Electronic Supplementary Material (ESI) for Chemical Communications

Aza-oxindole Synthesis by Oxidative Coupling of Csp^2-H and Csp^3-H Centers

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CONTENTS:

1. General Information:

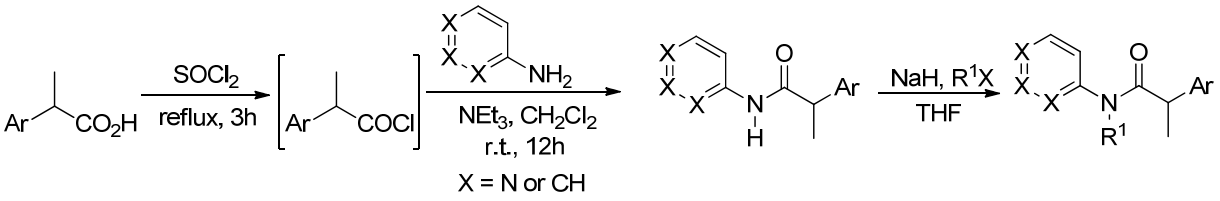
Toluene, THF, CH_2Cl_2, Et_3N were purified by filtration on Al_2O_3 drying columns (Solvtek® system). DMF (Acros) was dried over activated 4Å molecular sieves. Mesitylene, diglyme, $n$$Bu_2O$ were distilled over CaH_2 under nitrogen. $CuCl_2$ was dried at 100 ^oC under vacuum and stored in a glove box. NaO*t*Bu and KO*t*Bu were sublimed and stored in a glove box. Dry xylenes was purchased from Acros. All reactions were carried out under nitrogen in glassware dried by heating under high vacuum. Weighing of $CuCl_2$, NaO*t*Bu, KO*t*Bu was performed in the glove box. Proton and carbon NMR spectra were recorded on Bruker AMX-400 or AMX-300 FT spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane. Coupling constants *J* are quoted in Hz. Infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer using a diamond ATR Golden Gate sampling. Electron impact (EI) mass spectra were obtained using Varian CH–4 or SM–1 instruments operating at 40–70eV and for Electrospray ionization (ESI) HRMS analyses were measured on a VG analytical 7070E instrument. Flash chromatography (FC) was performed using silica gel 60 (40μm). Melting points were determined on a Büchi 510 apparatus.

2-phenylpropanoic acid, 2-(*p*-tolyl)propanoic acid, 2-(4-(trifluoromethyl)phenyl)acetic acid, 2-(4-methoxyphenyl)acetic acid, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-(methylamino)pyridine, 4-(methylamino)pyridine, 2-benzylaminopyridine, were bought and used as received. 2-(4-methoxyphenyl)propanoic acid,[1] 4-benzylaminopyridine[2] were prepared according to the literature procedures.

[1] E. P. Kündig, T. M. Seidel, Y.-X. Jia and G. Bernardinelli, *Angew. Chem. Int. Ed.*, 2007, **46**, 8484.
[2] A. M. Asencio, D. J. Ramón and M. Yus, *Tetrahedron Lett.*, 2010, **51**, 325.

2. Synthesis and analytical data of the substrates:

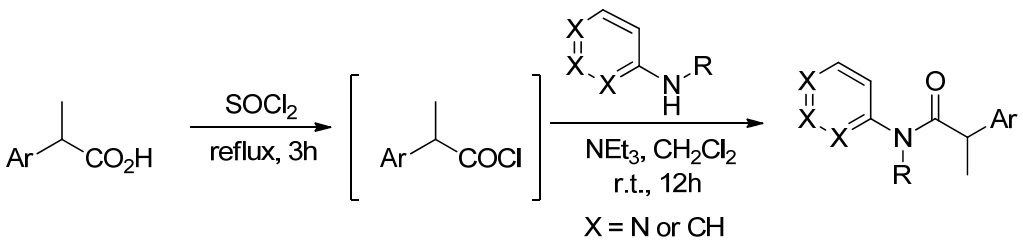
General procedure **A** for preparing substrates **1a-c** and **1k-o**.



The 2-arylylpropionic acid derivative (4.0 mmol, 1.0 equiv) was refluxed with $SOCl_2$ (8.0 mmol, 2.0 equiv) for 3 hours. After evaporating the excess $SOCl_2$ the reaction mixture was diluted with CH_2Cl_2 (5 mL) and cooled to 0 ^oC followed by the addition of NEt_3 (8.0 mmol, 2.0 equiv) and the solution of pyridyl amine (4.4 mmol, 1.1 equiv) in CH_2Cl_2 (5 mL). The mixture was stirred for 12 hours at room temperature (r.t.). The N-H amide was passed through a small pad of silica. The solvent was evaporated and the crude amide was used for the next step.

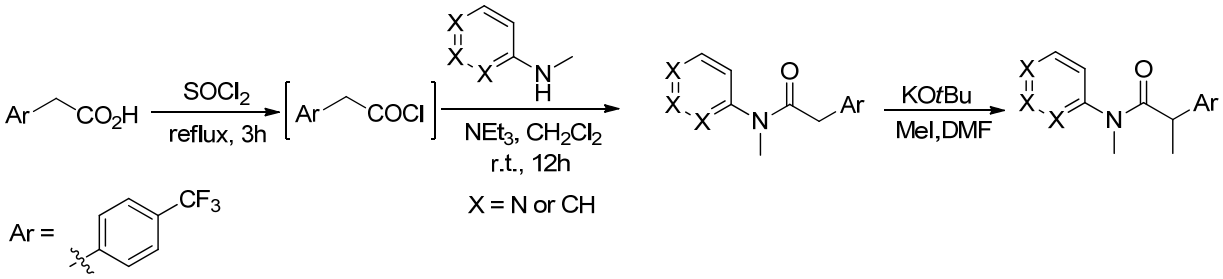
The solution of amide (3.0 mmol, 1.0 equiv) in THF (10 mL) was added to a suspension of NaH (3.3 mmol, 1.1 equiv) in THF (8 mL) at 0 ^oC and the mixture was stirred for 1 h at r.t., followed by the addition of MeI or benzylbromide (3.3 mmol, 1.1 equiv) at 0 ^oC. Stirring was continued for 24 hours at r.t.. The reaction mixture was quenched with brine and extracted with EtOAc (3 times). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The product was purified by flash chromatography. The yields of the products are based on three steps.

General procedure **B** for preparing substrates **1d**, **1f-h** and **1j**.



The 2-arylylpropionic acid derivative (4.0 mmol, 1.0 equiv) was refluxed with $SOCl_2$ (8.0 mmol, 2.0 equiv) for 3 hours. After evaporating the excess $SOCl_2$ the reaction mixture was diluted with CH_2Cl_2 (5 mL) and cooled to 0 ^oC followed by the addition of NEt_3 (8.0 mmol, 2.0 equiv) and the solution of *N*-Me-pyridyl amine or *N*-benzylpyridyl amine (4.4 mmol, 1.1 equiv) in CH_2Cl_2 (5 mL). The mixture was stirred for 12 hours at r.t.. The reaction mixture was extracted with water and EtOAc (3 times). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The product was purified by flash chromatography. The yields of the products are based on two steps.

General procedure **C** for preparing substrates **1e**, **1i** and **1p**.

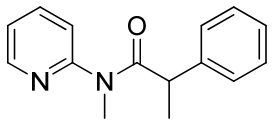


The 2-(4-(trifluoromethyl)phenyl)acetic acid (4.0 mmol, 1.0 equiv) was refluxed with $SOCl_2$ (8.0 mmol, 2.0 equiv) for 3 hours. After evaporating the excess $SOCl_2$ the reaction mixture was diluted with CH_2Cl_2 (5 mL) and cooled to 0 ^oC followed by the addition of NEt_3 (8.0 mmol, 2.0 equiv) and the solution of *N*-Me-pyridyl amine (4.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL). The mixture was stirred for 12 hours at r.t.. The amide was passed through a small pad of silica. The solvent was evaporated and the crude amide was used for next step.

The solution of the amide (2.0 mmol, 1.0 equiv) in DMF (10 mL) was added to a solution of KO*t*Bu (2.0 mmol, 1.0 equiv) in DMF (10 mL) at 0 ^oC and the mixture was stirred for 1 h at r.t., followed by the addition of MeI (2.0 mmol, 1.0 equiv) at 0 ^oC. Stirring was continued for 24 hours at r.t.. The reaction mixture was quenched with brine and extracted with EtOAc (3 times). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated.

The product was purified by flash chromatography. The yields of the products are based on three steps.

N-methyl-2-phenyl-*N*-(pyridin-2-yl)propanamide (**1a**):



1a

Purified by chromatography (cyclohexane/EtOAc = 3:2), 560 mg (70%), oil.

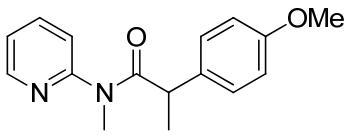
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.63 (td, *J* = 7.6, 2.0 Hz, 1H), 7.23-7.15 (m, 4H), 7.06-6.97 (m, 3H), 3.93 (q, *J* = 6.8 Hz, 1H), 3.33 (s, 3H), 1.45 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 156.1, 148.9, 141.7, 138.1, 128.5, 127.3, 126.7, 122.0, 121.4, 43.9, 35.9, 20.3.

IR (neat, cm^{-1}): 3060, 3021, 2977, 2931, 2877, 1658, 1584, 1569, 1469, 1433, 1372, 1292, 1128, 1050, 1027, 991, 787, 746, 699.

HRMS (ESI): calcd. for $C_{15}H_{17}N_2O$ ($[M+H]^+$): 241.1335, found: 241.1334.

2-(4-methoxyphenyl)-*N*-methyl-*N*-(pyridin-2-yl)propanamide (**1b**):



1b

Purified by chromatography (cyclohexane/EtOAc = 3:2), 657 mg (73%), oil. The product **1b** was obtained as a mixture of two isomers (89:11).

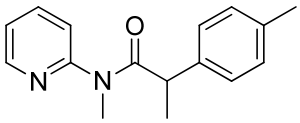
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (dd, *J* = 4.8 Hz, 1.2 Hz, 1.00H), 8.36 (dd, *J* = 4.8, 1.6 Hz, 0.13H), 7.65 (td, *J* = 8.0, 2.0 Hz, 1.02H), 7.44 (td, *J* = 8.0, 2.0 Hz, 0.14H), 7.19 (dd, *J* = 6.8, 5.2 Hz, 1.12H), 7.05-6.96 (m, 3.30H), 6.75 (d, *J* = 8.8 Hz, 2.35H), 3.86 (q, *J* = 6.8 Hz, 1.12H), 3.78 (s, 0.39H), 3.76 (s, 3.09H), 3.32 (s, 3.08H), 3.10 (s, 0.40H), 1.50 (d, *J* = 6.8 Hz, 0.31H), 1.42 (d, *J* = 6.8 Hz, 3.07H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 174.7, 158.4, 158.1, 156.6, 156.3, 149.0, 148.3, 138.2, 138.0, 137.3, 133.9, 128.7, 128.5, 126.5, 122.7, 122.1, 121.6, 114.1, 114.0, 55.3, 47.5, 43.1, 37.8, 36.0, 28.7, 25.7, 20.5.

IR (neat, cm^{-1}): 3058, 2974, 2962, 2932, 2835, 1657, 1610, 1584, 1569, 1509, 1469, 1433, 1373, 1293, 1242, 1177, 1129, 1064, 1050, 1030, 991, 833, 784, 746, 696, 678, 623.

HRMS (ESI): calcd. for $C_{16}H_{19}N_2O_2$ ($[M+H]^+$): 271.1441, found: 271.1446.

N-methyl-*N*-(pyridin-2-yl)-2-(*p*-tolyl)propanamide (**1c**):



1c

Purified by chromatography (cyclohexane/EtOAc = 3:1), 482 mg (57%), oil. The product **1c** was obtained as a mixture of two isomers (88:12).

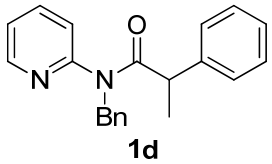
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (dd, *J* = 4.4, 1.2 Hz, 1.00H), 8.36 (dd, *J* = 4.8, 1.6 Hz, 0.14H), 7.64 (td, *J* = 7.6, 2.0 Hz, 1.02H), 7.43 (td, *J* = 7.6, 2.0 Hz, 0.15H), 7.25-7.23 (m, 0.17H), 7.18 (dd, *J* = 6.8, 5.2 Hz, 1.07H), 7.15-7.13 (m, 0.27H), 7.03-6.85 (m, 5.76H), 3.87 (q, *J* = 6.8 Hz, 1.02H), 3.71 (q, *J* = 6.8 Hz, 0.12H), 3.32 (s, 3.09H), 3.08 (s, 0.45H), 2.30 (s, 0.45H), 2.28 (s, 3.10H), 1.50 (d, *J* = 6.8 Hz, 0.44H), 1.43 (d, *J* = 6.8 Hz, 3.14H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 174.5, 156.5, 156.2, 149.0, 148.2, 138.8, 138.1, 137.3, 136.3, 135.9, 129.4, 129.3, 127.6, 127.3, 125.3, 122.6, 122.0, 121.6, 121.5, 47.8, 43.6, 37.7, 35.9, 28.5, 21.1, 21.0, 20.5.

IR (neat, cm^{-1}): 3056, 2931, 1663, 1585, 1512, 1471, 1434, 1373, 1130, 1062, 790.

HRMS (ESI): calcd. for $C_{16}H_{19}N_2O$ ($[M+H]^+$): 255.1491, found: 255.1486.

N-benzyl-2-phenyl-*N*-(pyridin-2-yl)propanamide (**1d**):



1d

Purified by chromatography (cyclohexane/EtOAc = 3:2), 797 mg (63%), oil.

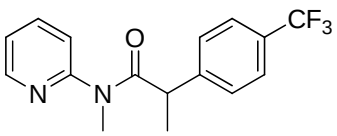
^1H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 3.6 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.25-7.14 (m, 9H), 7.03 (br s, 2H), 6.64 (br s, 1H), 5.09-4.93 (m, 2H), 3.87 (q, *J* = 6.8 Hz, 1H), 1.46 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 155.1, 149.2, 141.8, 137.9, 137.7, 128.6, 128.5, 128.0, 127.4, 127.2, 126.8, 122.6, 122.4, 51.7, 44.2, 20.4.

IR (neat, cm^{-1}): 3061, 3029, 2976, 2931, 1660, 1583, 1468, 1453, 1433, 1382, 1266, 1206, 1181, 1010, 992, 784, 732, 696.

HRMS (ESI): calcd. for $C_{21}H_{21}N_2O$ ($[M+H]^+$): 317.1648, found: 317.1642.

N-methyl-*N*-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)propanamide (**1e**):



1e

Purified by chromatography (EtOAc), 431 mg (56%), oil.

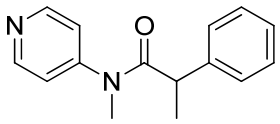
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.66 (td, *J* = 8.0, 2.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.23-7.16 (m, 3H), 6.97 (br s, 1H), 3.99 (q, *J* = 6.8 Hz, 1H), 3.31 (s, 3H), 1.44 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 156.1, 149.2, 145.9, 138.4, 129.0 (q, *J* = 32.4 Hz), 127.9, 125.5 (q, *J* = 3.7 Hz), 122.9, 122.4, 121.3, 43.8, 36.1, 20.2.

IR (neat, cm^{-1}): 3060, 2979, 2935, 1661, 1616, 1585, 1571, 1471, 1434, 1421, 1376, 1322, 1162, 1114, 1071, 1018, 992, 845, 793, 714, 622.

HRMS (ESI): calcd. for $C_{16}H_{16}F_3N_2O$ ($[M+H]^+$): 309.1209, found: 309.1209.

N-methyl-2-phenyl-*N*-(pyridin-4-yl)propanamide (**1f**):



1f

Purified by chromatography (CH_2Cl_2/MeOH = 18:1), 807 mg (84%), oil.

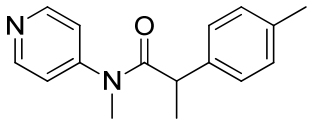
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* =5.6 Hz, 2H), 7.25-7.19 (m, 3H), 7.06 (d, *J* = 6.4 Hz, 2H), 6.99 (d, *J* = 5.6 Hz, 2H), 3.74 (q, *J* = 6.8 Hz, 1H), 3.26 (s, 3H), 1.43 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 151.3, 151.2, 141.4, 128.8, 127.4, 127.0, 122.0, 43.9, 37.3, 20.7.

IR (neat, cm^{-1}): 3059, 3028, 2975, 2931, 2873, 1661, 1584, 1560, 1494, 1453, 1411, 1374, 1274, 1124, 1060, 1024, 831, 746, 700, 661.

HRMS (ESI): calcd. for $C_{15}H_{17}N_2O$ ($[M+H]^+$): 241.1335, found: 241.1333.

N-methyl-*N*-(pyridin-4-yl)-2-(*p*-tolyl)propanamide (**1g**):



1g

Purified by chromatography (CH_2Cl_2/MeOH = 18:1), 905 mg (89%), solid, m.p. 87-89 ^oC.

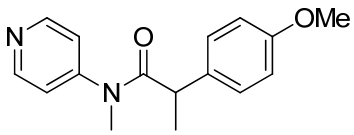
^1H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 6.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 5.4 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 3.70 (q, *J* = 6.8 Hz, 1H), 3.25 (s, 3H), 2.30 (s, 3H), 1.40 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 151.3, 151.1, 138.3, 136.6, 129.4, 127.2, 121.8, 43.3, 37.2, 21.0, 20.7.

IR (neat, cm^{-1}): 2975, 2929, 1665, 1586, 1512, 1496, 1374, 1273, 1126, 1062, 1024, 825, 780, 667.

HRMS (ESI): calcd. for $C_{16}H_{19}N_2O$ ($[M+H]^+$): 255.1491, found: 255.1487.

2-(4-methoxyphenyl)-*N*-methyl-*N*-(pyridin-4-yl)propanamide (**1h**):



1h

Purified by chromatography (CH_2Cl_2/MeOH = 18:1), 897 mg (83%), oil.

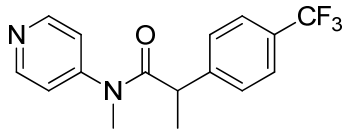
^1H NMR (400 MHz, $CDCl_3$): δ 8.59 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.00-6.96 (m, 4H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.68 (q, *J* = 6.8 Hz, 1H), 3.25 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 158.6, 151.4, 151.2, 133.4, 128.4, 121.9, 114.1, 55.3, 42.9, 37.2, 20.7.

IR (neat, cm^{-1}): 2968, 2932, 1659, 1610, 1584, 1509, 1456, 1372, 1302, 1243, 1177, 1123, 1061, 1027, 994, 831, 782, 683, 664.

HRMS (ESI): calcd. for $C_{16}H_{19}N_2O_2$ ($[M+H]^+$): 271.1441, found: 271.1442.

N-methyl-*N*-(pyridin-4-yl)-2-(4-(trifluoromethyl)phenyl)propanamide (**1i**):



1i

Purified by chromatography (CH_2Cl_2/MeOH = 36:1), 382 mg (53%), oil.

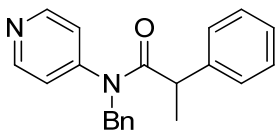
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 4.8, 2H), 7.50 (d, *J* = 8.0, 2H), 7.19 (d, *J* = 7.6, 2H), 6.99 (d, *J* = 5.2, 2H), 3.79 (q, *J* = 6.8, 1H), 3.26 (s, 3H), 1.43 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 151.4, 151.2, 145.3, 129.4 (q, *J* = 32.5 Hz), 127.8, 125.8 (q, *J* = 3.7 Hz), 122.8, 122.0, 43.6, 37.4, 20.6.

IR (neat, cm^{-1}): 2983, 2936, 1664, 1617, 1664, 1617, 1415, 1377, 1322, 1162, 1113, 1067, 1018, 836, 780, 710, 662, 629.

HRMS (ESI): calcd. for $C_{16}H_{16}F_3N_2O$ ($[M+H]^+$): 309.1209, found: 309.1194.

N-benzyl-2-phenyl-*N*-(pyridin-4-yl)propanamide (**1j**):



1j

Purified by chromatography (CH_2Cl_2/MeOH = 36:1), 746 mg (59%), oil.

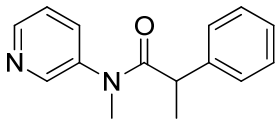
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 5.6 Hz, 2H), 7.26-7.17 (m, 6H), 7.12-7.09 (m, 2H), 7.03-7.01 (m, 2H), 6.75 (d, *J* = 4.0 Hz, 2H), 4.87 (s, 2H), 3.64 (q, *J* = 6.8 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 151.0, 149.8, 141.3, 136.8, 128.7, 128.6, 128.2, 127.6, 127.3, 127.0, 123.1, 52.8, 44.1, 20.6.

IR (neat, cm^{-1}): 3059, 3028, 2975, 2931, 1662, 1583, 1661, 1494, 1453, 1385, 1265, 1207, 1182, 1027, 834, 699, 628.

HRMS (ESI): calcd. for $C_{21}H_{21}N_2O$ ($[M+H]^+$): 317.1648, found: 317.1636.

N-methyl-2-phenyl-*N*-(pyridin-3-yl)propanamide (**1k**):



1k

Purified by chromatography (EtOAc), 670 mg (84%), oil.

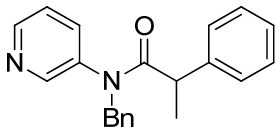
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (br s, 1H), 8.24 (br s, 1H), 7.23-7.15 (m, 5H), 6.90 (d, *J* = 5.6 Hz, 2H), 3.51 (q, *J* = 6.6 Hz, 1H), 3.21 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 149.2, 148.8, 141.3, 140.2, 135.3, 128.6, 127.3, 126.9, 123.9, 43.7, 37.9, 20.4.

IR (neat, cm^{-1}): 3056, 3028, 2976, 2932, 2866, 1657, 1478, 1419, 1375, 1275, 1125, 1024, 813, 753, 713, 699, 616.

HRMS (ESI): calcd. for $C_{15}H_{17}N_2O$ ($[M+H]^+$): 241.1335, found: 241.1335.

N-benzyl-2-phenyl-*N*-(pyridin-3-yl)propanamide (**1m**):



1m

Purified by chromatography (cyclohexane/EtOAc = 1:6), 642 mg (61%), oil.

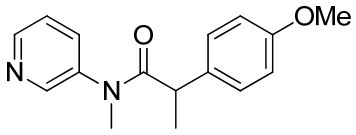
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.04 (br s, 1H), 7.24-7.20 (m, 6H), 7.13-7.11 (m, 3H), 6.95-6.88 (m, 3H), 4.90 (d, *J* = 14.4 Hz, 1H), 4.85 (d, *J* = 14.4 Hz, 1H), 3.50 (q, *J* = 6.8 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 150.3, 149.1, 141.5, 138.4, 136.9, 136.6, 128.9, 128.8, 128.7, 127.8, 127.5, 127.1, 123.7, 53.5, 44.3, 20.6.

IR (neat, cm^{-1}): 3063, 3030, 2980, 2931, 2865, 1660, 1477, 1453, 1421, 1389, 1266, 1184, 1028, 1009, 818, 755, 713, 699, 634.

HRMS (ESI): calcd. for $C_{21}H_{21}N_2O$ ($[M+H]^+$): 317.1648, found: 317.1660.

2-(4-methoxyphenyl)-*N*-methyl-*N*-(pyridin-3-yl)propanamide (**1n**):



1n

Purified by chromatography (cyclohexane/EtOAc = 1:6), 567 mg (63%), oil.

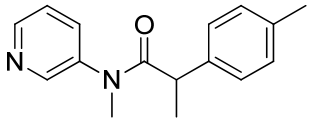
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (br s, 1H), 8.31 (br s, 1H), 7.30-7.25 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 3.77 (s, 3H), 3.49 (q, *J* = 6.6 Hz, 1H), 3.25 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 174.3, 158.6, 149.4, 149.0, 140.4, 135.5, 133.5, 128.5, 124.0, 114.1, 55.4, 42.9, 38.0, 20.6.

IR (neat, cm^{-1}): 3058, 2974, 2962, 2932, 2899, 2831, 1659, 1511, 1479, 1420, 1302, 1275, 1247, 1179, 1127, 1029, 835, 784, 714.

HRMS (ESI): calcd. for $C_{16}H_{19}N_2O_2$ ($[M+H]^+$): 271.1441, found: 271.1441.

N-methyl-*N*-(pyridin-3-yl)-2-(*p*-tolyl)propanamide (**1o**):



1o

Purified by chromatography (cyclohexane/EtOAc = 1:6), 564 mg (67%), oil. The product **1o** was obtained as a mixture of two isomers (93:7).

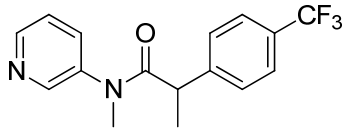
^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1.00H), 8.36-8.35 (m, 0.09H), 8.27 (s, 0.99H), 8.07 (s, 0.08H), 7.28-7.25 (m, 2.55H), 7.01 (d, *J* = 7.2 Hz, 2.38H), 6.83 (d, *J* = 7.0 Hz, 1.96H), 3.49 (q, *J* = 6.3 Hz, 1.00H), 3.24 (s, 3.07H), 3.08 (s, 0.24H), 2.32 (s, 0.26H), 2.28 (s, 3.09H), 1.37 (d, *J* = 6.7 Hz, 3.22H).

^{13}C NMR (100 MHz, $CDCl_3$): 176.7, 174.1, 149.4, 148.9, 147.7, 142.6, 140.4, 138.4, 136.6, 136.3, 135.4, 129.4, 127.3, 125.2, 124.0, 123.2, 47.3, 43.3, 38.0, 28.6, 21.1, 21.0, 20.5.

IR (neat, cm^{-1}): 3050, 3021, 2973, 2931, 2865, 1659, 1513, 1479, 1419, 1375, 1275, 1126, 1024, 818, 781, 714, 617.

HRMS (ESI): calcd. for $C_{16}H_{19}N_2O$ ($[M+H]^+$): 255.1491, found: 255.1491.

N-methyl-*N*-(pyridin-3-yl)-2-(4-(trifluoromethyl)phenyl)propanamide (**1p**):



1p

Purified by chromatography (EtOAc), 424 mg (52%), oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 3.2 Hz, 1H), 8.33 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.32-7.24 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.62 (q, *J* = 6.8 Hz, 1H), 3.27 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 173.1, 149.2, 145.4, 140.1, 135.2, 129.3 (q, *J* = 32.4 Hz), 127.8, 125.6 (q, *J* = 3.3 Hz), 125.5, 124.2, 122.8, 43.5, 38.0, 20.4.

IR (neat, cm^{-1}): 3059, 2974, 2935, 1664, 1617, 1583, 1480, 1420, 1325, 1164, 1121, 1072, 1019, 817, 715, 615.

HRMS (ESI): calcd. for $C_{16}H_{16}F_3N_2O$ ($[M+H]^+$): 309.1209, found: 309.1200.

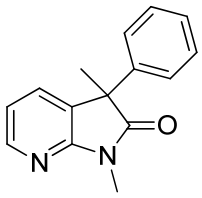
3. Oxidative coupling reactions to aza-oxindoles and analytical data for the products:

General procedure **D** for the oxidative coupling reaction.

In a dry Schlenk tube amide (0.40 mmol, 1.0 equiv), $CuCl_2$ (0.88 mmol, 2.2 equiv), and NaO*t*Bu (2.00 mmol, 5.0 equiv) were combined. Toluene (8 mL) was introduced to the Schlenk tube by syringe under N_2 atmosphere. The resulting mixture was stirred at 110 ^oC until completion of the reaction (monitored by TLC). After cooling to r.t., the mixture was filtered through a short pad of celite. The filtrate was washed with brine or water (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The product was purified by flash chromatography.

Compound **2o** is literature known.[3]

1,3-dimethyl-3-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (**2a**):



2a

The reaction was carried out starting with **1a** (192 mg, 0.8 mmol) according to the general procedure **D**. Purified by chromatography (cyclohexane/EtOAc = 3:2), 130 mg (68%), oil.

^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.45 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.34-7.25 (m, 5H), 7.01 (dd, *J* = 6.8, 5.2 Hz, 1H), 3.34 (s, 3H), 1.81 (s, 3H).

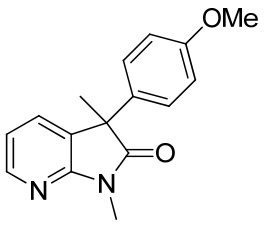
^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 156.9, 147.2, 139.7, 131.6, 129.3, 128.9, 127.7, 126.6, 118.5, 51.9, 25.8, 23.7.

IR (neat, cm^{-1}): 3056, 2969, 2933, 1722, 1593, 1468, 1342, 1255, 1123, 1019, 778, 697.

[3] L. Ackermann, R. Vicente and N. Hofmann, *Org. Lett.*, 2009, **11**, 4274.

HRMS (ESI): calcd. for $C_{15}H_{15}N_2O$ ($[M+H]^+$): 239.1178, found: 239.1185.

3-(4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (**2b**):



2b

The reaction was carried out starting with **1b** (108 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (cyclohexane/EtOAc = 3:2), 57 mg (53%), oil.

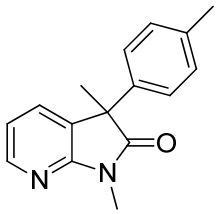
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.22 (d, *J* = 9.2 Hz, 2H), 7.01 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.33 (s, 3H), 1.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.4, 159.1, 156.9, 147.2, 131.8, 131.6, 129.5, 127.8, 118.5, 114.2, 55.4, 51.3, 25.7, 23.8.

IR (neat, cm^{-1}): 3058, 2983, 2957, 2933, 2907, 2836, 1721, 1604, 1593, 1511, 1468, 1341, 1251, 1181, 1108, 1029, 833, 803, 779, 666.

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_2$ ($[M+H]^+$): 269.1284, found: 269.1291.

1,3-dimethyl-3-(*p*-tolyl)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (**2c**):



2c

The reaction was carried out starting with **1c** (102 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (cyclohexane/EtOAc = 3:2), 58 mg (57%), oil.

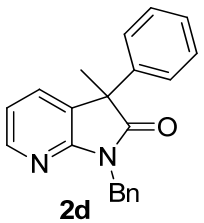
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.44 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.00 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.33 (s, 3H), 2.32 (s, 3H), 1.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 156.9, 147.1, 137.5, 136.8, 131.6, 129.6, 129.5, 126.5, 118.5, 51.7, 25.8, 23.6, 21.1.

IR (neat, cm^{-1}): 3059, 3025, 2970, 2928, 2860, 1725, 1593, 1512, 1469, 1341, 1112, 1020, 782.

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O$ ($[M+H]^+$): 253.1335, found: 253.1336.

1-benzyl-3-methyl-3-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (**2d**):



2d

The reaction was carried out starting with **1d** (127 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (cyclohexane/EtOAc = 3:2), 80 mg (64%), oil.

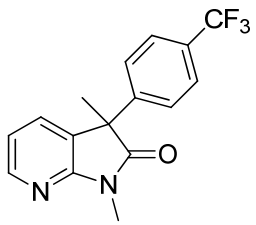
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.46-7.42 (m, 3H), 7.35-7.24 (m, 8H), 6.99 (dd, *J* = 7.2, 5.2 Hz, 1H), 5.08 (d, *J* = 14.8 Hz, 1H), 5.03 (d, *J* = 14.8 Hz, 1H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9, 156.3, 147.3, 139.8, 136.8, 131.6, 129.3, 128.9, 128.7, 128.3, 127.7, 127.6, 126.6, 118.6, 51.9, 42.9, 23.6.

IR (neat, cm^{-1}): 3059, 3033, 2974, 2925, 2856, 1722, 1595, 1495, 1453, 1371, 1345, 1195, 780, 698.

HRMS (ESI): calcd. for $C_{21}H_{19}N_2O$ ($[M+H]^+$): 315.1491, found: 315.1486.

1,3-dimethyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (**2e**):



2e

The reaction was carried out starting with **1e** (123 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (cyclohexane/EtOAc = 3:2), 66 mg (54%), oil.

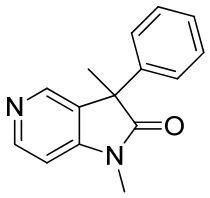
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (brs, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.46-7.43 (m, 3H), 7.05 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.35 (s, 3H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 165.4, 156.8, 147.6, 144.2, 143.7, 131.7, 131.5, 127.2, 125.8 (q, *J* = 3.8 Hz), 118.7, 51.9, 25.9, 23.8.

IR (neat, cm^{-1}): 3063, 2976, 2936, 1719, 1602, 1593, 1468, 1408, 1375, 1340, 1324, 1297, 1256, 1164, 1118, 1074, 1015, 840, 794, 779, 734, 699, 647.

HRMS (ESI): calcd. for $C_{16}H_{14}F_3N_2O$ ($[M+H]^+$): 307.1052, found: 307.1055.

1,3-dimethyl-3-phenyl-1*H*-pyrrolo[3,2-*c*]pyridin-2(3*H*)-one (**2f**):



2f

The reaction was carried out starting with **1f** (192 mg, 0.8 mmol) according to the general procedure **D**. Purified by chromatography (CH_2Cl_2/MeOH = 18:1), 179 mg (94%), oil.

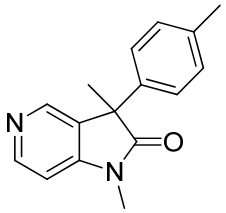
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 5.2 Hz, 1H), 8.40 (s, 1H), 7.37-7.36 (m, 4H), 7.33-7.29 (m, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 3.28 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.2, 150.6, 150.1, 144.7, 139.6, 130.3, 128.9, 127.8, 126.6, 104.2, 50.9, 26.6, 24.0.

IR (neat, cm^{-1}): 3055, 2970, 2936, 1724, 1604, 1495, 1373, 1339, 1115, 1017, 903, 821, 697, 633.

HRMS (ESI): calcd. for $C_{15}H_{15}N_2O$ ($[M+H]^+$): 239.1178, found: 239.1178.

1,3-dimethyl-3-(*p*-tolyl)-1*H*-pyrrolo[3,2-*c*]pyridin-2(3*H*)-one (**2g**):



2g

The reaction was carried out starting with **1g** (102 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (CH_2Cl_2/MeOH = 18:1), 100 mg (99%), solid, m.p. 90-92 ^{o}C.

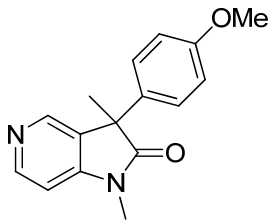
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 5.2 Hz, 1H), 8.35 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 5.2 Hz, 1H), 3.23 (s, 3H), 2.31 (s, 3H), 1.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 150.6, 150.0, 144.6, 137.6, 136.6, 130.4, 129.6, 126.4, 104.1, 50.6, 26.6, 24.0, 21.1.

IR (neat, cm^{-1}): 3033, 2957, 2923, 2854, 1724, 1602, 1510, 1494, 1371, 1338, 1109, 1018, 818, 713, 665.

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O$ ($[M+H]^+$): 253.1335, found: 253.1345.

3-(4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrrolo[3,2-*c*]pyridin-2(3*H*)-one (**2h**):



2h

The reaction was carried out starting with **1h** (108 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (CH_2Cl_2/MeOH = 18:1), 106 mg (99%), solid, m.p. 119-121 ^{o}C.

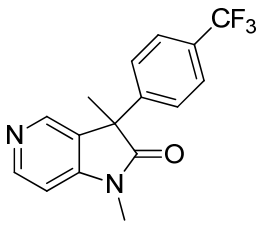
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 5.2 Hz, 1H), 8.34 (s, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 5.2 Hz, 1H), 6.83 (d, *J* = 9.2 Hz, 2H), 3.76 (s, 3H), 3.22 (s, 3H), 1.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.5, 159.2, 150.6, 150.0, 144.7, 131.6, 130.5, 127.8, 114.2, 104.2, 55.4, 50.3, 26.6, 24.2.

IR (neat, cm^{-1}): 3063, 3042, 2957, 2928, 2835, 1723, 1602, 1510, 1495, 1461, 1372, 1338, 1251, 1181, 1107, 1017, 805, 717, 666.

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_2$ ($[M+H]^+$): 269.1290, found: 269.1288.

1,3-dimethyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[3,2-*c*]pyridin-2(3*H*)-one (**2i**):



2i

The reaction was carried out starting with **1i** (123 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (CH_2Cl_2/MeOH = 36:1), 78 mg (64%), oil.

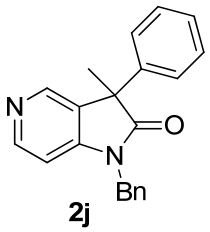
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J* = 4.8 Hz, 1H), 8.37 (s, 1H), 7.59-7.57 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 5.2 Hz, 1H), 3.26 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 150.7, 150.4, 144.6, 143.5, 130.1 (q, *J* = 32.6 Hz), 127.8, 127.2, 125.8 (q, *J* = 3.8 Hz), 125.4, 104.4, 50.9, 26.8, 24.2.

IR (neat, cm^{-1}): 3065, 2966, 2937, 1725, 1604, 1496, 1370, 1324, 1164, 1107, 1071, 1015, 839, 818, 765, 764, 756, 749, 747, 715, 604.

HRMS (ESI): calcd. for $C_{16}H_{14}F_3N_2O$ ($[M+H]^+$): 307.1052, found: 307.1061.

1-benzyl-3-methyl-3-phenyl-1*H*-pyrrolo[3,2-*c*]pyridin-2(3*H*)-one (**2j**):



2j

The reaction was carried out starting with **1j** (127 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (CH_2Cl_2/MeOH = 36:1), 99 mg (79%), oil.

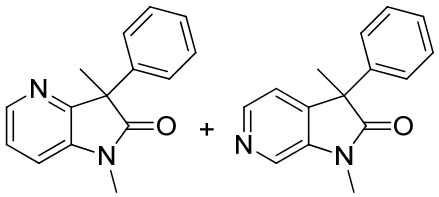
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43-8.37 (m, 2H), 7.35-7.29 (m, 8H), 7.27-7.25 (m, 2H), 6.77 (d, *J* = 4.0 Hz, 1H), 4.96 (d, *J* = 16.0 Hz, 1H), 4.91 (d, *J* = 16.0 Hz, 1H), 1.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 149.9, 149.8, 144.7, 139.6, 135.1, 129.1, 129.0, 128.2, 127.9, 127.4, 126.6, 51.0, 44.1, 24.0.

IR (neat, cm^{-1}): 3059, 3031, 2966, 2927, 2852, 1723, 1602, 1490, 1345, 1146, 1024, 819, 732, 697, 646.

HRMS (ESI): calcd. for $C_{21}H_{19}N_2O$ ($[M+H]^+$): 315.1491, found: 315.1484.

1,3-dimethyl-3-phenyl-1*H*-pyrrolo[3,2-*b*]pyridin-2(3*H*)-one (**2k**) + 1,3-dimethyl-3-phenyl-1*H*-pyrrolo[2,3-*c*]pyridin-2(3*H*)-one (**2l**):



2k **2l**

The reaction was carried out starting with **1k** (192 mg, 0.8 mmol) according to the general procedure **D**. Purified by chromatography (EtOAc), 181 mg (95%) (**2k**/**2l** = 84/16), oil.

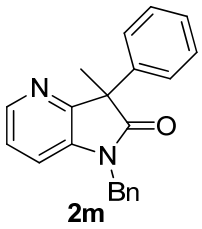
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 1.6 Hz, 0.16 H), 8.29 (dd, *J* = 5.2, 1.2 Hz, 0.84H), 7.51-7.49 (m, 0.36H), 7.46-7.43 (m, 1.70H), 7.37-7.20 (m, 4.52H), 7.13 (dd, *J* = 7.8, 1.6 Hz, 0.88H), 3.36 (s, 0.48H), 3.29 (s, 2.59H), 1.90 (s, 0.46H), 1.85 (s, 2.63H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.11, 178.06, 155.3, 143.3, 141.8, 139.3, 139.0, 138.8, 138.3, 133.6, 128.8, 128.7, 127.7, 127.5, 126.8, 122.8, 114.5, 113.1, 52.4, 52.3, 26.5, 26.3, 23.0, 22.9.

IR (neat, cm^{-1}): 3059, 3025, 2974, 2932, 2866, 1718, 1603, 1451, 1370, 1325, 1151, 1103, 1038, 794, 773, 697, 628.

HRMS (ESI): calcd. for $C_{15}H_{15}N_2O$ ($[M+H]^+$): 239.1178, found: 239.1178.

1-benzyl-3-methyl-3-phenyl-1*H*-pyrrolo[3,2-*b*]pyridin-2(3*H*)-one (**2m**):



2m

The reaction was carried out starting with **1m** (127 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (cyclohexane/EtOAc = 3:2), 89 mg (71%), oil.

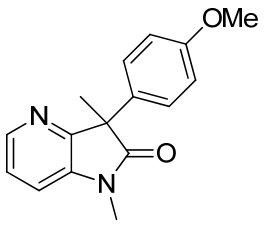
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.48-7.45 (m, 2H), 7.36-7.26 (m, 8H), 7.07 (dd, *J* = 8.0, 5.2 Hz , 1H), 6.97 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.03 (d, *J* = 15.6 Hz, 1H), 4.95 (d, *J* = 15.6 Hz, 1H), 1.91 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.1, 155.3, 143.5, 139.3, 137.4, 135.3, 129.1, 128.8, 128.1, 127.6, 127.4, 126.8, 122.7, 115.6, 52.5, 43.8, 23.0.

IR (neat, cm^{-1}): 3062, 2928, 2865, 1713, 1601, 1495, 1444, 1331, 1161, 1077, 1029, 996, 794, 773, 733, 697, 643, 618.

HRMS (ESI): calcd. for $C_{21}H_{19}N_2O$ ($[M+H]^+$): 315.1491, found: 315.1490.

3-(4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrrolo[3,2-*b*]pyridin-2(3*H*)-one (**2n**):



2n

The reaction was carried out starting with **1n** (108 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (cyclohexane/EtOAc = 3:2), 88 mg (82%), oil.

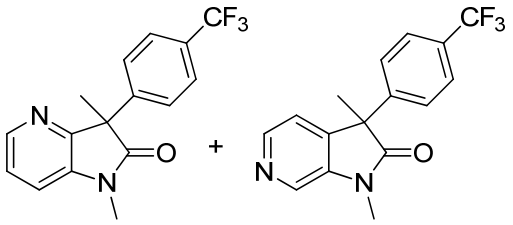
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.36 (d, *J* = 9.2 Hz, 2H), 7.20 (dd, *J* = 7.6, 5.1 Hz, 1H), 7.12 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 3.27 (s, 3H), 1.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 158.9, 155.5, 143.3, 138.2, 131.4, 127.9, 122.7, 114.4, 114.1, 55.4, 51.7, 26.2, 23.1.

IR (neat, cm^{-1}): 3064, 2969, 2933, 2837, 1713, 1602, 1509, 1451, 1368, 1325, 1308, 1247, 1181, 1150, 1098, 1029, 905, 832, 785, 729, 688.

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_2$ ($[M+H]^+$): 269.1284, found: 269.1284.

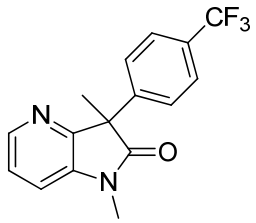
1,3-dimethyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[3,2-*b*]pyridin-2(3*H*)-one (**2p**) + 1,3-dimethyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[2,3-*c*]pyridin-2(3*H*)-one (**2q**):



2p **2q**

The reaction was carried out starting with **1p** (123 mg, 0.4 mmol) according to the general procedure **D**. Purified by chromatography (cyclohexane/EtOAc = 1:1), 98 mg (80%) (**2p**/**2q** = 82/18), oil.

1,3-dimethyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[3,2-*b*]pyridin-2(3*H*)-one (**2p**)



2p

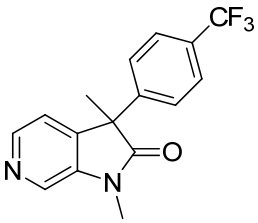
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.26-7.21 (m, 1H), 7.17 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.30 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 154.3, 143.5, 143.3, 138.3, 129.7 (q, *J* = 32.4 Hz), 127.4, 126.8, 125.6 (q, *J* = 3.8 Hz), 123.2, 114.8, 52.2, 26.4, 23.4.

IR (neat, cm^{-1}): 3065, 2974, 2934, 1718, 1601, 1453, 1372, 1325, 1165, 1120, 1072, 1017, 841, 794, 693, 602.

HRMS (ESI): calcd. for $C_{16}H_{14}F_3N_2O$ ($[M+H]^+$): 307.1052, found: 307.1052.

1,3-dimethyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrolo[2,3-*c*]pyridin-2(3*H*)-one (**2q**):



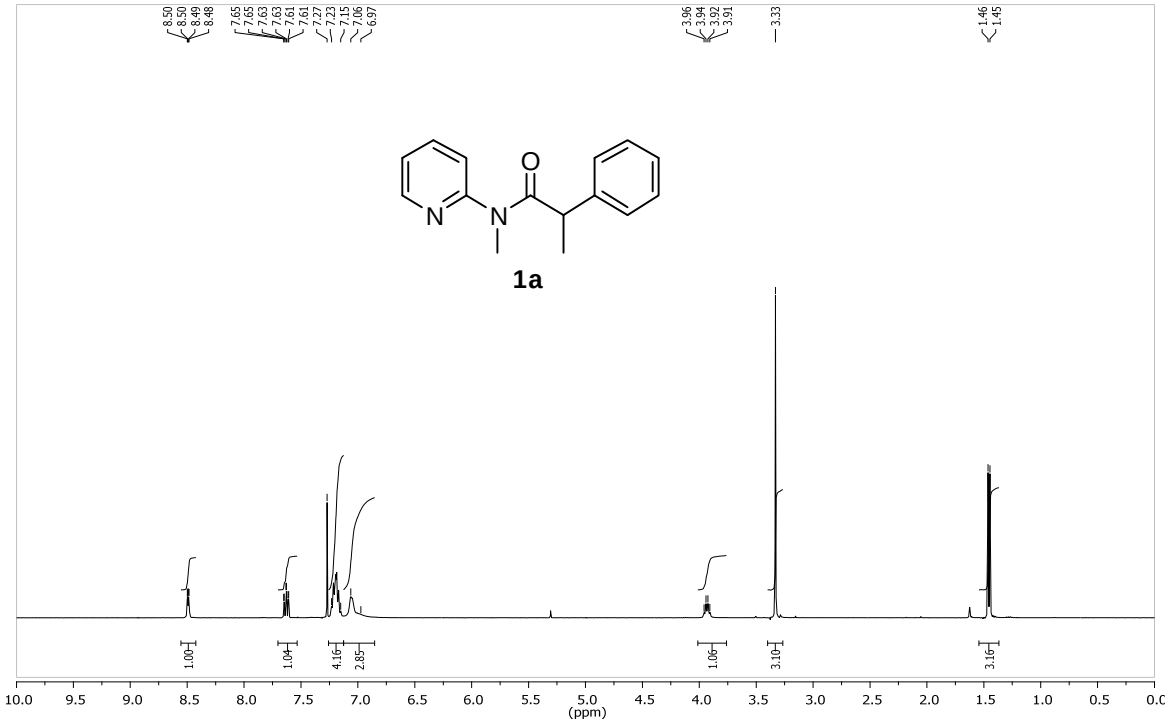
2q

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.58-7.53 (m, 1H), 7.32 (br d, *J* = 1.2 Hz, 1H), 3.38 (s, 3H), 1.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 154.4, 142.9, 142.0, 138.8, 133.8, 127.4, 126.8, 125.7 (q, *J* = 3.7 Hz), 113.4, 52.1, 26.6, 23.6.

IR (neat, cm^{-1}): 3046, 2974, 2931, 2873, 1720, 1607, 1454, 1371, 1325, 1165, 1120, 1073, 1016, 840, 735, 702, 647.

HRMS (ESI): calcd. for $C_{16}H_{14}F_3N_2O$ ($[M+H]^+$): 307.1053, found: 307.1049.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7.06
6.97
3.96
3.94
3.92
3.91
3.33
1.46
1.45
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N
N
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1.00
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4.16
2.85
1.06
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3.16
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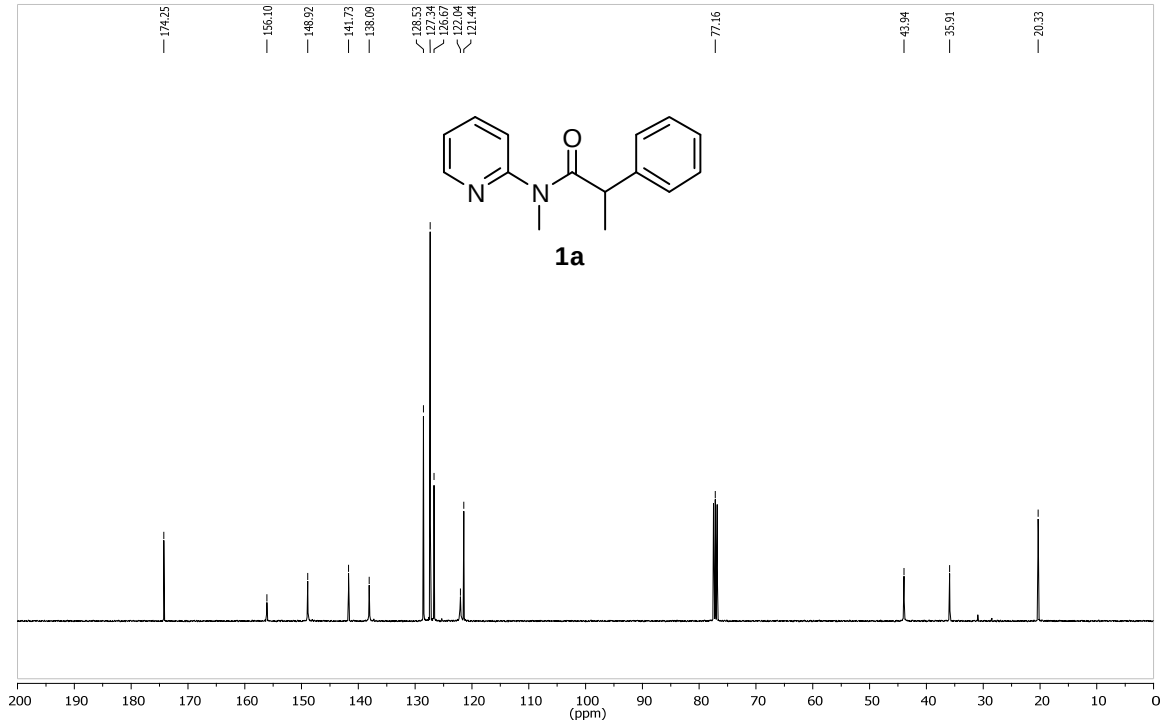
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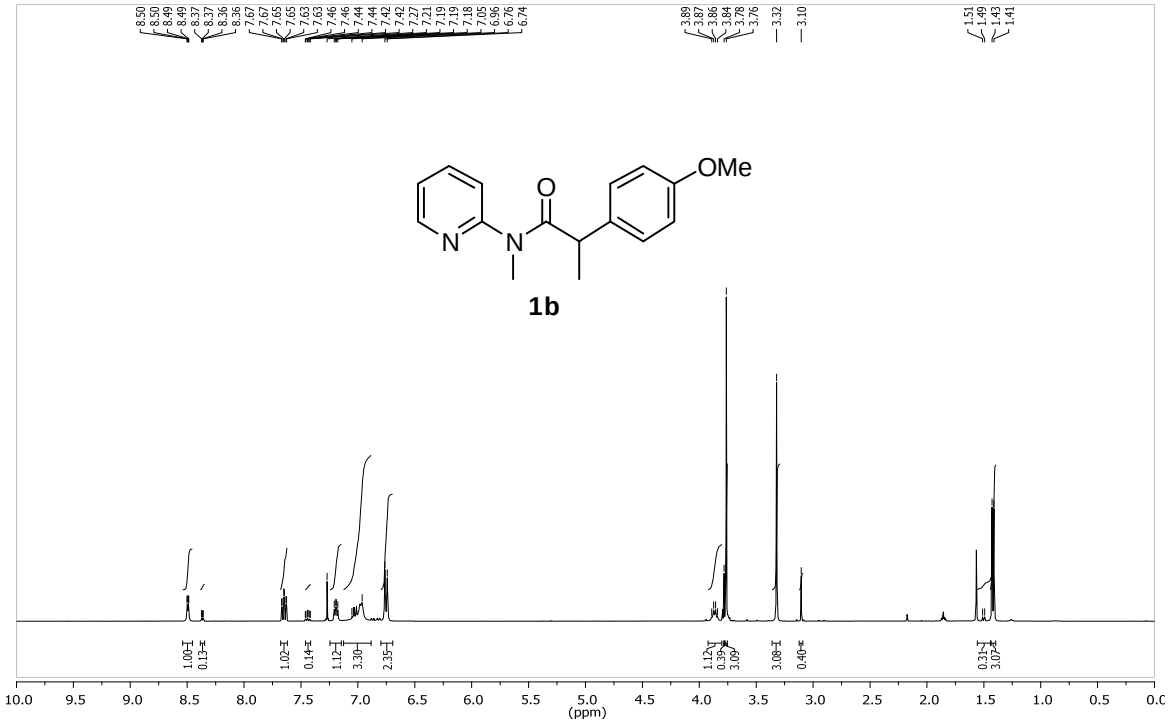
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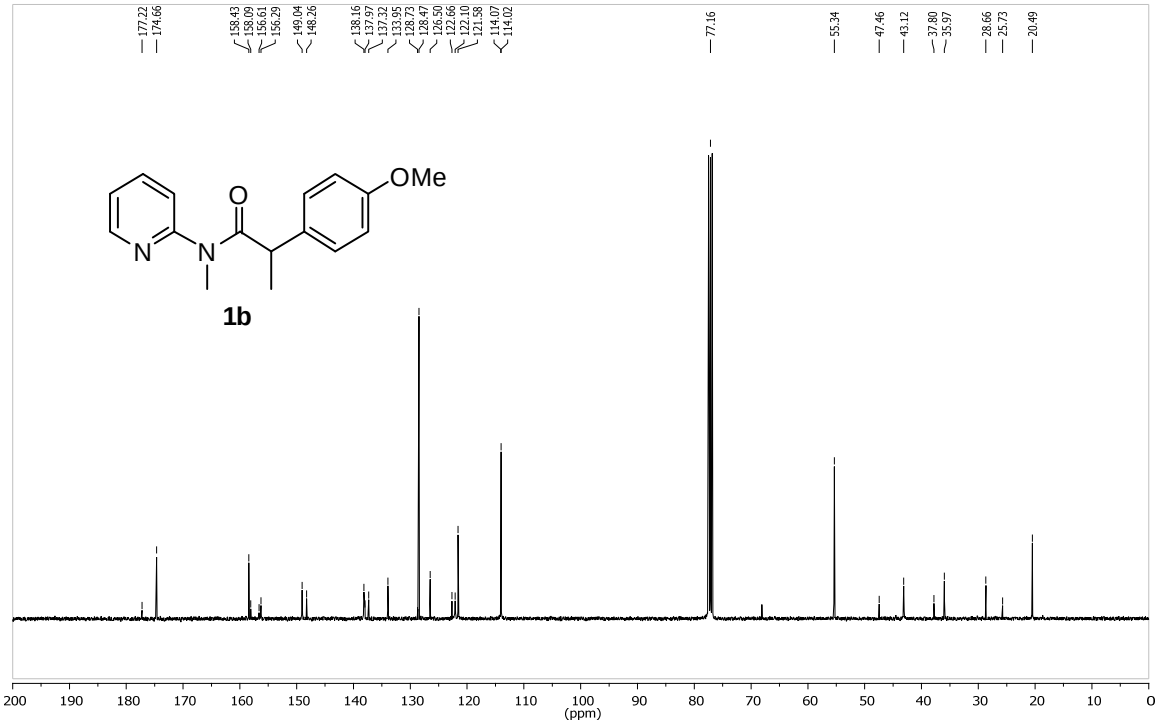
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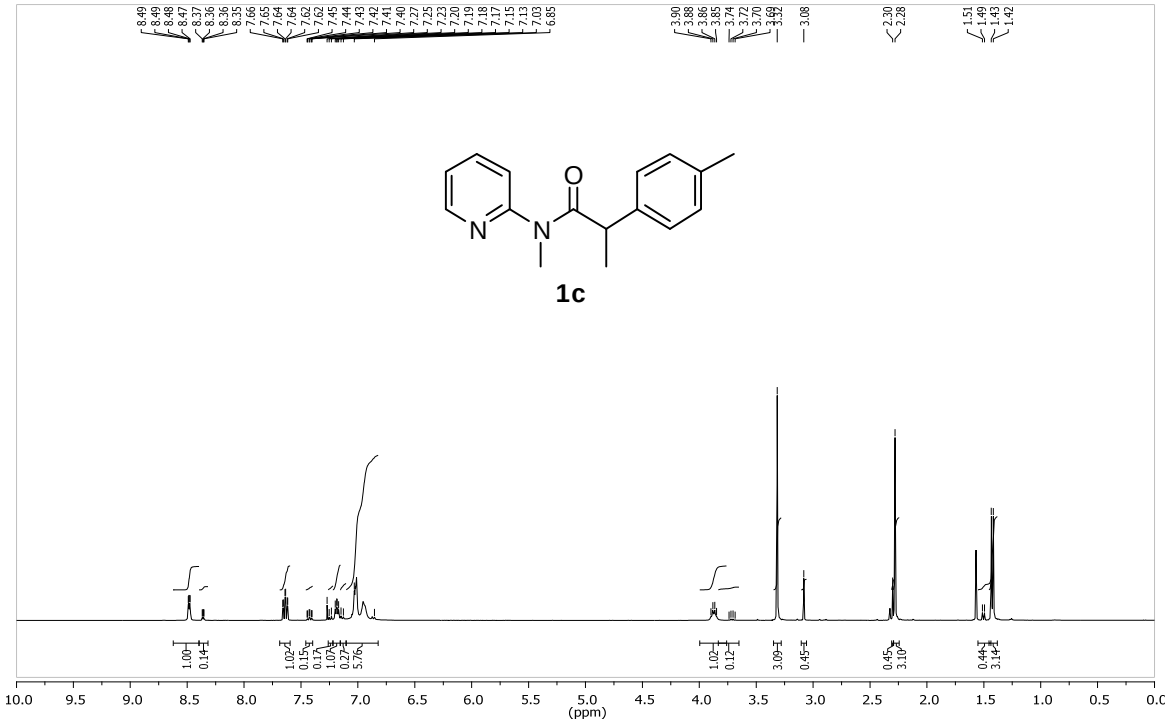
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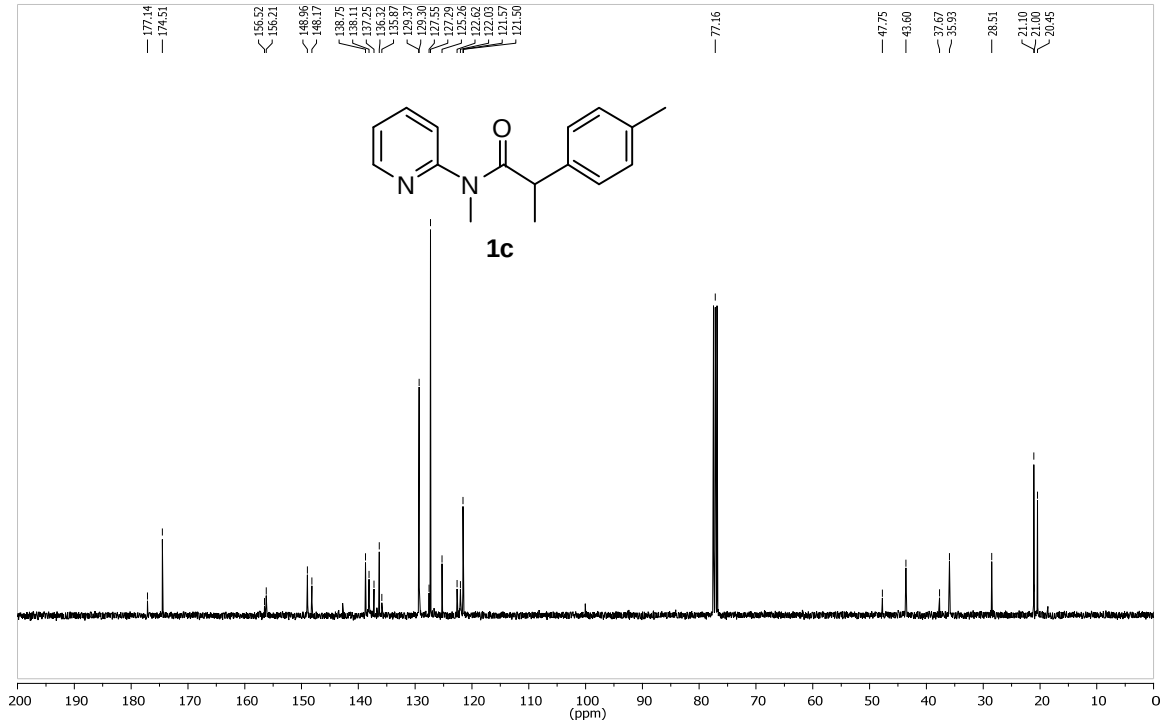
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125.26
122.62
122.03
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43.60
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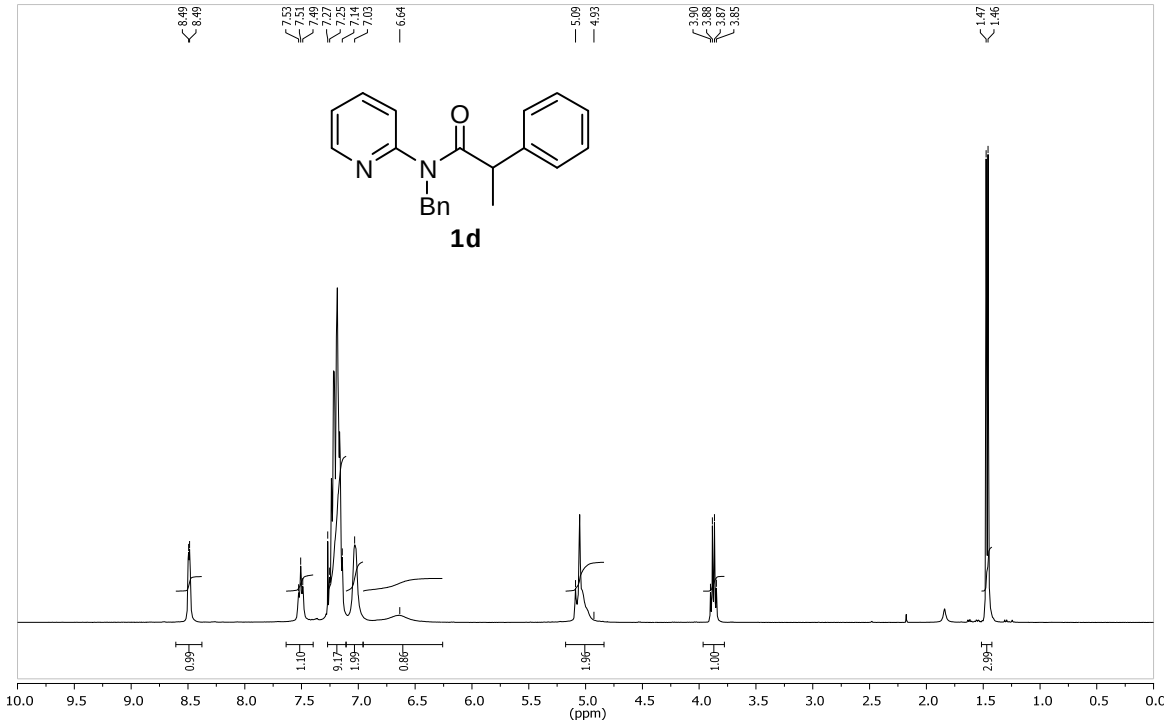
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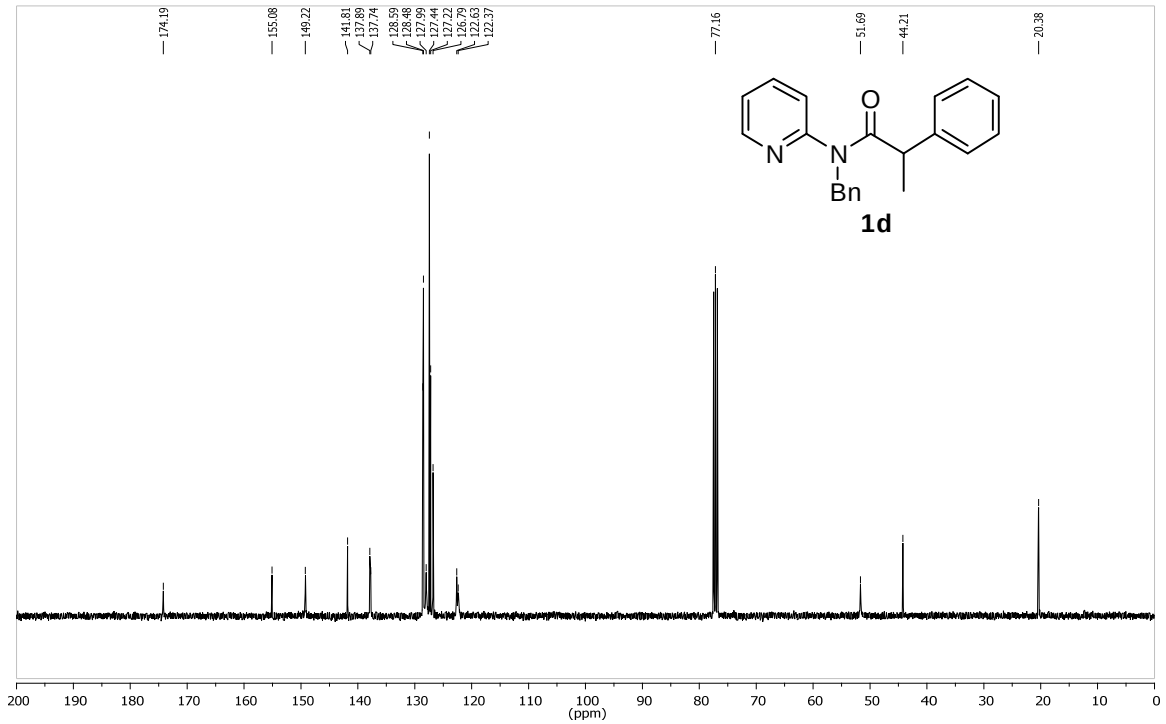
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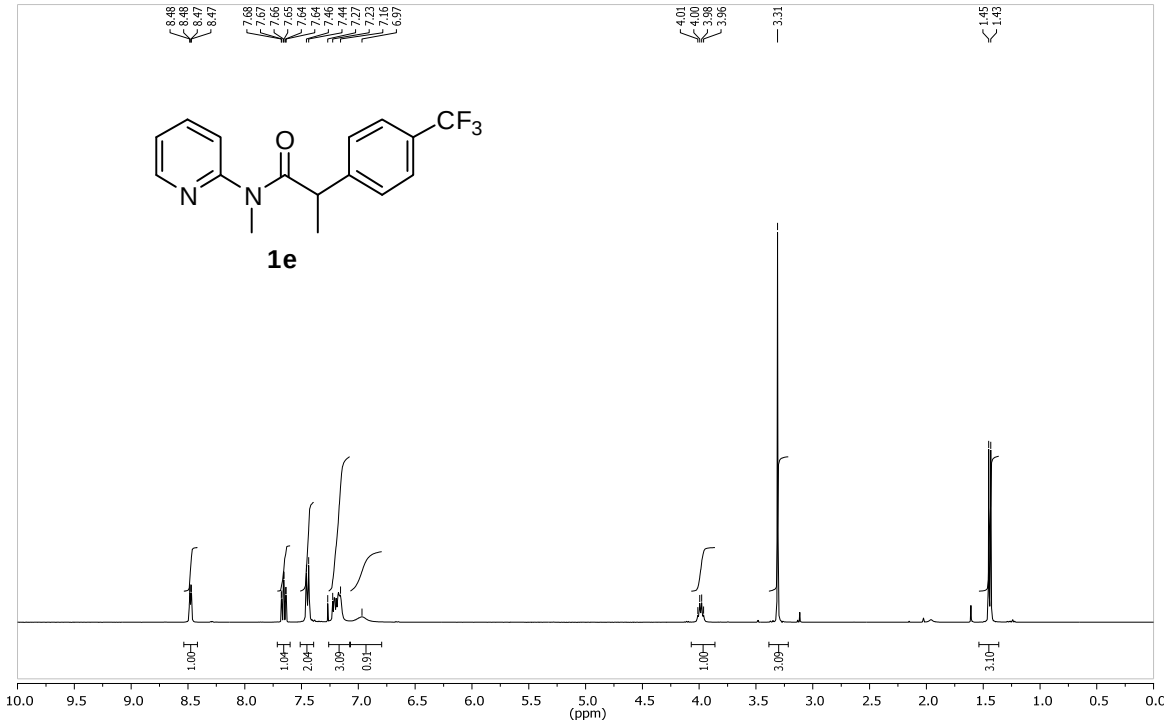
1d
(ppm)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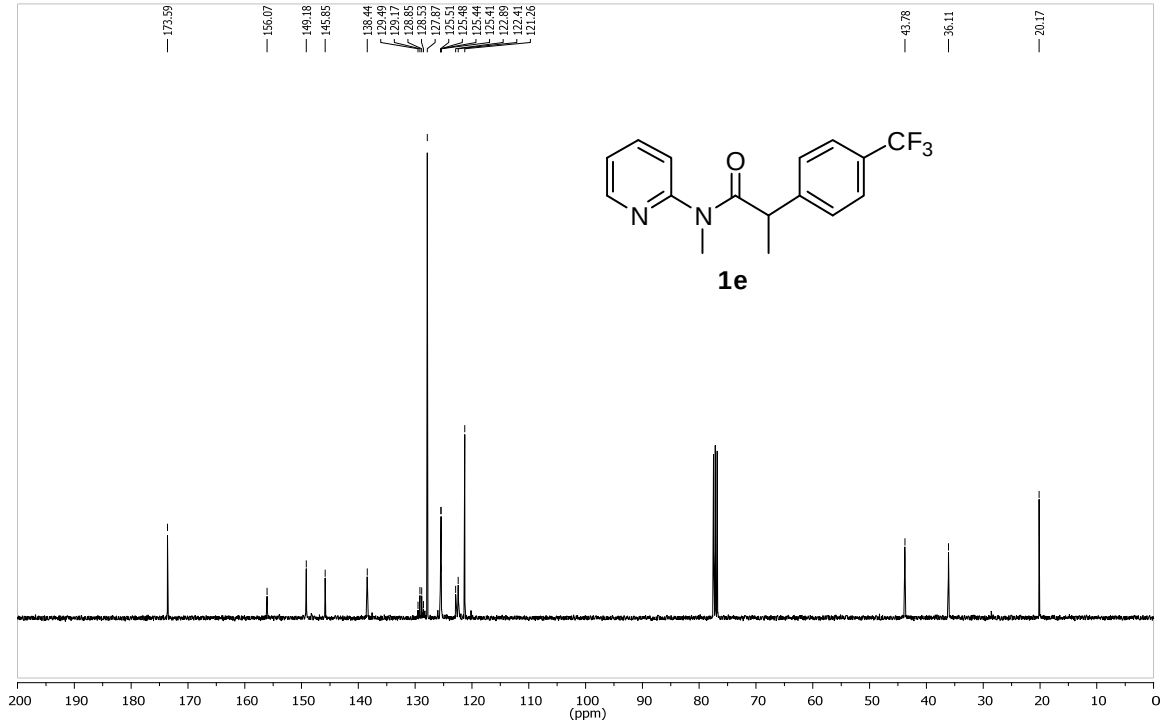
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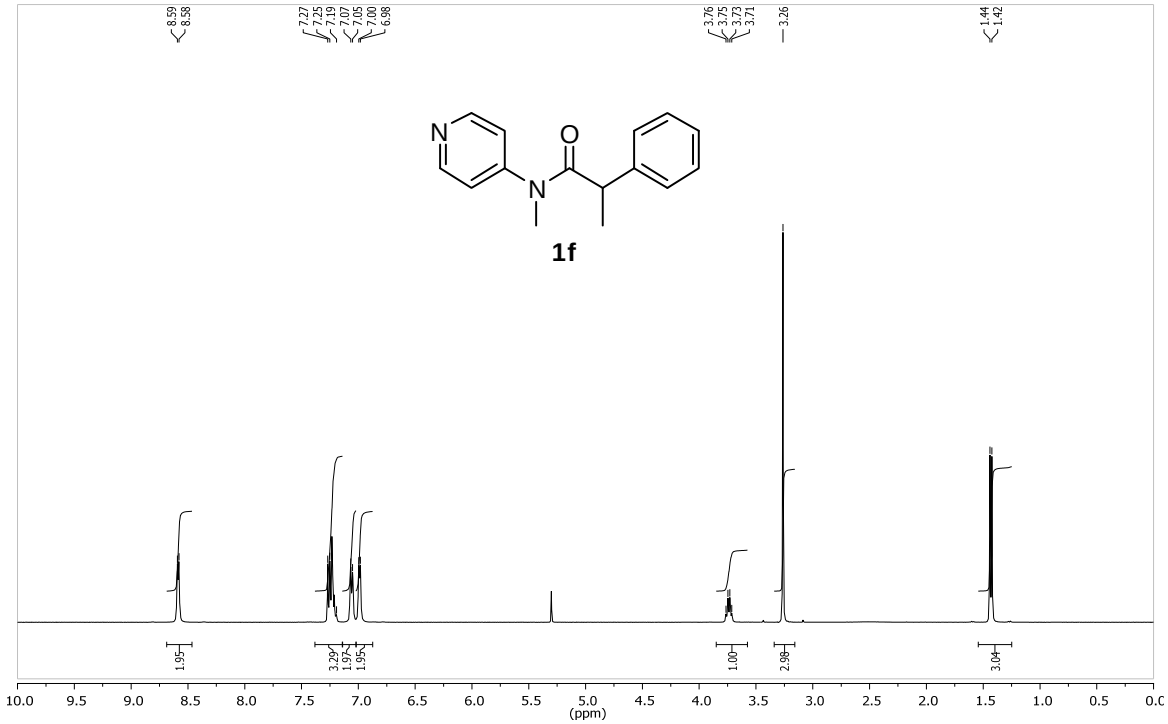
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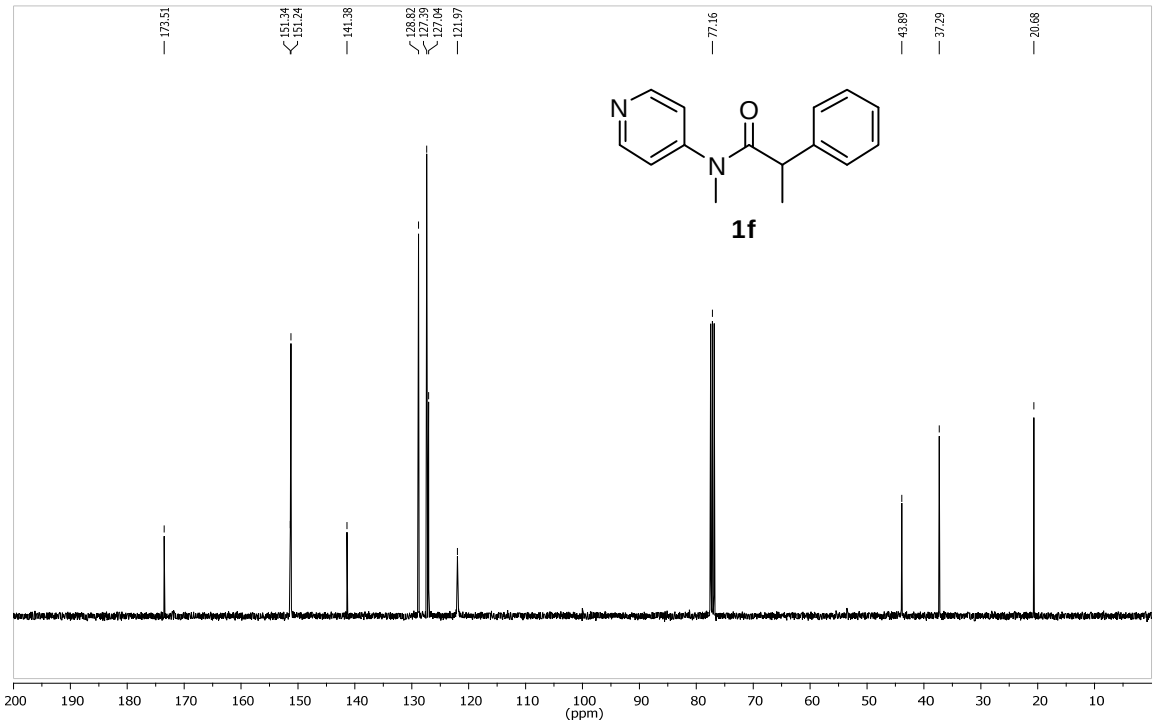
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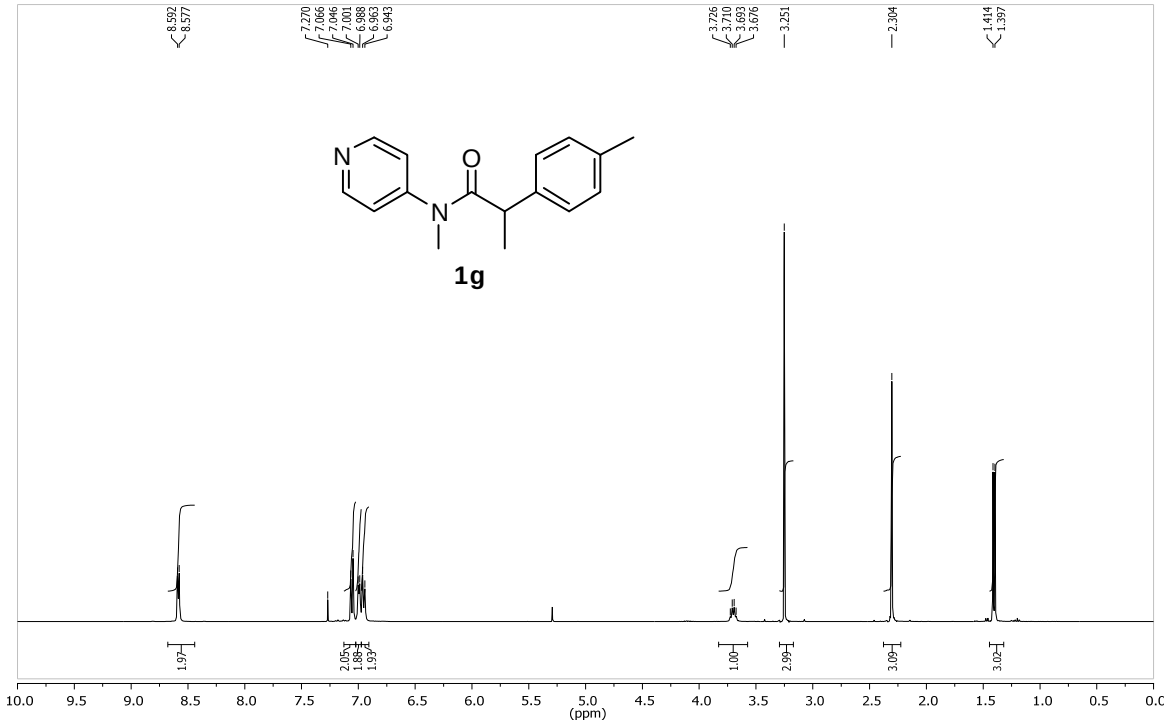
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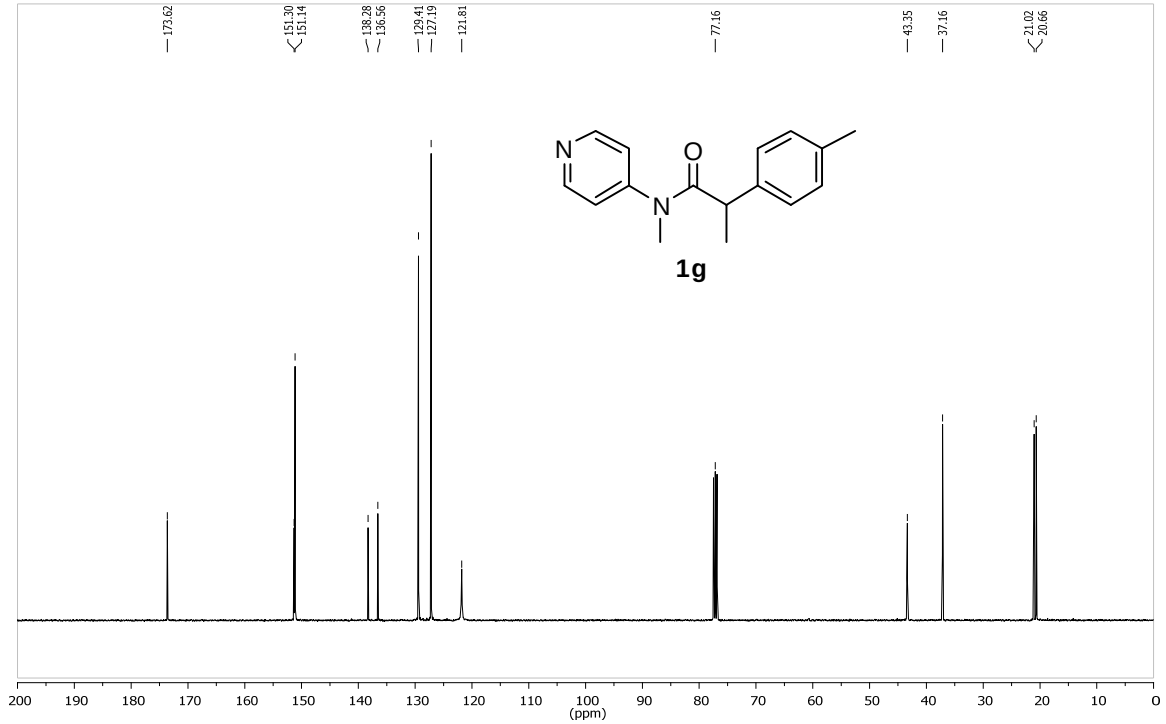
(ppm)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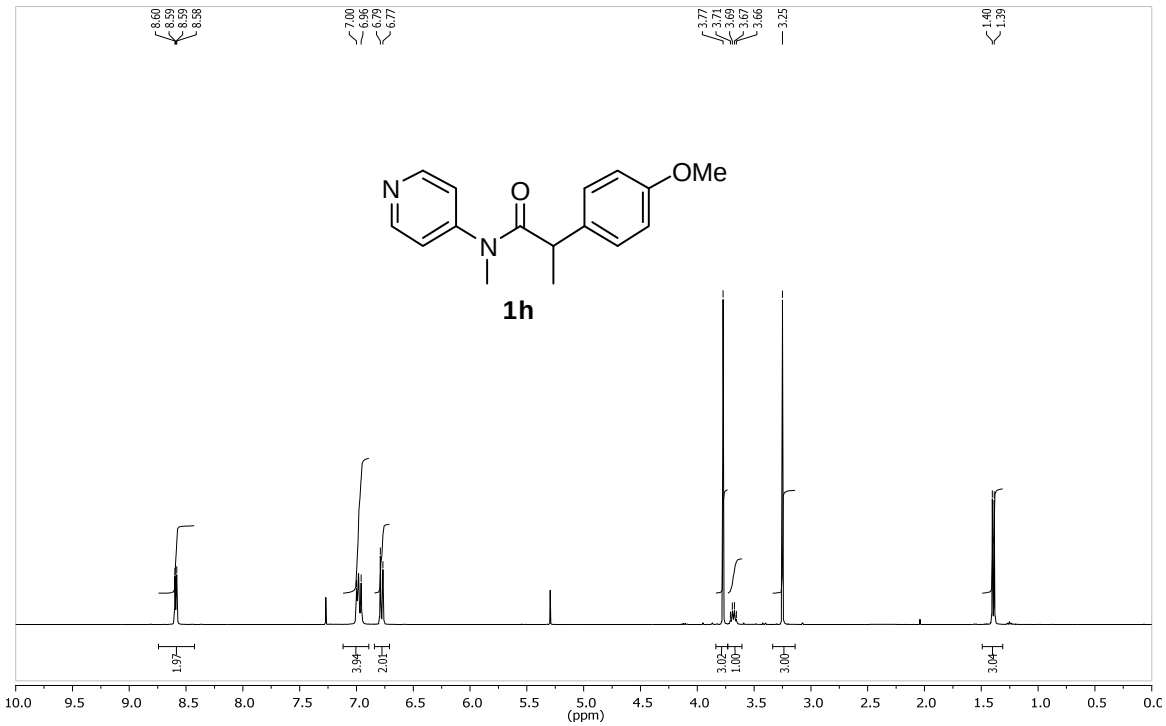
(ppm)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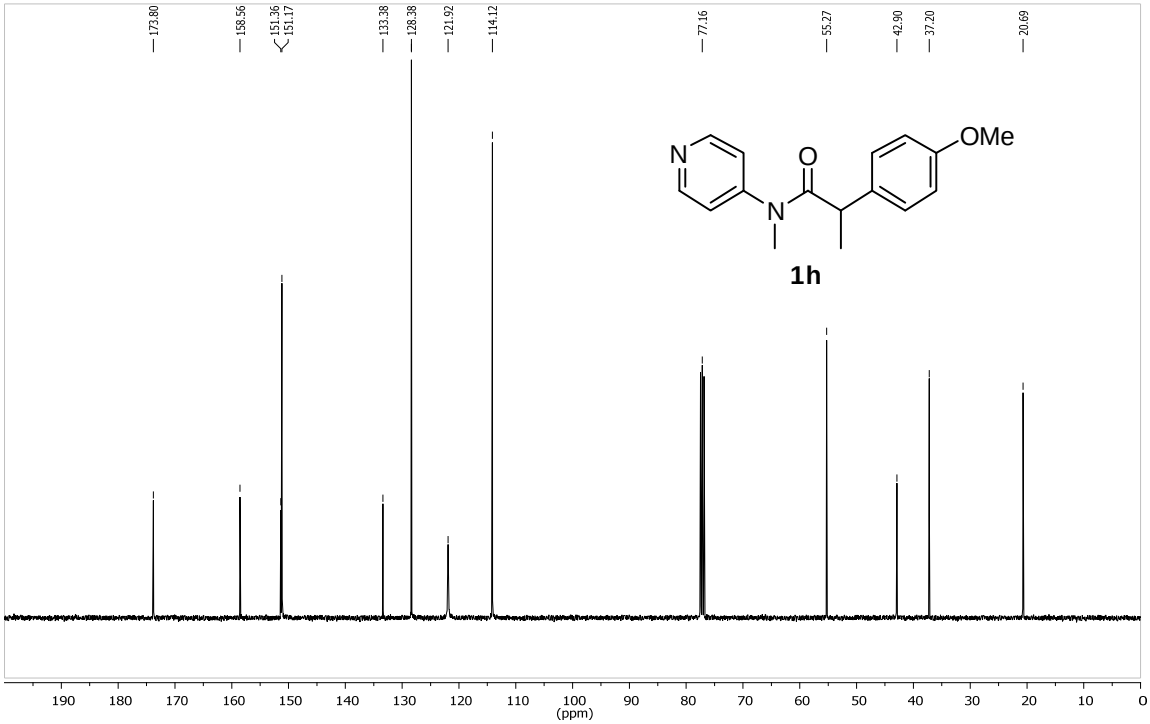
(ppm)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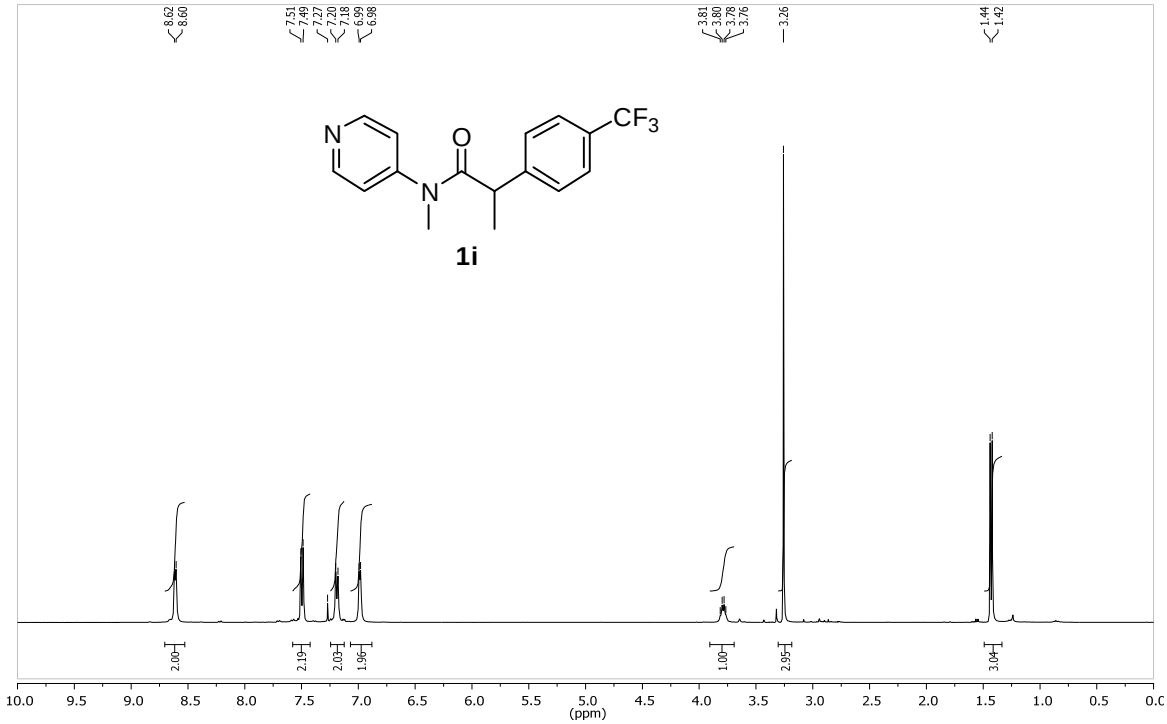
1h
(ppm)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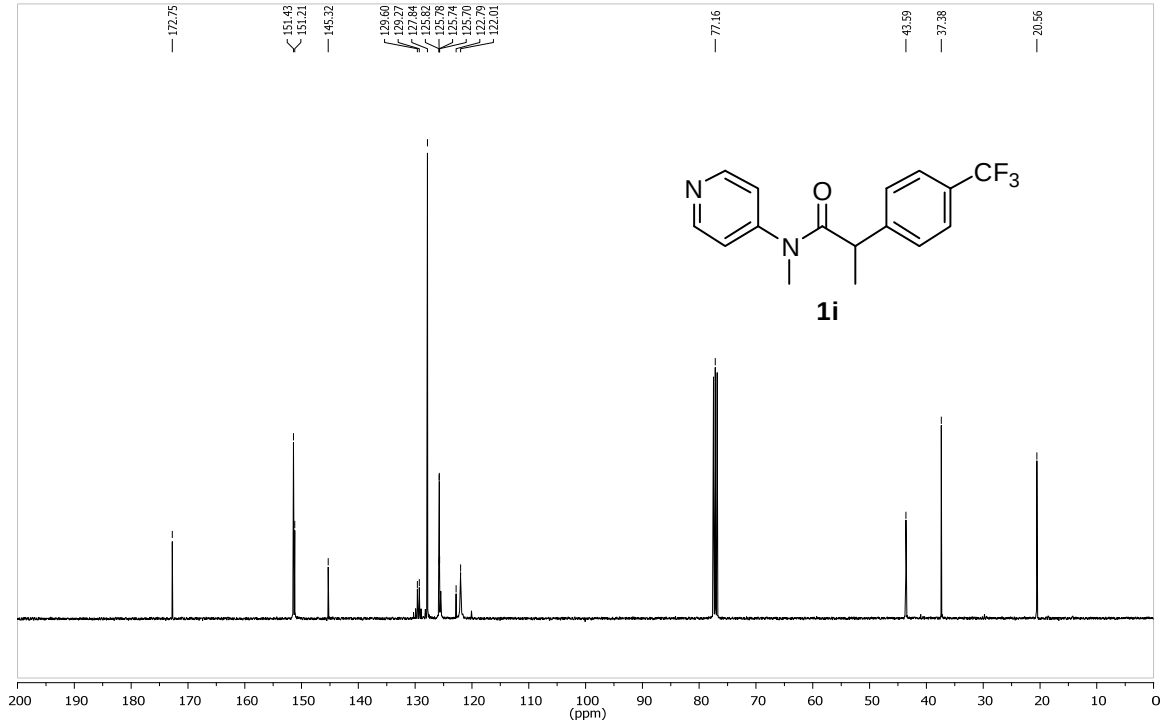
8.60
7.51
7.49
7.27
7.20
7.18
6.99
6.98
3.81
3.80
3.78
3.76
3.26
1.44
1.42
N
O
N
CF3
2.00
2.19
2.03
1.96
1.00
2.95
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

1i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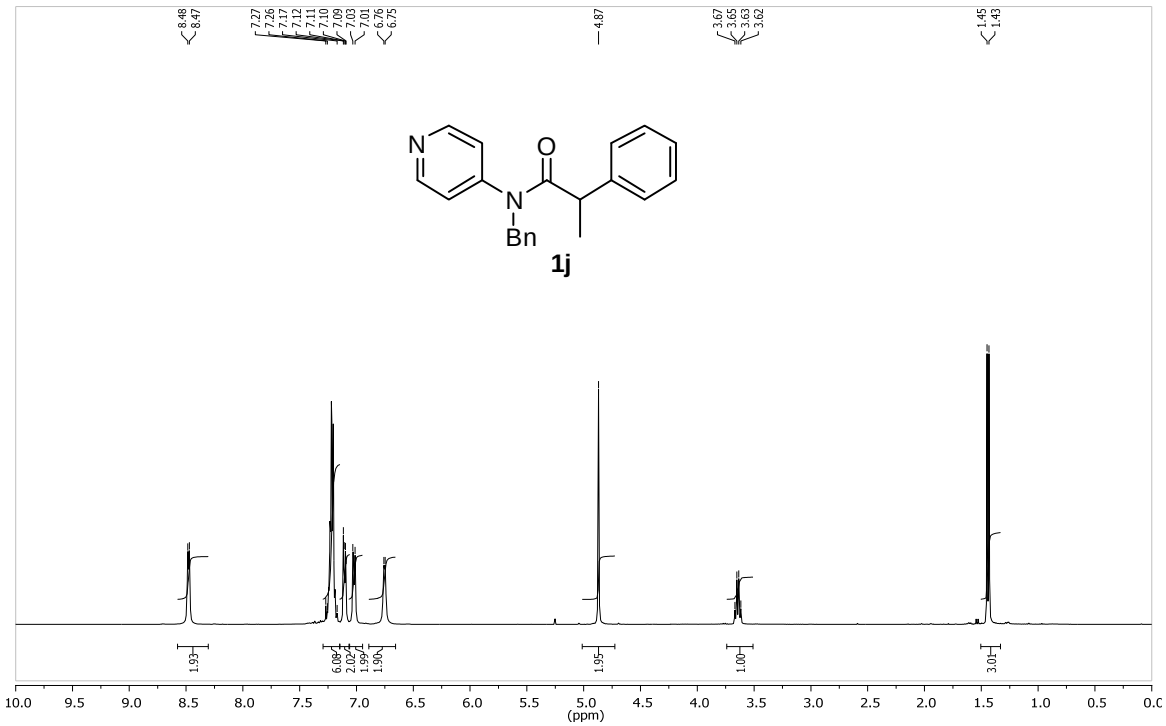
151.43
151.21
145.32
129.60
129.27
127.84
125.82
125.78
125.74
125.70
122.79
122.01
77.16
43.59
37.38
20.56
N
O
N
CF3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

1i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7.17
7.12
7.11
7.10
7.09
7.03
7.01
6.76
6.75
4.87
3.67
3.65
3.63
3.62
1.45
1.43
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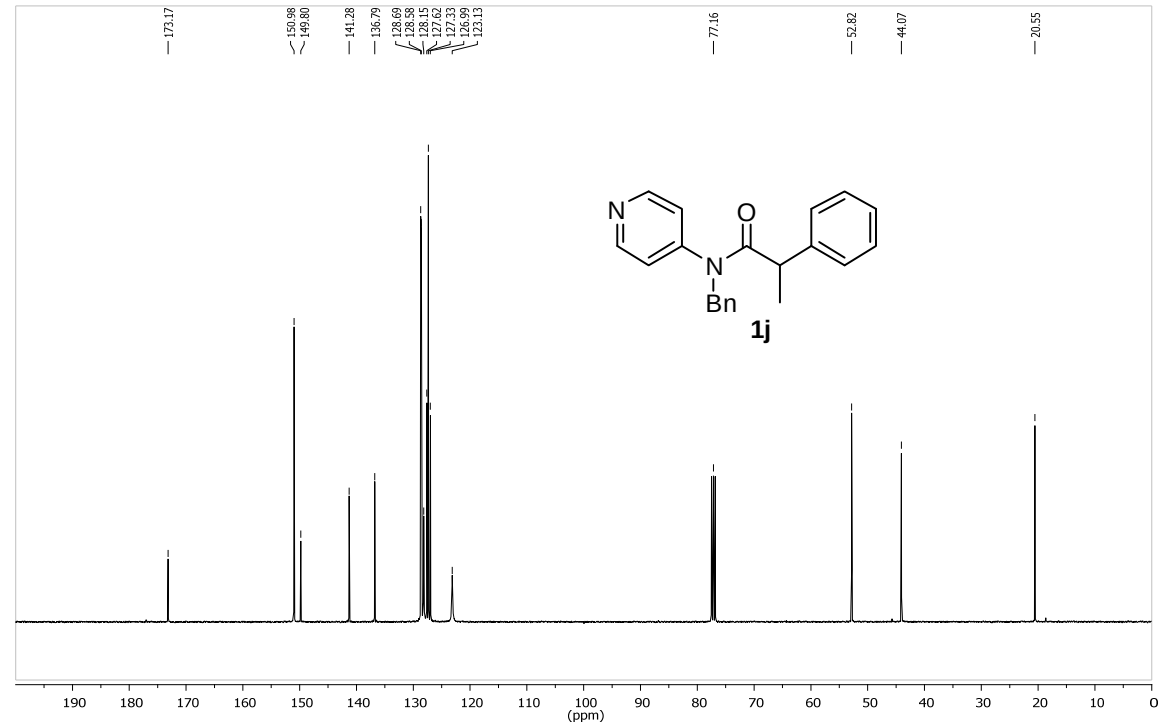
O
N
Bn
1j
1.93
6.08
2.02
1.99
1.90
1.95
1.00
3.01
(ppm)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128.15
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123.13
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52.82
44.07
20.55
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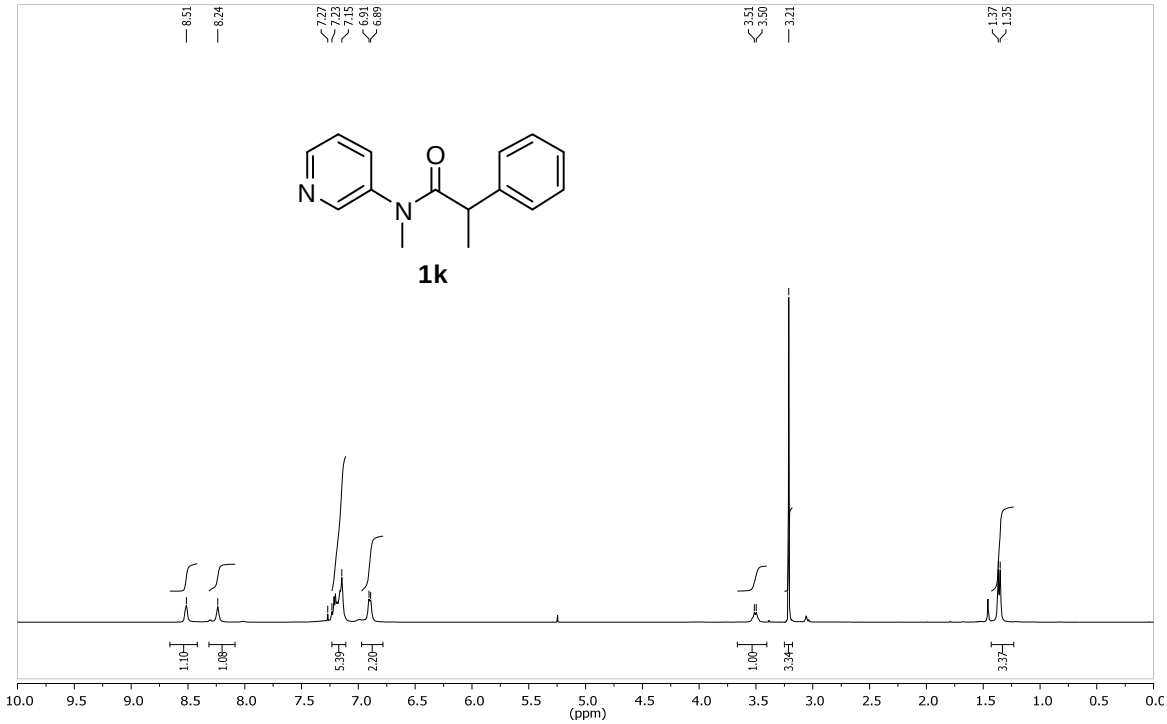
O
N
Bn
1j
(ppm)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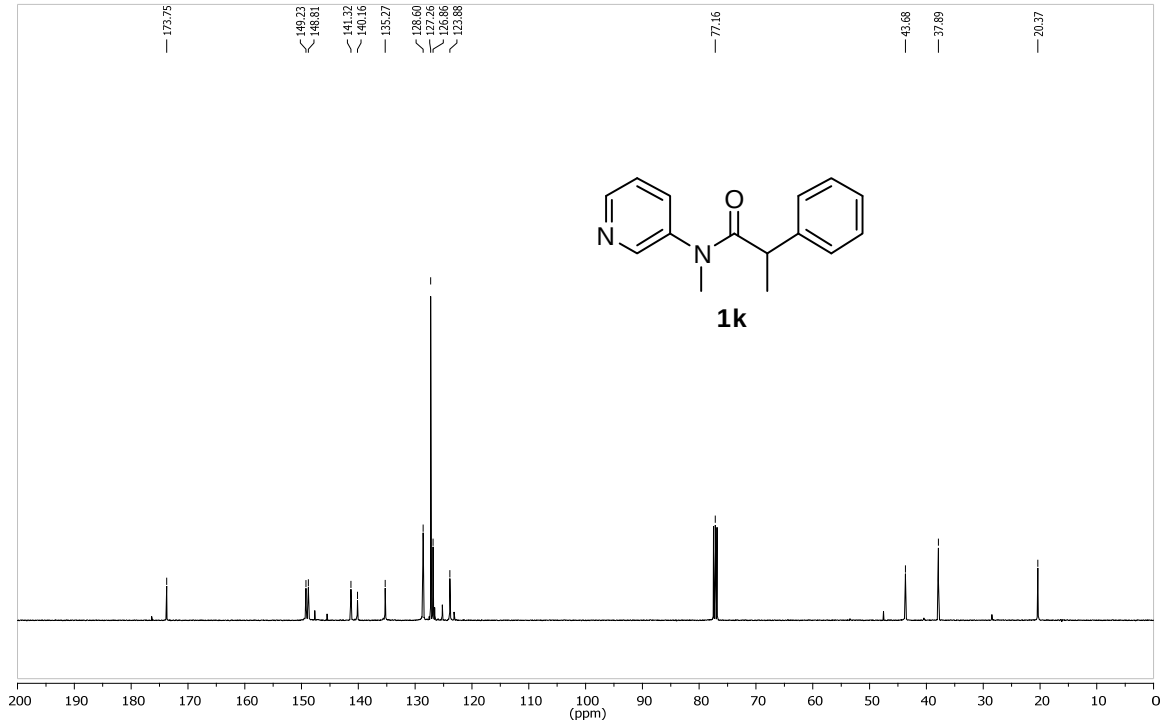
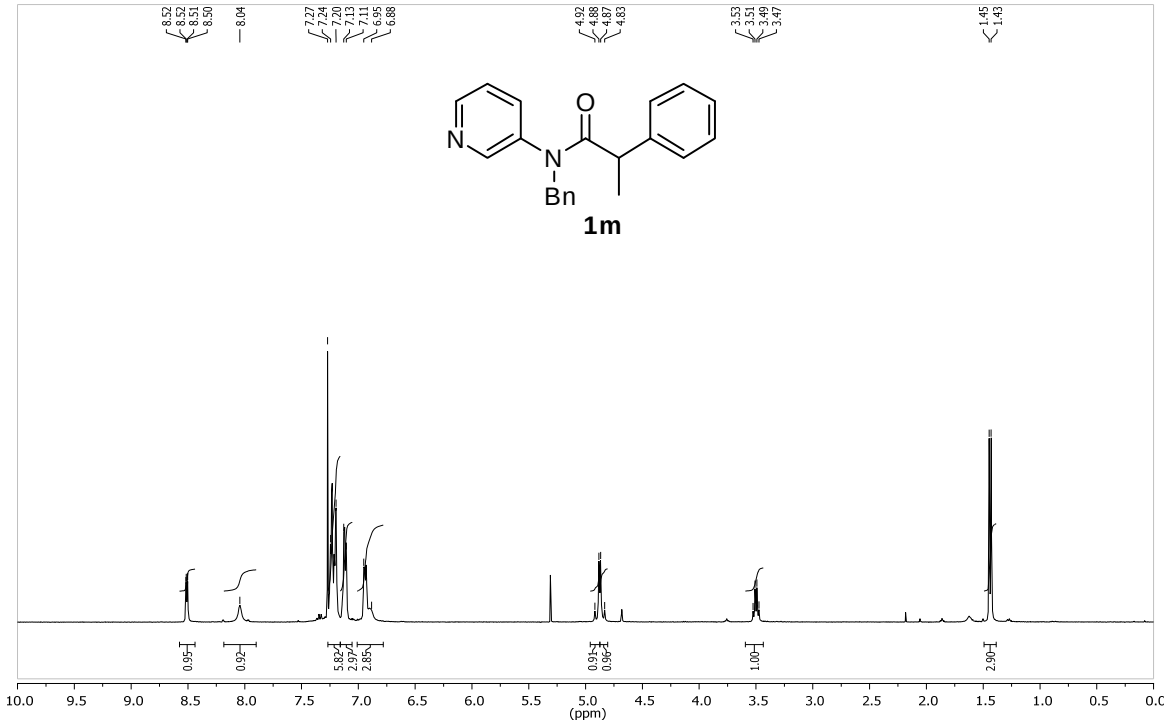
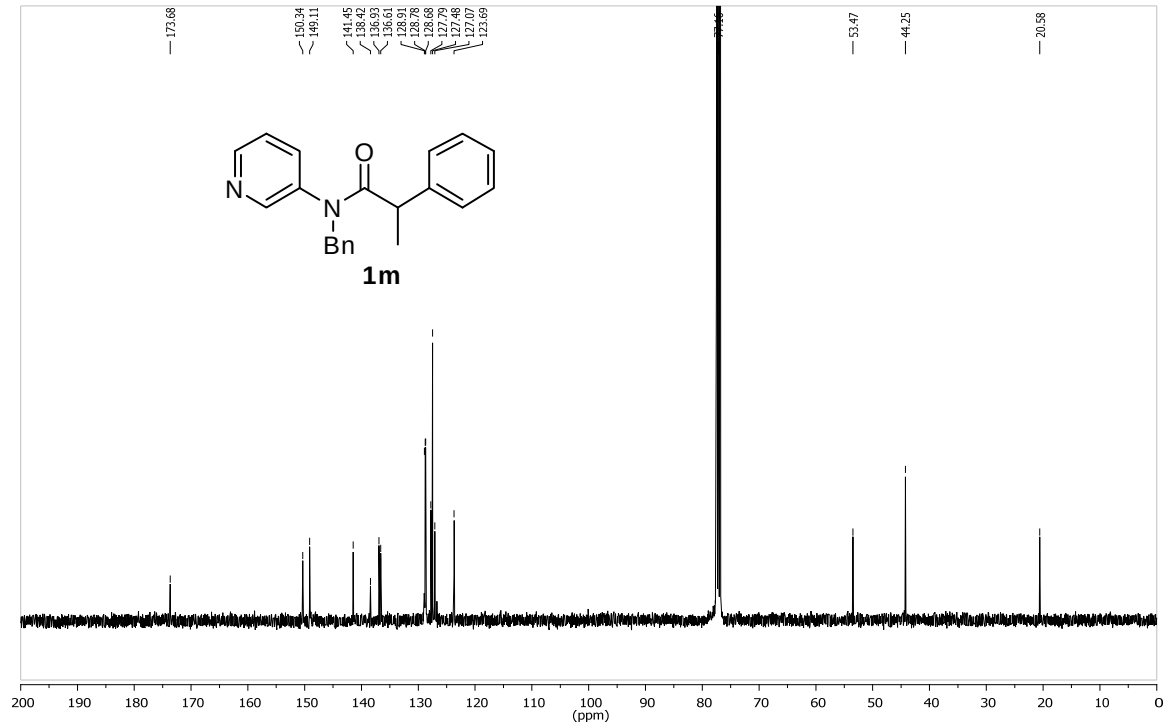
8.24
7.27
7.23
7.15
6.91
6.89
3.51
3.50
3.21
1.37
1.35
1.10
1.08
5.39
2.20
1.00
3.34
3.37
(ppm)

1k


173.75
149.23
148.81
141.32
140.16
135.27
128.60
127.26
126.86
123.88
77.16
43.68
37.89
20.37
(ppm)

1k


8.52
8.52
8.51
8.50
8.04
7.27
7.24
7.20
7.13
7.11
6.95
6.88
4.92
4.88
4.87
4.83
3.53
3.51
3.49
3.47
1.45
1.43
N
O
N
Bn
1m
0.95
0.92
5.82
2.97
2.85
0.91
0.96
1.00
2.90
(ppm)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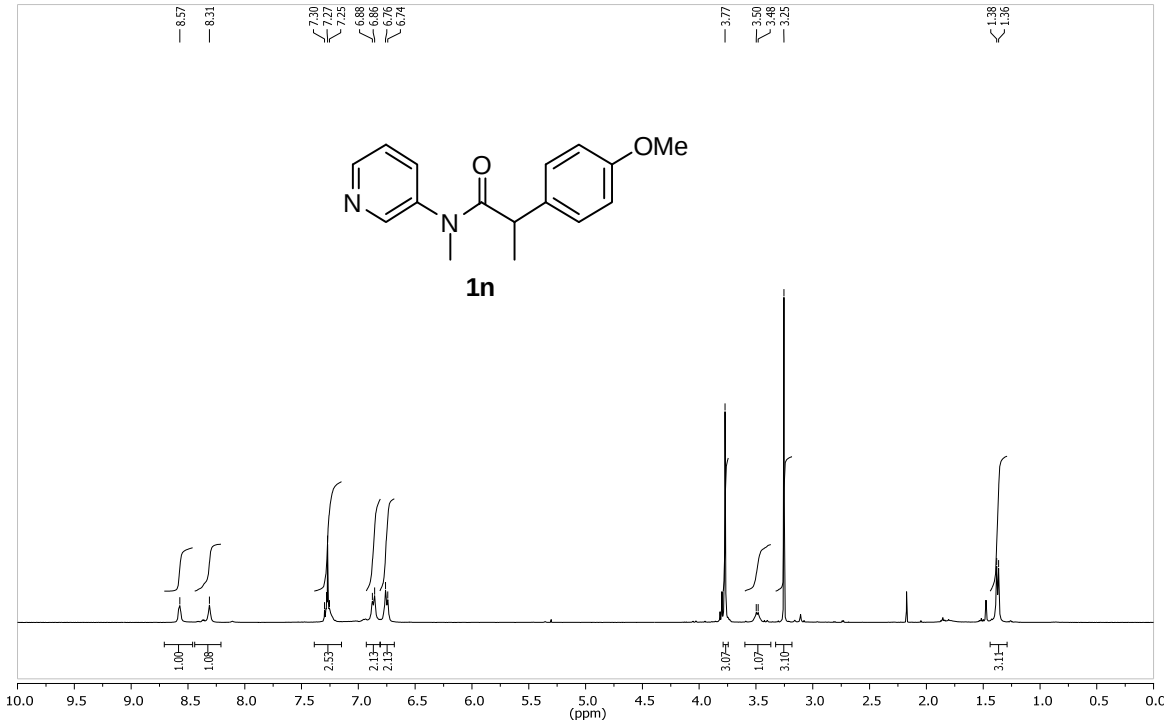
138.42
136.93
136.61
128.91
128.78
128.68
127.79
127.48
127.07
123.69
53.47
44.25
20.58
N
O
N
Bn
1m
(ppm)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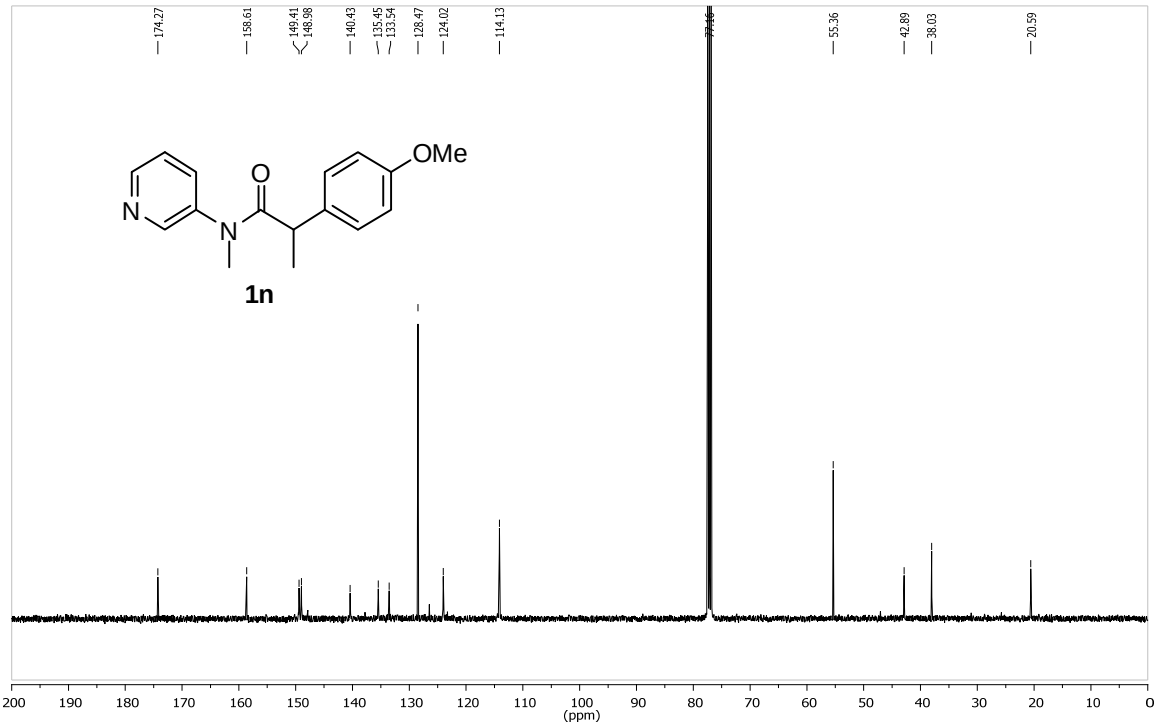
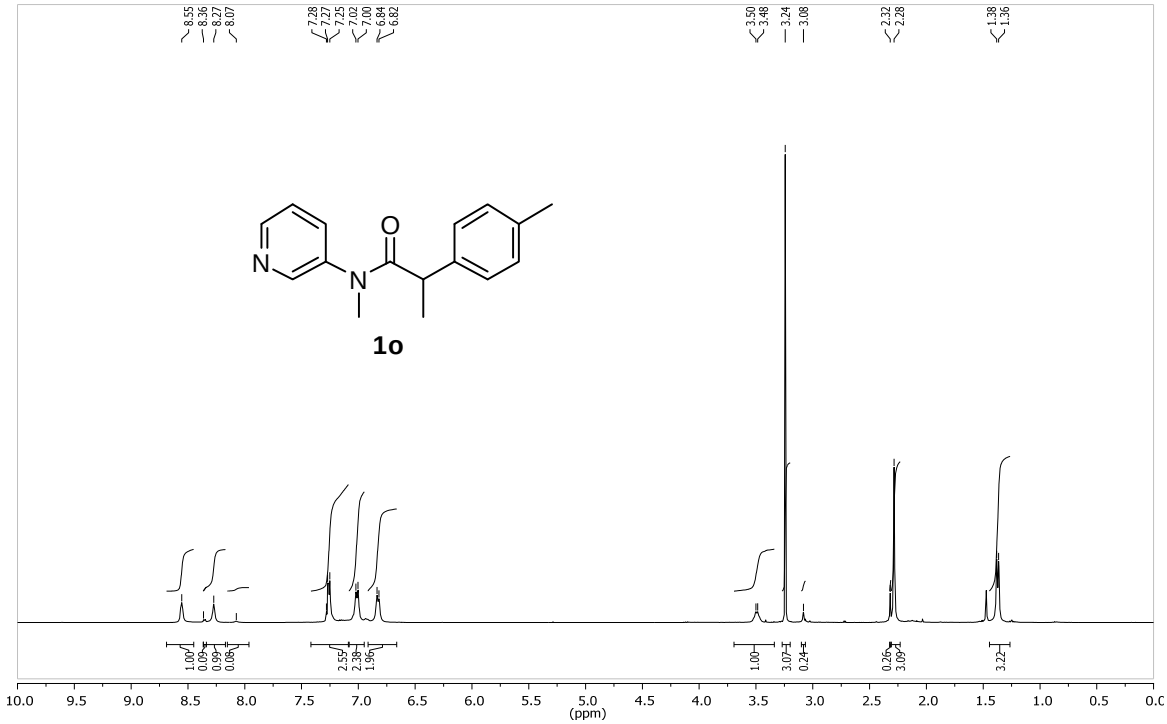
8.31
7.30
7.27
7.25
6.88
6.86
6.76
6.74
3.77
3.50
3.48
3.25
1.38
1.36
OMe
O
N
N
1n
1.00
1.08
2.53
2.13
2.13
3.07
1.07
3.10
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


174.27
158.61
149.41
148.98
140.43
135.45
133.54
128.47
124.02
114.13
77.16
55.36
42.89
38.03
20.59
OMe
O
N
N
1n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)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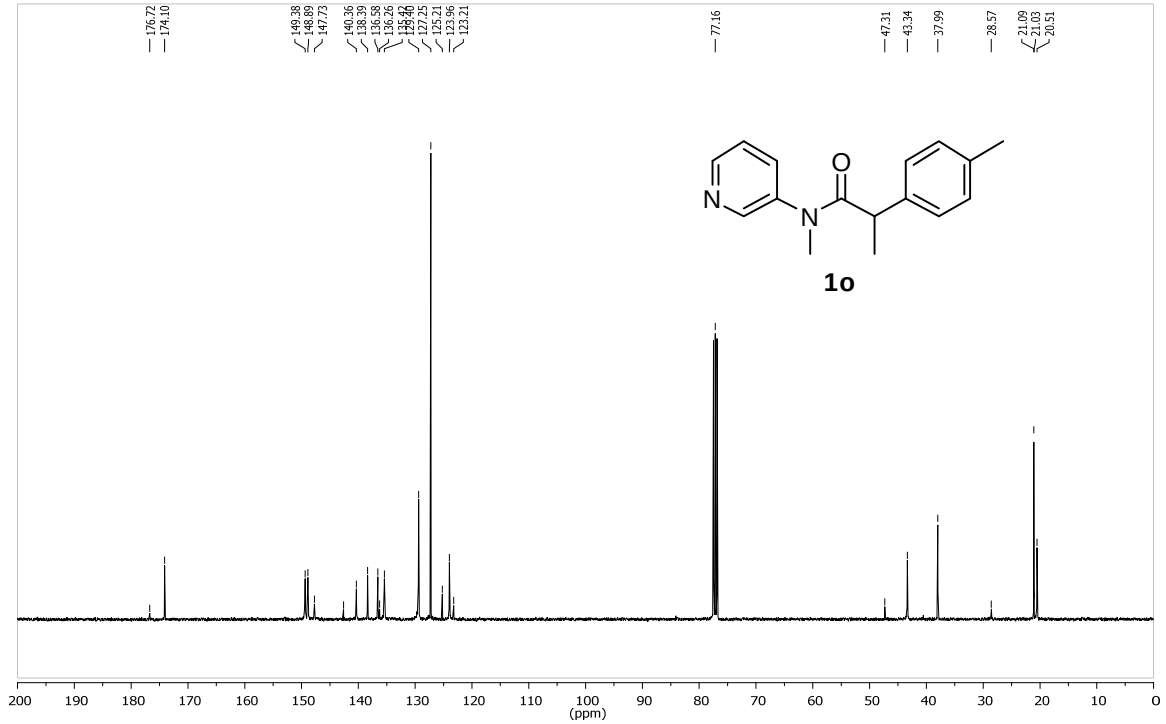
8.36
8.27
8.07
7.28
7.27
7.25
7.02
7.00
6.84
6.82
3.50
3.48
3.24
3.08
2.32
2.28
1.38
1.36
1.00
0.09
0.99
0.08
2.55
2.38
1.96
1.00
3.07
0.24
0.26
3.09
3.22
O
N
N
1o
(ppm)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174.10
149.38
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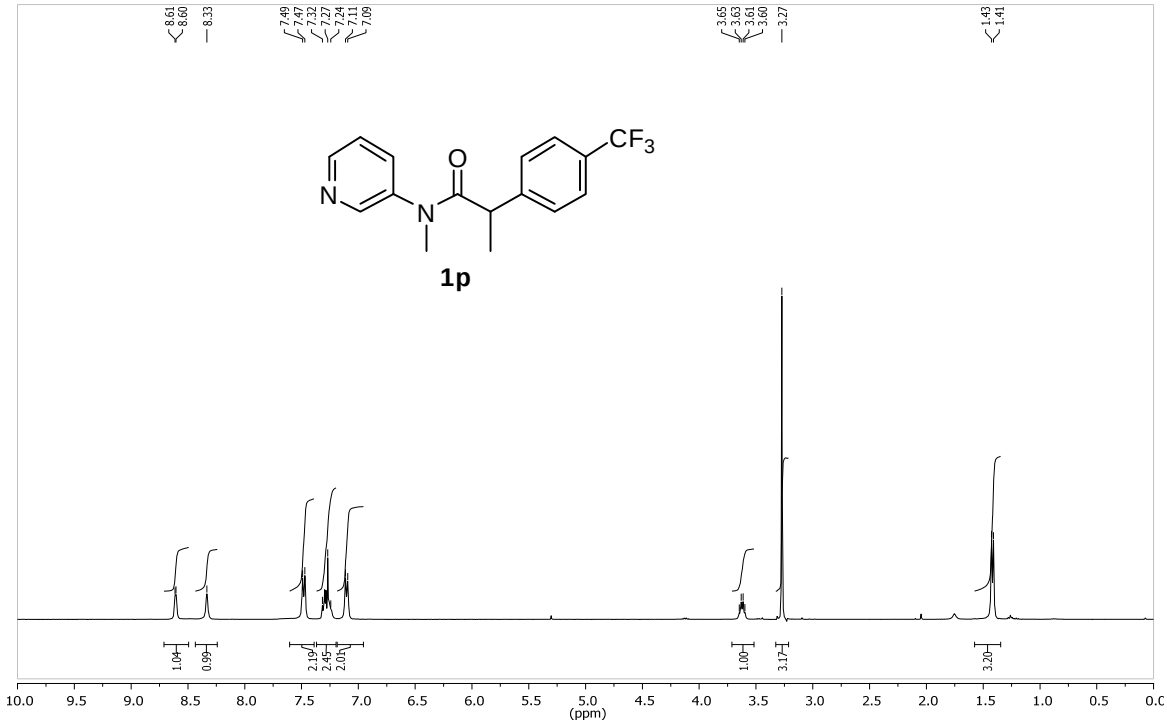
140.36
138.39
136.58
136.26
135.42
129.40
127.25
125.21
123.96
123.21
77.16
47.31
43.34
37.99
28.57
21.09
21.03
20.51
O
N
N
1o
(ppm)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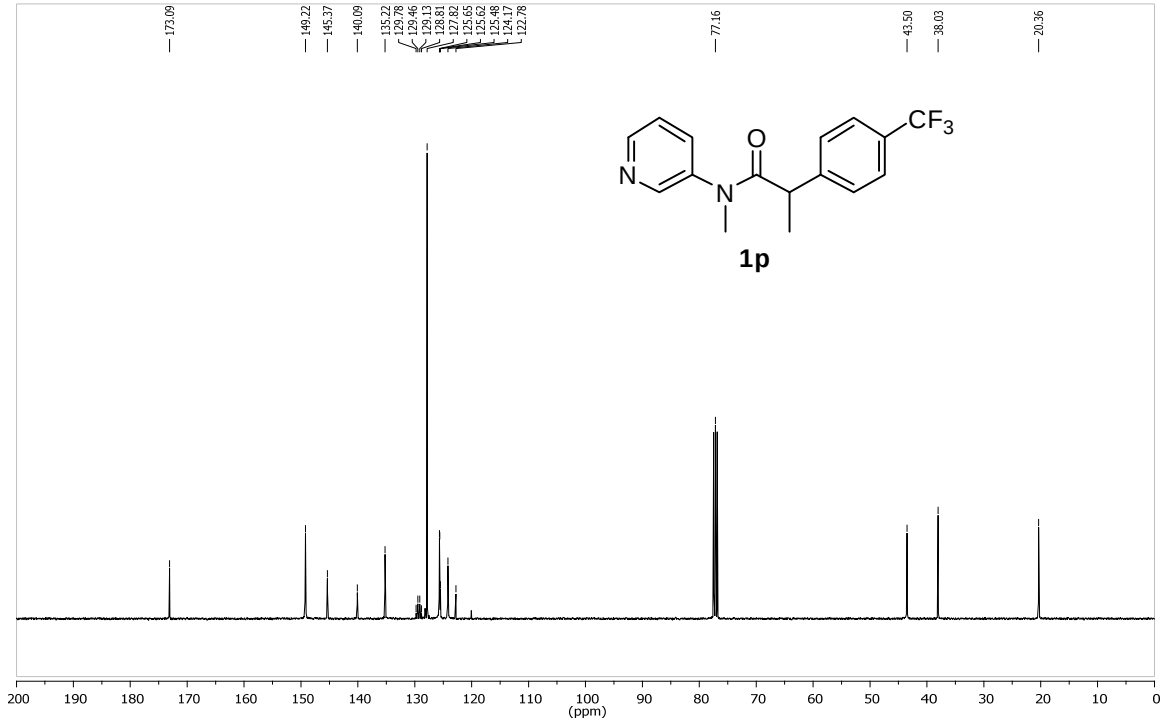
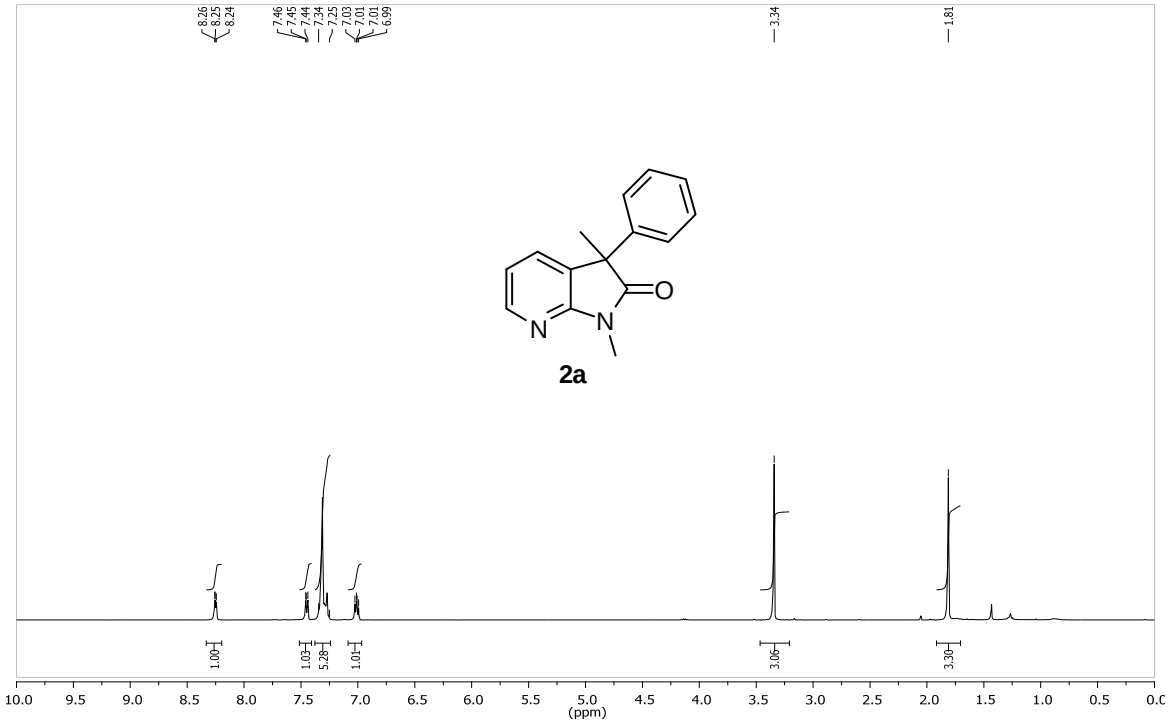
8.60
8.33
7.49
7.47
7.32
7.27
7.24
7.11
7.09
3.65
3.63
3.61
3.60
3.27
1.43
1.41
CF3
O
N
N
1p
1.04
0.99
2.19
2.45
2.01
1.00
3.17
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


173.09
149.22
145.37
140.09
135.22
129.78
129.46
129.13
128.81
127.82
125.65
125.62
125.48
124.17
122.78
77.16
43.50
38.03
20.36
CF3
O
N
N
1p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)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8.25
8.24
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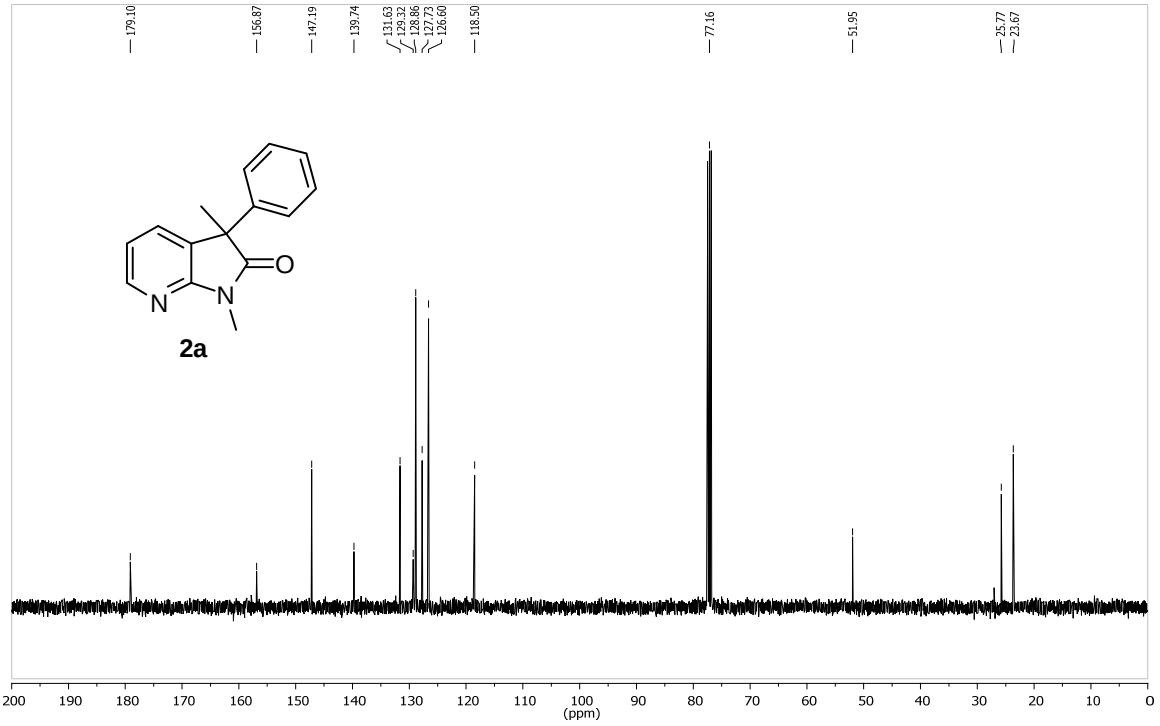
7.44
7.34
7.25
7.03
7.01
7.01
6.99
3.34
1.81
O
N
N
2a
1.00
1.03
5.28
1.01
3.06
3.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)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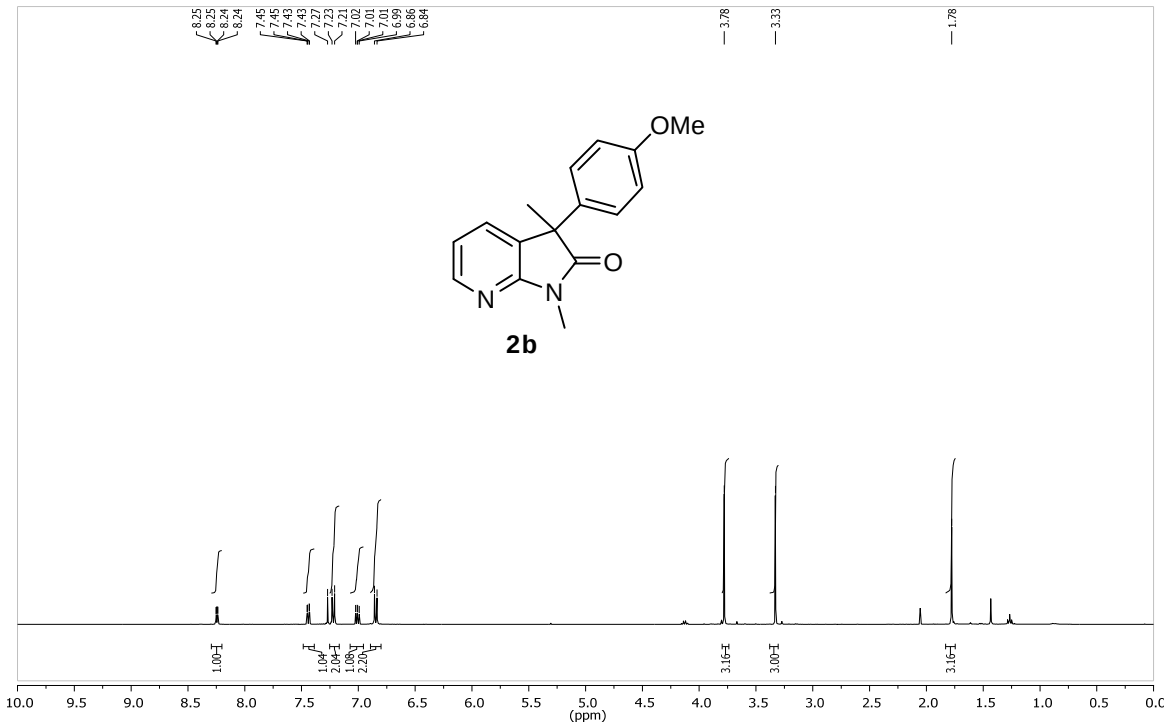
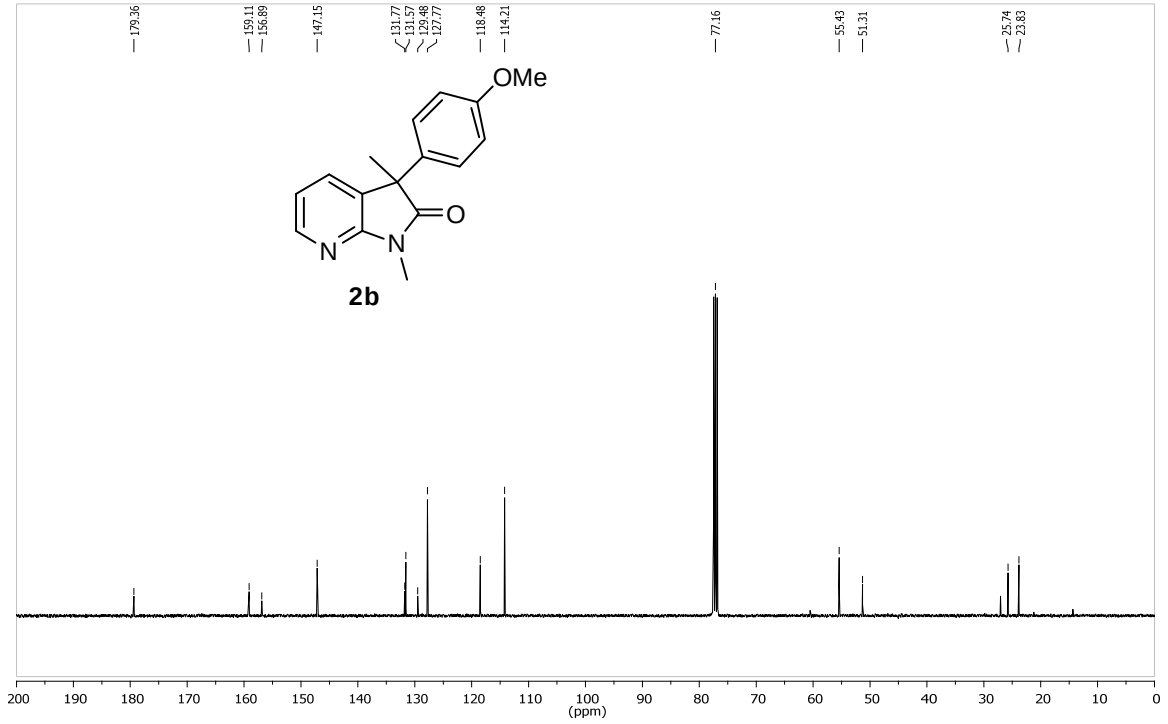
129.32
128.86
127.73
126.60
118.50
77.16
51.95
25.77
23.67
O
N
N
2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


8.25
8.25
8.24
8.24
7.45
7.45
7.43
7.43
7.27
7.23
7.21
7.02
7.01
7.01
6.99
6.86
6.84
3.78
3.33
1.78
OMe
O
N
N
2b
1.00
1.04
2.04
1.08
2.20
3.16
3.00
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)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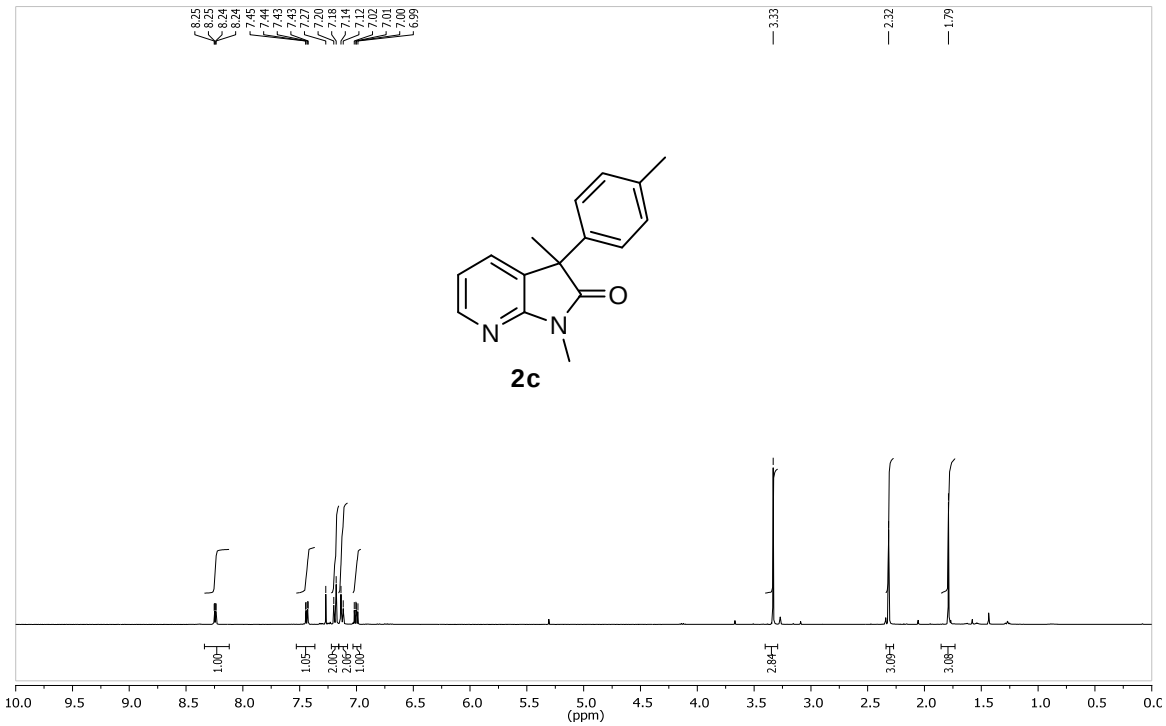
159.11
156.89
147.15
131.77
131.57
129.48
127.77
118.48
114.21
77.16
55.43
51.31
25.74
23.83
OMe
O
N
N
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)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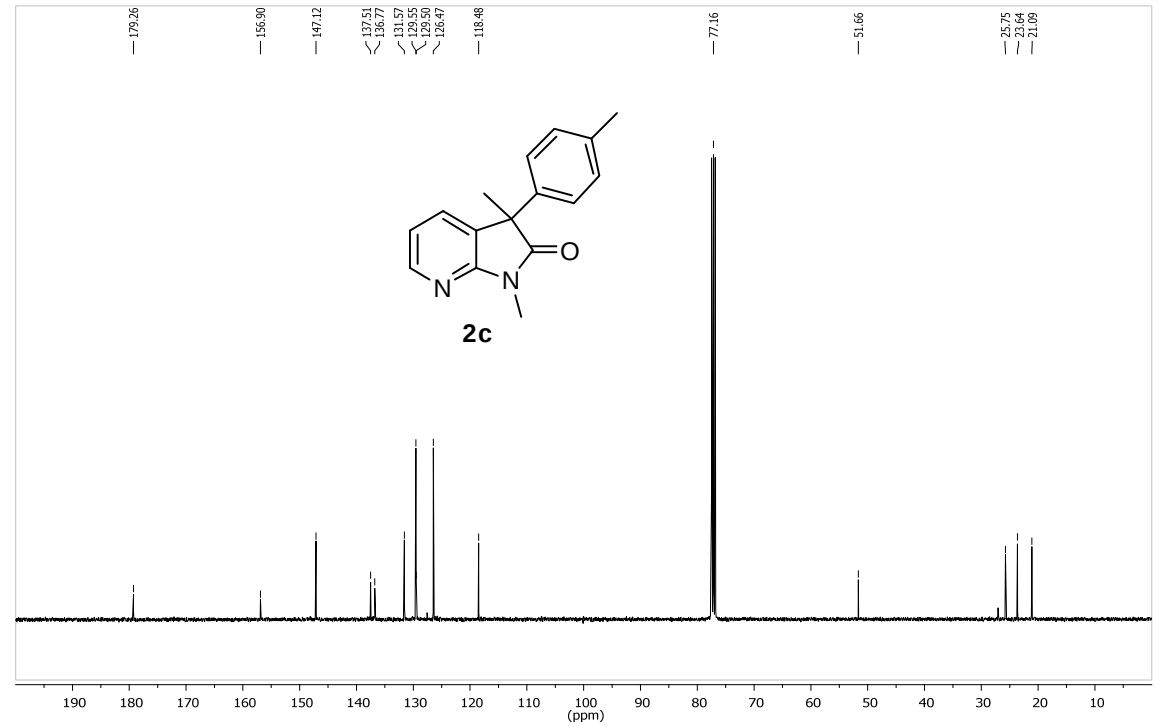
8.25
8.24
8.24
7.45
7.44
7.43
7.43
7.27
7.20
7.18
7.14
7.12
7.02
7.01
7.00
6.99
3.33
2.32
1.79
2c
1.00
1.05
2.00
2.06
1.00
2.84
3.09
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)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136.77
131.57
129.55
129.50
126.47
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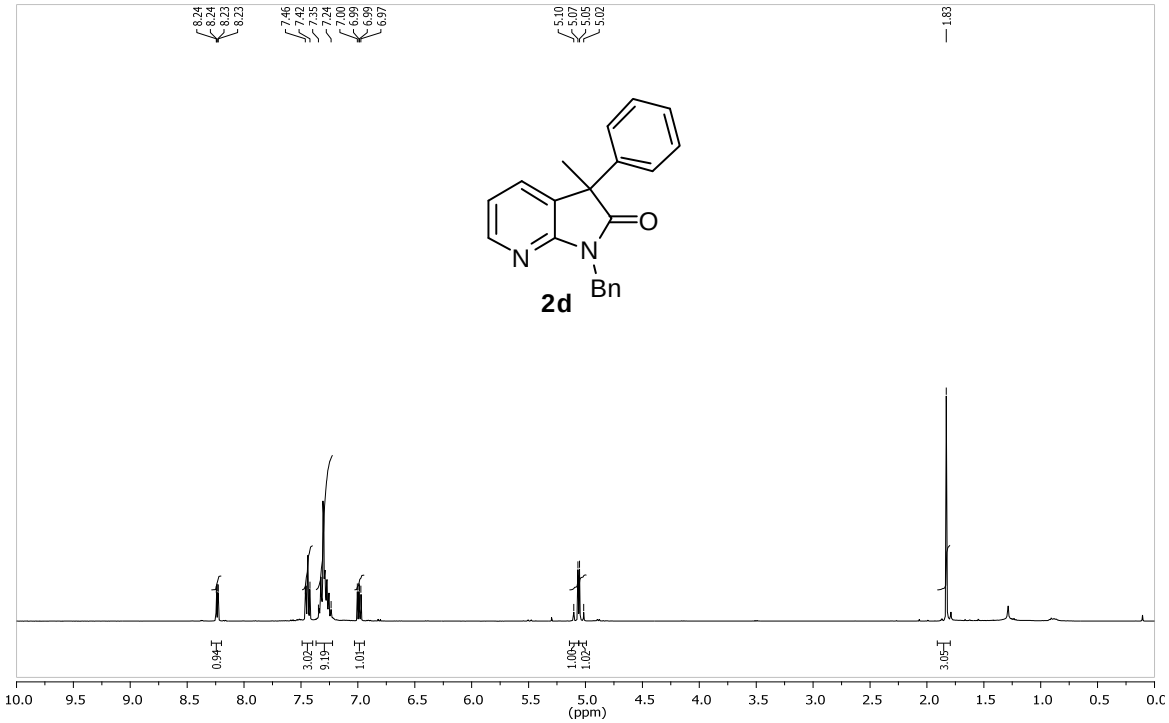
77.16
51.66
25.75
23.64
21.09
2c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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8.24
8.23
8.23
7.46
7.42
7.35
7.24
7.00
6.99
6.99
6.97
5.10
5.07
5.05
5.02
1.83
O
N
N
Bn
2d
0.94
3.02
9.19
1.01
1.00
1.02
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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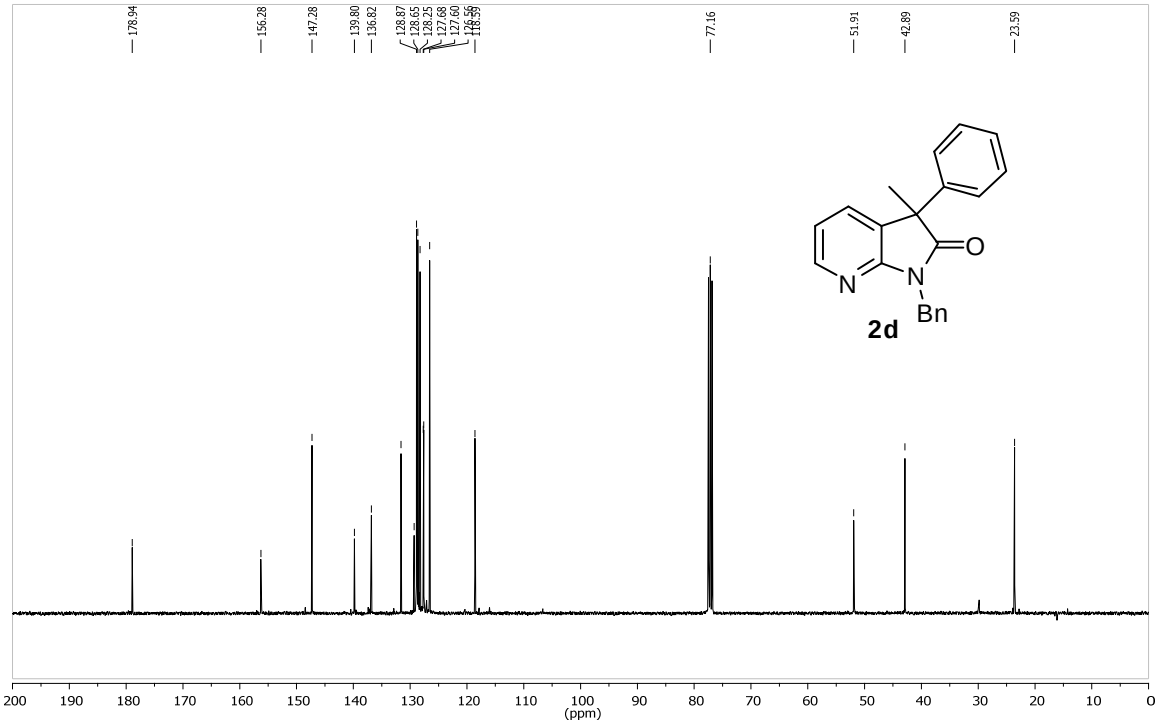
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)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128.87
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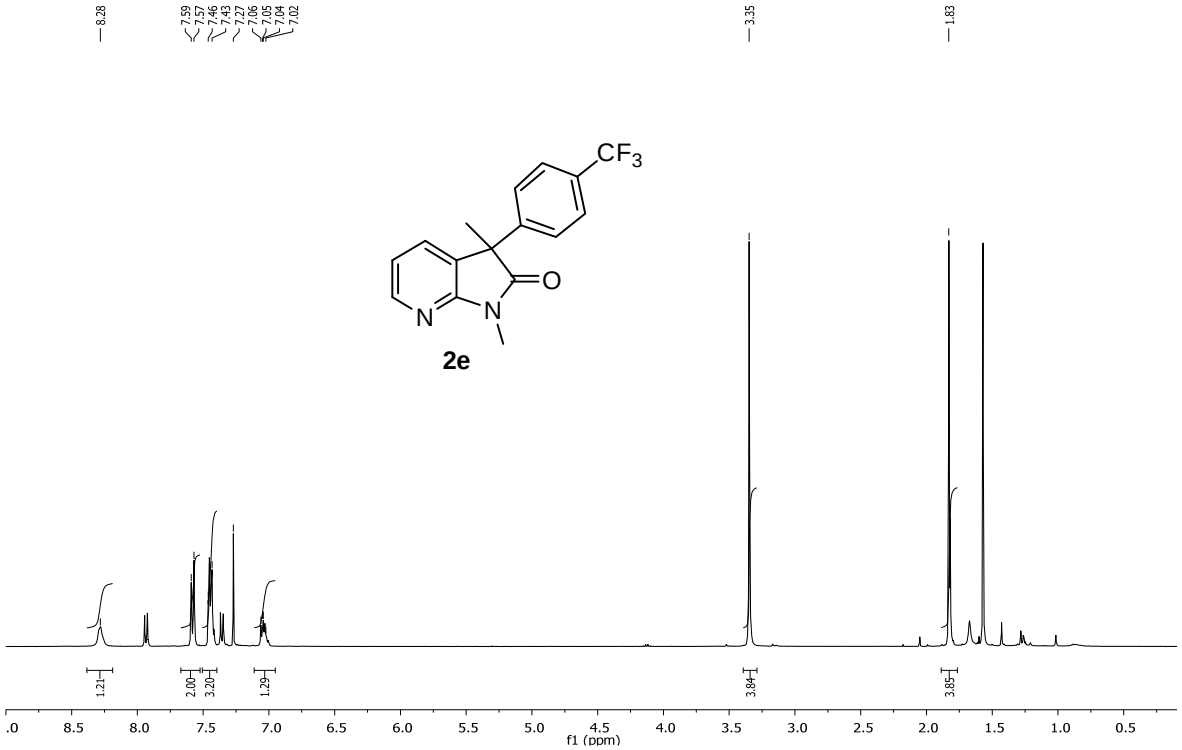
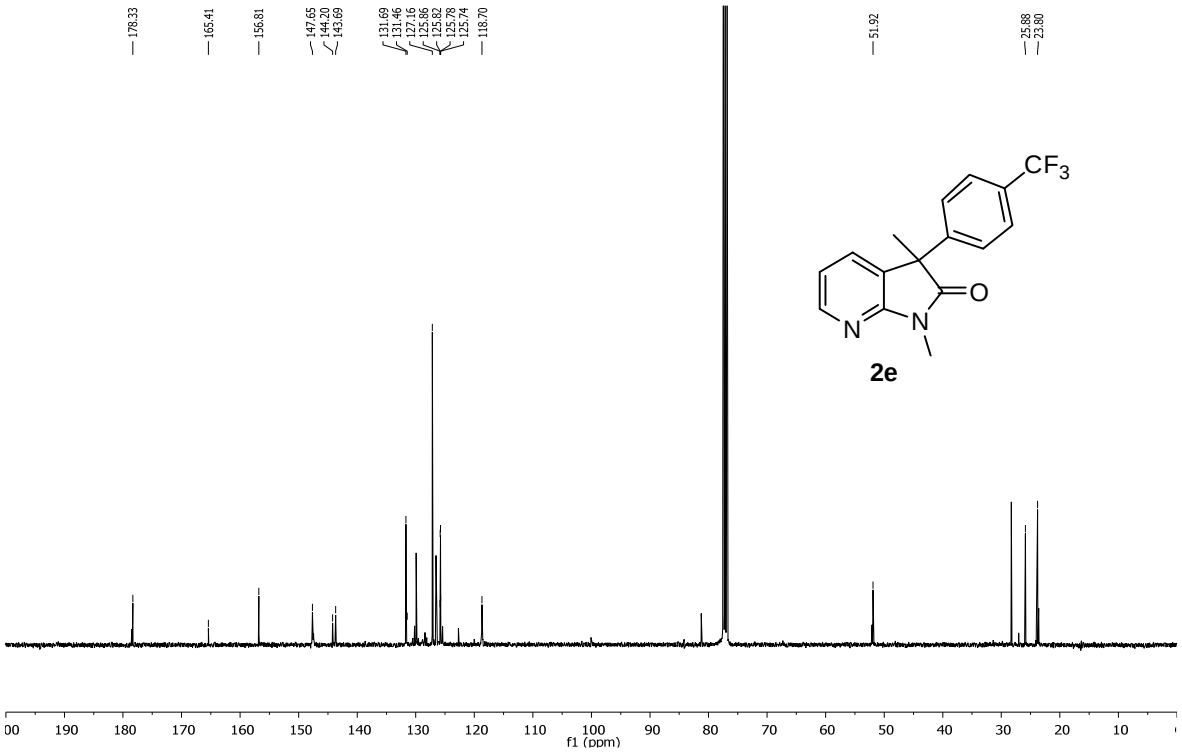
128.25
127.68
127.60
126.56
118.59
77.16
51.91
42.89
23.59
O
N
N
Bn
2d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


8.28
7.59
7.57
7.46
7.43
7.27
7.06
7.05
7.04
7.02
3.35
1.83
CF3
O
N
N
2e
1.21
2.00
3.20
1.29
3.84
3.85
f1 (ppm)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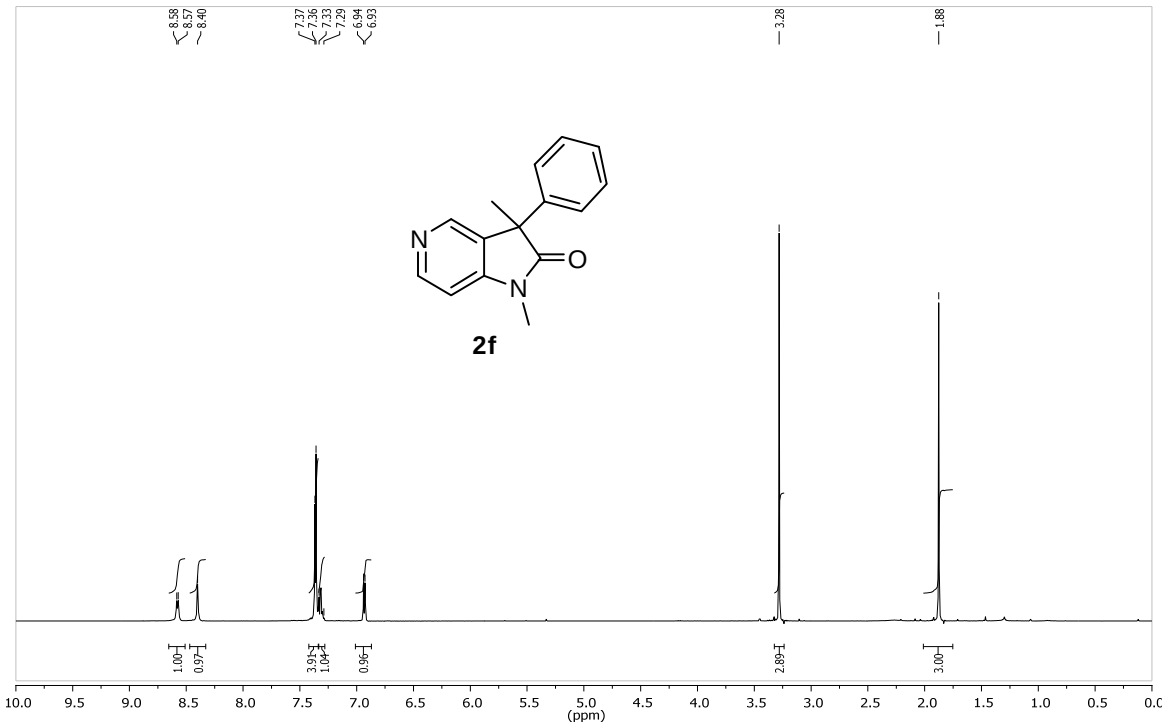
165.41
156.81
147.65
144.20
143.69
131.69
131.46
127.16
125.86
125.82
125.78
125.74
118.70
51.92
25.88
23.80
CF3
O
N
N
2e
f1 (ppm)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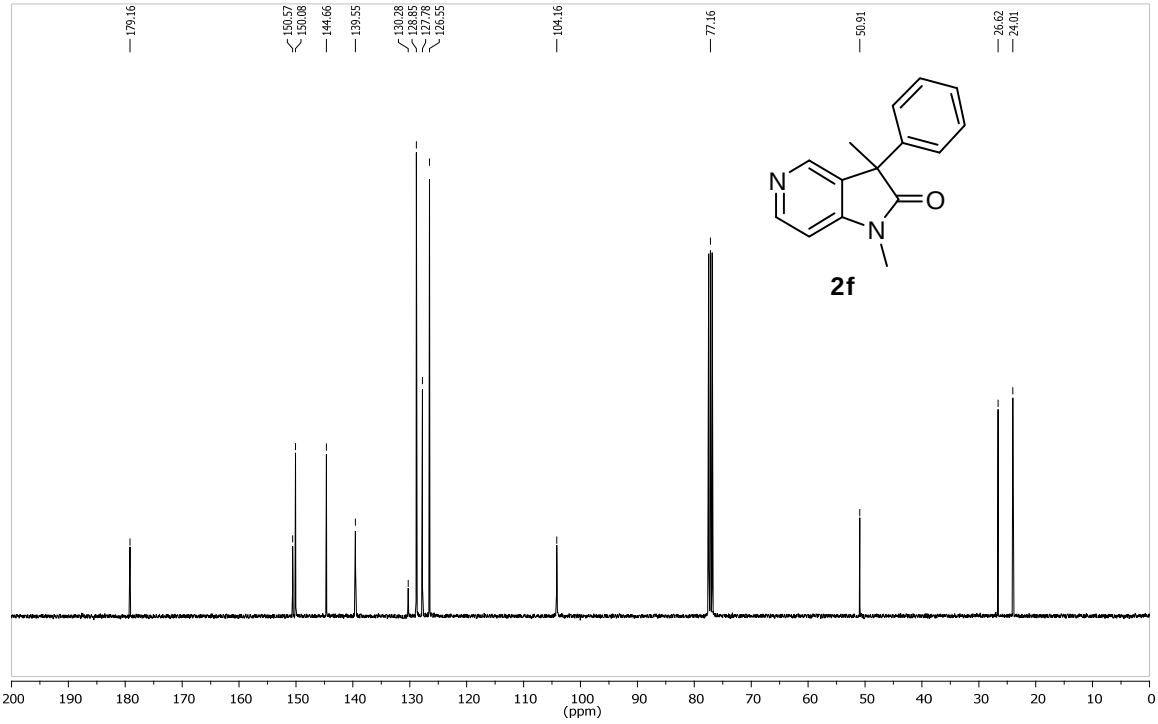
8.57
8.40
7.37
7.36
7.33
7.29
6.94
6.93
3.28
1.88
N
O
N
2f
1.00
0.97
3.91
1.04
0.96
2.89
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)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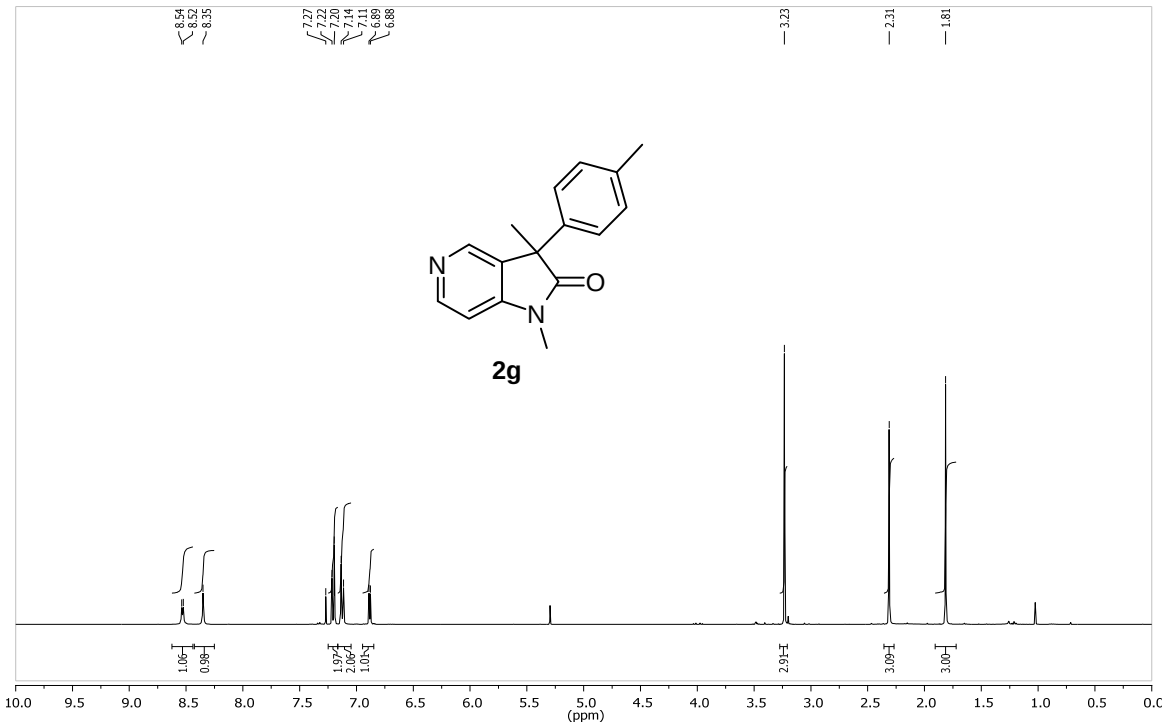
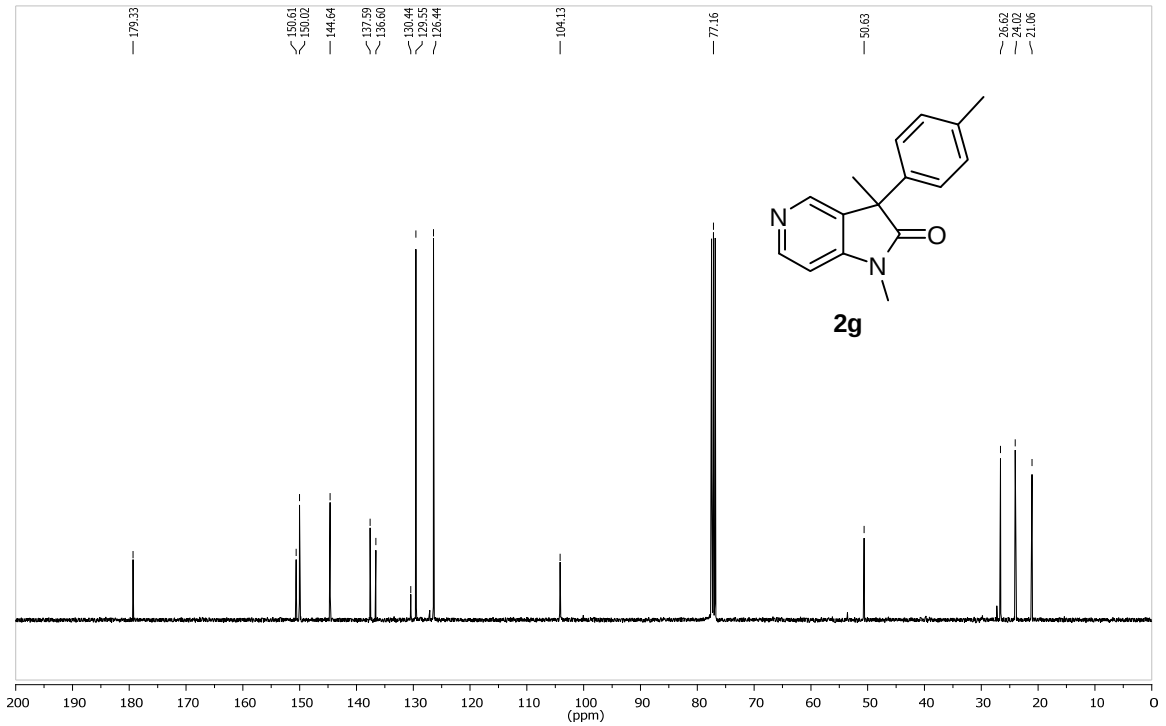
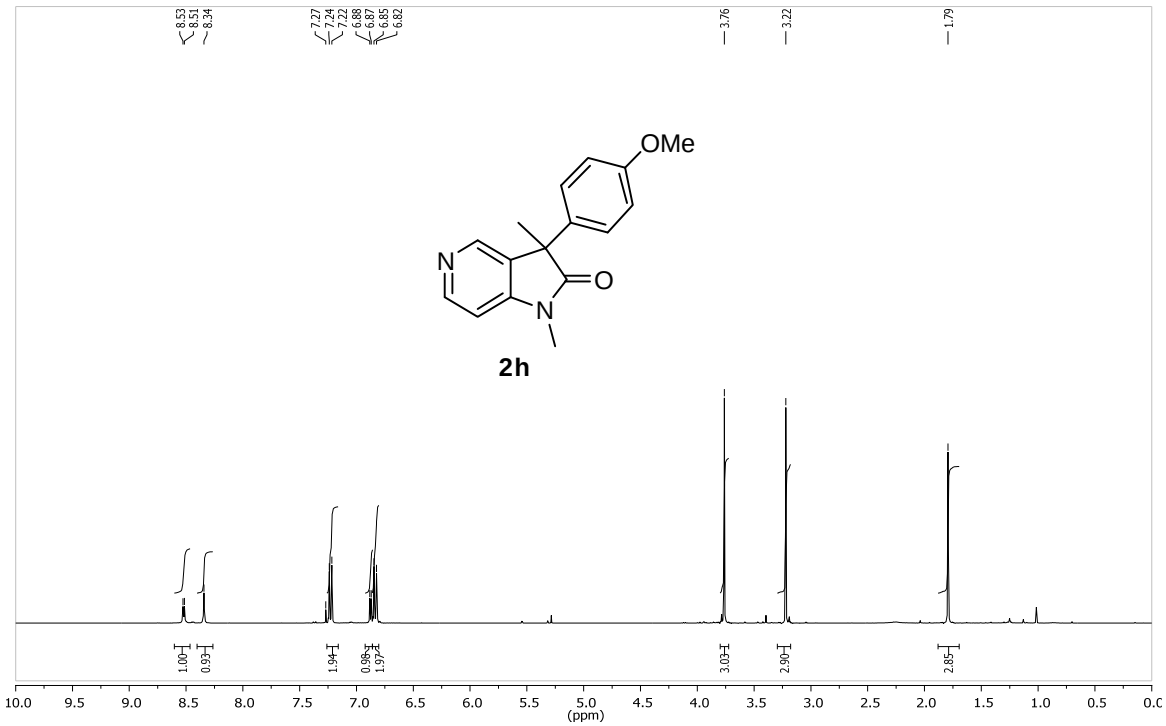
150.57
150.08
144.66
139.55
130.28
128.85
127.78
126.55
104.16
77.16
50.91
26.62
24.01
N
O
N
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

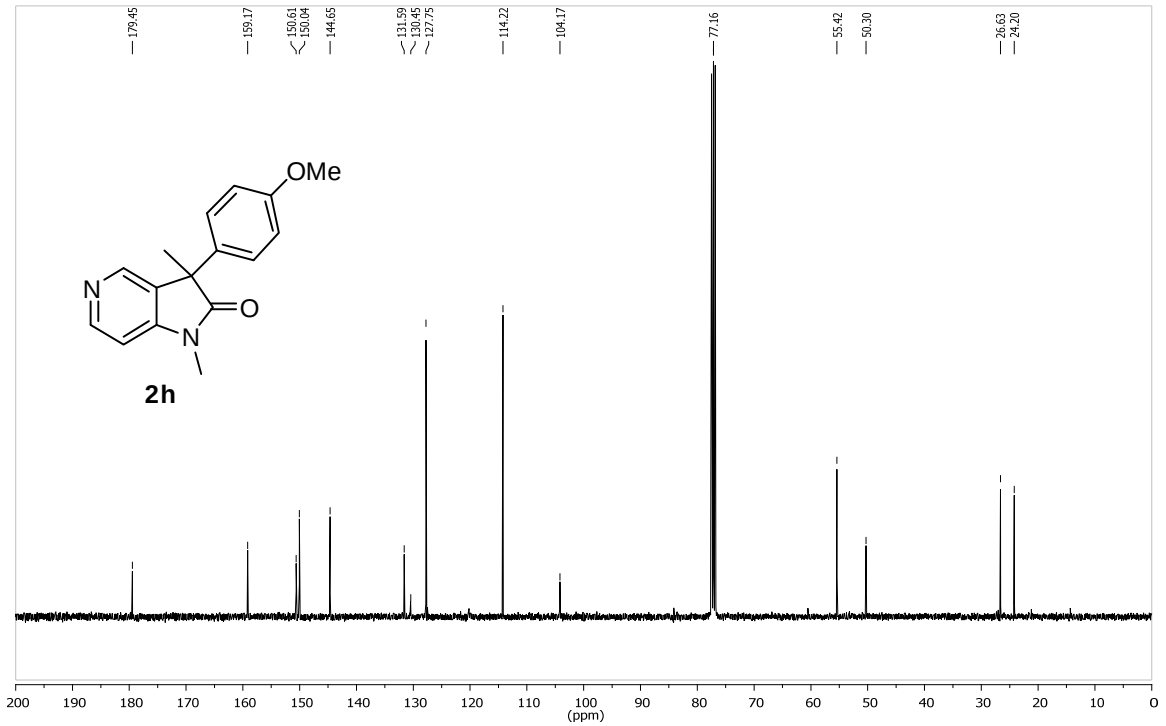

8.54
8.52
8.35
7.27
7.22
7.20
7.14
7.11
6.89
6.88
3.23
2.31
1.81
1.06
0.98
1.97
2.06
1.01
2.91
3.09
3.00
(ppm)

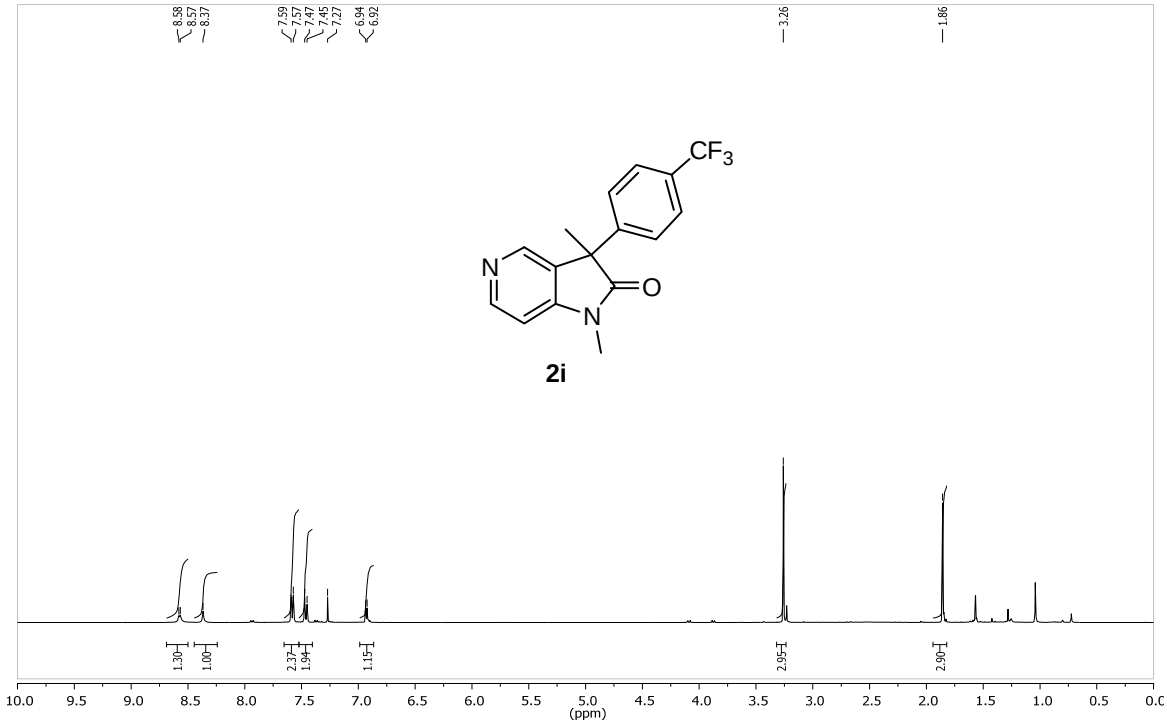
2g

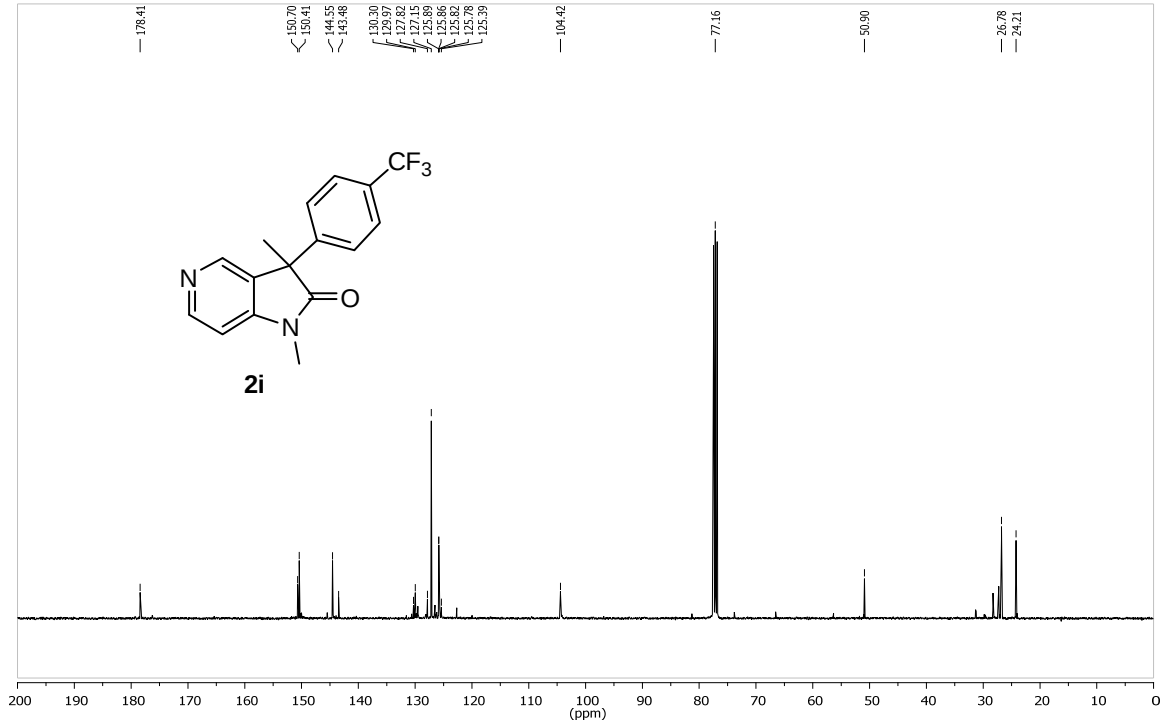

179.33
150.61
150.02
144.64
137.59
136.60
130.44
129.55
126.44
104.13
77.16
50.63
26.62
24.02
21.06
(ppm)

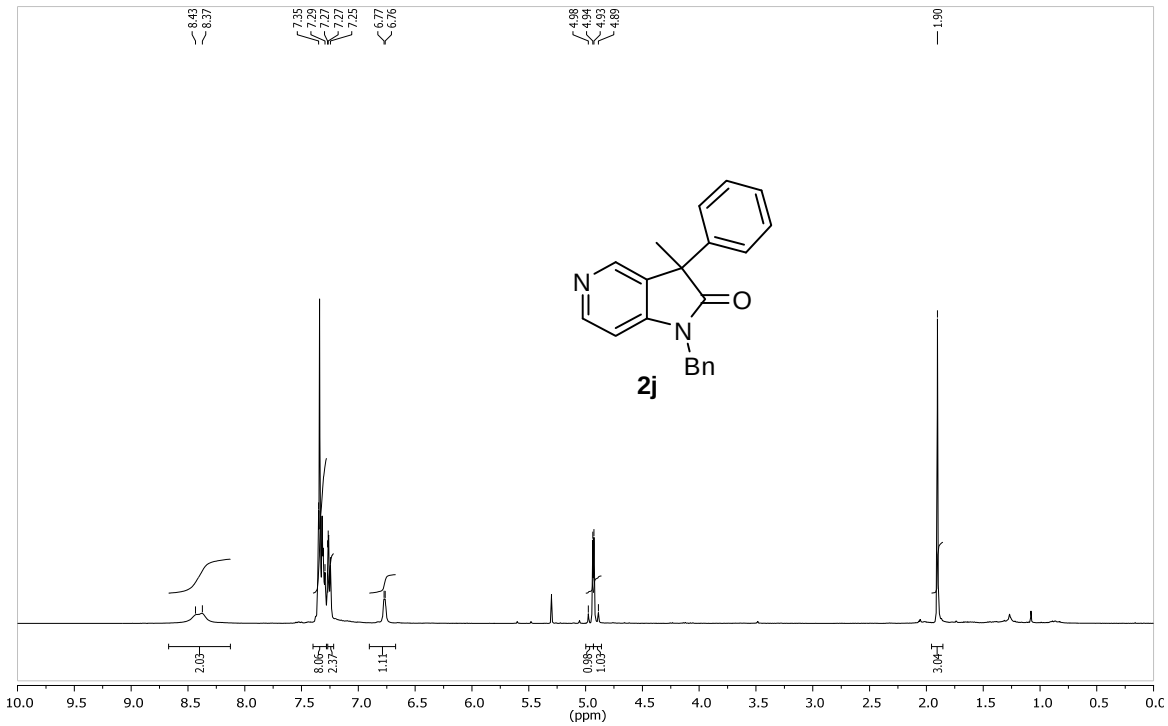
2g

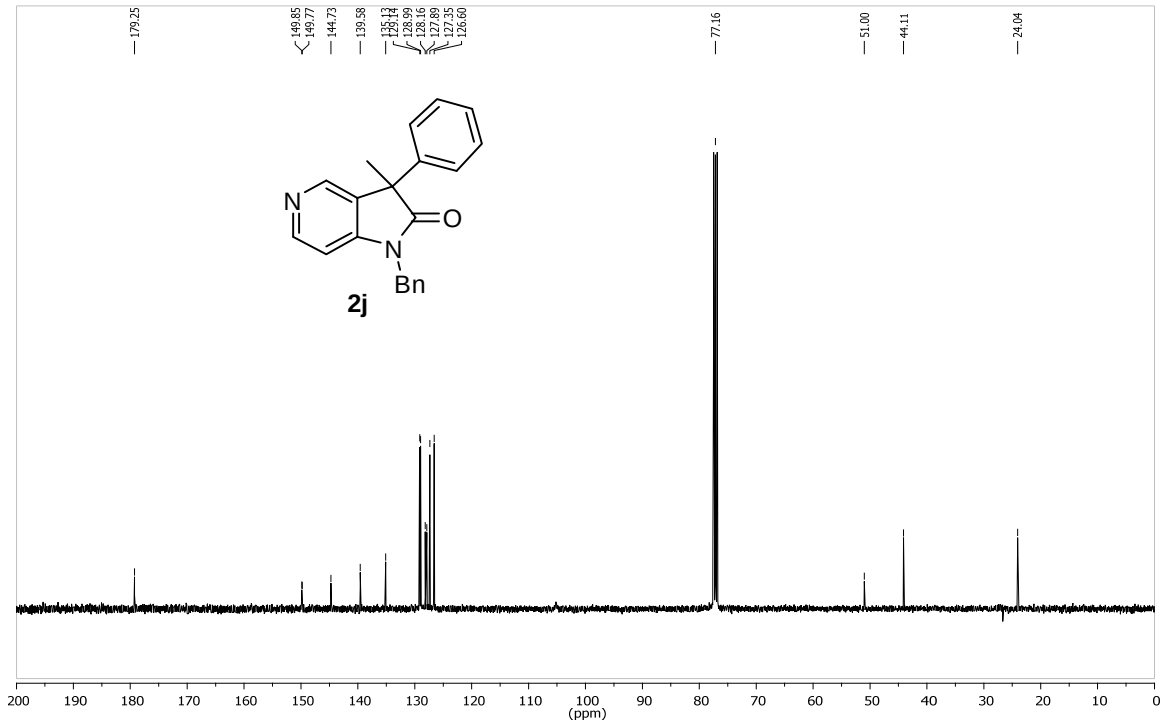

8.53
8.51
8.34
7.27
7.24
7.22
6.88
6.87
6.85
6.82
3.76
3.22
1.79
OMe
N
O
N
2h
1.00
0.93
1.94
0.98
1.97
3.03
2.90
2.85
(ppm)

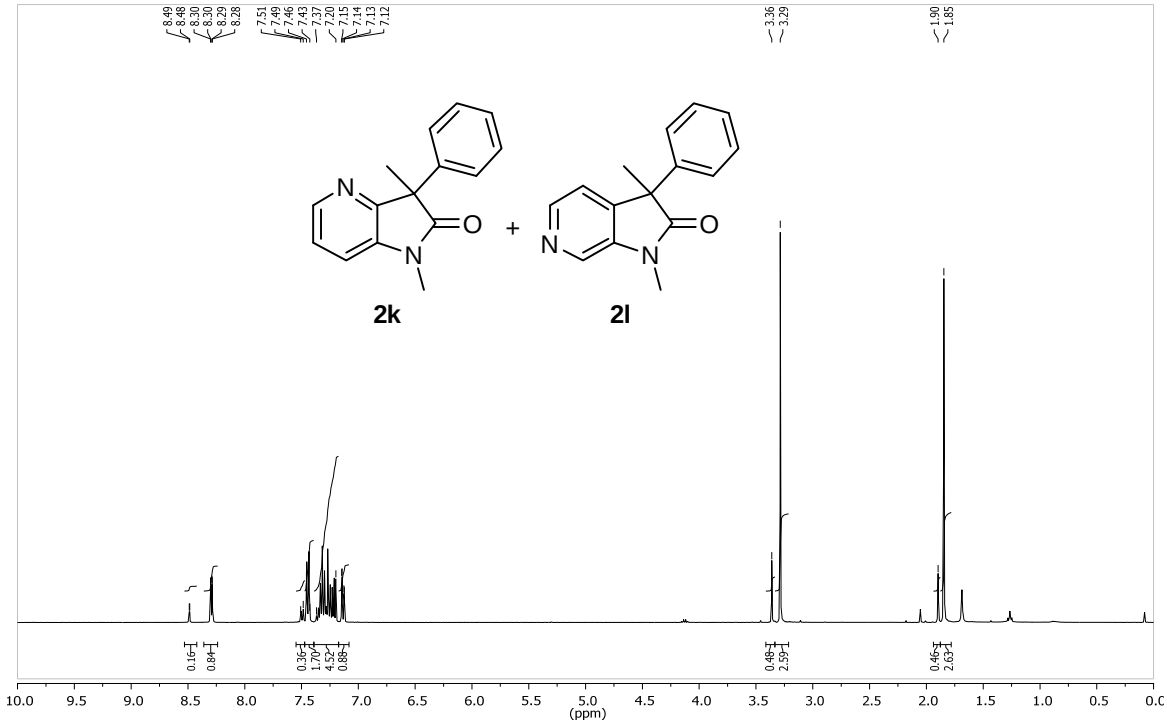

179.45
159.17
150.61
150.04
144.65
131.59
130.45
127.75
114.22
104.17
77.16
55.42
50.30
26.63
24.20
OMe
N
O
N
2h
(ppm)

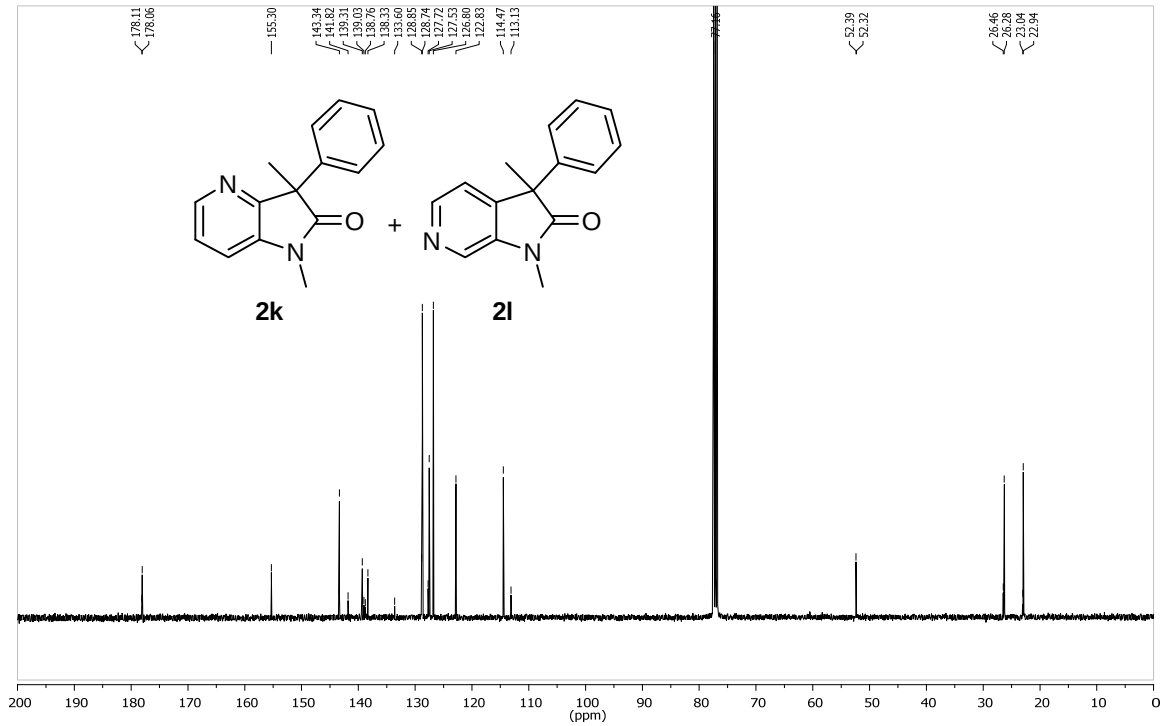

8.58
8.57
8.37
7.59
7.57
7.47
7.45
7.27
6.94
6.92
3.26
1.86
CF3
N
O
N
2i
1.30
1.00
2.37
1.94
1.15
2.95
2.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

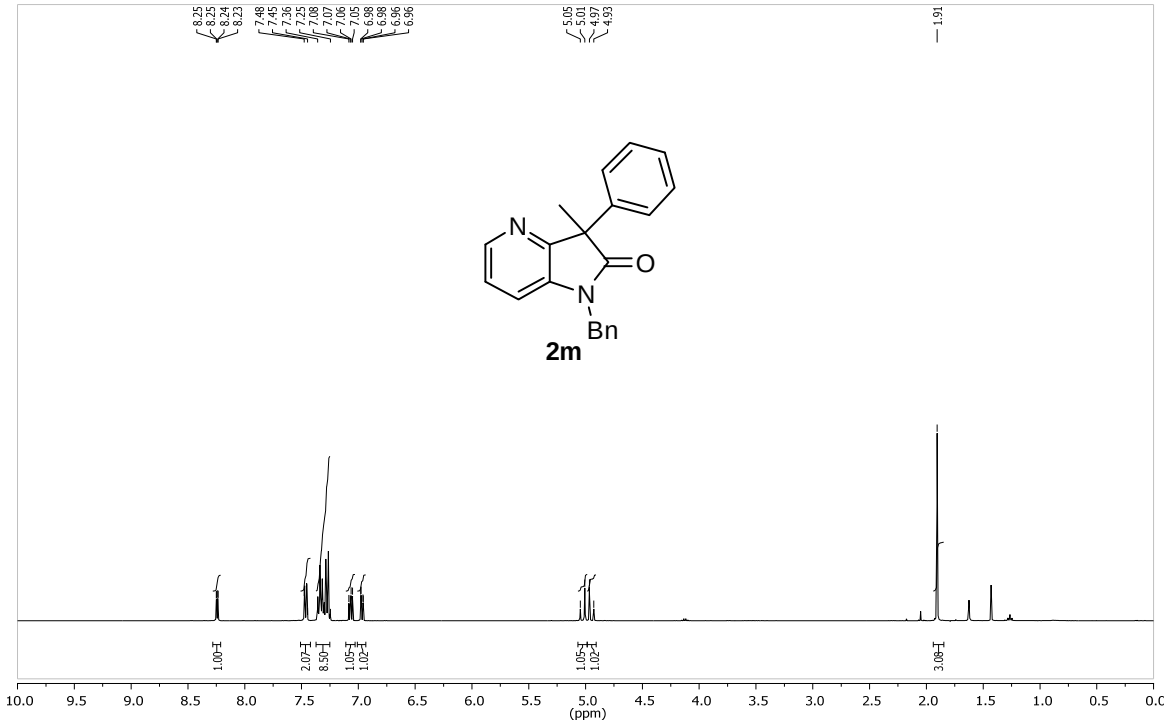

178.41
150.70
150.41
144.55
143.48
130.30
129.97
127.82
127.15
125.89
125.86
125.82
125.78
125.39
104.42
77.16
50.90
26.78
24.21
CF3
N
O
N
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

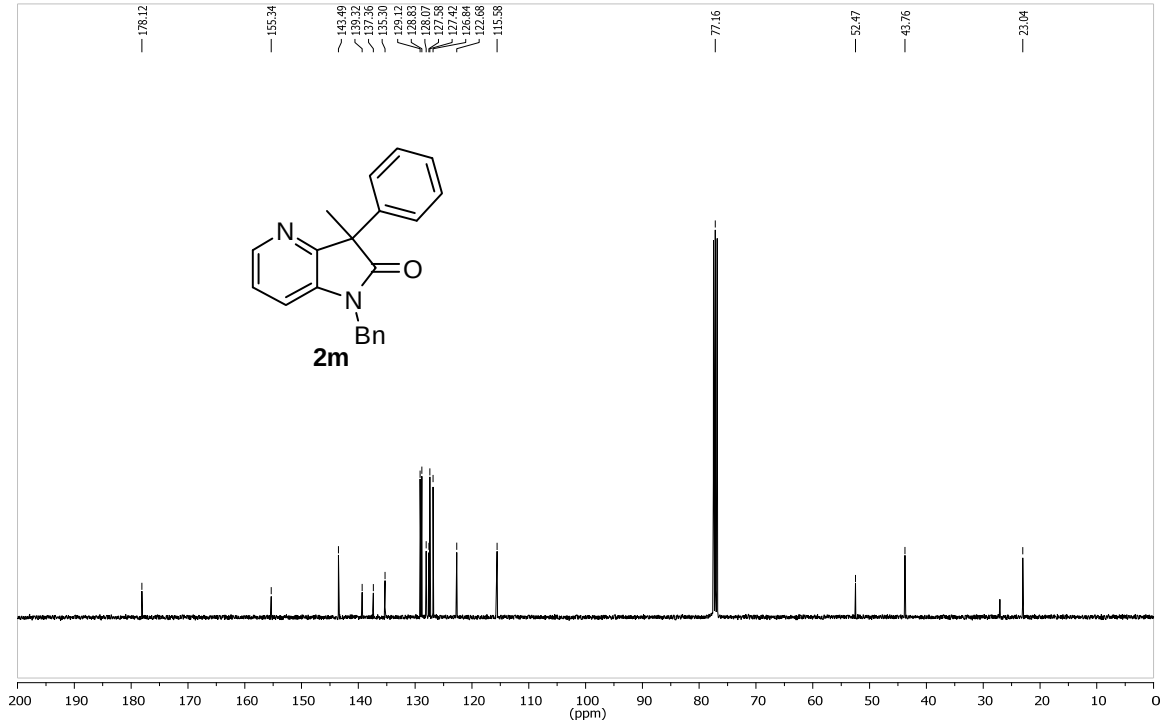

8.43
8.37
7.35
7.29
7.27
7.27
7.25
6.77
6.76
4.98
4.94
4.93
4.89
1.90
N
O
N
Bn
2j
2.03
8.06
2.37
1.11
0.98
1.03
3.04
(ppm)

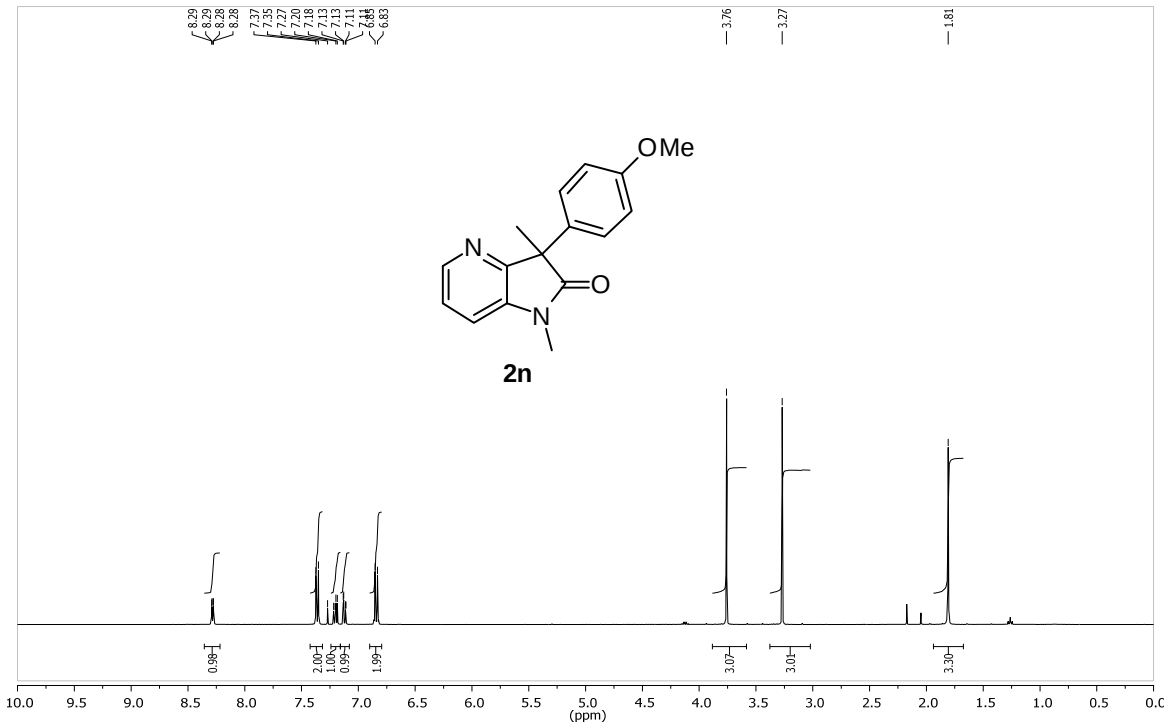

179.25
149.85
149.77
144.73
139.58
135.13
129.14
128.99
128.46
127.89
127.35
126.60
77.16
51.00
44.11
24.04
N
O
N
Bn
2j
(ppm)


8.49
8.48
8.30
8.30
8.29
8.28
7.51
7.49
7.46
7.43
7.37
7.20
7.15
7.14
7.13
7.12
3.36
3.29
1.90
1.85
2k
2l
0.16
0.84
0.36
1.70
4.52
0.88
0.48
2.59
0.46
2.63
(ppm)


178.11
178.06
155.30
143.34
141.82
139.31
139.03
138.76
138.33
133.60
128.85
128.74
127.72
127.53
126.80
122.83
114.47
113.13
77.16
52.39
52.32
26.46
26.28
23.04
22.94
2k
2l
(ppm)


8.25
8.25
8.24
8.23
7.48
7.45
7.36
7.25
7.08
7.07
7.06
7.05
6.98
6.98
6.96
6.96
5.05
5.01
4.97
4.93
1.91
N
O
N
Bn
2m
1.00
2.07
8.50
1.05
1.02
1.05
1.02
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


178.12
155.34
143.49
139.32
137.36
135.30
129.12
128.83
128.07
127.58
127.42
126.84
122.68
115.58
77.16
52.47
43.76
23.04
N
O
N
Bn
2m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)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8.29
8.28
8.28
7.37
7.35
7.27
7.20
7.18
7.13
7.11
6.85
6.83
3.76
3.27
1.81
OMe
N
O
N
2n
0.98
2.00
1.00
0.99
1.99
3.07
3.01
3.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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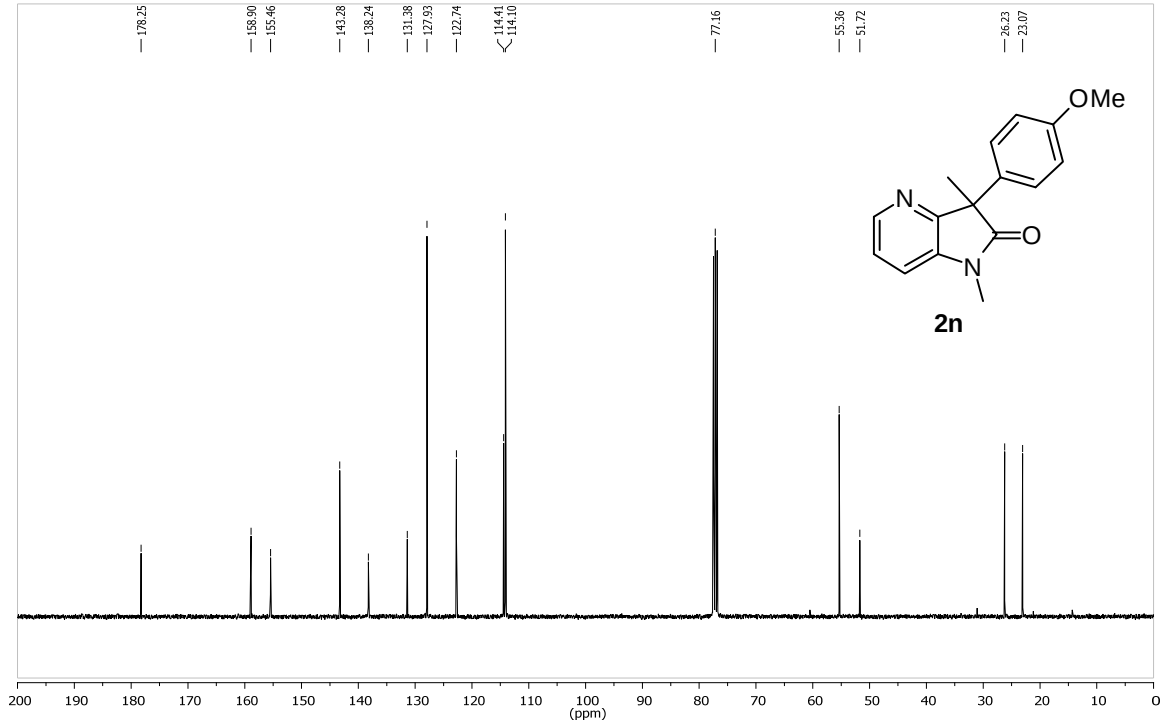
(ppm)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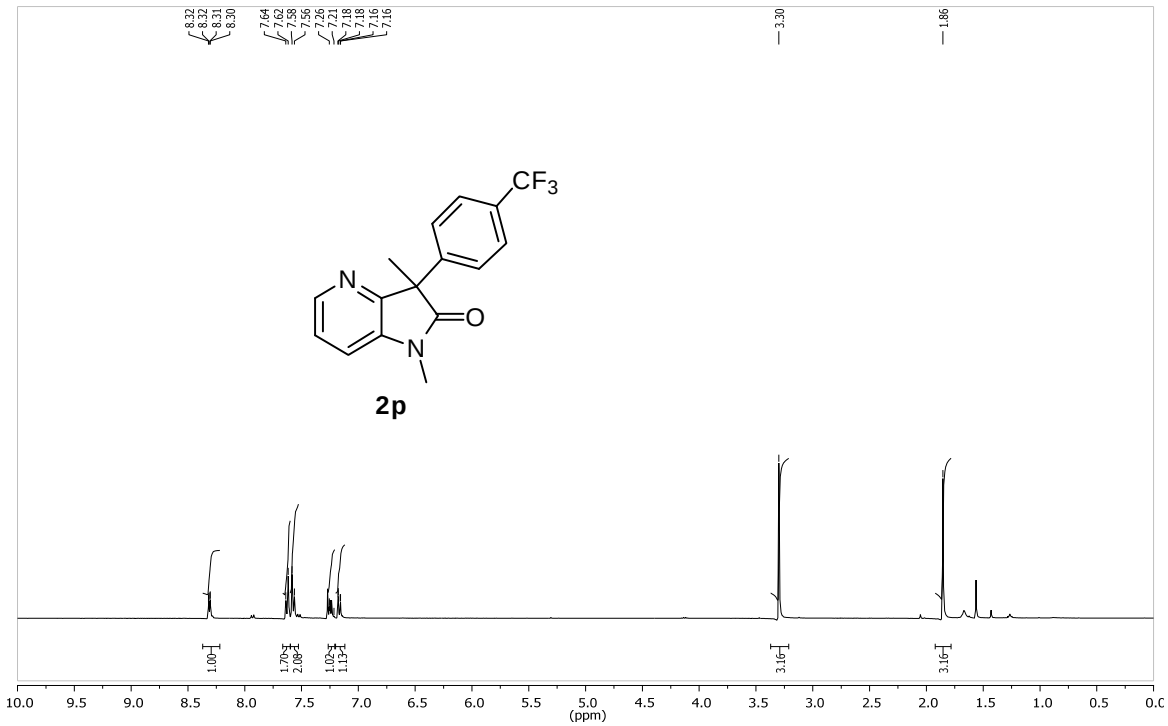
158.90
155.46
143.28
138.24
131.38
127.93
122.74
114.41
114.10
77.16
55.36
51.72
26.23
23.07
OMe
N
O
N
2n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)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8.32
8.31
8.30
7.64
7.62
7.58
7.56
7.26
7.21
7.18
7.18
7.16
7.16
3.30
1.86
CF3
N
O
N
2p
1.00
1.70
2.00
1.02
1.13
3.16
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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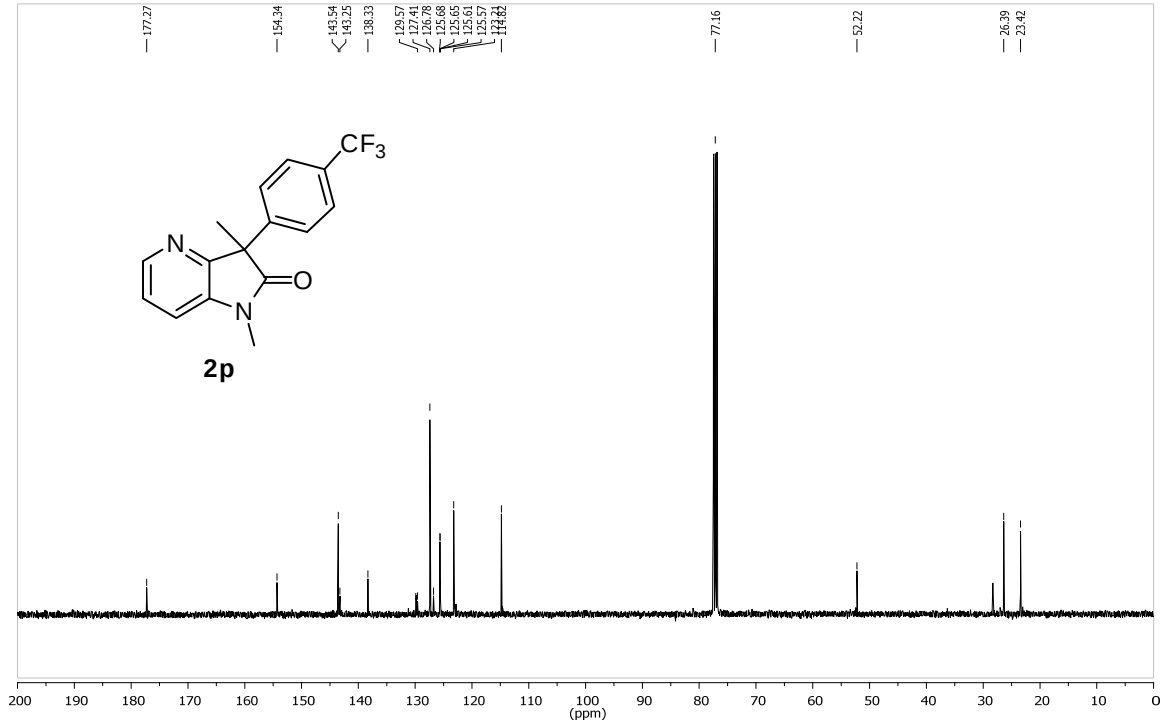
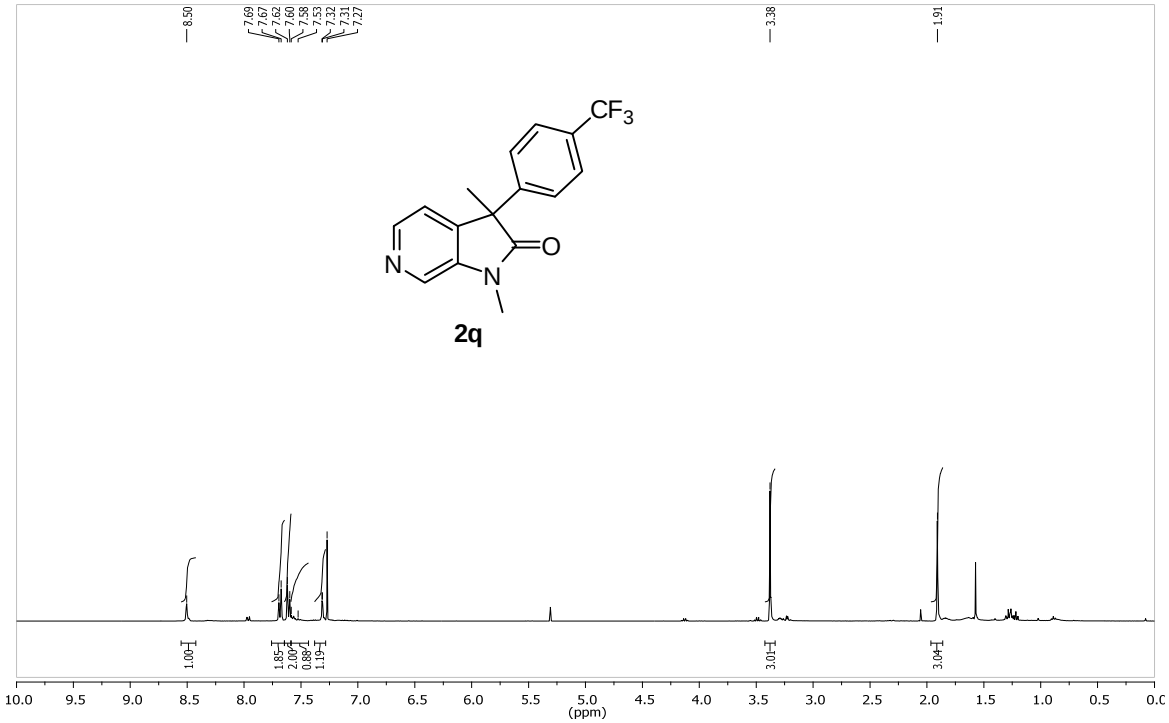
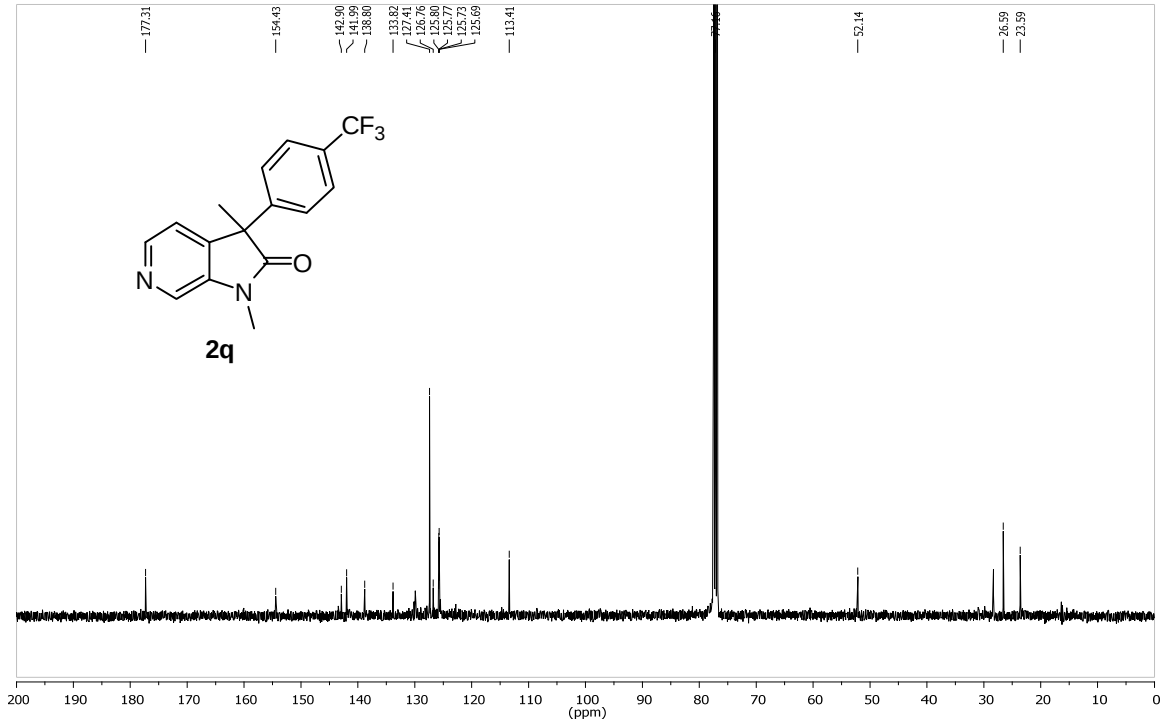
(ppm)


177.27
154.34
143.54
143.25
138.33
129.57
127.41
126.78
125.68
125.65
125.61
125.57
77.16
52.22
26.39
23.42
CF3
N
O
N
2p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


8.50
7.69
7.67
7.62
7.60
7.58
7.53
7.32
7.31
7.27
3.38
1.91
CF3
O
N
N
2q
1.00
1.85
2.00
0.88
1.19
3.01
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


177.31
154.43
142.90
141.99
138.80
133.82
127.41
126.76
126.60
125.77
125.73
125.69
113.41
77.16
52.14
26.59
23.59
CF3
O
N
N
2q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)