Electronic supplementary materials *Mendeleev Commun.*, 2012, **22**, 148−149

Basic ionic liquid-catalyzed one-pot synthesis of the spiroacenaphthylene derivatives in water medium

Jia Zheng and Yiqun Li*

General Information

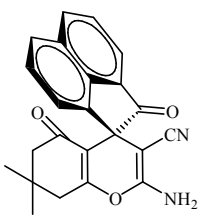
Melting points were measured on an Electrothemal X6 microscopy digital melting point apparatus. IR spectra were recorded on a Bruker Equinox-55 spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Bruker AVANCE 300 and 75 MHz instrument with TMS at δ=0.00 ppm as an internal standard. Mass spectra were performed on a AB 4000 Q TRAP (USA). Pyrazolones was prepared according to the method reported in the literature.[1] All other chemicals were of commercial grade without further purification.

General procedure for the synthesis of spiroacenaphthylene derivatives

An equimolar (1.0 mmol) mixture of acenaphthequinone **1**, malononitrile **2**, α-methylenecarbonyl compounds **3** and ionic liquid [BDDMA]Cl (15.0 mol%) in 5.0 ml water was stirred at 80 ºC for the specified time (Table 2). Upon completion (monitored by TLC), the solid was filtered off and washed with water (2×5 ml) and cold ethanol (2×2 ml) to obtain the product (TLC pure). Thus obtained substance was further purified by recrystallization from ethanol or ethanol–acetone. The catalyst contained in the filtrate can be used in the next run without further purification.

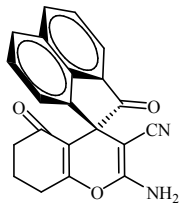
Spectral data

2'-Amino-7',7'-dimethyl-2,5'-dioxo-5',6',7',8'-tetrahydro-2*H*-spiro-(acenaphthylene-1,4'-chromene)-3'-carbonitrile 4a[2]



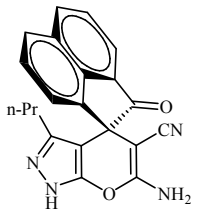
Yellow solid; mp 256−257 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.03 (3 H, s, Me), 1.04 (3 H, s, Me), 2.08 (2 H, q, J = 36.0 Hz, CH_2), 2.63 (2 H, s, CH_2), 7.34 (2 H, s, NH_2), 7.39-8.28 (6 H, m, ArH). IR (KBr): 3369, 3293, 3245, 3182, 2954, 2193, 1717, 1665, 1600, 1347 cm^{-1}.

2'-Amino-2,5'-dioxo-5',6',7',8'-tetrahydro-2*H*-spiro(acenaphthylene-1,4'-chromene)-3'-carbonitrile 4b[2]



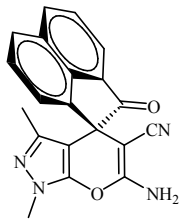
Yellow solid; mp 242−244 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.94 (2 H, q, J = 18.3 Hz, -CH$_2$CH$_2$-), 2.16 (3 H, m, -CH$_2$ CH$_2$CH$_2$-), 2.72 (2 H, t, J = 11.7 Hz, -CH$_2$CH$_2$-), 7.32 (2 H, s, NH$_2$), 7.40-8.27 (6 H, m, ArH). IR (KBr): 3373, 3314, 3242, 3199, 2194, 1717, 1668, 1599, 1348 cm^{-1}.

3'-Amino-7'-*n*-propyl-2-oxo-2*H*,5*H*'-spiro(acenaphthylene-1,1'-pyrano[2,3-*c*]-pyrazole)-2'-carbonite 4e



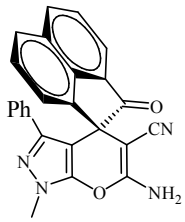
Yellow solid; mp 234−236 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 0.11 (3 H, t, J = 14.7 Hz, -CH$_2$Me), 0.66 (2 H, m, -CH$_2$CH$_2$Me), 1.33 (2 H, m, -CH$_2$CH$_2$Me), 7.32 (2 H, s, NH$_2$), 7.45-8.40 (6 H, m, ArH), 12.28 (1 H, s, NH). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 12.9, 21.1, 25.9, 51.7, 55.8, 96.0, 118.9, 121.3, 122.4, 124.9, 129.0, 129.4, 130.0, 130.7, 132.6, 139.1, 140.9, 141.5, 155.0, 162.4, 204.2. IR (KBr): 3420, 3298, 3157, 2200, 1708, 1641, 1594, 1487, 1404 cm^{-1}. MS, m/z (%): 479 (M$^+$, 100), 457 (57), 301 (28).

3'-Amino-5'- methyl -7'-methyl-2-oxo-2*H*,5*H*'-spiro(acenaphthylene-1,1'-pyrano[2,3-*c*]pyrazole)-2'-carbonite 4f



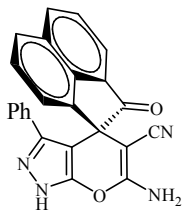
Yellow solid; mp 201−203 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 0.95 (3 H, s, Me), 3.66 (3 H, s, Me), 7.54 (2 H, s, NH$_2$), 7.46-8.41 (6 H, m, ArH). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 11.7, 33.6, 52.2, 56.8, 94.8, 118.3, 121.4, 122.5, 129.0, 129.4, 129.9, 130.5, 132.7, 140.8, 141.0, 141.2, 145.1, 161.2, 203.7. IR (KBr): 3387, 3302, 3214, 2194, 1722, 1644, 1599, 1560, 1392, 1361 cm^{-1}. MS, m/z (%): 365 (M$^+$, 100), 343 (85), 301 (40),253 (20), 113 (25).

3'-Amino-5'-methyl-7'-phenyl -2-oxo-2*H*,5*H*'-spiro(acenaphthylene-1,1'-pyrano[2,3-*c*]pyrazole)-2'-carbonite 4g



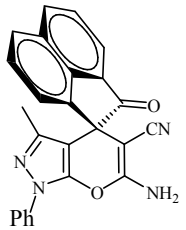
Yellow solid; mp 183−186 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 3.82 (3 H, s, Me), 7.56 (2 H, s, NH$_2$), 6.36-8.31 (11 H, m, ArH). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 34.1, 52.4, 57.8, 94.5, 118.1, 121.3, 122.3, 125.0, 126.8, 127.1, 127.4, 128.7, 129.2, 130.0, 131.0, 132.0, 132.4, 141.2, 142.0, 135.4, 145.9, 160.4, 203.8. IR (KBr): 3398, 3309, 2194, 1718, 1644, 1613, 1551, 1391 cm^{-1}. MS, m/z (%): 427 (M$^+$, 100), 405 (80), 301 (15), 175 (35).

3'-Amino-7'-phenyl -2-oxo-2*H*,5*H*'-spiro(acenaphthylene-1,1'- pyrano-[2,3-*c*]pyrazole)-2'-carbonite 4h



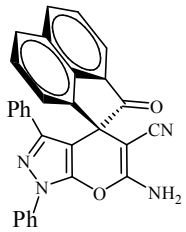
Yellow solid; mp 264−266 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 7.22 (2 H, s, NH$_2$), 6.35-8.27 (11 H, m, ArH), 12.76 (1 H, s, NH). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 51.7, 56.6, 96.7, 118.7, 121.1, 122.3, 124.8, 127.1, 127.4, 127.8, 128.4, 128.7, 129.2, 129.9, 130.9, 132.3, 139.0, 141.1, 142.2, 155.7, 161.9, 204.1. IR (KBr): 3445, 3297, 3166, 2192, 1715, 1632, 1586, 1496, 1405 cm^{-1}. MS, m/z (%): 413 (M$^+$, 100), 391 (60), 301 (20),139 (85), 113 (30).

3'-Amino-5'-phenyl-7'-methyl-2-oxo-2*H*,5*H*'-spiro(acenaphthylene-1,1'-pyrano[2,3-*c*]pyrazole)-2'-carbonite 4i



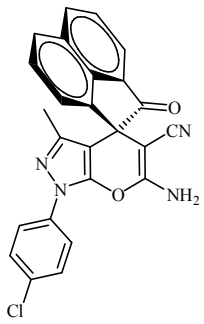
Yellow solid; mp 159−161 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.07 (3 H, s, Me), 7.69 (2 H, s, NH$_2$), 7.34-8.45 (11 H, m, ArH). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 11.9, 52.0, 56.8, 97.1, 118.0, 120.1, 121.8, 122.8, 125.3, 126.6, 129.1, 129.4, 130.0, 130.4, 132.9, 137.1, 140.4, 141.1, 143.8, 144.9, 161.0, 203.5. IR (KBr): 3354, 3297, 3187, 2200, 1716, 1645, 1599, 1521, 1493, 1382 cm^{-1}. MS, m/z (%): 427 (M$^+$, 100), 405 (70), 301 (10), 253 (10), 175 (35).

3'-Amino-5'-phenyl-7'-phenyl -2-oxo-2*H*,5*H*'-spiro(acenaphthylene-1,1'-pyrano[2,3-*c*]pyrazole)-2'-carbonite 4j



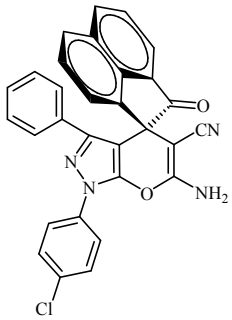
Yellow solid; mp 215−217 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 6.44-8.32 (18 H, m, ArH and NH$_2$). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 52.2, 57.7, 96.8, 117.9, 120.9, 121.6, 122.5, 125.1, 127.1, 127.2, 145.5, 147.6, 160.4, 203.6. IR (KBr): 3465, 3315, 2194, 1704, 1651, 1593, 1519, 1456, 1390 cm^{-1}. MS, m/z (%): 489 (M$^+$, 100), 467 (50), 301 (25), 253 (25), 237 (65), 139 (55), 113 (35).

3'-Amino-5'-(4-chlorophenyl)-7'-methyl-2-oxo-2*H*,5*H*'-spiro(acenaphthylene-1,1'-pyrano[2,3-*c*]pyrazole)-2'-carbonite 4k[3]



Yellow solid; mp 172−174 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.07 (3 H, s, Me), 7.71 (2 H, s, NH$_2$), 7.56-8.45 (10 H, m, ArH). IR (KBr): 3460, 3310, 2191, 1708, 1651, 1581, 1515, 1490, 1386 cm^{-1}.

3'-Amino-5'-(4-chlorophenyl)-7'-phenyl -2-oxo-2*H*,5*H*'-spiro(acenaphthylene-1,1'-pyrano[2,3-*c*]pyrazole)-2'-carbonite 4l



Yellow solid; mp 194−196 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.45-8.32 (17 H, m, ArH and NH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 52.2, 57.7, 97.1, 117.9, 121.6, 122.3, 122.6, 125.2, 127.1, 127.2, 128.0, 128.8, 129.2, 129.4, 130.0, 130.9, 131.2, 131.3, 132.5, 135.9, 141.2, 141.5, 145.6, 147.9, 160.3, 203.4. IR (KBr): 3393, 3320, 3197, 2201, 1712, 1654, 1614, 1517, 1482, 1395cm^{-1}. MS, m/z (%): 523 (M^+, 100), 501 (26), 379 (24), 301 (53), 271 (76), 253 (40).

References

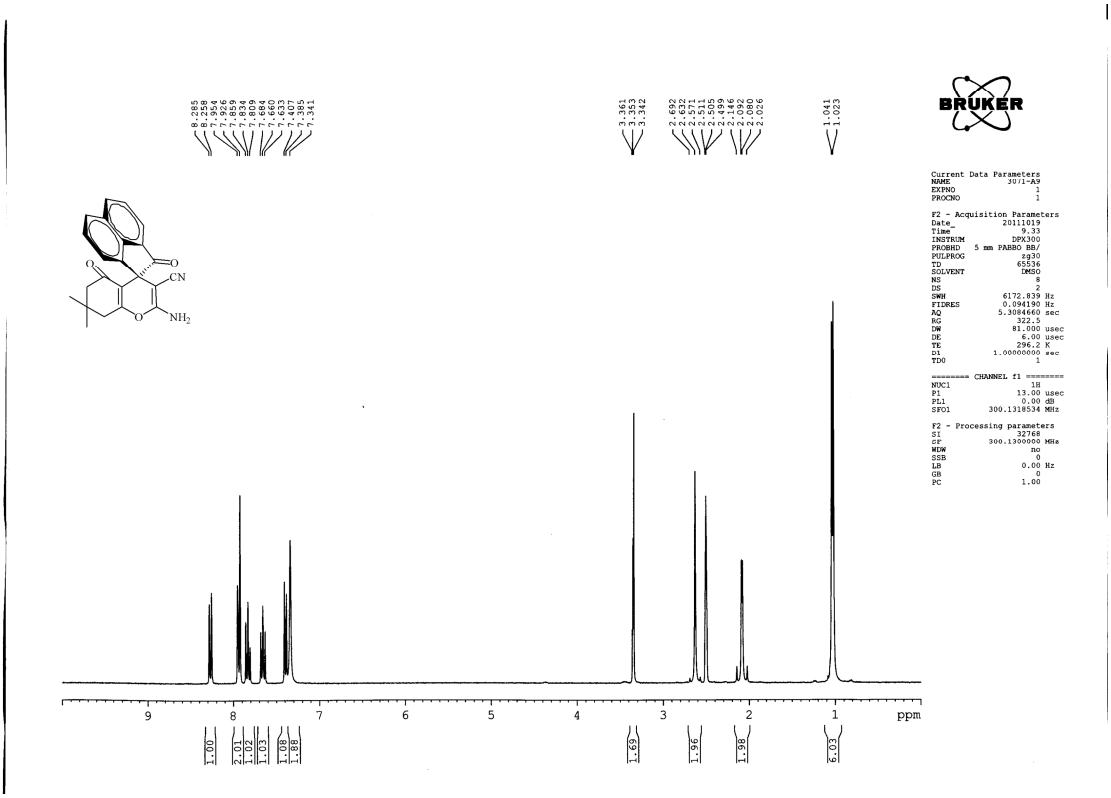
1. (*a*) F. Lehmann, M. Holm and S. Laufer, *J. Comb. Chem*., 2008, **10**, 364; (*b*) Y. Y. Huang, H. C. Lin, K. M. Cheng, W. N. Su, K. C. Sung, T. P. Li, J. J. Huang, S. K. Lin and F. F. Wong, *Tetrahedron*, 2009, **65**, 9592; (*c*) R. Ramajayam, K. P. Tan, H. G. Liu and P. H. Liang, *Bioorg. Med. Chem*., 2010, **18**, 7849.

2. M. Dabiri, M. Bahramnejad and M. Baghbanzadeh, *Tetrahedron*, 2009, **65**, 9443.

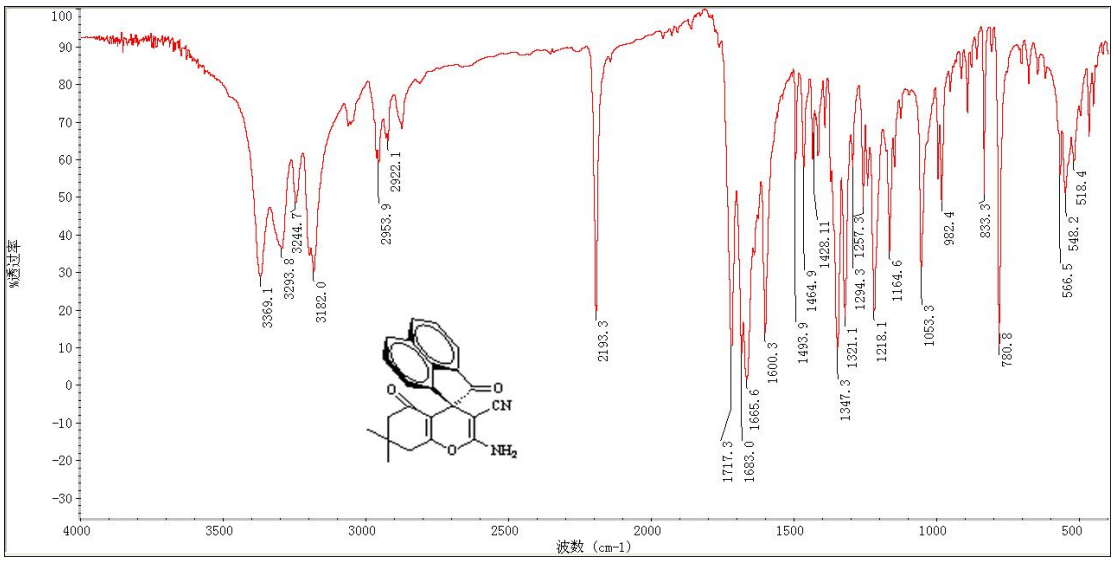
3. M. Saeedi, M. M. Heravi, Y. S. Beheshtiha and H. A. Oskooie, *Tetrahedron*, 2010, **66**, 5345.

Spectra (^{1}H NMR, ^{13}C NMR, IR, MS) of compounds

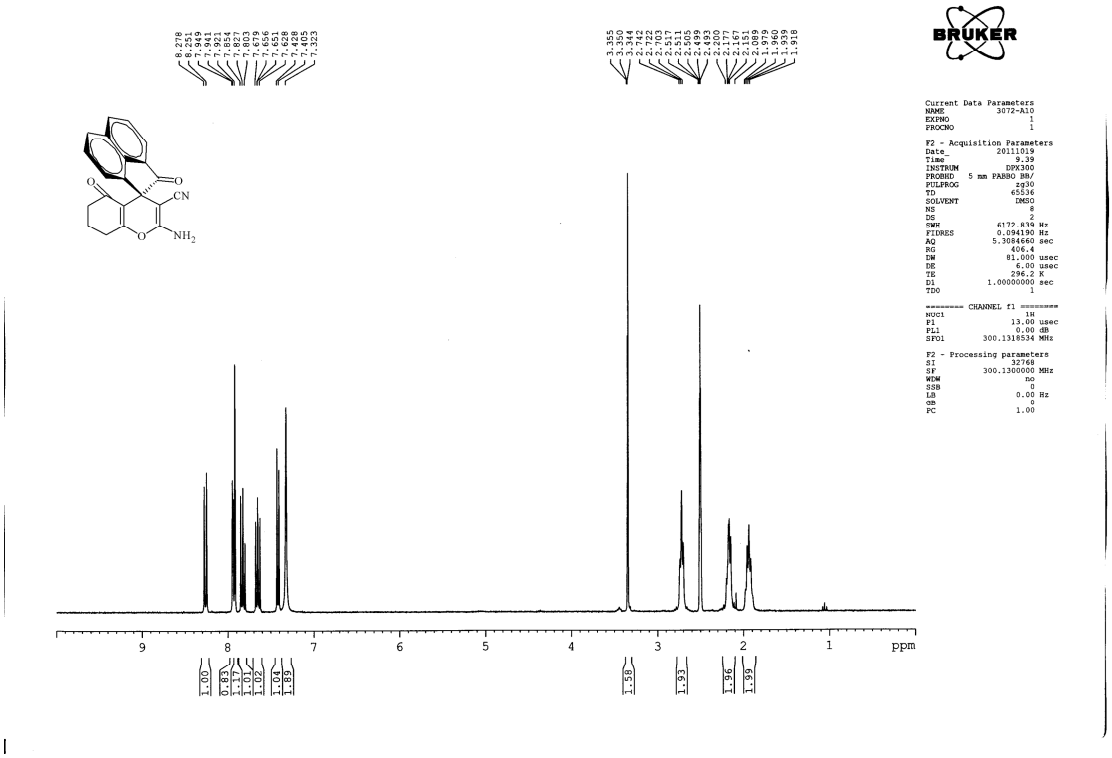
^{1}H NMR of **4a**



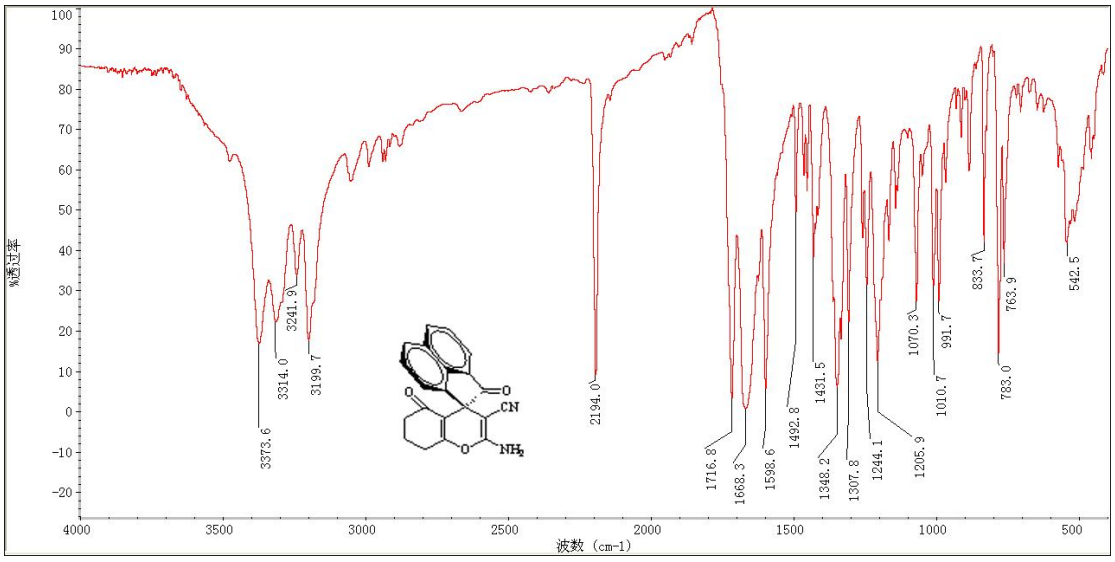
IR of **4a**



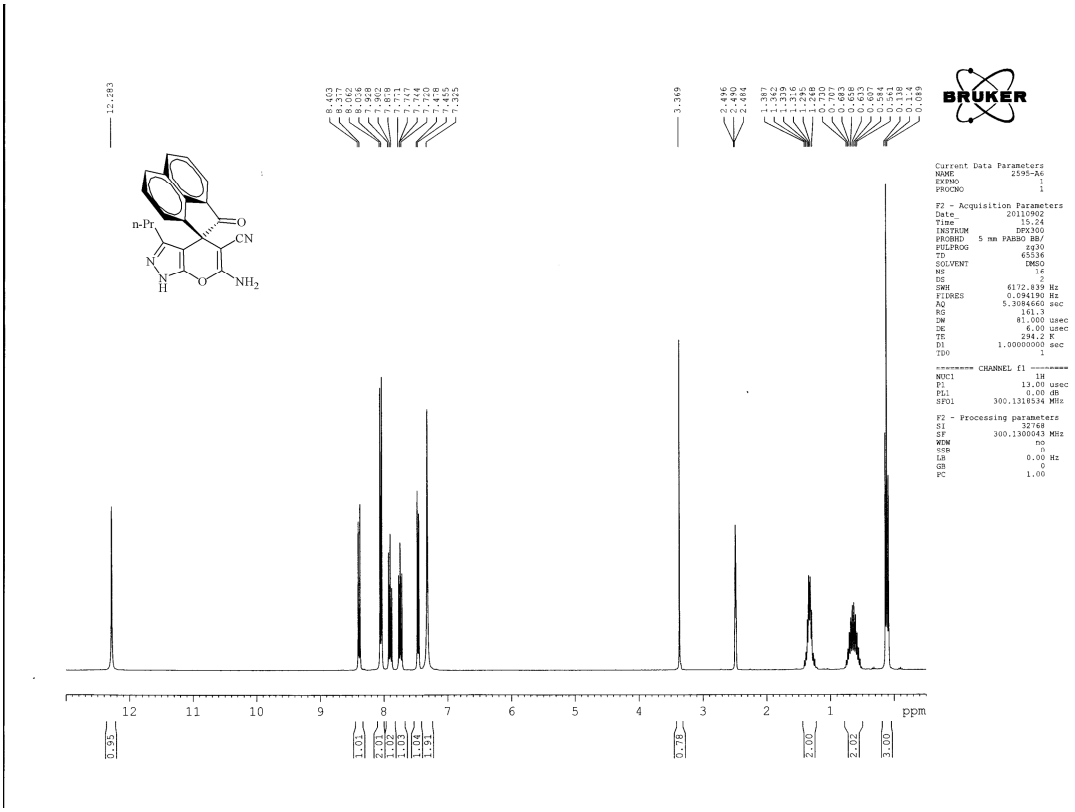
^{1}H NMR of **4b**



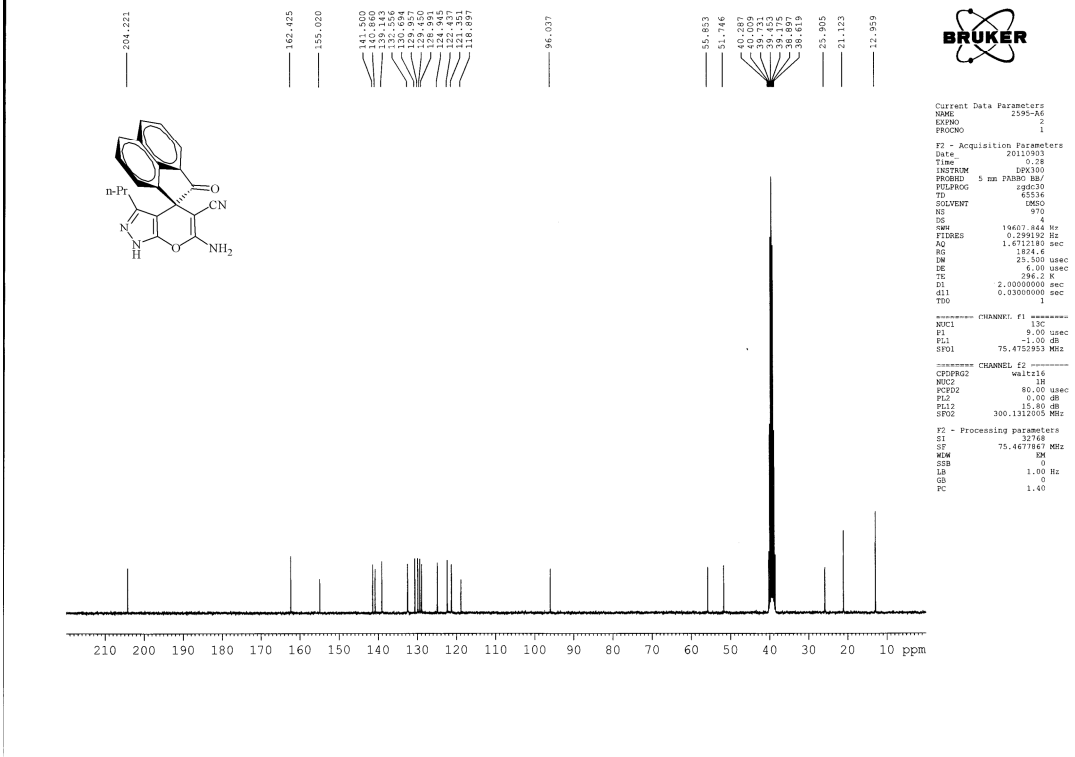
IR of **4b**



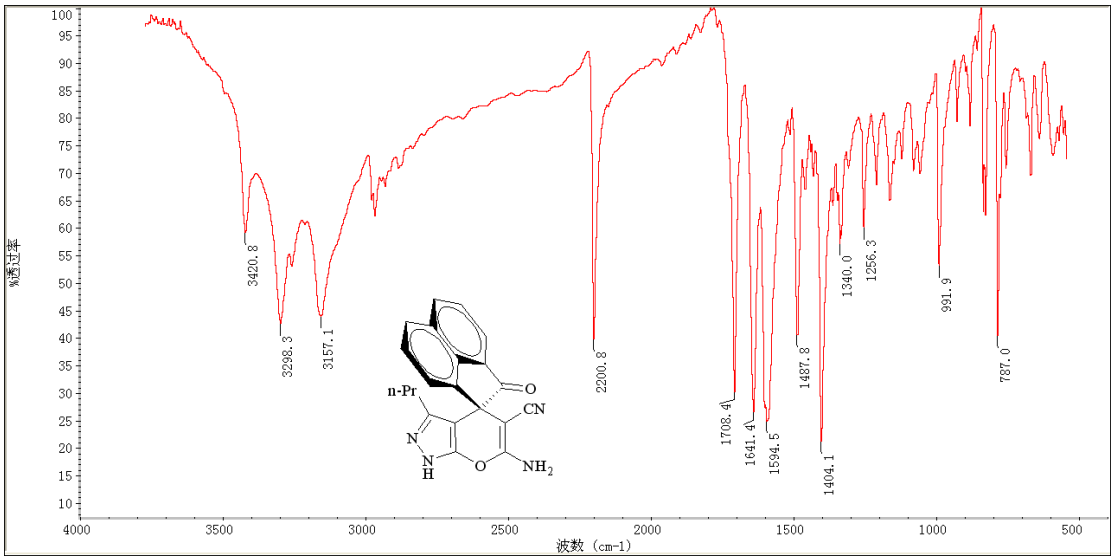
^{1}H NMR of **4e**



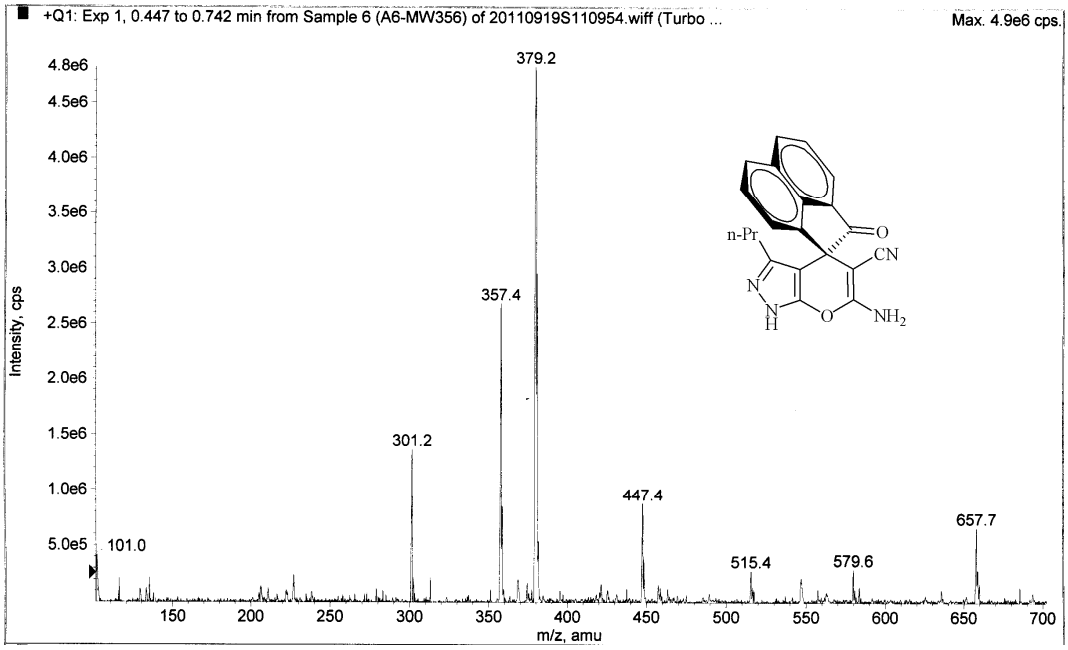
^{13}C NMR of **4e**



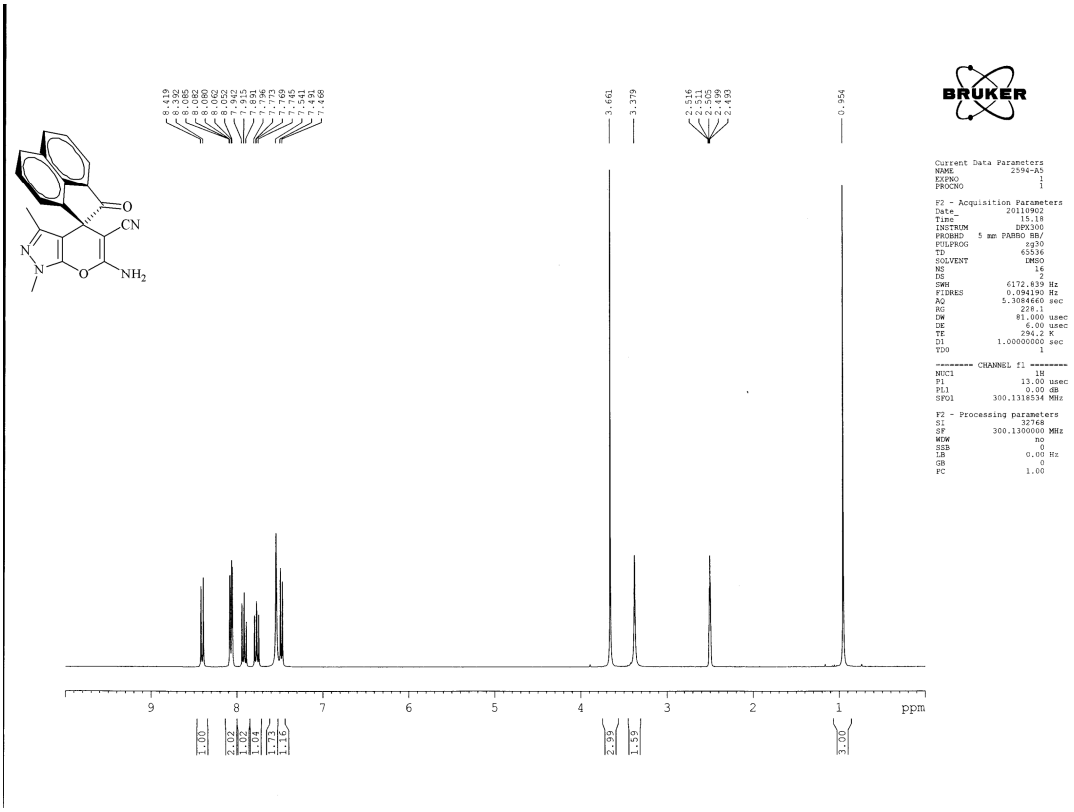
IR of **4e**



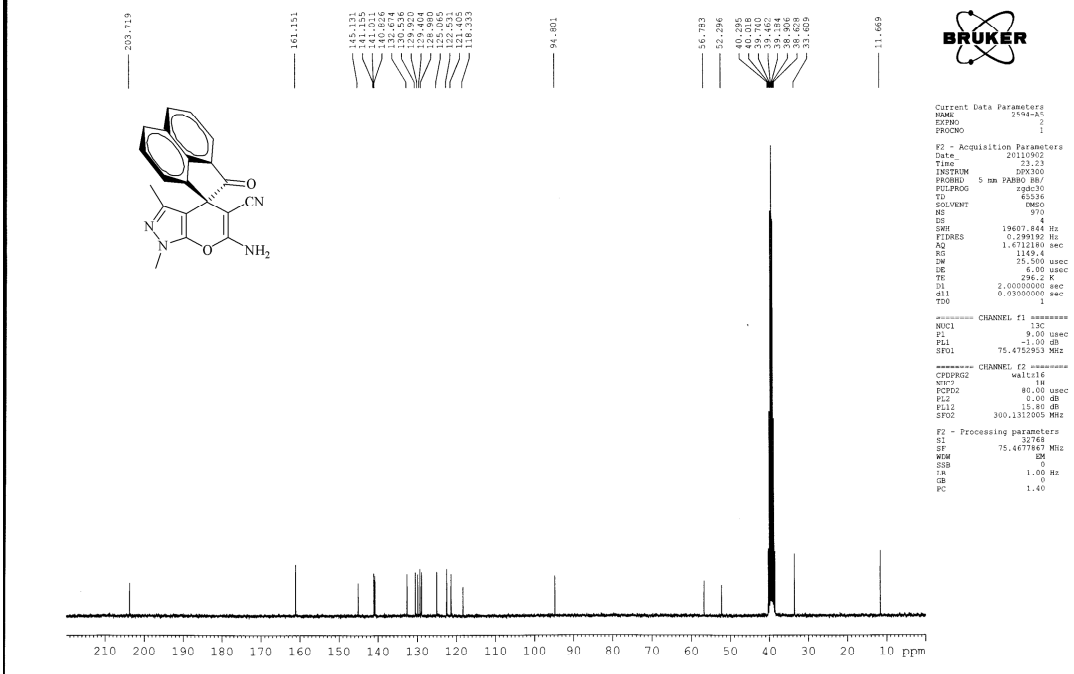
MS of **4e**



^{1}H NMR of **4f**



^{13}C NMR of **4f**



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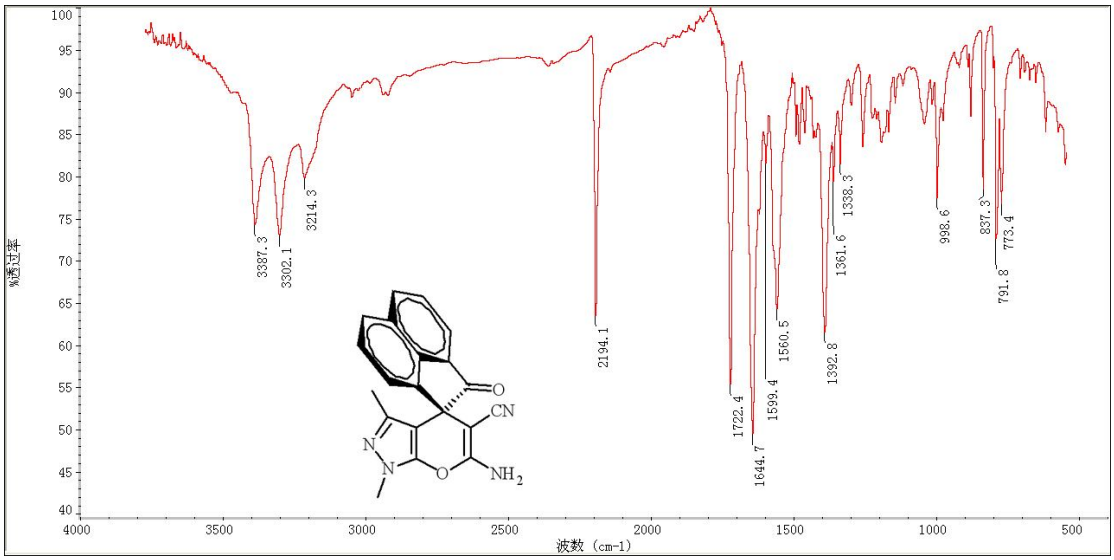
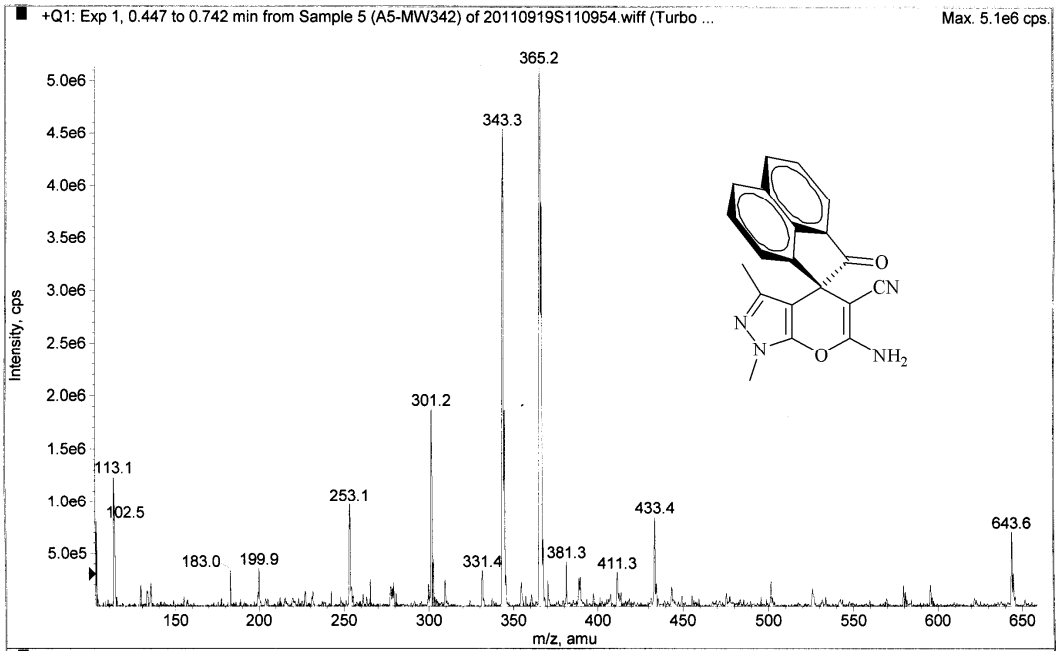
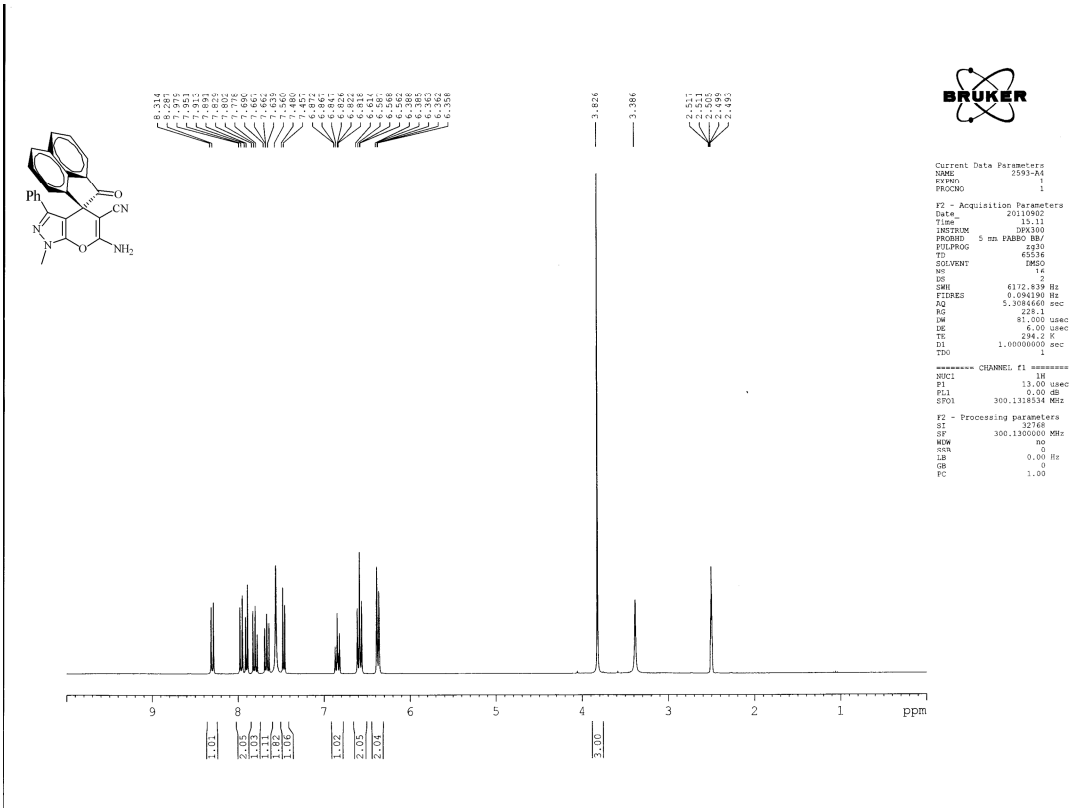


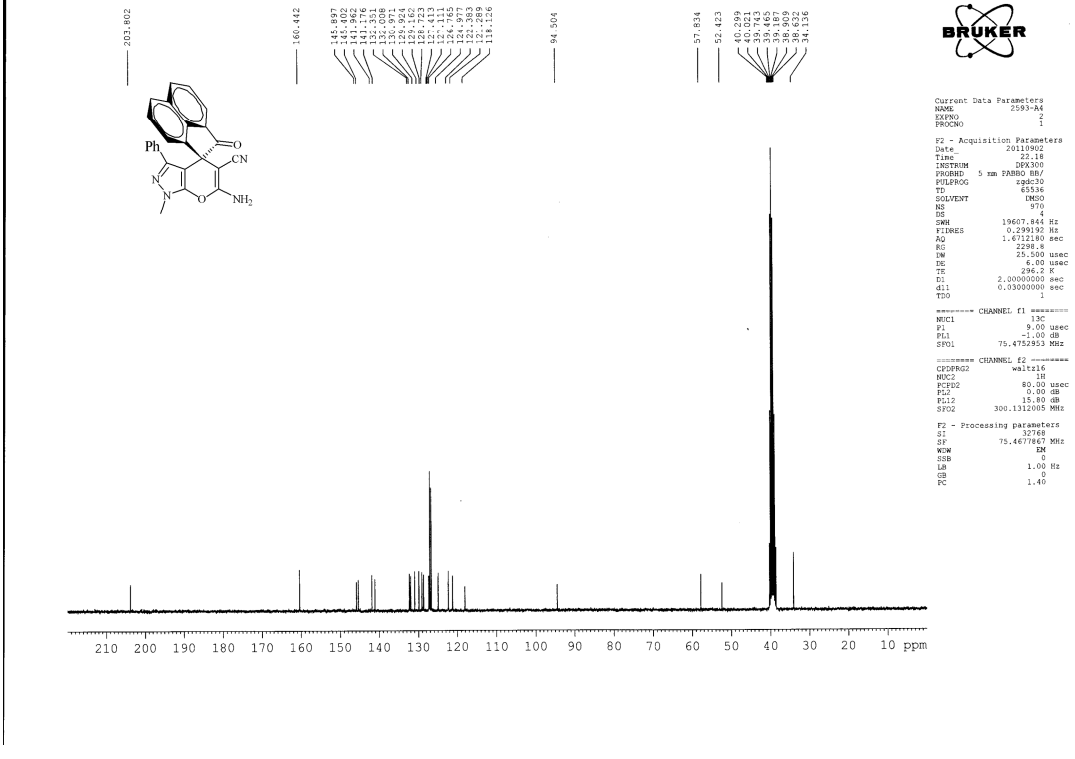
MS of **4f**



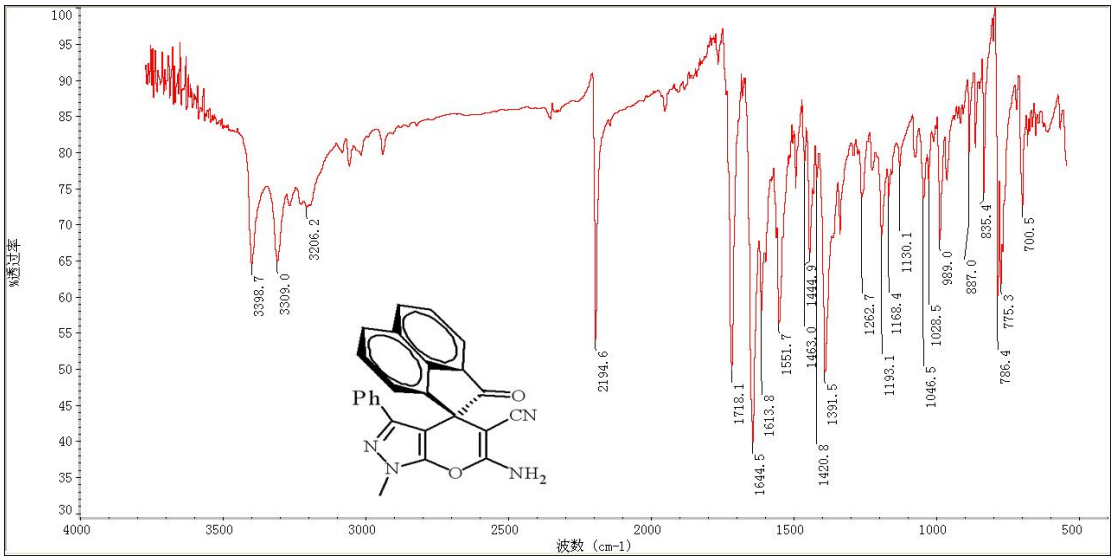
^{1}H NMR of **4g**



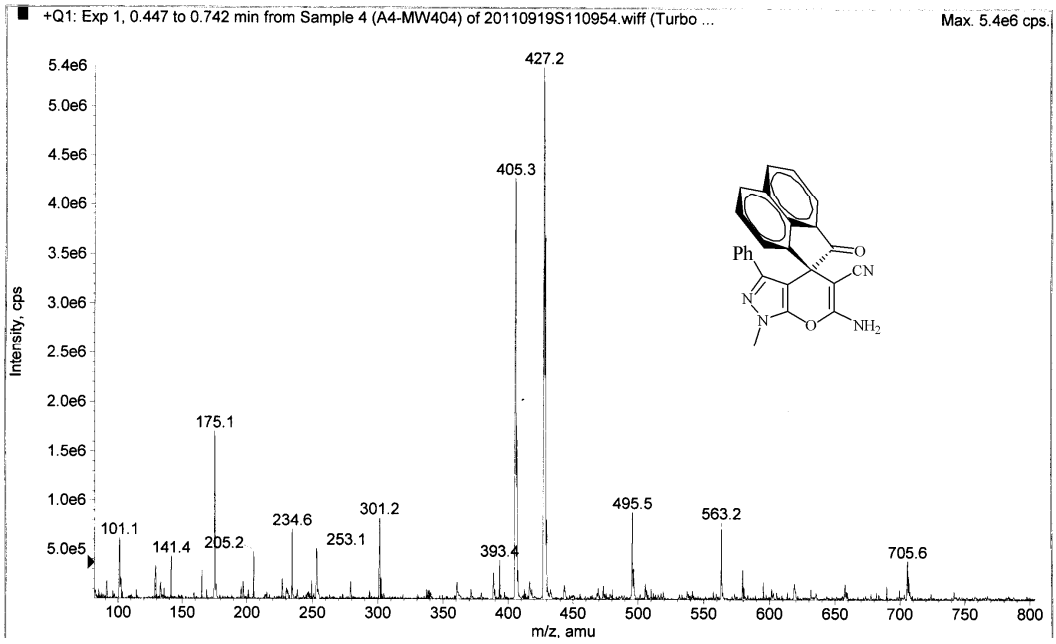
^{13}C NMR of **4g**



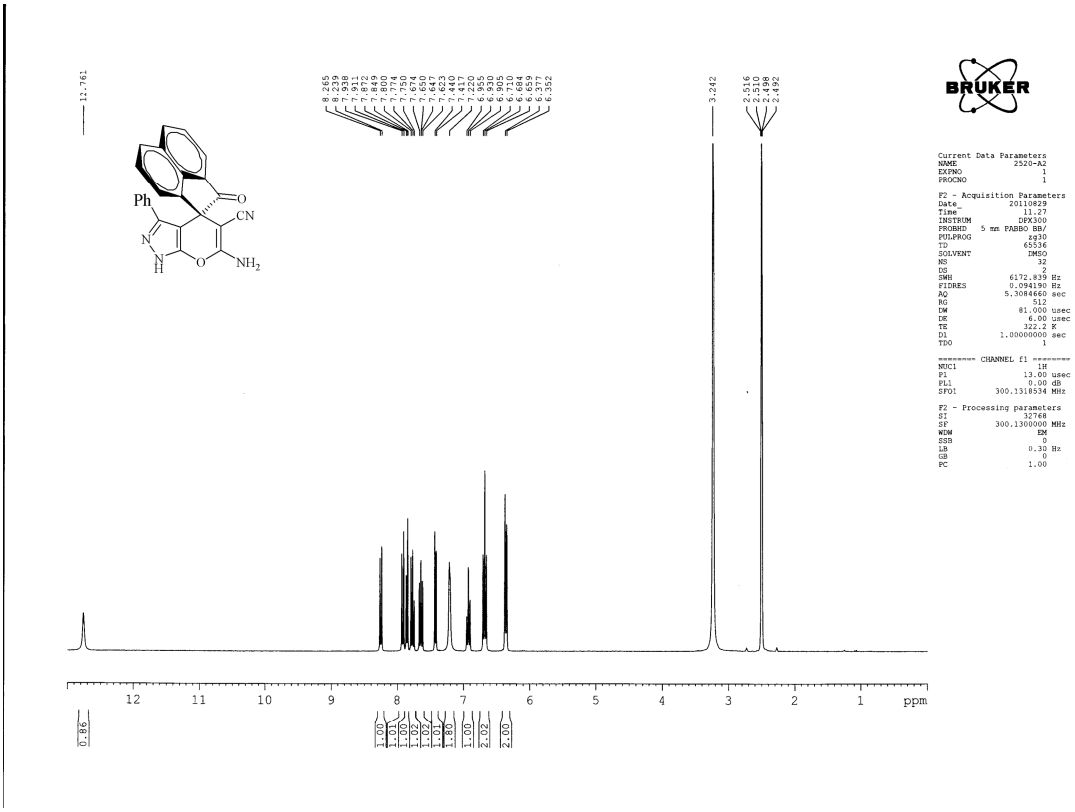
IR of **4g**



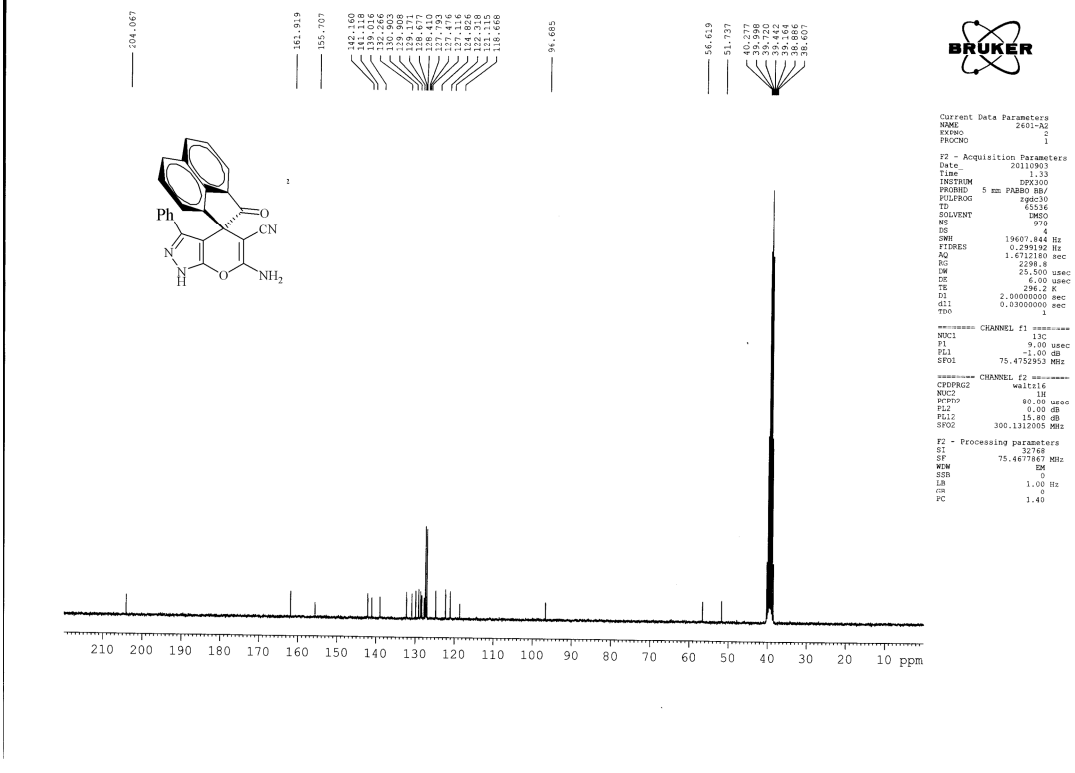
MS of **4g**



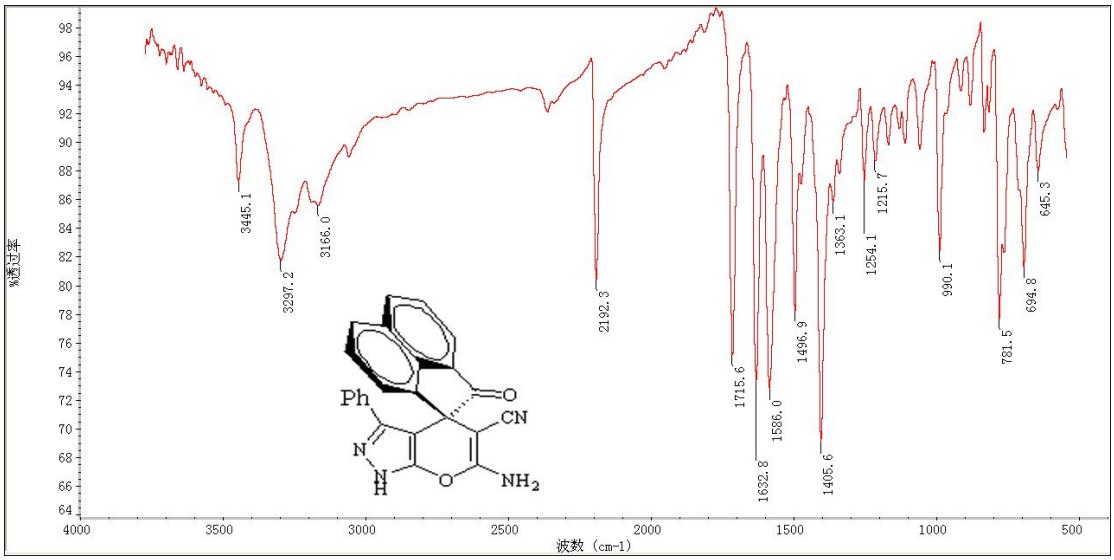
^{1}H NMR of **4h**



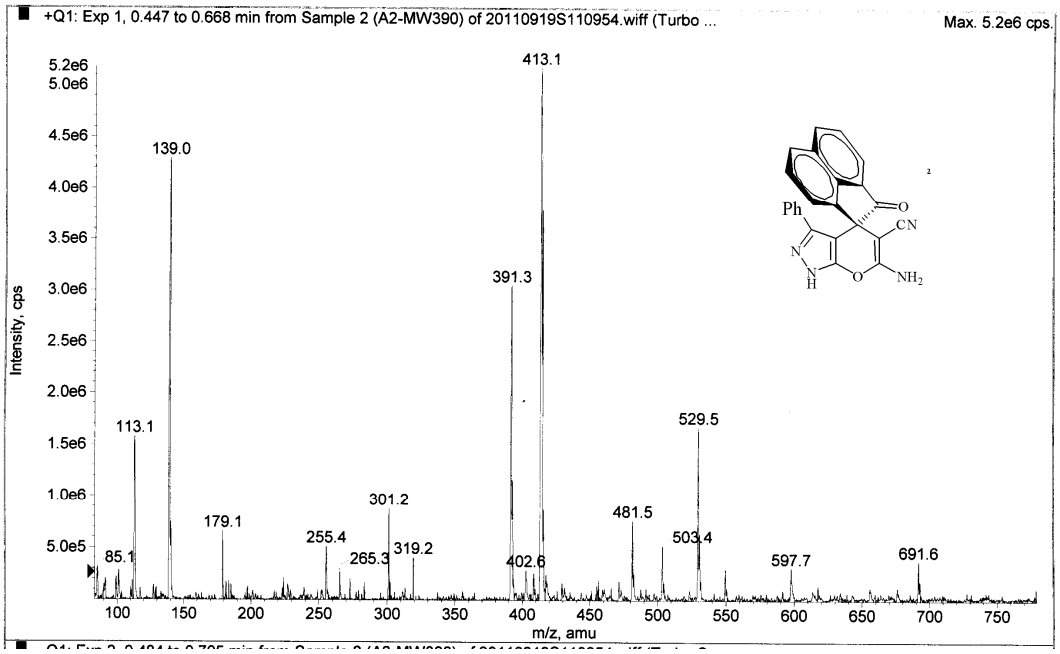
^{13}C NMR of **4h**



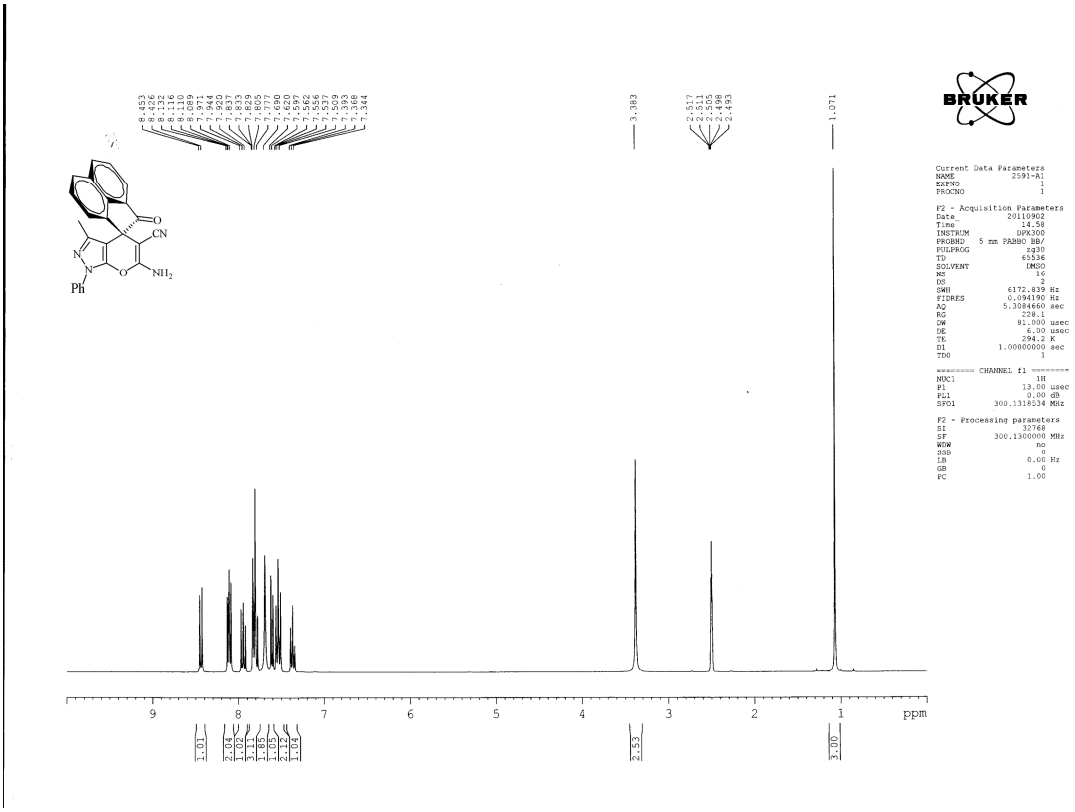
IR of **4h**



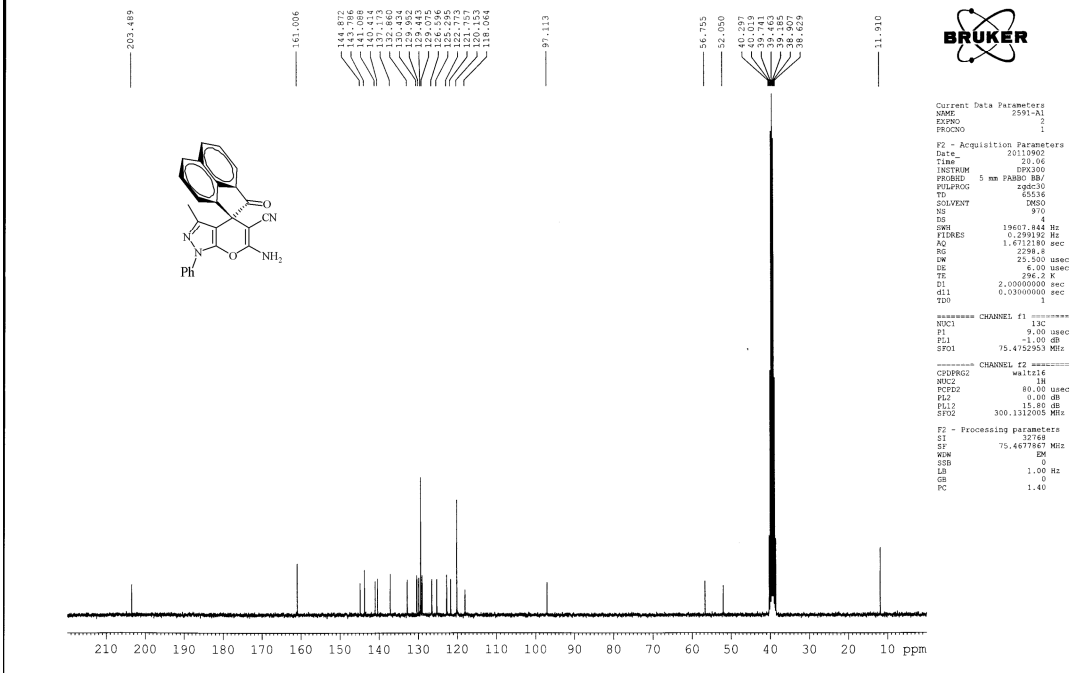
MS of **4h**



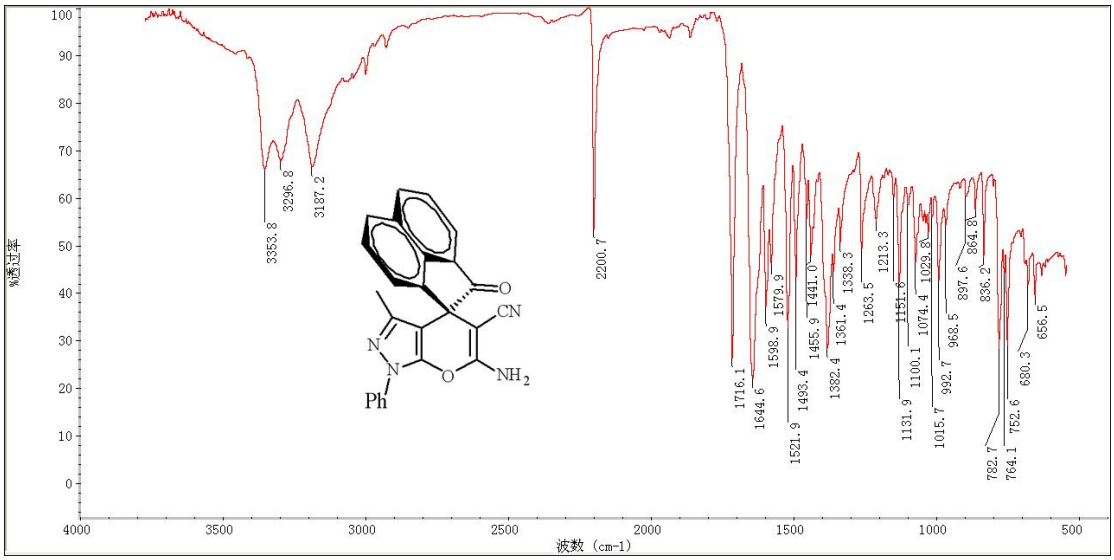
^{1}H NMR of **4i**



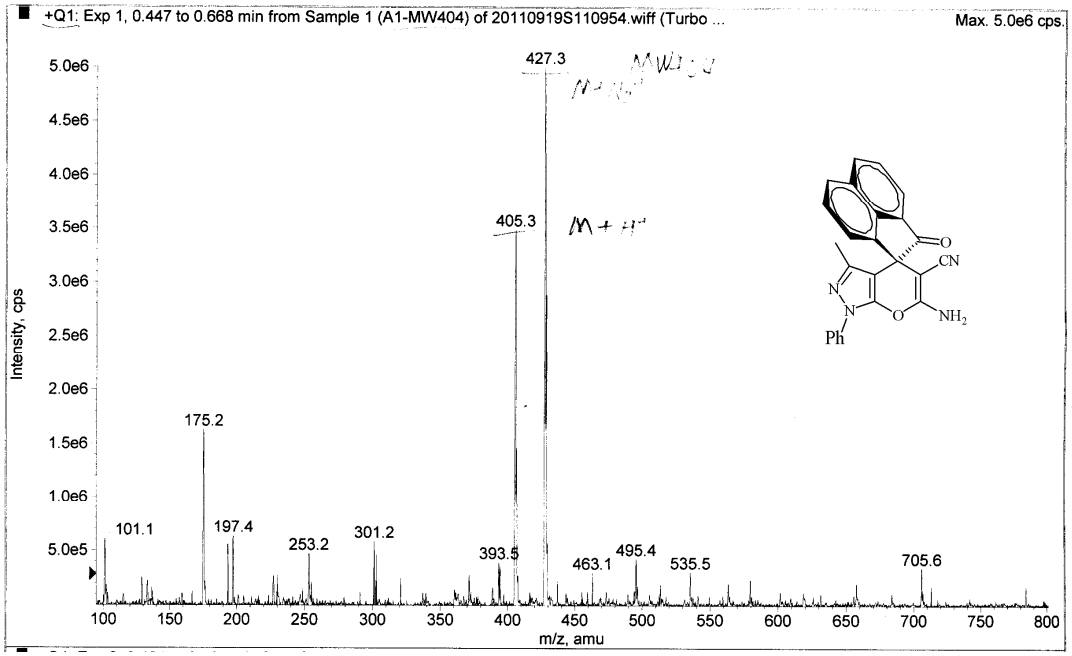
^{13}C NMR of **4i**



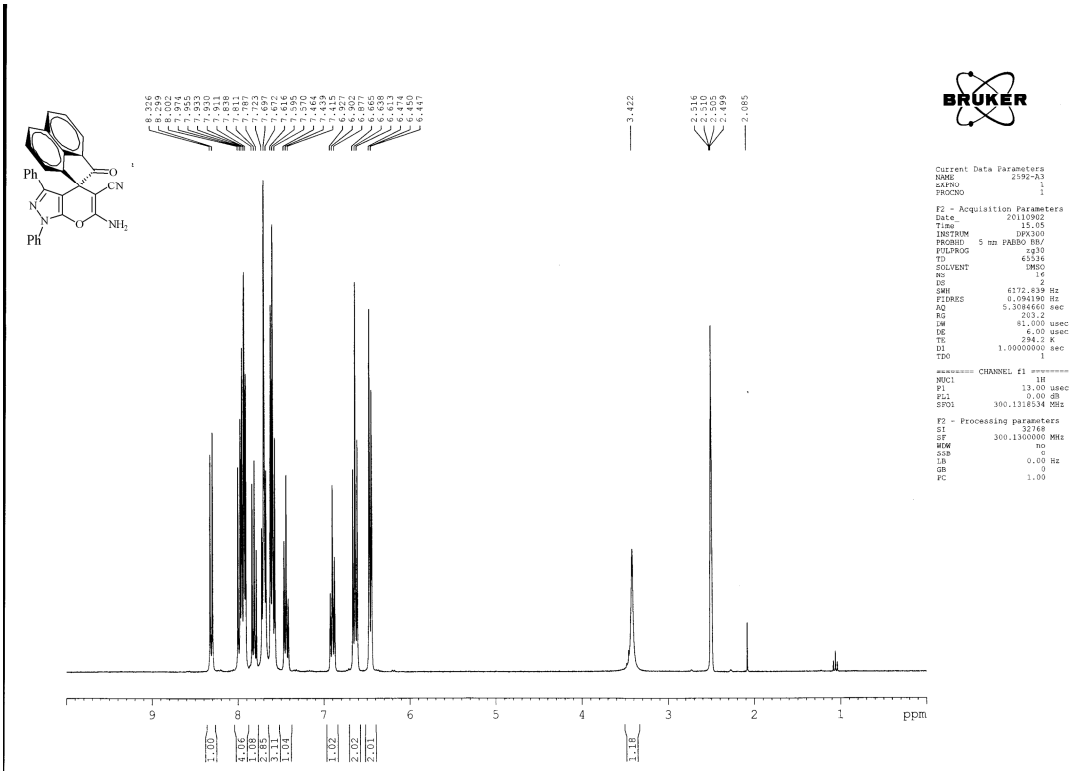
IR of **4i**



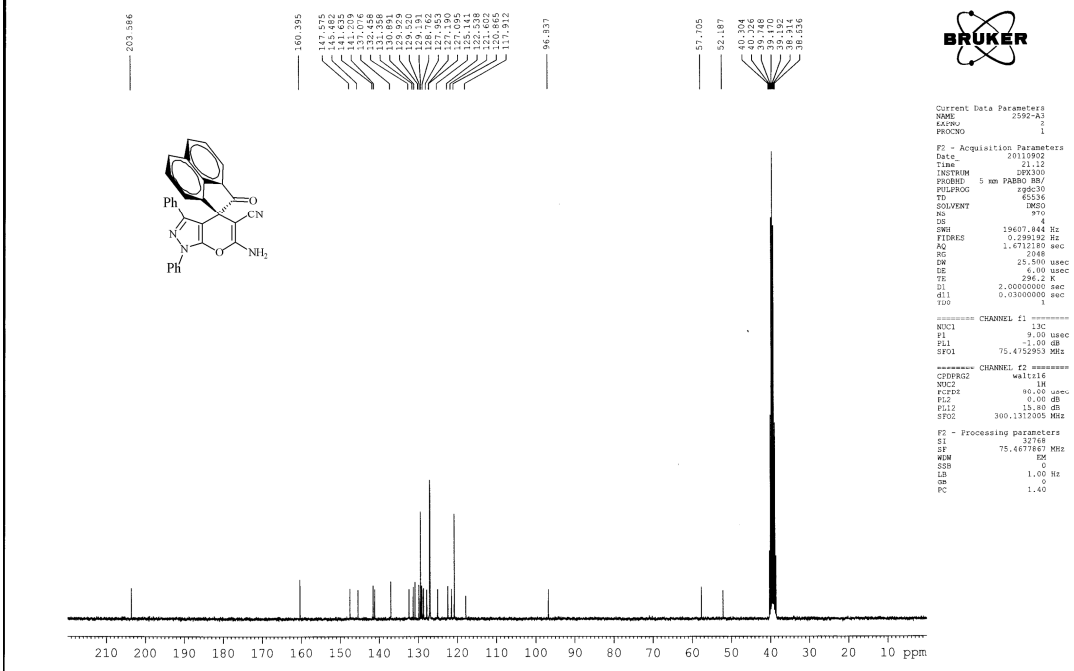
MS of **4i**



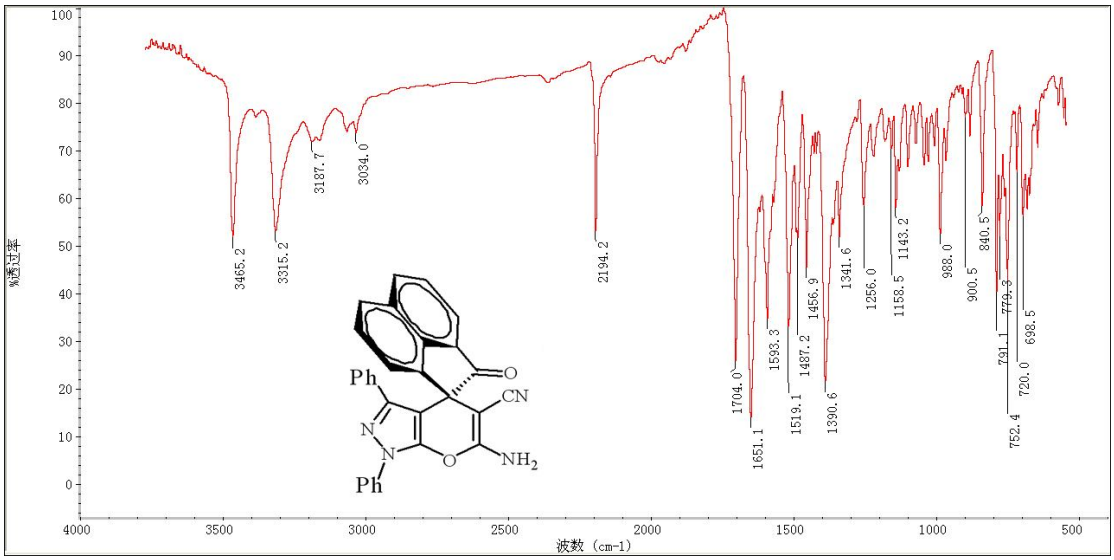
^{1}H NMR of **4j**



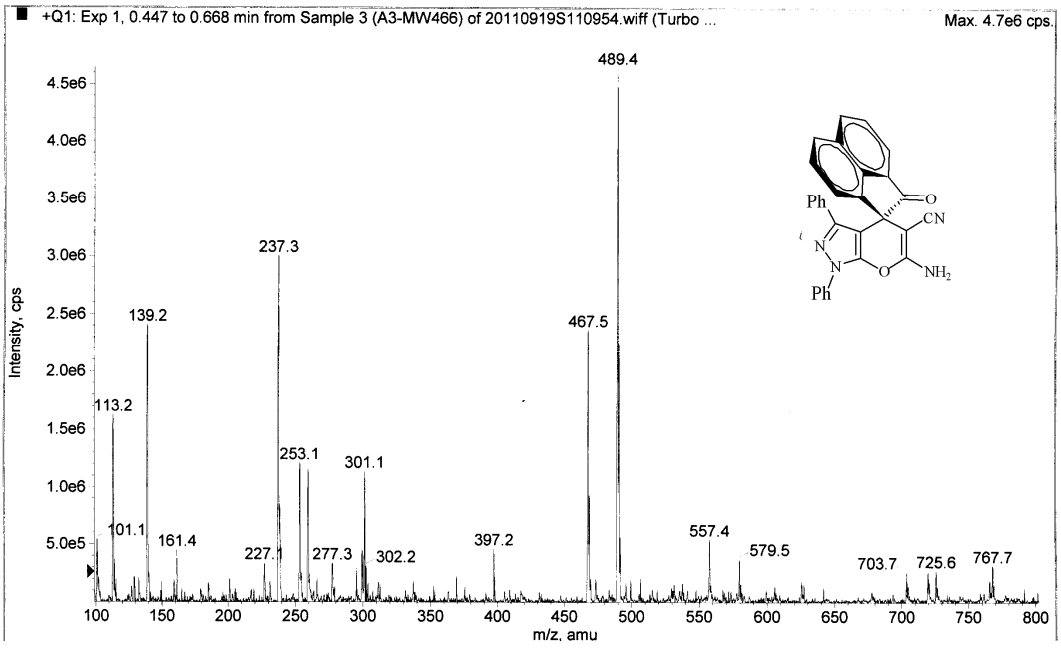
^{13}C NMR of **4j**



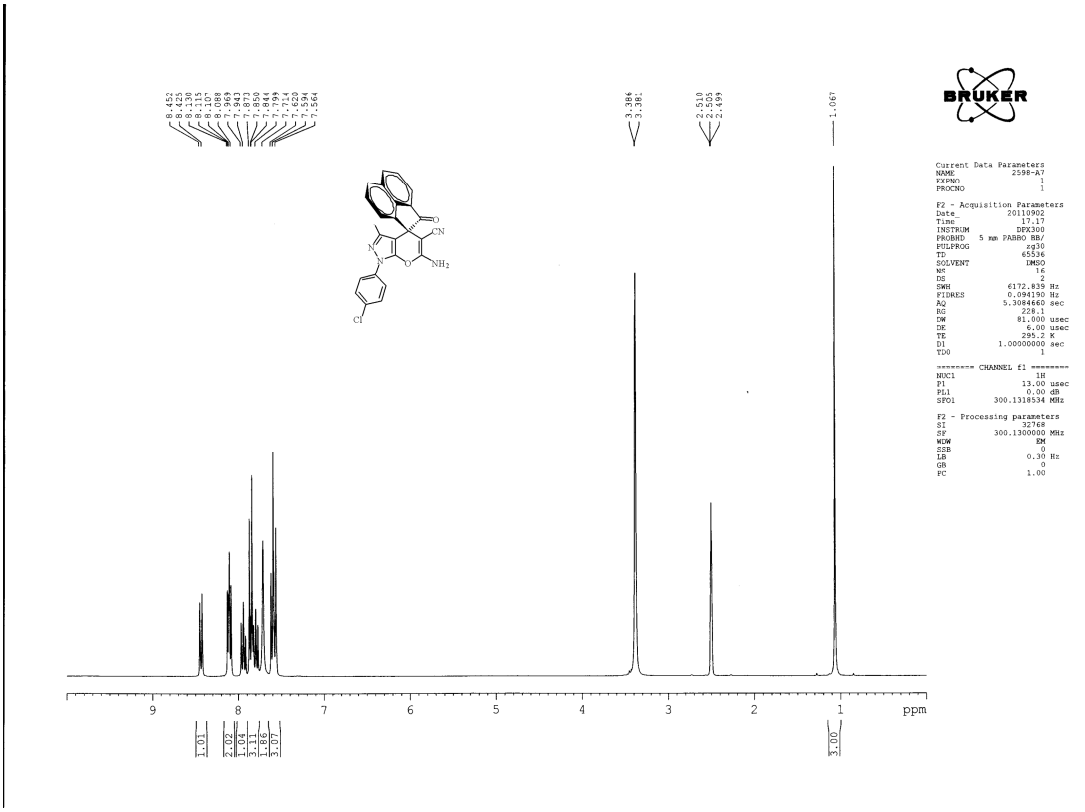
IR of **4j**



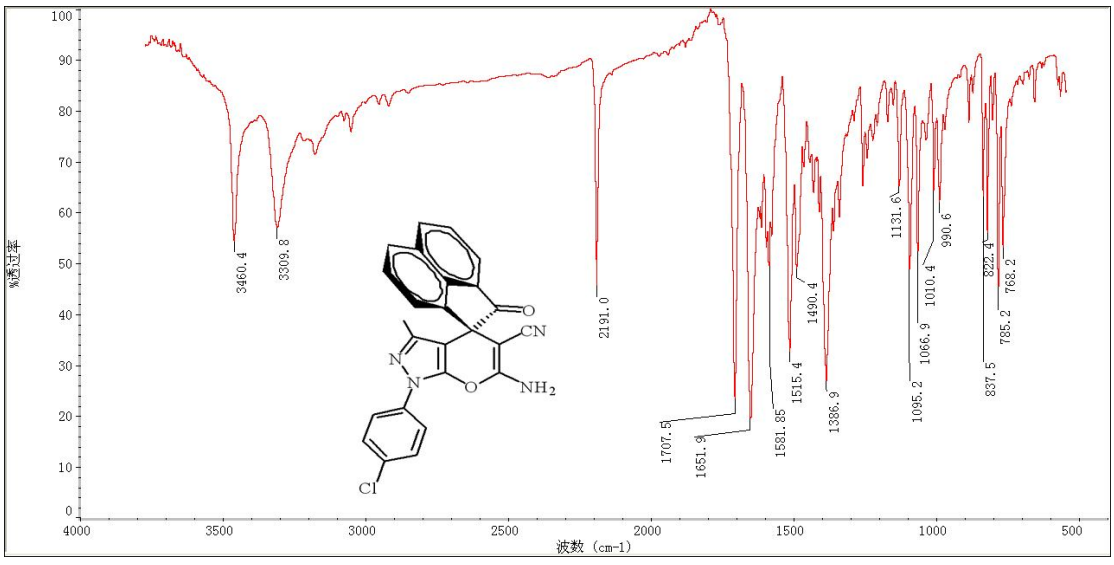
MS of **4j**



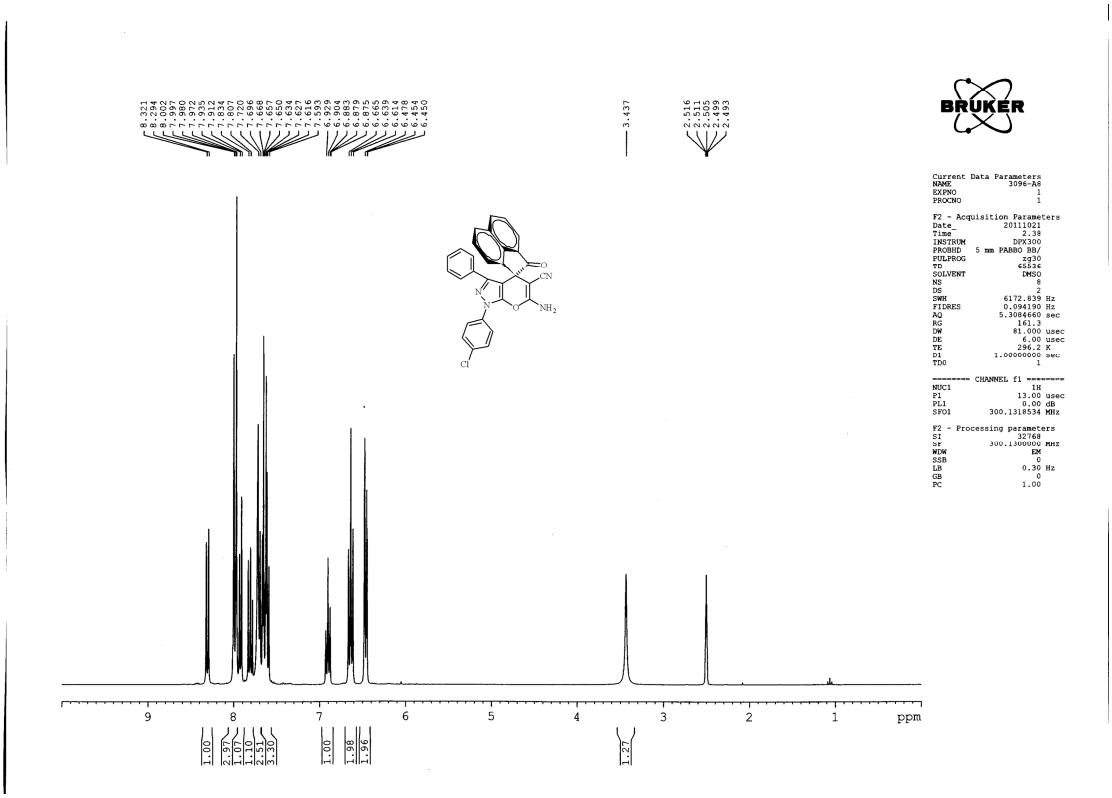
^{1}H NMR of **4k**



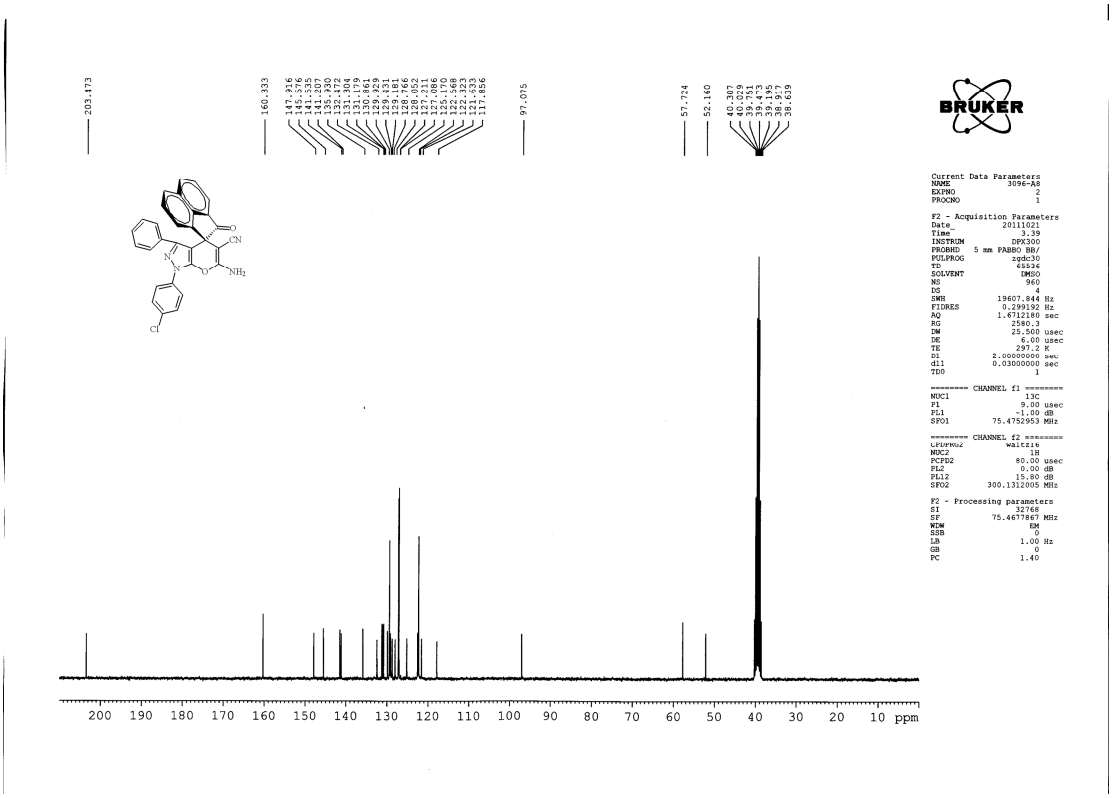
IR of **4k**



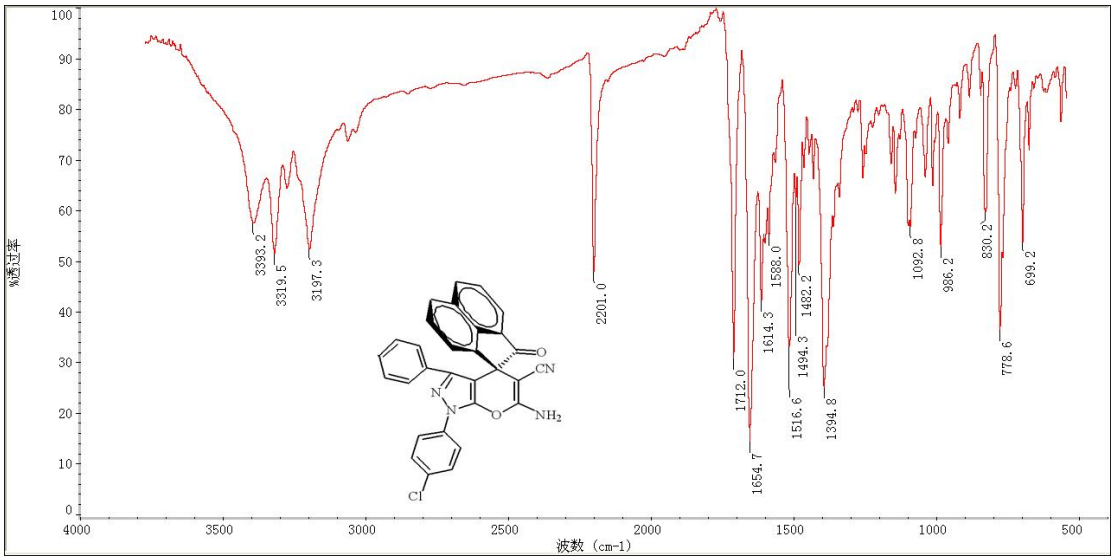
^{1}H NMR of **4l**



^{13}C NMR of **4l**



IR of **4l**



MS of **4l**