Supporting Information

Silver-Catalyzed Oxidative Decarboxylation of Difluoroacetates: Efficient Access to C-CF_2 Bond Formation

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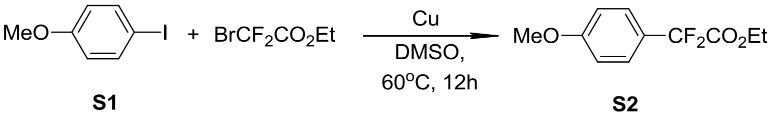
1. General Information

^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded in $CDCl_3$ on a Bruker AV-500 spectrometer. Chemical shifts for ^{1}H NMR spectra are reported in ppm relative to residual $CHCl_3$ as internal reference (δ 7.26 ppm for ^{1}H) downfield from TMS, chemical shifts for ^{13}C NMR spectra are reported in ppm relative to internal $CDCl_3$ (δ 77.16 ppm for ^{13}C), and chemical shifts for ^{19}F NMR spectra are reported in ppm downfield from internal fluorotrichloromethane ($CFCl_3$). Coupling constants (*J*) are given in Hertz (Hz). The terms m, s, d, t, q refer to multiplet, singlet, doublet, triplet, quartlet respectively; br refers to a broad signal. Infrared spectra (IR) were recorded on AVATAR 370 FT-IR spectrometer, absorbance frequencies are given at maximum of intensity in cm^{-1}. Melting points were obtained on a X-4 digital melting point apparatus without correction. High resolution mass spectra (HRMS) and Mass spectra (MS) were recorded using an Electron impact (EI) or Electrospray ionization (ESI) techniques.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. DMSO was distilled under reduced pressure from CaH_2 and stored with 4 Å molecular sieves.

2. Synthesis of potassium α,α-difluoroaryl acetate

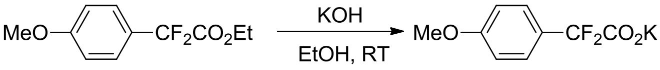
General procedure for Cu-promoted cross-coupling of aryl iodide with ethyl bromodifluoroacetate: [1]



S1 **S2**

In a 50 mL round bottom flask under an atmosphere of N_2, the appropriate aryl iodide **S1** (20 mmol, 1.0 equiv.) and ethyl bromodifluoroacetate (3.1 mL, 24 mmol, 1.2 equiv) were added to a suspension of activated Cu powder (3.4 g, 52 mmol, 2.6 equiv) in DMSO (50 mL). The reaction mixture was stirred at 60 °C for 12 h, after which time it was poured into a mixture of ice and sat. aq. NH_4Cl, the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with sat. aq. NH_4Cl (2 × 50 mL) and brine (2 × 50 mL), then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 100/1→50/1) to give **S2** 2.21g (48% yield) as a pale yellow oil.

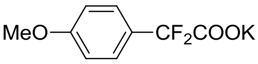
General procedure for saponification of ethyl α,α-difluoroaryl acetate: [2]



S2 **1a**

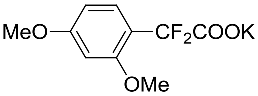
The substituted ethyl α,α-difluoroaryl acetate **S2** (2.21 g, 9.6 mmol) were reacted with KOH (0.54 g, 1.0 mmol) in ethanol for 12 h at room temperature, and the desired potassium α,α-difluoroaryl acetate **1a** was obtained in 96% yield as an off-white solid by removing the ethanol. This material was used for the subsequent decarboxylation without further purification. All other potassium salts were dried for 6h *in vacuo* at room temperature prior to use.

Potassium 2,2-difluoro-2-(4-methoxyphenyl)acetate (1a)



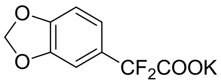
White solid, mp: 238-240 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.49 (d, *J* = 8.3 Hz, 2 H), 6.92 (d, *J* = 8.3 Hz, 2H), 3.75 (s, 3H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -96.64; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 165.84 (t, *J* = 27.5 Hz), 159.89 , 129.59 (t, *J* = 27.0 Hz), 126.97 (t, *J* = 5.8 Hz), 115.84 (t, *J* = 251.8 Hz), 113.20 , 55.22; **IR** (KBr): ν_{max} 2974, 2843, 1649, 1614, 1254, 1077, 840, 763 cm^{-1}.

Potassium 2-(2,4-dimethoxyphenyl)-2,2-difluoroacetate (1b)



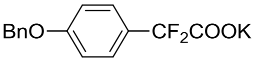
This compound was prepared via the same procedure described for **1a**, except that 1-iodo-2,4-dimethoxybenzene was used in place of 1-iodo-4-methoxybenzene. **1b** was obtained in 73% yield over two steps as an off-white solid, mp: 239-241 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.33 (d, *J* = 8.5 Hz, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 6.49 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.73(s, 3H), 3.68(s, 3H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -96.94; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 167.17 (t, *J* = 27.9 Hz), 162.08 , 158.89 (d, *J* = 3.2 Hz), 128.19 (t, *J* = 7.8 Hz), 118.28 (t, *J* = 25.3 Hz), 115.95 (t, *J* = 250.0 Hz), 104.63 , 99.48 , 56.27 , 55.91; **IR** (KBr): ν_{max} 2978, 2842, 1646, 1615, 1272, 1064, 836, 778 cm^{-1}.

Potassium 2-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoroacetate (1c)



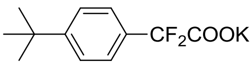
This compound was prepared via the same procedure described for **1a**, except that 5-iodobenzo[*d*][1,3]dioxole was used in place of 1-iodo-4-methoxybenzene. **1c** was obtained in 61% yield over two steps as an off-white solid, mp: 245-247 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.16-7.04 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -96.71; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 166.04 (t, *J* = 27.7 Hz), 148.12 , 147.19 , 131.10 (t, *J* = 26.8 Hz), 119.44 (t, *J* = 6.7 Hz), 115.68 (t, *J* = 252.4 Hz), 107.78 , 106.42 (t, *J* = 6.0 Hz), 101.47; **IR** (KBr): ν_{max} 2912, 1634, 1505, 1263, 1044, 825, 765 cm^{-1}.

Potassium 2-(4-(benzyloxy)phenyl)-2,2-difluoroacetate (1d)



This compound was prepared via the same procedure described for **1a**, except that 1-(benzyloxy)-4-iodobenzene was used in place of 1-iodo-4-methoxybenzene. **1d** was obtained in 66% yield over two steps as an off-white solid, mp: 270-272 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.70- 7.20 (m, 7H), 7.02 (d, *J* = 8.3 Hz, 2H), 5.12 (s, 2H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -96.77; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 165.85 (t, *J* = 27.7 Hz), 158.97 , 137.01 , 129.80 (t, *J* = 27.1 Hz), 128.54 , 127.93 , 127.70 , 127.00 (t, *J* = 5.9 Hz), 115.80 (t, *J* = 251.9 Hz), 114.16 , 69.31; **IR** (KBr): ν_{max} 2891, 1656, 1514, 1256, 1069, 827, 733 cm^{-1}.

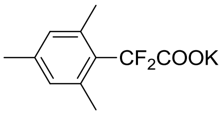
Potassium 2-(4-(tert-butyl)phenyl)-2,2-difluoroacetate (1e)



This compound was prepared via the same procedure described for **1a**, except that 1-(tert-butyl)-4-iodobenzene was used in place of 1-iodo-4-methoxybenzene. **1e** was obtained in 52% yield over two steps as an off-white solid, mp:

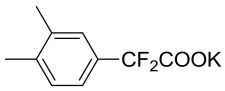
296-297 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.52 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 1.28 (s, 9H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -98.21; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 165.98 (t, *J* = 27.5 Hz), 151.60 , 134.50 (t, *J* = 26.5 Hz), 125.28 (t, *J* = 5.7 Hz), 124.58 , 115.85 (t, *J* = 251.7 Hz), 34.39 , 31.13; **IR** (KBr): ν_{max} 2961, 1661, 1615, 1272, 1078, 813, 702 cm^{-1}.

Potassium 2,2-difluoro-2-mesitylacetate (1f)



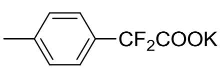
This compound was prepared via the same procedure described for **1a**, except that 2-iodo-1,3,5-trimethylbenzene was used in place of 1-iodo-4-methoxybenzene. **1f** was obtained in 68% yield over two steps as an off-white solid, mp: 279-281 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 6.76 (s, 2H), 2.39 (t, *J* = 4.0 Hz, 6H), 2.18 (s, 3H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -90.33; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 165.97 (t, *J* = 27.4 Hz), 136.70 , 136.45 (t, *J* = 3.4 Hz), 132.36 (t, *J* = 23.8 Hz), 129.90 , 118.70 (t, *J* = 254.8 Hz), 21.70 (t, *J* = 5.6 Hz), 20.30; **IR** (KBr): ν_{max} 2973, 1655, 1402, 1109, 1075, 820, 779 cm^{-1}.

Potassium 2-(3,4-dimethylphenyl)-2,2-difluoroacetate (1g)



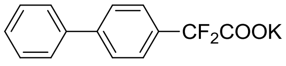
This compound was prepared via the same procedure described for **1a**, except that 4-iodo-1,2-dimethylbenzene was used in place of 1-iodo-4-methoxybenzene. **1g** was obtained in 63% yield over two steps as an off-white solid, mp: 247-249 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm ppm 7.33 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 2.24 (s, 3H), 2.22 (s, 3H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -95.74; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 165.70 (t, *J* = 27.1 Hz), 137.06 , 136.26 (t, *J* = 23.8 Hz), 134.35 (t, *J* = 3.2 Hz), 130.22 , 124.62 , 123.50 (t, *J* = 9.3 Hz), 116.59 (t, *J* = 253.3 Hz), 20.04 , 15.76. **IR** (KBr): ν_{max} 2943, 1652, 1405, 1276, 1037, 819, 749 cm^{-1}.

Potassium 2,2-difluoro-2-(p-tolyl)acetate (1h)



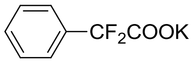
This compound was prepared via the same procedure described for **1a**, except that 1-iodo-4-methylbenzene was used in place of 1-iodo-4-methoxybenzene. **1h** was obtained in 53% yield over two steps as an off-white solid, mp: 258-260 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.47 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 2.30 (s, 3H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -97.86; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 166.00 (t, *J* = 27.4 Hz), 138.63 , 134.51 (t, *J* = 26.5 Hz), 128.44 , 125.46 (t, *J* = 5.9 Hz), 115.89 (t, *J* = 251.7 Hz), 20.90; **IR** (KBr): ν_{max} 3023, 1651, 1409, 1244, 1047, 812, 737 cm^{-1}.

Potassium 2-([1,1'-biphenyl]-4-yl)-2,2-difluoroacetate (1i)



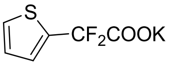
This compound was prepared via the same procedure described for **1a**, except that 4-iodo-1,1'-biphenyl was used in place of 1-iodo-4-methoxybenzene. **1i** was obtained in 76% yield over two steps as an off-white solid, mp: 298-300 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.72-7.64 (m, 6H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -98.37; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 165.55 (t, *J* = 27.5 Hz), 141.00 , 139.71 , 136.48 (t, *J* = 26.6 Hz), 129.06 , 127.78 , 126.84 , 126.25 , 126.10 (t, J = 5.8 Hz), 115.73 (t, J = 252.5 Hz); **IR** (KBr): ν_{max} 3033, 1636, 1404, 1264, 1066, 841, 742 cm^{-1}.

Potassium 2,2-difluoro-2-phenylacetate (1j)



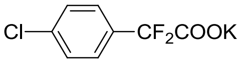
This compound was prepared via the same procedure described for **1a**, except that iodobenzene was used in place of 1-iodo-4-methoxybenzene. **1j** was obtained in 46% yield over two steps as an off-white solid, mp: 263-265 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.61-7.54 (m, 2H), 7.42-7.36 (m, 3H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -98.41; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 165.66 (t, J = 27.2 Hz), 137.34 (t, J = 26.3 Hz), 129.19 , 127.90 , 125.42 (t, J = 5.9 Hz), 115.71 (t, J = 252.3 Hz); **IR** (KBr): ν_{max} 3042, 1638, 1411, 1262, 1109, 820, 688 cm^{-1}.

Potassium 2,2-difluoro-2-(thiophen-2-yl)acetate (1k)



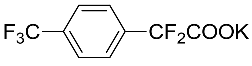
This compound was prepared via the same procedure described for **1a**, except that 2-iodothiophene was used in place of 1-iodo-4-methoxybenzene. **1k** was obtained in 38% yield over two steps as a pale yellow solid, mp: 215-217 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.60 (dd, J = 5.0, 1.3 Hz, 1H), 7.32 (dd, J = 3.4, 1.6 Hz, 1H), 7.02 (dd, J = 5.0, 3.6 Hz, 1H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -86.85; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 164.60 (t, J = 26.6 Hz), 138.85 (t, J = 30.8 Hz), 127.98 , 126.99 (t, J = 5.5 Hz), 126.45 , 113.62 (t, J = 250.3 Hz); **IR** (KBr): ν_{max} 3084, 1652, 1403, 1243, 1114, 1037, 809, 706 cm^{-1}.

Potassium 2-(4-chlorophenyl)-2,2-difluoroacetate (1l)



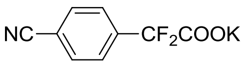
This compound was prepared via the same procedure described for **1a**, except that 1-chloro-4-iodobenzene was used in place of 1-iodo-4-methoxybenzene. **1l** was obtained in 76% yield over two steps as an off-white solid, mp: 285-287 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.61 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -98.67; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 165.41 (t, J = 27.2 Hz), 136.19 (t, J = 26.8 Hz), 134.12, 128.06 , 127.49 (t, J = 5.8 Hz), 115.26 (t, J = 252.7 Hz); **IR** (KBr): ν_{max} 3043, 1630, 1400, 1263, 1053, 833, 775 cm^{-1}.

Potassium 2,2-difluoro-2-(4-(trifluoromethyl)phenyl)acetate (1m)



This compound was prepared via the same procedure described for **1a**, except that 1-iodo-4-(trifluoromethyl)benzene was used in place of 1-iodo-4-methoxybenzene. **1m** was obtained in 72% yield over two steps as an off-white solid,, mp: 283-285 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ ppm 7.80-7.74 (m, 4H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -61.36 , -99.71; **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 164.64 (t, J = 26.7 Hz), 141.64 (t, J = 26.7 Hz), 129.67 (q, J = 31.8 Hz), 126.33 (t, J = 5.9 Hz), 124.90 (q, J = 3.9 Hz), 124.13 (q, J = 272.1 Hz), 115.00 (t, J = 253.7 Hz); **IR** (KBr): ν_{max} 3052, 1634, 1414, 1266, 1077, 844, 816, 721, 688 cm^{-1}.

Potassium 2-(4-cyanophenyl)-2,2-difluoroacetate (1n)



This compound was prepared via the same procedure described for **1a**, except that 4-iodobenzonitrile was used in place of 1-iodo-4-methoxybenzene. **1n** was obtained in 78% yield over two steps as a pale yellow solid, mp: 262-264 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ ppm 7.86 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H); **^{19}F NMR** (471 MHz, DMSO-*d*$_6$) δ ppm -100.18; **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ ppm 164.67 (t, *J* = 26.7 Hz), 142.02 (t, *J* = 26.7 Hz), 132.13 , 126.49 (t, *J* = 5.9 Hz), 118.63 , 114.89 (t, *J* = 253.9 Hz), 112.13; **IR** (KBr): ν_{max} 3042, 2246, 1647, 1385, 1245, 1087, 853, 761, 701 cm^{-1}.

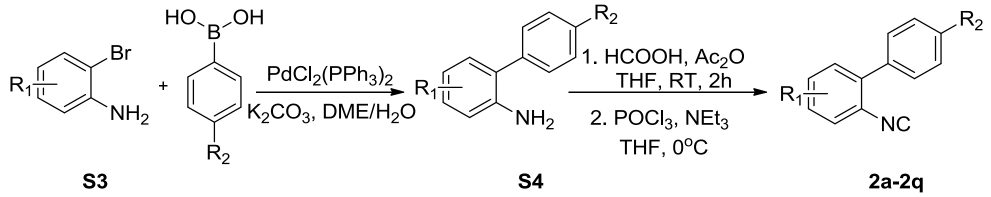
Potassium 2,2-difluoroacetate (1p)

$$HCF_2CO_2H + KOH \xrightarrow[\text{EtOH, RT}]{} HCF_2CO_2K$$

In a 50 mL round bottom flask, 2,2-difluoroacetic acid (10 mmol, 1.0 equiv) was added to a mixture of EtOH (15 mL) and KOH (10.5 mmol,1.05 equiv) and stirred for 6 h at room temperature. The desired potassium 2,2-difluoroacetate **1p** was obtained by removing the ethanol. Products were purified by washing with petroleum ether in 90% yield as an off-white solid, mp: 224-226 ^{o}C; **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ ppm 5.71 (t, *J* = 55.3 Hz, 1H); **^{19}F NMR** (471 MHz, DMSO-*d*$_6$) δ ppm -123.22 (d, *J* = 55.3 Hz); **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ ppm 167.99 (t, *J* = 23.6 Hz), 110.34 (t, *J* = 248.0 Hz); **IR** (KBr): ν_{max} 3011, 1639, 1339, 1049, 815 cm^{-1}.

3. General procedure for synthesis of isocyanides:

All the 2-isocyanobiaryls (**2a-2q**) were prepared according to the following procedure:[3]

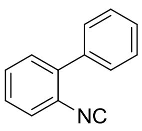


To an oven-dried three necked flask, 2-bromoaniline (20 mmol), phenylboronic acid (24 mmol), aqueous solution of K_2CO_3 (2M, 45 mL) and DME (40 mL) were added under a gentle stream of nitrogen, and the mixture was stirred for 30 min at room temperature under N_2 atmosphere. To the stirred mixture, $PdCl_2(PPh_3)_2$ (280 mg, 0.40 mmol) was added at room temperature, and the mixture was stirred for overnight at 80 ℃, under N_2. The reaction mixture was then cooled to room temperature and diluted with EtOAc. The organic layer was washed with water and dried over $MgSO_4$. After removing the volatiles in vacuo, the residue was subjected to column chromatography on silica gel (Petroleum ether/EtOAc = 30/1) to afford **S4**, (**S4a**, 89%).

To an oven-dried three necked flask equipped with a dropping funnel, **S4** (18 mmol) and THF (30 mL) were added under N_2 atmosphere and cooled to 0 ℃. Acetic formic anhydride, which was prepared from the reaction of acetic anhydride (3.8 mL) with formic acid (1.7 mL) at 55 ℃ for 2 h, was transferred to the dropping funnel and dropped to the solution of **S4** at 0 ℃. After the addition was complete, the mixture was warmed to room temperature and stirred for 2 h. Then, the mixture was quenched by sat. aqueous solution of $NaHCO_3$ and extracted with EtOAc three times. The extract was dried over Na_2SO_4 and concentrated under reduced pressure to give formamide as a pale yellow oil.

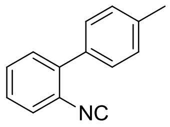
This material was used for the subsequent dehydration without further purification. To an oven-dried three necked flask equipped with a dropping funnel, THF (30 mL), NEt_3 (150 mmol) and the whole amount of formamide obtained above were added under N_2 atmosphere and cooled to 0 ℃. $POCl_3$ (36 mmol) was added dropwise, and the mixture was stirred for 2 h at 0 ℃ after the addition was complete. Then, the mixture was quenched by sat. aqueous solution of Na_2CO_3 and stirred for 1 h. The mixture was extracted with CH_2Cl_2three times, dried over $MgSO_4$ and evaporated under reduced pressure. The compound was purified by column chromatography on Florisil (Petroleum ether/EtOAc = 40/1) to give **2a** as a green oil (78% yield from **S4**).

2-isocyano-1,1'-biphenyl (2a)



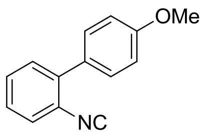
Green oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ7.58-7.54 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 3H), 7.48-7.43 (m, 3H), 7.41-7.36 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 166.73 , 138.58 , 136.84 , 130.41 , 129.44 , 128.82 , 128.41 , 128.22 , 128.03 , 127.66 , 124.36; **IR** (KBr): ν_{max} 3065, 2120, 1475, 1438, 762, 702 cm^{-1}.

2-isocyano-4'-methyl-1,1'-biphenyl (2b)



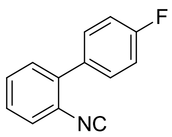
This compound was prepared via the same procedure described for **2a**, except that *p*-tolylboronic acid was used in place of phenylboronic acid. **2b** was obtained in 81% yield over two steps as a green oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.49 (d, *J* = 7.4 Hz, 1H), 7.48-7.42 (m, 4H), 7.38-7.34 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 166.52 , 138.74 , 138.17 , 134.04 , 130.46 , 129.47 , 129.23 , 128.79 , 127.85 , 127.76, 124.48, 21.22; **IR** (KBr): ν_{max} 3028, 2922, 2120, 1516, 1478, 1109, 819, 764 cm^{-1}.

2-isocyano-4'-methoxy-1,1'-biphenyl (2c)



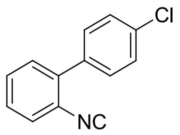
This compound was prepared via the same procedure described for **2a**, except that (4-methoxyphenyl)boronic acid was used in place of phenyl boronic acid. **2c** was obtained in 85% yield over two steps as a pale green solid, mp: 69-71 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.48-7.45(m, 3H), 7.45-7.39 (m, 2H), 7.36-7.31 (m, 1H), 7.02(d, *J* =8.8 Hz, 2H), 3.86 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 166.40 , 159.65 , 138.36 , 130.38 , 130.14 , 129.48 , 129.20 , 127.77 , 127.62 , 124.38 , 113.95 , 55.24; **IR** (KBr): ν_{max} 3030, 2982, 2124, 1610, 1476, 1248, 1033, 826, 748 cm^{-1}.

4'-fluoro-2-isocyano-1,1'-biphenyl (2d)



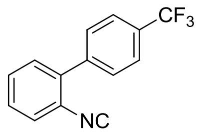
This compound was prepared via the same procedure described for **2a**, except that (4-fluorophenyl)boronic acid was used in place of phenyl boronic acid. **2d** was obtained in 78% yield over two steps as a green solid, mp: 60-62 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.52-7.44 (m, 4H), 7.42-7.36 (m, 2H), 7.17 (t, *J* = 8.8 Hz, 2H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -113.20- -113.30(m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 166.85 , 162.81 (d, *J* = 248.2 Hz), 137.79 , 133.03 (d, *J* = 3.5 Hz), 130.81 (d, *J* = 8.2 Hz), 130.50 , 129.66 , 128.35 , 127.86 , 124.59 , 115.63 (d, *J* = 21.6 Hz); **IR** (KBr): ν_{max} 3028, 2120, 1602, 1511, 1475, 1227, 832, 759 cm^{-1}.

4'-chloro-2-isocyano-1,1'-biphenyl (2e)



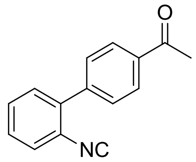
This compound was prepared via the same procedure described for **2a**, except that (4-chlorophenyl)boronic acid was used in place of phenyl boronic acid. **2e** was obtained in 88% yield over two steps as an off-white solid, mp: 98-100 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.55-7.46 (m, 6H), 7.45-7.39 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 167.08 , 137.53 , 135.41 , 134.57 , 130.38 , 130.33 , 129.71 , 128.82 , 128.55 , 127.91 , 124.49; **IR** (KBr): ν_{max} 3035, 2123, 1469, 1091, 824, 763 cm^{-1}.

2-isocyano-4'-(trifluoromethyl)-1,1'-biphenyl (2f)



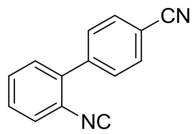
This compound was prepared via the same procedure described for **2a**, except that (4-(trifluoromethyl)phenyl)boronic acid was used in place of phenyl boronic acid. **2f** was obtained in 78% yield over two steps as a green solid, mp: 85-87 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.76 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.55-7.46 (m, 2H), 7.47-7.41 (m, 2H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -62.58; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 167.44 , 140.68 , 137.39 , 130.53 (q, J = 32.6 Hz), 130.49 , 129.87 , 129.51 , 129.10 , 128.03 , 125.63 (q, J = 3.8 Hz), 124.60 , 124.14 (q, J = 272.2 Hz); **IR** (KBr): ν_{max} 3033, 2124, 1622, 1473, 1328, 1116, 841, 764 cm^{-1}.

1-(2'-isocyano-[1,1'-biphenyl]-4-yl)ethan-1-one (2g)



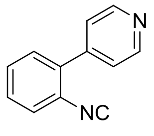
This compound was prepared via the same procedure described for **2a**, except that (4-acetylphenyl)boronic acid was used in place of phenyl boronic acid. **2g** was obtained in 82% yield over two steps as an off-white solid, mp: 117-119 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.03 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.46 (t, J = 7.8 Hz, 1H), 7.42-7.36 (m, 2H), 2.61 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 197.45 , 167.25 , 141.51 , 137.47 , 136.61 , 130.29 , 129.69 , 129.22 , 128.89 , 128.48 , 127.88 , 124.35 , 26.65; **IR** (KBr): ν_{max} 3035, 2122, 1676, 1466, 1264, 1152, 837, 764 cm^{-1}.

2'-isocyano-[1,1'-biphenyl]-4-carbonitrile (2h)



This compound was prepared via the same procedure described for **2a**, except that (4-cyanophenyl)boronic acid was used in place of phenyl boronic acid. **2h** was obtained in 70% yield over two steps as a green solid, mp: 123-125 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.75 (d, J = 6.4 Hz, 2H), 7.62 (d, J = 6.6 Hz, 2H), 7.55-7.47 (m, 2H), 7.47-7.38 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 167.60 , 141.48 , 136.62 , 132.27 , 130.20 , 129.88 , 129.74 , 129.38 , 127.97 , 124.26 , 118.41 , 112.11; **IR** (KBr): ν_{max} 3028, 2220, 2128, 1638, 1473, 1154, 847, 764 cm^{-1}; **HRMS** (EI) calcd. for $C_{14}H_8N_2$ 204.0687, found: 204.0698.

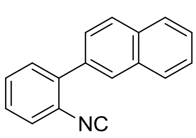
4-(2-isocyanophenyl)pyridine (2i)



This compound was prepared via the same procedure described for **2a**, except that pyridin-4-ylboronic acid was used in place of phenyl boronic acid. **2i** was obtained in 70% yield over two steps as a brown solid, mp: 61-63 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$)

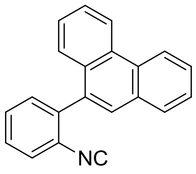
δ ppm 8.76-8.64 (m, 2H), 7.54-7.35 (m, 6H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ ppm 167.89 , 150.08 , 144.62 , 135.80 , 130.09 , 129.90 , 129.56 , 128.07 , 124.28 , 123.57; **IR** (KBr): ν_{max} 3030, 2122, 1599, 1472, 827, 765, 716 cm^{-1}.

2-(2-isocyanophenyl)naphthalene (2j)



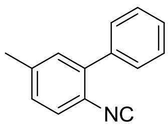
This compound was prepared via the same procedure described for **2a**, except that naphthalen-2-ylboronic acid was used in place of phenyl boronic acid. **2j** was obtained in 80% yield over two steps as pale yellow solid, mp: 124-126 ^{o}C; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ ppm 8.00 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.93 (q, *J* = 5.7 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.59-7.52 (m, 4H), 7.50 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 (td, *J* = 7.7, 1.6 Hz, 1H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ ppm 166.82 , 138.73 , 134.45 , 133.22 , 132.96 , 130.83 , 129.61 , 128.38 , 128.32 , 128.24 , 128.23 , 127.90 , 127.76 , 126.66 , 126.63 , 126.51 , 124.76; **IR** (KBr): ν_{max} 3061, 2110, 1489, 1349, 1160, 827, 762 cm^{-1}.

9-(2-isocyanophenyl)phenanthrene (2k)



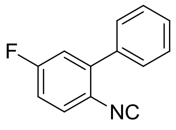
This compound was prepared via the same procedure described for **2a**, except that phenanthren-9-ylboronic acid was used in place of phenyl boronic acid. **2k** was obtained in 58% yield over two steps as a pale yelow solid, mp: 181-183 ^{o}C; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ ppm 8.84 (d, *J* = 8.3 Hz, 1H), 8.79 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.81-7.72 (m, 3H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.66-7.58 (m, 3H), 7.57-7.47 (m, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ ppm 166.49 , 138.02 , 133.69 , 131.75 , 131.18 , 130.56 , 130.52 , 130.38 , 129.31 , 128.91 , 128.68 , 128.38 , 127.25 , 127.21 , 126.99 , 126.87 , 126.84 , 126.43 , 126.13 , 123.15 , 122.68; **IR** (KBr): ν_{max} 3044, 2110, 1489, 1349, 1160, 827, 762 cm^{-1}.

2-isocyano-5-methyl-1,1'-biphenyl (2l)



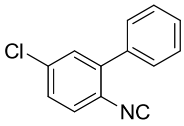
This compound was prepared via the same procedure described for **2a**, except that 2-bromo-4-methylaniline was used in place of 2-bromoaniline. **2l** was obtained in 88% yield over two steps as a pale yellow solid, mp: 93-95 ^{o}C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ7.55-7.52 (m, 2H), 7.52-7.47 (m, 2H), 7.44 (tt, *J* = 7.1, 2.4 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 2.43 (s, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ ppm 165.88 , 139.88 , 138.54 , 137.16 , 131.14 , 128.94 , 128.78 , 128.50 , 128.25 , 127.64 , 122.08 , 21.34; **IR** (KBr): ν_{max} 2914, 2115, 1639, 1472, 1127, 825, 705 cm^{-1}.

5-fluoro-2-isocyano-1,1'-biphenyl (2m)



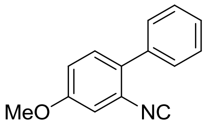
This compound was prepared via the same procedure described for **2a**, except that 2-bromo-4-fluoroaniline was used in place of 2-bromoaniline. **2m** was obtained in 82% yield over two steps as a green solid, mp: 58-60 ^{o}C; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ ppm 7.55-7.44 (m, 6H), 7.14 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.07 (ddd, *J* = 8.8, 7.6, 2.8 Hz, 1H); ^{19}**F NMR** (471 MHz, $CDCl_3$) δ ppm -108.56- -108.66 (m); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ ppm 166.91 , 162.19 (d, *J* = 252.1 Hz), 141.26 (d, *J* = 8.7 Hz), 136.00 , 129.79 (d, *J* = 9.2 Hz), 128.94 , 128.82 , 128.74 , 120.82 , 117.48 (d, *J* = 23.5 Hz), 115.30 (d, *J* = 23.3 Hz); **IR** (KBr): ν_{max} 3058, 2129, 1576, 1475, 1265, 1181, 822, 769, 705 cm^{-1}.

5-chloro-2-isocyano-1,1'-biphenyl (2n)



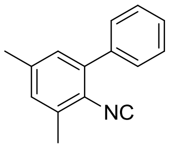
This compound was prepared via the same procedure described for **2a**, except that 2-bromo-4-chloroaniline was used in place of 2-bromoaniline. **2n** was obtained in 84% yield over two steps as an off-white solid, mp: 77-79 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.52-7.45 (m, 5H), 7.45-7.41 (m, 2H), 7.35 (dd, J = 8.6, 2.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 168.09 , 140.31 , 135.69 , 135.30 , 130.53 , 128.98 , 128.89 , 128.79 , 128.69 , 128.23 , 123.00; **IR** (KBr): ν_{max} 3022, 2120, 1642, 1469, 1090, 812, 761, 691 cm^{-1}.

2-isocyano-4-methoxy-1,1'-biphenyl (2o)



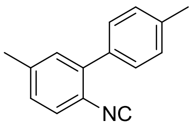
This compound was prepared via the same procedure described for **2a**, except that 2-bromo-5-methoxyaniline was used in place of 2-bromoaniline. **2o** was obtained in 86% yield over two steps as a green solid, mp: 57-59 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.53-7.45 (m, 4H), 7.40 (tt, J = 6.9, 2.6 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.05-6.99 (m, 2H), 3.85 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 166.37 , 159.09 , 136.83 , 131.42 , 131.28 , 128.98 , 128.50 , 127.91 , 125.01 , 116.10 , 112.71 , 55.68; **IR** (KBr): ν_{max} 3063, 2965, 2124, 1611, 1481, 1281, 1039, 764, 696 cm^{-1}.

2-isocyano-3,5-dimethyl-1,1'-biphenyl (2p)



This compound was prepared via the same procedure described for **2a**, except that 2-bromo-4,6-dimethylaniline was used in place of 2-bromoaniline. **2p** was obtained in 79% yield over two steps as a yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.53-7.50 (m, 2H), 7.50-7.45 (m, 2H), 7.42 (tt, J = 7.1, 1.6 Hz, 1H), 7.10 (s, 1H), 7.07 (s, 1H), 2.48 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 167.84 , 139.18 , 138.85 , 137.73 , 135.65 , 130.05 , 129.03 , 128.68 , 128.47 , 128.15 , 122.31 , 21.31, 19.34; **IR** (KBr): ν_{max} 3033, 2921, 2115, 1600, 1463, 1262, 1028, 861, 772, 704 cm^{-1}.

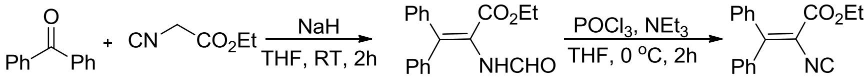
2-isocyano-4',5-dimethyl-1,1'-biphenyl (2q)



This compound was prepared via the same procedure described for **2a**, except that 2-bromo-4-methylaniline was used in place of 2-bromoaniline, *p*-tolylboronic acid was used in place of phenylboronic acid. **2q** was obtained in 85% yield over two steps as a pale green solid, mp: 63-65 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.45 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 7.9 Hz, 2H), 7.25 (s, 1H), 7.16 (dd, J = 8.1, 1.3 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 165.77 , 139.76 , 138.48 , 138.03 , 134.20 , 131.03 , 129.17, 128.76 , 128.49 , 127.57 , 122.02 , 21.29 , 21.21; **IR** (KBr): ν_{max} 3023, 2914, 2121, 1610, 1480, 815, 725 cm^{-1}.

Ethyl 2-isocyano-3,3-diphenylacrylate (2r)

Ethyl 2-isocyano-3,3-diphenylacrylate 2r was prepared according to the previously reported procedures:[4]

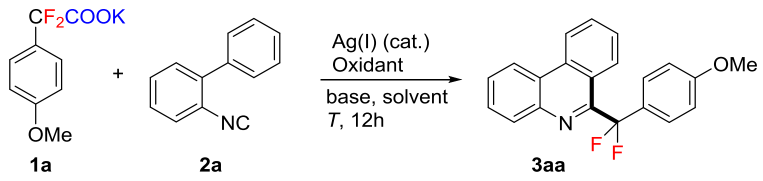


S5 **2r**

A mixture of benzophenone (1.82 g, 10.0 mmol) and ethyl isocyanoacetate (S2, 1.13 g, 10.0 mmol) in THF (10 ml) was added dropwise to a suspension of NaH (60% in oil) (0.48 g, 12.0 mmol) in THF (10.0 ml) at room temperature. After stirring for 2 h at room temperature, 10% AcOH was added to the mixture at 0 ℃ until there is no hydrogen release. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 three times and the extract was washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. Further recrystallization in MeOH afforded the product **S5** (2.3 g, 78%) as a white solid.

THF (10.0 mL), NEt_3 (5.6 mL, 40 mmol) and **S5** (1.48 g, 5.0 mmol) were added to an oven-dried three necked flask under N_2 atmosphere and cooled to 0 ℃. $POCl_3$ (0.93 mL, 10.0 mmol) was added dropwise and the mixture was stirred for 2 h at 0 ℃ after the addition was completed. Then the mixture was quenched by sat. Na_2CO_3 and stirred for another 1 h. The mixture was extracted with CH_2Cl_2 three times, dried over Na_2SO_4 and concentracted under reduced pressure. The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to give **2r** (1.20 g, 86%) as a yellow solid. Mp: 85-87 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.45-7.33 (m, 8H), 7.16 (d, J = 6.7 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 1.07 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 169.68 , 161.94 , 153.83 , 138.02 , 137.37 , 130.23 , 129.86 , 129.45 , 129.10 , 128.43 , 128.22 , 114.35 , 62.22 , 13.57; **IR** (KBr): ν_{max} 3030, 2987, 2113, 1723, 1639, 1447, 1260, 1116, 755, 699 cm^{-1}; **HRMS** (ESI-TOF) calcd. for $C_{18}H_{16}NO_2^+$ 278.1176, found: 278.1184.

4. Survey of reaction conditions. [a]

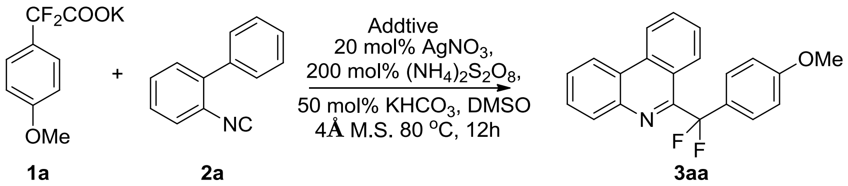


Entry	Catalyst [mol %]	Oxidant [equiv]	Base [equiv]	Solvent	Temp [°C]	Yield [%][b]
1	$AgNO_3$ (10)	$Na_2S_2O_8$ (2)		DMSO	120	39
2	$AgCO_3$ (10)	$Na_2S_2O_8$ (2)		DMSO	120	35
3	Ag_2O (10)	$Na_2S_2O_8$ (2)		DMSO	120	34
4	$AgBF_4$ (10)	$Na_2S_2O_8$ (2)		DMSO	120	29
5	$AgSbF_6$ (10)	$Na_2S_2O_8$ (2)		DMSO	120	21
6	AgOAc (10)	$Na_2S_2O_8$ (2)		DMSO	120	34
7	$AgNO_3$ (10)	$PhI(OAc)_2$ (2)		DMSO	120	0
8	$AgNO_3$ (10)	$K_2S_2O_8$ (2)		DMSO	120	48
9	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)		DMSO	120	56
10	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)		DMF	120	8
11	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)		DMPU	120	0
12	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)		NMP	120	0
13	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)		DMSO	100	66
14	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)		DMSO	80	73
15	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)		DMSO	60	65
16	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)	K_2CO_3 (0.5)	DMSO	80	43
17	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)	KOH (0.5)	DMSO	80	62
18	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)	Et_3N (0.5)	DMSO	80	60
19	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)	$KHCO_3$ (0.5)	DMSO	80	87
20[c]	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)	$KHCO_3$ (1)	DMSO	80	64
21[d]	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (2)	$KHCO_3$ (2)	DMSO	80	44
22	$AgNO_3$ (10)	$(NH_4)_2S_2O_8$ (1)	$KHCO_3$ (0.5)	DMSO	80	53
23	$AgNO_3$ (20)	$(NH_4)_2S_2O_8$ (2)	$KHCO_3$ (0.5)	DMSO	80	92
24	$AgNO_3$ (30)	$(NH_4)_2S_2O_8$ (2)	$KHCO_3$ (0.5)	DMSO	80	97
25[e]	---	$(NH_4)_2S_2O_8$ (2)	$KHCO_3$ (0.5)	DMSO	80	12
26[f]	$AgNO_3$ (10)	---	$KHCO_3$ (0.5)	DMSO	80	0

[a] Reaction conditions: potassium difluoroacetate **1a** (0.5 mmol), 2-isocyanobiphenyl **2a** (2.5 mmol), Ag(I) salt, oxidant and base in solvent (3.0 mL) under N_2 atmosphere. [b] Yields determined by ^{19}F NMR analysis with $PhCF_3$ as the internal standard. [c] 0.5 mmol loading of base and 0.5 mmol loading of oxidant. [d] 1.0 mmol loading of base and 1.0 mmol loading of oxidant. [e] Without catalyst. [f] Without oxidant.

5. Preliminary mechanistic study

Table S1. Effects of Additives on silver-catalyzed oxidative decarboxylation of difluoroacetates



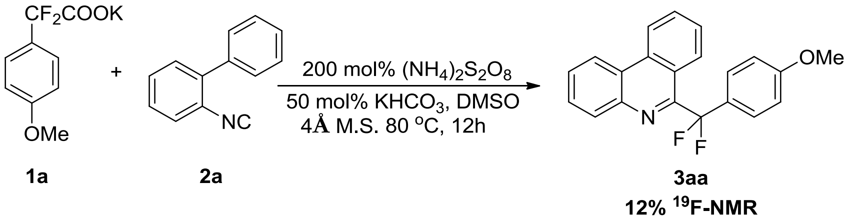
Entry	Additive	Yield (%)[a]
1	ambient light	92
2	dark	94
3	1.0 equiv 1,4-dinitrobenzene	26
4	1.0 equiv hydroquinone	trace
5	1.0 equiv TEMPO	46
6	2.0 equiv TEMPO	trace

[a] Yields determined by ^{19}F-NMR spectroscopy with $PhCF_3$ as internal standard.

General Procedure: An oven-dried 10 mL Schlenk tube was charged with $AgNO_3$ (10.2 mg, 0.06 mmol, 0.2 equiv), $(NH_4)_2S_2O_8$ (137 mg, 0.6 mmol, 2.0 equiv), anhydrous $KHCO_3$ (15 mg, 0.15 mmol, 0.5 equiv), pre-activated 4Å powdered molecular sieves (60 mg), additive (1.0 equiv or 2.0 equiv) and potassium 2,2-difluoro-2-(4-methoxyphenyl)acetate **1a** (72 mg, 0.3 mmol, 1.0 equiv) under air, followed by 2-isocyanobiphenyl **2a** (135 mg, 0.75 mmol, 2.5 equiv). The tube was sealed with a septum, evacuated and backfilled with N_2 for three times. Anhydrous DMSO (3.0 mL) was added with syringe under N_2. The reaction mixture was heated to 80 °C (oil bath). After stirring for 12 h, the reaction was cooled to room temperature and $PhCF_3$ (0.3 mmol) was added. The yield was determined by ^{19}F-NMR.

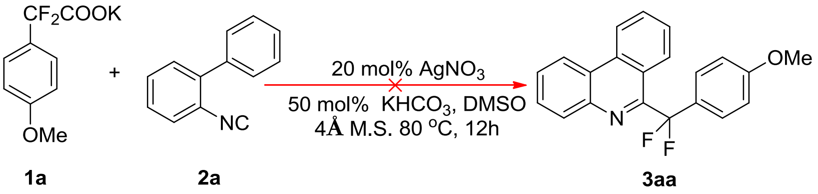
Control reactions to probe for the possible mechanism.

A 10 mL Schlenk tube was charged with $(NH_4)_2S_2O_8$ (137 mg, 0.6 mmol, 2.0 equiv), anhydrous $KHCO_3$ (15 mg, 0.15 mmol, 0.5 equiv), potassium 2,2-difluoro-2-(4-methoxyphenyl)acetate **1a** (72 mg, 0.3 mmol, 1.0 equiv), pre-activated 4Å powdered molecular sieves (60 mg) under air, followed by 2-isocyanobiphenyl **2a** (135 mg, 0.75 mmol, 2.5 equiv). The tube was sealed with a septum, evacuated and backfilled with N_2 for three times. Anhydrous DMSO (3.0 mL) was added with syringe under N_2. After 12 h of stirring at 80 °C, the resulting mixture was analyzed by ^{19}F-NMR, and the desired product **3aa** was detected only 12% yield. (Scheme 1)



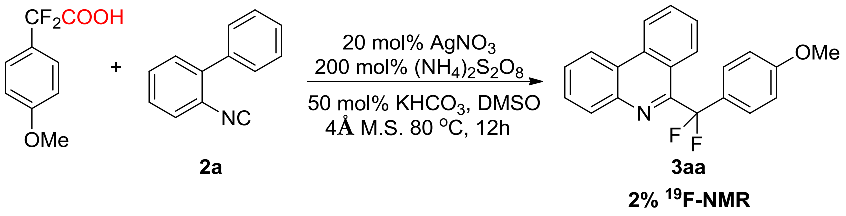
Scheme 1

A 10 mL Schlenk tube was charged with, $AgNO_3$ (10.2 mg, 0.06 mmol, 0.2 equiv), anhydrous $KHCO_3$ (15 mg, 0.15 mmol, 0.5 equiv), potassium 2,2-difluoro-2-(4-methoxyphenyl)acetate **1a** (72 mg, 0.3 mmol, 1.0 equiv), pre-activated 4Å powdered molecular sieves (60 mg) under air, followed by 2-isocyanobiphenyl **2a** (135 mg, 0.75 mmol, 2.5 equiv). The tube was sealed with a septum, evacuated and backfilled with N_2 for three times. Anhydrous DMSO (3.0 mL) was added with syringe under N_2. After 12 h of stirring at 80 °C, the resulting mixture was analyzed by ^{19}F-NMR, and the desired product **3aa** was not detected. (Scheme 2)



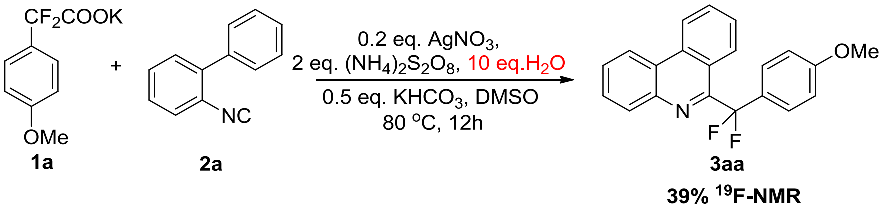
Scheme 2

An oven-dried 10mL Schlenk tube was charged with $AgNO_3$ (10.2 mg, 0.06 mmol, 0.2 equiv), $(NH_4)_2S_2O_8$ (137 mg, 0.6 mmol, 2.0 equiv), anhydrous $KHCO_3$ (15 mg, 0.15 mmol, 0.5 equiv), pre-activated 4Å powdered molecular sieves (60 mg), additive (1.0 equiv or 2.0 equiv) and 2,2-difluoro-2-(4-methoxyphenyl)acetic acid (62 mg, 0.3 mmol, 1.0 equiv) under air, followed by 2-isocyanobiphenyl **2a** (135 mg, 0.75 mmol, 2.5 equiv). The tube was sealed with a septum, evacuated and backfilled with N_2 for three times. Anhydrous DMSO (3.0 mL) was added with syringe under N_2. The reaction mixture was heated to 80 °C (oil bath). After stirring for 12 h, the reaction was cooled to room temperature and $PhCF_3$ (0.3 mmol) was added. The resulting mixture was analyzed by ^{19}F-NMR, and the desired product **3aa** was detected only 2% yield. (Scheme 3)



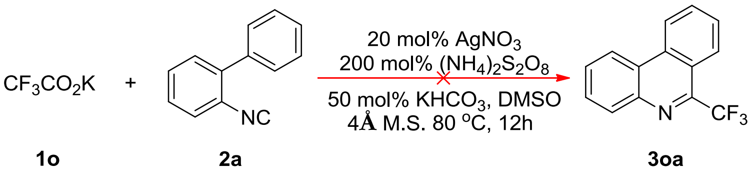
Scheme 3

The Effect of Water: A 10 mL Schlenk tube was charged with $AgNO_3$ (10.2 mg, 0.06 mmol, 0.2 equiv), $(NH_4)_2S_2O_8$ (137 mg, 0.6 mmol, 2.0 equiv), anhydrous $KHCO_3$ (15 mg, 0.15 mmol, 0.5 equiv), potassium 2,2-difluoro-2-phenylacetate **1a** (72 mg, 0.3 mmol, 1.0 equiv) under air, followed by 2-isocyanobiphenyl **2a** (135 mg, 0.75 mmol, 2.5 equiv). The tube was sealed with a septum, evacuated and backfilled with N_2 for three times. DMSO (3.0 mL) and H_2O (54 mg, 10.0 equiv) was added with syringe subsequently. The reaction mixture was heated to 80 °C (oil bath). After stirring for 12 h, the reaction was cooled to room temperature and $PhCF_3$ (0.3 mmol) was added. The resulting mixture was analyzed by ^{19}F-NMR, and the desired product **3aa** was detected 39% yield (Scheme 4).



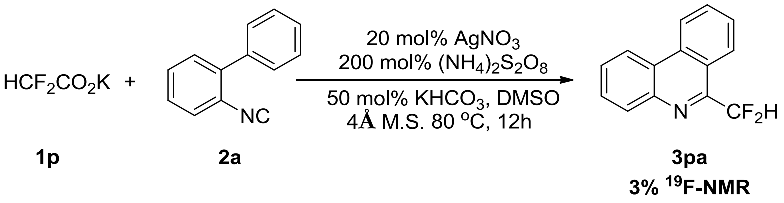
Scheme 4

A 10 mL Schlenk tube was charged with $AgNO_3$ (10.2 mg, 0.06 mmol, 0.2 equiv), $(NH_4)_2S_2O_8$ (137 mg, 0.6 mmol, 2.0 equiv), anhydrous $KHCO_3$ (15 mg, 0.15 mmol, 0.5 equiv), potassium trifluoroacetate **1o** (46 mg, 0.3 mmol, 1.0 equiv), pre-activated 4Å powdered molecular sieves (60 mg) under air, followed by 2-isocyanobiphenyl **2a** (135 mg, 0.75 mmol, 2.5 equiv). The tube was sealed with a septum, evacuated and backfilled with N_2 for three times. Anhydrous DMSO (3.0 mL) was added with syringe under N_2. After 12 h of stirring at 80 °C, the resulting mixture was analyzed by ^{19}F-NMR, and the desired product **3oa** was not detected (Scheme 5).



Scheme 5

A 10 mL Schlenk tube was charged with $AgNO_3$ (10.2 mg, 0.06 mmol, 0.2 equiv), $(NH_4)_2S_2O_8$ (137 mg, 0.6 mmol, 2.0 equiv), anhydrous $KHCO_3$ (15 mg, 0.15 mmol, 0.5 equiv), potassium 2,2-difluoroacetate **1p** (40 mg, 0.3 mmol, 1.0 equiv), pre-activated 4Å powdered molecular sieves (60 mg) under air, followed by 2-isocyanobiphenyl **2a** (135 mg, 0.75 mmol, 2.5 equiv). The tube was sealed with a septum, evacuated and backfilled with N_2 for three times. Anhydrous DMSO (3.0 mL) was added with syringe under N_2. After 12 h of stirring at 80 °C, the resulting mixture was analyzed by ^{19}F-NMR, and the desired product **3pa** was detected only 3% yield (Scheme 6).



Scheme 6

6. General procedure for synthesis of 6-difluoromethyl phenanthridines

A 10 mL Schlenk tube was charged with $AgNO_3$ (10.2 mg, 0.06 mmol, 0.2 equiv), $(NH_4)_2S_2O_8$ (137 mg, 0.6 mmol, 2.0 equiv), anhydrous $KHCO_3$ (15 mg, 0.15 mmol, 0.5 equiv), potassium 2,2-difluoro-2-phenylacetate **1a** (72 mg, 0.3 mmol, 1.0 equiv), pre-activated 4Å powdered molecular sieves (60 mg) under air, followed by 2-isocyanobiphenyl **2a** (135 mg, 0.75 mmol, 2.5 equiv). The tube was sealed with a septum, evacuated and backfilled with N_2 for three times. Anhydrous DMSO (3.0 mL) was added with syringe under N_2. The mixture was stirred at 80 ^{o}C for 12 h. It was quenched by water and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The pure product was obtained by flash column chromatography on silica gel (Petroleum ether/ EtOAc = 20:1) to afford **3aa** in 88% yield.

7. Reference

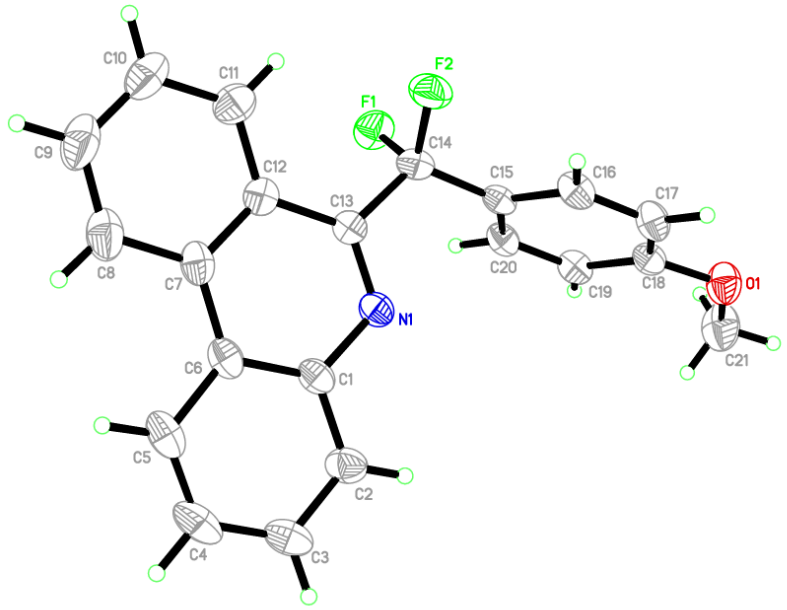
[1] a) K. Sato, M. Omote, A. Ando, I. Kumadaki, *J. Fluorine Chem*. **2004**, *125*, 509; b) S. Mizuta, I. S. R. Stenhagen, M. O'Duill, J. Wolstenhulme, A. K. Kirjavainen, S. J. Forsback, M. Tredwell, G. Sandford, P. R. Moore, M. Huiban, S. K. Luthra, J. Passchier, O. Solin, V. Gouverneur, *Org. Lett*. **2013**, *15*, 2648; c) K. Fujikawa, Y. Fujioka, A. Kobayashi, H. Amii, *Org. Lett*. **2011**, *13*, 5560.

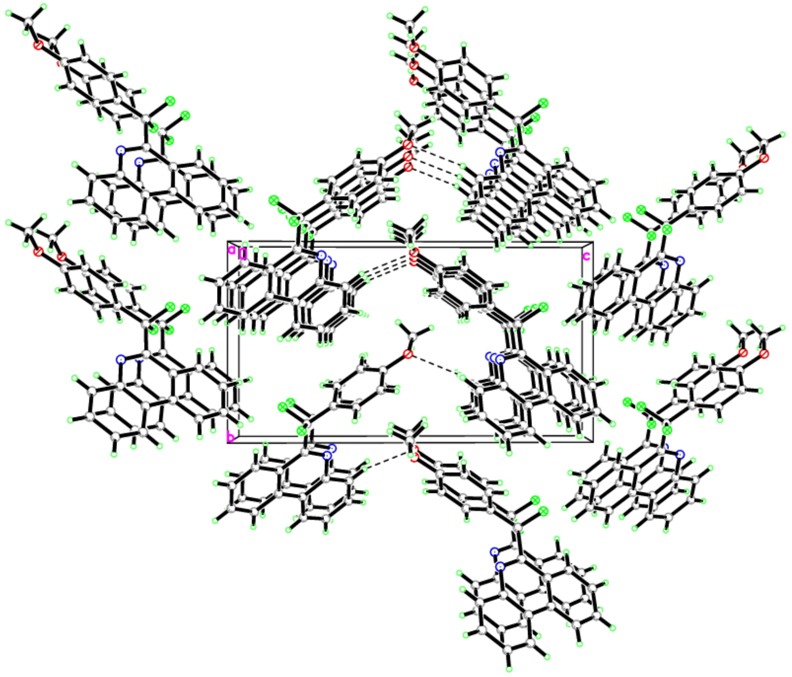
[2] L. J. Gooßen, F. Rudolphi, C. Oppel, N. Rodríguez, *Angew. Chem. Int. Ed*. **2008**, *47*, 3043.

[3] a) Q. Wang, X. Dong, T. Xiao, L. Zhou, *Org. Lett*. **2013**, *15*, 4846; b) Y. Cheng, H. Jiang, Y. Zhang, S. Yu, *Org. Lett*., **2013**, 5580; c) M. Tobisu, K. Koh, T. Furukawa, N. Chatani, *Angew. Chem. Int. Ed*. **2012**, *51*, 11363; d) B. Zhang, C. Mück-Lichtenfeld, C. G. Daniliuc, A. Studer, *Angew. Chem. Int. Ed*. **2013**, *52*, 10792; e) L. Wang, W. Sha, Q. Dai, X. Feng, W. Wu, H. Peng, B Chen., J. Cheng, *Org. Lett*. **2014**, *16*, 2088.

[4] H. Jiang, Y. Cheng, R. Wang, Y. Zhang, S. Yu, *Chem. Commun*. **2014**, *50*, 6164.

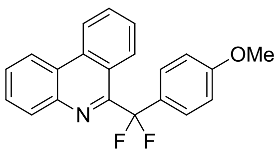
8. Single crystal X-ray analysis of 3aa





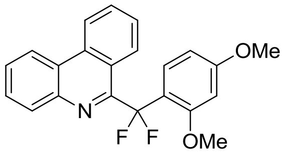
9. New Compounds Characterization

6-(difluoro(4-methoxyphenyl)methyl)phenanthridine (3aa)



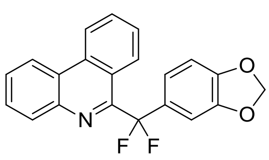
The product (91 mg, 90% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 120-122 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.64 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.34 (d, *J* = 7.5 Hz, 1H), 8.28 (dd, *J* = 8.4 1.3 Hz, 1H), 7.82-7.69 (m, 3H), 7.62-7.55 (m, 3H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.22; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.00 (t, *J* = 1.8 Hz), 153.31 (t, *J* = 28.2 Hz), 142.24 , 134.01 , 131.17 , 130.74 , 129.04 (t, *J* = 26.7 Hz), 129.03 , 128.47 , 127.83 (t, *J* = 5.4 Hz), 127.53 (t, *J* = 4.9 Hz), 127.47 , 124.76 , 123.02 , 122.46 , 122.02 , 120.30 (t, *J* = 243.2 Hz), 113.81 , 55.38; **IR** (KBr): ν_{max} 3072, 2948, 1612, 1515, 1252, 1028, 821, 758, 722 cm^{-1}; **MS** (EI): *m/z* (%) 314(100), 157(89), 335(71); **HRMS** (ESI-TOF) calcd. for $C_{21}H_{16}F_2NO^+$ 336.1194, found: 336.1198.

6-((2,4-dimethoxyphenyl)difluoromethyl)phenanthridine (3ba)



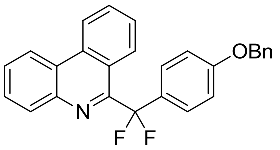
The product (94 mg, 86% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). **Mp**: 156-158 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.65 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 7.4 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 6.7 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.76-7.67 (m, 3H), 7.60 (t, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 1H), 6.47 (s, 1H), 3.84 (s, 3H), 3.43 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.89; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 162.68, 159.12 (t, *J* = 3.8 Hz), 153.46 (t, *J* = 28.9 Hz), 142.38, 133.88, 131.07, 130.49, 128.75, 128.25 (t, *J* = 7.6 Hz), 128.11, 127.32 (t, *J* = 4.5 Hz), 127.28, 124.70, 123.18, 122.32, 121.96, 120.45 (t, *J* = 242.7 Hz), 118.21 (t, *J* = 25.4 Hz), 104.31, 99.71, 55.85, 55.48; **IR** (KBr): ν_{max} 3066, 2934, 1611, 1454, 1134, 1041, 929, 766, 728 cm^{-1}; **LC-MS** (ESI): m/z 366.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{22}H_{18}F_2NO_2^+$ 366.1300, found: 366.1306.

6-(benzo[d][1,3]dioxol-5-yldifluoromethyl)phenanthridine (3ca)



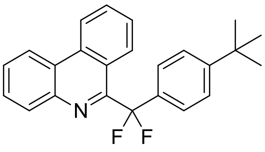
The product (47 mg, 45% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 158-160 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.65 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 8.3 Hz, 1H), 8.33 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 7.81 (t, *J* = 7.4 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.15 (s, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 5.98 (s, 2H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.18; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 153.09 (t, *J* = 28.0 Hz), 149.21, 147.88, 142.23, 134.03, 131.20, 130.79, 130.66 (t, *J* = 26.7 Hz), 129.07, 128.54, 127.52, 127.43 (t, *J* = 4.7 Hz), 124.78, 122.96, 122.50, 122.04, 120.62 (t, *J* = 6.3 Hz), 119.98 (t, *J* = 244.1 Hz), 108.13, 106.99 (t, *J* = 5.4 Hz), 101.65; **IR** (KBr): ν_{max} 3069, 1498, 1446, 1253, 1033, 811, 722 cm^{-1}; **LC-MS** (ESI): m/z 350.3 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{21}H_{14}F_2NO_2^+$ 350.0987, found: 350.0989.

6-((4-(benzyloxy)phenyl)difluoromethyl)phenanthridine (3da)



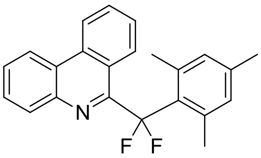
The product (86 mg, 70% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). **Mp**: 165-167 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ ppm 8.66 (d, J = 7.8 Hz, 1H), 8.58 (d, J = 8.2 Hz, 1H), 8.38 (d, J = 8.6 Hz, 1H), 8.30 (dd, J = 8.0, 1.5 Hz, 1H), 7.84-7.72 (m, 4H), 7.64-7.59 (m, 4H), 7.45-7.37 (m, 6H), 7.37-7.32 (m, 1H), 7.02 (d, J = 8.7 Hz, 3H), 5.06 (s, 2H); **^{19}F NMR** (471 MHz, CDCl$_3$) δ ppm -86.19; **^{13}C NMR** (125 MHz, CDCl$_3$) δ ppm 160.22, 153.29 (t, J = 28.2 Hz), 142.25, 136.57, 134.00, 131.18, 130.74, 129.29 (t, J = 26.8 Hz), 129.02, 128.71, 128.47, 128.20, 127.88 (t, J = 5.3 Hz), 127.59, 127.53 (d, J = 4.6 Hz), 127.48, 124.76, 123.02, 122.46, 122.02, 120.31 (t, J = 243.3 Hz), 114.68, 70.14; **IR** (KBr): $\nu_{\max}$ 3074, 2915, 1607, 1511, 1236, 1062, 918, 746, 705 cm^{-1}; **LC-MS** (ESI): m/z 412.4 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{27}H_{20}F_2NO^+$ 412.1507, found: 412.1510.

6-((4-(tert-butyl)phenyl)difluoromethyl)phenanthridine (3ea)



The product (69 mg, 64% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 194-196 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ ppm 8.64 (d, J = 8.3 Hz, 1H), 8.56 (d, J = 8.3 Hz, 1H), 8.40 (d, J = 8.3 Hz, 1H), 8.29 (d, J = 8.1 Hz, 1H), 7.82-7.69 (m, 3H), 7.65-7.57 (m, 3H), 7.45 (d, J = 8.3 Hz, 2H), 1.33 (s, 9H); **^{19}F NMR** (471 MHz, CDCl$_3$) δ ppm -87.32; **^{13}C NMR** (125 MHz, CDCl$_3$) δ ppm 153.42, 153.34 (t, J = 27.9 Hz), 142.31, 134.01, 133.86 (t, J = 26.4 Hz), 131.22, 130.72, 129.01, 128.45, 127.54 (t, J = 5.1 Hz), 127.49, 125.99 (t, J = 5.4 Hz), 125.45, 124.76, 123.05, 122.45, 122.02, 120.33 (t, J = 243.6 Hz), 34.86, 31.31; **IR** (KBr): $\nu_{\max}$ 3069, 2951, 2867, 1609, 1470, 1259, 1084, 837, 757, 718 cm^{-1}; **LC-MS** (ESI): m/z 362.4 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{24}H_{22}F_2N^+$ 362.1715, found: 362.1719.

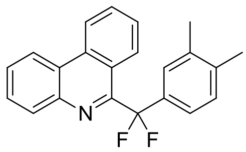
6-(difluoro(mesityl)methyl)phenanthridine (3fa)



The product (74 mg, 71% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 169-170 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ ppm 8.83 (d, J = 8.0 Hz, 1H), 8.71 (d, J = 8.0 Hz, 1H), 8.60 (d, J = 8.0 Hz, 1H), 8.02 (d, J =8.0 Hz, 1H), 7.90 (t, J = 7.6 Hz, 1H), 7.80-7.65 (m, 3H), 6.98 (s, 2H), 2.39 (s, 3H), 2.33 (t, J = 4.0 Hz, 6H); **^{19}F NMR** (471 MHz, CDCl$_3$) δ ppm -78.44; **^{13}C NMR** (125 MHz, CDCl$_3$) δ ppm 153.30 (t, J = 32.5 Hz), 142.30, 138.66, 137.86 (t, J = 3.2 Hz), 134.25, 131.41, 131.23 (t, J = 22.5 Hz), 130.78, 130.61, 128.71, 128.49, 127.59, 127.54, 125.74 (t, J = 243.7 Hz), 124.80, 123.27, 122.46, 121.96, 22.66 (t, J = 5.8 Hz), 21.01; **IR** (KBr): $\nu_{\max}$ 3075, 2973, 2929, 1612, 1454, 1243, 1128, 1016, 887, 753, 723 cm^{-1}; **LC-MS** (ESI): m/z 348.4 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{23}H_{20}F_2N^+$ 348.1558, found: 348.1553.

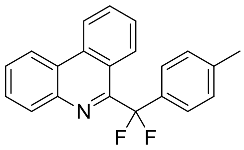
6-((3,4-dimethylphenyl)difluoromethyl)phenanthridine (3ga)

The product (60 mg, 63% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 151-153 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ ppm 8.68 (d, J = 8.3



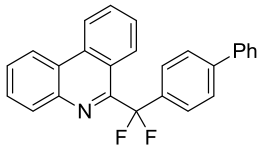
Hz, 1H), 8.63-8.57 (m, 2H), 8.18-8.11 (m, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.77-7.70 (m, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H); **^{19}F NMR** (471 MHz, CDCl$_3$) δ ppm -84.44; **^{13}C NMR** (125 MHz, CDCl$_3$) δ ppm 153.40 (t, *J* = 29.9 Hz), 142.18, 138.20, 136.42 (t, *J* = 2.5 Hz), 134.94 (t, *J* = 23.4 Hz), 134.09, 131.85, 131.20, 130.76, 128.87, 128.50, 127.70 (t, *J* = 5.1 Hz), 127.49, 125.08, 124.73, 124.70 (t, *J* = 8.7 Hz), 123.29, 122.46 (t, *J* = 243.7 Hz), 122.44, 121.99, 20.65, 16.93; **IR** (KBr): ν_{max} 3069, 2917, 1573, 1452, 1261, 1121, 1015, 757, 717 cm^{-1}; **LC-MS** (ESI): m/z 334.4 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{22}H_{18}F_2N^+$ 334.1402, found: 334.1405.

6-(difluoro(p-tolyl)methyl)phenanthridine (3ha)



The product (57 mg, 60% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 123-125 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ ppm 8.65 (d, *J* = 8.3 Hz, 1H), 8.58 (dd, *J* = 8.3, 2.2 Hz, 1H), 8.35 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.84-7.70 (m, 3H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H); **^{19}F NMR** (471 MHz, CDCl$_3$) δ ppm -87.44; **^{13}C NMR** (125 MHz, CDCl$_3$) δ ppm 153.29 (t, *J* = 28.0 Hz), 142.28, 140.37 (t, *J* = 1.9 Hz), 134.02, 133.97 (t, *J* = 26.4 Hz), 131.22, 130.74, 129.18, 129.03, 128.47, 127.50 (t, *J* = 4.8 Hz), 127.48, 126.18 (t, *J* = 5.4 Hz), 124.79, 123.02, 122.47, 122.03, 120.30 (t, *J* = 243.5 Hz), 21.44; **IR** (KBr): ν_{max} 3073, 2921, 1613, 1449, 1254, 1058, 923, 754, 717 cm^{-1}; **LC-MS** (ESI): m/z 320.4 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{21}H_{16}F_2N^+$ 320.1245, found: 320.1244.

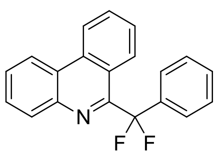
6-([1,1'-biphenyl]-4-yldifluoromethyl)phenanthridine (3ia)



The product (59 mg, 52% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 143-144 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ ppm 8.68 (d, *J* = 8.1 Hz, 1H), 8.60 (d, *J* = 8.2 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 7.84 (t, *J* = 8.5 Hz, 1H), 7.81-7.72 (m, 4H), 7.69-7.63 (m, 3H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H); **^{19}F NMR** (471 MHz, CDCl$_3$) δ ppm -87.57; **^{13}C NMR** (125 MHz, CDCl$_3$) δ ppm 153.14 (t, *J* = 28.2 Hz), 143.08, 142.26, 140.27, 135.62 (t, *J* = 26.6 Hz), 134.07, 131.23, 130.83, 129.07, 128.96, 128.56, 127.91, 127.58, 127.46 (t, *J* = 5.0 Hz), 127.30, 127.18, 126.80 (t, *J* = 5.5 Hz), 124.81, 123.02, 122.53, 122.05, 120.46 (t, *J* = 243.0 Hz) ; **IR** (KBr): ν_{max} 3037, 2922, 1607, 1477, 1255, 1064, 841, 757, 729, 685 cm^{-1}; **LC-MS** (ESI): m/z 382.4 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{26}H_{18}F_2N^+$ 382.1402, found: 382.1406.

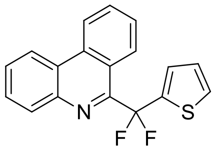
6-(difluoro(phenyl)methyl)phenanthridine (3ja)

30mol % of AgNO$_3$ was used. The product (46 mg, 50% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 147-149 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ ppm 8.62 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 7.8 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.83-7.68 (m, 5H), 7.60 (t, *J* = 8.4 Hz, 1H), 7.50-7.42 (m, 3H); **^{19}F NMR** (471 MHz,



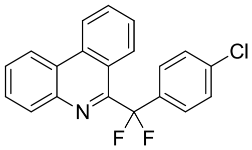
$CDCl_3$) δ ppm -87.80; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 153.11 (t, *J* = 28.1 Hz), 142.19, 136.75 (t, *J* = 26.2 Hz), 133.98, 131.15, 130.74, 130.25, 129.00, 128.49, 128.44, 127.49, 127.36 (t, *J* = 5.0 Hz), 126.26 (t, *J* = 5.6 Hz), 124.73, 122.94, 122.46, 122.00, 120.36 (t, *J* = 243.5 Hz); **IR** (KBr): ν_{max} 3051, 2922, 1609, 1448, 1247, 1101, 1006, 753, 710 cm^{-1}; **MS** (EI): *m/z* (%) 284(100), 304(82), 305(59); **HRMS** (ESI-TOF) calcd. for $C_{20}H_{13}F_2N^+$ 306.1089, found: 306.1087.

6-(difluoro(thiophen-2-yl)methyl)phenanthridine (3ka)



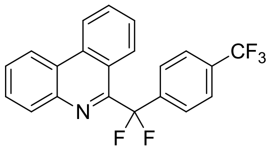
30mol % of $AgNO_3$ was used. The product (42 mg, 45% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). **Mp**: 126-128 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.63 (d, *J* = 8.3 Hz, 1H), 8.55 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.83-7.79 (m, 1H), 7.79-7.75 (m, 1H), 7.75-7.70 (m, 1H), 7.65-7.60 (m, 1H), 7.49 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.24-7.20 (m, 1H), 7.02-6.98 (m, 1H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -76.94; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 152.31 (t, *J* = 27.8 Hz), 142.07, 138.64 (t, *J* = 30.6 Hz), 134.02, 131.06, 130.88, 129.08, 128.74 (t, *J* = 5.6 Hz), 128.70, 128.66, 127.55, 127.35 (t, *J* = 5.2 Hz), 126.70, 124.81, 122.83, 122.47, 122.02, 118.41 (t, *J* = 241.4 Hz); **IR** (KBr): ν_{max} 3095, 2929, 1647, 1460, 1245, 1128, 1049, 983, 727 cm^{-1}; **LC-MS** (ESI): m/z 312.3 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{18}H_{12}F_2NS^+$ 312.0653, found: 312.0652.

6-((4-chlorophenyl)difluoromethyl)phenanthridine (3la)



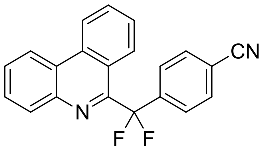
30mol % of $AgNO_3$ was used. The product (42 mg, 41% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). **Mp**: 120-122 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.63 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 7.7 Hz, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 8.18 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.77-7.68 (m, 2H), 7.67-7.59 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 2H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -87.47; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 152.71 (t, *J* = 29.1 Hz), 142.07, 136.32, 135.22 (t, *J* = 26.6 Hz), 134.04, 131.14, 130.87, 129.05, 128.64, 127.95 (t, *J* = 5.7 Hz), 127.61, 127.21 (t, *J* = 5.2 Hz), 124.73, 122.86, 122.54, 122.00, 120.48 (t, *J* = 244.2 Hz); **IR** (KBr): ν_{max} 3076, 2945, 1600, 1486, 1257, 1041, 812, 761, 722 cm^{-1}; **LC-MS** (ESI): m/z 340.3 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{20}H_{13}ClF_2N^+$ 340.0699, found: 340.0697.

6-(difluoro(4-(trifluoromethyl)phenyl)methyl)phenanthridine (3ma)



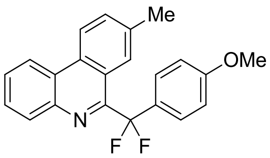
30mol % of $AgNO_3$ was used. The product (29 mg, 26% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). **Mp**: 110-112 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.69 (d, *J* = 8.3 Hz, 1H), 8.62-8.57 (m, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.14-8.09 (m, 1H), 7.91-7.85 (m, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.77-7.72 (m, 4H), 7.72-7. 67 (m, 1H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -62.77, -88.13; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 152.59 (t, *J* = 29.6 Hz), 142.07, 140.31 (t, *J* = 26.3 Hz), 134.17, 132.33 (q, *J* = 32.7 Hz), 131.23, 131.03, 129.12, 128.82, 127.78, 127.19 (t, *J* = 5.1 Hz), 127.15 (t, *J* = 5.6 Hz), 125.37 (q, *J* = 3.8 Hz), 124.81, 123.98 (q, *J* = 272.4 Hz), 122.93, 122.66, 122.08, 120.69 (t, *J* = 244.7 Hz); **IR** (KBr): ν_{max} 3071, 2926, 1640, 1516, 1325, 1125, 1041, 828, 756, 719 cm^{-1}; **LC-MS** (ESI): m/z 374.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{21}H_{13}F_5N^+$ 374.0963, found: 374.0969.

4-(difluoro(phenanthridin-6-yl)methyl)benzonitrile (3na)



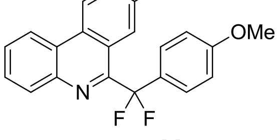
30mol % of $AgNO_3$ was used. The product (15 mg, 15% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). **Mp**: 209-211°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.68 (d, *J* = 8.3 Hz, 1H), 8.60-8.52 (m, 2H), 8.05-7.99 (m, 1H), 7.91-7.85 (m, 1H), 7.82-7.75 (m, 4H), 7.75-7.69 (m, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -88.42; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 152.27 (t, *J* = 30.3 Hz), 141.87, 141.17 (t, *J* = 26.3 Hz), 134.11, 132.02, 131.08, 129.09, 128.88, 127.80, 127.52 (t, *J* = 5.9 Hz), 127.01 (t, *J* = 5.5 Hz), 124.73, 122.81, 122.65, 122.05, 120.83 (t, *J* = 245.1 Hz), 118.40, 113.99; **IR** (KBr): ν_{max} 3071, 2944, 2228, 1609, 1247, 1027, 829, 759 cm^{-1}; **LC-MS** (ESI): m/z 331.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{21}H_{13}F_2N_2^+$ 331.1041, found: 331.1043.

6-(difluoro(4-methoxyphenyl)methyl)-8-methylphenanthridine (3ab)



The product (85 mg, 81% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 133-135 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.53-8.49 (m, 2H), 8.24 (dd, *J* = 7.9 1.5 Hz, 1H), 8.13 (s, 1H), 7.75-7.67 (m, 2H), 7.64-7.56 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.49 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.20; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 160.96, 152.98 (t, *J* = 28.2 Hz), 141.93, 137.44, 132.54, 131.92, 131.09, 129.12 (t, *J* = 26.7 Hz), 128.54, 128.36, 127.84 (t, *J* = 5.4 Hz), 126.88 (t, *J* = 4.8 Hz), 124.85, 123.21, 122.32, 121.83, 120.47 (t, *J* = 243.2 Hz), 113.77, 55.37, 22.04; **IR** (KBr): ν_{max} 3075, 2923, 1612, 1514, 1250, 1025, 821, 754 cm^{-1}; **LC-MS** (ESI): m/z 350.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{22}H_{18}F_2NO^+$ 350.1351, found: 350.1353.

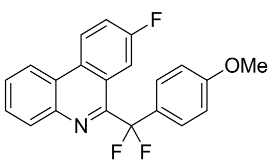
6-(difluoro(4-methoxyphenyl)methyl)-8-methoxyphenanthridine (3ac)



The product (88 mg, 80% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 182-184 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.49 (d, *J* = 9.1 Hz, 1H), 8.45-8.42 (m, 1H), 8.27-8.22 (m, 1H), 7.72-7.63 (m, 3H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.39 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.79 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -87.57; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 160.98 (t, *J* = 1.7 Hz), 158.35, 152.31 (t, *J* = 28.0 Hz), 141.45, 131.09, 129.00 (t, *J* = 26.7 Hz), 128.47, 128.41, 127.99, 127.71 (t, *J* = 5.4 Hz), 124.88, 124.25, 123.97, 121.59, 121.51, 120.28 (t, *J* = 243.4 Hz), 113.80, 107.45 (t, *J* = 4.8 Hz), 55.39, 55.35; **IR** (KBr): ν_{max} 3059, 2933, 1613, 1516, 1240, 1082, 831, 755, 636, 535 cm^{-1}; **MS** (EI): *m/z* (%) 157(100), 365(82); **LC-MS** (ESI): m/z 366.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for

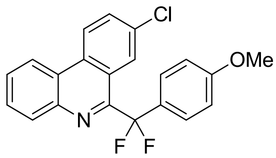
$C_{22}H_{18}F_2NO_2^+$ 366.1300, found: 366.1302.

6-(difluoro(4-methoxyphenyl)methyl)-8-fluorophenanthridine (3ad)



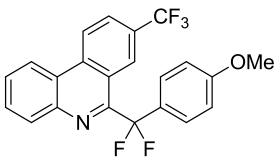
The product (91 mg, 86% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 132-134 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.61 (dd, *J* = 9.2, 5.4 Hz, 1H), 8.47 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.23 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.00 (dd, *J* = 10.4, 1.6 Hz, 1H), 7.78-7.69 (m, 2H), 7.59-7.52 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.86 (s, CF_2), -110.73- -110.80 (m, F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.11 (t, *J* = 1.8 Hz), 161.09 (d, *J* = 248.5 Hz), 152.58 (td, *J* = 29.1, 4.1 Hz), 141.90, 131.27, 130.73 (d, *J* = 1.7 Hz), 128.91 (d, *J* = 3.8 Hz), 128.51 (t, *J* = 26.6 Hz), 127.83 (t, *J* = 5.5 Hz), 124.98 (d, *J* = 8.7 Hz), 124.31, 124.14 (d, *J* = 8.6 Hz), 121.78, 120.32 (t, *J* = 243.3 Hz), 120.25, 120.05, 113.89, 112.29 (dt, *J* = 23.1, 5.2 Hz), 55.41; **IR** (KBr): ν_{max} 3077, 2945, 1614, 1516, 1253, 1033, 823, 761 cm^{-1}; **LC-MS** (ESI): m/z 354.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{21}H_{15}F_3NO^+$ 354.1100, found: 354.1103.

8-chloro-6-(difluoro(4-methoxyphenyl)methyl)phenanthridine (3ae)



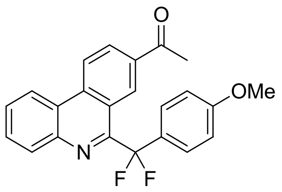
The product (93 mg, 84% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 180-181 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.57 (d, *J* = 8.9 Hz, 1H), 8.51 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.36 (d, *J* = 1.8 Hz, 1H), 8.22 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.80-7.71 (m, 3H), 7.56 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.46; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.12, 152.42 (t, *J* = 29.3 Hz), 142.16, 133.58, 132.44, 131.44, 131.34, 129.38, 128.95, 128.53 (t, *J* = 26.6 Hz), 127.86 (t, *J* = 5.4 Hz), 126.84 (t, *J* = 5.4 Hz), 124.19, 123.88, 121.92, 120.38 (t, *J* = 243.7 Hz), 113.90, 55.45; **IR** (KBr): ν_{max} 377, 2923, 1612, 1513, 1250, 1029, 820, 761, 729 cm^{-1}; **LC-MS** (ESI): m/z 370.3 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{21}H_{15}ClF_2NO^+$ 370.0805, found: 370.0811.

6-(difluoro(4-methoxyphenyl)methyl)-8-(trifluoromethyl)phenanthridine (3af)



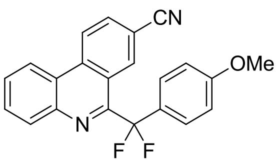
The product (85 mg, 70% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 8:1). **Mp**: 151-153 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.77-8.71 (m, 2H), 8.56 (d, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.85-7.74 (m, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -62.48, -86.51; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.17, 153.43 (t, *J* = 29.7 Hz), 142.87, 136.18, 131.43, 130.25, 129.39 (q, *J* = 32.9 Hz), 129.12, 128.43 (t, *J* = 26.5 Hz), 127.80 (t, *J* = 5.6 Hz), 126.65 (q, *J* = 3.2 Hz), 125.07 (q, *J* = 4.9 Hz), 123.81, 123.63, 122.86(q, *J* = 273.4 Hz), 122.40, 122.32, 120.47 (t, *J* = 243.5 Hz), 113.92, 55.45; **IR** (KBr): ν_{max} 3073, 2963, 1618, 1513, 1310, 1248, 1175, 1096, 835, 768, 726 cm^{-1}; **LC-MS** (ESI): m/z 404.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{22}H_{15}F_5NO^+$ 404.1068, found: 404.1071.

1-(6-(difluoro(4-methoxyphenyl)methyl)phenanthridin-8-yl)ethan-1-one (3ag)



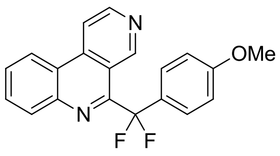
The product (68 mg, 60% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). **Mp**: 173-175 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.94 (s, 1H), 8.65 (d, J = 8.7 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.7 Hz, 1H), 8.27 (d, J = 8.2 Hz, 1H), 7.82 (t, J = 7.6 Hz, 1H), 7.76 (t, J = 8.3 Hz, 1H), 7.62 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 2.64 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.70; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 197.13, 161.14, 153.74 (t, J = 28.8 Hz), 143.06, 136.97, 135.33, 131.32, 130.27, 128.97(t, J = 4.6 Hz), 128.93, 128.92, 128.74 (t, J = 26.5 Hz), 127.67 (t, J = 5.5 Hz), 124.05, 123.06, 122.65, 122.38, 120.20, 113.95, 55.43, 26.60; **IR** (KBr): ν_{max} 2926, 1685 1611, 1514, 1250, 1060, 1015, 938, 768, 579 cm^{-1}; **LC-MS** (ESI): m/z 378.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{23}H_{18}F_2NO_2^+$ 378.1300, found: 378.1295.

6-(difluoro(4-methoxyphenyl)methyl)phenanthridine-8-carbonitrile (3ah)



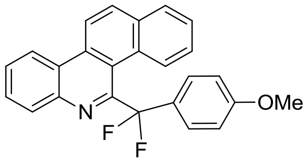
The product (70 mg, 65% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 4:1). **Mp**: 168-170 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.71 (s, 1H), 8.68 (d, J = 8.7 Hz, 1H), 8.52 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.83 (t, J = 7.6 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -85.76; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.25 , 152.71 (t, J = 29.9 Hz), 143.00 , 136.38 , 132.87 (t, J = 5.5 Hz), 131.88 , 131.46 , 130.81 , 129.37 , 128.00 (t, J = 26.4 Hz), 127.80 (t, J = 5.5 Hz), 123.81 , 123.38 , 122.52 , 122.36 , 120.32 (t, J = 243.4 Hz), 118.47 , 113.98 , 111.14 , 55.44; **IR** (KBr): ν_{max} 3075, 2940, 2226, 1610, 1511, 1254, 1086, 1016, 835, 766 cm^{-1}; **LC-MS** (ESI): m/z 361.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{22}H_{15}F_2N_2O^+$ 361.1147, found: 361.1143.

5-(difluoro(4-methoxyphenyl)methyl)benzo[c][2,7]naphthyridine (3ai)



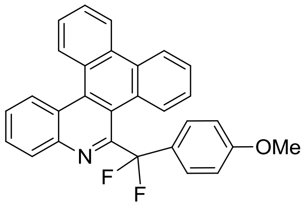
The product (50 mg, 51% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 6:1). **Mp**: 143-145 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 9.71 (s, 1H), 8.87 (d, J = 5.7 Hz, 1H), 8.51 (d, J = 8.2 Hz, 1H), 8.35 (d, J = 5.6 Hz, 1H), 8.24 (dd, J = 8.2, 1.3 Hz, 1H), 7.87-7.82 (m, 1H), 7.78-7.73 (m, 1H), 7.57 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.09; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.12, 153.22 (t, J = 30.2 Hz), 151.09 (t, J = 6.4 Hz), 148.32, 143.28, 138.60, 131.19, 131.17, 129.00, 128.20 (t, J = 26.5 Hz), 127.72 (t, J = 5.5 Hz), 122.52, 122.43, 119.98 (t, J = 243.7 Hz), 118.11, 115.53, 113.88, 55.33; **IR** (KBr): ν_{max} 3065, 2923, 1606, 1513, 1248, 1072, 841, 755, 728 cm^{-1}; **LC-MS** (ESI): m/z 337.4 $[M+1]^+$; **HRMS** (ESI-TOF) calcd. for $C_{20}H_{15}F_2N_2O^+$ 337.1147, found: 337.1150.

5-(difluoro(4-methoxyphenyl)methyl)benzo[i]phenanthridine (3aj)



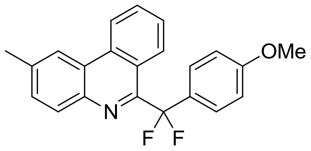
The product (60 mg, 52% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). **Mp**: 174-176 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) ***major***: δ ppm 8.66 (d, *J* = 8.6 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.9 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.82-7.75 (m, 3H), 7.75-7.70 (m, 1H), 7.58 (t, *J* = 7.3 Hz, 1H),7.50-7.44 (m, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) ***major***: δ ppm -79.52, ***minor***: 86.52; **^{13}C NMR** (125 MHz, $CDCl_3$) ***major***: δ ppm 161.01, 151.83 (t, *J* = 29.3 Hz), 142.72, 134.84, 132.90, 132.63, 130.30, 130.08 (t, *J* = 27.3 Hz), 129.73 (t, *J* = 7.6 Hz), 129.20, 129.09, 128.56 (t, *J* = 5.0 Hz), 128.27, 128.07, 126.98, 126.15, 124.22, 122.59, 121.31, 121.31 (t, *J* = 242.8 Hz), 119.77, 113.89, 55.44; **IR** (KBr): ν_{max} 2908, 1607, 1511, 1245, 1032, 821, 756 cm^{-1}; **LC-MS** (ESI): m/z 386.4 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{25}H_{18}F_2NO^+$ 386.1351, found: 386.1353.

5-(difluoro(4-methoxyphenyl)methyl)dibenzo[i,k]phenanthridine (3ak)



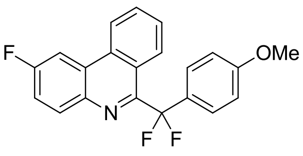
The product (72 mg, 55% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). **Mp**: 197-199 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.71 (d, *J* = 8.1 Hz, 1H), 8.68 (d, *J* = 8.6 Hz, 1H), 8.64 (d, *J* = 8.3 Hz, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 8.35 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.78-7.72 (m, 2H), 7.69-7.59 (m, 3H), 7.47-7.42 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -79.80; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 160.95, 151.17 (t, *J* = 29.7 Hz), 144.53, 136.26, 132.72, 130.25 (t, *J* = 6.2 Hz), 130.15 (t, *J* = 27.4 Hz), 130.05, 129.88, 129.36, 129.11, 128.81, 128.55, 128.54 (t, *J* = 5.2 Hz), 127.95, 127.70, 127.63, 127.31, 127.11, 126.42, 123.96, 123.50, 123.04, 121.81, 120.89 (t, *J* = 244.2 Hz), 113.80, 55.44; **IR** (KBr): ν_{max} 3064, 2923, 1607, 1511, 1246, 1036, 767, 730 cm^{-1}; **LC-MS** (ESI): m/z 436.5 [M+1]$^+$; **HRMS** (ESI-TOF) calcd. for $C_{29}H_{20}F_2NO^+$ 436.1507, found: 436.1506.

6-(difluoro(4-methoxyphenyl)methyl)-2-methylphenanthridine (3al)



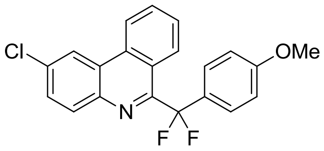
The product (89 mg, 85% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 114-116 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.66 (d, *J* = 9.1 Hz, 1H), 8.38 (s, 1H), 8.29 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.85-7.76 (m, 1H), 7.63-7.56 (m, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.65 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.00; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 160.92, 152.25 (t, *J* = 28.1 Hz), 140.50, 138.55, 133.64, 130.79, 130.71, 130.43, 129.12 (t, *J* = 26.7 Hz), 127.78 (t, *J* = 5.4 Hz), 127.36 (t, *J* = 4.7 Hz), 127.24, 124.55, 123.03, 122.36, 121.58, 120.35 (t, *J* = 243.6 Hz), 113.74, 55.29, 22.10; **IR** (KBr): ν_{max} 3063, 2916, 1612, 1514, 1250, 1027, 892, 825, 771 cm^{-1}; **MS** (EI): *m/z* (%) 328(100), 157(76), 349(75); **HRMS** (ESI-TOF) calcd. for $C_{22}H_{18}F_2NO^+$ 350.1351, found: 350.1354.

6-(difluoro(4-methoxyphenyl)methyl)-2-fluorophenanthridine (3am)



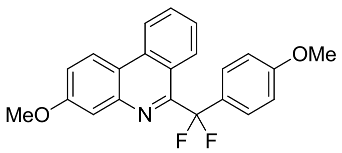
The product (87 mg, 82% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 134-136 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.51 (d, *J* = 8.3 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.23 (dd, *J* = 9.0, 5.6 Hz, 1H), 8.16 (dd, *J* = 10.0, 2.7 Hz, 1H), 7.85-7.79 (m, 1H), 7.66-7.61 (m, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.52-7.46 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.27, -110.35- -110.46 (m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 162.31 (d, *J* = 249.1 Hz), 161.06, 152.70 (t, *J* = 28.3 Hz), 139.09, 133.55 (d, *J* = 9.7 Hz), 133.46 (d, *J* = 4.2 Hz), 130.83, 128.93 (t, *J* = 26.6 Hz), 128.17, 127.85 (t, *J* = 5.5 Hz), 127.66, 126.33 (d, *J* = 9.3 Hz), 123.10, 122.65, 120.38 (t, *J* = 243.2 Hz), 118.04 (d, *J* = 24.4 Hz), 113.84, 107.09 (d, *J* = 23.5 Hz), 55.43; **IR** (KBr): ν_{max} 2932, 1615, 1451, 1246, 1174, 1029, 896, 828, 772, 678 cm^{-1}; **MS** (EI): *m/z* (%) 157(100), 332(79), 353(52); **HRMS** (ESI-TOF) calcd. for $C_{21}H_{15}F_3NO^+$ 354.1100, found: 354.1098.

2-chloro-6-(difluoro(4-methoxyphenyl)methyl)phenanthridine (3an)



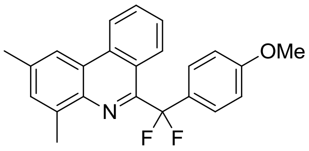
The product (78 mg, 70% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 141-142 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.58-8.46 (m, 2H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 9.2 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.35; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.07, 153.64 (t, *J* = 28.6 Hz), 140.64, 134.56, 133.02, 132.64, 131.06, 129.62, 128.81 (t, *J* = 26.6 Hz), 128.18, 127.83 (t, *J* = 5.4 Hz), 127.66 (t, *J* = 4.9 Hz), 125.87, 123.21, 122.50, 121.75, 120.30 (t, *J* = 243.7 Hz), 113.86, 55.43; **IR** (KBr): ν_{max} 3074, 2926, 1610, 1515, 1253, 1030, 822, 763, 679 cm^{-1}; **MS** (EI): *m/z* (%) 157(100), 348(54), 369(44); **HRMS** (ESI-TOF) calcd. for $C_{21}H_{15}ClF_2NO^+$ 370.0805, found: 370.0802.

6-(difluoro(4-methoxyphenyl)methyl)-3-methoxyphenanthridine (3ao)



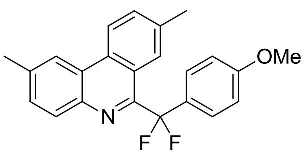
The product (85 mg, 78% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 6:1). **Mp**: 173-174 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.54 (d, *J* = 8.4 Hz, 1H), 8.45 (d, *J* = 9.0 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 2.7 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.50 (t, *J* = 8.3 Hz, 1H), 7.36 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.98 (s, 3H), 3.80 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.18; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.02, 160.42, 153.73 (t, *J* = 27.6 Hz), 143.95, 134.27, 130.79, 129.16 (t, *J* = 26.6 Hz), 127.79 (t, *J* = 5.3 Hz), 127.52 (t, *J* = 4.7 Hz), 126.39, 123.22, 122.13, 121.99, 120.14 (t, *J* = 243.1 Hz), 119.87, 118.89, 113.87, 110.62, 55.83, 55.41; **IR** (KBr): ν_{max} 2931, 1611, 1477, 1254, 1171, 1026, 837, 770, 678 cm^{-1}; **MS** (EI): *m/z* (%) 344(100), 157(97), 365(84); **HRMS** (ESI-TOF) calcd. for $C_{22}H_{18}F_2NO_2^+$ 366.1300, found: 366.1296.

6-(difluoro(4-methoxyphenyl)methyl)-2,4-dimethylphenanthridine (3ap)



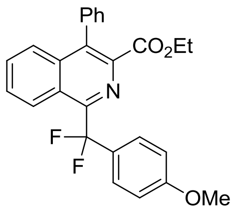
The product (88 mg, 81% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 120-122 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.62 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 8.5 Hz, 1H), 8.17 (s, 1H), 7.82-7.76 (m, 1H), 7.69-7.60 (m, 3H), 7.41 (s, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H), 2.61 (s, 3H), 2.57 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.15; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 160.70, 150.76 (t, *J* = 30.8 Hz), 139.04, 138.71, 137.99, 133.94, 131.29, 130.10, 129.30 (t, *J* = 26.4 Hz), 128.15 (t, *J* = 5.8 Hz), 127.19 (t, *J* = 5.2 Hz), 127.05, 124.35, 122.87, 122.59, 121.84 (t, *J* = 242.5 Hz), 119.25, 113.29, 55.31, 22.09, 17.72; **IR** (KBr): ν_{max} 2917, 1613, 1450, 1250, 1168, 1029, 821, 771, 627 cm^{-1}; **MS** (EI): *m/z* (%) 157(100), 363(99), 328(98); **HRMS** (ESI-TOF) calcd. for $C_{23}H_{20}F_2NO^+$ 364.1507, found: 364.1511.

6-(difluoro(4-methoxyphenyl)methyl)-2,8-dimethylphenanthridine (3aq)



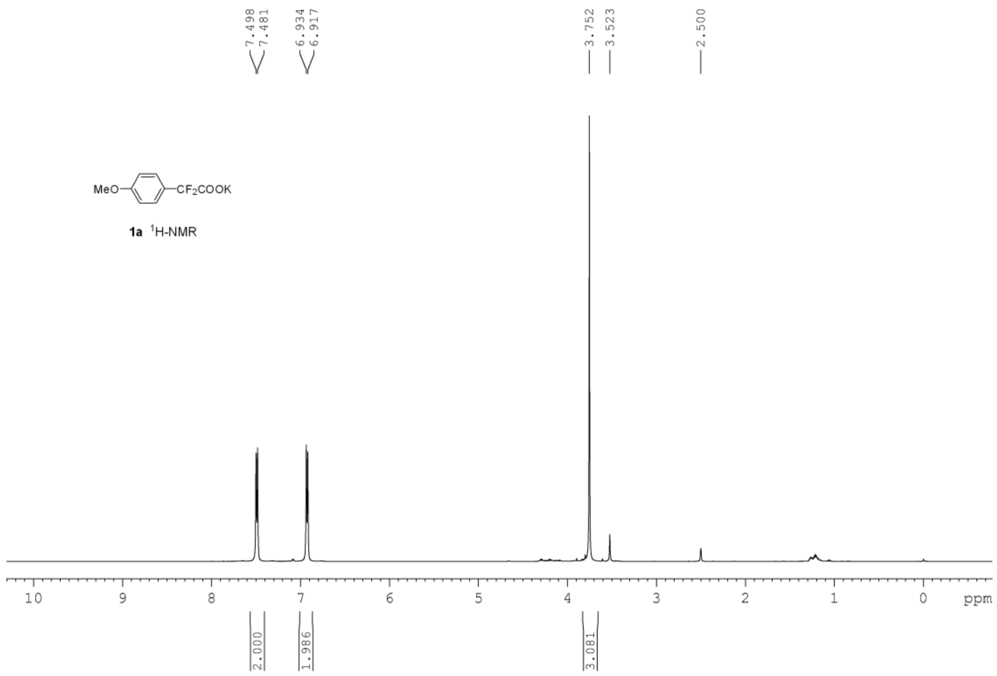
The product (83 mg, 76% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1). **Mp**: 150-152 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.50 (d, *J* = 8.5 Hz, 1H), 8.30 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H), 7.62-7.53 (m, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.62 (s, 3H), 2.49 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.09; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 160.91, 151.99 (t, *J* = 28.1 Hz), 140.27, 138.46, 137.23, 132.29, 131.63, 130.82, 130.29, 129.26 (t, *J* = 26.7 Hz), 127.85 (t, *J* = 5.3 Hz), 126.80 (t, *J* = 4.8 Hz), 124.70, 123.30, 122.28, 121.44, 120.52 (t, *J* = 242.9 Hz), 113.74, 55.37, 22.17, 22.03; **IR** (KBr): ν_{max} 3013, 2912, 1613, 1514, 1452, 1248, 1064, 829, 776, 560 cm^{-1}; **LC-MS** (ESI): m/z 364.4 [M+1]$^{+}$; **HRMS** (ESI-TOF) calcd. for $C_{23}H_{20}F_2NO^+$ 364.1507, found: 364.1502.

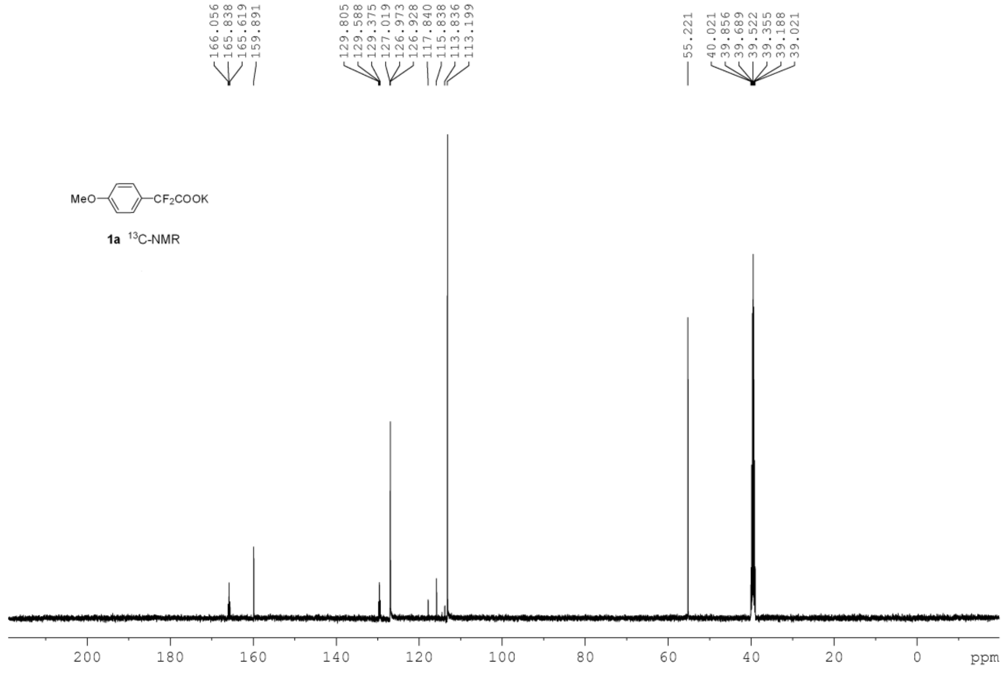
ethyl 1-(difluoro(4-methoxyphenyl)methyl)-4-phenylisoquinoline-3-carboxylate (3ar)

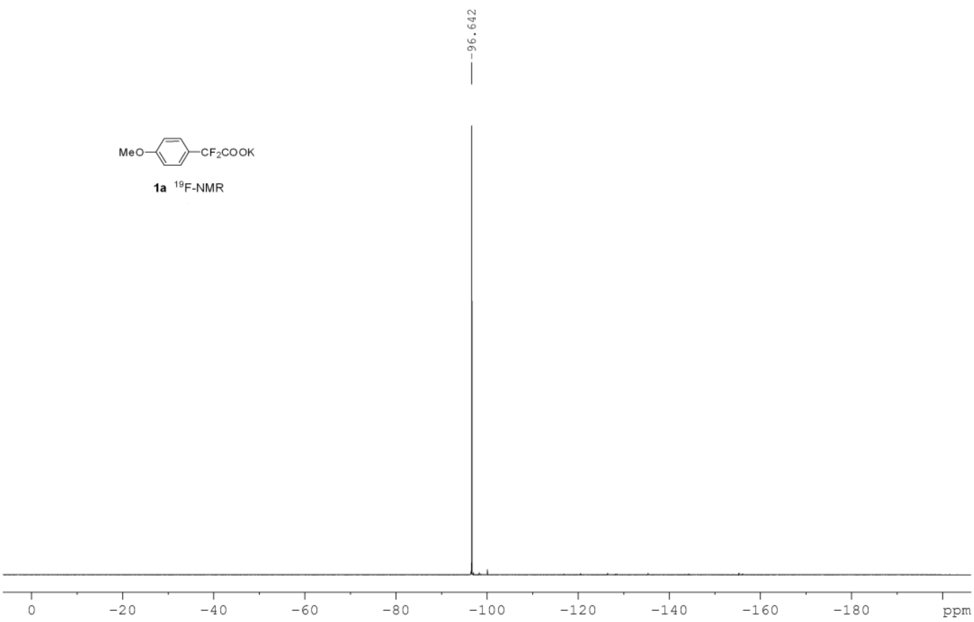


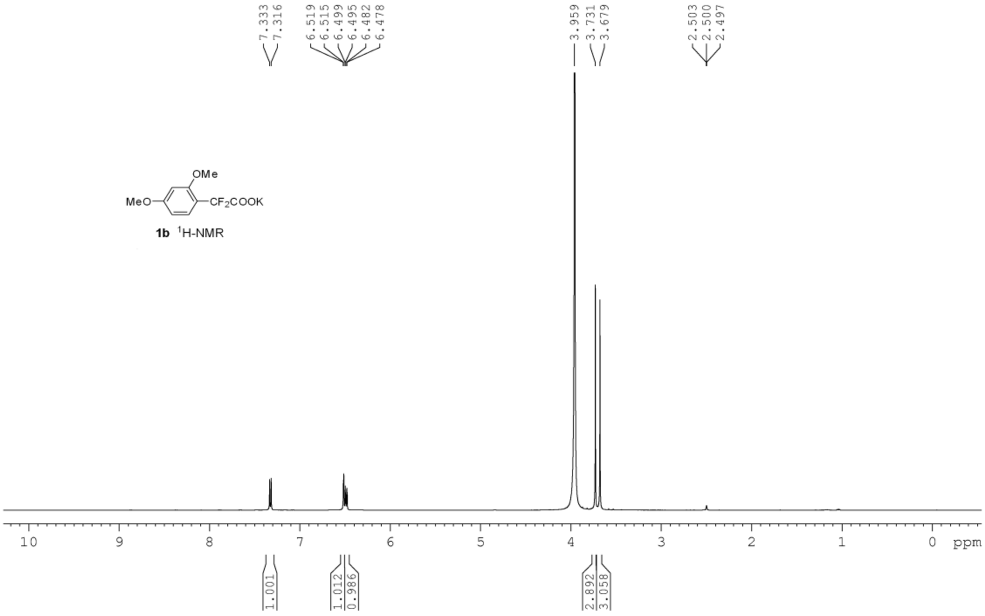
The product (94 mg, 72% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 4:1). **Mp**: 134-136 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.42-8.36 (m, 1H), 7.73-7.68 (m, 1H), 7.65-7.58 (m, 4H), 7.53-7.48 (m, 3H), 7.40-7.35 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -85.81; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 166.78, 160.93, 152.71 (t, *J* = 29.3 Hz), 140.83, 136.87, 135.56, 135.00, 130.69, 129.78,128.96 (t, *J* = 26.7 Hz), 128.77, 128.28, 127.79, 127.03, 126.12, 125.61, 120.12 (t, *J* = 243.6 Hz), 113.69, 61.30, 55.26, 13.61; **IR** (KBr): ν_{max} 3050, 2924, 1730, 1610, 1508, 1245, 1109, 1017, 831, 766, 698 cm^{-1}; **LC-MS** (ESI): m/z 434.5 [M+1]$^{+}$; **HRMS** (ESI-TOF) calcd. for $C_{26}H_{22}F_2NO_3^+$ 434.1562, found: 434.1567.

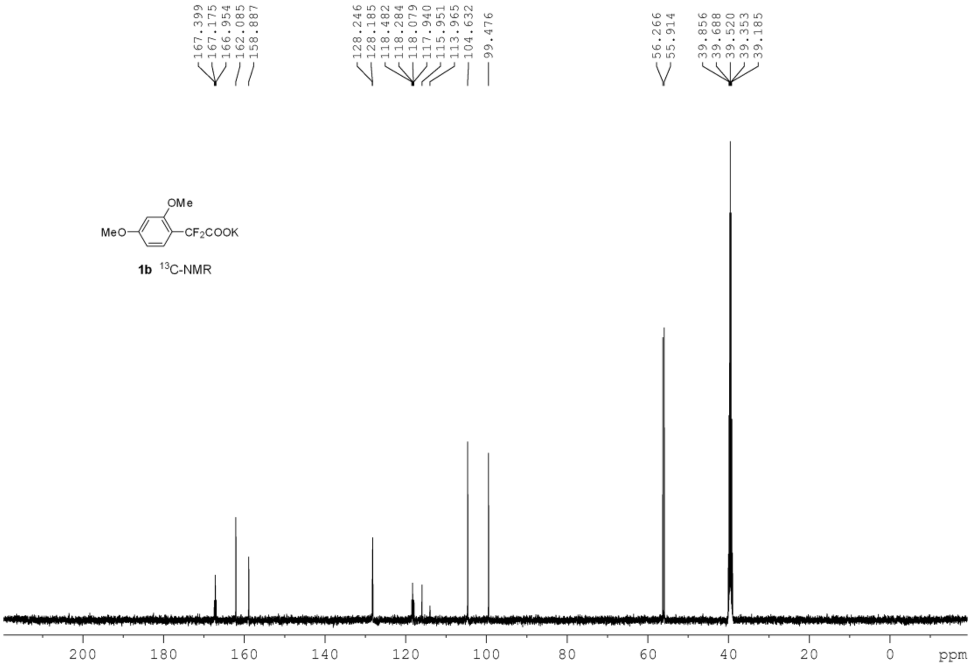
10. NMR spectra for potassium α,α-difluoroaryl acetate

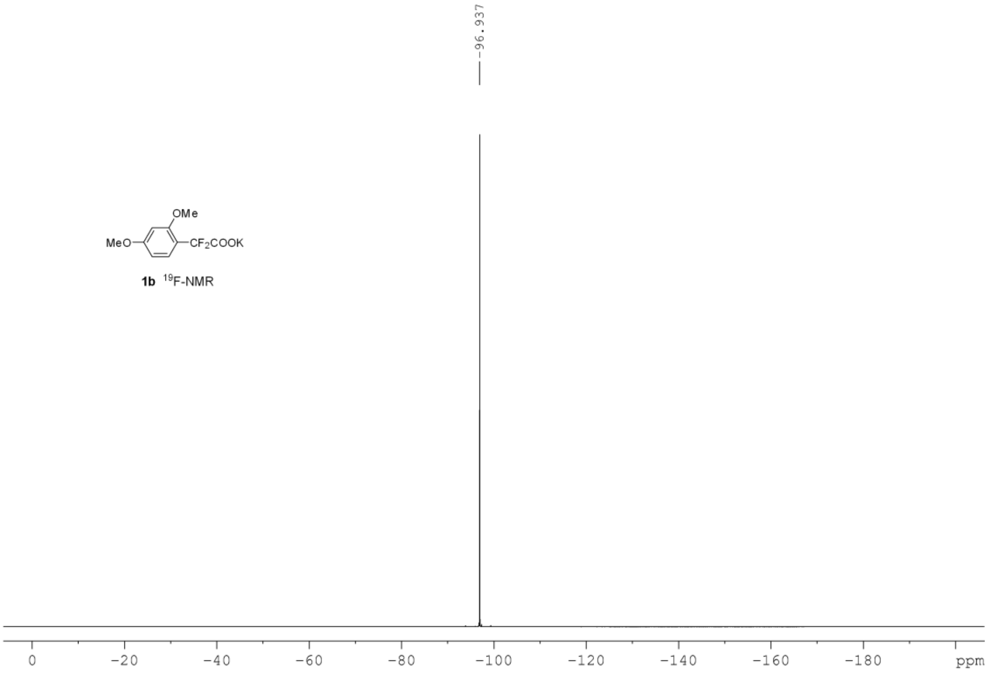


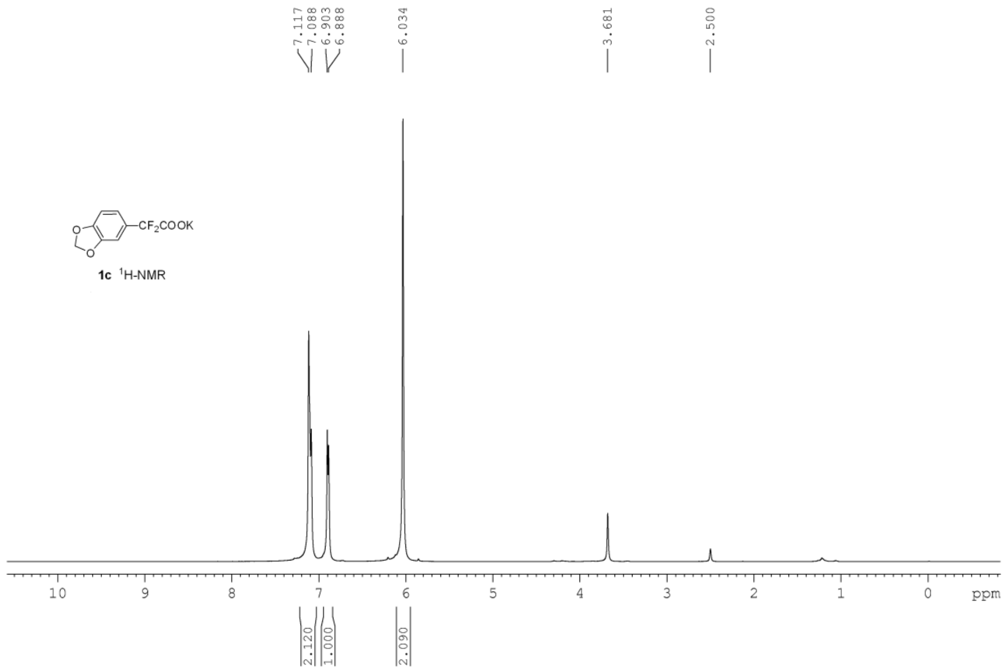


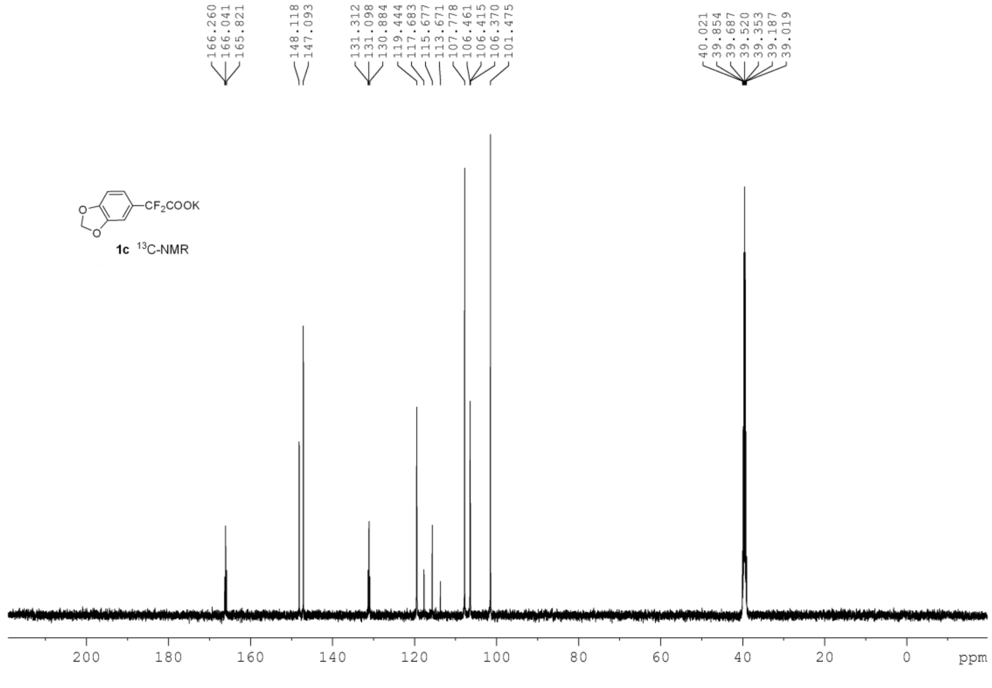

-96.642
MeO
CF2COOK
1a 19F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

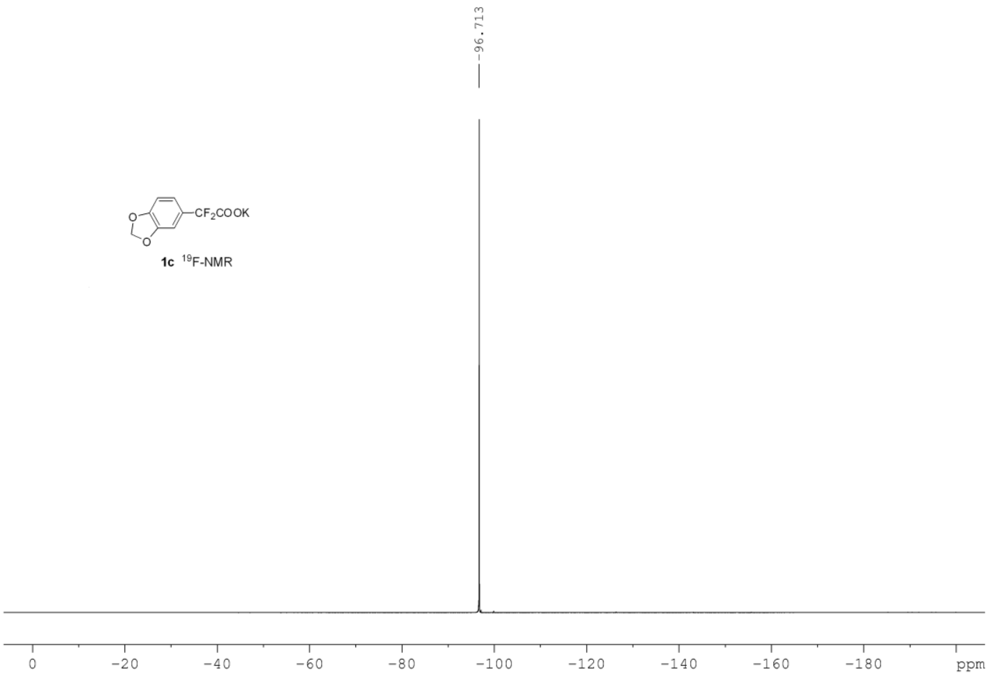

7.333
7.316
6.519
6.515
6.499
6.495
6.482
6.478
3.959
3.731
3.679
2.503
2.500
2.497
OMe
MeO
CF2COOK
1b 1H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm
1.001
1.012
0.986
2.892
3.058


167.399
167.175
166.954
162.085
158.887
128.246
128.185
118.482
118.284
118.079
117.940
115.951
113.965
104.632
99.476
56.266
55.914
39.856
39.688
39.520
39.353
39.185
OMe
MeO
CF2COOK
1b 13C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

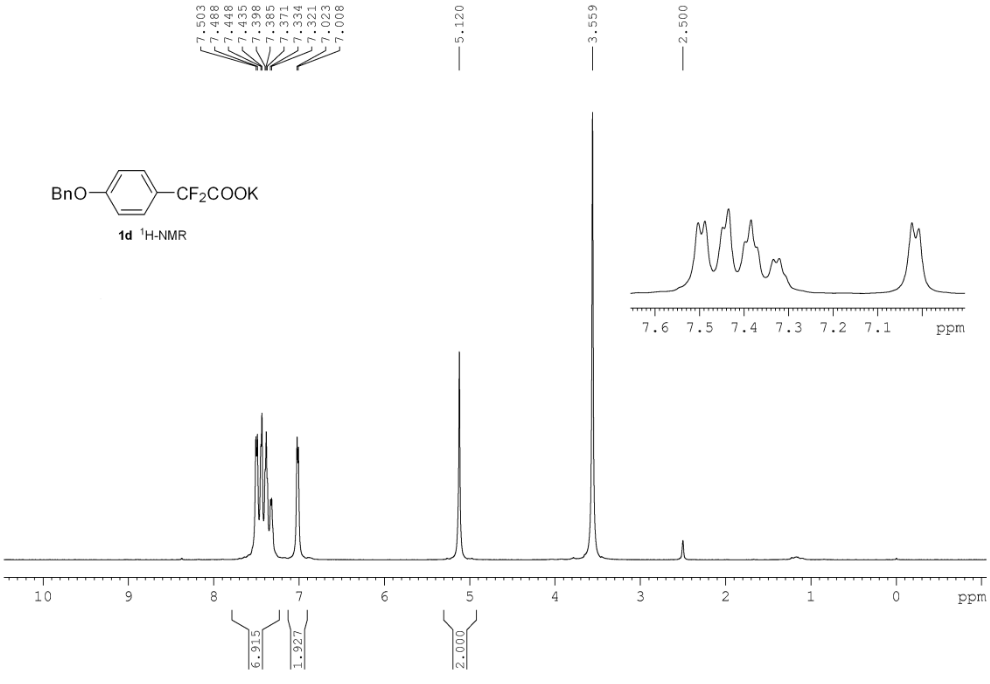

-96.937
OMe
MeO
CF2COOK
1b 19F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


7.117
7.088
6.903
6.888
6.034
3.681
2.500
CF2COOK
1c ¹H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm
2.120
1.000
2.090

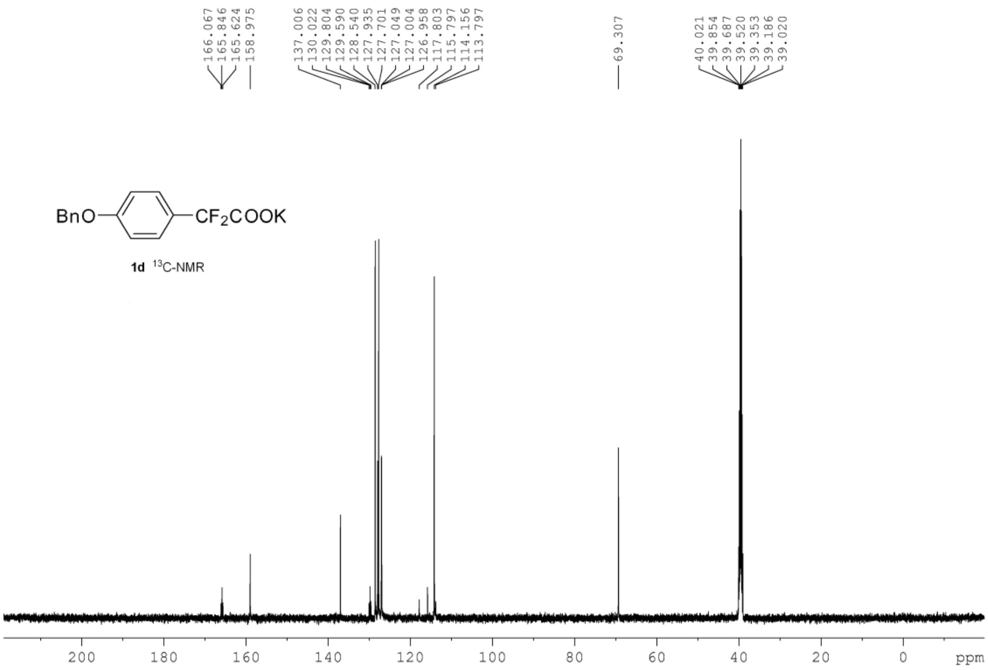

166.260
166.041
165.821
148.118
147.093
131.312
131.098
130.884
119.444
117.683
115.677
113.671
107.778
106.461
106.415
106.370
101.475
40.021
39.854
39.687
39.520
39.353
39.187
39.019
CF2COOK
1c ¹³C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

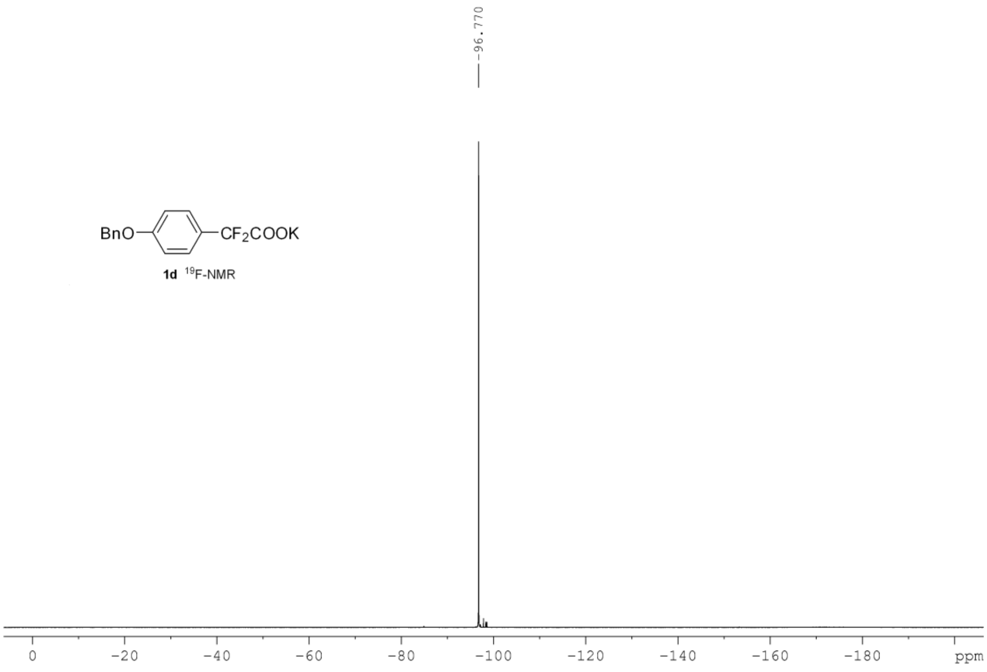


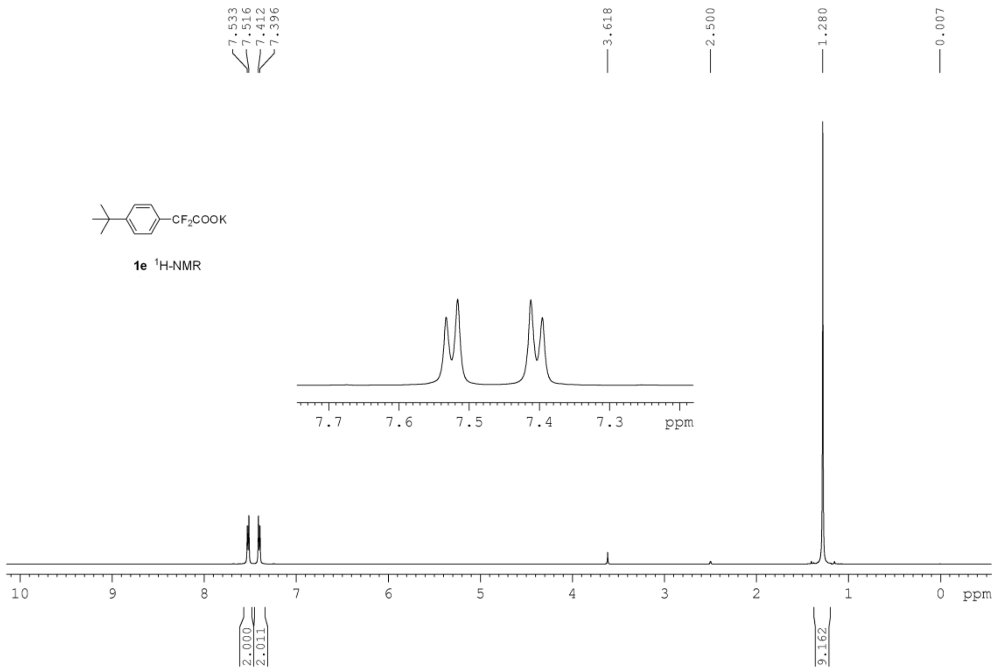
1c ^{19}F-NMR



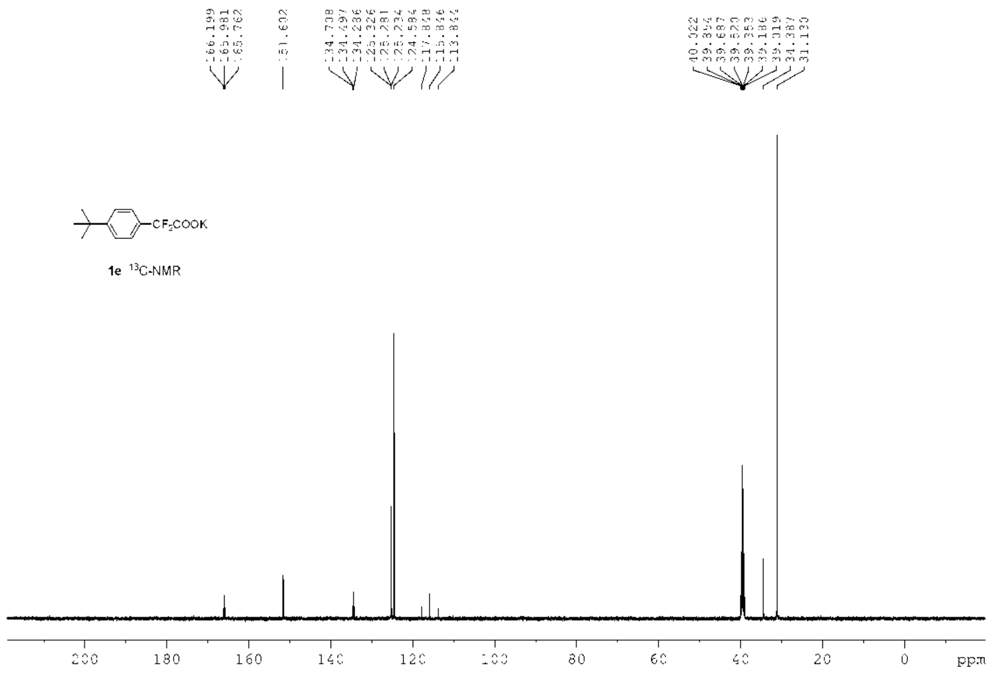
1d ^{1}H-NMR


166.067
165.846
165.624
158.975
137.006
130.022
129.804
129.590
128.540
127.935
127.701
127.049
127.004
126.958
117.803
115.797
114.156
113.797
69.307
40.021
39.854
39.687
39.520
39.353
39.186
39.020
BnO
CF2COOK
1d 13C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

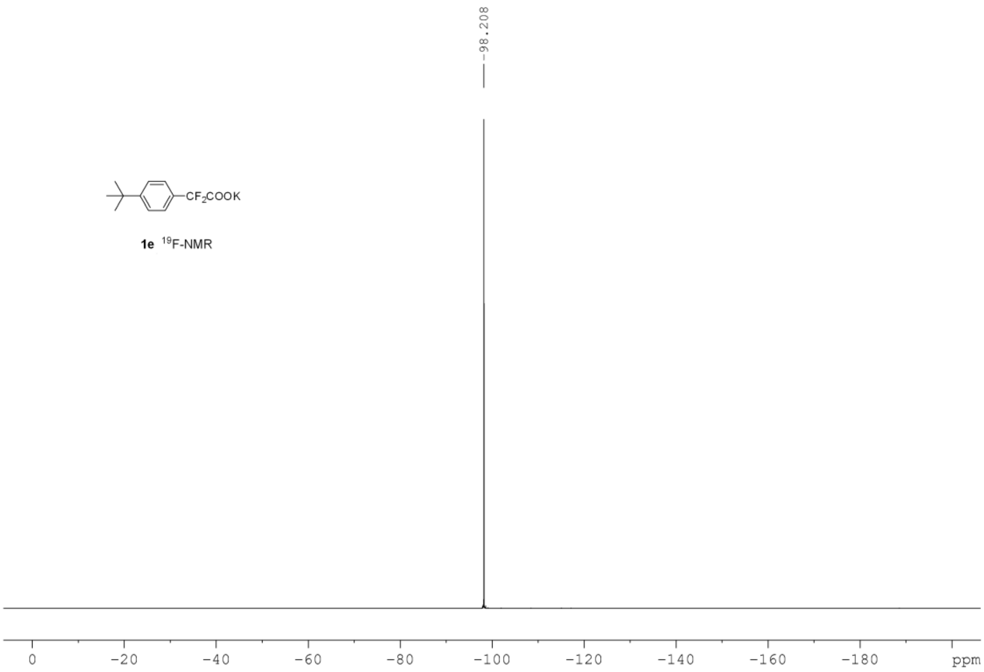

-96.770
BnO
CF2COOK
1d 19F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

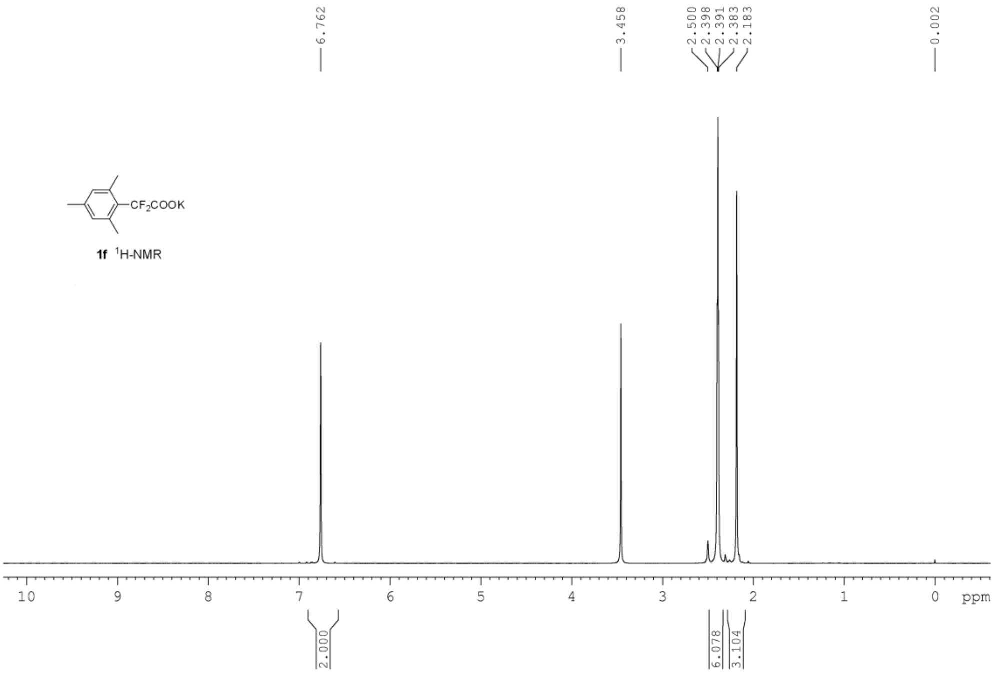


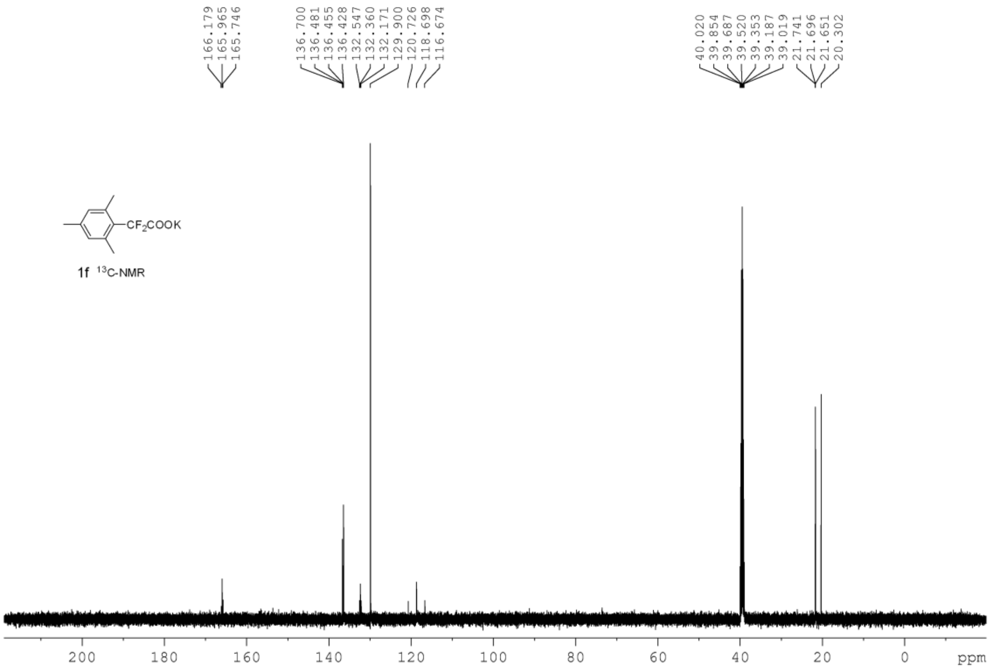
1e ^{1}H-NMR

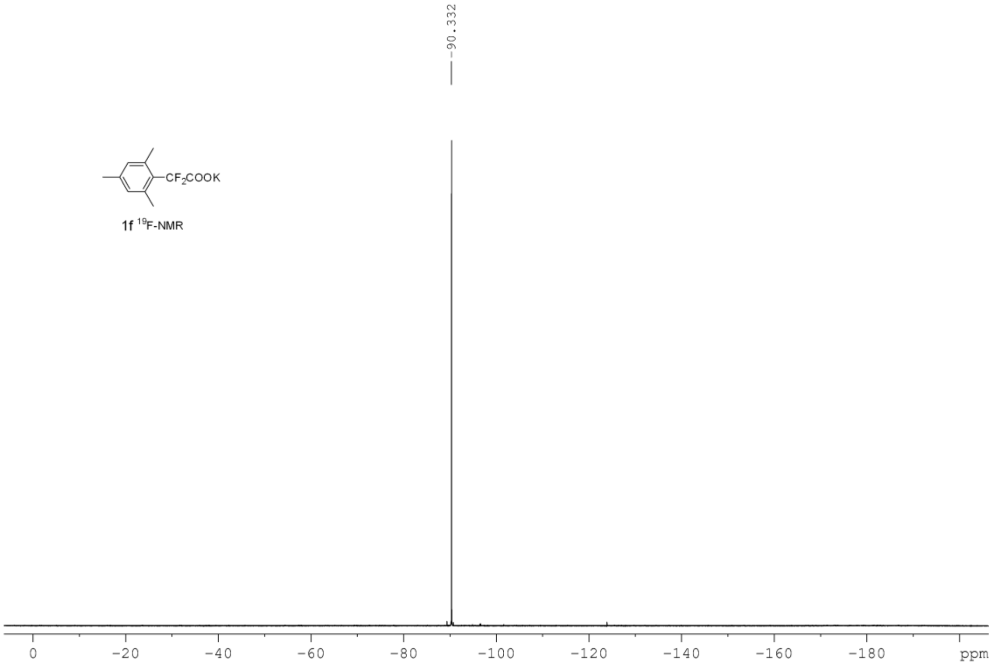


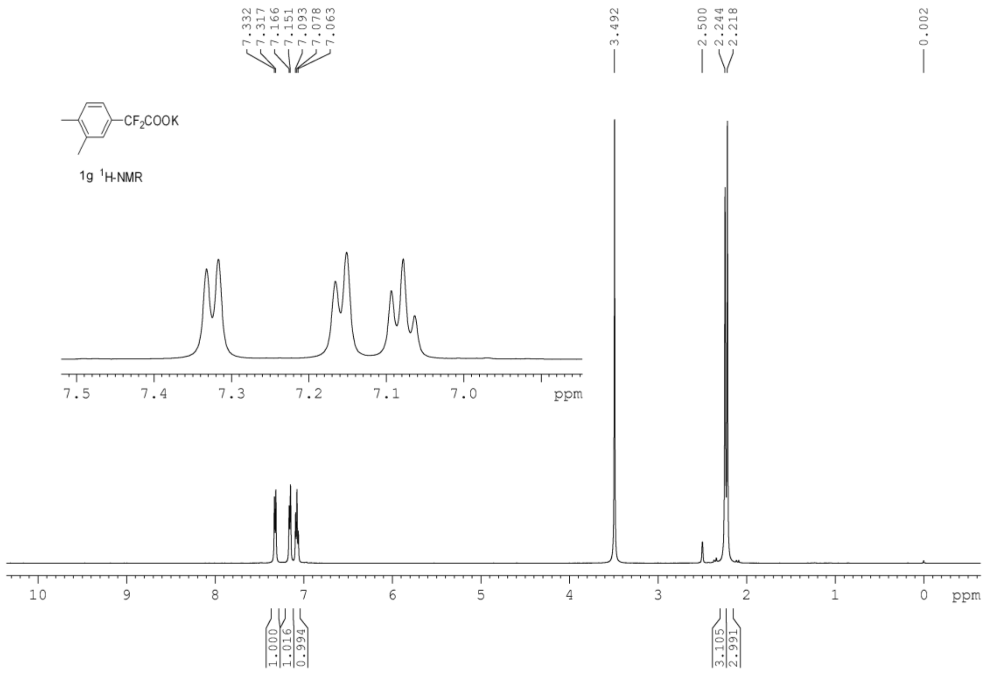
1e ^{13}C-NMR

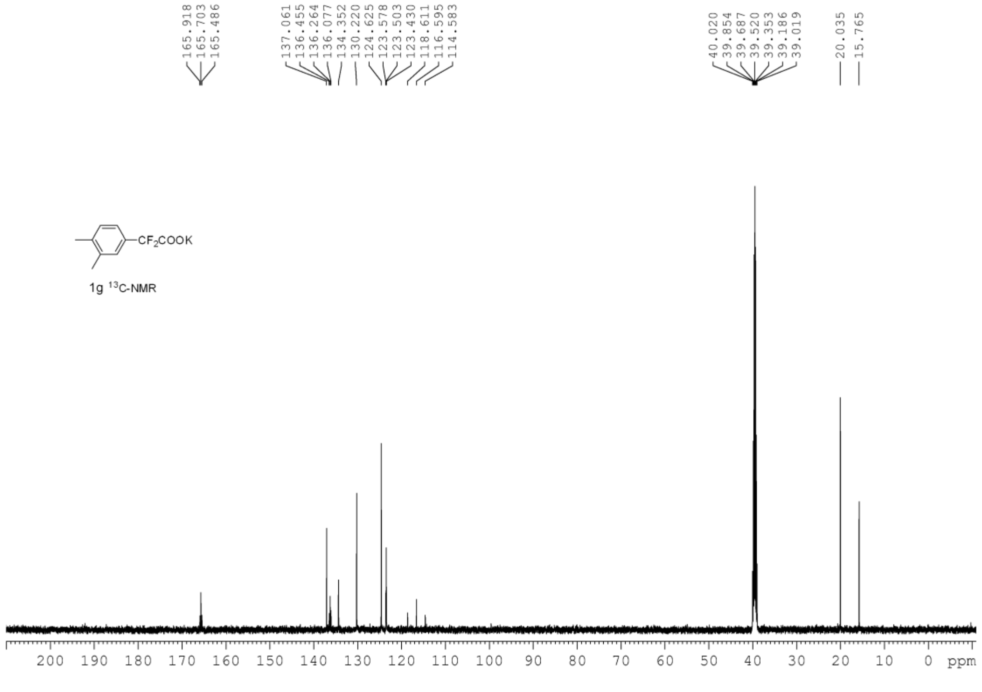

1e ^{19}F-NMR

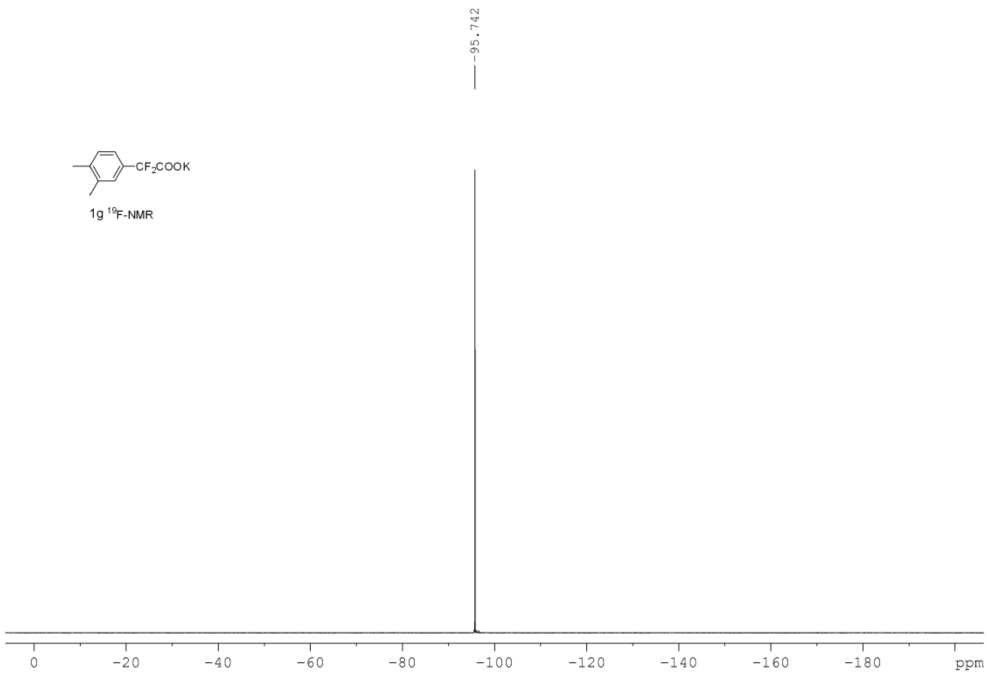

1f ^{1}H-NMR


166.179
165.965
165.746
136.700
136.481
136.455
136.428
132.547
132.360
132.171
129.900
120.726
118.698
116.674
40.020
39.854
39.687
39.520
39.353
39.187
39.019
21.741
21.696
21.651
20.302
CF2COOK
1f 13C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm


-90.332
CF2COOK
1f 19F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


7.332
7.317
7.166
7.151
7.093
7.078
7.063
3.492
2.500
2.244
2.218
0.002
CF2COOK
1g 1H-NMR
7.5
7.4
7.3
7.2
7.1
7.0
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.016
0.994
3.105
2.991


165.918
165.703
165.486
137.061
136.455
136.264
136.077
134.352
130.220
124.625
123.578
123.503
123.430
118.611
116.595
114.583
40.020
39.854
39.687
39.520
39.353
39.186
39.019
20.035
15.765
CF2COOK
1g 13C-NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-95.742
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1g 19F-NMR
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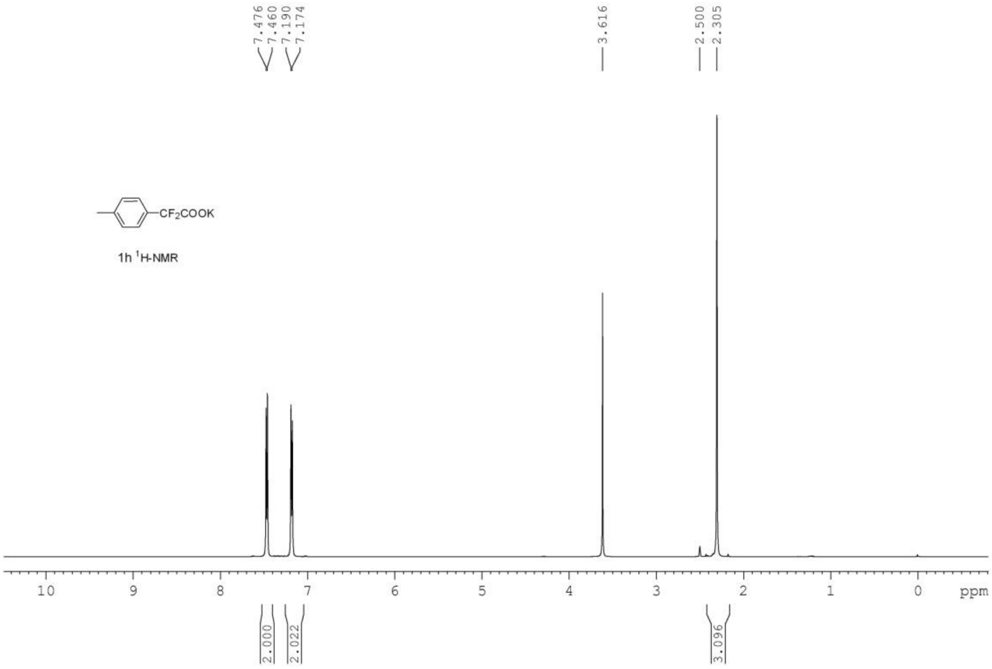
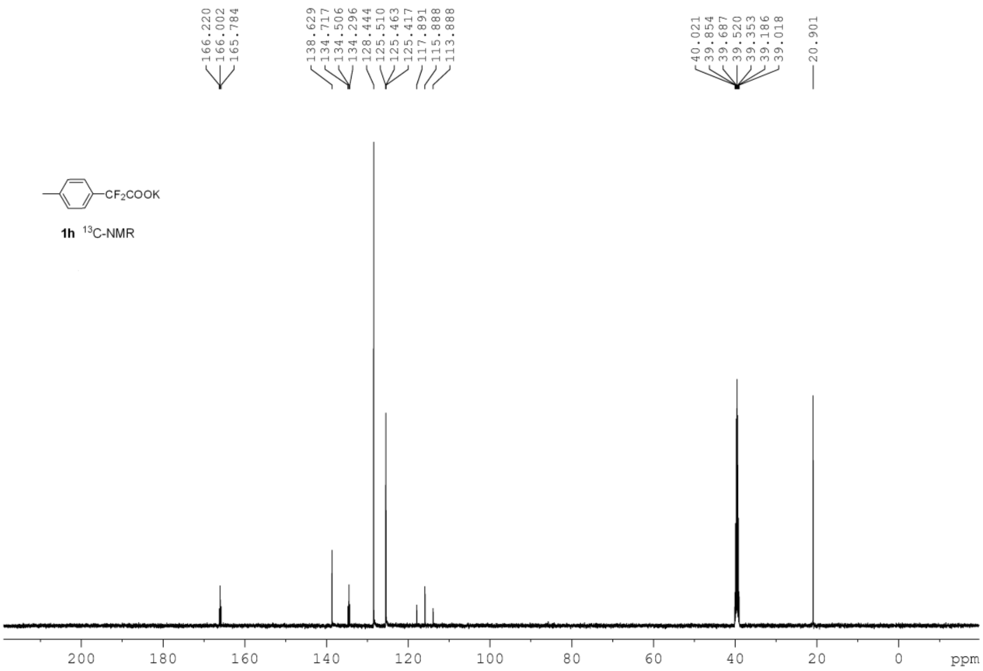
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


7.476
7.460
7.190
7.174
3.616
2.500
2.305
CF2COOK
1h 1H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.022
3.096


166.220
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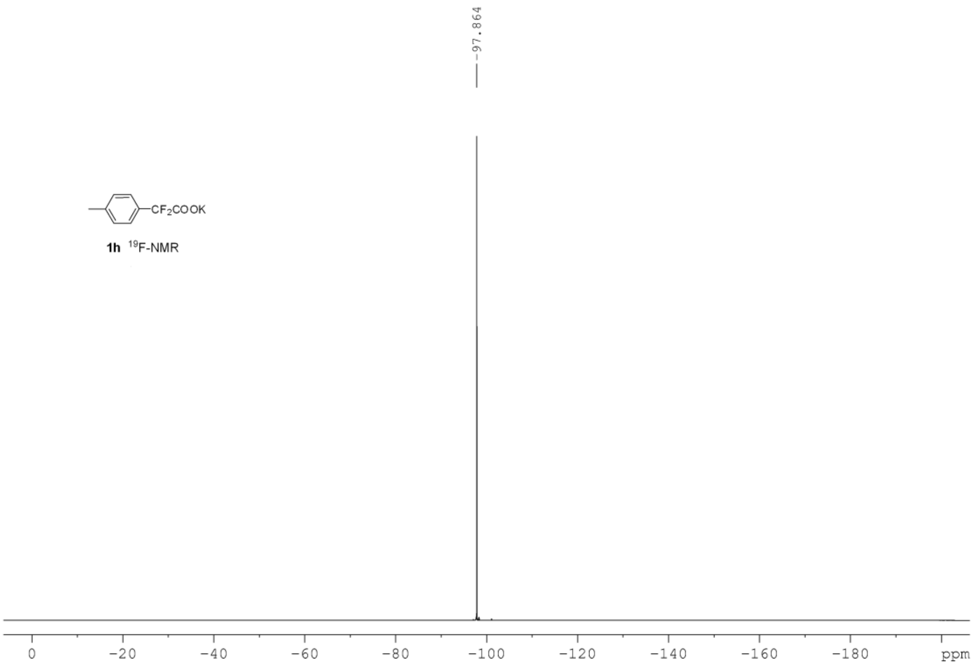
165.784
138.629
134.717
134.506
134.296
128.444
125.510
125.463
125.417
117.891
115.888
113.888
40.021
39.854
39.687
39.520
39.353
39.186
39.018
20.901
CF2COOK
1h 13C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm


-97.864
CF2COOK
1h 19F-NMR
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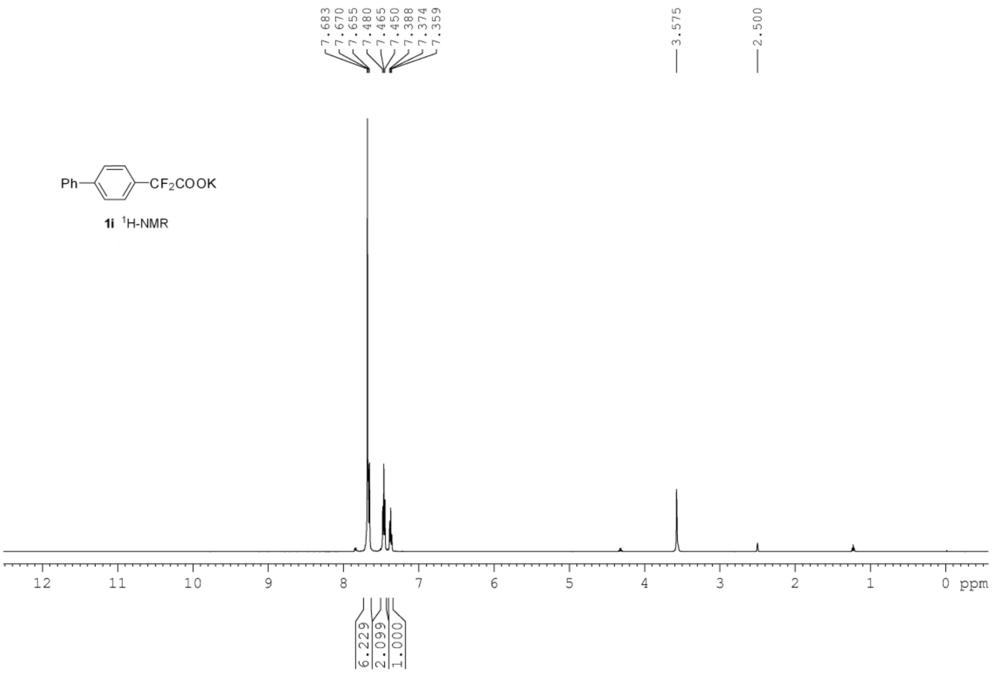
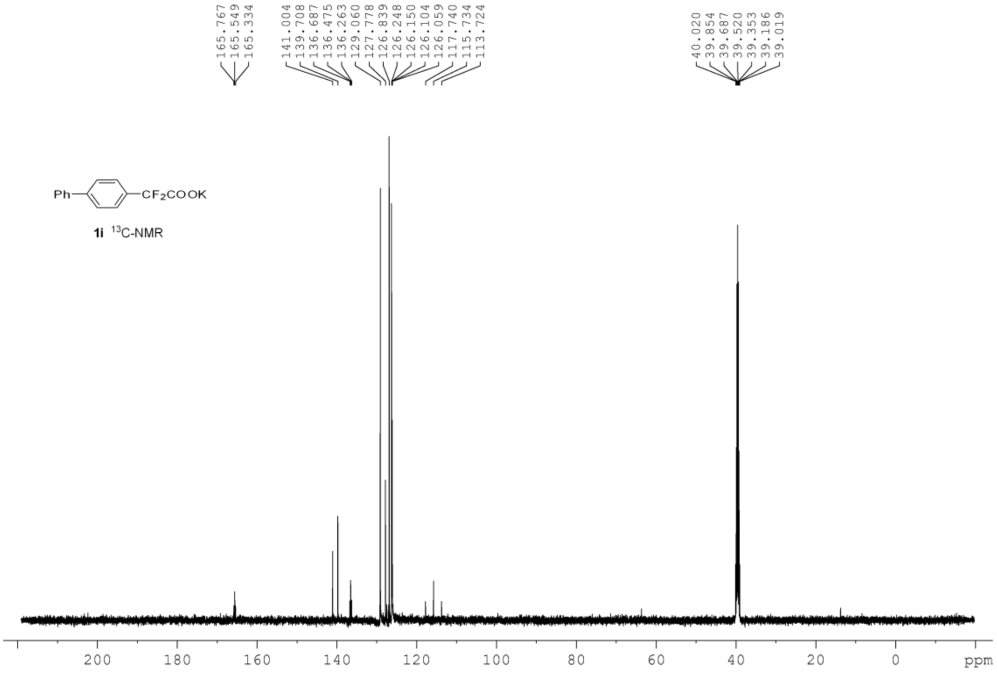
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


7.683
7.670
7.655
7.480
7.465
7.450
7.388
7.374
7.359
3.575
2.500
Ph
CF2COOK
1i ¹H-NMR
12
11
10
9
8
7
6
5
4
3
2
1
0 ppm
6.229
2.099
1.000


165.767
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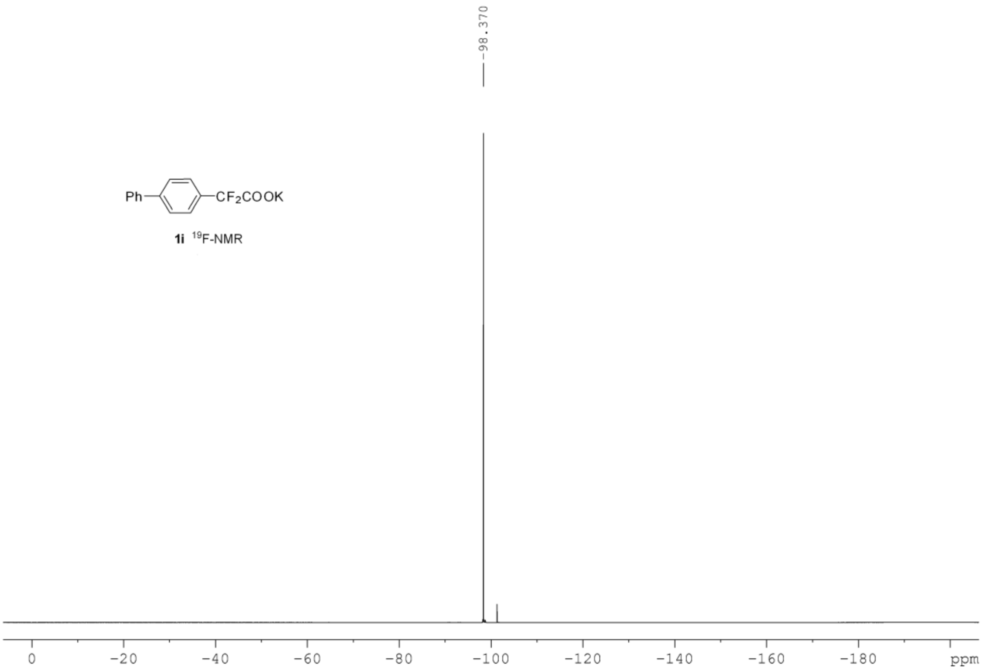
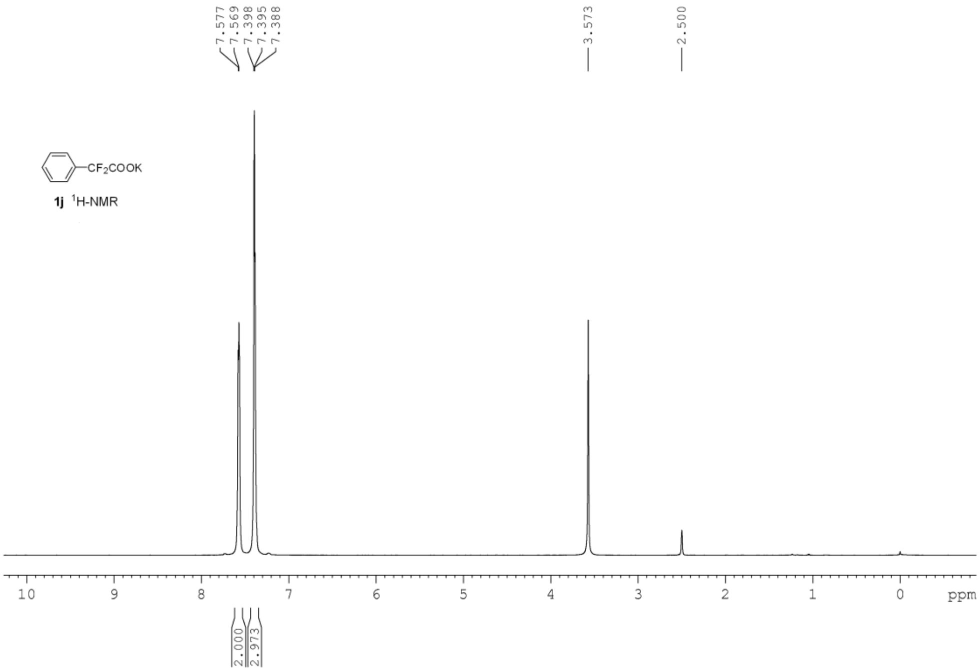
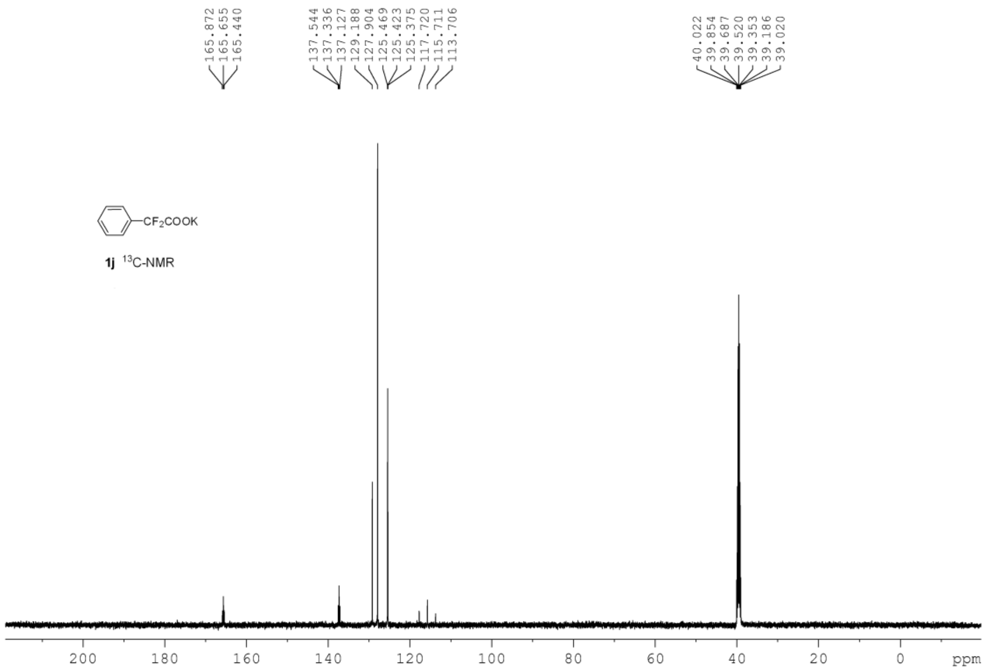
141.004
139.708
136.687
136.475
136.263
129.060
127.778
126.839
126.248
126.150
126.104
126.059
117.740
115.734
113.724
40.020
39.854
39.687
39.520
39.353
39.186
39.019
Ph
CF2COOK
1i ¹³C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm



1i ^{19}F-NMR



1j ^{1}H-NMR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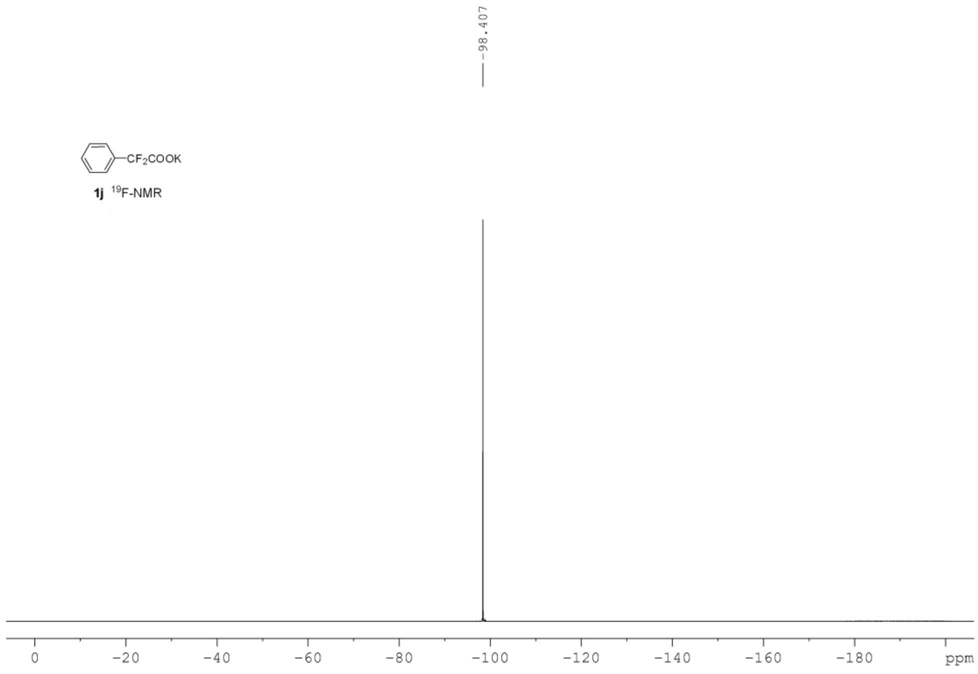
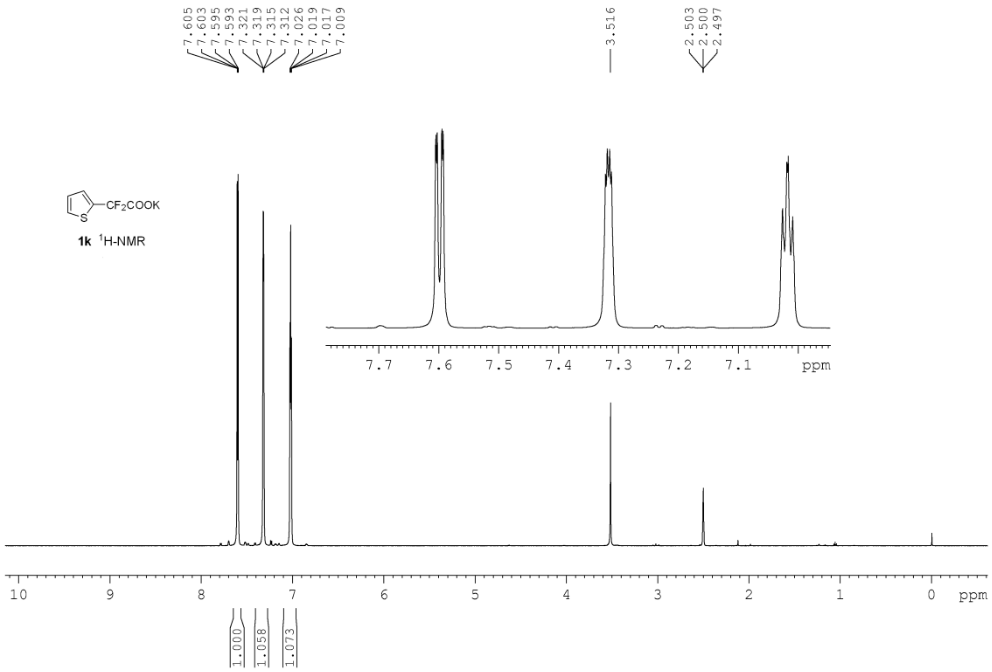
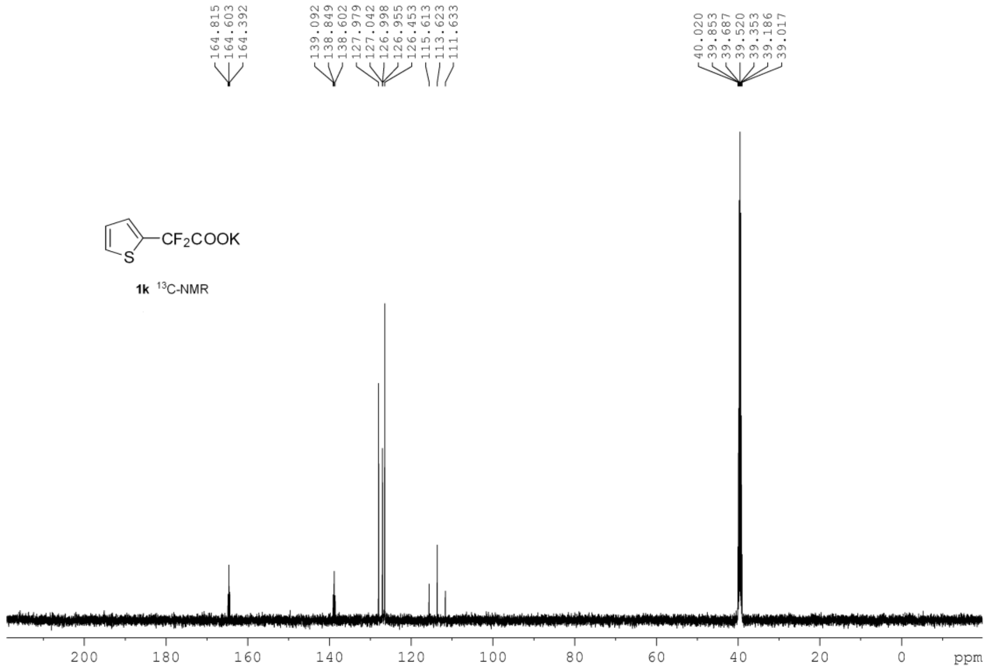
137.544
137.336
137.127
129.188
127.904
125.469
125.423
125.375
117.720
115.711
113.706
40.022
39.854
39.687
39.520
39.353
39.186
39.020
CF2COOK
1j 13C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm


-98.407
CF2COOK
1j 19F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


7.605
7.603
7.595
7.593
7.321
7.319
7.315
7.312
7.026
7.019
7.017
7.009
3.516
2.503
2.500
2.497
CF2COOK
S
1k ¹H-NMR
7.7
7.6
7.5
7.4
7.3
7.2
7.1
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.058
1.073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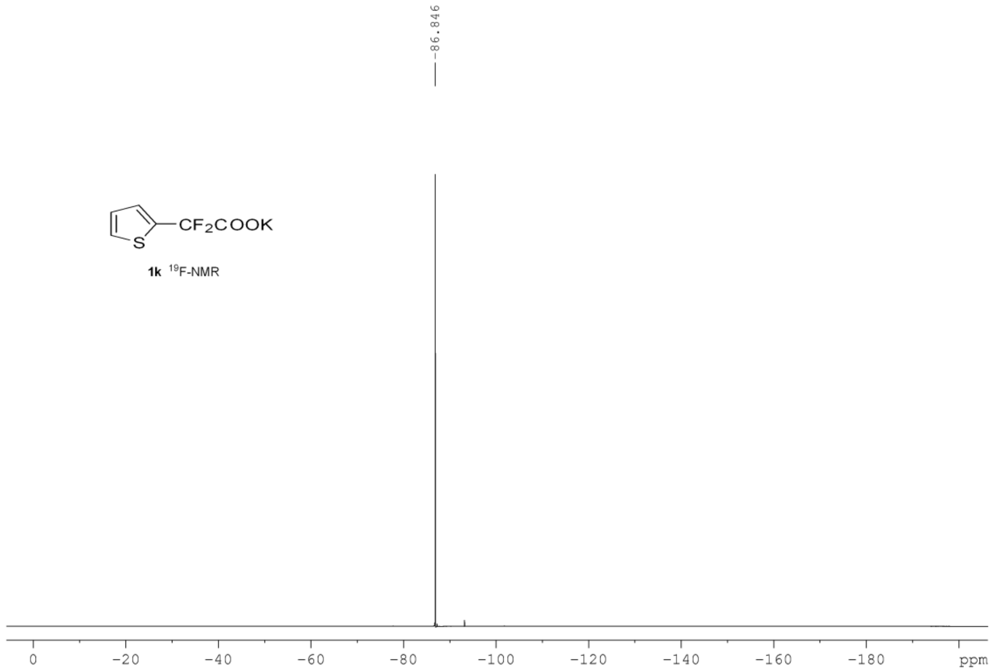
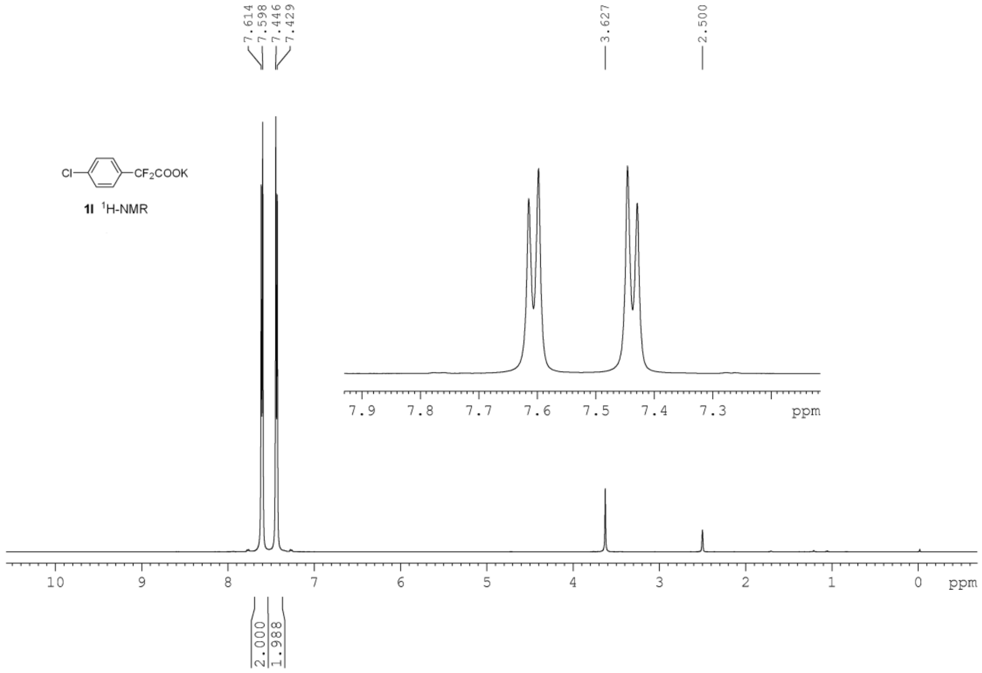
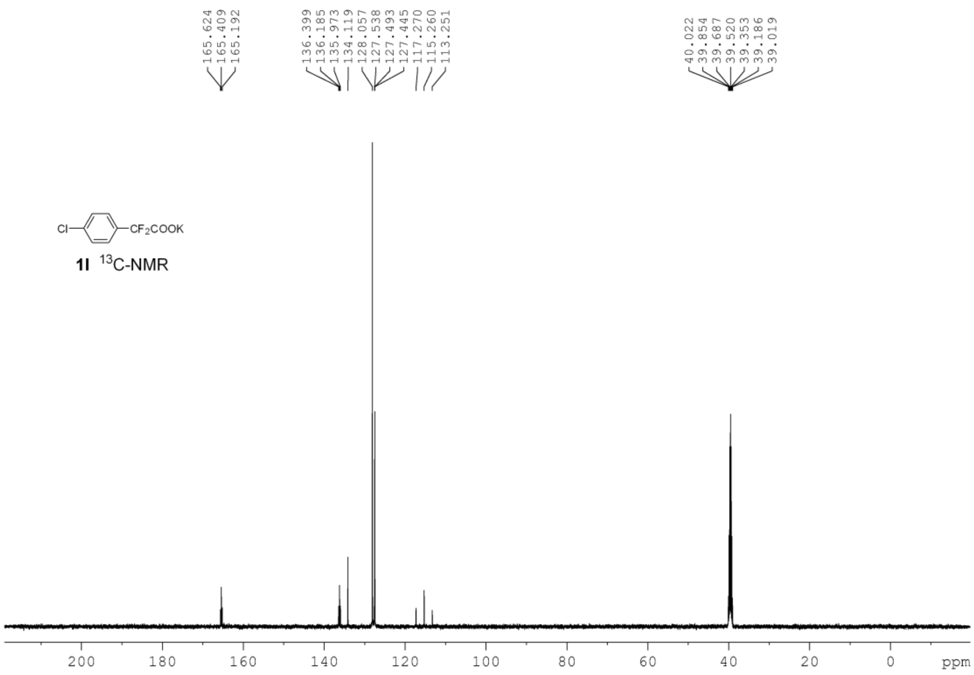
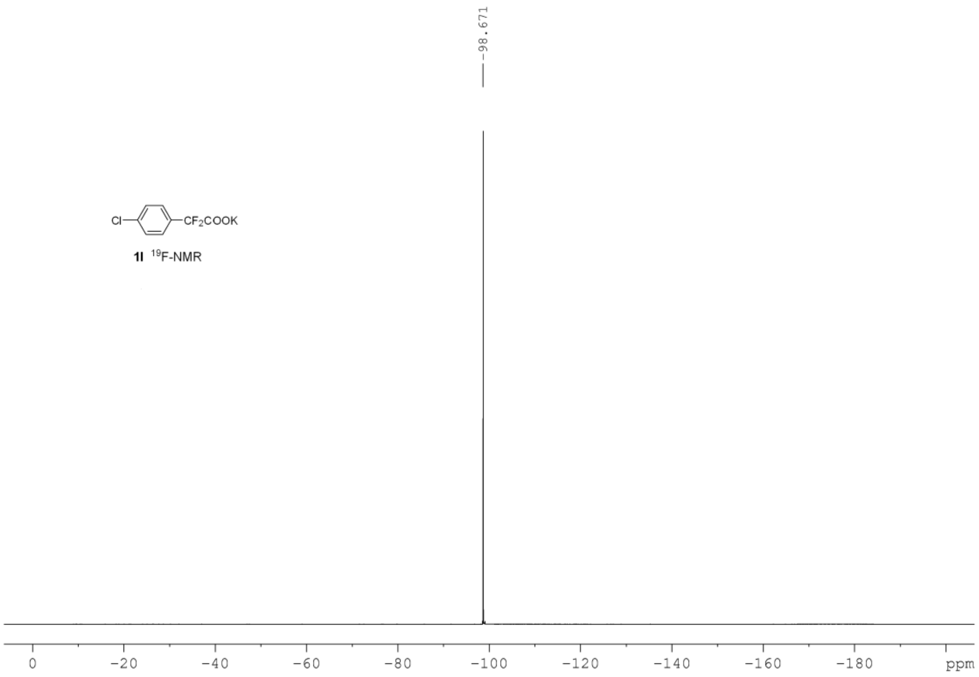
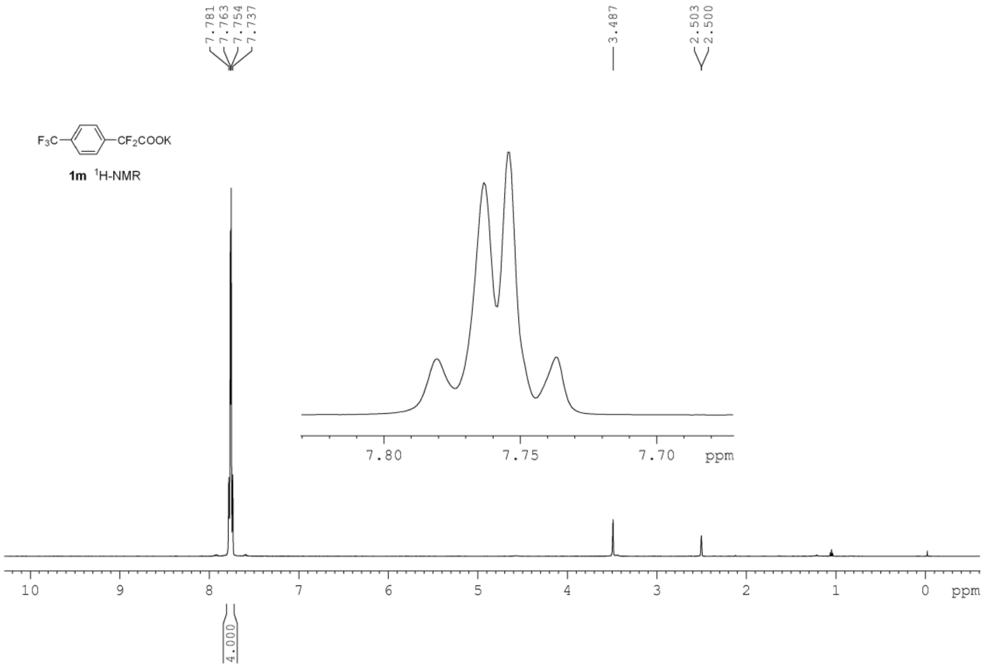
164.392
139.092
138.849
138.602
127.979
127.042
126.998
126.955
126.453
115.613
113.623
111.633
40.020
39.853
39.687
39.520
39.353
39.186
39.017
CF2COOK
S
1k ¹³C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

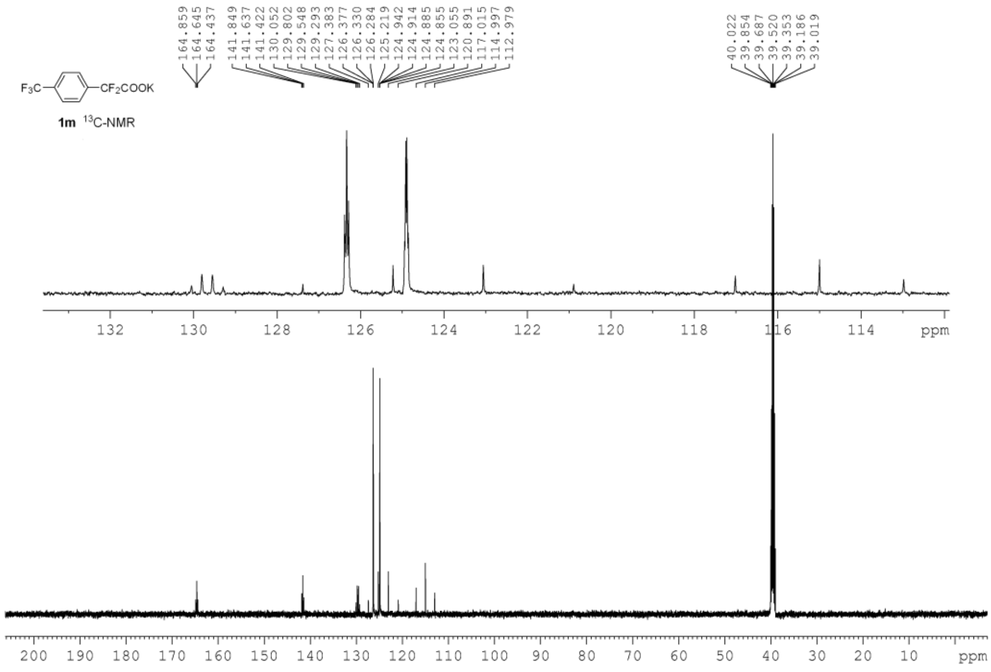

-86.846
CF$_2$COOK
S
1k ^{19}F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

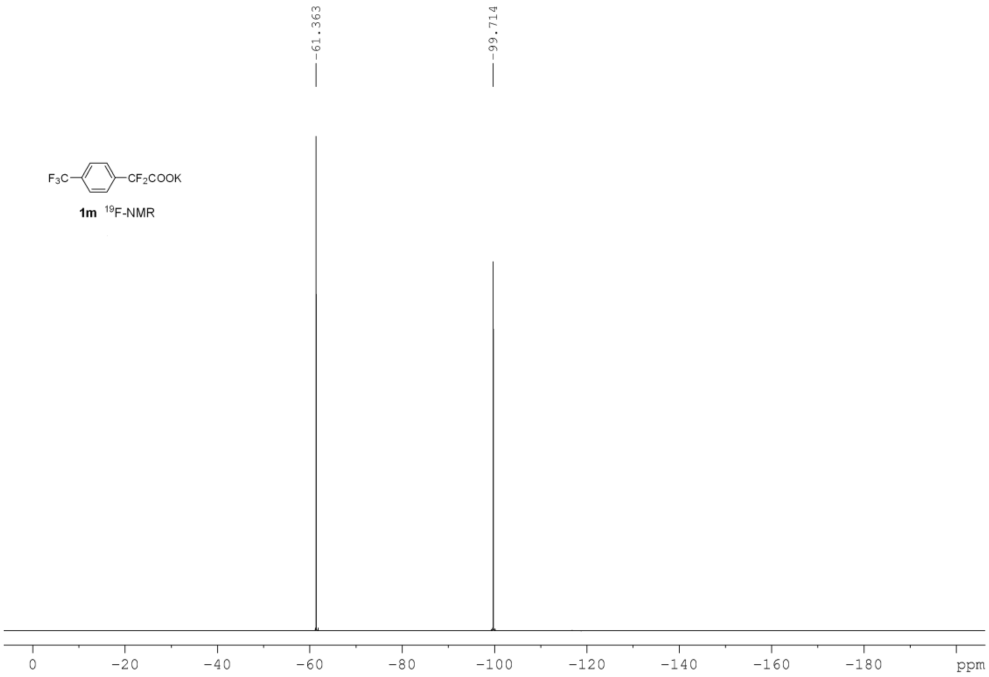

7.614
7.598
7.446
7.429
3.627
2.500
Cl
CF$_2$COOK
1l ^{1}H-NMR
7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
1.988


165.624
165.409
165.192
136.399
136.185
135.973
134.119
128.057
127.538
127.493
127.445
117.270
115.260
113.251
40.022
39.854
39.687
39.520
39.353
39.186
39.019
Cl
CF2COOK
1l 13C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

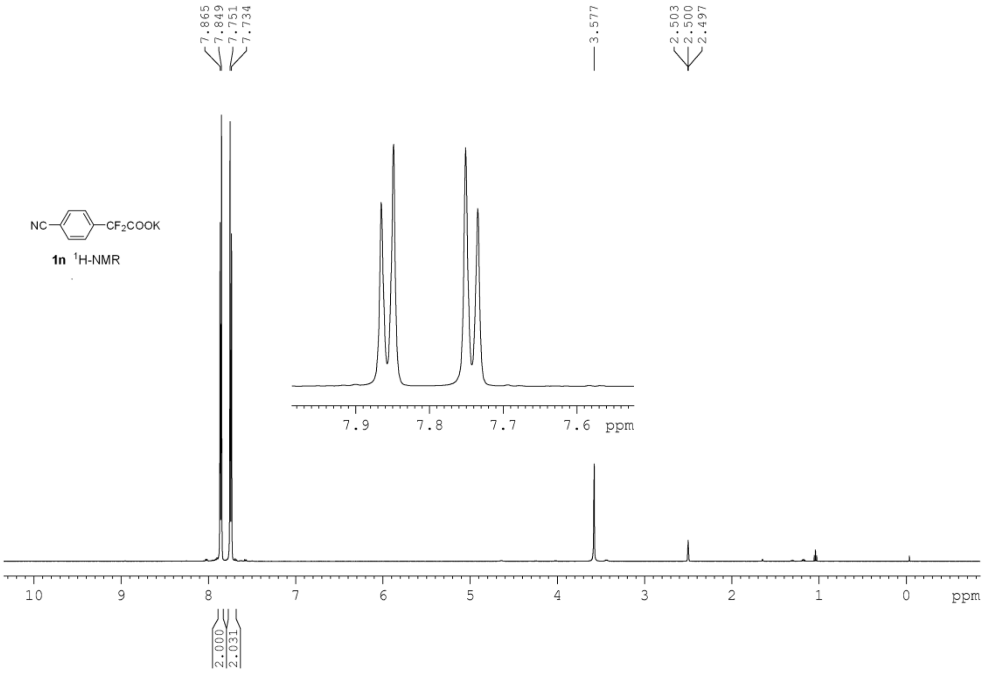

-98.671
Cl
CF2COOK
1l 19F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


7.781
7.763
7.754
7.737
3.487
2.503
2.500
F3C–C6H4–CF2COOK
1m ¹H-NMR
7.80
7.75
7.70
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
4.000

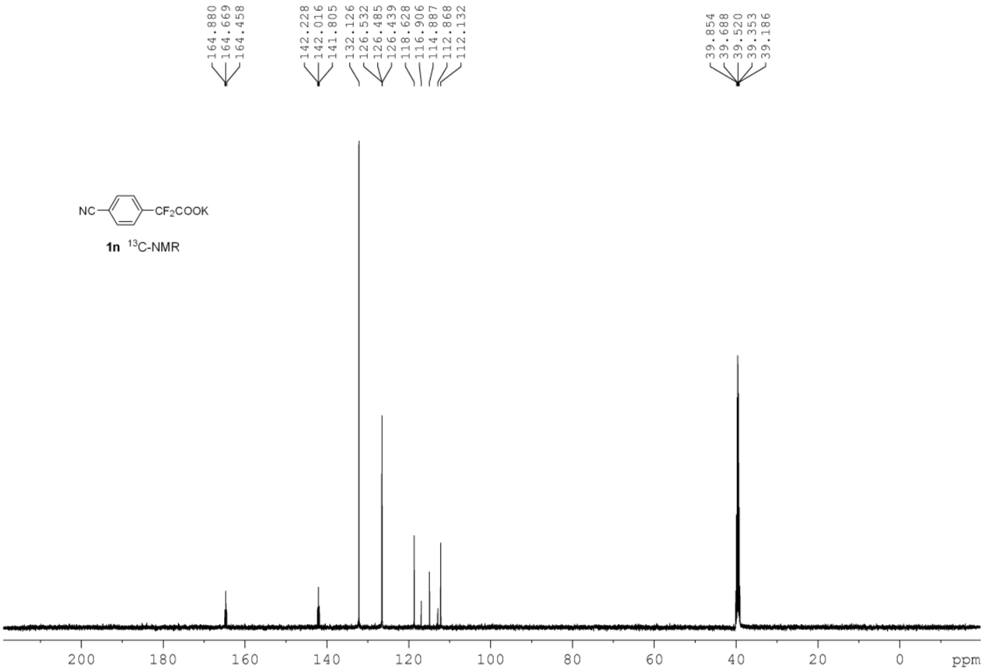

164.859
164.645
164.437
141.849
141.637
141.422
130.052
129.802
129.548
129.293
127.383
126.377
126.330
126.284
125.219
124.942
124.914
124.885
124.855
123.055
120.891
117.015
114.997
112.979
40.022
39.854
39.687
39.520
39.353
39.186
39.019
F3C–C6H4–CF2COOK
1m ¹³C-NMR
132
130
128
126
124
122
120
118
116
114
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

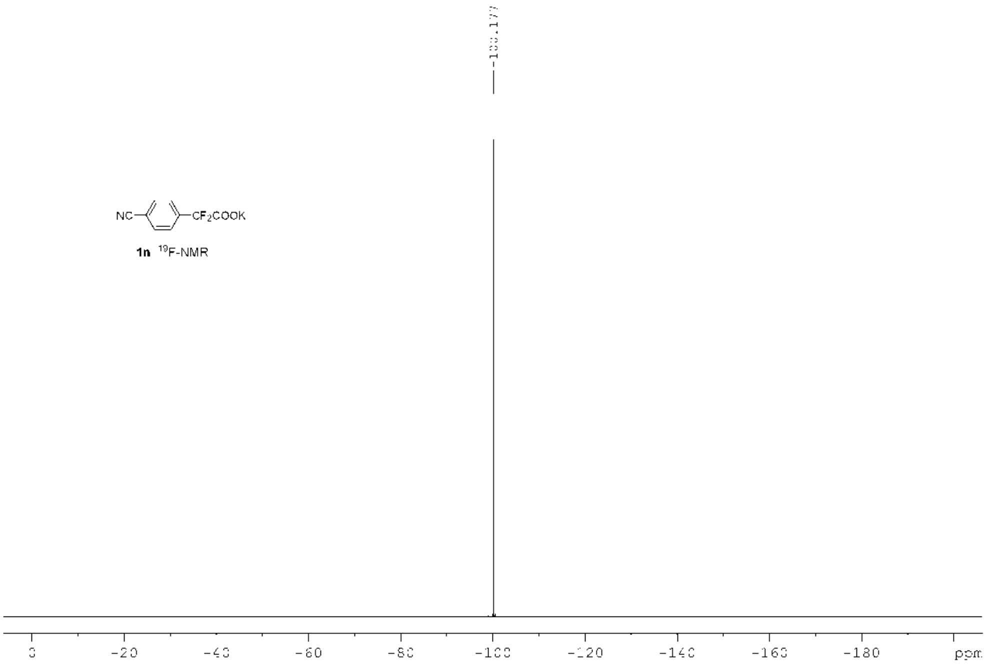


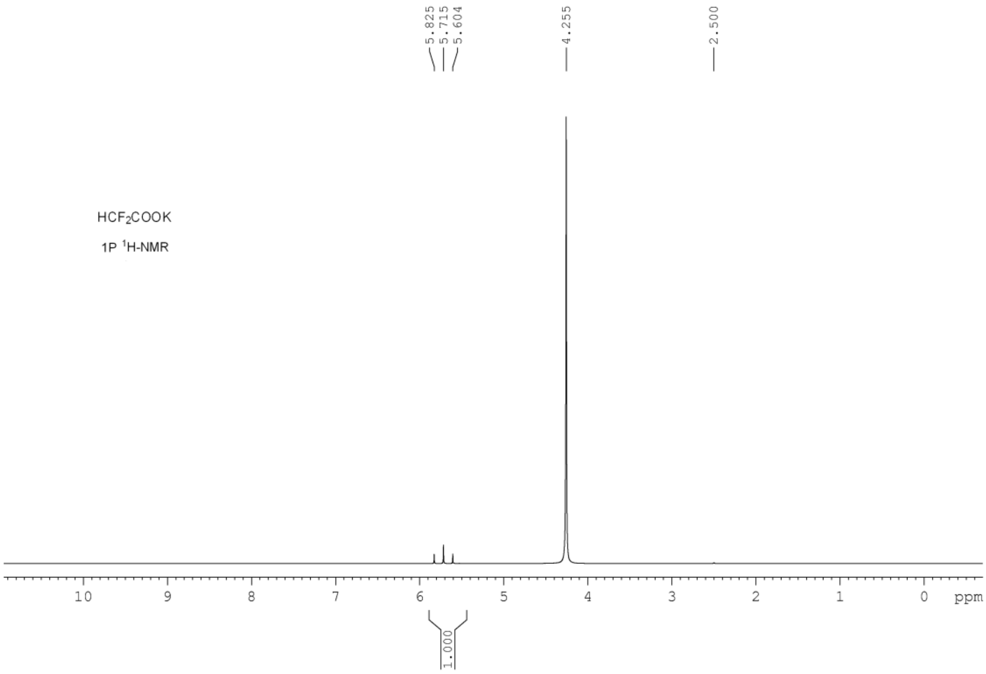
1m ^{19}F-NMR

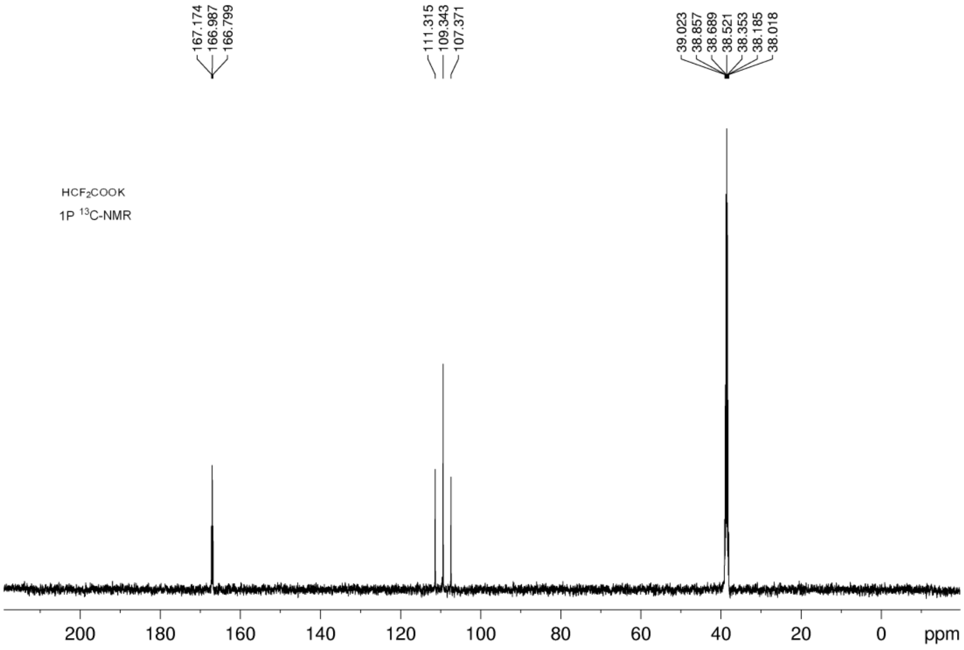


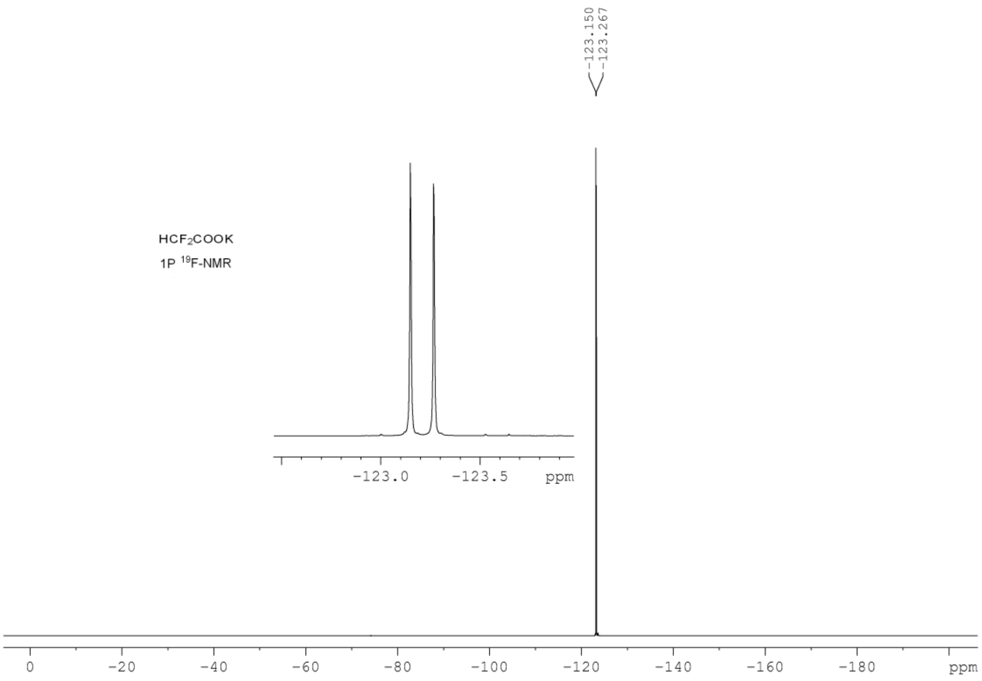
1n ^{1}H-NMR


164.880
164.669
164.458
142.228
142.016
141.805
132.126
126.532
126.485
126.439
118.628
116.906
114.887
112.868
112.132
39.854
39.688
39.520
39.353
39.186
NC
CF2COOK
1n 13C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

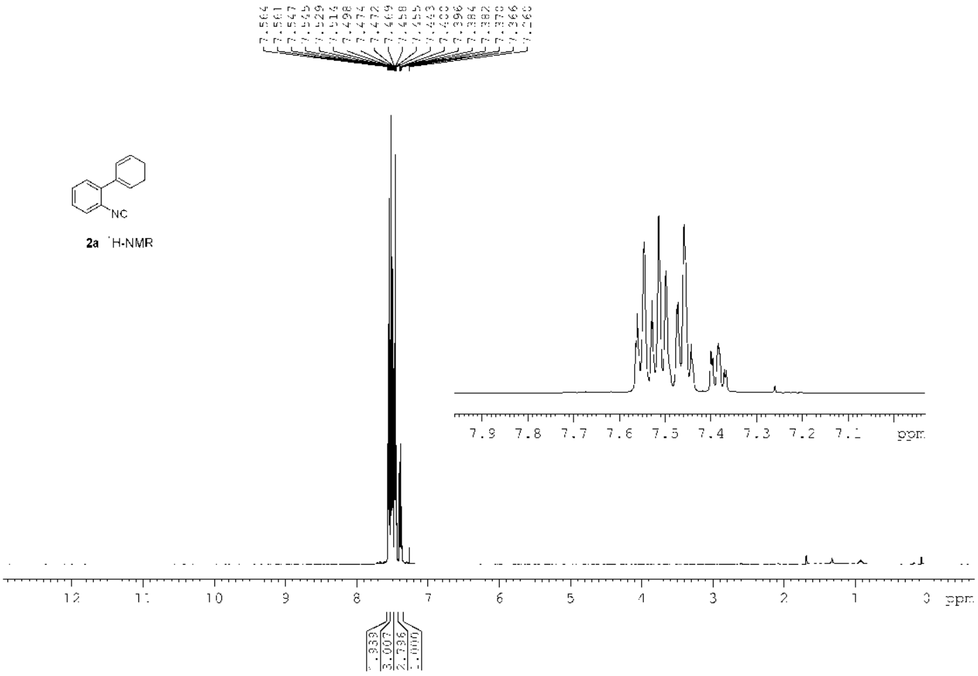

-100.177
NC
CF2COOK
1n 19F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

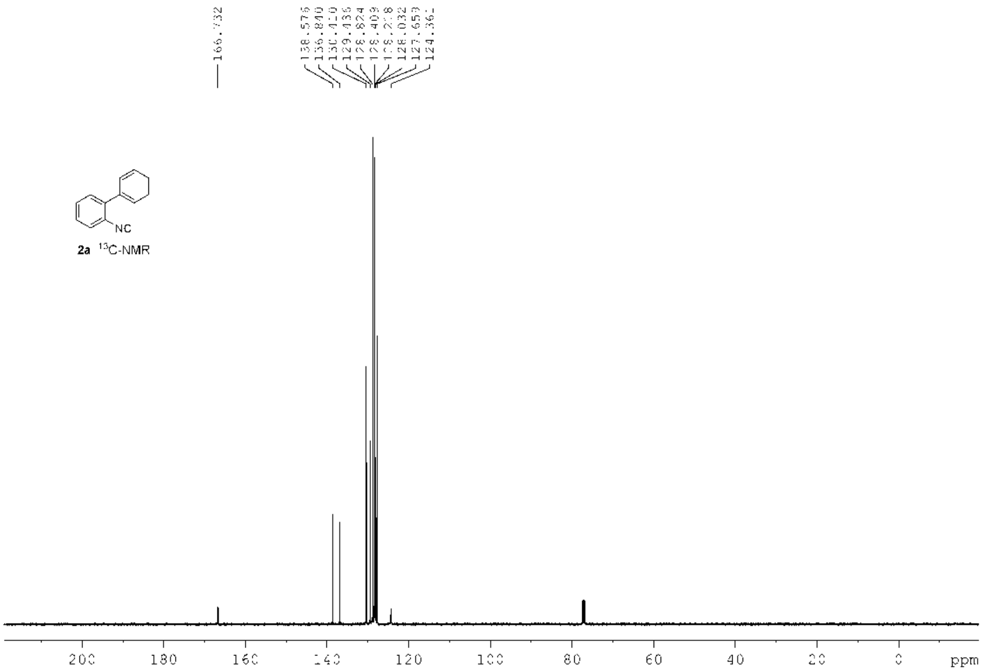

HCF₂COOK
1P ¹H-NMR
5.825
5.715
5.604
4.255
2.500
1.000
10
9
8
7
6
5
4
3
2
1
0
ppm

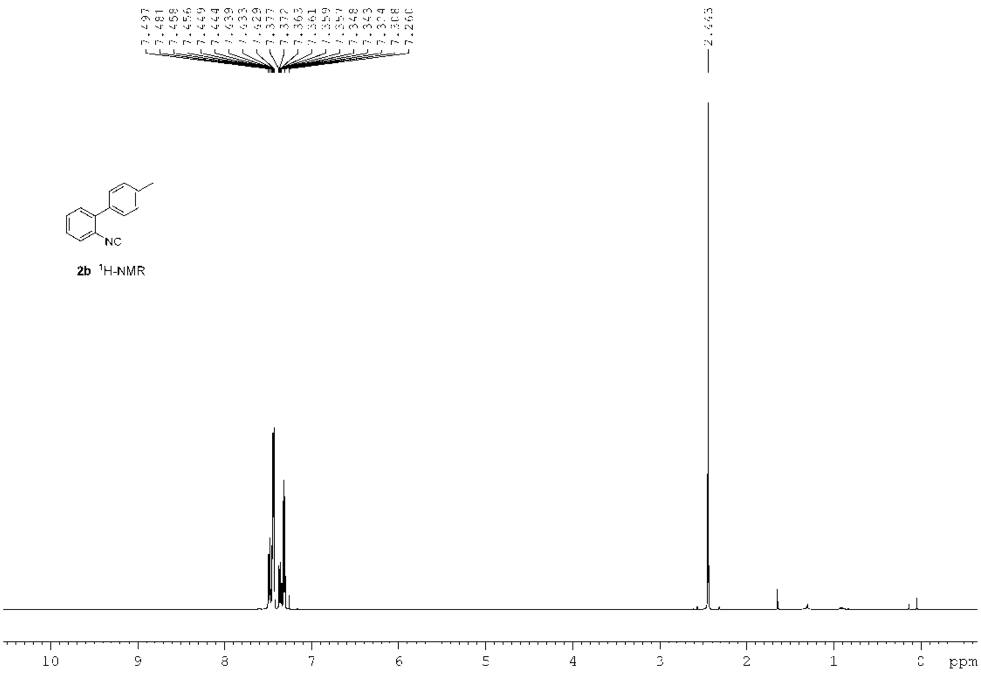

HCF₂COOK
1P ¹³C-NMR
167.174
166.987
166.799
111.315
109.343
107.371
39.023
38.857
38.689
38.521
38.353
38.185
38.018
200
180
160
140
120
100
80
60
40
20
0
ppm

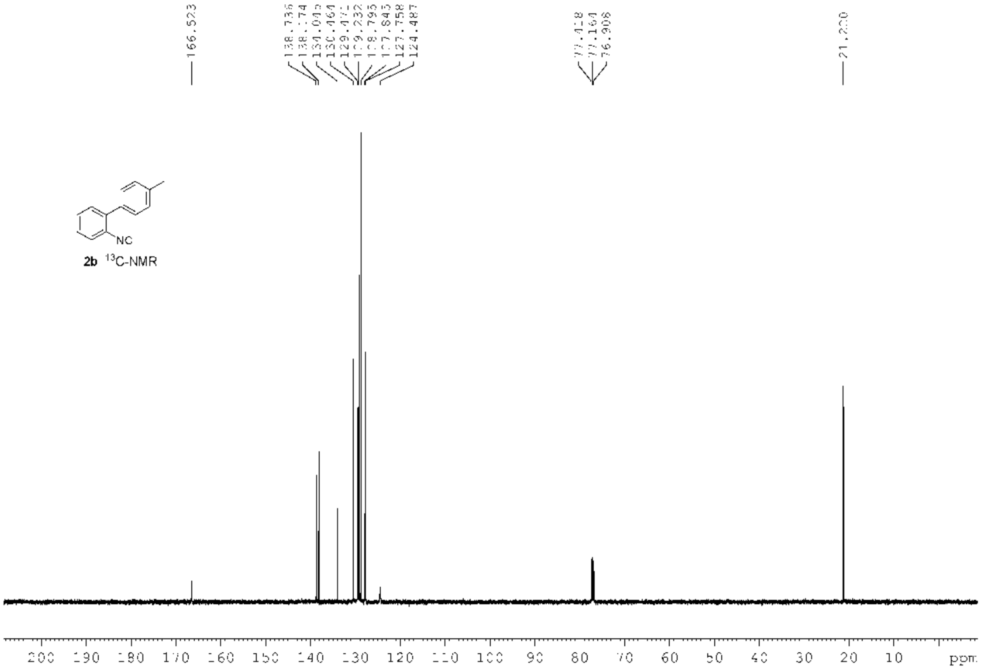

-123.150
-123.267
HCF$_2$COOK
1P ^{19}F-NMR
-123.0
-123.5
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

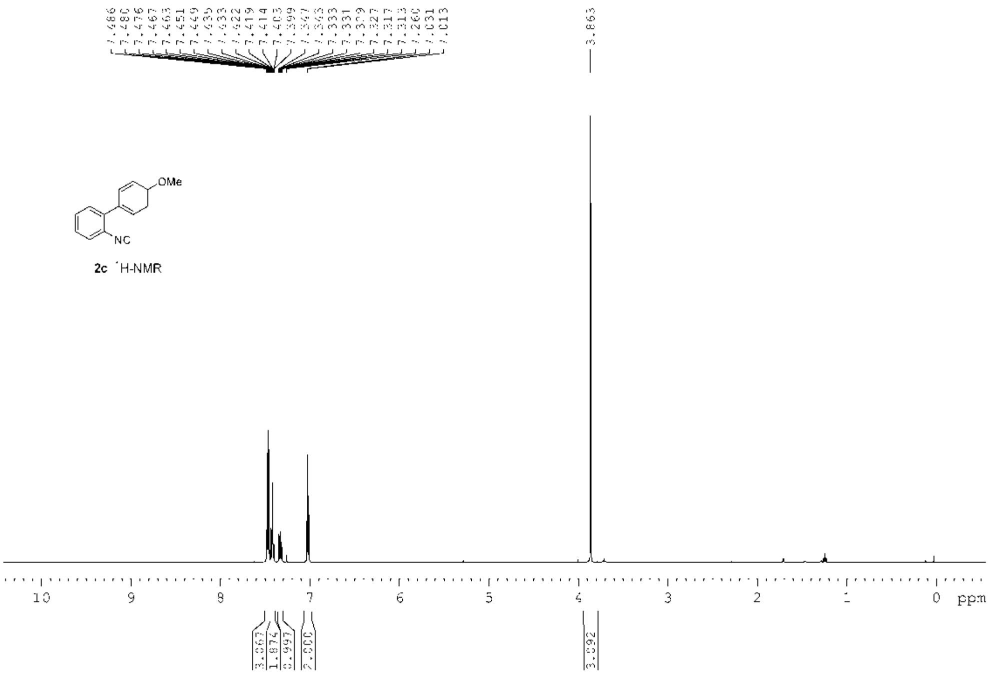
11. NMR spectra for isocyanides



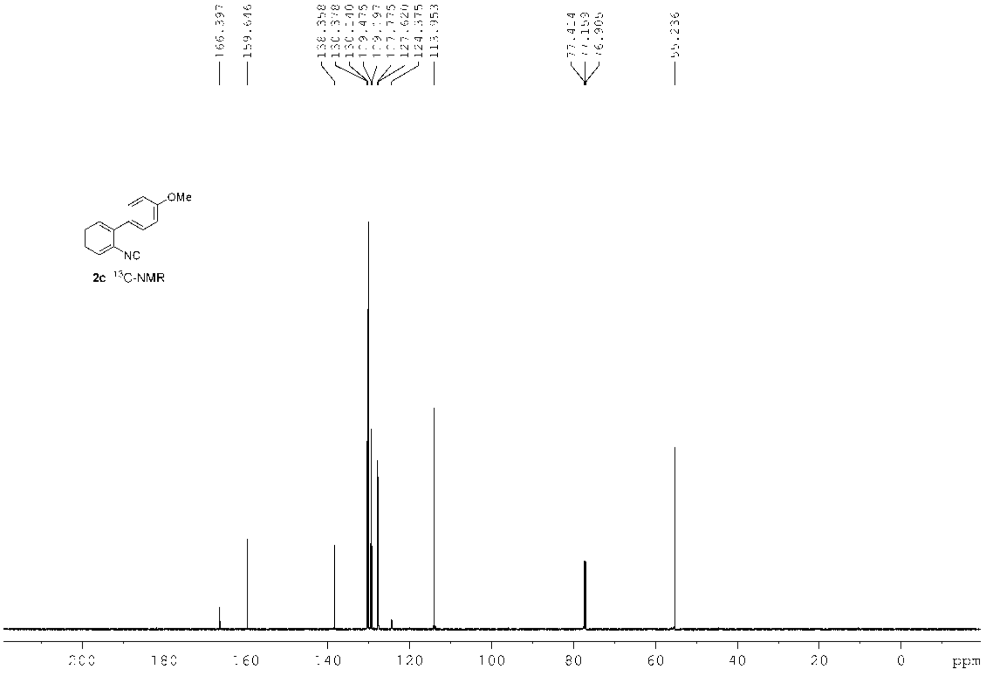



7.497
7.481
7.458
7.456
7.449
7.444
7.439
7.433
7.429
7.377
7.372
7.363
7.361
7.359
7.357
7.348
7.343
7.324
7.308
7.260
2.443
NC
2b ¹H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm

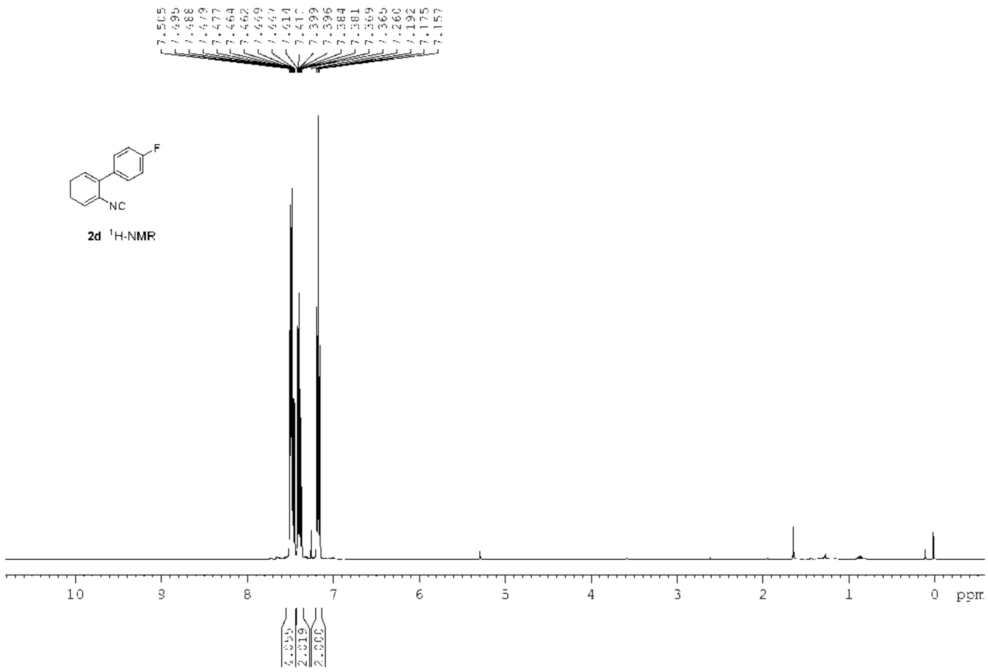

166.523
138.736
138.174
134.045
130.464
129.471
129.232
128.795
127.843
127.758
124.487
77.418
77.164
76.906
21.220
NC
2b ¹³C-NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

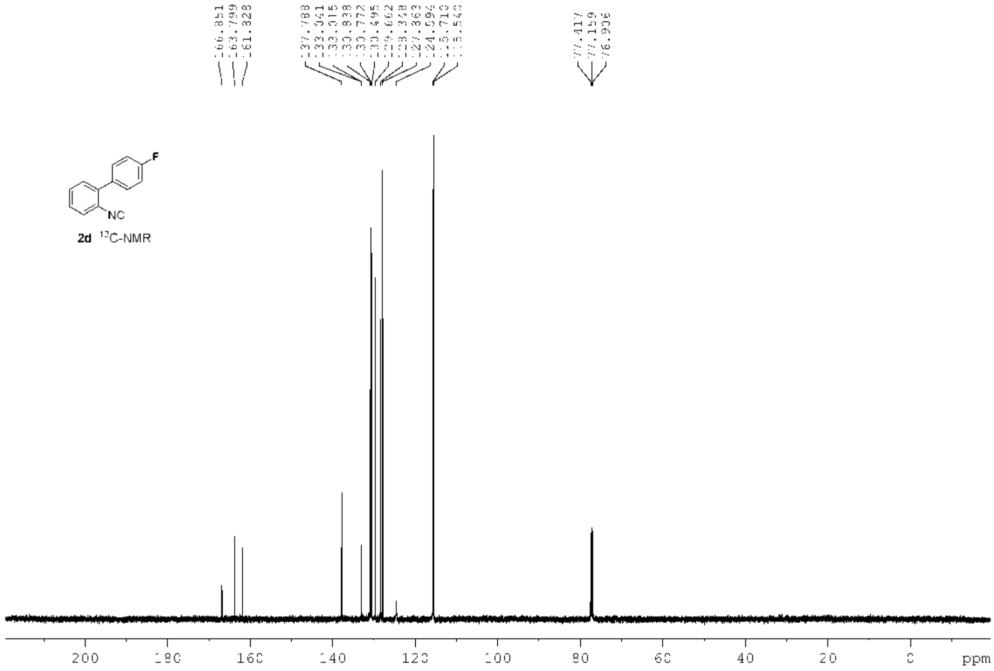


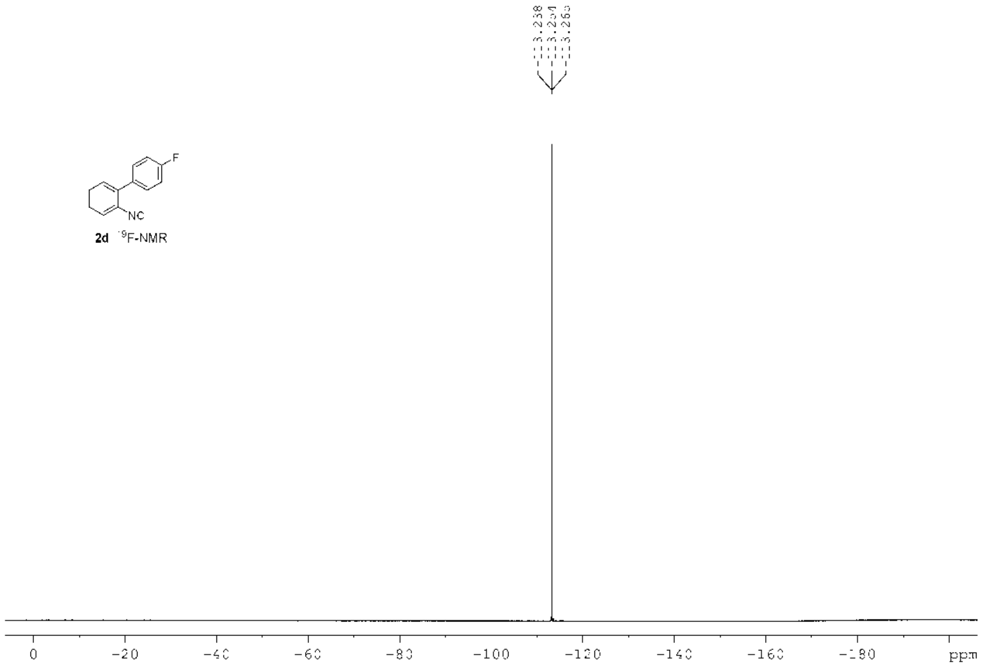
2c ^{1}H-NMR



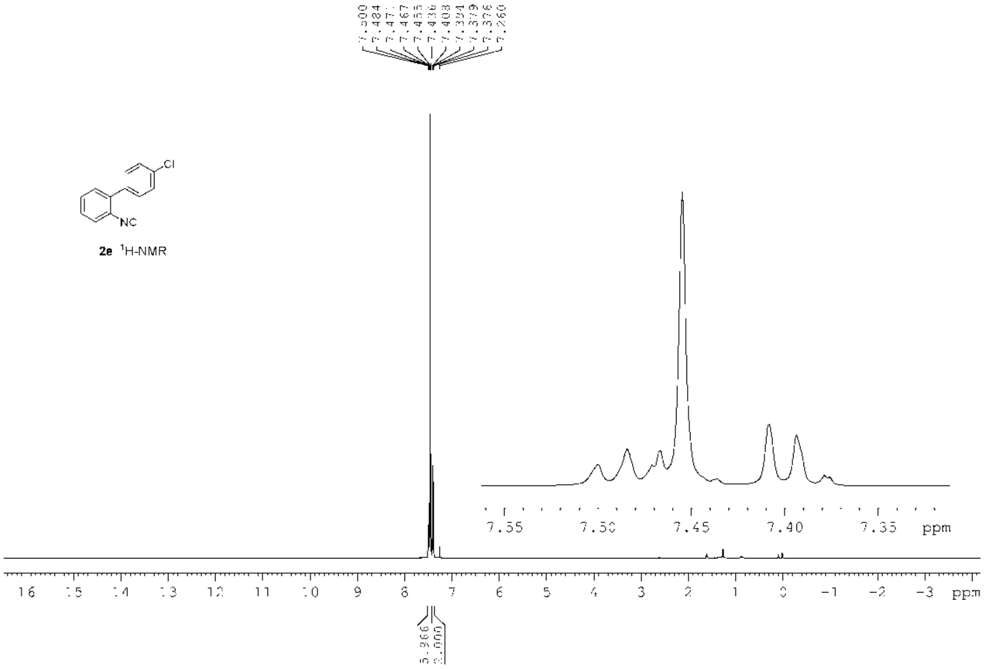
2c ^{13}C-NMR


7.505
7.495
7.488
7.479
7.477
7.464
7.462
7.449
7.447
7.414
7.41
7.399
7.396
7.384
7.381
7.369
7.365
7.260
7.192
7.175
7.157
F
NC
2d ^{1}H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm
4.055
2.019
2.000

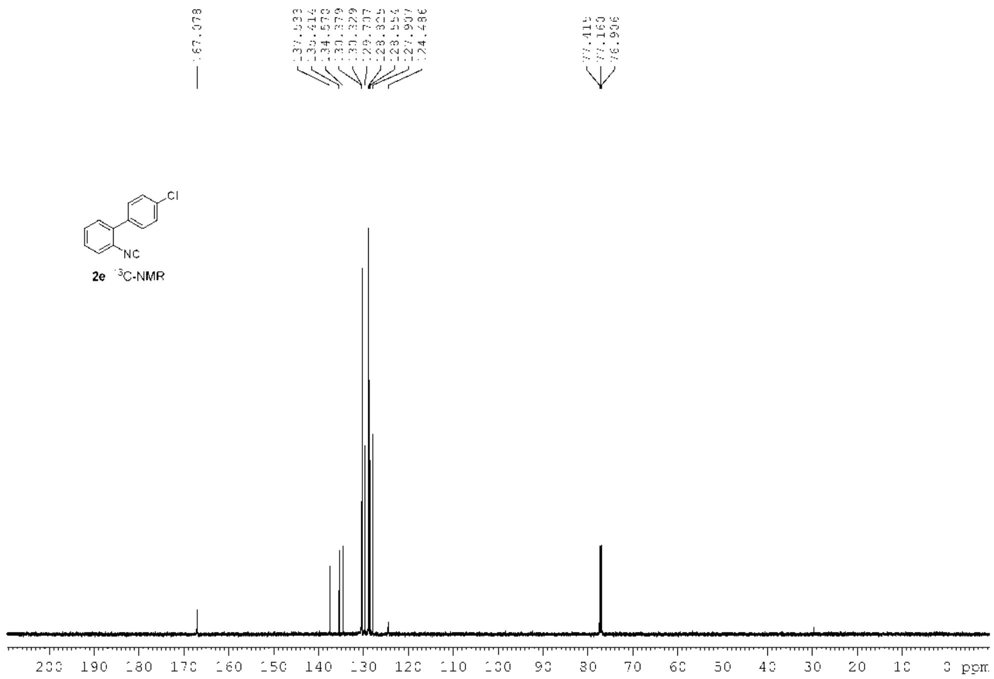

166.851
163.799
161.328
137.788
133.041
133.015
130.838
130.772
130.495
129.662
128.348
127.363
124.594
115.713
115.540
77.417
77.159
76.906
F
NC
2d ^{13}C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

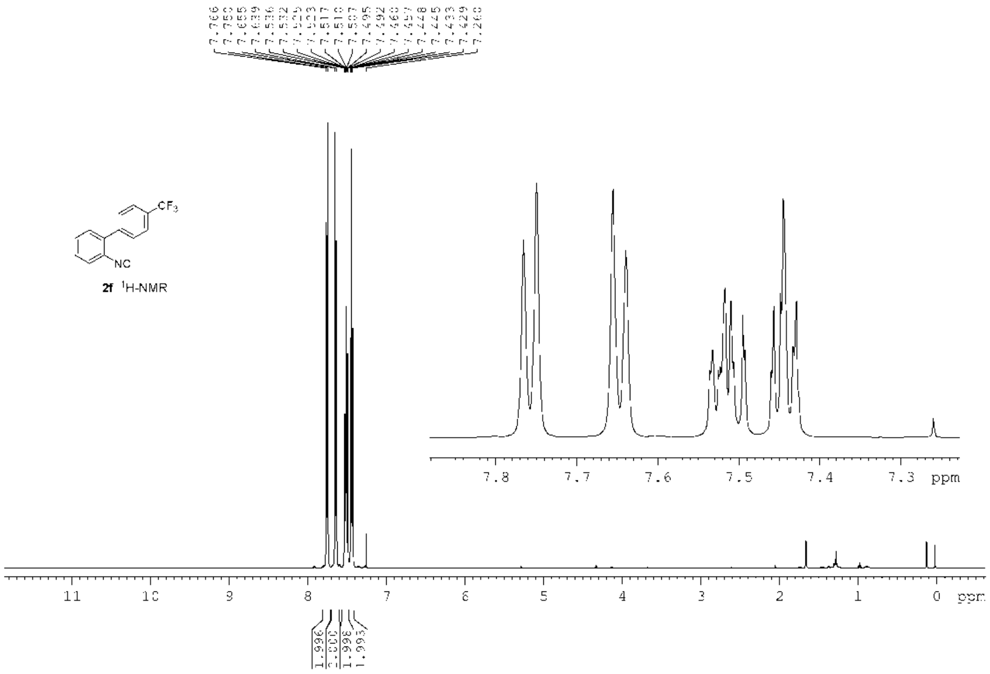


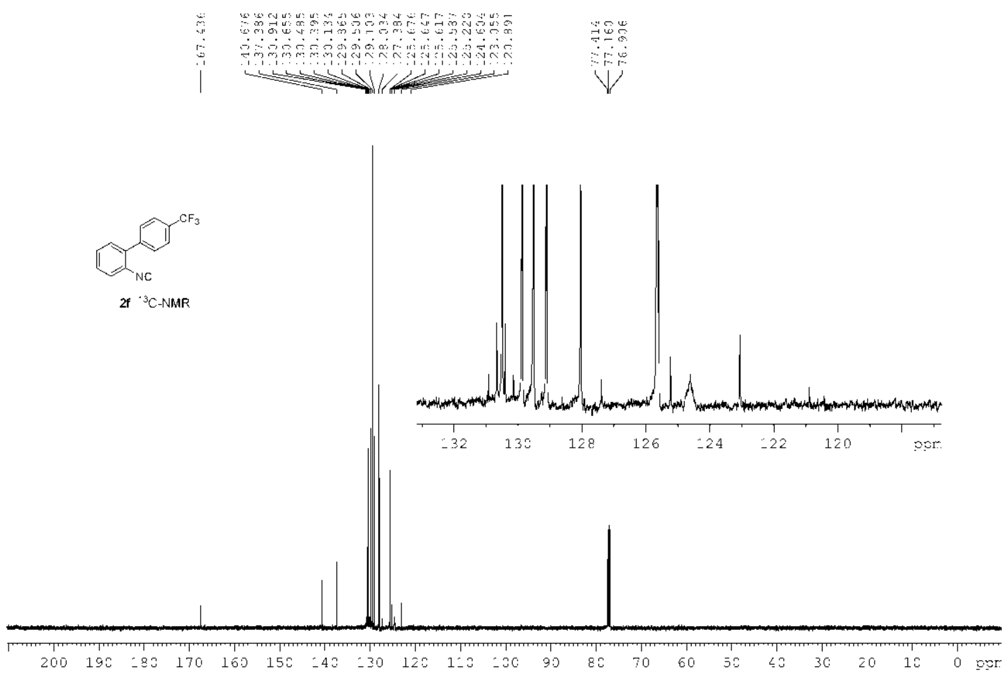
2d ^{19}F-NMR



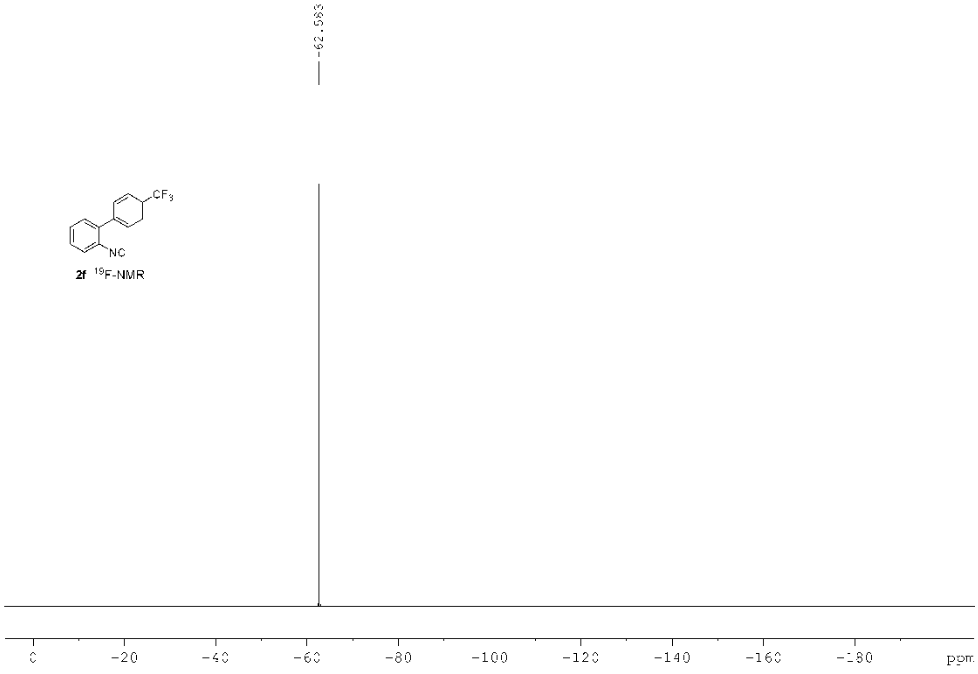
2e ^{1}H-NMR


167.078
137.533
135.414
134.573
130.379
130.329
129.707
128.925
128.554
127.907
124.486
77.415
77.160
76.906
Cl
NC
2e 13C-NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

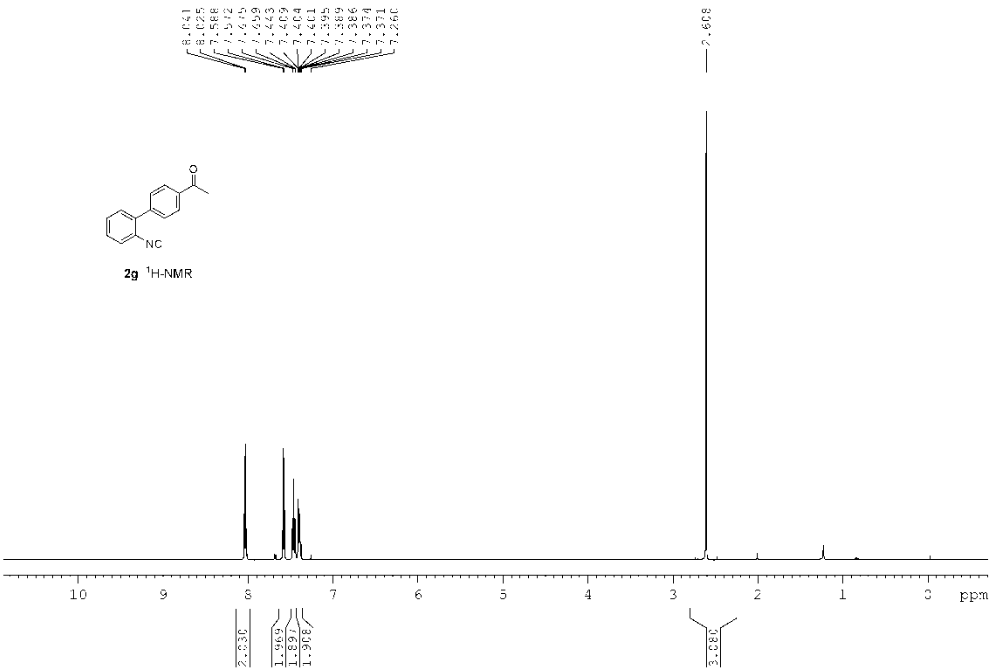

7.766
7.760
7.665
7.639
7.536
7.532
7.525
7.523
7.517
7.510
7.507
7.495
7.492
7.460
7.457
7.448
7.445
7.433
7.429
7.260
CF3
NC
2f 1H-NMR
7.8
7.7
7.6
7.5
7.4
7.3
ppm
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.996
2.000
1.998
1.993

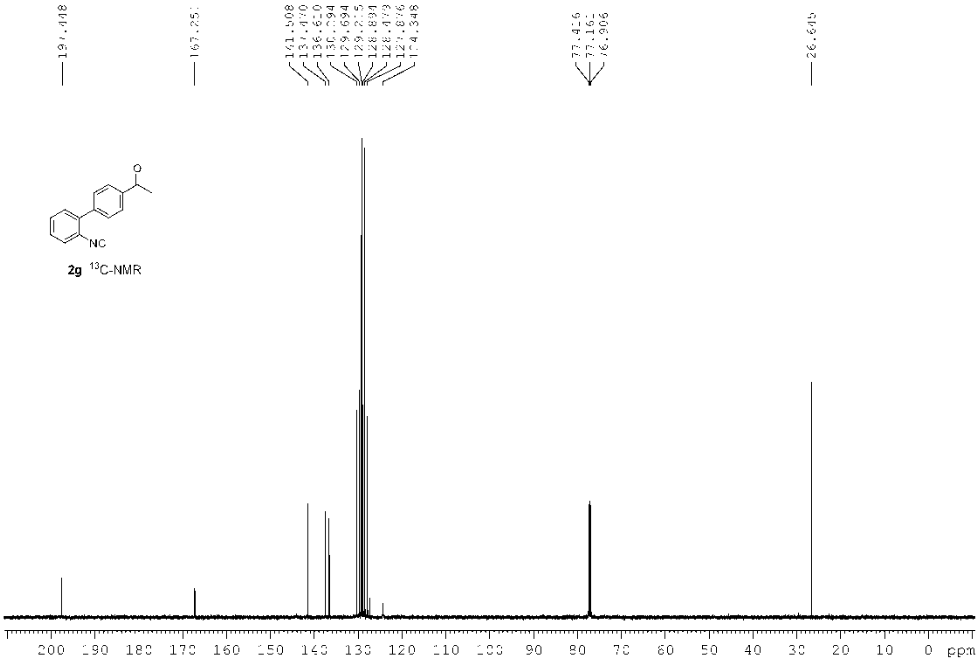


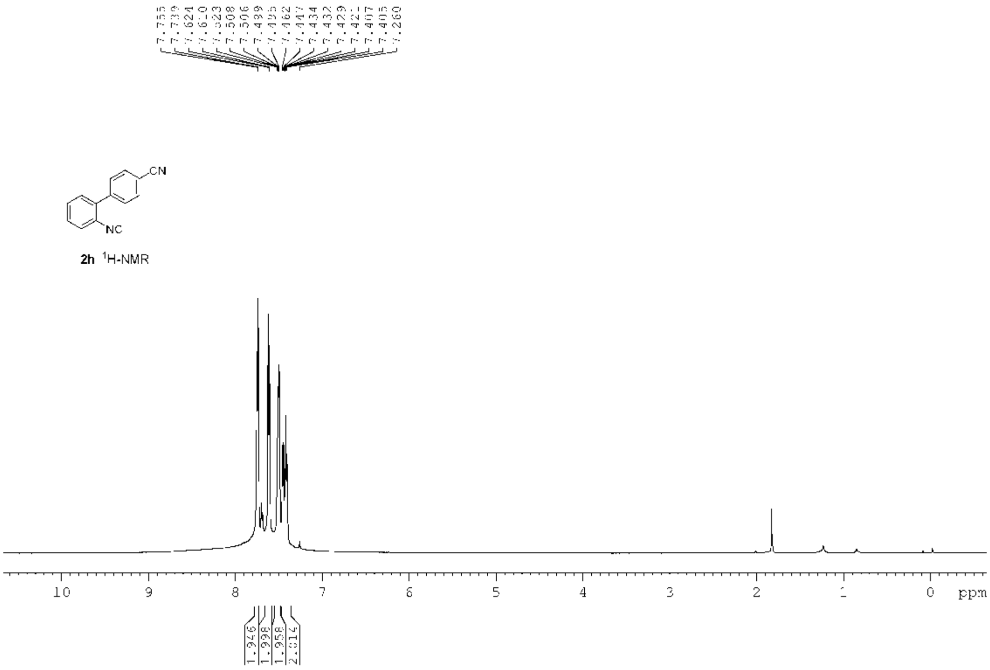
2f ^{13}C-NMR



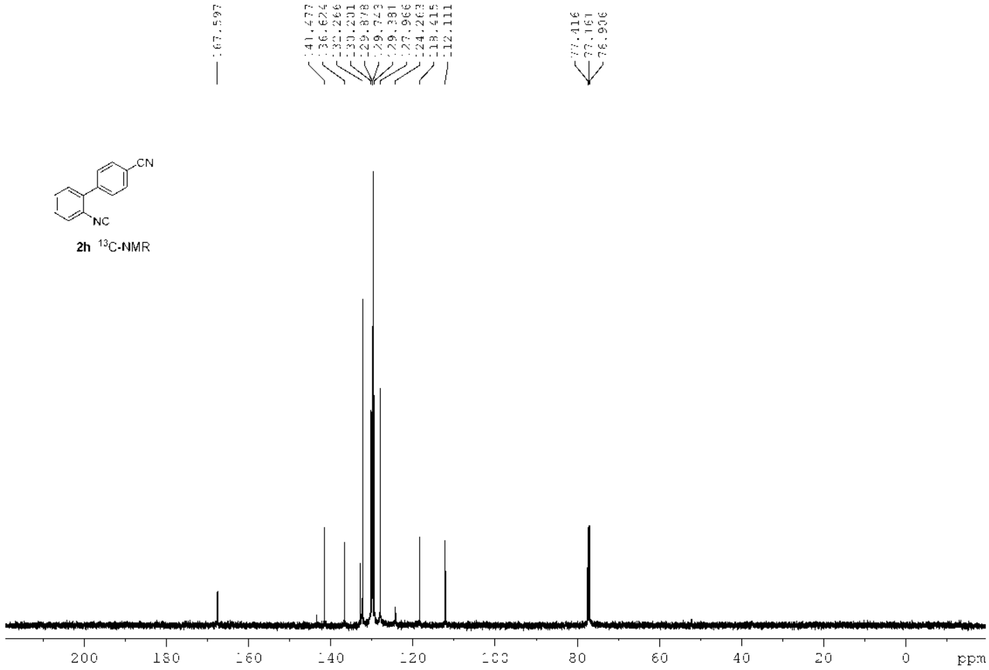
2f ^{19}F-NMR


8.041
8.025
7.588
7.572
7.475
7.459
7.443
7.409
7.404
7.401
7.395
7.389
7.386
7.374
7.371
7.260
2.608
O
NC
2g ¹H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm
2.030
1.969
1.897
1.908
3.080

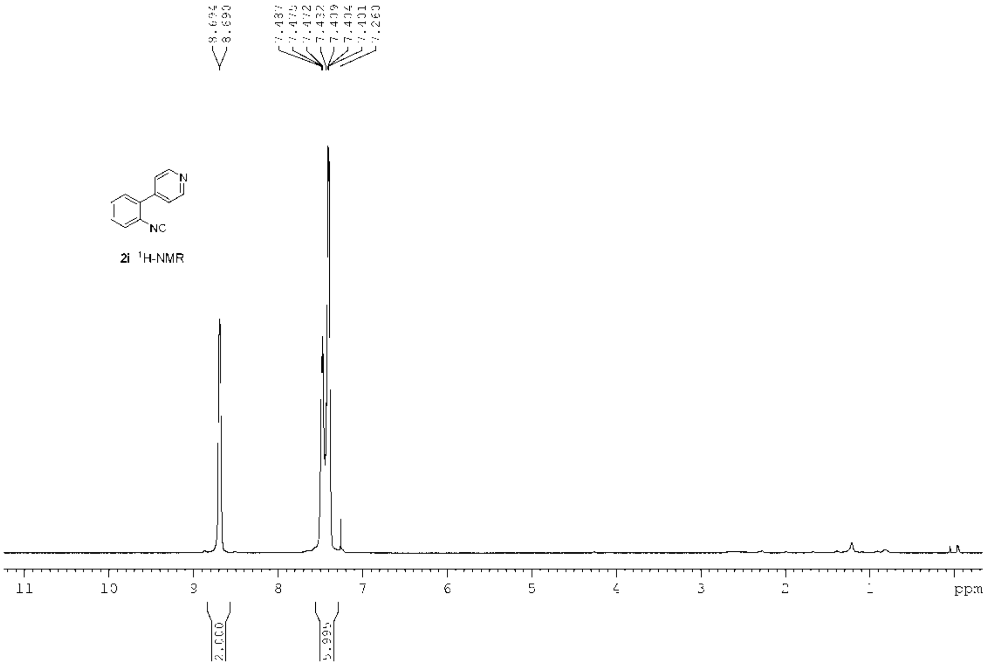

197.448
167.251
141.508
137.470
136.610
130.094
129.694
129.215
128.894
128.473
127.876
124.348
77.416
77.161
76.906
26.645
O
NC
2g ¹³C-NMR
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



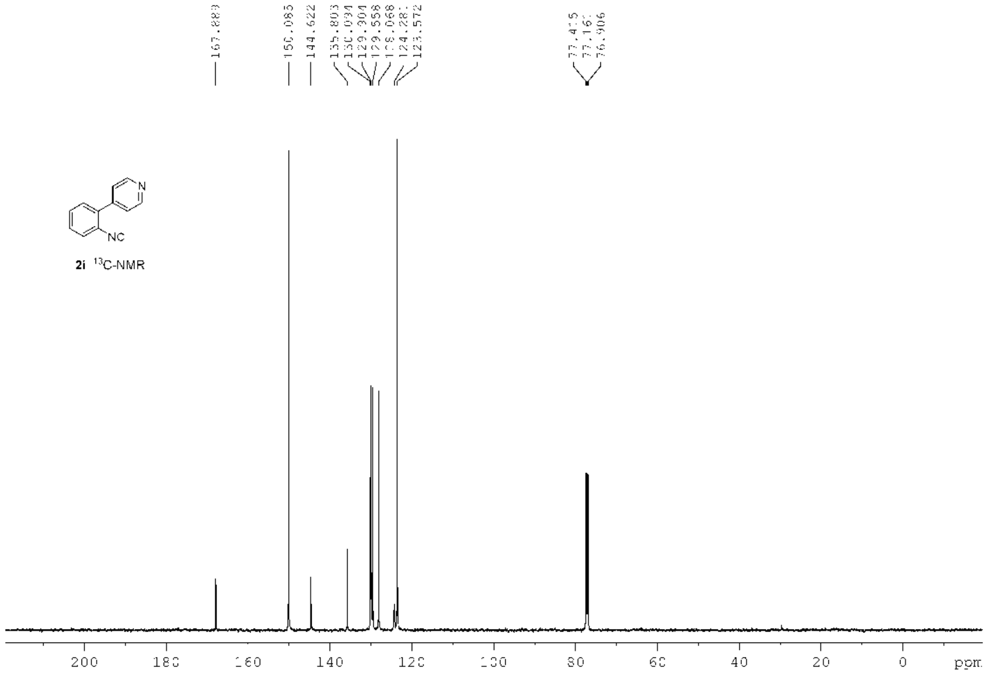
2h ^{1}H-NMR



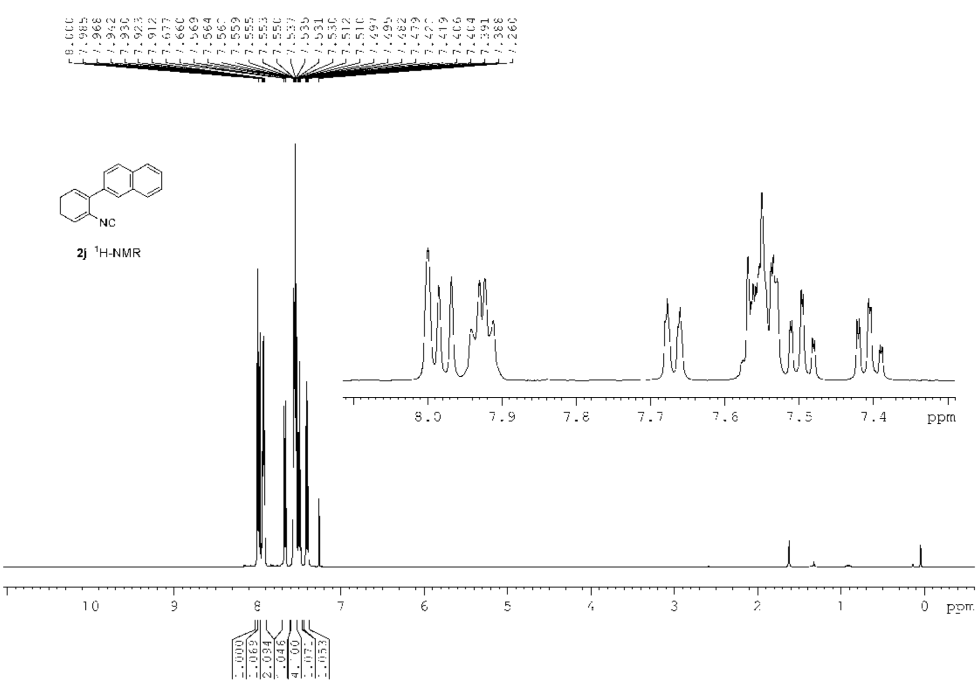
2h ^{13}C-NMR



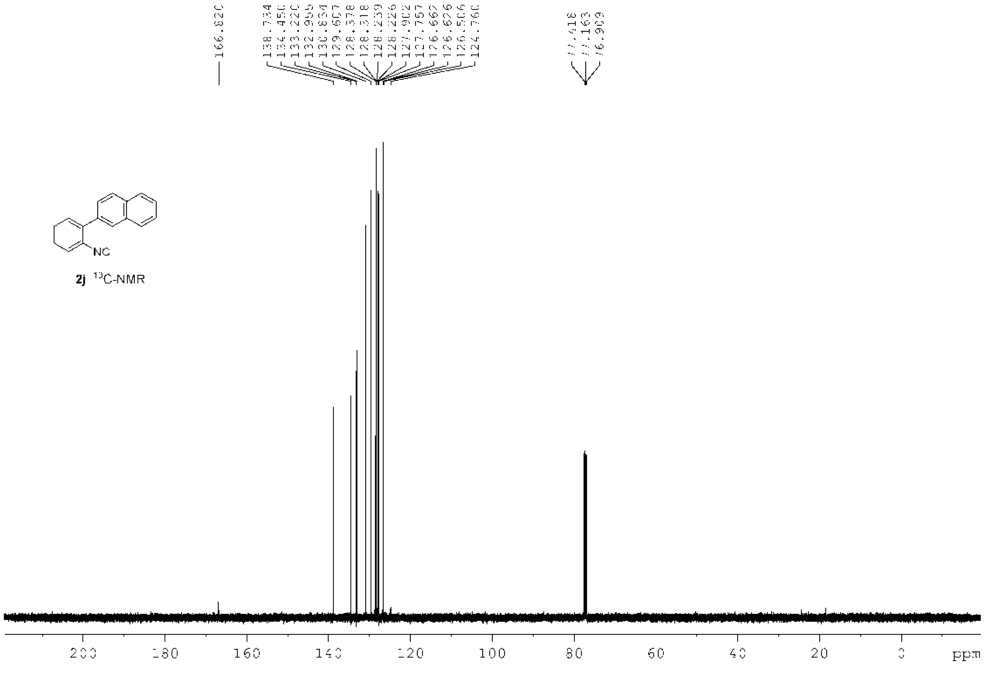
2i ^{1}H-NMR



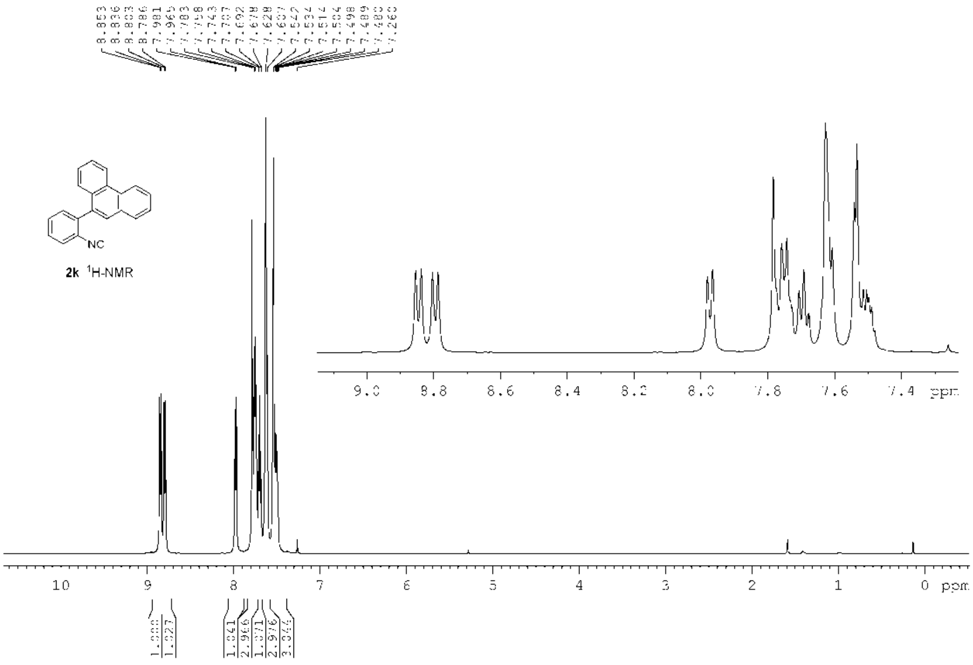
2i ^{13}C-NMR

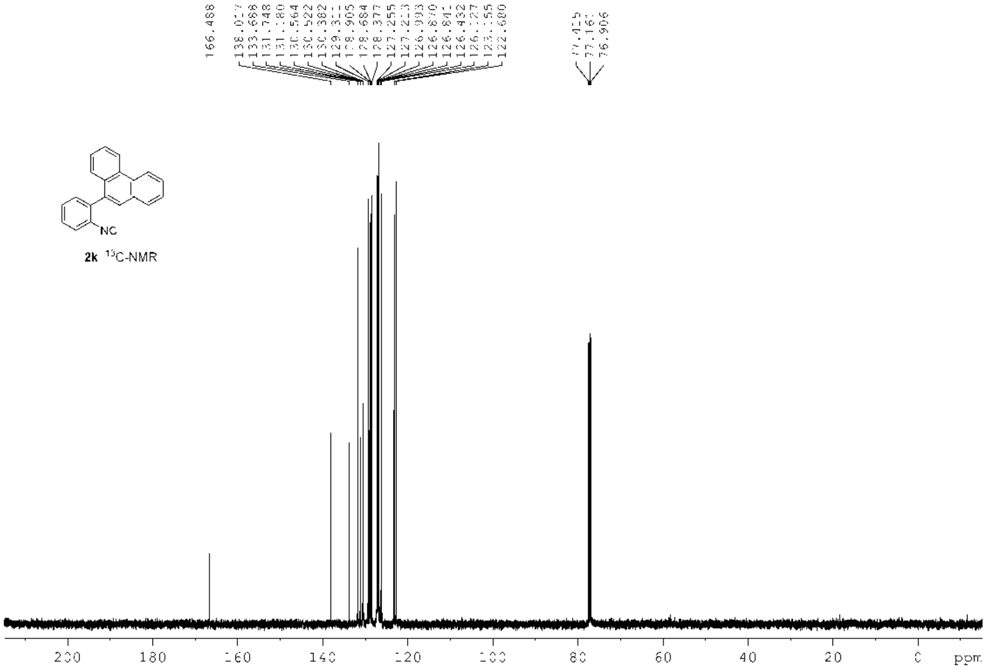


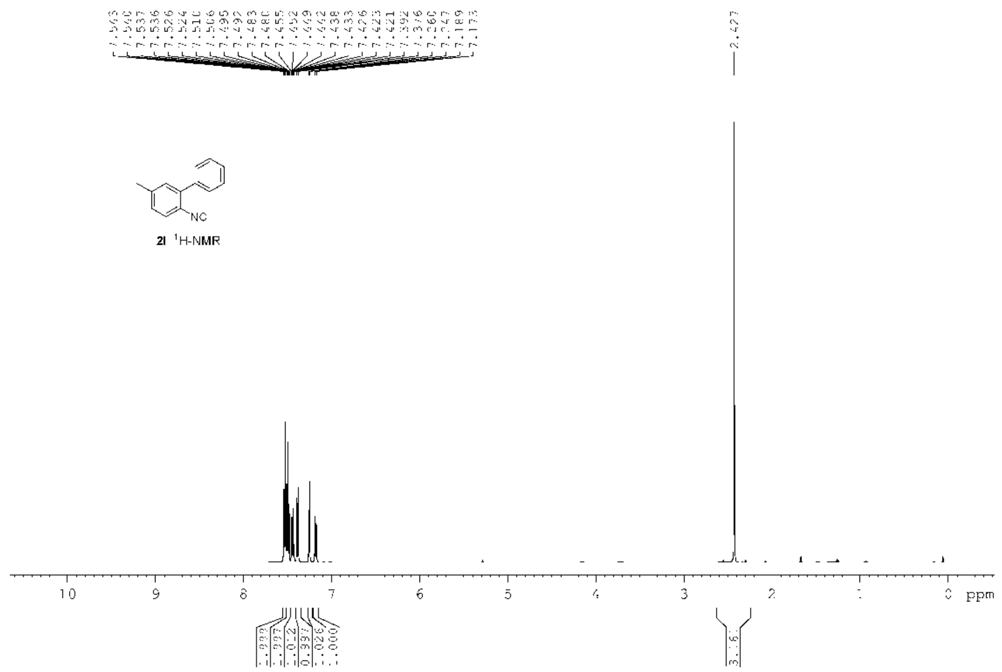
2j ^{1}H-NMR



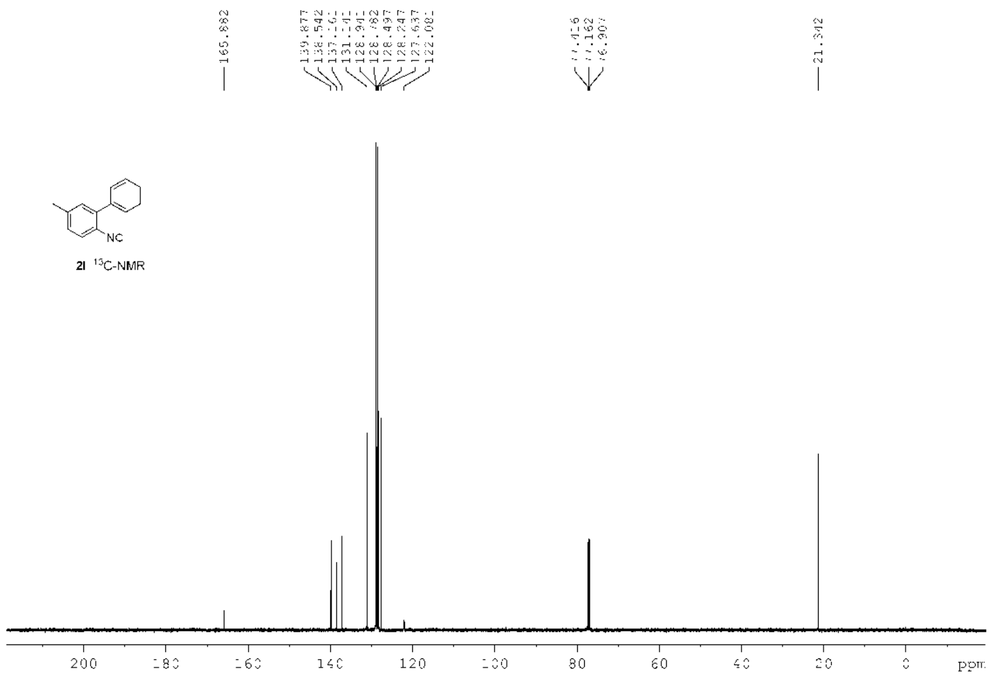
2j ^{13}C-NMR


8.853
8.836
8.803
8.786
7.981
7.965
7.783
7.758
7.743
7.707
7.692
7.678
7.628
7.607
7.542
7.534
7.514
7.504
7.498
7.489
7.480
7.260
NC
2k ¹H-NMR
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.027
1.041
2.966
1.071
2.976
3.344

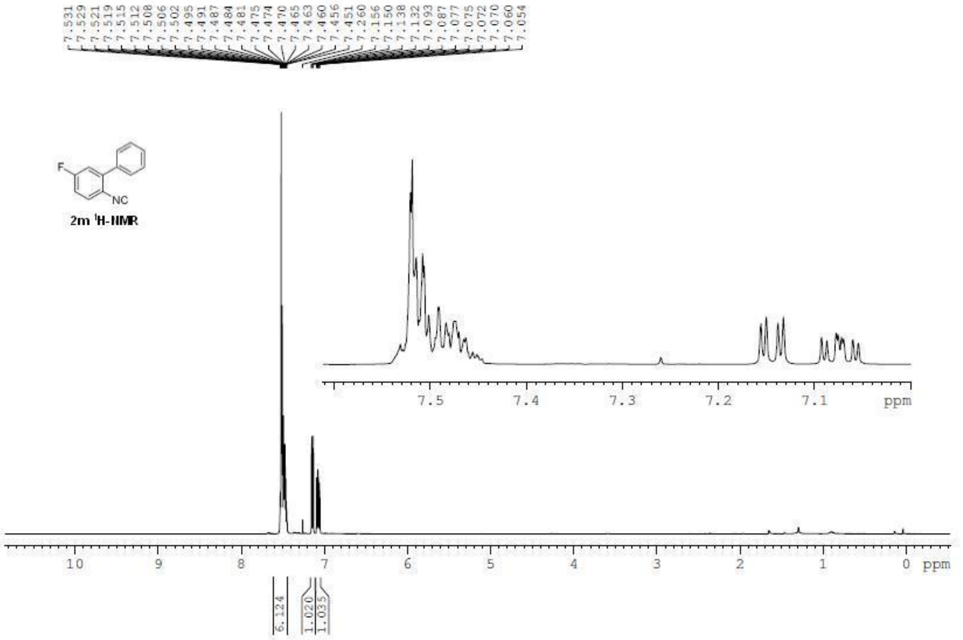

166.488
138.017
133.668
131.748
131.180
130.564
130.522
130.382
129.311
128.905
128.684
128.377
127.255
127.213
126.993
126.870
126.841
126.432
126.127
123.155
122.680
77.415
77.161
76.906
NC
2k ¹³C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm



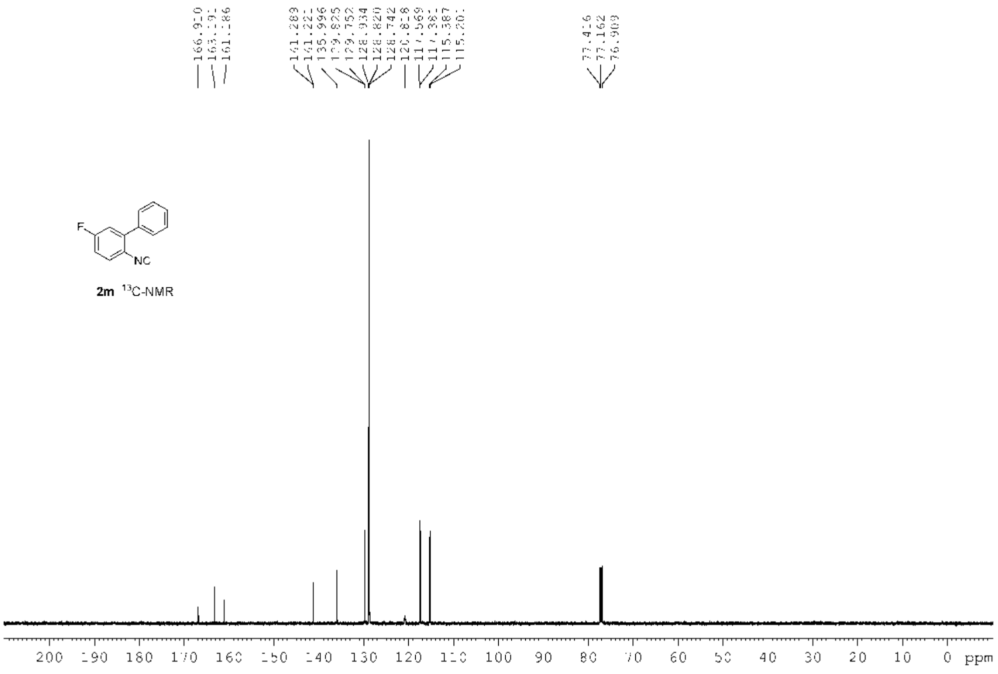
2l ^{1}H-NMR



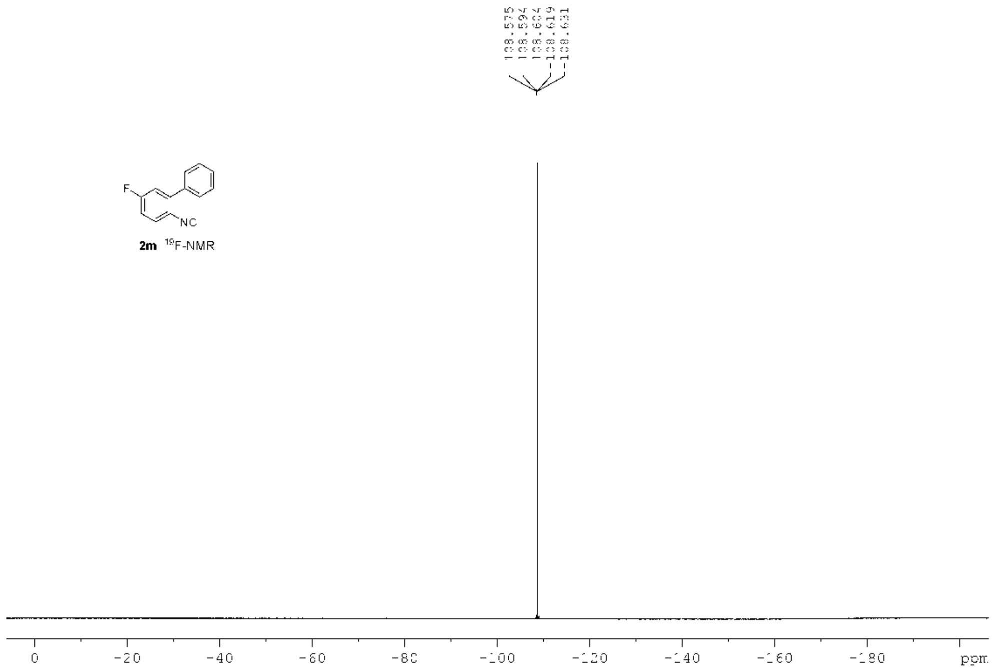
2l ^{13}C-NMR



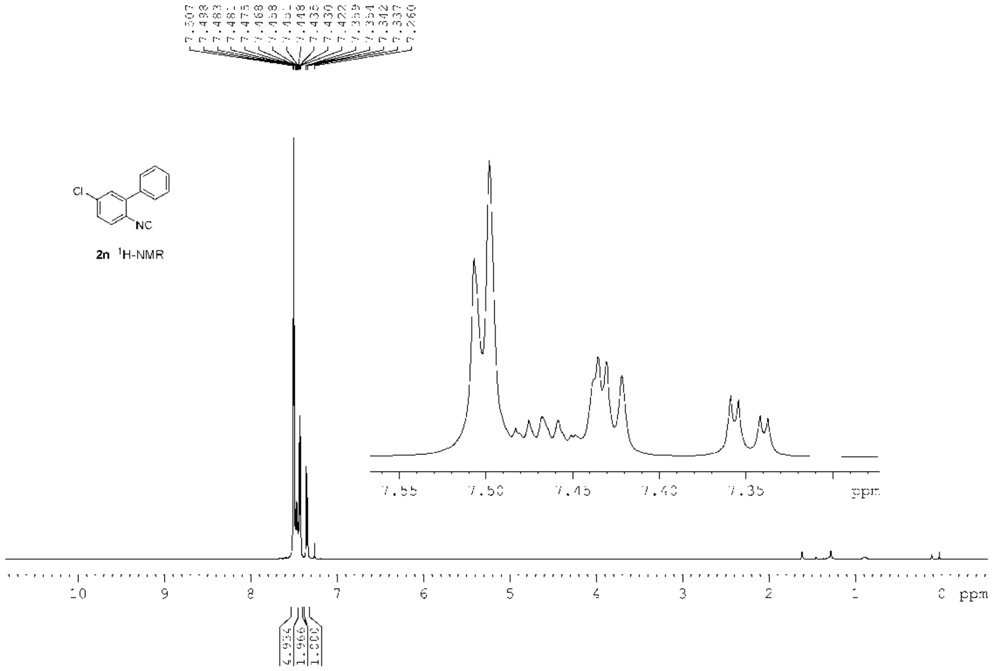
2m ^{1}H-NMR



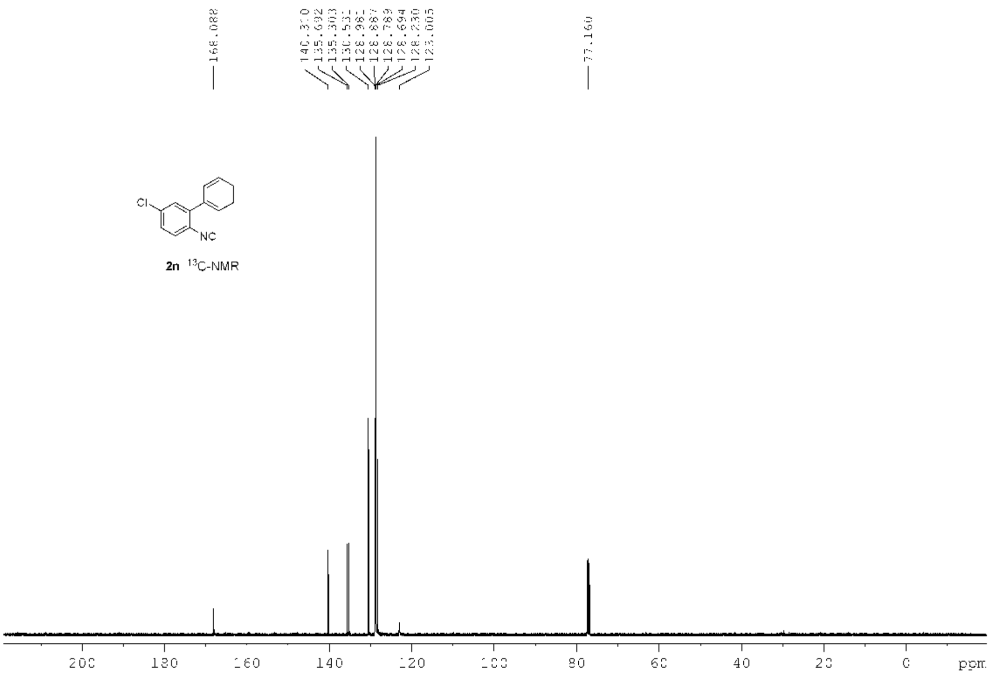
2m ^{13}C-NMR

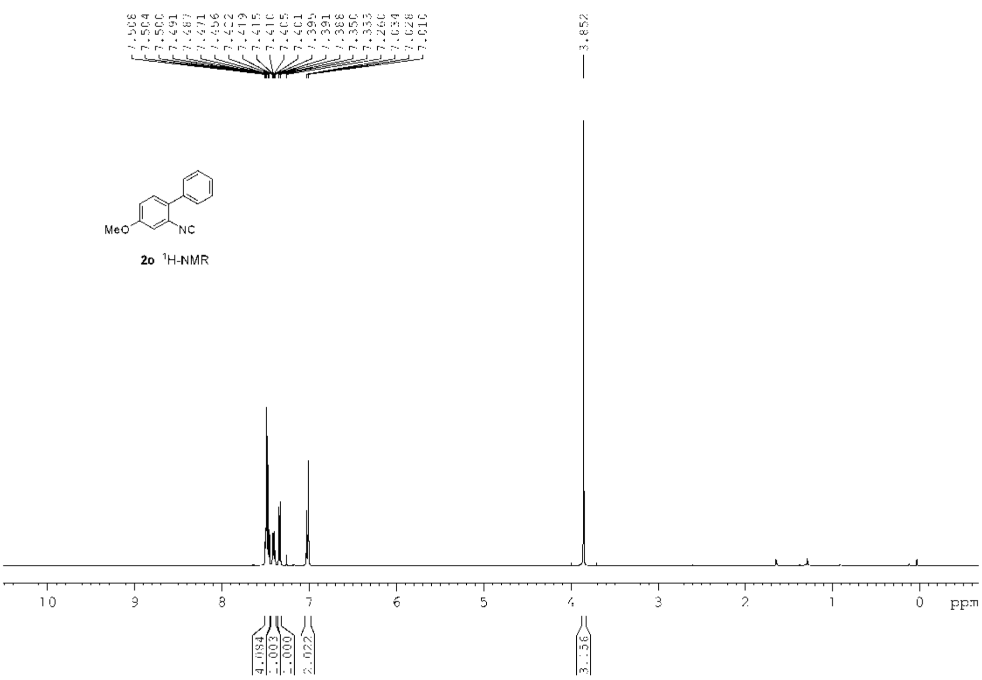


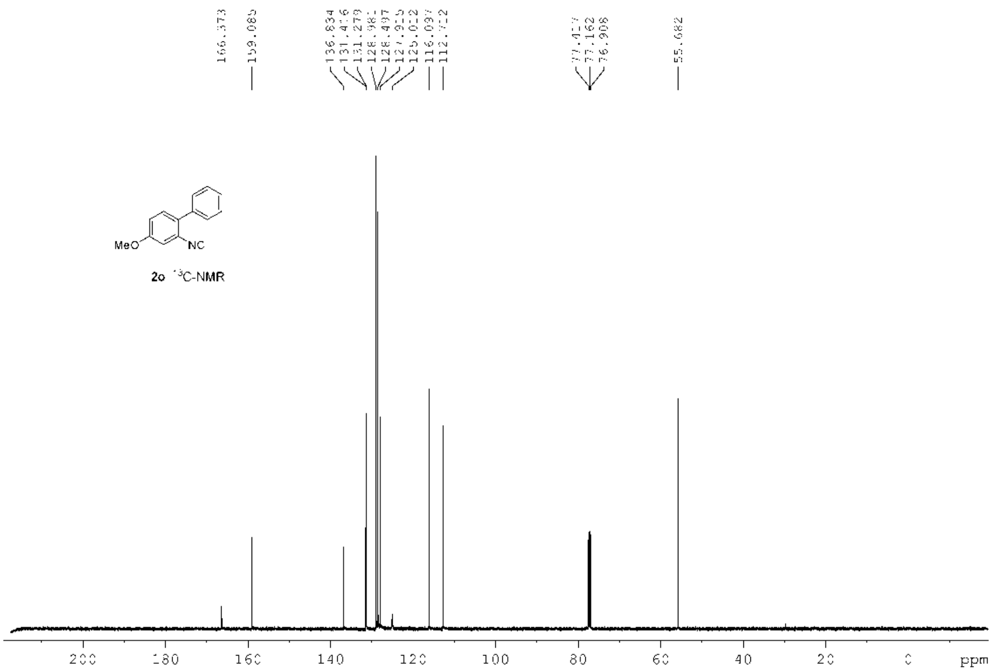
2m ^{19}F-NMR

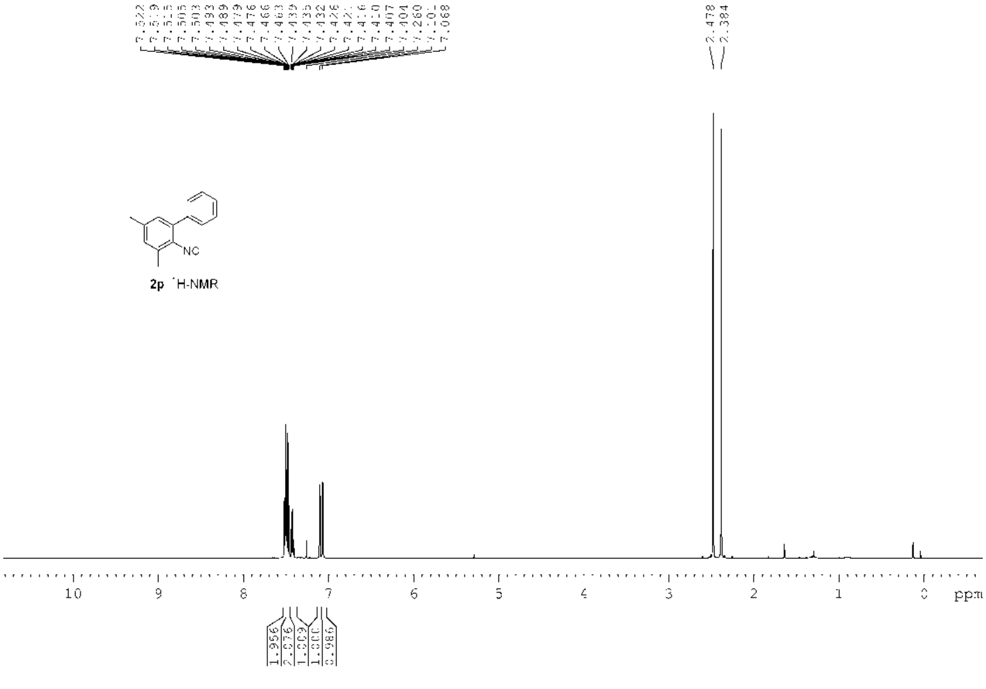


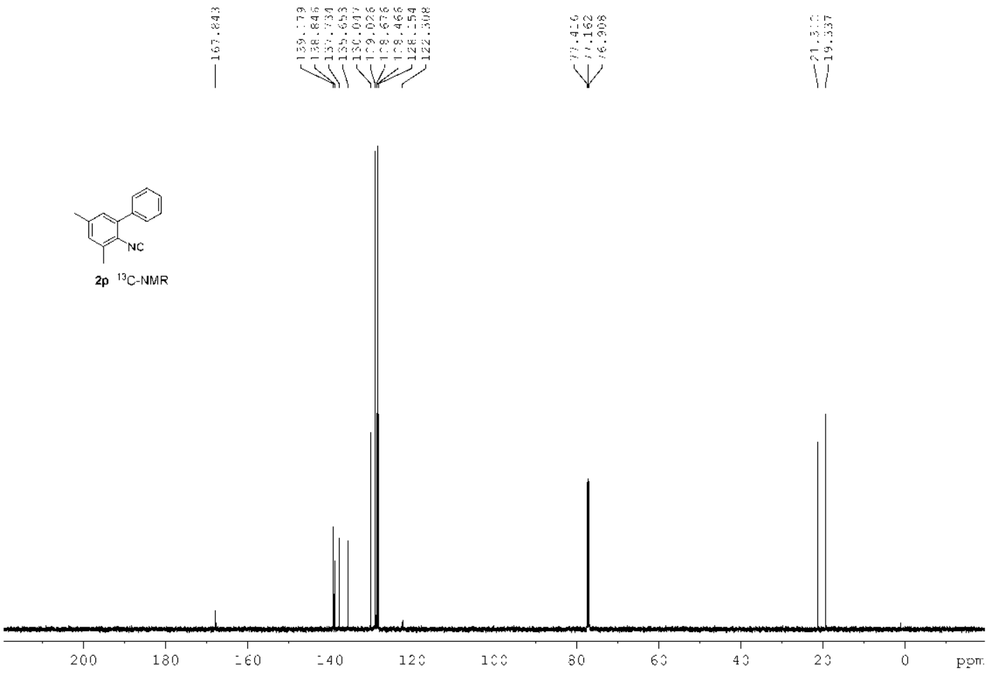
2n ^{1}H-NMR


168.088
140.370
135.692
135.303
130.531
128.961
128.867
128.789
128.694
128.230
123.005
77.160
Cl
NC
2n ^{13}C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

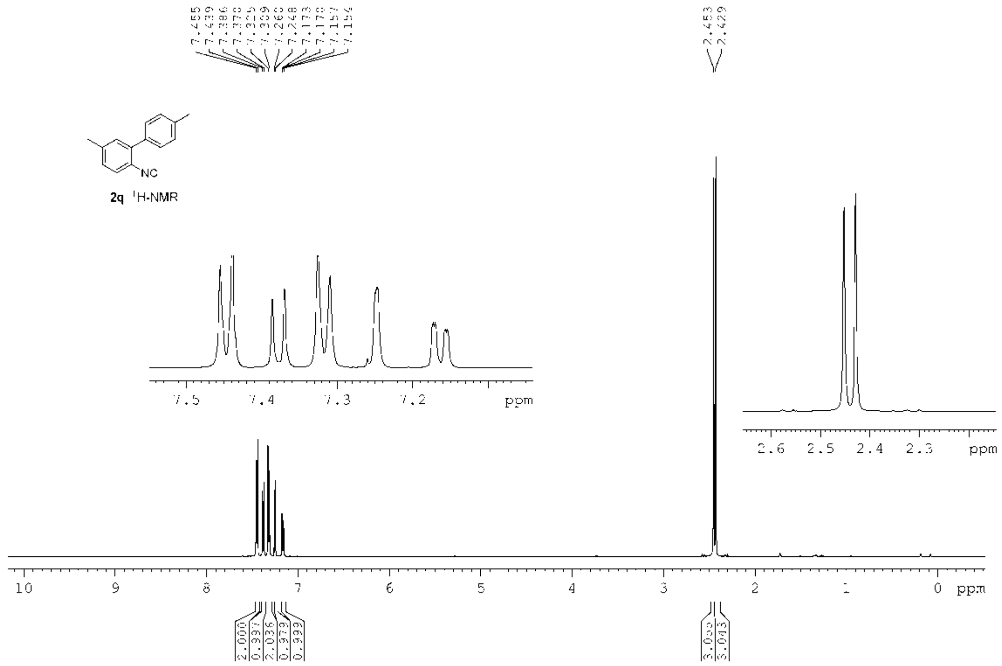

7.508
7.504
7.500
7.491
7.487
7.471
7.456
7.422
7.419
7.415
7.410
7.405
7.401
7.395
7.391
7.388
7.350
7.333
7.260
7.034
7.028
7.010
3.852
MeO
NC
2o ^{1}H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm
4.084
1.003
1.000
2.022
3.156


166.373
159.085
136.834
131.416
131.279
128.981
128.497
127.915
125.012
116.037
112.752
77.417
77.162
76.908
55.682
MeO
NC
2o ¹³C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

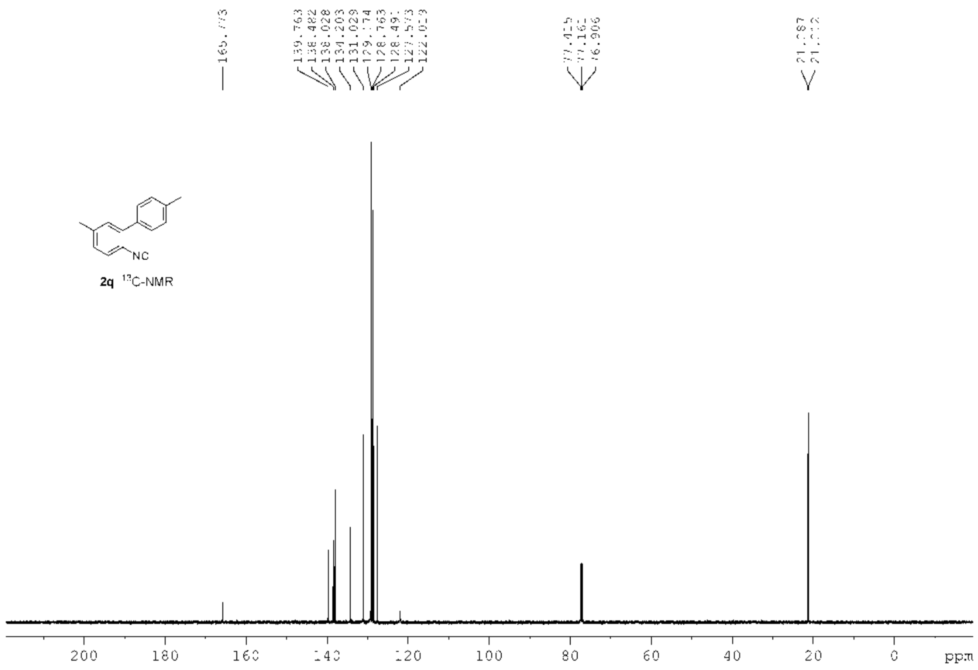

7.522
7.519
7.515
7.505
7.503
7.493
7.489
7.479
7.476
7.466
7.463
7.439
7.435
7.432
7.426
7.421
7.416
7.410
7.407
7.404
7.260
7.101
7.068
2.478
2.384
NC
2p ¹H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm
1.956
2.076
1.009
1.000
0.986

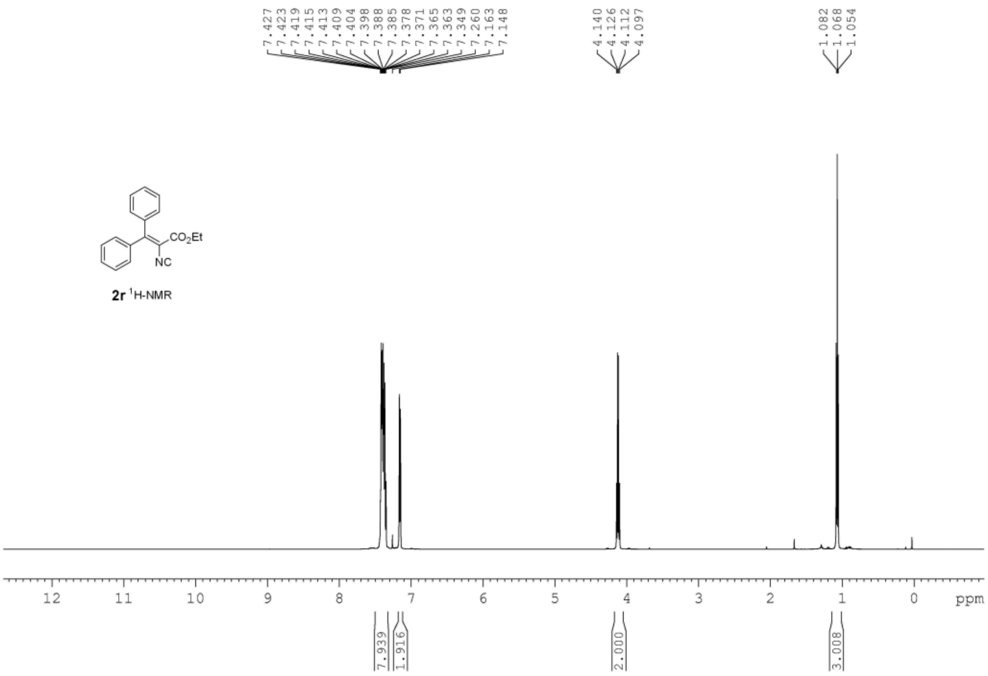


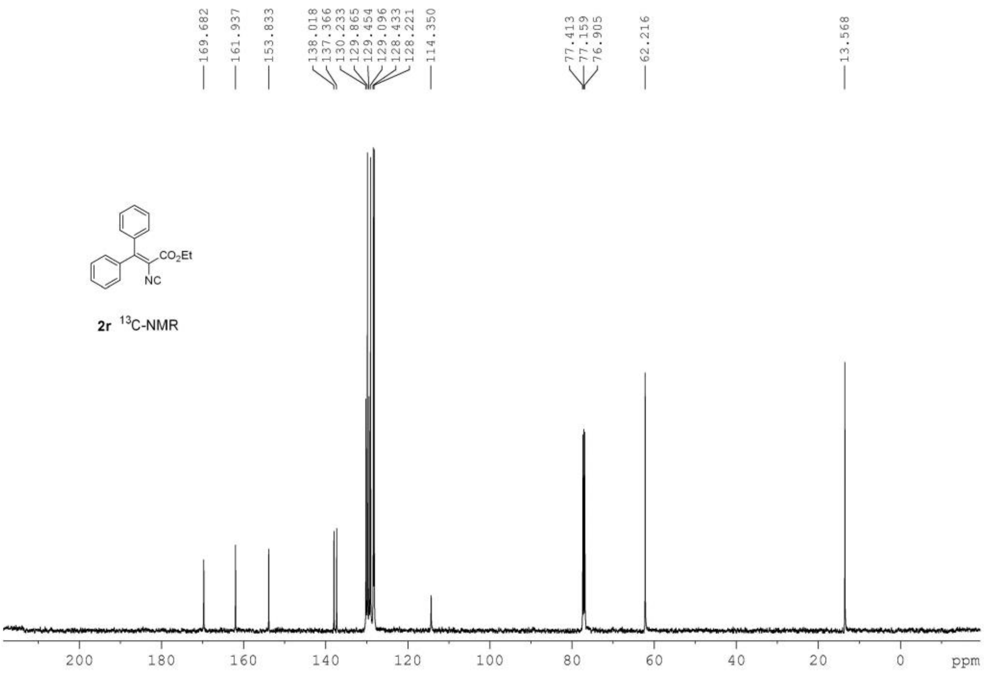
2p ^{13}C-NMR



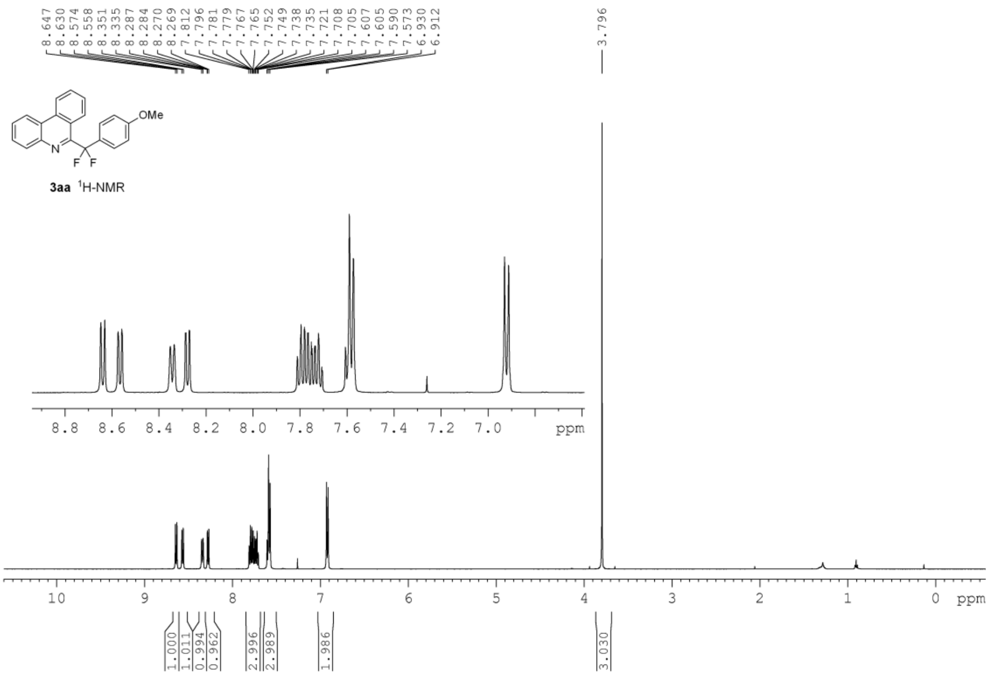
2q ^{1}H-NMR

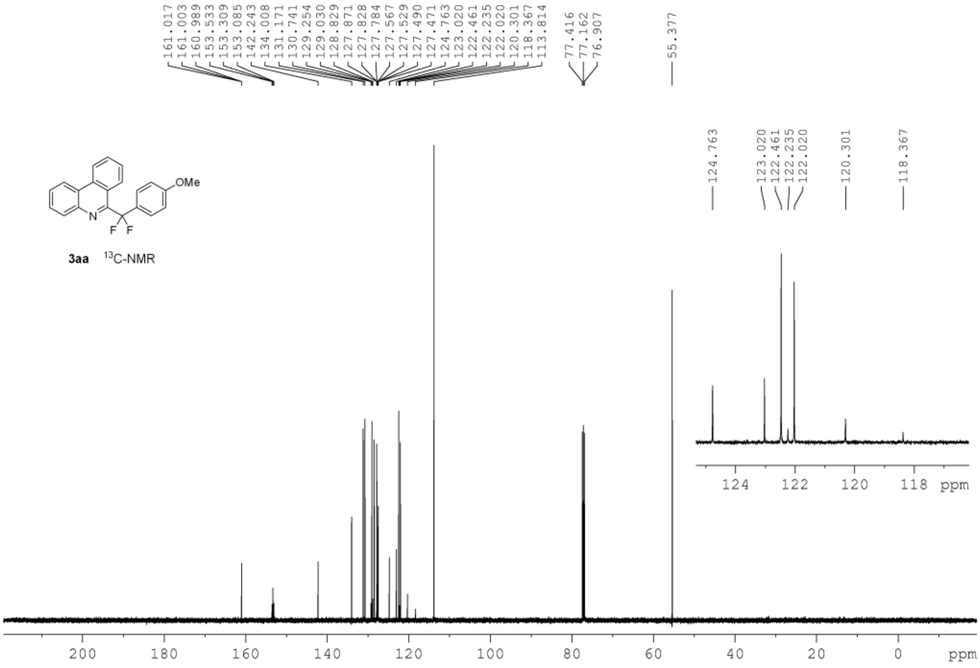

2q ^{13}C-NMR

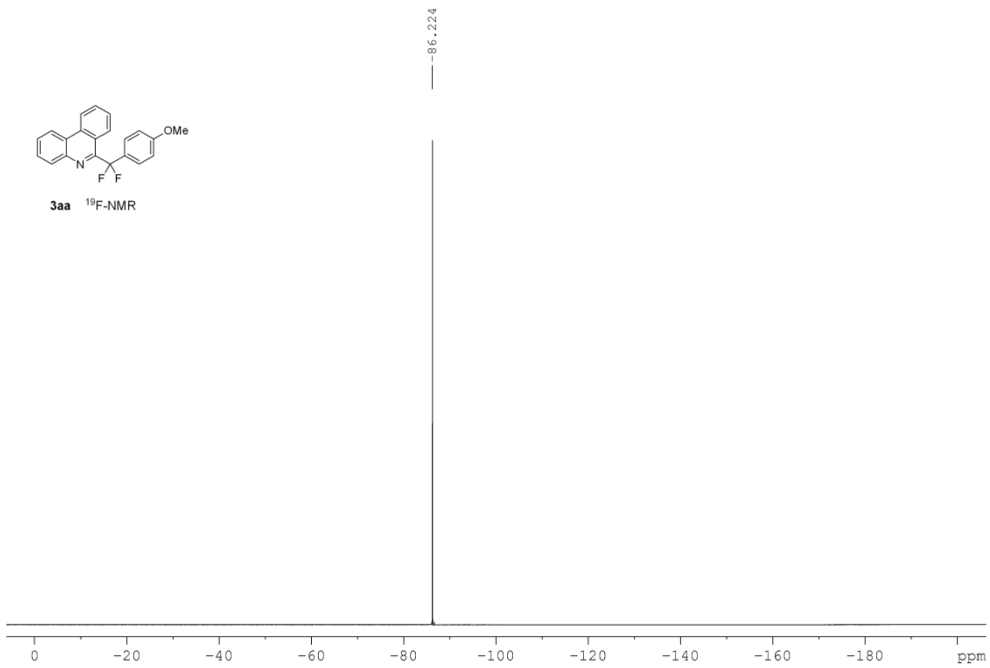

2r ^{1}H-NMR


169.682
161.937
153.833
138.018
137.366
130.233
129.865
129.454
129.096
128.433
128.221
114.350
77.413
77.159
76.905
62.216
13.568
CO2Et
NC
2r 13C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

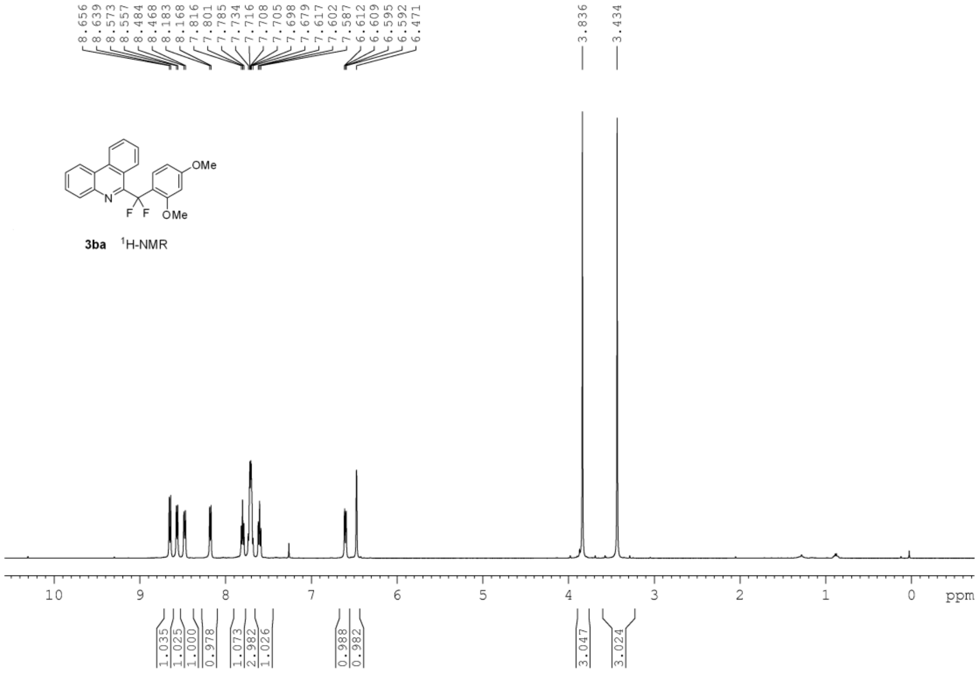
12. NMR spectra for 6-difluoromethyl phenanthridines 3aa-3ar



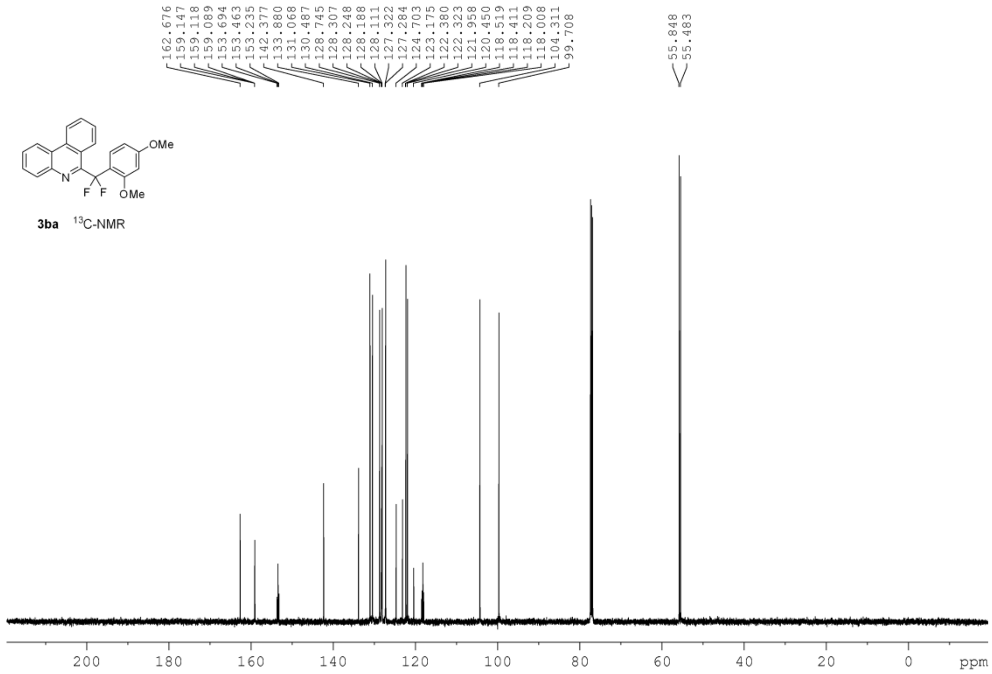




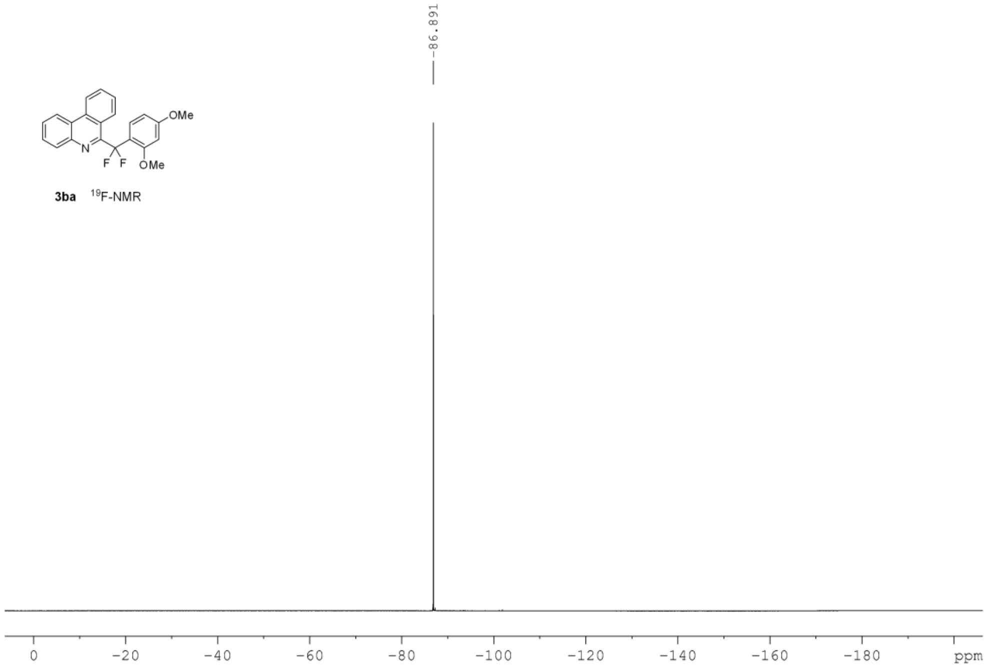
3aa ^{19}F-NMR



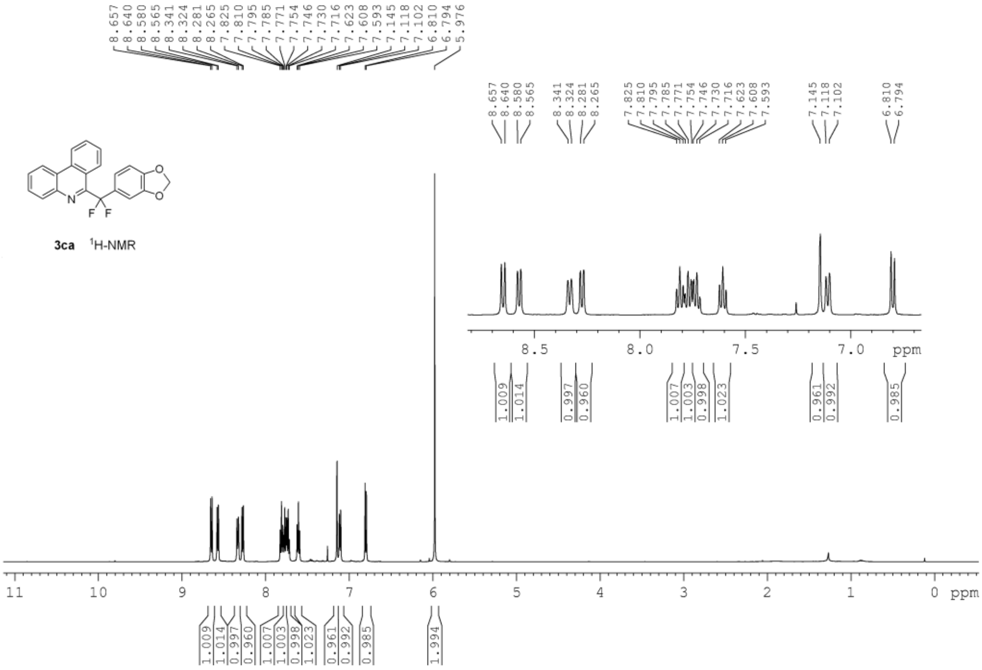
3ba ^{1}H-NMR



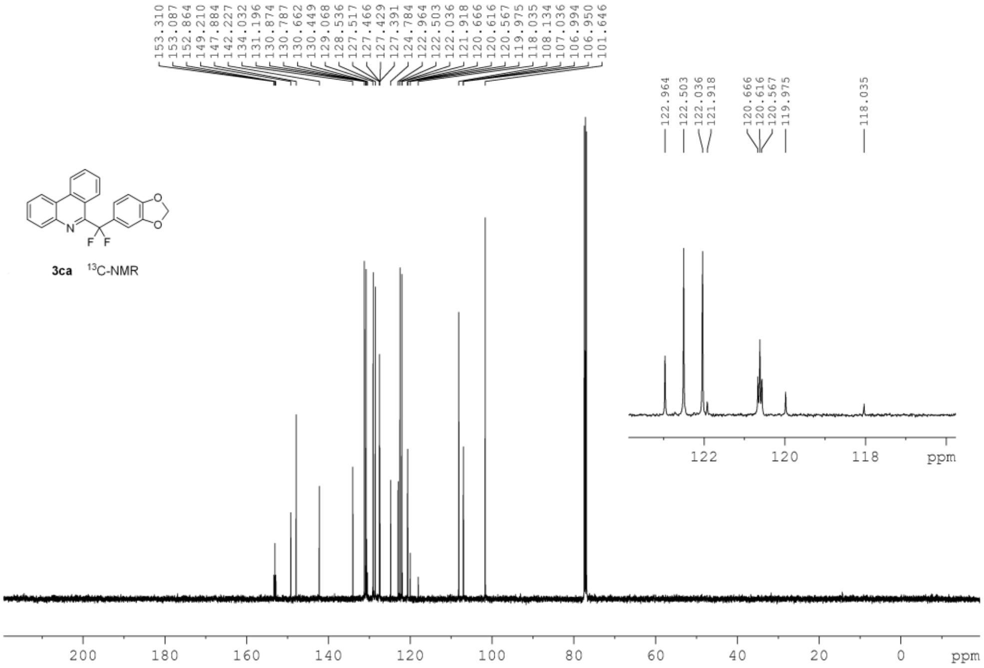
3ba ^{13}C-NMR



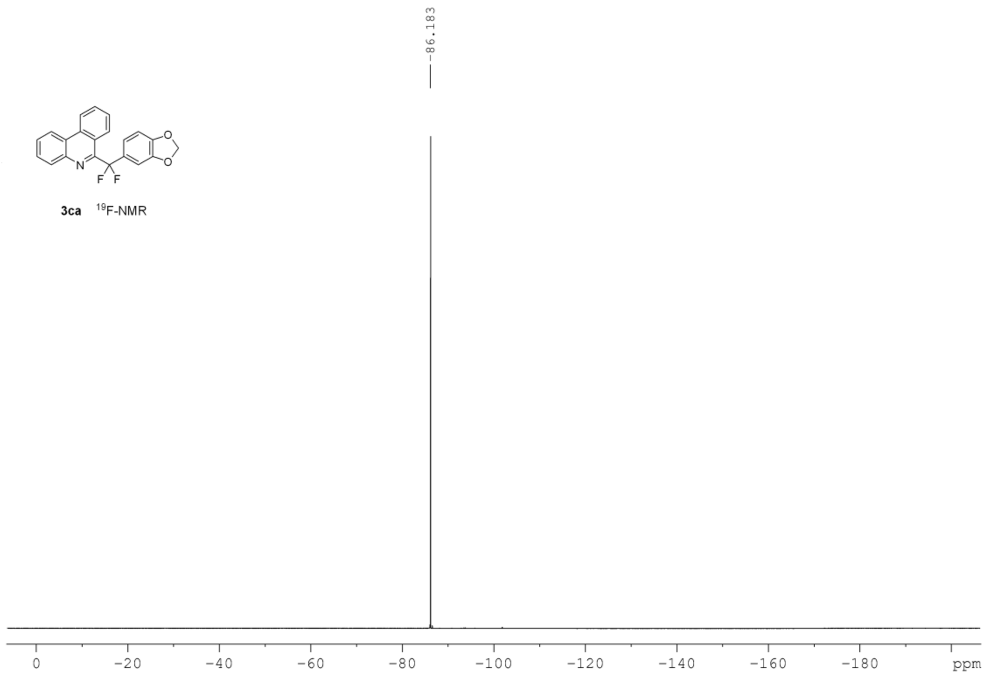
3ba ^{19}F-NMR

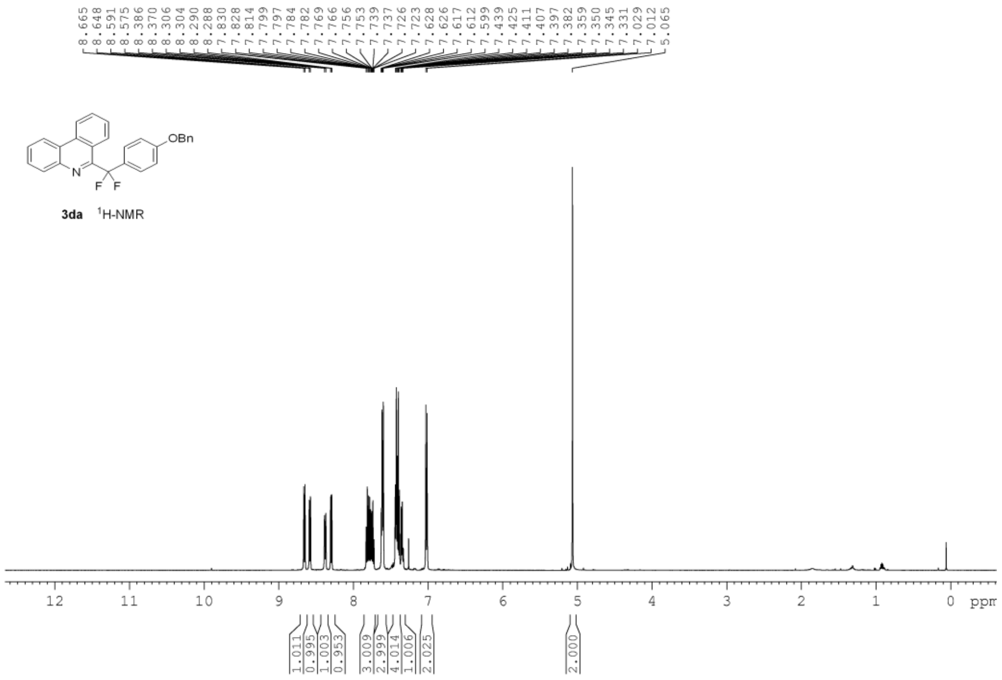


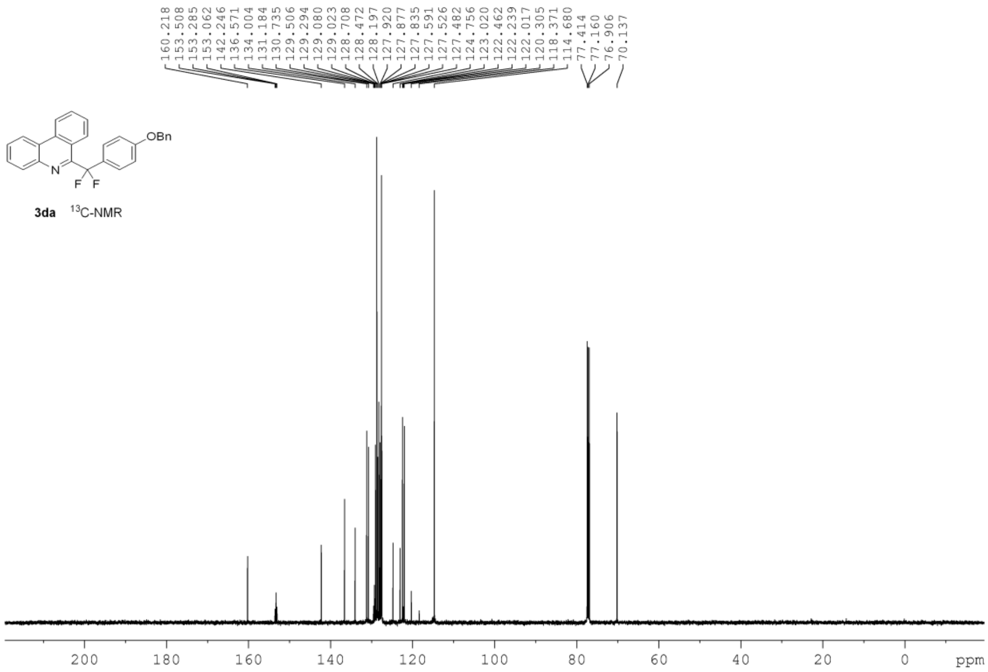
3ca ^{1}H-NMR

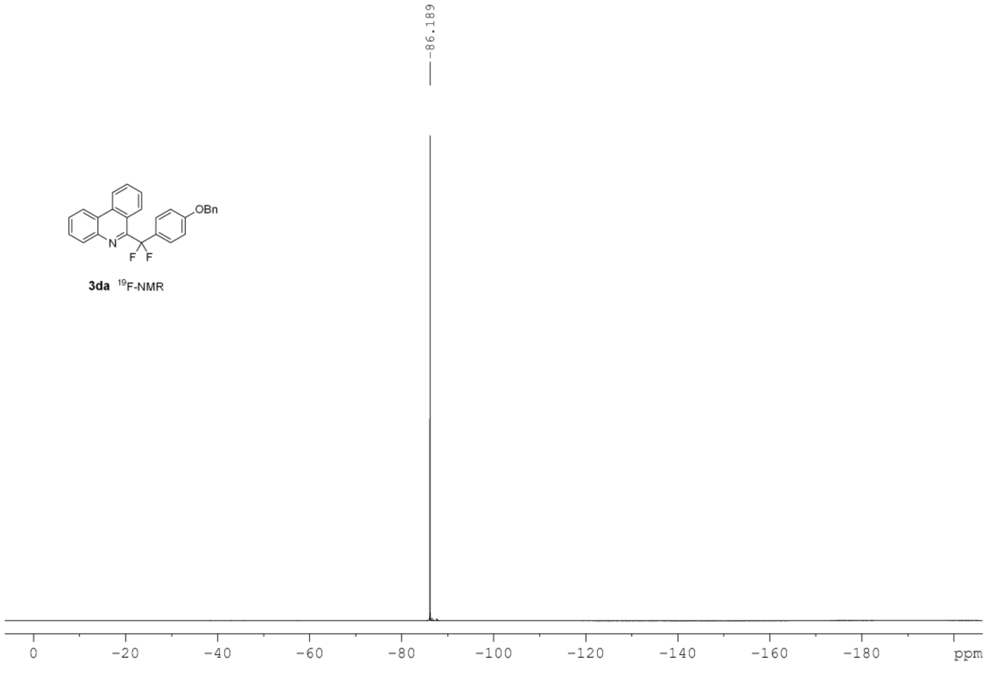


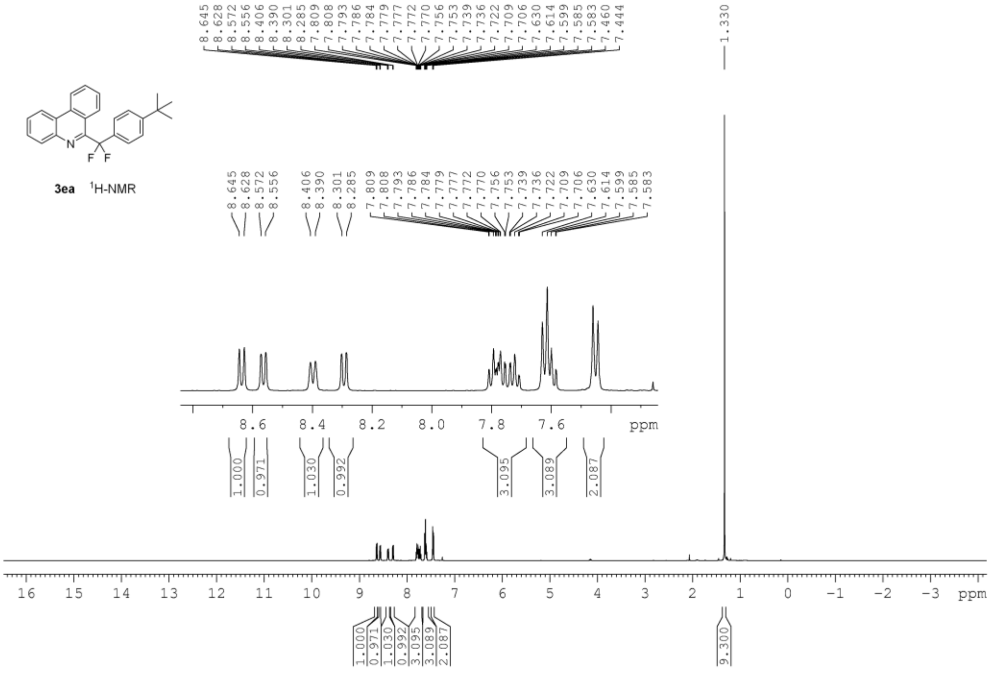
3ca ^{13}C-NMR

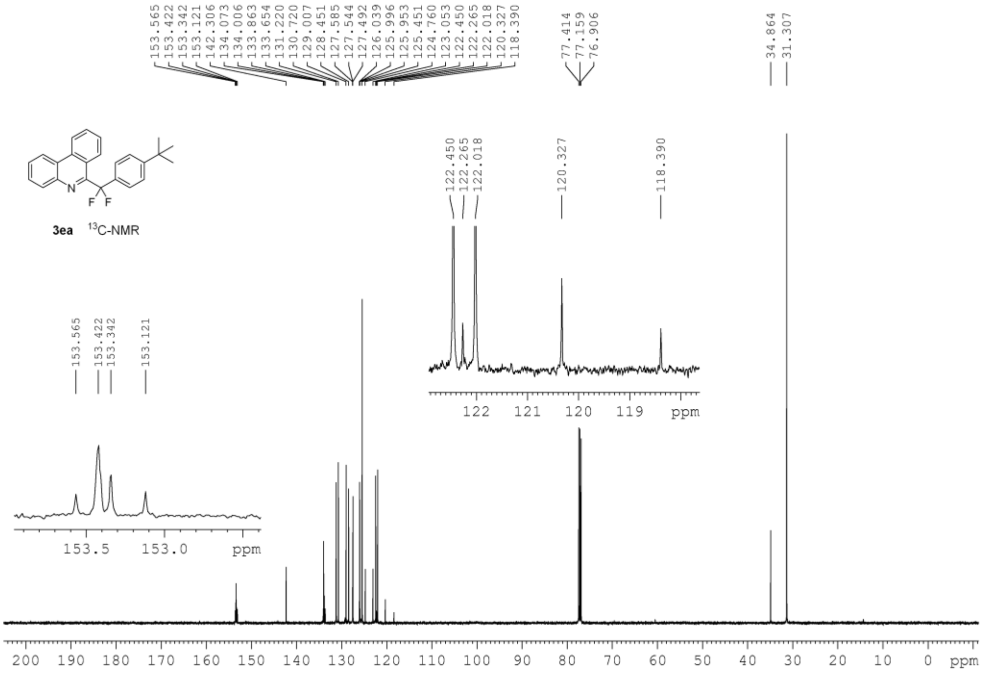

-86.183
N
F F
3ca ¹⁹F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

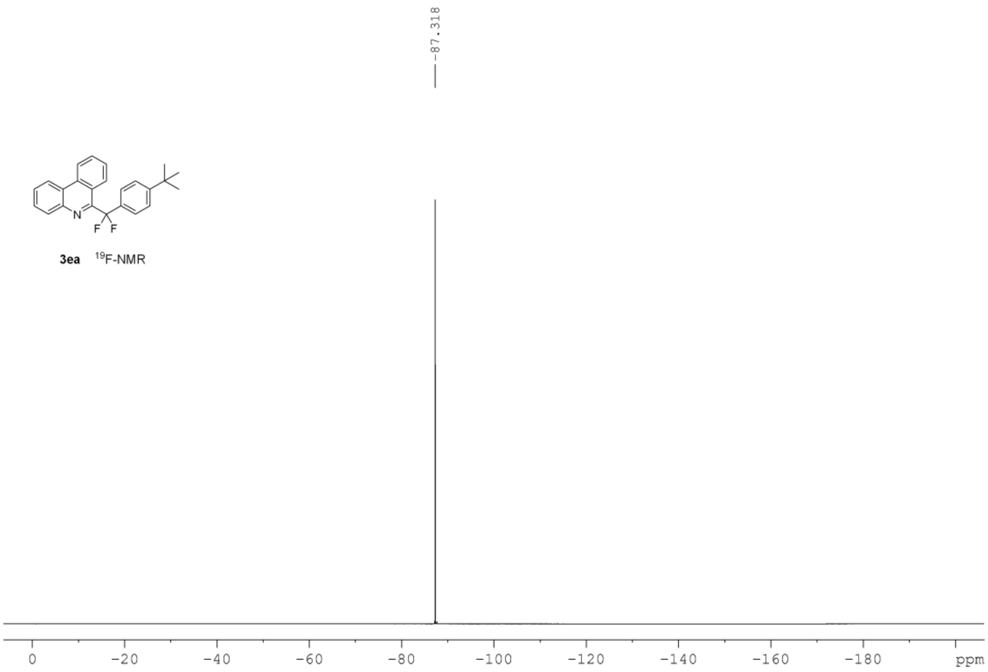

8.665
8.648
8.591
8.575
8.386
8.370
8.306
8.304
8.290
8.288
7.830
7.828
7.814
7.799
7.797
7.784
7.782
7.769
7.766
7.756
7.753
7.739
7.737
7.726
7.723
7.628
7.626
7.617
7.612
7.599
7.439
7.425
7.411
7.407
7.397
7.382
7.359
7.350
7.345
7.331
7.029
7.012
5.065
OBn
N
F F
3da ¹H-NMR
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.011
0.995
1.003
0.953
3.009
2.999
4.014
1.006
2.025
2.000

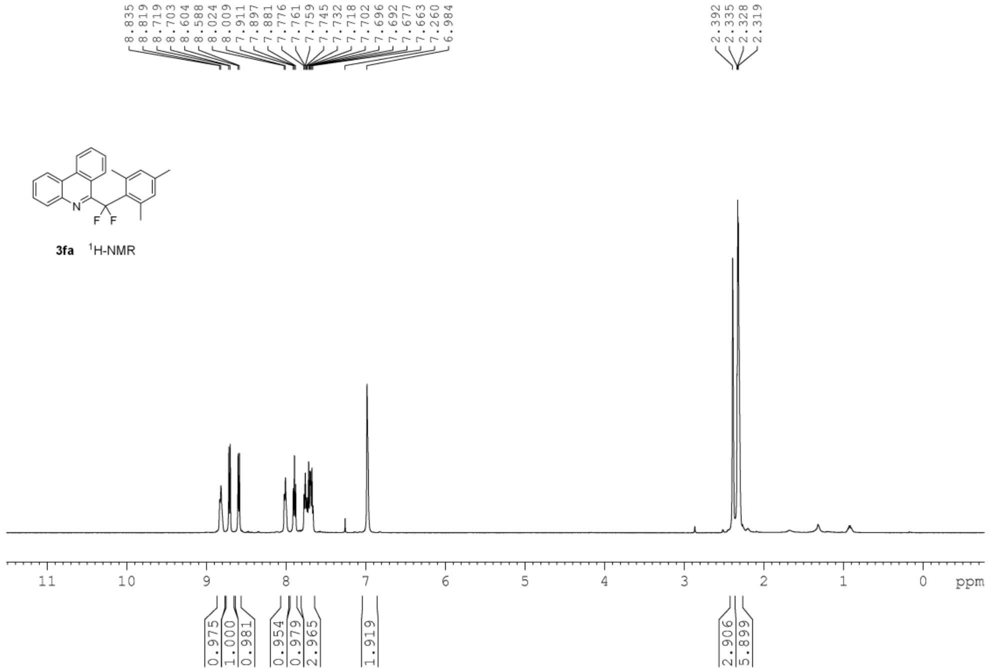

3da ^{13}C-NMR

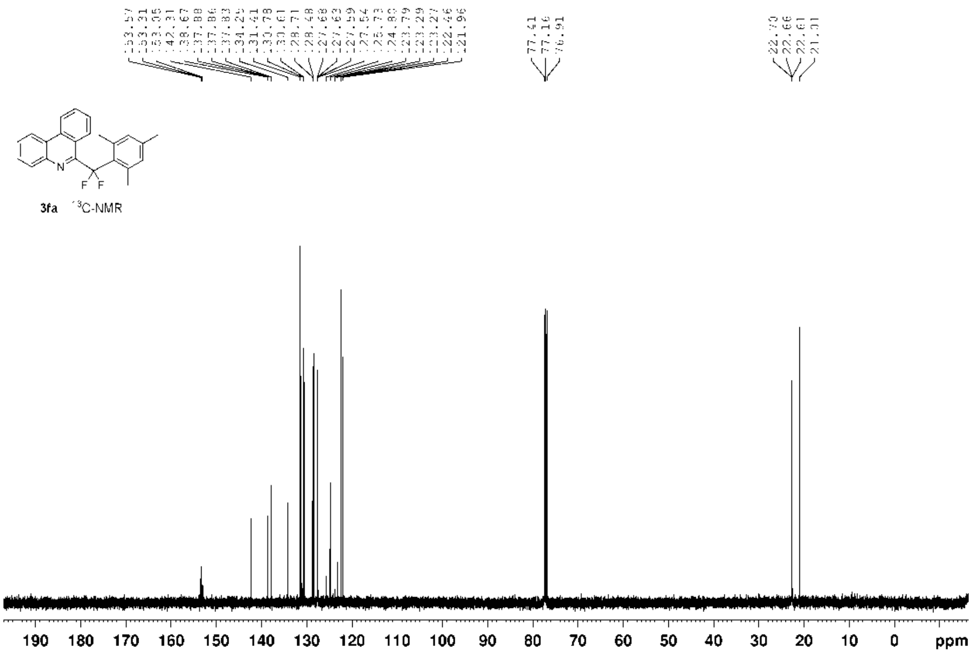

3da ^{19}F-NMR


8.645
8.628
8.572
8.556
8.406
8.390
8.301
8.285
7.809
7.808
7.793
7.786
7.784
7.779
7.777
7.772
7.770
7.756
7.753
7.739
7.736
7.722
7.709
7.706
7.630
7.614
7.599
7.585
7.583
7.460
7.444
1.330
F F
N
3ea ¹H-NMR
8.6
8.4
8.2
8.0
7.8
7.6
ppm
1.000
0.971
1.030
0.992
3.095
3.089
2.087
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
ppm
9.300

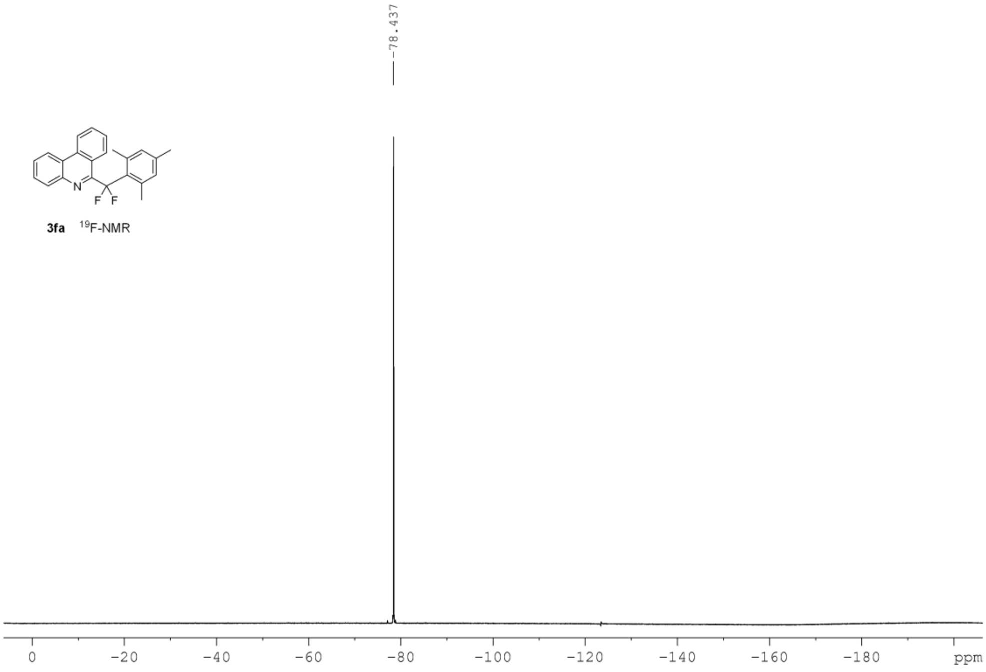

153.565
153.422
153.342
153.121
142.306
134.073
134.006
133.863
133.654
131.220
130.720
129.007
128.451
127.585
127.544
127.492
126.039
125.996
125.953
125.451
124.760
123.053
122.450
122.265
122.018
120.327
118.390
77.414
77.159
76.906
34.864
31.307
F F
N
3ea ¹³C-NMR
122.450
122.265
122.018
120.327
118.390
122
121
120
119
ppm
153.565
153.422
153.342
153.121
153.5
153.0
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


3ea ^{19}F-NMR

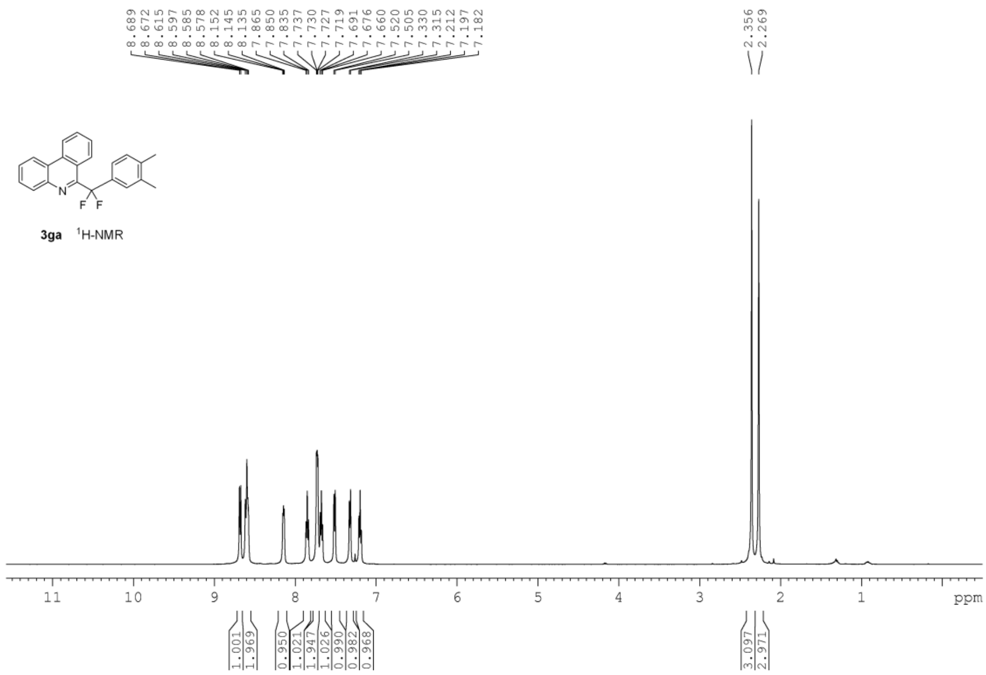

3fa ^{1}H-NMR

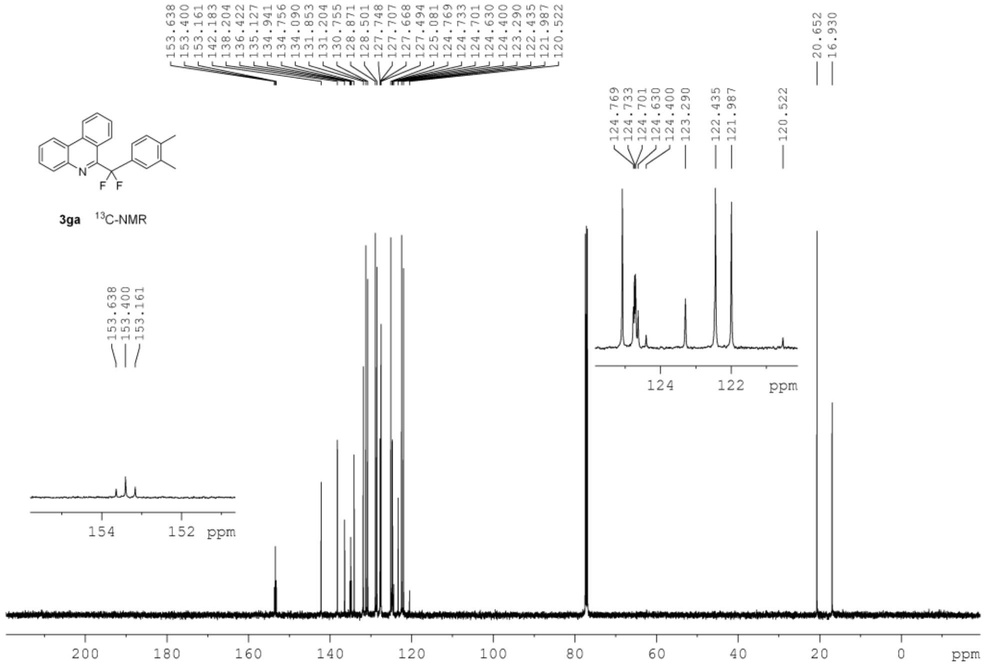


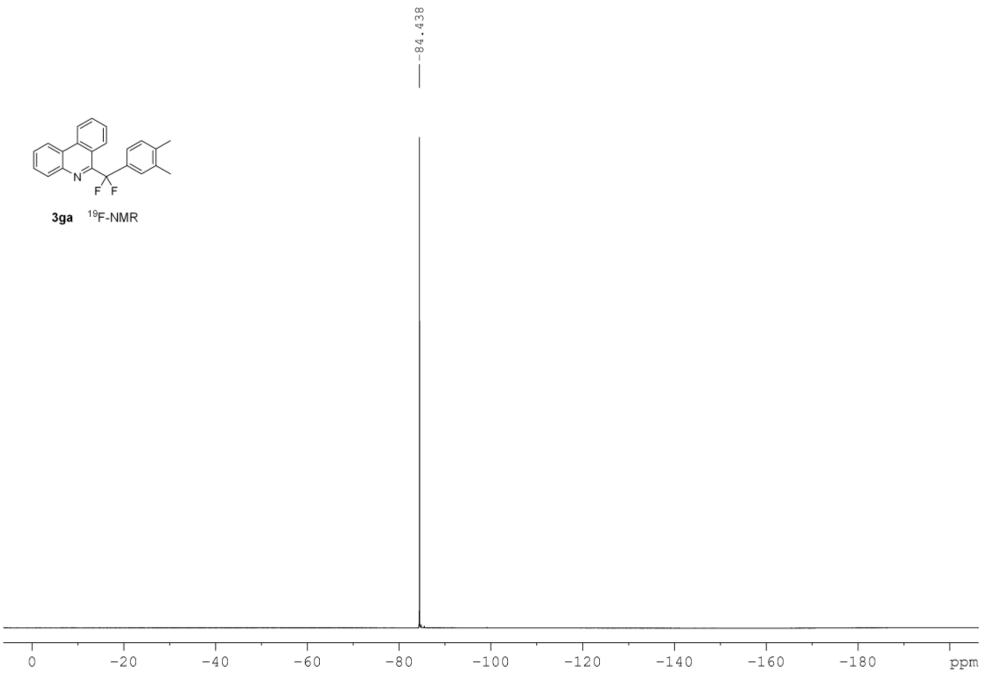
3fa ^{13}C-NMR



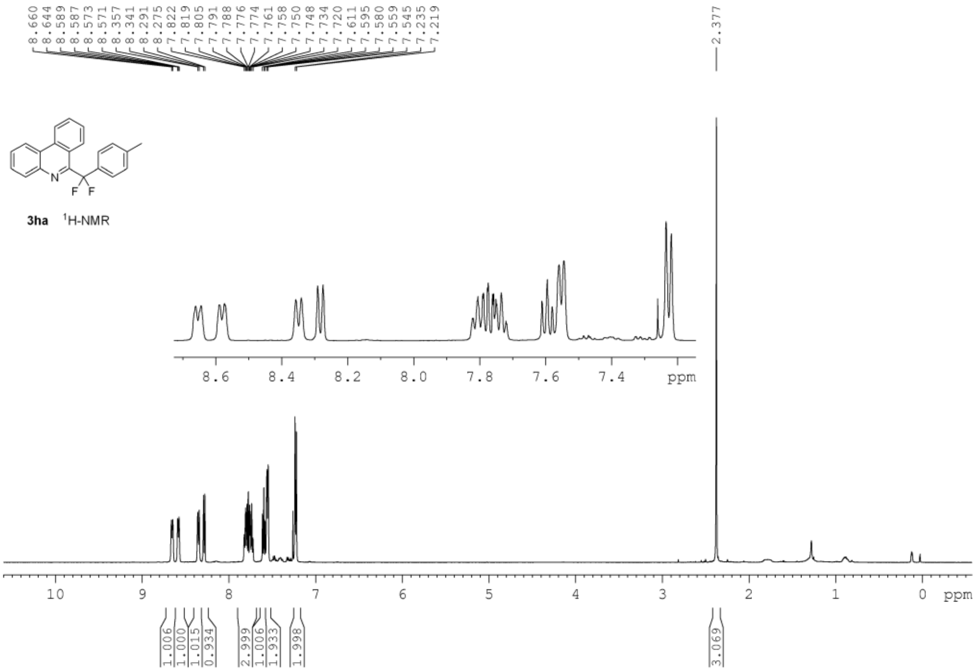
3fa ^{19}F-NMR


8.689
8.672
8.615
8.597
8.585
8.578
8.152
8.145
8.135
7.865
7.850
7.835
7.737
7.730
7.727
7.719
7.691
7.676
7.660
7.520
7.505
7.330
7.315
7.212
7.197
7.182
2.356
2.269
N
F F
3ga ¹H-NMR
11
10
9
8
7
6
5
4
3
2
1
ppm
1.001
1.969
0.950
1.021
1.947
1.026
0.990
0.982
0.968
3.097
2.971

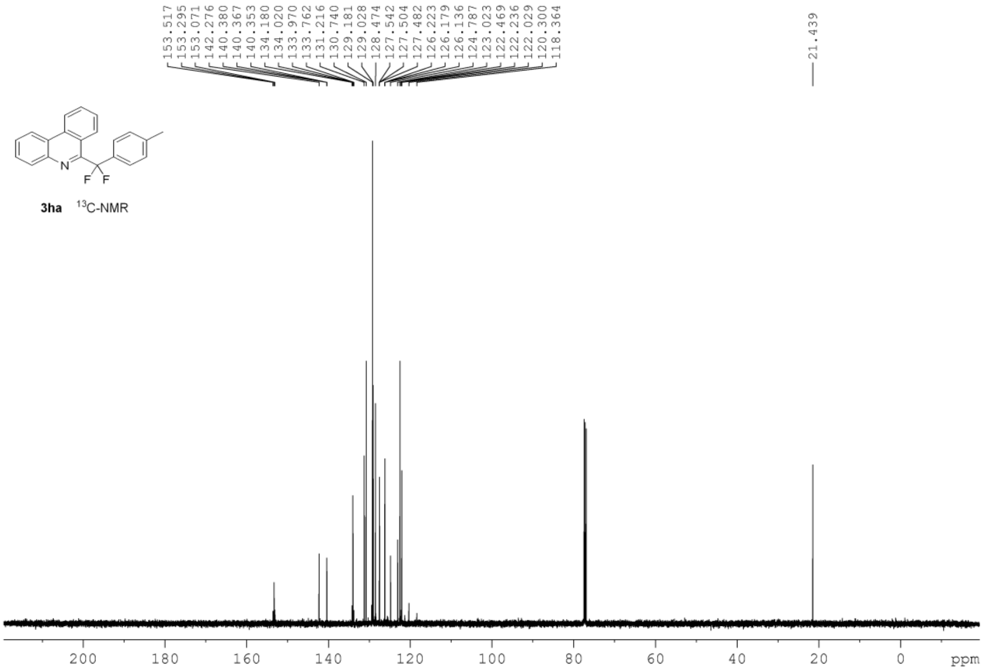

153.638
153.400
153.161
142.183
138.204
136.422
135.127
134.941
134.756
134.090
131.853
131.204
130.755
128.871
128.501
127.748
127.707
127.668
127.494
125.081
124.769
124.733
124.701
124.630
124.400
123.290
122.435
121.987
120.522
20.652
16.930
N
F F
3ga ¹³C-NMR
124.769
124.733
124.701
124.630
124.400
123.290
122.435
121.987
120.522
124
122
ppm
153.638
153.400
153.161
154
152
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

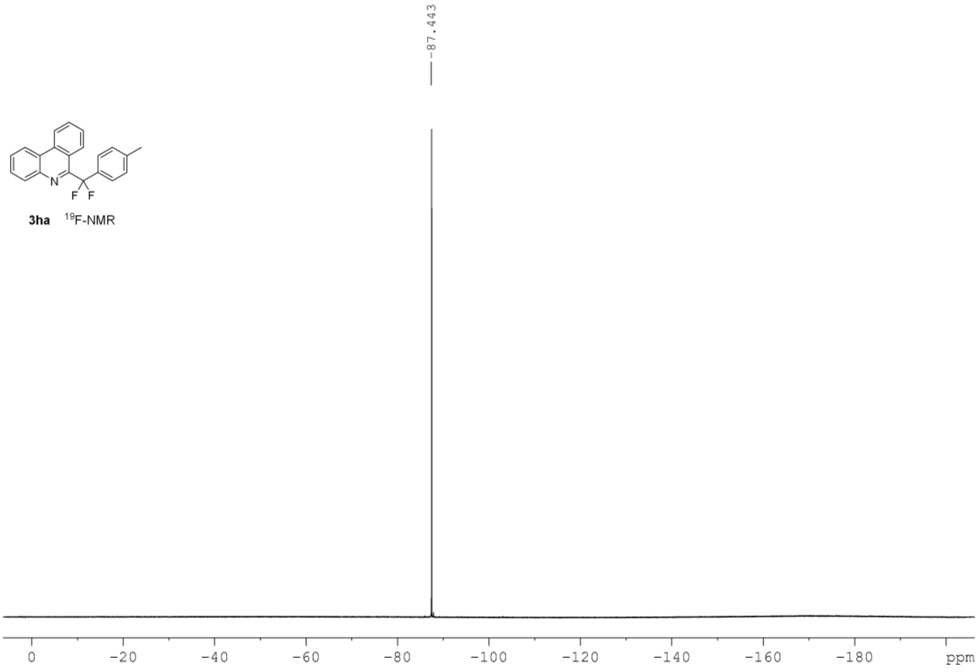


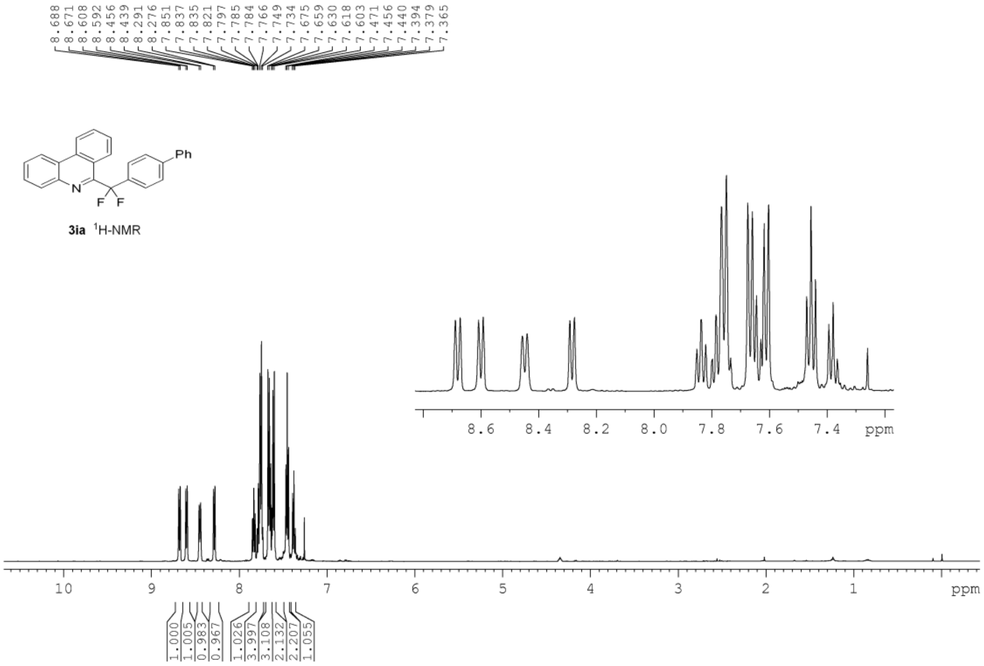
3ga ^{19}F-NMR



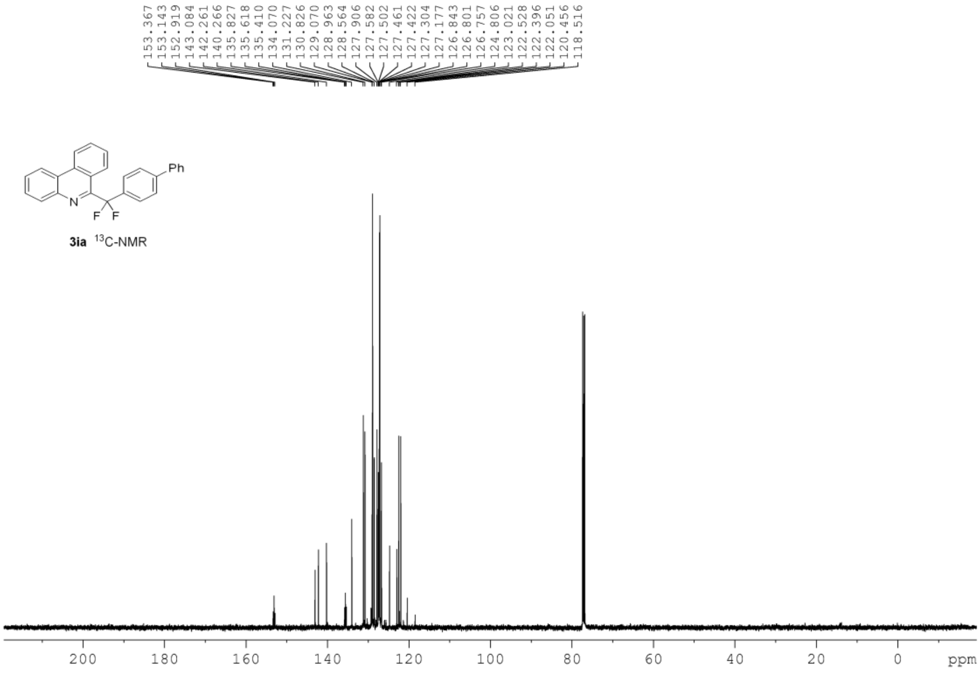
3ha ^{1}H-NMR


153.517
153.295
153.071
142.276
140.380
140.367
140.353
134.180
134.020
133.970
133.762
131.216
130.740
129.181
129.028
128.474
127.542
127.504
127.482
126.223
126.179
126.136
124.787
123.023
122.469
122.236
122.029
120.300
118.364
21.439
N
F
F
3ha ¹³C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm

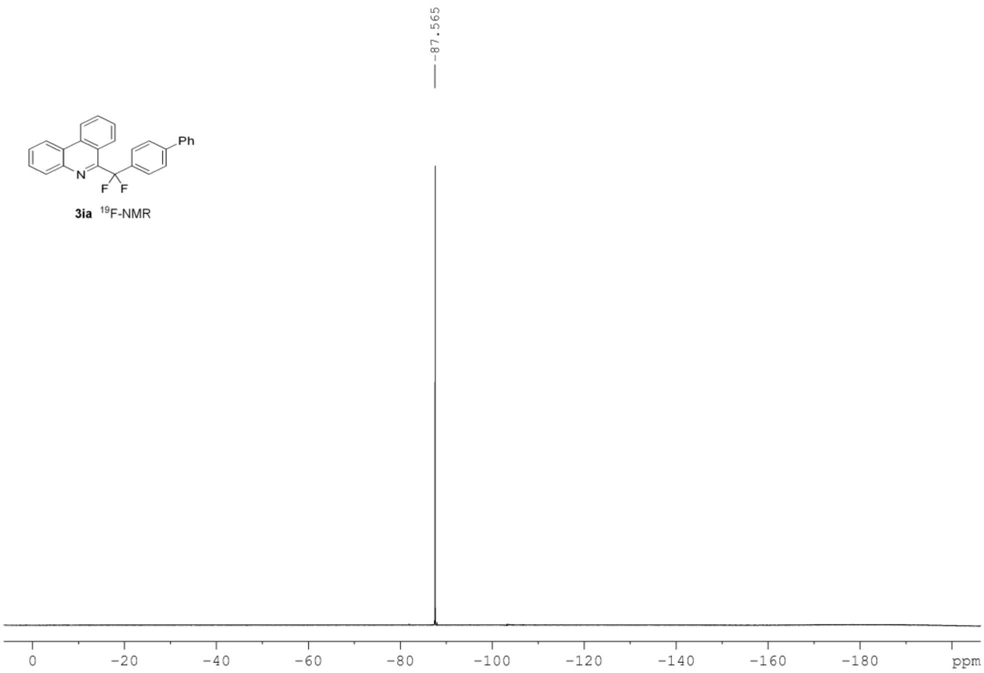

-87.443
N
F
F
3ha ¹⁹F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

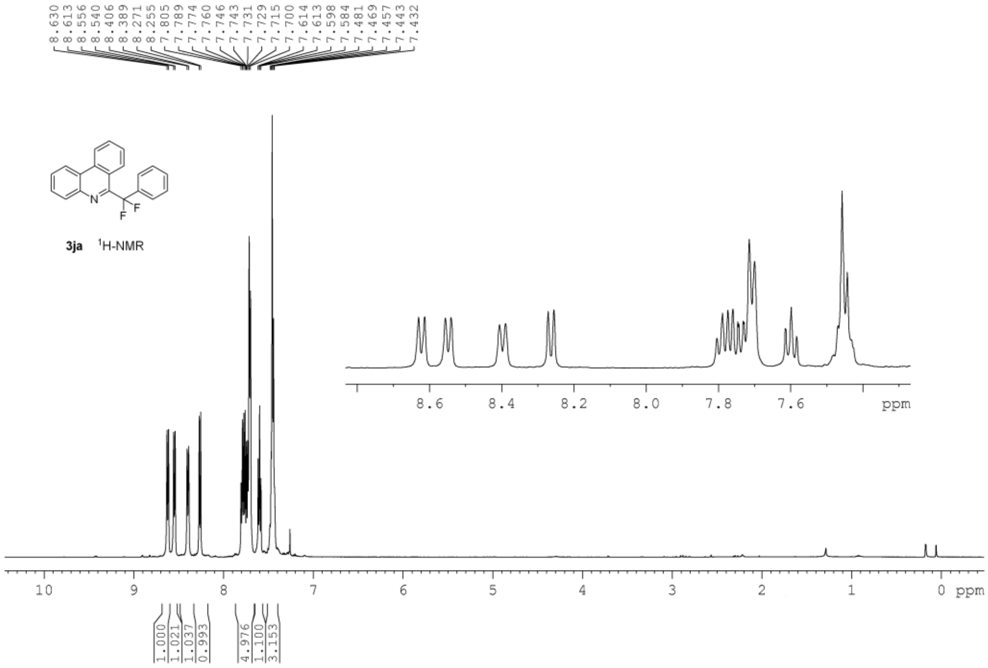


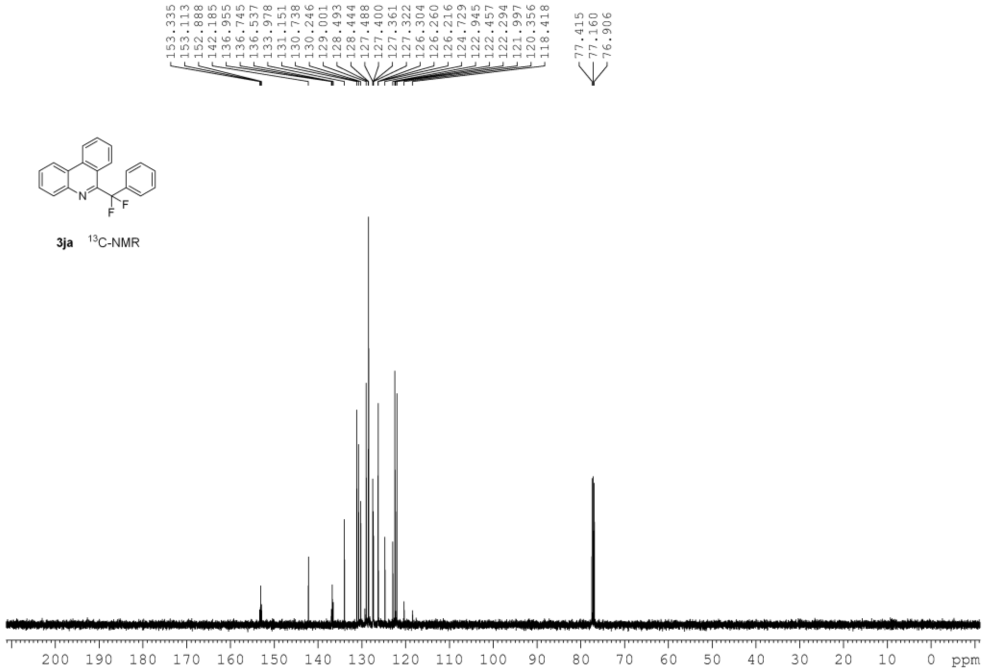
3ia ¹H-NMR



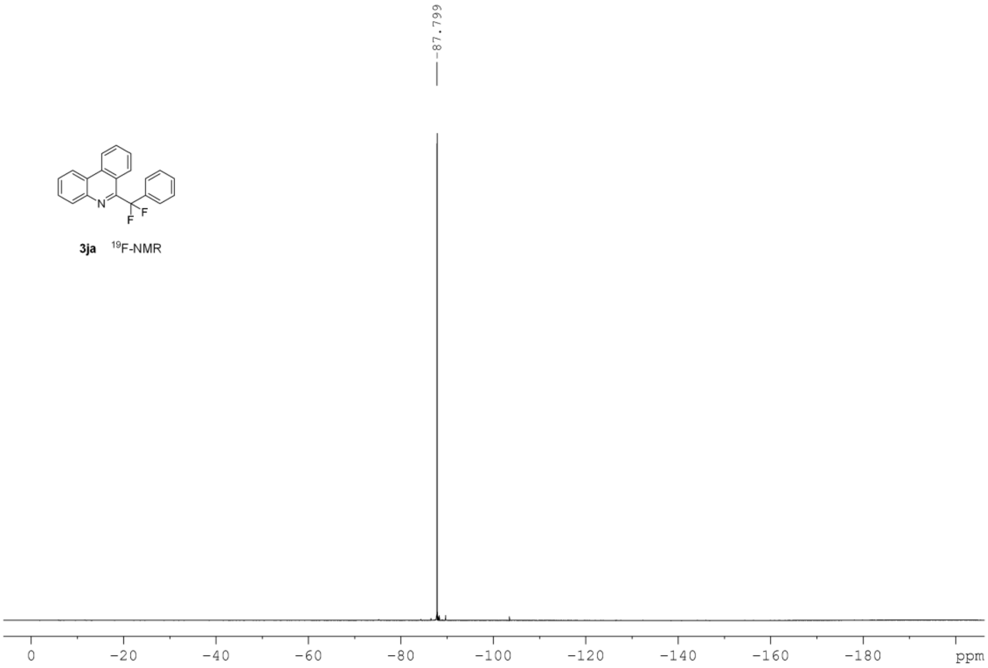
3ia ¹³C-NMR


-87.565
Ph
N
F F
3ia ¹⁹F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

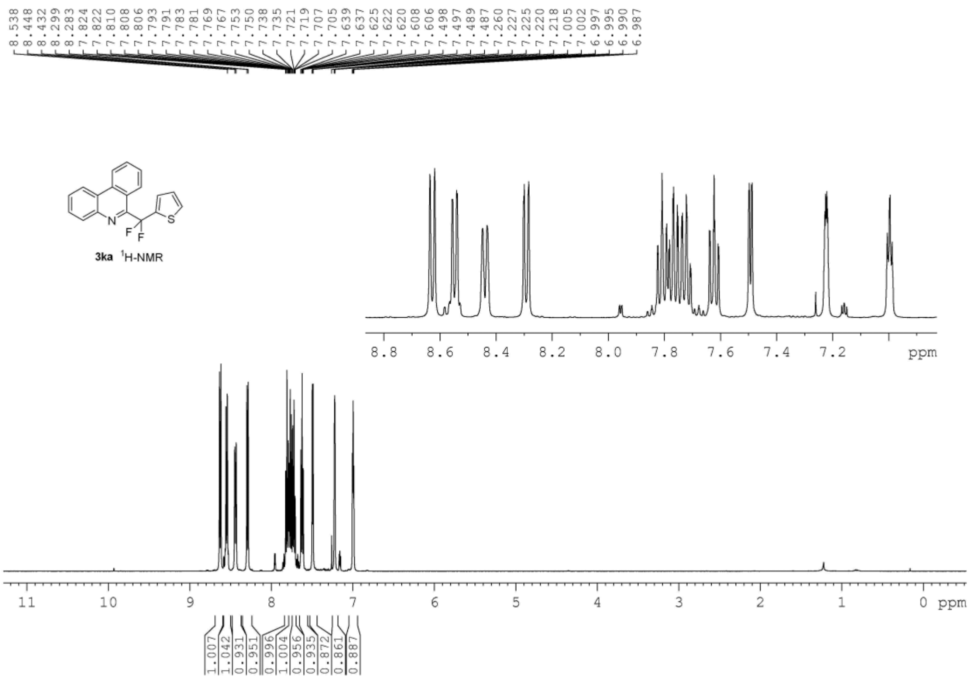

8.630
8.613
8.556
8.540
8.406
8.389
8.271
8.255
7.805
7.789
7.774
7.760
7.746
7.743
7.731
7.729
7.715
7.700
7.614
7.613
7.598
7.584
7.481
7.469
7.457
7.443
7.432
N
F F
3ja ¹H-NMR
8.6
8.4
8.2
8.0
7.8
7.6
ppm
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
1.021
1.037
0.993
4.976
1.100
3.153



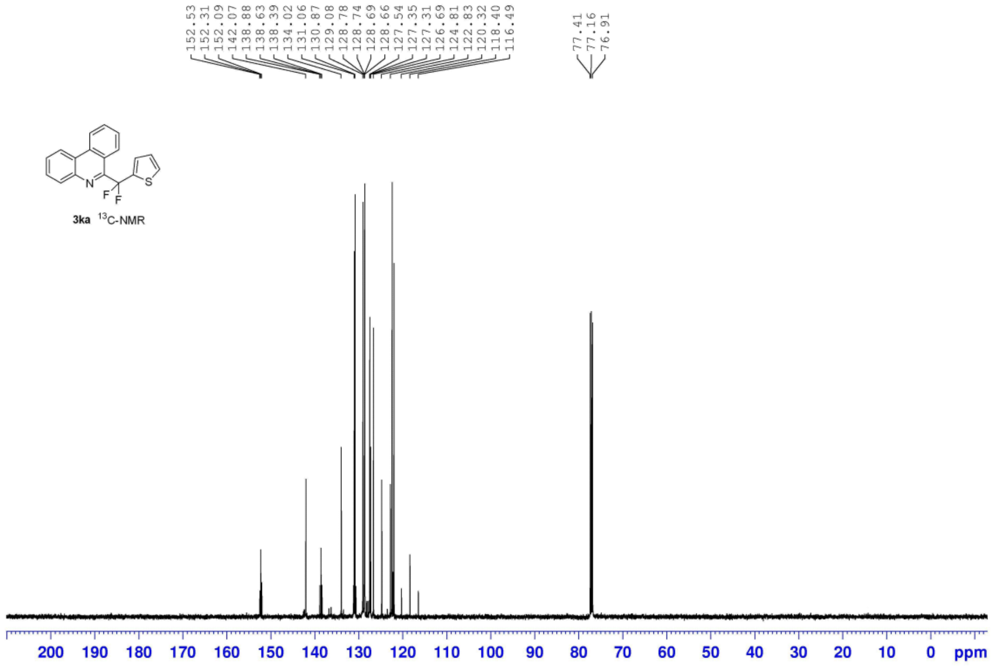
3ja ^{13}C-NMR



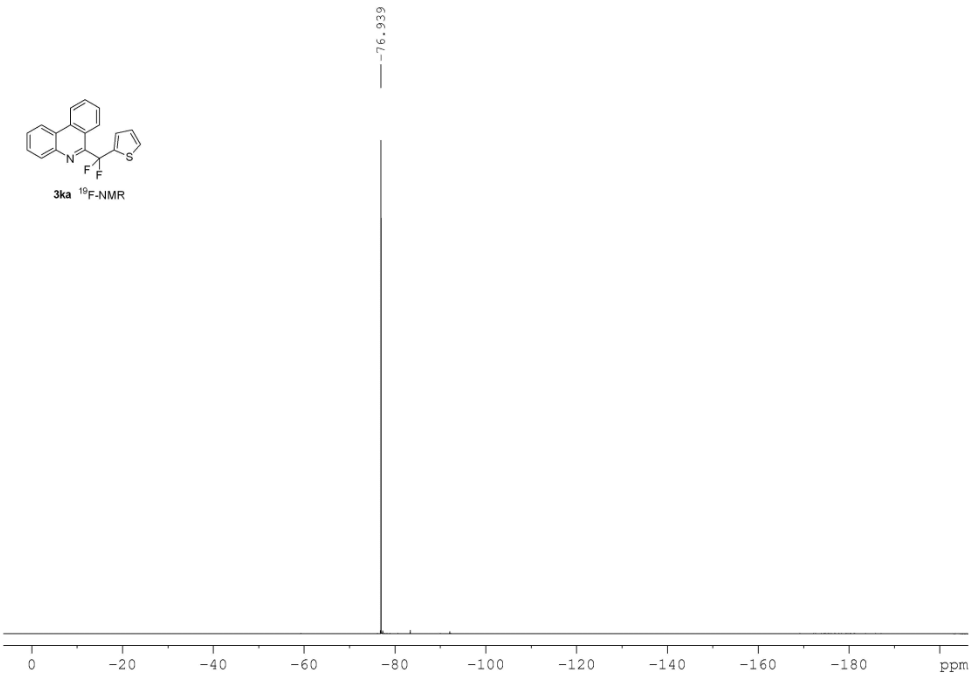
3ja ^{19}F-NMR



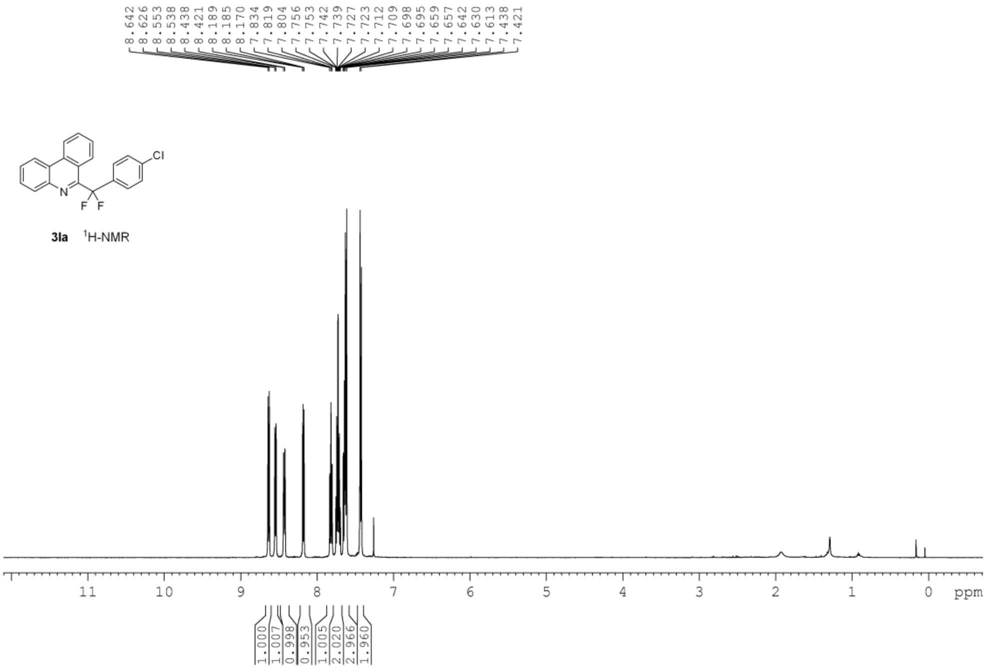
3ka ¹H-NMR



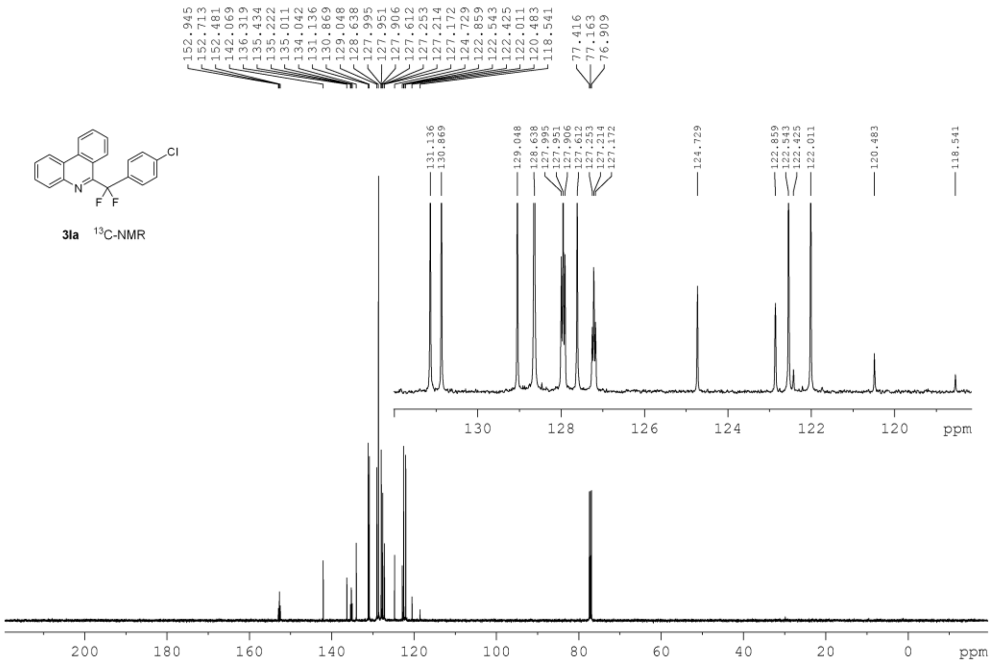
3ka ¹³C-NMR

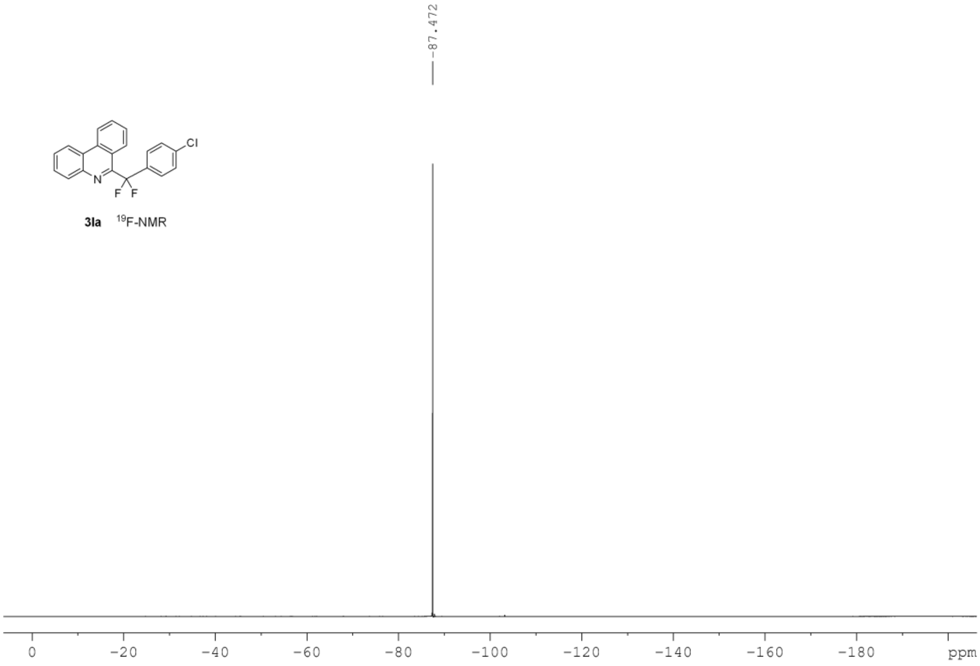


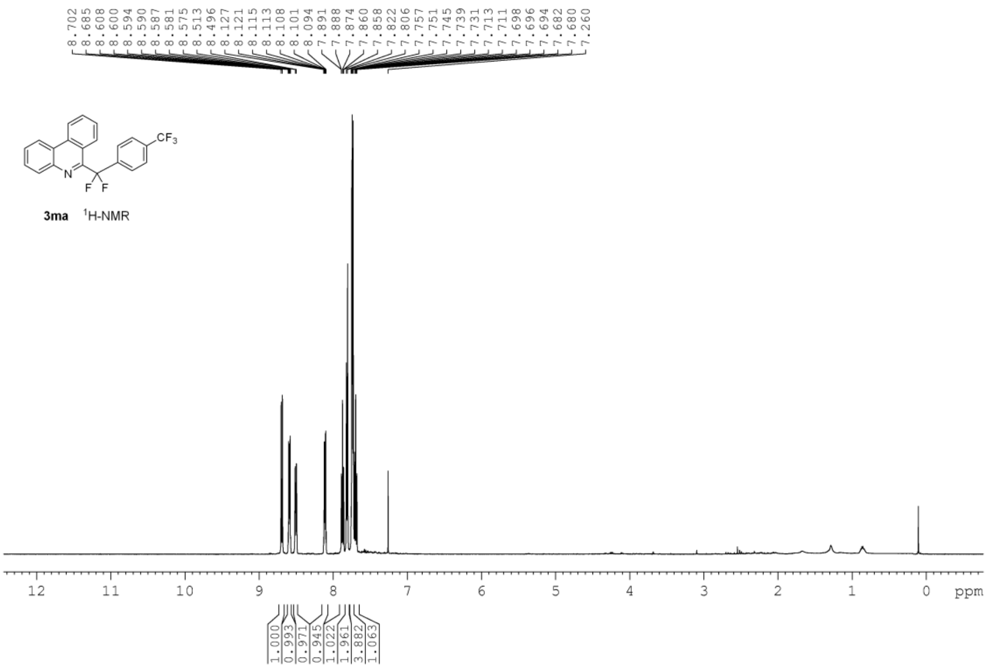
3ka ^{19}F-NMR



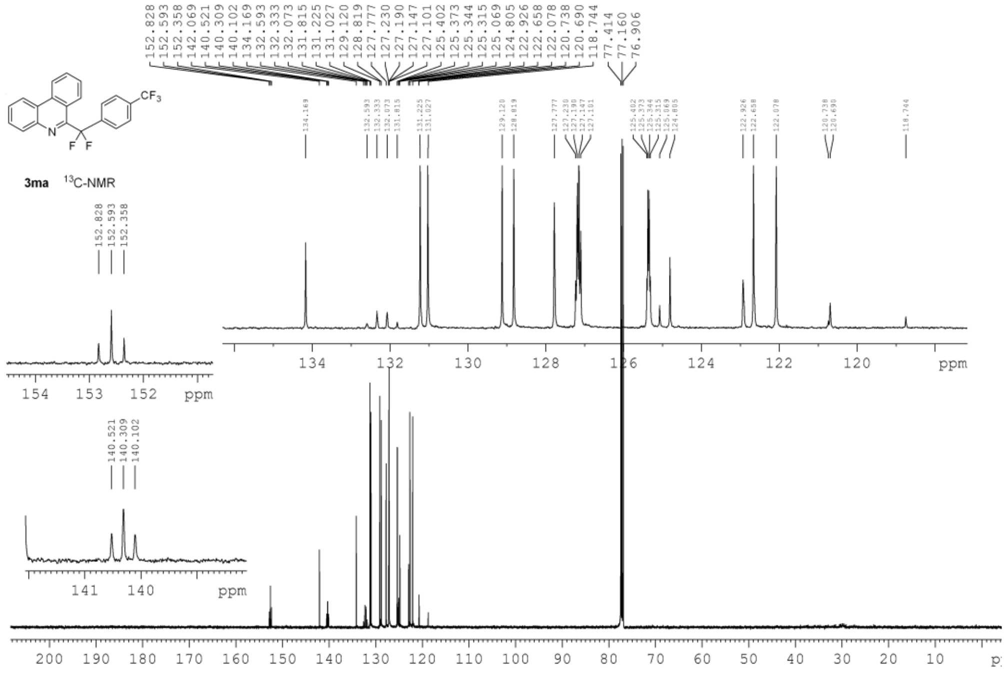
3la ^{1}H-NMR


3la ^{13}C-NMR

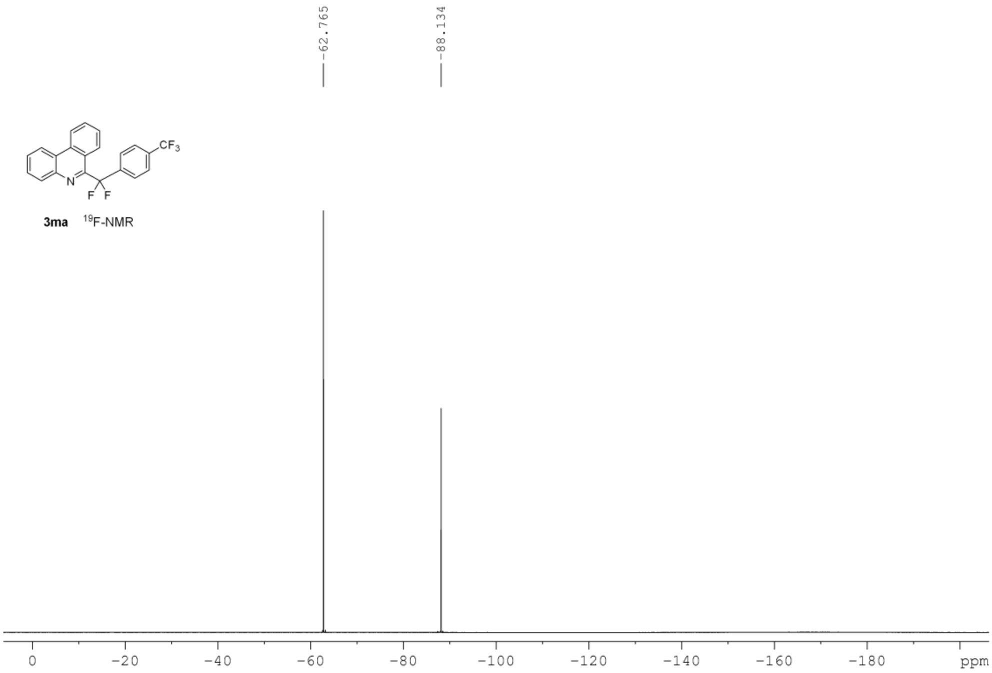

3la ^{19}F-NMR



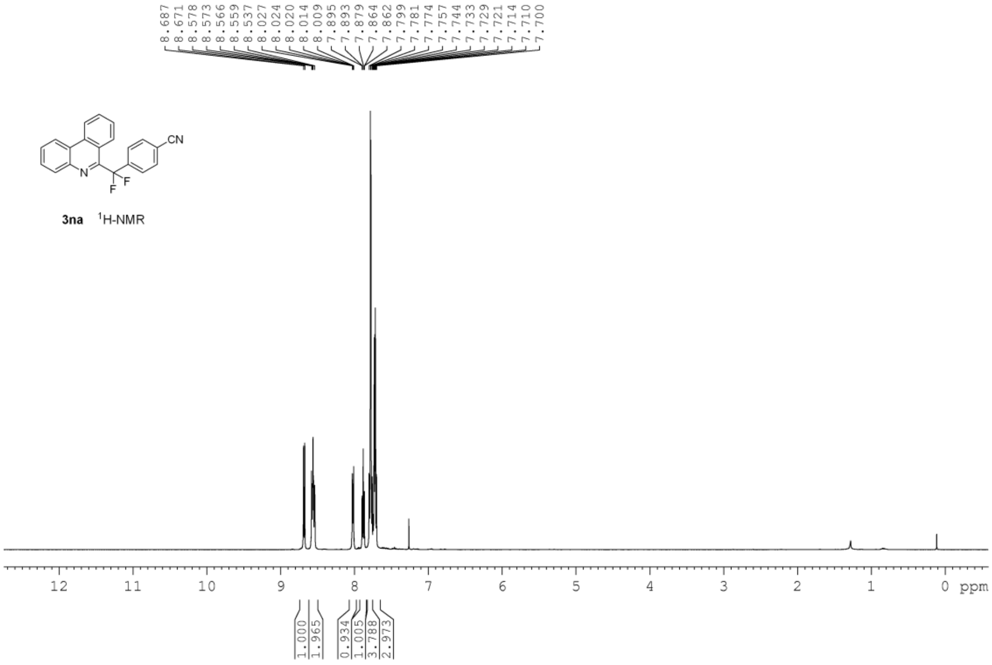
3ma ^{1}H-NMR



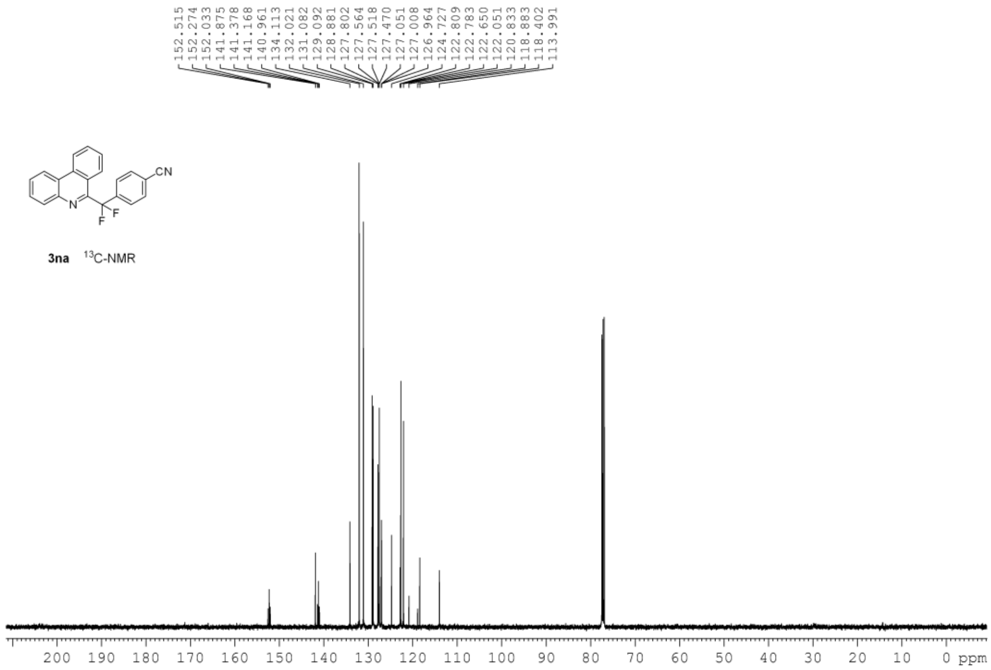
3ma ^{13}C-NMR



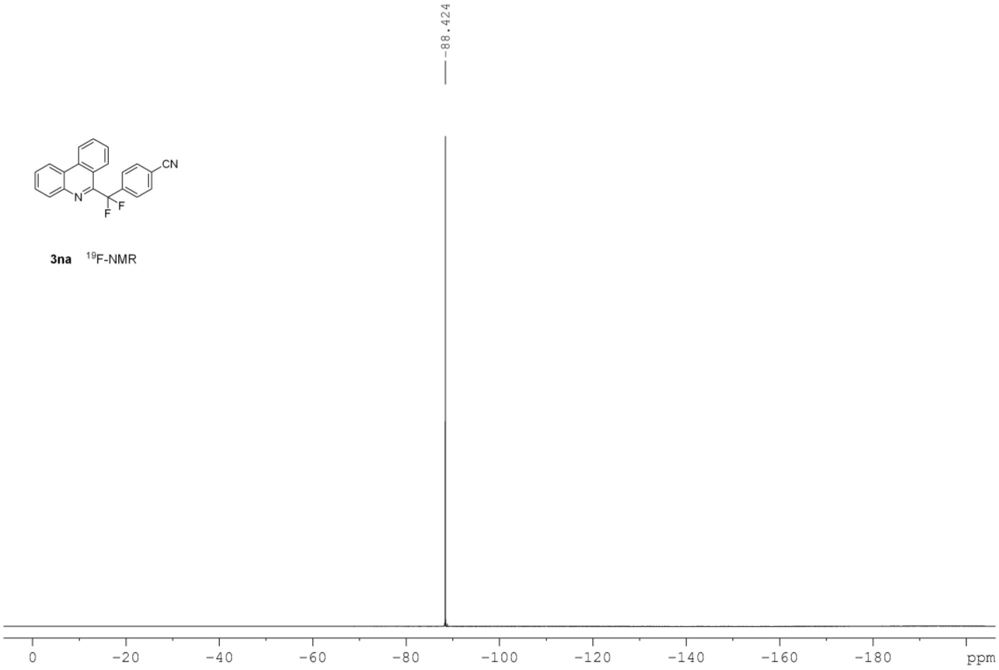
3ma ^{19}F-NMR



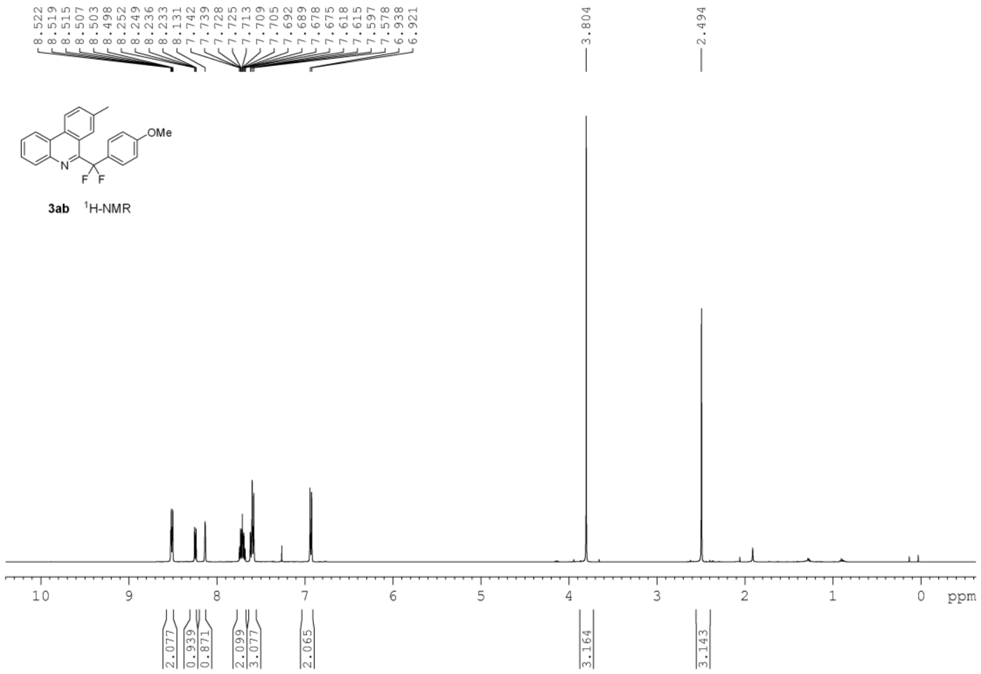
3na ^{1}H-NMR

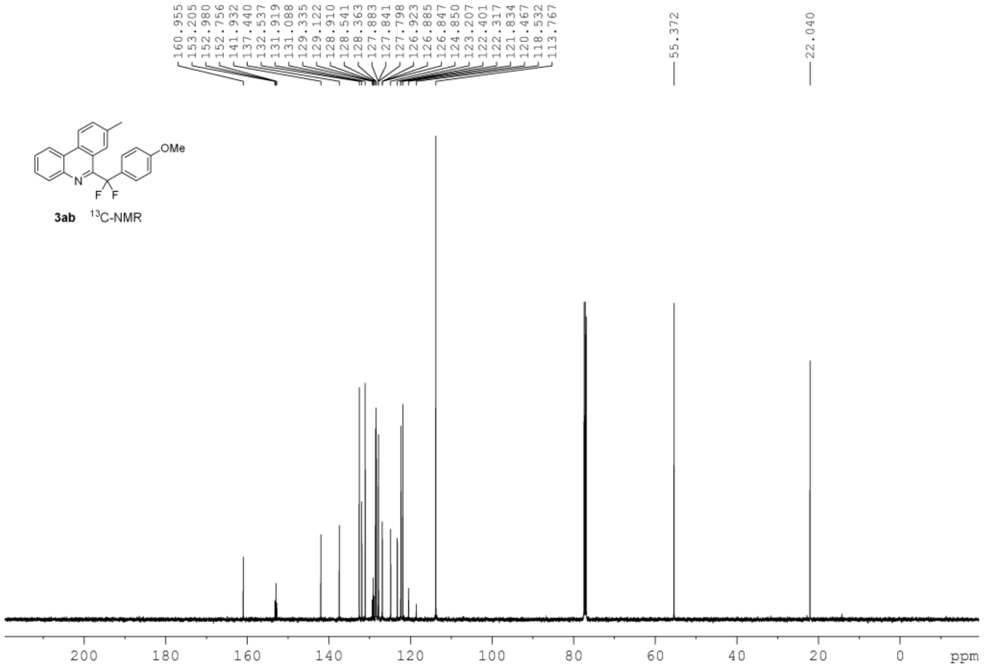


3na ^{13}C-NMR



3na ^{19}F-NMR


8.522
8.519
8.515
8.507
8.503
8.498
8.252
8.249
8.236
8.233
8.131
7.742
7.739
7.728
7.725
7.713
7.709
7.705
7.692
7.689
7.678
7.675
7.618
7.615
7.597
7.578
6.938
6.921
3.804
2.494
OMe
N
F F
3ab ^{1}H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm
2.077
0.939
0.871
2.099
3.077
2.065
3.164
3.143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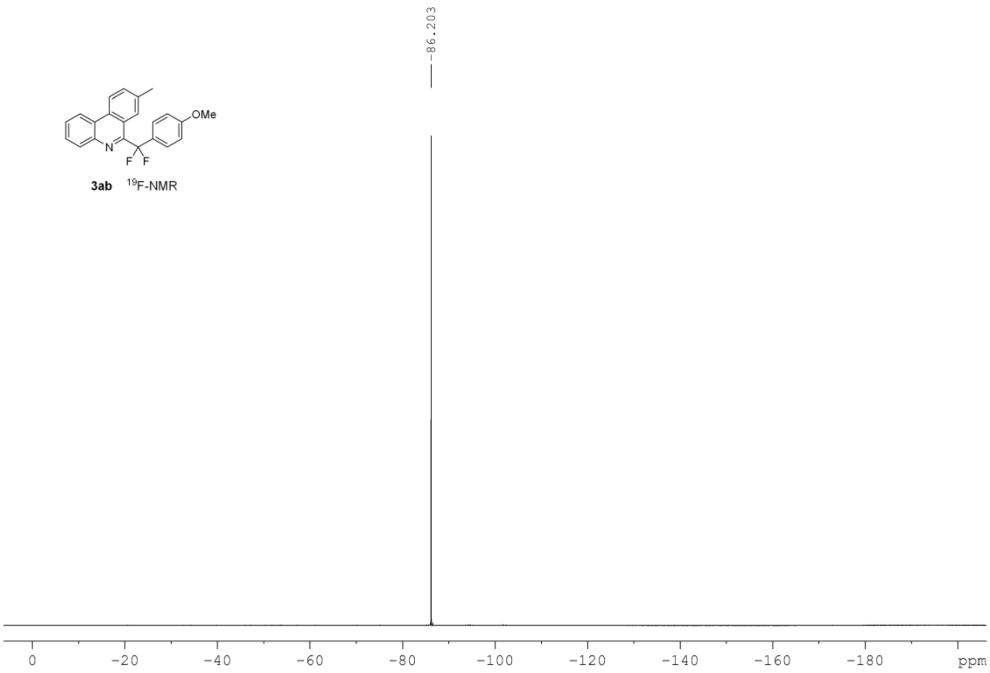
152.980
152.756
141.932
137.440
132.537
131.919
131.088
129.335
129.122
128.910
128.541
128.363
127.883
127.841
127.798
126.923
126.885
126.847
124.850
123.207
122.401
122.317
121.834
120.467
118.532
113.767
55.372
22.040
OMe
N
F F
3ab ^{13}C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm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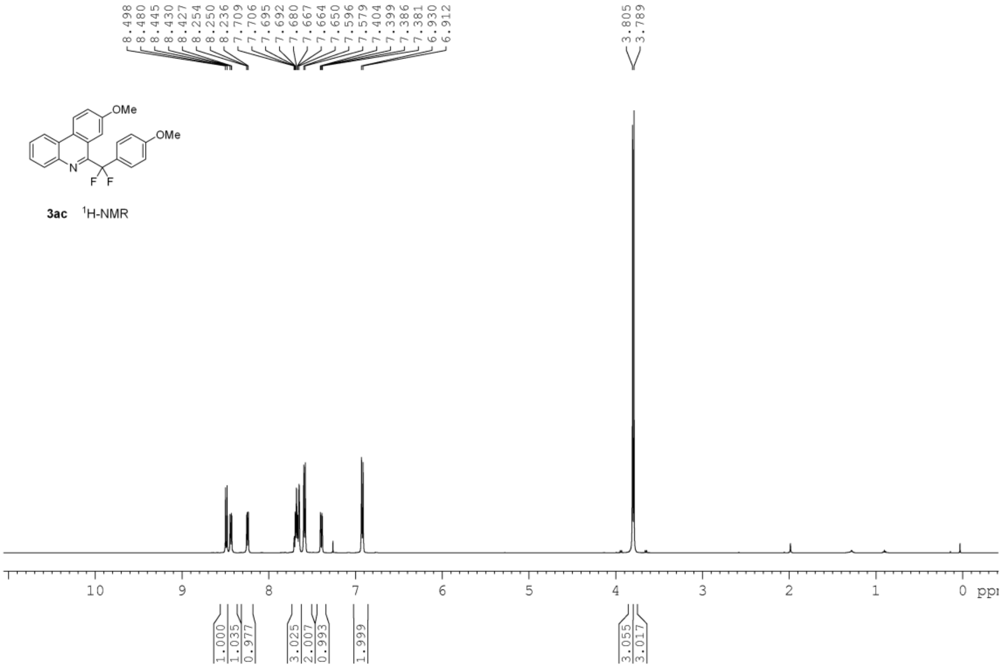
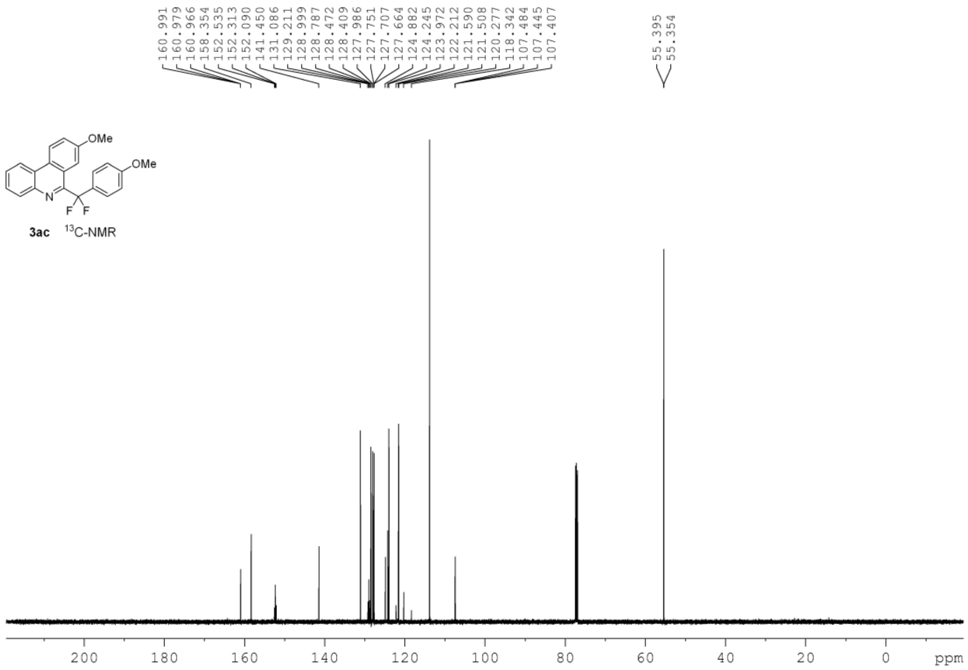

3ac ^{1}H-NMR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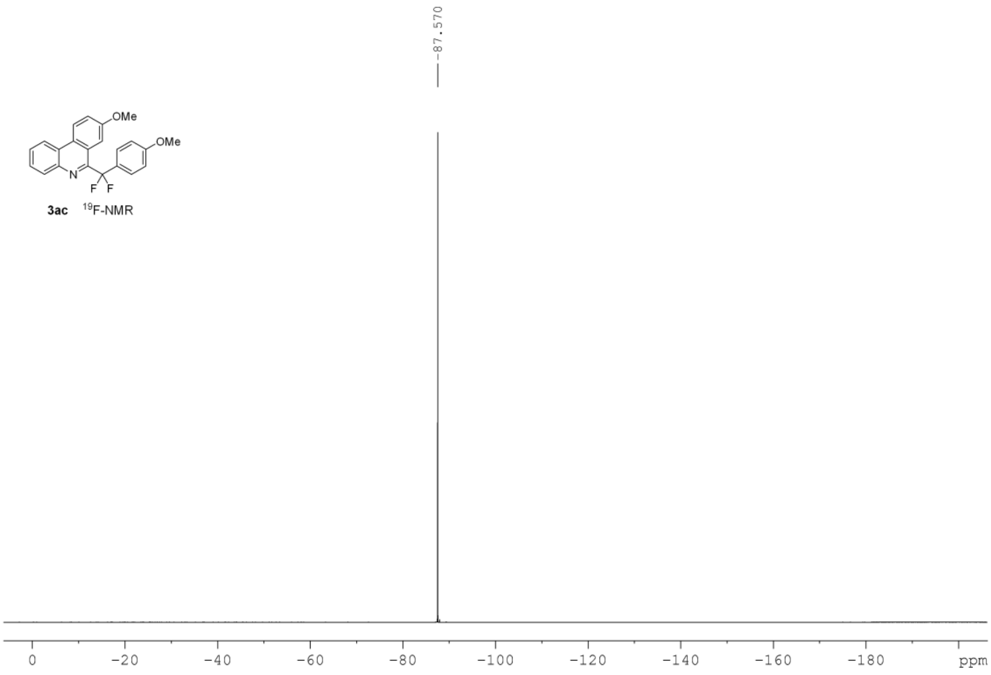
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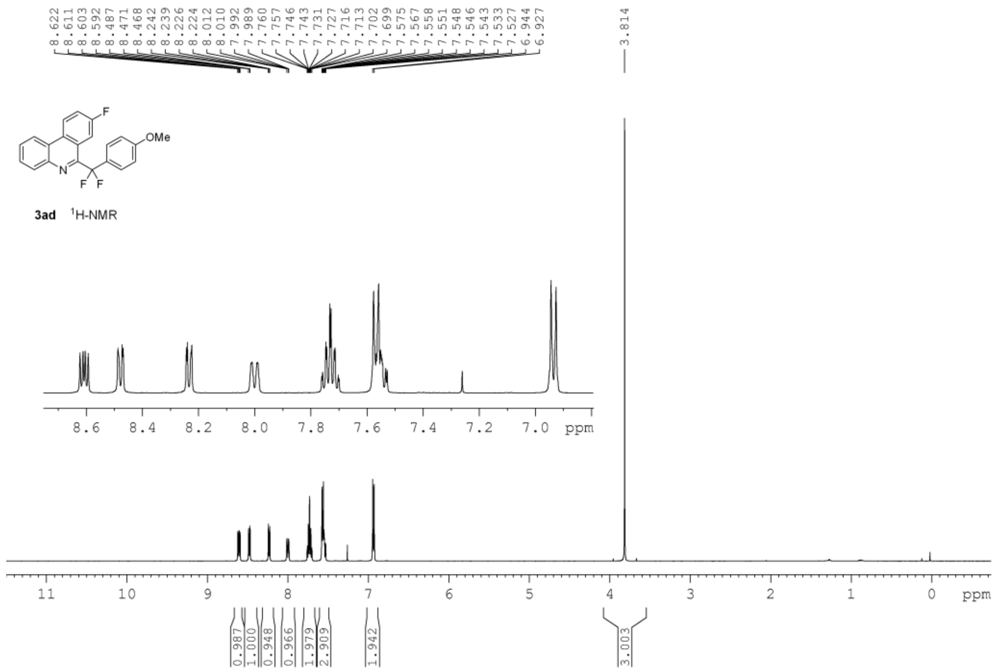
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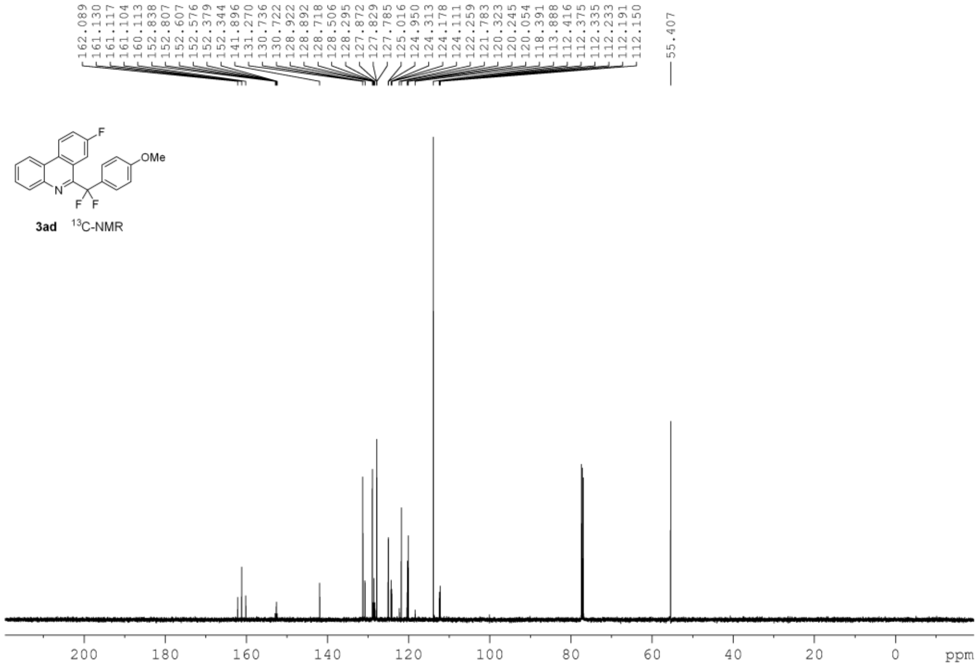
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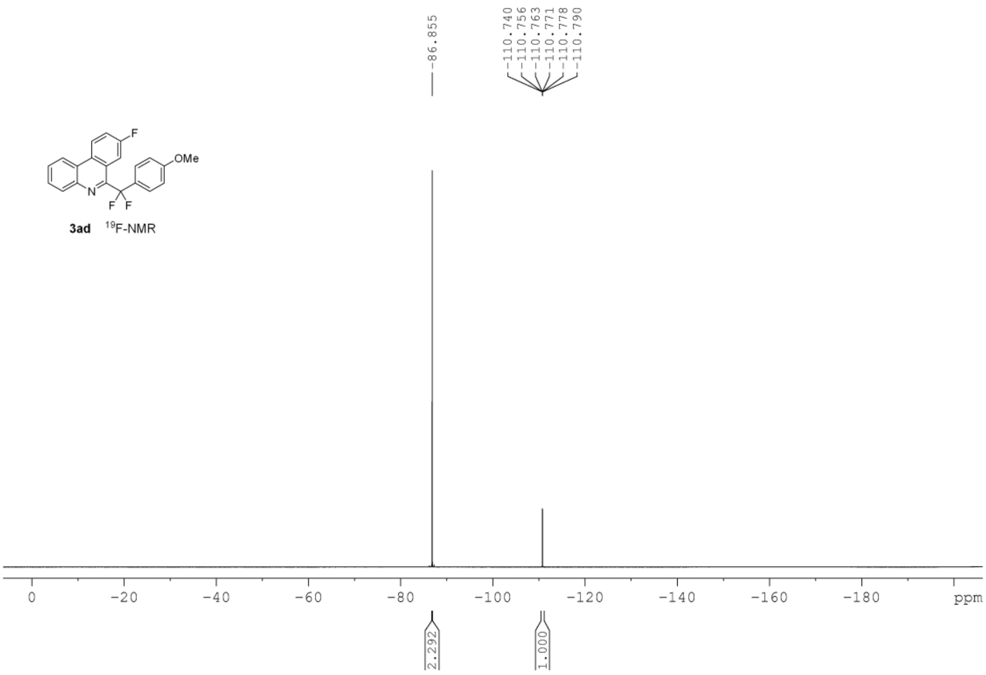
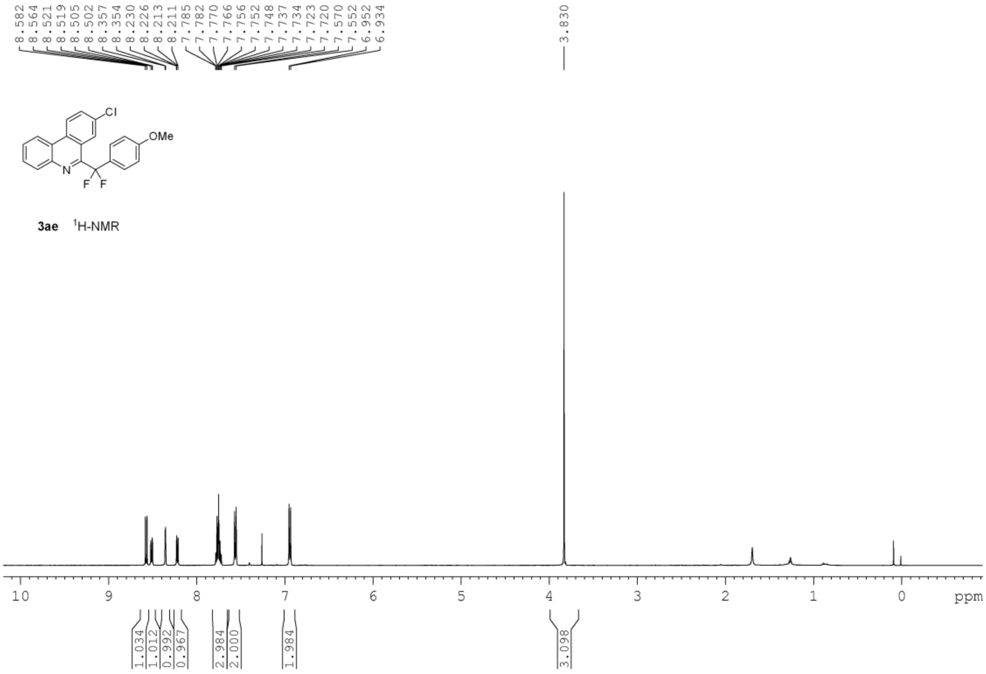


3ad ^{19}F-NMR



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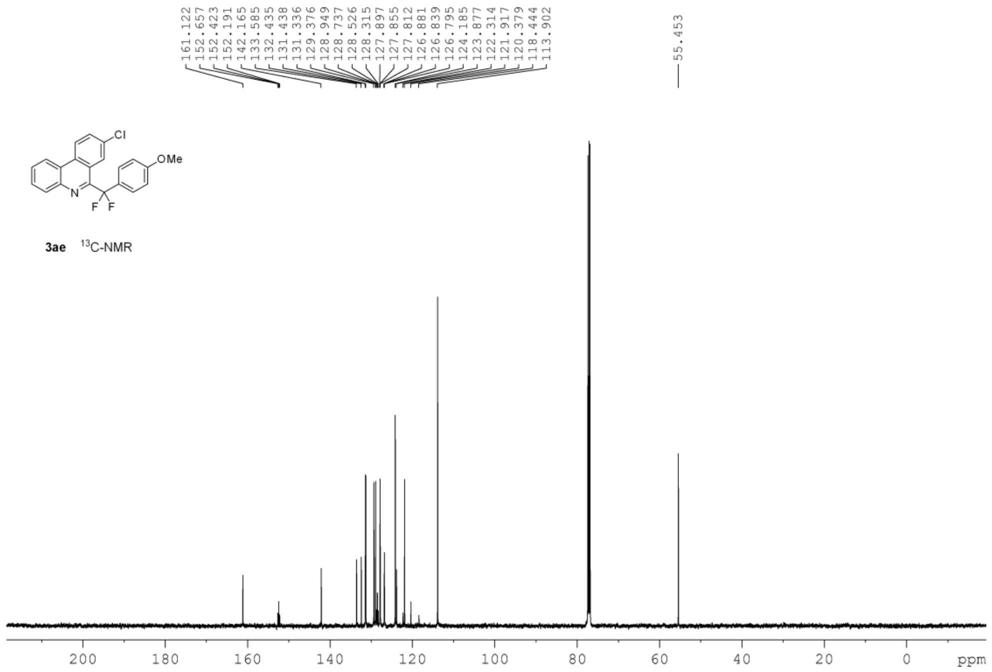

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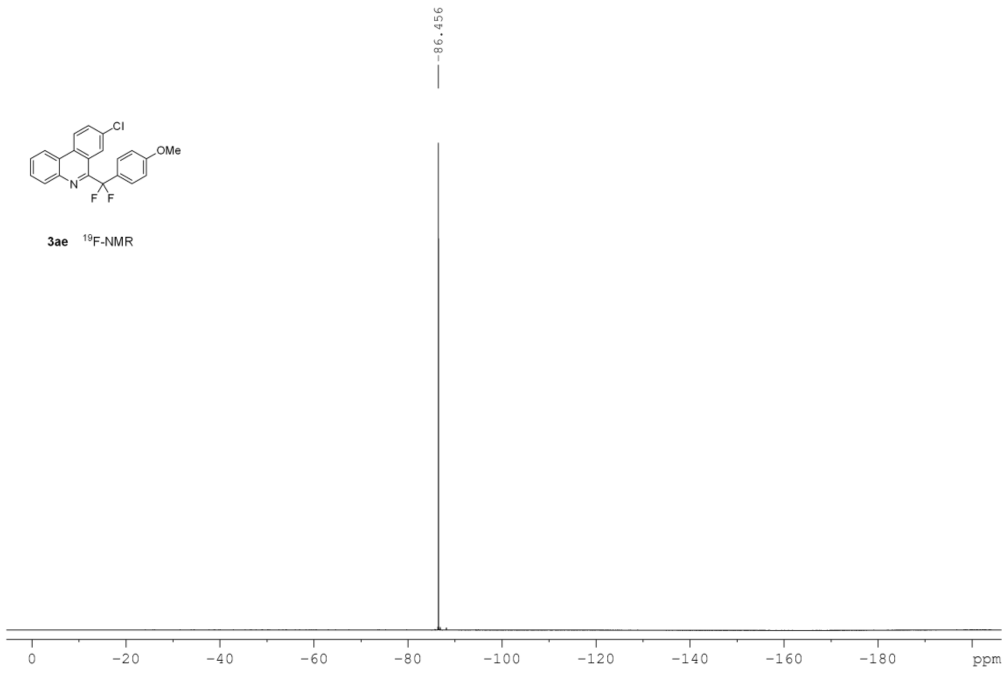
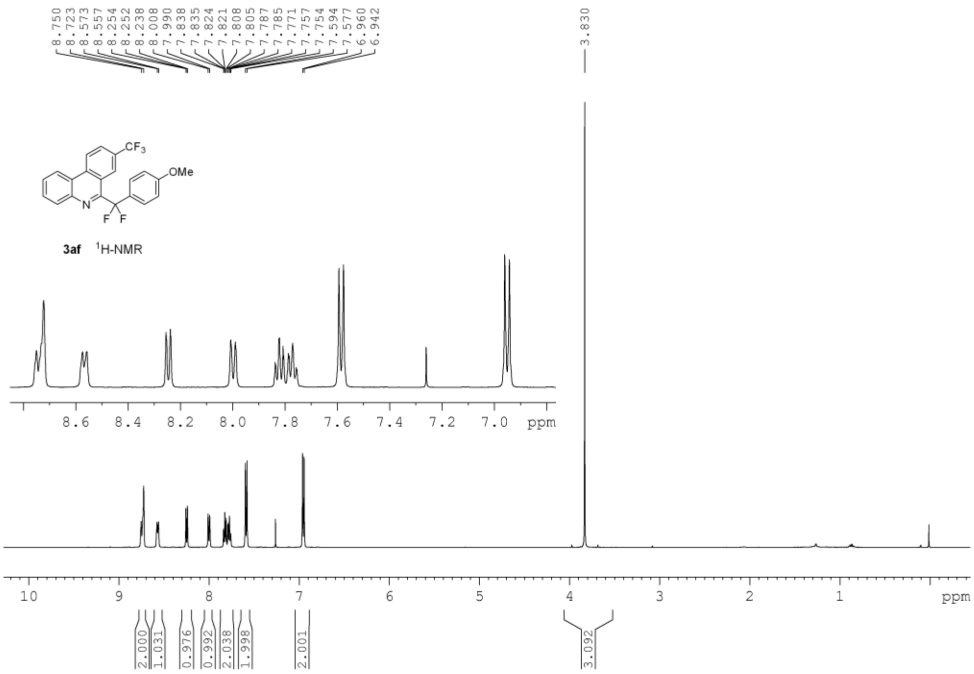


3ae ^{19}F-NMR



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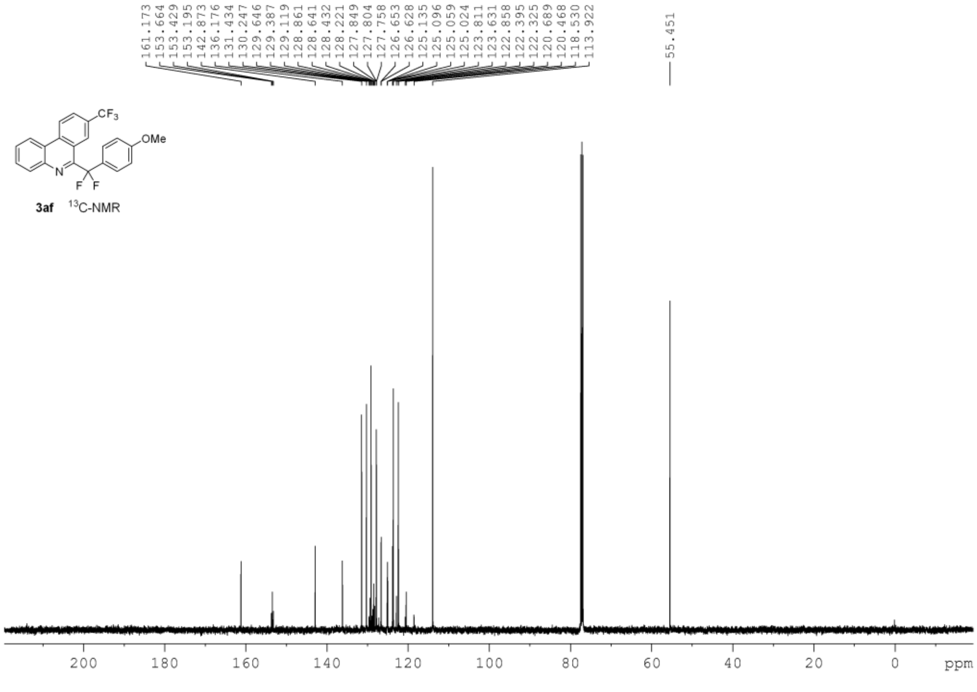
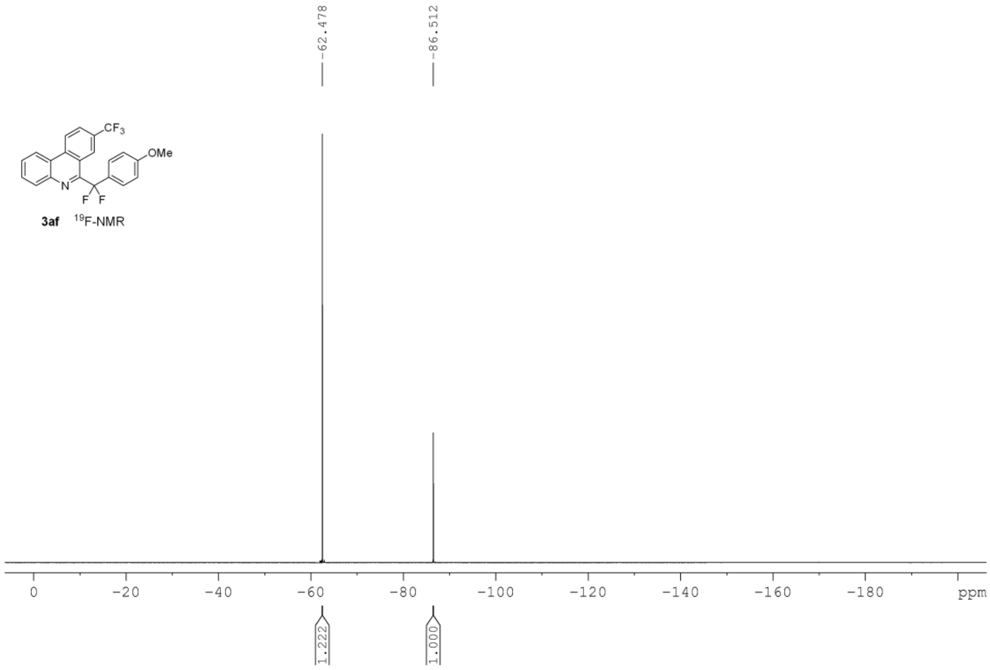
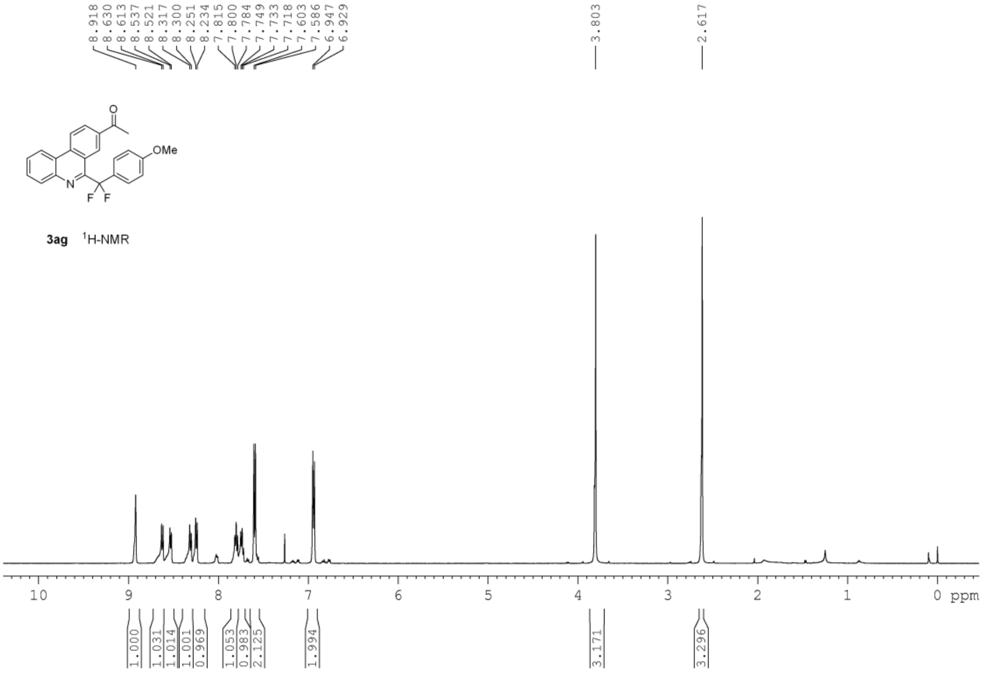


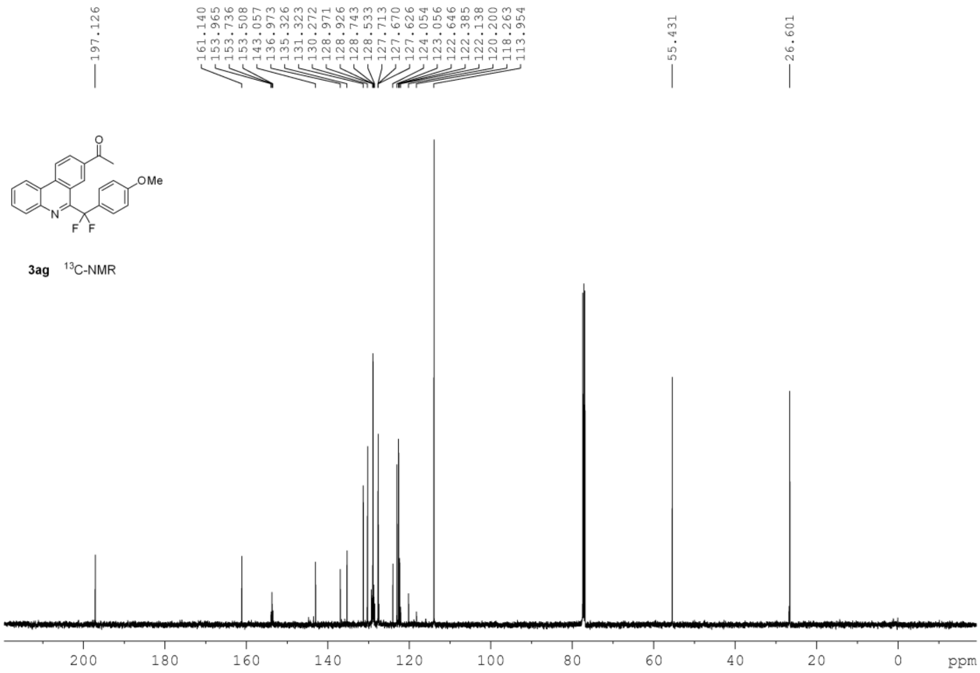
3af ^{13}C-NMR



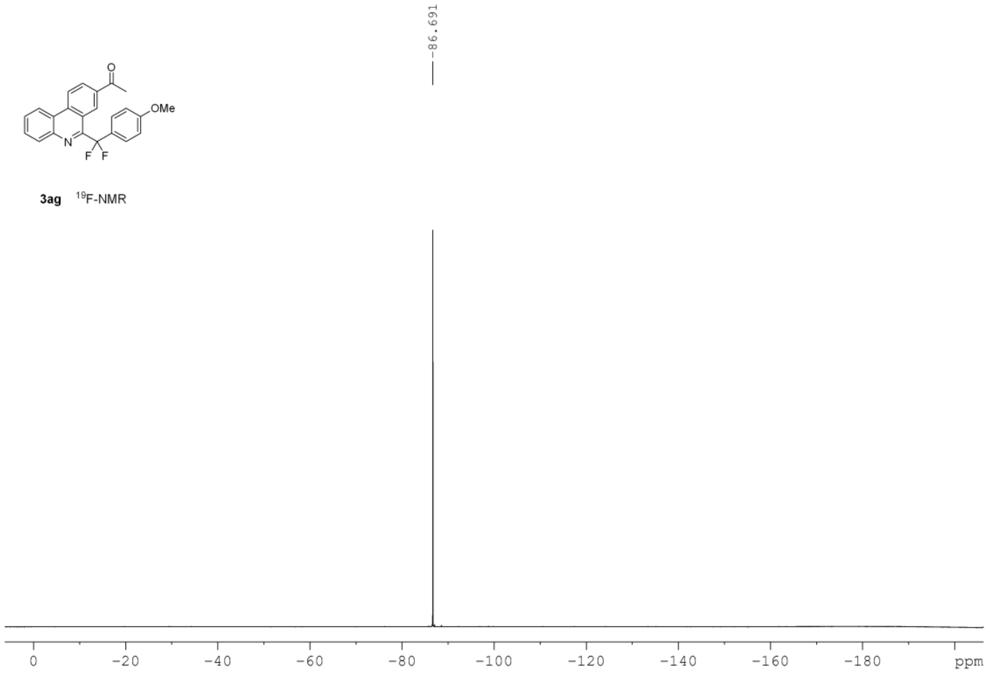
3af ^{19}F-NMR



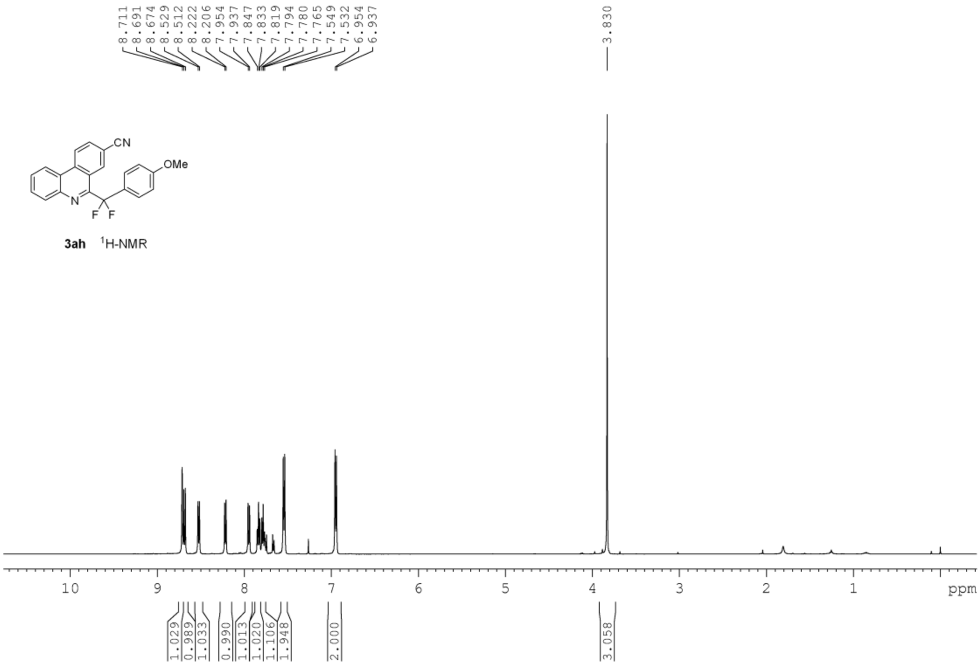
3ag ^{1}H-NMR



3ag ^{13}C-NMR



3ag ^{19}F-NMR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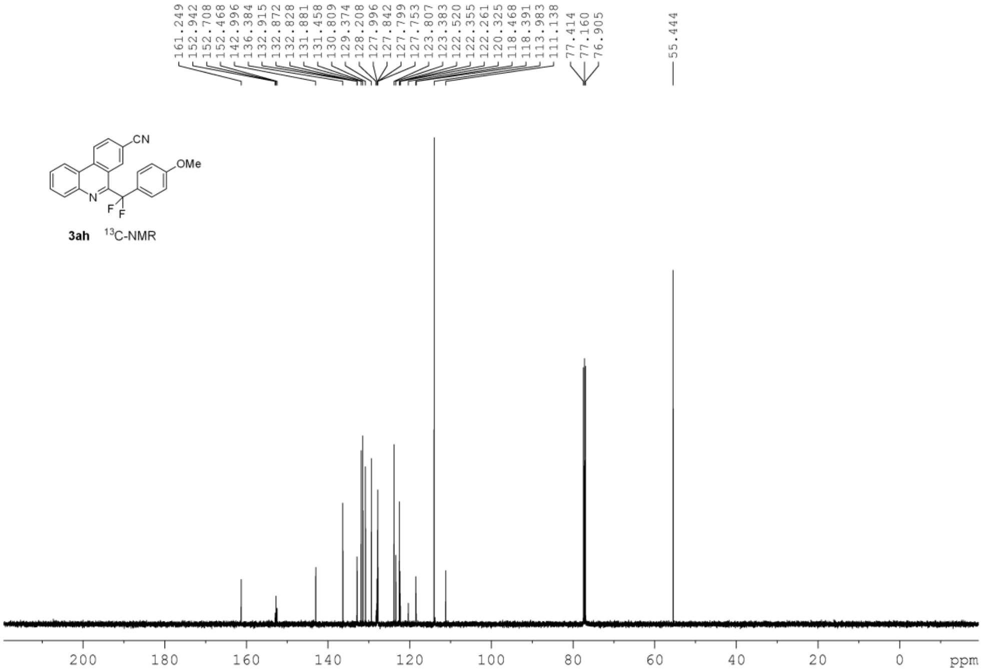
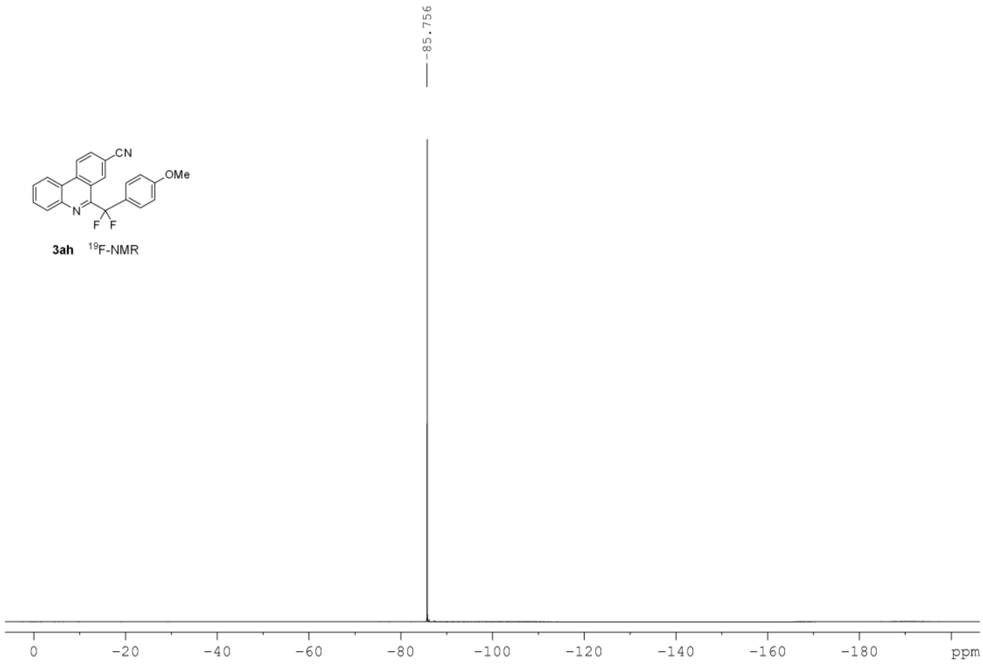
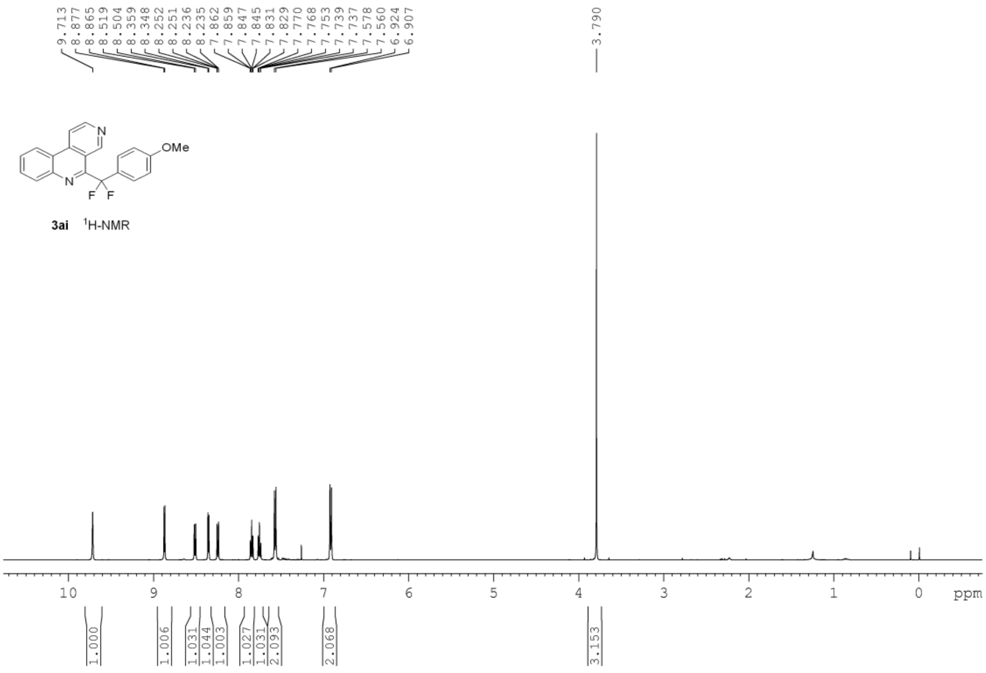
8.691
8.674
8.529
8.512
8.222
8.206
7.954
7.937
7.847
7.833
7.819
7.794
7.780
7.765
7.549
7.532
6.954
6.937
3.830
CN
OMe
N
F
F
3ah ¹H-NMR
10
9
8
7
6
5
4
3
2
1
ppm
1.029
0.989
1.033
0.990
1.013
1.020
1.106
1.948
2.000
3.058

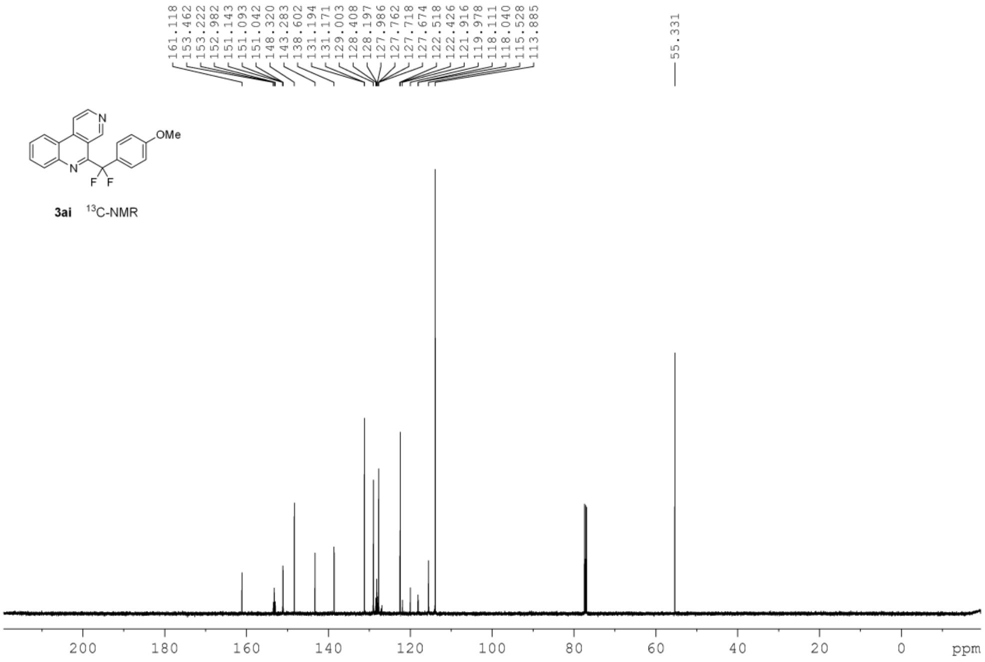

161.249
152.942
152.708
152.468
142.996
136.384
132.915
132.872
132.828
131.881
131.458
130.809
129.374
128.208
127.996
127.842
127.799
127.753
123.807
123.383
122.520
122.355
122.261
120.325
118.468
118.391
113.983
111.138
77.414
77.160
76.905
55.444
CN
OMe
N
F
F
3ah ¹³C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm



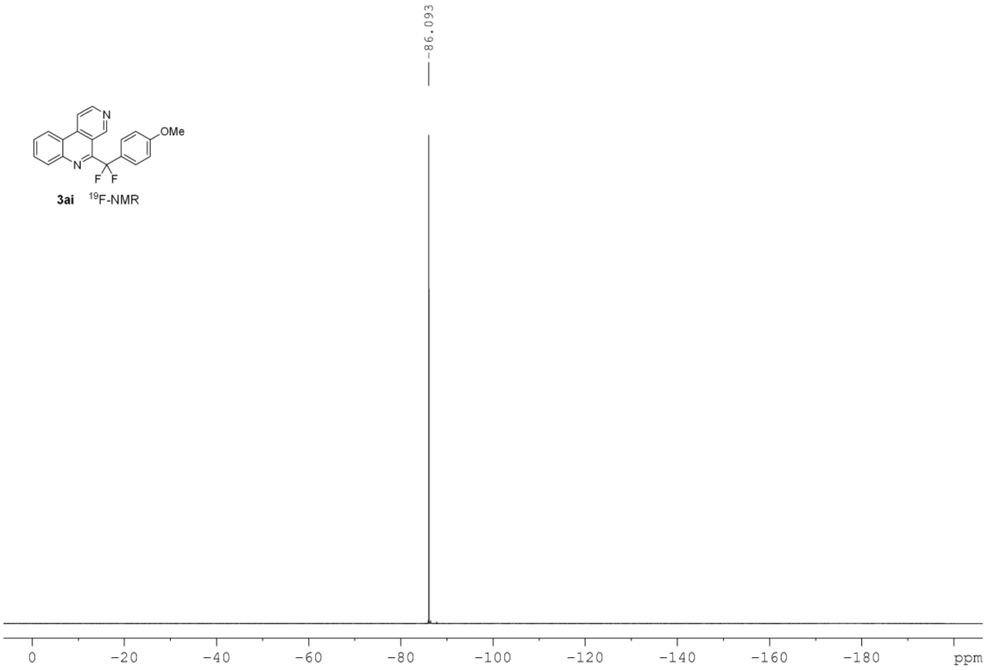
3ah ^{19}F-NMR



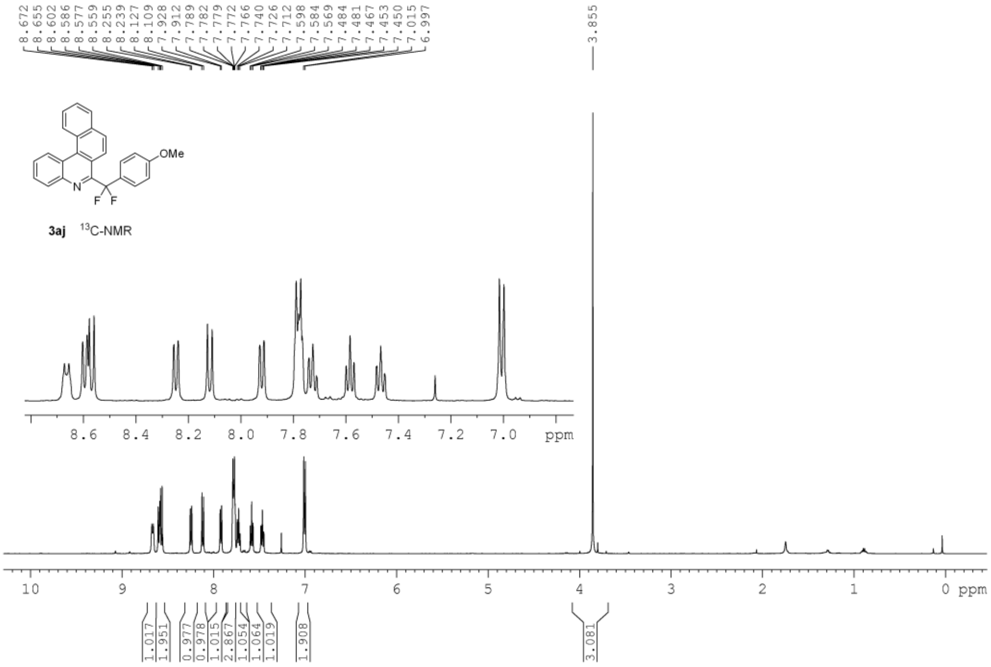
3ai ^{1}H-NMR



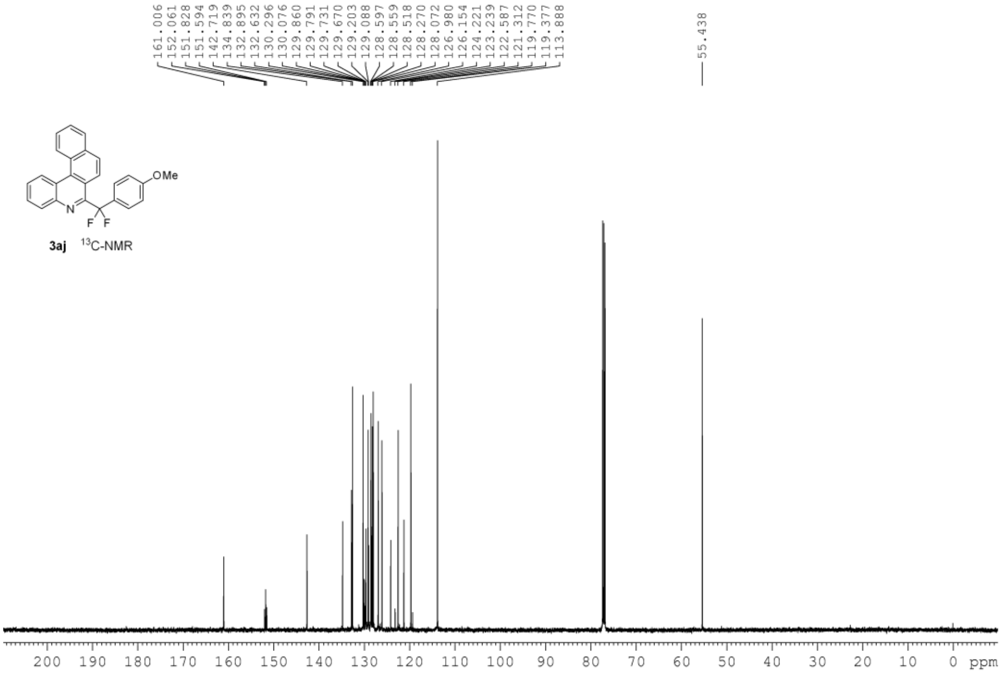
3ai ^{13}C-NMR



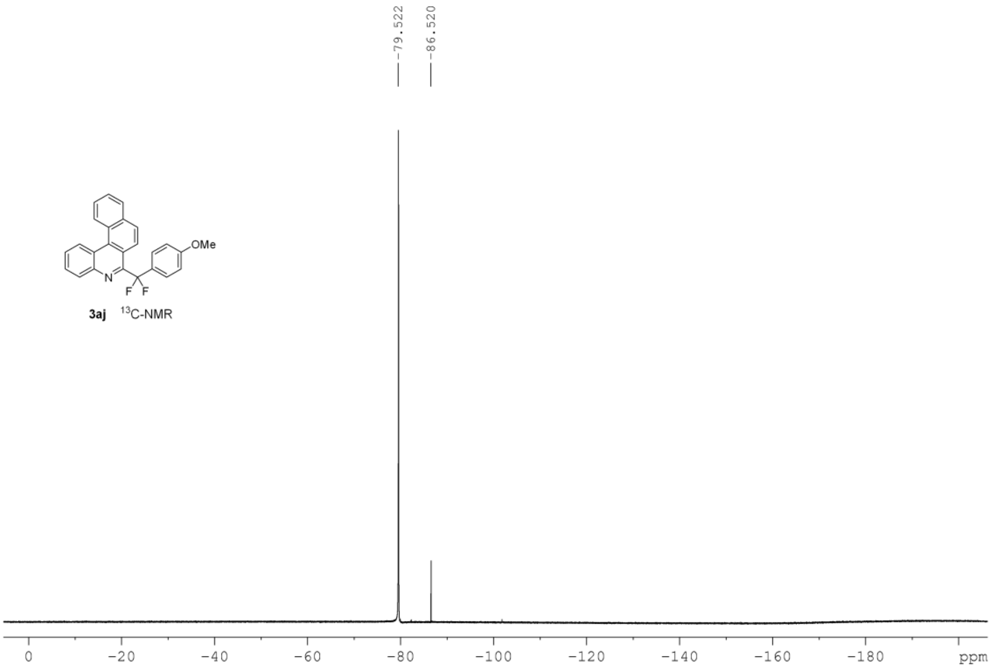
3ai ^{19}F-NMR

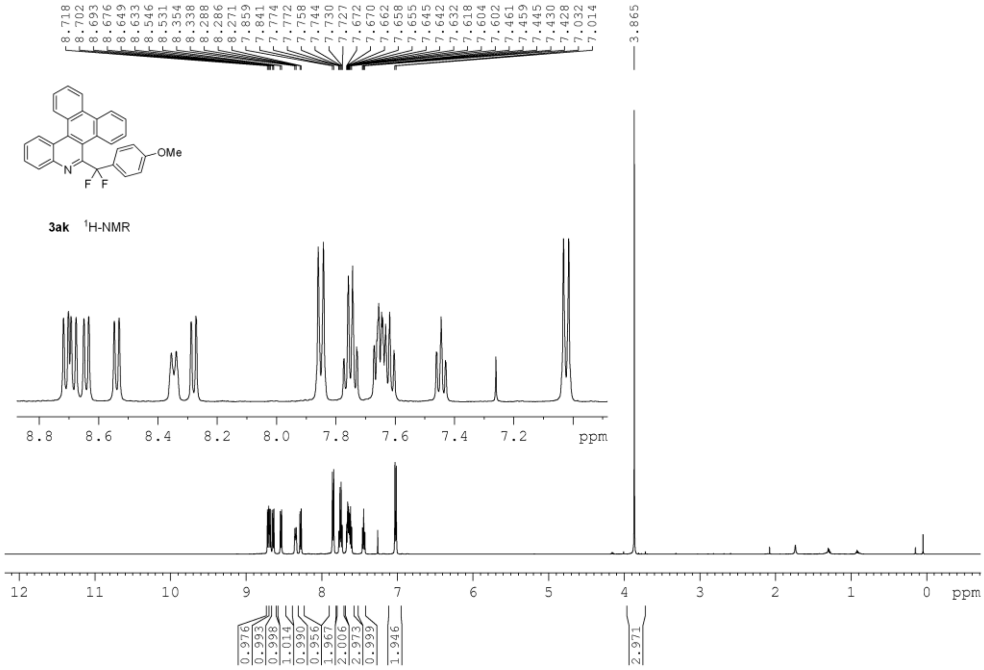


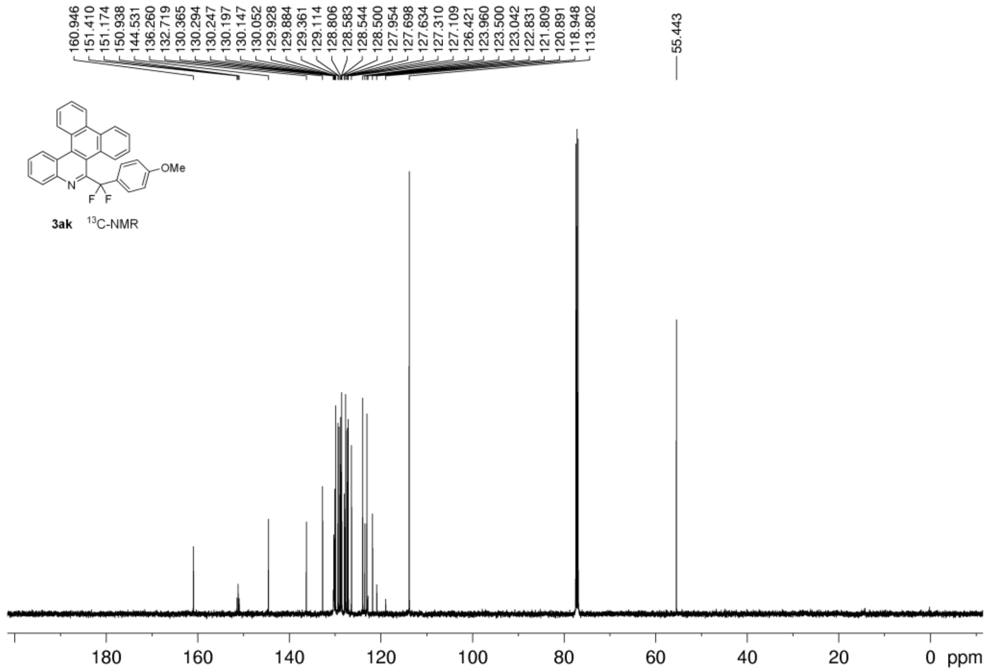
3aj ^{13}C-NMR



3aj ^{13}C-NMR


3aj ^{13}C-NMR


3ak ^{1}H-NMR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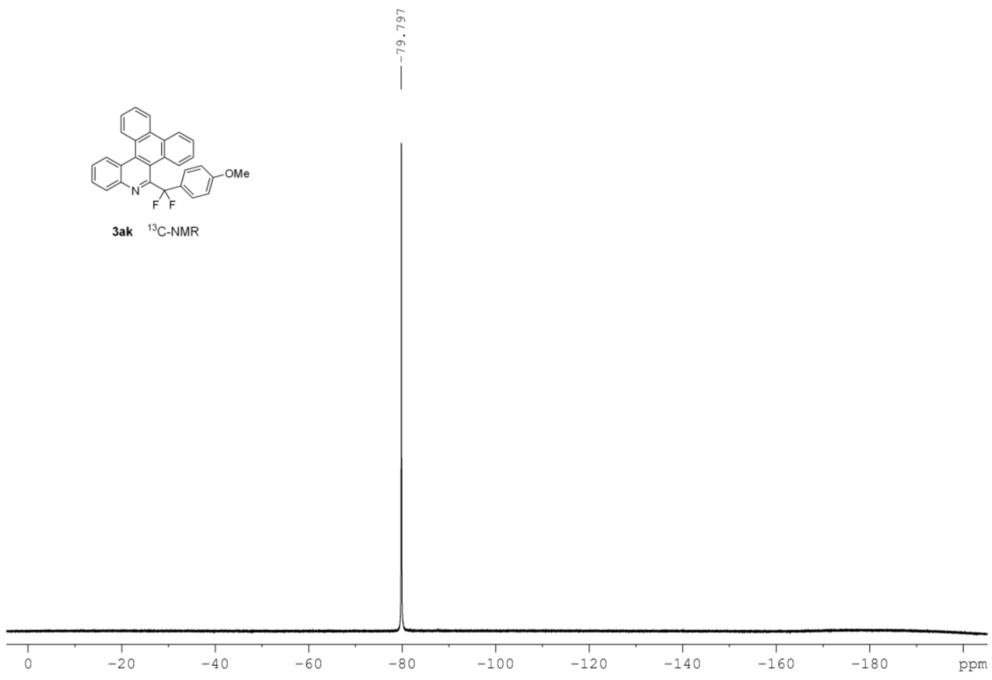
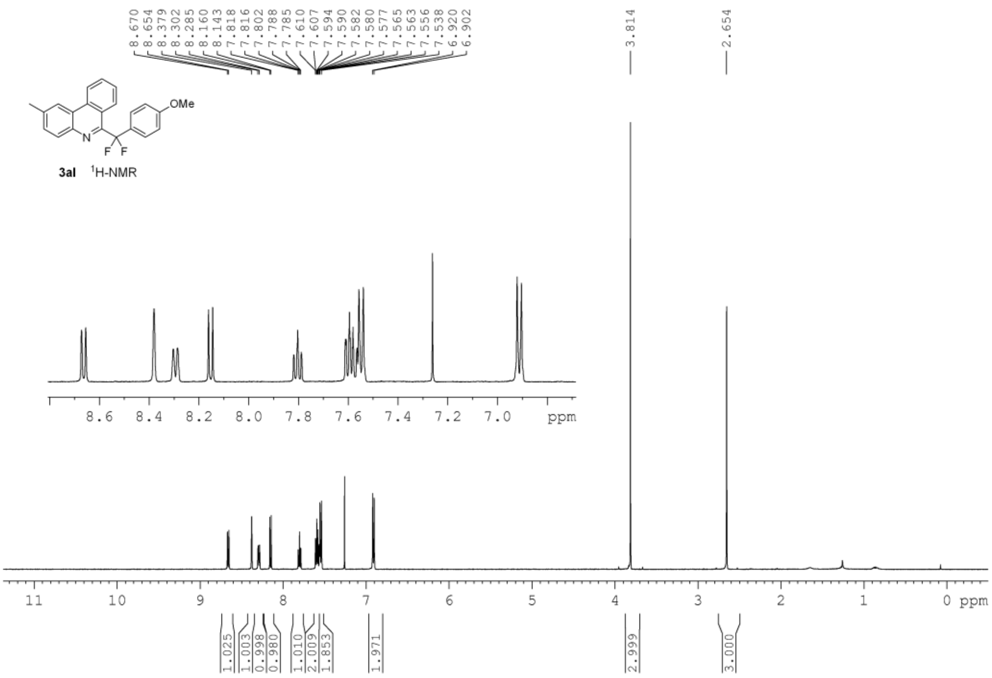
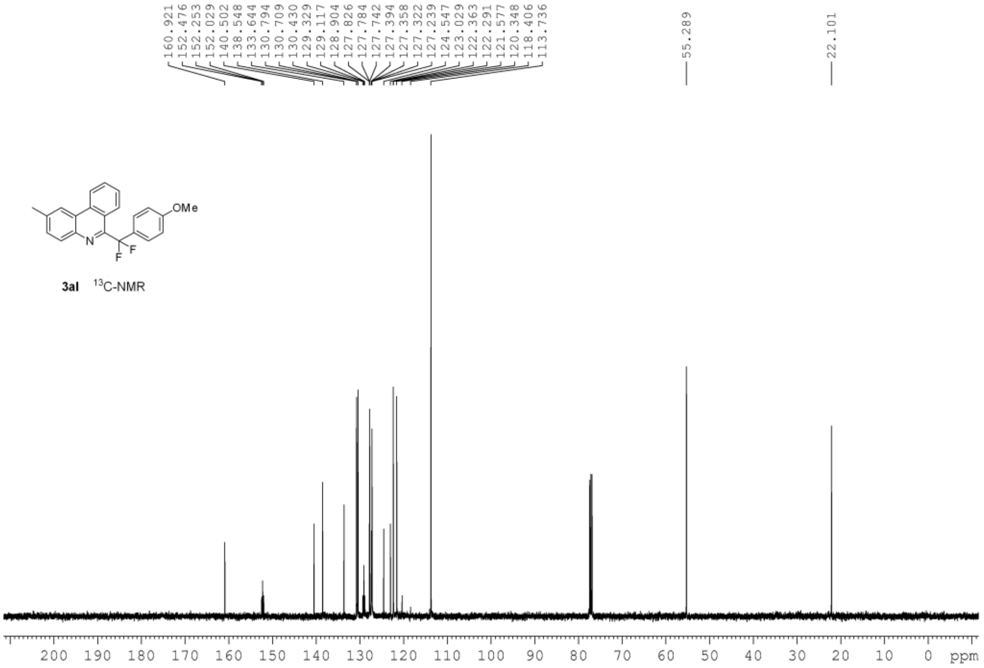
151.410
151.174
150.938
144.531
136.260
132.719
130.365
130.294
130.247
130.197
130.147
130.052
129.928
129.884
129.361
129.114
128.806
128.583
128.544
128.500
127.954
127.698
127.634
127.310
127.109
126.421
123.960
123.500
123.042
122.831
121.809
120.891
118.948
113.802
55.443
OMe
N
F F
3ak ¹³C-NMR
180
160
140
120
100
80
60
40
20
0 ppm


-79.797
OMe
N
F F
3ak ¹³C-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


3al ¹H-NMR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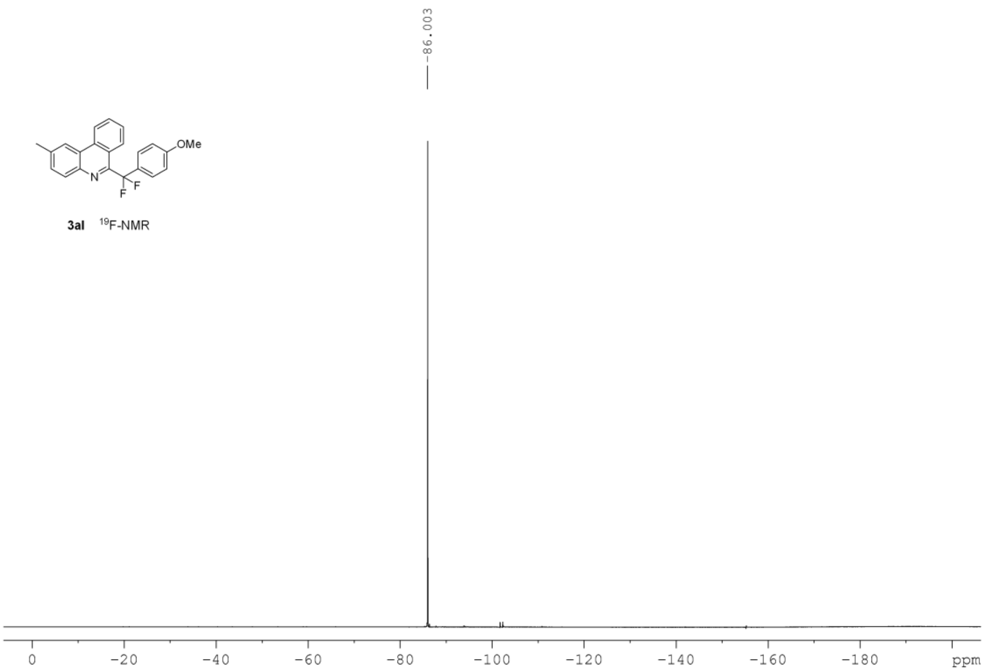
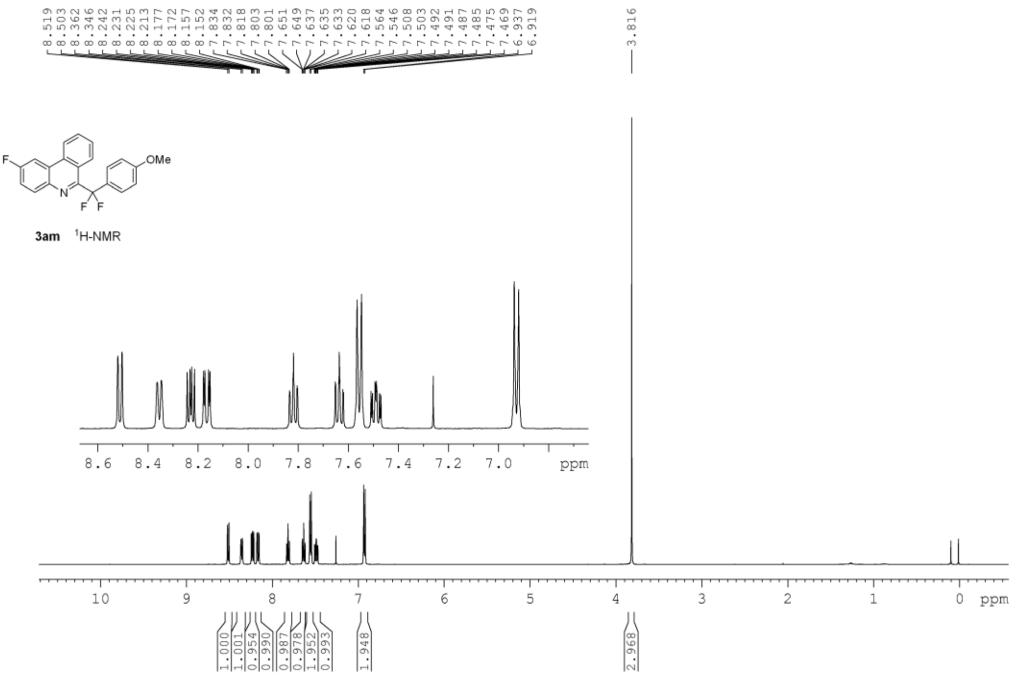
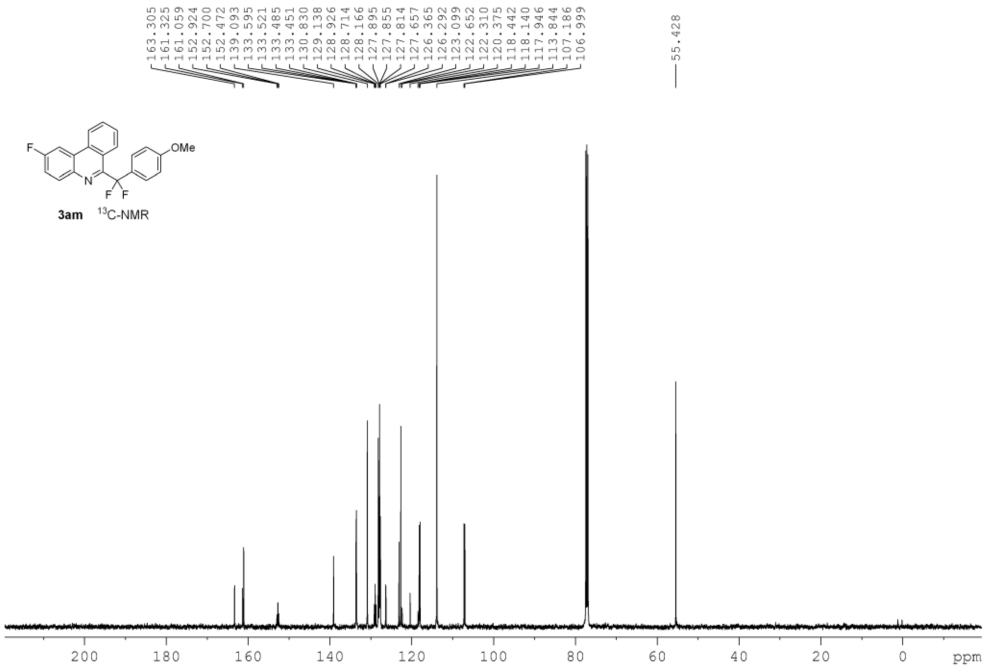

3al ^{19}F-NMR


3am ^{1}H-NMR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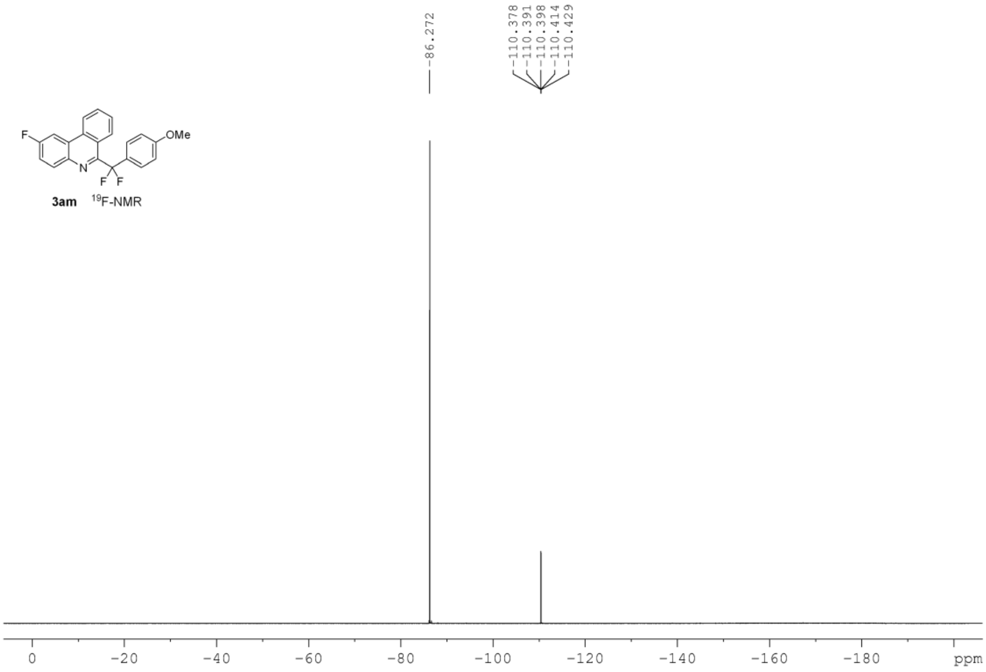
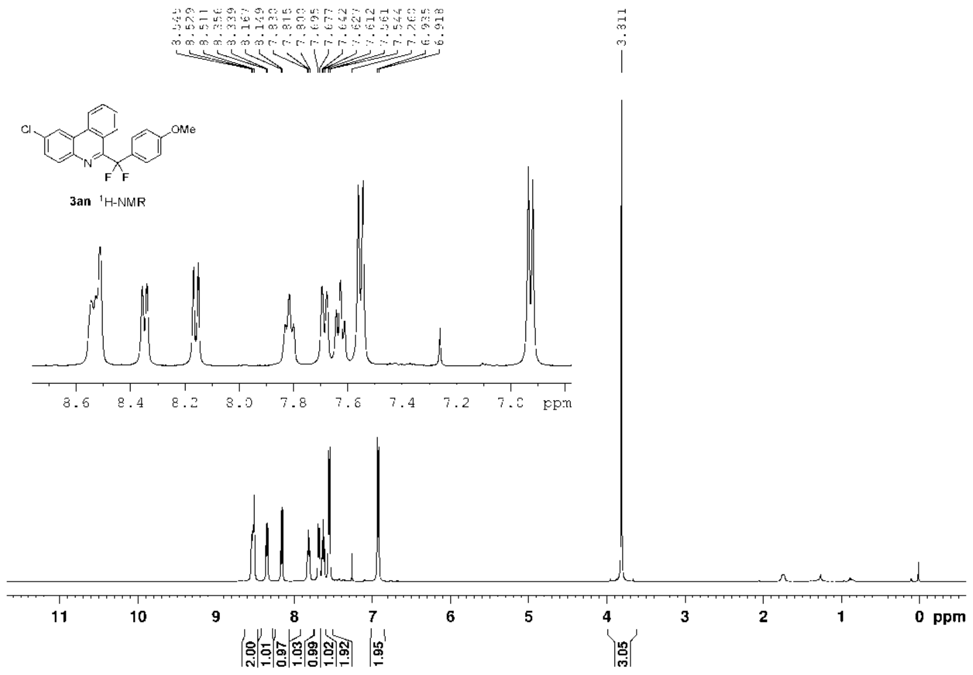
152.472
139.093
133.595
133.521
133.485
133.451
130.830
129.138
128.926
128.714
128.166
127.895
127.855
127.814
127.657
126.365
126.292
123.099
122.652
122.310
120.375
118.442
118.140
117.946
113.844
107.186
106.999
55.428
F
OMe
N
F F
3am 13C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm


-86.272
-110.378
-110.391
-110.398
-110.414
-110.429
F
OMe
N
F F
3am 19F-NMR
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm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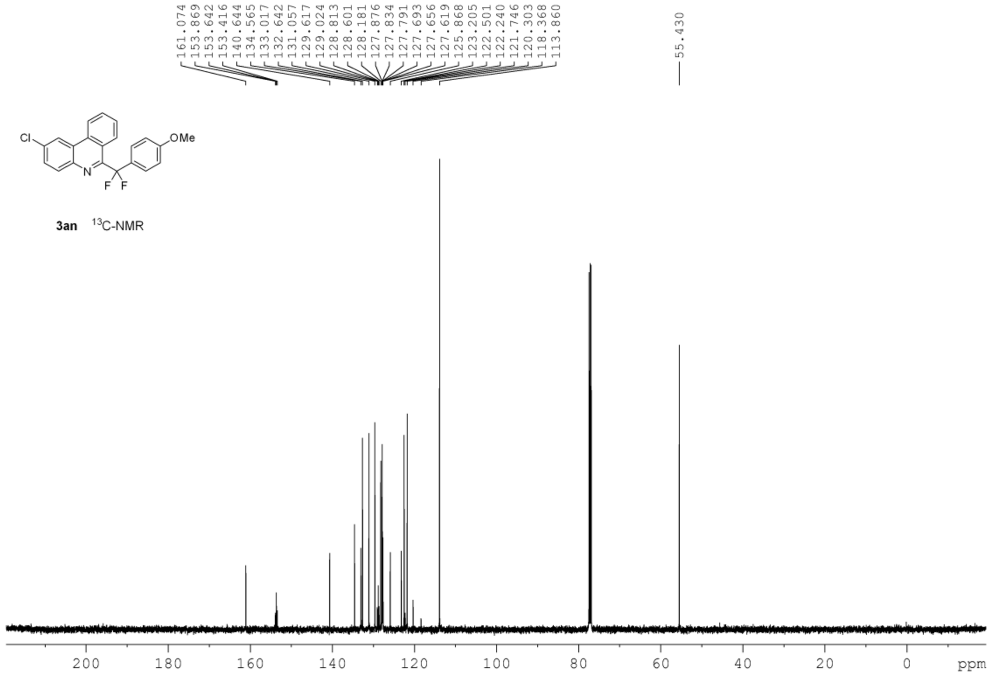
8.529
8.511
8.356
8.339
8.167
8.149
7.833
7.815
7.800
7.695
7.677
7.642
7.627
7.612
7.561
7.544
7.260
6.935
6.918
3.811
Cl
N
F F
OMe
3an ^{1}H-NMR
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
11
10
9
8
7
6
5
4
3
2
1
0 ppm
2.00
1.01
0.97
1.03
0.99
1.02
1.92
1.95
3.05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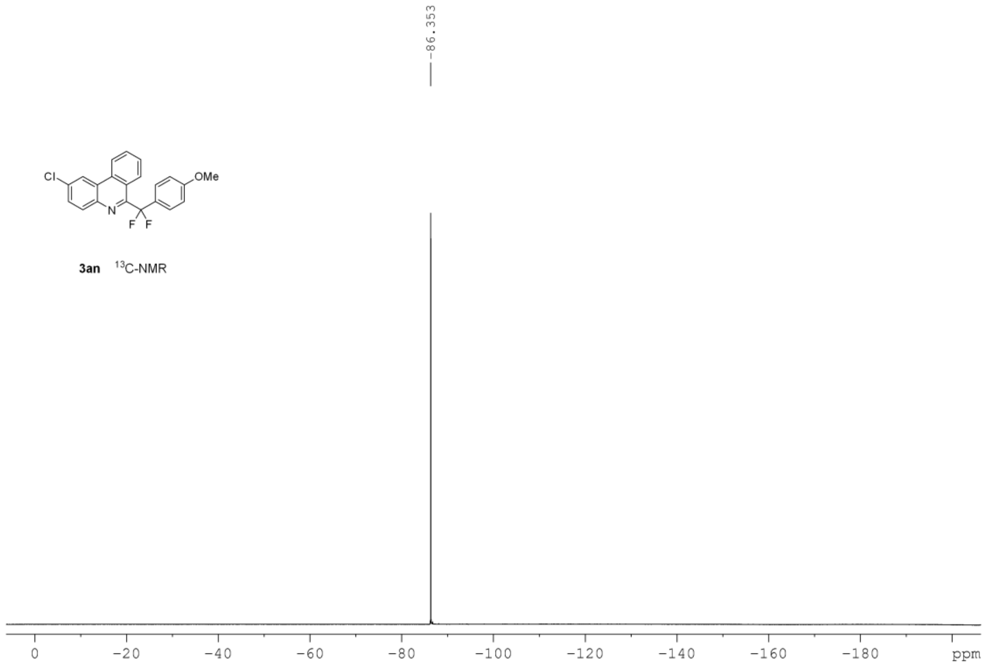
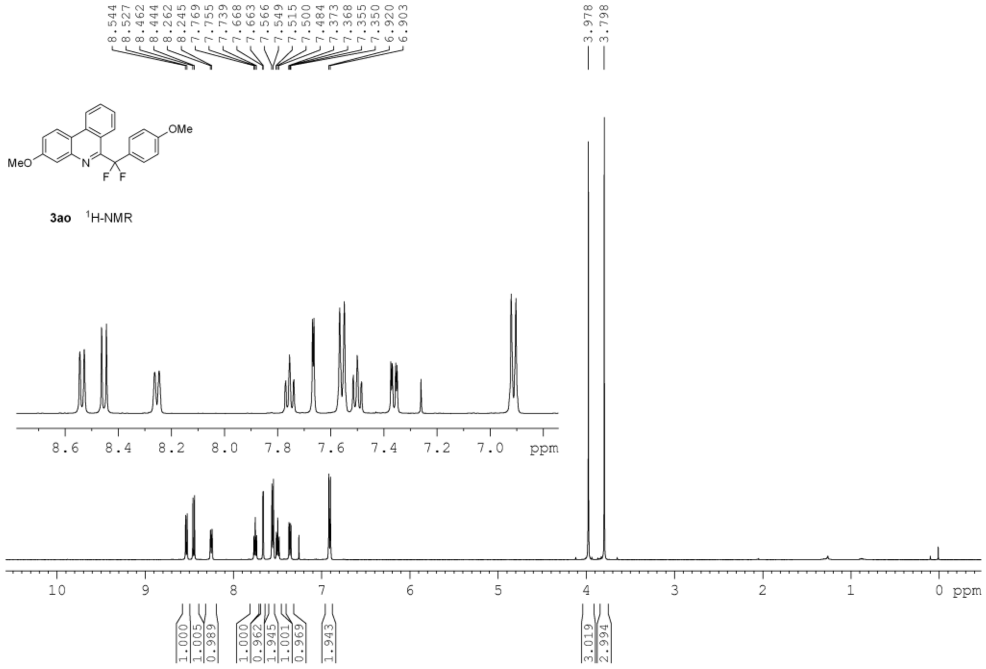
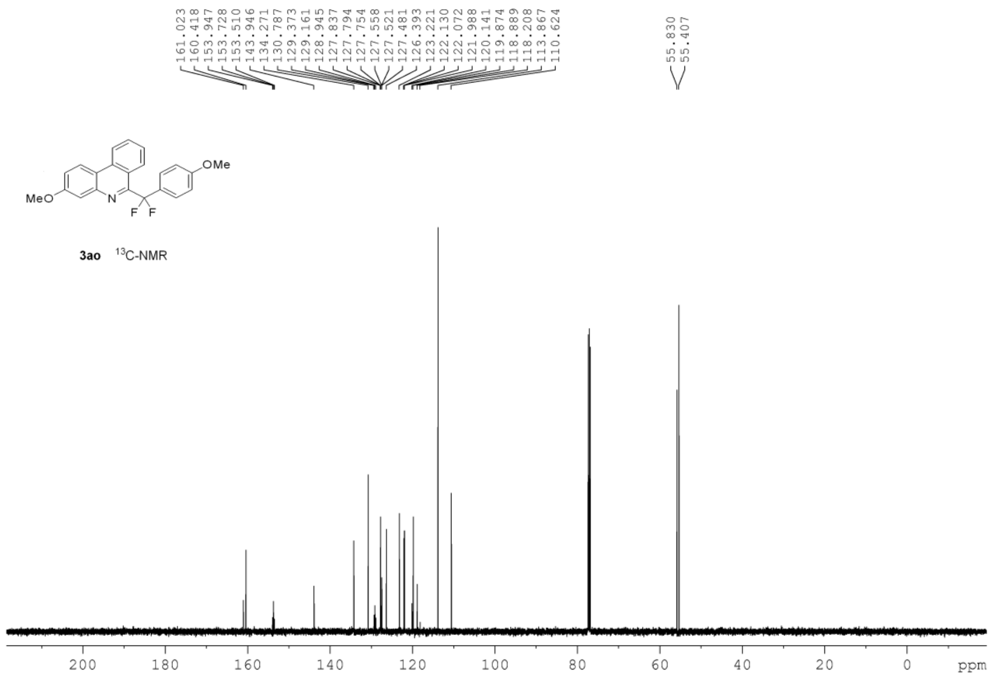
140.644
134.565
133.017
132.642
131.057
129.617
129.024
128.813
128.601
128.181
127.876
127.834
127.791
127.693
127.656
127.619
125.868
123.205
122.501
122.240
121.746
120.303
118.368
113.860
55.430
Cl
N
F F
OMe
3an ^{13}C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm



3an ^{13}C-NMR



3ao ^{1}H-NMR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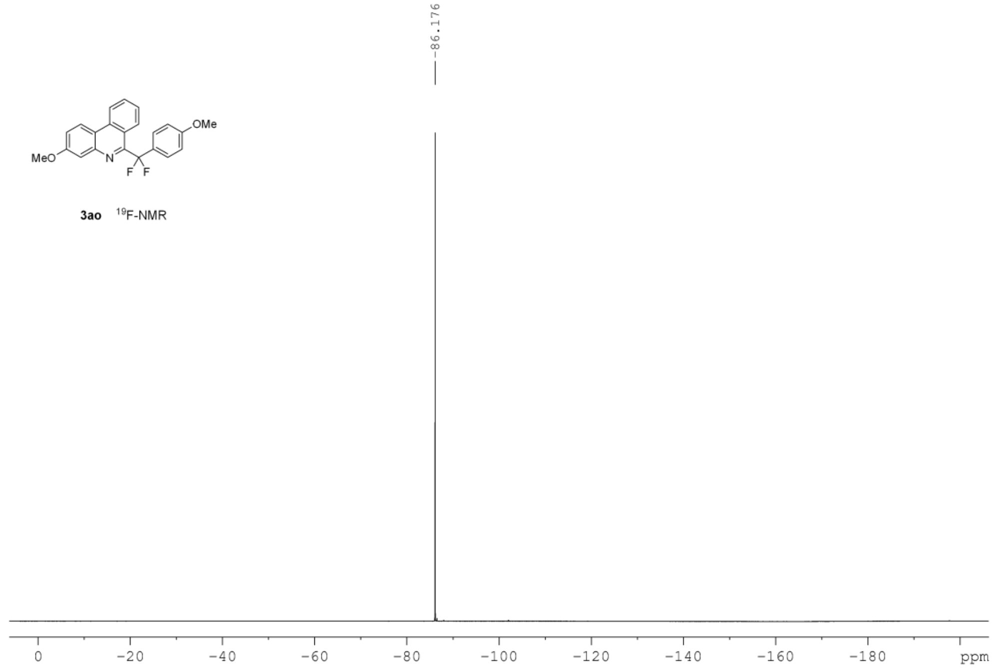
153.510
143.946
134.271
130.787
129.373
129.161
128.945
127.837
127.794
127.754
127.558
127.521
127.481
126.393
123.221
122.130
122.072
121.988
120.141
119.874
118.889
118.208
113.867
110.624
55.830
55.407
OMe
MeO
N
F
F
3ao ¹³C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm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OMe
MeO
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F
F
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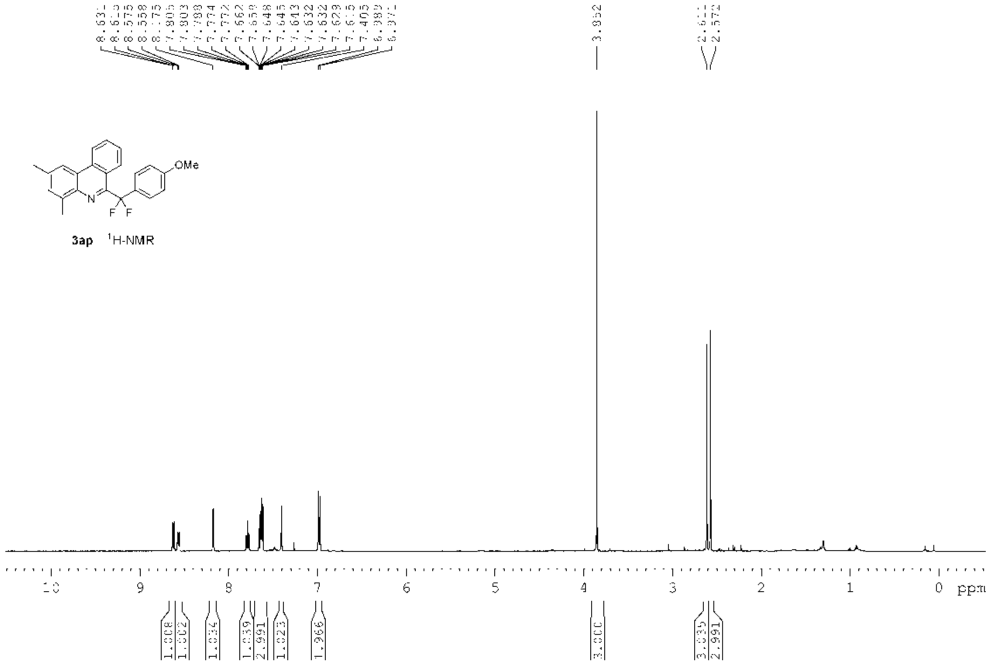
-100
-120
-140
-160
-180
ppm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8.175
7.805
7.803
7.788
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7.772
7.662
7.659
7.648
7.645
7.643
7.632
7.632
7.629
7.615
7.405
6.989
6.971
3.852
2.611
2.572
OMe
N
F
F
3ap ¹H-NMR
10
9
8
7
6
5
4
3
2
1
0
ppm
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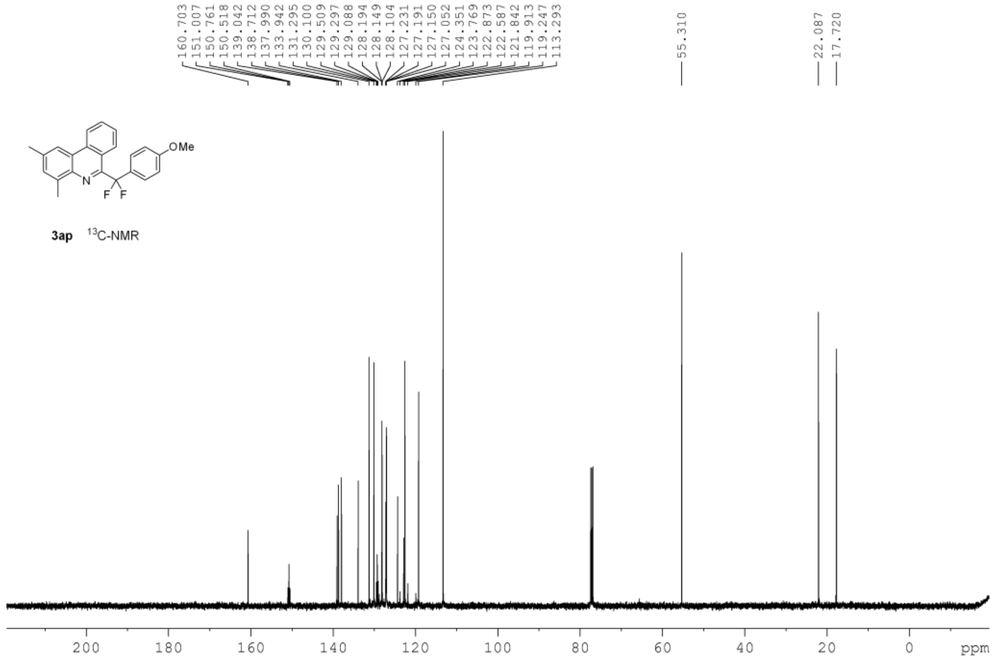
1.002
1.034
1.039
2.991
1.023
1.966
3.000
3.035
2.991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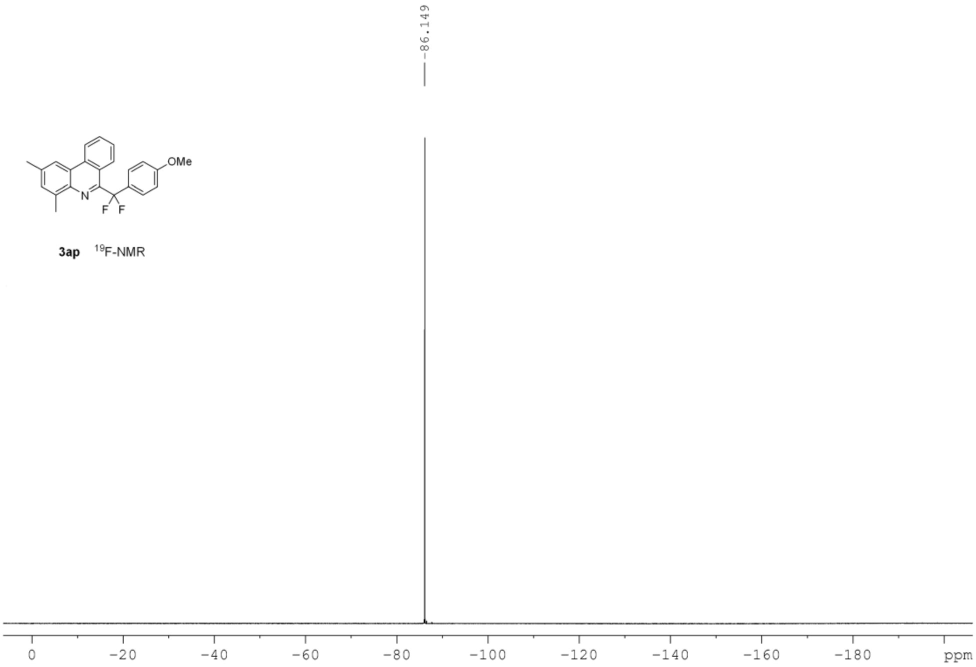
150.518
139.042
138.712
137.990
133.942
131.295
130.100
129.509
129.297
129.088
128.194
128.149
128.104
127.231
127.191
127.150
127.052
124.351
123.769
122.873
122.587
121.842
119.913
119.247
113.293
55.310
22.087
17.720
OMe
N
F
F
3ap ¹³C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm


-86.149
OMe
N
F F
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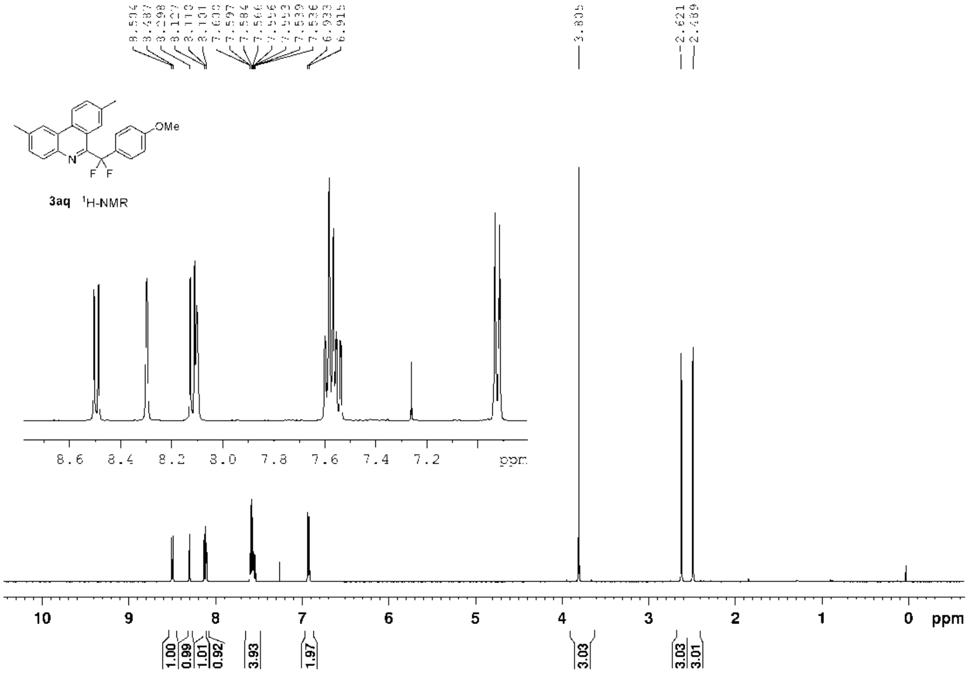
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm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8.487
8.298
8.127
8.113
8.101
7.602
7.597
7.584
7.566
7.556
7.553
7.539
7.536
6.933
6.915
3.805
2.621
2.489
OMe
N
F F
3aq ^{1}H-NMR
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
10
9
8
7
6
5
4
3
2
1
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ppm
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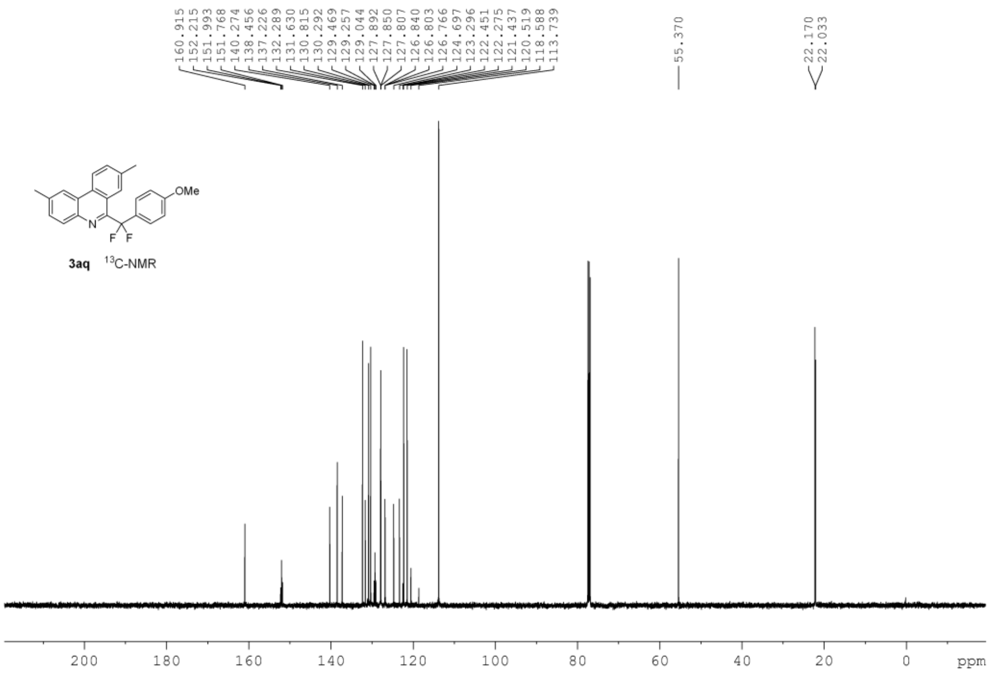
0.99
1.01
0.92
3.93
1.97
3.03
3.03
3.01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152.215
151.993
151.768
140.274
138.456
137.226
132.289
131.630
130.815
130.292
129.469
129.257
129.044
127.892
127.850
127.807
126.840
126.803
126.766
124.697
123.296
122.451
122.275
121.437
120.519
118.588
113.739
55.370
22.170
22.033
OMe
N
F
F
3aq
13C-NMR
200
180
160
140
120
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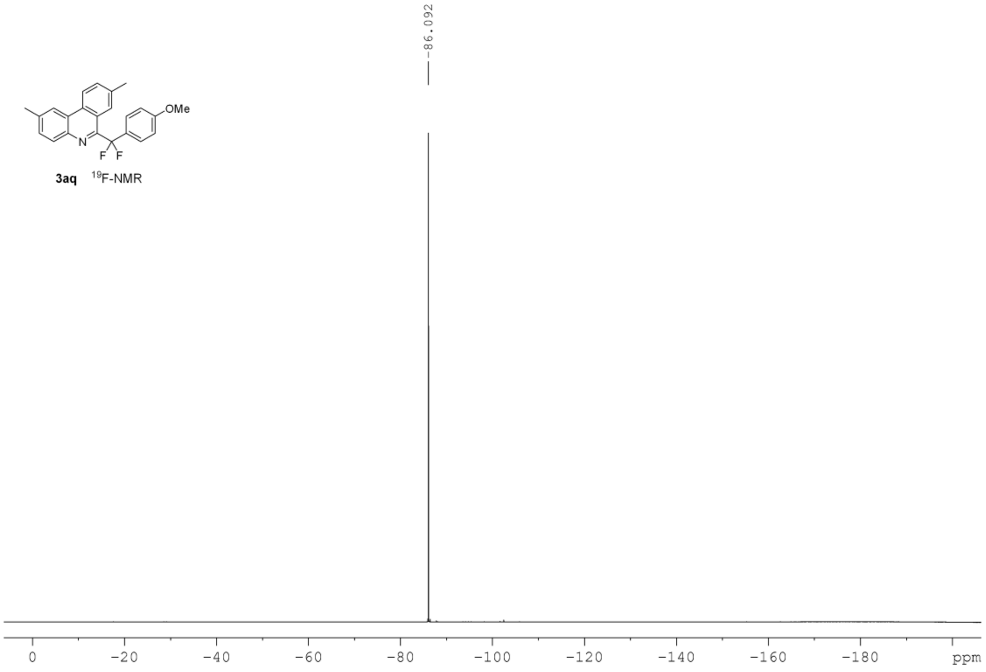
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19F-NMR
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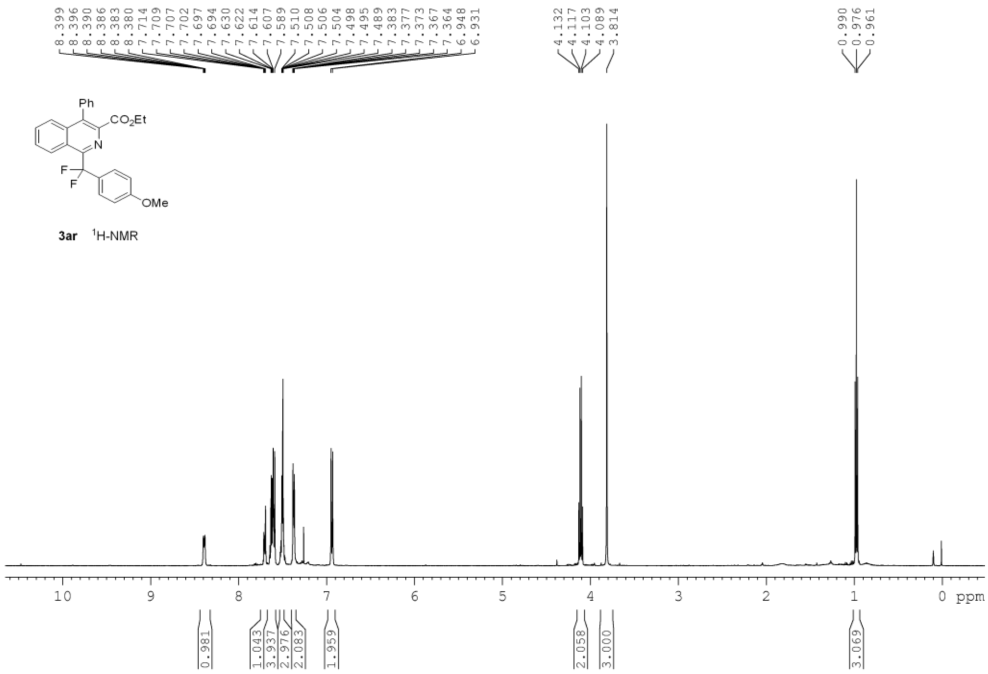
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6.931
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4.117
4.103
4.089
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0.961
Ph
CO$_2$Et
N
F
F
OMe
3ar ^{1}H-NMR
10
9
8
7
6
5
4
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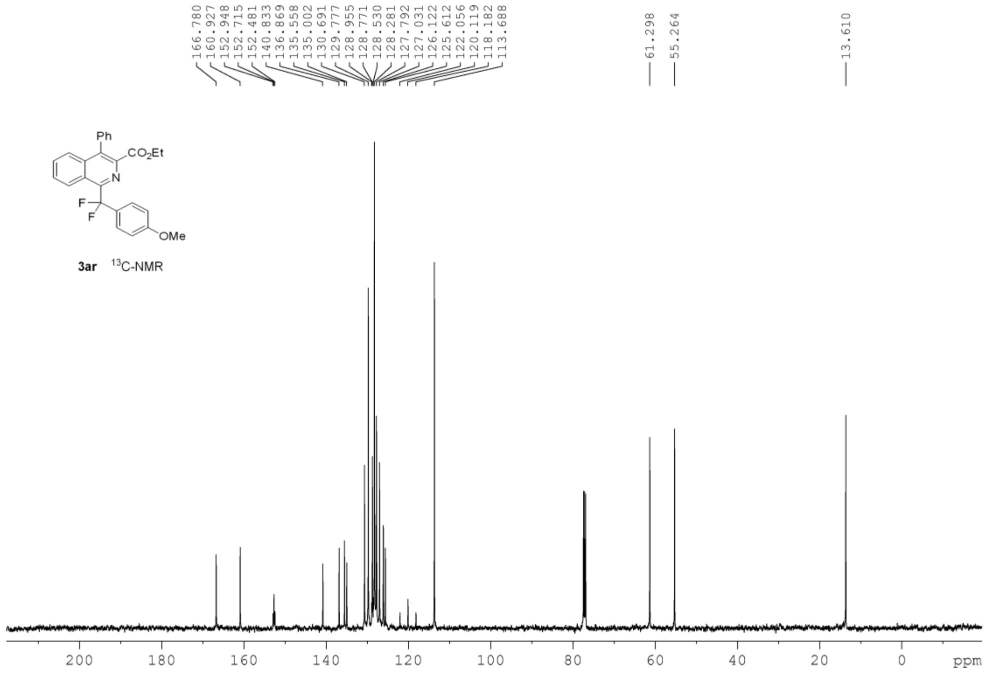
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Ph
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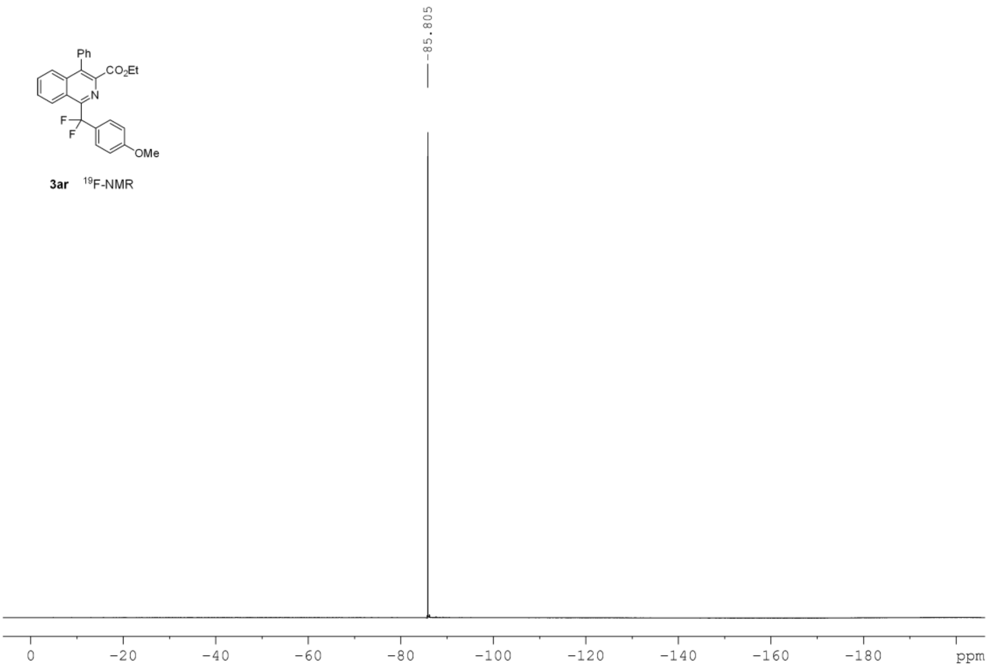

3ar ^{19}F-NMR

13. X-ray Crystal data for product 3aa

Table 1. Crystal data and structure refinement for 3aa.

Identification code	**3aa**
Empirical formula	$C_{21}H_{15}F_2NO$
Formula weight	335.34
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 5.498(5) A alpha = 90 deg.
	b = 9.083(8) A beta = 92.524(10) deg.
	c = 16.538(15) A gamma = 90 deg.
Volume	825.1(13) A^3
Z, Calculated density	2, 1.350 Mg/m^3
Absorption coefficient	0.098 mm^{-1}
F(000)	348
Crystal size	0.28 x 0.19 x 0.08 mm
Theta range for data collection	2.47 to 25.04 deg.
Limiting indices	-6<=h<=6, -10<=k<=10, -19<=l<=11
Reflections collected / unique	4258 / 2878 [R(int) = 0.0154]
Completeness to theta = 25.04	99.20%
Absorption correction	None
Max. and min. transmission	0.9922 and 0.9730
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2878 / 1 / 228
Goodness-of-fit on F^2	1.603
Final R indices [I>2sigma(I)]	R_1 = 0.0311, wR_2 = 0.0536
R indices (all data)	R_1 = 0.0354, wR_2 = 0.0549
Absolute structure parameter	0.0(6)
Extinction coefficient	0.049(2)
Largest diff. peak and hole	0.106 and -0.092 e.A^{-3}
Largest diff. peak and hole	0.106 and -0.092 e.A^{-3}

Table 2. Atomic coordinates (Å x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 3aa. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	6366(3)	7056(2)	7420(1)	47(1)
C(2)	7939(3)	7279(2)	6784(1)	59(1)
C(3)	9599(4)	8410(2)	6816(1)	71(1)
C(4)	9694(4)	9349(2)	7476(2)	75(1)
C(5)	8153(3)	9180(2)	8095(1)	67(1)
C(6)	6431(3)	8015(2)	8086(1)	50(1)
C(7)	4752(3)	7753(2)	8720(1)	52(1)
C(8)	4599(4)	8677(2)	9405(1)	76(1)
C(9)	2994(4)	8388(3)	9990(1)	85(1)
C(10)	1451(4)	7174(2)	9931(1)	74(1)
C(11)	1567(3)	6255(2)	9283(1)	64(1)
C(12)	3227(3)	6509(2)	8666(1)	48(1)
C(13)	3432(3)	5566(2)	7961(1)	43(1)
C(14)	2026(3)	4115(2)	7886(1)	48(1)
C(15)	2327(3)	3206(2)	7143(1)	43(1)
C(16)	605(3)	3259(2)	6504(1)	52(1)
C(17)	838(3)	2387(2)	5825(1)	56(1)
C(18)	2807(3)	1437(2)	5780(1)	49(1)
C(19)	4549(3)	1380(2)	6412(1)	51(1)
C(20)	4292(3)	2266(2)	7082(1)	49(1)
C(21)	4969(4)	-267(2)	4959(1)	86(1)
F(1)	2715(2)	3282(1)	8563(1)	66(1)
F(2)	-419(2)	4383(1)	7977(1)	68(1)
N(1)	4846(2)	5826(1)	7368(1)	46(1)
O(1)	2846(2)	606(1)	5085(1)	68(1)

Table 3. Bond lengths [Å] and angles [°] for 3aa.

C(1)-N(1)	1.396(2)
C(1)-C(2)	1.406(2)
C(1)-C(6)	1.403(2)
C(2)-C(3)	1.374(3)
C(2)-H(2)	0.93
C(3)-C(4)	1.385(3)
C(3)-H(3)	0.93
C(4)-C(5)	1.366(3)
C(4)-H(4)	0.93
C(5)-C(6)	1.420(2)
C(5)-H(5)	0.93
C(6)-C(7)	1.447(2)
C(7)-C(12)	1.408(2)
C(7)-C(8)	1.416(2)
C(8)-C(9)	1.363(3)
C(8)-H(8)	0.93
C(9)-C(10)	1.392(3)
C(9)-H(9)	0.93
C(10)-C(11)	1.363(3)
C(10)-H(10)	0.93
C(11)-C(12)	1.418(2)
C(11)-H(11)	0.93
C(12)-C(13)	1.454(2)
C(13)-N(1)	1.300(2)
C(13)-C(14)	1.530(2)
C(14)-F(2)	1.381(2)
C(14)-F(1)	1.3903(19)
C(14)-C(15)	1.496(2)
C(15)-C(20)	1.384(2)
C(15)-C(16)	1.388(2)
C(16)-C(17)	1.384(2)
C(16)-H(16)	0.93
C(17)-C(18)	1.389(2)
C(17)-H(17)	0.93
C(18)-O(1)	1.377(2)
C(18)-C(19)	1.387(2)
C(19)-C(20)	1.382(2)
C(19)-H(19)	0.93
C(20)-H(20)	0.93
C(21)-O(1)	1.434(2)
C(21)-H(21A)	0.96

C(21)-H(21B)	0.96
C(21)-H(21C)	0.96
N(1)-C(1)-C(2)	117.07(15)
N(1)-C(1)-C(6)	122.68(15)
C(2)-C(1)-C(6)	120.20(16)
C(3)-C(2)-C(1)	120.52(19)
C(3)-C(2)-H(2)	119.7
C(1)-C(2)-H(2)	119.7
C(2)-C(3)-C(4)	119.58(19)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(5)-C(4)-C(3)	121.23(19)
C(5)-C(4)-H(4)	119.4
C(3)-C(4)-H(4)	119.4
C(4)-C(5)-C(6)	120.73(19)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(1)-C(6)-C(5)	117.72(17)
C(1)-C(6)-C(7)	118.18(15)
C(5)-C(6)-C(7)	124.11(16)
C(12)-C(7)-C(8)	118.12(18)
C(12)-C(7)-C(6)	118.83(15)
C(8)-C(7)-C(6)	123.04(17)
C(9)-C(8)-C(7)	121.1(2)
C(9)-C(8)-H(8)	119.5
C(7)-C(8)-H(8)	119.5
C(8)-C(9)-C(10)	121.0(2)
C(8)-C(9)-H(9)	119.5
C(10)-C(9)-H(9)	119.5
C(11)-C(10)-C(9)	119.4(2)
C(11)-C(10)-H(10)	120.3
C(9)-C(10)-H(10)	120.3
C(10)-C(11)-C(12)	121.4(2)
C(10)-C(11)-H(11)	119.3
C(12)-C(11)-H(11)	119.3
C(7)-C(12)-C(11)	119.00(16)
C(7)-C(12)-C(13)	117.21(15)
C(11)-C(12)-C(13)	123.77(16)
N(1)-C(13)-C(12)	124.59(15)
N(1)-C(13)-C(14)	114.29(14)
C(12)-C(13)-C(14)	121.06(14)
F(2)-C(14)-F(1)	103.90(12)
F(2)-C(14)-C(15)	109.30(13)

F(1)-C(14)-C(15)	108.99(14)
F(2)-C(14)-C(13)	109.26(13)
F(1)-C(14)-C(13)	106.50(13)
C(15)-C(14)-C(13)	117.95(13)
C(20)-C(15)-C(16)	118.33(16)
C(20)-C(15)-C(14)	121.02(15)
C(16)-C(15)-C(14)	120.63(15)
C(17)-C(16)-C(15)	120.84(16)
C(17)-C(16)-H(16)	119.6
C(15)-C(16)-H(16)	119.6
C(16)-C(17)-C(18)	119.93(16)
C(16)-C(17)-H(17)	120
C(18)-C(17)-H(17)	120
O(1)-C(18)-C(19)	124.94(16)
O(1)-C(18)-C(17)	115.22(15)
C(19)-C(18)-C(17)	119.84(16)
C(20)-C(19)-C(18)	119.35(16)
C(20)-C(19)-H(19)	120.3
C(18)-C(19)-H(19)	120.3
C(19)-C(20)-C(15)	121.70(16)
C(19)-C(20)-H(20)	119.2
C(15)-C(20)-H(20)	119.2
O(1)-C(21)-H(21A)	109.5
O(1)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(1)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(13)-N(1)-C(1)	118.34(14)
C(18)-O(1)-C(21)	117.85(14)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^2 x 10^3) for 3aa. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[$h^2a^{*2}U_{11}$+...+$2hka^*b^*U_{12}$]

Atom	U11	U22	U33	U23	U13	U12
C(1)	46(1)	35(1)	60(1)	4(1)	-2(1)	-2(1)
C(2)	65(1)	45(1)	68(1)	7(1)	11(1)	-5(1)
C(3)	70(1)	52(1)	92(2)	16(1)	10(1)	-13(1)
C(4)	64(1)	49(1)	110(2)	18(1)	-9(1)	-18(1)
C(5)	67(1)	45(1)	87(1)	-6(1)	-14(1)	-8(1)
C(6)	48(1)	38(1)	63(1)	0(1)	-9(1)	2(1)
C(7)	52(1)	47(1)	58(1)	-8(1)	-13(1)	8(1)
C(8)	72(1)	72(1)	82(2)	-28(1)	-9(1)	7(1)
C(9)	82(2)	100(2)	73(2)	-35(1)	-5(1)	26(2)
C(10)	78(2)	89(2)	55(1)	-7(1)	9(1)	23(1)
C(11)	64(1)	66(1)	60(1)	2(1)	8(1)	11(1)
C(12)	48(1)	47(1)	48(1)	1(1)	-2(1)	7(1)
C(13)	42(1)	39(1)	48(1)	2(1)	1(1)	2(1)
C(14)	42(1)	47(1)	56(1)	9(1)	5(1)	-2(1)
C(15)	39(1)	35(1)	55(1)	4(1)	2(1)	-7(1)
C(16)	43(1)	43(1)	70(1)	0(1)	-3(1)	2(1)
C(17)	49(1)	54(1)	63(1)	-3(1)	-12(1)	2(1)
C(18)	49(1)	40(1)	57(1)	1(1)	2(1)	-5(1)
C(19)	44(1)	42(1)	67(1)	0(1)	0(1)	5(1)
C(20)	42(1)	47(1)	58(1)	4(1)	-7(1)	-3(1)
C(21)	85(2)	84(2)	90(2)	-31(1)	-2(1)	21(1)
F(1)	87(1)	53(1)	59(1)	13(1)	8(1)	-4(1)
F(2)	46(1)	73(1)	85(1)	-12(1)	16(1)	-6(1)
N(1)	48(1)	37(1)	53(1)	1(1)	2(1)	-2(1)
O(1)	70(1)	67(1)	67(1)	-18(1)	-3(1)	8(1)

Table 5. Hydrogen coordinates (Å x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 3aa

Atom	x	y	z	U(eq)
H(2)	7856	6655	6337	71
H(3)	10652	8544	6398	86
H(4)	10827	10110	7499	90
H(5)	8234	9835	8528	80
H(8)	5611	9495	9457	91
H(9)	2927	9011	10434	102
H(10)	352	6992	10331	89
H(11)	536	5444	9244	76
H(16)	-723	3888	6532	63
H(17)	-321	2438	5399	67
H(19)	5878	751	6384	61
H(20)	5469	2230	7503	59
H(21A)	5123	-1012	5370	130
H(21B)	6386	352	4987	130
H(21C)	4822	-725	4436	130