Supporting Information

Catalyst-free chemoselective reduction of the carbon-carbon double bond in conjugated alkenes with Hantzsch esters in water

Qi He[b], Zhihong Xu[a], Dehong Jiang[b], Wensi Ai[b], Ronghua Shi[b], Shan Qian*[b], Zhouyu Wang*[a]

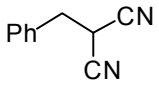
[a] Department of Chemistry, Xihua University, Chengdu, 610039, China
[b] Department of Pharmaceutics Engineering, Xihua University, Chengdu, 610039, China
E-mail: zhouyuwang77@gmail.com; qians33@163.com;

Fax: +86-028-8772-3006; Tel: +86-028-8772-9463

General Methods: All starting materials were of the commercially available (analytical grade) and used without further purification. All the solvents are used after redistillation. Reactions were monitored by thin layer chromatography using silica gel HSGF254 plates. Flash chromatography was performed using silica gel HG/T2354-92. Melting points were measured with SGW X-4 melting point apparatus. ^{1}H NMR (300, 400 or 600 MHz) spectra were recorded in $CDCl_3$. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ = 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (Hz) and integration.^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, 77.0ppm). Chemical yields refer to pure isolated substances. All products were prepared according to the general procedure. Products **1'**, **2'**, **4', 13'-32', 35'**, **36'**, **38' - 47'** are known compounds and their ^{1}H NMR data matched the literature data.[1-5]

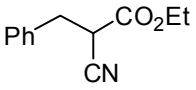
General Experimental Procedures for reduction of the carbon-carbon double bond in conjugated alkenes: A solution of alkenes (0.4 mmol) and Hantzsch esters (0.48mmol) in water (2.0 mL) was stirred at 100 □ for 24 h. After the reaction mixtures were cooled to room temperature, the crude solution was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After removal of

solvents under reduced pressure, the residue was purified through column chromatograph on silica gel to give the pure products.



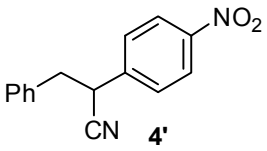
1'

2-benzylmalononitrile (1'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield **1'** as white solid in 91% yield. Mp.: 86-87 °C; 1HNMR (600 MHz, $CDCl_3$): 3.28 (d, J = 6.96 Hz, 2H), 3.91 (t, J = 6.96 Hz, 2H), 7.32 (d, J = 6.72 Hz, 2H), 7.38-7.42 (m, 3H).



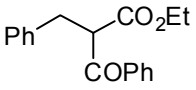
2'

ethyl 2-cyano-3-phenylpropanoate (2') : The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield **2'** as colorless oil in 94% yield. ^{1}HNMR (400 MHz, $CDCl_3$): 1.29 (t, J = 7.16 Hz, 3H), 3.19 - 3.33 (m, 2H), 3.74 (t, J = 8.36 Hz, 1H), 4.27 (q, J = 7.12 Hz, 2H), 7.29-7.37 (m, 5H).



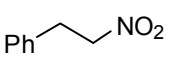
4'

2-(4-nitrophenyl)-3-phenylpropanenitrile (4'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 5' as yellow solid in 98% yield. Mp.: 89-91 °C; ^{1}HNMR (600 MHz, CDCl3): 3.10 (dd, J = 6.72, 13.62 Hz, 1H), 3.19 (dd, J = 7.68, 13.68 Hz, 1H), 4.07 (t, J = 7.20 Hz, 1H), 7.01 (d, J = 5.16 Hz, 2H), 7.22 (d, J = 5.70 Hz, 3H), 7.32 (d, J = 8.22 Hz, 2H), 8.13 (d, J = 8.16 Hz, 2H),



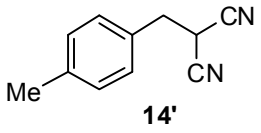
9'

ethyl 2-benzyl-3-oxo-3-phenylpropanoate (9'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 10' as yellow solid in 35% yield. ^{1}HNMR (600 MHz, $CDCl_3$): 1.11 (t, J = 7.02 Hz, 3H), 3.33-3.35 (m, 2H), 4.10 (q, J = 7.02 Hz, 2H), 4.62 (t, J = 7.26 Hz, 1H), 7.15-7.27 (m, 5H), 7.44 (t, J = 7.50 Hz, 2H), 7.56 (t, J = 7.26 Hz, 1H), 7.95 (d, J = 7.98 Hz, 2H).



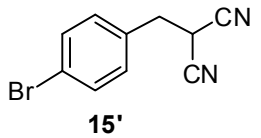
13'

1-(2-nitroethyl)benzene (13'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 13' as colorless oil in 96% yield. ^{1}HNMR (300MHz, $CDCl_3$): 3.35 (t, J = 7.42 Hz, 2H), 4.63 (t, J = 7.38 Hz, 2H), 7.21 – 7.34 (m, 2H).



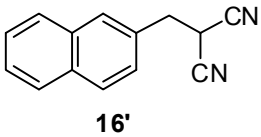
14'

2-(4-methylbenzyl)malononitrile (14'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 14' white solid in 86% yield. Mp.: 86 °C; ^{1}HNMR (400 MHz, $CDCl_3$): 2.39 (s, 3H), 3.27 (d, J = 6.92 Hz, 2H), 3.90 (t, J = 6.92 Hz, 1H), 7.23-7.28 (m, 4H).



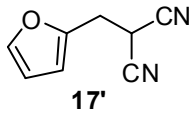
15'

2-(4-bromobenzyl)malononitrile (15') : The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 15' as white solid in 78% yield. Mp.: 96-98 °C; ^{1}HNMR (400 MHz, $CDCl_3$): 3.27 (d, J = 6.80 Hz, 2H), 3.93 (d, J = 6.76 Hz, 1H), 7.23 (d, J = 8.32 Hz, 2H), 7.57 (d, J = 8.40 Hz, 2H).



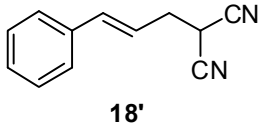
16'

2-(naphthalen-2-ylmethyl)malononitrile (16'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 16' as white solid in 83% yield. Mp.: 62-66 °C; ^{1}HNMR (400 MHz, $CDCl_3$): 3.83 (d, J = 7.60 Hz, 2H), 4.10 (t, J = 7.60 Hz, 3H), 7.50 - 7.67 (m, 4H), 7.88 - 7.98 (m, 3H).



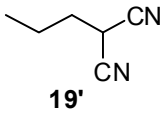
17'

2-(furan-2-ylmethyl)malononitrile (17'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 17' as white solid in 70% yield. ^{1}HNMR (400 MHz, $CDCl_3$): 3.28 - 3.42 (m, 2H), 3.75 (t, J = 6.76 Hz, 1H), 6.29 (d, J = 3.12 Hz, 1H), 6.36 (t, J = 2.84 Hz, 1H), 7.40 (s, 1H).



18'

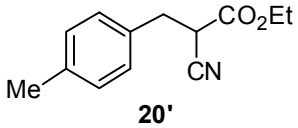
2-cinnamylmalononitrile (18'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 18' as colorless oil in 82% yield. ^{1}HNMR (400 MHz, $CDCl_3$): a 5/1 mixture of E/Z isomers, 2.95 (t, J = 6.92 Hz, 2H), 3.85 (t, J = 6.68 Hz, 1H), 6.17 - 6.24 (m, 1H), 6.73 (d, J = 15.68 Hz, 1H), 7.19 - 7.44 (m, 5H), 7.55 (d, J = 8.64 Hz, 2H), 8.27 (d, J = 8.70 Hz, 2H).



19'

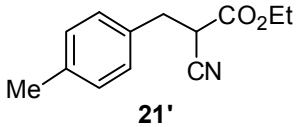
2-propylmalononitrile (19'): P The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 19' as brown solid

in 40% yield. Mp.: 124 °C; ^{1}HNMR (400 MHz, $CDCl_3$): 1.02 (t, J = 7.36 Hz, 3H), 1.56 - 1.61 (m, 2H), 1.94 - 2.01 (m, 2H), 3.40 - 3.44 (m, 1H). ^{13}CNMR (200 MHz, $CDCl_3$): 13.3, 20.2, 31.9, 37.9, 118.2.



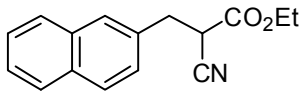
20'

ethyl 2-cyano-3-p-tolylpropanoate (20'): The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 20' as colorless oil in 90% yield. ^{1}HNMR (400 MHz, $CDCl_3$): 1.30 (t, J = 7.12 Hz, 3H), 2.36 (s, 3H), 3.14 - 3.28 (m, 2H), 3.72 (dd, J = 5.92, 8.40 Hz, 1H), 4.27 (q, J = 7.16 Hz, 2H), 7.15-7.20 (m, 4H).



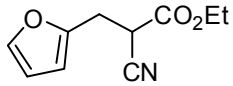
21'

ethyl 3-(4-bromophenyl)-2-cyanopropanoate (21'): The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 21' as colorless oil in 94% yield. ^{1}HNMR (400 MHz, $CDCl_3$): 1.30 (t, J = 7.12 Hz, 3H), 3.15 - 3.27 (m, 2H), 3.73 (dd, J = 5.88, 8.08 Hz, 1H), 4.27 (q, J = 7.12 Hz, 2H), 7.17 (d, J = 8.28 Hz, 2H).



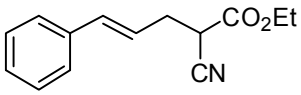
22'

ethyl 2-cyano-3-(naphthalen-2-yl)propanoate (22'): The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 22' as colorless oil in 96% yield. ^{1}HNMR (400 MHz, $CDCl_3$): 1.30 (t, J = 7.16 Hz, 3H), 3.57 (dd, J = 10.08, 15.44 Hz, 2H), 3.93 (t, J = 5.44 Hz, 2H), 4.28 (q, J = 7.08 Hz, 2H), 7.46-7.62 (m, 4H), 7.85 (d, J = 7.76 Hz, 1H), 7.93 (d, J = 7.92 Hz, 1H), 7.97 (d, J = 8.32 Hz, 1H).



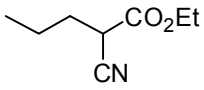
23'

ethyl 2-cyano-3-(furan-2-yl)propanoate (23'): The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 23' as colorless oil in 86% yield.^{1}HNMR (400 MHz, $CDCl_3$): 1.33 (t, J = 7.12 Hz, 3H), 3.26 - 3.38 (m, 2H), 3.84 (dd, J = 6.24, 7.80 Hz, 1H), 4.29 (q, J = 7.16, 2H), 6.27 (d, J = 3.12 Hz, 1H), 6.35 (t, J = 2.80 Hz, 1H), 7.38 (s, 1H).



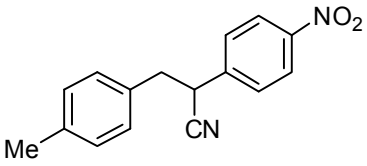
24'

ethyl 2-cyano-5-phenylpent-4-enoate (24'): The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 24' as colorless oil in 93% yield. ^{1}HNMR (400 MHz, $CDCl_3$): a 3/1 mixture of E/Z isomers, 1.34 (t, J = 7.16 Hz, 3H), 2.88 (t, J = 7.20 Hz, 2H), 3.65 (t, J = 6.72 Hz, 1H), 4.25 – 4.33 (m, 1H), 6.17 - 6.24 (m, 1H), 6.61 (d, J = 15.72 Hz, 1H), 7.23 - 7.40 (m, 5H).



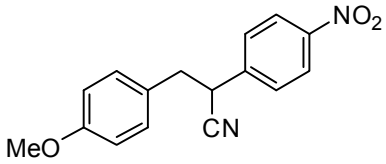
25'

ethyl 2-cyanopentanoate (25'): The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 25' as colorless oil in 70% yield.



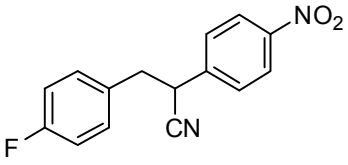
26'

2-(4-Nitro-phenyl)-5-phenyl-pentanenitrile (26'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 26' as white solid in 89% yield. Mp.: 68 °C; ^{1}HNMR (600 MHz, $CDCl_3$): 2.33 (s, 3H), 3.12 (dd, J = 6.96, 13.74 Hz, 1H), 3.21 (dd, J = 6.06, 13.68 Hz, 1H), 4.12 (t, J = 7.20 Hz, 1H), 6.96 (d, J = 7.74 Hz, 2H), 7. 09 (d, J = 7.74 Hz, 2H), 7.40 (d, J = 8.58 Hz, 2H), 8.20 (d, J = 8.64 Hz, 2H).



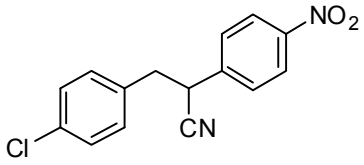
27'

3-(4-methoxyphenyl)-2-(4-nitrophenyl)propanenitrile (27'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 27' as yellow oil in 91% yield. ^{1}HNMR (600 MHz, $CDCl_3$): 3.11 (dd, J = 6.66, 13.74 Hz, 1H), 3.20 (dd, J = 6.30, 13.80 Hz, 1H), 3.79 (s, 3H), 4.11 (t, J = 7.20 Hz, 1H), 6.81 (d, J = 8.46 Hz, 2H), 6.98 (d, J = 8.40 Hz, 2H), 7.38 (d, J = 8.58 Hz, 2H), 8.20 (d, J = 8.58 Hz, 2H).



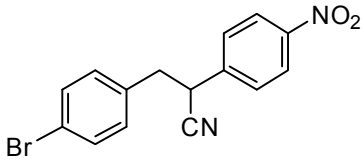
28'

3-(4-fluorophenyl)-2-(4-nitrophenyl)propanenitrile (28'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 28' as white solid in 92% yield. Mp.: 98 °C; ^{1}HNMR (600 MHz, $CDCl_3$): 3.15 - 3.23 (m, 2H), 4.13 (t, J = 6.96 Hz, 1H), 6.99 (t, J = 8.52 Hz, 2H), 7. 04 - 7.06 (m, 2H), 7.40 (d, J = 8.58 Hz, 2H), 8.21 (d, J = 8.64 Hz, 2H).



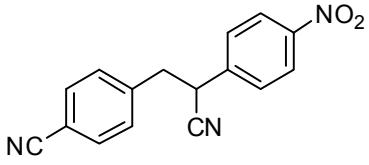
29'

3-(4-chlorophenyl)-2-(4-nitrophenyl)propanenitrile (29'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 29' as white solid in 88% yield. Mp.: 70 °C; 1HNMR (600 MHz, CDCl3): 3.15 - 3.23 (m, 2H), 4.10 – 4.14 (m, 1H), 7.01 (d, J = 8.10 Hz, 2H), 7.27 (d, J = 8.16 Hz, 2H), 7.40 (d, J = 8.46 Hz, 2H), 8.22 (d, J = 8.52 Hz, 2H).



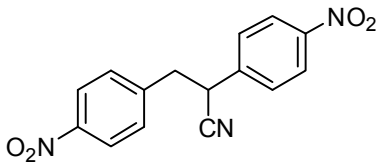
30'

3-(4-bromophenyl)-2-(4-nitrophenyl)propanenitrile (30'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 30' as yellow oil in 93% yield.[1]HNMR (600 MHz, $CDCl_3$): 3.12 - 3.21 (m, 2H), 4.10 – 4.15 (m, 1H), 6.96 (d, J = 8.16 Hz, 2H), 7.40 - 7.43 (m, 4H), 8.22 (d, J = 8.58 Hz, 2H).



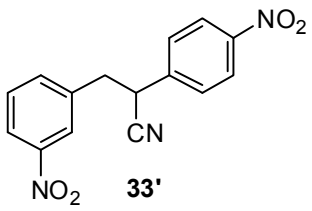
31'

4-(2-cyano-2-(4-nitrophenyl)ethyl)benzonitrile (31'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 31' as yellow solid in 95% yield. Mp.: 137-139 °C; [1]HNMR (600 MHz, $CDCl_3$): 3.28 (d, J = 6.66 Hz, 2H), 4.19 (t, J = 7.08 Hz, 1H), 7.23 (d, J = 8.04 Hz, 2H), 7.43 (d, J = 8.64 Hz, 2H), 7.61 (d, J = 8.10 Hz, 2H), 8.24 (d, J = 8.58 Hz, 2H).



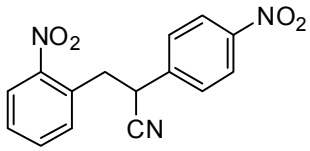
32'

2,3-bis(4-nitrophenyl)propanenitrile (32'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 32' as yellow solid in 95% yield. Mp.: 137-138 °C; [1]HNMR (400 MHz, $CDCl_3$): 3.35 (d, J = 7.08 Hz, 2H), 4.26 (t, J = 7.08 Hz, 1H), 7.32 (d, J = 8.48 Hz, 2H), 7.47 (d, J = 8.56 Hz, 2H), 8.20 (d, J = 8.44 Hz, 2H), 8.27 (d, J = 8.48 Hz, 2H).



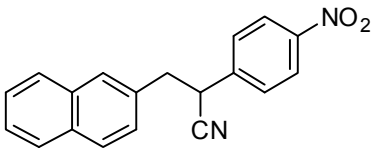
33'

3-(3-nitrophenyl)-2-(4-nitrophenyl)propanenitrile (33'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 33' as white solid in 92% yield. Mp.: 85 °C; [1]HNMR (600 MHz, $CDCl_3$): 3.33 (d, J = 7.44 Hz, 2H), 4.23 (t, J = 7.20 Hz, 1H), 7.48 - 7.54 (m, 5H), 8.02 (s, 1H), 8.18 (d, J = 8.04 Hz, 1H), 8.26 (d, J = 8.58 Hz, 2H).



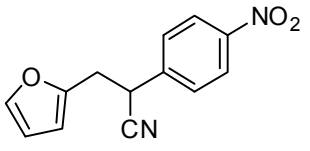
34'

3-(2-nitrophenyl)-2-(4-nitrophenyl)propanenitrile (34'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 34' as yellow solid in 45% yield. Mp.: 110°C; HNMR (600 MHz, $CDCl_3$): 3.25 (t, J = 10.74 Hz, 1H), 3.59 (dd, J = 4.86, 10.56 Hz, 1H), 4.54 (t, J = 10.56 Hz, 1H), 6.10 (d, J = 2.88 Hz, 1H), 6.29 (s, 1H), 7.35 (d, J = 0.66 Hz, 1H), 7.43 (d, J = 8.40 Hz, 2H), 8.22 (d, J = 8.40 Hz, 2H). ^{13}CNMR (200 MHz, $CDCl_3$): 38.5, 40.2, 124.5, 125.7, 128.5, 129.5, 133.6, 134.1, 141.9 ; ESI HRMS exact mass calcd for $(C_{15}H_{10}N_3O_4 - H)^-$ requires m/z 296.0677, found m/z 296.0677.



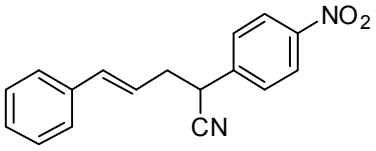
35'

3-(naphthalen-2-yl)-2-(4-nitrophenyl)propanenitrile (35'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 35' as yellow solid in 97% yield. Mp.: 137-138 °C; 1HNMR (600 MHz, $CDCl_3$): 3.58 (d, J = 7.32 Hz, 1H), 3.76 (d, J = 7.98 Hz, 1H), 4.30 (t, J = 7.68 Hz, 1H), 7.19 (d, J = 6.96 Hz, 1H), 7.36-7.40 (m, 3H), 7.53-7.56 (m, 2H), 7.81 (d, J = 8.28 Hz, 1H), 7.88 (d, J = 8.04 Hz, 1H), 7.91 (d, J = 8.28 Hz, 1H), 8.17 (d, J = 8.52Hz, 2H).



36'

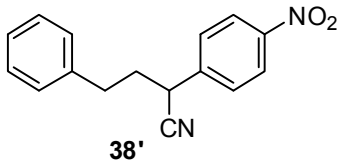
3-(furan-2-yl)-2-(4-nitrophenyl)propanenitrile (36'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 36' as white solid in 94% yield. Mp.: 150 °C; ^{1}HNMR (600 MHz, $CDCl_3$): 3.20 (dd, J = 7.02, 14.94 Hz, 1H), 3.35 (dd, J = 7.50, 14.94 Hz, 1H), 4.28 (t, J = 7.32 Hz, 1H), 6.10 (d, J = 2.88 Hz, 1H), 6.29 (s, 1H), 7.35 (d, J = 0.66 Hz, 1H), 7.43 (d, J = 8.40 Hz, 2H), 8.22 (d, J = 8.40 Hz, 2H).



37'

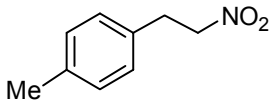
2-(4-nitrophenyl)-5-phenylpent-4-enenitrile (37'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 37' as yellow solid in 88% yield. Mp.: 80-82 °C; ^{1}HNMR (600 MHz, $CDCl_3$): 2.84 (t, J = 6.96 Hz, 1H), 4.06 (t, J = 6.90 Hz, 1H), 6.12 (t, J = Petroleum ether /EtOAc 7.50 Hz, 1H), 6.49 (d, J = 15.78 Hz, 1H), 7.26 - 7.32 (m, 5H), 7.55 (d, J = 8.64 Hz, 2H), 8.27 (d, J = 8.70 Hz, 2H);

^{13}CNMR (200 MHz, $CDCl_3$): 37.8, 38.9, 119.1, 122.4, 124.4, 126.4, 128.1, 128.5, 128.7, 135.4, 136.1, 142.1; ESI HRMS exact mass calcd for $(C_{17}H_{13}N_2O_2 - H)^-$ requires m/z 277.0983, found m/z 277.0971.



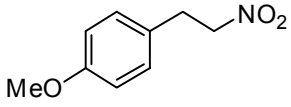
38'

2-(4-nitrophenyl)-4-phenylbutanenitrile (38'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 38' as white solid in 85% yield. ^{1}HNMR (600 MHz, $CDCl_3$): 2.16 - 2.22 (m, 1H), 2.28 - 2.32 (m, 1H), 2.81 - 2.90 (m, 2H), 3.84 - 3.86 (m, 1H), 7.20 (d, J = 7.38 Hz, 2H), 7.24 (d, J = 7.50 Hz, 1H), 7.33 (t, J = 7.44 Hz, 2H), 7.50 (d, J = 8.58 Hz, 2H), 8.24 (d, J = 8.64 Hz, 2H).



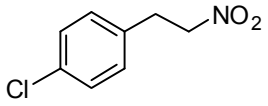
39'

1-methyl-4-(2-nitroethyl)benzene(39'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 39' as yellow oil in 94% yield. ^{1}HNMR (600MHz, CDCl3): 2.34 (s, 3H), 3.28 (t, J = 7.38 Hz, 2H), 4.58 (J = 7.38 Hz, t, 2H), 7.11 (d, J = 7.92 Hz, 2H), 7.15 (d, J = 7.80 Hz, 2H).



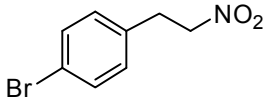
40'

1-methoxy-4-(2-nitroethyl)benzene(40'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 40' as colorless oil in 93% yield. ^{1}HNMR (600MHz, $CDCl_3$): 3.25 (t, J = 7.32 Hz, 2H), 3.79 (s, 3H), 4.56 (t, J = 7.38 Hz, 2H), 6.86 (d, J = 8.52 Hz, 2H), 7.12 (d, J = 8.46 Hz, 2H).



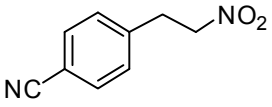
41'

1-chloro-4-(2-nitroethyl)benzene(41'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 41' as colorless oil in 94% yield. ^{1}HNMR (600MHz, $CDCl_3$): 3.28 (t, J = 7.26 Hz, 2H), 4.59 (J = 7.26 Hz, t, 2H), 7.14 (d, J = 8.28 Hz, 2H), 7.30 (d, J = 8.34 Hz, 2H).



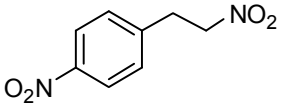
42'

1-bromo-4-(2-nitroethyl)benzene(42'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 42' as colorless oil in 93% yield. ^{1}HNMR (600MHz, $CDCl_3$): 3.27 (t, J = 7.26 Hz, 2H), 4.59 (t, J = 7.20 Hz, 2H), 7.08 (d, J = 8.28 Hz, 3H), 7.46 (d, J = 8.34 Hz, 2H).



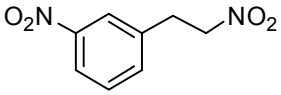
43'

4-(2-nitroethyl)benzonitrile(43'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 43' as white solid in 96% yield. Mp.: 80 °C; ^{1}HNMR (600MHz, $CDCl_3$): 3.38 (t, J = 7.08 Hz, 2H), 4.64 (t, J = 7.02 Hz, 2H), 7.33 (d, J = 8.10 Hz, 2H), 7.63 (d, J = 8.16 Hz, 2H).



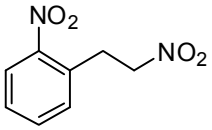
44'

1-nitro-4-(2-nitroethyl)benzene(44'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 44' as white solid in 90% yield. Mp.: 102 °C; ^{1}HNMR (600MHz, $CDCl_3$): 3.43 (t, J = 6.96 Hz, 2H), 4.67 (t, J = 6.96 Hz, 2H), 7.40 (d, J = 8.46 Hz, 2H), 8.20 (d, J = 8.52 Hz, 2H).



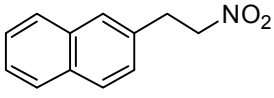
45'

1-nitro-3-(2-nitroethyl)benzene(45'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 49' as white solid in 83% yield. Mp.: 61-62 °C; ^{1}HNMR (600 MHz, $CDCl_3$): 3.43 (t, J = 7.02 Hz, 2H), 4.69 (t, J = 7.02 Hz, 2H), 7.51 – 7.57 (m, 2H), 8.11 (s, 1H), 8.14 (d, J = 8.10 Hz, 1H).



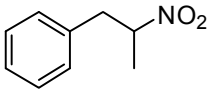
46'

1-nitro-2-(2-nitroethyl)benzene(46'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 46' as colorless oil in 75% yield. ^{1}HNMR (600MHz, $CDCl_3$): 3.61 (t, J = 6.78 Hz, 2H), 4.77 (t, J = 6.78 Hz, 2H), 7.39 (d, J = 7.62 Hz, 1H), 7.49 (t, J = 8.04 Hz, 1H), 7.60 (t, J = 7.50 Hz, 1H), 8.07 (d, J = 8.16 Hz, 1H).



47'

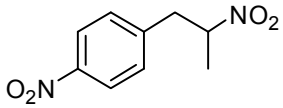
2-(2-nitroethyl)naphthalene(47'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 47' as white solid in 94% yield. Mp.: 47-48 °C; 1HNMR (600 MHz, CDCl3): 3.80 (t, J = 7.74 Hz, 2H), 4.72 (t, J = 7.56 Hz, 2H), 7.36 (d, J = 6.96 Hz, 1H), 7.42 (t, J = 7.98 Hz, 1H), 7.54 (t, J = 7.74 Hz, 1H), 7.59 (t, J = 7.68 Hz, 1H), 7.80 (d, J = 8.16 Hz, 1H), 7.91 (d, J = 8.04 Hz, 1H), 7.99 (d, J=8.40 Hz, 1H).



48'

1-(2-nitropropyl)benzene(48'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 48' as colorless

oil in 83% yield. ^{1}HNMR (600 MHz, $CDCl_3$): 1.55 (d, J = 6.66 Hz, 3H), 3.01 (dd, J = 6.84, 13.92 Hz, 1H), 3.33 (qq, J = 7.44, 13.92 Hz, 1H), 4.76 – 4.81 (m, 1H), 7.17 (d, J = 7.38 Hz, 2H), 7.26 – 7.33 (m, 3H).



49'

1-nitro-4-(2-nitropropyl)benzene(49'): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 49' as colorless oil in 88% yield. ^{1}HNMR (600 MHz, $CDCl_3$): 1.61 (d, J = 6.60 Hz, 3H), 3.14 (dd, J = 5.7, 14.34 Hz, 1H), 3.37 – 3.43 (m, 1H), 4.79 – 4.84 (m, 1H), 7.34 (d, J = 8.28 Hz, 2H), 8.17 (d, J = 8.40 Hz, 2H).

References

1. (a) B. C. Ranu and S. Samanta, *Tetrahedron Lett*., 2002, **43**, 7405. (b)D. Xue, Y. C. Chen, X Cui, Q. W. Wang, J. Zhu and J. G. Deng, *J. Org. Chem*., 2005, **70**, 3584.

2. (a) X. Q. Zhu, H. L. Zou, P. L. Yuan, *J. Chem. Soc*., 2000, **2**, 1857. (b) BC. Ranu, S Samanta, *J. Org. Chem*., 2003, **68**, 18.

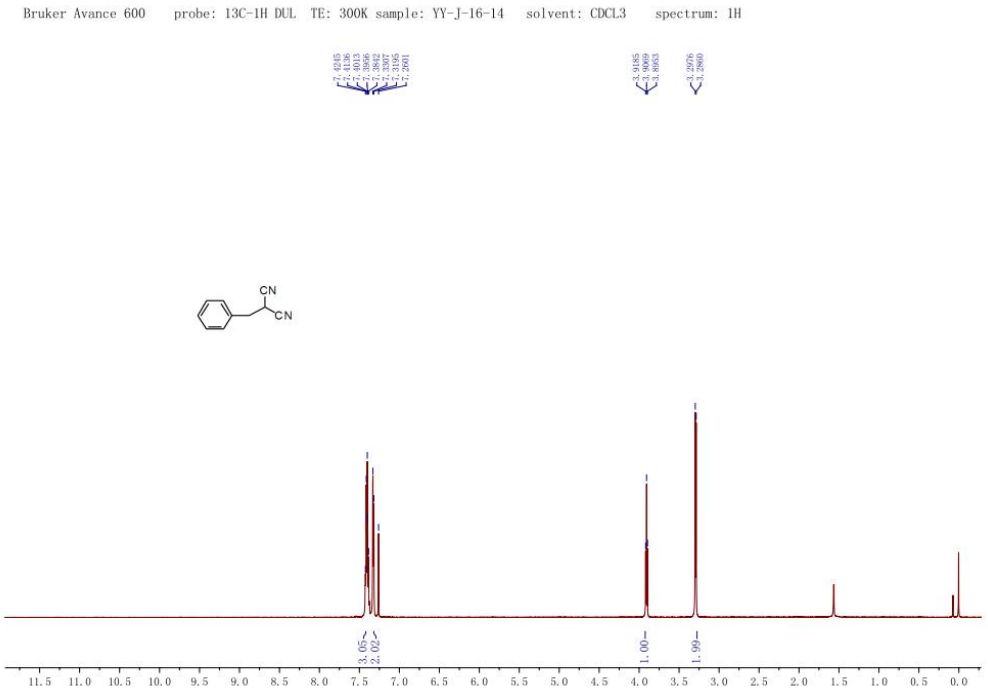
3. D. B. Ramachary, M. Kishor and Y. V. Reddy, *Eur. J. Org. Chem*., 2008, 975.

4. (a)Q. P. B. Nguyen, J. N. Kim, T. H. Kim, *Tetrahedron*., 2012, **68**, 6513. (b) J. Xiang, E. X. Sun, C. X. Lian, Q. W. Wang and J. G. Deng, *Tetrahedron*., 2012, **68**, 4609. (c) Z. G. Zhang and P. R. Schreiner, *Synthesis*., 2007, **16**, 2559.

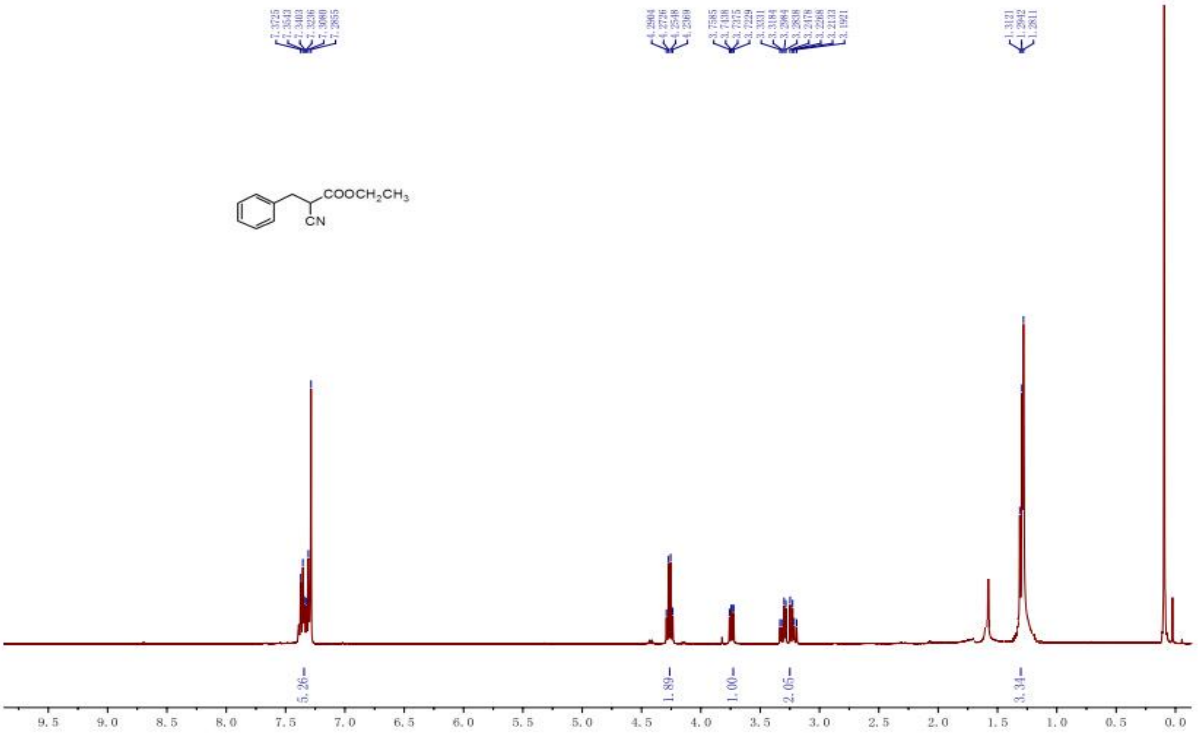
5. D. B. Ramachary and M. S. Prasad, *Tetrahedron Lett*., 2010, **51**, 5246.

^{1}H and ^{13}C NMR Spectra:

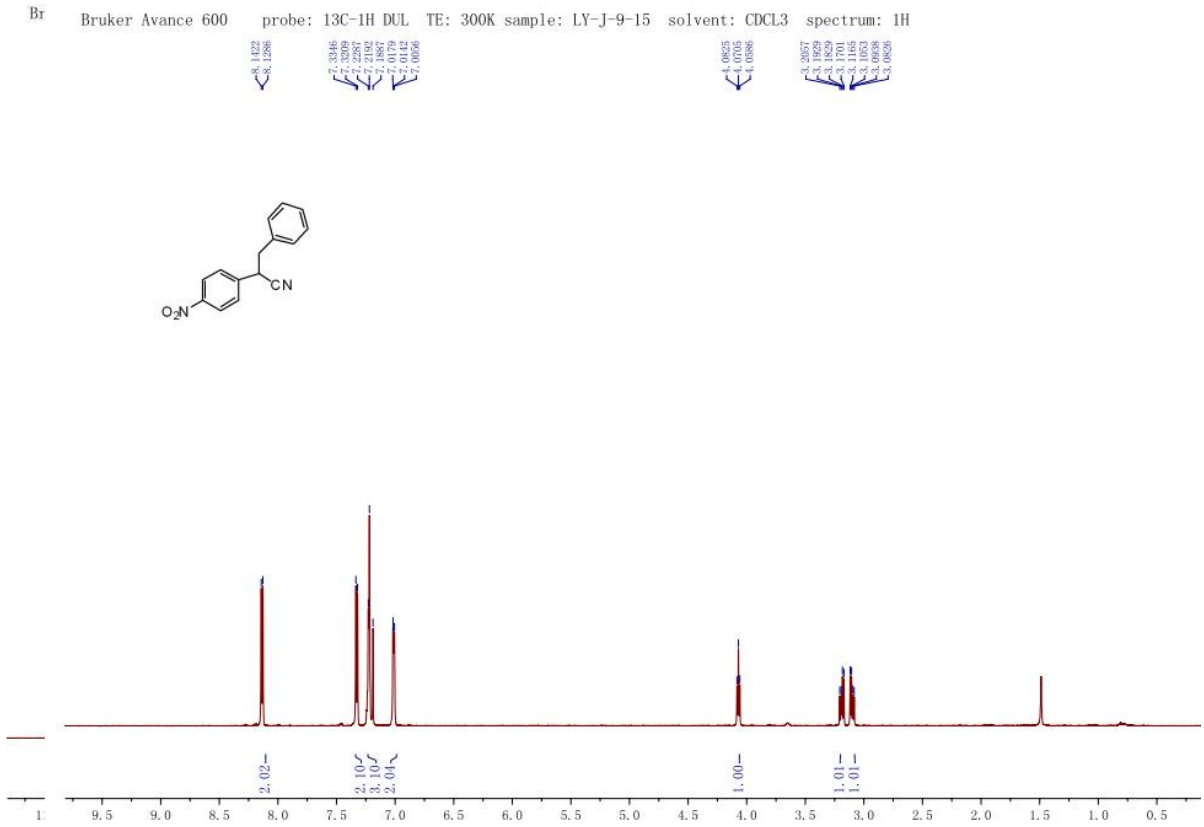
The ^{1}H NMR Spectra of 1'



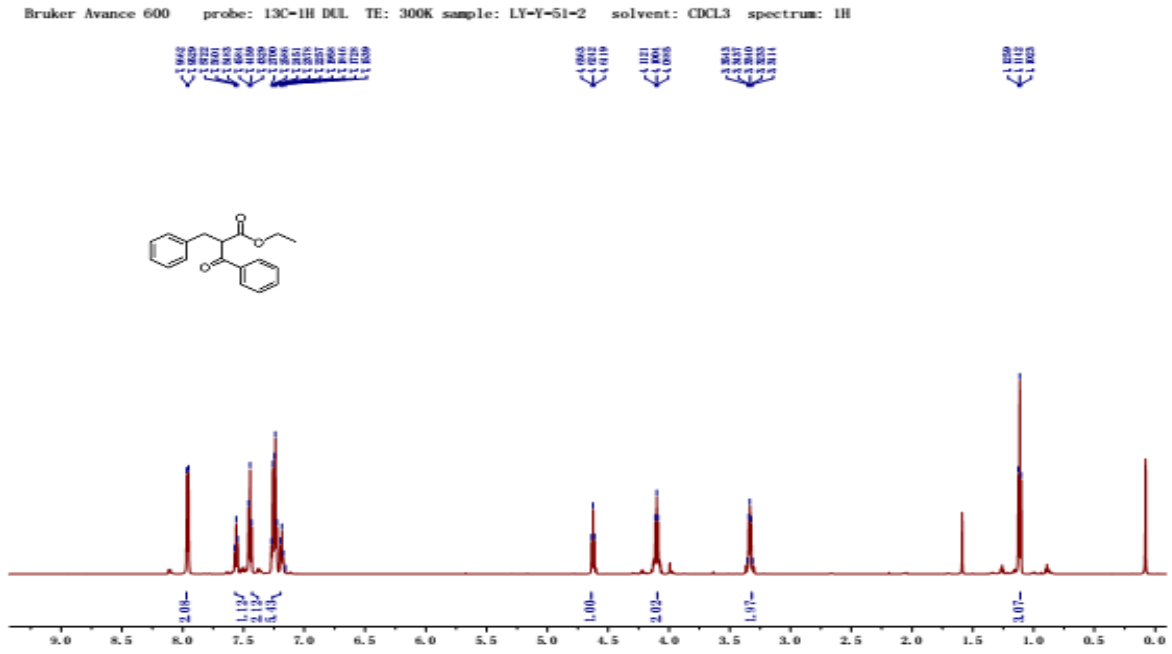
The ^{1}H NMR Spectra of 2'



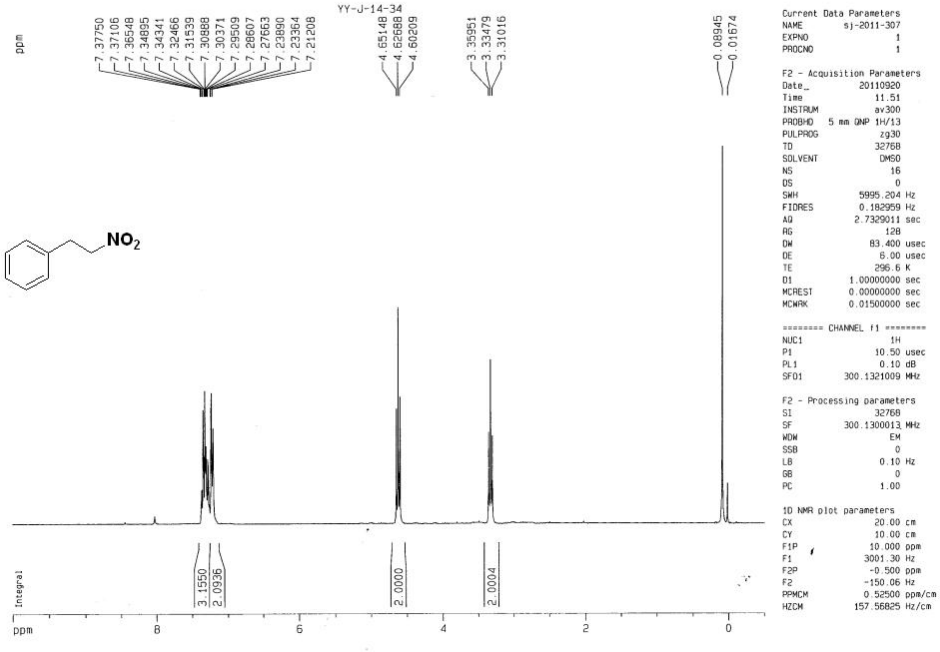
The ^{1}H NMR Spectra of 4'



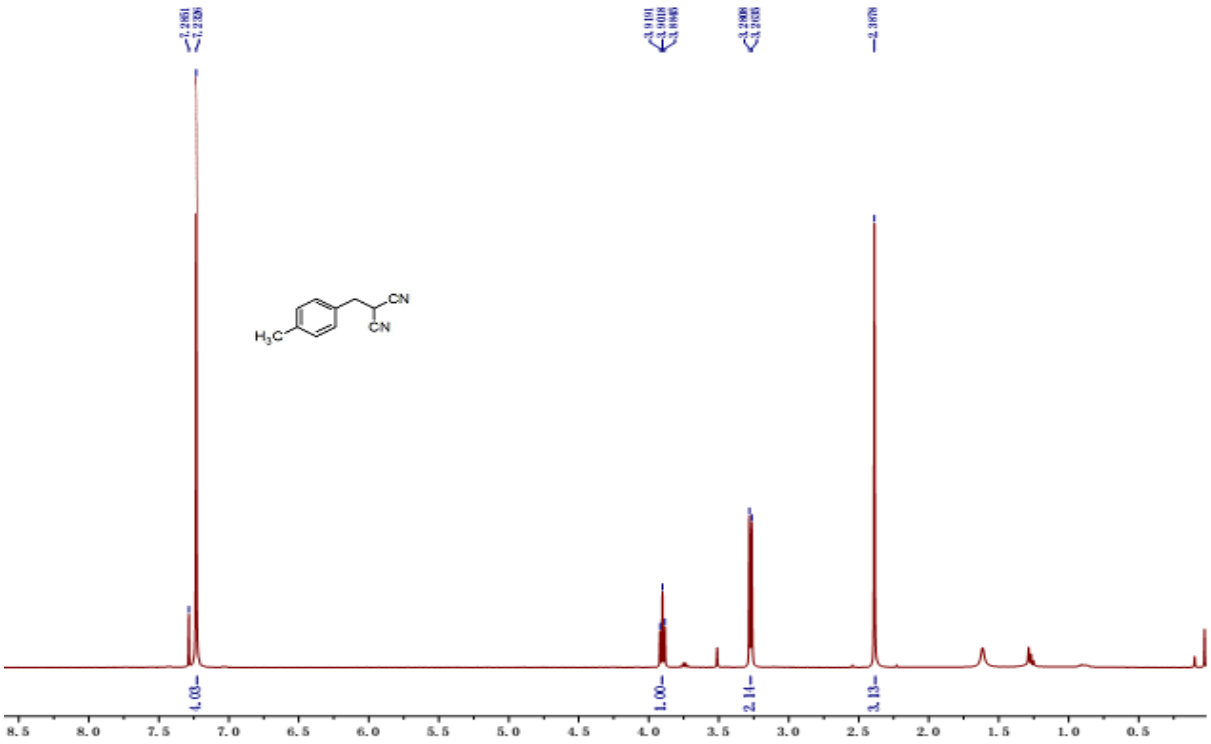
The ^{1}H NMR Spectra of 9'



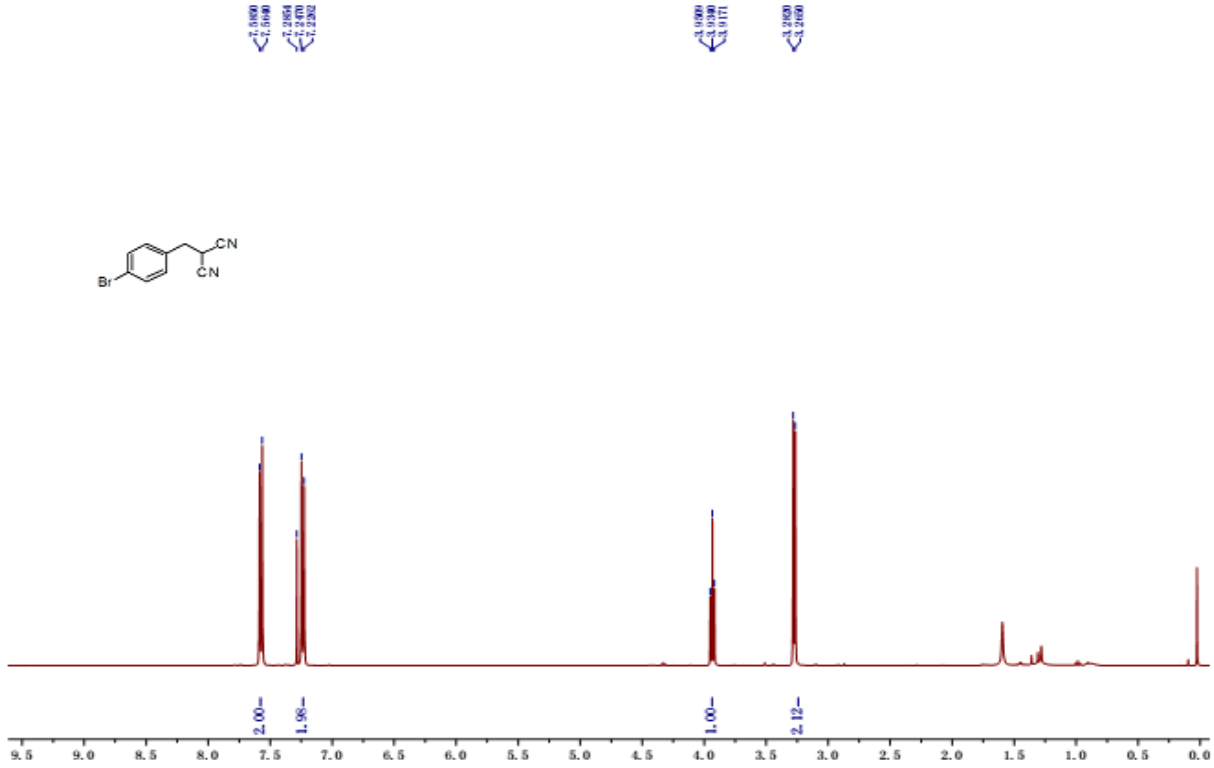
The ^{1}H NMR Spectra of 13'



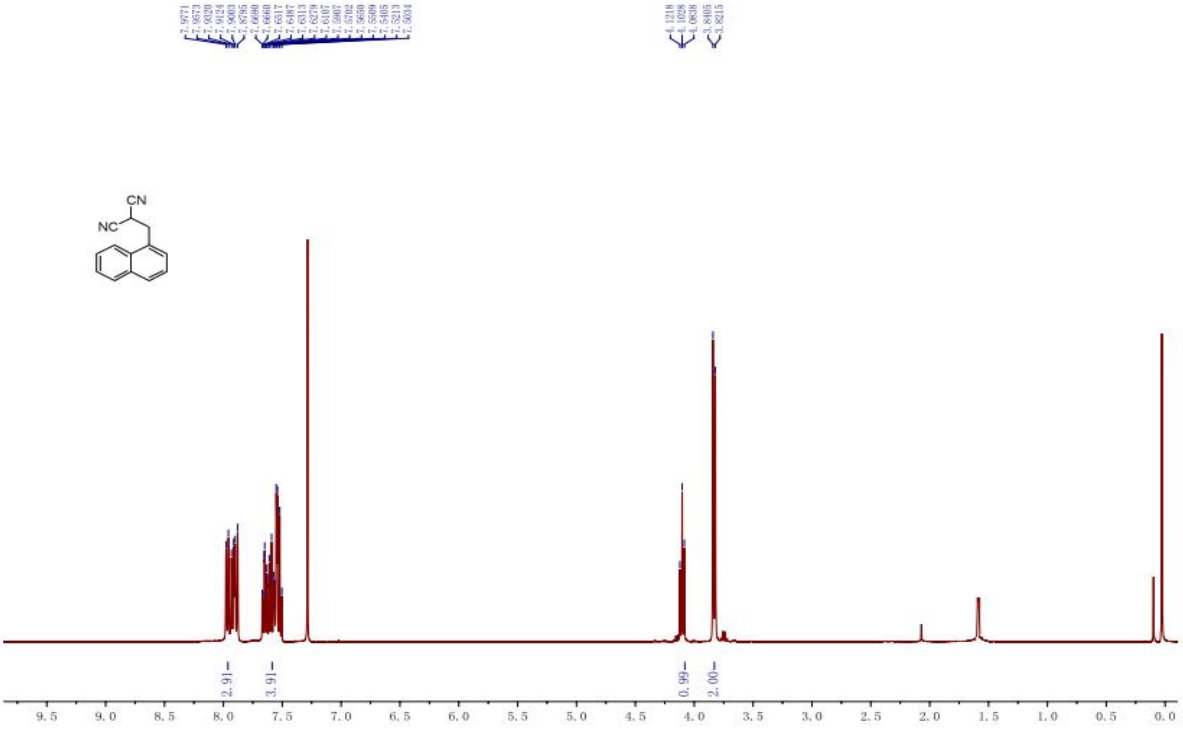
The ^{1}H NMR Spectra of 14'



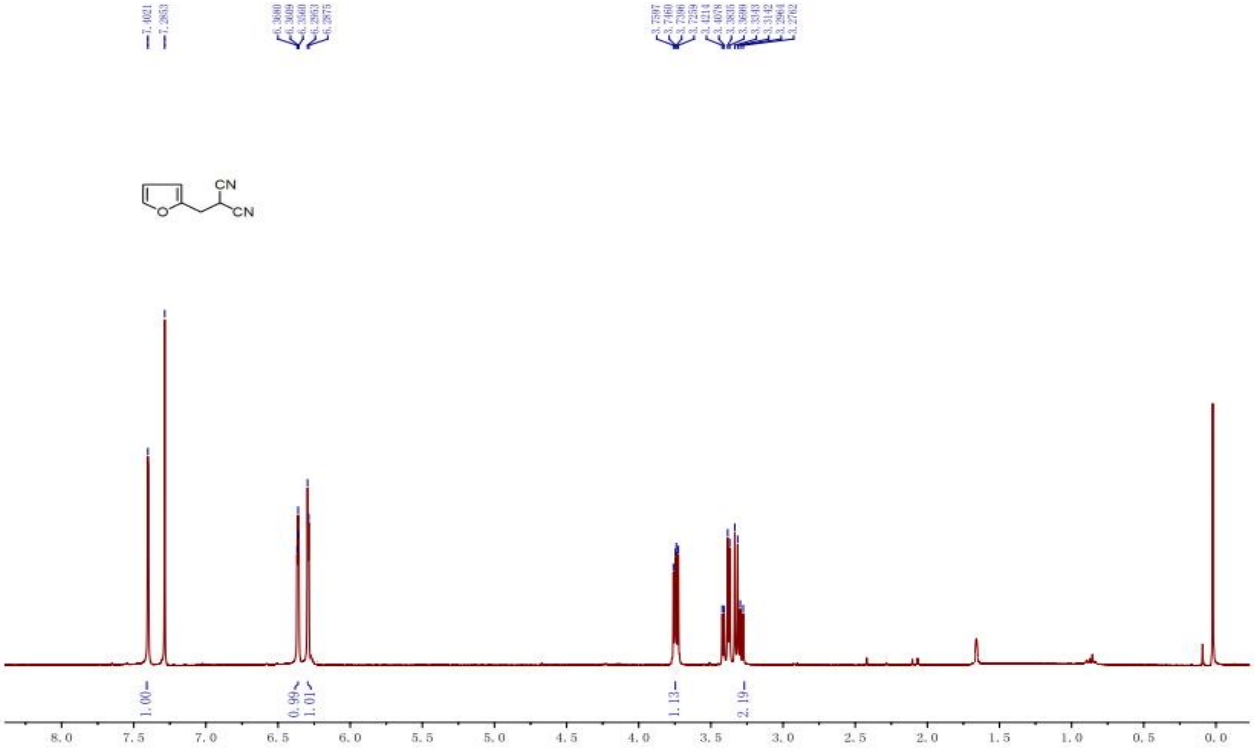
The ^{1}H NMR Spectra of 15'



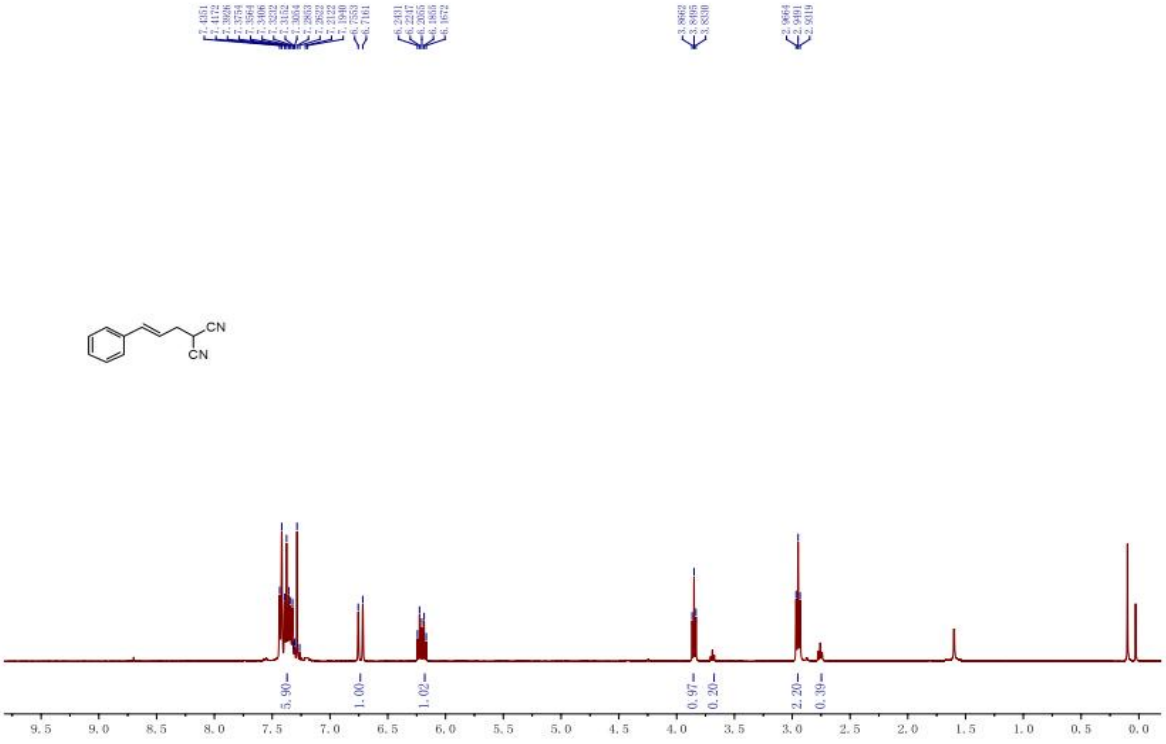
The ^{1}H NMR Spectra of 16'



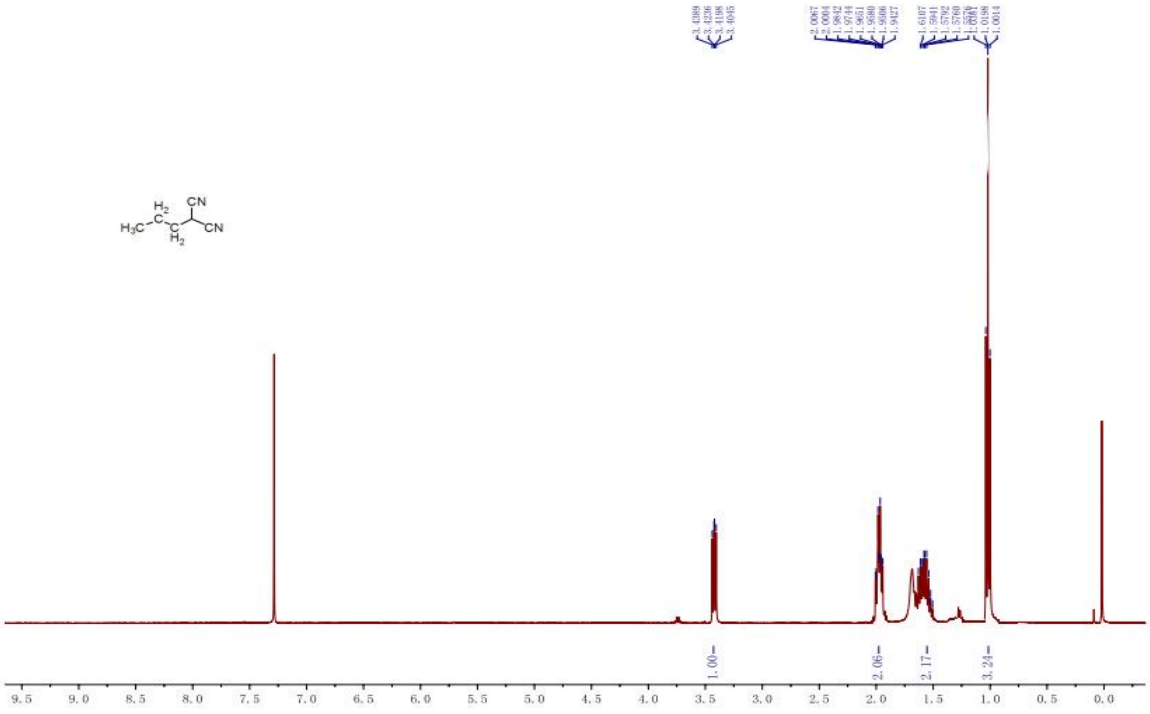
The ^{1}H NMR Spectra of 17'



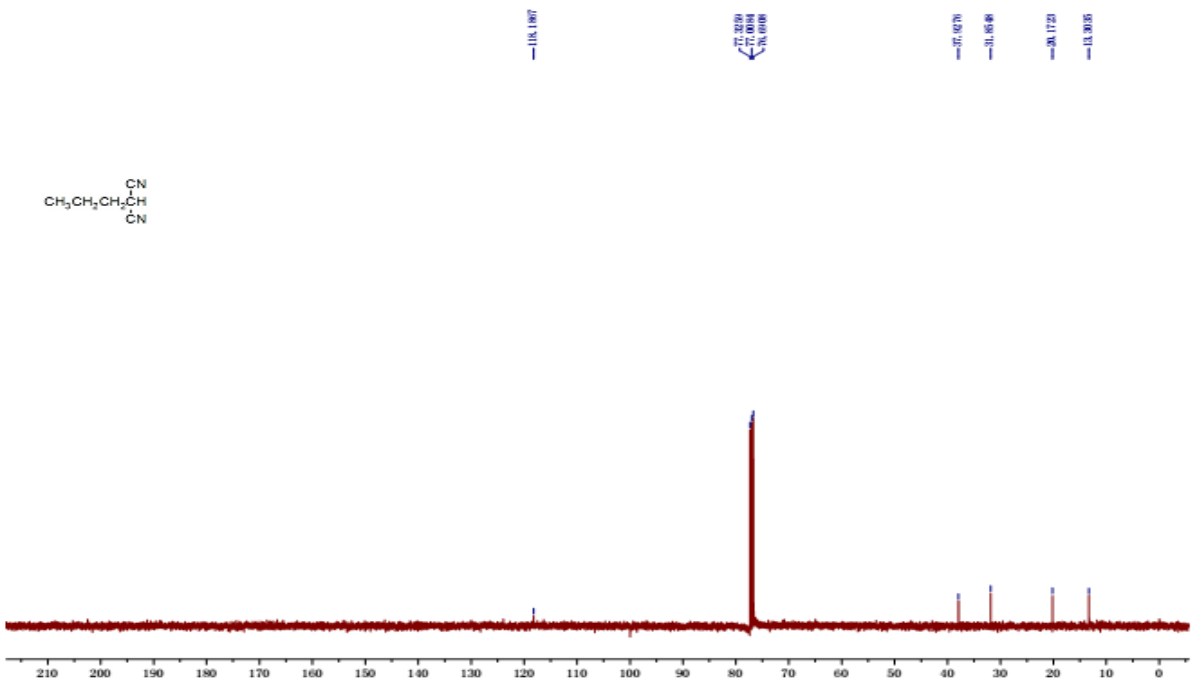
The ^{1}H NMR Spectra of 18'



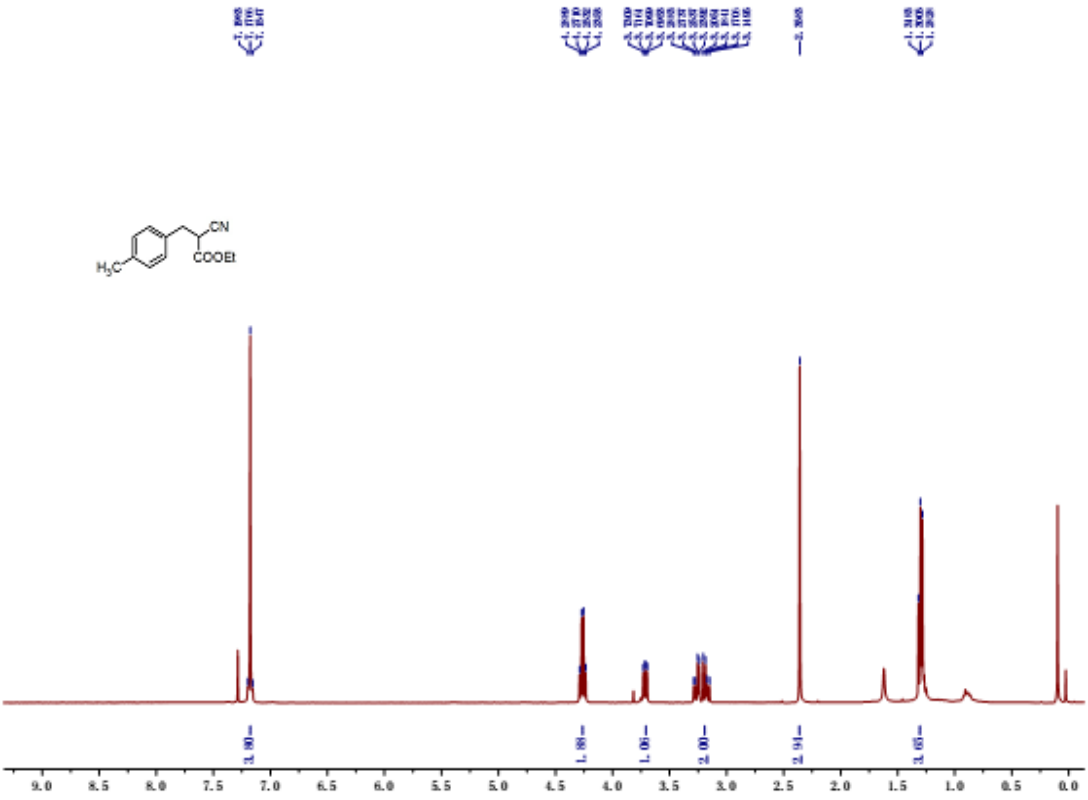
The ^{1}H NMR Spectra of 19'



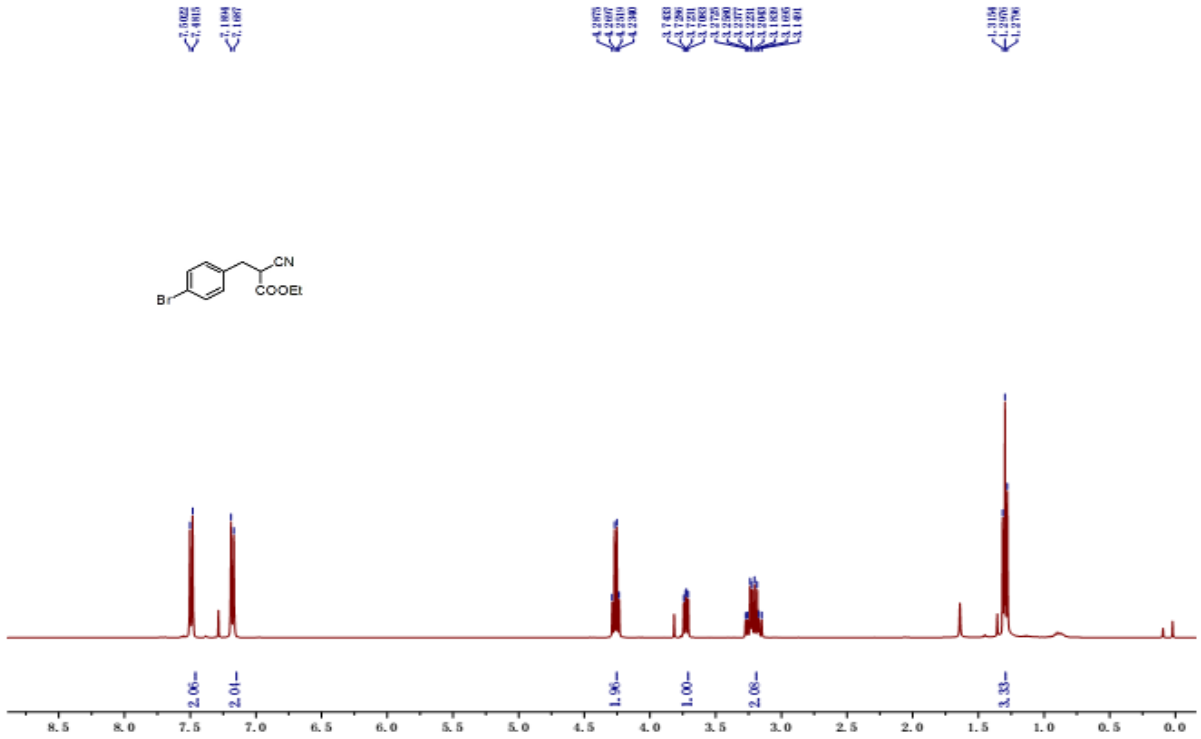
The ^{13}C NMR Spectra of 19'



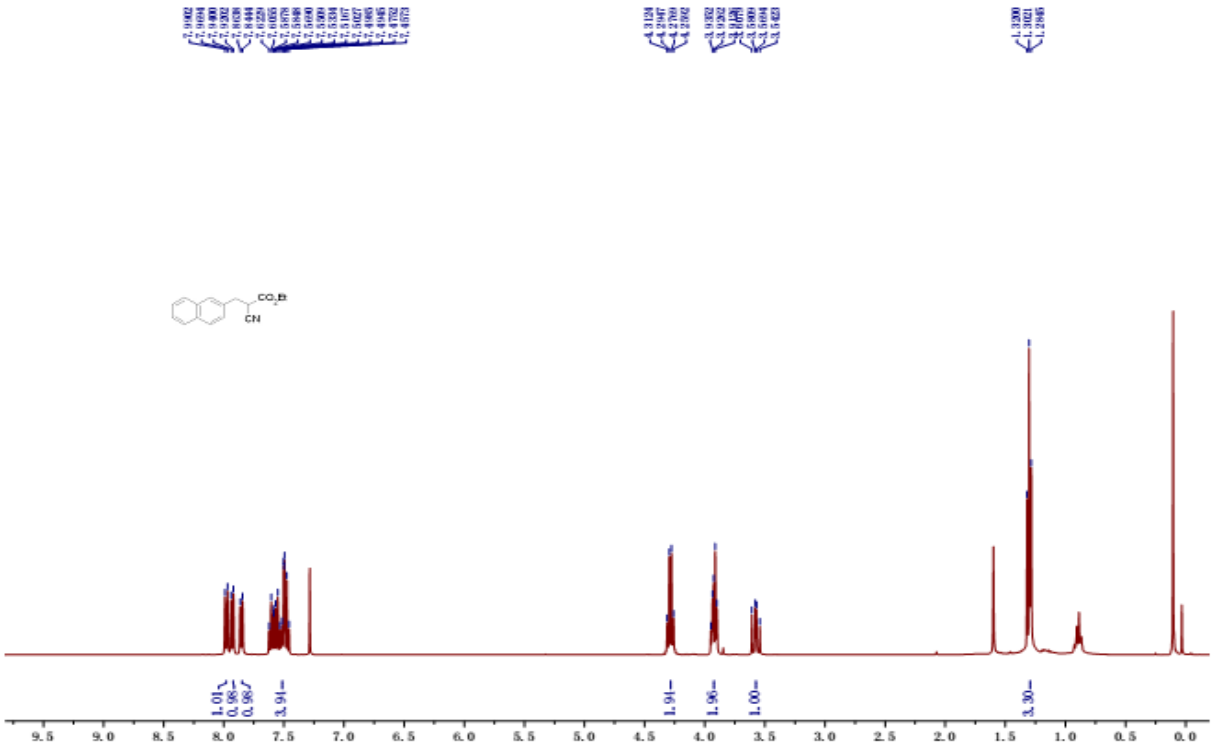
The ^{1}H NMR Spectra of 20'



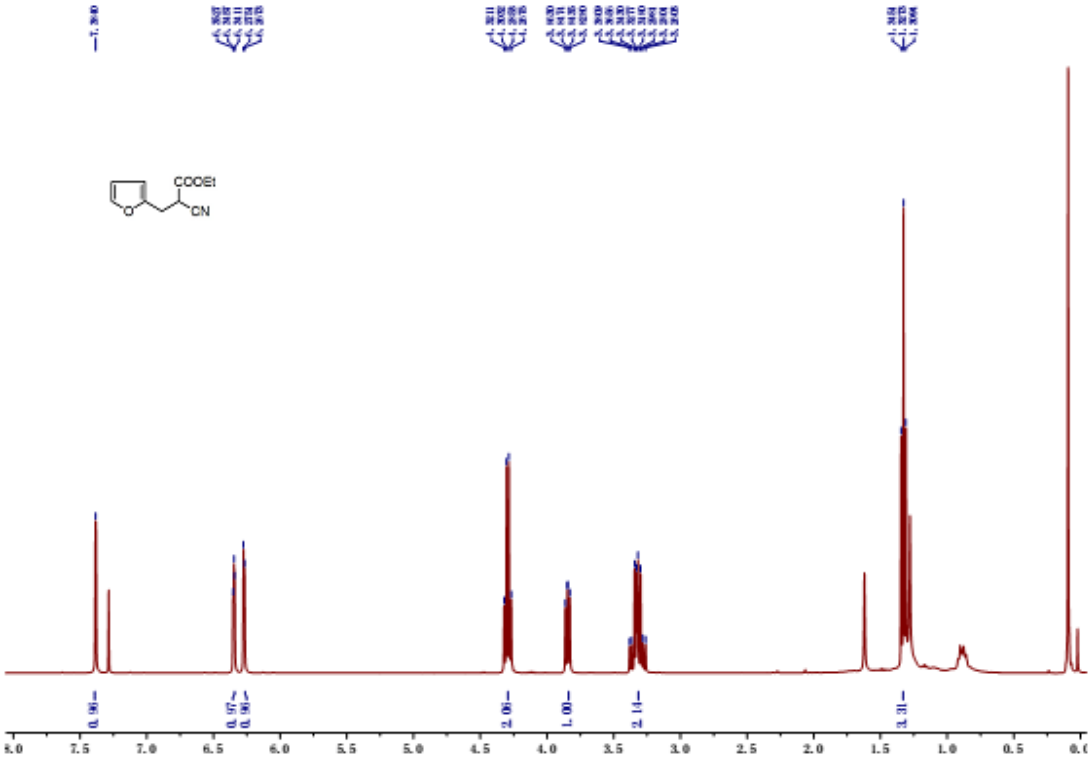
The ^{1}H NMR Spectra of 21'



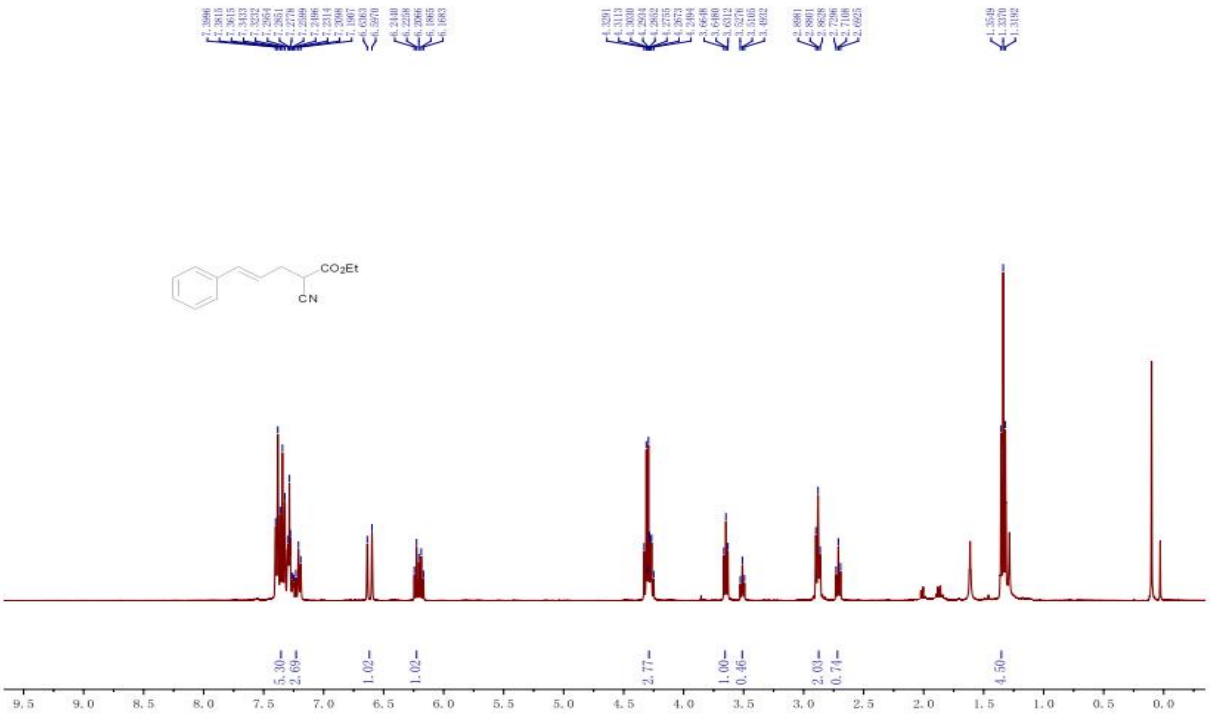
The ^{1}H NMR Spectra of 22'



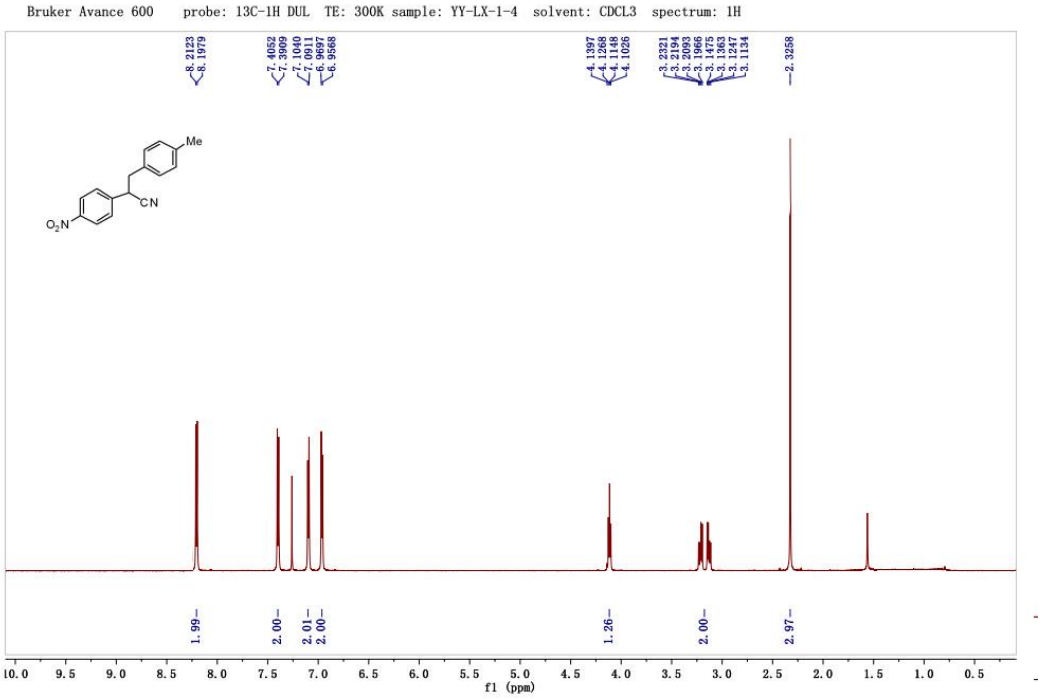
The ^{1}H NMR Spectra of 23'



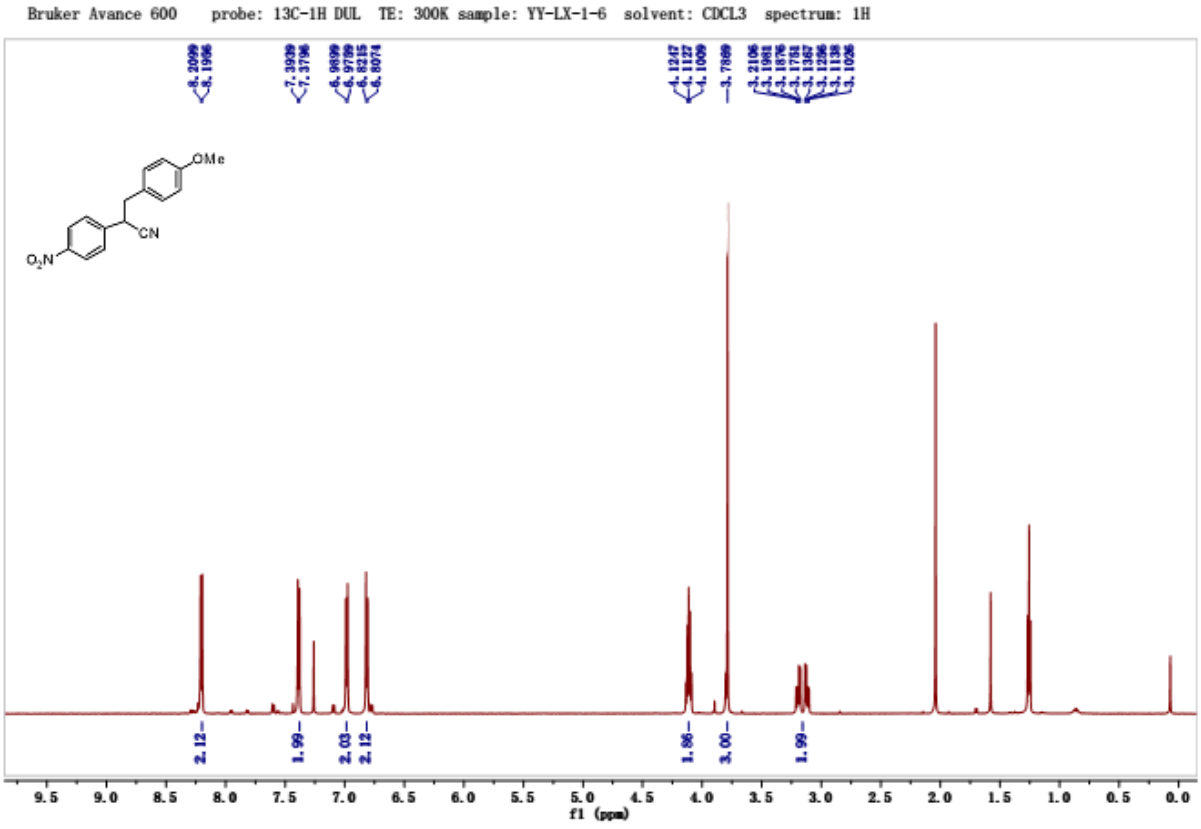
The ^{1}H NMR Spectra of 24'



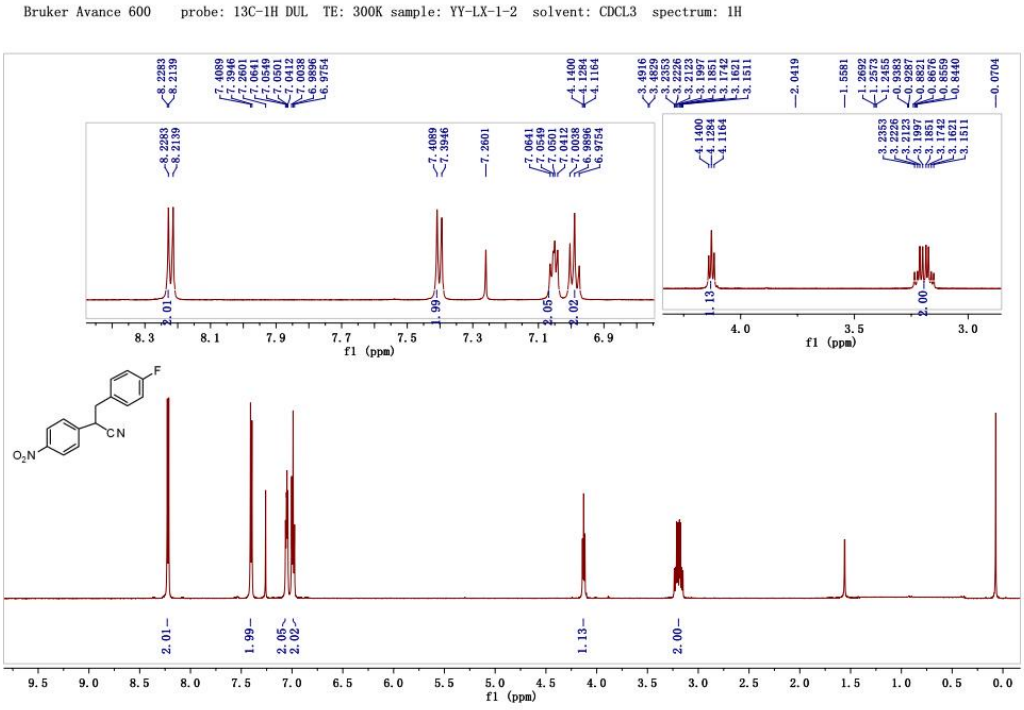
The ^{1}H NMR Spectra of 26'



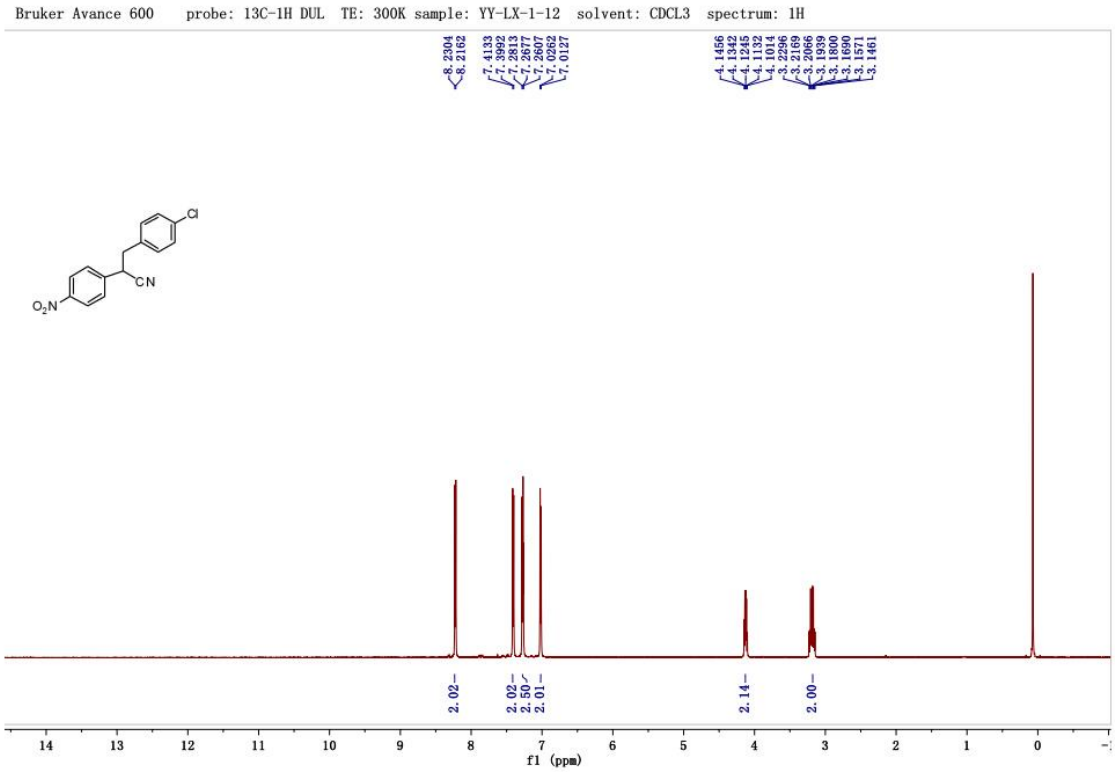
The ^{1}H NMR Spectra of 27'



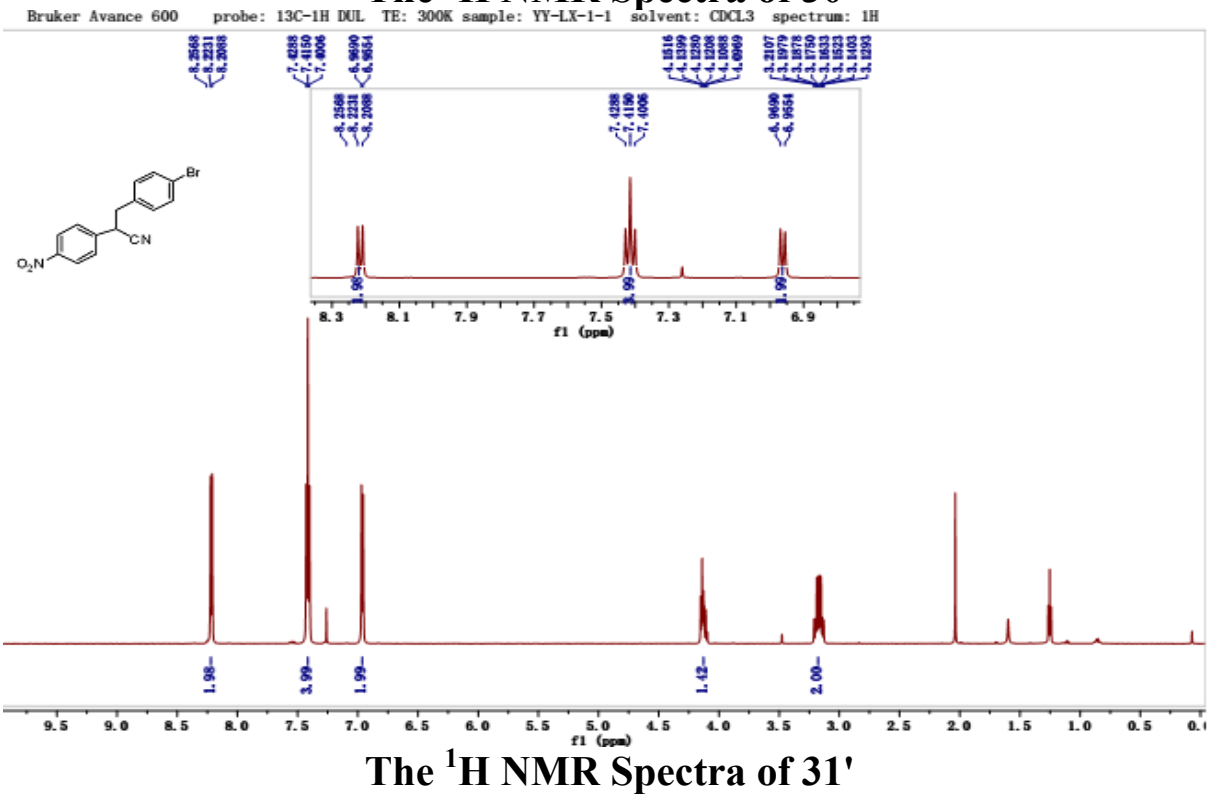
The ^{1}H NMR Spectra of 28'



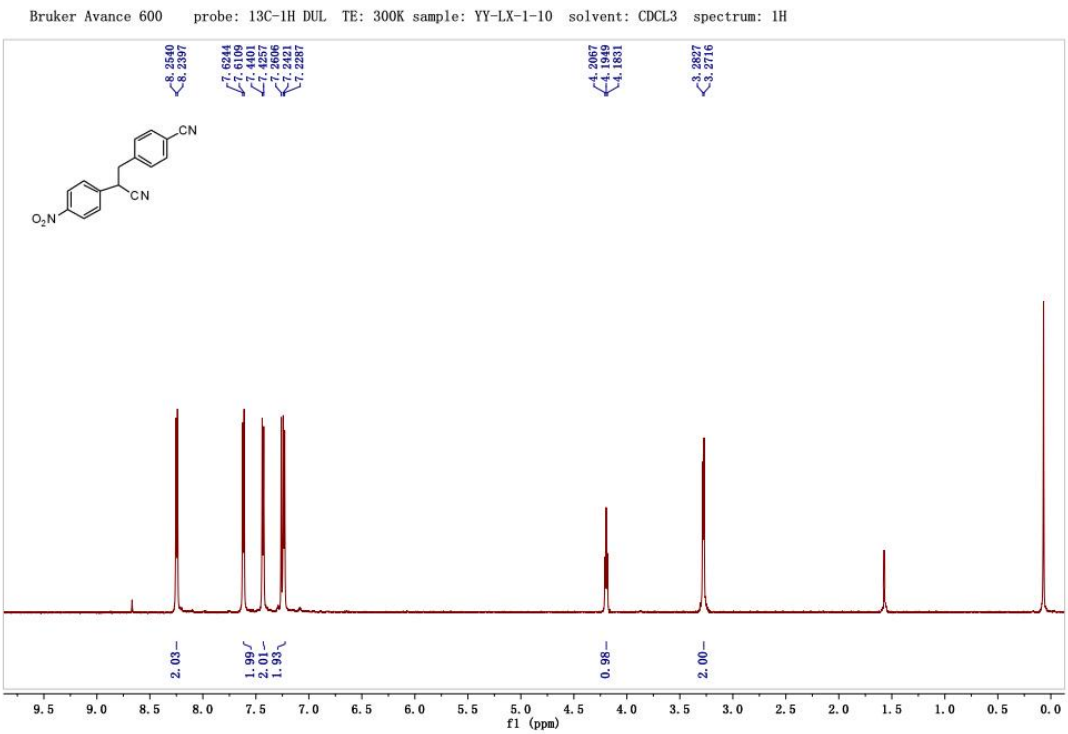
The ^{1}H NMR Spectra of 29'



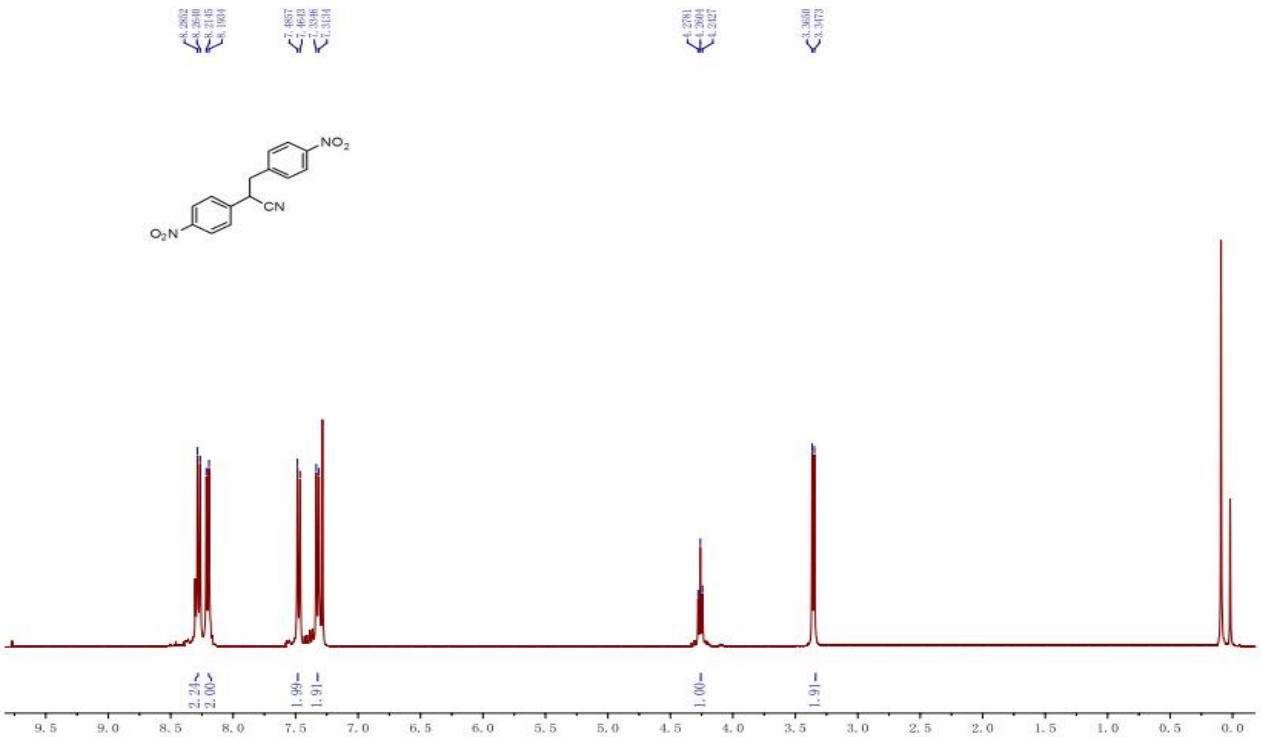
The ^{1}H NMR Spectra of 30'



The ^{1}H NMR Spectra of 31'

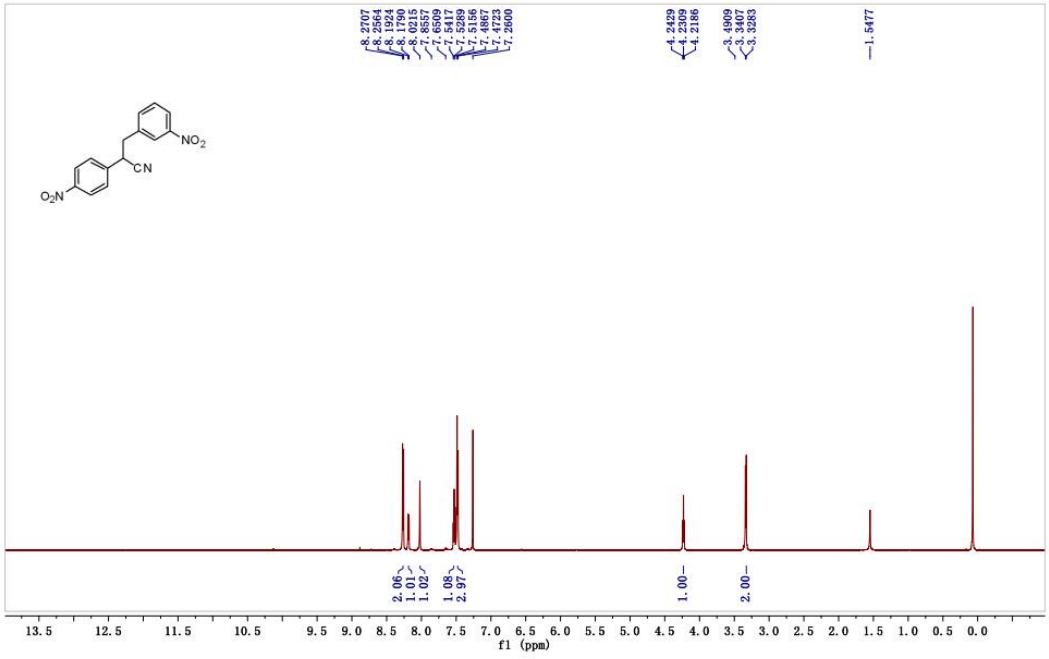


The ^{1}H NMR Spectra of 32'

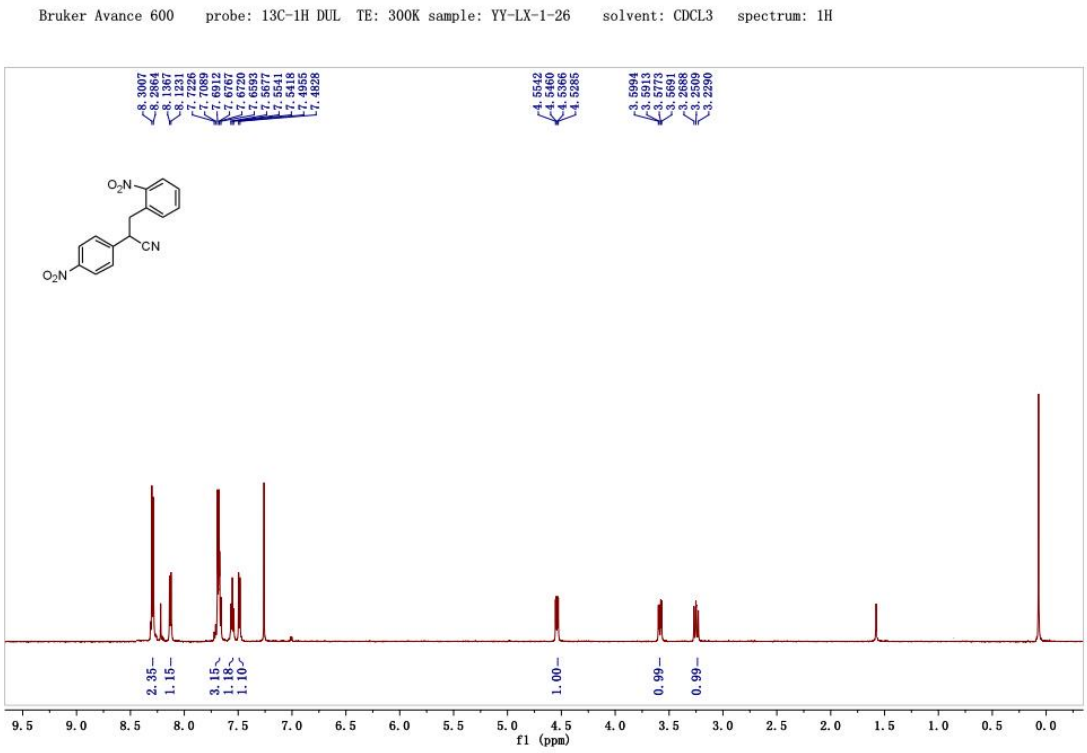


The ^{1}H NMR Spectra of 33'

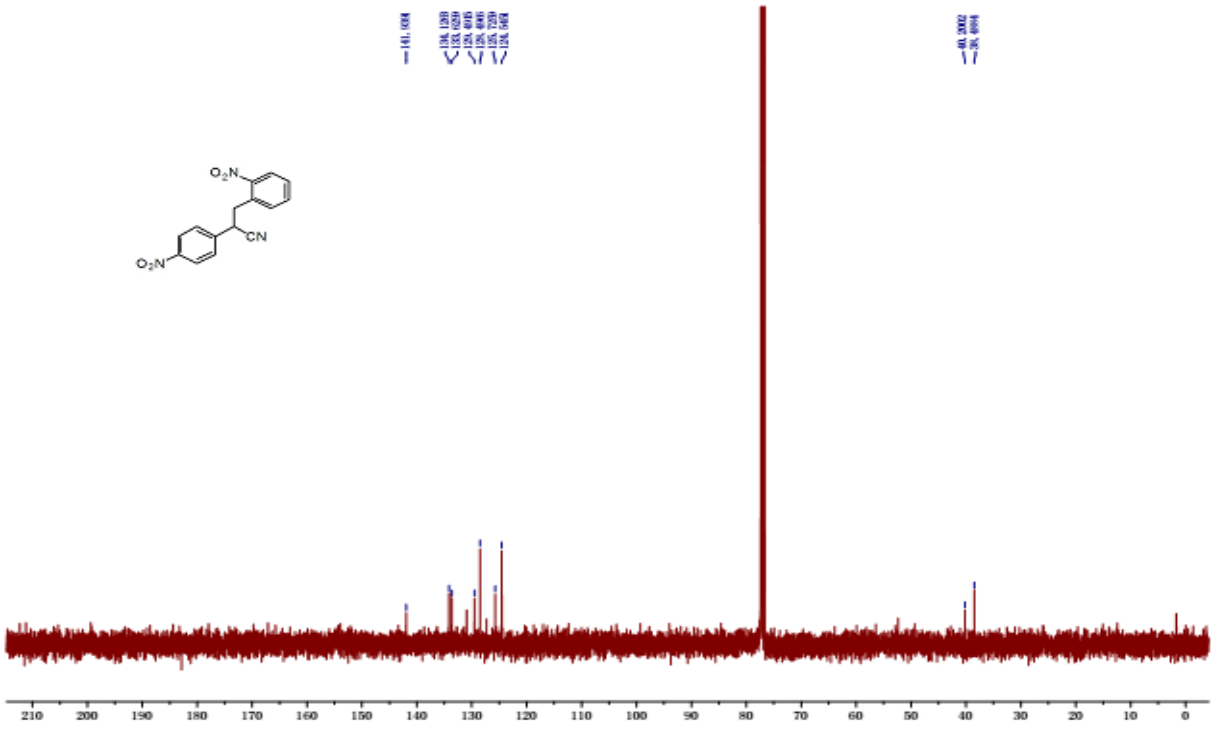
Bruker Avance 600 probe: 13C-1H DUL TE: 300K sample: YY-LX-1-24 solvent: CDCL3 spectrum: 1H



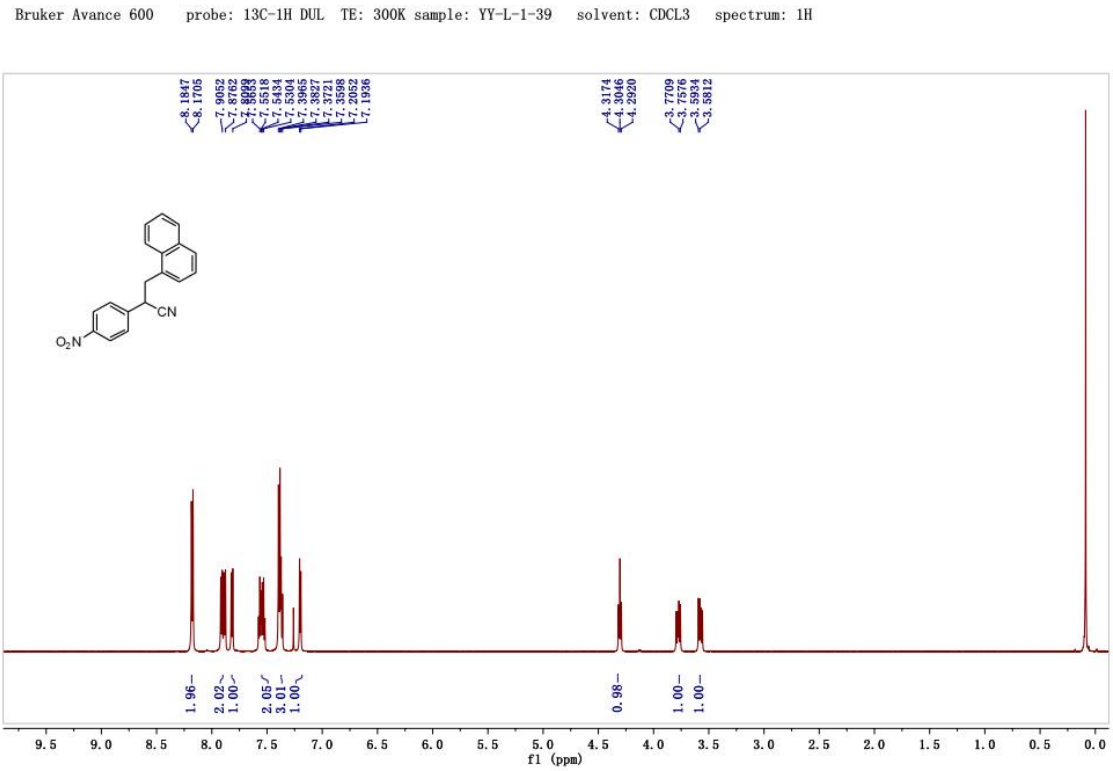
The ^{1}H NMR Spectra of 34'



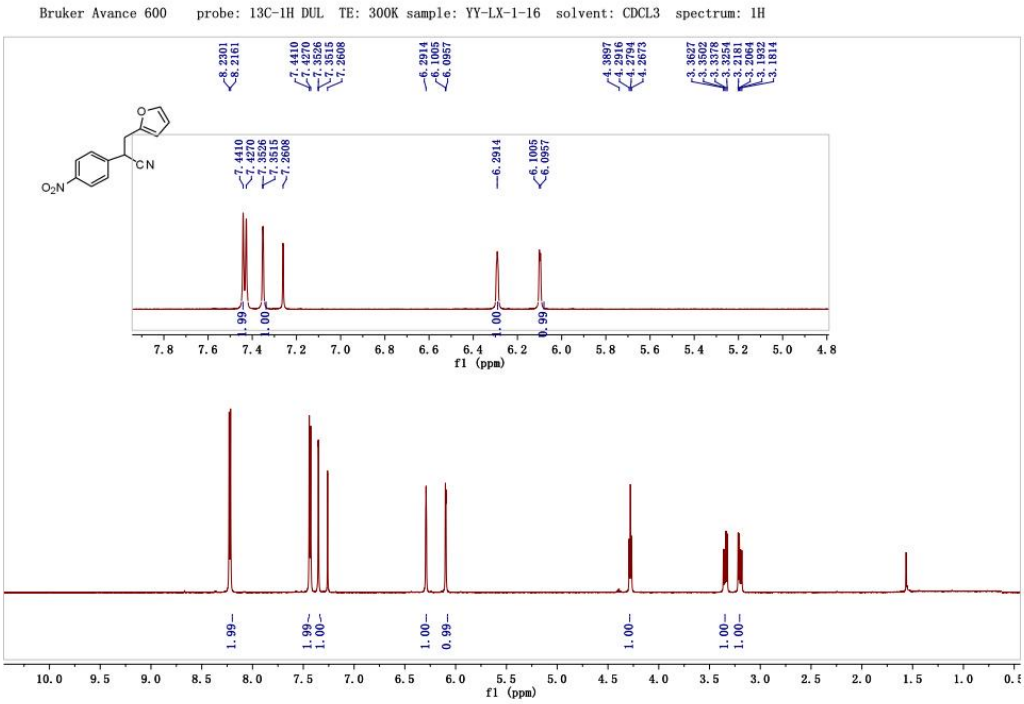
The ^{13}C NMR Spectra of 34'



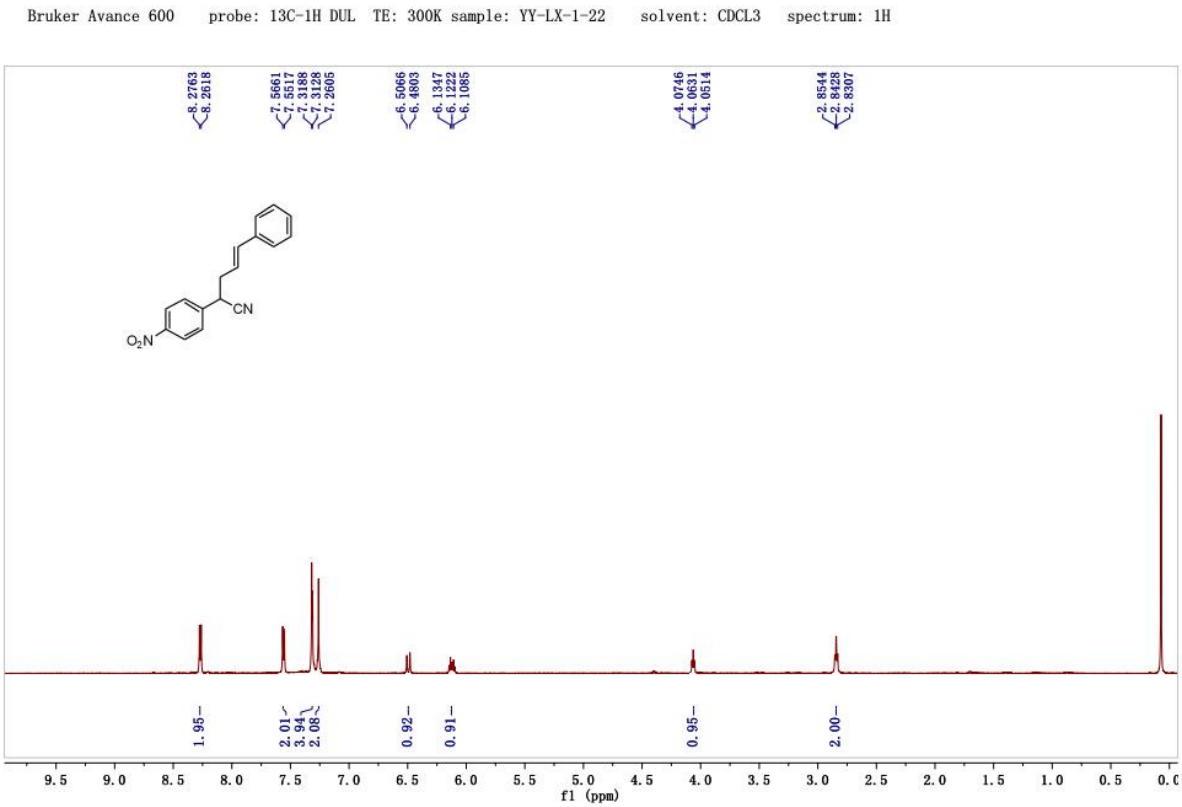
The ^{1}H NMR Spectra of 35'



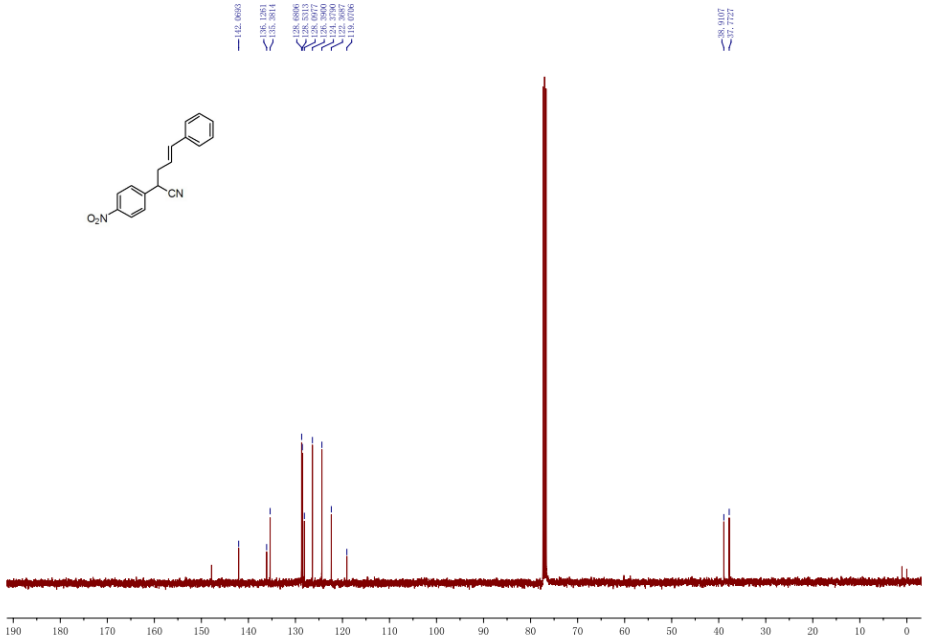
The ^{1}H NMR Spectra of 36'



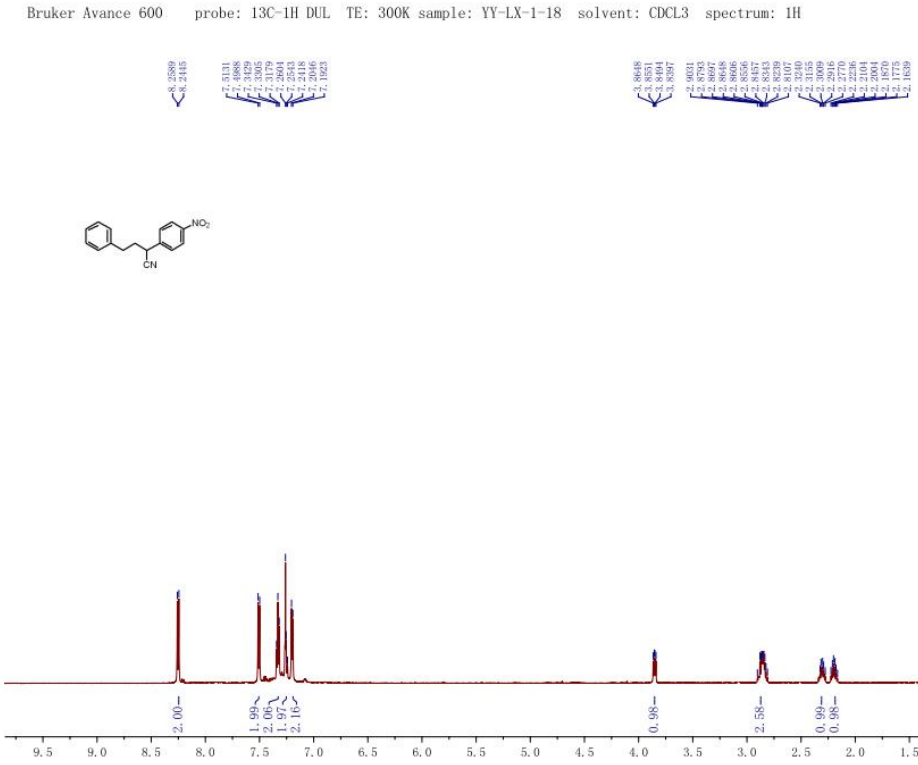
The ^{1}H NMR Spectra of 37'



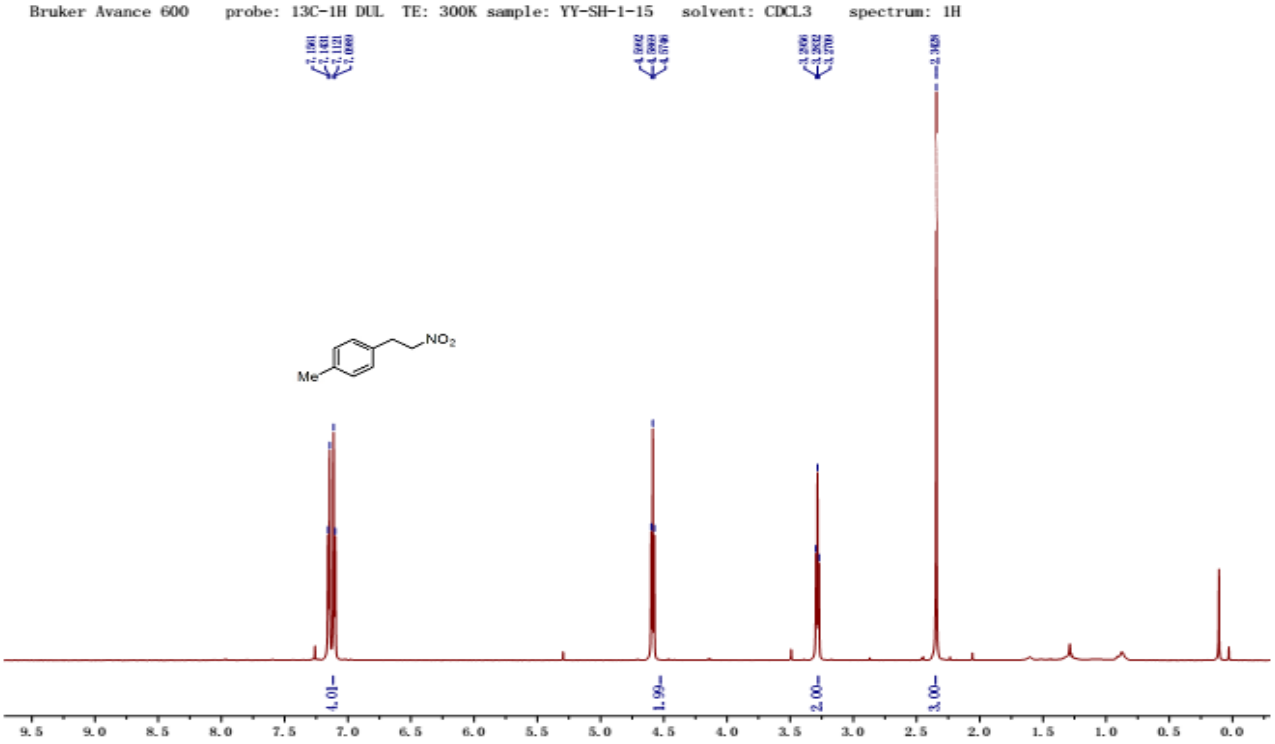
The ^{13}C NMR Spectra of 37'



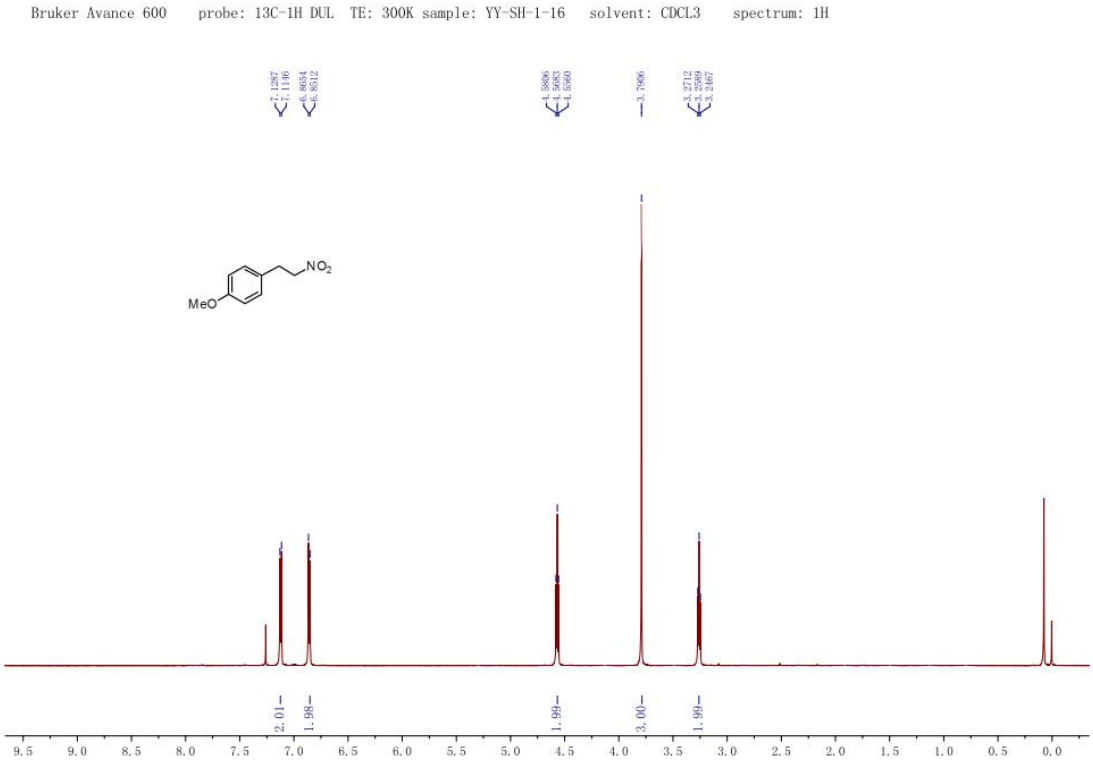
The ^{1}H NMR Spectra of 38'



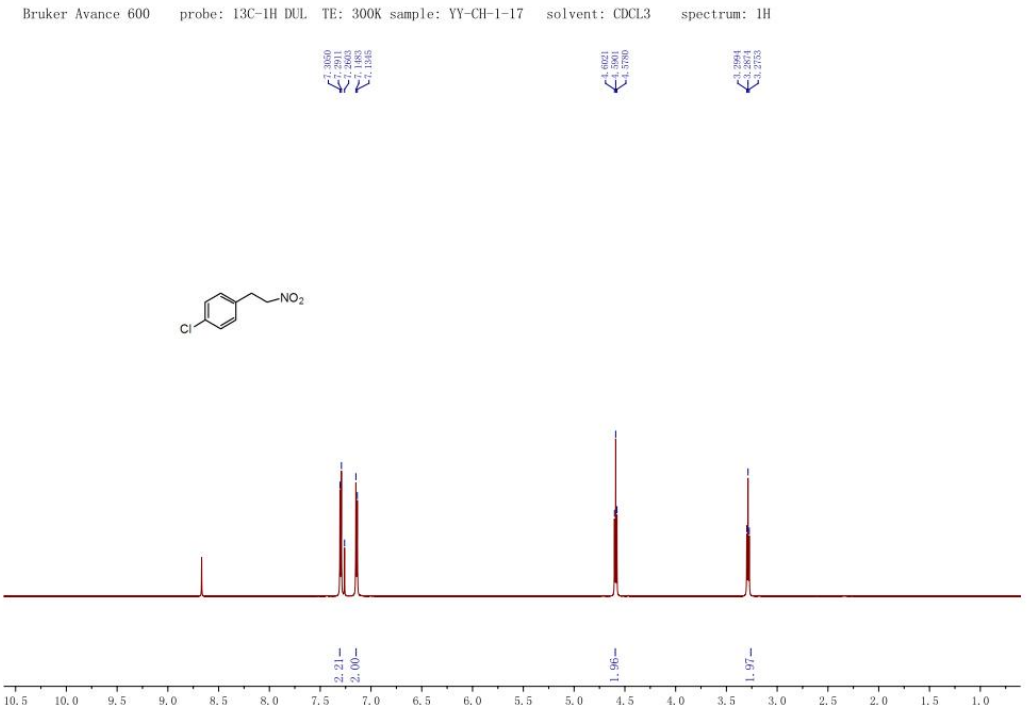
The ^{1}H NMR Spectra of 39'



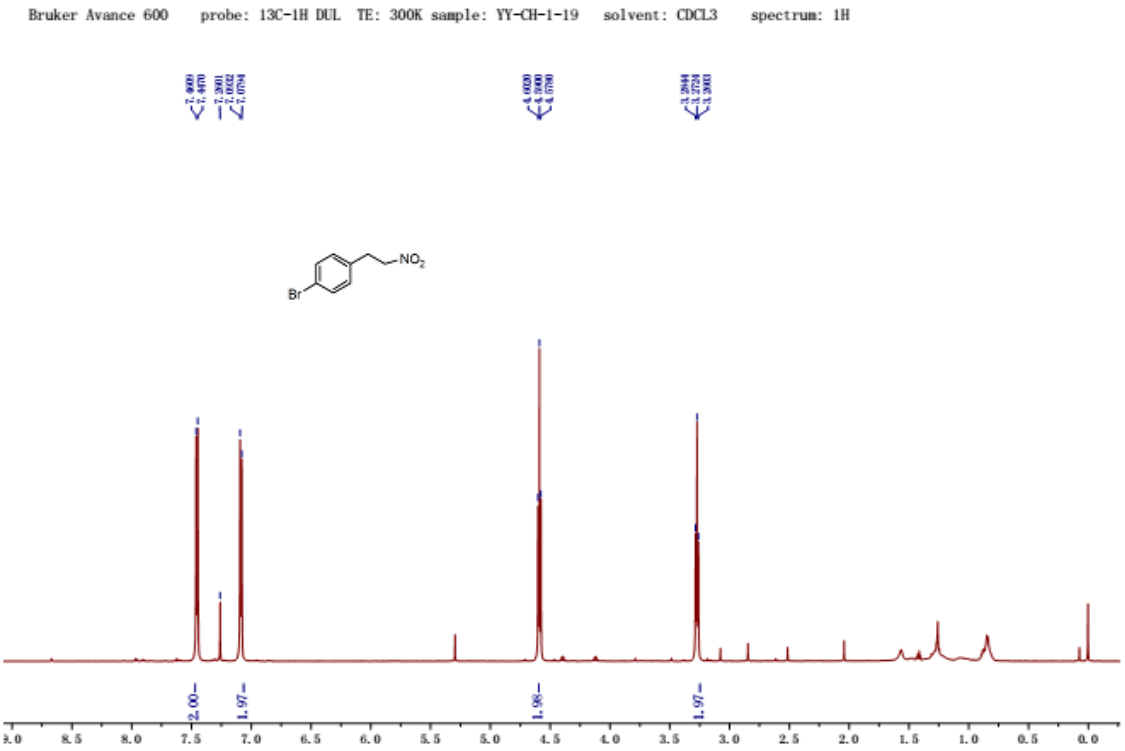
The ^{1}H NMR Spectra of 40'



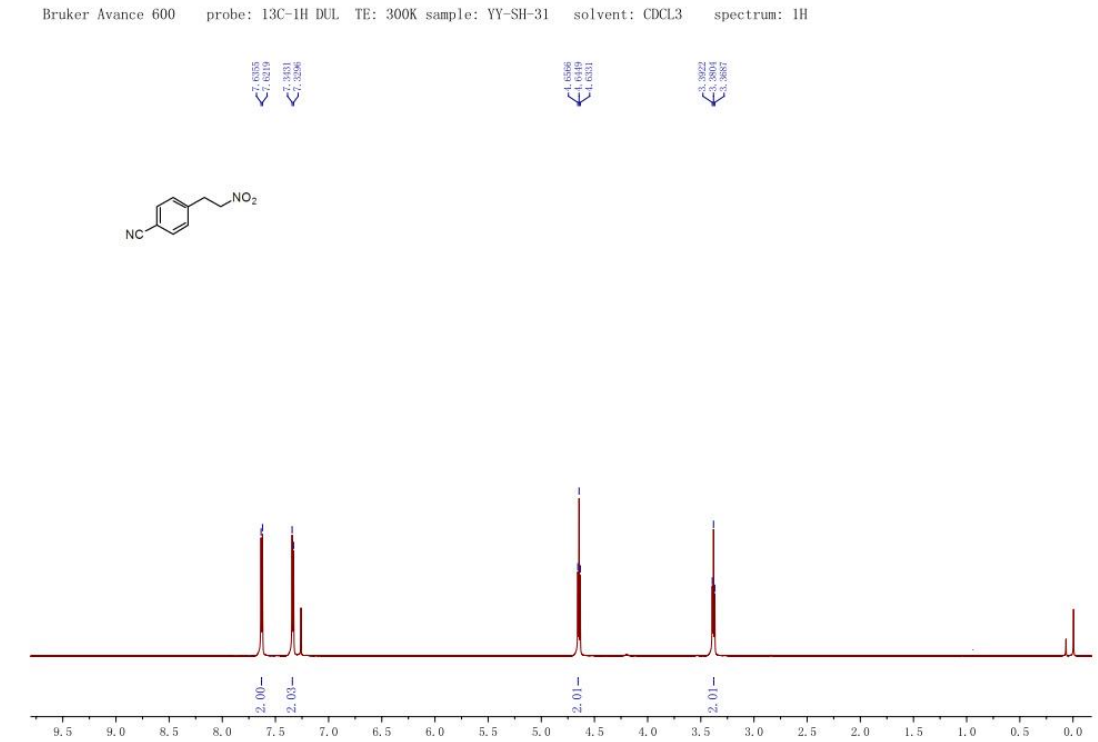
The ^{1}H NMR Spectra of 41'



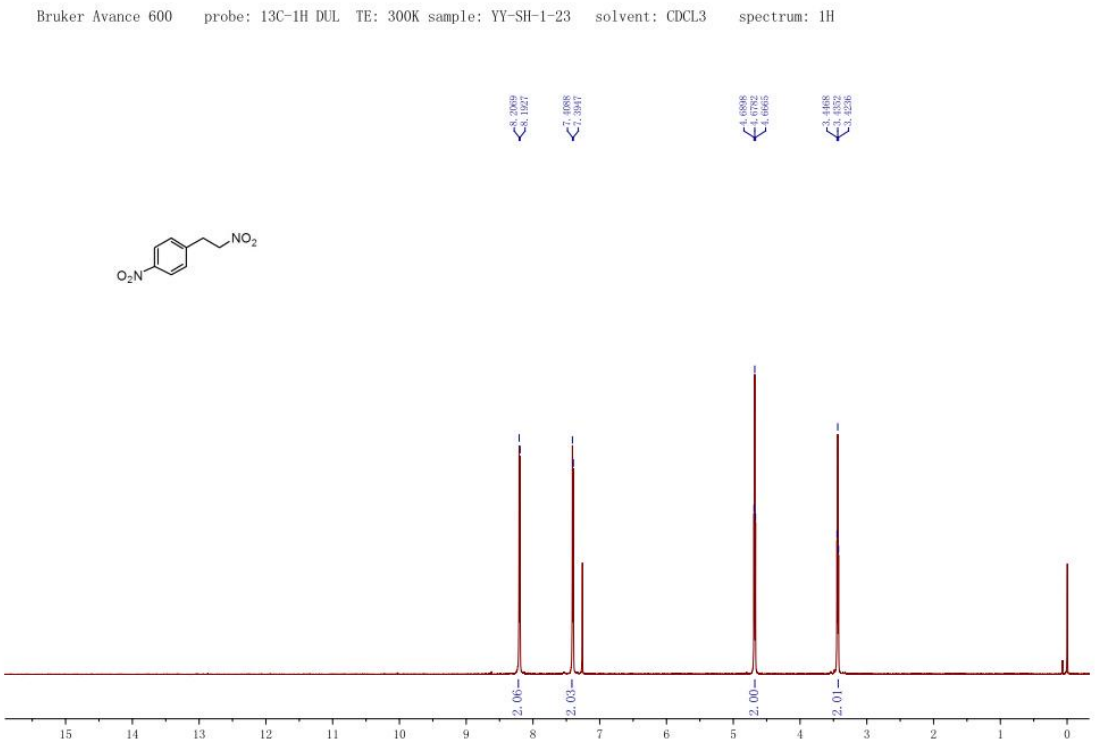
The ^{1}H NMR Spectra of 42'



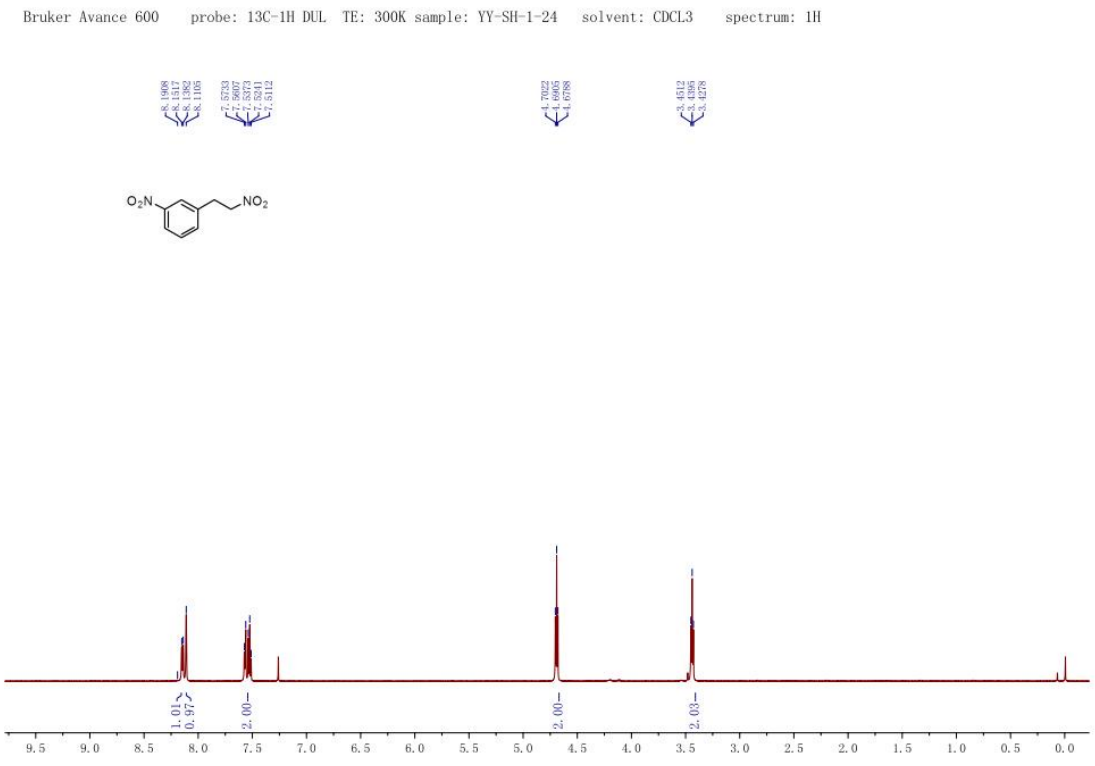
The ^{1}H NMR Spectra of 43'



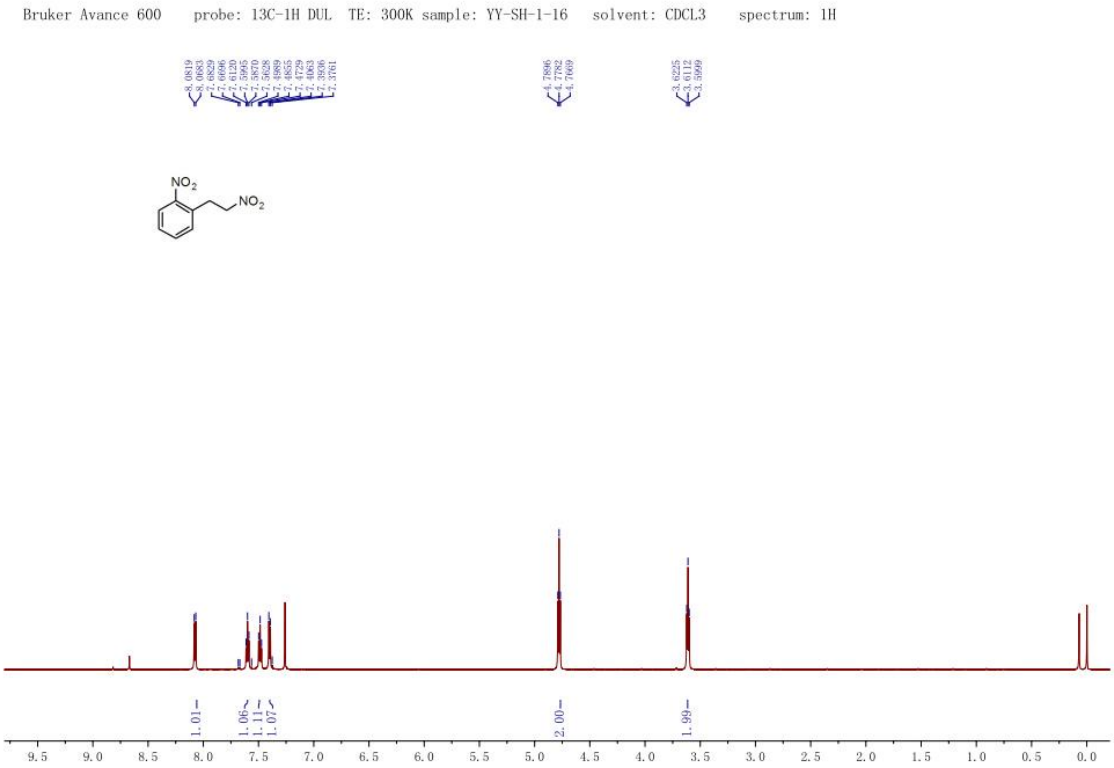
The ^{1}H NMR Spectra of 44'



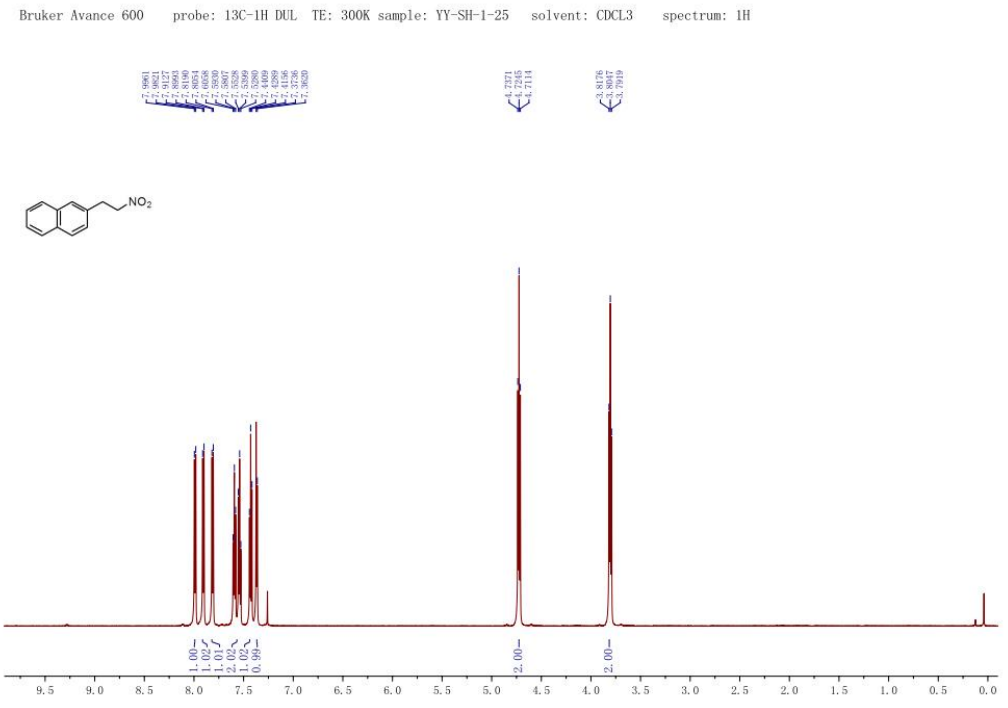
The ^{1}H NMR Spectra of 45'



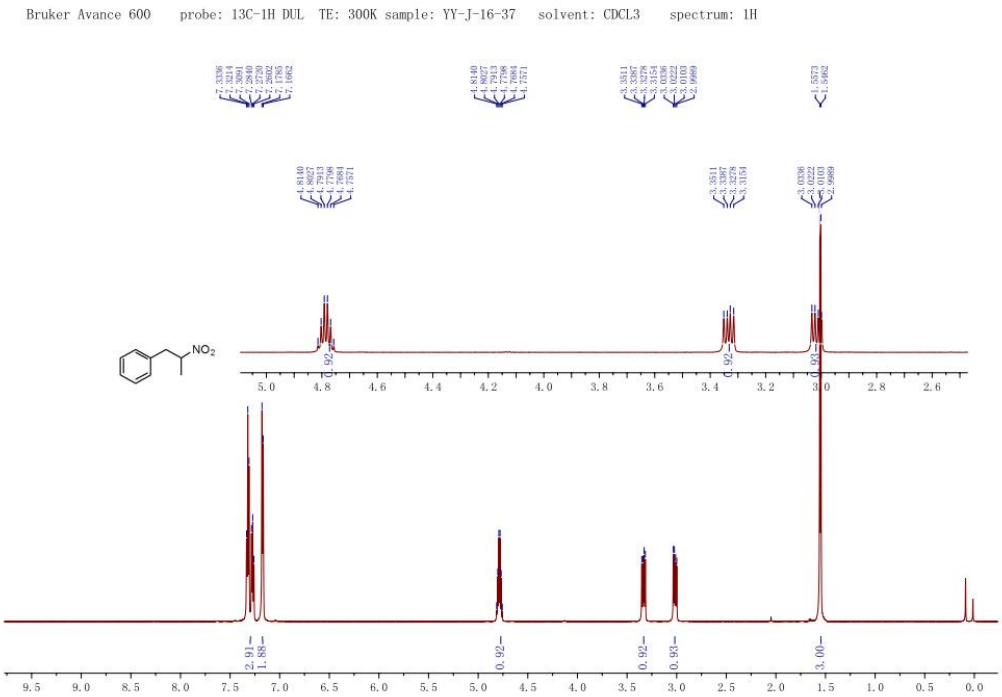
The ^{1}H NMR Spectra of 46'



The ^{1}H NMR Spectra of 47'



The ^{1}H NMR Spectra of 48'



The ^{1}H NMR Spectra of 49'