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Support information

Visible-light induced three-component reaction of α-aminobutyronitrile synthesis by C-C bond formation using quantum dots as photocatalyst

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1. Synthesis of CdSeS/CdZnSeS(Al)/ZnS QDs

Chemicals.
Cadmium acetate dihydrate ($Cd(Ac)_2.2H_2O$, 98%), zinc acetate ($Zn(Ac)_2$, 99.99%), selenium power (200 mesh, 99.999%), 1-octadecene (ODE, 90%), and oleic acid (99% or 90%) were purchased from either Aldrich or Alfa Aesar. Trioctylphosphine (TOP) and tributylphosphine (TBP) were purchased from Acros. Sulfur powder (S, 99.98%) and oleylamine (98+%) were purchased from Aldrich. All organic solvents were obtained from Sinopharm Reagents. All chemicals were used directly without any further purification.

Synthesis of CdSe Sally quantum dots. Se-S-ODE solution was prepared by dissolving sulfur powder (0.032g, 0.001mol) and selenium power (0.079g, 0.001mol) in ODE (5 mL) by sonication. In a typical synthesis, $Cd(Ac)_2.2H_2O$ (0.53g, 0.002mol) and oleic acid (1.4g, 0.005mol)were loaded into a 100 mL three-neck flask with 40 mL of ODE. After stirring and argon bubbling for 10 min, the mixture was heated to 200 °C to obtain a colorless solution. The temperature was heated to 250 °C, and 5 mL of Se-S-ODE was injected quickly into the hot solution. The reaction temperature was kept at 250 °C for further growth for 10 min. For precipitation of the core QDs from the reaction solution, a mixed solution of acetone and methanol (volume ratio 3:1) was prepared as the precipitation solution. The crude reaction solution was loaded into a 500 mL vial. The precipitation solution (100 mL) was added into the vial. The vial was rapidly placed in a centrifugation and centrifuged at 4000 rpm for 3 min. The supernatant was removed quickly and the nanocrystal precipitate was dissolved in 5 mL of ODE.

Synthesis of CdSeS/CdZnSeS(Al)/ZnS core/shell quantum dots. S-TBP solution was prepared by dissolving sulfur powder (0.64g, 0.002mol) in TBP (10 mL) by sonication. Se-S-TOP solution was prepared by dissolving sulfur powder (0.32g, 0.01mol) and selenium power (0.79g, 0.01mol) in TOP (10 mL) by sonication. In a typical synthesis, $Zn(Ac)_2$ (1.83g, 0.01mol) and oleic acid (1.4g, 0.05mol) were loaded into a 100 mL three-neck flask with 20mL of ODE. After stirring and argon bubbling for 10 min, the mixture was heated to 200 °C to obtain a colorless solution. Purified CdSeS core QDs dissolved in 0.5 mL ODE was injected into the reaction solution. The temperature was heated to 300 °C, 1 mL of Se-S-TOP and 1ml cadmium oleate-ODE (0.2mmol/mL) solution was injected quickly into the hot solution. The reaction temperature was kept at 300 °C for further growth for 10 min. And then 4 mL S-TBP was loaded into a syringe and drop wise added to the reaction flask at 20 mL/h. After the S-TBP was added, the reaction solution was allowed to react for 5 min. And then the reaction was stopped by allowing the reaction mixture to cool in air for purification. For precipitation of the core QDs from the reaction solution, a mixed solution of acetone and methanol (volume ratio 3:1) was prepared as the precipitation solution. The crude reaction solution was loaded into a 500 mL vial. The precipitation solution (100 mL) was added into the vial. The vial was rapidly placed in a centrifugation and centrifuged at 4000 rpm for 3 min. The supernatant was removed quickly and the nanocrystal precipitate

was dissolved in 5 mL of toluene.

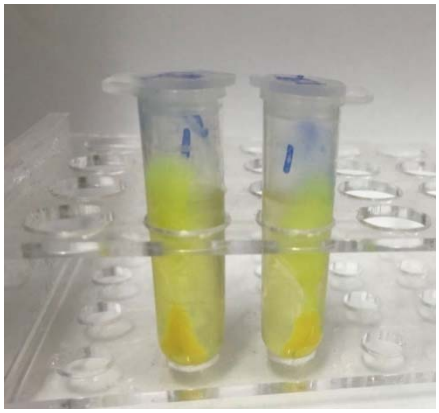
Quantify the QDs. The total number of core/shell QDs was the same with the one of core QDs. The density of CdSe and CdS were 5810 kg/m^3 and 4820 kg/m^3. In our experiment, the proportion of Se and S was 1:1. Thus it was reasonable that the density of bulk of CdSeS was about 5315 kg/m^3. And the size of CdSeS was about 3 nm. Therefore the mass of one CdSeS quantum dot was about 6×10^{-19}g. the molecular mass of CdSeS (Se:S=1:1) in our experiment was about 167. In other words, the molar weight of Cd-Se-S in one quantum dot was about 4.4×10^{-24}mol. In our experiment, if the reaction progress was completely, the total molar weight of Cd-Se-S was about 0.002mol. Combined with Avogadro constant, the total molar weight of CdSeS was 7.5×10^{-5} mol. Considering the dose of CdSeS for core/shell QDs, the total molar weight of core/shell QDs was about 7.5×10^{-6}mol in 10mL tolune. Considering that the density is the bulk density and the reaction is complete, the value is too large. So, the concentration of quantum dot solution is 7.5×10^{-7}mol/L. We use 100uL of QDs into the reaction solution (1.5mL), so the quantum dot concentration in the reaction solution is about 5×10^{-5}mol/L. It should be noted that the concentration derived by this computation is approximately and greater than the actual concentration, so that the TON of this reaction must be greater than what we have reported.

2. General Procedure for Synthesis of Products 4

To three 4 mL vials respectively equipped with a Teflon septum and magnetic stir bar were added 0.5 mL H_2O (1.5 mL H_2O in total), **1** (0.03 mmol per bottle, 0.09 mmol in

total), **2** (0.03 mmol per bottle, 0.09 mmol in total), than added 1.5 mL toluene (4.5 mL toluene in total), **3** (0.18 mmol per bottle, 0.54 mmol in total) and CdSeS/CdZnSeS(Al)/ZnS QDs (100uL per bottle). The solution was purged with argon gas for 20 minutes irradiated with two 3W blue LEDs. After 24 hours, add 10 mL of acetone to precipitate and centrifuge to remove the QDs. Take the organic layer for concentration. The crude mixture was subjected to silica gel (ethyl acetate/petroleum ether 1:10) flash column chromatography, anhydrous magnesium sulfate drying, concentration in vacuum and purification to obtain the desired product **4**.

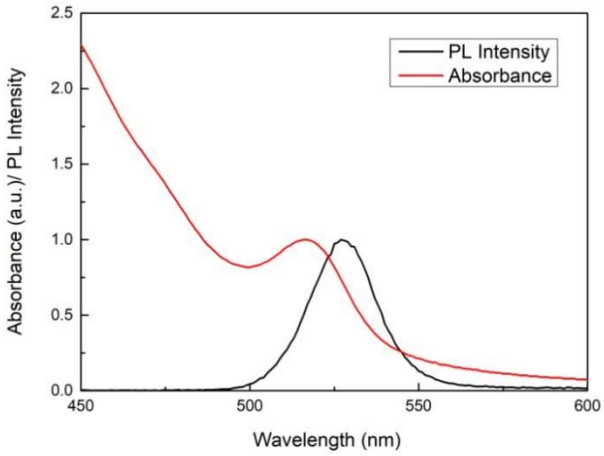
3. Recycling of quantum dots



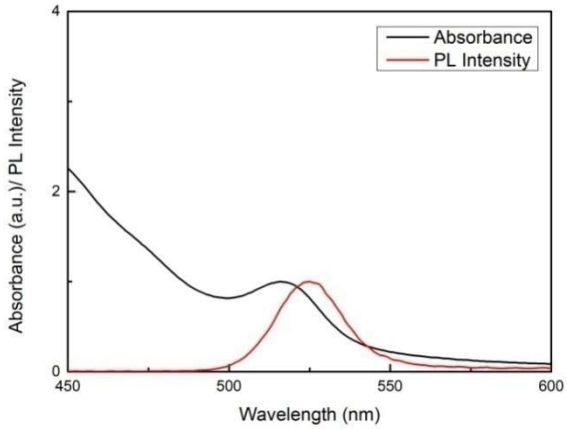
Reutilization of the core/shell quantum dots. For reutilization of the QDs from the catalysis solution, a simple procedure was applied to recover their PL properties. Briefly, $Zn(Ac)_2$ (0.366g, 0.002mol) and oleic acid (1.4g, 0.005mol) were loaded into 25mL three neck flask with 5 mL of ODE. After stirring and argon bubbling for 10 min, the mixture was heated to 180 °C to obtain a colorless solution. Into this mixture was injected 1 mL of TBP. The core/shell QDs from the catalysis solution was dissolved in 0.5 mL of ODE and injected into the flask. The mixture was heated to 280 °C and kept for five minutes. And then the reaction was stopped by allowing the reaction mixture to cool in air for purification. The crude reaction solution was loaded into a 50 mL vial. Acetone solution (20 mL) was added into the vial. The vial was rapidly placed in a centrifugation and centrifuged at 4000 rpm for 3 min. The supernatant was removed quickly and the nanocrystal precipitate was dissolved in 1 mL of toluene. To 4 mL vials respectively equipped with a Teflon septum and magnetic stir bar were added 0.5 mL H_2O, **1** (0.03mmol per bottle, 0.09mmol in total), **2** (0.03mmol), than added 1.5 mL toluene and **3** (0.18mmol), the recovered QDs. The solution was purged with argon gas for 20 minutes irradiated with two 3W blue LEDs, TLC is used to confirm that the reaction is complete, add 10 mL of acetone to precipitate and centrifuge to remove the QDs. Take the organic layer for concentration. The crude mixture was subjected to silica gel (ethyl acetate/petroleum ether 1:10) flash column chromatography, anhydrous magnesium sulfate drying, concentration in vacuum and purification to obtain the desired product **4**.

entry	Time(h)	Yield(%)
1	24	98
2	24	94
3	72	88

4. Absorption and photoluminescence spectra of CdSeS/CdZnSeS(Al)/ZnS QDs before and after three reactions

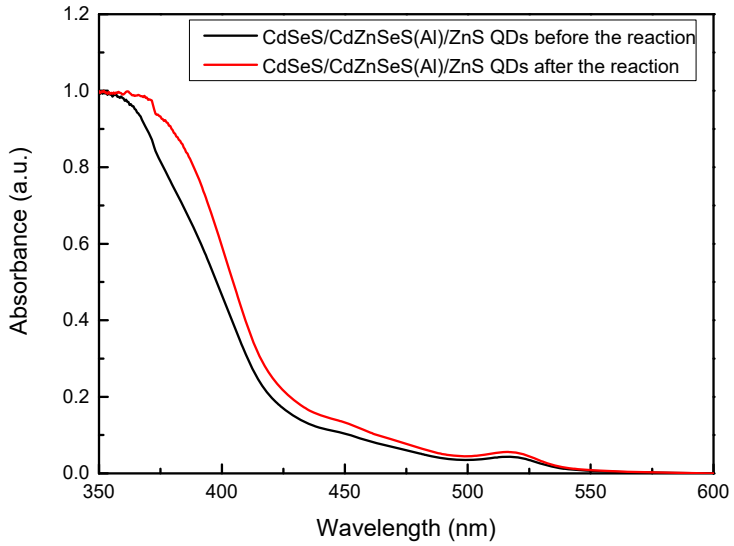


Absorption and photoluminescence spectra of CdSeS/CdZnSeS(Al)/ZnS QDs before three reactions



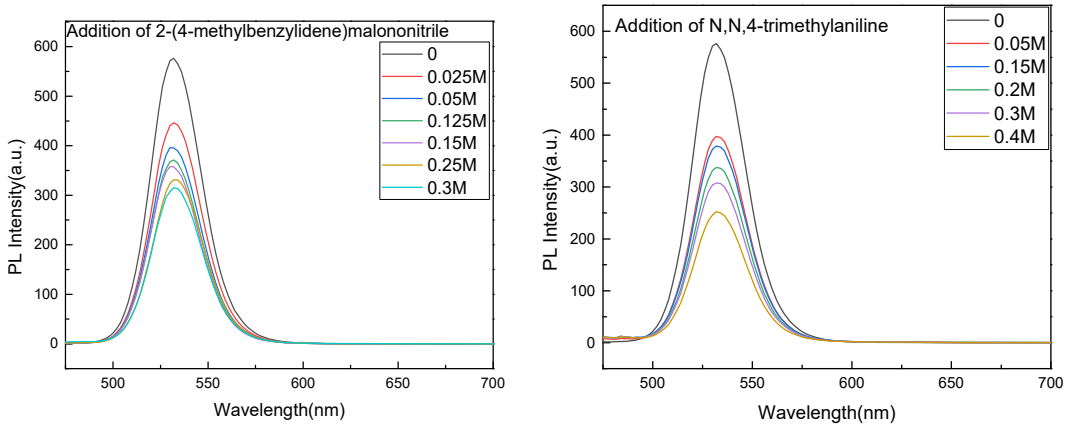
Absorption and photoluminescence spectra of CdSeS/CdZnSeS(Al)/ZnS QDs after three reactions

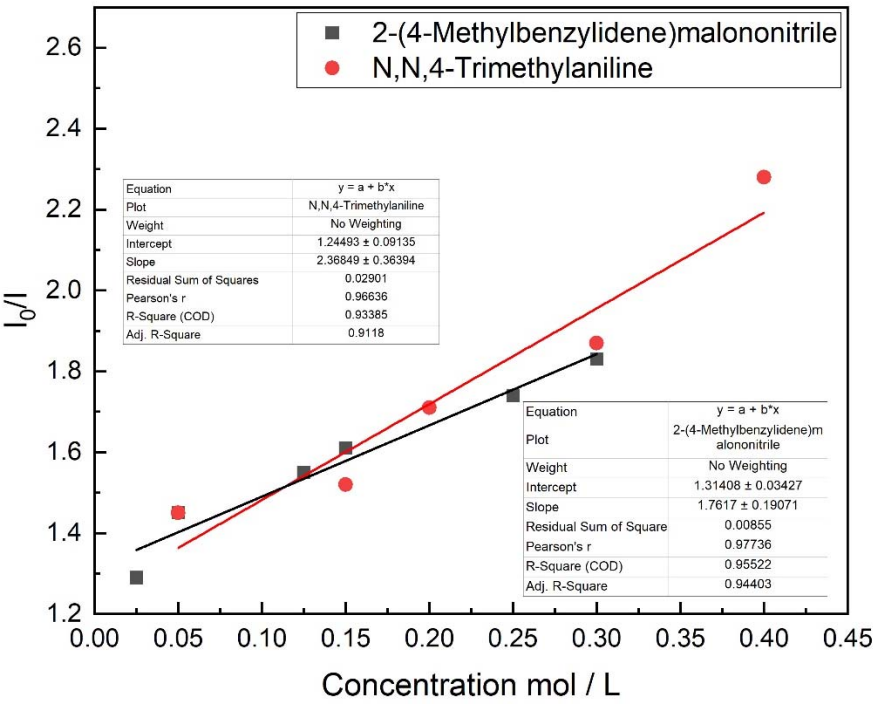
5. UV image of CdSeS/CdZnSeS(Al)/ZnS QDs before and after three reactions which was measured in toluene solution



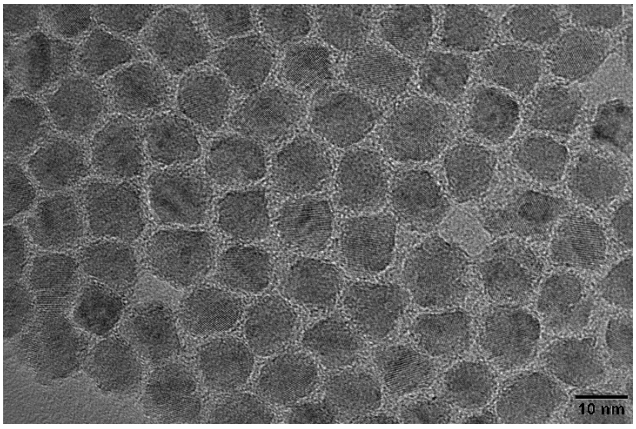
6. Fluorescence Quenching Studies

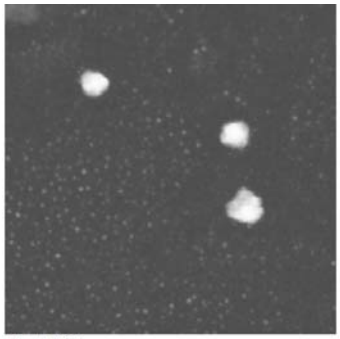
Fluorescence quenching experiments were performed on an Edinburgh instruments FLS920 spectrofluorometer with an excitation wavelength of 450 nm. QDs diluent was prepared by dissoluting 200uL quantum dots in 10mL toluene, adding different qualities of p-methylbenzene methylene malonitrile, 4, N, N-trimethylaniline and CH_3COOCs, 100uL QDs diluent, and then diluted to 10mL with toluene. After testing, both p-methylbenzene-methylene and 4, N, N-trimethylaniline can quench QDs, and 4, N, N-trimethylaniline is a better quench agent.

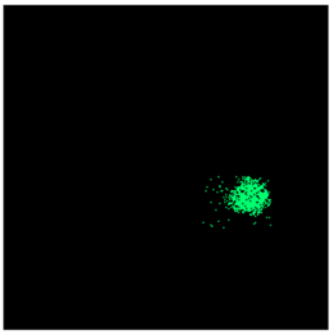


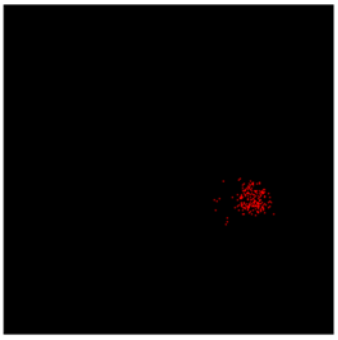


7. HRTEM-EDS mapping results

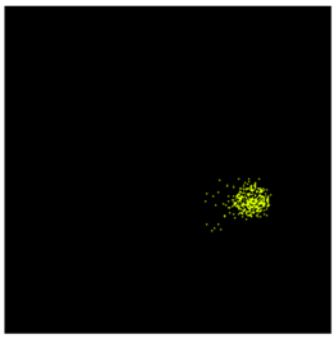



电子图像 1

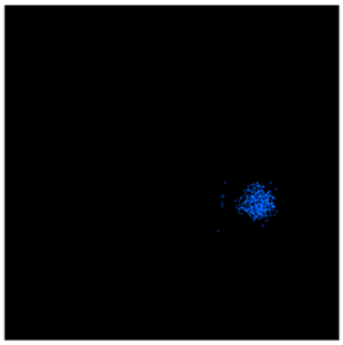

Zn Ka1



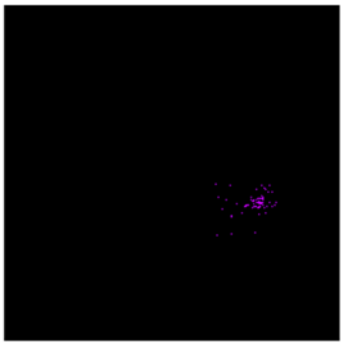
Al Ka1



S Ka1

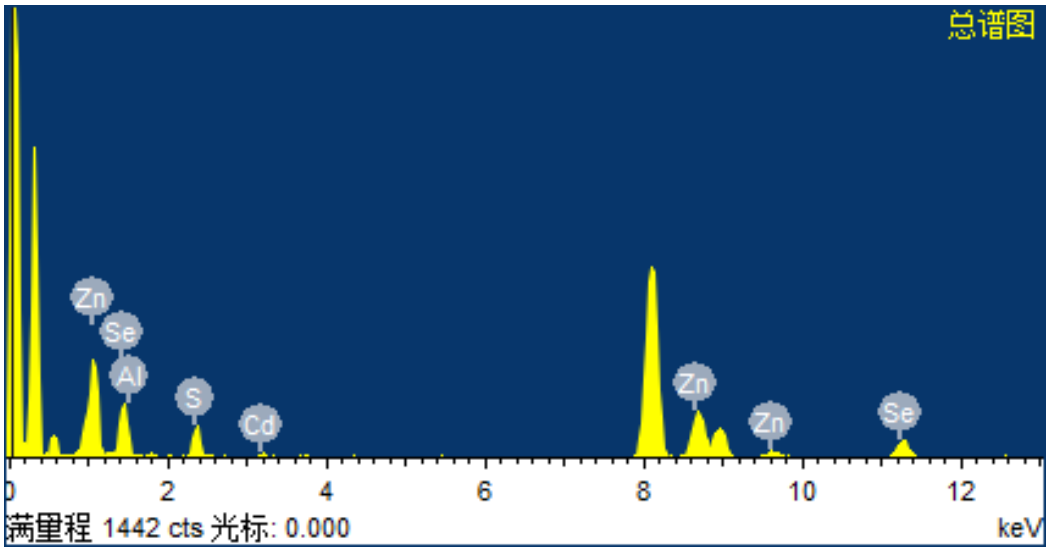


Se Ka1

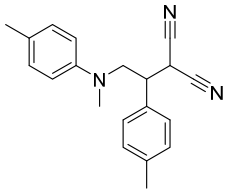


Cd La1

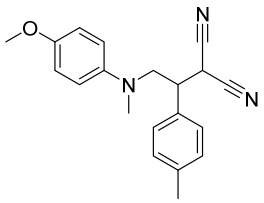
Element	Weight percentage	Atomic percent
Al K	-0.20	-0.46
S K	14.42	27.42
Zn K	50.34	46.95
Se K	29.84	23.05
Cd L	5.60	3.04
Total quantity	100.00	



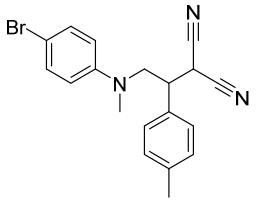
8. Characterization Data



2-(2-(methyl(p-tolyl)amino)-1-(p-tolyl)ethyl)malononitrile（4a）:The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (98%, 25.9mg). The compound data was in agreement with the literature (*J. Am. Chem. Soc.*, 2013, **135**, 1823-1829.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.2 Hz, 3H), 7.23 (s, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.26 (d, *J* = 4.3 Hz, 1H), 3.79 (dt, *J* = 15.9, 8.0 Hz, 1H), 3.58 (ddd, *J* = 15.1, 12.5, 4.9 Hz, 2H), 2.94 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 139.3, 131.9, 130.1, 128.6, 128.0, 114.7, 112.4, 111.9, 55.7, 44.6, 41.4, 27.1, 21.2, 20.3.

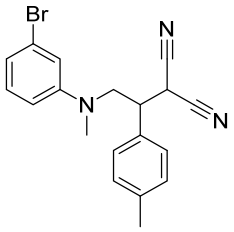


2-(2-((4-methoxyphenyl)(methyl)amino)-1-(p-tolyl)ethyl)malononitrile（4b）：The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (>99%, 30.9mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.19 (m, 2H), 6.91 – 6.80 (m, 4H), 4.38 (d, *J* = 3.7 Hz, 1H), 3.78 (s, 3H), 3.71 – 3.65 (m, 1H), 3.55 – 3.44 (m, 2H), 2.89 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9, 143.5, 139.2, 131.9, 130.0, 128.0, 117.7, 115.0, 112.5, 111.9, 56.5, 55.7, 44.5, 42.4, 27.1, 21.2. HRMS (ESI-TOF) for $C_{20}H_{21}N_3O$ ($[M+H]^+$): calcd.320.1757; found: 320.1760. IR (neat): ν(cm^{-1})=3133, 2999, 1607, 1390.

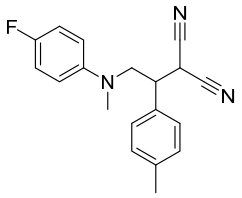


2-(2-((4-bromophenyl)(methyl)amino)-1-(p-tolyl)ethyl)malononitrile（4c）：The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (77%, 28.7mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 9.0 Hz, 2H), 7.27 – 7.20 (m, 4H), 6.64 (d, *J* = 9.0 Hz, 2H), 4.17 – 4.06 (m, 1H), 3.96 – 3.80 (m, 1H), 3.65 (dd, *J* = 15.0, 5.6 Hz, 1H), 3.59 – 3.50 (m, 1H), 2.91 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 139.5, 132.3, 131.8, 130.1, 129.0, 127.9, 115.2, 112.1, 111.8, 110.7, 55.4, 44.3, 40.7, 27.2, 21.2. HRMS (ESI-TOF) for $C_{19}H_{19}BrN_3$ ($[M+H]^+$):

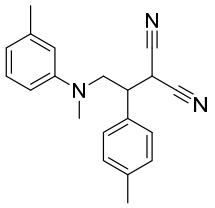
calcd.368.0757; found: 368.0760. IR (neat): ν(cm^{-1})=3133, 3019, 1620, 1505, 1403.



2-(2-((3-bromophenyl)(methyl)amino)-1-(p-tolyl)ethyl)malononitrile（4d）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (66%, 17.1mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.4 Hz, 1H), 7.21 (s, 4H), 7.13 (t, *J* = 8.1 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.87 (s, 1H), 6.69 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.12 (d, *J* = 4.9 Hz, 1H), 3.90 (dt, *J* = 12.4, 6.2 Hz, 1H), 3.69 (dd, *J* = 15.1, 5.7 Hz, 1H), 3.61 – 3.52 (m, 1H), 2.93 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 139.5, 131.7, 130.8, 130.1, 129.0, 127.9, 123.8, 121.3, 116.3, 111.8, 55.2, 44.4, 40.6, 27.2, 21.2. HRMS (ESI-TOF) for $C_{19}H_{19}BrN_3$ ($[M+H]^+$): calcd.368.0757; found: 368.0754. IR (neat): ν(cm^{-1})=3133, 3006, 1588, 1537, 1396.

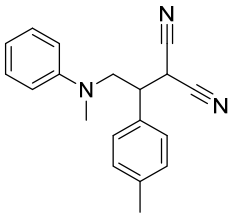


2-(2-((4-fluorophenyl)(methyl)amino)-1-(p-tolyl)ethyl)malononitrile（4e）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (86%, 26.4mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 10.7 Hz, 2H), 7.09 – 6.98 (m, 2H), 6.88 – 6.73 (m, 2H), 4.31 (d, *J* = 4.4 Hz, 1H), 3.85 (dd, *J* = 14.3, 9.9 Hz, 1H), 3.65 – 3.49 (m, 2H), 2.96 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 155.5, 145.7, 139.3, 132.1, 130.1, 129.2, 28.0, 116.1,115.9,112.6,56.2, 44.3, 41.2, 27.2, 21.2.^{19}F NMR (377 MHz, $CDCl_3$). δ -125.69. HRMS (ESI-TOF) for $C_{19}H_{19}FN_3$ ($[M+H]^+$): calcd.308.1558; found: 308.1569. IR (neat): ν(cm^{-1})=3153, 3006, 1671, 1620.

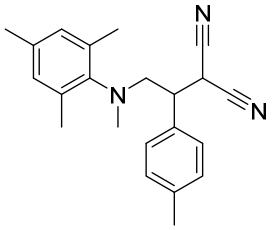


2-(2-(methyl(m-tolyl)amino)-1-(p-tolyl)ethyl)malononitrile（4f）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (81%, 21.8mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.1 Hz, 3H), 7.24 (s, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.65 (dd, *J* = 25.9, 7.7 Hz, 3H), 4.21 (d, *J* = 4.5 Hz, 1H), 3.86 (dd, *J* = 14.9, 10.2 Hz, 1H), 3.69 – 3.52 (m, 2H), 2.96 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 139.4, 131.9, 130.1, 129.5, 128.0, 119.7, 114.8,

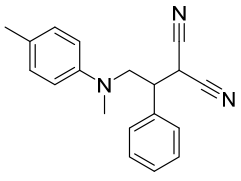
112.3, 111.9, 111.0, 55.4, 44.6, 40.9, 27.1, 21.9, 21.2. HRMS (ESI-TOF) for $C_{20}H_{21}N_3$ ($[M+H]^+$): calcd.304.1808; found: 304.1812. IR (neat): ν(cm^{-1})=3140, 3006, 1658, 1594, 1396.



2-(2-(methyl(phenyl)amino)-1-(p-tolyl)ethyl)malononitrile（4g）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (>99%, 29.7mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 3H), 7.22 (dd, *J* = 12.4, 10.5 Hz, 3H), 6.88 – 6.77 (m, 3H), 4.19 (d, *J* = 4.6 Hz, 1H), 3.87 (dd, *J* = 14.9, 10.1 Hz, 1H), 3.66 (dd, *J* = 14.9, 5.2 Hz, 1H), 3.58 (dt, *J* = 9.9, 4.9 Hz, 1H), 2.95 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 139.3, 131.9, 130.1, 129.6, 128.0, 118.8, 113.9, 112.3, 111.9, 55.5, 44.5, 40.8, 27.2, 21.2. HRMS (ESI-TOF) for $C_{19}H_{19}N_3$ ($[M+H]^+$):calcd.290.1652; found: 290.1653. IR (neat): ν(cm^{-1})=3140, 3006, 1665, 1594, 1396.

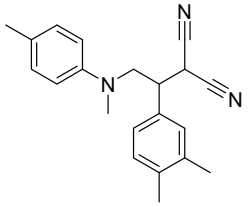


2-(2-(mesityl(methyl)amino)-1-(p-tolyl)ethyl)malononitrile（4h）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (86%, 31.2mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 2H), 4.52 (d, *J* = 4.3 Hz, 1H), 3.61 (dd, *J* = 13.5, 5.3 Hz, 1H), 3.44 (dd, *J* = 13.4, 10.5 Hz, 1H), 3.28 – 3.17 (m, 1H), 2.77 (s, 3H), 2.35 (s, 3H), 2.24 (d, *J* = 3.6 Hz, 6H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 139.0, 136.1, 135.6, 132.4, 130.3, 129.9, 128.2, 112.8, 111.7, 57.4, 45.7, 41.4, 27.1, 21.2, 20.7, 19.3. HRMS (ESI-TOF) for $C_{22}H_{25}N_3$ ($[M+H]^+$): calcd.332.2048; found:332.2123. IR (neat): ν(cm^{-1})=3140, 3012, 1601, 1473, 1409.

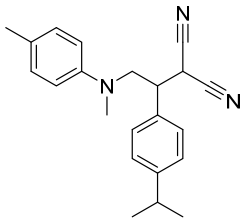


2-(2-(methyl(p-tolyl)amino)-1-phenylethyl)malononitrile（4i）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (>99%, 31.0mg). The compound data was in agreement with the literature (*J. Am. Chem. Soc.*, 2013, **135**, 1823-1829.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.34 (m, 5H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 4.29 (d, *J* = 4.3 Hz, 1H), 3.82

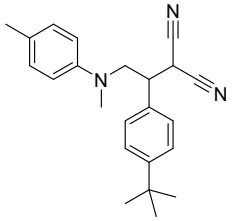
(dd, *J* = 14.4, 10.3 Hz, 1H), 3.61 (ddd, *J* = 15.1, 12.0, 4.8 Hz, 2H), 2.94 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 134.9, 130.1, 129.3, 128.6, 128.1, 114.7, 112.2, 111.8, 55.6, 44.8, 41.4, 26.9, 20.3.



2-(1-(3,4-dimethylphenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4j）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (81%, 27.2mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.9 Hz, 1H), 7.18 – 7.10 (m, 4H), 6.77 (d, *J* = 8.4 Hz, 2H), 4.28 (d, *J* = 4.4 Hz, 1H), 3.80 (dd, *J* = 14.7, 10.7 Hz, 1H), 3.63 (dd, *J* = 14.8, 4.8 Hz, 1H), 3.58 – 3.50 (m, 1H), 2.97 (s, 3H), 2.31 (d, *J* = 5.6 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 137.9, 137.7, 132.3, 130.5, 130.1, 129.3, 128.5, 125.4, 114.7, 112.4, 111.9, 55.7, 44.5, 41.4, 27.1, 20.3, 19.9, 19.54. HRMS (ESI-TOF) for $C_{21}H_{23}N_3$ ($[M+H]^+$): calcd.318.1965; found: 318.1965. IR (neat): ν(cm^{-1})=3140, 3006, 1671, 1582, 1390.

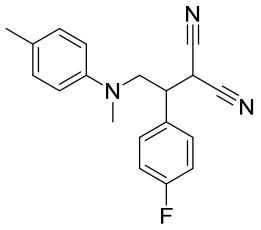


2-(1-(4-isopropylphenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4k）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (51%, 11.3mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (q, *J* = 8.4 Hz, 4H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 4.27 (d, *J* = 4.3 Hz, 1H), 3.79 (dd, *J* = 14.6, 10.6 Hz, 1H), 3.66 – 3.47 (m, 2H), 2.94 (s, 3H), 2.28 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 6H), 0.07 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 145.8, 131.3, 129.3, 127.7, 127.2, 126.5, 113.9, 111.5, 111.0, 54.8, 43.7, 40.5, 33.0, 26.2, 23.0, 19.4. HRMS (ESI-TOF) for $C_{22}H_{25}N_3$ ($[M+H]^+$): calcd.332.2121; found: 332.2125. IR (neat): ν(cm^{-1})=3133, 2999, 1658, 1594, 1531.

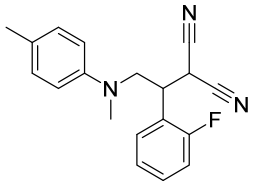


2-(1-(4-(tert-butyl)phenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4l）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (57%, 20.5mg). The compound data was in

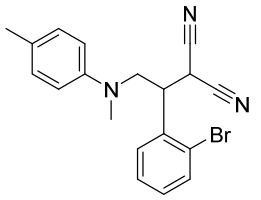
agreement with the literature (*J. Am. Chem. Soc.*, 2013, **135**, 1823-1829.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.29 (d, *J* = 4.0 Hz, 1H), 3.79 (dd, *J* = 14.6, 10.8 Hz, 1H), 3.67 – 3.52 (m, 2H), 2.96 (s, 3H), 2.28 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 146.7, 131.8, 130.1, 128.7, 127.8, 126.3, 114.8, 112.4, 111.9, 55.6, 44.5, 41.4, 34.7, 31.3, 27.0, 20.3.



2-(1-(4-fluorophenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4m）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (66%, 26.1mg). The compound data was in sgreement with the literature(*J. Am. Chem. Soc.*, 2013, **135**, 1823-1829.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 2H), 7.24 – 7.09 (m, 4H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.35 (d, *J* = 3.8 Hz, 1H), 3.86 – 3.73 (m, 1H), 3.63 (ddd, *J* = 13.0, 9.0, 4.7 Hz, 2H), 2.99 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 162.0, 146.6, 130.7, 130.4, 128.9, 116.6, 116.3, 114.9, 112.2, 111.6, 55.7, 44.2, 41.5, 27.0, 20.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.56 – -111.94 (m).

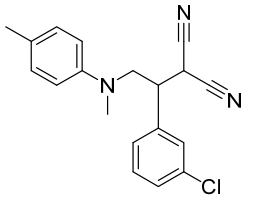


2-(1-(2-fluorophenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4n）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (86%, 25.7mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 19.2, 7.4 Hz, 2H), 7.27 – 7.10 (m, 4H), 6.78 (d, *J* = 8.4 Hz, 2H), 4.33 (d, *J* = 6.0 Hz, 1H), 4.12 – 4.00 (m, 1H), 3.88 (dd, *J* = 14.7, 9.7 Hz, 1H), 3.68 (dd, *J* = 14.7, 5.7 Hz, 1H), 2.95 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.10 (s), 159.65 (s), 146.39 (s), 130.91 (d, *J* = 8.6 Hz), 130.14 (s), 129.05 (d, *J* = 3.4 Hz), 128.5, 125.1, 116.4, 116.2, 114.5, 111.9, 55.1, 41.1, 38.4, 25.8, 20.3.HRMS (ESI-TOF) for $C_{19}H_{18}FN_4$([M+H]$^+$): calcd.308.1558; found: 308,1572. ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.88 – -110.96 (m). IR (neat): ν(cm^{-1})=3133, 2993, 1602, 1588, 1529, 1055.

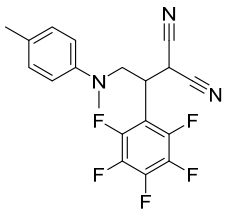


2-(1-(2-bromophenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4o）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1

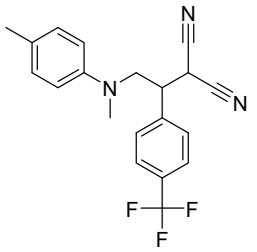
Gradient elution chromatography). Yellow oil (90%, 33.3mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 16.7, 7.8 Hz, 1H), 7.42 – 7.31 (m, 1H), 7.21 (dd, *J* = 14.6, 7.1 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 2H), 4.34 (dd, *J* = 9.5, 4.9 Hz, 1H), 4.20 (d, *J* = 4.8 Hz, 1H), 3.67 (ddd, *J* = 20.0, 14.7, 7.8 Hz, 2H), 2.93 (s, 3H), 2.26 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 130.9, 130.1, 129.0, 128.5, 125.1, 122.4, 116.4, 116.2, 114.5, 111.9, 55.1, 41.1, 38.4, 25.8, 20.3. HRMS (ESI-TOF) for $C_{19}H_{18}BrN_3$ ($[M+H]^+$): calcd.368.0757; found: 368.2870. IR (neat): ν(cm^{-1})=3146, 3006, 1582, 1404.



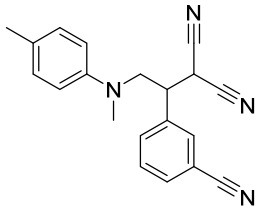
2-(1-(3-chlorophenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4p）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (82%, 25.0mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 3H), 7.30 (dd, *J* = 7.0, 1.7 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.29 (d, *J* = 4.5 Hz, 1H), 3.76 (dd, *J* = 14.6, 10.3 Hz, 1H), 3.63 (d, *J* = 5.0 Hz, 1H), 3.56 (ddd, *J* = 15.1, 9.8, 4.9 Hz, 1H), 2.93 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 137.0, 135.3, 130.7, 130.2, 129.6, 128.4, 126.3, 115.0, 112.0, 111.6, 55.6, 44.4, 41.6, 26.7, 20.4. HRMS (ESI-TOF) for $C_{19}H_{18}ClN_3$ ($[M+H]^+$): calcd.324.1262; found: 324.1266. IR (neat): ν(cm^{-1})=3146, 3006, 1582, 1403, 1599.



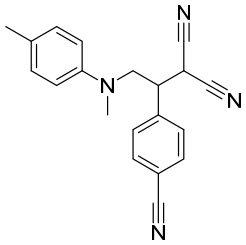
2-(2-(methyl(p-tolyl)amino)-1-(perfluorophenyl)ethyl)malononitrile（4q）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (76%, 21.0mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 4.26 (d, *J* = 9.0 Hz, 1H), 4.16 – 4.07 (m, 1H), 3.92 (dd, *J* = 14.7, 7.5 Hz, 1H), 3.83 – 3.73 (m, 1H), 2.90 (s, 3H), 2.25 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 130.1, 128.9, 114.4, 111.2, 110.8, 54.3, 40.4, 36.1, 24.7, 20.3.^{19}F NMR (377 MHz, $CDCl_3$) δ -139.33 (d, *J* = 15.9 Hz), -150.35 (s), -150.43 (d, *J* = 20.9 Hz), -150.46–-150.57 (m), -159.10(dd, *J* = 20.9, 15.0 Hz). HRMS (ESI-TOF) for $C_{19}H_{15}F_5N_3$ ($[M+H]^+$): calcd.380.1181; found: 380.1180. IR (neat): ν(cm^{-1})=3146, 3019, 1588, 1480, 1403.



2-(2-(methyl(p-tolyl)amino)-1-(4-(trifluoromethyl)phenyl)ethyl)malononitrile（4r）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (76%, 12.6mg). The compound data was in sgreement with the literature (*J. Am. Chem. Soc.*, 2013, **135**, 1823-1829.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.34 (d, *J* = 4.1 Hz, 1H), 3.86 – 3.72 (m, 1H), 3.64 (td, *J* = 11.3, 4.8 Hz, 2H), 2.93 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 138.9, 130.2, 128.8, 126.4, 115.1, 112.0, 111.5, 55.5, 44.6, 41.6, 26.6, 20.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.75 (s).

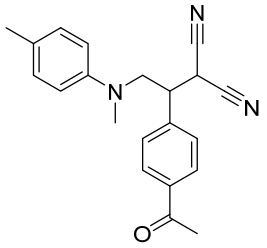


2-(1-(3-cyanophenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4s）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (41%, 14.6mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 19.7, 6.9 Hz, 3H), 7.58 (t, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 4.41 (d, *J* = 2.5 Hz, 1H), 3.80 (dd, *J* = 15.4, 11.4 Hz, 1H), 3.69 – 3.56 (m, 2H), 2.95 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 133.0, 132.6, 132.0, 130.3, 118.0, 115.4, 113.8, 111.8, 111.4, 55.6, 44.3, 41.9, 26.7, 20.4. HRMS (ESI-TOF) for $C_{20}H_{18}N_4$ ($[M+H]^+$): calcd.315.1531; found: 315.1604. IR (neat): ν(cm^{-1})=3127, 3012, 1665, 1588, 1396.

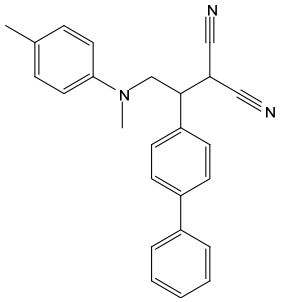


2-(1-(4-cyanophenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4t）: The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (56%, 16.8mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 4.36 (d, *J* = 4.3 Hz, 1H), 3.77 (ddd, *J* = 47.0, 26.4, 20.7 Hz, 1H), 3.64 (td, *J* = 11.4, 4.9 Hz, 2H), 2.93

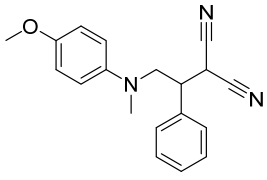
(s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 140.1, 133.1, 130.3, 129.2, 118.0, 115.1, 113.5, 111.8, 111.4, 55.4, 44.7, 41.6, 26.5, 20.4. HRMS (ESI-TOF) for $C_{20}H_{18}N_4$ ($[M+H]^+$): calcd.315.1604; found: 315.1608. IR (neat): ν(cm^{-1})=3140, 3006, 1665, 1588, 1409.



2-(1-(4-acetylphenyl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4u）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (71%, 18.2mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.41 (d, *J* = 4.0 Hz, 1H), 3.88 (dd, *J* = 16.1, 11.8 Hz, 1H), 3.75 – 3.61 (m, 2H), 2.98 (s, 3H), 2.67 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 146.5, 140.2, 137.8, 130.2, 129.2, 128.6, 114.8, 112.1, 111.7, 55.5, 44.6, 41.4, 26.7, 20.4. HRMS (ESI-TOF) for $C_{21}H_{21}N_3O$ ($[M+H]^+$): calcd.332.1757; found: 331.1664. IR (neat): ν(cm^{-1})=3100, 3006, 1707, 1604, 1589, 1396.

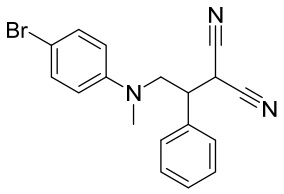


2-(1-([1,1'-biphenyl]-4-yl)-2-(methyl(p-tolyl)amino)ethyl)malononitrile（4v）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (48%, 14.2mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 6.7 Hz, 4H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 2H), 4.23 (d, *J* = 2.9 Hz, 1H), 3.81 (dd, *J* = 15.2, 11.8 Hz, 1H), 3.67 – 3.54 (m, 2H), 2.89 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3 133.8, 130.2, 128.9, 128.6, 128.0, 127.8, 127.2, 114.8, 112.3, 55.7, 44.6, 29.7, 27.0, 20.3. HRMS (ESI-TOF) for $C_{25}H_{23}N_3$ ($[M+H]^+$): calcd.366.1965; found: 366.1965. IR (neat): ν(cm^{-1})=3146, 3019, 1658, 1594, 1390.

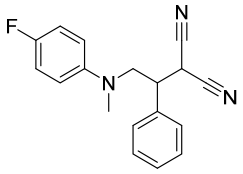


2-(2-((4-methoxyphenyl)(methyl)amino)-1-phenylethyl)malononitrile（4w）: The product

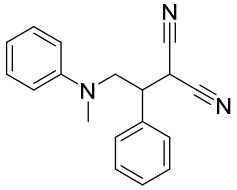
was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (64%, 17.3mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 5H), 6.92 – 6.80 (m, 4H), 4.40 (d, *J* = 4.2 Hz, 1H), 3.78 (s, 3H), 3.58 – 3.44 (m, 2H), 2.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 143.5, 135.0, 129.3, 128.2, 117.7, 115.0, 112.4, 111.8, 56.4, 55.7, 44.8, 42.4, 26.9. HRMS (ESI-TOF) for $C_{19}H_{19}N_3O$ ($[M+H]^+$): calcd.306.1601; found: 306.1603. IR (neat): ν(cm^{-1})=3133, 2999, 1588, 1446, 1390.



2-(2-((4-bromophenyl)(methyl)amino)-1-phenylethyl)malononitrile（4x）：The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (29%, 11.1mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 8H), 6.81 – 6.53 (m, 2H), 4.16 (d, *J* = 4.8 Hz, 1H), 3.91 (dd, *J* = 15.1, 9.6 Hz, 1H), 3.63 (ddd, *J* = 15.3, 14.8, 5.5 Hz, 2H), 2.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 134.8, 132.3, 129.5, 128.0, 115.2, 111.9, 111.6, 110.8, 55.3, 44.6, 40.8, 29.7, 27.0. HRMS (ESI-TOF) for $C_{18}H_{16}BrN_3$ ($[M+H]^+$): calcd.354.1600; found: 354.1620. IR (neat): ν(cm^{-1})=3127, 3012, 1671, 1614, 1403.

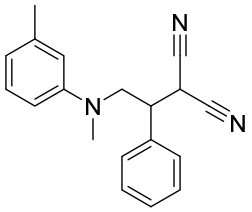


2-(2-((4-fluorophenyl)(methyl)amino)-1-phenylethyl)malononitrile（4y）：The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (45%, 11.1mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 5H), 6.98 (t, *J* = 8.7 Hz, 2H), 6.84 – 6.69 (m, 2H), 4.25 (d, *J* = 4.5 Hz, 1H), 3.91 – 3.73 (m, 1H), 3.56 (tt, *J* = 10.0, 5.2 Hz, 2H), 2.87 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 155.7, 145.5, 134.8, 129.4, 128.1, 116.1, 112.1, 111.7, 56.1, 44.7, 41.6, 29.7, 27.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -125.01 (s). HRMS (ESI-TOF) for $C_{18}H_{16}FN_3$ ($[M+H]^+$): calcd.294.1401; found: 294.1412. IR (neat): ν(cm^{-1})=3146, 2999, 1665, 1594, 1390.

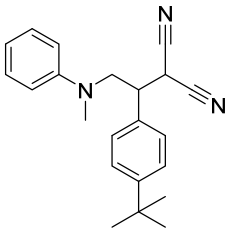


2-(2-(methyl(phenyl)amino)-1-phenylethyl)malononitrile（4z）;The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (67%, 25.5mg).The compound data was in sgreement with the literature(*J. Am. Chem. Soc.*, 2013, **135**, 1823-1829.).^{1}H NMR (400 MHz, $CDCl_3$) δ

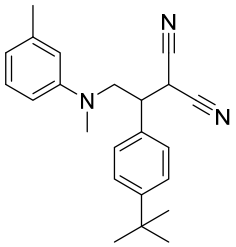
7.44 – 7.35 (m, 5H), 7.28 (t, *J* = 7.9 Hz, 2H), 6.87 – 6.73 (m, 3H), 4.18 (d, *J* = 4.7 Hz, 1H), 3.92 – 3.75 (m, 1H), 3.69 – 3.53 (m, 2H), 2.92 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 134.9, 129.6, 129.6, 128.1, 118.8, 113.8, 112.1, 111.7, 55.3, 44.8, 40.9, 29.7, 27.0.



2-(2-(methyl(m-tolyl)amino)-1-phenylethyl)malononitrile（4aa）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (44%, 14.2mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 5H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 4.24 (d, *J* = 4.4 Hz, 1H), 3.87 (dt, *J* = 19.9, 9.9 Hz, 1H), 3.63 (ddd, *J* = 14.7, 12.2, 7.2 Hz, 2H), 2.94 (s, 3H), 2.34 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.56 (s), 139.50 (s), 135.03 (s), 129.43 (t, *J* = 7.0 Hz), 128.17 (s), 119.89 (s), 114.85 (s), 112.26 (s), 111.86 (s), 111.09 (s), 77.37 (d, *J* = 11.6 Hz), 77.11 (s), 76.79 (s), 55.44 (s), 44.87 (s), 40.95 (s), 27.05 (s), 21.91 (s). HRMS (ESI-TOF) for $C_{19}H_{19}N_3$ ($[M+H]^+$): calcd.290.1652; found: 290.1669. IR (neat): ν(cm^{-1})=3127, 3012, 1665, 1594, 1396.

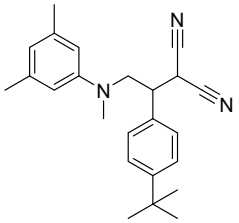


2-(1-(4-(tert-butyl)phenyl)-2-(methyl(phenyl)amino)ethyl)malononitrile （4ab）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (60%, 15.2mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.23 (m, 4H), 6.83 (dd, *J* = 20.1, 7.6 Hz, 3H), 4.22 (d, *J* = 4.1 Hz, 1H), 3.87 (dd, *J* = 14.7, 10.7 Hz, 1H), 3.73 – 3.52 (m, 2H), 2.99 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 148.6, 131.7, 129.6, 127.8, 126.3, 118.8, 113.9, 112.3, 111.9, 55.4, 44.5, 40.9, 34.7, 31.3, 27.1. HRMS (ESI-TOF) for $C_{22}H_{25}N_3$ ($[M+H]^+$): calcd.332.2121; found: 332.2122. IR (neat): ν(cm^{-1})=3146, 3006, 1665, 1588, 1396.

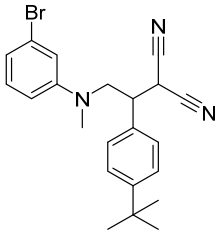


2-(1-(4-(tert-butyl)phenyl)-2-(methyl(m-tolyl)amino)ethyl)malononitrile （4ac）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate

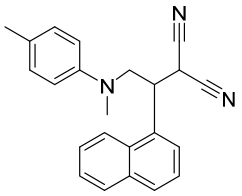
(10:1 Gradient elution chromatography). Yellow oil (60%, 19.5mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.69 (dd, *J* = 23.8, 7.7 Hz, 3H), 4.27 (d, *J* = 4.3 Hz, 1H), 3.90 (dd, *J* = 14.9, 10.5 Hz, 1H), 3.68 (ddd, *J* = 15.0, 12.7, 5.1 Hz, 2H), 3.02 (s, 3H), 2.38 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 148.7, 139.4, 131.8, 129.5, 127.8, 126.3, 119.7, 114.8, 112.4, 111.9, 111.0, 55.3, 44.6, 40.9, 34.7, 31.3, 27.1, 21.9. HRMS (ESI-TOF) for $C_{23}H_{27}N_3$ ([M+H]$^+$): calcd.346.2278; found: 346.2272. IR (neat): ν(cm^{-1})=3140, 3006, 1658, 1594, 1403.



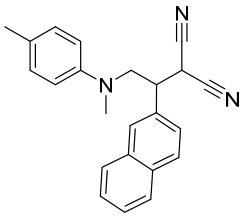
2-(1-(4-(tert-butyl)phenyl)-2-((3,5-dimethylphenyl)(methyl)amino)ethyl)malononitrile（4ad）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (36%, 11.5mg).The compound data was in agreement with the literature(*J. Am. Chem. Soc.*, 2013, **135**, 1823-1829.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.38 – 7.21 (m, 2H), 6.52 (s, 1H), 6.44 (s, 2H), 4.23 (d, *J* = 4.3 Hz, 1H), 3.85 (dd, *J* = 14.9, 10.5 Hz, 1H), 3.62 (ddd, *J* = 14.9, 12.6, 4.8 Hz, 2H), 2.96 (s, 3H), 2.29 (s, 6H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 148.8, 139.3, 131.8, 127.8, 126.3, 120.8, 112.4, 112.0, 55.3, 44.6, 40.9, 34.7, 31.3, 27.1, 21.8.



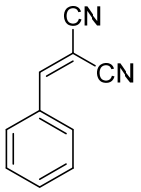
2-(2-((3-bromophenyl)(methyl)amino)-1-(4-(tert-butyl)phenyl)ethyl)malononitrile（4ae）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (23%, 8.9mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.37 (m, 2H), 7.32 (s, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 8.1 Hz, 1H), 6.94 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.89 – 6.83 (m, 1H), 6.69 (dd, *J* = 8.3, 2.4 Hz, 1H), 4.13 (d, *J* = 4.7 Hz, 1H), 3.99 – 3.86 (m, 1H), 3.71 (dd, *J* = 15.1, 5.5 Hz, 1H), 3.59 (dt, *J* = 9.9, 5.1 Hz, 1H), 2.96 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 149.6, 131.6, 130.8, 128.8, 127.7, 126.4, 123.8, 121.2, 116.3, 111.9, 55.2, 44.2, 40.6, 34.7, 31.2, 27.1. HRMS (ESI-TOF) for $C_{22}H_{24}N_3$ ([M+H]$^+$): calcd.410.1226; found: 410.1228. IR (neat): ν(cm^{-1})=3133, 3012, 1588, 1403.



2-(2-(methyl(p-tolyl)amino)-1-(naphthalen-1-yl)ethyl)malononitrile（4af）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (87%, 19.9mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.82 (m, 3H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.63 – 7.50 (m, 3H), 7.22 – 7.08 (m, 2H), 6.87 (dd, *J* = 19.4, 8.2 Hz, 2H), 4.72 – 4.62 (m, 1H), 4.19 – 3.99 (m, 2H), 3.91 – 3.77 (m, 1H), 3.04 (d, *J* = 22.0 Hz, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 134.2, 131.5, 130.2, 129.6, 128.6, 127.3, 126.4, 125.4, 124.8, 121.7, 114.7, 112.2, 56.2, 41.8, 27.0, 20.4. HRMS (ESI-TOF) for $C_{23}H_{21}N_3$ ($[M+H]^+$): calcd.339.1808; found: 339.1735. IR (neat): ν(cm^{-1})=3152, 2999, 1670, 1601, 1409.



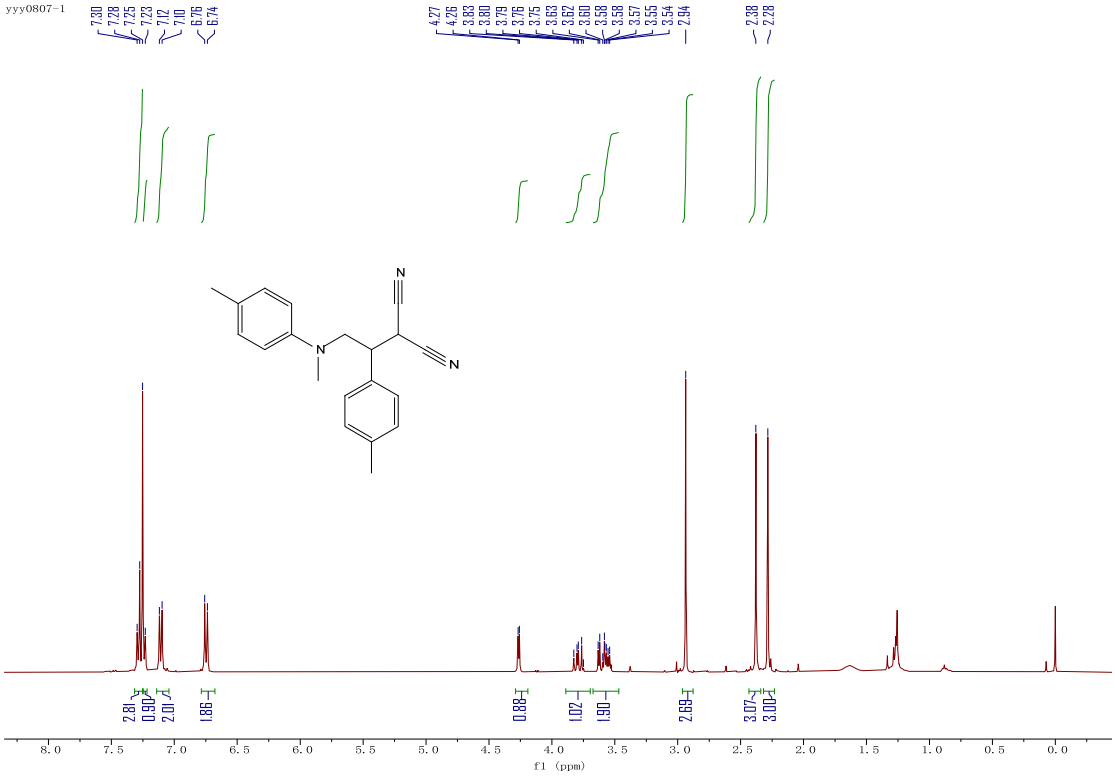
2-(2-(methyl(p-tolyl)amino)-1-(naphthalen-2-yl)ethyl)malononitrile（4ag）： The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). Yellow oil (74%, 15.6mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.82 (m, 4H), 7.59 – 7.40 (m, 3H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.37 (d, *J* = 3.9 Hz, 1H), 3.94 (dd, *J* = 13.2, 8.9 Hz, 1H), 3.83 – 3.65 (m, 2H), 2.95 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.42, 132.34, 130.21, 129.35, 128.17, 127.82, 126.89, 125.14, 114.86, 112.28, 111.85, 55.85, 44.94, 41.57, 27.06, 20.38. HRMS (ESI-TOF) for $C_{23}H_{21}N_3$ ($[M+H]^+$): calcd.339.1808; found: 340.1818. IR (neat): ν(cm^{-1})=3133, 3006, 1658, 1588, 1390.



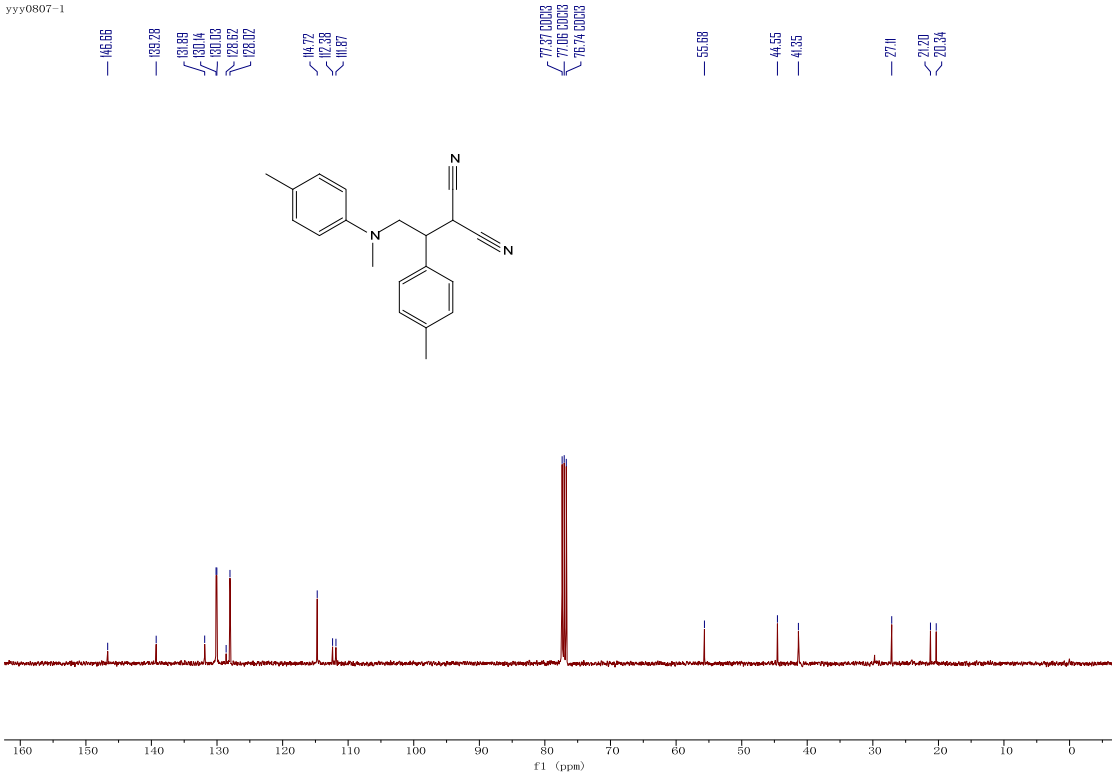
2-benzylidenemalononitrile （ 5 ） The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1 Gradient elution chromatography). White solid. ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 2H), 7.78 (s, 1H), 7.64 (t, J = 7.4Hz, 1H), 7.55(t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 134.7, 131.0, 130.8, 129.7, 113.7, 112.6, 83.0, 77.4, 77.0, 76.7.

9. NMR spectra

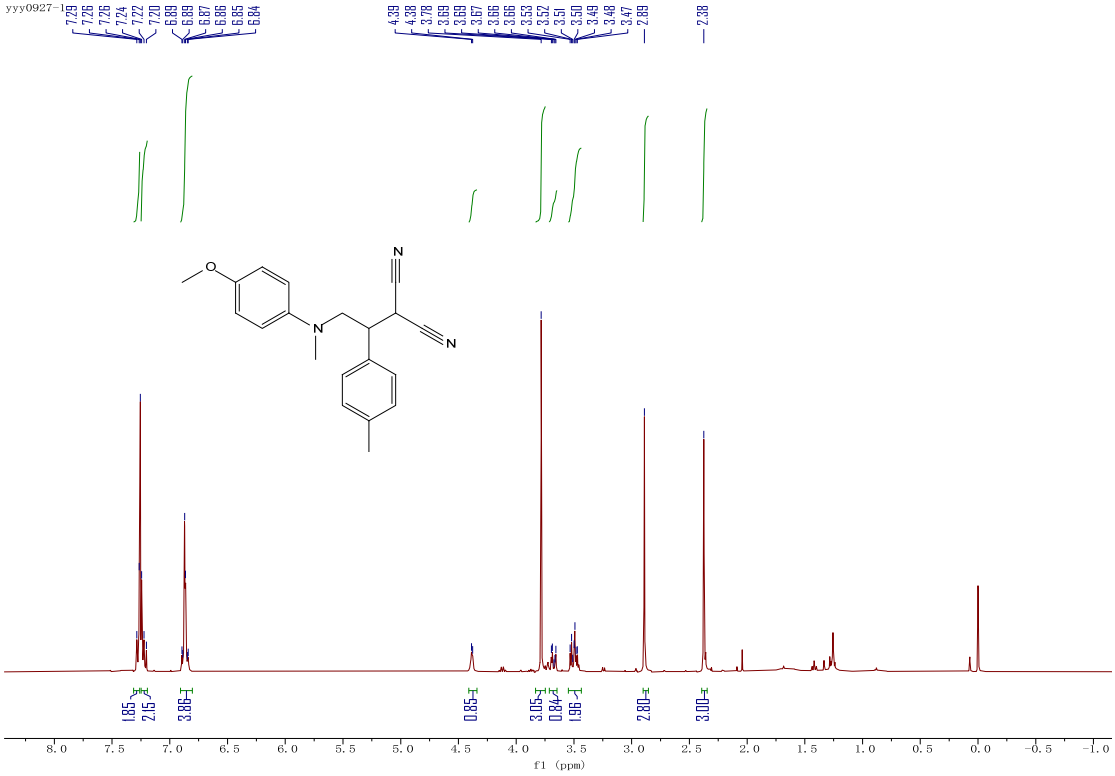
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4a**



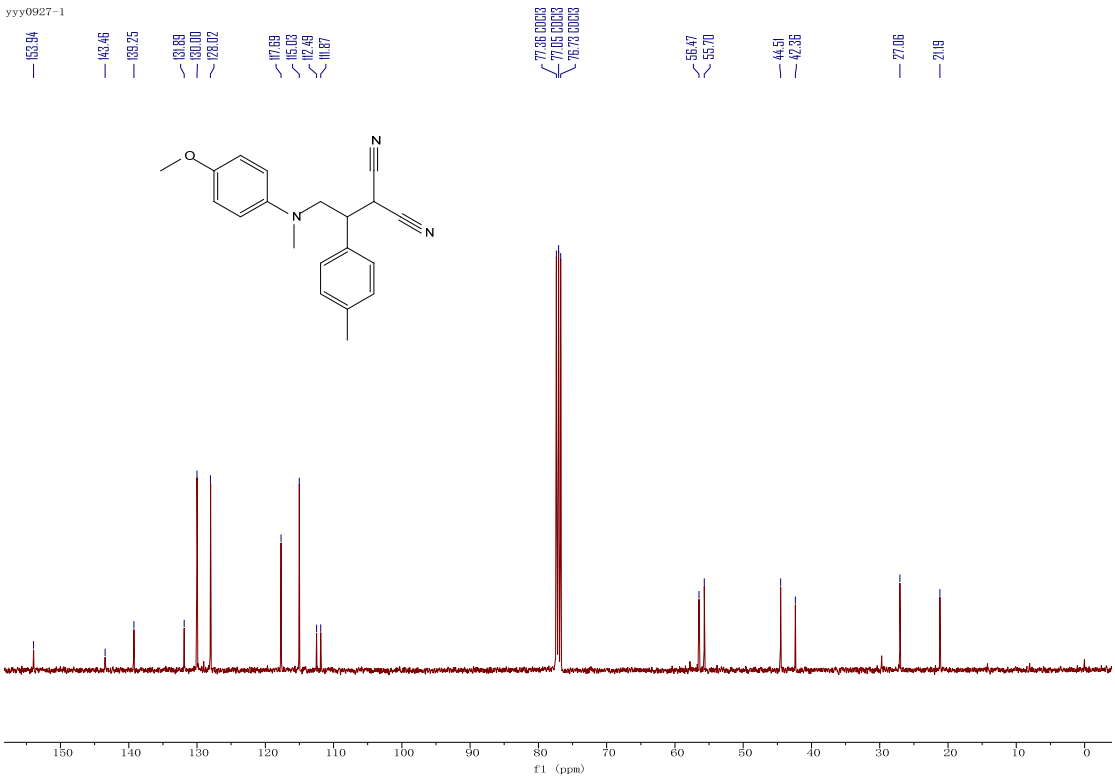
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4a**



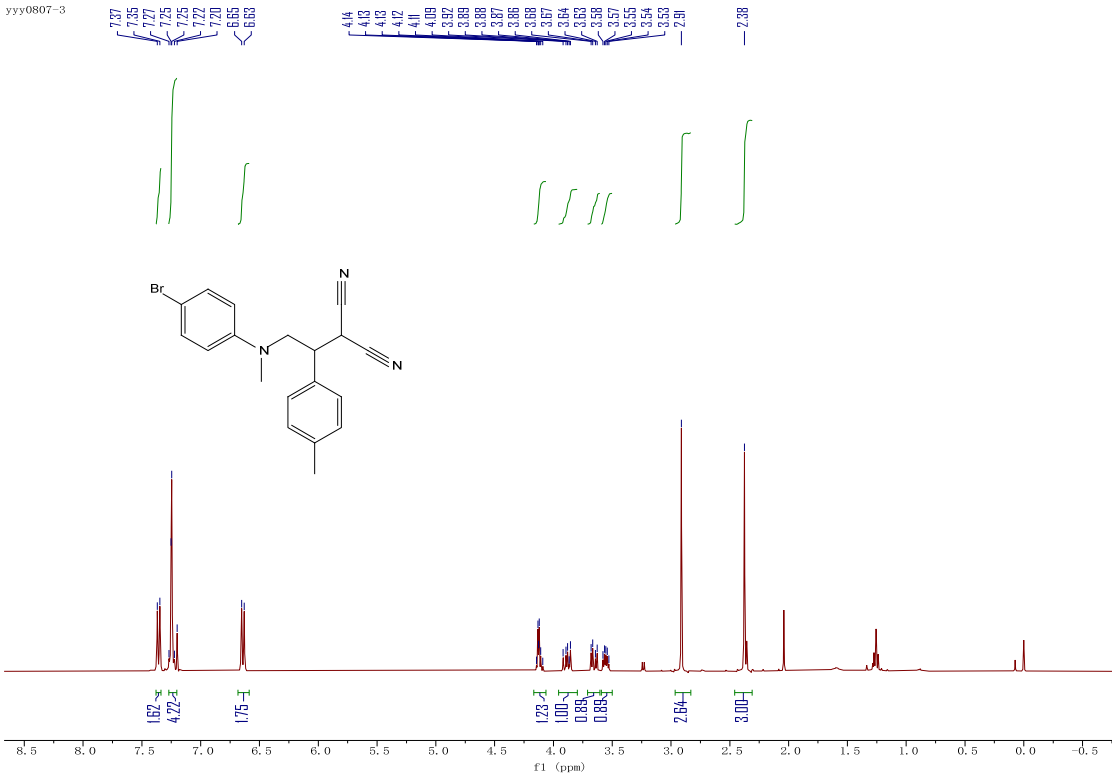
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4b**



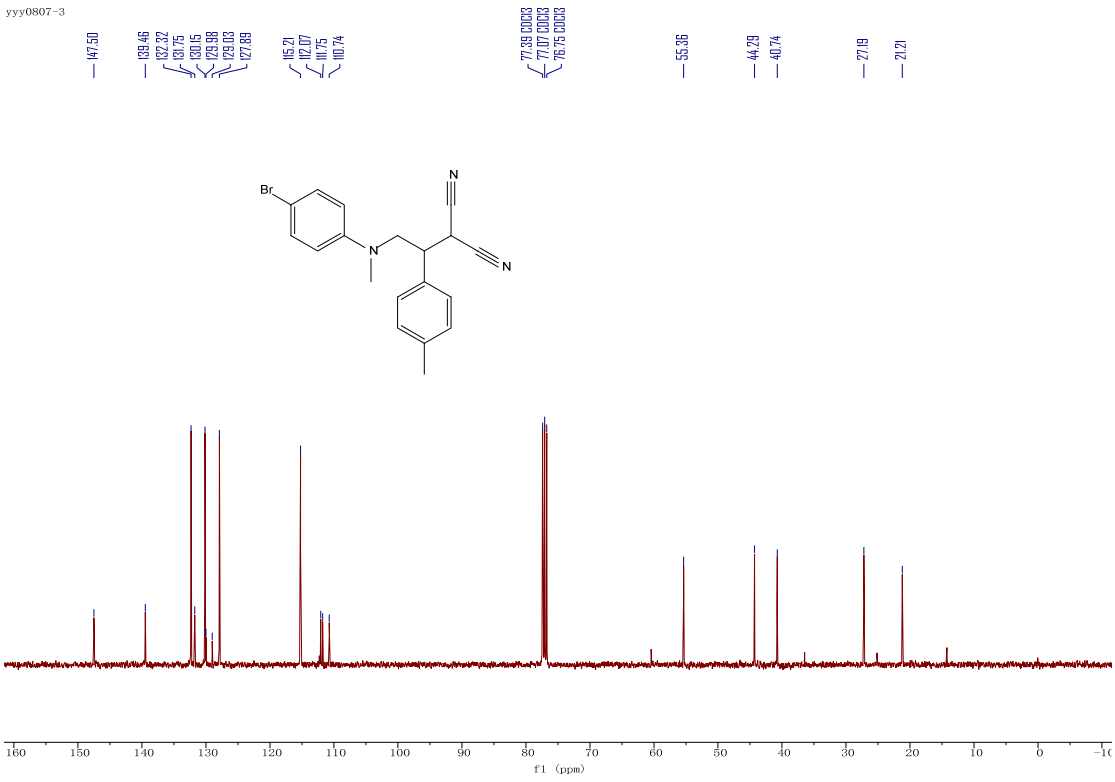
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4b**



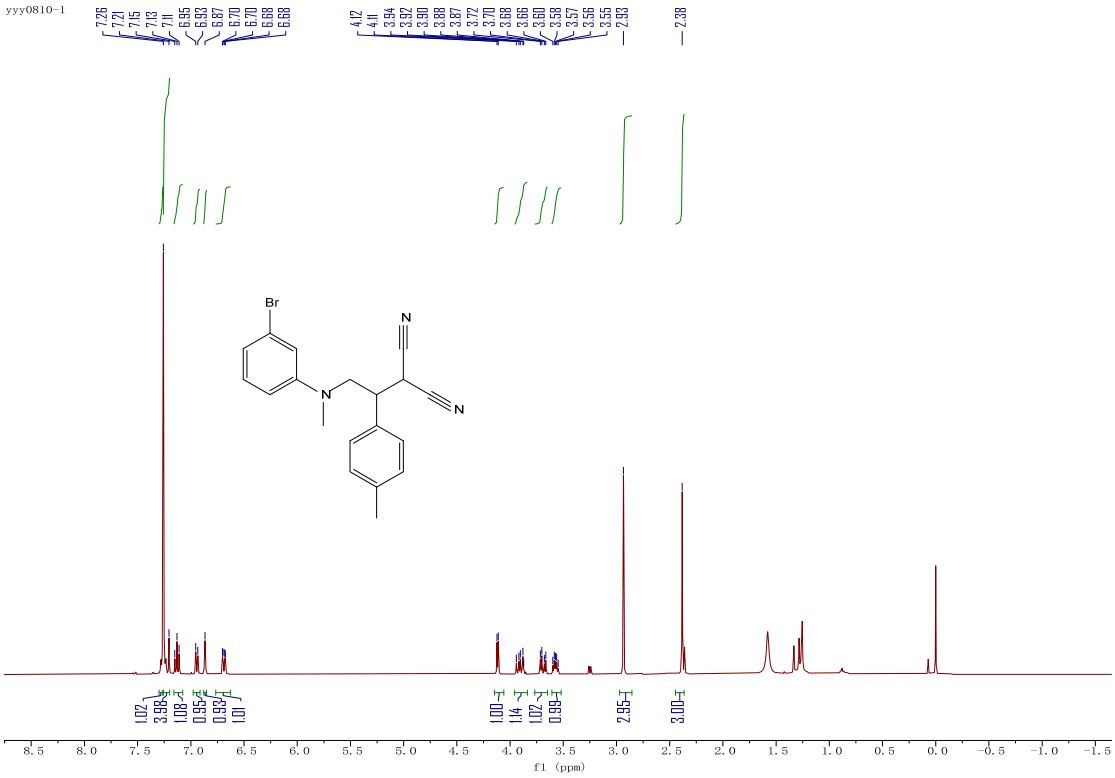
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4c**



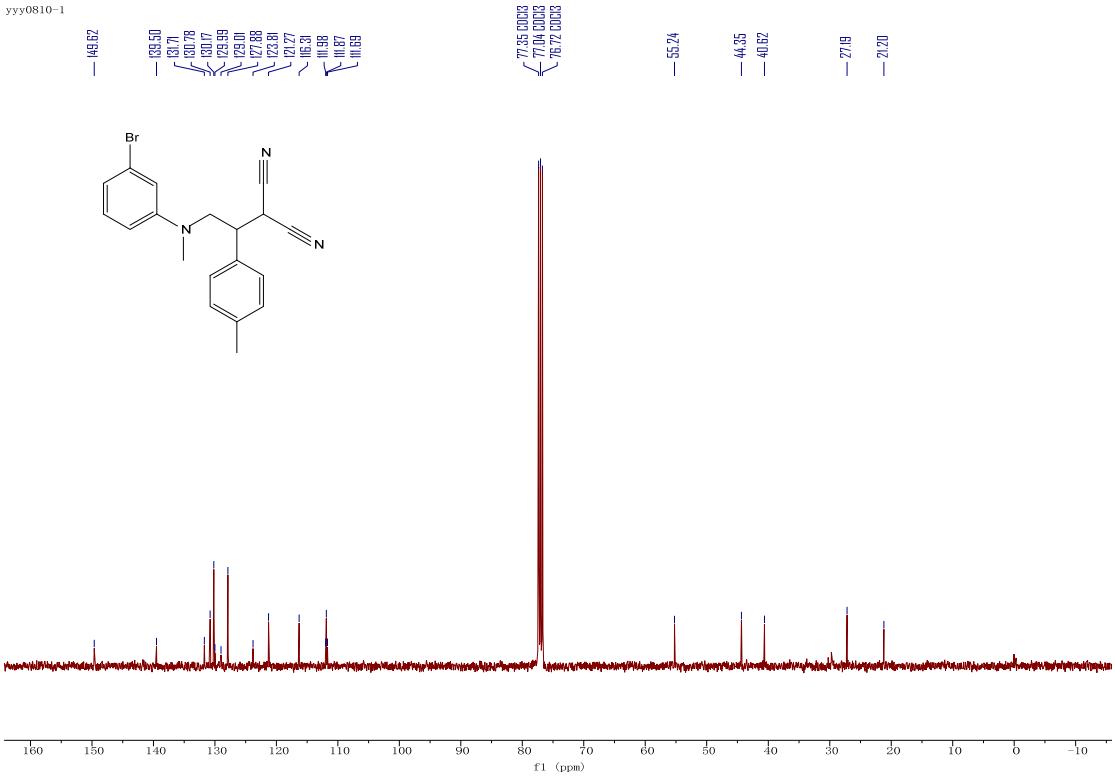
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4c**



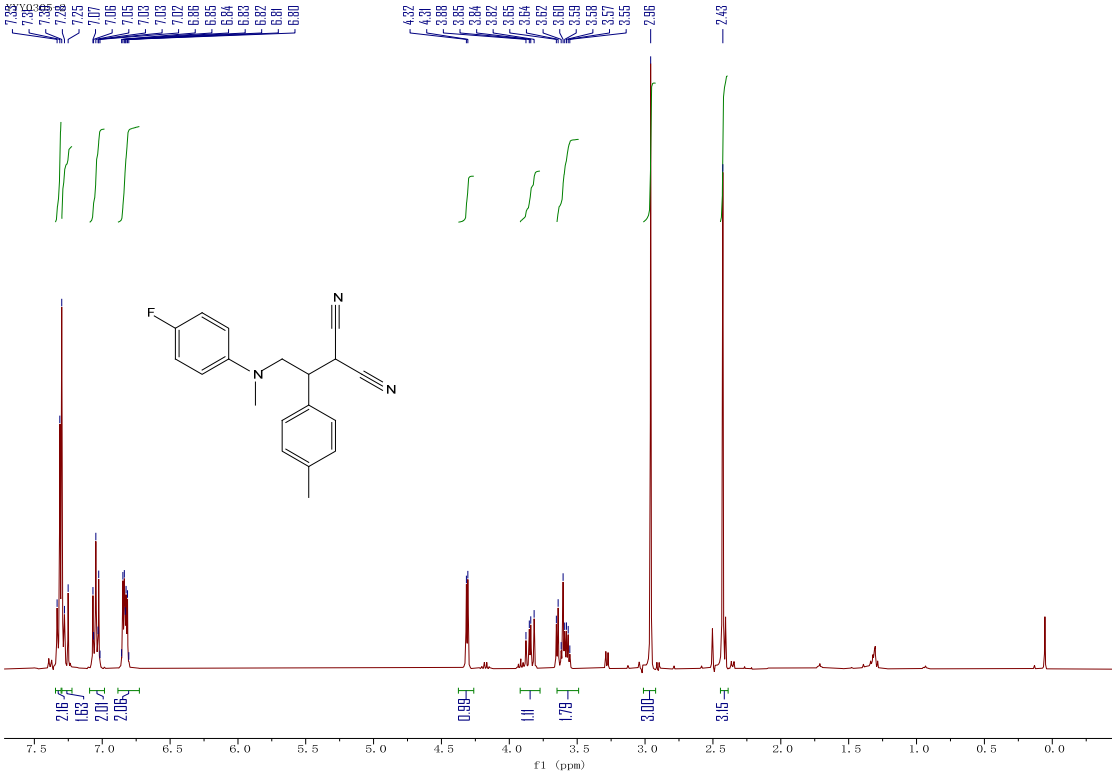
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4d**



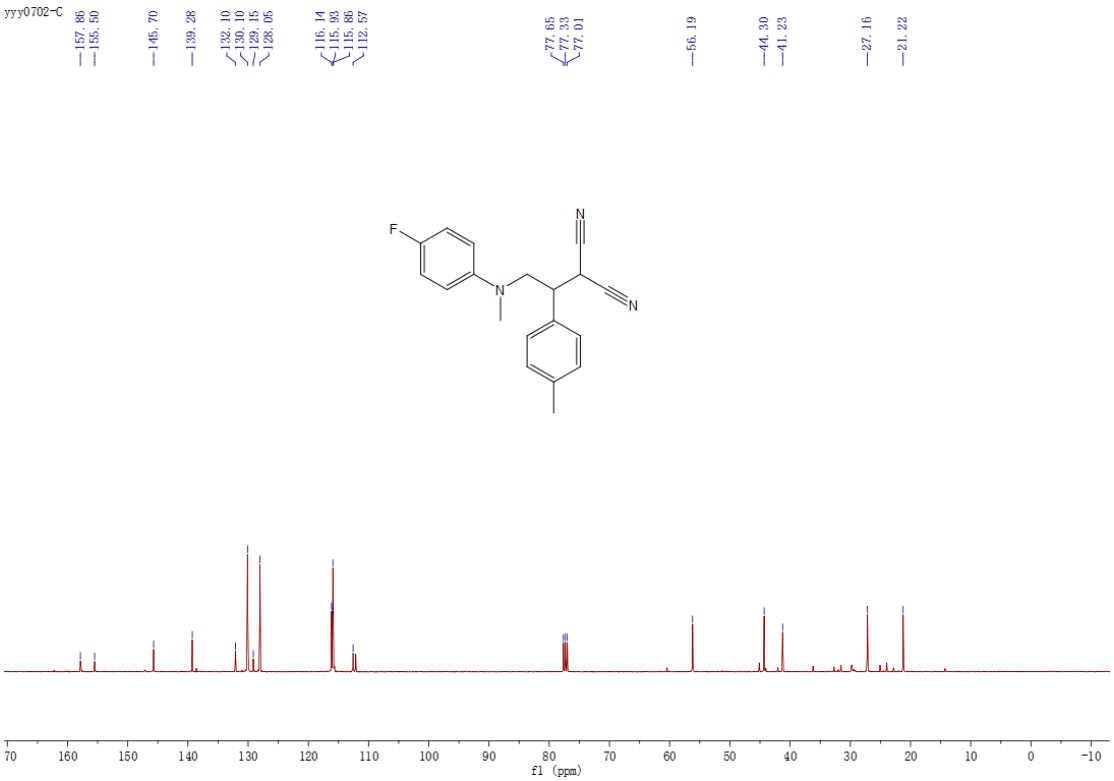
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4d**



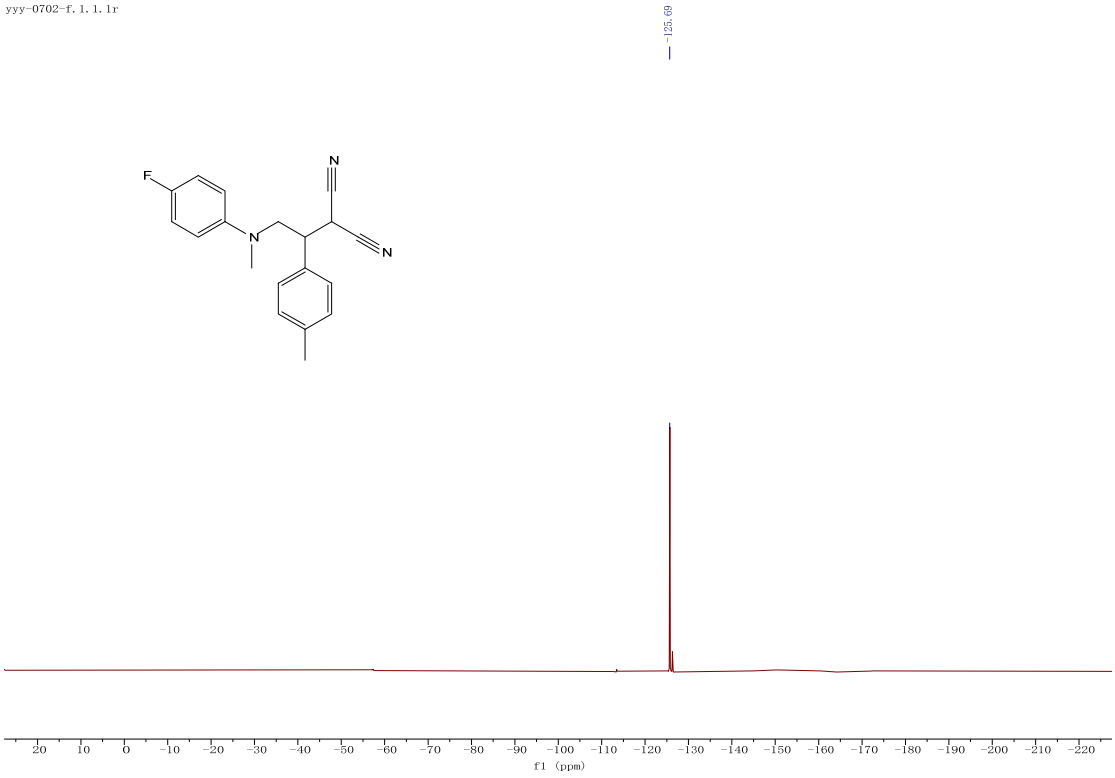
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4e**



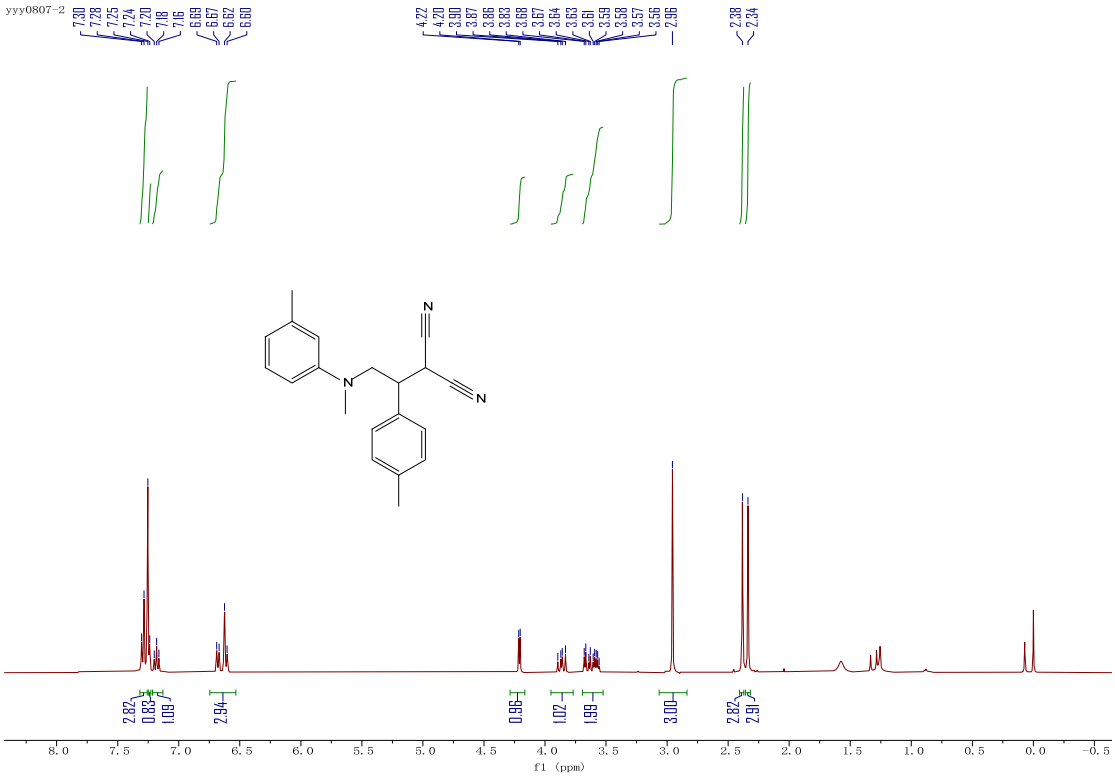
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4e**



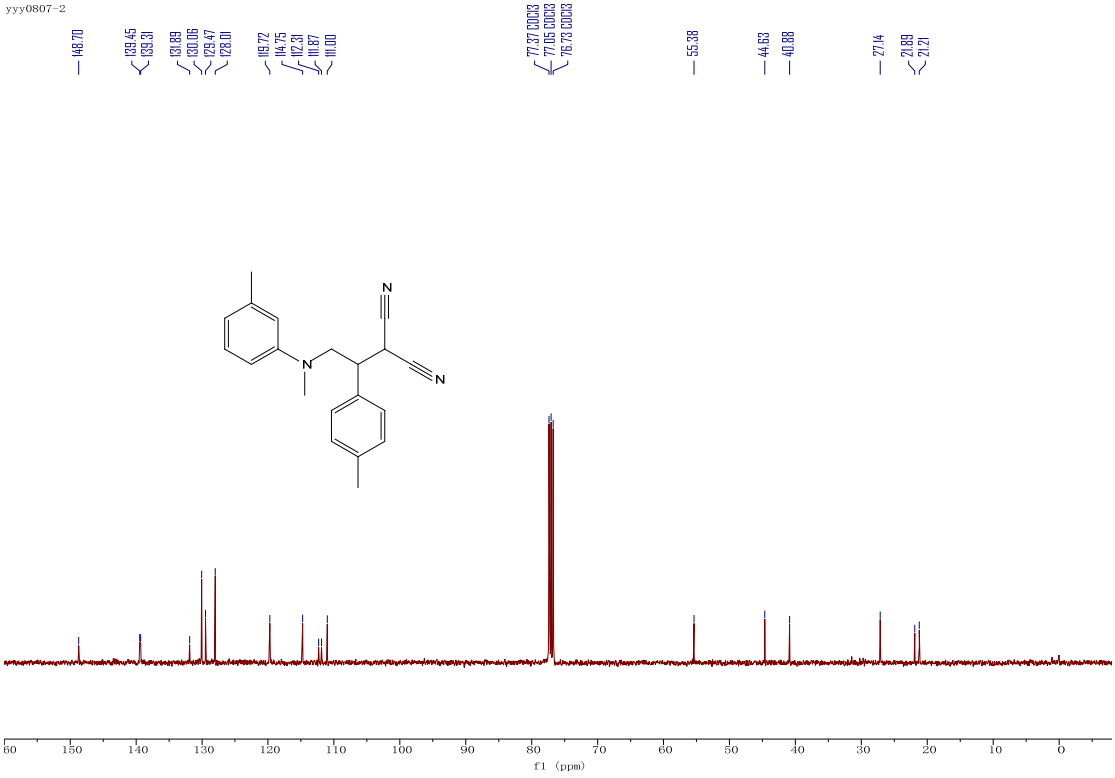
^{19}F NMR-spectrum (377MHz, $CDCl_3$) of **4e**



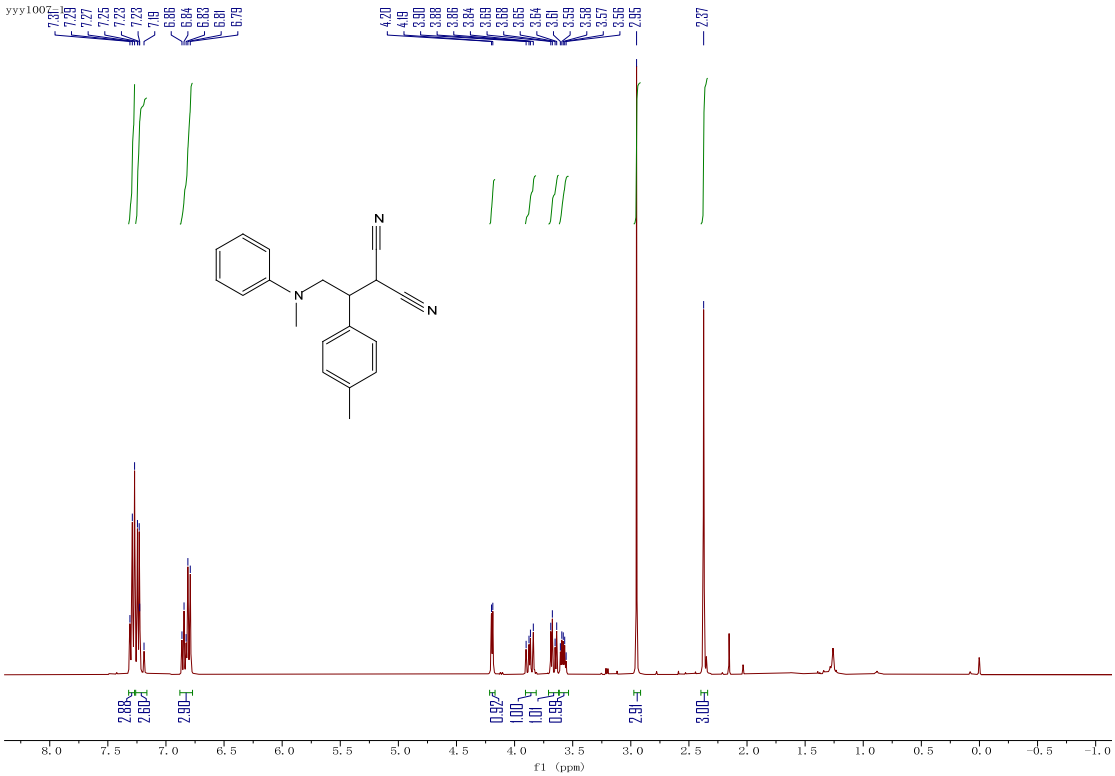
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4f**



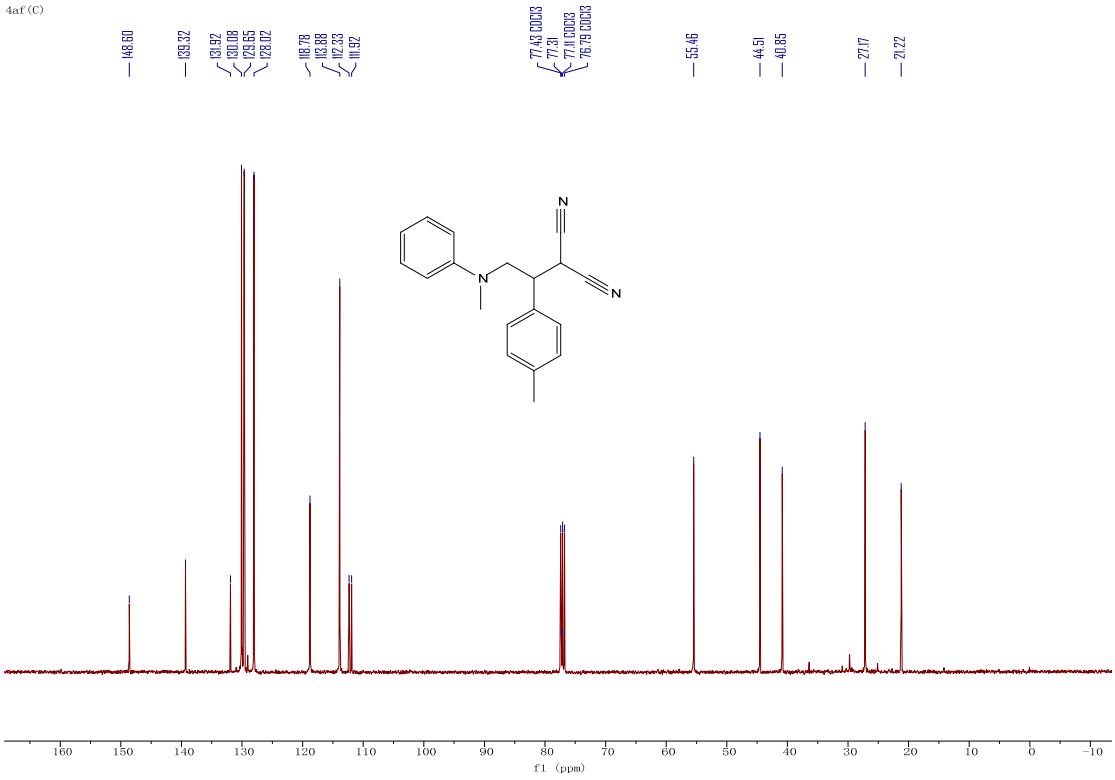
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4f**



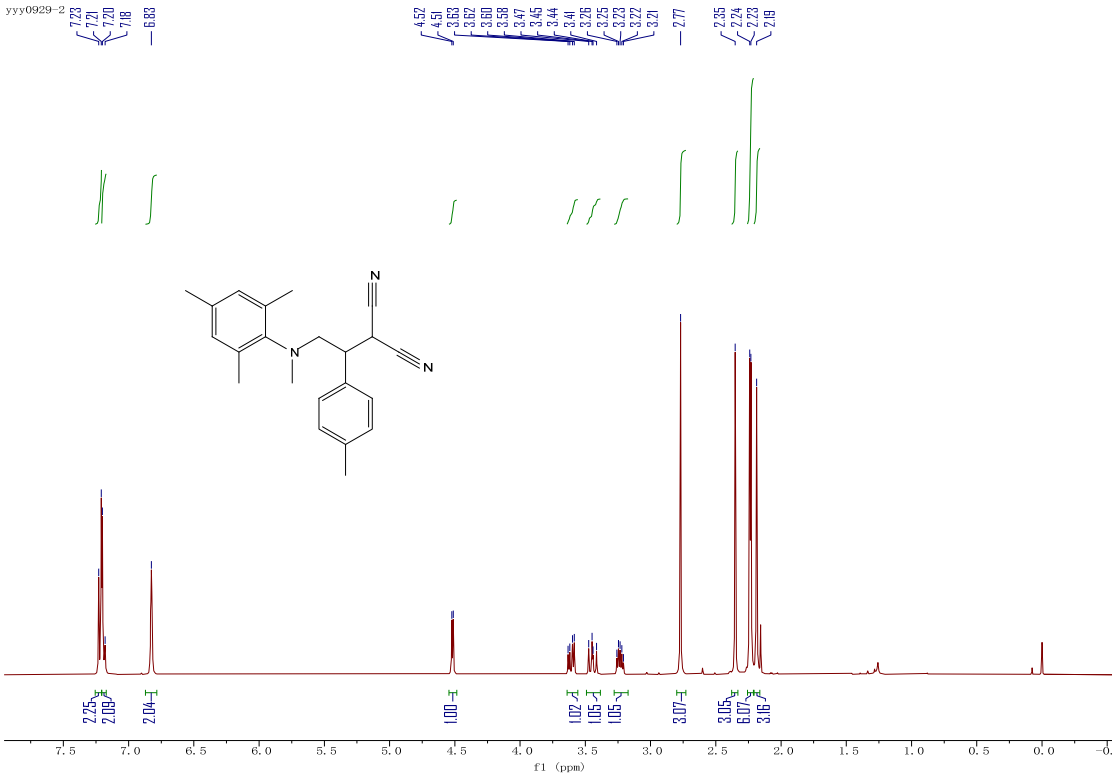
^{1}H NMR-spectrum (400MHz,$CDCl_3$) of **4g**



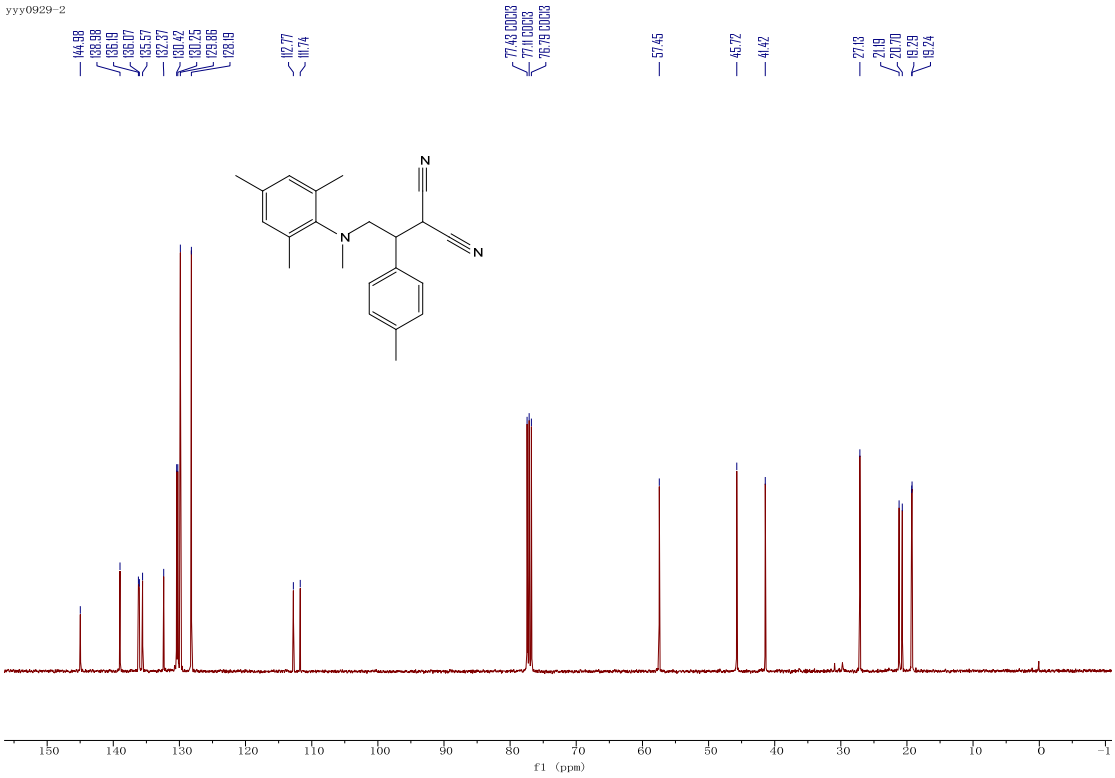
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4g**



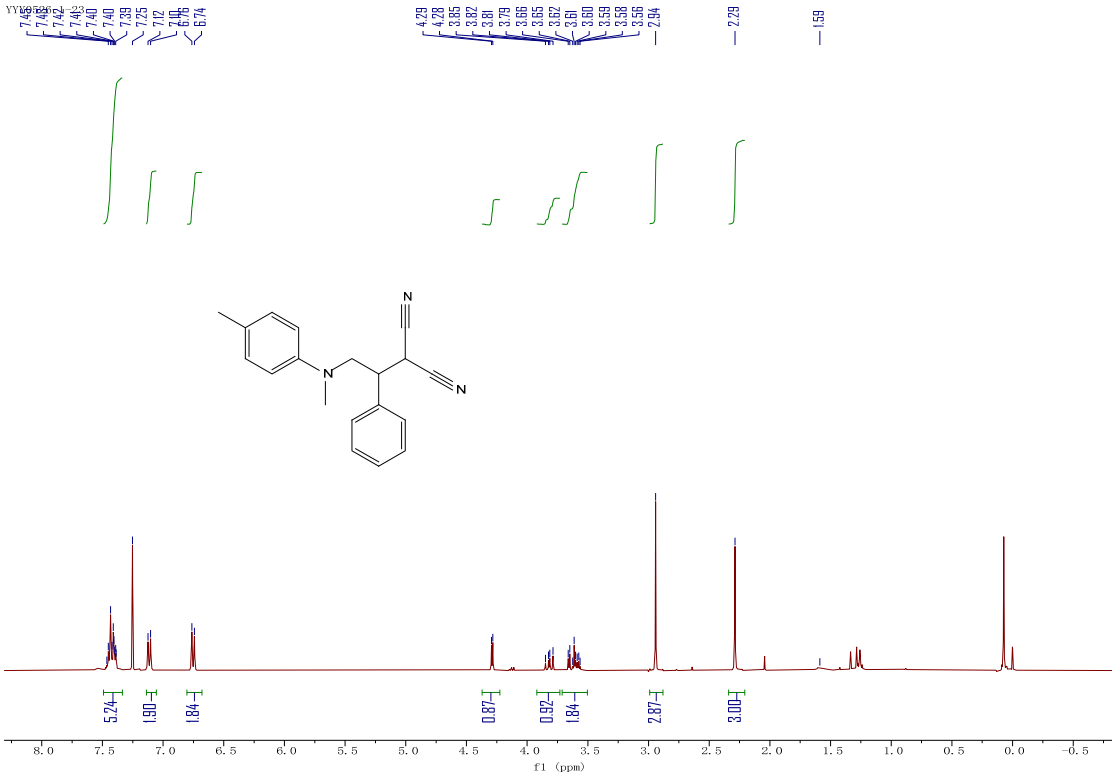
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4h**



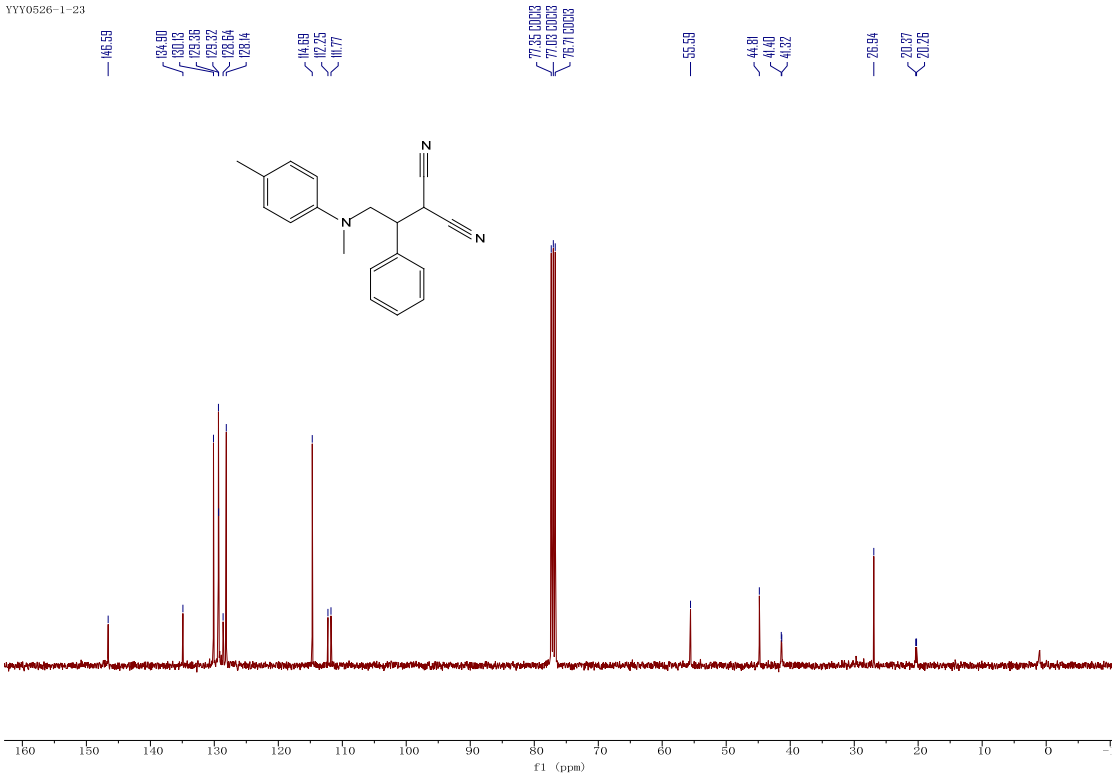
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4h**



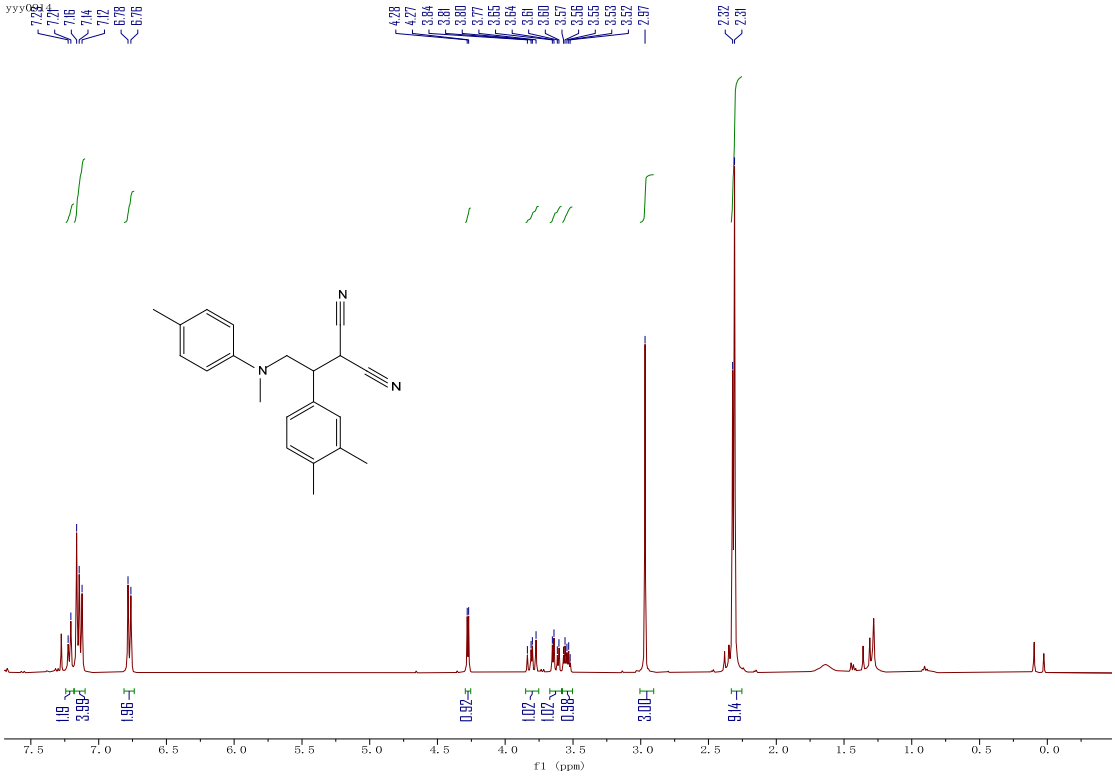
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4i**



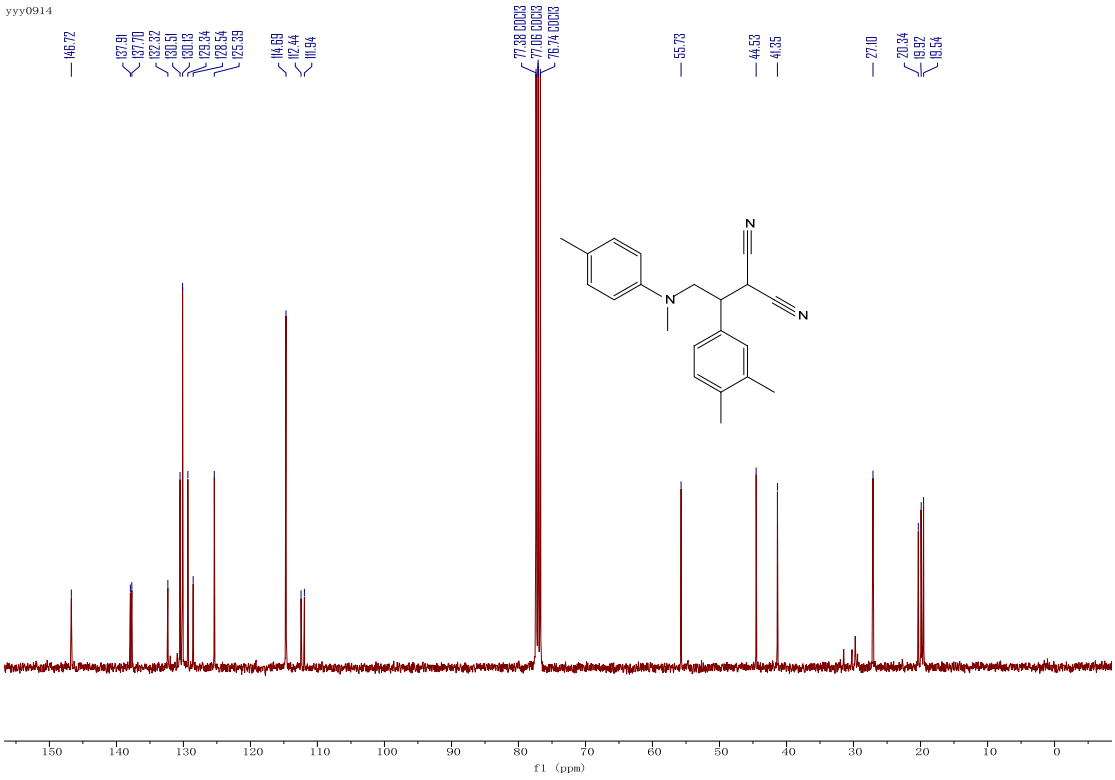
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4i**



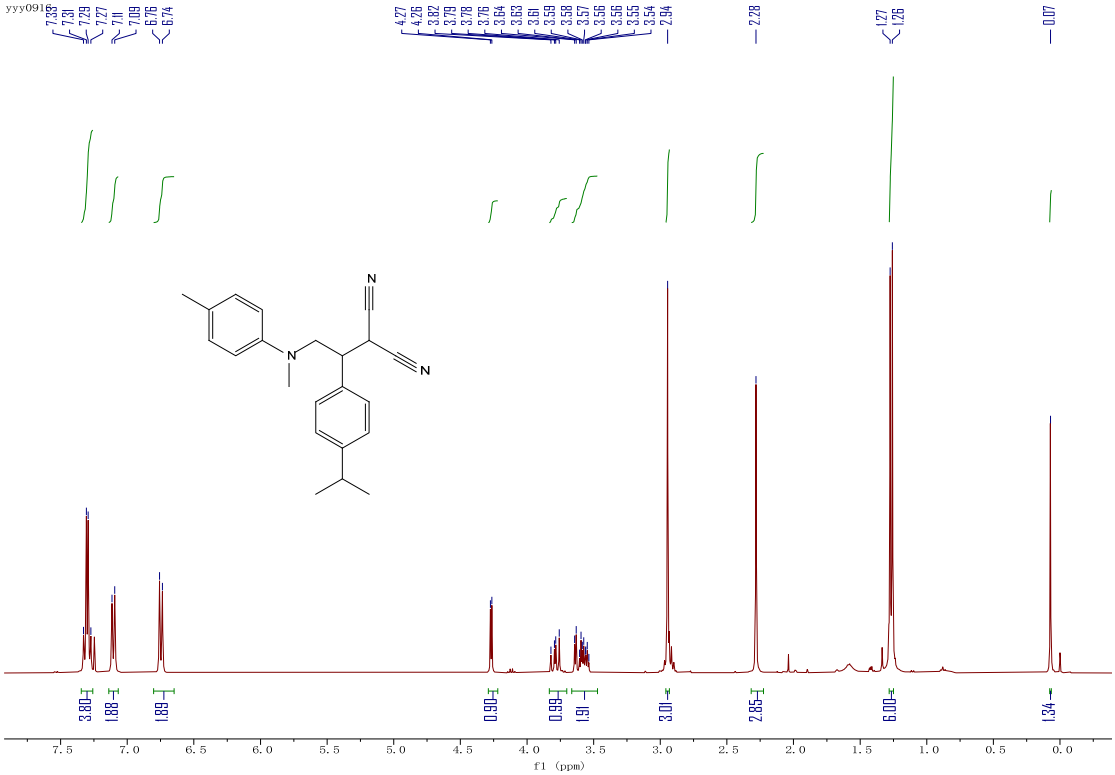
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4j**



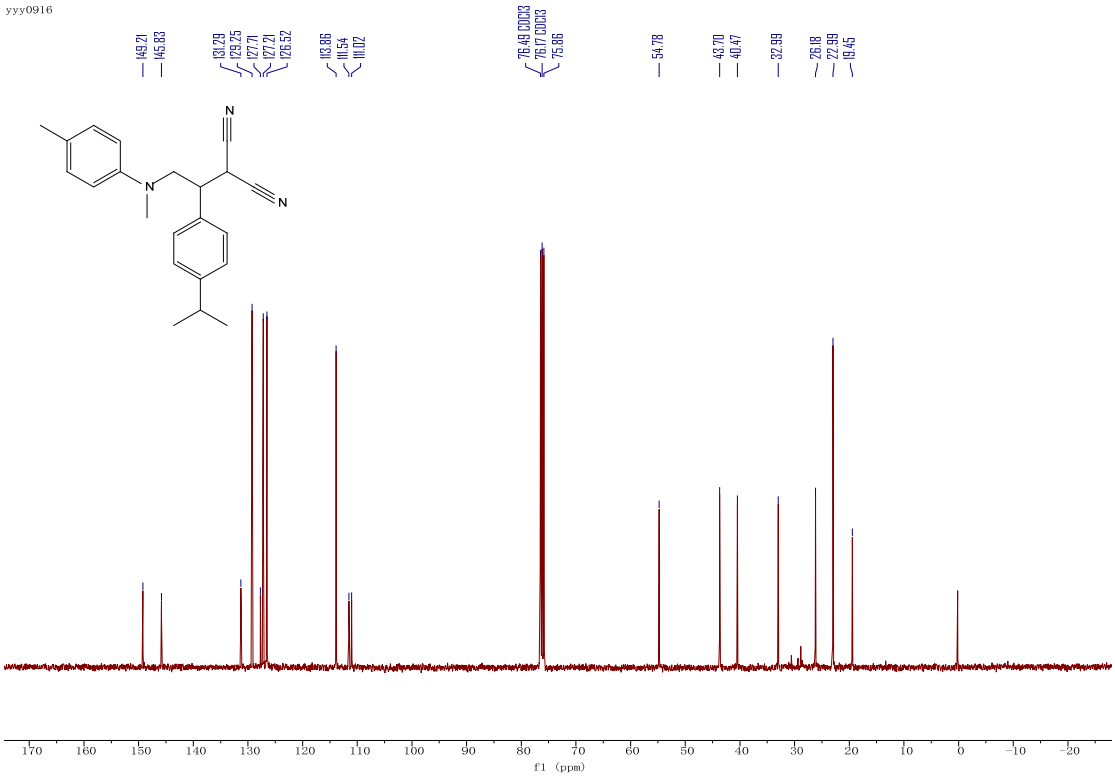
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4j**



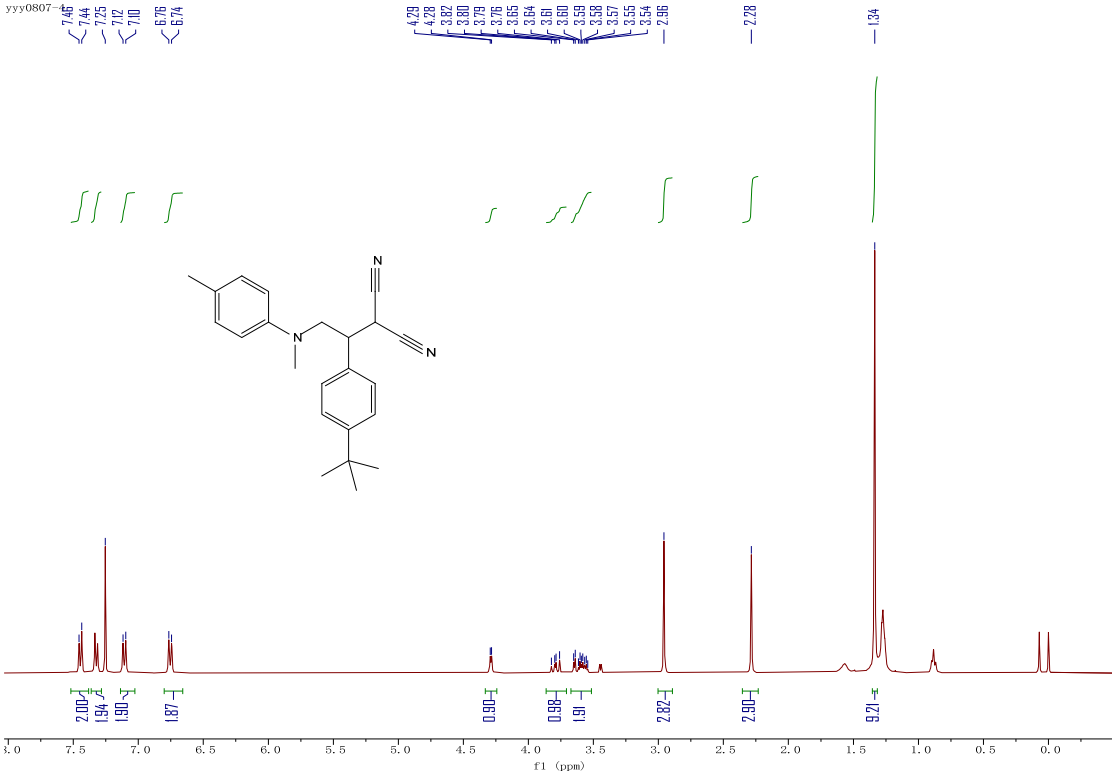
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4k**



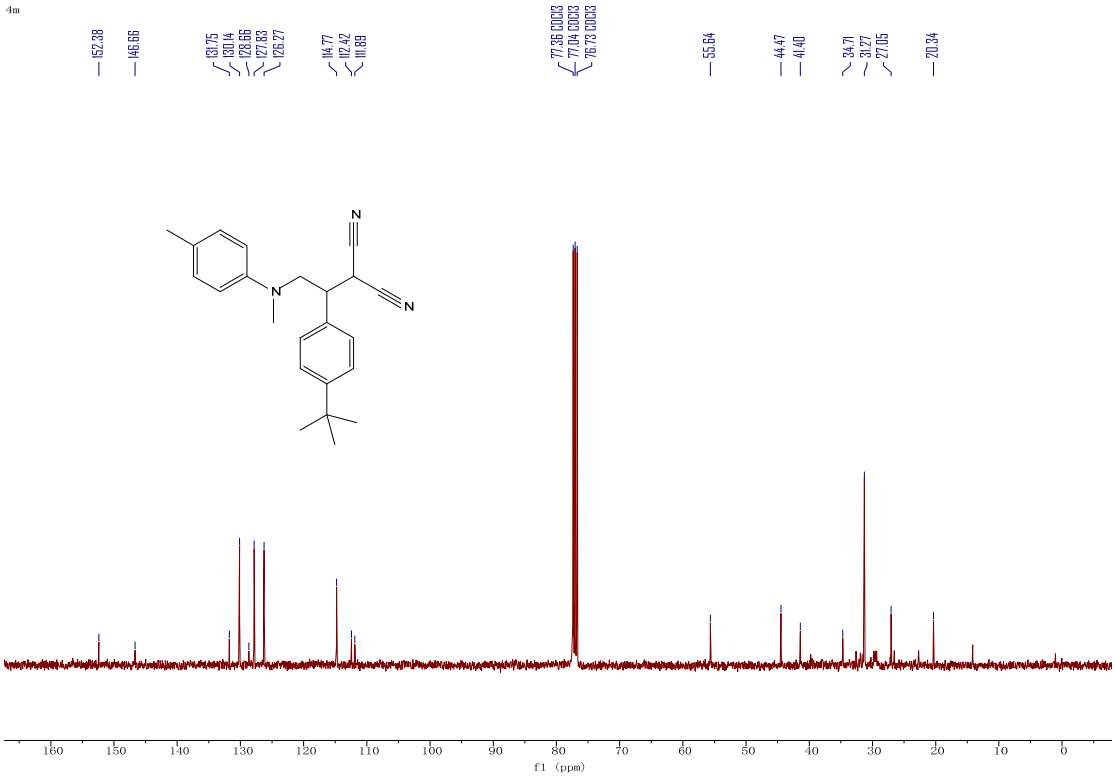
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4k**



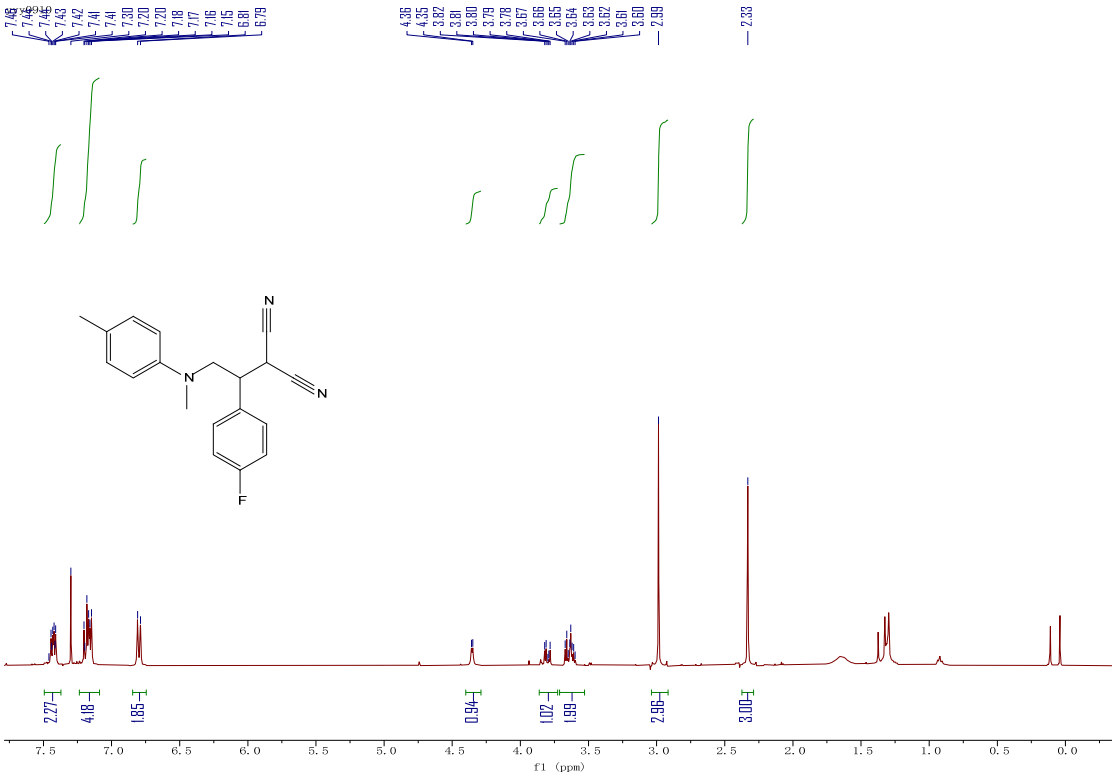
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4l**



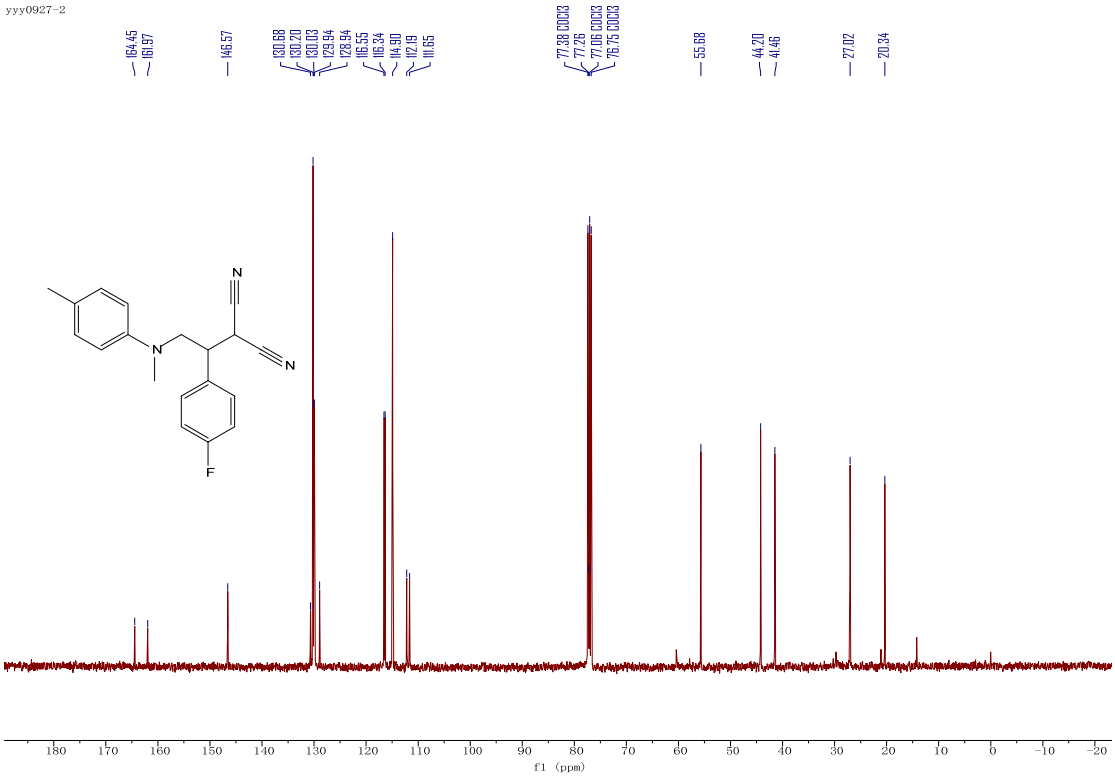
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4l**



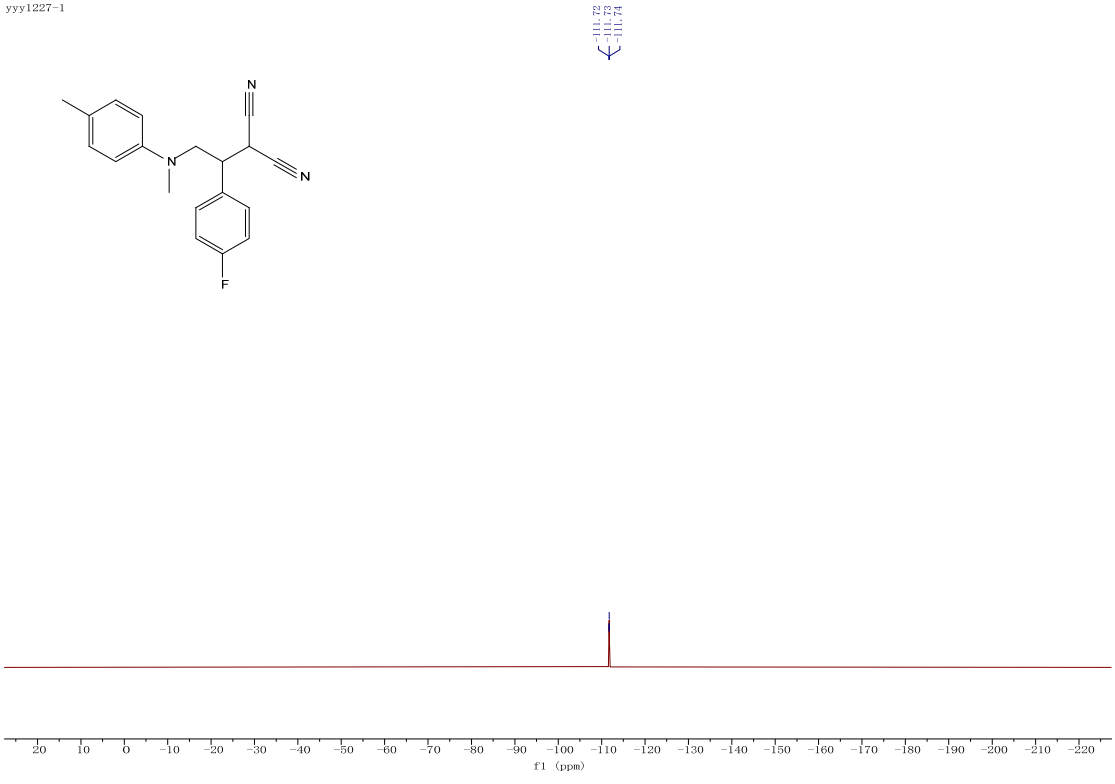
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4m**



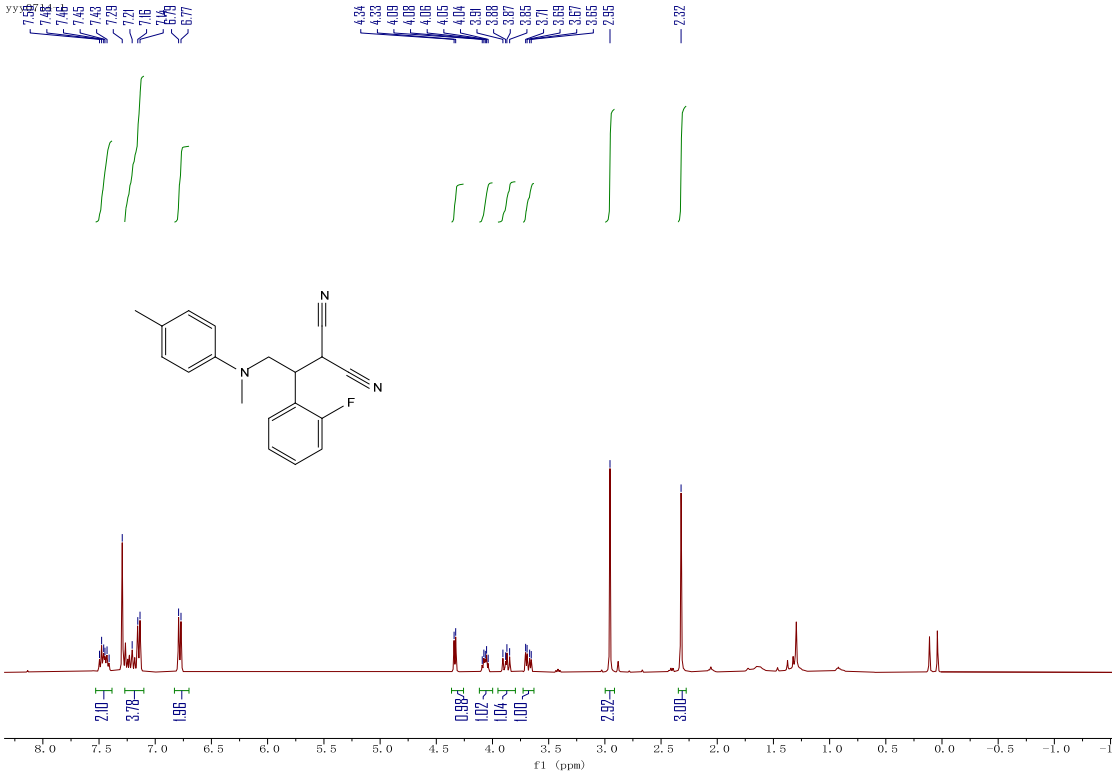
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4m**



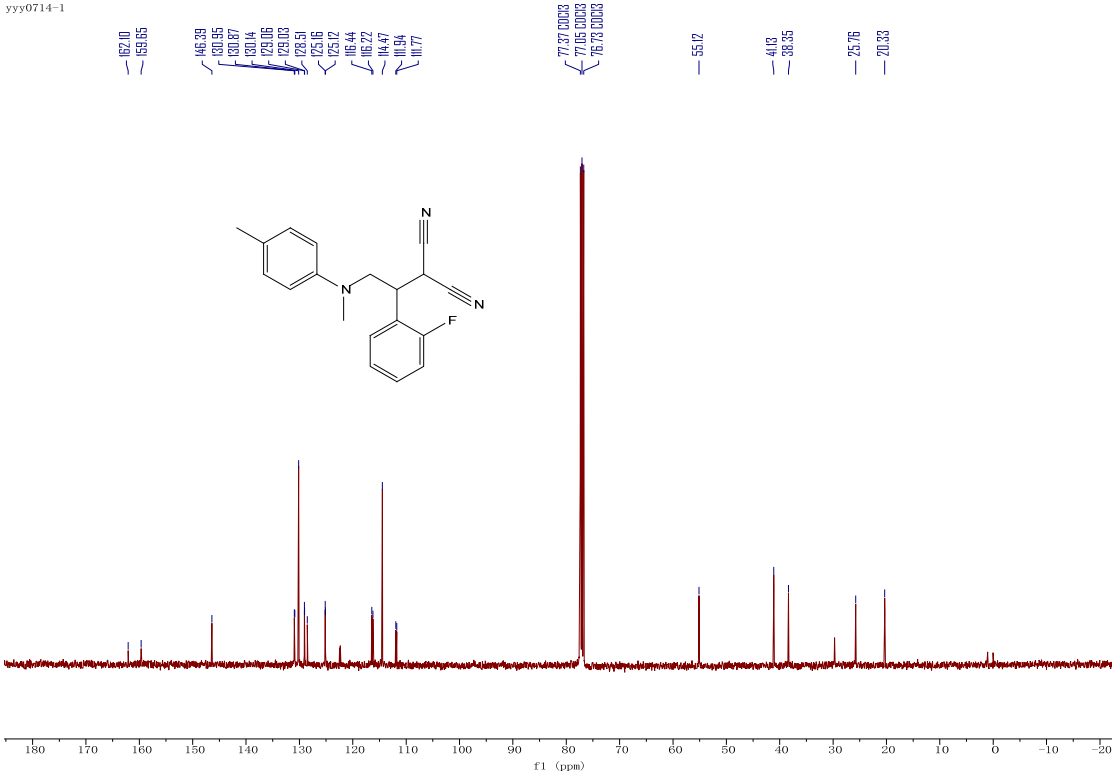
^{19}F NMR-spectrum (377MHz, $CDCl_3$) of **4m**



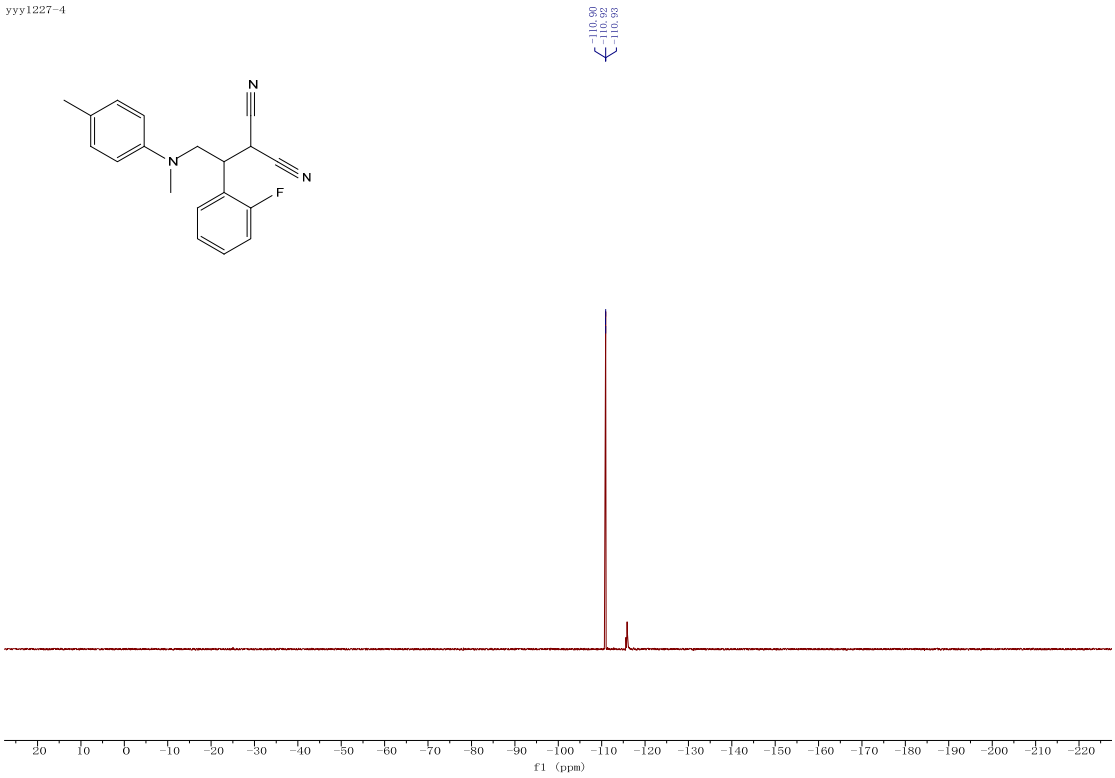
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4n**



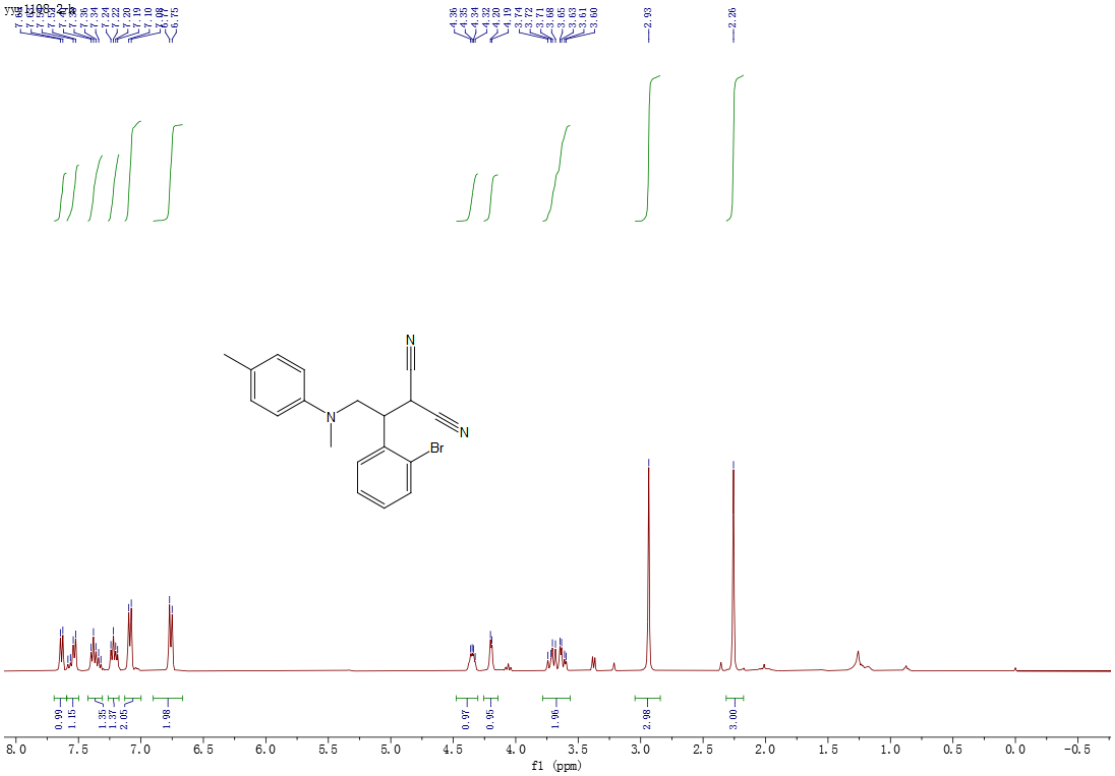
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4n**



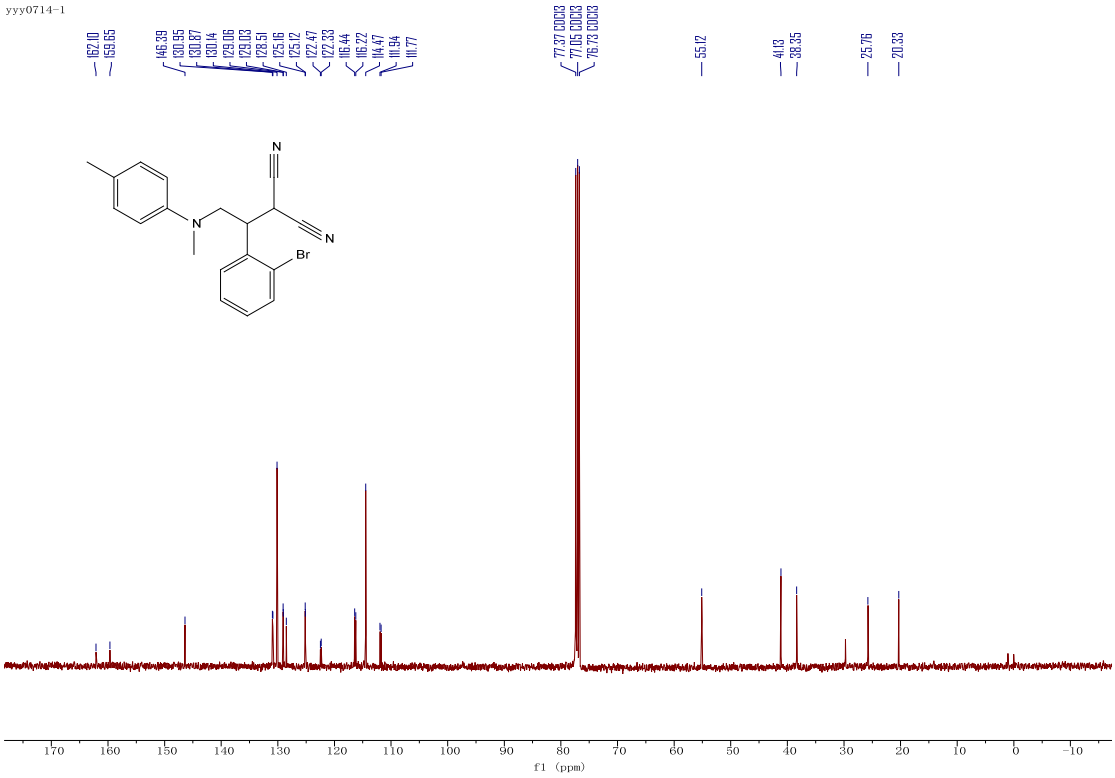
^{19}F NMR-spectrum (377MHz, $CDCl_3$) of **4n**



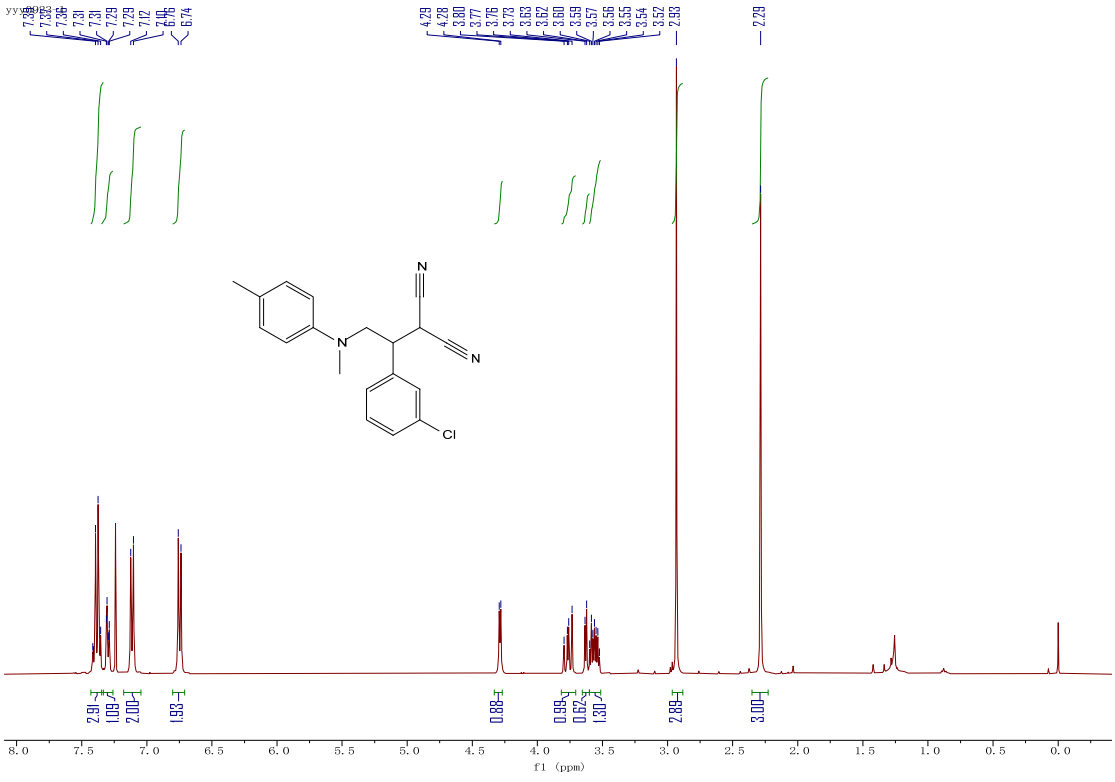
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4o**



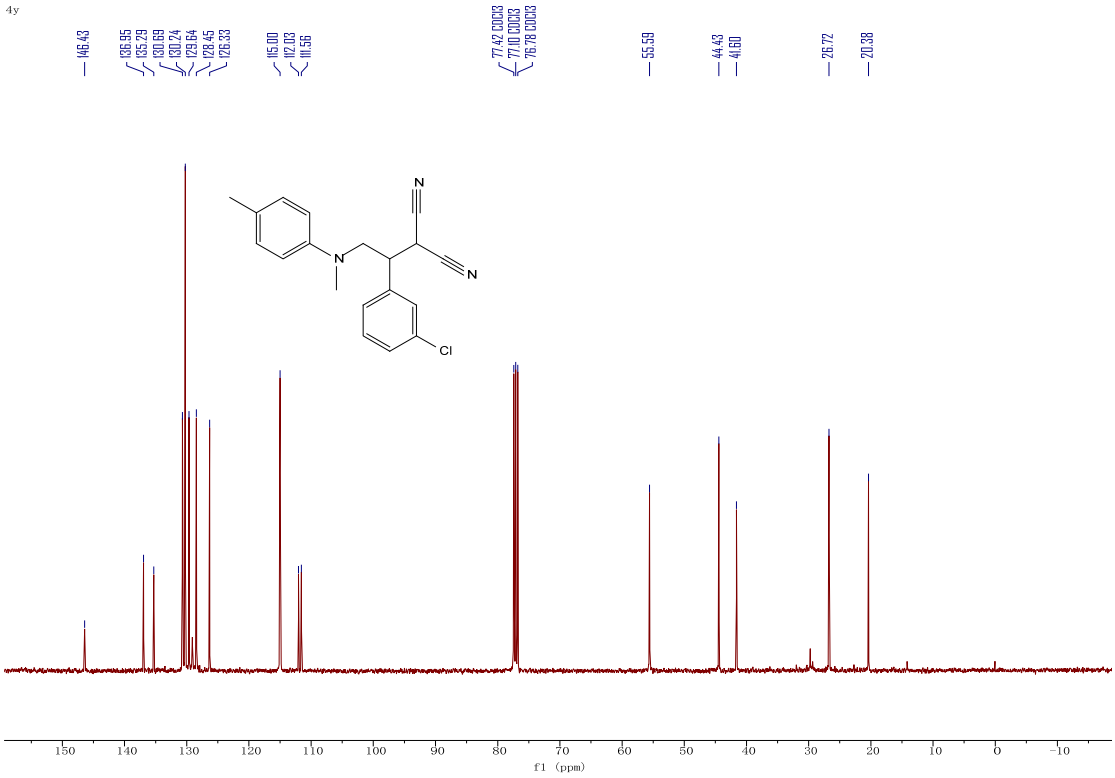
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4o**



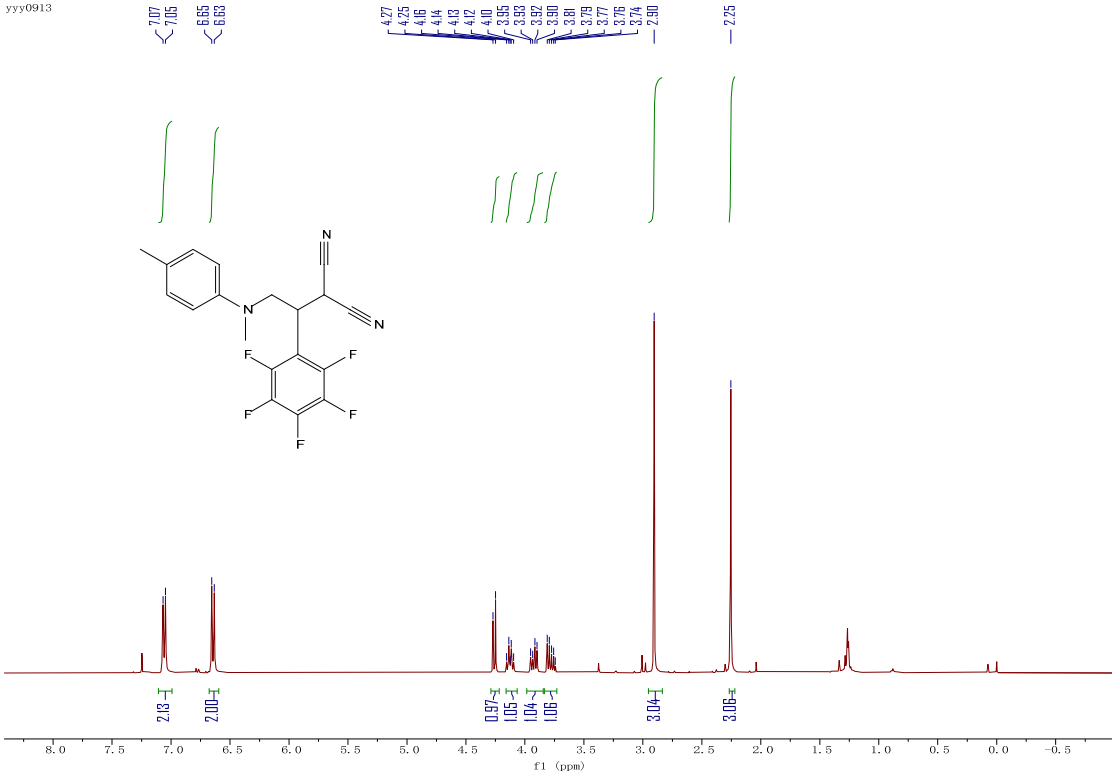
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4p**



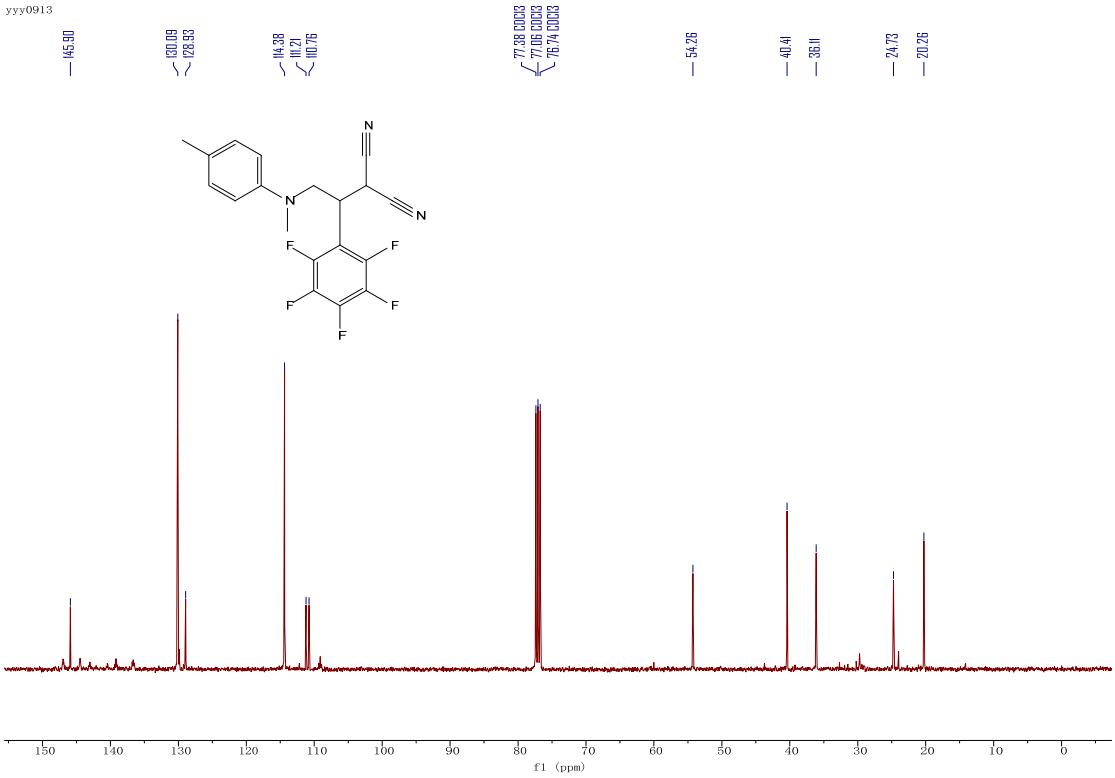
^{13}C NMR-spectrum (101MHz,$CDCl_3$) of **4p**



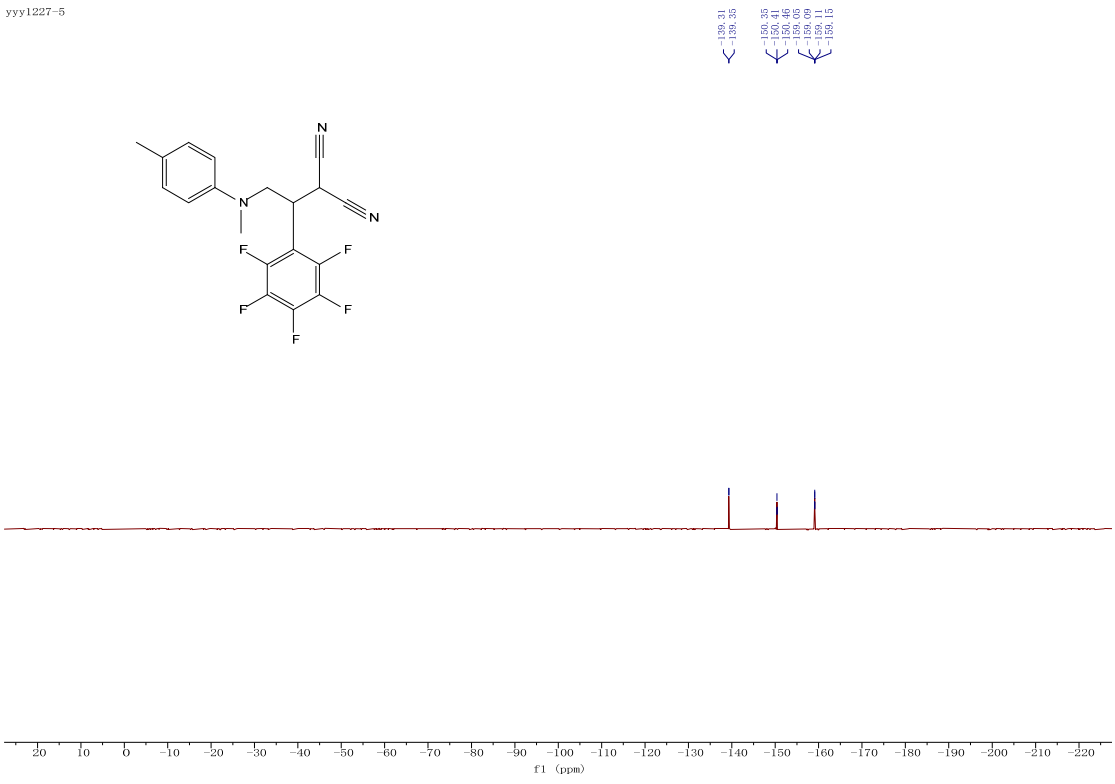
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4q**



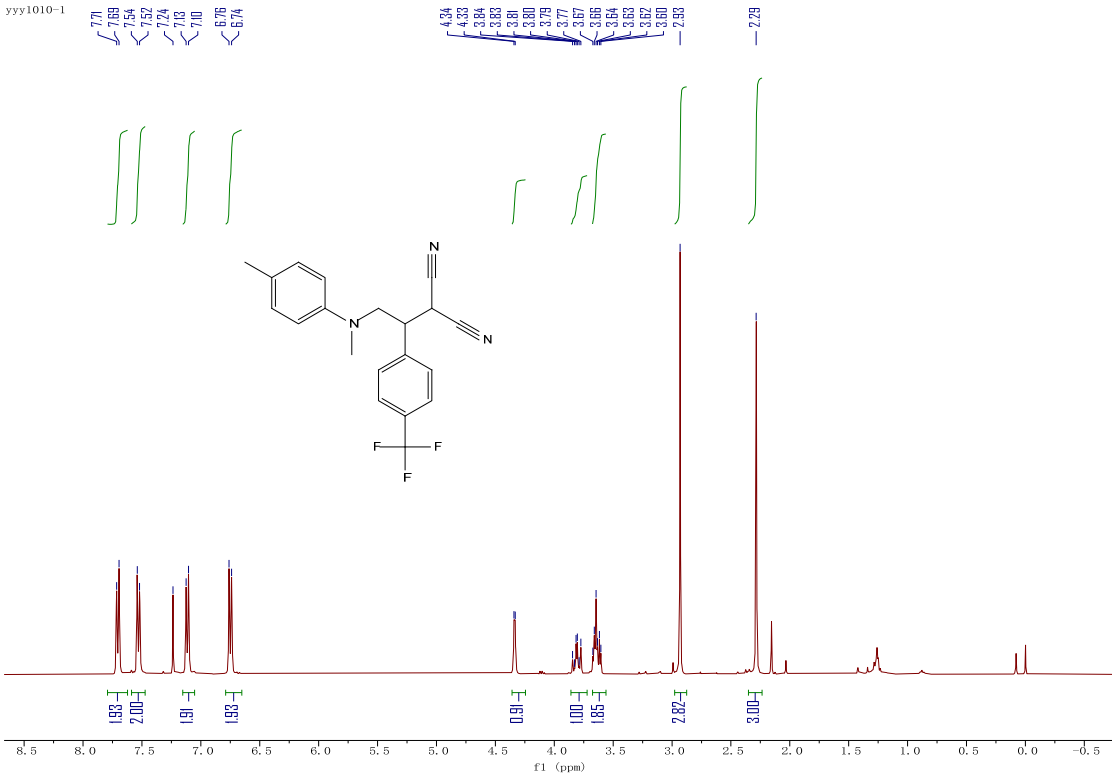
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4q**



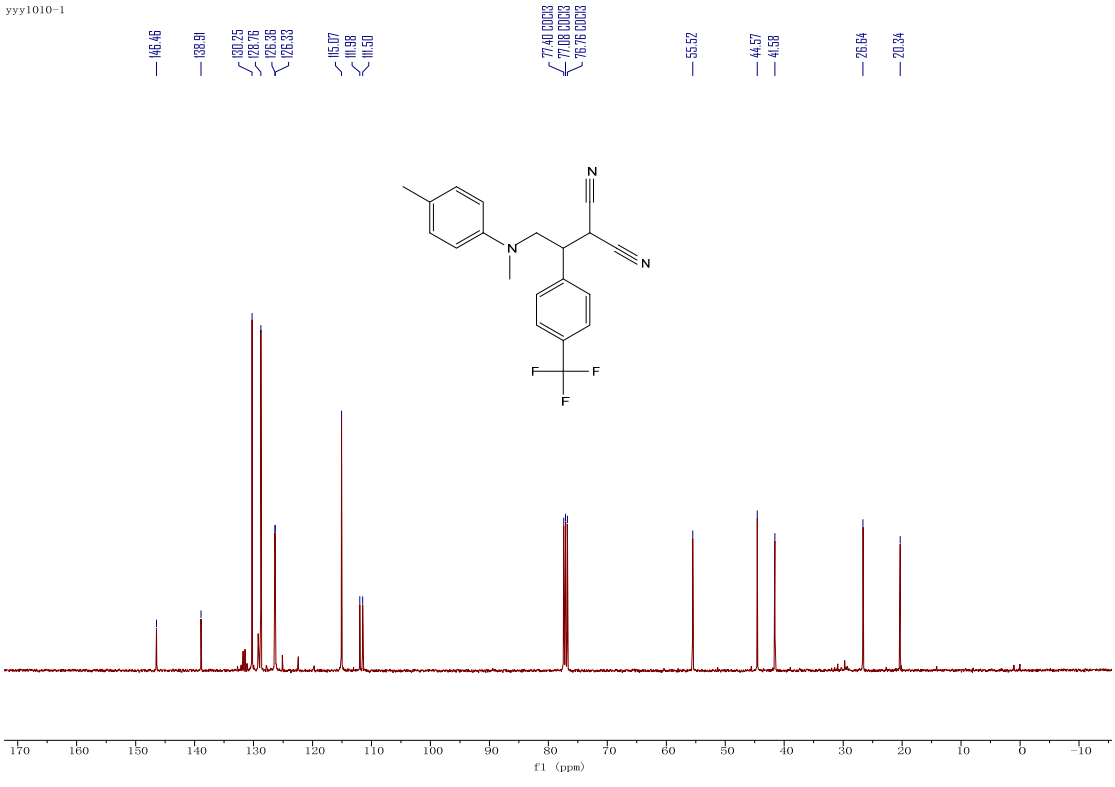
^{19}F NMR-spectrum (377MHz, $CDCl_3$) of **4q**



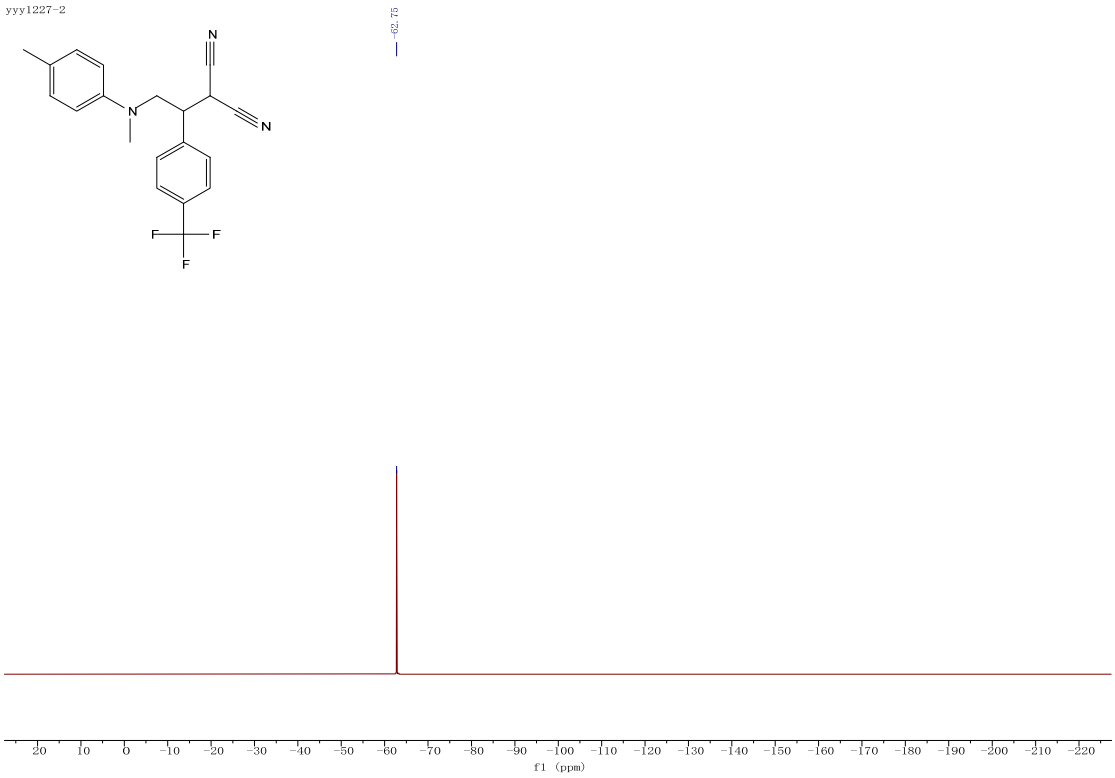
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4r**



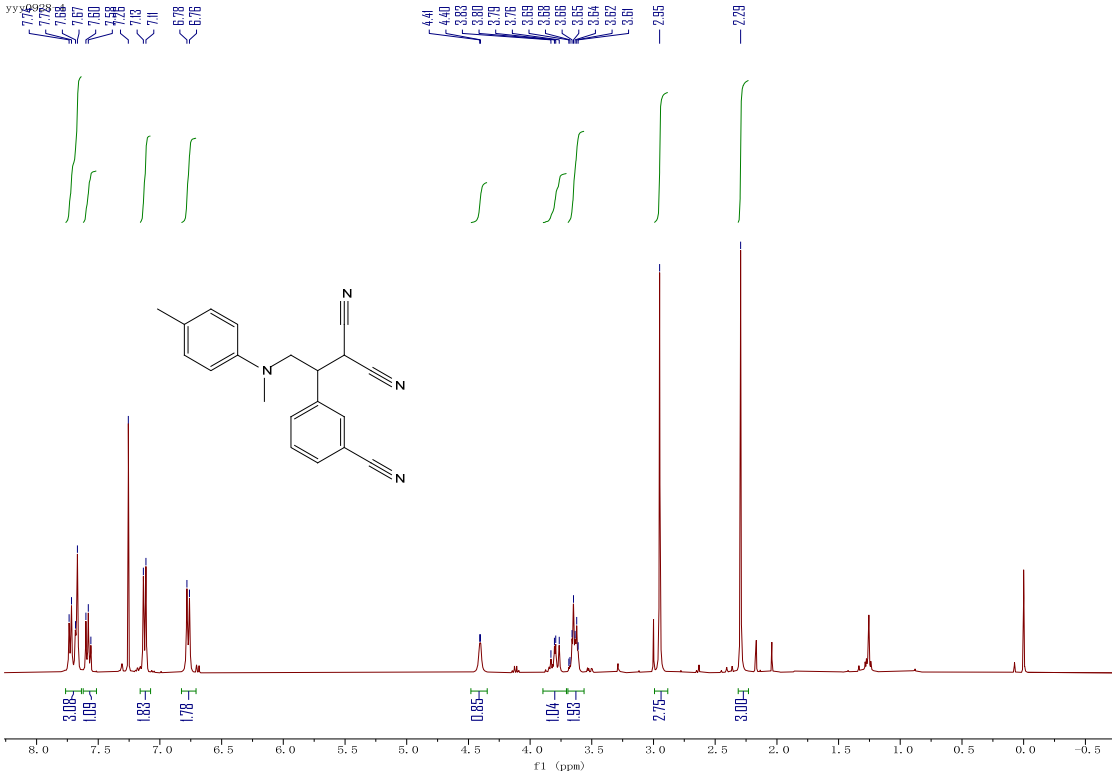
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4r**



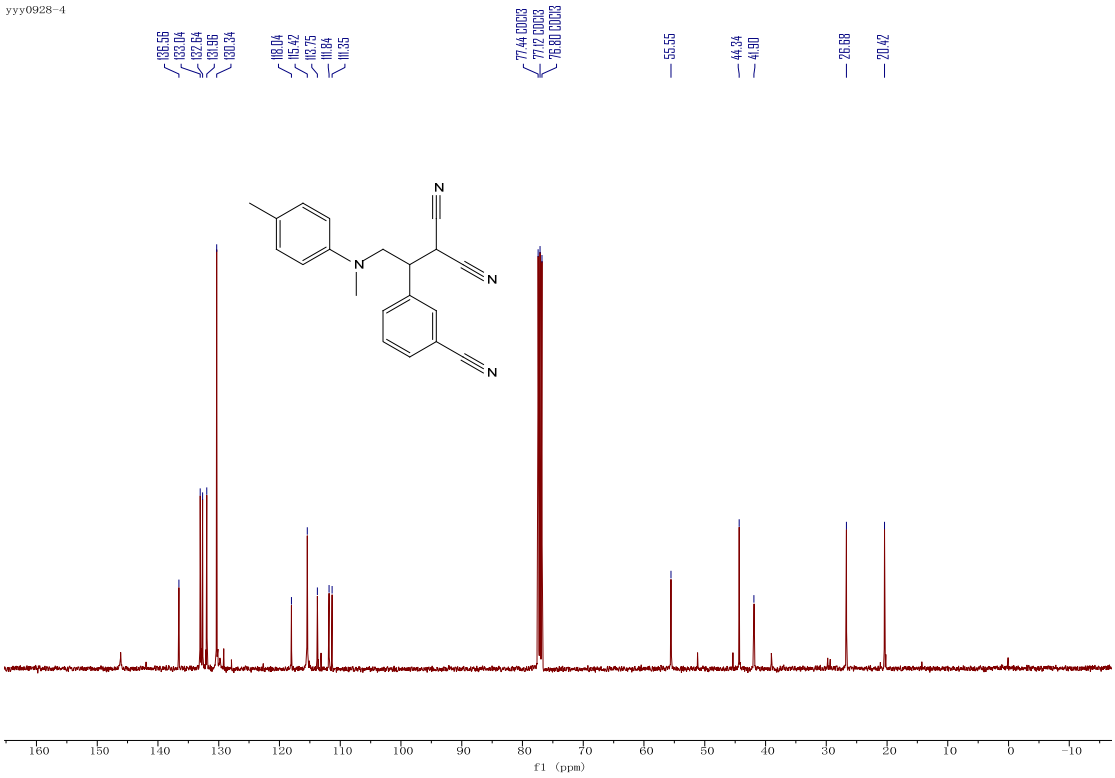
^{19}F NMR-spectrum (377MHz, $CDCl_3$) of **4r**



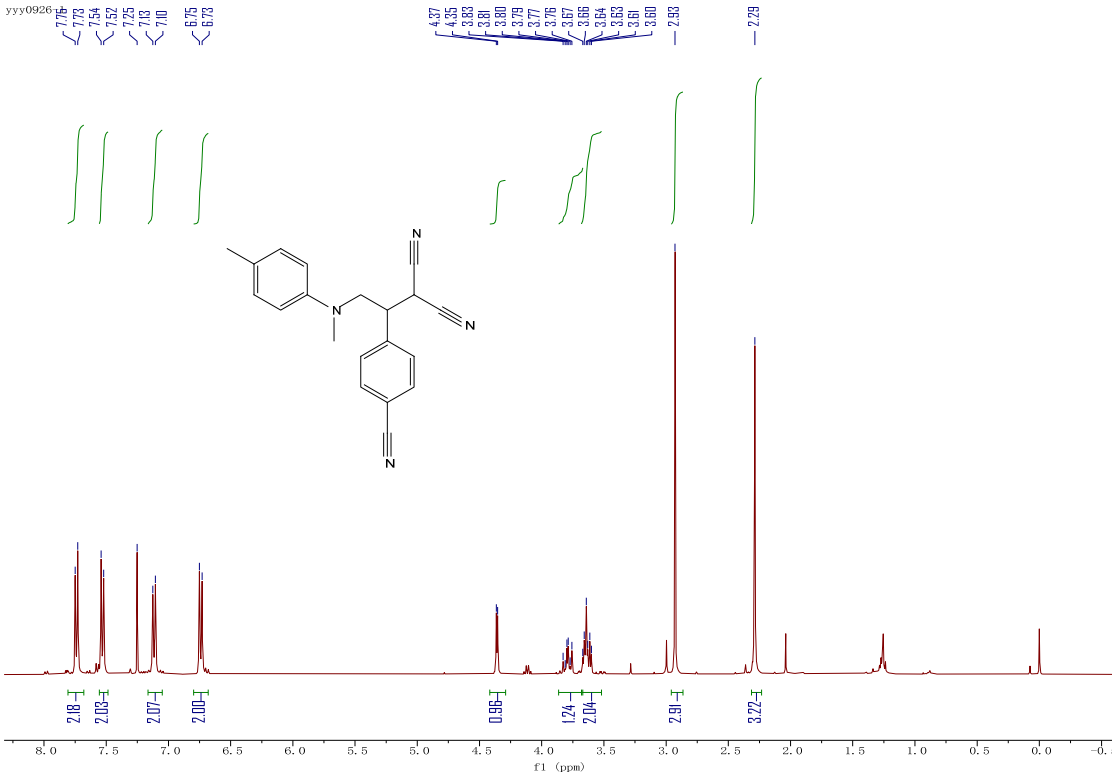
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4s**



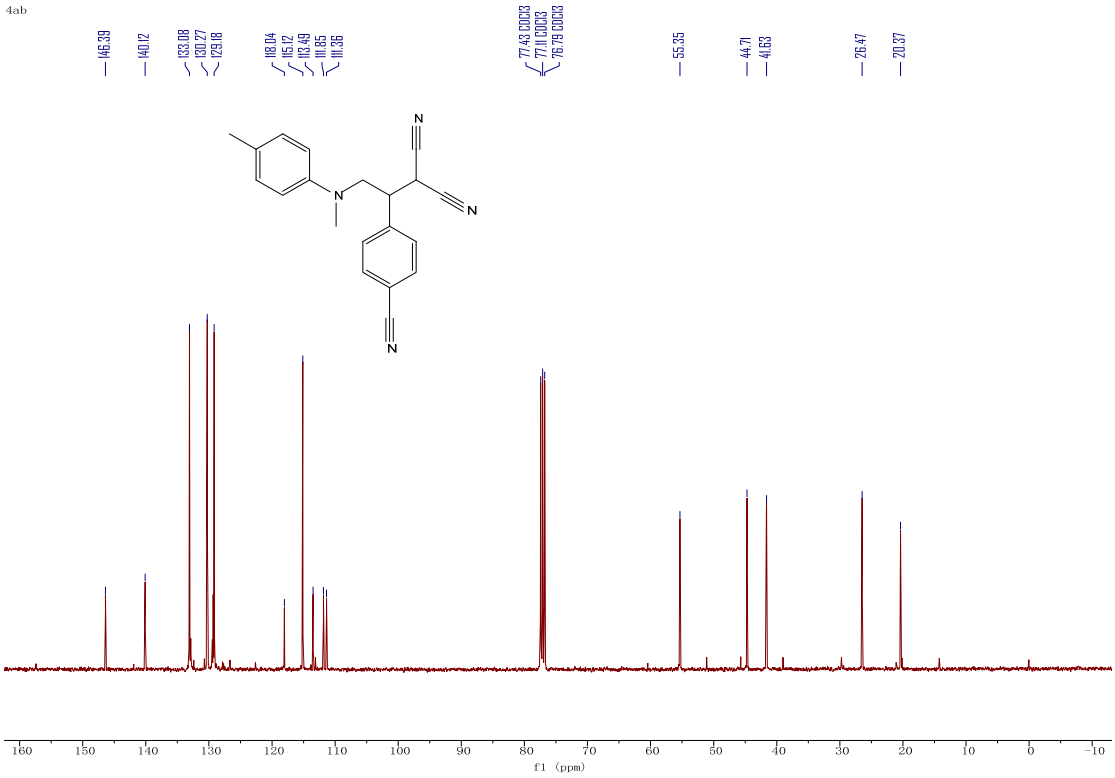
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4s**



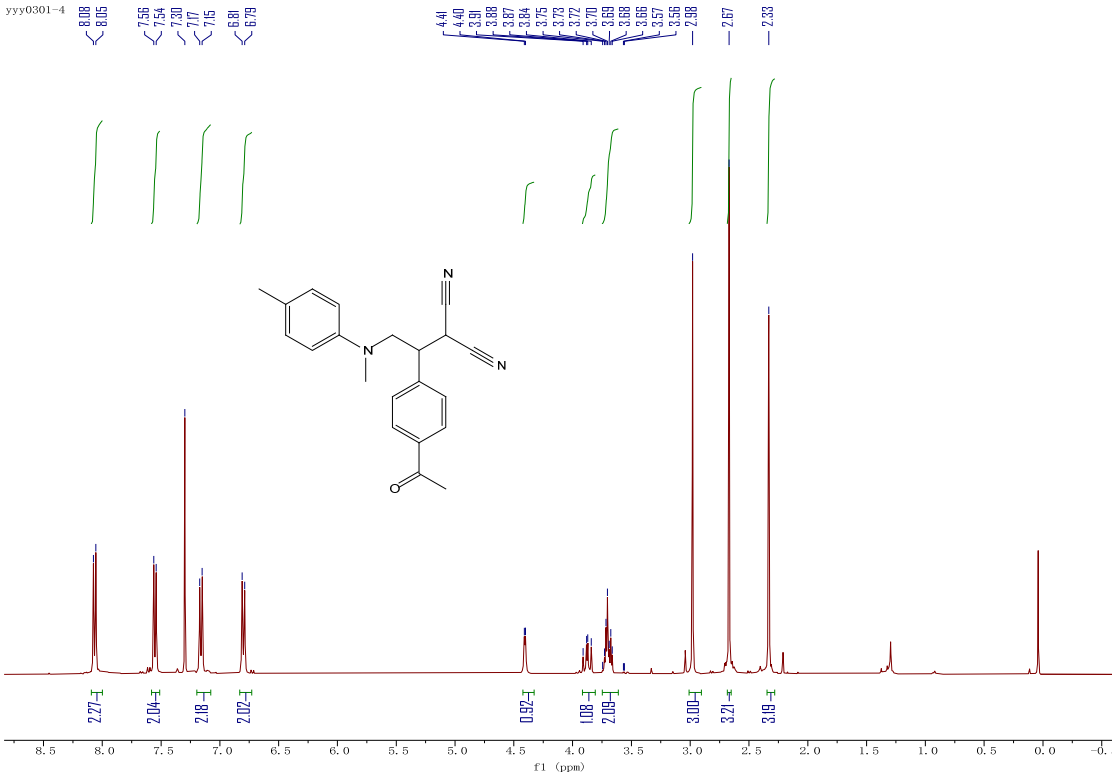
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4t**



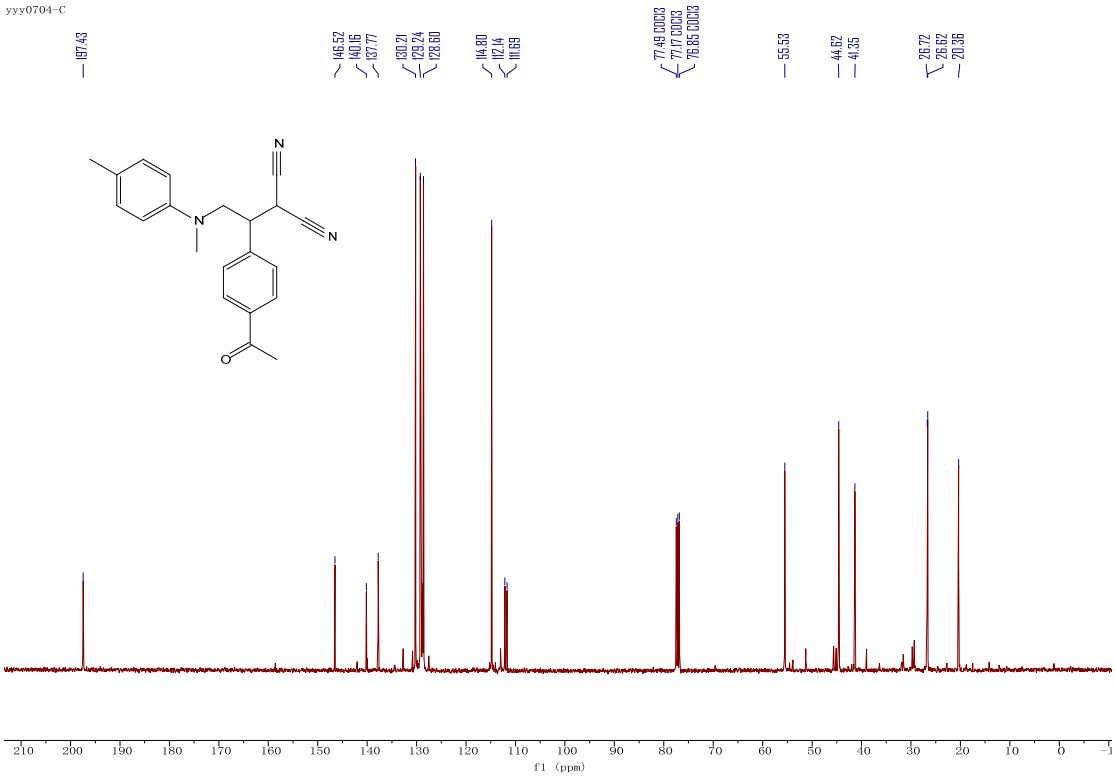
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4t**



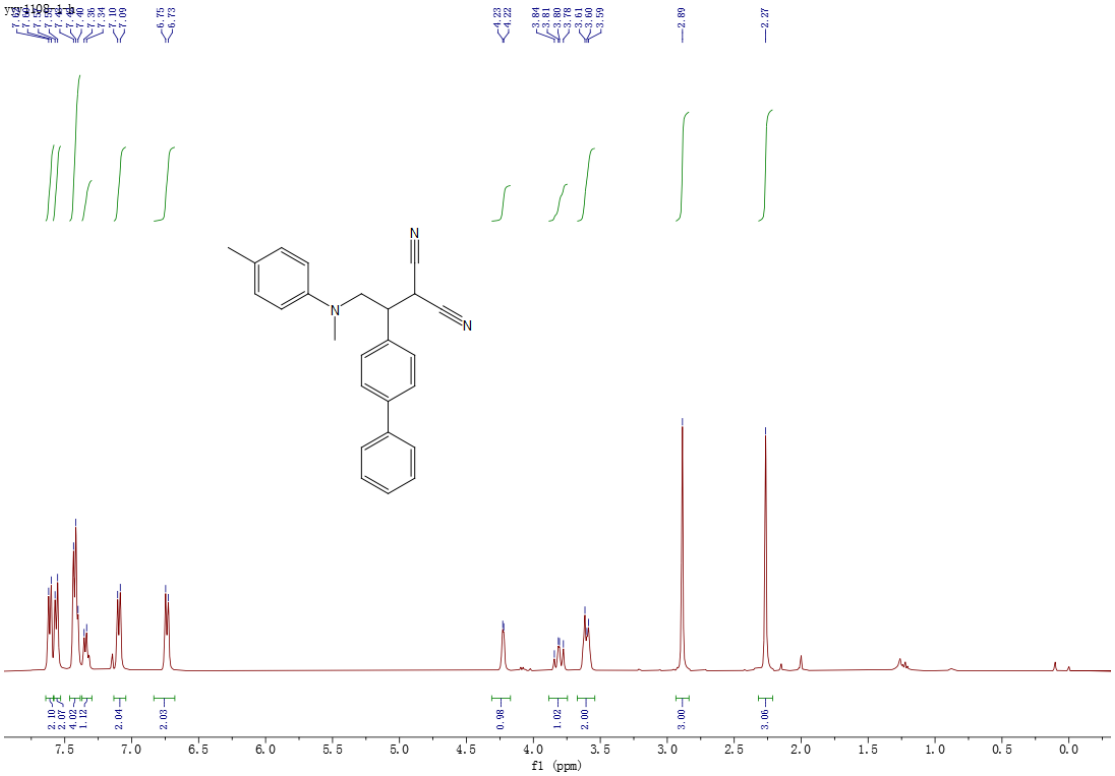
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4u**



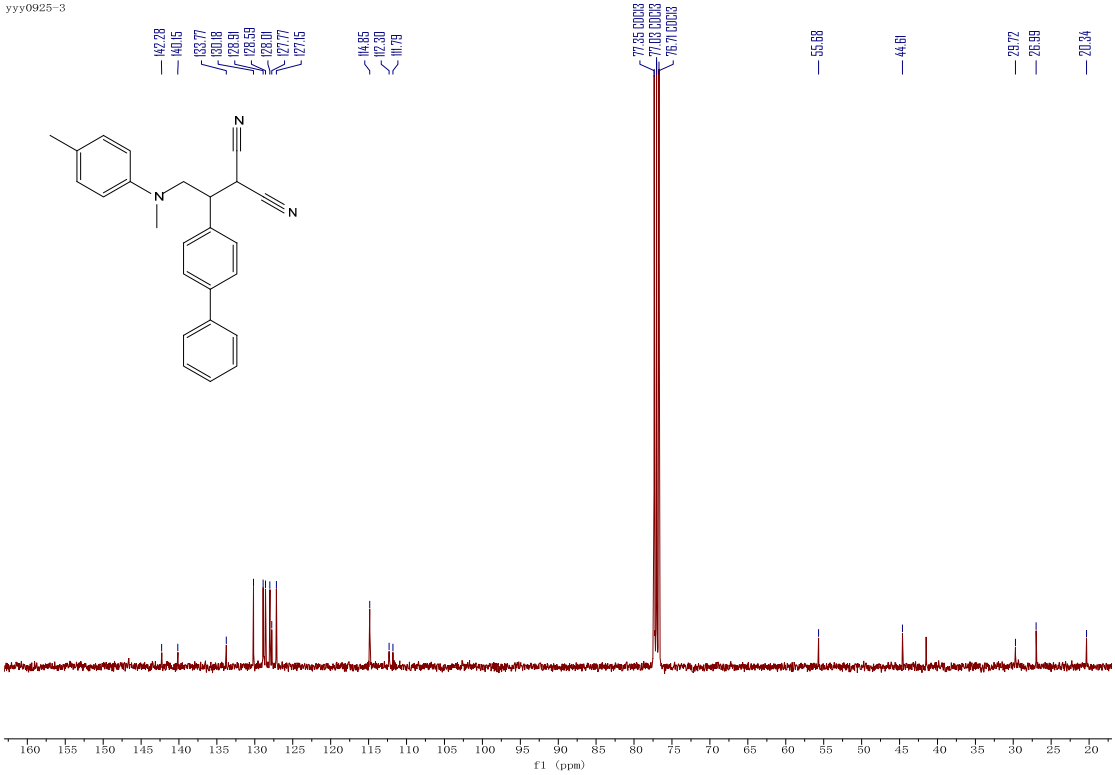
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4u**



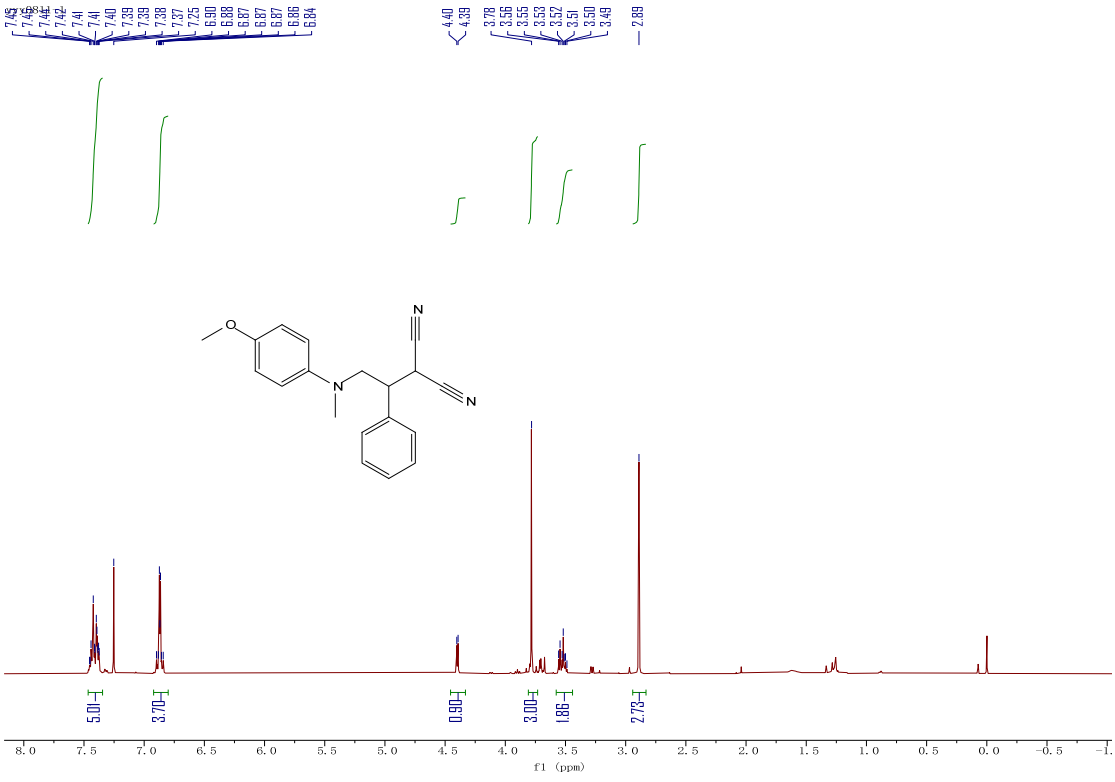
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4v**



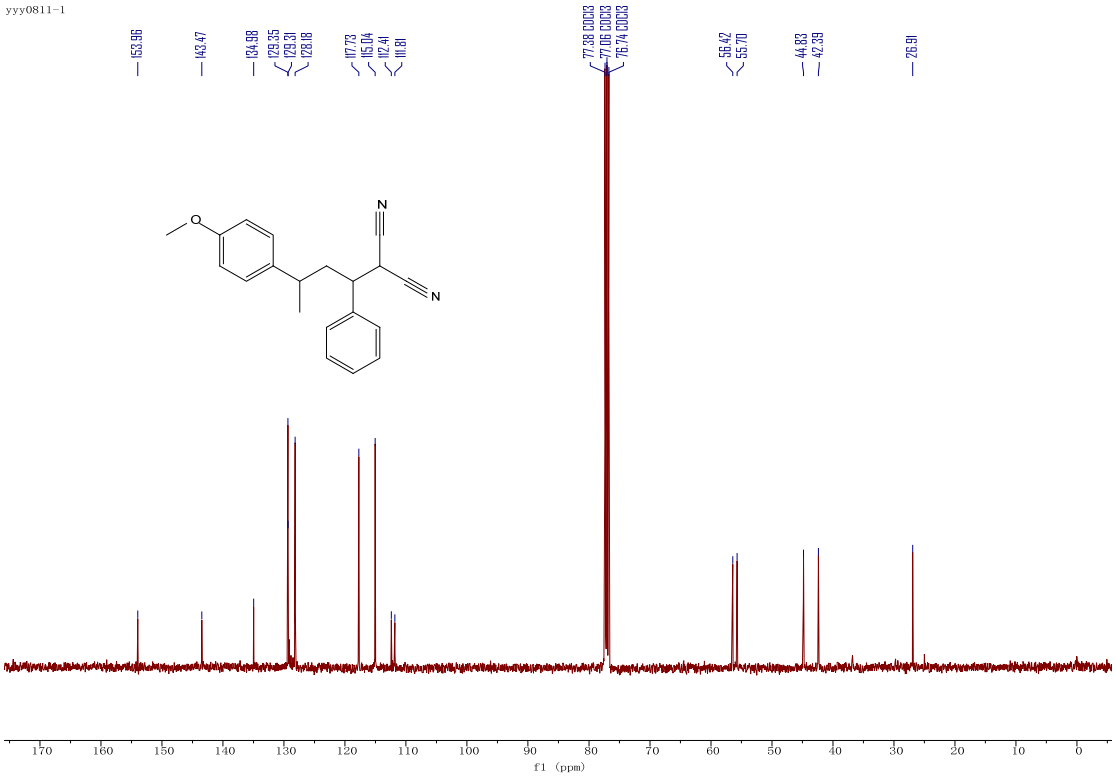
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4v**



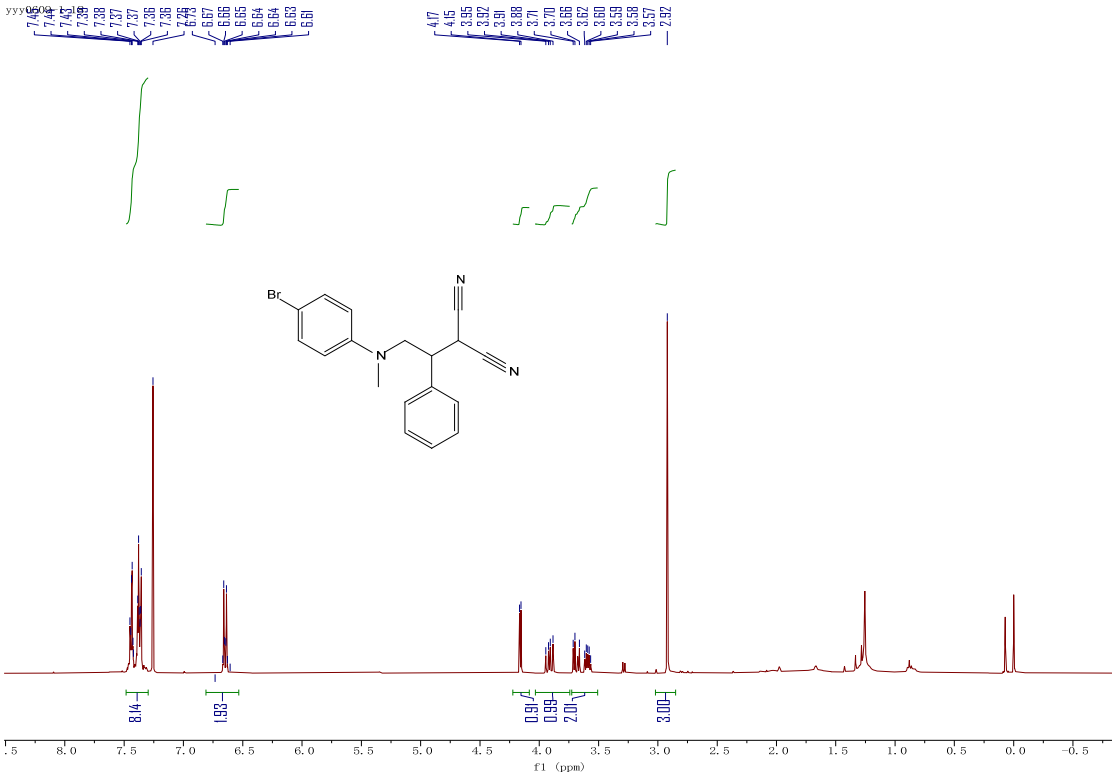
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4w**



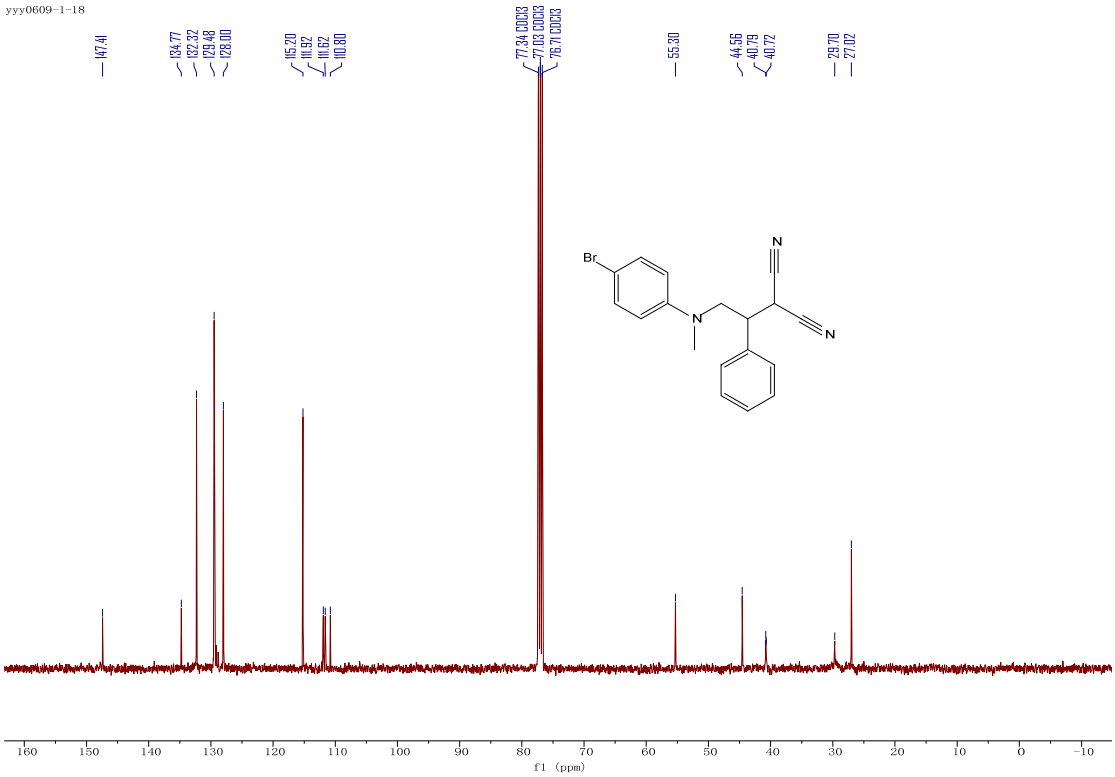
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4w**



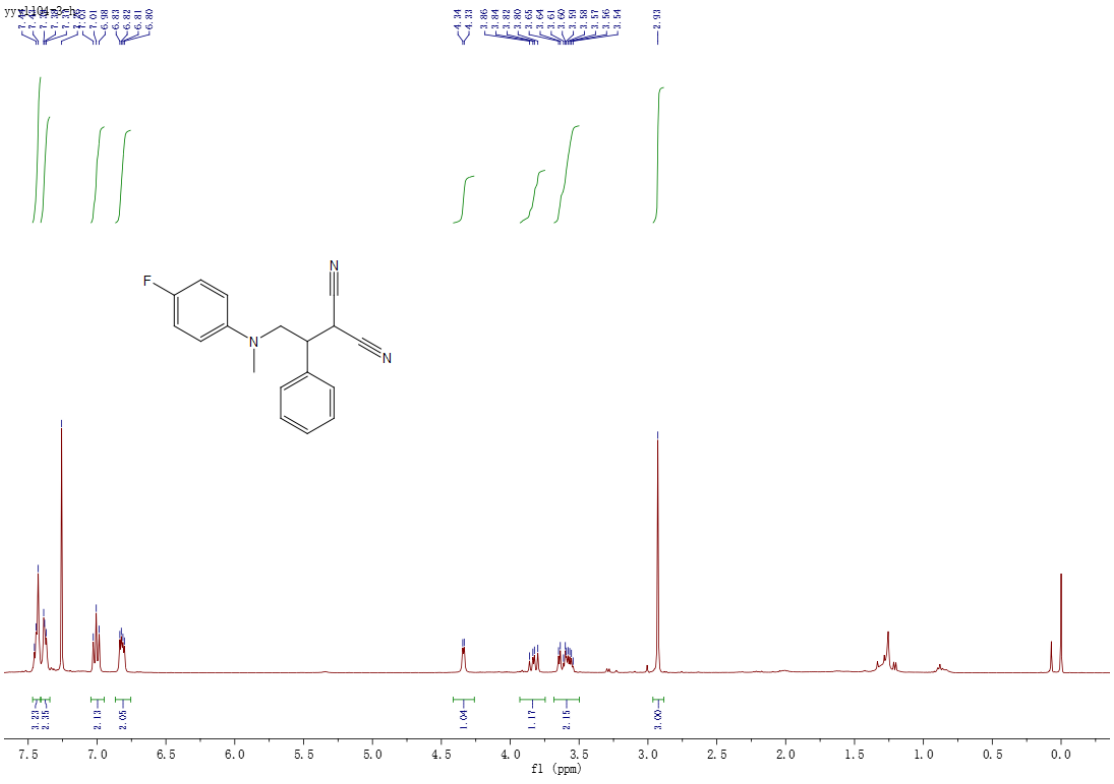
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4x**



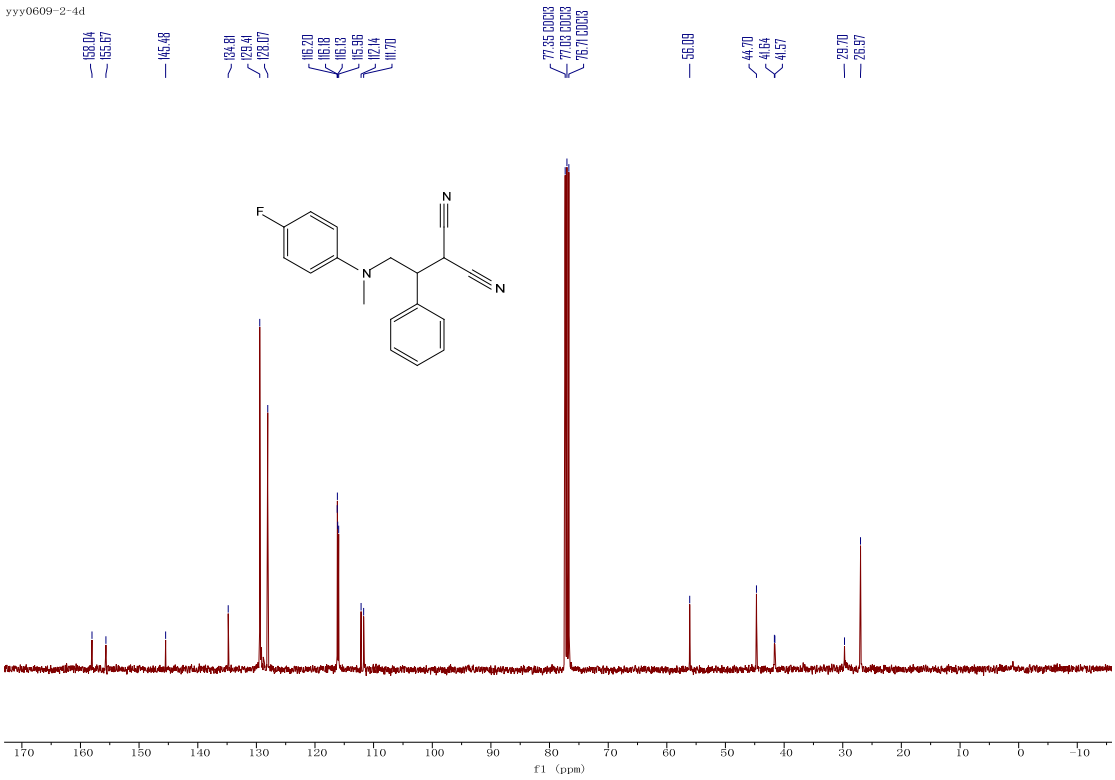
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4x**



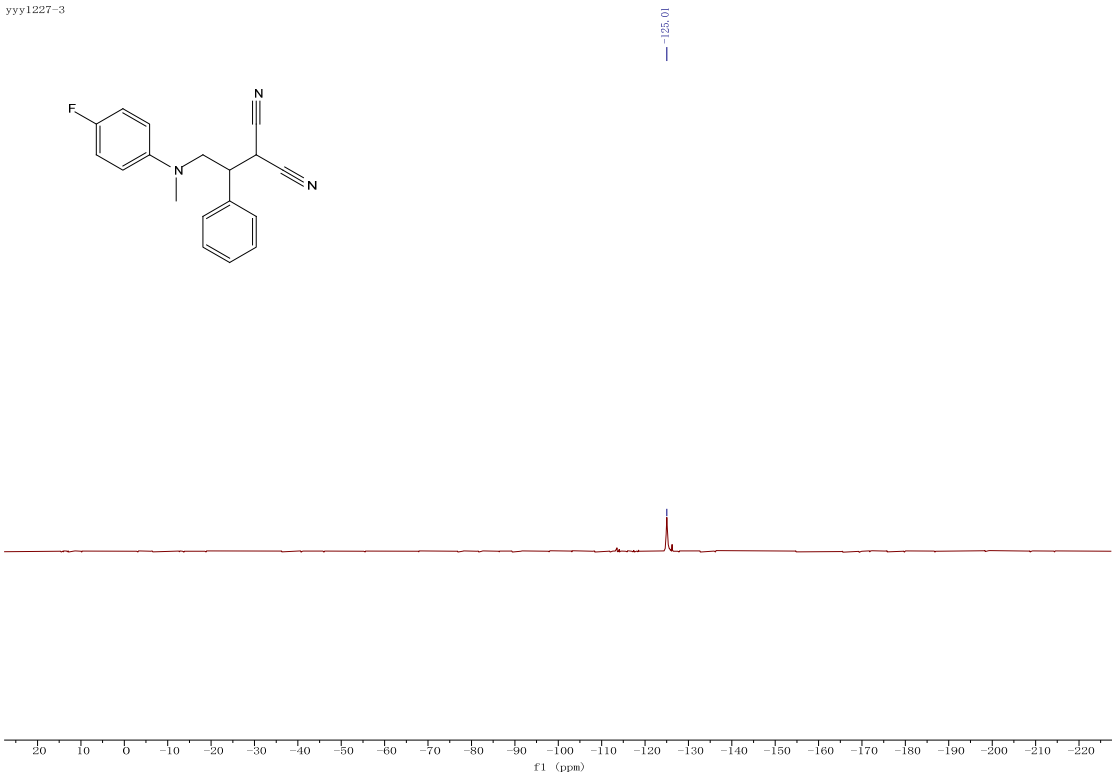
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4y**



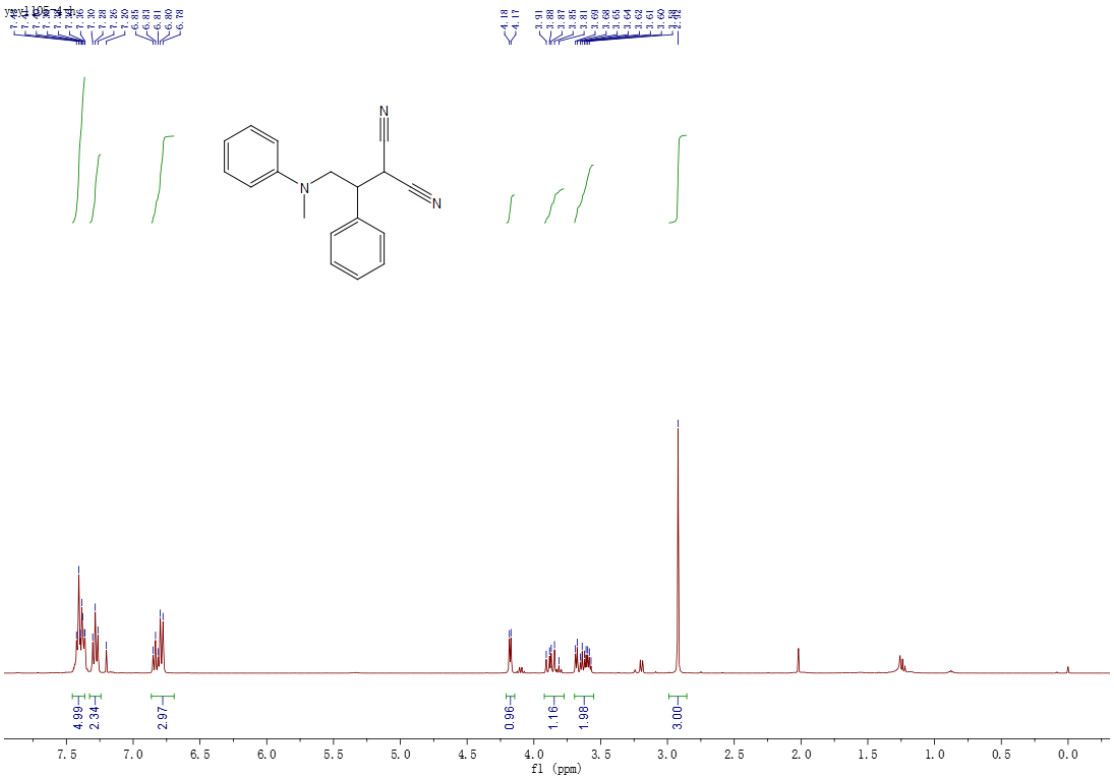
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4y**



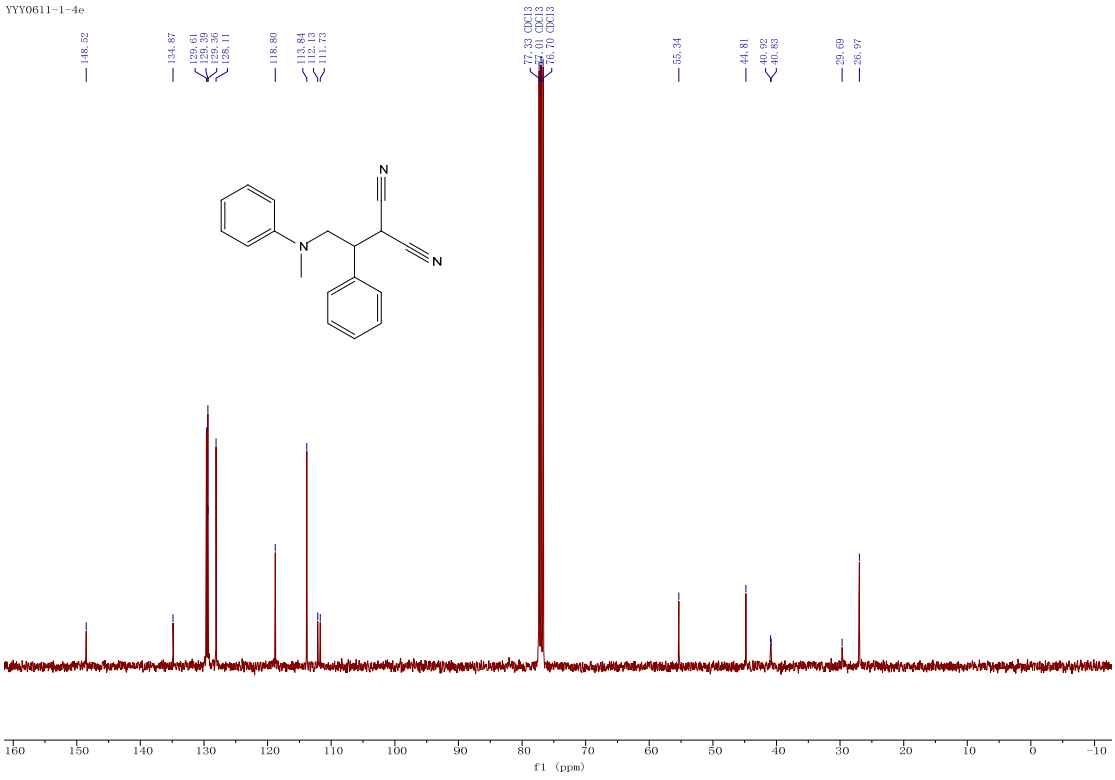
^{19}F NMR-spectrum (377MHz, $CDCl_3$) of **4y**



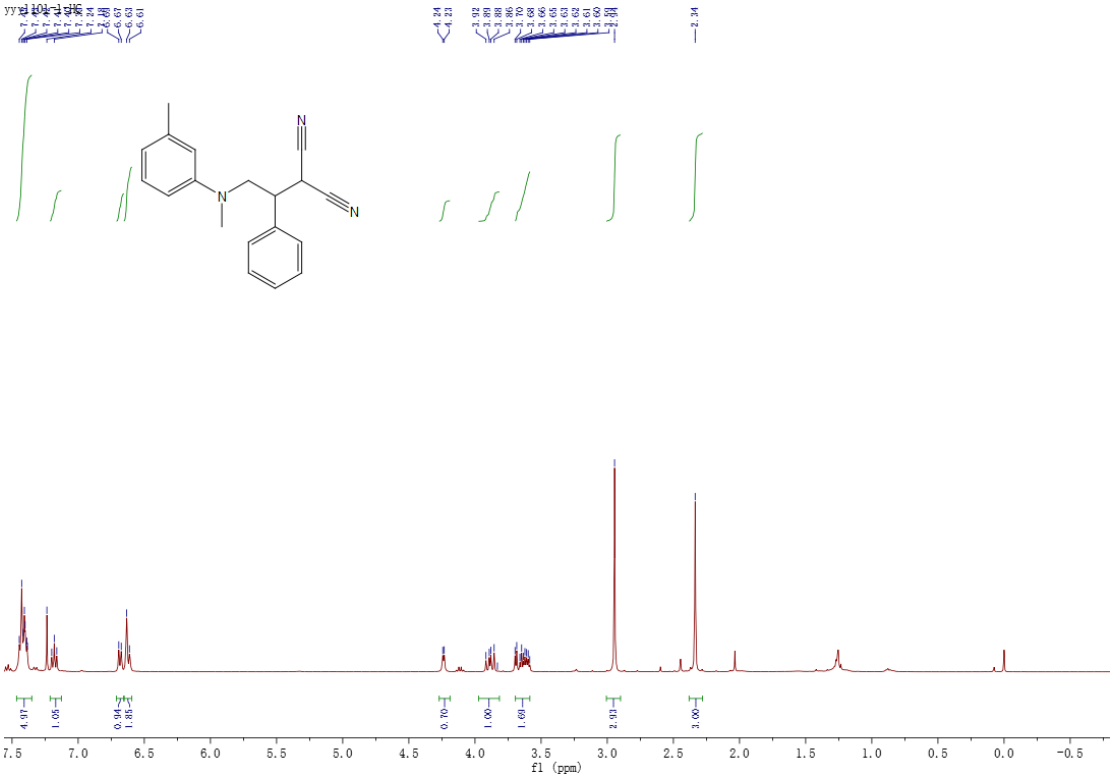
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4z**



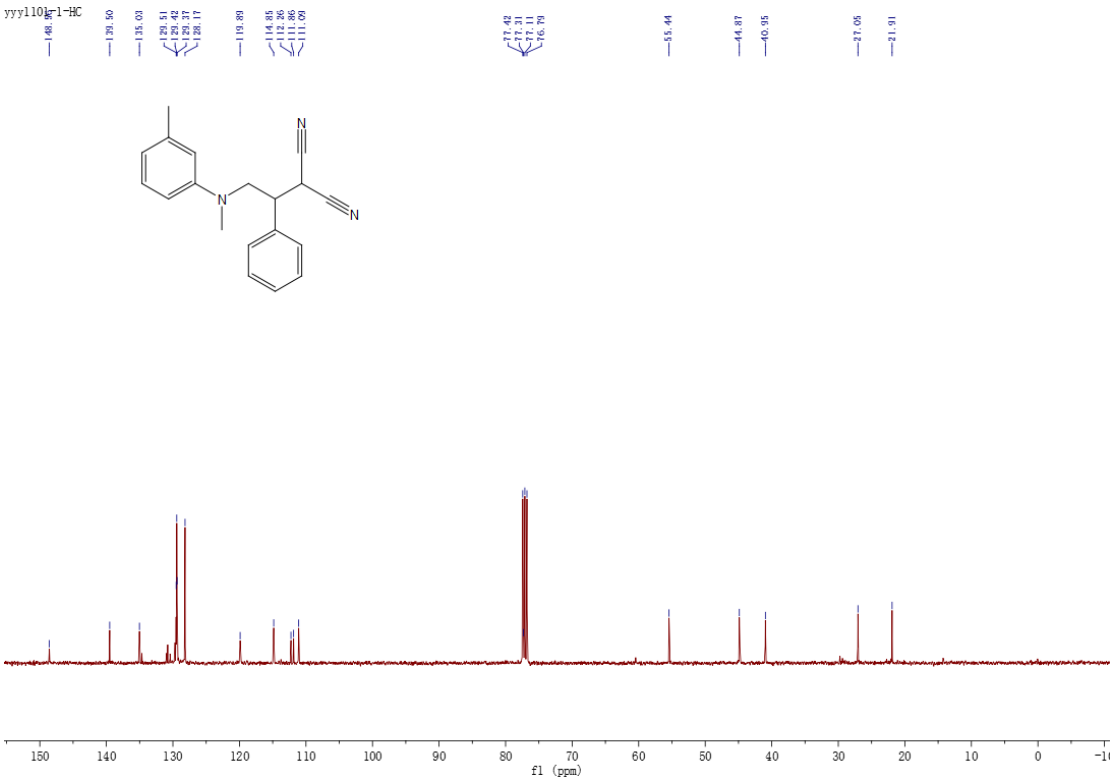
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4z**



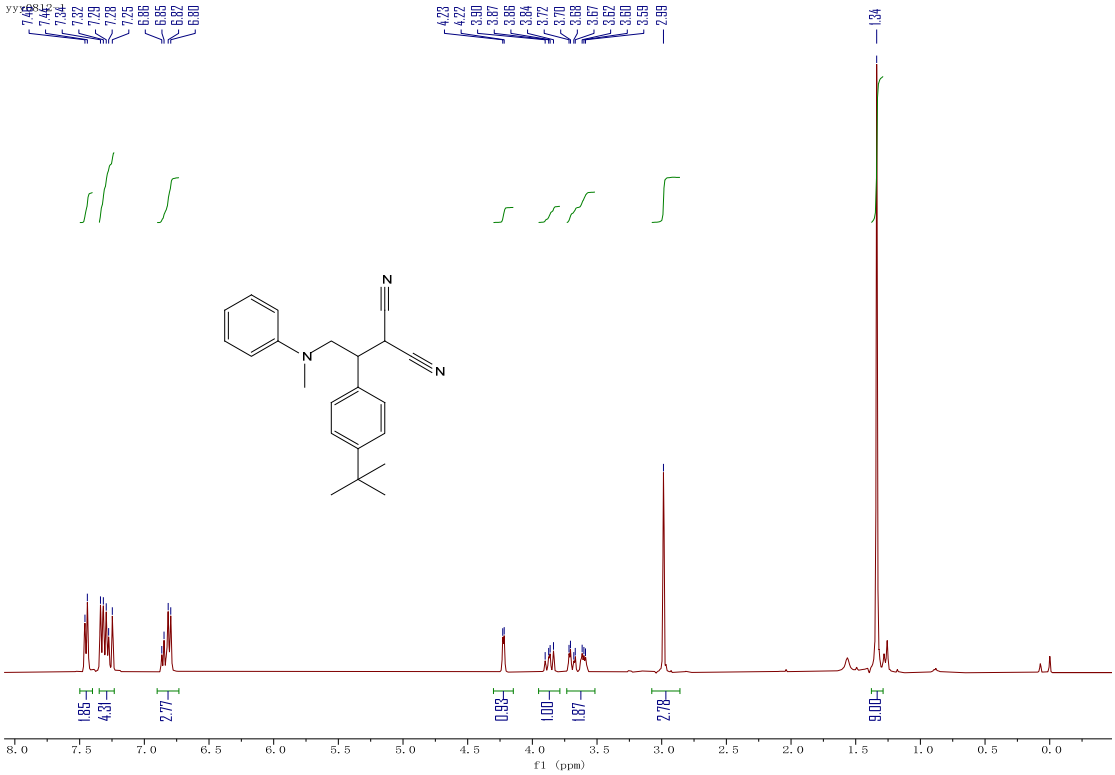
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4aa**



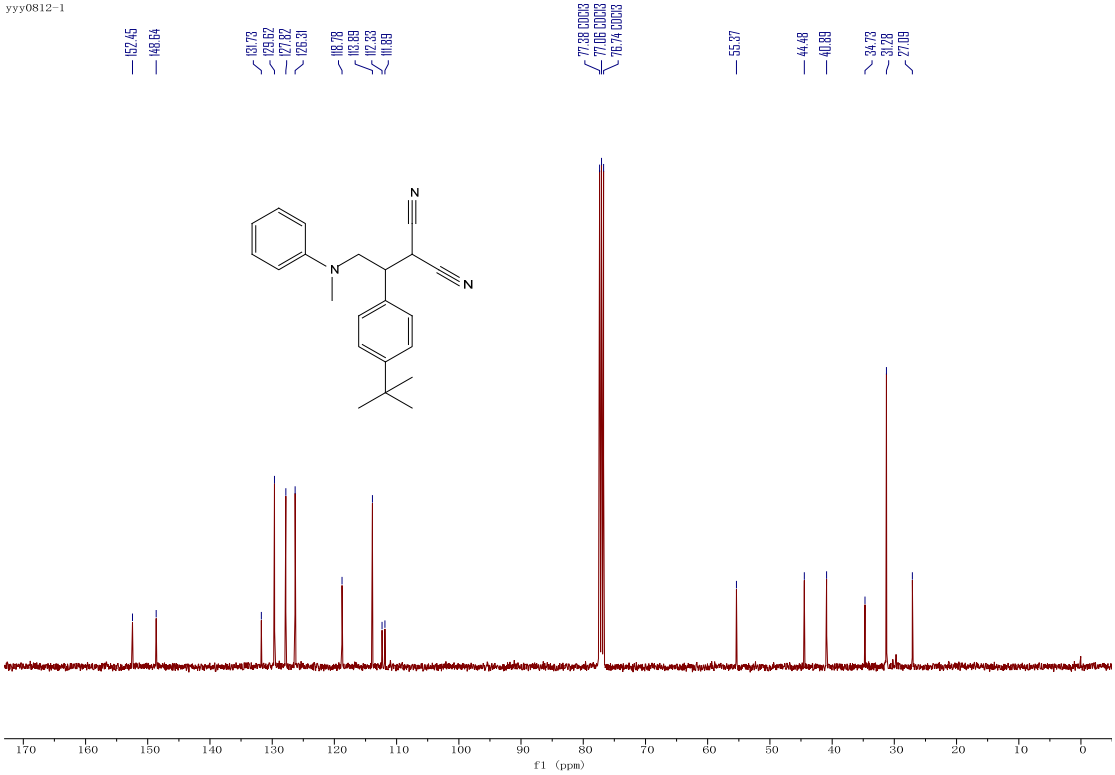
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4aa**



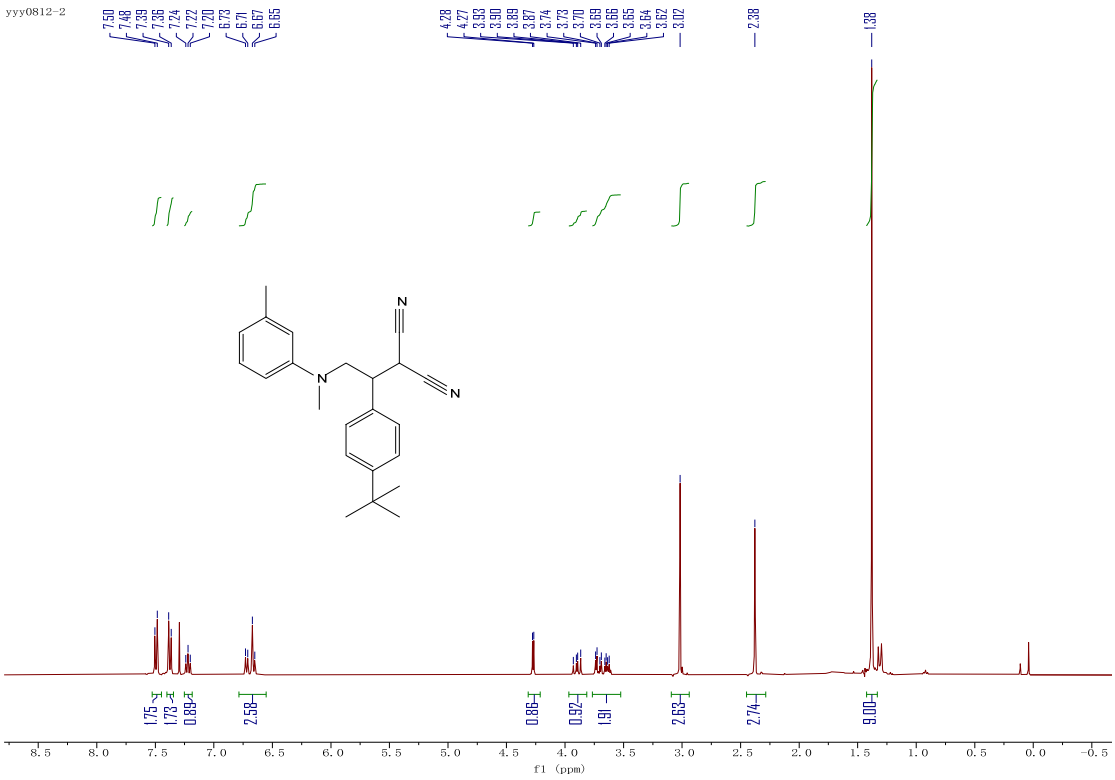
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4ab**



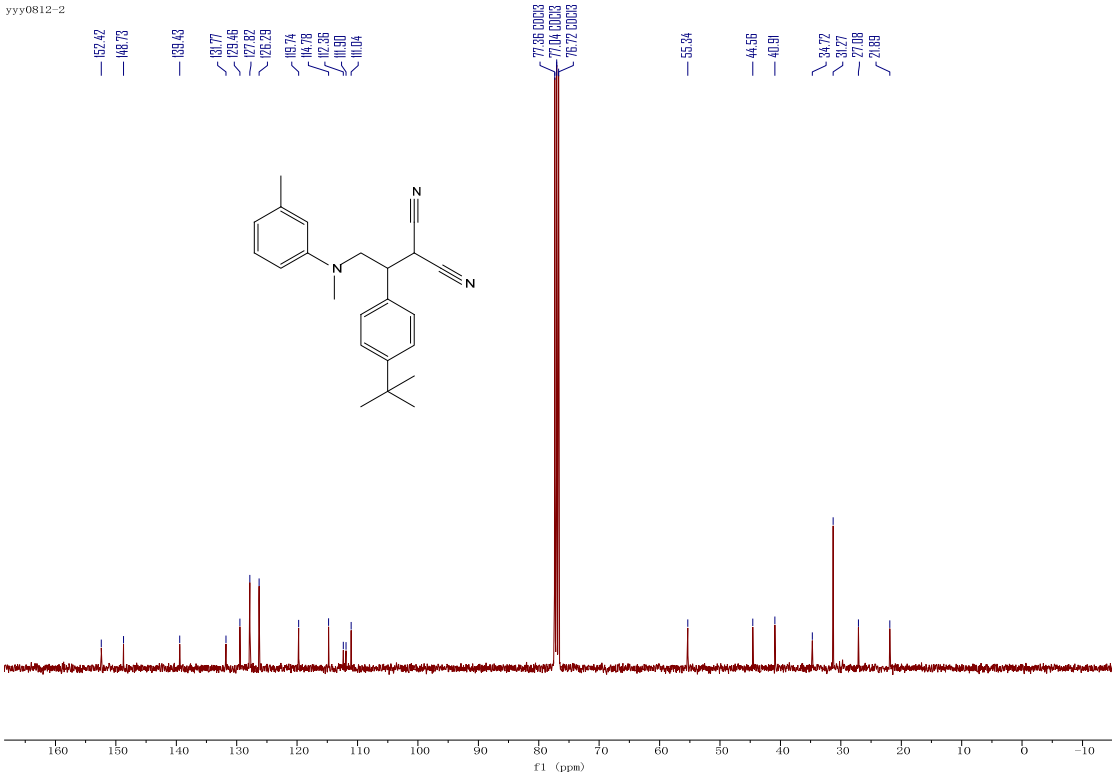
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4ab**



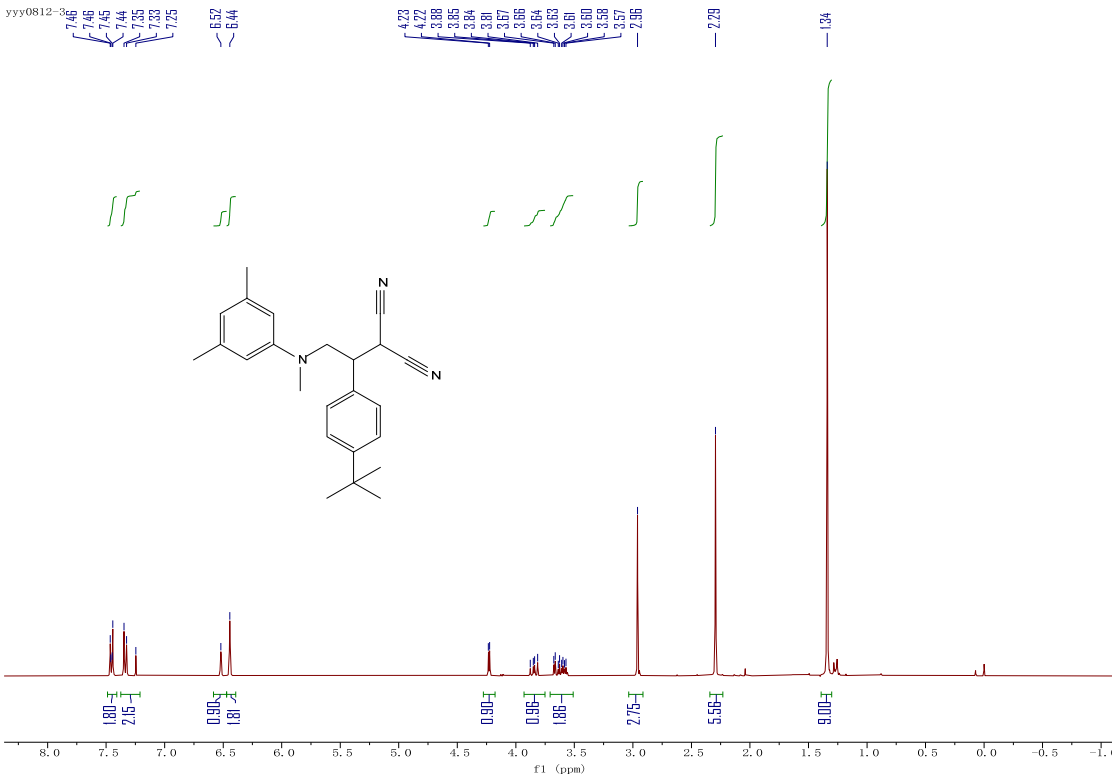
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4ac**



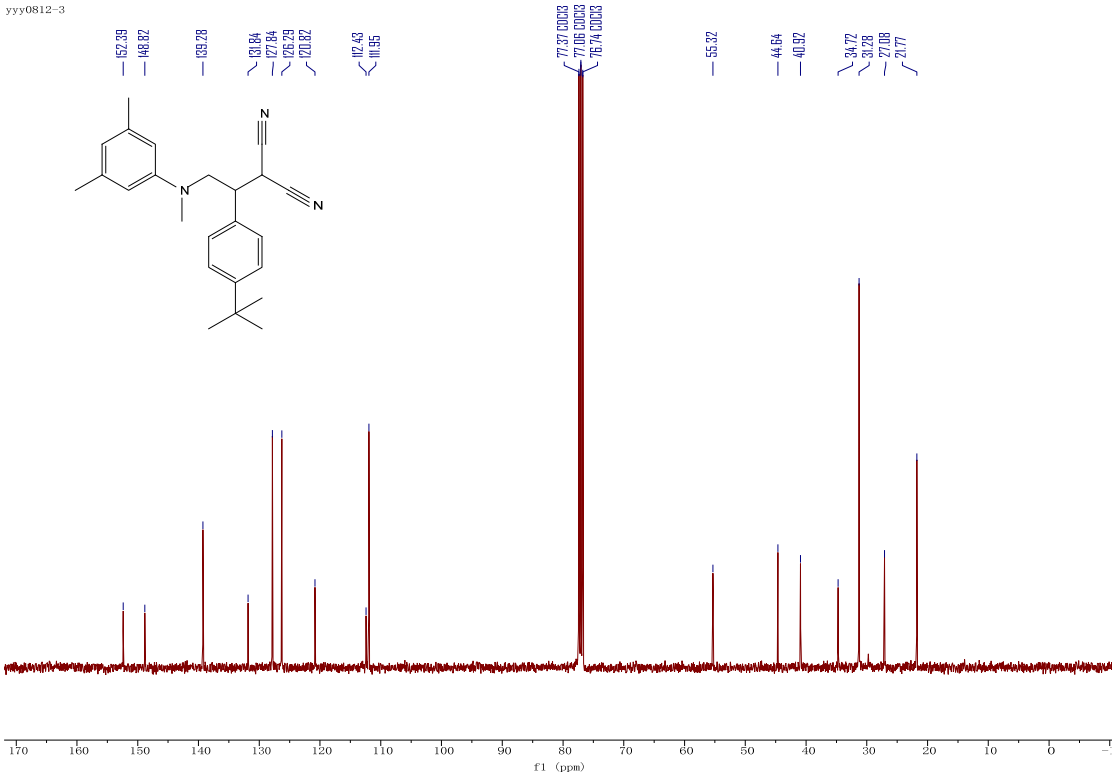
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4ac**



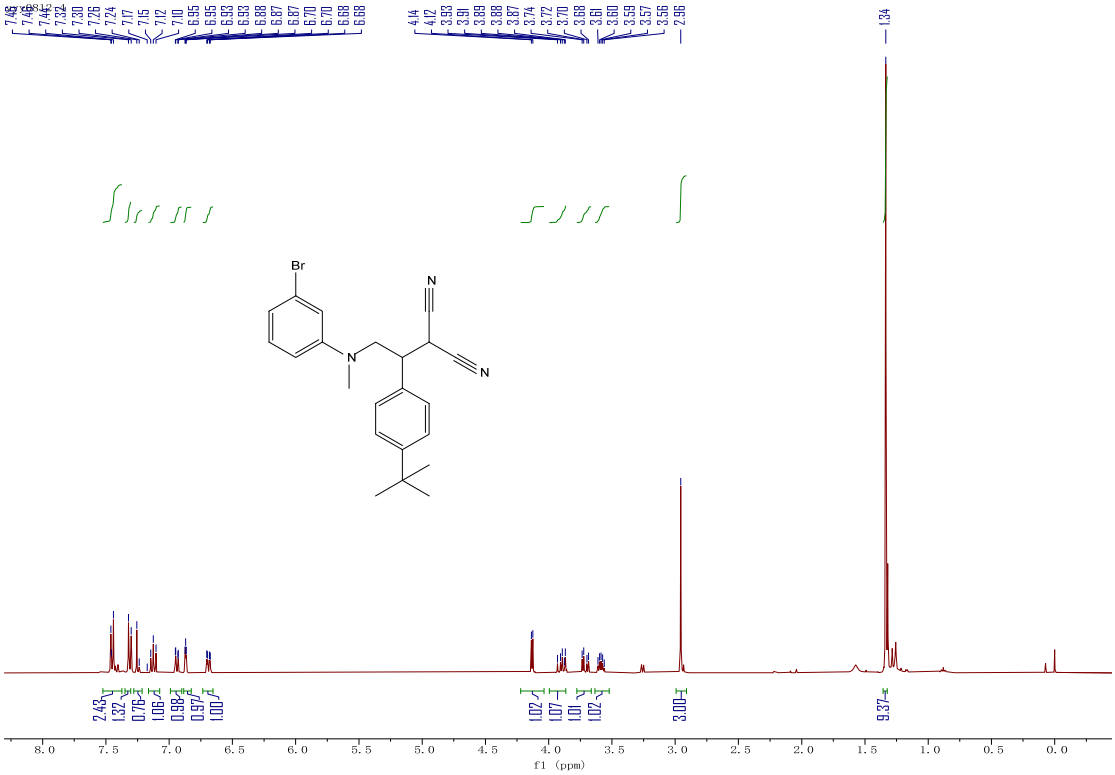
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4ad**



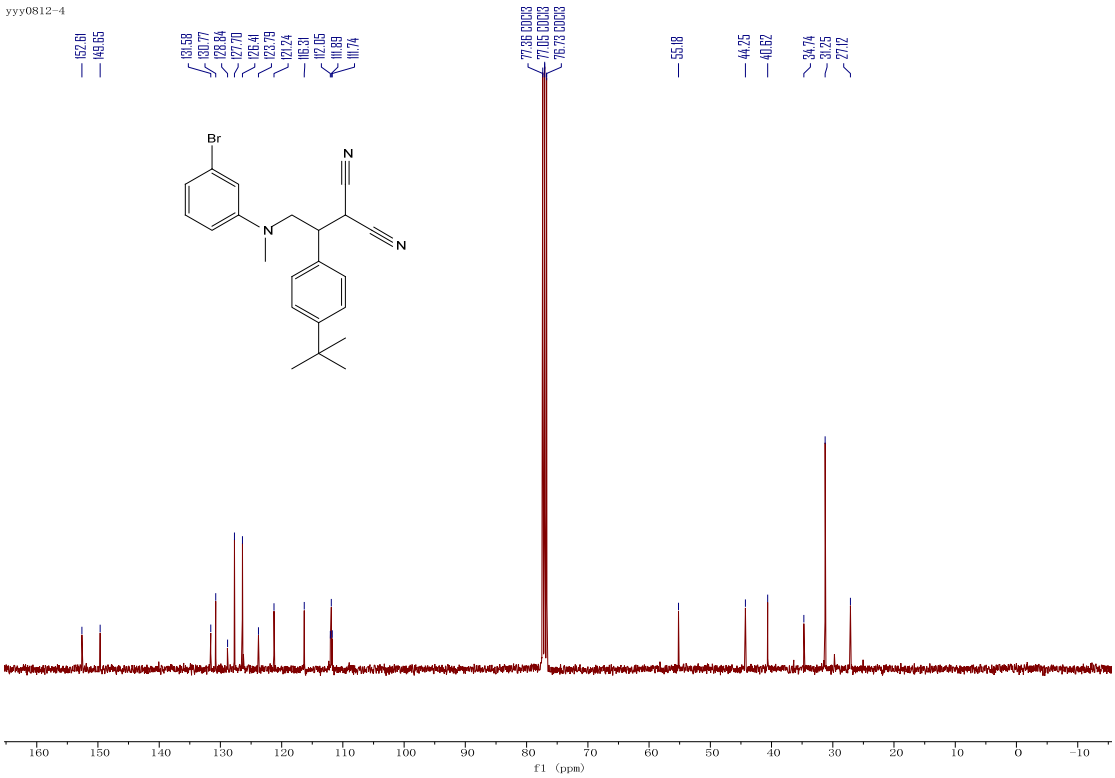
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4ad**



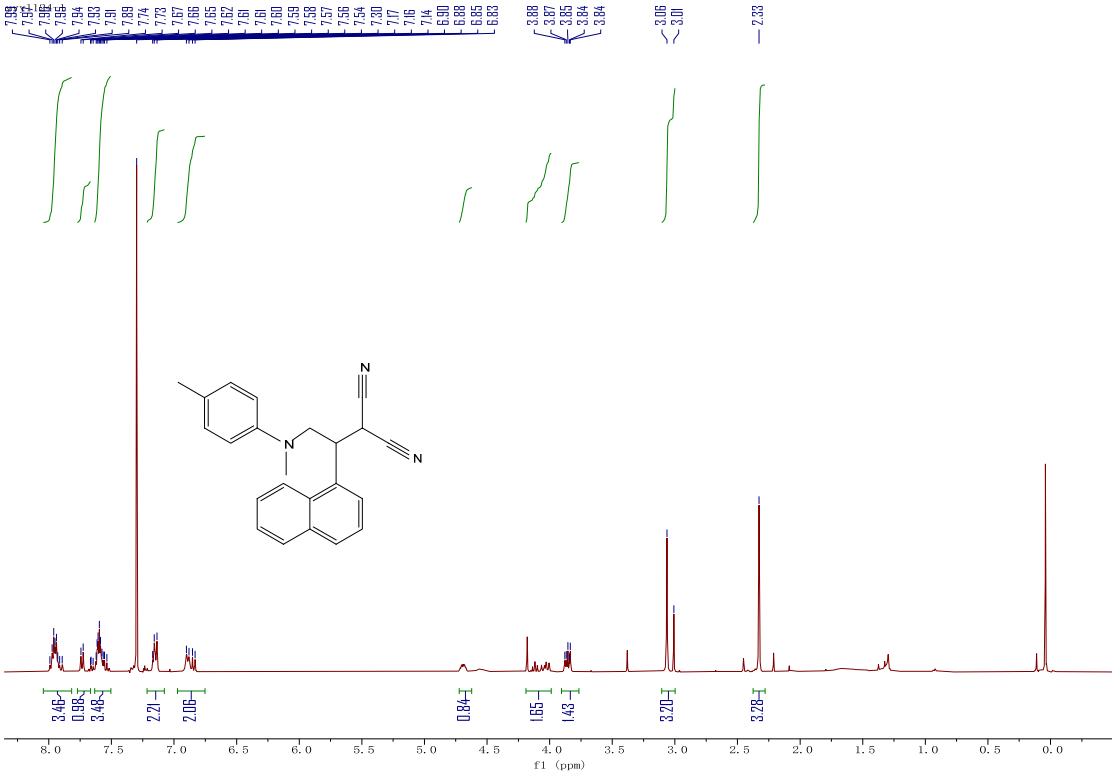
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4ae**



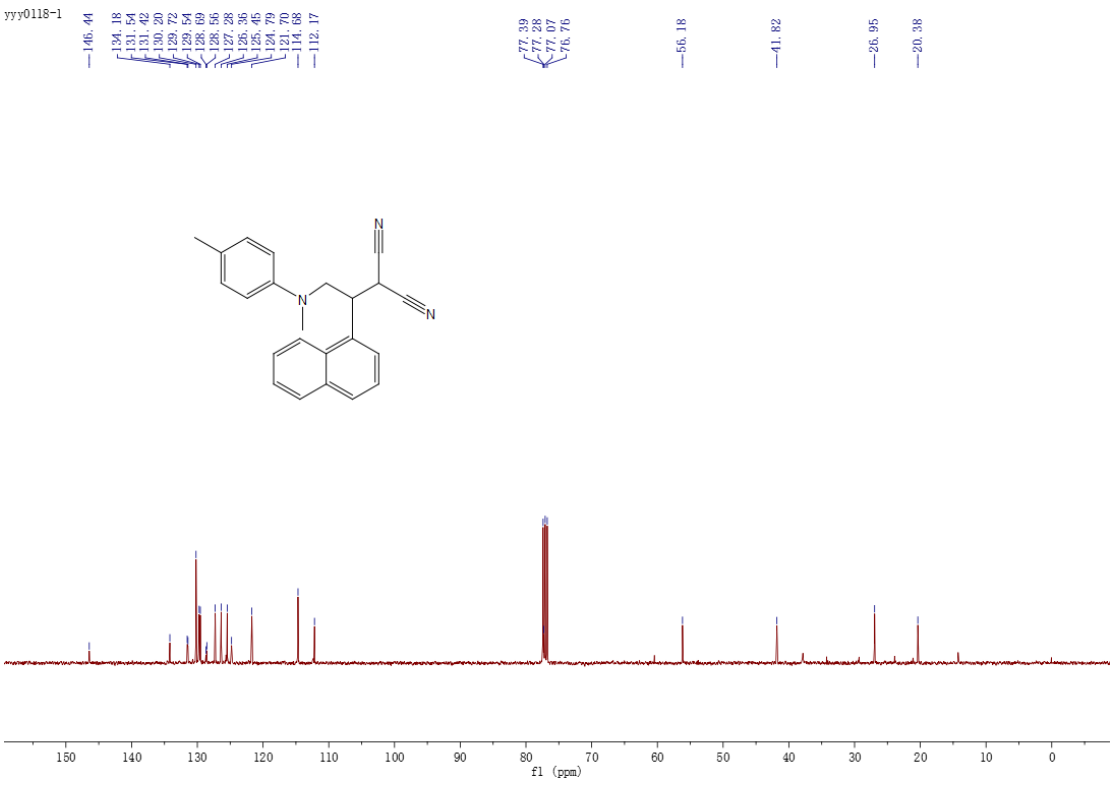
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4ae**



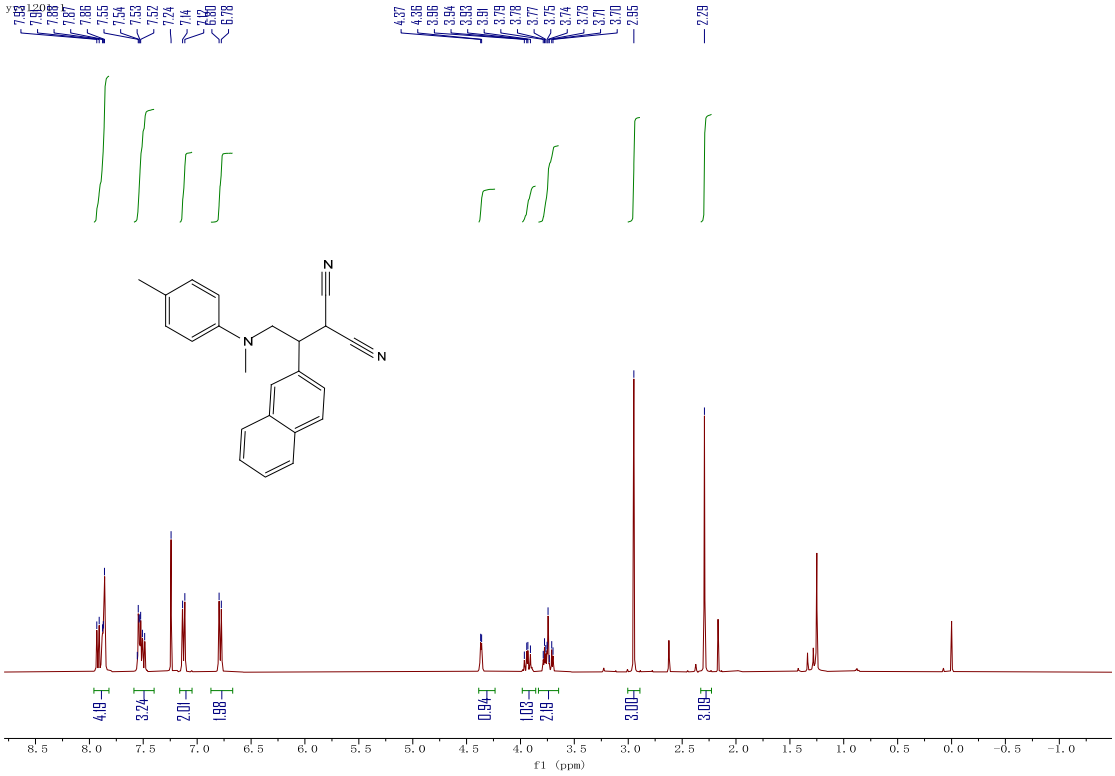
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4af**



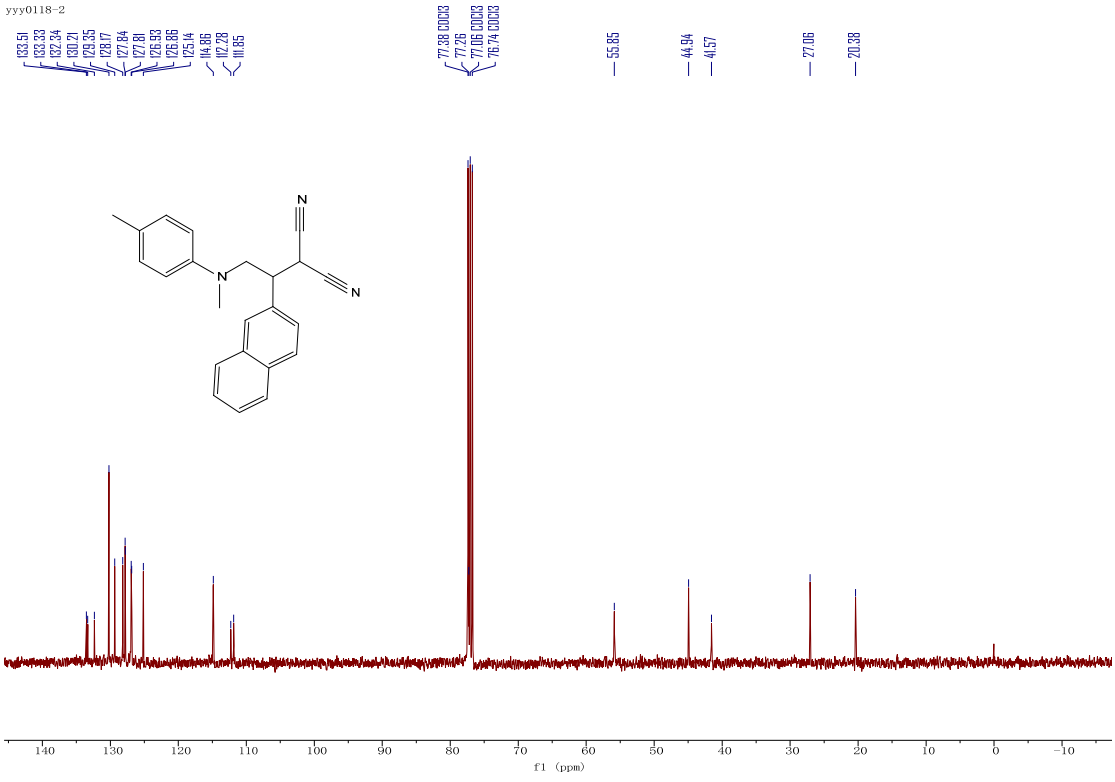
^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4af**



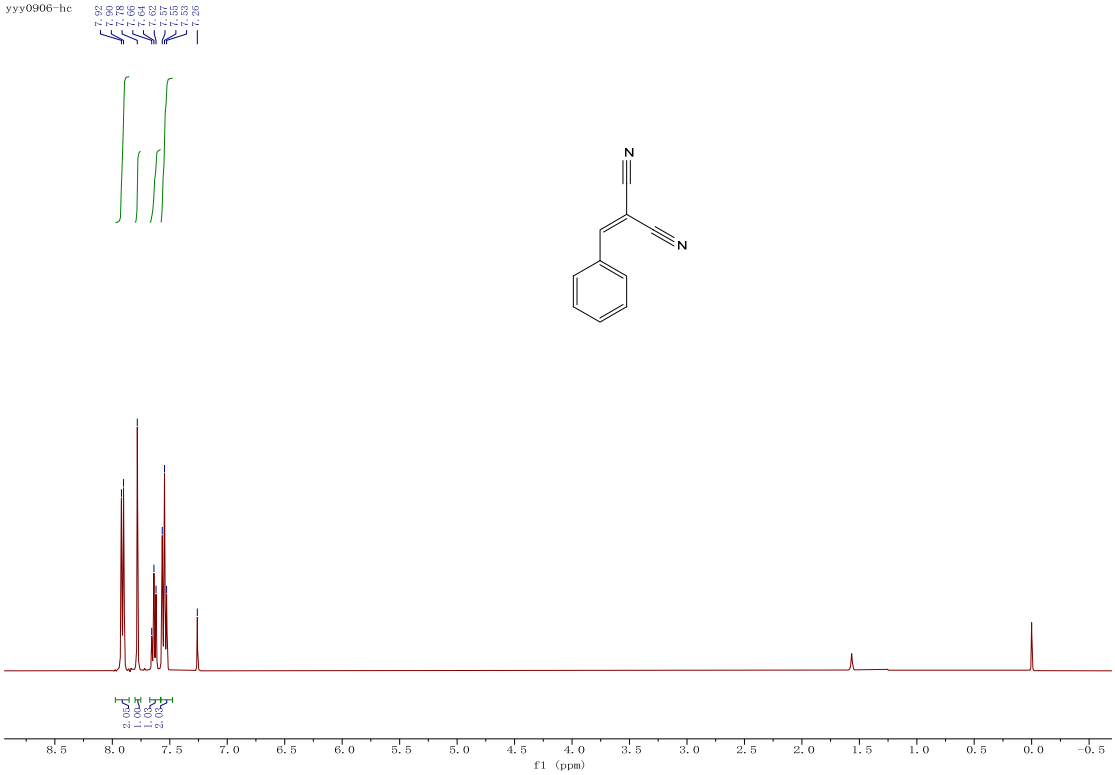
^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **4ag**



^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **4ag**



^{1}H NMR-spectrum (400MHz, $CDCl_3$) of **5**



^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **5**