Benzoyl Peroxide (BPO)-promoted Oxidative Trifluoromethylation of Tertiary Amines with Trimethyl(trifluoromethyl)silane

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Supporting information

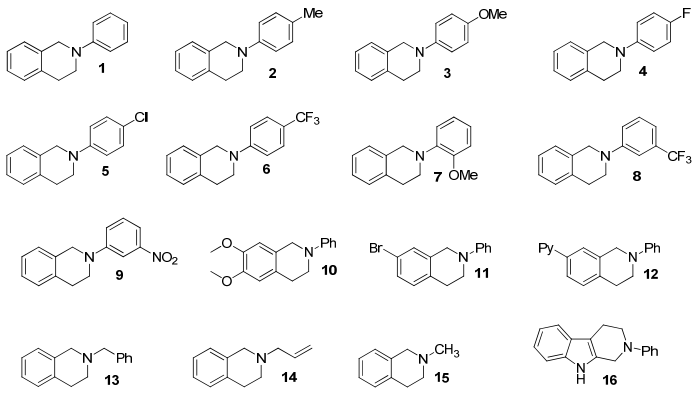
General information: ^{1}H NMR and ^{19}F NMR spectra ($CFCl_3$ as outside standard and low field is positive) were recorded on a Bruker AM300 spectrometer. ^{13}C NMR was recorded on a Bruker AM400 spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. THF was distilled from sodium and benzophenone immediately before use. DCM, CH_3CN, DCE and DME were distilled from CaH_2.

Preparation of substrates:

N-aryl-1,2,3,4-tetrahydroisoquinolines **1-11** and 2-phenyl-2,3,4,9-tetrahydro-1*H* -pyrido[3,4-*b*] indole **16** were prepared according to the procedure of Li and Buchwald.[1] Substrate **12** was prepared via Stille coupling of 2-(tributylstannyl)pyridine and substrate **11** using a literature procedure.[2] *N*-benzyl-1,2,3,4-tetrahydroisoquinoline **13** and *N*-allyl-1,2,3,4-tetrahydroisoquinoline **14** were prepared according to the procedure of Grigg.[3] *N*-methyl-1,2,3,4-tetrahydroisoquinoline **15** was prepared according to the procedure of Lasne.[4]

Substrate Structures



[1] (a) Kwong, F. Y.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2002**, *4,* 581; (b) Li, C.-J. Li, Z. *J. Am. Chem. Soc.* **2005***, 127,* 6968.

[2] Zhou, G.-J.; Wang, X.-Z.; Wong, W.-Y.; Yu, X.-M.; Kwok, H.-S.; Lin, Z. *J. Orgmet. Chem.* **2007***, 692,* 3461.

[3] Grigg, R.; Myers, P.; Somasunderam, A.; Sridharan, V. *Tetrahedron* **1992,** *48*, 9735.

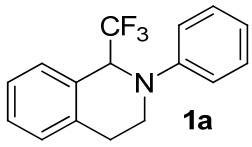
[4] Lemoucheux, L.; Rouden, J.; Ibazizene, M.; Sobrio, F.; Lasne, M.–C. *J. Org. Chem.* **2006***, 68,* 7289.

General procedure for trifluoromethylation of tetrahydroisoquinolines:

In a glove box, KF (1.5 mmol) was added to a reaction vessel that was equipped with a stirrer bar. The tube was then sealed with a screw-cap and taken out of the glove box. Tertiary amine (0.5 mmol) and 1 mL dichloromethane (DCM) were added to the reaction tube under a nitrogen atomosphere. The solution of BPO (0.75 mmol) was added dropwise to the mixture at 0 ^{o}C and then CF_3TMS (1.5 mmol) was added dropwise. The resulting mixture was heated to reflux and stirred for 5-10 h. The resulting reaction mixture was mixed with a small amount of silica gel and concentrated, and then purified by flash column chromatography on silica gel to give the desired product. Compounds **3a**/**3b**, **4a**/**4b**, **5a**/**5b**, **7a**/**7b**, **8a**/**8b**, **9a**/**9b**, **10a**/**10b**, **12a**/**12b**, **16a**/**16b** were not easily separated by flash chromatography, and the mixtures of **a**/**b** were used for the next step.

General procedure for the Hydrogenation (For the mixtures of **3a**/**3b**, **4a**/**4b**, **5a**/**5b**, **7a**/**7b**, **8a**/**8b**, **9a**/**9b**, **10a**/**10b**, **12a**/**12b**, **16a**/**16b**):

A solution of the mixture of 3**a** and 3**b** (~ 0.45 mmol) in MeOH at 23 ^{o}C was treated with 10% Pd-C (~ 60 mg) under air atmosphere. The reaction mixture was evacuated and flushed with H_2 gas (four times) and the stirred vigorously under an atmosphere of H_2 (1 atom, H_2 balloon) at 23 ^{o}C. After 24 h, the reaction mixture was filtered through Celite and concentrated in vacuo, and then purified by flash column chromatography on silica gel to give the pure **3a** in a quantitative yield.

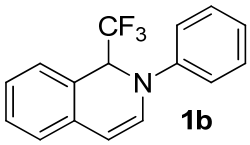


1a

2-phenyl-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **1a:**

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.30-7.21 (m, 6H), 6.98 (d, J = 8.1 Hz, 2H), 6.86 (t, J = 7.5 Hz, 1H), 5.17 (q, J = 7.5 Hz, 1H), 3.83-3.75 (m, 1H), 3.55-3.47 (m, 1H), 3.03 (br, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -71.0 (d, J= 7.3 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 149.44, 136.96, 129.44, 128.98 (d, J = 1.3 Hz), 128.91(q, J = 7.1 Hz), 126.50, 126.23(q, J = 286.0 Hz), 119.24, 114.58, 114.57, 61.20 (q, J = 29.4 Hz), 43.59,

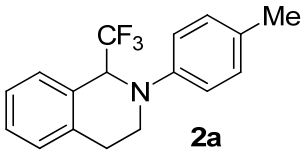
27.44 (d, J = 1.4 Hz). IR (ATR): ν_{max} 3061, 2924, 1625, 1505, 1296, 1239, 773 cm^{-1}. MS (EI): *m/z* (%) 277, 208(100), 77. HRMS: Calculated for $C_{16}H_{14}F_3N$: 277.1078; Found: 277.1080.



1b

2-phenyl-1-(trifluoromethyl)-1,2-dihydroisoquinoline **1b:**

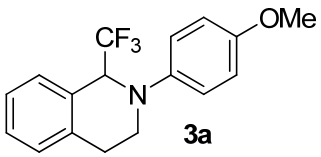
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.32 (q, J = 7.5 Hz, 3H), 7.19-7.02 (m, 6H), 6.64 (d, J = 6.6 Hz, 1H), 6.00 (d, J = 7.5 Hz, 1H), 5.42 (q, J = 6.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -75.2 (d, J= 5.4 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 145.69, 132.50, 129.47, 129.45, 129.35, 129.33, 128.88, 128.15 (d, J = 0.9 Hz), 126.34, 125.40 (q, J = 288.1 Hz), 124.20, 122.51, 121.51, 117.76 (t, J = 1.4 Hz), 106.87 (d, J = 1.2 Hz), 61.92 (q, J = 31.7 Hz). IR (ATR): ν_{max} 2942, 1599, 1504, 1297, 1124, 760, 686 cm^{-1}. MS (EI): *m/z* (%) 275, 206(100), 77. HRMS: Calculated for $C_{16}H_{12}F_3N$: 275.0922; Found: 275.0926.



2a

2-p-tolyl-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **2a:**

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.29-7.20 (m, 4H), 7.10 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.13 (q, J = 7.8 Hz, 1H), 3.80-3.72 (m, 1H), 3.50-3.42 (m, 1H), 3.00 (t, J = 5.7 Hz, 2H), 2.27 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -71.0 (d, J= 7.3 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 147.36, 136.99, 129.88, 128.97, 128.85, 128.64, 128.60, 126.37, 126.18 (q, J = 285.0 Hz), 115.02, 61.34 (q, J = 29.6 Hz), 43.83, 27.33, 20.33. IR (ATR): ν_{max} 3022, 2924, 1519, 1248, 1164, 1124, 799 cm^{-1}. MS (EI): *m/z* (%) 291, 222(100). HRMS: Calculated for $C_{17}H_{16}F_3N$: 291.1235; Found: 291.1228.

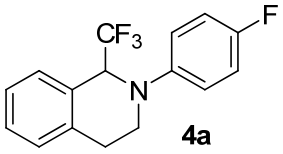


3a

2-(4-methoxyphenyl)-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **3a:**

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.44-7.30 (m, 4H), 7.03 (d, J = 9.3 Hz, 2H), 6.97 (d, J = 9.6 Hz, 2H), 5.14 (q, J = 7.8 Hz, 1H), 3.89 (s, 3H), 3.86-3.81 (m, 1H), 3.57-3.49

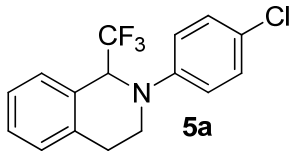
(m, 1H), 3.08 (t, *J* = 6.0 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -71.4 (d, *J*= 7.9 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 153.60, 144.07, 137.02, 128.86 (td, *J* = 2.0 Hz, *J* = 3.8 Hz, *J* = 5.7 Hz), 128.68, 138.56, 126.15 (q, *J* = 284.9 Hz), 117.55, 114.69, 61.91 (q, *J* = 29.3 Hz), 55.62, 44.68 (d, *J* = 1.2 Hz), 27.51 (d, *J* = 1.0 Hz). IR (ATR): ν_{max} 3033, 2961, 1512, 1465, 1032, 949, 807, 683 cm^{-1}. MS (EI): *m/z* (%) 307, 238(100), 119, 77. HRMS: Calculated for $C_{17}H_{16}F_3NO$: 307.1184; Found: 307.1180.



4a

2-(4-fluorophenyl)-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **4a**:

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.32-7.20 (m, 4H), 7.01-6.88 (m, 4H), 5.05 (q, *J* = 7.8 Hz, 1H), 3.78-3.70 (m, 1H), 3.45-3.37 (m, 1H), 2.99 (br, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -71.4 (d, *J*= 7.1 Hz, 3F), -125.8~-125.9 (m, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 156.86 (d, *J* =237.2 Hz), 146.11 (d, *J* =2.3 Hz), 136.76, 128.84 (q, *J* =1.6 Hz), 128.75, 128.71 (q, *J* =0.7 Hz), 128.63, 126.45, 126.04 (q, *J* = 285.6 Hz), 116.56 (d, *J* = 0.9 Hz), 116.48 (d, *J* =0.8 Hz), 115.84, 115.61, 61.70 (q, *J* =29.4 Hz), 44.31 (d, *J* = 0.9 Hz), 27.23 (d, *J* = 1.2 Hz). IR (ATR): ν_{max} 3059, 2929, 1511, 1246, 1162, 1122, 812, 746 cm^{-1}. MS (EI): *m/z* (%) 295, 226(100). HRMS: Calculated for $C_{16}H_{13}F_4N$: 295.0984; Found: 295.0983.

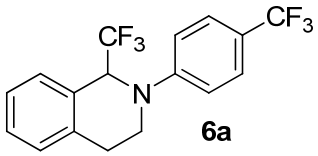


5a

2-(4-chlorophenyl)-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **5a**:

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.35-7.20 (m, 6H), 6.89 (d, *J* = 9.0 Hz, 2H), 5.10 (q, *J* = 7.8 Hz, 1H), 3.80-3.72 (m, 1H), 3.48-3.39 (m, 1H), 3.13-2.95 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -71.4 (d, *J*= 8.7 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 147.90, 136.59, 129.32, 129.09, 128.86, 128.82 (q, *J* =1.7 Hz), 128.57 (d, *J* =1.3 Hz), 128.52, 126.52, 125.90 (q, *J* =285.3 Hz), 124.02, 115.59 (d, *J* = 0.6 Hz), 61.10 (d, *J* =30.2 Hz), 43.73, 27.34 (t, *J* = 1.4 Hz). IR (ATR): ν_{max} 3059, 2929, 1511, 1246, 1162, 1122, 812, 746 cm^{-1}. MS (EI): *m/z* (%) 311, 242 (100), 77. HRMS: Calculated for $C_{16}H_{13}F_3NCl$:

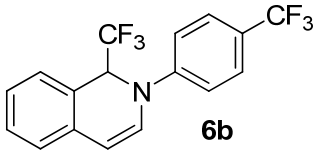
311.0689; Found: 311.0692.



6a

1-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline **6a**:

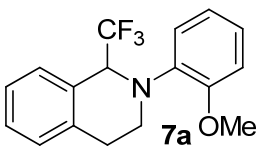
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.53 (d, *J* = 8.7 Hz, 2H), 7.36-7.24 (m, 4H), 7.00 (d, *J* = 8.4 Hz, 2H), 5.23 (q, *J* = 7.5 Hz, 1H), 3.86-3.78 (m, 1H), 3.55-3.47 (m, 1H), 3.20-2.30 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -61.7 (s, 3F), -71.5 (d, *J*= 7.3 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 151.34 (d, *J* =0.9 Hz), 136.39, 129.06, 128.82 (dd, *J* =1.8 Hz, *J* =3.0 Hz), 128.47, 128.41 (t, *J* =235.0 Hz), 127.21 (q, *J* =285.8 Hz), 126.67, 126.56 (q, *J* = 3.8 Hz), 113.12 (d, *J* = 1.2 Hz), 60.58 (q, *J* =30.5 Hz), 43.47, 27.44 (q, *J* = 2.0 Hz). IR (ATR): ν_{max} 3071, 2927, 1620, 1317, 820, 695 cm^{-1}. MS (EI): *m/z* (%) 345, 276 (100). HRMS: Calculated for $C_{17}H_{13}F_6N$: 345.0952; Found: 345.0956.



6b

1-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinoline **6b**:

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.60 (d, *J* = 8.7 Hz, 2H), 7.37 (t, *J* = 1.5 Hz, 1H), 7.36-7.15 (m, 5H), 6.66 (d, *J* = 6.9 Hz, 1H), 6.12 (d, *J* = 7.5 Hz, 1H), 5.44 (q, *J* = 6.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -62.2 (s, 3F), -75.3 (d, *J*= 7.6 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 147.86, 131.93, 129.59, 128.14 (q, *J* = 1.0 Hz), 127.48, 126.85, 126.70 (q, *J* = 3.9 Hz), 124.59, 124.29 (q, *J* =269.6 Hz), 124.09, 123.76, 123.68, 116.54 (q, *J* = 1.4 Hz), 108.84, 61.16 (q, *J* = 31.0 Hz). IR (ATR): ν_{max} 3059, 2926, 1614, 1328, 777, 684 cm^{-1}. MS (EI): *m/z* (%) 343, 274(100). HRMS: Calculated for $C_{17}H_{11}F_6N$: 343.0796; Found: 343.0801.

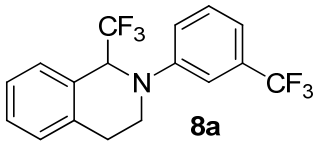


7a

2-(2-methoxyphenyl)-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **7a**:

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.34-7.18 (m, 4H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 2H), 5.14 (q, *J* = 8.1 Hz, 1H), 3.78 (s, 3H), 3.71-3.67 (m, 1H), 3.50-3.43

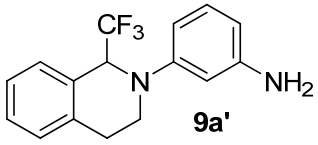
(m, 1H), 3.04-2.85 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -69.4 (d, J= 5.6 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 153.19, 139.87, 136.62, 129.28 (dd, J = 0.8 Hz, J = 2.2 Hz), 128.99, 128.68 (q, J = 1.8 Hz), 128.11, 126.60 (q, J = 287.7 Hz), 125.86, 124.23, 123.87, 121.21, 112.16, 60.67 (q, J = 26.5 Hz), 55.58, 45.15 (d, J = 1.3 Hz), 28.01. IR (ATR): ν_{max} 3059, 2962, 1595, 1503, 1261, 1106, 1027, 802, 749 cm^{-1}. MS (EI): *m/z* (%) 307, 238(100), 77. HRMS: Calculated for $C_{17}H_{16}F_3NO$: 307.1184; Found: 307.1183.



8a

1-(trifluoromethyl)-2-(3-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline **8a**:

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.41-7.30 (m, 3H), 7.25 (t, J = 6.9 Hz, 2H), 7.16-7.08 (m, 3H), 5.18 (q, J = 7.8 Hz, 1H), 3.85-3.77 (m, 1H), 3.53-3.44 (m, 1H), 3.18-2.98 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -63.1 (s, 3F), -71.5 (d, J= 8.5 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 149.37, 136.47, 131.63 (q, J =31.9 Hz), 129.78, 129.00, 128.86 (q, J =1.8 Hz), 128.50, 128.44 (q, J =0.5 Hz), 125.86 (q, J =285.4 Hz), 123.69 (q, J = 271.4 Hz), 117.07 (t, J = 1.4 Hz), 115.43 (q, J =4.0 Hz), 110.42 (q, J = 4.4 Hz), 60.93 (q, J = 30.7 Hz), 43.60, 27.41 (q, J = 1.7 Hz). IR (ATR): ν_{max} 3037, 2933, 1612, 1455, 1338, 1165, 1121, 755, 696 cm^{-1}. MS (EI): *m/z* (%) 345, 276 (100). HRMS: Calculated for $C_{17}H_{13}F_6N$: 345.0952; Found: 345.0956.

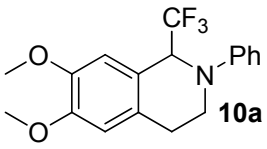


9a'

3-(1-(trifluoromethyl)-3,4-dihydroisoquinolin-2(1H)-yl)aniline **9a'** :

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.32-7.20 (m, 4H), 7.06 (t, J = 8.4 Hz, 1H), 6.40 (d, J = 8.4 Hz, 1H), 6.30 (s, 1H), 6.22 (d, J = 7.8 Hz, 1H), 5.14 (q, J = 7.8 Hz, 1H), 3.79-3.71 (m, 1.5H), 3.53-3.45 (m, 1.5H), 3.01 (t, J = 6.0 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -70.8 (d, J= 7.3 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 150.62, 147.47, 136.89, 130.10, 128.95 (q, J = 1.0 Hz), 128.75 (q, J = 1.4 Hz), 128.59, 128.50, 126.33, 126.02 (q, J = 285.3 Hz), 106.52, 105.30 (d, J = 0.8 Hz), 101.48, 61.03 (q, J = 30.0 Hz), 43.48, 27.32 (d, J = 0.8 Hz). IR (ATR): ν_{max} 3459, 3341, 3022, 2928, 1609, 1502, 1249,

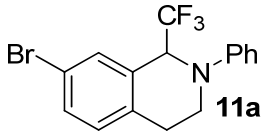
1162, 756, 690 cm^{-1}. MS (EI): *m/z* (%) 292, 223 (100). HRMS: Calculated for $C_{16}H_{15}F_3N_2$: 292.1187; Found: 292.1186.



10a

6,7-dimethoxy-2-phenyl-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **10a**:

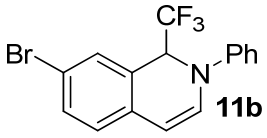
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.30 (t, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.90-6.84 (m, 2H), 6.71 (s, 1H), 5.12 (q, *J* = 7.5 Hz, 1H), 3.89 (s, 6H), 3.82-3.74 (m, 1H), 3.61-3.53 (m, 1H), 2.97-2.92 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -71.2 (d, *J*= 6.5 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 149.48, 129.20, 147.41, 129.26, 126.20 (q, *J* = 285.4 Hz), 120.36, 120.35, 119.23, 114.84, 111.51 (q, *J* = 2.1 Hz), 111.22, 60.68 (q, *J* = 29.3 Hz), 56.05, 55.87, 43.4, 26.66 (q, *J* = 1.4 Hz). IR (ATR): ν_{max} 3067, 2934, 1600, 1521, 1257, 1115, 750 cm^{-1}. MS (EI): *m/z* (%) 337, 268 (100). HRMS: Calculated for $C_{18}H_{18}F_3NO_2$: 337.1290; Found: 337.1284.



11a

7-bromo-2-phenyl-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **11a**:

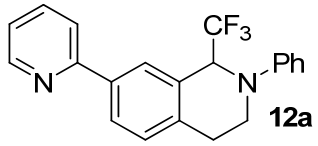
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.48(s, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.31-7.23 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.88 (t, *J* = 6.9 Hz, 1H), 5.11 (q, *J* = 7.5 Hz, 1H), 3.79-3.71 (m, 1H), 3.58-3.50 (m, 1H), 2.96-2.93 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -71.0 (d, *J*= 9.3 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 149.08, 135.82, 131.74, 131.52 (q, *J* =2.2 Hz), 130.84 (q, *J* =1.5 Hz), 130.19, 129.40, 125.78 (q, *J* =285.6 Hz), 119.75, 119.61, 114.88 (d, *J* = 1.0 Hz), 60.65 (d, *J* =30.1 Hz), 43.16 (d, *J* = 0.7 Hz), 26.67 (d, *J* = 1.5 Hz). IR (ATR): ν_{max} 3037, 2927, 1599, 1509, 949, 749 cm^{-1}. MS (EI): *m/z* (%) 355, 286 (100), 77. HRMS: Calculated for $C_{16}H_{13}F_3NBr$: 355.0183; Found: 355.0178.



11b

7-bromo-2-phenyl-1-(trifluoromethyl)-1,2-dihydroisoquinoline **11b**:

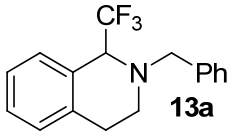
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.45-7.31(m, 4H), 7.11-7.02 (m, 4H), 6.67 (d, *J* = 7.2 Hz, 1H), 5.97 (d, *J* = 7.5 Hz, 2H), 5.37 (q, *J* = 6.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -75.5 (d, *J*= 6.6 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 149.18, 145.38, 132.30, 131.49, 130.88 (q, *J* =1.0 Hz), 129.51, 129.46, 125.56, 125.01 (q, *J* = 287.4 Hz), 122.93, 119.16, 118.00 (q, *J* = 1.7 Hz), 106.00, 61.55 (q, *J* =31.6 Hz). IR (ATR): ν_{max} 3037, 2927, 1599, 1509, 949, 749 cm^{-1}. MS (EI): *m/z* (%) 353, 284 (100), 77. HRMS: Calculated for $C_{16}H_{11}F_3NBr$: 353.0027; Found: 353.0028.



12a

2-phenyl-7-(pyridin-2-yl)-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **12a**:

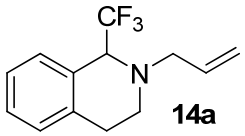
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.69 (d, *J* = 3.0 Hz, 1H), 8.00 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.79-7.73 (m, 2H), 7.35-7.23 (m, 4H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 5.28 (q, *J* = 7.8 Hz, 1H), 3.85-3.79 (m, 1H), 3.60-3.52 (m, 1H), 3.11-3.09 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -70.6 (d, *J*= 7.9 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 156.62, 149.63, 149.32, 137.82, 137.01, 129.47, 129.35, 129.05, 127.37, 127.14, 125.96 (q, *J* =284.1 Hz), 122.30, 120.49, 119.33, 114.76, 61.14 (q, *J* = 30.1 Hz), 43.48, 27.15. IR (ATR): ν_{max} 3054, 2929, 1603, 1519, 949, 759 cm^{-1}. MS (EI): *m/z* (%) 354, 285 (100), 77. HRMS: Calculated for $C_{21}H_{17}F_3N_2$: 354.1344; Found: 354.1349.



13a

2-benzyl-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **13a**:

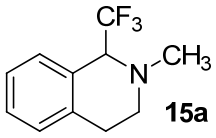
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.32-7.07 (m, 9H), 4.16 (q, *J* = 7.8 Hz, 1H), 3.87 (dd, *J* = 13.2 Hz, *J* = 41.7 Hz, 2H), 3.21-3.13 (m, 1H), 2.75-2.69 (m, 2H), 2.65-2.56 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -72.2 (d, *J*= 8.2 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 137.58, 136.40, 128.44 (d, *J* =1.6 Hz), 127.61, 127.57, 127.38, 127.10, 126.30, 125.22 (q, *J* =282.5 Hz), 124.98, 61.62 (q, *J* =26.9 Hz), 59.52, 44.53, 25.79. IR (ATR): ν_{max} 3067, 2961, 1494, 1453, 1259, 751 cm^{-1}. MS (EI): *m/z* (%) 291, 222 (100), 91. HRMS: Calculated for $C_{17}H_{16}F_3N$: 291.1235; Found: 291.1245.



14a

2-allyl-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **14a**:

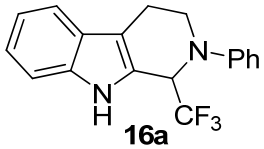
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.41-7.29 (m, 4H), 6.08-5.97 (m, 1H), 5.35-5.29 (m, 2H), 4.34 (q, *J* = 9.0 Hz, 1H), 3.54 (d, *J* = 6.6 Hz, 2H), 3.46-3.40 (m, 1H), 2.96-2.86 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -72.4 (d, *J*= 7.8 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 137.44, 134.87, 129.47 (dd, *J* =1.7 Hz, *J* =3.5 Hz), 128.55, 128.31 (dd, *J* =0.9 Hz, *J* =1.2 Hz), 128.12, 127.53 (q, *J* =283.2 Hz), 126.05, 118.26, 61.54 (q, *J* =27.3 Hz), 59.14 (q, *J* = 1.3 Hz), 46.18 (q, *J* = 1.9 Hz), 28.82. IR (ATR): ν_{max} 3030, 2960, 1258, 1156, 1114, 917, 751 cm^{-1}. MS (EI): *m/z* (%) 241, 172 (100), 77. HRMS: Calculated for $C_{13}H_{14}F_3N$: 241.1078; Found: 241.1087.



15a

2-methyl-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline **15a**:

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.22-7.08(m, 4H), 3.98 (q, *J* = 7.8 Hz, 1H), 3.20-3.14 (m, 1H), 2.87-2.79 (m, 1H), 2.75-2.67 (m, 1H), 2.60 (s, 3H), 2.55-2.51 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -73.6 (d, *J*= 8.5 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 137.53, 129.42 (q, *J* = 2.0 Hz), 128.30, 128.25 (q, *J* = 1.4 Hz), 128.09, 126.11 (q, *J* = 281.5 Hz), 126.05, 64.80 (q, *J* = 30.1 Hz), 49.90, 45.39 (t, *J* = 1.6 Hz), 28.06. IR (ATR): ν_{max} 3059, 2926, 1257, 1157, 1116, 752 cm^{-1}. MS (EI): *m/z* (%) 215, 146 (100), 77. HRMS: Calculated for $C_{11}H_{12}F_3N$: 215.0922; Found: 215.0918.



16a

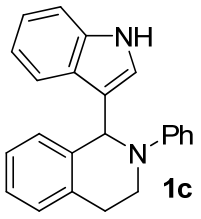
2-phenyl-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole **16a**:

^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.98 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.29-7.20 (m, 3H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.89 (t, *J* = 6.4 Hz, 1H), 5.12 (d, *J* = 7.8 Hz, 1H), 4.01 (dd, *J* = 4.8 Hz, *J* = 14.4 Hz, 1H), 3.81-3.71

(m, 1H), 3.05-2.95 (m, 1H), 2.71 (dd, J = 3.6 Hz, J = 15.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -72.6 (d, J= 7.1 Hz, 3F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 150.14, 136.41, 129.44, 126.43, 125.62 (q, J = 284.4 Hz), 124.26, 123.06, 120.54, 119.85, 118.86, 117.18, 113.78, 58.66 (q, J = 31.6 Hz), 43.87, 19.00. IR (ATR): ν_{max} 3422, 3059, 2963, 1778, 1594, 1490, 1119, 744, 688 cm^{-1}. MS (ESI): *m/z* 317 $(M + H)^+$; HRMS Calculated for $C_{18}H_{16}F_3N_2^+$ 317.1271; Found: 317.1260 (M + H)

Procedure for the oxidative coupling of 1,2,3,4-tetrahydroisoquioline with indole:

1,2,3,4-tetrahydroisoquinoline **1** (0.5 mmol), indole (1.5 mmol) and 1 mL DCM were added to a reaction tube under a nitrogen atomosphere. The solution of BPO (0.75 mmol) was added dropwise to the mixture at 0 ^{o}C. The resulting mixture was heated to reflux and stirred for 10 h. At the end of reaction, the resulting reaction mixture was allowed to cool room temperature, diluted with DCM, washed with saturated $NaHCO_3$ and then brine, and dried with anhydrous Na_2SO_4. The crude product was concentrated and then purified by flash column chromatography on silica gel to give the desired product.



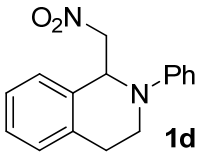
1c

1-(1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline **1c**:
Known compound
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.90 (s, 1 H), 7.60 (d, J = 26.1 Hz, 1H), 7.35-7.12 (m, 8H), 7.03-7.01 (m, 3H), 6.78 (t, J = 6.6 Hz, 1H), 6.61 (s, 1H), 6.17 (s, 1H), 3.64-3.60 (m, 2 H), 3.11-3.01 (m, 1 H), 2.83-2.77 (m, 1 H).

Procedure for the oxidative coupling of 1,2,3,4-tetrahydroisoquioline with nitromethane:

1,2,3,4-tetrahydroisoquinoline **1** (0.5 mmol), CH_3NO_2 (1.5 mmol) and 1 mL DCM were added to a reaction tube under a nitrogen atomosphere. The solution of BPO (0.75 mmol) was added dropwise to the mixture at 0 ^{o}C. The resulting mixture was heated to reflux and stirred for 10 h. At the end of reaction, the resulting reaction mixture was allowed to cool room

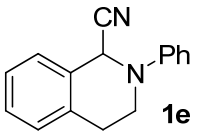
temperature, diluted with DCM, washed with saturated $NaHCO_3$ and then brine, and dried with anhydrous Na_2SO_4. The crude product was concentrated and then purified by flash column chromatography on silica gel to give the desired product.



1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline **1d**:
Known compound
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.23-7.05 (m, 6 H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.77 (t, *J* = 7.2 Hz, 1H), 5.47 (t, *J* = 7.8 Hz, 1H), 4.80 (dd, *J* = 8.1 Hz, *J* = 11.7 Hz, 1H), 4.49 (dd, *J* = 6.9 Hz, *J* = 12.0 Hz, 1H), 3.59-3.54 (m, 2 H), 3.06-2.96 (m, 1 H), 2.76-2.67 (m, 1 H).

Procedure for the oxidative cyanation of 1,2,3,4-tetrahydroisoquioline with TMSCN:

1,2,3,4-tetrahydroisoquinoline **1** (0.5 mmol), TMSCN (1.5 mmol) and 1 mL DCM were added to a reaction tube under a nitrogen atomosphere. The solution of BPO (0.75 mmol) was added dropwise to the mixture at 0 ^{o}C. The resulting mixture was heated to reflux and stirred for 10 h. At the end of reaction, the resulting reaction mixture was allowed to cool room temperature, diluted with DCM, washed with saturated $NaHCO_3$ and then brine, and dried with anhydrous Na_2SO_4. The crude product was concentrated and then purified by flash column chromatography on silica gel to give the desired product.



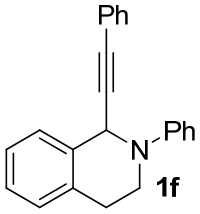
2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile **1e**:

Known compound
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.21-6.93 (m, 9 H), 5.39 (s, 1 H), 3.67-3.61 (m, 1 H), 3.42-3.33 (m, 1 H), 3.15-3.04 (m, 1 H), 3.90-2.85 (m, 1 H).

Procedure for the oxidative coupling of 1,2,3,4-tetrahydroisoquioline with phenylacetylene:

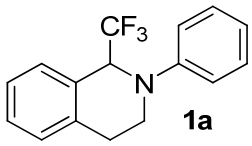
1,2,3,4-tetrahydroisoquinoline **1** (0.5 mmol), CuBr (0.1 mmol), phenylacetylene (1.5 mmol)

and 1 mL DCM were added to a reaction tube under a nitrogen atomosphere. The solution of BPO (0.75 mmol) was added dropwise to the mixture at 0 ^{o}C. The resulting mixture was heated to reflux and stirred for 10 h. At the end of reaction, the resulting reaction mixture was allowed to cool room temperature, diluted with DCM, washed with saturated $NaHCO_3$ and then brine, and dried with anhydrous Na_2SO_4. The crude product was concentrated and then purified by flash column chromatography on silica gel to give the desired product.



1f

2-phenyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline **1f**:
Known compound.
^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.46-6.78 (m, 14 H), 5.57 (s, 1H), 3.69-3.55 (m, 2 H), 3.12-2.92 (m, 1 H), 2.91-2.87 (m, 1 H).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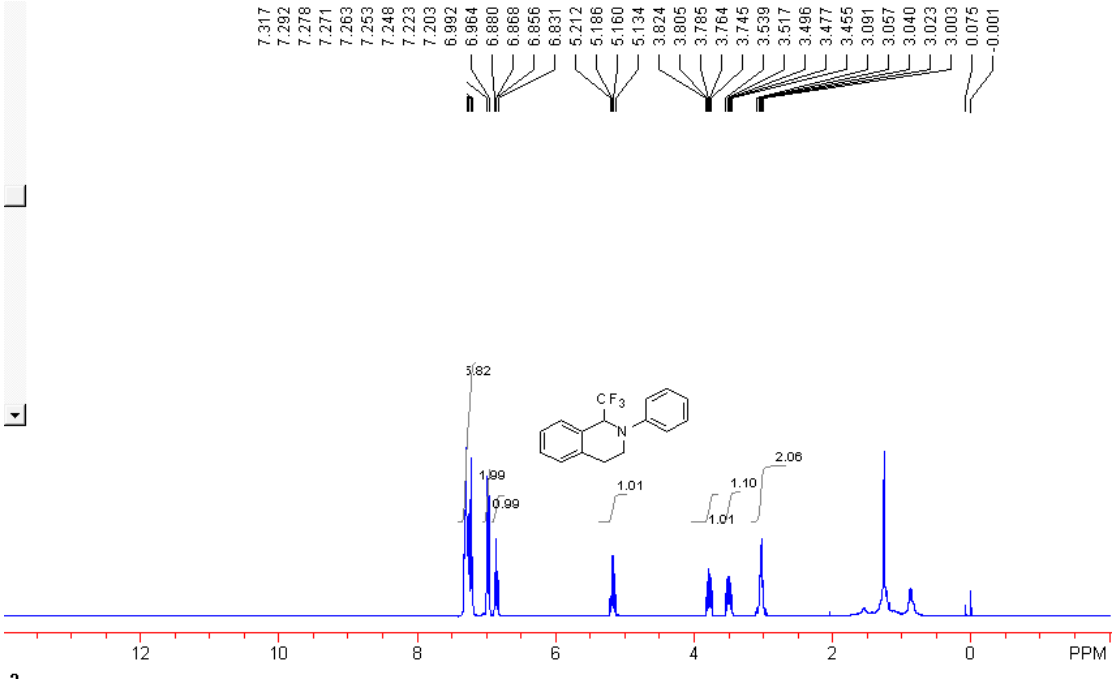
1a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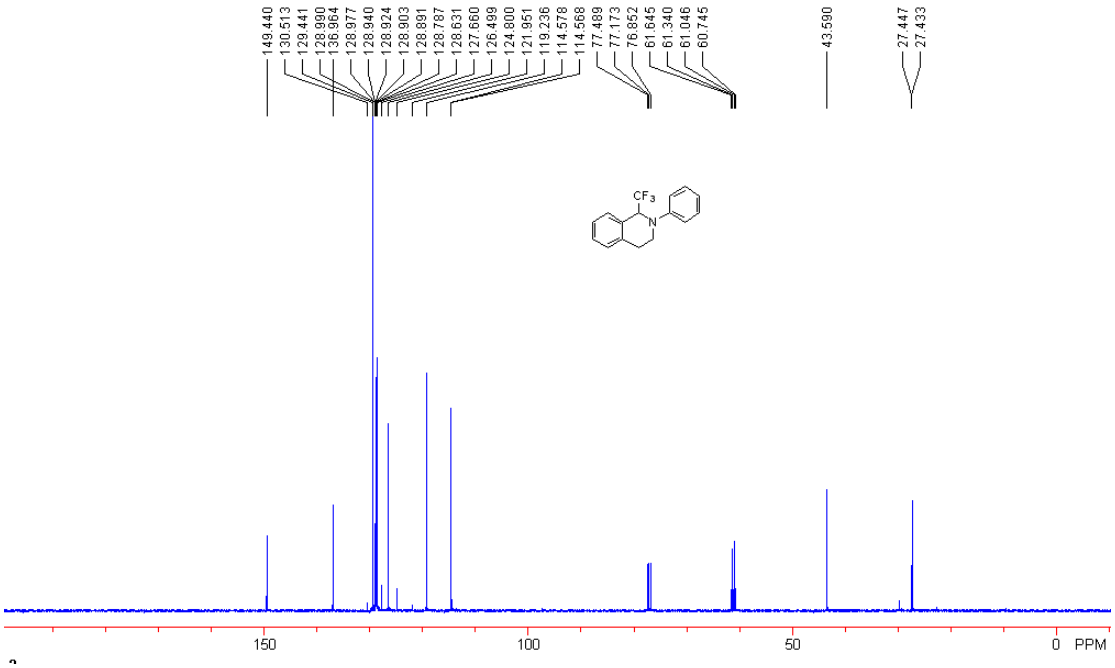
PPM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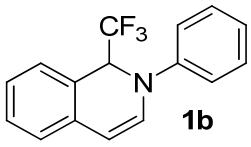
CF3
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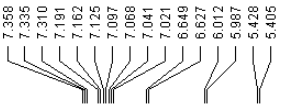
1b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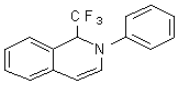
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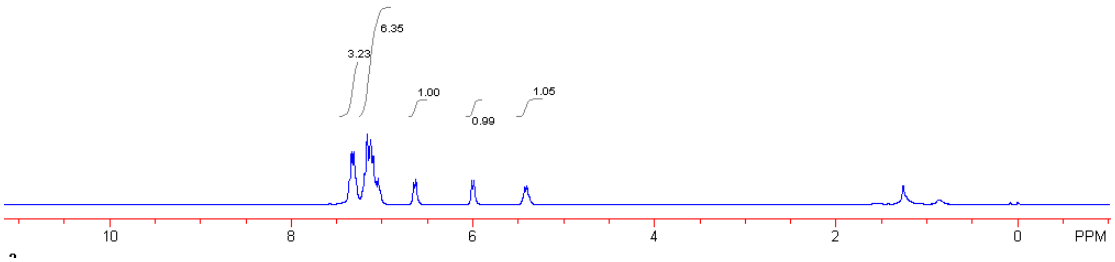
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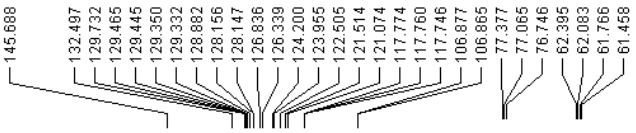
PPM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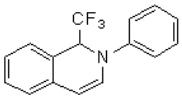
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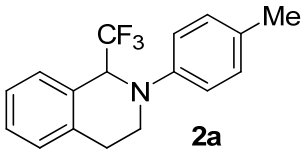
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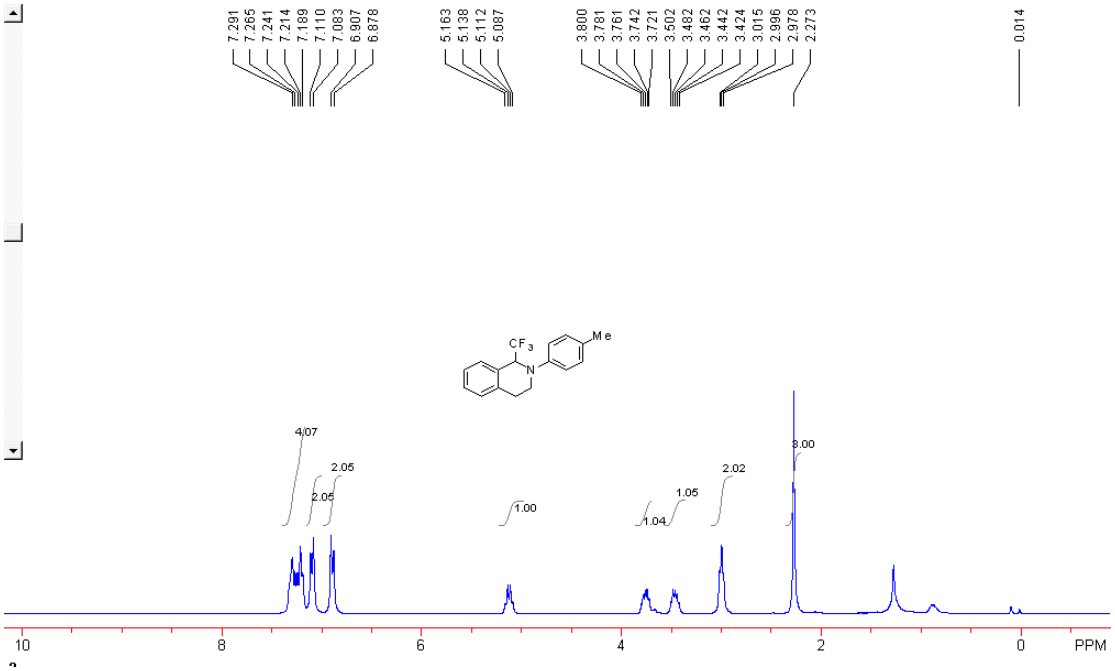
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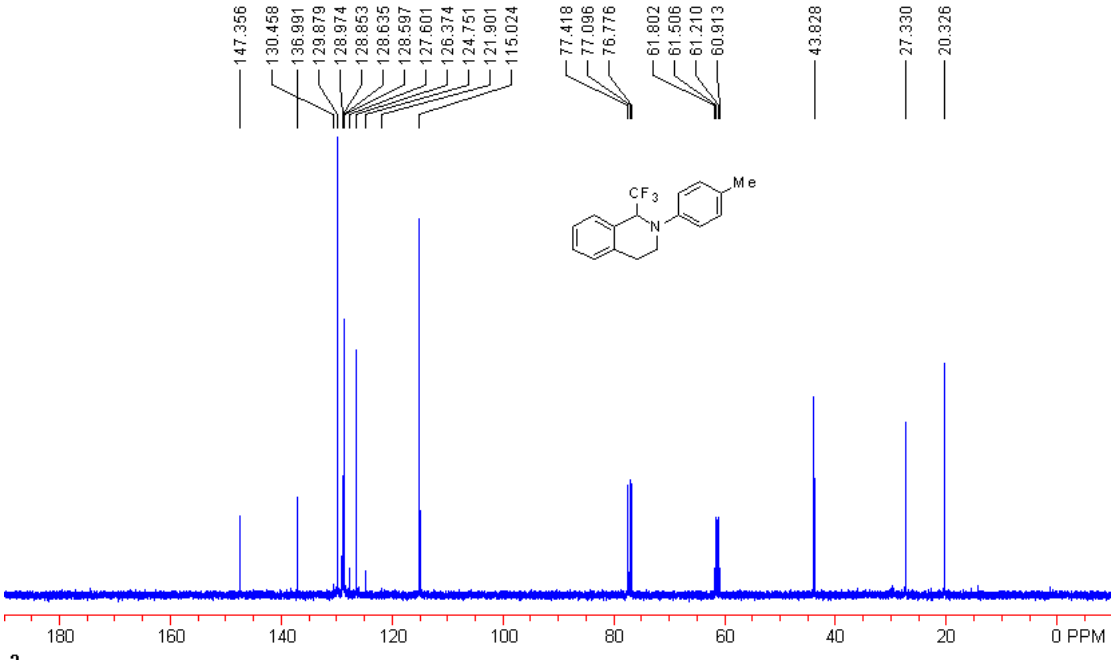
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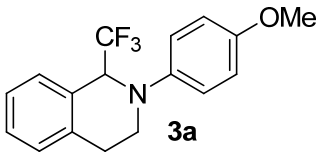
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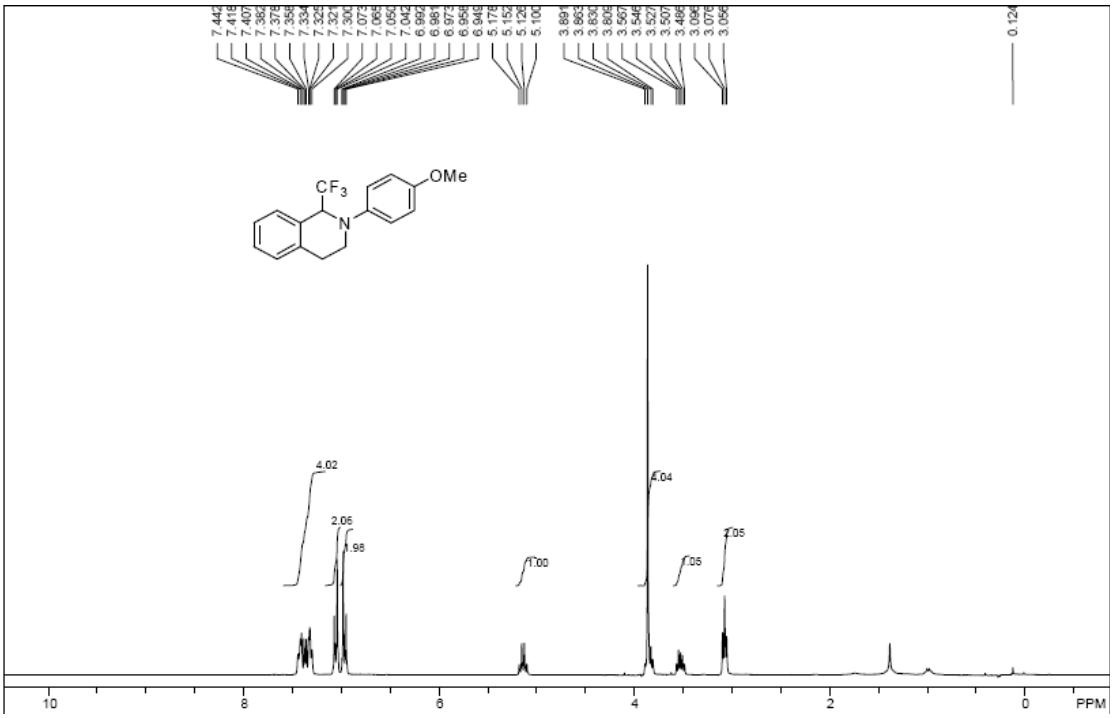
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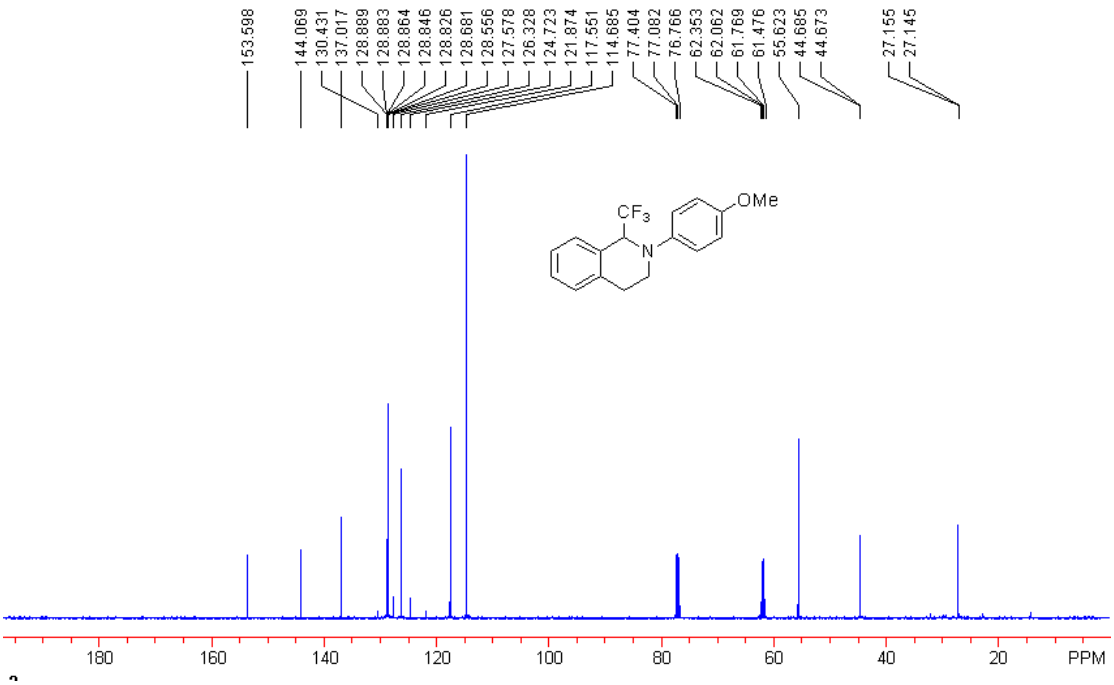
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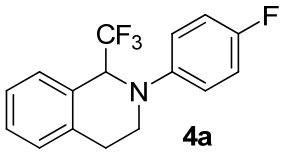
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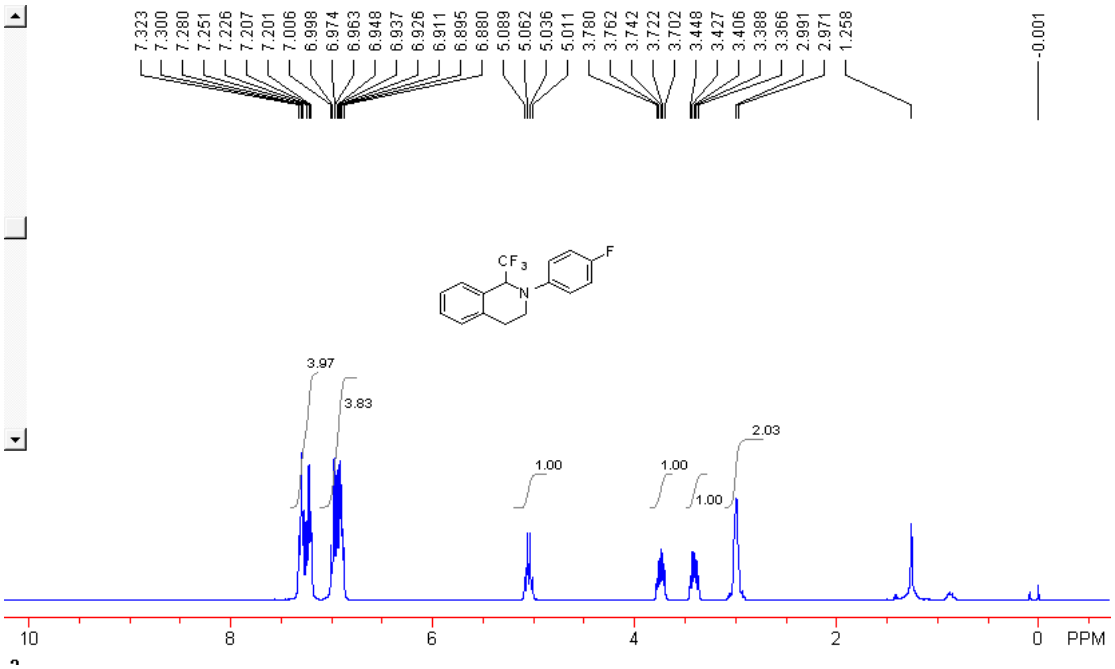
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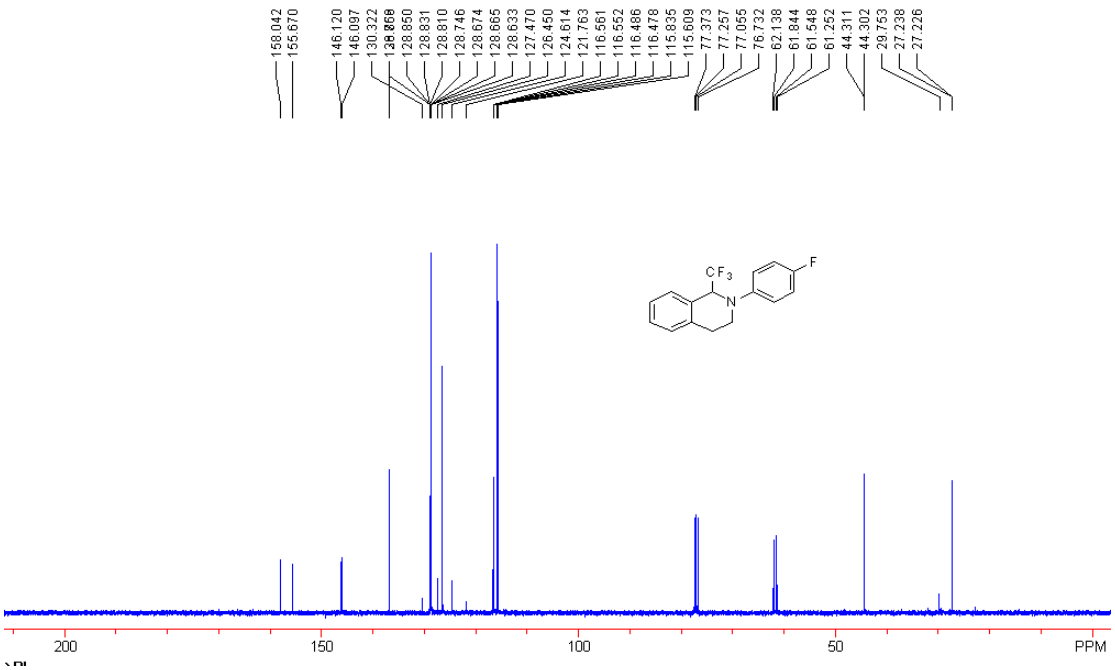
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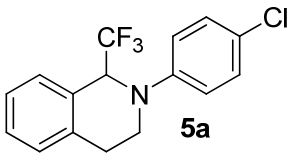
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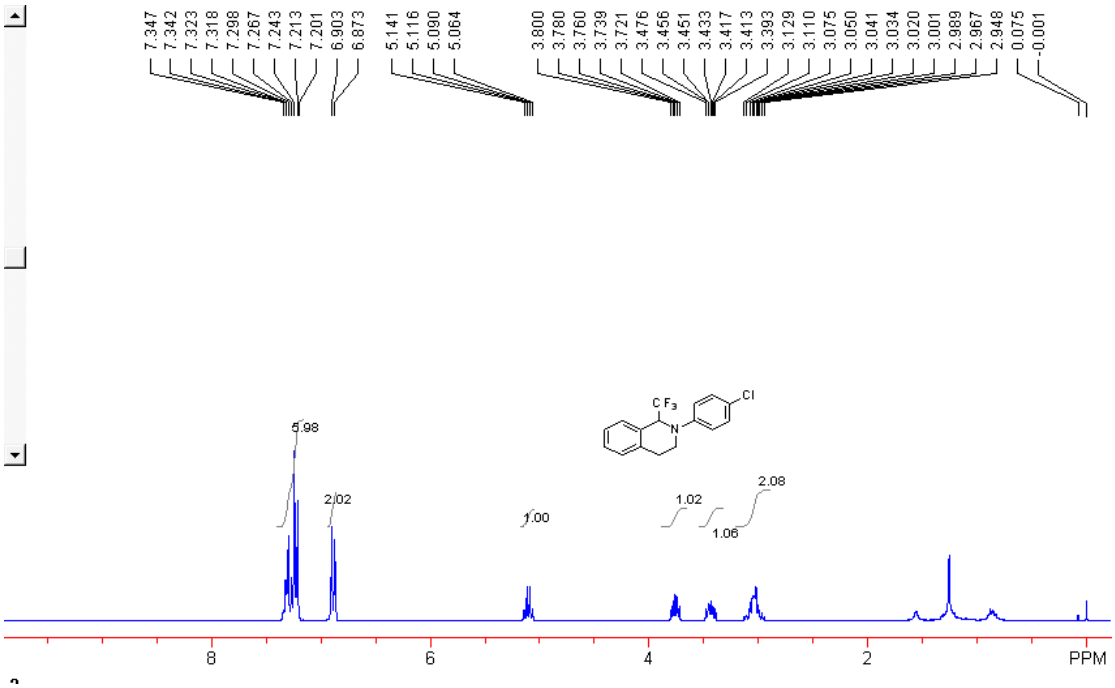
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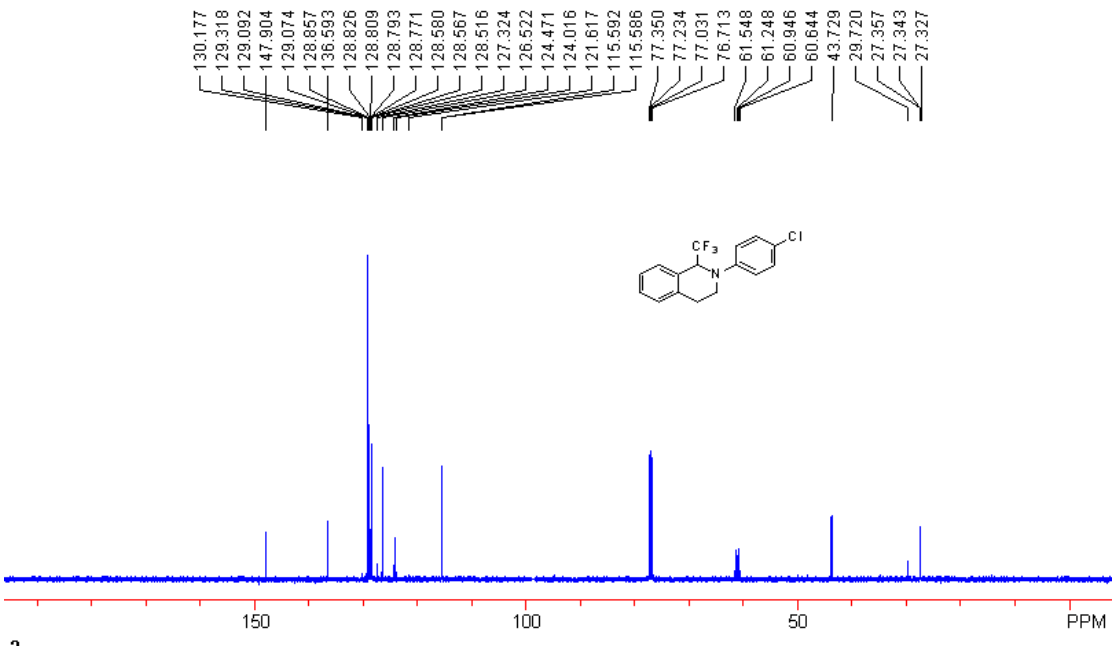
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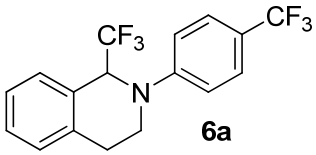
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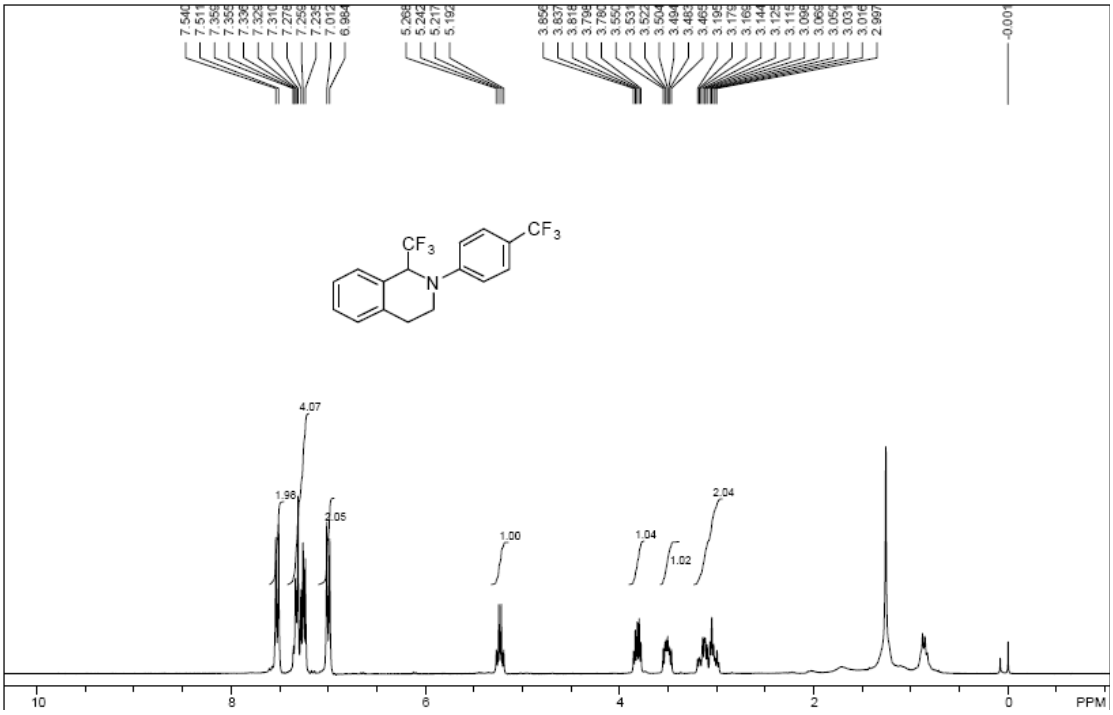
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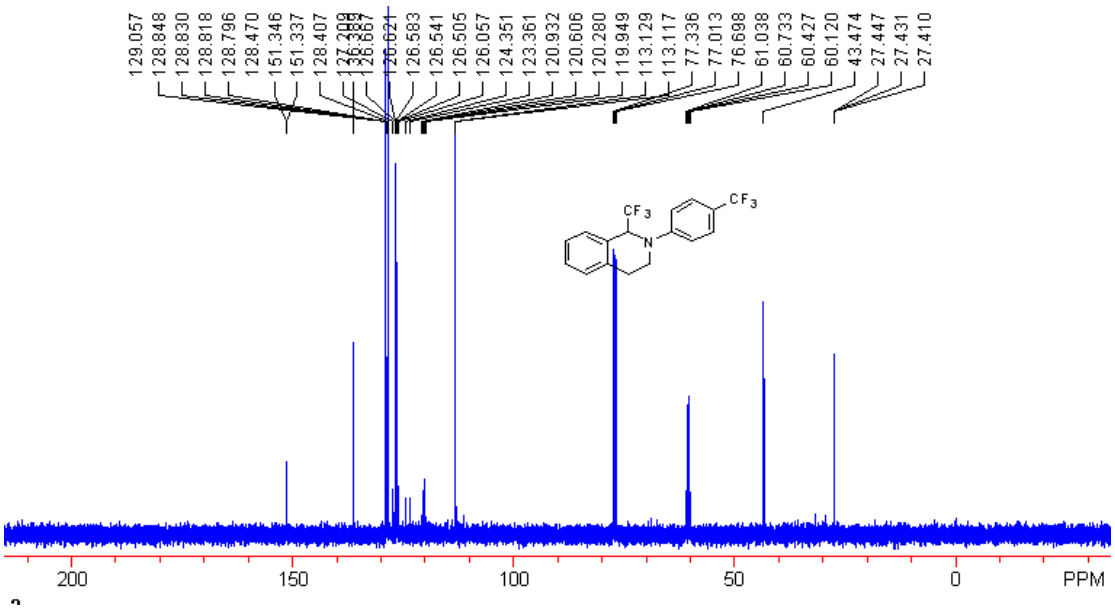
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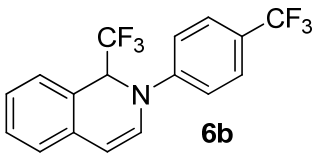
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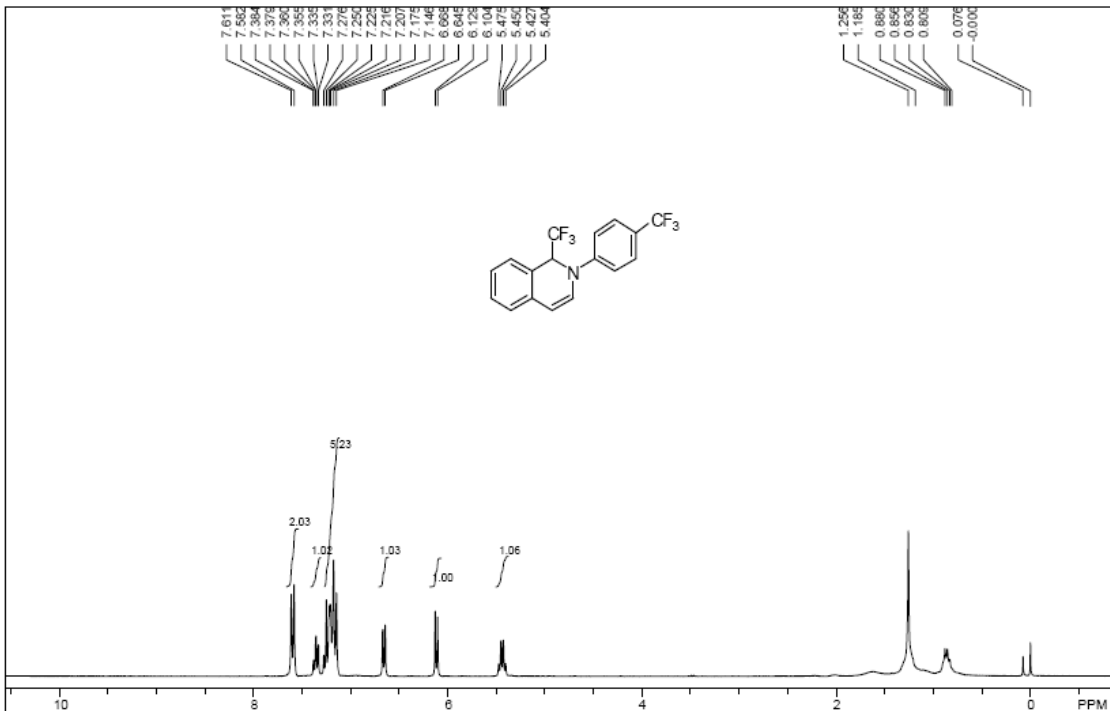
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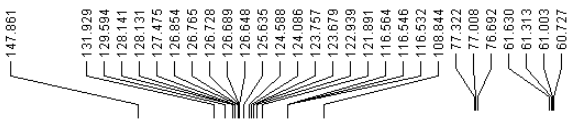
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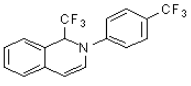
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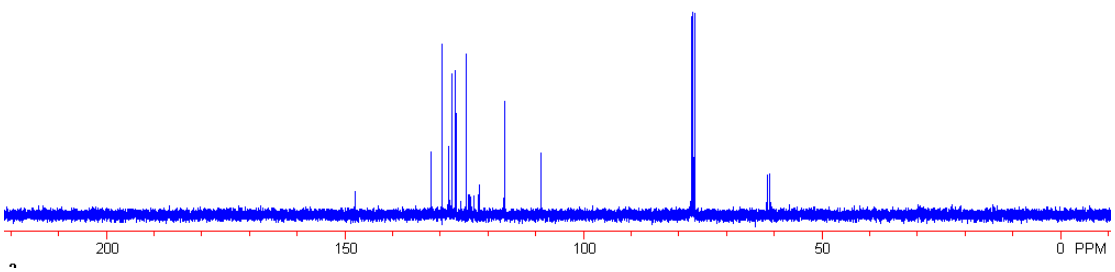
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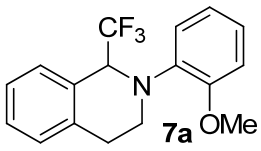
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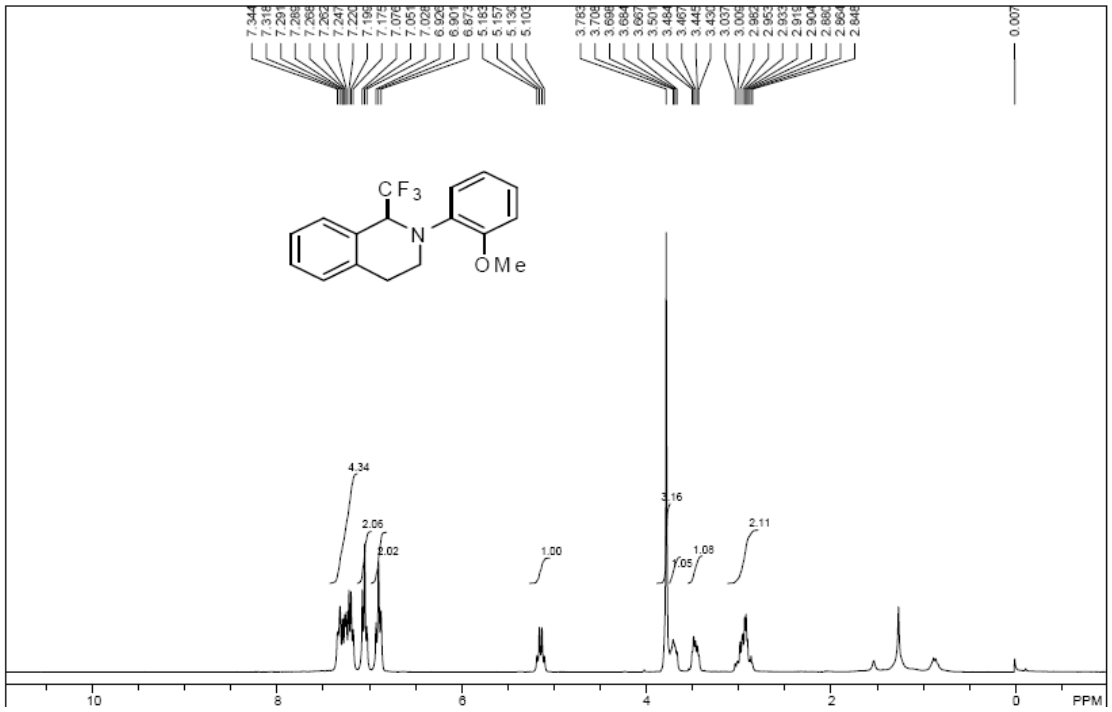
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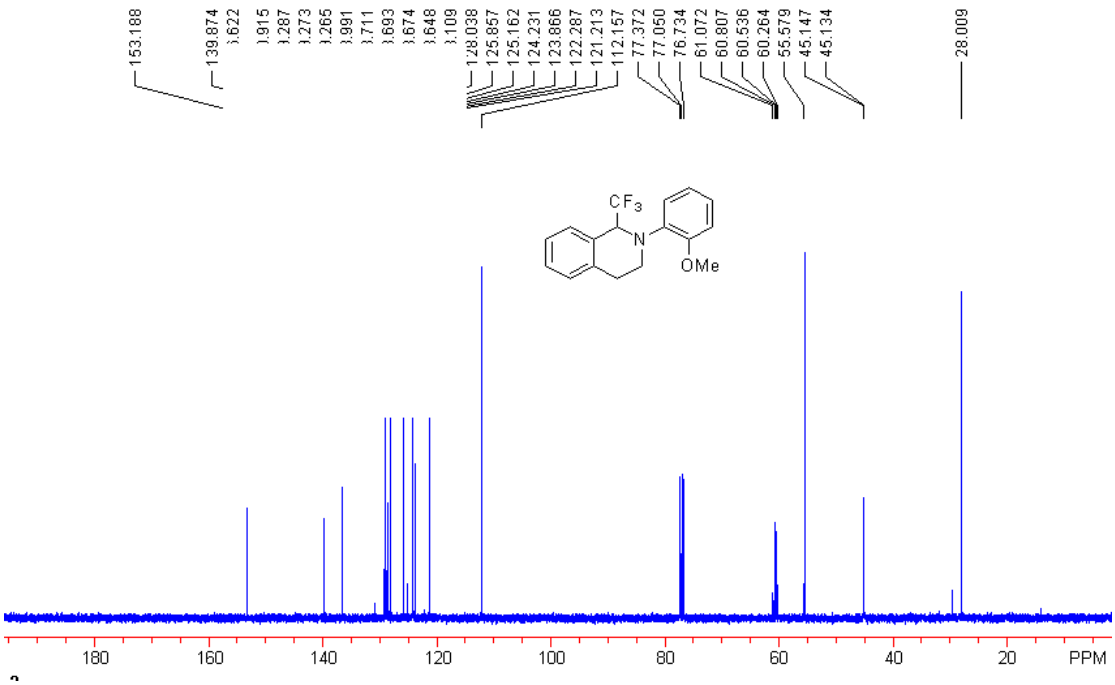
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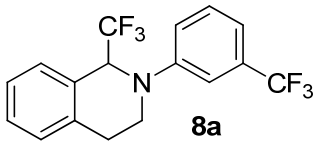
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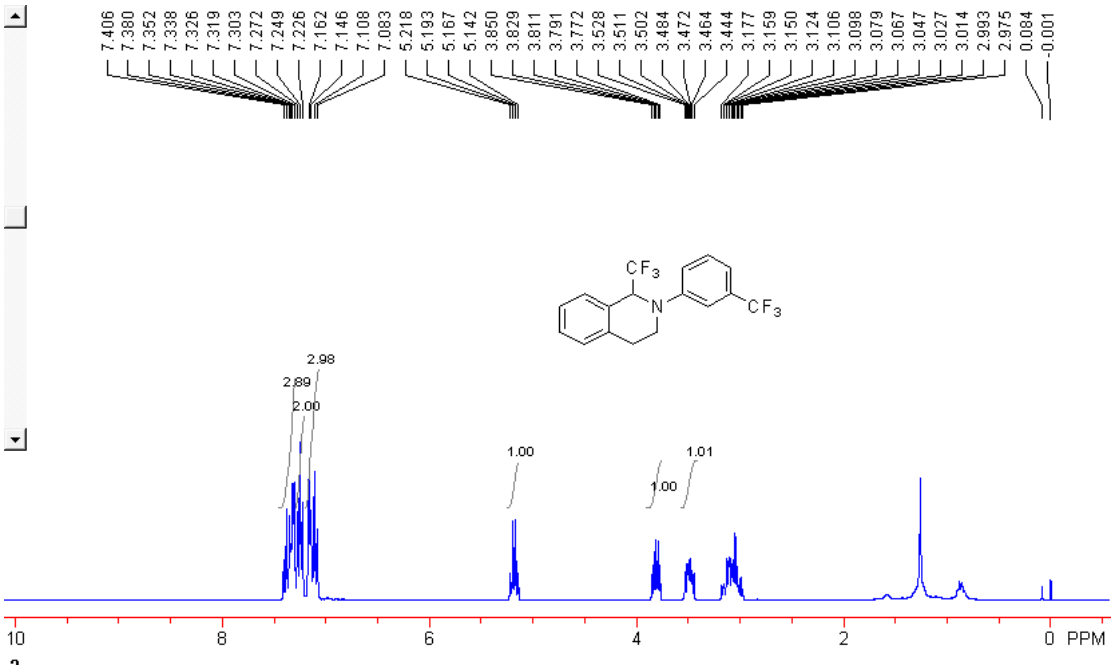
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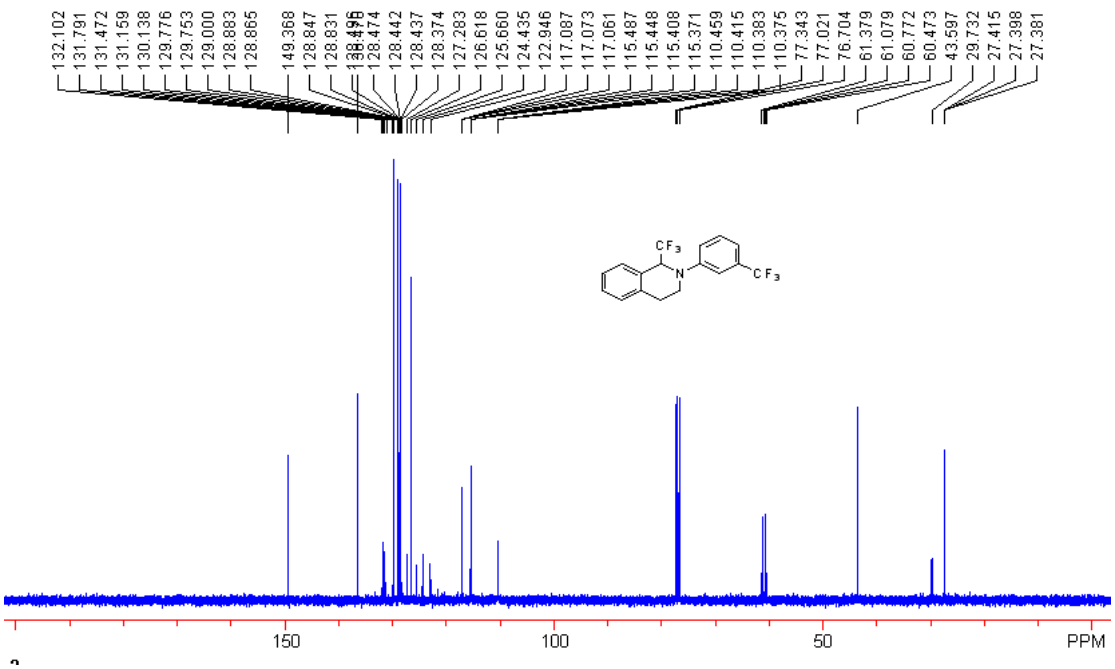
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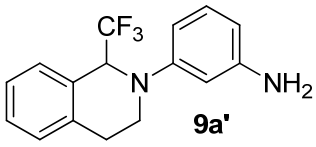
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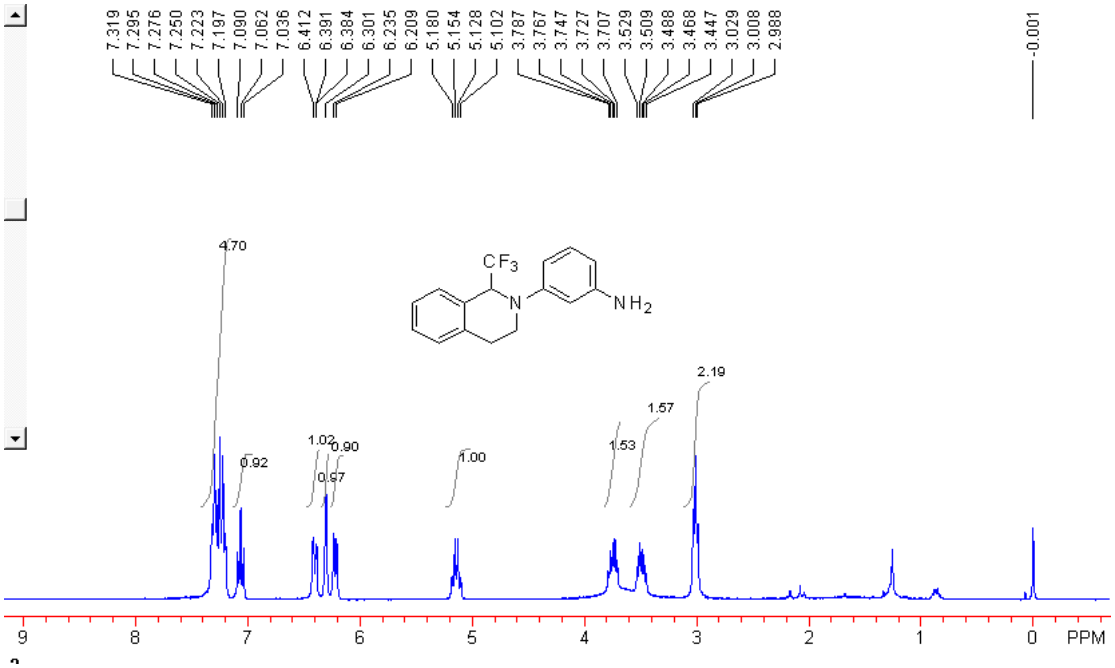
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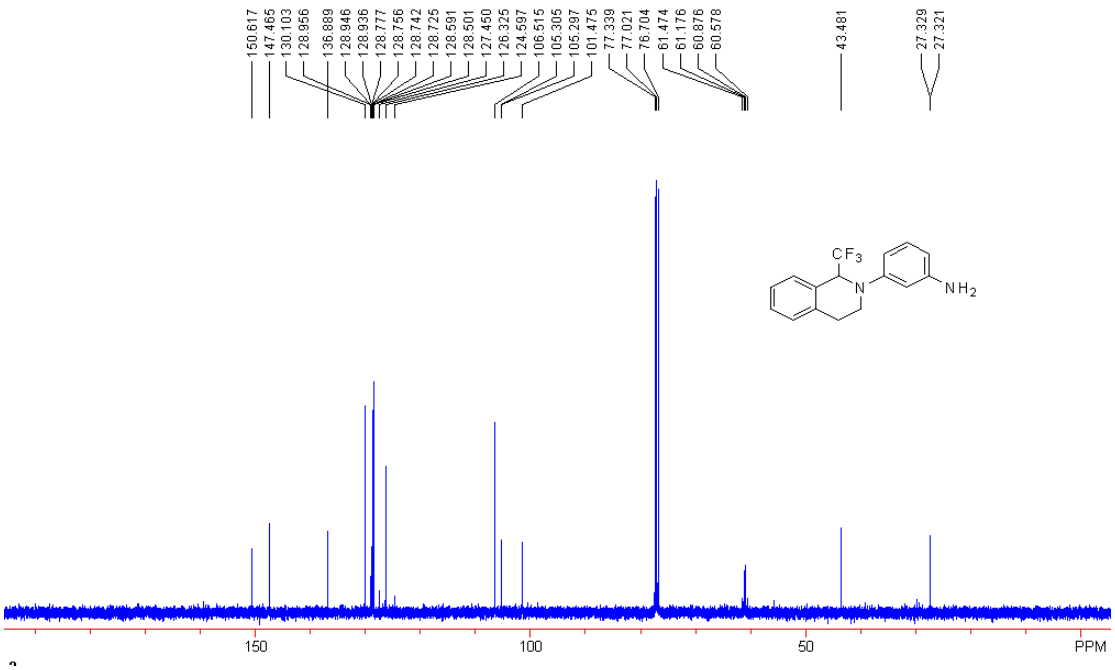
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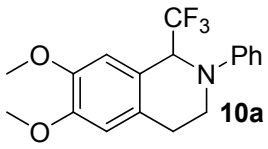
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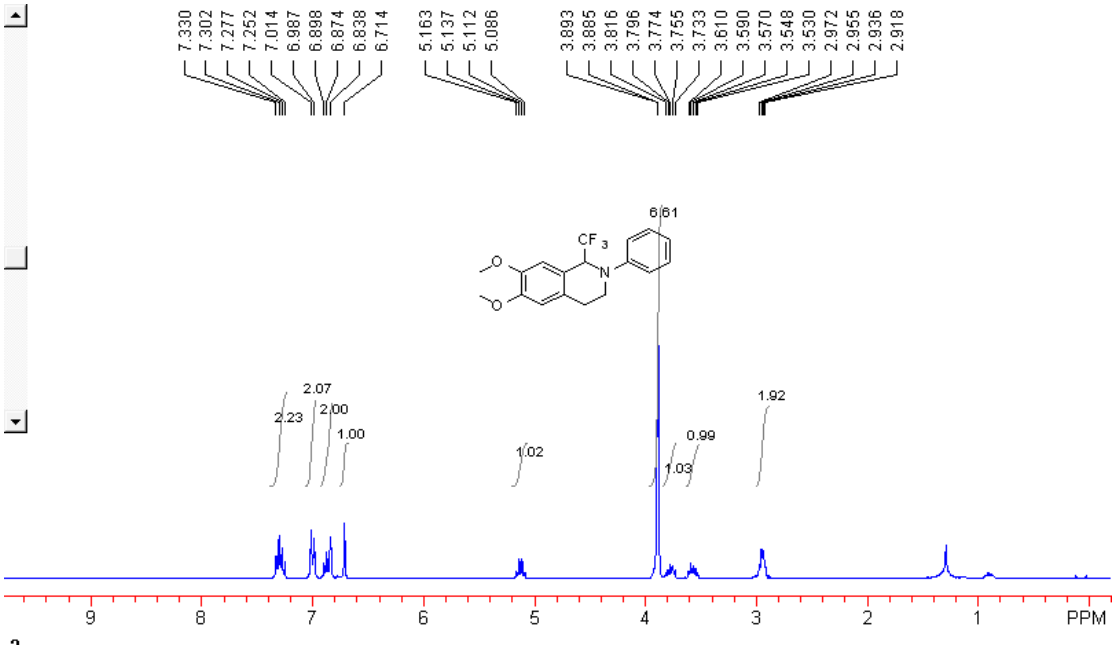
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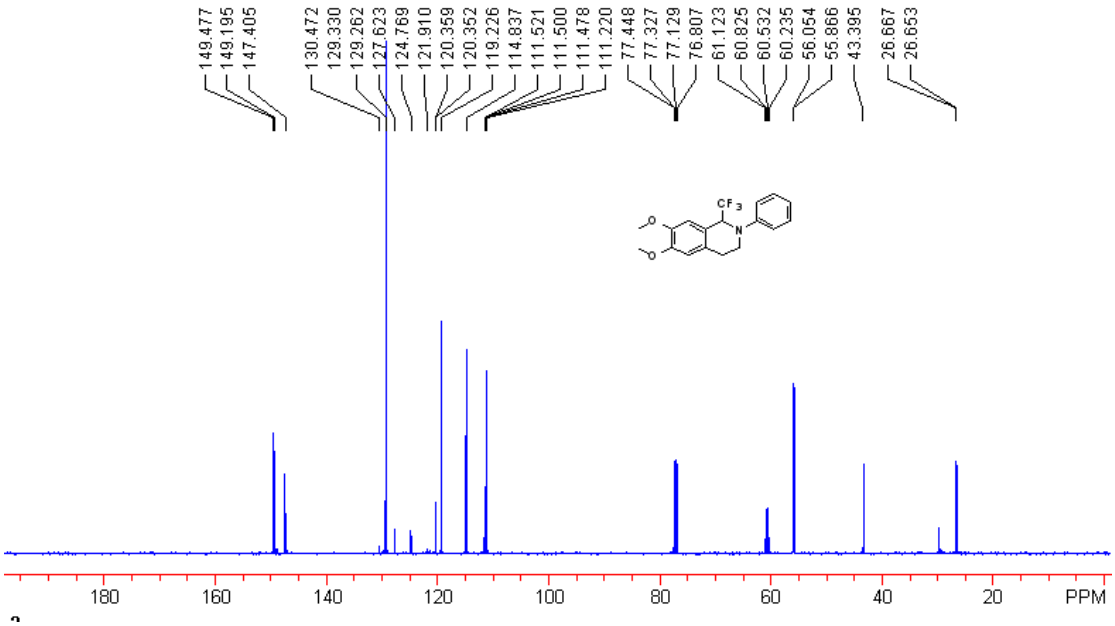
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111.521
111.500
111.478
111.220
77.448
77.327
77.129
76.807
61.123
60.825
60.532
60.235
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26.653
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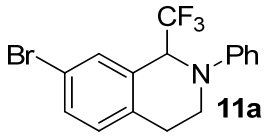
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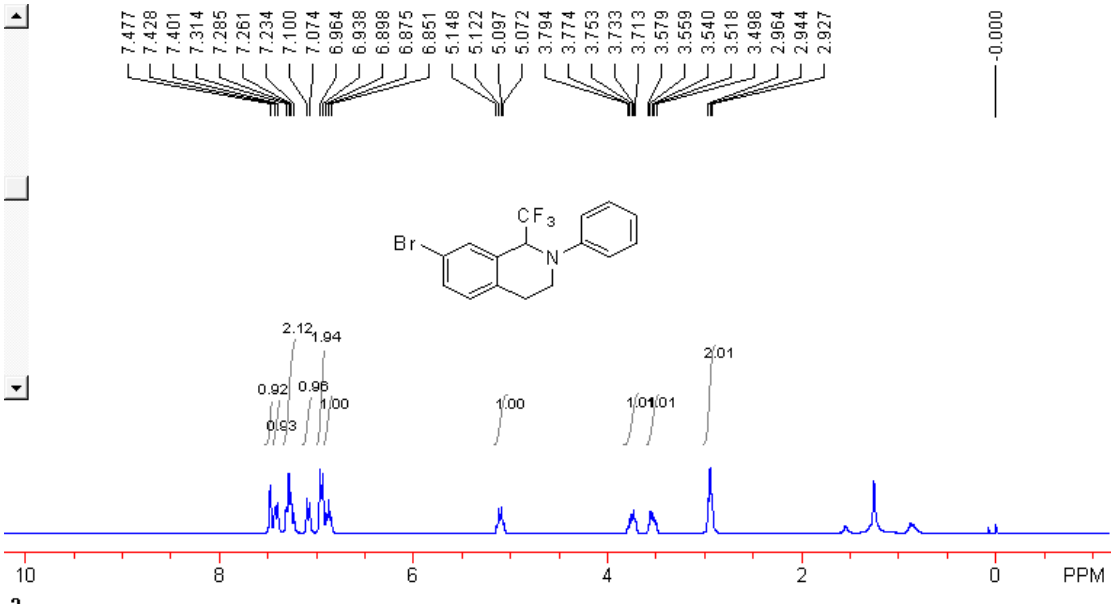
11a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7.100
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6.875
6.851
5.148
5.122
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5.072
3.794
3.774
3.753
3.733
3.713
3.579
3.559
3.540
3.518
3.498
2.964
2.944
2.927
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CF3
Br
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1.94
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1.01
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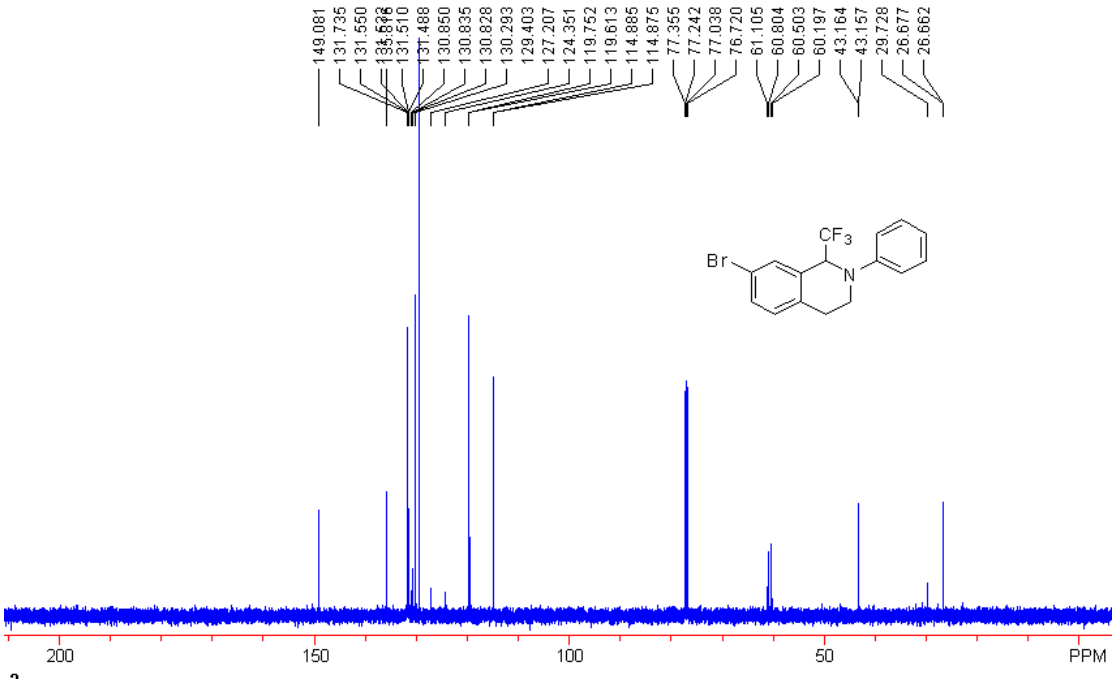
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130.835
130.828
130.293
129.403
127.207
124.351
119.752
119.613
114.885
114.875
77.355
77.242
77.038
76.720
61.105
60.804
60.503
60.197
43.164
43.157
29.728
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100
50
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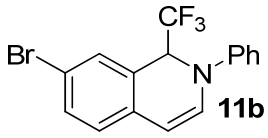
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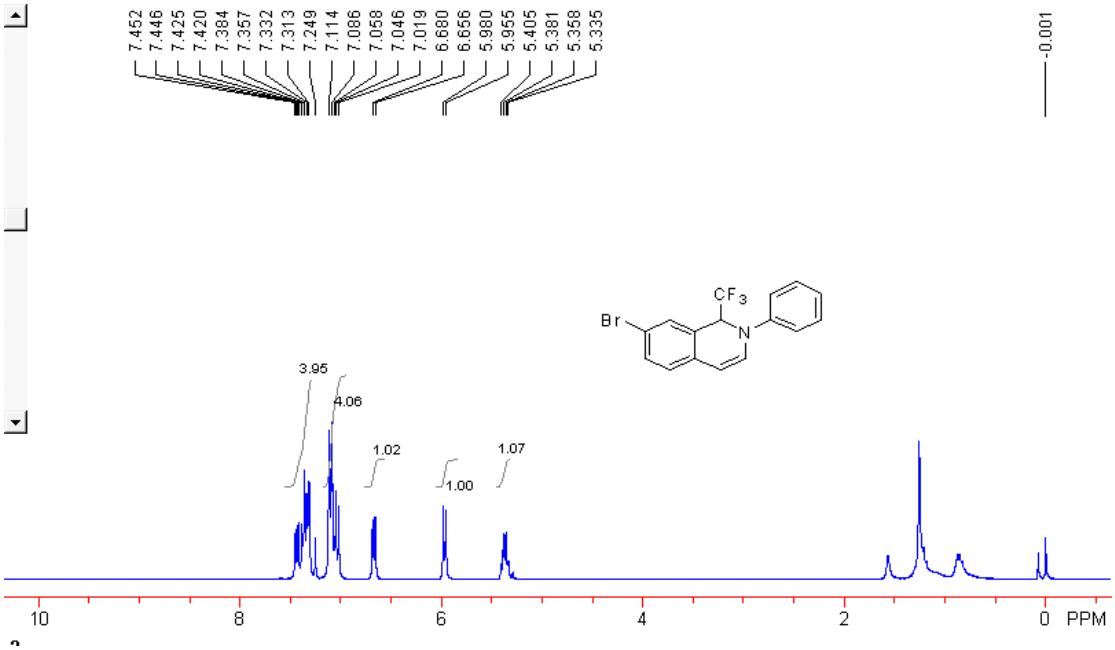
Ph

11b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7.313
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7.114
7.086
7.058
7.046
7.019
6.680
6.656
5.980
5.955
5.405
5.381
5.358
5.335
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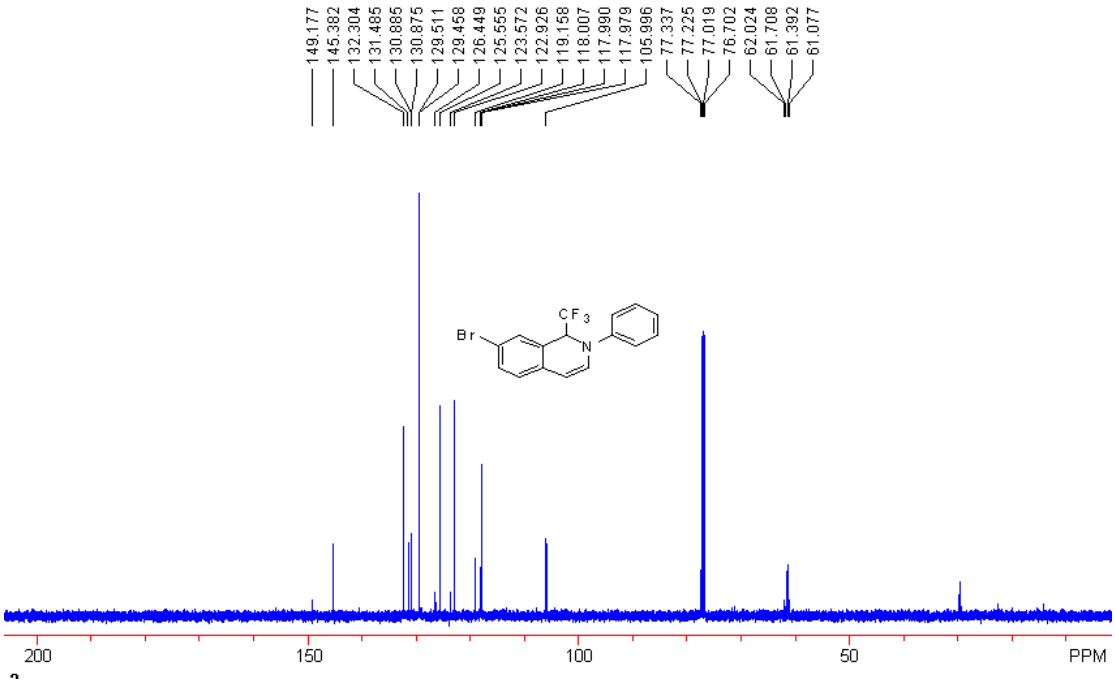
2
0
PPM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130.875
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125.555
123.572
122.926
119.158
118.007
117.990
117.979
105.996
77.337
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62.024
61.708
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CF3
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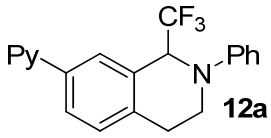
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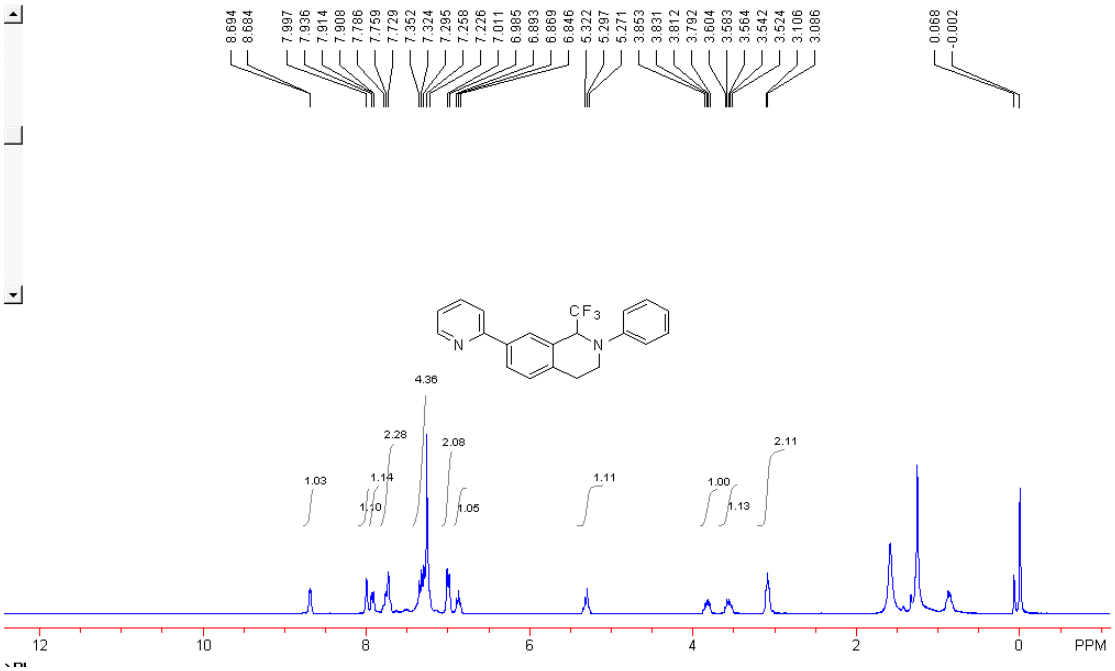
Py
N
Ph

12a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7.324
7.295
7.258
7.226
7.011
6.985
6.893
6.869
6.846
5.322
5.297
5.271
3.853
3.831
3.812
3.792
3.604
3.583
3.564
3.542
3.524
3.106
3.086
0.068
-0.002
CF3
N
N
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2.28
2.08
2.11
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1.05
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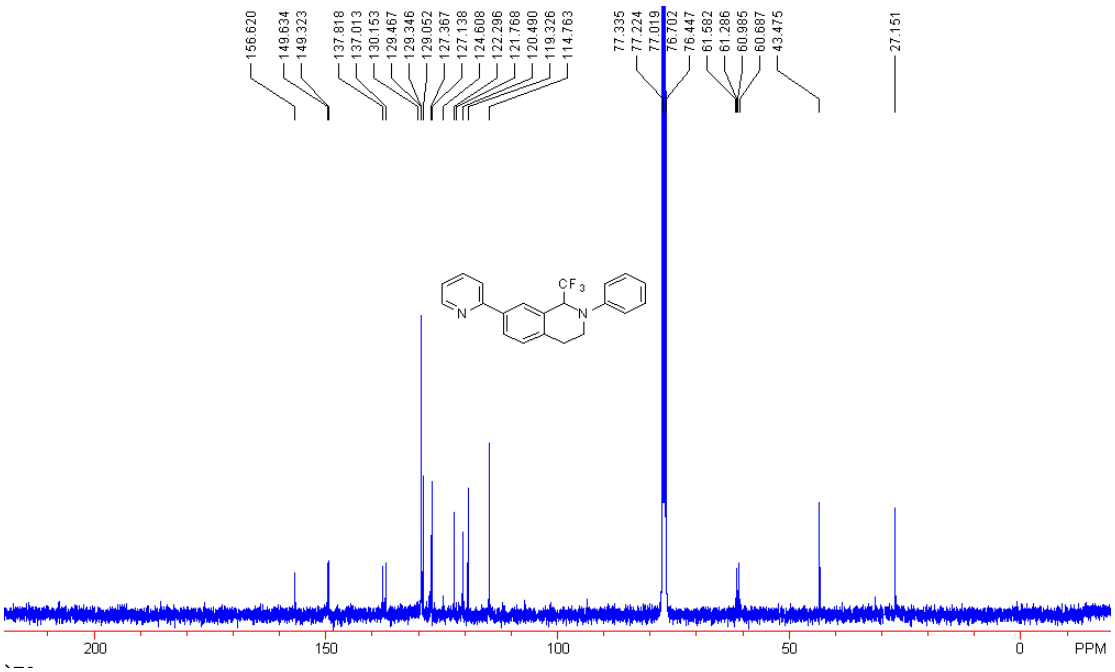
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122.296
121.768
120.490
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114.763
77.335
77.224
77.019
76.702
76.447
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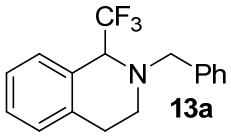
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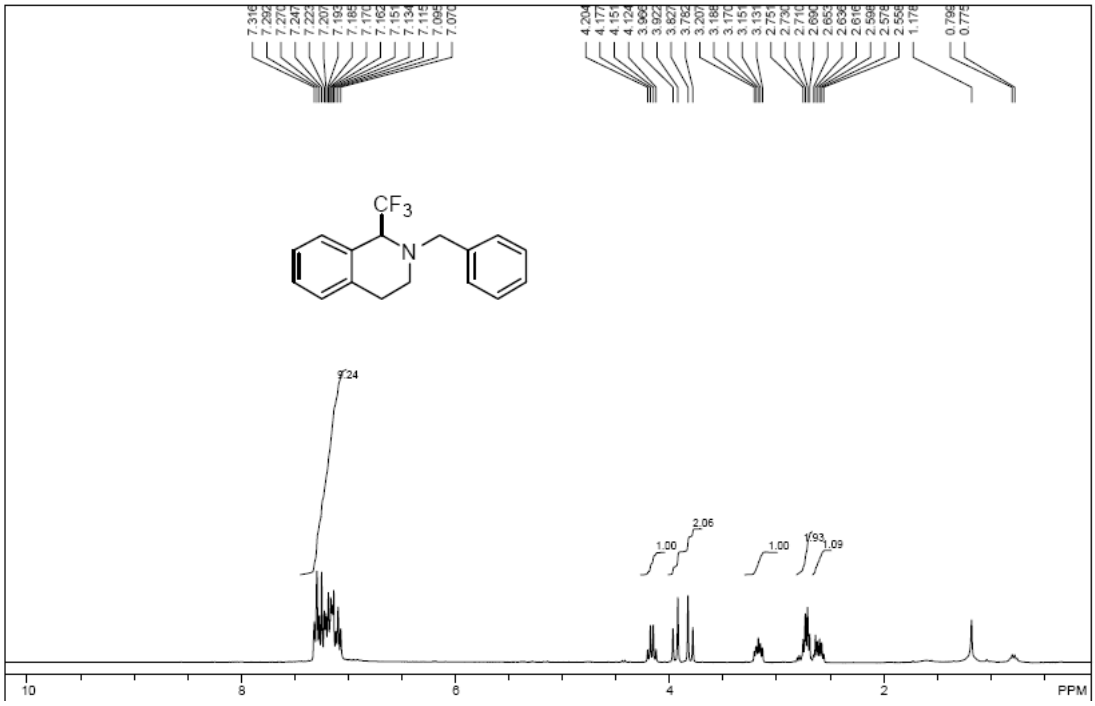
13a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8
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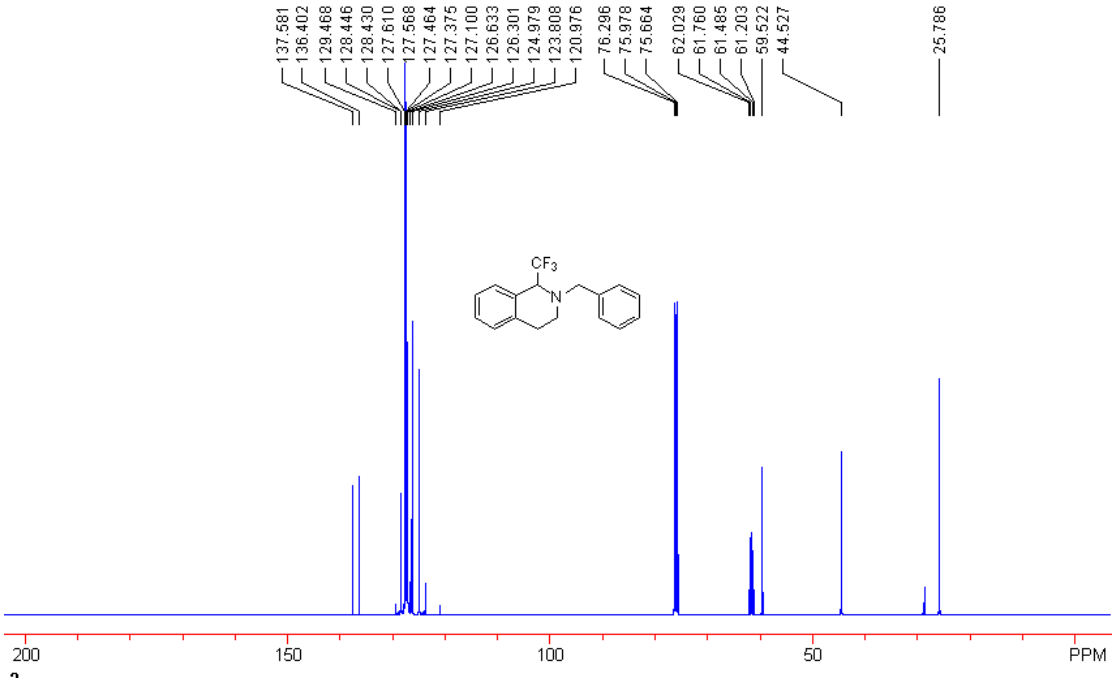
2
PPM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127.464
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124.979
123.808
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76.296
75.978
75.664
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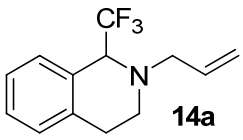
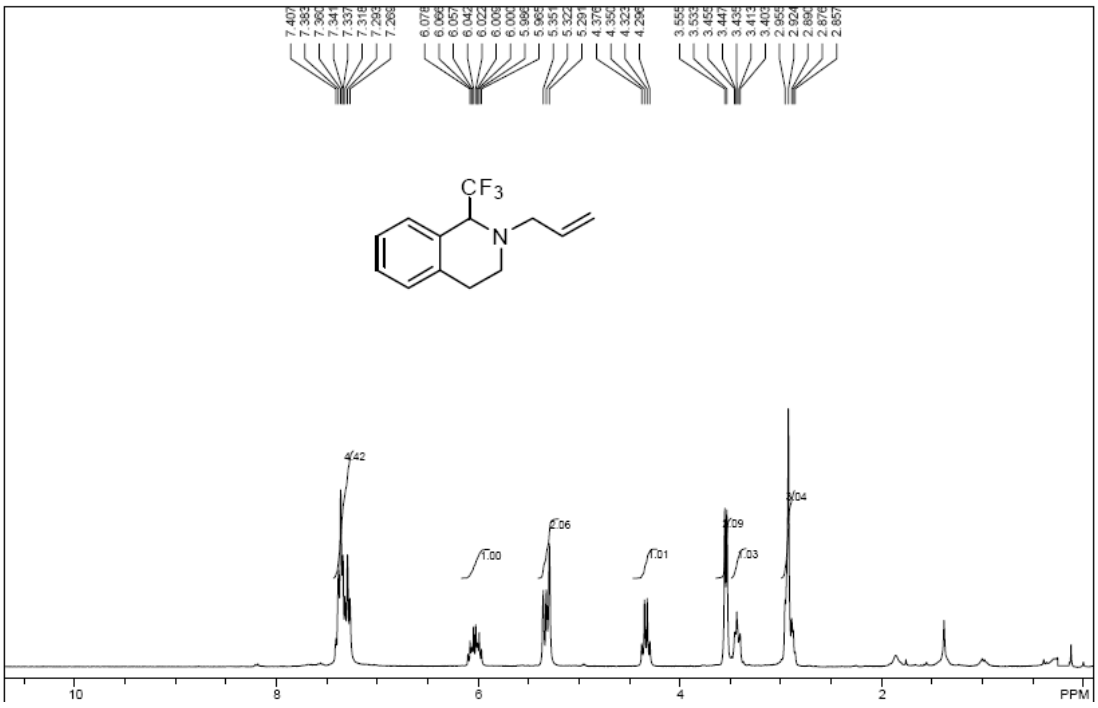
PPM


CF3
N

14a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6.022
6.008
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5.965
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5.922
5.291
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4.350
4.323
4.296
3.555
3.533
3.455
3.447
3.438
3.413
3.403
2.955
2.924
2.890
2.876
2.857
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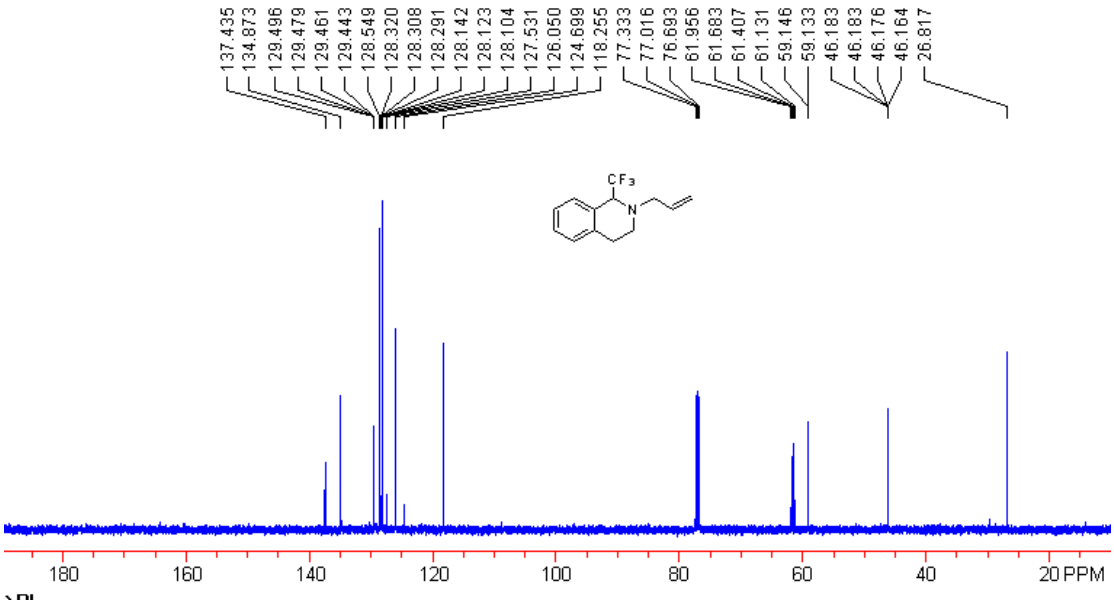
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77.016
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61.683
61.407
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59.146
59.133
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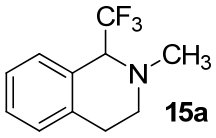
20 PPM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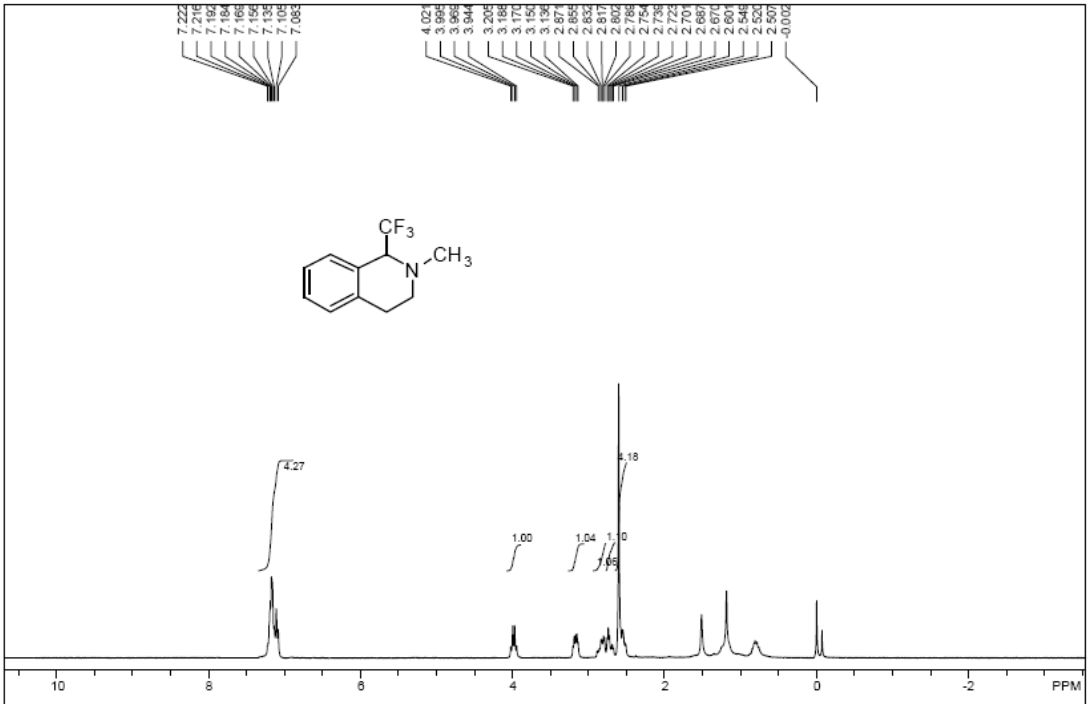
CH3
N

15a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8
6
4
2
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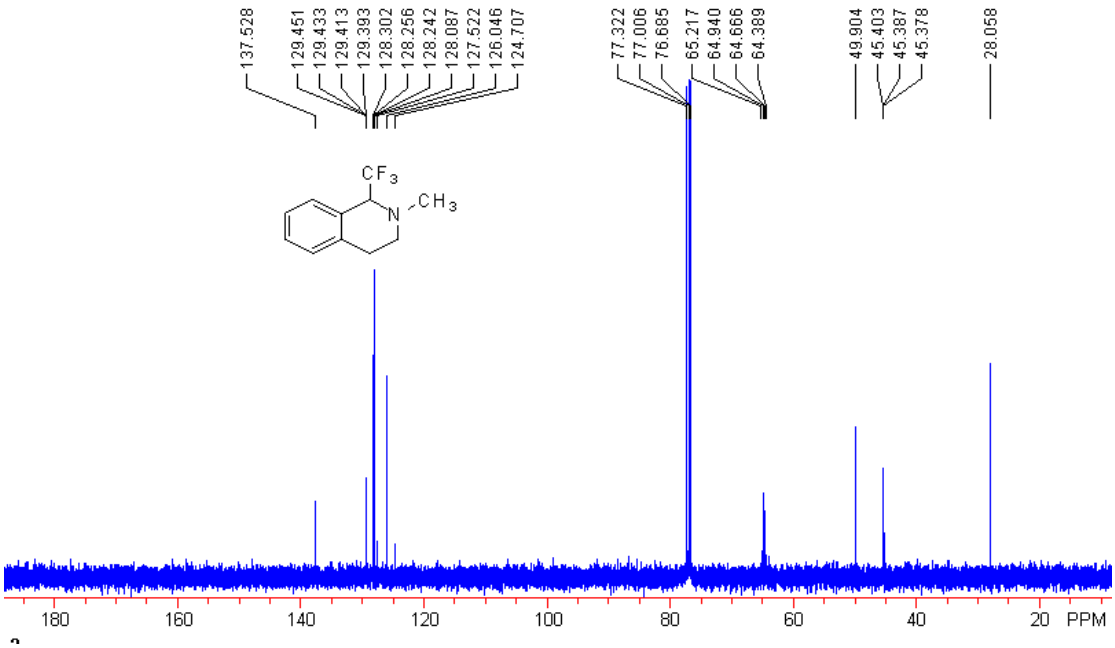
-2
PPM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64.940
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64.389
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CH3
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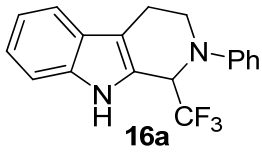
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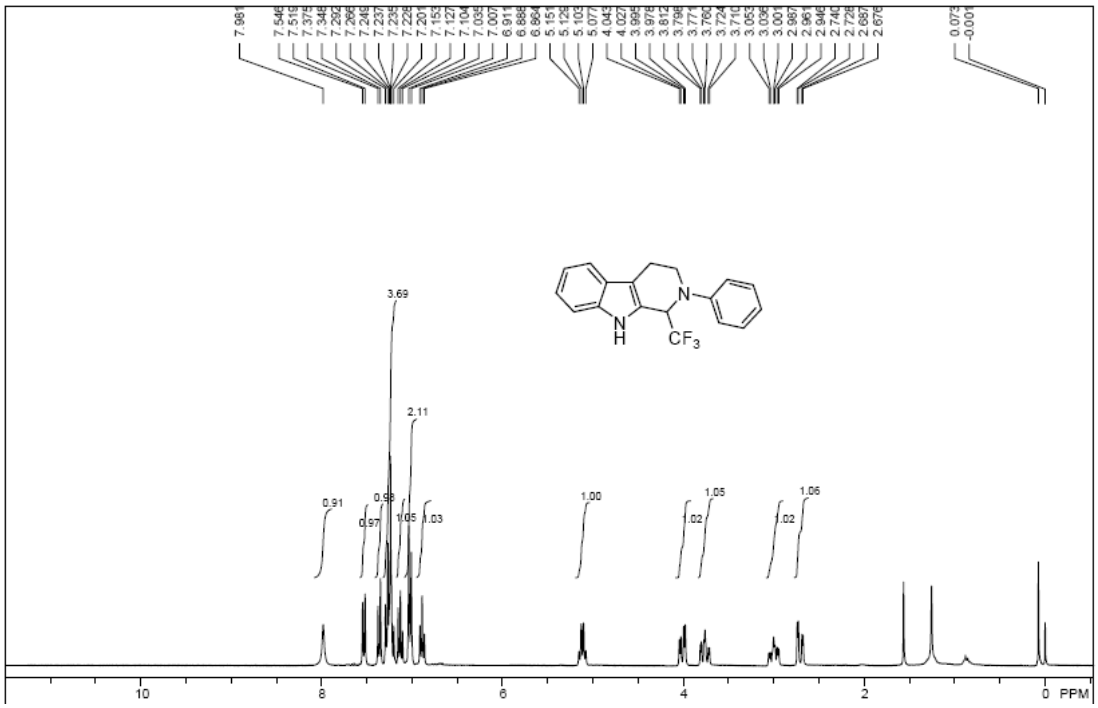
Ph
N
H
CF3

16a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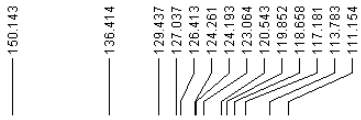
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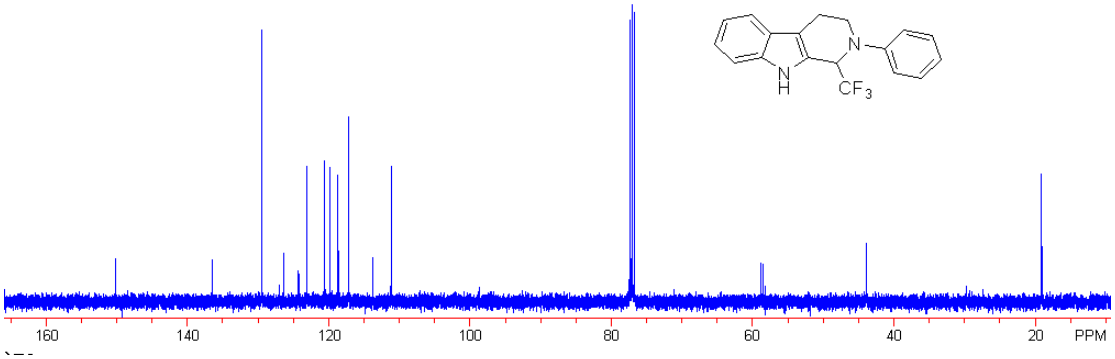
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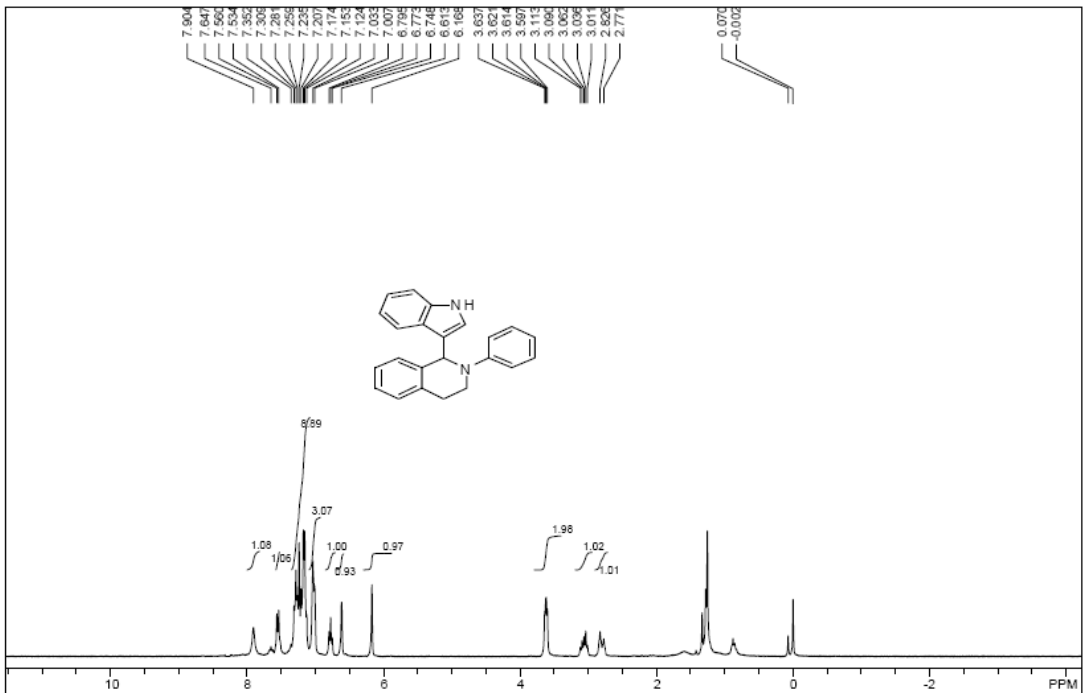
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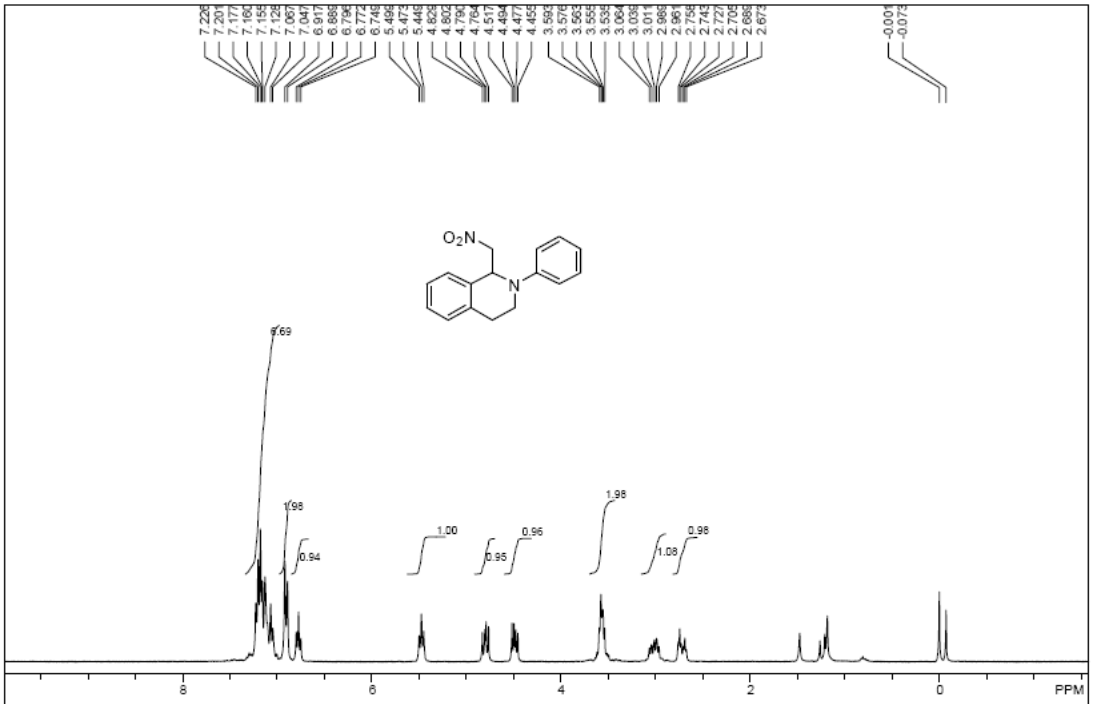
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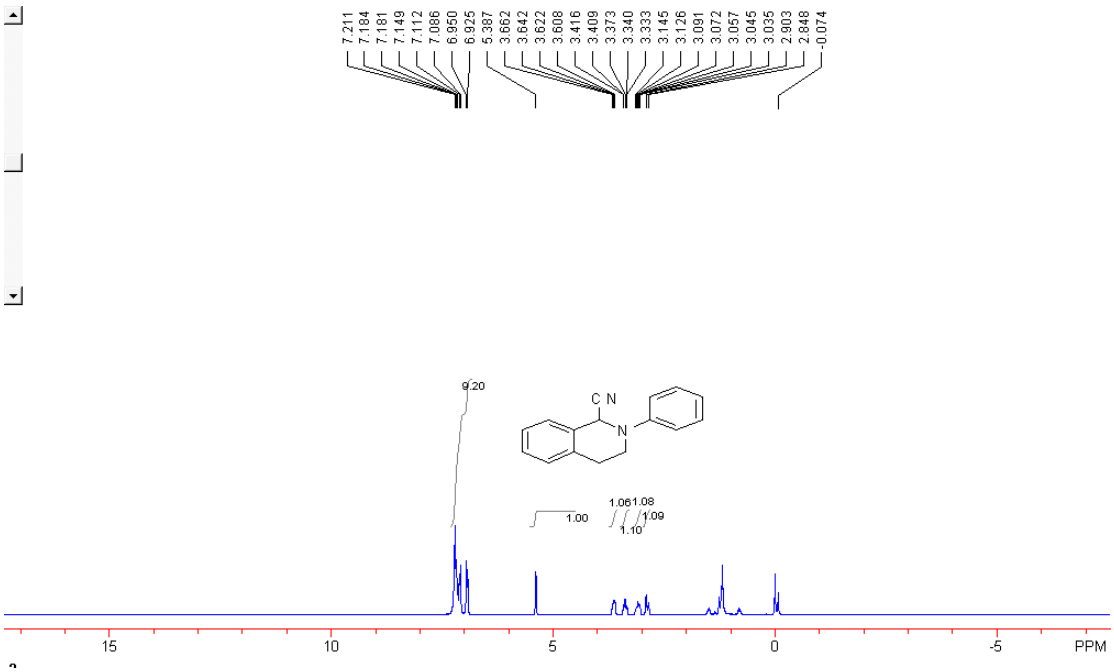
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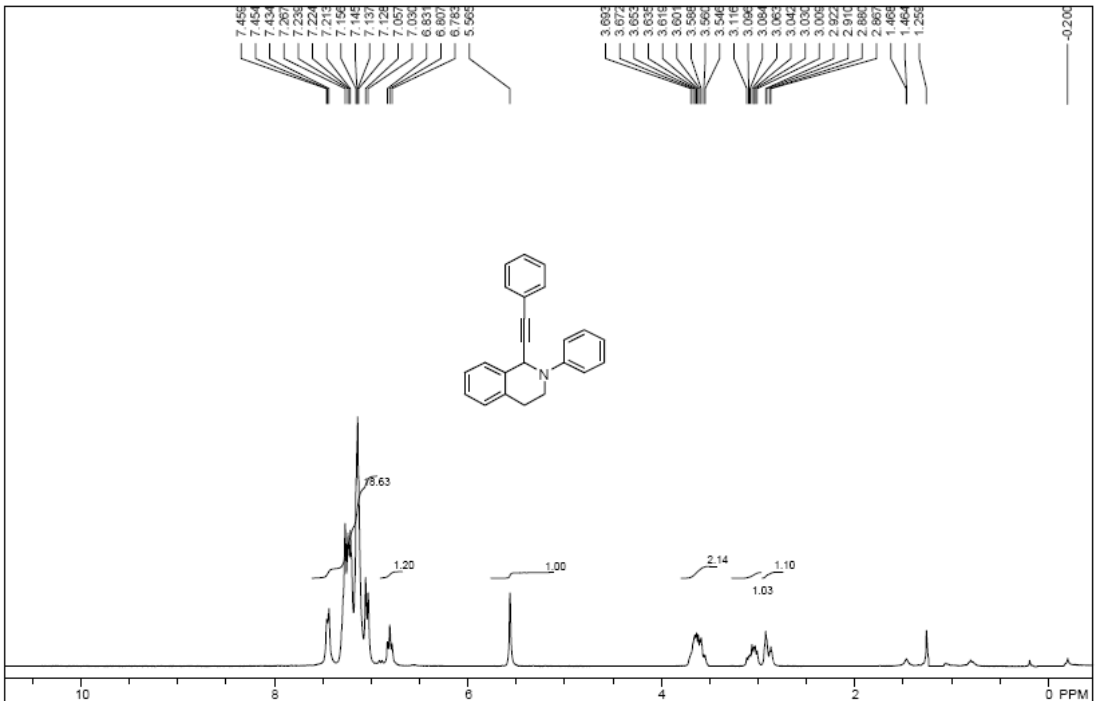
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1.10
1.03
10
8
6
4
2
0 PPM