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Palladium-Catalyzed Dearomative Cyclization by Norbornene-Mediated Sequence: A Route to Spiroindolenine Derivatives

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Supporting Information

Content:

1. General considerations.

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90) are used. ^{1}H NMR spectra were recorded on a Bruker advance Ⅲ 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using TMS as internal standard. Data for 1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for 13C NMR is reported in terms of chemical shift (δ, ppm). IR spectra were obtained on a Perkin-Elmer Model 2000 FT-IR using KBr plates (thin film). High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II.

2. Preparation of starting materials.

Compounds **2** were prepared according to the known procedures[1]. All other starting materials were commercially available.

3-1. General procedure for the preparation of the product 3.

1 (0.1 mmol), **2** (0.15 mmol), $[Pd(C_3H_5)Cl]_2$ (5 mol %), tri(2-furyl)phosphine （**L2**） (10 mol %), K_2CO_3 (3.0 equiv.), norbornene (3.0 equiv.) were added to a sealed tube, MeCN (3 mL) was added via syringe. The mixture was flushed with N_2 and stirred at 90 ℃ until completion (monitored by TLC). After cooling at room temperature, the mixture was diluted with diethyl ether, washed with water, dried over magnesium sulfate and purified by flash chromatography on silica gel (Hex/EA: 20/1-10/1).

3-2. General procedure for the preparation of the products 3aa, 3oo, 3mm.

To a solution of indolenine derivative (0.2 mmol, 1.0 equiv.) in MeOH (4.0 mL) at 0 ℃ was added $NaBH_3CN$ (12.8 mg, 0.2 mmol). The reaction mixture was stirred at room temperature until completion (monitored by TLC). Then saturated $NaHCO_3$ (2.0 mL) was added and concentrated in vacuo. The mixture was extracted with ethyl acetate and dried with Na_2SO_4. The residue was purified by silica gel column chromatography to afford the desired product (Hex/EA: 5/1-3/1).

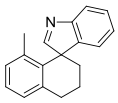
3-3. General procedure for the preparation of the product 3aa'.

To a solution of indolenine derivative **3a** (0.2 mmol, 1.0 equiv.) in MeOH (4.0 mL) at 0 ℃ was added $NaBH_3CN$ (12.8 mg, 0.2 mmol). The reaction mixture was stirred at room temperature until completion (monitored by TLC). Then saturated $NaHCO_3$ (2.0 mL) was added and concentrated in vacuo. The mixture was extracted with ethyl acetate and dried with Na_2SO_4. Then, the mixture was concentrated in vacuo. CH_2Cl_2 (4.0 mL) was added and the mixture was cooled to 0 ℃, after that Et_3N (111 μL, 0.8 mmol), $(CH_3CO)_2O$ (38 μL, 0.4 mmol) were added in sequence. The reaction mixture was stirred at room temperature until completion (monitored by TLC). Then saturated $NaHCO_3$ (2.0 mL) was added. The mixture was extracted with CH_2Cl_2 and dried with Na_2SO_4. The mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the desired product (Hex/EA: 5/1-3/1).

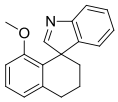
3-4. General procedure for the preparation of the product 3dd.

A carousel reaction tube under nitrogen atmosphere was charged with Xphos (0.004 mmol, 2 mol %), $Pd_2(dba)_3$ (0.002 mmol, 1 mol %), Li^{t}OBu (0.44 mmol), tosylhydrazone (0.2 mmol) and dioxane (1.2 mL). After 1 minute, the indolenine derivative **3d** (0.2 mmol) was added. The system was heated at 90 ℃ with stirring and reflux. The reaction was monitored by TLC analysis. When the reaction was completed, the crude reaction mixture was allowed to cool to room temperature, taken up in dry pentane, hexanes or dichloromethane (5 mL), and filtered through celite. The solvents were evaporated under reduced pressure, the residue was purified by flash chromatography on silica gel to afford pure product **3dd**.

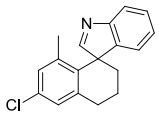
4. Spectra Data.



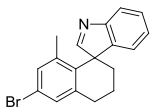
8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3a): solid; m.p. 100-102 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.22 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.39-7.35 (m, 1H), 7.22-7.14 (m, 2H), 7.09 (d, *J* = 4.8 Hz, 2H), 6.83 (t, *J* = 4.4 Hz, 1H), 3.10-2.94 (m, 2H), 2.12-2.02 (m, 2H), 2.00-1.92 (m, 1H), 1.50-1.46 (m, 1H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.8, 154.6, 145.5, 138.7, 138.2, 130.8, 129.3, 128.0, 127.7, 127.0, 126.3, 122.4, 121.6, 61.7, 34.4, 31.0, 20.7, 18.5. IR: 3399, 2934, 2868, 1544, 1458, 944, 776,755. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{18}N$: 248.1434; Found, 248.1437.



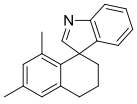
8'-methoxy-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3b): solid; m.p. 114-116 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.11 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.34-7.29 (m, 1H), 7.17-7.11 (m, 3H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 3.27 (s, 3H), 3.08-2.92 (m, 2H), 2.15-1.94 (m, 3H), 1.45-1.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.2, 157.9, 155.0, 145.8, 139.7, 127.7, 127.2, 125.5, 122.4, 122.1, 121.7, 120.7, 108.8, 58.6, 55.2, 32.0, 29.9, 20.3. IR: 3339, 2929, 2853, 1579, 1467, 1261, 1105, 1015, 774, 755,740. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{18}NO$: 264.1383; Found, 264.1380.



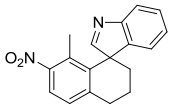
6'-chloro-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3c): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.18 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 6.8 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.13-7.09 (m, 2H), 6.82 (s, 1H), 3.02-2.97 (m, 2H), 2.07-1.93 (m, 3H), 1.50-1.47 (m, 1H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.2, 154.5, 145.0, 140.5, 140.1, 132.5, 129.4, 129.1, 128.0, 127.5, 126.5, 122.3, 121.8, 61.2, 34.2, 31.0, 20.4, 18.3. IR: 3282, 2933, 2869, 1582, 1462, 1265, 1007, 861, 751,739. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{17}ClN$: 282.1044; Found, 282.1047.



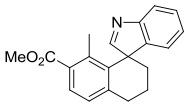
6'-bromo-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3d): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.18 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 3.02-2.97 (m, 2H), 2.06-1.92 (m, 3H), 1.49 (dd, *J* = 9.2 Hz, *J* = 3.2 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.0, 154.6, 145.0, 140.9, 140.4, 132.0, 130.6, 130.0, 128.0, 126.5, 122.3, 121.8, 120.9, 61.3, 34.2, 30.9, 20.4, 18.3. IR: 3291, 2928, 2853, 1575, 1461, 1265, 1015, 953, 857, 752. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{17}BrN$: 326.0539; Found, 326.0542.



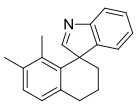
6',8'-dimethyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3e): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.21 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.39-7.35 (m, 1H), 7.22-7.15 (m, 2H), 6.93 (s, 1H), 6.67 (s, 1H), 3.06-2.93 (m, 2H), 2.26 (s, 3H), 2.08-1.93 (m, 3H), 1.51-1.46 (m, 1H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.1, 154.6, 145.7, 138.7, 138.1, 136.6, 130.3, 128.6, 127.7, 126.3, 122.4, 121.6, 61.5, 34.5, 31.0, 20.8, 20.7, 18.4. IR: 3298, 2930, 1611, 1545, 1474, 1450, 1014, 854, 753, 581. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{20}N$: 262.1590; Found, 262.1588.



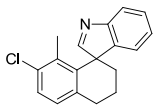
8'-methyl-7'-nitro-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3f): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8. 27 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.44-7.40 (m, 1H), 7.26-7.21 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 3.17-3.03 (m, 2H), 2.12-1.97 (m, 3H), 1.46-1.42 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.8, 154.3, 150.6, 144.7, 143.3, 133.9, 132.0, 128.4, 128.3, 126.8, 122.3, 122.3, 122.2, 61.8, 34.5, 31.3, 20.0, 13.2. IR: 3303, 2955, 2925, 2853, 1736, 1524, 1460, 1377, 1018, 742. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{17}N_2O_2$: 293.1285; Found, 293.1281.



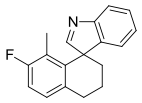
methyl 8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene]-7'-carboxylate (3g): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8. 27 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.41-7.37 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.15-7.11 (m, 2H), 3.80 (s, 3H), 3.12-2.99 (m, 2H), 2.09-1.92 (m, 3H), 1.56 (s, 3H), 1.40-1.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.0, 169.1, 154.2, 145.3, 142.2, 138.9, 132.7, 130.8, 128.2, 127.9, 127.6, 126.4, 122.3, 122.0, 61.9, 51.9, 34.8, 31.3, 20.1, 15.0. IR: 3322, 2931, 1721, 1594, 1455, 1435, 1264, 776, 738, 703. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{20}H_{20}NO_2$: 306.1489; Found, 306.1490.



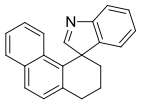
7',8'-dimethyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3h): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8. 28 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.40-7.36 (m, 1H), 7.22-7.15 (m, 2H), 7.03 (dd, *J* = 12.4 Hz, *J* = 8.0 Hz, 2H), 3.06-2.94 (m, 2H), 2.12 (s, 3H), 2.09-2.02 (m, 2H), 1.99-1.90 (m, 1H), 1.39-1.35 (m, 1H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 180.0, 154.3, 146.3, 136.7, 136.3, 135.1, 130.9, 129.1, 127.7, 127.5, 126.2, 122.4, 121.9, 62.2, 35.0, 31.0, 20.8, 20.6, 14.1. IR: 3291, 2931, 1544, 1451, 1266, 1096, 806, 752, 703. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{20}N$: 262.1590; Found, 262.1592.



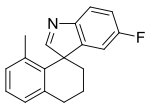
7'-chloro-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3i): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8. 25 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.26-7.20 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 3.07-2.93 (m, 2H), 2.07-1.94 (m, 3H), 1.46 (s, 3H), 1.42-1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.8, 154.3, 145.5, 137.4, 135.8, 133.1, 133.0, 128.7, 128.2, 128.0, 126.5, 122.3, 122.0, 62.2, 34.6, 30.8, 20.3, 14.8. IR: 3309, 2929, 2854, 1727, 1543, 1459, 1265, 1047, 807, 744, 584. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{17}ClN$: 282.1044; Found, 282.1041.



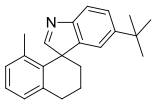
7'-fluoro-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3j): solid; m.p. 100-102 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8. 23 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 3.04-2.92 (m, 2H), 2.07-1.93 (m, 3H), 1.48-1.43 (m, 1H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.4, 160.6, 158.2, 154.4, 145.3, 134.0, 134.0, 132.7, 132.7, 128.4, 128.3, 128.0, 126.5, 124.7, 124.6, 122.3, 121.9, 114.2, 114.0, 61.9, 61.8, 34.3, 30.6, 20.7, 8.7, 8.6. IR: 3285, 2938, 1545, 1477, 1452, 1245, 1188, 911, 809, 734. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{17}NF$: 266.1340; Found, 266.1337.



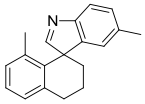
2',3'-dihydro-1'H-spiro[indole-3,4'-phenanthrene] (3k): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.39 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 8.4 Hz, 2H), 7.43-7.39 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.18-7.15 (m, 2H), 7.07-7.03 (m, 1H), 6.58 (d, *J* = 8.8 Hz, 1H), 3.19-3.16 (m, 2H), 2.22-2.12 (m, 2H), 2.09-2.01 (m, 1H), 1.47-1.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 181.2, 153.8, 147.2, 136.9, 132.6, 132.3, 128.5, 128.4, 128.3, 128.0, 127.2, 126.5, 126.4, 124.9, 123.4, 122.5, 122.2, 61.7, 34.5, 31.4, 20.3. IR: 3295, 3048, 2931, 1728, 1543, 1453, 1265, 1016, 808, 739. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{21}H_{18}N$: 284.1434; Found, 284.1431.



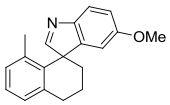
5-fluoro-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3l): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8. 20 (s, 1H), 7.63 (dd, *J* = 8.4 Hz, *J* = 4.8 Hz, 1H), 7.14-7.04 (m, 3H), 6.88-6.84 (m, 2H), 3.09-2.97 (m, 2H), 2.07-1.95 (m, 3H), 1.51-1.47 (m, 1H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.7, 178.6, 163.1, 160.7, 150.5, 147.7, 147.6, 138.7, 138.1, 130.2, 129.4, 128.1, 127.3, 122.4, 122.3, 114.6, 114.4, 110.4, 110.1, 62.2, 62.1, 34.5, 31.0, 20.6, 18.5. IR: 3340, 2929, 1597, 1460, 1259, 1162, 823, 773, 563. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{17}FN$: 266.1340; Found, 266.1337.



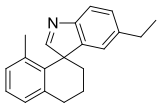
5-(tert-butyl)-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3m): solid; m.p. 110-112 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.16 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.41-7.39 (m, 1H), 7.16 (d, *J* = 1.6 Hz, 1H), 7.11 (d, *J* = 4.8Hz, 2H), 6.84 (t, *J* = 4.8 Hz, 1H), 3.12-2.98 (m, 2H), 2.12-1.93 (m, 3H), 1.61-1.56 (m, 1H), 1.39 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.8, 152.3, 149.9, 145.5, 138.8, 138.4, 131.1, 129.3, 128.0, 126.9, 124.6, 120.8, 119.2, 61.7, 35.0, 34.9, 31.6, 31.2, 21.0, 18.7. IR: 3291, 2958, 2868, 1731, 1549, 1462, 1263, 890, 828, 775, 738, 565. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{22}H_{26}N$: 304.2060; Found, 304.2057.



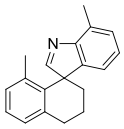
5,8'-dimethyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3n): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.15 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 4.8 Hz, 2H), 6.96 (s, 1H), 6.85-6.83 (m, 1H), 3.09-2.97 (m, 2H), 2.34 (s, 3H), 2.10-1.93 (m, 3H), 1.50-1.45 (m, 1H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.8, 152.4, 145.7, 138.7, 138.3, 136.3, 131.2, 129.3, 128.4, 128.0, 127.0, 123.2, 121.2, 61.5, 34.5, 31.1, 21.5, 20.7, 18.5. IR: 3370, 2930, 1548, 1461, 1266, 1003, 820, 773, 738. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{20}N$: 262.1590; Found, 262.1588.



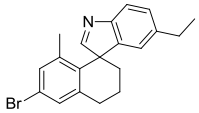
5-methoxy-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3o): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.10 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.11-7.09 (m, 2H), 6.90-6.83 (m, 2H), 6.70 (d, *J* = 2.0 Hz, 1H), 3.77 (s, 3H), 3.08-2.96 (m, 2H), 2.10-1.91 (m, 3H), 1.56-1.51 (m, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.5, 158.8, 148.3, 147.4, 138.7, 138.4, 131.0, 129.3, 128.0, 127.0, 122.0, 112.5, 108.9, 61.8, 55.7, 34.8, 31.1, 20.6, 18.6. IR: 2936, 1721, 1546, 1469, 1335, 1271, 1212, 1030, 814, 738, 703. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{20}NO$: 278.1539; Found, 278.1537.



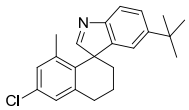
5-ethyl-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3p): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.16 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 5.2 Hz, 2H), 6.98 (s, 1H), 6.85-6.83 (m, 1H), 3.09-2.99 (m, 2H), 2.63 (dd, *J* = 15.2 Hz, *J* = 7.6 Hz, 2H), 2.10-1.92 (m, 3H), 1.54-1.51 (m, 1H), 1.49 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.8, 152.4, 145.7, 142.9, 138.7, 138.3, 131.1, 129.3, 128.0, 127.2, 127.0, 122.0, 121.2, 61.5, 34.6, 31.1, 28.9, 20.7, 18.5, 15.8. IR: 3289, 2963, 2933, 1548, 1465, 1266, 889, 829, 775, 737. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{20}H_{22}N$: 276.1747; Found, 276.1751.



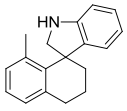
7,8'-dimethyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3q): solid; m.p. 73-74 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.22 (s, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.12-7.09 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.84-6.82 (m, 1H), 3.05-3.00 (m, 2H), 2.64 (s, 3H), 2.09-1.93 (m, 3H), 1.50-1.48 (m, 1H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.7, 153.0, 145.5, 138.7, 138.3, 131.3, 131.1, 129.3, 129.1, 128.0, 127.0, 126.3, 120.0, 61.9, 34.6, 31.1, 20.7, 18.6, 16.8. IR: 3256, 2926, 1736, 1548, 1459, 1378, 909, 784, 734, 542. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{20}N$: 262.1590; Found, 262.1587.



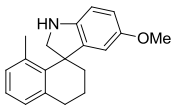
6'-bromo-5-ethyl-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3r): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.12 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 6.99 (d, *J* = 1.6 Hz, 1H), 6.95 (s, 1H), 3.06-2.93 (m, 2H), 2.63 (dd, *J* = 15.2 Hz, *J* = 7.6 Hz, 2H), 2.10-1.90 (m, 3H), 1.53-1.46 (m, 1H), 1.38 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.0, 152.4, 145.2, 143.2, 140.9, 140.5, 132.0, 130.5, 130.3, 127.4, 121.9, 121.4, 120.8, 61.1, 34.3, 30.9, 28.9, 20.4, 18.3, 15.8. IR: 3257, 2963, 2933, 1720, 1575, 1463, 1265, 1005, 891, 830, 738, 570. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{20}H_{21}BrN$: 354.0852; Found, 354.0856.



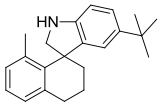
5-(tert-butyl)-6'-chloro-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3s): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8. 12 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.12-7.11 (m, 2H), 6.84 (s, 1H), 3.07-2.94 (m, 2H), 2.07-1.92 (m, 3H), 1.60-1.54 (m, 1H), 1.35 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.2, 152.3, 150.1, 145.0, 140.6, 140.3, 132.4, 129.7, 129.1, 127.5, 124.8, 121.0, 119.1, 61.2, 34.9, 34.7, 31.6, 31.1, 20.7, 18.5. IR: 3396, 2960, 1583, 1463, 1364, 1263, 1005, 892, 739, 575. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{22}H_{25}NCl$: 338.1670; Found, 338.1673.



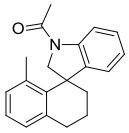
8'-methyl-3',4'-dihydro-2'H-spiro[indoline-3,1'-naphthalene] (3aa): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.07-6.98 (m, 3H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.76-6.74 (m, 1H), 6.65-6.62(m, 2H), 3.76 (d, *J* = 10.0 Hz, 1H), 3.60 (d, *J* = 9.6 Hz, 1H), 2.99-2.83 (m, 2H), 2.17-2.14 (m, 1H), 1.88-1.70 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.0, 138.7, 138.6, 138.6, 138.5, 130.4, 127.3, 127.2, 126.2, 122.9, 118.7, 109.4, 59.3, 50.3, 39.8, 31.5, 22.0, 19.6. IR: 3387, 2928, 1605, 1490, 1462, 1249, 1026, 773, 741, 638. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{20}N$: 250.1590; Found, 250.1588.



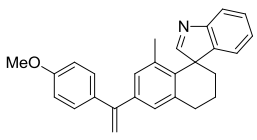
5-methoxy-8'-methyl-3',4'-dihydro-2'H-spiro[indoline-3,1'-naphthalene] (3oo): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.06 (d, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.64 (dd, *J* = 8.0 Hz, *J* = 6.4 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 3.79-3.76 (m, 1H), 3.67-3.64 (m, 4H), 13.04-2.84 (m, 2H), 2.19-2.15 (m, 1H), 1.88 (s, 3H), 1.86-1.74 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.3, 143.2, 140.9, 138.7, 138.4, 138.1, 130.5, 127.3, 126.3, 112.6, 111.0, 109.4, 59.6, 56.0, 51.0, 39.5, 31.5, 22.1, 19.8. IR: 3369, 2930, 1595, 1495, 1268, 1208, 1034, 909, 774, 735, 647. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{22}NO$: 280.1696; Found, 280.1693.



5-(tert-butyl)-8'-methyl-3',4'-dihydro-2'H-spiro[indoline-3,1'-naphthalene] (3mm): solid; m.p. 116-118 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.08-7.00 (m, 3H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 1.6 Hz, 1H), 6.61(d, *J* = 8.0 Hz, 1H), 3.71 (d, *J* = 10.0 Hz, 1H), 3.61 (d, *J* = 10.0 Hz, 1H), 3.02-2.84 (m, 2H), 2.19-2.15 (m, 1H), 1.87-1.73 (m, 6H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.5, 142.4, 138.8, 138.7, 138.6, 138.5, 130.4, 127.3, 126.2, 123.6, 120.1, 109.2, 59.5, 50.7, 39.4, 34.2, 31.7, 31.5, 22.2, 19.8. IR: 3379, 2958, 2244, 1612, 1496, 1362, 1259, 1208, 909, 813, 774, 735. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{22}H_{28}N$: 306.2216; Found, 306.2212.



1-(8'-methyl-3',4'-dihydro-2'H-spiro[indoline-3,1'-naphthalen]-1-yl)ethanone (3aa') solid; m.p. 197-199 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.25 (d, *J* = 8.0 Hz, 1H), 7.24-7.18 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.98-6.92 (m, 2H), 6.85 (d, *J* = 7.2 Hz, 1H), 4.12 (d, *J* = 11.2 Hz, 1H), 4.05 (d, *J* = 10.8 Hz, 1H), 3.02-2.87 (m, 2H), 2.24 (s, 3H), 2.05-2.01 (m, 1H), 1.94-1.80 (m, 3H), 1.70 (S, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.7, 142.1, 140.8, 138.6, 138.0, 137.0, 130.6, 127.5, 126.8, 123.9, 122.7, 116.9, 62.4, 48.2, 41.7, 31.2, 24.3, 21.7, 19.6. IR: 2931, 1663, 1595, 1481, 1399, 1336, 1276, 1129, 834, 776, 757, 629, 498. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{20}H_{22}NO$: 292.1696; Found, 292.1693.



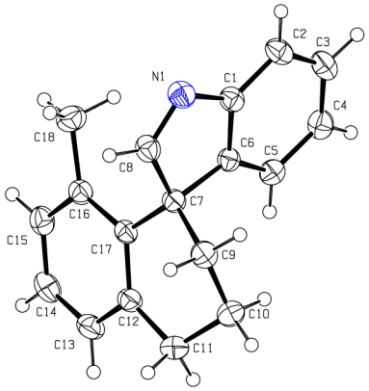
6'-(1-(4-methoxyphenyl)vinyl)-8'-methyl-3',4'-dihydro-2'H-spiro[indole-3,1'-naphthalene] (3dd): viscous oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.29 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.44-7.36 (m, 1H), 7.29-7.19 (m, 4H), 7.07 (s, 1H), 6.88-6.81 (m, 3H), 5.34 (d, *J* = 5.2 Hz, 2H), 3.83(s, 3H), 3.03-2.98 (m, 2H), 2.06-1.95 (m, 3H), 1.53-1.48 (m, 1H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.1, 159.3, 148.9, 140.3, 138.5, 137.9, 133.8, 130.6, 130.1, 129.4, 129.2, 129.2, 127.9, 127.7, 126.5, 122.6, 121.6, 113.7, 113.5, 112.9, 61.6, 55.3, 34.4, 31.1, 20.8, 18.6. IR:

3371, 2931, 1607, 1510, 1249, 1178, 1033, 837, 736, 585. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{27}H_{26}NO$: 380.2009; Found, 380.2008.

5. References.

(1) (a) S. Wang, Y. Chen, X. Liu, X. Xu, X. Liu, B. F. Liu and G. Zhang, *Arch. Pharm. Chem. Life Sci.* 2014, **347**, 32; (b) K. R. Campos, J. C. S. Woo, S. Lee and R. D. Tillyer, *Org. Lett.* 2004, **6**, 79; (c) K. Oisaki, J. Abea and M. Kanai, *Org. Biomol. Chem.*, 2013, **11**, 4569.

6. Crystallographic data of 3a and 3m.



Structure of 3a

Datablock:

Bond precision:	C-C = 0.0020 A		Wavelength=1.54184
Cell:	a=7.7592(8)	b=21.8617(17)	c=8.2702(8)
	alpha=90	beta=113.794(12)	gamma=90
Temperature:	295 K		
	Calculated		Reported
Volume	1283.6(2)		1283.6(2)
Space group	P 21/c		P 1 21/c 1
Hall group	-P 2ybc		-P 2ybc
Moiety formula	C18 H17 N		C18 H17 N
Sum formula	C18 H17 N		C18 H17 N
Mr	247.33		247.33
Dx,g cm-3	1.280		1.280
Z	4		4
Mu (mm-1)	0.562		0.562
F000	528.0		528.0
F000’	529.35		
h,k,lmax	9,26,10		9,26,10
Nref	2438		2339
Tmin,Tmax	0.821,0.840		0.958,1.000
Tmin’	0.821		

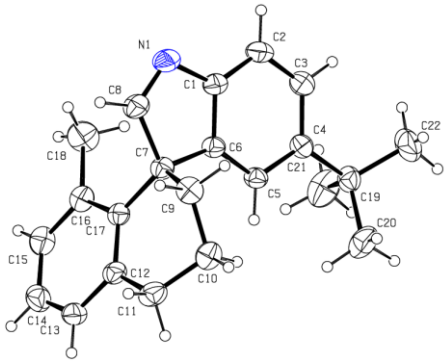
Correction method= # Reported T Limits: Tmin=0.958 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.959 Theta(max)= 69.940

R(reflections)= 0.0454(2042) wR2(reflections)= 0.1197(2339)

S = 1.067 Npar= 173



Structure of 3m

Datablock:

Bond precision:	C-C = 0.0033 A		Wavelength=1.54184
Cell:	a=8.3630(6)	b=16.4293(8)	c=25.6720(15)
	alpha=90	beta=90	gamma=90
Temperature:	295 K		
	Calculated		Reported
Volume	3527.3(4)		3527.3(4)
Space group	P b c a		P b c a
Hall group	-P 2ac 2ab		-P 2ac 2ab
Moiety formula	C22 H25 N		C22 H25 N
Sum formula	C22 H25 N		C22 H25 N
Mr	303.43		303.43
Dx,g cm-3	1.143		1.143
Z	8		8
Mu (mm-1)	0.492		0.492
F000	1312.0		1312.0
F000’	1315.24		
h,k,lmax	10,20,31		10,19,30
Nref	3356		3289
Tmin,Tmax	0.838,0.859		0.799,1.000
Tmin’	0.838		

Correction method= # Reported T Limits: Tmin=0.799 Tmax=1.000

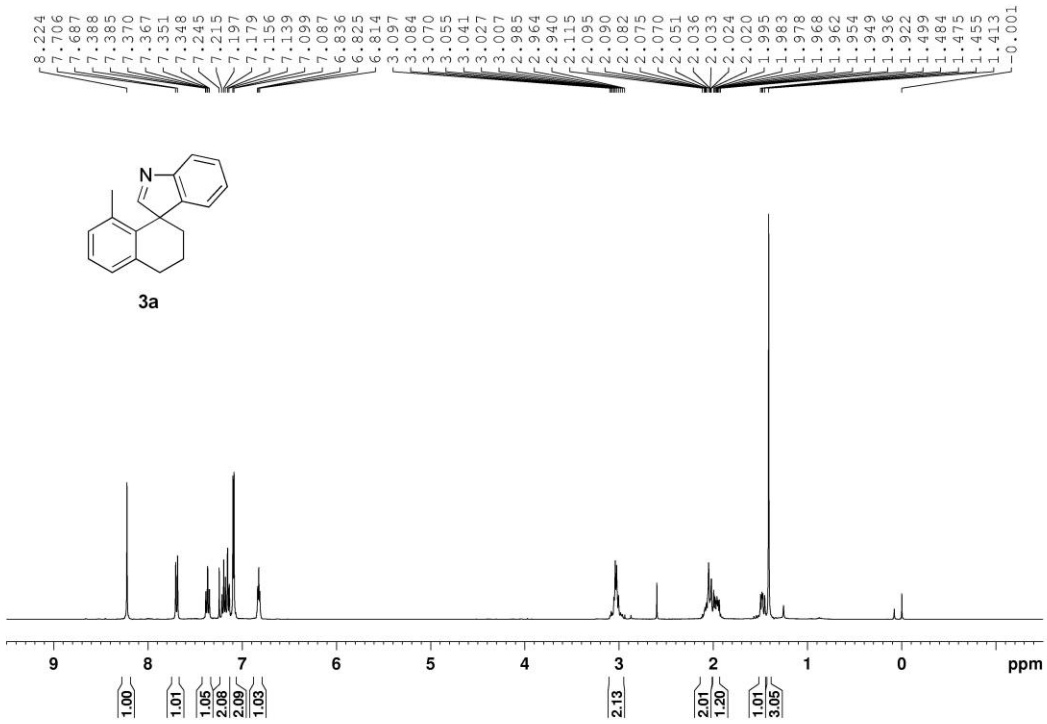
AbsCorr = MULTI-SCAN

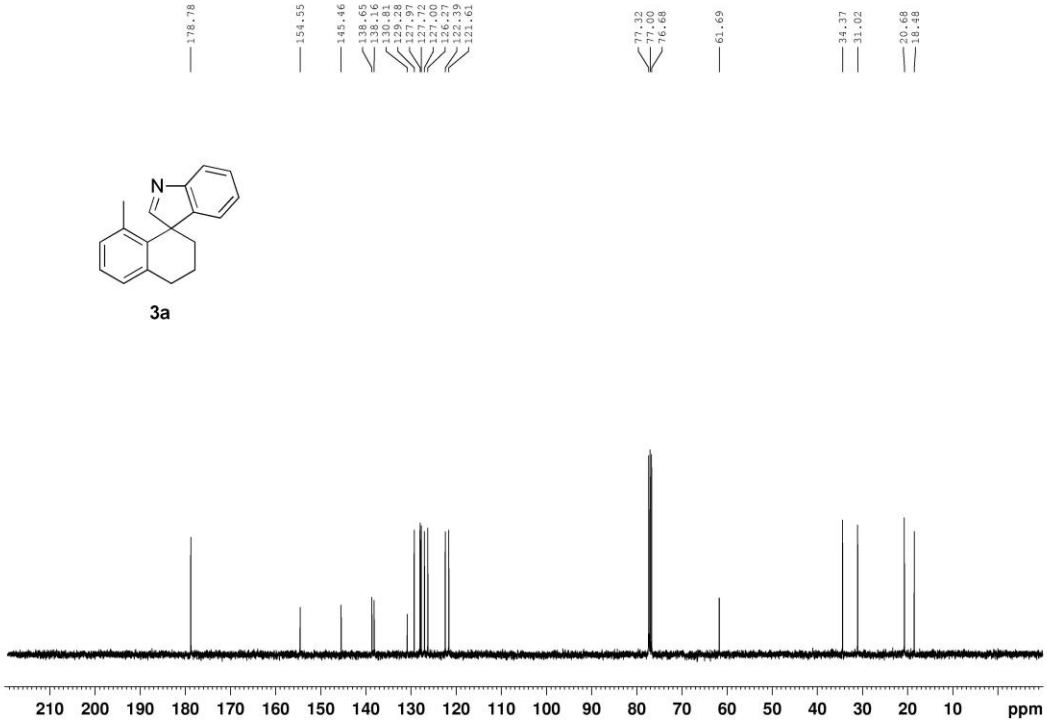
Data completeness= 0.980 Theta(max)= 70.165

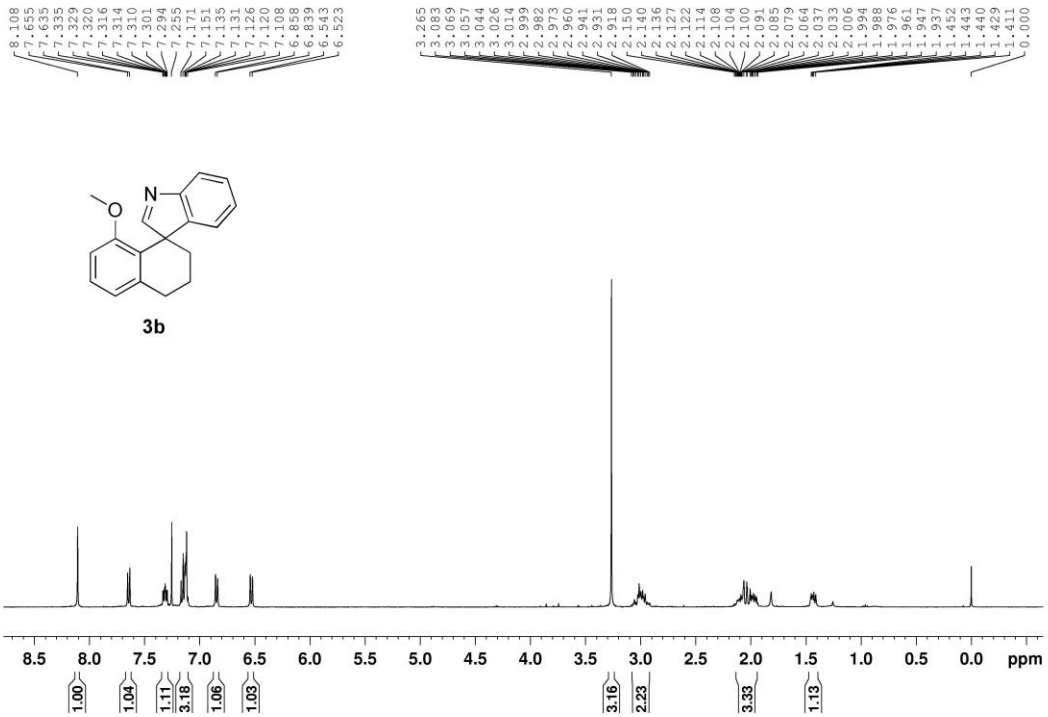
R(reflections)= 0.0630(2168) wR2(reflections)= 0.2038(3289)

S = 1.018 Npar= 212

7. Copies of ^{1}H and ^{13}C Spectra



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1.452
1.443
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O
3b
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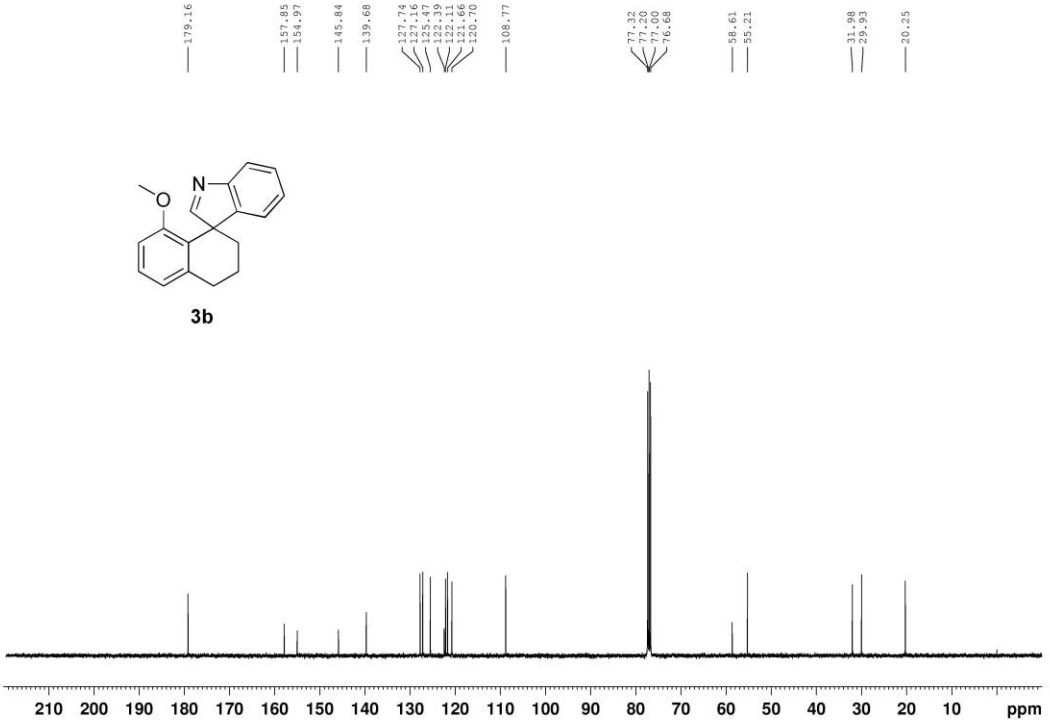
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O
3b
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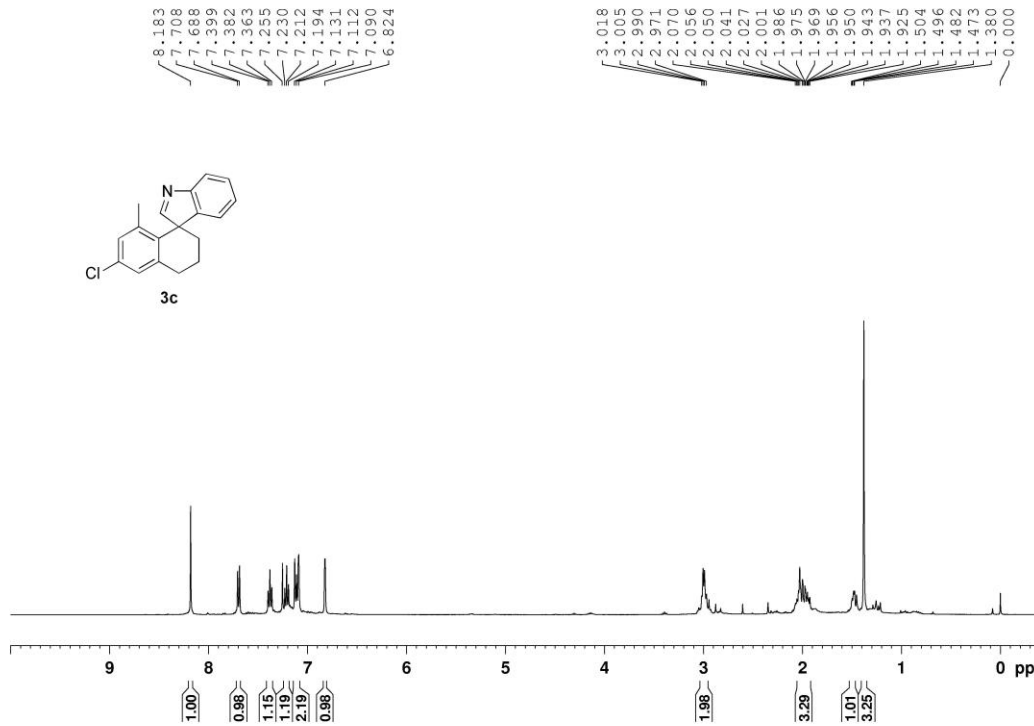
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Cl
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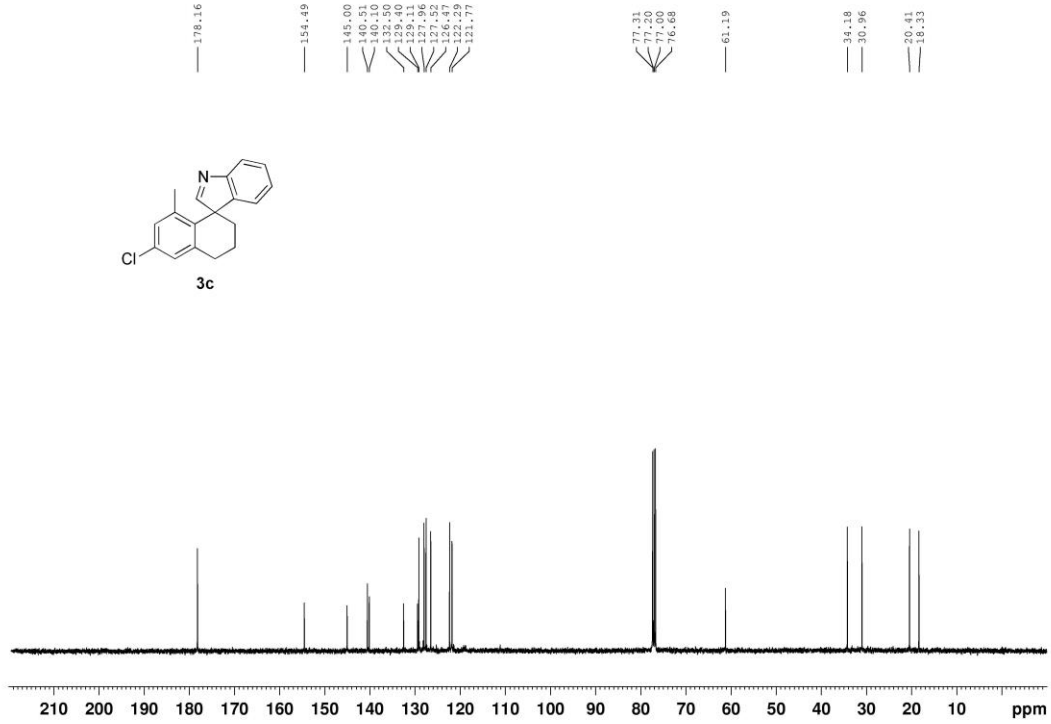
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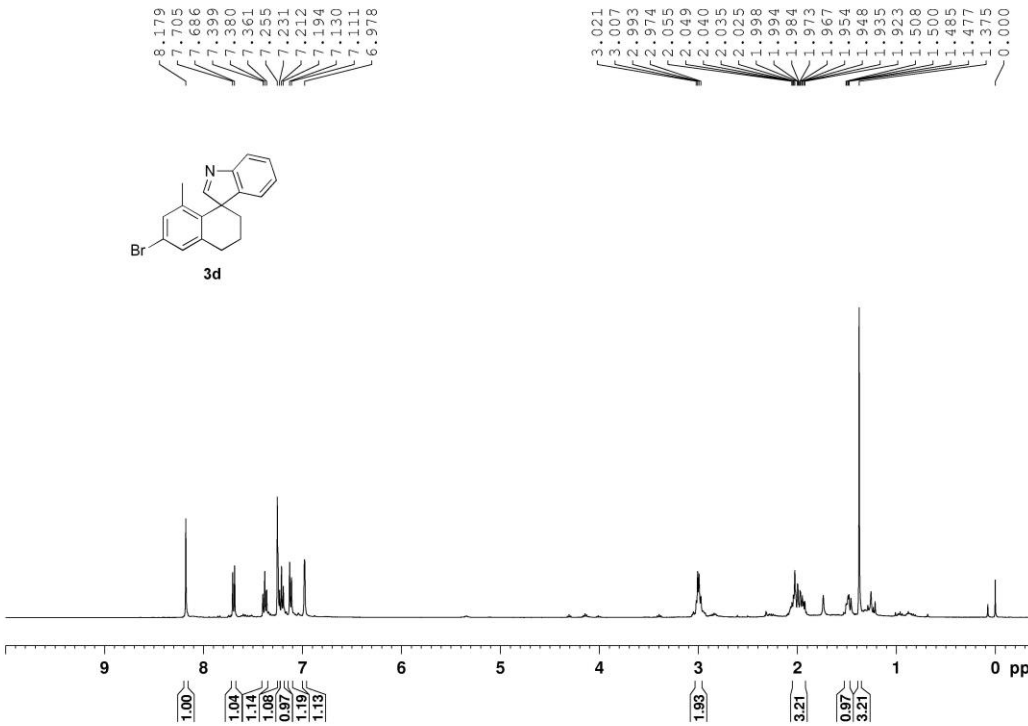
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Br
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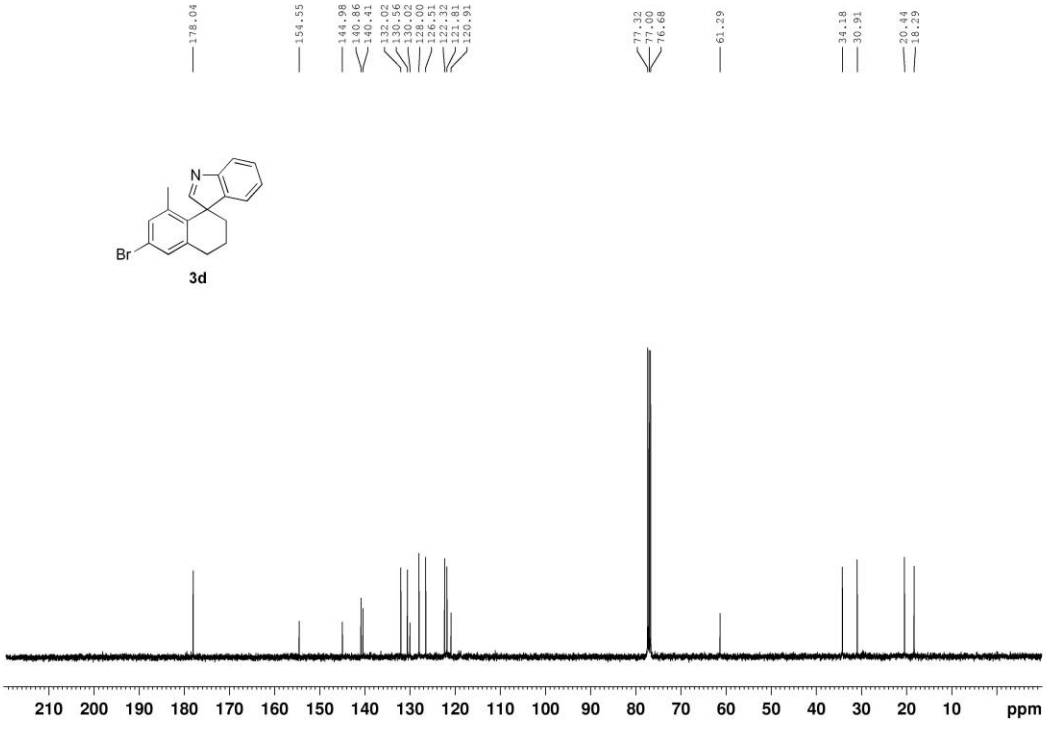
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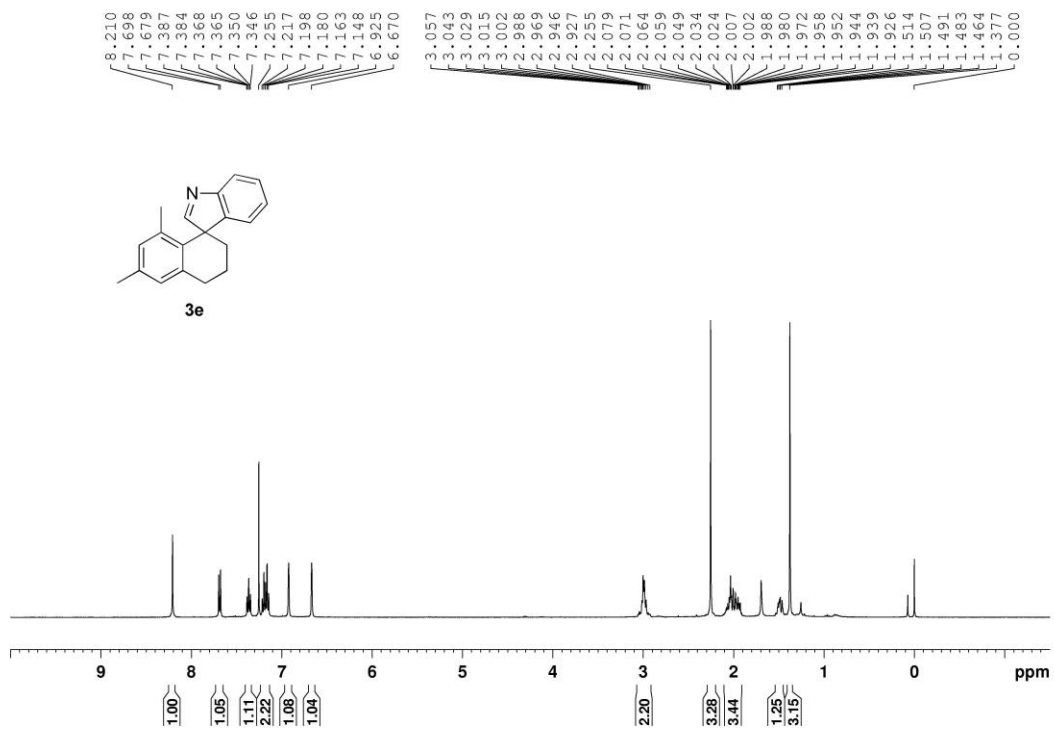
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2.024
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6
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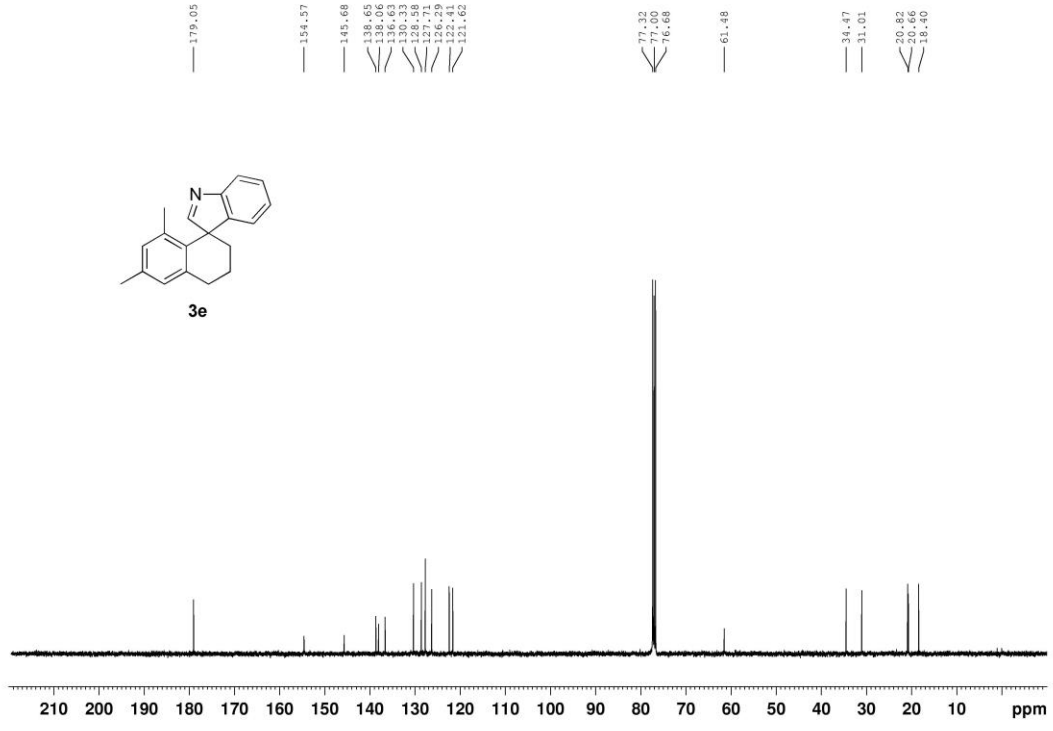
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3e
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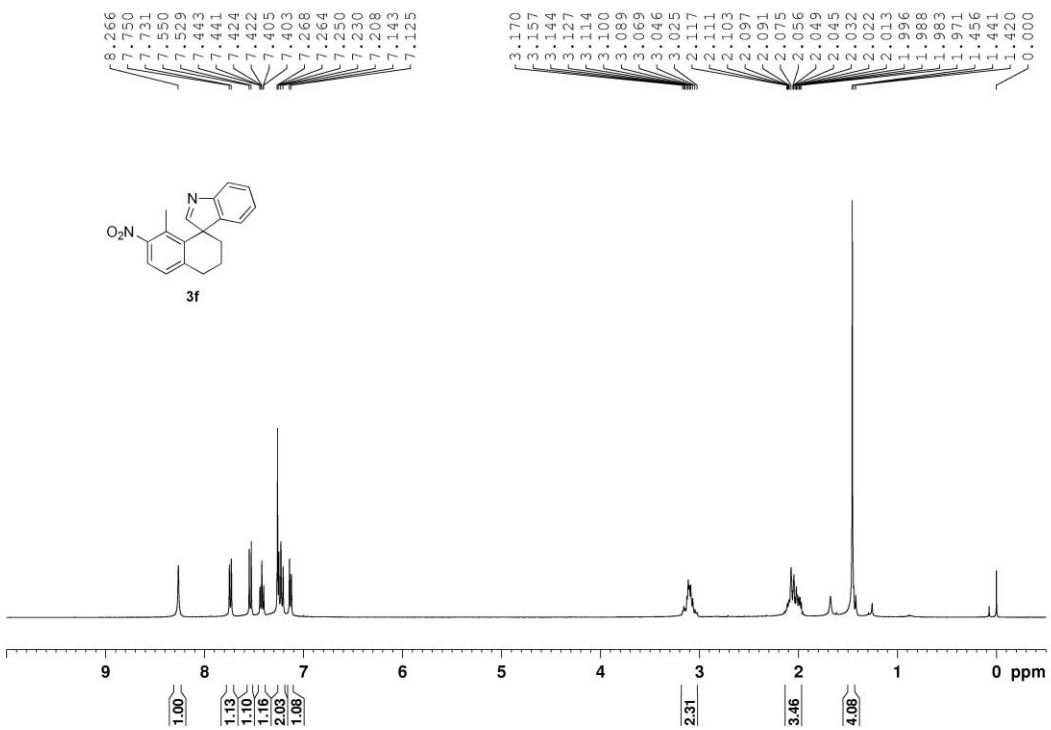
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7.403
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7.264
7.250
7.230
7.208
7.143
7.125
3.170
3.157
3.144
3.127
3.114
3.100
3.089
3.069
3.046
3.025
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2.091
2.075
2.056
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2.045
2.032
2.022
2.013
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1.988
1.983
1.971
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1.420
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O2N
3f
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8
7
6
5
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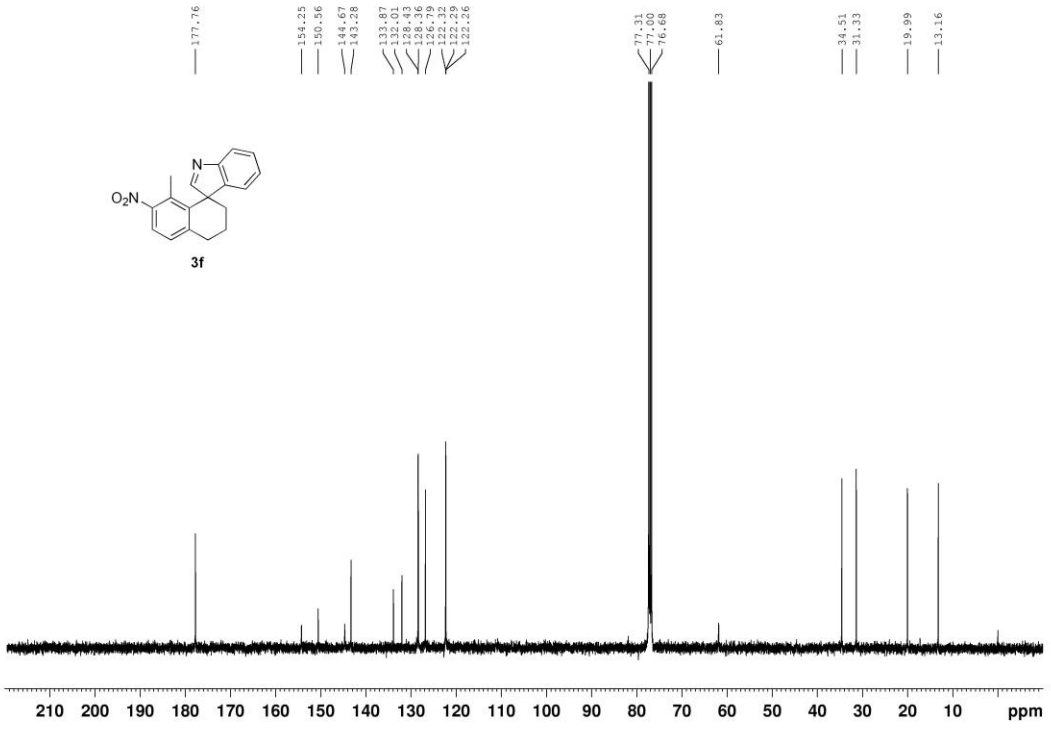
4.08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O2N
3f
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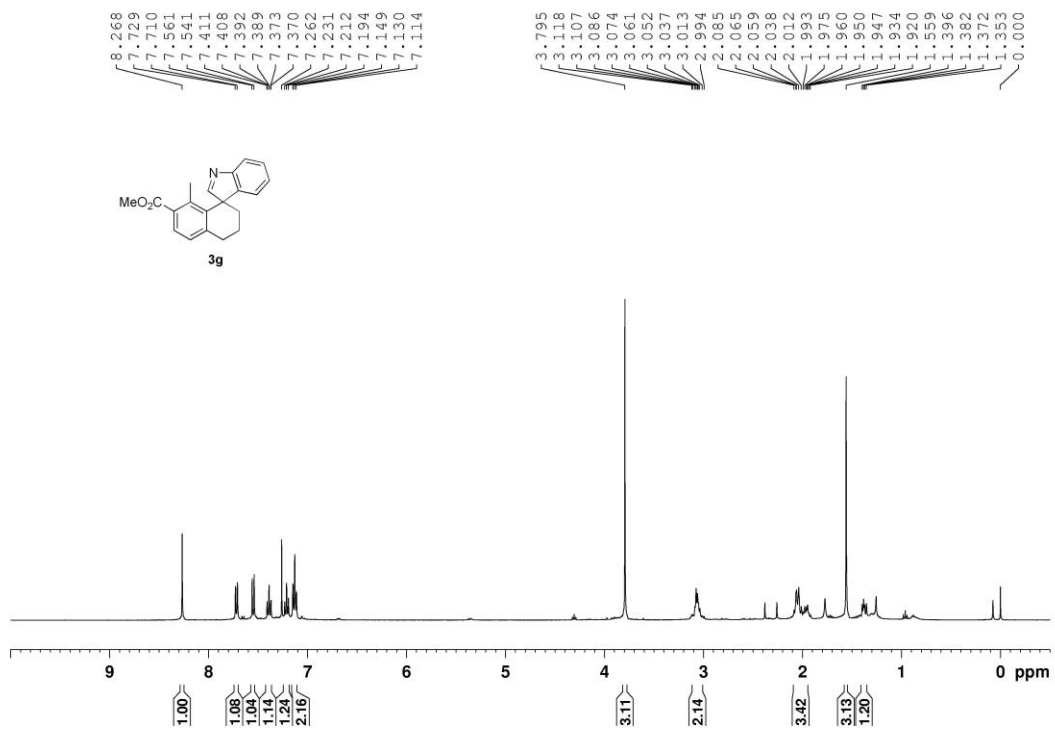
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3.074
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3.052
3.037
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2.085
2.065
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7
6
5
4
3
2
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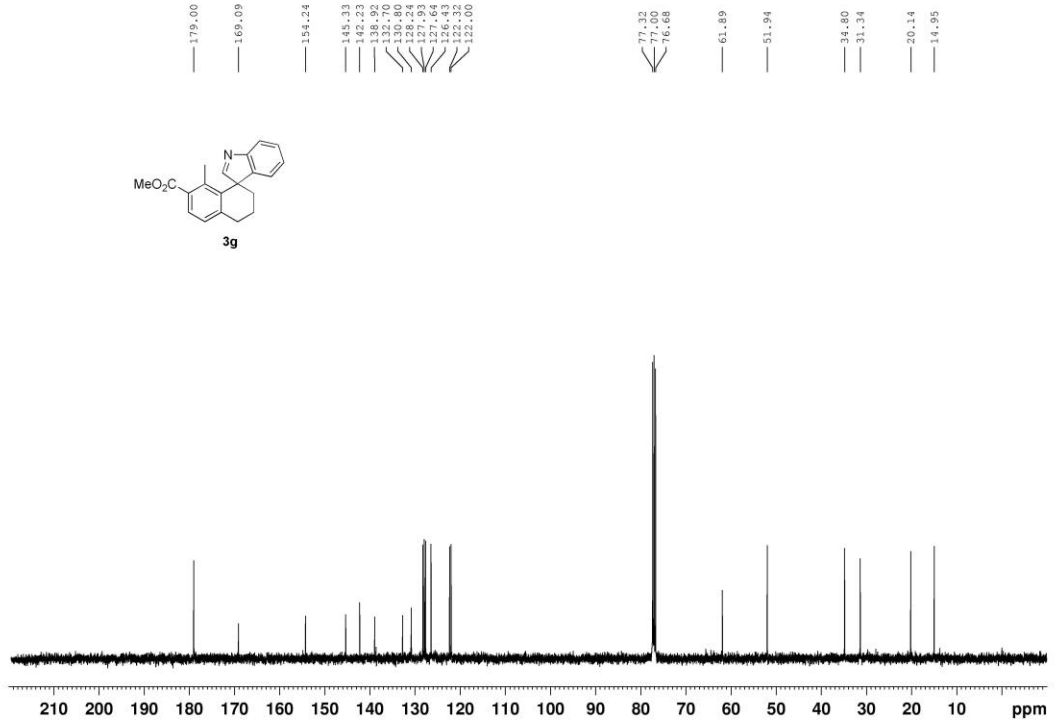
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77.32
77.00
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MeO2C
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3g
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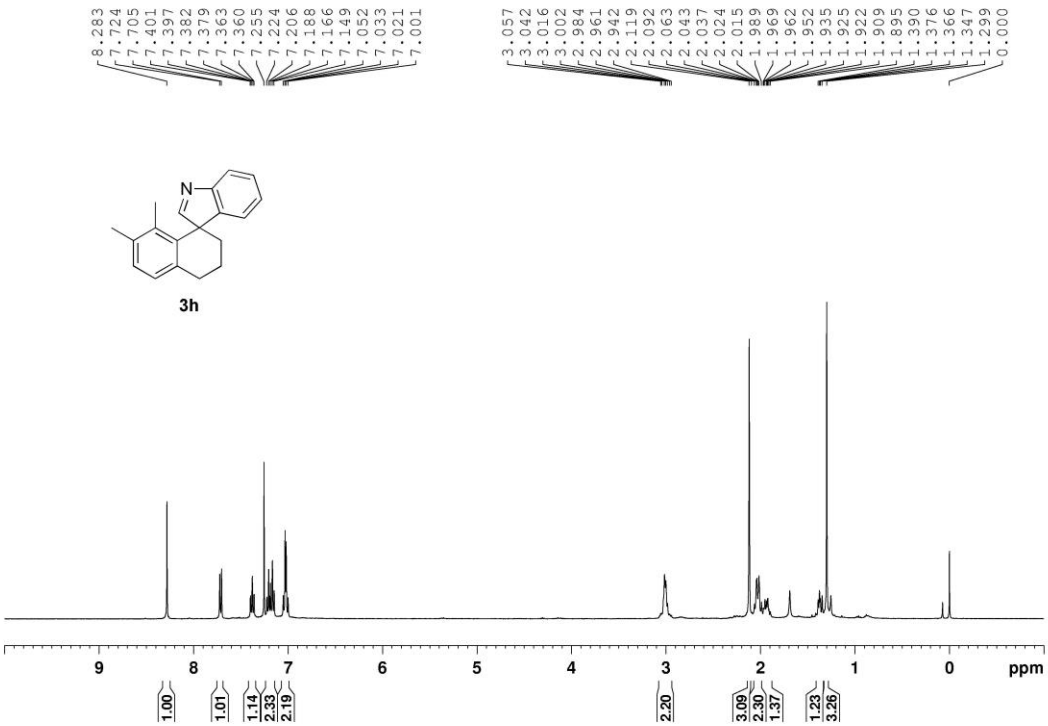
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1.925
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3h
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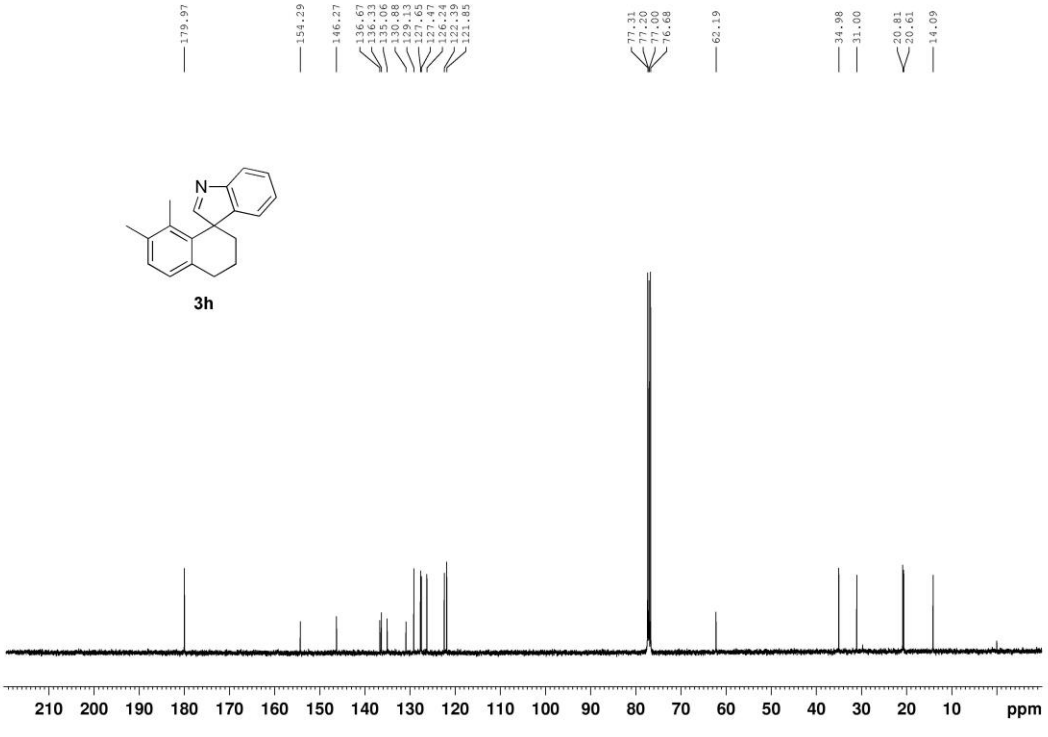
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3h
210
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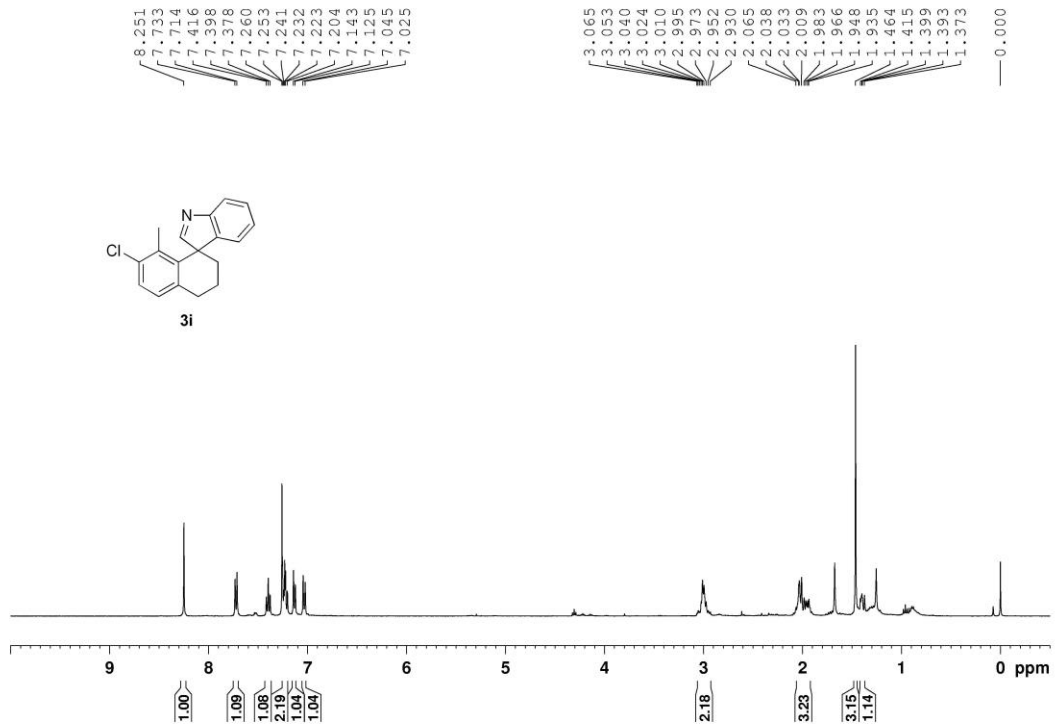
ppm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Cl
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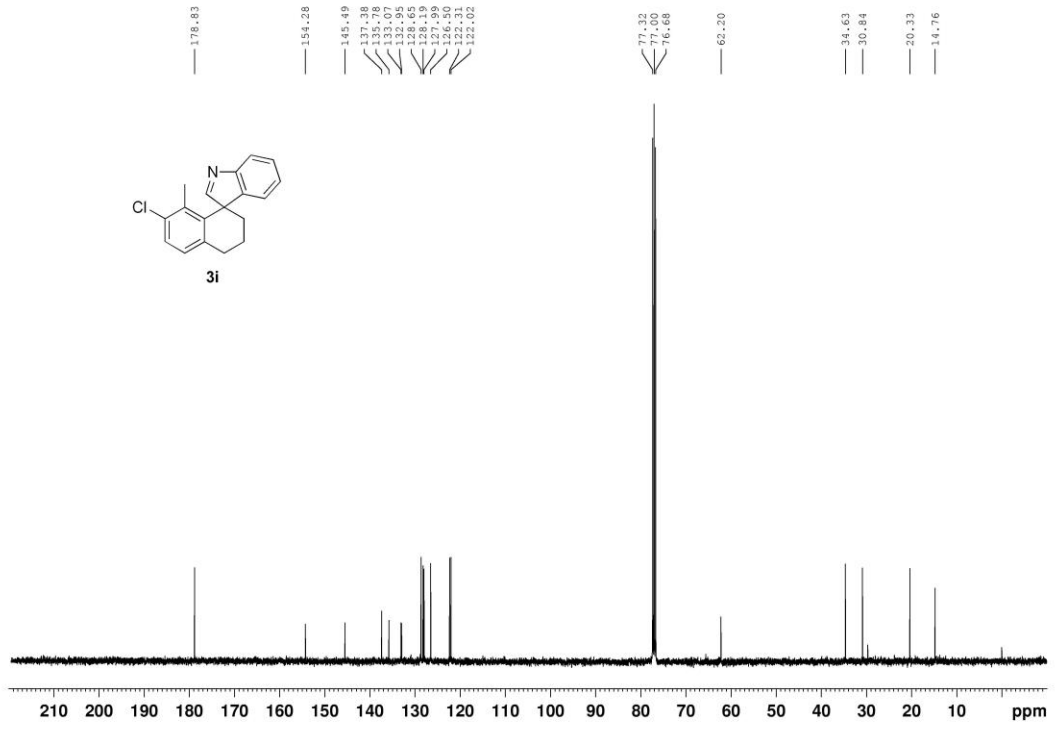
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34.63
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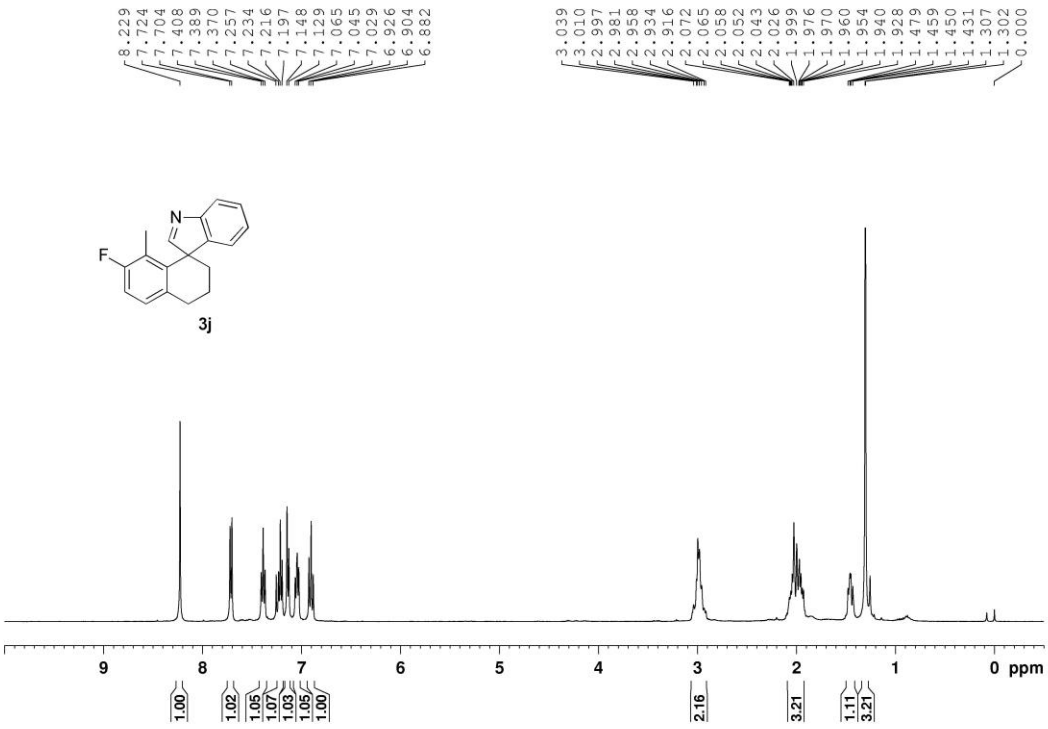
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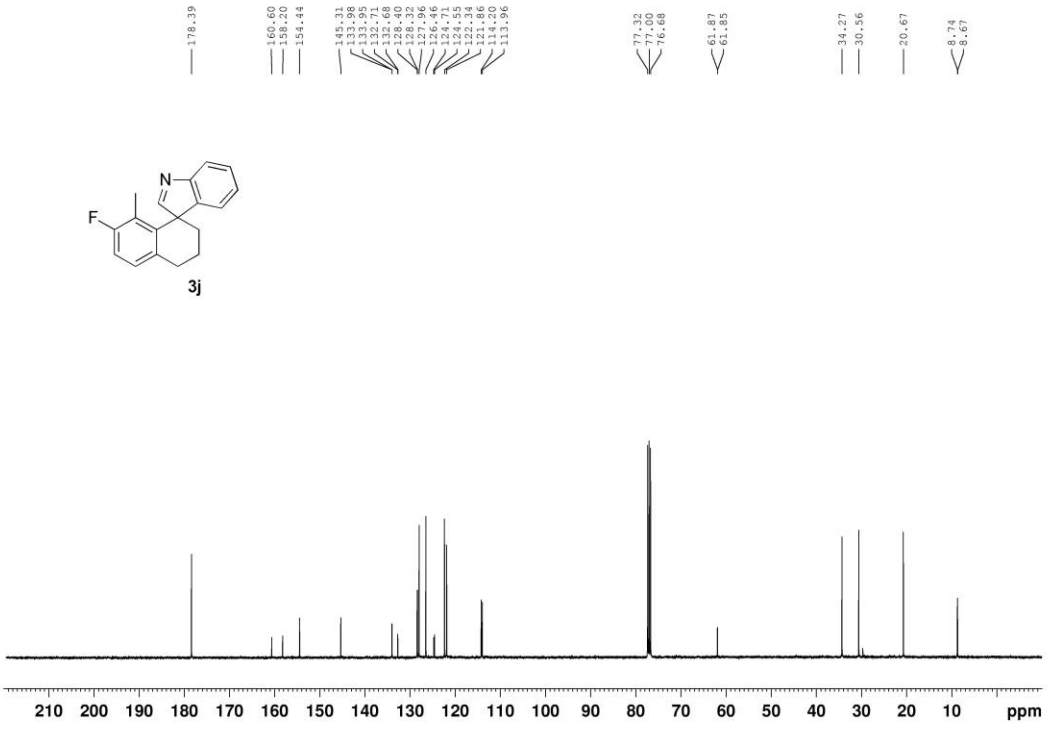
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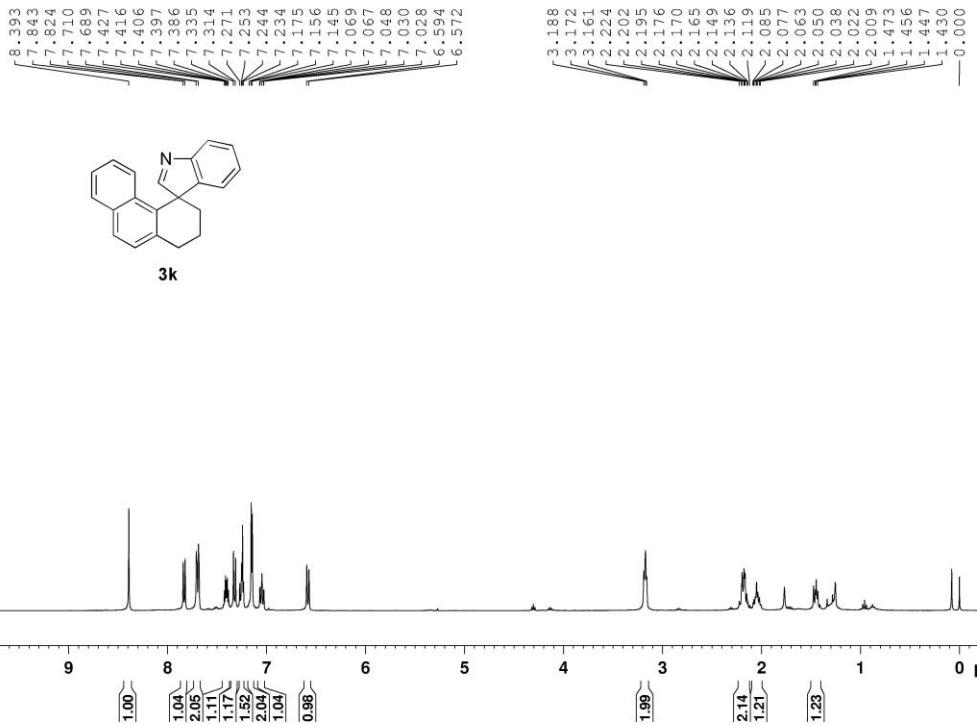
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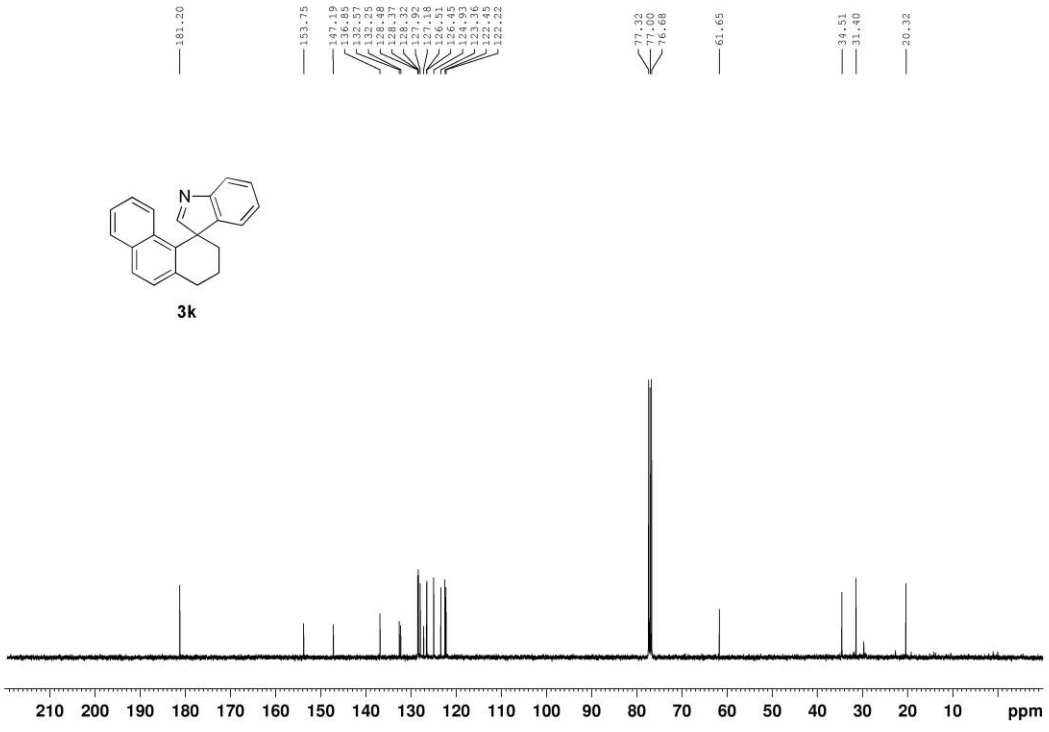
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77.32
77.00
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20.32
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3k
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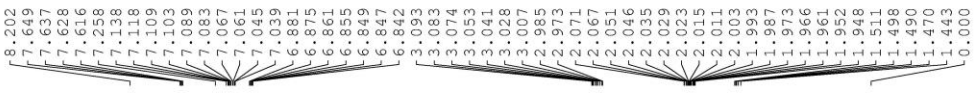
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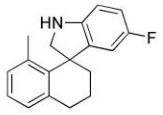
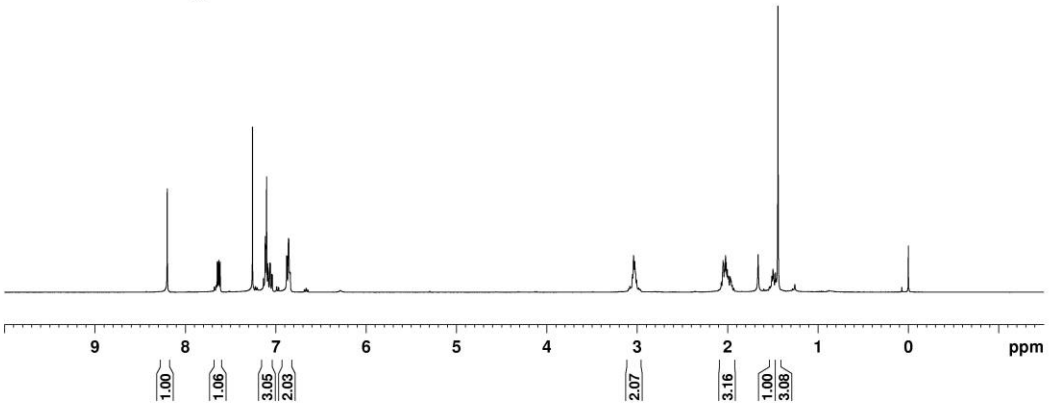

HN
F

3l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ppm
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2.07
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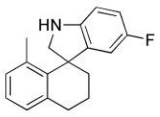
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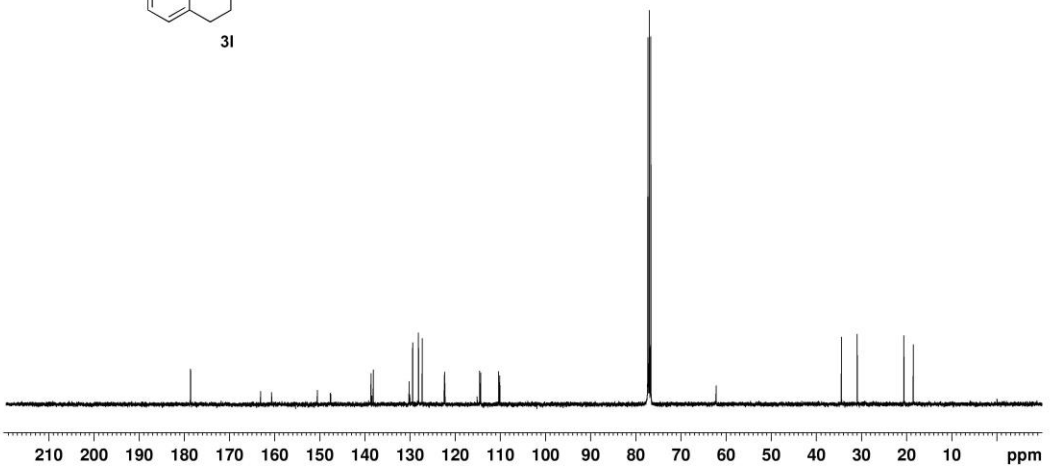
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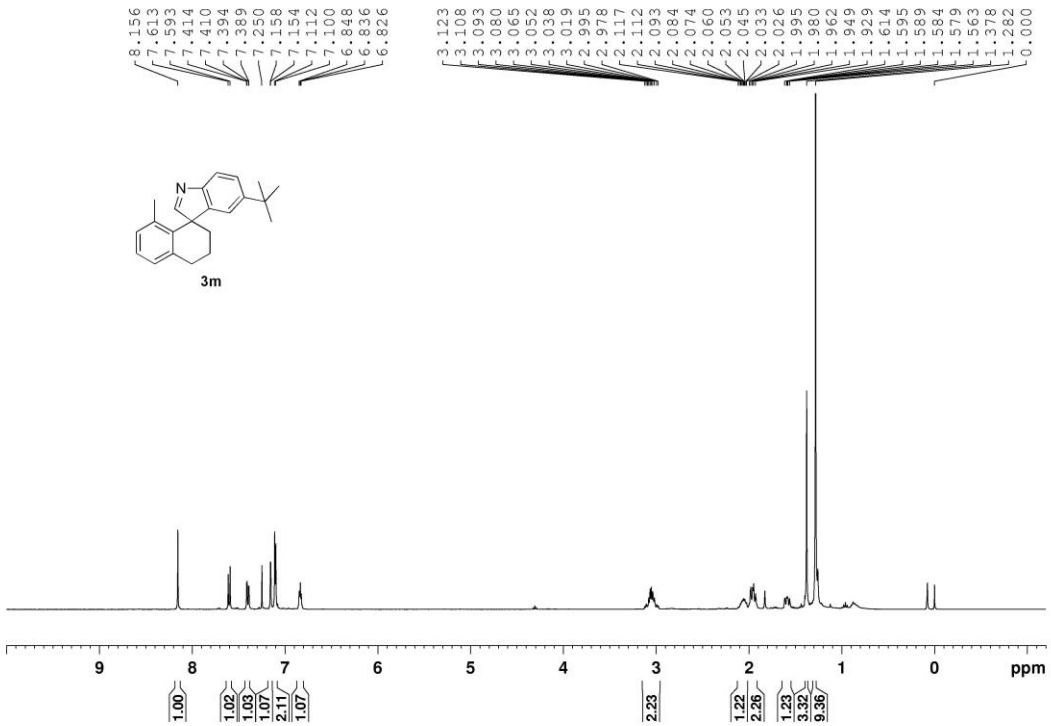
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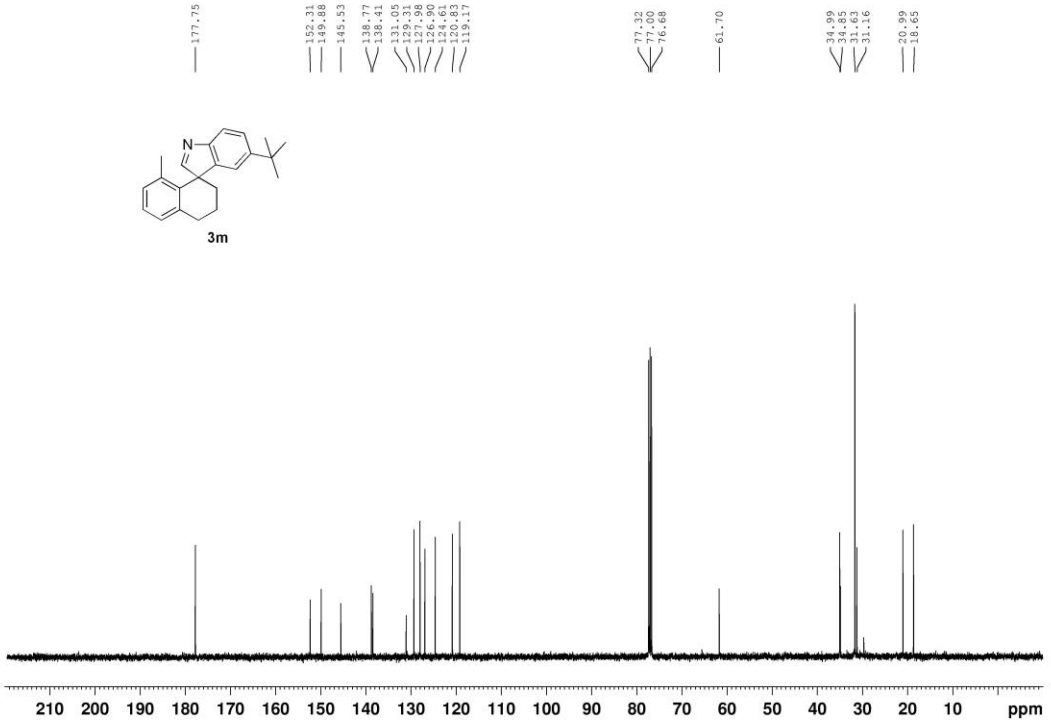
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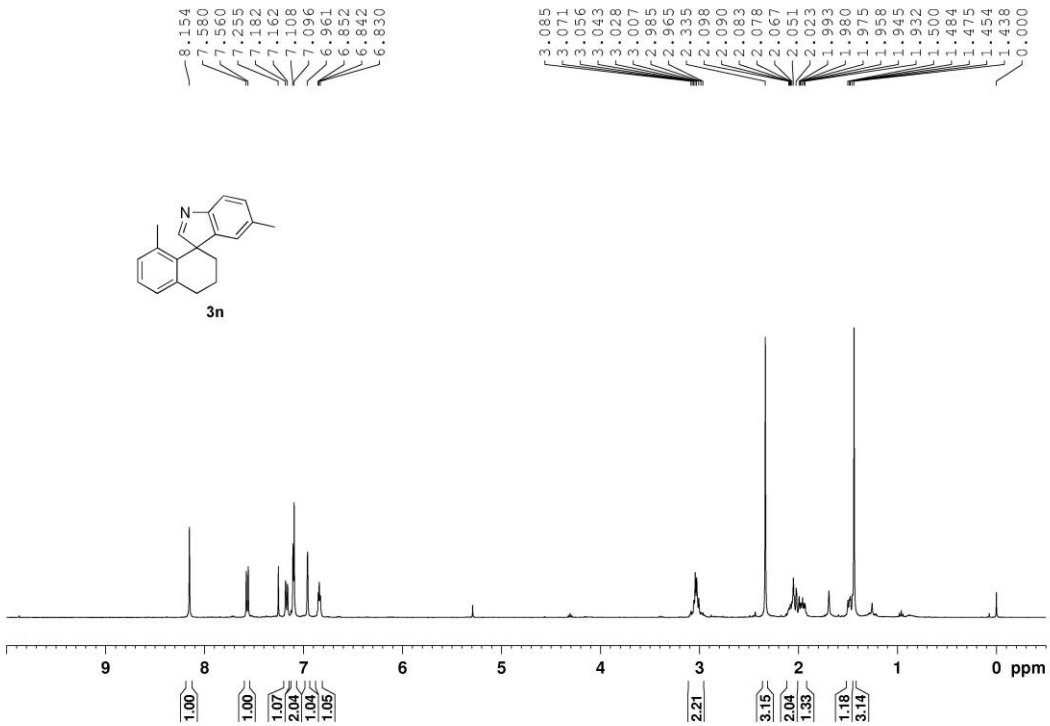
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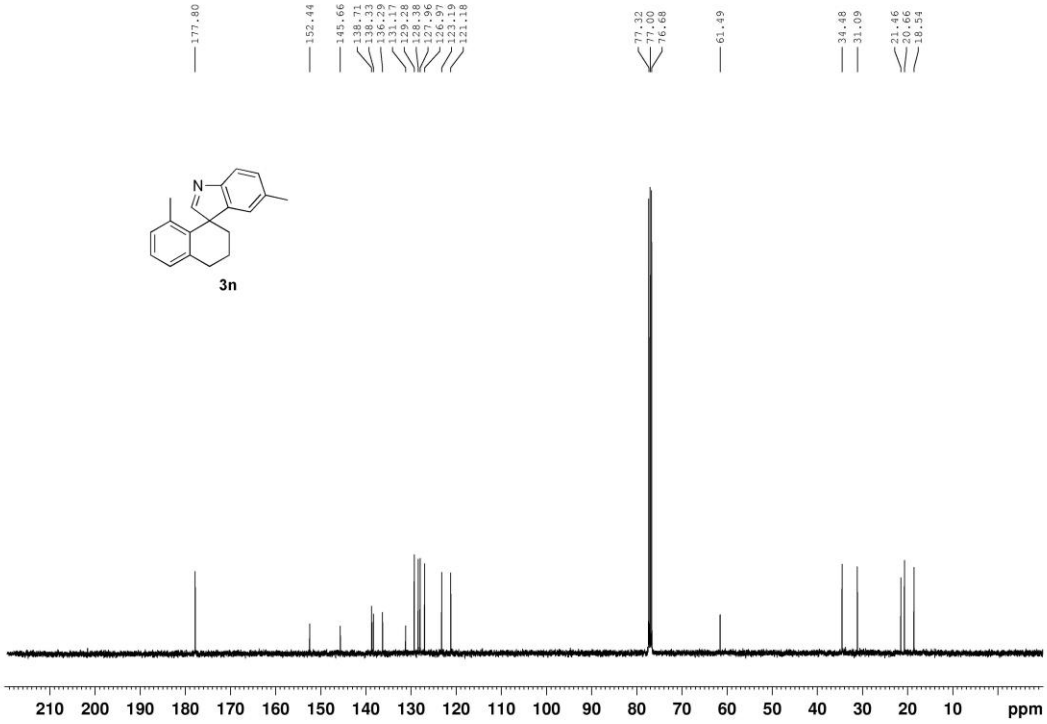
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3n
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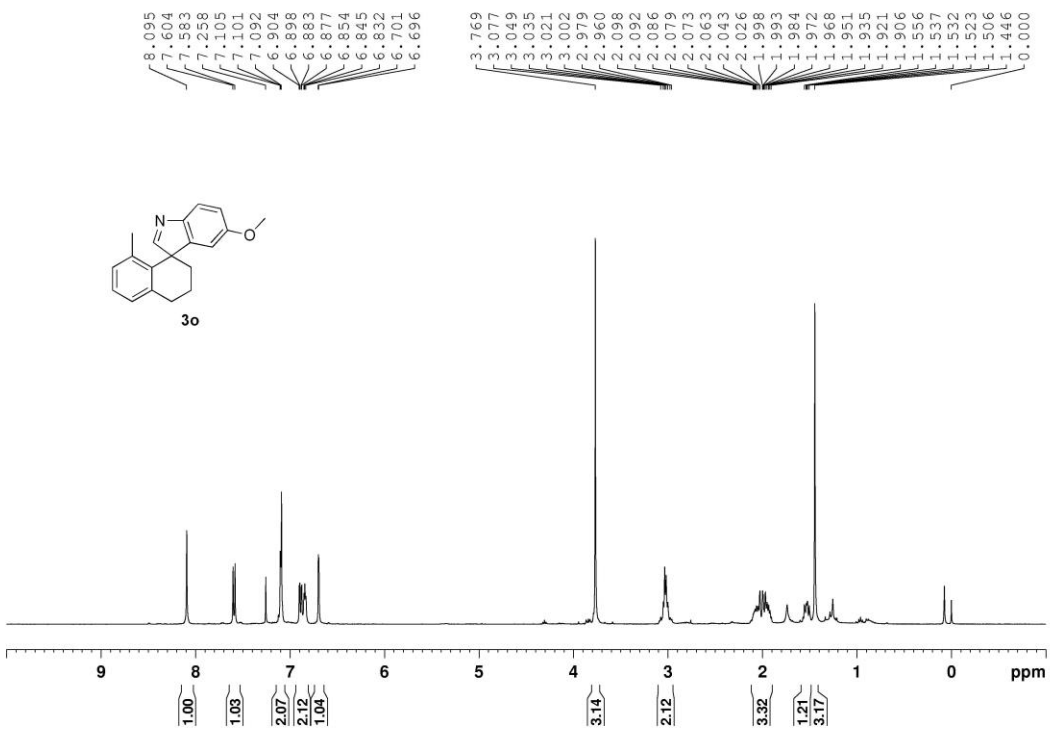
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6.701
6.696
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3.035
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3.002
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2.086
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2.073
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1.984
1.972
1.968
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1.935
1.921
1.906
1.556
1.537
1.532
1.523
1.506
1.446
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O
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9
8
7
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5
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3
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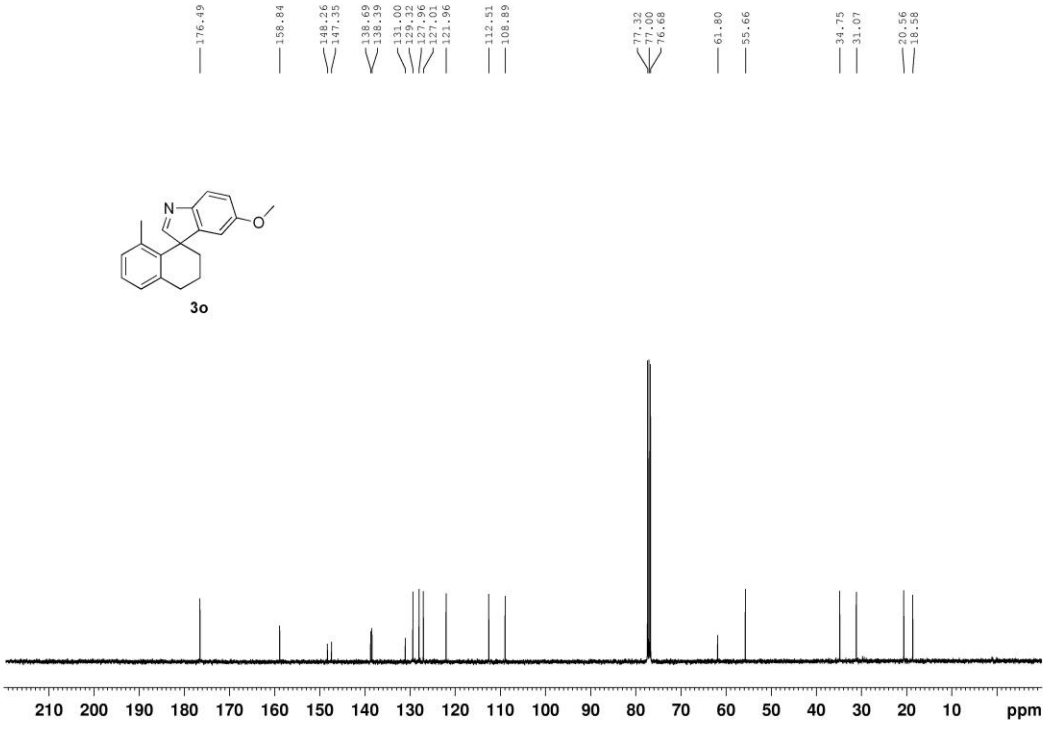
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O
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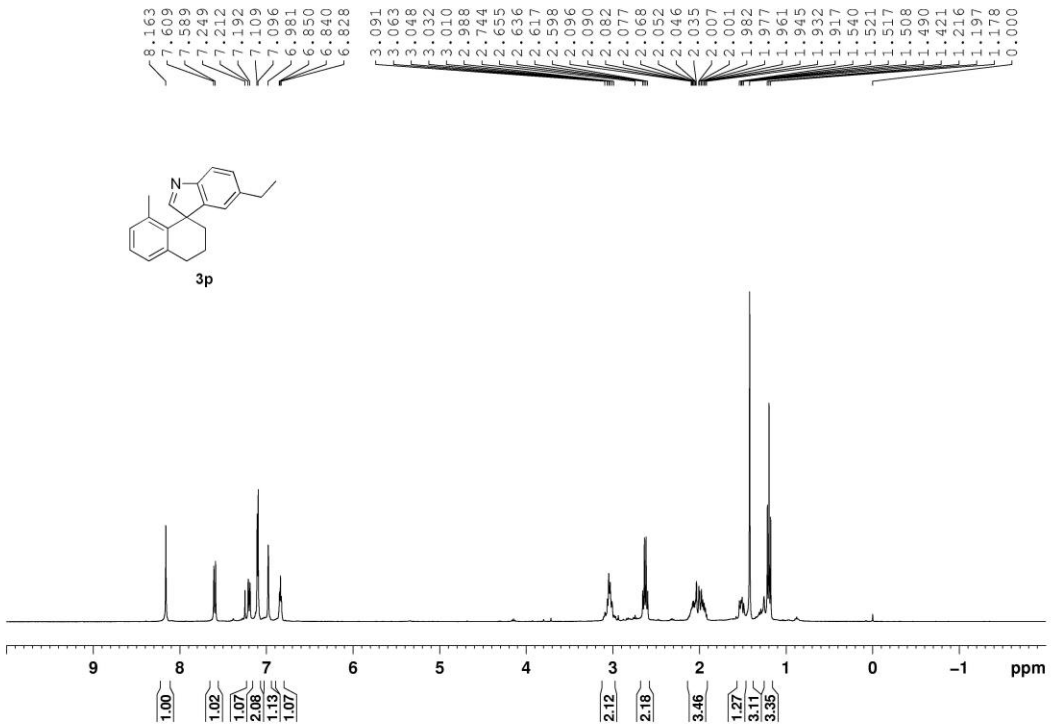
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1.517
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−1
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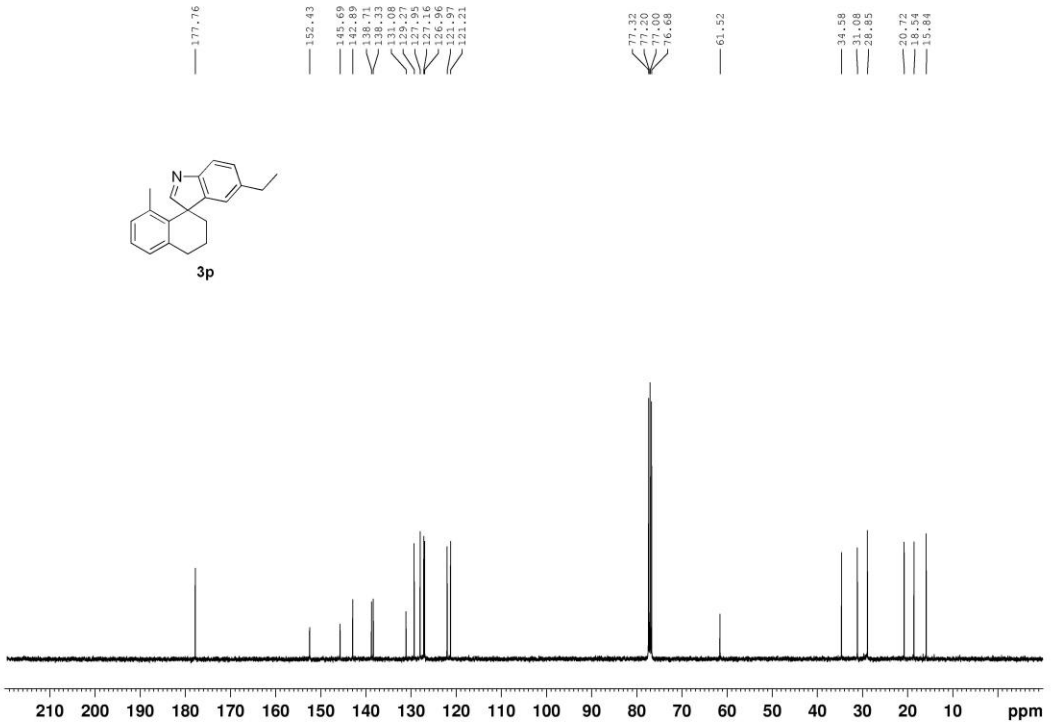
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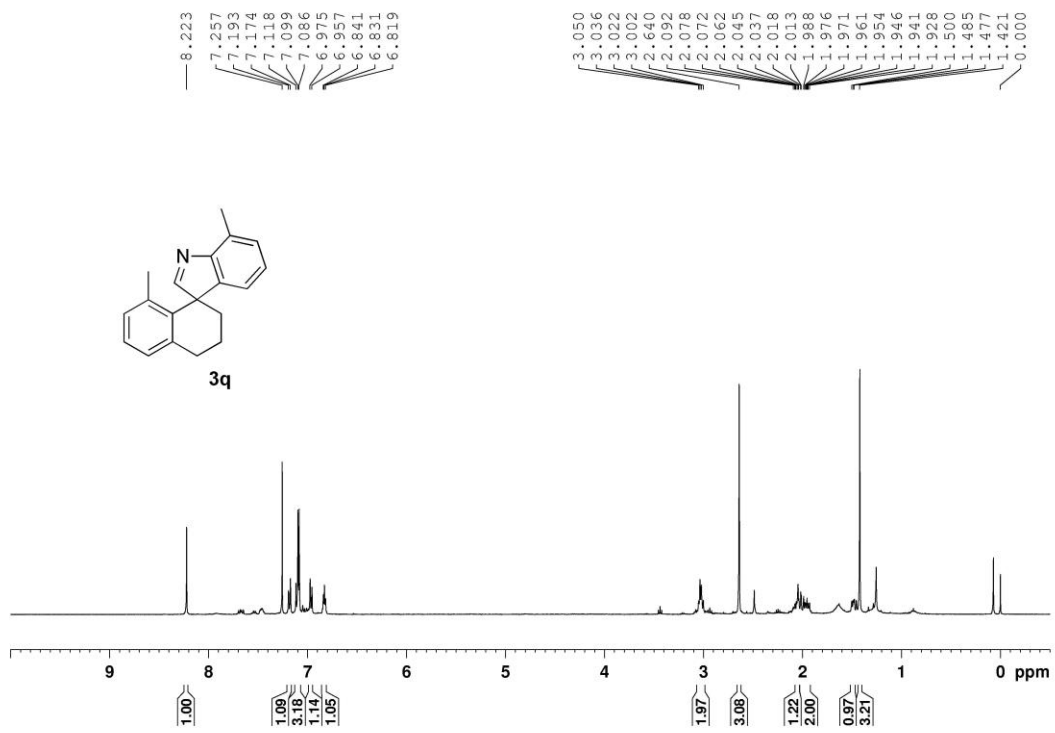
ppm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4
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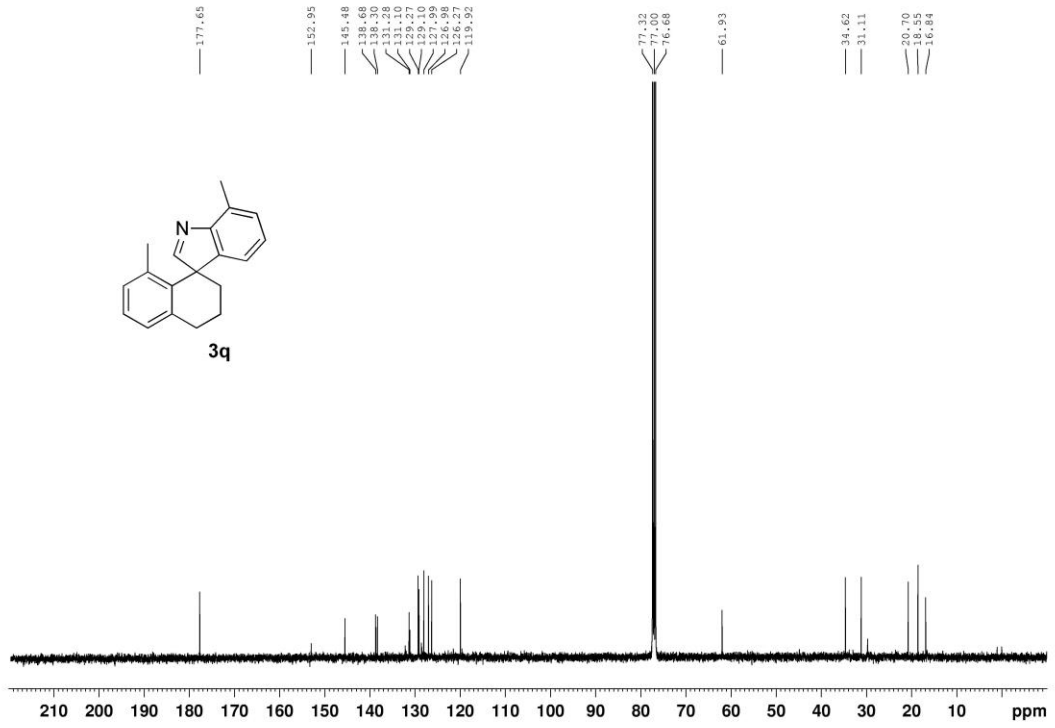
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3q
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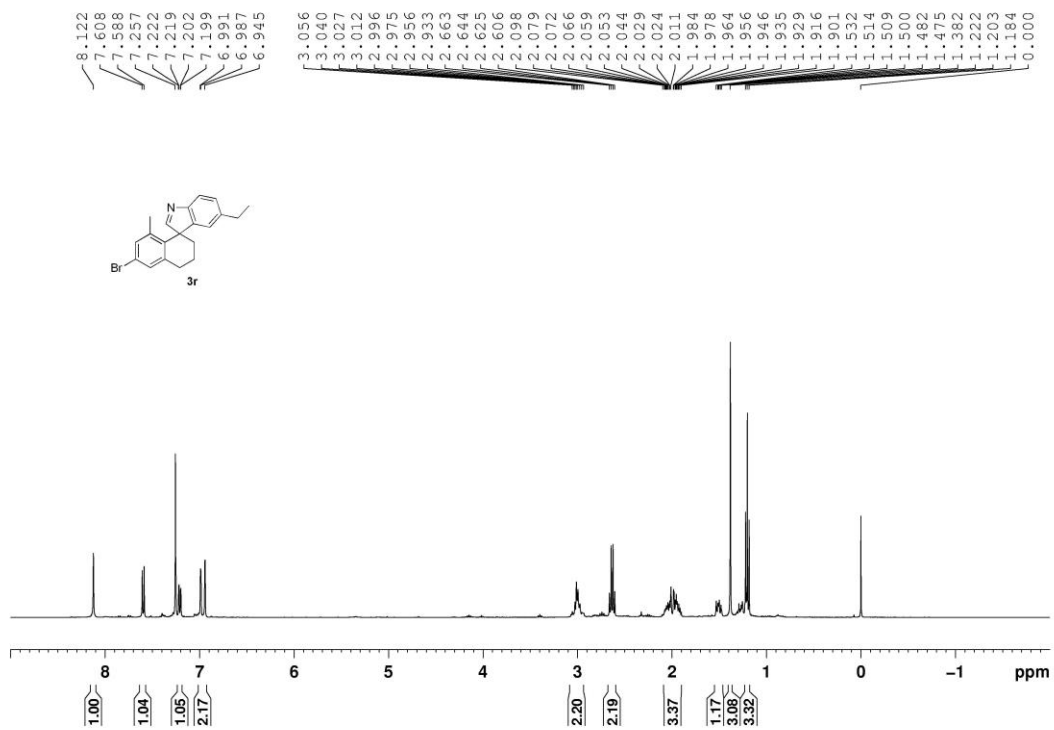
ppm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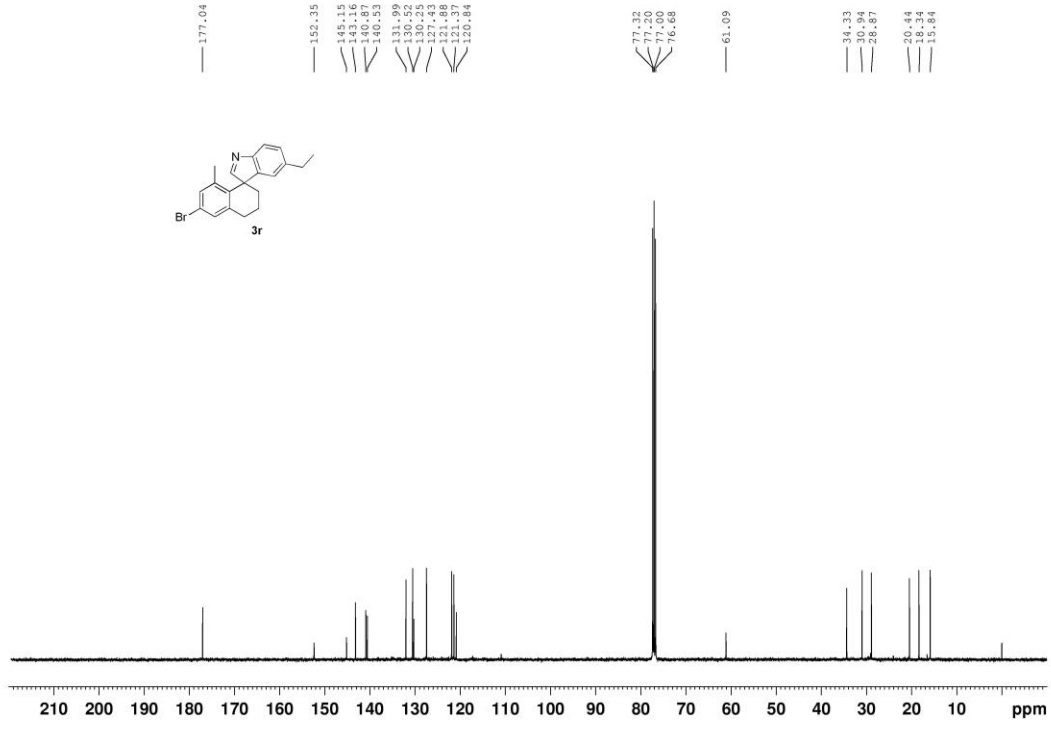
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77.20
77.00
76.68
61.09
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30.94
28.87
20.44
18.34
15.84
N
Br
3r
210
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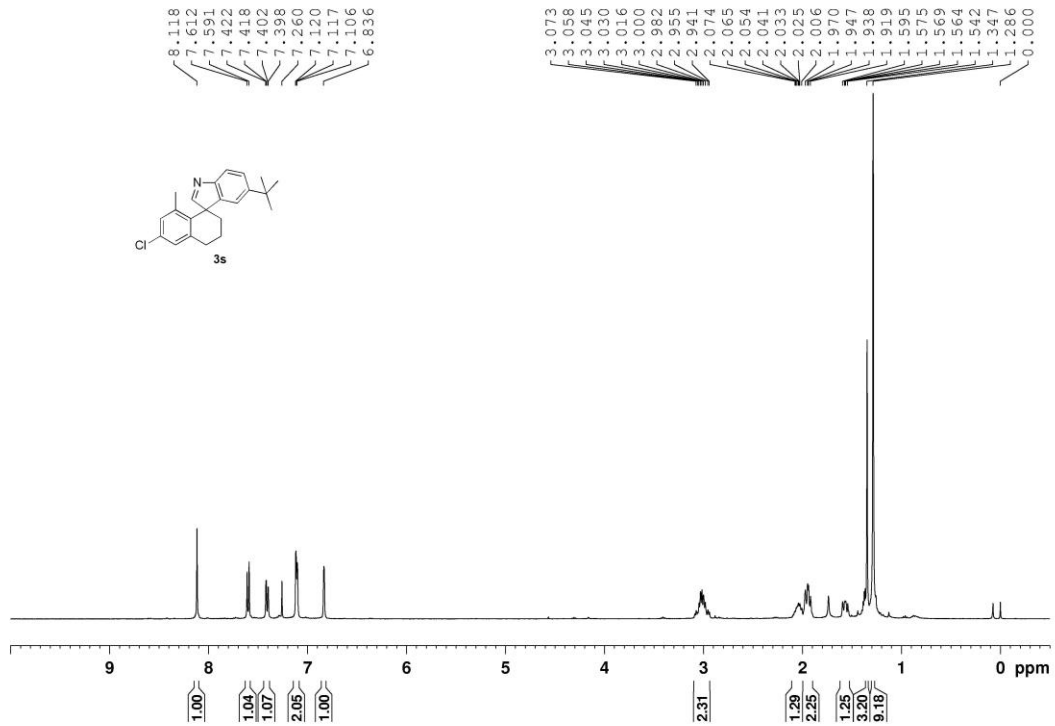
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Cl
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2
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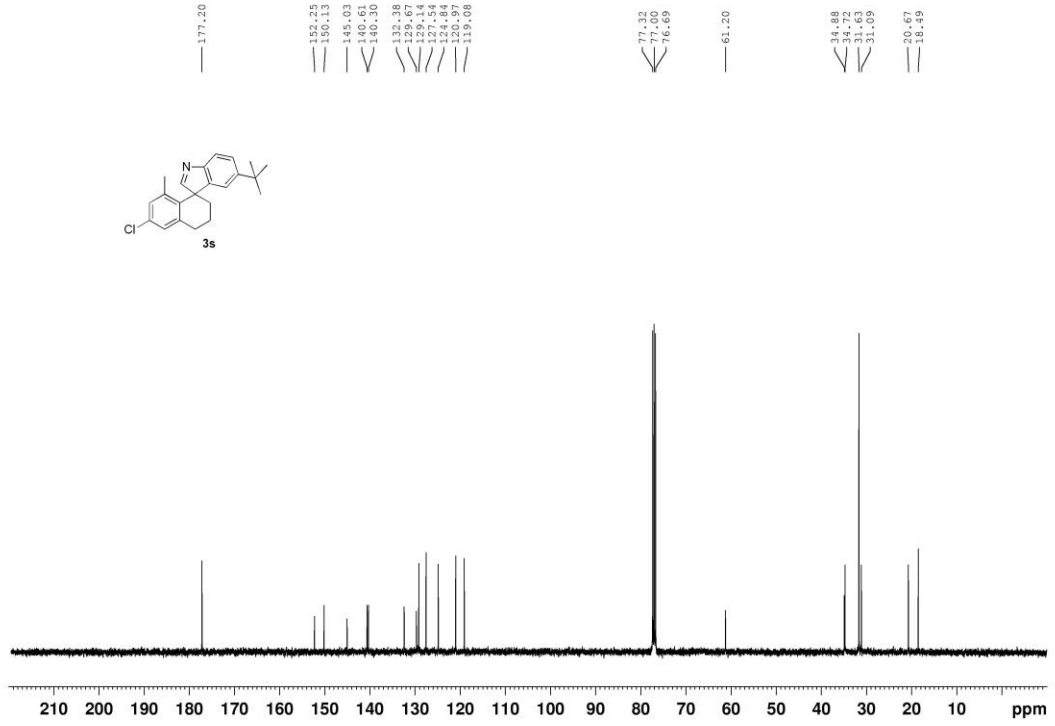
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77.00
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34.88
34.72
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20.67
18.49
N
Cl
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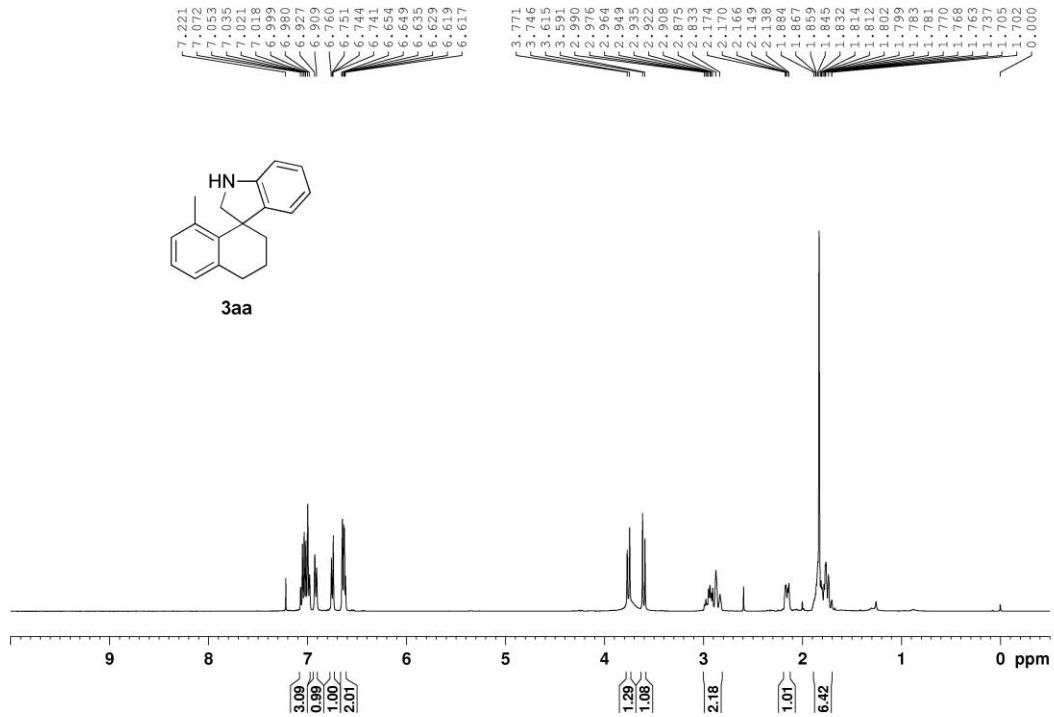
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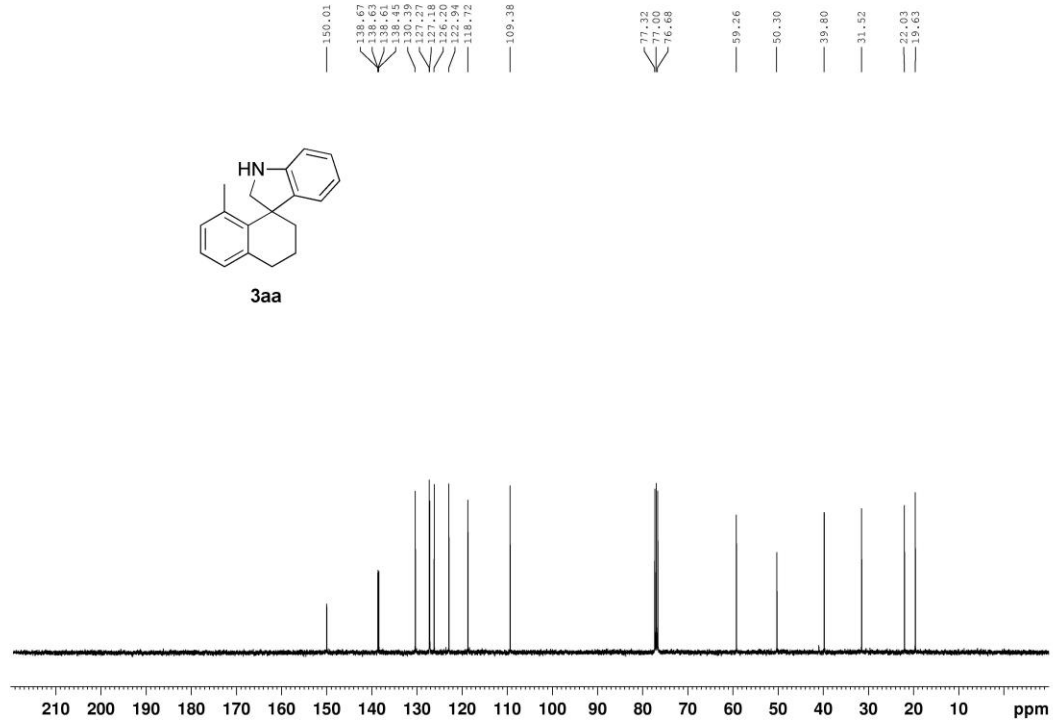
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77.00
76.68
59.26
50.30
39.80
31.52
22.03
19.63
HN
3aa
210
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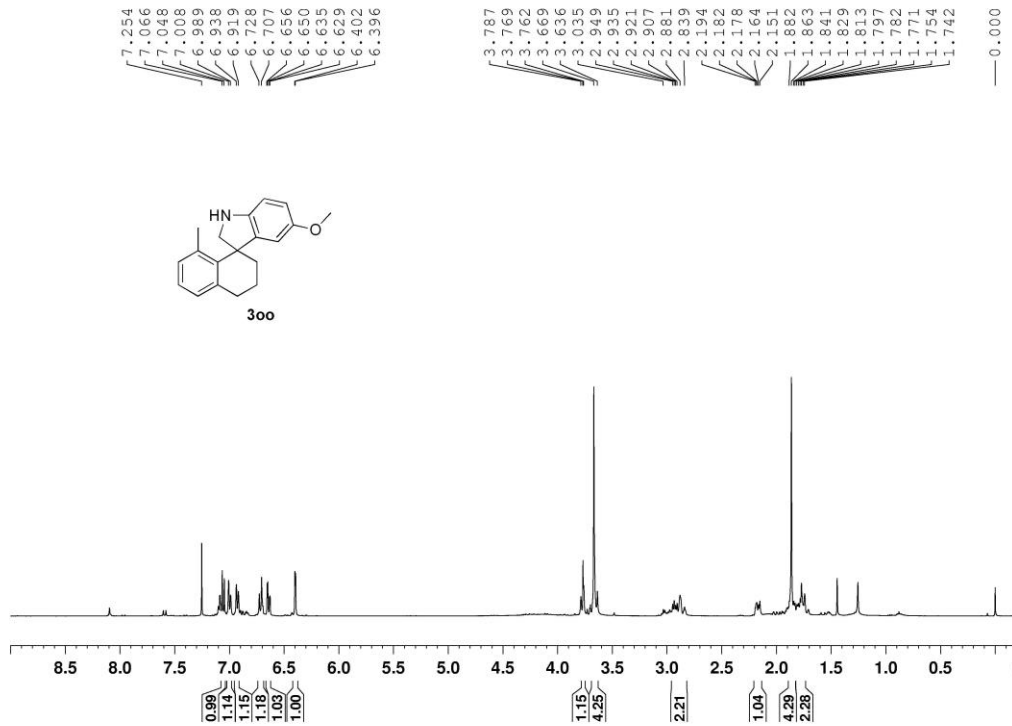
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3.762
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2.921
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HN
O
3oo
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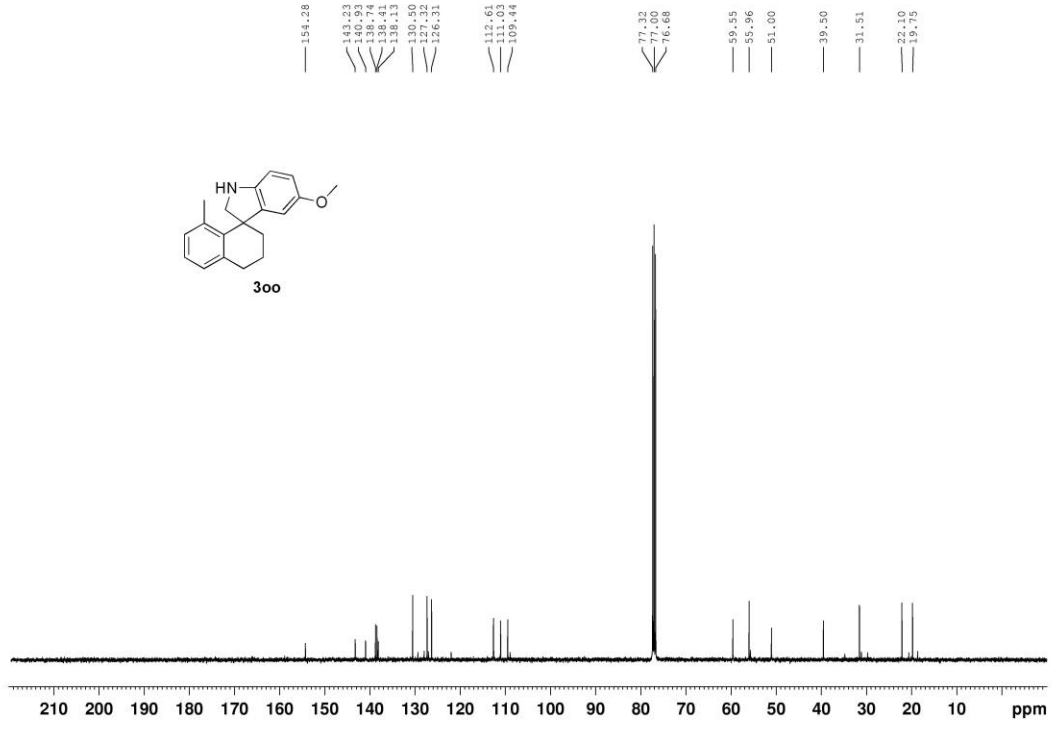
4.29
2.28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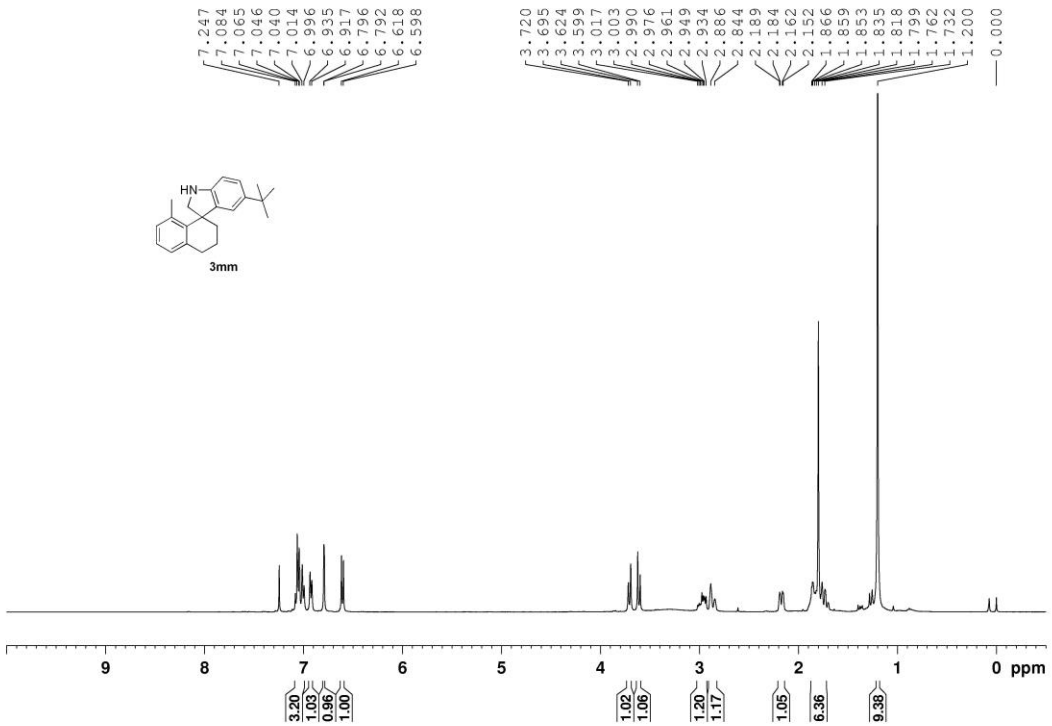
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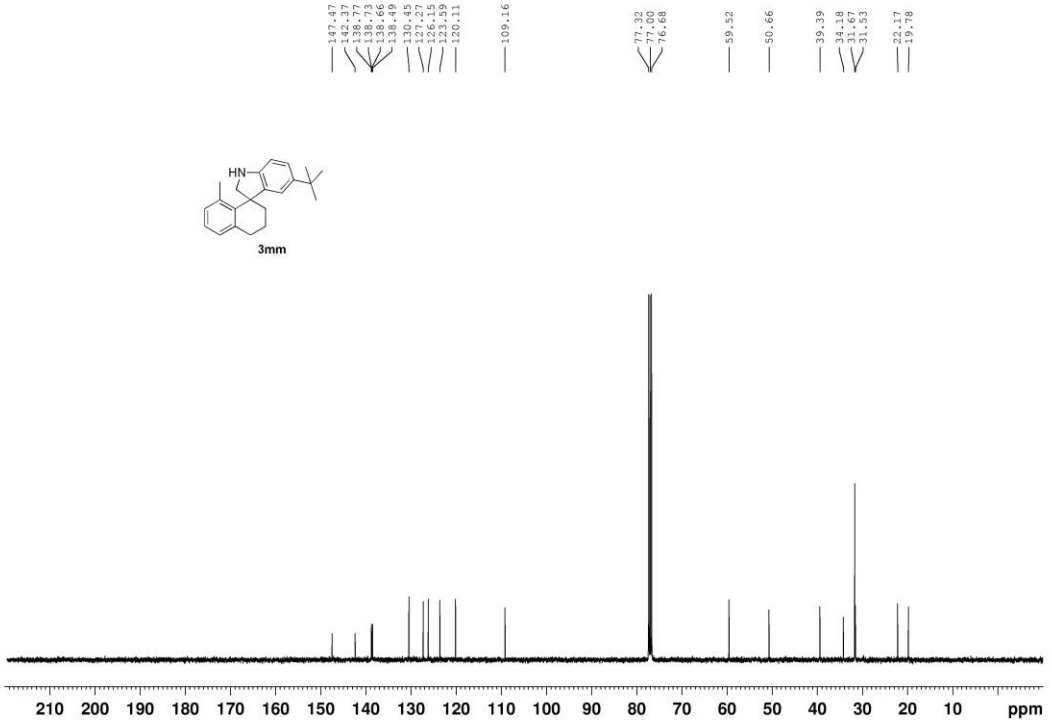
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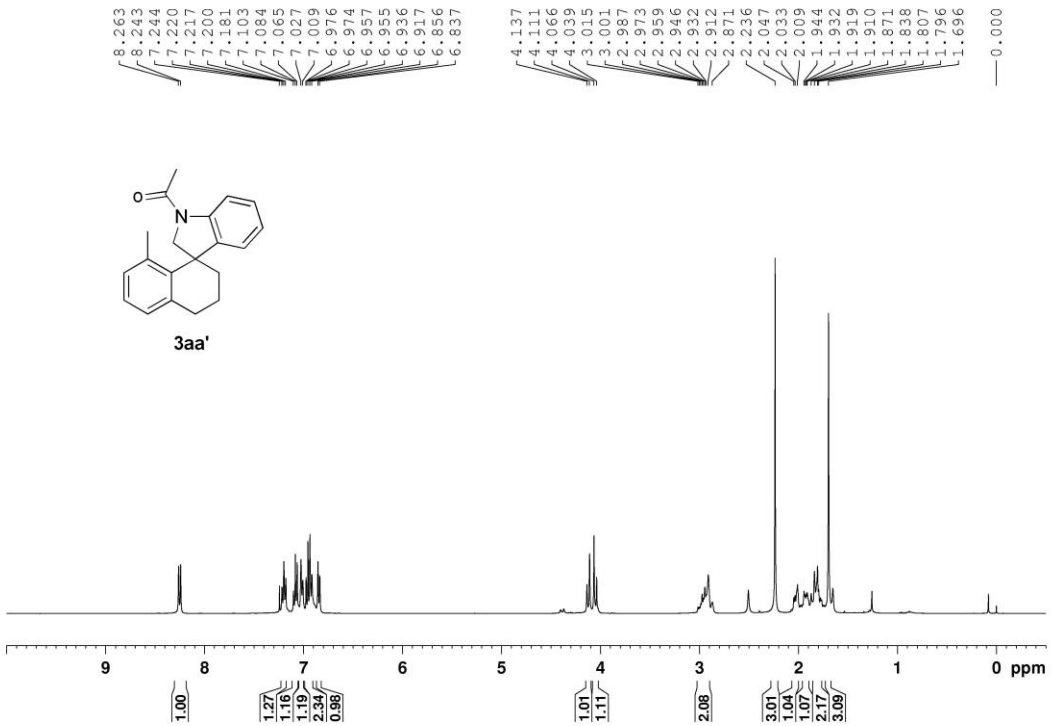
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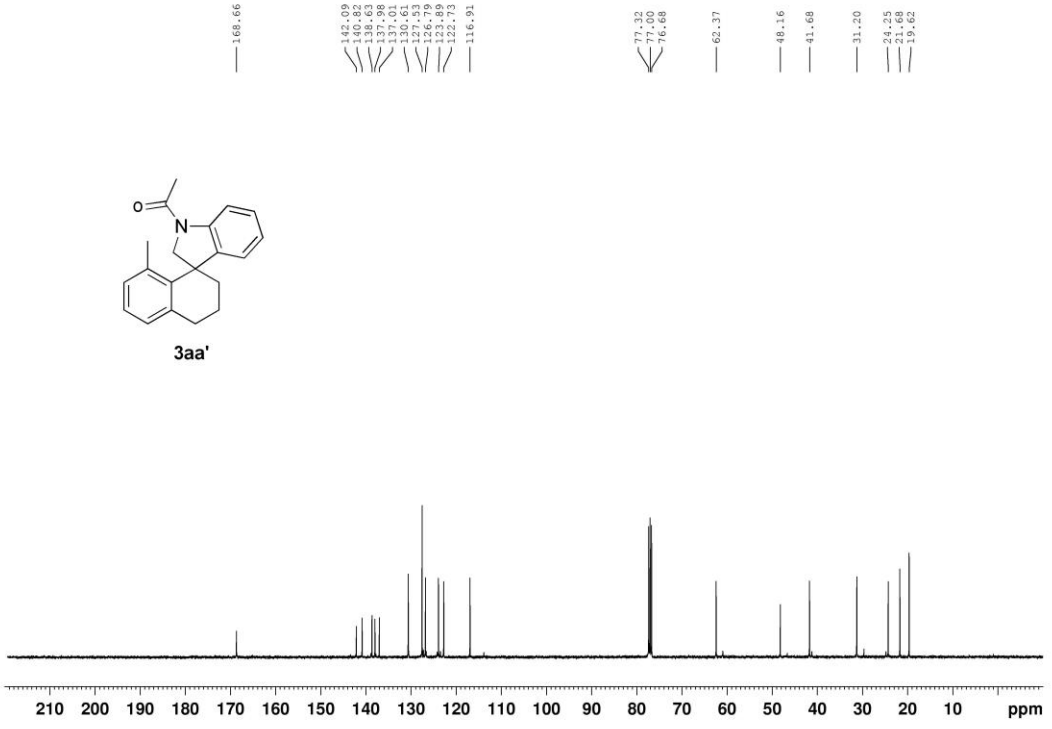
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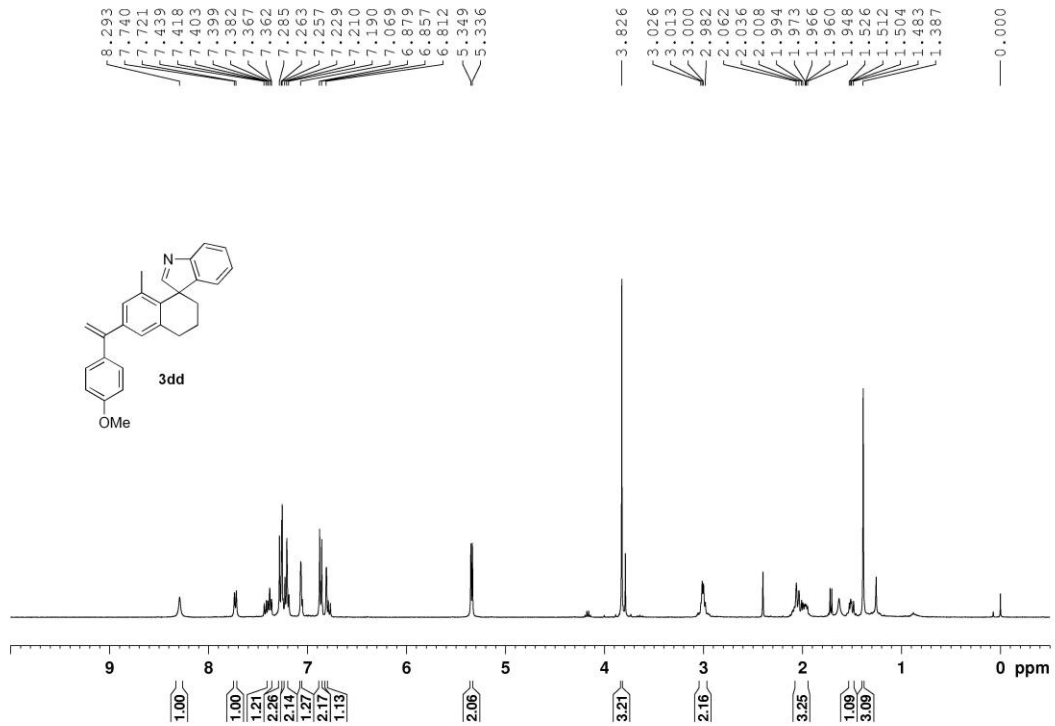
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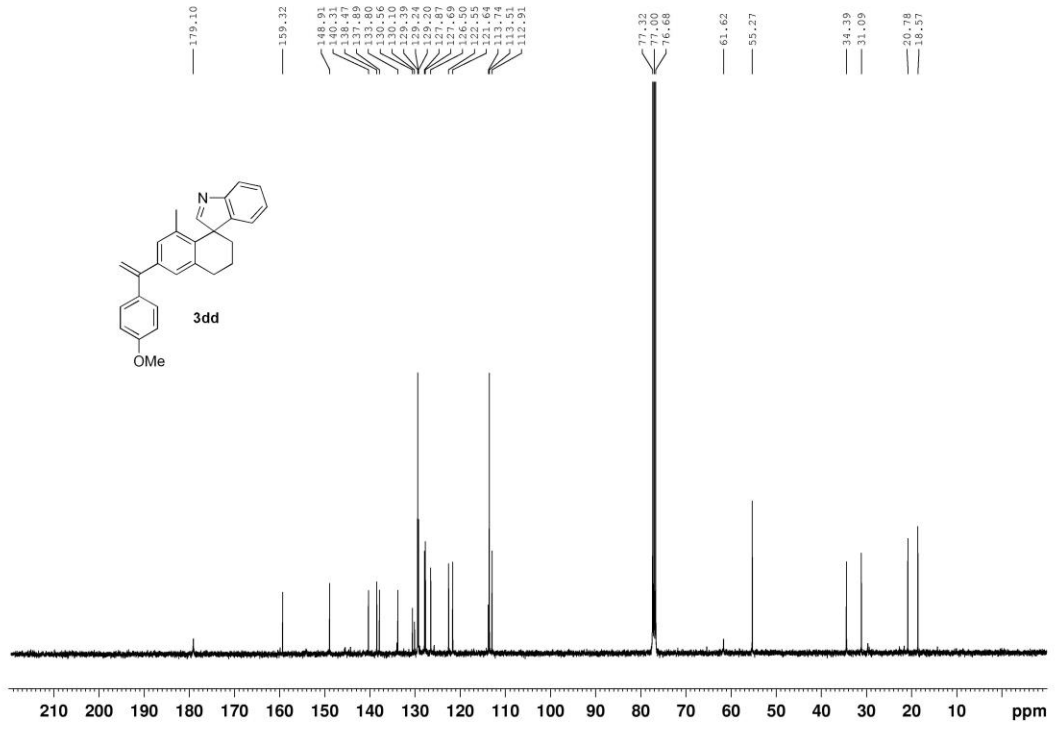
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ppm