Electronic Supplementary Material (ESI) for Chemical Communications

Aza-oxindole synthesis *via* base promoted Truce-Smiles rearrangement

Chandan Dey, Dmitry Katayev, Kai E. O. Ylijoki, and E. Peter Kündig[a]*

[a] *Department of Organic Chemistry, University of Geneva*
30 Quai Ernest Ansermet, CH-1211, Geneva 4, Switzerland
E-mail: peter.kündig@unige.ch

CONTENTS:

1. General Information:

Toluene, THF, and CH_2Cl_2 were purified by filtration on Al_2O_3 drying columns (Solvtek® system). Pyridine and triethylamine were dried over CaH_2 and distilled under nitrogen. DME was dried over sodium/benzophenone and distilled under nitrogen. NaO*t*Bu was sublimed and stored in a glove box. All reactions were carried out under nitrogen in glassware dried by heating under vacuum. Weighing of NaO*t*Bu was performed in the glove box. Proton and carbon NMR spectra were recorded on Bruker AMX-400 or AMX-500 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 sampler. Electron impact (EI) mass spectra were obtained using Varian CH–4 or SM–1 instruments operating at 40–70eV. Electrospray ionization (ESI) HRMS measurements were obtained 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-amino-3-bromopyridine, 3-aminopyridine, 4-amino-3-bromopyridine, 4-amino-3-chloropyridine, 4-(methylamino)pyridine were bought and used as received. 2-(4-methoxyphenyl)propanoic acid,[1] 1-indanecarboxylic acid,[2] 1,2,3,4-tetrahydro-1-naphthoic acid,[3] 3-amino-4-bromopyridine,[4] and (^{2}H)-4-aminopyridine[5] were prepared according to the literature procedures.

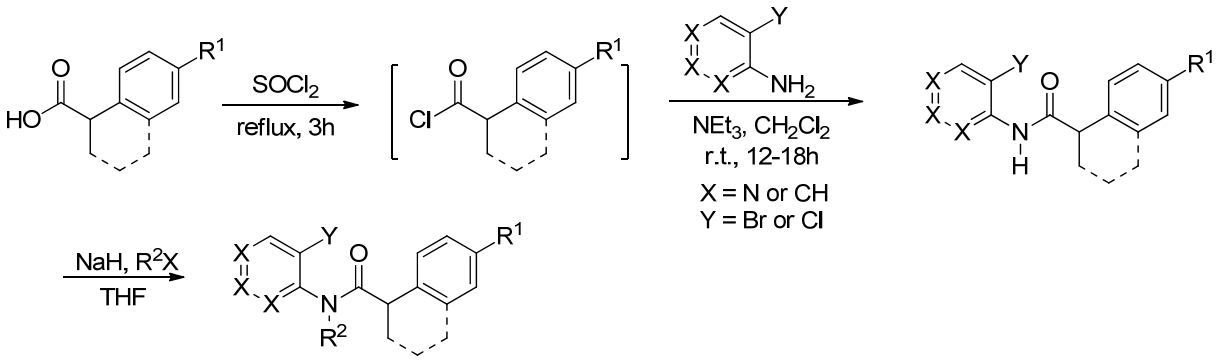
All computations were conducted with the *Spartan'10* computational software package.[6] Initial stationary point searches were carried out with the semiempirical AM1 method.[7] Low energy conformers INT1 and INT3b were located via a semiempirical AM1 conformational search. These structures were then used as starting points for geometry optimization at the B3LYP[8]/6-

[1] E. P. Kündig, T. M. Seidel, Y.-X. Jia and G. Bernardinelli, *Angew. Chem. Int. Ed.*, 2007, **46**, 8484.
[2] A. H. Mermerian and G. C. Fu, *J. Am. Chem. Soc.*, 2005, **127**, 5604.
[3] J. L. Belletire, H. Howard and K. Donahue, *Synth. Commun.*, 1982, **12**, 763.
[4] V. Stockmann, J. M. Bakke, P. Bruheim and A. Fiksdahl, *Tetrahedron*, 2009, **65**, 3668.
[5] H. Esaki, N. Ito, S. Sakai, T. Maegawa, Y. Monguchi and H. Sajiki, *Tetrahedron*, 2006, **62**, 10954.
[6] *Spartan '10*; Wavefunction, Inc.; Irvine, CA; http://www.wavefun.com.
[7] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
[8] (a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

31G* level. Improved geometries and energies were obtained by successive B3LYP/6-311G* and B3LYP/6-311++G** level optimizations. Vibrational analyses were carried out to confirm the nature of all stationary points and to calculate the thermal corrections (enthalpy and entropy) for 298 K, 1 bar, gas phase. Solvent corrections were not applied; the gas phase results provide an accurate approximation given the low dielectric constant of the DME solvent employed. A .zip file containing atomic coordinates in the .pdb file format for all stationary points listed is provided as Supporting Information.

2. Synthesis and analytical data of the substrates:

General procedure for preparing substrates **1a-k**.



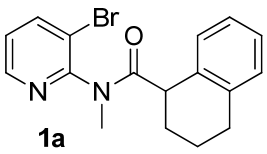
The carboxylic acid (1.0 equiv.) was heated under reflux with $SOCl_2$ (2.0 equiv.) for 3 hours. After evaporating the excess $SOCl_2$, the reaction mixture was diluted with CH_2Cl_2 (0.8M with respect to (w.r.t.) the carboxylic acid). The acid chloride solution was added to the solution of pyridyl amine (1.0 equiv.) and pyridine or triethyl amine (2.0 equiv.) in CH_2Cl_2 (0.8M w.r.t. the pyridyl amine) at 0 ^oC. The mixture was stirred for overnight (12-18 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 (1.0 equiv.) in THF (0.3M w.r.t. the amide) was added to a suspension of NaH (1.1 equiv.) in THF (0.3M w.r.t. the NaH) at 0 ^oC and the mixture was stirred for 1 h at r.t., followed by the addition of MeI or benzylbromide (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. Spectroscopically, the amide exists in a mixture of two rotamers.

Compound **4** is literature known.[9]

N-(3-bromopyridin-2-yl)-*N*-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxamide (**1a**):



1a

Purified by chromatography (cyclohexane/EtOAc = 3:1), 64% yield, White solid, m.p.= 160-162 °C.

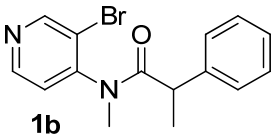
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, *J* = 4.5, 1.3 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.24 (brs, 2H), 7.12-7.05 (m, 3H), 3.50-3.40 (m, 1H), 3.33 (s, 3H), 2.90-2.83 (m, 1H), 2.69-2.65 (m, 1H), 2.03 (brs, 3H), 1.54-1.50 (m, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 175.6, 175.5, 154.8, 148.8, 148.6, 148.5, 143.0, 142.9, 137.7, 137.5, 135.1, 129.3, 128.9, 126.5, 126.0, 125.8, 124.9, 119.9, 44.6, 43.7, 34.7, 29.3, 27.8, 27.5, 21.3, 21.2.

IR (neat, cm^{-1}): 2934, 1652, 1561, 1442, 1411, 1372, 1277, 1130, 1069, 1020, 816, 743, 571.

HRMS (ESI): calcd. for $C_{17}H_{18}BrN_2O$ ($[M+H]^+$): 345.0597, found: 345.0599.

N-(3-bromopyridin-4-yl)-*N*-methyl-2-phenylpropanamide (**1b**):



1b

[9] C. Dey and E. P. Kündig, *Chem. Commun.*, 2012, **48**, 3064.

Purified by chromatography (cyclohexane/EtOAc = 1:1), 85% yield, Oil.

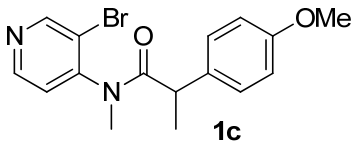
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1.0H), 8.70 (s, 0.4H), 8.65 (d, *J* = 4.9 Hz, 0.4H), 8.35 (d, *J* = 4.9 Hz, 0.9H), 7.32 (d, *J* = 5.0 Hz, 0.6H), 7.21-7.16 (m, 4.1H), 6.93-6.91 (m, 2.6H), 6.59 (d, *J* = 5.0 Hz, 0.9H), 3.52 (q, *J* = 6.9 Hz, 0.4H), 3.28 (q, *J* = 6.8 Hz, 1.0H), 3.18 (s, 1.1H), 3.16 (s, 3.0H), 1.44-1.41 (m, 4.3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 172.9, 154.1, 153.6, 149.94, 149.88, 141.3, 140.0, 128.8, 128.6, 127.8, 127.3, 127.14, 127.12, 125.6, 125.1, 122.0, 44.8, 44.0, 36.0, 35.9, 20.7, 20.2.

IR (neat, cm^{-1}): 3029, 2976, 2931, 1667, 1569, 1478, 1452, 1397, 1373, 1275, 1250, 1129, 1020, 910, 839, 750, 720, 698.

HRMS (ESI): calcd. for $C_{15}H_{16}N_2BrO$ ($[M+H]^+$): 319.0441, found: 319.0433.

N-(3-bromopyridin-4-yl)-2-(4-methoxyphenyl)-*N*-methylpropanamide (**1c**):



1c

Purified by chromatography (Cyclohexane/EtOAc = 1/1), 83% yield, solid, m.p.= 114-116 °C.

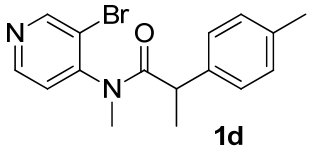
^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.85 (brs, 0.8H), 8.70 (s, 0.3H), 8.62 (d, *J* = 4.5 Hz, 0.3H), 8.38 (d, *J* = 2.5 Hz, 0.8H), 7.30 (d, *J* = 4.6 Hz, 0.4H), 6.82 (d, *J* = 6.7 Hz, 2.5H), 6.73-6.69 (m, 2.7H), 6.63 (brs, 0.8H), 3.75 (s, 3.0H), 3.73 (s, 0.8H), 3.44 (q, *J* = 6.6 Hz, 0.3H), 3.22 (brs, 1.0H), 3.14 (s, 4.1H), 1.38 (d, *J* = 6.5 Hz, 4.0H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 173.3, 173.1, 158.7, 158.6, 154.0, 153.5, 150.1, 149.9, 133.3, 132.1, 128.8, 128.3, 125.5, 125.0, 122.2, 121.9, 114.1, 113.9, 55.3, 43.8, 42.9, 35.9, 35.8, 20.7, 20.2.

IR (neat, cm^{-1}): 2970, 2932, 1666, 1570, 1510, 1479, 1398, 1374, 1245, 1025, 835.

HRMS (ESI): calcd. for $C_{16}H_{18}N_2BrO_2$ ($[M+H]^+$): 349.0546, found: 349.0545.

N-(3-bromopyridin-4-yl)-*N*-methyl-2-(*p*-tolyl)propanamide (**1d**):



1d

Purified by chromatography (Cyclohexane/EtOAc = 1/1), 70% yield, solid, m.p.= 109-111 °C.

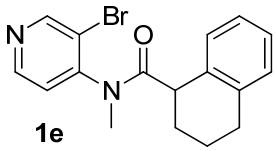
^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.87 (brs, 0.8H), 8.71 (brs, 0.3H), 8.63 (d, *J* = 3.9 Hz, 0.2H), 8.37 (brs, 0.8H), 7.31 (d, *J* = 3.9 Hz, 0.3H), 7.01-6.97 (m, 2.6H), 6.81 (brs, 2.3H), 6.63 (brs, 0.7H), 3.47 (q, *J* = 6.5 Hz, 0.2H), 3.25 (brs, 1.0H), 3.15 (brs, 3.9H), 2.29 (s, 3.1H), 2.27 (s, 0.8H), 1.41 (d, *J* = 6.4 Hz, 3.9H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 173.3, 173.0, 154.1, 153.5, 150.1, 149.9, 138.2, 137.0, 136.7, 129.4, 129.2, 127.7, 127.2, 125.6, 125.0, 122.2, 121.9, 44.3, 43.4, 36.0, 35.8, 21.1, 20.7, 20.1.

IR (neat, cm^{-1}): 2976, 2930, 1669, 1571, 1479, 1398, 1374, 1276, 1022, 823.

HRMS (ESI): calcd. for $C_{16}H_{18}N_2BrO$ ($[M+H]^+$): 333.0597, found: 333.0586.

N-(3-bromopyridin-4-yl)-*N*-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxamide (**1e**):



1e

Purified by chromatography (Cyclohexane/EtOAc = 1/1), 73% yield, solid, m.p.= 168-170 °C.

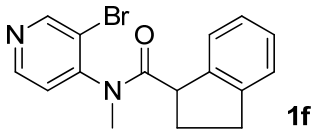
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1.0H). 8.64 (dd, *J* = 11.6, 5.0 Hz, 1.0H), 7.43 (d, *J* = 4.9 Hz, 0.5H), 7.32 (d, *J* = 5.0 Hz, 0.6H), 7.24-7.22 (m, 0.6H), 7.15-7.01 (m, 3.7H),), 3.53-3.50 (m, 1H), 3.32 (s, 1.5H), 3.28 (s, 1.5H), 2.89-2.83 (m, 1.1H), 2.70-2.66 (m, 1.1H), 2.03-1.88 (m, 3.0H), 1.58-1.53 (m, 1.0H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 174.7, 154.3, 154.2, 150.6, 150.4, 137.8, 137.5, 134.9, 134.3, 129.7, 129.4, 129.3, 127.6, 126.83, 126.77, 126.03, 125.97, 124.9, 124.8, 121.6, 121.5, 43.8, 43.7, 36.1, 29.2, 29.1, 28.0, 27.6, 21.3, 21.2.

IR (neat, cm^{-1}): 3034, 2938, 2834, 1653, 1566, 1479, 1397, 1375, 1278, 1252, 1131, 1082, 1024, 854, 840, 759, 742, 660, 593.

HRMS (ESI): calcd. for $C_{17}H_{18}BrN_2O$ ($[M+H]^+$): 345.0597, found: 345.0606.

N-(3-bromopyridin-4-yl)-*N*-methyl-2,3-dihydro-1*H*-indene-1-carboxamide (**1f**):



1f

Purified by chromatography (Cyclohexane/EtOAc = 1/1), 68% yield, solid, m.p.= 127-129 °C.

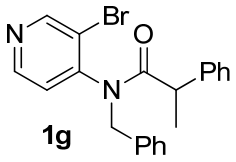
^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.91 (s, 1.0H), 8.66 (d, *J* = 4.9 Hz, 1.1H), 7.24-7.11 (m, 5.1H), 3.77 (brs, 0.7H), 3.30 (s, 3.2H), 3.10 (brs, 1.3H), 2.84-2.78 (m, 1.1H), 2.46-2.06 (m, 2.2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 175.4, 174.1, 154.0, 153.2, 150.6, 150.5, 149.4, 147.5, 144.7, 144.3, 142.1, 141.8, 127.7, 127.5, 127.1, 126.5, 125.1, 124.9, 124.6, 123.7, 123.6, 121.6, 49.2, 48.8, 36.2, 35.9, 32.1, 31.3, 30.9, 30.6.

IR (neat, cm^{-1}): 2939, 2849, 1668, 1570, 1478, 1398, 1375, 1256, 1129, 1081, 1023, 744.

HRMS (ESI): calcd. for $C_{16}H_{16}N_2BrO$ ($[M+H]^+$): 331.0440, found: 331.0435.

N-benzyl-*N*-(3-bromopyridin-4-yl)-2-phenylpropanamide (**1g**):



1g

Purified by chromatography (Cyclohexane/EtOAc = 3/1), 65% yield, oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1.0H), 8.73 (s, 0.4H), 8.46 (d, *J* = 5.1 Hz, 0.4H), 8.15 (d, *J* = 5.1 Hz, 1.0H), 7.28-7.26 (m, 1.0H), 7.22-7.18 (m, 7.7H), 7.09-7.07 (m, 2.1H), 6.98-6.96 (m, 0.8H), 6.93-6.90 (m, 2.0H), 6.82 (d, *J* = 5.1 Hz, 0.4H), 6.06 (d, *J* = 5.1 Hz, 1.0H), 5.73 (d, *J* =

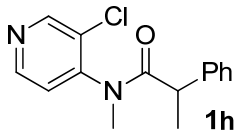
14.5 Hz, 0.4H), 5.52 (d, *J* = 14.5 Hz, 1.0H), 4.12 (d, *J* = 14.5 Hz, 1.0H), 3.95 (d, *J* = 14.5 Hz, 0.4H), 3.45 (q, *J* = 6.9 Hz, 0.4H), 3.30 (q, *J* = 6.8 Hz, 1.0H), 1.48 (d, *J* = 6.8 Hz, 3.0H), 1.44 (d, *J* = 6.9 Hz, 1.1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 172.8, 172.7, 154.1, 153.5, 149.4, 149.3, 147.99, 147.96, 141.3, 139.9, 136.5, 136.4, 129.3, 129.1, 128.8, 128.7, 128.65, 128.61, 128.0, 127.99, 127.9, 127.4, 127.3, 127.2, 126.7, 122.8, 122.6, 51.6, 51.0, 45.3, 44.2, 20.7, 20.4.

IR (neat, cm^{-1}): 3062, 3029, 2981, 2932, 1670, 1568, 1476, 1453, 1385, 1263, 1246, 1208, 1078, 1017, 840, 747.

HRMS (ESI): calcd. for $C_{21}H_{20}N_2BrO$ ($[M+H]^+$): 395.0753, found: 395.0756.

N-(3-chloropyridin-4-yl)-*N*-methyl-2-phenylpropanamide (**1h**):



1h

Purified by chromatography (Cyclohexane/EtOAc = 1/1), 77% yield, oil.

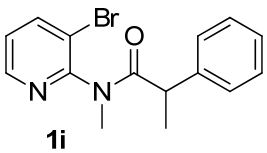
^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.74 (s, 1.0H), 8.59 (d, *J* = 4.1 Hz, 0.5H), 8.51 (s, 0.5H), 8.33 (s, 1.0H), 7.30 (d, *J* = 4.1 Hz, 0.5H), 7.19-7.14 (m, 5.1H), 6.93-6.86 (m, 3.1H), 6.60 (s, 0.7H), 3.55 (q, *J* = 6.5 Hz, 0.4H), 3.30 (brs, 1.0H), 3.16 (s, 4.6H), 1.42 (d, *J* = 6.5 Hz, 4.8H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 173.10, 173.06, 151.5, 151.1, 149.3, 148.3, 141.3, 140.0, 131.4, 130.7, 128.8, 128.5, 127.6, 127.3, 127.1, 125.1, 124.7, 44.5, 44.0, 36.1, 35.7, 20.6, 20.1.

IR (neat, cm^{-1}): 3030, 2974, 2932, 1667, 1572, 1484, 1453, 1399, 1374, 1267, 1247, 1136, 1088, 1021, 839, 730, 698.

HRMS (ESI): calcd. for $C_{15}H_{16}N_2ClO$ ($[M+H]^+$): 275.0945, found: 275.0947.

N-(3-bromopyridin-2-yl)-*N*-methyl-2-phenylpropanamide (**1i**):



1i

Purified by chromatography (Cyclohexane/EtOAc =3/1), 70% yield, solid, m.p.= 84-86 °C.

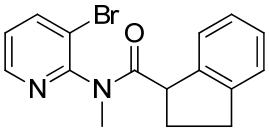
^{1}H-NMR (400 MHz, $CDCl_3$): 8.52 (brs, 1.1H), 8.34 (brs, 0.7H), 8.05 (brs, 0.7H), 7.80 (d, *J* = 5.4 Hz, 0.9H), 7.18-7.14 (m, 7.0H), 6.96-6.86 (m, 3.5H), 3.67 (brs, 1.0H), 3.39 (brs, 0.7H), 3.22 (s, 5.4H), 1.44 (brs, 5.5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 173.9, 154.3, 148.3, 147.93, 147.91, 142.8, 142.7, 140.8, 140.7, 128.4, 127.6, 127.5, 126.8, 124.7, 120.52, 120.49, 44.5, 44.2, 35.0, 34.8, 29.8, 20.0.

IR (neat, cm^{-1}): 3049, 3030, 2929, 1657, 1565, 1440, 1414, 1375, 1285, 1140, 1059, 1025, 810, 788, 751, 722, 694.

HRMS (ESI): calcd. for $C_{15}H_{16}N_2BrO$ ($[M+H]^+$): 319.0441, found: 319.0440.

N-(3-bromopyridin-2-yl)-*N*-methyl-2,3-dihydro-1*H*-indene-1-carboxamide (**1j**):



1j

Purified by chromatography (Cyclohexane/EtOAc = 3/1), 65% yield, solid, m.p.= 160-162 °C.

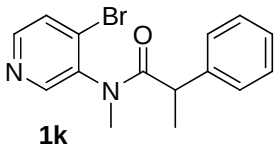
^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.60 (brs, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.42 (brs, 1H), 7.24-7.15 (m, 4H), 3.75-3.69 (m, 1H), 3.34 (s, 3H), 3.11 (brs, 1H), 2.79 (brs, 1H), 2.52-2.34 (m, 1H), 2.20-2.19 (m, 1H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 174.9, 174.6, 154.8, 148.5, 144.4, 142.7, 142.4, 127.2, 126.4, 125.0, 124.7, 124.6, 124.5, 120.5, 49.8, 49.2, 34.7, 32.1, 31.8, 31.3, 30.2, 28.8.

IR (neat, cm^{-1}): 3059, 2942, 2843, 1666, 1565, 1436, 1423, 1373, 1298, 1139.1074, 1021, 801, 745.

HRMS (ESI): calcd. for $C_{16}H_{16}N_2BrO$ ($[M+H]^+$): 331.0440, found: 331.0429.

N-(4-bromopyridin-3-yl)-*N*-methyl-2-phenylpropanamide (**1k**):



1k

Purified by chromatography (EtOAc), 43% yield, oil.

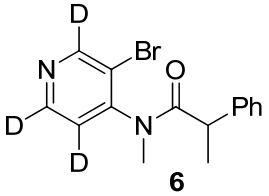
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 0.5H), 8.40 (d, *J* = 5.2 Hz, 0.5H), 8.37 (d, *J* = 5.2 Hz, 1.0H), 7.81 (s, 1.0H), 7.66 (d, *J* = 5.2 Hz, 1.0H), 7.49(d, *J* = 5.2 Hz, 0.5H), 7.23-7.21 (m, 3.0H), 7.18-7.16 (m, 1.5H), 6.93-6.88 (m, 3.0H), 3.51 (q, *J* = 6.9 Hz, 0.5H), 3.24 (q, *J* = 6.9 Hz, 1.0H, N-CH_3 peak of minor isomer overlap), 3.21 (s, 1.4H, benzylic proton peak of major isomer overlap), 3.19 (s, 3.2H), 1.43 (d, *J* = 6.9 Hz, 4.8H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.8, 173.7, 151.6, 150.8, 149.7, 141.2, 140.2, 139.9, 139.5, 134.9, 134.3, 128.9, 128.8, 128.6, 128.3, 127.9, 127.3, 127.2, 127.1, 44.7, 44.1, 36.6, 36.5, 20.6, 20.4.

IR (neat, cm^{-1}): 2974, 2932, 1666, 1470, 1402, 1373, 1280, 1132, 1067, 1049, 745, 699, 665.

HRMS (EI): calcd. for $C_{15}H_{15}N_2BrO$ ($[M]^+$): 318.0362, found: 318.0360.

N-(3-bromopyridin(D3)-4-yl)-*N*-methyl-2-phenylpropanamide (**6**)



6

Compound **6** was synthesized starting from 4-amino-3-bromopyridine(D3) according to the general procedure. 4-amino-3-bromopyridine(D3) was synthesized according to the procedure described for the preparation of 4-amino-3-bromopyridine.[10]

Purified by chromatography (Cyclohexane/EtOAc = 1/1), 79% yield, oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.36 (brs, 0.5H), 7.20-7.16 (m, 4.2H), 6.92-6.91 (m, 2.7H), 3.51 (q, *J* = 6.9 Hz, 0.4H), 3.28 (q, *J* = 6.8 Hz, 1.0H), 3.17 (s, 1.1H), 3.16 (s, 3.1H), 1.43-1.41 (m, 4.3H).

^{2}H-NMR (76 MHz, $CDCl_3$): δ 8.94 (brs, 1.0D), 8.76 (brs, 0.4D), 8.72 (brs, 0.4D), 8.42 (brs, 1.0D), 6.66 (brs, 1.0D; minor isomer of this corresponding D may overlapped with $CDCl_3$ peak).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 173.0, 172.8, 153.8 (t, *J* = 29.0 Hz), 153.2 (t, *J* = 28.5 Hz), 150.0, 149.8, 149.5 (t, *J* = 27.9 Hz), 141.3, 140.0, 128.8, 128.6, 127.8, 127.3, 127.10, 127.09, 125.4-125.0 (m), 122.0 (broad), 44.8, 43.9, 36.0, 35.9, 20.7, 20.2.

IR (neat, cm^{-1}): 3029, 2974, 2931, 1666, 1547, 1452, 1408, 1369, 1359, 1287, 1241, 1118, 1019, 745, 699.

HRMS (ESI): calcd. for $C_{15}H_{13}D_3N_2BrO$ ($[M+H]^+$): 322.0628, found: 322.0630.

[10] V. Canibano, J. F. Rodriguez, M. Santos, M. A. Sanz-Tejedor, M. C. Carreno, G. Gonzalez and J. L. Garcia Ruano, *Synthesis*, 2001, 2175.

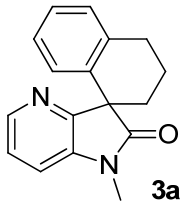
3. Base promoted aza-oxindole synthesis and analytical data for the products:

General procedure for the synthesis of aza-oxindoles.

A dried Schlenk tube was loaded with NaO*t*Bu (0.42 mmol, 2.1 equiv.). Dry DME (2 mL) was introduced to the Schlenk tube by syringe under N_2 atmosphere and the solution was stirred for 5 minute. Substrate (0.20 mmol, 1.0 equiv.) was then added as a solution in DME (2 mL). The resulting mixture was stirred at 50 ^oC until completion of the reaction (monitored by TLC). After cooling to r.t., the reaction mixture was quenched with 4 mL of water or brine and extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The product was purified by flash chromatography.

The data for compound **3i**[11] and **3k**[9] are in agreement with the literature.

1'-methyl-3,4-dihydro-2*H*-spiro[naphthalene-1,3'-pyrrolo[3,2-*b*]pyridin]-2'(1'*H*)-one (**3a**):



3a

The reaction was carried out starting with **1a** (0.3 mmol) according to the general procedure. Purified by chromatography (Cyclohexane/EtOAc = 1/1), 74 mg (94% yield), solid, m.p.= 126-128 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.20-7.11 (m, 4H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 7.7 Hz, 1H), 3.31 (s, 3H), 3.01 (t, *J* = 6.2 Hz, 2H), 2.35-2.29 (m, 2H), 2.18-2.13 (m, 2H),

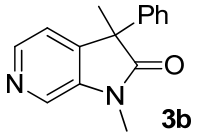
^{13}C-NMR (100 MHz, $CDCl_3$): δ 179.0, 157.5, 143.4, 138.4, 138.1, 133.4, 130.2, 127.5, 127.4, 126.4, 122.6, 114.2, 52.5, 32.4, 29.3, 26.3, 18.5.

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

IR (neat, cm^{-1}): 2933, 1714, 1600, 1491, 1461, 1429, 1365, 1330, 1108, 1029, 755, 625.

HRMS (ESI): calcd. for $C_{17}H_{17}N_2O$ ($[M+H]^+$): 265.1335, found: 265.1333.

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

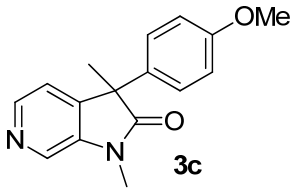


3b

The reaction was carried out starting with **1b** (0.4 mmol) according to the general procedure. Purified by chromatography (EtOAc), 95 mg (99% yield), solid, m.p.= 90-92 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 4.7 Hz, 1H), 8.30 (s, 1H), 7.34–7.26 (m, 5H), 7.17 (d, *J* = 4.8 Hz, 1H), 3.30 (s, 3H), 1.80 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 145.2, 143.6, 140.3, 139.0, 129.8, 128.9, 127.9, 126.5, 119.3, 52.3, 26.8, 23.4.
IR (neat, cm^{-1}): 3052, 2930, 1714, 1606, 1493, 1464, 1432, 1364, 1330, 1282, 1236, 1115, 1037, 900, 831, 806, 734, 697, 624.
HRMS (ESI): calcd. for $C_{15}H_{15}N_2O$ ($[M+H]^+$): 239.1179, found: 239.1169.

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



3c

The reaction was carried out starting with **1c** (0.4 mmol) according to the general procedure. Purified by chromatography (EtOAc), 106 mg (99% yield), solid, m.p.= 80-82 °C.

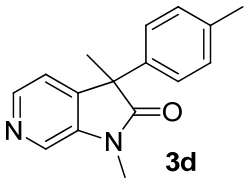
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, *J* = 4.5 Hz, 1H), 8.28 (s, 1H), 7.18 (d, *J* = 8.9 Hz, 2H), 7.16 (d, *J* = 4.7 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 3.28 (s, 3H), 1.76 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$): 178.7, 159.2, 145.2, 143.7, 140.3, 131.1, 129.8, 127.7, 119.2, 114.3, 55.4, 51.6, 26.8, 23.5.

IR (neat, cm^{-1}): 3046, 2962, 2934, 2837, 1714, 1605, 1510, 1463, 1434, 1330, 1250, 1182, 1109, 1034, 831, 806, 749, 602.

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_2$ ($[M+H]^+$): 269.1284, found: 269.1287.

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



3d

The reaction was carried out starting with **1d** (0.3 mmol) according to the general procedure. Purified by chromatography (EtOAc), 75 mg (99% yield), semi solid.

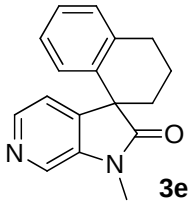
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, J = 4.4 Hz, 1H), 8.29 (s, 1H), 7.17-7.15 (m, 3H), 7.13-7.11 (m, 2H), 3.30 (s, 3H), 2.31 (s, 3H), 1.78 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$): 178.6, 145.2, 143.7, 140.3, 137.7, 136.2, 129.8, 129.6, 126.4, 119.2, 52.0, 26.8, 23.4, 21.1.

IR (neat, cm^{-1}): 3042, 2968, 2928, 2864, 1714, 1603, 1493, 1432, 1362, 1330, 1257, 1109, 1037, 1019, 903, 823, 800, 721, 651, 601.

HRMS (ESI): calcd. for $C_{16}H_{17}N_2O$ ($[M+H]^+$): 253.1335, found: 253.1332.

1'-methyl-3,4-dihydro-2*H*-spiro[naphthalene-1,3'-pyrrolo[2,3-*c*]pyridin]-2'(1'*H*)-one (**3e**):



3e

The reaction was carried out starting with **1e** (0.2 mmol) according to the general procedure. Purified by chromatography (EtOAc), 52 mg (99% yield), solid, m.p.= 115-118 °C.

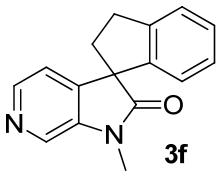
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 4.7 Hz, 1H), 8.30 (s, 1H), 7.20–7.14 (m, 2H), 7.03 (d, *J* = 4.7 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 3.35 (s, 3H), 3.08–2.93 (m, 2H), 2.41–2.32 (m, 1H), 2.25-2.18 (m, 1H), 2.06–1.92 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.4, 145.7, 145.3, 140.1, 137.9, 133.5, 130.0, 129.5, 127.8, 127.7, 126.6, 118.9, 52.3, 33.6, 29.1, 26.8, 18.7.

IR (neat, cm^{-1}): 3088, 3018, 2933, 2864, 1714, 1600, 1491, 1461, 1429, 1365, 1365, 1330, 1269, 1233, 1152, 1108, 1029, 965, 828, 772, 755, 721, 625.

HRMS (ESI): calcd. for $C_{17}H_{17}N_2O$ ($[M+H]^+$): 265.1337, found: 265.1334.

1'-methyl-2,3-dihydrospiro[indene-1,3'-pyrrolo[2,3-*c*]pyridin]-2'(1'*H*)-one (**3f**):



3f

The reaction was carried out starting with **1f** (0.2 mmol) according to the general procedure. Purified by chromatography (EtOAc), 49 mg (97% yield), oil.

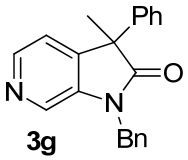
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (brs, 1H), 8.28 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 4.6 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 3.49-3.43 (m, 1H), 3.32 (s, 3H), 3.26-3.20 (m, 1H), 2.73-2.68 (m, 1H), 2.44-2.38 (m, 1H).

^{13}C-NMR (125 MHz, $CDCl_3$): 178.5, 145.4, 145.1, 143.3, 142.7, 140.5, 129.3, 128.6, 127.3, 125.3, 123.3, 118.4, 60.1, 37.6, 31.9, 26.8.

IR (neat, cm^{-1}): 3029, 2942, 1715, 1632, 1602, 1493, 1466, 1433, 1363, 1331, 1236, 1158, 1111, 1035, 828, 751.

HRMS (ESI): calcd. for $C_{16}H_{15}N_2O$ ($[M+H]^+$): 251.1178, found: 251.1173.

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



3g

The reaction was carried out starting with **1g** (0.2 mmol) according to the general procedure. Purified by chromatography (EtOAc), 42 mg (66% yield), oil.

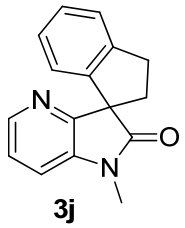
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J = 3.3 Hz, 1H), 8.17 (s, 1H), 7.37-7.28 (m, 10H), 7.16 (d, J = 4.6 Hz, 1H), 5.01 (d, J = 15.5 Hz, 1H), 4.94 (d, J = 15.5 Hz, 1H), 1.87 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 178.5, 145.2, 143.7, 139.4, 139.1, 135.3, 130.8, 129.1, 129.0, 128.1, 127.9, 127.6, 126.6, 119.2, 52.3, 44.3, 23.4.

IR (neat, cm^{-1}): 3031, 2970, 2924, 1713, 1602, 1490, 1435, 1344, 1183, 1153, 1078, 995, 913, 830, 734, 697.

HRMS (ESI): calcd. for $C_{21}H_{19}N_2O$ ($[M+H]^+$): 315.1491, found: 315.1495.

1'-methyl-2,3-dihydrospiro[indene-1,3'-pyrrolo[3,2-*b*]pyridin]-2'(1'*H*)-one (**3j**):



3j

The reaction was carried out starting with **1j** (0.2 mmol) according to the general procedure. Purified by chromatography (Cyclohexane/EtOAc = 1/1), 30 mg (60% yield), solid, m.p.= 129-131 °C.

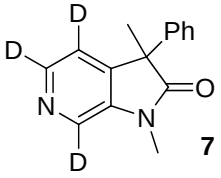
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.20 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.25-7.18 (m, 2H), 7.14 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 3.47-3.33 (m, 2H), 3.30 (s, 3H), 2.67-2.63 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 178.3, 155.5, 145.6, 143.6, 142.5, 138.6, 128.4, 127.0, 125.4, 123.0, 122.8, 114.2, 60.9, 35.8, 32.1, 26.3.

IR (neat, cm^{-1}): 2929, 1707, 1598, 1445, 1323, 1304, 1131, 1080, 1032, 947, 790, 774, 754, 654, 579.

HRMS (ESI): calcd. for $C_{16}H_{15}N_2O$ ($[M+H]^+$): 251.1178, found: 251.1186.

1,3-dimethyl-3-phenyl-1*H*-pyrrolo[2,3-*c*]pyridine(D3)-2(3*H*)-one (**7**):



7

The reaction was carried out starting with **6** (0.3 mmol) according to the general procedure. Purified by chromatography (EtOAc), 71 mg (99% yield), solid, m.p.= 88-90 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): 7.33-7.26 (m, 5H), 3.30 (s, 3H), 1.80 (s, 3H).

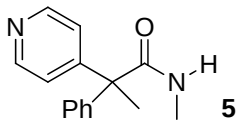
^{2}H-NMR (76 MHz, CD_2Cl_2): δ 8.43 (brs, 1D), 8.32 (brs, 1D), 7.20 (brs, 1D).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 178.5, 144.9 (t, *J* = 27.7 Hz), 143.5, 140.2,139.1, 129.5 (t, *J* = 27.1 Hz), 128.9, 127.9, 126.5, 118.8 (t, *J* = 25.1 Hz), 52.3, 26.8, 23.4.

IR (neat, cm^{-1}): 3054, 2983, 2933, 1715, 1588, 1493, 1462, 1446, 1363, 1320, 1242, 1081, 1027, 769, 734, 700, 617, 554.

HRMS (ESI): calcd. for $C_{15}H_{12}D_3N_2O$ ($[M+H]^+$): 242.1373, found: 242.1368.

N-methyl-2-phenyl-2-(pyridin-4-yl)propanamide (**5**):



5

The reaction was carried out starting with **4** (0.2 mmol) according to the general procedure. Purified by chromatography (CH_2Cl_2/MeOH = 95/5), 40 mg (82% yield), oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (brs, 2H), 7.38-7.30 (m, 3H), 7.20-7.18 (m, 4H), 5.45 (brs, 1H), 2.83 (d, *J* = 4.8 Hz, 3H), 2.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 154.7, 149.7, 143.1, 129.0, 128.2, 127.8, 56.8, 27.1, 26.6.

IR (neat, cm^{-1}): 3359, 3047, 2983, 2935, 2887, 1652, 1595, 1522, 1410, 1263, 1068, 1028, 821, 700, 659, 568.

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

4. Computational thermodynamic data:

Computations for the production of INT4 from INT1 were conducted at the B3LYP/6-311++G** level. The H°, zero-point energies (ZPE), S°, and G° values are collected in Table S1. Select transition states are shown in Figure S2.

Table S1: Thermodynamic data for Figure S1 in main text.

	H° (a.u.)	ZPE (kJ/mol)	S° (J/mol°)	G° (a.u.)
INT1	-3338.87028	670.95	500.66	-3338.92713
INT1a	-3338.87031	670.82	500.87	-3338.92719
INT1b	-3338.86501	670.18	499.77	-3338.92176
INT1c	-3338.86060	669.14	500.17	-3338.91740
INT1d	-3338.86501	670.18	499.76	-3338.92176
TS1a-2a	-3338.84187	664.38	508.77	-3338.89965
TS1b-2b	-3338.83862	665.14	506.89	-3338.89618
TS1c-5	-3338.83356	665.48	505.24	-3338.89093
TS1d-5	-3338.83294	665.22	505.43	-3338.89033
INT2a	-3338.84633	668.34	504.78	-3338.90366
INT2b	-3338.84680	669.20	501.18	-3338.90371
TS2a-3a	-3338.84076	666.48	507.42	-3338.89839
TS2b-3b	-3338.84295	665.55	504.72	-3338.90027
INT3a	-3338.86512	669.88	499.31	-3338.92183
INT3b	-3338.86537	669.51	498.00	-3338.92192
INT3c	-3338.86428	669.86	500.26	-3338.92109
INT3d	-3338.86265	668.99	499.15	-3338.91934
TS3a-4	-3338.84068	666.38	504.02	-3338.89791
TS3b-4	-3338.84263	666.23	503.29	-3338.89978
TS3c-6	-3338.83396	667.46	503.26	-3338.89111
TS3d-6	-3338.83633	667.33	501.93	-3338.89332
INT4	-3338.94995	678.18	498.54	-3339.00657
INT5	-3338.95175	678.47	499.50	-3339.00848
INT6	-3338.90564	676.53	496.56	-3338.96203
INT1-Br	-765.327627	697.73	474.31	-765.381489
TS1-Br-2-Br	-765.288012	690.85	481.46	-765.342686

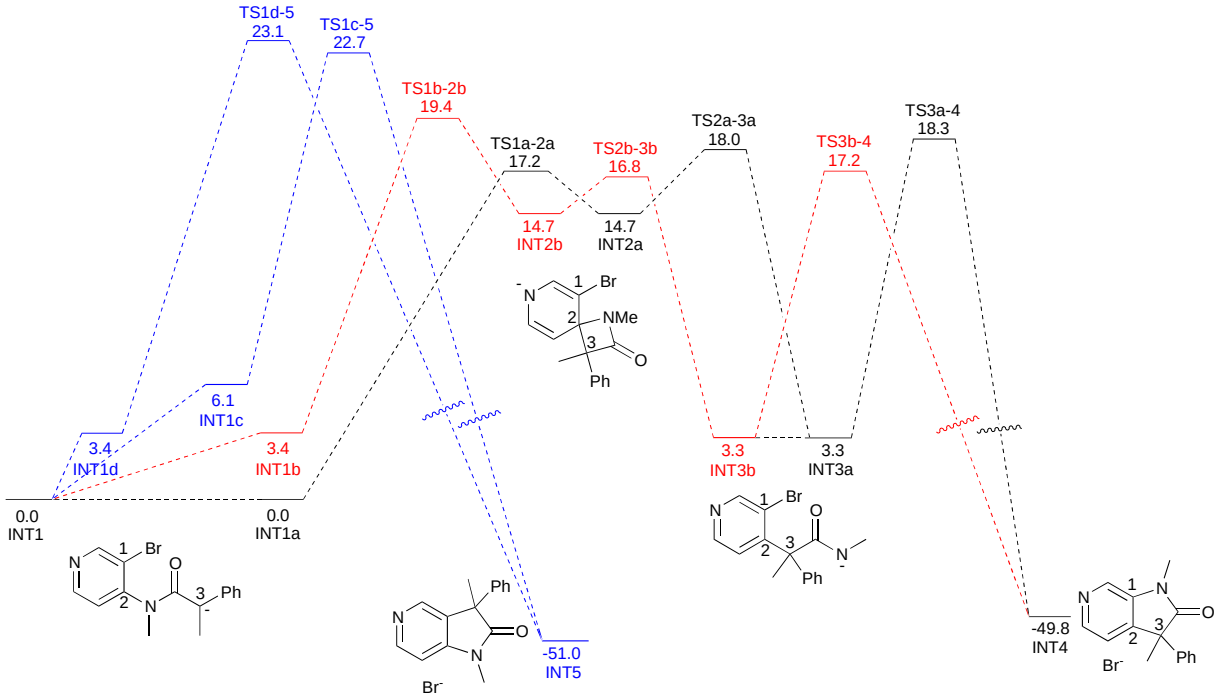


Figure S1: B3LYP/6-311++G** energy surface (free energies, kcal/mol)

It is interesting that we do not observe products **INT5** arising from direct nucleophilic substitution at **INT1**. Our calculations agree with this observation, suggesting this competing pathway (**TS1c-5** and **TS1d-5**, in blue) is of significantly higher energy (ca. 23 kcal/mol) than the observed rearrangement (Figure S1). To further understand this result, the NPA charges for the relevant atoms in the computed intermediates were measured (Table S2).[12] From this data, it is clear that the highest degree of positive charge and therefore the most electrophilic position of the pyridine moiety in INT1 is at C2; C1 carries a comparatively high degree of negative charge. Presumably, this higher electrophilicity favours the C2-rearrangement pathway over the "competitive" C1-nucleophilic substitution. The degree of negative charge at C1 decreases as the reaction proceeds to INT3, as the C2 position becomes correspondingly less positive, presumably facilitating the previously disfavoured substitution pathway.

[12] H. Sun, J. Li, D. Zhang, C. Ma and C. Liu, *J. Phys. Org. Chem.*, 2008, **21**, 215.

Table S2: Calculated NPA charges for select atoms (au)

	C1	C2	C3	N
INT1	-0.189	0.211	-0.274	-0.525
INT2a	-0.236	0.112	-0.151	-0.515
INT2b	-0.232	0.112	-0.152	-0.520
INT3a	-0.118	0.046	-0.168	-0.733
INT3b	-0.112	0.046	-0.169	-0.703
INT3c	-0.120	0.043	-0.164	-0.705
INT3d	-0.114	0.047	-0.168	-0.735

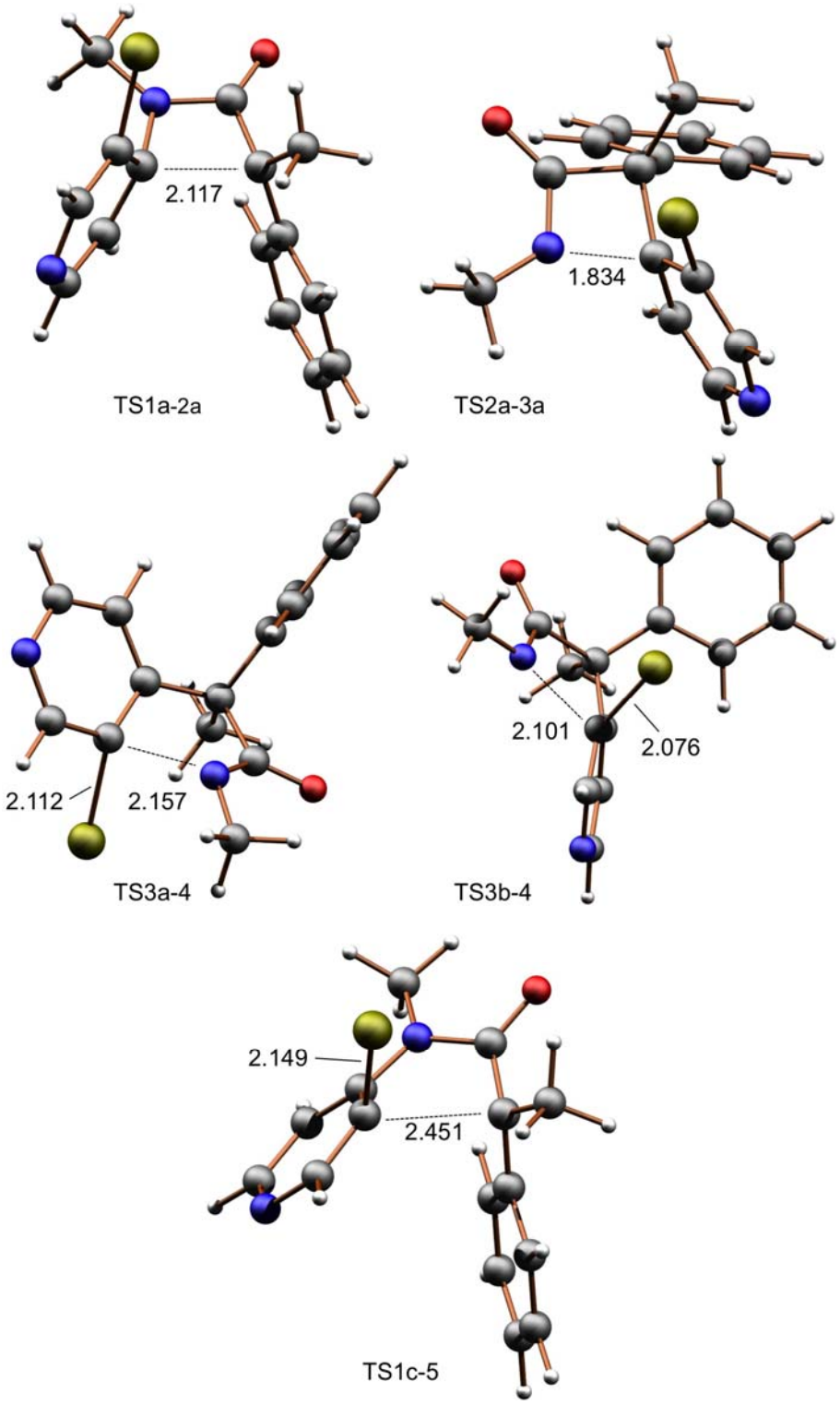
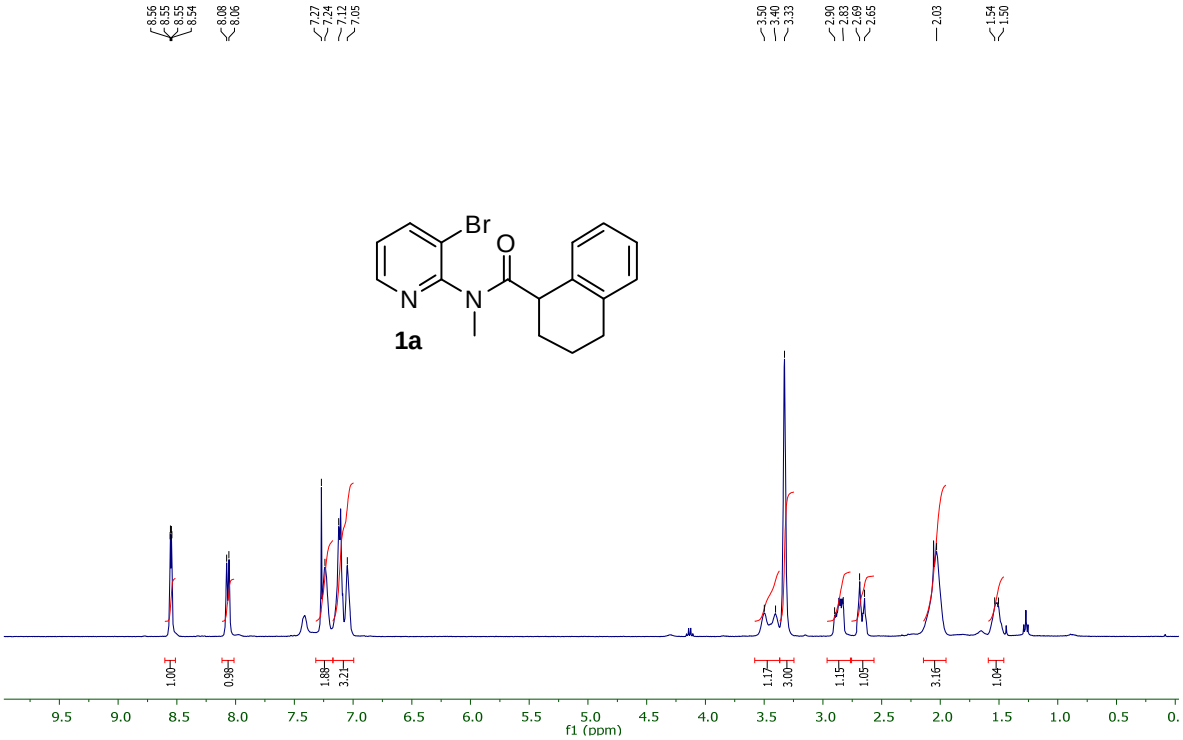
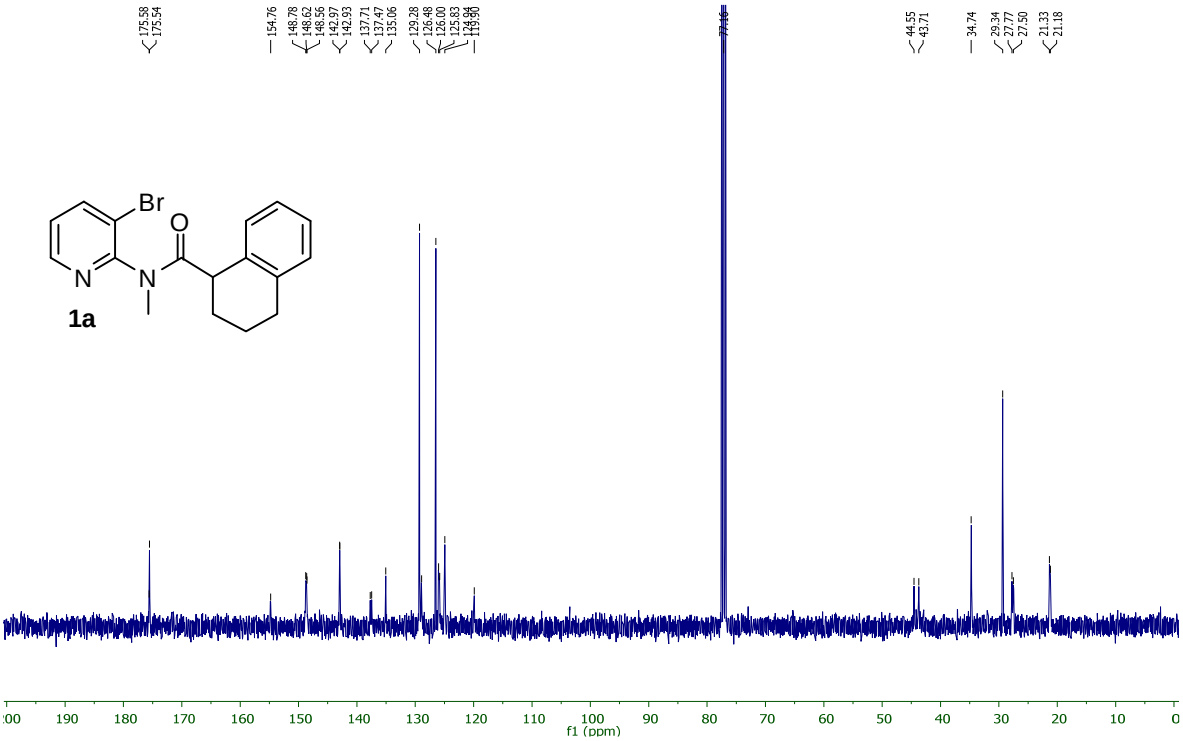
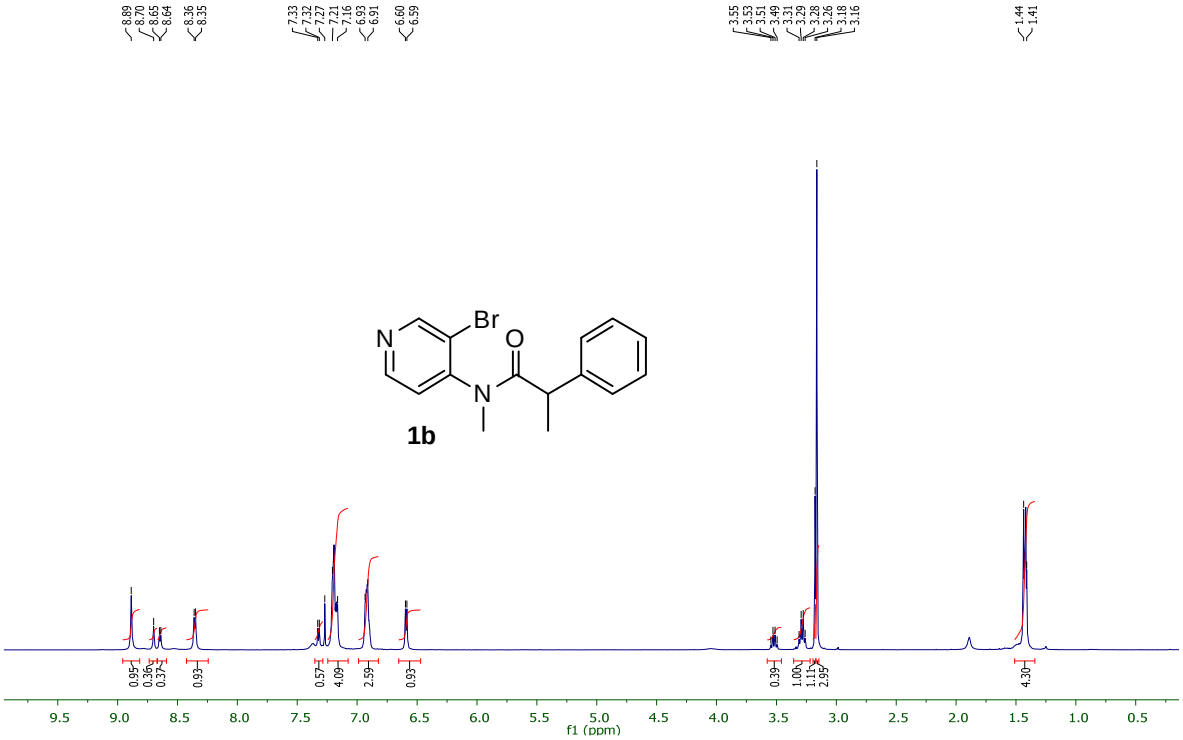
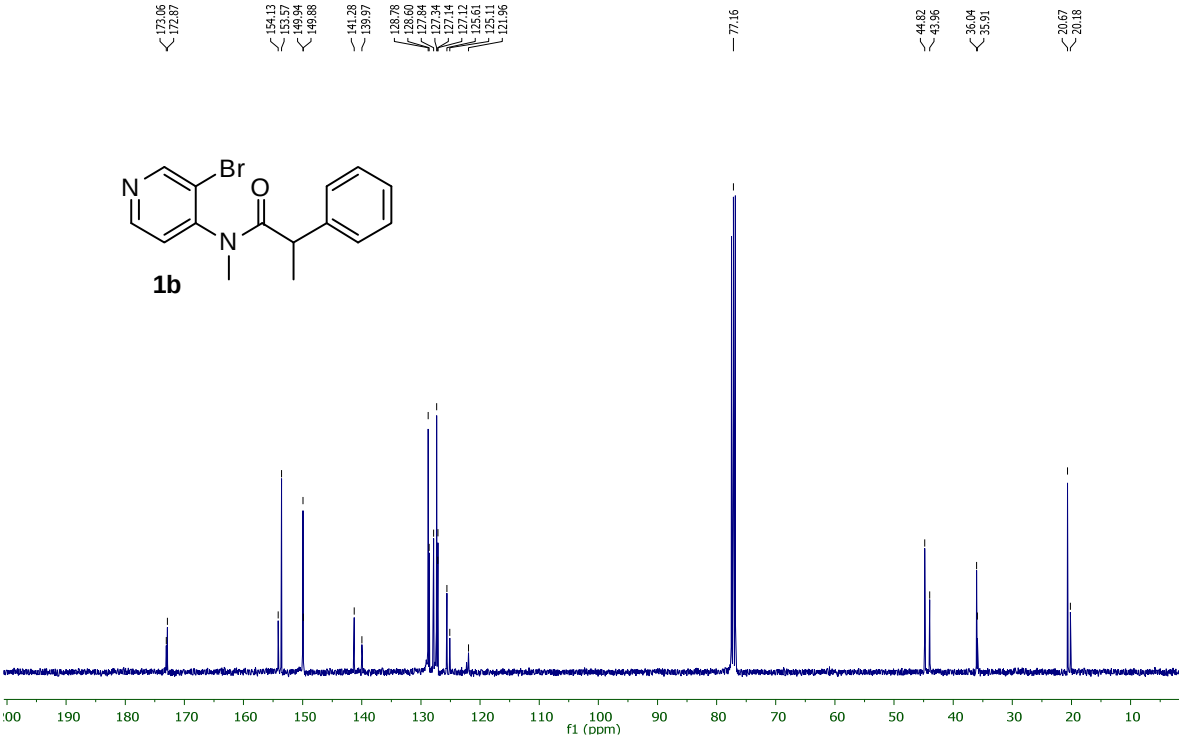


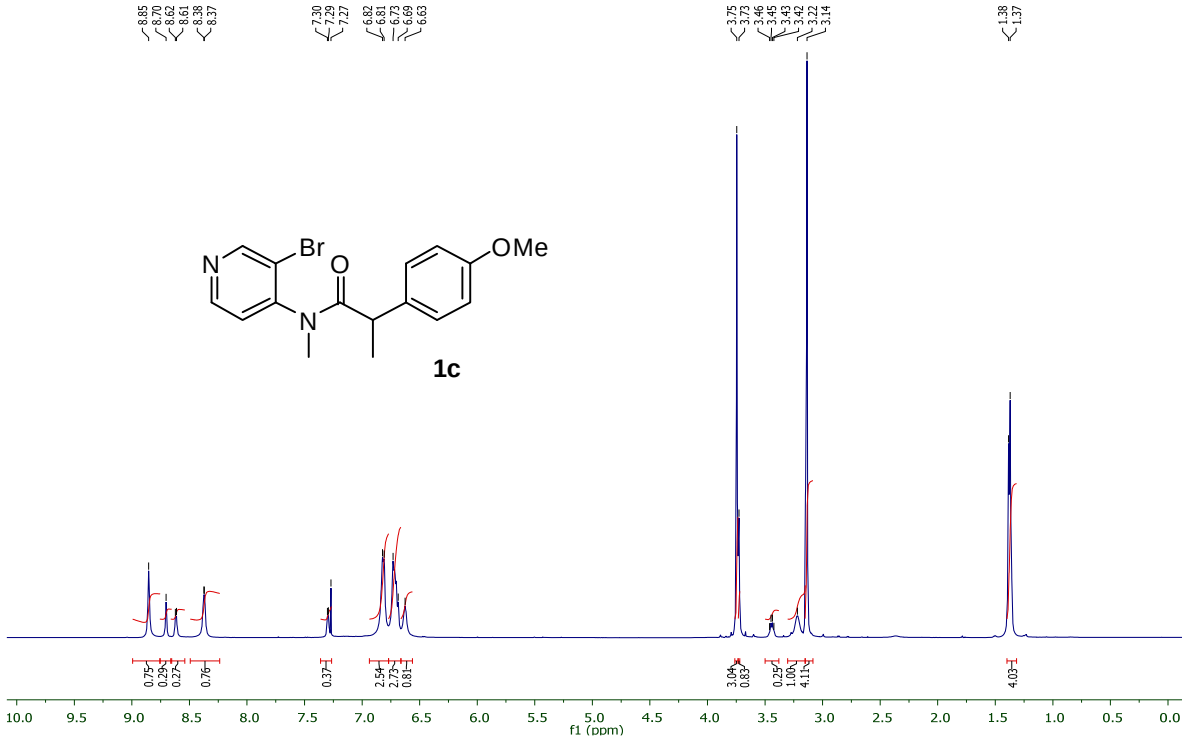
Figure S2: Optimized transition-state structures from Figure S1 (distances in Å)

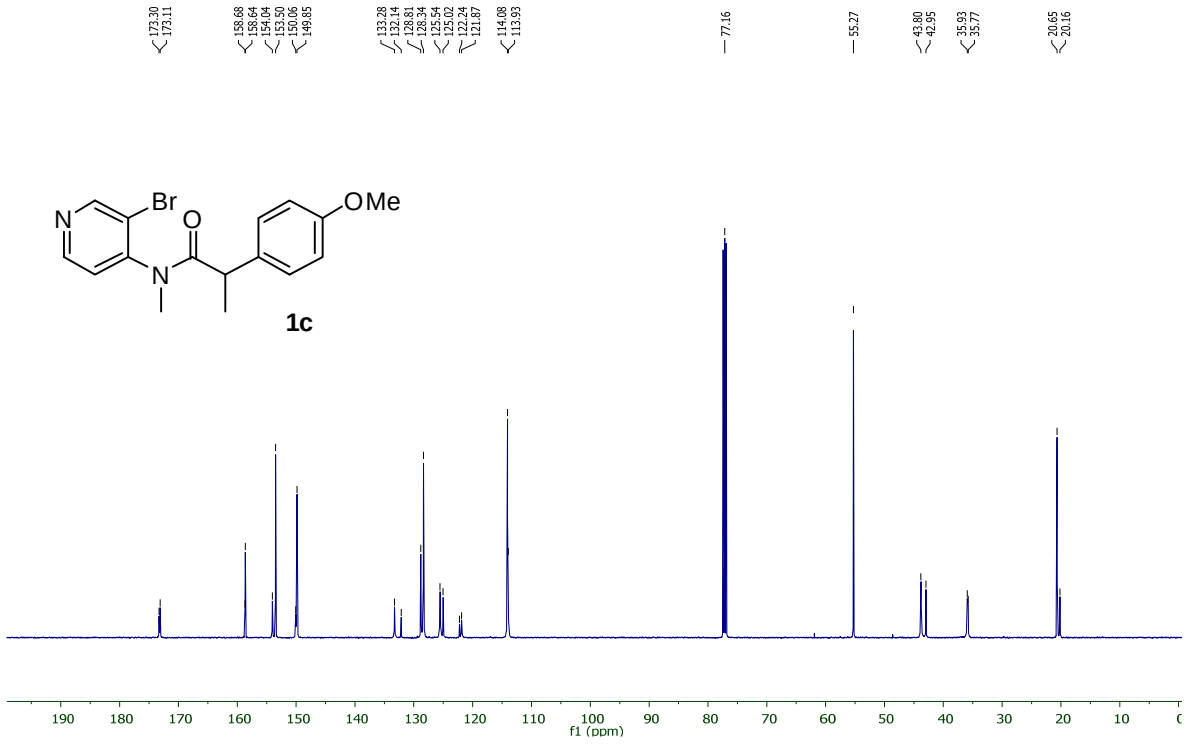

8.56
8.55
8.55
8.54
8.08
8.06
7.27
7.24
7.12
7.05
3.50
3.40
3.33
2.90
2.83
2.69
2.65
2.03
1.54
1.50
Br
O
N
N
1a
1.00
0.98
1.88
3.21
1.17
3.00
1.15
1.05
3.16
1.04
f1 (ppm)

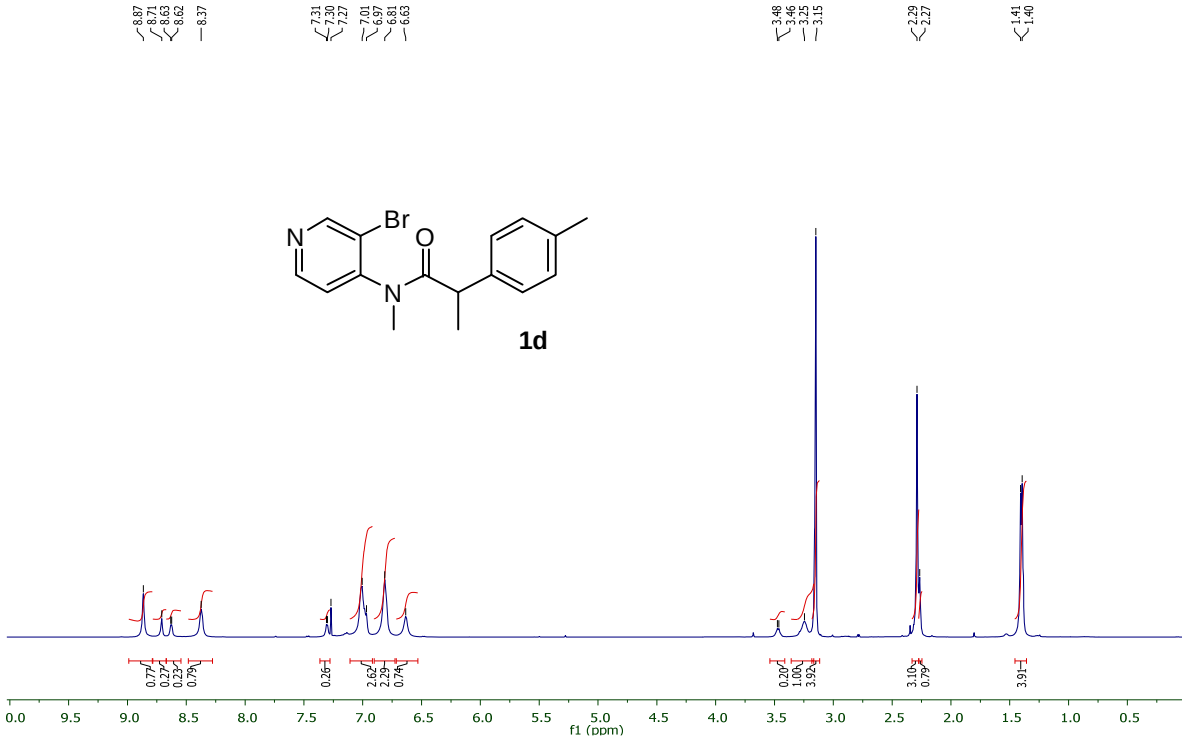

175.58
175.54
154.76
148.78
148.62
148.56
142.97
142.93
137.71
137.47
135.06
129.28
126.48
126.00
125.83
124.83
119.90
77.46
44.55
43.71
34.74
29.34
27.77
27.50
21.33
21.18
Br
O
N
N
1a
f1 (ppm)

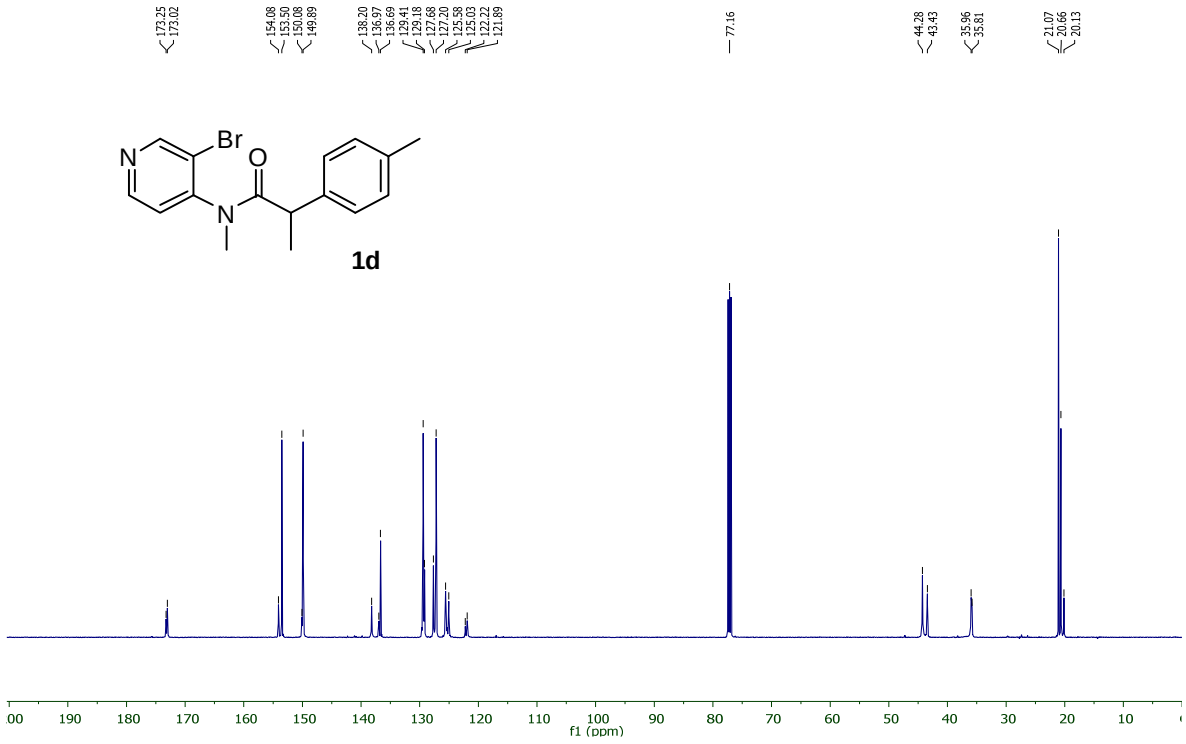

8.89
8.70
8.65
8.64
8.36
8.35
7.33
7.32
7.27
7.21
7.16
6.93
6.91
6.60
6.59
3.55
3.53
3.51
3.49
3.31
3.29
3.28
3.26
3.18
3.16
1.44
1.41
Br
N
O
N
1b
0.95
0.36
0.37
0.93
0.57
4.09
2.59
0.93
0.39
1.00
1.11
2.99
4.30
f1 (ppm)

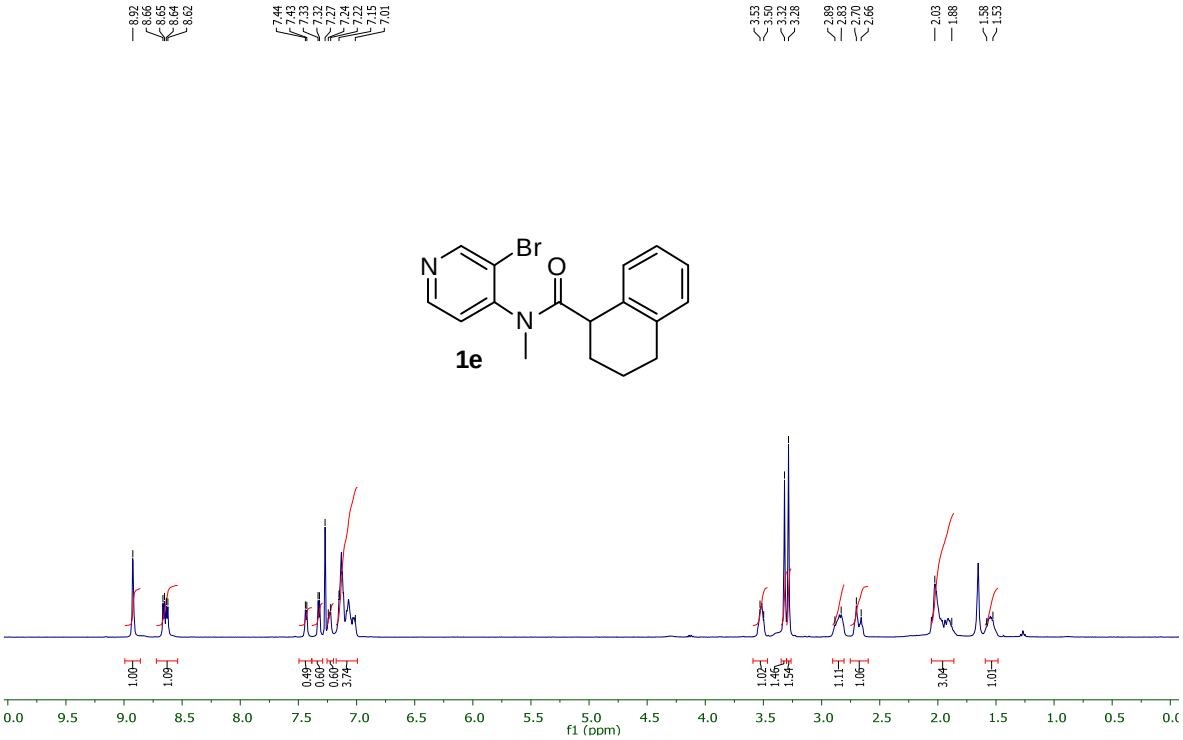

173.06
172.87
154.13
153.57
149.94
149.88
141.28
139.97
128.78
128.60
127.84
127.34
127.14
127.12
125.61
125.11
121.96
77.16
44.82
43.96
36.04
35.91
20.67
20.18
Br
N
O
N
1b
f1 (ppm)

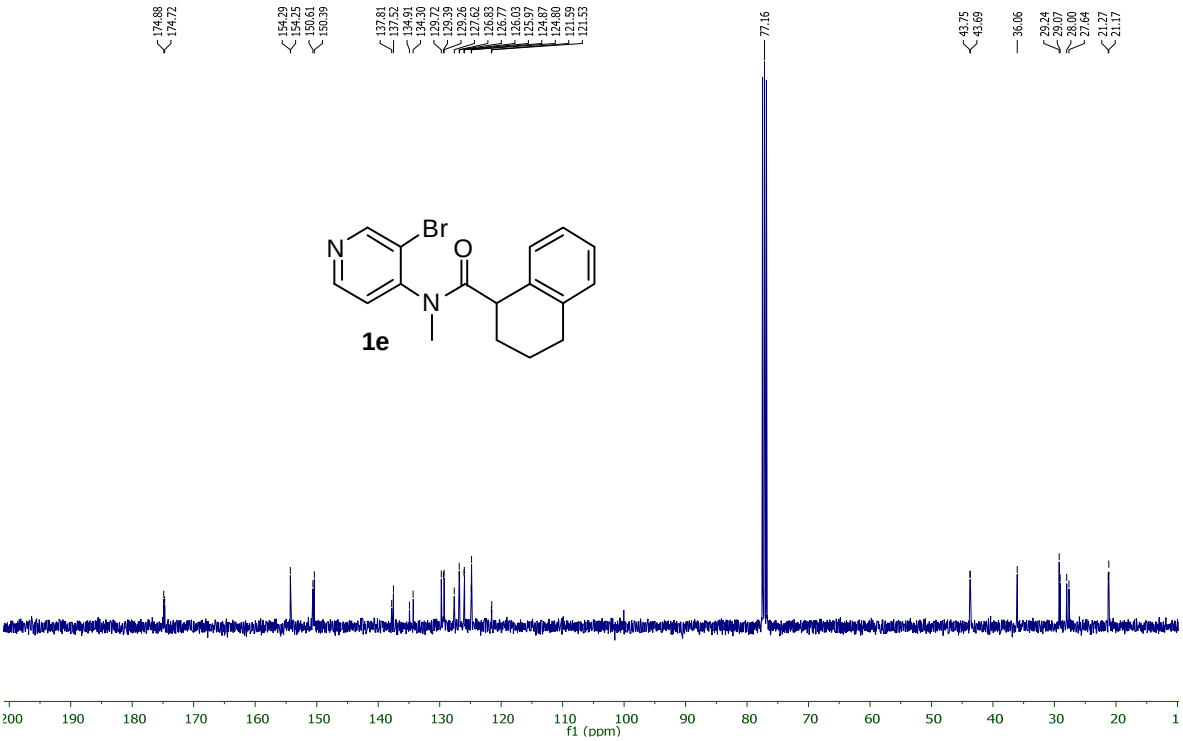

8.85
8.70
8.62
8.61
8.38
8.37
7.30
7.29
7.27
6.82
6.81
6.73
6.69
6.63
3.75
3.73
3.46
3.45
3.43
3.42
3.22
3.14
1.38
1.37
Br
O
N
N
OMe
1c
0.75
0.29
0.27
0.76
0.37
2.54
2.73
0.81
3.04
0.83
0.25
1.00
4.11
4.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

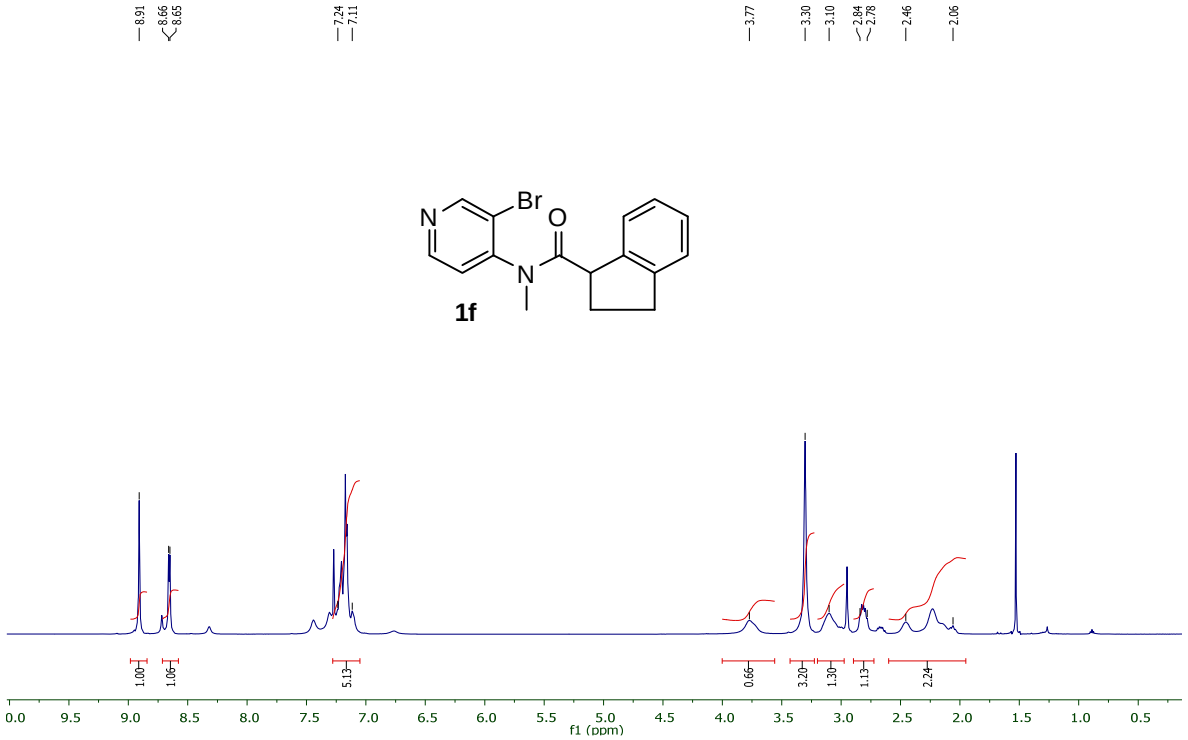

173.30
173.11
158.68
158.64
154.04
153.50
150.06
149.85
133.28
132.14
128.81
128.34
125.54
125.02
122.24
121.87
114.08
113.93
77.16
55.27
43.80
42.95
35.93
35.77
20.65
20.16
Br
O
N
N
OMe
1c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

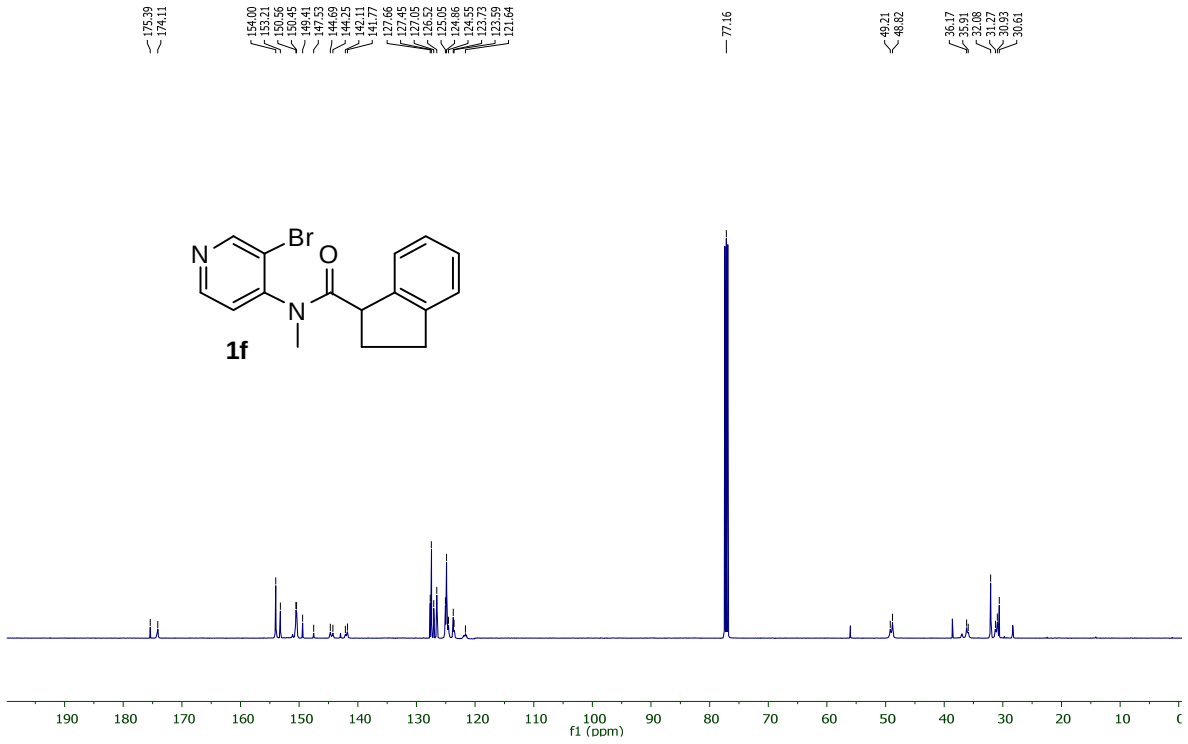

8.87
8.71
8.63
8.62
8.37
7.31
7.30
7.27
7.01
6.97
6.81
6.63
3.48
3.46
3.25
3.15
2.29
2.27
1.41
1.40
Br
N
O
N
1d
0.77
0.27
0.25
0.79
0.26
2.62
2.29
0.74
0.20
1.00
3.92
3.10
0.79
3.91
f1 (ppm)

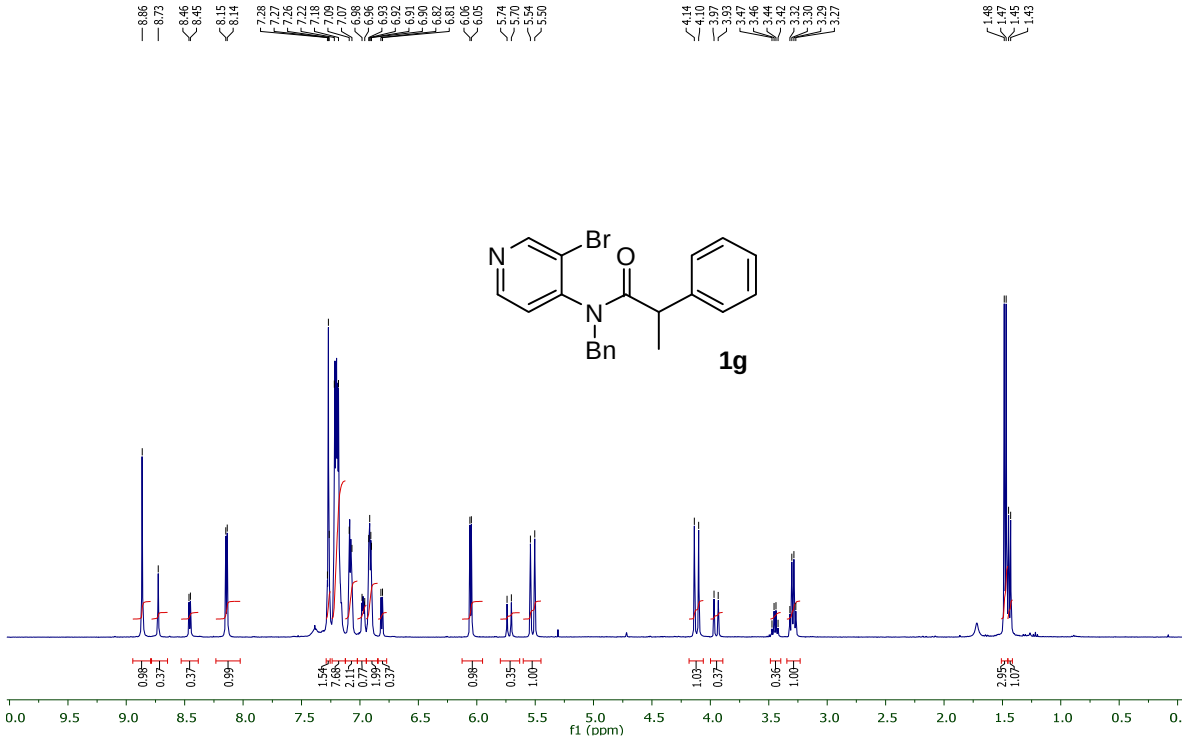

173.25
173.02
154.08
153.50
150.08
149.89
138.20
136.97
136.69
129.41
129.18
127.66
127.20
125.58
125.03
122.22
121.89
77.16
44.28
43.43
35.96
35.81
21.07
20.66
20.13
Br
N
O
N
1d
f1 (ppm)

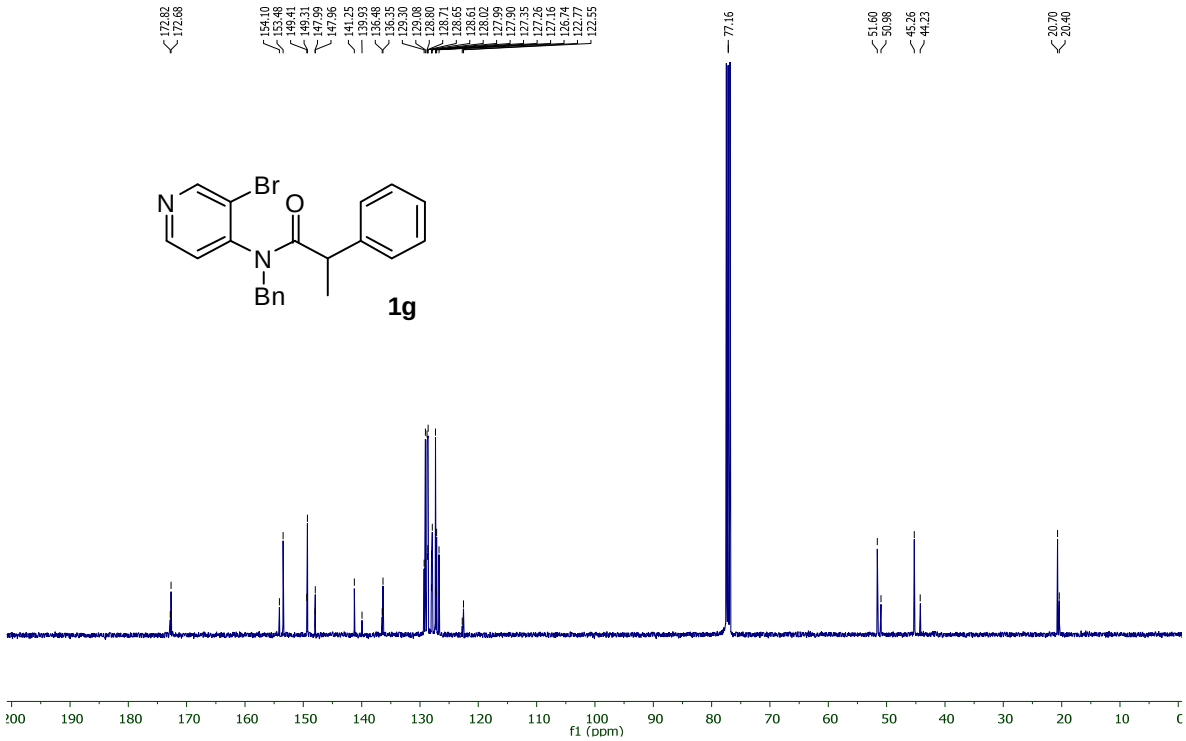

8.92
8.66
8.65
8.64
8.62
7.44
7.43
7.33
7.32
7.27
7.24
7.22
7.15
7.01
3.53
3.50
3.32
3.28
2.89
2.83
2.70
2.66
2.03
1.88
1.58
1.53
Br
N
O
N
1e
1.00
1.09
0.49
0.60
0.69
3.74
1.02
1.46
1.54
1.11
1.06
3.04
1.01
f1 (ppm)

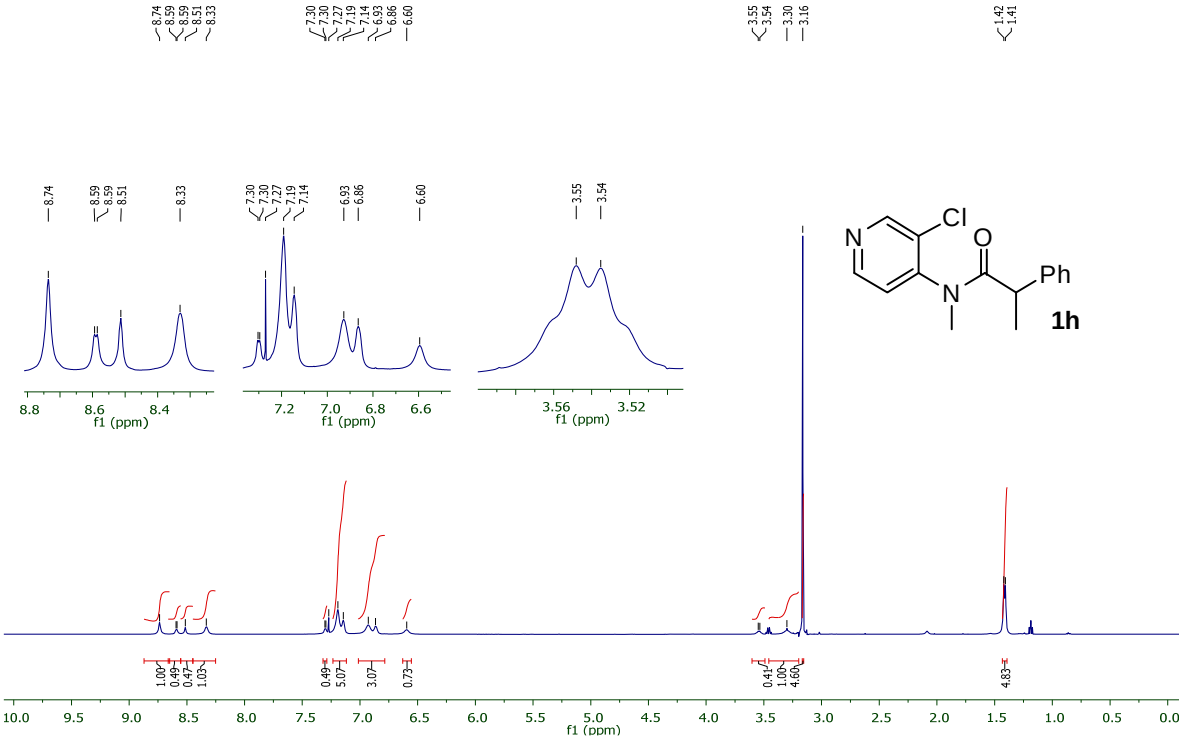

174.88
174.72
154.29
154.25
150.61
150.39
137.81
137.52
134.91
134.30
129.72
129.39
129.26
127.62
126.83
126.77
126.03
125.97
124.87
124.80
121.59
121.53
77.16
43.75
43.69
36.06
29.24
29.07
28.00
27.64
21.27
21.17
Br
N
O
N
1e
f1 (ppm)

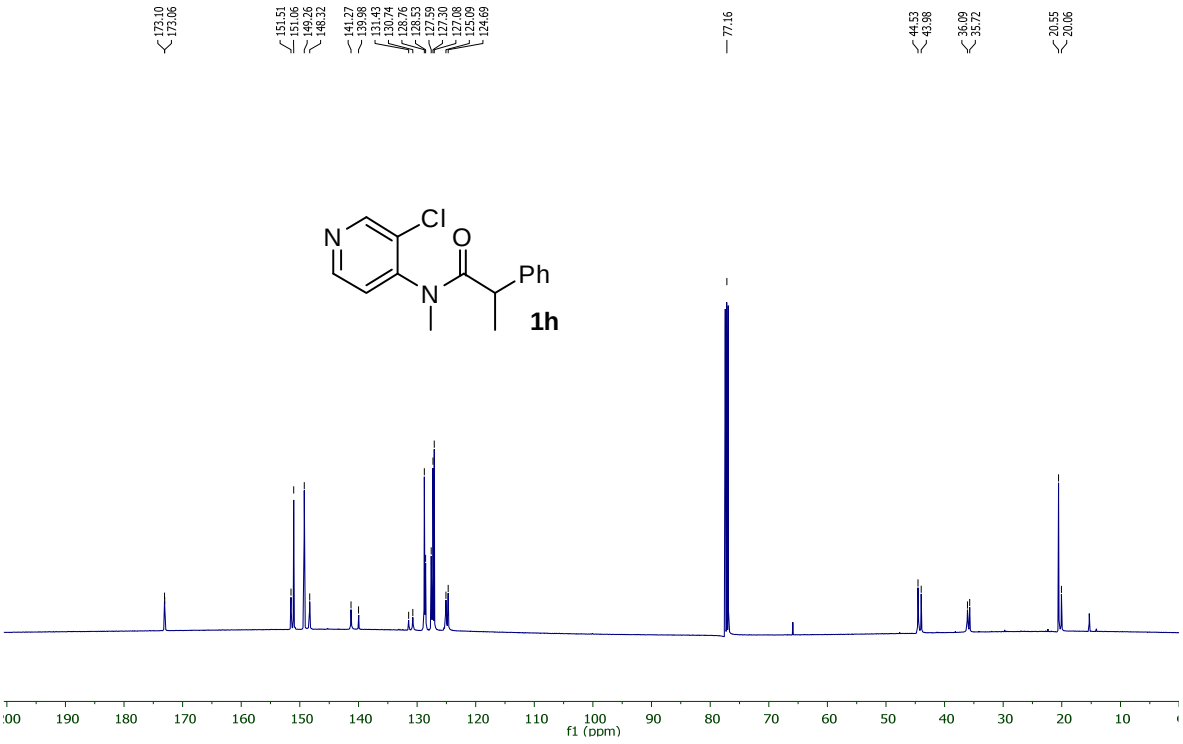

8.91
8.66
8.65
7.24
7.11
3.77
3.30
3.10
2.84
2.78
2.46
2.06
Br
N
O
N
1f
1.00
1.06
5.13
0.66
3.20
1.30
1.13
2.24
f1 (ppm)

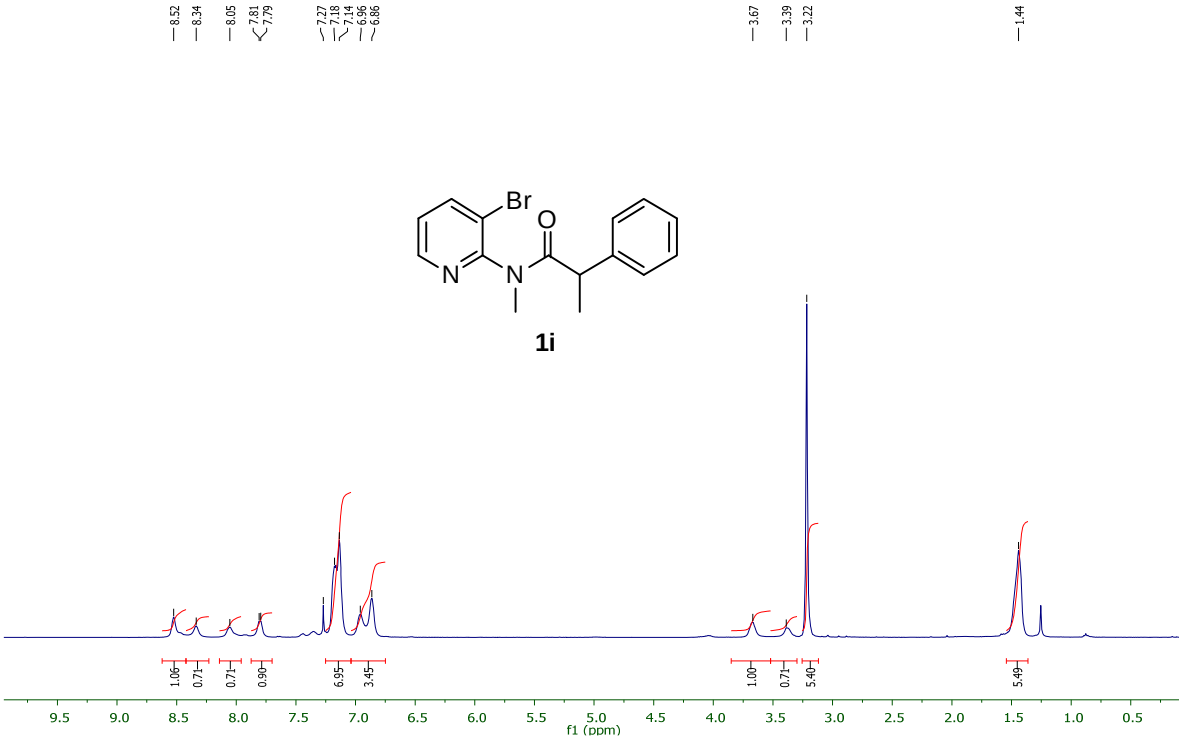

175.39
174.11
154.00
153.21
150.56
150.45
149.41
147.53
144.69
144.25
142.11
141.77
127.66
127.45
127.05
126.52
125.05
124.86
124.55
123.73
123.59
121.64
77.16
49.21
48.82
36.17
35.91
32.08
31.27
30.93
30.61
Br
N
O
N
1f
f1 (ppm)

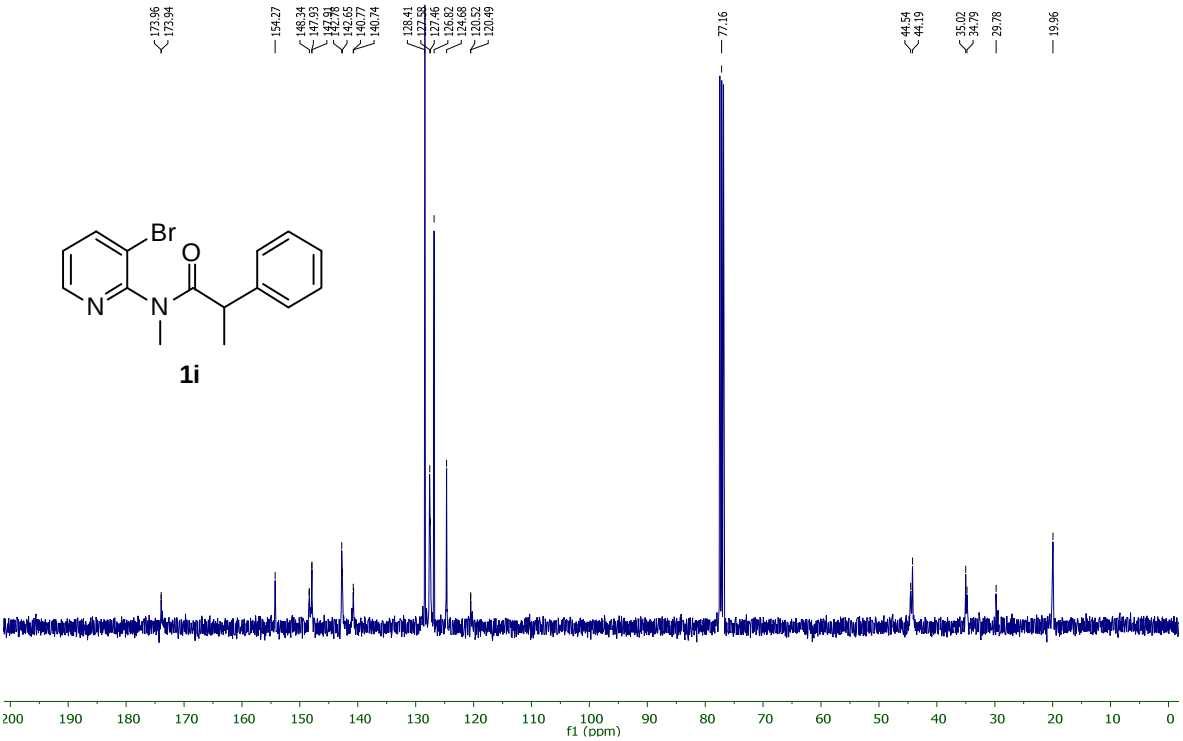

8.86
8.73
8.46
8.45
8.15
8.14
7.28
7.27
7.26
7.22
7.18
7.09
7.07
6.98
6.96
6.93
6.92
6.91
6.90
6.82
6.81
6.06
6.05
5.74
5.70
5.54
5.50
4.14
4.10
3.97
3.93
3.47
3.46
3.44
3.42
3.32
3.30
3.29
3.27
1.48
1.47
1.45
1.43
Br
O
N
N
Bn
1g
0.98
0.37
0.37
0.99
1.54
7.68
2.11
0.77
1.99
0.37
0.98
0.35
1.00
1.03
0.37
0.36
1.00
2.95
1.07
f1 (ppm)

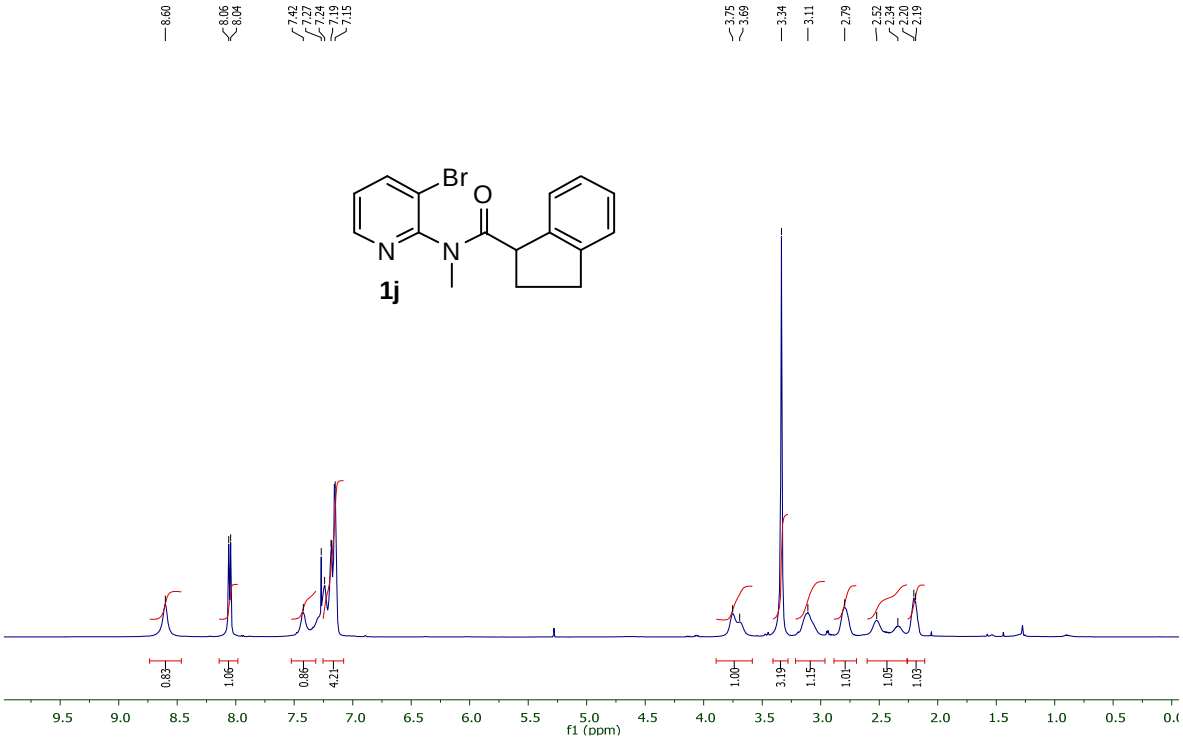

172.82
172.68
154.10
153.48
149.41
149.31
147.99
147.96
141.25
139.93
136.48
136.35
129.30
129.08
128.90
128.71
128.65
128.61
128.02
127.99
127.90
127.35
127.26
127.16
126.74
122.77
122.55
77.16
51.60
50.98
45.26
44.23
20.70
20.40
Br
O
N
N
Bn
1g
f1 (ppm)

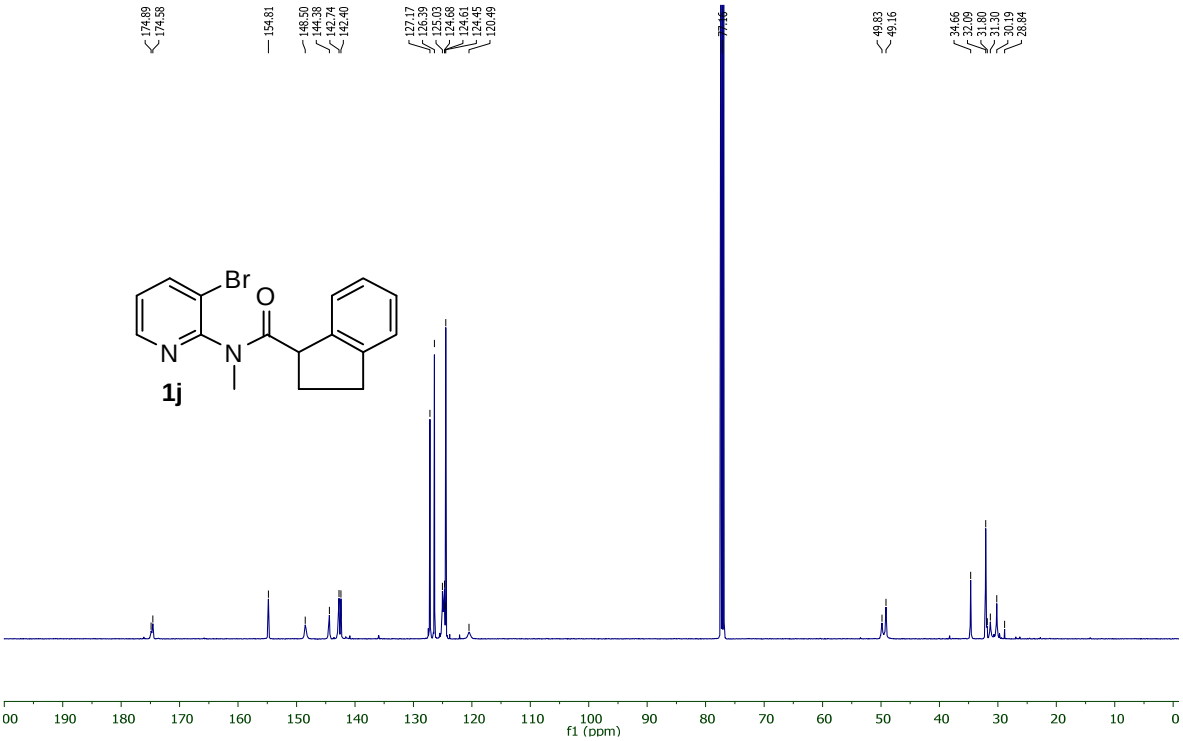

8.74
8.59
8.59
8.51
8.33
7.30
7.30
7.27
7.19
7.14
6.93
6.86
6.60
3.55
3.54
3.30
3.16
1.42
1.41
Cl
N
O
Ph
N
1h
f1 (ppm)

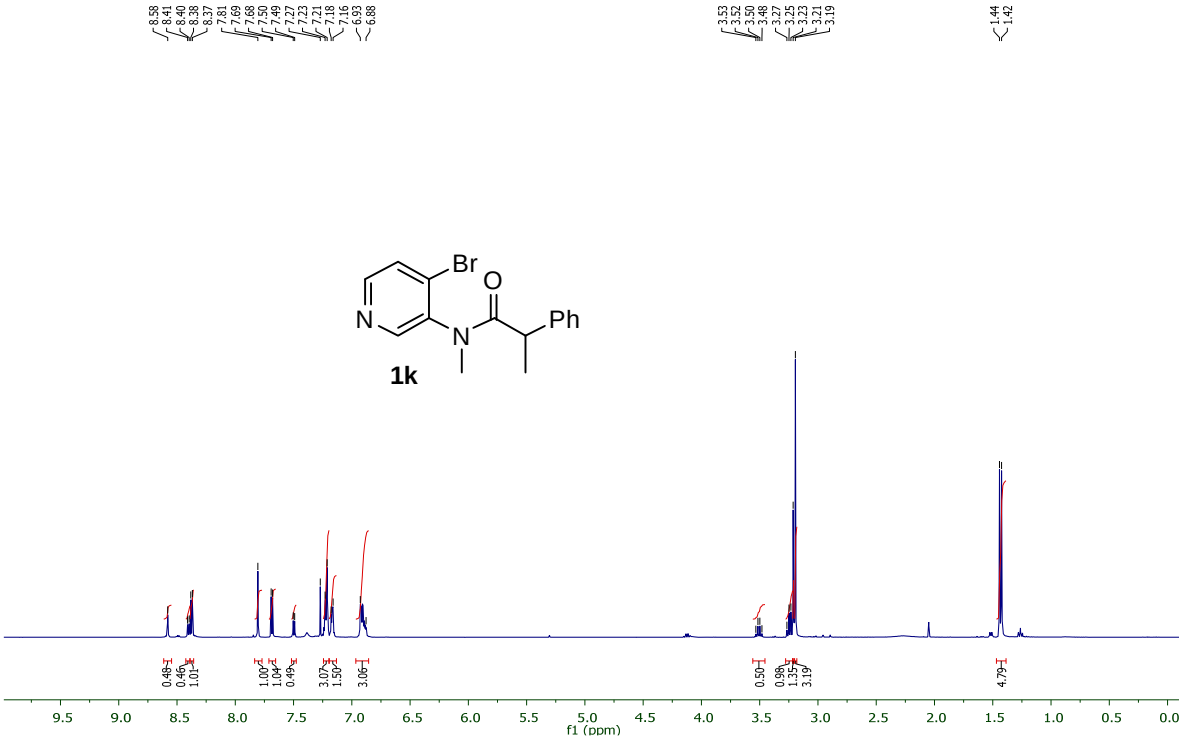

173.10
173.06
151.51
151.06
149.26
148.32
141.27
139.98
131.43
130.74
128.76
128.53
127.59
127.30
127.08
125.09
124.69
77.16
44.53
43.98
36.09
35.72
20.55
20.06
Cl
N
O
Ph
N
1h
f1 (ppm)

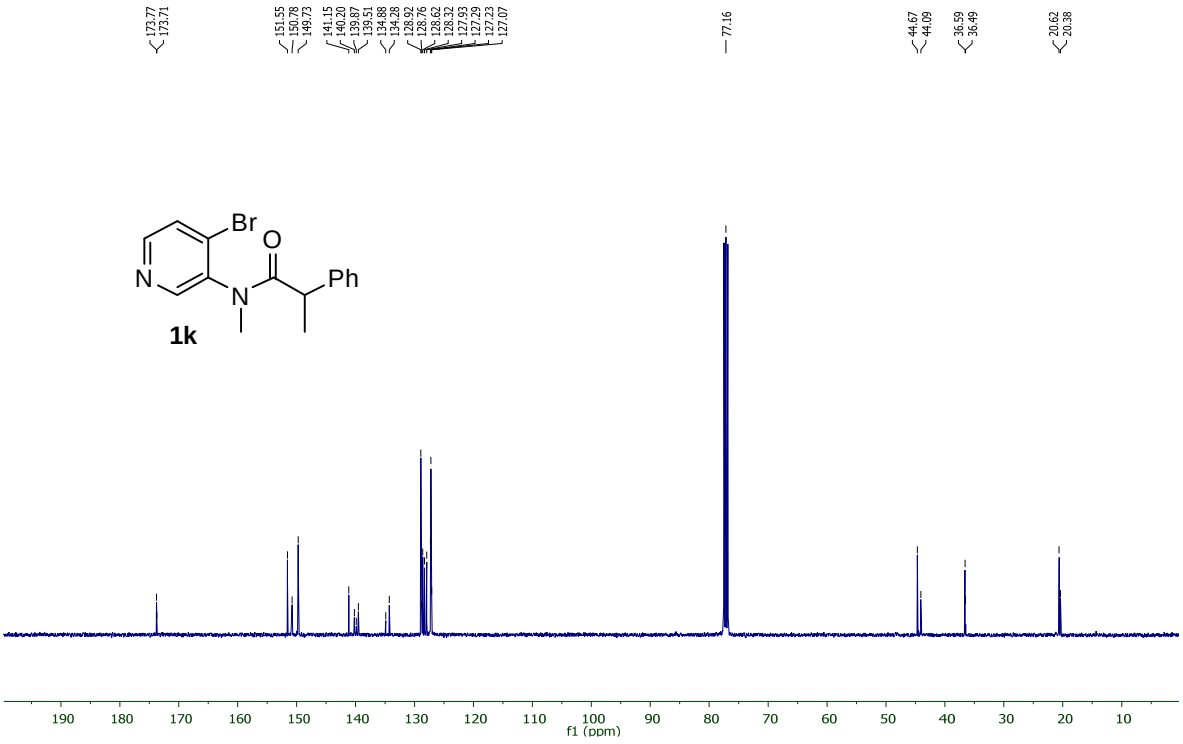

8.52
8.34
8.05
7.81
7.79
7.27
7.18
7.14
6.96
6.86
3.67
3.39
3.22
1.44
Br
O
N
N
1i
1.06
0.71
0.71
0.90
6.95
3.45
1.00
0.71
5.40
5.49
f1 (ppm)

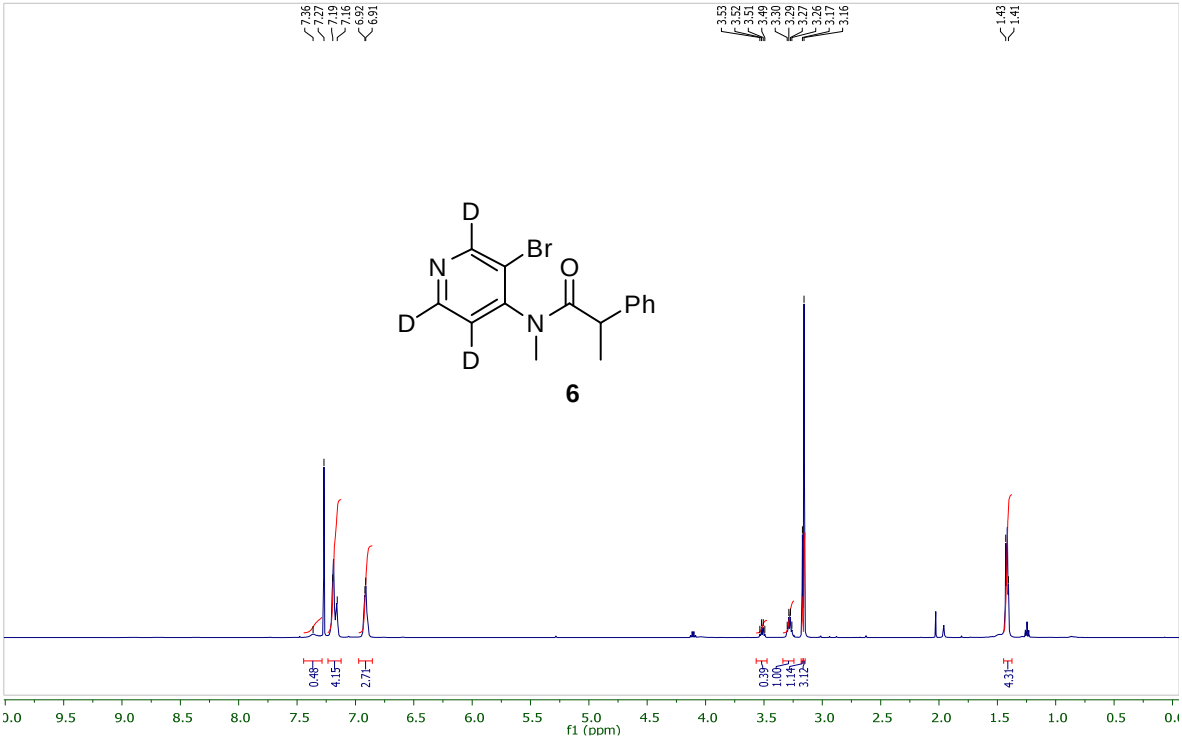

173.96
173.94
154.27
148.34
147.93
147.91
142.78
142.65
140.77
140.74
128.41
127.58
127.46
126.82
124.68
120.52
120.49
77.16
44.54
44.19
35.02
34.79
29.78
19.96
Br
O
N
N
1i
f1 (ppm)

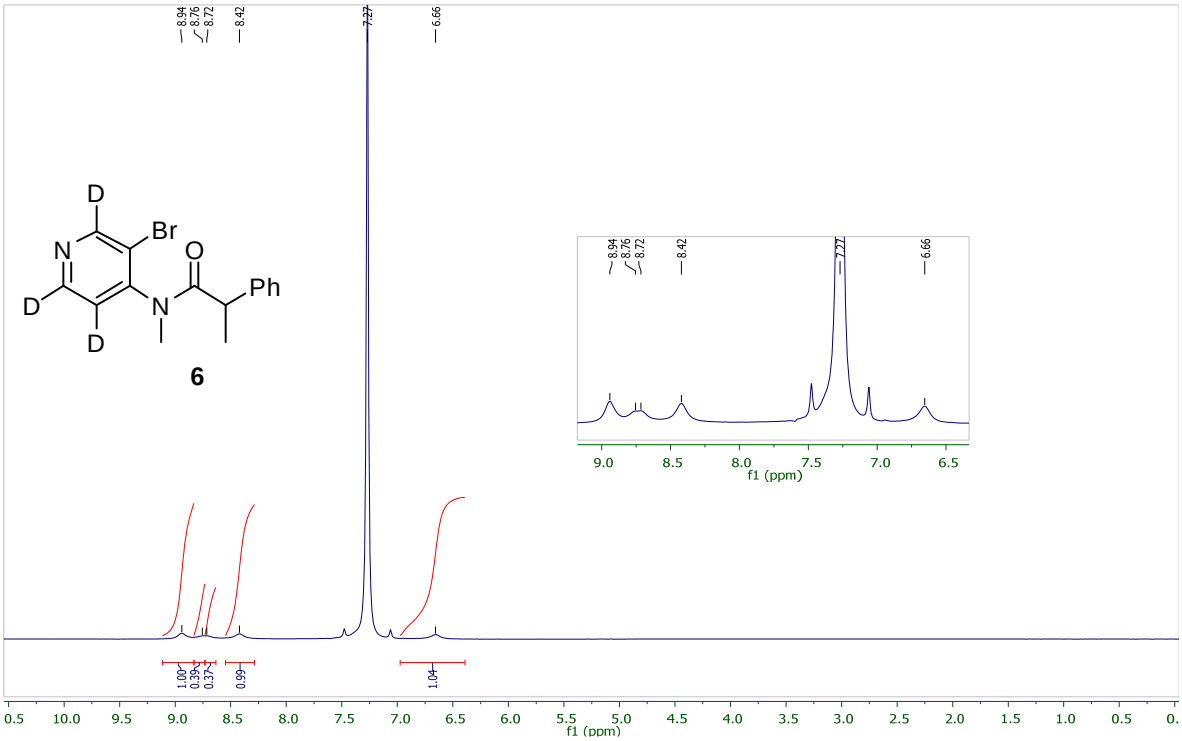

8.60
8.06
8.04
7.42
7.27
7.24
7.19
7.15
3.75
3.69
3.34
3.11
2.79
2.52
2.34
2.20
2.19
Br
O
N
N
1j
0.83
1.06
0.86
4.21
1.00
3.19
1.15
1.01
1.05
1.03
f1 (ppm)

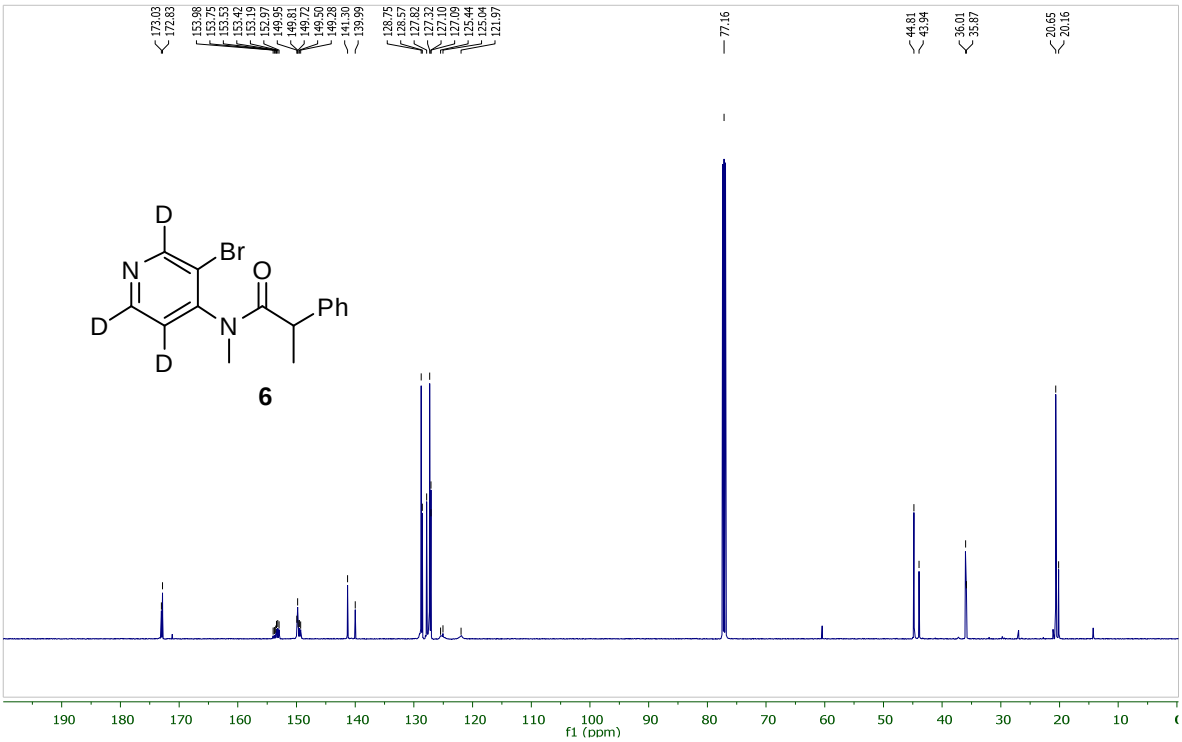

174.89
174.58
154.81
148.50
144.38
142.74
142.40
127.17
126.39
125.03
124.68
124.61
124.45
120.49
77.16
49.83
49.16
34.66
32.09
31.80
31.30
30.19
28.84
Br
O
N
N
1j
f1 (ppm)

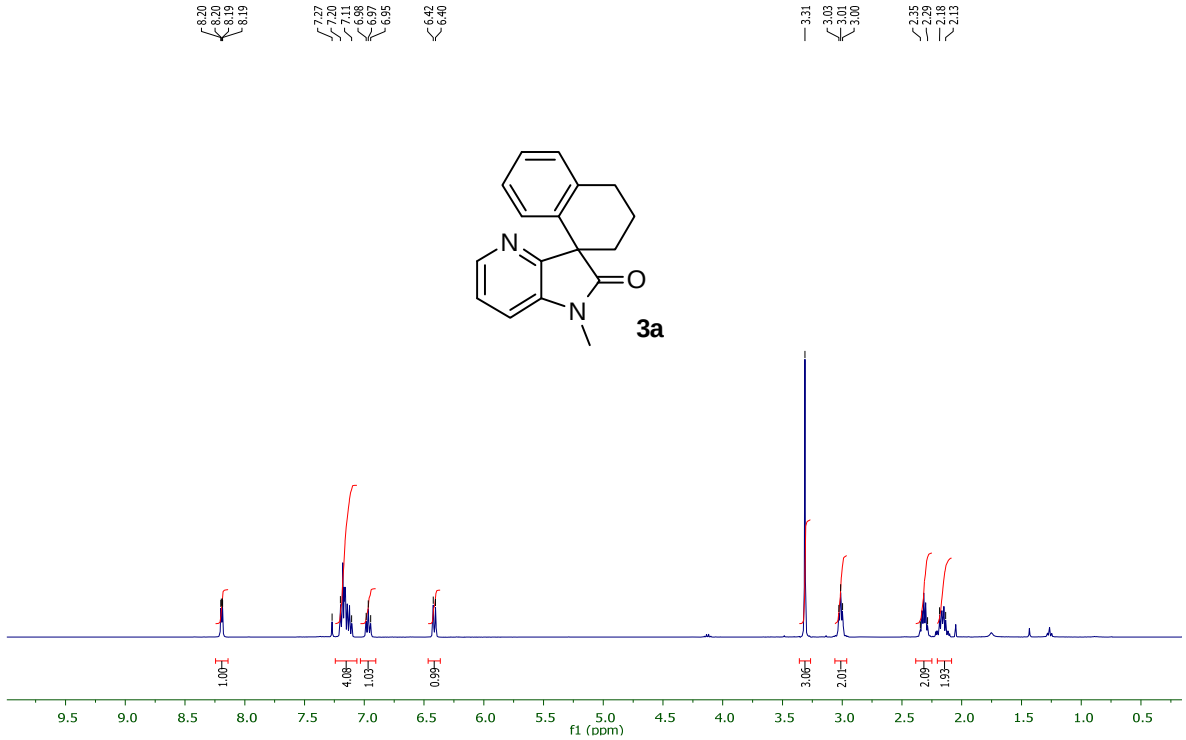

8.58
8.41
8.40
8.38
8.37
7.81
7.69
7.68
7.50
7.49
7.27
7.23
7.21
7.18
7.16
6.93
6.88
3.53
3.52
3.50
3.48
3.27
3.25
3.23
3.21
3.19
1.44
1.42
Br
O
N
N
Ph
1k
0.48
0.46
1.01
1.00
1.04
0.49
3.07
1.50
3.06
0.50
0.98
1.35
3.19
4.79
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

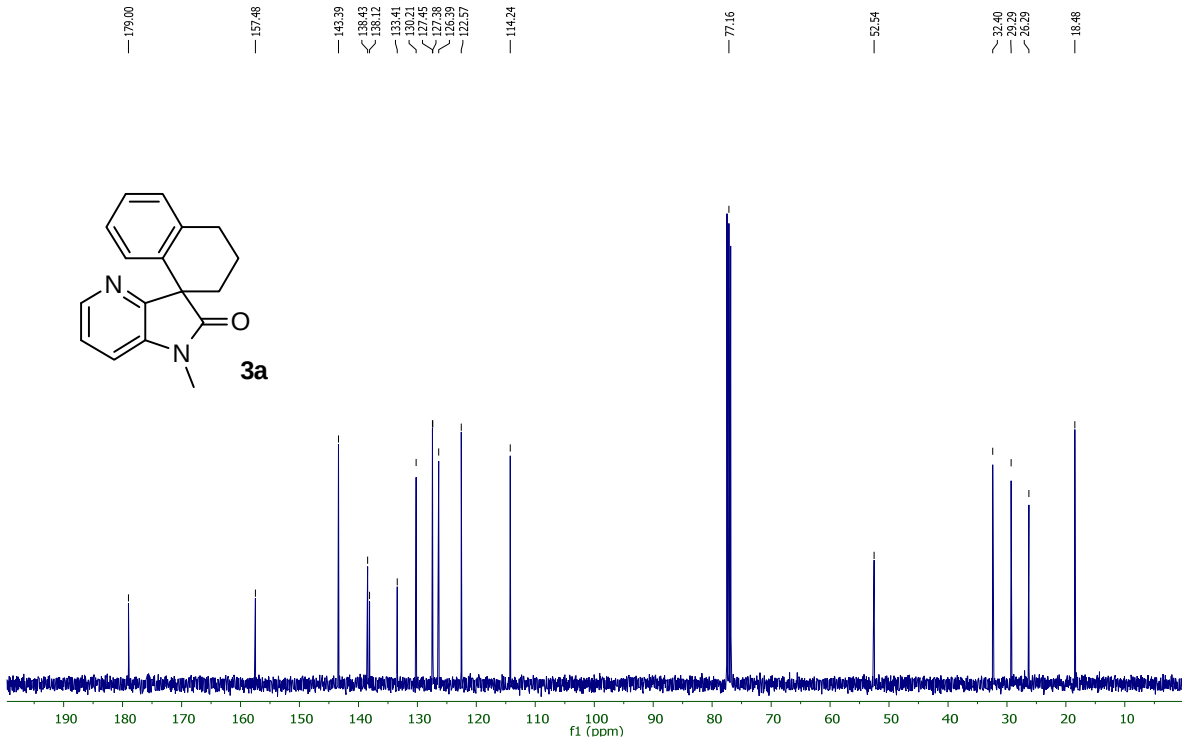

173.77
173.71
151.55
150.78
149.73
141.15
140.20
139.87
139.51
134.88
134.28
128.92
128.76
128.62
128.32
127.93
127.29
127.23
127.07
77.16
44.67
44.09
36.59
36.49
20.62
20.38
Br
O
N
N
Ph
1k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

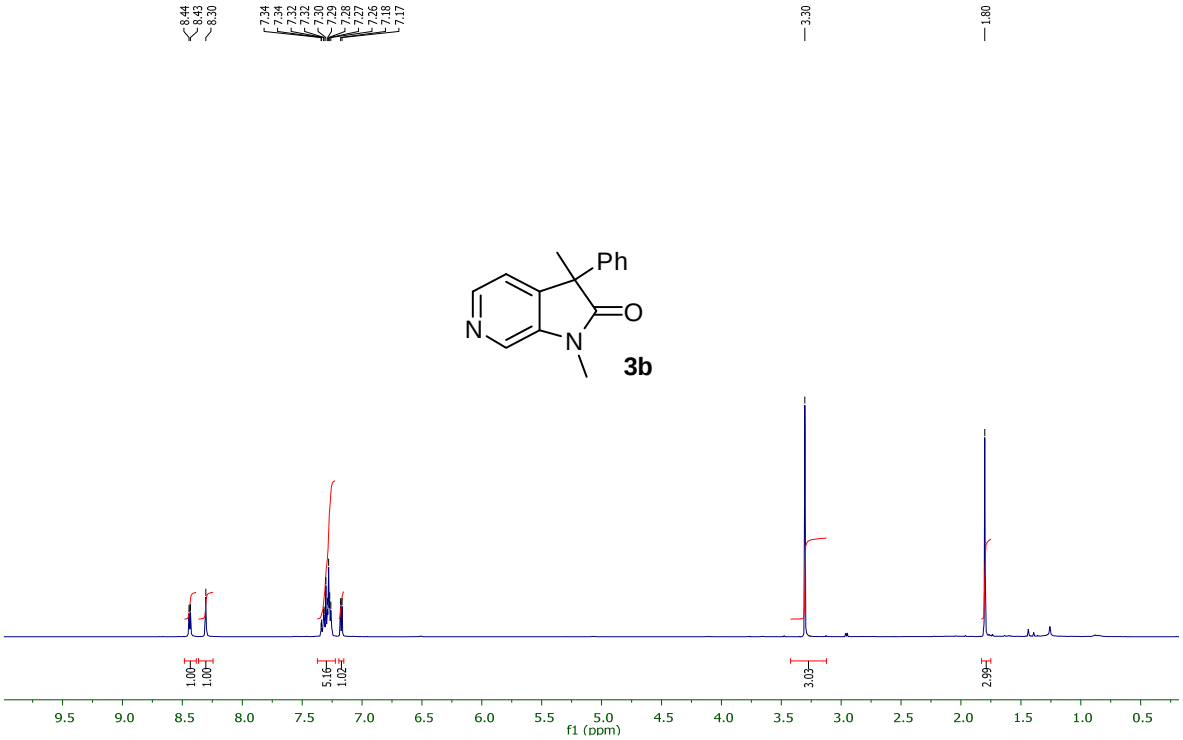

7.36
7.27
7.19
7.16
6.92
6.91
3.53
3.52
3.51
3.49
3.30
3.29
3.27
3.26
3.17
3.16
1.43
1.41
D
Br
N
O
D
N
Ph
D
6
0.48
4.15
2.71
0.39
1.00
1.14
3.12
4.31
f1 (ppm)

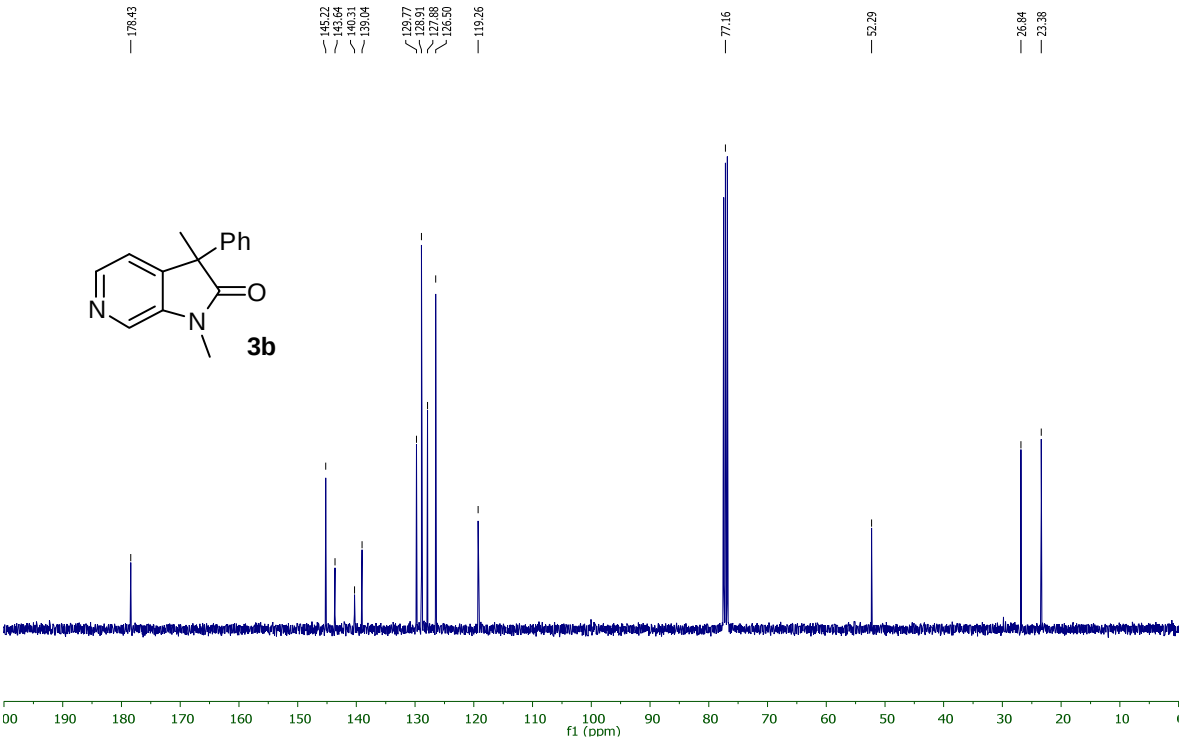

8.94
8.76
8.72
8.42
7.27
6.66
D
Br
N
O
D
N
Ph
D
6
f1 (ppm)
1.00
0.39
0.37
0.99
1.04
f1 (ppm)

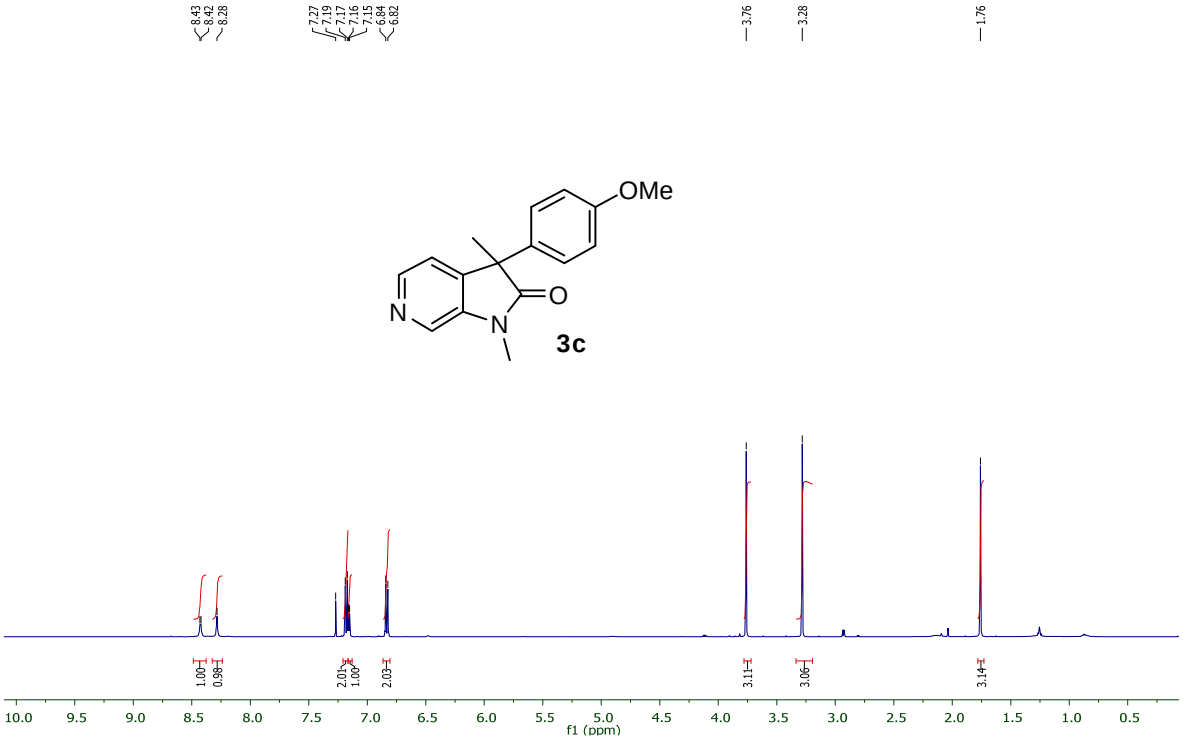

173.03
172.83
153.98
153.75
153.53
153.42
153.19
152.97
149.95
149.81
149.72
149.50
149.28
141.30
139.99
128.75
128.57
127.82
127.32
127.10
127.09
125.44
125.04
121.97
77.16
44.81
43.94
36.01
35.87
20.65
20.16
D
Br
N
O
Ph
D
N
D
6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

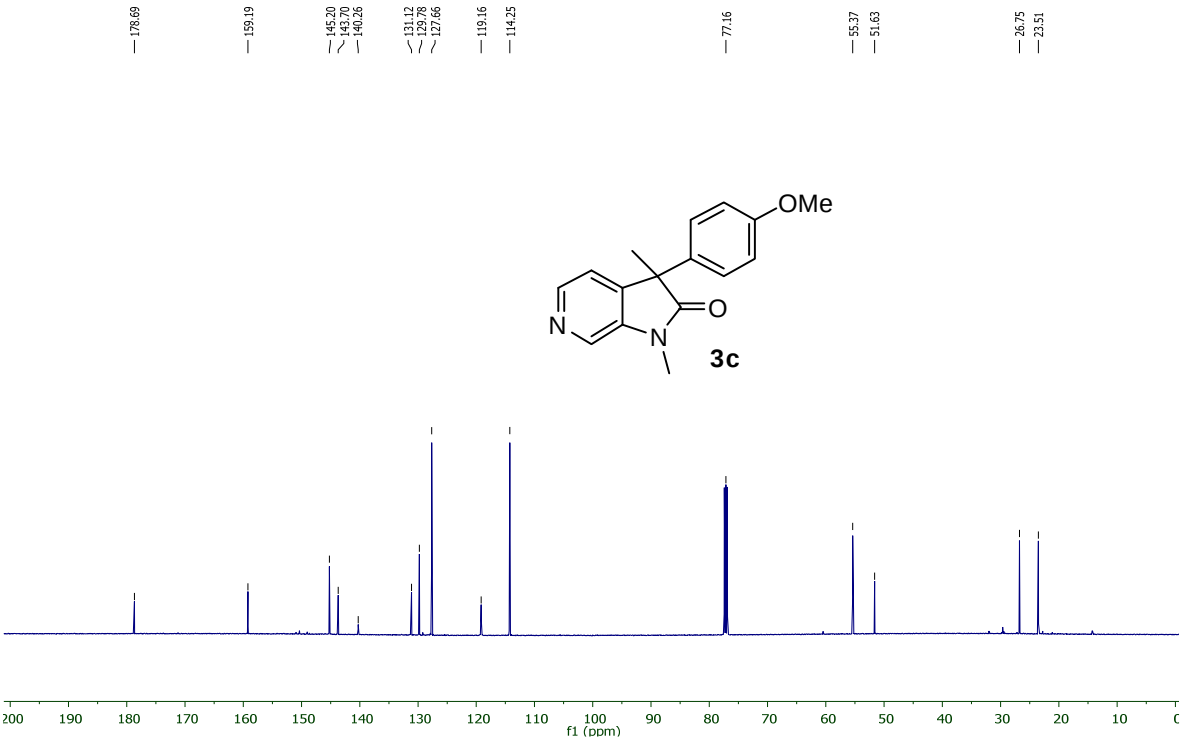

8.20
8.20
8.19
8.19
7.27
7.20
7.11
6.98
6.97
6.95
6.42
6.40
3.31
3.03
3.01
3.00
2.35
2.29
2.18
2.13
N
O
N
3a
1.00
4.08
1.03
0.99
3.06
2.01
2.09
1.93
f1 (ppm)

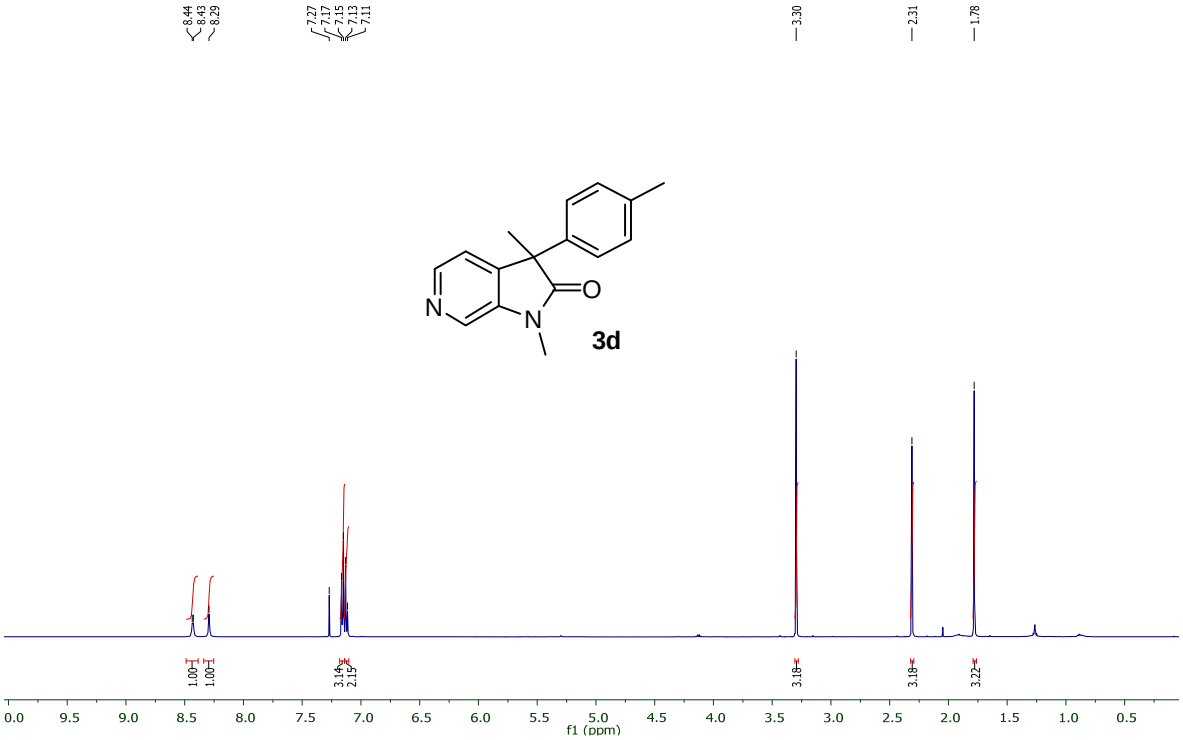

179.00
157.48
143.39
138.43
138.12
133.41
130.21
127.45
127.38
126.39
122.57
114.24
77.16
52.54
32.40
29.29
26.29
18.48
N
O
N
3a
f1 (ppm)

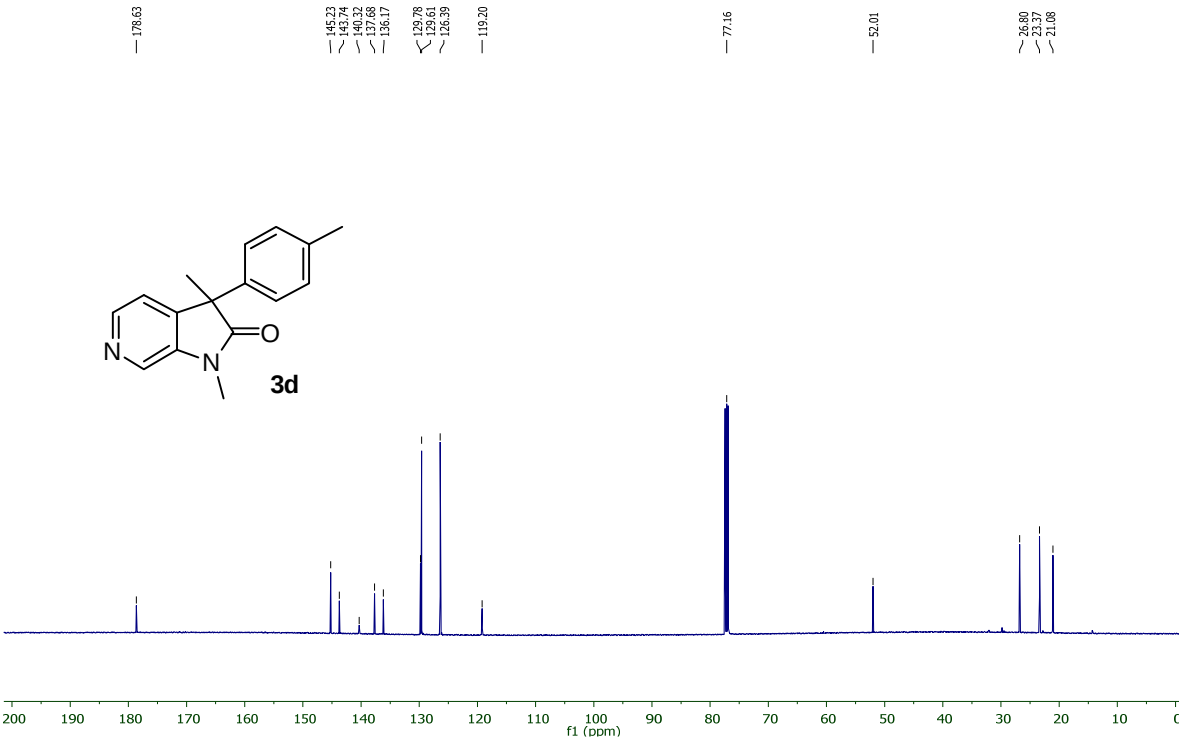

8.44
8.43
8.30
7.34
7.34
7.32
7.32
7.30
7.29
7.28
7.27
7.26
7.18
7.17
3.30
1.80
Ph
O
N
N
3b
1.00
1.00
5.16
1.02
3.03
2.99
f1 (ppm)

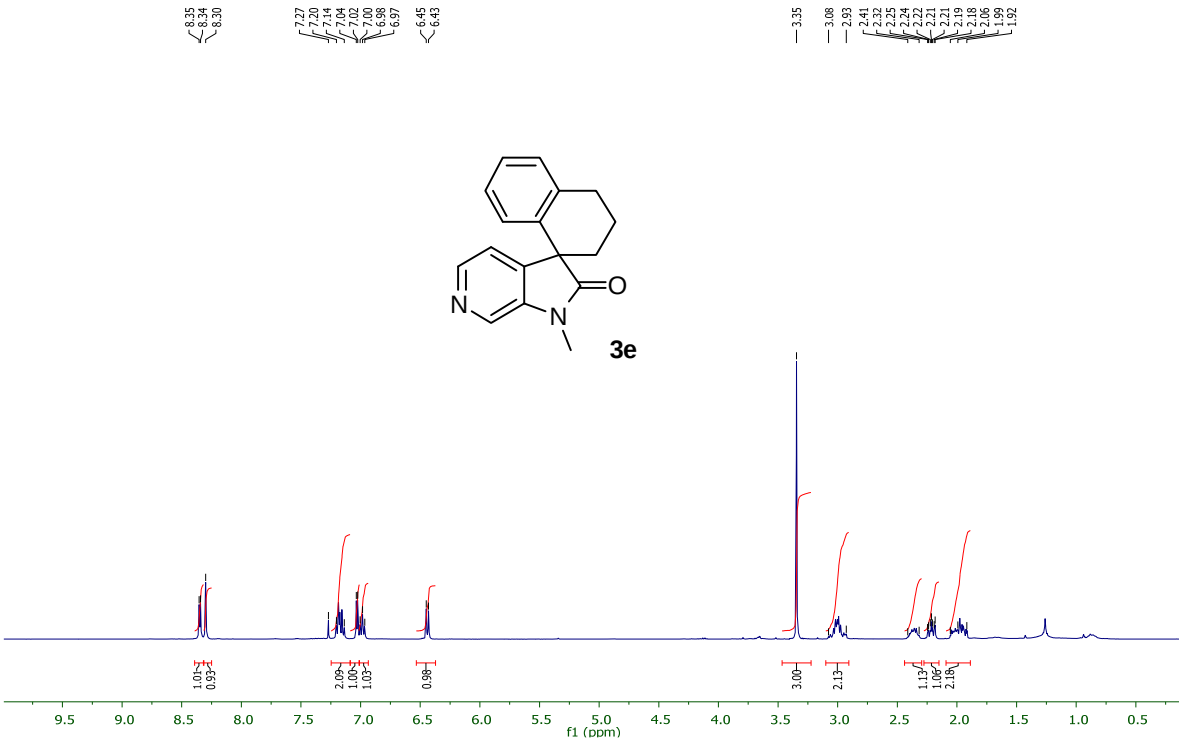

178.43
145.22
143.64
140.31
139.04
129.77
128.91
127.88
126.50
119.26
77.16
52.29
26.84
23.38
Ph
O
N
N
3b
f1 (ppm)

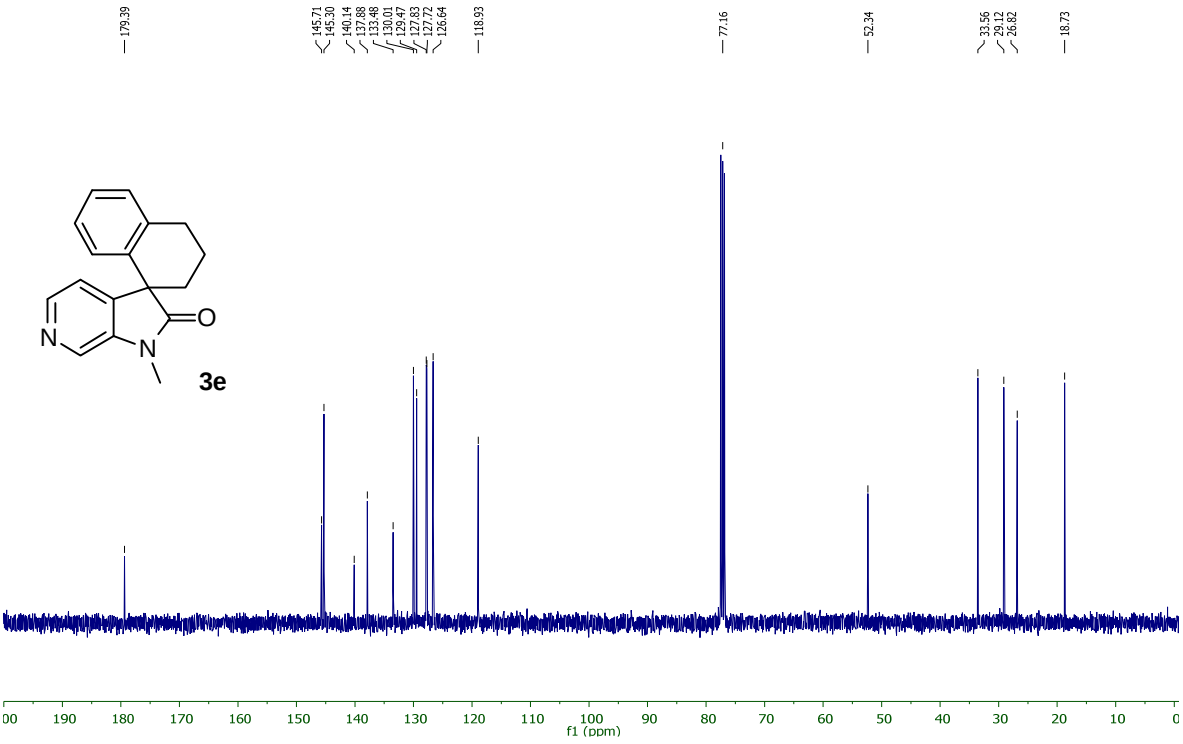

8.43
8.42
8.28
7.27
7.19
7.17
7.16
7.15
6.84
6.82
3.76
3.28
1.76
OMe
O
N
N
3c
1.00
0.98
2.01
1.00
2.03
3.11
3.06
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

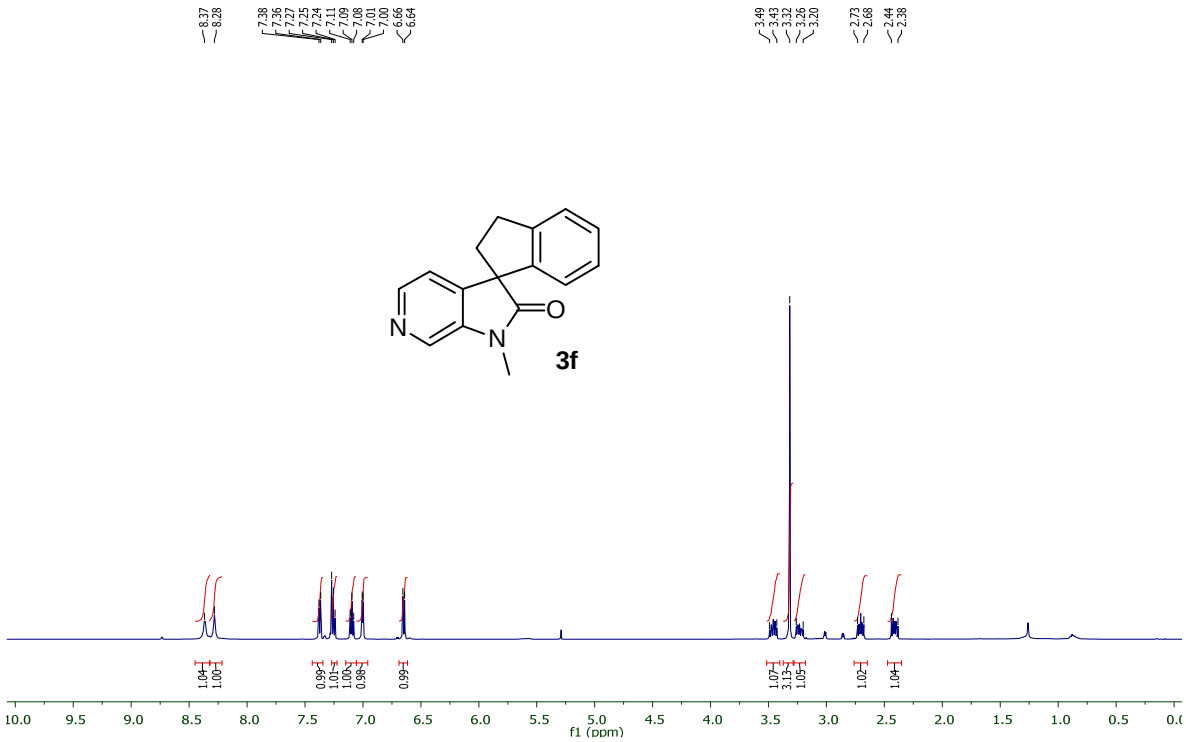

178.69
159.19
145.20
143.70
140.26
131.12
129.78
127.66
119.16
114.25
77.16
55.37
51.63
26.75
23.51
OMe
O
N
N
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

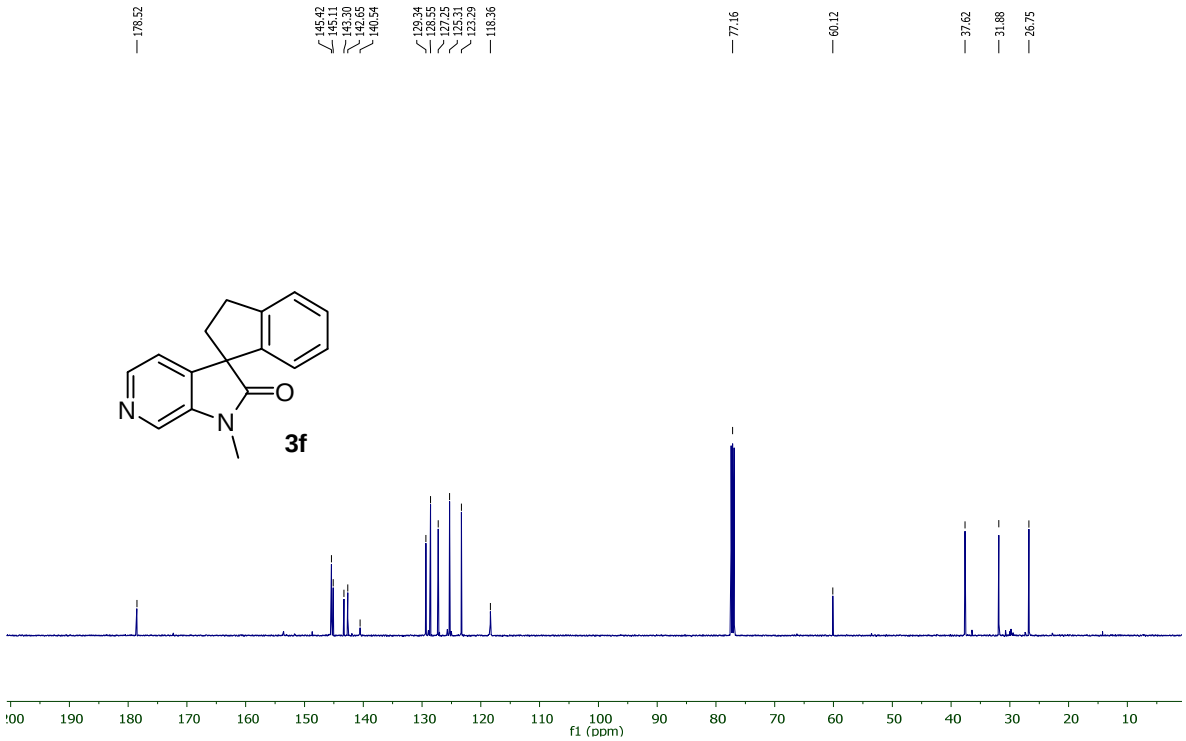

8.44
8.43
8.29
7.27
7.17
7.15
7.13
7.11
3.30
2.31
1.78
3d
1.00
1.00
3.14
2.15
3.18
3.18
3.22
f1 (ppm)

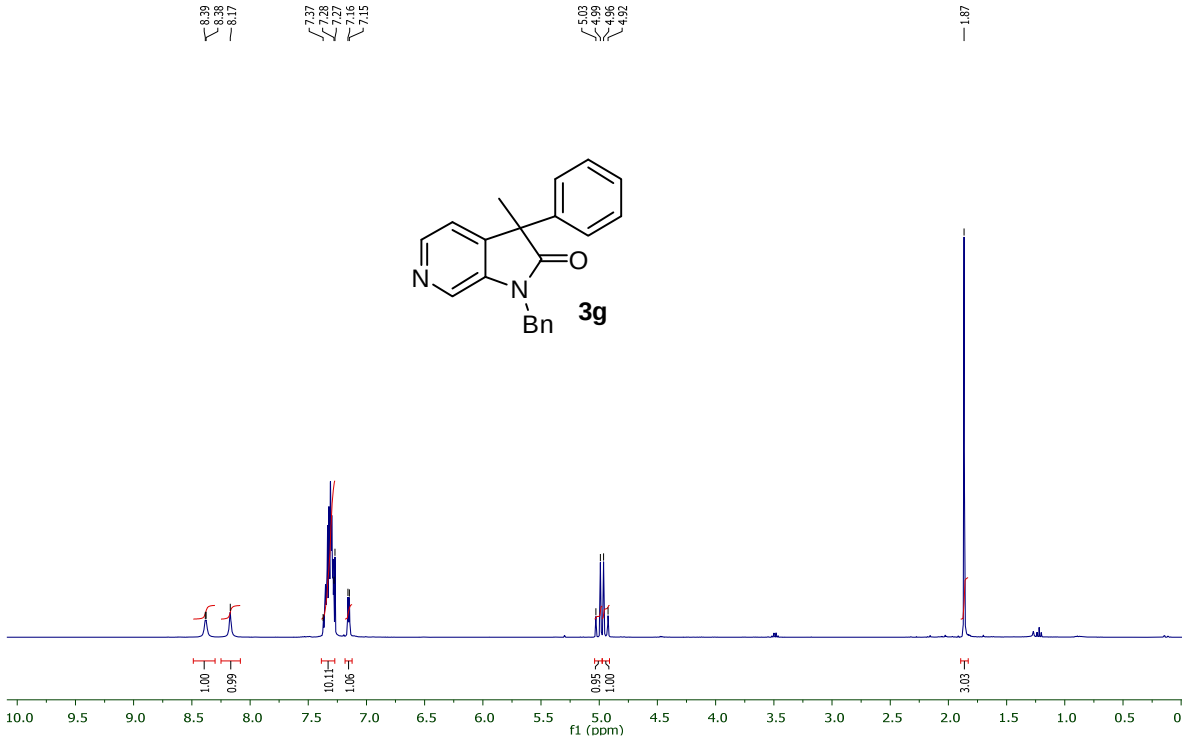

178.63
145.23
143.74
140.32
137.68
136.17
129.78
129.61
126.39
119.20
77.16
52.01
26.80
23.37
21.08
3d
f1 (ppm)

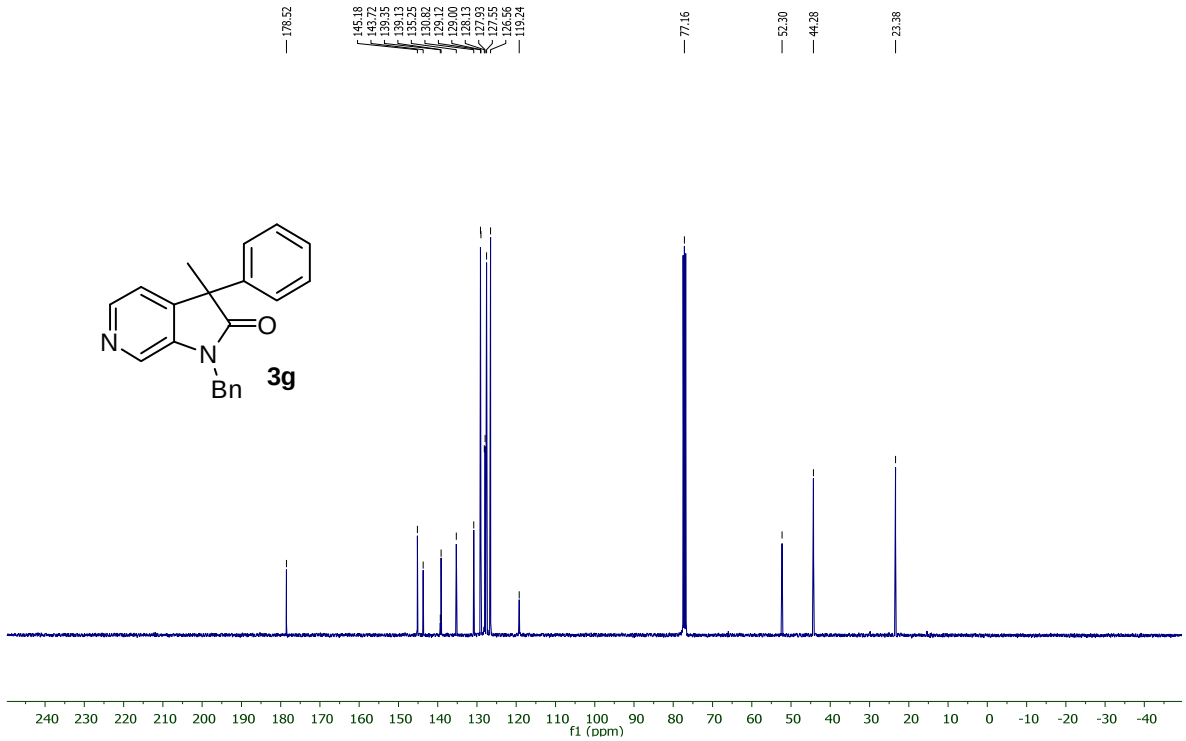

8.35
8.34
8.30
7.27
7.20
7.14
7.04
7.02
7.00
6.98
6.97
6.45
6.43
3.35
3.08
2.93
2.41
2.32
2.25
2.24
2.22
2.21
2.21
2.19
2.18
2.06
1.99
1.92
O
N
N
3e
1.01
0.93
2.09
1.00
1.03
0.98
3.00
2.13
1.13
1.06
2.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

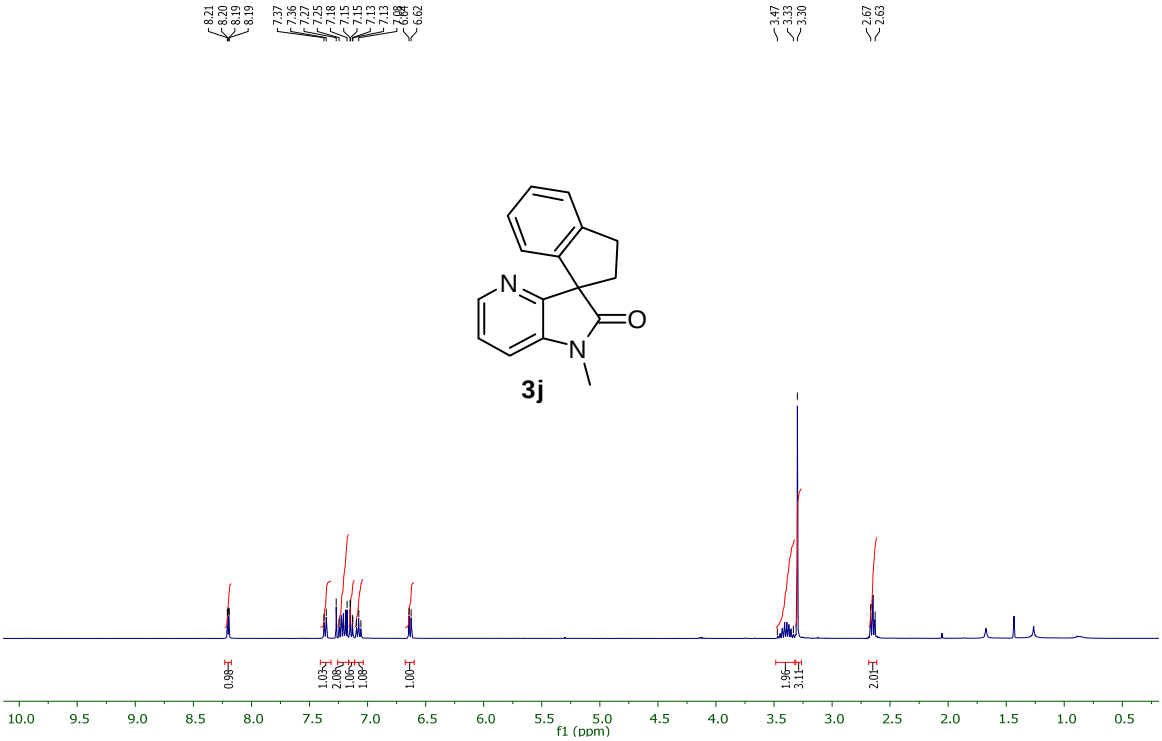

179.39
145.71
145.30
140.14
137.88
133.48
130.01
129.47
127.83
127.72
126.64
118.93
77.16
52.34
33.56
29.12
26.82
18.73
O
N
N
3e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

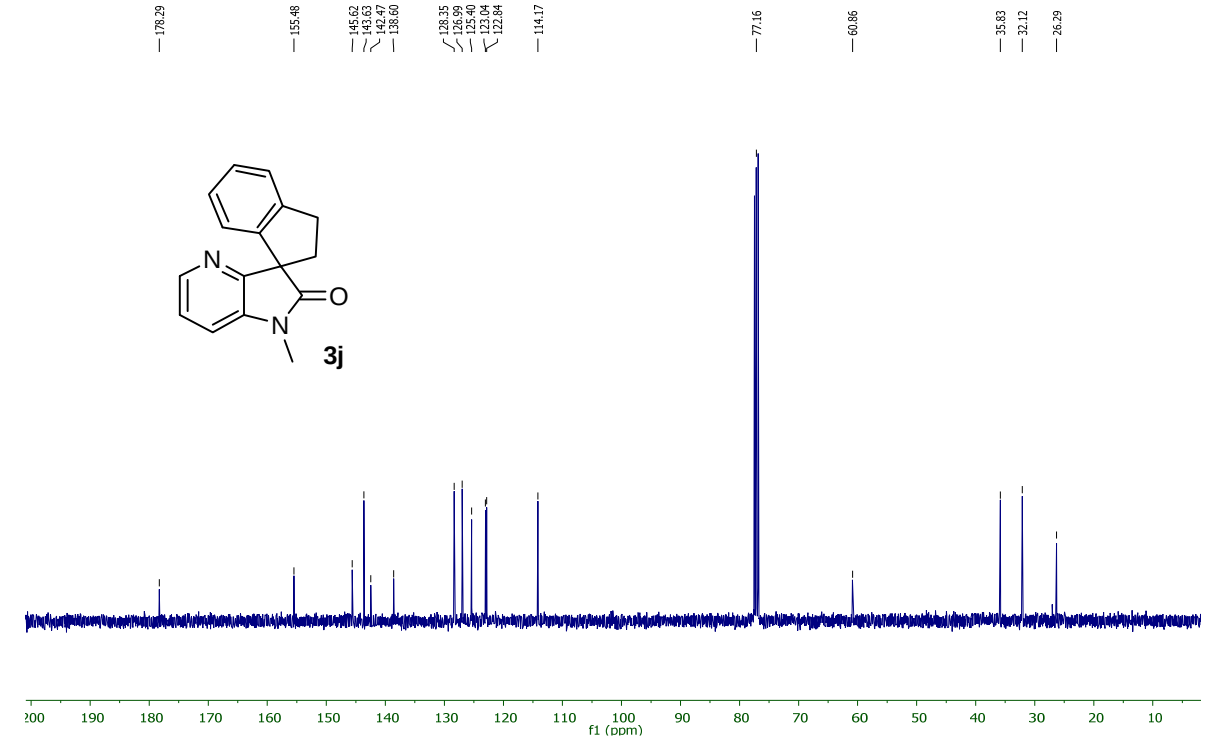

8.37
8.28
7.38
7.36
7.27
7.25
7.24
7.11
7.09
7.08
7.01
7.00
6.66
6.64
3.49
3.43
3.32
3.26
3.20
2.73
2.68
2.44
2.38
O
N
N
3f
1.04
1.00
0.99
1.01
1.00
0.98
0.99
1.07
3.13
1.05
1.02
1.04
f1 (ppm)

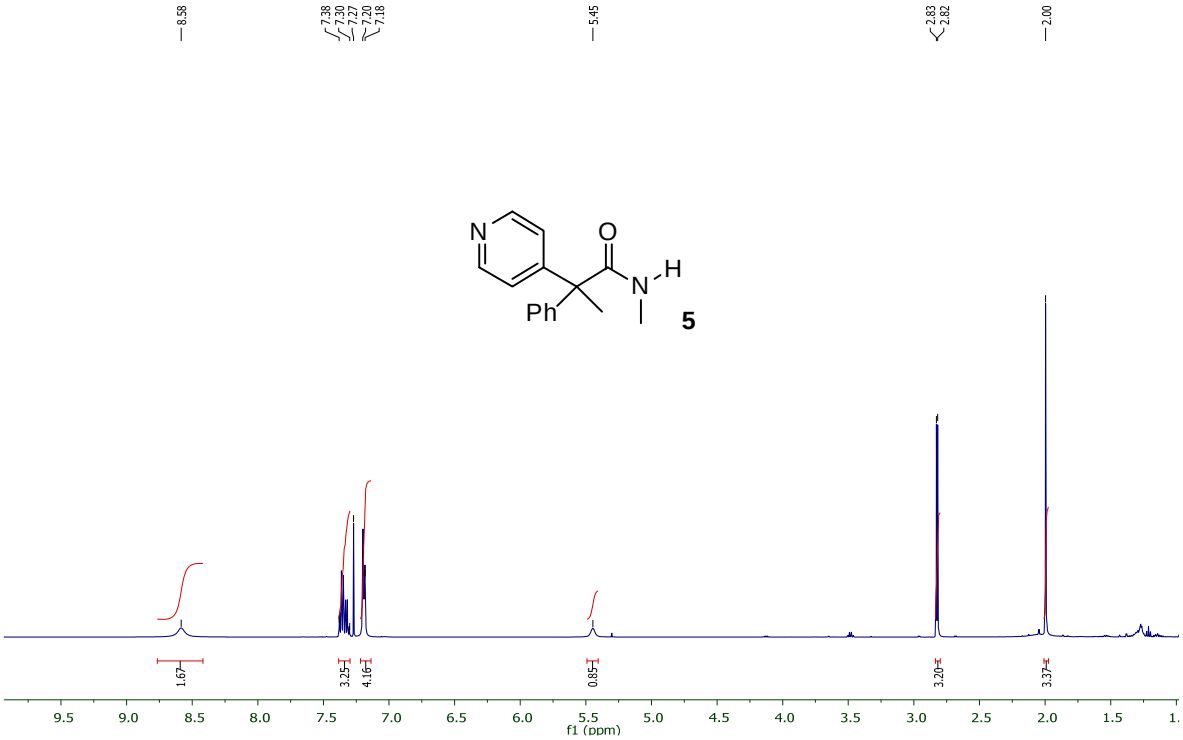

178.52
145.42
145.11
143.30
142.65
140.54
129.34
128.55
127.25
125.31
123.29
118.36
77.16
60.12
37.62
31.88
26.75
O
N
N
3f
f1 (ppm)

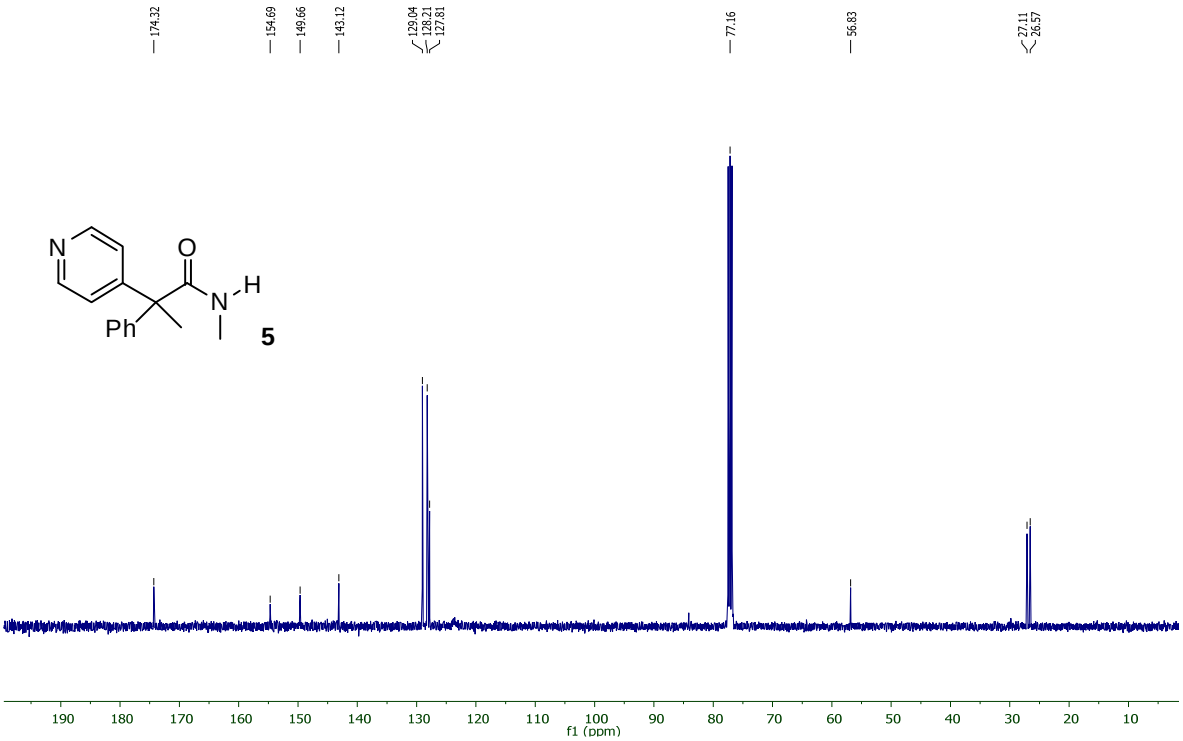

8.39
8.38
8.17
7.37
7.28
7.27
7.16
7.15
5.03
4.99
4.96
4.92
1.87
N
O
N
Bn
3g
1.00
0.99
10.11
1.06
0.95
1.00
3.03
f1 (ppm)

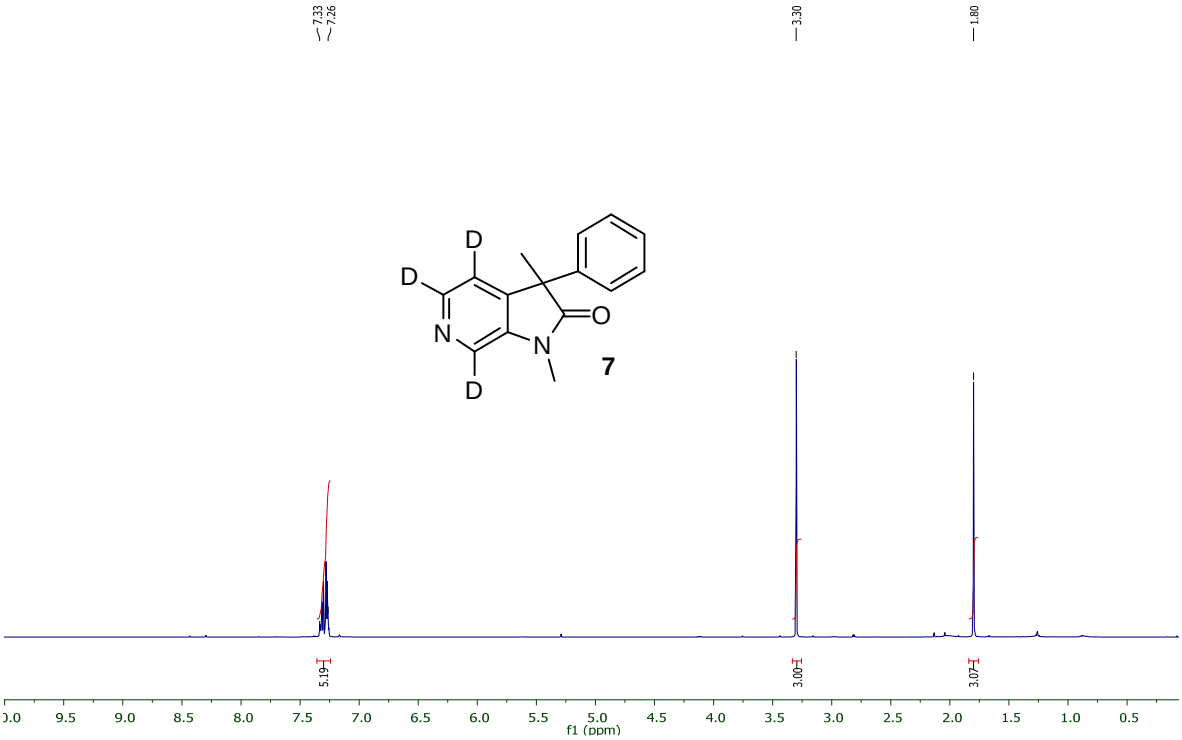

178.52
145.18
143.72
139.35
139.13
135.25
130.82
129.12
129.00
128.13
127.93
127.55
126.56
119.24
77.16
52.30
44.28
23.38
N
O
N
Bn
3g
f1 (ppm)

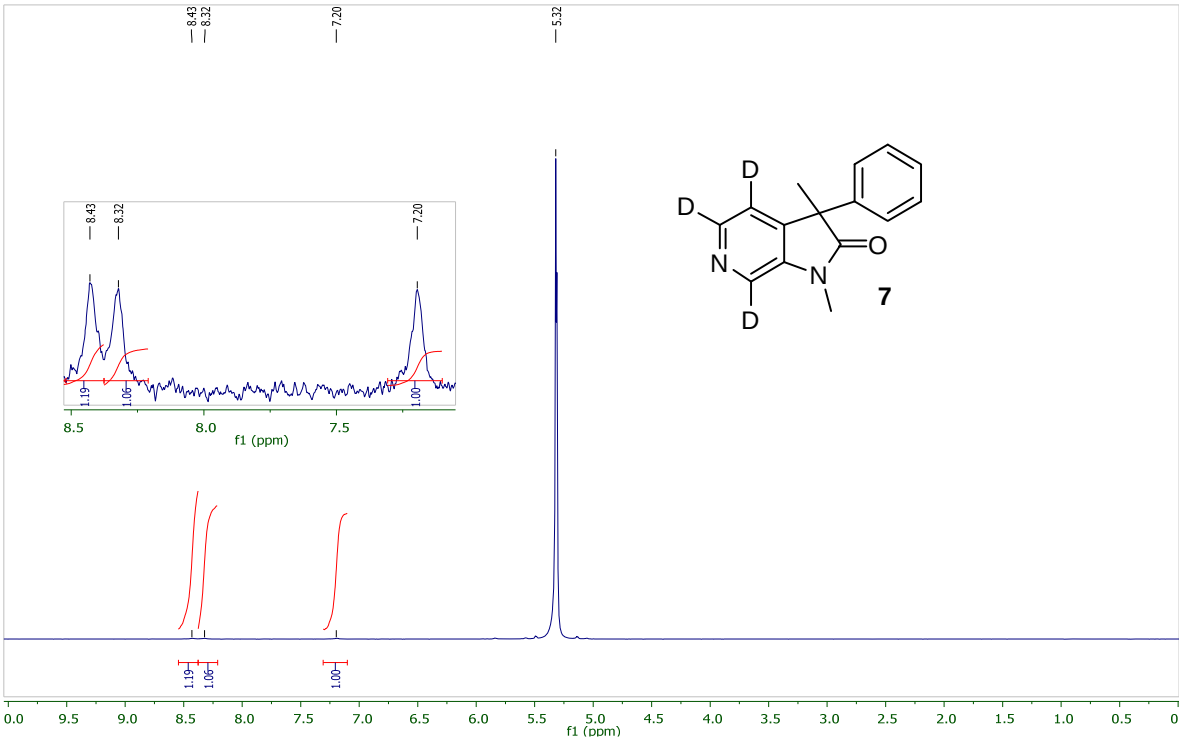

8.21
8.20
8.19
8.19
7.37
7.36
7.27
7.25
7.18
7.15
7.15
7.13
7.13
6.62
3.47
3.33
3.30
2.67
2.63
N
O
N
3j
0.98
1.03
2.05
1.08
1.00
1.96
3.11
2.01
f1 (ppm)

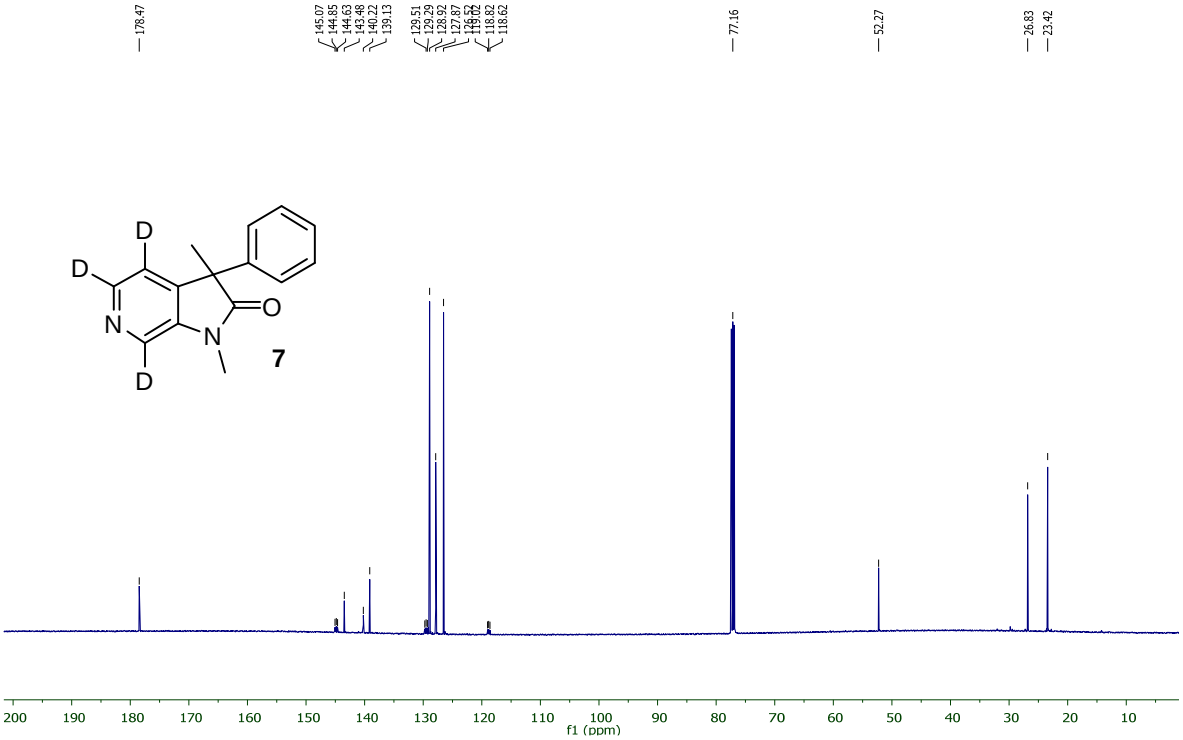

178.29
155.48
145.62
143.63
142.47
138.60
128.35
126.99
125.40
123.04
122.84
114.17
77.16
60.86
35.83
32.12
26.29
N
O
N
3j
f1 (ppm)


8.58
7.38
7.30
7.27
7.20
7.18
5.45
2.83
2.82
2.00
N
O
N
H
Ph
5
1.67
3.25
4.16
0.85
3.20
3.37
f1 (ppm)


174.32
154.69
149.66
143.12
129.04
128.21
127.81
77.16
56.83
27.11
26.57
N
O
N
H
Ph
5
f1 (ppm)


7.33
7.26
3.30
1.80
D
D
N
O
N
D
7
5.19
3.00
3.07
f1 (ppm)


8.43
8.32
7.20
5.32
D
D
N
O
N
D
7
1.19
1.06
1.00
f1 (ppm)


178.47
145.07
144.85
144.63
143.48
140.22
139.13
129.51
129.29
128.92
127.87
119.52
119.02
118.82
118.62
77.16
52.27
26.83
23.42
D
D
N
N
O
D
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)