

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supporting Information for

A novel three-component [5+1] heterocyclization leading to 2-azafluorenone synthesis and its polyfunctionalizations

Ying Li, Wei Fan, Hai-Wei Xu, Bo Jiang,* Shu-Liang Wang, Shu-Jiang Tu*

School of Chemistry and Chemical Engineering, and Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Jiangsu, P.R. China.

E-mail: jiangchem@jsnu.edu.cn (B. Jiang); laotu@jsnu.edu.cn (S.-J. Tu)

General

Microwave irradiation was carried out with initiator from Biotage Company, Sweden. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1} . ^1H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in $\text{DMSO}-d_6$ with chemical shift (δ) given in ppm relative to TMS as internal standard. HRMS (ESI) was determined by using microTOF-Q II HRMS/MS instrument (Bruker). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

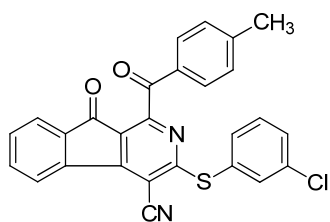
Example for the synthesis of **4a**:

3-((3-chlorophenyl)thio)-1-(4-methylbenzoyl)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4a)

Typically, 2,2-dihydroxy-1-*p*-tolylethanone (**1a**, 1 mmol, 0.166 g, 1.0 equiv.) was introduced in a 10-mL InitiatorTM reaction vial, 3-chlorobenzenethiol (**2a**, 1.0 mmol, 0.144 g, 1.0 equiv.) and 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (**3**, 1.0 mmol, 0.194 g, 1.0 equiv.) as well as acetic acid (1.0 mL) were then successively added. Subsequently, the reaction vial was closed and then pre-stirred for 10 second. The mixture was irradiated (Time: 28 min, Temperature: 120 °C; Absorption Level: High; Fixed Hold Time) until TLC (petroleum ether : acetone 3:1) revealed that conversion of the starting material **1a** was complete. The reaction mixture was then cooled to room temperature and then diluted with cold water (20 ml). The solid product was collected by Büchner filtration and was purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetone, 7:1, v/v) to afford the desired pure 2-azafluorenonones **4a** as a green solid (mp: 190-191 °C)

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3-((3-Chlorophenyl)thio)-1-(4-methylbenzoyl)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4a)



A green solid; mp: 190-191 °C

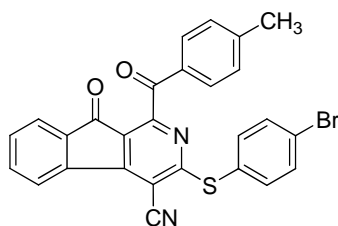
^1H NMR (400 MHz, DMSO- d_6) δ 8.25 (d, J = 7.6 Hz, 1H, ArH), 7.94-7.90 (m, 1H, ArH), 7.77 (s, 2H, ArH), 7.70 (d, J = 8.0 Hz, 3H, ArH), 7.56 (d, J = 7.6 Hz, 1H, ArH), 7.46-7.37 (m, 2H, ArH), 7.33 (d, J = 7.6 Hz, 2H, ArH), 2.39 (s, 3H, CH₃).

^{13}C NMR (100 MHz, DMSO- d_6) δ 199.5, 190.3, 187.6, 166.8, 155.5, 154.1, 145.5, 138.5, 136.1, 134.0, 133.9, 133.5, 133.0, 131.5, 130.9, 129.9, 129.5, 129.0, 124.9, 123.6, 122.7, 114.0, 99.8, 94.0, 21.3.

IR (KBr, ν , cm^{-1}): 3415, 2218, 1720, 1674, 1655, 1569, 1491, 1459, 1283, 1182, 1088, 941, 849.

HRMS (ESI): m/z calcd for C₂₇H₁₅ClN₂NaSO₂, 489.0435 [M+Na]⁺, found: 489.0461.

3-((4-Bromophenyl)thio)-1-(4-methylbenzoyl)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4b)



A green solid; mp: 194-194.3 °C

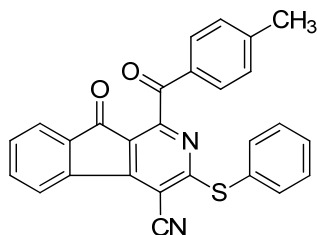
^1H NMR (400 MHz, DMSO- d_6) δ 8.24 (d, J = 7.6 Hz, 1H, ArH), 8.00 – 7.82 (m, 1H, ArH), 7.76-7.73 (m, 2H, ArH), 7.66 (d, J = 8.0 Hz, 2H, ArH), 7.58-7.52 (m, 4H, ArH), 7.32 (d, J = 8.0 Hz, 2H, ArH), 2.40 (s, 3H, CH₃).

^{13}C NMR (100 MHz, DMSO- d_6) δ 190.2, 187.6, 167.1, 155.5, 154.0, 145.5, 138.5, 136.7, 136.1, 134.0, 133.9, 132.4, 131.5, 129.9, 129.4, 126.2, 124.9, 123.8, 123.6, 122.7, 114.0, 99.6, 21.3.

IR (KBr, ν , cm^{-1}): 3439, 2221, 1725, 1673, 1602, 1560, 1472, 1454, 1386, 1364, 1286, 1237, 1182, 1118, 1086, 1007, 933, 821, 750, 693.

HRMS (ESI): m/z calcd for C₂₇H₁₅BrN₂NaSO₂, 534.9912 [M+Na]⁺, found: 534.9924.

1-(4-Methylbenzoyl)-9-oxo-3-(phenylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4c)



A pale yellow solid, mp: 200-201 °C

^1H NMR (400 MHz, DMSO- d_6) δ 8.23 (d, J = 7.6 Hz, 1H, ArH), 7.95 – 7.84 (m, 1H, ArH), 7.74-7.73 (m, 2H, ArH), 7.65 (d, J = 8.0 Hz, 2H, ArH), 7.61 – 7.53 (m, 2H, ArH), 7.40 – 7.28 (m,

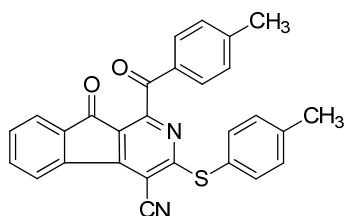
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5H, ArH), 2.37 (s, 3H, CH₃).

IR (KBr, ν , cm⁻¹): 3440, 2217, 1719, 1667, 1603, 1569, 1442, 1369, 1284, 1242, 1180, 1120, 1022, 944, 848, 757, 694.

HRMS (ESI): m/z calcd for C₂₇H₁₇N₂SO₂, 433.1005 [M+H]⁺, found: 433.1033.

1-(4-Methylbenzoyl)-9-oxo-3-(p-tolylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4d)



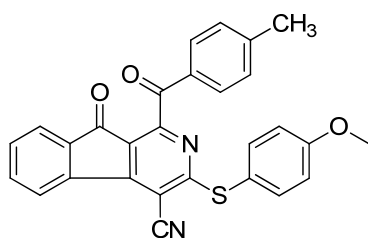
A yellow solid, mp: 197-197.5°C

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24 (d, J = 7.6 Hz, 1H, ArH), 7.92-7.88 (m, 1H, ArH), 7.75-7.74(m, 2H, ArH), 7.67 (d, J = 7.6 Hz, 2H, ArH), 7.46 (d, J = 7.6 Hz, 2H, ArH), 7.31 (d, J = 7.6 Hz, 2H, ArH), 7.19 (d, J = 7.6 Hz, 2H, ArH), 2.39 (s, 3H, CH₃), 2.26 (s, 3H, CH₃).

IR (KBr, ν , cm⁻¹): 3437, 2219, 1724, 1669, 1601, 1559, 1494, 1453, 1364, 1285, 1364, 1285, 1237, 1180, 1085, 1016, 938, 848, 812, 770, 753.

HRMS (ESI): m/z calcd for C₂₈H₁₉N₂O₂S, 447.1162 [M+H]⁺, found: 447.1182.

3-((4-Methoxyphenyl)thio)-1-(4-methylbenzoyl)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4e)



A yellow solid, mp: 181-181.5°C

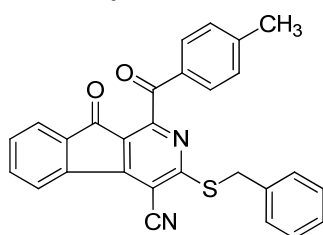
¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24 (d, J = 7.6 Hz, 1H, ArH), 7.97 – 7.83 (m, 3H, ArH), 7.78 – 7.70 (m, 2H, ArH), 7.53 – 7.46 (m, 2H, ArH), 7.41 – 7.28 (m, 2H, ArH), 7.00 – 6.86 (m, 2H, ArH), 3.72 (s, 3H, CH₃), 2.09 (s, 3H, CH₃).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 189.3, 187.6, 168.7, 164.5, 160.7, 155.4, 153.3, 138.5, 136.8, 136.1, 134.0, 133.0, 130.7, 124.9, 123.5, 122.5, 116.5, 116.2, 116.0, 115.1, 114.0, 99.0, 55.2, 18.5.

IR (KBr, ν , cm⁻¹): 3448, 2216, 1719, 1681, 1592, 1563, 1495, 1467, 1243, 1178, 1088, 1023, 942, 837, 757.

HRMS (ESI): m/z calcd for C₂₈H₁₉N₂O₃S, 463.1111 [M+H]⁺, found: 463.1139.

3-(Benzylthio)-1-(4-methylbenzoyl)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4f)



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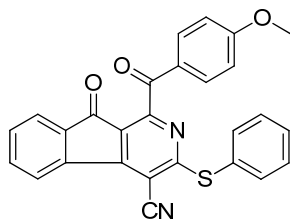
A pale yellow solid, mp: 194-195°C

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.20 (d, $J = 7.6$ Hz, 1H, ArH), 7.91-7.87 (m, 1H, ArH), 7.80-7.73 (m, 4H, ArH), 7.38 (d, $J = 8.0$ Hz, 2H, ArH), 7.34 – 7.27 (m, 2H, ArH), 7.22-7.18 (m, 3H, ArH), 4.51 (s, 2H, CH_2), 2.43 (s, 3H, CH_3).

IR (KBr, ν , cm^{-1}): 3439, 2215, 1722, 1671, 1601, 1558, 1451, 1370, 1289, 1240, 1180, 1087, 1025, 942, 846, 755.

HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{18}\text{N}_2\text{NaSO}_2$, 469.0981 $[\text{M}+\text{Na}]^+$, found: 469.0989.

1-(4-Methoxybenzoyl)-9-oxo-3-(phenylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4g)



A green solid, mp: 196-197°C

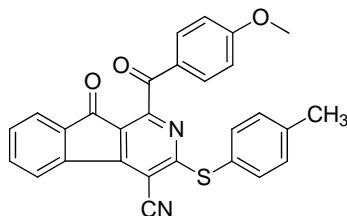
^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.22 (d, $J = 7.6$ Hz, 1H, ArH), 7.90 – 7.86 (m, 1H, ArH), 7.75-7.72(m, 4H, ArH), 7.59-7.57 (m, 2H, ArH), 7.39-7.36 (m, 3H, ArH), 7.00 (d, $J = 8.8$ Hz, 2H, ArH), 3.84 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 189.2, 187.7, 167.6, 164.3, 155.4, 154.3, 138.5, 136.0, 134.7, 133.9, 132.3, 130.0, 129.5, 126.9, 126.6, 124.8, 123.5, 122.3, 114.1, 114.0, 99.3, 55.7

IR (KBr, ν , cm^{-1}): 3430, 2218, 1726, 1668, 1595, 1561, 1441, 1363, 1285, 1243, 1120, 850, 756.

HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$, 449.0954 $[\text{M}+\text{H}]^+$, found: 449.0959.

1-(4-Methoxybenzoyl)-9-oxo-3-(p-tolylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4h)



A green solid, mp: 184-185°C

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.24 (d, $J = 7.6$ Hz, 1H, ArH), 7.90 (s, 1H, ArH), 7.74 (d, $J = 5.2$ Hz, 4H, ArH), 7.47 (d, $J = 7.6$ Hz, 2H, ArH), 7.21 (d, $J = 7.6$ Hz, 2H, ArH), 7.02 (d, $J = 8.0$ Hz, 2H, ArH), 3.86 (s, 3H, CH_3), 2.27 (s, 3H, CH_3).

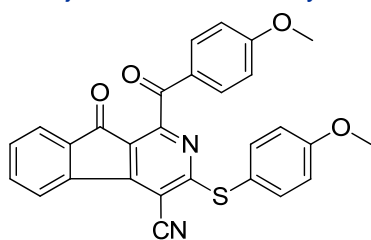
^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 189.2, 187.7, 175.6, 168.0, 164.3, 155.3, 154.3, 140.0, 138.5, 136.0, 134.7, 133.9, 133.8, 132.3, 130.1, 127.0, 124.8, 123.5, 123.0, 122.2, 114.2, 55.7, 20.8

IR (KBr, ν , cm^{-1}): 3441, 2210, 1721, 1679, 1599, 1561, 1491, 1369, 1287, 1244, 1171, 1086, 848, 778.

HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{19}\text{N}_2\text{O}_3\text{S}$, 463.1111 $[\text{M}+\text{H}]^+$, found: 463.1139.

1-(4-Methoxybenzoyl)-3-((4-methoxyphenyl)thio)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4i)

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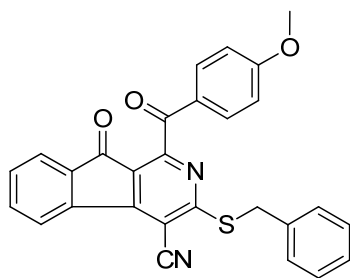
A yellow solid, mp: 205-206°C

^1H NMR (400 MHz, DMSO- d_6) δ 8.22 (d, J = 7.6 Hz, 1H, ArH), 7.97 – 7.81 (m, 1H, ArH), 7.77 – 7.64 (m, 4H, ArH), 7.49 (d, J = 8.8 Hz, 2H, ArH), 7.01 (d, J = 8.8 Hz, 2H, ArH), 6.93 (d, J = 8.8 Hz, 2H, ArH), 3.85 (s, 3H, CH₃), 3.71 (s, 3H, CH₃).

^{13}C NMR (100 MHz, DMSO- d_6) δ 189.2, 187.6, 168.6, 164.2, 160.7, 155.3, 154.3, 138.5, 136.8, 136.0, 133.9, 133.8, 132.3, 126.9, 124.8, 123.5, 122.2, 116.6, 115.1, 114.2, 114.0, 98.7, 55.7, 55.2
IR (KBr, v, cm⁻¹): 3445, 2211, 1721, 1665, 1596, 1561, 1494, 1270, 1245, 1180, 1020, 1087, 936, 858, 832, 756.

HRMS (ESI): m/z calcd for C₂₈H₁₈N₂NaSO₄, 501.0879 [M+Na]⁺, found: 501.0908.

3-(Benzylthio)-1-(4-methoxybenzoyl)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4j)



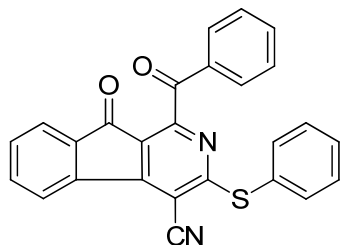
A pale yellow solid, mp: 181-182°C

^1H NMR (400 MHz, DMSO- d_6) δ 8.19 (d, J = 7.6 Hz, 1H, ArH), 7.86 (d, J = 8.8 Hz, 3H, ArH), 7.77 – 7.69 (m, 2H, ArH), 7.36 – 7.27 (m, 2H, ArH), 7.20 (d, J = 6.8 Hz, 3H, ArH), 7.07 (d, J = 8.8 Hz, 2H, ArH), 4.51 (s, 2H, CH₂), 3.88 (s, 3H, CH₃).

IR (KBr, v, cm⁻¹): 3420, 2215, 1720, 1671, 1593, 1559, 1494, 1368, 1290, 1242, 1170, 1121, 1086, 941, 848, 759.

HRMS (ESI): m/z calcd for C₂₈H₁₈N₂NaSO₃, 485.0936 [M+Na]⁺, found: 485.0919.

1-Benzoyl-9-oxo-3-(phenylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4k)



A yellow solid, 186.4-187.3°C

^1H NMR (400 MHz, DMSO- d_6) δ 8.25 (d, J = 7.2 Hz, 1H, ArH), 7.97 – 7.86 (m, 1H, ArH), 7.84 – 7.66 (m, 5H, ArH), 7.64 – 7.47 (m, 4H, ArH), 7.37-7.36 (m, 3H, ArH).

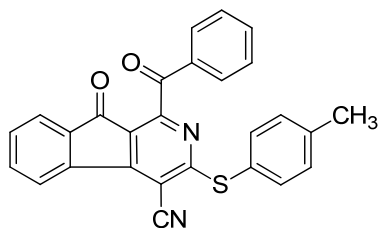
^{13}C NMR (100 MHz, DMSO- d_6) δ 190.8, 187.7, 167.7, 155.4, 153.8, 138.5, 136.1, 134.7, 133.9, 133.9, 133.8, 130.0, 129.8, 129.4, 128.9, 126.5, 124.9, 123.6, 122.6, 114.0, 99.4,

IR (KBr, v, cm⁻¹): 3435, 2218, 1720, 1673, 1597, 1561, 1451, 1365, 1283, 1240, 1183, 1086, 1019, 941, 836, 745.

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HRMS (ESI): m/z calcd for $C_{26}H_{15}N_2O_2S$, 419.0849 $[M+H]^+$, found: 419.0818.

1-Benzoyl-9-oxo-3-(p-tolylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4l)



A yellow solid, mp: 178-179°C

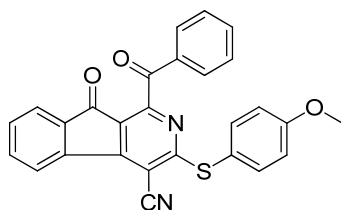
1H NMR (400 MHz, DMSO- d_6) δ 8.25 (d, $J = 6.8$ Hz, 1H, ArH), 7.91 (s, 1H, ArH), 7.79-7.71 (m, 5H, ArH), 7.53-7.45 (m, 4H, ArH), 7.18 (d, $J = 6.8$ Hz, 2H, ArH), 2.25 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO- d_6) δ 190.9, 187.6, 168.1, 155.3, 153.8, 140.0, 138.5, 136.0, 134.7, 134.6, 133.9, 133.9, 130.1, 129.8, 128.9, 124.8, 123.6, 122.9, 122.5, 114.0, 99.2, 20.8

IR (KBr, ν , cm^{-1}): 3413, 2218, 1720, 1687, 1560, 1451, 1367, 1239, 1182, 1015, 942, 867, 760, 656.

HRMS (ESI): m/z calcd for $C_{27}H_{17}N_2O_2S$, 433.1005 $[M+H]^+$, found: 433.1015.

1-Benzoyl-3-((4-methoxyphenyl)thio)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4m)



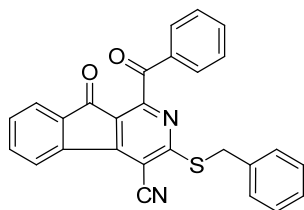
An orange solid, mp: 204-205°C

1H NMR (400 MHz, DMSO) δ 8.25 (d, $J = 7.6$ Hz, 1H, ArH), 7.98 – 7.87 (m, 1H, ArH), 7.83 – 7.74 (m, 4H, ArH), 7.73 – 7.66 (m, 1H, ArH), 7.56 – 7.47 (m, 4H, ArH), 6.95 – 6.87 (m, 2H, ArH), 3.72 (s, 3H, CH_3)

IR (KBr, ν , cm^{-1}): 3413, 2218, 1720, 1687, 1560, 1451, 1367, 1239, 1182, 1015, 942, 867, 760, 656.

HRMS (ESI): m/z calcd for $C_{27}H_{17}N_2O_3S$, 449.0954 $[M+H]^+$, found: 449.0931.

1-Benzoyl-3-(benzylthio)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4n)



A pale yellow solid, mp: 236-237°C

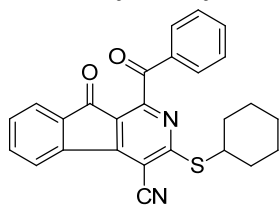
1H NMR (400 MHz, DMSO- d_6) δ 8.19 (d, $J = 7.6$ Hz, 1H, ArH), 7.93 – 7.85 (m, 3H, ArH), 7.80 – 7.68 (m, 3H, ArH), 7.60-7.56 (m, 2H, ArH), 7.3-7.28 (m, 2H, ArH), 7.22 – 7.10 (m, 3H, ArH), 4.50 (s, 2H, CH_2).

IR (KBr, ν , cm^{-1}): 3415, 2219, 1716, 1674, 1565, 1466, 1283, 1234, 1182, 1121, 1086, 1018, 943, 837, 745.

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HRMS (ESI): m/z calcd for $C_{27}H_{16}N_2NaSO_2$, 455.0830 $[M+Na]^+$, found: 455.0839.

1-Benzoyl-3-(cyclohexylthio)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4o)



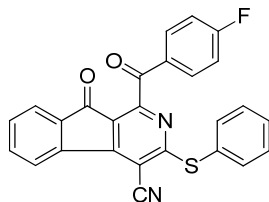
A pale yellow solid, mp: 174-175°C

1H NMR (400 MHz, DMSO- d_6) δ 8.19 (d, $J = 7.6$ Hz, 1H, ArH), 7.93-7.86 (m, 3H, ArH), 7.74 (d, $J = 6.4$ Hz, 3H, ArH), 7.59-7.55 (m, 2H, ArH), 1.96 (d, $J = 10.8$ Hz, 2H, CH₂), 1.70 – 1.39 (m, 5H, CH₂), 1.25 (d, $J = 7.6$ Hz, 3H, CH₂).

IR (KBr, ν , cm^{-1}): 3425, 2214, 1714, 1681, 1567, 1450, 1285, 1238, 1088, 1020, 947, 866, 774.

HRMS (ESI): m/z calcd for $C_{26}H_{20}N_2NaSO_2$, 447.1143 $[M+Na]^+$, found: 447.1139.

1-(4-Fluorobenzoyl)-9-oxo-3-(phenylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4p)



A pale yellow solid, mp: 191-192°C

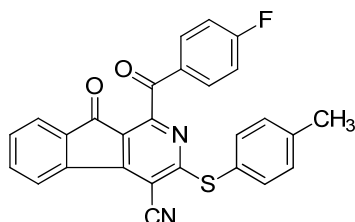
1H NMR (400 MHz, DMSO- d_6) δ 8.25 (d, $J = 7.6$ Hz, 1H, ArH), 8.00 – 7.84 (m, 3H, ArH), 7.81 – 7.71 (m, 2H, ArH), 7.65 – 7.54 (m, 2H, ArH), 7.39-7.33 (m, 5H, ArH).

^{13}C NMR (100 MHz, DMSO- d_6) δ 189.3, 187.6, 167.8, 165.8 ($J_{CF} = 253.3$ Hz), 155.5, 153.4, 138.5, 136.1, 134.8, 133.9, 133.0 ($J_{CF} = 10.0$ Hz), 130.6 ($J_{CF} = 2.8$ Hz), 130.0, 129.4, 126.5, 124.9, 123.6, 122.7, 116.1 ($J_{CF} = 22.1$ Hz), 114.0, 112.7, 99.5.

IR (KBr, ν , cm^{-1}): 3414, 2216, 1718, 1675, 1597, 1567, 1284, 1240, 1157, 1121, 1021, 941, 861, 761.

HRMS (ESI): m/z calcd for $C_{26}H_{13}FN_2NaSO_2$, 459.0574 $[M+Na]^+$, found: 459.0551.

1-(4-Fluorobenzoyl)-9-oxo-3-(p-tolylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4q)



A yellow solid, mp: 196-197°C

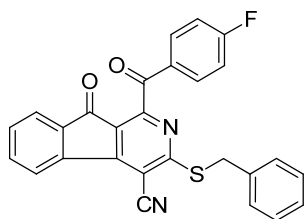
1H NMR (400 MHz, DMSO- d_6) δ 8.23 (d, $J = 7.6$ Hz, 1H, ArH), 7.89-7.73 (m, 3H, ArH), 7.76-7.73 (m, 2H, ArH), 7.45 (d, $J = 8.0$ Hz, 2H, ArH), 7.36-7.31 (m, 2H, ArH), 7.18 (d, $J = 8.0$ Hz, 2H, ArH), 2.25 (s, 3H, CH₃).

IR (KBr, ν , cm^{-1}): 3413, 2220, 1717, 1687, 1594, 1563, 1410, 1285, 1244, 1230, 1152, 941, 851, 810, 760.

HRMS (ESI): m/z calcd for $C_{27}H_{16}FN_2SO_2$, 451.0911 $[M+H]^+$, found: 451.0900.

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3-(Benzylthio)-1-(4-fluorobenzoyl)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4r)



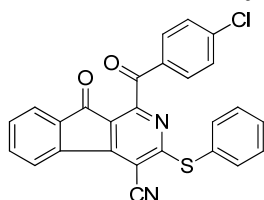
A pale orange solid, mp: 250-252°C

$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.20 (d, $J = 7.6$ Hz, 1H, ArH), 8.07 – 7.95 (m, 2H, ArH), 7.95 – 7.86 (m, 1H, ArH), 7.82 – 7.70 (m, 2H, ArH), 7.43-7.39 (m, 2H, ArH), 7.36 – 7.27 (m, 2H, ArH), 7.25 – 7.10 (m, 2H, ArH), 4.51 (s, 2H, CH_2).

IR (KBr, ν , cm^{-1}): 3425, 2216, 1722, 1683, 1598, 1561, 1413, 1285, 1240, 1025, 943, 855, 759.

HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{15}\text{FN}_2\text{SNaO}_2$, 473.0730 $[\text{M}+\text{Na}]^+$, found: 473.0704.

1-(4-Chlorobenzoyl)-9-oxo-3-(phenylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4s)



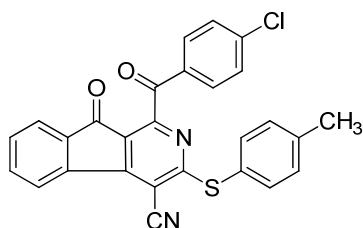
A pale yellow solid, mp: 170-172°C

$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.26 (d, $J = 7.6$ Hz, 1H, ArH), 8.01 – 7.87 (m, 1H, ArH), 7.82-7.75 (m, 4H, ArH), 7.59 (d, $J = 8.0$ Hz, 4H, ArH), 7.39-7.37 (m, 3H, ArH).

IR (KBr, ν , cm^{-1}): 3412, 2214, 1719, 1674, 1618, 1570, 1475, 1283, 1239, 1187, 1089, 1022, 944, 852, 752.

HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{13}\text{ClN}_2\text{SNaO}_2$, 475.0278 $[\text{M}+\text{Na}]^+$, found: 475.0264.

1-(4-Chlorobenzoyl)-9-oxo-3-(p-tolylthio)-9H-indeno[2,1-c]pyridine-4-carbonitrile (4t)



A yellow solid, mp: 223-224°C

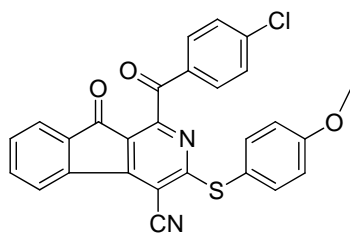
$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.25 (d, $J = 7.6$ Hz, 1H, ArH), 8.00 – 7.85 (m, 1H, ArH), 7.86 – 7.69 (m, 4H, ArH), 7.61 – 7.53 (m, 2H, ArH), 7.46 (d, $J = 8.0$ Hz, 2H, ArH), 7.19 (d, $J = 8.0$ Hz, 2H, ArH), 2.27 (s, 3H, CH_3).

IR (KBr, ν , cm^{-1}): 3425, 2220, 1719, 1691, 1562, 1486, 1398, 1367, 1286, 1242, 1182, 1084, 1015, 941, 848, 810, 752.

HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{15}\text{ClN}_2\text{SNaO}_2$, 489.0435 $[\text{M}+\text{Na}]^+$, found: 489.0432.

1-(4-Chlorobenzoyl)-3-((4-methoxyphenyl)thio)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4u)

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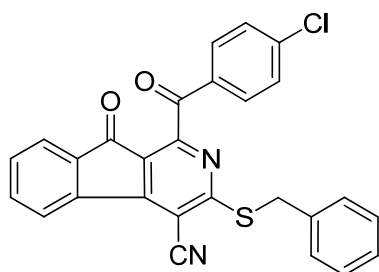
A yellow solid, mp: 206-207°C

^1H NMR (400 MHz, DMSO- d_6) δ 8.25 (d, $J = 7.6$ Hz, 1H, ArH), 7.93-7.89 (m, 1H, ArH), 7.85 – 7.69 (m, 4H, ArH), 7.60-7.58 (m, 2H, ArH), 7.50-7.48 (m, 2H, ArH), 6.93 (d, $J = 8.4$ Hz, 2H, ArH), 3.73 (s, 3H, CH₃).

IR (KBr, ν , cm^{-1}): 3415, 2219, 1720, 1686, 1592, 1566, 1496, 1399, 1367, 1288, 1258, 1241, 1178, 1086, 1021, 942, 850, 756.

HRMS (ESI): m/z calcd for C₂₇H₁₅ClN₂SNaO₃, 505.0384 [M+Na]⁺, found: 505.0366.

3-(Benzylthio)-1-(4-chlorobenzoyl)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4v)



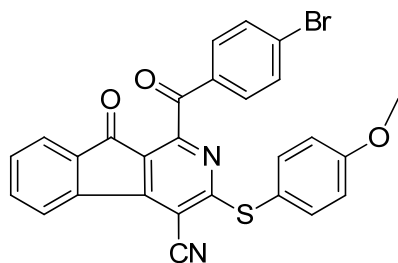
A pale orange solid, 246-247°C

^1H NMR (400 MHz, DMSO- d_6) δ 8.20 (d, $J = 7.6$ Hz, 1H, ArH), 8.01 – 7.82 (m, 3H, ArH), 7.77-7.74 (m, 2H, ArH), 7.65 (d, $J = 8.8$ Hz, 2H, ArH), 7.36 – 7.25 (m, 2H, ArH), 7.22-7.18 (m, 2H, ArH), 4.51 (s, 2H, CH₂).

IR (KBr, ν , cm^{-1}): 3430, 2215, 1719, 1679, 1561, 1402, 1238, 1174, 1087, 1023, 1014, 942, 852, 756.

HRMS (ESI): m/z calcd for C₂₇H₁₅FN₂SNaO₂, 489.0435 [M+Na]⁺, found: 489.0434.

1-(4-Bromobenzoyl)-3-((4-methoxyphenyl)thio)-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile (4w)



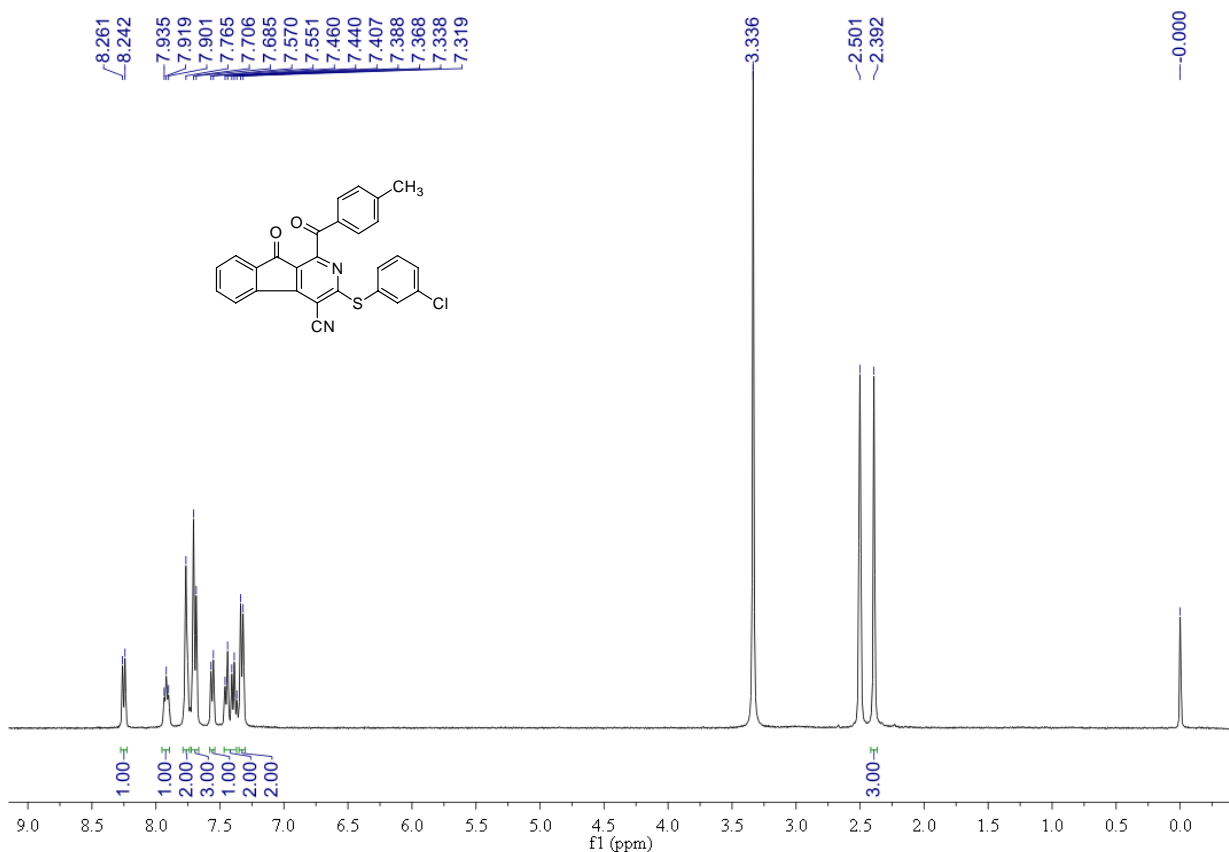
A yellow solid, mp: 207-208°C

^1H NMR (400 MHz, DMSO- d_6) δ 8.21 (d, $J = 7.6$ Hz, 1H, ArH), 7.93 – 7.80 (m, 1H, ArH), 7.75 – 7.61 (m, 6H, ArH), 7.52 – 7.39 (m, 2H, ArH), 7.01 – 6.72 (m, 2H, ArH), 3.70 (s, 3H, CH₃).

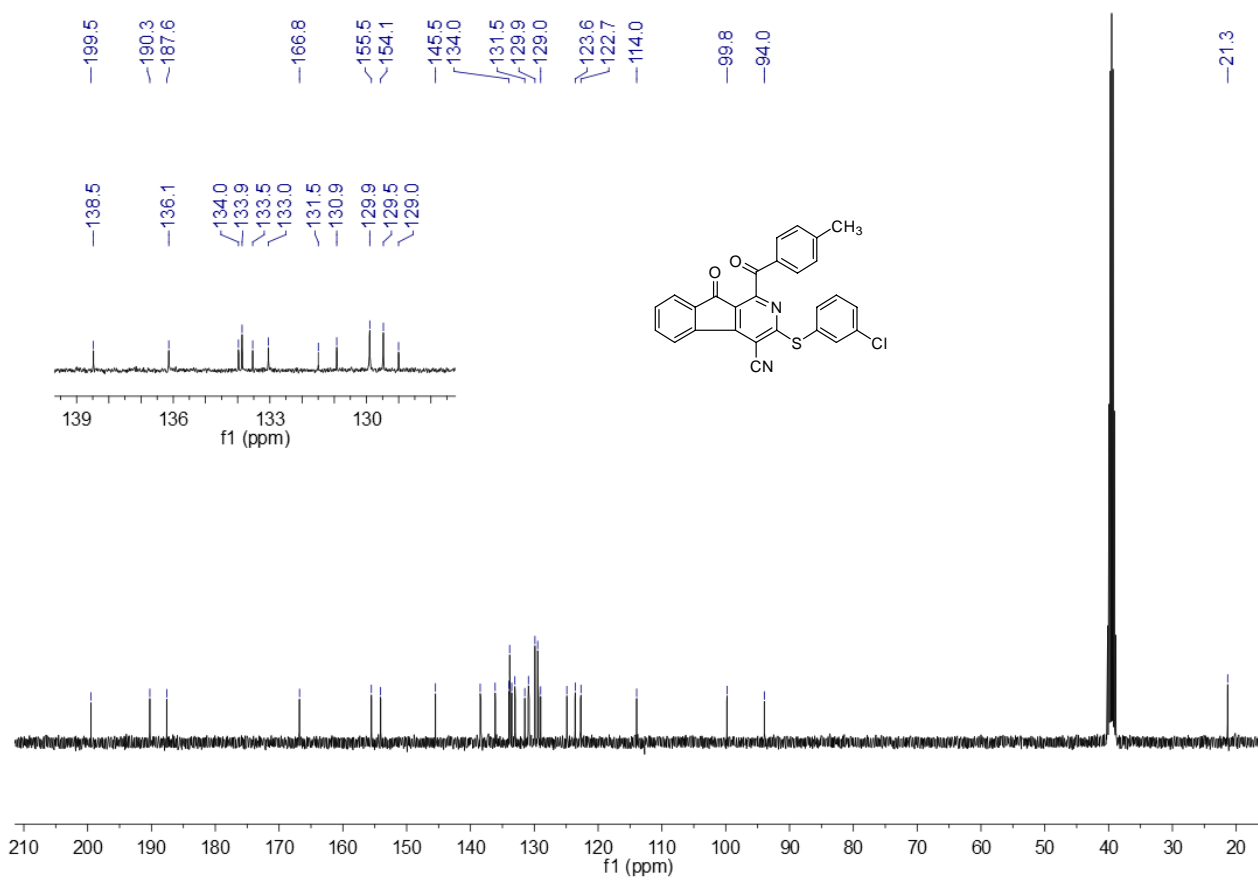
IR (KBr, ν , cm^{-1}): 3443, 2221, 1720, 1687, 1564, 14095, 1397, 1242, 1177, 1089, 1021, 940, 849, 756.

HRMS (ESI): m/z calcd for C₂₇H₁₅BrN₂SNaO₃, 529.0042 [M+Na]⁺, found: 529.0055.

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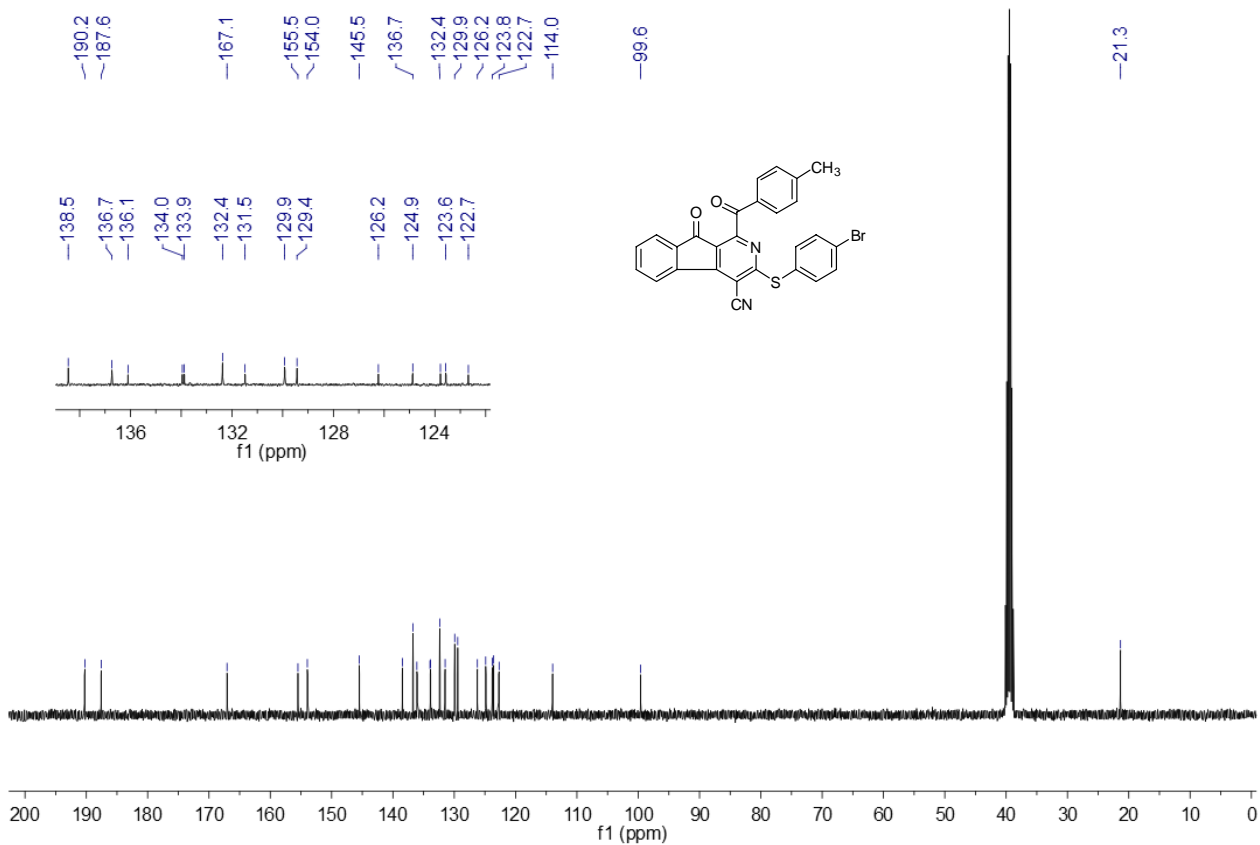
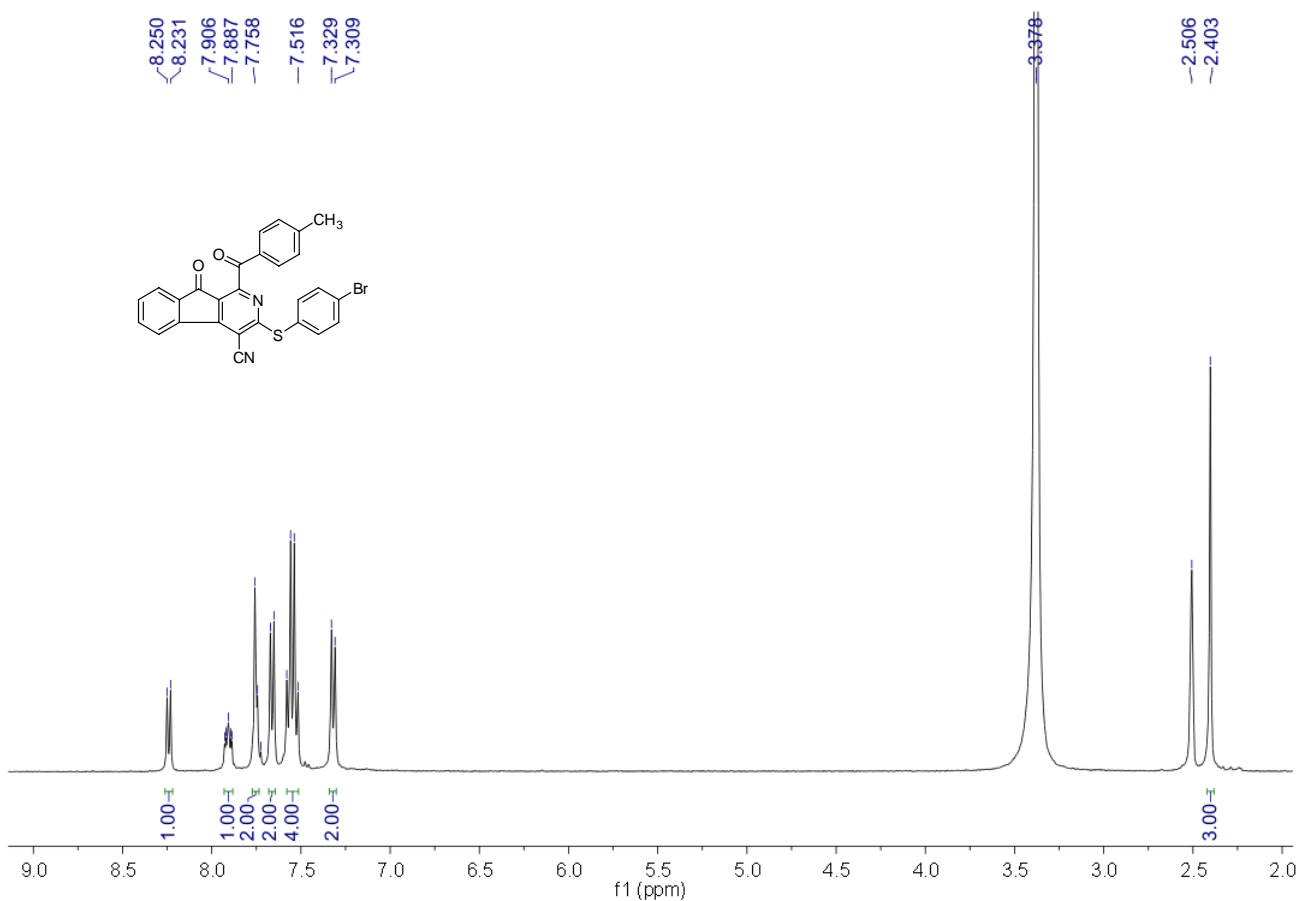


¹H NMR Spectrum of Compound 4a



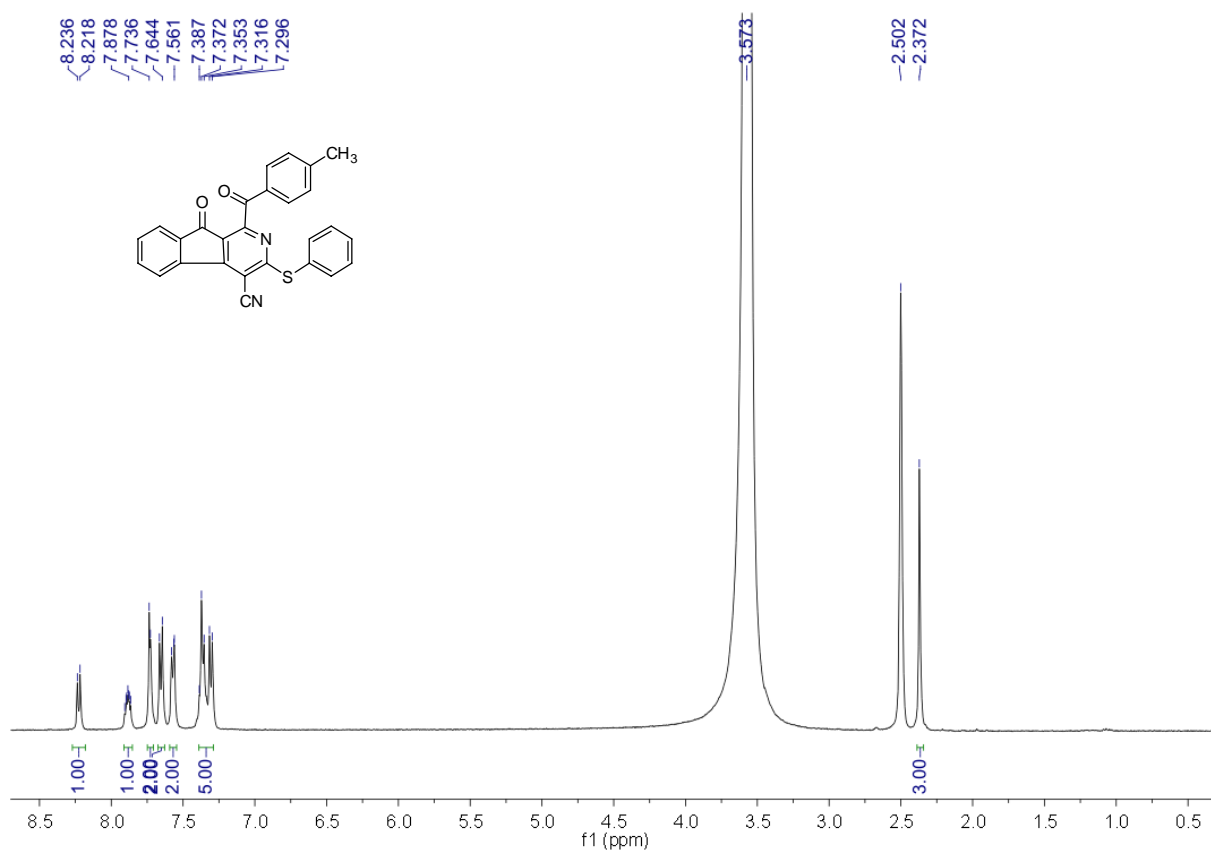
¹³C NMR Spectrum of Compound 4a

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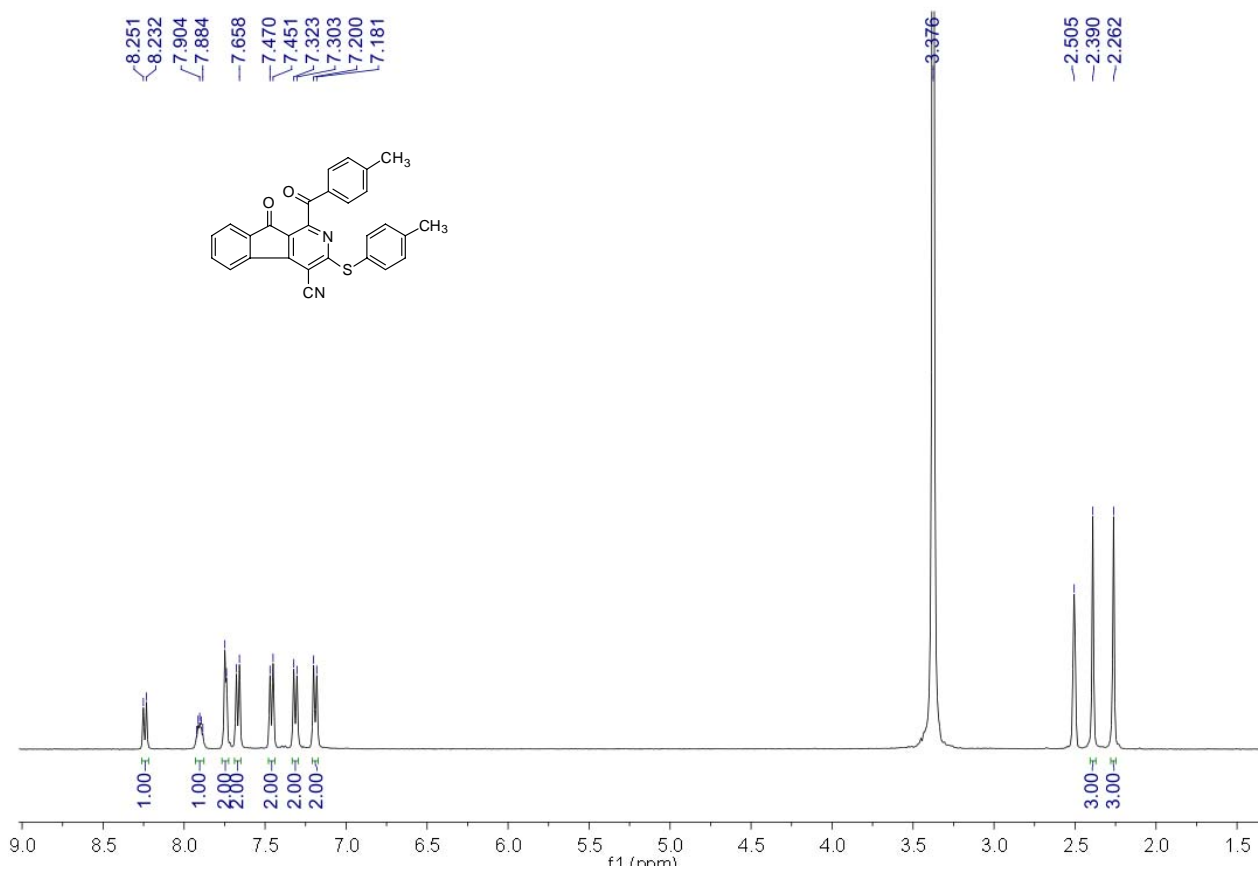


¹³C NMR Spectrum of Compound 4b

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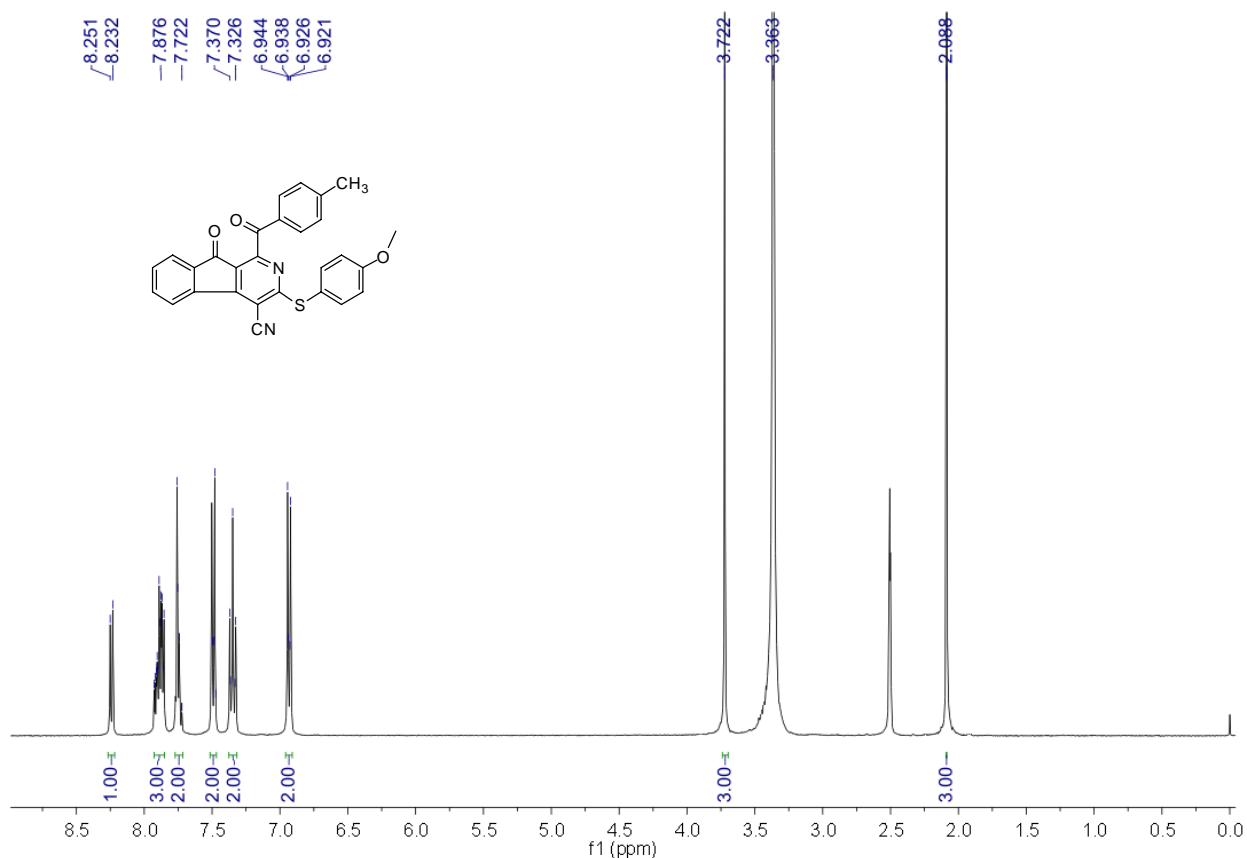


¹H NMR Spectrum of Compound 4c

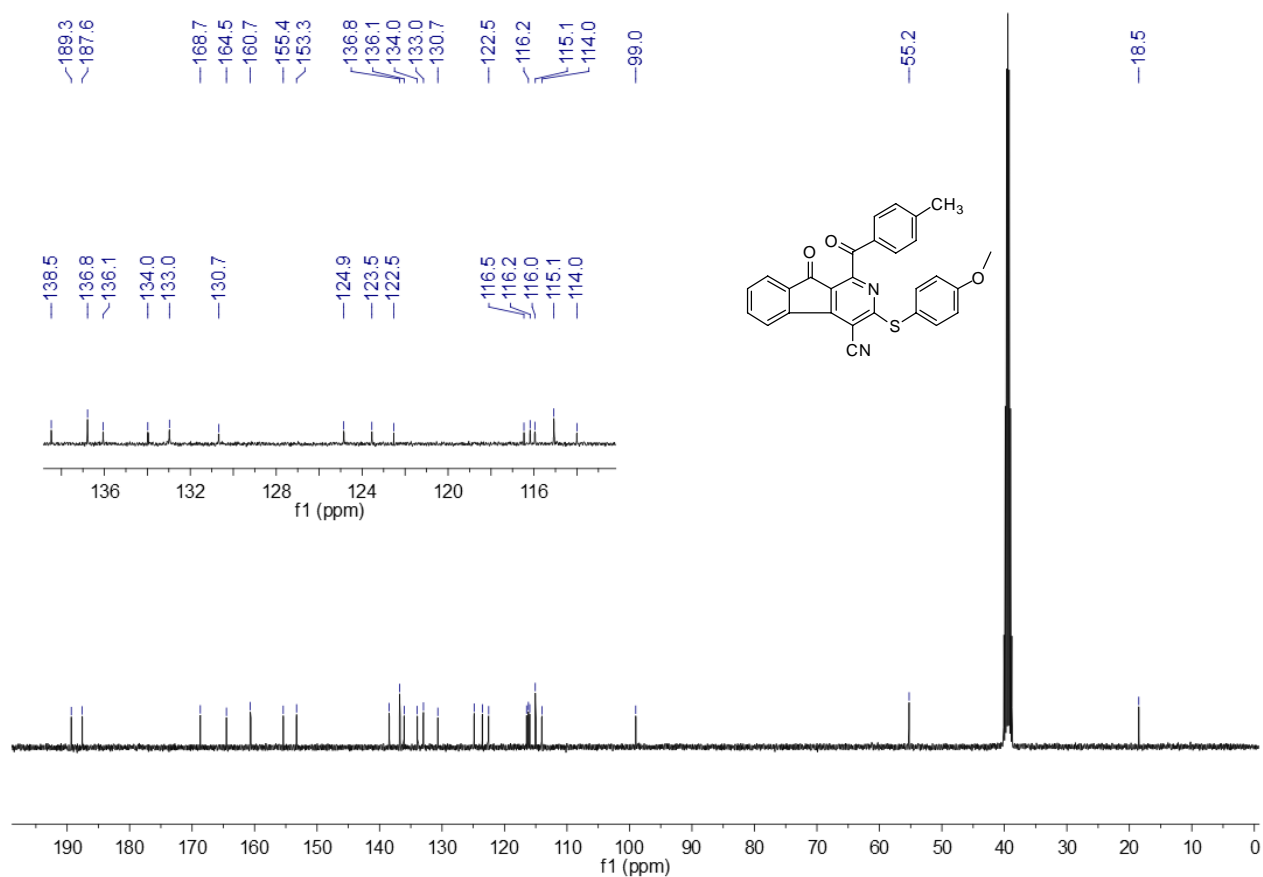


¹H NMR Spectrum of Compound 4d

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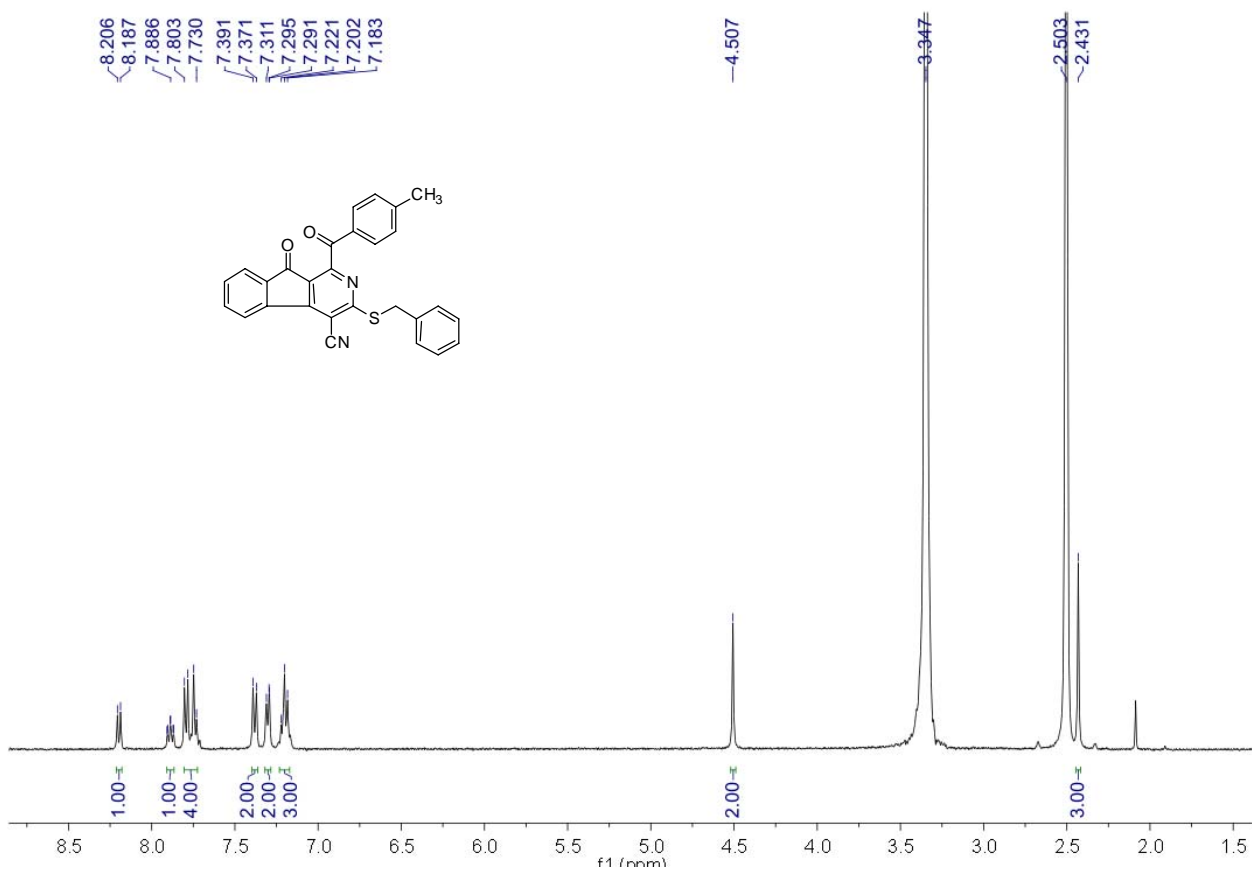


¹H NMR Spectrum of Compound 4e

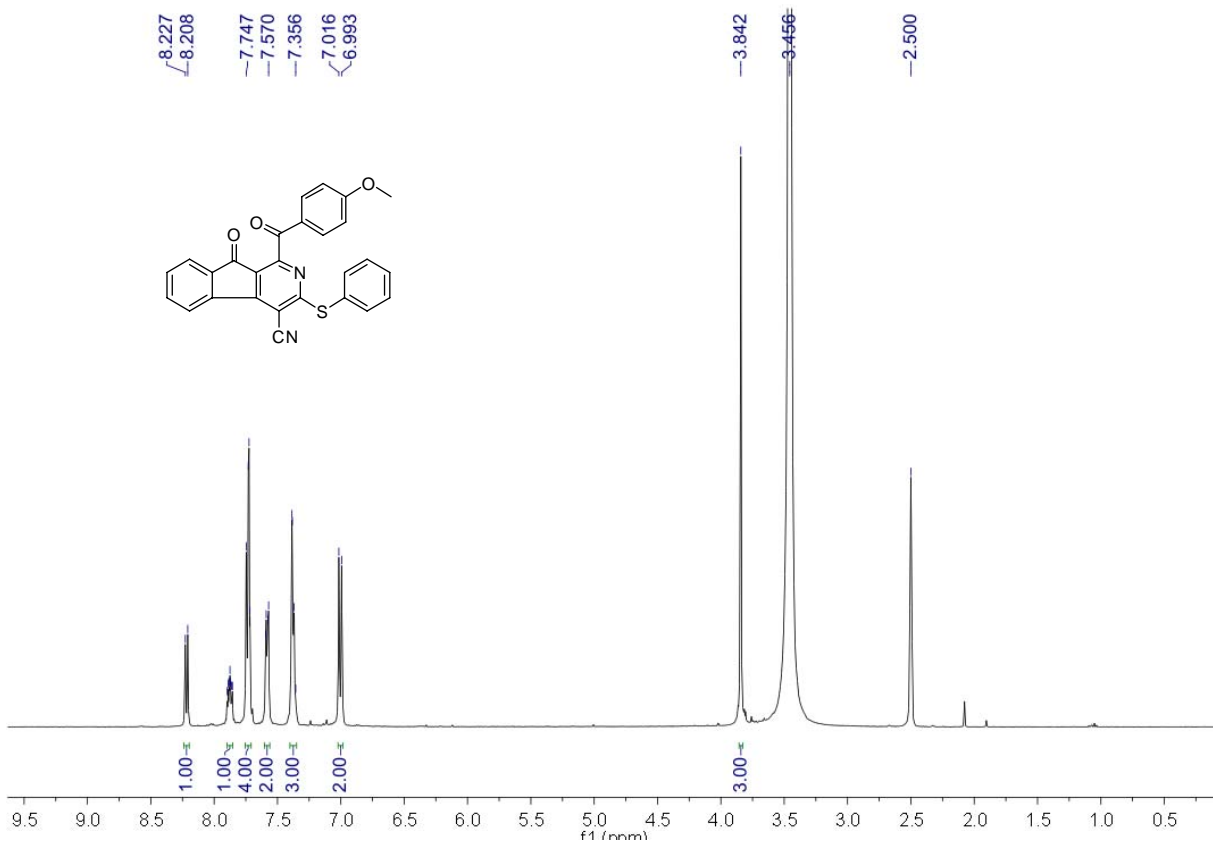


¹³C NMR Spectrum of Compound 4e

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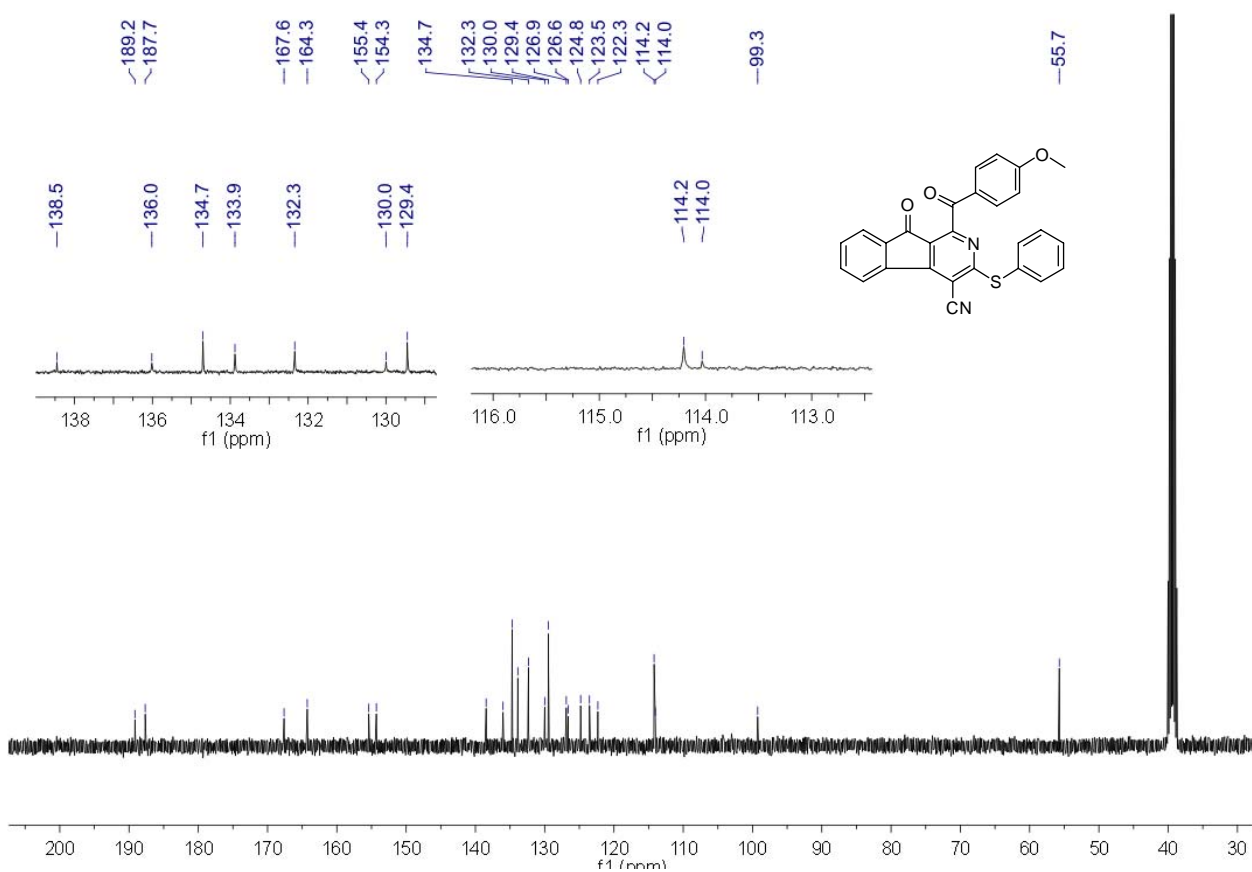


¹H NMR Spectrum of Compound 4f

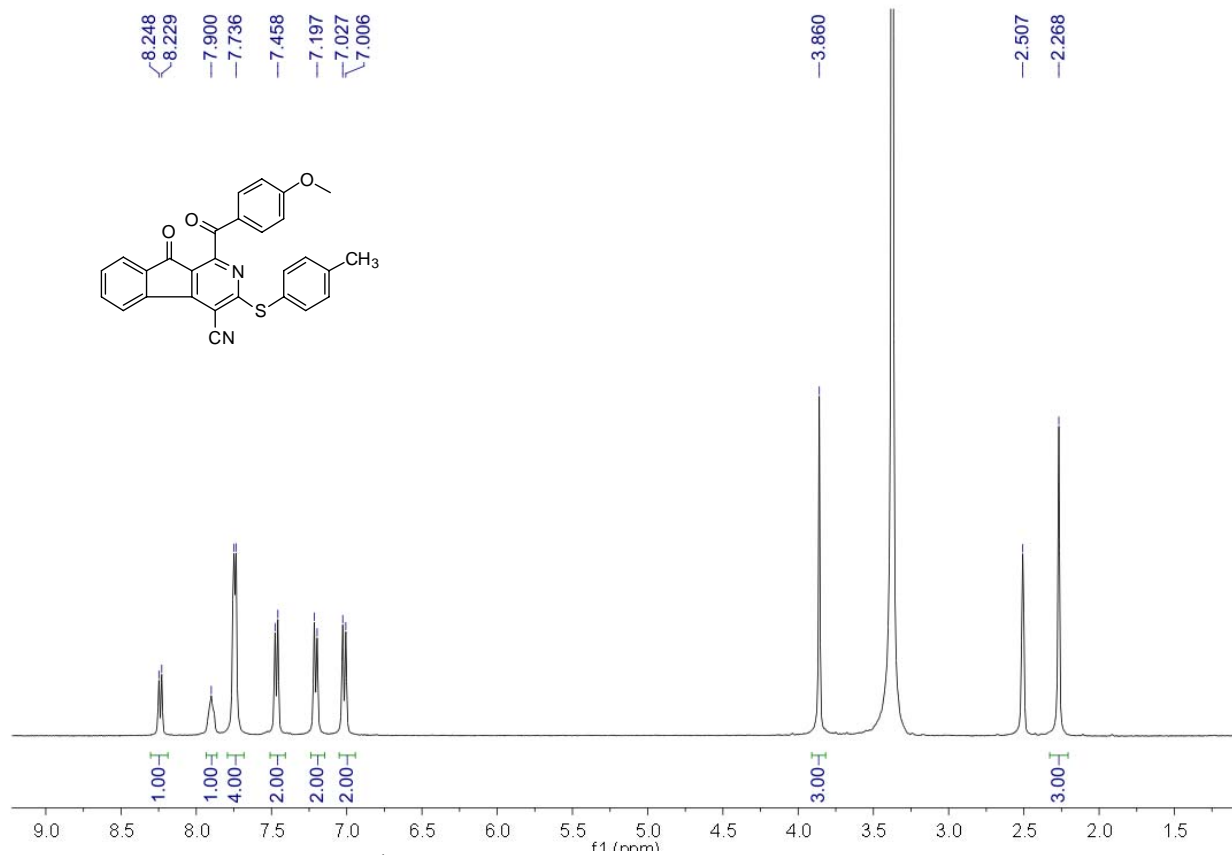


¹H NMR Spectrum of Compound 4g

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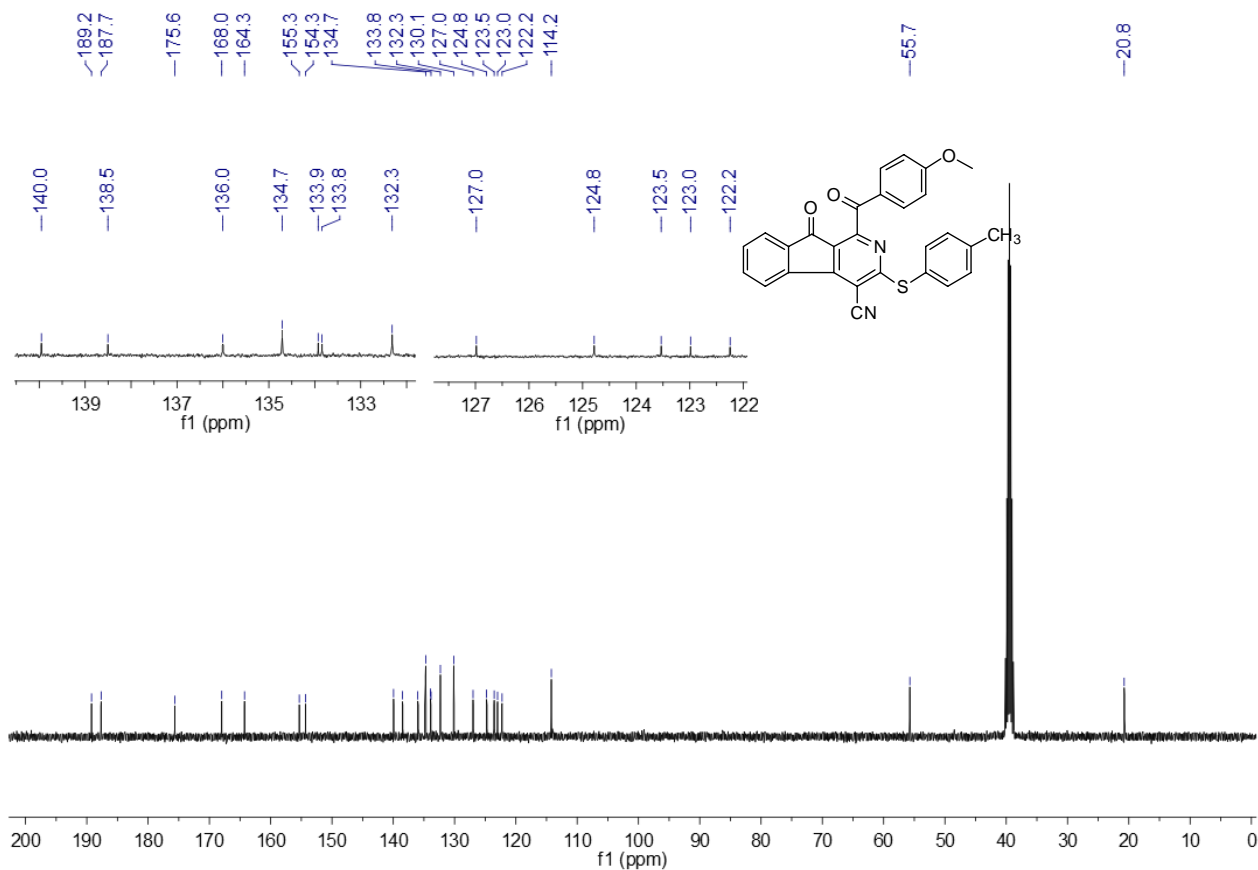


¹³C NMR Spectrum of Compound 4g

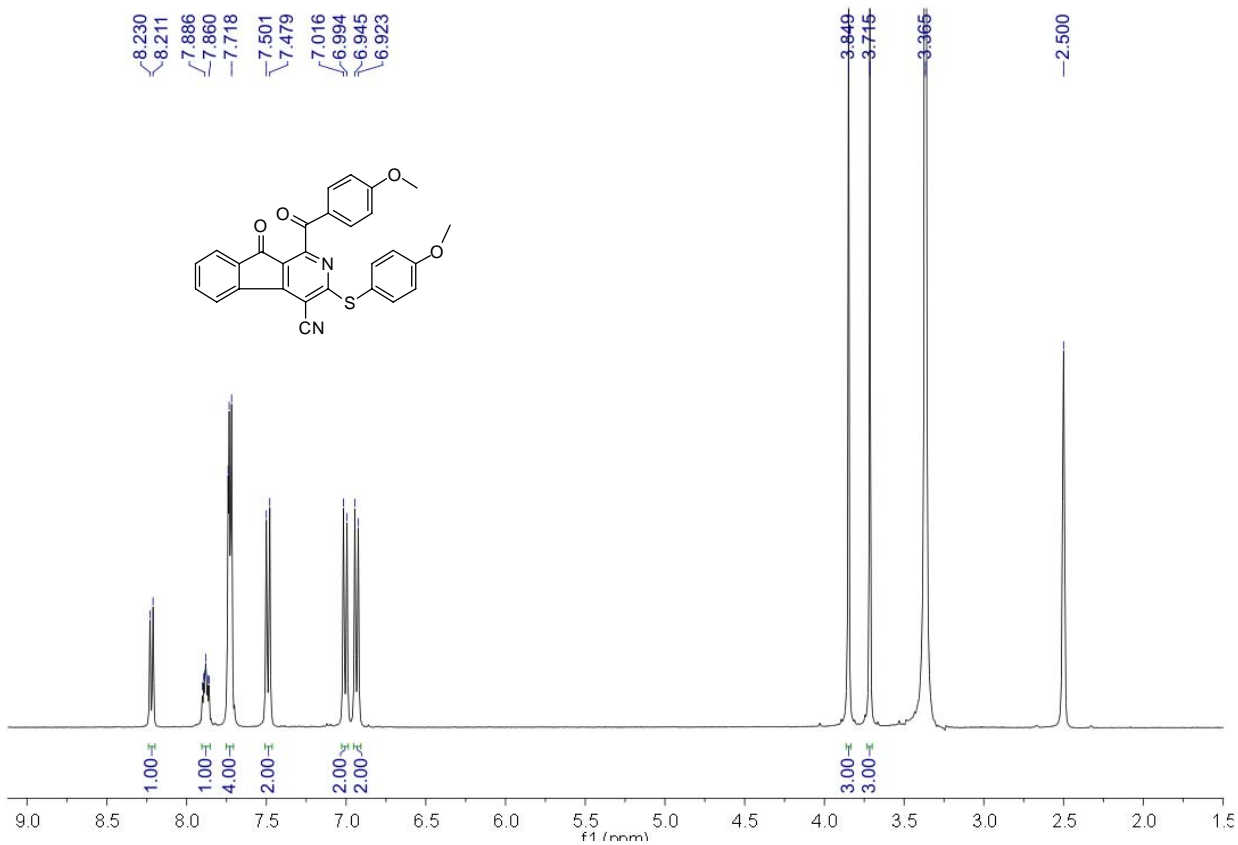


¹H NMR Spectrum of Compound 4h

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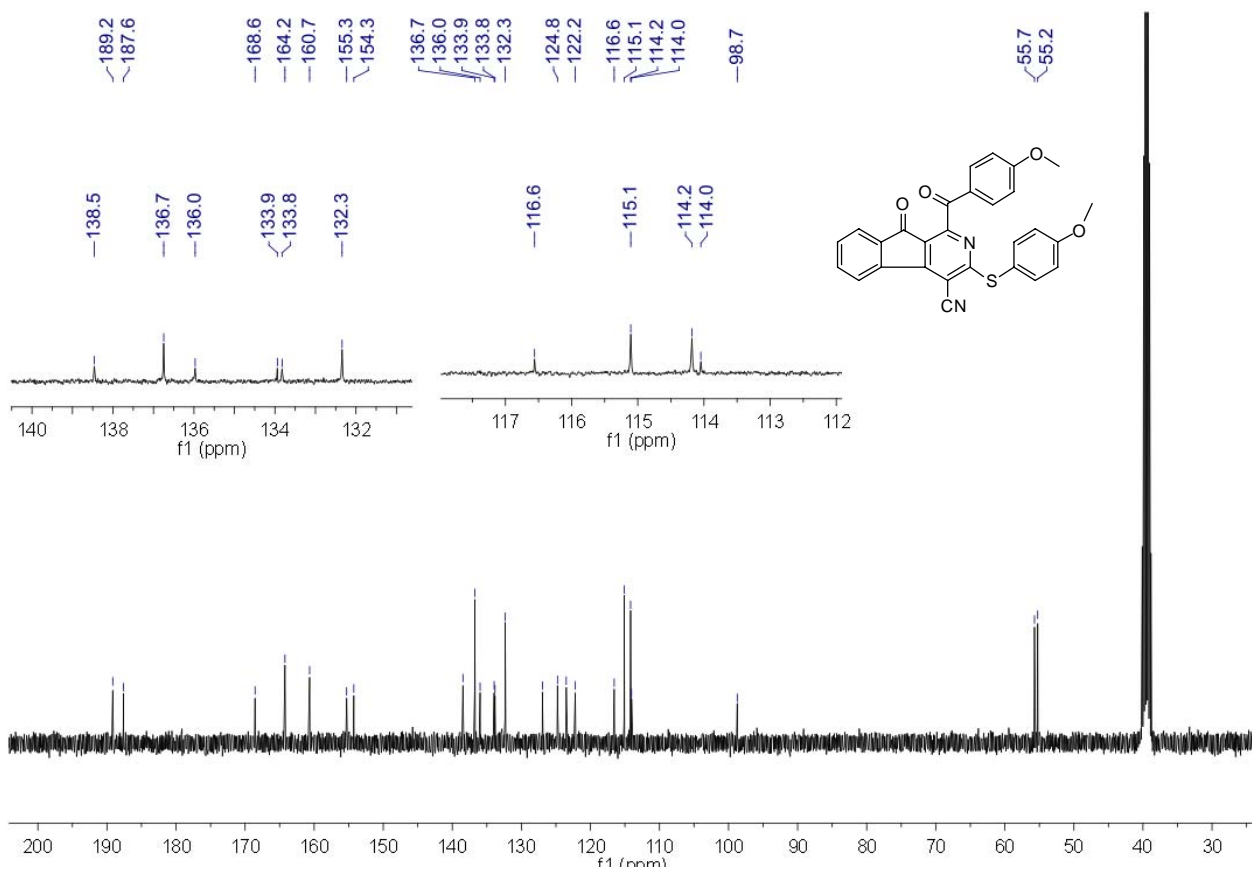


¹³C NMR Spectrum of Compound 4h

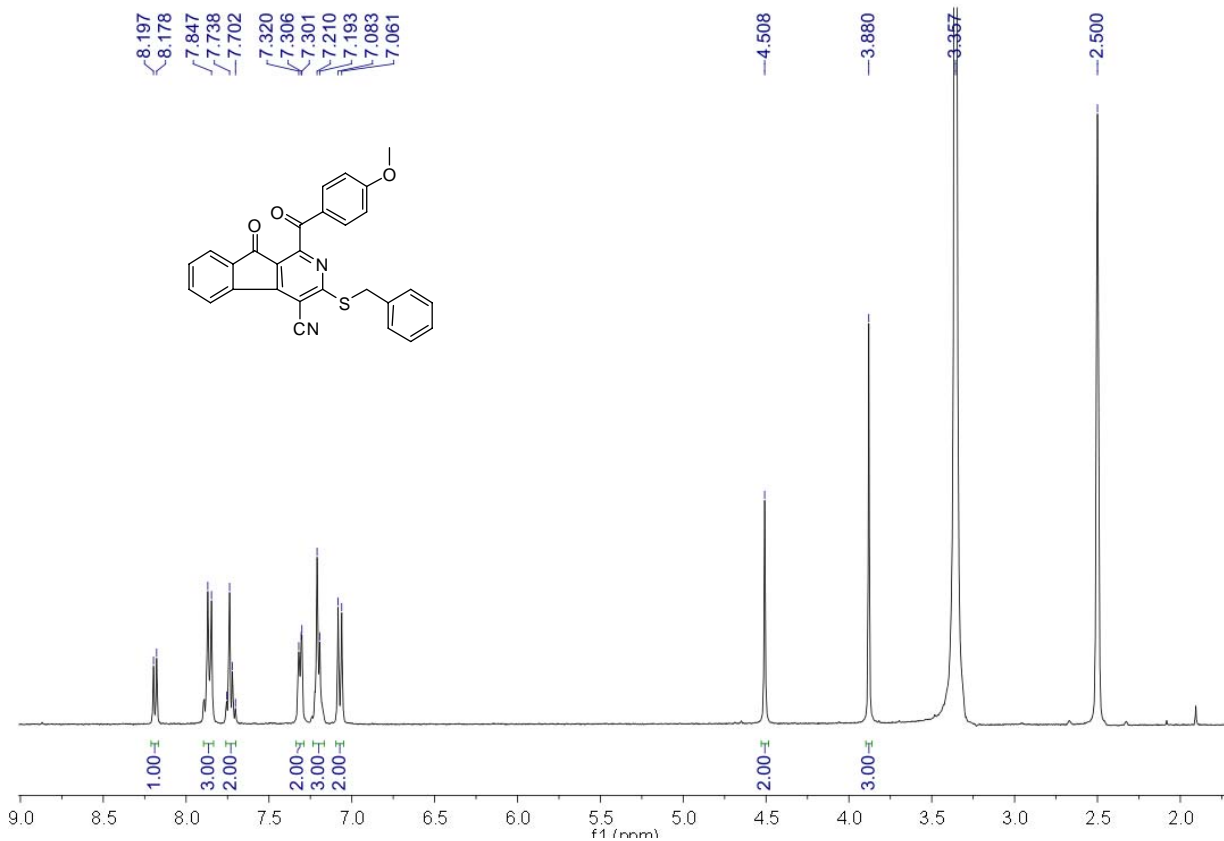


¹H NMR Spectrum of Compound 4i

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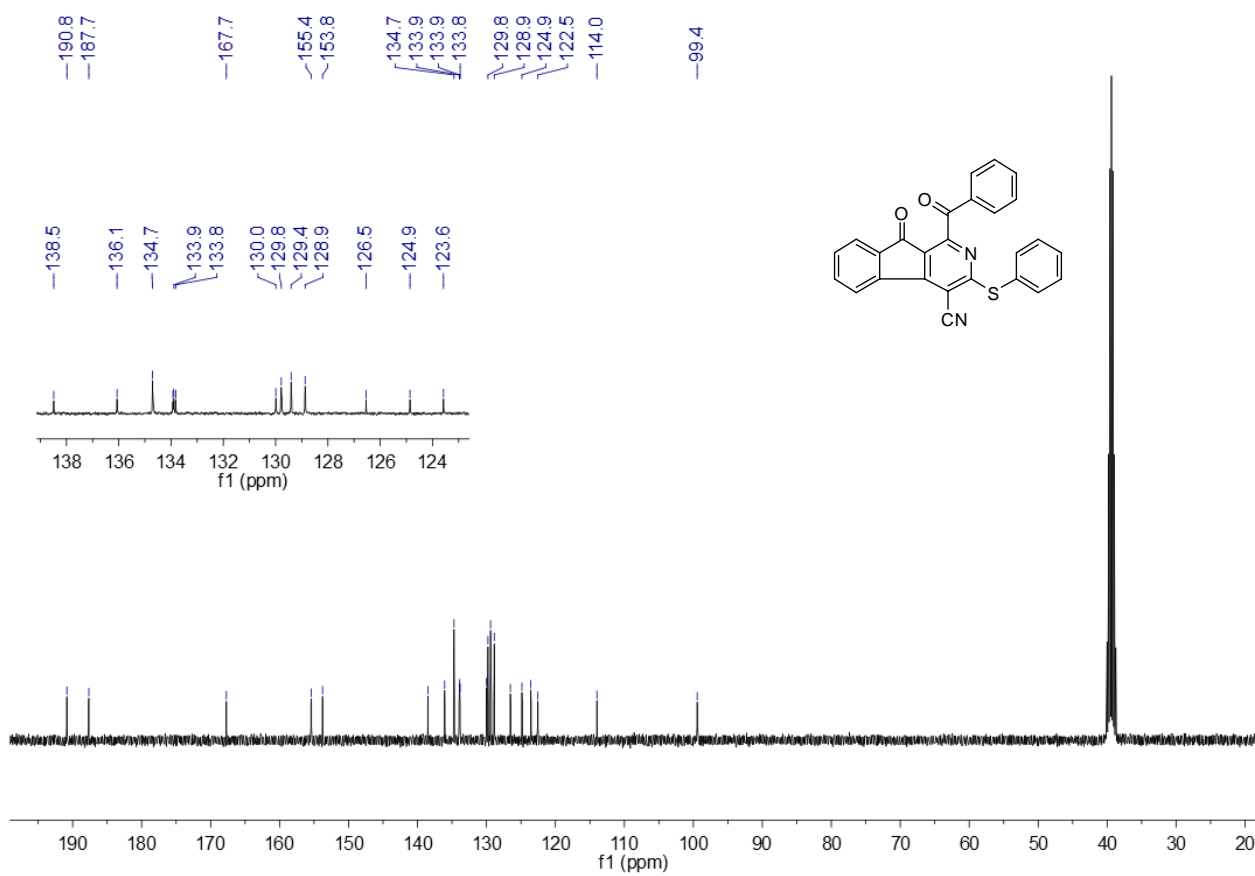
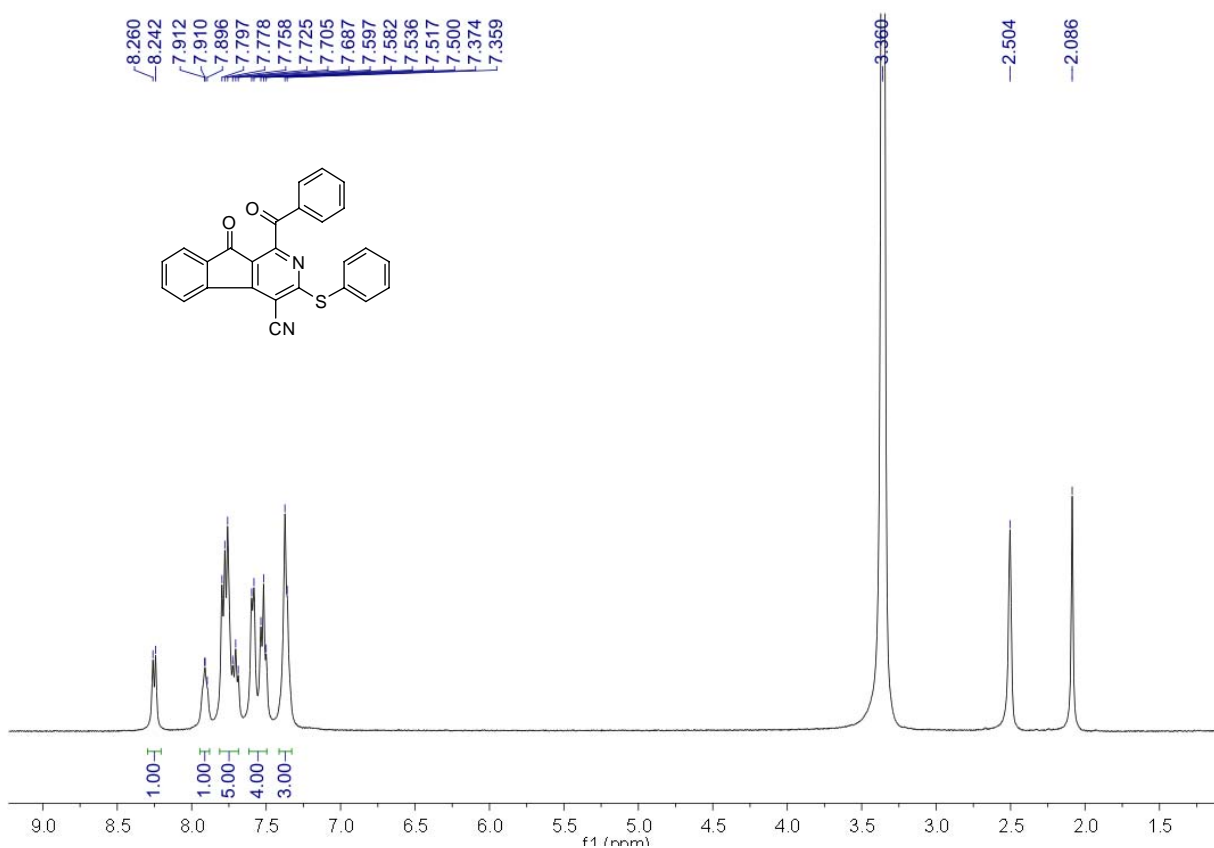


¹³C NMR Spectrum of Compound 4i



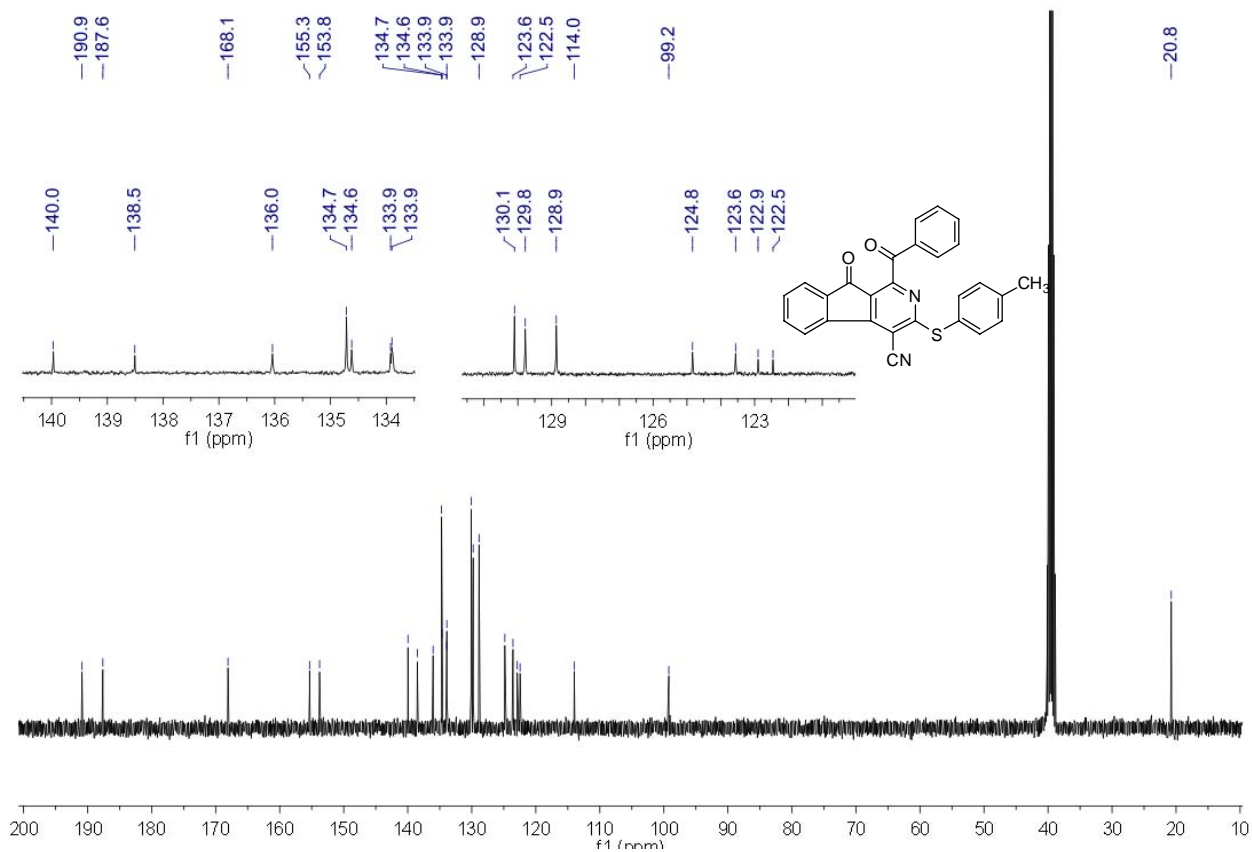
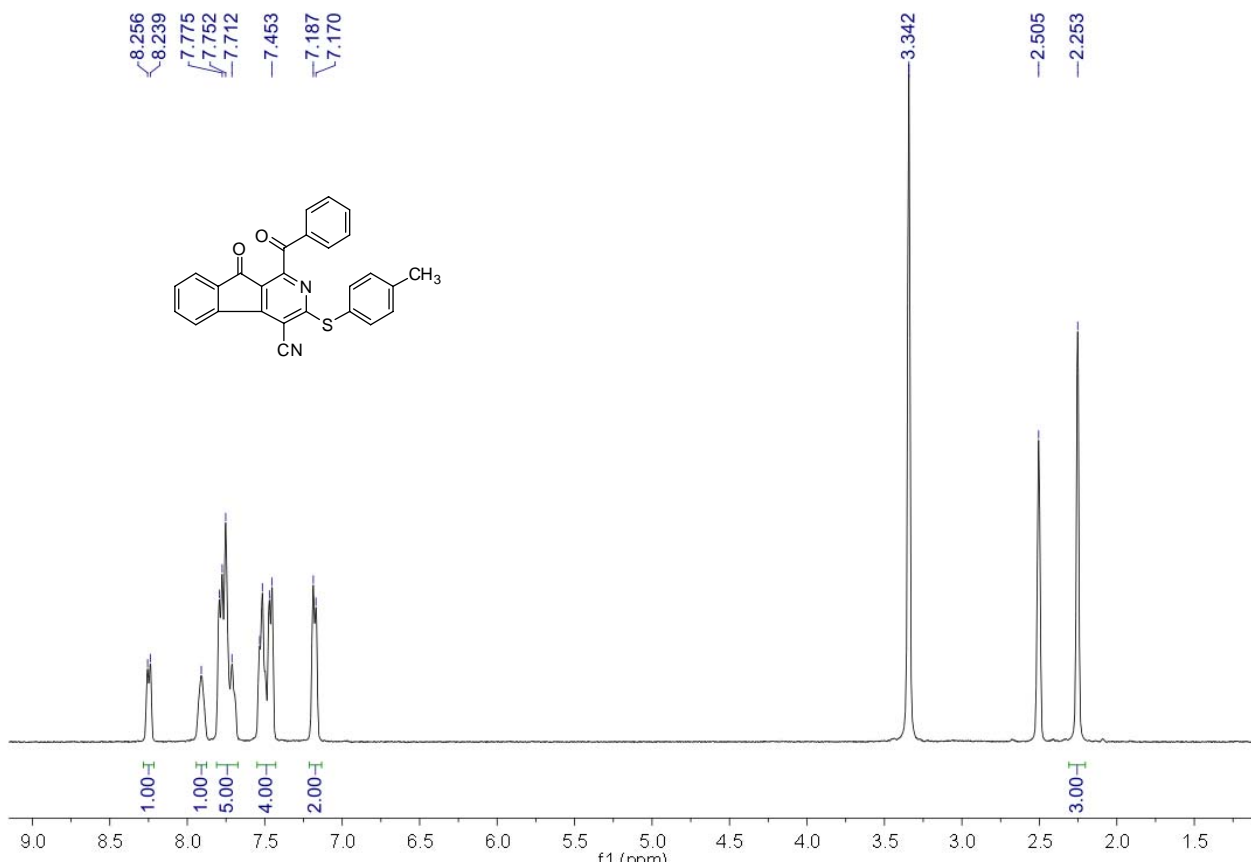
¹H NMR Spectrum of Compound 4j

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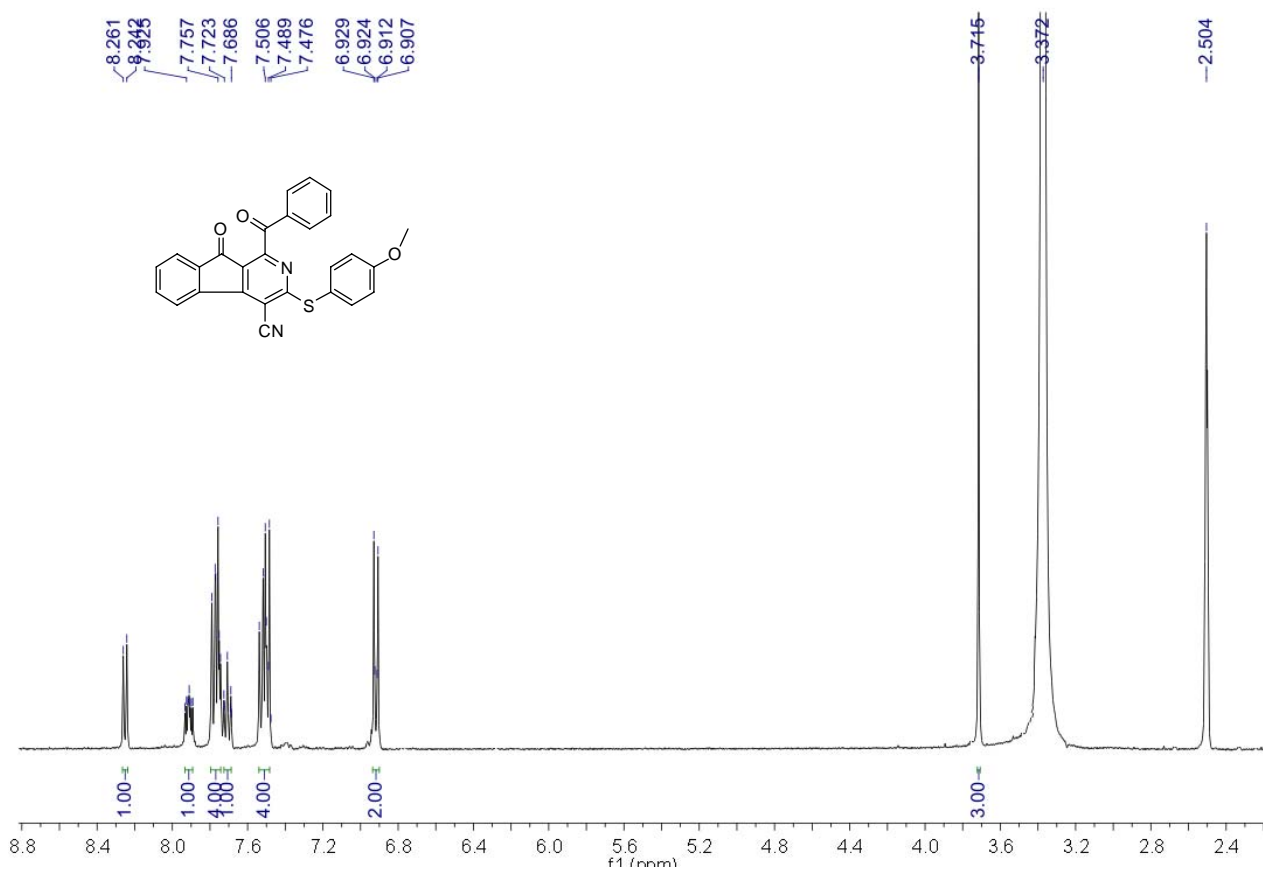


¹³C NMR Spectrum of Compound 4k

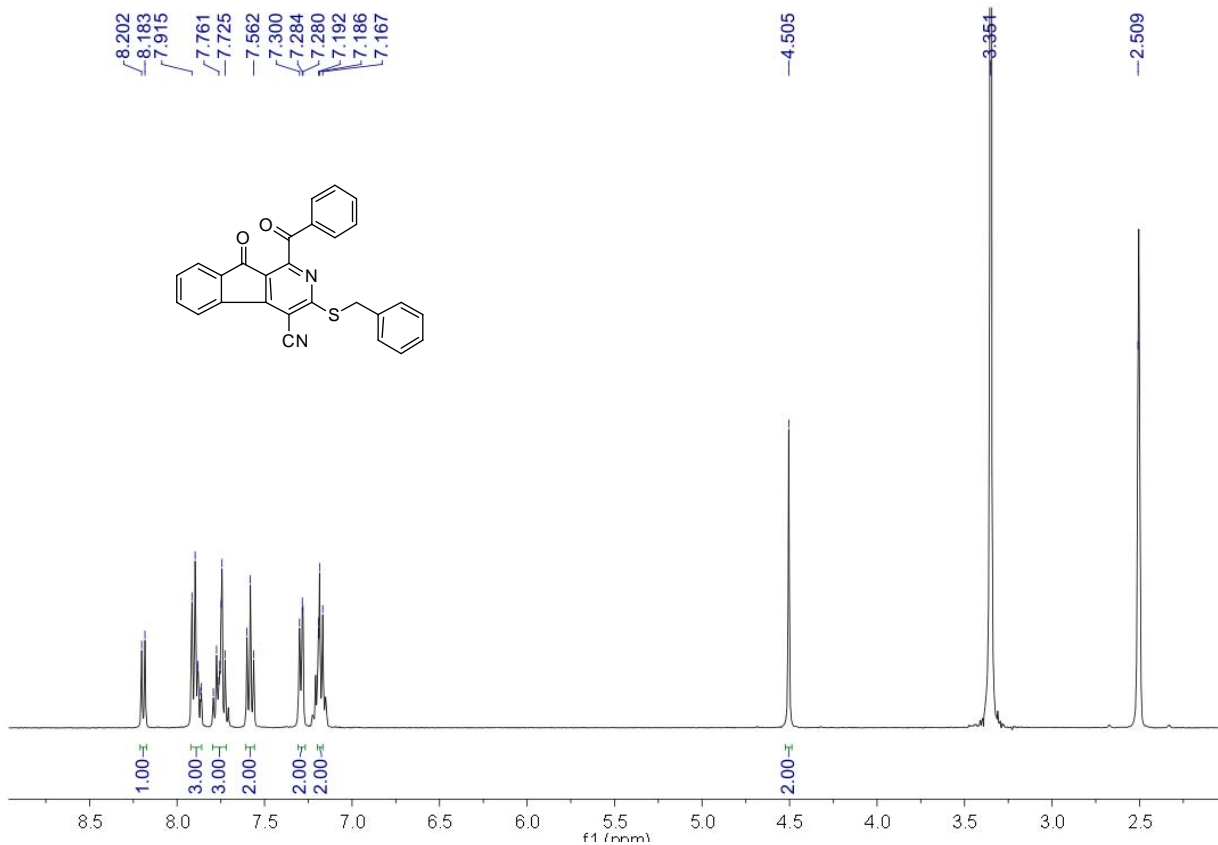
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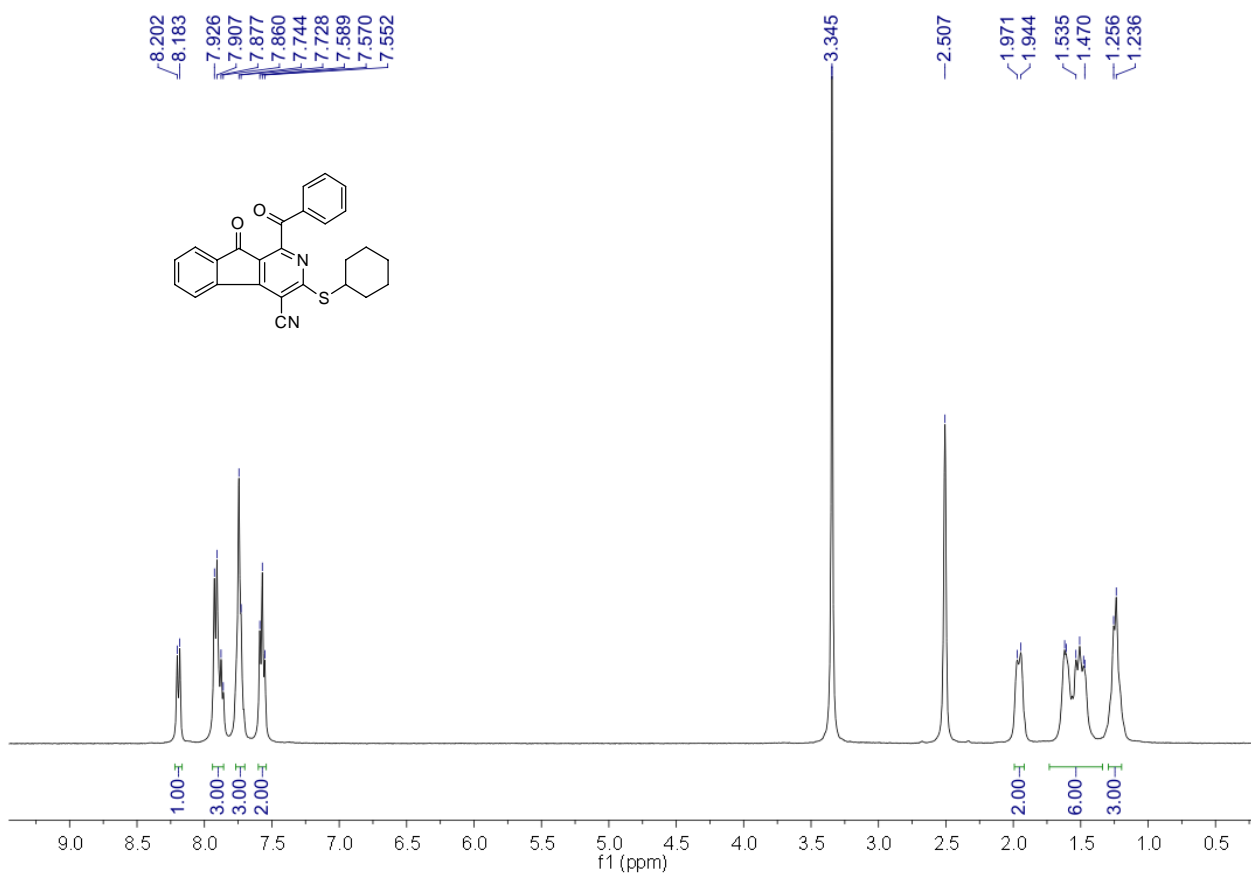


¹H NMR Spectrum of Compound 4m

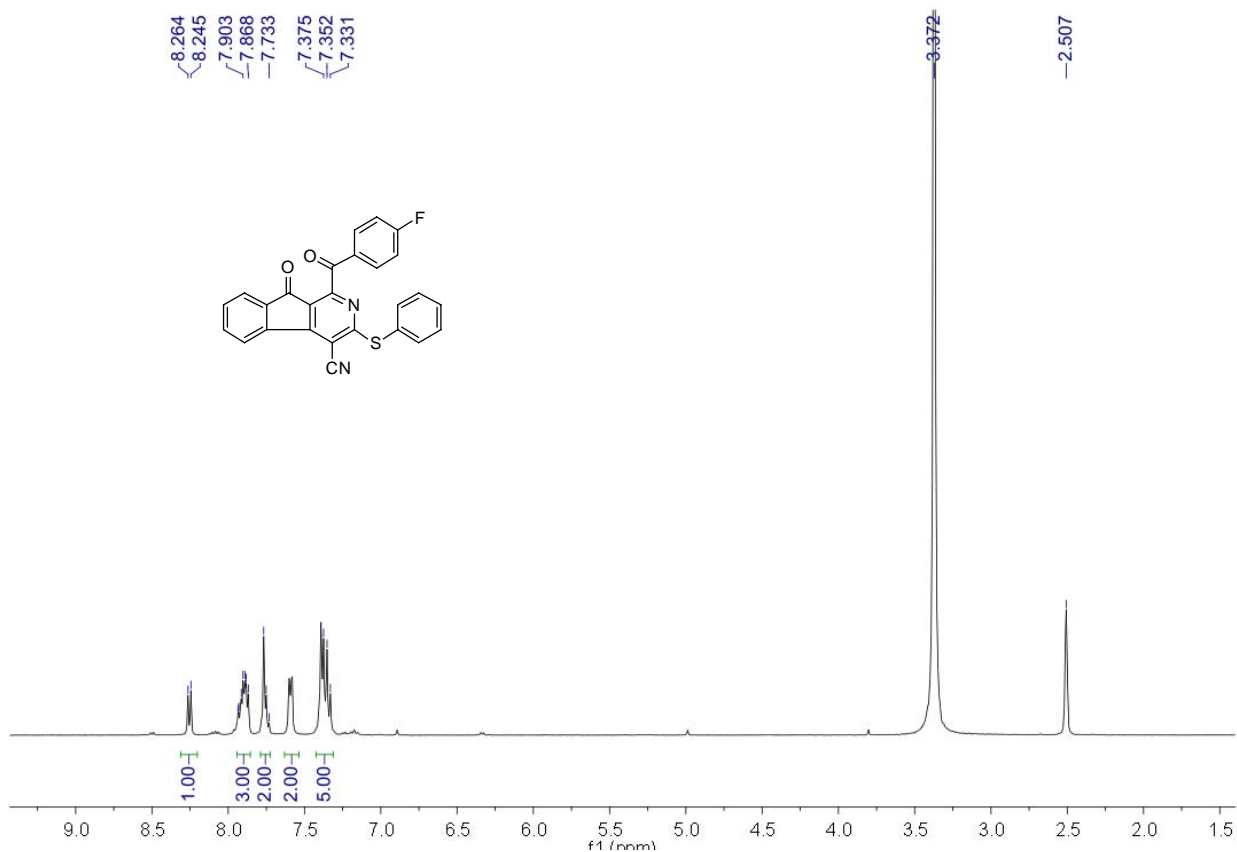


¹H NMR Spectrum of Compound 4n

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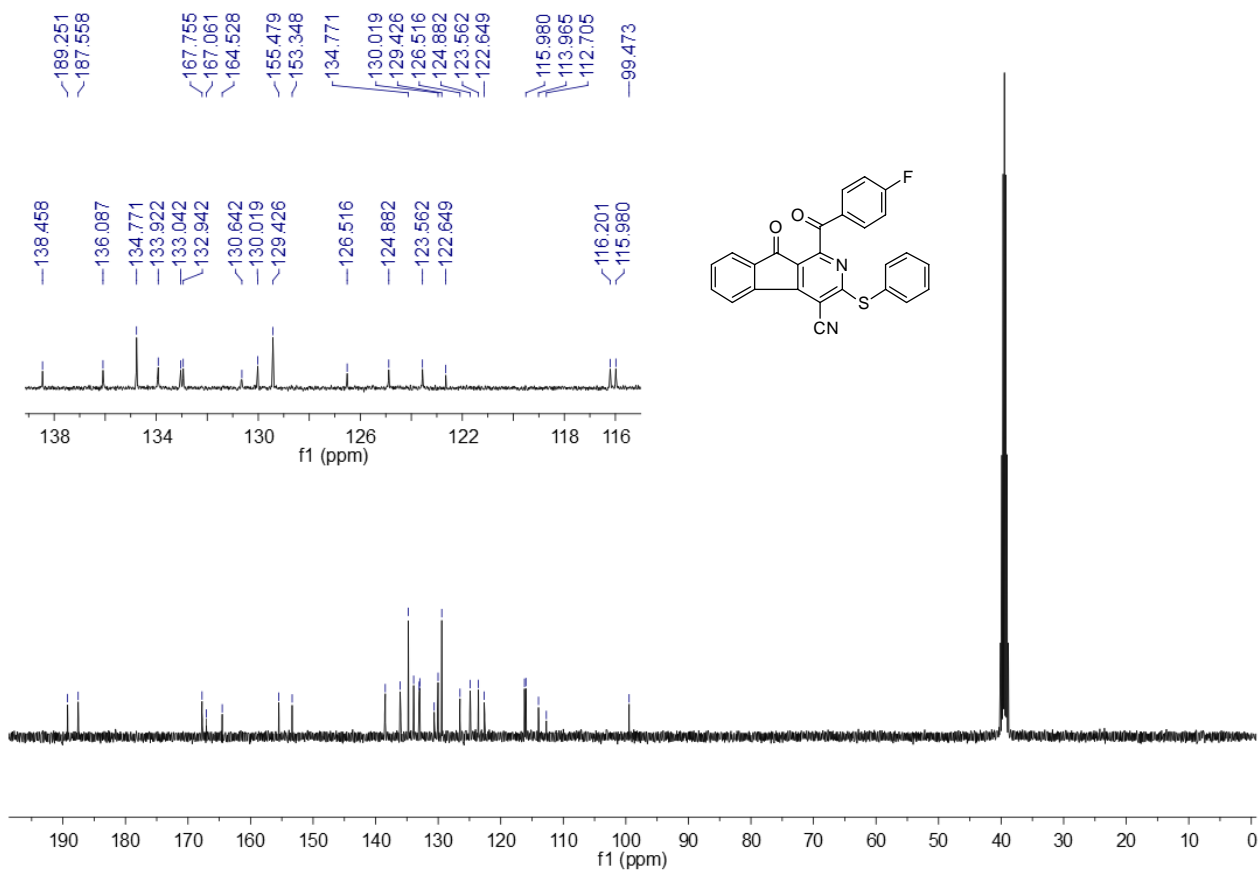


¹H NMR Spectrum of Compound 4o

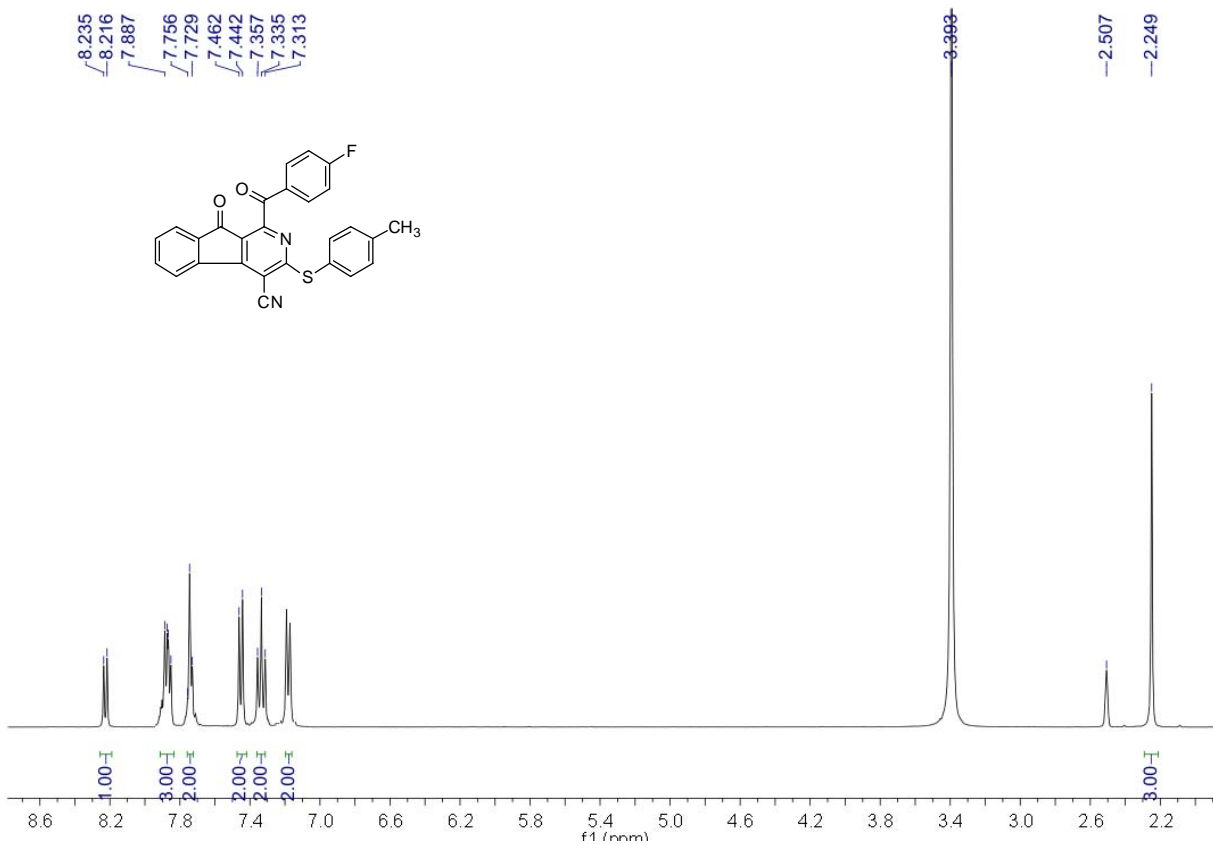


¹H NMR Spectrum of Compound 4p

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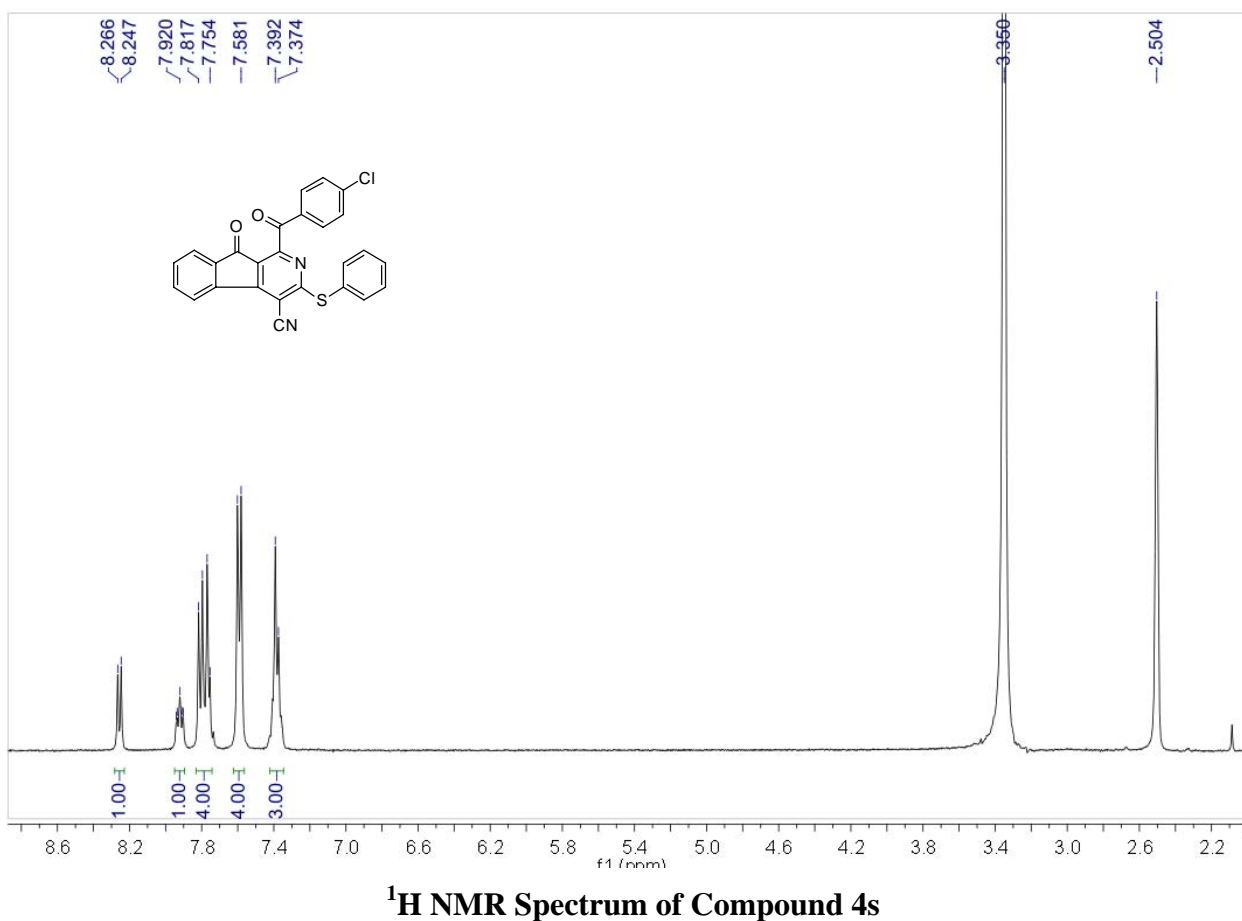
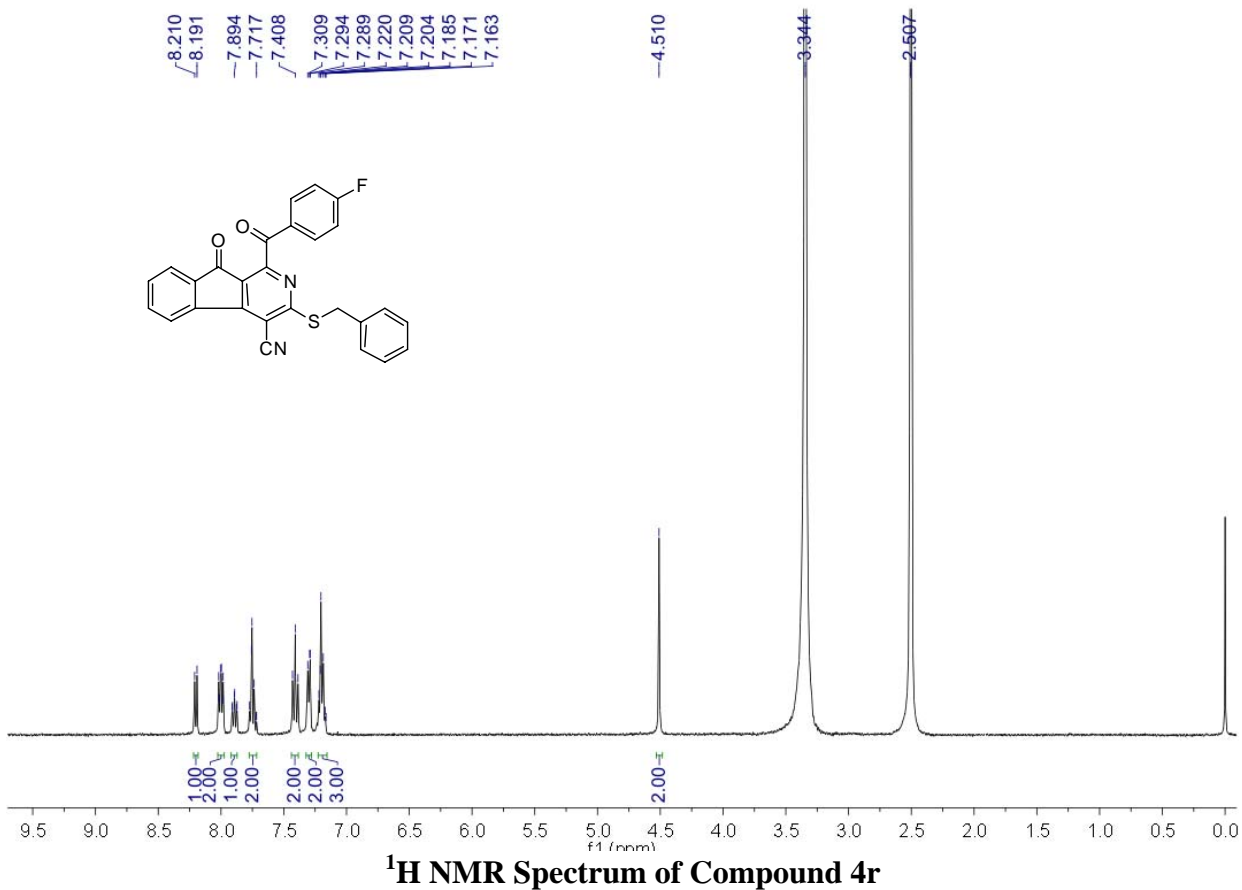


¹³C NMR Spectrum of Compound 4p

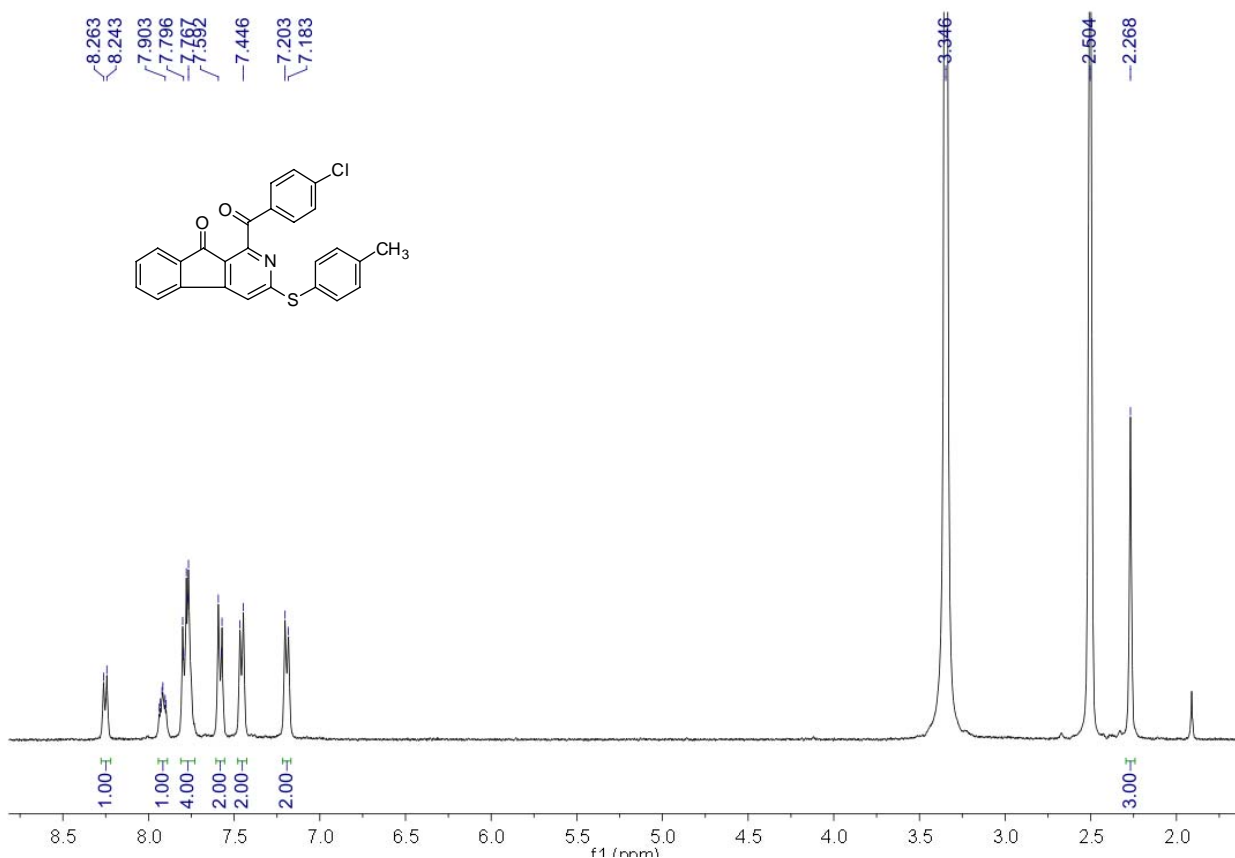


¹H NMR Spectrum of Compound 4q

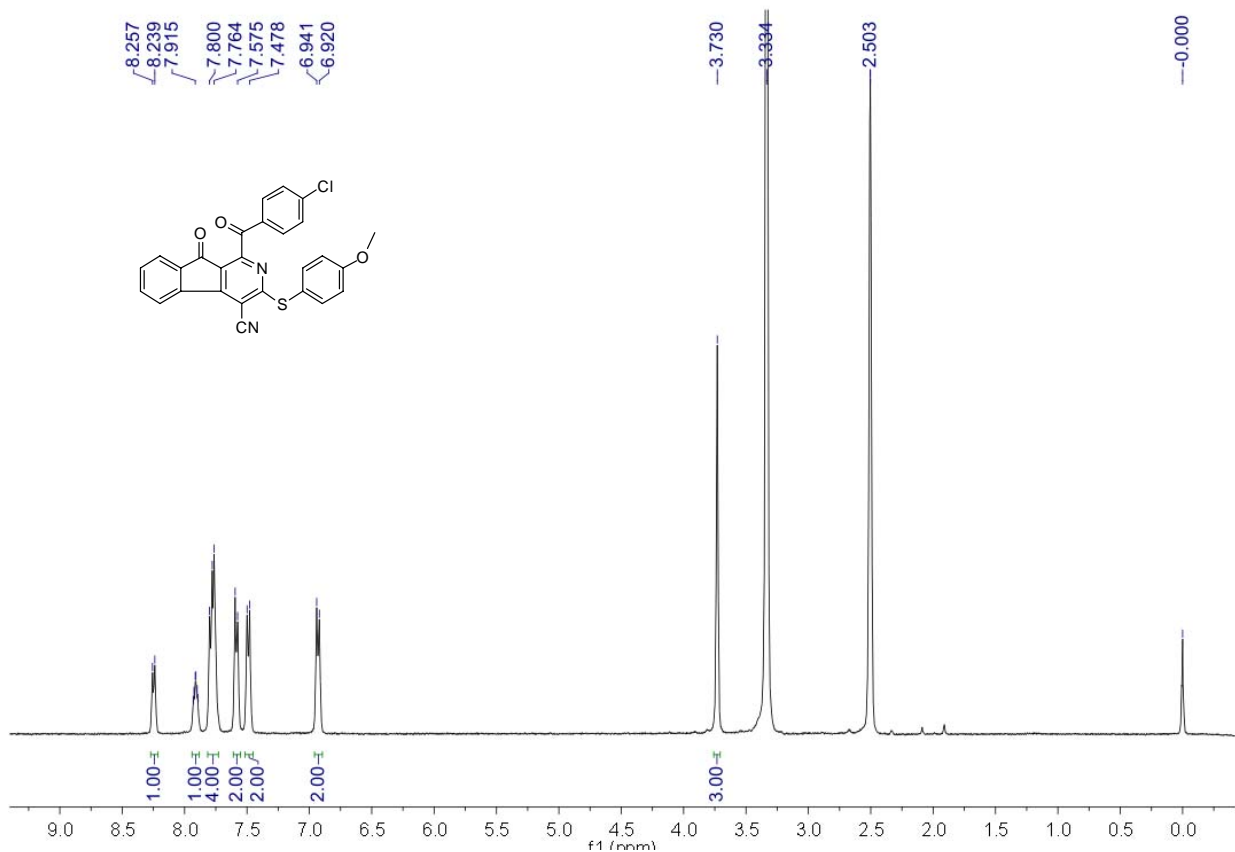
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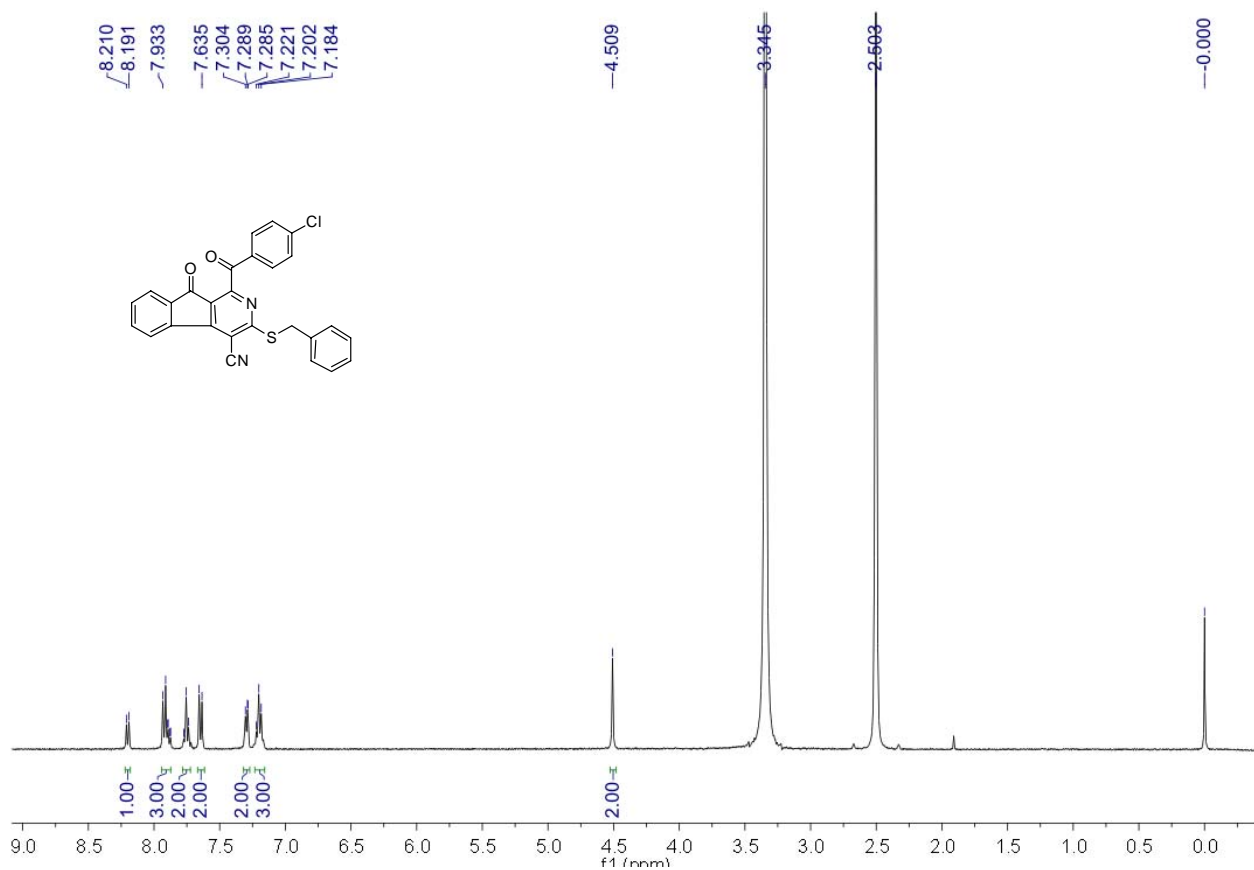


¹H NMR Spectrum of Compound 4t

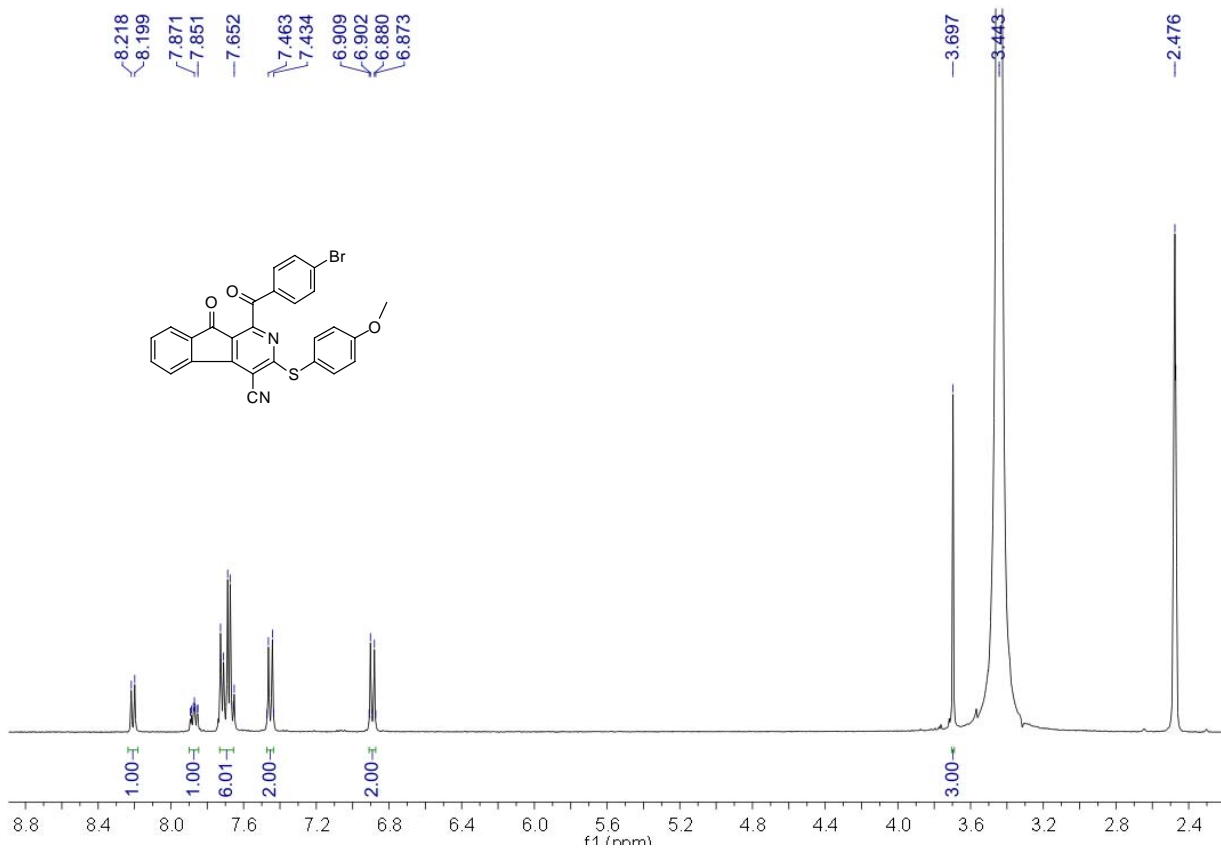


¹H NMR Spectrum of Compound 4u

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¹H NMR Spectrum of Compound 4v



¹H NMR Spectrum of Compound 4w