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Supplementary Information for

Silver-Catalyzed Radical Ring-Opening Reaction of Cyclopropanols with Sulfonyl Oxime Ethers

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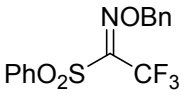
List

Structures of Starting Materials 1a-e



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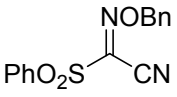

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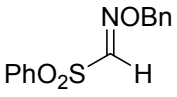

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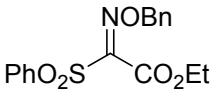

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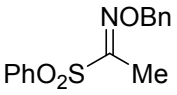

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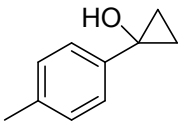
Structures of Starting Materials 2a-o



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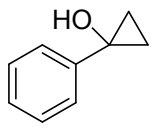

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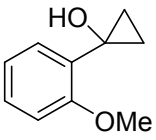

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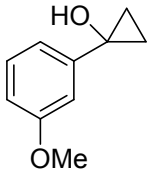

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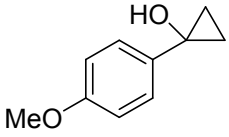

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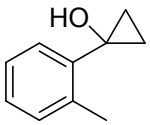

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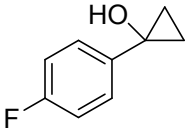

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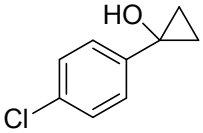

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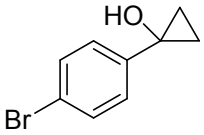

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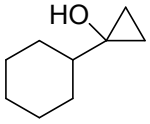

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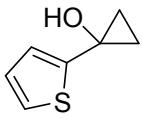

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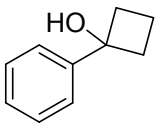

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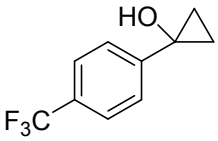

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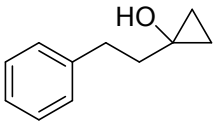

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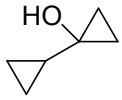

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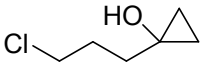

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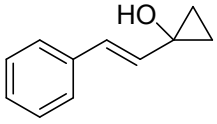

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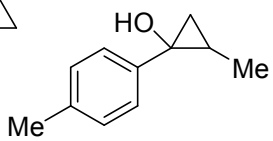

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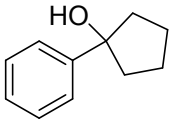


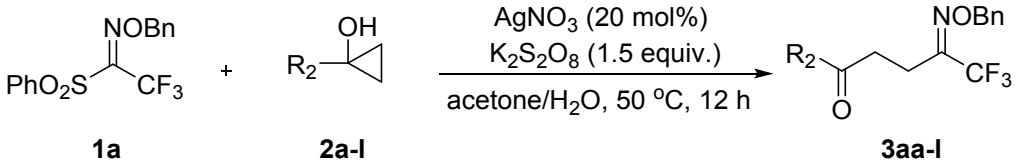
2s

2. 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 sulfonyl oxime ethers (**1a-e**)[1] and cyclopropanols (**2a-o**)[2] 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.

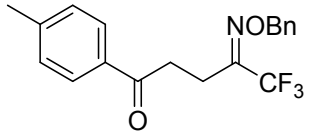
3. Preparation and characterizations of compounds 3aa-i, 3aj-w

3.1 Preparation and characterizations of compounds 3aa-i



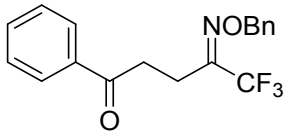
A mixture of CF_3-containing sulfonyl oxime ethers (**1a**) (0.3 mmol, 103 mg), cyclopropanols (**2a-l**) (0.45 mmol), $AgNO_3$ (0.06 mmol, 10.2 mg) and $K_2S_2O_8$ (0.45 mmol, 122 mg) in acetone:H_2O (1:1, 2 mL) was stirred at 50 °C for 12 h (monitored by TLC). After it was cooled down to room temperature, 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 preparative thin layer

chromatograpy (PTLC) (5% acetone in PE) to give the corresponding products.



3aa, 65%

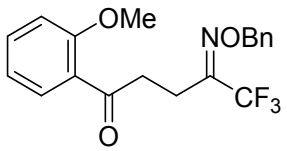
***E*-4-((benzyloxy)imino)-5,5,5-trifluoro-1-(*p*-tolyl)pentan-1-one (3aa)**. 68 mg (65%); yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.79 (d, J = 8.1 Hz, 2H), 7.34 (s, 5H), 7.22 (d, J = 8.0 Hz, 2H), 5.22 (s, 2H), 3.22-3.13 (m, 2H), 2.89 -2.80 (m, 2H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.1, 148.9 (q, J_{C-F} = 32 Hz), 144.2, 136.1, 133.7, 129.3, 128.6, 128.5, 128.4, 128.1, 120.8 (q, J_{C-F} = 272 Hz), 77.8, 33.8, 21.6, 19.7. **^{19}F NMR: (376 MHz, $CDCl_3$)** δ -69.3 (s, 3F); HRMS *m/z* (ESI) calcd. for $C_{19}H_{19}F_3NO_2$ $(M + H)^+$ 350.1362, found 350.1365.



3ab, 63%

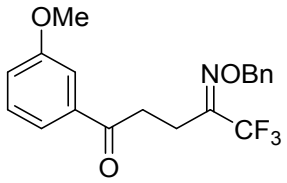
***E*-4-((benzyloxy)imino)-5,5,5-trifluoro-1-phenylpentan-1-one (3ab)**. 64 mg (63%); yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.88 (d, J = 7.6 Hz, 2H), 7.57-7.53 (m, 1H), 7.44-7.40 (m, 2H), 7.37-7.32 (m, 5H), 5.22 (s, 2H), 3.23-3.17 (m, 2H), 2.89-2.81 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.4, 148.8 (q, J_{C-F} = 32 Hz), 136.1 (2C), 133.3, 128.6, 128.5, 128.4, 128.3, 127.9, 120.8 (q, J_{C-F} = 272 Hz), 77.8, 33.9, 19.6. **^{19}F NMR: (376 MHz, $CDCl_3$)** δ -69.3 (s, 3F); HRMS *m/z* (ESI) calcd. for $C_{18}H_{17}F_3NO_2$ (M

+ H)$^+$ 336.1206, found 336.1203.



3ac, 46%

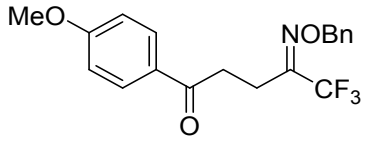
***E*-4-((benzyloxy)imino)-5,5,5-trifluoro-1-(2-methoxyphenyl)pentan-1-one** (**3ac**). 51 mg (46%); yellow oil; **^{1}H NMR (400MHz, CDCl$_3$)** δ 7.72 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.52-7.43 (m, 1H), 7.35-7.30 (m, 5H), 7.03-6.91 (m, 2H), 5.22 (s, 2H), 3.82 (s, 3H), 3.28-3.17 (m, 2H), 2.90-2.78 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 199.4, 158.8, 149.1 (q, $J_{C\text{-}F}$ = 31 Hz), 136.4, 133.9, 130.5, 128.5, 128.3, 128.2, 127.2, 120.9 (q, $J_{C\text{-}F}$ = 273 Hz), 120.7, 111.5, 77.6, 55.4, 39.0, 19.8. **^{19}F NMR: (376 MHz, CDCl$_3$)** δ -69.2 (s, 3F); HRMS *m/z* (ESI) calcd. for $C_{19}H_{19}F_3NO_3$ (M + H)$^+$ 366.1312, found 366.1315.



3ad, 53%

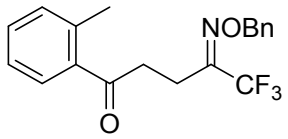
***E*-4-((benzyloxy)imino)-5,5,5-trifluoro-1-(3-methoxyphenyl)pentan-1-one** (**3ad**). 58 mg (53%); yellow oil; **^{1}H NMR (400MHz, CDCl$_3$)** δ 7.48-7.40 (m, 2H), 7.36-7.30 (m, 6H), 7.12-7.09 (m, 2.7 Hz, 1H), 5.22 (s, 2H), 3.84 (s, 3H), 3.23-3.15 (m, 2H), 2.89-2.80 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 197.3, 159.8, 148.8 (q, $J_{C\text{-}F}$ = 32 Hz), 137.5, 136.1, 129.6, 128.6, 128.5, 128.4, 120.8 (q, $J_{C\text{-}F}$ = 272 Hz), 120.6, 119.8, 112.2, 77.9, 55.4, 34.1,

19.6. **^{19}F NMR: (376 MHz, $CDCl_3$)** δ -69.3 (s, 3F); HRMS *m/z* (ESI) calcd. for $C_{19}H_{19}F_3NO_3$ $(M + H)^+$ 366.1312, found 366.1310.



3ae, 61%

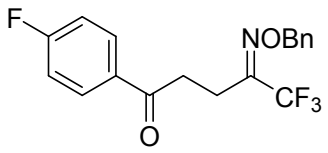
***E*-4-((benzyloxy)imino)-5,5,5-trifluoro-1-(4-methoxyphenyl)pentan-1-one** (**3ae**). 67 mg (61%); yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.90-7.84 (m, 2H), 7.37-7.33 (m, 5H), 6.91-6.85 (m, 2H), 5.22 (s, 2H), 3.86 (s, 3H), 3.18-3.11 (m, 2H), 2.87-2.80 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.0, 163.6, 149.0 (q, J_{C-F} = 32 Hz), 136.1, 130.3, 129.2, 128.5 (2C), 128.4, 120.8 (q, J_{C-F} = 273 Hz), 113.8, 77.9, 55.5, 33.6, 19.8. **^{19}F NMR: (376 MHz, $CDCl_3$)** δ -69.3 (s, 3F); HRMS *m/z* (ESI) calcd. for $C_{19}H_{19}F_3NO_3$ $(M + H)^+$ 366.1312, found 366.1313.



3af, 45%

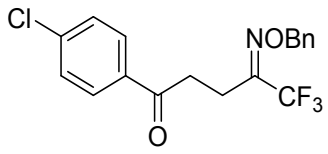
***E*-4-((benzyloxy)imino)-5,5,5-trifluoro-1-(*o*-tolyl)pentan-1-one** (**3af**). 47 mg (45%); yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.35 (s, 6H), 7.26-7.17 (m, 2H), 5.23 (s, 2H), 3.23-3.09 (m, 2H), 2.90 -2.77 (m, 2H), 2.48 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.9, 148.7 (q, J_{C-F} = 32 Hz), 138.6, 136.7, 136.2, 132.1, 131.7, 128.6, 128.5 (2C), 128.4, 125.7, 120.8 (q, J_{C-F} = 273 Hz), 77.9, 36.4, 21.5, 19.7. **^{19}F NMR: (376 MHz, $CDCl_3$)** δ -69.3 (s, 3F); HRMS *m/z* (ESI) calcd. for

$C_{19}H_{19}F_3NO_2$ $(M + H)^+$ 350.1362, found 350.1364.



3ag, 51%

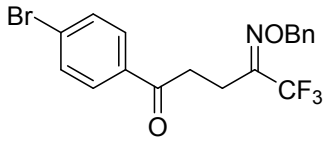
***E*-4-((benzyloxy)imino)-5,5,5-trifluoro-1-(4-fluorophenyl)pentan-1-one** (**3ag**). 54 mg (51%); yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.91 (dd, J = 8.7, 5.4 Hz, 2H), 7.36-73.4 (m, 5H), 7.10-7.06 (m, 2H), 5.23 (s, 2H), 3.20-3.13 (m, 2H), 2.89-2.80 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.9, 165.8 (d, J_{C-F} = 254 Hz), 148.7 (q, J_{C-F} = 32 Hz), 136.1, 132.6 (d, J_{C-F} = 3 Hz), 130.7, 130.6, 128.6, 128.5, 120.8 (q, J_{C-F} = 273 Hz), 115.8 (d, J_{C-F} = 21 Hz), 78.0, 33.9, 19.6. **^{19}F NMR: (376 MHz, $CDCl_3$)** δ -69.4 (s, 3F), -104.7(tt, J = 8.4, 5.5 Hz, 1F); HRMS *m/z* (ESI) calcd. for $C_{18}H_{16}F_4NO_2$ $(M + H)^+$ 354.1112, found 354.1115.



3ah, 54%

***E*-4-((benzyloxy)imino)-1-(4-chlorophenyl)-5,5,5-trifluoropentan-1-one** (**3ah**). 60 mg (54%); yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.81 (d, J = 8.5 Hz, 2H), 7.41-7.31 (m, 7H), 5.22 (s, 2H), 3.20-3.12 (m, 2H), 2.87-2.80 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.2, 148.6 (q, J_{C-F} = 32 Hz), 139.8, 136.0, 134.4, 129.4, 129.0, 128.6 (2C), 128.5, 120.8 (q, J_{C-F} = 273 Hz), 78.0, 34.0, 19.6. **^{19}F NMR: (376 MHz, $CDCl_3$)** δ -69.3 (s,

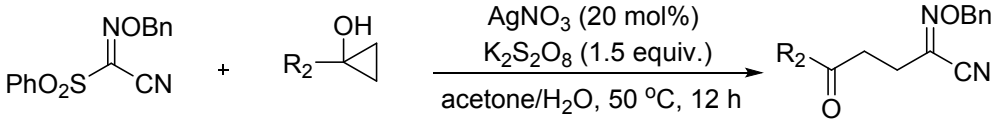
3F); HRMS *m/z* (ESI) calcd. for $C_{18}H_{16}ClF_3NO_2$ $(M + H)^+$ 370.0816, found 370.0815.



3ai, 53%

***E*-4-((benzyloxy)imino)-1-(4-bromophenyl)-5,5,5-trifluoropentan-1-one** (**3ai**). 66 mg (53%); yellow oil; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.37-7.32 (m, 5H), 5.22 (s, 2H), 3.19-3.12 (m, 2H), 2.87-2.80 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.4, 148.6 (q, J_{C-F} = 32 Hz), 136.0, 134.8, 131.9, 129.5, 128.6 (2C), 128.5, 128.4, 120.8 (q, J_{C-F} = 273 Hz), 78.0, 33.9, 19.5. **^{19}F NMR: (376 MHz, $CDCl_3$)** δ -69.3 (s, 3F); HRMS *m/z* (ESI) calcd. for $C_{18}H_{16}BrF_3NO_2$ $(M + H)^+$ 414.0311, found 414.0313.

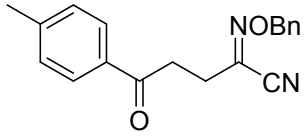
3.2 Preparation and characterizations of compounds 3aj-w



1b **2a-j, 2m-o** **3aj-w**

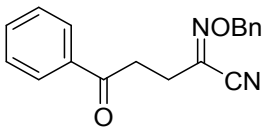
A mixture of CN-containing sulfonyl oxime ethers (**1b**) (0.3 mmol, 90 mg), cyclopropanols (**2a-j, 2m-o**) (0.45 mmol), $AgNO_3$ (0.06 mmol, 10.2 mg) and $K_2S_2O_8$ (0.45 mmol, 122 mg) in acetone:H_2O (1:1, 2 mL) was stirred at 50 °C for 12 h (monitored by TLC). After it was cooled down to room temperature, 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 preparative thin layer chromatograpy (PTLC) (5% EA in PE) to give the corresponding products.



3aj, 71%

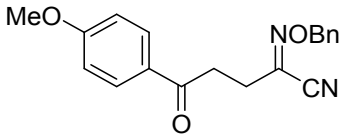
***N*-(benzyloxy)-4-oxo-4-(*p*-tolyl)butanimidoyl cyanide** (**3aj**). 65 mg (71%). 1.9:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.85-7.82 (m, 2H), 7.40-7.21 (m, 7H), 5.26 (s, $2H_{minor}$), 5.19 (s, $2H_{major}$), 3.28-3.24 (m, 2H), 2.89-2.86 (m, 2H), 2.41 (s, $3H_{major}$), 2.40 (s, $3H_{minor}$). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.5, 196.4, 144.4, 144.3, 138.3, 135.8, 135.6, 133.7, 133.5, 131.2, 129.3, 129.2, 128.6, 128.5 (2C), 128.4 (2C), 128.3, 128.1, 114.3, 110.3, 78.5, 77.8, 34.0, 33.7, 26.5, 22.7, 21.6. HRMS *m/z* (ESI) calcd. For $C_{19}H_{19}N_2O_2$ $(M + H)^+$ 307.1441, found 307.1443.



3ak, 68%

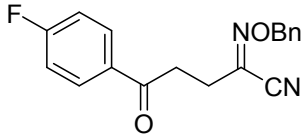
***N*-(benzyloxy)-4-oxo-4-phenylbutanimidoyl cyanide** (**3ak**). 60 mg (68%). 1.8:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.93-7.91 (m, 2H), 7.59-7.55 (m, 1H), 7.47-7.42 (m, 2H), 7.34-7.29 (m, 5H), 5.25 (s, $2H_{minor}$), 5.17 (s, $2H_{major}$), 3.29-3.25 (m, 2H), 2.88-2.85 (m,

2H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.9, 196.7, 138.2, 136.1, 135.9, 135.8, 135.6, 133.5, 133.4, 131.1, 128.6, 128.5(3C), 128.4, 128.3 (2C), 127.9, 114.3, 110.2, 78.5, 77.8, 34.1, 33.9, 26.4, 22.6. HRMS *m/z* (ESI) calcd. For $C_{18}H_{17}N_2O_2$ $(M + H)^+$ 293.1285, found 293.1283.



3al, 65%

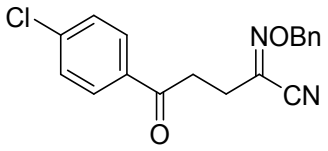
***N*-(benzyloxy)-4-(4-methoxyphenyl)-4-oxobutanimidoyl cyanide** (**3al**). 63 mg (65%). 1.9:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.96-7.89 (m, 2H), 7.41-7.27 (m, 5H), 6.96-6.90 (m, 2H), 5.27 (s, $2H_E$), 5.20 (s, $2H_Z$), 3.87 (s, $3H_{minor}$), 3.86 (s, $3H_{major}$) 3.27-3.23 (m, 2H), 2.90-2.86 (m, 2H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.4, 195.3, 163.7, 163.6, 138.4, 135.9, 135.7, 131.4, 130.3, 129.3, 129.1, 128.6 (3C), 128.5, 128.4, 128.3, 113.8, 113.7, 110.3, 78.5, 77.8, 55.5, 33.9, 33.5, 26.6, 22.8. HRMS *m/z* (ESI) calcd. For $C_{19}H_{19}N_2O_3$ $(M + H)^+$ 323.1390, found 323.1393.



3am, 55%

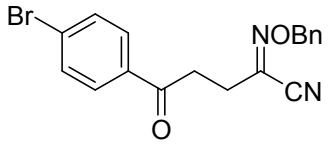
***N*-(benzyloxy)-4-(4-fluorophenyl)-4-oxobutanimidoyl cyanide** (**3am**). 51 mg (55%). 1.5:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.98-7.95 (m, 2H), 7.43-7.26 (m, 5H), 7.17-7.11 (m, 2H), 5.28

(s, $2H_{minor}$), 5.20 (s, $2H_{major}$), 3.29-3.25 (m, 2H), 2.92-2.87 (m, 2H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.3, 195.2, 167.2 (2C), 164.7, 164.6, 138.0, 135.9, 135.6, 132.7, 132.6, 132.5, 132.4, 131.1, 130.7 (2C), 130.6 (2C), 128.7, 128.6, 128.5, 128.4, 116.0, 115.9, 115.8, 115.7, 114.3, 110.3, 78.6, 77.9, 34.1, 33.9, 26.5, 22.6. HRMS *m/z* (ESI) calcd. For $C_{18}H_{16}FN_2O_2$ $(M + H)^+$ 311.1190, found 311.1193.



3an, 57%

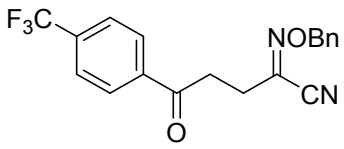
***N*-(benzyloxy)-4-(4-chlorophenyl)-4-oxobutanimidoyl cyanide (3an)**. 56 mg (57%). 2.3:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.88-7.86 (m, 2H), 7.45-7.40 (m, 2H), 7.39-7.27 (m, 5H), 5.27 (s, $2H_{minor}$), 5.19 (s, $2H_{major}$), 3.28-3.24 (m, 2H), 2.91-2.86 (m, 2H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.7, 195.6, 140.0, 139.9, 137.9, 135.8, 135.6, 134.5, 134.2, 131.0, 129.4, 129.0 (2C), 128.7, 128.6, 128.4 (3C), 114.3, 110.2, 78.6, 77.9, 34.1, 33.9, 26.4, 22.6. HRMS *m/z* (ESI) calcd. For $C_{18}H_{16}ClN_2O_2$ $(M + H)^+$ 327.0895, found 327.0893.



3ao, 51%

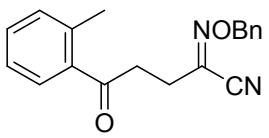
***N*-(benzyloxy)-4-(4-bromophenyl)-4-oxobutanimidoyl cyanide (3ao)**. 57 mg (51%). 2.3:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.63-7.55 (m, 2H), 7.41-7.25 (m, 5H),

5.26 (s, 2H$_{minor}$), 5.17 (s, 2H$_{major}$), 3.30-3.19 (m, 2H), 2.89-2.85 (m, 2H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.9, 195.7, 137.9, 135.8, 135.5, 134.8, 134.6, 131.9, 131.8, 130.9, 129.4, 128.6, 128.5(2C), 128.4, 128.3, 128.2, 114.2, 110.2, 78.5, 77.8, 34.0, 33.8, 26.3, 22.5. HRMS *m/z* (ESI) calcd. For $C_{18}H_{16}BrN_2O_2$ $(M + H)^+$ 371.0390, found 371.0392.



3ap, 49%

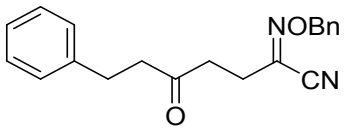
***N*-(benzyloxy)-4-oxo-4-(4-(trifluoromethyl)phenyl)butanimidoyl cyanide** (**3ap**). 53 mg (49%). 1.9:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 8.03-8.01 (m, 2H), 7.74-7.71 (m, 2H), 7.41-7.24 (m, 5H), 5.27 (s, 2H$_{minor}$), 5.18 (s, 2H$_{major}$), 3.34-3.29 (m, 2H), 2.93-2.89 (m, 2H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.0, 195.9, 138.8, 138.5, 137.8, 135.8, 135.6, 135.1, 134.9, 134.7, 134.5, 134.4, 134.3, 134.1, 130.8, 129.2, 128.9, 128.8, 128.7, 128.6, 128.4 (2C), 128.3 (2C), 125.8 (2C), 125.7 (3C), 114.2, 110.2, 78.6, 77.8, 34.4, 34.3, 26.3, 22.5. **^{19}F NMR: (376 MHz, $CDCl_3$)** δ -63.1 (s, 3F$_{minor}$), -63.1(s, 3F$_{major}$); HRMS *m/z* (ESI) calcd. For $C_{19}H_{16}F_3N_2O_2$ $(M + H)^+$ 361.1158, found 361.1157.



3aq, 46%

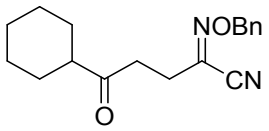
***N*-(benzyloxy)-4-oxo-4-(*o*-tolyl)butanimidoyl cyanide** (**3aq**). 43 mg

(46%). 2.5:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.65-7.63 (m, 1H), 7.43-7.22 (m, 8H), 5.28 (s, $2H_{minor}$), 5.20 (s, $2H_{major}$), 3.25-3.20 (m, 2H), 2.91-2.81 (m, 2H), 2.50 (s, $3H_{minor}$), 2.48 (s, $3H_{major}$). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.3 (2C), 138.7, 138.5, 138.3, 136.9, 136.4, 135.9, 135.7, 132.2, 132.1, 131.8, 131.7, 131.2, 128.6 (4C), 128.5, 128.4, 128.3, 125.8, 125.7, 114.3, 110.3, 78.6, 77.8, 36.7, 36.3, 26.7, 22.7, 21.5, 21.4. HRMS *m/z* (ESI) calcd. For $C_{19}H_{19}N_2O_2$ $(M + H)^+$ 307.1441, found 307.1443.



3ar, 63%

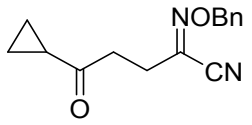
***N*-(benzyloxy)-4-oxo-6-phenylhexanimidoyl cyanide** (**3ar**). 61 mg (63%). 1.9:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.43-7.22 (m, 7H), 7.20-7.14 (m, 3H), 5.23 (s, $2H_{minor}$), 5.17 (s, $2H_{major}$), 2.91-2.84 (m, 2H), 2.77-2.60 (m, 6H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 206.7, 206.5, 140.6, 140.5, 137.9, 135.9, 135.6, 131.0, 128.6, 128.5 (2C), 128.4, 128.3 (2C), 128.2 (2C), 126.1, 114.1, 110.1, 78.4, 77.7, 44.1, 44.0, 37.9, 37.7, 29.5, 29.4, 26.0, 22.0. HRMS *m/z* (ESI) calcd. For $C_{20}H_{21}N_2O_2$ $(M + H)^+$ 321.1598, found 321.1596.



3as, 52%

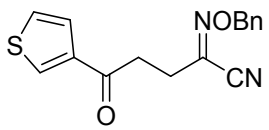
***N*-(benzyloxy)-4-cyclohexyl-4-oxobutanimidoyl cyanide** (**3as**). 47 mg

(52%). 9.6:1 of two isomers, colorless oil; **major isomer**: **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.38-7.31 (m, 5H), 5.21 (s, 2H), 2.81-2.65 (m, 4H), 1.86-1.63 (m, 5H), 1.41-1.10 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 210.6, 136.0, 131.3, 128.5, 128.4, 128.3, 110.2, 77.8, 50.7, 35.9, 28.4, 26.1, 25.7, 25.5. HRMS *m/z* (ESI) calcd. For $C_{18}H_{23}N_2O_2$ $(M + H)^+$ 299.1754, found 299.1756.



3at, 49%

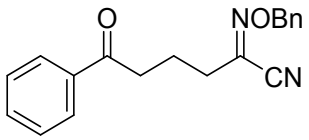
***N*-(benzyloxy)-4-cyclopropyl-4-oxobutanimidoyl cyanide** (**3at**). 38 mg (49%). 2.2:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.38-7.33 (m, 5H), 5.25 (s, $2H_{minor}$), 5.22 (s, $2H_{major}$), 2.92-2.87 (m, 2H), 2.74-2.70 (m, 2H), 1.95-1.88 (m, 1H), 1.07-1.00 (m, 2H), 0.92-0.87 (m, 2H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.6, 207.4, 138.2, 135.9, 135.7, 131.2, 128.6, 128.5 (3C), 128.3 (2C), 114.1, 110.2, 78.5, 77.8, 38.6, 38.2, 26.2, 22.2, 20.5, 20.4, 11.1, 10.9. HRMS *m/z* (ESI) calcd. For $C_{15}H_{17}N_2O_2$ $(M + H)^+$ 257.1285, found 257.1283.



3au, 49%

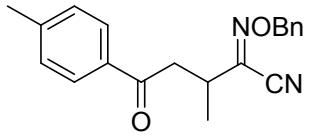
***N*-(benzyloxy)-4-oxo-4-(thiophen-3-yl)butanimidoyl cyanide** (**3au**). 38 mg (49%). 2.0:1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 8.05-8.03 (m, 1H), 7.54-7.51 (m, 1H), 7.36-7.30 (m, 6H), 5.27

(s, $2H_{minor}$), 5.19 (s, $2H_{major}$), 3.21-3.18 (m, 2H), 2.88-2.84 (m, 2H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ13C NMR (101 MHz, CDCl3) δ 191.1 (2C), 141.4, 141.2, 138.0, 135.8, 135.6, 132.3, 132.2, 131.1, 128.6 (3C), 128.4 (2C), 128.3, 126.7, 126.6 (3C), 114.3, 110.2, 78.5, 77.8, 35.3, 34.9, 26.3, 22.6. HRMS *m/z* (ESI) calcd. For $C_{16}H_{15}N_2O_2S$ $(M + H)^+$ 299.0849, found 299.0846.



3av, 46%

***N*-(benzyloxy)-5-oxo-5-phenylpentanimidoyl cyanide** (**3av**). 43 mg (46%). 1:2.1 of two isomers, colorless oil; **^{1}H NMR: (400 MHz, $CDCl_3$)** δ 7.91-7.88 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.35-7.26 (m, 5H), 5.21 (s, $2H_{major}$), 5.18 (s, $2H_{minor}$), 3.00-2.94 (m, 2H), 2.63-2.52 (m, 2H), 2.11-2.04 (m, 2H). **Detectable signals of ^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.6, 198.4, 138.7, 136.5 (2C), 136.0, 135.6, 133.1, 132.0, 128.6 (2C), 128.5 (4C), 128.4, 128.3, 127.9, 127.8, 114.4, 110.3, 78.3, 77.7, 36.9, 36.5, 31.3, 27.2, 20.2, 19.6. HRMS *m/z* (ESI) calcd. For $C_{19}H_{19}N_2O_2$ $(M + H)^+$ 307.1441, found 307.1445.

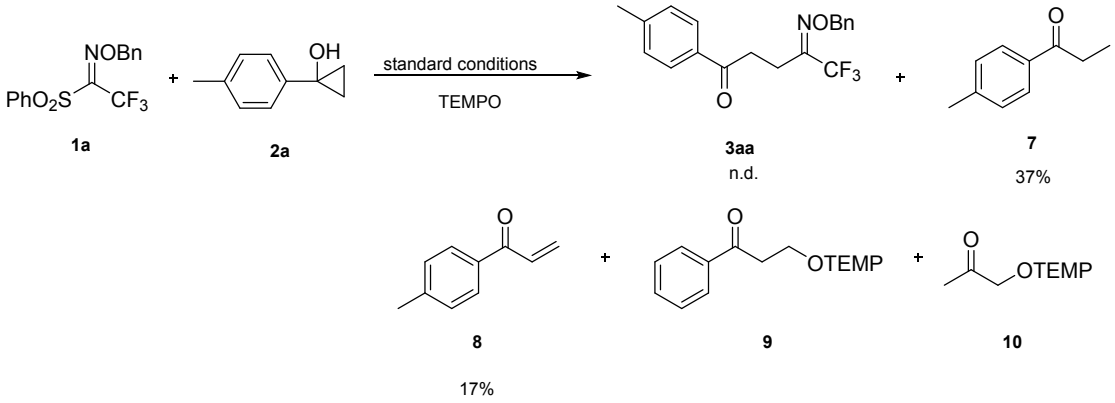


3aw, 36%

***N*-(benzyloxy)-2-methyl-4-oxo-4-(*p*-tolyl)butanimidoyl cyanide** (**3aw**). 35 mg (36%). colorless oil; **Major isomer** : **^{1}H NMR: (400 MHz, $CDCl_3$)**

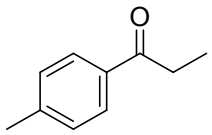
δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.37-7.26 (m, 7H), 5.18 (s, 2H), 3.43-3.31 (m, 2H), 3.07-2.98 (m, 1H), 2.42 (s, 3H), 1.30 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.4, 144.2, 136.1, 135.9, 134.1, 129.3, 128.4 (2C), 128.3, 128.1, 109.8, 77.8, 41.6, 32.8, 21.7, 18.2. HRMS *m/z* (ESI) calcd. For $C_{20}H_{21}N_2O_2$ $(M + H)^+$ 321.1598, found 321.1596.

3.3 Radical-capturing experiments



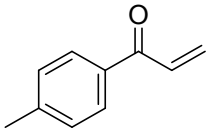
A mixture of CF_3-containing sulfonyl oxime ethers (**1a**) (0.3 mmol, 103 mg), cyclopropanols (**2a**) (0.45 mmol, 67 mg), $AgNO_3$ (0.06 mmol, 10.2 mg) and $K_2S_2O_8$ (0.45 mmol, 122 mg)， TEMPO (4 eq. 187 mg) in acetone:H_2O (1:1, 2 mL) was stirred at 50 °C for 2 h (monitored by TLC). After it was 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 MgSO4. The solvent was removed by vacuum and the residue was purified by preparative thin layer chromatograpy (PTLC) (5% acetone in PE) to give

the corresponding products.



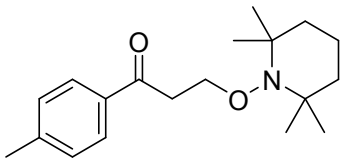
7

1-(*p*-tolyl)propan-1-one (**7**). colorless oil; The data is in accordance with reported lit. 3. **^{1}H NMR: (400 MHz, $CDCl_3$) δ** 7.86 (d, J = 8.2 Hz, 2H), 7.27-7.22 (m, 2H), 2.97 (d, J = 7.3 Hz, 2H), 2.40 (s, 3H), 1.21 (t, J = 7.3 Hz, 3H).



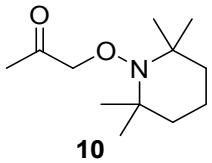
8

1-(*p*-tolyl)prop-2-en-1-one (**8**). colorless oil; The data is in accordance with reported lit. 4. **^{1}H NMR: (400 MHz, $CDCl_3$) δ** 7.87 (d, J = 8.1 Hz, 2H), 7.32-7.25 (m, 2H), 7.17 (dd, J = 17.1, 10.5 Hz, 1H), 6.43 (dd, J = 17.0, 1.8 Hz, 1H), 5.90 (dd, J = 10.6, 1.8 Hz, 1H), 2.42 (s, 3H).



9

3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-1-(p-tolyl)propan-1-one (**9**). colorless oil; The data is in accordance with reported lit. 5. **^{1}H NMR: (400 MHz, $CDCl_3$) δ** 7.90 (d, J = 7.7 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 4.14 (t, J = 6.6 Hz, 2H), 3.14 (t, J = 6.6 Hz, 2H), 2.42 (s, 3H), 1.47-1.1.42 (m, 6H), 1.16-1.01 (m, 12H).



10

1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propan-2-one (**10**). colorless oil; The data is in accordance with reported lit. 6. **^{1}H NMR: (400 MHz, $CDCl_3$) δ** 4.38 (s, 2H), 2.21 (s, 3H), 1.47-1.42 (m, 6H), 1.16-1.01 (m, 12H).

4. Reference

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[3] Q. Tong, Y. Liu, X. Gao, Z. Fan, T. Liu, B. Li, D. Su, Q. Wang and M. Cheng, *Adv. Synth. Catal.*, 2019, **361**, 3137.

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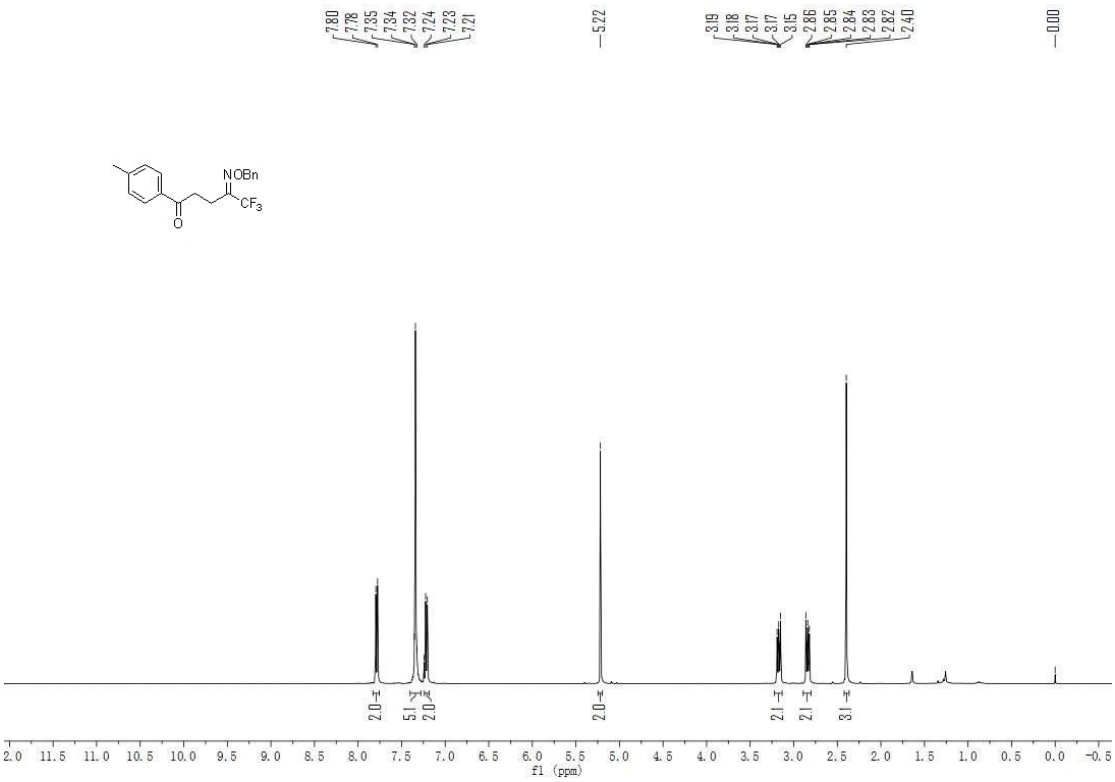
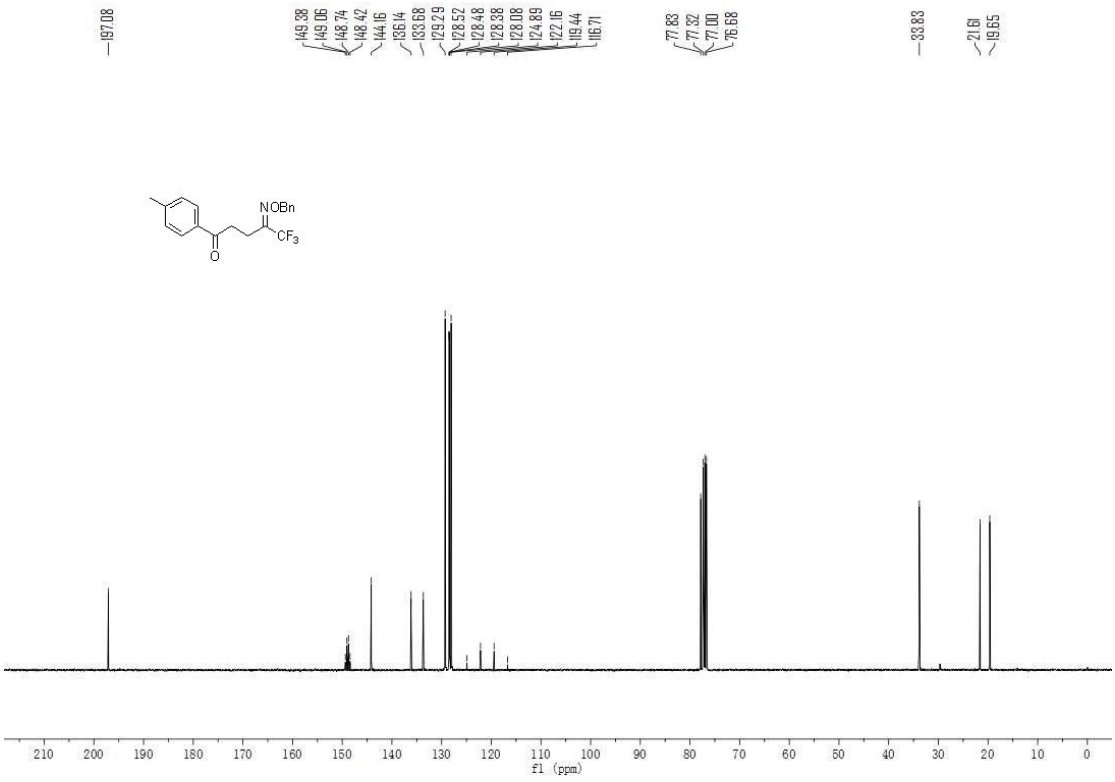
5. ^{1}H NMR and ^{13}C NMR spectra of compounds 3aa-i, 3am-w

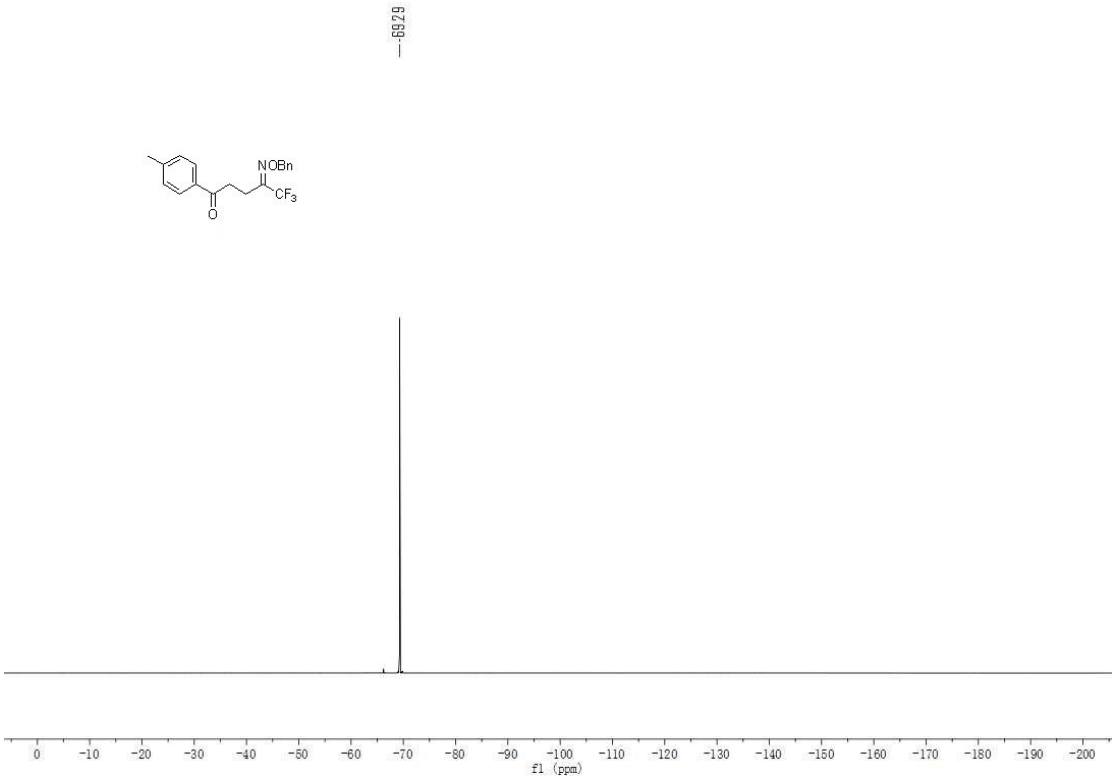
^{1}H NMR spectrum of 3aa



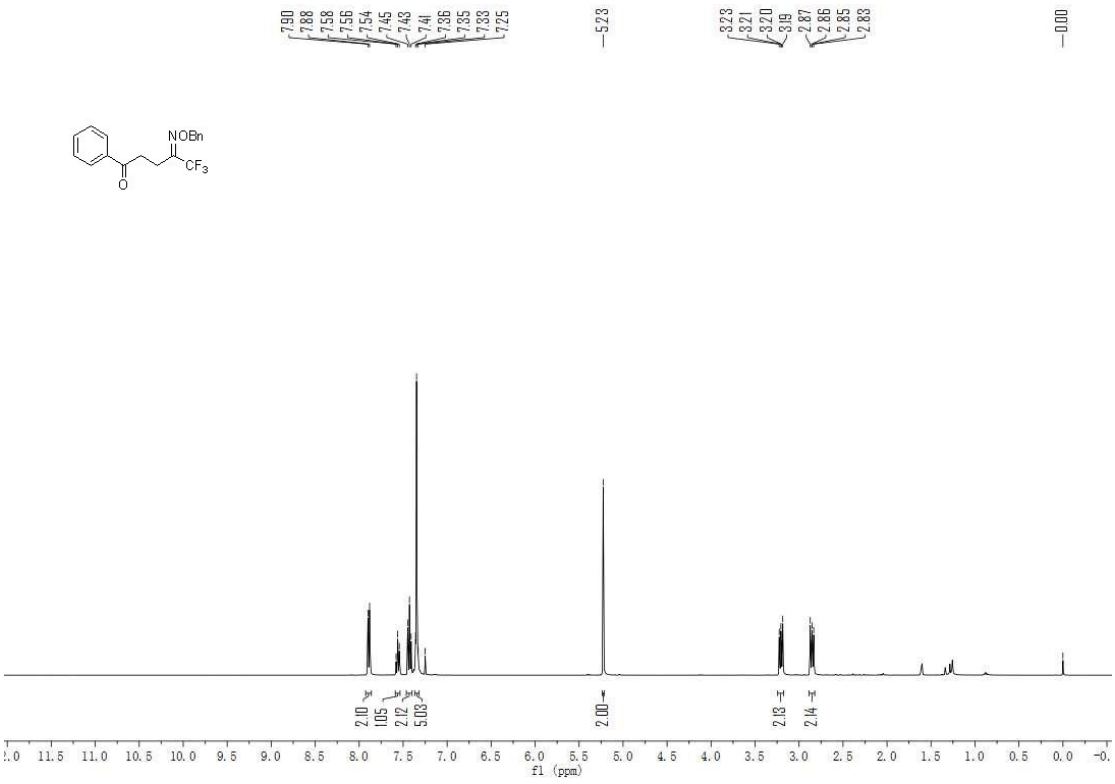
^{13}C NMR spectrum of 3aa



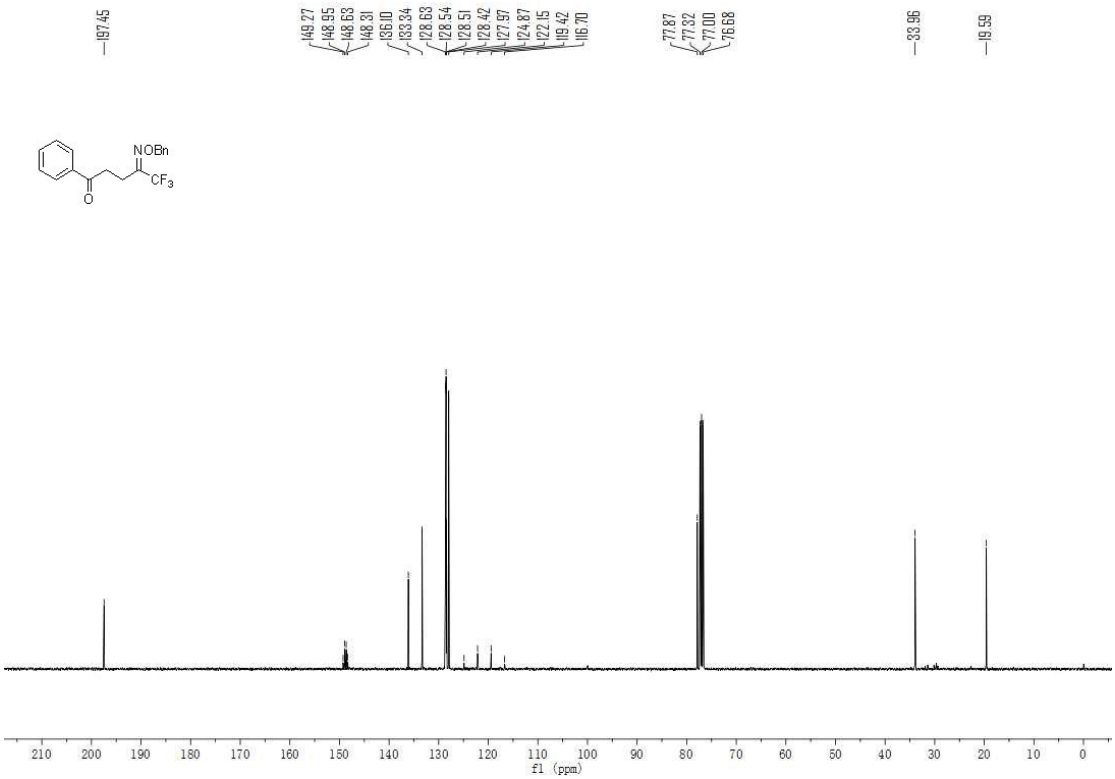
^{19}F NMR spectrum of 3aa



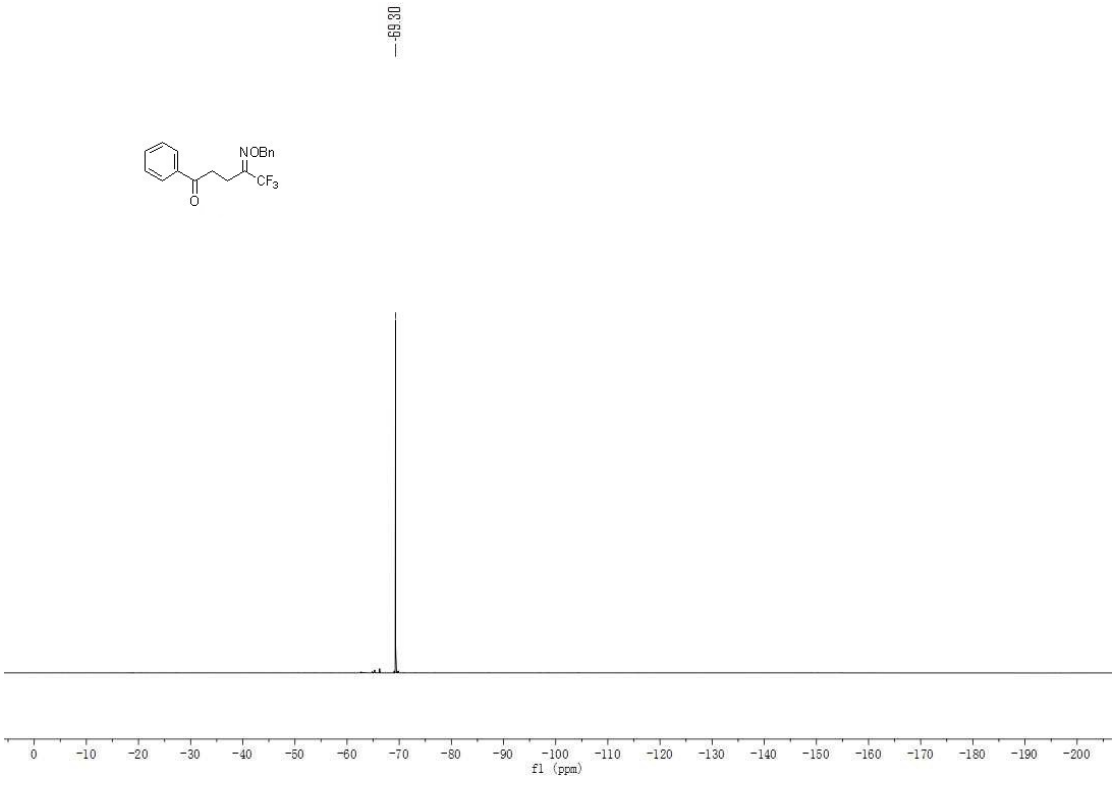
^{1}H NMR spectrum of 3ab



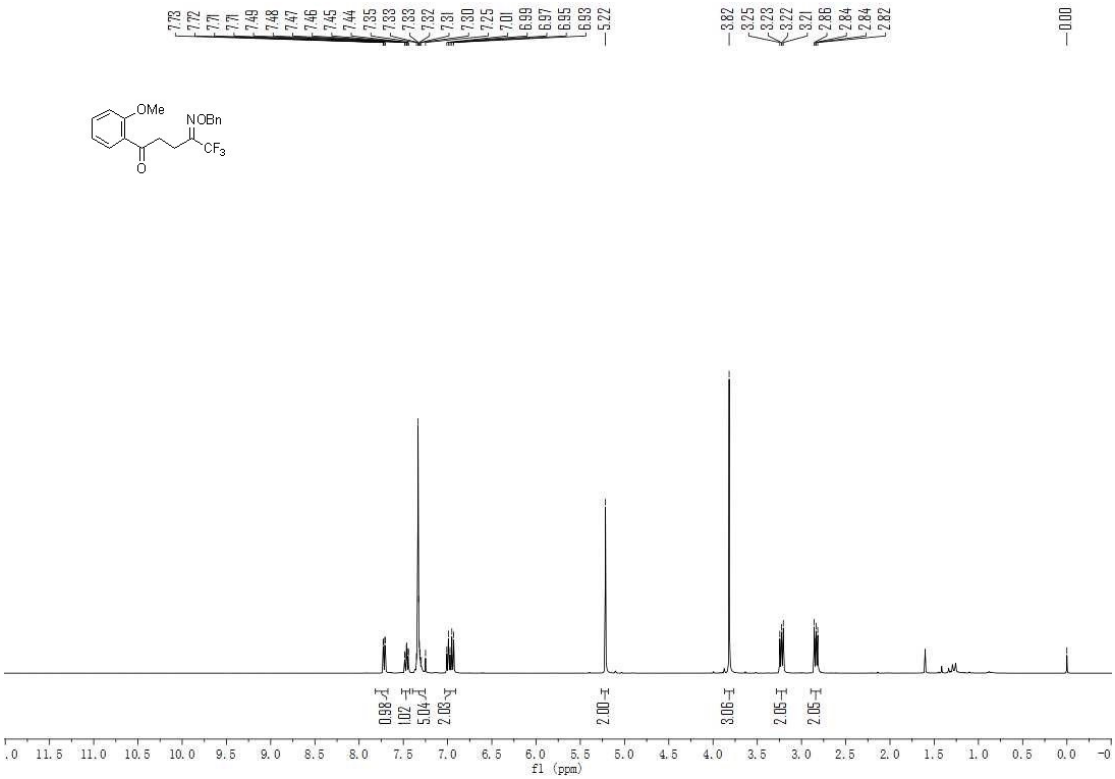
^{13}C NMR spectrum of 3ab



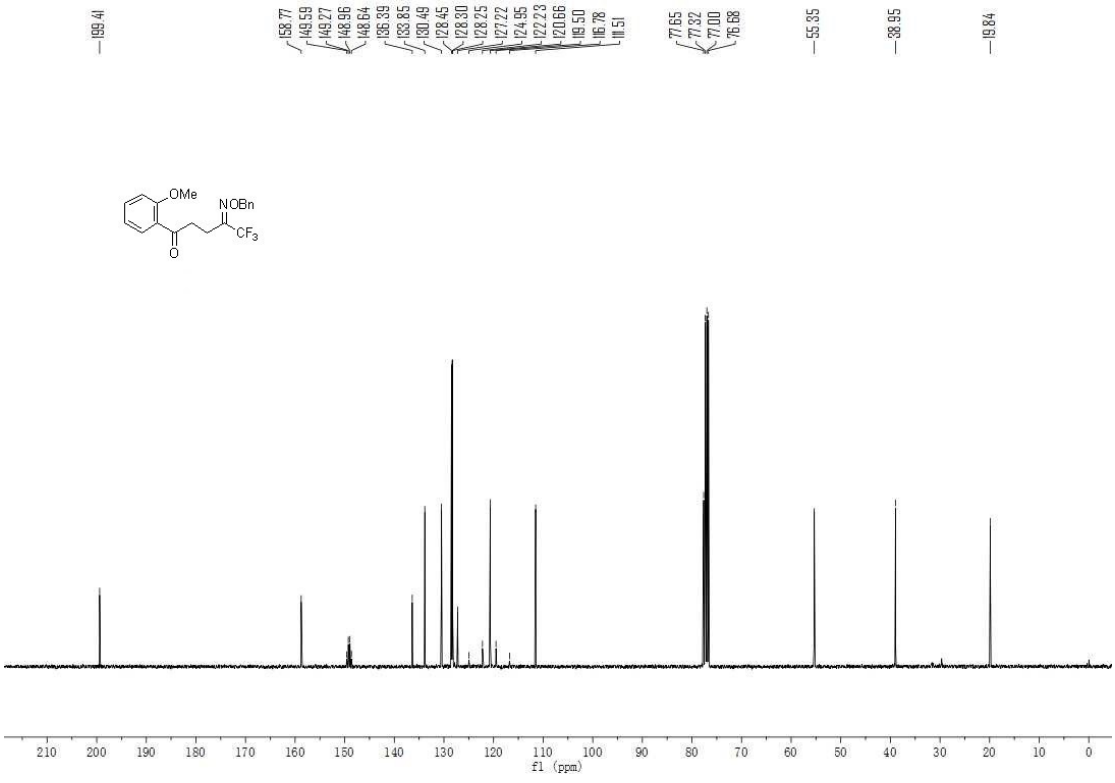
^{19}F NMR spectrum of 3ab



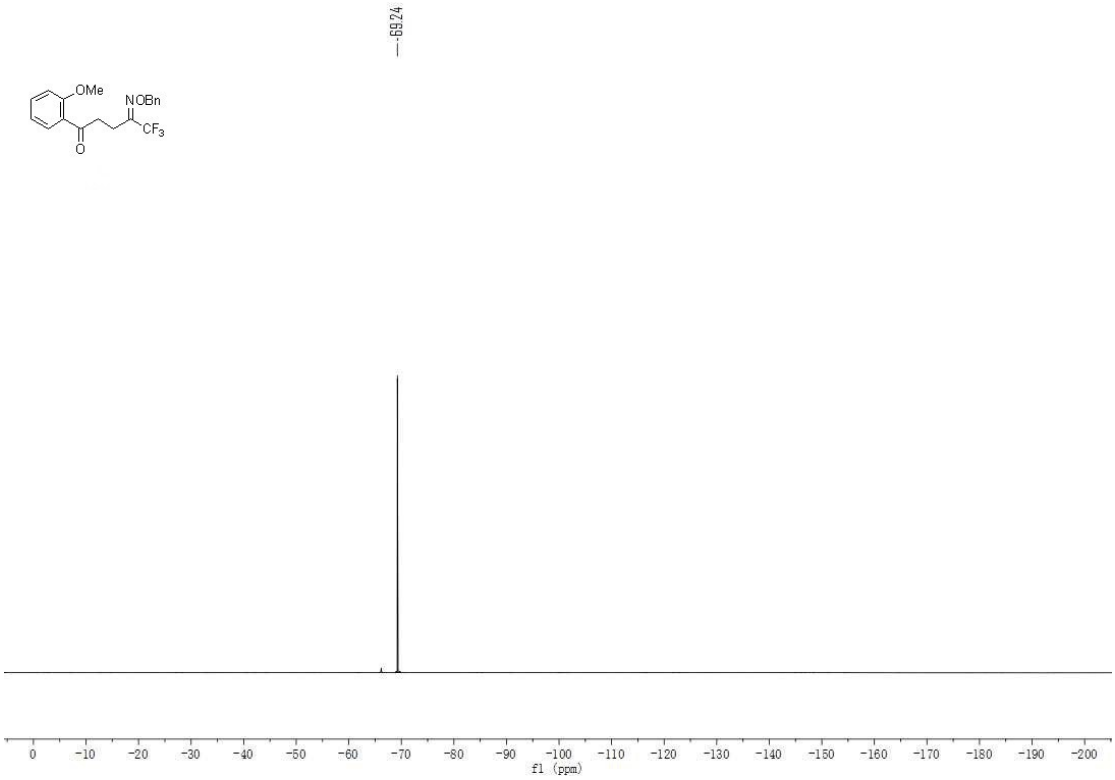
^{1}H NMR spectrum of 3ac



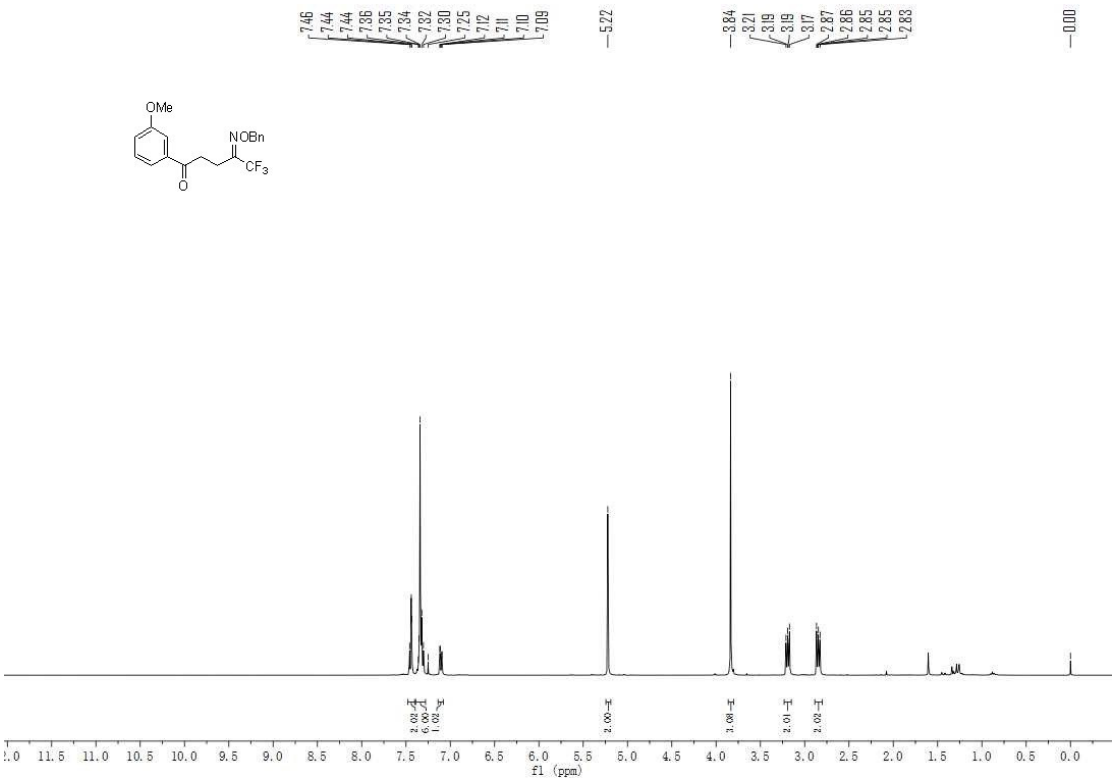
^{13}C NMR spectrum of 3ac



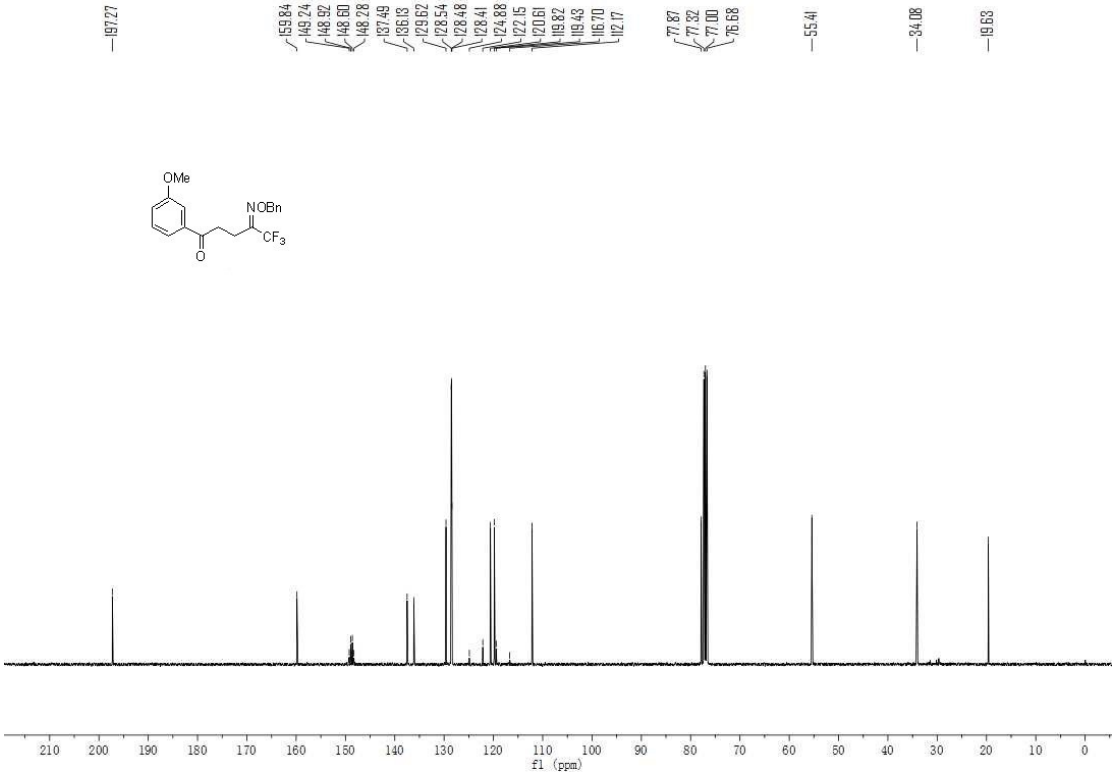
^{19}F NMR spectrum of 3ac



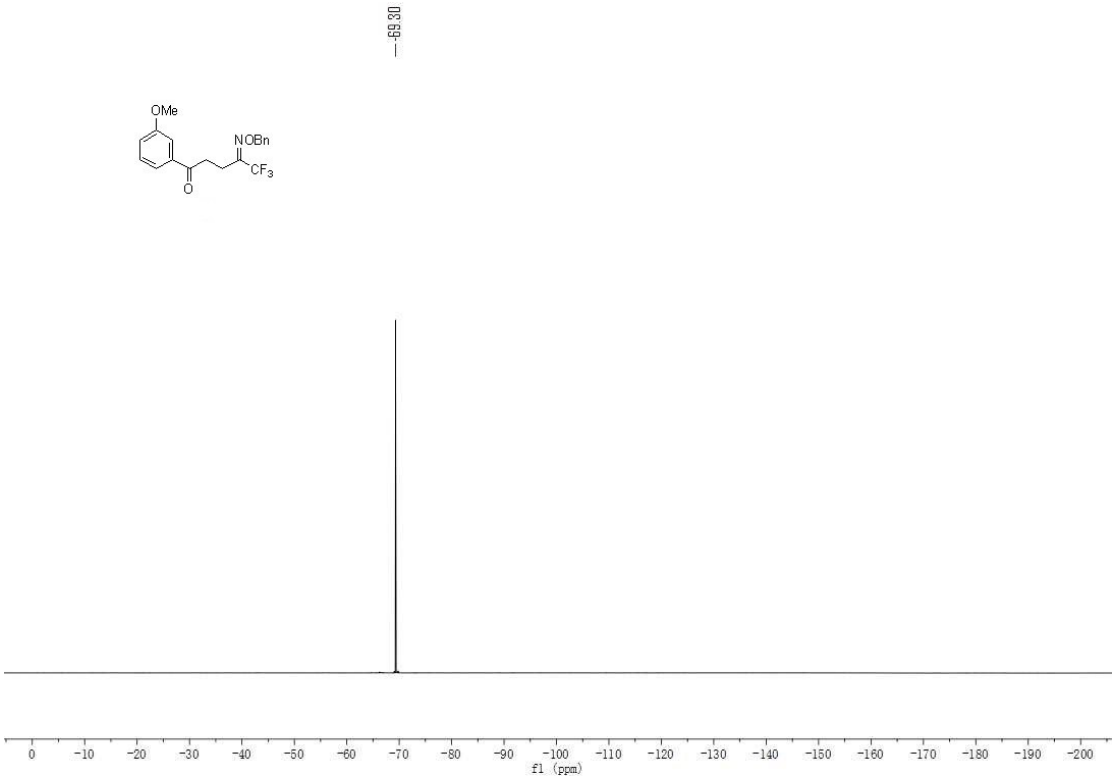
^{1}H NMR spectrum of 3ad



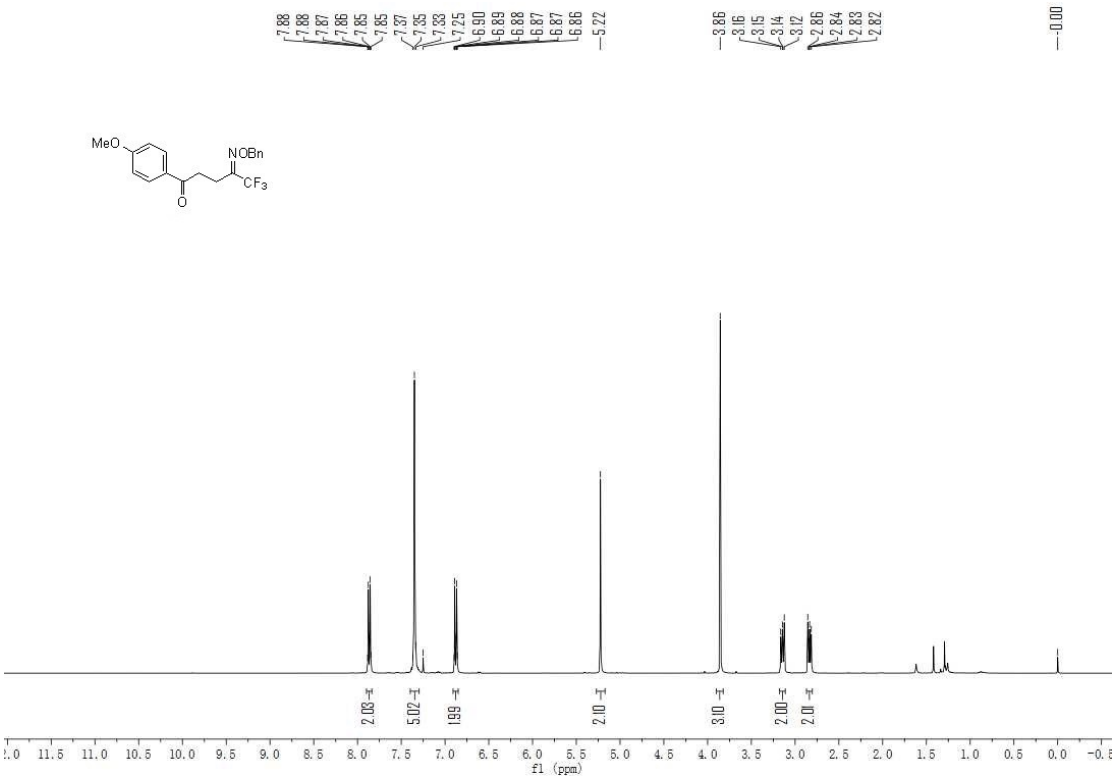
^{13}C NMR spectrum of 3ad



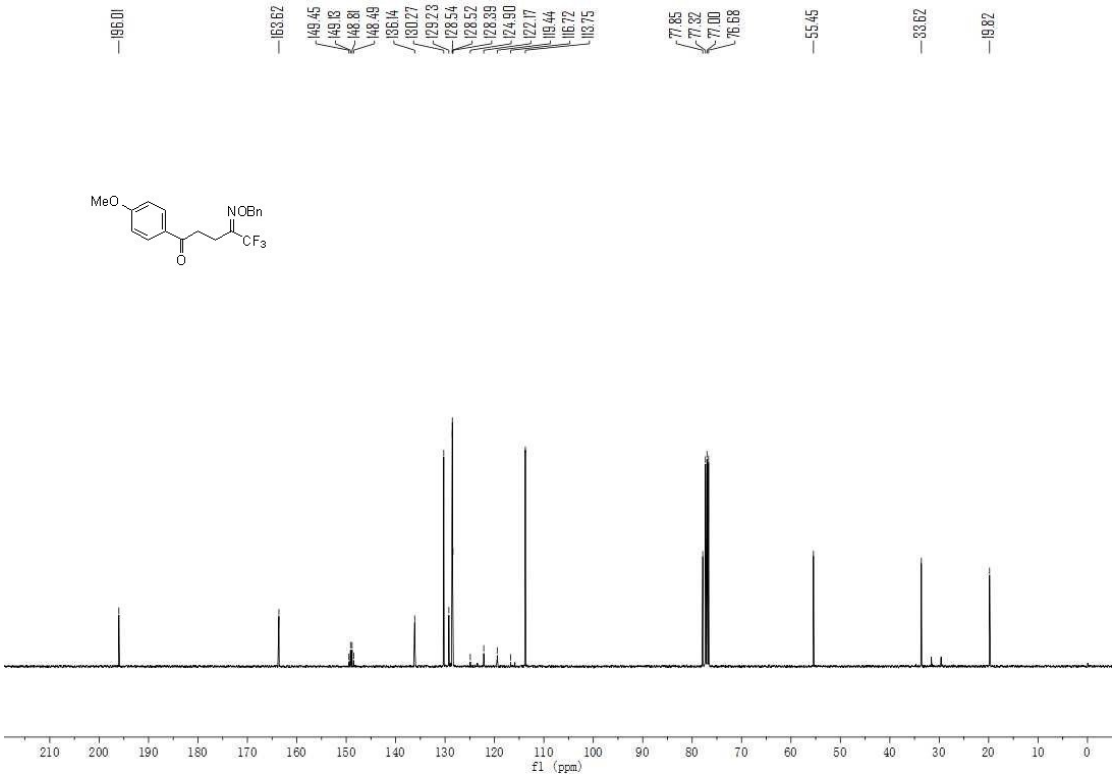
^{19}F NMR spectrum of 3ad



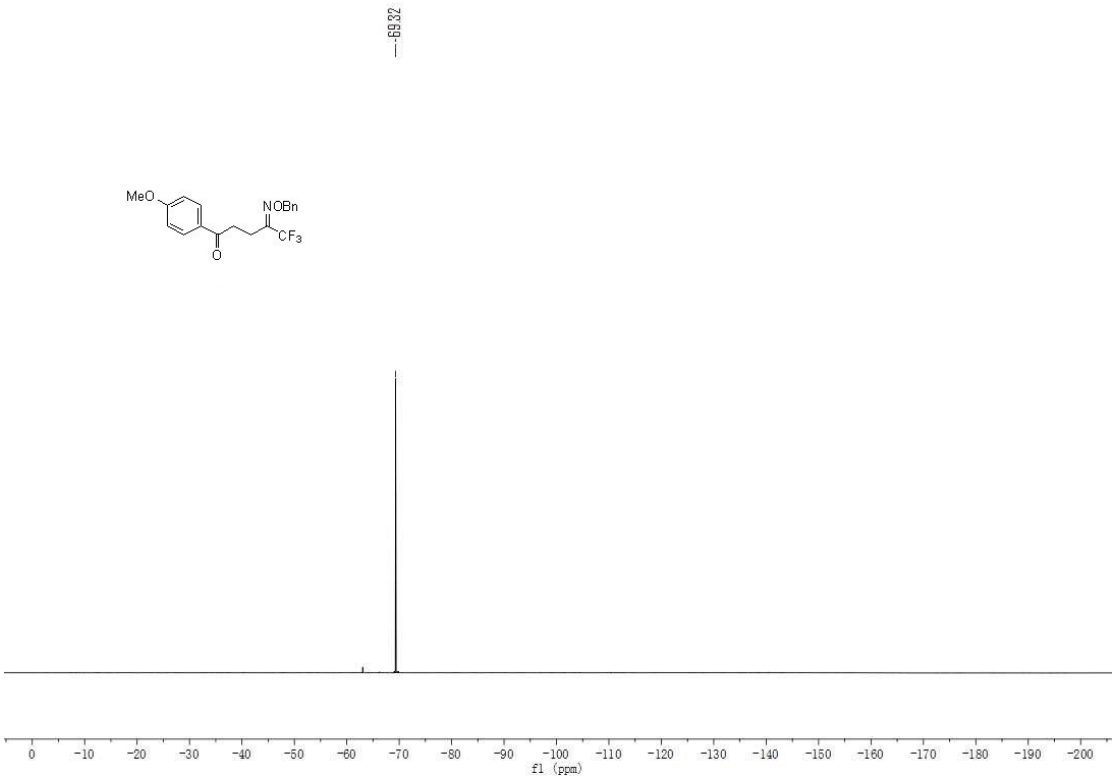
^{1}H NMR spectrum of 3ae



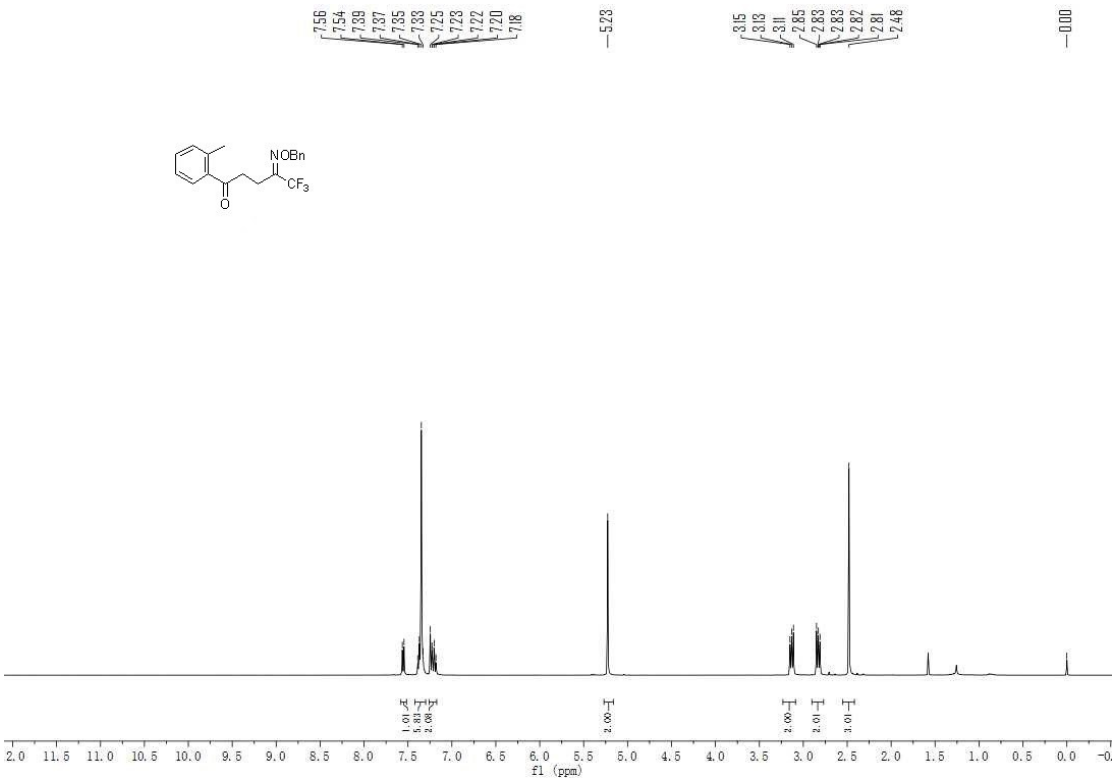
^{13}C NMR spectrum of 3ae



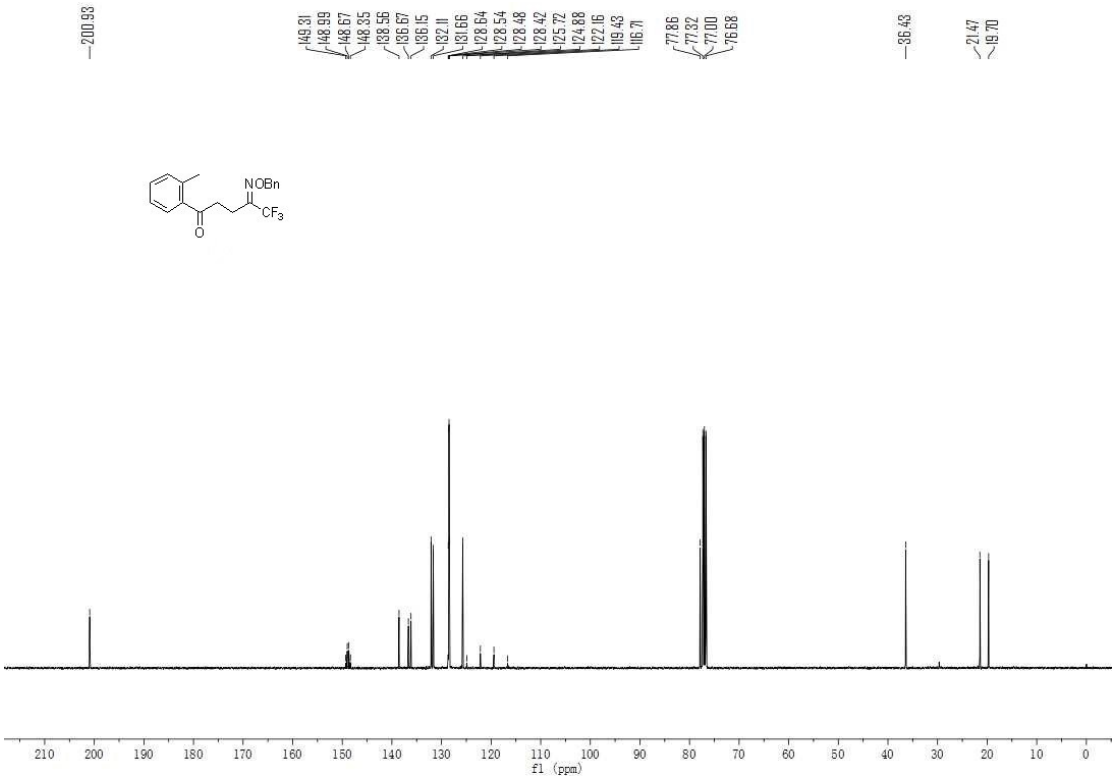
^{19}F NMR spectrum of 3ae



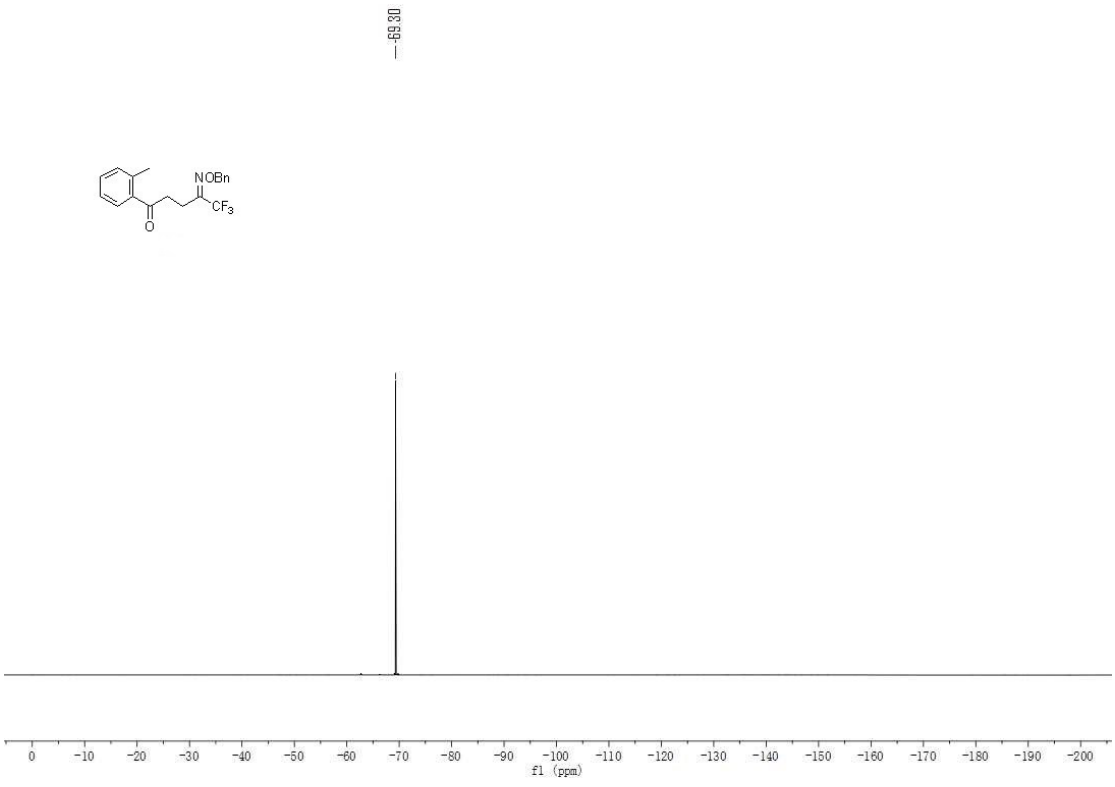
^{1}H NMR spectrum of 3af



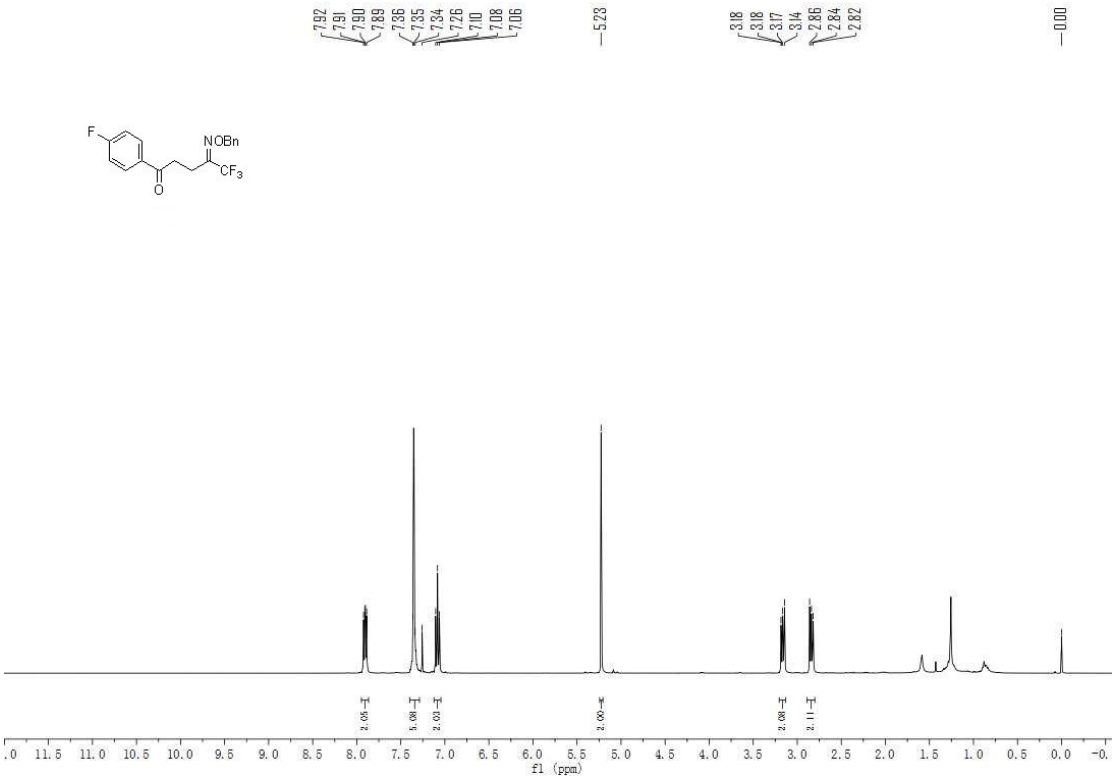
^{13}C NMR spectrum of 3af



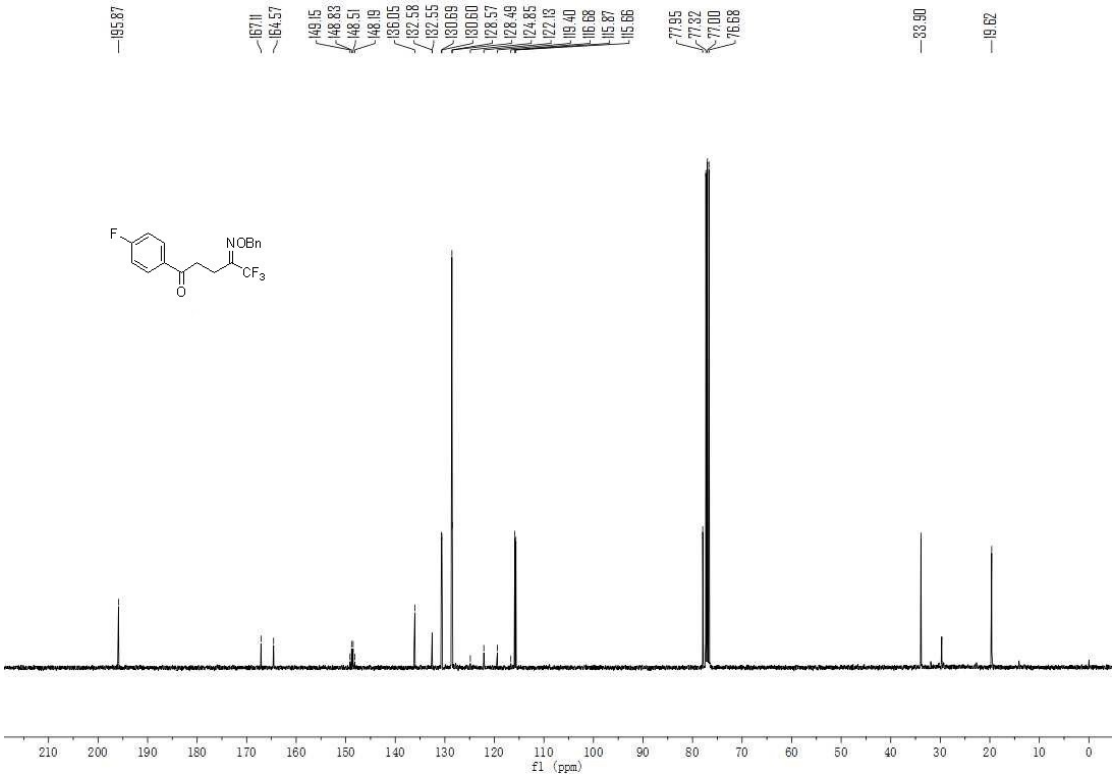
^{19}F NMR spectrum of 3af



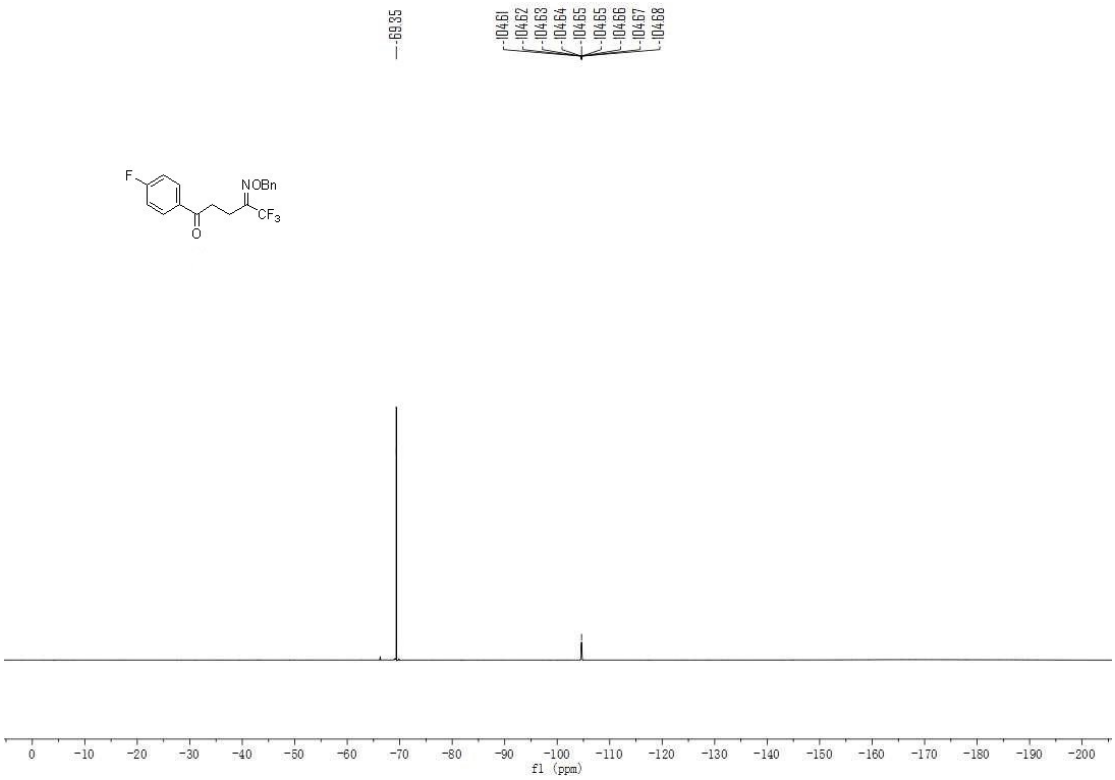
^{1}H NMR spectrum of 3ag



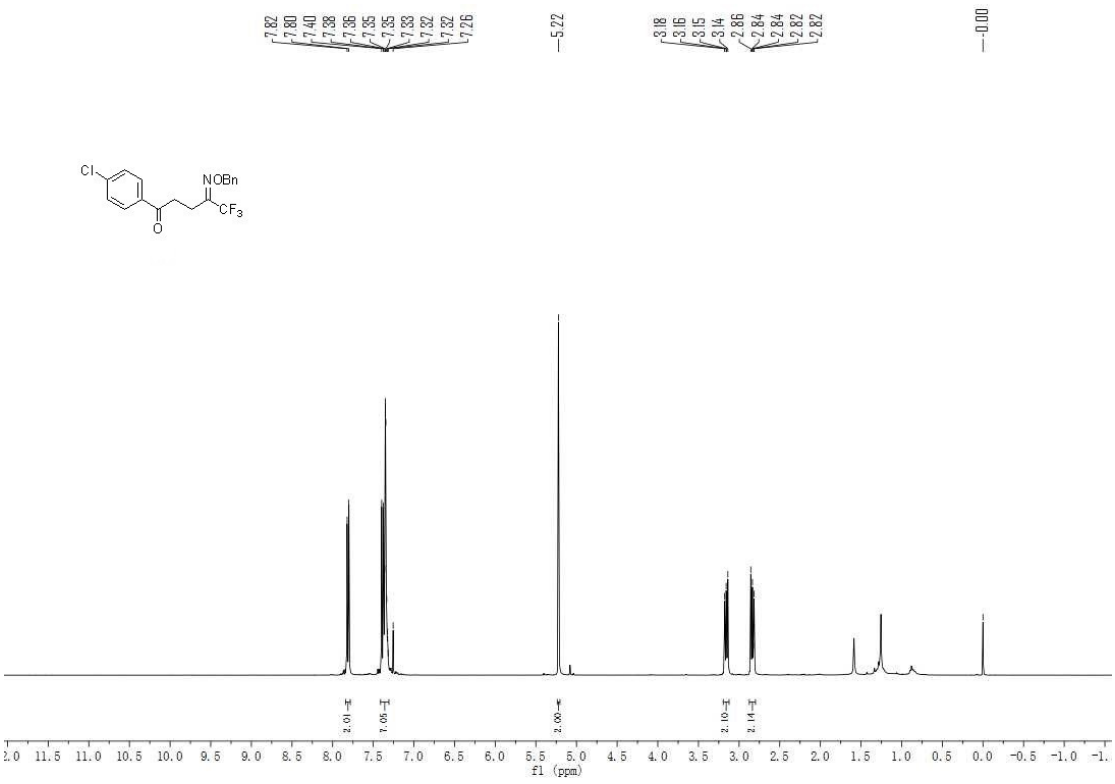
^{13}C NMR spectrum of 3ag



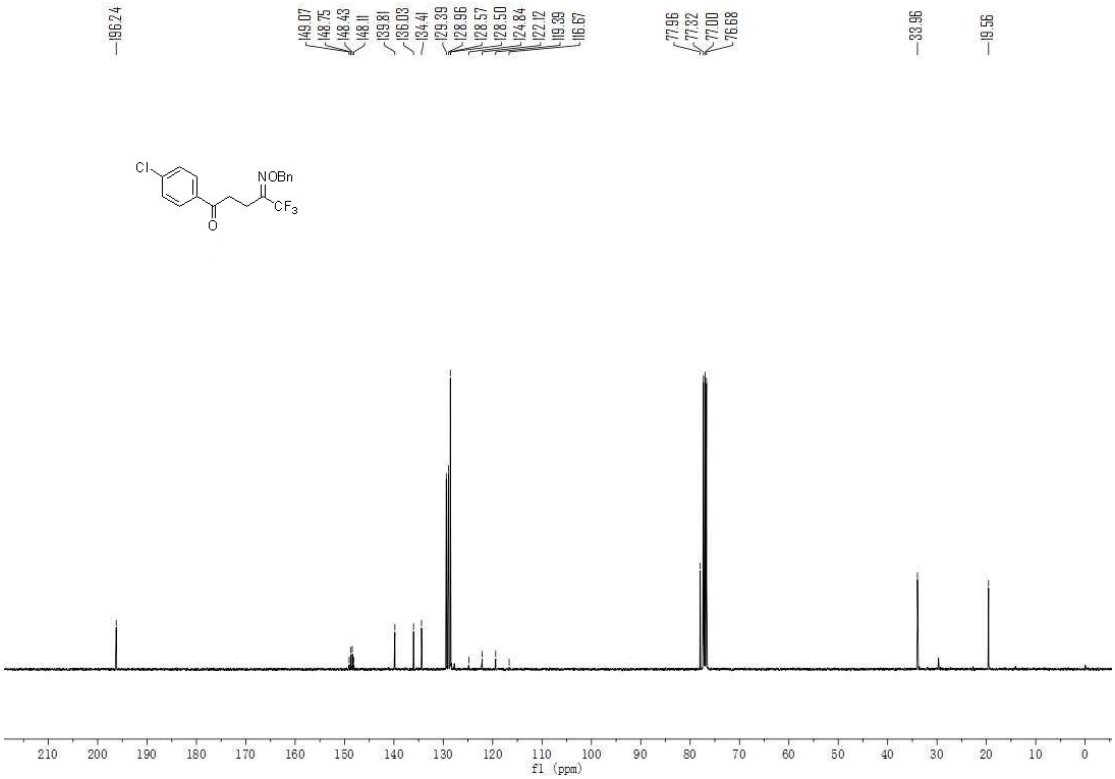
^{19}F NMR spectrum of 3ag



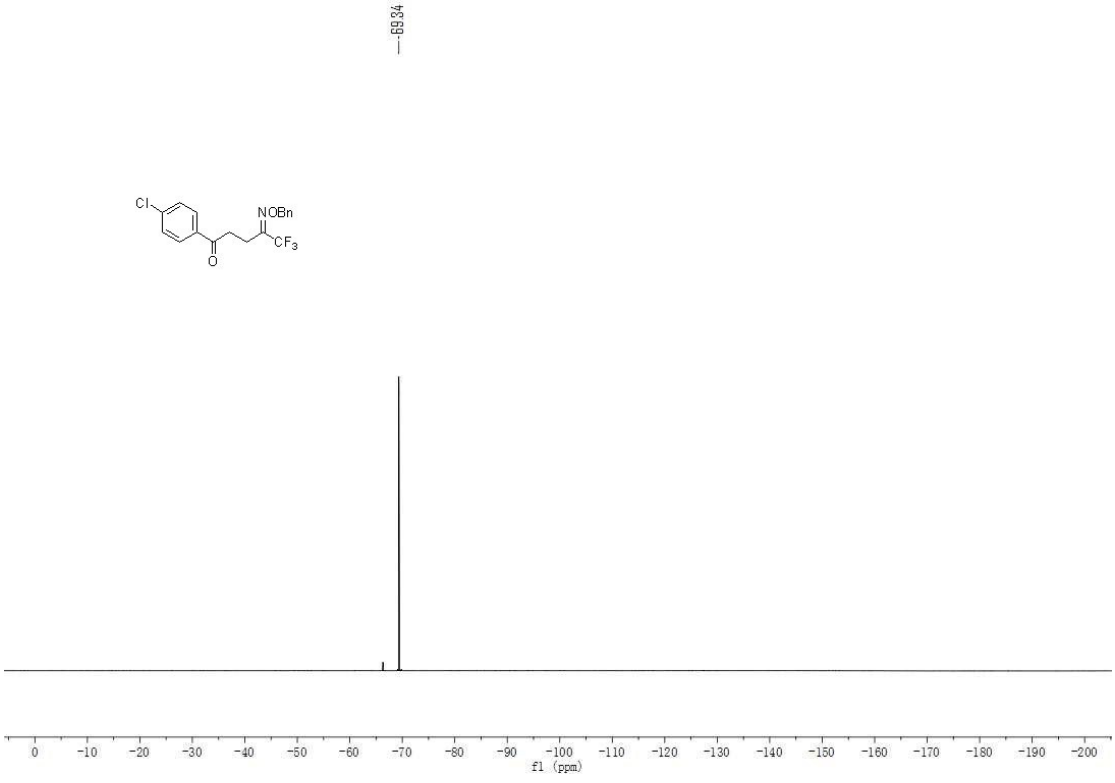
^{1}H NMR spectrum of 3ah



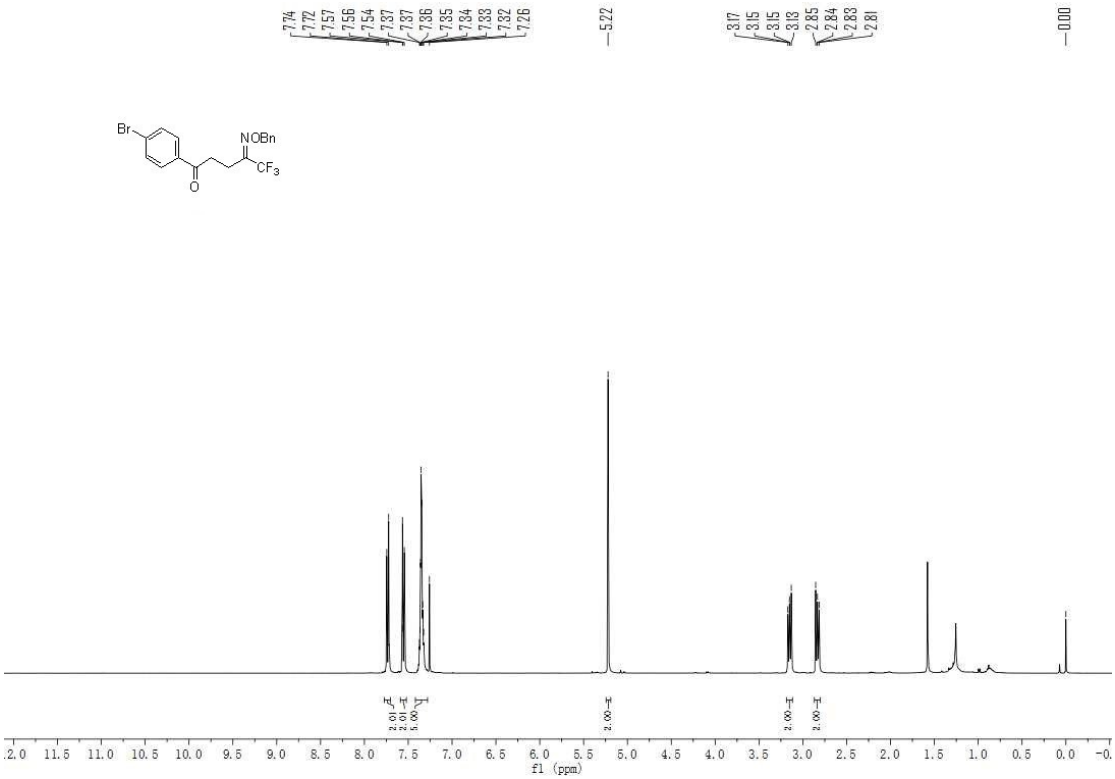
^{13}C NMR spectrum of 3ah



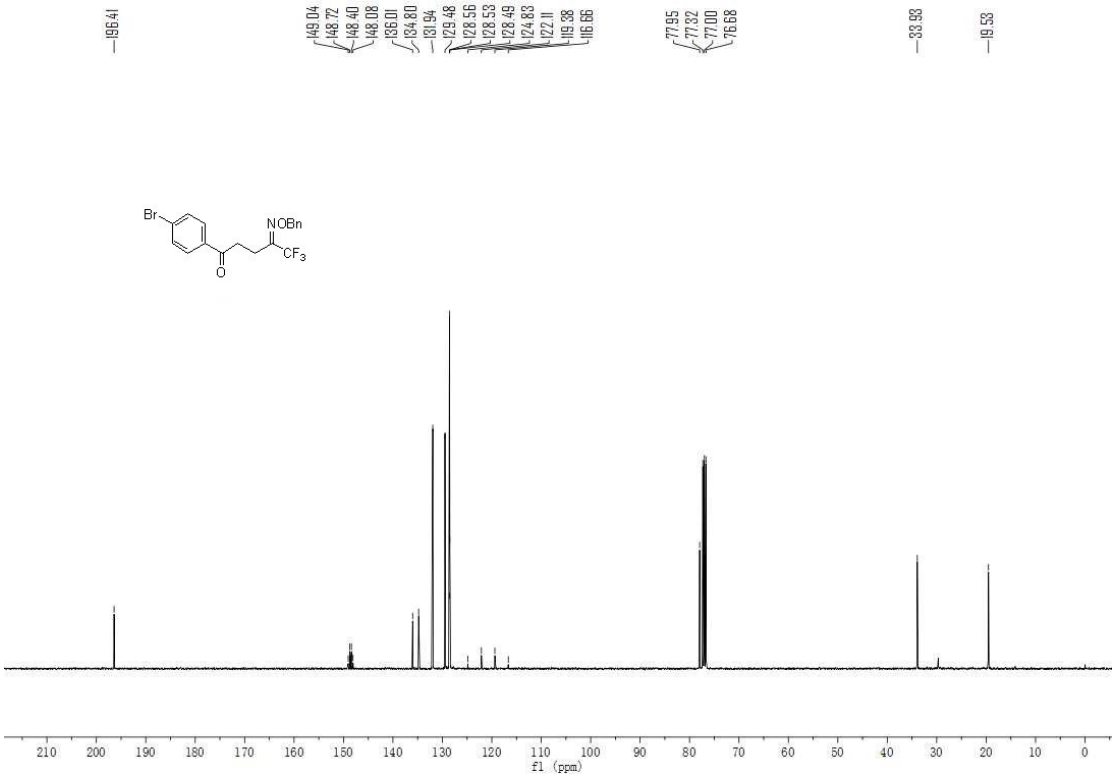
^{19}F NMR spectrum of 3ah



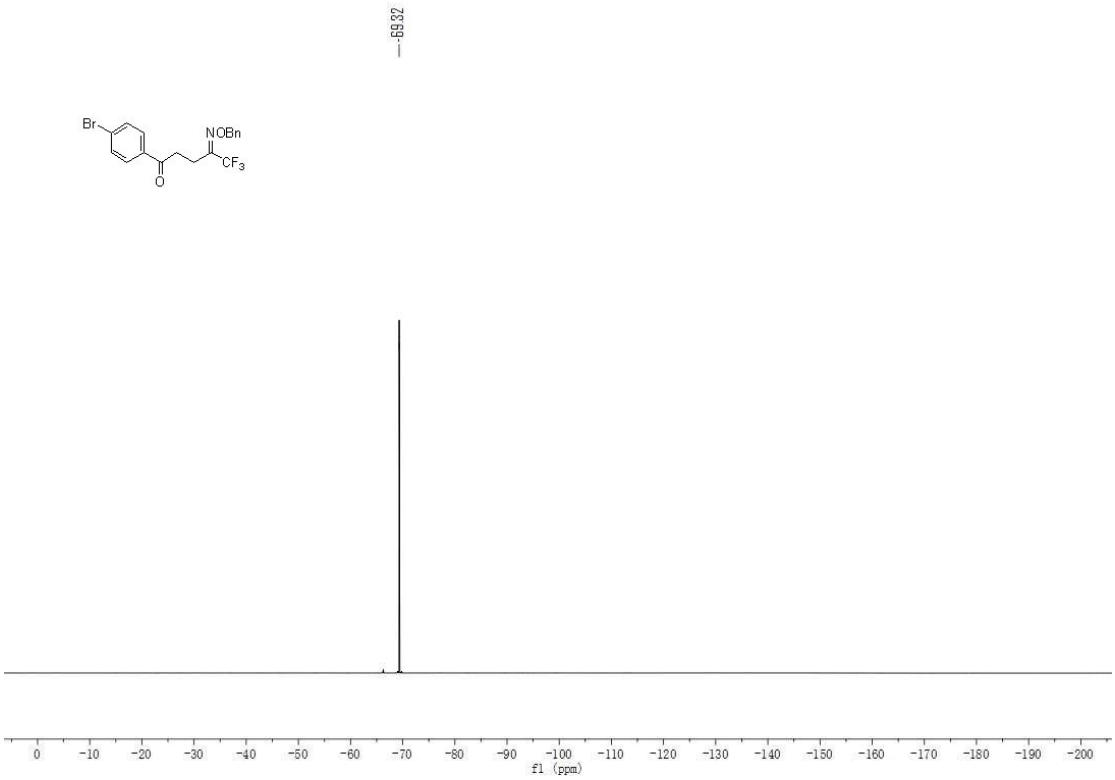
^{1}H NMR spectrum of 3ai



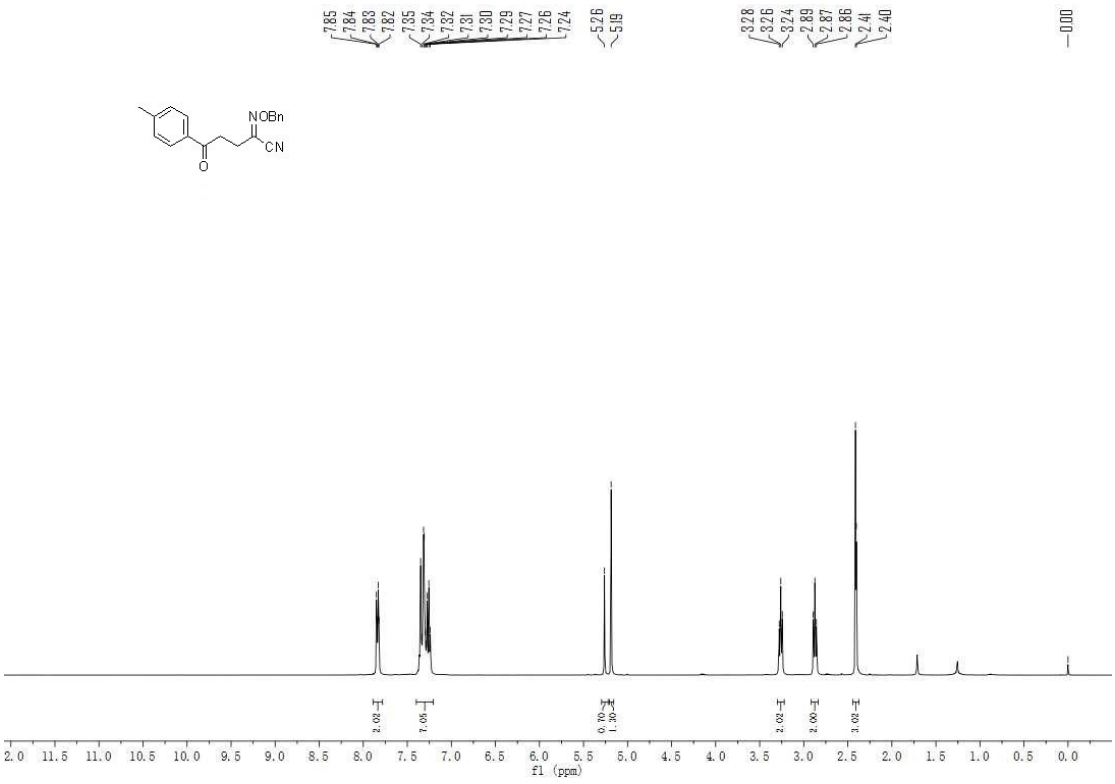
^{13}C NMR spectrum of 3ai



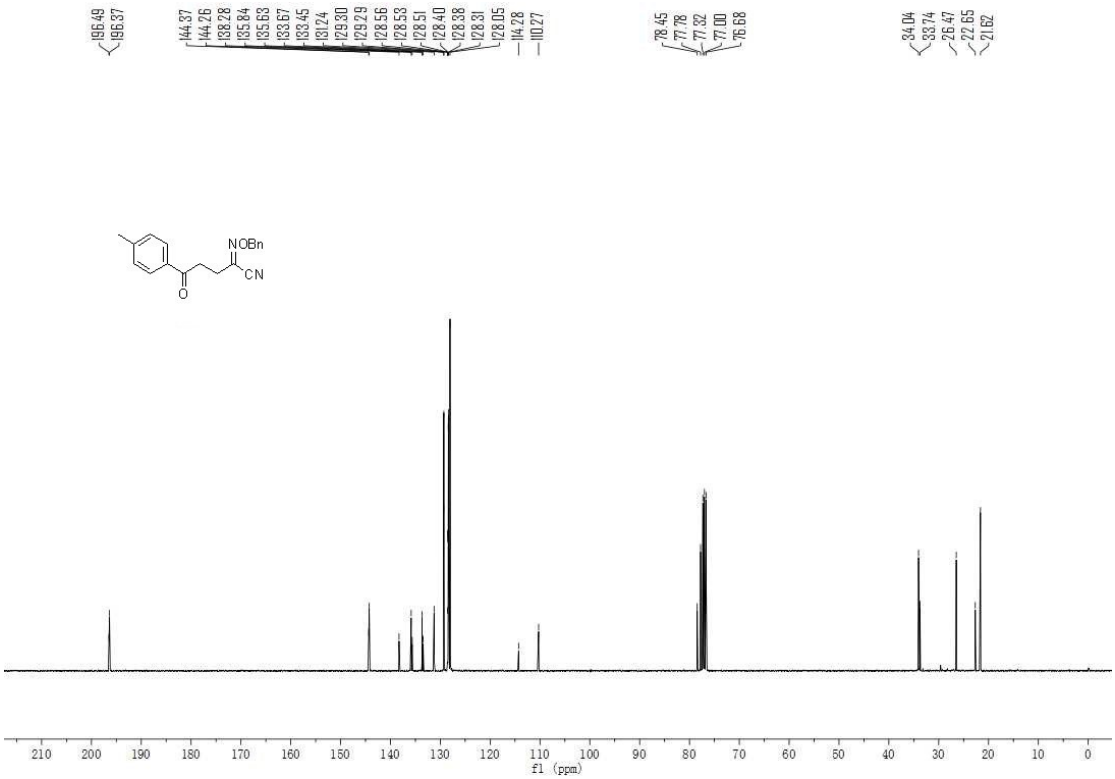
^{19}F NMR spectrum of 3ai



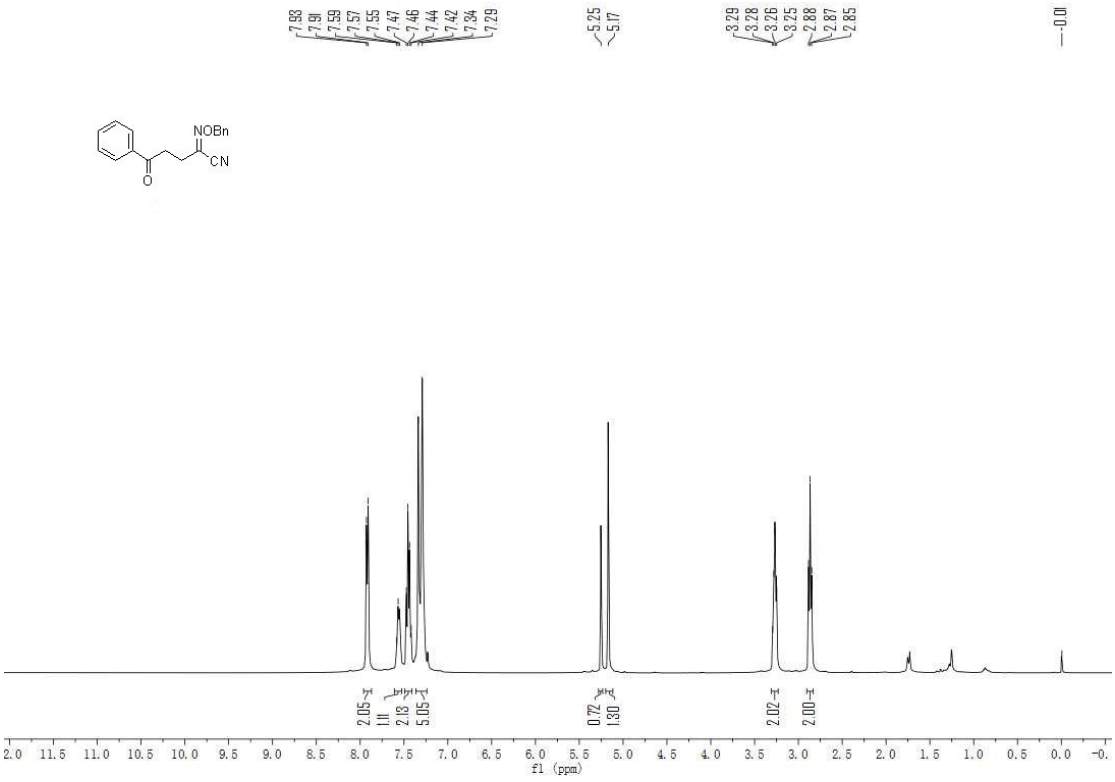
^{1}H NMR spectrum of 3aj



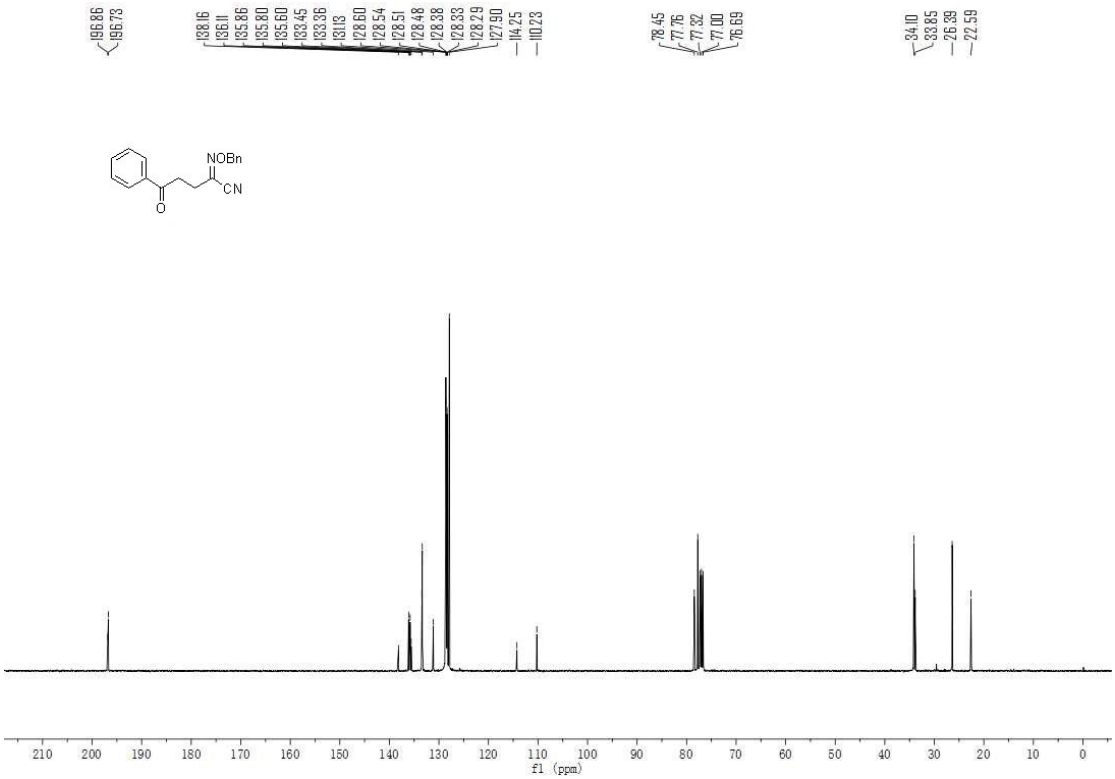
^{13}C NMR spectrum of 3aj



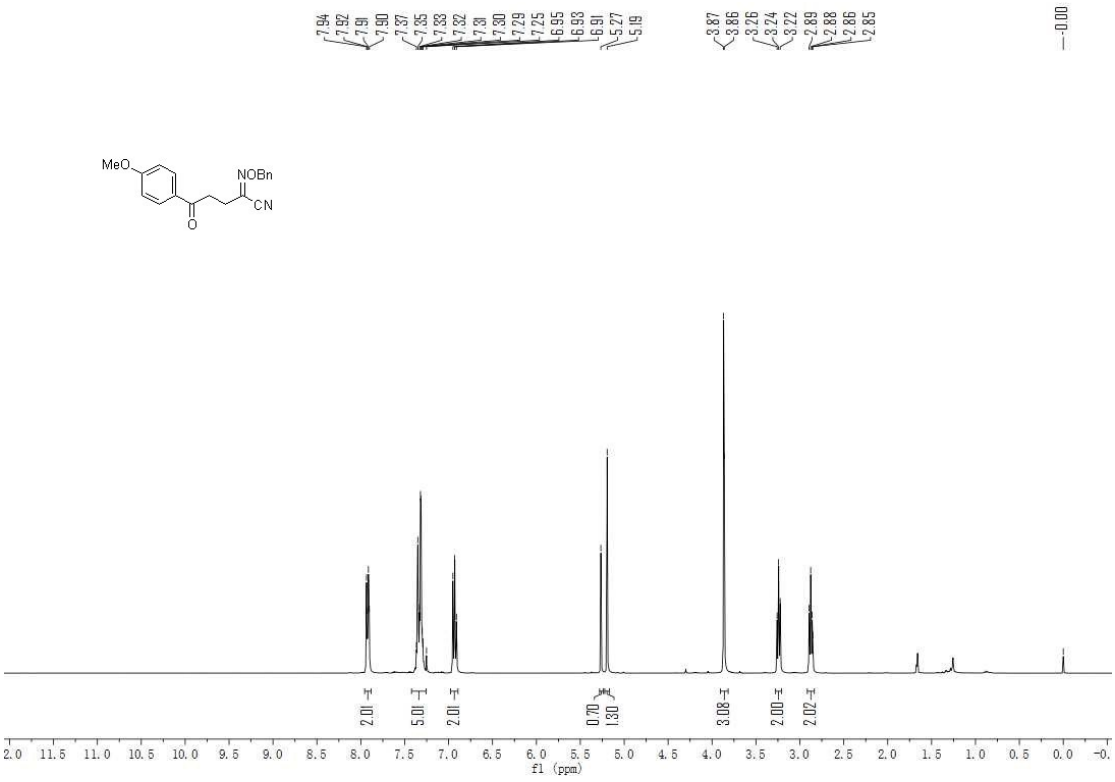
^{1}H NMR spectrum of 3ak



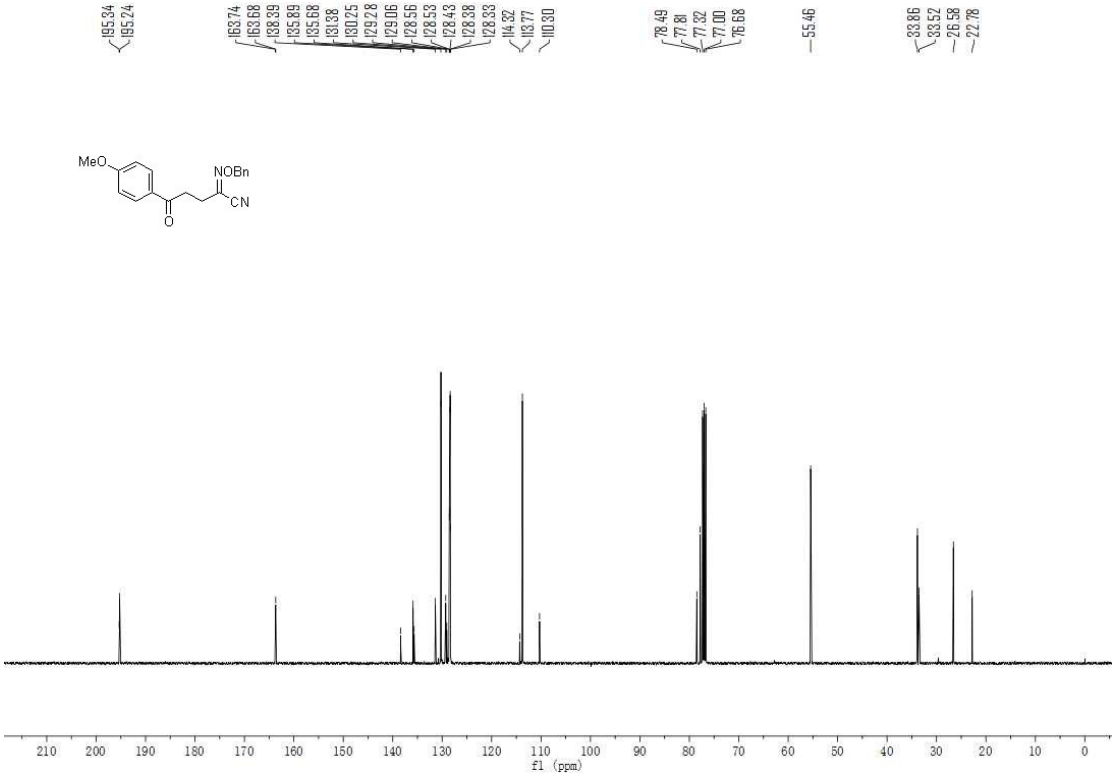
^{13}C NMR spectrum of 3ak



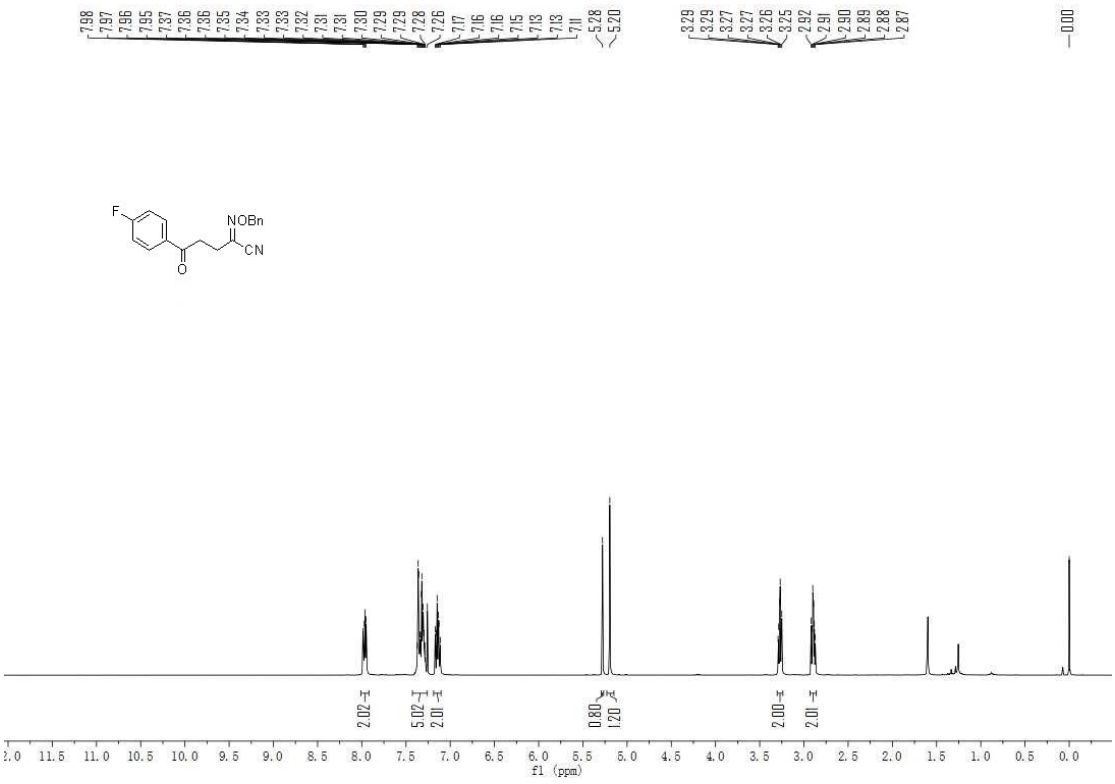
^{1}H NMR spectrum of 3al



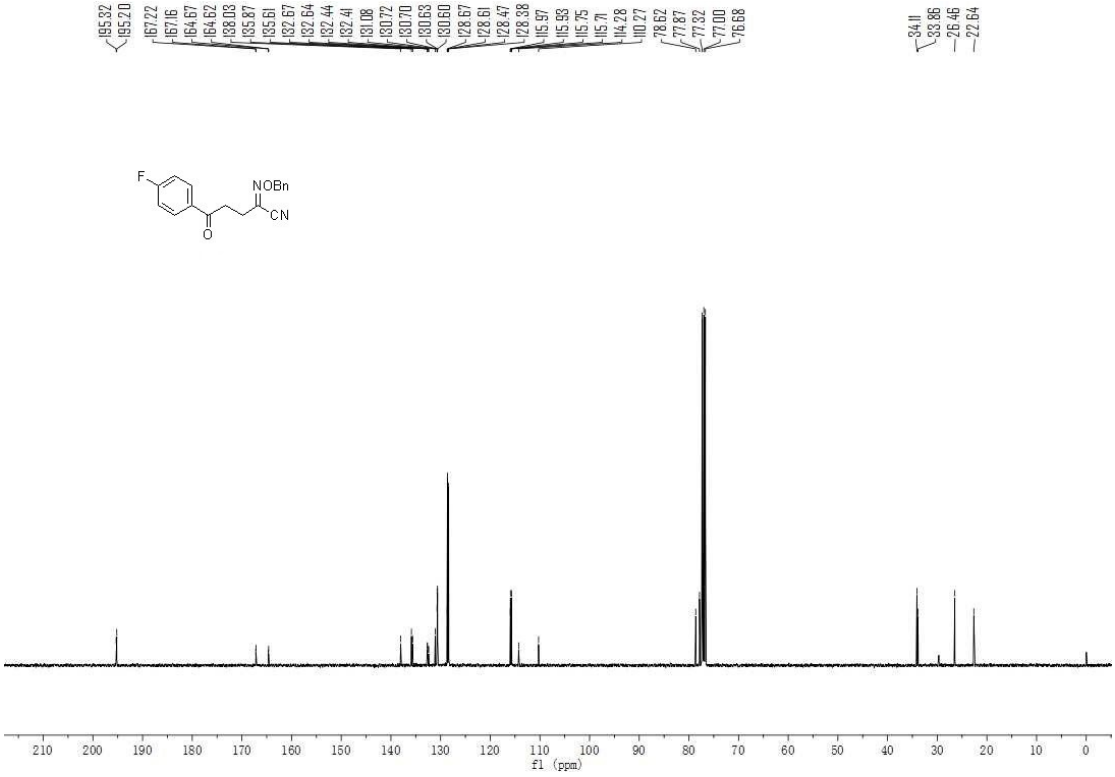
^{13}C NMR spectrum of 3al



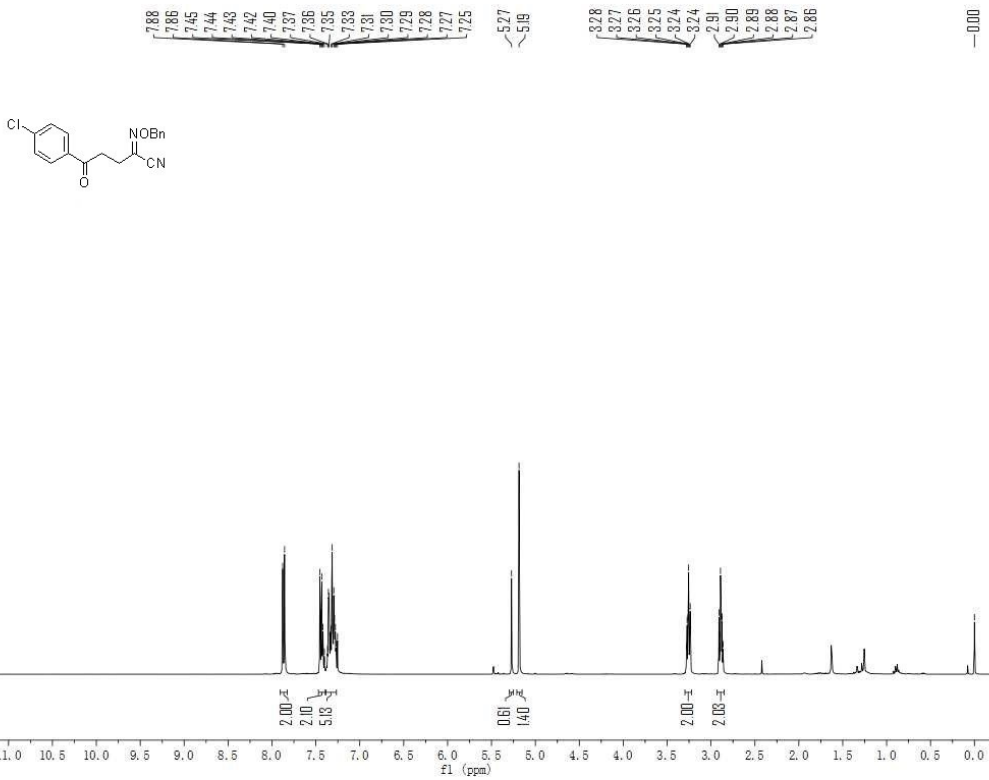
^{1}H NMR spectrum of 3am



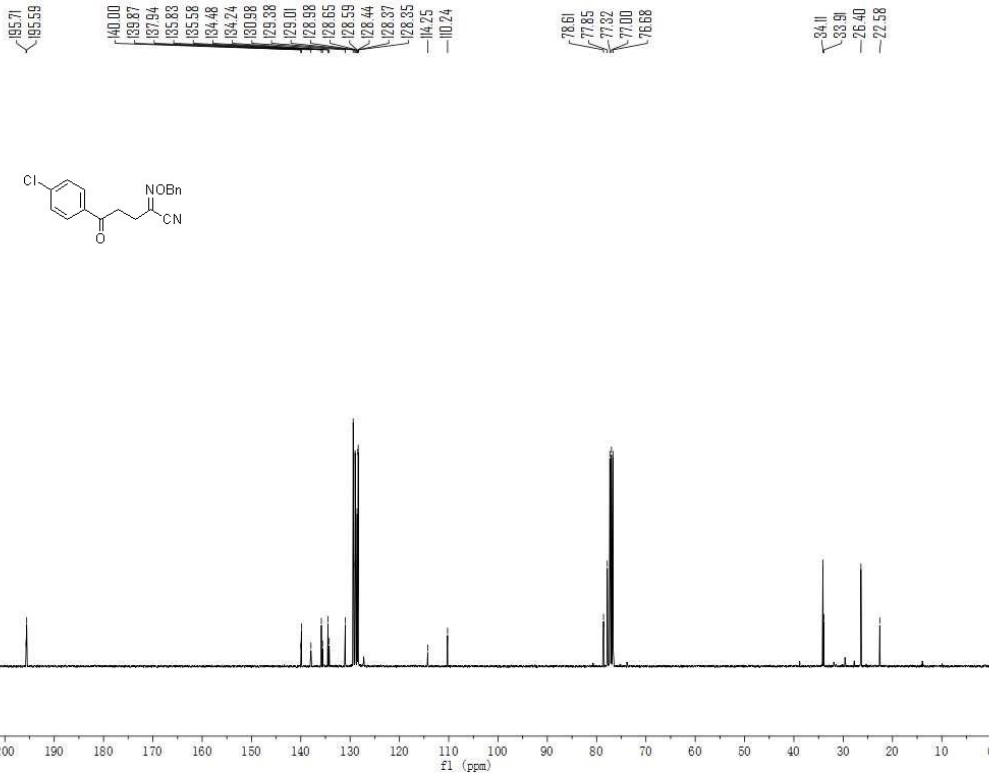
^{13}C NMR spectrum of 3am



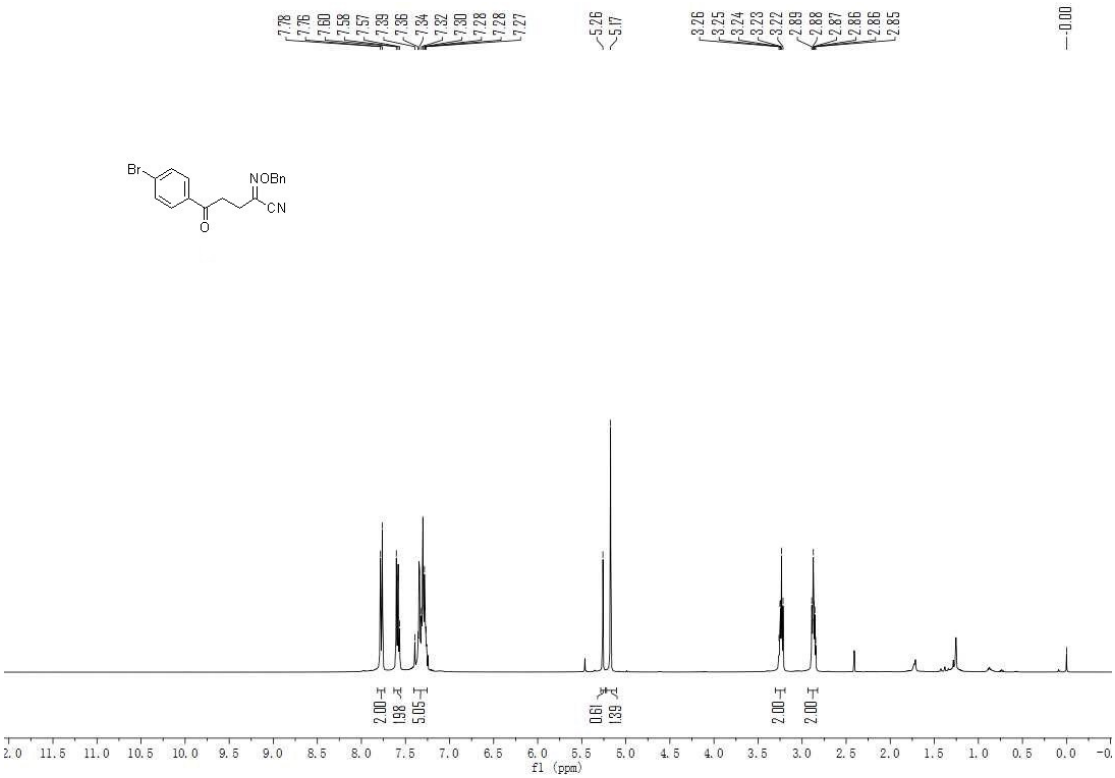
^{1}H NMR spectrum of 3an



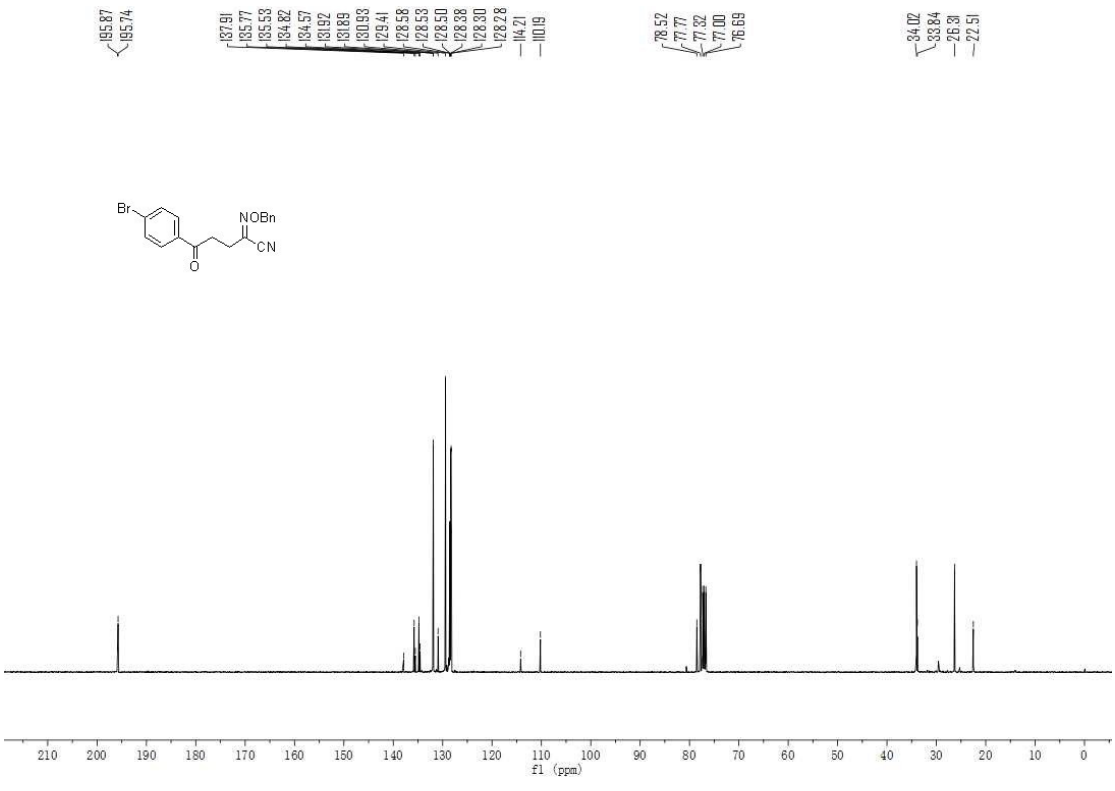
^{13}C NMR spectrum of 3an



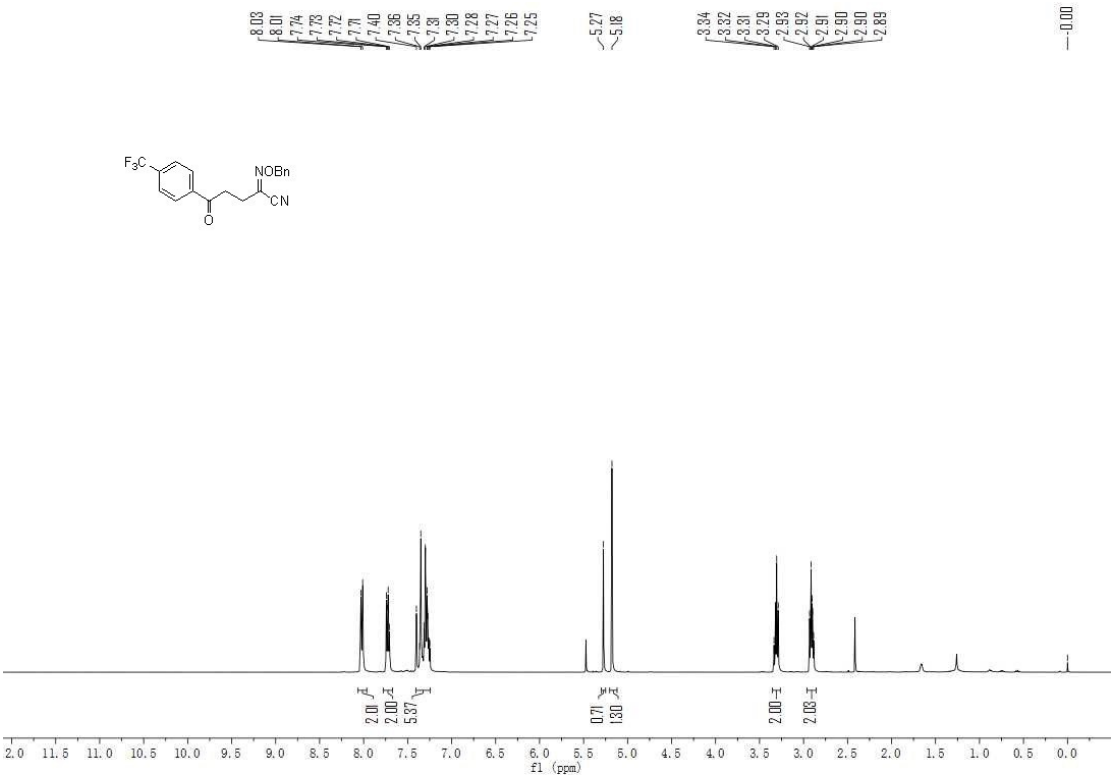
^{1}H NMR spectrum of 3ao



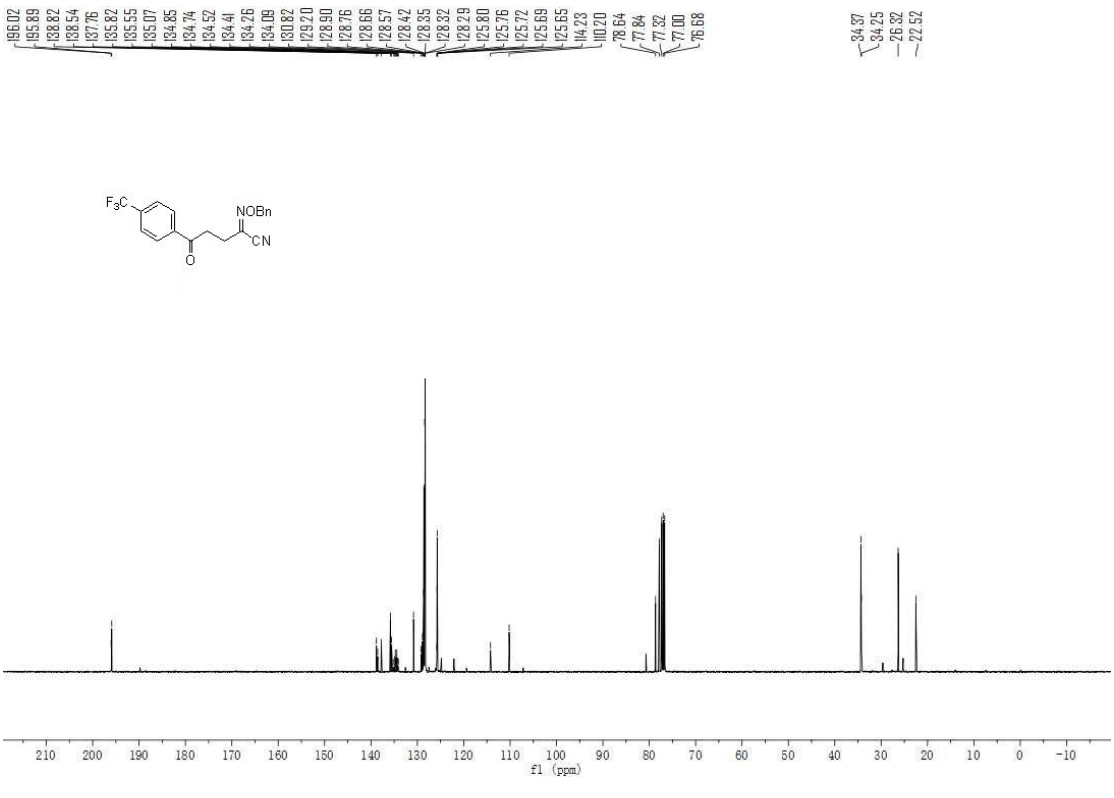
^{13}C NMR spectrum of 3ao



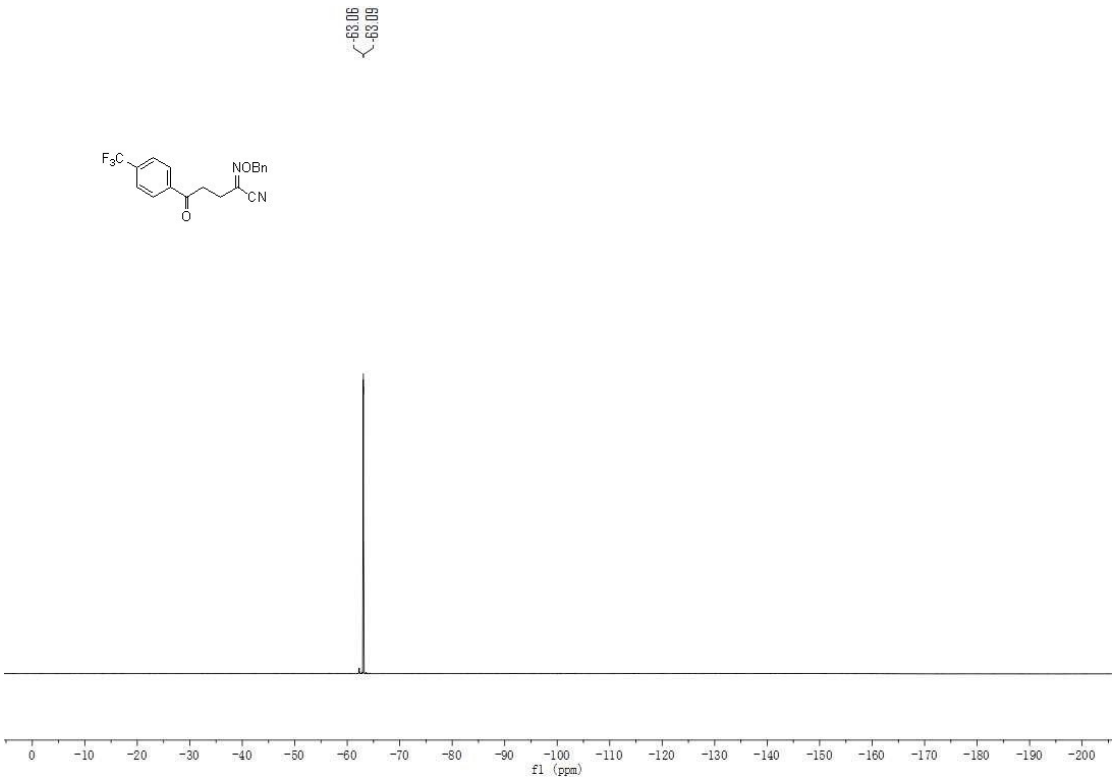
^{1}H NMR spectrum of 3ap



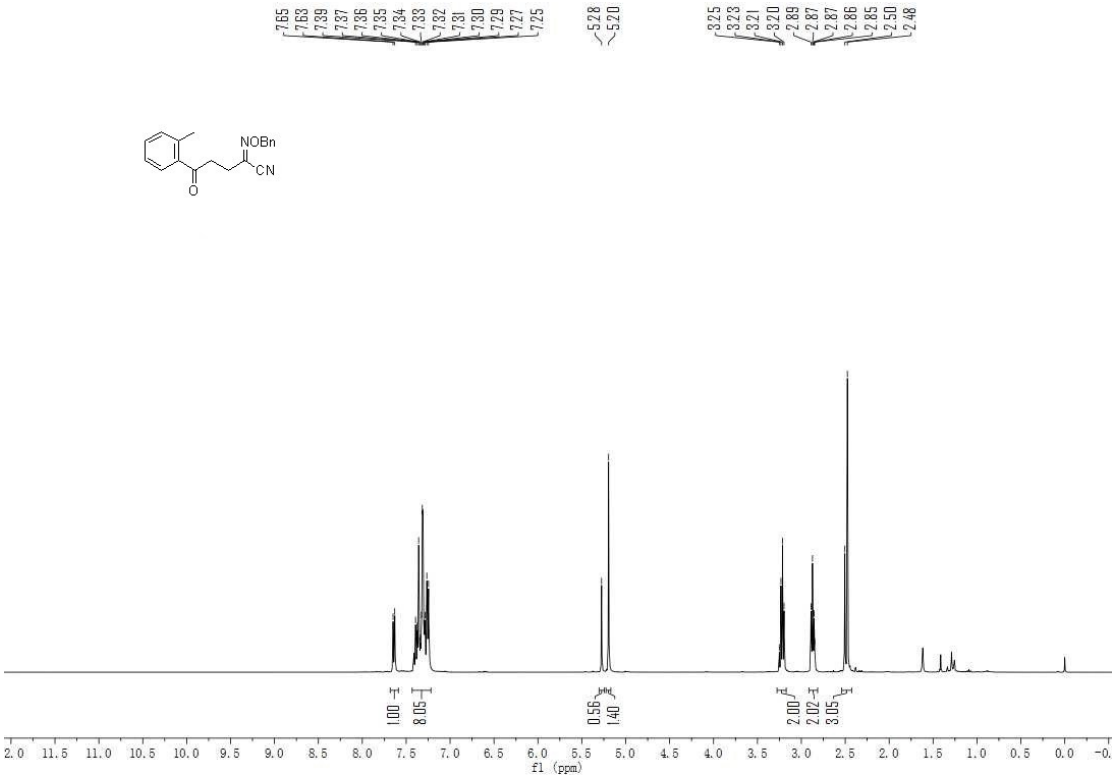
^{13}C NMR spectrum of 3ap



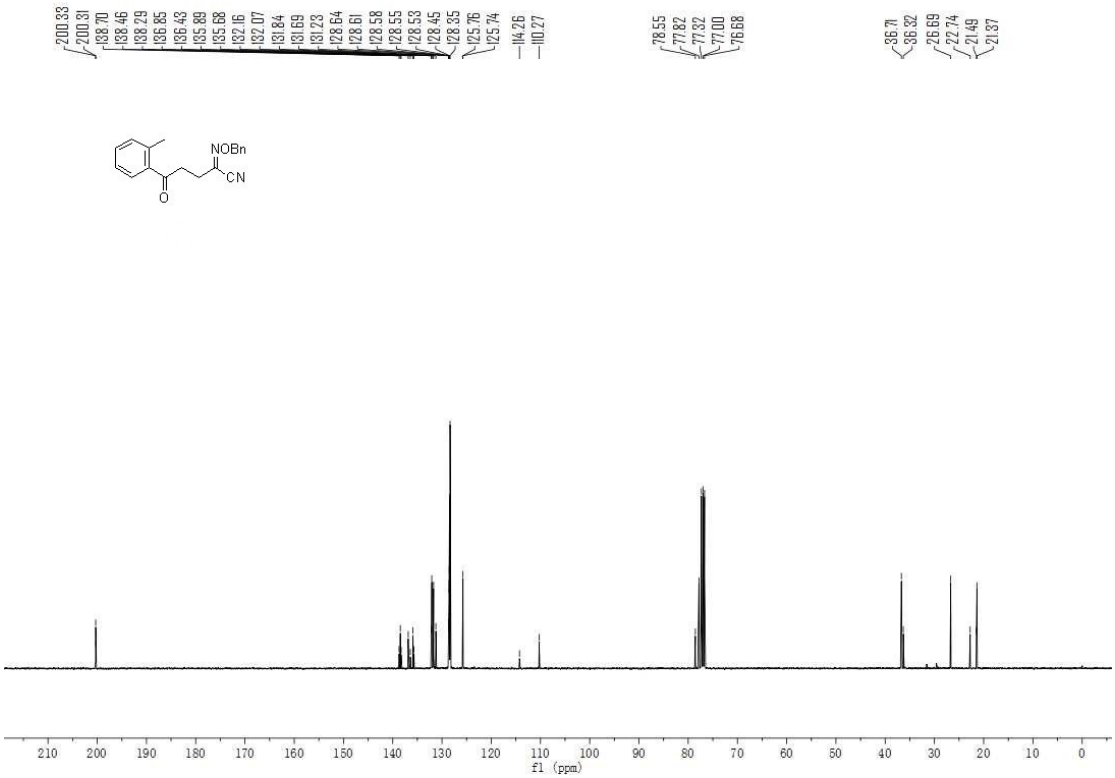
^{19}F NMR spectrum of 3ap



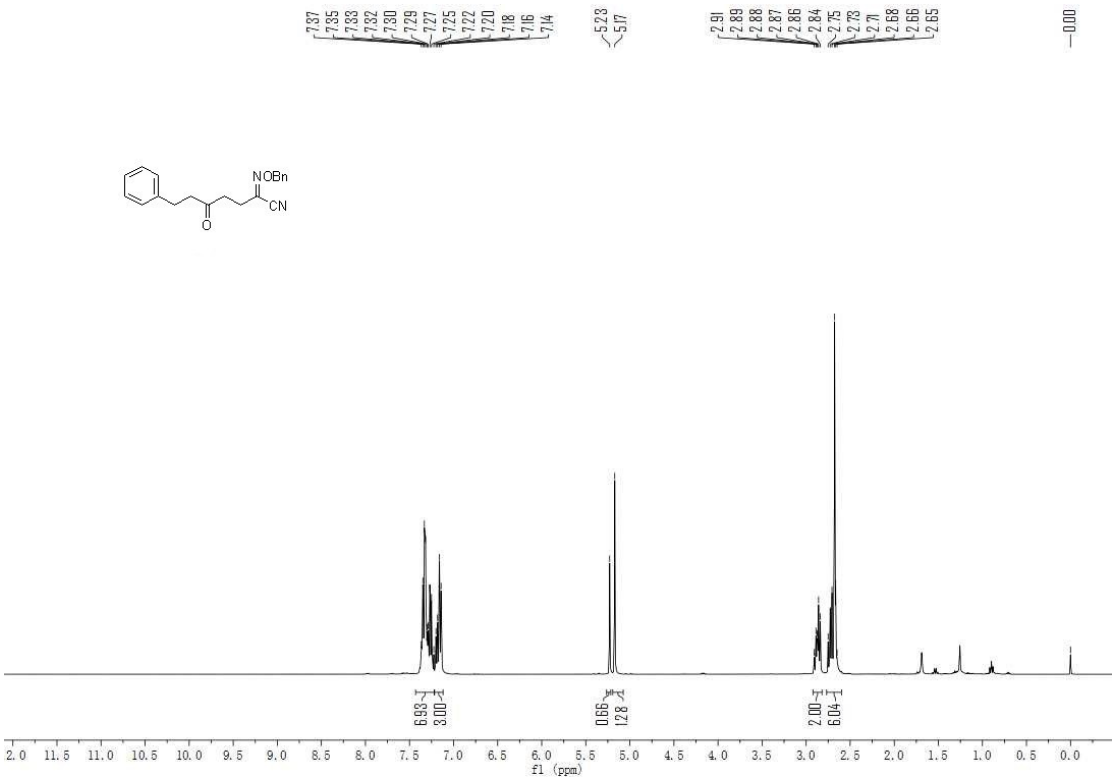
^{1}H NMR spectrum of 3aq



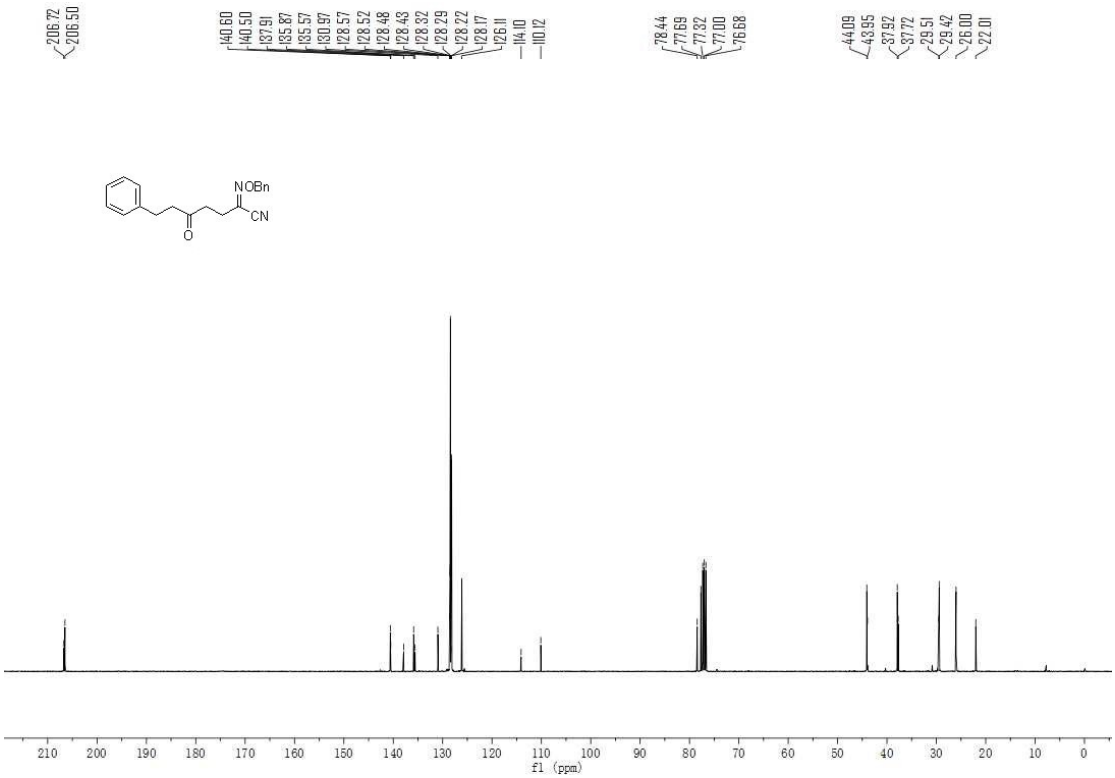
^{13}C NMR spectrum of 3aq



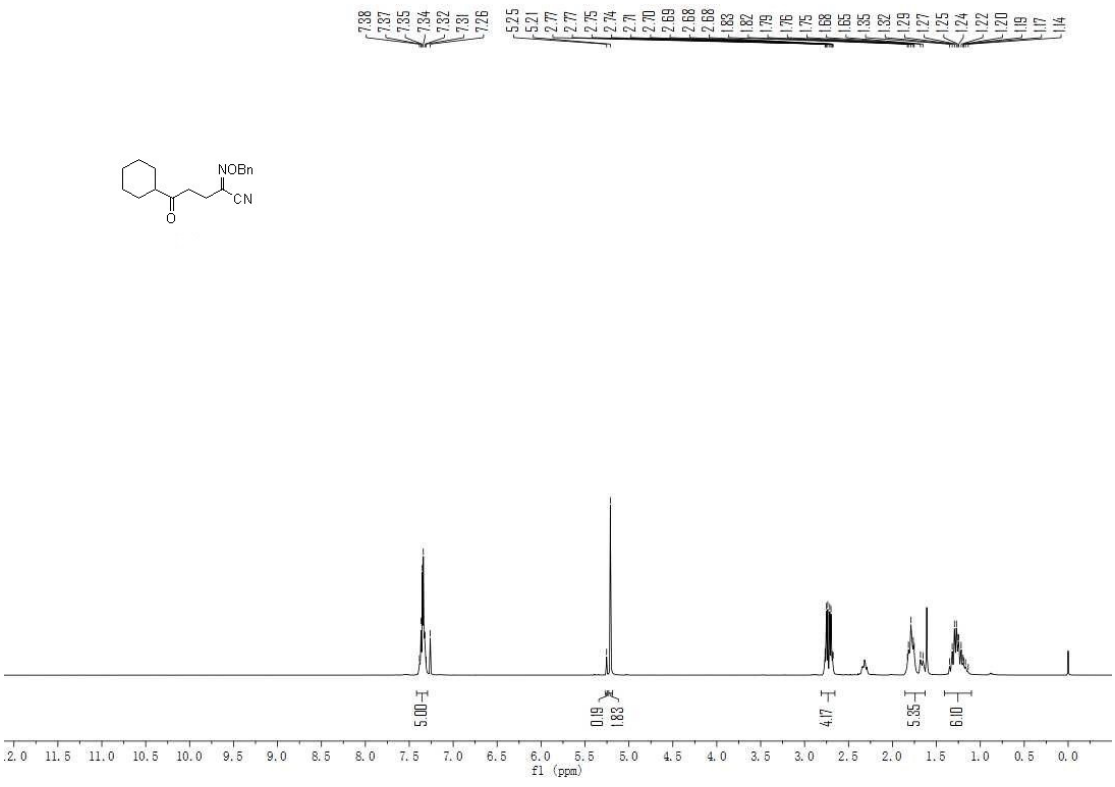
^{1}H NMR spectrum of 3ar



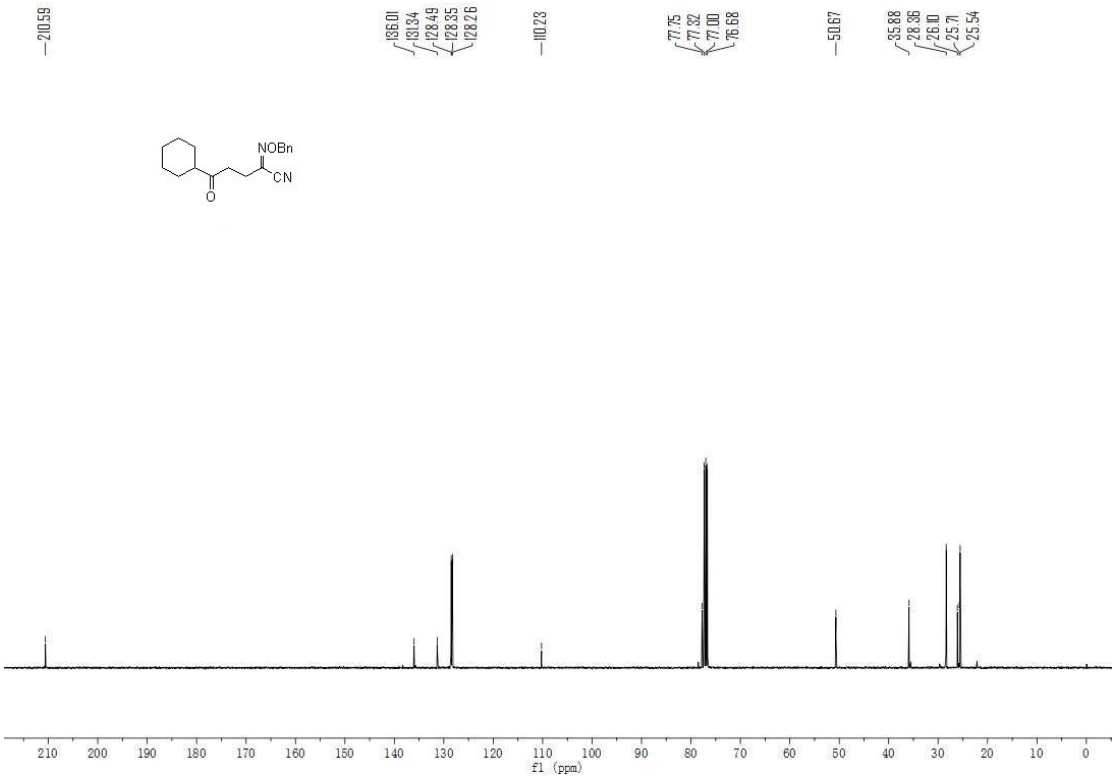
^{13}C NMR spectrum of 3ar



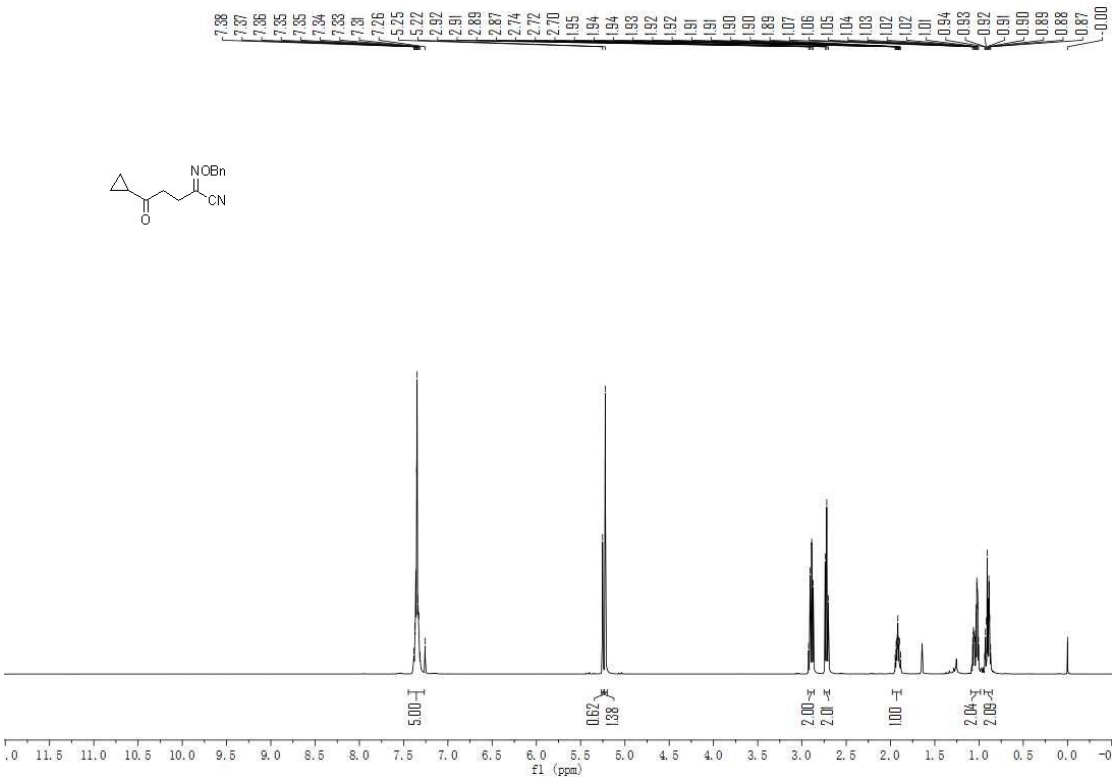
^{1}H NMR spectrum of 3as



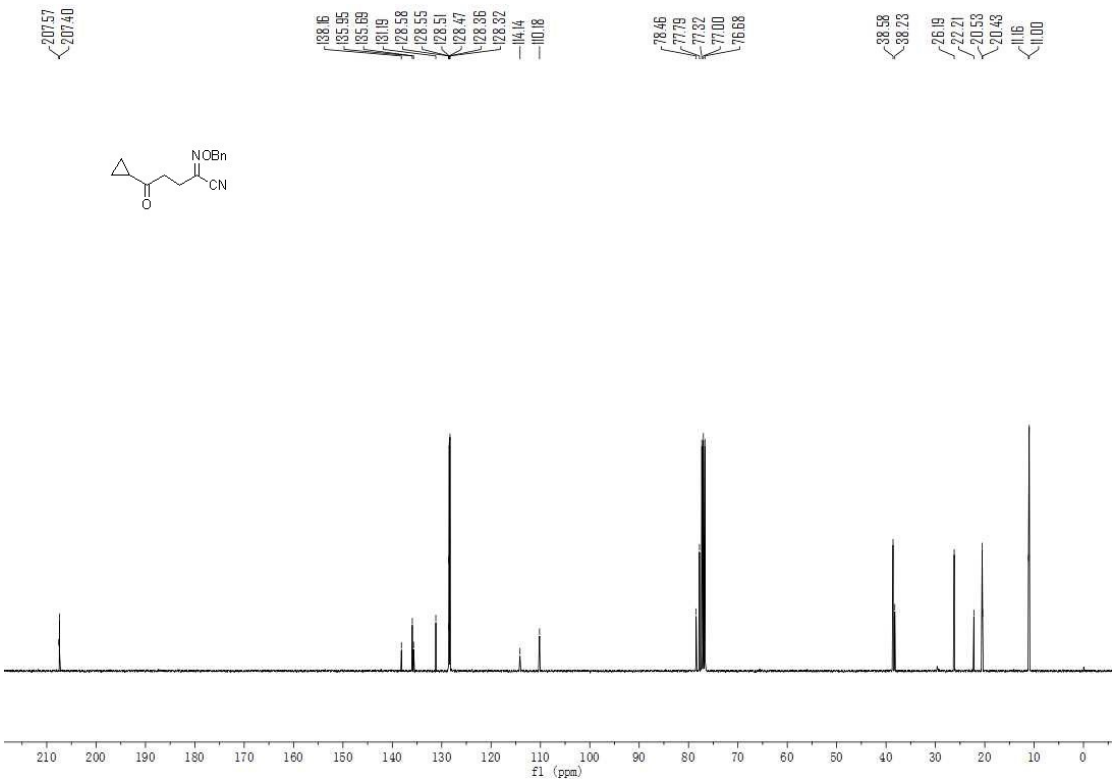
^{13}C NMR spectrum of 3as



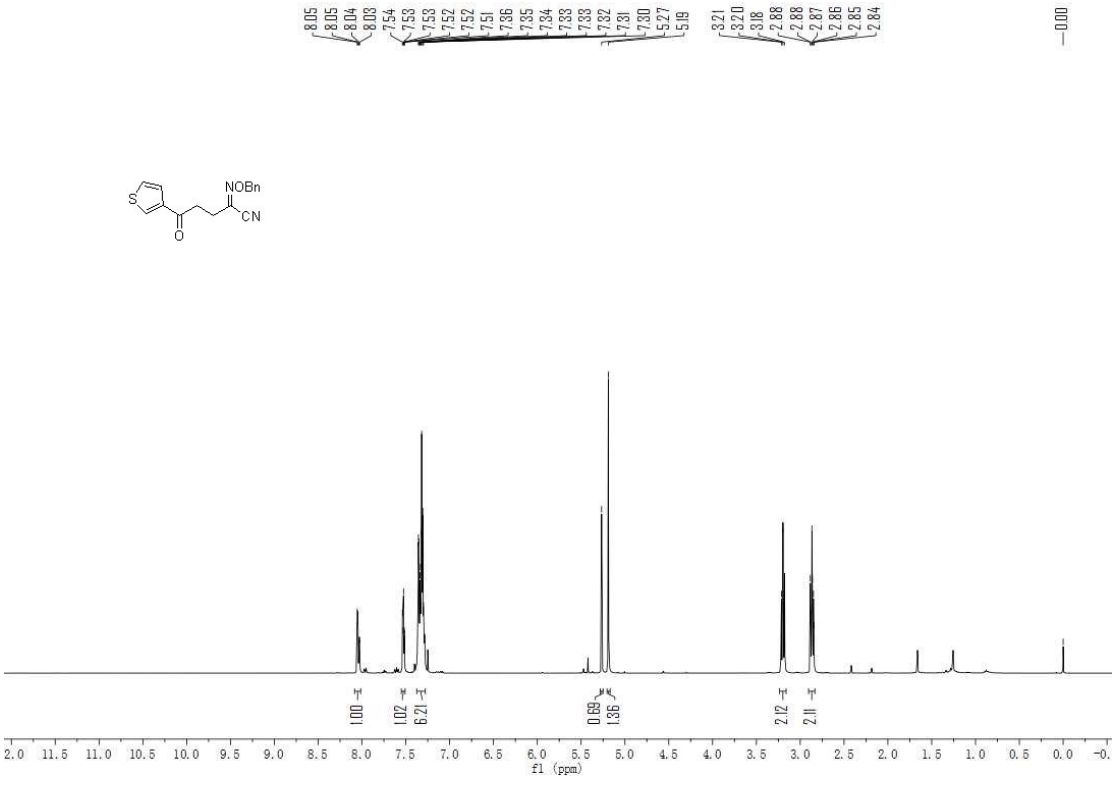
^{1}H NMR spectrum of 3at



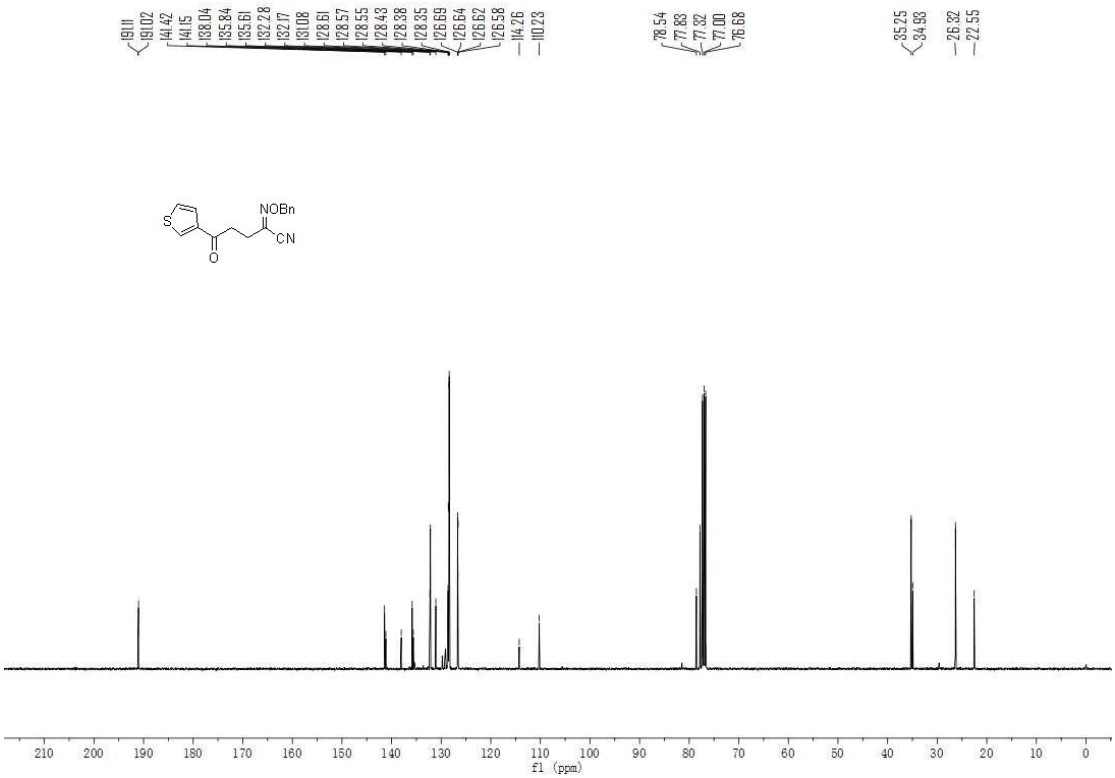
^{13}C NMR spectrum of 3at



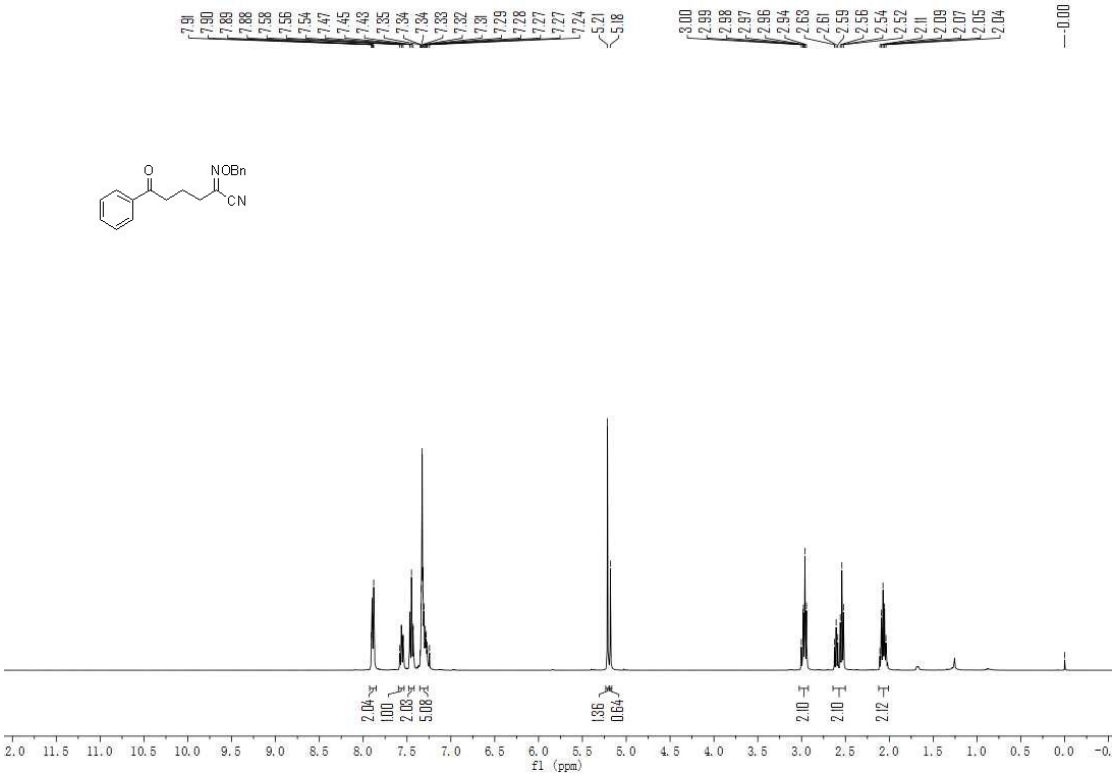
^{1}H NMR spectrum of 3au



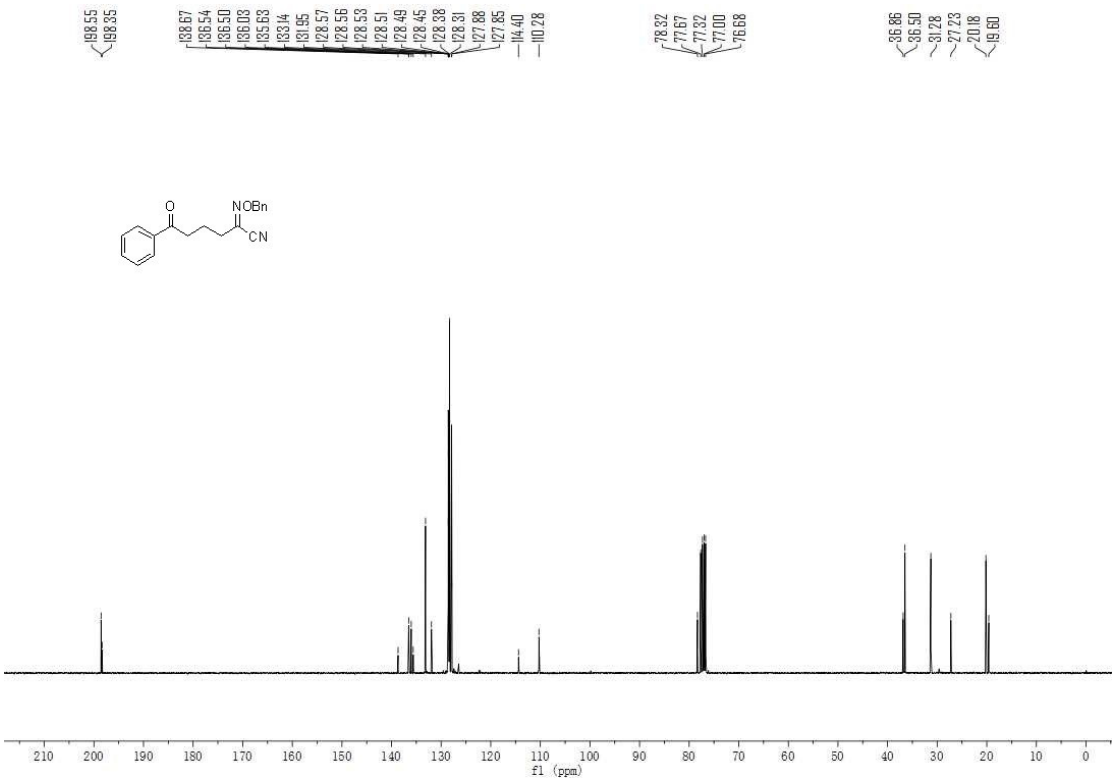
^{13}C NMR spectrum of 3au



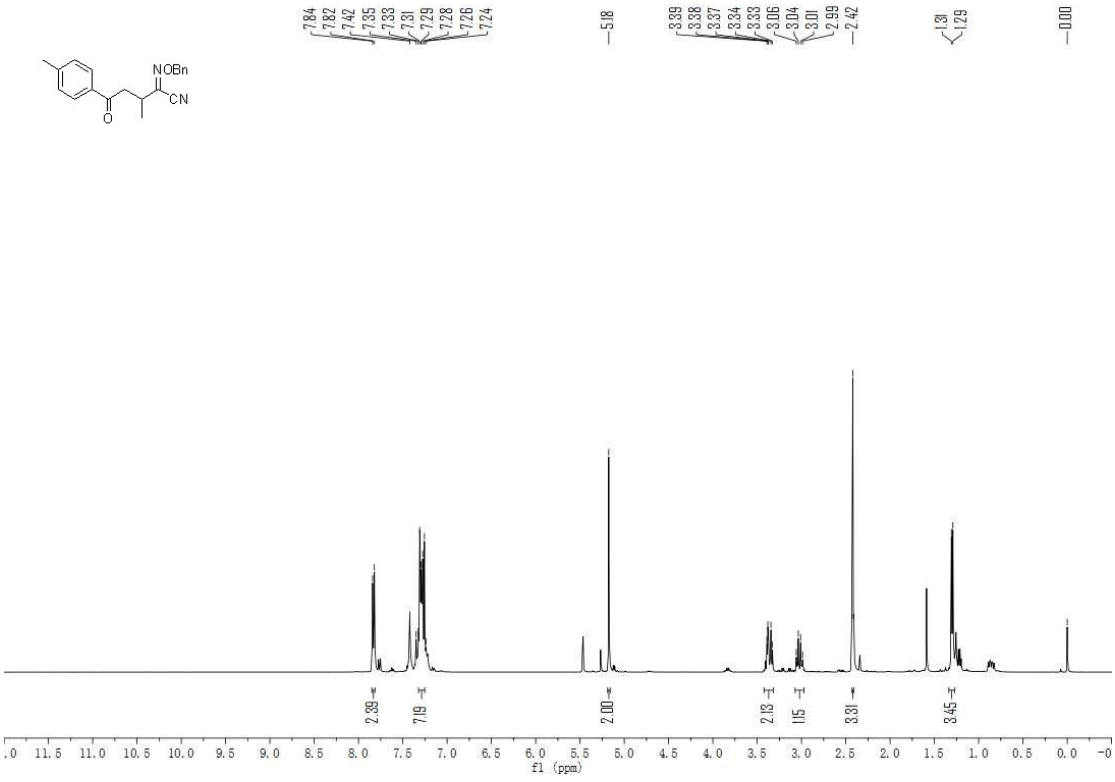
^{1}H NMR spectrum of 3av



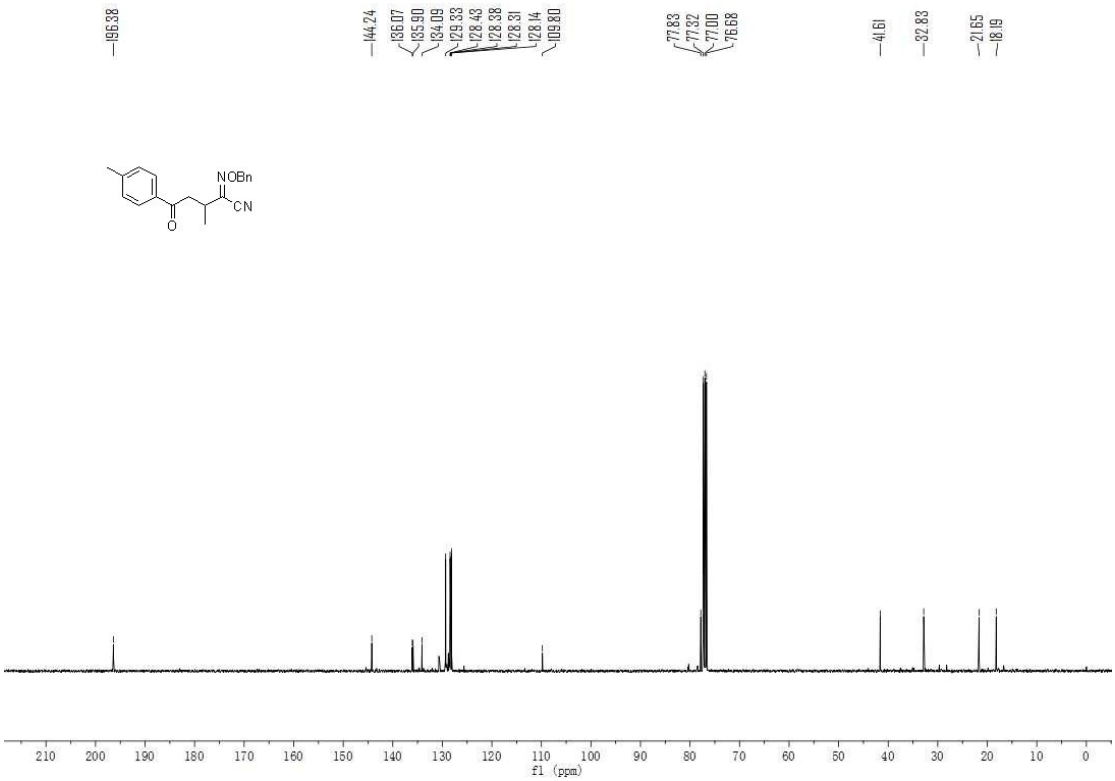
^{13}C NMR spectrum of 3av



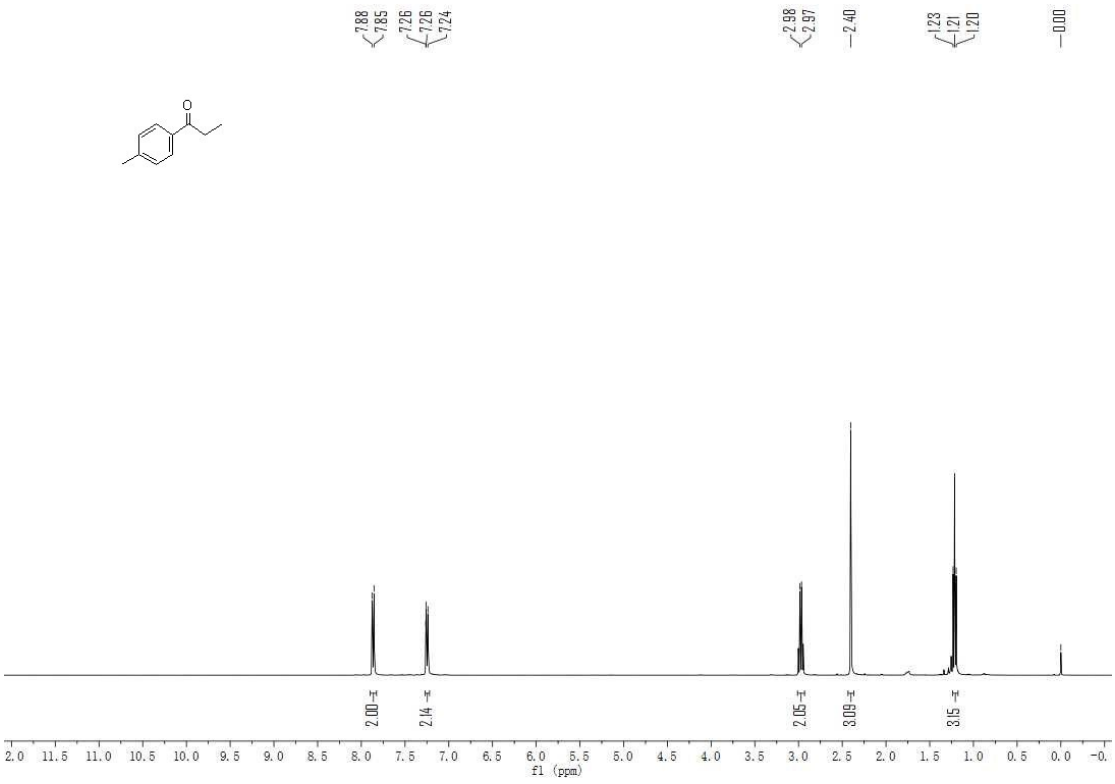
^{1}H NMR spectrum of 3aw



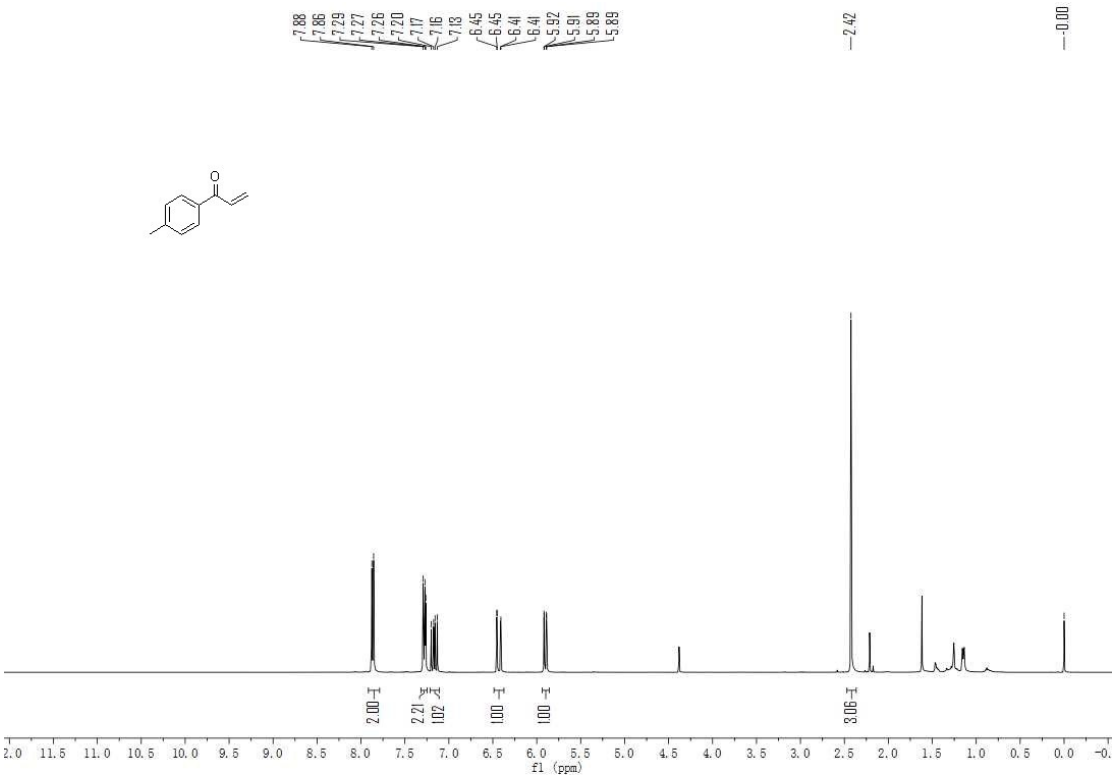
^{13}C NMR spectrum of 3aw



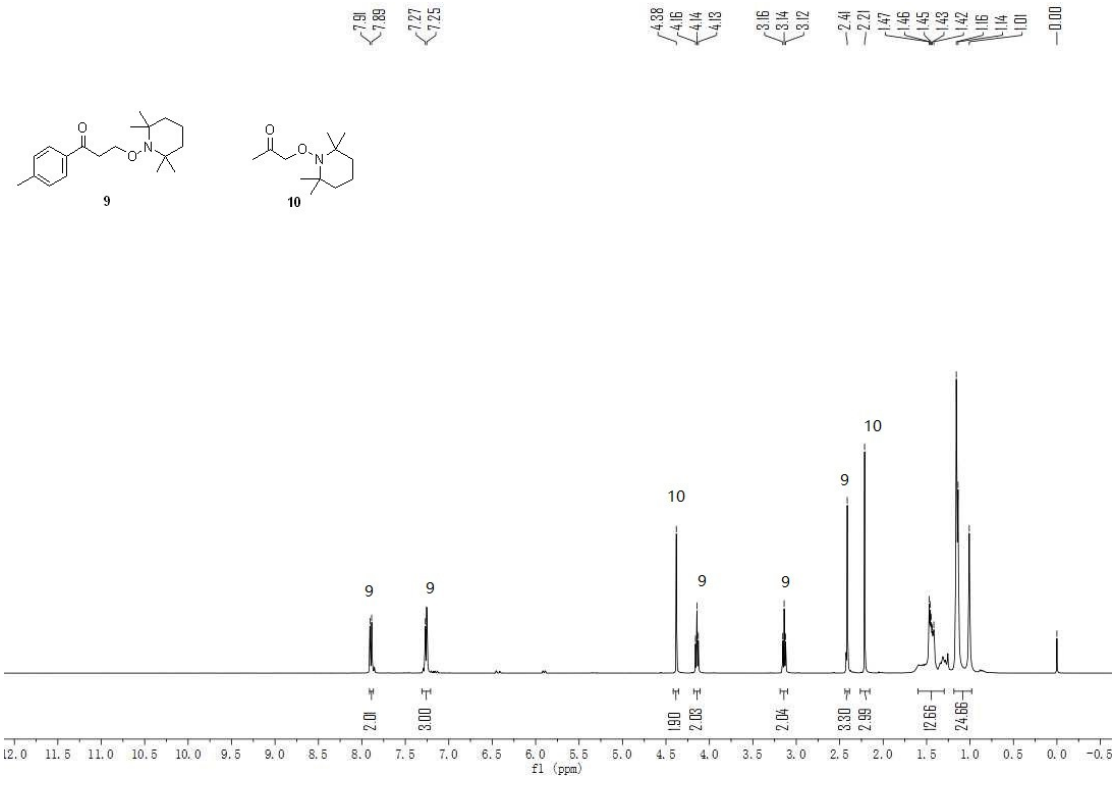
^{1}H NMR spectrum of 7



^{1}H NMR spectrum of 8



^{1}H NMR spectrum of 9 and 10



^{1}H NMR spectrum of 11