Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Silver-Mediated Oxidative C-H Difluoromethylation of Phenanthridines and 1,10-Phenanthrolines

Sheng-Qing Zhu,[†] Xiu-Hua Xu,[†] and Feng-Ling Qing[*,†,‡]

[†]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Science, Chinese Academy of Science, 345 Lingling Lu, Shanghai 200032, China
[‡]College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China

Email: flq@mail.sioc.ac.cn

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1. General information.

^{1}H NMR (TMS as the internal standard) and ^{19}F NMR spectra ($CFCl_3$ as the outside standard and low field is positive) were recorded on a Bruker AM400 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. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure.

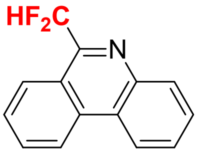
Materials. 1a and **3a-g** were received from commercial sources. The phenanthridines **1b-1k** were prepared as reported procedures.[1-3] Solvents were freshly dried and degassed before using.

References

(1) W. Han, X. Zhou, S. Yang, G. Xiang, B. Cui and Y. Chen, *J. Org. Chem.*, 2015, **80**, 11580.
(2) W.-L. Chen, C.-Y. Chen, Y.-F. Chen and J.-C. Hsieh, *Org. Lett.*, 2015, **17**, 1613.
(3) X.-D. An and S. Yu, *Org. Lett.*, 2015, **17**, 2692.

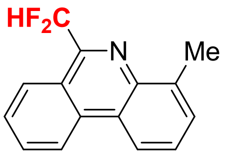
2. General Procedures for Silver-Mediated Oxidative Difluoromethylation of Phenanthridines

In a glove box, ^{t}BuOK (3.0 mmol, 336.6 mg), phenanthridine (1.0 mmol), and AgOAc (1.0 mmol, 166.9 mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum. Tetraethylene glycol dimethyl ether (10 mL) was added under Ar atmosphere and the mixture was stirred at room temperature for 10 minutes. Next, TMSCF$_2$H (3.0 mmol, 372.6 mg) was added and the mixture was stirred for 5 minutes, followed by the addition of [bis(trifluoroacetoxy)iodo]benzene (3.0 mmol, 1290.1 mg). Then, the reaction mixture was stirred at room temperature for 10 h. The reaction was quenched by water and extracted with ethyl acetate (3×30 mL), and the combined organic layer was washed with water and brine (3×50 mL), dried over Na$_2$SO$_4$ and concentrated. The resulting residue was purified by flash column chromatography.



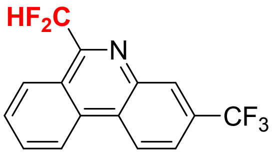
2a

6-(Difluoromethyl)phenanthridine (**2a**) was obtained as a light yellow solid (145.0 mg, 63%), with hexane/ethyl acetate = 5:1 as eluent for the column chromatography. mp 87-89 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, 293K, TMS): δ ppm 8.61 (d, J = 8.4 Hz, 1H), 8.54 (t, J = 8.8 Hz, 2H), 8.17 (d, J = 7.6 Hz, 1H), 7.85 (t, J = 7.2 Hz, 1H), 7.77-7.69 (m, 3H), 7.02 (t, J = 54.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl$_3$): δ ppm -110.57 (d, J = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$, 293K, TMS): δ ppm 151.4 (t, J = 26.3 Hz), 142.5, 133.8, 131.2, 130.6, 129.1, 128.6, 127.8, 126.4 (t, J = 4.4 Hz), 124.9, 122.4, 122.1, 118.4 (t, J = 242.1 Hz). IR (ATR): ν_{max} 1613, 1578, 1528, 1445, 1380, 1140, 1124, 1092, 1055, 1021, 857, 783, 755, 720, 674, 509 cm^{-1}. MS (EI): m/z (%) 229 (100). HRMS: Calculated for C$_{14}$H$_9$F$_2$N: 229.0703; Found: 229.0708.



2b

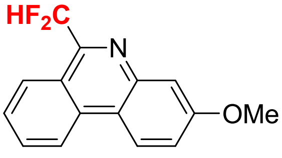
6-(Difluoromethyl)-4-methylphenanthridine (**2b**) was obtained as a light yellow solid (162.0 mg, 67%), with hexane/ethyl acetate = 10:1 as eluent for the column chromatography. mp 68-70 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 293K, TMS): δ ppm 8.61 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.8 Hz, 1H), 8.38 (s, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.59-7.58 (m, 2H), 7.03 (t, *J* = 54.4 Hz, 1H), 2.85 (s, 3H). ^{19}F NMR (376 MHz, CDCl$_3$): δ ppm -109.95 (d, *J* = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$, 293K, TMS): δ ppm 149.8 (t, *J* = 25.5 Hz), 141.1, 138.7, 134.0, 130.8, 129.7, 128.1, 127.5, 126.3, 124.7, 122.6, 122.1, 119.8, 119.1 (t, *J* = 242.1 Hz), 18.2. IR (ATR): ν_{max} 3075, 3034, 2993, 2924, 1614, 1528, 1474, 1449, 1379, 1351, 1157, 1113, 1072, 1033, 779, 758, 741, 675, 559, 505 cm^{-1}. MS (EI): *m/z* (%) 243 (100). HRMS: Calculated for $C_{15}H_{11}F_2N$: 243.0860; Found: 243.0855. Anal. Calcd. for $C_{15}H_{11}F_2N$: C, 74.06; H, 4.56; F, 15.62; N, 5.76. Found: C, 73.64; H, 4.54; F, 15.42; N, 5.73.



2c

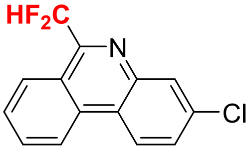
6-(Difluoromethyl)-3-(trifluoromethyl)phenanthridine (**2c**) was obtained as a light yellow solid (224.0 mg, 76%), with hexane as eluent for the column chromatography. mp 81-83 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 293K, TMS): δ ppm 8.60-8.54 (m, 3H), 8.43 (s, 1H), 7.92-7.87 (m, 2H), 7.78 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 54.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl$_3$): δ ppm -62.42 (s, 3F), -110.91 (d, *J* = 54.1 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$, 293K, TMS): δ ppm 152.7 (t, *J* = 26.2 Hz), 141.6, 132.8, 131.7, 130.9 (q, *J* = 32.8 Hz), 128.9, 128.1 (q, *J* = 3.9 Hz), 127.0, 126.6, 124.4, 123.9 (q, *J* = 270.5 Hz), 123.1, 122.8, 122.6, 118.0 (t, *J* = 242.8 Hz). IR (ATR): ν_{max} 3009, 1613, 1446, 1364, 1331, 1277, 1186, 1152, 1109, 1071, 1047, 898, 833, 788, 773, 747, 728, 682 cm^{-1}. MS (EI): *m/z* (%) 297 (100). HRMS: Calculated for $C_{15}H_8F_5N$: 297.0577; Found: 297.0568. Anal. Calcd. For $C_{15}H_8F_5N$: C, 60.61; H, 2.95; F, 31.96;

N, 4.71. Found: C, 60.41; H, 2.95, F, 31.22; N, 4.80.



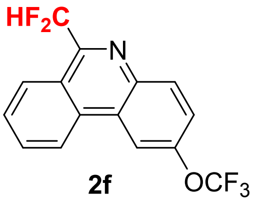
2d

6-(Difluoromethyl)-3-methoxyphenanthridine (**2d**) was obtained as a light yellow solid (150.0 mg, 58%), with hexane/ethyl acetate = 5:1 as eluent for the column chromatography. mp 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.55 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 8.8 Hz, 1H), 7.84 (t, *J* = 7.2 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.99 (t, *J* = 54.4 Hz, 1H), 3.98 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -110.65 (d, *J* = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 160.4, 151.7 (t, *J* = 26.2 Hz), 144.1, 134.0, 131.3, 126.7, 126.4 (t, *J* = 3.7 Hz), 123.4, 121.9, 121.6, 119.9, 119.1, 118.2 (t, *J* = 242.1 Hz), 110.0, 55.7. IR (ATR): ν_{max} 3081, 3008, 2964, 2837, 1619, 1489, 1472, 1444, 1413, 1307, 1252, 1218, 1202, 1172, 1129, 1090, 1051, 1022, 847, 822, 794, 763, 735, 721, 676, 575, 534, 527 cm^{-1}. MS (EI): *m/z* (%) 259 (100). HRMS: Calculated for $C_{15}H_{11}F_2NO$: 259.0809; Found: 259.0805.



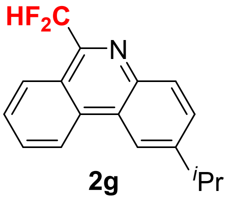
2e

3-Chloro-6-(difluoromethyl)phenanthridine (**2e**) was obtained as a light yellow solid (181.0 mg, 69%), with hexane/ethyl acetate = 5:1 as eluent for the column chromatography. mp 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.51 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 8.09 (s, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 6.95 (t, *J* = 54.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -110.78 (dd, *J* = 54.4, 8.9 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 152.4 (t, *J* = 27.0 Hz), 143.0, 134.7, 133.3, 131.5, 129.7, 129.1, 128.0, 126.5 (t, *J* = 4.4 Hz), 123.4, 123.3, 122.2, 118.1 (t, *J* = 242.1 Hz). IR (ATR): ν_{max} 1604, 1571, 1482, 1442, 1378, 1174, 1132, 1101, 1036, 878, 823, 805, 781, 762, 722, 715, 629, 530, 431 cm^{-1}. MS (EI): *m/z* (%) 263 (100). HRMS: Calculated for $C_{14}H_8ClF_2N$: 263.0313; Found: 263.0318.



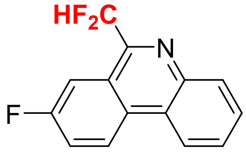
2f

6-(Difluoromethyl)-2-(trifluoromethoxy)phenanthridine (**2f**) was obtained as a light yellow solid (125.2 mg, 40%), with hexane as eluent for the column chromatography. mp 74-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.56 (t, *J* = 8.4 Hz, 2H), 8.35 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 7.91 (t, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 9.2, 1.6 Hz, 1H), 6.99 (t, *J* = 54.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -57.60 (s, 3F), -110.76 (d, *J* = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 151.9 (t, *J* = 27.0 Hz), 148.9, 148.9, 140.6, 133.2, 132.6, 131.6, 128.7, 126.7 (t, *J* = 4.4 Hz), 126.1, 122.5, 122.4, 120.6 (q, *J* = 256.7 Hz), 118.1 (t, *J* = 242.1 Hz), 113.7. IR (ATR): ν_{max} 3026, 2921, 1618, 1531, 1496, 1452, 1388, 1307, 1211, 1154, 1098, 1025, 868, 836, 820, 773, 690, 677, 517 cm^{-1}. MS (EI): *m/z* (%) 313 (100). HRMS: Calculated for $C_{15}H_8F_5NO$: 313.0526; Found: 313.0536.



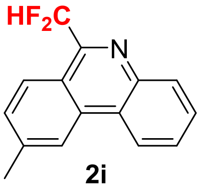
2g

6-(Difluoromethyl)-2-isopropylphenanthridine (**2g**) was obtained as a light yellow solid (183.0 mg, 68%), with hexane/ethyl acetate = 10:1 as eluent for the column chromatography. mp 75-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.63 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 8.8 Hz, 1H), 8.37 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 54.4 Hz, 1H), 3.22-3.15 (m, 1H), 1.40 (d, *J* = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -110.28 (d, *J* = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 150.5 (t, *J* = 26.2 Hz), 149.6, 141.1, 133.7, 130.9, 130.5, 128.3, 127.5, 126.3 (t, *J* = 4.3 Hz), 124.8, 122.5, 122.3, 119.1, 118.6 (t, J = 242.1 Hz), 34.7, 24.1. IR (ATR): ν_{max} 2962, 2871, 2360, 1615, 1525, 1449, 1380, 1343, 1137, 1098, 1060, 1032, 835, 804, 770, 754, 676, 509 cm^{-1}. MS (EI): *m/z* (%) 271, 256 (100). HRMS: Calculated for $C_{17}H_{15}F_2N$: 271.1173; Found: 271.1177.



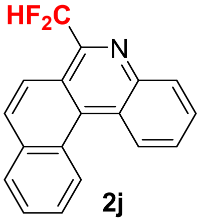
2h

6-(Difluoromethyl)-8-fluorophenanthridine (**2h**) was obtained as a light yellow solid (79.1 mg, 32%), with hexane/ethyl acetate = 5:1 as eluent for the column chromatography. mp 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.67 (q, J = 4.9 Hz, 1H), 8.54-8.52 (m, 1H), 8.21-8.18 (m, 2H), 7.79-7.74 (m, 2H), 7.64 (td, J = 8.4, 2.4 Hz, 1H), 6.98 (t, J = 54.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -110.66-(-110.73) (m, 1F), -111.03 (d, J = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 161.4 (d, J = 247.9 Hz), 150.6 (td, J = 27.0, 4.4 Hz), 142.1, 130.8, 130.6, 129.1, 129.0, 125.0 (d, J = 8.8 Hz), 124.6, 123.5 (d, J = 8.7 Hz), 121.9, 120.7 (d, J = 24.1 Hz), 118.2 (t, J = 242.1 Hz), 111.3 (dt, J = 22.6, 4.4 Hz). IR (ATR): ν_{max} 1624, 1579, 1533, 1436, 1196, 1125, 1091, 1033, 1008, 922, 827, 761, 733, 570, 491 cm^{-1}. MS (EI): *m/z* (%) 247 (100). HRMS: Calculated for $C_{14}H_8F_3N$: 247.0609; Found: 247.0601.



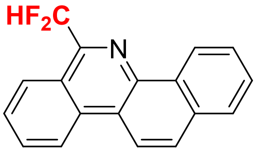
2i

6-(Difluoromethyl)-9-methylphenanthridine (**2i**) was obtained as a white solid (178.0 mg, 74%), with hexane/ethyl acetate = 5:1 as eluent for the column chromatography. mp 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.51 (d, J = 7.2 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.37 (s, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.75-7.67 (m, 2H), 7.51 (d, J = 8.4 Hz, 1H), 6.99 (t, J = 54.4 Hz, 1H), 2.61 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -110.59 (d, J = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 151.2 (t, *J* = 25.5 Hz), 142.6, 141.8, 134.0, 130.5, 129.5, 128.9, 128.3, 126.2 (t, *J* = 3.7 Hz), 124.8, 122.1, 122.0, 120.5, 118.4 (t, *J* = 241.4 Hz), 22.4. IR (ATR): ν_{max} 1621, 1466, 1369, 1122, 1090, 1020, 873, 840, 817, 760, 733, 491, 422 cm^{-1}. MS (EI): *m/z* (%) 243 (100). HRMS: Calculated for $C_{15}H_{11}F_2N$: 243.0860; Found: 243.0849.



2j

6-(Difluoromethyl)benzo[*k*]phenanthridine (**2j**) was obtained as a light yellow solid (202.0 mg, 72%), with hexane as eluent for the column chromatography. mp 109-110 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 293K, TMS): δ ppm 8.94 (d, *J* = 7.6 Hz, 1H), 8.88 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.8 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.96-7.91 (m, 2H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.71-7.62 (m, 3H), 7.14 (t, *J* = 54.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl$_3$): δ ppm -109.51 (d, *J* = 56.0 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$, 293K, TMS): δ ppm 150.2 (t, *J* = 25.5 Hz), 144.4, 134.7, 133.1, 130.4, 128.8, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 127.1, 126.9, 125.1, 121.8 (t, *J* = 4.3 Hz), 121.7, 118.6 (t, *J* = 242.1 Hz). IR (ATR): ν_{max} 3063, 1602, 1580, 1498, 1462, 1394, 1361, 1165, 1123, 1081, 1034, 901, 829, 774, 757, 612, 538, 518 cm^{-1}. MS (EI): *m/z* (%) 279 (100). HRMS: Calculated for $C_{18}H_{11}F_2N$: 279.0860; Found: 279.0864. Anal. Calcd. for $C_{18}H_{11}F_2N$: C, 77.41; H, 3.97; N, 5.02. Found: C, 76.05; H, 4.10; N, 4.71.



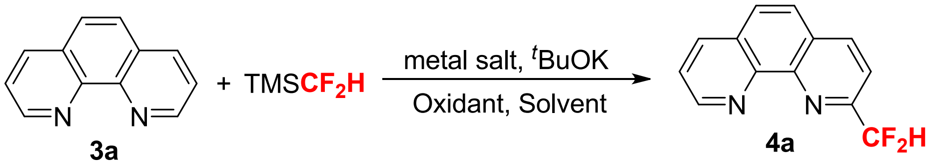
2k

6-(Difluoromethyl)benzo[*c*]phenanthridine (**2k**) was obtained as a white solid (217.0 mg, 78%), with hexane as eluent for the column chromatography. mp 151-153 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 293K, TMS): δ ppm 9.32 (d, *J* = 8.4 Hz, 1H), 8.63 (dd, *J* = 7.6, 5.2 Hz, 2H), 8.41 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.91 (d, *J* = 8.0

Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.75-7.64 (m, 3H), 7.18 (t, *J* = 54.8 Hz, 1H). ^{19}F NMR (376 MHz, CDCl$_3$): δ ppm -109.46 (d, *J* = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$, 293K, TMS): δ ppm 149.7 (t, *J* = 26.2 Hz), 139.3, 134.0, 133.2, 131.9, 130.9, 129.4, 127.7, 127.5, 127.3, 126.2 (t, *J* = 3.6 Hz), 124.7, 123.0, 122.7, 122.4, 119.5, 118.9 (t, *J* = 241.3 Hz). IR (ATR): ν_{max} 1386, 1340, 1161, 1116, 1081, 1014, 870, 823, 798, 782, 758, 724, 686, 666, 627, 575, 547 cm^{-1}. MS (EI): *m/z* (%) 279 (100). HRMS: Calculated for $C_{18}H_{11}F_2N$: 279.0860; Found: 279.0859.

3. Optimization of Reaction Conditions for Silver-Mediated

Oxidative Difluoromethylation of 1,10-Phenanthroline with $TMSCF_2H$.[a]



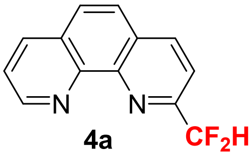
Entry	Metal salts	Oxidant/equiv.	Solvent	Yield[b]
1	CuI	NCS/1.0	THF	0%
2	AgF	NCS/1.0	THF	15%
3	Ag_2CO_3	NCS/1.0	THF	18%
4	AgCl	NCS/1.0	THF	24%
5	AgOAc	NCS/1.0	THF	0%
6	AgCl	$PhI(OCOCF_3)_2$/1.0	THF	7%
7	AgCl	DDQ/1.0	THF	18%
8	AgCl	NBS/1.0	THF	20%
9	AgCl	NIS/1.0	THF	15%
10	AgCl	NCS/1.0	MeCN	0%
11	AgCl	NCS/1.0	DMF	0%
12	AgCl	NCS/1.0	CH_2Cl_2	0%
13	AgCl	NCS/1.0	Dioxane	36%
14	AgCl	NCS/1.0	Diglyme	29%
15[c]	AgCl	NCS/2.0	Dioxane	52%
16[d]	**AgCl**	**NCS/3.0**	**Dioxane**	**69%**
17[e]	AgCl	NCS/4.0	Dioxane	37%
18[f]	AgCl	NCS/3.0	Dioxane	20%
19[g]	AgCl	NCS/3.0	Dioxane	42%
20[h]	AgCl	NCS/3.0	Dioxane	5%

[a] Reaction conditions: **3a** (0.1 mmol, 1.0 eq.), metal salt (0.1 mmol, 1.0 eq.), *t*BuOK (0.1 mmol, 1.0 eq.), $TMSCF_2H$ (0.1 mmol, 1.0 eq.), Oxidant (0.1 mmol, 1.0 eq.) in 1 mL solvent under Ar atomosphere. [b] Yields determined by ^{19}F NMR spectroscopy using difluoromethylbenzene as internal standard. [c] *t*BuOK (0.2 mmol, 2.0 eq.), $TMSCF_2H$ (0.2 mmol, 2.0 eq.). [d] *t*BuOK (0.3 mmol, 3.0 eq.), $TMSCF_2H$ (0.3 mmol, 3.0 eq.). [e] *t*BuOK (0.4 mmol, 4.0 eq.), $TMSCF_2H$ (0.4 mmol, 4.0 eq.). [f] *t*BuOK (0.2 mmol, 2.0 eq.), $TMSCF_2H$ (0.3 mmol, 3.0 eq.). [g] *t*BuOK (0.3 mmol, 3.0 eq.), $TMSCF_2H$ (0.2 mmol, 2.0 eq.). [h] *t*BuOK (0.3 mmol, 3.0 eq.), $TMSCF_2H$ (0.1 mmol, 1.0 eq.).

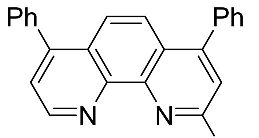
4. General Procedures for Silver-Mediated Oxidative

Difluoromethylation of 1,10-Phenanthrolines

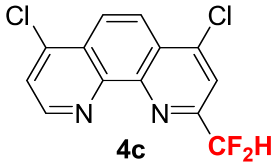
In a glove box, ^{t}BuOK (3.0 mmol, 336.6 mg), 1,10-phenanthroline (1.0 mmol), and AgCl (1.0 mmol, 143.5 mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum. Dioxane (10 mL) was added under Ar atmosphere and the mixture was stirred at room temperature for 10 minutes. Next, $TMSCF_2H$ (3.0 mmol, 372.6 mg) was added and the mixture was stirred for 5 minutes, followed by the addition of *N*-chlorosuccinimide (3.0 mmol, 400.5 mg). Then, the reaction mixture was stirred at room temperature for 10 h. The reaction was quenched by water and extracted with ethyl acetate (3×30 mL), and the combined organic layer was washed with water and brine (3×50 mL), dried over Na_2SO_4 and concentrated. The resulting residue was purified by flash column chromatography.



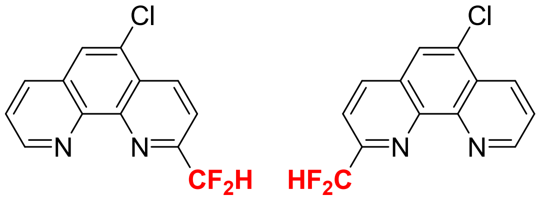
2-(Difluoromethyl)-1,10-phenanthroline (**4a**) was obtained as a light yellow solid (154.0 mg, 67%), with chloroform/methanol/triethylamine = 100:1:1 as eluent for the column chromatography. mp 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 9.16 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.72 (q, *J* = 8.8 Hz, 2H), 7.58 (t, *J* = 3.6 Hz, 1H), 7.07 (t, *J* = 55.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -112.69 (d, *J* = 54.1 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 152.9 (t, *J* = 27.0 Hz), 150.7, 145.8, 145.2, 137.8, 136.3, 129.5, 129.0, 128.1, 126.1, 123.4, 119.1, 114.9 (t, *J* = 238.5 Hz). IR (ATR): ν_{max} 2987, 2189, 1620, 1590, 1494, 1397, 1342, 1111, 1085, 1029, 908, 855, 835, 802, 777, 746, 723, 624, 514 cm^{-1}. MS (EI): *m/z* (%) 230 (100). HRMS: Calculated for $C_{13}H_8F_2N_2$: 230.0656; Found: 230.0658.


4b

2-(Difluoromethyl)-4,7-diphenyl-1,10-phenanthroline (**4b**) was obtained as a light yellow solid (280.0 mg, 73%), with chloroform as eluent for the column chromatography. mp 65-67 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 293K, TMS): δ ppm 9.27 (d, *J* = 4.8 Hz, 1H), 7.94-7.85 (m, 3H), 7.59 (d, *J* = 4.8 Hz, 1H), 7.51-7.49 (m, 10H), 7.17 (t, *J* = 55.2 Hz, 1H). ^{19}F NMR (376 MHz, CDCl$_3$): δ ppm -112.58 (d, *J* = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$, 293K, TMS): δ ppm 152.4 (t, *J* = 27.7 Hz), 150.5, 150.2, 148.8, 146.5, 146.0, 137.6, 137.4, 129.6, 128.9, 128.8, 128.7, 127.5, 126.9, 125.6, 123.9, 123.8, 119.6, 115.1 (t, *J* = 239.1 Hz). IR (ATR): ν_{max} 3058, 3032, 2958, 2211, 1954, 1811, 1711, 1618, 1591, 1557, 1512, 1491, 1445, 1410, 1378, 1343, 1212, 1201, 1110, 1076, 1041, 896, 857, 836, 814, 789, 751, 702, 661, 641, 561, 475 cm^{-1}. MS (EI): *m/z* (%) 382 (100). HRMS: Calculated for $C_{25}H_{16}F_2N_2$: 382.1282; Found: 382.1290.

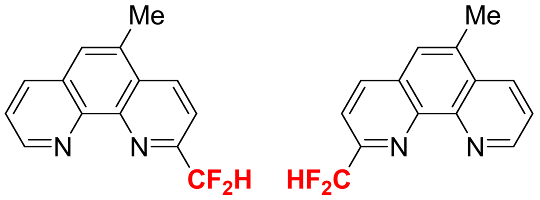

4c

4,7-Dichloro-2-(difluoromethyl)-1,10-phenanthroline (**4c**) was obtained as a light yellow solid (96.0 mg, 32%), with chloroform/methanol/triethylamine = 100:1:1 as eluent for the column chromatography. mp 204-206 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 293K, TMS): δ ppm 9.13 (dd, *J* = 6.4, 4.8 Hz, 1H), 8.41-8.30 (m, 2H), 8.10 (d, *J* = 6.8 Hz, 1H), 7.78 (dd, *J* = 7.2, 4.8 Hz, 1H), 7.08 (td, *J* = 54.8, 4.0 Hz, 1H). ^{19}F NMR (376 MHz, CDCl$_3$): δ ppm -113.43 (d, *J* = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, CDCl$_3$, 293K, TMS): δ ppm 153.3 (td, *J* = 28.0, 3.6 Hz), 150.8, 146.6 (d, *J* = 3.6 Hz), 146.0, 144.6 (d, *J* = 2.7 Hz), 143.2 (d, *J* = 4.5 Hz), 127.7 (d, *J* = 4.5 Hz), 127.3 (d, *J* = 4.5 Hz), 124.7 (d, *J* = 3.6 Hz), 124.3 (d, *J* = 1.8 Hz), 122.9 (d, *J* = 5.5 Hz), 120.2 (d, *J* = 1.8 Hz), 114.0 (t, *J* = 240.2 Hz). IR (ATR): ν_{max} 1609, 1578, 1543, 1487, 1405, 1317, 1211, 1080, 1039, 1024, 880, 846, 803, 729, 633, 544 cm^{-1}. MS (EI): *m/z* (%) 298 (100). HRMS: Calculated for $C_{13}H_6Cl_2F_2N_2$: 298.9876; Found: 298.9881.



4d + 4d'

5-Chloro-2-(difluoromethyl)-1,10-phenanthroline (**4d**) and 6-chloro-2-(difluoromethyl)-1,10-phenanthroline (**4d'**) were obtained as a white solid (163.7 mg, 62%), with chloroform/methanol/triethylamine = 100:1:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 9.22 (dd, *J* = 4.4, 1.6 Hz, 0.8H), 9.16 (dd, *J* = 4.0, 1.6 Hz, 0.2H), 8.77 (dt, *J* = 8.8, 2.0 Hz, 0.2 H), 8.62 (dt, *J* = 8.4, 2.2 Hz, 0.8H), 8.25 (dd, *J* = 8.8, 2.0 Hz, 0.8H), 8.12 (dt, *J* = 8.0, 2.0 Hz, 0.2H), 8.03 (dd, *J* = 8.4, 1.6 Hz, 0.2H), 7.93 (dd, *J* = 8.4, 1.6 Hz, 0.8H), 7.87 (d, *J* = 2.8 Hz, 0.2H), 7.84 (d, *J* = 2.8 Hz, 0.8H), 7.72 (qd, *J* = 4.0, 1.6 Hz, 0.8H), 7.61 (qd, *J* = 4.0, 1.6 Hz, 0.2H), 7.08 (t, *J* = 54.8 Hz, 0.2H), 7.05 (t, *J* = 54.8 Hz, 0.8H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -113.02 (d, *J* = 54.5 Hz, 1.6F), -113.29 (d, *J* = 54.5 Hz, 0.4F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 153.5 (t, *J* = 12.6 Hz), 153.2 (t, *J* = 27.1 Hz), 151.3, 151.0, 146.2, 145.7, 144.8, 144.2, 137.0, 135.5, 135.3, 133.5, 131.7, 129.7, 129.1, 128.6, 127.8, 127.3, 127.1, 125.3, 124.1, 124.0, 119.8, 119.6, 114.6 (t, *J* = 239.3 Hz), 114.5 (t, *J* = 239.2 Hz). IR (ATR): ν_{max} 2921, 2202, 1609, 1589, 1488, 1457, 1395, 1349, 1252, 1115, 1075, 1032, 942, 926, 876, 803, 754, 721, 665, 626, 430 cm^{-1}. MS (EI): *m/z* (%) 264 (100). HRMS: Calculated for $C_{13}H_7ClF_2N_2$: 264.0266; Found: 264.0272.

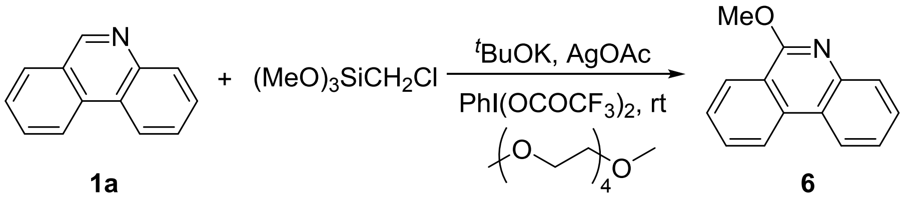


4e + 4e'

2-(Difluoromethyl)-5-methyl-1,10-phenanthroline (**4e**) and 2-(difluoromethyl)-6-methyl-1,10-phenanthroline (**4e'**) were obtained as a white solid (138.2 mg, 57%), with chloroform as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 9.19-9.18 (m, 0.33 H), 9.13-9.11 (m, 0.67H), 8.48-8.44

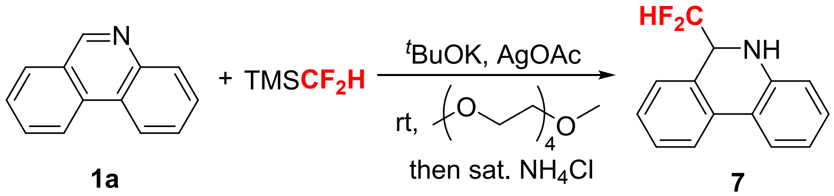
(m, 0.67H), 8.36-8.32 (m, 0.33H), 8.24-8.20 (m, 0.33H), 8.12-8.08 (m, 0.67H), 8.00-7.94 (m, 0.67H), 7.90-7.87 (m, 0.33H), 7.66-7.62 (m, 0.33H), 7.58-7.54 (m, 1.67H), 7.09 (t, *J* = 54.8 Hz, 0.67H), 7.07 (t, *J* = 54.8 Hz, 0.33H), 2.69 (s, 0.33H), 2.68 (s, 0.67H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -113.02 (d, *J* = 54.5 Hz, 1.33F), -113.29 (d, *J* = 54.5 Hz, 0.67F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 152.4, 152.2, 150.2, 150.0, 145.8, 145.3, 145.1, 144.5, 137.0, 135.5, 134.8, 134.3, 132.8, 132.7, 129.8, 129.5, 129.2, 128.9, 127.2, 125.4, 123.5, 123.2, 119.2, 118.9, 115.0 (t, *J* = 238.5 Hz), 114.9 (t, *J* = 239.2 Hz), 29.7, 19.2. IR (ATR): ν_{max} 3445, 2924, 2195, 1624, 1562, 1489, 1406, 1377, 1351, 1117, 1078, 1034, 936, 910, 879, 838, 793, 725, 666, 523 cm^{-1}. MS (EI): *m/z* (%) 244 (100). HRMS: Calculated for $C_{14}H_{10}F_2N_2$: 244.0812; Found: 244.0807.

5. Methoxylation of Phenanthridine 1a

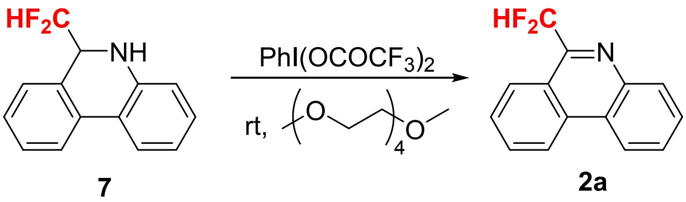


In a glove box, ^{t}BuOK (3.0 mmol, 336.6 mg), phenanthridine (1.0 mmol, 179.1 mg), and AgOAc (1.0 mmol, 166.9 mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum. Tetraethylene glycol dimethyl ether (10 mL) was added under Ar atmosphere and the mixture was stirred at room temperature for 10 minutes. Next, $(MeO)_3SiCH_2Cl$ (3.0 mmol, 512.0 mg) was added and the mixture was stirred for 5 minutes, followed by the addition of [bis(trifluoroacetoxy)iodo]benzene (3.0 mmol, 1290.1 mg). Then, the reaction mixture was stirred at room temperature for 10 h. The reaction was quenched by water and extracted with ethyl acetate (3×30 mL), and the combined organic layer was washed with water and brine (3×50 mL), dried over Na_2SO_4 and concentrated. The resulting residue was purified by flash column chromatography (chloroform) to afford **6** as a light yellow solid (113.1 mg, 0.54 mmol, 54%). ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 8.44 (d, *J* = 8.4 Hz, 1H), 8.37 (t, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.75 (td, *J* = 6.8, 1.2 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 4.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 159.2, 143.4, 134.8, 130.8, 128.8, 127.9, 127.2, 125.1, 124.4, 122.6, 122.2, 121.9, 120.1, 53.6. IR (ATR): ν_{max} 3446, 3075, 3013, 2984, 2946, 2895, 2847, 1942, 1621, 1589, 1578, 1531, 1488, 1473, 1434, 1356, 1323, 1242, 1227, 1184, 1164, 1145, 1090, 1039, 983, 899, 861, 758, 726, 669, 661, 567, 506, 450 cm^{-1}. MS (EI): *m/z* (%) 209, 208 (100). HRMS: Calculated for $C_{14}H_{11}NO$: 209.0841; Found: 209.0840.

6. Addition of Phenanthridine 1a with TMSCF$_2$H and Aromatization

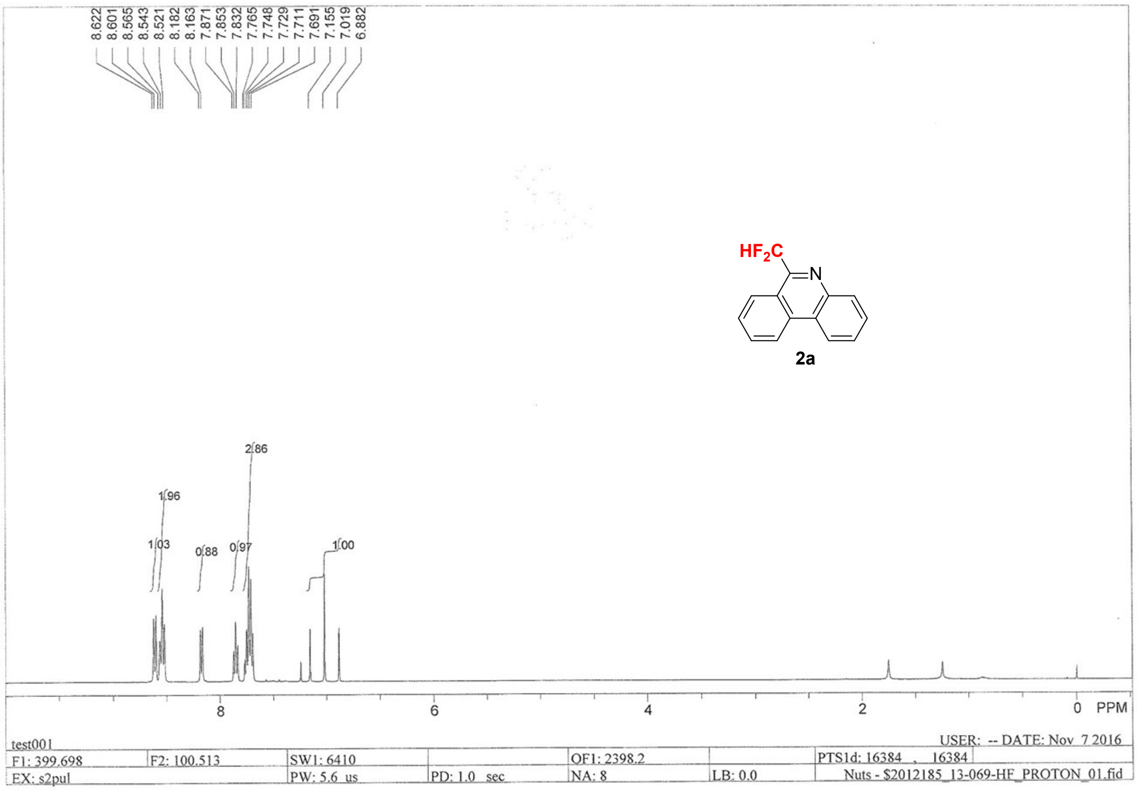


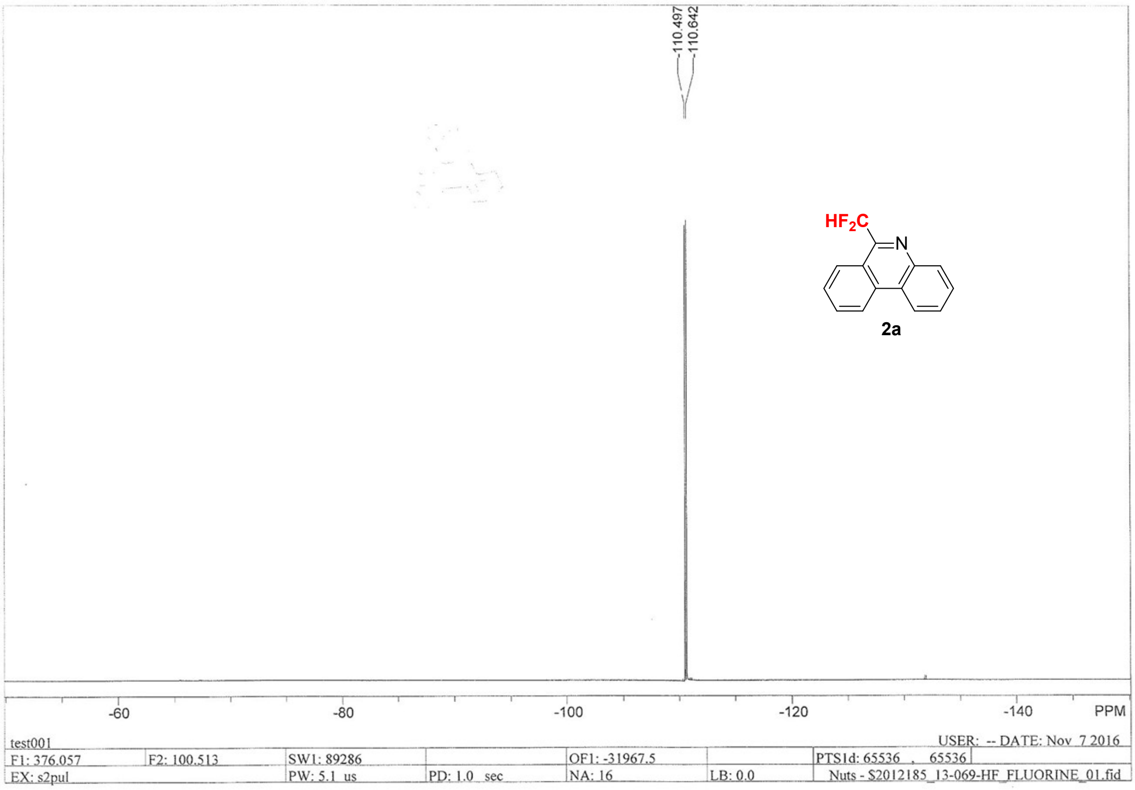
Addition of Phenanthridine 1a with TMSCF$_2$H: In a glove box, ^{t}BuOK (3.0 mmol, 336.6 mg), phenanthridine (1.0 mmol, 179.1 mg), and AgOAc (1.0 mmol, 166.9 mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum. Tetraethylene glycol dimethyl ether (10 mL) was added under Ar atmosphere and the mixture was stirred at room temperature for 10 minutes. Next, TMSCF$_2$H (3.0 mmol, 372.6 mg) was added and the mixture was stirred for 10 minutes, followed by the addition of saturated NH_4Cl (10 mL). Then, the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by water and extracted with ethyl acetate (3×30 mL), and the combined organic layer was washed with water and brine (3×50 mL), dried over Na_2SO_4 and concentrated. The resulting residue was purified by flash column chromatography (hexane/ethyl acetate = 5:1) to afford **7** as light yellow solid (141.0 mg, 0.61 mmol, 61%). Mp 76-78 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.81 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.44 (td, *J* = 7.4, 1.6 Hz, 1H), 7.34-7.26 (m, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 7.2 (d, *J* = 8.0 Hz, 1H), 5.71 (td, *J* = 56.8, 6.4 Hz, 1H), 4.51-4.45 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -126.82 (ddd, *J* = 282.0, 57.2, 10.9 Hz, 1F), -127.85 (ddd, *J* = 282.0, 56.0, 8.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$, 293K, TMS): δ ppm 142.2, 131.9, 129.5, 129.3, 128.8, 127.6, 127.4, 123.6, 122.7, 120.3, 119.6, 115.2, 114.7 (t, *J* = 224.5 Hz), 57.5 (t, *J* = 23.5 Hz). IR (ATR): ν_{max} 3400, 3069, 3029, 2968, 2923, 1925, 1609, 1492, 1474, 1448, 1384, 1353, 1311, 1292, 1223, 1099, 1062, 884, 753, 732, 671, 620, 542 cm^{-1}. MS (EI): *m/z* (%) 231, 180 (100). HRMS: Calculated for $C_{14}H_{11}F_2N$: 231.0860; Found: 231.0862.

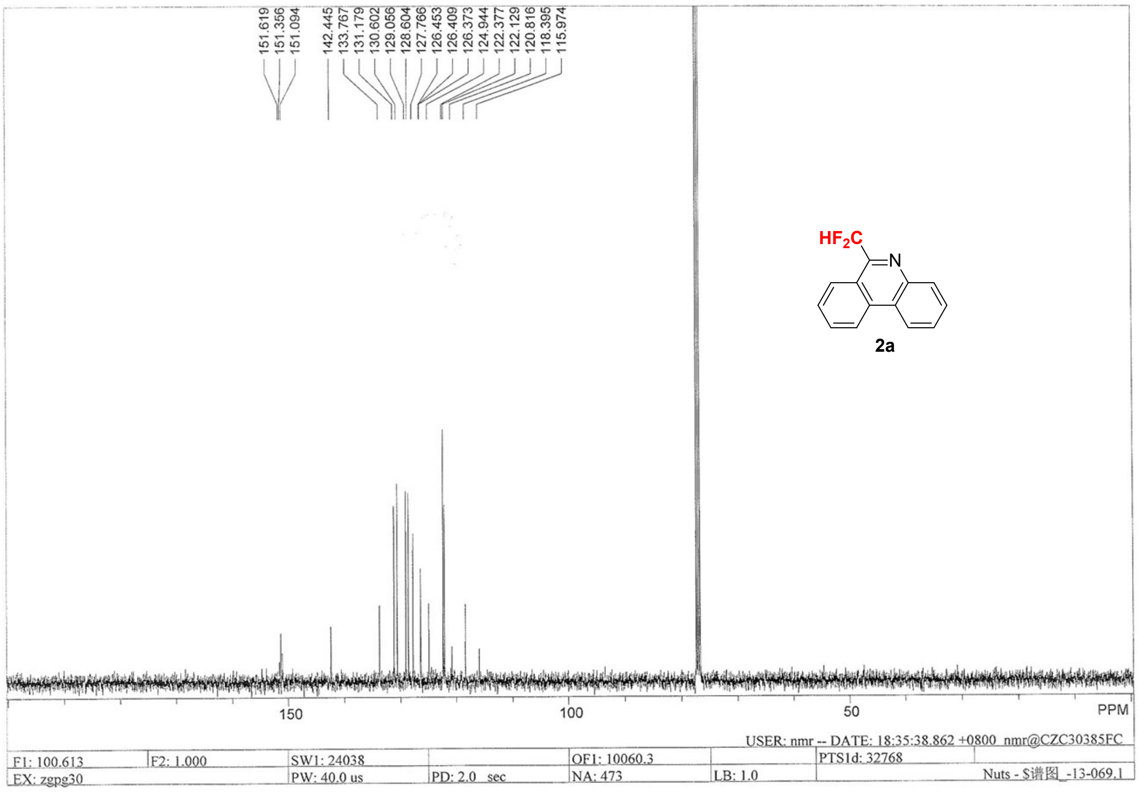


Aromatization: In a glove box, **7** (0.2 mmol, 46.2 mg) was added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum. Tetraethylene glycol dimethyl ether (2 mL) was added under Ar atmosphere and the mixture was stirred at room temperature for 10 minutes. Next, [bis(trifluoroacetoxy)iodo]benzene (0.6 mmol, 258.0 mg) was added and the mixture was stirred for 10 h. The reaction was quenched by water and extracted with ethyl acetate (3×10 mL), and the combined organic layer was washed with water and brine (3×15 mL), dried over Na_2SO_4 and concentrated. The resulting residue was purified by flash column chromatography (hexane/ethyl acetate = 5:1) to afford **2a** as a light yellow solid (45.8 mg, 0.2 mmol, quantitative).

7. Copies of ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR Spectra of products



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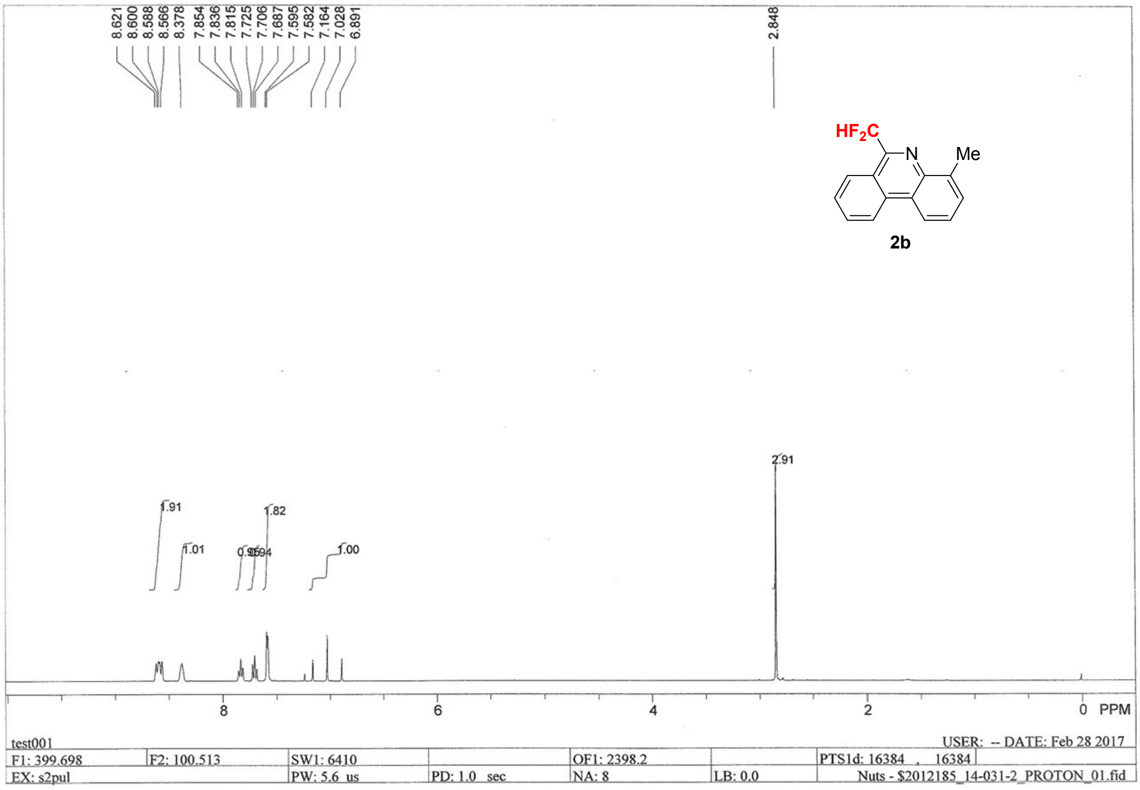
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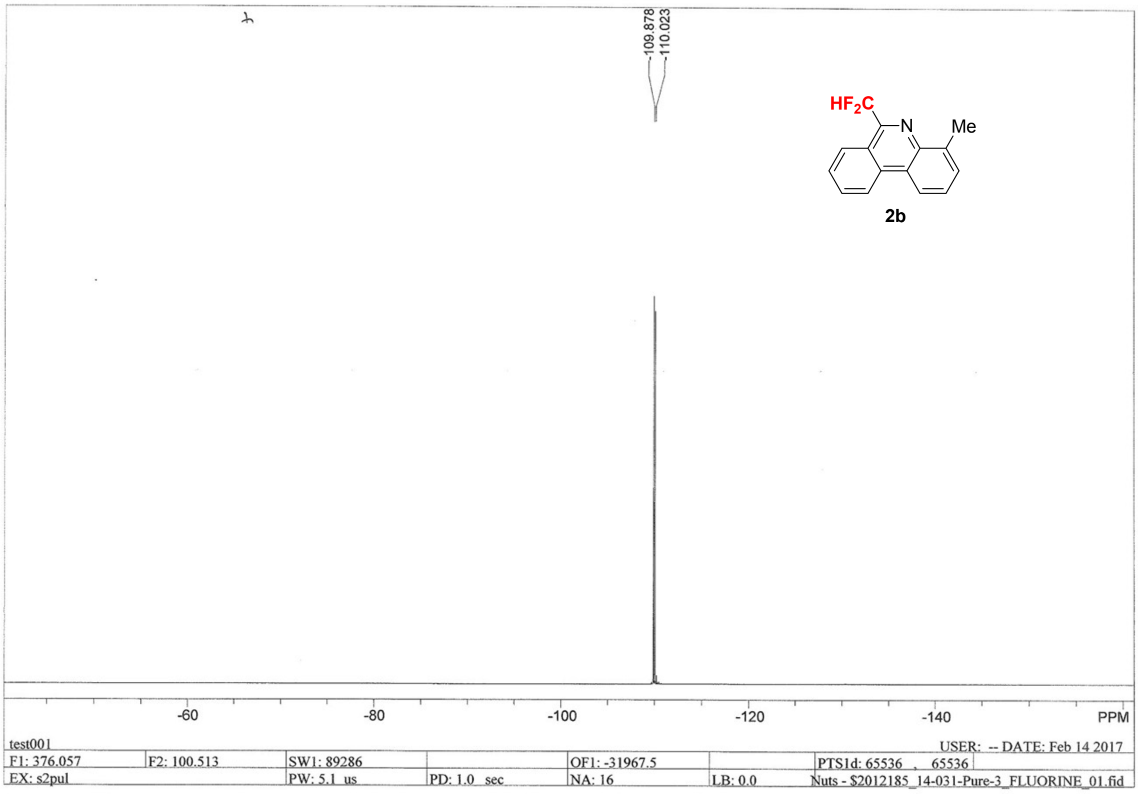
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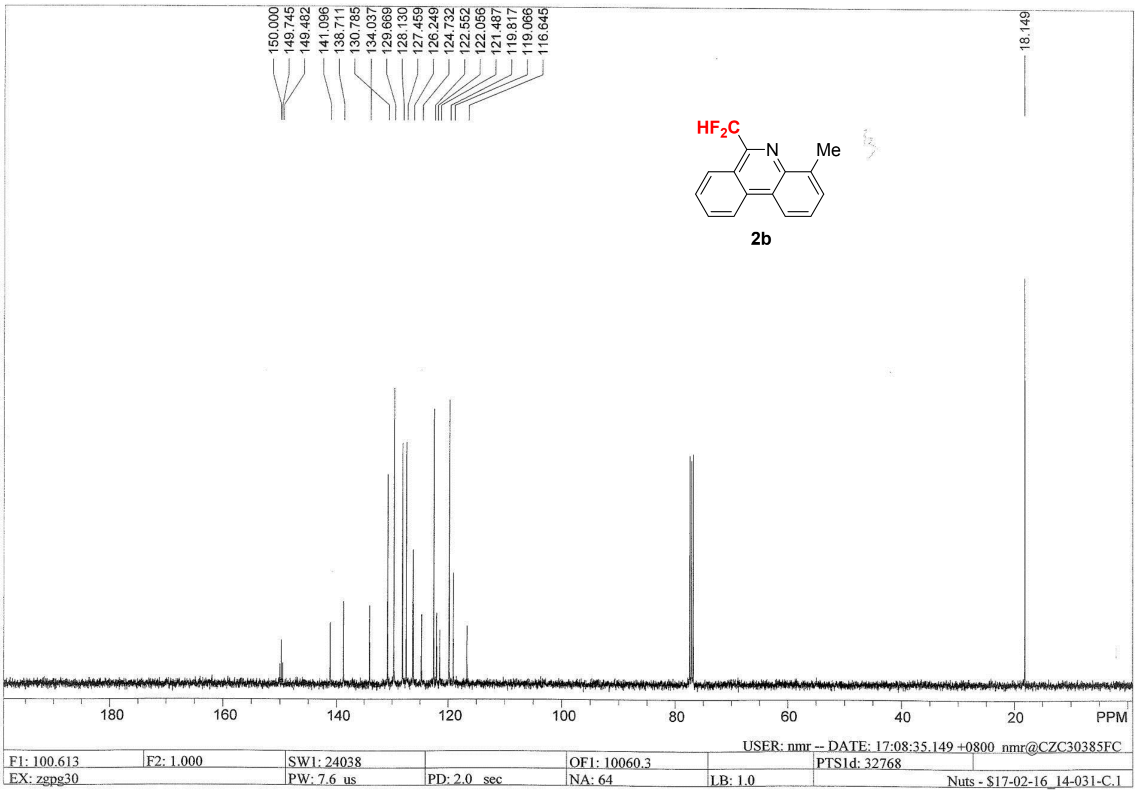
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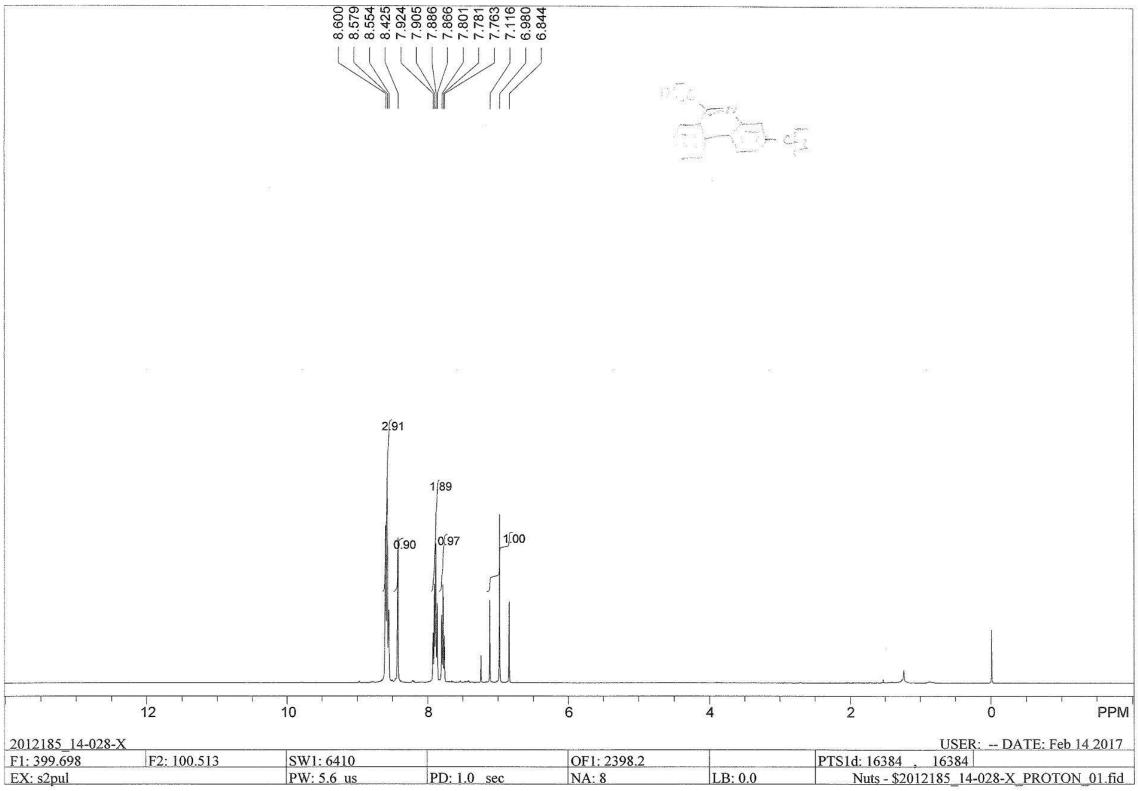
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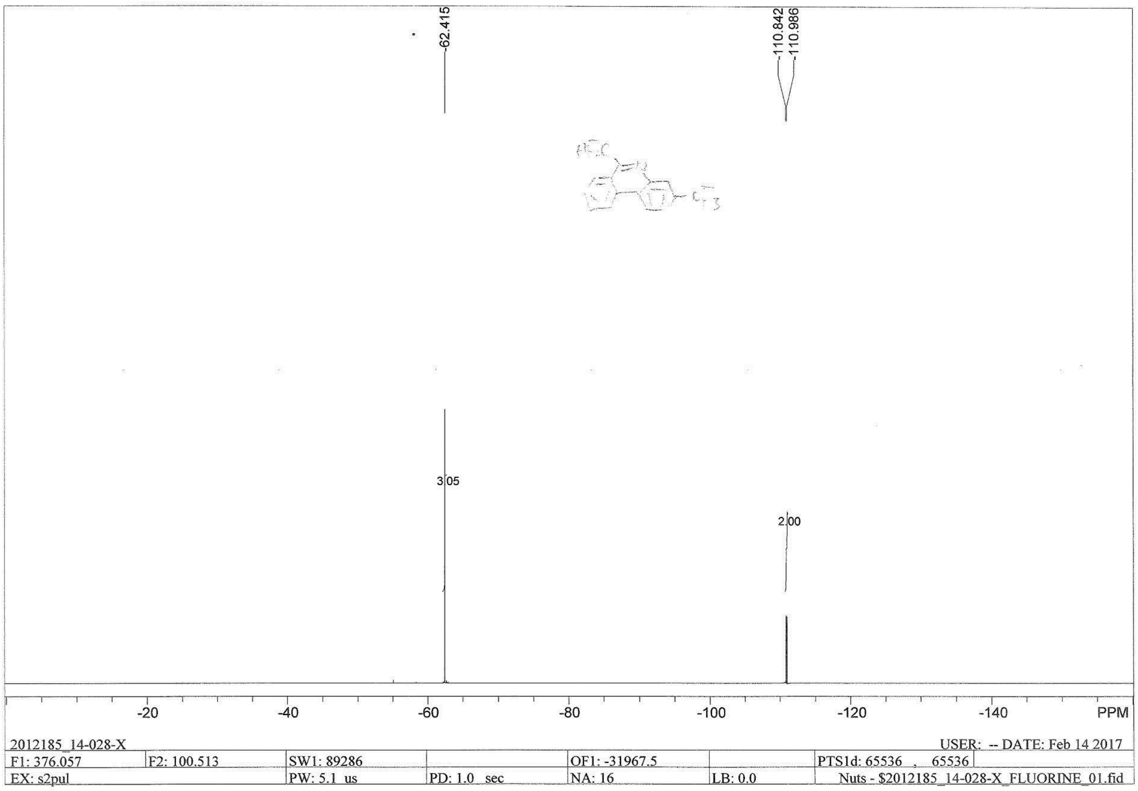
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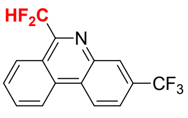
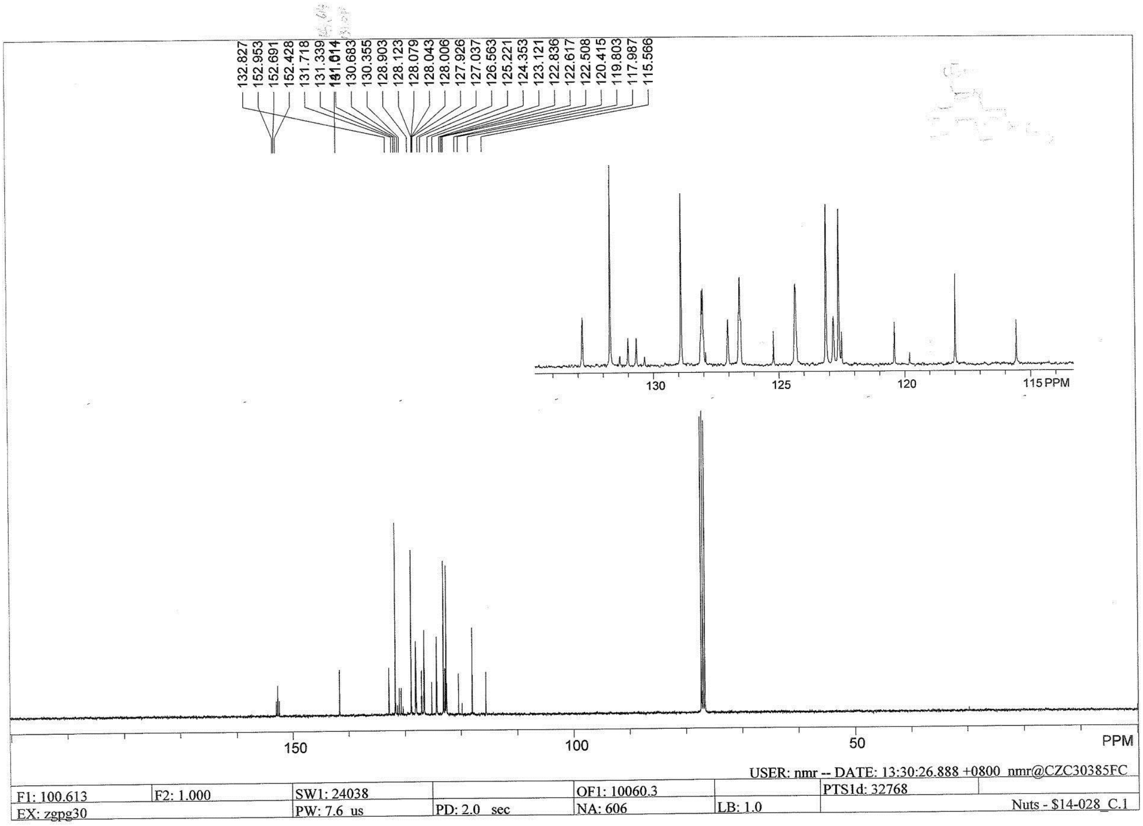
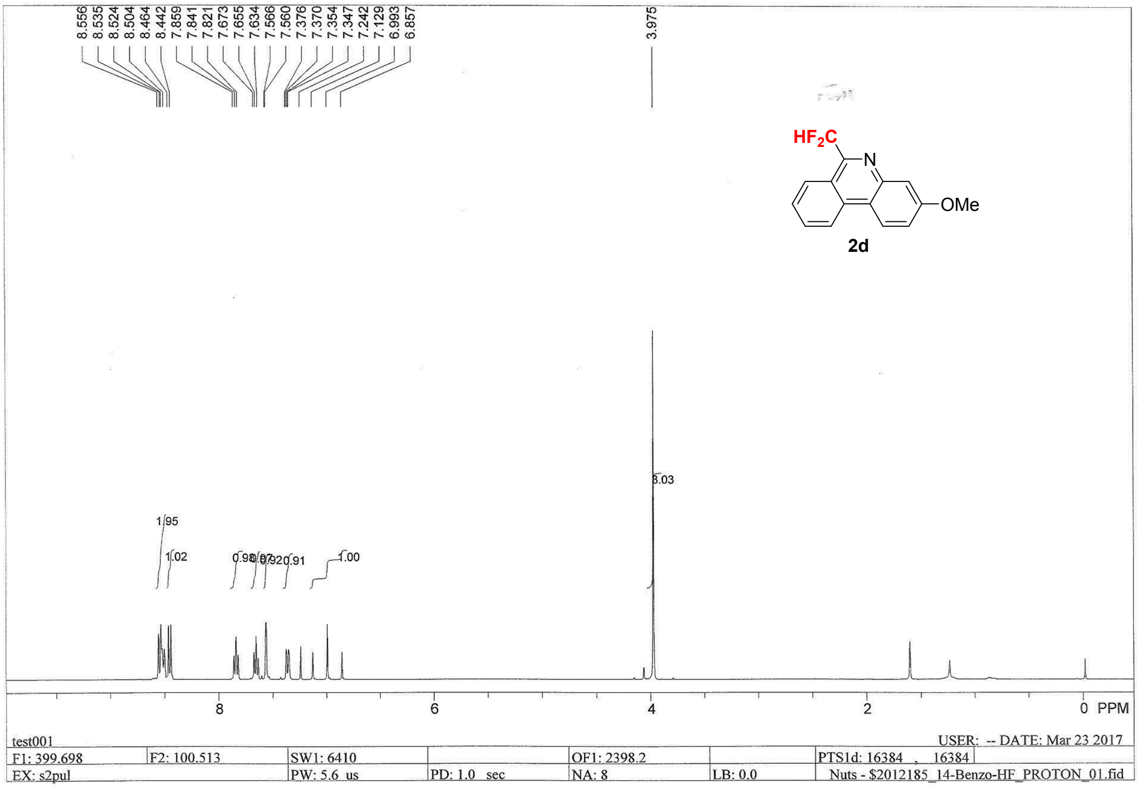
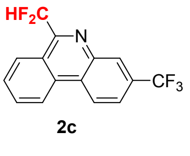
-40
-60
-80
-100
-120
-140
PPM
2012185_14-028-X
USER: -- DATE: Feb 14 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185_14-028-X_FLUORINE_01.fid


HF2C
N
CF3

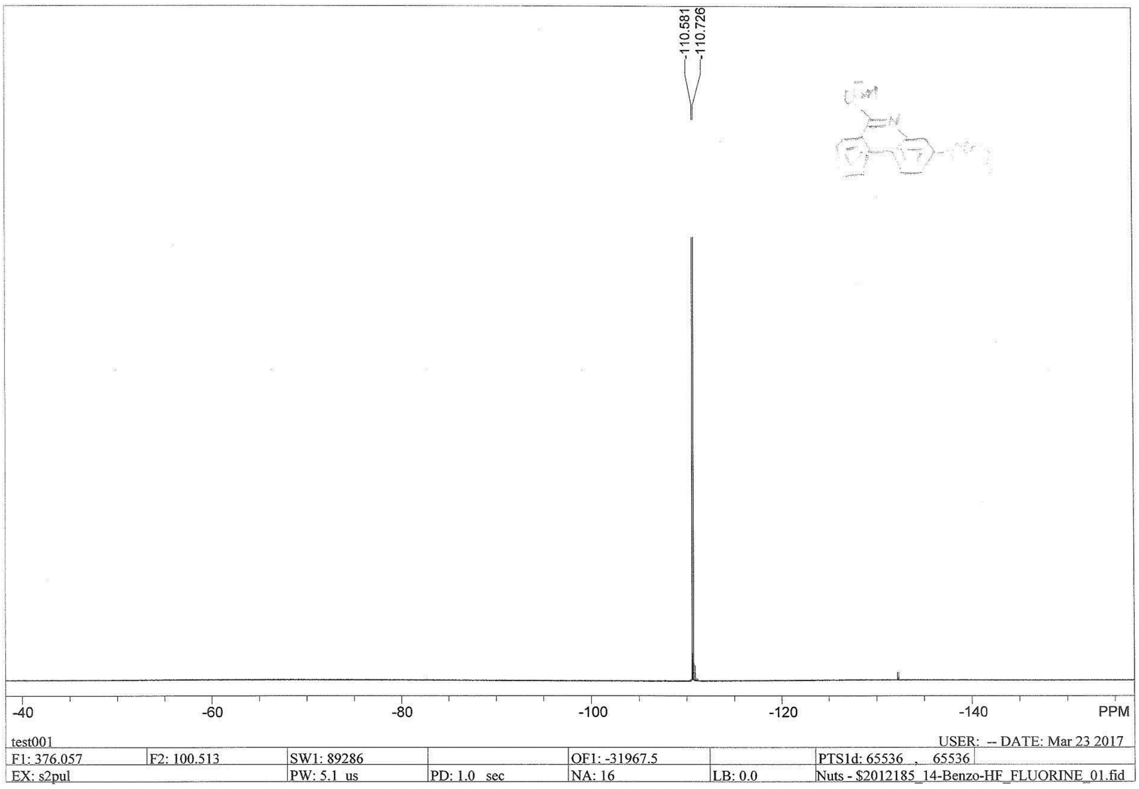
2c

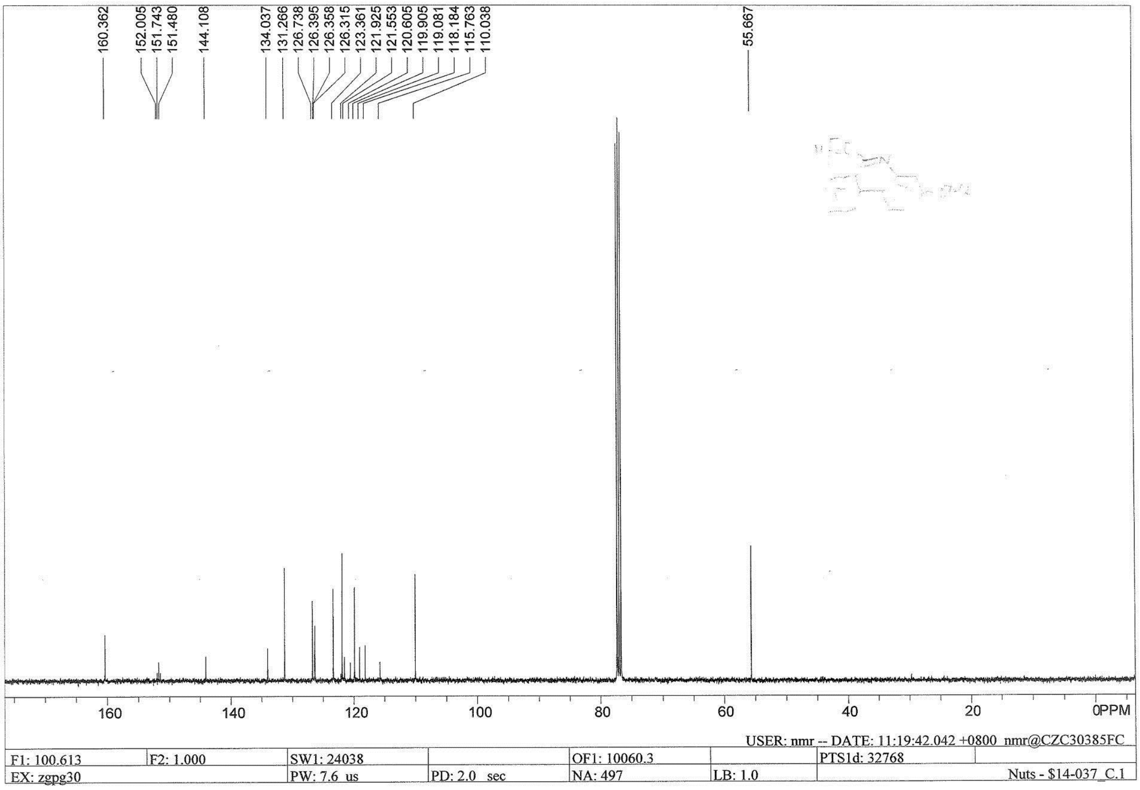

132.827
152.953
152.691
152.428
131.718
131.339
131.614
130.683
130.355
128.903
128.123
128.079
128.043
128.006
127.926
127.037
126.563
125.221
124.353
123.121
122.836
122.617
122.508
120.415
119.803
117.987
115.566
130
125
120
115 PPM
150
100
50
PPM
USER: nmr -- DATE: 13:30:26.888 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 606
LB: 1.0
Nuts - $14-028_C.1

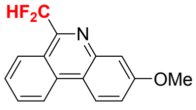

8.556
8.535
8.524
8.504
8.464
8.442
7.859
7.841
7.821
7.673
7.655
7.634
7.566
7.560
7.376
7.370
7.354
7.347
7.242
7.129
6.993
6.857
3.975
HF2C
N
OMe
2d
1.95
1.02
0.98
0.97
0.92
0.91
1.00
3.03
8
6
4
2
0 PPM
test001
USER: -- DATE: Mar 23 2017
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_14-Benzo-HF_PROTON_01.fid


HF2C
N
CF3

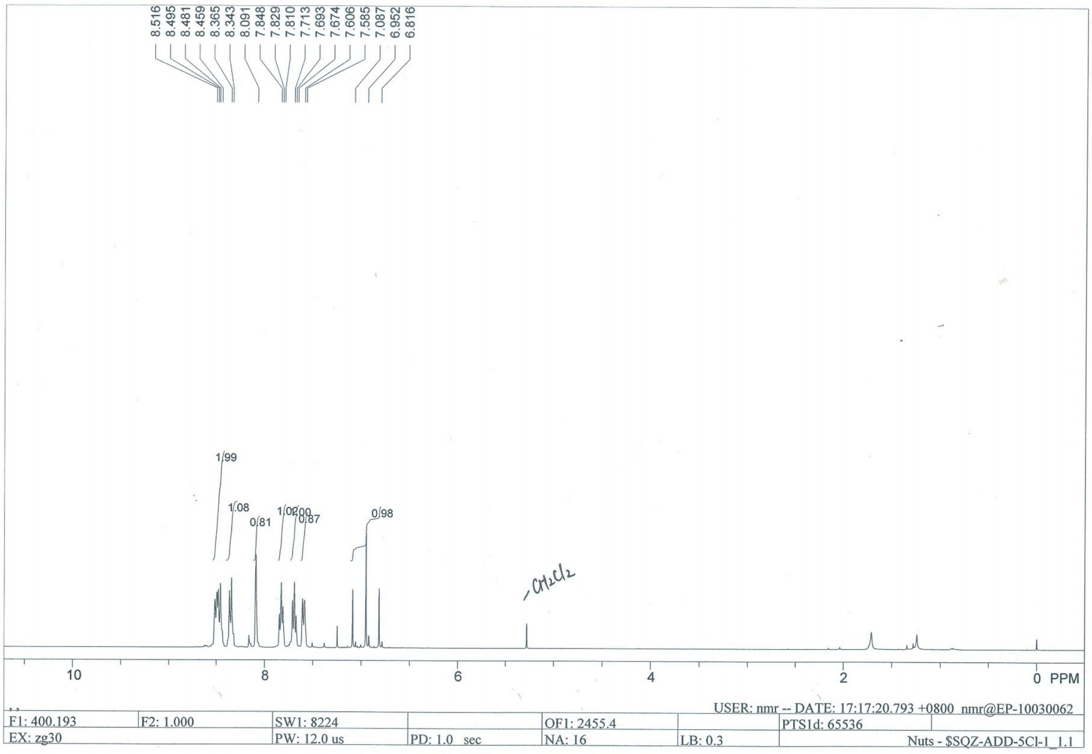
2c

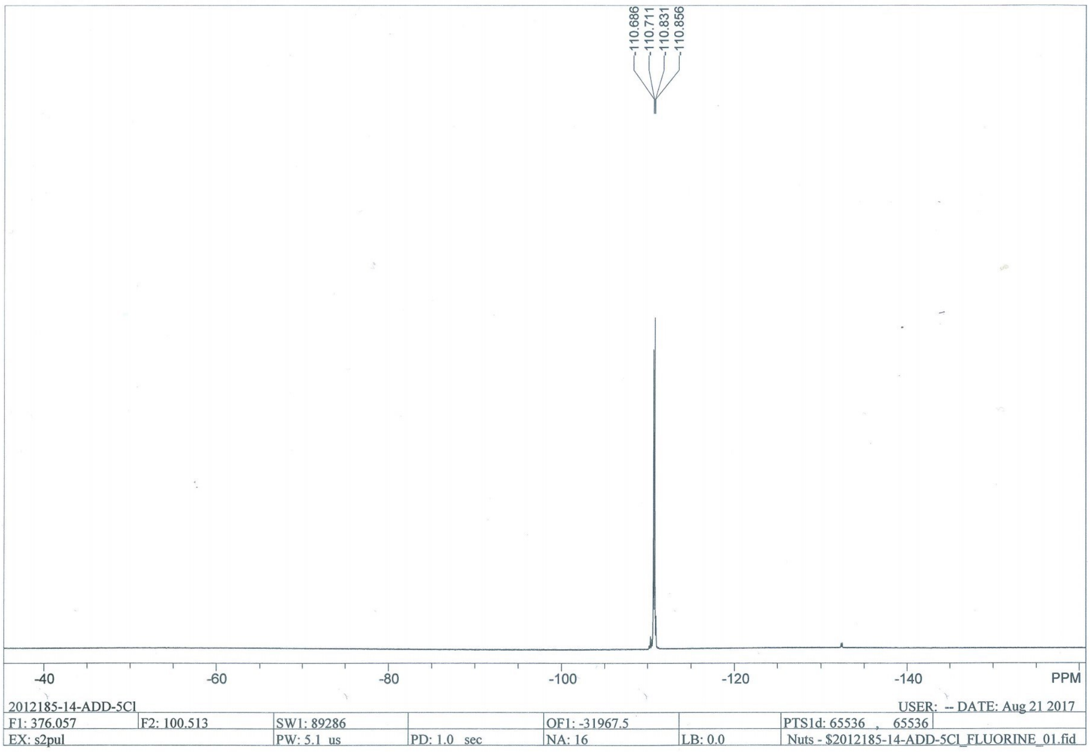

-110.581
-110.726
-40
-60
-80
-100
-120
-140
PPM
test001
USER: -- DATE: Mar 23 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185_14-Benzo-HF_FLUORINE_01.fid

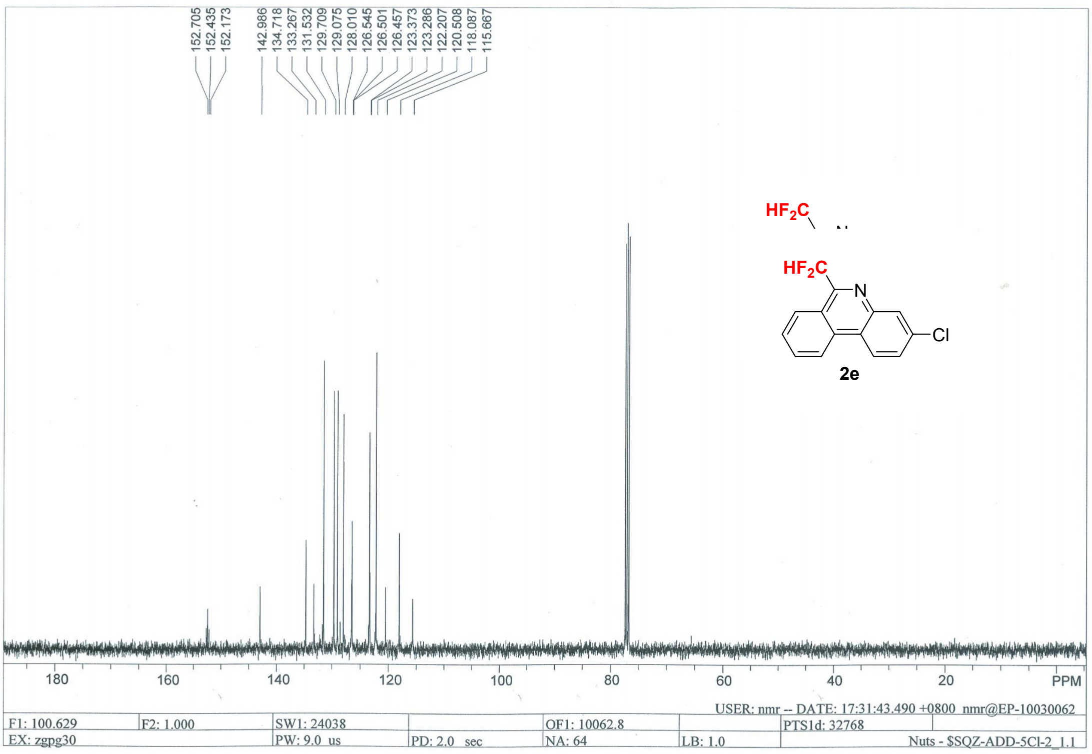

160.362
152.005
151.743
151.480
144.108
134.037
131.266
126.738
126.395
126.358
126.315
123.361
121.925
121.553
120.605
119.905
119.081
118.184
115.763
110.038
55.667
160
140
120
100
80
60
40
20
0PPM
USER: nmr -- DATE: 11:19:42.042 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 497
LB: 1.0
Nuts - $14-037_C.1

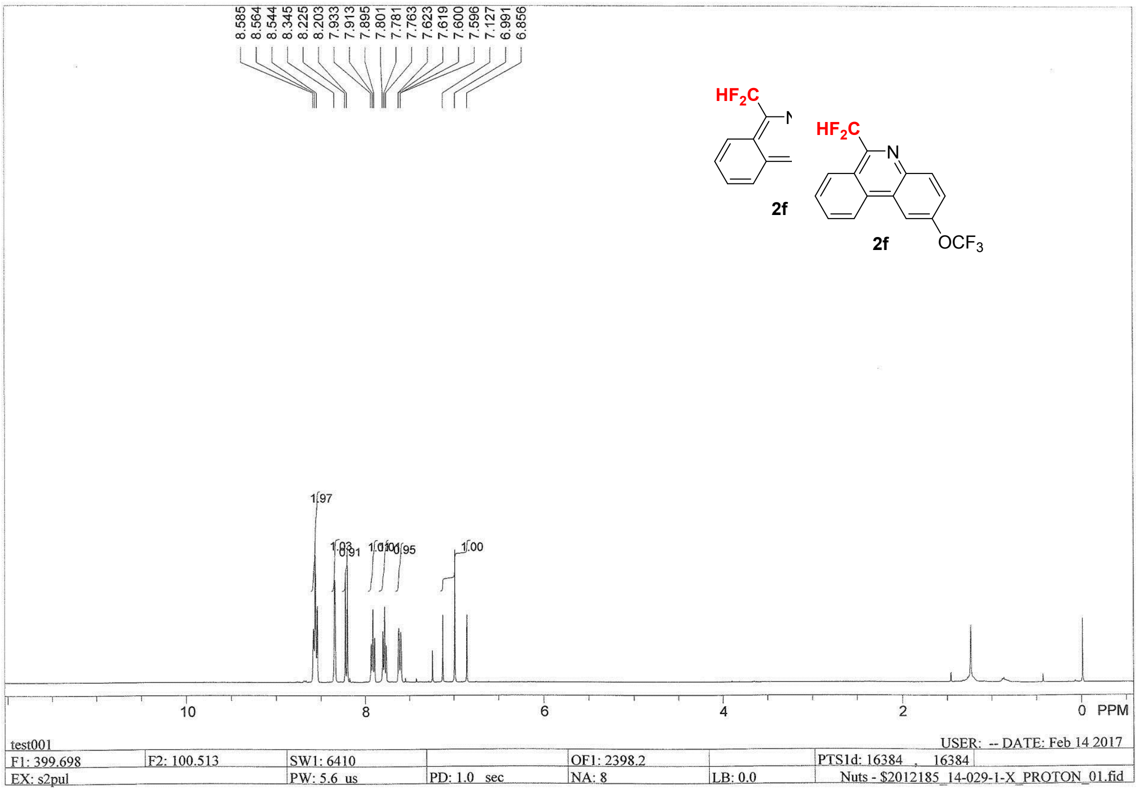

HF2C
N
OMe

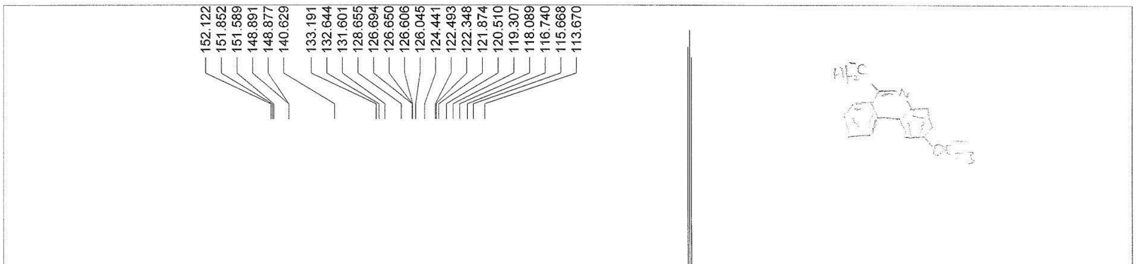
2d

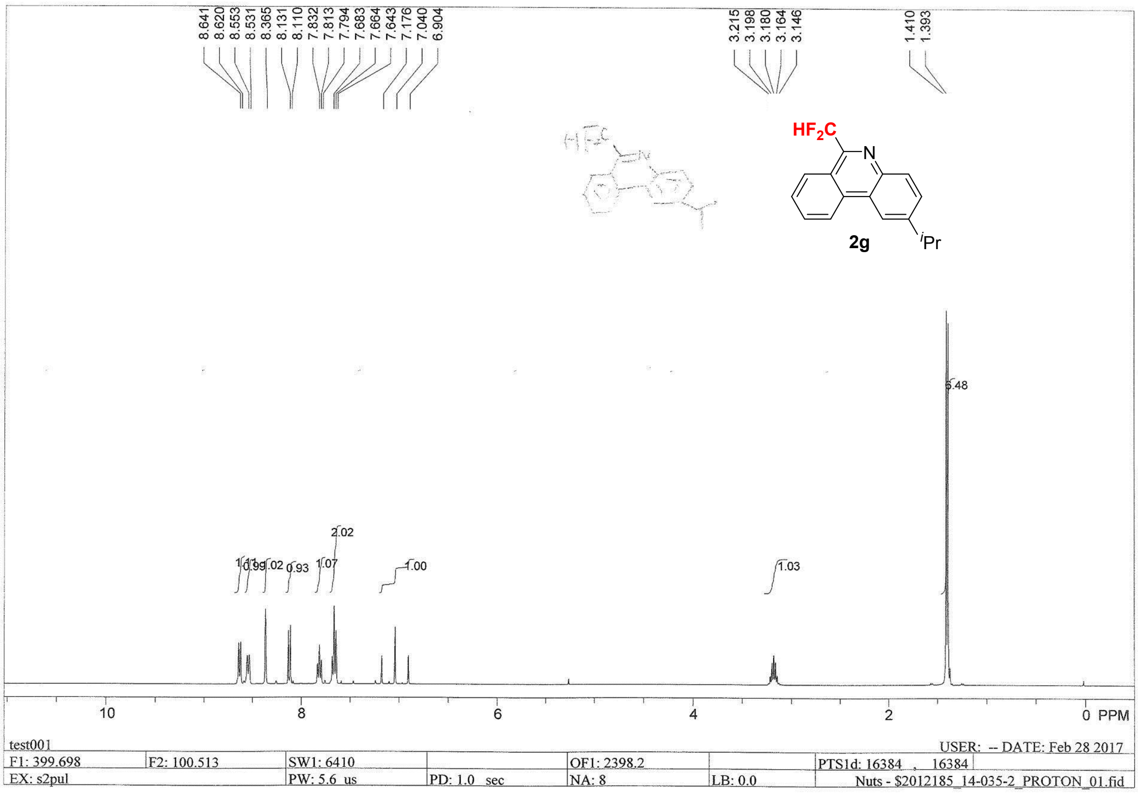

8.516
8.495
8.481
8.459
8.365
8.343
8.091
7.848
7.829
7.810
7.713
7.693
7.674
7.606
7.585
7.087
6.952
6.816
1.99
1.08
0.81
1.02
1.00
0.87
0.98
CH2Cl2
10
8
6
4
2
0 PPM
USER: nmr -- DATE: 17:17:20.793 +0800 nmr@EP-10030062
F1: 400.193
F2: 1.000
SW1: 8224
OF1: 2455.4
PTS1d: 65536
EX: zg30
PW: 12.0 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $SQZ-ADD-5Cl-1_1.1

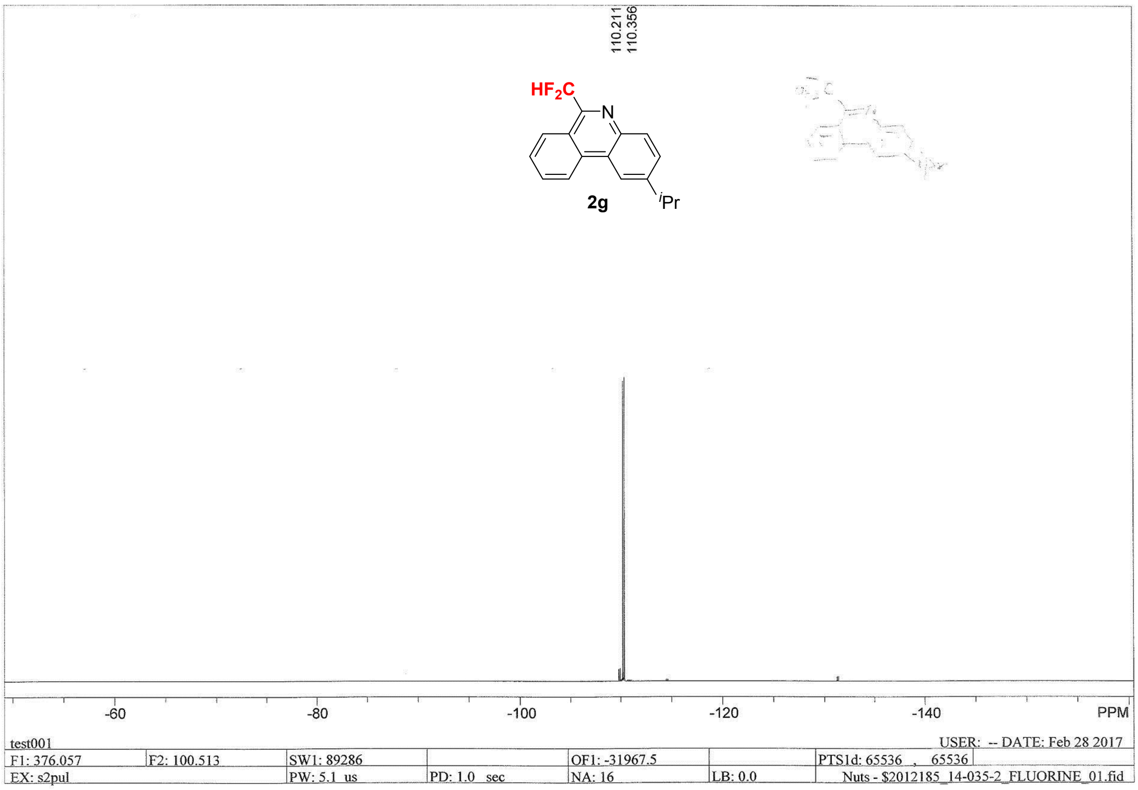

-110.686
-110.711
-110.831
-110.856
-40
-60
-80
-100
-120
-140
PPM
2012185-14-ADD-5Cl
USER: -- DATE: Aug 21 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185-14-ADD-5Cl_FLUORINE_01.fid

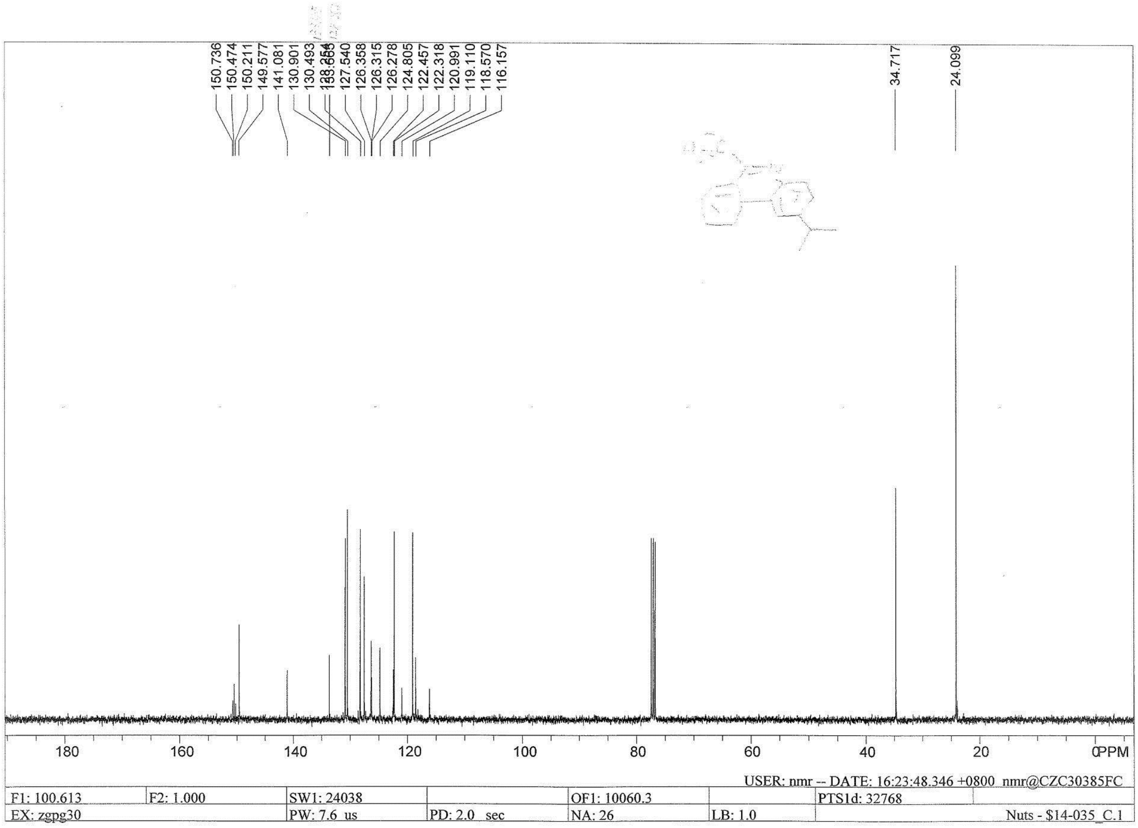

152.705
152.435
152.173
142.986
134.718
133.267
131.532
129.709
129.075
128.010
126.545
126.501
126.457
123.373
123.286
122.207
120.508
118.087
115.667
HF2C
HF2C
N
Cl
2e
180
160
140
120
100
80
60
40
20
PPM
USER: nmr -- DATE: 17:31:43.490 +0800 nmr@EP-10030062
F1: 100.629
F2: 1.000
SW1: 24038
OF1: 10062.8
PTS1d: 32768
EX: zgpg30
PW: 9.0 us
PD: 2.0 sec
NA: 64
LB: 1.0
Nuts - $SQZ-ADD-5Cl-2_1.1

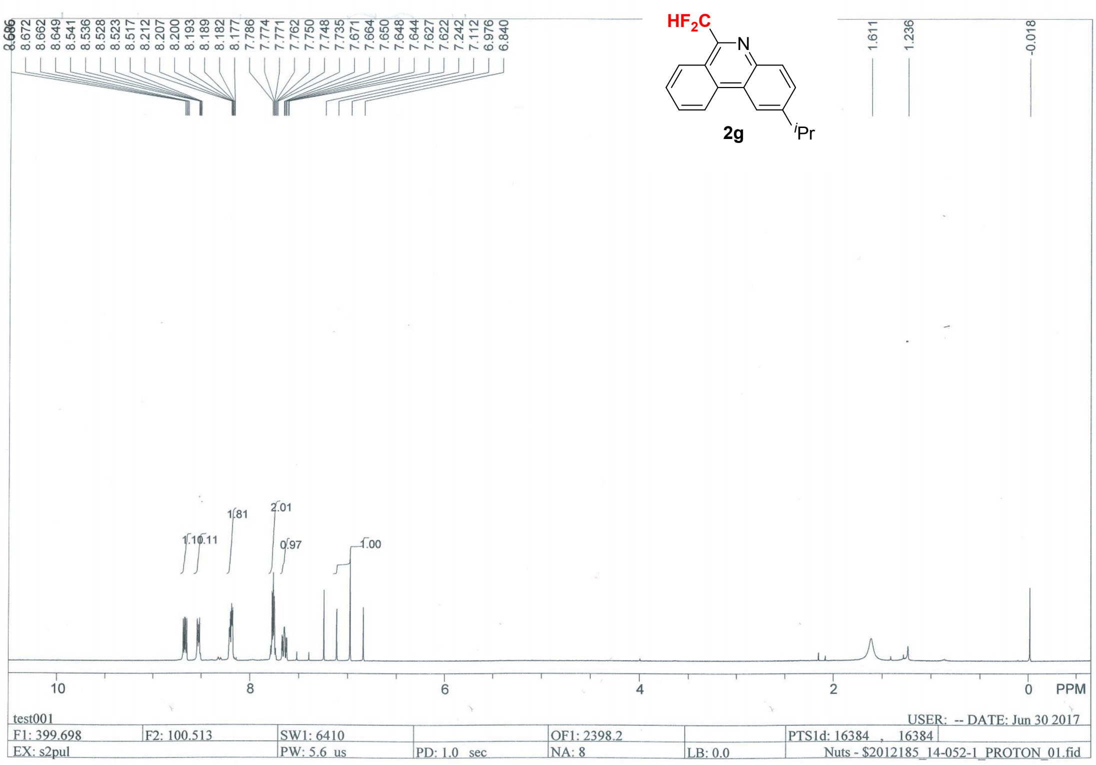

8.585
8.564
8.544
8.345
8.225
8.203
7.933
7.913
7.895
7.801
7.781
7.763
7.623
7.619
7.600
7.596
7.127
6.991
6.856
HF2C
N
2f
HF2C
N
2f
OCF3
1.97
1.03
0.91
1.01
1.00
0.95
1.00
10
8
6
4
2
0 PPM
test001
USER: -- DATE: Feb 14 2017
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_14-029-1-X_PROTON_01.fid

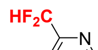

152.122
151.852
151.589
148.891
148.877
140.629
133.191
132.644
131.601
128.655
126.694
126.650
126.606
126.045
124.441
122.493
122.348
121.874
120.510
119.307
118.089
116.740
115.668
113.670
HF2C
N
OCF3

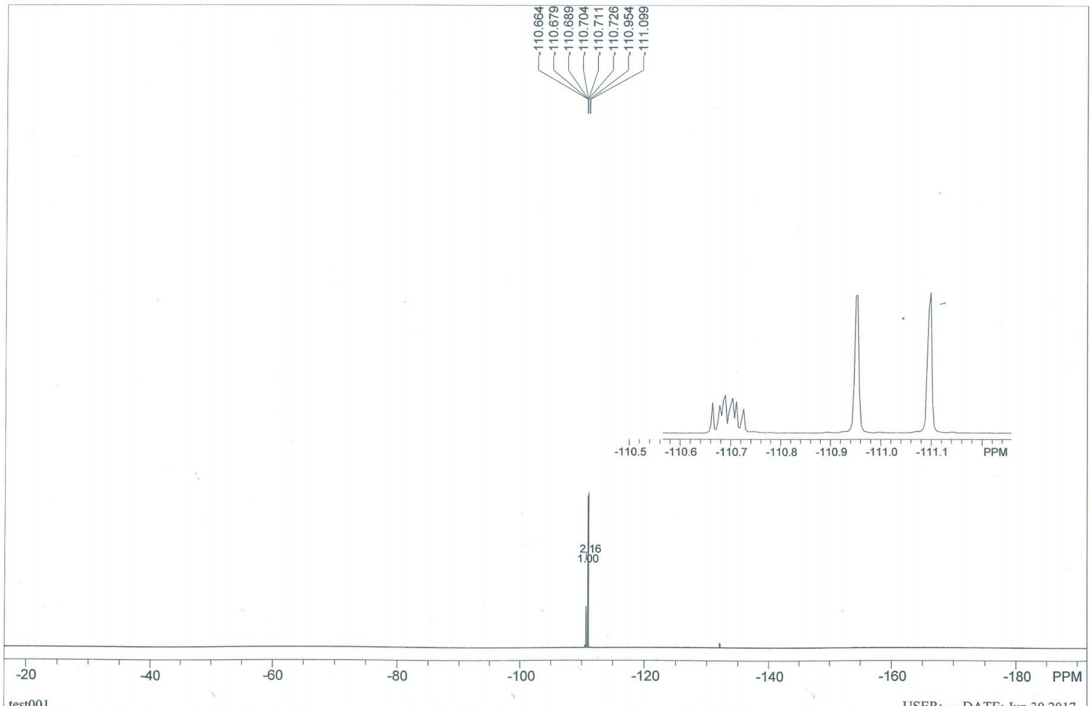

8.641
8.620
8.553
8.531
8.365
8.131
8.110
7.832
7.813
7.794
7.683
7.664
7.643
7.176
7.040
6.904
3.215
3.198
3.180
3.164
3.146
1.410
1.393
HF_2C
N
2g
^{i}Pr
6.48
2.02
1.11
0.99
1.02
0.93
1.07
1.00
1.03
10
8
6
4
2
0 PPM
test001
USER: -- DATE: Feb 28 2017
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_14-035-2_PROTON_01.fid


110.211
110.356
HF_2C
N
2g
^{i}Pr
-60
-80
-100
-120
-140
PPM
test001
USER: -- DATE: Feb 28 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185_14-035-2_FLUORINE_01.fid

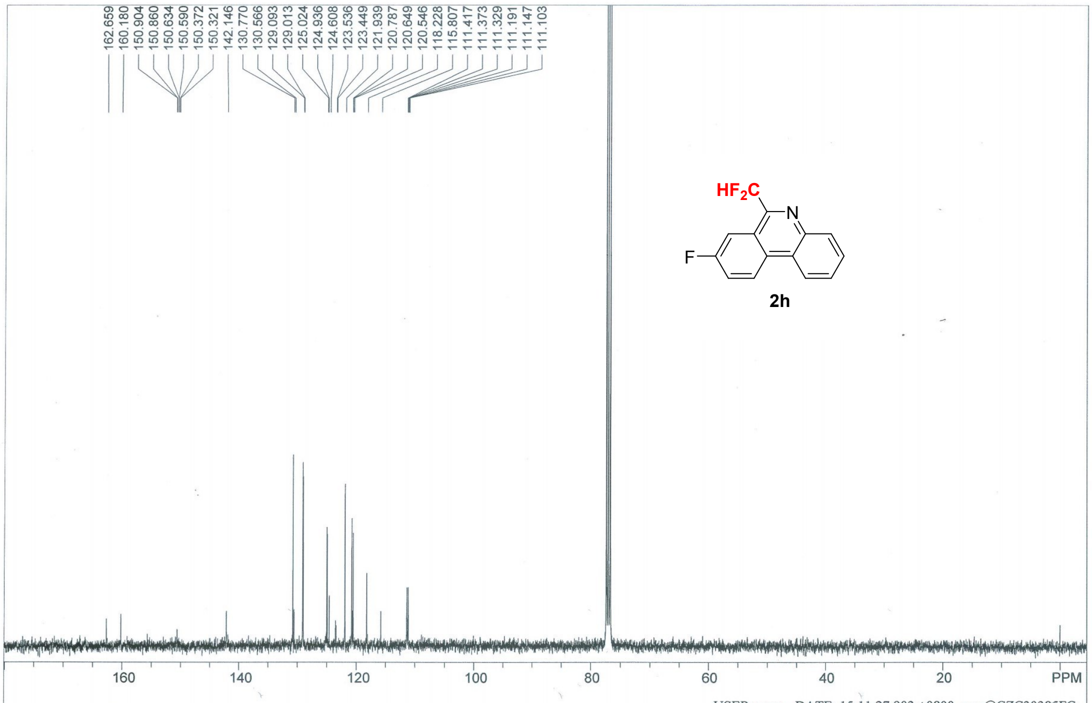

150.736
150.474
150.211
149.577
141.081
130.901
130.493
128.665
128.254
127.540
126.358
126.315
126.278
124.805
122.457
122.318
120.991
119.110
118.570
116.157
34.717
24.099
180
160
140
120
100
80
60
40
20
0
PPM
USER: nmr -- DATE: 16:23:48.346 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 26
LB: 1.0
Nuts - $14-035_C.1


8.686
8.672
8.662
8.649
8.541
8.536
8.528
8.523
8.517
8.212
8.207
8.200
8.193
8.189
8.182
8.177
7.786
7.774
7.771
7.762
7.750
7.748
7.735
7.671
7.664
7.650
7.648
7.644
7.627
7.622
7.242
7.112
6.976
6.840
1.611
1.236
-0.018
HF2C
N
2g
iPr
1.10
0.11
1.81
2.01
0.97
1.00
10
8
6
4
2
0
PPM
test001
USER: -- DATE: Jun 30 2017
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_14-052-1_PROTON_01.fid

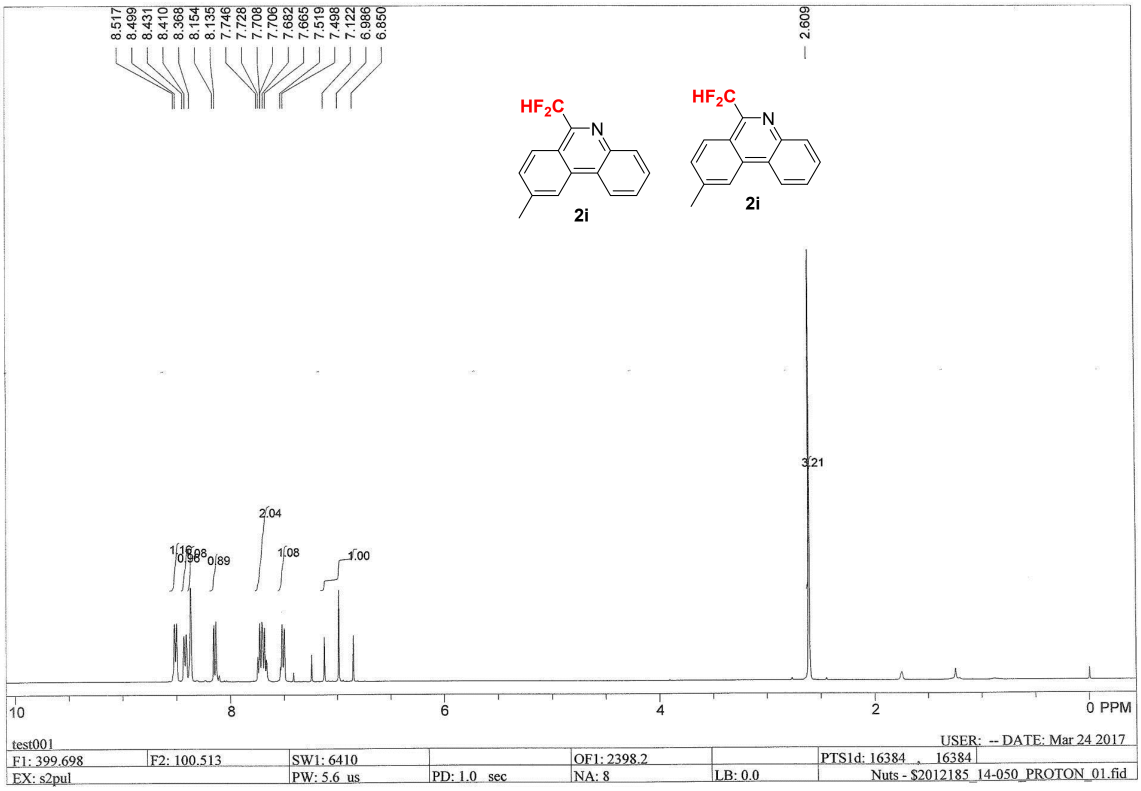

HF2C
N

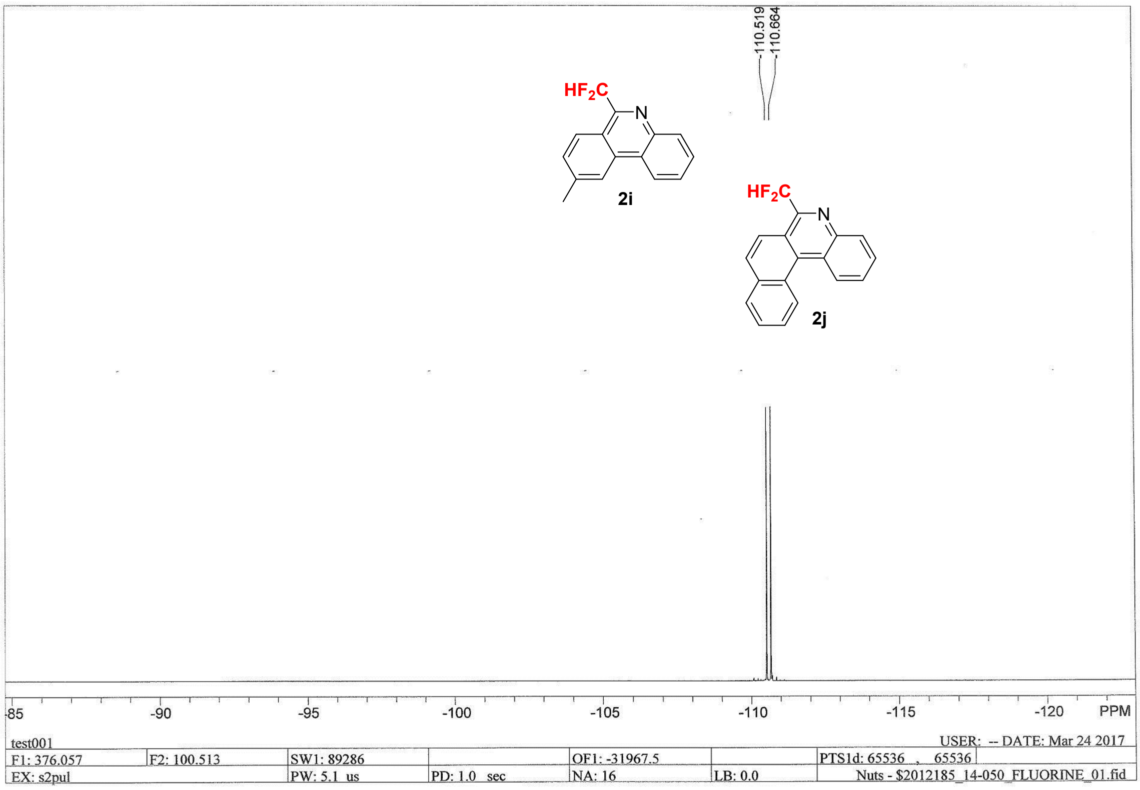


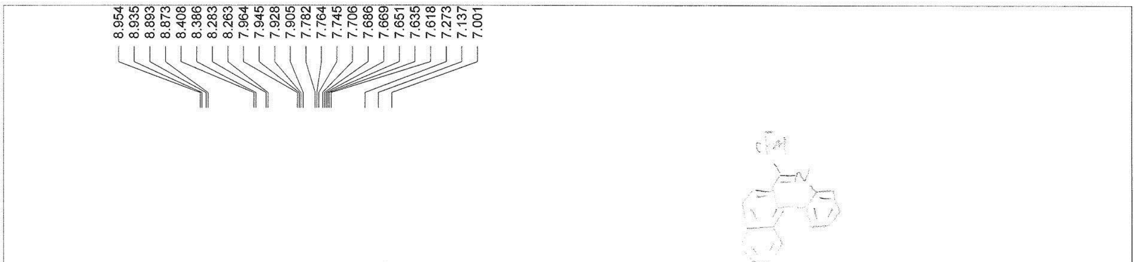
test001 USER: -- DATE: Jun 30 2017
F1: 376.057 F2: 100.513 SW1: 89286 OF1: -31967.5 PTS1d: 65536 , 65536
EX: s2pul PW: 5.1 us PD: 1.0 sec NA: 16 LB: 0.0 Nuts - $2012185_14-052-1_FLUORINE_01.fid

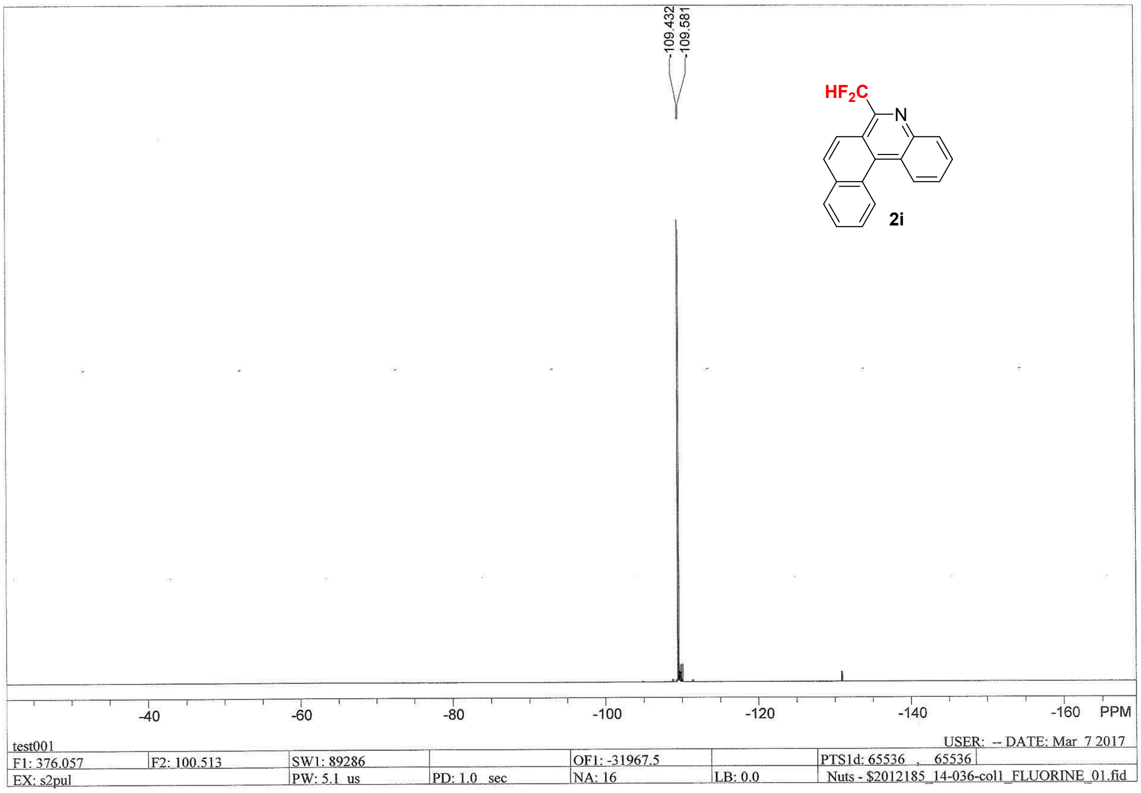


USER: nmr -- DATE: 15:11:27.903 +0800 nmr@CZC30385FC
F1: 100.613 F2: 1.000 SW1: 24038 OF1: 10060.3 PTS1d: 32768
EX: zgpg30 PW: 7.6 us PD: 2.0 sec NA: 1247 LB: 1.0 Nuts - $14-052-1_C.1

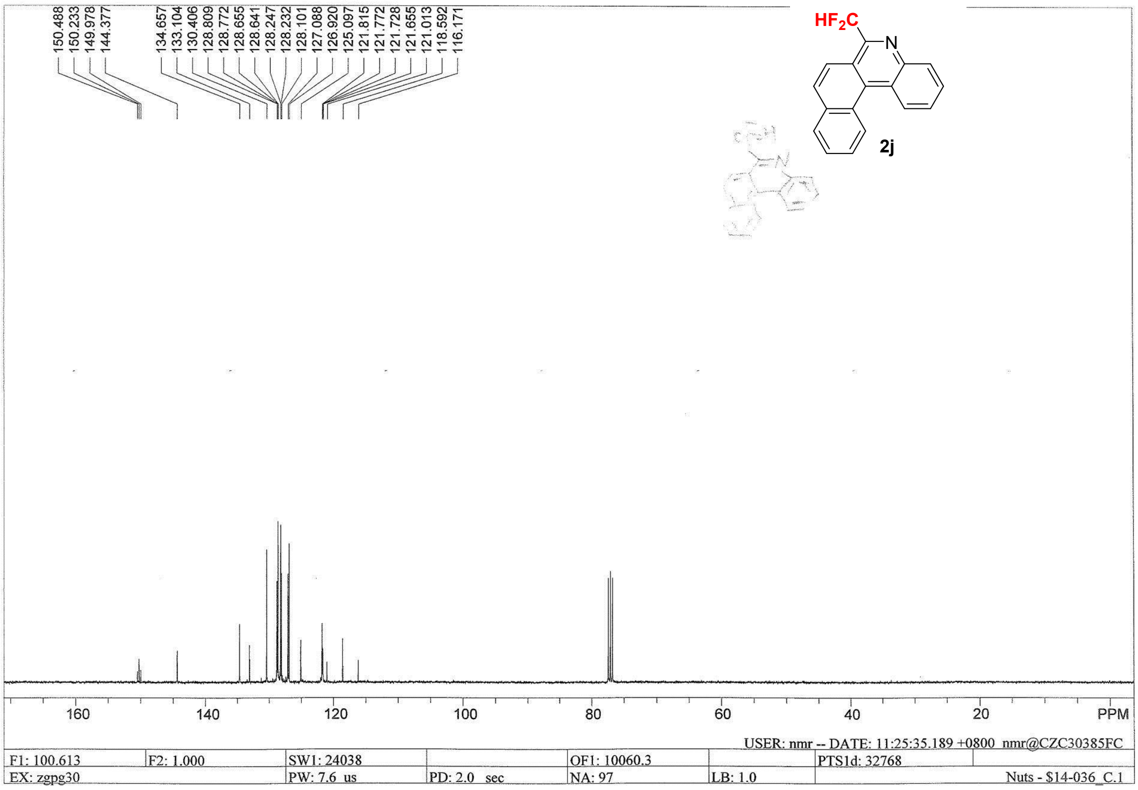

8.517
8.499
8.431
8.410
8.368
8.154
8.135
7.746
7.728
7.708
7.706
7.682
7.665
7.519
7.498
7.122
6.986
6.850
2.609
HF2C
N
2i
HF2C
N
2i
3.21
2.04
1.16
0.98
1.08
0.89
1.08
1.00
10
8
6
4
2
0 PPM
test001
USER: -- DATE: Mar 24 2017
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_14-050_PROTON_01.fid


-110.519
-110.664
HF2C
N
2i
HF2C
N
2j
-85
-90
-95
-100
-105
-110
-115
-120
PPM
test001
USER: -- DATE: Mar 24 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185_14-050_FLUORINE_01.fid

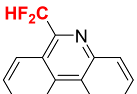

8.954
8.935
8.893
8.873
8.408
8.386
8.283
8.263
7.964
7.945
7.928
7.905
7.782
7.764
7.745
7.706
7.686
7.669
7.651
7.635
7.618
7.273
7.137
7.001



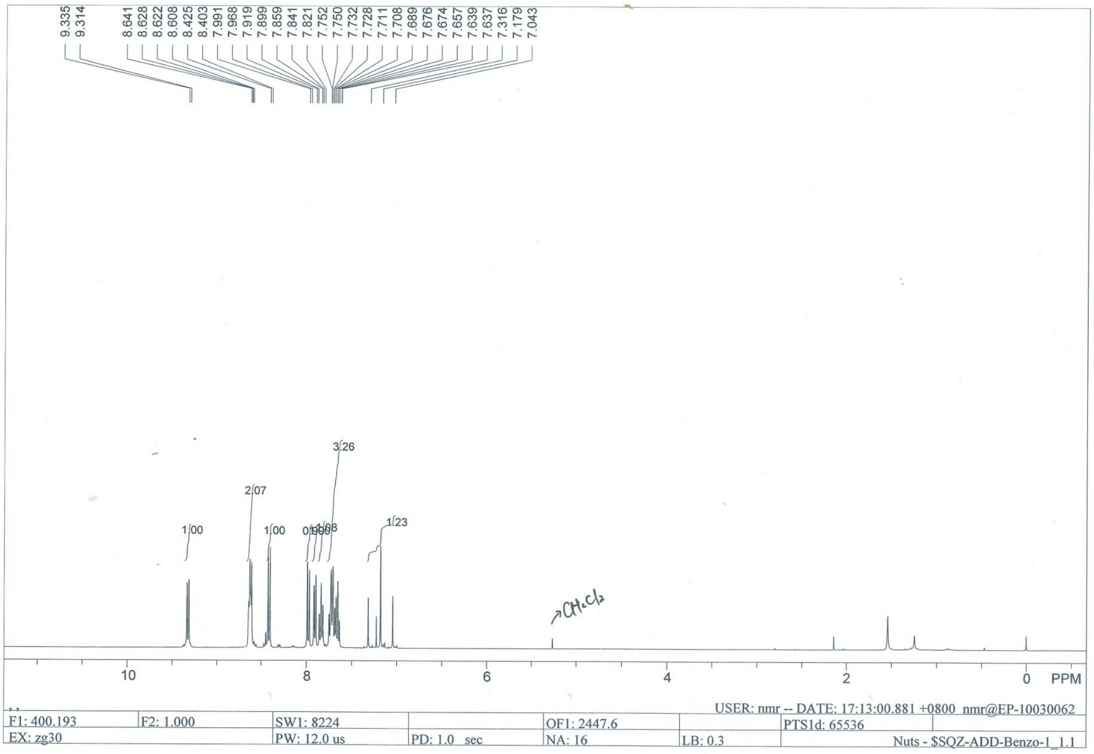
-109.432
-109.581
HF2C
N
2i
-40
-60
-80
-100
-120
-140
-160
PPM
test001
USER: -- DATE: Mar 7 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185_14-036-col1_FLUORINE_01.fid

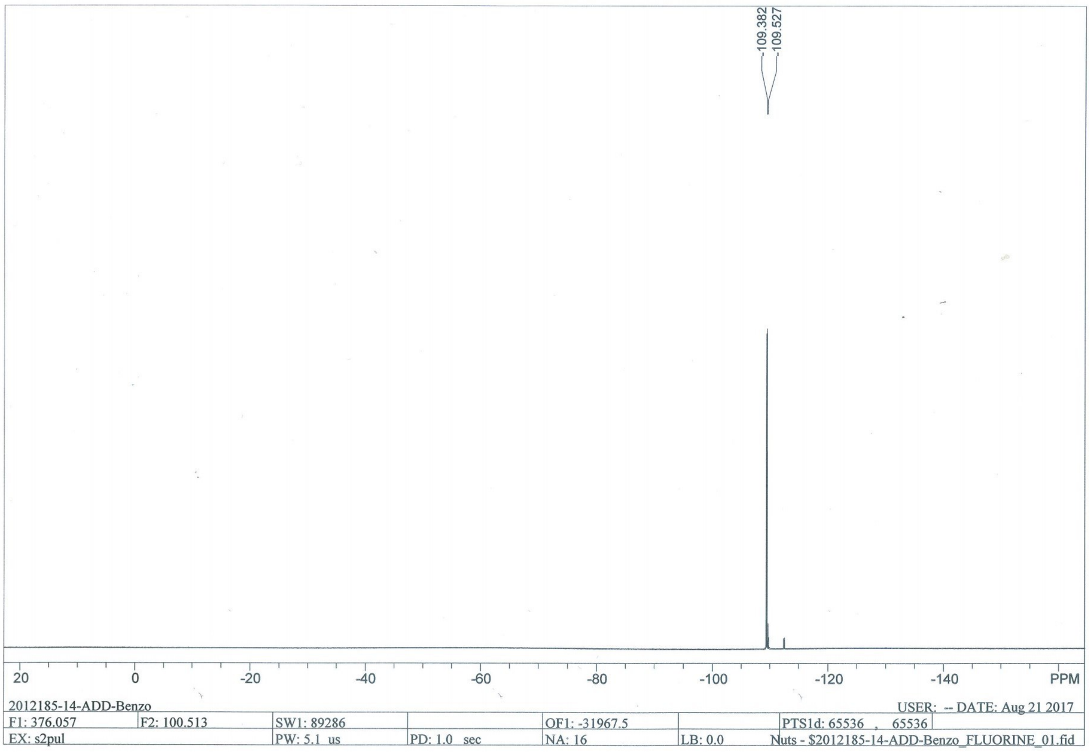


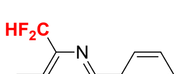
150.488
150.233
149.978
144.377
134.657
133.104
130.406
128.809
128.772
128.655
128.641
128.247
128.232
128.101
127.088
126.920
125.097
121.815
121.772
121.728
121.655
121.013
118.592
116.171
HF2C
N
2j
160
140
120
100
80
60
40
20
PPM
USER: nmr -- DATE: 11:25:35.189 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 97
LB: 1.0
Nuts - $14-036_C.1

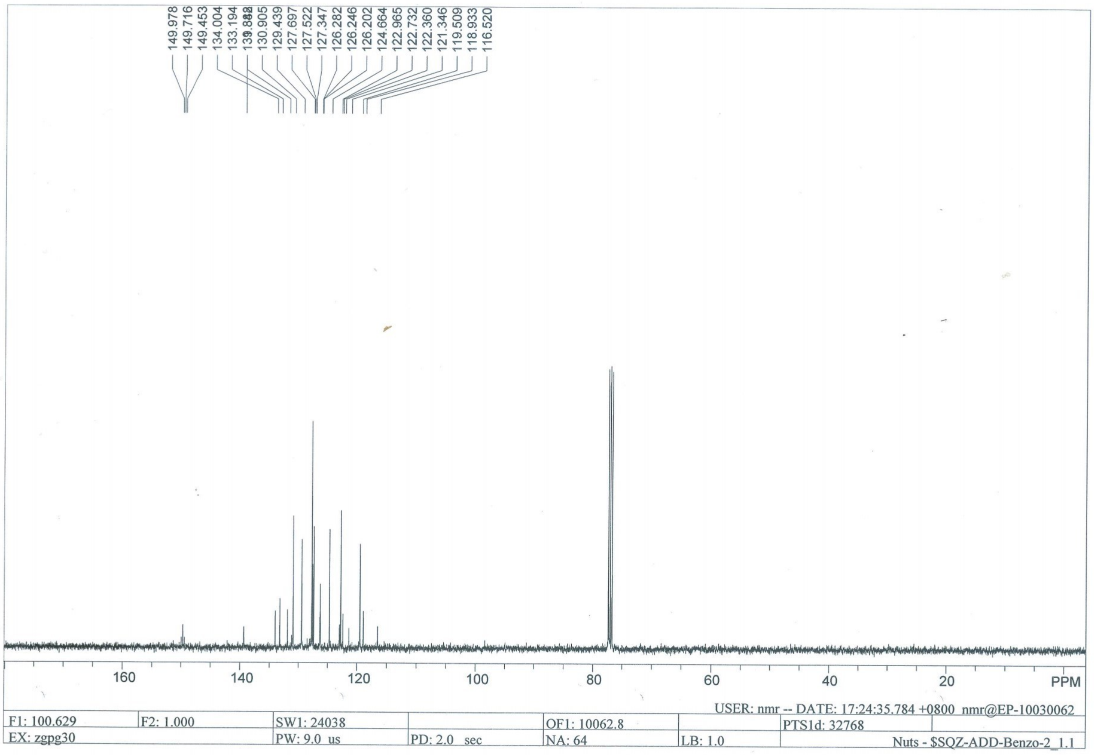


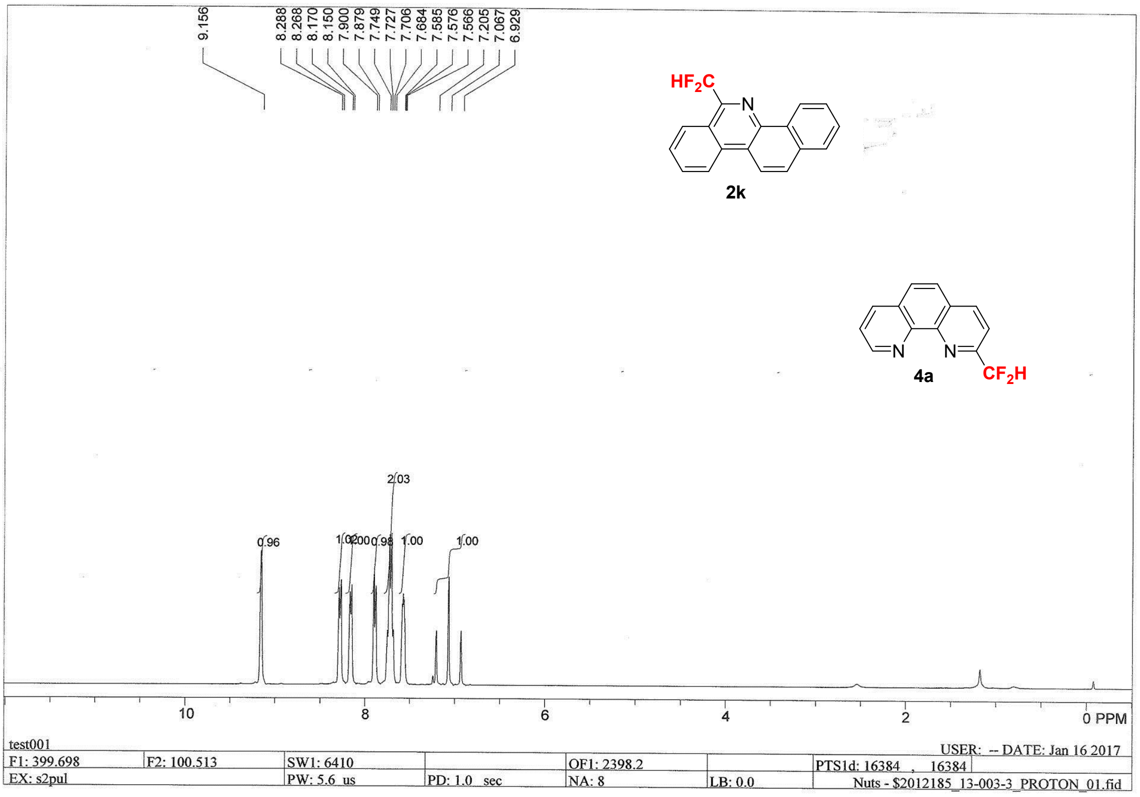
HF2C
N

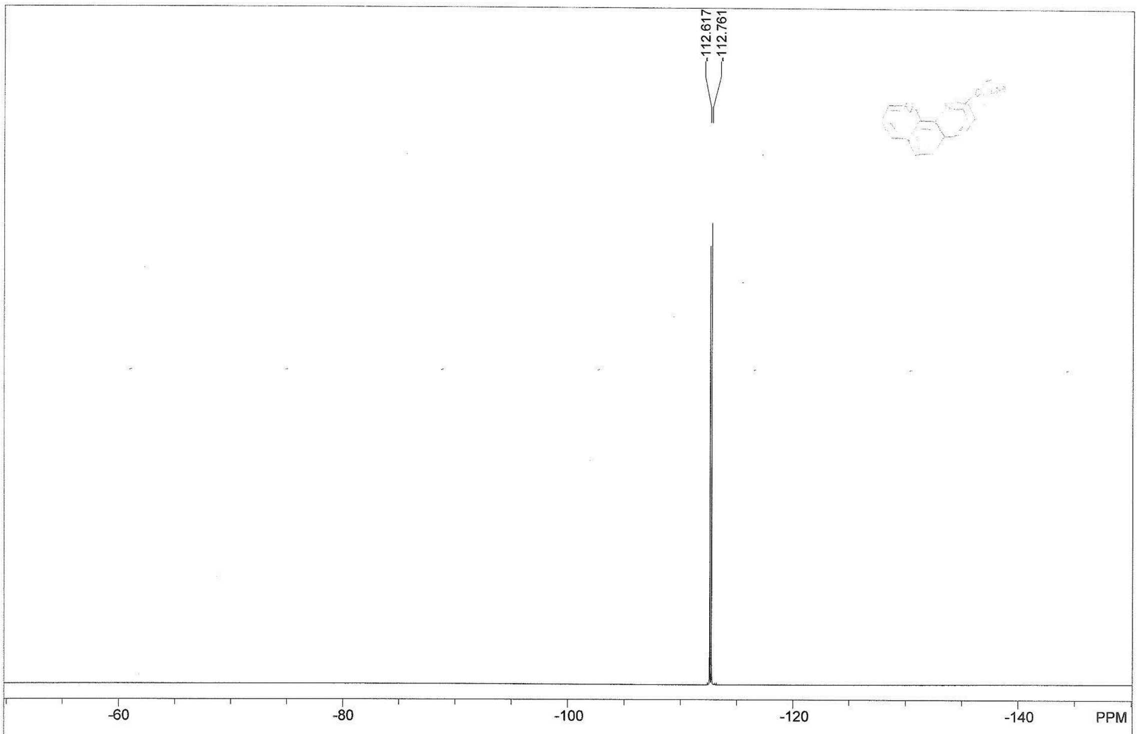

9.335
9.314
8.641
8.628
8.622
8.608
8.425
8.403
7.991
7.968
7.919
7.899
7.859
7.841
7.821
7.752
7.750
7.732
7.728
7.711
7.708
7.689
7.676
7.674
7.657
7.639
7.637
7.316
7.179
7.043
1.00
2.07
1.00
3.26
1.23
→CH2Cl2
10
8
6
4
2
0
PPM
USER: nmr -- DATE: 17:13:00.881 +0800 nmr@EP-10030062
F1: 400.193
F2: 1.000
SW1: 8224
OF1: 2447.6
PTS1d: 65536
EX: zg30
PW: 12.0 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $SQZ-ADD-Benzo-1_1.1


-109.382
-109.527
20
0
-20
-40
-60
-80
-100
-120
-140
PPM
2012185-14-ADD-Benzo
USER: -- DATE: Aug 21 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185-14-ADD-Benzo_FLUORINE_01.fid


HF2C
N

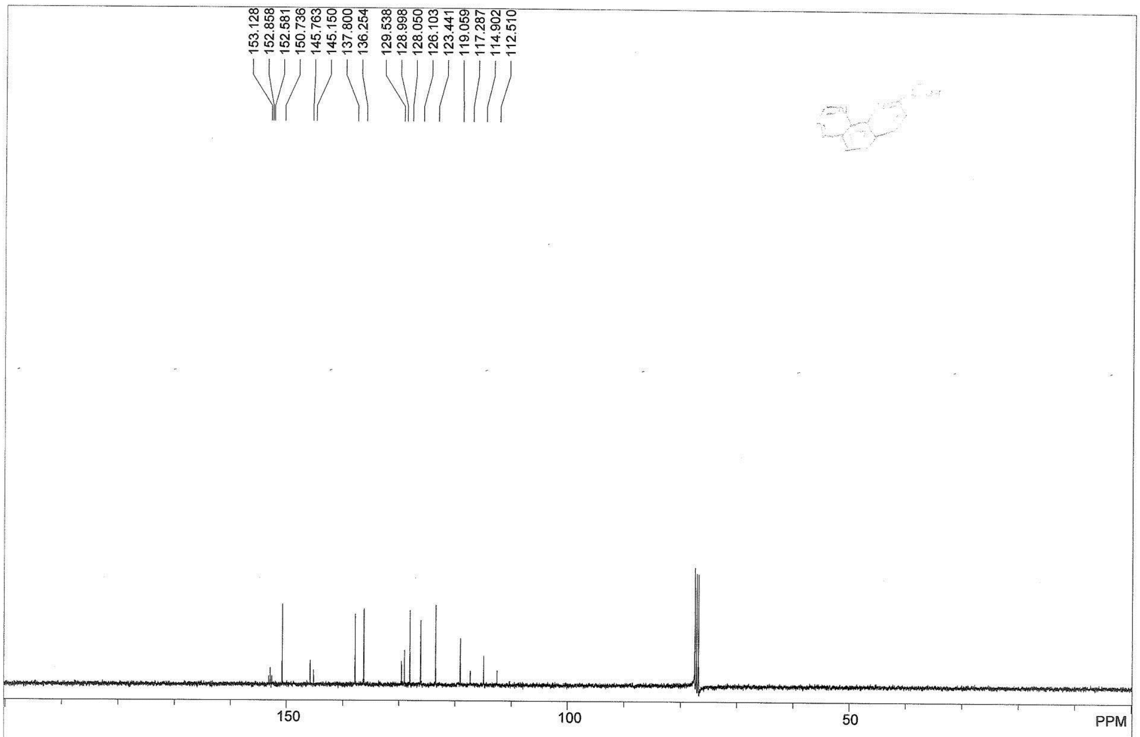

149.978
149.716
149.453
134.004
133.194
139.882
130.905
129.439
127.697
127.522
127.347
126.282
126.246
126.202
124.664
122.965
122.732
122.360
121.346
119.509
118.933
116.520
160
140
120
100
80
60
40
20
PPM
USER: nmr -- DATE: 17:24:35.784 +0800 nmr@EP-10030062
F1: 100.629
F2: 1.000
SW1: 24038
OF1: 10062.8
PTS1d: 32768
EX: zgpg30
PW: 9.0 us
PD: 2.0 sec
NA: 64
LB: 1.0
Nuts - $SQZ-ADD-Benzo-2_1.1


9.156
8.288
8.268
8.170
8.150
7.900
7.879
7.749
7.727
7.706
7.684
7.585
7.576
7.566
7.205
7.067
6.929
HF2C
N
2k
N
N
CF2H
4a
0.96
1.02
1.00
0.98
2.03
1.00
1.00
10
8
6
4
2
0 PPM
test001
USER: -- DATE: Jan 16 2017
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_13-003-3_PROTON_01.fid



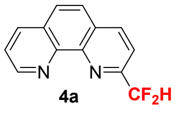
test001 USER: -- DATE: Jan 16 2017

F1: 376.057	F2: 100.513	SW1: 89286		OF1: -31967.5		PTS1d: 65536 , 65536
EX: s2pul		PW: 5.1 us	PD: 1.0 sec	NA: 16	LB: 0.0	Nuts - $2012185_13-003-3_FLUORINE_01.fid

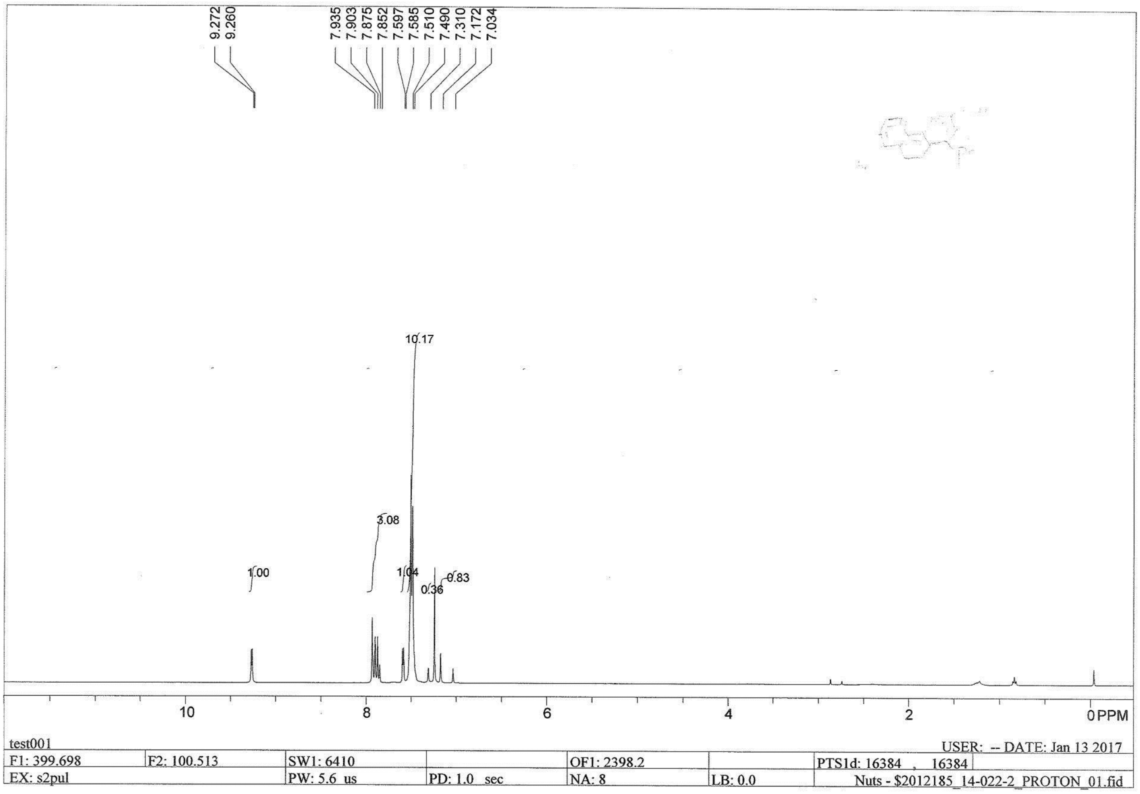


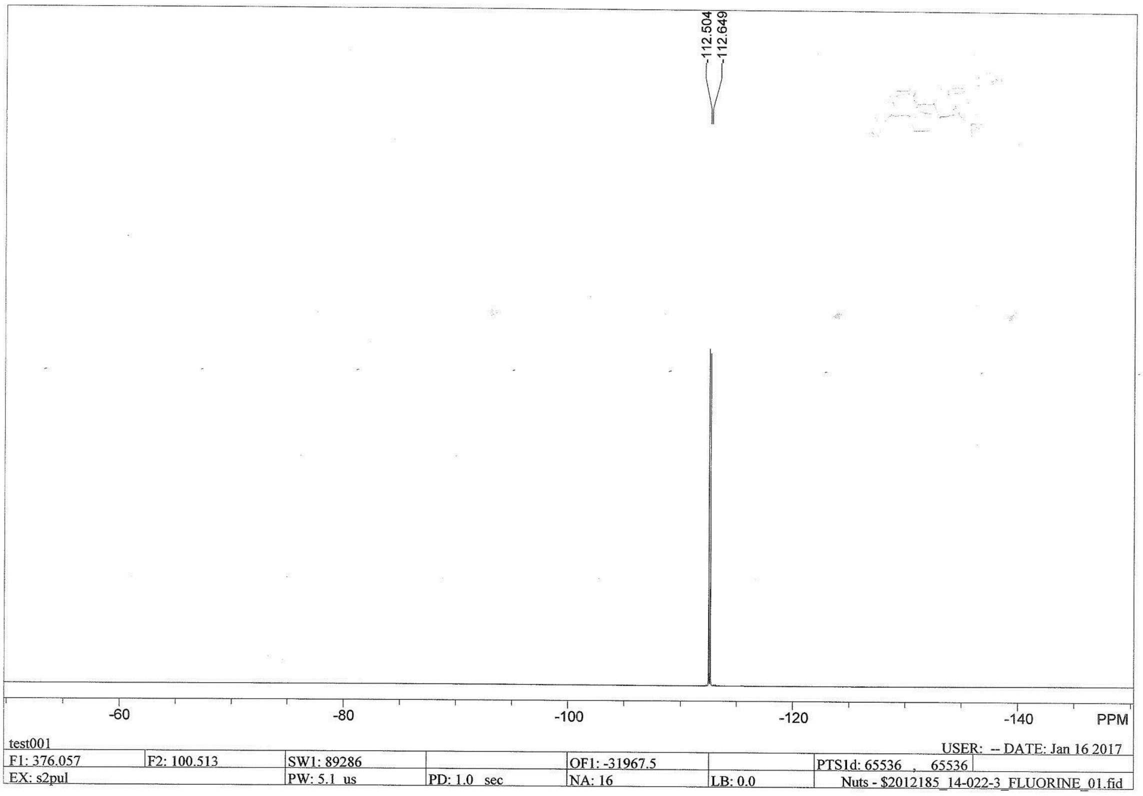
USER: nmr -- DATE: 10:25:56.952 +0800 nmr@CZC30385FC

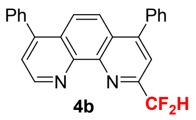
F1: 100.613	F2: 1.000	SW1: 24038		OF1: 10060.3		PTS1d: 32768
EX: zgpg30		PW: 7.6 us	PD: 2.0 sec	NA: 23	LB: 1.0	Nuts - $13-003_C.1



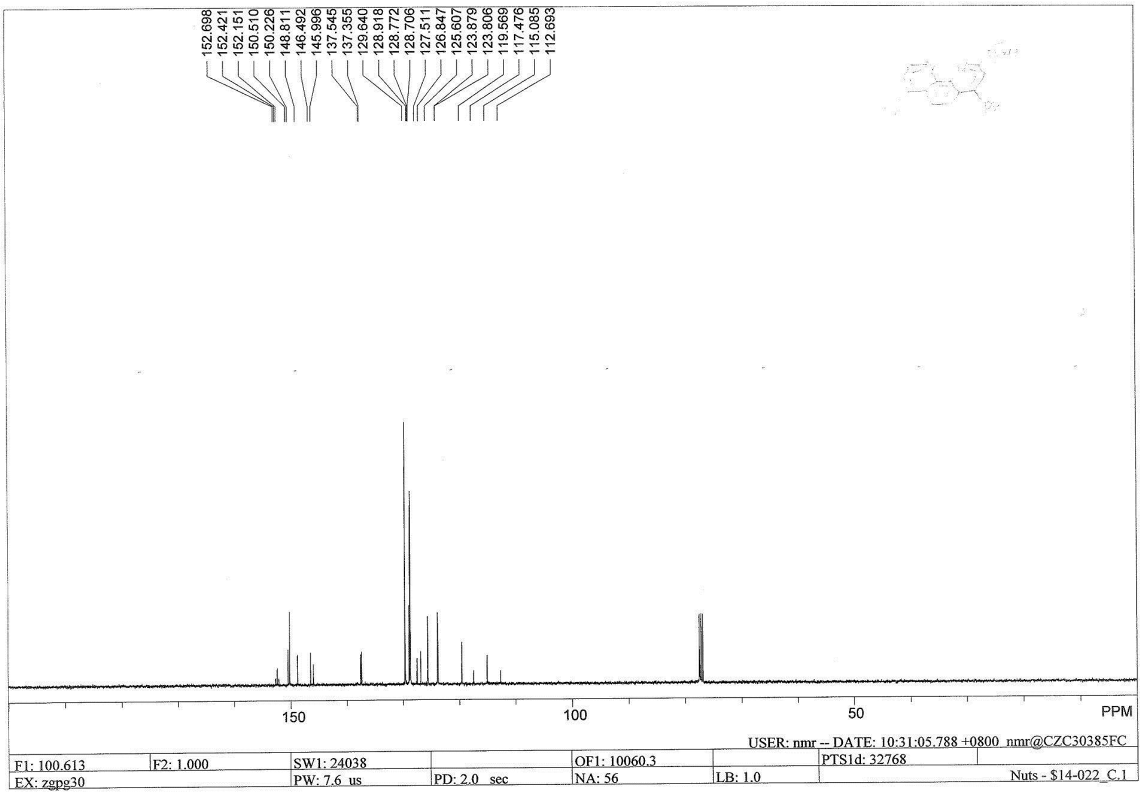
4a

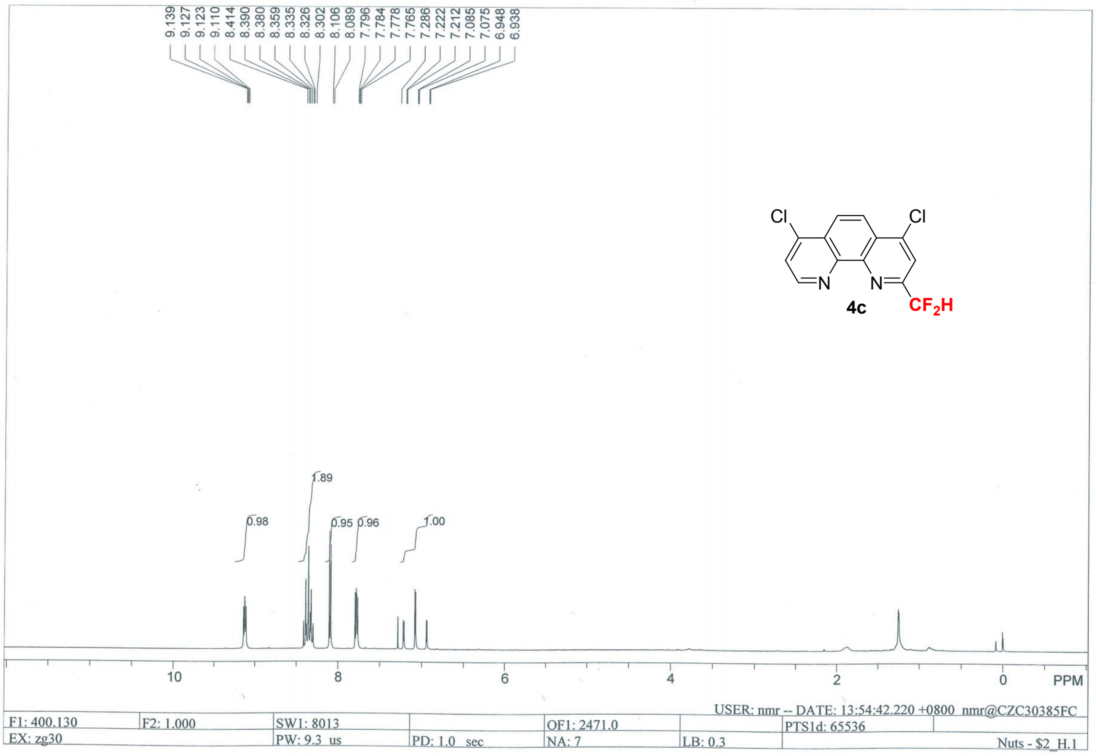

9.272
9.260
7.935
7.903
7.875
7.852
7.597
7.585
7.510
7.490
7.310
7.172
7.034
10.17
3.08
1.00
1.04
0.36
0.83
10
8
6
4
2
0 PPM
test001
USER: -- DATE: Jan 13 2017
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_14-022-2_PROTON_01.fid

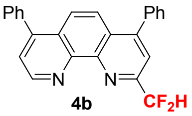

-112.504
-112.649
-60
-80
-100
-120
-140
PPM
test001
USER: -- DATE: Jan 16 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185_14-022-3_FLUORINE_01.fid


Ph
Ph
N
N
CF2H

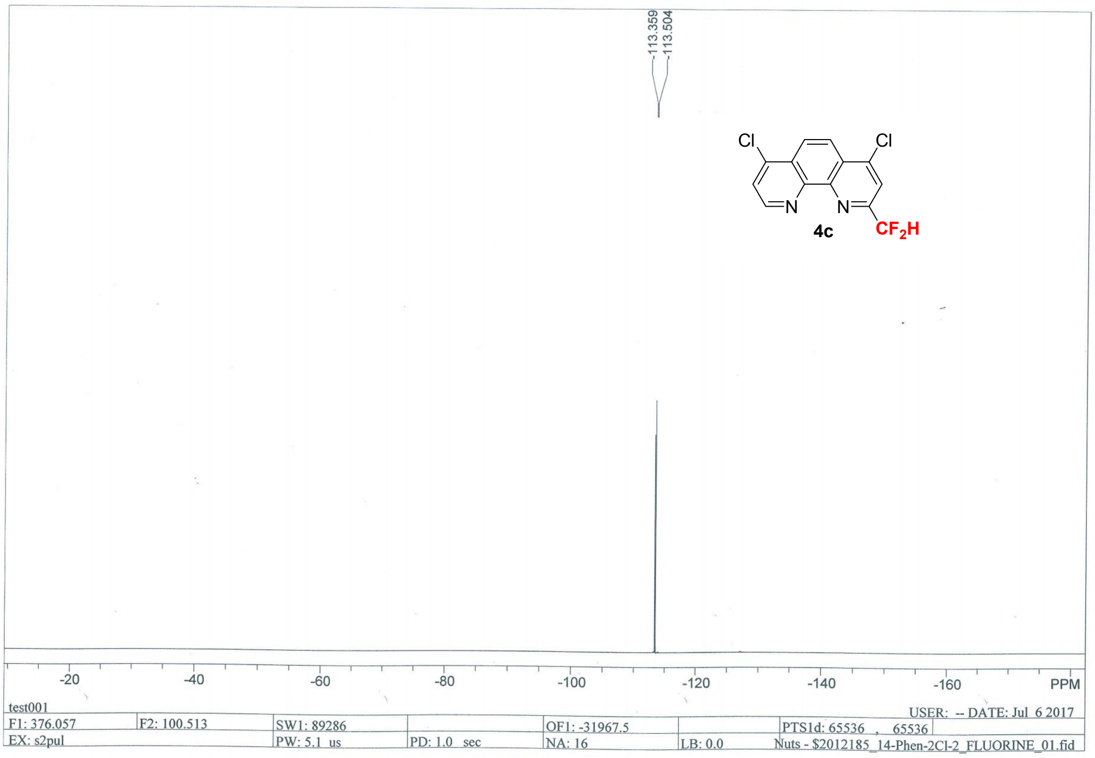
4b

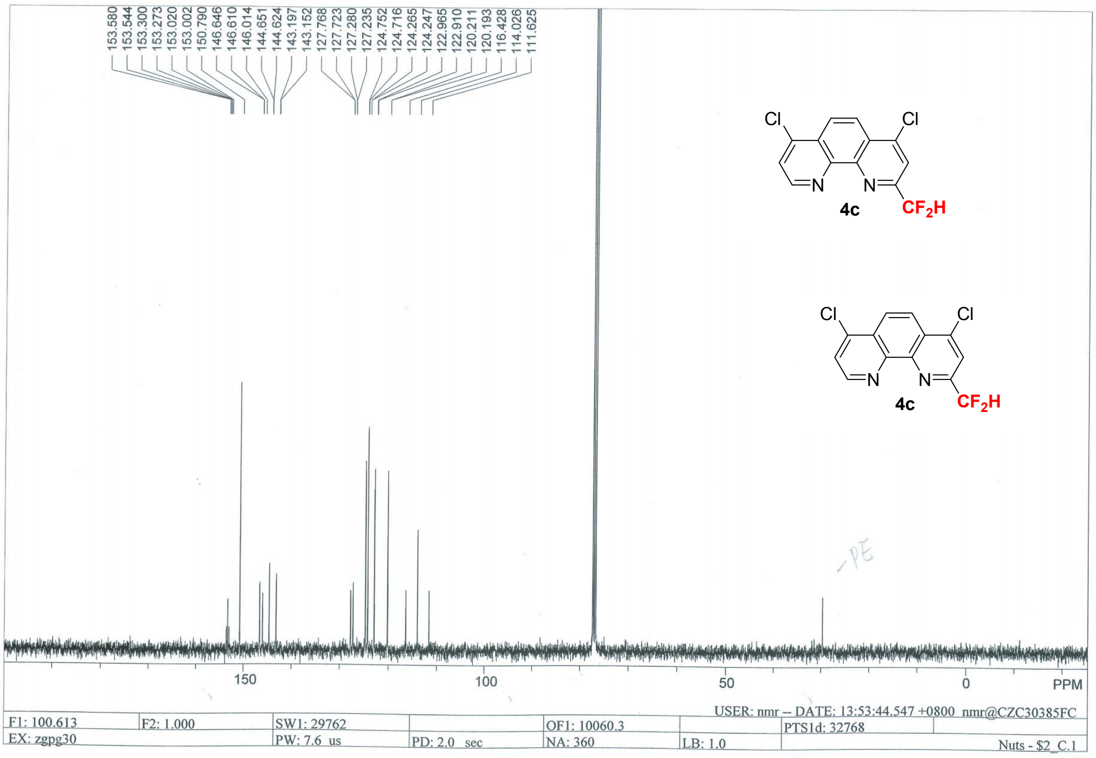

152.698
152.421
152.151
150.510
150.226
148.811
146.492
145.996
137.545
137.355
129.640
128.918
128.772
128.706
127.511
126.847
125.607
123.879
123.806
119.569
117.476
115.085
112.693
150
100
50
PPM
USER: nmr -- DATE: 10:31:05.788 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 56
LB: 1.0
Nuts - $14-022_C.1

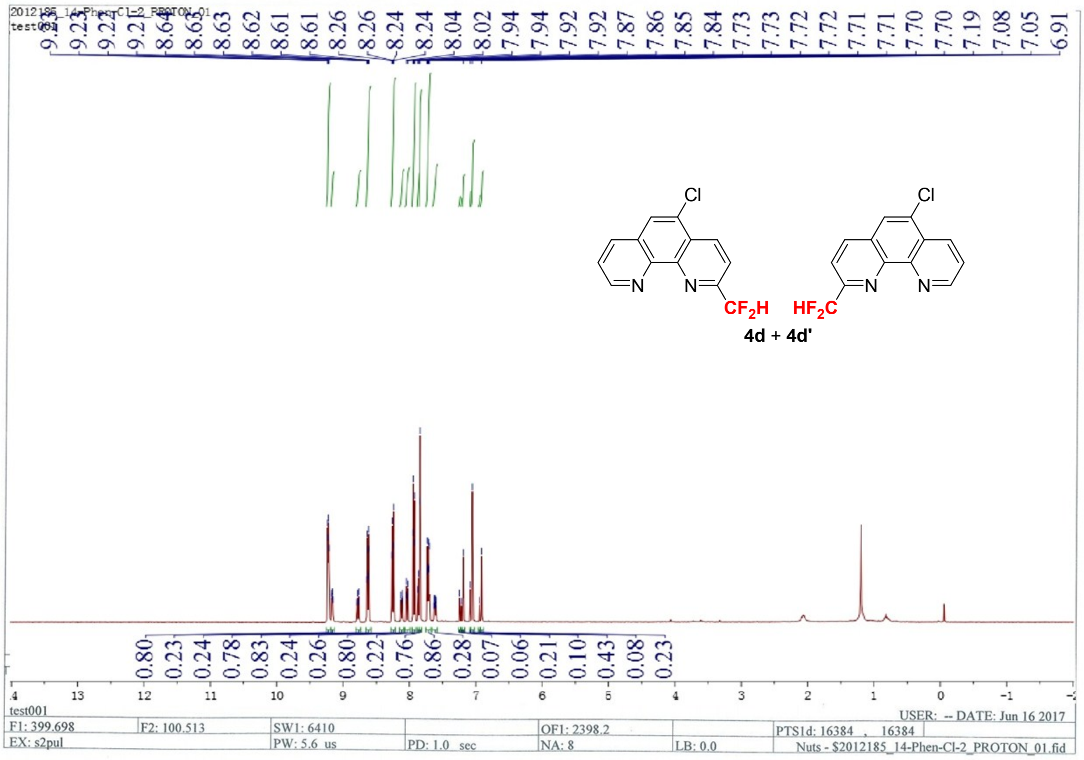

9.139
9.127
9.123
9.110
8.414
8.390
8.380
8.359
8.335
8.326
8.302
8.106
8.089
7.796
7.784
7.778
7.765
7.286
7.222
7.212
7.085
7.075
6.948
6.938
Cl
Cl
N
N
4c
CF2H
0.98
1.89
0.95
0.96
1.00
10
8
6
4
2
0
PPM
USER: nmr -- DATE: 13:54:42.220 +0800 nmr@CZC30385FC
F1: 400.130
F2: 1.000
SW1: 8013
OF1: 2471.0
PTS1d: 65536
EX: zg30
PW: 9.3 us
PD: 1.0 sec
NA: 7
LB: 0.3
Nuts - $2_H.1

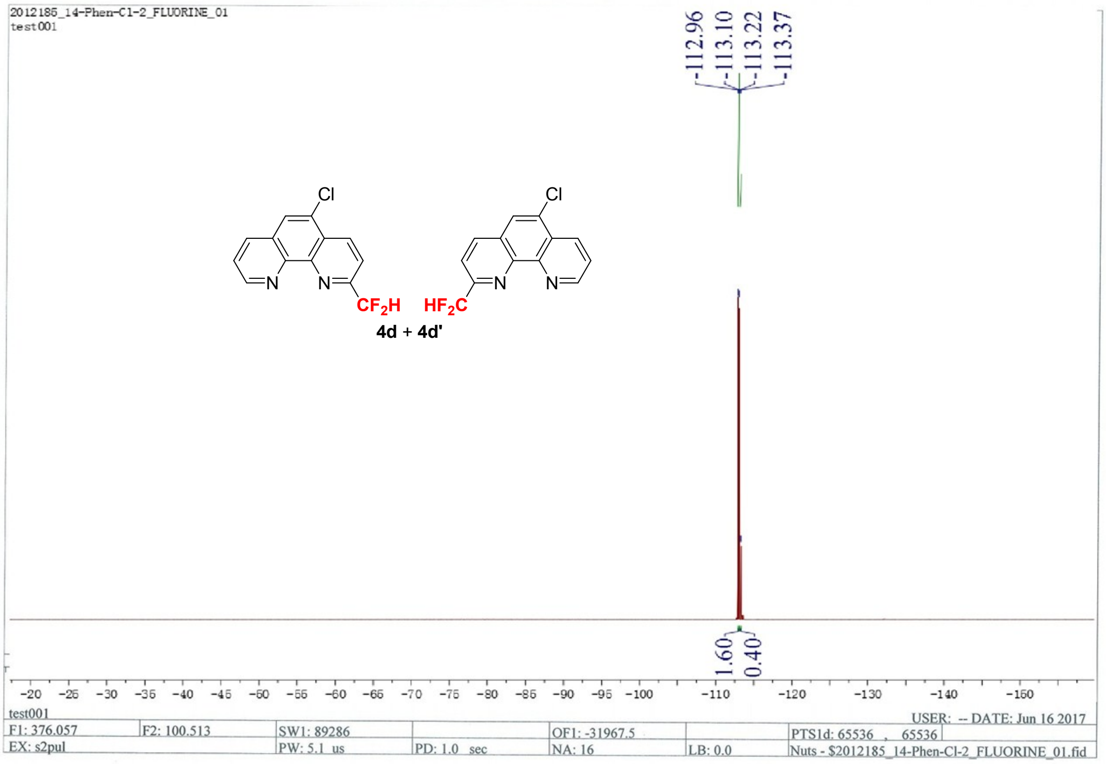

Ph
Ph
N
N
CF2H

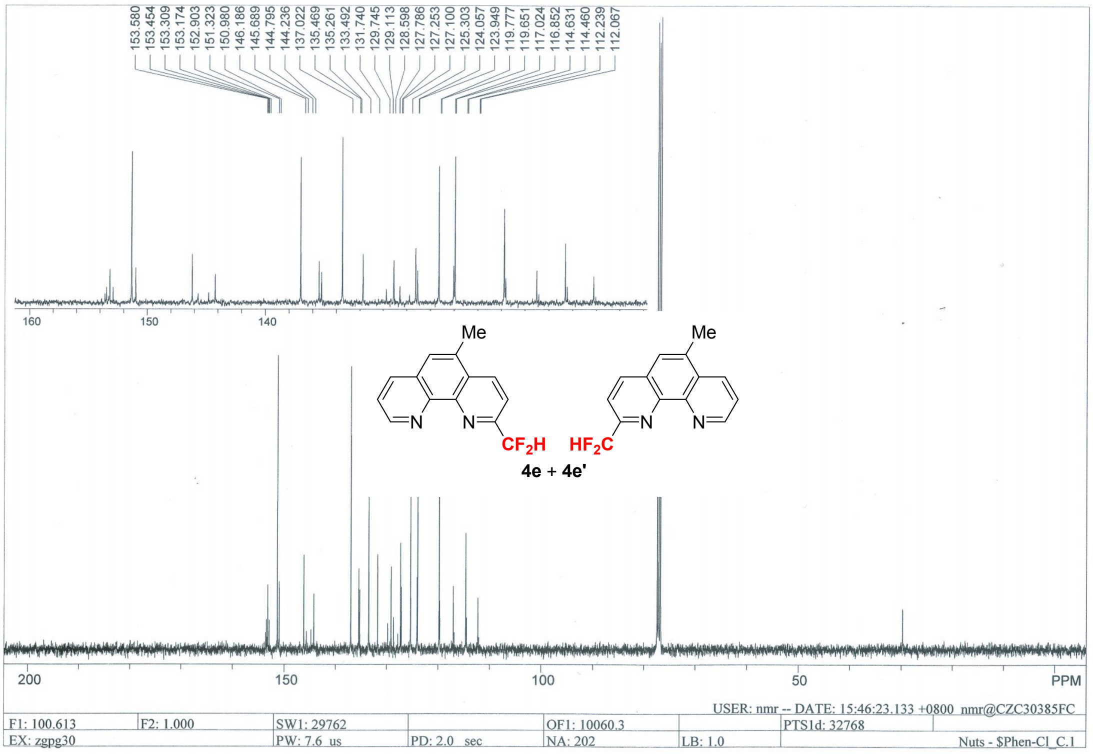
4b


-113.359
-113.504
Cl
Cl
N
N
4c
CF2H
-20
-40
-60
-80
-100
-120
-140
-160
PPM
test001
USER: -- DATE: Jul 6 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185_14-Phen-2Cl-2_FLUORINE_01.fid

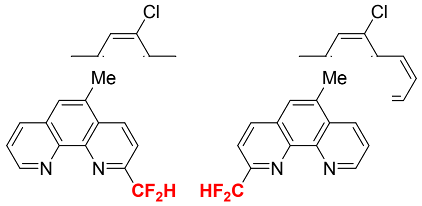

153.580
153.544
153.300
153.273
153.020
153.002
150.790
146.646
146.610
146.014
144.651
144.624
143.197
143.152
127.768
127.723
127.280
127.235
124.752
124.716
124.265
124.247
122.965
122.910
120.211
120.193
116.428
114.026
111.625
Cl
Cl
N
N
4c
CF2H
Cl
Cl
N
N
4c
CF2H
-PE
150
100
50
0
PPM
USER: nmr -- DATE: 13:53:44.547 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 29762
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 360
LB: 1.0
Nuts - $2_C.1


2012185_14-Phen-Cl-2_PROTON_01
test001
9.23
9.23
9.22
9.21
8.64
8.63
8.63
8.62
8.61
8.61
8.26
8.26
8.24
8.24
8.04
8.02
7.94
7.94
7.92
7.92
7.87
7.86
7.85
7.84
7.73
7.73
7.72
7.72
7.71
7.71
7.70
7.70
7.19
7.08
7.05
6.91
Cl
N
N
CF2H
Cl
HF2C
N
N
4d + 4d'
0.80
0.23
0.24
0.78
0.83
0.24
0.26
0.80
0.22
0.76
0.86
0.28
0.07
0.06
0.21
0.10
0.43
0.08
0.23
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
test001
USER: -- DATE: Jun 16 2017
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_14-Phen-Cl-2_PROTON_01.fid

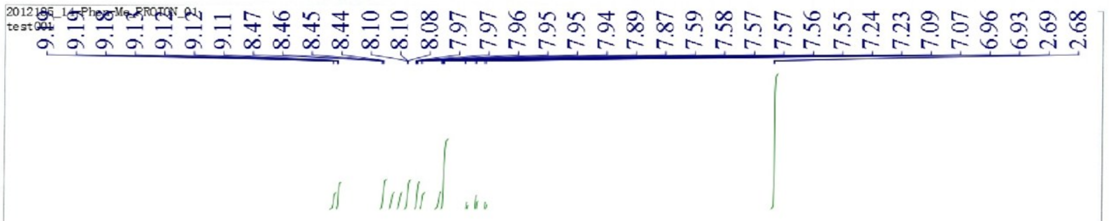

2012185_14-Phen-Cl-2_FLUORINE_01
test001
-112.96
-113.10
-113.22
-113.37
Cl
N
N
CF2H
Cl
HF2C
N
N
4d + 4d'
1.60
0.40
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
test001
USER: -- DATE: Jun 16 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185_14-Phen-Cl-2_FLUORINE_01.fid

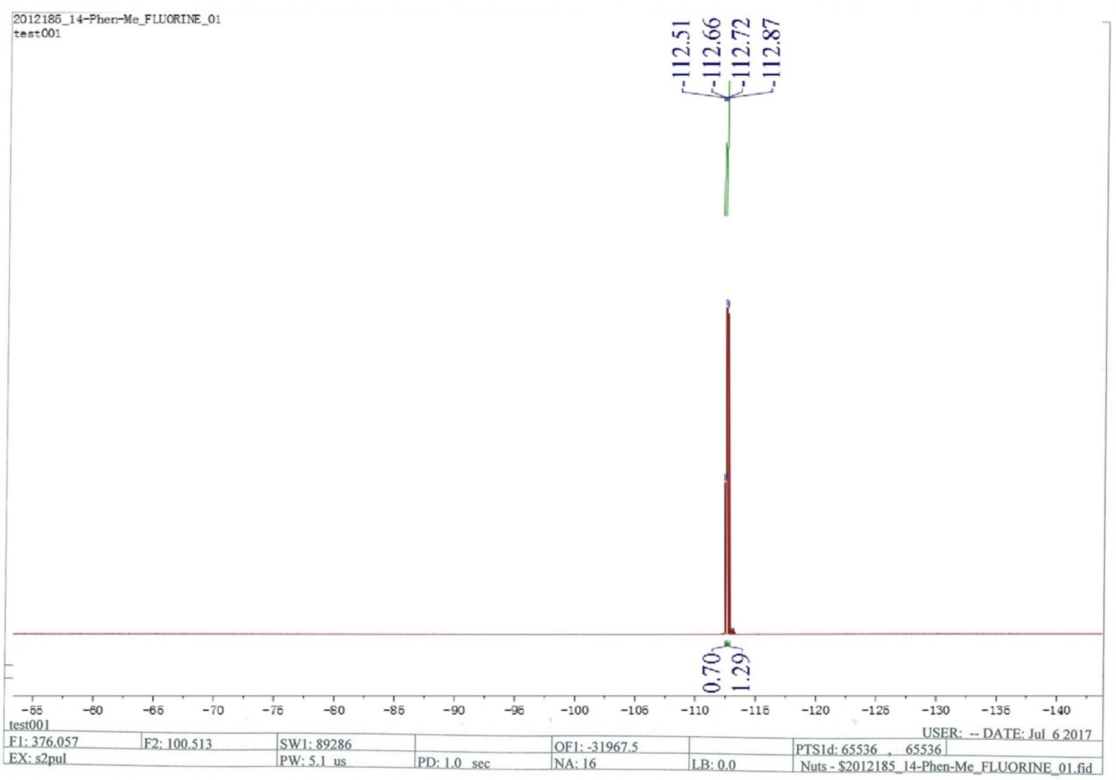

153.580
153.454
153.309
153.174
152.903
151.323
150.980
146.186
145.689
144.795
144.236
137.022
135.469
135.261
133.492
131.740
129.745
129.113
128.598
127.786
127.253
127.100
125.303
124.057
123.949
119.777
119.651
117.024
116.852
114.631
114.460
112.239
112.067
160
150
140
Me
N
N
CF2H
Me
HF2C
N
N
200
150
100
50
PPM
USER: nmr -- DATE: 15:46:23.133 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 29762
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 202
LB: 1.0
Nuts - $Phen-Cl_C.1

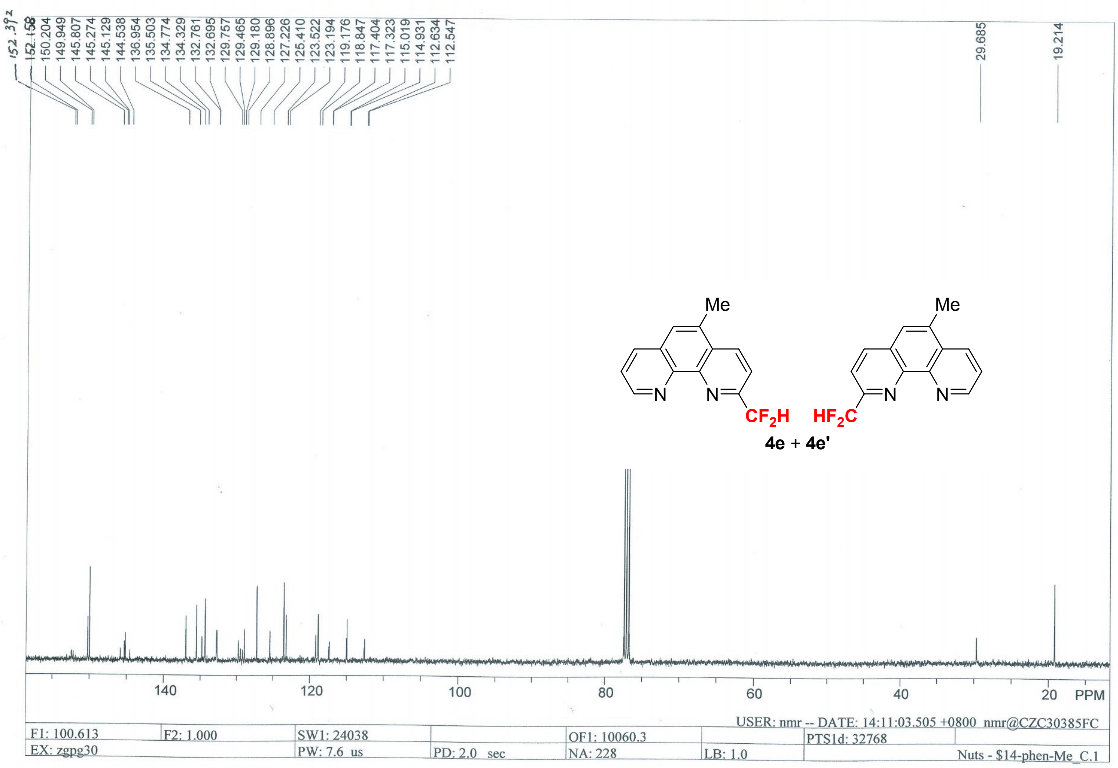
4e + 4e'

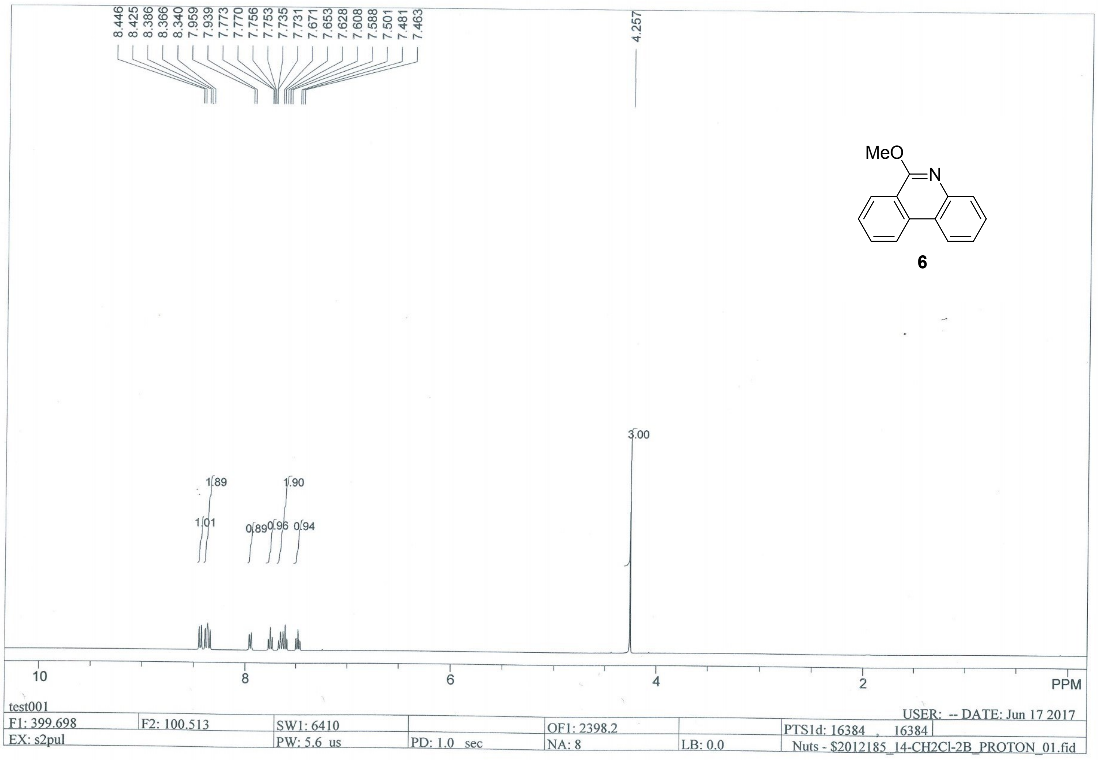

Cl
Cl
Me
Me
N
N
CF2H
HF2C
N
N

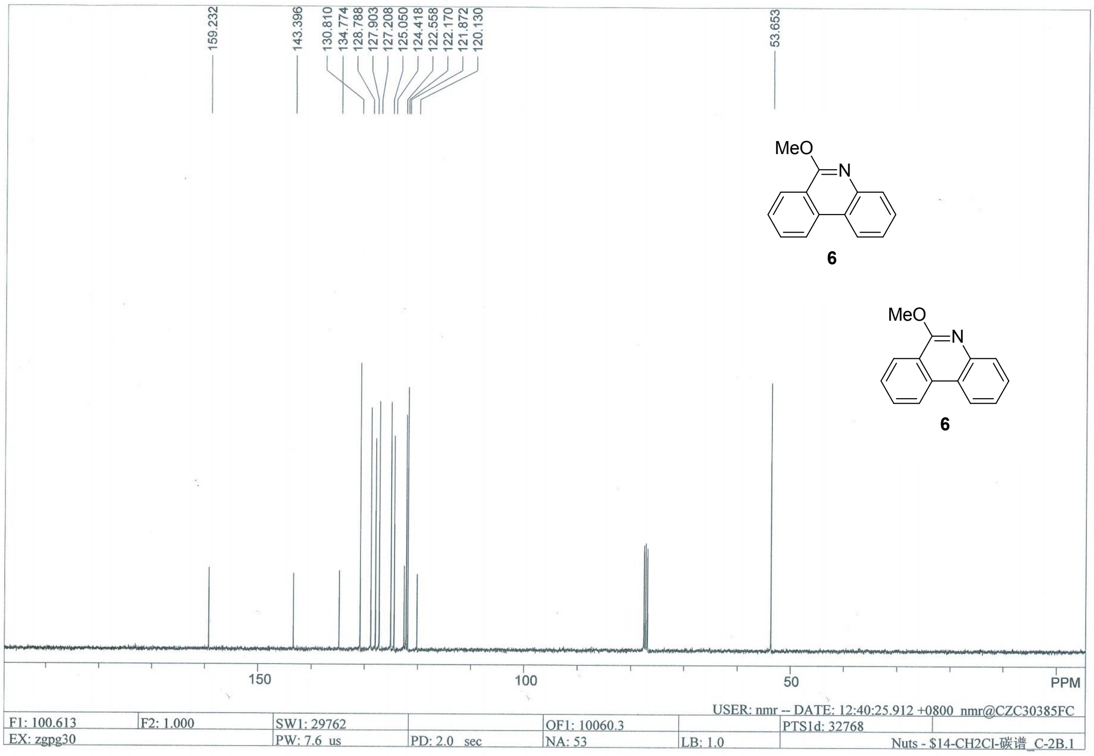
4e + 4e'

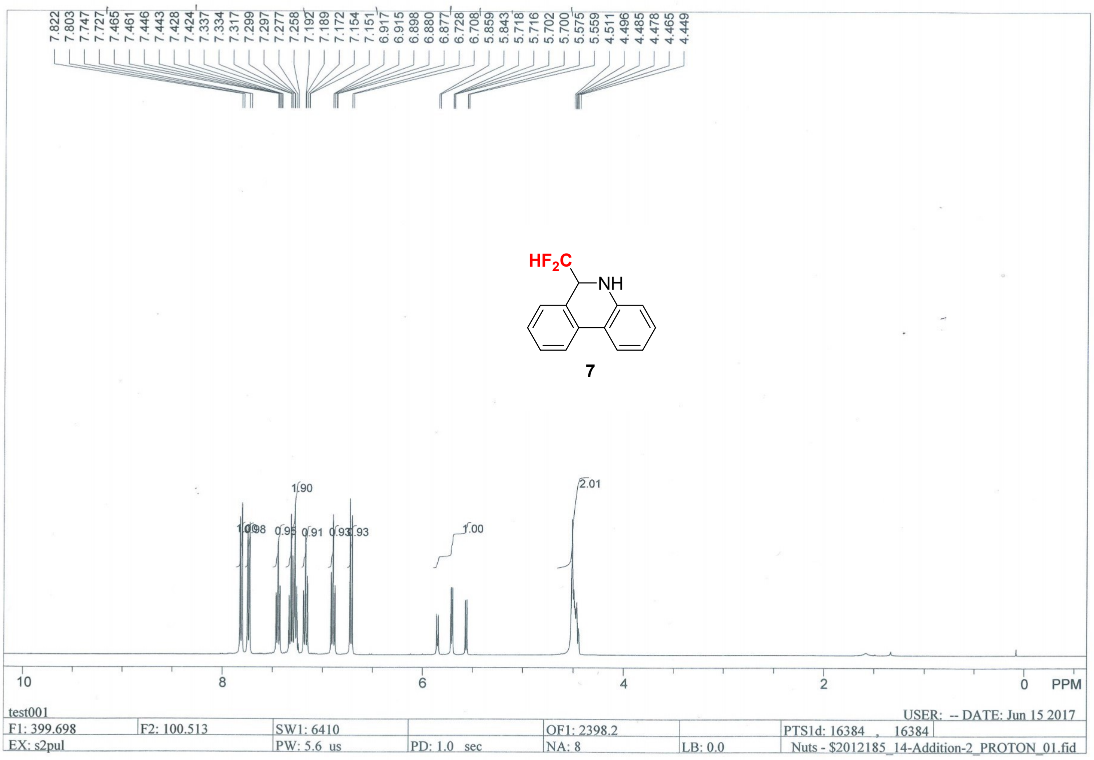

2012185_14-Phen-Me_PROTON_01
test001
9.19
9.19
9.18
9.13
9.12
9.12
9.11
8.47
8.46
8.45
8.44
8.10
8.10
8.08
7.97
7.97
7.96
7.95
7.95
7.94
7.89
7.87
7.59
7.58
7.57
7.57
7.56
7.55
7.24
7.23
7.09
7.07
6.96
6.93
2.69
2.68

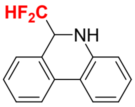

2012185_14-Phen-Me_FLUORINE_01
test001
-112.51
-112.66
-112.72
-112.87
0.70
1.29
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
test001
USER: -- DATE: Jul 6 2017
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $2012185_14-Phen-Me_FLUORINE_01.fid


152.392
152.158
150.204
149.949
145.807
145.274
145.129
144.538
136.954
135.503
134.774
134.329
132.761
132.695
129.757
129.465
129.180
128.896
127.226
125.410
123.522
123.194
119.176
118.847
117.404
117.323
115.019
114.931
112.634
112.547
29.685
19.214
Me
N
N
CF2H
Me
HF2C
N
N
4e + 4e'
140 120 100 80 60 40 20 PPM
USER: nmr -- DATE: 14:11:03.505 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 228
LB: 1.0
Nuts - $14-phen-Me_C.1

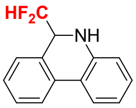

8.446
8.425
8.386
8.366
8.340
7.959
7.939
7.773
7.770
7.756
7.753
7.735
7.731
7.671
7.653
7.628
7.608
7.588
7.501
7.481
7.463
4.257
MeO
N
6
3.00
1.89
1.90
1.01
0.89
0.96
0.94
10
8
6
4
2
PPM
test001
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
USER: -- DATE: Jun 17 2017
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_14-CH2Cl-2B_PROTON_01.fid


159.232
143.396
130.810
134.774
128.788
127.903
127.208
125.050
124.418
122.558
122.170
121.872
120.130
53.653
MeO
N
6
MeO
N
6
150
100
50
PPM
USER: nmr -- DATE: 12:40:25.912 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 29762
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 53
LB: 1.0
Nuts - $14-CH2Cl-碳谱_C-2B.1


7.822
7.803
7.747
7.727
7.465
7.461
7.446
7.443
7.428
7.424
7.337
7.334
7.317
7.299
7.297
7.277
7.258
7.192
7.189
7.172
7.154
7.151
6.917
6.915
6.898
6.880
6.877
6.728
6.708
5.859
5.843
5.718
5.716
5.702
5.575
5.559
4.511
4.496
4.485
4.478
4.465
4.449
HF2C
NH
7
1.00 0.98 0.95 0.91 0.93 0.93
1.90
1.00
2.01
10
8
6
4
2
0
PPM
test001
USER: -- DATE: Jun 15 2017
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2398.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 5.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $2012185_14-Addition-2_PROTON_01.fid

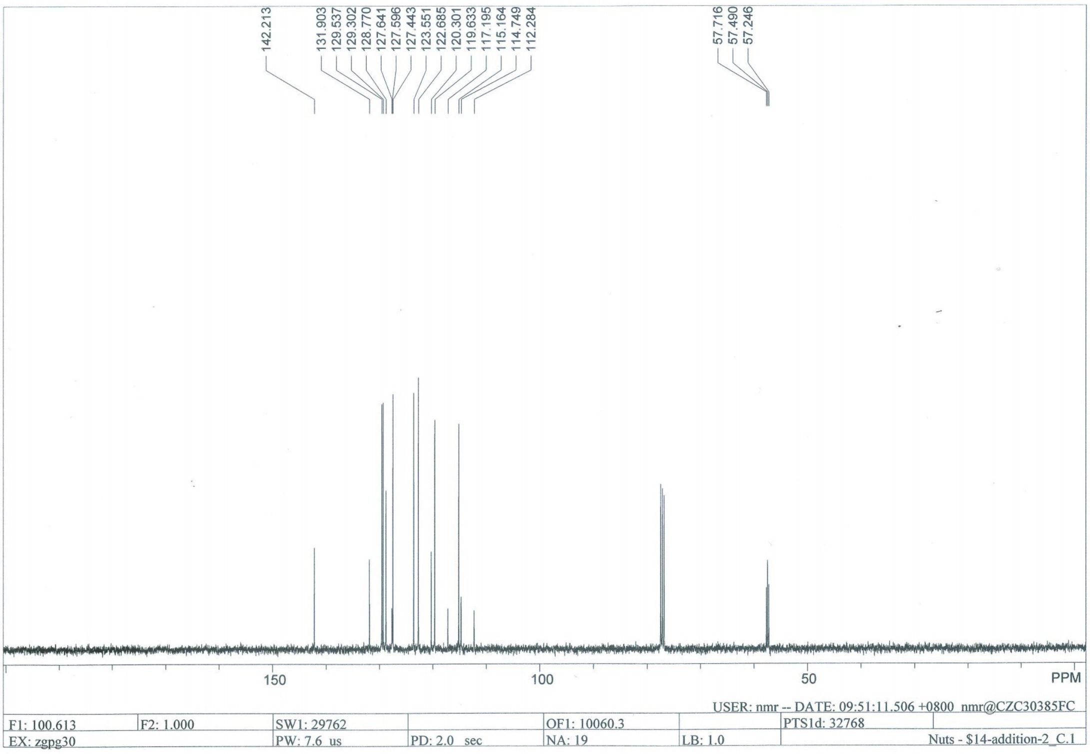


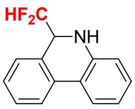
7



7


2012185_14-Addition-2_FLUORINE_01
test001
-126.36
-126.39
-126.51
-126.54
-127.11
-127.14
-127.26
-127.29
-127.40
-127.42
-127.55
-127.57
-128.15
-128.17
-128.30
-128.32
7500
7000
6500
6000
5500
5000
4500
4000


142.213
131.903
129.537
129.302
128.770
127.641
127.596
127.443
123.551
122.685
120.301
119.633
117.195
115.164
114.749
112.284
57.716
57.490
57.246
150
100
50
PPM
USER: nmr -- DATE: 09:51:11.506 +0800 nmr@CZC30385FC
F1: 100.613
F2: 1.000
SW1: 29762
OF1: 10060.3
PTS1d: 32768
EX: zgpg30
PW: 7.6 us
PD: 2.0 sec
NA: 19
LB: 1.0
Nuts - $14-addition-2_C.1


HF2C
NH

7