

Supplementary Information

PhI(OAc)₂-promoted metal-free oxidation of 2-oxoaldehydes: A facile one-pot synthesis of cyanoforamides

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(A) General Details

All the direct oxidative reactions of aldehydes were carried out under sealed tube. ^1H and ^{13}C NMR spectra were recorded with tetramethylsilane as the internal standard. TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with EtOAc/petroleum ether). ^1H NMR spectra were recorded at 400 or 600 MHz (Varian) and ^{13}C NMR spectra were recorded at 150 MHz (Varian). Chemical shifts are reported in ppm downfield from CDCl_3 ($\delta = 7.26$ ppm) for ^1H NMR and relative to the central CDCl_3 resonance ($\delta = 77.0$ ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. All the 2-oxoaldehydes **1** were prepared according to the reported procedures.¹ General chemicals were purchased from commercial suppliers and used without further purification.

(B) Experimental Procedure and Analytical Data of Products

1. General reaction procedure for the indosobenzene diacetate-promoted metal free synthesis of cyanoforamides from 2-oxoaldehydes

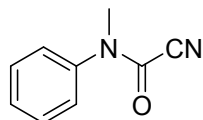
A 5 mL sealed tube was charged with NH_4OAc (3.0 mmol) and 2.0 mL of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v:v = 4:1). The mixture was stirred at room temperature until the solid was completely dissolved. Then 2-oxoaldehyde (1.0 mmol) was added. After stirring for 5 min, $\text{PhI}(\text{OAc})_2$ (2.0 mmol) was added. The reaction was carried out at room temperature in a sealed tube for 3h. The mixture was diluted with ethyl acetate, washed with water and brine. The combined organic phase was dried over anhydrous Na_2SO_4 . Removal of the organic solvent in a vacuum followed by flash silica gel column chromatographic purification (petroleum/ethyl acetate) afforded the corresponding product.

2. General reaction procedure for the synthesis of **2z** from **2n**

Compound **2n** (533 mg, 2.0 mmol) was dissolved in TFA (3.0 mL) under an atmosphere of nitrogen and anisole (0.44 mL, 4.0 mmol) was added. The reaction was carried out at 60 °C for 12 hours. After the reaction was complete (TLC), the mixture was diluted with ethyl acetate, washed with brine and triethylamine (1.5 mL). The combined organic phase was dried over anhydrous Na_2SO_4 . Removal of the organic solvent in a vacuum followed by flash silica gel column chromatographic purification (petroleum/ethyl acetate) afforded the product **2z**.

3. Spectroscopic characterization data of products

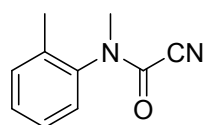
Methyl(phenyl)carbamoyl cyanide (2a)^[2]



2a

White solid, mp. 60-62 °C (Lit² 61-63 °C); ¹H NMR (CDCl₃, 400 MHz): δ 7.53-7.48 (m, 3H), 7.33-7.26 (m, 2H), 3.37 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.5, 139.8, 130.1, 129.7, 126.9, 110.6, 36.7. ESI HRMS: calcd. for C₉H₈N₂O+Na⁺ 183.1652, found 183.1653. Elemental Analysis: C, 67.49; H, 5.03; N, 17.49, found C, 67.54; H, 5.01; N, 17.45. IR (KBr, cm⁻¹): 3064, 2935, 2232, 1682, 1590, 1488, 1390, 996, 702.

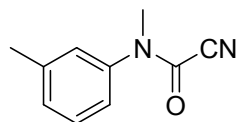
Methyl(o-tolyl)carbamoyl cyanide (2b)



2b

Yellow solid, mp. 70-74 °C; ¹H NMR (CDCl₃, 600 MHz): δ 7.40 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 3.39 (s, 3H), 2.31 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 145.1, 138.5, 136.0, 131.9, 130.3, 128.3, 127.8, 110.5, 35.8, 17.2. ESI HRMS: calcd. for C₁₀H₁₀N₂O+Na⁺ 197.0685, found 197.0687. Elemental Analysis: C, 68.95; H, 5.79; N, 16.08, found C, 69.02; H, 5.87; N, 15.92. IR (KBr, cm⁻¹): 3066, 2937, 2233, 1679, 1590, 1486, 1394, 1015, 699.

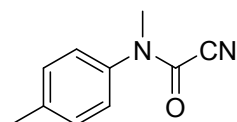
Methyl(m-tolyl)carbamoyl cyanide (2c)



2c

Yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 7.38-7.36 (m, 1H), 7.29-7.27 (m, 1H), 7.11-7.09 (m, 2H), 3.35 (s, 3H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.6, 140.4, 139.7, 130.5, 129.9, 127.5, 124.0, 110.7, 36.7, 21.2. ESI HRMS: calcd. for C₁₀H₁₀N₂O+Na⁺ 197.0685, found 197.0688. Elemental Analysis: C, 68.95; H, 5.79; N, 16.08, found C, 69.03; H, 5.72; N, 16.05. IR (KBr, cm⁻¹): 3067, 2945, 2231, 1683, 1587, 1489, 1392, 1017, 690.

Methyl(p-tolyl)carbamoyl cyanide (2d)

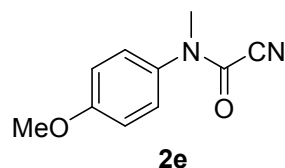


2d

Pale yellow solid, mp. 72-76 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.16 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.34 (s, 3H), 2.41 (s, 3H). ESI HRMS: calcd. for C₁₀H₁₀N₂O+Na⁺ 197.0685,

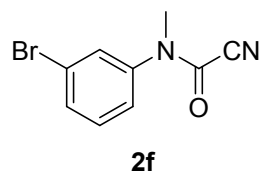
found 197.0688. Elemental Analysis: C, 68.95; H, 5.79; N, 16.08, found C, 69.01; H, 5.75; N, 16.04. IR (KBr, cm^{-1}): 3064, 2948, 2236, 1686, 1585, 1485, 1387, 1011, 700.

(4-Methoxyphenyl)(methyl)carbamoyl cyanide (2e)



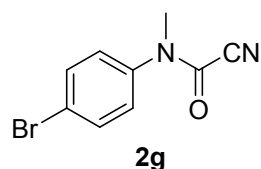
White solid, mp. 80-86 °C; ^1H NMR (CDCl_3 , 400 MHz): δ 7.23 (d, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 8.4$ Hz, 2H), 3.85 (s, 3H), 3.32 (s, 3H). ESI HRMS: calcd. for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2 + \text{Na}^+$ 213.0634, found 213.0638. Elemental Analysis: C, 63.15; H, 5.30; N, 14.73, found C, 63.24; H, 5.37; N, 14.55. IR (KBr, cm^{-1}): 3062, 2944, 2848, 2234, 1687, 1609, 1511, 1389, 1016, 723.

(3-Bromophenyl)(methyl)carbamoyl cyanide (2f)



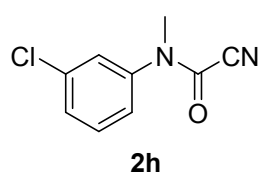
Yellow liquid; ^1H NMR (CDCl_3 , 600 MHz): δ 7.63 (d, $J = 8.4$ Hz, 1H), 7.50-7.49 (m, 1H), 7.39 (t, $J = 8.4$ Hz, 1H), 7.28 (d, $J = 8.4$ Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 144.3, 140.9, 133.0, 131.4, 130.2, 125.9, 123.4, 110.3, 36.8. ESI HRMS: calcd. for $\text{C}_9\text{H}_7\text{BrN}_2\text{O} + \text{Na}^+$ 260.9634, found 260.9639. Elemental Analysis: C, 45.22; H, 2.95; N, 11.72, found C, 45.30; H, 2.90; N, 11.70. IR (KBr, cm^{-1}): 3068, 2924, 2231, 1683, 1585, 1475, 1373, 1044, 692.

(4-Bromophenyl)(methyl)carbamoyl cyanide (2g)



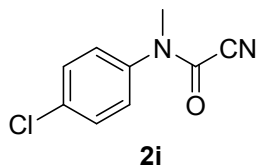
Pale yellow solid, mp. 100-102 °C; ^1H NMR (CDCl_3 , 400 MHz): δ 7.66-7.57 (m, 2H), 7.26-7.18 (m, 2H), 3.35 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 144.3, 138.8, 133.4, 128.6, 123.9, 110.4, 36.7. ESI HRMS: calcd. for $\text{C}_9\text{H}_7\text{BrN}_2\text{O} + \text{Na}^+$ 260.9634, found 260.9637. Elemental Analysis: C, 45.22; H, 2.95; N, 11.72, found C, 45.35; H, 2.89; N, 11.70. IR (KBr, cm^{-1}): 3067, 2923, 2233, 1682, 1583, 1474, 1373, 1044, 699.

(3-Chlorophenyl)(methyl)carbamoyl cyanide (2h)



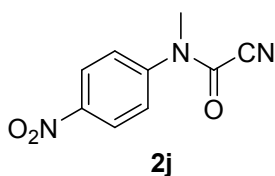
Yellow liquid; ^1H NMR (CDCl_3 , 400 MHz): δ 7.48-7.44 (m, 2H), 7.34-7.33 (m, 1H), 7.25-7.22 (m, 1H), 3.37 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 144.3, 140.8, 135.8, 131.1, 130.1, 127.3, 125.4, 110.3, 36.8. ESI HRMS: calcd. for $\text{C}_9\text{H}_7\text{ClN}_2\text{O}+\text{Na}^+$ 217.0139, found 217.0140. Elemental Analysis: C, 55.54; H, 3.63; N, 14.39, found C, 55.60; H, 3.59; N, 14.37. IR (KBr, cm^{-1}): 3066, 2925, 2231, 1685, 1586, 1477, 1373, 1028, 677.

(4-Chlorophenyl)(methyl)carbamoyl cyanide (2i)



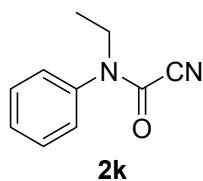
Pale yellow liquid; ^1H NMR (CDCl_3 , 400 MHz): δ 7.49 (d, $J = 8.8$ Hz, 2H), 7.27 (d, $J = 8.8$ Hz, 2H), 3.35 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 144.4, 138.3, 135.9, 130.4, 128.4, 110.4, 36.8. ESI HRMS: calcd. for $\text{C}_9\text{H}_7\text{ClN}_2\text{O}+\text{Na}^+$ 217.0139, found 217.0141. Elemental Analysis: C, 55.54; H, 3.63; N, 14.39, found C, 55.62; H, 3.58; N, 14.36. IR (KBr, cm^{-1}): 3060, 2948, 2233, 1680, 1591, 1485, 1378, 1012, 713.

Methyl(4-nitrophenyl)carbamoyl cyanide (2j)



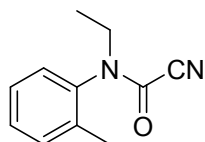
Pale yellow solid, mp. 98-102 °C; ^1H NMR (CDCl_3 , 400 MHz): δ 7.65 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 3.35 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 144.3, 138.8, 133.4, 128.6, 123.9, 110.4, 36.7. ESI HRMS: calcd. for $\text{C}_9\text{H}_7\text{N}_3\text{O}_3+\text{Na}^+$ 228.0380, found 228.0382. Elemental Analysis: C, 52.69; H, 3.44; N, 20.48, found C, 52.77; H, 3.39; N, 20.43. IR (KBr, cm^{-1}): 3063, 2936, 2233, 1689, 1587, 1489, 1392, 1014, 719.

Ethyl(phenyl)carbamoyl cyanide (2k)



Yellow solid, mp. 90-92 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 7.53-7.50 (m, 3H), 7.29-7.28 (m, 2H), 3.83 (q, $J = 7.2$ Hz, 2H), 1.18 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 144.3, 138.2, 130.1, 129.9, 128.1, 110.6, 44.4, 12.3. ESI HRMS: calcd. for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}+\text{Na}^+$ 197.0685, found 197.0689. Elemental Analysis: C, 68.95; H, 5.79; N, 16.08, found C, 69.02; H, 5.77; N, 16.02. IR (KBr, cm^{-1}): 3062, 2933, 2235, 1686, 1586, 1488, 1389, 1032, 696.

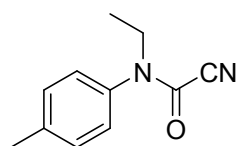
Ethyl(o-tolyl)carbamoyl cyanide (2l)



2l

Yellow liquid; ^1H NMR (CDCl_3 , 400 MHz): δ 7.43-7.34 (m, 2H), 7.33-7.31 (m, 1H), 7.19-7.17 (m, 1H), 4.06-3.99 (m, 1H), 3.50-3.43 (m, 1H), 2.31 (s, 3H), 1.19 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 144.8, 136.9, 136.5, 131.9, 130.3, 129.4, 127.5, 110.7, 43.6, 17.5, 12.2. ESI HRMS: calcd. for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}+\text{Na}^+$ 211.0842, found 211.0846. Elemental Analysis: C, 70.19; H, 6.43; N, 14.88, found C, 70.26; H, 6.51; N, 14.72. IR (KBr, cm^{-1}): 3065, 2944, 2233, 1684, 1584, 1500, 1379, 1020, 688.

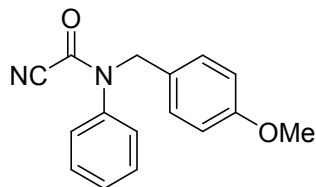
Ethyl(p-tolyl)carbamoyl cyanide (2m)



2m

White solid, mp. 56-60 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 7.31-7.26 (m, 2H), 7.25-7.15 (m, 2H), 3.80 (q, $J = 7.2$ Hz, 2H), 2.42 (s, 3H), 1.82 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 144.4, 140.1, 135.5, 130.7, 127.9, 110.8, 44.3, 21.1, 12.3. ESI HRMS: calcd. for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}+\text{Na}^+$ 211.0842, found 211.0845. Elemental Analysis: C, 70.19; H, 6.43; N, 14.88, found C, 70.27; H, 6.38; N, 14.83. IR (KBr, cm^{-1}): 3068, 2936, 2231, 1676, 1589, 1485, 1394, 1016, 698.

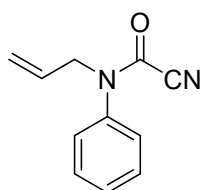
(4-Methoxybenzyl)(phenyl)carbamoyl cyanide (2n)



2n

Yellow liquid; ^1H NMR (CDCl_3 , 600 MHz): δ 7.45-7.40 (m, 3H), 7.08-7.07 (m, 4H), 6.81 (d, $J = 8.4$ Hz, 2H), 4.85 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 159.6, 144.7, 138.1, 130.5, 129.9, 129.8, 128.4, 126.6, 114.1, 110.5, 55.2, 52.5. ESI HRMS: calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2+\text{Na}^+$ 289.0947, found 289.0954. Elemental Analysis: C, 72.17; H, 5.30; N, 10.52, found C, 72.25; H, 5.23; N, 10.59. IR (KBr, cm^{-1}): 3066, 2936, 2840, 2230, 1676, 1610, 1594, 1512, 1442, 1395, 1032, 698.

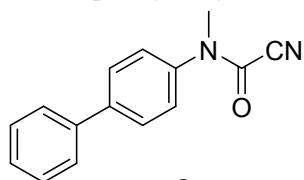
Allyl(phenyl)carbamoyl cyanide (2o)



2o

Pale yellow solid, mp. 50-54 °C; ¹H NMR (CDCl₃, 600 MHz): δ 7.51-7.49 (m, 3H), 7.30-7.25 (m, 2H), 5.84-5.77 (m, 1H), 5.25-5.18 (m, 2H), 4.35 (d, *J* = 6.0 Hz, 2H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.4, 138.4, 130.2, 130.0, 129.9, 128.0, 120.3, 110.5, 52.0. ESI HRMS: calcd. for C₁₁H₁₀N₂O+Na⁺ 209.0685, found 209.0687. Elemental Analysis: C, 70.95; H, 5.41; N, 15.04, found C, 71.02; H, 5.49; N, 14.94. IR (KBr, cm⁻¹): 3090, 3064, 2927, 2230, 1674, 1589, 1489, 1394, 997, 700.

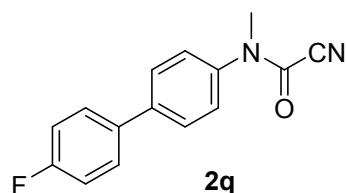
[1,1'-Biphenyl]-4-yl(methyl)carbamoyl cyanide (2p)



2p

Pale yellow solid, mp. 140-144 °C; ¹H NMR (CDCl₃, 600 MHz): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.39-7.38 (m, 1H), 3.41 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.5, 142.8, 139.4, 138.8, 129.0, 128.7, 128.1, 127.3, 127.2, 110.7, 36.8. ESI HRMS: calcd. for C₁₅H₁₂N₂O+Na⁺ 259.0842, found 259.0843. Elemental Analysis: C, 76.25; H, 5.12; N, 11.86, found C, 76.32; H, 5.10; N, 11.80. IR (KBr, cm⁻¹): 3060, 2938, 2230, 1687, 1604, 1518, 1480, 1390, 1021, 708.

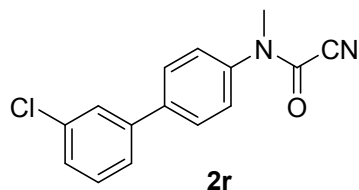
(4'-Fluoro-[1,1'-biphenyl]-4-yl)(methyl)carbamoyl cyanide (2q)



2q

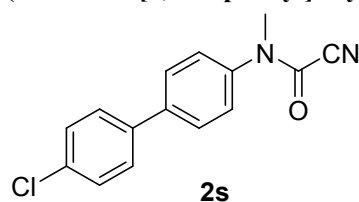
Yellow solid, mp. 108-112 °C; ¹H NMR (CDCl₃, 600 MHz): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 3.40 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 162.0, 144.5, 141.7, 138.8, 135.5, 128.8, 128.6, 127.3, 116.0, 115.9, 110.7, 36.8. ESI HRMS: calcd. for C₁₅H₁₁FN₂O+Na⁺ 277.0748, found 277.0753. Elemental Analysis: C, 70.86; H, 4.36; N, 11.02, found C, 70.95; H, 4.43; N, 10.86. IR (KBr, cm⁻¹): 3057, 2945, 2230, 1678, 1600, 1520, 1481, 1385, 1097, 715.

(3'-Chloro-[1,1'-biphenyl]-4-yl)(methyl)carbamoyl cyanide (2r)



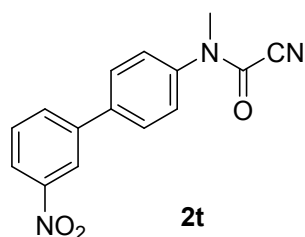
White solid, mp. 122-126 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.58 (s, 1H), 7.48-7.47 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 4H), 3.41 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.4, 141.3, 141.2, 139.3, 134.9, 130.2, 128.7, 128.1, 127.4, 127.3, 125.3, 110.6, 36.8. ESI HRMS: calcd. for C₁₅H₁₁ClN₂O+Na⁺ 293.0452, found 293.0453. Elemental Analysis: C, 66.55; H, 4.10; N, 10.35, found C, 66.64; H, 4.17; N, 10.21. IR (KBr, cm⁻¹): 3060, 2948, 2235, 1688, 1604, 1521, 1483, 1388, 1098, 710.

(4'-Chloro-[1,1'-biphenyl]-4-yl)(methyl)carbamoyl cyanide (2s)



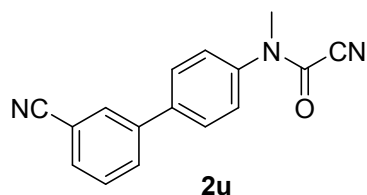
White solid, mp. 84-88 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 3.40 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.5, 141.5, 139.0, 137.8, 134.3, 129.2, 128.6, 128.4, 127.4, 110.6, 36.8. ESI HRMS: calcd. for C₁₅H₁₁ClN₂O+Na⁺ 293.0452, found 293.0463. Elemental Analysis: C, 66.55; H, 4.10; N, 10.35, found C, 66.62; H, 4.18; N, 10.30. IR (KBr, cm⁻¹): 3059, 2949, 2236, 1689, 1602, 1520, 1483, 1389, 1099, 711.

Methyl(3'-nitro-[1,1'-biphenyl]-4-yl)carbamoyl cyanide (2t)



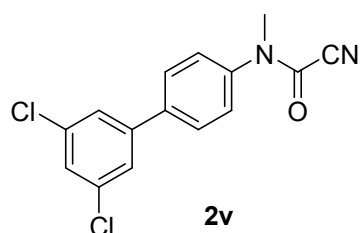
White solid, mp. 142-146 °C; ¹H NMR (CDCl₃, 600 MHz): δ 8.47 (s, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.47-7.46 (m, 2H), 3.34 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 148.8, 144.4, 141.1, 140.2, 140.0, 133.0, 130.1, 128.9, 127.7, 122.9, 122.1, 110.6, 36.8. ESI HRMS: calcd. for C₁₅H₁₁N₃O₃+Na⁺ 304.0693, found 304.0696. Elemental Analysis: C, 64.05; H, 3.94; N, 14.94, found C, 64.18; H, 3.88; N, 14.86. IR (KBr, cm⁻¹): 3067, 2933, 2230, 1678, 1608, 1510, 1477, 1392, 1012, 699.

(3'-Cyano-[1,1'-biphenyl]-4-yl)(methyl)carbamoyl cyanide (2u)



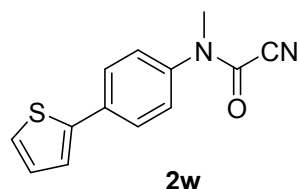
White solid, mp. 136-138 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.88 (s, 1H), 7.85-7.82 (m, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.62-7.58 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 3.42 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.4, 140.7, 140.3, 139.8, 131.5, 130.7, 129.9, 128.8, 127.7, 125.5, 118.5, 113.3, 110.5, 36.8. ESI HRMS: calcd. for C₁₆H₁₁N₃O+Na⁺ 284.0794, found 284.0794. Elemental Analysis: C, 73.55; H, 4.24; N, 16.08, found C, 73.62; H, 4.32; N, 15.98. IR (KBr, cm⁻¹): 3068, 2925, 2230, 1682, 1607, 1514, 1479, 1393, 1016, 688.

(3',5'-Dichloro-[1,1'-biphenyl]-4-yl)(methyl)carbamoyl cyanide (2v)



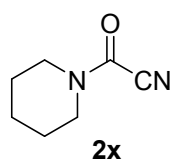
White solid, mp. 146-152 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.68-7.62 (m, 3H), 7.47-7.40 (m, 4H), 3.41 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.4, 142.3, 140.0, 139.8, 135.6, 128.8, 128.0, 127.6, 125.7, 110.5, 36.8. ESI HRMS: calcd. for C₁₅H₁₀Cl₂N₂O+Na⁺ 327.0062, found 327.0066. Elemental Analysis: C, 59.04; H, 3.30; N, 9.18, found C, 59.11; H, 3.38; N, 9.32. IR (KBr, cm⁻¹): 3065, 2940, 2233, 1683, 1599, 1498, 1390, 1014, 718.

Methyl(4-(thiophen-2-yl)phenyl)carbamoyl cyanide (2w)



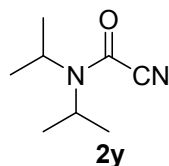
Pale yellow solid, mp. 150-156 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.74-7.72 (m, 2H), 7.38-7.31 (m, 4H), 7.13-7.11 (m, 1H), 3.38 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.5, 142.3, 138.5, 135.9, 128.3, 127.4, 127.3, 126.1, 124.3, 110.6, 36.7. ESI HRMS: calcd. for C₁₃H₁₀N₂SO+Na⁺ 265.0406, found 265.0406. Elemental Analysis: C, 64.44; H, 4.16; N, 11.56; S, 13.23, found C, 64.53; H, 4.23; N, 11.50; S, 13.03. IR (KBr, cm⁻¹): 3065, 2943, 2231, 1683, 1592, 1489, 1379, 1012, 699.

Piperidine-1-carbonyl cyanide (2x)^[2]



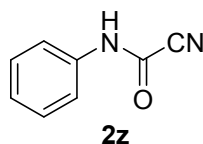
Colorless oil (Lit²); ¹H NMR (CDCl₃, 400 MHz): δ 3.71-3.70 (m, 2H), 3.57 (t, *J* = 6.0 Hz, 2H), 1.71-1.69 (m, 4H), 1.62-1.59 (m, 2H).

Diisopropylcarbamoyl cyanide (2y)^[3]



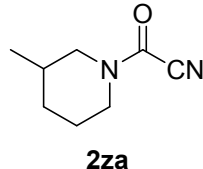
Colorless oil (Lit³); ¹H NMR (CDCl₃, 400 MHz): δ 4.47-4.39 (m, 2H), 1.43-1.36 (m, 6H), 1.31-1.24 (m, 6H).

Phenylcarbamoyl cyanide (2z)^[2]



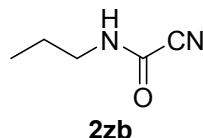
Pale yellow solid, mp. 100-104 °C (Lit² 104-106 °C); ¹H NMR (CDCl₃, 600 MHz): δ 8.29 (bs, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H).

3-Methylpiperidine-1-carbonyl cyanide (2za)



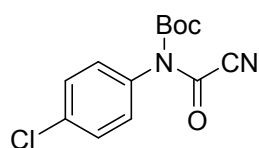
Colorless oil; ¹H NMR (CDCl₃, 400 MHz): δ 4.29-4.02 (m, 2H), 3.25-2.44 (m, 2H), 1.92-1.44 (m, 4H), 1.29-1.17 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.3, 110.6, 54.8, 48.0, 34.2, 28.8, 23.4, 18.6. ESI HRMS: calcd. for C₈H₁₂N₂O+Na⁺ 175.0842, found 175.0845. Elemental Analysis: C, 63.13; H, 7.95; N, 18.41; found C, 63.21; H, 7.90; N, 18.36. IR (KBr, cm⁻¹): 3040, 2895, 2854, 2229, 1689, 1186.

Propylcarbamoyl cyanide (2zb)



Colorless oil; ¹H NMR (CDCl₃, 400 MHz): δ 6.67 (s, 1H), 3.35-3.30 (m, 2H), 1.68-1.57 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.5, 110.4, 42.5, 23.2, 11.2. ESI HRMS: calcd. for C₅H₈N₂O+Na⁺ 135.0529, found 135.0530. Elemental Analysis: C, 53.56; H, 7.19; N, 24.98; found C, 53.69; H, 7.13; N, 24.90. IR (KBr, cm⁻¹): 3436, 2923, 2853, 2237, 1684, 1255.

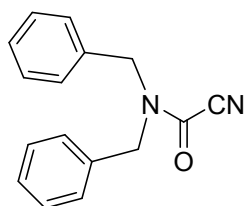
***tert*-Butyl (4-chlorophenyl)(cyanocarbonyl)carbamate (2zc)**



2zc

White solid, mp. 80-84 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.32-7.30 (m, 2H), 7.25-7.23 (m, 2H), 1.51 (s, 9H). ¹³C NMR (CDCl₃, 150 MHz): δ 151.2, 144.2, 138.1, 134.7, 130.2, 128.2, 110.5, 84.5, 33.4. ESI HRMS: calcd. for C₁₃H₁₃ClN₂O₃+Na⁺ 303.0507, found 303.0511. Elemental Analysis: C, 55.62; H, 4.67; N, 9.98; found C, 55.68; H, 4.63; N, 9.94. IR (KBr, cm⁻¹): 2933, 2231, 1704, 1682, 1584, 1476, 1372, 1250, 1040, 710.

Dibenzylcarbamoyl cyanide (2zd)



2zd

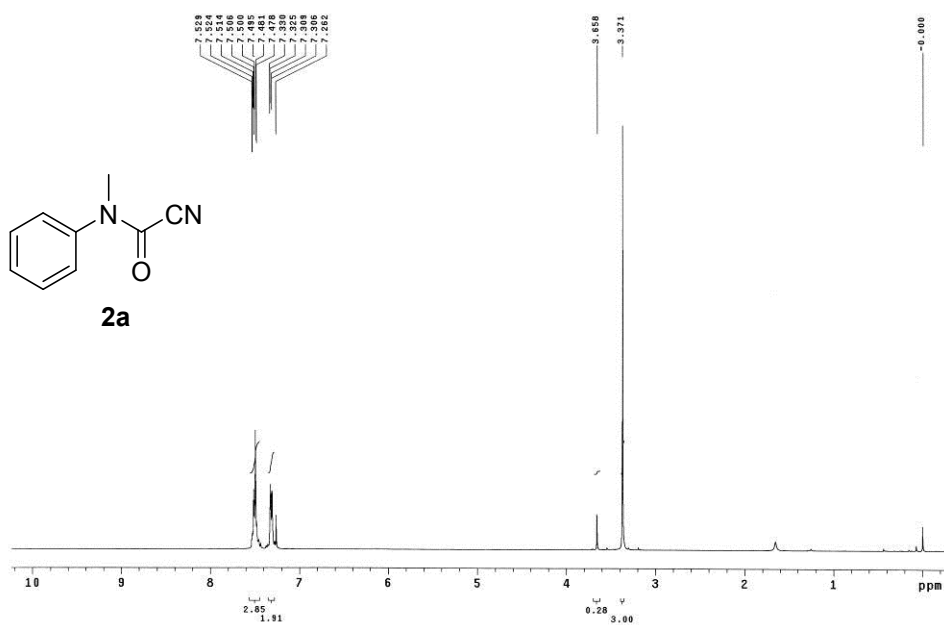
Yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 7.44-7.36 (m, 5H), 7.26-7.19 (m, 5H), 4.65 (s, 2H), 4.49 (s, 2H); ¹³C NMR (CDCl₃, 150 MHz): δ 144.4, 139.8, 136.9, 136.1, 128.5, 128.2, 128.0, 127.8, 127.7, 127.3, 127.1, 126.5, 126.1, 110.7, 52.1, 50.3. ESI HRMS: calcd. for C₁₆H₁₄N₂O+Na⁺ 273.0998, found 273.1003. Elemental Analysis: C, 76.78; H, 5.64; N, 11.19; found C, 76.85; H, 5.62; N, 11.13. IR (KBr, cm⁻¹): 3065, 2230, 1688, 1618, 1489, 1470, 1381, 1235, 1024, 718, 694.

(C) References

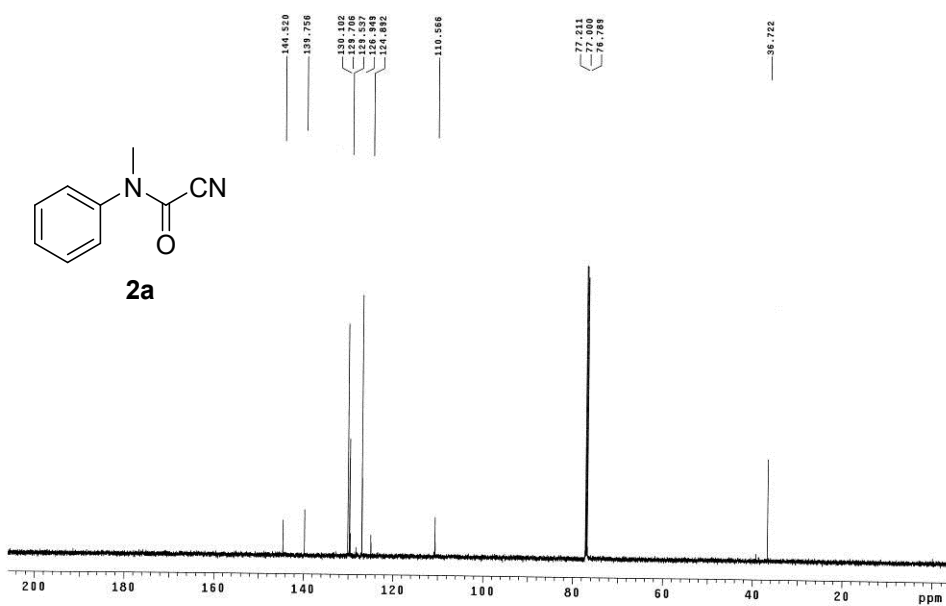
- [1] Marc, M.; Johannes, C.; Vogel, W. T. *Org. Biomol. Chem.*, **2009**, *7*, 589.
- [2] Yang, J. M.; Xiang, D. X.; Zhang, R.; Zhang, N.; Liang Y. J.; Dong, D. *Org. Lett.*, **2015**, *17*, 809.
- [3] Fu, X. P.; Chen, J. J.; Li, G. Y.; Liu, Y. H. *Angew. Chem. Int. Ed.*, **2009**, *48*, 5500.

(D) ^1H NMR and ^{13}C NMR Spectra of Products

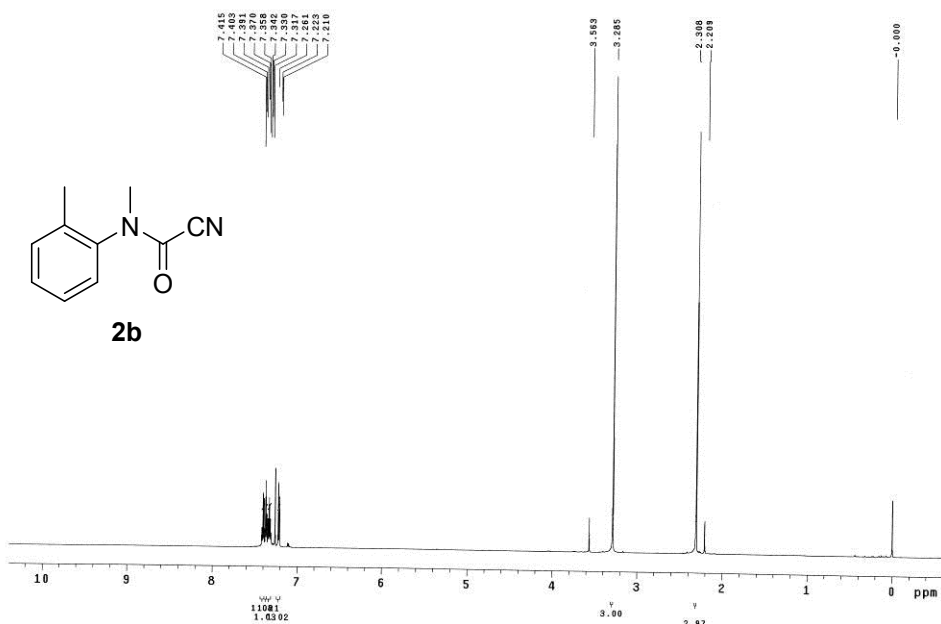
CK-2 H1 CDC13 2015-4-16
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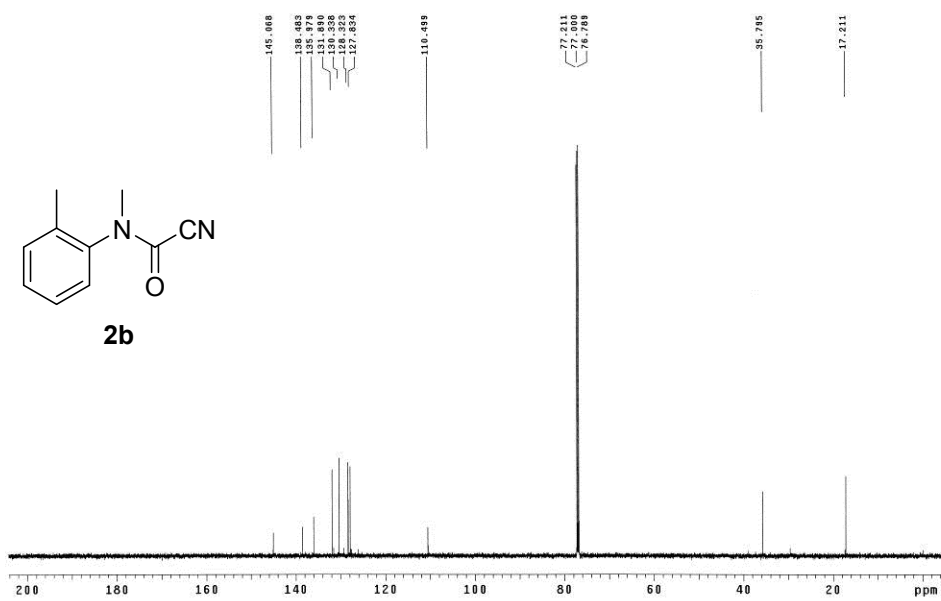
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Pulse Sequence: s2pu1



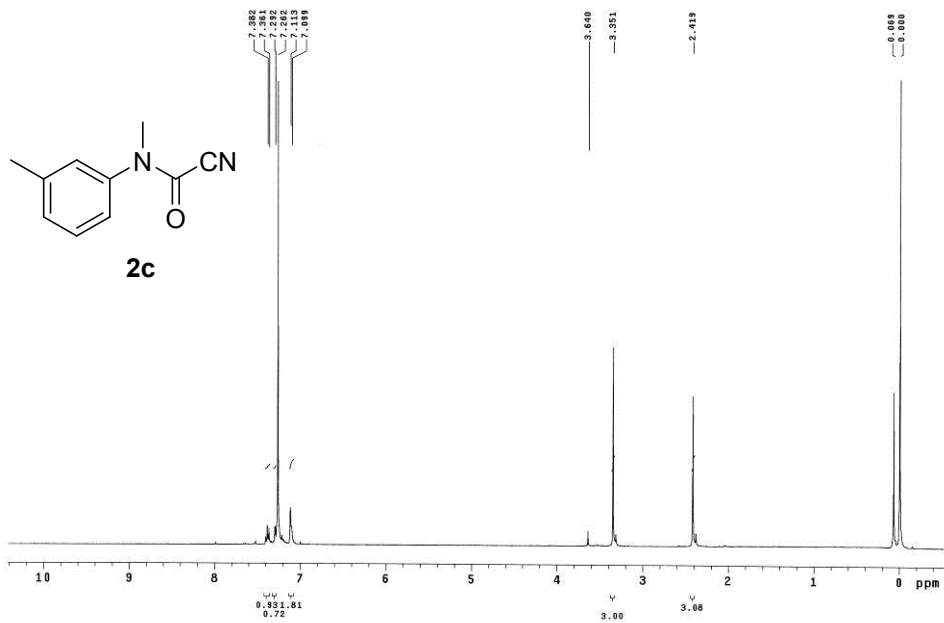
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Sample directory: OneProbe_calib_20140603_05
Pulse Sequence: s2pu1



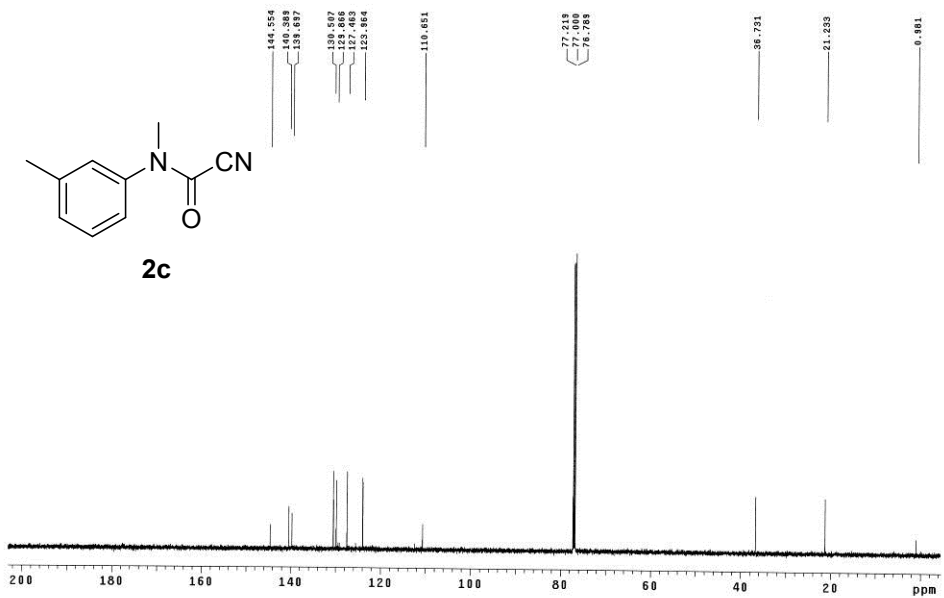
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Pulse Sequence: s2pu1



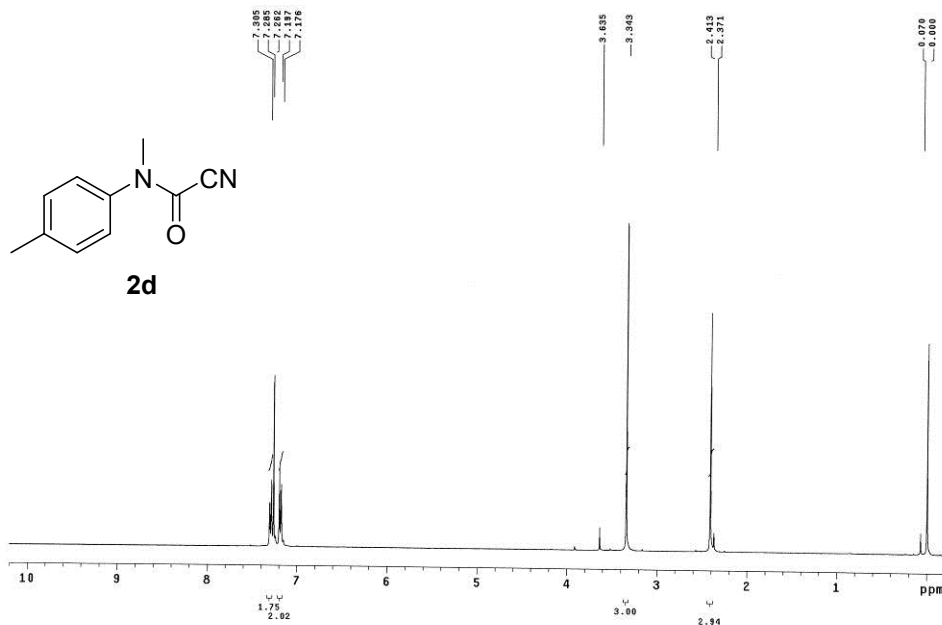
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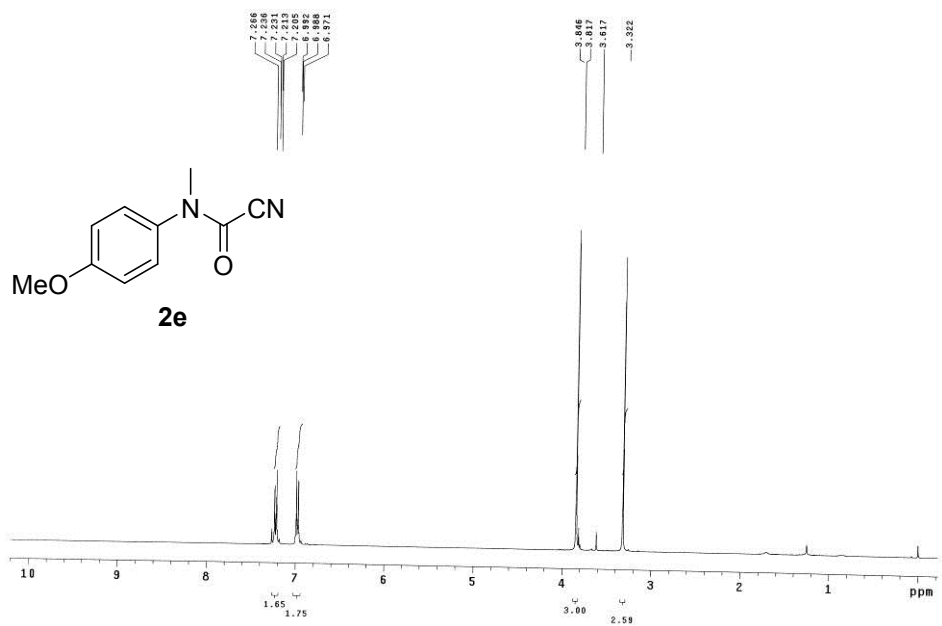
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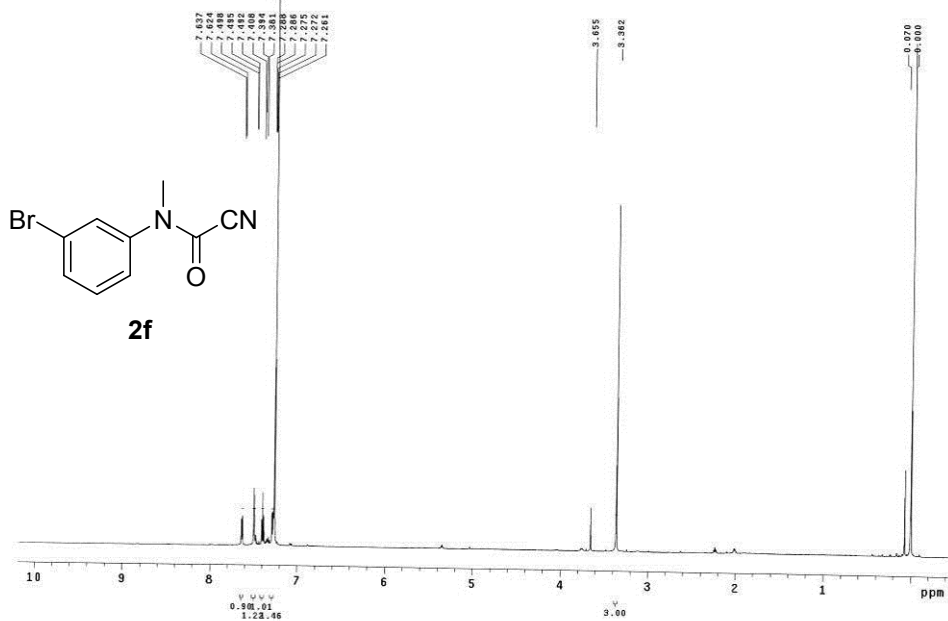
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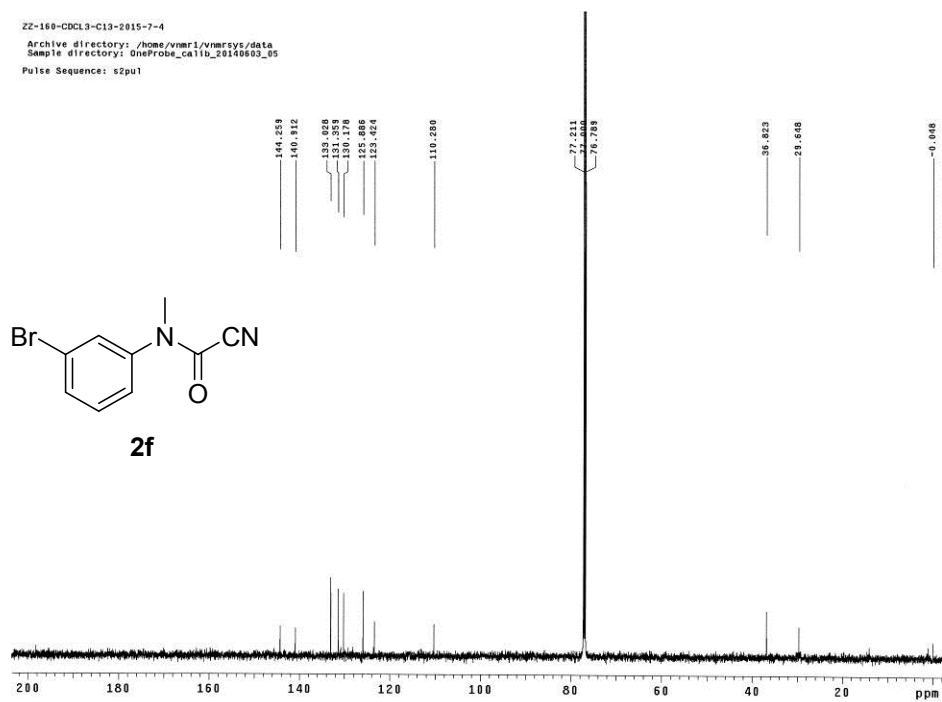
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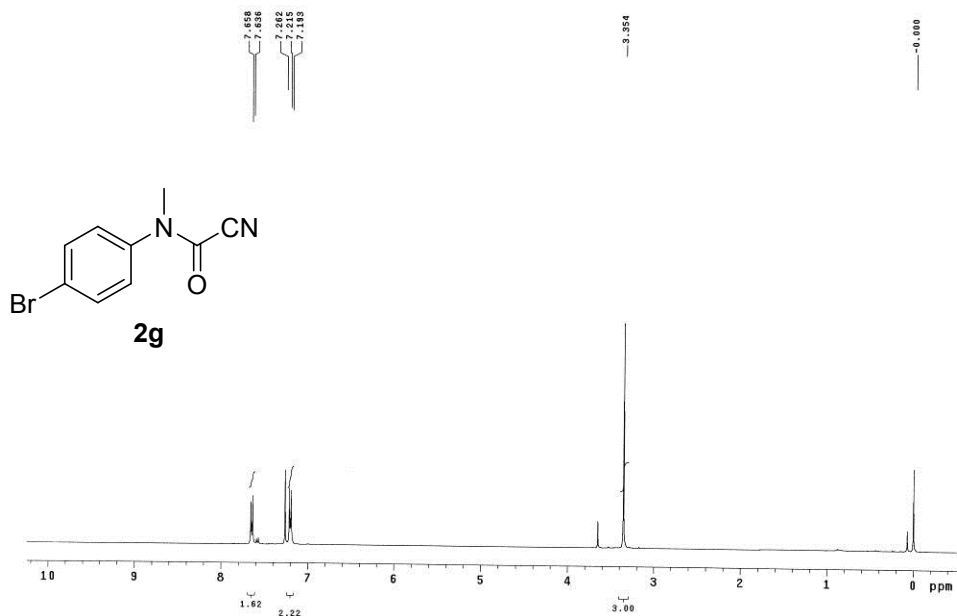
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Pulse Sequence: s2pu1



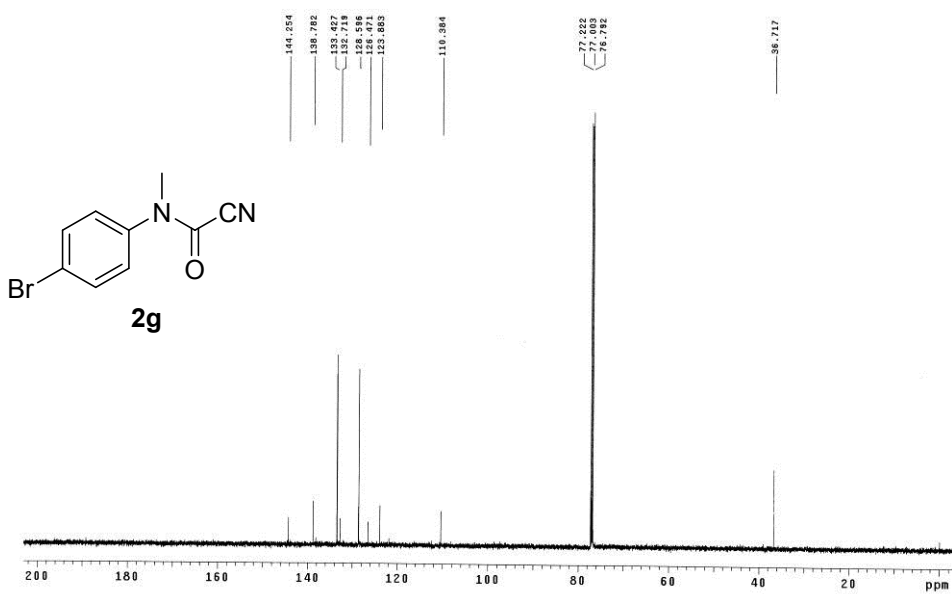
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Pulse Sequence: s2pu1



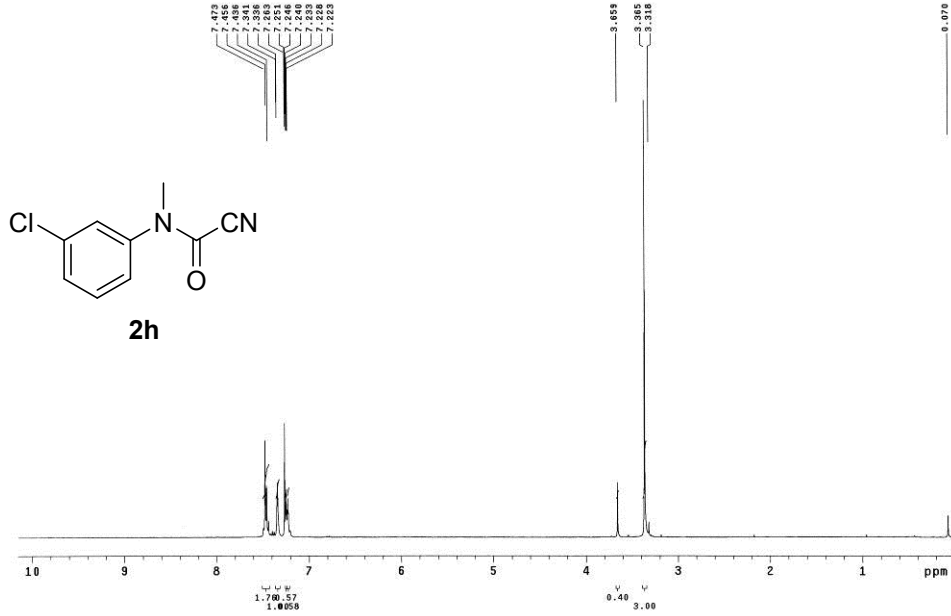
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Pulse Sequence: s2pu1



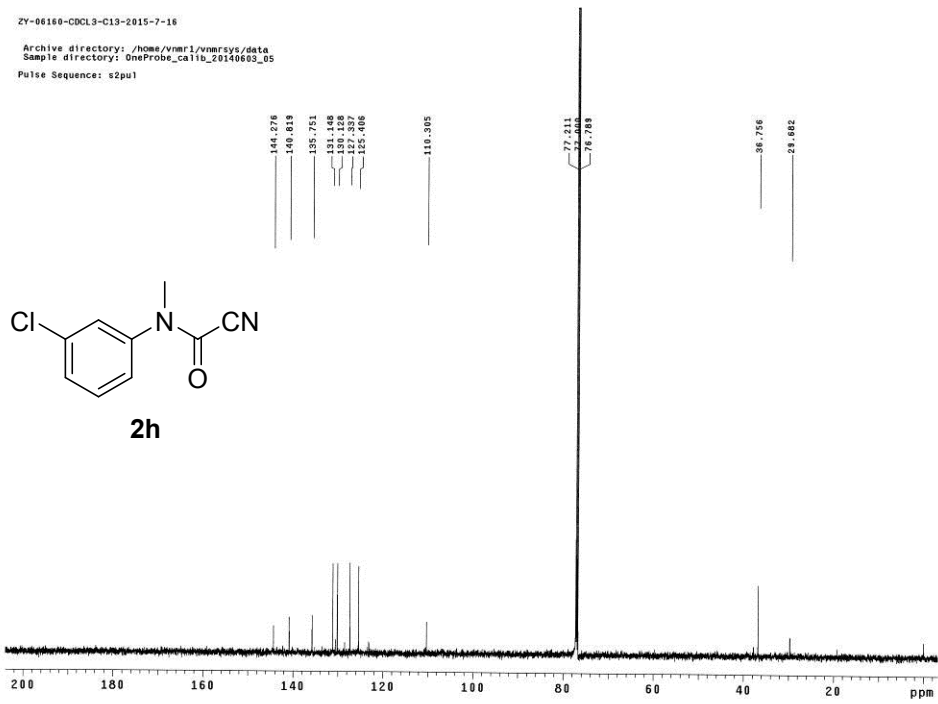
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Pulse Sequence: s2pu1



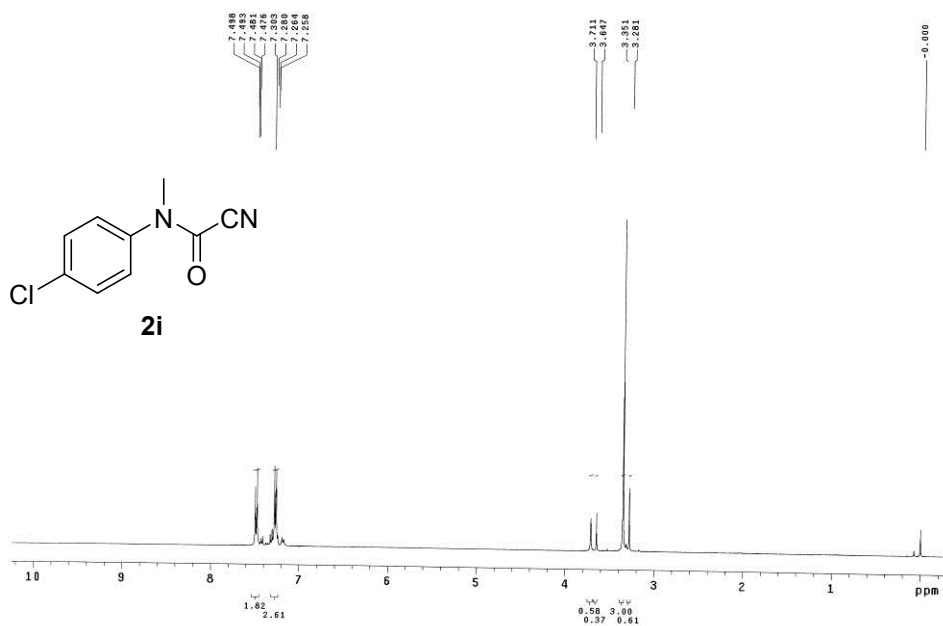
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Pulse Sequence: s2pu1



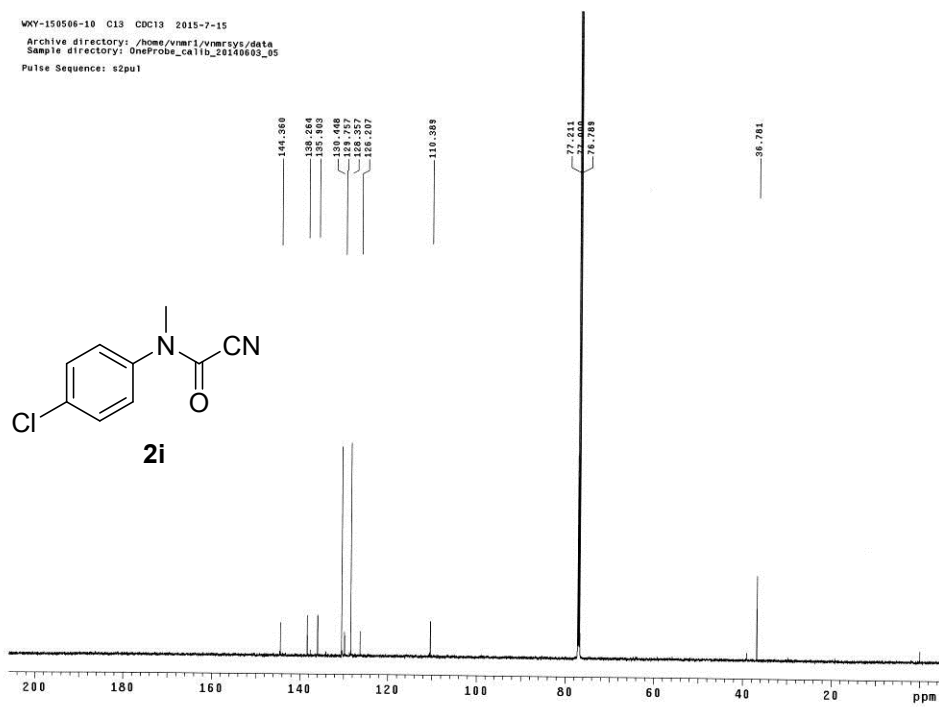
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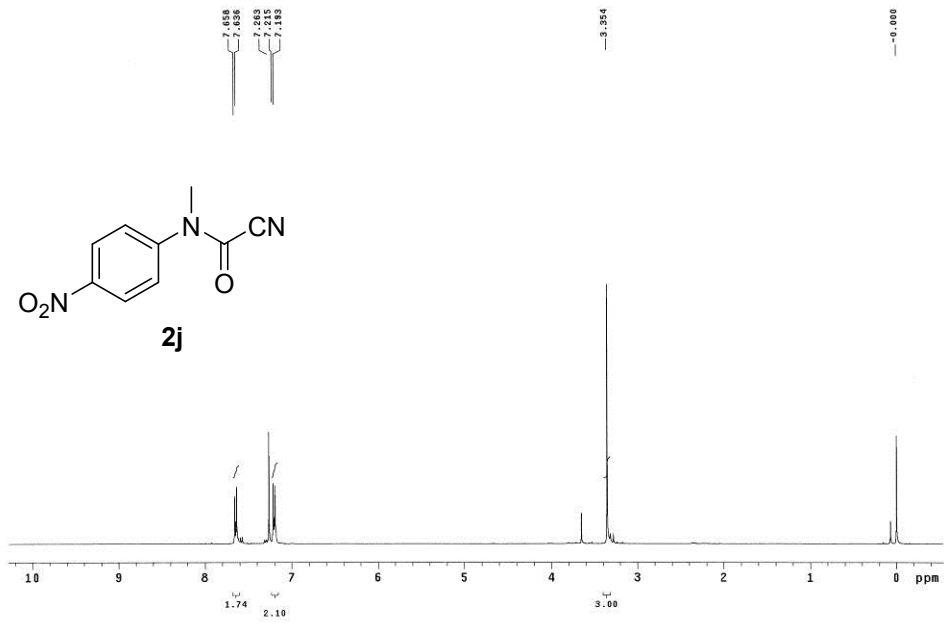
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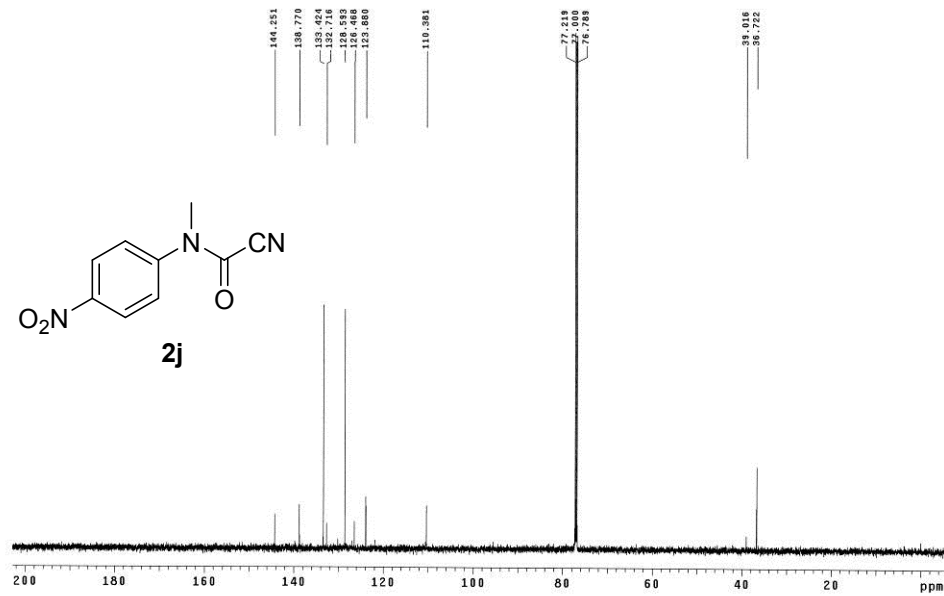
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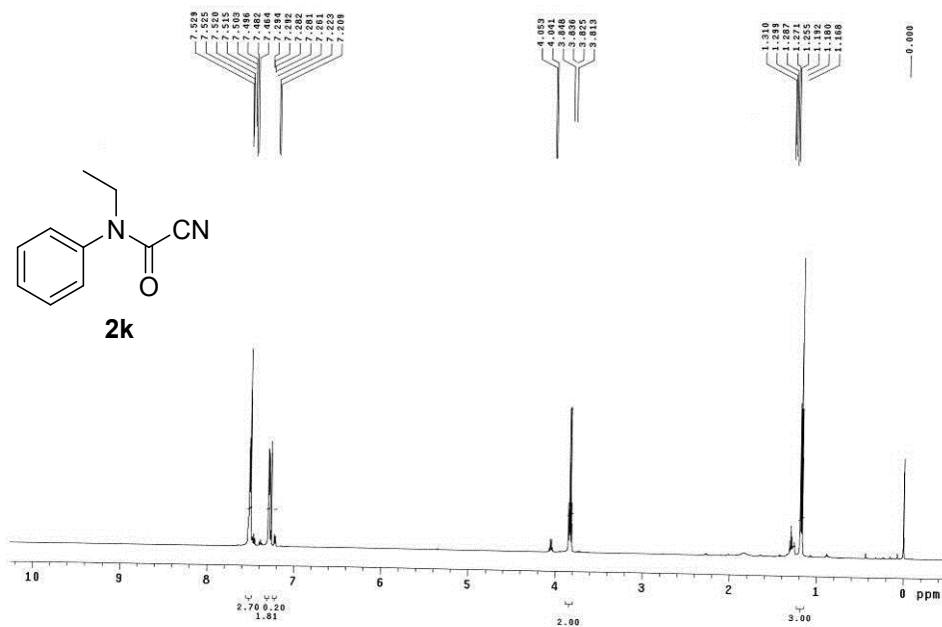
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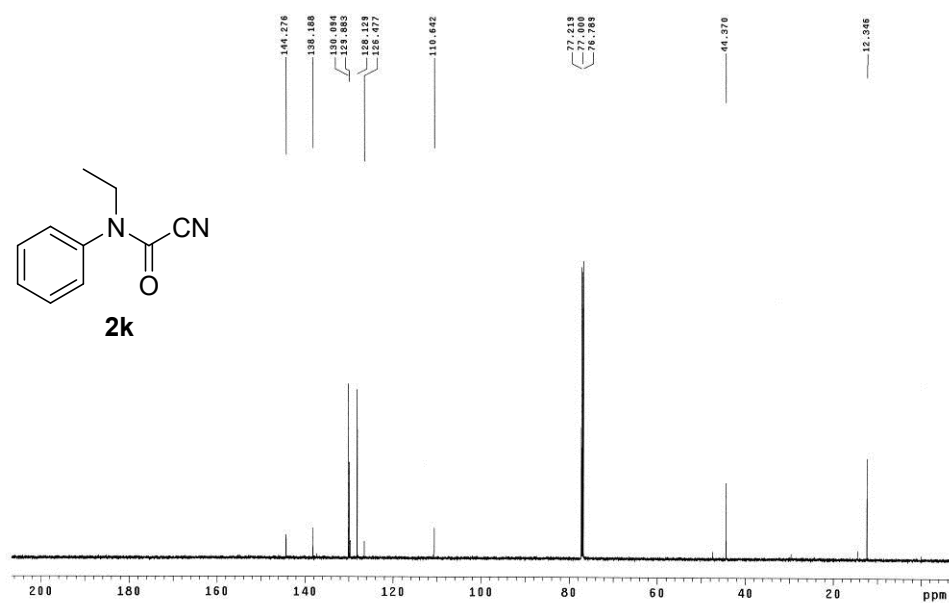
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Pulse Sequence: s2pu1



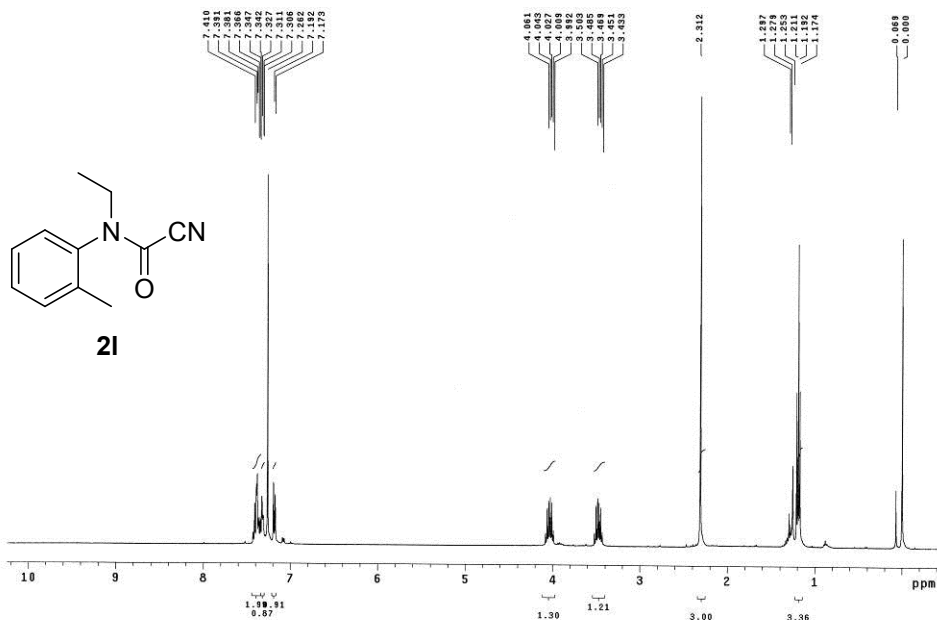
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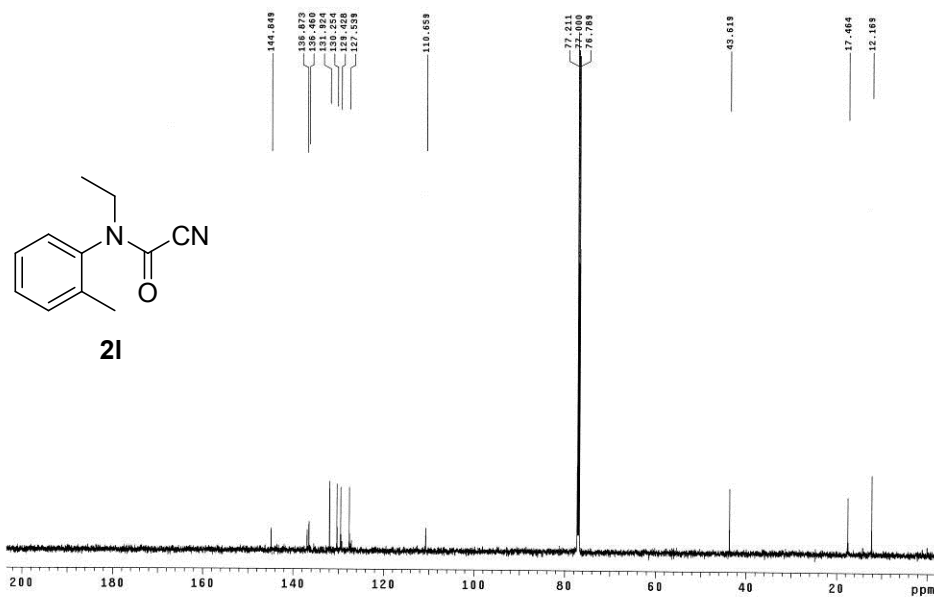
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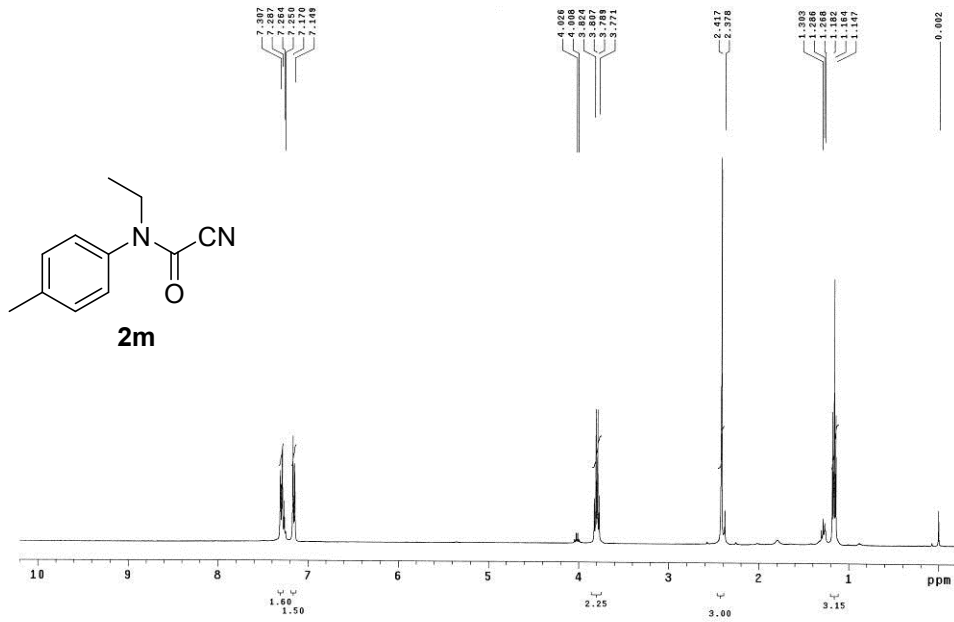
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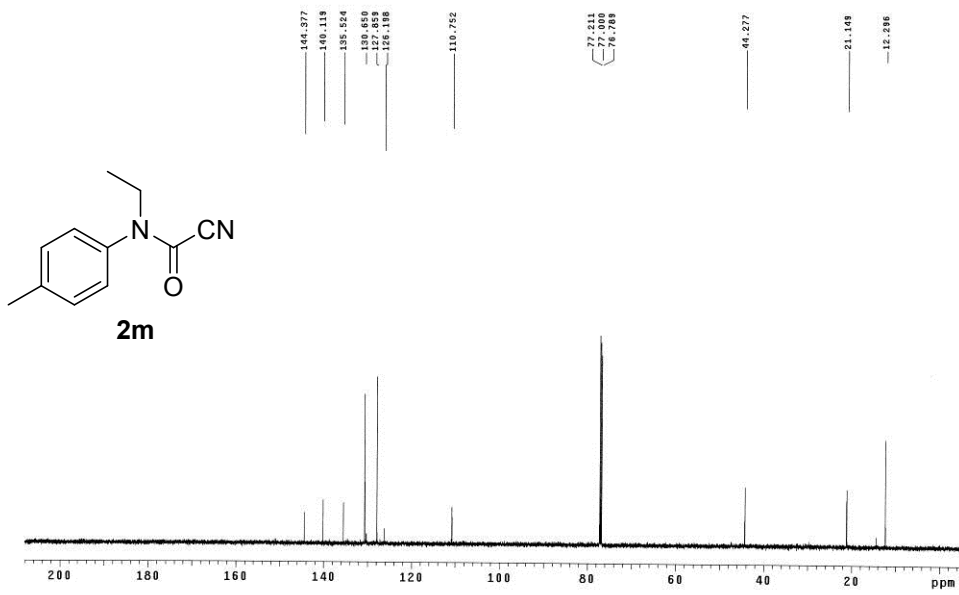
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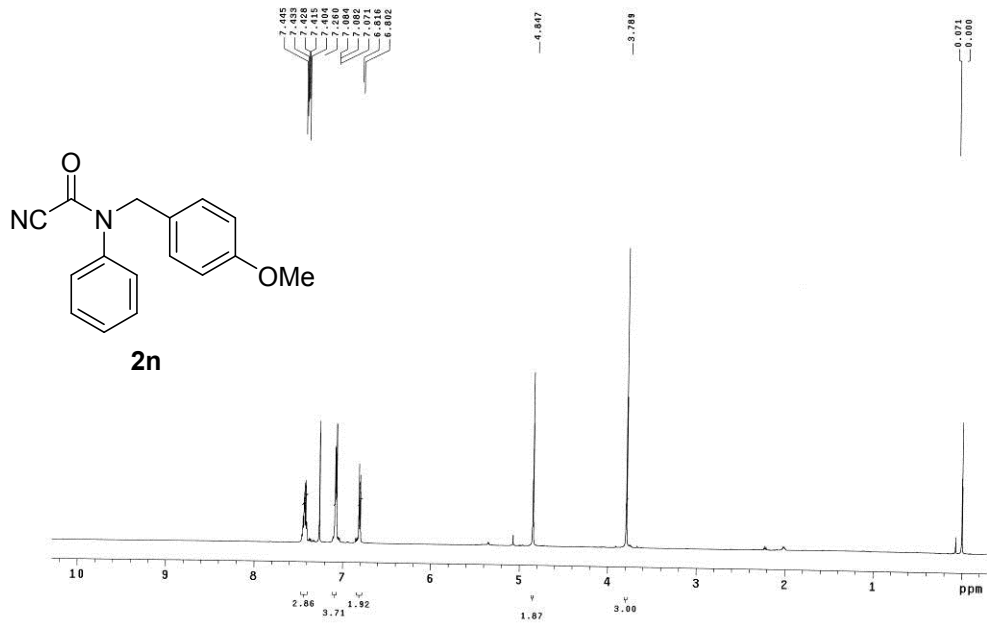
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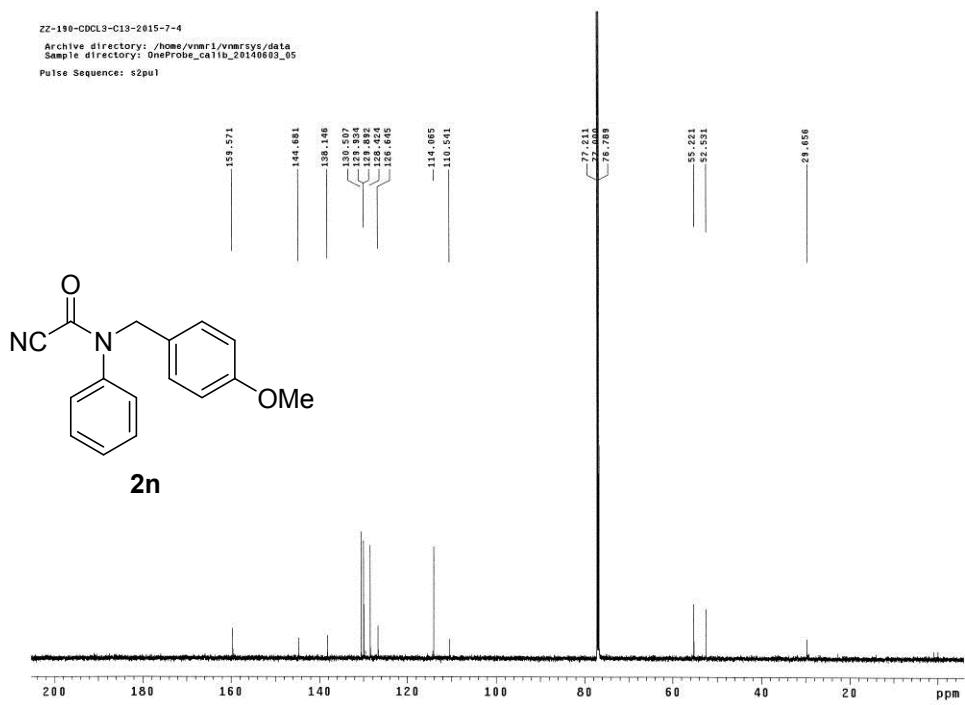
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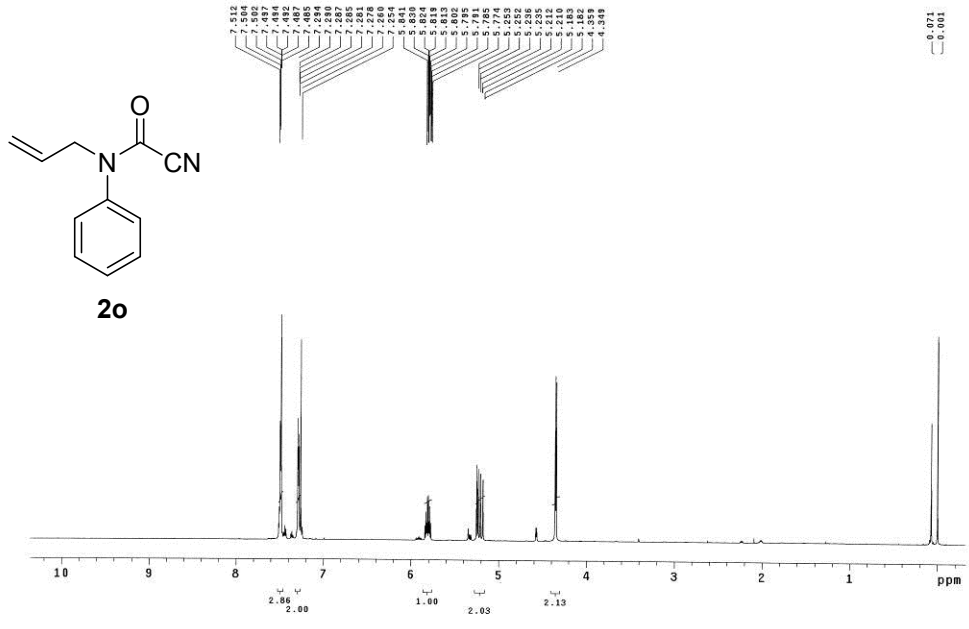
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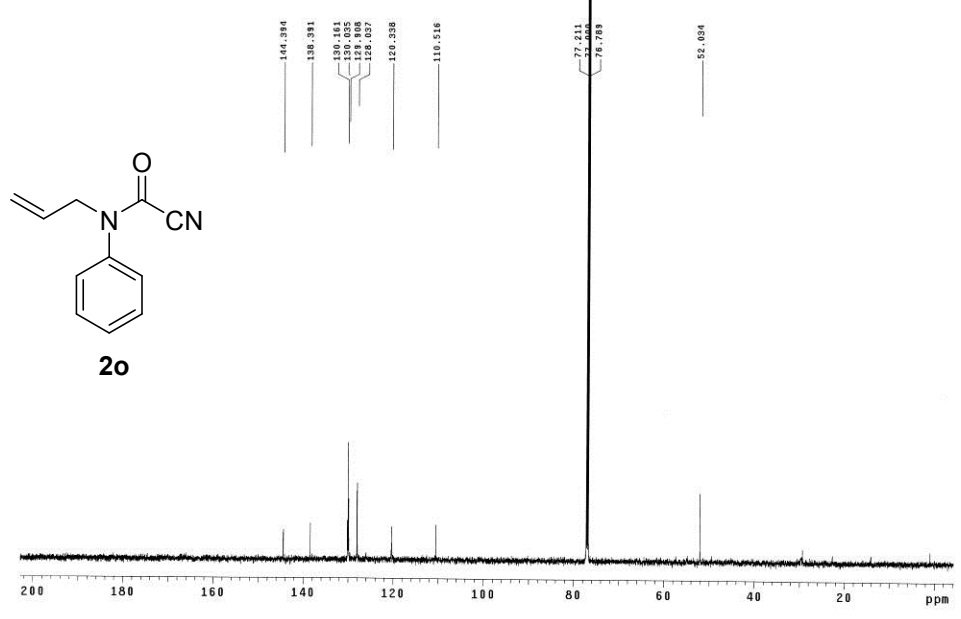
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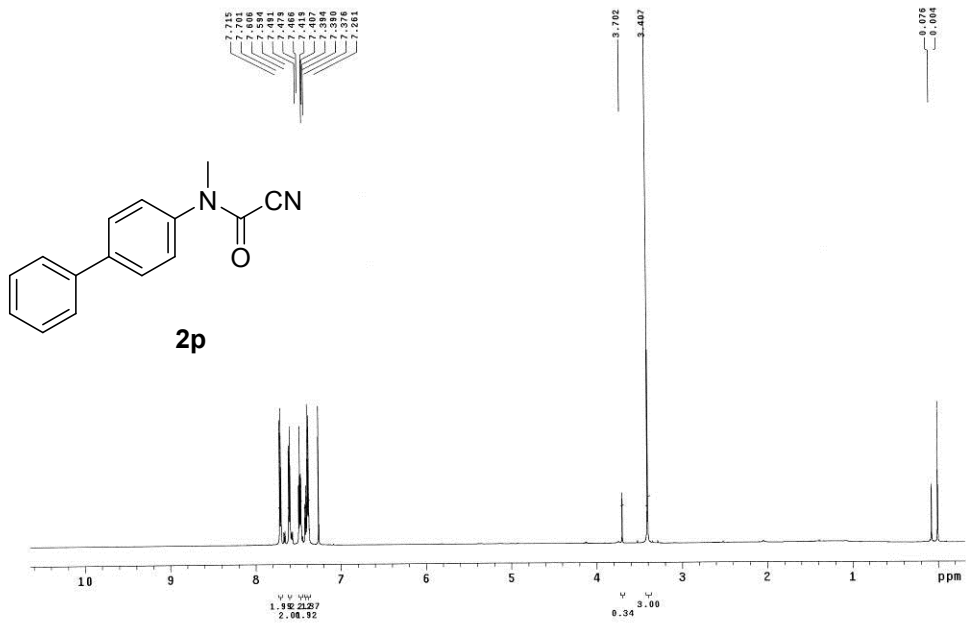
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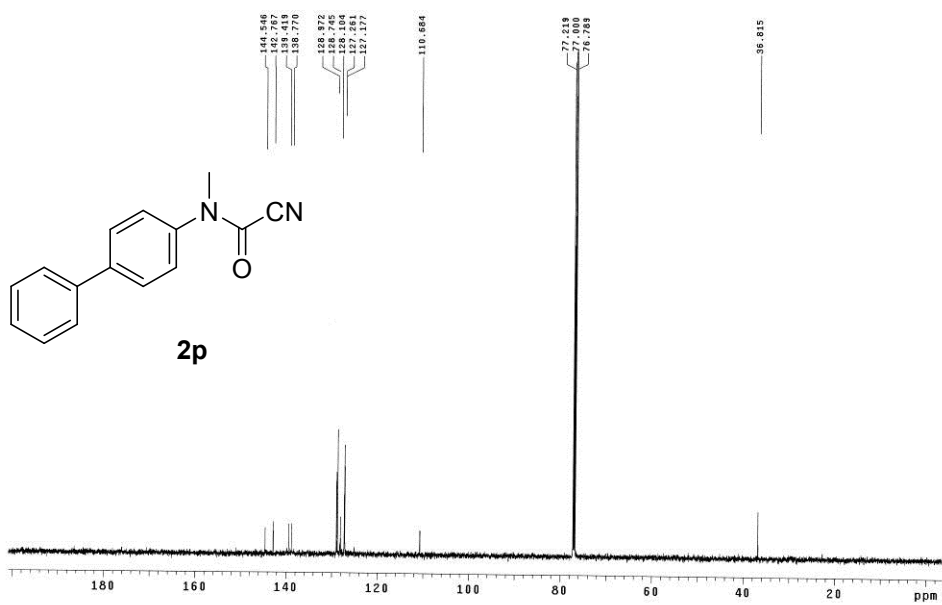
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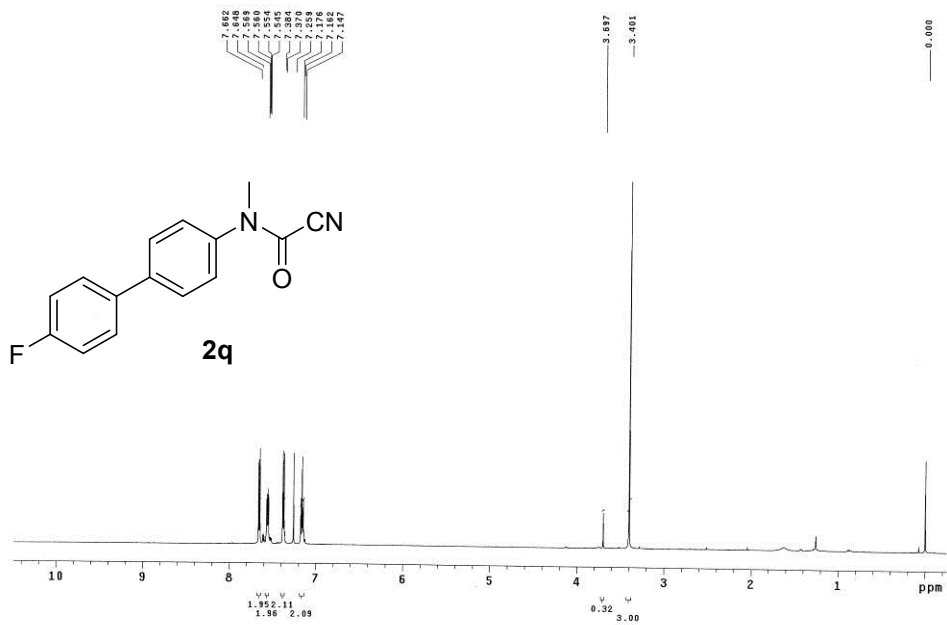
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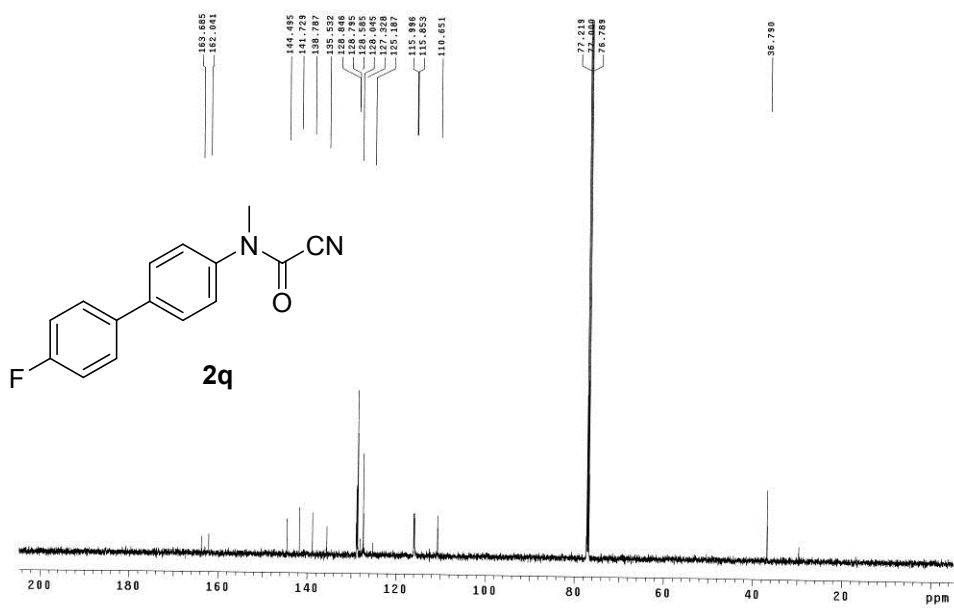
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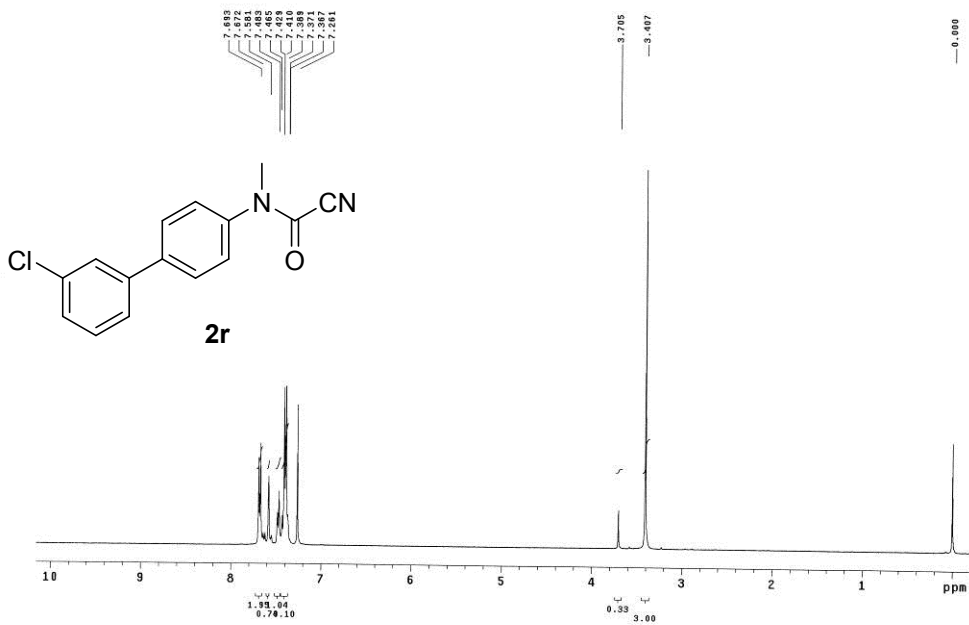
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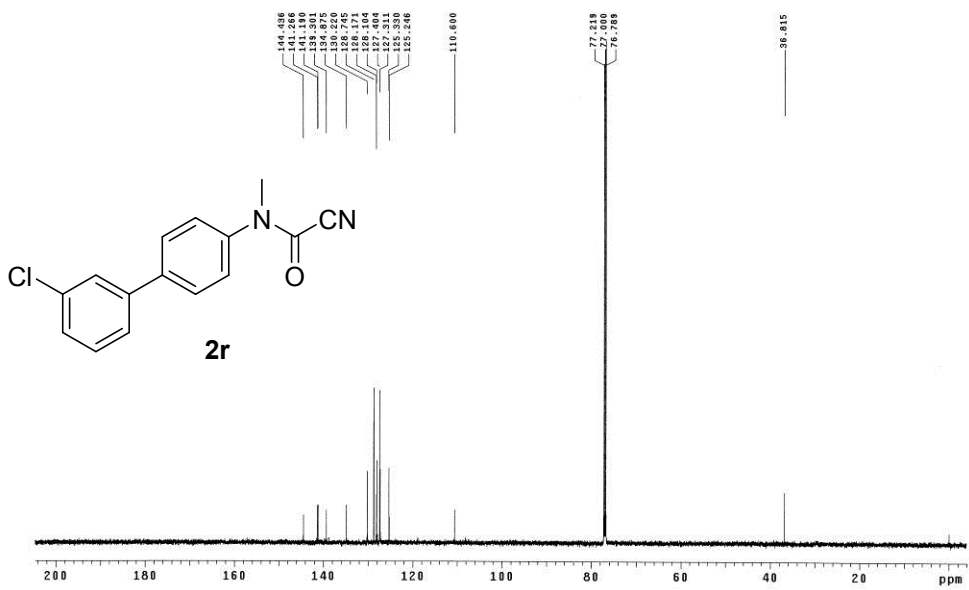
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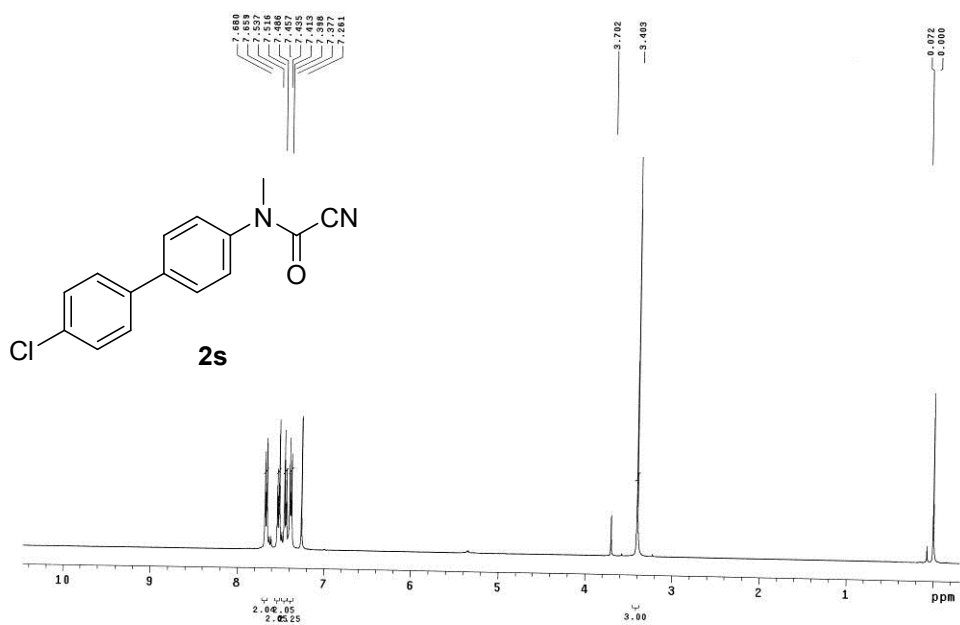
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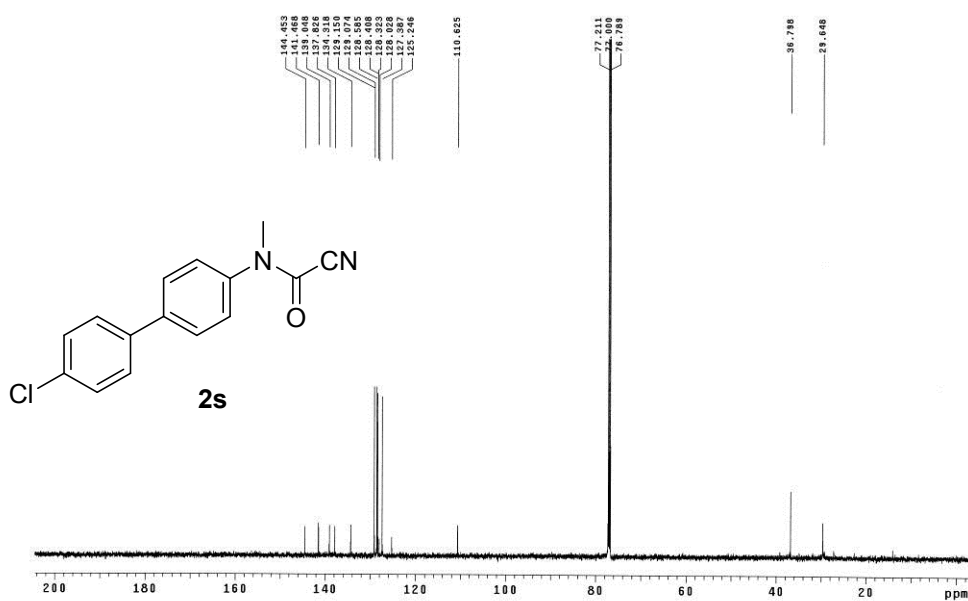
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Sample directory: OneProbe_calib_20140603_05
Pulse Sequence: s2pu1



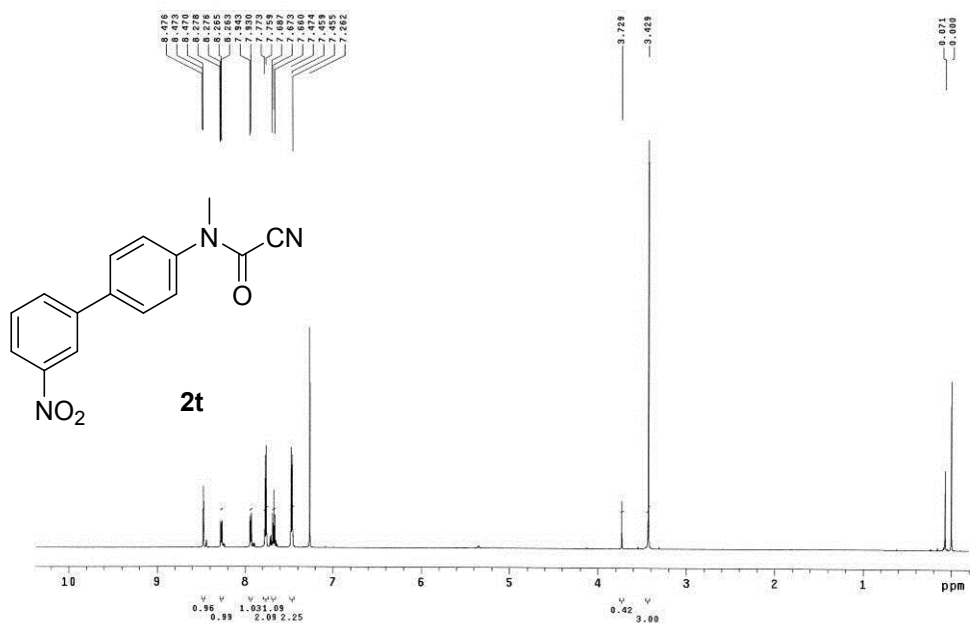
ZZ-24 H1 CDCl3 2015-7-7
Pulse Sequence: s2pu1



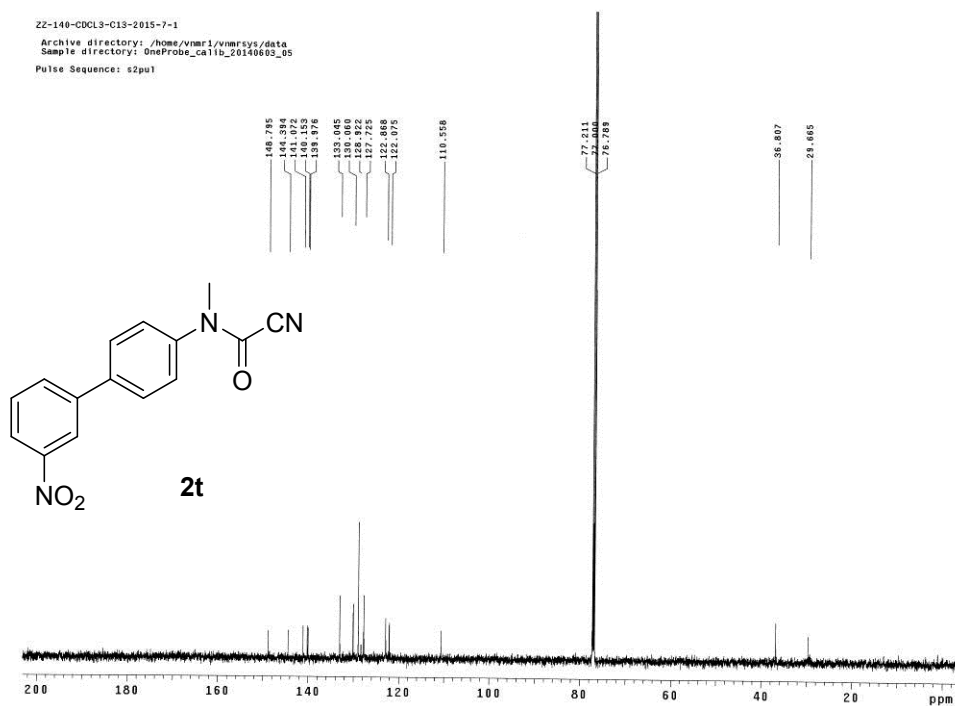
ZZ-240-CDCl3-C13-2015-7-11
Archive directory: /home/vmmr1/vnmrsys/data
Sample directory: OneProbe_cat1b_20140603_05
Pulse Sequence: s2pu1



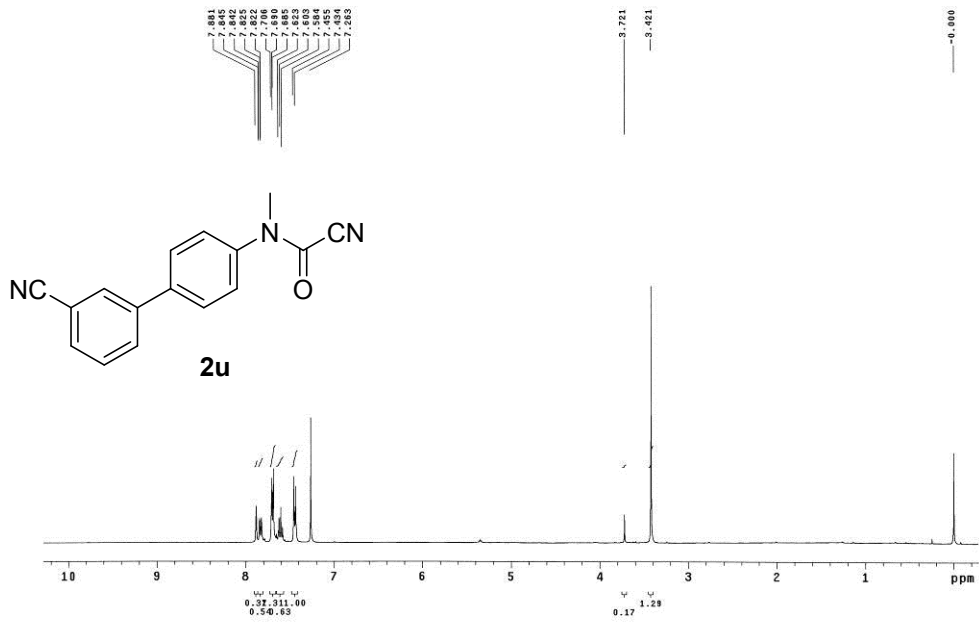
ZZ-14 H1 CDCl3 2015-6-29
Archive directory: /home/vmr1/vmr/sys/data
Sample directory: OneProbe_callb_20140603_05
Pulse Sequence: s2pu1



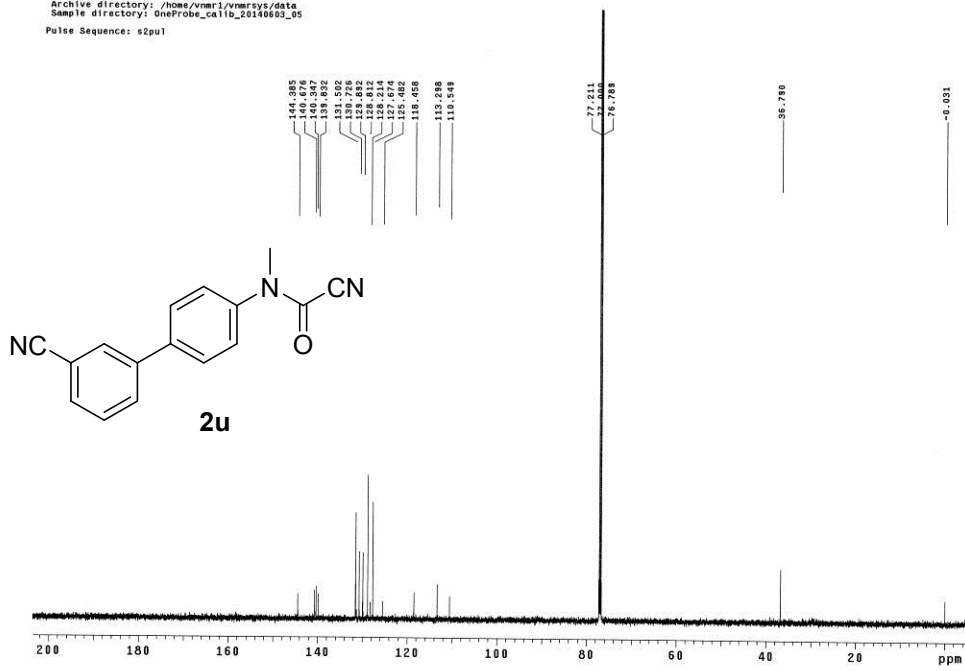
ZZ-140-CDCl3-C13-2015-7-1
Archive directory: /home/vmr1/vmr/sys/data
Sample directory: OneProbe_callb_20140603_05
Pulse Sequence: s2pu1



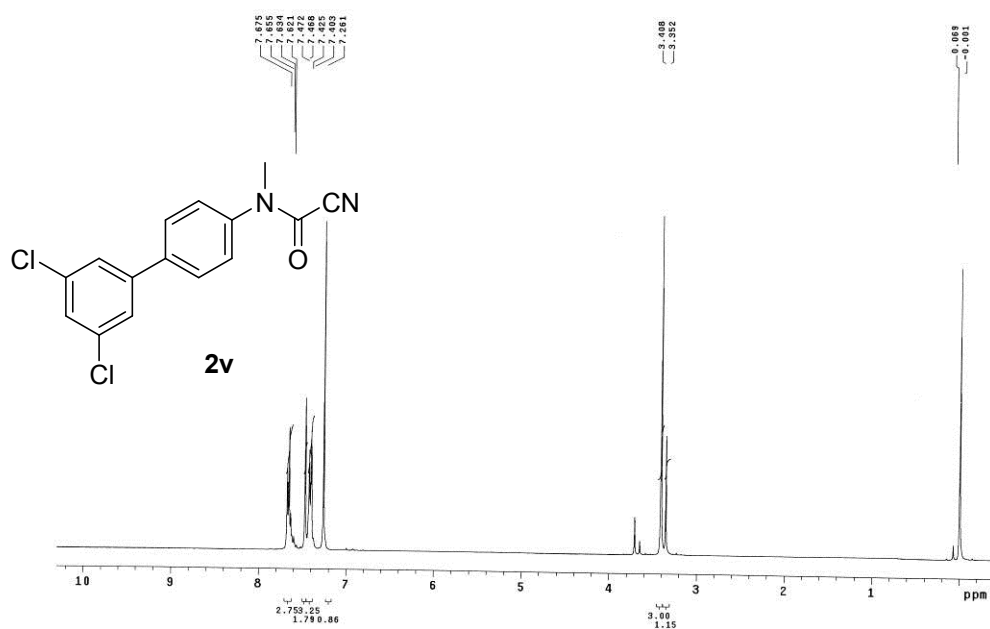
ZZ-26 H1 CDCl3 2015-7-8
Pulse Sequence: s2pu1



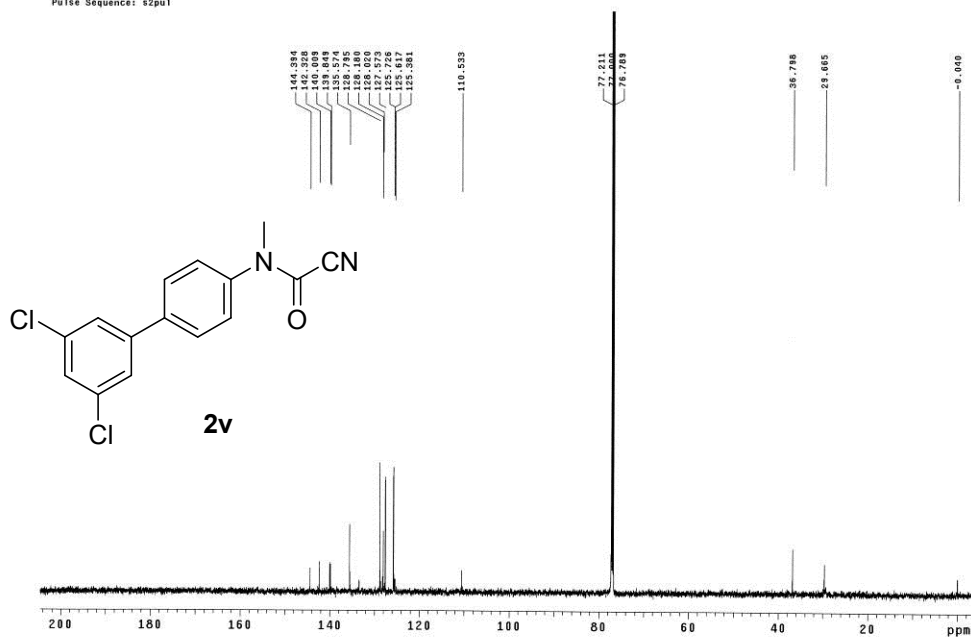
ZZ-266-CDCl3-C13-2015-7-11
Archive directory: /home/vmr1/vmr/sys/data
Sample directory: OneProbe_calib_20140603_05
Pulse Sequence: s2pu1



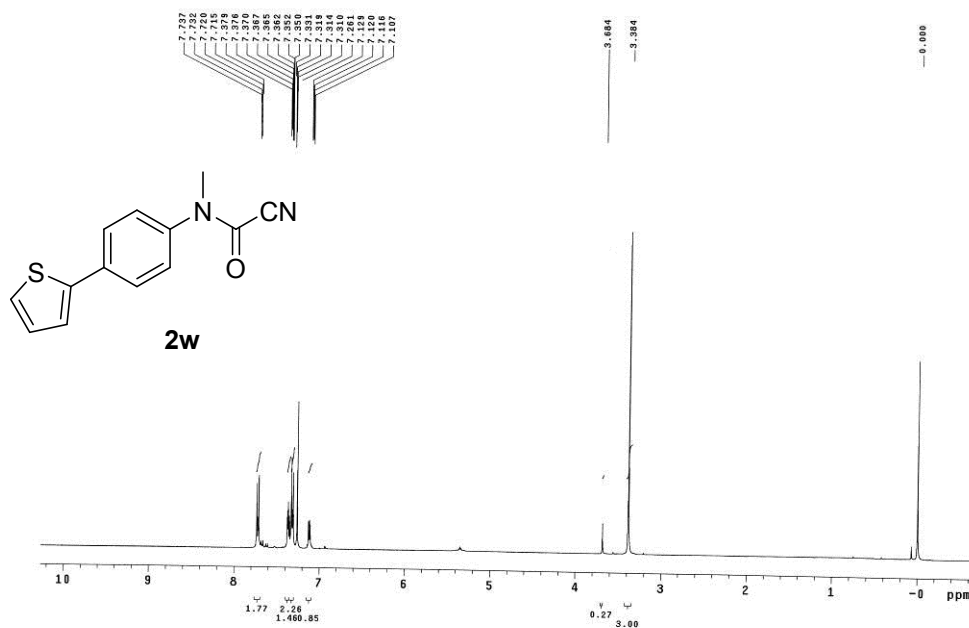
ZZ-22 H1 CDCl3 2015-7-6
Pulse Sequence: s2pu1



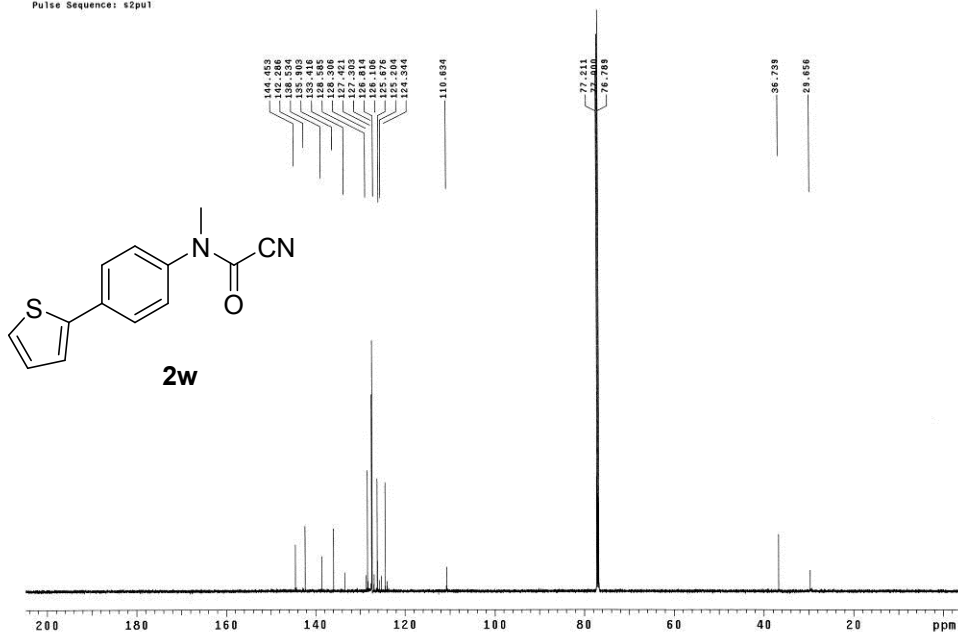
ZZ-220-CDCl3-C13-2015-7-8
Archive directory: /home/vmr1/vmrsys/data
Sample directory: OneProbe_calib_20146693_05
Pulse Sequence: s2pu1



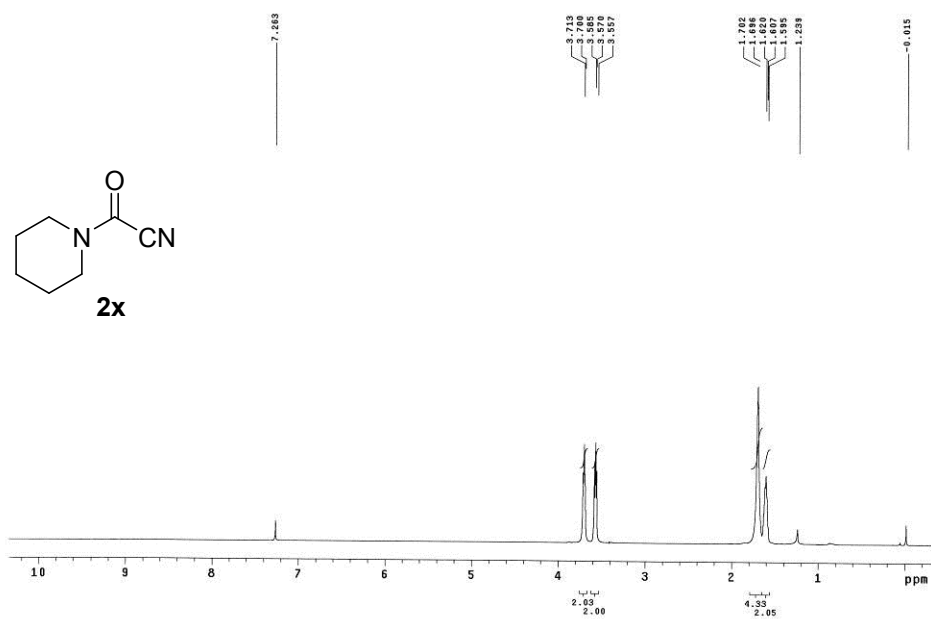
ZZ-27 H1 CDC13 2015-7-10
Pulse Sequence: s2pu1



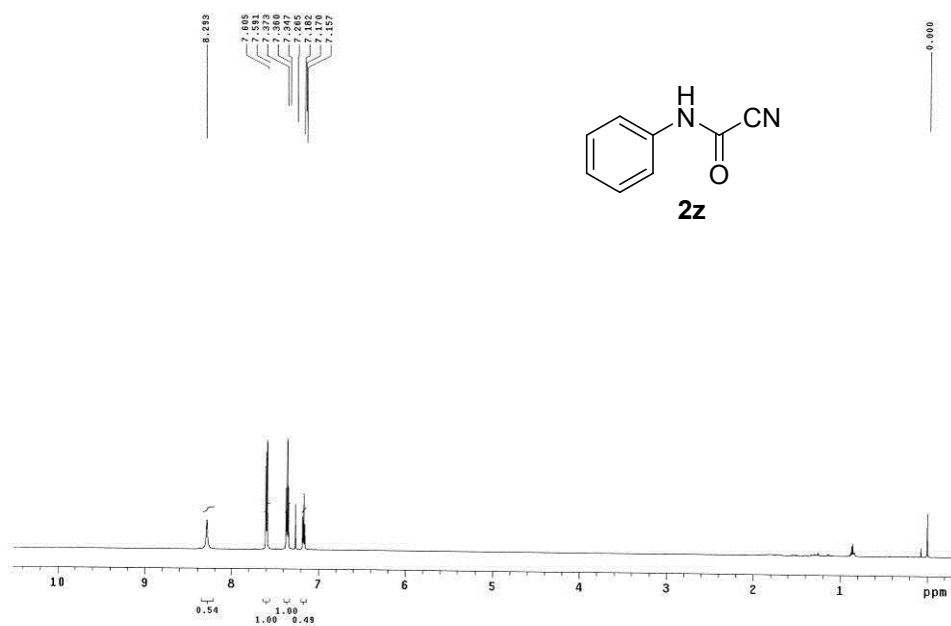
ZZ-270 C13 CDC13 2015-7-15
Archive directory: /home/vmr1/vmr/sys/data
Sample directory: OneProbe_calib_20150803_05
Pulse Sequence: s2pu1



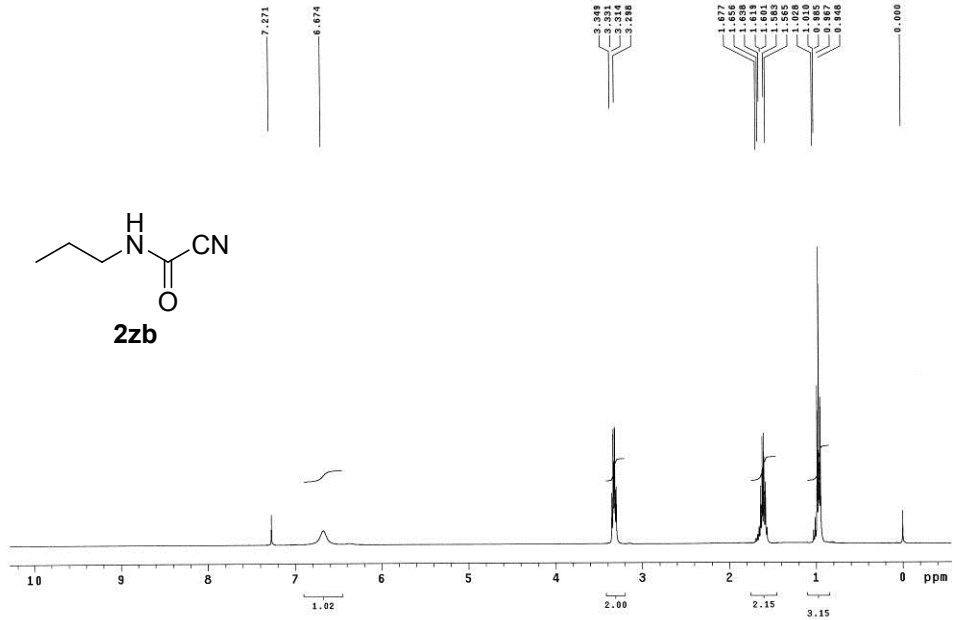
ZZ-93-CDCL3-H1-2015-8-19
Pulse Sequence: s2pu1



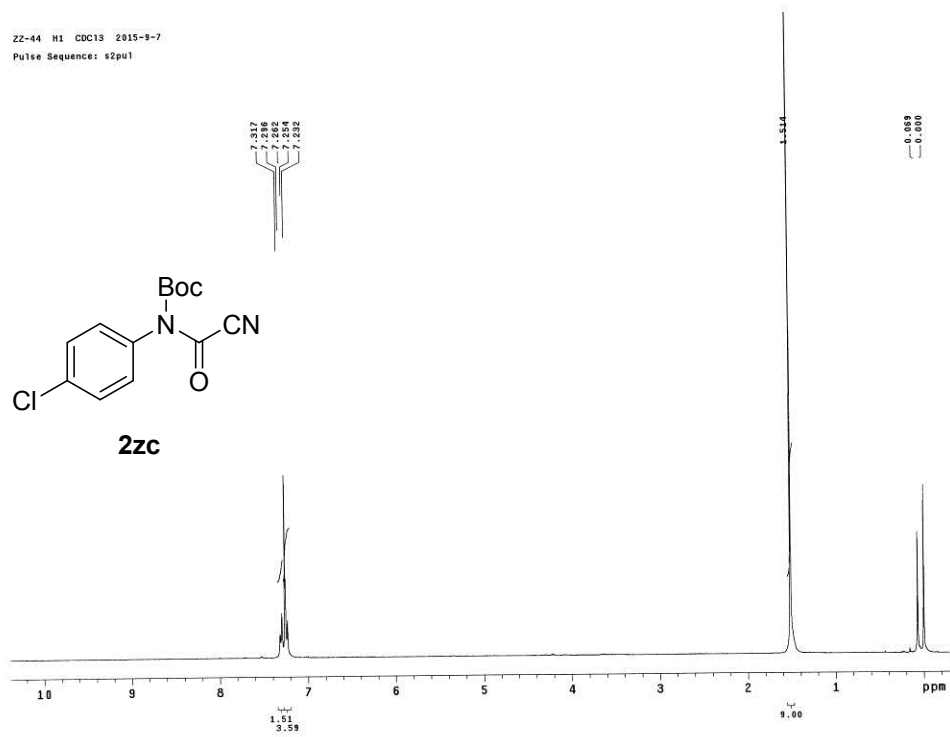
P03-03a H1 CDCl3 2015-5-24
Archive directory: /home/vmr1/vmr/sys/data
Sample directory: OneProbe_calib_20140603_05
Pulse Sequence: s2pu1



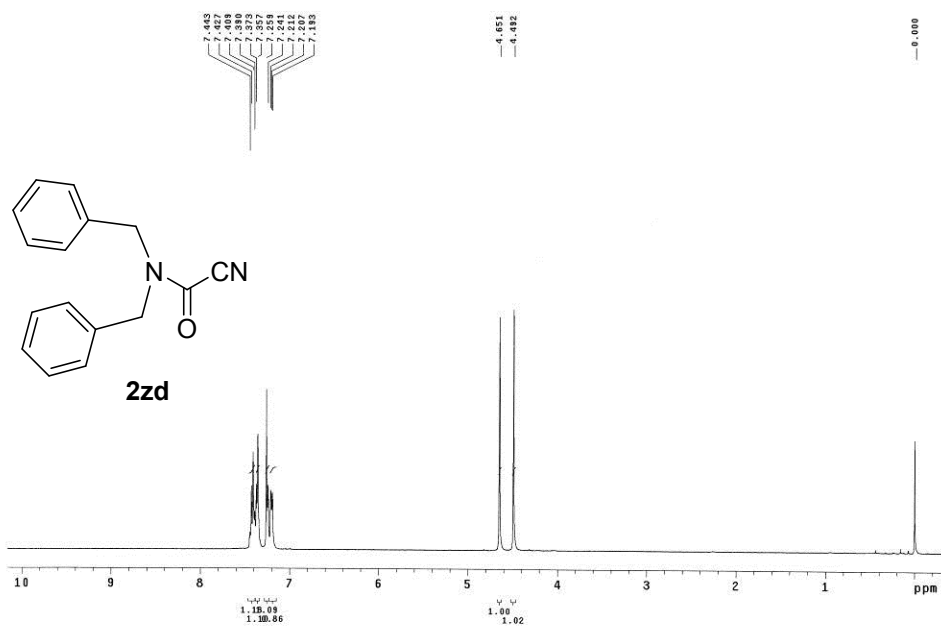
ZZ-43 H1 CDC13 2015-9-6
Pulse Sequence: s2pu1



ZZ-44 H1 CDC13 2015-9-7
Pulse Sequence: s2pu1

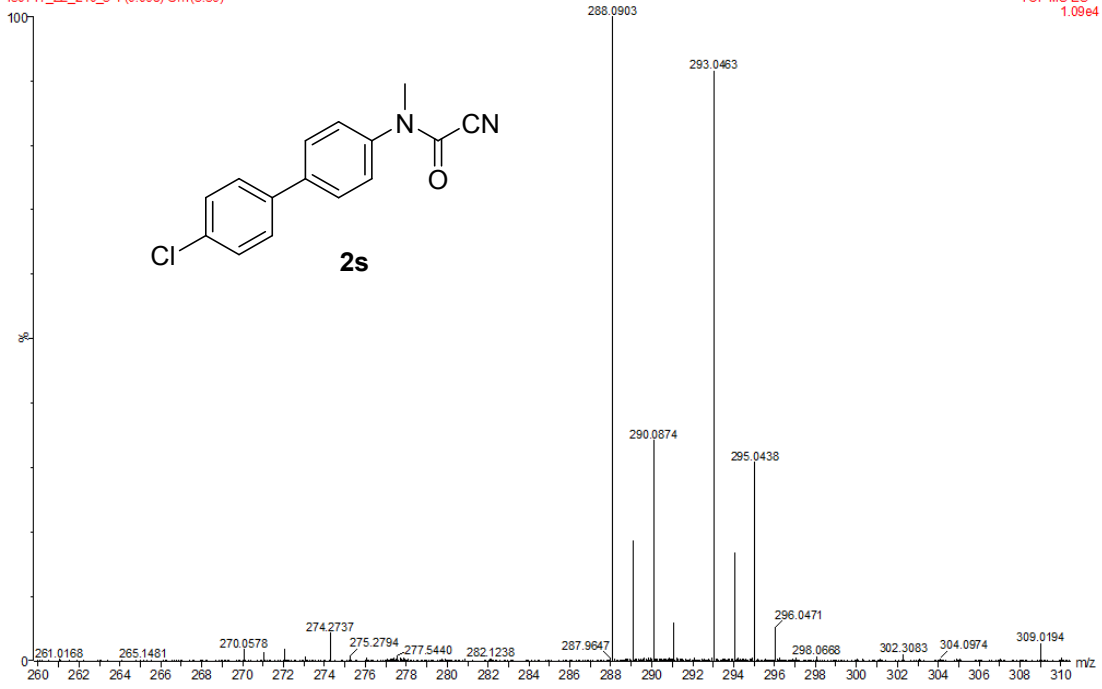


ZZ-45 H1 CDC13 2015-9-8
Pulse Sequence: s2pu1



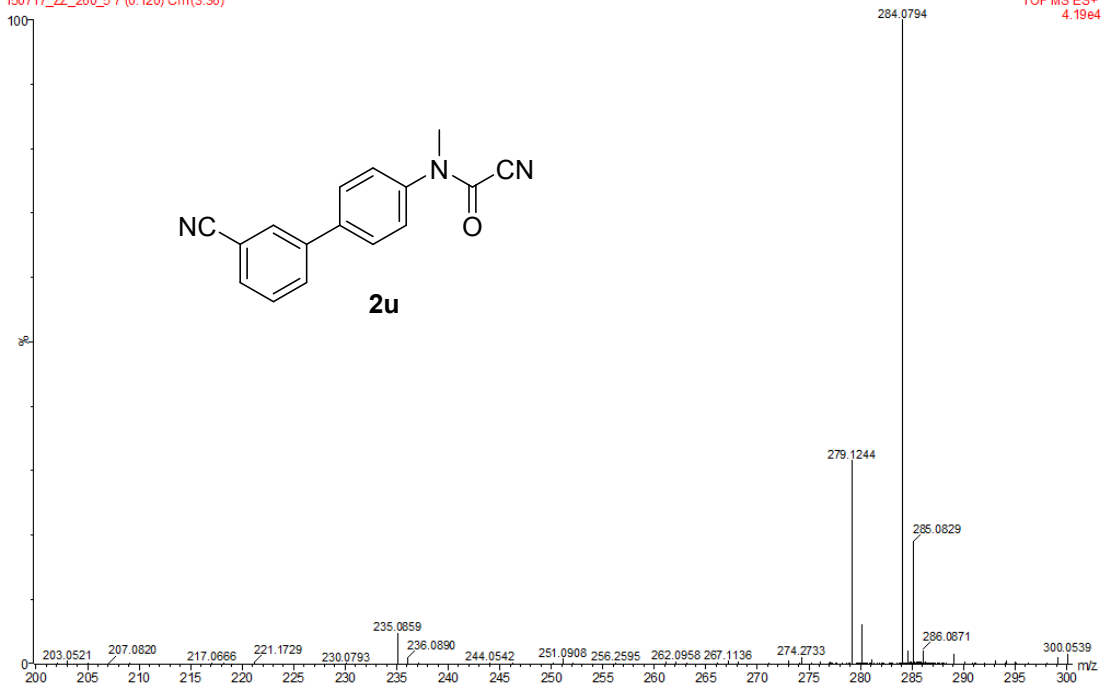
16:12:48
150717_ZZ_240_3_4 (0.068) Cm(3:36)

17-Jul-2015
TOF MS ES+
1.09e4



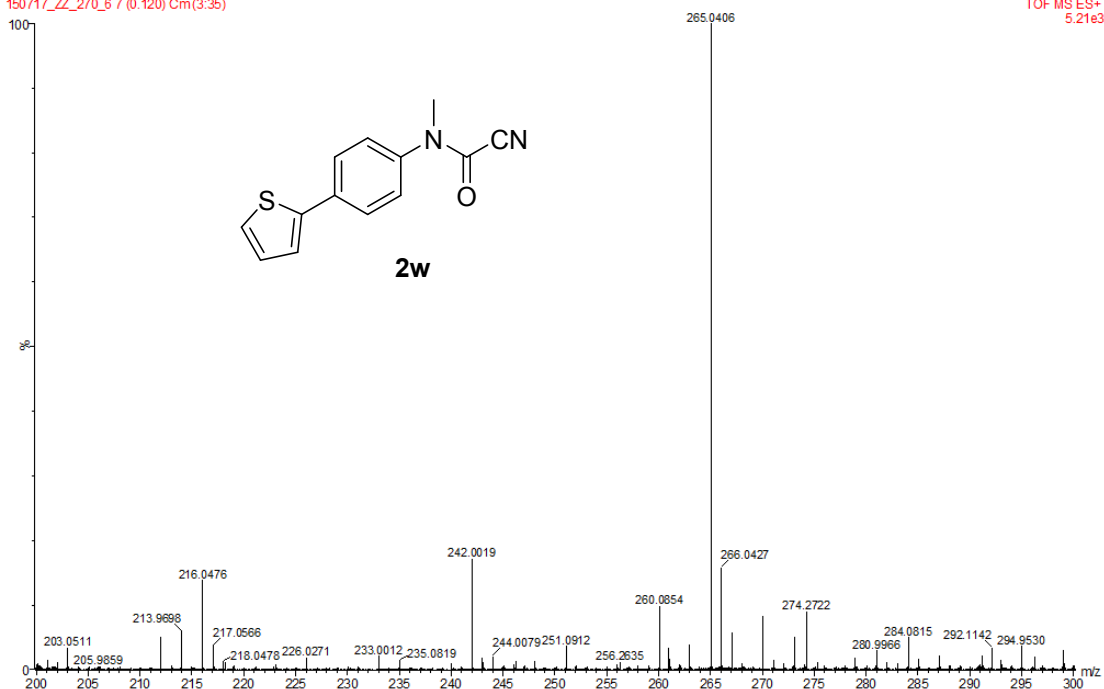
16:17:27
150717_ZZ_260_5_7 (0.120) Cm(3:36)

17-Jul-2015
TOF MS ES+
4.19e4



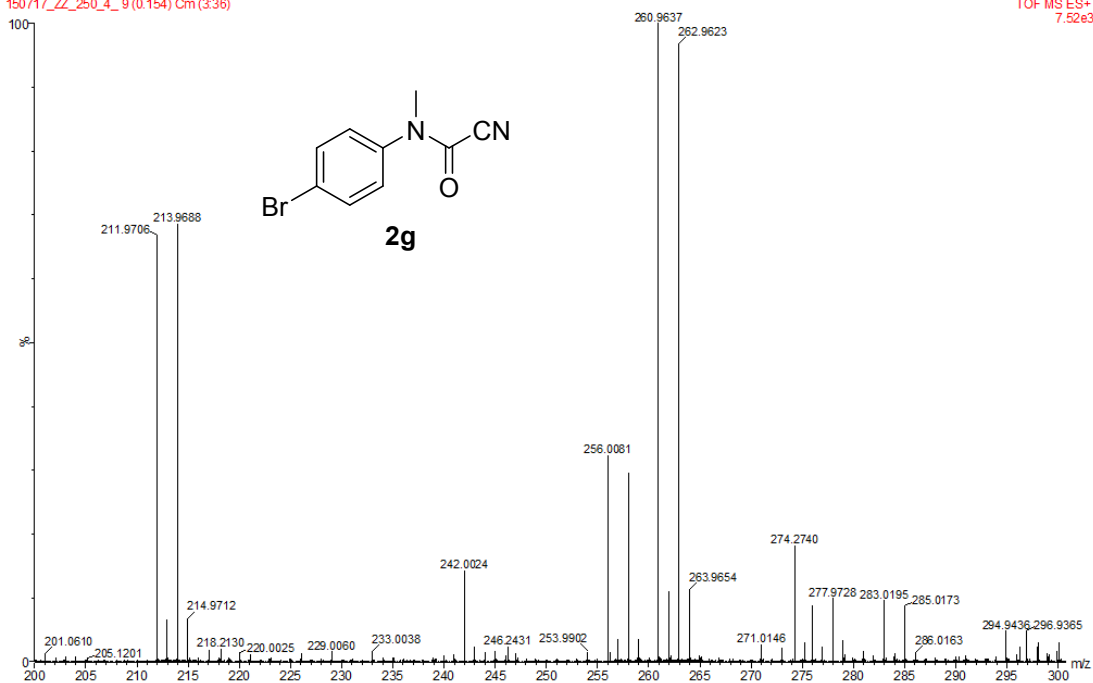
16:20:27
150717_ZZ_270_6_7 (0.120) Cm (3:35)

17-Jul-2015
TOF MS ES+
5.21e3



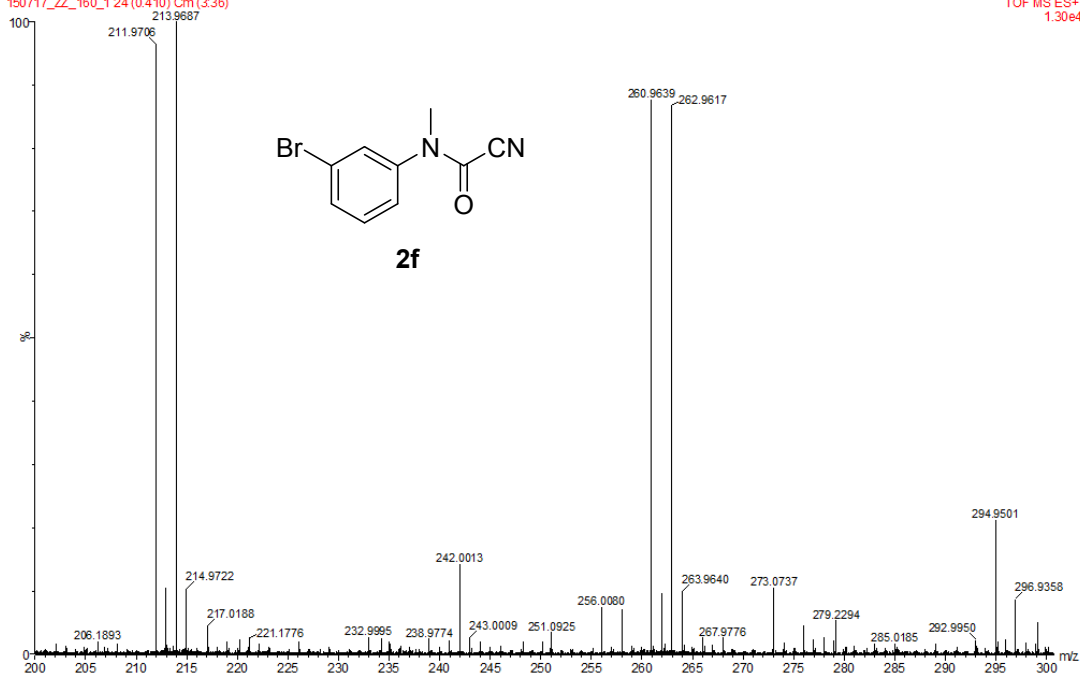
16:27:25
150717_ZZ_250_4_9 (0.154) Cm (3:36)

17-Jul-2015
TOF MS ES+
7.52e3



16:31:30
150717_ZZ_160_1 24 (0.410) Cm (3:36)

17-Jul-2015
TOF MS ES+
1.30e4



16:34:13
150717_ZZ_190_2 17 (0.291) Cm (2:35)

17-Jul-2015
TOF MS ES+
4.53e4

