Supporting Information for

Titanium-Mediated Cross-Coupling Reactions of 1,3-Butadiynes with α-Iminonitriles to 3-Aminopyrroles: Observation of an Imino Aza-Nazarov Cyclization

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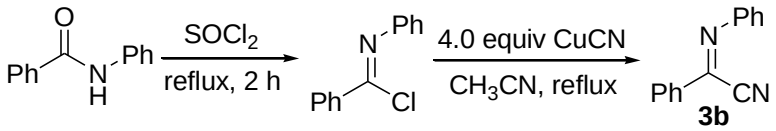
Contents: Pages

General Methods. All reactions were carried out using standard Schlenk technique under argon. Tetrahydrofuran was distilled from sodium and benzophenone. Zirconocene dichloride was purchased from Aldrich Chemical Company. *n*-BuLi (1.6 M solution in hexane) was purchased from Acros Chemical Company. Unless noted, all commercial reagents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03%, 0.3%, or 1% TMS), or C_6D_6 (containing 0.03% TMS), or THF-d_8 solutions on Varian, or Agilent XL-400 MHz, or Agilent vnmrs 600 MHz spectrometer. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00

ppm) or solvent residual peak (chloroform, δ = 7.26 ppm; tetrahydrofuran, δ = 1.72, 3.58 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) or THF-d_8 (δ = 25.31 ppm) as internal reference. High-resolution mass spectra was obtained by using Waters Micromass GCT Premier or Agilent Technologies 6224 TOF LC/MS mass spectrometers. Single crystal X-ray diffraction data were collected at 293(2) K (for **3b**, **4a**, *N*-tosylated derivatives of **4l** and **4p**, **15**) and 273(2) K (for **5**) on Bruker SMART diffractometer .

Synthesis of (*Z*)-*N*-phenylbenzimidoyl cyanide (3b).



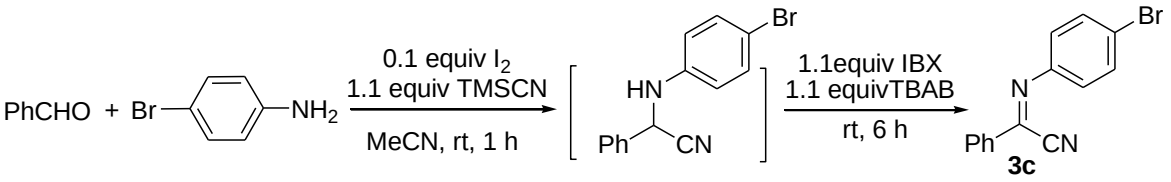
In a 100 mL round bottom flask, equipped with a condenser and drying tube, a mixture of *N*-phenylbenzamide (5.92 g, 30.0 mmol) and $SOCl_2$ (60 mL) was heated to reflux in oil-bath. After 2 hours the excess $SOCl_2$ was removed, and the resulting residue was further purified by distillation under reduced pressure to give pure imidoyl chloride as a light yellow solid in 92% yield (5.984 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.38-7.40 (m, 2H), 7.42-7.48 (m, 2H), 7.51-7.54 (m, 1H), 8.15-8.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.37, 125.01, 128.41, 128.83, 129.39, 132.01, 135.40, 143.20, 147.60. The NMR data is in agreement with that previously reported.[1]

To a solution of (*Z*)-*N*-phenylbenzimidoyl chloride (1.075g, 5.0 mmol) in acetonitrile (10 mL) was added CuCN(1.791g, 20.0 mmol) at room temperature, and then the mixture was heated to reflux for 4 h. The resulting mixture was cooled down to room temperature, and filtered over celite. The filtrate was concentrated to give a viscous residue which was purified by flash chromatograph on silica gel (eluent: petroleum ether) to afford (*Z*)-*N*-phenylbenzimidoyl cyanide **3b** as a light yellow solid in 88% yield (909 mg). M.p. = 79-80 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.44-7.58 (m, 5H), 8.13-8.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.80, 120.28, 127.26, 128.16, 128.98, 129.23, 132.83, 133.52, 139.75, 149.04. IR (neat): 3063, 2962,

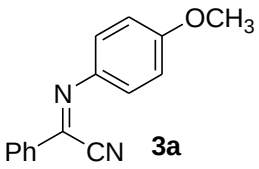
2220, 1594, 1574, 1479, 1450, 1275, 1200, 1069, 1006, 835, 773, 721, 687 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{10}N_2$ $[M]^+$: 206.0844, found 206.0842. The structure and the Z-configuration of **3b** was also determined by X-ray single-crystal analysis.

Synthesis of α-iminonitriles 3a, 3c and 3f-3j.[2]

Typical procedure for the synthesis of (*Z*)-*N*-(4-bromophenyl)benzimidoyl cyanide (3c)

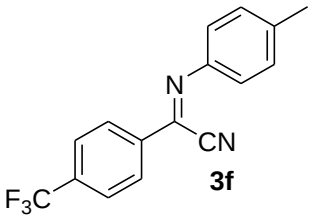


To a solution of benzaldehyde (0.51 mL, 5.0 mmol), 4-bromoaniline (0.86 g, 5.0 mmol) and I_2 (0.13 g, 0.5 mmol) in acetonitrile (5 mL) was added TMSCN (0.74 mL, 5.5 mmol) at room temperature, and the mixture was then stirred for one hour. Then the IBX (1.54 g, 5.5 mmol) and tetrabutylammonium bromide (1.77 g, 5.5 mmol) were added (under water bath if necessary) and stirring was maintained at room temperature. After the reaction was complete as monitored by TLC, the reaction mixture was then filtered over celite and concentrated. The crude product was purified by flash chromatograph on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) to afford the α-iminonitrile **3c** as a yellow-green solid in 83% yield (1.177 g). M.p. = 115 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.01-7.05 (m, 2H), 7.45-7.57 (m, 5H), 8.07-8.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.46, 120.70, 122.00, 128.08, 128.89, 132.19, 132.94, 133.11, 139.93, 147.65. IR (neat): 2221, 1892, 1594, 1573, 1477, 1449, 1278, 1201, 1068, 1003, 834, 773, 739, 680 cm^{-1}. HRMS(EI) calcd for $C_{14}H_9BrN_2$ $[M]^+$: 283.9949, found 283.9952.



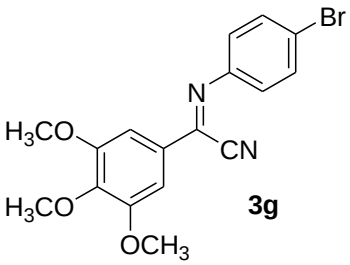
(*Z*)-*N*-(4-Methoxyphenyl)benzimidoyl cyanide (3a). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the title product as a yellow solid in 77% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 3.84(s, 3H),

6.98 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.48-7.55 (m, 3H), 8.11-8.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.43, 111.58, 114.37, 122.99, 127.81, 128.88, 132.28, 134.03, 136.74, 141.63, 159.42. The NMR data is in agreement with that previously reported.[2]



3f

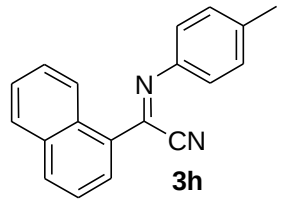
(*Z*)-*N*-(*p*-Tolyl)-4-(trifluoromethyl)benzimidoyl cyanide (3f). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) followed by recrystallization in petroleum ether afforded the title product as an orange crystal in 58% yield. M.p. = 102-103 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.21 (d, *J* = 8.4, 2H), 7.28 (d, *J* = 8.4, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 8.24 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.17, 110.93, 120.94, 123.53 (q, *J* = 272.4 Hz), 125.90 (q, *J* = 3.8 Hz), 128.31, 129.93, 133.85 (q, *J* = 35.2 Hz), 136.73, 136.79 (q, *J* = 1.5 Hz), 138.63, 145.77. ^{19}F NMR (376MHz, $CDCl_3$) δ -62.99. IR (neat): 3029, 2926, 2869, 2224, 1615, 1603, 1572, 1500, 1411, 1325, 1274, 1167, 1127, 1113, 1068, 1005, 853, 826, 803, 667 cm^{-1}. HRMS(EI) calcd for $C_{16}H_{11}F_3N_2$ [M] $^{+}$: 288.0874, found 288.0870.



3g

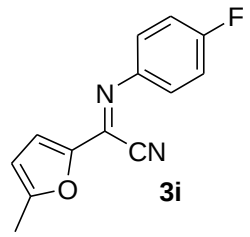
(*Z*)-*N*-(4-Bromophenyl)-3,4,5-trimethoxybenzimidoyl cyanide (3g). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) followed by recrystallization in hexane/ethyl acetate afforded the title product as a yellow solid in 73% yield. M.p. = 126-127 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.959 (s, 3H), 3.961 (s, 6H), 7.04-7.08 (m, 2H), 7.38 (s, 2H), 7.58-7.61 (m, 2H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 56.17, 60.91, 105.27, 110.53, 120.54, 121.95, 128.37, 132.24, 139.53, 142.41, 147.81, 153.33. IR (neat): 2962, 2941, 2927, 2831, 1585, 1567, 1505, 1471, 1456, 1416, 1344, 1258, 1236, 1170, 1135, 1070, 997, 850, 829, 740, 701 cm^{-1}. HRMS(ESI) calcd for $C_{17}H_{16}BrN_2O_3$ $[M+H]^+$: 375.0344, found 375.0339.



3h

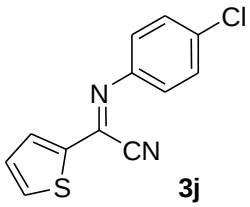
(*Z*)-*N*-(*p*-Tolyl)-1-naphthimidoyl cyanide (3h). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) followed by recrystallization in petroleum ether afforded the title product as an orange solid in 50% yield. M.p. = 114 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.50-7.55 (m, 2H), 7.58-7.62 (m, 1H), 7.86-7.88 (m, 1H), 7.96 (d, *J* = 8.0 Hz, 1H) , 8.18-8.20 (m, 1H), 9.15 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.07, 111.71, 120.25, 124.64, 125.38, 126.75, 128.39, 128.79, 129.80, 129.87, 130.17, 131.50, 133.30, 133.98, 137.30, 139.97, 146.76. IR (neat): 3049, 2915, 2855, 1581, 1568, 1510, 1499, 1286, 1210, 1184, 1108, 949, 824, 803, 769, 734 cm^{-1}. HRMS(ESI) calcd for $C_{19}H_{15}N_2$ $[M+H]^+$: 271.1235, found 271.1230.



3i

(*Z*)-*N*-(4-Fluorophenyl)-5-methylfuran-2-carbimidoyl cyanide (3i). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded the title product as an orange solid in 67% yield. M.p. = 82 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 6.26 (d, *J* = 3.2 Hz, 1H), 7.09-7.22 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.05, 109.75, 110.28, 116.04 (d, *J* = 22.8 Hz), 120.93, 122.73 (d, *J* = 8.7 Hz), 128.04 (d, *J* = 1.8 Hz), 144.58 (d, *J* = 3.4 Hz), 148.27, 159.14, 161.58 (d, *J* = 247.7

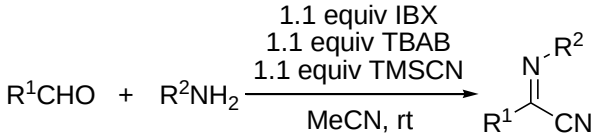
Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.61--114.54(m). IR (neat): 3113, 3072, 2225, 1892, 1755, 1602, 1573, 1529, 1497, 1301, 1212, 1194, 1157, 1061, 1029, 919, 839, 815, 803, 757, 742 cm^{-1}. HRMS(ESI) calcd for $C_{13}H_{10}FN_2O$ $[M+H]^+$: 229.0777, found 229.0773.



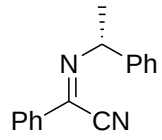
3j

(*Z*)-*N*-(4-Chlorophenyl)thiophene-2-carbimidoyl cyanide (3j). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) followed by recrystallization in petroleum ether/ethyl acetate afforded the title product as a yellow solid in 60% yield. M.p. = 103-104 ^oC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.17 (m, 3H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 5.2 Hz, 1H), 7.79 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.20, 122.28, 128.27, 129.32, 133.00, 133.10, 133.42, 133.66, 140.46, 146.49. IR (neat): 3115, 3080, 1889, 1591, 1570, 1481, 1420, 1401, 1357, 1282, 1198, 1083, 1011, 945, 856, 832, 748, 731, 713, 685 cm^{-1}. HRMS(EI) calcd for $C_{12}H_7ClN_2S$ $[M]^+$: 246.0018, found 246.0016.

Synthesis of α-iminonitrile (R)-3d, rac-3d and 3e.[2]

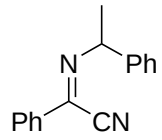


To a solution of aldehyde (5 mmol), amine (5 mmol, 1.0 equiv) and TMSCN (0.74 mL, 5.5 mmol, 1.1 equiv) in acetonitrile (5 mL) were added IBX (1.54 g, 5.5 mmol, 1.1 equiv) and tetrabutylammonium bromide (1.773 g, 5.5 mmol, 1.1 equiv) at room temperature, and stirring was maintained at room temperature. After the reaction was complete as monitored by TLC, the reaction mixture was then filtered over celite and concentrated. The crude product was purified by flash chromatograph on silica gel to afford pure α-iminonitrile.



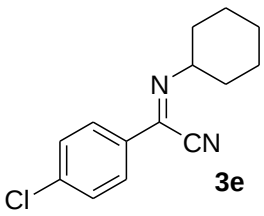
(R)-**3d**

(*R*)-*Z*-*N*-(1-Phenylethyl)benzimidoyl cyanide (R)-3d. Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 200/1) afforded the title product as a light yellow solid in 75% yield. M.p. = 54 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, *J* = 6.4 Hz, 3H), 5.24-5.26 (m, 1H), 7.31-7.35 (m, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.49-7.55 (m, 5H), 8.08-8.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.58, 67.61, 109.67, 126.64, 127.49, 127.68, 128.64, 128.79, 132.14, 133.42, 139.74, 143.29. IR (neat) 3066, 3032, 2973, 2922, 2876, 1605, 1576, 1490, 1449, 1361, 1262, 1246, 1073, 1014, 776, 760, 689, 675 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{14}N_2$ [M] $^{+}$: 234.1157, found 234.1159. $[\alpha]_D^{20}$ = -22.4 (c = 1.0 g/100 mL, $CHCl_3$). The enantiomeric excess was determined by Chiralcel OD-H (0.46×25 cm): >99% ee, detected at 214 nm; flow rate 0.4 mL/min; eluent: hexanes/isoproanol = 80:20 (v/v %); t (major) = 9.957 min, t (minor) = 9.418 min.



rac-**3d**

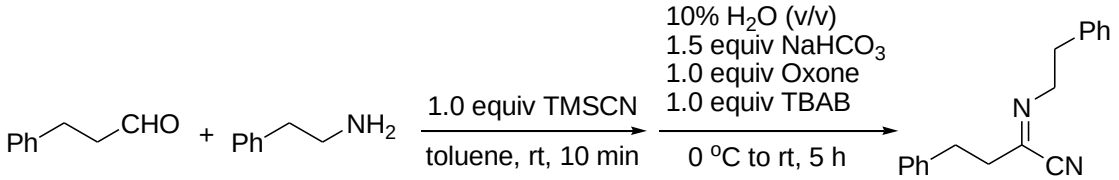
(*Z*)-*N*-(1-Phenylethyl)benzimidoyl cyanide (rac-3d). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 200/1) afforded the title product as a light yellow solid in 81% yield. M.p. = 35-37 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (d, *J* = 6.4 Hz, 3H), 5.21 (q, *J* = 6.4 Hz, 1H), 7.29-7.32 (m, 1H), 7.37-7.41 (m, 2H), 7.47-7.56 (m, 5H), 8.05-8.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.62, 67.60, 109.69, 126.67, 127.52, 127.72, 128.67, 128.82, 132.19, 133.45, 139.76, 143.32. IR (neat): 3065, 3031, 2973, 2923, 2875, 2216, 1605, 1577, 1491, 1448, 1361, 1317, 1262, 1181, 1109, 1072, 1014, 910, 851, 775, 760, 689, 675 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{15}N_2$ [M+H]$^{+}$: 235.1235, found 235.1232.



3e

(*Z*)-4-Chloro-*N*-cyclohexylbenzimidoyl cyanide (3e). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded the title product as a colorless crystal in 41% yield. M.p. = 71-72 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25-1.37 (m, 1H), 1.40-1.51 (m, 2H), 1.57-1.88 (m, 7H), 3.84-3.91 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.88, 25.22, 33.27, 67.31, 109.31, 128.57, 128.89, 132.01, 137.77, 138.00. IR (neat): 2932, 2858, 1605, 1592, 1568, 1490, 1446, 1401, 1259, 1091, 1074, 1015, 994, 835, 799, 721 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{15}N_2Cl$ [M] $^{+}$: 246.0924, found 246.0921.

Synthesis of α-iminonitrile 3k.[3]

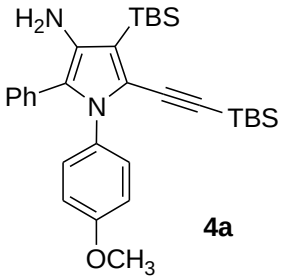


3k

3k was synthesized by a modified procedure of the published method.[3] To a solution of 3-phenylpropanal (0.40 mL, 3.0 mmol) and 2-phenylethanamine (0.38 mL, 3.0 mmol) in toluene (40 mL) was added TMSCN (0.40 mL, 3.0 mmol) at room temperture. About 10 min later, H_2O (4 mL, 10% by volume), $NaHCO_3$ (378 mg, 4.5 mmol), oxone (922 mg, 3.0 mmol) and TBAB (967 mg, 3.0 mmol) were added to the mixture successively at 0 ℃, then the solution was warmed up to room temperature and stirred vigorously at the same temperature until the reaction was complete. Then the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with ethyl acetate. The combined organic extracts were washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (wet loading; eluent: petroleum ether/ethyl acetate/triethylamine = 30/1/0.3) to afford the product **3k** as a light yellow oil in 50% yield (393 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76-2.80 (m, 2H), 2.90-2.94 (m, 4H),

3.95-3.98 (m, 2H), 7.15-7.30 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.51, 36.30, 39.96, 59.82, 110.20, 126.41, 128.33, 128.38, 128.51, 128.89, 138.43, 139.34, 143.60. The NMR data is in agreement with that previously reported.[3]

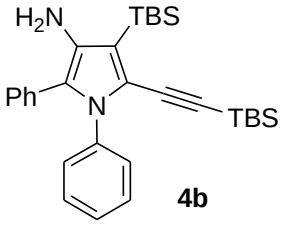
A typical procedure for the titanium-mediated cross-coupling reactions of 1,3-butadiynes with α-iminonitriles. To a stirred solution of 1,4-bis(*tert*-butyldimethylsilyl)buta-1,3-diyne **1a** (139 mg, 0.5 mmol) and $Ti(O^iPr)_4$ (0.19 mL, 0.65 mmol) in THF (5 mL) was added *n*-BuLi (0.81 mL, 1.6 M solution in hexane, 1.3 mmol) dropwise at -78 ℃ under argon. Then the reaction mixture was warmed up to room temperature and stirred at the same temperature for 1 h. (*Z*)-*N*-(4-Methoxyphenyl)benzimidoyl cyanide **3a** (130 mg, 0.55 mmol) was added at -78 ℃ and stirred at this temperature until the reaction was complete as monitored by TLC. Then the dry-ice-acetone bath was removed, and the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ solution and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2. Then silica gel was added, and the mixture was evaporated to dryness. The silica gel with absorbed product was loaded onto a silica gel column and eluted with petroleum ether/ethyl acetate, 100:1, to provide the desired product **4a** as a yellow solid in 72% yield (185 mg).



4a

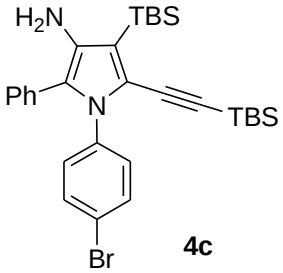
4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-1-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrol-3-amine (4a). M.p. = 94 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.46 (s, 6H), 0.82 (s, 9H), 1.04 (s, 9H), 3.28 (s, 2H), 3.77 (s, 3H), 6.77-6.79 (m, 2H), 7.10-7.13 (m, 5H), 7.21-7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.96, -4.07, 16.60, 19.02, 25.95, 26.68, 55.34, 98.22, 100.65, 110.49, 113.37, 121.19, 121.51, 125.90, 128.27,

129.11, 129.15, 131.59, 131.80, 135.45, 158.16. IR (neat): 2952, 2925, 2882, 2852, 2147, 1601, 1510, 1495, 1460, 1240, 1029, 822, 811, 762, 699, 669 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{45}N_2OSi_2$ $[M+H]^+$: 517.3070, found 517.3063. The structure of **4a** was determined by X-ray single-crystal analysis.



4b

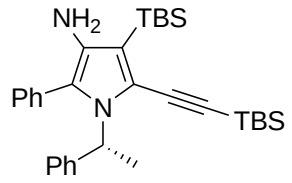
4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-1,2-diphenyl-1*H*-pyrrol-3-amine (4b). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 200/1 to 100/1) afforded the title product as a yellow solid in 88% yield (213 mg). M.p. = 107 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 0.003 (s, 6H), 0.44 (s, 6H), 0.78 (s, 9H), 1.01 (s, 9H), 3.28 (s, 2H), 7.07-7.12 (m, 3H), 7.16-7.26 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.01, -4.06, 16.62, 19.05, 25.95, 26.68, 98.44, 100.49, 110.95, 120.97, 121.32, 125.97, 126.67, 128.10, 128.13, 128.29, 129.12, 131.56, 135.73, 138.62. IR (neat): 2952, 2927, 2883, 2854, 2143, 1600, 1542, 1493, 1462, 1367, 1249, 1007, 878, 822, 809, 762, 694 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{43}N_2Si_2$ $[M+H]^+$: 487.2965, found 487.2958.



4c

1-(4-Bromophenyl)-4-(*tert*-butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-2-phenyl-1*H*-pyrrol-3-amine (4c). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 200/1 to 100/1) afforded the title product as a yellow solid in 85% yield (241 mg). M.p. = 123-124 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 6H), 0.43 (s, 6H), 0.80 (s, 9H), 1.00 (s, 9H), 3.27 (s, 2H), 7.04-7.08 (m,

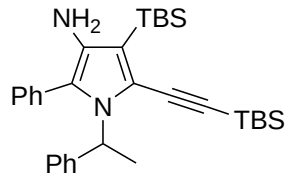
4H), 7.11-7.15 (m, 1H), 7.22-7.26 (m, 2H), 7.35-7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.01, -4.12, 16.62, 19.01, 25.89, 26.64, 99.02, 100.16, 111.56, 120.34, 120.66, 121.29, 126.21, 128.50, 129.10, 129.63, 131.21, 131.29, 136.00, 137.69. IR (neat): 2951, 2924, 2881, 2852, 2142, 1603, 1551, 1489, 1460, 1372, 1248, 1067, 1011, 882, 822, 777, 763, 695 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{42}BrN_2Si_2$ $[M+H]^+$: 565.2070, found 565.2075.



(R)-**4d**

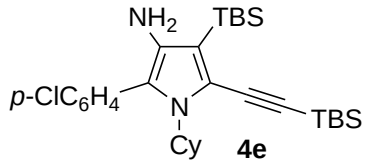
(*R*)-4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-2-phenyl-1-(1-phenylethyl)-1*H*-pyrrol-3-amine (R)-4d. After the reaction was complete, the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in THF (5 mL). To this mixture was added 4.0 equiv of BF_3 Et_2O (252 μL, 2.0 mmol) at room temperature, and stirred at 50 ^{o}C for 1 h. Then the reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silical gel (eluent: petroleum ether/ethyl acetate = 100/1) to provide the product (R)-**4d** as a yellow solid in 73% yield (187 mg, 99% ee). M.p. = 96-98 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.05 (s, 3H), -0.03 (s, 3H), 0.38 (s, 3H), 0.40 (s, 3H), 0.78 (s, 9H), 0.96 (s, 9H), 1.89 (d, *J* = 6.8 Hz, 3H), 3.02 (bs, 2H), 5.45-5.51 (m, 1H), 6.97-6.99 (m, 2H), 7.16-7.27 (m, 6H), 7.30-7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.01, -4.95, -4.03, -3.88, 16.58, 19.10, 19.44, 26.08, 26.71, 54.49, 99.10, 101.44, 111.14, 118.95, 122.33, 125.93, 126.35, 127.26, 127.99, 128.65, 130.44, 131.69, 134.42, 142.65. IR (neat): 2947, 2925, 2882, 2851, 2138, 1611, 1599, 1545, 1492, 1470, 1408, 1340, 1249, 1026, 1006, 892, 824, 810, 793, 763, 730, 694, 671 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{47}N_2Si_2$ $[M+H]^+$: 515.3278, found 515.3262. $[\alpha]_D^{20}$ = -6.8 (c = 1.0 g/100 mL, $CHCl_3$). The enantiomeric excess was determined by Lux 5μ cellulose-2 (0.46×25 cm): >99% ee, detected at 220 nm; flow rate 0.5 mL/min; eluent:

ACN / H_2O = 75/25 (v/v %); t (major) = 31.877 min, t (minor) = 32.999 min.



rac-**4d**

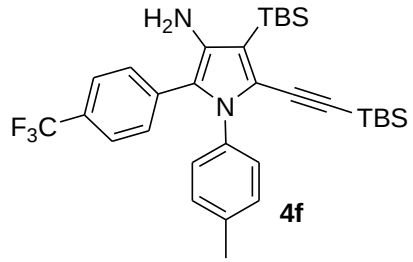
4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-2-phenyl-1-(1-phenylethyl)-1*H*-pyrrol-3-amine (rac-4d). After the reaction was complete, the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in THF (5 mL). To this mixture was added 4.0 equiv of BF_3 Et_2O (252 μL, 2.0 mmol), and stirred at 50 ^oC for 1 h. Then the reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silical gel (eluent: petroleum ether/ethyl acetate = 100/1) to provide the product rac-**4d** as a yellow oil in 65% yield (168 mg). ^1H NMR (400 MHz, $CDCl_3$) δ -0.05 (s, 3H), -0.03 (s, 3H), 0.38 (s, 3H), 0.40 (s, 3H), 0.78 (s, 9H), 0.96 (s, 9H), 1.90 (d, *J* = 6.8 Hz, 1H), 3.00 (bs, 2H), 5.48 (q, *J* = 6.0 Hz, 1H), 6.97-6.99 (m, 2H), 7.14-7.27 (m, 6H), 7.30-7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.02, -4.96, -4.05, -3.89, 16.61, 19.12, 19.44, 26.07, 26.70, 54.49, 99.13, 101.38, 111.15, 118.95, 122.33, 125.94, 126.36, 127.28, 128.01, 128.67, 130.45, 131.66, 134.37, 142.66. IR (neat): 3415, 3339, 2925, 2882, 2852, 2361, 2341, 2137, 1611, 1599, 1544, 1492, 1470, 1408, 1338, 1296, 1249, 1026, 1005, 893, 822, 809, 762, 730, 693, 670 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{47}N_2Si_2$ $[M+H]^+$: 515.3278, found 515.3252.



4e

4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-2-(4-chlorophenyl)-1-cy

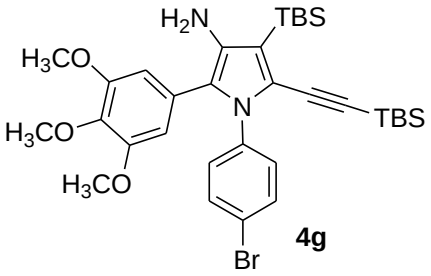
clohexyl-1*H*-pyrrol-3-amine (4e). After the reaction was complete, the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in THF (5 mL). To this mixture was added 4.0 equiv of BF_3 Et_2O (252 μL, 2.0 mmol), and stirred at 50 ^oC for 1 h. Then the reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silical gel (eluent: petroleum ether/ethyl acetate = 100/1) to provide the product **4e** as a yellow solid in 75% yield (198 mg). M.p. = 115-117 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 6H), 0.39 (s, 6H), 0.95 (s, 9H), 1.00 (s, 9H), 1.15-1.17 (m, 3H), 1.59 (s, 1H), 1.76 (s, 2H), 1.78 (s, 2H), 2.42 (s, 2H), 2.93 (s, 2H), 3.86 (t, *J* = 11.6 Hz, 1H), 7.21-7.23 (m, 2H), 7.38-7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.80, -3.88, 16.90, 19.08, 25.09, 26.24, 26.67, 31.80, 57.80, 99.00, 102.18, 110.99, 118.26, 120.28, 128.93, 130.52, 131.74, 133.06, 134.42. IR (neat): 3424, 3347, 2952, 2925, 2883, 2852, 2131, 1613, 1538, 1488, 1469, 1413, 1355, 1329, 1250, 1088, 1047, 1011, 924, 880, 824, 770, 722, 690, 674, 638, 623 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{48}ClN_2Si_2$ $[M+H]^+$: 527.3045, found 527.3033.



4f

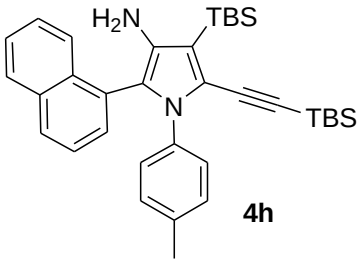
4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-1-(*p*-tolyl)-2-(4-(trifluor omethyl)phenyl)-1*H*-pyrrol-3-amine (4f). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded the title product as a yellow solid in 84% yield (239 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 6H), 0.44 (s, 6H), 0.78 (s, 9H), 1.01 (s, 9H), 2.30 (s, 3H), 3.33 (s, 2H), 7.05 (s, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.05, -4.07, 16.60, 19.03, 21.00, 25.88, 26.66, 99.06, 100.11, 110.72, 119.38, 122.86, 124.19 (q, *J* =

271.6 Hz), 125.19 (q, *J* = 3.8 Hz), 127.21 (q, *J* = 32.8 Hz), 127.82, 128.66, 129.04, 135.36 (q, *J* = 1.5 Hz), 135.90, 136.87, 136.92. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.32(s). IR (neat): 2952, 2927, 2884, 2855, 2143, 1613, 1513, 1363, 1322, 1248, 1164, 1123, 1071, 1015, 823, 772, 671 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{44}F_3N_2Si_2$ $[M+H]^+$: 569.2995, found 569.2988.



4g

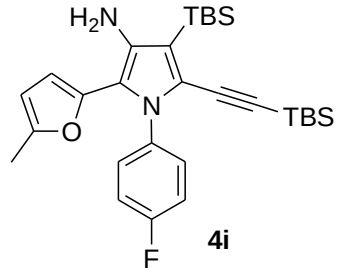
1-(4-Bromophenyl)-4-(*tert*-butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-2-(3, 4,5-trimethoxyphenyl)-1*H*-pyrrol-3-amine (4g). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1 to 10/1) afforded the title product as a yellow solid in 77% yield (252 mg). M.p = 176-177 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.43 (s, 6H), 0.80(s, 9H), 1.01 (s, 9H), 3.33 (bs, 2H), 3.63 (s, 6H), 3.80 (s, 3H), 6.27 (s, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.11, -4.21, 16.49, 18.88, 25.78, 26.56, 55.75, 60.70, 98.95, 100.00, 106.02, 111.25, 120.24, 120.31, 121.06, 126.44, 129.56, 131.21, 135.85, 136.10, 137.82, 152.94. IR (neat): 3439, 3335, 2927, 2855, 2141, 1600, 1582, 1505, 1490, 1462, 1410, 1370, 1248, 1122, 1068, 1009, 832, 808, 774, 681 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{48}BrN_2O_3Si_2$ $[M+H]^+$: 655.2387, found 655.2376.



4h

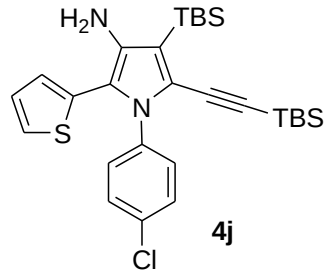
4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-2-(naphthalen-1-yl)-1-(*p*-tolyl)-1*H*-pyrrol-3-amine (4h). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum to petroleum ether/ethyl acetate = 100/1) followed by

recycling preparative HPLC afforded the title product as a yellow solid in 72% yield (199 mg). M.p. = 172-174 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 3H), 0.03 (s, 3H), 0.45 (s, 3H), 0.49 (s, 3H), 0.79 (s, 9H), 1.06 (s, 9H), 2.12 (s, 3H), 2.86 (bs, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 8.8 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.37-7.46 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.94, -4.93, -4.10, -3.99, 16.60, 19.12, 20.84, 25.94, 26.78, 97.90, 100.82, 110.53, 119.51, 121.12, 125.30, 125.78, 125.99, 126.48, 127.25, 127.79, 128.34, 128.46, 129.05, 129.83, 132.24, 133.62, 135.96, 136.07, 136.34. IR (neat): 2951, 2926, 2883, 2853, 2143, 1610, 1545, 1515, 1463, 1372, 1248, 1007, 823, 807, 774, 680, 666 cm^{-1}. HRMS (ESI) calcd for $C_{35}H_{47}N_2Si_2$ $[M+H]^+$: 551.3278, found 551.3274.



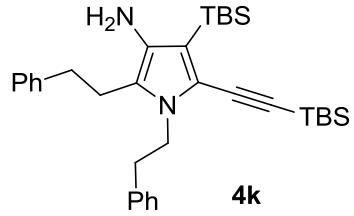
4i

4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-1-(4-fluorophenyl)-2-(5-methylfuran-2-yl)-1*H*-pyrrol-3-amine (4i). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded the title product as a yellow solid in 73% yield (186 mg). M.p. = 113-115 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.03 (s, 6H), 0.41 (s, 6H), 0.75 (s, 9H), 0.99 (s, 9H), 2.23 (s, 3H), 3.84 (s, 2H), 5.16 (d, *J* = 3.2 Hz, 1H), 5.79 (dd, *J* = 1.2, 3.2 Hz, 1H), 7.04-7.08 (m, 2H), 7.24-7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.07, -4.23, 13.49, 16.50, 18.96, 25.83, 26.62, 98.90, 99.95, 105.35, 106.69, 110.30, 112.93, 115.28 (d, *J* = 23.2 Hz), 122.34, 130.24 (d, *J* = 7.9 Hz), 135.11 (d, *J* = 2.9 Hz), 136.60, 145.79, 149.58, 161.97 (d, *J* = 247.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.02--113.95. IR (neat): 2950, 2925, 2881, 2852, 2148, 1606, 1509, 1463, 1379, 1247, 1221, 1024, 837, 823, 803, 771, 678 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{42}FN_2OSi_2$ $[M+H]^+$: 509.2820, found 509.2826.



4j

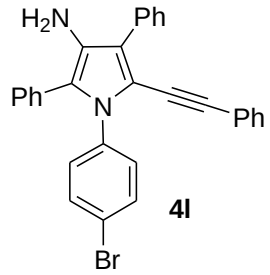
4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-1-(4-chlorophenyl)-2-(thiophen-2-yl)-1*H*-pyrrol-3-amine (4j). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) afforded the title product as a yellow solid in 79% yield (208 mg). M.p. = 97 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.44 (s, 6H), 0.80 (s, 9H), 1.02 (s, 9H), 3.39 (bs, 2H), 6.75 (dd, *J* = 0.8, 3.6 Hz, 1H), 6.93 (dd, *J* = 3.6, 5.2 Hz, 1H), 7.15-7.21 (m, 3H), 7.27-7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.05, -4.19, 16.55, 18.98, 25.85, 26.63, 99.17, 99.81, 110.85, 114.92, 122.00, 125.04, 125.98, 126.93, 128.45, 129.78, 132.67, 133.17, 137.01. IR (neat): 2952, 2926, 2882, 2854, 2137, 1607, 1538, 1492, 1463, 1375, 1249, 1088, 1011, 831, 807, 772, 687 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{40}ClN_2SSi_2$ $[M+H]^+$: 527.2139, found 527.2132.



4k

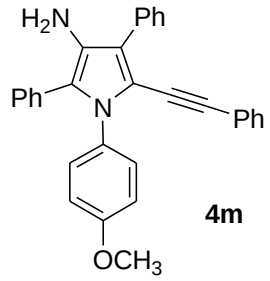
4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)ethynyl)-1,2-diphenethyl-1*H*-pyrrol-3-amine (4k). After the reaction was complete, the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ and stirred for 0.5 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in THF (5 mL). To this mixture was added 4.0 equiv of BF_3 Et_2O (252 μL, 2.0 mmol), and stirred at 50 ^{o}C for 30 min. Then the reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. Purification of the crude product by flash chromatography on silica gel (wet loading; eluent: petroleum ether/ethyl acetate/triethylamine = 30/1/0.3) afforded the product **4k** as a brown oil in 55% yield (148

mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 6H), 0.34 (s, 6H), 0.92 (s, 9H), 0.99 (s, 9H), 2.66-2.71 (m, 4H), 2.94-2.98 (m, 2H), 4.04-4.08 (m, 2H), 7.05-7.30 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.58, -4.13, 16.74, 18.82, 26.22, 26.60, 29.64, 35.67, 37.63, 46.50, 97.34, 100.69, 110.70, 117.31, 120.55, 126.08, 126.47, 128.39, 128.47, 128.53, 128.73, 133.34, 138.48, 141.12. IR (film): 3028, 2927, 2884, 2855, 2134, 1709, 1603, 1547, 1496, 1462, 1359, 1248, 1178, 1006, 823, 810, 774, 740, 697 cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{51}N_2Si_2$ $[M+H]^+$: 543.3585, found 543.3583.



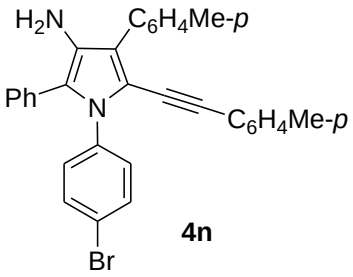
4l

1-(4-Bromophenyl)-2,4-diphenyl-5-(phenylethynyl)-1*H*-pyrrol-3-amine (4l). After the reaction was complete, the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2 (5 mL). To this mixture was added 4.0 equiv of BF_3 Et_2O (252 μL, 2.0 mmol), and stirred at room temperature for 5 min. Then the reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with dichloromethane, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by washing with cold hexane and ether to afford the product **4l** as an orange solid in 48% yield (118 mg). M.p. = 211-213 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (bs, 2H), 7.19-7.35 (m, 13H), 7.45-7.52 (m, 4H), 7.81 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.59, 95.26, 113.42, 120.11, 120.40, 121.01, 123.27, 126.40, 126.65, 127.67, 128.23, 128.60, 128.66, 128.73, 128.92, 128.97, 129.20, 130.50, 131.09, 131.51, 133.45, 137.60. IR (film): 3410, 3362, 3057, 2957, 2926, 2855, 2361, 2199, 1952, 1891, 1669, 1597, 1488, 1444, 1370, 1264, 1176, 1069, 1009, 914, 832, 755, 734, 693 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{22}BrN_2$ $[M+H]^+$: 489.0966, found 489.0947.



4m

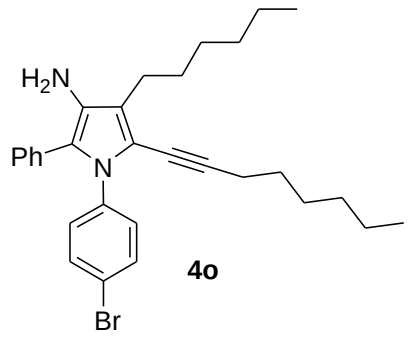
1-(4-Methoxyphenyl)-2,4-diphenyl-5-(phenylethynyl)-1*H*-pyrrol-3-amine (4m). After the reaction was complete, the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2 (5 mL). To this mixture was added 4.0 equiv of BF_3 Et_2O (252 μL, 2.0 mmol), and stirred at room temperature for 5 min. Then the reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with dichloromethane, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by washing with cold hexane and ether to afford the product **4m** as a grey solid in 44% yield (96 mg). M.p. = 214-215 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (bs, 2H), 3.80 (s, 3H), 6.85 (d, *J* = 8.8 Hz, 2H), 7.13-7.33 (m, 13H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.37, 83.07, 94.87, 113.53, 113.66, 120.12, 120.73, 123.61, 126.11, 126.39, 127.39, 128.13, 128.22, 128.44, 128.53, 128.72, 128.85, 128.98, 130.48, 131.46, 131.63, 133.83, 158.22. IR (neat): 3364, 3293, 3053, 2217, 1597, 1510, 1442, 1396, 1380, 1295, 1246, 1181, 1159, 1102, 1030, 837, 783, 772, 754, 697, 667 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{25}N_2O$ $[M+H]^+$: 441.1967, found 441.1962.



4n

1-(4-Bromophenyl)-2-phenyl-4-(*p*-tolyl)-5-(*p*-tolylethynyl)-1*H*-pyrrol-3-amine (4n). After the reaction was complete, the reaction mixture was quenched with 5 mL sat.

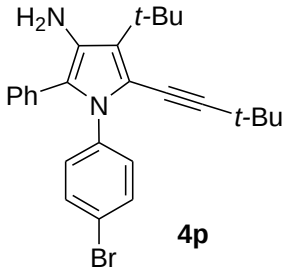
$NaHCO_3$ and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2 (5 mL). To this mixture was added 4.0 equiv of BF_3 Et_2O (252 μL, 2.0 mmol), and stirred at room temperature for 5 min. Then the reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with dichloromethane, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by washing with cold hexane and ether to afford the product **4n** as a grey solid in 42% yield (108 mg). M.p. = 200-202 ^oC. ^1H NMR (400 MHz, THF-d_8) δ 2.28 (s, 3H), 2.37 (s, 3H), 3.73 (s, 2H), 7.05-7.12 (m, 5H), 7.17-7.26 (m, 8H), 7.49 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, THF-d_8) δ 21.35, 21.43, 83.21, 96.05, 114.37, 120.33, 120.76, 121.56, 121.80, 126.65, 129.20, 129.44, 129.73, 129.75, 129.77, 130.39, 131.16, 131.29, 132.08, 132.31, 132.80, 136.52, 138.46, 139.26. IR (film): 3358, 3300, 3025, 2958, 2918, 2857, 2199, 1738, 1667, 1596, 1514, 1490, 1454, 1409, 1379, 1261, 1102, 1069, 1013, 816, 771, 732, 721, 697, 666 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{26}BrN_2$ $[M+H]^+$: 517.1279, found 517.1272.



4o

1-(4-Bromophenyl)-4-hexyl-5-(oct-1-yn-1-yl)-2-phenyl-1*H*-pyrrol-3-amine (4o). After the reaction was complete, the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in THF (5 mL). To this mixture was added 4.0 equiv of BF_3 Et_2O (252 μL, 2.0 mmol), and stirred at 50 ^oC for 30 min. Then the reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was

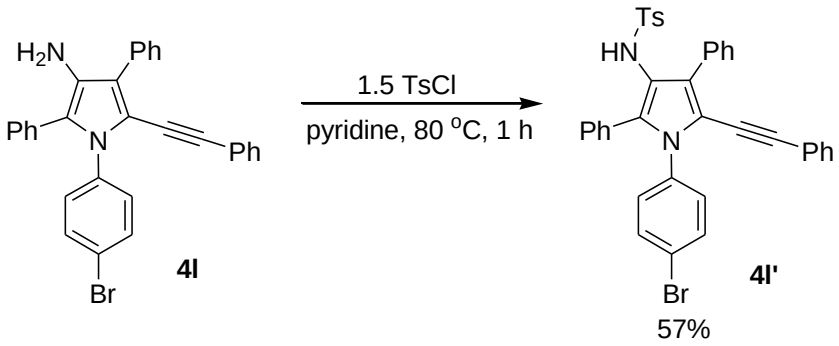
purified by flash chromatography on silical gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford the product **4o** as a yellow solid in 39% yield (99 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87-0.91 (m, 6H), 1.26-1.48 (m, 14H), 1.59-1.64 (m, 2H), 2.33 (t, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 3.10 (bs, 2H), 7.01-7.12 (m, 5H), 7.20-7.24 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.09, 14.13, 19.67, 22.58, 22.66, 24.46, 28.41, 28.57, 29.34, 29.82, 31.36, 31.71, 72.36, 96.64, 114.77, 118.46, 119.54, 120.51, 125.71, 128.43, 128.68, 129.02, 129.10, 131.24, 131.71, 138.07. IR (film): 3386, 3059, 2955, 2927, 2855, 2360, 2341, 1726, 1615, 1572, 1491, 1465, 1370, 1326, 1069, 1012, 834, 723, 698, 669 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{38}BrN_2$ $[M+H]^+$: 505.2218, found 505.2211.



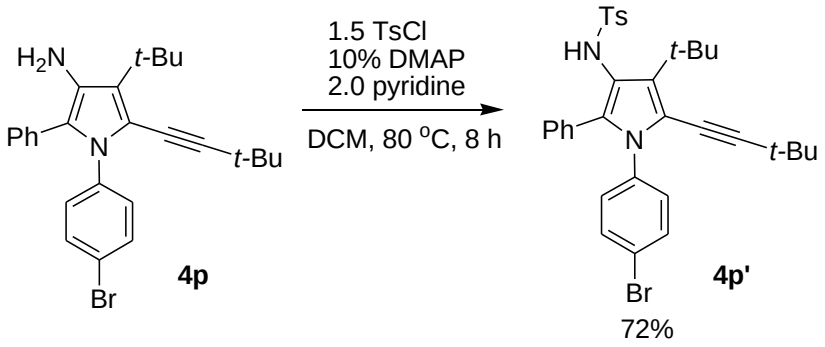
4p

1-(4-Bromophenyl)-4-(*tert*-butyl)-5-(3,3-dimethylbut-1-yn-1-yl)-2-phenyl-1*H*-pyrrol-3-amine (4p). After the reaction was complete, the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dissolved in THF (5 mL). To this mixture was added 4.0 equiv of BF_3 Et_2O (252 μL, 2.0 mmol), and stirred at 50 ^{o}C for 30 min. Then the reaction mixture was quenched with sat. $NaHCO_3$ solution, extracted with ether, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by flash chromatography on silical gel (eluent: petroleum ether/ethyl acetate = 100/1 to 50/1) to afford the product **4p** as a yellow solid in 55% yield (123 mg). M.p. = 163-164 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (s, 9H), 1.53 (s, 9H), 3.21 (s, 2H), 6.99-7.12 (m, 5H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.16, 30.29, 30.90, 32.65, 73.58, 105.17, 112.61, 119.67, 120.29, 125.72, 126.05, 128.36, 128.41, 129.32, 129.90, 130.83, 131.49, 137.84. IR (neat): 2962, 2927, 2901, 2861, 2356, 2220, 2137, 1599, 1545, 1489, 1392, 1362, 1248, 1202, 1178, 1067, 1008, 839, 821,

772, 727, 700, 669 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{30}BrN_2$ $[M+H]^+$: 449.1592, found 449.1584.

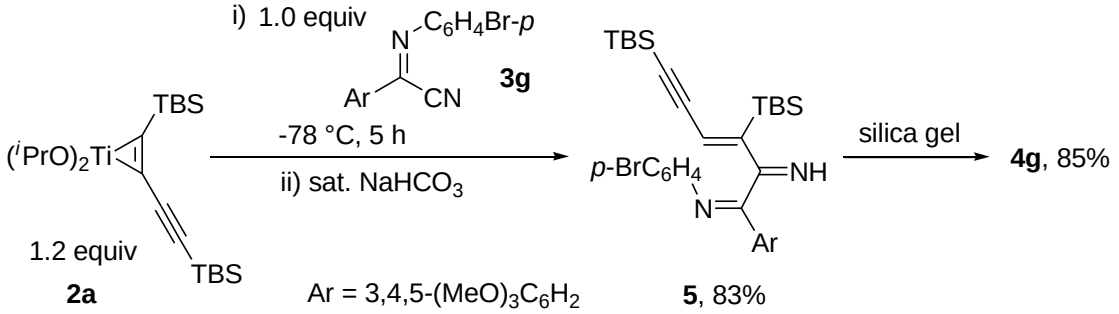


***N*-(1-(4-Bromophenyl)-2,4-diphenyl-5-(phenylethynyl)-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (4l').** To a stirred solution of 3-aminopyrrole **4l** (310 mg, 0.63 mmol) in pyridine (2.0 mL) was added 4-methylbenzene-1-sulfonyl chloride (181 mg, 0.95 mmol) at room temperature, then the mixture was warmed to 80 °C and stirred for 1 h. After evaporation of the solvent, the resulting mixture was quenched by H_2O (5 mL), and stirred for 30 min. The mixture was extracted with dichloromethane, washed separately with water and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by washing with hexane and ether to afford the product **4l'** as a brown solid in 57% yield (233 mg). M.p. = 277-278 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 6.33 (s, 1H), 6.81 (d, *J* = 7.6 Hz, 2H), 7.06-7.31 (m, 17H), 7.43-7.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.43, 81.39, 95.45, 114.01, 115.84, 121.51, 122.86, 126.68, 126.93, 127.66, 128.00, 128.18, 128.25, 128.50, 128.92, 128.95, 129.43, 129.66, 130.12, 130.62, 131.62, 132.54, 134.24, 136.38, 136.87, 142.66. IR (film): 3250, 3056, 2920, 2360, 2341, 2202, 1960, 1892, 1597, 1491, 1474, 1443, 1408, 1370, 1320, 1154, 1091, 1070, 1013, 911, 834, 812, 786, 758, 732, 717, 689, 662 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{31}BrN_3O_2S$ $[M+NH_4]^+$: 660.1320, found 660.1315.



***N*-(1-(4-Bromophenyl)-4-(*tert*-butyl)-5-(3,3-dimethylbut-1-yn-1-yl)-2-phenyl-1*H*-pyrrol -3-yl)-4-methylbenzenesulfonamide (4p').** To a stirred solution of 3-aminopyrrole **4p** (90 mg, 0.2 mmol) in dichloromethane (2.0 mL) were added 4-methylbenzene-1-sulfonyl chloride (57 mg, 0.3 mmol), DMAP (2.4 mg, 0.02 mmol) and pyridine (32 μL, 0.4 mmol) sequentially at room temperature. The flask was sealed and immersed into an oil bath at 80 ^{o}C. After stirring for 8 h, the solvent was evaporated in vacuo and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1 to 4/1) to afford **4p'** as a yellow solid in 72% yield (87 mg). M.p. = 243-244 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.61 (s, 9H), 2.24 (s, 3H), 6.05 (s, 1H), 6.59-6.61 (m, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.83-6.89 (m, 4H), 6.93-6.97(m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.36, 28.21, 30.27, 31.19, 32.97, 72.62, 106.93, 114.38, 114.50, 120.90, 126.55, 126.91, 127.65, 128.89, 129.99, 130.02, 130.26, 131.01, 132.42, 134.60, 137.15, 137.38, 142.18. IR (film): 3266, 2965, 2925, 2864, 2361, 2341, 1894, 1597, 1542, 1490, 1449, 1395, 1375, 1361, 1328, 1265, 1249, 1185, 1173, 1158, 1092, 1069, 1011, 889, 835, 811, 729, 690, 664 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{36}BrN_2O_2S$ $[M+H]^+$: 603.1681, found 603.1674.

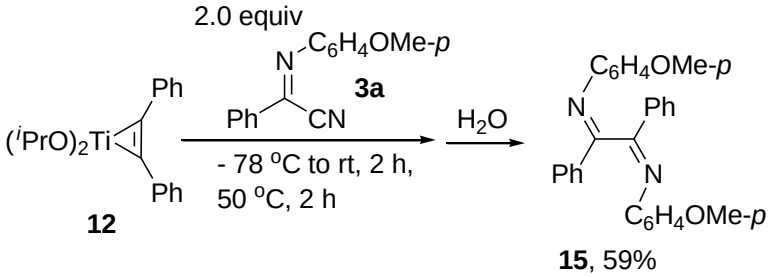
Synthesis of compound 5.



To a stirred solution of 1,4-bis(*tert*-butyldimethylsilyl)buta-1,3-diyne **1a** (167 mg, 0.6 mmol) and $Ti(O^iPr)_4$ (0.23 mL, 0.78 mmol) in THF (5 mL) was added *n*-BuLi (0.98 mL, 1.6 M solution in hexane, 1.56 mmol) dropwise at -78 ℃ under argon. The mixture was warmed up to room temperature and stirred at the same temperature for 1 h. α-Iminonitrile **3g** (188 mg, 0.5 mmol) was added at -78 ℃ and stirred at this temperature for 5 h. Then the reaction mixture was quenched with 5 mL sat. $NaHCO_3$ solution, and stirred for 1 h at room temperature. The mixture was extracted with ethyl acetate, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by flash chromatography on neutral alumina (wet loading; eluent: petroleum ether/ethyl acetate = 20/1 to 10/1) to afford the product **5** as a yellow solid in 83% yield (273 mg). M.p. = 136-137 ^oC. ^1H NMR (400 MHz, C_6D_6) δ 0.18 (s, 6H), 0.49 (s, 6H), 1.01 (s, 9H), 1.21 (s, 9H), 3.50 (s, 6H), 3.90 (s, 3H), 6.59 (d, *J* = 8.4 Hz, 2H), 6.98 (s, 1H), 7.27-7.30 (m, 2H), 7.33 (s, 2H), 10.00 (s, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ -4.79, -1.69, 16.87, 18.72, 26.29, 28.11, 55.64, 60.55, 105.37, 106.23, 109.38, 117.34, 122.23, 130.97, 132.05, 133.05, 142.59, 150.26, 153.69, 154.15, 167.30, 179.30. IR (neat): 3244, 3225, 2928, 2887, 2855, 1608, 1577, 1505, 1463, 1414, 1362, 1335, 1251, 1234, 1201, 1122, 1071, 1006, 938, 823, 808, 771, 681 cm^{-1}. HRMS(ESI) calcd for $C_{33}H_{48}BrN_2O_3Si_2$ $[M+H]^+$: 655.2387, found 655.2393. The structure of **5** was determined by X-ray single-crystal analysis.

To a solution of **5** (130 mg, 0.20 mmol) in CH_2Cl_2 was added silica gel, and the mixture was evaporated to dryness. Then the silica gel with absorbed product was loaded onto a silica gel column and eluted with petroleum ether/ethyl acetate, 10:1, to provide the product **4g** as an orange solid in 85% yield (111 mg).

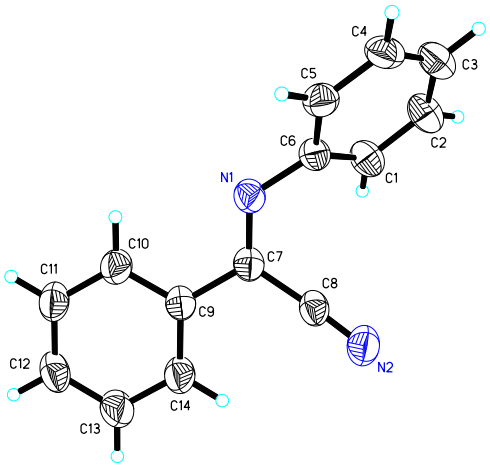
Titanium-mediated cross-coupling reactions of monoynes with α-iminonitriles.



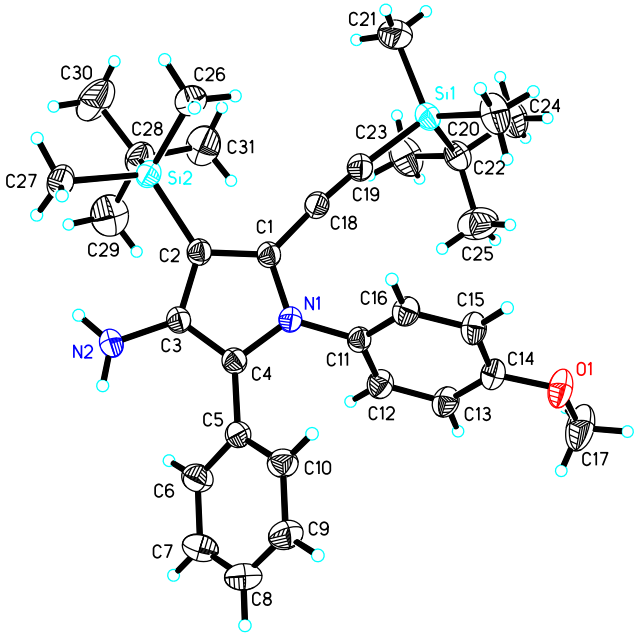
To a stirred solution of diphenylacetylene (89 mg, 0.5 mmol) and $Ti(O^iPr)_4$ (190 μL, 0.65 mL) in THF (5 mL) was added *n*-BuLi (0.81 mL, 1.6 M solution in hexane, 1.3 mmol) dropwise at -78 ℃ under argon. The solution was warmed up to room temperature and stirred at the room temperature for 1 h. Then α-Iminonitrile **3a** (1.0 mmol, 236 mg) was added at -78 ℃, then the mixture was warmed up to room temperature and stirred for 2 h, and at 50 ^oC for another 2 h. Then the reaction mixture was quenched with 5 mL water, and stirred for 30 min at room temperature. The mixture was extracted with diethyl ether, washed with water and brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1 to 30/1) on silica gel to afford the product **15** as a yellow solid in 59% yield (124 mg). In addition, diphenylacetylene was also isolated in 74% yield (66 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 6H), 6.65-6.73 (m, 8H), 7.36-7.41 (m, 6H), 7.89-7.91 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.18, 113.60, 122.04, 127.94, 128.61, 130.74, 137.26, 142.32, 157.21, 163.13. The NMR data is in agreement with that previously reported.[4] The structure of **15** was also determined by X-ray single-crystal analysis.

References:

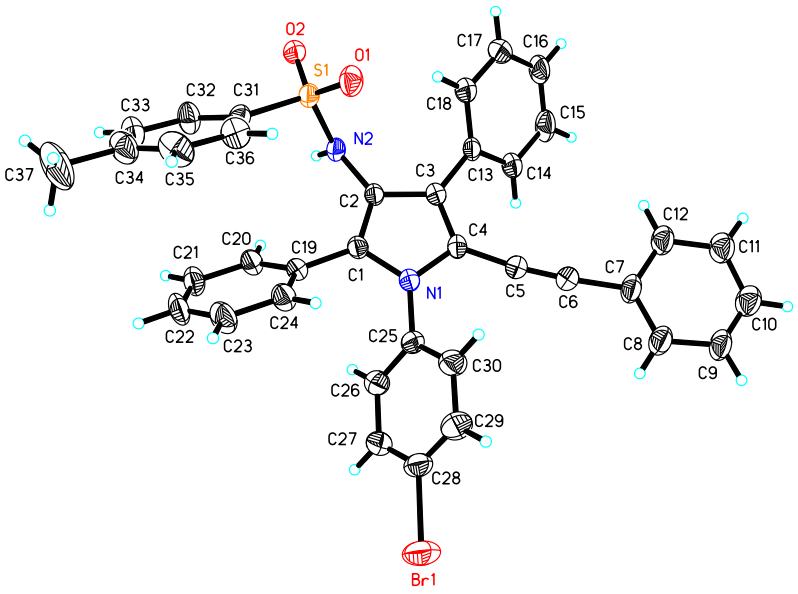
1) R. F. Cunico, R. K. Pandey, *J. Org. Chem*., 2005, **70**, 5344.
2) P. Fontaine, A. Chiaroni, G. Masson, J.-P. Zhu, *Org. Lett.*, 2008, **10**, 1509.
3) J. B. Gualtierotti, X. Schumacher, Q. Wang, J. -P. Zhu, *Synthesis*, 2013, **45**, 1380.
4) W.-S. Jin, Y. Makioka, T. Kitamura, Y. Fujiwara, *J. Org. Chem*., 2001, **66**, 514.



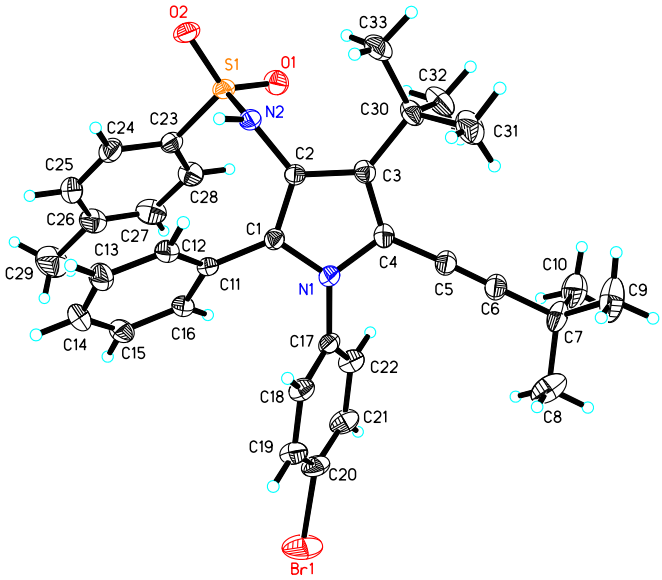
X-ray crystal structure of compound **3b**



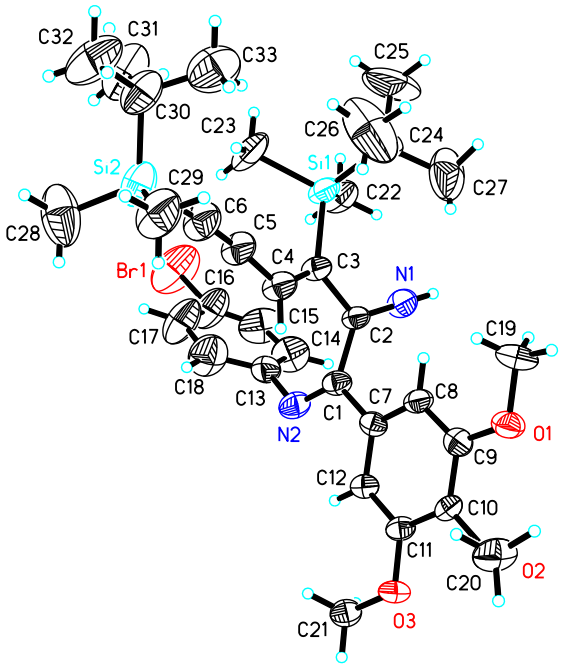
X-ray crystal structure of complex **4a**



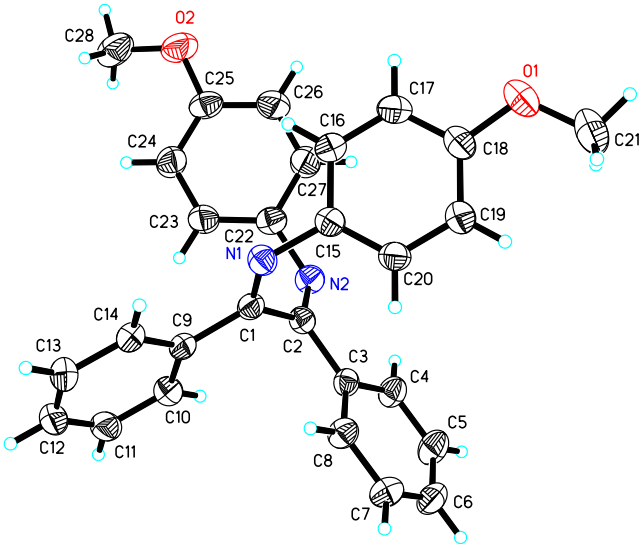
X-ray crystal structure of complex **4l'** (*N*-tosylated derivative of **4l**)



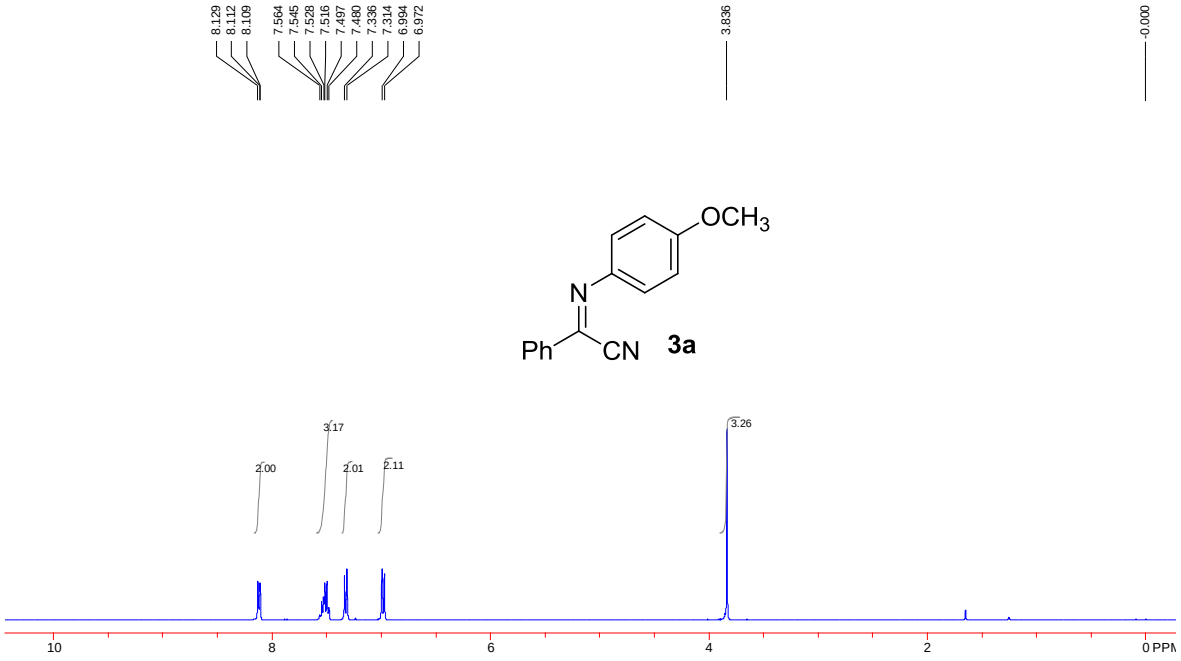
X-ray crystal structure of complex **4p'** (*N*-tosylated derivative of **4p**)



X-ray crystal structure of compound **5**



X-ray crystal structure of complex **15**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7.528
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7.497
7.480
7.336
7.314
6.994
6.972
3.836
0.000
OCH3
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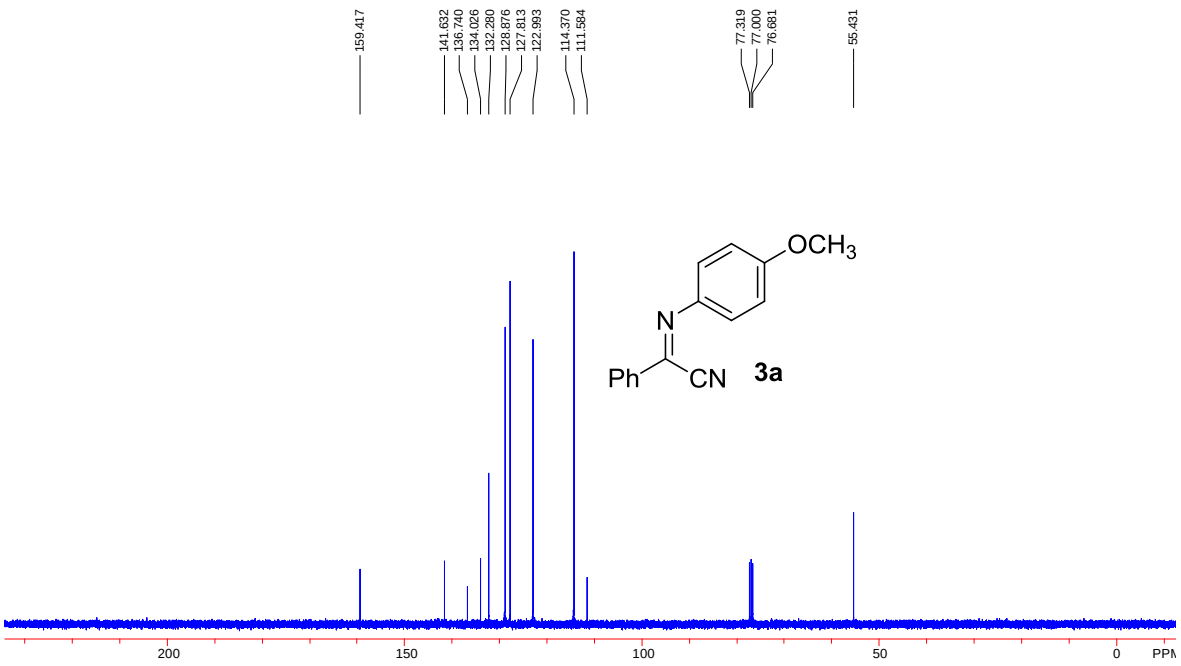
Ph
CN
3a
3.17
3.26
2.00
2.01
2.11
10
8
6
4
2
0 PPM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122.993
114.370
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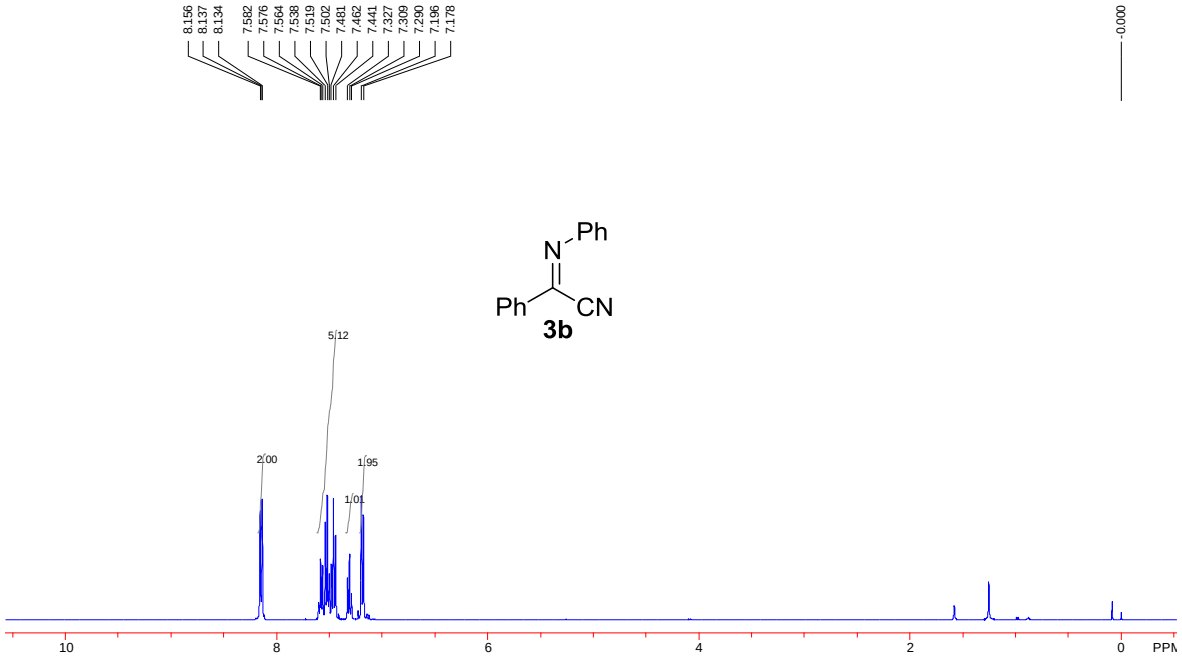
77.000
76.681
55.431
OCH3
N
Ph
CN
3a
200
150
100
50
0 PPM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8.137
8.134
7.582
7.576
7.564
7.538
7.519
7.502
7.481
7.462
7.441
7.327
7.309
7.290
7.196
7.178
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N
Ph
CN
3b
5.12
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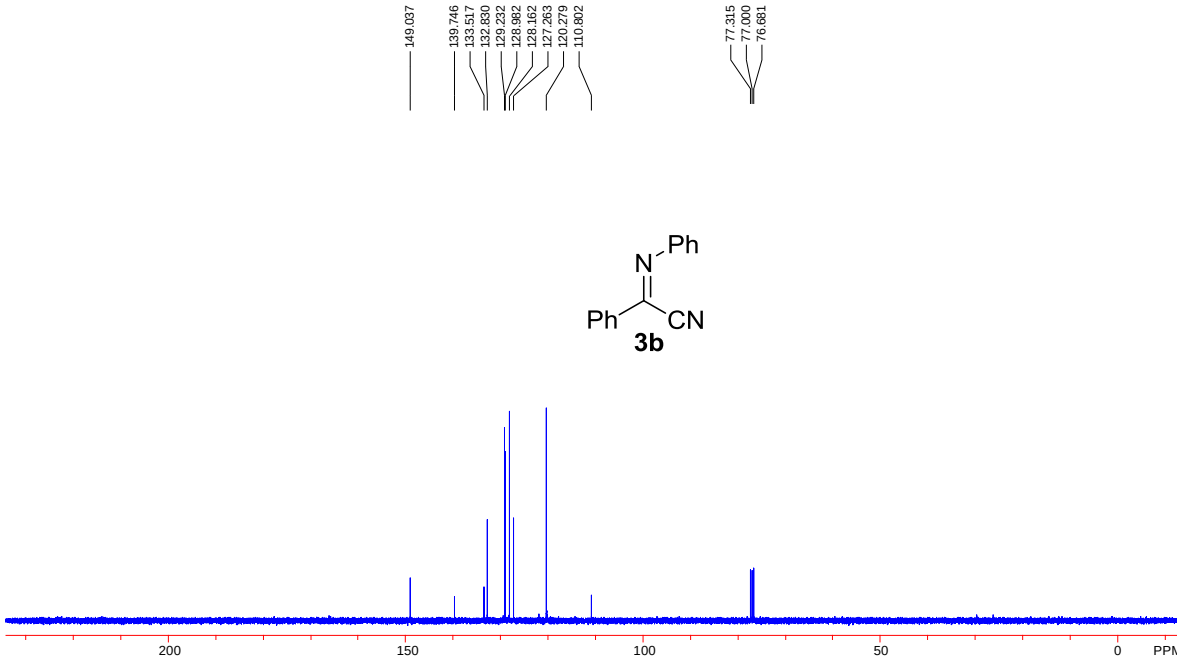
1.01
10
8
6
4
2
0
PPM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139.746
133.517
132.830
129.232
128.982
128.162
127.263
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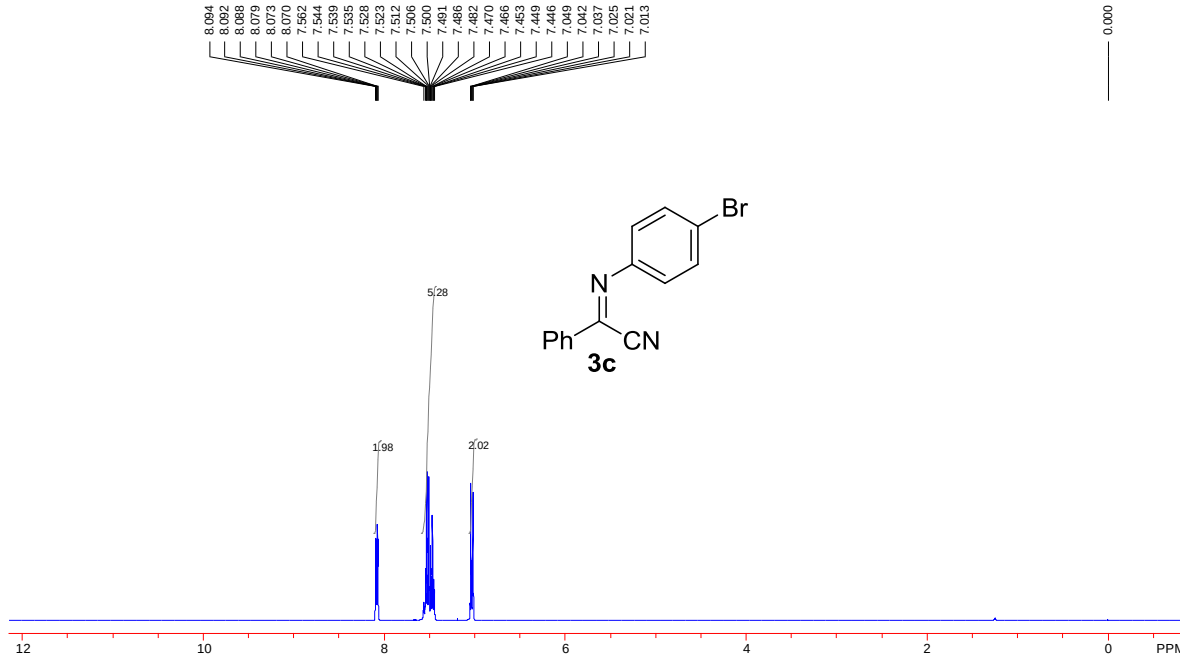
77.315
77.000
76.681
Ph
N
Ph
CN
3b
200
150
100
50
0
PPM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8.092
8.088
8.079
8.073
8.070
7.562
7.544
7.539
7.535
7.528
7.523
7.512
7.506
7.500
7.491
7.486
7.482
7.470
7.466
7.453
7.449
7.446
7.049
7.042
7.037
7.025
7.021
7.013
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N
Ph
CN
3c
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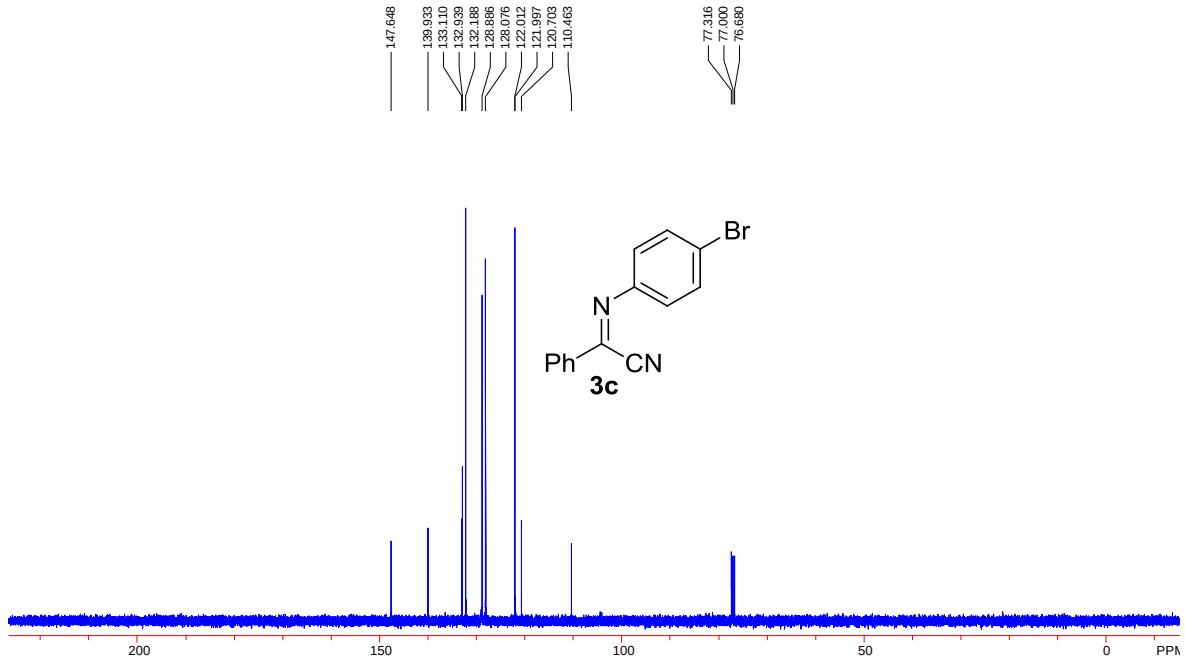
12
10
8
6
4
2
0
PPM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132.939
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122.012
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77.000
76.680
Br
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Ph
CN
3c
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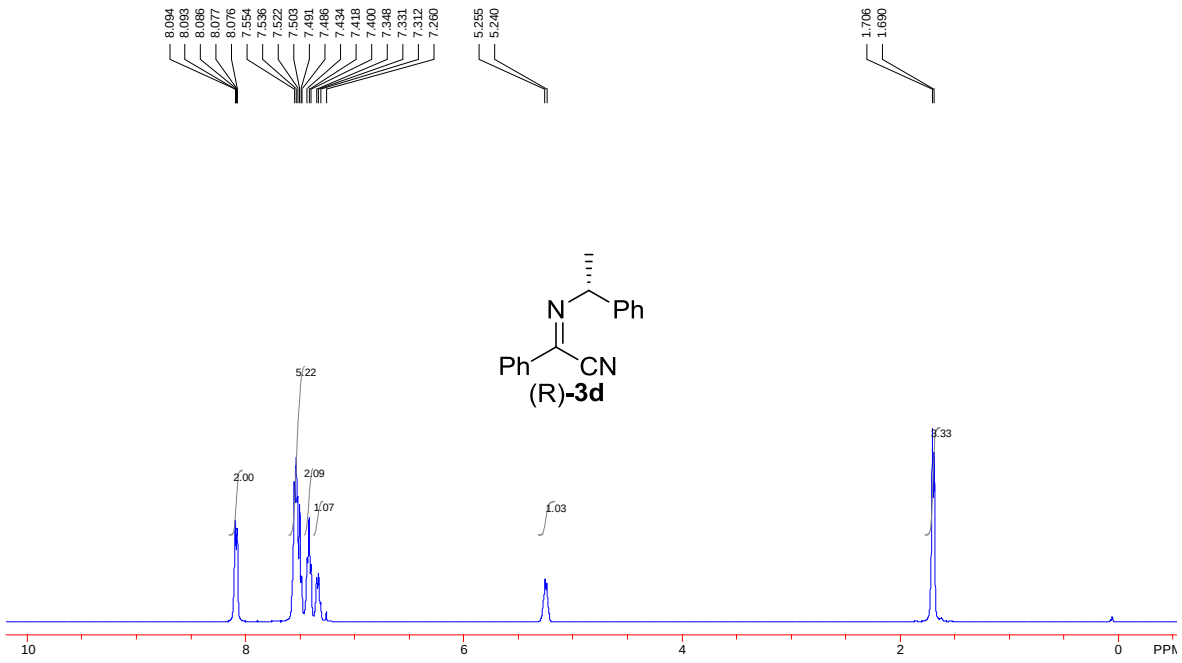
150
100
50
0
PPM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8.093
8.086
8.077
8.076
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7.536
7.522
7.503
7.491
7.486
7.434
7.418
7.400
7.348
7.331
7.312
7.260
5.255
5.240
1.706
1.690
N
Ph
Ph
CN
(R)-3d
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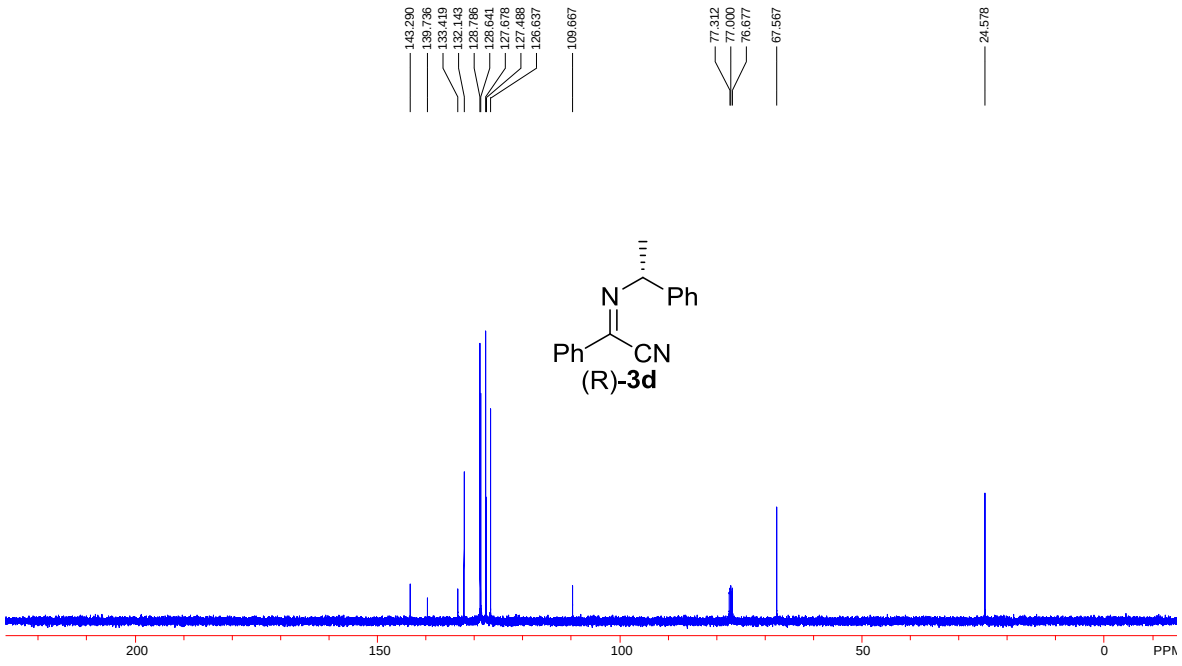
2.00
2.09
1.07
1.03
3.33
10
8
6
4
2
0
PPM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133.419
132.143
128.786
128.641
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127.488
126.637
109.667
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76.677
67.567
24.578
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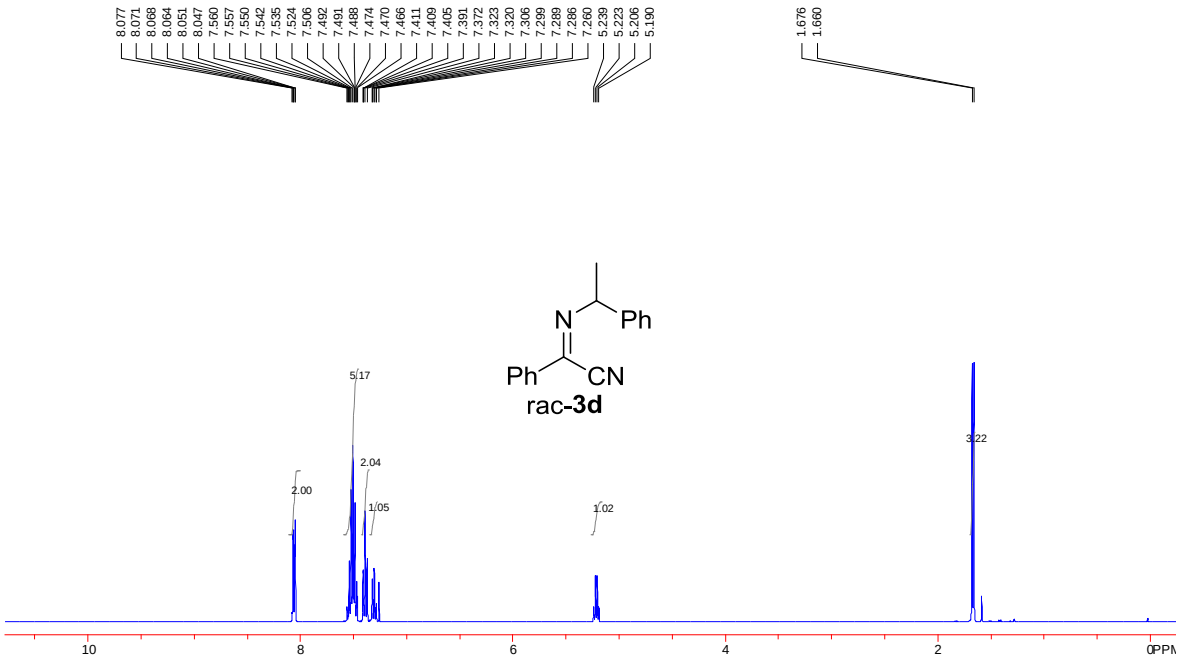
Ph
Ph
CN
(R)-3d
200
150
100
50
0
PPM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8.071
8.068
8.064
8.051
8.047
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7.557
7.550
7.542
7.535
7.524
7.506
7.492
7.491
7.488
7.474
7.470
7.466
7.411
7.409
7.405
7.391
7.372
7.323
7.320
7.306
7.299
7.289
7.286
7.260
5.239
5.223
5.206
5.190
1.676
1.660
N
Ph
Ph
CN
rac-3d
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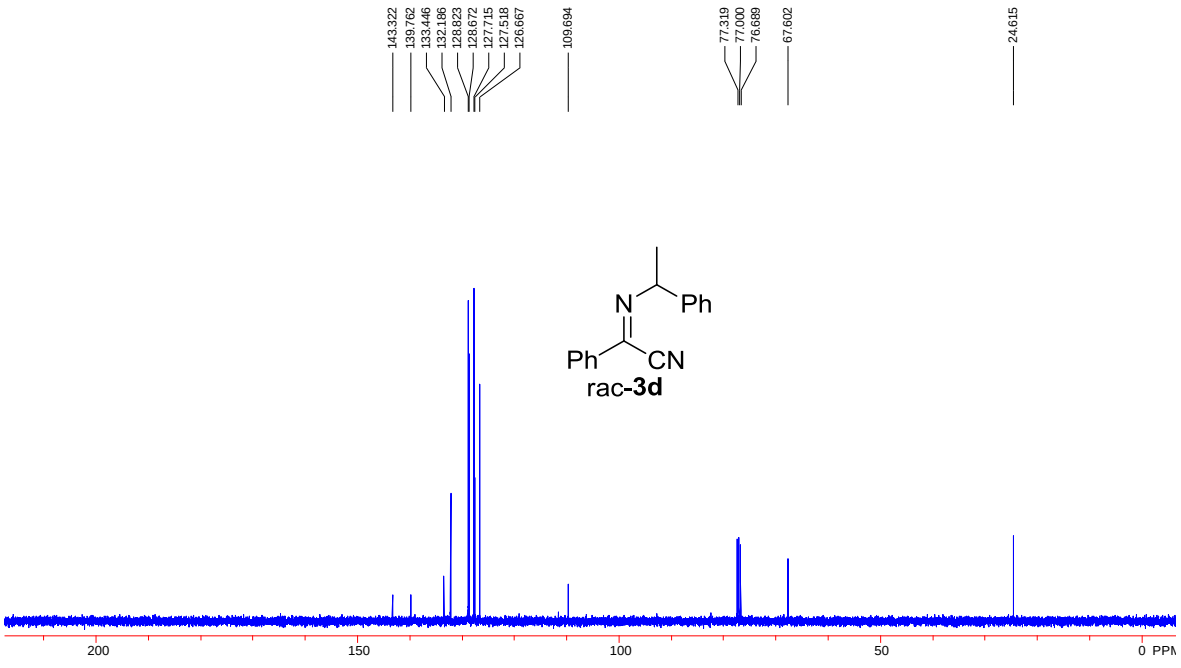
2.04
2.00
1.05
1.02
3.22
10
8
6
4
2
0PPM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127.715
127.518
126.667
109.694
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77.000
76.689
67.602
24.615
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Ph
Ph
CN
rac-3d
200
150
100
50
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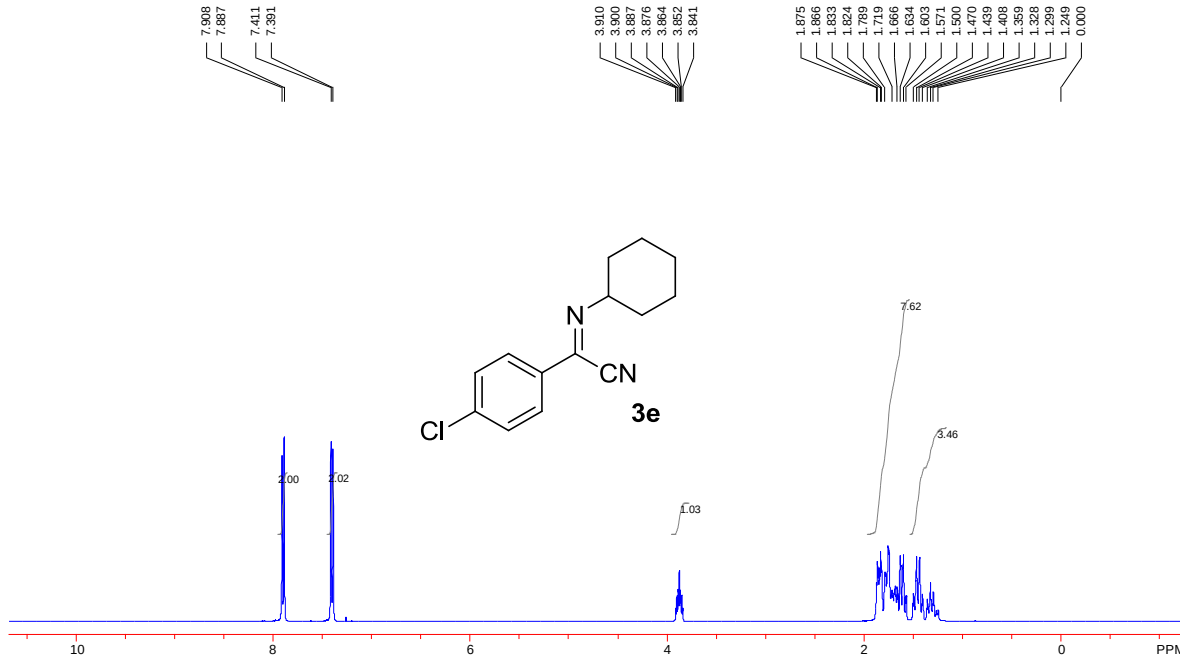
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7.411
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3.900
3.887
3.876
3.864
3.852
3.841
1.875
1.866
1.833
1.824
1.789
1.719
1.666
1.634
1.603
1.571
1.500
1.470
1.439
1.408
1.359
1.328
1.299
1.249
0.000
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CN
Cl
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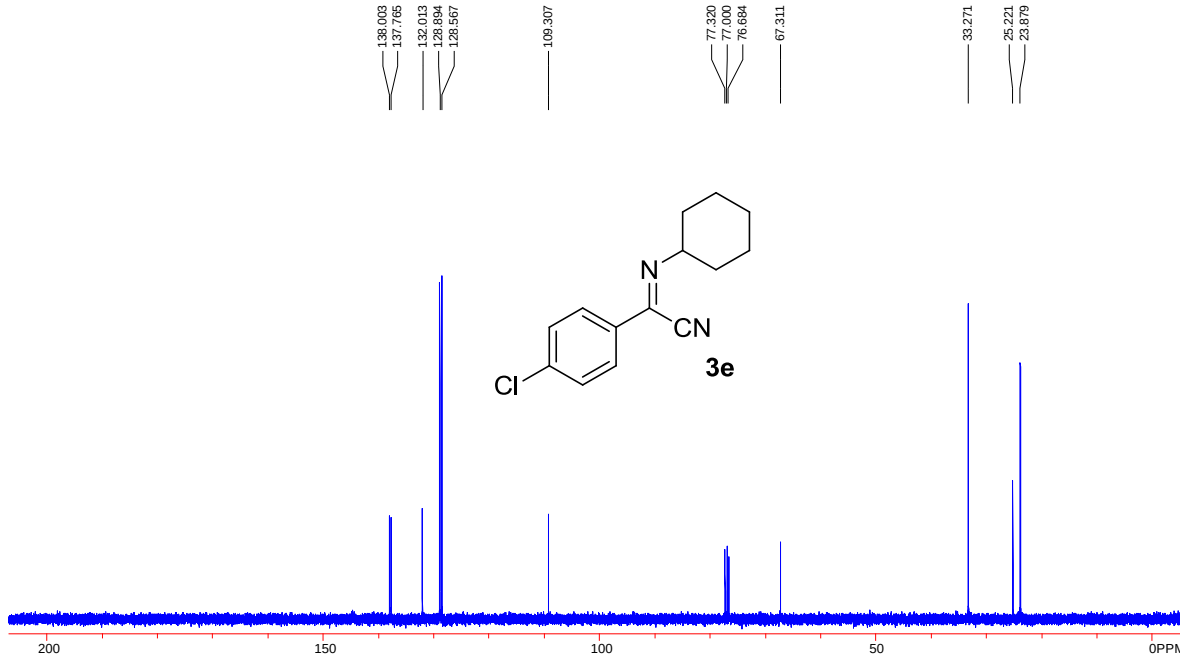
7.62
3.46
2.00
2.02
1.03
10
8
6
4
2
0
PPM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Cl
3e
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50
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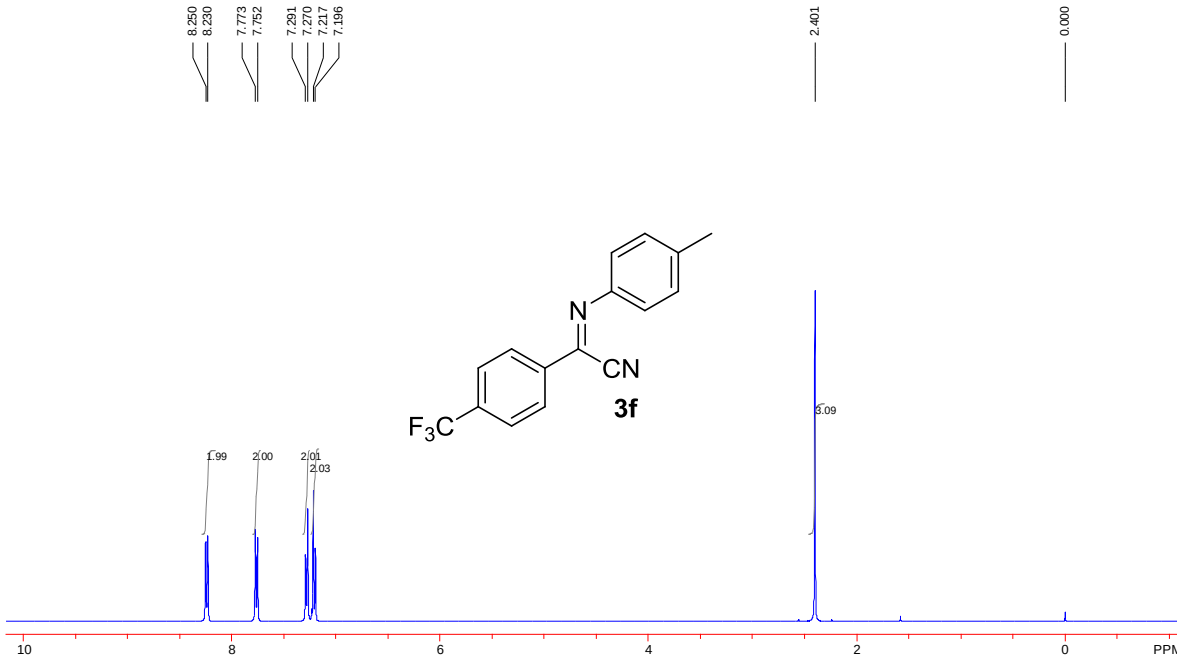
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8.230
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7.752
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7.270
7.217
7.196
2.401
0.000
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CN
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3f
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2.00
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3.09
10
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6
4
2
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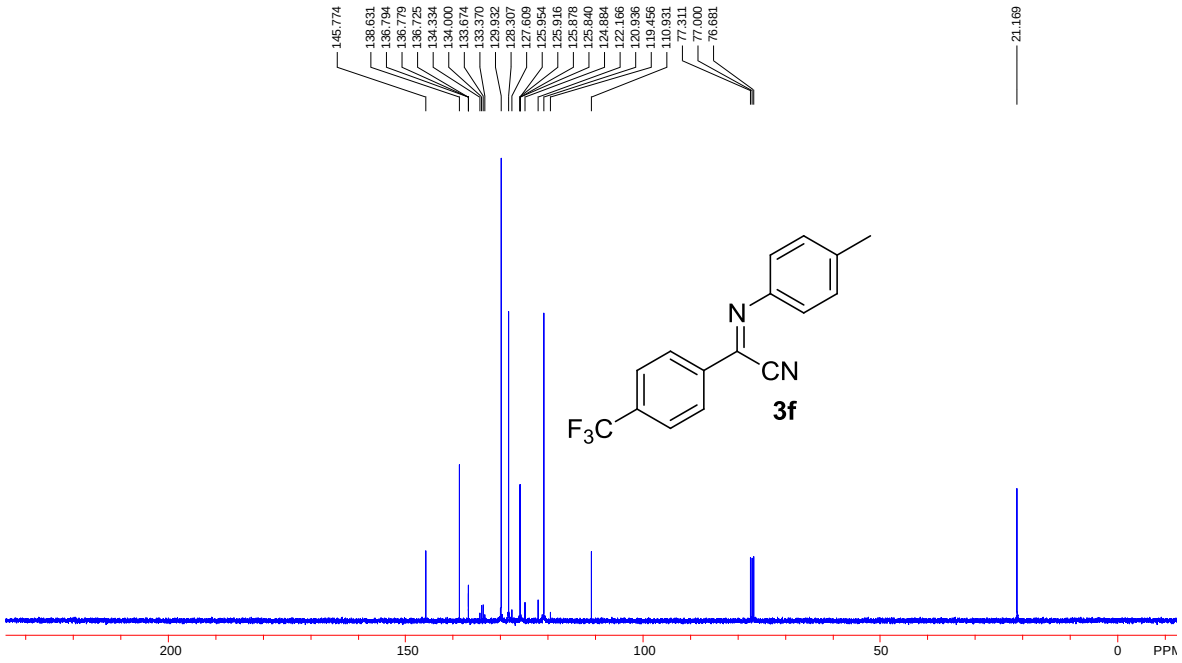
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125.878
125.840
124.884
122.166
120.936
119.456
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3f
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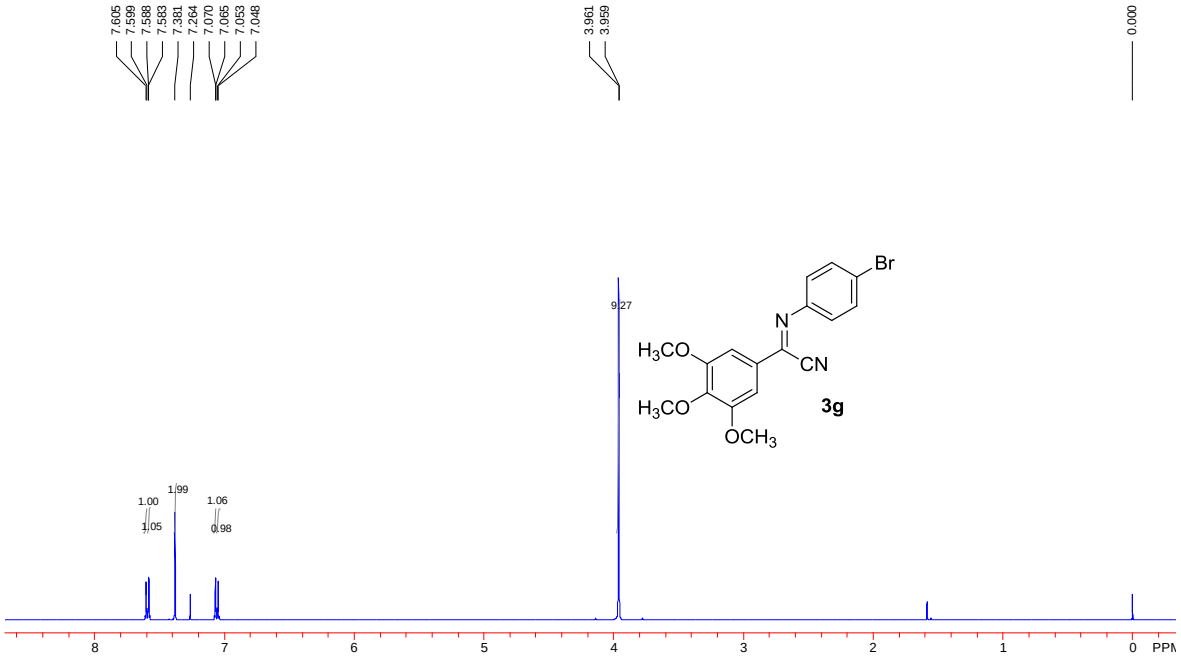
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7.070
7.065
7.053
7.048
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3.959
0.000
9.27
1.00
1.99
1.06
1.05
0.98
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CN
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H3CO
OCH3
3g
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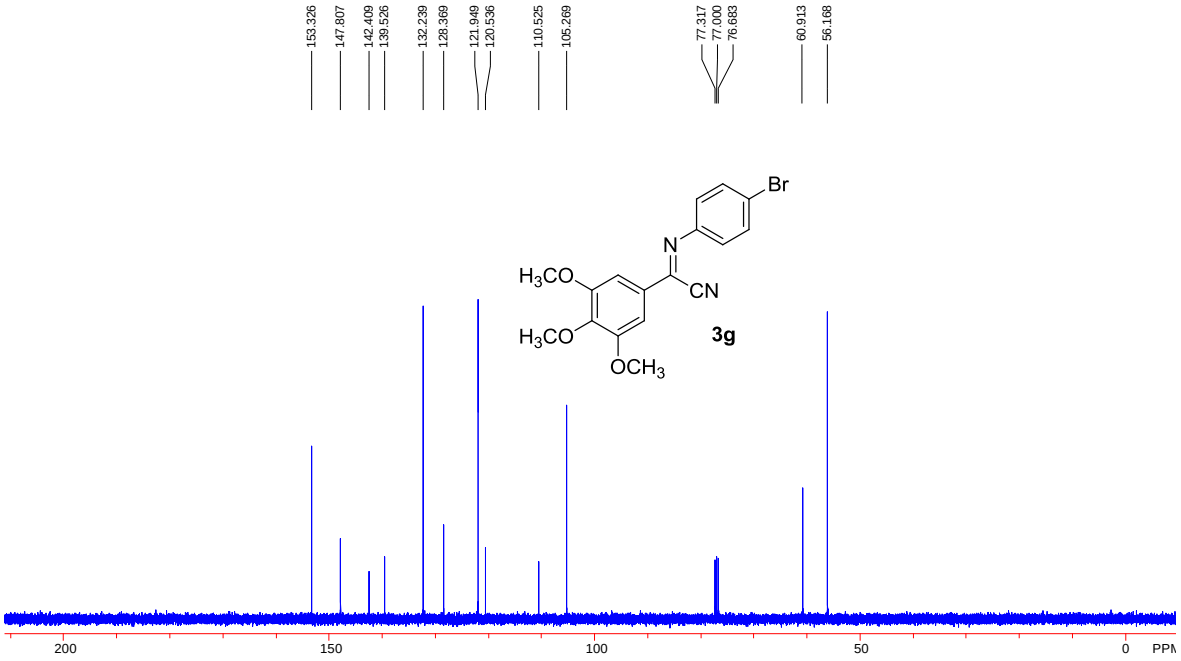
5
4
3
2
1
0
PPM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H3CO
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3g
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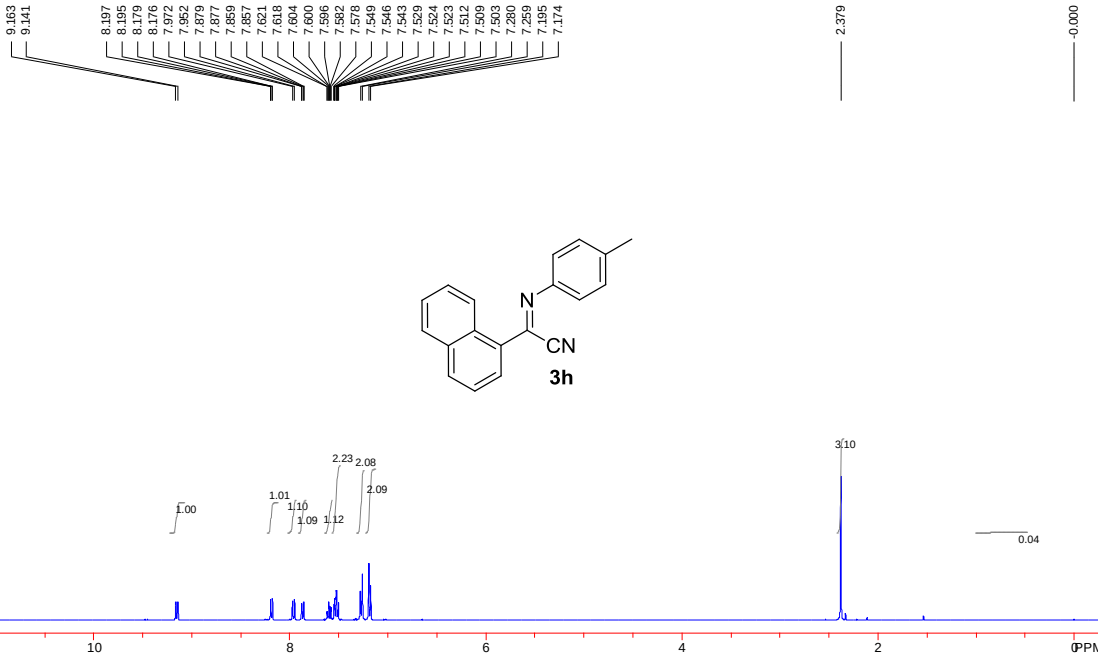
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7.877
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7.857
7.621
7.618
7.604
7.600
7.596
7.582
7.578
7.549
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7.543
7.529
7.524
7.523
7.512
7.509
7.503
7.280
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7.195
7.174
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CN
3h
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1.01
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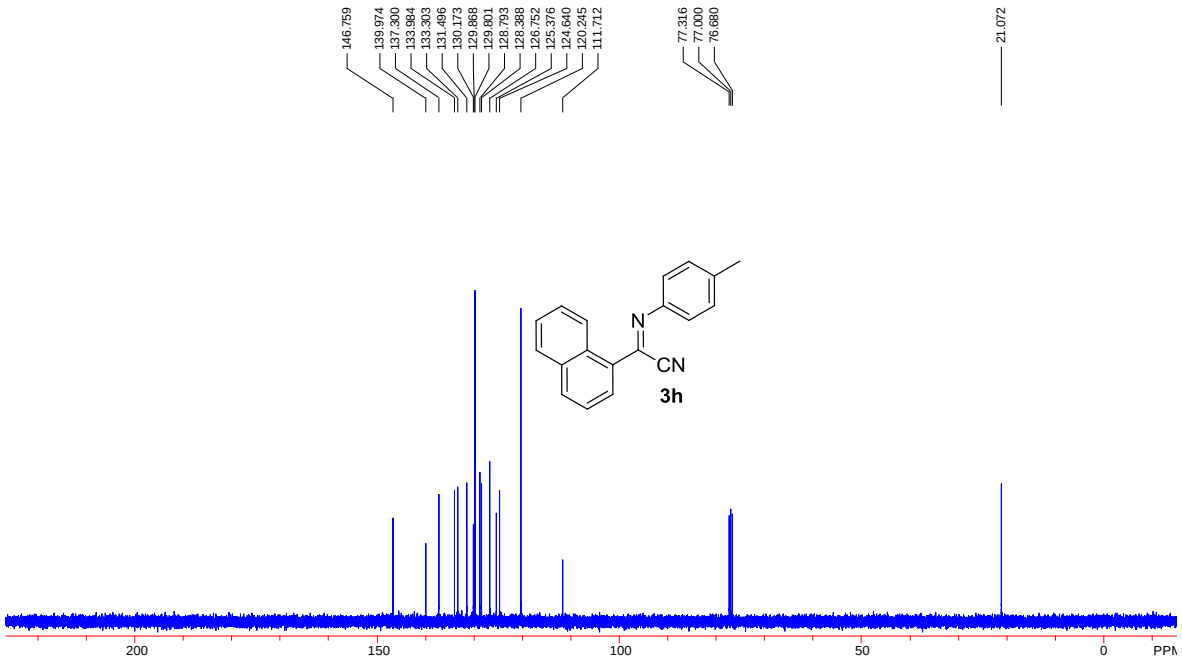
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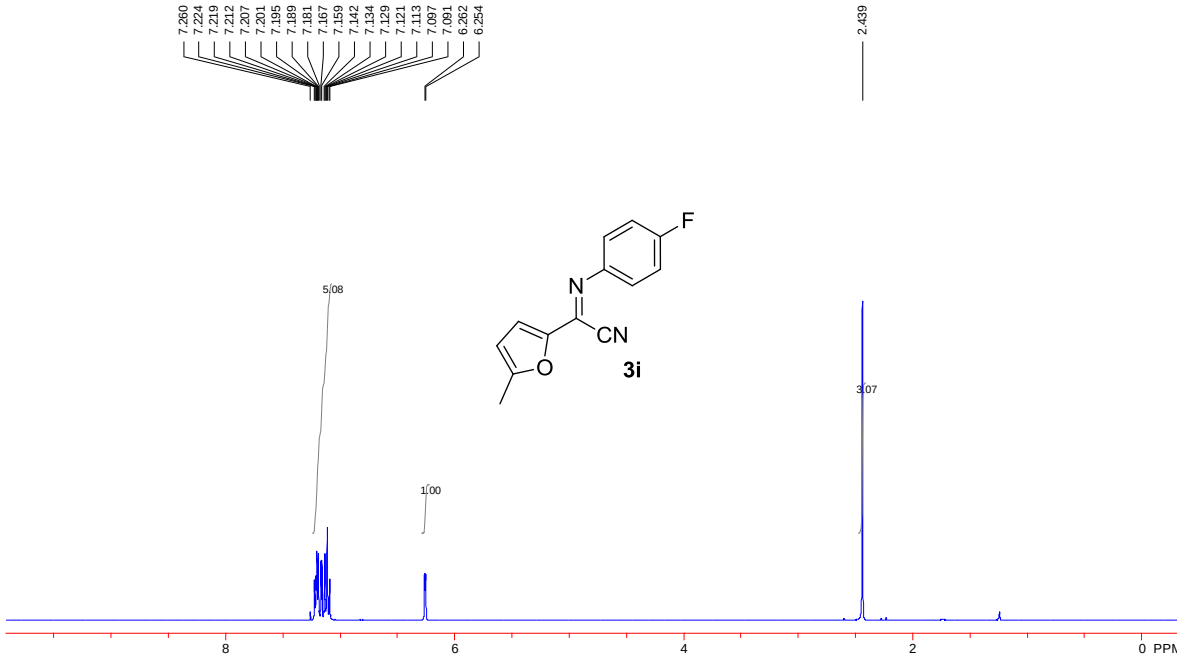
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7.189
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7.167
7.159
7.142
7.134
7.129
7.121
7.113
7.097
7.091
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N
CN
O
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3.07
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4
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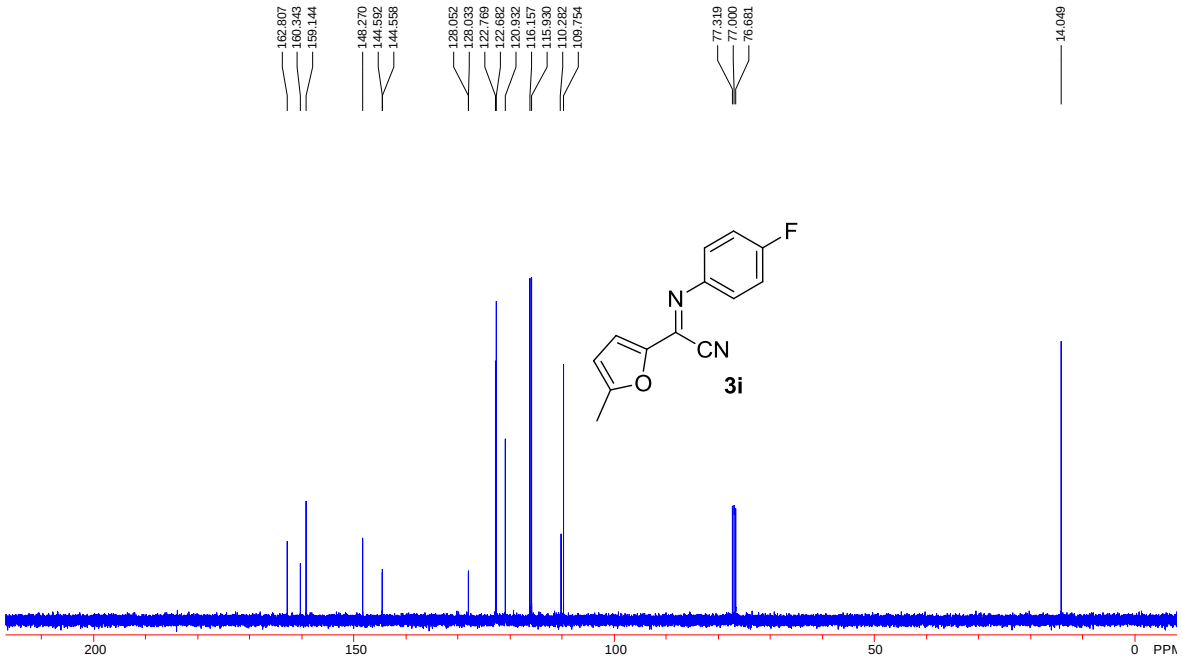
0 PPM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115.930
110.282
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77.000
76.681
14.049
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N
CN
O
3i
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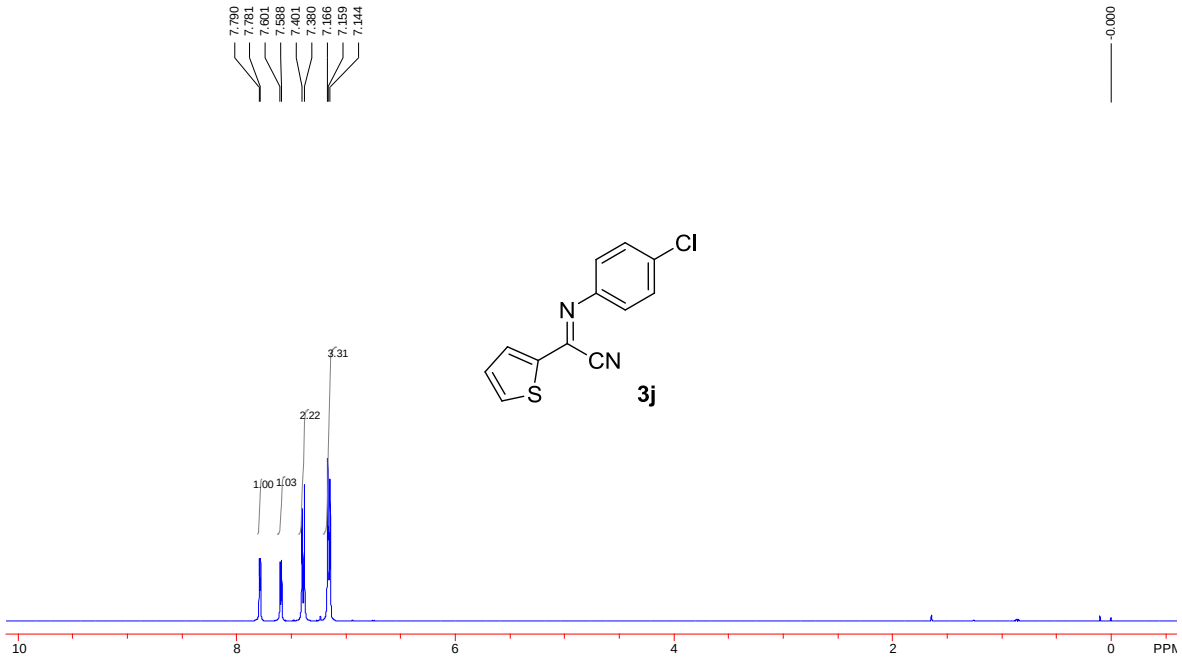
150
100
50
0 PPM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7.159
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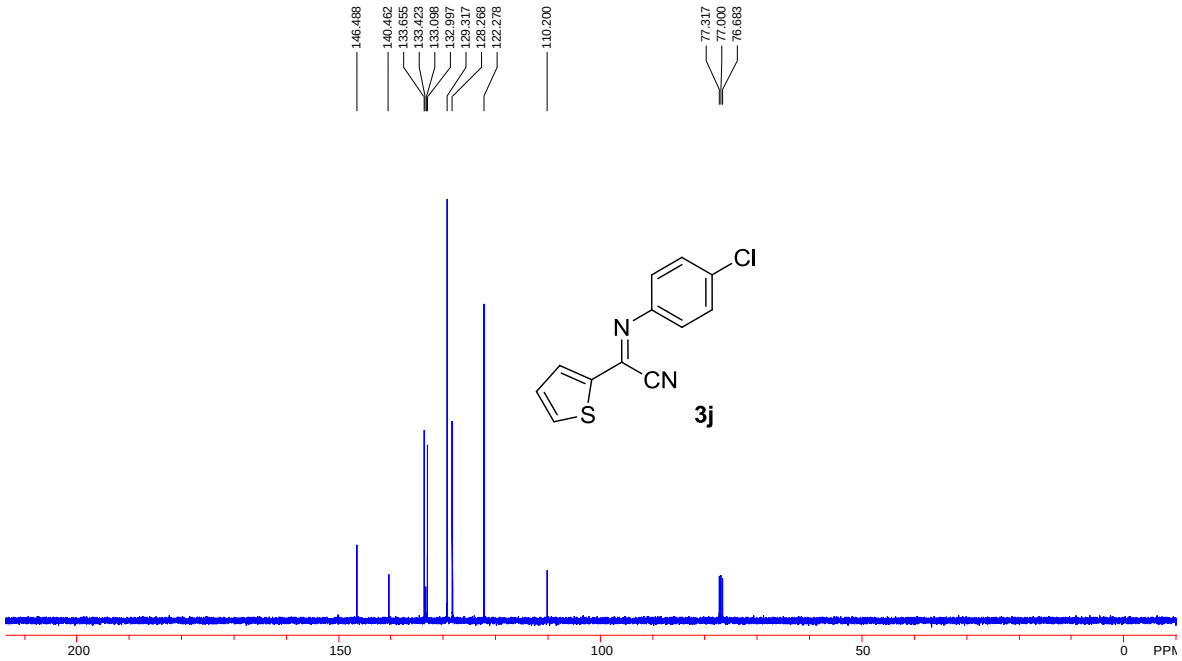
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3j
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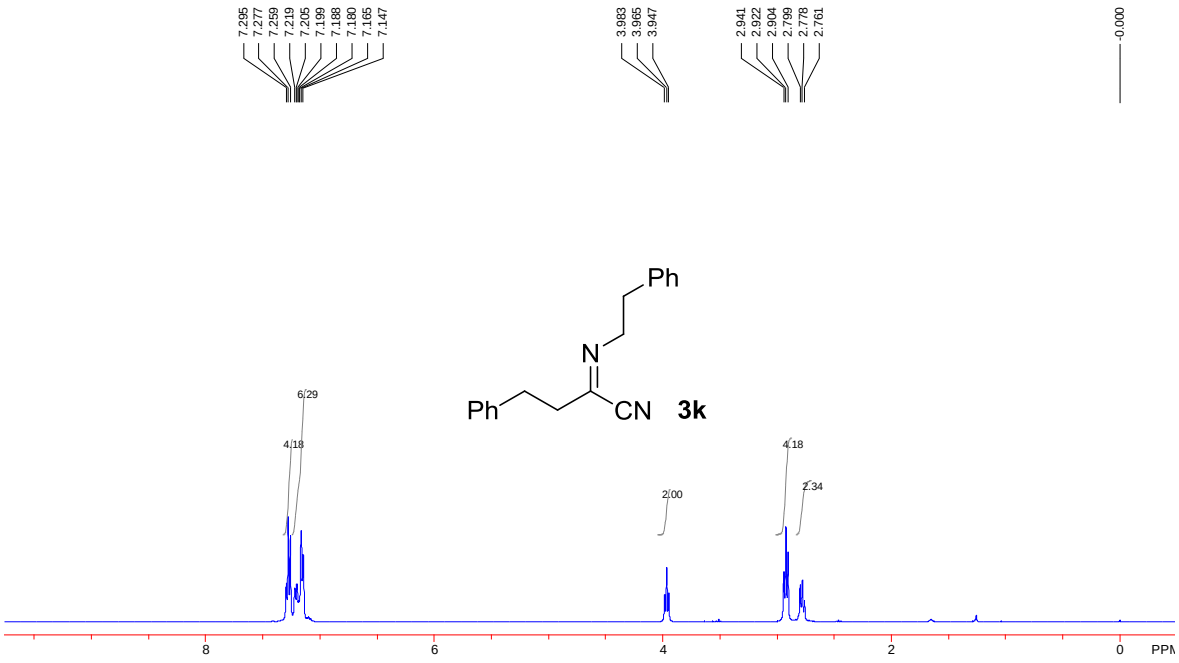
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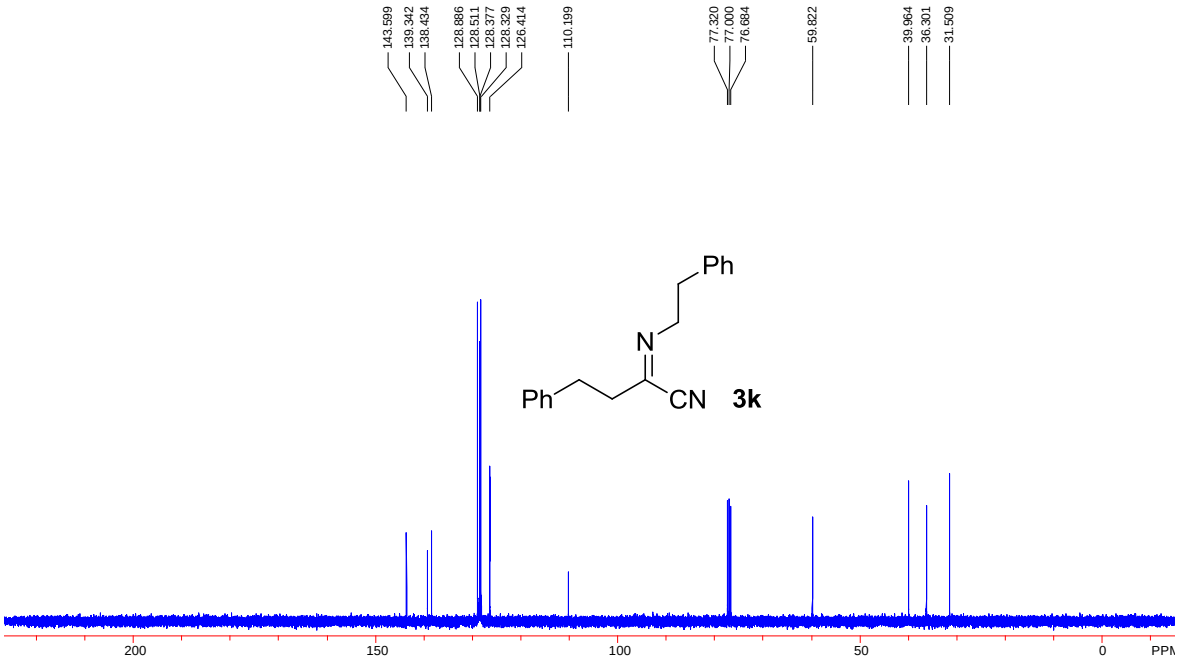
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3k
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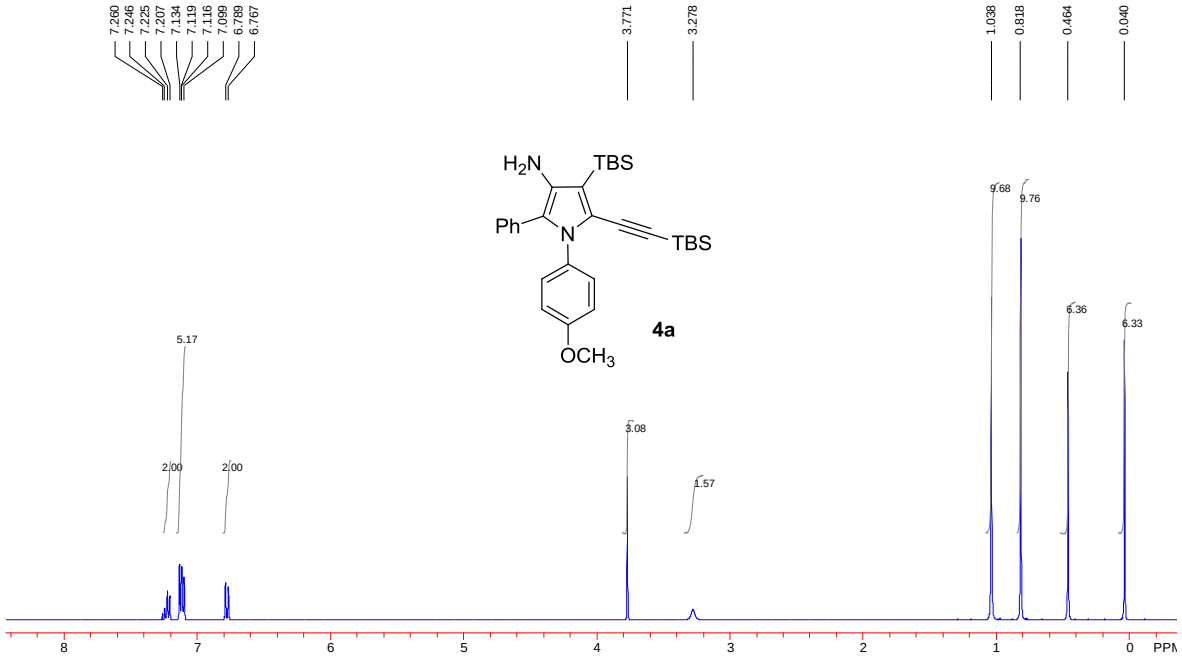
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6.767
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3.278
1.038
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0.040
H2N
TBS
Ph
N
TBS
OCH3
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9.76
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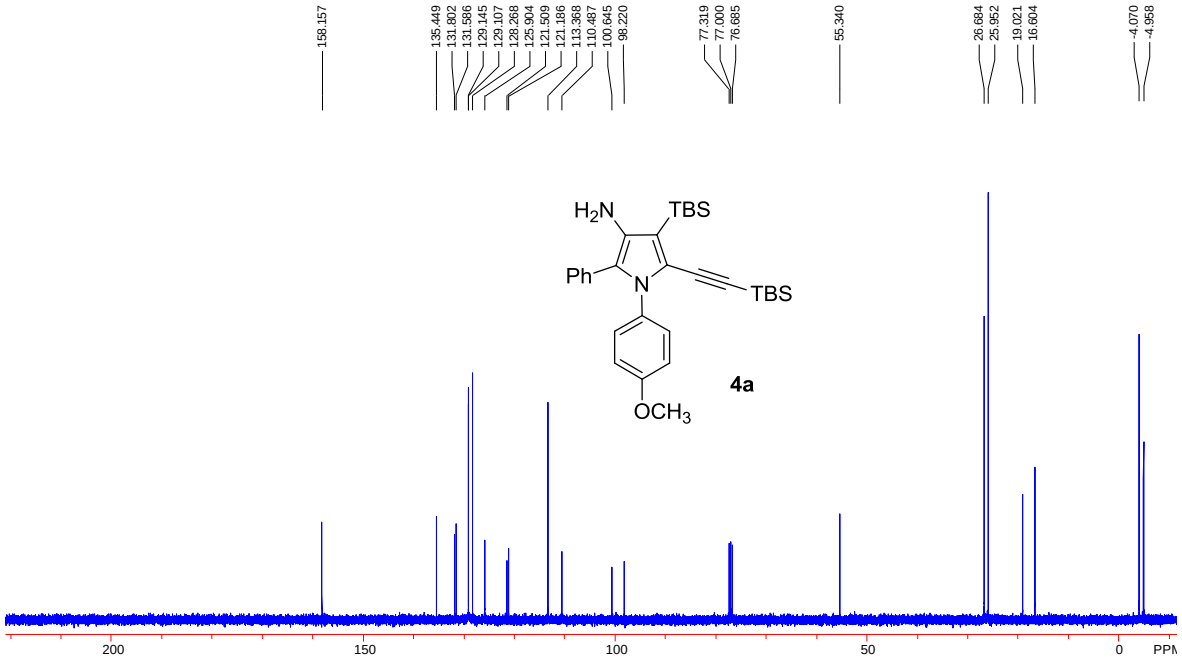
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121.186
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110.487
100.645
98.220
77.319
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55.340
26.684
25.952
19.021
16.604
-4.070
-4.958
H2N
TBS
Ph
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TBS
OCH3
4a
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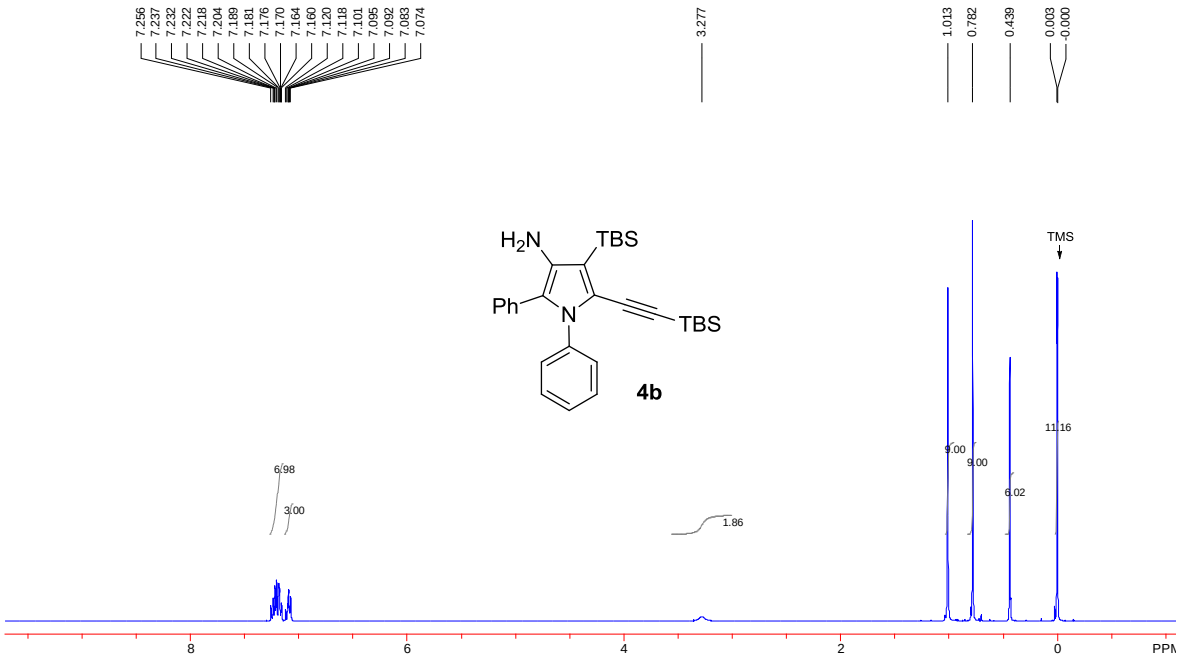
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7.120
7.118
7.101
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7.092
7.083
7.074
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1.013
0.782
0.439
0.003
-0.000
H2N
TBS
Ph
N
TBS
4b
TMS
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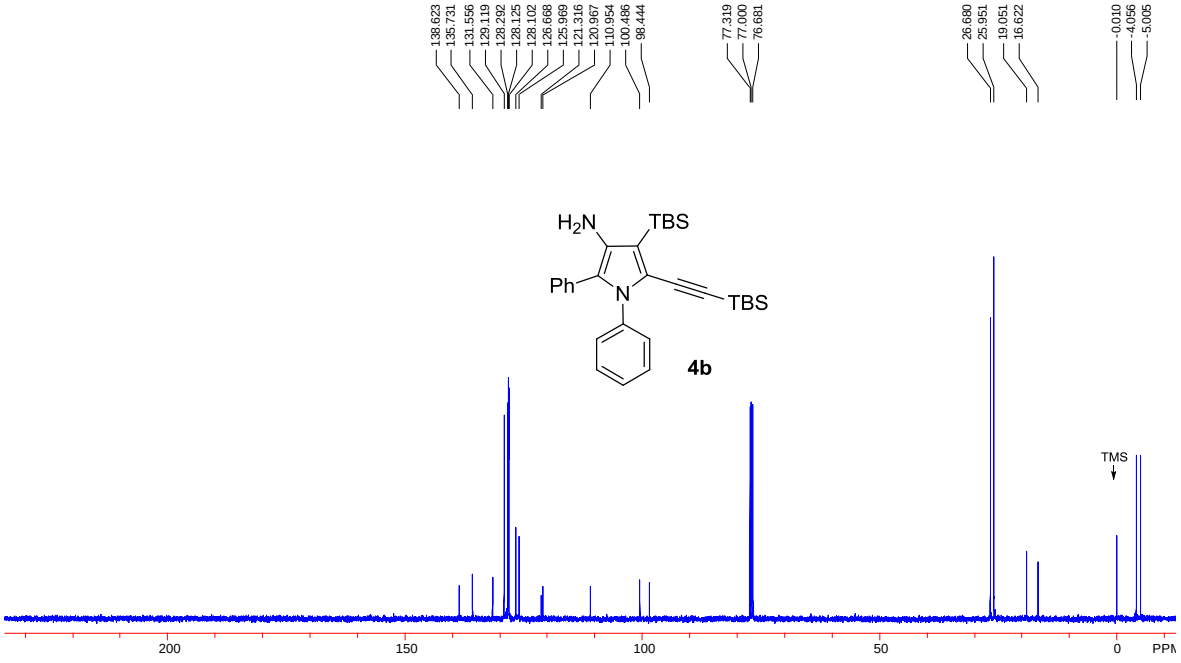
PPM

1% TMS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98.444
77.319
77.000
76.681
26.680
25.951
19.051
16.622
-0.010
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TBS
Ph
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TBS
4b
TMS
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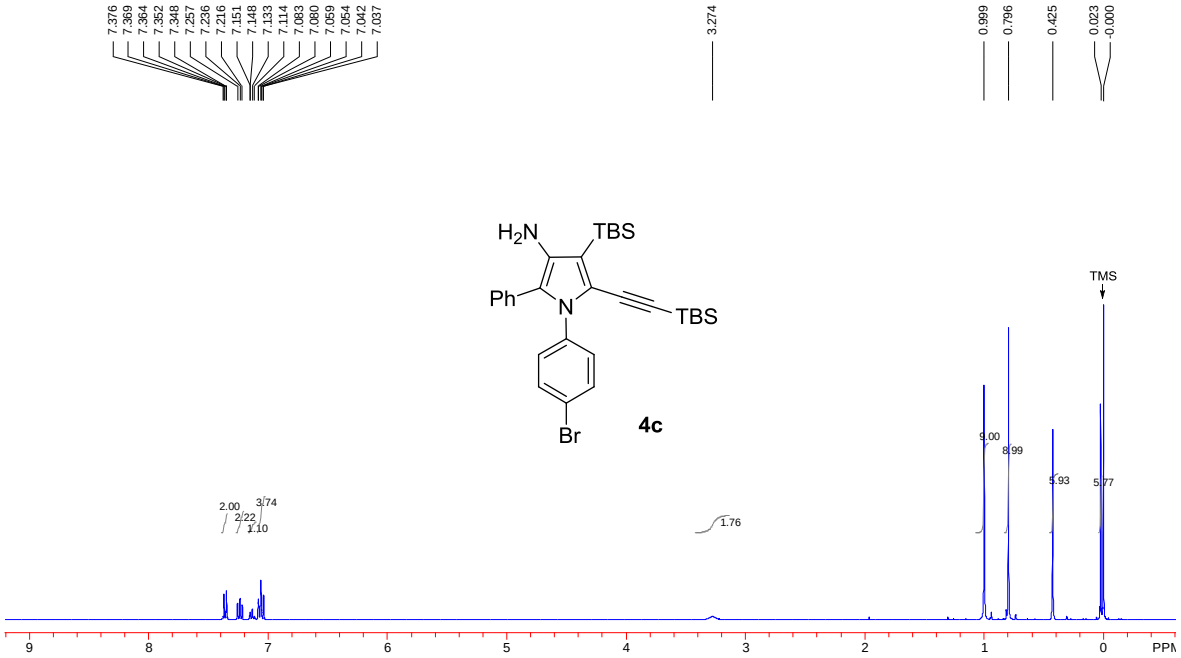
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7.083
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7.054
7.042
7.037
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0.796
0.425
0.023
-0.000
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TBS
Ph
N
TBS
Br
4c
TMS
9.00
8.99
5.93
5.77
2.00
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1.76
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8
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6
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4
3
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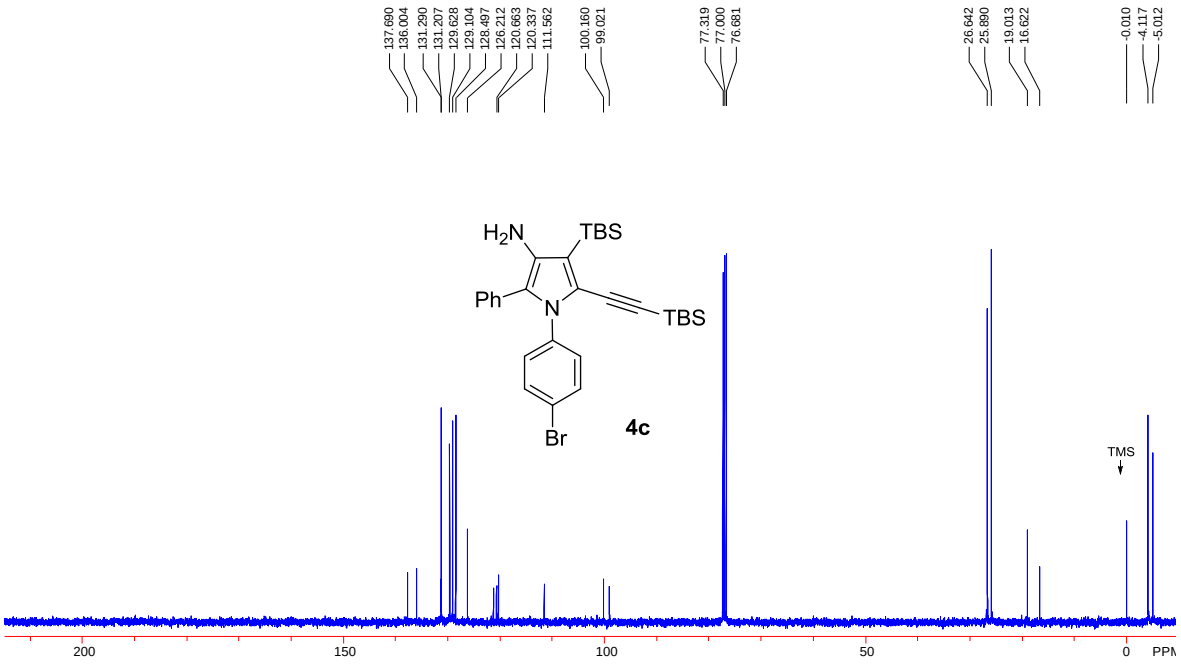
PPM

1% TMS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19.013
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-0.010
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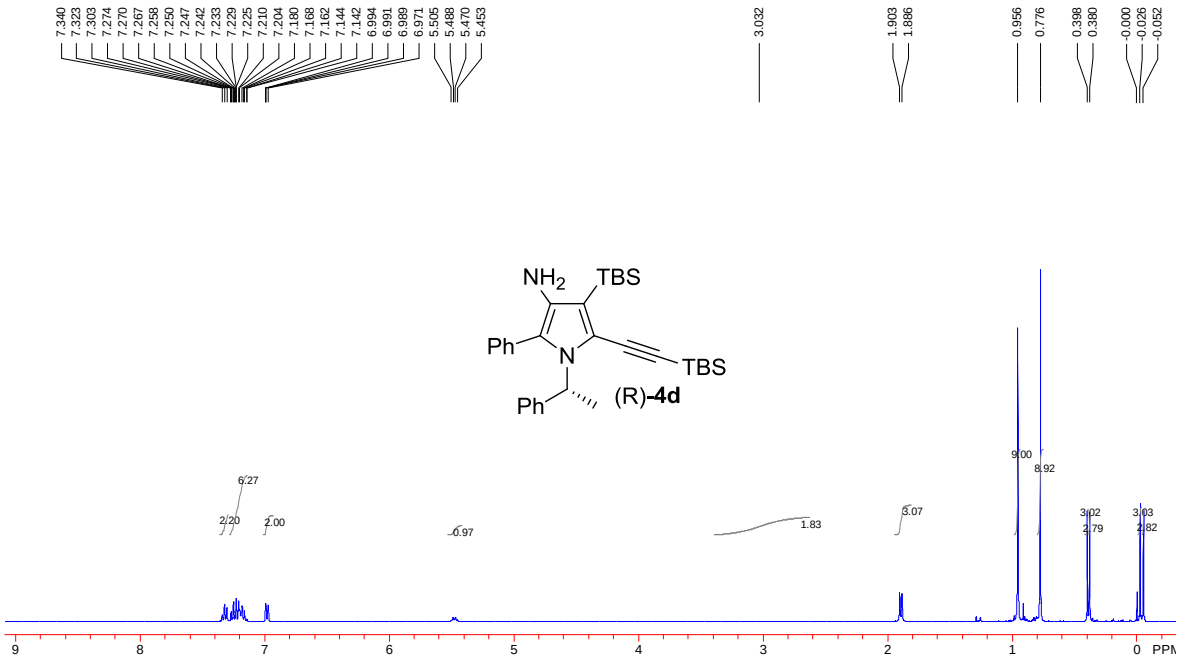
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7.250
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7.233
7.229
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7.210
7.204
7.180
7.168
7.162
7.144
7.142
6.994
6.991
6.989
6.971
5.505
5.488
5.470
5.453
3.032
1.903
1.886
0.956
0.776
0.398
0.380
-0.000
-0.026
-0.052
NH2
TBS
Ph
N
TBS
Ph
(R)-4d
6.27
2.20
2.00
0.97
1.83
3.07
9.00
8.92
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2.82
9
8
7
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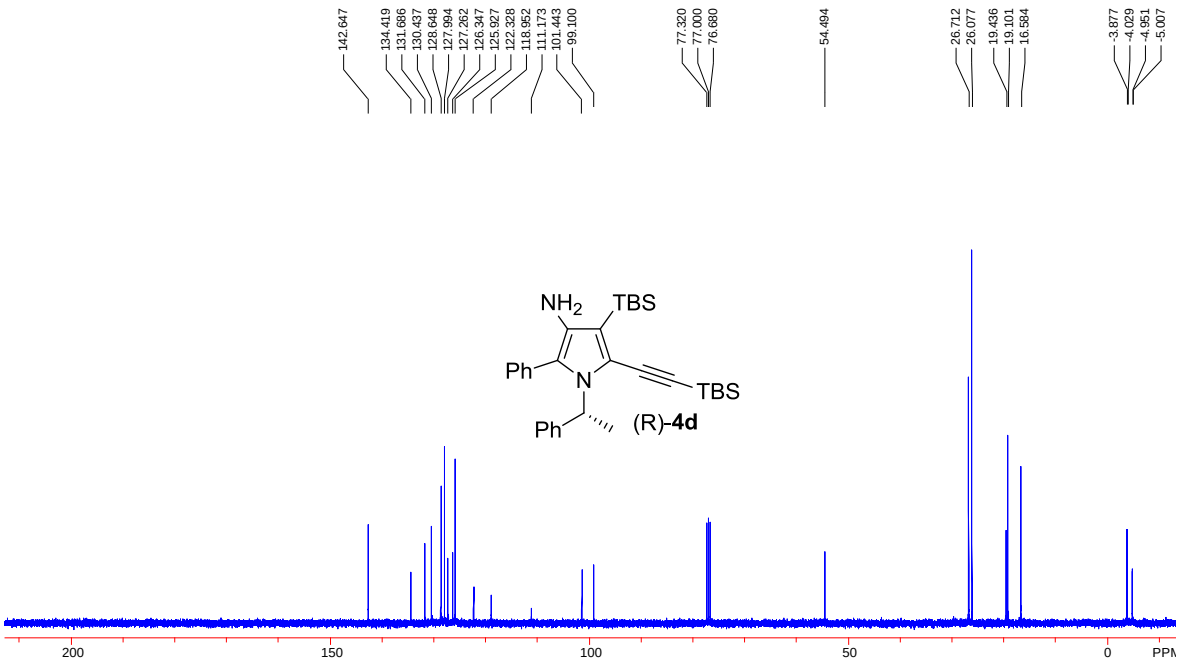
5
4
3
2
1
0
PPM

0.3% TMS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101.443
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77.000
76.680
54.494
26.712
26.077
19.436
19.101
16.584
-3.877
-4.029
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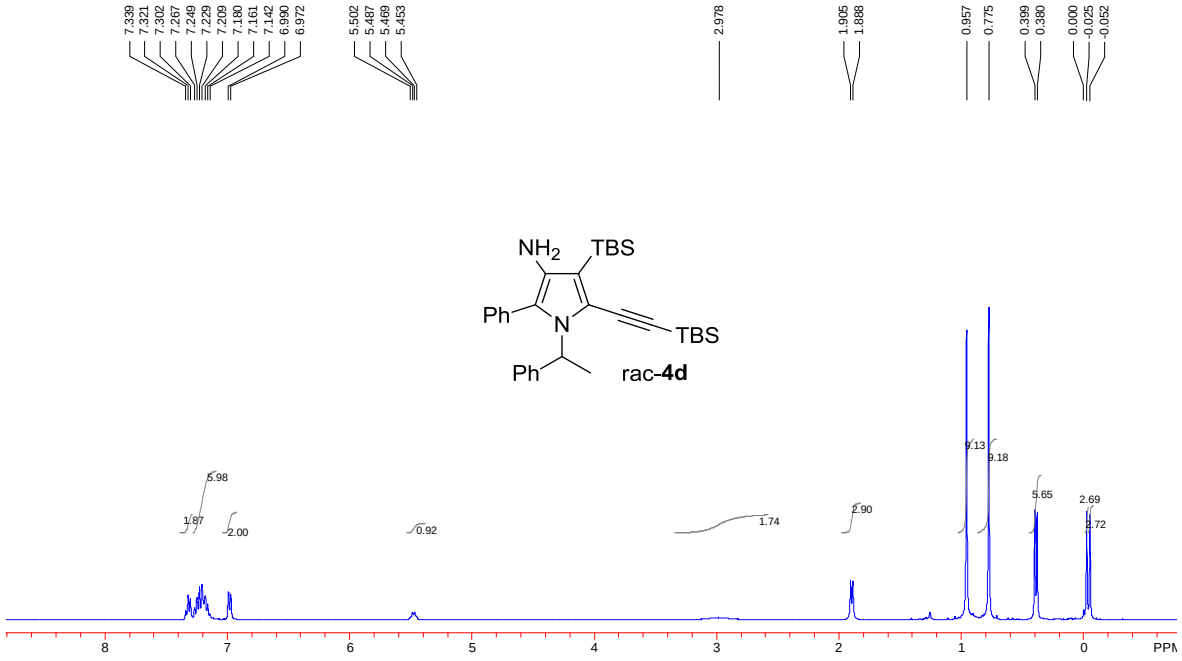
NH2
TBS
Ph
N
TBS
Ph
(R)-4d
200
150
100
50
0
PPM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7.267
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7.229
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7.180
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7.142
6.990
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5.502
5.487
5.469
5.453
2.978
1.905
1.888
0.957
0.775
0.399
0.380
0.000
-0.025
-0.052
NH2
TBS
Ph
N
TBS
Ph
rac-4d
5.98
1.87
2.00
0.92
1.74
2.90
9.13
9.18
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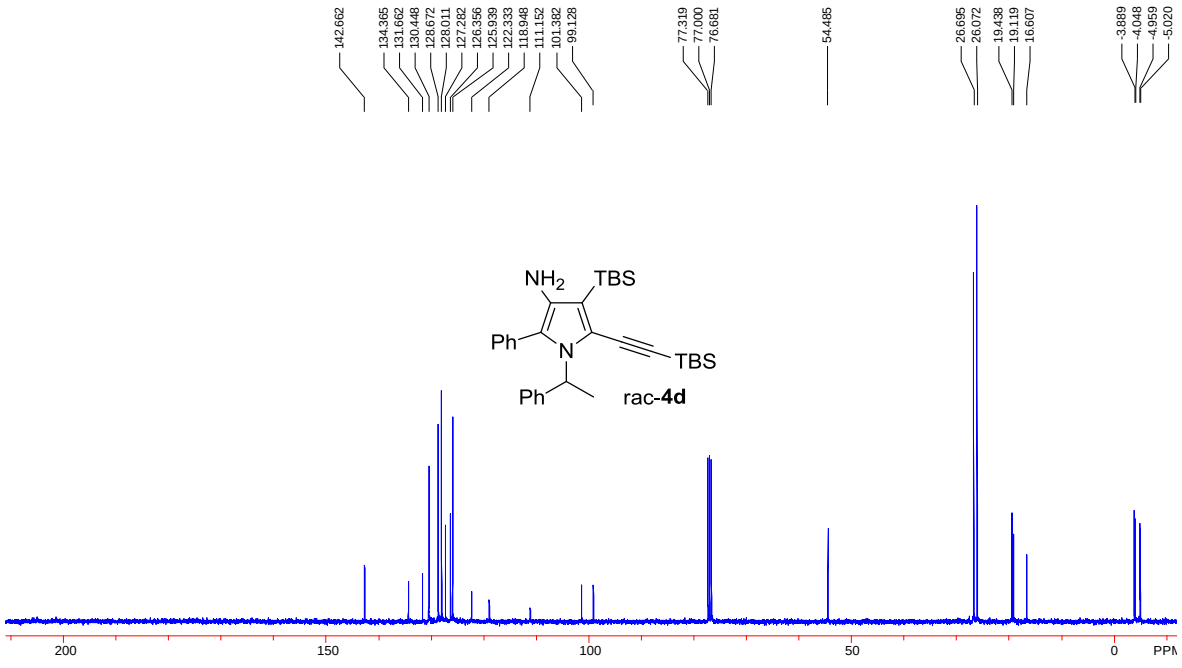
2.69
2.72
8
7
6
5
4
3
2
1
0
PPM

0.1% TMS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126.356
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122.333
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111.152
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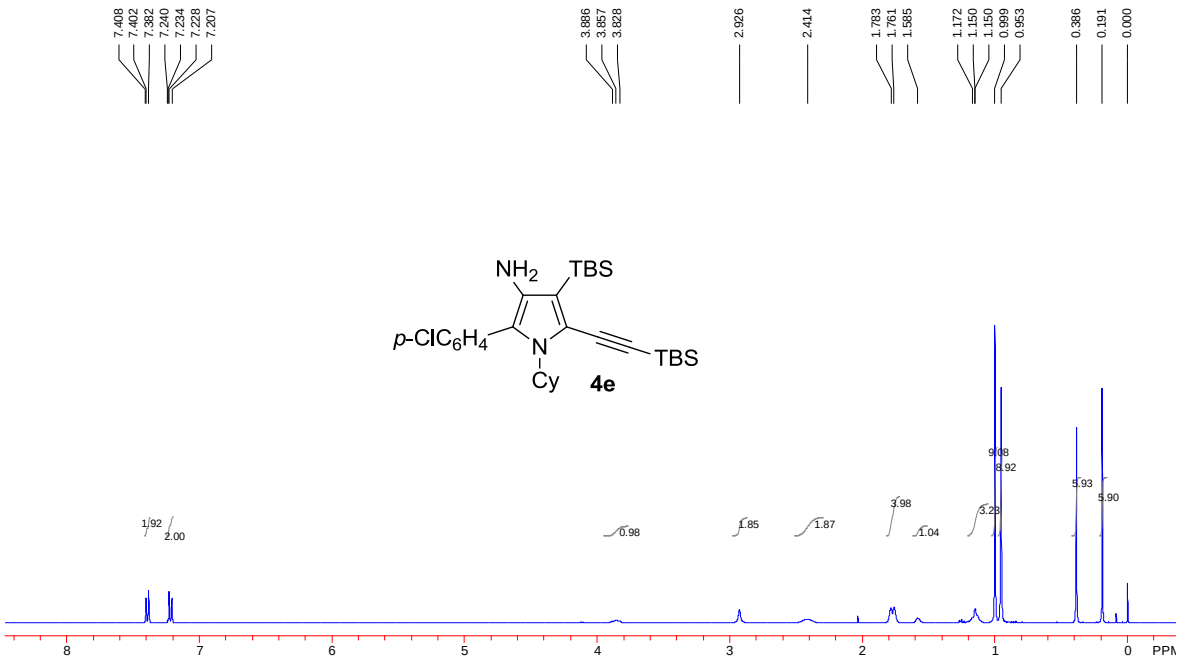
99.128
77.319
77.000
76.681
54.485
26.695
26.072
19.438
19.119
16.607
-3.889
-4.048
-4.959
-5.020
NH2
TBS
Ph
N
TBS
Ph
rac-4d
200
150
100
50
0
PPM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7.228
7.207
3.886
3.857
3.828
2.926
2.414
1.783
1.761
1.585
1.172
1.150
1.150
0.999
0.953
0.386
0.191
0.000
NH2
TBS
p-ClC6H4
N
Cy
TBS
4e
1.92
2.00
0.98
1.85
1.87
3.98
1.04
3.23
9.08
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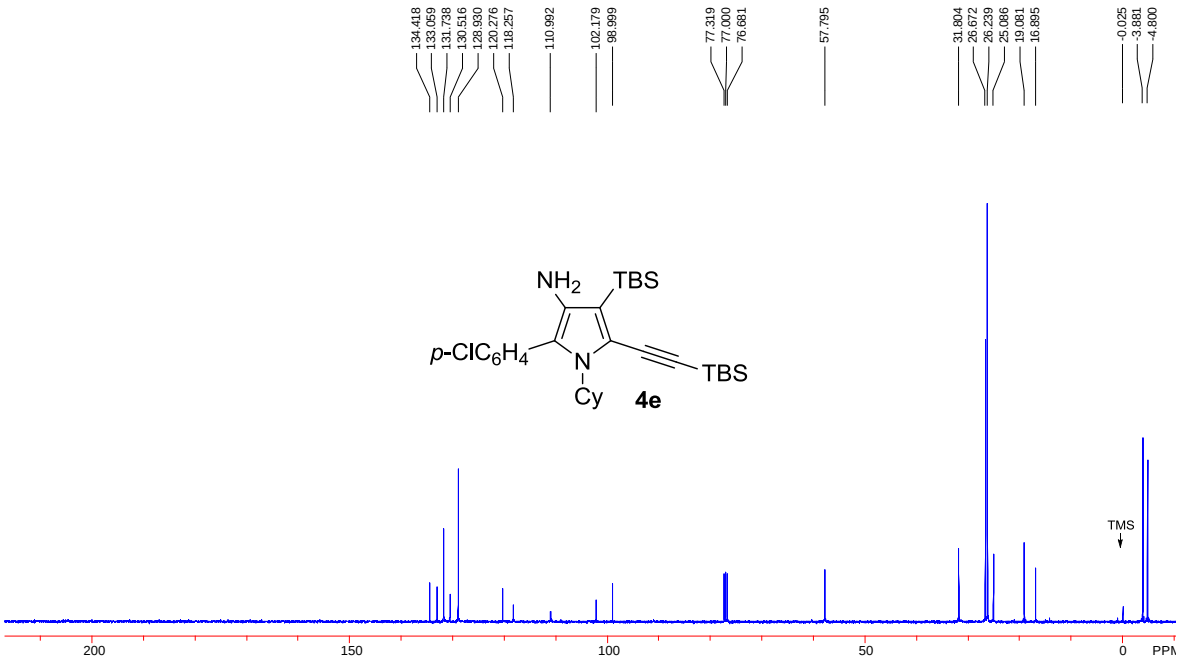
5.93
5.90
8
7
6
5
4
3
2
1
0
PPM

1% TMS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118.257
110.992
102.179
98.999
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77.000
76.681
57.795
31.804
26.672
26.239
25.086
19.081
16.895
-0.025
-3.881
-4.800
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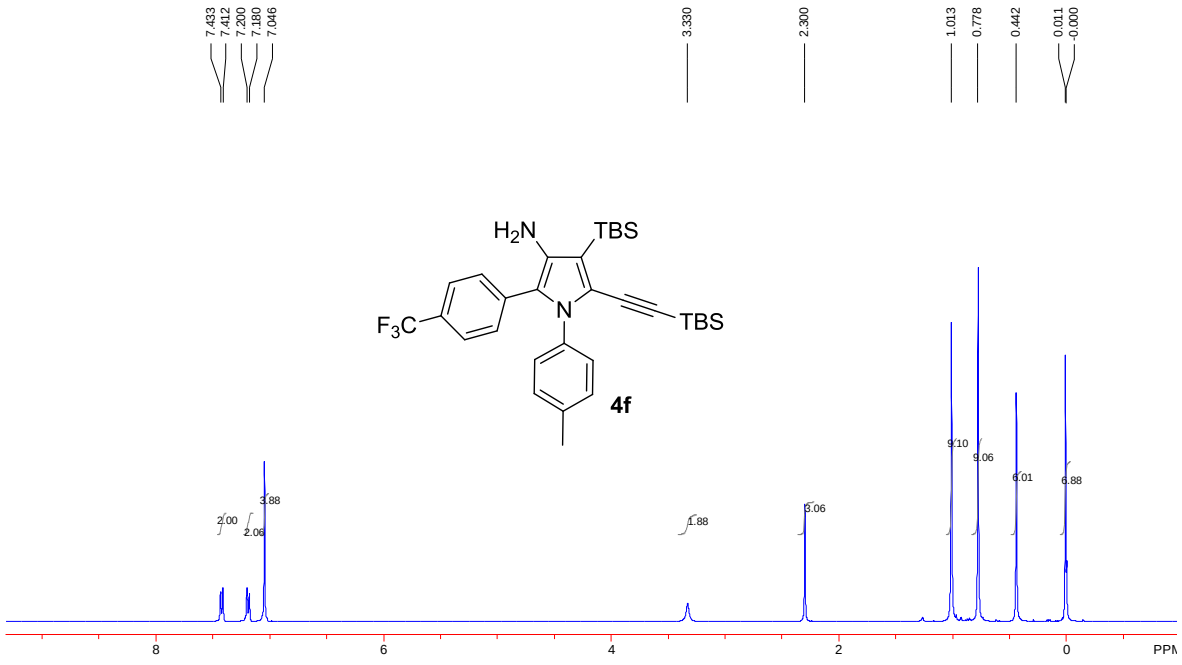
TBS
p-ClC6H4
N
Cy
TBS
4e
TMS
200
150
100
50
0
PPM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7.180
7.046
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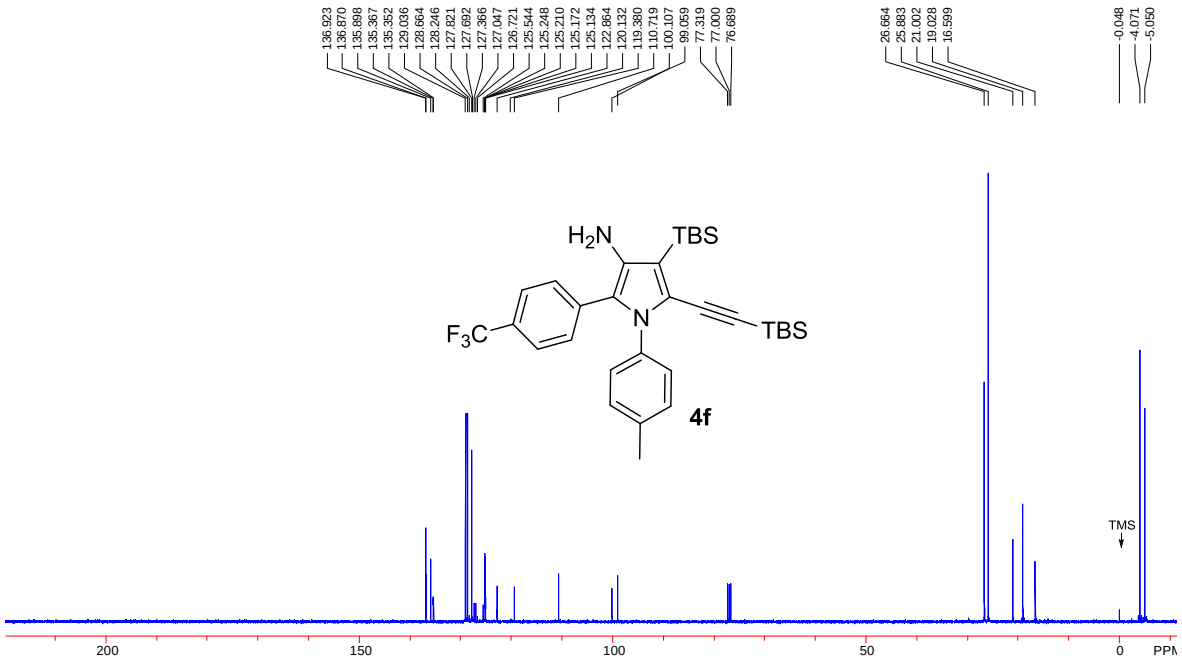
2.300
1.013
0.778
0.442
0.011
-0.000
H2N
TBS
F3C
N
TBS
4f
2.00
2.06
3.88
1.88
3.06
9.10
9.06
6.01
6.88
8
6
4
2
0
PPM

1% TMS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127.047
126.721
125.544
125.248
125.210
125.172
125.134
122.864
120.132
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110.719
100.107
99.059
77.319
77.000
76.689
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25.883
21.002
19.028
16.599
-0.048
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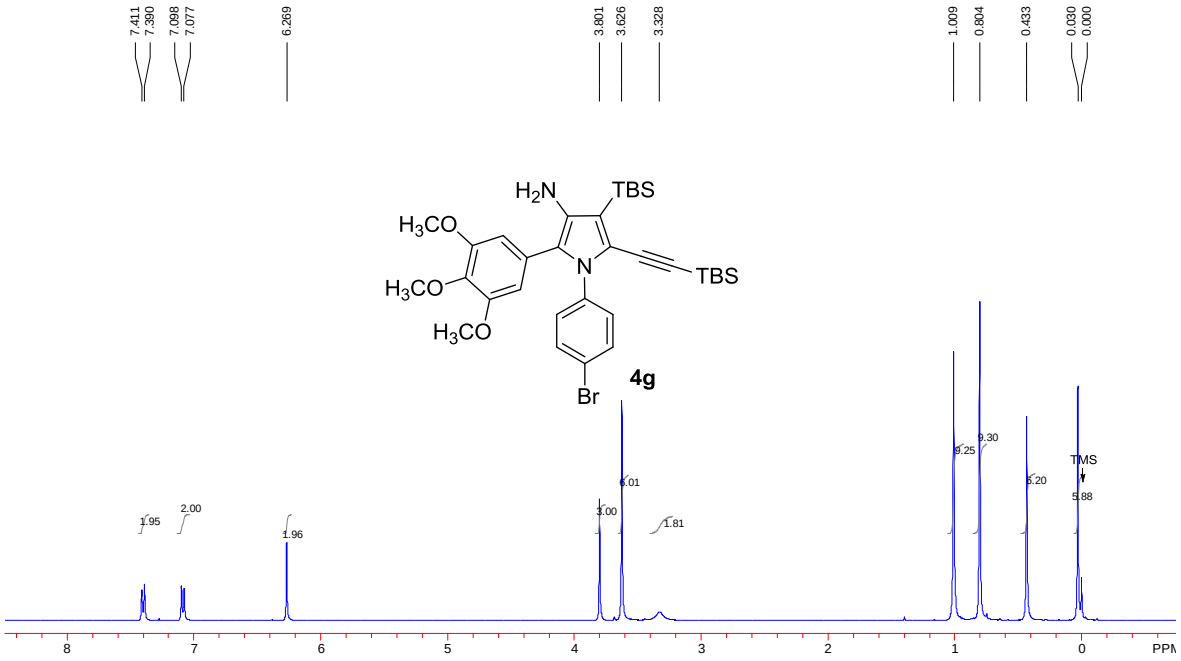
TBS
F3C
N
TBS
4f
TMS
200
150
100
50
0
PPM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0.000
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TBS
H3CO
H3CO
H3CO
N
TBS
Br
4g
1.95
2.00
1.96
3.00
6.01
1.81
9.25
9.30
6.20
TMS
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8
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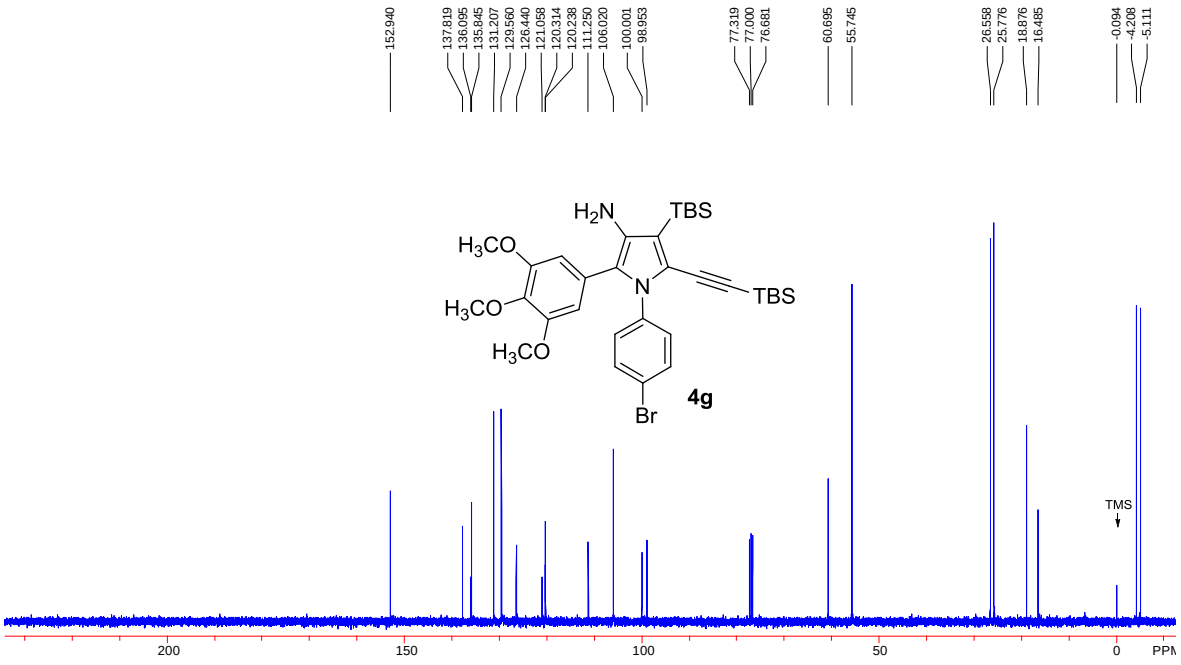
6
5
4
3
2
1
0
PPM

1% TMS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120.238
111.250
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100.001
98.953
77.319
77.000
76.681
60.695
55.745
26.558
25.776
18.876
16.485
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-4.208
-5.111
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H3CO
H3CO
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Br
4g
TMS
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100
50
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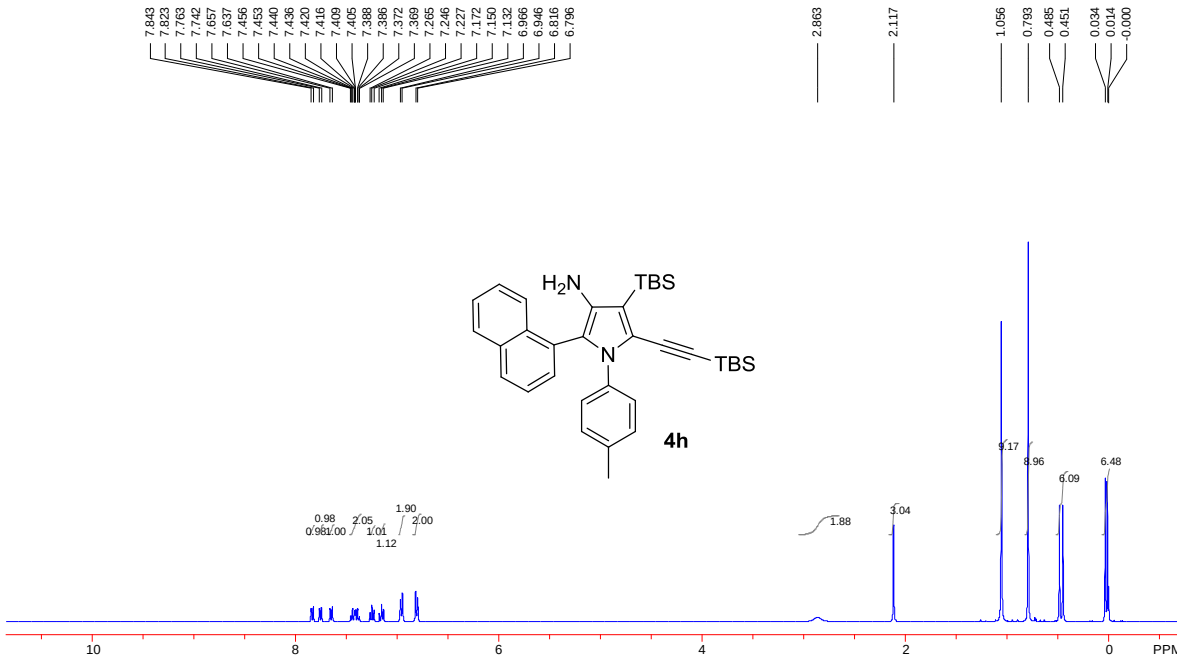
PPM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7.246
7.227
7.172
7.150
7.132
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6.946
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6.796
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2.117
1.056
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0.034
0.014
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TBS
N
TBS
4h
0.98
0.98
2.05
1.01
1.90
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3.04
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10
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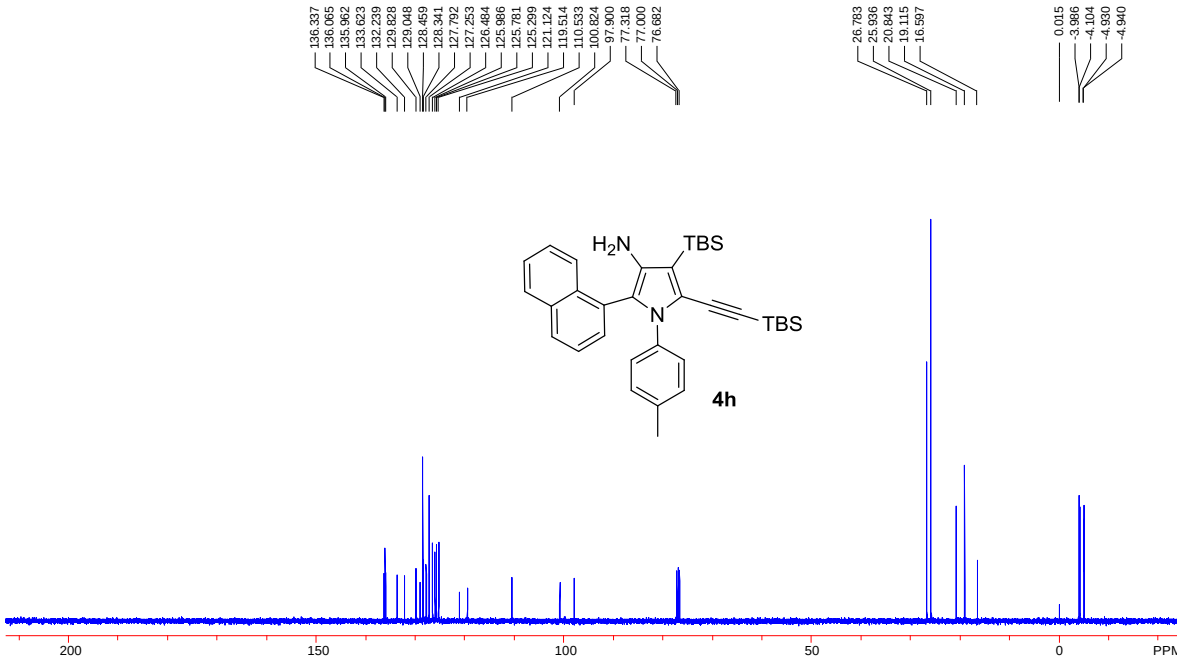
PPM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125.299
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110.533
100.824
97.900
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77.000
76.682
26.783
25.936
20.843
19.115
16.597
0.015
-3.986
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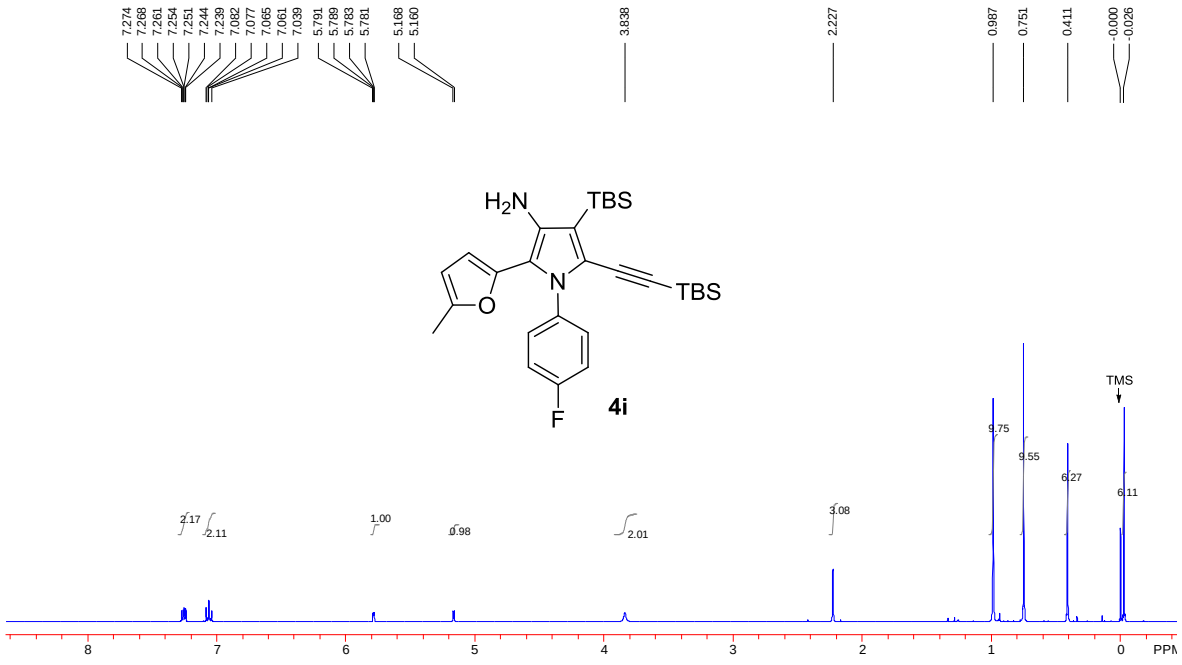
N
TBS
4h
200
150
100
50
0
PPM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7.039
5.791
5.789
5.783
5.781
5.168
5.160
3.838
2.227
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0.751
0.411
-0.000
-0.026
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TBS
TBS
N
O
F
4i
TMS
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6.27
6.11
2.17
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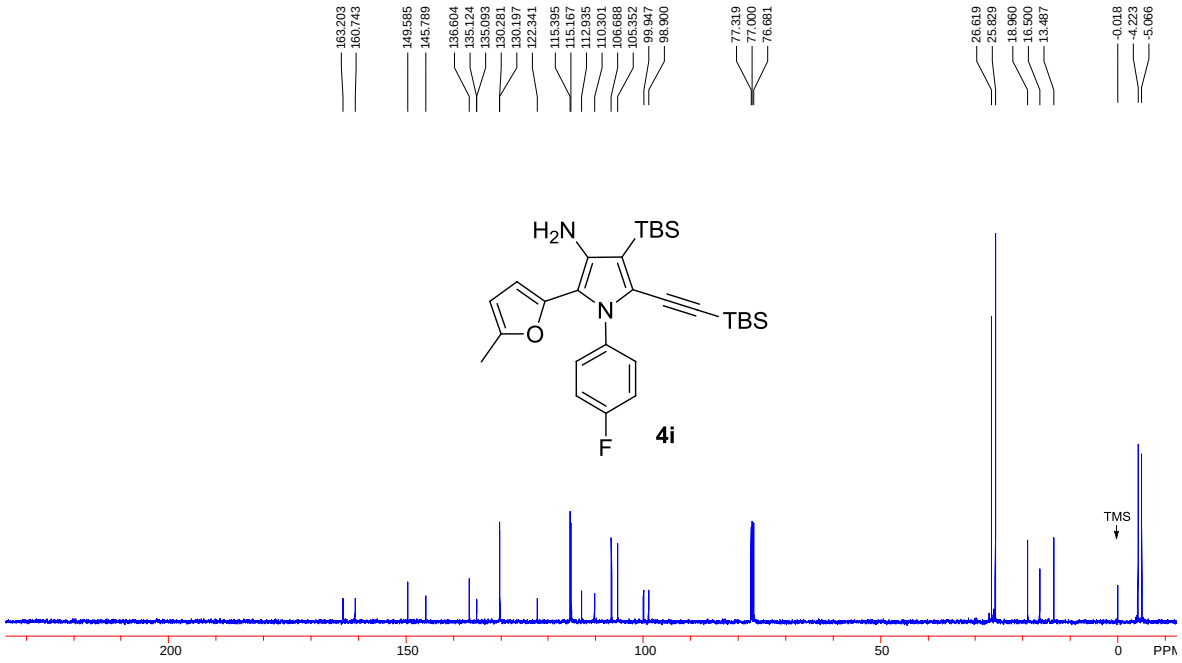
0
PPM

1% TMS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TMS
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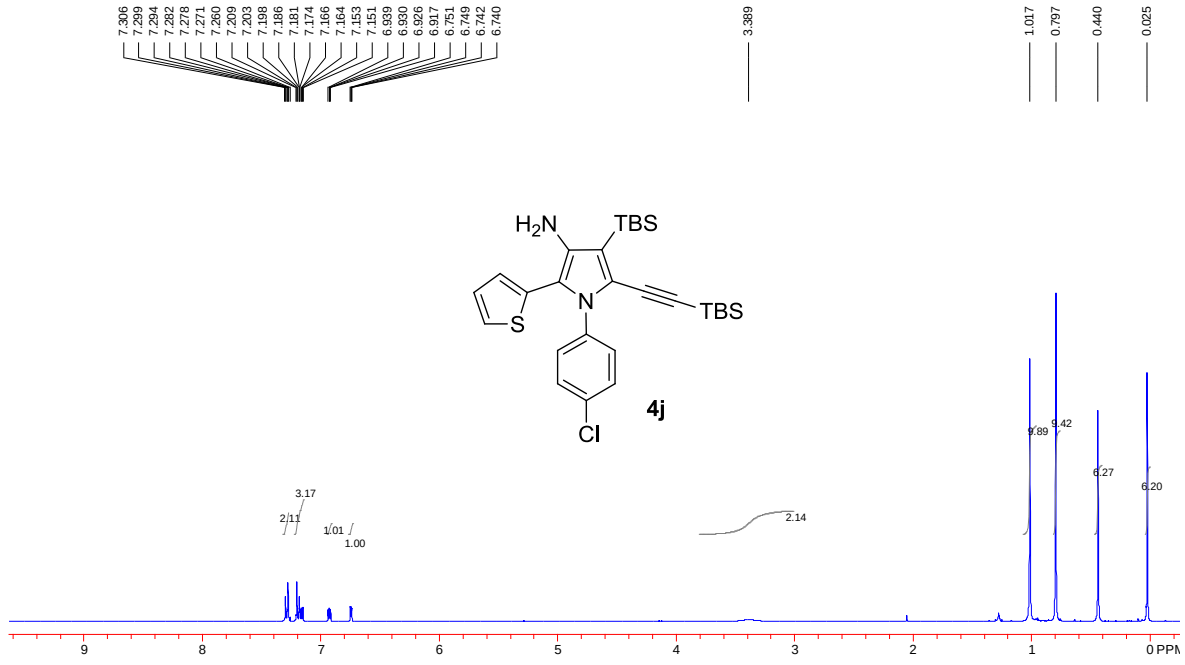
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7.164
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0.797
0.440
0.025
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TBS
TBS
N
S
Cl
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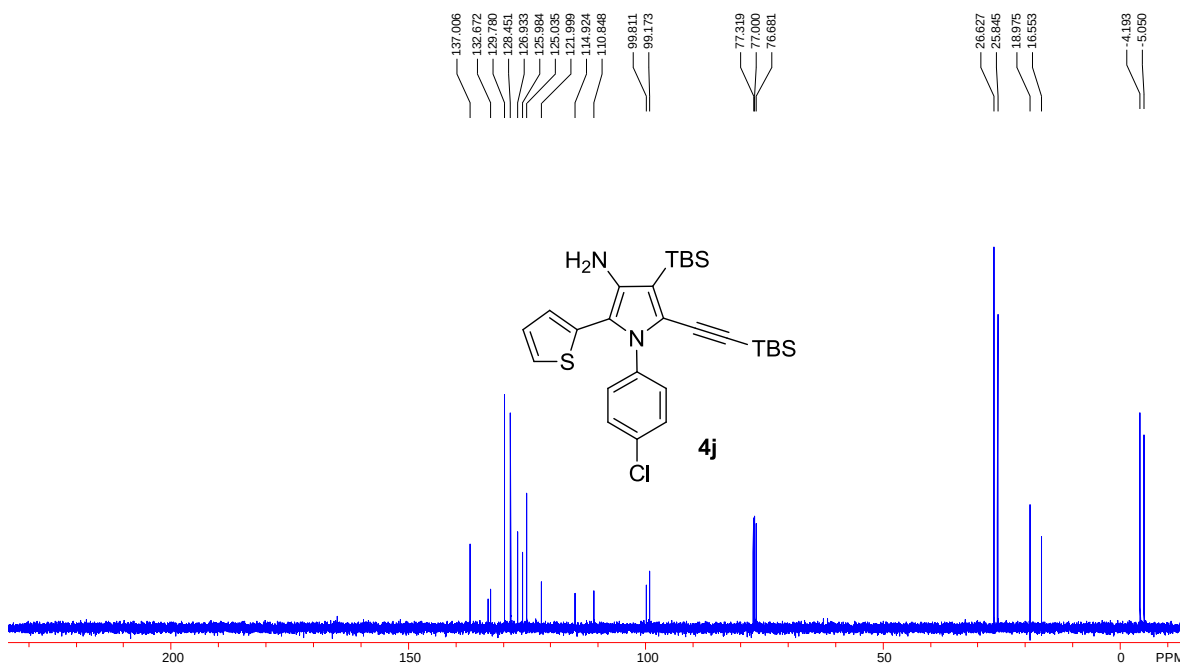
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77.000
76.681
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TBS
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4j
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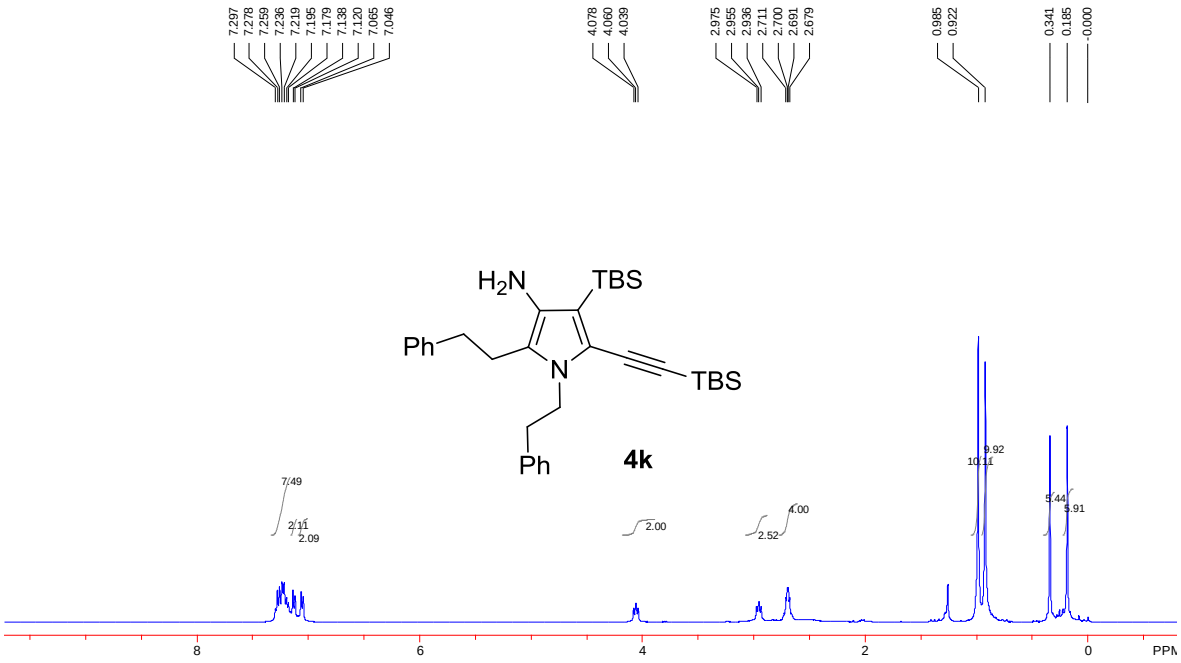
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0.185
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TBS
Ph
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TBS
Ph
4k
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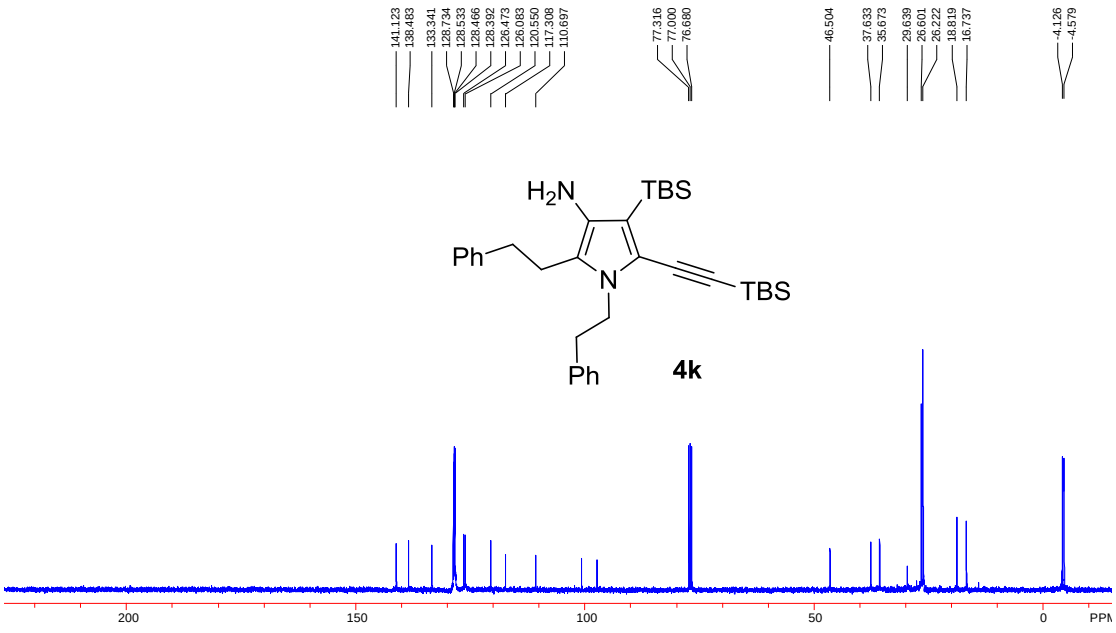
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77.000
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35.673
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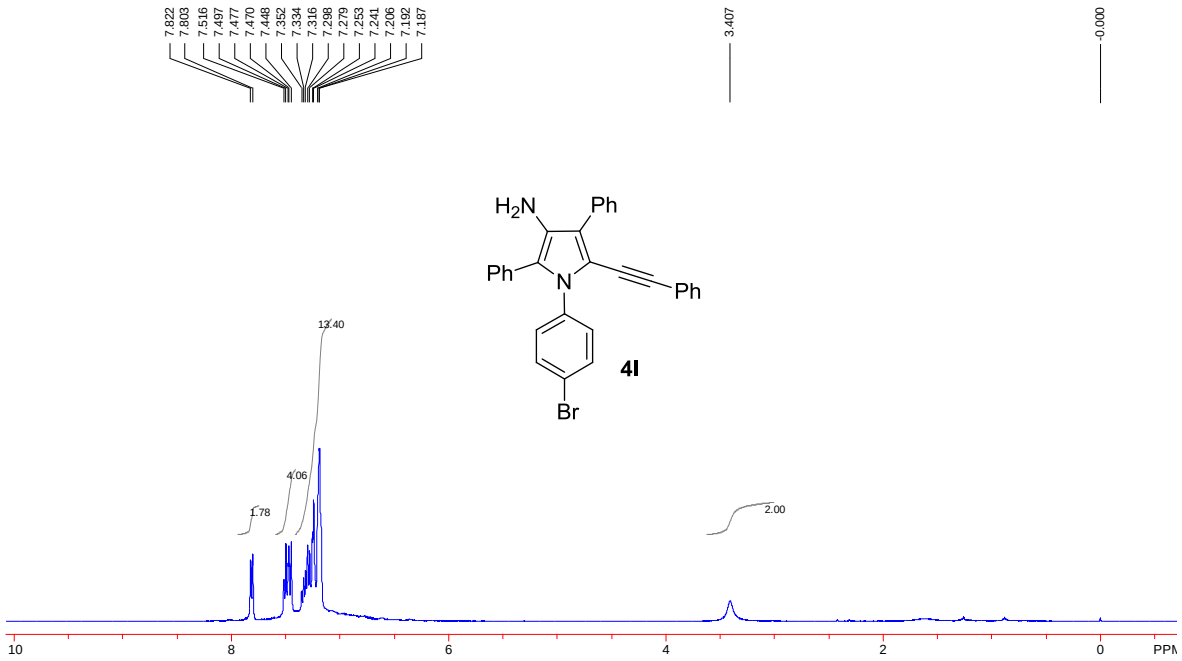
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7.298
7.279
7.253
7.241
7.206
7.192
7.187
3.407
0.000
H2N
Ph
Ph
N
Ph
Br
4l
13.40
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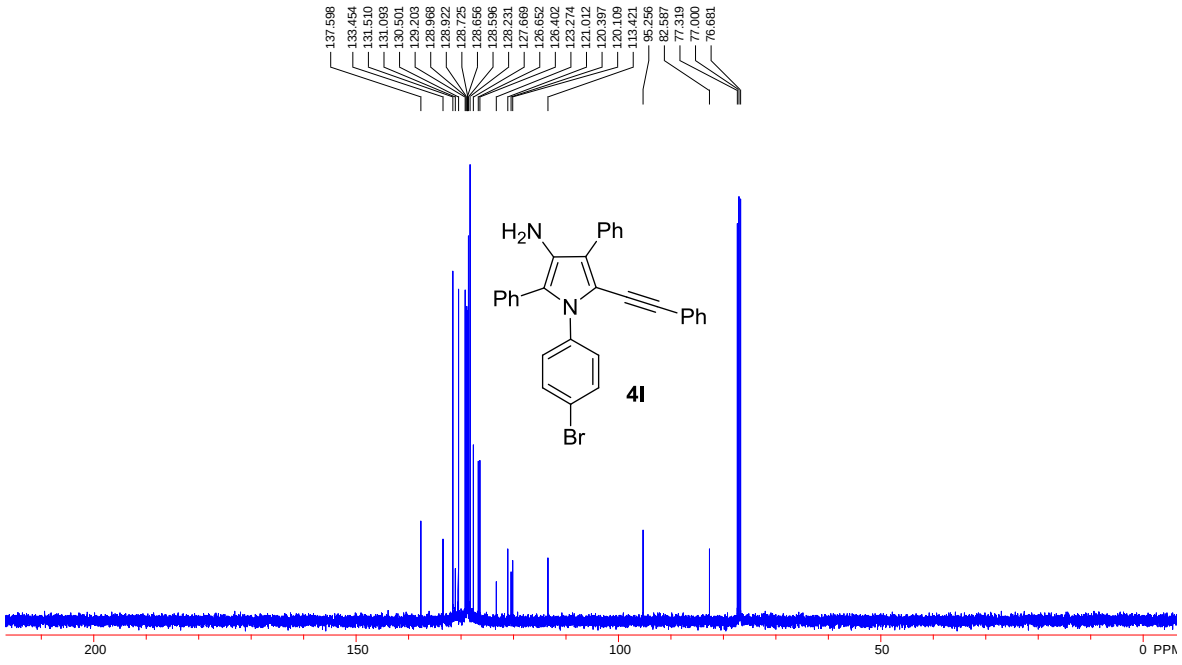
2.00
10
8
6
4
2
0
PPM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128.922
128.725
128.656
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127.669
126.652
126.402
123.274
121.012
120.397
120.109
113.421
95.256
82.587
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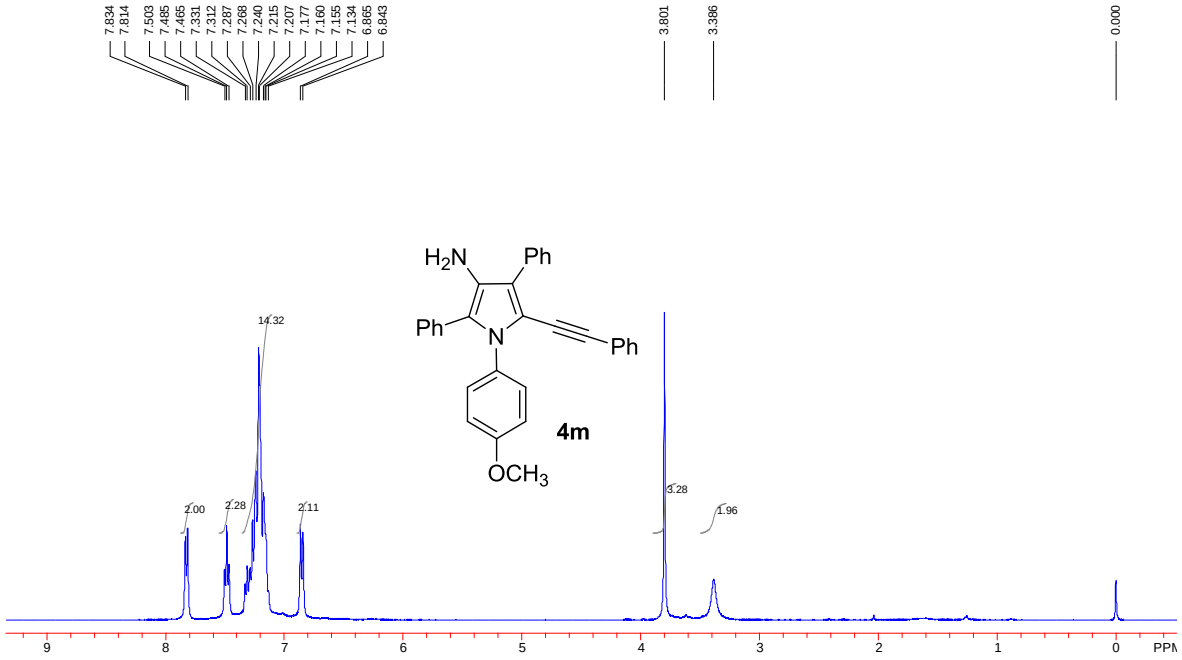
77.000
76.681
H2N
Ph
Ph
N
Ph
Br
4l
200
150
100
50
0 PPM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7.287
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7.240
7.215
7.207
7.177
7.160
7.155
7.134
6.865
6.843
3.801
3.386
0.000
H2N
Ph
Ph
N
Ph
4m
OCH3
14.32
2.00
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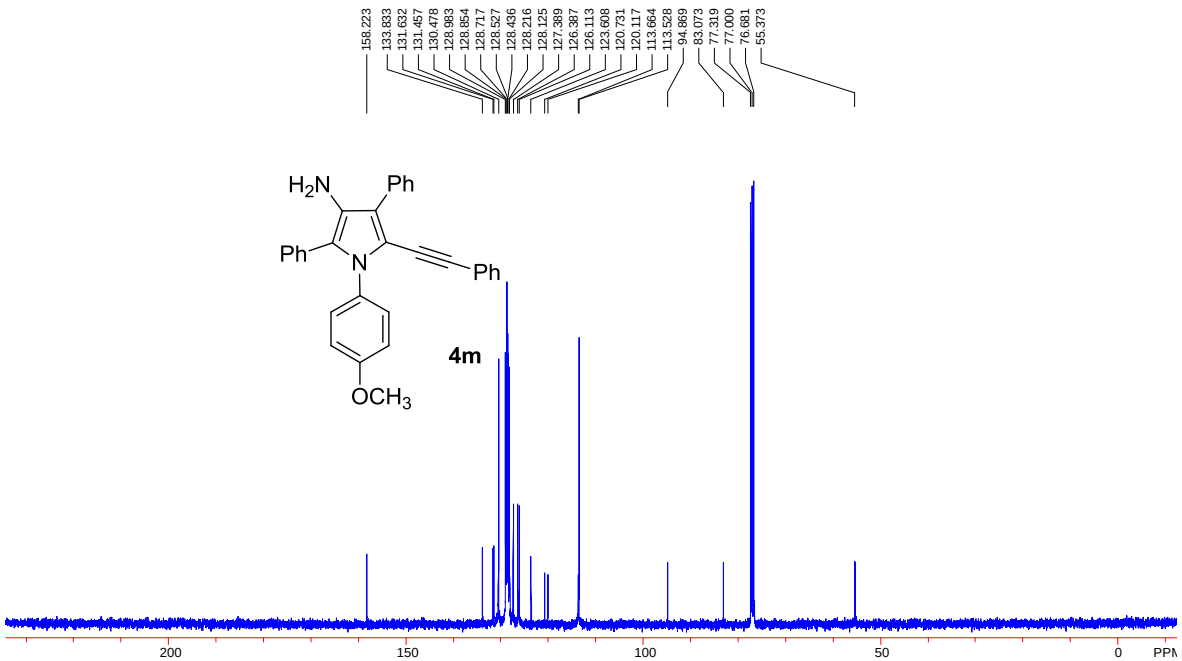
2.11
3.28
1.96
9
8
7
6
5
4
3
2
1
0
PPM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128.717
128.527
128.436
128.216
128.125
127.389
126.387
126.113
123.608
120.731
120.117
113.664
113.528
94.869
83.073
77.319
77.000
76.681
55.373
H2N
Ph
Ph
N
Ph
4m
OCH3
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100
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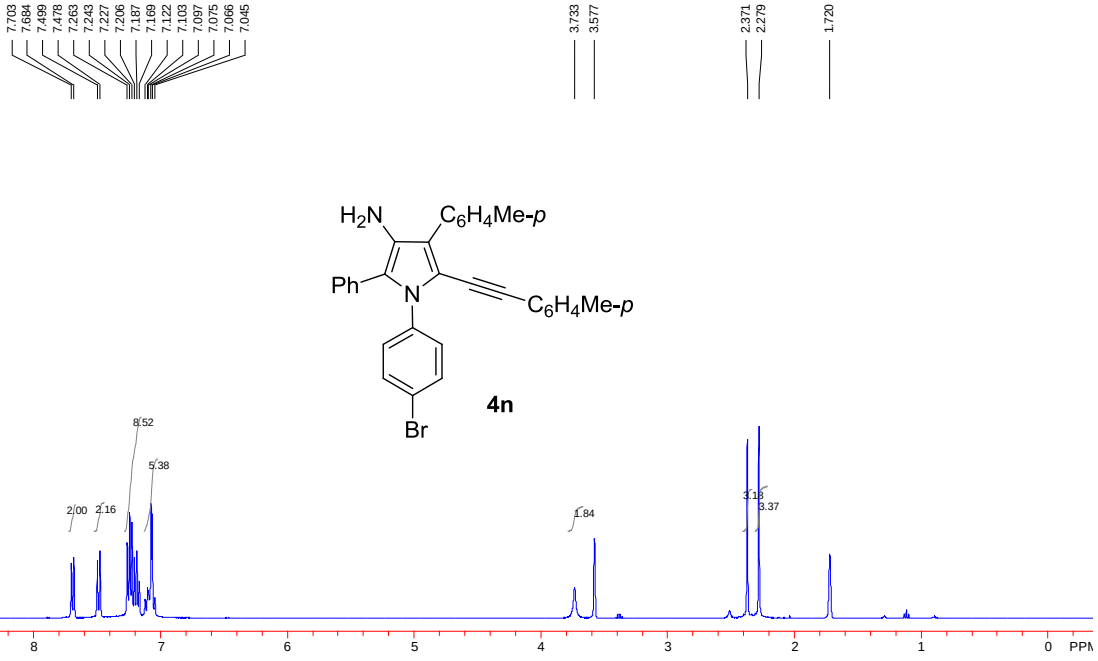
PPM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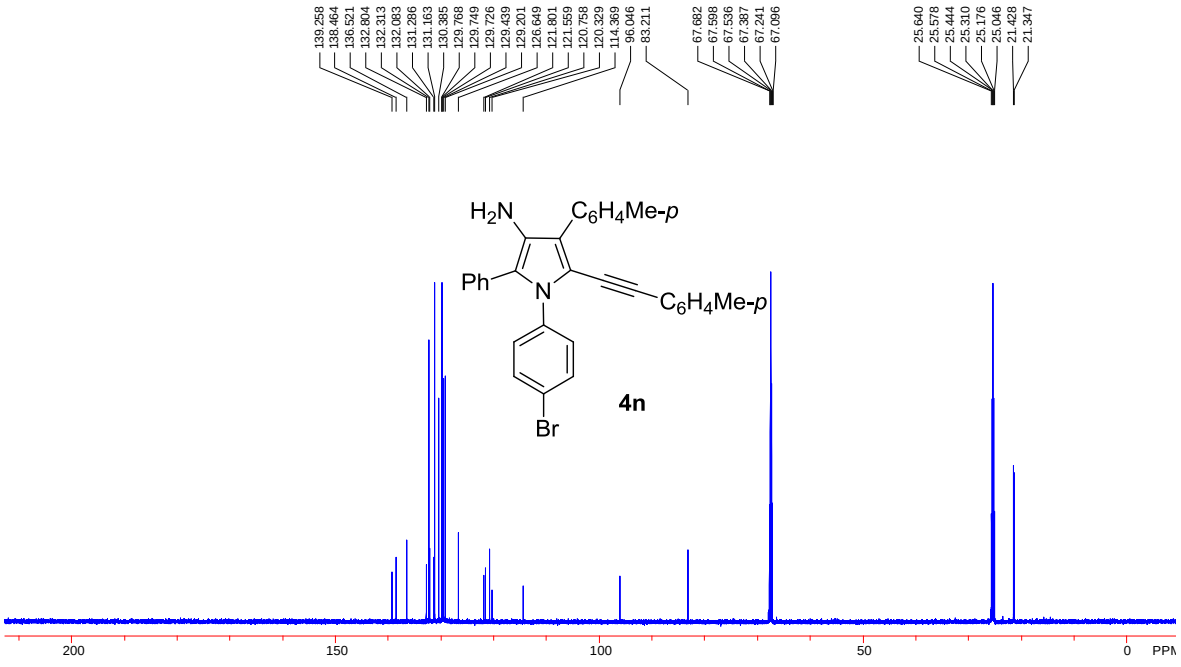
7.478
7.263
7.243
7.227
7.206
7.187
7.169
7.122
7.103
7.097
7.075
7.066
7.045
3.733
3.577
2.371
2.279
1.720
H2N
C6H4Me-p
Ph
N
C6H4Me-p
Br
4n
8.52
5.38
2.00
2.16
1.84
3.18
3.37
8
7
6
5
4
3
2
1
0
PPM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136.521
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131.163
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129.768
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129.439
129.201
126.649
121.801
121.559
120.758
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96.046
83.211
67.682
67.598
67.536
67.387
67.241
67.096
25.640
25.578
25.444
25.310
25.176
25.046
21.428
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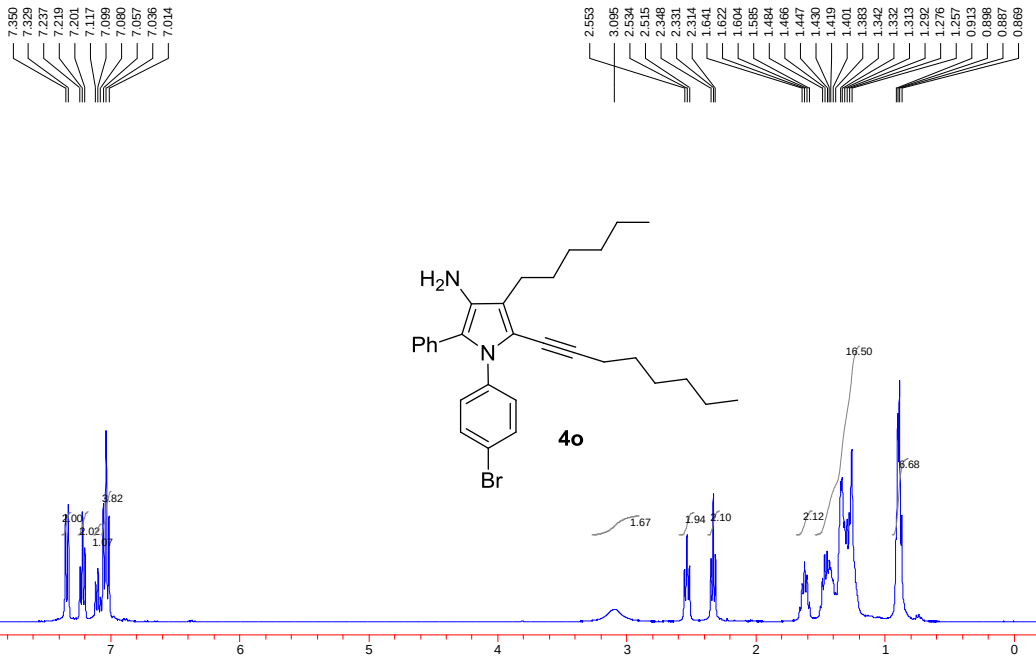
C6H4Me-p
Ph
N
C6H4Me-p
Br
4n
200
150
100
50
0
PPM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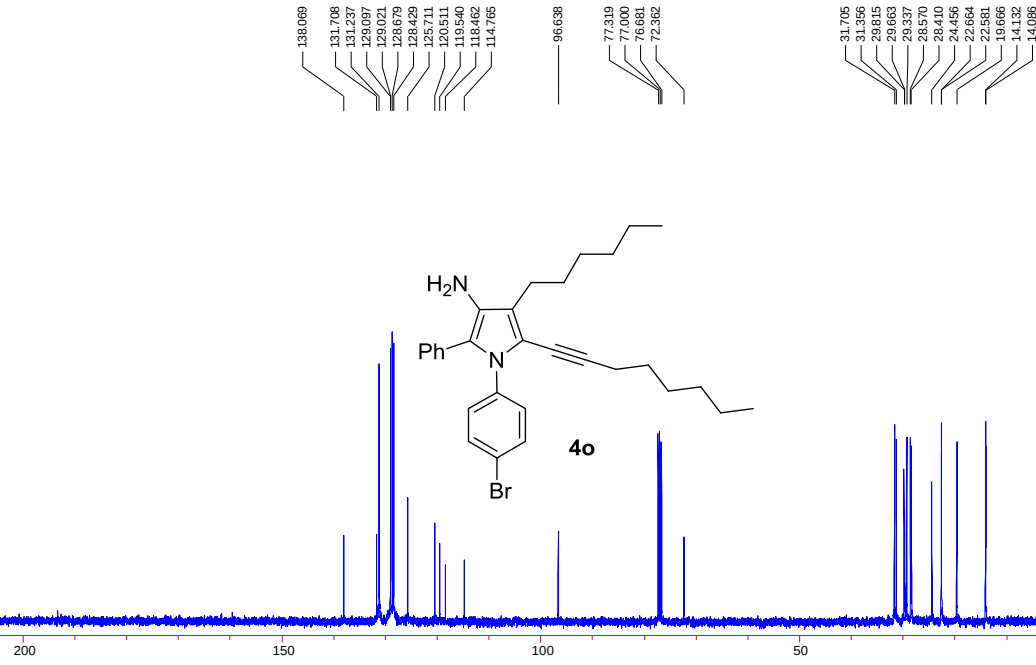
7.329
7.237
7.219
7.201
7.117
7.099
7.080
7.057
7.036
7.014
2.553
3.095
2.534
2.515
2.348
2.331
2.314
1.641
1.622
1.604
1.585
1.484
1.466
1.447
1.430
1.419
1.401
1.383
1.342
1.332
1.313
1.292
1.276
1.257
0.913
0.898
0.887
0.869
H2N
Ph
N
Br
4o
16.50
6.68
3.82
2.00
2.02
1.07
1.67
1.94
2.10
2.12
8
7
6
5
4
3
2
1
0
PPM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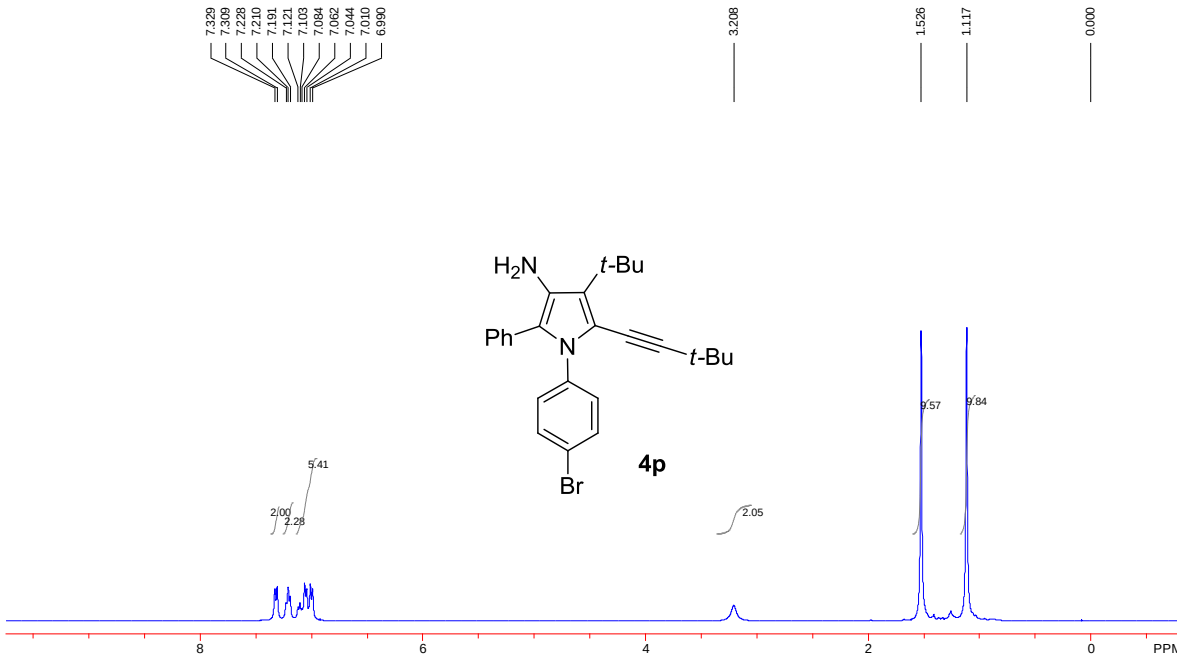
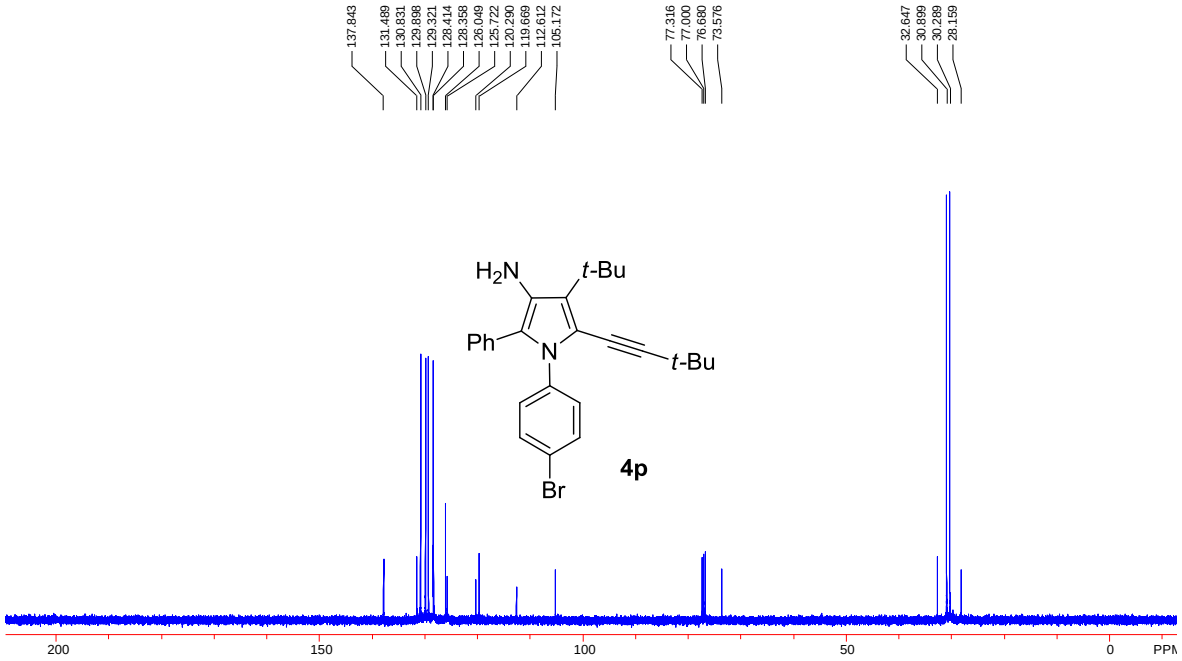
131.237
129.097
129.021
128.679
128.429
125.711
120.511
119.540
118.462
114.765
96.638
77.319
77.000
76.681
72.362
31.705
31.356
29.815
29.663
29.337
28.570
28.410
24.456
22.664
22.581
19.666
14.132
14.086
H2N
Ph
N
Br
4o
200
150
100
50
0
PPM


7.329
7.309
7.228
7.210
7.191
7.121
7.103
7.084
7.062
7.044
7.010
6.990
3.208
1.526
1.117
0.000
H_2N
t-Bu
Ph
N
t-Bu
Br
4p
5.41
2.09
2.28
2.05
9.57
9.84
8
6
4
2
0
PPM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129.898
129.321
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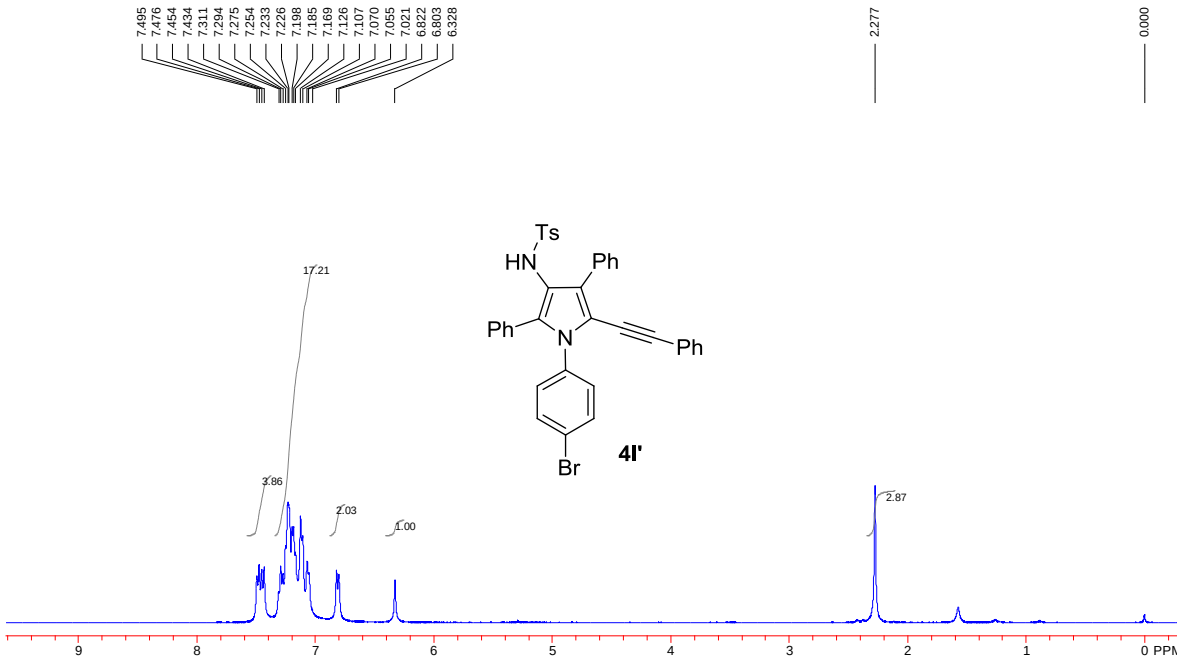
128.358
126.049
125.722
120.290
119.669
112.612
105.172
77.316
77.000
76.680
73.576
32.647
30.899
30.289
28.159
H_2N
t-Bu
Ph
N
t-Bu
Br
4p
200
150
100
50
0
PPM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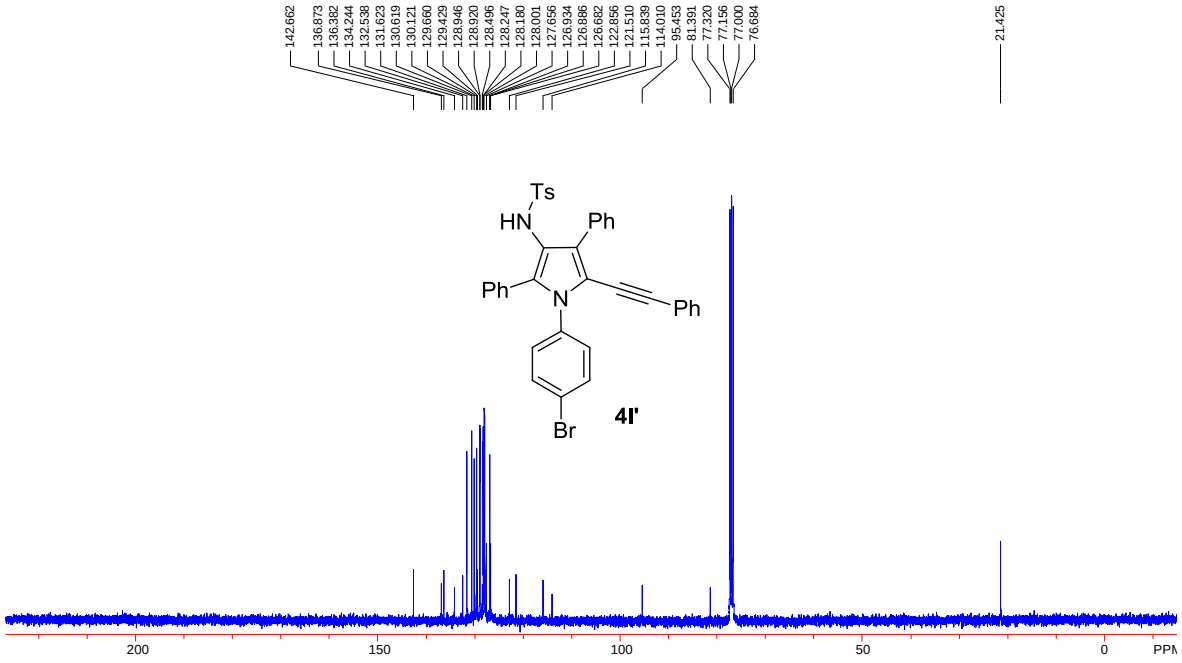
7.454
7.434
7.311
7.294
7.275
7.254
7.233
7.226
7.198
7.185
7.169
7.126
7.107
7.070
7.055
7.021
6.822
6.803
6.328
2.277
0.000
Ts
HN
Ph
Ph
N
Ph
Br
4l'
17.21
3.86
2.03
1.00
2.87
9
8
7
6
5
4
3
2
1
0 PPM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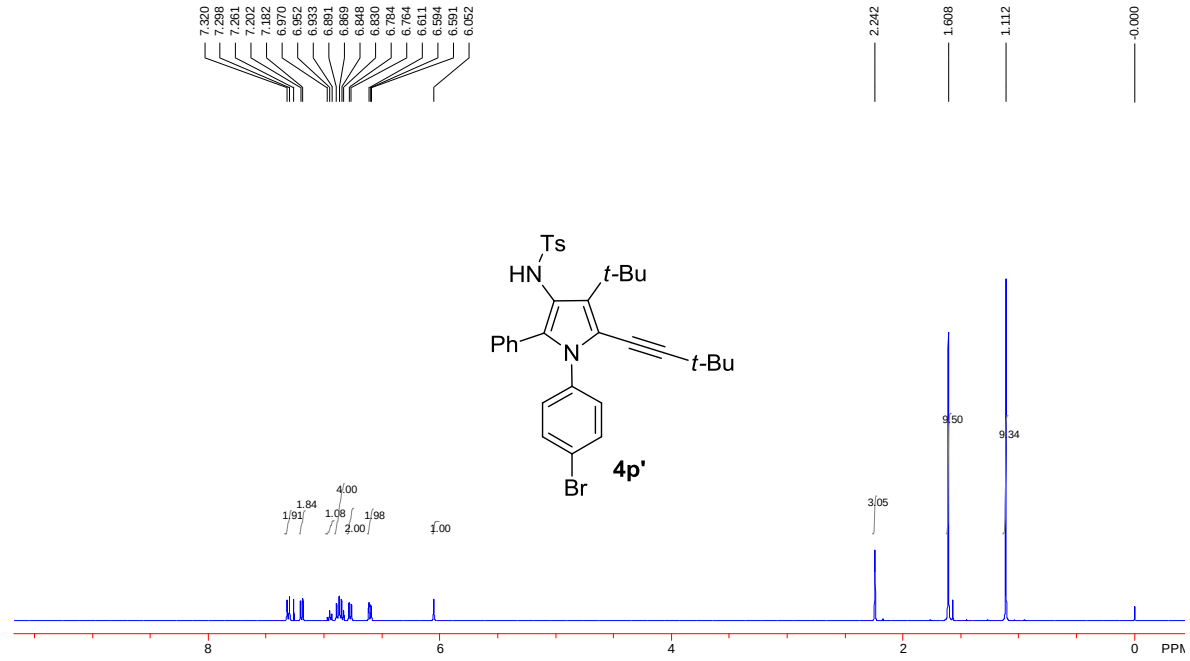
136.382
134.244
132.538
131.623
130.619
130.121
129.660
129.429
128.946
128.920
128.496
128.247
128.180
128.001
127.656
126.934
126.886
126.682
122.856
121.510
115.839
114.010
95.453
81.391
77.320
77.156
77.000
76.684
21.425
Ts
HN
Ph
Ph
N
Ph
Br
4l'
200
150
100
50
0
PPM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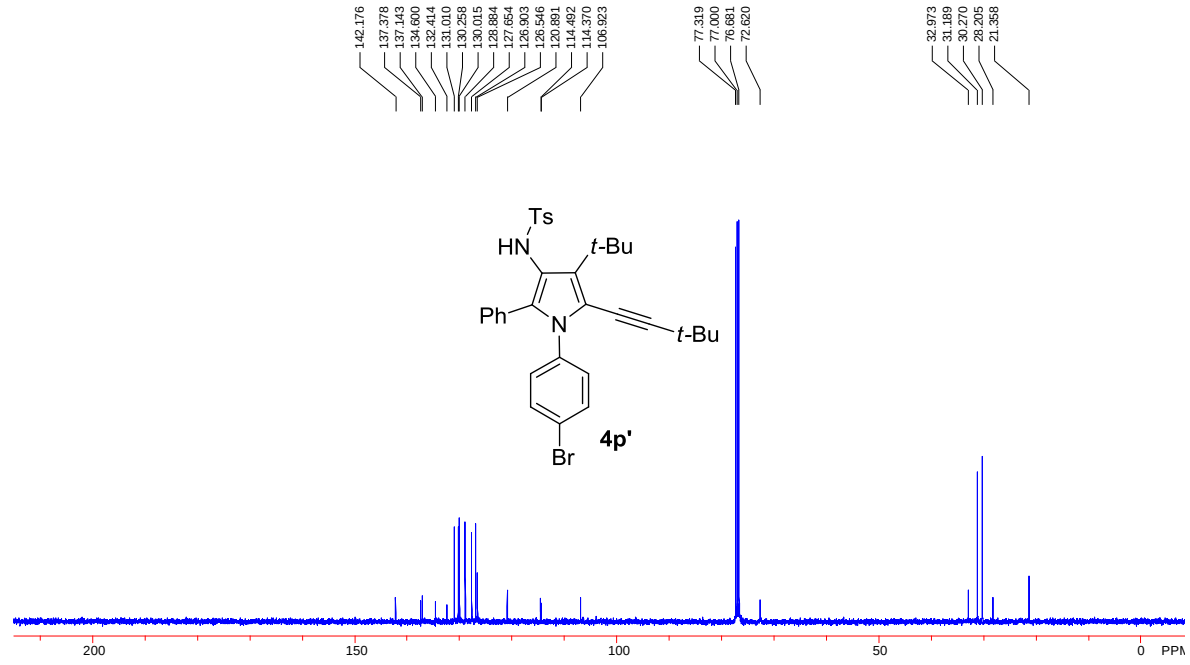
6.952
6.933
6.891
6.869
6.848
6.830
6.784
6.764
6.611
6.594
6.591
6.052
2.242
1.608
1.112
-0.000
Ts
HN
t-Bu
Ph
N
t-Bu
Br
4p'
4.00
1.84
1.91
1.08
2.00
1.98
1.00
3.05
9.50
9.34
8
6
4
2
0
PPM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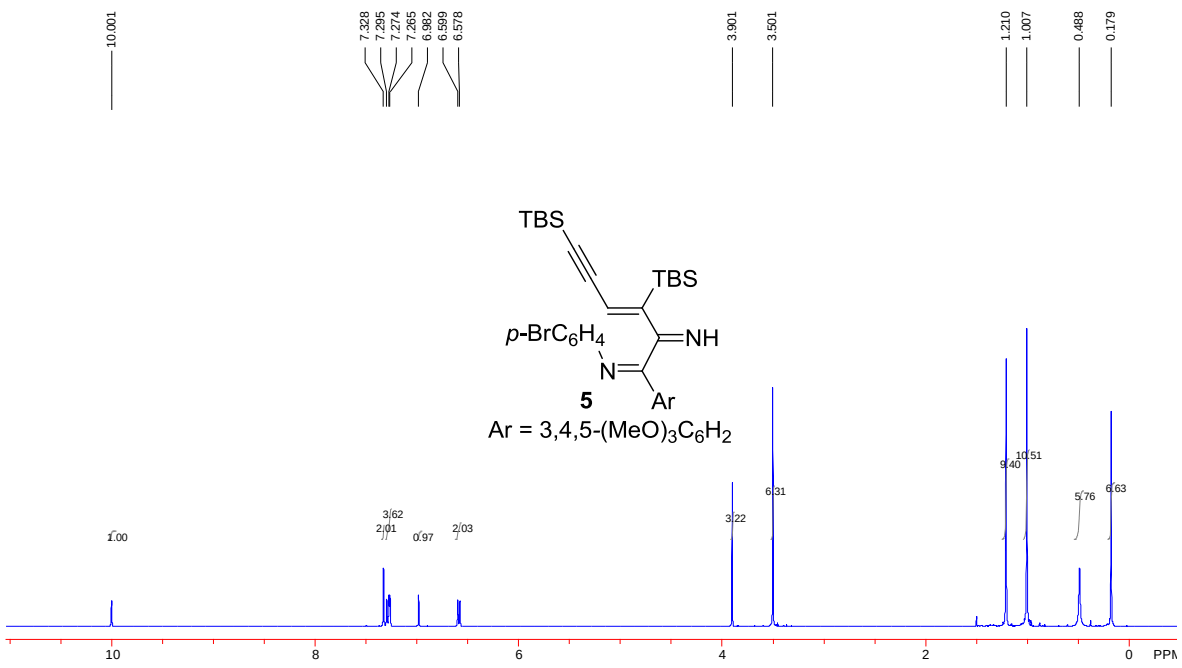
137.143
134.600
132.414
131.010
130.258
130.015
128.884
127.654
126.903
126.546
120.891
114.492
114.370
106.923
77.319
77.000
76.681
72.620
32.973
31.189
30.270
28.205
21.358
Ts
HN
t-Bu
Ph
N
t-Bu
Br
4p'
200
150
100
50
0
PPM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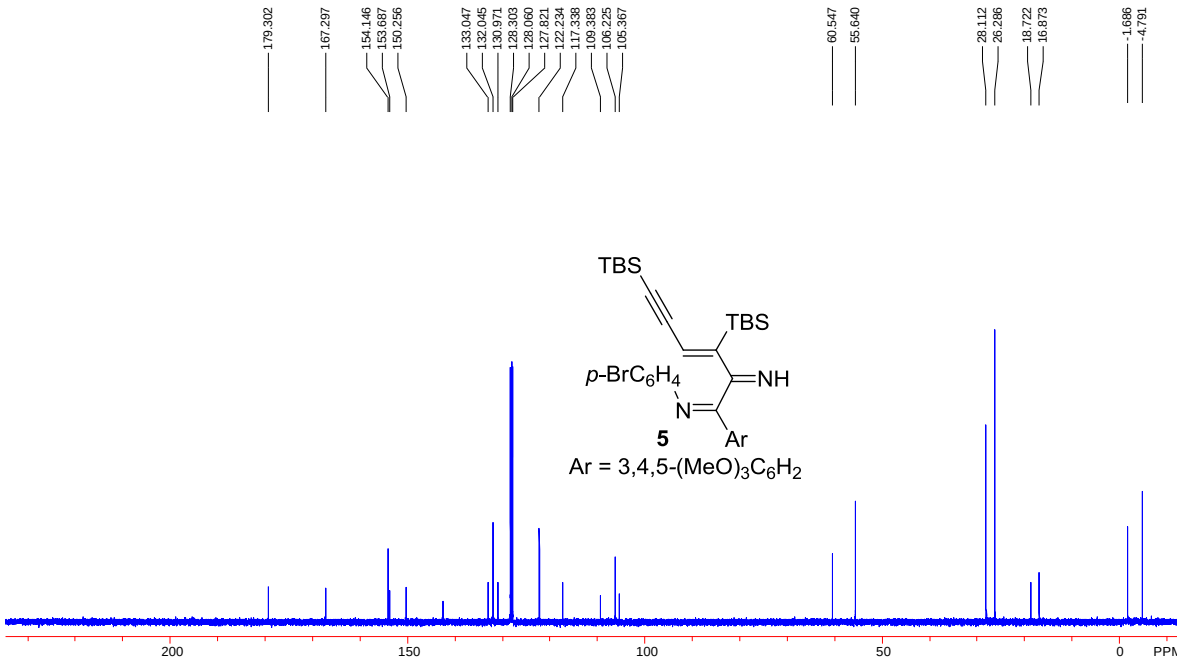
7.295
7.274
7.265
6.982
6.599
6.578
3.901
3.501
1.210
1.007
0.488
0.179
TBS
TBS
p-BrC6H4
NH
N
5
Ar
Ar = 3,4,5-(MeO)3C6H2
1.00
3.62
2.01
0.97
2.03
3.22
6.31
9.40
10.51
5.76
6.63
10
8
6
4
2
0
PPM


179.302
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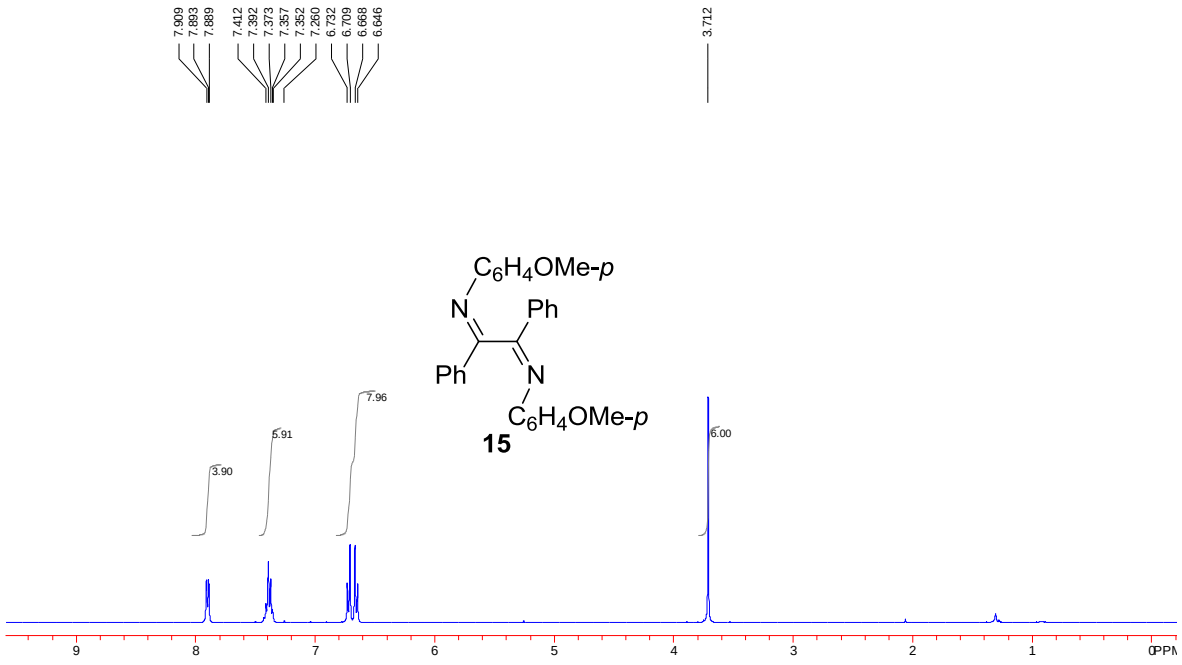
154.146
153.687
150.256
133.047
132.045
130.971
128.303
128.060
127.821
122.234
117.338
109.383
106.225
105.367
60.547
55.640
28.112
26.286
18.722
16.873
-1.686
-4.791
TBS
TBS
p-BrC6H4
NH
N
5
Ar
Ar = 3,4,5-(MeO)3C6H2
200
150
100
50
0
PPM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7.889
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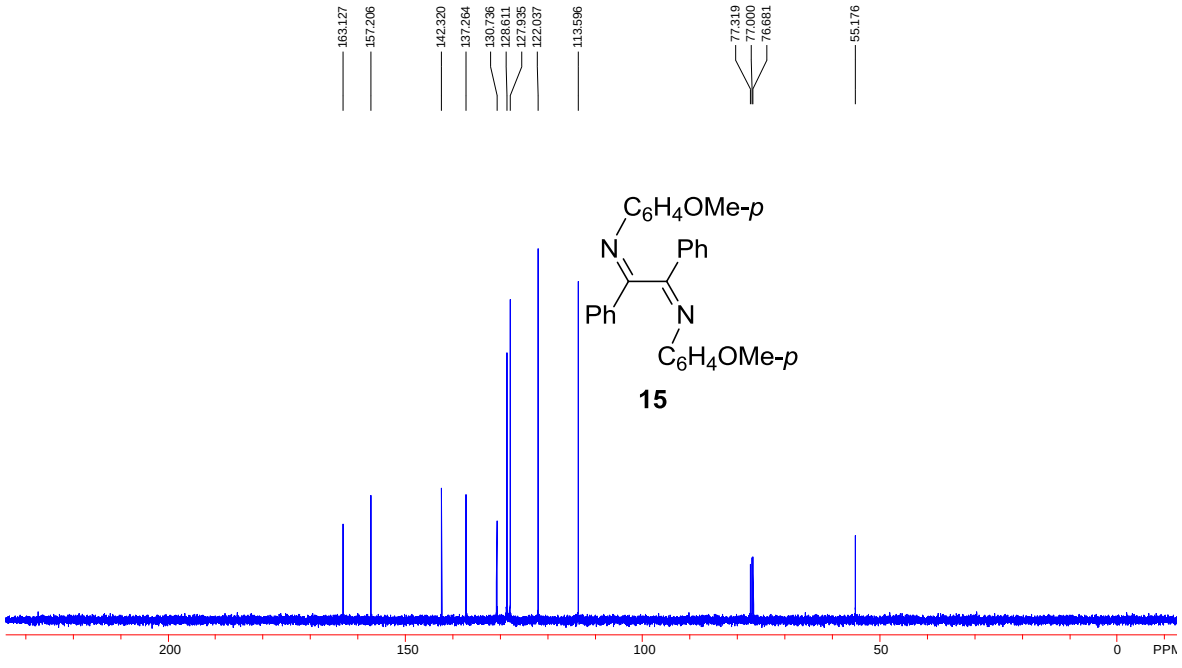
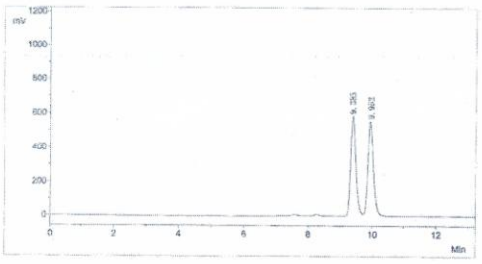
7.392
7.373
7.357
7.352
7.260
6.732
6.709
6.668
6.646
3.712
C6H4OMe-p
N
Ph
Ph
N
C6H4OMe-p
15
7.96
5.91
3.90
6.00
9
8
7
6
5
4
3
2
1
0
PPM

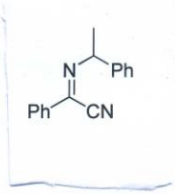

163.127
157.206
142.320
137.264
130.736
128.611
127.935
122.037
113.596
77.319
77.000
76.681
55.176
C6H4OMe-p
N
Ph
Ph
N
C6H4OMe-p
15
200
150
100
50
0
PPM

HPLC Report

Sample Name:
Operator:
Time:14:13

Data File:YX-14-11+- AD-H 82 214 0.4.che
Date:2013-12-30



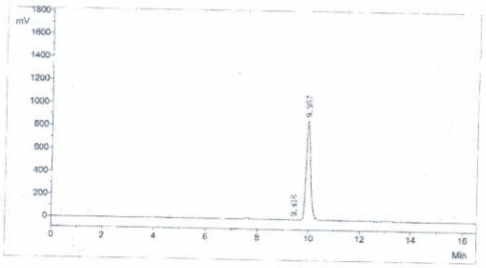


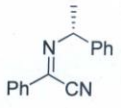
No.	PeakNo	ID Name	R Time	PeakHeight	PeakArea	PerCent
1	1		9.385	578127.0	6673341.6	49.7232
2	2		9.962	547167.9	6747647.5	50.2768
Total				1125294.9	13420989.1	100.0000

HPLC Report

Sample Name:
Operator:
Time:14:41

Data File:YX-7-5..che
Date:2013-12-30

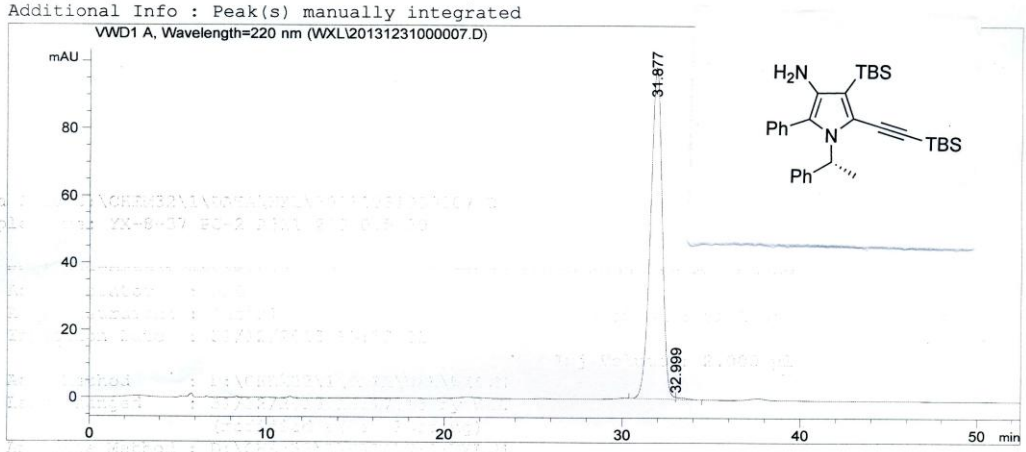




No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		9.418	685.7	8928.7	0.0851
2	2		9.957	866275.5	10482979.8	99.9149
Total				866961.3	10491908.5	100.0000

Data File D:\CHEM32\1\DATA\WXL\20131231000007.D
Sample Name: YX-8-37 PC-2 A3W1 220 0.5 20

Acq. Operator : WXL
Acq. Instrument : instr1 Location : Vial 54
Injection Date : 31/12/2013 13:18:21 Inj Volume : 2.000 µl
Acq. Method : D:\CHEM32\1\DATA\WXL\WXL.M
Last changed : 31/12/2013 13:17:15 by WXL
(modified after loading)
Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
Last changed : 31/12/2013 14:54:32 by WXL
(modified after loading)
Additional Info : Peak(s) manually integrated



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

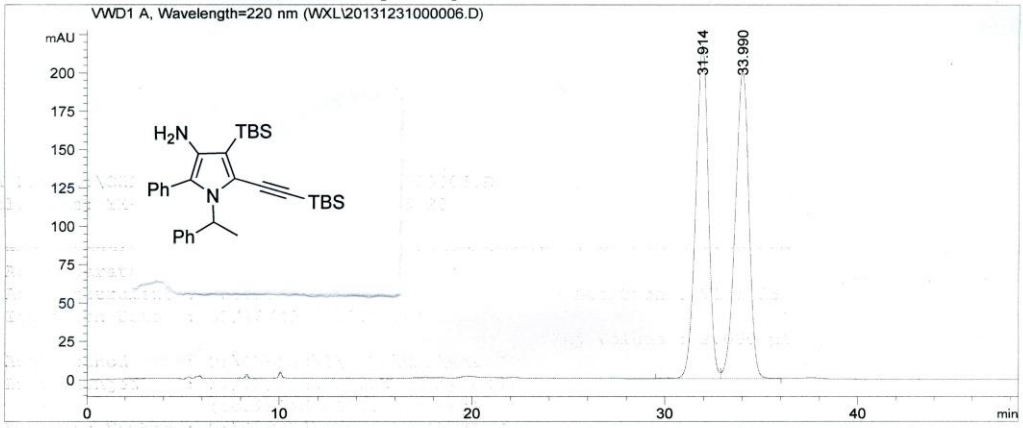
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.877	MF	0.7578	4476.55469	98.45500	99.5001
2	32.999	FM	0.6139	22.48872	6.10521e-1	0.4999
Totals :				4499.04341	99.06552	

*** End of Report ***

Data File D:\CHEM32\1\DATA\WXL\20131231000006.D
Sample Name: YX-8-37+- PC-2 A3W1 220 0.5 20

```
Acq. Operator    : WXL
Acq. Instrument  : instr1                          Location : Vial 53
Injection Date   : 31/12/2013 12:28:41
                                                   Inj Volume : 2.000 µl
Acq. Method      : D:\CHEM32\1\DATA\WXL\WXL.M
Last changed     : 31/12/2013 12:25:20 by WXL
                   (modified after loading)
Analysis Method  : D:\CHEM32\1\DATA\WXL\WXL.M
Last changed     : 31/12/2013 14:54:32 by WXL
                   (modified after loading)
Additional Info  : Peak(s) manually integrated
```



Area Percent Report

```
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.914	MF	0.7644	9934.23340	216.59384	50.1184
2	33.990	FM	0.8215	9887.31348	200.58691	49.8816
Totals :				1.98215e4	417.18076	

*** End of Report ***