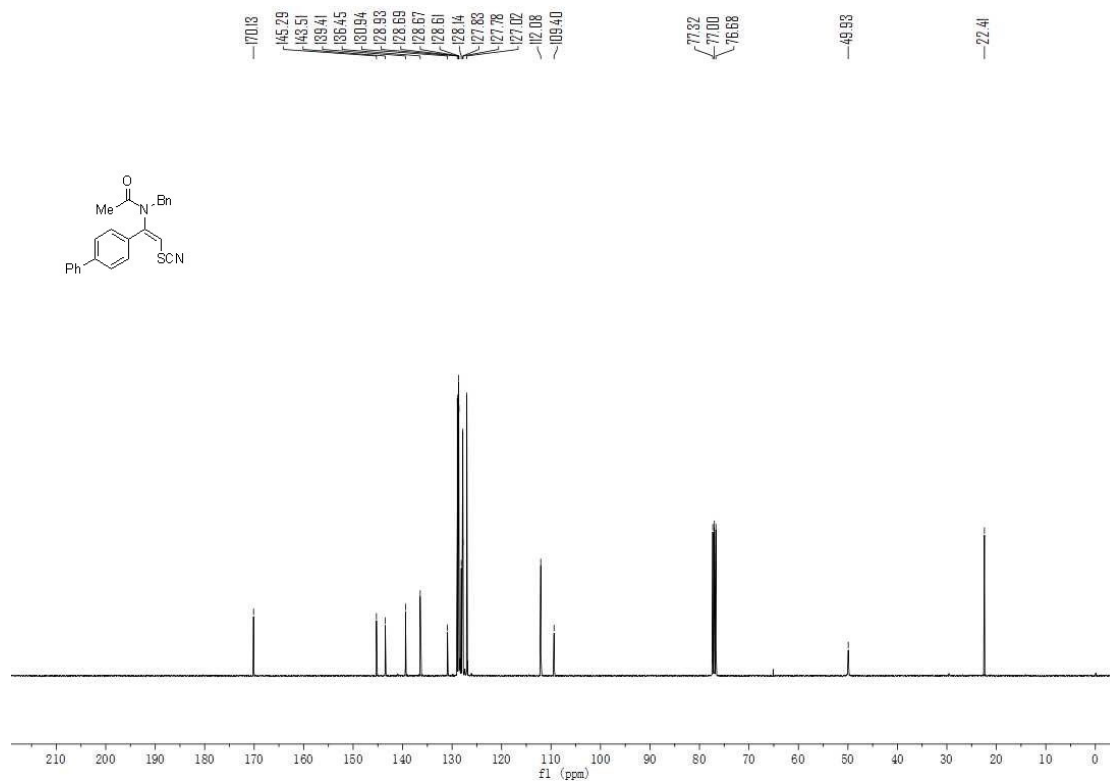
¹³C NMR spectrum of 3ac



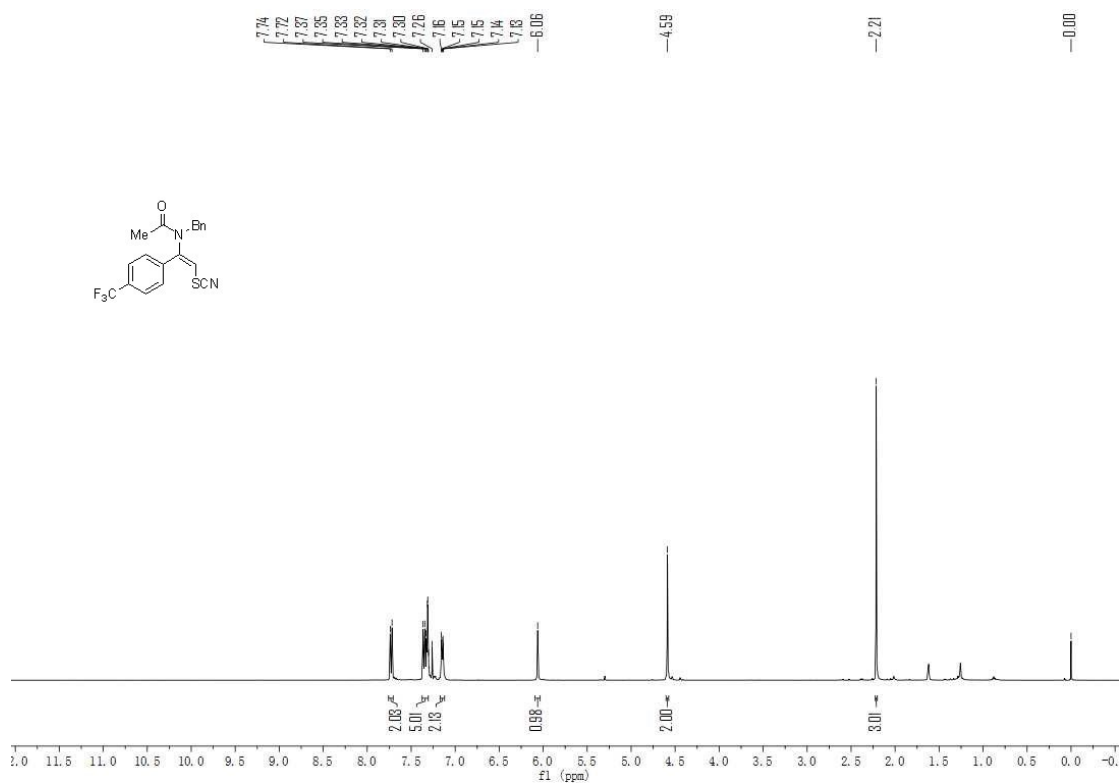
¹H NMR spectrum of 3ad



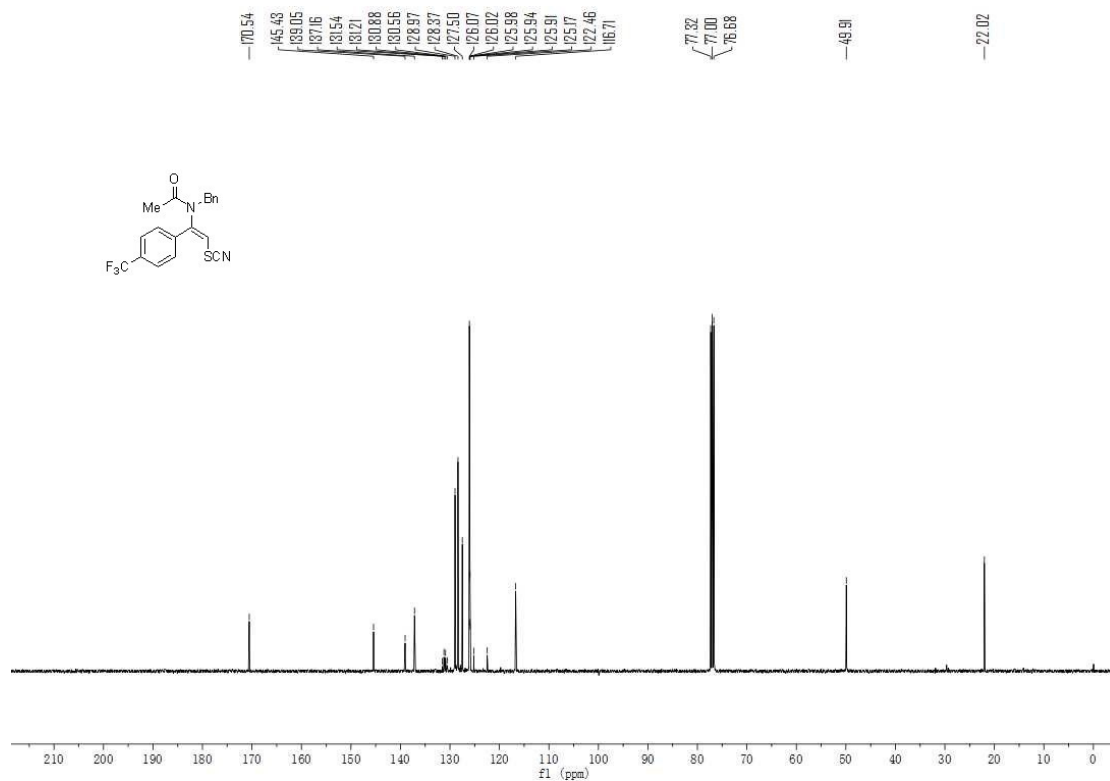
¹³C NMR spectrum of 3ad



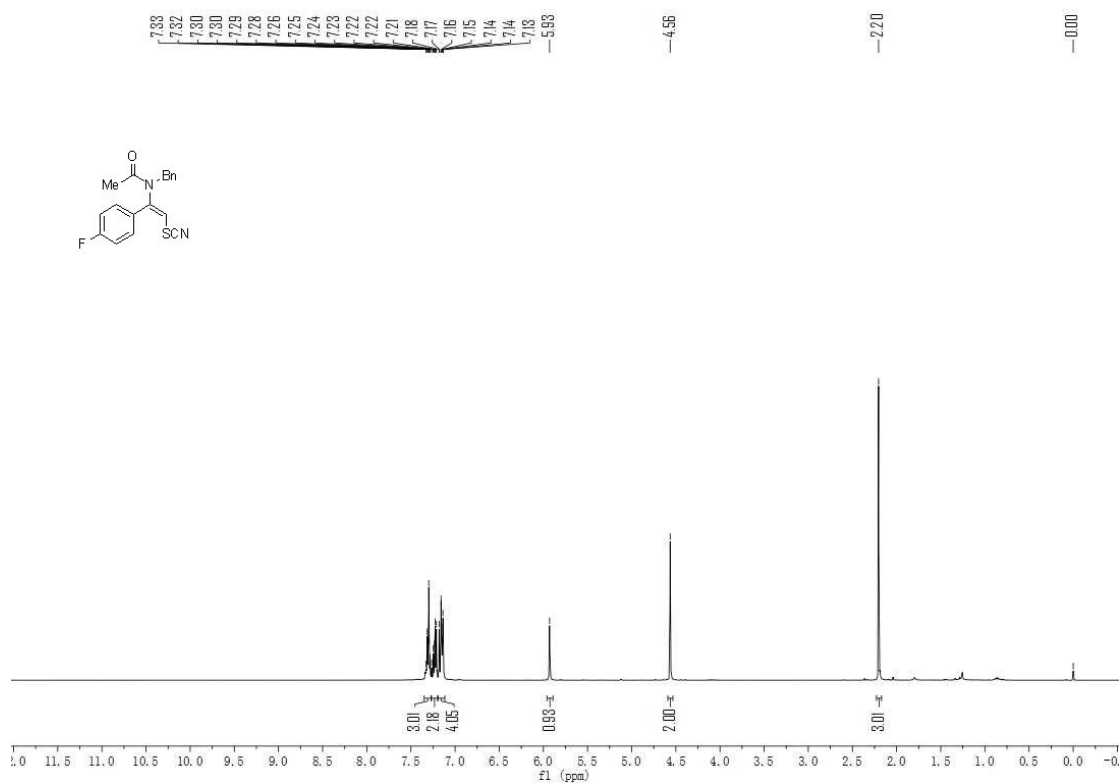
¹H NMR spectrum of 3ae



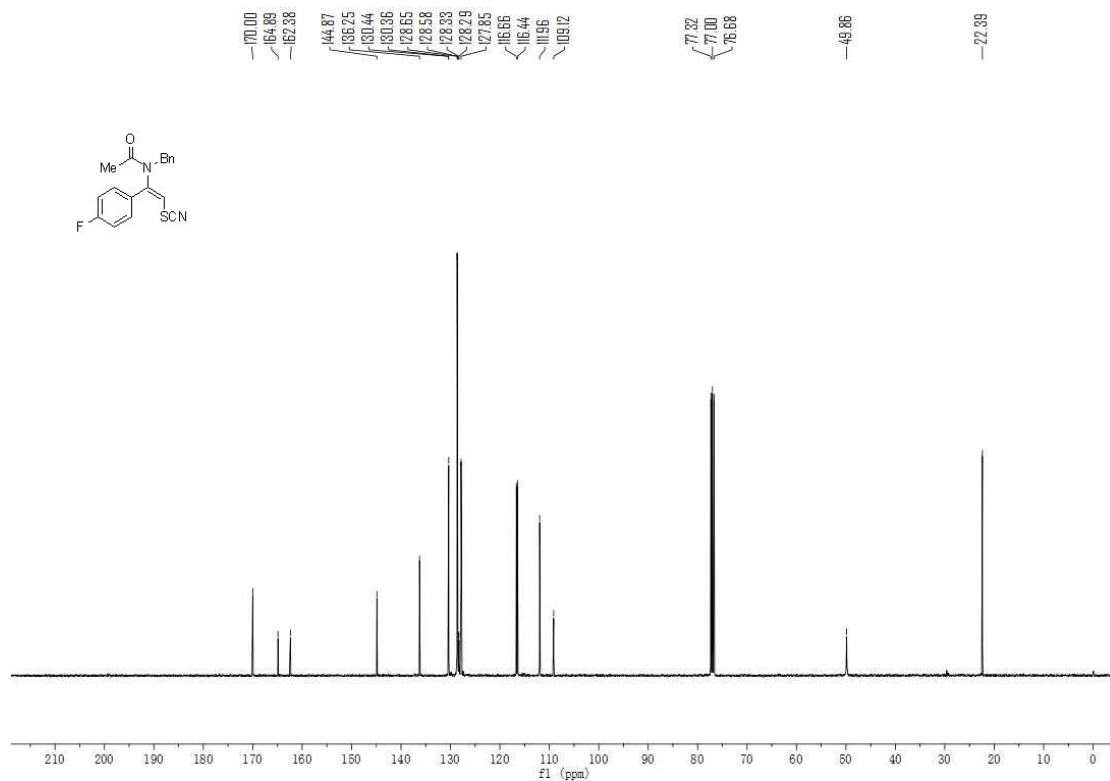
¹³C NMR spectrum of 3ae



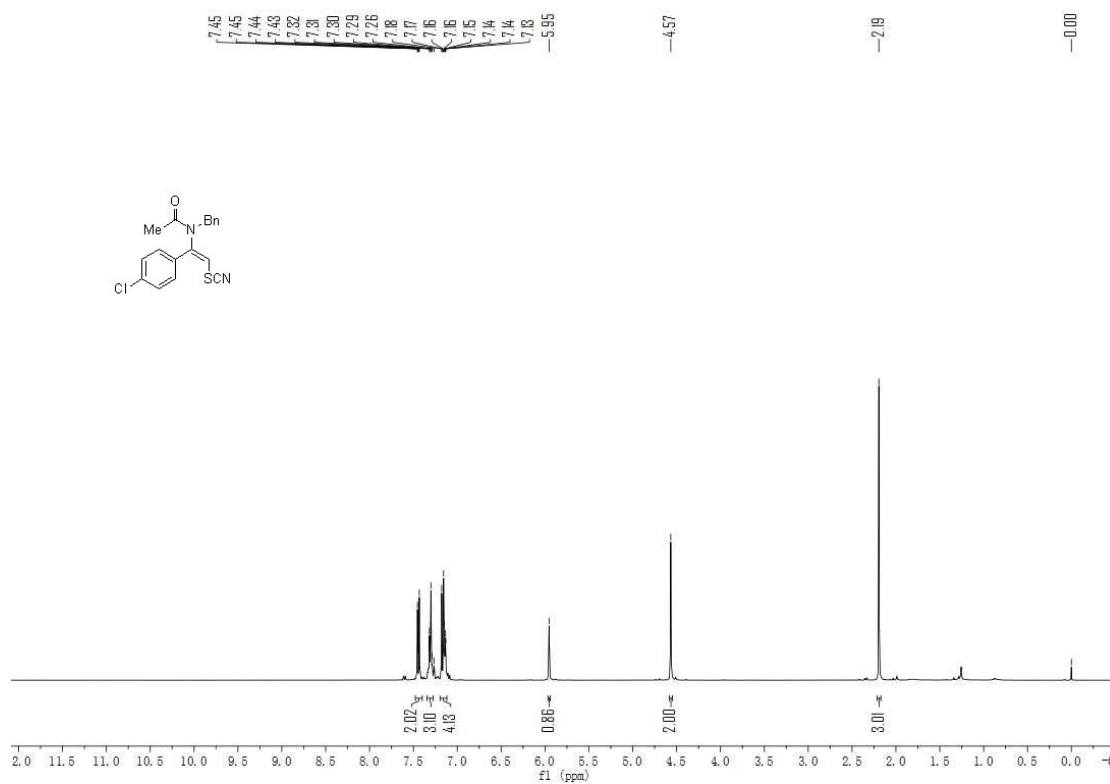
¹H NMR spectrum of 3af



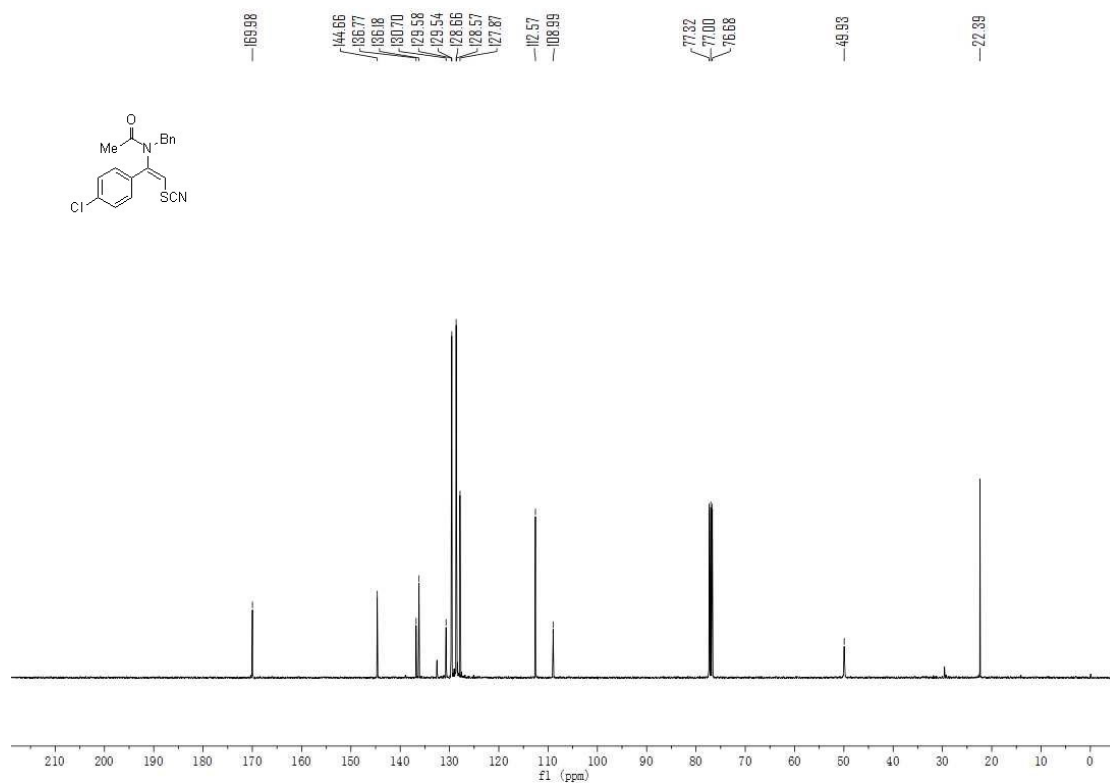
¹³C NMR spectrum of 3af



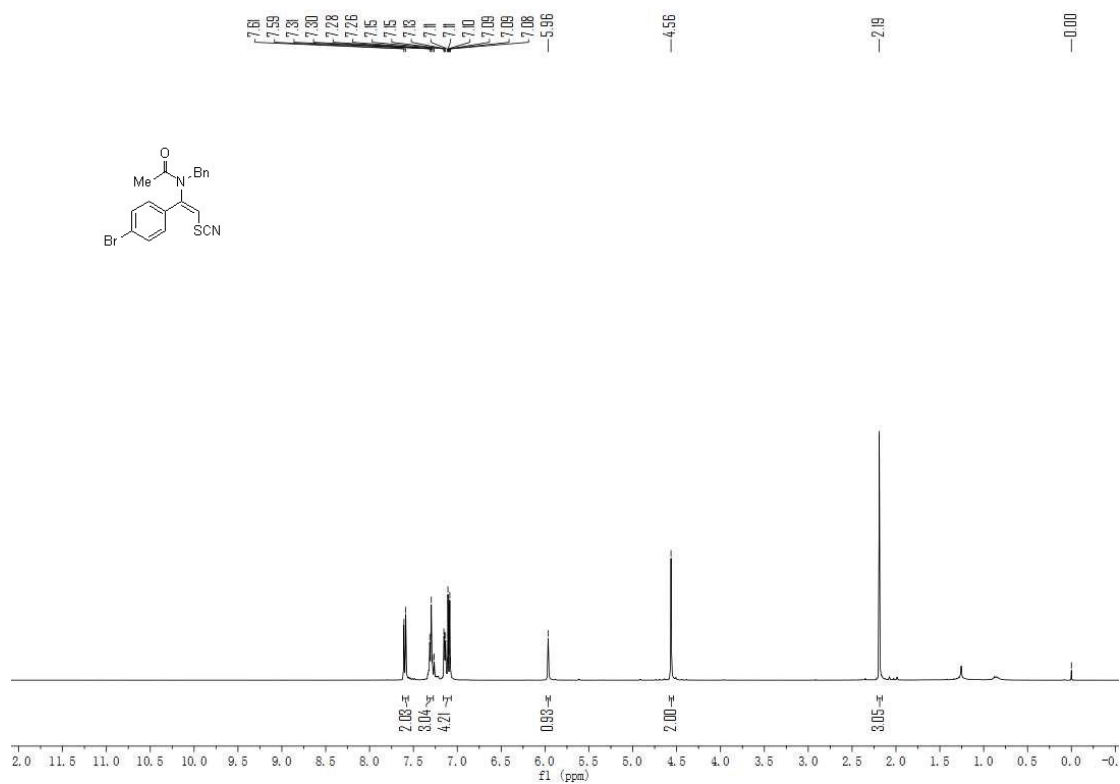
¹H NMR spectrum of 3ag



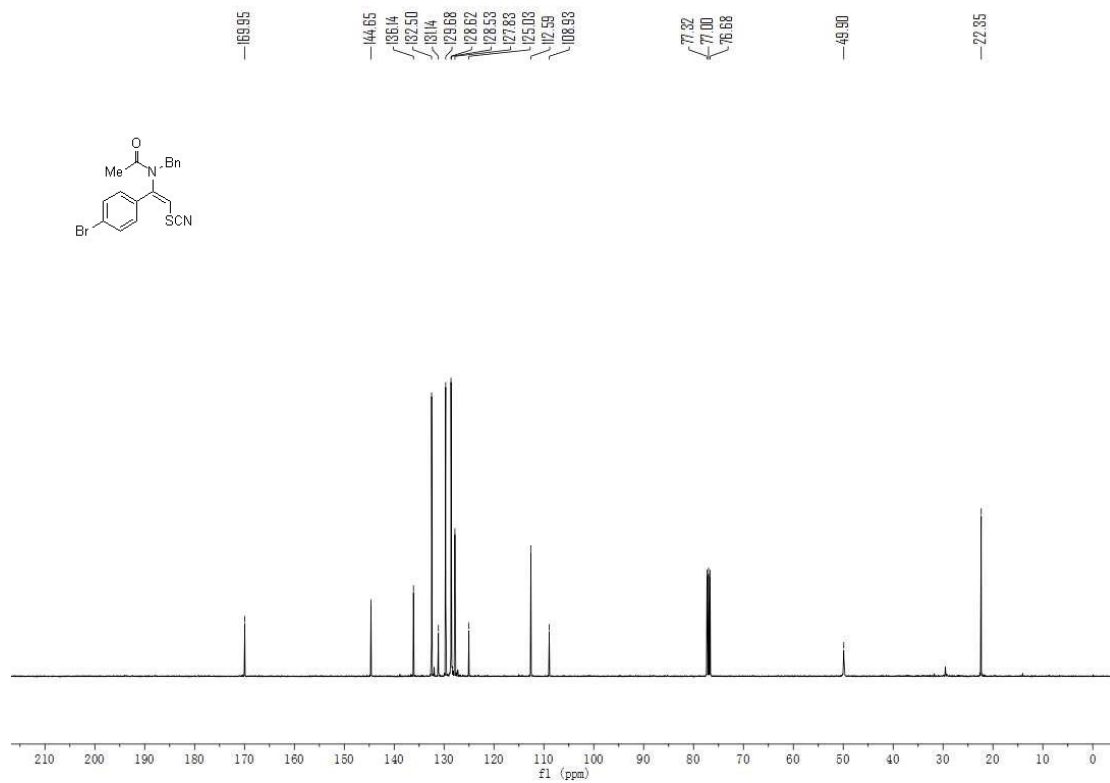
¹³C NMR spectrum of 3ag



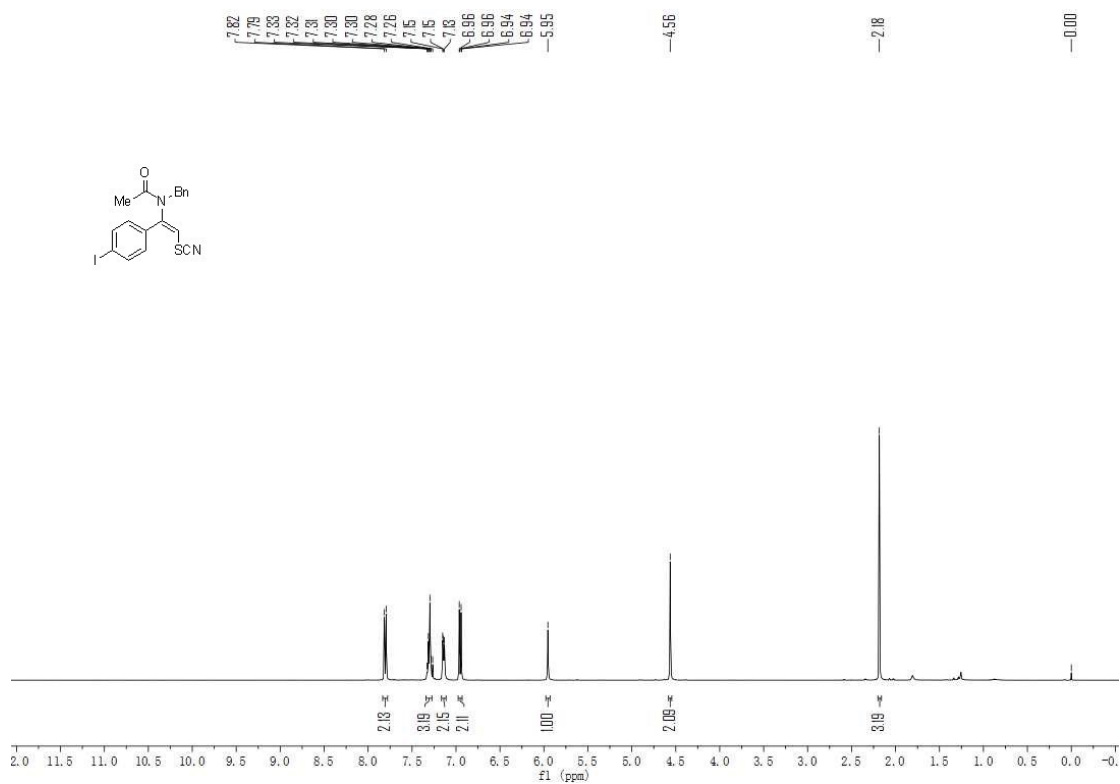
¹H NMR spectrum of 3ah



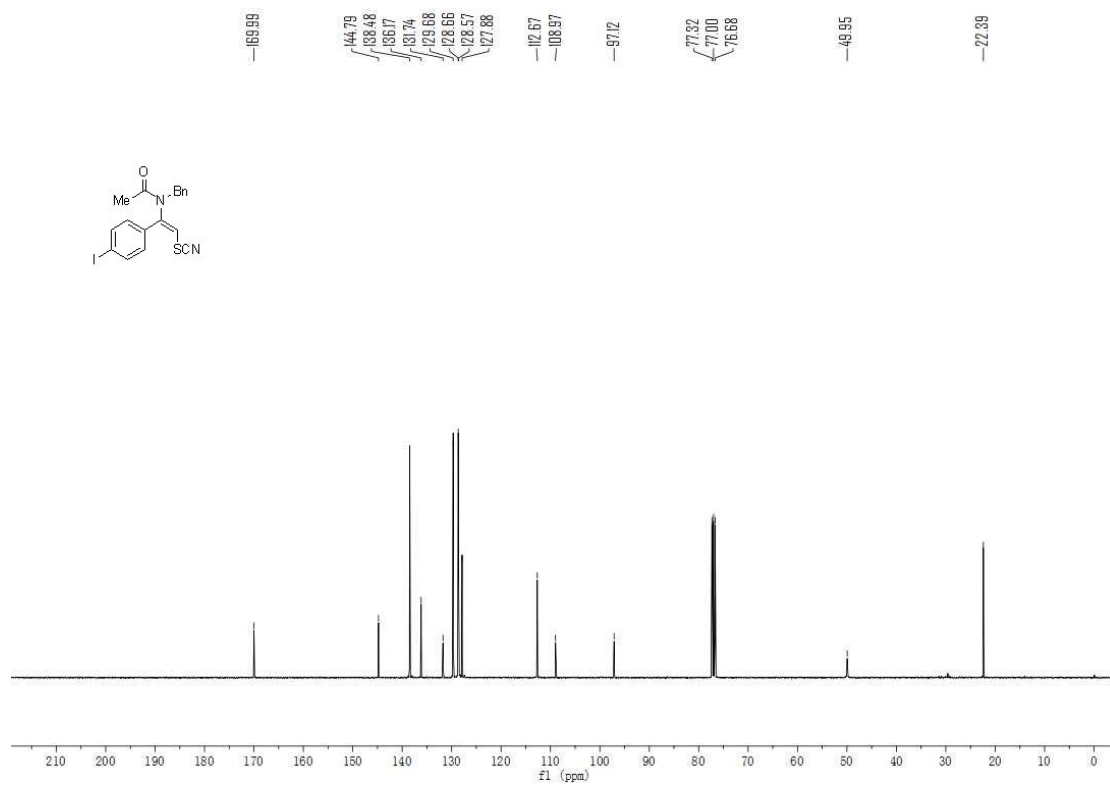
¹³C NMR spectrum of 3ah



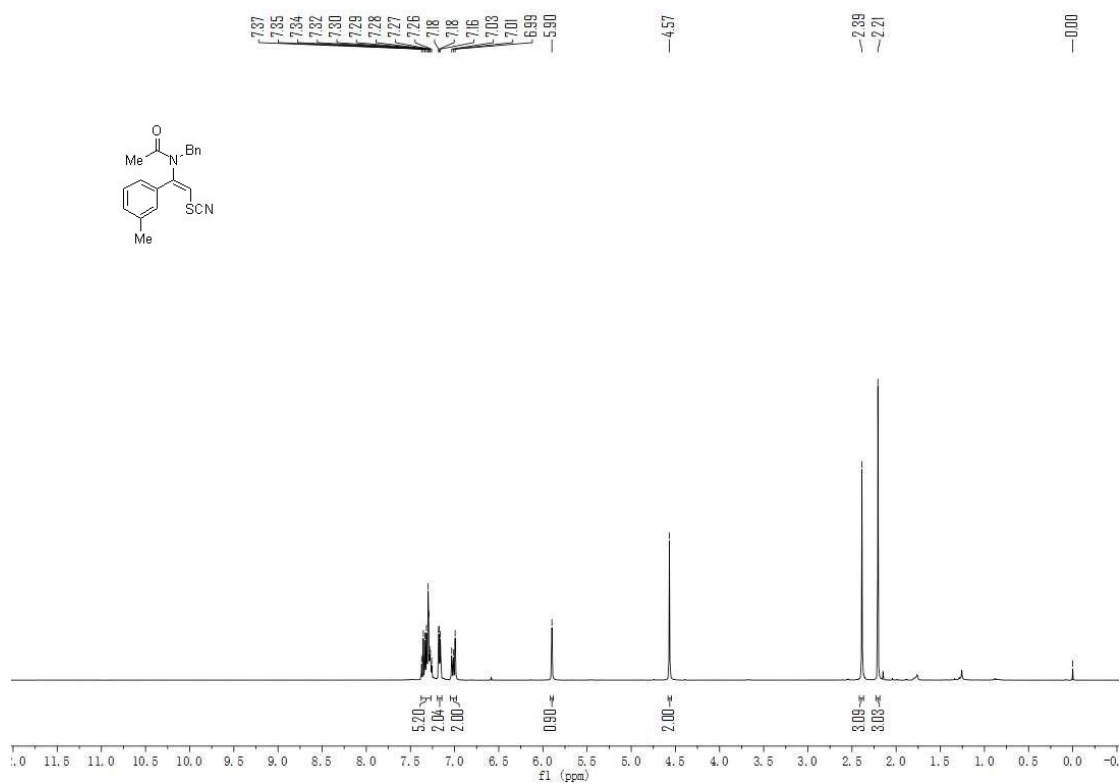
¹H NMR spectrum of 3ai



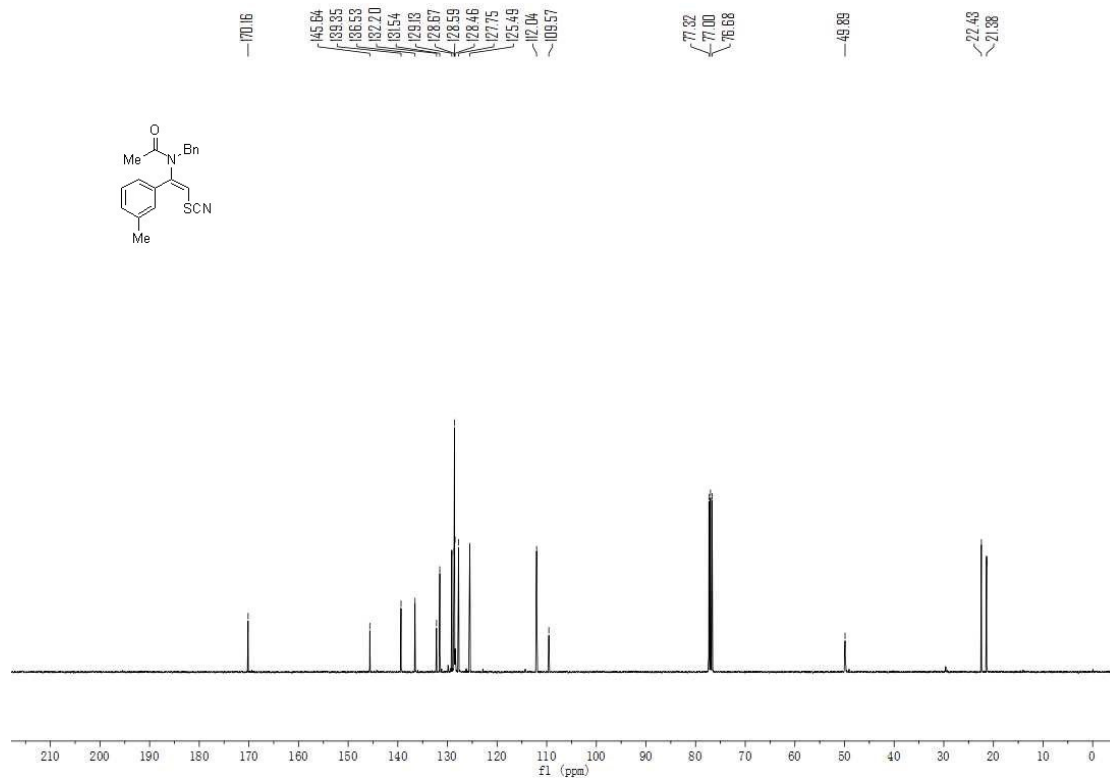
¹³C NMR spectrum of 3ai



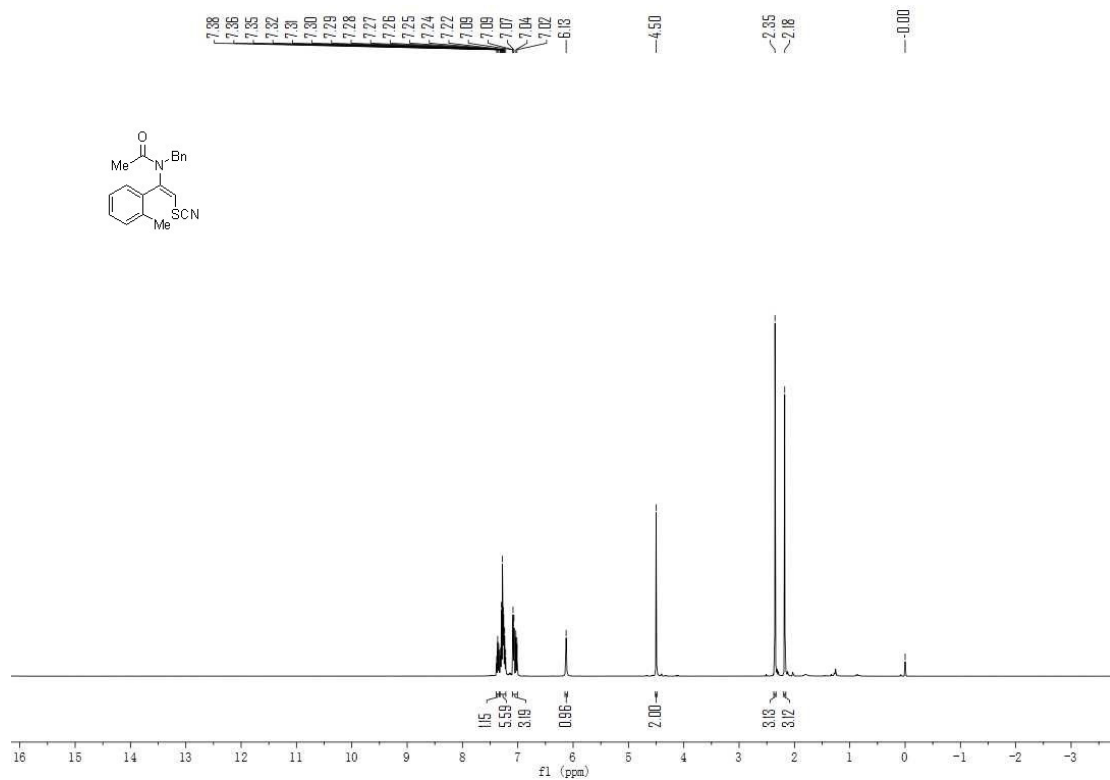
¹H NMR spectrum of 3aj



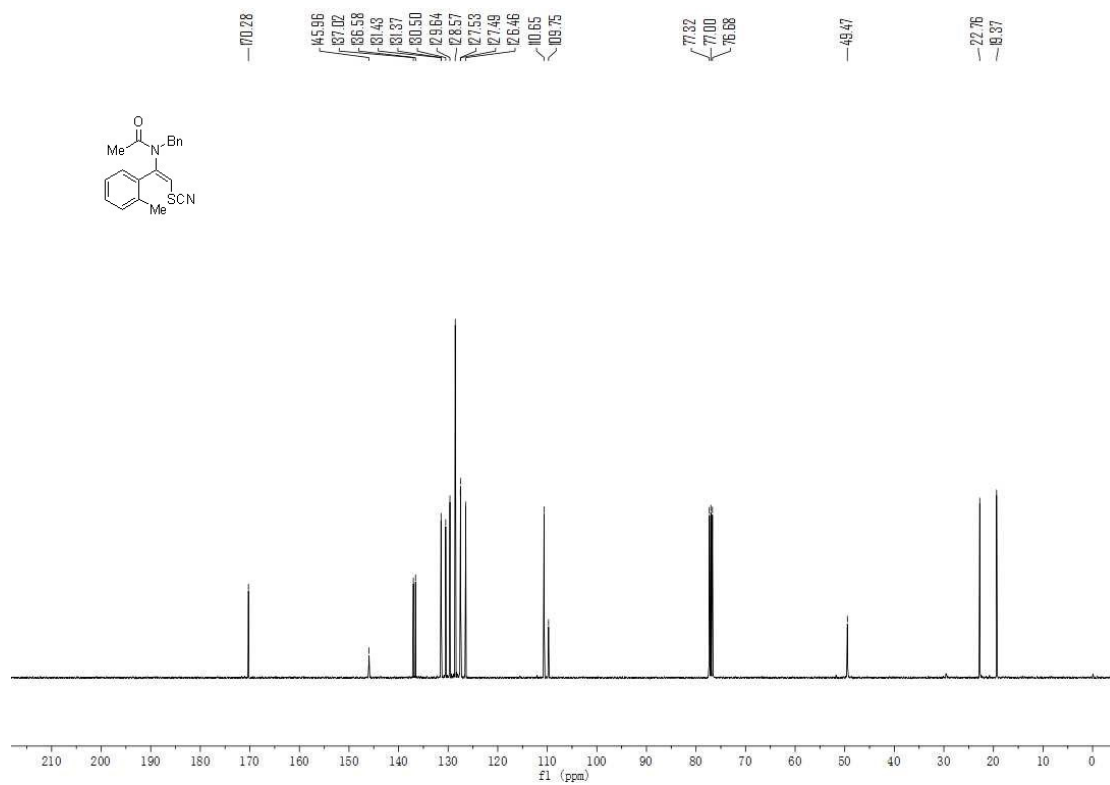
¹³C NMR spectrum of 3aj



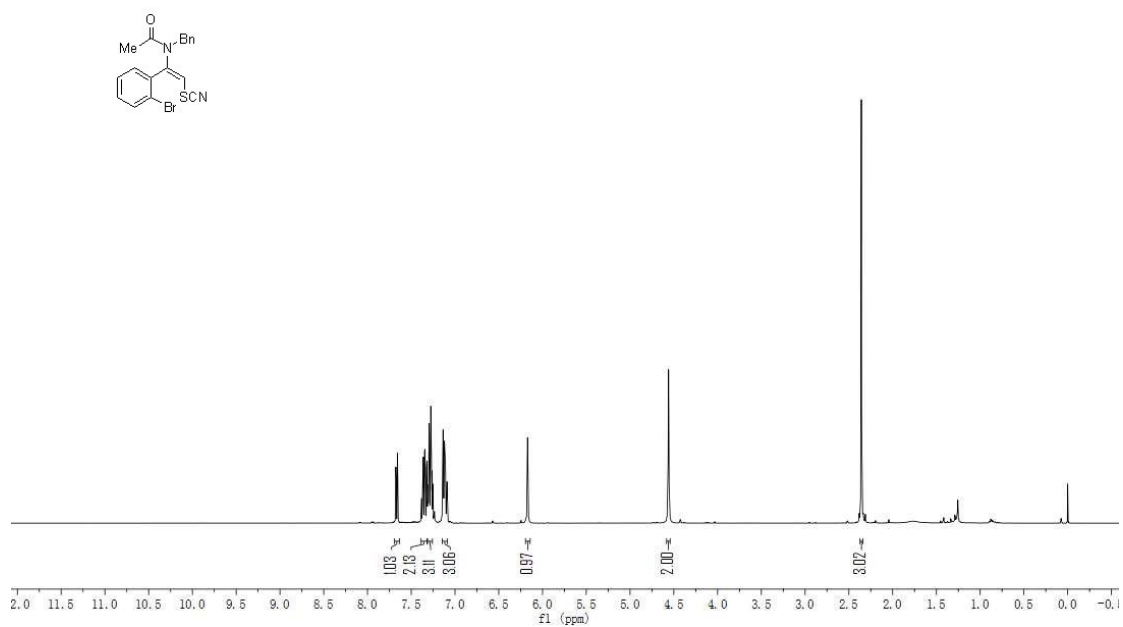
¹H NMR spectrum of 3ak



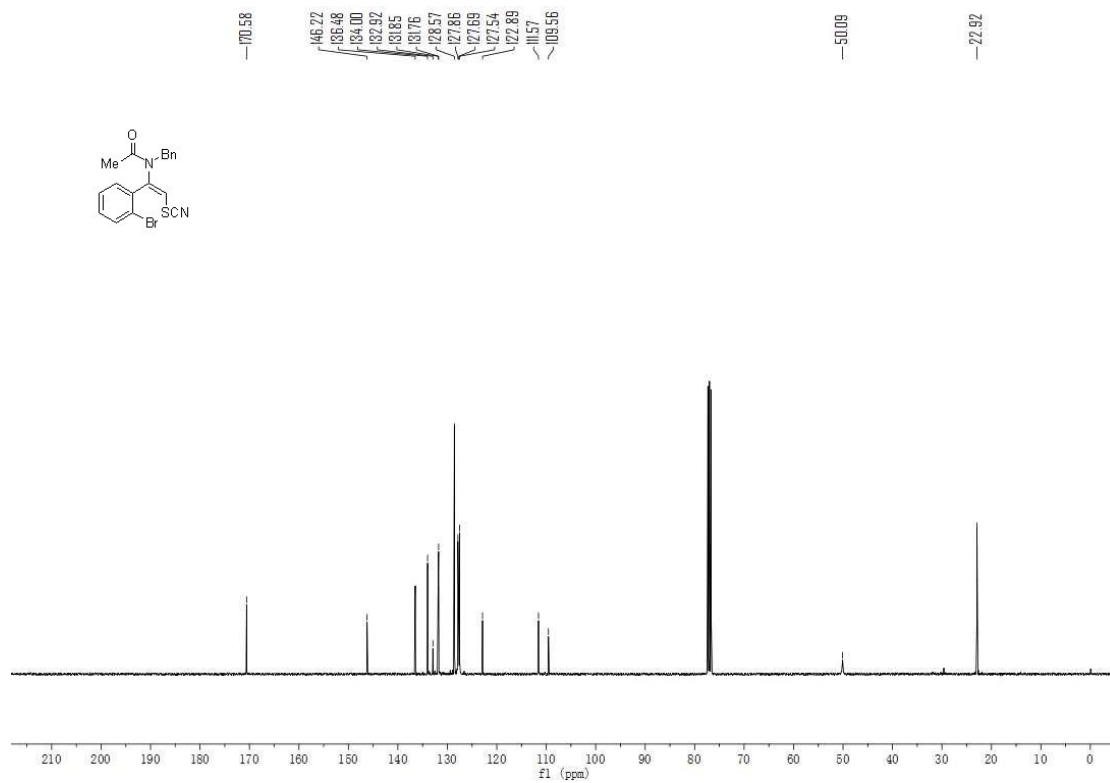
¹³C NMR spectrum of 3ak



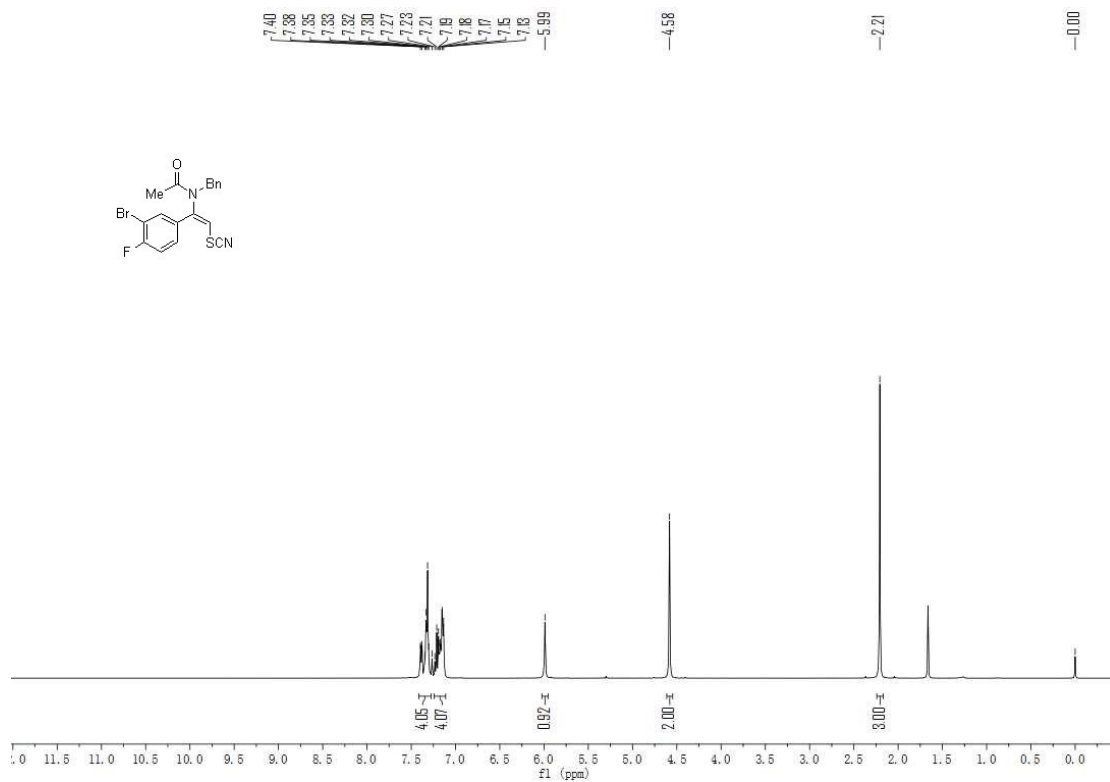
¹H NMR spectrum of 3a



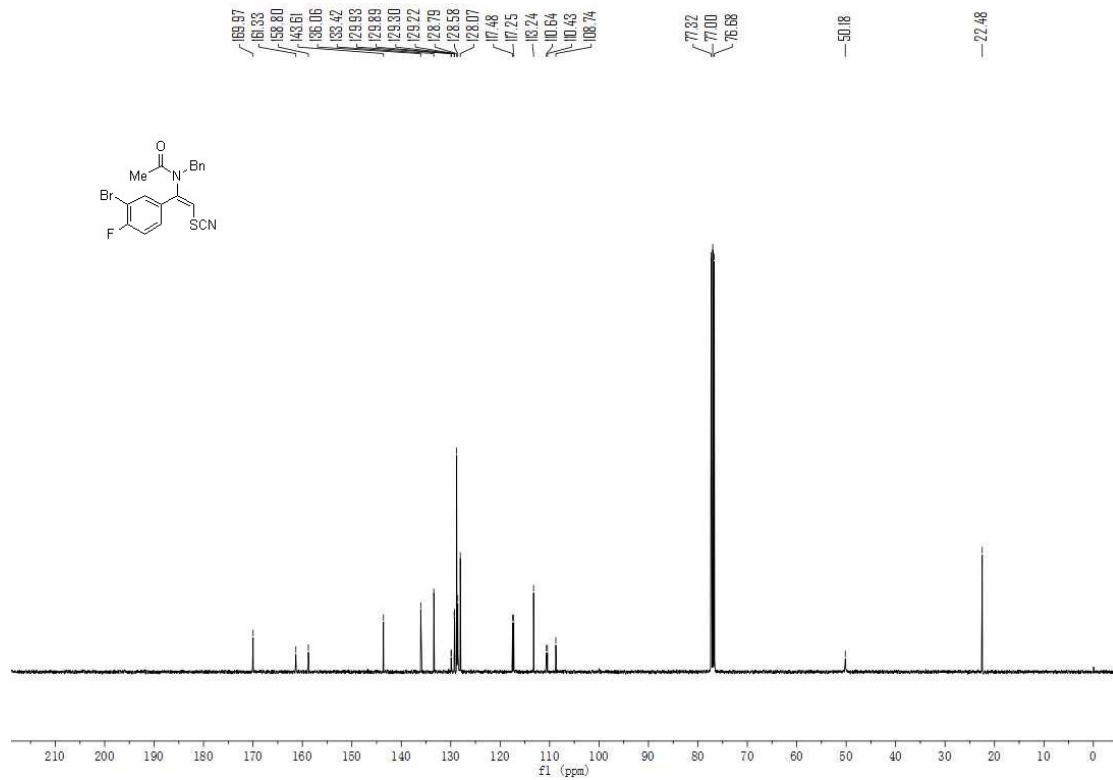
¹³C NMR spectrum of 3a



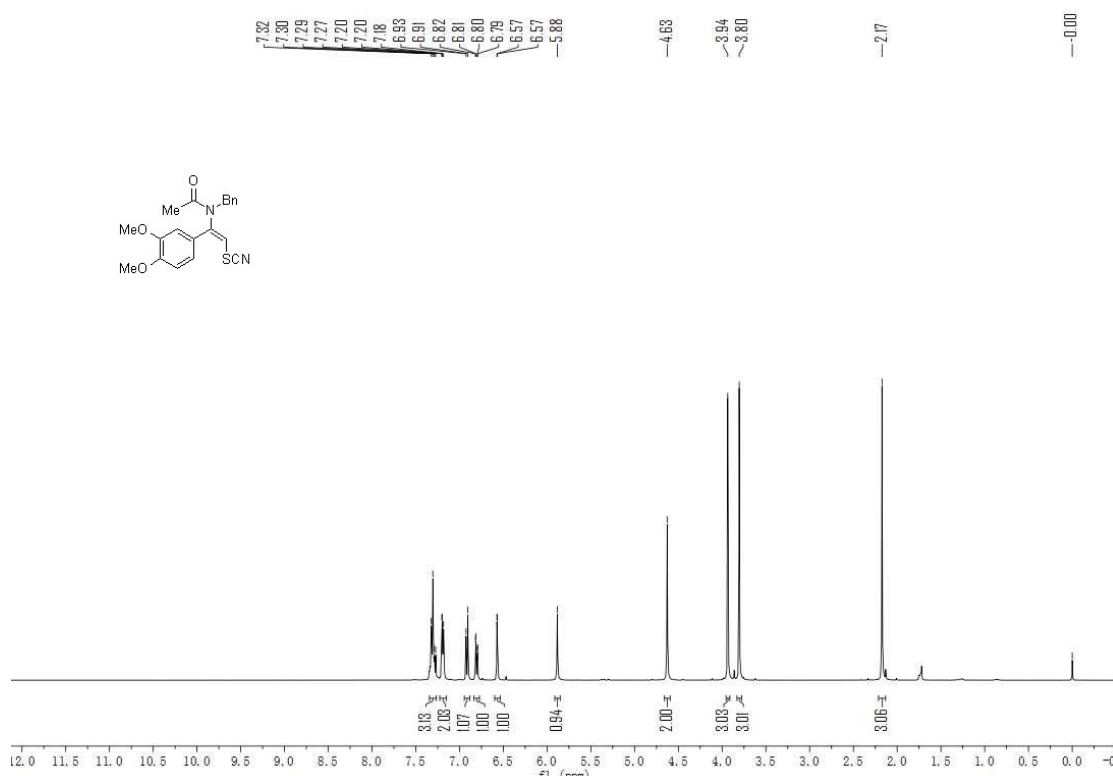
¹H NMR spectrum of 3am



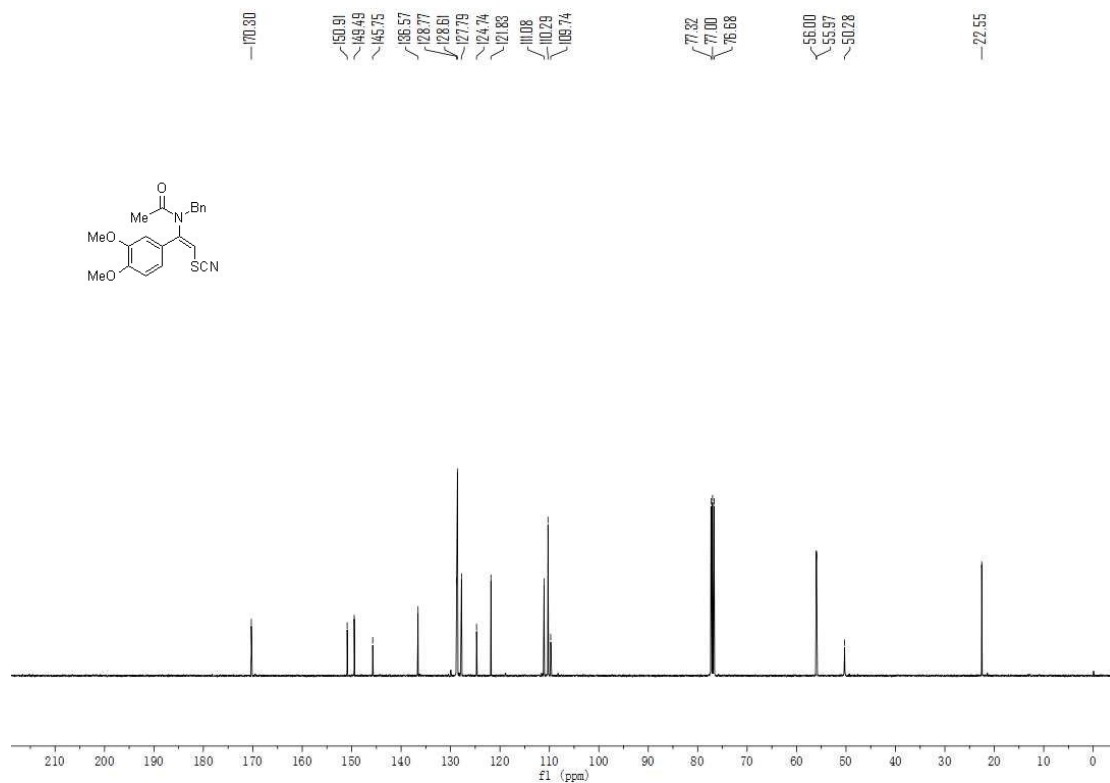
¹³C NMR spectrum of 3am



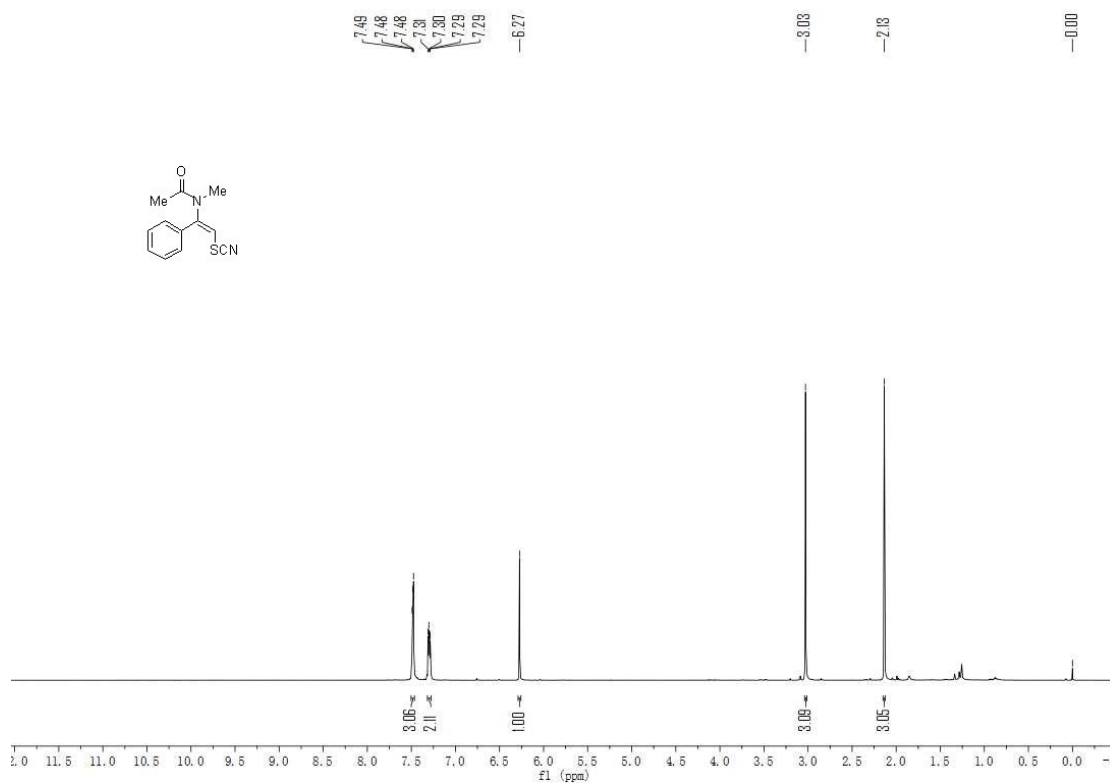
¹H NMR spectrum of 3an



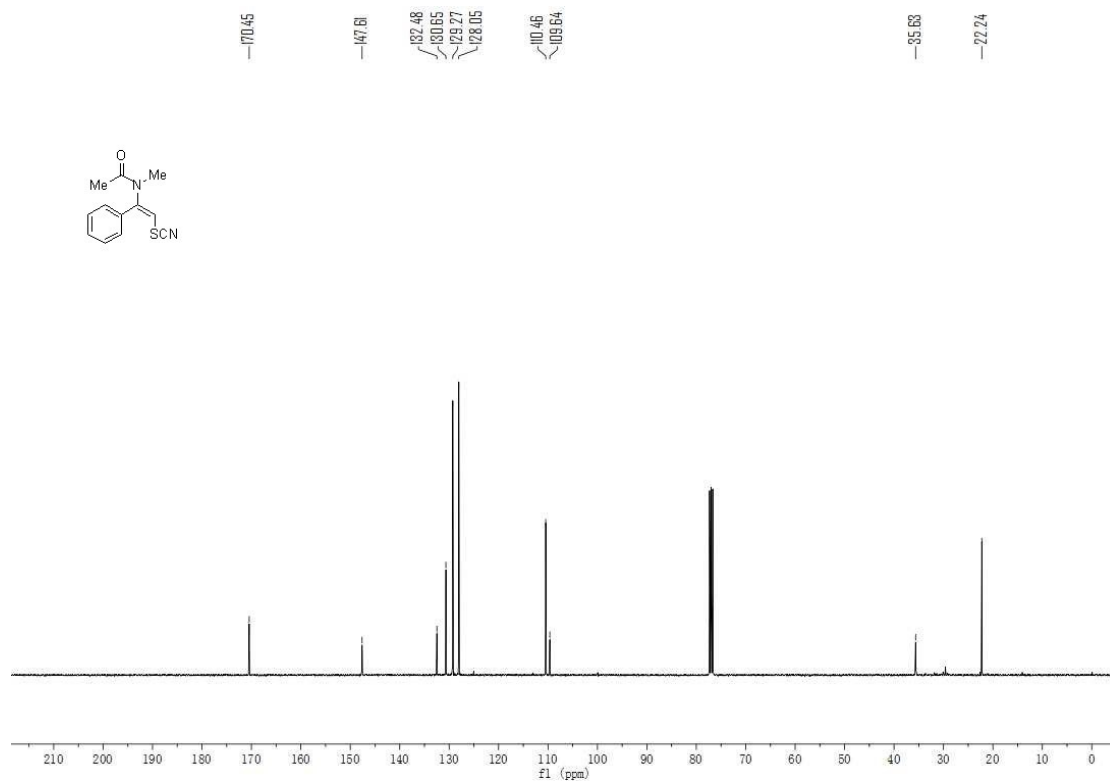
¹³C NMR spectrum of 3an



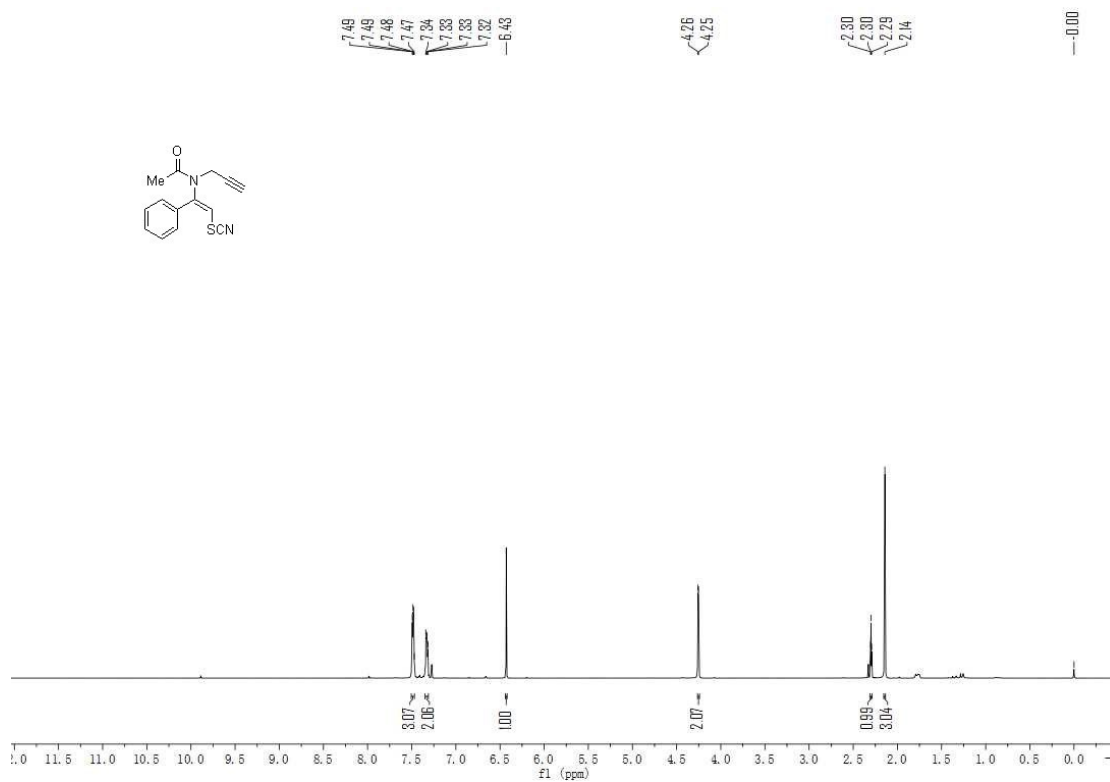
¹H NMR spectrum of 3ao



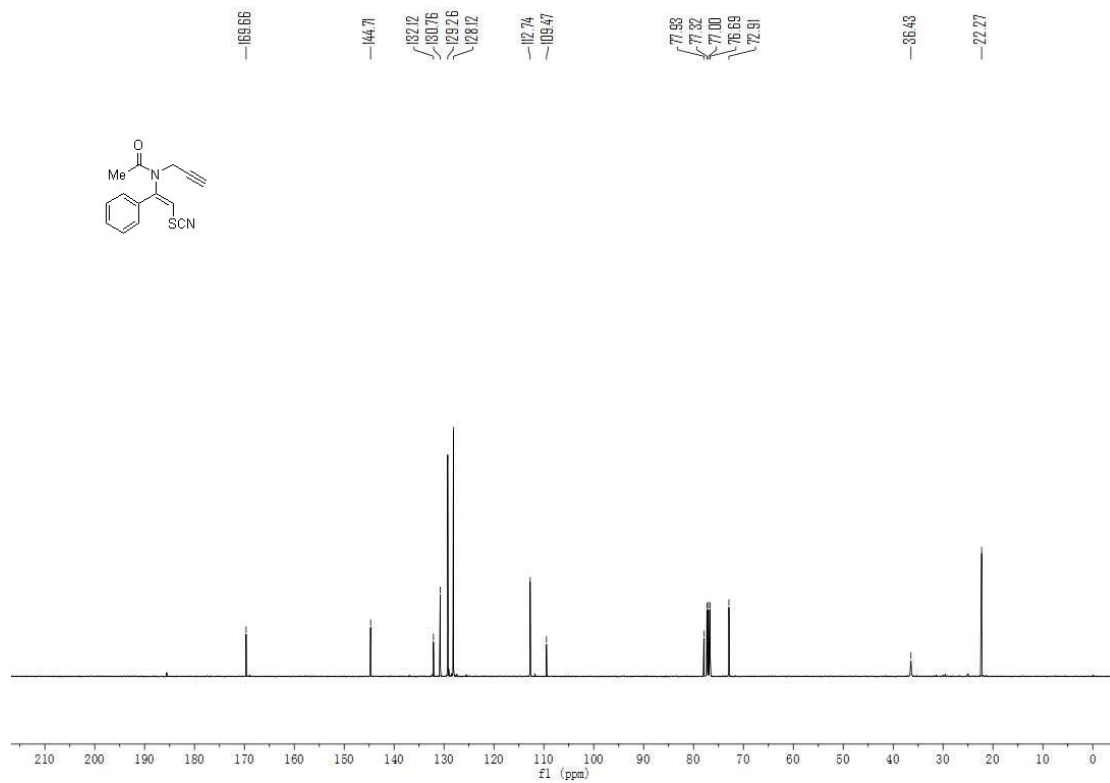
¹³C NMR spectrum of 3ao



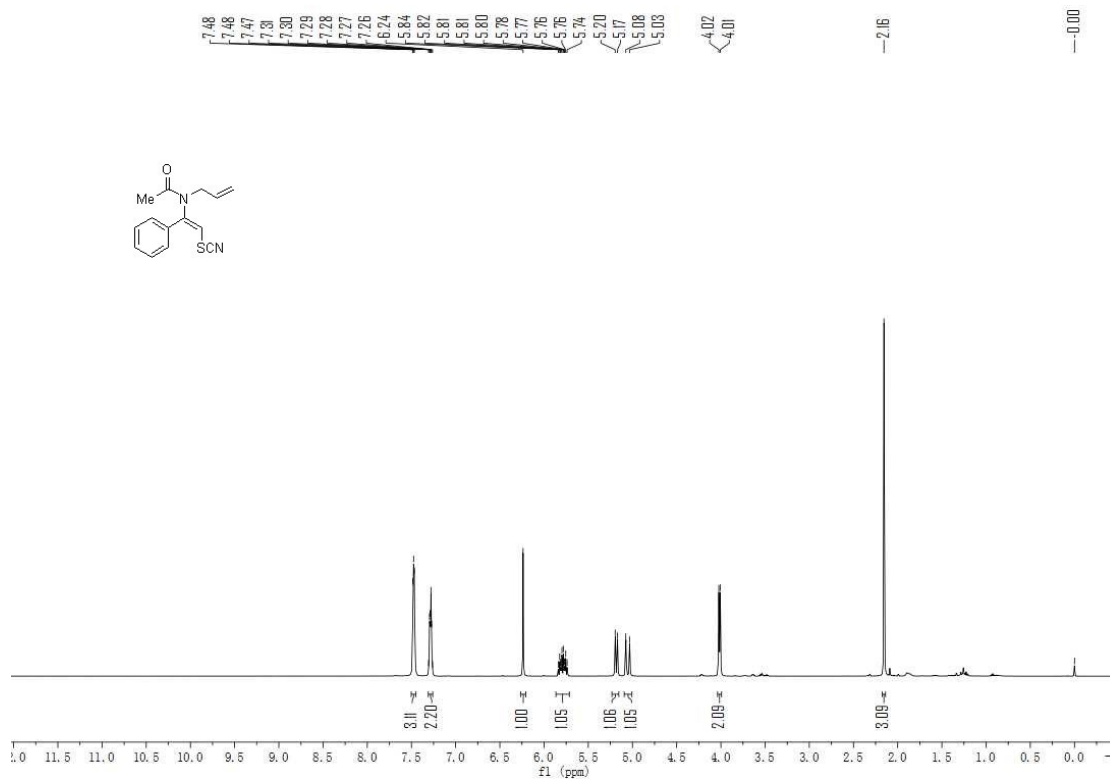
¹H NMR spectrum of 3ap



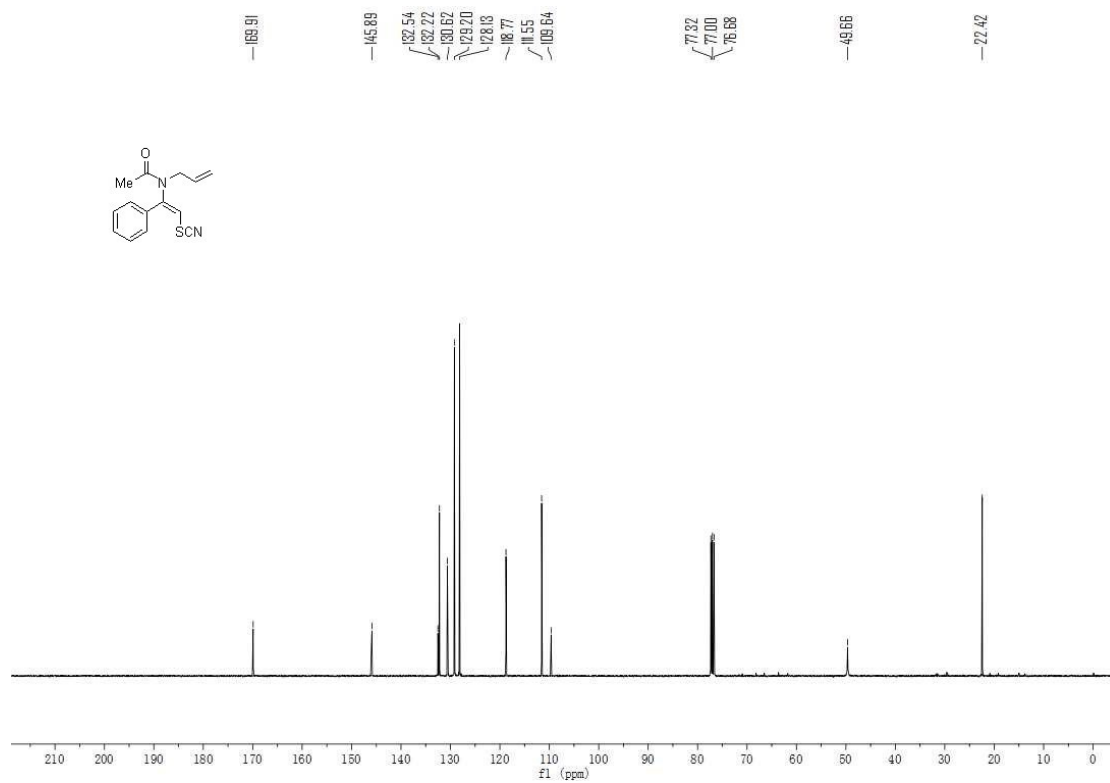
¹³C NMR spectrum of 3ap



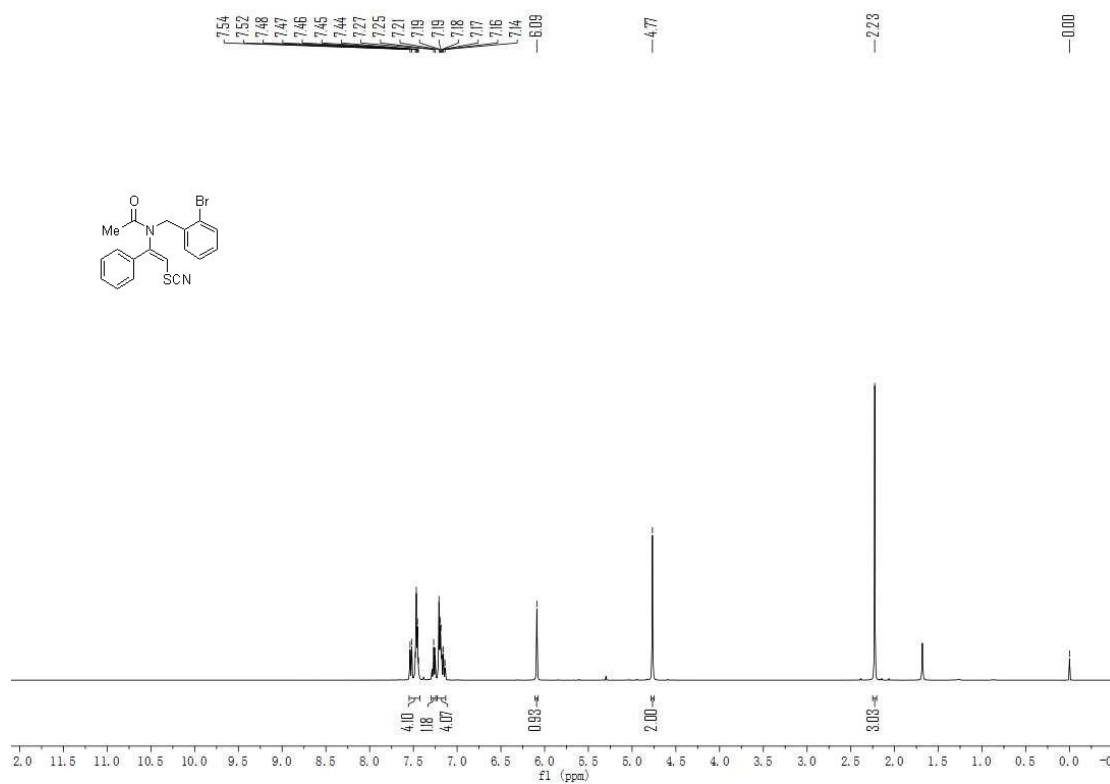
¹H NMR spectrum of 3a



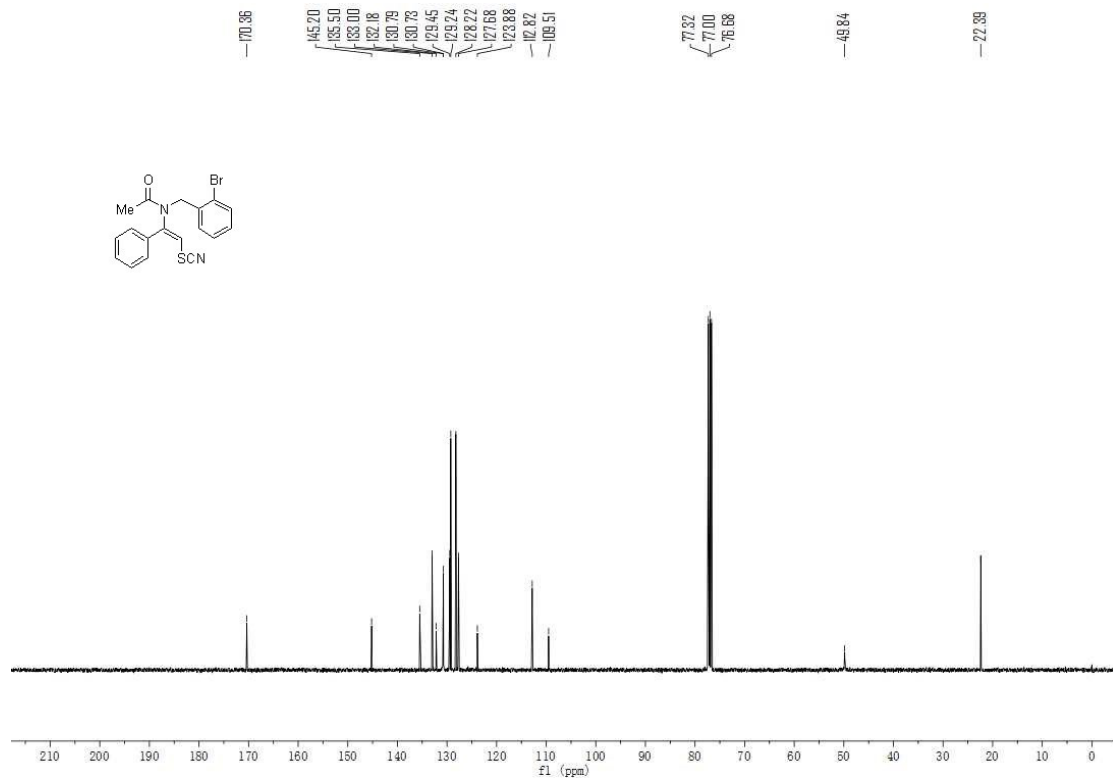
¹³C NMR spectrum of 3a



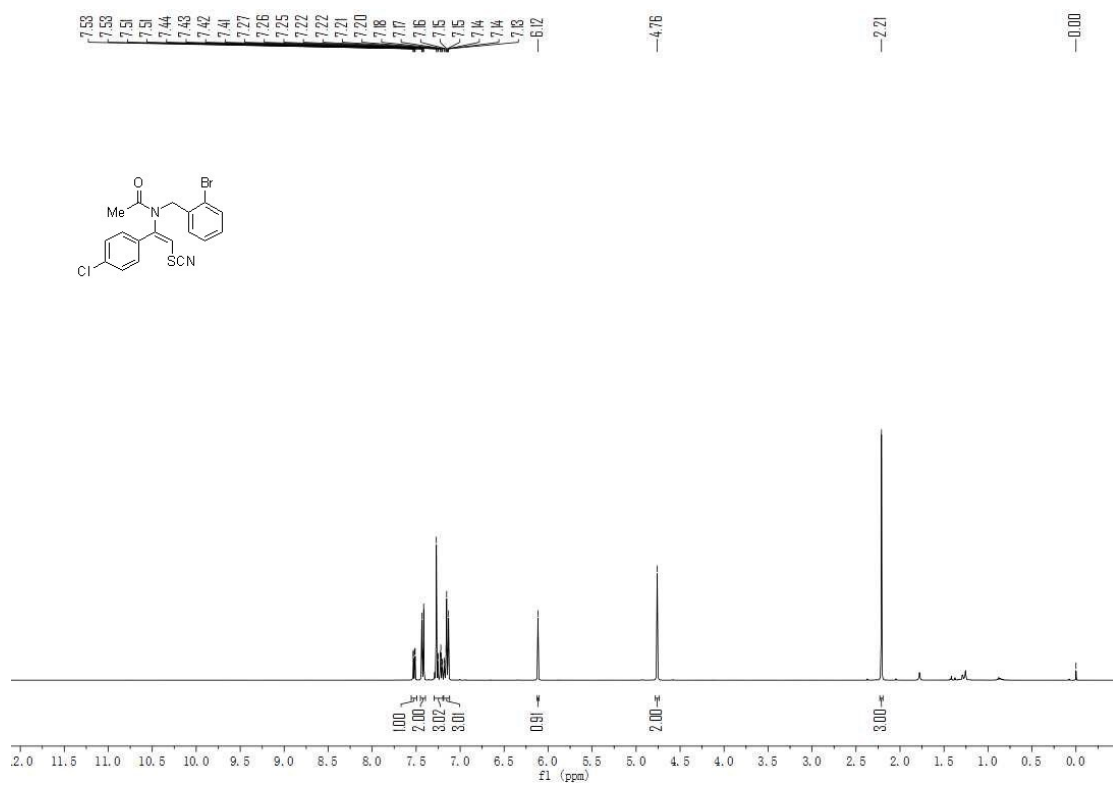
¹H NMR spectrum of 3ar



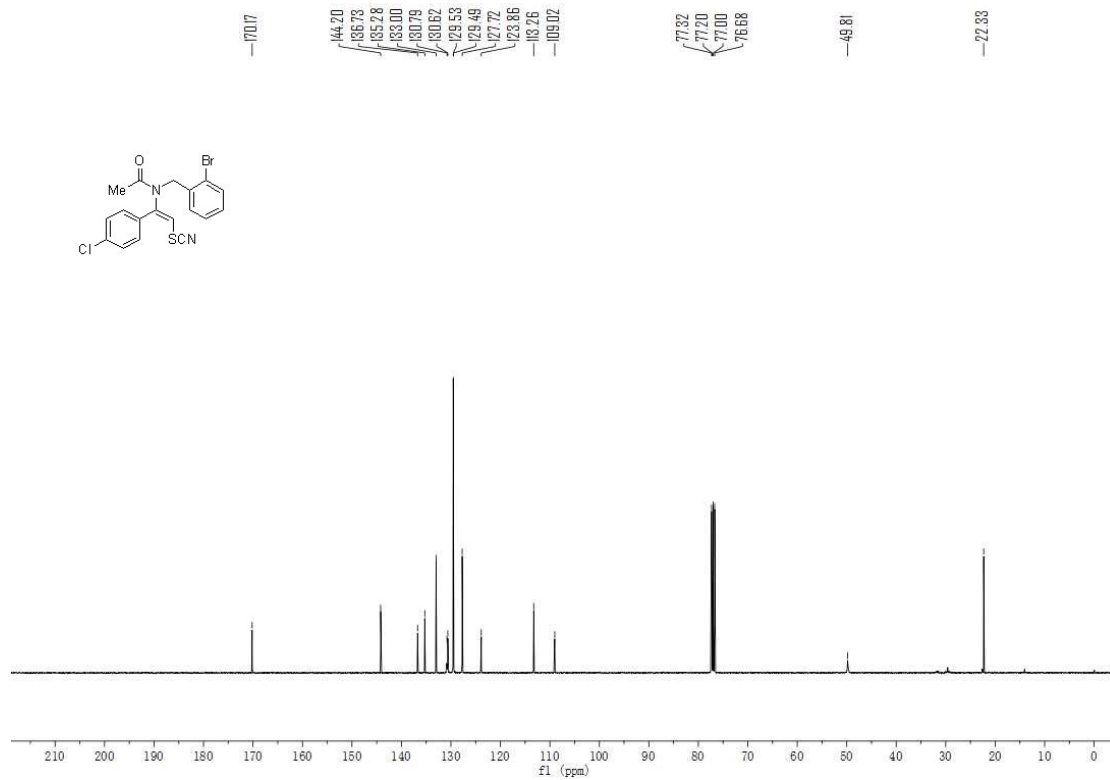
¹³C NMR spectrum of 3ar



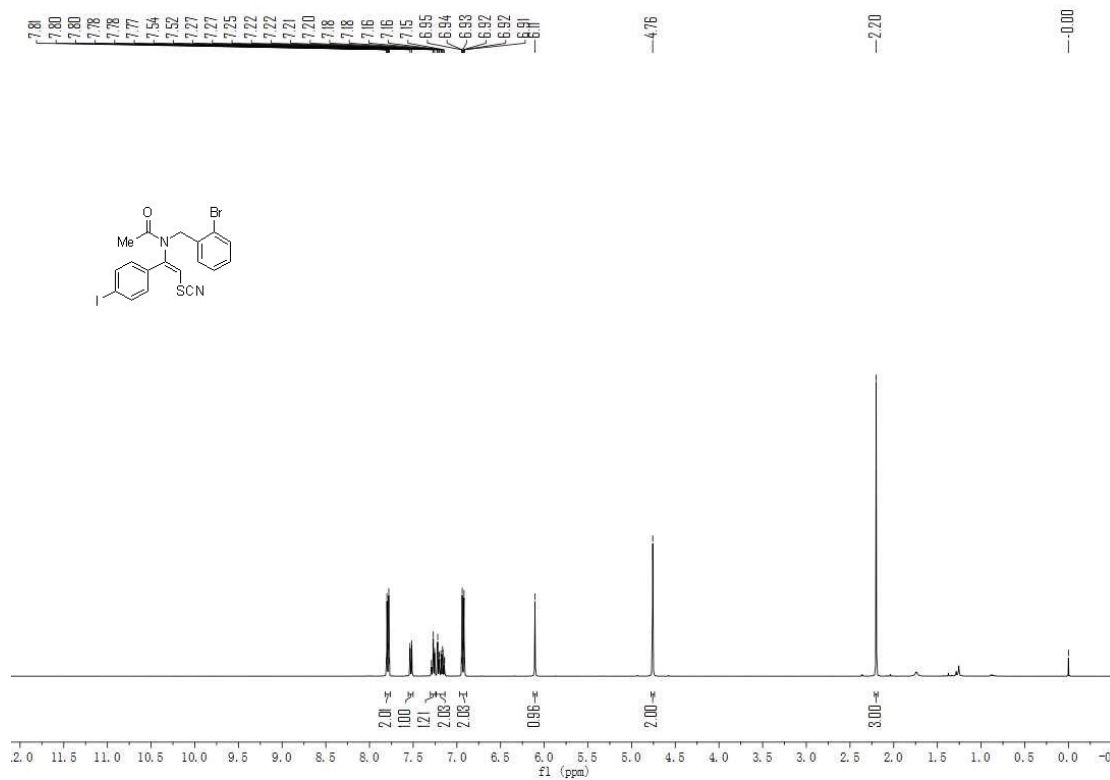
¹H NMR spectrum of 3as



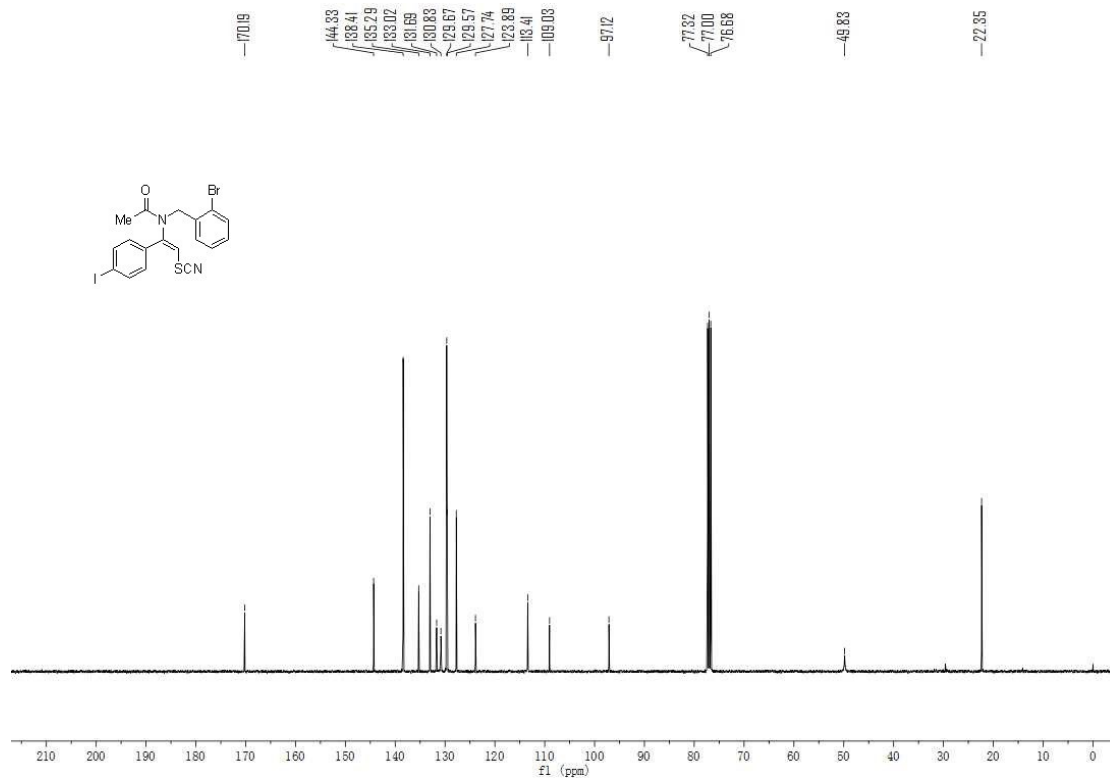
¹³C NMR spectrum of 3as



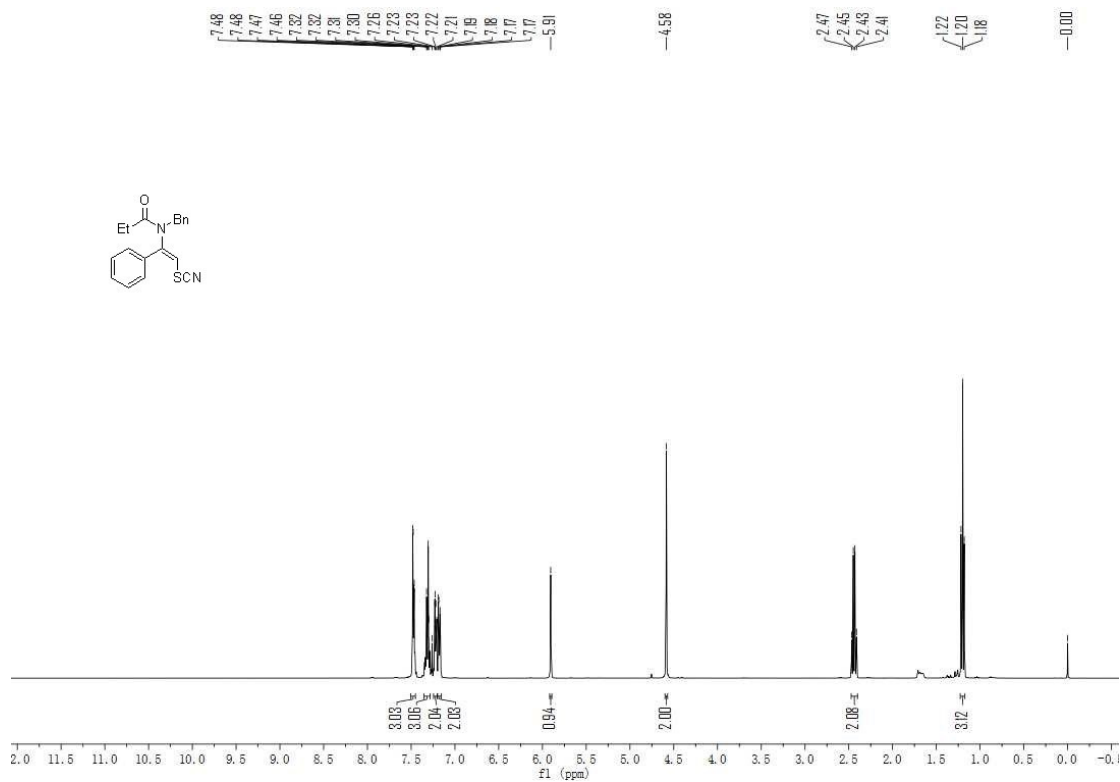
¹H NMR spectrum of 3at



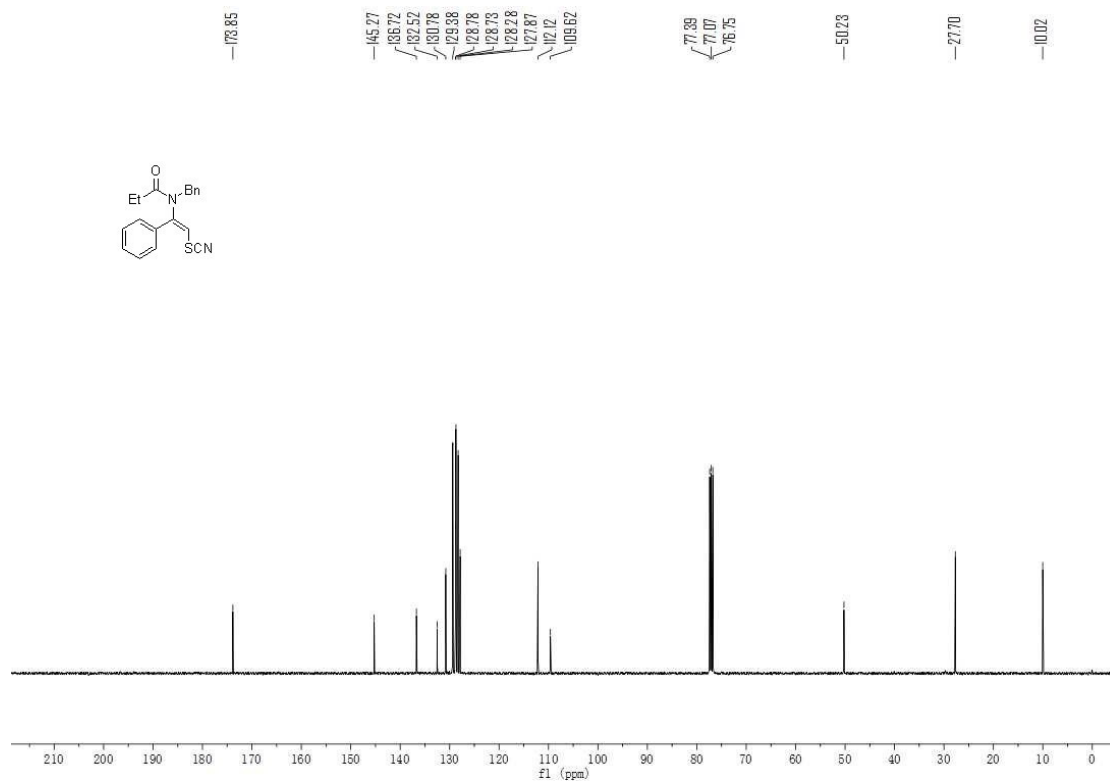
¹³C NMR spectrum of 3at



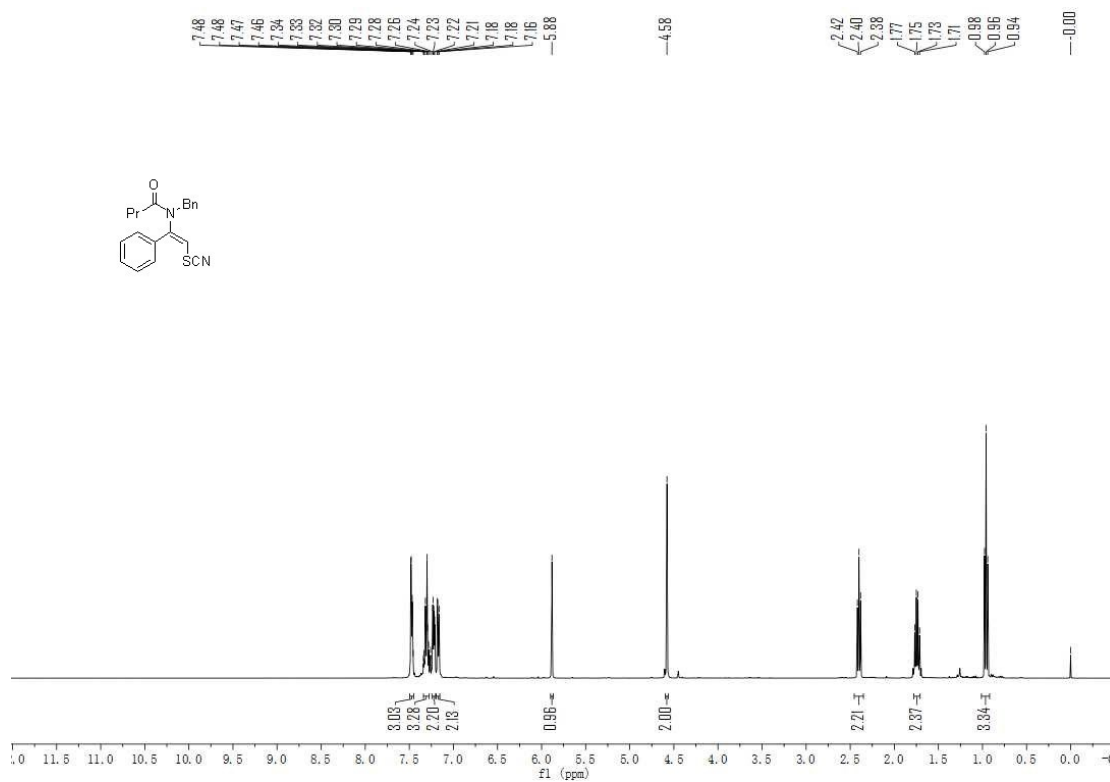
¹H NMR spectrum of 3au



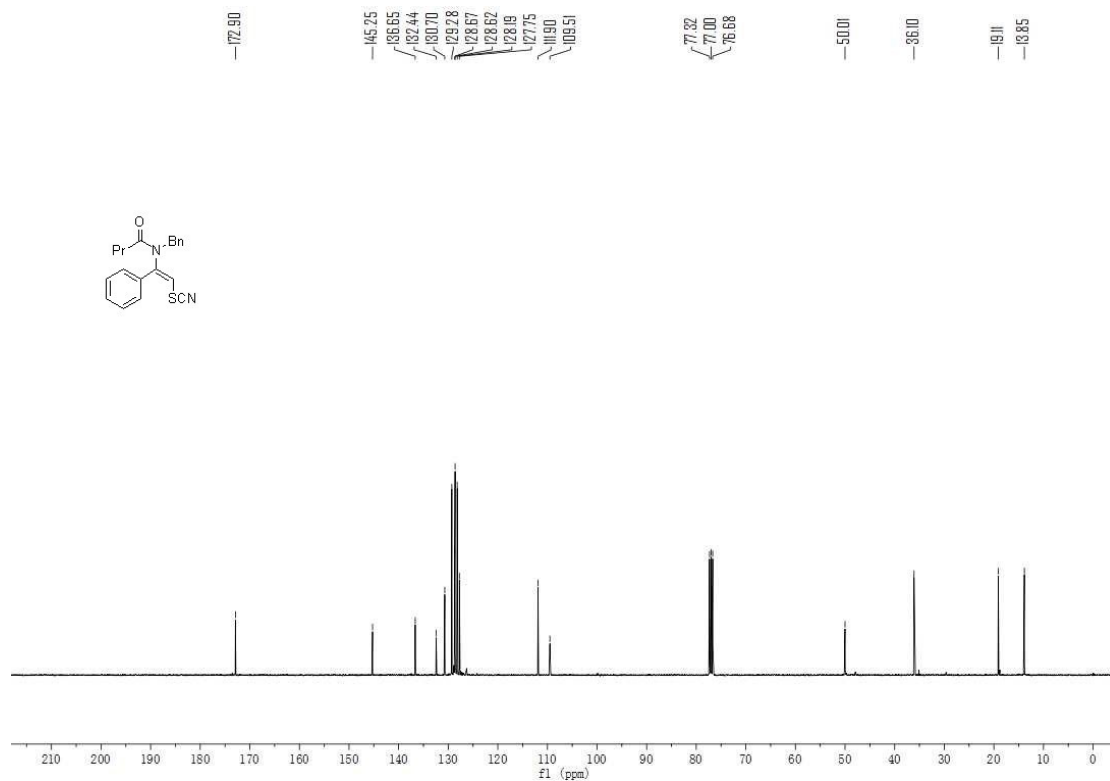
¹³C NMR spectrum of 3au



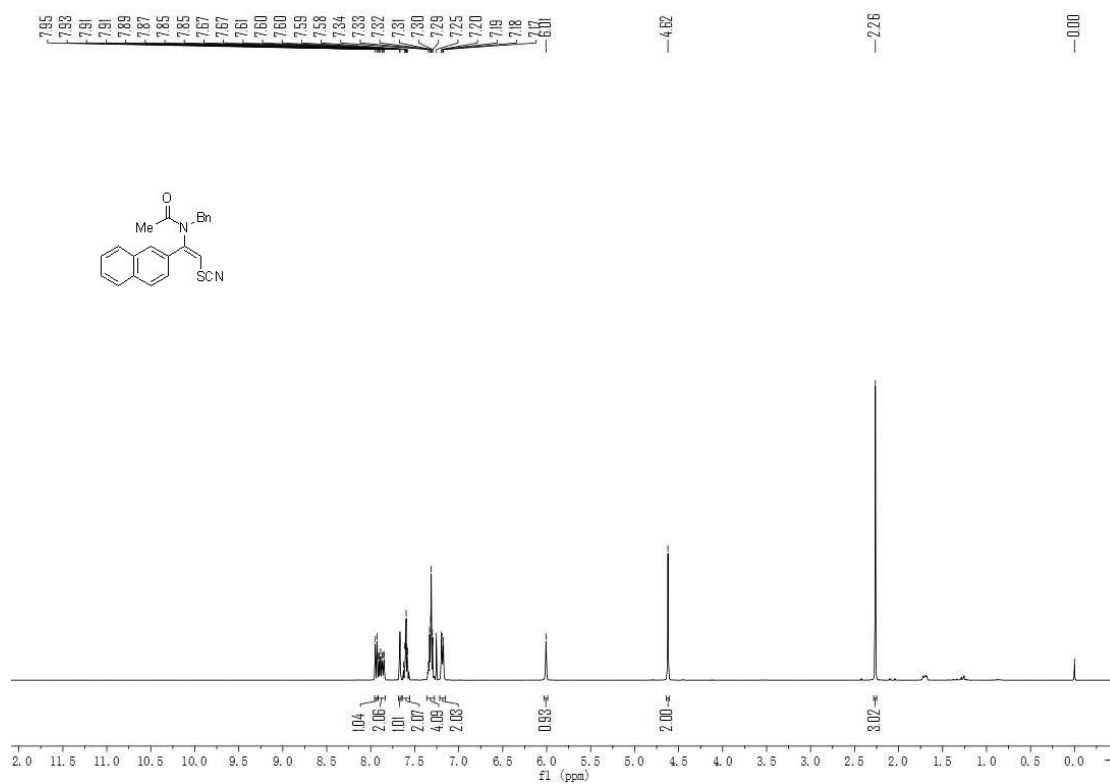
¹H NMR spectrum of 3av



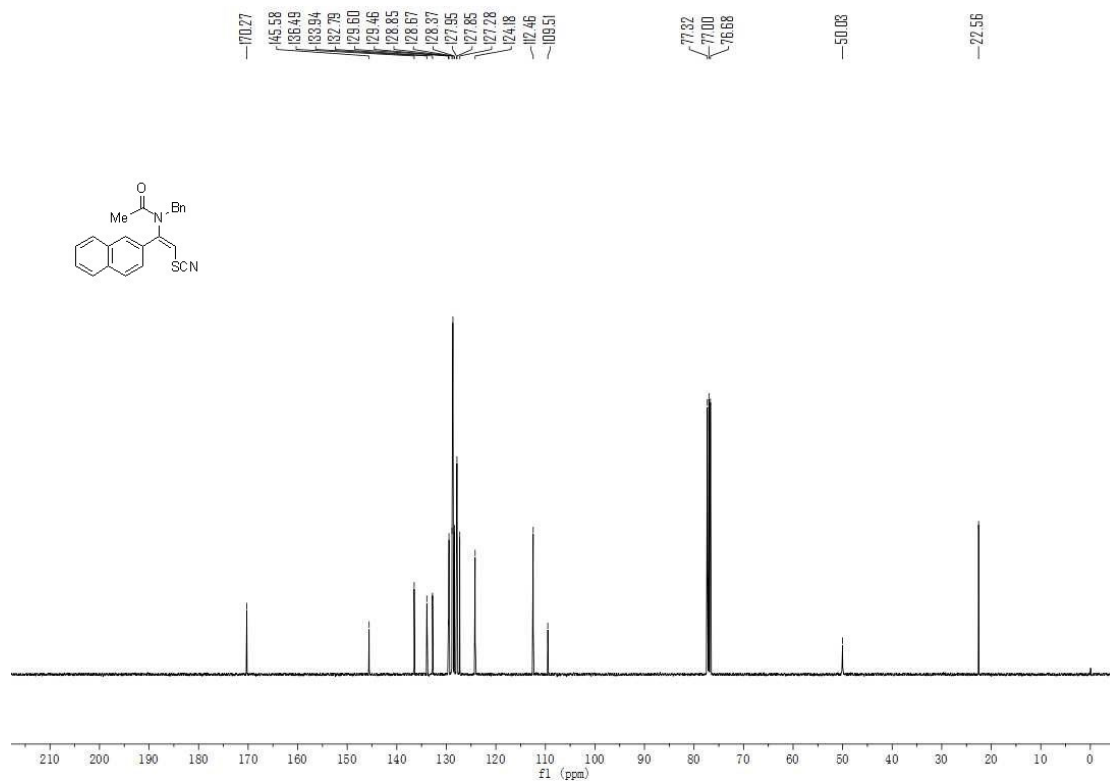
¹³C NMR spectrum of 3av



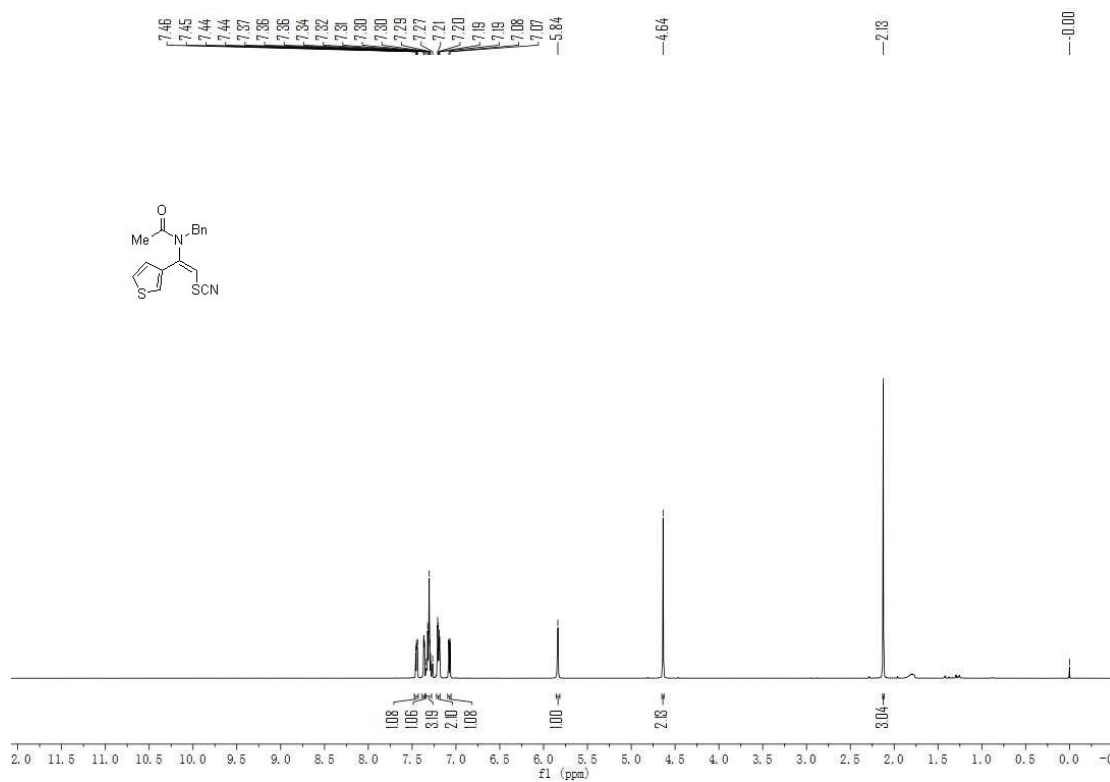
¹H NMR spectrum of 3aw



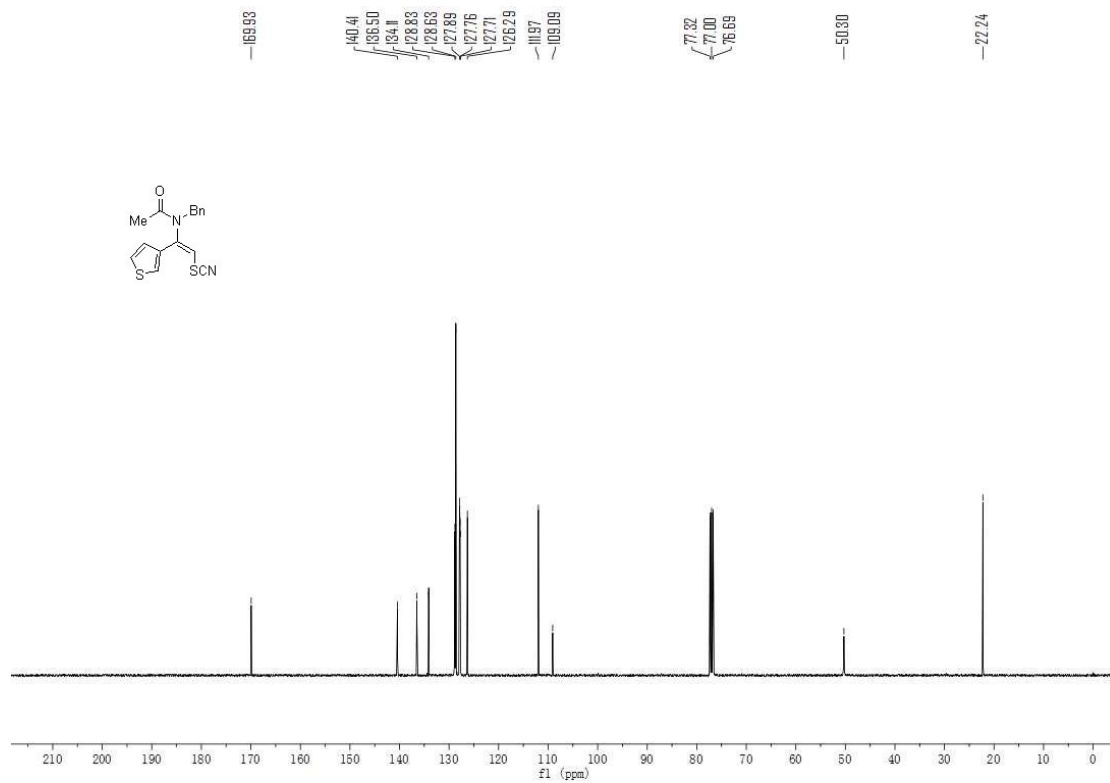
¹³C NMR spectrum of 3aw



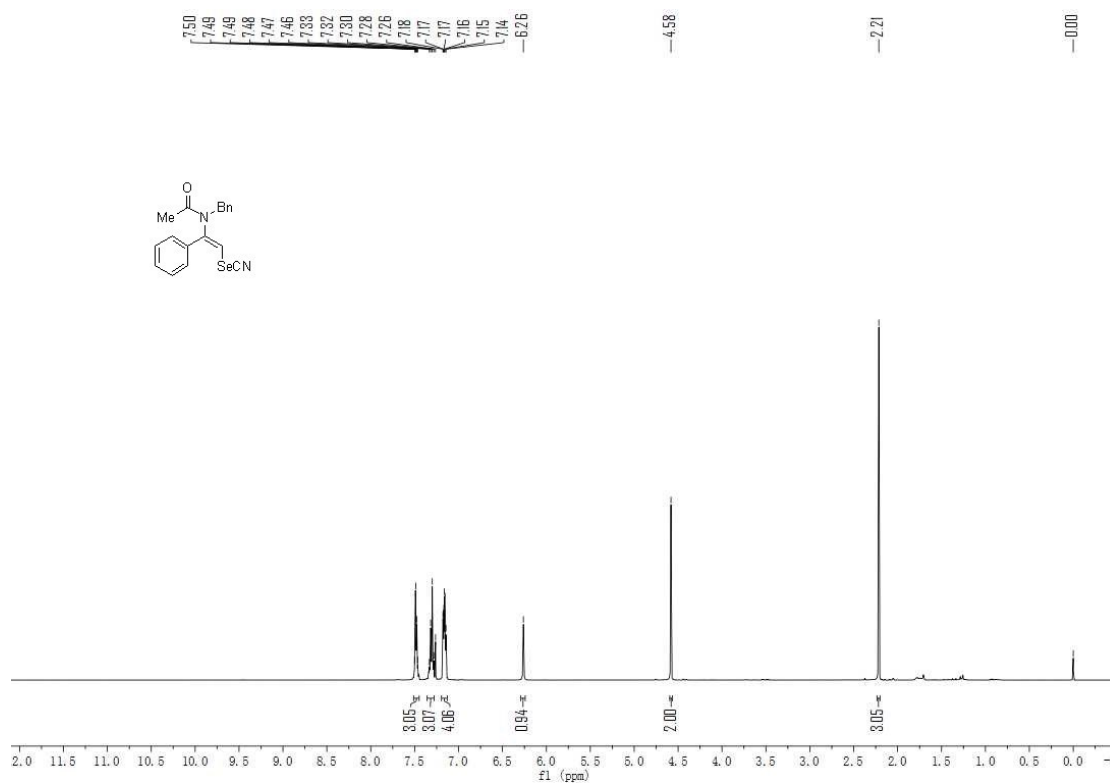
¹H NMR spectrum of 3ax



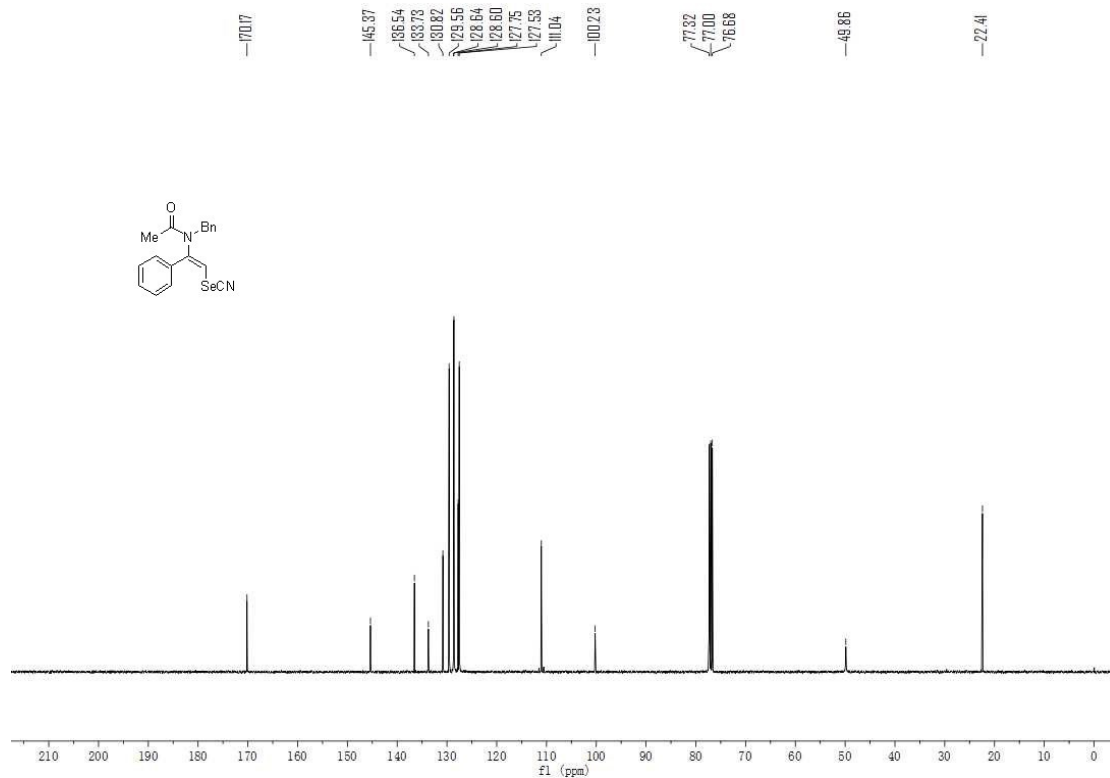
¹³C NMR spectrum of 3ax



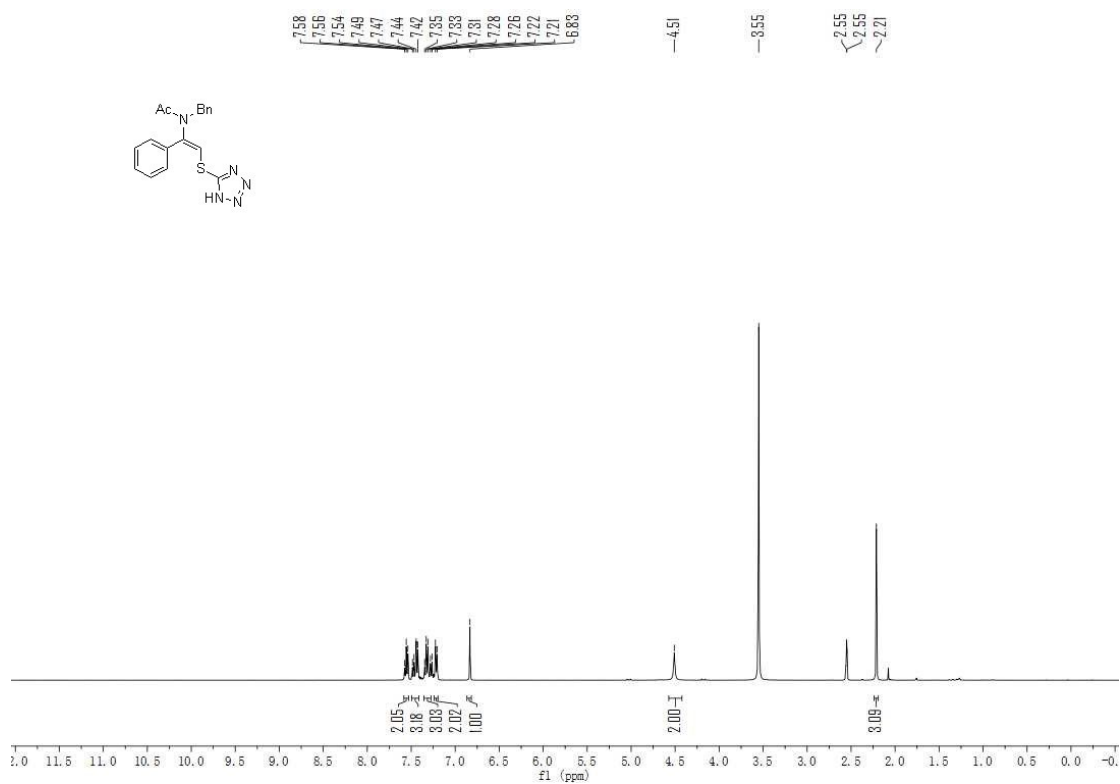
¹H NMR spectrum of 3ay



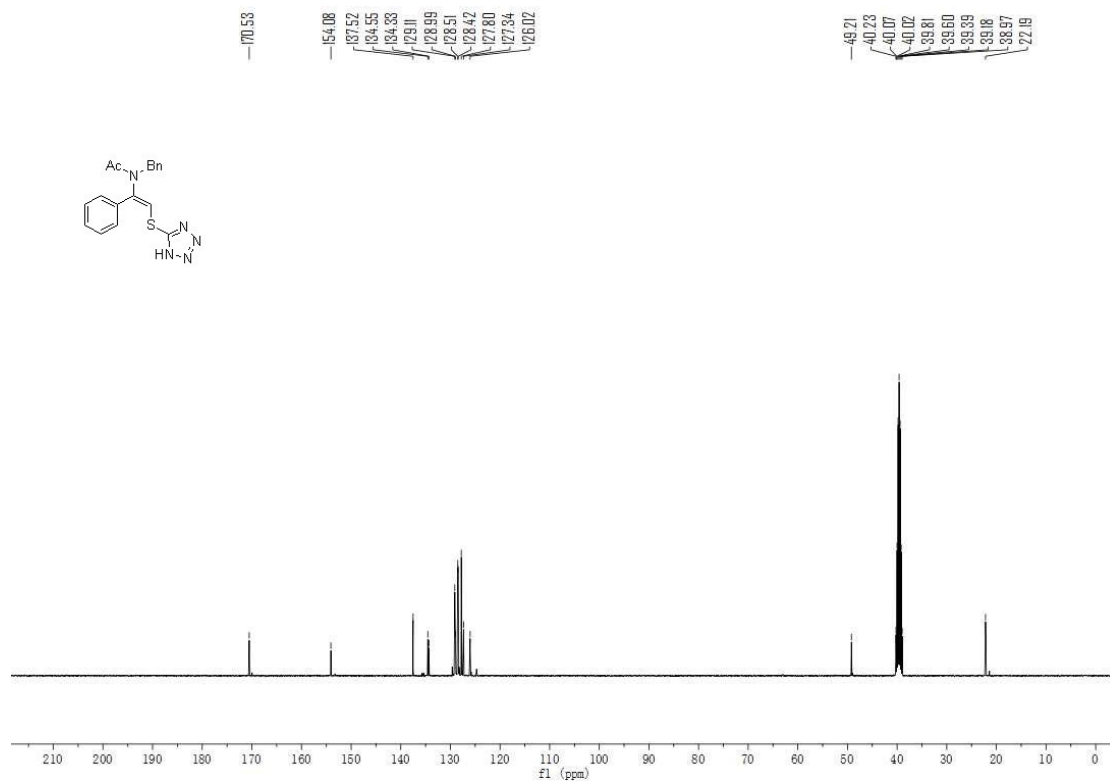
¹³C NMR spectrum of 3ay



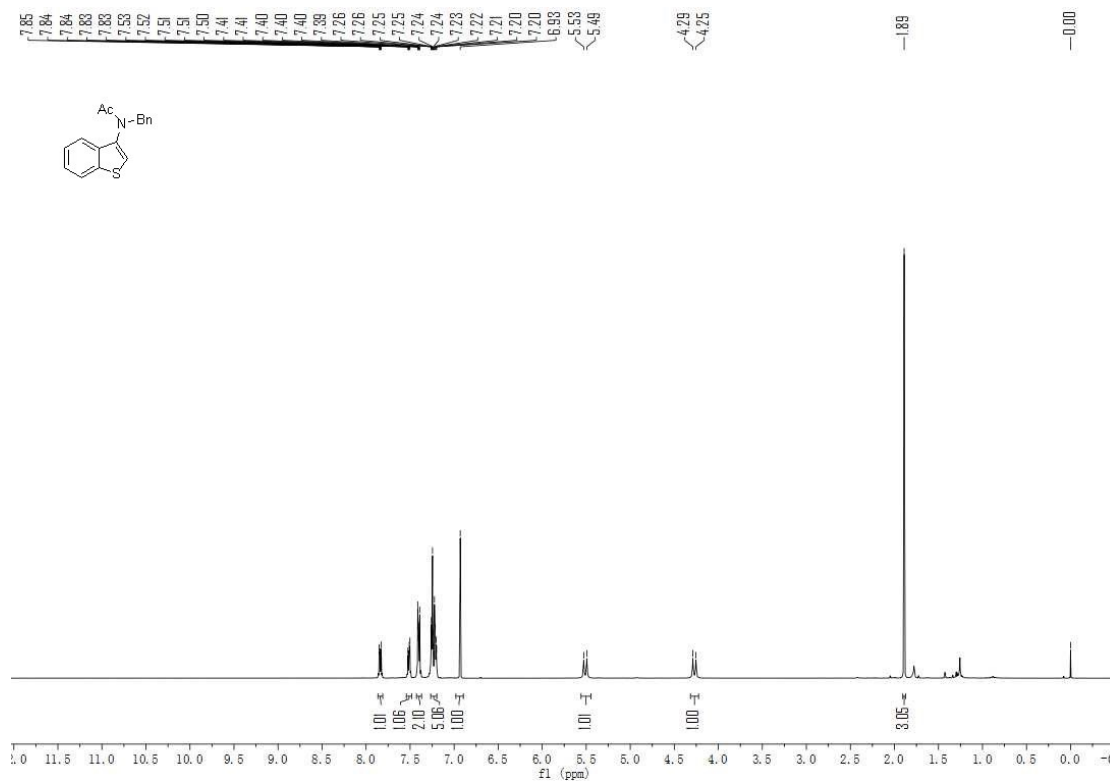
¹H NMR spectrum of 4



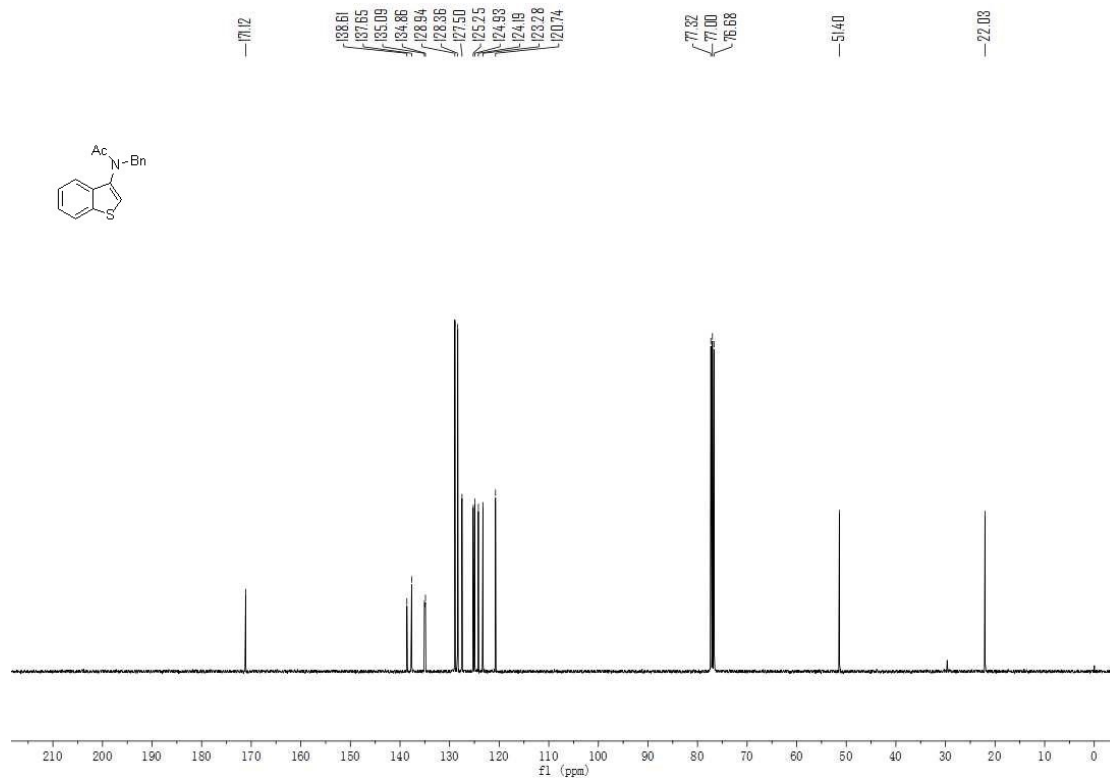
¹³C NMR spectrum of 4



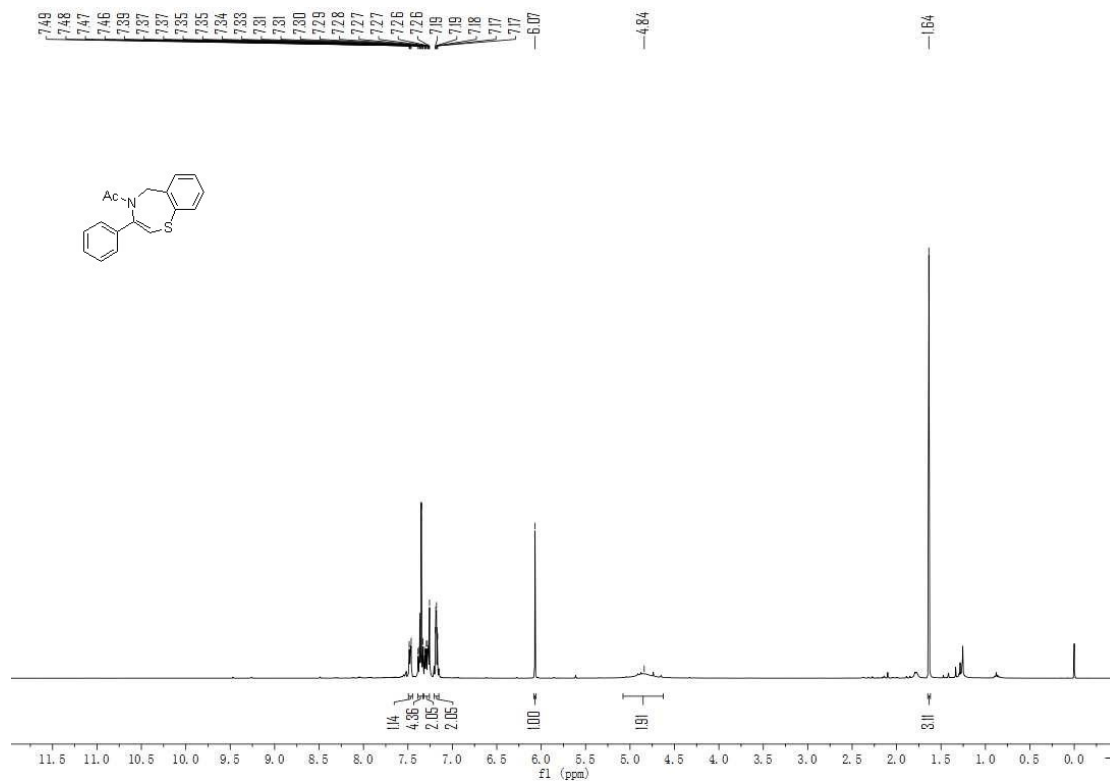
¹H NMR spectrum of 5



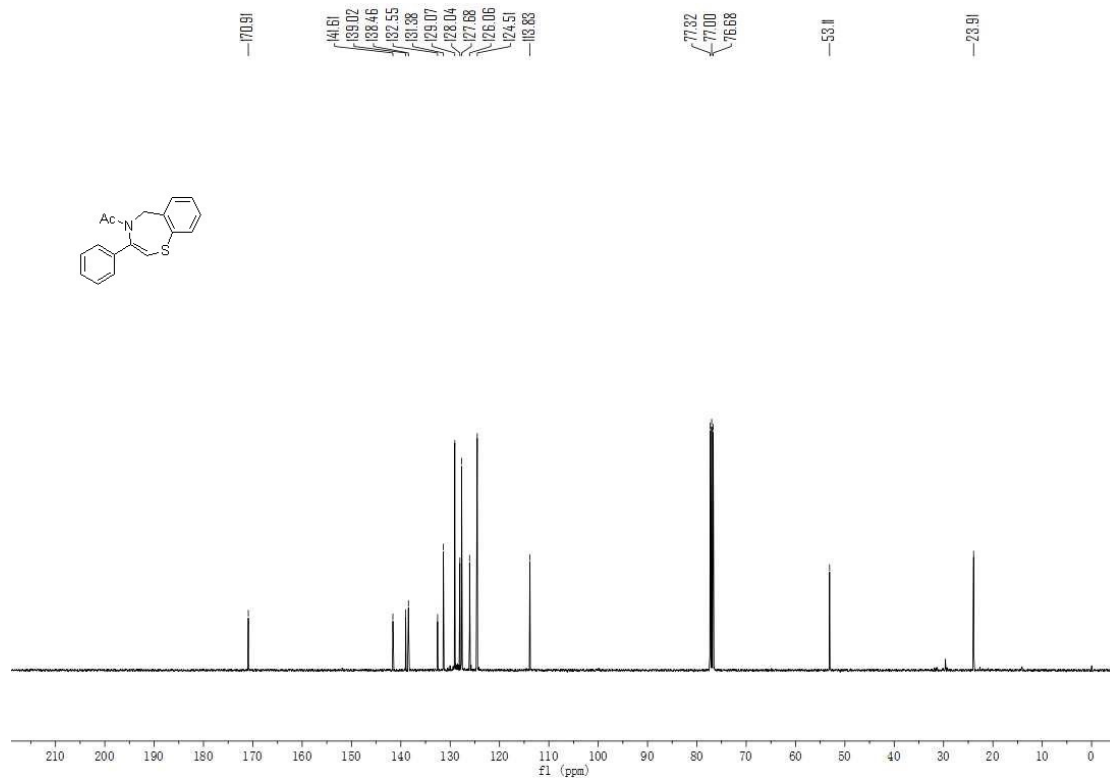
¹³C NMR spectrum of 5



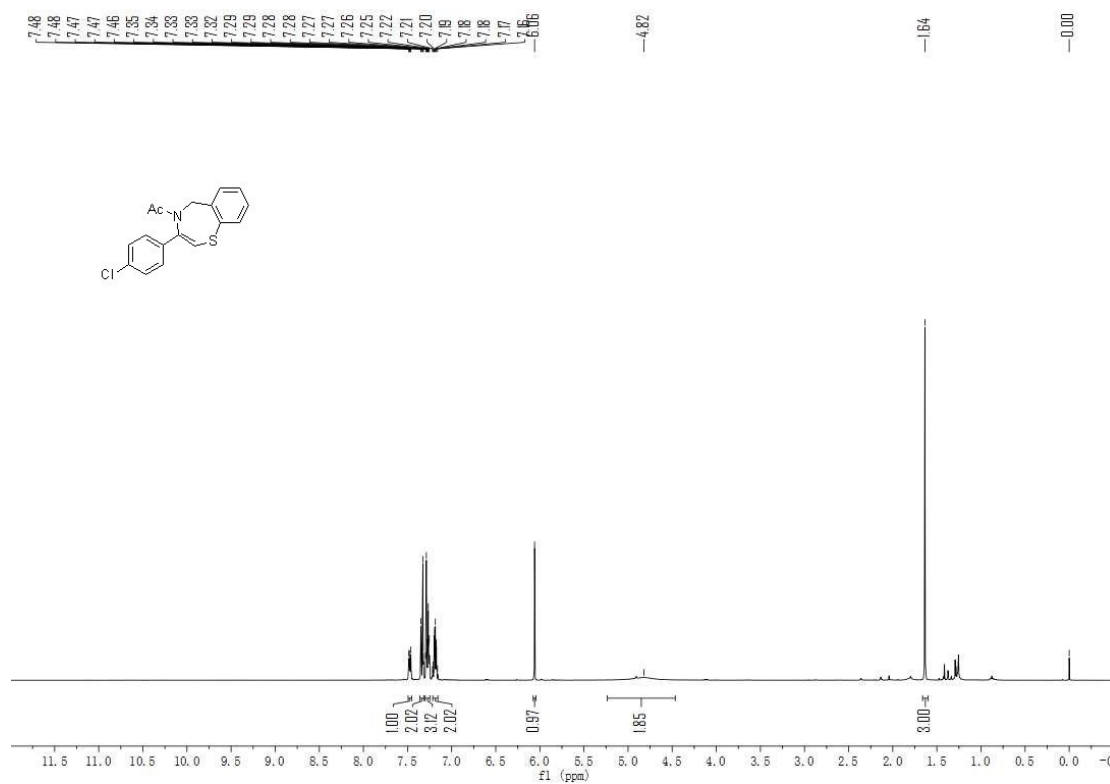
¹H NMR spectrum of 6



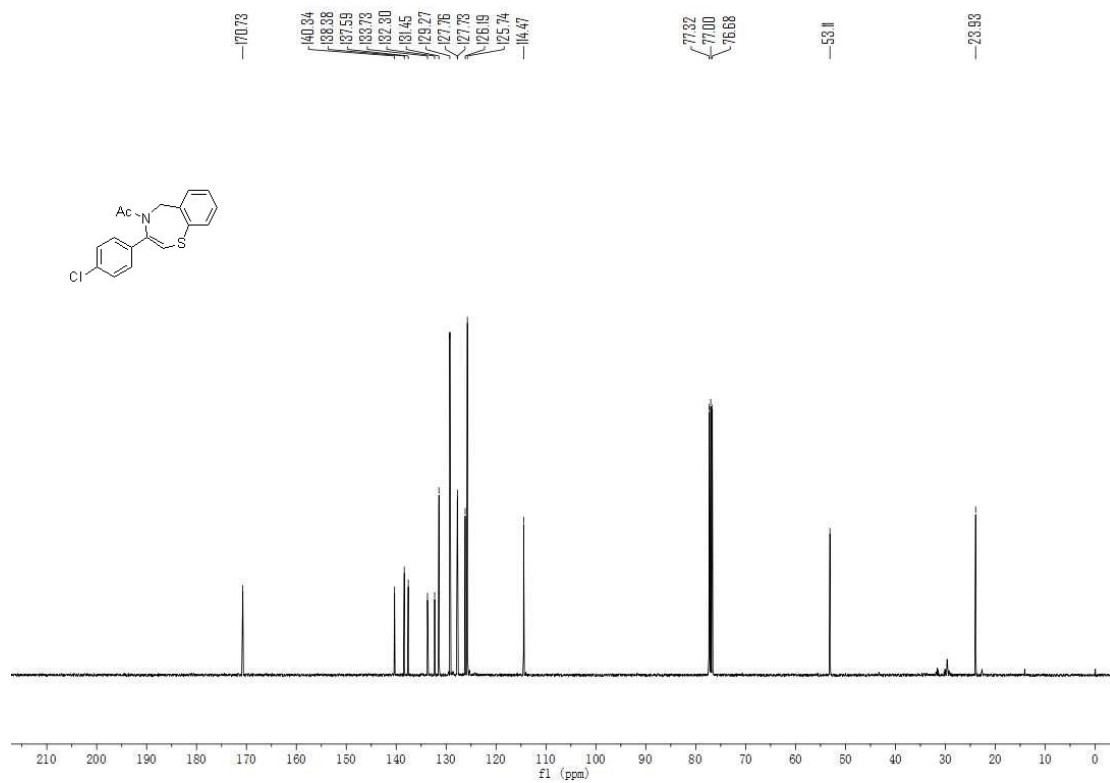
¹³C NMR spectrum of 6



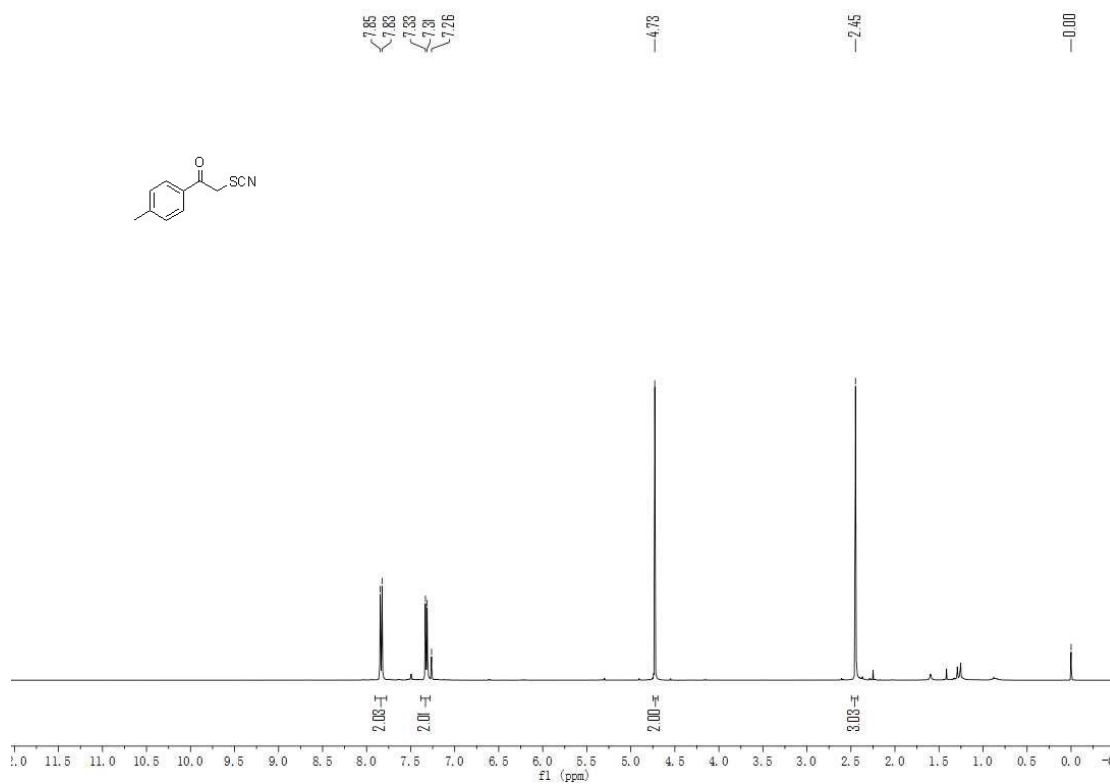
¹H NMR spectrum of 7



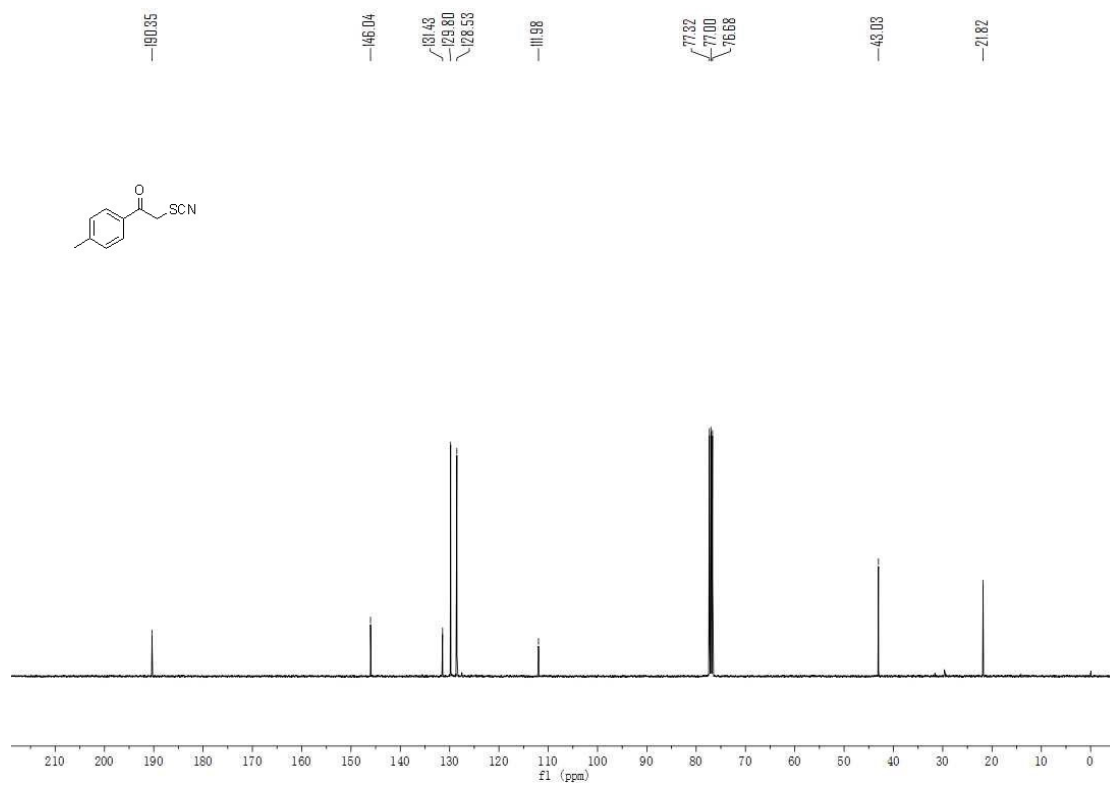
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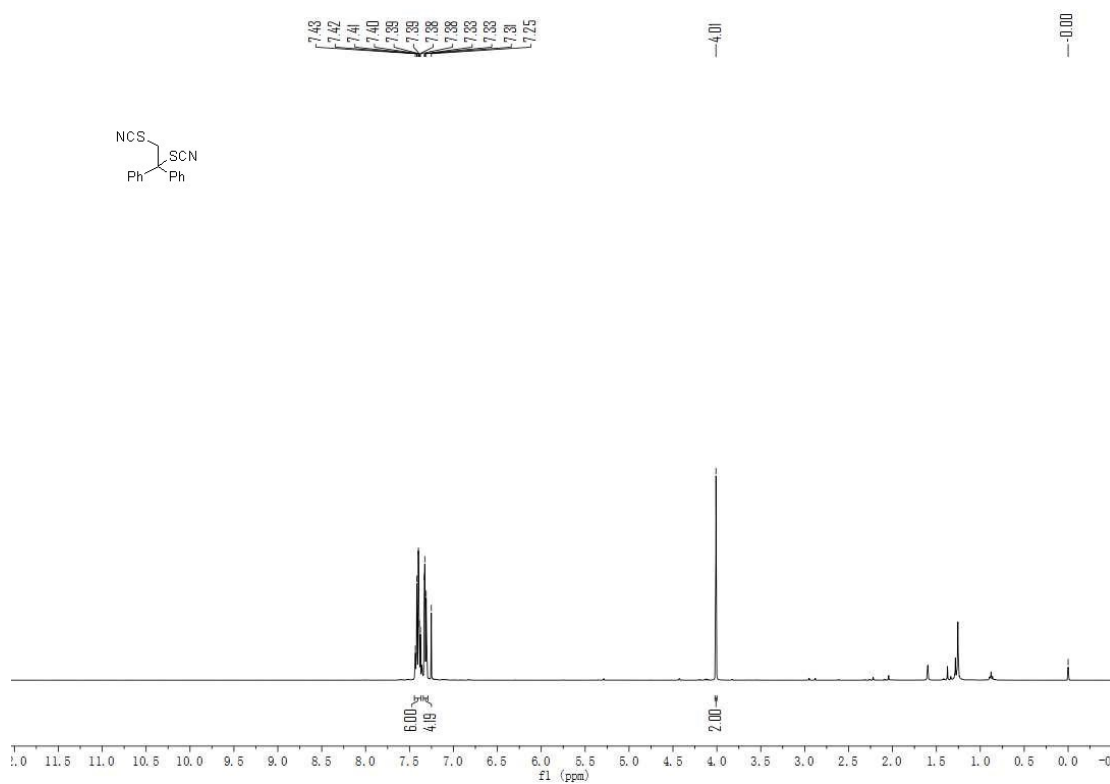
¹H NMR spectrum of 9



¹³C NMR spectrum of 9



¹H NMR spectrum of 10



¹³C NMR spectrum of 10

