Access to cyano-substituted pyrazolines through copper-catalyzed cascade cyanation/cyclization of unactivated olefins

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Supporting Information

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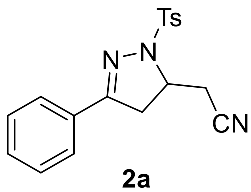
General information. All commercially available reagents were used without further purification. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (J) were given in Hertz (Hz). Data were reported as s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were recorded on an AB SCIEX Triple TOF 5600+ mass spectrometer. Substrates **1a**–**1r** and **1t** were synthesized via the allylation[1] of the corresponding aldehyde, oxidation,[2] and hydrazonation.[3] Alkenyl hydrazone **1s** was obtained according to the literature procedure.[4,2,3] Substrate **1u** was prepared following the reported methods.[5] Alkenyl hydrazone **1v** was synthesized according to the literature methods.[6,3]

General procedure for the domino cyanation/cyclization reaction (Scheme 1). To a reaction tube equipped with a magnetic stir bar were added alkenyl hydrazone **1** (0.20 mmol), $Zn(CN)_2$ (47.0 mg, 0.40 mmol), $Cu(acac)_2$ (5.2 mg, 0.020 mmol), $K_2S_2O_8$ (135.2 mg, 0.50 mmol), $NaHCO_3$ (25.2 mg, 0.30 mmol), and DMSO (1.6 mL). The reaction mixture was vigorously stirred at room temperature until the reaction was completed as monitored by TLC analysis, diluted with water (15 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1 or 3:1) to give product **2**.

Procedure for the radical trapping experiment (Scheme 3B). To a reaction tube equipped with a magnetic stir bar were added alkenyl hydrazone **1a** (62.9 mg, 0.20 mmol), $Zn(CN)_2$ (47.0 mg, 0.40 mmol), $Cu(acac)_2$ (5.2 mg, 0.020 mmol), $K_2S_2O_8$ (135.2 mg, 0.50 mmol), $NaHCO_3$ (25.2 mg, 0.30 mmol), TEMPO (62.5 mg, 0.40 mmol), and DMSO (1.6 mL). The reaction mixture was stirred at room temperature for 12 h, diluted with water (15 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to give TEMPO-trapped pyrazoline **3**.

Characterization data

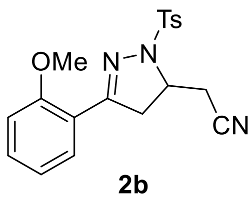
2-(3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2a)



2a

White solid (0.20 mmol scale: 51.4 mg, 76%; 5.0 mmol scale: 1.22 g, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.67 – 7.61 (m, 2H), 7.48 – 7.34 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.15 – 4.02 (m, 1H), 3.36 (dd, *J* = 17.3, 10.9 Hz, 1H), 3.24 (dd, *J* = 17.0, 3.6 Hz, 1H), 3.12 (dd, *J* = 17.3, 9.5 Hz, 1H), 3.05 (dd, *J* = 17.0, 8.2 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 145.0, 131.1, 131.0, 129.9, 129.7, 128.7, 128.6, 126.9, 116.4, 57.5, 39.3, 24.5, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}N_3NaO_2S$ 362.0934, found 362.0937.

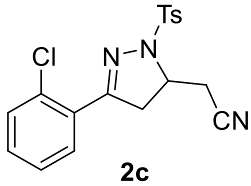
2-(3-(2-methoxyphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2b)



2b

White solid (57.7 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.06 – 3.93 (m, 1H), 3.78 (s, 3H), 3.45 (dd, *J* = 18.2, 10.7 Hz, 1H), 3.27 (dd, *J* = 18.3, 10.0 Hz, 1H), 3.20 (dd, *J* = 17.0, 3.0 Hz, 1H), 3.02 (dd, *J* = 16.9, 8.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 157.3, 144.8, 132.2, 131.1, 129.6, 129.4, 128.7, 120.7, 119.0, 111.3, 57.6, 55.4, 42.6, 24.4, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}N_3NaO_3S$ 392.1039, found 392.1032.

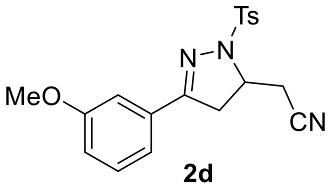
2-(3-(2-chlorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2c)



2c

White solid (52.4 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.40 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 4.17 – 4.05 (m, 1H), 3.51 (dd, *J* = 17.7, 10.6 Hz, 1H), 3.30 (dd, *J* = 17.7, 9.8 Hz, 1H), 3.21 (dd, *J* = 17.0, 3.6 Hz, 1H), 3.08 (dd, *J* = 17.0, 7.7 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 145.1, 132.7, 131.5, 131.1, 130.6, 130.5, 129.8, 129.4, 128.7, 127.0, 116.2, 57.9, 42.2, 24.3, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}ClN_3NaO_2S$ 396.0544, found 396.0551.

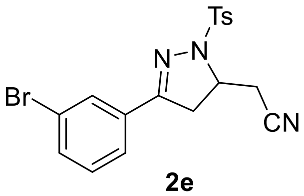
2-(3-(3-methoxyphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2d)



2d

White solid (49.6 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.22 (s, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.13 – 4.00 (m, 1H), 3.83 (s, 3H), 3.34 (dd, *J* = 17.3, 10.9 Hz, 1H), 3.23 (dd, *J* = 17.0, 3.7 Hz, 1H), 3.10 (dd, *J* = 17.2, 9.4 Hz, 1H), 3.04 (dd, *J* = 16.8, 8.1 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 157.1, 145.0, 131.2, 131.1, 129.7, 129.7, 128.6, 119.6, 117.1, 116.4, 111.6, 57.5, 55.4, 39.4, 24.5, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}N_3NaO_3S$ 392.1039, found 392.1035.

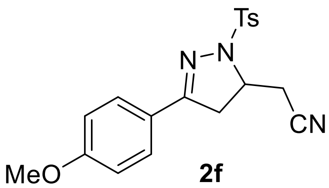
2-(3-(3-bromophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2e)



2e

White solid (65.4 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 3H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 1H), 4.19 – 4.06 (m, 1H), 3.36 (dd, *J* = 17.3, 10.9 Hz, 1H), 3.24 (dd, *J* = 16.9, 3.7 Hz, 1H), 3.15 – 3.01 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 145.2, 133.9, 131.9, 131.1, 130.3, 129.9, 129.7, 128.6, 125.4, 122.9, 116.2, 57.6, 39.2, 24.5, 21.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}BrN_3NaO_2S$ 440.0039, found 440.0031.

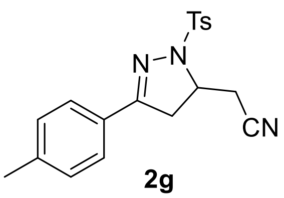
2-(3-(4-methoxyphenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2f)



2f

White solid (58.5 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.10 – 3.96 (m, 1H), 3.82 (s, 3H), 3.31 (dd, *J* = 17.2, 10.8 Hz, 1H), 3.21 (dd, *J* = 17.0, 3.7 Hz, 1H), 3.07 (dd, *J* = 17.3, 9.0 Hz, 1H), 3.03 (dd, *J* = 17.0, 8.3 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 157.0, 144.8, 131.0, 129.7, 128.62, 128.55, 122.4, 116.5, 114.0, 57.3, 55.3, 39.3, 24.4, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}N_3NaO_3S$ 392.1039, found 392.1047.

2-(3-(*p*-tolyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2g)

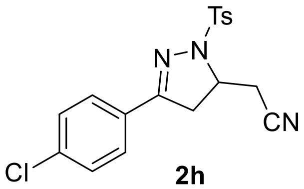


2g

White solid (59.2 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 4.14 –

4.00 (m, 1H), 3.34 (dd, J = 17.3, 10.8 Hz, 1H), 3.24 (dd, J = 17.0, 3.7 Hz, 1H), 3.09 (dd, J = 17.3, 9.6 Hz, 1H), 3.01 (dd, J = 17.0, 8.5 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 144.9, 141.5, 131.3, 129.7, 129.4, 128.7, 127.2, 126.9, 116.4, 57.5, 39.5, 24.5, 21.6, 21.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}N_3NaO_2S$ 376.1090, found 376.1098.

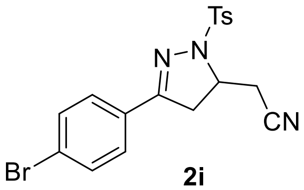
2-(3-(4-chlorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2h)



2h

White solid (48.1 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.16 – 4.04 (m, 1H), 3.34 (dd, J = 17.3, 10.9 Hz, 1H), 3.22 (dd, J = 17.0, 3.6 Hz, 1H), 3.10 (dd, J = 12.8, 8.8 Hz, 1H), 3.06 (dd, J = 12.5, 8.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 145.1, 137.1, 131.1, 129.8, 129.0, 128.6, 128.4, 128.1, 116.3, 57.6, 39.2, 24.4, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}ClN_3NaO_2S$ 396.0544, found 396.0542.

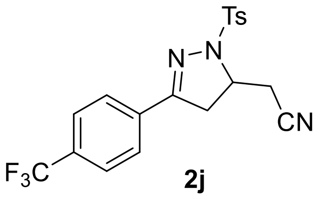
2-(3-(4-bromophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2i)



2i

White solid (56.3 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.56 – 7.47 (m, 4H), 7.32 (d, J = 7.9 Hz, 2H), 4.19 – 4.05 (m, 1H), 3.35 (dd, J = 17.3, 10.9 Hz, 1H), 3.23 (dd, J = 17.0, 3.6 Hz, 1H), 3.09 (dd, J = 19.1, 8.5 Hz, 1H), 3.05 (dd, J = 17.4, 7.9 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 145.1, 132.0, 131.3, 129.8, 128.9, 128.7, 128.3, 125.6, 116.2, 57.7, 39.2, 24.5, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}BrN_3NaO_2S$ 440.0039, found 440.0047.

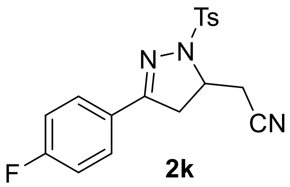
2-(1-tosyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2j)



2j

White solid (65.8 mg, 81%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.22 – 4.08 (m, 1H), 3.40 (dd, J = 17.3, 11.0 Hz, 1H), 3.24 (dd, J = 17.0, 3.6 Hz, 1H), 3.15 (dd, J = 21.0, 8.8 Hz, 1H), 3.10 (dd, J = 20.5, 8.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.7, 145.2, 133.3 (q, J = 0.9 Hz), 132.5 (q, J = 32.6 Hz), 131.2, 129.8, 128.6, 127.2, 125.7 (q, J = 3.7 Hz), 123.6 (q, J = 272.4 Hz), 116.2, 57.8, 39.1, 24.5, 21.6; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{19}H_{16}F_3N_3NaO_2S$ 430.0808, found 430.0800.

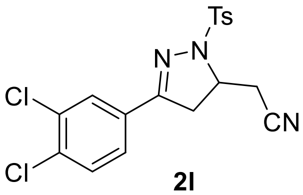
2-(3-(4-fluorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2k)



2k

White solid (50.8 mg, 71%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.64 (dd, J = 8.5, 5.3 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.07 (t, J = 8.4 Hz, 2H), 4.17 – 4.02 (m, 1H), 3.35 (dd, J = 17.3, 10.9 Hz, 1H), 3.22 (dd, J = 17.0, 3.6 Hz, 1H), 3.11 (dd, J = 16.6, 9.0 Hz, 1H), 3.07 (dd, J = 16.6, 8.3 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.2 (d, J = 252.5 Hz), 156.2, 145.0, 131.1, 129.8, 129.0 (d, J = 8.7 Hz), 128.6, 126.2 (d, J = 3.3 Hz), 116.3, 115.9 (d, J = 22.1 Hz), 57.5, 39.3, 24.4, 21.6; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{18}H_{16}FN_3NaO_2S$ 380.0839, found 380.0835.

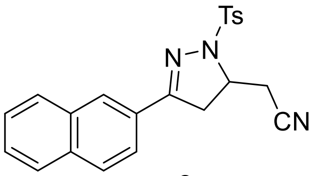
2-(3-(3,4-dichlorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2l)



2l

White solid (50.5 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.71 (s, 1H), 7.46 (s, 2H), 7.33 (d, J = 7.9 Hz, 2H), 4.20 – 4.05 (m, 1H), 3.34 (dd, J = 17.4, 11.1 Hz, 1H), 3.22 (d, J = 16.8 Hz, 1H), 3.15 – 3.02 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 145.2, 135.2, 133.2, 131.1, 130.8, 129.9, 129.8, 128.6, 128.5, 125.9, 116.2, 57.7, 39.1, 24.5, 21.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}Cl_2N_3NaO_2S$ 430.0154, found 430.0150.

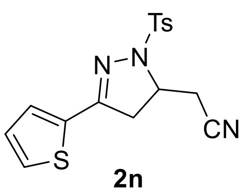
2-(3-(naphthalen-2-yl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2m)



2m

White solid (49.7 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 1H), 7.88 – 7.78 (m, 6H), 7.57 – 7.49 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.20 – 4.07 (m, 1H), 3.50 (dd, J = 17.1, 10.3 Hz, 1H), 3.34 – 3.18 (m, 2H), 3.07 (dd, J = 17.0, 8.3 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 145.0, 134.3, 132.6, 131.1, 129.7, 128.7, 128.6, 128.5, 127.8, 127.7, 127.6, 127.5, 126.9, 123.2, 116.5, 57.6, 39.3, 24.5, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}N_3NaO_2S$ 412.1090, found 412.1098.

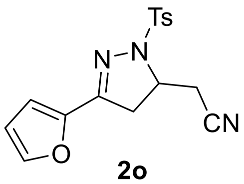
2-(3-(thiophen-2-yl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2n)



2n

White solid (49.8 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.45 (dd, J = 5.1, 1.2 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.18 (dd, J = 3.7, 1.2 Hz, 1H), 7.04 (dd, J = 5.1, 3.7 Hz, 1H), 4.11 – 4.01 (m, 1H), 3.34 (dd, J = 17.1, 10.8 Hz, 1H), 3.23 (dd, J = 17.0, 3.7 Hz, 1H), 3.13 (dd, J = 17.1, 9.5 Hz, 1H), 3.02 (dd, J = 17.0, 8.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 145.0, 133.3, 131.0, 130.0, 129.7, 129.6, 128.8, 127.6, 116.3, 57.6, 40.1, 24.4, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{15}N_3NaO_2S_2$ 368.0498, found 368.0489.

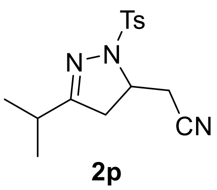
2-(3-(furan-2-yl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2o)



2o

White solid (40.1 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 1.7 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 3.5 Hz, 1H), 6.49 (dd, J = 3.7, 1.7 Hz, 1H), 4.11 – 4.01 (m, 1H), 3.33 (dd, J = 17.4, 10.9 Hz, 1H), 3.22 (dd, J = 17.0, 3.3 Hz, 1H), 3.09 (dd, J = 17.5, 9.5 Hz, 1H), 3.01 (dd, J = 17.0, 8.3 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 145.6, 145.1, 145.0, 131.2, 129.8, 128.7, 116.2, 113.2, 112.1, 57.0, 39.3, 24.4, 21.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{15}N_3NaO_3S$ 352.0726, found 352.0721.

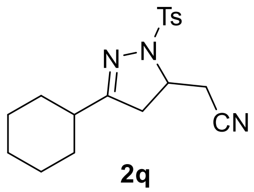
2-(3-isopropyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2p)



2p

White solid (47.4 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 3.94 – 3.81 (m, 1H), 3.08 (dd, J = 17.0, 3.7 Hz, 1H), 2.92 (dd, J = 17.0, 7.9 Hz, 1H), 2.84 (dd, J = 17.6, 10.6 Hz, 1H), 2.68 (dd, J = 17.6, 9.2 Hz, 1H), 2.63 – 2.53 (m, 1H), 2.43 (s, 3H), 1.06 (d, J = 3.7 Hz, 3H), 1.04 (d, J = 3.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.7, 131.0, 129.5, 128.8, 116.3, 56.8, 39.4, 29.7, 24.5, 21.6, 19.8, 19.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{19}N_3NaO_2S$ 328.1090, found 328.1093.

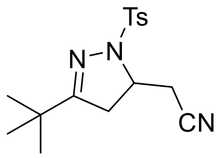
2-(3-cyclohexyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2q)



2q

Colorless oil (51.8 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.89 – 3.78 (m, 1H), 3.08 (dd, *J* = 17.0, 3.7 Hz, 1H), 2.91 (dd, *J* = 16.9, 8.0 Hz, 1H), 2.83 (dd, *J* = 17.6, 10.7 Hz, 1H), 2.67 (dd, *J* = 17.6, 9.1 Hz, 1H), 2.43 (s, 3H), 2.33 – 2.21 (m, 1H), 1.74 – 1.60 (m, 5H), 1.33 – 1.10 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.8, 130.7, 129.5, 128.7, 116.4, 56.5, 39.8, 39.0, 30.1, 29.8, 25.6, 25.5, 25.4, 24.5, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{23}N_3NaO_2S$ 368.1403, found 368.1409.

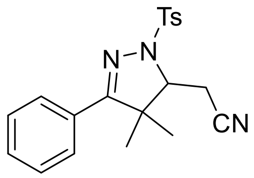
2-(3-(tert-butyl)-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2r)



2r

Colorless oil (58.1 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.90 – 3.77 (m, 1H), 3.06 (dd, *J* = 16.9, 3.7 Hz, 1H), 2.92 (dd, *J* = 15.3, 6.0 Hz, 1H), 2.86 (dd, *J* = 15.9, 8.9 Hz, 1H), 2.67 (dd, *J* = 17.6, 9.2 Hz, 1H), 2.42 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 144.8, 130.5, 129.4, 128.7, 116.4, 57.2, 38.4, 34.2, 27.7, 24.5, 21.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{21}N_3NaO_2S$ 342.1247, found 342.1241.

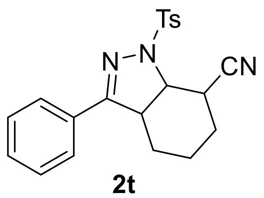
2-(4,4-dimethyl-3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2s)



2s

White solid (42.7 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.47 – 7.32 (m, 5H), 3.55 (dd, J = 17.2, 3.7 Hz, 1H), 3.40 (dd, J = 10.5, 3.7 Hz, 1H), 2.92 (dd, J = 17.2, 10.5 Hz, 1H), 2.44 (s, 3H), 1.43 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 145.1, 130.3, 129.73, 129.65, 129.0, 128.6, 127.6, 116.5, 67.3, 51.7, 26.1, 21.7, 19.5, 18.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{21}N_3NaO_2S$ 390.1247, found 390.1252.

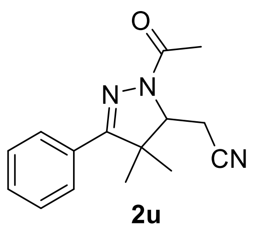
3-phenyl-1-tosyl-3a,4,5,6,7,7a-hexahydro-1*H*-indazole-7-carbonitrile (2t)



2t

White solid (53.7 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 7.72 – 7.65 (m, 2H), 7.46 – 7.36 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 4.31 – 4.24 (m, 1H), 3.46 – 3.33 (m, 2H), 2.39 (s, 3H), 2.09 – 1.99 (m, 3H), 1.84 – 1.68 (m, 2H), 1.36 – 1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 145.1, 131.0, 129.69, 129.59, 129.1, 128.8, 127.1, 120.2, 62.9, 42.6, 27.7, 26.1, 22.9, 21.6, 18.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{21}N_3NaO_2S$ 402.1247, found 402.1239.

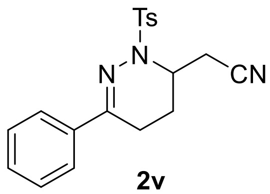
2-(1-acetyl-4,4-dimethyl-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)acetonitrile (2u)



2u

White solid (28.5 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.5 Hz, 2H), 7.48 – 7.38 (m, 3H), 4.34 (dd, J = 7.2, 2.6 Hz, 1H), 3.04 (dd, J = 17.1, 7.1 Hz, 1H), 2.79 (dd, J = 17.1, 2.6 Hz, 1H), 2.40 (s, 3H), 1.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 162.1, 130.3, 130.1, 128.7, 127.6, 117.0, 64.2, 50.0, 28.1, 21.7, 19.0, 16.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{17}N_3NaO$ 278.1264, found 278.1270.

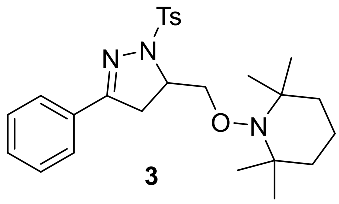
2-(6-phenyl-2-tosyl-2,3,4,5-tetrahydropyridazin-3-yl)acetonitrile (2v)



2v

White solid (28.4 mg, 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.3 Hz, 2H), 7.69 (dd, J = 6.7, 2.9 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.32 (d, J = 8.1 Hz, 2H), 4.75 – 4.65 (m, 1H), 2.88 (dd, J = 16.9, 4.5 Hz, 1H), 2.79 – 2.67 (m, 1H), 2.56 (dd, J = 16.9, 10.5 Hz, 1H), 2.51 – 2.31 (m, 5H), 1.88 – 1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 144.5, 136.1, 134.9, 129.7, 129.7, 128.5, 128.0, 125.3, 116.3, 47.4, 21.6, 20.63, 20.60, 17.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}N_3NaO_2S$ 376.1090, found 376.1098.

2,2,6,6-tetramethyl-1-((3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-5-yl)methoxy)piperidine (3)



3

White solid (72.9 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.73 – 7.66 (m, 2H), 7.44 – 7.35 (m, 3H), 7.27 (d, J = 7.8 Hz, 2H), 4.31 (dd, J = 9.2, 3.8 Hz, 1H), 4.12 (dd, J = 9.2, 7.3 Hz, 1H), 4.01 – 3.88 (m, 1H), 3.18 (dd, J = 17.2, 8.9 Hz, 1H), 3.10 (dd, J = 17.2, 11.0 Hz, 1H), 2.38 (s, 3H), 1.58 – 1.29 (m, 6H), 1.23 (s, 6H), 1.07 (d, J = 8.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 144.1, 131.9, 130.8, 130.5, 129.4, 128.51, 128.50, 126.9, 77.9, 60.0, 59.8, 39.5, 37.3, 33.2, 33.0, 21.5, 20.0, 17.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{26}H_{35}N_3NaO_3S$ 492.2291, found 492.2285.

S. Chen, W. Chen, X. Chen, G. Chen, L. Ackermann and X. Tian, Copper (I)-catalyzed oxyamination of β,γ-unsaturated hydrazones: synthesis of dihydropyrazoles, *Org. Lett.*, 2019, **21**, 7787-7790.

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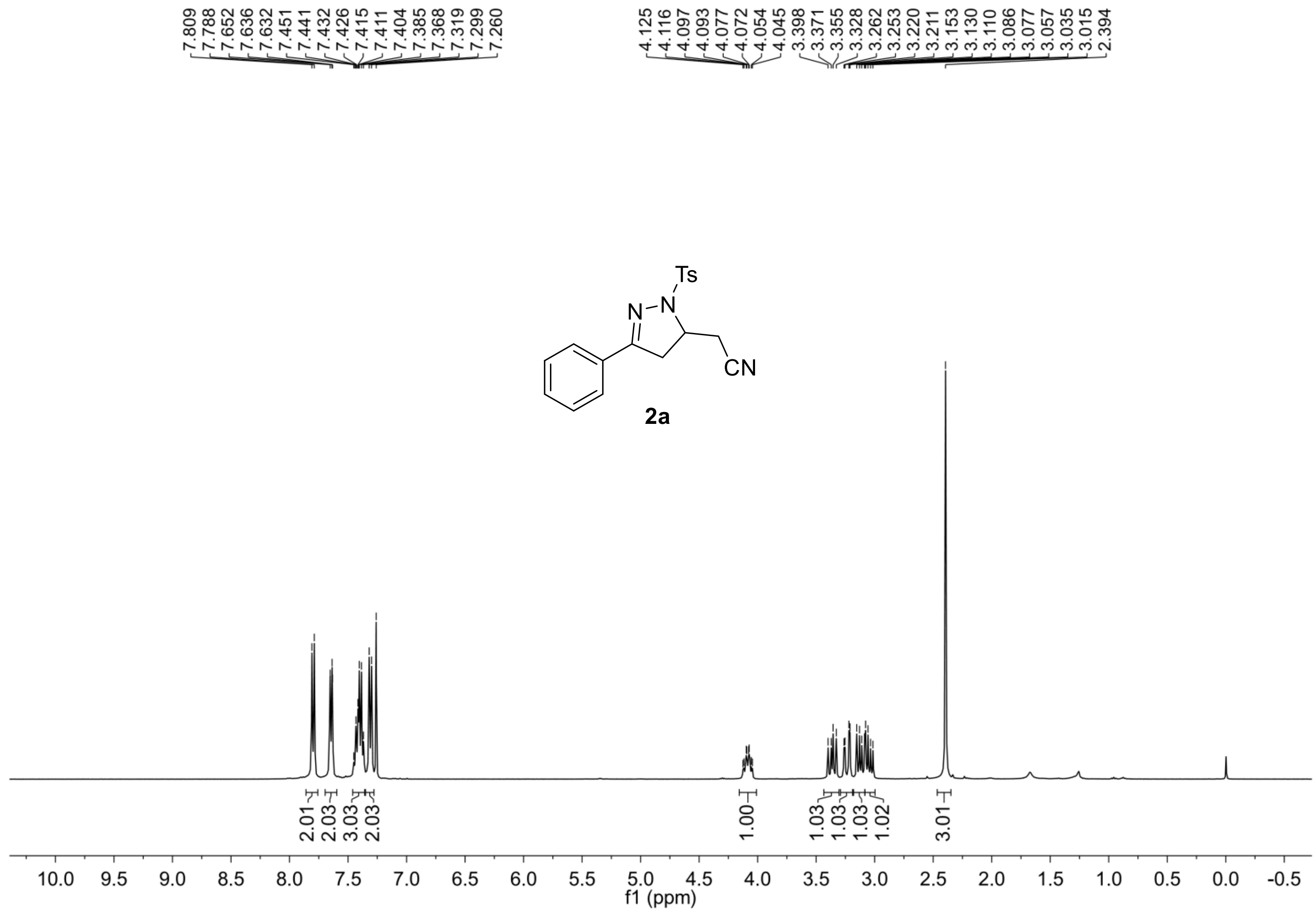
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7.368
7.319
7.299
7.260
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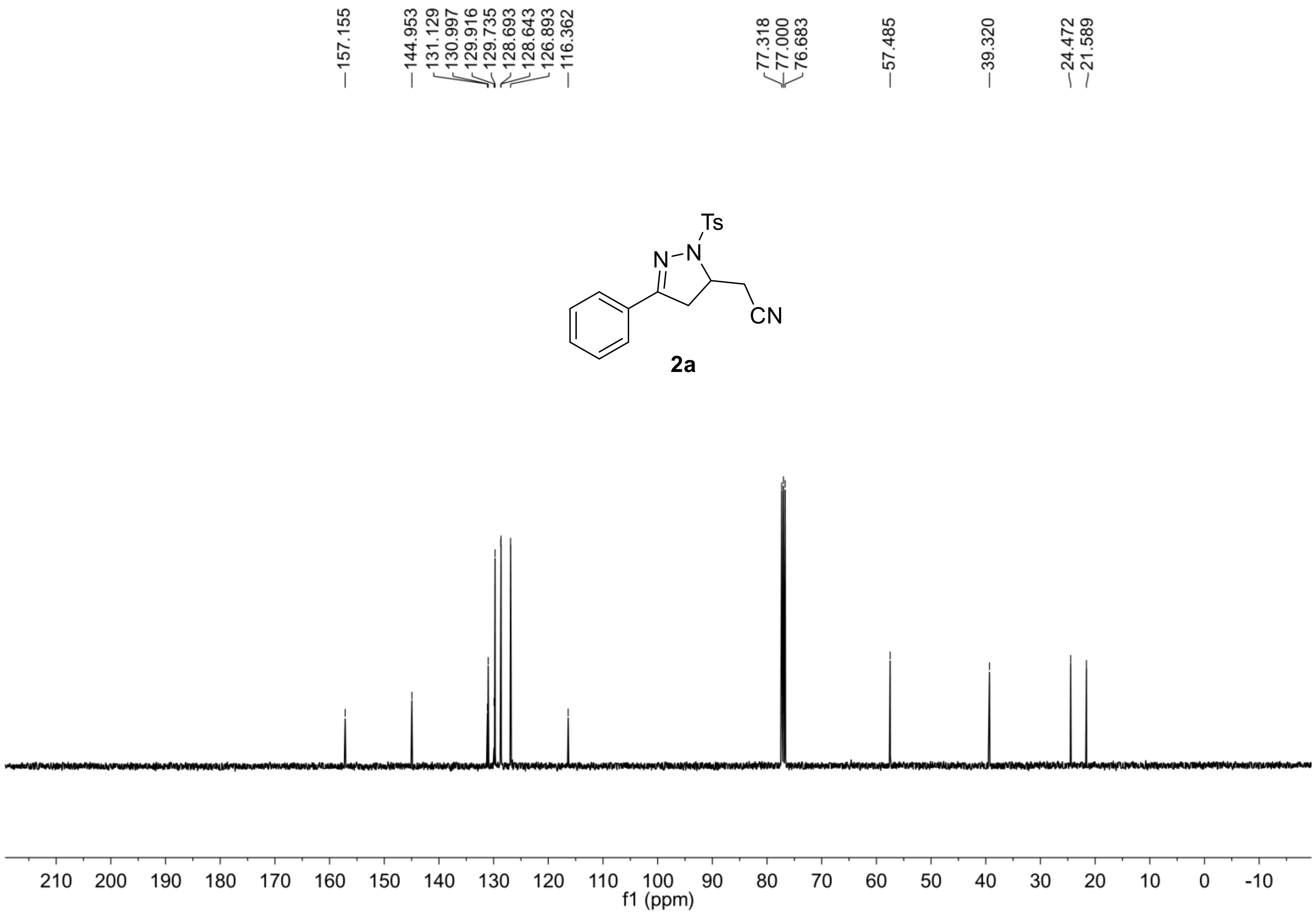
4.116
4.097
4.093
4.077
4.072
4.054
4.045
3.398
3.371
3.355
3.328
3.262
3.253
3.220
3.211
3.153
3.130
3.110
3.086
3.077
3.057
3.035
3.015
2.394
Ts
N
N
CN
2a
2.01
2.03
3.03
2.03
1.00
1.03
1.03
1.03
1.02
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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76.683
57.485
39.320
24.472
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Ts
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N
CN
2a
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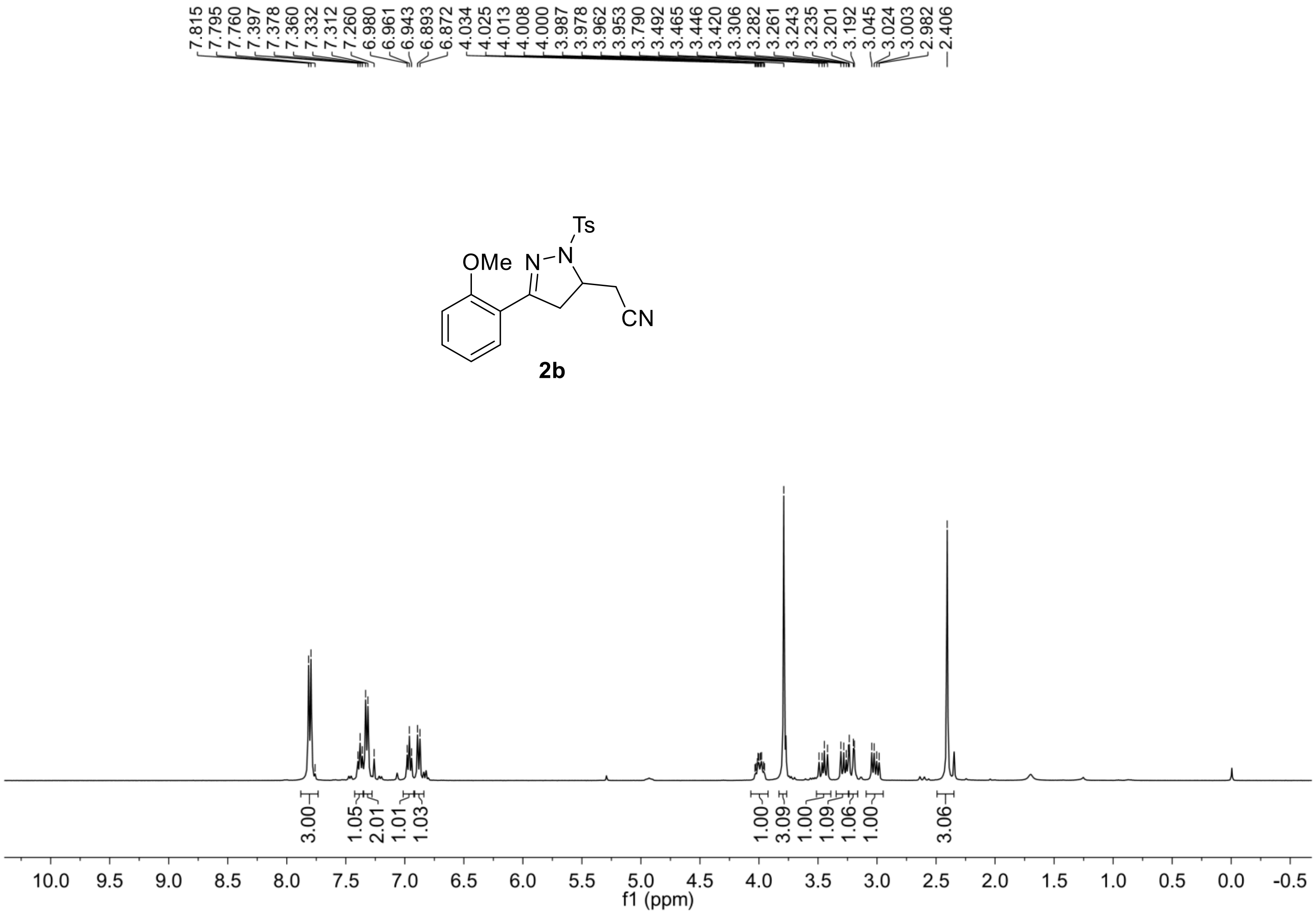
f1 (ppm)



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2.982
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CN
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8.0
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7.0
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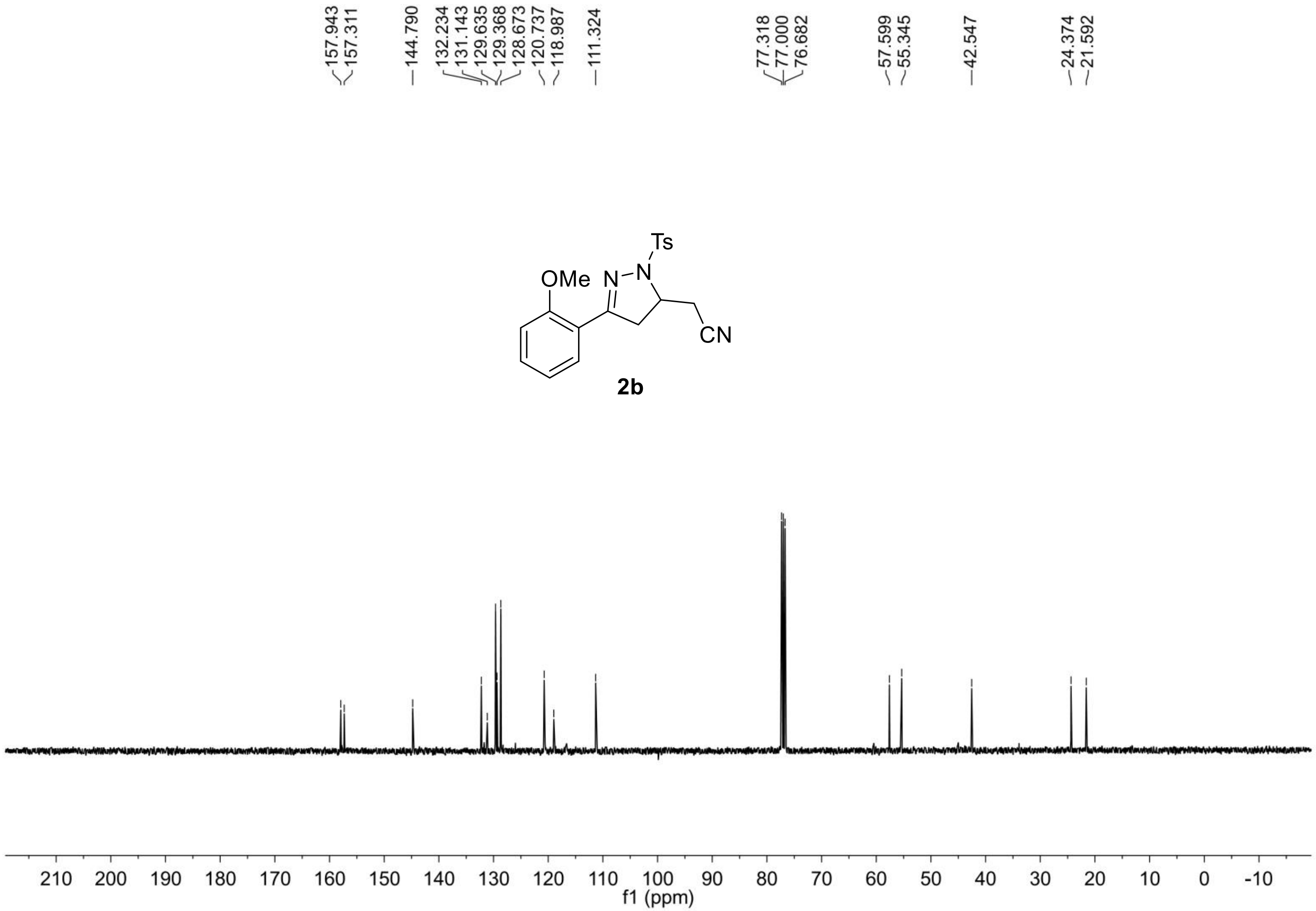
f1 (ppm)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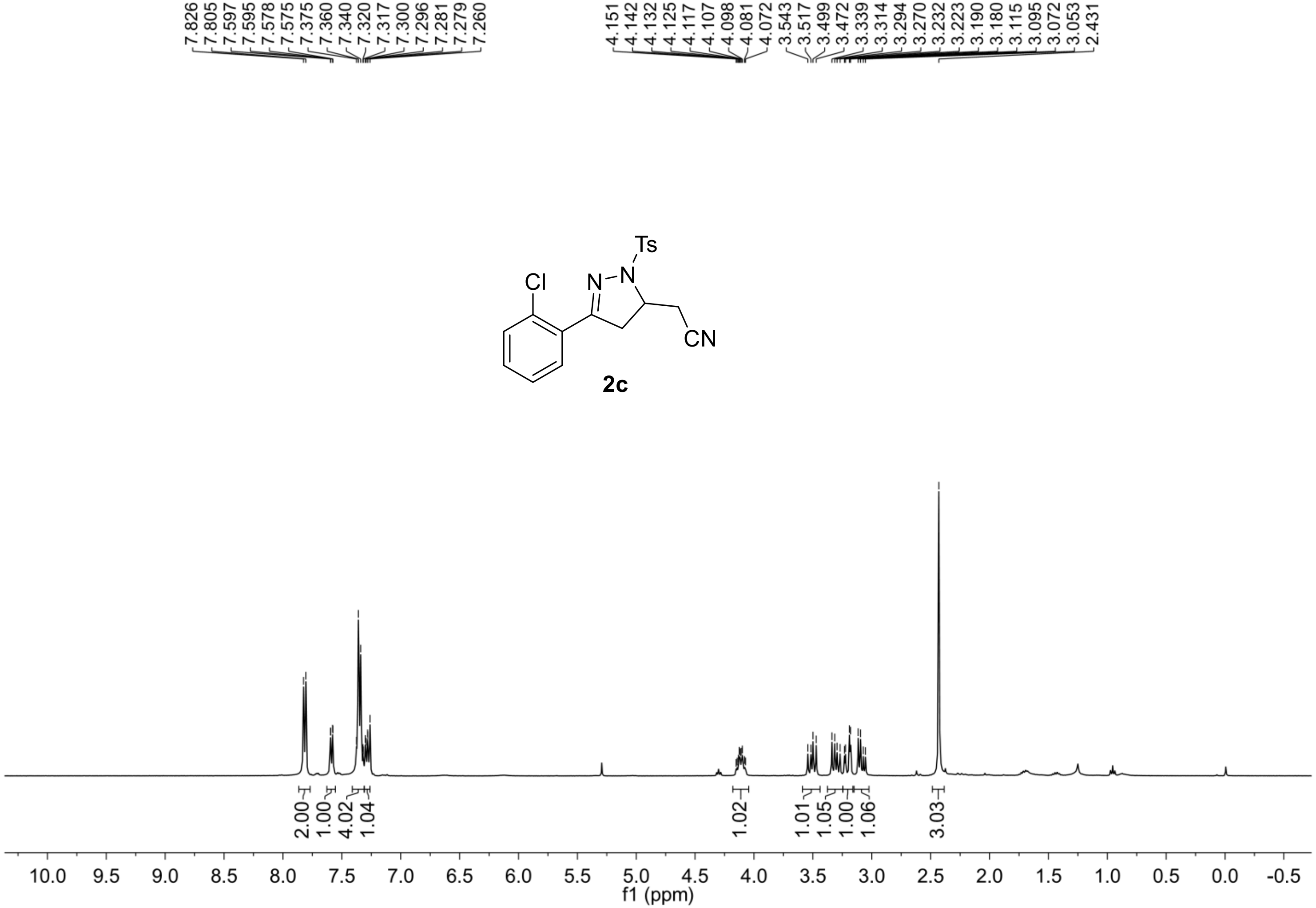
f1 (ppm)

2b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3.294
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Cl
CN
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1.05
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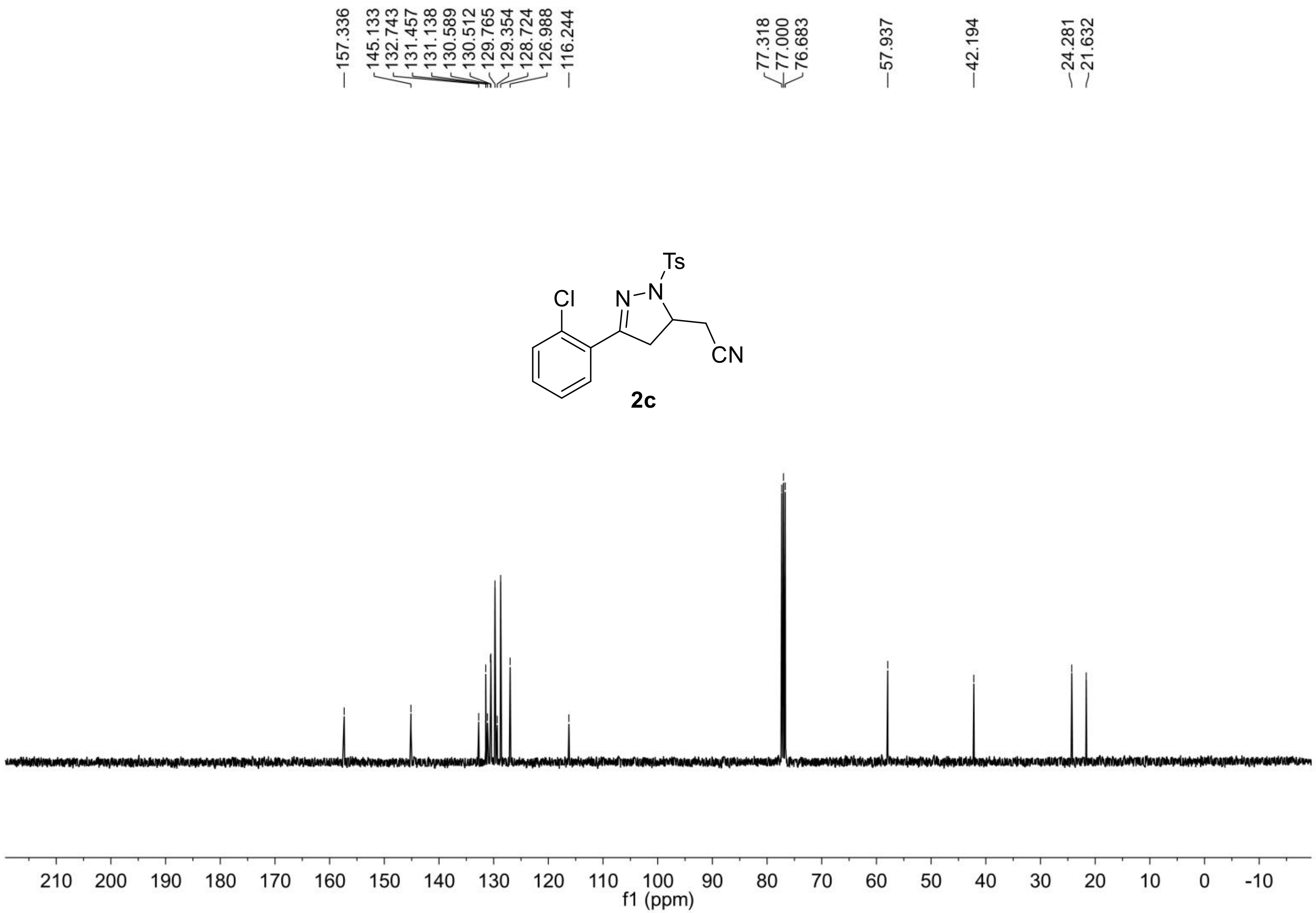
1.06
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2c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77.000
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Cl
CN
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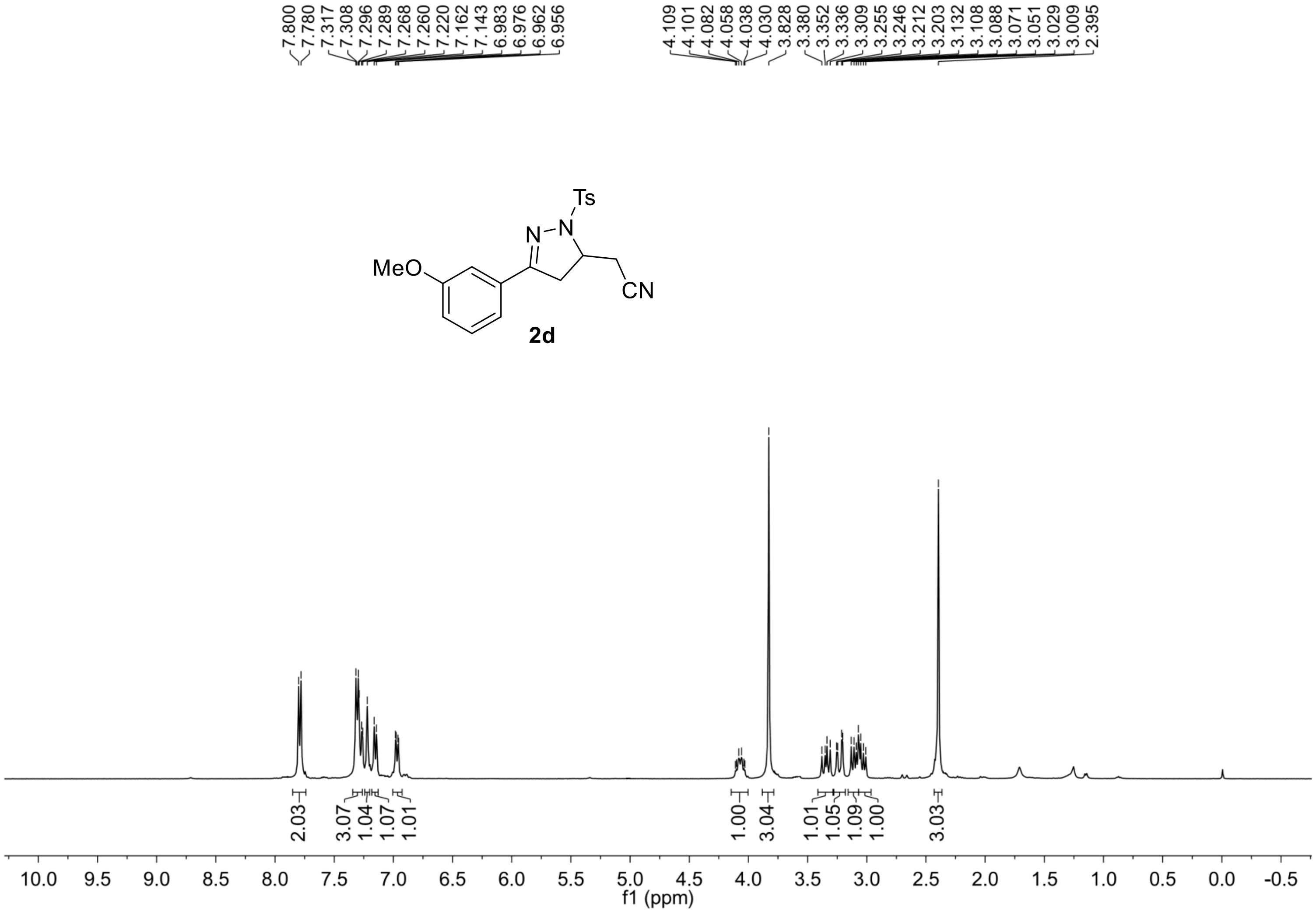
f1 (ppm)

2c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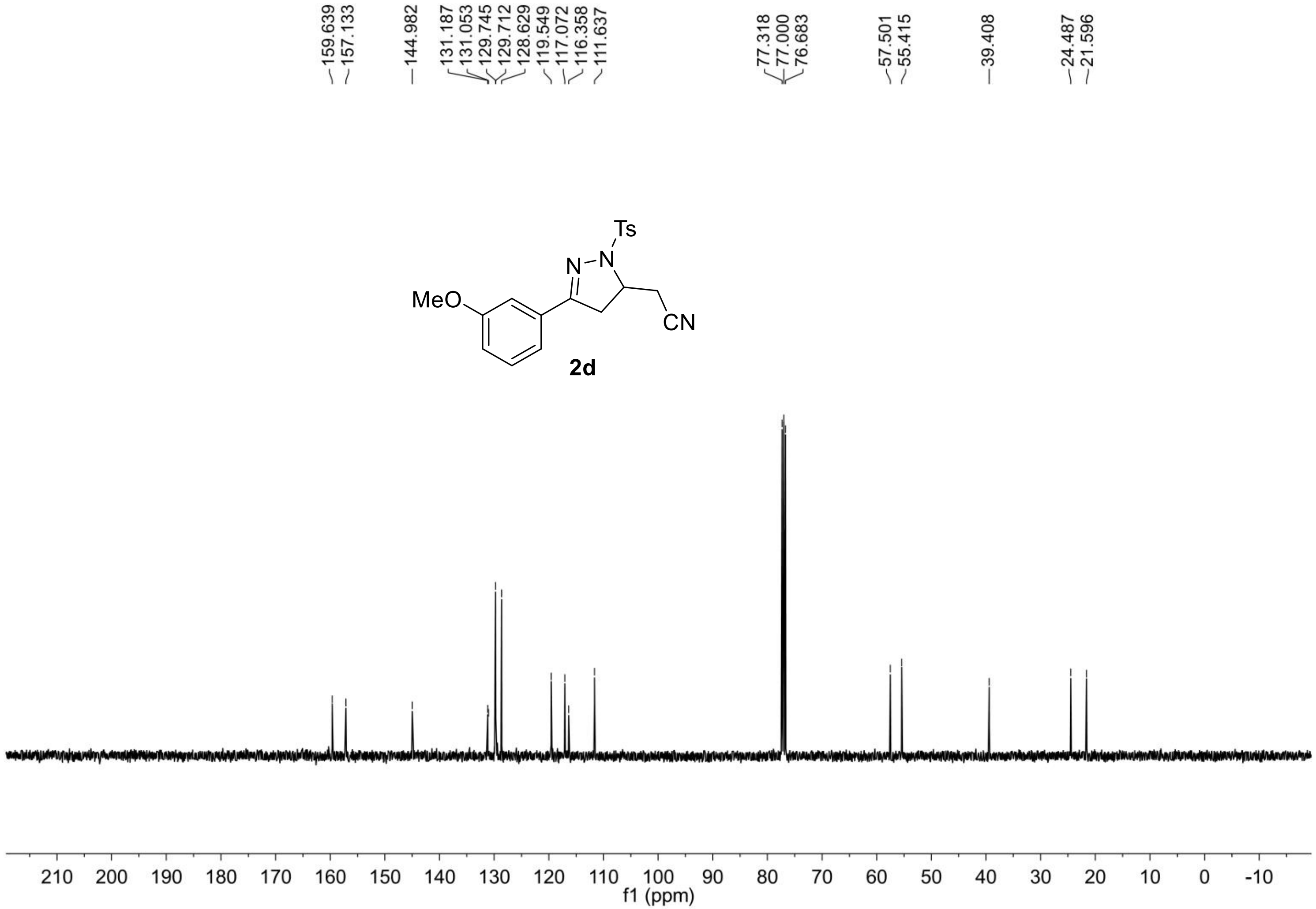
f1 (ppm)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55.415
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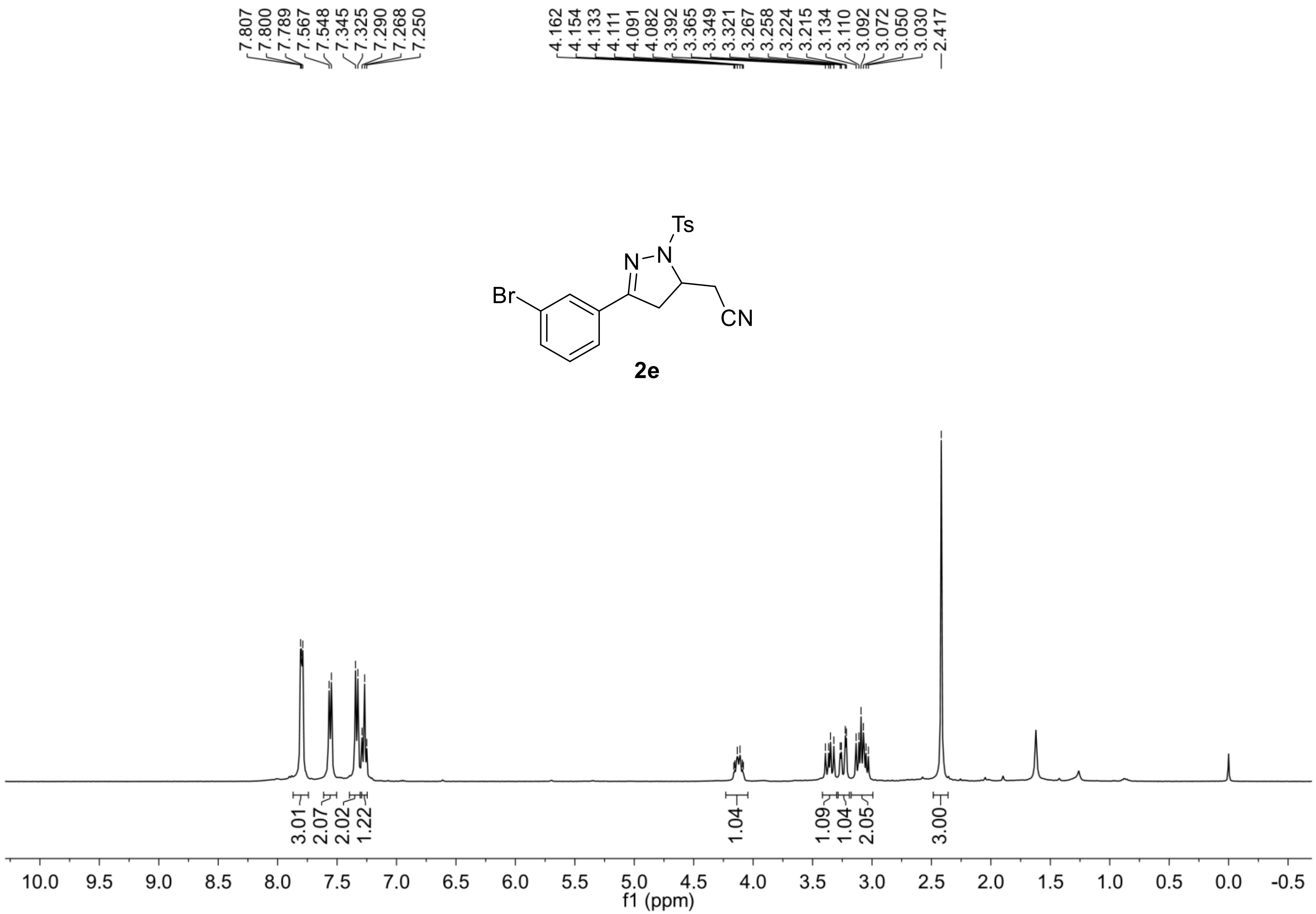
f1 (ppm)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2.02
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1.04
2.05
3.00
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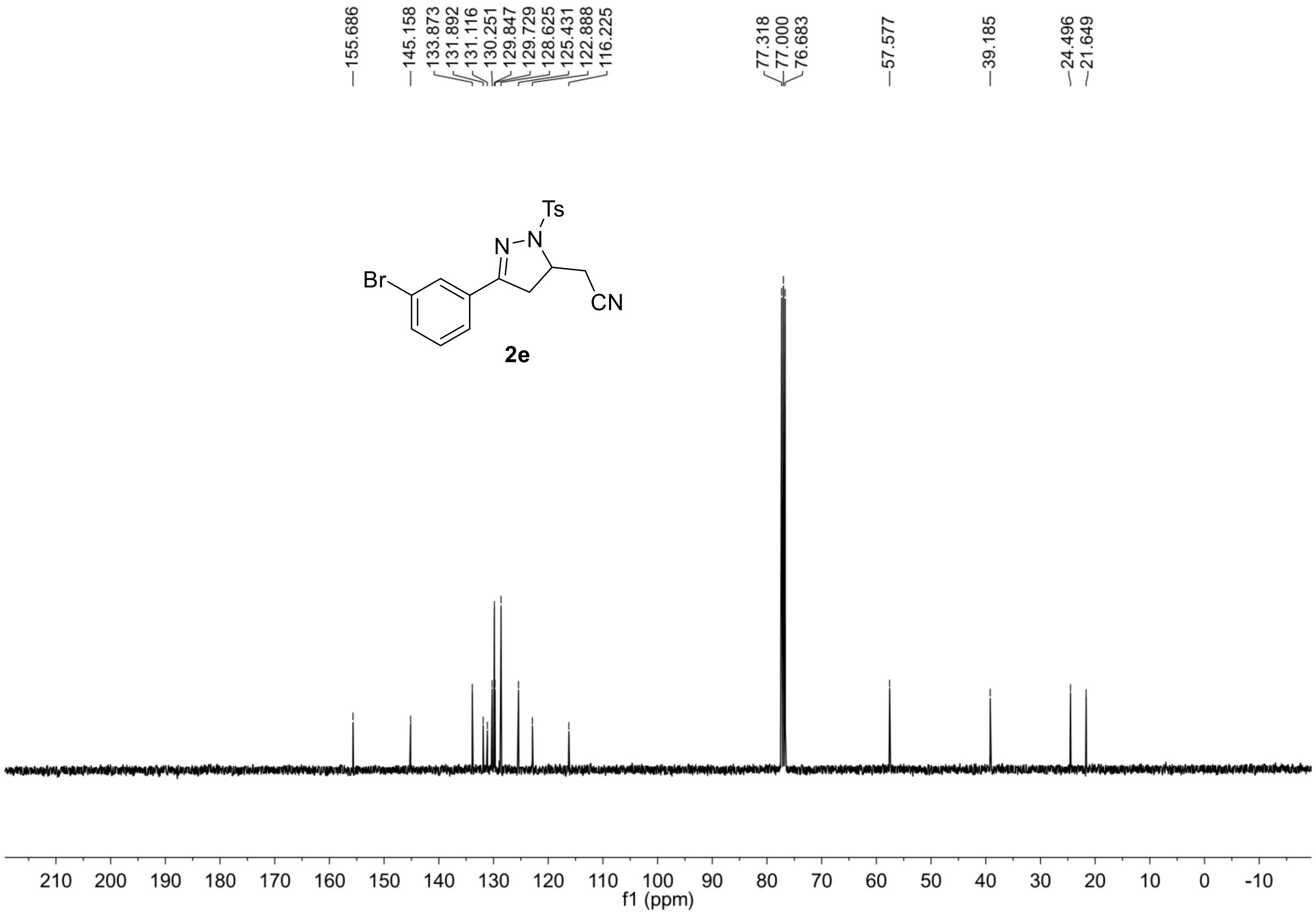
f1 (ppm)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77.000
76.683
57.577
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21.649
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N
Br
CN
2e
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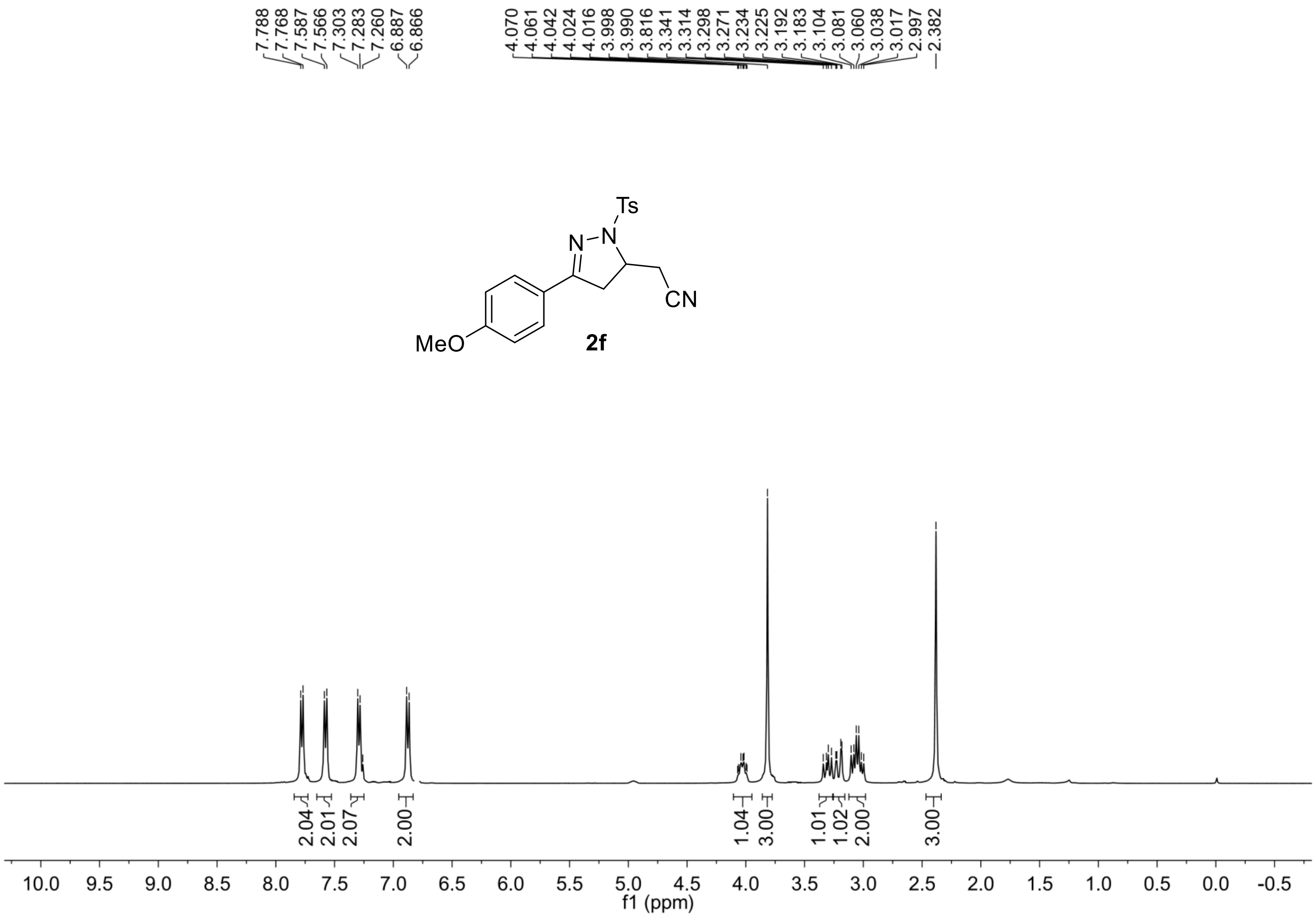
f1 (ppm)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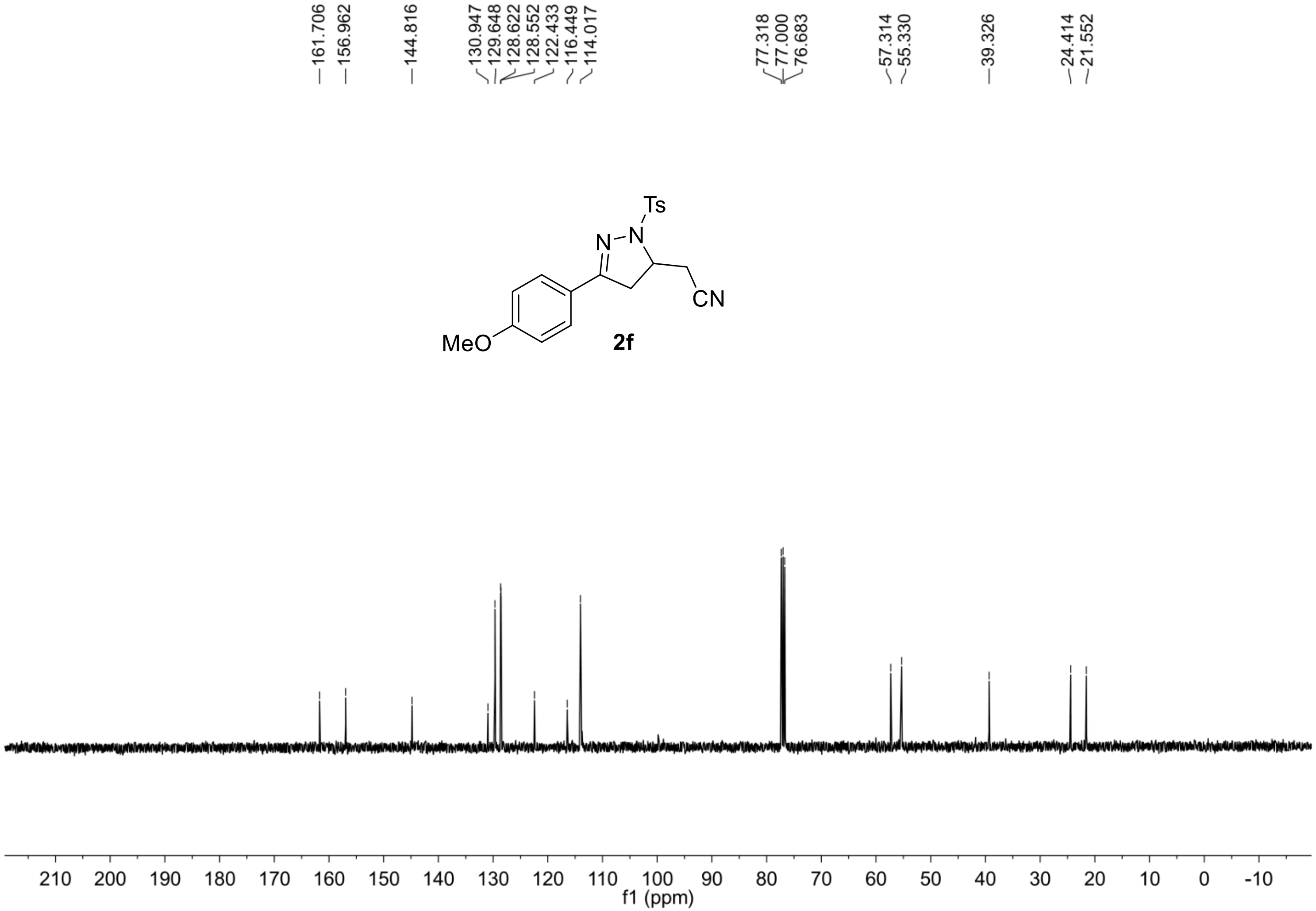
6.887
6.866
4.070
4.061
4.042
4.024
4.016
3.998
3.990
3.816
3.341
3.314
3.298
3.271
3.234
3.225
3.192
3.183
3.104
3.081
3.060
3.038
3.017
2.997
2.382
Ts
N
N
CN
MeO
2f
2.04
2.01
2.07
2.00
1.04
3.00
1.01
1.02
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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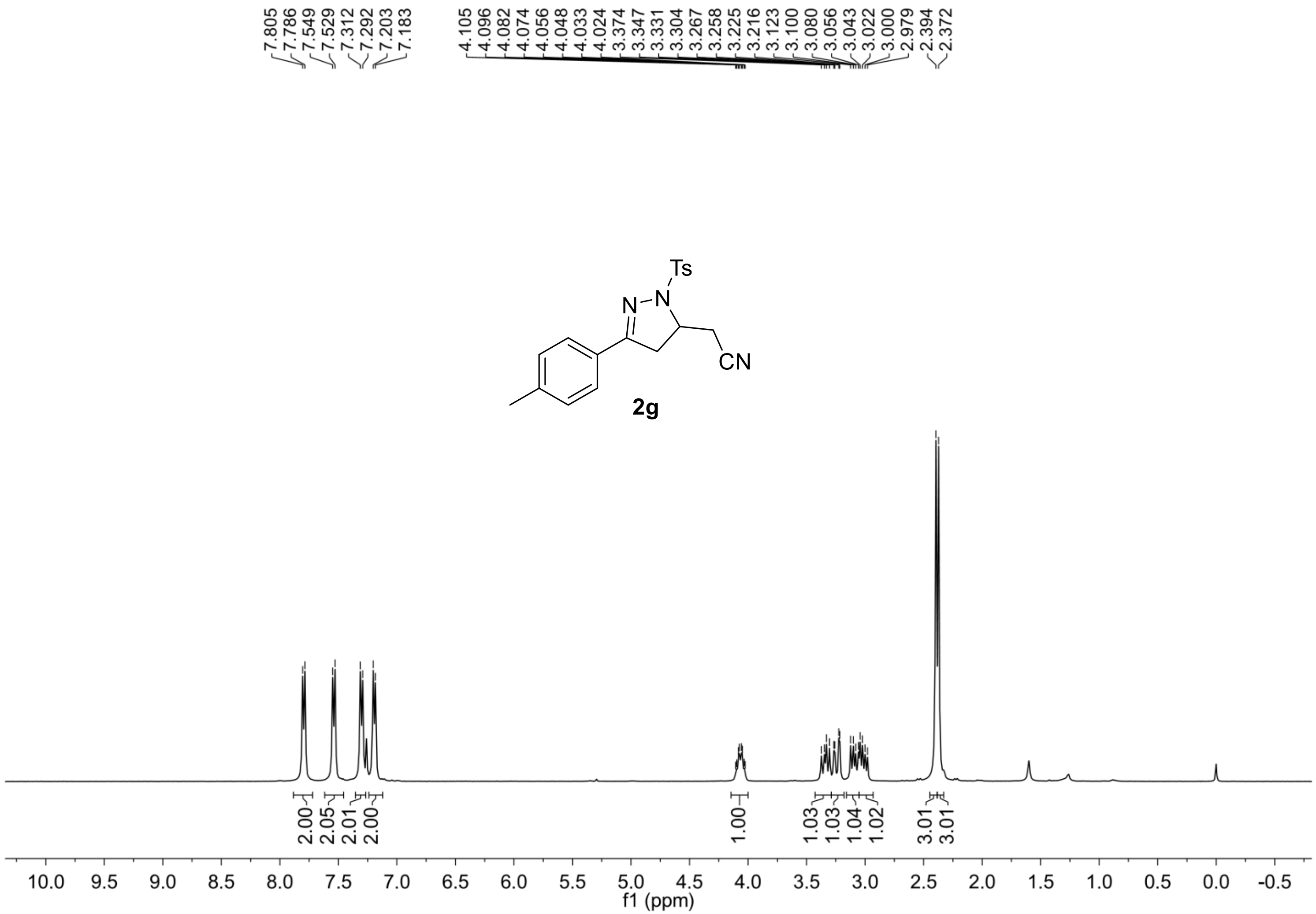
156.962
144.816
130.947
129.648
128.622
128.552
122.433
116.449
114.017
77.318
77.000
76.683
57.314
55.330
39.326
24.414
21.552
Ts
N
N
CN
MeO
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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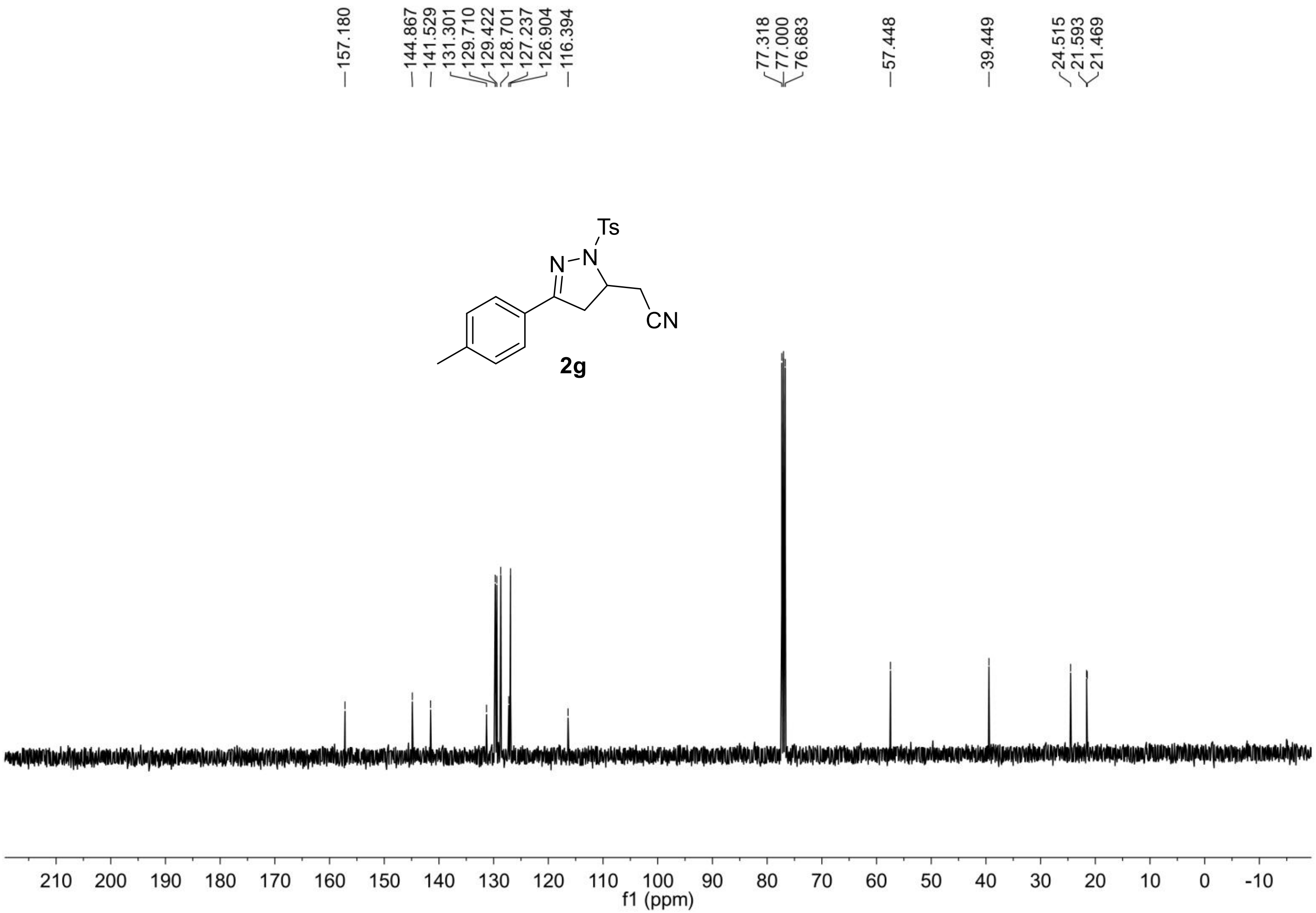
7.786
7.549
7.529
7.312
7.292
7.203
7.183
4.105
4.096
4.082
4.074
4.056
4.048
4.033
4.024
3.374
3.347
3.331
3.304
3.267
3.258
3.225
3.216
3.123
3.100
3.080
3.056
3.043
3.022
3.000
2.979
2.394
2.372
Ts
N
N
CN
2g
2.00
2.05
2.01
2.00
1.00
1.03
1.03
1.04
1.02
3.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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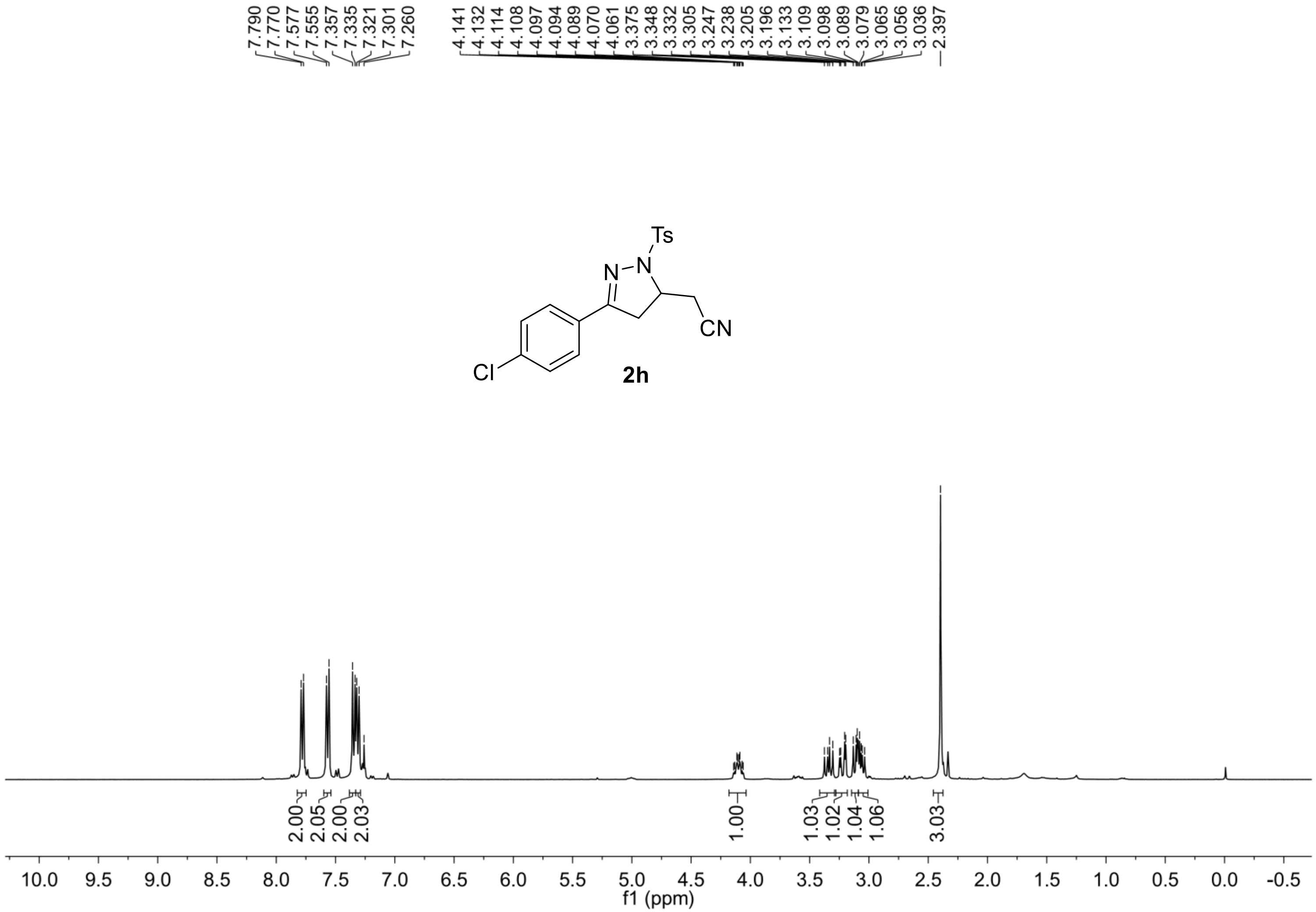
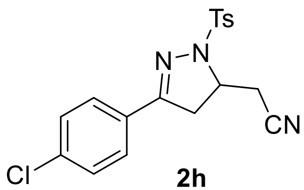
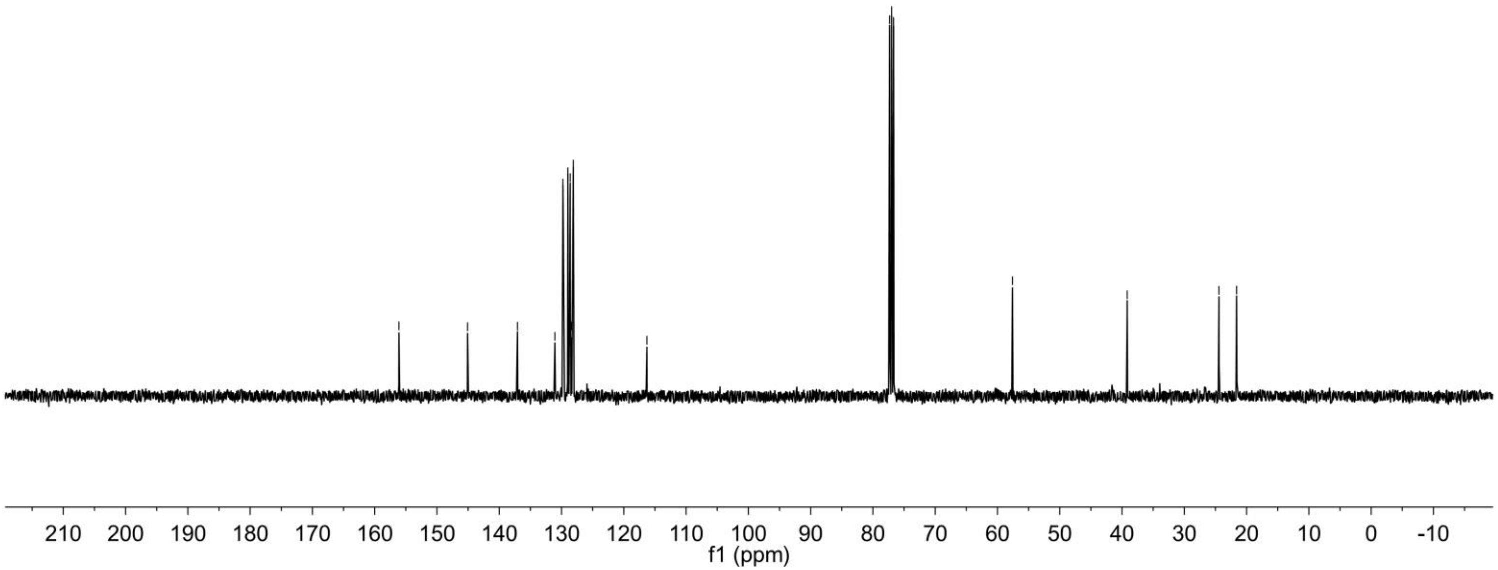
141.529
131.301
129.710
129.422
128.701
127.237
126.904
116.394
77.318
77.000
76.683
57.448
39.449
24.515
21.593
21.469
Ts
N
N
CN
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.790
7.770
7.577
7.555
7.357
7.335
7.321
7.301
7.260
4.141
4.132
4.114
4.108
4.097
4.094
4.089
4.070
4.061
3.375
3.348
3.332
3.305
3.247
3.238
3.205
3.196
3.133
3.109
3.098
3.089
3.079
3.065
3.056
3.036
2.397
Ts
N
N
CN
Cl
2h
2.00
2.05
2.00
2.03
1.00
1.03
1.02
1.04
1.06
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



2h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145.086
137.075
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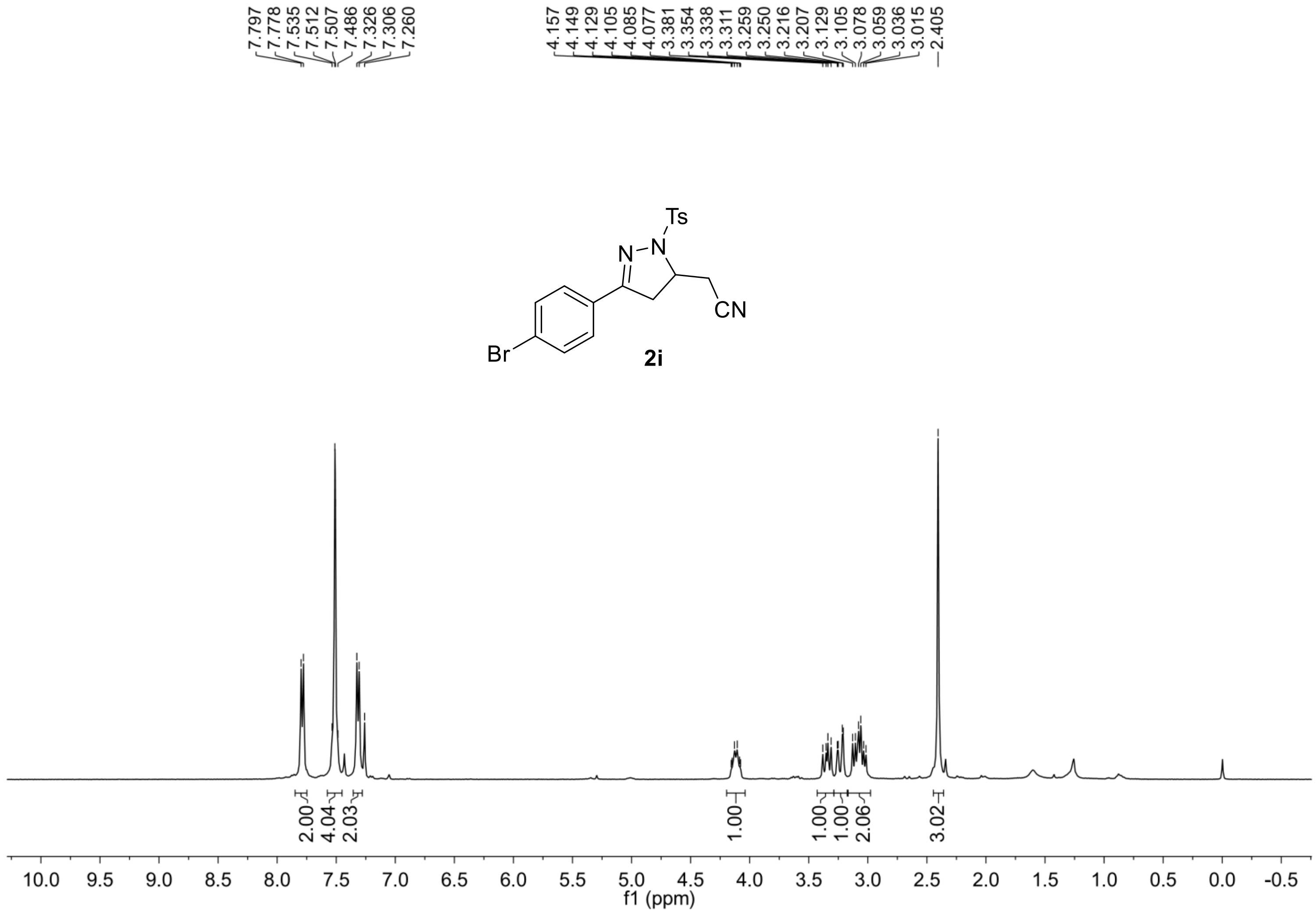
129.773
128.986
128.605
128.382
128.110
116.291
77.319
77.000
76.682
57.594
39.172
24.431
21.607
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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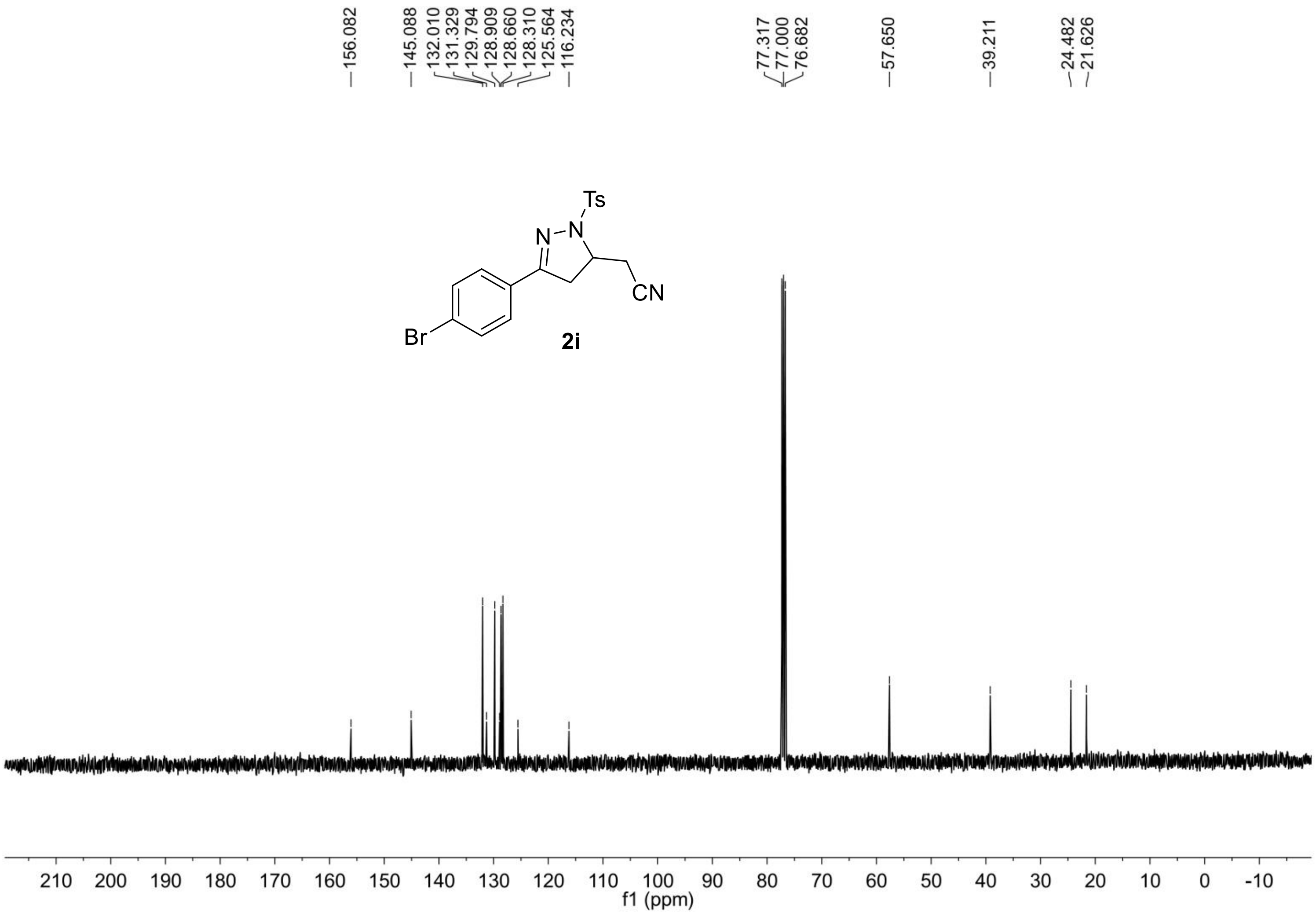
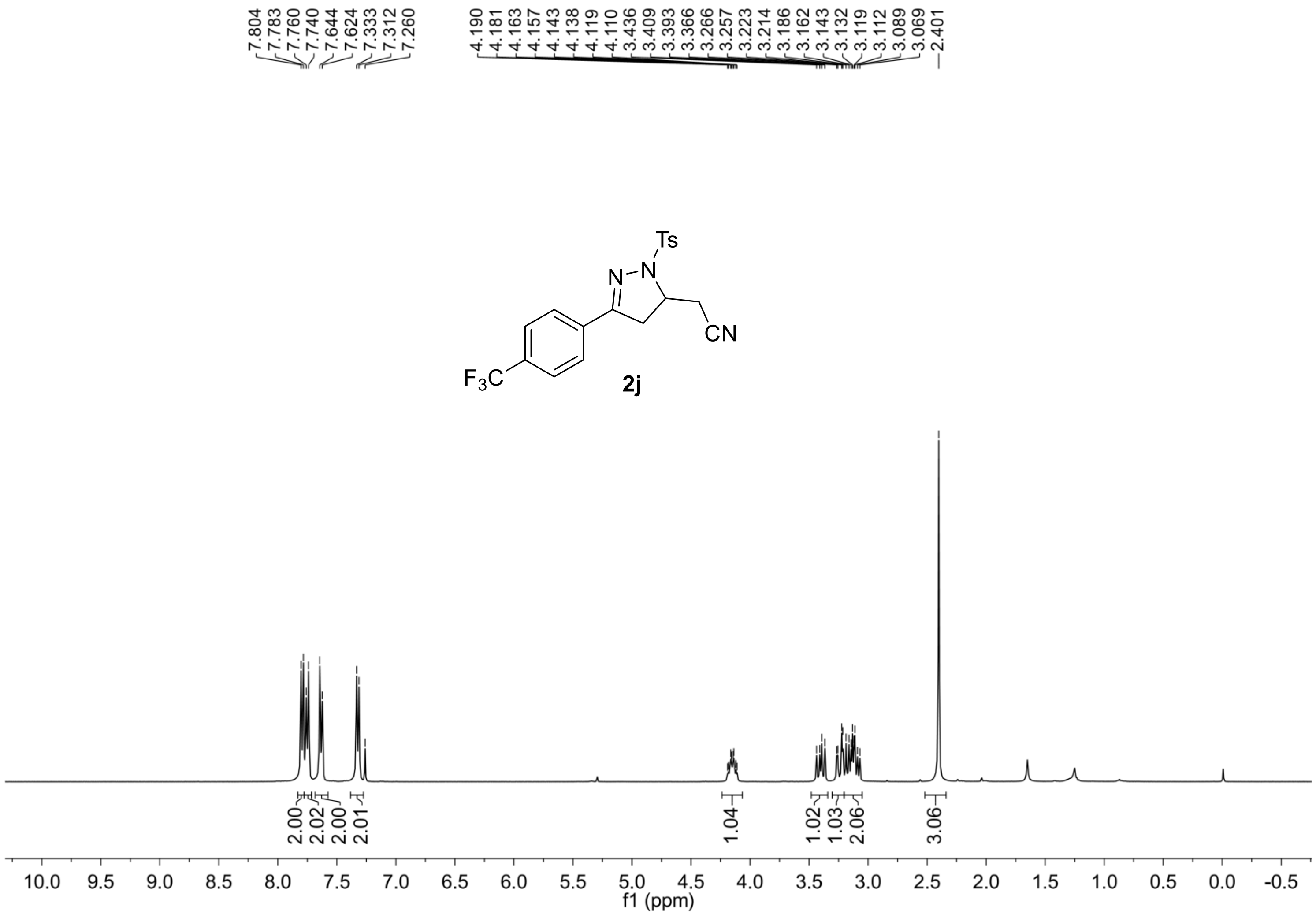
7.778
7.535
7.512
7.507
7.486
7.326
7.306
7.260
4.157
4.149
4.129
4.105
4.085
4.077
3.381
3.354
3.338
3.311
3.259
3.250
3.216
3.207
3.129
3.105
3.078
3.059
3.036
3.015
2.405
Ts
N
N
Br
CN
2.00
4.04
2.03
1.00
1.00
1.00
2.06
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2i


156.082
145.088
132.010
131.329
129.794
128.909
128.660
128.310
125.564
116.234
77.317
77.000
76.682
57.650
39.211
24.482
21.626
Ts
N
N
CN
Br
2i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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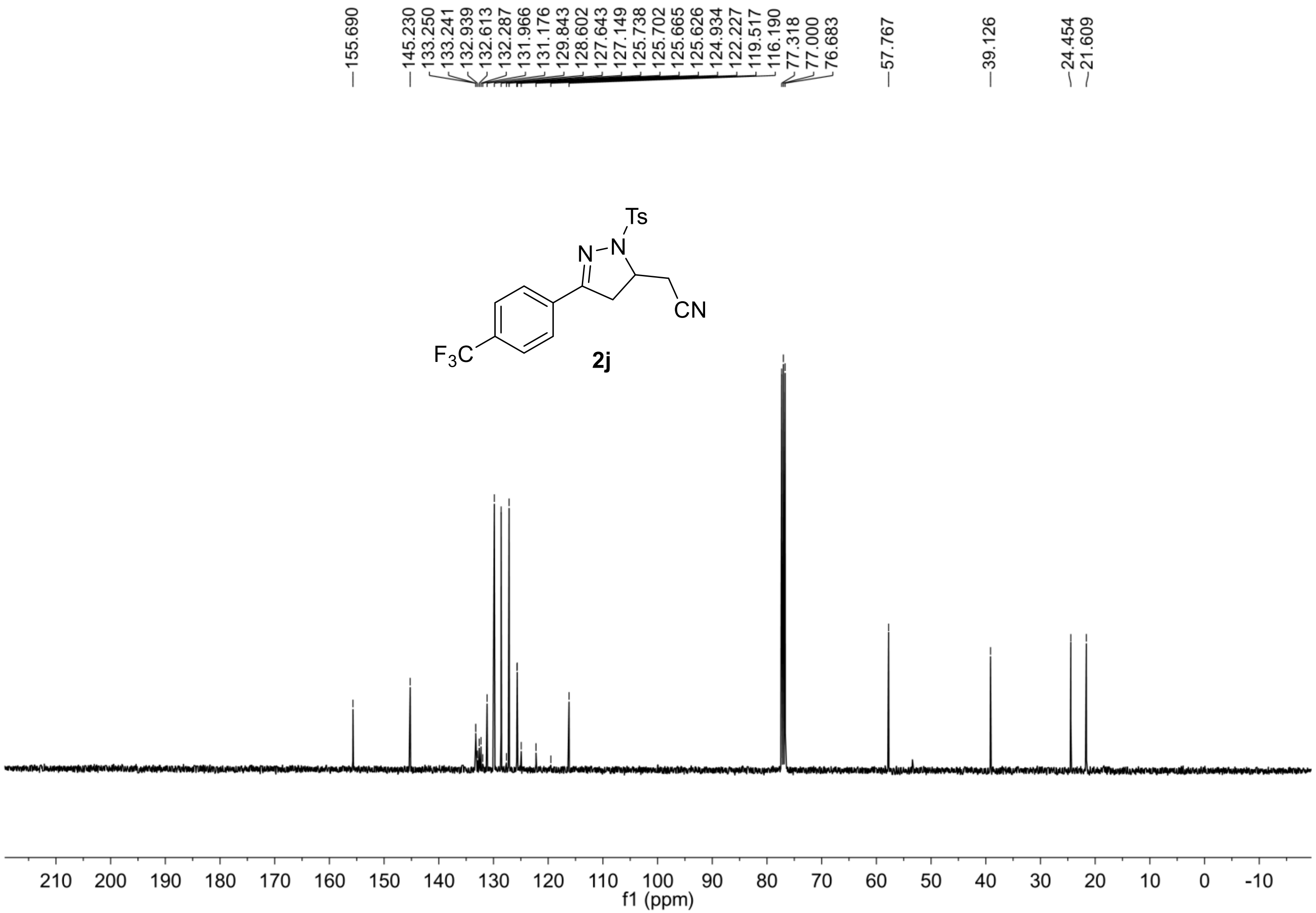
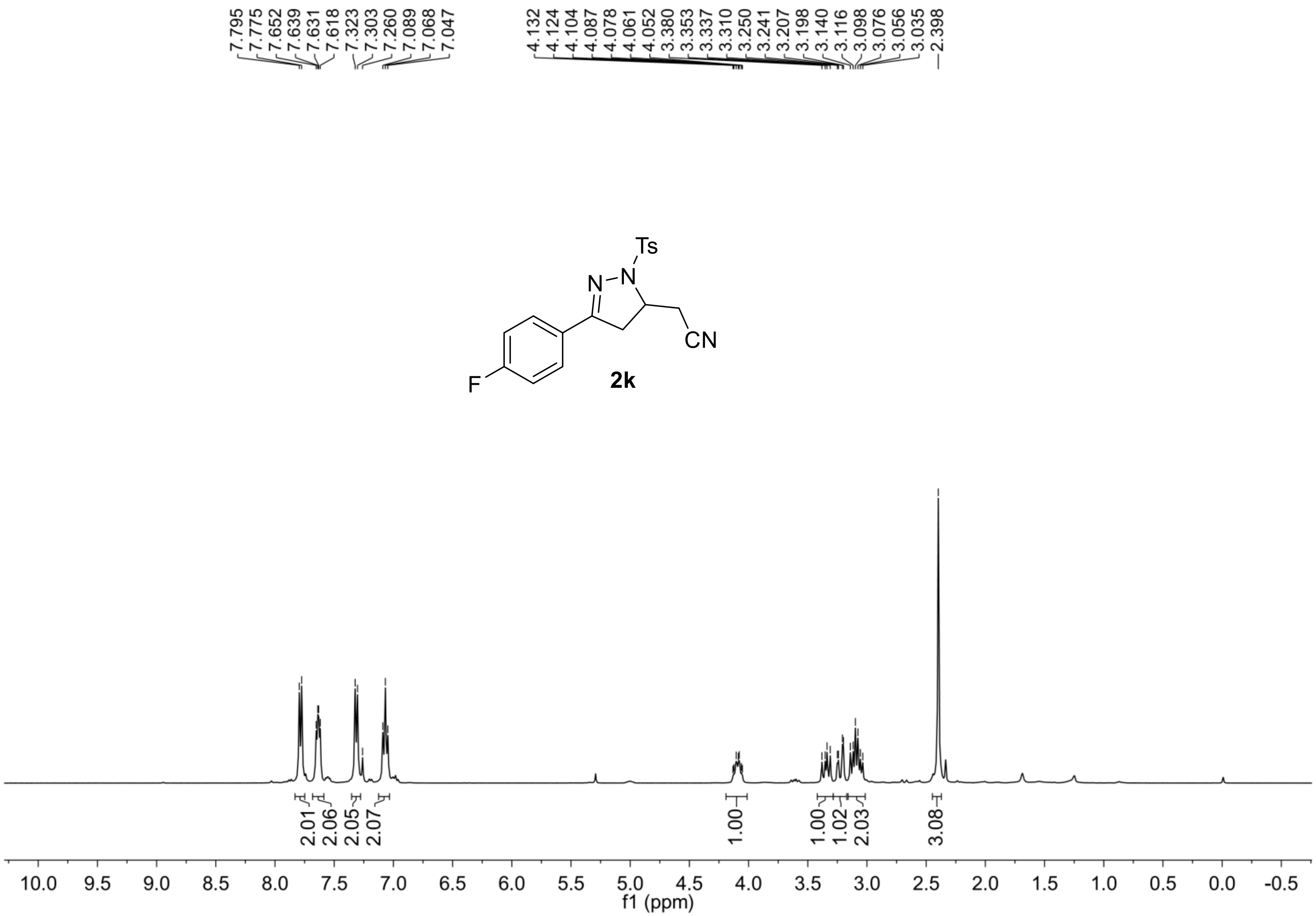
7.783
7.760
7.740
7.644
7.624
7.333
7.312
7.260
4.190
4.181
4.163
4.157
4.143
4.138
4.119
4.110
3.436
3.409
3.393
3.366
3.266
3.257
3.223
3.214
3.186
3.162
3.143
3.132
3.119
3.112
3.089
3.069
2.401
Ts
N
N
CN
F3C
2j
2.00
2.02
2.00
2.01
1.04
1.02
1.03
2.06
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


155.690
145.230
133.250
133.241
132.939
132.613
132.287
131.966
131.176
129.843
128.602
127.643
127.149
125.738
125.702
125.665
125.626
124.934
122.227
119.517
116.190
77.318
77.000
76.683
57.767
39.126
24.454
21.609
Ts
N
N
CN
F3C
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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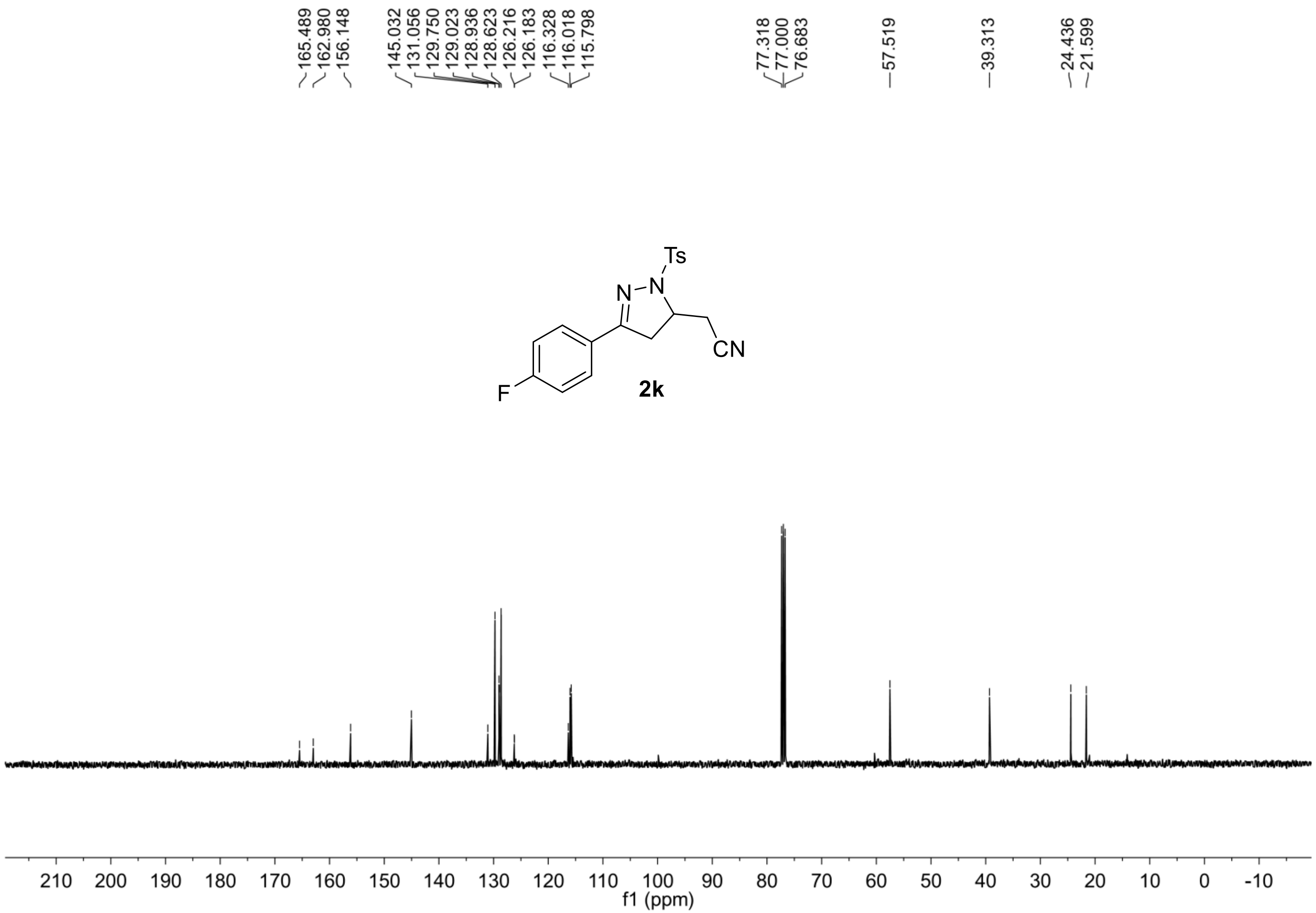
7.775
7.652
7.639
7.631
7.618
7.323
7.303
7.260
7.089
7.068
7.047
4.132
4.124
4.104
4.087
4.078
4.061
4.052
3.380
3.353
3.337
3.310
3.250
3.241
3.207
3.198
3.140
3.116
3.098
3.076
3.056
3.035
2.398
Ts
N
N
CN
F
2k
2.01
2.06
2.05
2.07
1.00
1.00
1.02
2.03
3.08
f1 (ppm)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145.032
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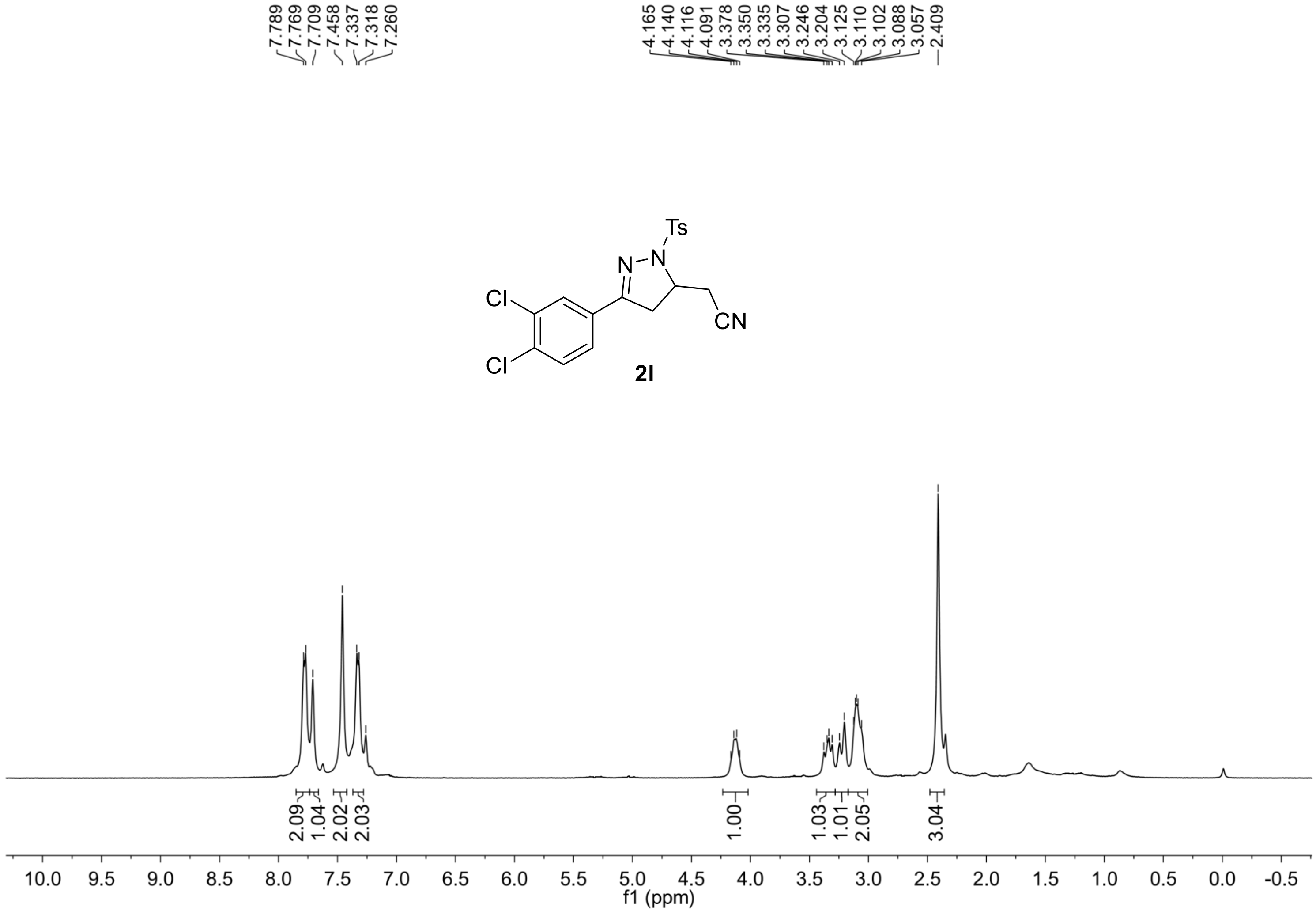
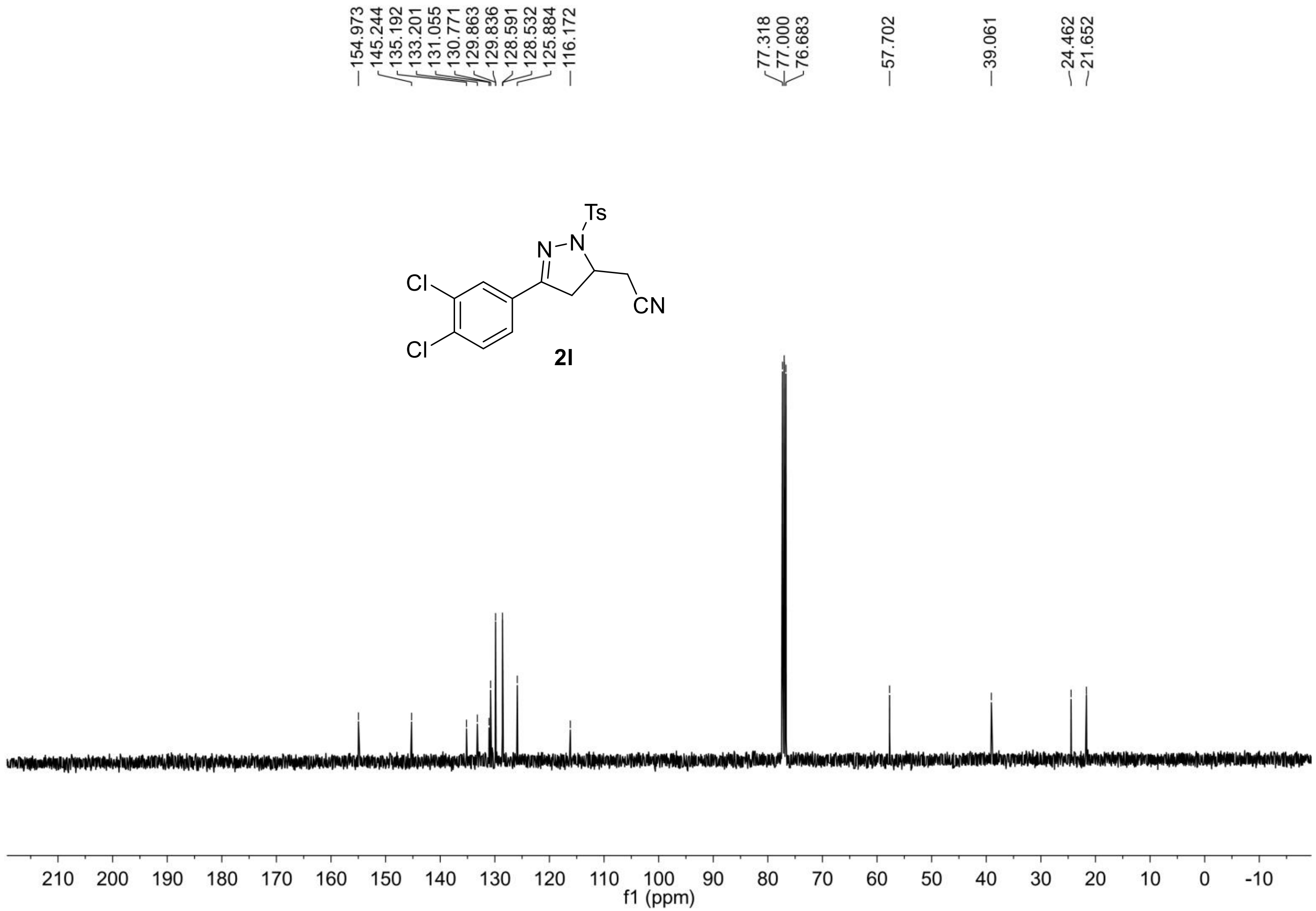
129.023
128.936
128.623
126.216
126.183
116.328
116.018
115.798
77.318
77.000
76.683
57.519
39.313
24.436
21.599
Ts
N
N
CN
F
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



7.789
7.769
7.709
7.458
7.337
7.318
7.260
4.165
4.140
4.116
4.091
3.378
3.350
3.335
3.307
3.246
3.204
3.125
3.110
3.102
3.088
3.057
2.409
Ts
N
N
Cl
Cl
CN
2l
2.09
1.04
2.02
2.03
1.00
1.03
1.01
2.05
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



154.973
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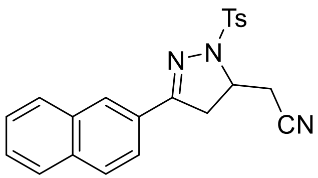
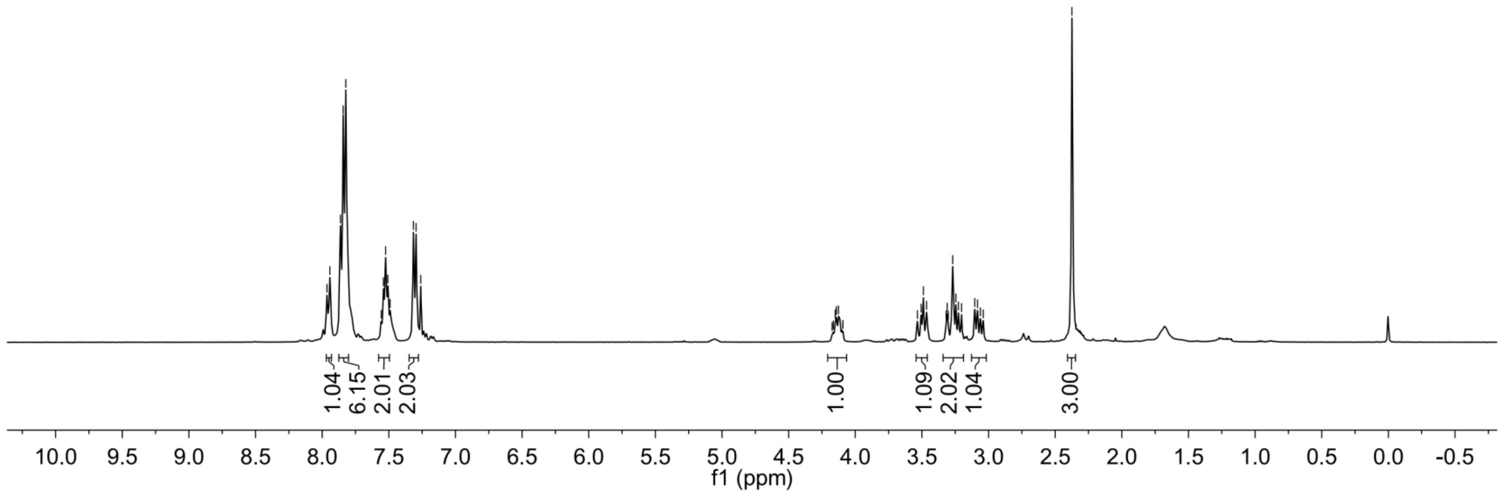
133.201
131.055
130.771
129.863
129.836
128.591
128.532
125.884
116.172
77.318
77.000
76.683
57.702
39.061
24.462
21.652
Ts
N
N
Cl
Cl
CN
2l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ts
N
N
CN

2m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7.823
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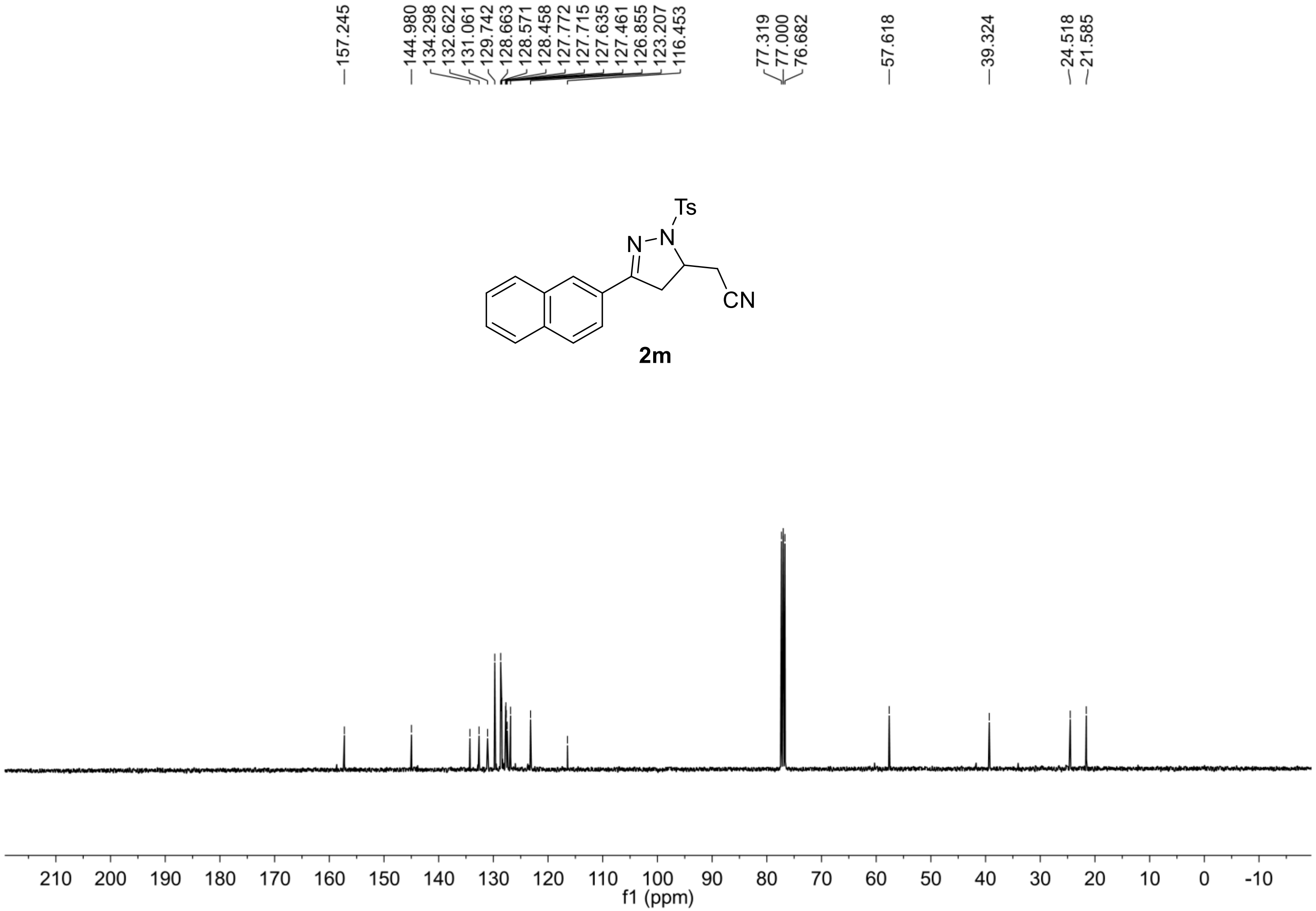
7.540
7.524
7.507
7.490
7.315
7.295
7.260
4.174
4.165
4.151
4.141
4.126
4.093
3.534
3.506
3.489
3.465
3.318
3.310
3.303
3.269
3.245
3.226
3.202
3.103
3.083
3.061
3.040
2.375
1.04
6.15
2.01
2.03
1.00
1.09
2.02
1.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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134.298
132.622
131.061
129.742
128.663
128.571
128.458
127.772
127.715
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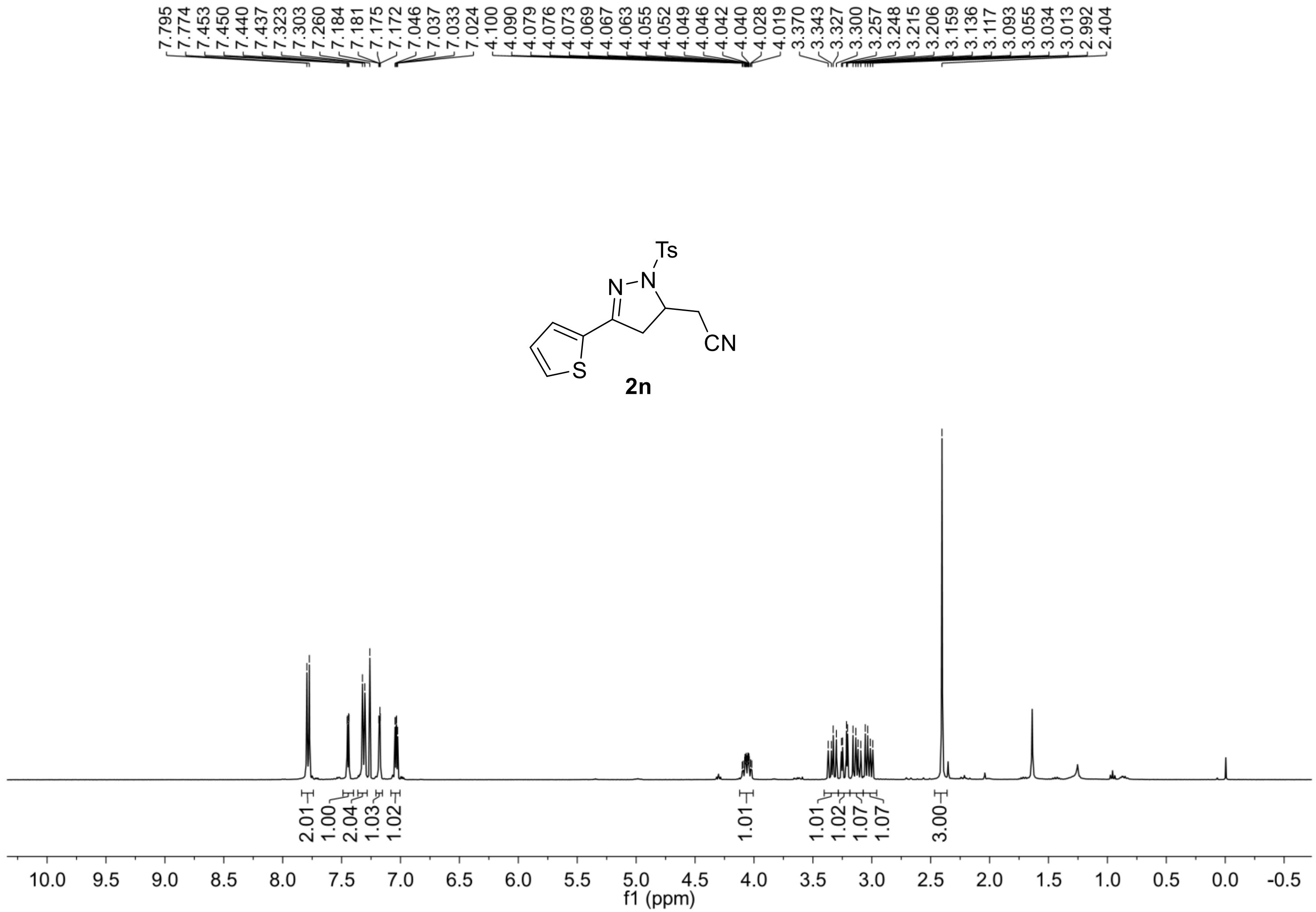
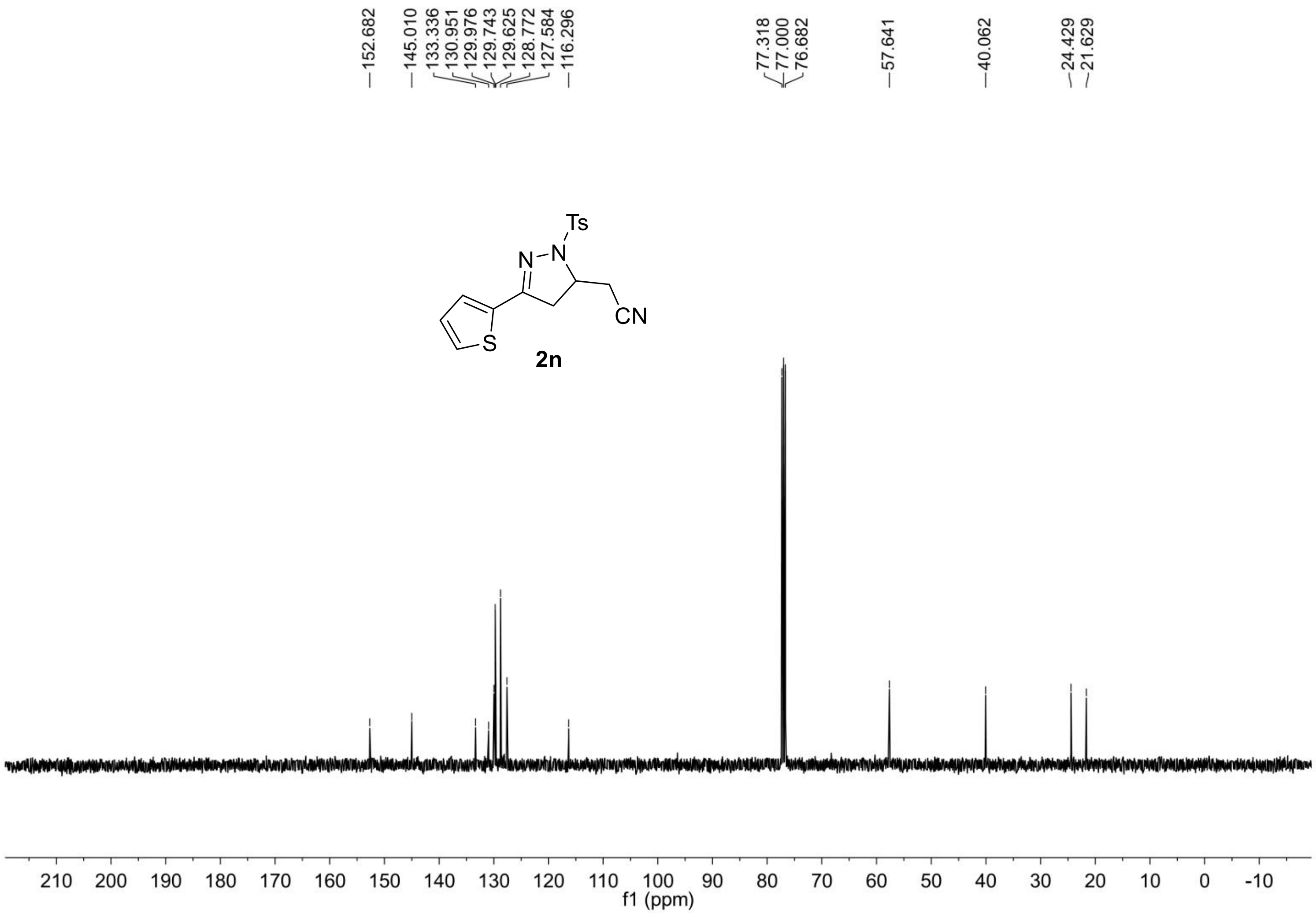
127.461
126.855
123.207
116.453
77.319
77.000
76.682
57.618
39.324
24.518
21.585
Ts
N
N
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

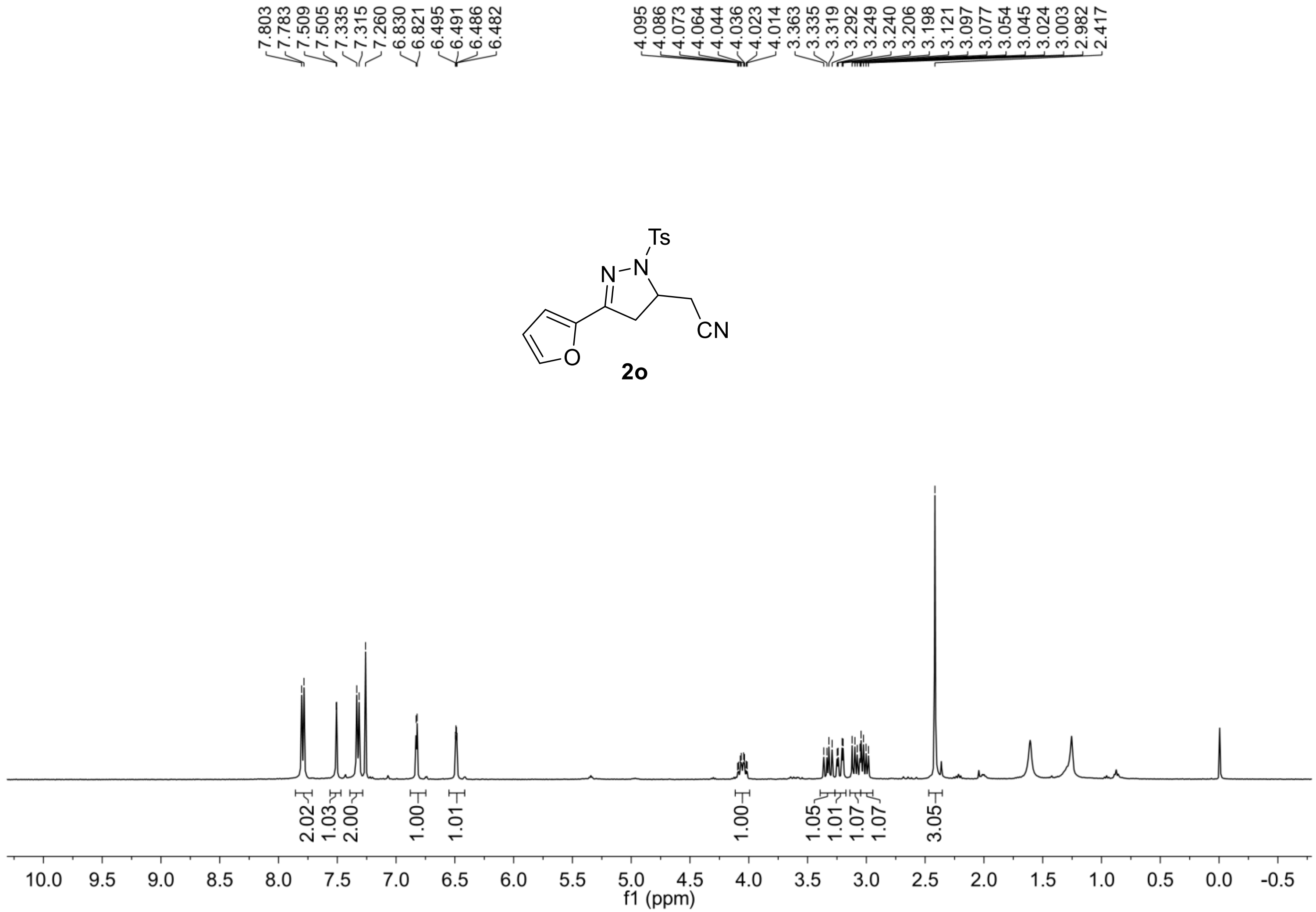
2m

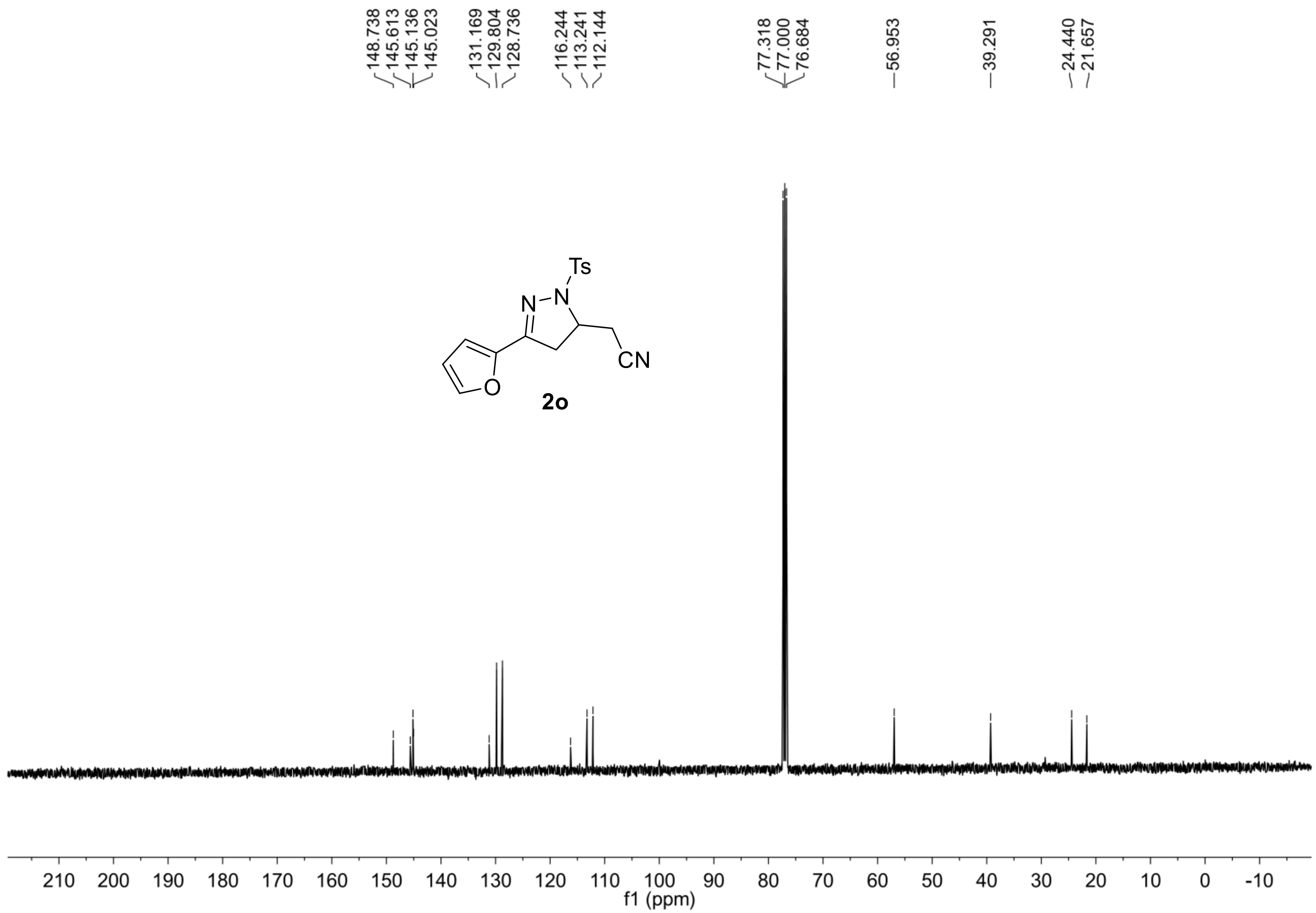

7.795 7.774 7.453 7.450 7.440 7.437 7.323 7.303 7.260 7.184 7.181 7.175 7.172 7.046 7.037 7.033 7.024 4.100 4.090 4.079 4.076 4.073 4.069 4.067 4.063 4.055 4.052 4.049 4.046 4.042 4.040 4.028 4.019 3.370 3.343 3.327 3.300 3.257 3.248 3.215 3.206 3.159 3.136 3.117 3.093 3.055 3.034 3.013 2.992 2.404
Ts
N
N
S
CN
2n
2.01
1.00
2.04
1.03
1.02
1.01
1.01
1.02
1.07
1.07
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



152.682
145.010
133.336
130.951
129.976
129.743
129.625
128.772
127.584
116.296
77.318
77.000
76.682
57.641
40.062
24.429
21.629
Ts
N
N
CN
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2n


7.803
7.783
7.509
7.505
7.335
7.315
7.260
6.830
6.821
6.495
6.491
6.486
6.482
4.095
4.086
4.073
4.064
4.044
4.036
4.023
4.014
3.363
3.335
3.319
3.292
3.249
3.240
3.206
3.198
3.121
3.097
3.077
3.054
3.045
3.024
3.003
2.982
2.417
Ts
N
N
CN
O
2o
2.02
1.03
2.00
1.00
1.01
1.00
1.05
1.01
1.07
1.07
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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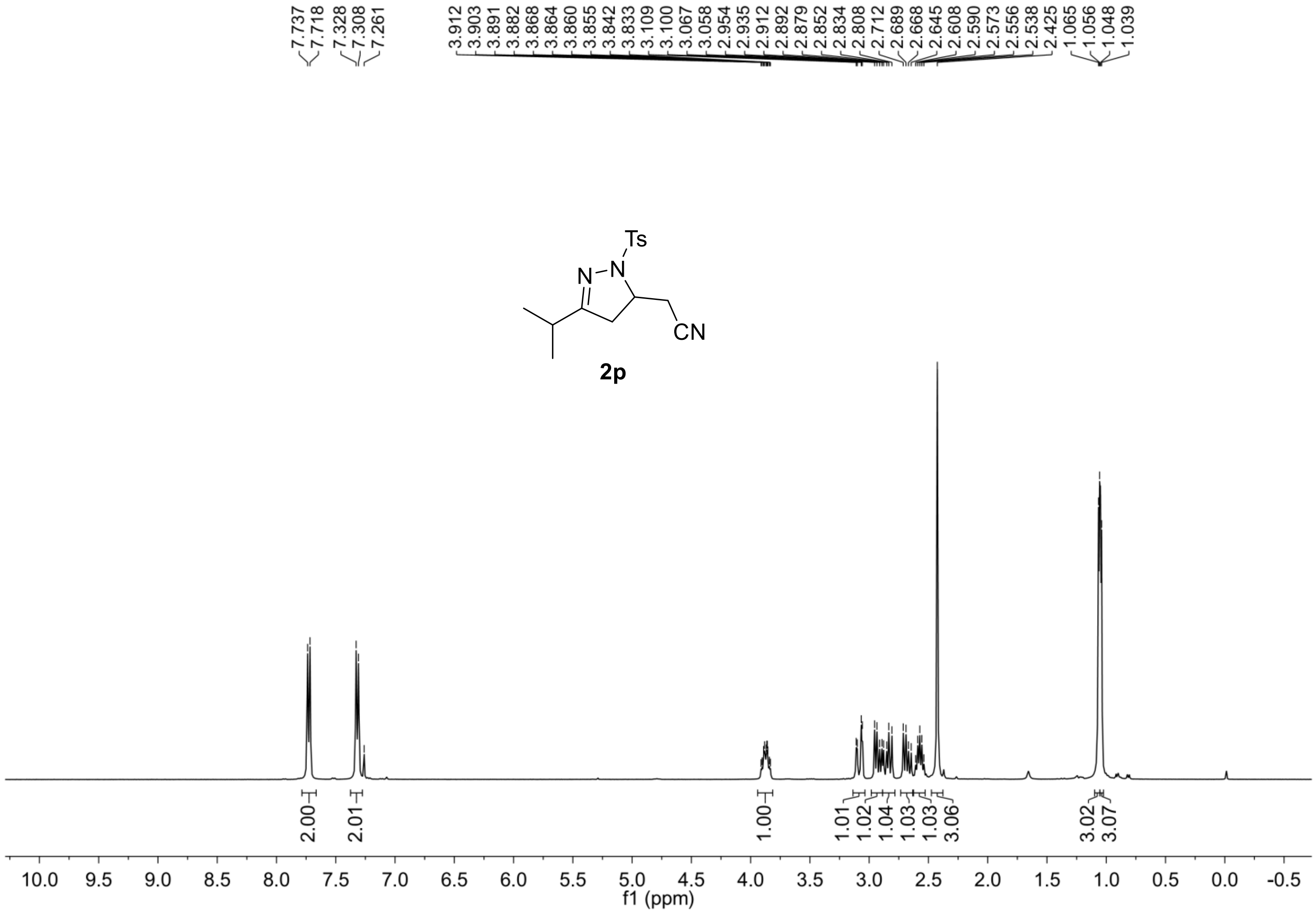
145.023
131.169
129.804
128.736
116.244
113.241
112.144
77.318
77.000
76.684
56.953
39.291
24.440
21.657
Ts
N
N
CN
O
2o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.903
3.891
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3.868
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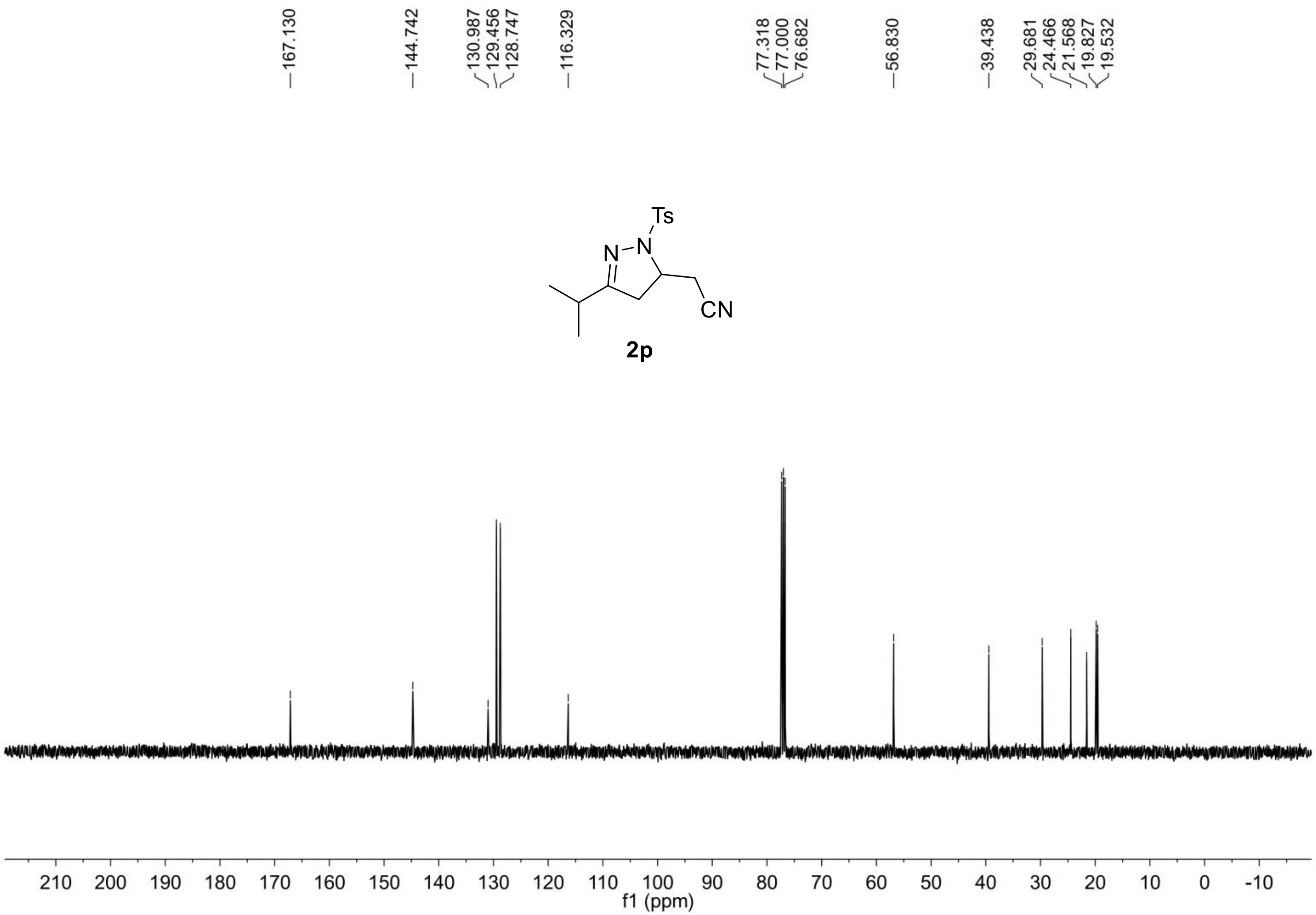
3.860
3.855
3.842
3.833
3.109
3.100
3.067
3.058
2.954
2.935
2.912
2.892
2.879
2.852
2.834
2.808
2.712
2.689
2.668
2.645
2.608
2.590
2.573
2.556
2.538
2.425
1.065
1.056
1.048
1.039
Ts
N
N
CN
2p
2.00
2.01
1.00
1.01
1.02
1.04
1.03
1.03
3.06
3.02
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



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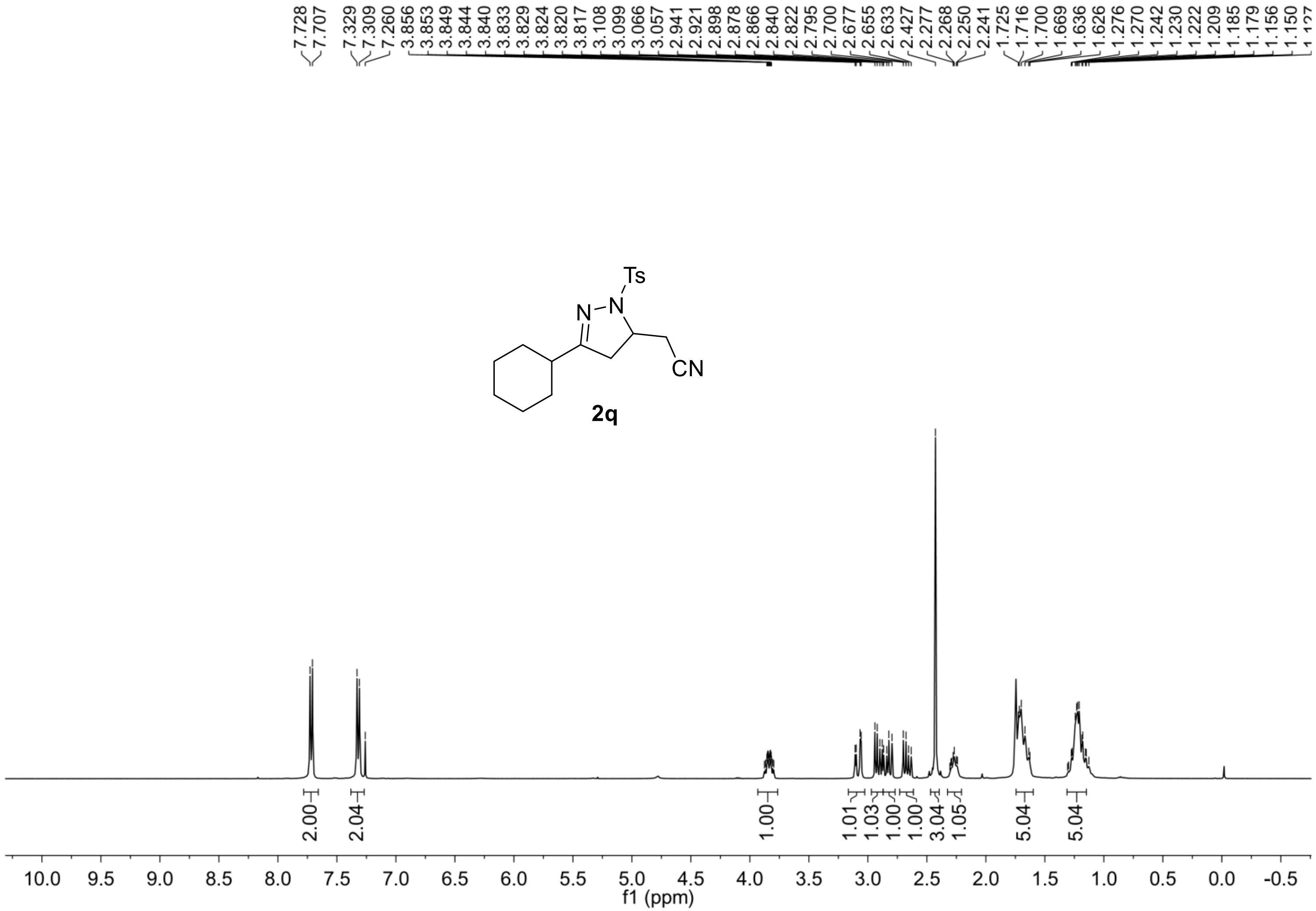
144.742
130.987
129.456
128.747
116.329
77.318
77.000
76.682
56.830
39.438
29.681
24.466
21.568
19.827
19.532
Ts
N
N
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2p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7.329
7.309
7.260
3.856
3.853
3.849
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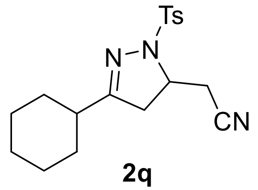
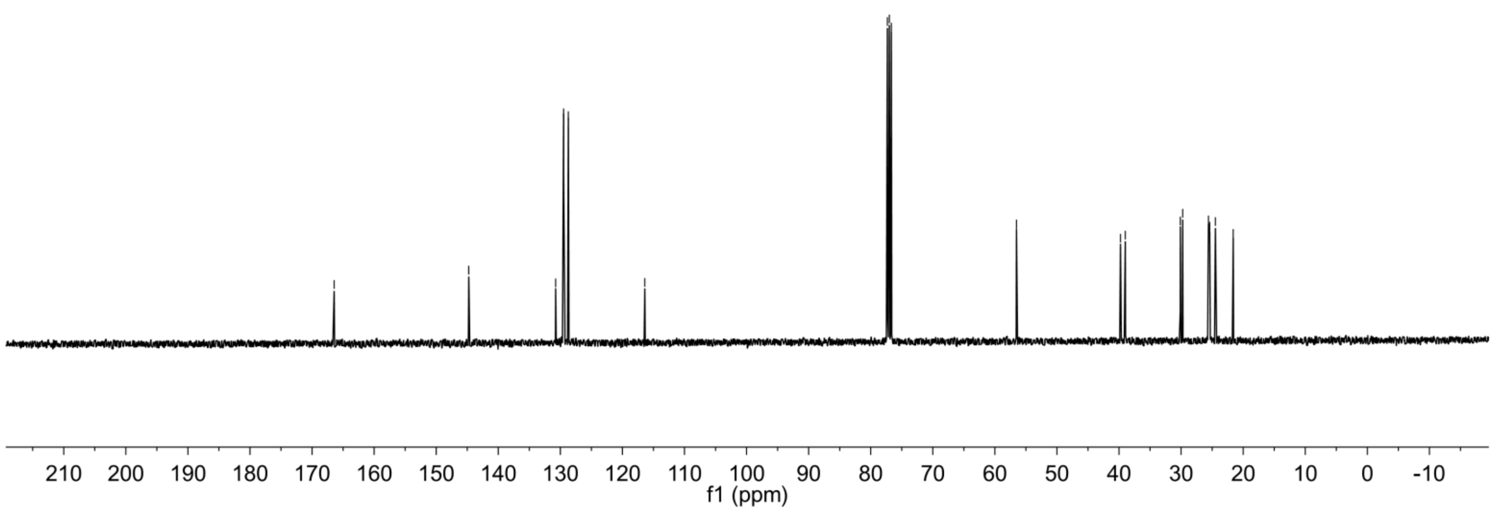
3.840
3.833
3.829
3.824
3.820
3.817
3.108
3.099
3.066
3.057
2.941
2.921
2.898
2.878
2.866
2.840
2.822
2.795
2.700
2.677
2.655
2.633
2.427
2.277
2.268
2.250
2.241
1.725
1.716
1.700
1.669
1.636
1.626
1.276
1.270
1.242
1.230
1.222
1.209
1.185
1.179
1.156
1.150
Ts
N
N
CN
2q
2.00
2.04
1.00
1.01
1.03
1.00
1.00
3.04
1.05
5.04
5.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


N
N
Ts
CN

2q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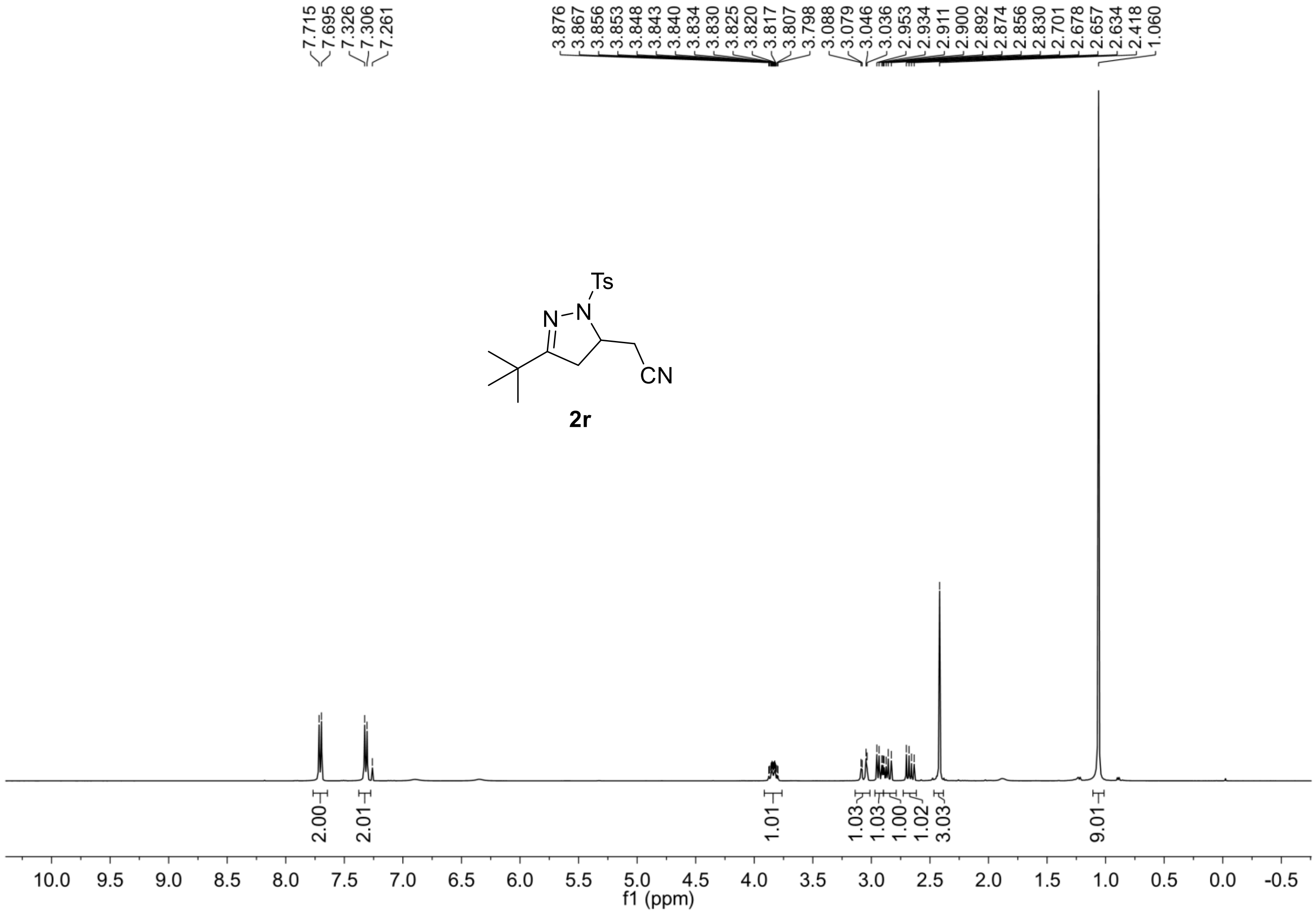
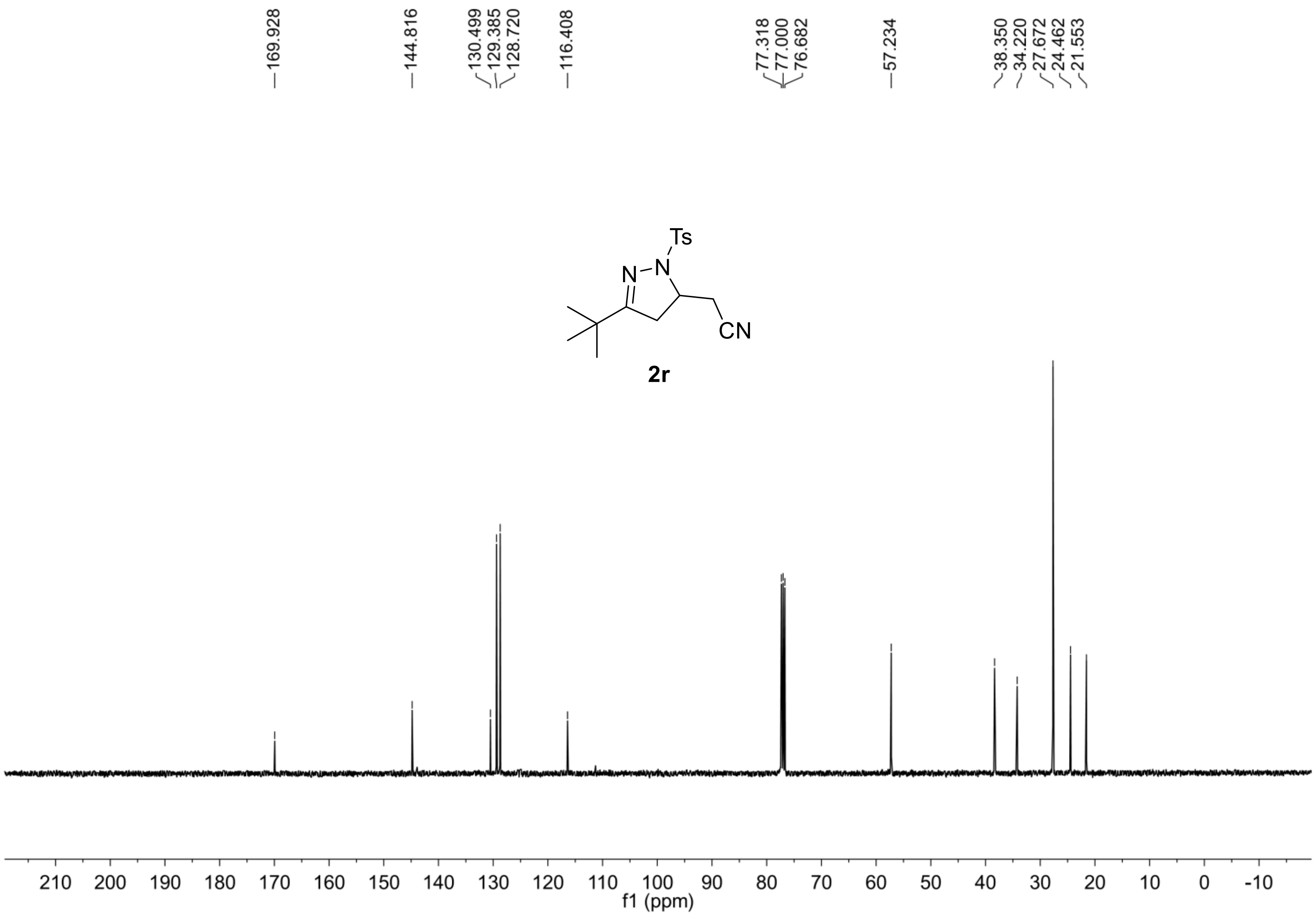
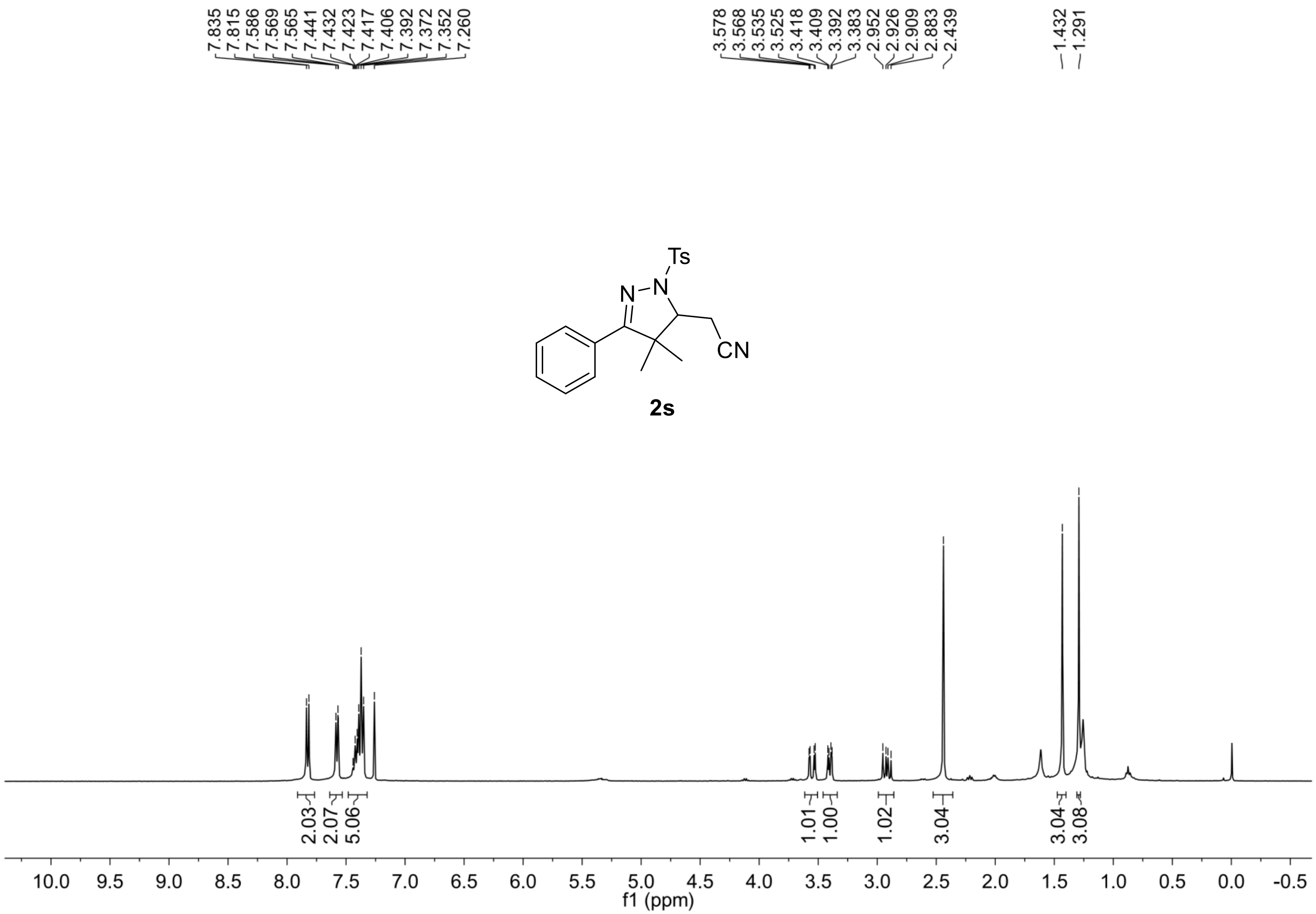
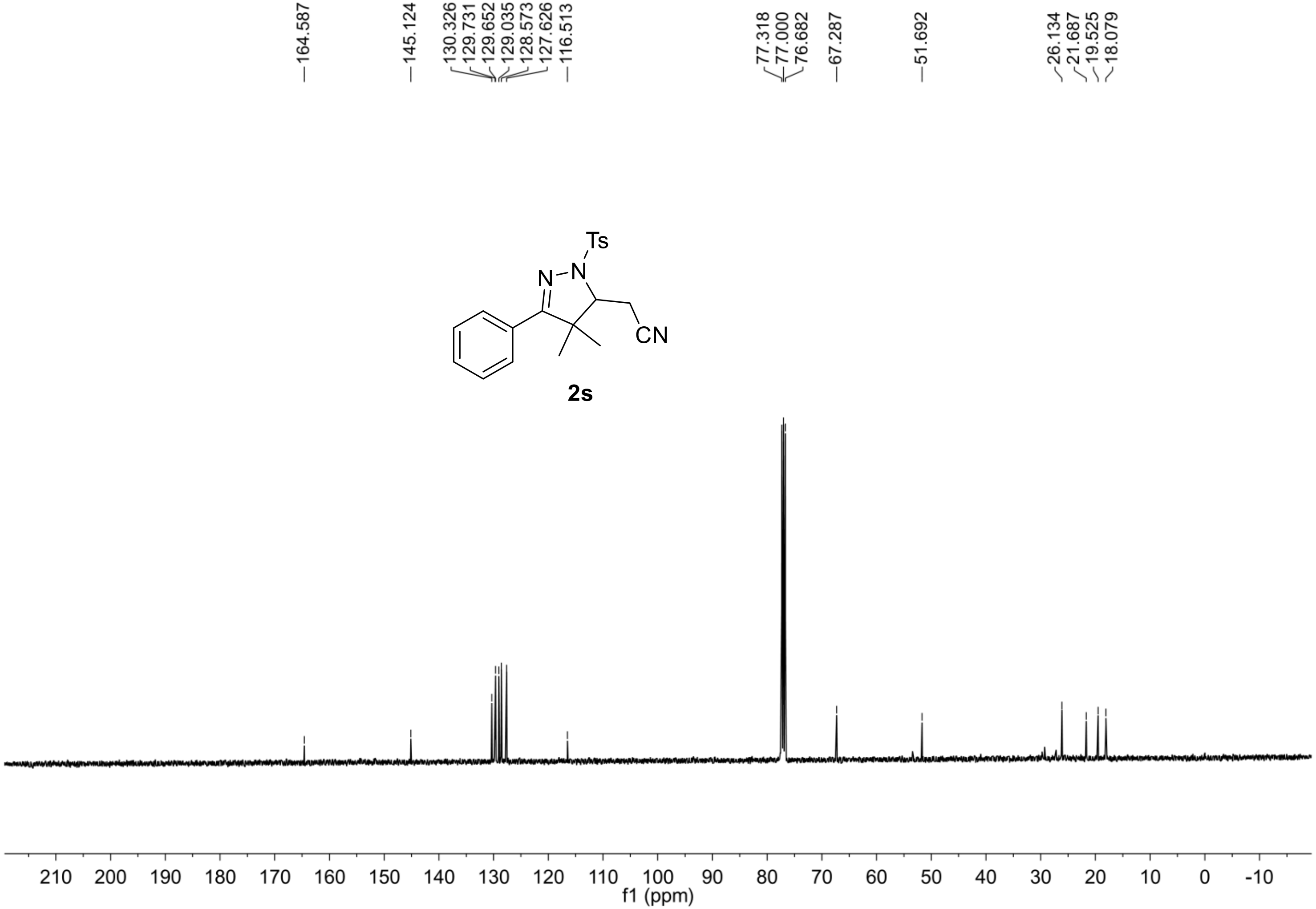
144.756
130.757
129.480
128.715
116.398
77.318
77.000
76.682
56.525
39.766
38.991
30.126
29.748
25.596
25.473
25.391
24.480
21.609
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

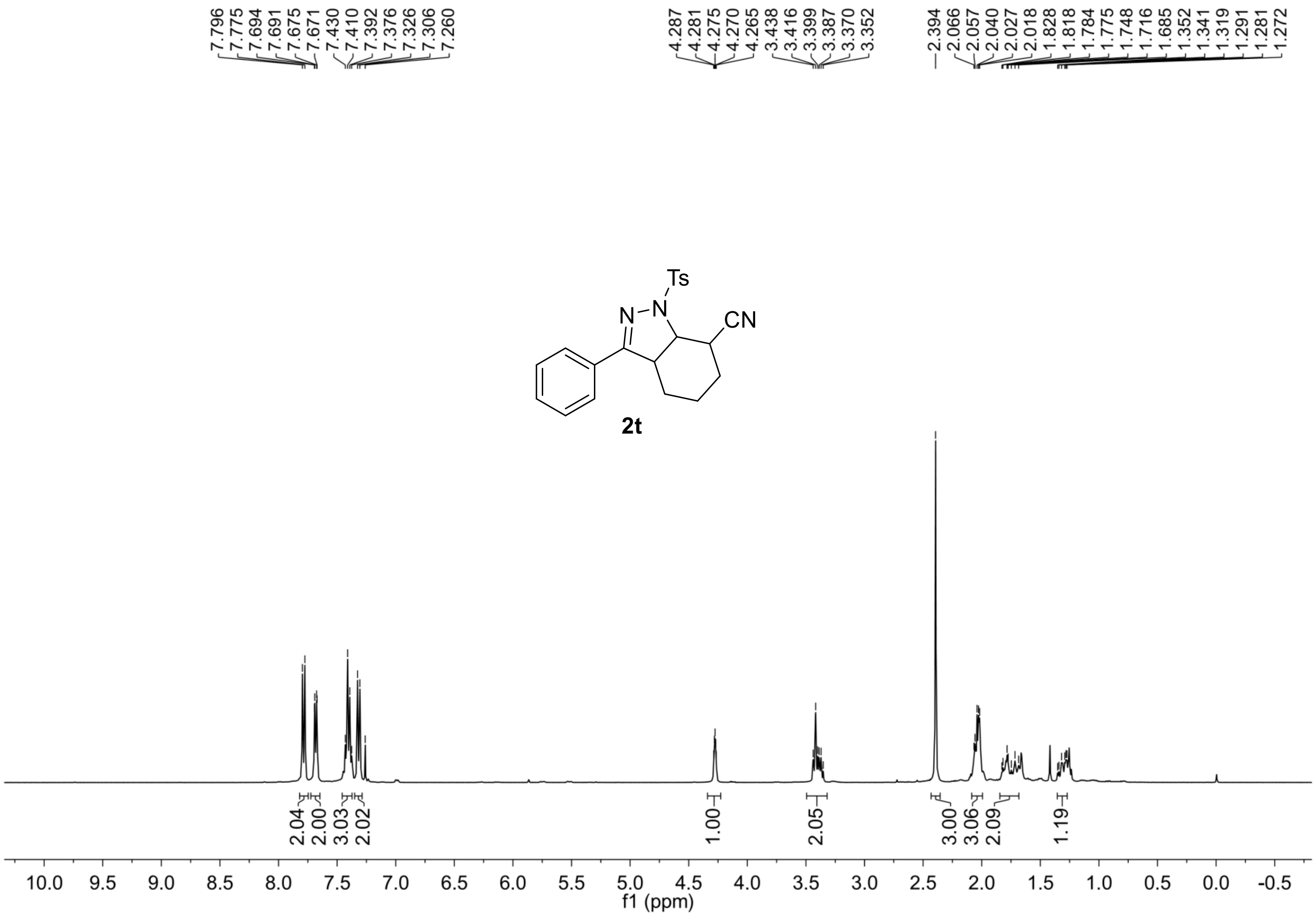

7.715
7.695
7.326
7.306
7.261
3.876
3.867
3.856
3.853
3.848
3.843
3.840
3.834
3.830
3.825
3.820
3.817
3.807
3.798
3.088
3.079
3.046
3.036
2.953
2.934
2.911
2.900
2.892
2.874
2.856
2.830
2.701
2.678
2.657
2.634
2.418
1.060
Ts
N
N
CN
2r
2.00
2.01
1.01
1.03
1.03
1.00
1.02
3.03
9.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

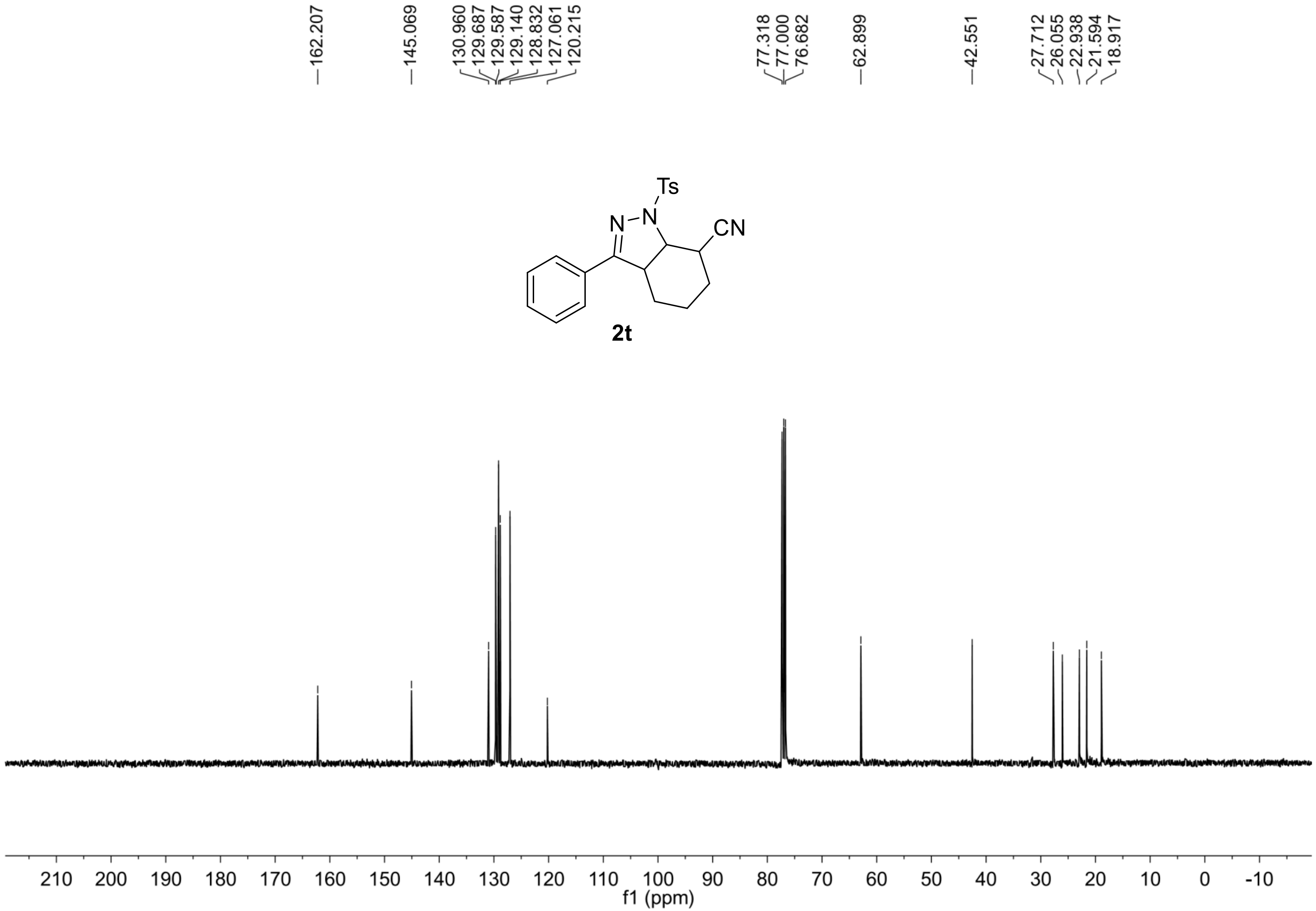

169.928
144.816
130.499
129.385
128.720
116.408
77.318
77.000
76.682
57.234
38.350
34.220
27.672
24.462
21.553
Ts
N
N
CN
2r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.835
7.815
7.586
7.569
7.565
7.441
7.432
7.423
7.417
7.406
7.392
7.372
7.352
7.260
3.578
3.568
3.535
3.525
3.418
3.409
3.392
3.383
2.952
2.926
2.909
2.883
2.439
1.432
1.291
Ts
N
N
CN
2s
2.03
2.07
5.06
1.01
1.00
1.02
3.04
3.04
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

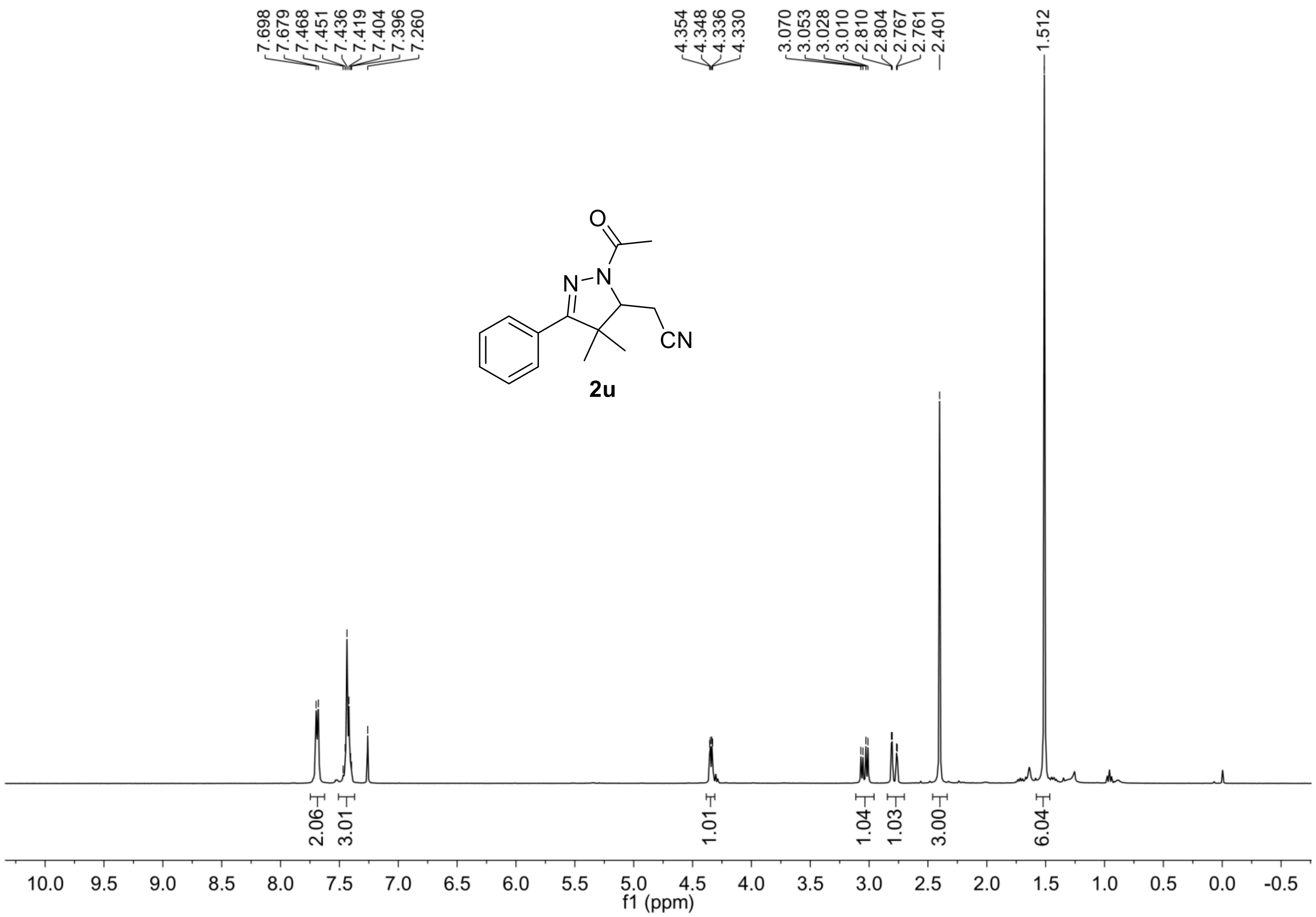


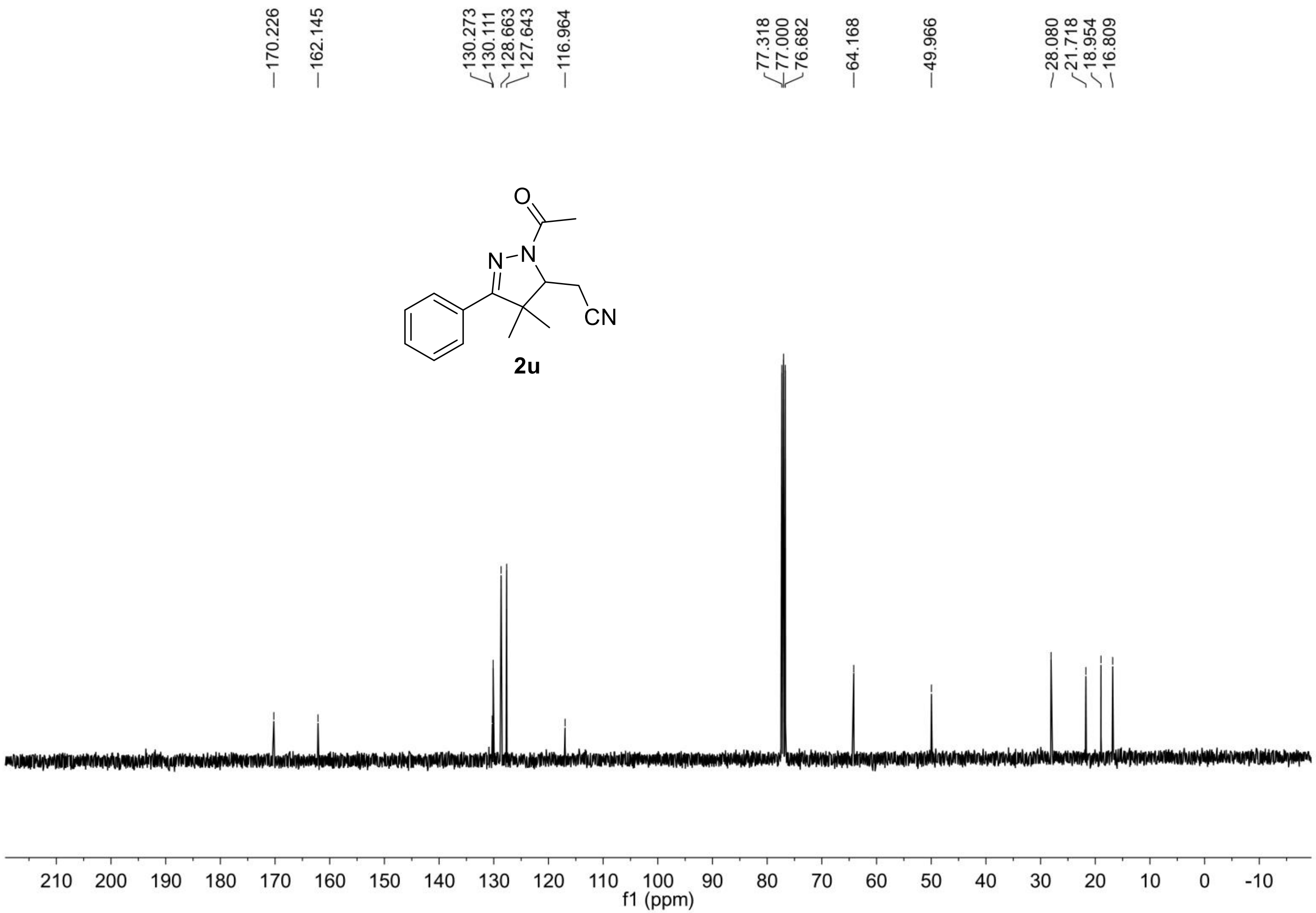
164.587
145.124
130.326
129.731
129.652
129.035
128.573
127.626
116.513
77.318
77.000
76.682
67.287
51.692
26.134
21.687
19.525
18.079
Ts
N
N
CN
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

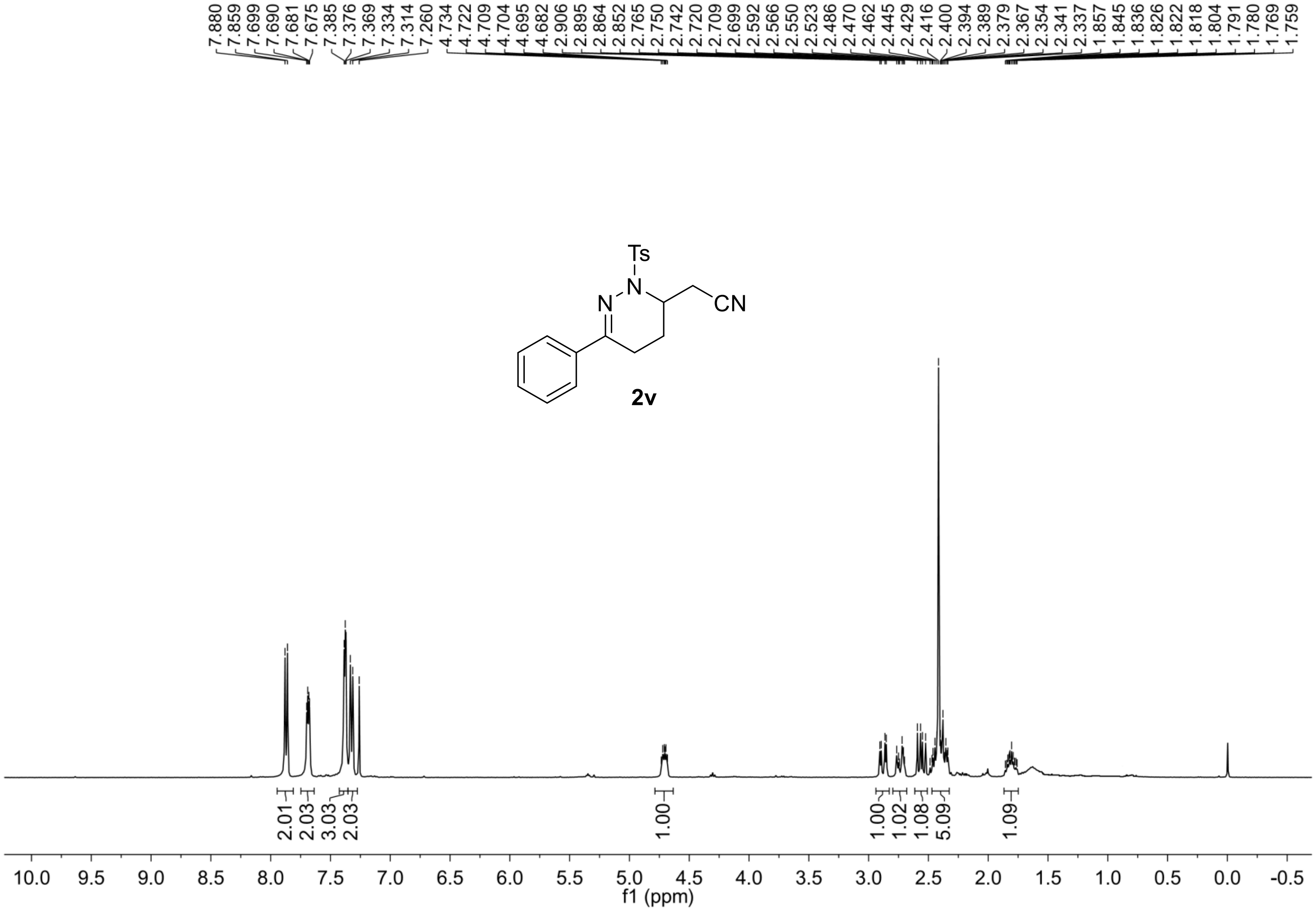

7.796 7.775 7.694 7.691 7.675 7.671 7.430 7.410 7.392 7.376 7.326 7.306 7.260
4.287 4.281 4.275 4.270 4.265 3.438 3.416 3.399 3.387 3.370 3.352
2.394 2.066 2.057 2.040 2.027 2.018 1.828 1.818 1.784 1.775 1.748 1.716 1.685 1.352 1.341 1.319 1.291 1.281 1.272
Ts
N
N
CN
2t
2.04 2.00 3.03 2.02
1.00
2.05
3.00 3.06 2.09
1.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

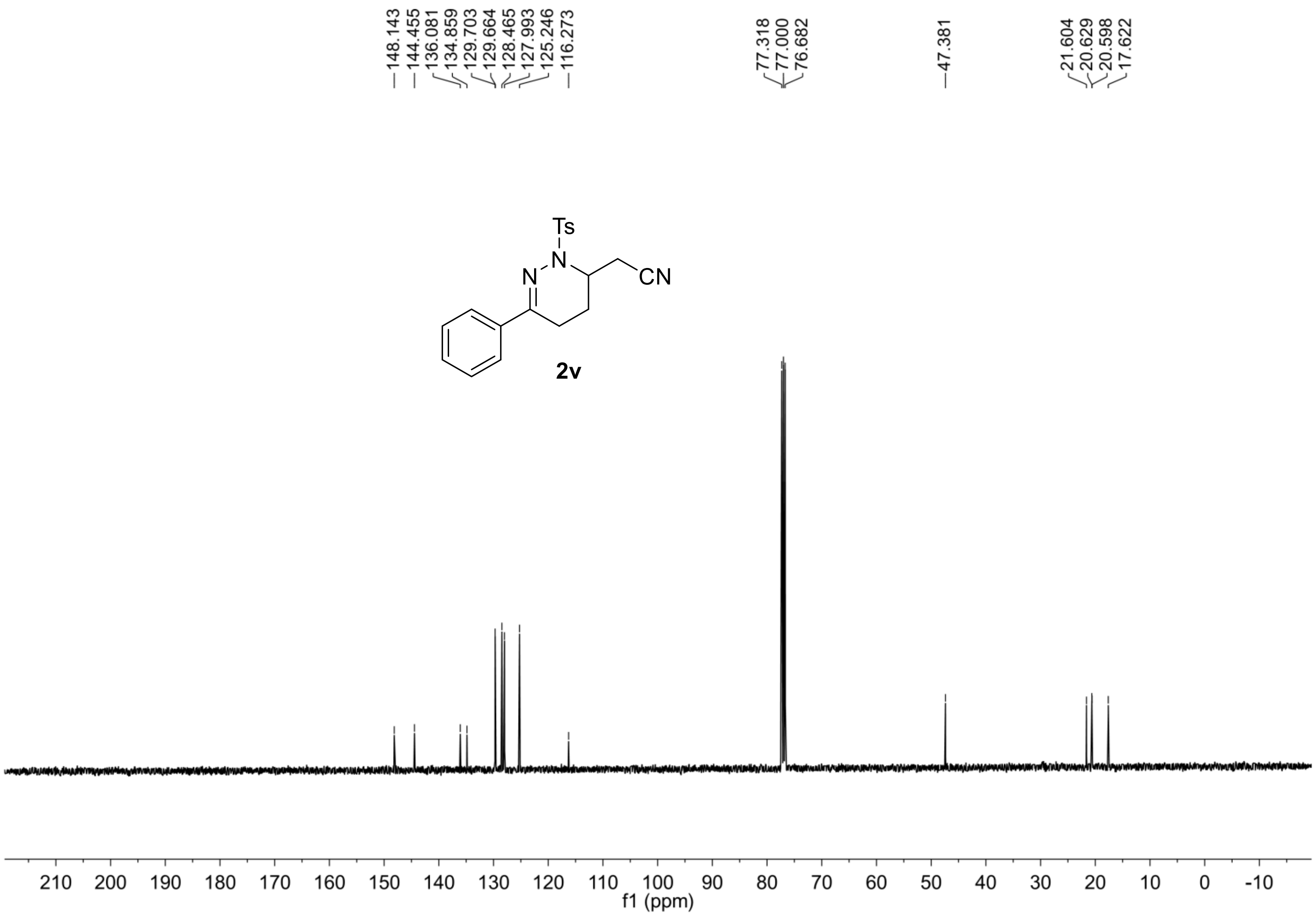


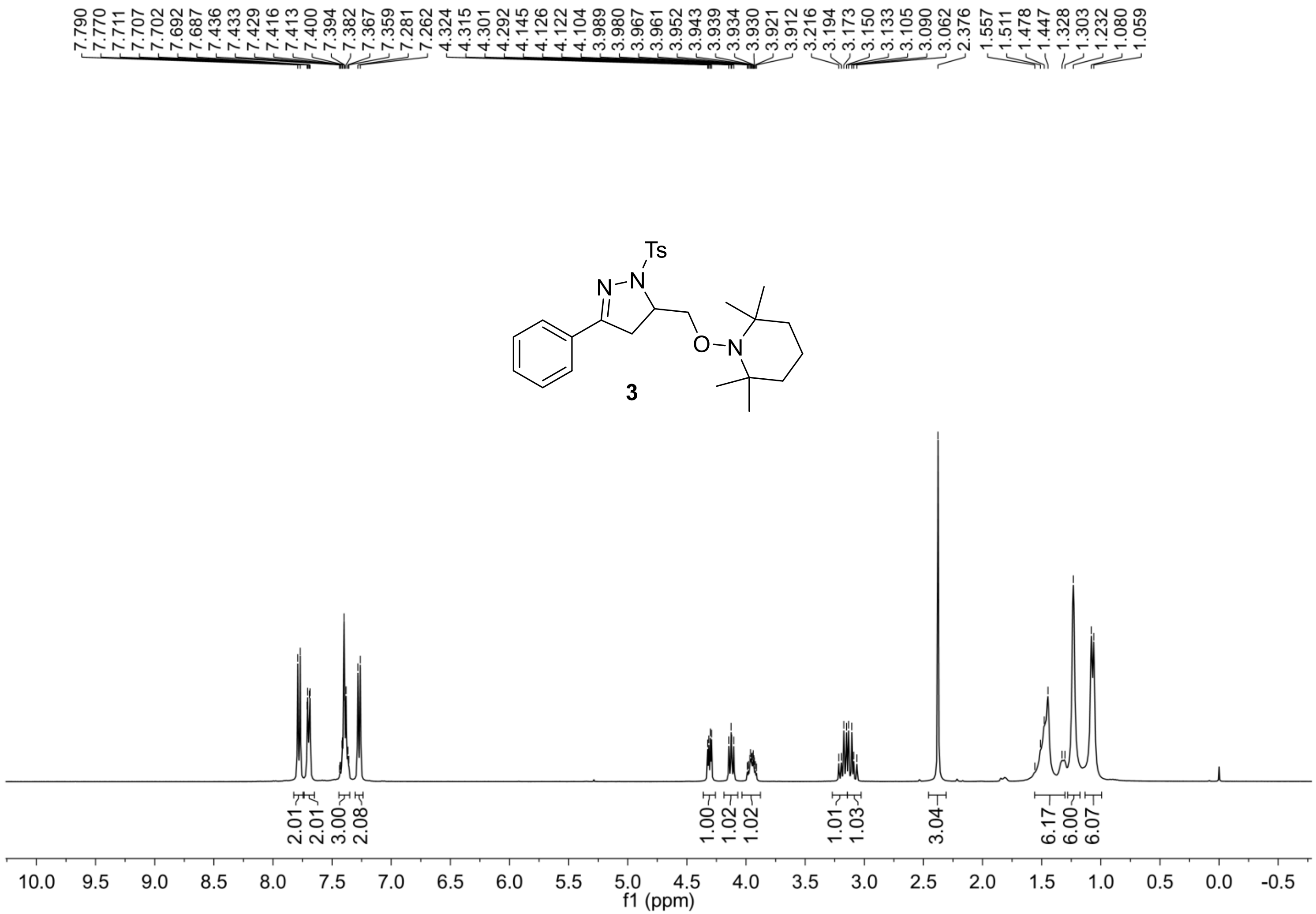
162.207
145.069
130.960
129.687
129.587
129.140
128.832
127.061
120.215
77.318
77.000
76.682
62.899
42.551
27.712
26.055
22.938
21.594
18.917
Ts
N
N
CN
2t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.698
7.679
7.468
7.451
7.436
7.419
7.404
7.396
7.260
4.354
4.348
4.336
4.330
3.070
3.053
3.028
3.010
2.810
2.804
2.767
2.761
2.401
1.512
O
N
N
CN
2u
2.06
3.01
1.01
1.04
1.03
3.00
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


170.226
162.145
130.273
130.111
128.663
127.643
116.964
77.318
77.000
76.682
64.168
49.966
28.080
21.718
18.954
16.809
O
N
N
CN
2u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

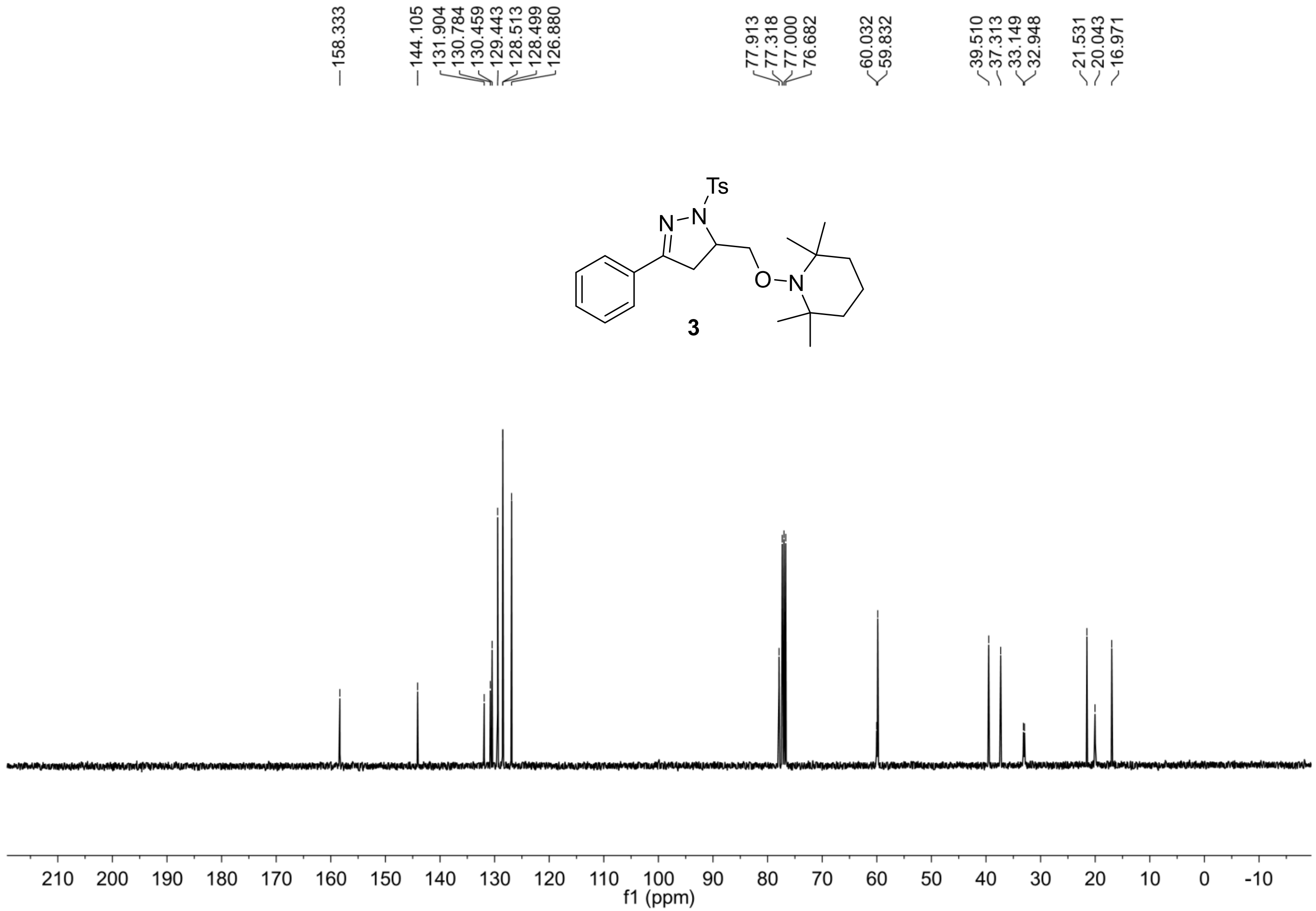

7.880 7.859 7.699 7.690 7.681 7.675 7.385 7.376 7.369 7.334 7.314 7.260 4.734 4.722 4.709 4.704 4.695 4.682 2.906 2.895 2.864 2.852 2.765 2.750 2.742 2.720 2.709 2.699 2.592 2.566 2.550 2.523 2.486 2.470 2.462 2.445 2.429 2.416 2.400 2.394 2.389 2.379 2.367 2.354 2.341 2.337 1.857 1.845 1.836 1.826 1.822 1.818 1.804 1.791 1.780 1.769 1.759
Ts
N
N
CN
2.01
2.03
3.03
2.03
1.00
1.00
1.02
1.08
5.09
1.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
2v


148.143
144.455
136.081
134.859
129.703
129.664
128.465
127.993
125.246
116.273
77.318
77.000
76.682
47.381
21.604
20.629
20.598
17.622
Ts
N
N
CN
2v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ts
N
N
O
N

3

7.790
7.770
7.711
7.707
7.702
7.692
7.687
7.436
7.433
7.429
7.416
7.413
7.400
7.394
7.382
7.367
7.359
7.281
7.262
4.324
4.315
4.301
4.292
4.145
4.126
4.122
4.104
3.989
3.980
3.967
3.961
3.952
3.943
3.939
3.934
3.930
3.921
3.912
3.216
3.194
3.173
3.150
3.133
3.105
3.090
3.062
2.376
1.557
1.511
1.478
1.447
1.328
1.303
1.232
1.080
1.059
2.01
2.01
3.00
2.08
1.00
1.02
1.02
1.01
1.03
3.04
6.17
6.00
6.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.333
144.105
131.904
130.784
130.459
129.443
128.513
128.499
126.880
77.913
77.318
77.000
76.682
60.032
59.832
39.510
37.313
33.149
32.948
21.531
20.043
16.971
Ts
N
N
O
N
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)