**Electronic Supplementary Information**

# Synthesis, Structure and N-N Bonding Character of 1,1-Disubstituted Indazolium Hexafluorophosphate

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## Table of Contents

## Experimental Procedures

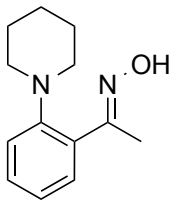
### General Methods:

All reactions were carried out under argon atmosphere in oven-dried glassware. All commercially available compounds and solvents were used as received unless otherwise mentioned.

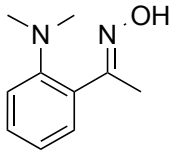
Open column chromatography was carried out using Kanto chemical silica gel (silica gel 60 N (100-210 μm)). Melting points were determined with a Yanaco micro melting point apparatus without correction. $^{1}$H- (400 MHz) and $^{13}$C- (100 MHz) NMR spectra were recorded on a Bruker Avance 400. Chemical shifts were calibrated with tetramethylsilane and solvent as an internal standard or with the solvent peak, and are shown in ppm (δ) values, and coupling constants are shown in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double triplet, dq = double quartet, h = hextet, m = multiplet, brs = broad singlet, br = broad signal. Electron spray ionization time-of-flight mass spectra (ESI-TOF MS) were recorded on a Bruker micrOTOF-05 to give high-resolution mass spectra (HRMS). The combustion analyses were carried out in the microanalytical laboratory of this department.

### Synthesis of *peri*-amino oxime 7

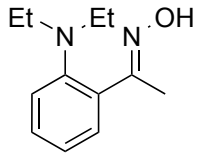
### synthesis of 7a, 7d, 7e, 7g and 7l



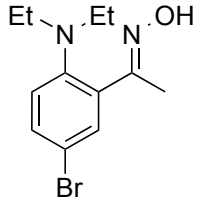

**7a**. A solution of 1-(2-(piperidin-1-yl)phenyl)ethan-1-one[S1] (1500.0 mg, 7.40 mmol), pyridine (1.5 mL), hydroxylamine hydrochloride (1000.0 mg, 2.0 equiv.) in 15 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 6: 1) to afford **7a** (white solid, 1000.2 mg, 62%).
Mp.: 151.0-152.0 ºC. $^{1}$H NMR ($CDCl_3$): δ 8.36 (1H, brs), 7.36-7.28 (2H, m), 7.08-7.01 (2H, m), 2.95 (4H, t, *J*= 5.2 Hz), 2.33 (3H, s), 1.73-1.67 (4H, m), 1.59-1.55 (2H, m) $^{13}$C NMR ($CDCl_3$): δ 159.9, 152.2, 131.9, 130.0, 129.7, 122.2, 118.9, 53.4, 26.5, 24.3, 14.3. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{13}H_{19}N_2O^+$: 219.1492. Found: 219.1505. Anal. Calcd. for Chemical Formula: $C_{13}H_{18}N_2O$
Elemental Analysis: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.20; H, 8.40; N, 12.77.



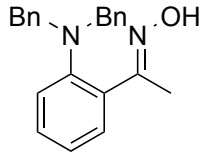

**7d.** A solution of 1-(2-(dimethylamino)phenyl)ethan-1-one[S2] (852.3 mg, 5.22 mmol), pyridine (1.7 mL), hydroxylamine hydrochloride (725.0 mg, 2.0 equiv.) in 10 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 6: 1) to afford **7d** (white solid, 409.7 mg, 44%).
Mp.: 75.5-77.0 ºC. $^{1}$H NMR ($CDCl_3$): δ 7.35-7.28 (2H, m), 7.03 (1H, d, *J*= 7.6 Hz), 6.97 (1H, dt, *J*= 1.2, 7.6 Hz), 2.77 (6H, s), 2.27 (3H, s). $^{13}$C NMR ($CDCl_3$): δ 159.6, 151.5, 130.3, 130.1, 129.6, 121.3, 117.6, 43.6, 13.9. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{10}H_{15}N_2O^+$: 179.1179. Found: 179.1186. Anal. Calcd. for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.25; H, 7.96; N, 15.58.



**7e.** A solution of 1-(2-(diethylamino)phenyl)ethan-1-one[S2] (485.6 mg, 2.54 mmol), pyridine (0.5 mL), hydroxylamine hydrochloride (350.0 mg, 2.0 equiv.) in 5 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 4: 1) to afford **7e** (colorless oil, 287.6 mg, 55%).
$^1$H NMR ($CDCl_3$): δ 7.38-7.30 (2H, m), 7.15-7.10 (2H, m), 3.10 (4H, q, *J*= 7.2), 2.31 (3H, s), 1.09 (6H, t, *J*= 7.2 Hz). $^{13}$C NMR ($CDCl_3$): δ 159.6, 151.5, 130.3, 130.1, 129.6, 121.3, 117.6, 43.6, 21.1, 13.9. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{12}H_{19}N_2O^+$: 207.1492. Found 207.1499.

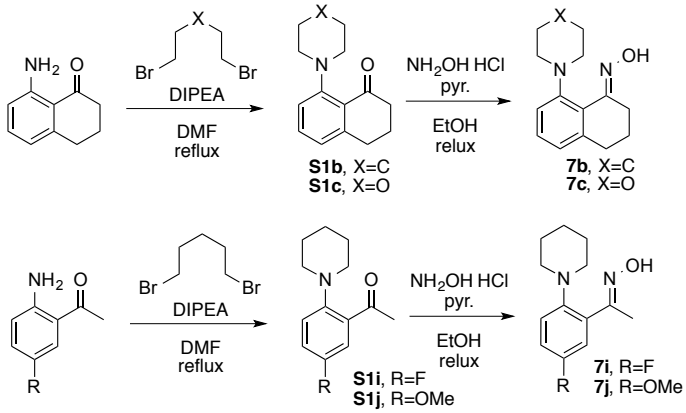


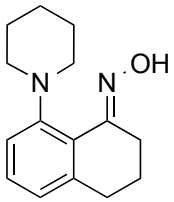
**7g.** A solution of 1-(5-bromo-2-(diethylamino)phenyl)ethan-1-one[S3] (683.4 mg, 2.53 mmol), pyridine (1.0 mL), hydroxylamine hydrochloride (350.0 mg, 2.0 equiv.) in 10 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 6: 1) to afford **7g** (off-white solid, 430.7 mg, 60%).
Mp.: 85.0-85.5 ºC. $^1$H NMR ($CDCl_3$): δ 9.23 (1H, brs), 7.43-7.39 (2H, m), 6.94 (1H, d, *J*= 8.4 Hz), 3.08 (4H, q, *J*= 6.8), 2.24 (3H, s), 1.01 (6H, t, *J*= 6.8 Hz). $^{13}$C NMR ($CDCl_3$): δ 157.9, 147.4, 131.5, 129.4, 129.3, 122.9, 121.0, 46.8, 21.1, 11.8. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{12}H_{18}BrN_2O^+$: 285.0597. Found: 285.0602. Anal. Calcd. for $C_{12}H_{17}BrN_2O$: C, 50.54; H, 6.01; N, 9.82. Found: C, 50.30; H, 6.03; N, 9.69.



**7l.** A solution of 1-(2-(dibenzylamino)phenyl)ethan-1-one [S4] (2166.1 mg, 6.87 mmol), pyridine (3.0 mL), hydroxylamine hydrochloride (1000.0 mg, 2.1 equiv.) in 40 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 6: 1) to afford **7g** (white solid, 1730.2 mg, 76%).
Mp.: 173.5-174.0 ºC. $^1$H NMR ($CDCl_3$): δ 8.96 (1H, brs), 7.34-7.22 (8H, m), 7.15-7.13 (4H, m), 7.04 (1H, dt, *J*= 0.8, 7.6 Hz), 6.91 (1H, d, *J*= 8.0 Hz), 4.13 (4H, s), 2.41 (3H, s). $^{13}$C NMR ($CDCl_3$): δ 159.6, 149.3, 137.4, 132.4, 130.3, 129.3, 129.2, 128.2, 127.1, 122.6, 121.7, 55.9, 15.3. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{22}H_{23}N_2O^+$: 331.1805. Found: 331.1828. Anal. Calcd. for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48. Found C, 79.81; H, 6.87; N, 8.44.

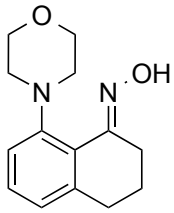
**synthesis of 7b**, **7c**, **7i**, **7j**.



**7b**. A solution of 8-amino-3,4-dihydronaphthalen-1(2*H*)-one (400.0 mg, 2.48 mmol), 1,5-dibromopentane (1150.0 mg, 2.0 equiv.) and DIPEA (2.5 ml) in 10 mL of DMF was heated to reflux for 2 hr. The reaction was quenched by slow addition of water and the whole was extracted with $Et_2O$. The combined organic layers were concentrated and purified by column chromatography (hexane: ethyl acetate= 9: 1) to afford an inseparable mixture of **S1b** and reactant (**S1b** : reactant = 2: 1, 391.3 mg, yellow oil).

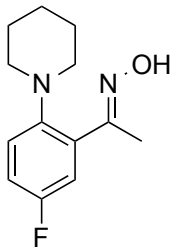
A solution of crude **S1b** (391.3 mg, calcd. 1.17 mmol), pyridine (1.0 mL), hydroxylamine hydrochloride (190.0 mg, 2.3 equiv.) in 5 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 4: 1) to afford **7b** (white solid, 196.5 mg, 33% in 2 steps).
Mp.: 185.0-185.5 ºC. $^1$H NMR ($CDCl_3$): δ 7.20-7.13 (2H, m), 7.00 (1H, d, *J*= 7.2 Hz), 2.99-2.77 (8H, m), 1.92-1.82 (8H, m). $^{13}$C NMR ($CDCl_3$): δ 151.2, 149.4, 140.4, 128.6, 126.1, 121.4, 119.5, 54.2, 30.9, 26.2, 24.6, 23.6, 20.5. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{15}H_{21}N_2O^+$: 245.16484. Found: 245.1639. Anal. Calcd. for $C_{15}H_{20}N_2O$: C, 73.74; H, 8.25; N, 11.47. Found C, 73.46; H, 8.16; N, 11.32.



**7c**. A solution of 8-amino-3,4-dihydronaphthalen-1(2*H*)-one (1000.0 mg, 6.20 mmol), 1,5-dibromopentane (2900.0 mg, 2.0 equiv.) and DIPEA (2.7 ml) in 15 mL of DMF was heated to reflux for 2hr. The reaction was quenched by slow addition of water and the whole was extracted with $Et_2O$. The combined organic layers were concentrated and purified by column chromatography (hexane: ethyl acetate= 4: 1) to afford **S1c** (yellow oil, 866.8 mg, 60%).
$^1$H NMR ($CDCl_3$): δ 7.35 (1H, t, *J*= 7.6 Hz), 6.89-6.84 (2H, m), 3.94-3.91 (4H, m), 3.05 (4H, t, *J*= 4.4 Hz), 2.94 (2H, t, *J*= 6.4 Hz), 2.62 (2H, t, *J*= 6.8 Hz), 2.08-2.01 (2H, m). $^{13}$C NMR ($CDCl_3$): δ 197.3, 153.4,147.8, 133.7, 124.2, 122.0, 116.4, 67.2, 53.0, 41.3, 31.6, 22.6. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{14}H_{17}NNaO_2^+$: 254.1151. Found: 254.1164.

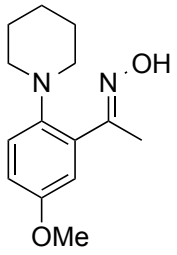
A solution of 8-morpholino-3,4-dihydronaphthalen-1(2*H*)-one (**S1c**, 542.9 mg, 2.34 mmol), DABCO (660.0 mg, 2.5 equiv.), hydroxylamine hydrochloride (325.0 mg, 2.0 equiv.) in 4 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 4: 1) to afford **7c** (white solid, 501.2 mg, 87%).

Mp.: 188.0-189.5 ºC. $^1$H NMR ($CDCl_3$): δ 7.20 (1H, t, *J*= 8.0 Hz), 6.98 (1H, d, *J*= 8.0 Hz), 6.90 (1H, d, *J*= 7.6 Hz), 3.94-3.91 (4H, m), 3.05-3.03 (4H, m), 2.90 (2H, t, *J*= 6.8 Hz), 2.68 (2H, t, *J*= 6.0 Hz), 1.85-1.79 (2H, m). $^{13}$C NMR ($CDCl_3$): δ 153.1, 150.9, 143.3, 129.1, 123.2, 122.8, 116.6, 66.4, 52.4, 31.1, 25.1, 20.9. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{14}H_{19}N_2O_2^+$: 247.1441. Found: 247.1440. Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.26; H, 7.38; N, 11.30.




**7i**. A solution of 1-(2-amino-5-fluorophenyl)ethan-1-one (422.7 mg, 2.76 mmol), 1,5-dibromopentane (750.0 mg, 1.2 equiv.) and DIPEA (2.0 ml) in 10 mL of DMF was heated to reflux for 10hr. The reaction was quenched by slow addition of water and the whole was extracted with $Et_2O$. The combined organic layers were concentrated and purified by column chromatography (hexane: ethyl acetate= 4: 1) to afford **S1i** (yellow oil, 328.2 mg, 54%). $^1$H NMR ($CDCl_3$): δ 7.15-7.05 (3H, m), 2.92 (4H, brs), 2.90 (3H, s), 1.76-1.70 (4H, m), 1.60-1.56 (2H, m) $^{13}$C NMR ($CDCl_3$): δ 203.4, 158.2 (d, *J*=241.4 Hz), 149.0, 137.1 (d, *J*= 5.8 Hz), 120.7 (d, *J*= 7.6 Hz), 118.2 (d, *J*=22.0 Hz), 115.8 (d, *J*=9.5 Hz), 115.5 (d, *J*=23.3 Hz), 60.4, 55.0, 29.2, 26.3, 23.9. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{13}H_{17}FNO^+$: 222.1289. Found: 222.1311.

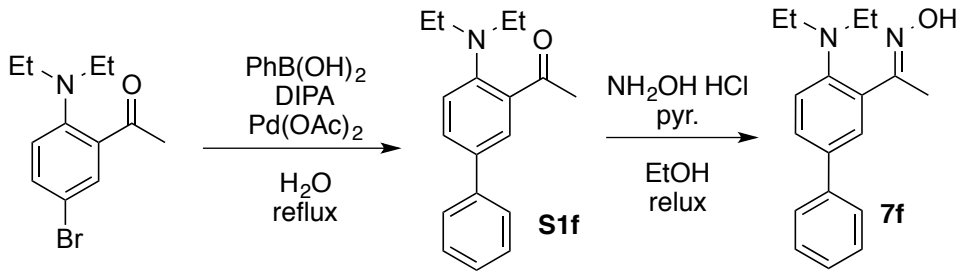
A solution of 1-(5-fluoro-2-(piperidin-1-yl)phenyl)ethan-1-one (315.6 mg, 1.43 mmol), pyridine (1.0 mL), hydroxylamine hydrochloride (200.0 mg, 2.0 equiv.) in 5 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 6: 1) to afford **7i** (white solid, 250.1 mg, 72%).
Mp.: 123.0-125.5 ºC. $^1$H NMR ($CDCl_3$): δ 7.04-7.02 (3H, m), 2.88 (4H, t, *J*= 5.2 Hz), 2.32 (3H, s), 1.72-1.67 (4H, m), 1.58-1.53 (2H, m). $^{13}$C NMR ($CDCl_3$): δ 158.7, 158.3 (d, *J*= 237.4 Hz), 148.5, 133.7 (d, *J*= 7.4 Hz), 120.4 (d, *J*= 8.2 Hz), 116.6 (d, *J*= 23.1 Hz), 115.9 (d, *J*= 21.5 Hz) 53.9, 26.4, 24.1, 14.4. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{13}H_{18}FN_2O^+$: 237.1398. Found 237.1406.




**7j.** A solution of 1-(2-amino-5-methoxyphenyl)ethan-1-one (374.8 mg, 2.27 mmol), 1,5-dibromopentane (630.0 mg, 1.2 equiv.) and DIPEA (1.5 ml) in 10 mL of DMF was heated to reflux for 6hr. The reaction was quenched by slow addition of water and the whole was extracted with $Et_2O$. The combined organic layers were concentrated and purified by column chromatography (hexane: ethyl acetate= 6: 1) to afford **S1j** (yellow oil, 422.7 mg, 80%). $^1$H NMR ($CDCl_3$): δ 7.09-7.06 (1H, m), 6.99-6.96 (2H, m), 3.80 (3H, s), 2.88 (4H, t, *J*=5.6 Hz), 2.72 (3H, s), 1.75-1.69 (4H, m), 1.58-1.53 (2H, m). $^{13}$C NMR ($CDCl_3$): δ 204.7, 155.1, 146.6, 136.9, 120.7, 118.0, 113.0, 55.6, 51.1, 29.6, 26.4, 24.0 HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{14}H_{20}NO_2^+$: 234.1489. Found 234.1492.

A solution of 1-(5-methoxy-2-(piperidin-1-yl)phenyl)ethan-1-one (414.4 mg, 1.78 mmol), pyridine (1.0 mL), hydroxylamine hydrochloride (250.0 mg, 2.0 equiv.) in 5 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 6: 1) to afford **7j** (white solid, 273.5 mg, 62%).
Mp.: 114.5-116.0 ºC. $^1$H NMR ($CDCl_3$): δ 7.04-7.00 (1H, m), 6.89-6.85 (2H, m), 3.78 (3H, s), 2.84 (4H, t, *J*=5.2 Hz), 2.31 (3H, s), 1.68-1.64 (4H, m), 1.54-1.48 (2H, m). $^{13}$C NMR ($CDCl_3$): δ 159.6, 155.1, 146.0, 133.6, 120.5, 115.1, 114.9, 55.6, 54.0, 26.6, 24.2, 14.7. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{14}H_{21}N_2O_2^+$: 249.1598. Found 249.1606. Anal. Calcd. for $C_{14}H_{20}N_2O_2$: C, 67.72; H, 8.12; N, 11.28. Found: C, 67.36; H, 8.04; N, 11.17.

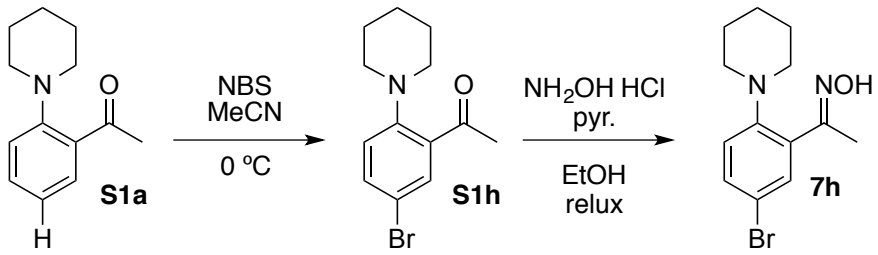
**Synthesis of 7f**




**7f**. A solution of 1-(5-bromo-2-(diethylamino)phenyl)ethan-1-one (1171.4 mg, 4.34 mmol), DIPA (1.0 mL), $PhB(OH)_2$ (800.0 mg, 1.5 equiv.) and $Pd(OAc)_2$ (50.0 mg, 5% equiv.) in 20 mL of water was heated to reflux for 1hr. The reaction mixture was extracted with dichloromethane and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 9: 1) to afford **S1f** (yellow oil, 733.7 mg, 63%).
$^1$H NMR ($CDCl_3$): δ 7.64 (1H, dd, *J*=2.4, 8.0 Hz), 7.65-7.59 (3H, m), 7.46-7.42 (2H, m) 7.36-7.32 (1H, m), 7.16 (1H, d, *J*=8.4 Hz) 3.19 (4H, q, *J*=6.8 Hz), 2.69 (3H, s), 1.10 (6H, t, *J*=7.2 Hz). $^{13}$C NMR ($CDCl_3$): δ 204.8, 148.9, 140.1, 136.8, 134.6, 129.6, 128.8, 127.7, 127.0, 126.7, 121.5, 47.6, 29.3, 11.8. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{18}H_{22}NO^+$: 268.1696. Found 268.1704.

A solution of 1-(4-(diethylamino)-[1,1'-biphenyl]-3-yl)ethan-1-one (**S1f**, 357.4 mg, 1.34 mmol), pyridine (0.5 mL), hydroxylamine hydrochloride (180.0 mg, 2.0 equiv.) in 5 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 4: 1) to afford **7f** (white solid, 214.4 mg, 57%).
Mp.: 122.5-124.0 ºC. $^1$H NMR ($CDCl_3$): δ 7.63-7.60 (2H, m), 7.58-7.55 (2H, m), 7.43 (2H, m), 7.34-7.30 (1H, m), 7.14 (1H, d, *J*= 8.0 Hz) 3.16 (4H, q, *J*= 6.8 Hz), 2.31 (3H, s), 1.07 (6H, t, *J*= 6.8 Hz). $^{13}$C NMR ($CDCl_3$): δ 159.8, 148.2, 140.5, 135.0, 133.4, 128.7, 128.7, 127.6, 126.82, 126.81, 121.6, 46.7, 14.5, 11.9. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{18}H_{23}N_2O^+$: 283.1805. Found: 283.1829. Anal. Calcd. for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found C, 76.23; H, 7.96; N, 9.80.

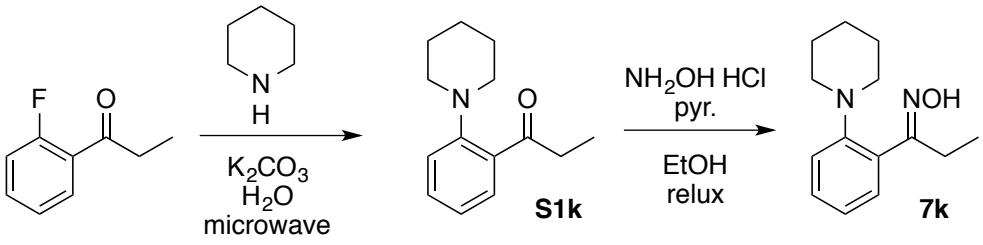
**Synthesis of 7h, 7k**




**7h.** To a solution of **S1a** (630.0 mg, 3.10 mmol) in 15 mL of MeCN was added NBS (550.0 mg, 1.0 equiv.) at 0 ºC. The solution was stirred at room temperature for 2 hr and the whole was concentrated. The residue was purified with column chromatography (hexane: ethyl acetate= 20: 1) to afford **S1h** (yellow oil, 752.5 mg, 86%).
$^1$H NMR ($CDCl_3$): δ 7.51-7.46 (2H, m), 6.95 (1H, d, *J*=8.4 Hz), 2.93 (4H, t, *J*= 5.2 Hz), 2.66 (3H, s), 1.75-1.69 (4H, m), 1.60-1.56 (2H, m). $^{13}$C NMR ($CDCl_3$): δ 203.1, 151.5, 136.6, 134.4, 131.8, 120.5, 114.7, 54.5, 28.8, 26.1, 23.9. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{13}H_{17}BrNO^+$: 282.0488. Found 282.0489.
A solution of 1-(5-bromo-2-(piperidin-1-yl)phenyl)ethan-1-one (597.4 mg, 2.12 mmol), pyridine (2.0 mL), hydroxylamine hydrochloride (300.0 mg, 2.0 equiv.) in 10 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 6: 1) to afford **7h** (white solid, 431.8 mg, 69%).
Mp.: 155.0-155.5 ºC. $^1$H NMR ($CDCl_3$): δ 9.01 (1H, brs) 7.45 (1H, dd, *J*= 2.0, 8.4 Hz), 7.38 (1H, d, *J*= 2.0 Hz), 6.98 (1H, d, *J*= 8.4 Hz), 2.92 (4H, t, *J*= 5.2 Hz), 2.29 (3H, s), 1.75-1.70 (4H, m), 1.60-1.57 (2H, m). $^{13}$C NMR ($CDCl_3$): δ 156.7, 149.6, 132.5, 131.9, 131.8, 120.8, 115.4, 53.7, 26.2, 23.9, 20.5. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{13}H_{17}BrN_2NaO^+$: 319.0417. Found: 319.0430. Anal. Calcd. for $C_{13}H_{17}BrN_2O$: C, 52.54; H, 5.77; N, 9.43.

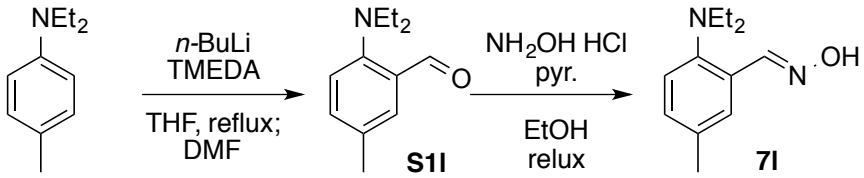
Found C, 52.30; H, 5.89; N, 9.42.

**Synthesis of 7k**




**7k.** A mixture of 1-(2-fluorophenyl)propan-1-one (1000.0 mg, 6.57 mmol), $K_2CO_3$ (1000.0 mg, 1.1 equiv.), piperidine (3.3 mL, 5.0 equiv.) in 10 mL of water was heated to 150 ºC for 1hr with microwave irradiation. The reaction mixture was acidified to pH=1 with 2M hydrochloric acid and washed with ethyl acetate. The aqueous layer was neutralized by saturated $NaHCO_3$ solution and the whole was extracted with ethyl acetate. The solvent was evaporated to afford **S1k** (yellow oil, 901.1 mg, 63%).
$^1$H NMR ($CDCl_3$): δ 7.38 (1H, d, *J*=7.6 Hz), 7.31 (1H, d, *J*=7.2 Hz), 7.08-7.02 (2H, m), 3.10 (2H, q, *J*= 7.2 Hz), 2.94 (4H, br), 1,71 (4H, br), 1.57 (2H, br), 1.18 (3H, t, *J*= 7.2 Hz). $^{13}$C NMR ($CDCl_3$): δ 209.1, 152.1, 135.8, 131.3, 128.6, 122.2, 118.7, 54.4, 34.6, 26.3, 24.0, 8.7. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{14}H_{20}NO^+$: 218.1539. Found 218.1546

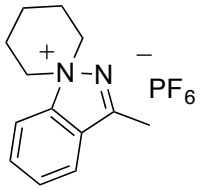
A solution of 1-(2-(piperidin-1-yl)phenyl)propan-1-one (734.4 mg, 3.39 mmol), pyridine (3.5 mL), hydroxylamine hydrochloride (470.0 mg, 2.0 equiv.) in 10 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 9: 1) to afford **7k** (white solid, 462.7 mg, 59%). Mp.: 107.5-108.5 ºC. $^1$H NMR ($CDCl_3$): δ 7.33 (1H, dt, *J*= 1.2, 8.0 Hz), 7.23 (1H, dd, *J*= 1.2 Hz), 7.07-7.01 (2H, m), 2.67-2.90 (6H, m), 1.69-1.66 (4H, m), 1.58-1.55 (2H, m). 0.97 (3H, t, *J*= 7.6 Hz). $^{13}$C NMR ($CDCl_3$): δ 164.9, 152.1, 130.9, 130.6, 129.6, 112.4, 118.9, 53.5, 26.4, 24.3, 20.4, 10.3. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{14}H_{21}N_2O^+$: 233.1648. Found: 233.1622. Anal. Calcd. for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found C, 72.49; H, 8.74; N, 11.70.




**7l.** A solution of *N*,*N*-diethyl-4-methylaniline (6.44 g, 39.4 mmol) and TMEDA (4.24 g, 36.4 mmol) in 50 mL of THF was cooled to 0 ºC. *n*-BuLi (1.46 M solution in hexane, 24 mL, 35.0 mmol) was added dropwise, and the solution was heated to reflux for 8 hr. The solution was cooled to ambient temperature and a solution of DMF (3.1 mL, 39.4 mmol) in 20 mL of THF was added dropwise. The reaction mixture was stirred at room temperature for 12 hr. The reaction was quenched by slow addition of saturated $NH_4Cl$ solution, and the whole was extrated with $Et_2O$. The solvent was evaporated and the residue was purified with distillation (82 ºC/ 2 mmHg) to afford **S1l** (3.36 g, 45%, yellow oil)
$^1$H NMR ($CDCl_3$): δ 10.4 (1H, s), 7.64 (1H, d, *J*= 2.0 Hz), 7.35 (1H, dd, *J*= 2.4, 8.4 Hz), 7.12 (1H, d, *J*= 8.4 Hz), 3.15 (4H, q, *J*= 7.2 Hz), 2.35 (3H, s), 1.05 (6H, t, *J*= 7.2 Hz). $^{13}$C NMR ($CDCl_3$): δ 192.6, 152.4, 135.3, 132.4, 131.2, 128.6, 122.1, 49.3, 20.6, 12.4. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{12}H_{18}NO^+$: 192.1383. Found: 192.1389

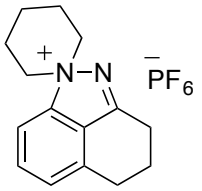
A solution of 2-(diethylamino)-5-methylbenzaldehyde (**S1l**, 519.1 mg, 2.71 mmol), pyridine (2 mL), hydroxylamine hydrochloride (380.0 mg, 2.0 equiv.) in 20 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated and the residue was purified by column chromatography (hexane: ethyl acetate= 4: 1) to afford **7l** (colorless oil, 430.9 mg, 77%). $^1$H NMR ($CDCl_3$): δ 8.60 (1H, s), 7.58 (1H, s), 7.18 (1H, dd, *J*= 2.0, 8.4 Hz), 7.06 (1H, d, *J*= 8.0 Hz), 3.01 (4H, q, *J*= 7.2 Hz), 2.38 (3H, s), 0.98 (6H, t, *J*= 7.2 Hz). $^{13}$C NMR ($CDCl_3$): δ 149.2, 148.0, 133.2, 131.1, 128.6, 126.8, 122.5, 48.6, 20.8, 12.3. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{12}H_{19}N_2O^+$: 207.1497. Found: 207.1497.

**Synthesis of 1,1-disubstituted indazolium hexafluorophosphates 3**



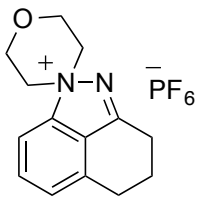
**3a**. To a solution of **7a** (218.3 mg, 1.0 mmol), pyridine (320.0 µL, 4.0 equiv.) and $KPF_6$ (370.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (5.0 mL) was added TsCl (210.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3a** (314.4 mg, 91%, colorless solid).

Mp.: 208.0-210.0 ºC. $^1$H NMR ($CD_2Cl_2$): δ 8.05 (1H, d, *J*=8.0 Hz), 7.92-7.88 (1H, m), 7.84-7.83 (2H, m), 4.14 (2H, dt, *J*=2.8, 12.4 Hz), 3.14-.3.10 (2H, m), 2.67 (3H, s), 2.50-2.37 (2H, m), 2.10-2.05 (2H, m), 2.00-1.91 (2H, m). $^{13}$C NMR ($CD_2Cl_2$): δ 173.8, 155.4, 136.1, 134.9, 131.2, 126.7, 119.5, 66.6, 24.4, 22.0, 15.2. HRMS (ESI-TOF, [M-$PF_6^-$]$^+$): Calcd. for $C_{13}H_{17}N_2^+$, 201.1386. Found: 201.1385. Anal. Calcd. for $C_{13}H_{17}F_6N_2P$: C, 45.09; H, 4.95; N, 8.09. Found C, 44.87; H, 5.01; N, 8.08.



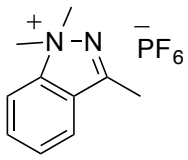
**3b**. To a solution of **7b** (122.5 mg, 0.5 mmol), $NEt_3$ (280.0 µL, 4.0 equiv.) and $KPF_6$ (185.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (2.5 mL) was added TsCl (105.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3b** (171.8 mg, 92%, colorless solid).

Mp.: 213.5-215.0 ºC. $^1$H NMR ($CDCl_3$): δ 7.96 (1H, d, *J*=8.0 Hz), 7.74 (1H, t, *J*=8.0 Hz), 7.55 (1H, d, *J*=7.6 Hz) 4.28-4.21 (2H, m), 3.16-3.13 (2H, br), 3.07 (2H, t, *J*=6.4 Hz), 2.98 (2H, t, *J*=6.0 Hz), 2.42-2.39 (2H, m), 2.25 (2H, quint, *J*=6.0 Hz), 2.09-2.02 (4H, br). $^{13}$C NMR ($CDCl_3$): δ 172.4, 152.1, 140.2, 134.8, 130.8, 126.8, 115.7, 63.7, 25.2, 24.1, 23.0, 22.7, 19.8. HRMS (ESI-TOF, [M-$PF_6^-$]$^+$): Calcd. for: $C_{15}H_{19}N_2^+$, 227.1543. Found: 227.1534. Anal. Calcd. for $C_{15}H_{19}F_6N_2P$: C, 48.39; H, 5.14; N, 7.52. Found C, 48.12; H, 5.05; N, 7.50.

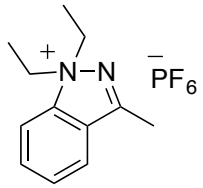


**3c**. To a solution of **7b** (123.0 mg, 0.5 mmol), $NEt_3$ (280.0 µL, 4.0 equiv.) and $KPF_6$ (185.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (2.5 mL) was added TsCl (105.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3c** (166.3 mg, 89%, colorless solid).

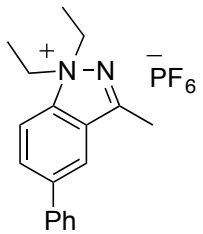
Mp.: 208.0-208.5 ºC. $^1$H NMR ($CD_3OD$): δ 8.01 (1H, d, *J*=8.0 Hz), 7.89 (1H, t, *J*=8.0 Hz), 7.73 (1H, d, *J*=7.6 Hz) 4.53-4.43 (4H, m), 4.28-4.24 (2H, m), 3.43-3.41 (2H, m), 3.15 (2H, t, *J*=6.4), 3.04 (2H, t, *J*=6.0 Hz), 2.28 (2H, quint, *J*=6.4 Hz).$^{13}$C NMR ($CD_3OD$): δ 173.5, 150.5, 141.5, 134.9, 131.5, 127.3, 114.9, 63.1, 61.9, 25.2, 24.1, 22.9. Calcd. for $C_{14}H_{17}N_2O^+$, 229.1335. Found: 229.1329. Anal. Calcd. for $C_{14}H_{17}F_6N_2OP$: C, 44.93; H, 4.58; N, 7.49. Found C, 44.76; H, 4.63; N, 7.42.



**3d**. To a solution of **7d** (65.5 mg, 0.37 mmol), pyridine (120.0 μL, 2.0 equiv.) and $KPF_6$ (135.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (2.0 mL) was added TsCl (80.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3d** (96.6 mg, 86%, colorless solid).
Mp.: 174.5-175.0 ºC. $^1$H NMR ($CD_2Cl_2$): δ 8.15 (1H, d, *J*=8.0 Hz), 8.01-7.97 (1H, m), 7.94-7.89 (2H, m), 3.72 (6H, s), 2.72 (3H, s). $^{13}$C NMR ($CD_2Cl_2$): δ 171.8, 152.8, 134.4, 133.0, 128.8, 124.9, 117.2, 54.0, 12.9. HRMS (ESI-TOF, $[M\text{-}PF_6^-]^+$): Calcd. for $C_{10}H_{13}N_2^+$: 161.1073. Found: 161.1080. Anal. Calcd. for $C_{10}H_{13}F_6N_2P$: C, 39.23; H, 4.28; N, 9.15. Found C, 39.02; H, 4.29; N, 8.97.

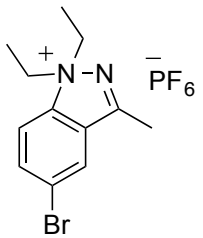


**3e**. To a solution of **7e** (90.7 mg, 0.44 mmol), DABCO (200.0 mg, 4.0 equiv.) and $KPF_6$ (160.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (2.0 mL) was added TsCl (90.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3e** (122.9 mg, 84%, colorless solid).
Mp.: 205.5-207.0 ºC. $^1$H NMR ($CDCl_3$): δ 8.18 (1H, d, *J*=8.4 Hz), 7.43 (1H, dt, *J*=1.2, 8.0 Hz), 7.85-7.78 (2H, m) 4.32-4.19 (4H, m), 2.71 (3H, s), 0.87 (6H, t, *J*=7.2 Hz). $^{13}$C NMR ($CDCl_3$): δ 172.9, 148.6, 134.8, 132.8, 131.3, 124.0, 118.7, 61.3, 13.0, 7.7. HRMS (ESI-TOF, $[M\text{-}PF_6^-]^+$): Calcd. for: $C_{12}H_{17}N_2^+$: 189.1386. Found: 189.1405. Anal. Calcd. for $C_{12}H_{17}F_6N_2P$: C, 43.12; H, 5.13; N, 8.38. Found: C, 43.32; H, 5.07; N, 8.37.



**3f.** To a solution of **7f** (60.0 mg, 0.21 mmol), pyridine (70 μL, 4.0 equiv.) and $KPF_6$ (80.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (1.5 mL) was added TsCl (50.0 mg, 1.2 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3f** (66.1 mg, 76%, colorless solid).

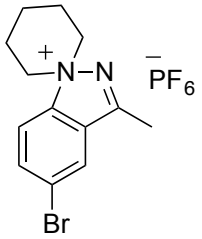
Mp.: 141.5-142.5 ºC. $^1$H NMR ($CD_2Cl_2$): δ 8.18 (1H, dd, *J*=1.6, 8.4 Hz), 8.07 (1H, d, *J*=8.4 Hz), 8.02 (1H, d, *J*=1.6 Hz), 7.73-7.70 (2H, m), 7.61-7.52 (3H, m), 4.35-4.18 (4H, m), 2.80 (3H, s), 0.98 (6H, *J*=7.2 Hz) $^{13}$C NMR ($CD_2Cl_2$): δ 173.8, 147.4, 147.0, 138.2, 133.7, 132.9, 129.8, 129.6, 127.9, 123.0, 118.6, 61.9, 13.4, 8.0. HRMS (ESI-TOF, $[M\text{-}PF_6^-]^+$): Calcd. for $C_{18}H_{21}N_2^+$: 265.16993. Found: 265.1707.



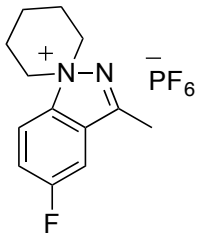
**3g**. To a solution of **7g** (121.0 mg, 0.42 mmol), pyridine (140 μL, 4.0 equiv.) and $KPF_6$ (155.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (2.0 mL) was added TsCl (90.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The

reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3g** (135.6 mg, 77%, colorless solid).

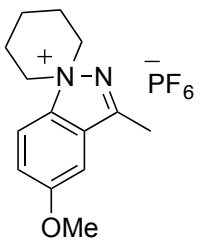
Mp.: 175.0-178.5 ºC. $^1$H NMR ($CD_2Cl_2$): δ 8.08 (1H, dd, *J*=1.6, 8.0 Hz), 7.07-7.92 (2H, m), 4.27-4.14 (4H, m), 2.69 (3H, s), 0.91 (6H, t, *J*=6.8 Hz). $^{13}$C NMR ($CD_2Cl_2$): δ 172.5, 147.3, 137.4, 133.4, 127.5, 126.9, 119.5, 61.6, 13.0, 7.6. HRMS (ESI-TOF, $[M\text{-}PF_6^-]^+$): Calcd. for $C_{12}H_{16}BrN_2^+$, 267.0491. Found: 267.0491. Anal. Calcd. for $C_{12}H_{16}BrF_6N_2P$: C, 34.89; H, 3.90; N, 6.78. Found C, 34.71; H, 3.90; N, 6.79.




**3h**. To a solution of **7h** (150.5 mg, 0.51 mmol), pyridine (160.0 µL, 4.0 equiv.) and $KPF_6$ (190.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (2.5 mL) was added TsCl (106.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3h** (199.9 mg, 93%, colorless solid).
Mp.: 211.0-211.5 ºC. $^1$H NMR ($CDCl_3$): δ 8.23 (1H, d, *J*=8.8 Hz), 8.05 (1H, dd, *J*=2.0, 8.8 Hz), 7.93 (1H, d, *J*=1.6 Hz), 4.42-4.35 (2H, m), 3.11 (2H, d, *J*=12.0 Hz), 2.71 (3H, s), 2.48-2.38 (2H, m), 2.15-2.07 (4H, m). $^{13}$C NMR ($CDCl_3$): δ 170.7, 152.6, 137.5, 130.7, 127.2, 127.0, 119.8, 64.8, 22.6, 19.6, 13.5. HRMS (ESI-TOF, $[M\text{-}PF_6^-]^+$): Calcd. for: $C_{13}H_{16}BrN_2^+$279.0491. Found: 227.0496. Anal. Calcd. for $C_{13}H_{16}BrF_6N_2P$: C, 36.73; H, 3.79; N, 6.59. Found: C, 36.76; H, 3.84; N, 6.55.

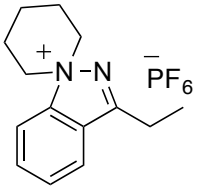



**3i.** To a solution of **7i** (119.3 mg, 0.50 mmol), pyridine (160.0 µL, 4.0 equiv.) and $KPF_6$ (190.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (2.5 mL) was added TsCl (106.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3i** (159.2 mg, 87%, colorless solid).
Mp.: 179.5-181.5 ºC. NMR ($CDCl_3$): δ 8.17-8.13 (1H, m), 7.67-7.62 (1H, m), 7.58-7.55 (1H, m), 4.20 (2H, t, *J*=12.4 Hz), 3.22 (2H, dd, *J*=1.6, 12.0 Hz), 2.72 (3H, s), 2.54-2.41 (2H, m), 2.16-2.11 (3H, m), 2.04-1.97 (1H, m). $^{13}$C NMR ($CDCl_3$): δ 171.4, 164.7 (d, *J*=253.5 Hz), 149.4 (d, *J*=2.2 Hz), 131.6 (d, *J*=10.1 Hz), 121.6 (d, *J*=25.9 Hz), 119.5 (d, *J*=9.6 Hz), 111.6 (d, *J*=25.5 Hz), 64.9, 22.6, 20.0,13.3. HRMS (ESI-TOF, $[M\text{-}PF_6^-]^+$): Calcd. for: $C_{13}H_{16}FN_2^+$: 219.1292. Found: 219.1292. Anal. Calcd. for $C_{13}H_{16}F_7N_2P$: C, 42.87; H, 4.43; N, 7.69. Found C 42.68; H, 4.43; N, 7.69.



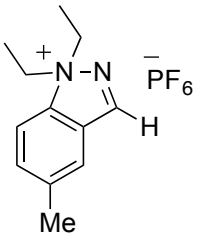

**3j**. To a solution of **7j** (79.4 mg, 0.32 mmol), pyridine (100.0 µL, 4.0 equiv.) and $KPF_6$ (120.0 mg, 2.0 equiv.) in $CH_2Cl_2$ (1.5 mL) was added TsCl (70.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The

reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **3i** (110.1 mg, 91%, colorless solid).
Mp.: 169-170 ºC. $^1$H NMR ($CD_2Cl_2$): δ 7.91 (1H, d, *J*=8.8 Hz), 7.37 (1H, dd, *J*=2.8, 9.2 Hz), 7.20 (1H, d, *J*=2.4 Hz), 4.08 (2H, dt, *J*=3.2, 12.0 Hz), 3.92 (3H, s), 3.11-3.08 (2H, m), 2.63 (3H, s), 2.45-2.34 (2H, m), 2.09-2.03 (3H, m), 1.95-1.87 (1H, m). $^{13}$C NMR ($CD_2Cl_2$): δ 173.8, 165.1, 148.2, 132.8, 122.4, 120.2, 110.1, 66.8, 58.5, 24.5, 22.0, 15.2. HRMS (ESI-TOF, [M-$PF_6^-$]$^+$): Calcd. for $C_{14}H_{19}N_2O^+$: 231.1492. Found: 231.1498. Anal. Calcd. for $C_{14}H_{19}F_6N_2OP$: C, 44.69; H, 5.09; N, 7.44. Found C, 44.68; H, 5.10; N, 7.35.



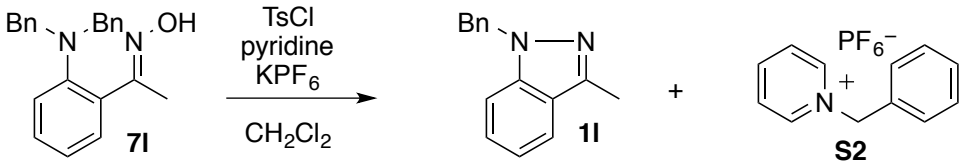
**3k**. To a solution of **7k** (126.7 mg, 0.55 mmol), pyridine (180.0 µL, 4 equiv.) and $KPF_6$ (200.0 mg, 2 equiv.) in $CH_2Cl_2$ (3.0 mL) was added TsCl (115.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **7f** (162.7 mg, 83%, white solid).

Mp.: 136-138 ºC. $^1$H NMR ($CD_2Cl_2$): δ 8.14 (1H, d, *J*=8.0 Hz), 8.00-7.96 (1H, m), 7.91-7.89 (2H, m), 4.23 (2H, dt, *J*=3.2, 12.8 Hz), 3.19-.3.10 (4H, m), 2.58-2.45 (2H, m), 2.19-2.13 (3H, m), 2.08-2.00 (1H, m), 1.51 (3H, t, *J*=7.6 Hz). $^{13}$C NMR ($CD_2Cl_2$): δ 176.1, 154.1, 134.6, 133.3, 129.1, 124.9, 118.2, 65.2, 22.9, 22.2, 20.5, 10.1. HRMS (ESI-TOF, [M-$PF_6^-$]$^+$): Calcd. for $C_{14}H_{19}N_2^+$, 215.1543. Found: 215.1535. Anal. Calcd. for $C_{14}H_{19}F_6N_2P$: C, 46.67; H, 5.32; N, 7.78. Found C, 46.60; H, 5.35; N, 7.69.



**3j**. To a solution of **7k** (224.2 mg, 1.09 mmol), pyridine (350.0 µL, 4 equiv.) and $KPF_6$ (400.0 mg, 2 equiv.) in $CH_2Cl_2$ (3.0 mL) was added TsCl (230.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **7f** (300.3 mg, 83%, white solid).
Mp.: 142-143 ºC. $^1$H NMR ($CD_2Cl_2$): δ 9.11 (1H, s), 7.89 (1H, d, *J*=8.4 Hz), 7.81-7.83 (2H, m), 4.34-4.18 (4H, m), 2.61 (3H, s), 0.92 (6H, t, *J*=6.8 Hz) $^{13}$C NMR ($CD_2Cl_2$): δ 163.6, 145.6, 144.5, 135.6, 131.1, 126.0, 117.4, 61.4, 21.2, 7.4. HRMS (ESI-TOF, [M-$PF_6^-$]$^+$): Calcd. for $C_{12}H_{17}N_2^+$: 189.1386. Found: 189.1389. Anal. Calcd. for $C_{12}H_{17}F_6N_2P$: C, 43.12; H, 5.13; N, 8.38. Found C, 43.18; H, 5.16; N, 8.34.

**Reaction of 7l with TsCl.**

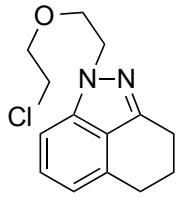



To a solution of **7l** (200.0 mg, 0.61 mmol), pyridine (200.0 µL, 4 equiv.) and $KPF_6$ (220.0 mg, 2 equiv.) in $CH_2Cl_2$ (3.0 mL) was added TsCl (130.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to give **S2** (122.0 mg, 64%, white solid). The residue was purified with column chromatography (hexane: ethyl acetate= 9: 1) to afford **1l** (122.2 mg, off-white solid, 91%)
**S2**. Mp.: 150.0-152.0 ºC. $^1$H NMR ($CDCl_3$): δ 8.76 (2H, d, *J*= 5.6 Hz), 8.53 (1H, t, *J*= 8.0 Hz), 8.08 (2H, t, *J*= 7.2

Hz), 7.54-7.52 (3H, m), 7.48-7.46 (2H, m), 5.78 (2H, s) $^{13}$C NMR ($CDCl_3$): δ 146.0, 144.0, 131.4, 130.5, 130.0, 129.4, 128.8, 65.6. HRMS (ESI-TOF, [M-$PF_6^-$]$^+$): Calcd. for $C_{12}H_{12}N^+$: 170.0964. Found: 170.0971. Anal. Calcd. for $C_{12}H_{12}F_6NP$: C, 45.73; H, 3.84; N, 4.44. Found C, 45.70; H, 3.96; N, 4.40.

**1l**.[5] Mp.: 51.5-53.0 ºC. $^1$H NMR ($CDCl_3$): δ 7.70 (1H, dt, *J*= 1.2, 8.4 Hz), 7.37-7.27 (5H, m), 7.21 (2H, dd, *J*= 2.0, 8.0 Hz), 7.17-7.13 (1H, m), 5.57 (2H, s), 2.64 (3H, s) $^{13}$C NMR ($CDCl_3$): δ 141.9, 140.5, 137.3, 128.7, 127.6, 127.1, 126.4, 123.7, 120.5, 119.8, 109.2, 52.6, 12.0.

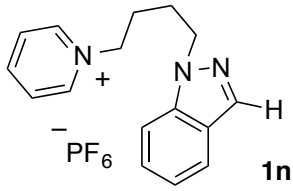
**Decomposition of 3c in concentrated HCl.**




**1c**. A solution of **3c** (112.3 mg, 0.30 mmol) in 1,4-dioxane (1.5 mL) and concentrated hydrochloric acid (1.5 ml) was heated to reflux. The mixture was for 4 hr and cooled to room temperature. $^1$H NMR confirmed the presence of unreacted **3c** (59%, dichloroethane as internal standard) in the reaction mixture. The reaction mixture was diluted with water, neutralized with saturated solution of $NaHCO_3$, and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with column chromatography (hexane: ethyl acetate= 3: 1) to afford **1c** (22.4 mg, 28%, colorless oil).

$^1$H NMR ($CDCl_3$): δ 7.33-7.31 (1H, m), 7.21 (1H, dd, *J*= 0.4, 8.4 Hz), 6.84 (1H, dd, *J*= 0.4, 6.8 Hz), 4.52 (2H, t, *J*= 5.6 Hz), 3.97 (2H, t, *J*=6.0 Hz), 3.65 (2H, t, *J*= 6.0 Hz), 3.52 (2H, t, *J*= 6.0 Hz), 3.03 (2H, t, *J*= 6.0 Hz), 2.96 (2H, t, *J*= 6.0Hz), 2.19 (2H, quint., *J*= 6.0 Hz). $^{13}$C NMR ($CDCl_3$): δ 145.4, 139.3, 134.6, 127.7, 123.3, 115.8, 106.5, 71.3, 70.4, 40.0, 42.6, 26.7, 24.7, 23.3. HRMS (ESI-TOF, [M+Na]$^+$): Calcd. for: $C_{14}H_{17}ClN_2NaO^+$: 287.0922. Found: 287.0942.

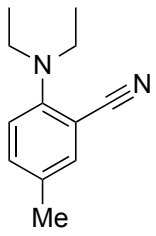
**Reaction of 7l with TsCl**




**1n**

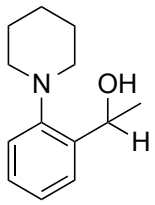
To a solution of **7n** (102.0 mg, 0.53 mmol), pyridine (170.0 µL, 4 equiv.) and $KPF_6$ (200.0 mg, 2 equiv.) in $CH_2Cl_2$ (3.0 mL) was added TsCl (110.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to give **1n** (110.8 mg, 53%, off-white solid).
**1n**. Mp.: 170.0-171.0 ºC. $^1$H NMR ($CD_3OD$): δ 8.91 (2H, d, *J*= 5.6 Hz), 8.58 (1H, tt, *J*= 8.0, 1.2 Hz), 8.09 (2H, t, *J*= 7.2 Hz), 8.04 (1H, d, *J*= 0.8 Hz), 7.77 (1H, dt, *J*= 8.4, 1.2 Hz), 7.59 (1H, dd, *J*= 8.4, 0.8 Hz), 7.45-7.41 (1H, m), 7.20-7.16 (1H, m), 4.64-4.60 (2H, m), 4.54-4.52 (2H, m), 2.03-2.00 (4H, m).$^{13}$C NMR (DMSO-d$^6$): δ 146.0, 145.2, 139.6, 133.2, 128.6, 126.5, 123.9, 121.4, 120.9, 109.9, 60.8, 47.7, 28.6, 26.4. HRMS (ESI-TOF, [M-$PF_6^-$]$^+$): Calcd. for $C_{16}H_{18}N_3^+$: 252.1495. Found: 252.1492.

**Conversion of 3l into 7l.**



**7l**. A solution of **3l** (30.0 mg, 0.09 mmol) and $K_2CO_3$ (50.0 mg, 4 equiv.) in water (0.5 mL) was stirred at ambient temperature for 2 hr. The mixture was extracted with dichloromethane and concentrated. The residue was purified with column chromatography (hexane: ethyl acetate= 4: 1) to afford **7l** (16.2 mg, 94%, yellow oil). $^1$H NMR ($CDCl_3$): δ 7.35 (1H, d, *J*=1.6 Hz), 7.24 (1H, dd, *J*=1.6, 8.8 Hz), 6.90 (1H, d, *J*=8.4), 3.34 (4H, q, *J*=7.2 Hz), 2.29 (3H, s), 1.15 (6H, t, *J*=7.2 Hz). $^{13}$C NMR ($CDCl_3$): δ 151.5, 134.8, 134.1, 129.7, 119.5, 110.6, 104.4, 46.7, 20.1, 12.6. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for: $C_{12}H_{17}N_2^+$: 189.1386. Found: 189.1373.

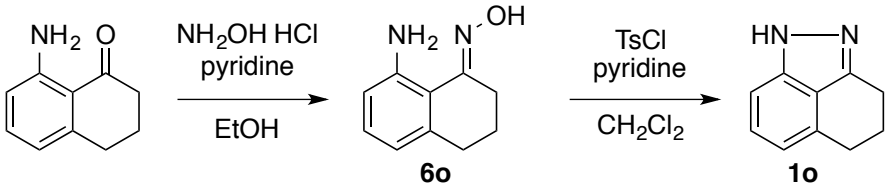
**Hydrogenation of 3a**.




**8a**. A solution of **3a** (103.9 mg, 0.30 mmol) and Pd/C (10%, 10.0 mg) in methanol (3.0 mL) was stirred at 20 ºC under hydrogen atmosphere for 2hr. The reaction mixture was filtered through a pad of Celite and concentrated. The mixture was purified with column chromatography (hexane: ethyl acetate= 4: 1) to afford **8a** (49.7 mg, 81%, colorless oil).

$^1$H NMR ($CDCl_3$): δ 7.40 (1H, brs), 7.27-7.22 (2H, m), 7.18-7.12 (2H, m), 5.06 (1H, q, *J*= 6.4 Hz), 2.95-2.89 (4H, br), 1.79-1.73 (4H, m), 1.61-1.53 (5H, m). $^{13}$C NMR ($CDCl_3$): δ 151.4, 140.2, 127.8, 127.0, 125.6, 122.4, 69.6, 54.9, 26.6, 24.4, 23.9. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for: $C_{13}H_{20}NO^+$: 206.1539. Found: 206.1550.

**synthesis of 1o**.



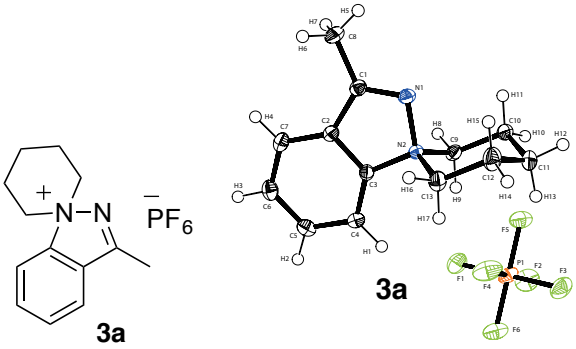

**6o** **1o**

A solution of 8-amino-3,4-dihydronaphthalen-1(2*H*)-one (160.0 mg, 1.00 mmol), pyridine (1.0 mL), hydroxylamine hydrochloride (140.0 mg, 2.0 equiv.) in 5 mL of ethanol was heated to reflux for 1hr. The reaction mixture was evaporated, diluted with dichloromethane and washed with water. The solvent was evaporated to afford **6o** (yellow solid, 155.7 mg, 88%). The crude product was used in further steps without purification.
Mp.: 107.5-110.0 ºC. $^1$H NMR ($CDCl_3$): δ 7.00 (1H, t, *J*= 8.0 Hz), 6.53 (1H, d, *J*= 8.4 Hz), 6.49 (1H, d, *J*= 7.6 Hz), 5.77 (2H, brs), 2.86 (2H, t, *J*= 6.4 Hz), 2.70 (2H, t, *J*= 6.0 Hz), 1.84-1.77 (2H, m). $^{13}$C NMR ($CDCl_3$): δ 159.4, 146.7, 141.8, 129.3, 117.3, 114.7, 113.6, 31.2, 24.6, 21.1. HRMS (ESI-TOF, $[M+H]^+$): Calcd. for $C_{10}H_{13}N_2O^+$: 177.1022. Found: 177.1020

To a solution of **6o** (126.9 mg, 0.72 mmol), pyridine (230.0 µL, 4 equiv.) in $CH_2Cl_2$ (3.5 mL) was added TsCl (150.0 mg, 1.1 equiv.) at 0 ºC. The whole was stirred at 0 ºC for 1 hr. The reaction was quenched with water and the mixture was extracted with $CH_2Cl_2$. The solvent was evaporated and the residue was purified with recrystallization (ethanol) to afford **1o** (white solid, 54.3 mg, 48%)
Mp.: 116.0-117.0 ºC. $^1$H NMR ($CDCl_3$): δ 10.42 (1H, brs), 7.31-7.27 (1H, m), 7.20 (1H, dd, *J*= 0.8, 8.0 Hz), 6.85 (1H, d, *J*= 6.4 Hz), 3.05 (2H, t, *J*= 5.6 Hz), 2.95 (2H, t, *J*= 6.0 Hz), 2.21-2.15 (2H, m) $^{13}$C NMR ($CDCl_3$): δ 146.7, 139.1, 134.6, 128.0, 122.7, 116.2, 106.9, 26.7, 24.8, 23.4. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{10}H_{10}N_2Na^+$: 181.0736. Found: 181.0748. Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.87; H, 6.47; N, 17.80.

**Single crystal X-ray diffraction experiment**

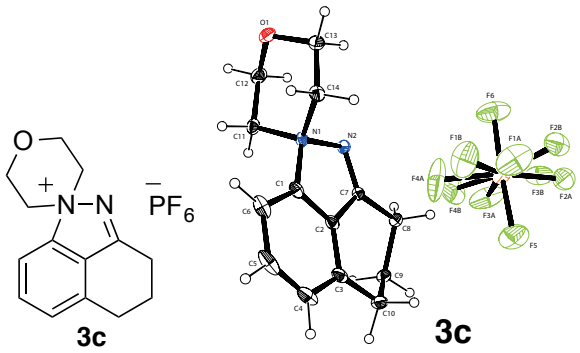
Single crystal of **3a** was obtained by recrystallization from ethanol. Single crystal of **3c** was obtained by recrystallization from $CH_2Cl_2$/EtOAc. Single crystal of **3g** was obtained by recrystallization from $CH_2Cl_2$/$CHCl_3$. Single crystal of **1o** was obtained by recrystallization from $CH_2Cl_2$/Hexane.




The crystal was immersed in Paraton-N oil and placed in the $N_2$ cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuKα : λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[s5] Structure solution and refinement were performed by using SHELXT-2014/5[s6] and SHELXL-2016/6 [s7].

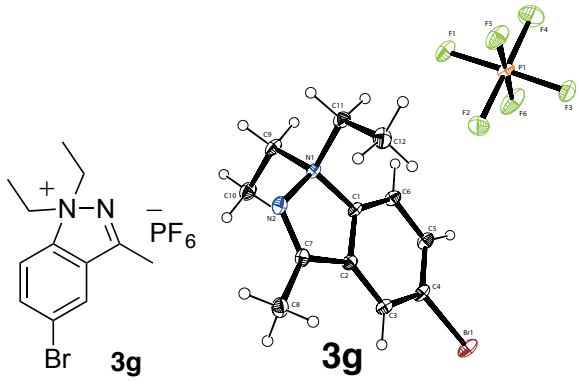
$C_{13}H_{17}F_6N_2P$, *Mr* = 346.25; monoclinic, space group $P2_1/n$, $Z = 4$, $D_{calc} = 1.511$ g·cm$^{-3}$, $a = 8.8739(5)$, $b = 12.9265(7)$, $c = 13.4682(7)$ Å, ∢= 99.885(2)°, $V = 1521.98(14)$ Å$^3$, 20163 observed and 2860 independent [$I > 2\sigma(I)$] reflections, 267 parameters, final $R_1 = 0.0333$, $wR_2 = 0.0809$, $S = 1.065$ [$I > 2\sigma(I)$].
All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found by the Fourier map and refined isotropically.

Empirical formula C13 H17 F6 N2 P
Formula weight 346.25
Temperature 100(2) K
Wavelength 1.54178 Å
Crystal system Monoclinic
Space group $P2_1/n$
Unit cell dimensions a = 8.8739(5) Å a= 90°.
b = 12.9265(7) Å b= 99.885(2)°.
c = 13.4682(7) Å g = 90°.
Volume 1521.98(14) Å3
Z 4
Density (calculated) 1.511 Mg/m3
Absorption coefficient 2.206 mm-1
F(000) 712
Crystal size 0.100 x 0.080 x 0.050 mm3
Theta range for data collection 4.776 to 78.669°.
Index ranges -10<=h<=11, -15<=k<=16, -16<=l<=16
Reflections collected 20163
Independent reflections 3206 [R(int) = 0.0399]
Completeness to theta = 67.679° 100.0 %
Absorption correction Empirical
Max. and min. transmission 0.8835 and 0.8350
Refinement method Full-matrix least-squares on F2
Data / restraints / parameters 3206 / 0 / 267
Goodness-of-fit on F2 1.065
Final R indices [I>2sigma(I)] R1 = 0.0333, wR2 = 0.0809
R indices (all data) R1 = 0.0382, wR2 = 0.0870
Extinction coefficient n/a
Largest diff. peak and hole 0.356 and -0.599 e.Å-3

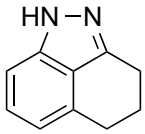



All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 23 and 43) with $U_{iso}$ values constrained to 1.2 $U_{eq}$ of their parent atoms. A pair of disordered fluorine atoms (F1-F4) of the hexafluorophosphate anion was refined with PART, and the ratio was ca. 50/50.

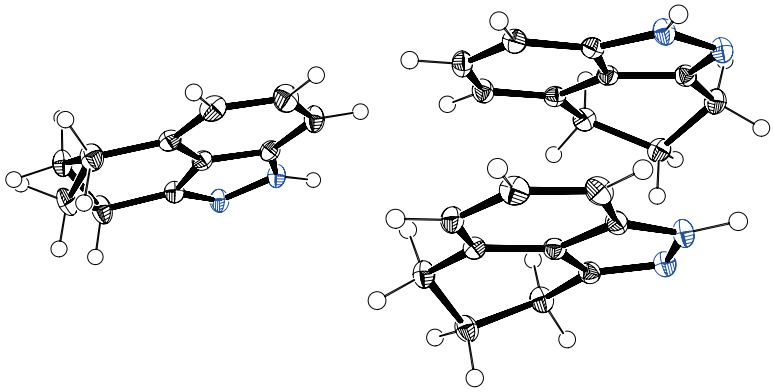
| | |
|---|---|
| Empirical formula | C14 H17 F6 N2 O P |
| Formula weight | 374.26 |
| Temperature | 100(2) K |
| Wavelength | 1.54178 Å |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions | a = 9.3512(9) Å a= 90°. |
| | b = 14.2117(14) Å b= 110.717(2)°. |
| | c = 12.5086(12) Å g = 90°. |
| Volume | 1554.9(3) Å3 |
| Z | 4 |
| Density (calculated) | 1.599 Mg/m3 |
| Absorption coefficient | 2.261 mm-1 |
| F(000) | 768 |
| Crystal size | 0.220 x 0.220 x 0.100 mm3 |
| Theta range for data collection | 4.896 to 78.787°. |
| Index ranges | -11<=h<=11, -17<=k<=18, -15<=l<=15 |
| Reflections collected | 19337 |
| Independent reflections | 3254 [R(int) = 0.0337] |
| Completeness to theta = 67.679° | 99.7 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.7508 and 0.6422 |
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 3254 / 0 / 254 |
| Goodness-of-fit on F2 | 1.048 |
| Final R indices [I>2sigma(I)] | R1 = 0.0516, wR2 = 0.1277 |
| R indices (all data) | R1 = 0.0529, wR2 = 0.1287 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.827 and -0.516 e.Å-3 |




Formula weight 413.15
Temperature 100(2) K
Wavelength 1.54178 Å
Crystal system Monoclinic
Space group $P2_1/n$
Unit cell dimensions a = 8.4310(7) Å a= 90°.
b = 10.6455(9) Å b= 91.537(2)°.
c = 17.7568(14) Å g = 90°.
Volume 1593.1(2) Å3
Z 4
Density (calculated) 1.723 Mg/m3
Absorption coefficient 5.047 mm-1
F(000) 824
Crystal size 0.100 x 0.060 x 0.030 mm3
Theta range for data collection 4.844 to 79.243°.
Index ranges -10<=h<=10, -13<=k<=13, -21<=l<=22
Reflections collected 20246
Independent reflections 3374 [R(int) = 0.0426]
Completeness to theta = 67.679° 99.9 %
Absorption correction Empirical
Max. and min. transmission 0.7958 and 0.6766
Refinement method Full-matrix least-squares on F2
Data / restraints / parameters 3374 / 0 / 202
Goodness-of-fit on F2 1.044
Final R indices [I>2sigma(I)] R1 = 0.0309, wR2 = 0.0766
R indices (all data) R1 = 0.0342, wR2 = 0.0787
Extinction coefficient n/a
Largest diff. peak and hole 0.776 and -0.893 e.Å-3




**1o**



Empirical formula C10 H10 N2
Formula weight 158.20
Temperature 100 K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P -1
Unit cell dimensions a = 8.9125(14) Å a= 69.182(2)°.
b = 11.3351(18) Å b= 74.864(2)°.
c = 13.323(2) Å g = 87.348(2)°.
Volume 1212.8(3) Å3
Z 6
Density (calculated) 1.300 Mg/m3
Absorption coefficient 0.079 mm-1
F(000) 504
Crystal size 0.48 x 0.32 x 0.18 mm3
Theta range for data collection 1.925 to 27.282°.
Index ranges -11<=h<=11, -14<=k<=14, -17<=l<=16
Reflections collected 12590
Independent reflections 4933 [R(int) = 0.0150]
Completeness to theta = 25.000° 99.4 %
Absorption correction None
Refinement method Full-matrix least-squares on F2
Data / restraints / parameters 4933 / 0 / 347
Goodness-of-fit on F2 1.049
Final R indices [I>2sigma(I)] R1 = 0.0359, wR2 = 0.0950
R indices (all data) R1 = 0.0391, wR2 = 0.0978
Extinction coefficient n/a
Largest diff. peak and hole 0.303 and -0.207 e.Å-3

**Computational Studies**

DFT calculations were performed with Gaussian 09.[S9] For energy calculations (**Scheme 1c**), geometries of molecules were fully optimized at B3LYP/def2-TZVPP level. This calculation level is able to reproduce the N-N bond length of indazole derivatives (**Figure S1**). For other computational studies (**Table 1** and **Figure 2**), Wave functions were generated at B3LYP/def2-TZVPP level using the structure obtained from X-ray diffraction experimetnts. Wave function analysis was conducted using Multiwfn.[S10] Topological analysis was conducted on the structure of charge neutral spiecies, and ESP was calculated on the corresponding cations without counter ion ($PF_6^-$). NICS value was calculated with GIAO-NMR method.

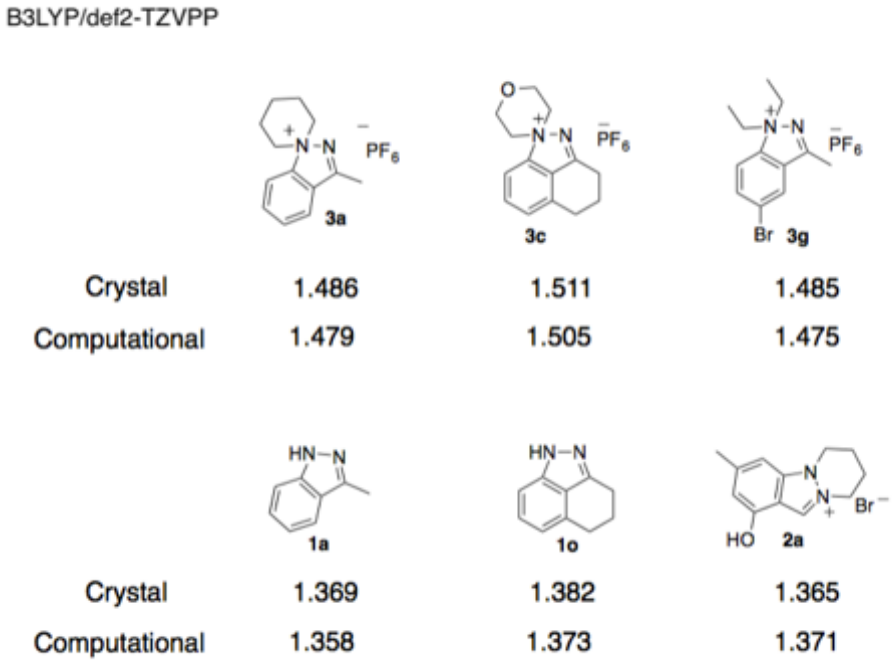
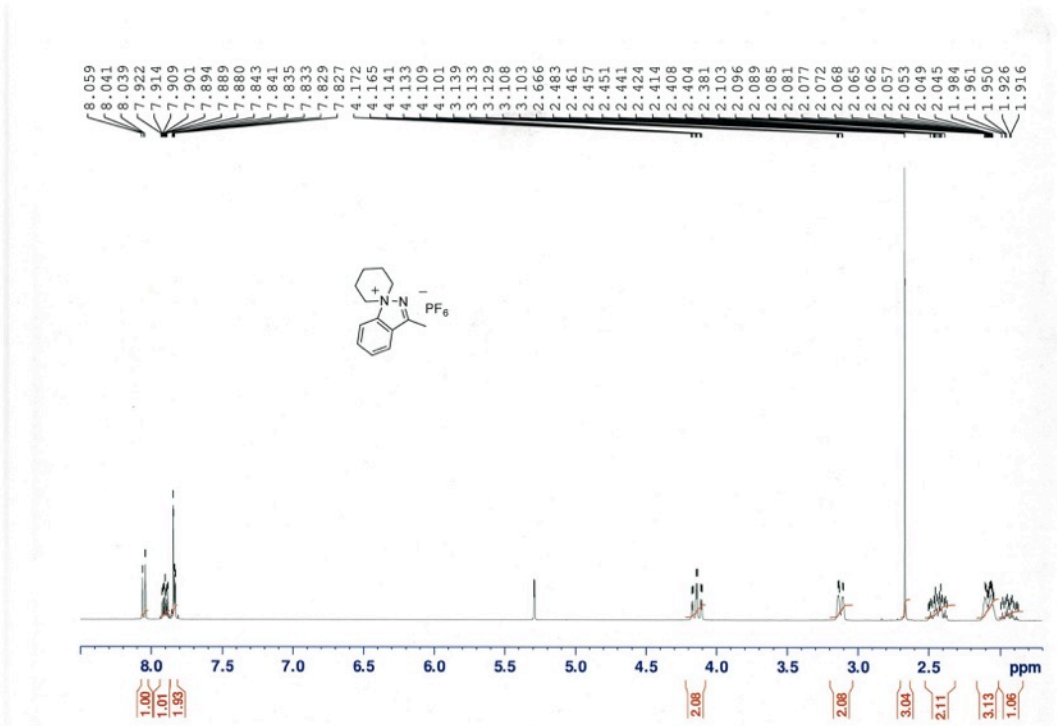
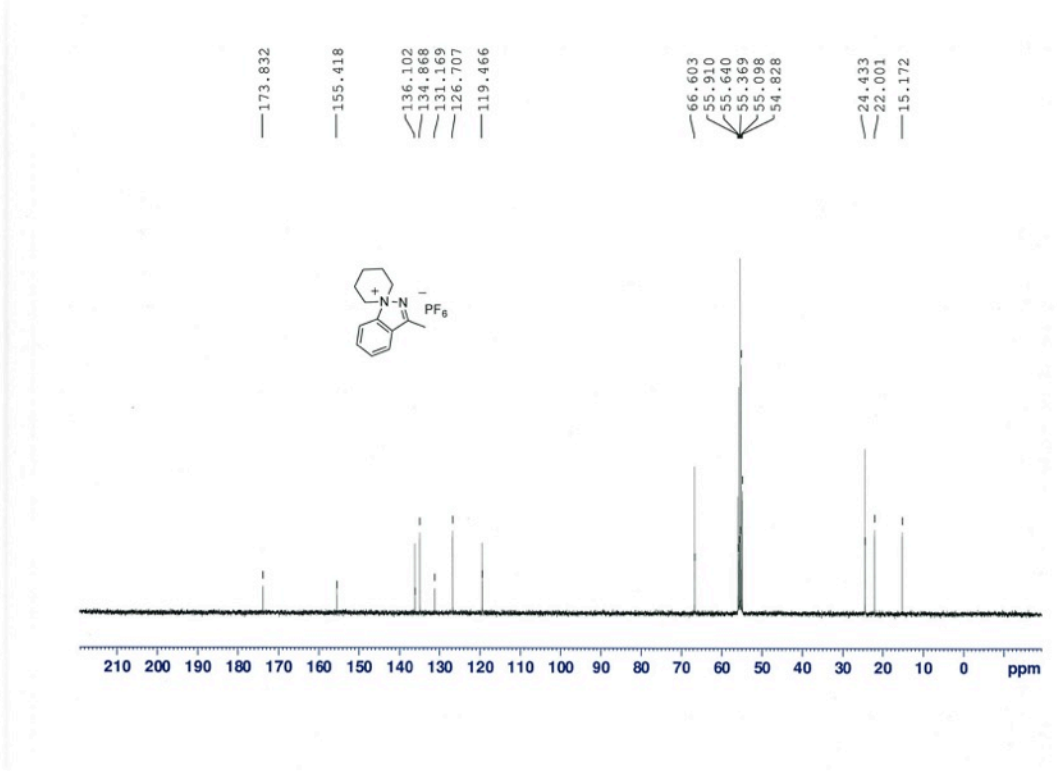
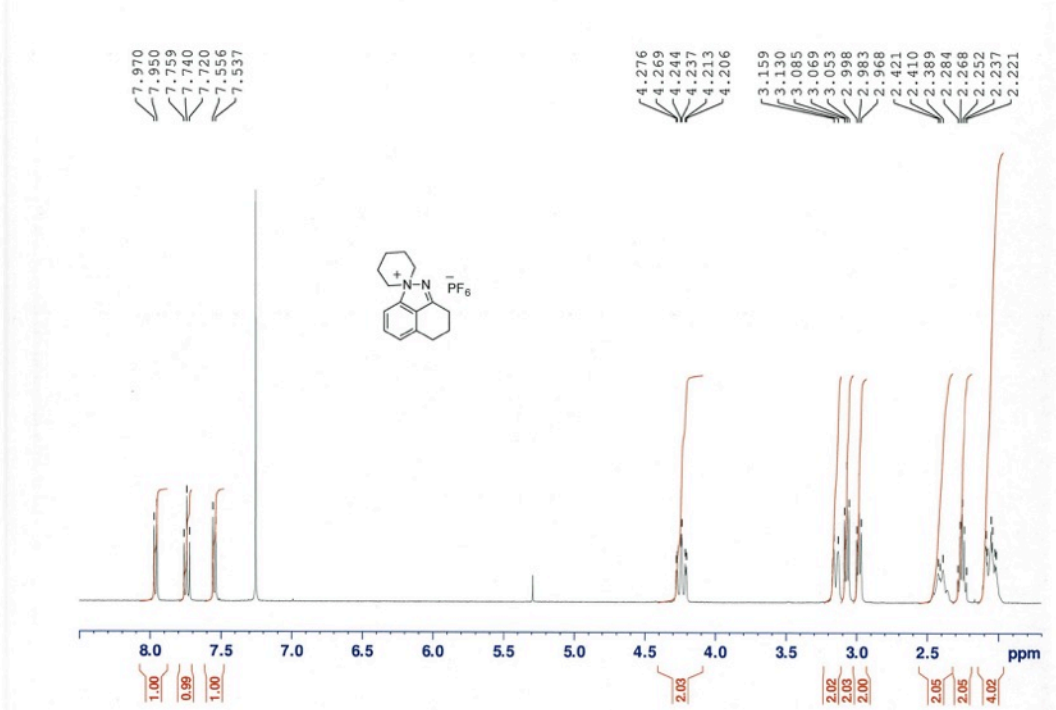



**Figure S1**. N-N bond lengths of indazoles, obtained from crystal structures and calculations (at the level of B3LYP/def2-TZVPP )

**NMR spectral of compounds**

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7.556
7.537
4.276
4.269
4.244
4.237
4.213
4.206
3.159
3.130
3.085
3.069
3.053
2.998
2.983
2.968
2.421
2.410
2.389
2.284
2.268
2.252
2.237
2.221
PF6
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
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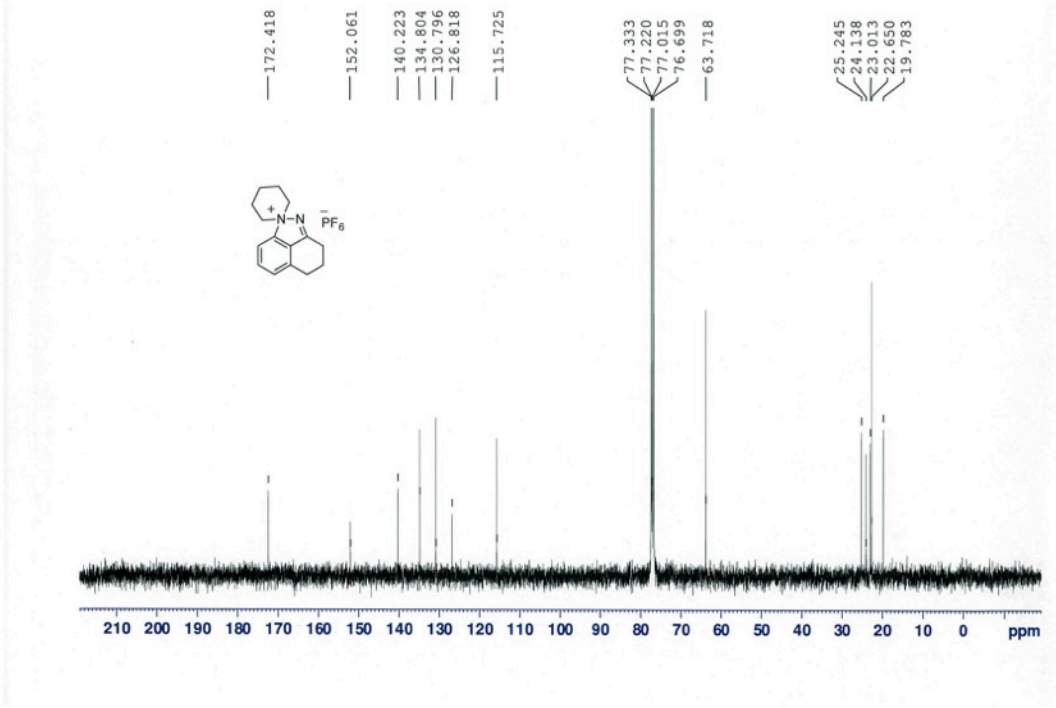
2.02
2.03
2.00
2.05
2.05
4.02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134.804
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126.818
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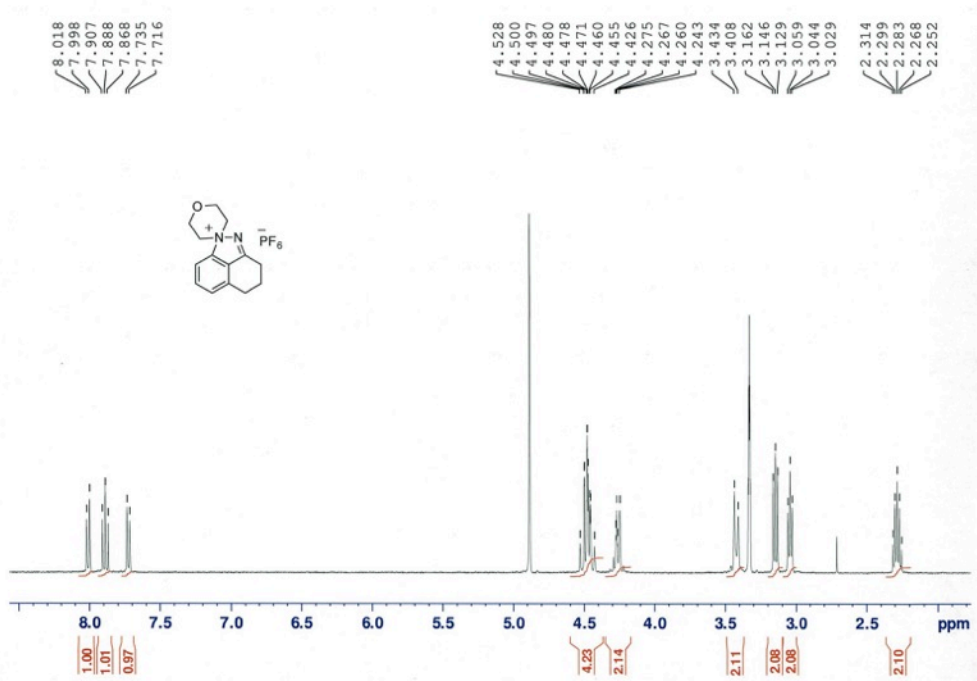
77.333
77.220
77.015
76.699
63.718
25.245
24.138
23.013
22.650
19.783
PF6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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7.998
7.907
7.888
7.868
7.735
7.716
4.528
4.500
4.497
4.480
4.478
4.471
4.460
4.455
4.426
4.275
4.267
4.260
4.243
3.434
3.408
3.162
3.146
3.129
3.059
3.044
3.029
2.314
2.299
2.283
2.268
2.252
PF6
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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ppm
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1.01
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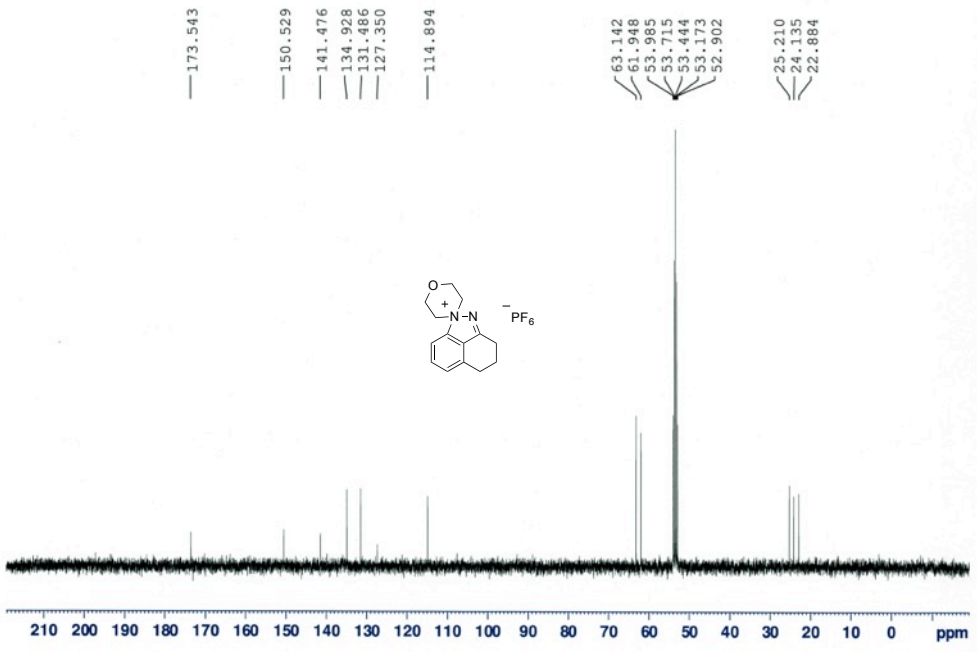
2.14
2.11
2.08
2.08
2.10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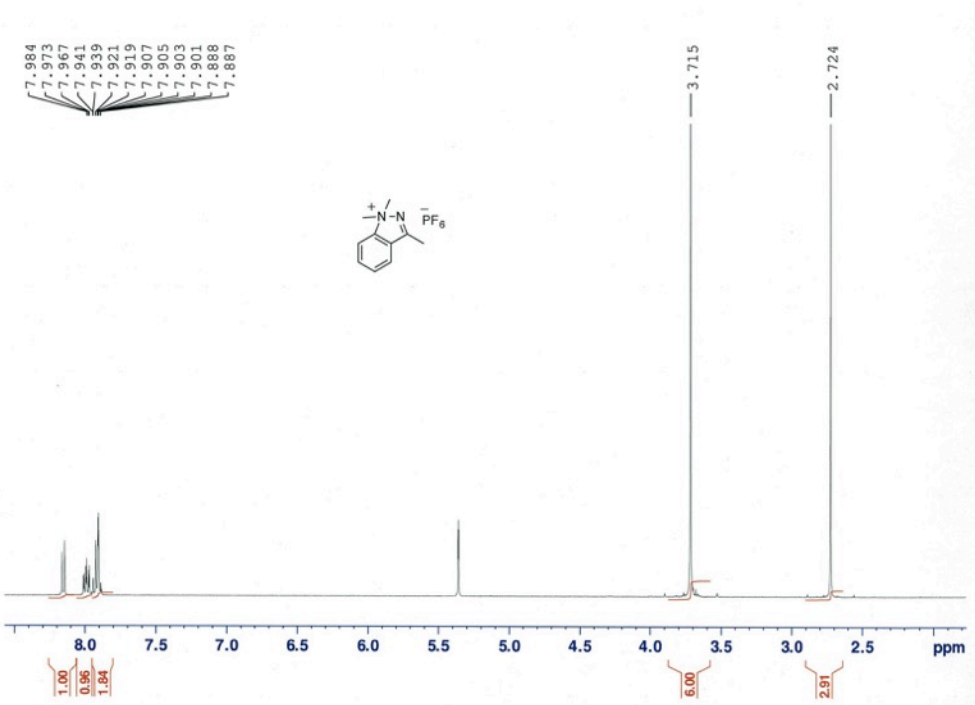
141.476
134.928
131.486
127.350
114.894
63.142
61.948
53.985
53.715
53.444
53.173
52.902
25.210
24.135
22.884
PF6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.973
7.967
7.941
7.939
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7.919
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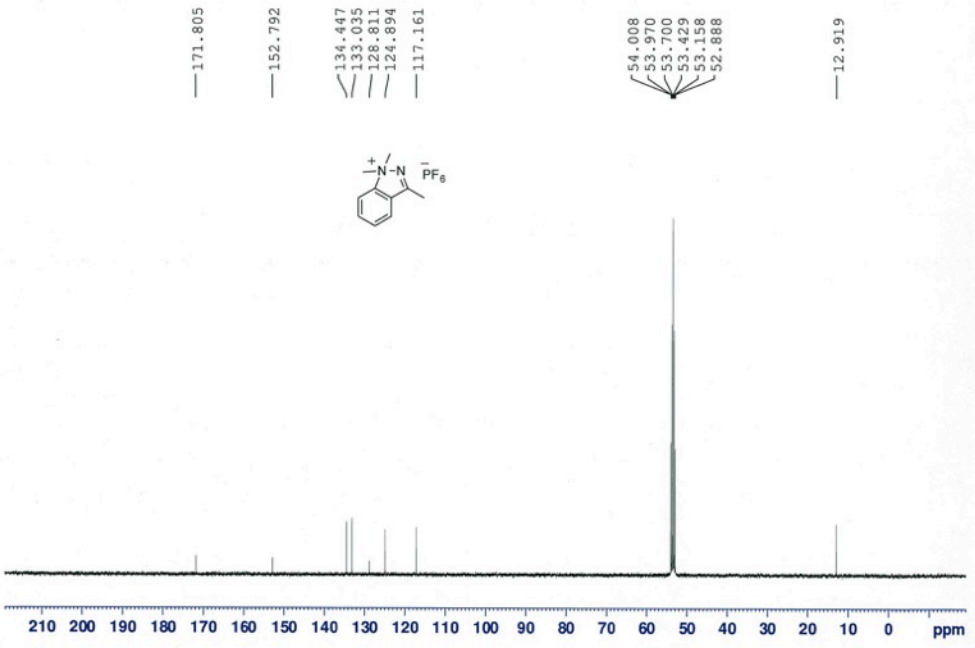
7.905
7.903
7.901
7.888
7.887
3.715
2.724
PF6
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.00
0.96
1.84
6.00
2.91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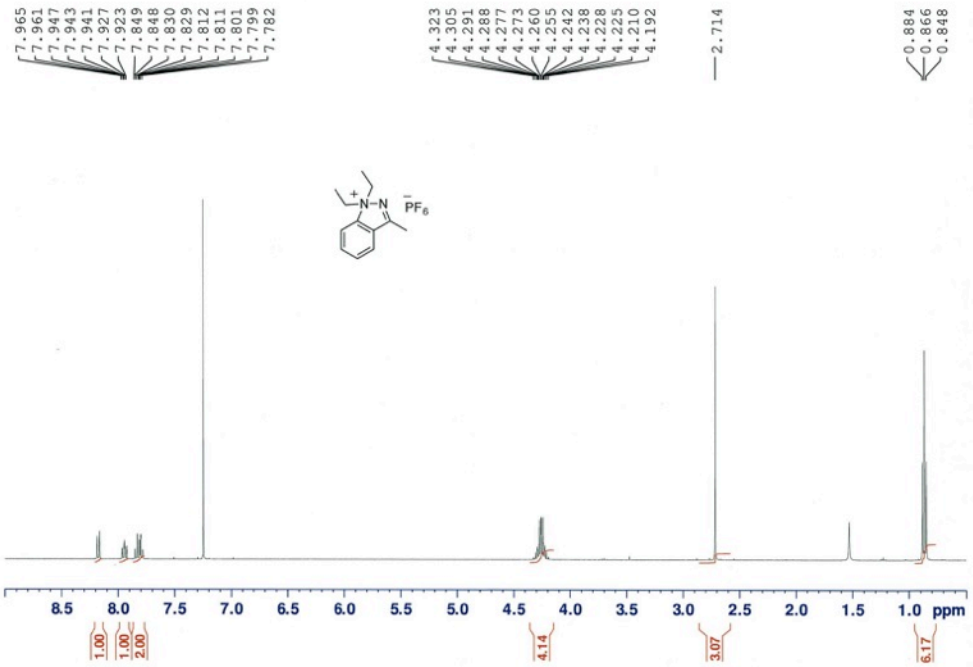
134.447
133.035
128.811
124.894
117.161
54.008
53.970
53.700
53.429
53.158
52.888
12.919
PF6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.941
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7.923
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7.848
7.830
7.829
7.812
7.811
7.801
7.799
7.782
4.323
4.305
4.291
4.288
4.277
4.273
4.260
4.255
4.242
4.238
4.228
4.225
4.210
4.192
2.714
0.884
0.866
0.848
PF6
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0 ppm
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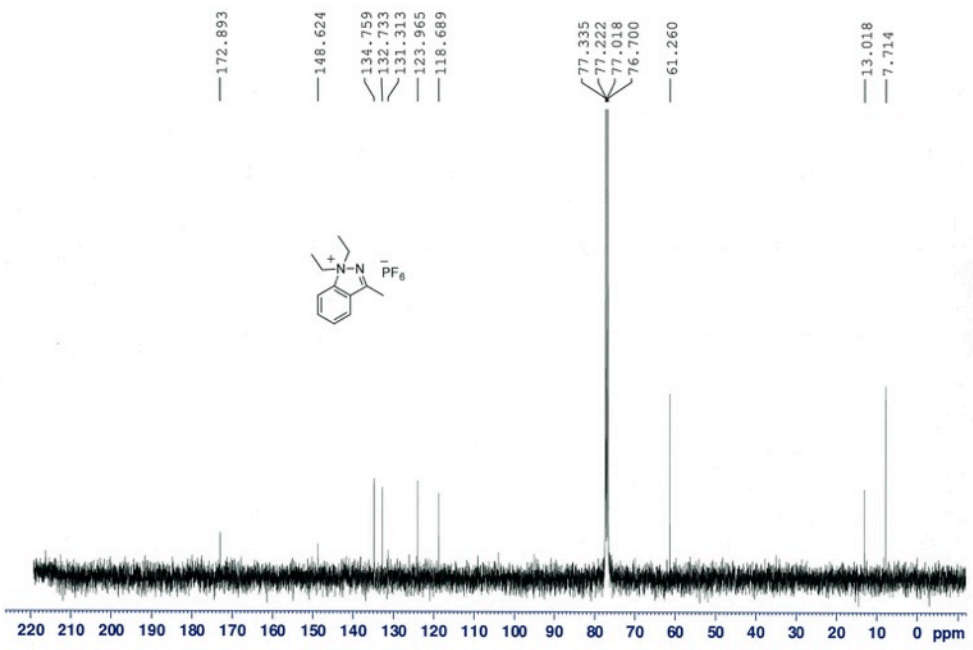
1.00
2.00
4.14
3.07
6.17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134.759
132.733
131.313
123.965
118.689
77.335
77.222
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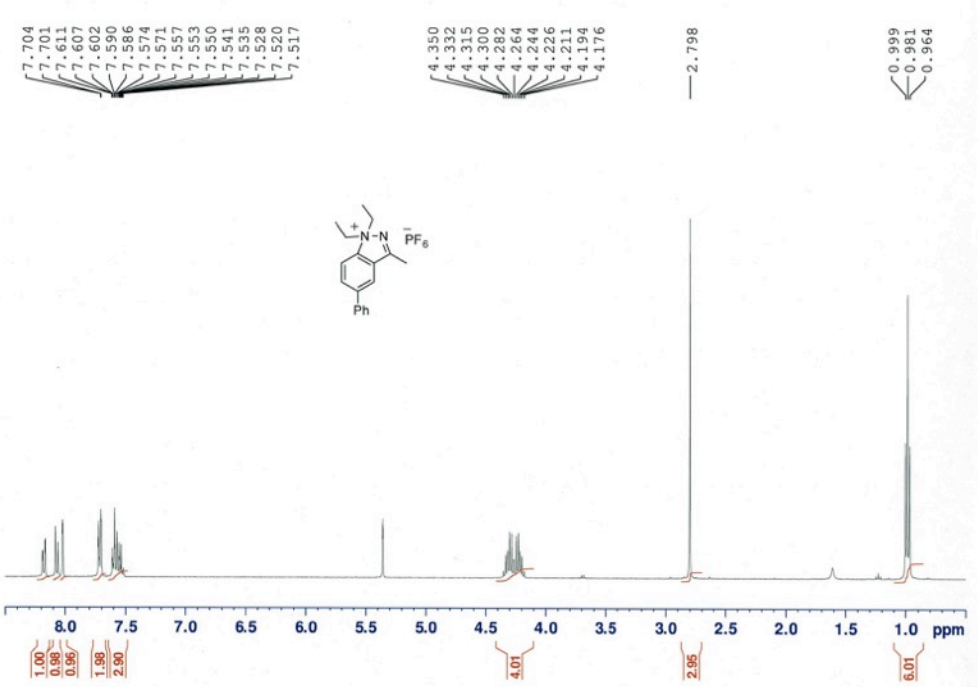
76.700
61.260
13.018
7.714
PF6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.611
7.607
7.602
7.590
7.586
7.574
7.571
7.557
7.553
7.550
7.541
7.535
7.528
7.520
7.517
4.350
4.332
4.315
4.300
4.282
4.264
4.244
4.226
4.211
4.194
4.176
2.798
0.999
0.981
0.964
PF6
Ph
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 ppm
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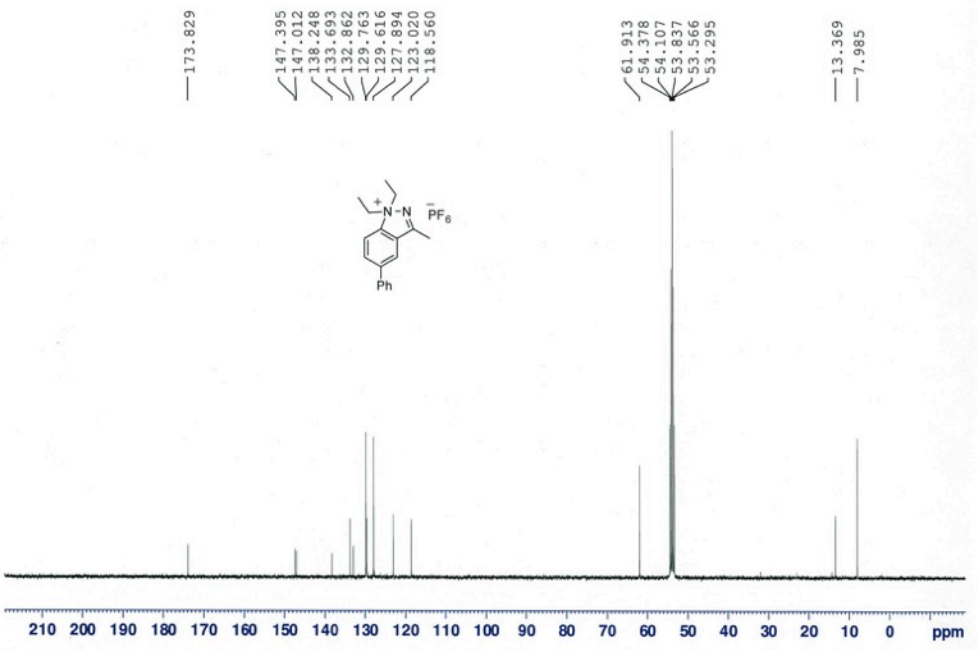
0.96
1.98
2.90
4.01
2.95
6.01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133.693
132.862
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123.020
118.560
61.913
54.378
54.107
53.837
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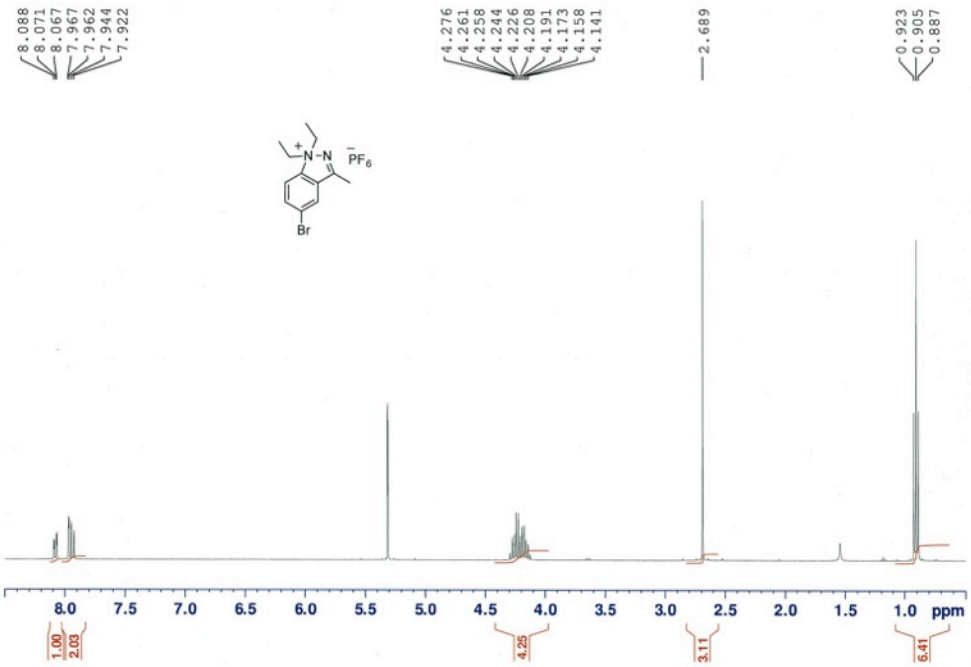
53.295
13.369
7.985
PF6
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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8.067
7.967
7.962
7.944
7.922
4.276
4.261
4.258
4.244
4.226
4.208
4.191
4.173
4.158
4.141
2.689
0.923
0.905
0.887
PF6
Br
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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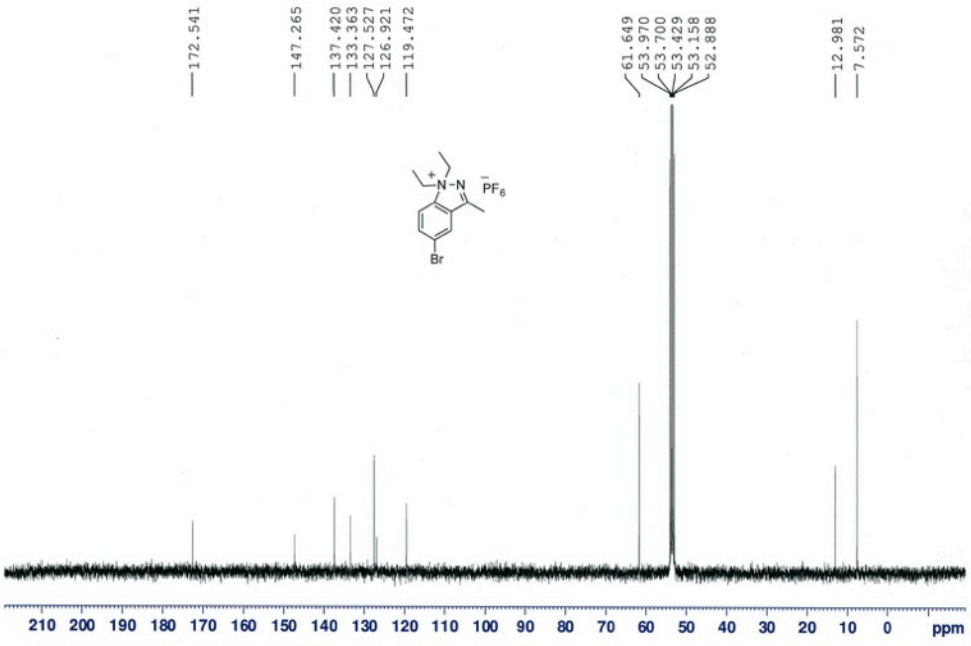
4.25
3.11
6.41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127.527
126.921
119.472
61.649
53.970
53.700
53.429
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52.888
12.981
7.572
PF6
Br
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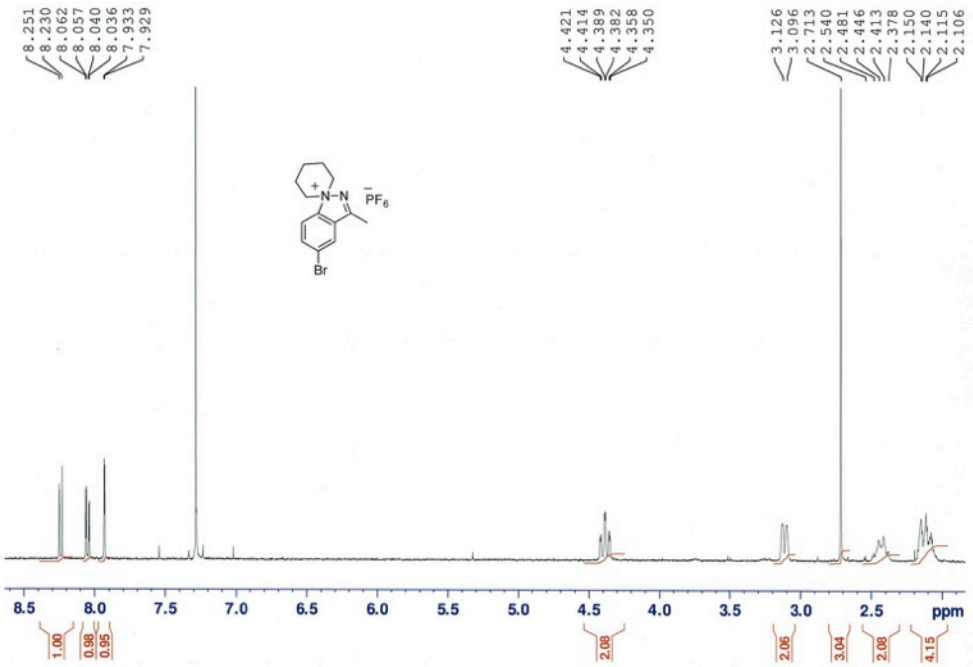
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8.057
8.040
8.036
7.933
7.929
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4.414
4.389
4.382
4.358
4.350
3.126
3.096
2.713
2.540
2.481
2.446
2.413
2.378
2.150
2.140
2.115
2.106
PF6
Br
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
ppm
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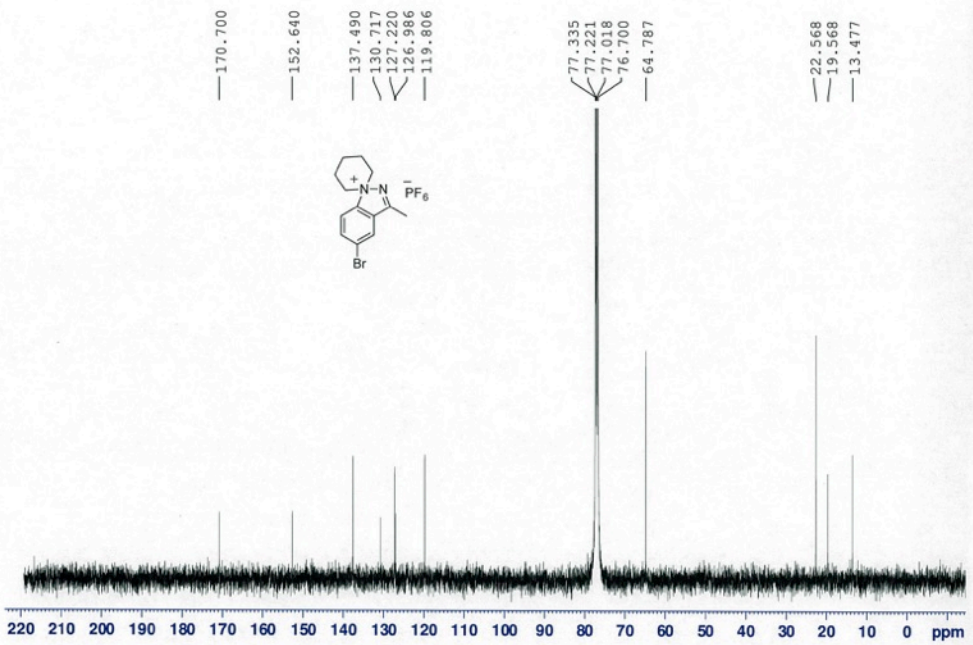
0.95
2.08
2.06
3.04
2.08
4.15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126.986
119.806
77.335
77.221
77.018
76.700
64.787
22.568
19.568
13.477
PF6
Br
220
210
200
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180
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140
130
120
110
100
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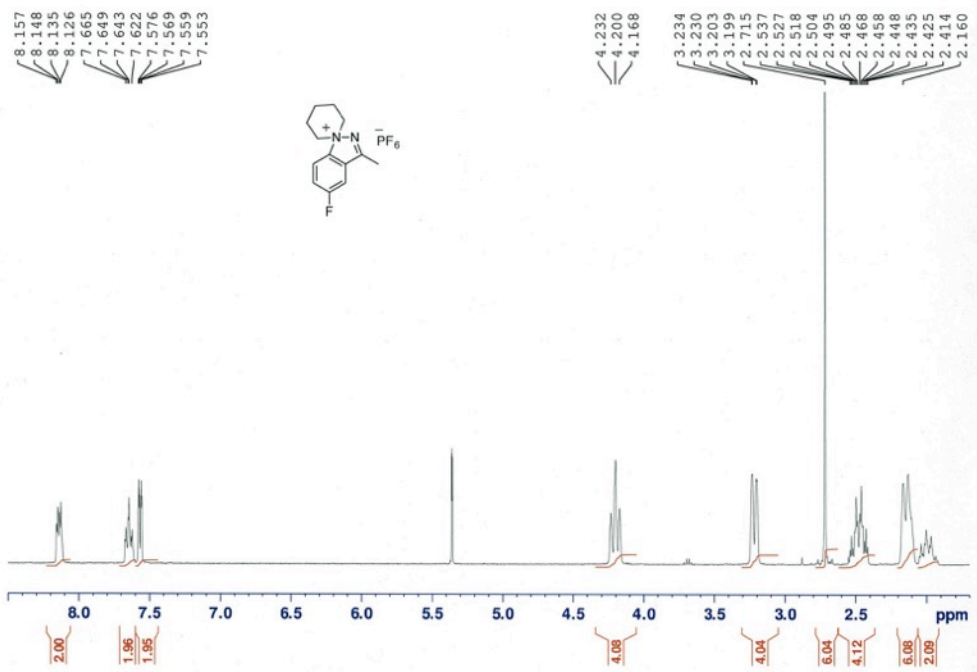
60
50
40
30
20
10
0
ppm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7.649
7.643
7.622
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7.569
7.559
7.553
4.232
4.200
4.168
3.234
3.230
3.203
3.199
2.715
2.537
2.527
2.518
2.504
2.495
2.485
2.468
2.458
2.448
2.435
2.425
2.414
2.160
PF6
F
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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ppm
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4.04
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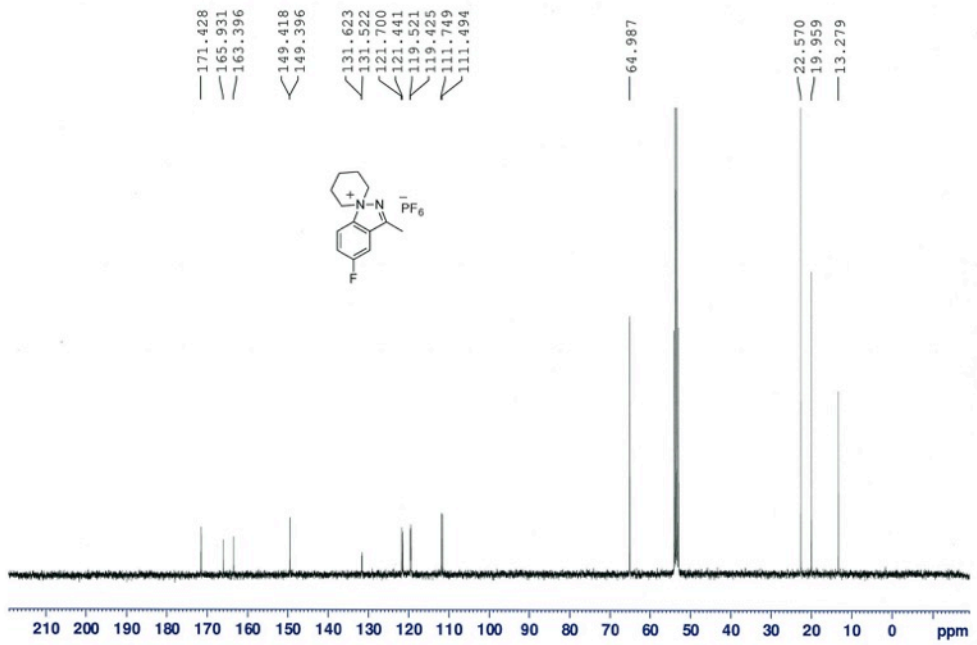
2.09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149.396
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121.700
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119.521
119.425
111.749
111.494
64.987
22.570
19.959
13.279
PF6
F
210
200
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180
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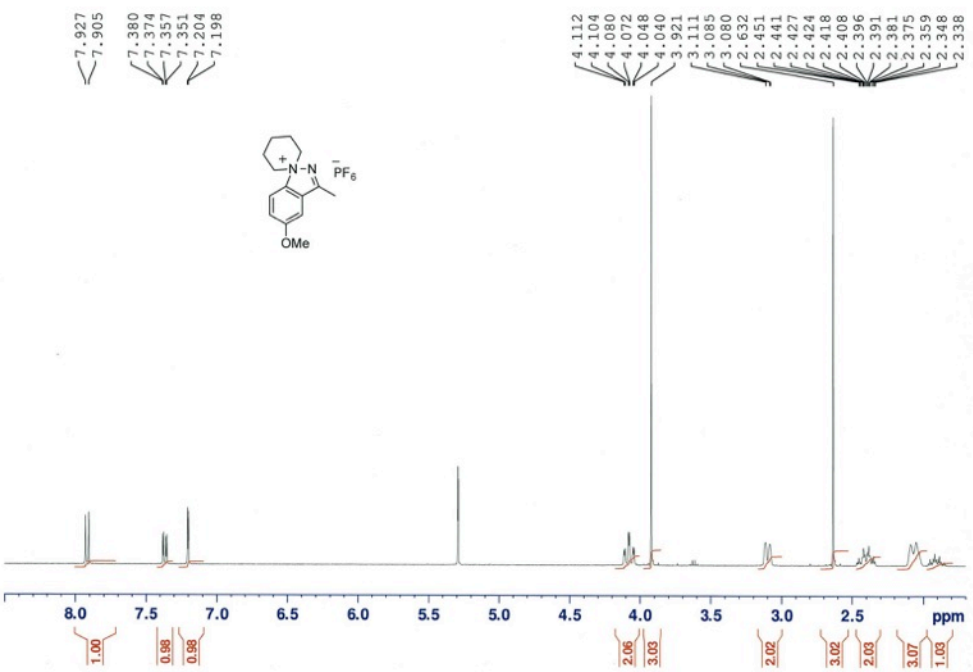
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.198
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4.104
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4.072
4.048
4.040
3.921
3.111
3.085
3.080
2.632
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2.441
2.427
2.424
2.418
2.408
2.396
2.391
2.381
2.375
2.359
2.348
2.338
PF6
OMe
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.02
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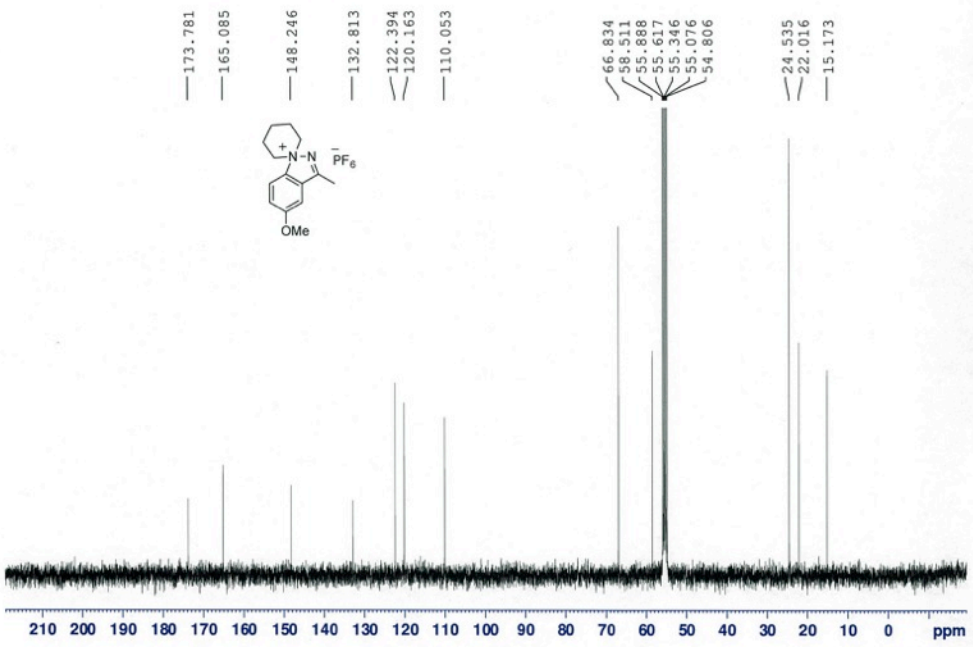
2.03
3.07
1.03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120.163
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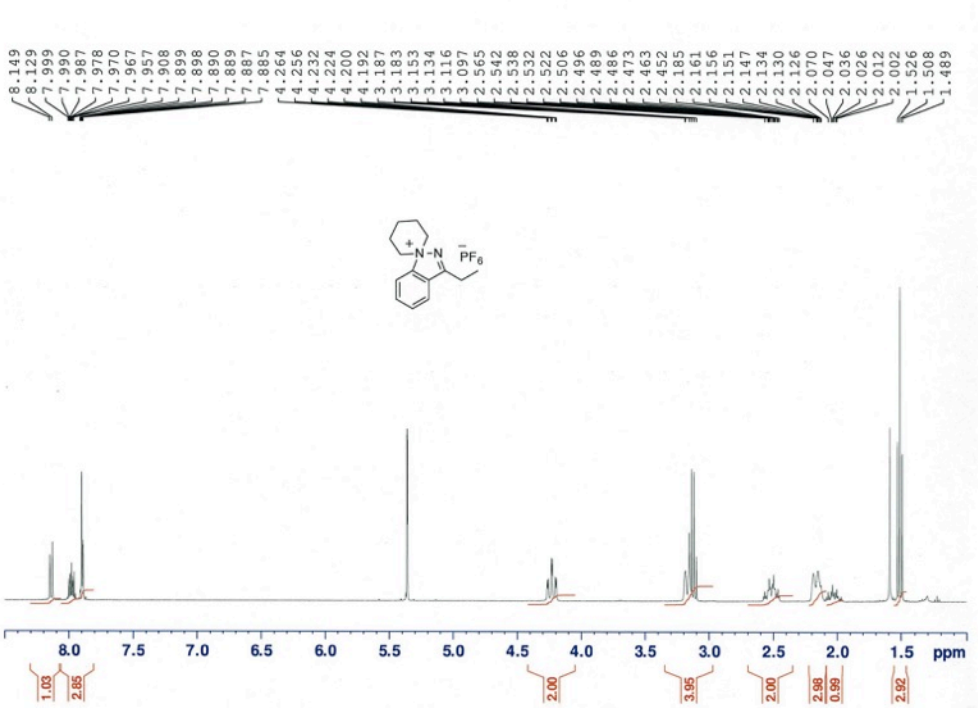
66.834
58.511
55.888
55.617
55.346
55.076
54.806
24.535
22.016
15.173
PF6
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.987
7.978
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7.890
7.889
7.887
7.885
4.264
4.256
4.232
4.224
4.200
4.192
3.187
3.183
3.153
3.134
3.116
3.097
2.565
2.542
2.538
2.532
2.522
2.506
2.496
2.489
2.486
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2.161
2.156
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2.147
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2.130
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2.036
2.026
2.012
2.002
1.526
1.508
1.489
PF6
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
ppm
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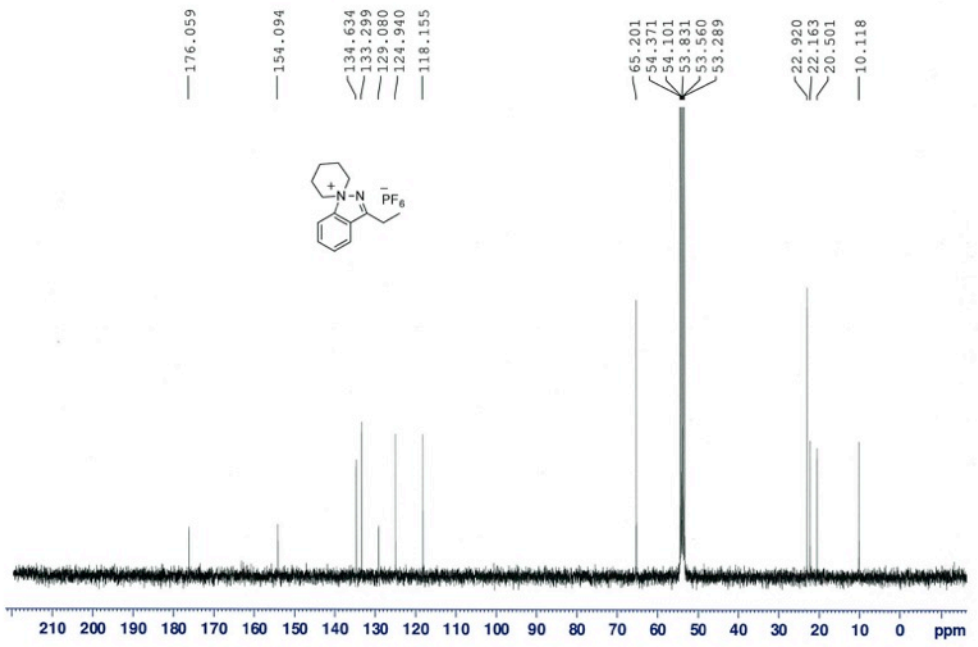
3.95
2.00
2.98
0.99
2.92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22.920
22.163
20.501
10.118
PF6
210
200
190
180
170
160
150
140
130
120
110
100
90
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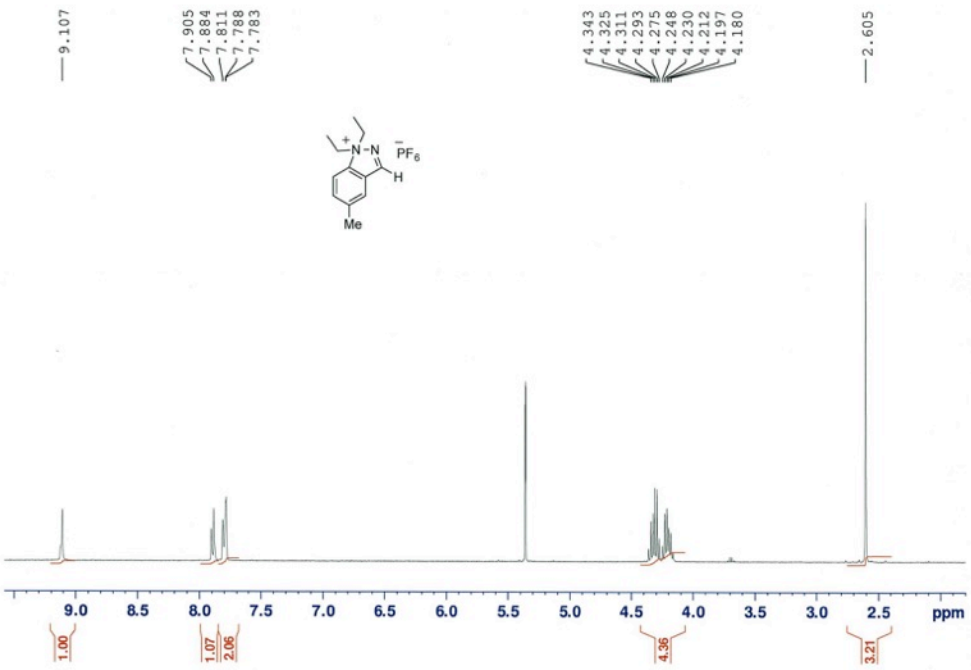
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4.248
4.230
4.212
4.197
4.180
2.605
PF6
H
Me
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.5
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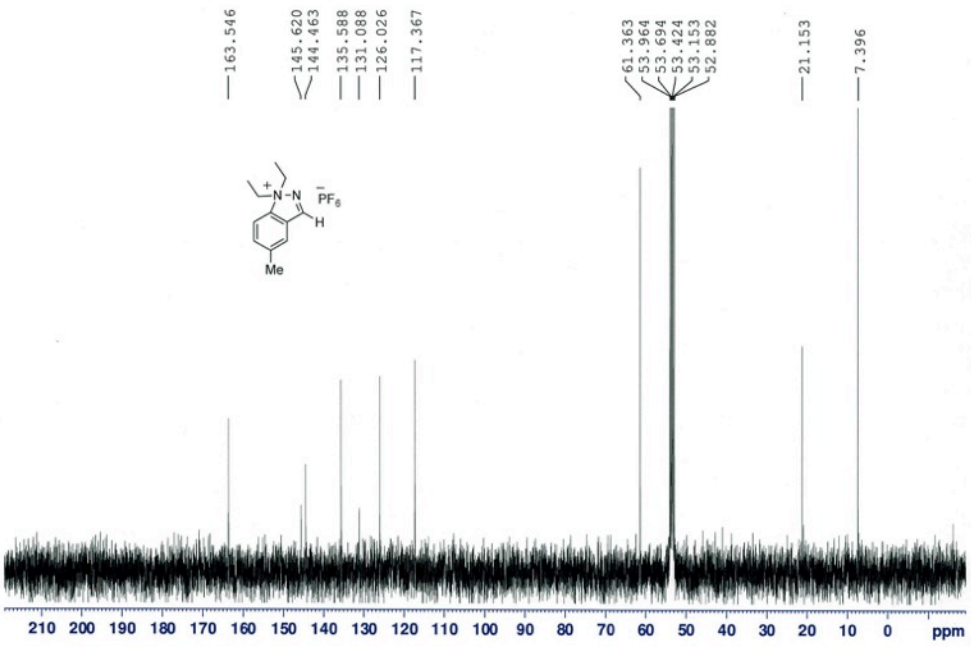
3.21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61.363
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53.694
53.424
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52.882
21.153
7.396
PF6
H
Me
210
200
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60
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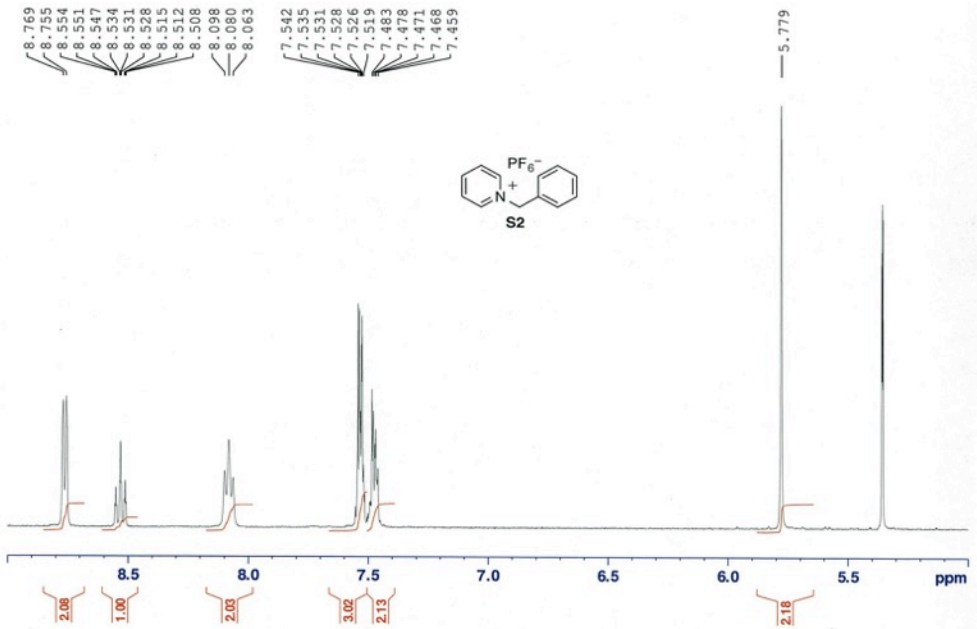
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8.063
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7.535
7.531
7.528
7.526
7.519
7.483
7.478
7.471
7.468
7.459
5.779
PF6−
N+
S2
8.5
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6.5
6.0
5.5
ppm
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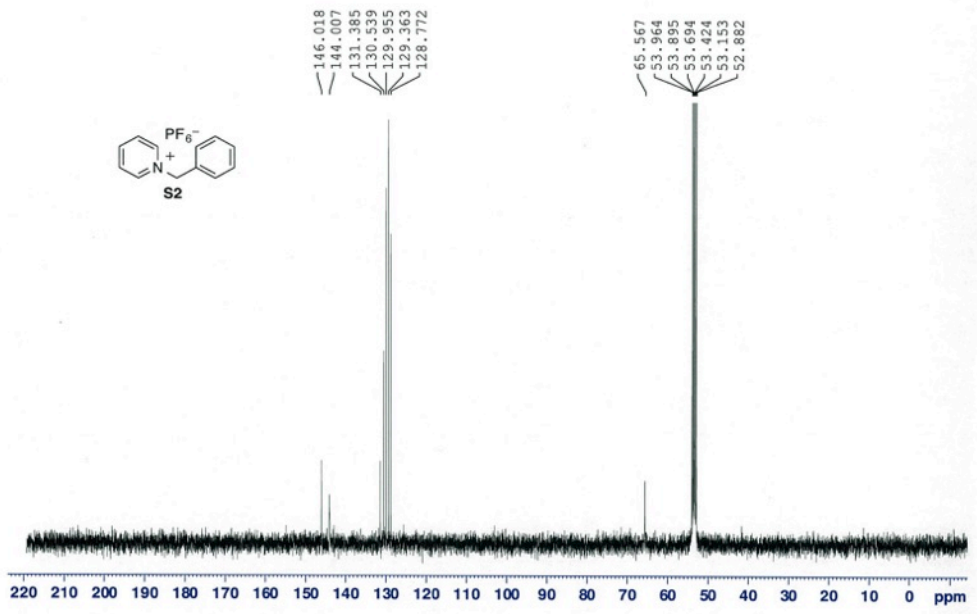
3.02
2.13
2.18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129.955
129.363
128.772
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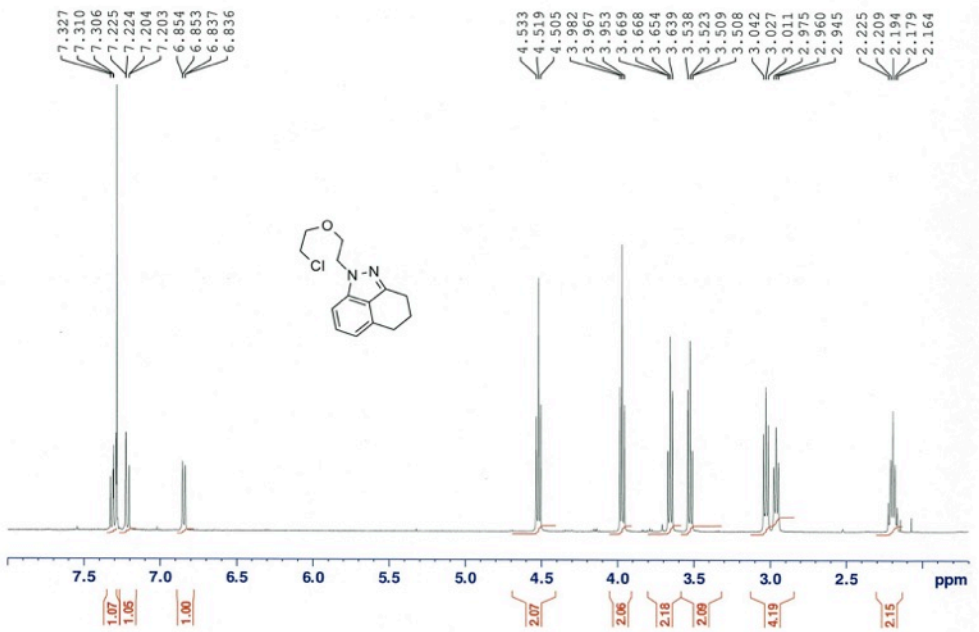
53.153
52.882
PF6−
N+
S2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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6.836
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4.519
4.505
3.982
3.967
3.953
3.669
3.668
3.654
3.639
3.538
3.523
3.509
3.508
3.042
3.027
3.011
2.975
2.960
2.945
2.225
2.209
2.194
2.179
2.164
Cl
N-N
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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ppm
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2.06
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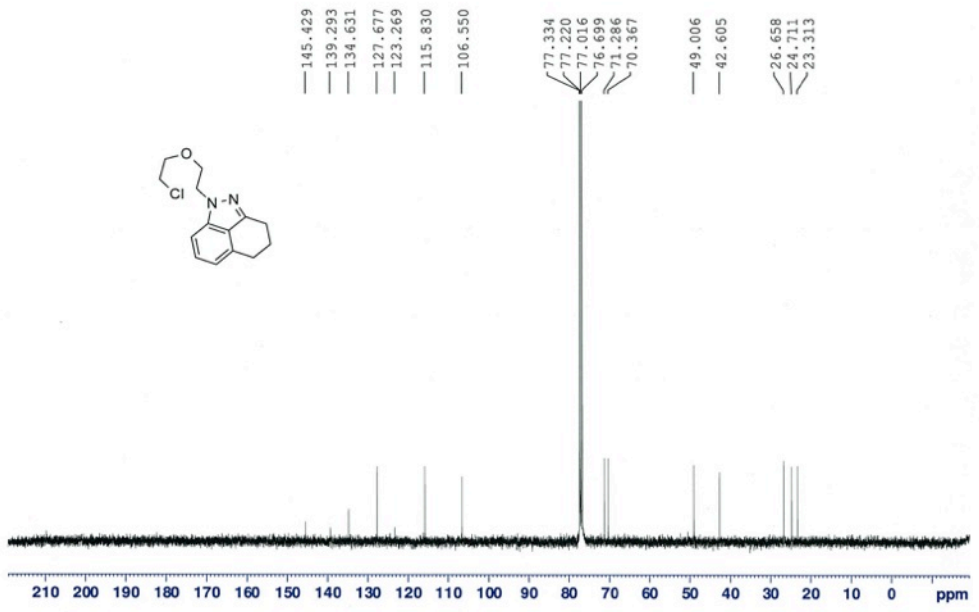
2.15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77.334
77.220
77.016
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70.367
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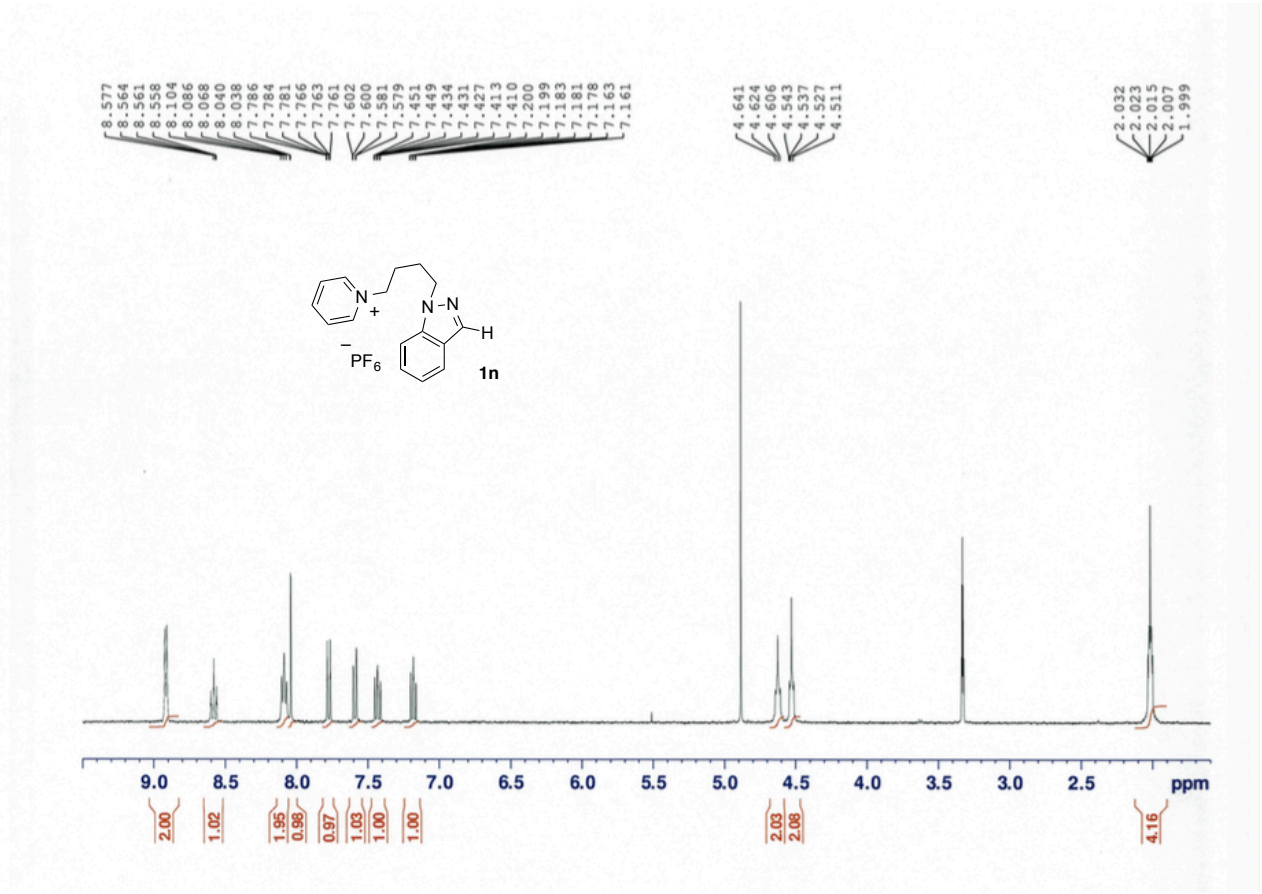
24.711
23.313
Cl
N-N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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8.040
8.038
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7.784
7.781
7.766
7.763
7.761
7.602
7.600
7.581
7.579
7.451
7.449
7.434
7.431
7.427
7.413
7.410
7.200
7.199
7.183
7.181
7.178
7.163
7.161
4.641
4.624
4.606
4.543
4.537
4.527
4.511
2.032
2.023
2.015
2.007
1.999
N
+
N-N
H
PF6
1n
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
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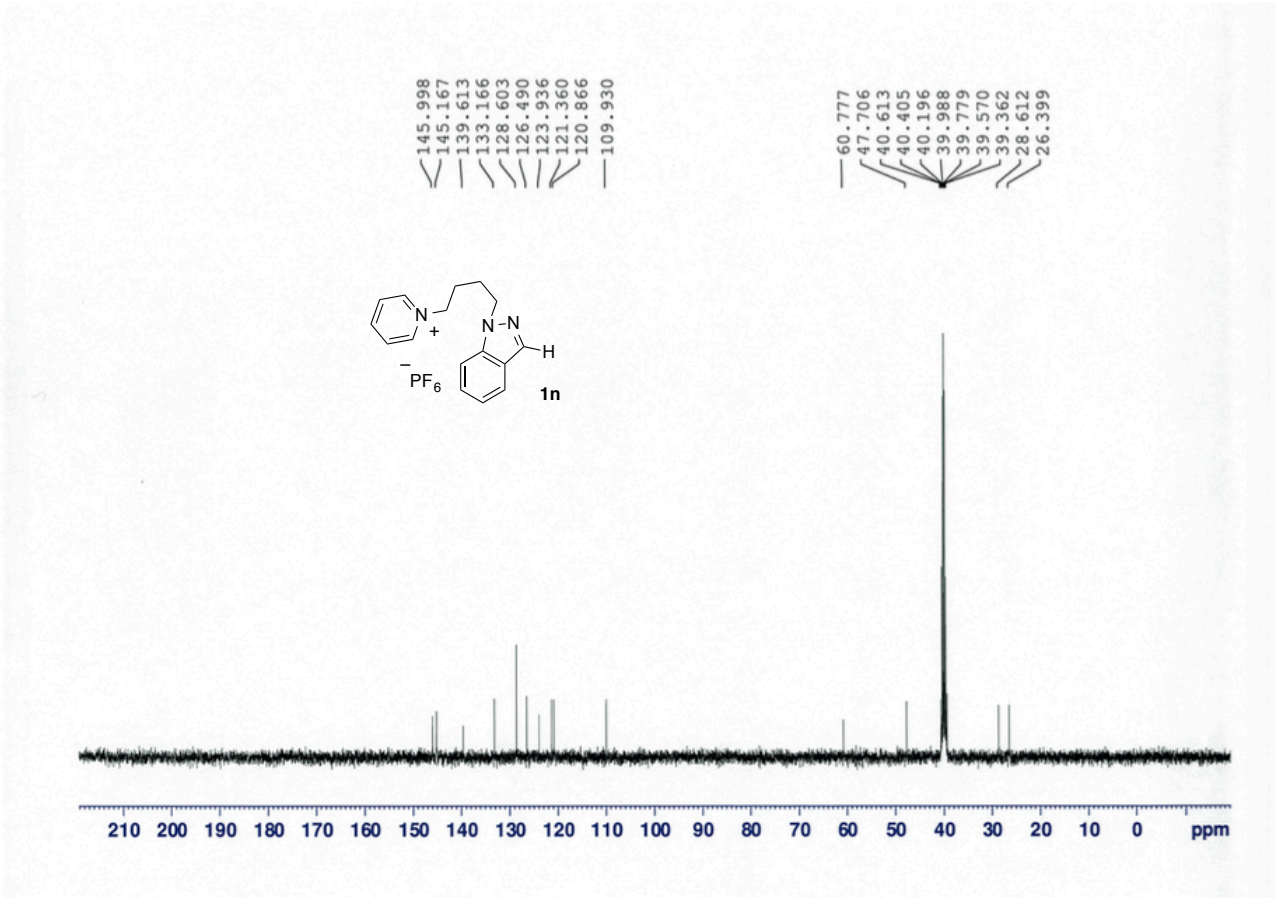
1.00
1.00
2.03
2.08
4.16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123.936
121.360
120.866
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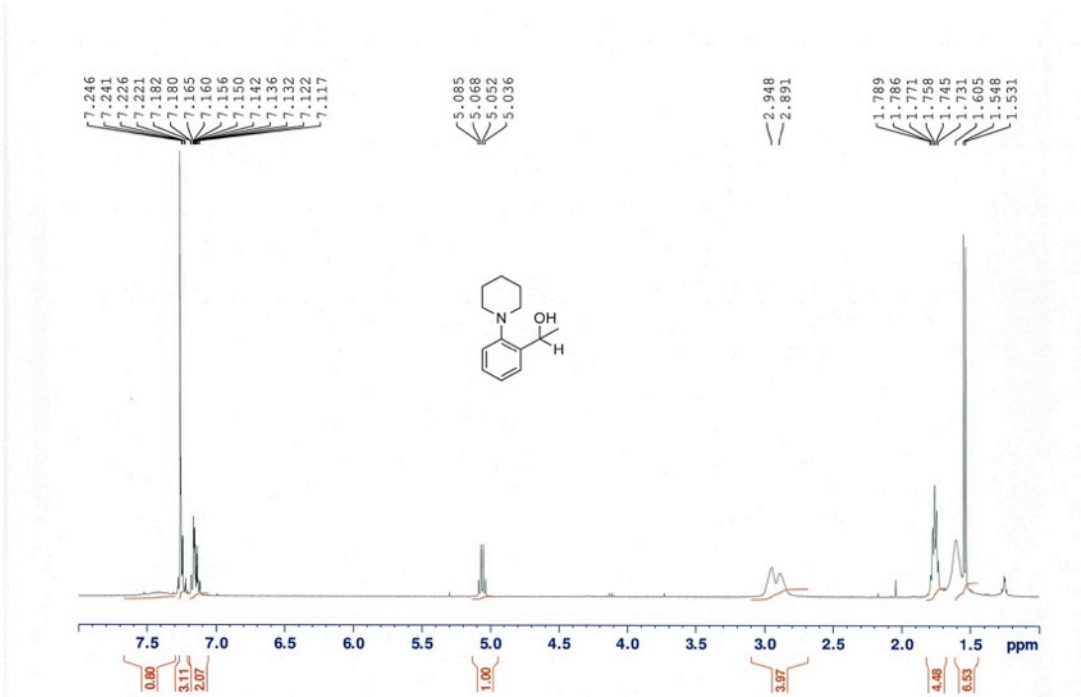
40.613
40.405
40.196
39.988
39.779
39.570
39.362
28.612
26.399
N
+
N-N
H
PF6
1n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.180
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7.160
7.156
7.150
7.142
7.136
7.132
7.122
7.117
5.085
5.068
5.052
5.036
2.948
2.891
1.789
1.786
1.771
1.758
1.745
1.731
1.605
1.548
1.531
OH
H
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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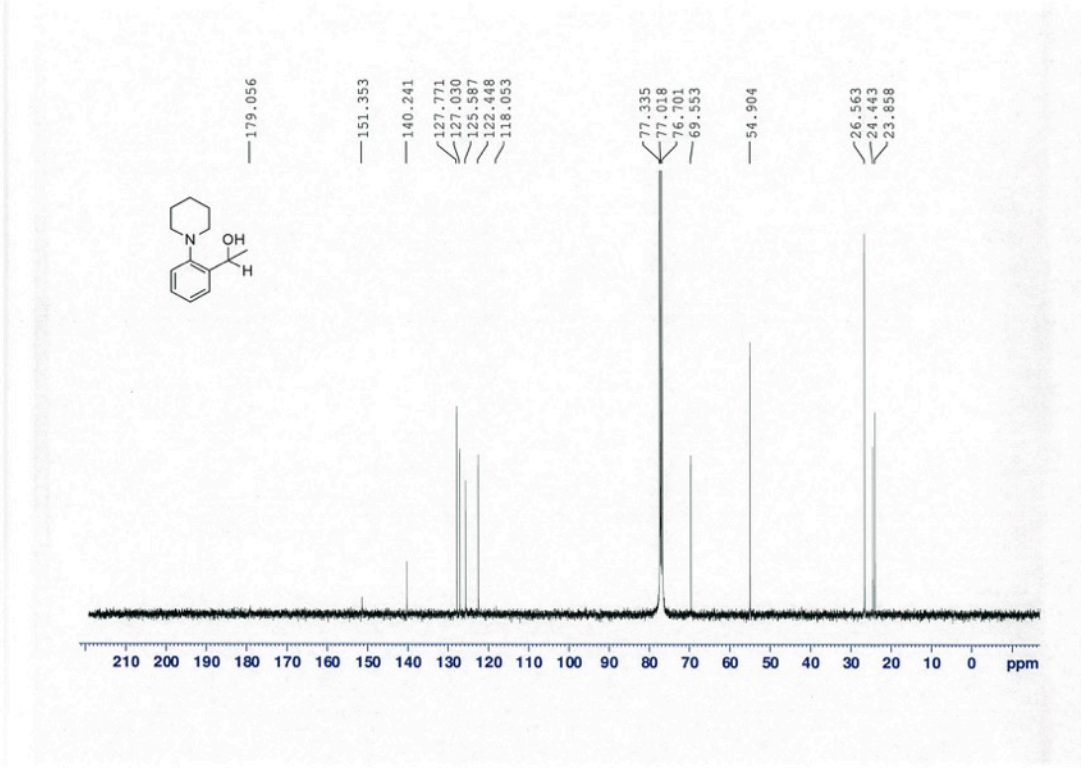
6.53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76.701
69.553
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26.563
24.443
23.858
OH
H
210
200
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180
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150
140
130
120
110
100
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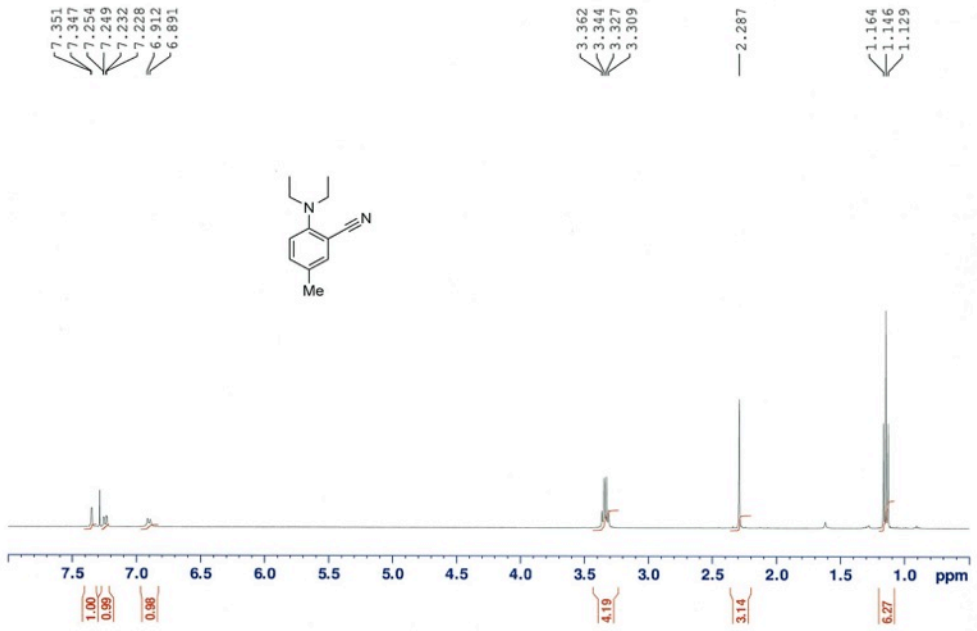
80
70
60
50
40
30
20
10
0
ppm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2.287
1.164
1.146
1.129
N
N
Me
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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1.5
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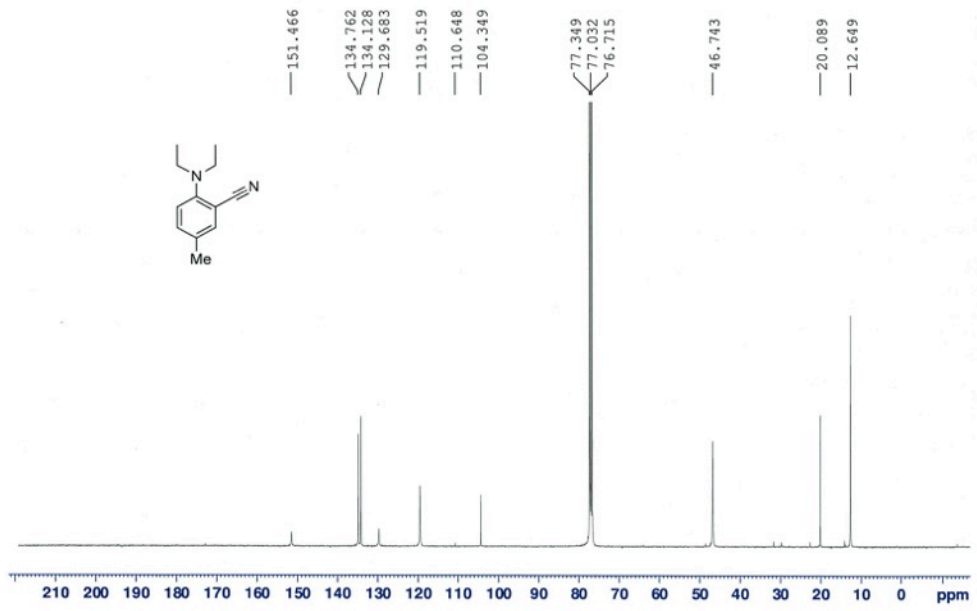
6.27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12.649
N
N
Me
210
200
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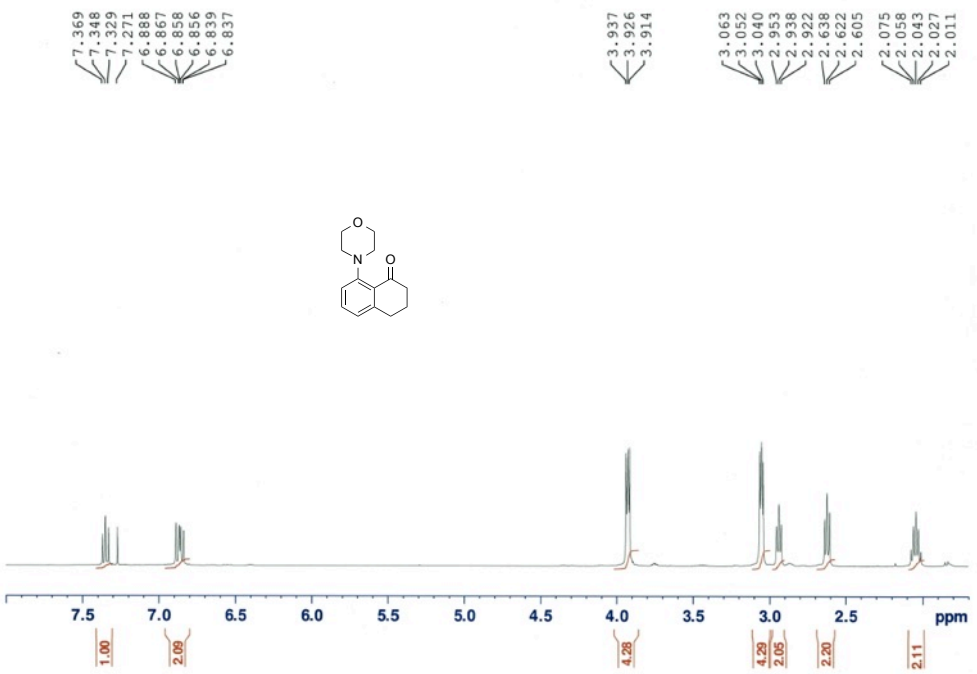
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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3.914
3.063
3.052
3.040
2.953
2.938
2.922
2.638
2.622
2.605
2.075
2.058
2.043
2.027
2.011
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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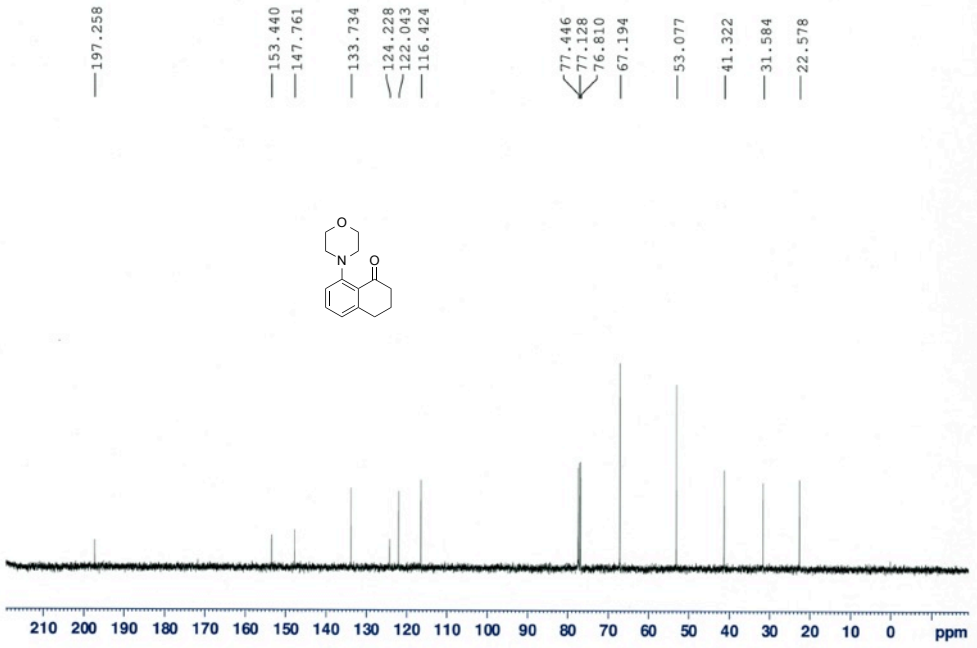
2.20
2.11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53.077
41.322
31.584
22.578
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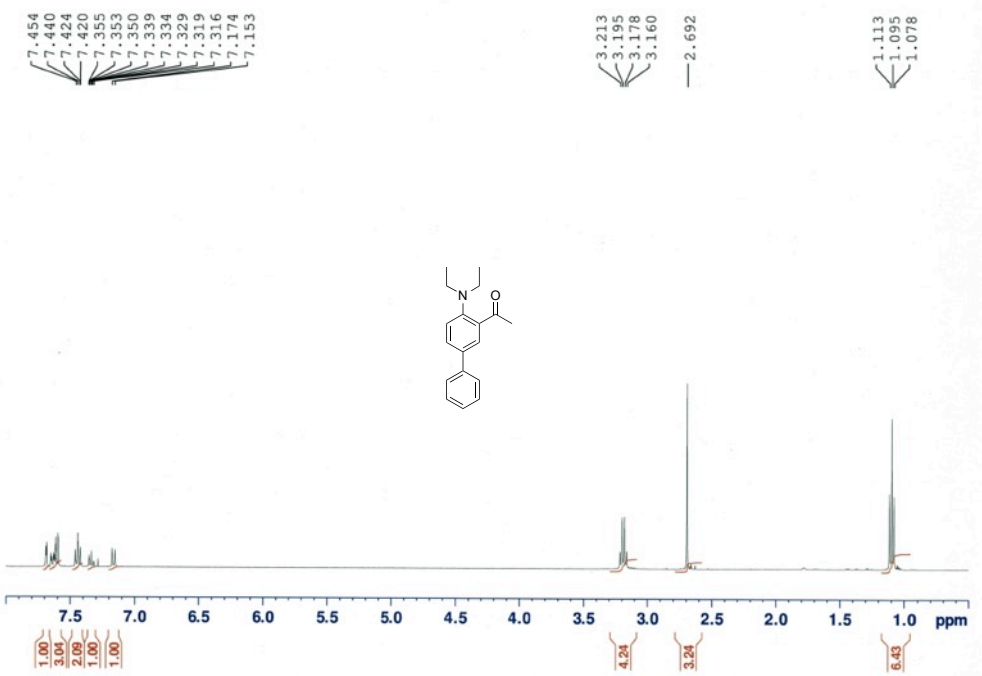
ppm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7.153
3.213
3.195
3.178
3.160
2.692
1.113
1.095
1.078
N
O
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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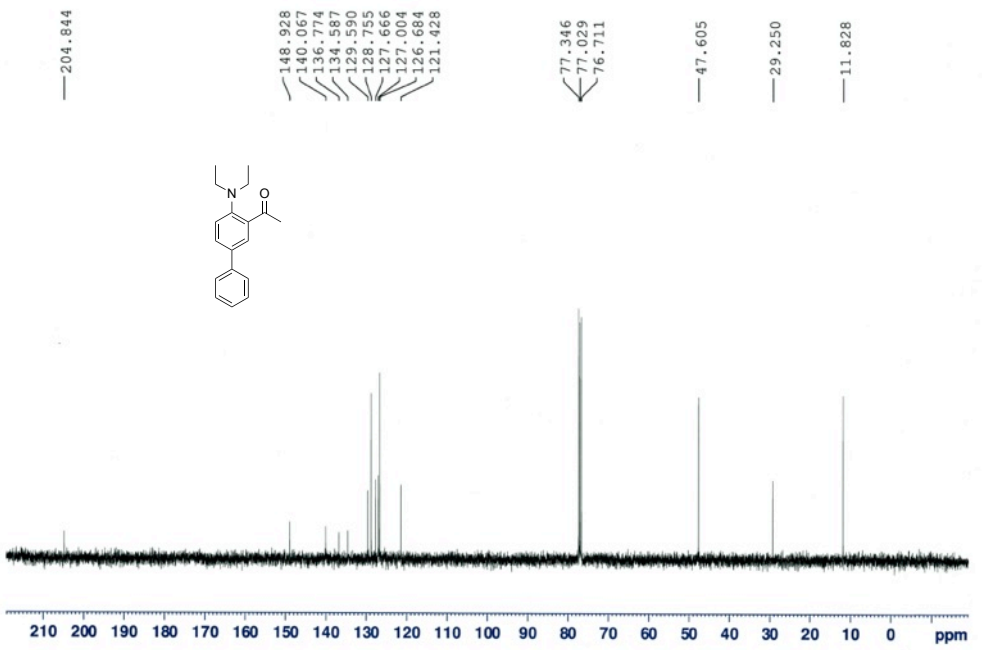
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77.029
76.711
47.605
29.250
11.828
N
O
210
200
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130
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60
50
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30
20
10
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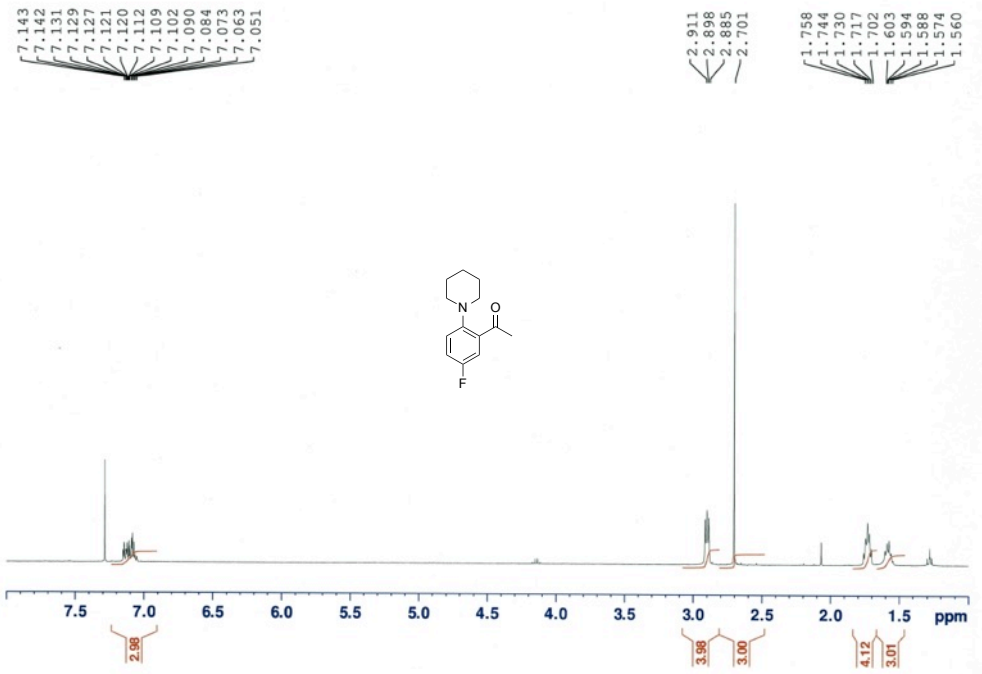
ppm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7.090
7.084
7.073
7.063
7.051
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2.701
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1.744
1.730
1.717
1.702
1.603
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1.588
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O
F
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6.5
6.0
5.5
5.0
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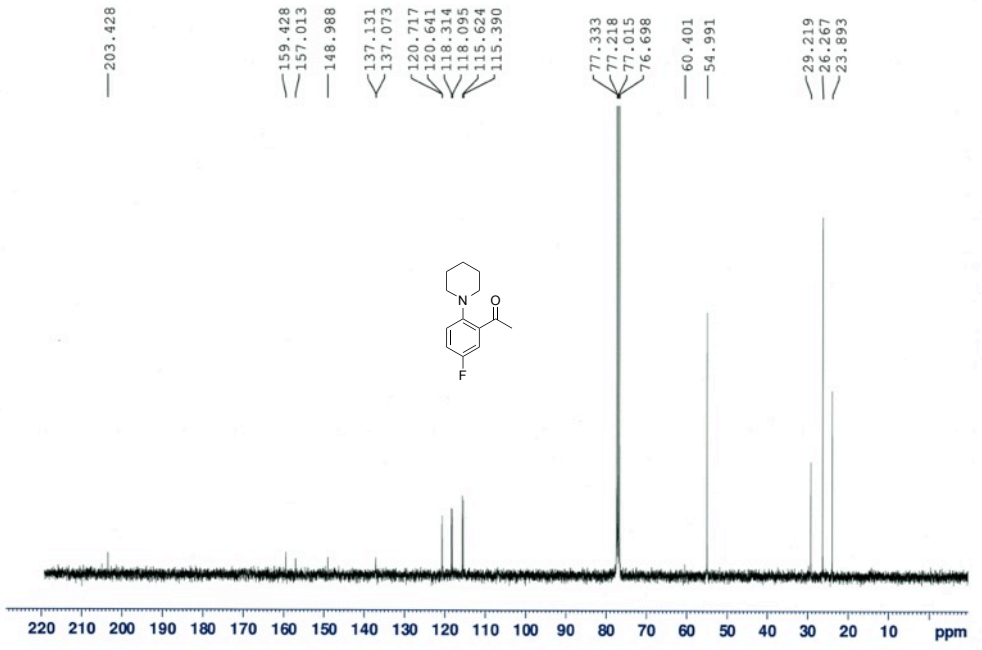
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115.390
77.333
77.218
77.015
76.698
60.401
54.991
29.219
26.267
23.893
N
O
F
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210
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150
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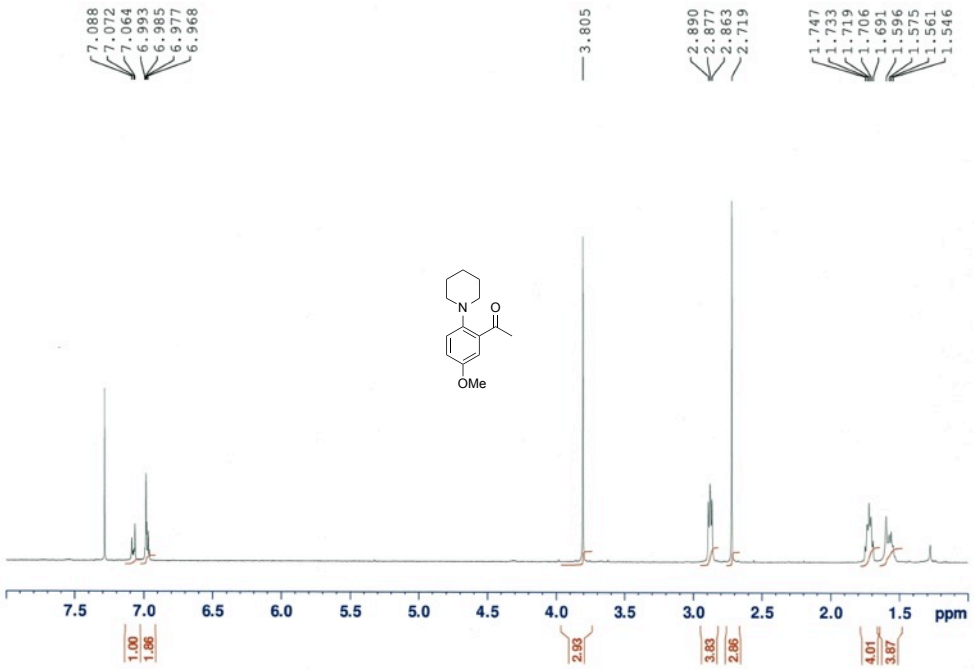
40
30
20
10
ppm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1.596
1.575
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1.546
N
O
OMe
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6.5
6.0
5.5
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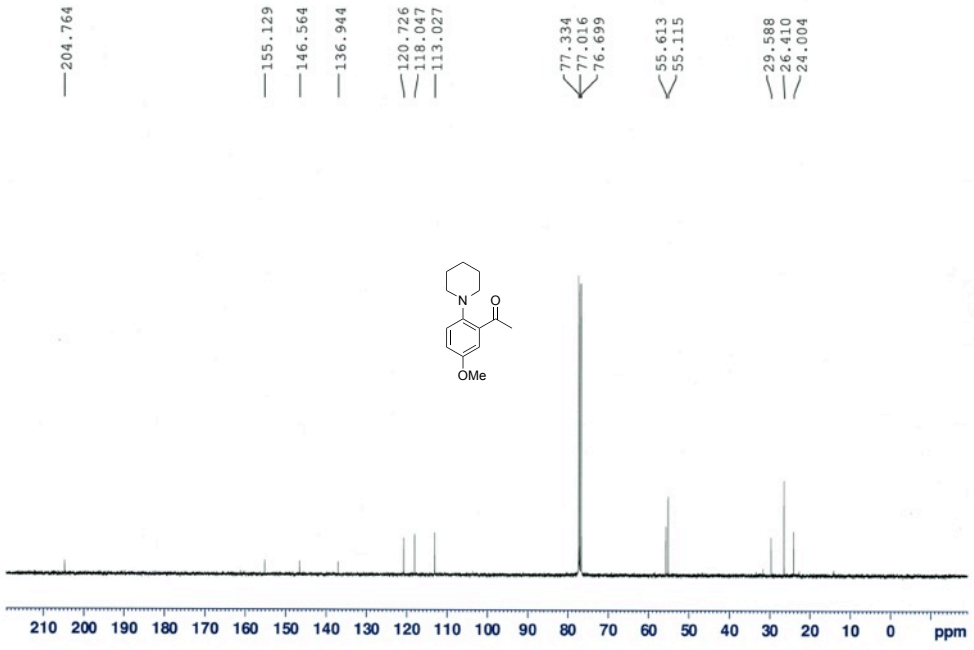
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76.699
55.613
55.115
29.588
26.410
24.004
N
O
OMe
210
200
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130
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60
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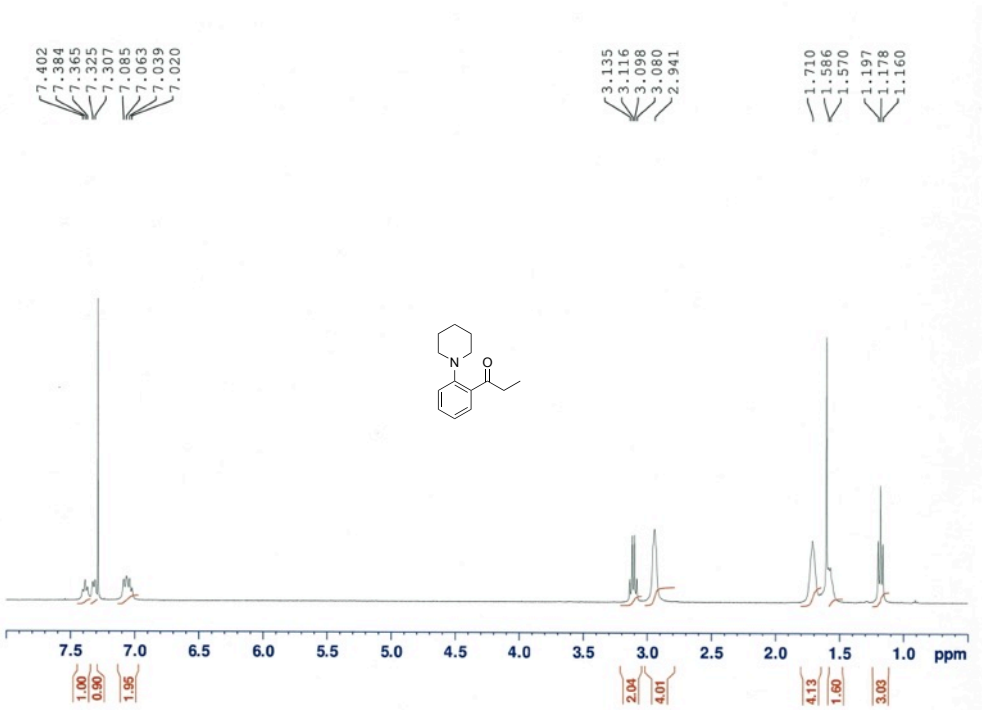
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7.039
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3.080
2.941
1.710
1.586
1.570
1.197
1.178
1.160
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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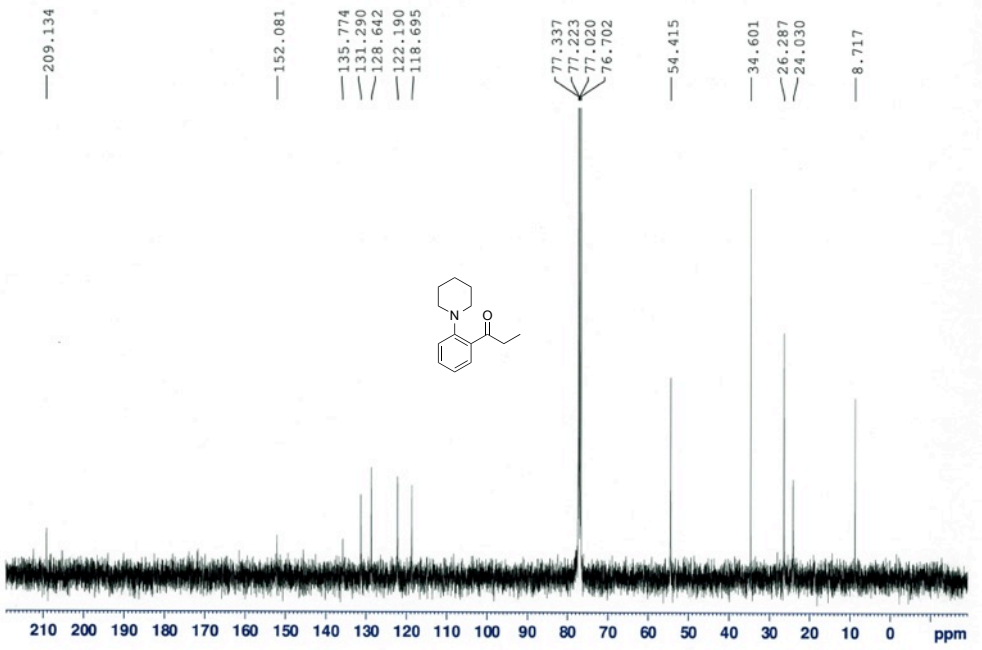
3.03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24.030
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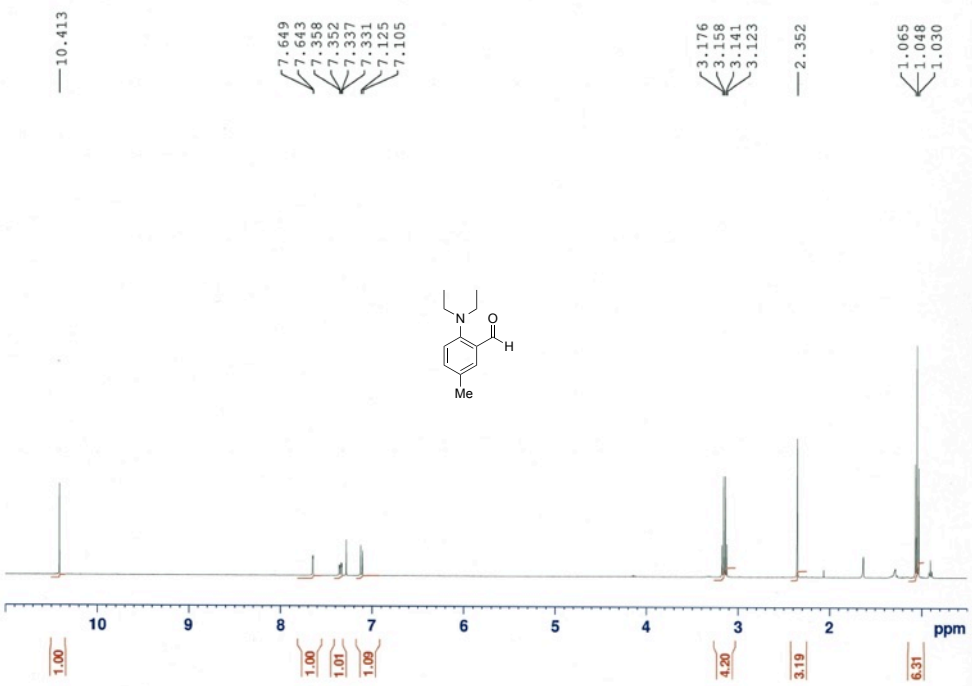
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2.352
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1.048
1.030
N
O
H
Me
10
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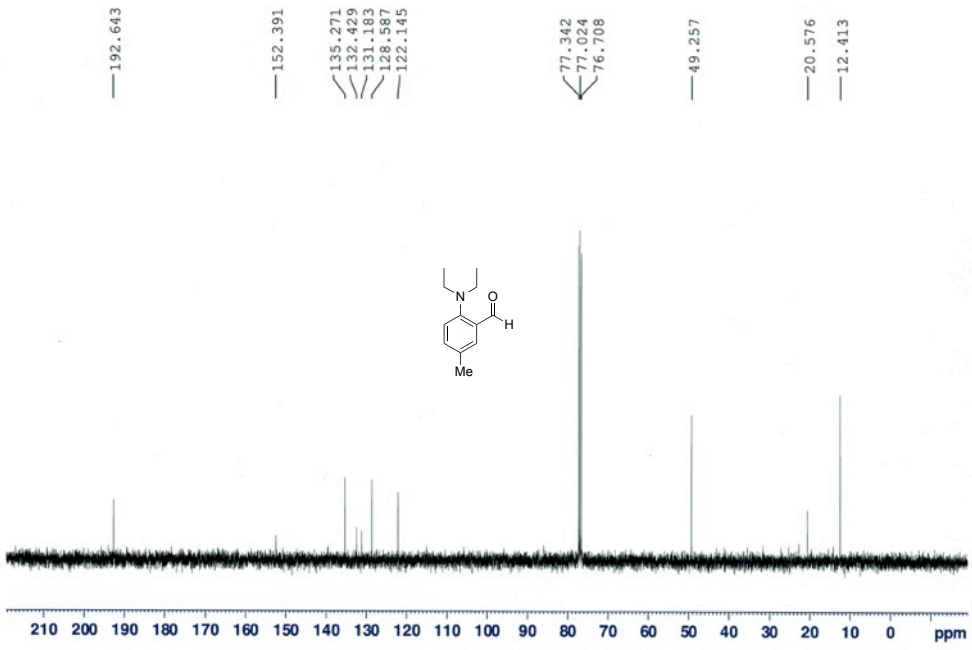
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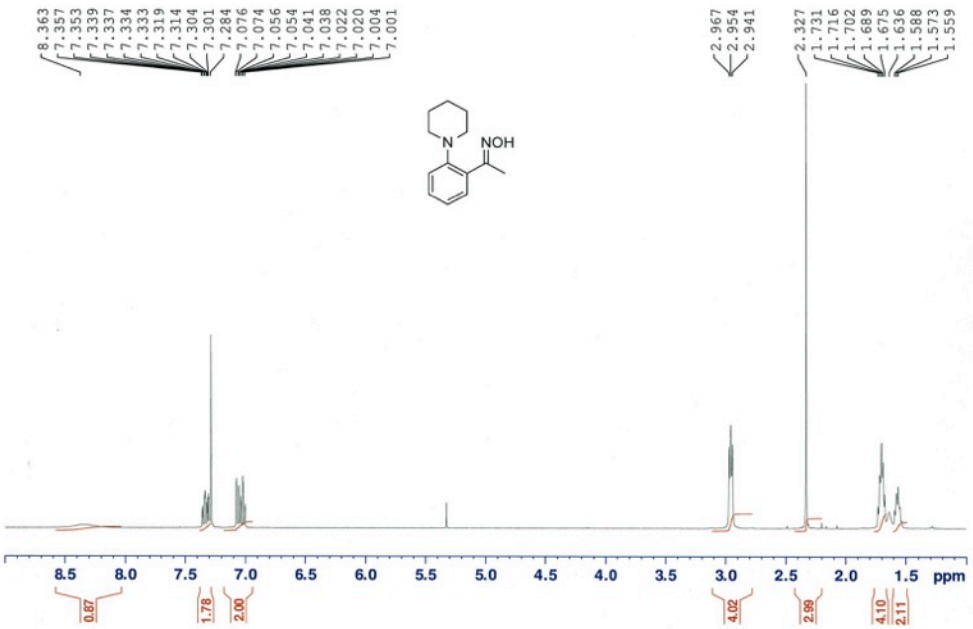
O
H
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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2.327
1.731
1.716
1.702
1.689
1.675
1.636
1.588
1.573
1.559
N
NOH
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
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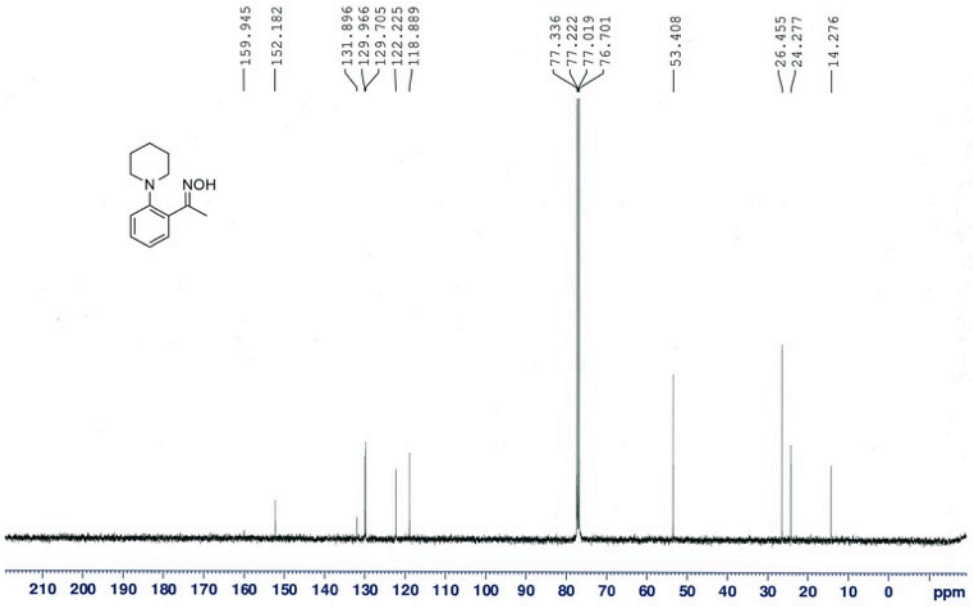
1.78
2.00
4.02
2.99
4.10
2.11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129.966
129.705
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77.336
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26.455
24.277
14.276
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NOH
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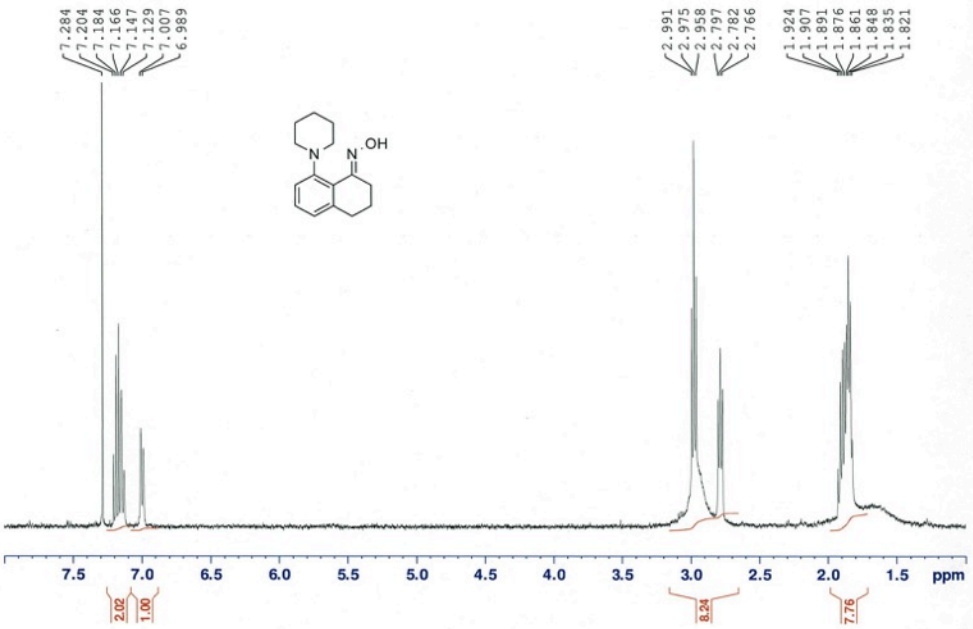
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7.184
7.166
7.147
7.129
7.007
6.989
2.991
2.975
2.958
2.797
2.782
2.766
1.924
1.907
1.891
1.876
1.861
1.848
1.835
1.821
N
N
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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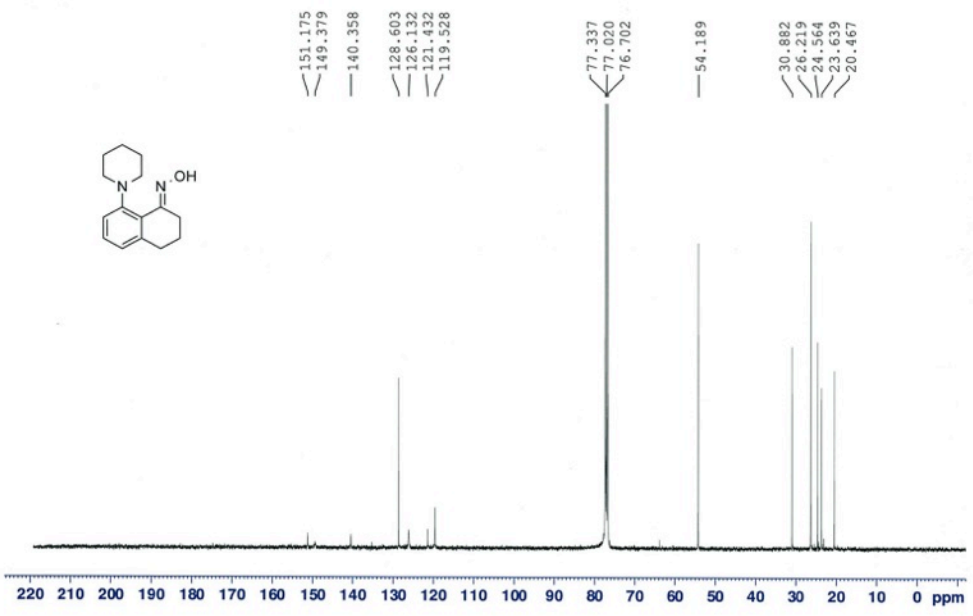
1.00
8.24
7.76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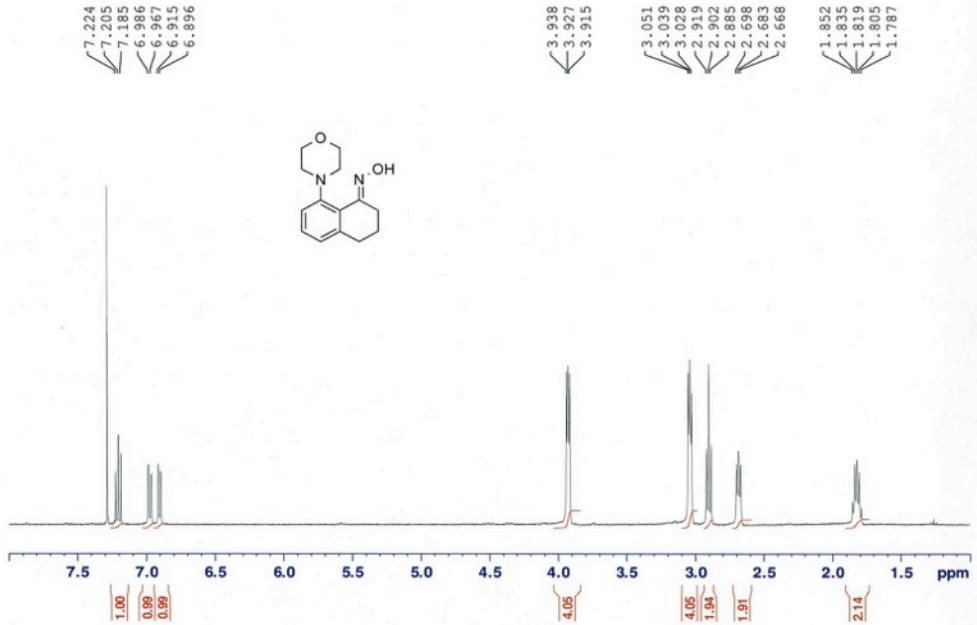
77.337
77.020
76.702
54.189
30.882
26.219
24.564
23.639
20.467
N
N
OH
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.205
7.185
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6.915
6.896
3.938
3.927
3.915
3.051
3.039
3.028
2.919
2.902
2.885
2.698
2.683
2.668
1.852
1.835
1.819
1.805
1.787
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.5
ppm
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0.99
4.05
4.05
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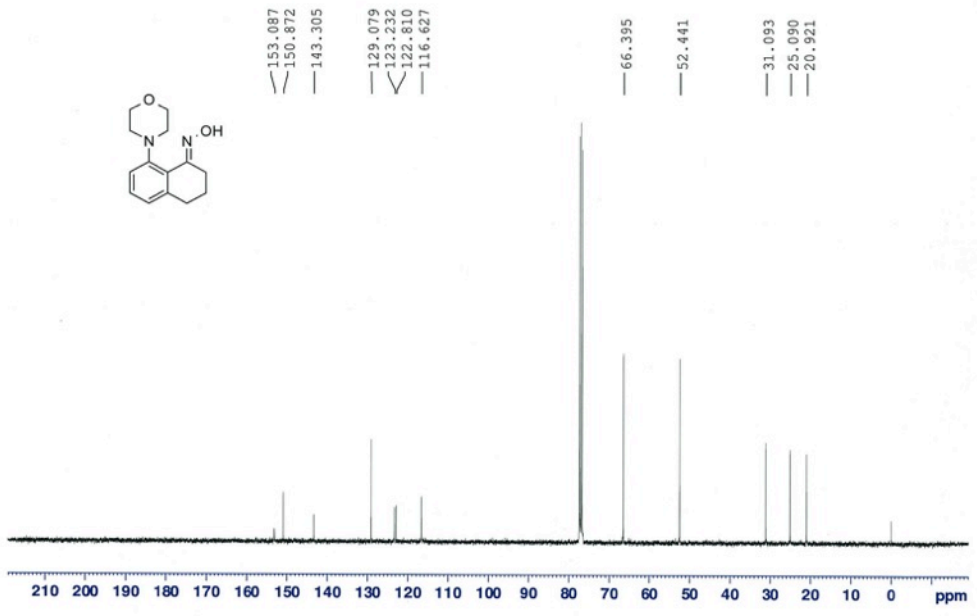
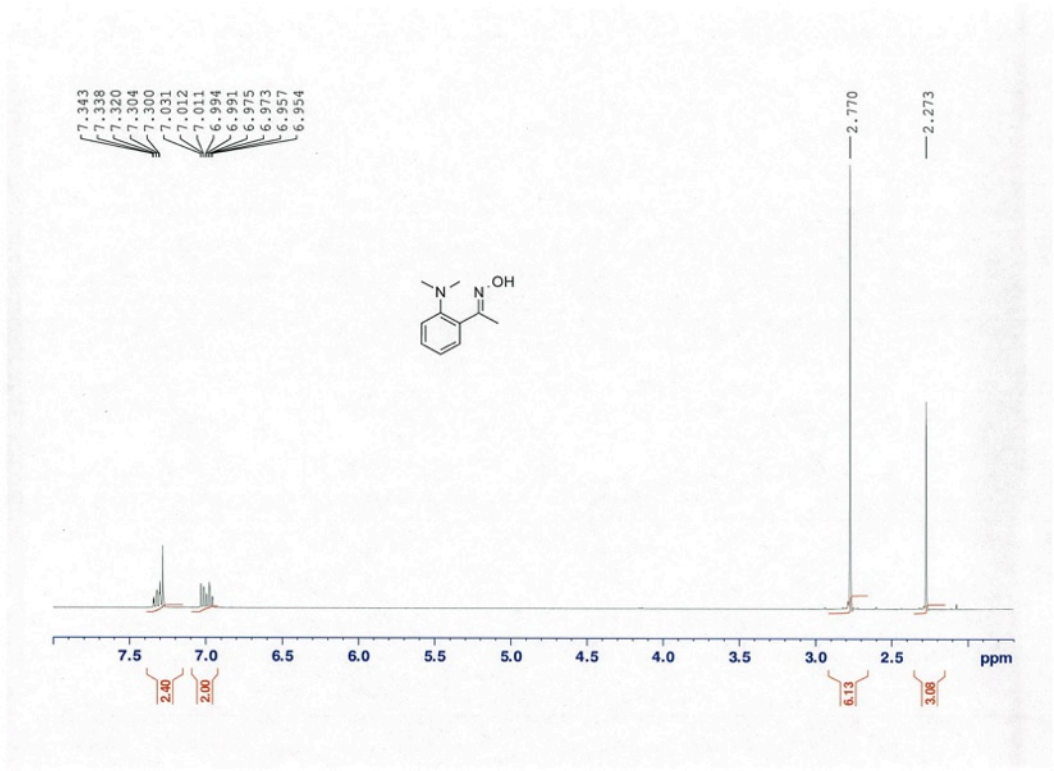
1.91
2.14


153.087
150.872
143.305
129.079
123.232
122.810
116.627
66.395
52.441
31.093
25.090
20.921
OH
210
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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7.338
7.320
7.304
7.300
7.031
7.012
7.011
6.994
6.991
6.975
6.973
6.957
6.954
2.770
2.273
OH
N
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
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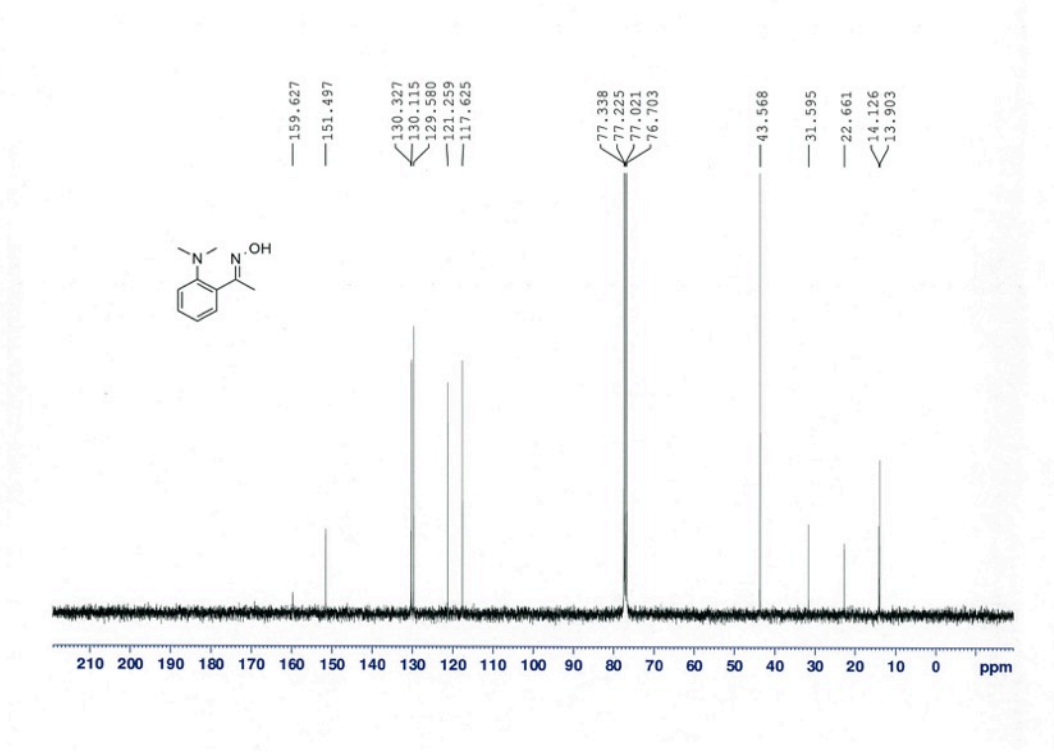
2.00
6.13
3.08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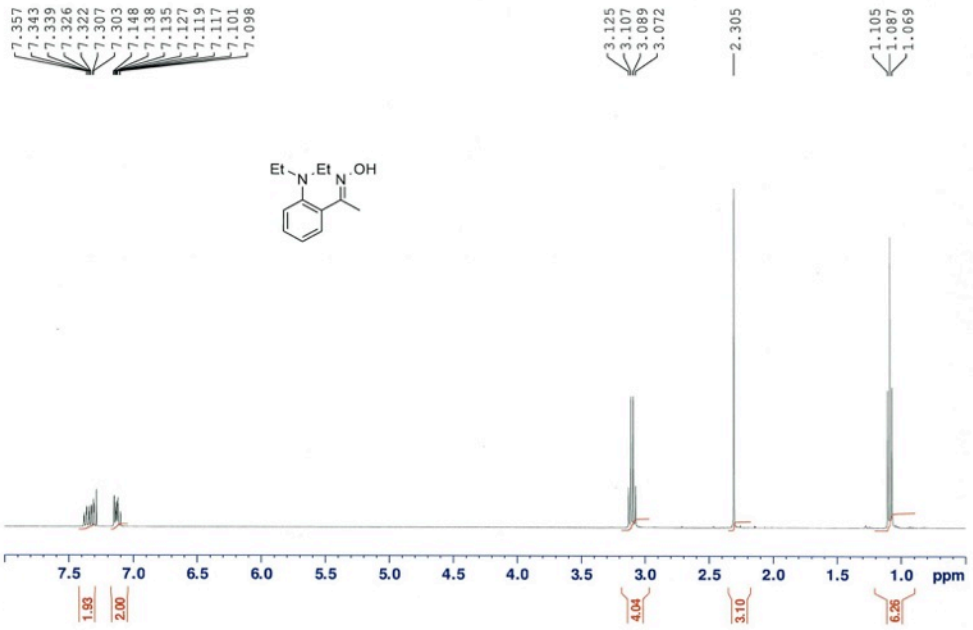
130.327
130.115
129.580
121.259
117.625
77.338
77.225
77.021
76.703
43.568
31.595
22.661
14.126
13.903
OH
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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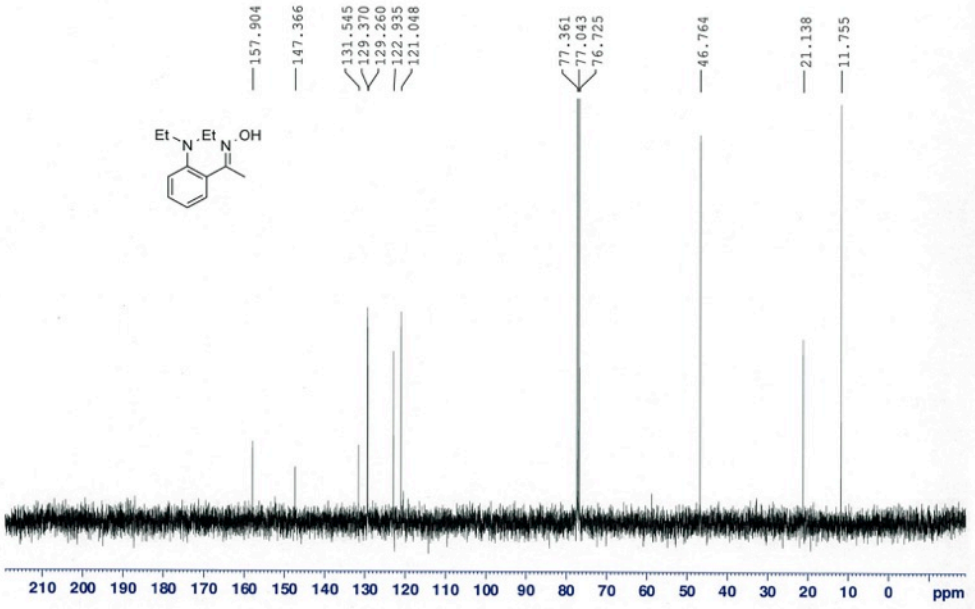
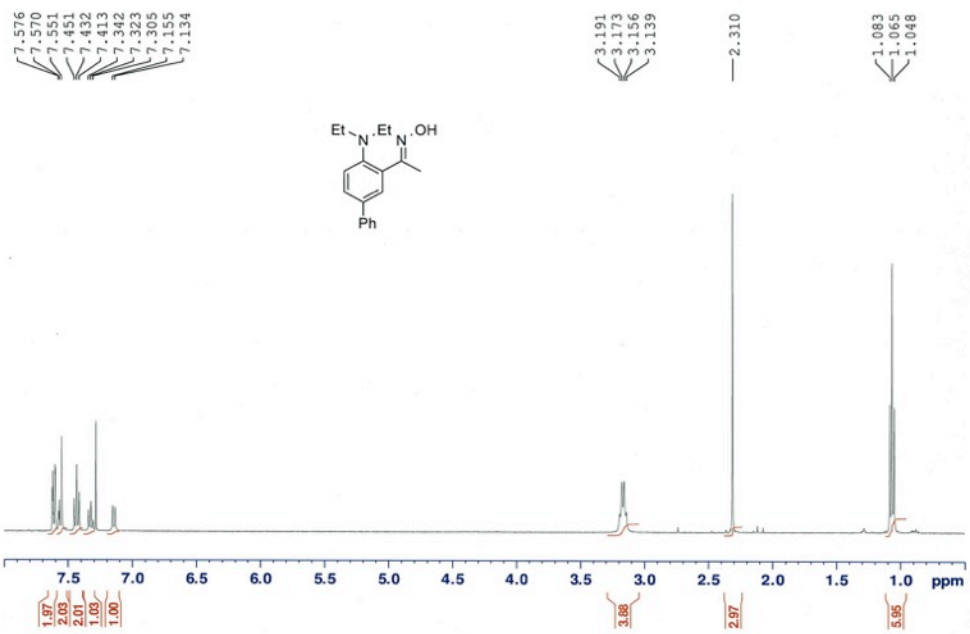
7.343
7.339
7.326
7.322
7.307
7.303
7.148
7.138
7.135
7.127
7.119
7.117
7.101
7.098
3.125
3.107
3.089
3.072
2.305
1.105
1.087
1.069
Et
N
Et
N
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.93
2.00
4.04
3.10
6.26


157.904
147.366
131.545
129.370
129.260
122.935
121.048
77.361
77.043
76.725
46.764
21.138
11.755
Et
N
Et
N
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.576
7.570
7.551
7.451
7.432
7.413
7.342
7.323
7.305
7.155
7.134
3.191
3.173
3.156
3.139
2.310
1.083
1.065
1.048
Et
N
Et
N
OH
Ph
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
ppm
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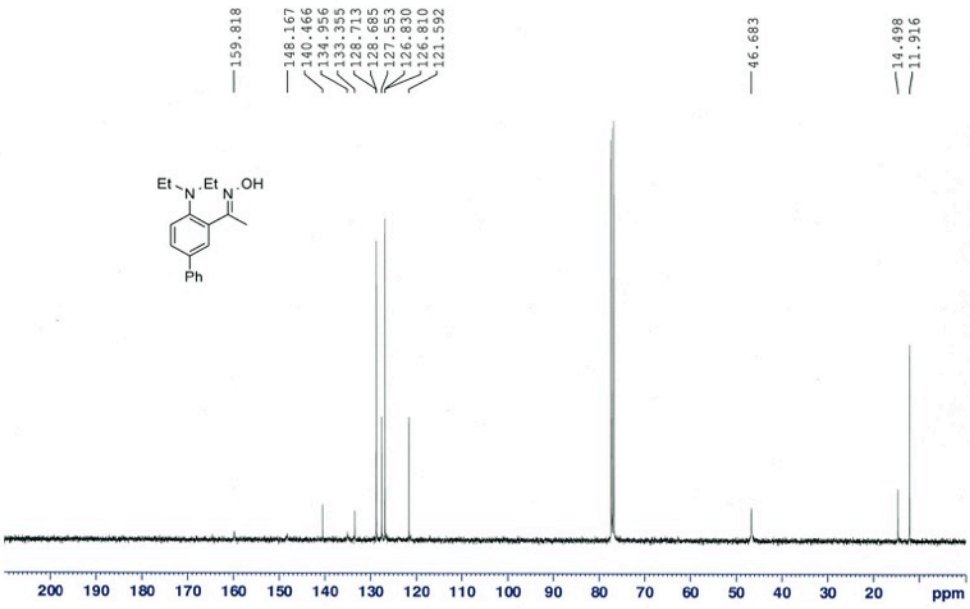
2.08
2.01
1.03
1.00
3.88
2.97
5.95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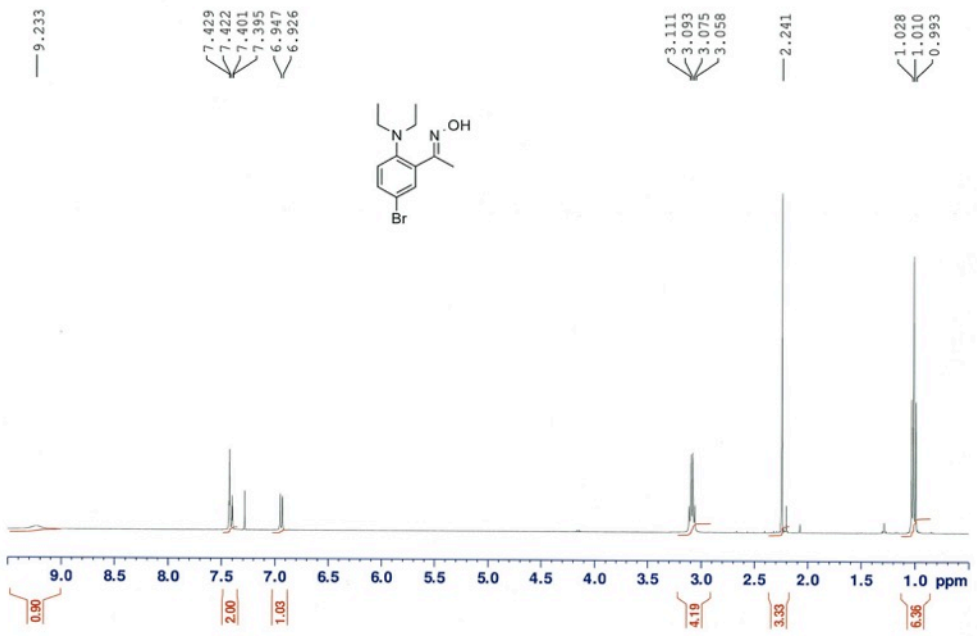
140.466
134.956
133.355
128.713
128.685
127.553
126.830
126.810
121.592
46.683
14.498
11.916
Et
N
Et
N
OH
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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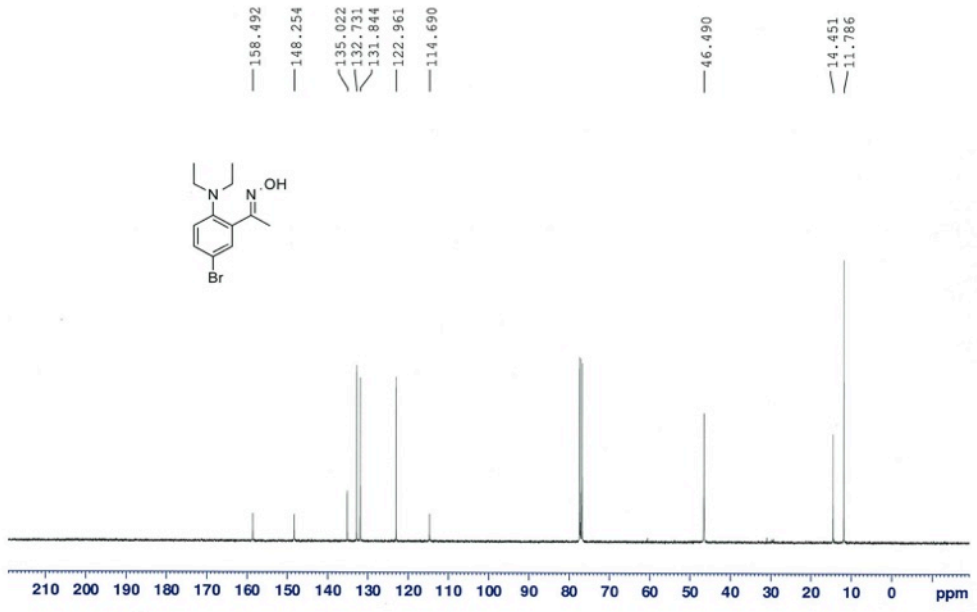
7.429
7.422
7.401
7.395
6.947
6.926
3.111
3.093
3.075
3.058
2.241
1.028
1.010
0.993
N
N
OH
Br
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.90
2.00
1.03
4.19
3.33
6.36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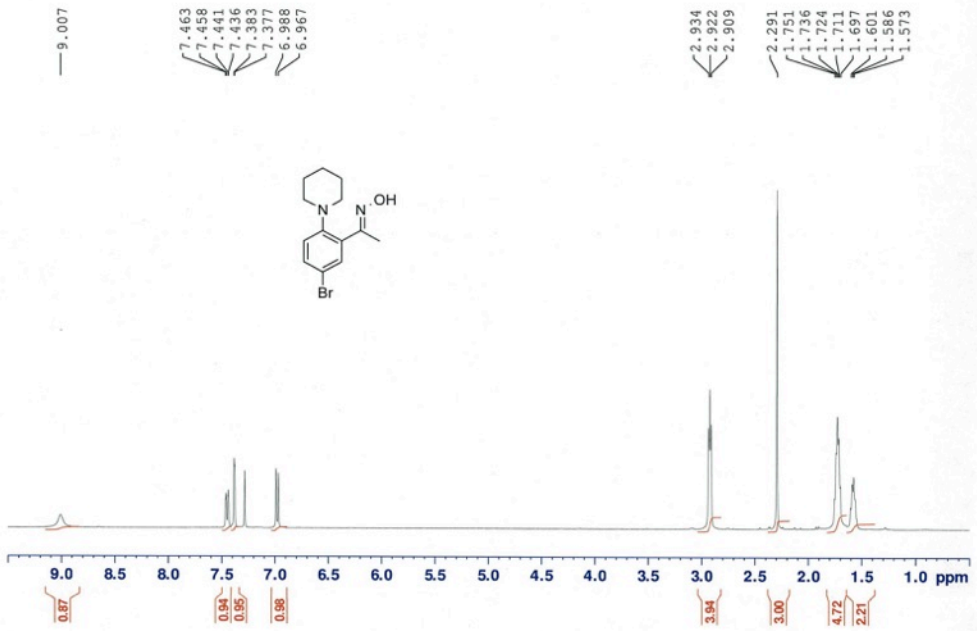
148.254
135.022
132.731
131.844
122.961
114.690
46.490
14.451
11.786
N
N
OH
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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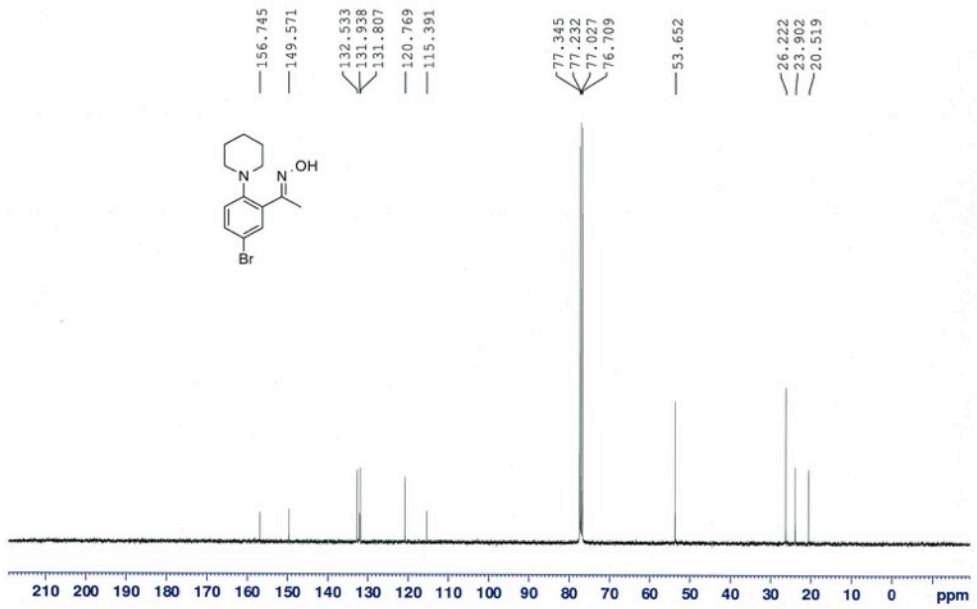
7.463
7.458
7.441
7.436
7.383
7.377
6.988
6.967
2.934
2.922
2.909
2.291
1.751
1.736
1.724
1.711
1.697
1.601
1.586
1.573
N
N
OH
Br
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.87
0.94
0.95
0.98
3.94
3.00
4.72
2.21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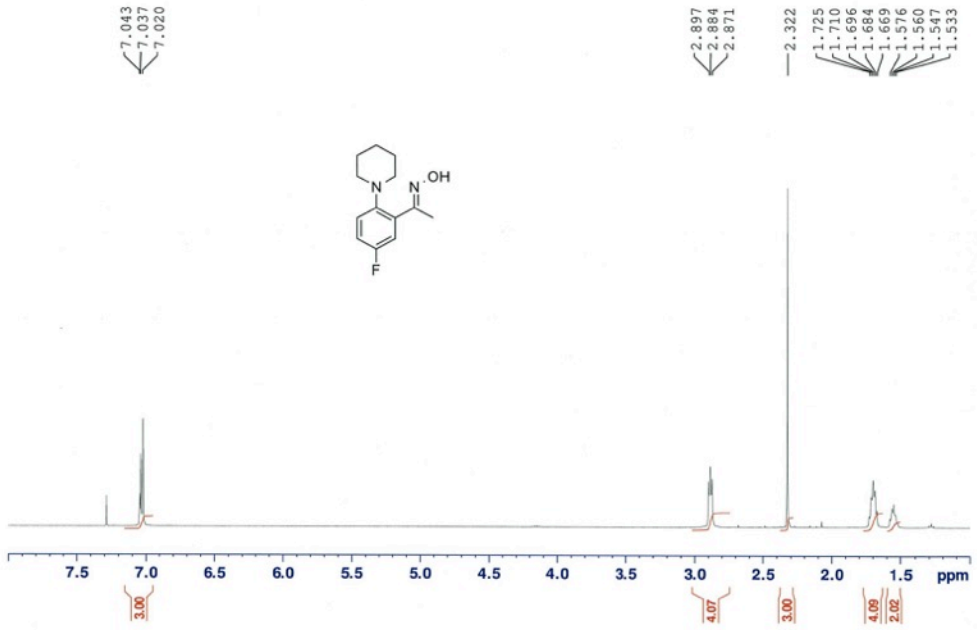
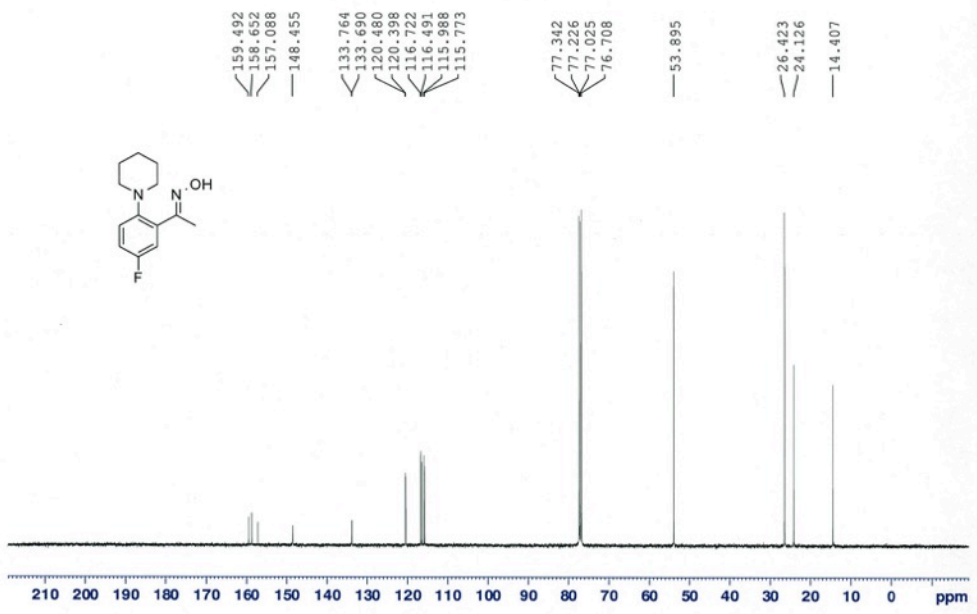
132.533
131.938
131.807
120.769
115.391
77.345
77.232
77.027
76.709
53.652
26.222
23.902
20.519
N
N
OH
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.043
7.037
7.020
2.897
2.884
2.871
2.322
1.725
1.710
1.696
1.684
1.669
1.576
1.560
1.547
1.533
N
OH
F
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
ppm
3.00
4.07
3.00
4.09
2.02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157.088
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133.764
133.690
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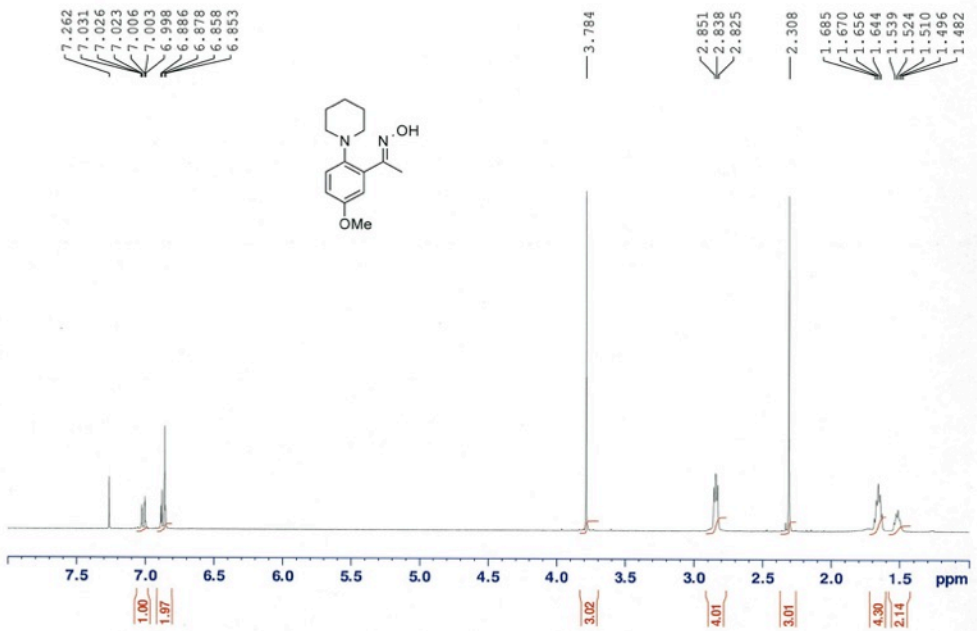
120.398
116.722
116.491
115.988
115.773
77.342
77.226
77.025
76.708
53.895
26.423
24.126
14.407
N
OH
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.003
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6.878
6.858
6.853
3.784
2.851
2.838
2.825
2.308
1.685
1.670
1.656
1.644
1.539
1.524
1.510
1.496
1.482
OH
N
N
OMe
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
ppm
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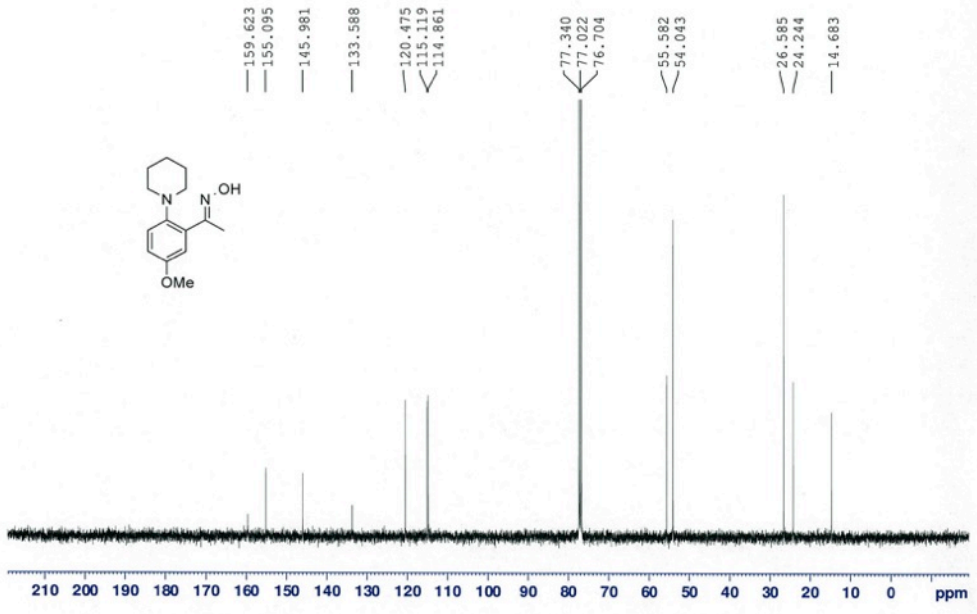
3.02
4.01
3.01
4.30
2.14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133.588
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115.119
114.861
77.340
77.022
76.704
55.582
54.043
26.585
24.244
14.683
OH
N
N
OMe
210
200
190
180
170
160
150
140
130
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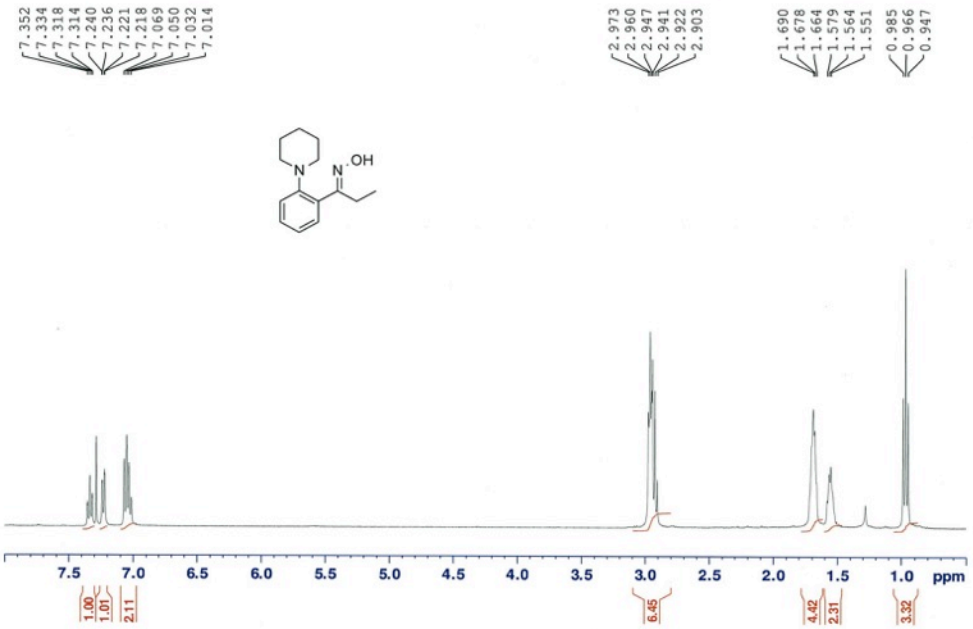
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.236
7.221
7.218
7.069
7.050
7.032
7.014
2.973
2.960
2.947
2.941
2.922
2.903
1.690
1.678
1.664
1.579
1.564
1.551
0.985
0.966
0.947
OH
N
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
ppm
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1.01
2.11
6.45
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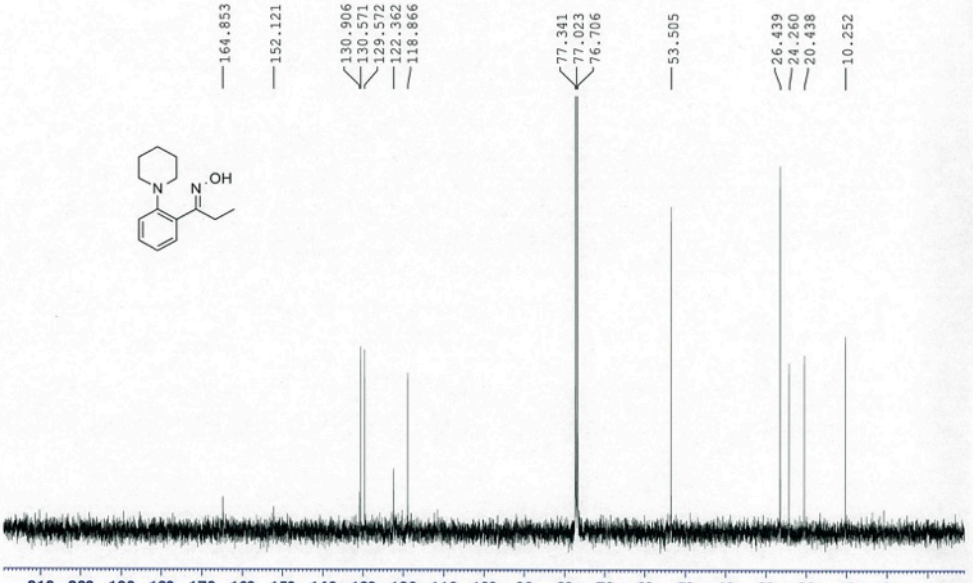
2.31
3.32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130.571
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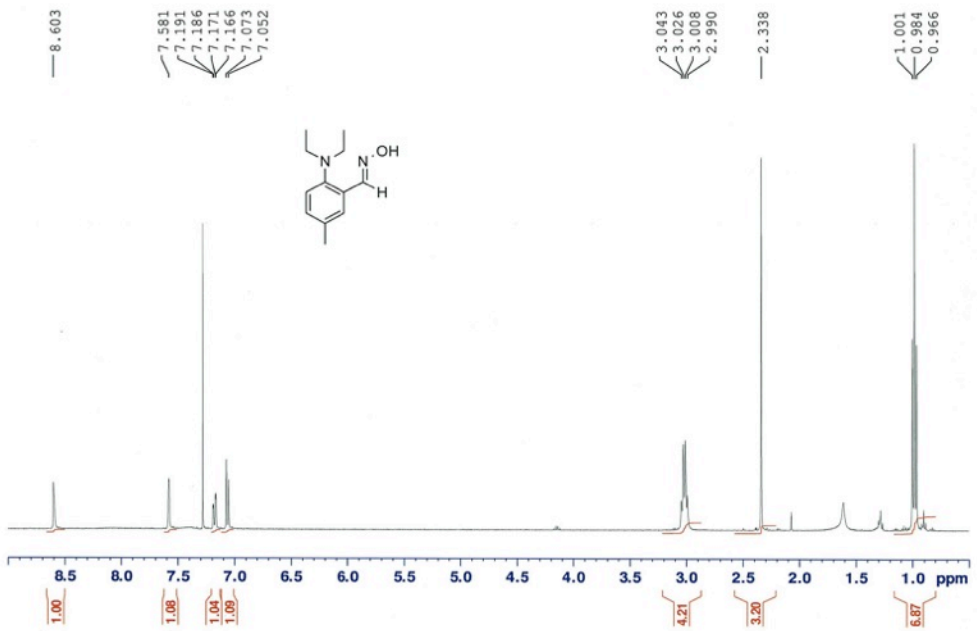
122.362
118.866
77.341
77.023
76.706
53.505
26.439
24.260
20.438
10.252
OH
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.186
7.171
7.166
7.073
7.052
3.043
3.026
3.008
2.990
2.338
1.001
0.984
0.966
OH
N
H
8.5 8.0 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 ppm
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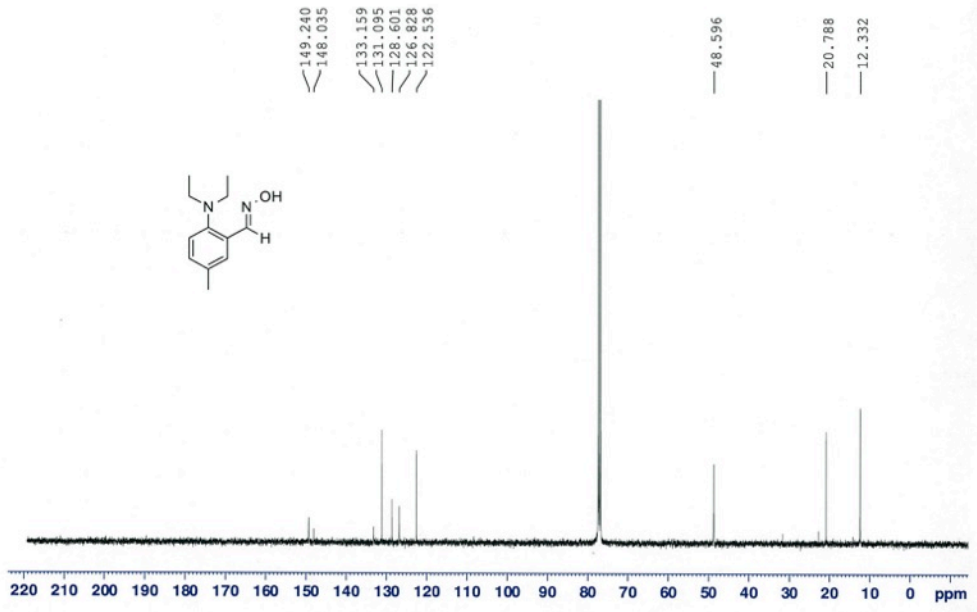
1.08
1.04
1.09
4.21
3.20
6.87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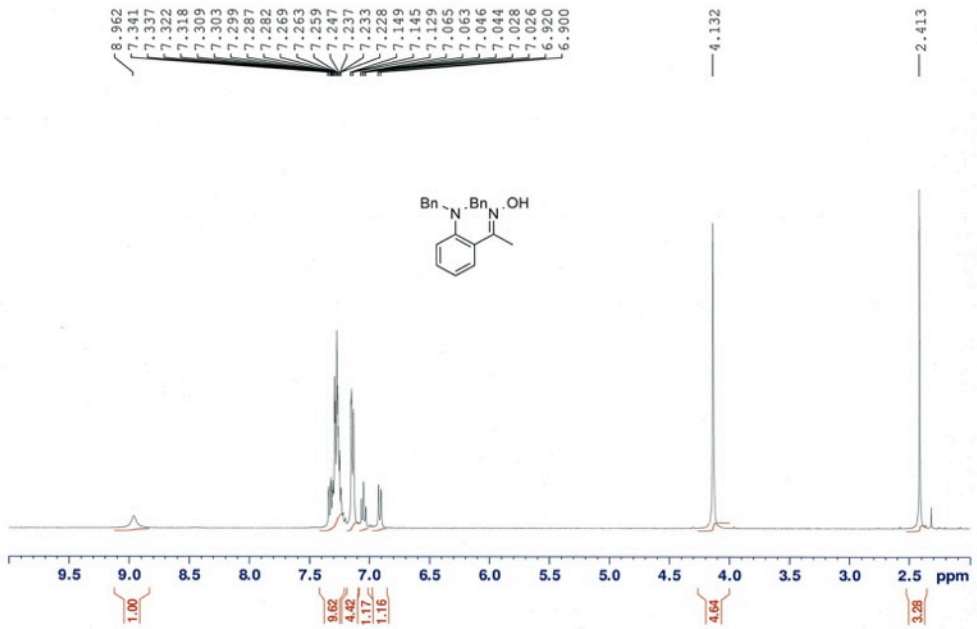
148.035
133.159
131.095
128.601
126.828
122.536
48.596
20.788
12.332
OH
N
H
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.299
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7.282
7.269
7.263
7.259
7.247
7.237
7.233
7.228
7.149
7.145
7.129
7.065
7.063
7.046
7.044
7.028
7.026
6.920
6.900
4.132
2.413
Bn
N
Bn
N
OH
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
ppm
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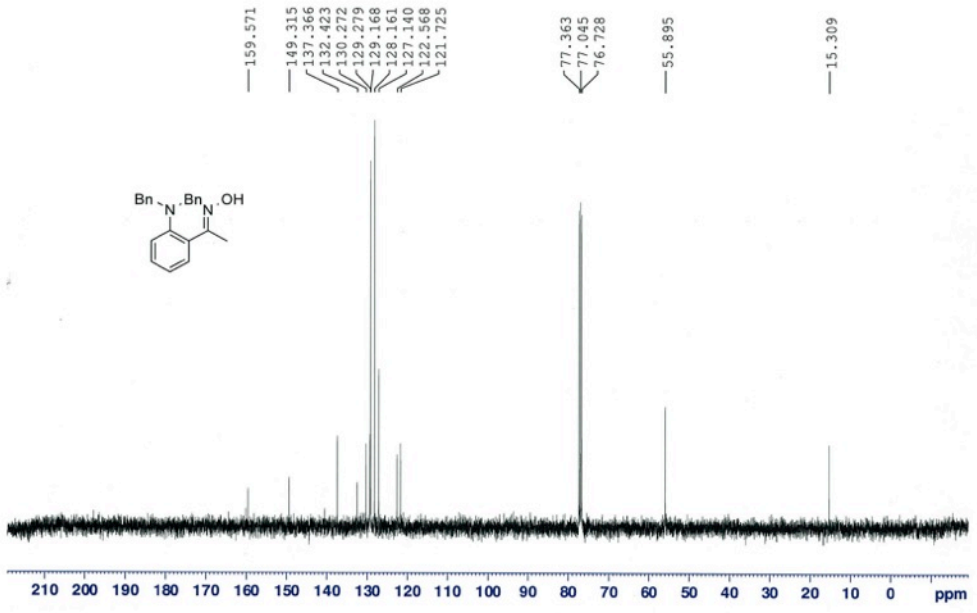
3.28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149.315
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128.161
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122.568
121.725
77.363
77.045
76.728
55.895
15.309
Bn
N
Bn
N
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

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