

Basic ionic liquid-catalyzed multicomponent synthesis of tetrahydrobenzo[*b*]pyrans and pyrano[*c*]chromenes

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Ethylenediammonium acetate ([EDA]Ac). IR (KBr) ν : 3423, 3093, 1637, 1563, 1481, 1409, 1341, 1172, 1121 cm^{-1} . ^1H NMR (D_2O , 300 MHz) δ : 1.51 (s, 3H), 2.65 (s, 4H) ppm. ^{13}C NMR (D_2O , 75.5 MHz) δ : 23.2, 38.8, 180.8 ppm.

Triethylenetetrammonium acetate ([TETA]Ac). IR (KBr) ν : 3271, 3232, 2926, 2834, 1690, 1549, 1397, 1333, 1133 cm^{-1} . ^1H NMR (D_2O , 300 MHz) δ : 1.60 (s, 3H), 2.48-2.61 (m, 12H) ppm. ^{13}C NMR (D_2O , 75.5 MHz) δ : 38.7, 46.8, 47.9, 180.6 ppm.

Triethylenetetrammonium *p*-toluenesulfonate ([TETA]PTS). IR (KBr) ν : 3349, 3291, 2944, 2839, 1602, 1489, 1458, 1211, 1183, 1122, 1034, 1010 cm^{-1} . ^1H NMR (D_2O , 300 MHz) δ : 2.18 (s, 3H), 2.54-2.68 (m, 12H), 7.15 (d, $J=8.1$ Hz, 1H), 7.53 (d, $J=8.4$ Hz, 1H) ppm. ^{13}C NMR (D_2O , 75.5 MHz) δ : 20.5, 39.0, 47.0, 48.4, 125.3, 129.4, 139.8, 142.1 ppm.

Triethylenetetrammonium tetrafluoroborate ([TETA]BF₄). IR(KBr) ν : 3368, 3250, 2933, 2837, 1605, 1462, 1362, 1289, 1087 cm^{-1} . ^1H NMR (D_2O , 300 MHz) δ : 2.69-2.81 (m, 12H) ppm. ^{13}C NMR (D_2O , 75.5 MHz) δ : 38.8, 46.9, 48.0 ppm.

Triethylenetetrammonium trifluoroacetate ([TETA]TFA). IR(KBr) ν : 3490, 3322, 3080, 2837, 2694, 1790, 1672, 1624, 1521, 1458, 1316, 1194, 1120, 1007, 822 cm^{-1} . ^1H NMR (D_2O , 300 MHz) δ : 2.62-2.77 (m, 12H) ppm. ^{13}C NMR (D_2O , 75.5 MHz) δ : 37.4, 47.0, 48.5, 116.1(q, $J=11.6$ MHz, 1C), 162.3(q, $J=1.3$ MHz, 1C) ppm. ^{19}F NMR (D_2O , 282 MHz) δ : -75.5 (s, 3F) ppm.

2-Amino-3-cyano--7,7-dimethyl-4-(4-nitrophenyl)-4*H*-5,6,7,8-tetrahydrobenzo[

b]pyran-5-one (5d). IR (KBr) ν : 3407, 3317, 3176, 2183, 1671, 1630, 1594, 1521, 1350, 1216, 1031 cm^{-1} . ^1H NMR (DMSO- d_6 , 300 MHz) δ : 0.94 (s, 3H), 1.02 (s, 3H), 2.07 (d, $J=16.07$ Hz, 1H), 2.21 (d, $J=16.03$ Hz, 1H), 2.52 (s, 2H), 4.35 (s, 1H), 7.17 (s, 2H), 7.44 (d, $J=8.35$ Hz, 2H), 8.14 (d, $J=8.35$ Hz, 2H) ppm.

2-Amino-3-cyano-7,7-dimethyl-4-phenyl-4H-5,6,7,8-tetrahydrobenzo[b]pyran-5-one (5f). IR (KBr) ν : 3397, 3325, 3213, 2961, 2200, 1680, 1661, 1604, 1371, 1214, 1139, 1036 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ : 1.04 (s, 3H), 1.12 (s, 3H), 2.22 (d, $J=16.3$ Hz, 1H), 2.23 (d, $J=16.3$ Hz, 1H), 2.46 (s, 2H), 4.41 (s, 1H), 4.57 (s, 2H), 7.18-7.32 (m, 5H) ppm.

2-Amino-3-cyano-4-(4-methoxyphenyl)-7,7-dimethyl-4H-5,6,7,8-tetrahydrobenzo[b]pyran-5-one (5h). IR (KBr) ν : 3377, 3322, 3187, 2964, 2198, 1684, 1655, 1606, 1509, 1370, 1248, 1212, 1034 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ : 1.03 (s, 3H), 1.11 (s, 3H), 2.21 (d, $J=16.0$ Hz, 1H), 2.22 (d, $J=16.0$ Hz, 1H), 2.43 (s, 2H), 3.77 (s, 3H), 4.36 (s, 3H), 4.55 (s, 2H), 6.84 (d, $J=8.7$ Hz, 2H), 7.15 (d, $J=8.7$ Hz, 2H) ppm.

2-Amino-3-cyano-4-phenyl-4H-5,6,7,8-tetrahydrobenzo[b]pyran-5-one (5l). IR (KBr) ν : 3322, 3170, 3001, 2956, 2933, 2920, 2193, 1683, 1651, 1610, 1369, 1210, 1169, 1134, 1065, 1001 cm^{-1} . ^1H NMR (300 MHz, DMSO- d_6) δ : 1.80-2.20 (m, 2H), 2.19-2.38 (m, 2H), 2.61-2.64 (m, 2H), 4.19 (s, 1H), 7.01 (s, 2H), 7.13-7.21 (m, 3H), 7.29 (t, $J=17.4$ Hz, 2H) ppm.

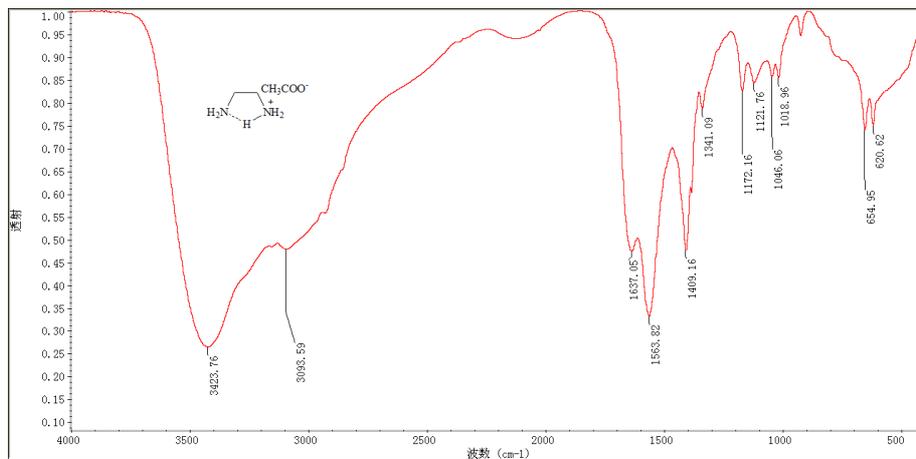
2-Amino-3-cyano-4-(4-nitrophenyl)-4H,5H-pyrano[3,2-c]chromen-5-one (6a). IR (KBr) ν : 3481, 3429, 3369, 3334, 2195, 1718, 1672, 1606, 1504, 1372, 1347, 1055 cm^{-1} . ^1H NMR (300 MHz, DMSO- d_6) δ : 4.68 (s, 1H), 7.22-7.59 (m, 5H), 7.62 (s, 2H), 7.71-7.77 (m, 1H), 7.90-7.93 (m, 1H), 8.18 (d, $J=8.7$ Hz, 2H) ppm.

2-Amino-3-cyano-4-phenyl-4H,5H-pyrano[3,2-c]chromen-5-one (6b). IR (KBr) ν : 3378, 3285, 3180, 2199, 1710, 1675, 1638, 1607, 1491, 1382, 1059 cm^{-1} . ^1H NMR (300 MHz, DMSO- d_6) δ : 4.45 (s, 1H), 7.21-7.35 (m, 5H), 7.42 (s, 2H), 7.44-7.52 (m, 2H), 7.74-7.68 (m, 1H), 7.89 (d, $J=1.5$ Hz, 1H), 7.92 (d, $J=1.5$ Hz, 1H) ppm.

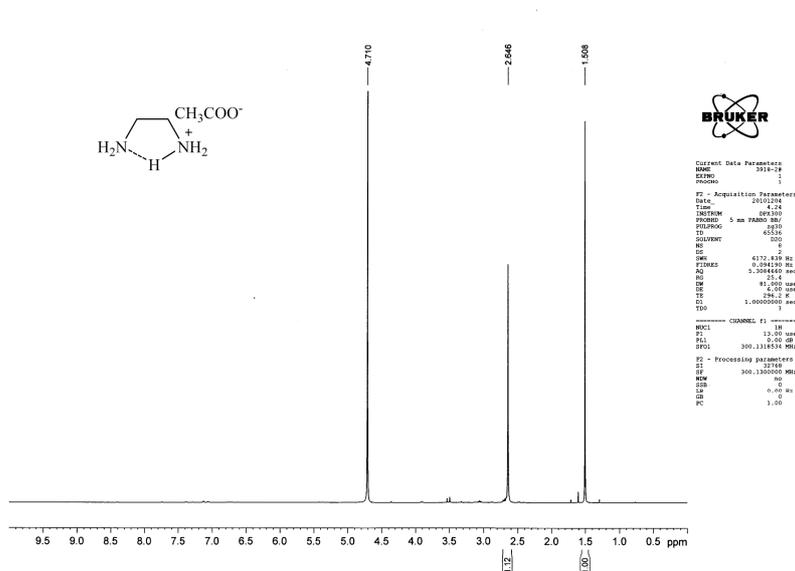
1. Copies of the IR, ^1H NMR, ^{19}F NMR, and ^{13}C NMR spectra

5.1 Ionic liquids

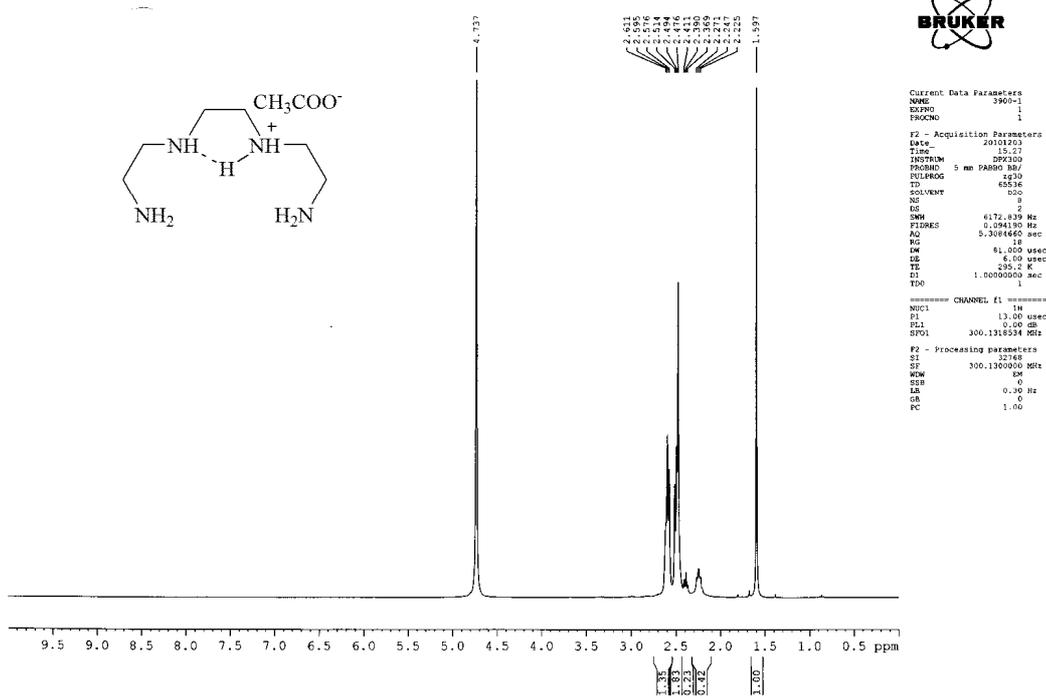
5.1.1 [EDA]Ac



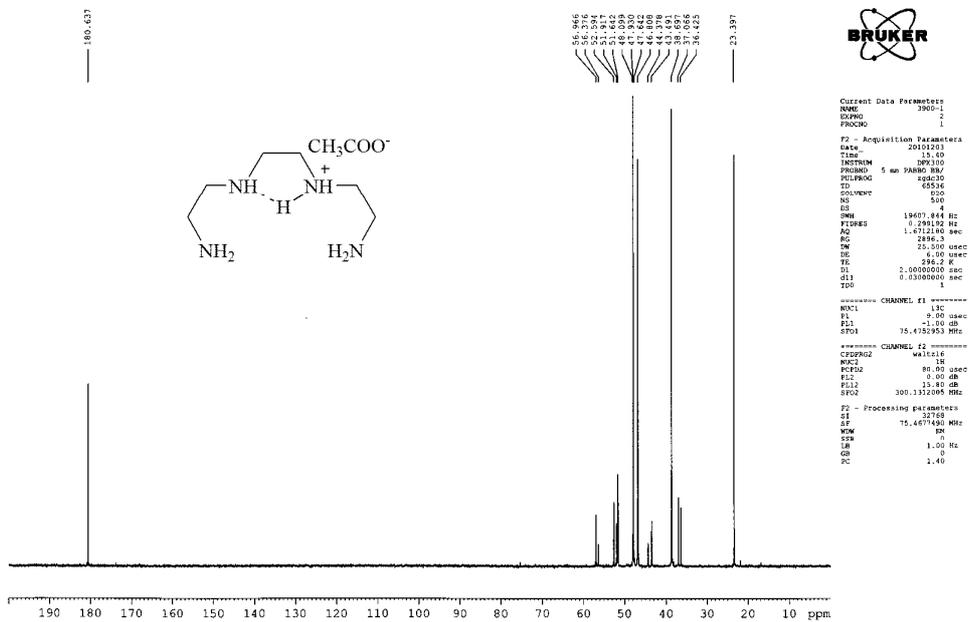
IR of [EDA]Ac



¹H NMR of [EDA]Ac

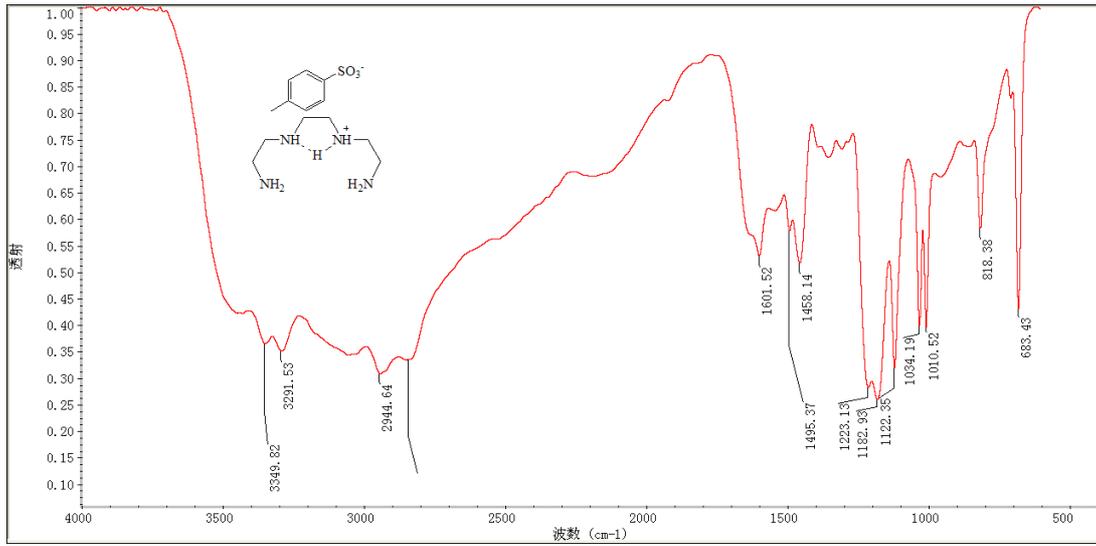


¹H NMR of [TETA]Ac

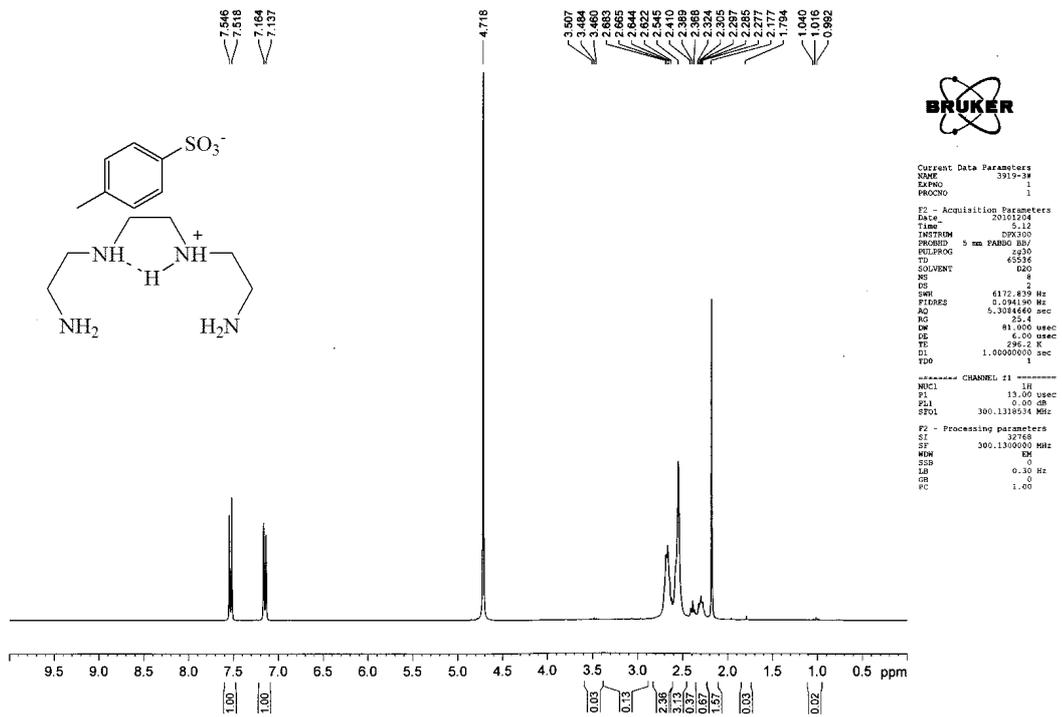


¹³C NMR of [TETA]Ac

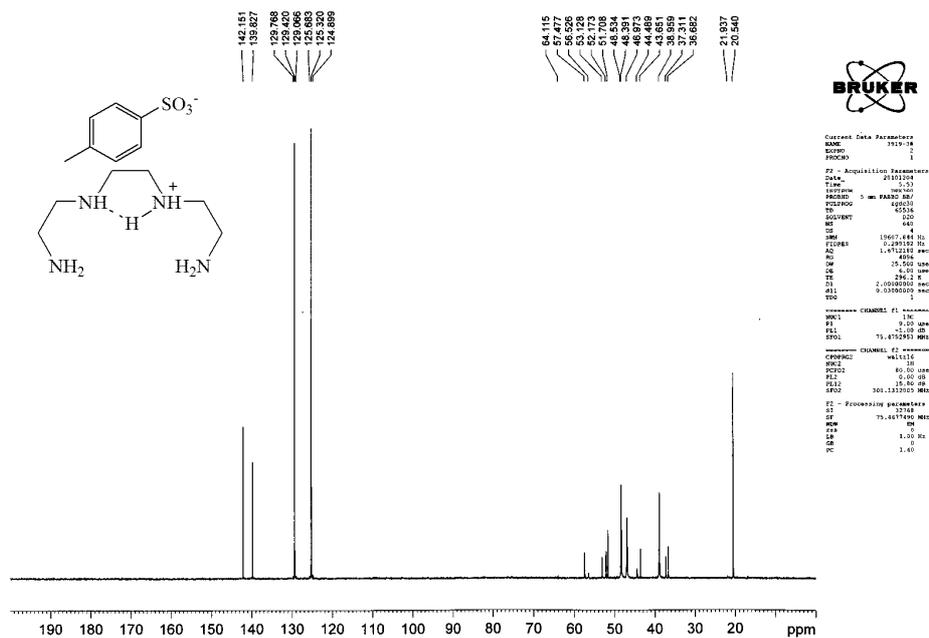
5.1.3 [TETA]Ts



IR of [TETA]Ts

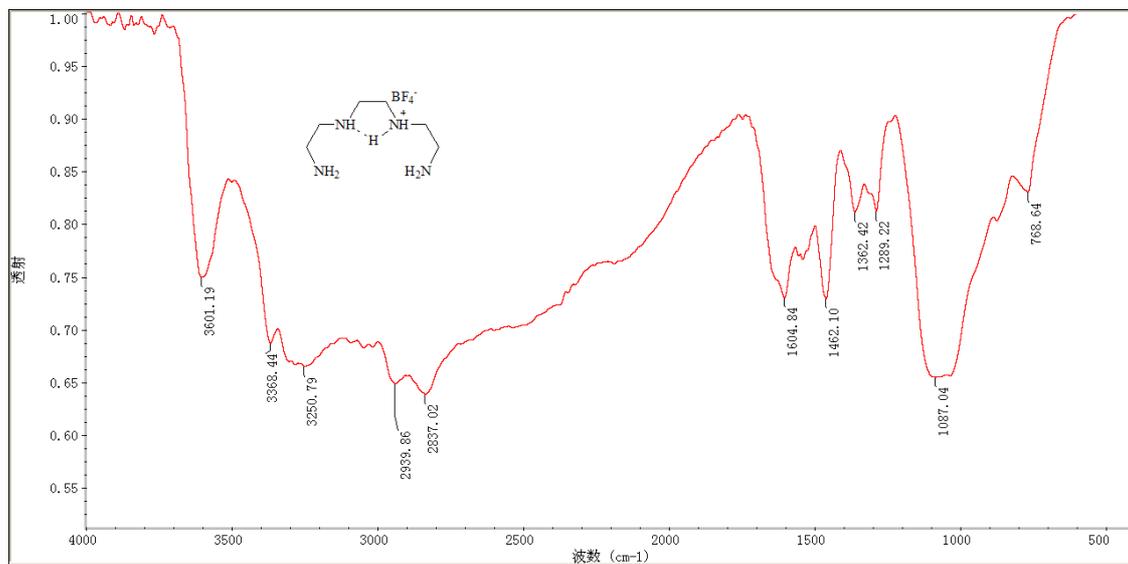


¹H NMR of [TETA]Ts

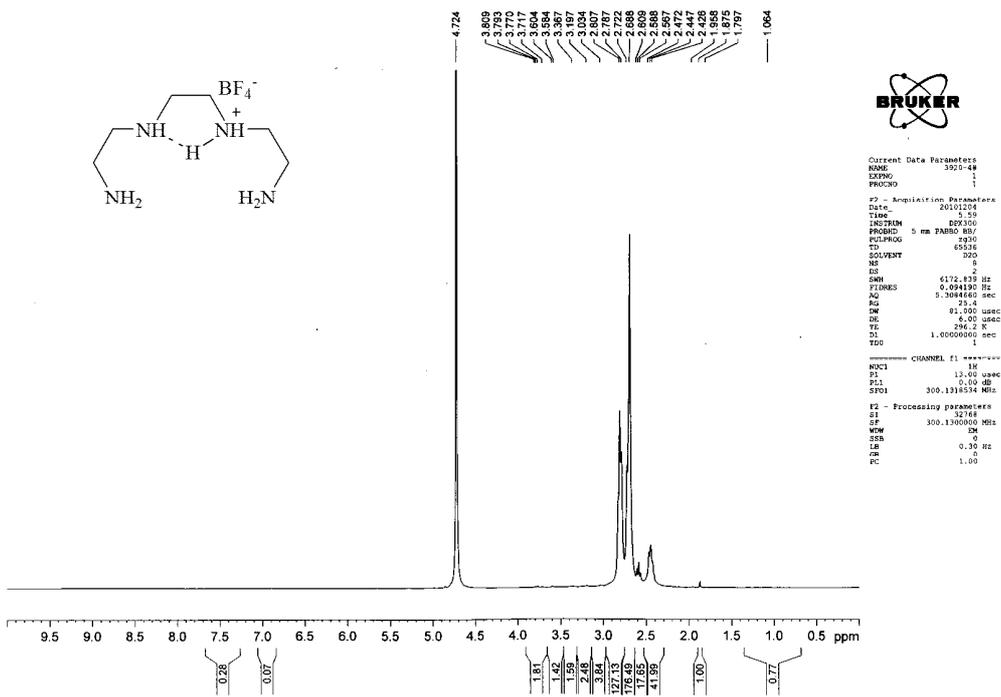


¹³C NMR of [TETA]Ts

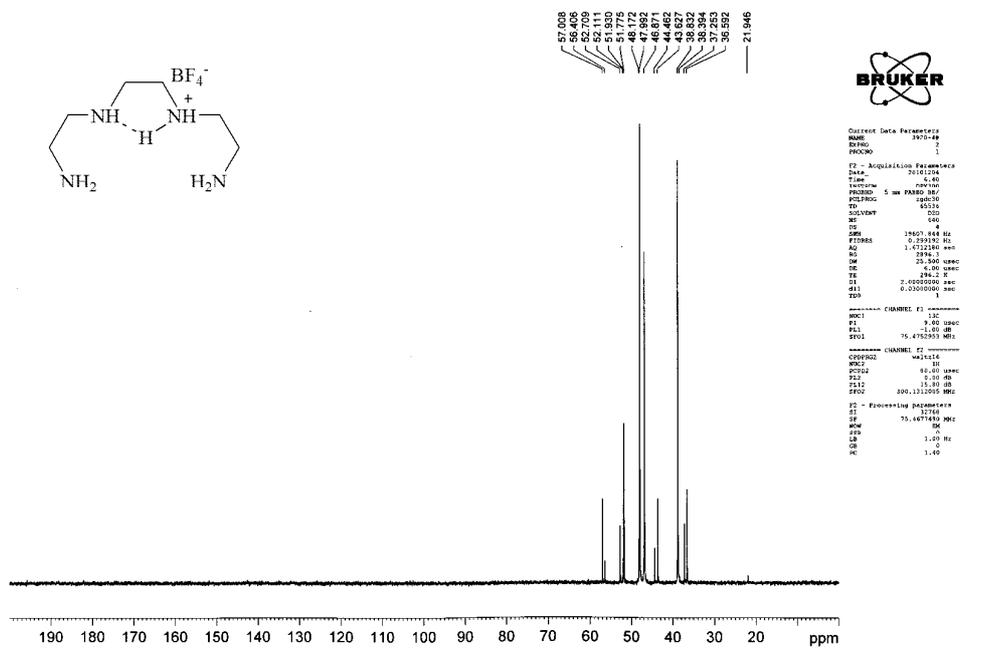
5.1.4 [TETA]BF₄



IR of [TETA]BF₄

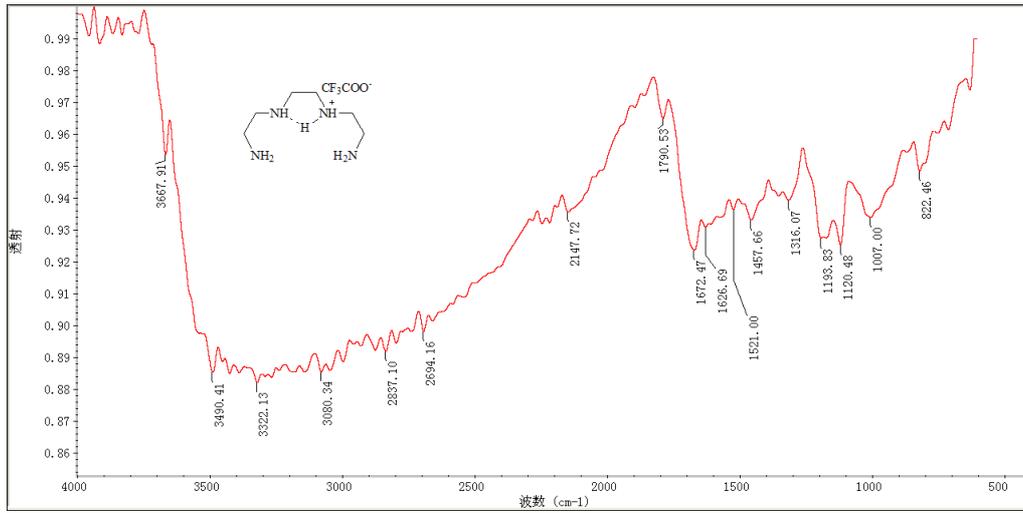


¹H NMR of [TETA]BF₄

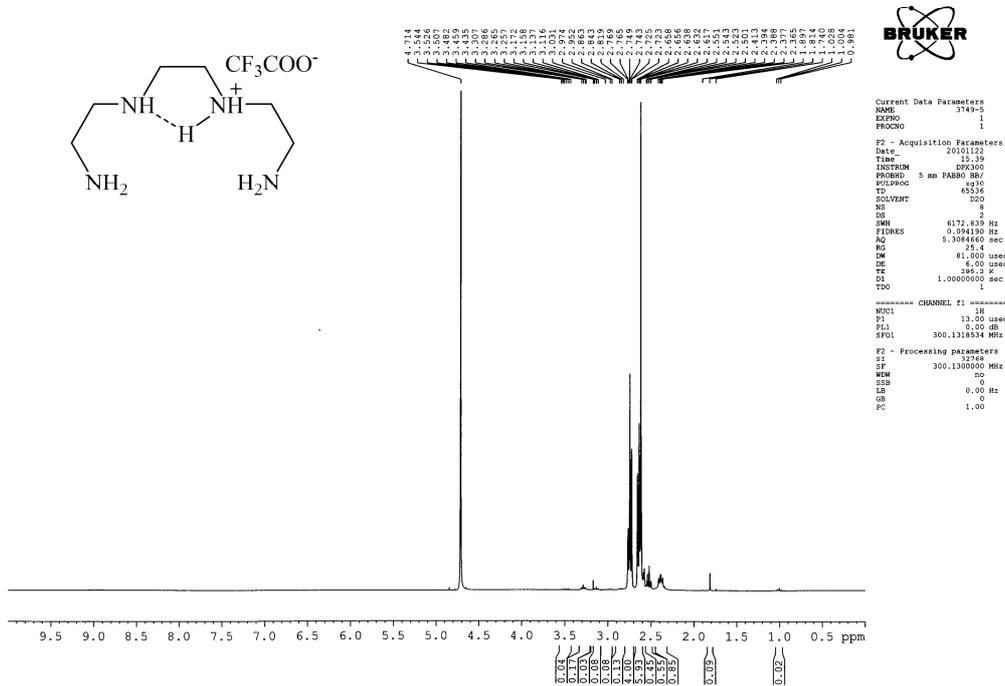


¹³C NMR of [TETA]BF₄

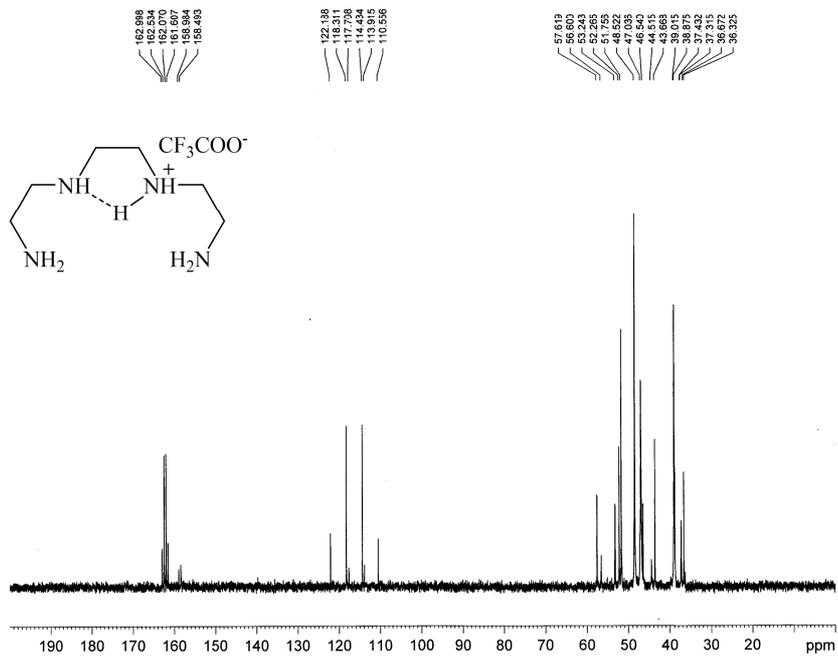
5.1.5 [TETA]TFA



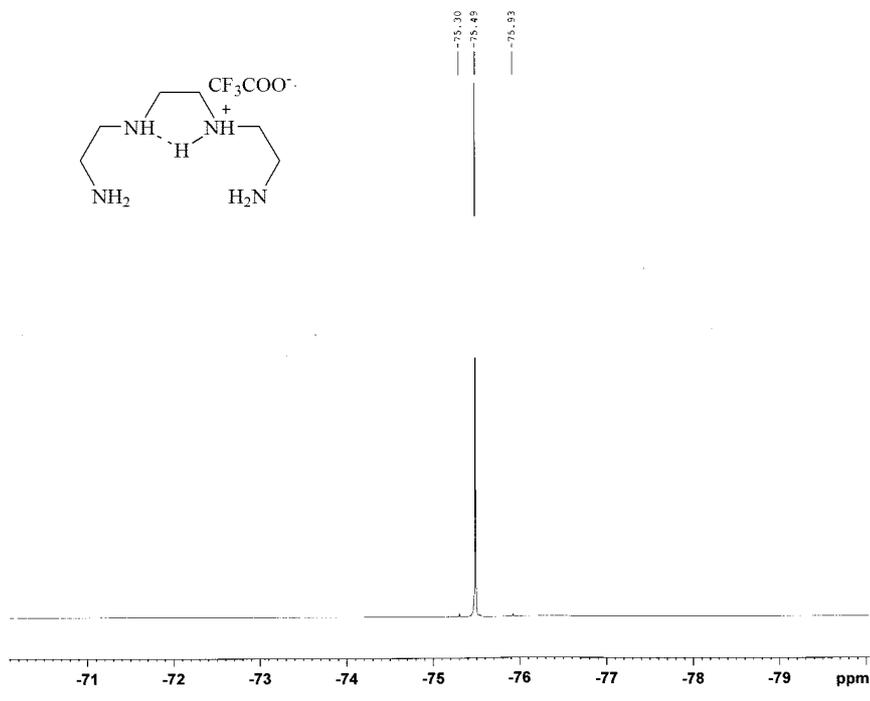
IR of [TETA]TFA



¹H NMR of [TETA]TFA

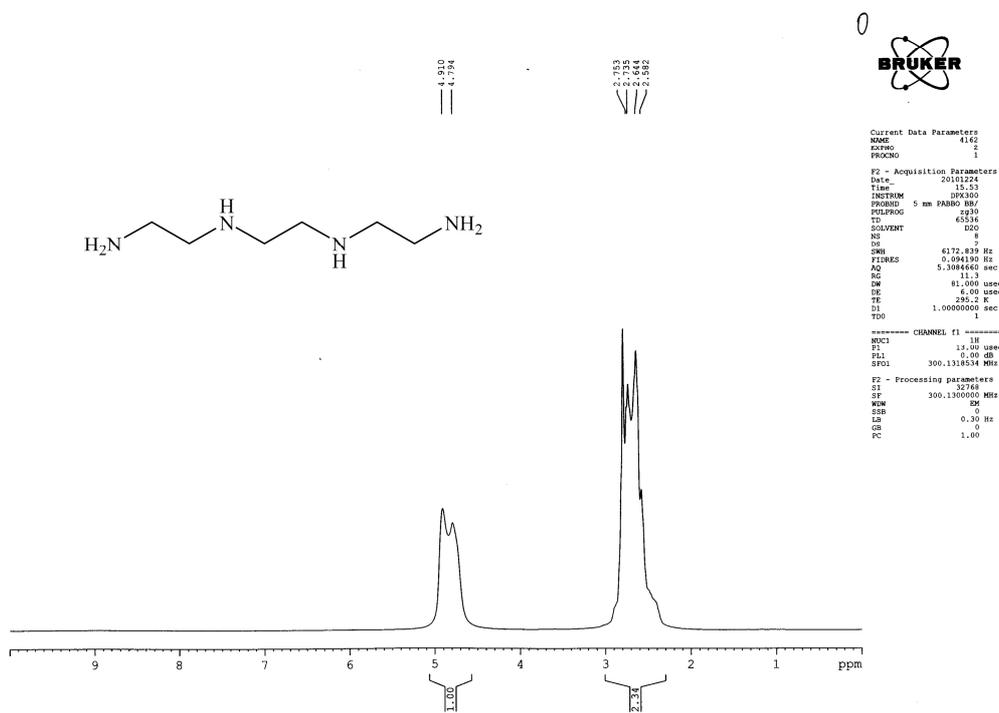


¹³C NMR of [TETA]TFA

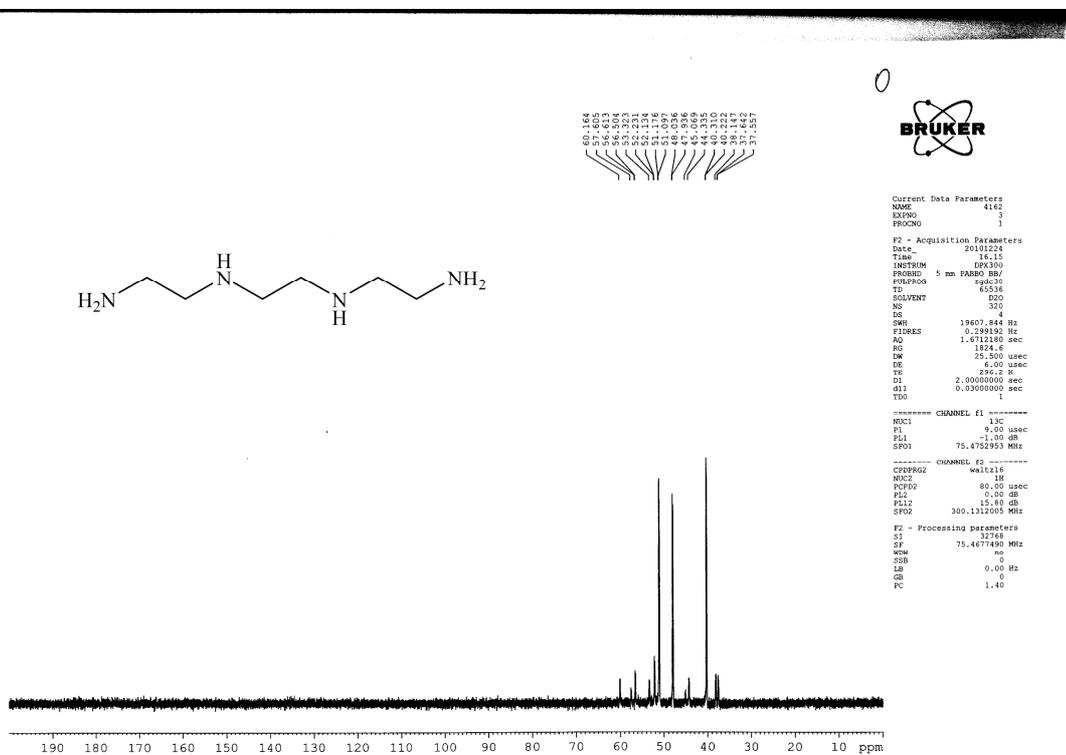


¹⁹F NMR of [TETA]TFA

5.1.6 Triethylenetetramine (TETA) as reference



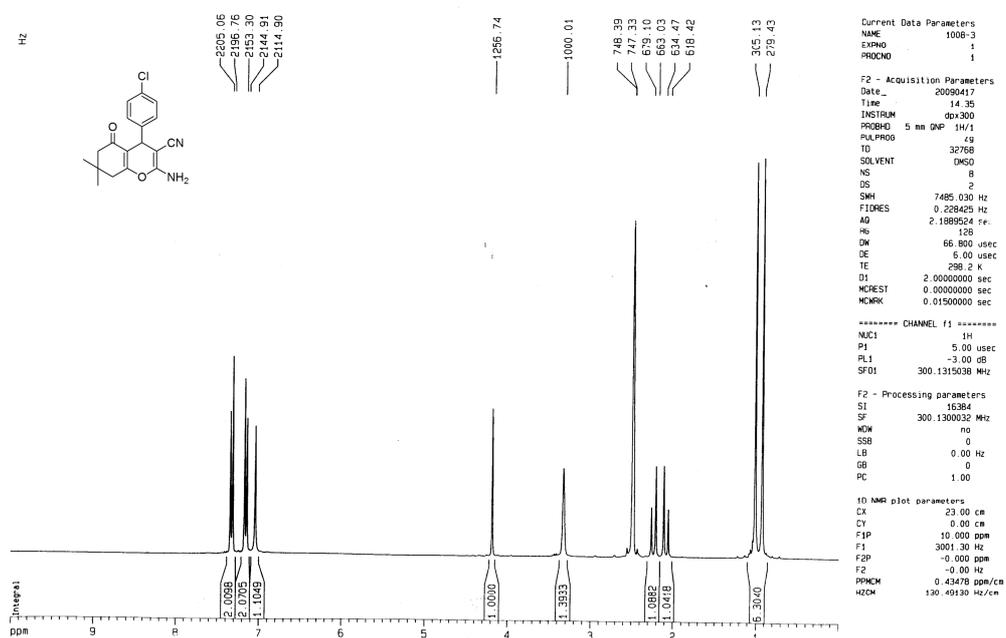
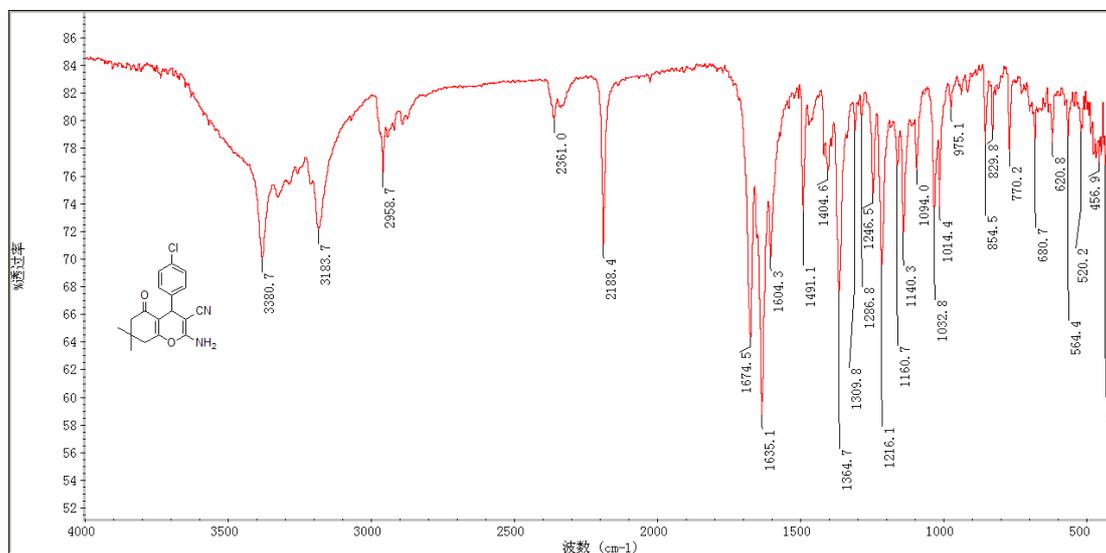
¹H NMR of TETA



¹³C NMR of TETA

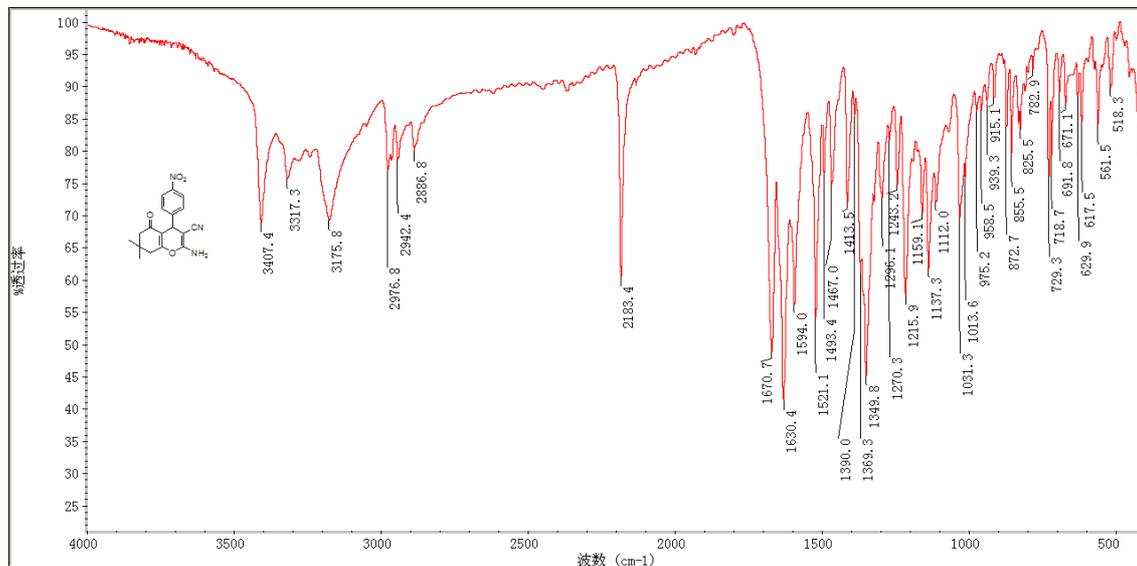
1.2 Tetrahydrobenzo[*b*]pyran derivatives

1.2.1 2-Amino-4-(4-chlorophenyl)-3-cyano-7,7-dimethyl-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran-5-one (5a)

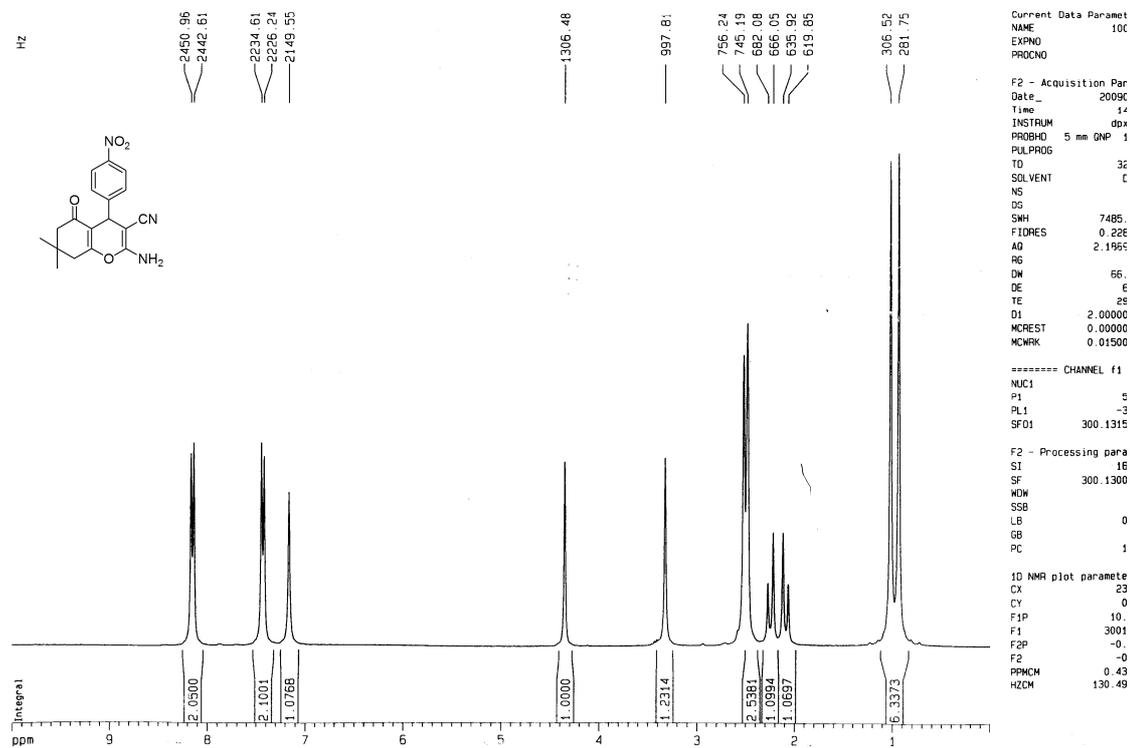


¹H NMR of 5a

1.2.2 2-Amino-3-cyano-7,7-dimethyl-4-(4-nitrophenyl)-4H-5,6,7,8-tetrahydrobenzo[b]pyran-5-one (5d)

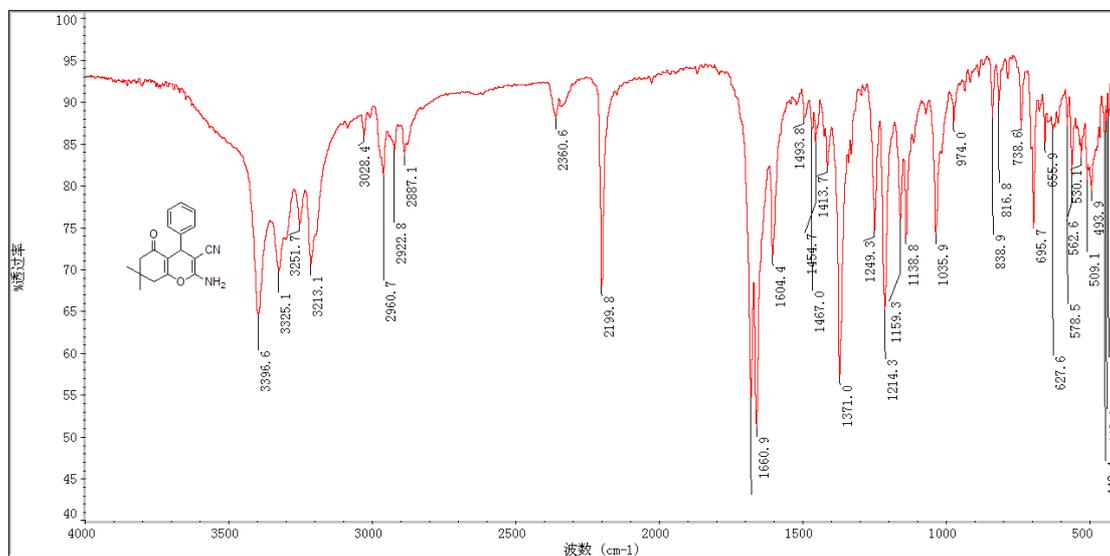


IR of 5d

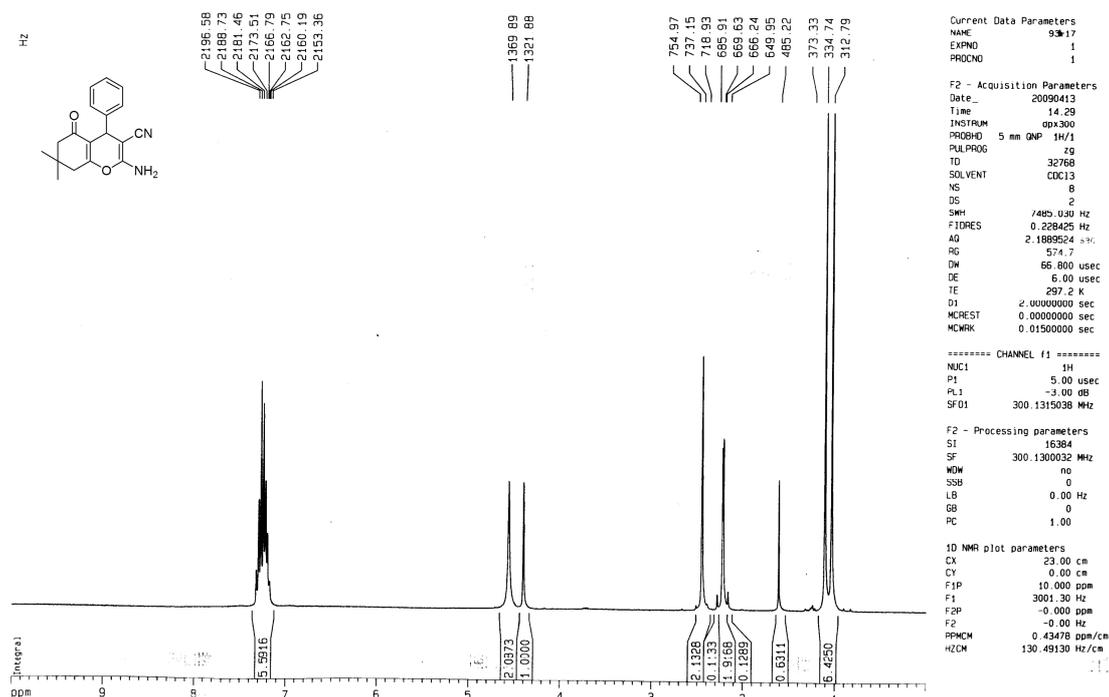


¹H NMR of 5d

1.2.3 2-Amino-3-cyano-7,7-dimethyl-4-phenyl-4H-5,6,7,8-tetrahydrobenzo[b]pyran-5-one (5f)

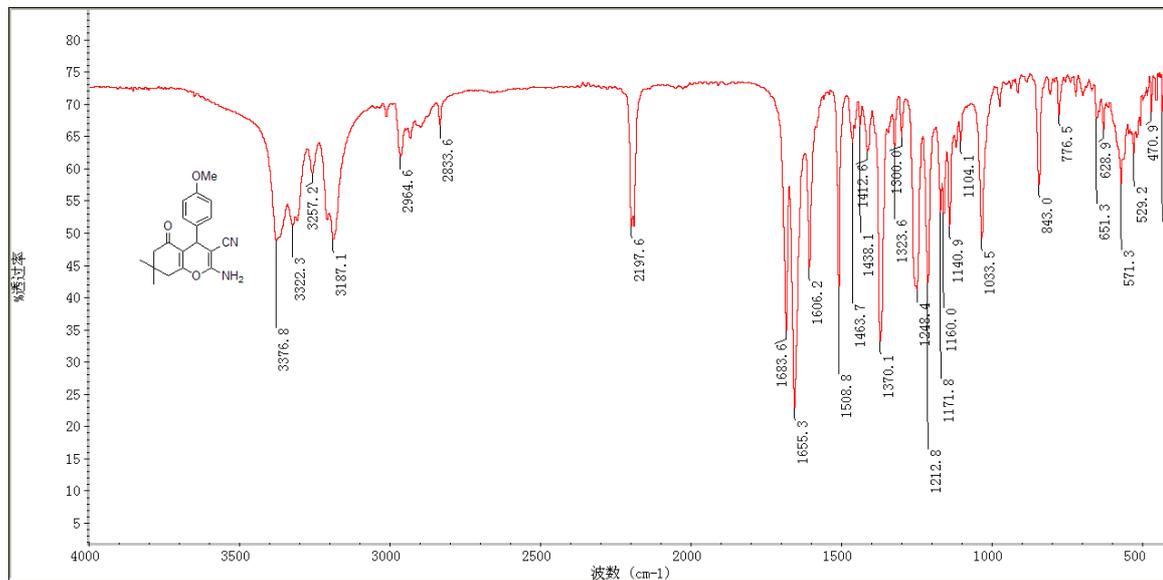


IR of 5f

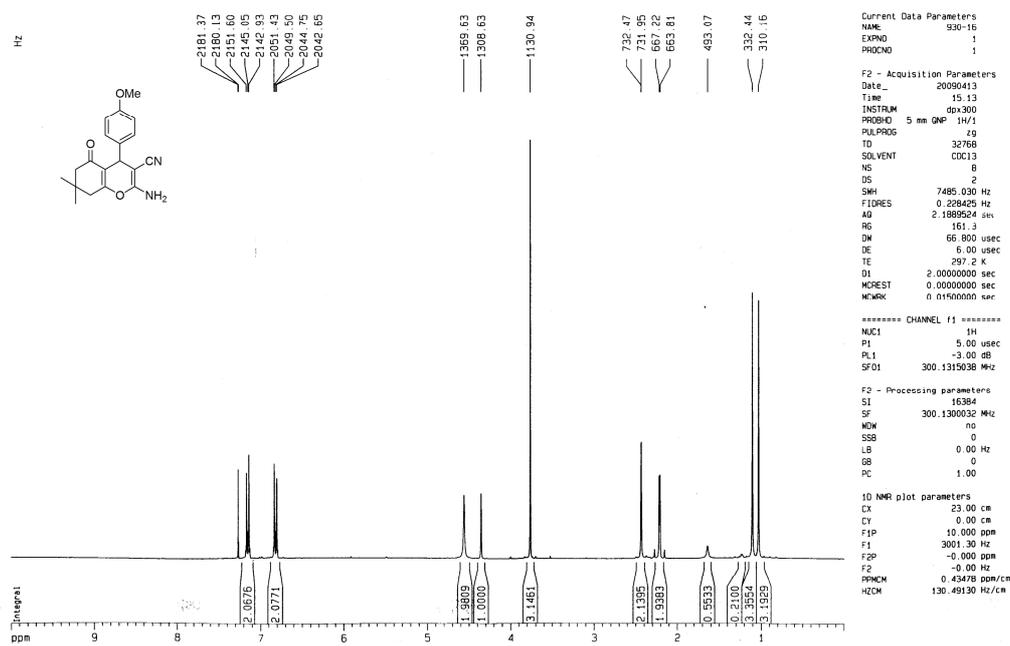


¹H NMR of 5f

1.2.4 2-Amino-3-cyano-4-(4-methoxyphenyl)-7,7-dimethyl-4H-5,6,7,8-tetrahydrobenzo[b]pyran-5-one (5h)



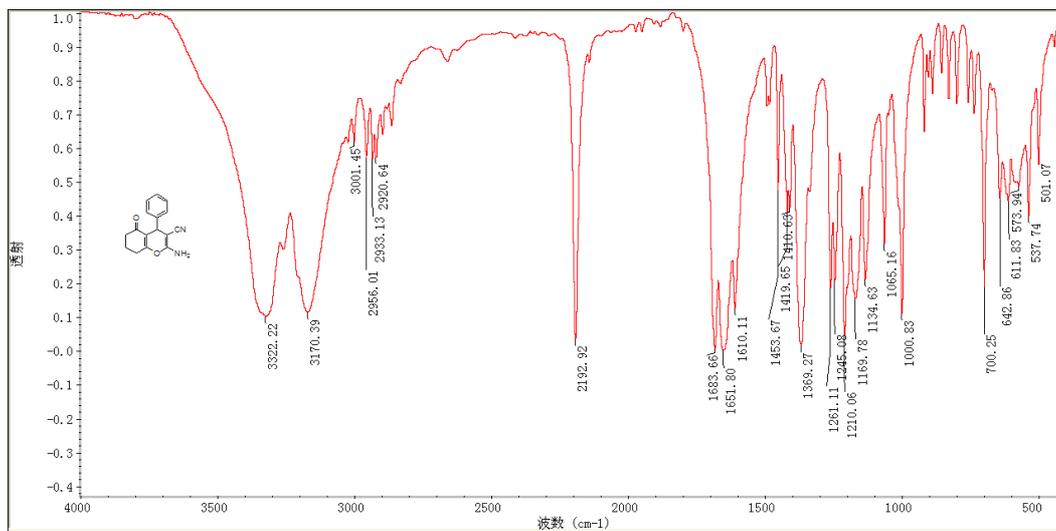
IR of 5h



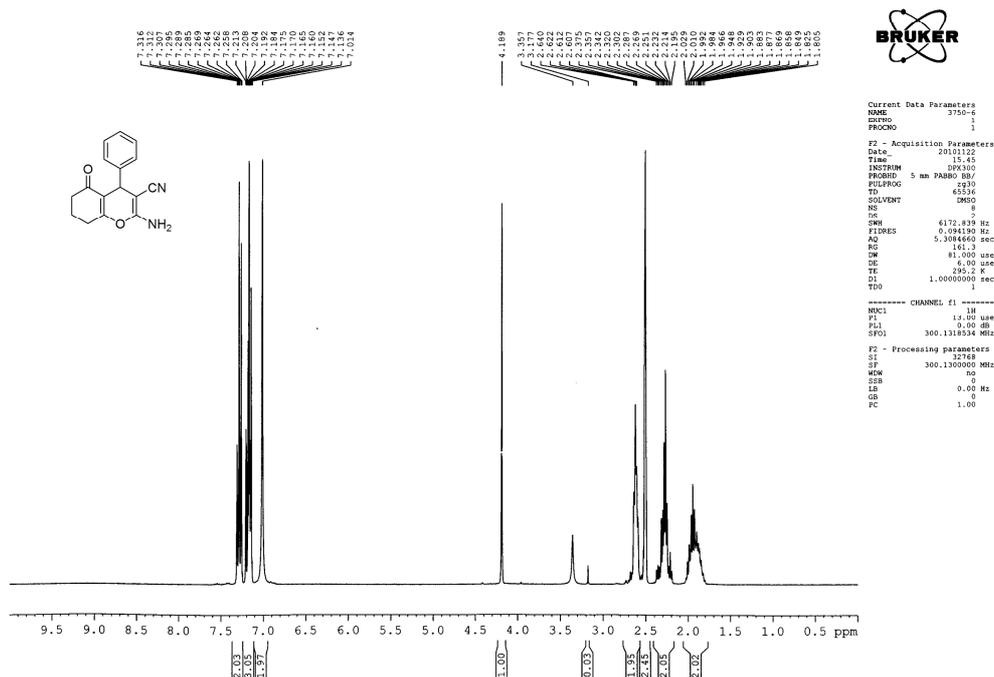
¹H NMR of 5h

1.2.5 2-Amino-3-cyano-4-phenyl-4H-5,6,7,8-tetrahydrobenzo[b]pyran-5-one

(51)



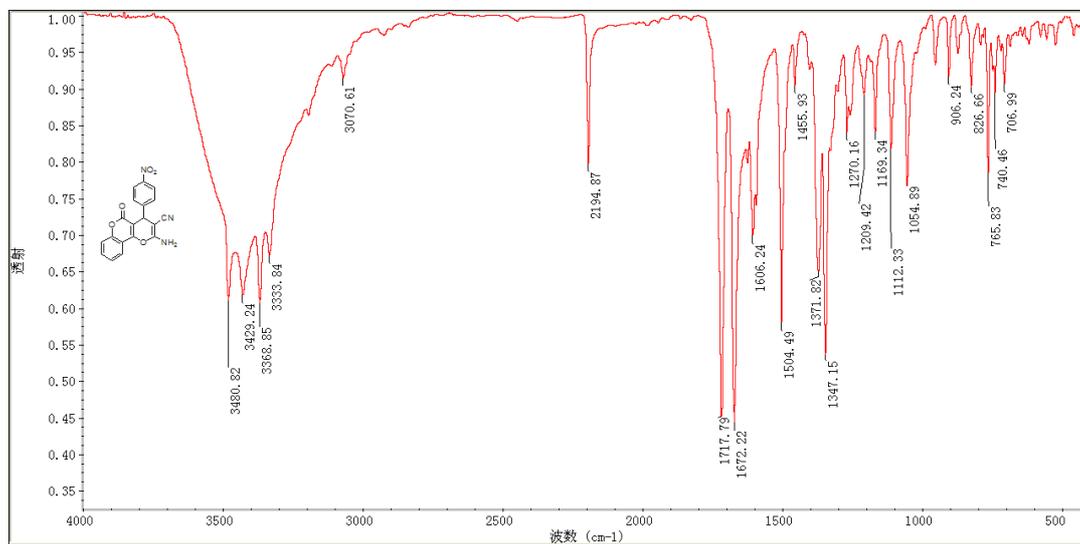
IR of 51



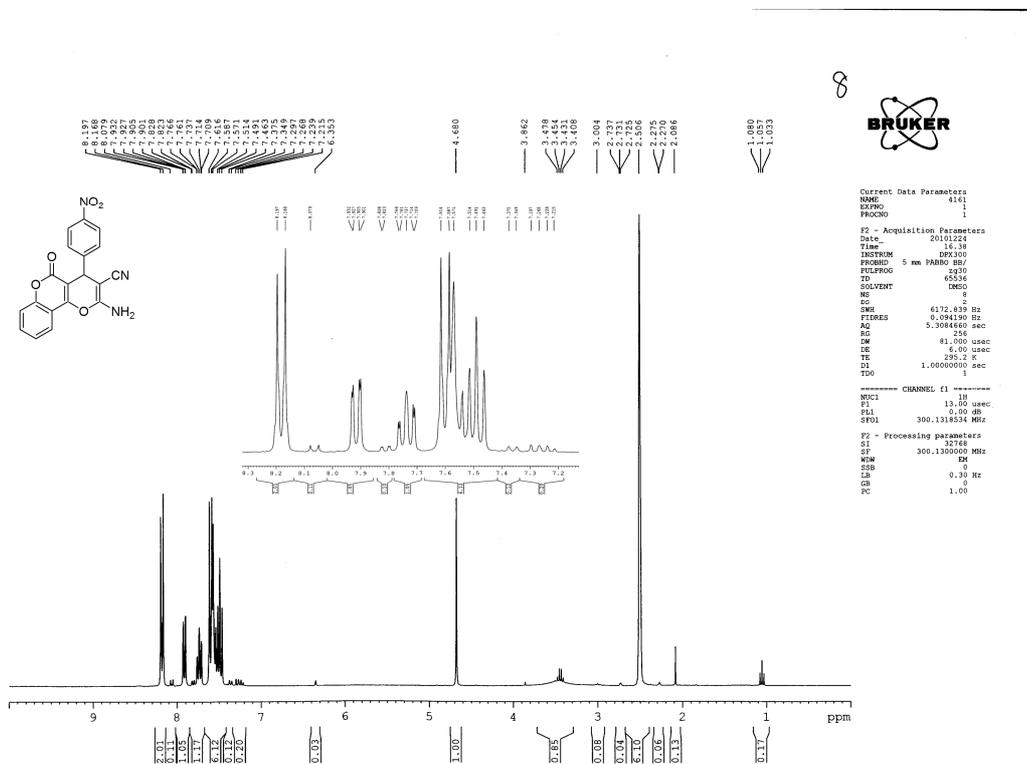
1.3 Pyrano[c]chromenes 6

1.3.1 2-Amino-3-cyano-4-(4-nitrophenyl)-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one

(6a)

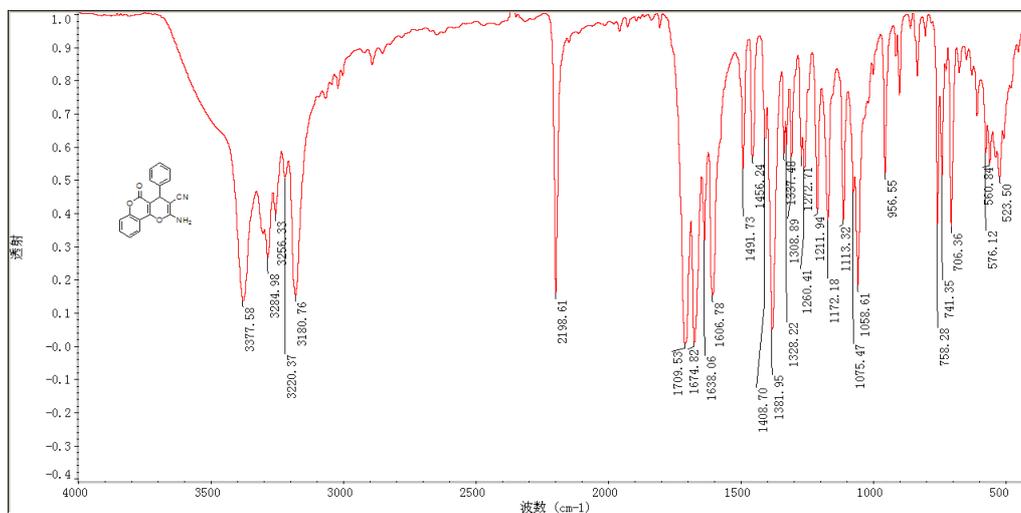


IR of 6a

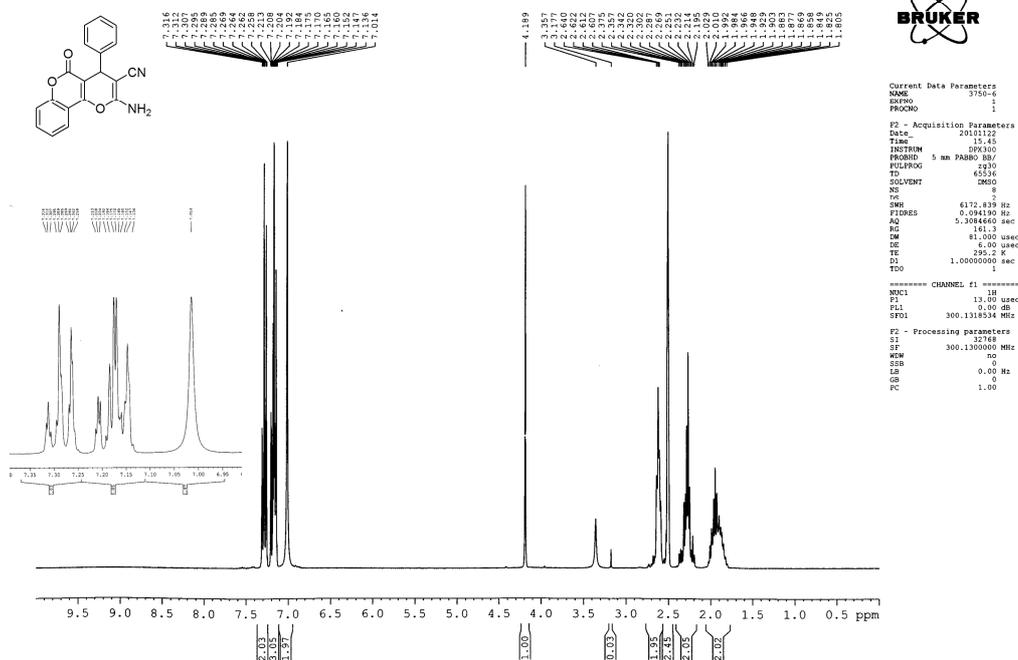


¹H NMR of 6a

1.3.2 2-Amino-3-cyano-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (6b)



IR of 6b



¹H NMR of 6b