Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electrochemical Initiation of Electron-Catalyzed Formation of Phenanthridines by Trifluoromethylation of Isonitriles

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1. General

All reactions containing air- or moisture-sensitive compounds were performed under argon atmosphere in oven-dried glassware using *Schlenk* techniques.

Tetrabutylammonium hexafluorophosphate (≥ 99.0%), 1,2-dimethoxyethane (≥ 99%) and $PdCl_2(PPh_3)_2$ (≥ 98%) were purchased from *Sigma Aldrich* and used as received. 1,4-Dioxan (99.5%, AcroSeal) was purchased from *Acros Organics* and used as received. Other chemicals were purchased from *ABCR*, *Acros Organics*, *Alfa Aesar*, *Fluka* and *Sigma Aldrich* and used as received. Solvents for extraction and flash chromatography (FC) were distilled.

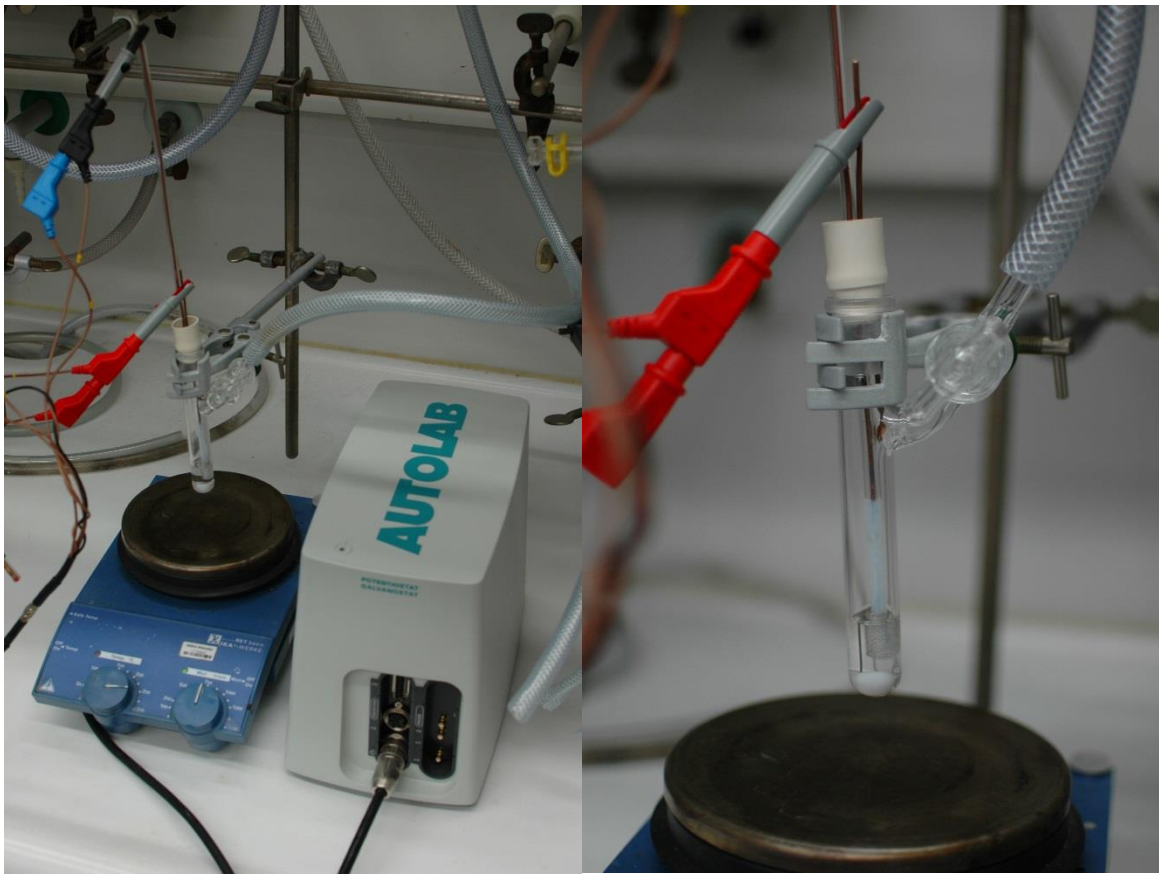
^{1}H-NMR (300 MHz and 400 MHz), **^{13}C-NMR** (75 MHz, 76 MHz and 101 MHz), **^{19}F-NMR** (282 MHz) measurements were carried out on a *Bruker DPX 300*, *Bruker AV 300* or *Bruker AV 400* spectrometer. The chemical shifts were referred to the solvent ($CDCl_3$) residual peak (^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm) and to an external standard ($CFCl_3$: δ = 0 ppm) for ^{19}F-NMR spectra. The multiplicity was described by s (singlet), d (doublet), t (triplet), q (quartet), sext (sextet) and m (multiplet). All melting points (**MP**) were determined by a *Stuart SMP10* and are uncorrected. Infrared spectra (**IR**) were recorded by a *Digilab 3100 FT-IR Excalibur Series* spectrometer. The IR signals are listed as *s* (strong), *m* (medium) and *w* (weak) in cm^{-1}. **HRMS ESI** (*m/z*) spectra were measured on a *Bruker MicroTof.*

For thin layer chromatography (TLC) *Merck* silica gel 60 F_{254} plates were used and UV light was used for detection. For FC *Acros Organics* silica gel (60 Å, 35-70 µm) was used with an argon excess pressure up to 0.5 bar.

Cyclic voltammetry experiments were conducted in a *Schlenk* tube that contained the substance dissolved in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile. A platinum wire working electrode and a platinum mesh counter electrode were used. The voltage was measured via a *Luggin* capillary against an Ag/Ag^+ reference and was referenced externally against the ferrocene/ferrocenium ion pair. The relevant parameters were controlled by a *Metrohm Autolab PGSTAT204* potentiostat.

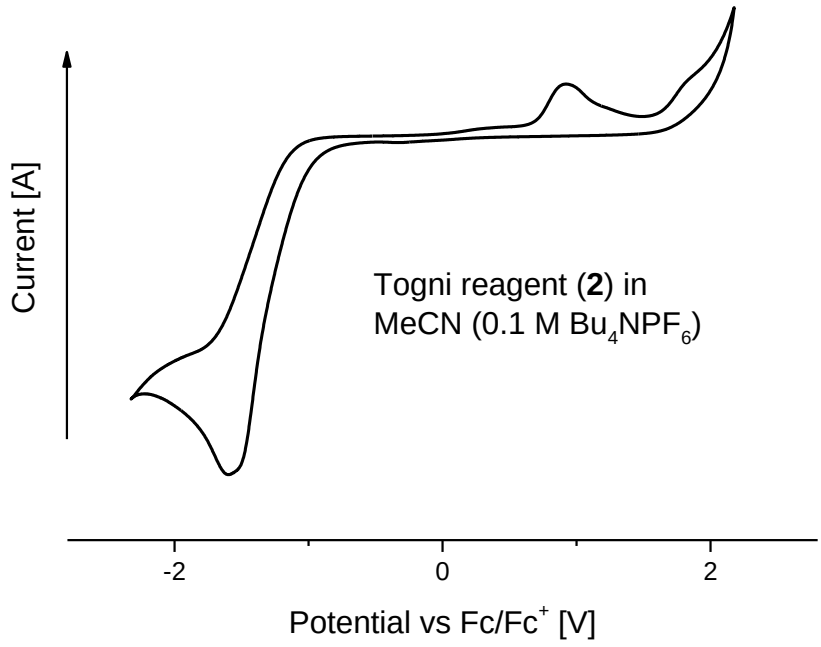
Electrochemical experiments were conducted under argon atmosphere in oven-dried *Schlenk* tubes. The platinum wire counter electrode (length: 1.5 cm) was protected by a synthetic flexible tube that was twined around by the platinum mesh working electrode (length: 1.4 cm; width:

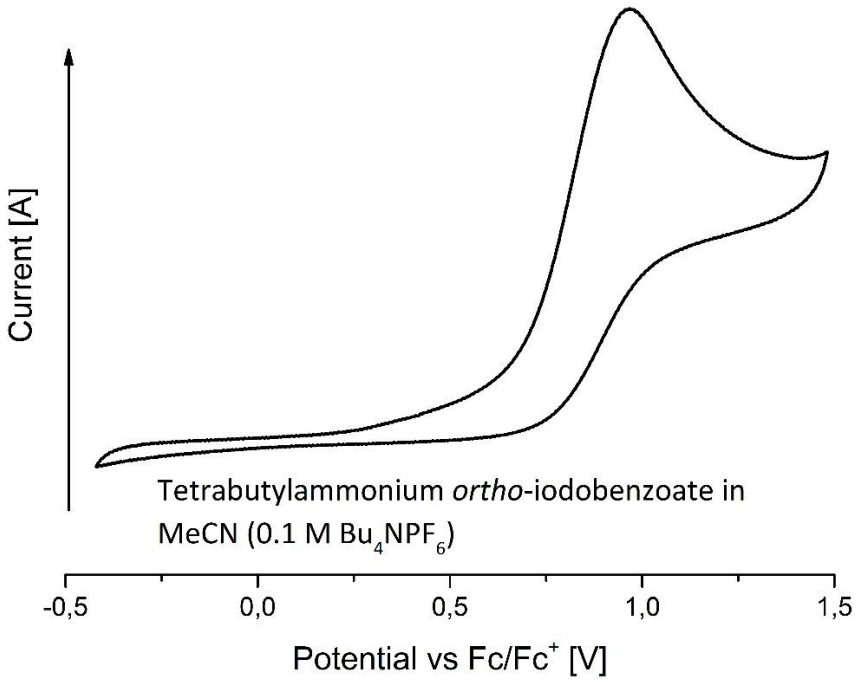
1.8 cm; distance to platinum wire approx. 3 mm). The electrodes were attached to platinum and copper wires (the wire leading to the counter electrode was additionally protected by melting it into a glass capillary) which were pushed through a septum to maintain an oxygen-free environment in the course of the reactions. For heating during the reactions the Schlenk tube was put into a heating block. The setup is depicted below. The relevant parameters were controlled by a *Metrohm Autolab PGSTAT204* potentiostat.

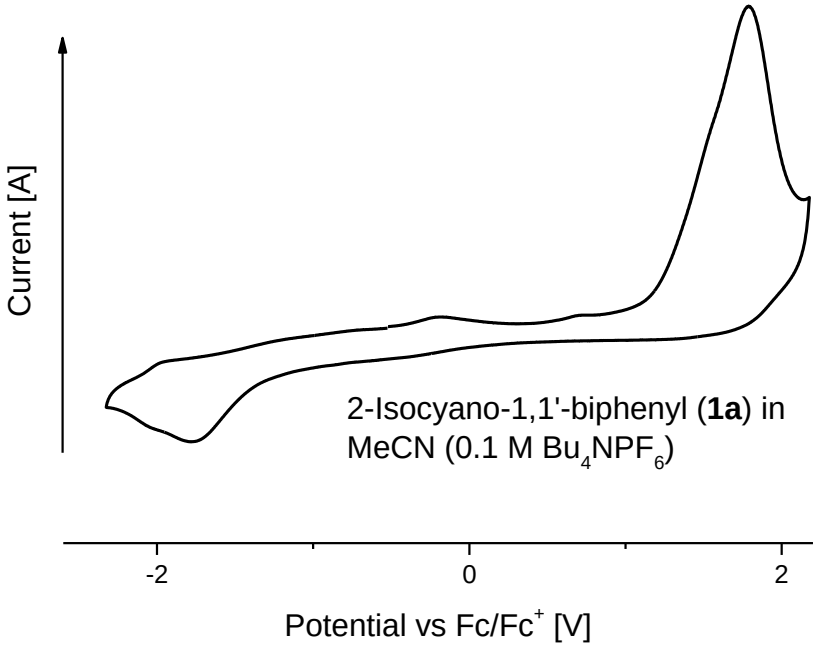


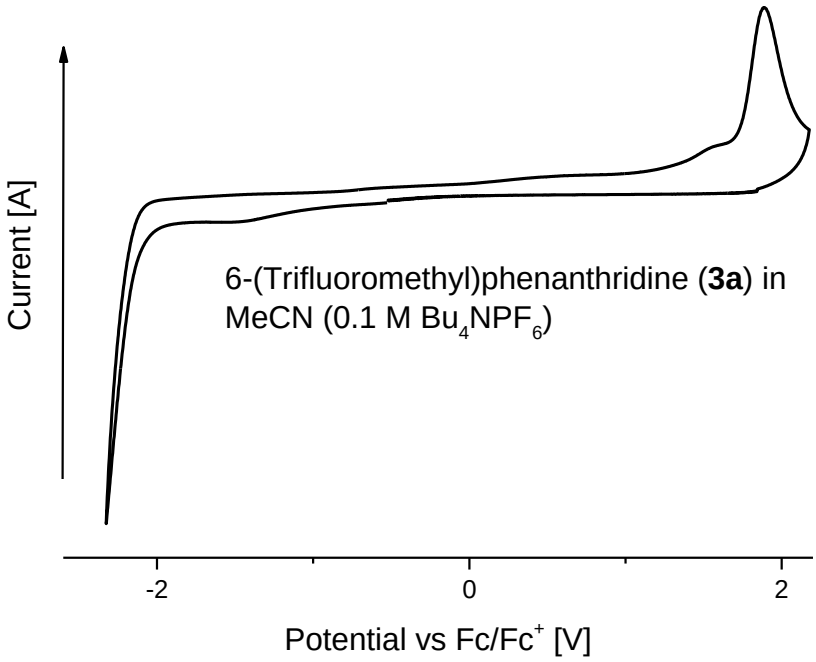
The large scale reaction (4 mmol) was performed under Argon atmosphere in an oven-dried glass tube. Two carbon electrodes which were pushed through a septum were utilized (working electrode: 1.9 cm × 0.4 cm × 3.0 cm; counter electrode: 1.9 cm × 0.5 cm × 3.0 cm; distance: 0.5 cm). The headspace was flushed with Argon via a canula during the reaction. For heating the tube was placed into an oil bath. The setup is depicted below. The relevant parameters were controlled by a *Metrohm Autolab PGSTAT204* potentiostat.

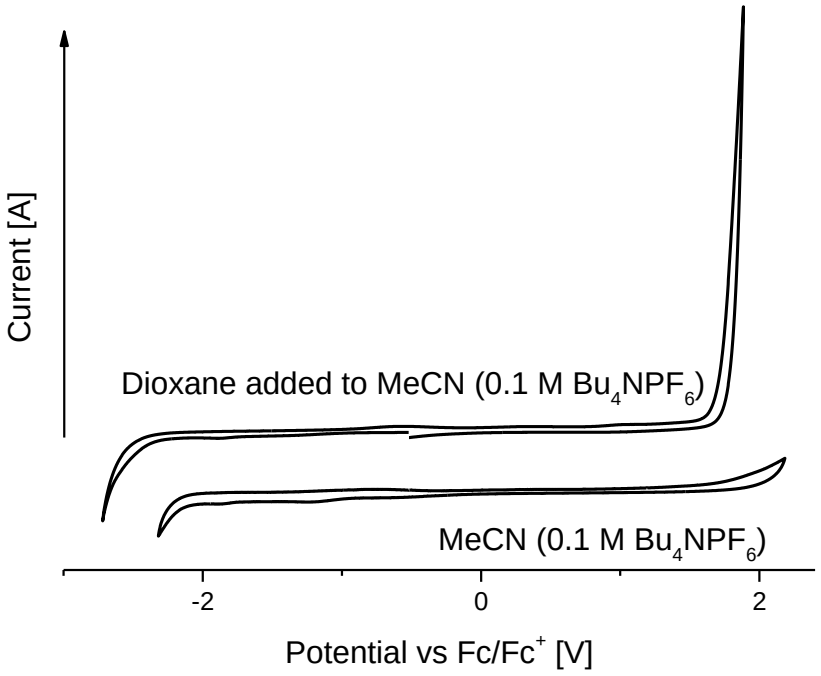
2. Cyclic voltammetry





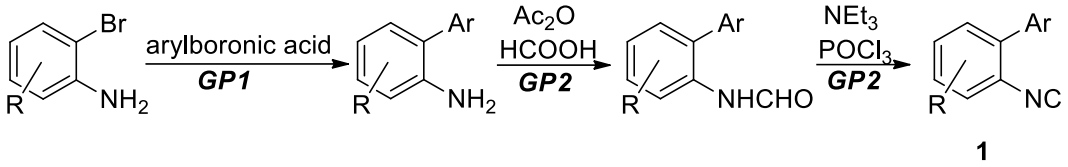

Current [A]
2-Isocyano-1,1'-biphenyl (**1a**) in
MeCN (0.1 M Bu_4NPF_6)
-2
0
2
Potential vs Fc/Fc^+ [V]


Current [A]
6-(Trifluoromethyl)phenanthridine (**3a**) in
MeCN (0.1 M Bu_4NPF_6)
-2
0
2
Potential vs Fc/Fc^+ [V]


Current [A]
Dioxane added to MeCN (0.1 M Bu4NPF6)
MeCN (0.1 M Bu4NPF6)
-2
0
2
Potential vs Fc/Fc+ [V]

3. Procedures

According to a literature procedure by *Chatani et al.*[1] 2-isocyanobiphenyls **1** were synthesized *via* a three step route (see scheme below).



*3.1. General procedure for the synthesis of 2-aminobiphenyls (**GP1**)*

Phenylboronic acid (1.2 equiv.) and an aq. solution of K_2CO_3 (2 M, 4.5 equiv.) were added to a mixture of 2-bromoaniline (1.0 equiv.) in 1,2-dimethoxyethane (0.5 M) and the reaction mixture was stirred for 30 min. After adding bis(triphenylphosphine)palladium(II)chloride (2 mol%), the mixture was heated to 80 °C and stirred overnight at this temperature. The reaction mixture was cooled to room temperature, filtered through a short pad of silica and eluted with EtOAc. The filtrate was washed with water and the organic phase was dried over $MgSO_4$. Filtration, concentration *in vacuo* and FC (P/EtOAc) afforded the desired 2-aminobiphenyl.

*3.2. General procedure for the synthesis of 2-isocyanobiphenyls **1** (**GP2**)*

An equimolar mixture of acetic anhydride and formic acid was stirred at 55 °C to form *in situ* acetic formic anhydride (2.0 equiv.). After cooling to room temperature it was added dropwise to a stirred solution of 2-aminobiphenyl in THF (0.3 – 0.6 M) at 0 °C. After stirring 2 h at room temperature, the reaction was stopped by the addition of a saturated aq. solution of $NaHCO_3$. The aqueous phase was extracted three times with EtOAc and the combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*.

Without further purification the residue was dissolved in THF (0.6 M) and triethylamine (6.0 equiv.) was added. The reaction mixture was cooled to 0 °C and phosphoryl chloride (1.5 equiv.) was added dropwise. After stirring two hours at this temperature a saturated solution of aq. Na_2CO_3 was added to the mixture and stirred for 1 h at room temperature. The aqueous phase was extracted three times with DCM. The combined organic phases were dried over $MgSO_4$ and filtered. Purification *via* FC (P/EtOAc) afforded the desired 2-isocyanobiphenyl **1**.

*3.3. General procedure for the synthesis of phenanthridines **3** (**GP3**)*

2-Isocyanobiphenyl **1** (0.20 mmol, 1.0 equiv.), Togni-Reagent (0.4 mmol, 2.0 equiv.) and tetrabutylammonium hexafluorophosphate (0.25 mmol) were suspended in 1,4-dioxane (2.5 mL). The electrodes were placed in the suspension which was subsequently heated to 80 °C. The solution was electrolyzed under constant current conditions (0.12 mA) until a charge of 1.45 C (0.075 equiv.) was reached.

Afterwards the reaction mixture was cooled to room temperature. The crude product was quantified by ^{19}F-NMR analysis using trifluorotoluene as internal standard. After concentration *in vacuo* the desired phenanthridine was afforded by FC (P/Et_2O).

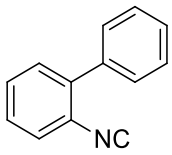
*3.4. Procedure for the synthesis of phenanthridine **3a** (**GP4**)*

2-Isocyanobiphenyl **1a** (717 mg, 4.00 mmol, 1.0 equiv.), Togni-Reagent (2.528 g, 8.000 mmol, 2.0 equiv.) and tetrabutylammonium hexafluorophosphate (1.937 g, 5.000 mmol) were suspended in 1,4-dioxane (50 mL). The electrodes were placed in the suspension which was subsequently heated to 80 °C. The solution was electrolyzed under constant current conditions (0.600 mA) until a charge of 13.6 C (0.035 equiv.) was reached.

Afterwards the reaction mixture was cooled to room temperature. The crude product was quantified by ^{19}F-NMR analysis using trifluorotoluene as internal standard. After concentration *in vacuo* the desired phenanthridine was afforded by FC (P/Et_2O).

4. Analytic data of starting materials

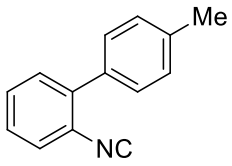
2-Isocyano-1,1'-biphenyl (1a)



According to ***GP2*** with [1,1'-biphenyl]-2-amine (508 mg, 3.00 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.80 mL), triethylamine (2.5 mL, 18 mmol, 6.0 equiv.) and phosphoryl chloride (0.41 mL, 4.5 mmol, 1.5 equiv.). FC (P/EtOAc = 40/1) afforded the desired 2-isocyanobiphenyl **1p** (456 mg, 2.54 mmol, 85%) as a green liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.57 – 7.34 (m, 9H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.6 (C), 138.9 (C), 137.1 (C), 130.7 (CH), 129.6 (CH), 129.1 (2 × CH), 128.7 (2 × CH), 128.5 (CH), 128.2 (CH), 127.9 (CH), 124.7 (C). **HRMS (ESI)** *m/z* = 202.06272 calcd. for $C_{13}H_9NNa^+$ $[M+Na]^+$, found: 202.06247. Spectroscopic data are in accordance with those described in the literature.[2]

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

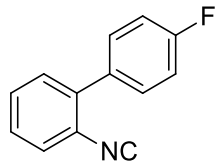


According to ***GP1*** with 2-bromoaniline (516 mg, 3.00 mmol, 1.0 equiv.), 4-methylphenylboronic acid (491 mg, 3.60 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.867 g, 13.51 mmol, 4.5 equiv.). FC (P/EtOAc = 10/1) afforded the desired 4'-methyl-[1,1'-biphenyl]-2-amine (425 mg, 2.32 mmol, 77%) as a yellow liquid.

According to ***GP2*** with 4'-methyl-[1,1'-biphenyl]-2-amine (425 mg, 2.32 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.61 mL), triethylamine (1.9 mL, 14 mmol, 6.0 equiv.) and phosphoryl chloride (0.32 mL, 3.5 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1m** (419 mg, 2.17 mmol, 94%) as a green liquid.

IR (neat): 3064*w*, 3028*w*, 2921*w*, 2865*w*, 2120*s*, 1616*w*, 1518*w*, 1479*s*, 1444*w*, 1410*w*, 1186*w*, 1107*w*, 1046*w*, 1007*w*, 946*w*, 820*m*, 759*s*, 680*w*, 562*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52 – 7.40 (m, 5H, $C_{arom}H$), 7.38 – 7.28 (m, 3H, $C_{arom}H$), 2.44 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.6 (C), 138.9 (C), 138.3 (C), 134.2 (C), 130.6 (CH), 129.6 (CH), 129.4 (2 × CH), 128.9 (2 × CH), 127.9 (CH), 127.9 (CH), 124.7 (C), 21.3 (CH3). **HRMS (ESI)** *m/z* = 216.0784 calcd. for $C_{14}H_{11}NNa^+$ $[M+Na]^+$, found: 216.0790.

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

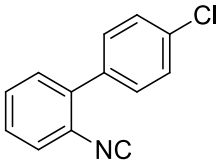


According to ***GP1*** with 2-bromoaniline (516 mg, 3.00 mmol, 1.0 equiv.), 4-fluorophenylboronic acid (506 mg, 3.62 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.867 g, 13.51 mmol, 4.5 equiv.). FC (P/EtOAc = 10/1) afforded the desired 4'-fluoro-[1,1'-biphenyl]-2-amine (345 mg, 1.84 mmol, 61%) as an orange liquid.

According to ***GP2*** with 4'-fluoro-[1,1'-biphenyl]-2-amine (339 mg, 1.81 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.48 mL), triethylamine (1.5 mL, 11 mmol, 6.1 equiv.) and phosphoryl chloride (0.25 mL, 2.7 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1p** (322 mg, 1.63 mmol, 90%) as a green liquid.

IR (neat): 3069*w*, 2120*s*, 1609*m*, 1598*w*, 1514*s*, 1479*s*, 1447*m*, 1405*w*, 1226*s*, 1186*w*, 1160*m*, 1110*w*, 1096*m*, 1047*w*, 1010*m*, 953*w*, 874*w*, 836*s*, 822*m*, 784*m*, 757*s*, 715*w*, 682*w*, 579*m*, 561*s*, 508*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 – 7.43 (m, 4H, $C_{arom}H$), 7.43 – 7.34 (m, 2H, $C_{arom}H$), 7.22 – 7.13 (m, 2H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7 (C), 162.9 (d, *J* = 248.1 Hz, C), 137.9 (C), 133.1 (d, *J* = 3.4 Hz, C), 130.9 (d, *J* = 8.3 Hz, 2 × CH), 130.6 (CH), 129.7 (CH), 128.4 (CH), 128.0 (CH), 124.7 (C), 115.7 (d, *J* = 21.7 Hz, 2 × CH). **^{19}F-NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -113.4 (s, CF). **HRMS (ESI)** *m/z* = 220.0533 calcd. for $C_{13}H_8FNNa^+$ $[M+Na]^+$, found: 220.0539.

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

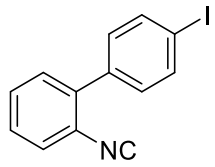


According to ***GP1*** with 2-bromoaniline (516 mg, 3.00 mmol, 1.0 equiv.), 4-chlorophenylboronic acid (563 mg, 3.60 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.862 g, 13.47 mmol, 4.5 equiv.). FC (P/EtOAc = 40/1) afforded the desired 4'-chloro-[1,1'-biphenyl]-2-amine (512 mg, 2.51 mmol, 84%) as a yellow liquid.

According to ***GP2*** with 4'-chloro-[1,1'-biphenyl]-2-amine (511 mg, 2.51 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.66 mL), triethylamine (2.1 mL, 15 mmol, 6.0 equiv.) and phosphoryl chloride (0.34 mL, 3.7 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1q** (491 mg, 2.30 mmol, 92%) as a light green solid.

MP: 97 °C. **IR** (neat): 3059*m*, 2292*w*, 2127*s*, 1980*w*, 1947*w*, 1906*w*, 1835*w*, 1729*w*, 1654*w*, 1594*w*, 1499*m*, 1475*s*, 1443*m*, 1397*m*, 1352*w*, 1298*w*, 1284*m*, 1267*w*, 1181*m*, 1100*m*, 1090*s*, 1049*m*, 1019*m*, 1006*m*, 909*m*, 878*m*, 829*s*, 819*s*, 796*m*, 762*s*, 739*s*, 653*w*, 632*m*, 562*s*, 535*m*, 506*m*. **^{1}H-NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52–7.37 (m, 8H, CH_{arom}). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.0 (C), 137.7 (C), 135.5 (C), 134.7 (C), 130.5 (CH), 130.4 (2 × CH), 129.8 (CH), 128.9 (2 × CH), 128.6 (CH), 128.0 (CH), 124.6 (C). **HRMS (ESI)** *m/z* = 236.0237 calcd. for $C_{13}H_8ClNNa^+$ $[M+Na]^+$, found: 236.0247.

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



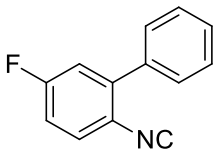
According to ***GP1*** with 2-aminophenylboronic acid hydrochloride (520 mg, 3.00 mmol, 1.0 equiv.), 1,4-diiodobenzene (3.959 g, 12.00 mmol, 4.0 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.874 g, 13.47 mmol, 4.5 equiv.). FC (P → P/EtOAc = 10/1) afforded the desired 4'-iodo-[1,1'-biphenyl]-2-amine (237 mg, 0.803 mmol, 27%) as a yellow oil.

IR (neat): 3456*w*, 3371*m*, 3208*w*, 3056*w*, 3022*w*, 1904*w*, 1791*w*, 1614*s*, 1581*m*, 1500*m*, 1478*s*, 1450*m*, 1386*m*, 1308*m*, 1293*m*, 1158*w*, 1100*w*, 1063*m*, 1000*s*, 936*w*, 821*s*, 749*s*, 730*m*, 625*w*, 562*m*, 517*w*. **^{1}H-NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 – 7.54 (m, 2H, $C_{arom}H$), 7.04 – 6.94 (m, 3H, $C_{arom}H$), 6.89 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H, $C_{arom}H$), 6.63 (td, *J* = 7.5 Hz, *J* = 1.2 Hz, 1H, $C_{arom}H$), 6.55 (dd, *J* = 8.0 Hz, *J* = 0.9 Hz, 1H, $C_{arom}H$), 3.47 (s, 2H, NH_2). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.3 (C), 139.1 (C), 138.0 (2 × CH), 131.1 (2 × CH), 130.3 (CH), 128.9 (CH), 126.4 (C), 118.9 (CH), 115.9 (CH), 92.9 (C). **HRMS (ESI)** *m/z* = 295.9931 calcd. for $C_{12}H_{11}IN^+$ $[M+H]^+$, found: 295.9937.

According to ***GP2*** with 4'-iodo-[1,1'-biphenyl]-2-amine (237 mg, 0.803 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.24 mL), triethylamine (0.67 mL, 4.8 mmol, 6.0 equiv.) and phosphoryl chloride (0.11 mL, 1.2 mmol, 1.5 equiv.). FC (P/EtOAc = 20/1) afforded the desired 2-isocyanobiphenyl **1e** (224.4 mg, 0.736 mmol, 92%) as a colorless solid.

MP: 125 °C. **IR** (neat): 3057*w*, 2128*s*, 1585*w*, 1498*w*, 1473*s*, 1443*w*, 1387*w*, 1297*w*, 1280*w*, 1182*w*, 1098*w*, 1063*w*, 1001*m*, 879*w*, 821*m*, 793*w*, 764*s*, 743*w*, 723*w*, 561*m*. **^{1}H-NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 – 7.79 (m, 2H), 7.51 – 7.43 (m, 2H), 7.42 – 7.35 (m, 2H), 7.27 – 7.22 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.1 (C), 137.9 (CH), 137.8 (C), 136.6 (C), 130.9 (CH), 130.4 (CH), 129.8 (CH), 128.7 (CH), 128.1 (CH), 124.5 (C), 94.7 (C). **HRMS (ESI)** *m/z* = 327.9594 calcd. for $C_{13}H_8INNa^+$ $[M+Na]^+$, found: 327.9593.

5-Fluoro-2-isocyano-1,1'-biphenyl (1f)

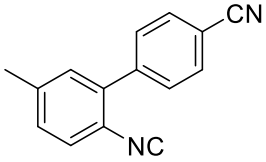


According to ***GP1*** with 2-bromo-4-fluoroaniline (760 mg, 4.00 mmol, 1.0 equiv.), phenylboronic acid (585 mg, 4.80 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (56 mg, 80 µmol, 2.0 mol%) and K_2CO_3 (2.492 g, 18.03 mmol, 4.5 equiv.). FC (P/EtOAc = 10/1) afforded the desired 5-fluoro-[1,1'-biphenyl]-2-amine (727 mg, 3.88 mmol, 97%) as an orange liquid.

According to ***GP2*** with 5-fluoro-[1,1'-biphenyl]-2-amine (721 mg, 3.85 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.97 mL), triethylamine (3.1 mL, 22 mmol, 5.7 equiv.) and phosphoryl chloride (0.50 mL, 5.5 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired 2-isocyanobiphenyl **1f** (617 mg, 3.13 mmol, 81%) as a green liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 – 7.41 (m, 6H, $C_{arom}H$), 7.14 (dd, *J* = 9.0 Hz, *J* = 2.8 Hz, 1H, $C_{arom}H$), 7.07 (ddd, *J* = 8.7 Hz, *J* = 7.6 Hz, *J* = 2.8 Hz, 1H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8 (C), 162.2 (d, *J* = 252.1 Hz, C), 141.3 (d, *J* = 8.7 Hz, C), 136.0 (d, *J* = 1.6 Hz, C), 129.8 (d, *J* = 9.2 Hz, CH), 129.0 (CH), 128.9 (2 × CH), 128.8 (2 × CH), 120.9 (C), 117.5 (d, *J* = 23.5 Hz, CH), 115.3 (d, *J* = 23.3 Hz, CH). **^{19}F-NMR** (282 MHz, $CDCl_3$, 300 K): δ (ppm) = -108.7 (s, CF). **HRMS (ESI)** *m/z* = 220.0533 calcd. for $C_{13}H_8FNNa^+$ $[M+Na]^+$, found: 220.0544. Spectroscopic data are in accordance with those described in the literature.[1]

2'-Isocyano-5'-methyl-[1,1'-biphenyl]-4-carbonitrile (1g)

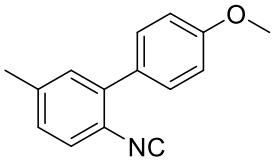


According to ***GP1*** with 2-bromo-4-methylaniline (0.37 mL, 3.0 mmol, 1.0 equiv.), 4-cyanophenylboronic acid (523 mg, 3.60 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.866 g, 13.50 mmol, 4.5 equiv.). FC (P/EtOAc = 25/1 → 5/1) afforded the desired 2'-amino-5'-methyl-[1,1'-biphenyl]-4-carbonitrile (460 mg, 2.21 mmol, 74%) as a colorless solid.

According to ***GP2*** with 2'-amino-5'-methyl-[1,1'-biphenyl]-4-carbonitrile (417 mg, 2.00 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.53 mL), triethylamine (1.7 mL, 12 mmol, 6.1 equiv.) and phosphoryl chloride (0.28 mL, 3.0 mmol, 1.5 equiv.). FC (P/Et_2O = 5/1) afforded the desired 2-isocyanobiphenyl **1g** (400 mg, 1.83 mmol, 92%) as a pale yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (d, *J* = 8.4 Hz, 2H, $C_{arom}H$), 7.62 (d, *J* = 8.4 Hz, 2H, $C_{arom}H$), 7.41 (d, *J* = 8.0 Hz, 1H, $C_{arom}H$), 7.28 – 7.18 (m, 2H, $C_{arom}H$), 2.43 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.2 (NC), 141.9 (C), 140.5 (C), 136.7 (C), 132.4 (2 × C), 130.9 (C), 130.1 (C), 129.9 (2 × C), 128.0 (C), 122.1 (C), 118.6 (CN), 112.4 (C), 21.5 (CH_3). **HRMS (ESI)** *m/z* = 241.0736 calcd. for $C_{15}H_{10}N_2Na^+$ $[M+Na]^+$, found: 241.0742. Spectroscopic data are in accordance with those described in the literature.[4]

2-Isocyano-4'-methoxy-5-methyl-1,1'-biphenyl (1h)

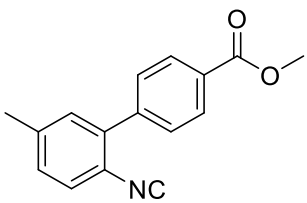


According to ***GP1*** with 2-bromo-4-methylaniline (0.37 mL, 3.0 mmol, 1.0 equiv.), 4-methoxyphenylboronic acid (547 mg, 3.60 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (42 mg, 60 µmol, 2.0 mol%) and K_2CO_3 (1.866 g, 13.50 mmol, 4.5 equiv.). FC (P/EtOAc = 15/1 → 8/1) afforded the desired 4'-methoxy-5-methyl-[1,1'-biphenyl]-2-amine (520 mg, 2.44 mmol, 81%) as a yellow liquid.

According to ***GP2*** with 4'-methoxy-5-methyl-[1,1'-biphenyl]-2-amine (427 mg, 2.00 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.53 mL), triethylamine (1.7 mL, 12 mmol, 6.1 equiv.) and phosphoryl chloride (0.28 mL, 3.0 mmol, 1.5 equiv.). FC (P/Et_2O = 8/1) afforded the desired 2-isocyanobiphenyl **1h** (375 mg, 1.68 mmol, 84%) as a colorless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.49 – 7.42 (m, 2H, $C_{arom}H$), 7.35 (d, *J* = 8.0 Hz, 1H, $C_{arom}H$), 7.21 (s, 1H, $C_{arom}H$), 7.13 (d, *J* = 8.2 Hz, 1H, $C_{arom}H$), 7.04 – 6.97 (m, 2H, $C_{arom}H$), 3.86 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.8 (NC), 159.8 (C), 139.9 (C), 138.4 (C), 131.1 (CH), 130.3 (CH), 129.6 (C), 128.4 (CH), 127.8 (CH), 122.2 (C), 114.09 (CH), 55.43 (OCH_3), 21.43 (CH_3). **HRMS (ESI)** *m/z* = 246.0889 calcd. for $C_{15}H_{13}NNaO^+$ $[M+Na]^+$, found: 246.0891. Spectroscopic data are in accordance with those described in the literature.[1]

Methyl 2'-isocyano-5'-methyl-[1,1'-biphenyl]-4-carboxylate (1i)



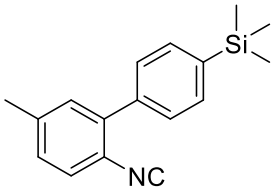
According to ***GP1*** with 2-bromo-4-methylaniline (0.25 mL, 2.0 mmol, 1.0 equiv.), 4-methoxycarbonylphenylboronic acid acid pinacol ester (629 mg, 2.40 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (28 mg, 40 µmol, 2.0 mol%) and K_2CO_3 (1.24 g, 8.97 mmol, 4.5 equiv.). FC

(P/EtOAc = 6/1 → 5/1) afforded the desired methyl 2'-amino-5'-methyl-[1,1'-biphenyl]-4-carboxylate (475 mg, 1.97 mmol, 98%) as a yellow liquid.

According to ***GP2*** with methyl 2'-amino-5'-methyl-[1,1'-biphenyl]-4-carboxylate (434 mg, 1.90 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.50 mL), triethylamine (1.6 mL, 12 mmol, 6.1 equiv.) and phosphoryl chloride (0.27 mL, 2.9 mmol, 1.5 equiv.). FC (P/Et_2O = 5/1) afforded the desired 2-isocyanobiphenyl **1i** (370 mg, 1.47 mmol, 78%) as a colorless solid.

MP: 146 °C. **IR** (neat): 2958*w*, 2927*w*, 2362*w*, 2125*m*, 1718*s*, 1612*w*, 1432*m*, 1286*s*, 1187*m*, 1111*m*, 1018*w*, 964*w*, 857*m*, 815*m*, 775*m*, 716*m*, 697*w*, 582*w*, 558*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.14 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H, $C_{arom}H$), 7.24 – 7.16 (m, 2H, $C_{arom}H$), 3.94 (s, 3H, CH_3), 2.41 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8 (C), 166.7 (C), 141.8 (C), 140.2 (C), 137.6 (C), 131.0 (CH), 130.0 (C), 129.9 (CH), 129.6 (CH), 129.1 (CH), 127.9 (CH), 122.1 (C), 52.3 (OCH_3), 21.41 (CH_3). **HRMS (ESI)** *m/z* = 274.0838 calcd. for $C_{16}H_{13}NNaO_2^+$ $[M+Na]^+$, found: 274.0836.

(2'-Isocyano-5'-methyl-[1,1'-biphenyl]-4-yl)trimethylsilane (1j)



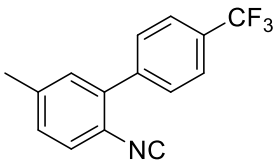
According to ***GP1*** with 2-bromo-4-methylaniline (0.15 mL, 1.2 mmol, 1.0 equiv.), 4-(trimethylsilyl)phenylboronic acid (280 mg, 1.44 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (17 mg, 24 µmol, 2.0 mol%) and K_2CO_3 (0.75 g, 5.4 mmol, 4.5 equiv.). FC (P/EtOAc = 10/1) afforded the desired 5-methyl-4'-(trimethylsilyl)-[1,1'-biphenyl]-2-amine (258 mg, 1.01 mmol, 84%) as a pale yellow oil.

According to ***GP2*** with 5-methyl-4'-(trimethylsilyl)-[1,1'-biphenyl]-2-amine (255 mg, 1.00 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.27 mL), triethylamine (0.83 mL, 5.8 mmol, 5.8 equiv.) and phosphoryl chloride (0.14 mL, 1.5 mmol, 1.5 equiv.). FC (P/Et_2O = 8/1) afforded the desired 2-isocyanobiphenyl **1j** (240 mg, 0.905 mmol, 91%) as a pale yellow liquid.

IR (neat): 3021*w*, 2955*w*, 2894*w*, 2361*w*, 2119*m*, 1599*w*, 1543*w*, 1488*w*, 1385*w*, 1312*w*, 1248*m*, 1199*w*, 1129*w*, 1107*m*, 1040*w*, 837*s*, 817*s*, 761*m*, 734*m*, 726*m*, 692*w*, 666*m*, 636*w*, 623*m*, 585*m*, 566*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63 (d, *J* = 8.1 Hz, 2H, $C_{arom}H$), 7.49 (d, *J* = 8.1 Hz, 2H, $C_{arom}H$), 7.37 (d, *J* = 8.0 Hz, 1H, $C_{arom}H$), 7.25 – 7.10 (m, 2H, $C_{arom}H$), 2.41 (s, 3H, CH_3), 0.32 (s, 9H, 3 × CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.0 (NC), 140.8 (C), 140.0 (C), 138.7 (C), 137.6 (C), 133.6 (CH), 131.3 (CH), 128.9 (CH), 128.3 (CH), 127.8

(CH), 122.3 (C), 21.5 (CH_3), -1.0 ($3 \times CH_3$). **HRMS (ESI)** *m/z* = 288.1179 calcd. for $C_{17}H_{19}NNaSi^+$ $[M+Na]^+$, found: 288.1180.

2-Isocyano-5-methyl-4'-(trifluoromethyl)-1,1'-biphenyl (1k)

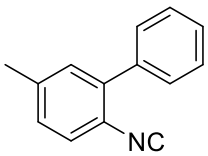


According to ***GP1*** with 2-bromo-4-methylaniline (0.15 mL, 1.2 mmol, 1.0 equiv.), 4-(trifluoromethyl)phenylboronic acid pinacol ester (392 mg, 1.44 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (17 mg, 24 µmol, 2.0 mol%) and K_2CO_3 (0.75 g, 5.4 mmol, 4.5 equiv.). FC (P/EtOAc = 10/1) afforded the desired 5-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (260 mg, 1.03 mmol, 86%) as a pale yellow solid.

According to ***GP2*** with 5-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (251 mg, 1.00 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.27 mL), triethylamine (0.83 mL, 5.8 mmol, 5.8 equiv.) and phosphoryl chloride (0.14 mL, 1.5 mmol, 1.5 equiv.). FC (P/Et_2O = 8/1) afforded the desired 2-isocyanobiphenyl **1j** (175 mg, 0.670 mmol, 67%) as a pale yellow/greenish solid.

MP: 78 °C. **IR** (neat): 2119*m*, 1620*w*, 1572*w*, 1491*w*, 1397*w*, 1322*s*, 1165*m*, 1122*s*, 1109*s*, 1068*s*, 1040*w*, 1019*m*, 958*w*, 844*m*, 820*m*, 715*w*, 654*w*, 636*w*, 609*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.75 (d, *J* = 8.1 Hz, 2H, $C_{arom}H$), 7.62 (d, *J* = 8.1 Hz, 2H, $C_{arom}H$), 7.41 (d, *J* = 8.6 Hz, 1H, $C_{arom}H$), 7.25 – 7.20 (m, 2H, $C_{arom}H$), 2.43 (s, 3H, CH_3) **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8 (NC), 140.9 (C), 140.3 (C), 137.2 (C), 131.1 (CH), 130.5 (q, *J* = 32 Hz, C), 129.7 (CH), 129.5 (CH), 127.9 (CH), 125.6 (q, *J* = 3.8 Hz, CH), 124.2 (q, *J* = 272 Hz, CF_3), 122.2 (C), 21.4 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -62.6 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 284.0658 calcd. for $C_{15}H_{10}NNa^+$ $[M+Na]^+$, found: 284.0656.

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

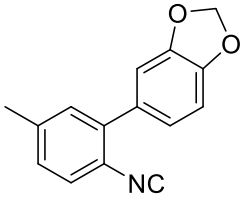


According to ***GP1*** with 2-bromo-4-methylaniline (0.25 mL, 2.0 mmol, 1.0 equiv.), phenylboronic acid (293 mg, 2.40 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (28 mg, 40 µmol, 2.0 mol%) and K_2CO_3 (1.2 g, 9.0 mmol, 4.5 equiv.). FC (P/EtOAc = 8/1) afforded the desired 5-methyl-[1,1'-biphenyl]-2-amine (330 mg, 1.80 mmol, 90%) as a pale brown liquid.

According to ***GP2*** with 5-methyl-[1,1'-biphenyl]-2-amine (324 mg, 1.77 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.47 mL), triethylamine (1.5 mL, 11 mmol, 6.1 equiv.) and phosphoryl chloride (0.26 mL, 2.8 mmol, 1.6 equiv.). FC (P/Et_2O = 5/1) afforded the desired 2-isocyanobiphenyl **1l** (307 mg, 1.59 mmol, 90%) as a pale green solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 – 7.34 (m, 6H, $C_{arom}H$), 7.24 – 7.21 (m, 1H, $C_{arom}H$), 7.20 – 7.13 (m, 1H, $C_{arom}H$), 2.41 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.0 (NC), 140.0 (C), 138.8 (C), 137.4 (C), 131.3 (CH), 129.1 (CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 127.8 (CH), 120.1 (C), 21.5 (CH_3). **HRMS (ESI)** *m/z* = 216.0784 calcd. for $C_{14}H_{11}NNa^+$ $[M+Na]^+$, found: 216.0800. Spectroscopic data are in accordance with those described in the literature.[1]

5-(2-Isocyano-5-methylphenyl)benzo[d][1,3]dioxole (1m)

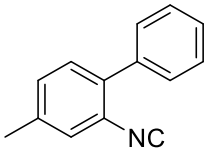


According to ***GP1*** with 2-bromo-4-methylaniline (0.25 mL, 2.0 mmol, 1.0 equiv.), 3,4-(methylenedioxy)benzeneboronic acid (398 mg, 2.40 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (28 mg, 40 µmol, 2.0 mol%) and K_2CO_3 (1.24 g, 8.97 mmol, 4.5 equiv.). FC (P/EtOAc = 5/1) afforded the desired 2-(benzo[d][1,3]dioxol-5-yl)-4-methylaniline (424 mg, 1.87 mmol, 93%) as a pale yellow liquid.

According to ***GP2*** with 2-(benzo[d][1,3]dioxol-5-yl)-4-methylaniline (409 mg, 1.80 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.48 mL), triethylamine (1.5 mL, 11 mmol, 6.0 equiv.) and phosphoryl chloride (0.25 mL, 2.7 mmol, 1.5 equiv.). FC (P/Et_2O = 8/1) afforded the desired 2-isocyanobiphenyl **1m** (320 mg, 1.35 mmol, 75%) as a pale yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.34 (d, *J* = 8.1 Hz, 1H, $C_{arom}H$), 7.19 – 7.16 (m, 1H, $C_{arom}H$), 7.16 – 7.10 (m, 1H, $C_{arom}H$), 6.99 – 6.93 (m, 2H, $C_{arom}H$), 6.92 – 6.87 (m, 1H, $C_{arom}H$), 6.02 (s, 2H, CH2), 2.40 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.0 (NC), 147.9 (C), 147.8 (C), 139.9 (C), 138.4 (C), 131.2 (CH), 131.1 (C), 128.7 (CH), 127.8 (CH), 122.9 (CH), 122.2 (C), 109.6 (CH), 108.5 (CH), 101.4 (CH_2), 21.4 (CH_3). **HRMS (ESI)** *m/z* = 260.0682 calcd. for $C_{15}H_{11}NNaO_2^+$ $[M+Na]^+$, found: 260.0682. Spectroscopic data are in accordance with those described in the literature.[4]

2-Isocyano-4-methyl-1,1'-biphenyl (3n)

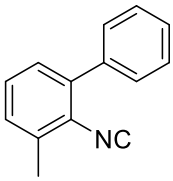


According to ***GP1*** with 2-bromo-5-methylaniline (0.25 mL, 2.0 mmol, 1.0 equiv.), phenylboronic acid (293 mg, 2.40 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (28 mg, 40 µmol, 2.0 mol%) and K_2CO_3 (1.2 g, 9.0 mmol, 4.5 equiv.). FC (P/EtOAc = 8/1) afforded the desired 4-methyl-[1,1'-biphenyl]-2-amine (315 mg, 1.72 mmol, 86%) as a pale yellow liquid.

According to ***GP2*** with 4-methyl-[1,1'-biphenyl]-2-amine (310 mg, 1.69 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.45 mL), triethylamine (1.4 mL, 10 mmol, 6.0 equiv.) and phosphoryl chloride (0.24 mL, 2.6 mmol, 1.5 equiv.). FC (P/Et_2O = 5/1) afforded the desired 2-isocyanobiphenyl **3n** (311 mg, 1.61 mmol, 95%) as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 – 7.37 (m, 5H, $C_{arom}H$), 7.34 – 7.24 (m, 3H, $C_{arom}H$), 2.41 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.3 (NC), 138.5 (C), 137.2 (C), 136.1 (C), 130.5 (CH), 130.5 (CH), 129.1 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 124.5 (C), 20.9 (CH_3). **HRMS (ESI)** *m/z* = 216.0784 calcd. for $C_{14}H_{11}NNa^+$ $[M+Na]^+$, found: 216.0806. Spectroscopic data are in accordance with those described in the literature.[4]

2-Isocyano-3-methyl-1,1'-biphenyl (3o)

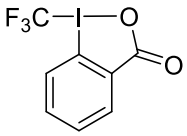


According to ***GP1*** with 2-bromo-6-methylaniline (238 mg, 1.28 mmol, 1.0 equiv.), phenylboronic acid (188 mg, 1.54 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (18 mg, 26 µmol, 2.0 mol%) and K_2CO_3 (0.80 g, 5.8 mmol, 4.5 equiv.). FC (P/EtOAc = 8/1) afforded the desired 3-methyl-[1,1'-biphenyl]-2-amine (208 mg, 1.14 mmol, 89%) as a white solid.

According to ***GP2*** with 3-methyl-[1,1'-biphenyl]-2-amine (200 mg, 1.09 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (0.29 mL), triethylamine (0.90 mL, 6.5 mmol, 6.0 equiv.) and phosphoryl chloride (0.15 mL, 1.6 mmol, 1.5 equiv.). FC (P/Et_2O = 8/1) afforded the desired 2-isocyanobiphenyl **3o** (183 mg, 0.95 mmol, 87%) as a white solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 – 7.38 (m, 5H, $C_{arom}H$), 7.38 – 7.22 (m, 3H, $C_{arom}H$), 2.51 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.8 (NC), 139.2 (C), 137.7 (C), 136.0 (C), 129.4 (CH), 129.1 (CH), 129.0 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 124.9 (C), 19.5 (CH_3). **HRMS (ESI)** *m/z* = 216.0784 calcd. for $C_{14}H_{11}NNa^+$ $[M+Na]^+$, found: 216.0787. Spectroscopic data are in accordance with those described in the literature.[4]

Togni reagent (2)



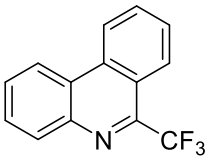
Togni reagent was synthesized according to a literature procedure.[3]

2-Iodobenzoic acid (3.47 g, 14.0 mmol, 1.0 equiv.) was placed into a dry three necked flask under argon and acetonitrile (30 mL) was added. The solution was heated to 75 °C and a solution of trichloroisocyanuric acid (1.11 g, 4.76 mmol, 1.0 equiv.) in acetonitrile (8 mL) was added within 5 min. Afterwards the mixture is cooled to room temperature.Dry KOAc (2.75 g, 28.0 mmol, 2.0 equiv.; the powder was dried at 105 °C over night) was added at once and the suspension was heated again at 75 °C for 1.5 h and then cooled to room temperature. Then trifluormethyltrimethylsilane (2.90 mL, 19.6 mmol, 1.4 equiv.) was added at once and the resulting mixture was stirred vigorously for 4.5 h at room temperature. After addition of acetonitrile (12.5 mL) the suspension was brought to reflux. The hot suspension was quickly filtered over a celite pad which was washed with hot acetonitrile afterwards. The brown filtrate was concentrated to a third of its initial volume and cooled to -15 °C while stirring. The formed crystals were filtered off and washed with little amount of cold acetonitrile. The filtrate is concentrated again to receive a second fraction of crystals.

According to the described procedure with the denoted amounts of substrate the crystallization afforded Togni reagent **2** (3.41 g, 10.8 mmol, 77%) as a colorless solid. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.47 – 8.40 (m, 1H, $C_{arom}H$), 7.85 – 7.70 (m, 3H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.0 (C), 135.8 (C), 133.9 (C), 132.2 (C), 132.1 (C), 127.4 (q, *J* = 3.1 Hz, C), 115.0 (C), 107.2 (q, *J* = 380.4 Hz, CF_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -33.81 (s, 3F, CF_3).

5. Analytic data of products

6-(Trifluoromethyl)phenanthridine (3a)

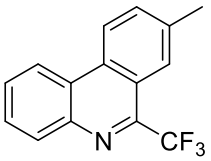


According to ***GP3*** with **1a** (36 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 100/1) afforded phenanthridine **3a** (38.0 mg, 0.154 mmol, 77%) as a yellow solid.

According to ***GP4*** phenanthridine **3a** (613 mg, 2.48 mmol, 62%) was obtained after FC (P/Et_2O = 50/1 → 40/1) as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.73 – 8.66 (m, 1H, $C_{arom}H$), 8.62 – 8.56 (m, 1H, $C_{arom}H$), 8.43 – 8.35 (m, 1H, $C_{arom}H$), 8.33 – 8.25 (m, 1H, $C_{arom}H$), 7.96 – 7.88 (m, 1H, $C_{arom}H$), 7.86 – 7.71 (m, 3H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 146.7 (m, C), 141.9 (C), 134.1 (C), 131.5 (C), 131.3 (C), 129.5 (C), 129.3 (C), 128.2 (C), 126.1 (q, *J* = 3.4 Hz, C), 125.3 (C), 122.7 (C), 122.2 (C), 122.1 (q, *J* = 277.6 Hz, CF_3), 121.9 (C). **^{19}F-NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.5 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 248.0682 calcd. for $C_{14}H_9F_3N^+$ $[M+H]^+$, found: 248.0690. Spectroscopic data are in accordance with those described in the literature.[4]

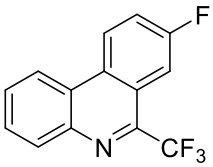
8-Methyl-6-(trifluoromethyl)phenanthridine (3b)



According to ***GP3*** with **1b** (36 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 50/1) afforded phenanthridine **3b** (36.4 mg, 0.139 mmol, 70%) as a colorless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.61 – 8.51 (m, 2H, $C_{arom}H$), 8.31 – 8.23 (m, 1H, $C_{arom}H$), 8.14 (s, 1H, $C_{arom}H$), 7.81 – 7.69 (m, 3H, $C_{arom}H$), 2.63 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 146.3 (m, C), 141.6 (C), 138.4 (C), 133.3 (C), 132.1 (C), 131.2 (C), 129.2 (C), 129.0 (C), 125.4 (q, *J* = 3.3 Hz, C), 122.5 (C), 122.1 (C), 122.1 (q, *J* = 277.7 Hz, CF_3), 122.0 (C), 22.1 (CH_3).**^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.5 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 262.0838 calcd. for $C_{15}H_{11}F_3N^+$ $[M+H]^+$, found: 262.0861. Spectroscopic data are in accordance with those described in the literature.[5]

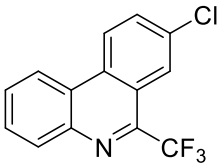
8-Fluoro-6-(trifluoromethyl)phenanthridine (3c)



According to ***GP3*** with **1c** (39 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 50/1) afforded phenanthridine **3c** (37.3 mg, 0.141 mmol, 70%) as a colorless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.66 (dd, *J* = 9.2, 5.3 Hz, 1H, $C_{arom}H$), 8.54 – 8.47 (m, 1H, $C_{arom}H$), 8.30 – 8.23 (m, 1H, $C_{arom}H$), 8.03 – 7.95 (m, 1H, $C_{arom}H$), 7.83 – 7.75 (m, 2H, $C_{arom}H$), 7.65 (m, 1H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 161.6 (d, *J* = 250.1 Hz, CF), 145.9 (m, C), 141.6 (C), 131.4 (C), 130.8 (d, *J* = 1.8 Hz, C), 129.8 (C), 129.4 (C), 125.3 (d, *J* = 8.7 Hz, C), 124.8 (C), 123.0 (d, *J* = 8.7 Hz, C), 121.9 (C), 121.9 (q, *J* = 276.9 Hz, CF_3), 121.0 (d, *J* = 24.1 Hz, C), 110.9 (dq, *J* = 23.3, 3.5 Hz, C). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -64.0 (s, 3F, CF_3), -109.9 (s, 1F, Ar-F). **HRMS (ESI)** *m/z* = 266.0587 calcd. for $C_{14}H_8F_4N^+$ $[M+H]^+$, found: 266.0574. Spectroscopic data are in accordance with those described in the literature.[6]

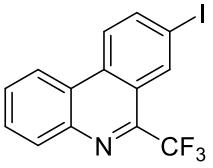
8-Chloro-6-(trifluoromethyl)phenanthridine (3d)



According to ***GP3*** with **1d** (42.7 mg, 0.200 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 50/1) afforded phenanthridine **3d** (42.1 mg, 0.149 mmol, 75%) as a colorless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.56 (d, *J* = 9.0 Hz, 1H, $C_{arom}H$), 8.52 – 8.45 (m, 1H, $C_{arom}H$), 8.33 – 8.28 (m, 1H, $C_{arom}H$), 8.28 – 8.22 (m, 1H, $C_{arom}H$), 7.86 – 7.74 (m, 3H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.5 (m, C), 141.8 (C), 134.4 (C), 132.4 (C), 132.1 (C), 131.4 (C), 129.8 (C), 129.8 (C), 125.3 (q, *J* = 3.6 Hz, C), 124.6 (C), 124.3 (C), 122.7 (C), 122.0 (C), 121.8 (q, *J* = 276.8 Hz, CF_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.6 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 282.0292 calcd. for $C_{14}H_8ClF_3N^+$ $[M+H]^+$, found: 282.0305. Spectroscopic data are in accordance with those described in the literature.[5]

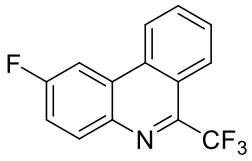
8-Iodo-6-(trifluoromethyl)phenanthridine (3e)



According to ***GP3*** with **1e** (61.0 mg, 0.200 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 50/1) afforded phenanthridine **3e** (56.2 mg, 0.151 mmol, 75%) as a colorless solid.

MP: 150 °C. **IR** (neat): 1571*w*, 1521*w*, 1465*w*, 1406*w*, 1374*w*, 1334*w*, 1250*m*, 1183*s*, 1168*s*, 1156*m*, 1122*s*, 978*m*, 858*w*, 829*w*, 802*w*, 762*s*, 734*m*, 588*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.71 – 8.65 (m, 1H, $C_{arom}H$), 8.56 – 8.48 (m, 1H, $C_{arom}H$), 8.37 (d, *J* = 8.8 Hz, 1H, $C_{arom}H$), 8.29 – 8.23 (m, 1H, $C_{arom}H$), 8.15 (dd, *J* = 8.8, 1.6 Hz, 1H, $C_{arom}H$), 7.86 – 7.74 (m, 2H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.3 (m, C), 141.8 (C), 140.2 (C), 134.8 (q, *J* = 3.7 Hz, C), 133.1 (C), 131.5 (C), 130.0 (C), 129.8 (C), 124.7 (C), 124.2 (C), 123.3 (C), 121.9 (C), 121.8 (q, *J* = 277.3 Hz, CF_3), 94.0 (CI). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.4 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 373.9648 calcd. for $C_{14}H_8F_3IN^+$ $[M+H]^{+,}$ found: 373.9648.

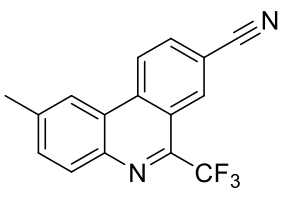
2-Fluoro-6-(trifluoromethyl)phenanthridine (3f)



According to ***GP3*** with **1f** (39 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 50/1) afforded phenanthridine **3f** (42.1 mg, 0.159 mmol, 79%) as a colorless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.57 (d, *J* = 8.3 Hz, 1H, $C_{arom}H$), 8.43 – 8.36 (m, 1H, $C_{arom}H$), 8.29 (dd, *J* = 9.0, 5.6 Hz, 1H, $C_{arom}H$), 8.20 (dd, *J* = 9.9, 2.7 Hz, 1H, $C_{arom}H$), 7.98 – 7.90 (m, 1H, $C_{arom}H$), 7.85 – 7.77 (m, 1H, $C_{arom}H$), 7.59 – 7.50 (m, 1H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.8 (d, *J* = 250.7 Hz, CF), 146.1 (m, C), 138.8 (C), 133.8 (d, *J* = 9.5 Hz, C), 133.6 (d, *J* = 4.4 Hz, C), 131.6 (C), 128.9 (C), 126.9 (d, *J* = 9.6 Hz, C), 126.2 (q, *J* = 3.2 Hz, C), 122.9 (C), 122.5 (q, J = 277.4 Hz, CF_3), 122.0 (C), 118.6 (d, *J* = 24.5 Hz, C), 107.3 (d, *J* = 23.7 Hz, C). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.5 (s, 3F, CF_3), -108.8 (s, 1F, Ar-F). **HRMS (ESI)** *m/z* = 266.0587 calcd. for $C_{14}H_8F_4N^+$ $[M+H]^{+,}$ found: 266.0596. Spectroscopic data are in accordance with those described in the literature.[4]

2-Methyl-6-(trifluoromethyl)phenanthridine-8-carbonitrile (3g)

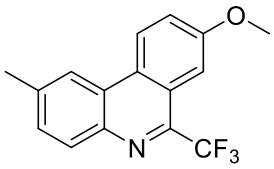


According to ***GP3*** with **1g** (44 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 5/1) afforded phenanthridine **3g** (41 mg, 0.14 mmol, 72%) as a colorless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.74 (d, *J* = 8.7 Hz, 1H, $C_{arom}H$), 8.68 – 8.63 (m, 1H, $C_{arom}H$), 8.35 (s, 1H, $C_{arom}H$), 8.19 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$),

8.04 (dd, *J* = 8.7, 1.6 Hz, 1H, $C_{arom}H$), 7.73 (dd, *J* = 8.4, 1.8 Hz, 1H, $C_{arom}H$), 2.69 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.9 (q, *J* = 33.9 Hz, C), 141.1 (C), 141.0 (C), 136.0 (C), 133.1 (CH), 132.3 (CH), 131.3 (CH), 131.2 (q, *J* = 3.7 Hz, CH), 124.0 (CH), 123.8 (C), 122.3 (CH), 121.7 (q, *J* = 277 Hz, CF_3), 121.3 (C), 118.1 (C), 111.9 (C), 22.3 (C). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.1 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 309.0610 calcd. for $C_{16}H_9F_3N_2Na^+$ $[M+Na]^{+,}$ found: 309.0609. Spectroscopic data are in accordance with those described in the literature.[4]

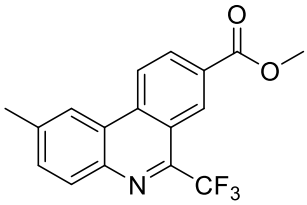
8-Methoxy-2-methyl-6-(trifluoromethyl)phenanthridine (3h)



According to ***GP3*** with **1h** (45 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 8/1) afforded phenanthridine **3h** (40 mg, 0.14 mmol, 69%) as a pale yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.50 (d, *J* = 9.2 Hz, 1H, $C_{arom}H$), 8.21 (s, 1H, $C_{arom}H$), 8.11 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 7.64 – 7.59 (m, 1H, $C_{arom}H$), 7.53 (dd, *J* = 8.4, 1.8 Hz, 1H, $C_{arom}H$), 7.47 (dd, *J* = 9.2, 2.6 Hz, 1H, $C_{arom}H$), 3.98 (s, 3H, OCH_3), 2.61 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.0 (C), 144.7 (q, *J* = 32.5 Hz, C), 139.6 (C), 139.5 (C), 130.9 (CH), 130.2 (CH), 128.2 (C), 125.3 (C), 124.2 (CH), 123.3 (C), 122.3 (q, *J* = 277 Hz, CF_3), 122.3 (CH), 121.2 (CH), 105.6 (q, *J* = 3.5 Hz, CH), 55.6 (OCH_3), 22.3 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -64.0 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 314.0763 calcd. for $C_{16}H_{12}NOF_3Na^+$ $[M+Na]^{+,}$ found: 314.0759. Spectroscopic data are in accordance with those described in the literature.[4]

Methyl 2-methyl-6-(trifluoromethyl)phenanthridine-8-carboxylate (3i)

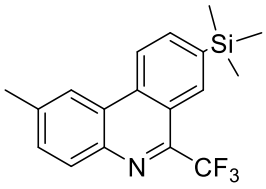


According to ***GP3*** with **1i** (50 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 5/1) afforded phenanthridine **3i** (49 mg, 0.15 mmol, 77%) as a colorless solid.

MP: 190 °C. **IR** (neat): 2953*w*, 1720*s*, 1620*w*, 1574*w*, 1528*w*, 1494*w*, 1440*w*, 1382*w*, 1331*w*, 1302*m*, 1251*s*, 1197*w*, 1176*s*, 1117*s*, 1010*w*, 969*w*, 913*w*, 852*m*, 824*m*, 763*m*, 733*w*, 716*w*, 685*w*, 583*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.04 – 8.97 (m, 1H, $C_{arom}H$), 8.66 (d, *J* = 8.8 Hz, 1H, $C_{arom}H$), 8.44 (dd, *J* = 8.8, 1.7 Hz, 1H, $C_{arom}H$), 8.34 (s, 1H, $C_{arom}H$), 8.15 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 7.66 (dd, *J* = 8.4, 1.8 Hz, 1H, $C_{arom}H$), 4.04 (s,

3H, OCH_3), 2.65 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.2 (C), 146.0 (q, J = 33.3 Hz, C), 140.9 (C), 140.2 (C), 136.5 (C), 132.3 (CH), 131.1 (CH), 131.0 (CH), 129.5 (C), 128.1 (q, J = 3.5 Hz, CH)), 124.4 (C), 122.9 (CH), 122.3 (CH), 121.9 (q, J = 277 Hz, CF_3), 121.4 (C), 52.8 (OCH_3), 22.3 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.1 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 342.0712 calcd. for $C_{17}H_{12}NO_2F_3Na^+$ $[M+Na]^{+,}$ found: 342.0711.

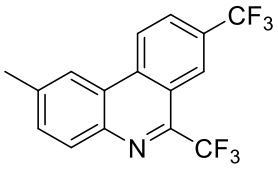
2-Methyl-6-(trifluoromethyl)-8-(trimethylsilyl)phenanthridine (3j)



According to ***GP3*** with **1j** (53 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 300/1) afforded phenanthridine **3j** (50 mg, 0.15 mmol, 75%) as a pale yellow liquid.

IR (neat): 3069*w*, 2957*w*, 2361*w*, 2338*w*, 1576*w*, 1522*w*, 1457*w*, 1397*w*, 1347*w*, 1305*w*, 1251*s*, 1169*s*, 1117*s*, 1037*w*, 984*m*, 856*s*, 840*s*, 824*s*, 791*w*, 754*m*, 735*w*, 725*w*, 712*m*, 700*w*, 655*m*, 628*w*, 590*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.63 (d, *J* = 7.9 Hz, 1H, $C_{arom}H$), 8.54 – 8.48 (m, 1H, $C_{arom}H$), 8.37 (s, 1H, $C_{arom}H$), 8.16 (d, *J* = 8.3 Hz, 1H, $C_{arom}H$), 8.02 (dd, *J* = 8.3, 1.2 Hz, 1H, $C_{arom}H$), 7.62 (dd, *J* = 7.9, 1.8 Hz, 1H, $C_{arom}H$), 2.66 (s, 3H, CH_3), 0.41 (s, 9H, 3 × CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.9 (q, *J* = 32.8 Hz, C), 141.2 (C), 140.4 (C), 139.6 (C), 135.5 (CH), 134.0 (C), 131.3 (CH), 131.2 (q, *J* = 3.4 Hz, CH), 130.9 (CH), 125.1 (C), 122.3 (q, *J* = 277 Hz, C), 121.8 (CH), 121.6 (CH), 121.5 (C), 22.3 (CH_3), -1.1 (3 × CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.1 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 356.1053 calcd. for $C_{18}H_{18}NF_3SiNa^+$ $[M+Na]^{+,}$ found: 356.1047.

2-Methyl-6,8-bis(trifluoromethyl)phenanthridine (3k)

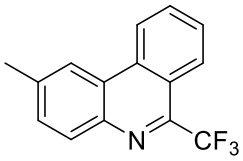


According to ***GP3*** with **1k** (52 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 50/1) afforded phenanthridine **3k** (53 mg, 0.16 mmol, 80%) as a colorless solid.

MP: 132 °C. **IR** (neat): 2930*w*, 1631*w*, 1531*w*, 1436*w*, 1382*w*, 1322*s*, 1287*m*, 1258*m*, 1180*s*, 1172*s*, 1144*m*, 1112*s*, 1085*s*, 987*m*, 905*w*, 843*w*, 832*s*, 804*w*, 741*w*, 717*m*, 621*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.76 (d, *J* = 8.8 Hz, 1H, $C_{arom}H$), 8.60 (s, 1H, $C_{arom}H$), 8.36 (s, 1H, $C_{arom}H$), 8.18 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.06 (dd, *J* = 8.8, 1.8 Hz, 1H, $C_{arom}H$), 7.69 (dd, *J* = 8.4, 1.8 Hz, 1H, $C_{arom}H$), 2.68 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.5 (q, *J* = 33.6 Hz, C), 140.9 (C), 140.6 (C), 135.8 (C), 132.5 (CH),

131.2 (CH), 130.0 (q, J = 33.2 Hz, C), 127.1 (q, J = 3.2 Hz, CH), 124.2 (C), 123.8 (CH), 123.8 (q, *J* = 273 Hz, CF_3), 123.6 – 123.3 (m, CH), 122.1 (CH), 121.9 (q, *J* = 277 Hz, CF_3), 121.3 (C), 22.3 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -62.6 (s, 3F, CF_3), -63.2 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 352.0531 calcd. for $C_{16}H_9NF_6Na^+$ $[M+Na]^{+,}$ found: 352.0525.

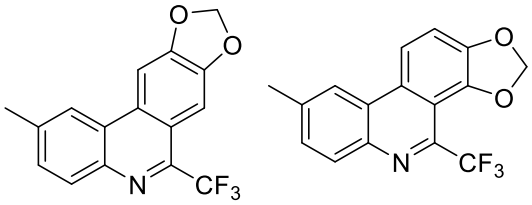
2-Methyl-6-(trifluoromethyl)phenanthridine (3l)



According to ***GP3*** with **1l** (39 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 15/1) afforded phenanthridine **3l** (40 mg, 0.15 mmol, 77%) as a pale yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.63 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.38 – 8.31 (m, 2H, $C_{arom}H$), 8.15 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 7.91 - 7.82 (m, 1H, $C_{arom}H$), 7.76 – 7.68 (m, 1H, $C_{arom}H$), 7.61 (dd, *J* = 8.4, 1.8 Hz, 1H, $C_{arom}H$), 2.64 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.7 (q, *J* = 32.9 Hz, CCF_3), 140.2 (C), 139.6 (C), 133.8 (C), 131.2 (CH), 131.2 (CH), 130.9 (CH), 128.0 (CH), 125.9 (q, *J* = 3.4 Hz, CH), 125.1 (C), 122.6 (CH), 122.2 (q, *J* = 277.0 Hz, CF_3), 122.0 (C), 121.8 (CH), 22.3 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.3 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 262.0838 calcd. for $C_{15}H_{11}F_3N^+$ $[M+H]^+$, found: 262.0852. Spectroscopic data are in accordance with those described in the literature.[4]

2-Methyl-6-(trifluoromethyl)-[1,3]dioxolo[4,5-j]phenanthridine (3m) and 8-methyl-4-(trifluoromethyl)-[1,3]dioxolo[4,5-i]phenanthridine (3m')

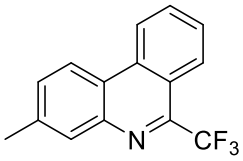


According to ***GP3*** with **1m** (47 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 8/1) afforded a mixture of phenanthridine **3m and 3m'** (46 mg, 0.15 mmol, 75%, **3m** / **3m'** = 3:1) as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): **3l** δ (ppm) = 8.18 – 8.13 (m, 2H, $C_{arom}H$), 7.96 (s, 1H, $C_{arom}H$), 7.67 – 7.63 (m, 1H, $C_{arom}H$), 7.60 – 7.55 (m, 1H, $C_{arom}H$), 6.20 (s, 2H, CH_2), 2.64 (s, 3H, CH_3). **3l'** δ (ppm) = 8.26 – 8.22 (m, 2H, $C_{arom}H$), 8.09 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 7.55 – 7.52 (m, 1H, $C_{arom}H$), 7.48 (d, *J* = 8.7 Hz, 1H, $C_{arom}H$), 6.26 (s, 2H, CH_2), 2.63 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): **3l** and **3l'**; CF_3-signal could not be assigned δ (ppm) = 151.7, 148.9, 140.1, 140.0, 139.2, 132.2, 131.2, 130.8, 130.4, 125.3, 121.7, 121.5, 118.7, 116.6, 113.9,

103.23 (q, *J* = 3.7 Hz), 102.4, 102.3, 100.4, 22.4 (CH_3), 22.3 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) **3l** δ (ppm) = -63.6 (s, 3F, CF_3). **3l'** δ (ppm) = -65.9 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 328.0550 calcd. for $C_{16}H_{10}NO_2F_3Na^+$ $[M+Na]^{+,}$ found: 328.0550. Spectroscopic data are in accordance with those described in the literature.[4]

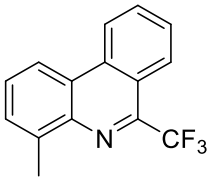
3-Methyl-6-(trifluoromethyl)phenanthridine (3n)



According to ***GP3*** with **1n** (39 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 20/1) afforded phenanthridine **3n** (35 mg, 0.13 mmol, 67%) as a colorless solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.63 (d, *J* = 8.5 Hz, 1H, $C_{arom}H$), 8.46 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 8.39 – 8.32 (m, 1H, $C_{arom}H$), 8.08 (s, 1H, $C_{arom}H$), 7.93 – 7.84 (m, 1H, $C_{arom}H$), 7.75 – 7.68 (m, 1H, $C_{arom}H$), 7.60 (dd, *J* = 8.5, 1.8 Hz, 1H, $C_{arom}H$), 2.60 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 146.6 (q, *J* = 33.0 Hz, CCF_3), 142.1 (C), 139.8 (C), 134.2 (C), 131.4 (CH), 131.1 (CH), 130.7 (CH), 127.7 (CH), 126.0 (q, *J* = 3.3 Hz, CH), 122.9 (C), 122.5 (CH), 122.1 (q, *J* = 277 Hz, CF_3), 121.9 (CH), 121.6 (C), 21.6 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.4 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 262.0838 calcd. for $C_{15}H_{11}F_3N^+$ $[M+H]^+$, found: 262.0848. Spectroscopic data are in accordance with those described in the literature.[4]

4-Methyl-6-(trifluoromethyl)phenanthridine (3o)

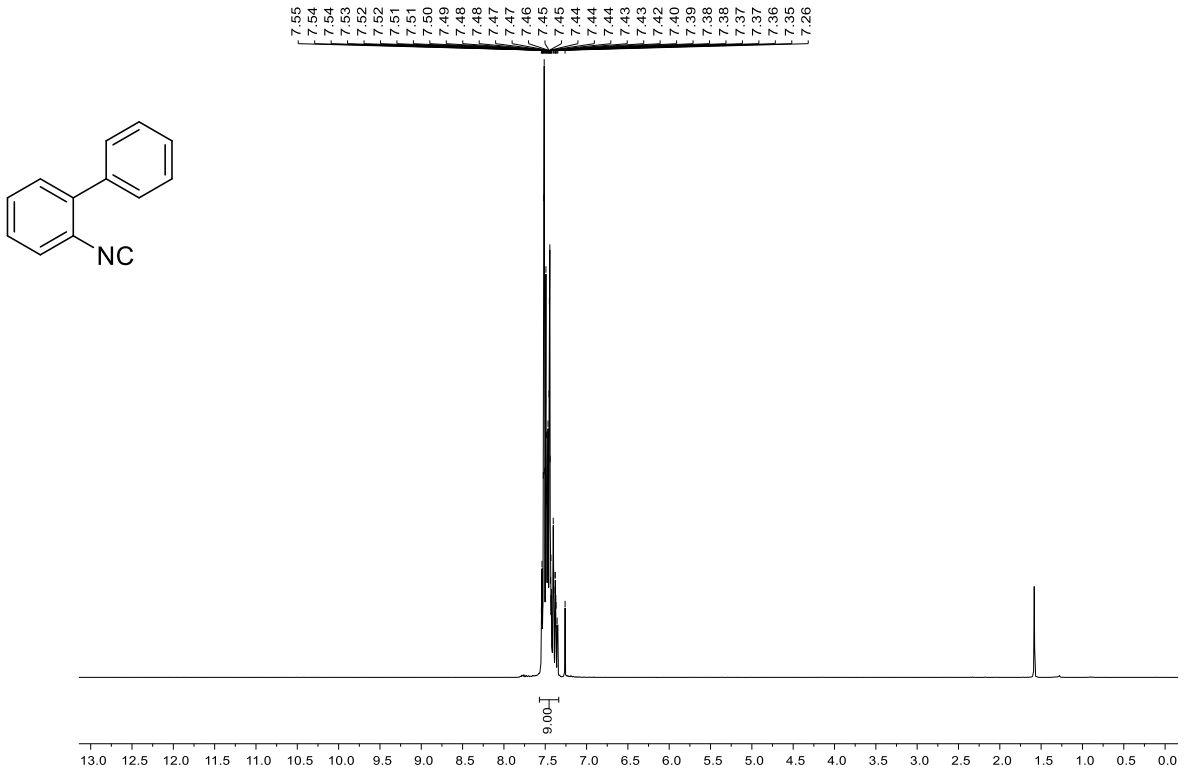


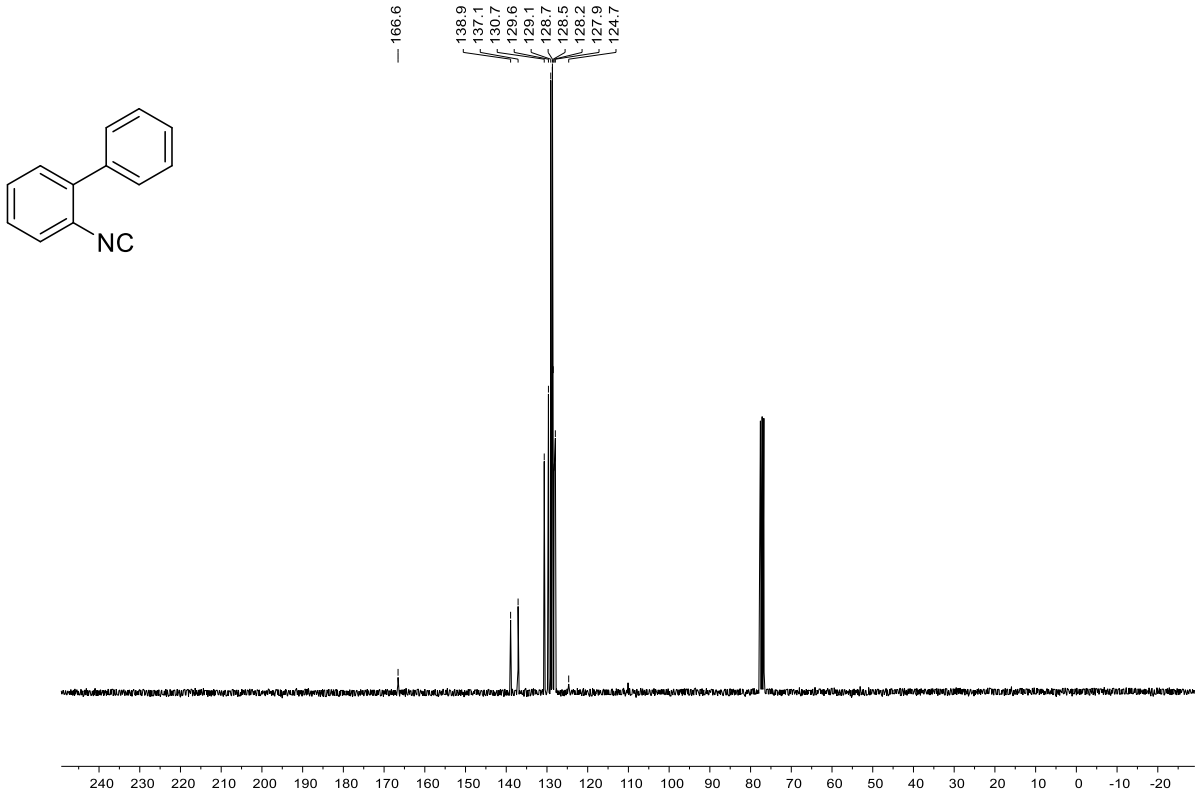
According to ***GP3*** with **1o** (39 mg, 0.20 mmol, 1.0 equiv.) and Togni reagent (126 mg, 0.400 mmol, 2.0 equiv.). FC (P/Et_2O = 50/1) afforded phenanthridine **3o** (33 mg, 0.13 mmol, 63%) as a pale yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.66 (d, *J* = 8.3 Hz, 1H, $C_{arom}H$), 8.45 – 8.34 (m, 2H, $C_{arom}H$), 7.92 – 7.84 (m, 1H, $C_{arom}H$), 7.79 – 7.70 (m, 1H, $C_{arom}H$), 7.68 – 7.62 (m, 2H, $C_{arom}H$), 2.90 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.0 (q, J = 33.0 Hz, CCF_3), 140.7 (C), 139.6 (C), 134.4 (C), 131.1 (CH), 130.1 (CH), 128.9 (CH), 127.9 (CH), 125.9 (q, J = 3.3 Hz, CH), 125.2 (C), 122.9 (CH), 122.3 (q, J = 277 Hz, CF_3), 121.7 (C), 119.9 (CH), 18.1 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.4 (s, 3F, CF_3). **HRMS (ESI)** *m/z* = 262.0838 calcd. for $C_{15}H_{11}F_3N^+$ $[M+H]^+$, found: 216.0840. Spectroscopic data are in accordance with those described in the literature.[4]

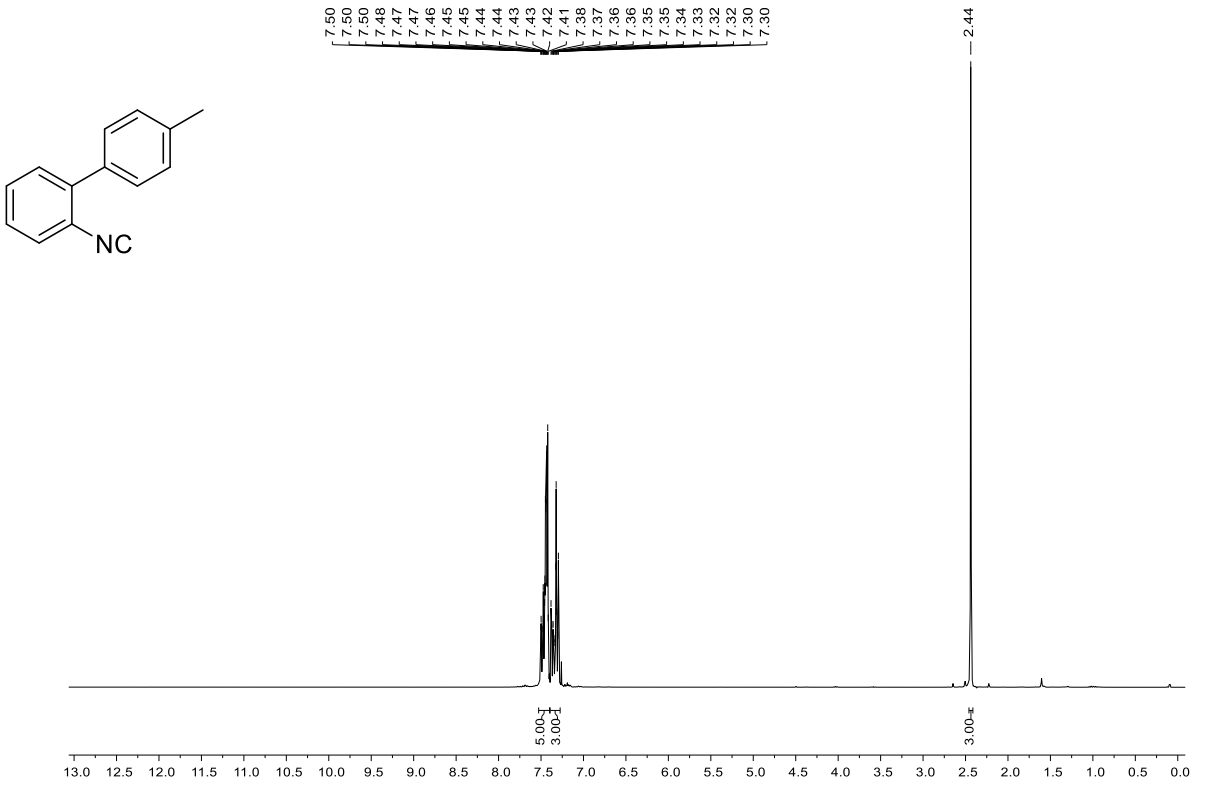
6. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra

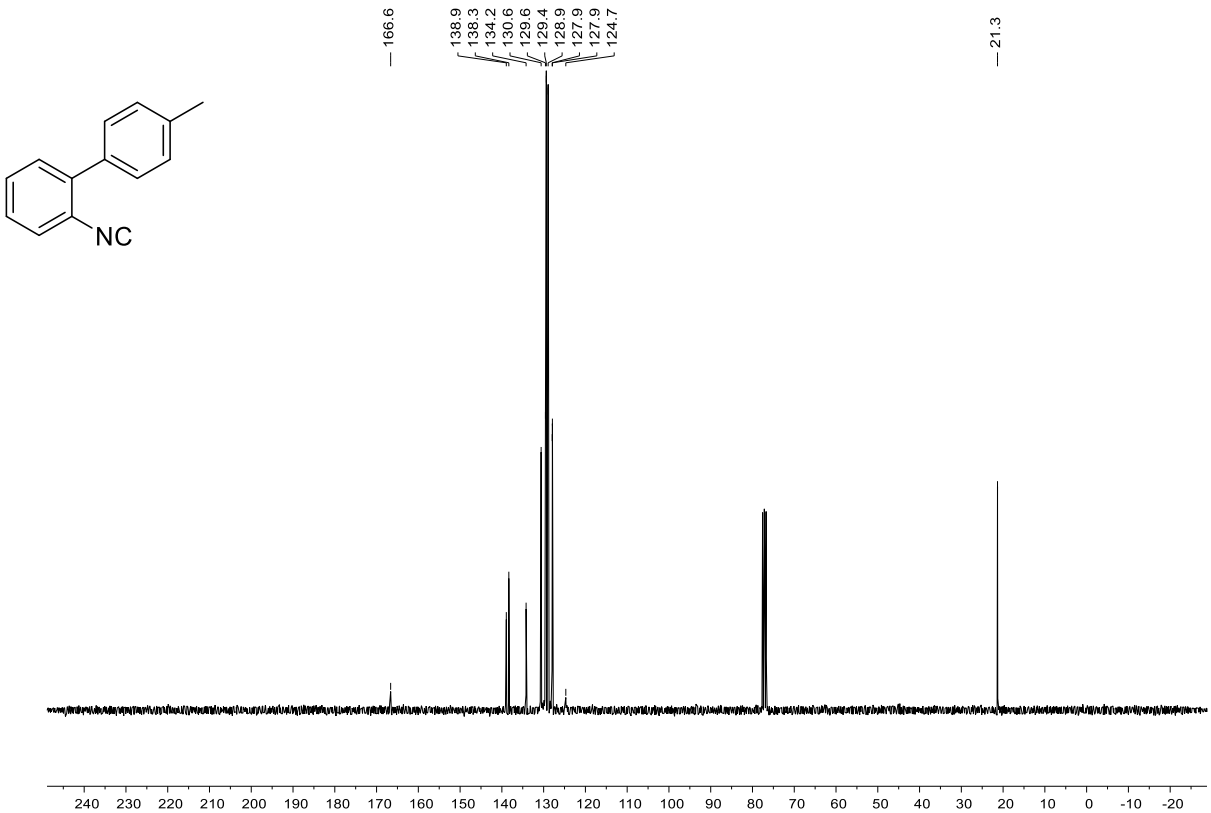
2-Isocyano-1,1'-biphenyl (1a)



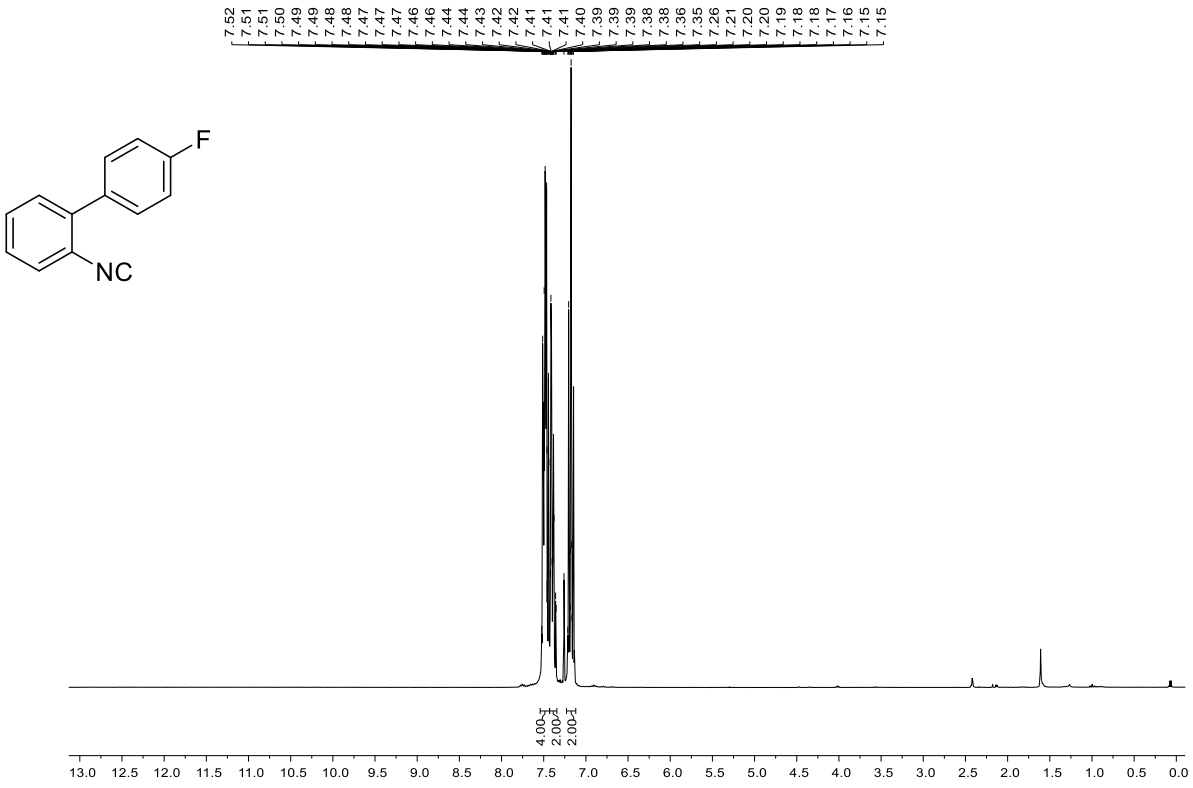


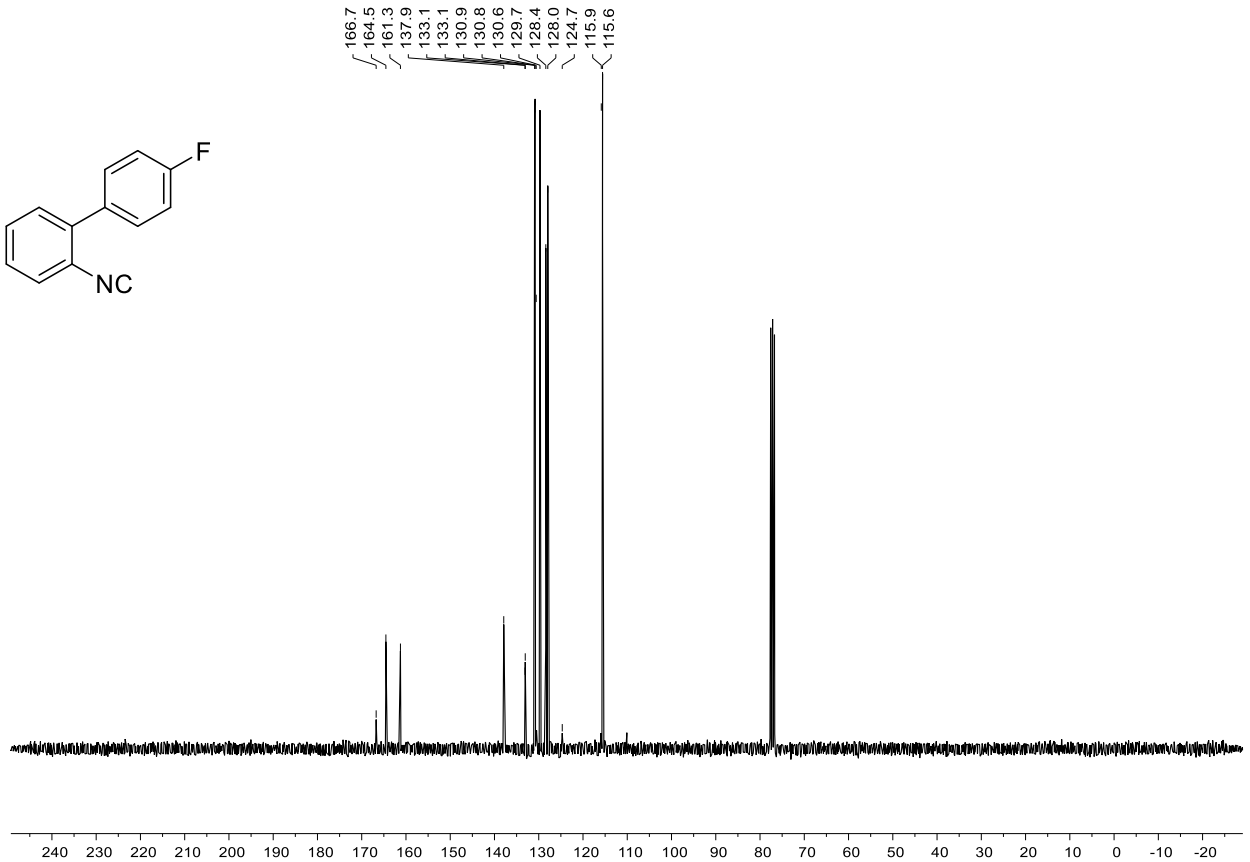
2-Isocyano-4'-methyl-1,1'-biphenyl (1b)

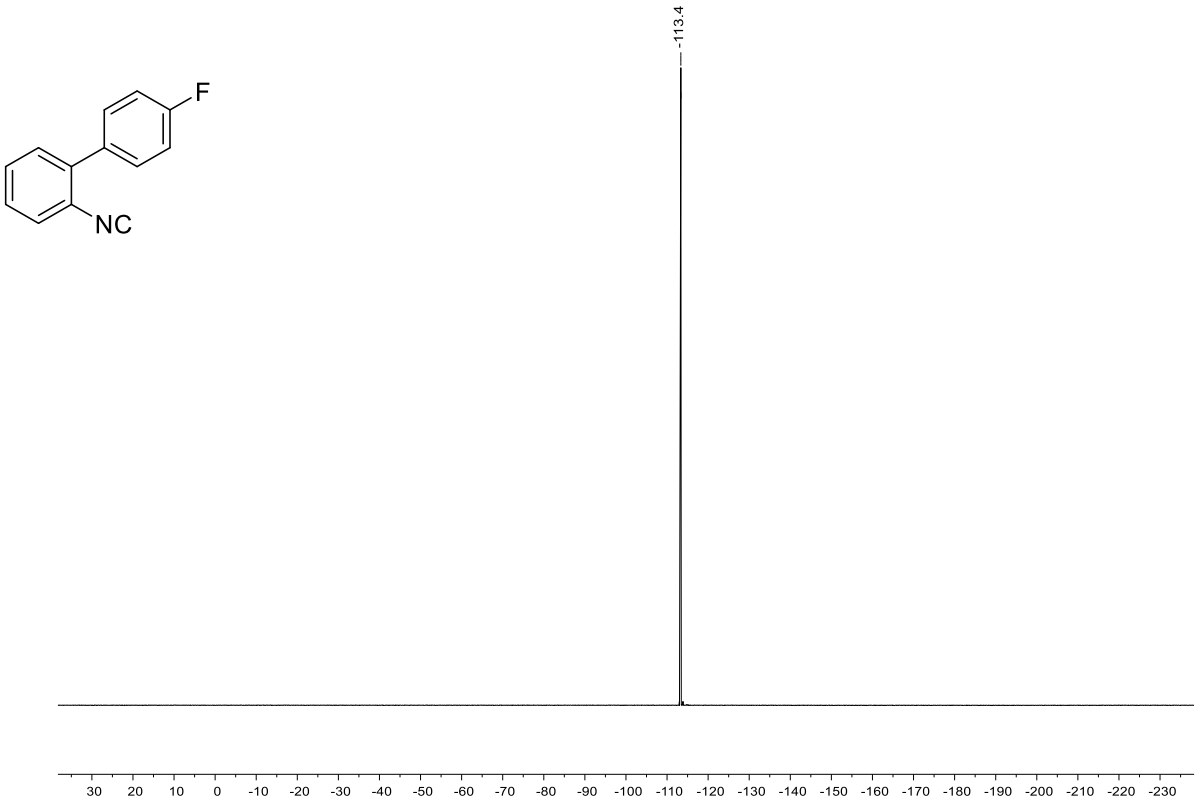




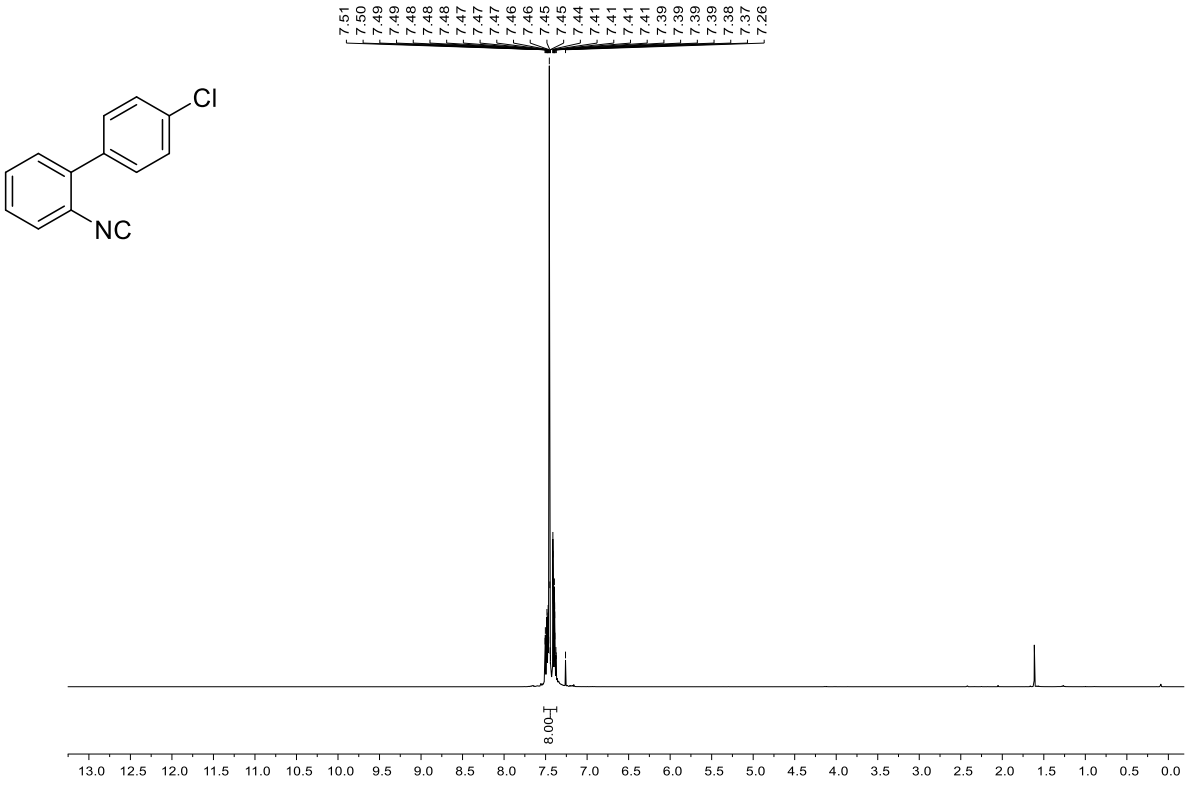
4'-Fluoro-2-isocyano-1,1'-biphenyl (1c)

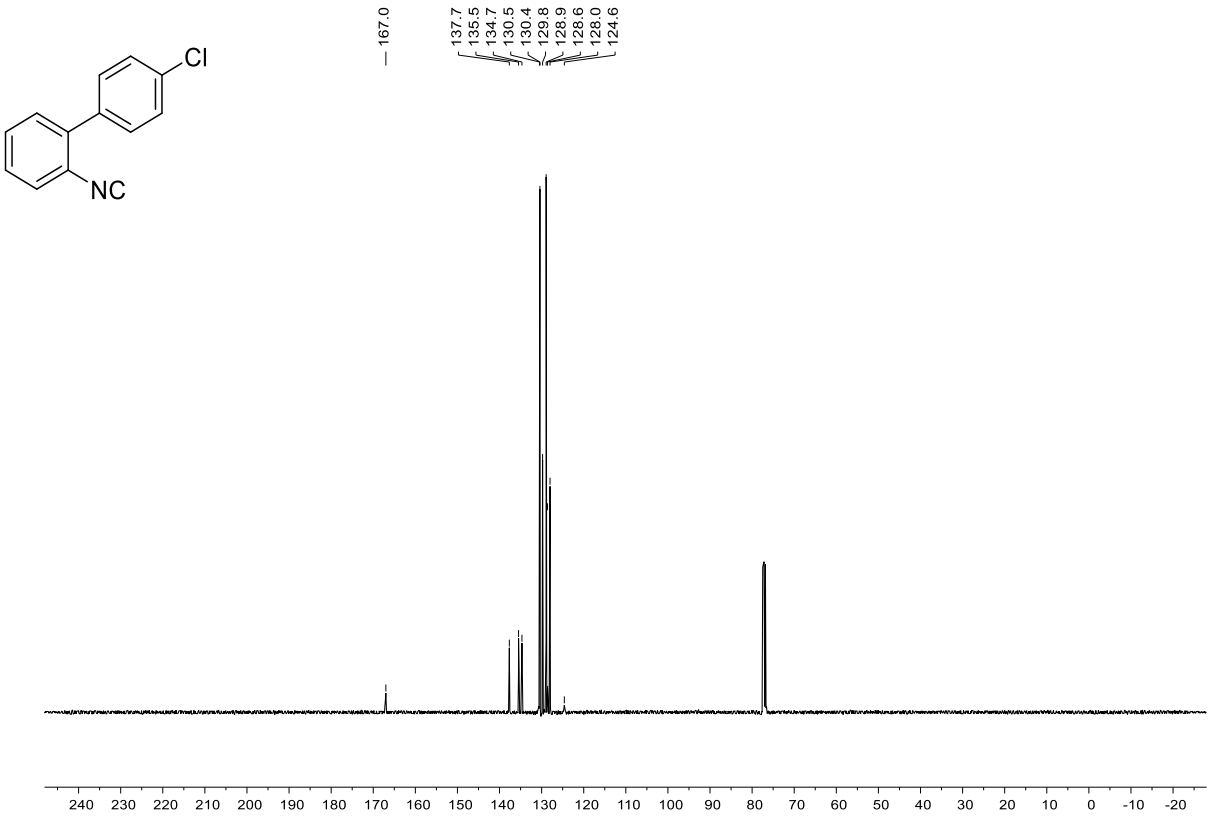




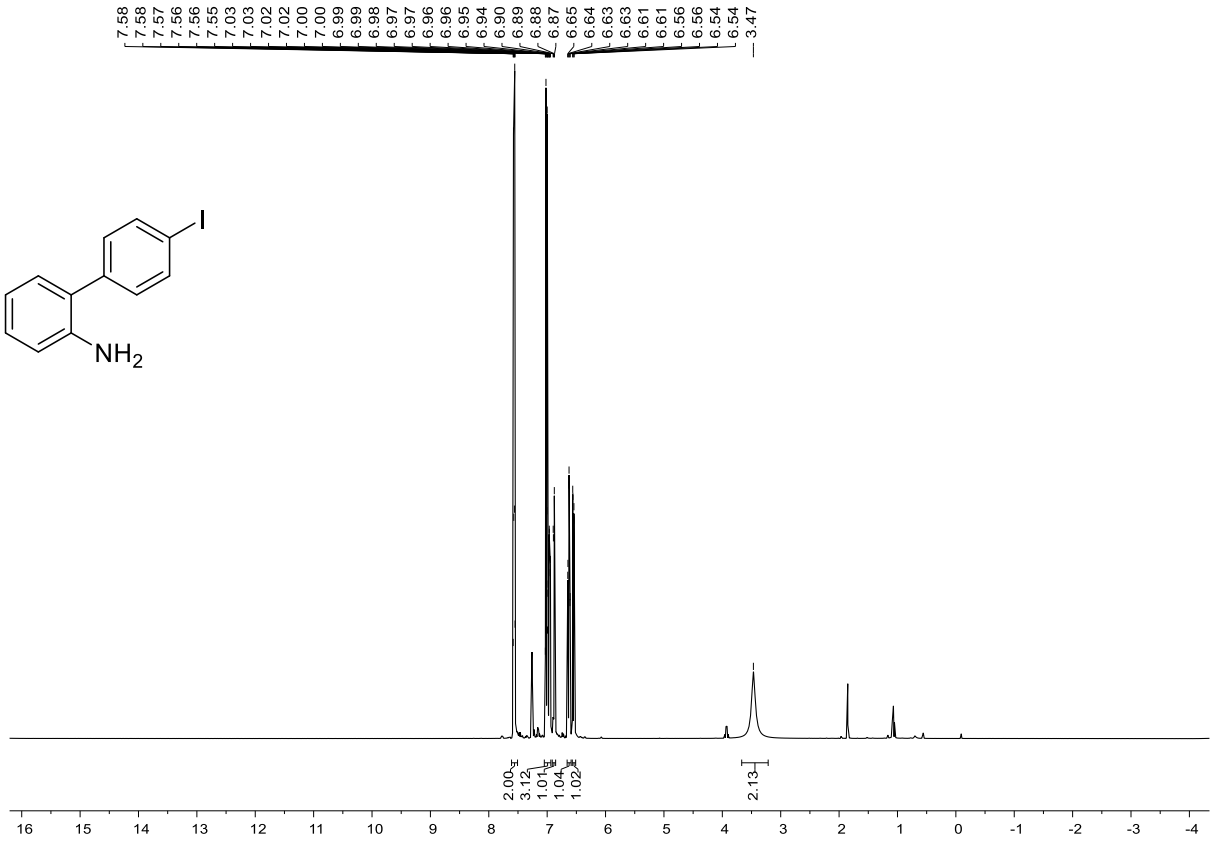


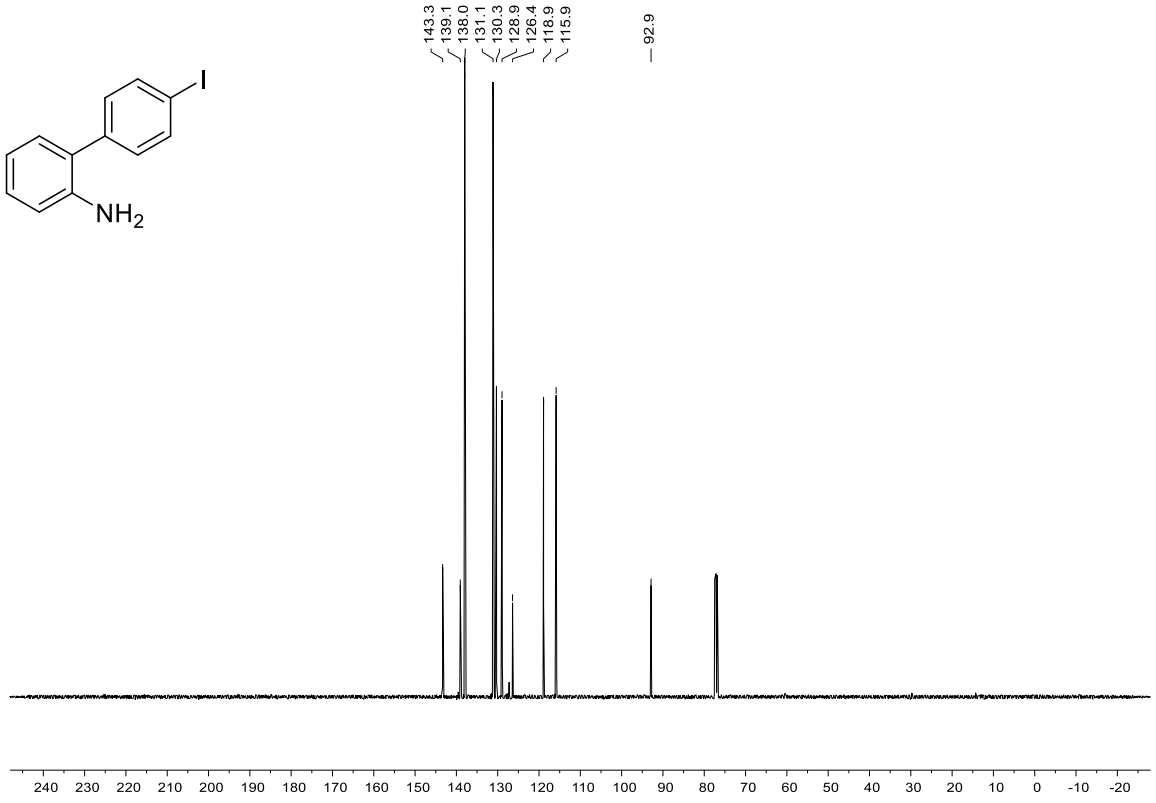
4'-Chloro-2-isocyano-1,1'-biphenyl (1d)



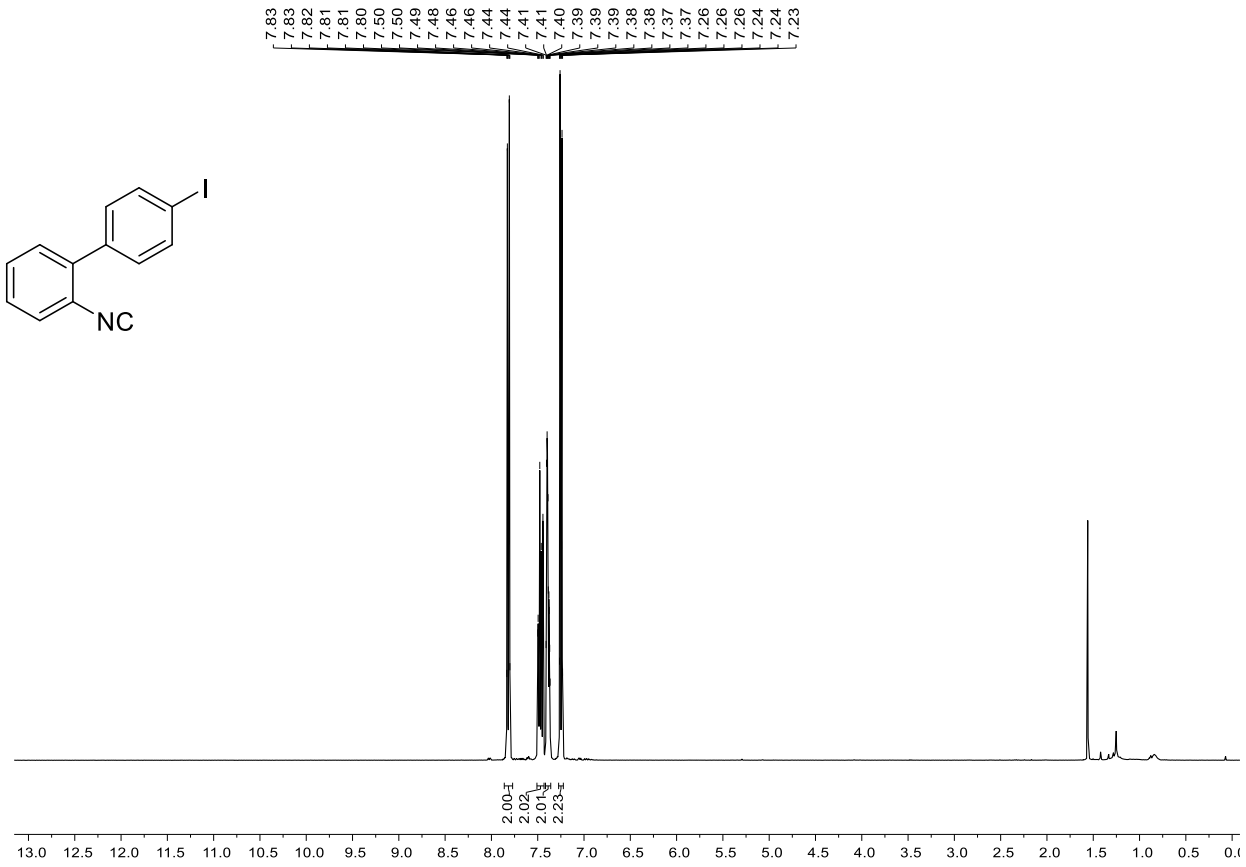


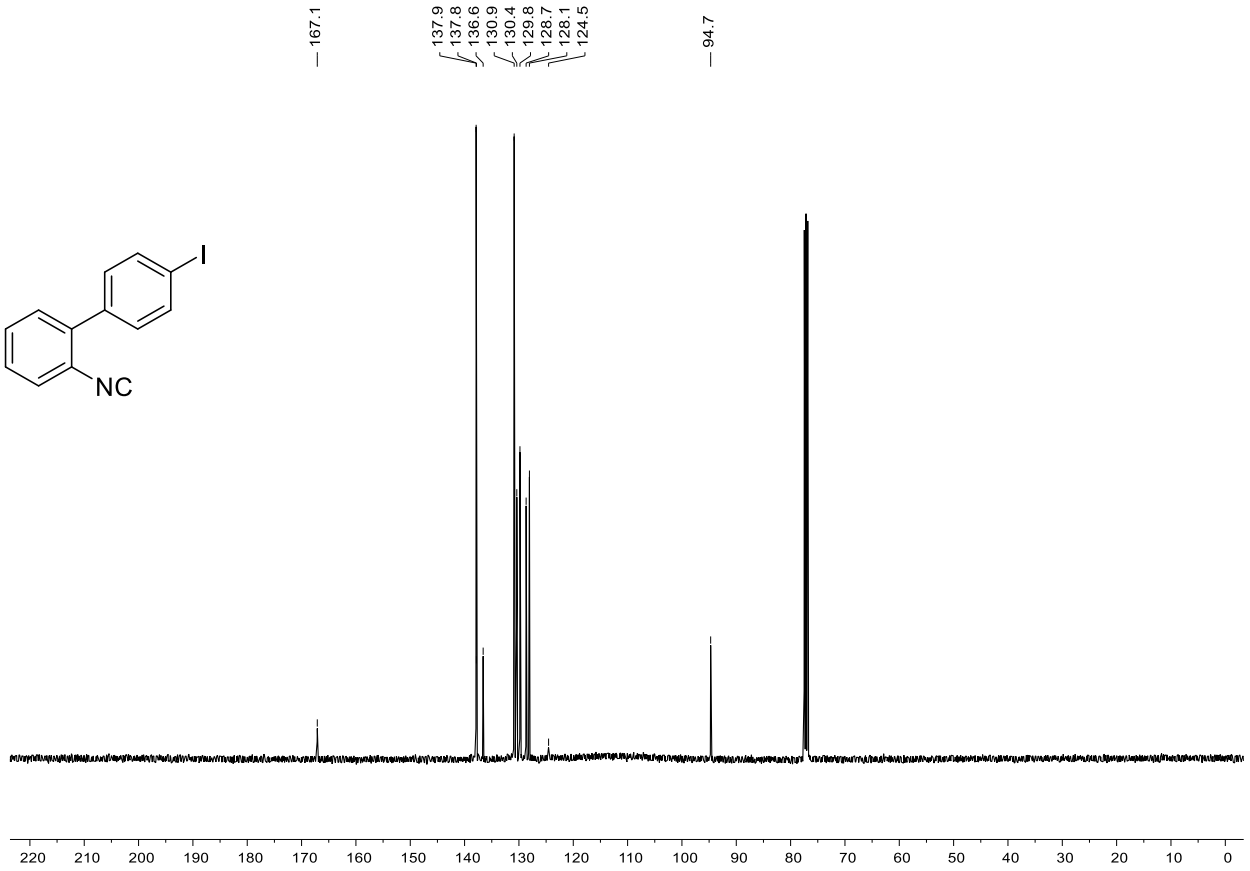
4'-iodo-[1,1'-biphenyl]-2-amine



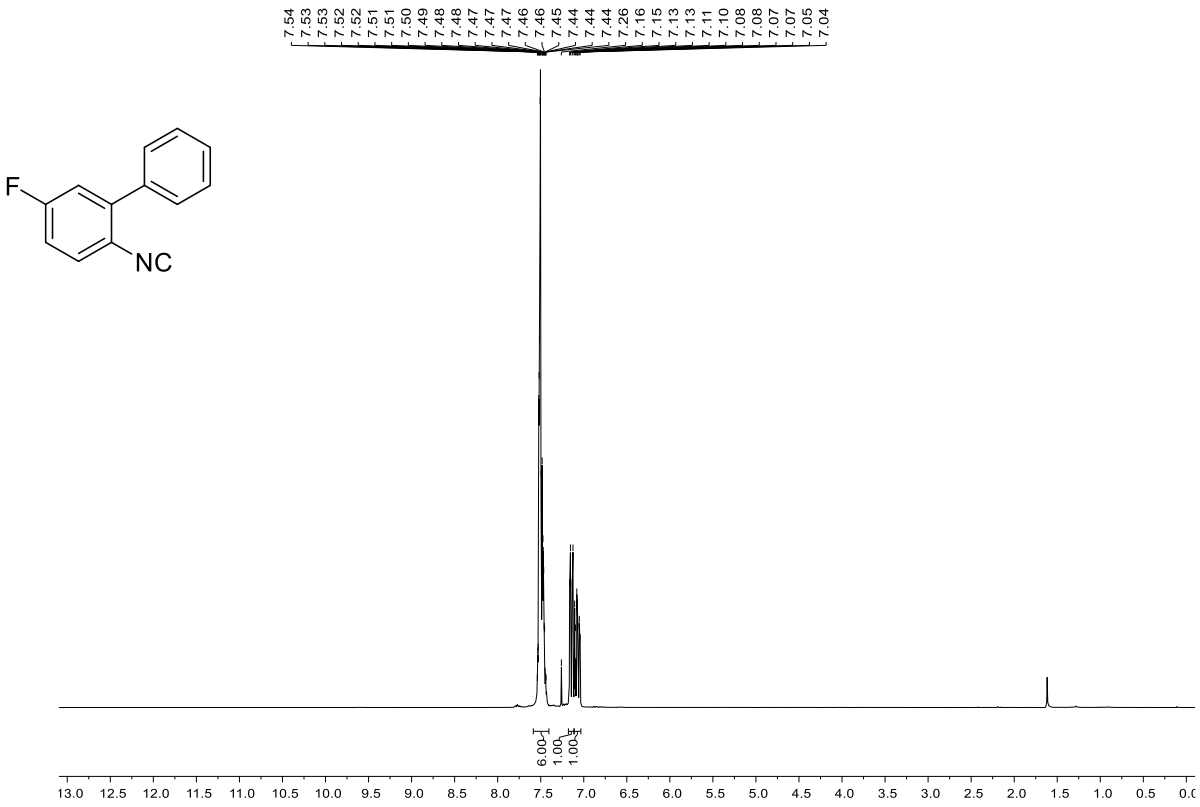


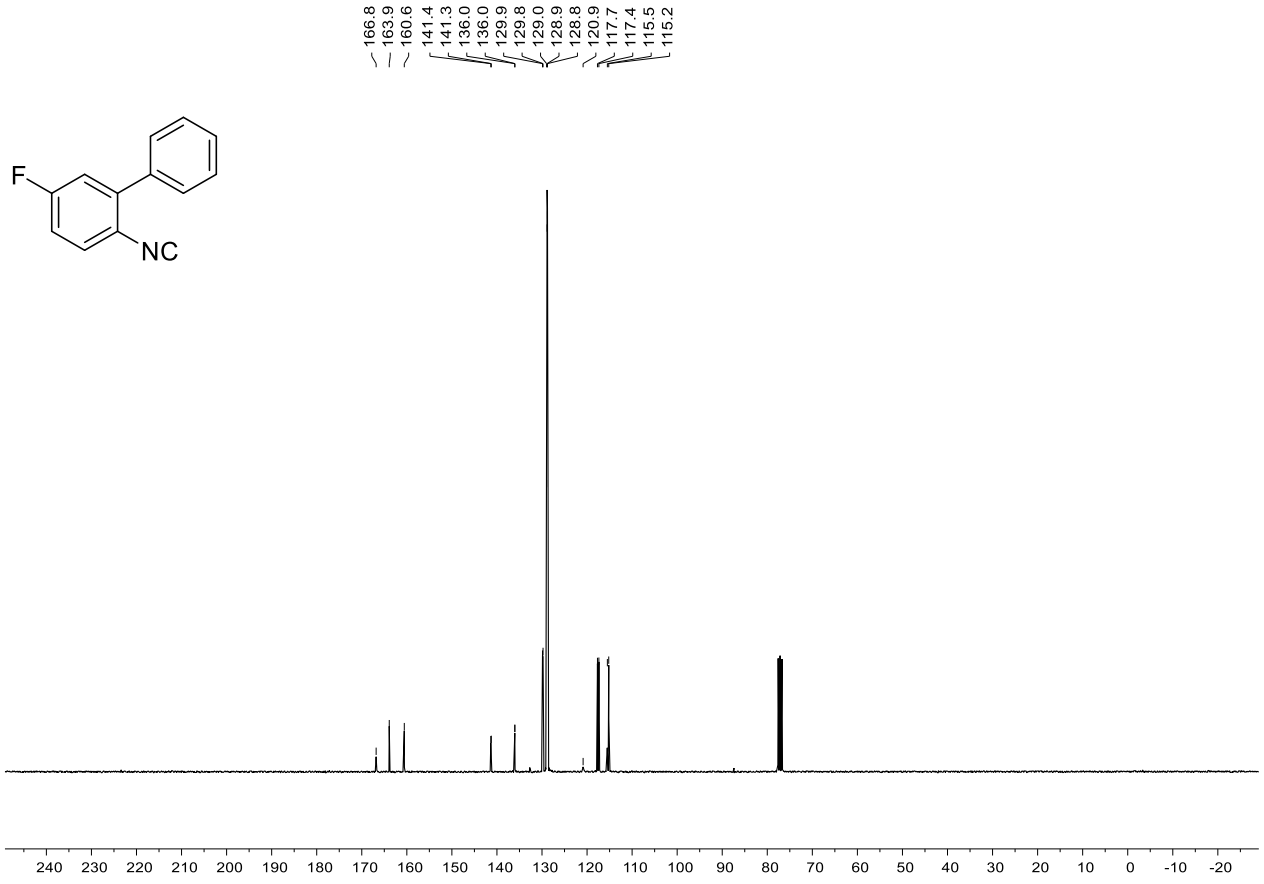
4'-Iodo-2-isocyano-1,1'-biphenyl (1e)

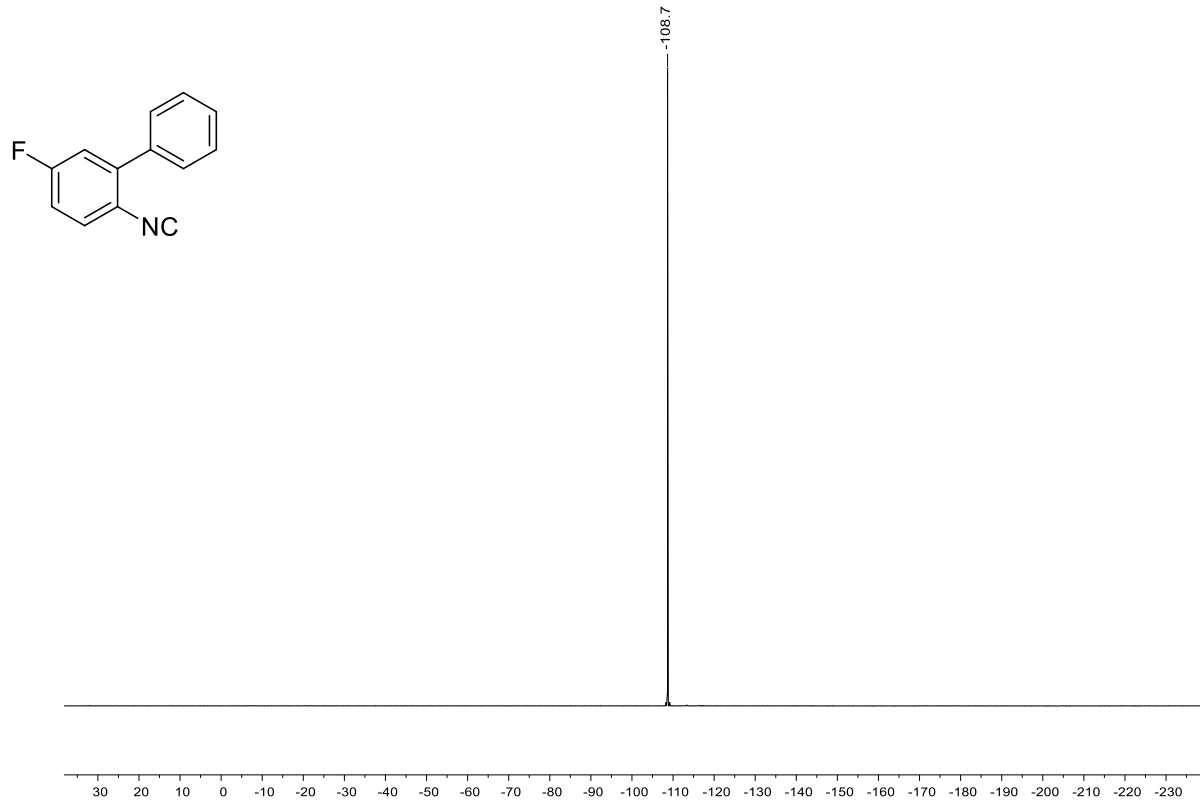




5-Fluoro-2-isocyano-1,1'-biphenyl (1f)




166.8
163.9
160.6
141.4
141.3
136.0
136.0
129.9
129.8
129.0
128.9
128.8
120.9
117.7
117.4
115.5
115.2
F
NC
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20


-108.7
F
NC
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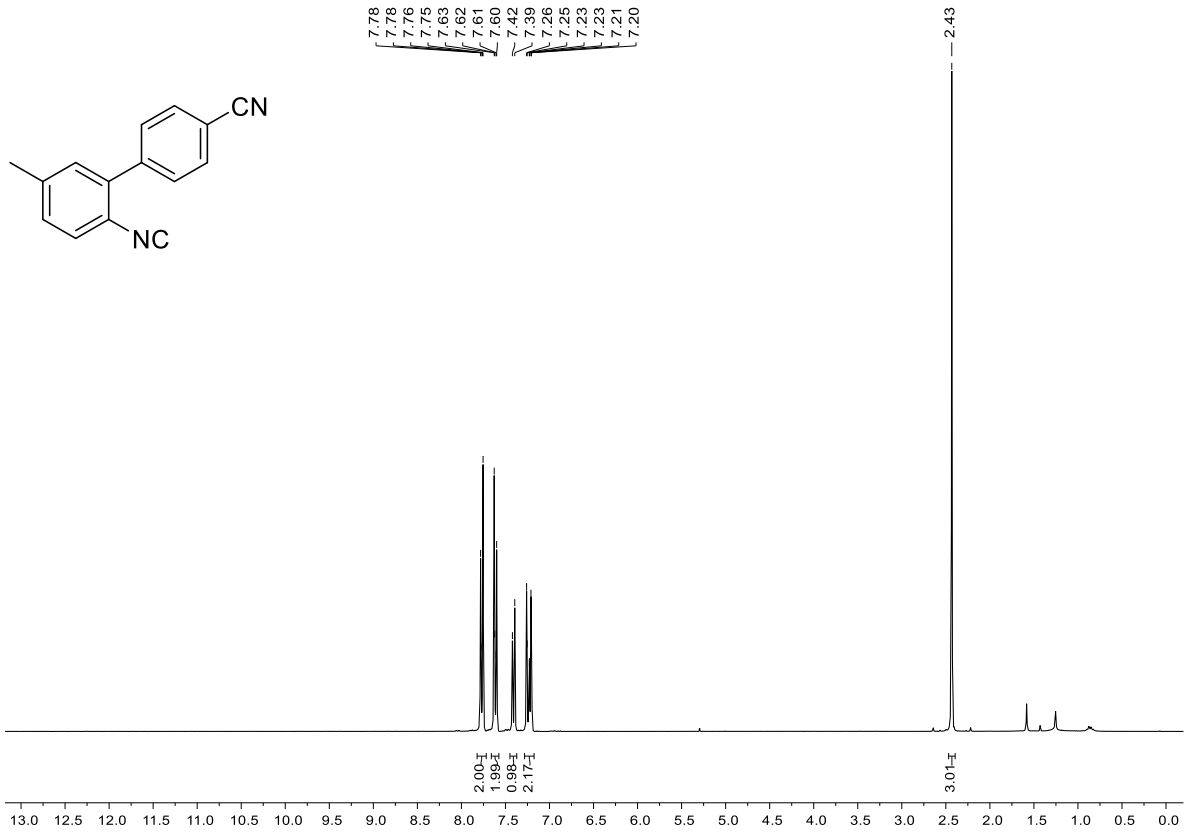
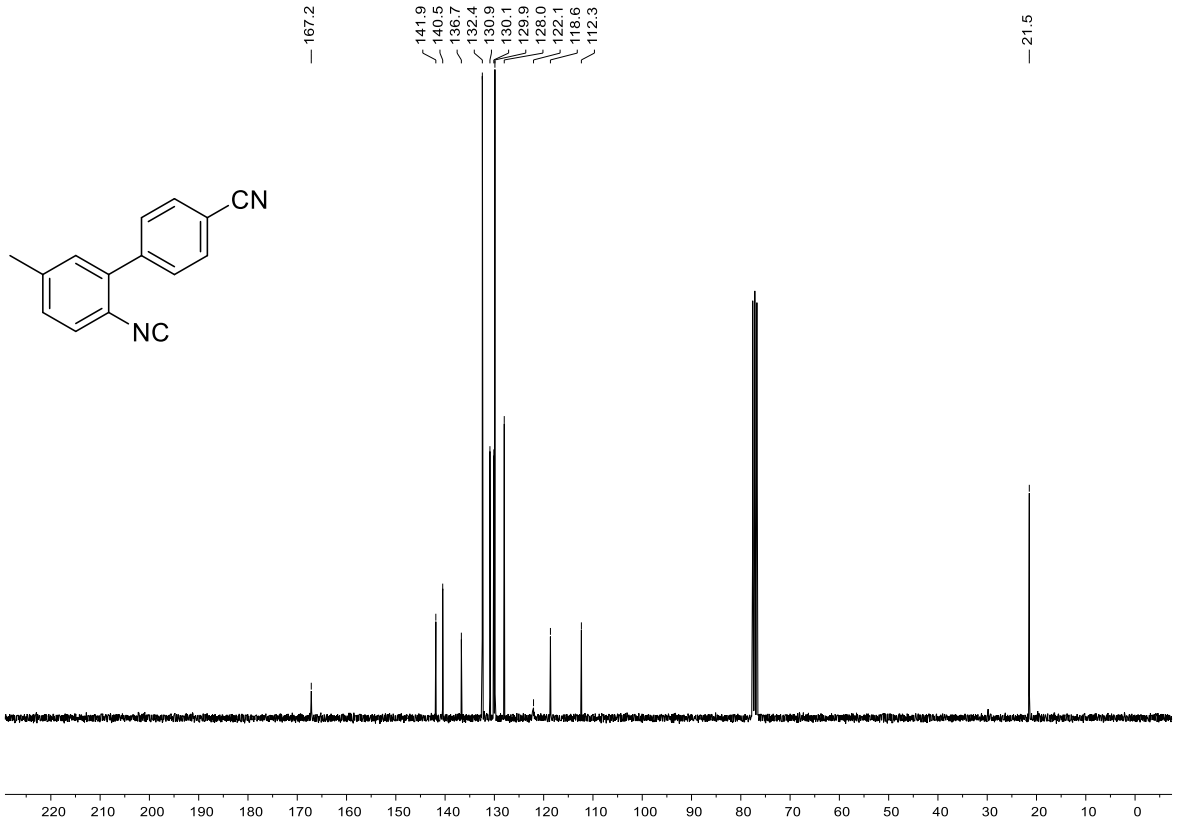
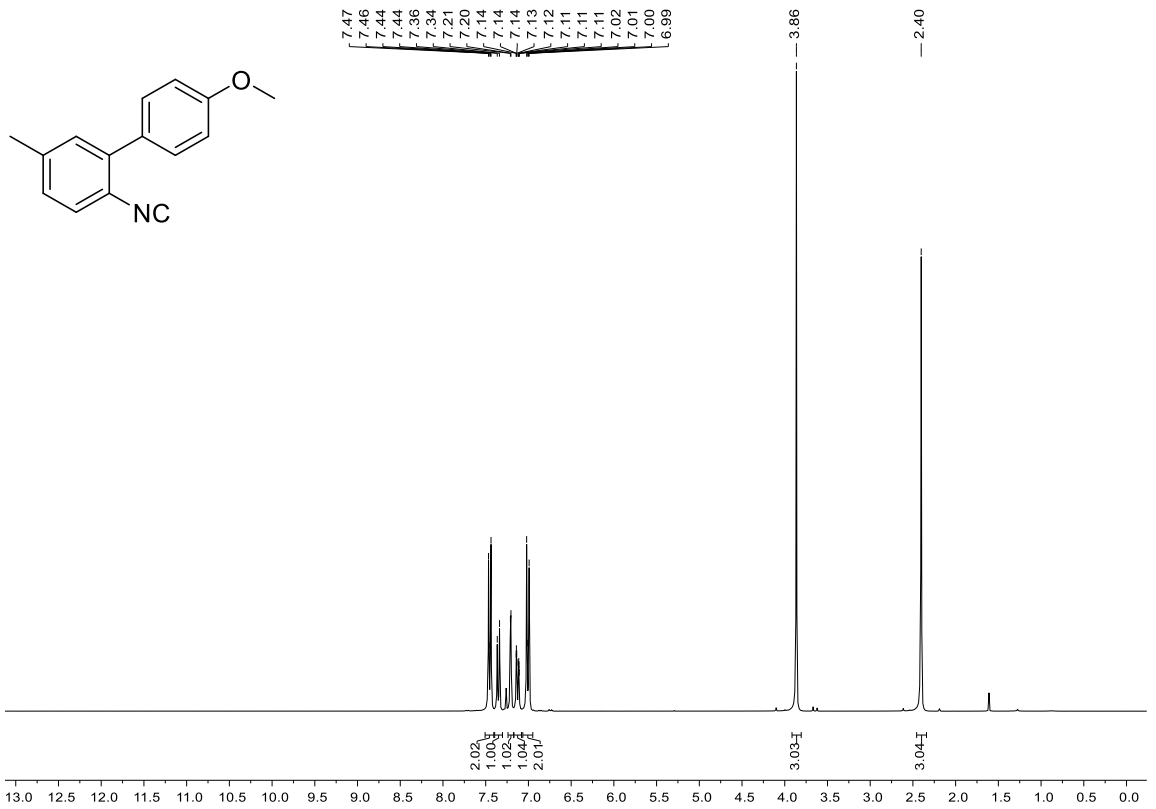
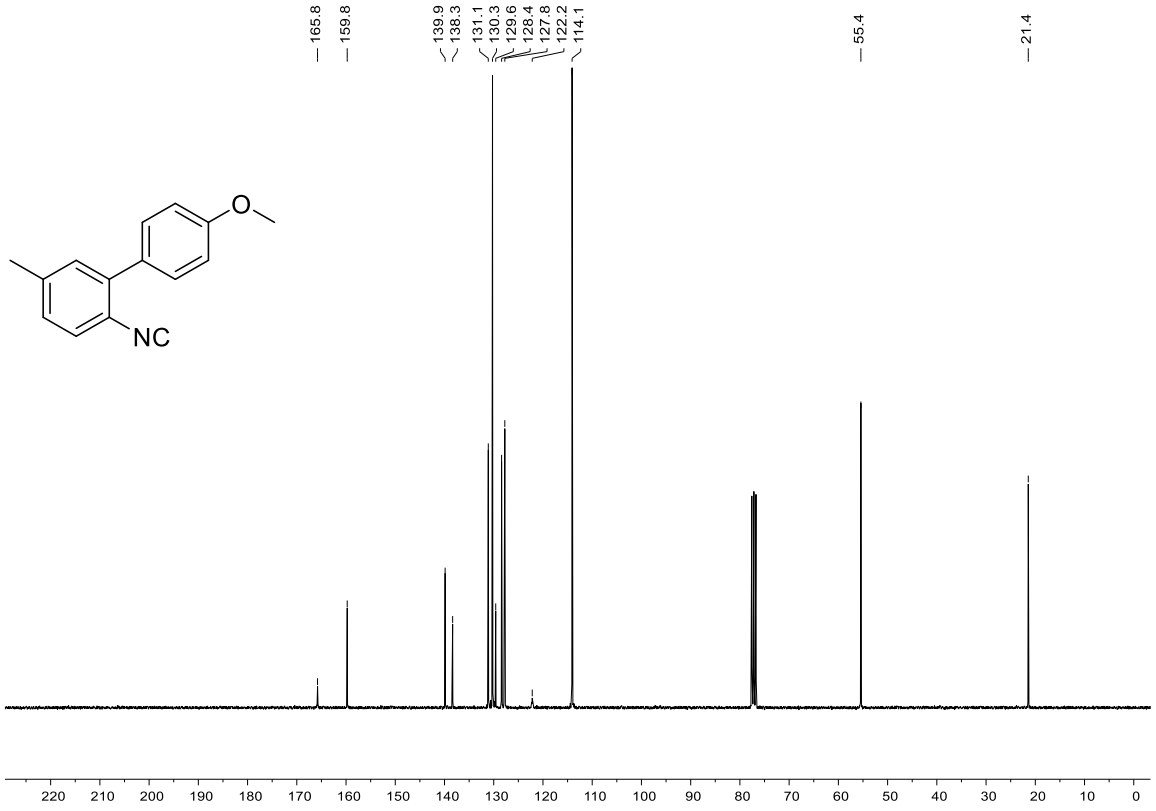
2'-Isocyano-5'-methyl-[1,1'-biphenyl]-4-carbonitrile (1g)



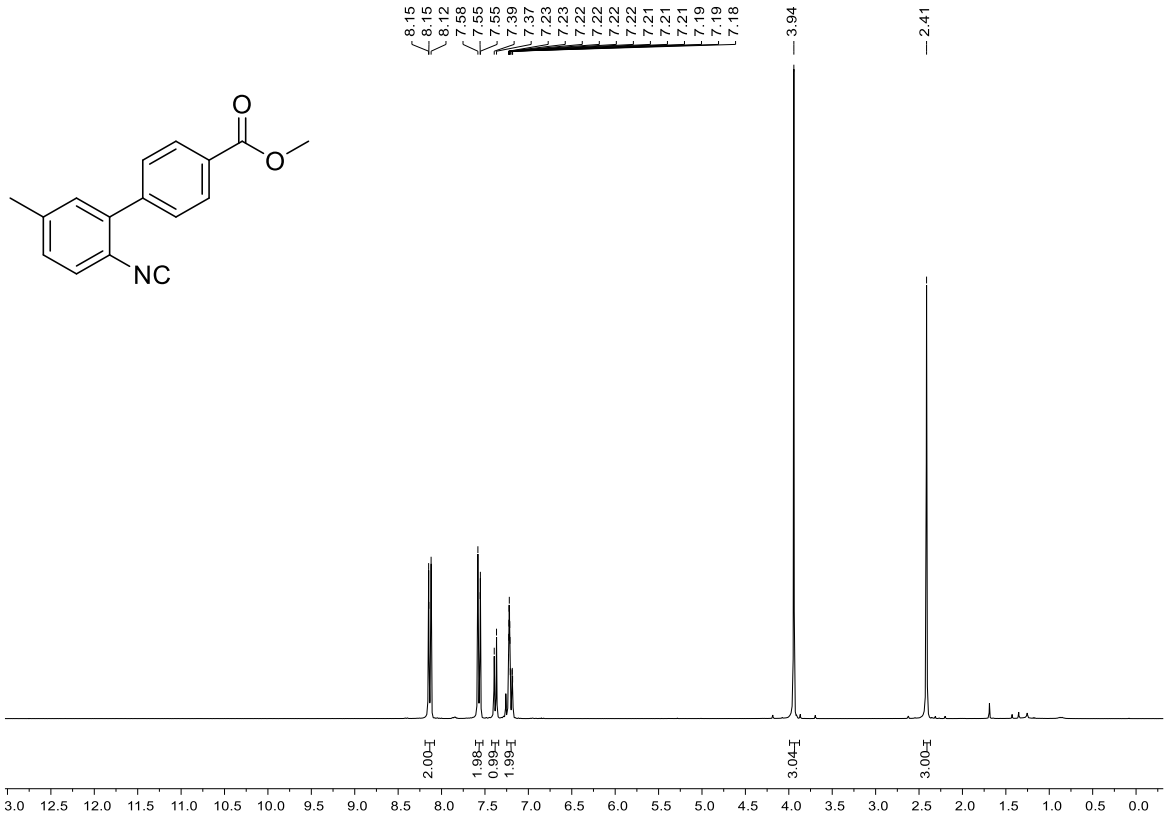


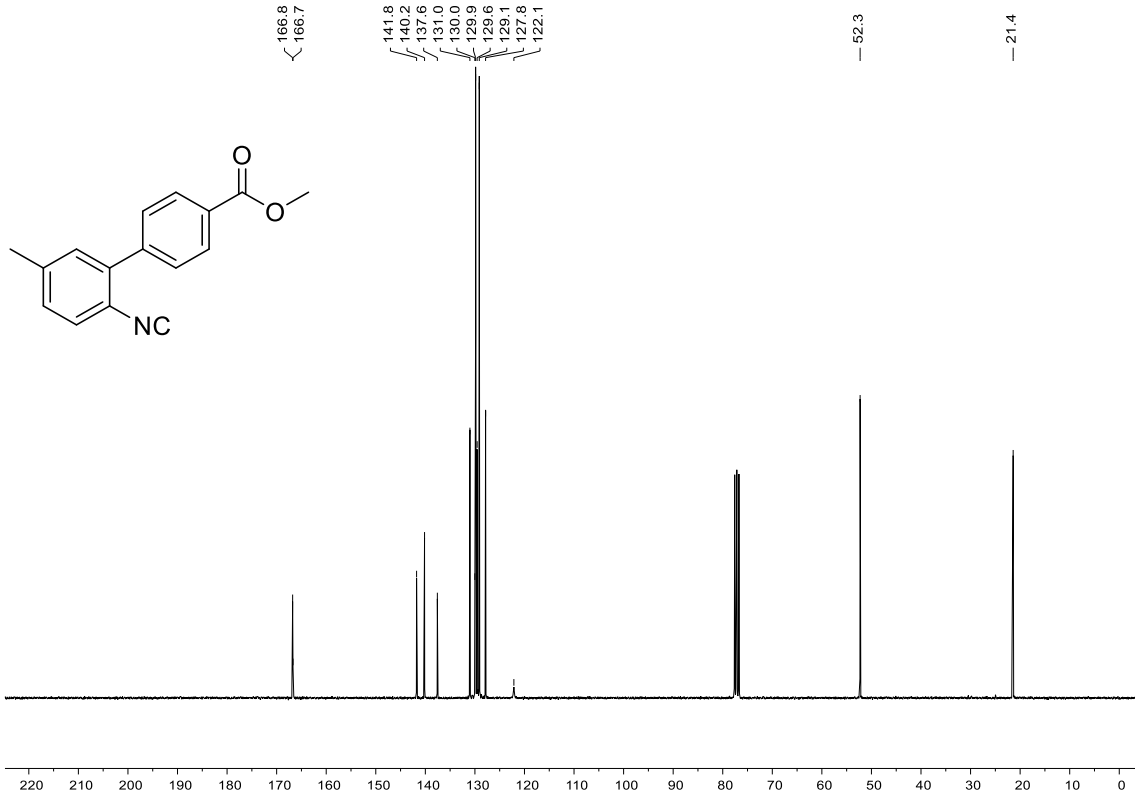
2-isocyano-4'-methoxy-5-methyl-1,1'-biphenyl (1h)



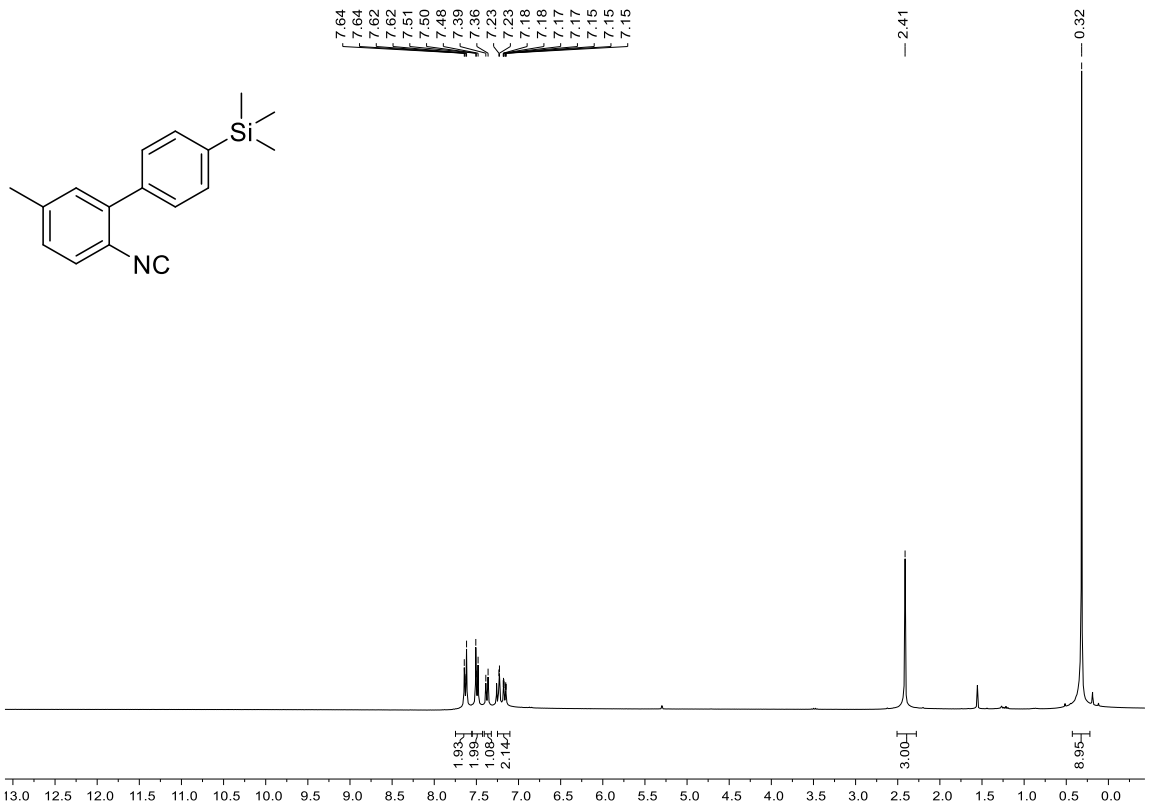


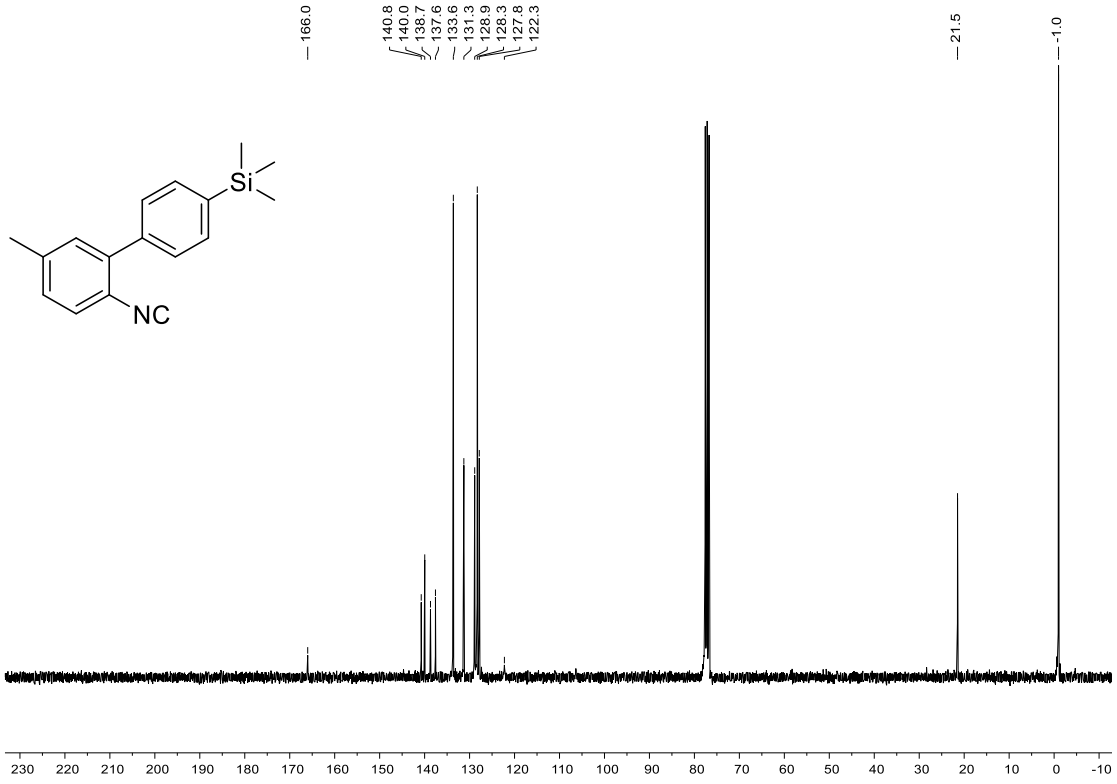
Methyl 2'-isocyano-5'-methyl-[1,1'-biphenyl]-4-carboxylate (1i)



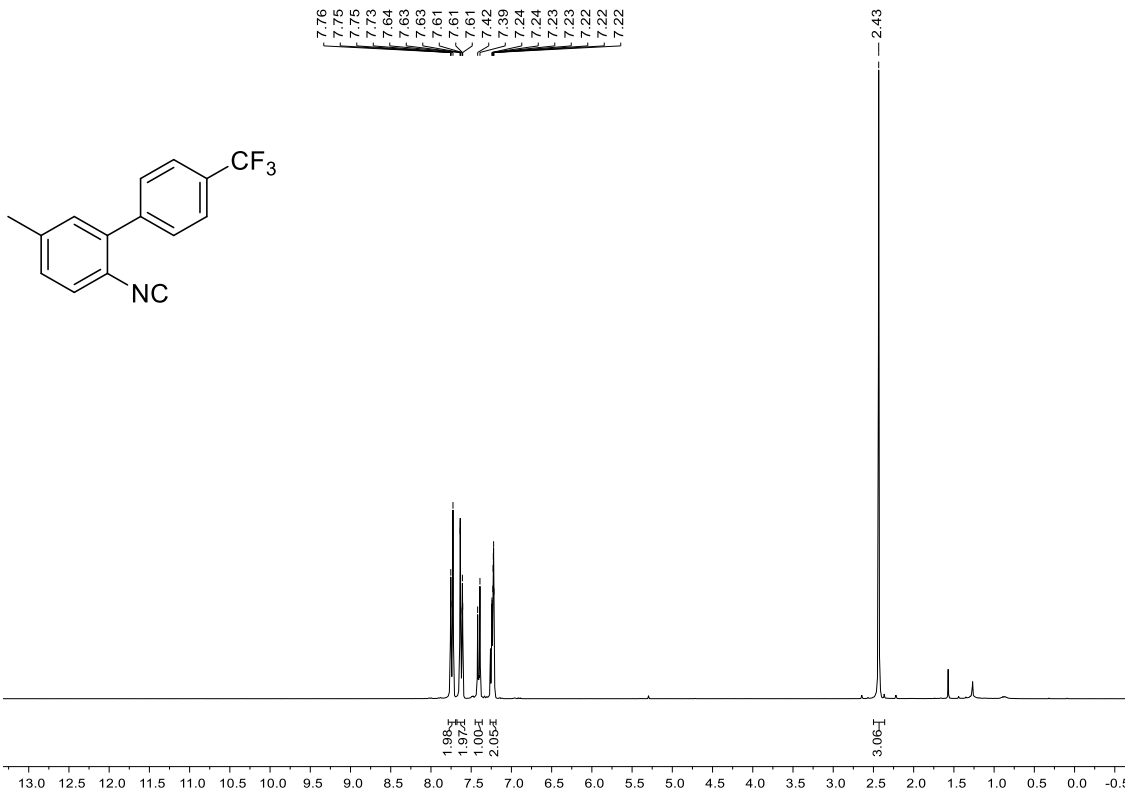


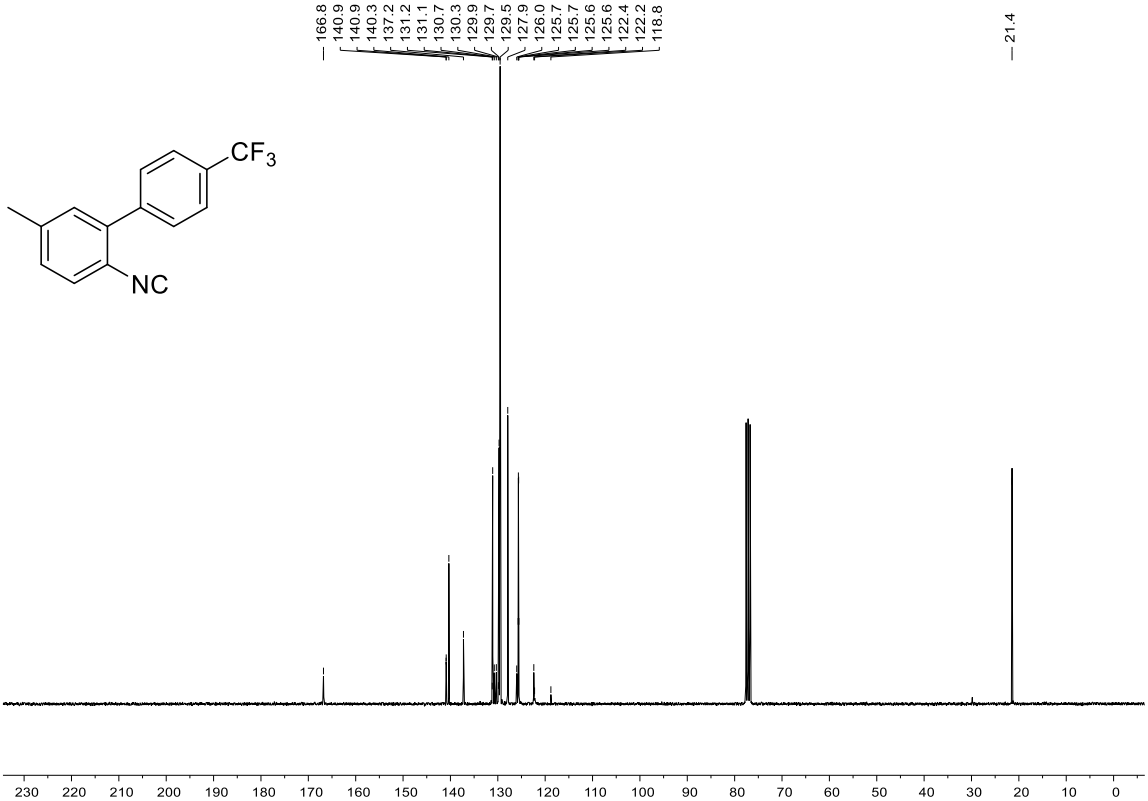
(2'-Isocyano-5'-methyl-[1,1'-biphenyl]-4-yl)trimethylsilane (1j)

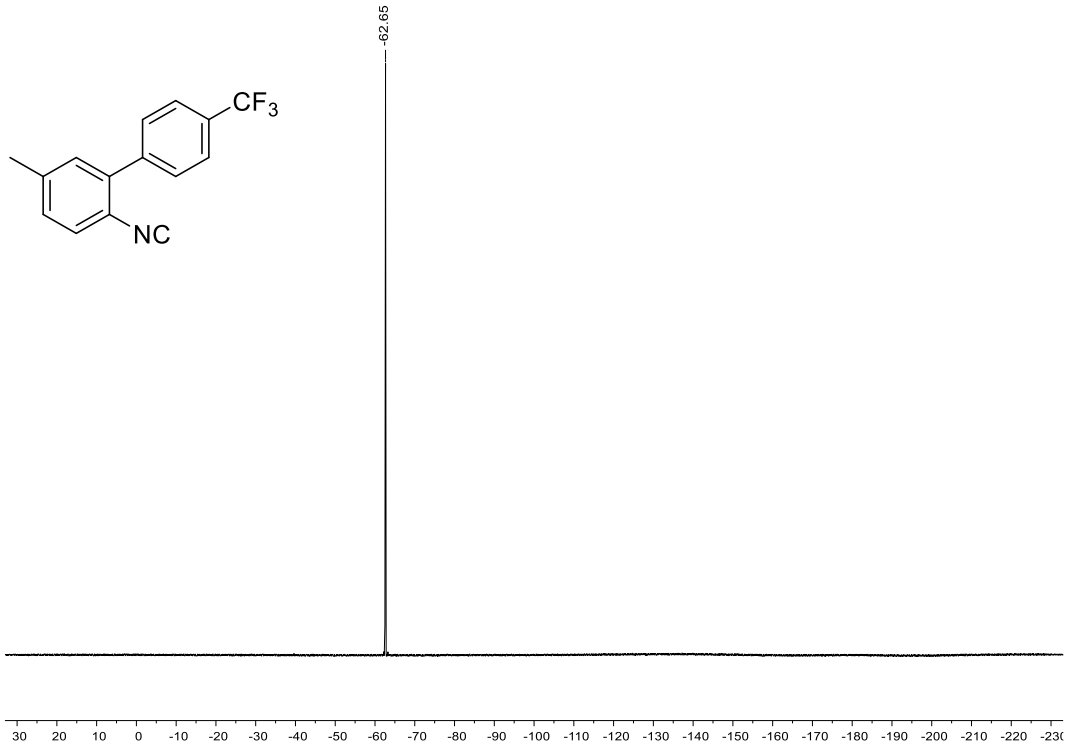




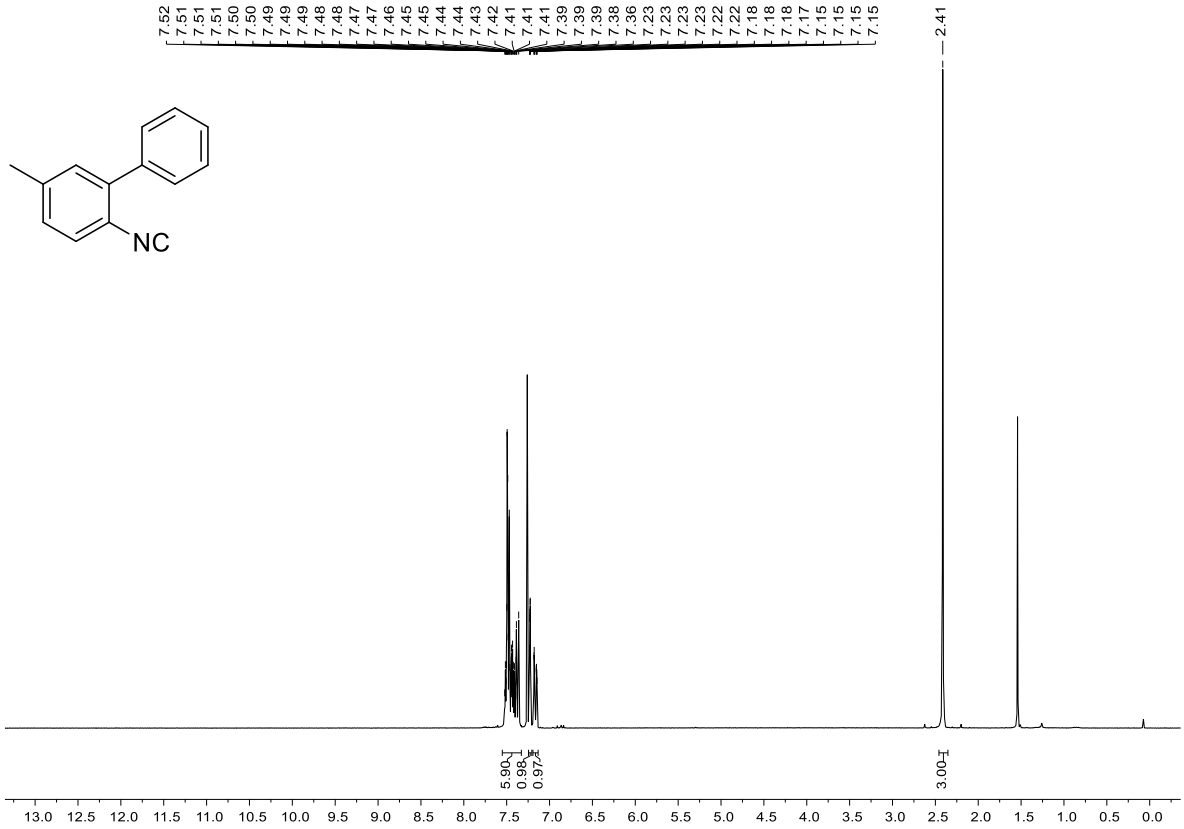
2-Isocyano-5-methyl-4'-(trifluoromethyl)-1,1'-biphenyl (1k)

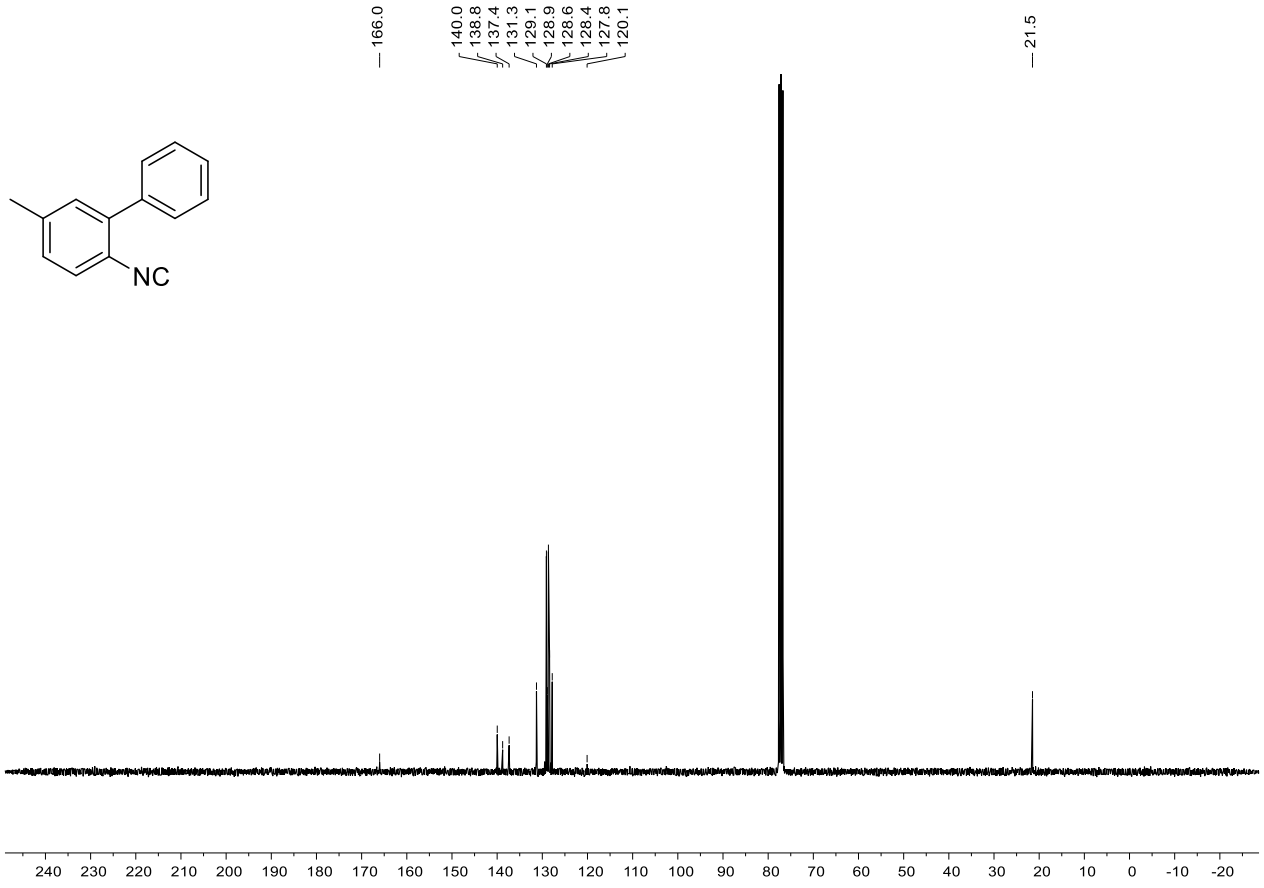




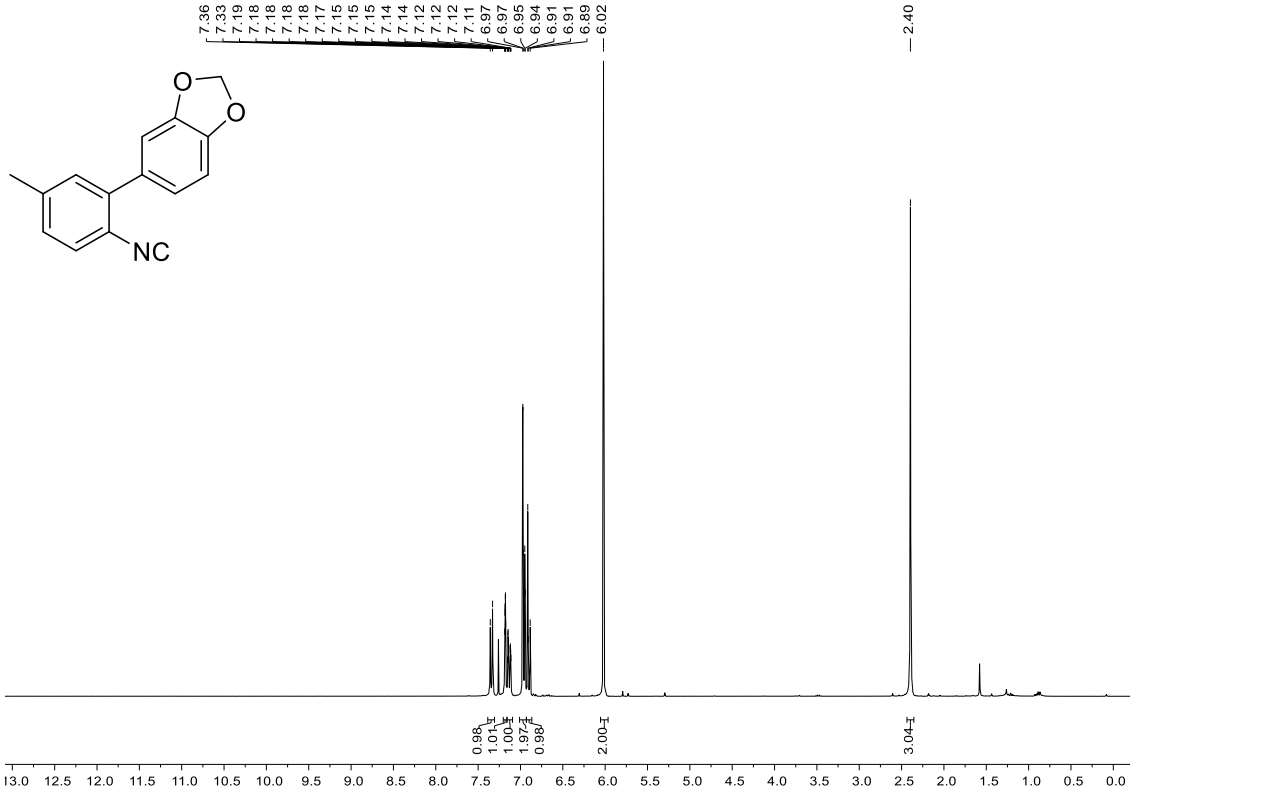


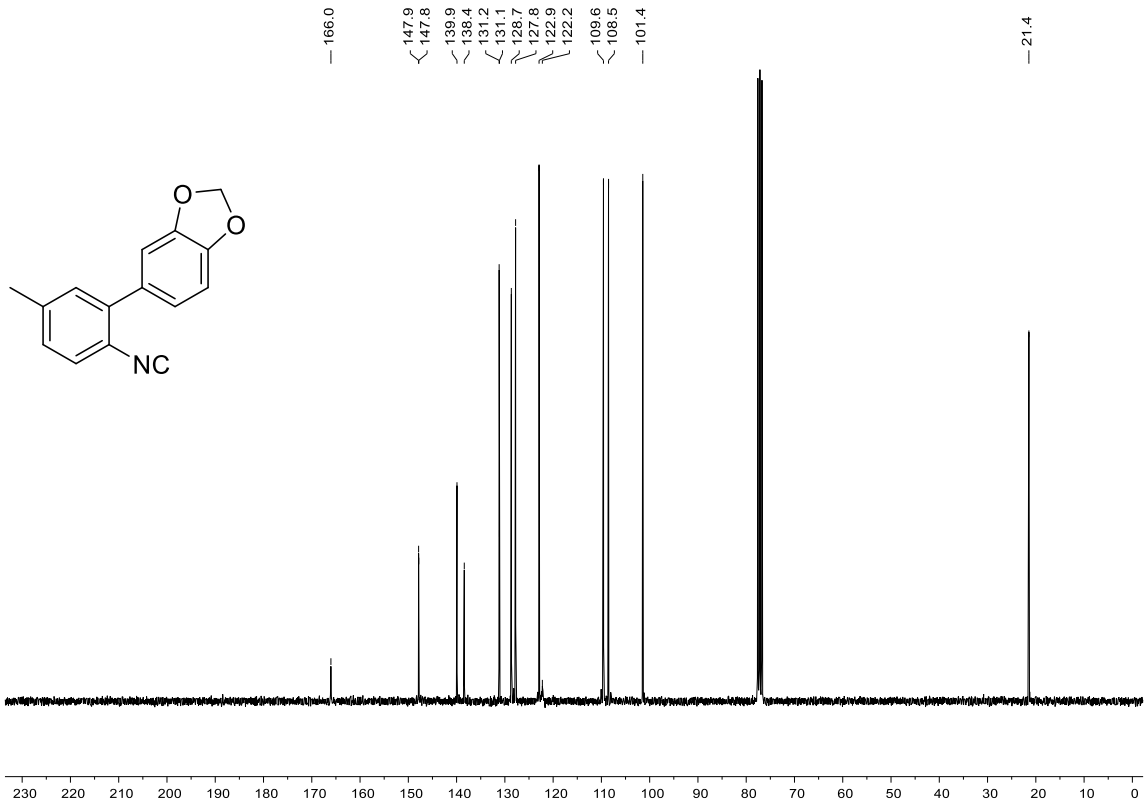
2-Isocyano-5-methyl-1,1'-biphenyl (1l)



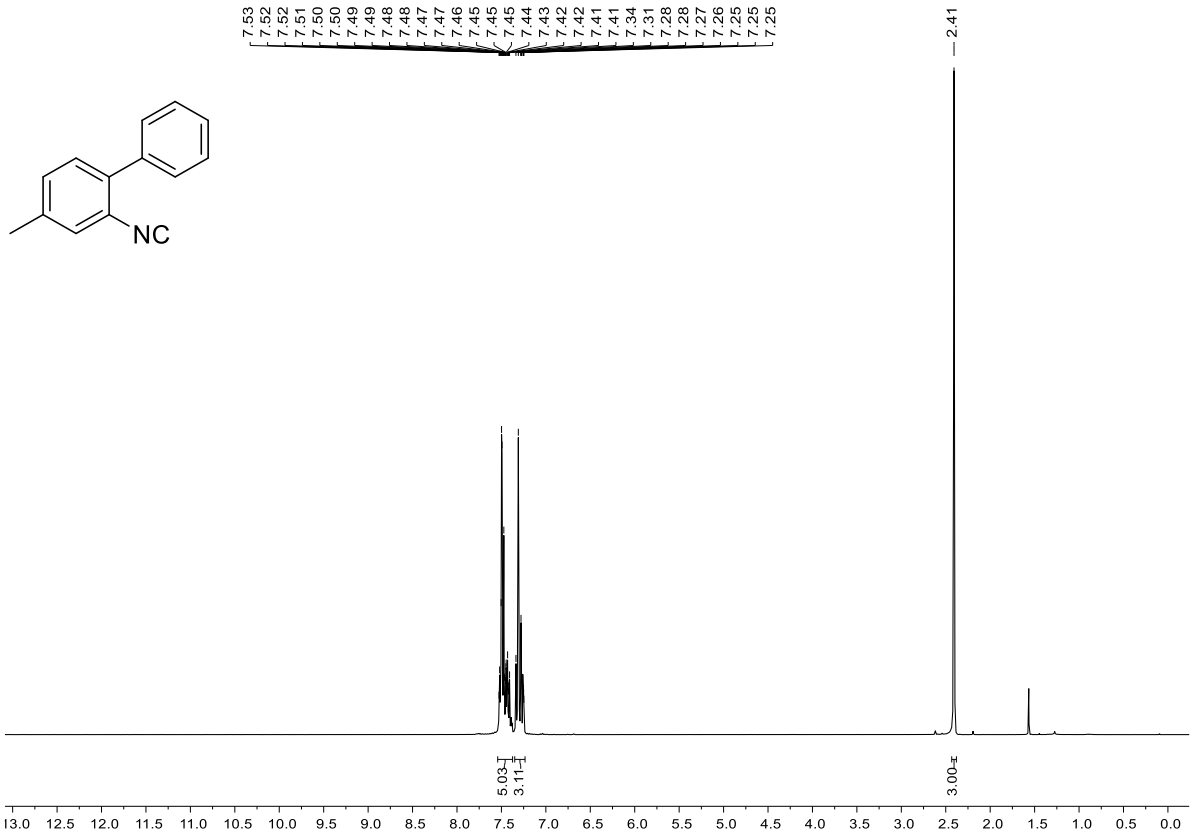


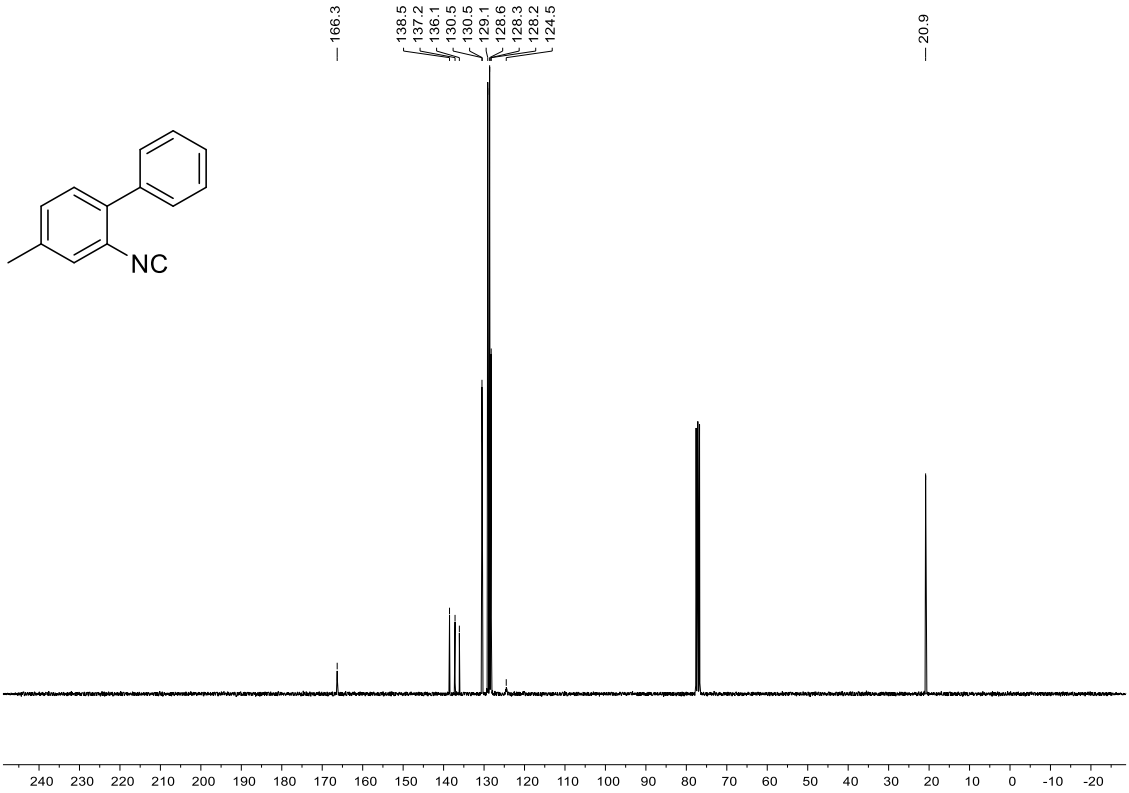
5-(2-Isocyano-5-methylphenyl)benzo[d][1,3]dioxole (1m)



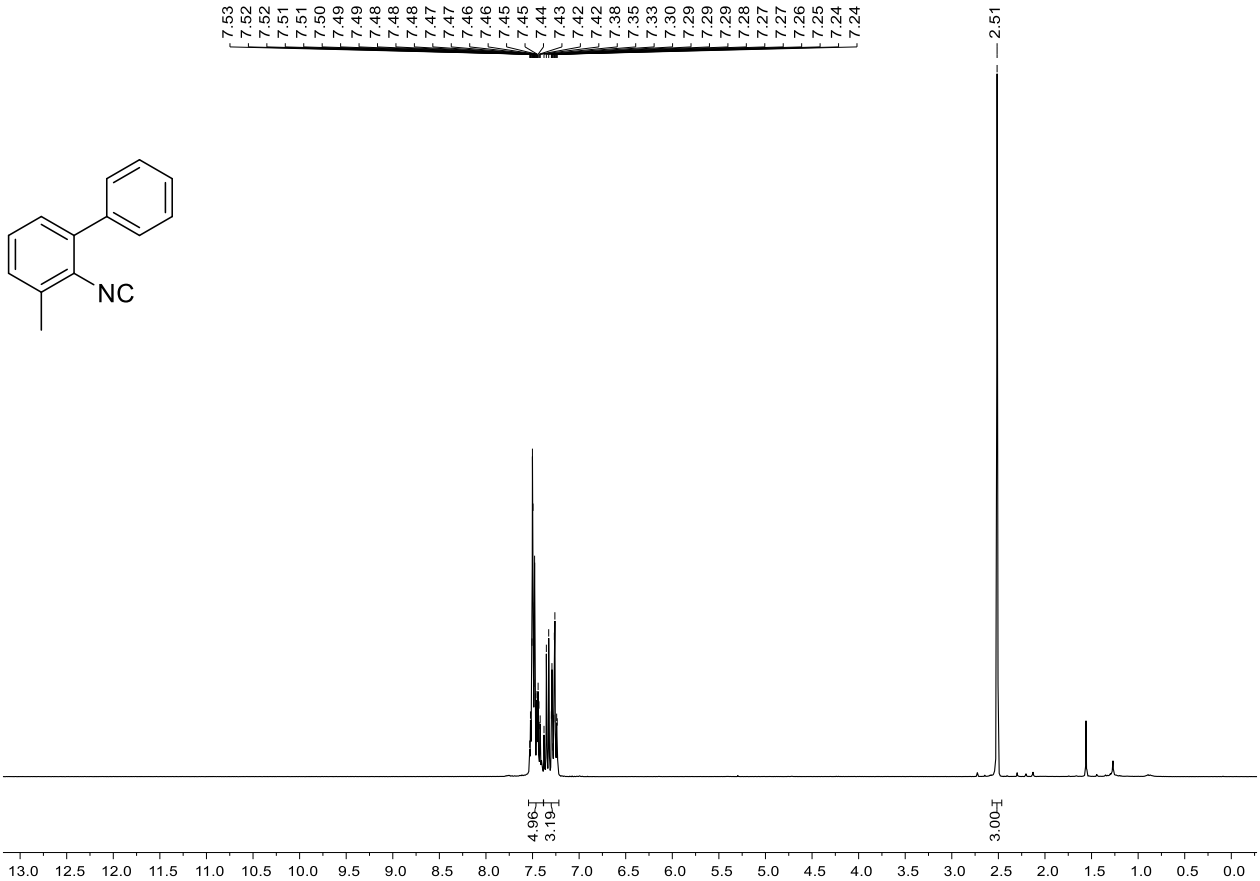


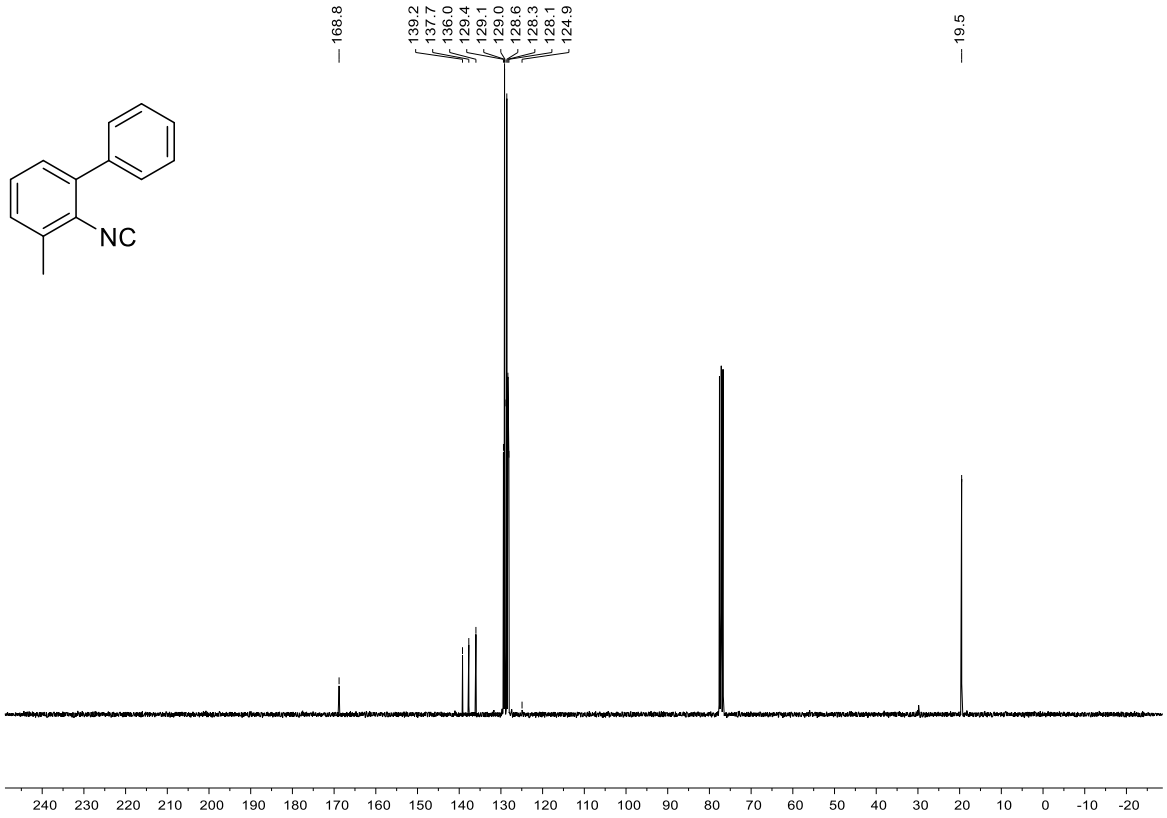
2-Isocyano-4-methyl-1,1'-biphenyl (1n)





2-Isocyano-3-methyl-1,1'-biphenyl (1o)




168.8
139.2
137.7
136.0
129.4
129.1
129.0
128.6
128.3
128.1
124.9
19.5
NC
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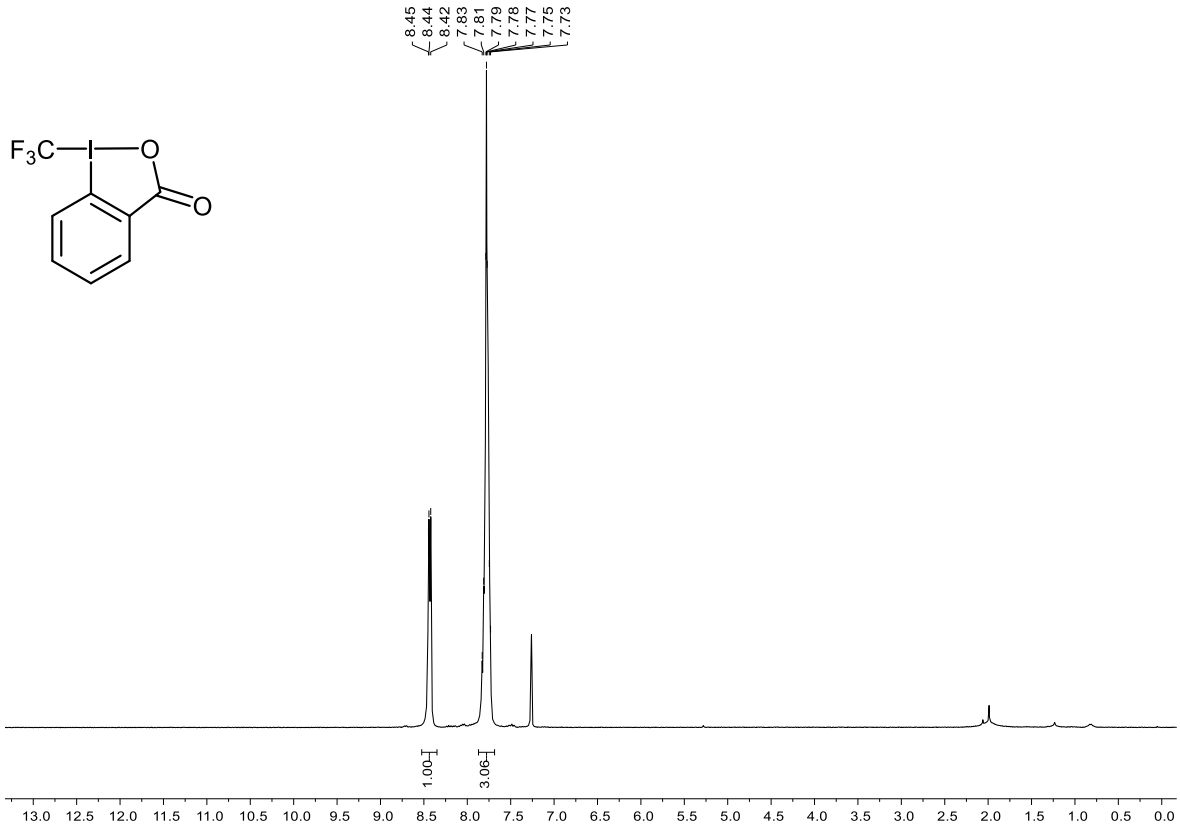
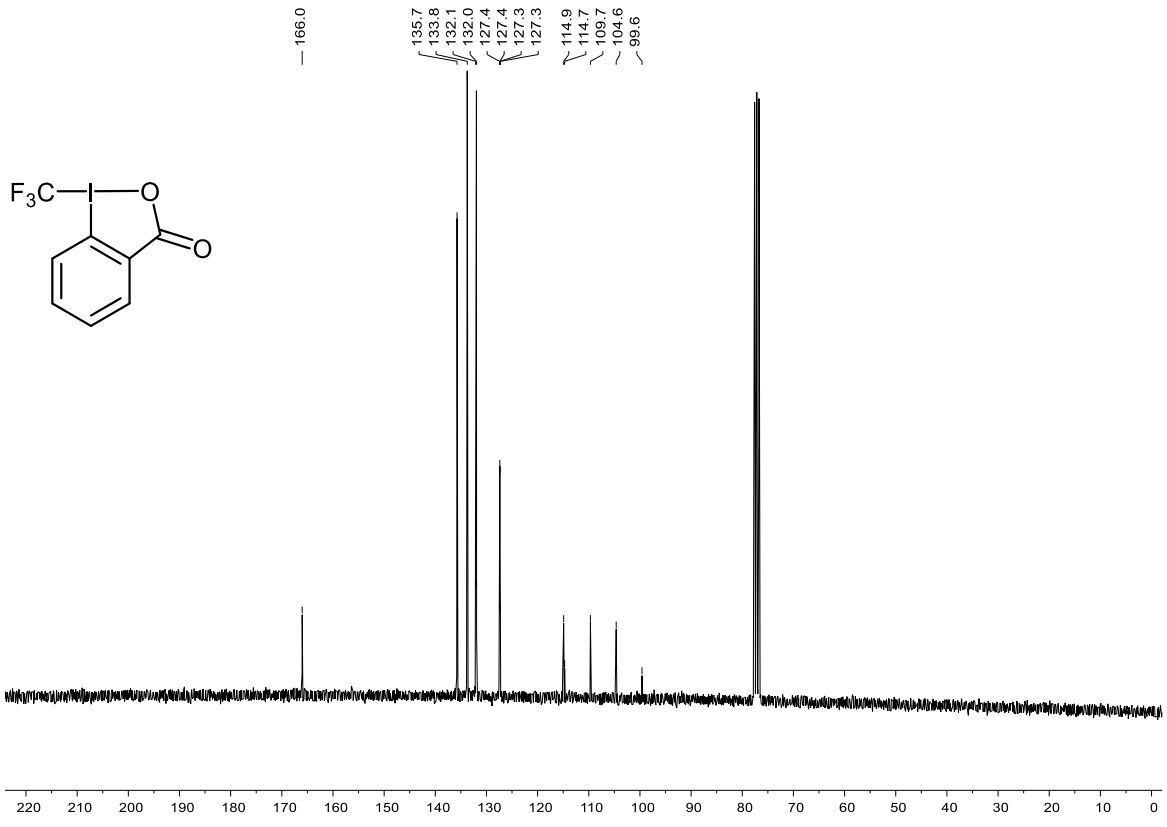
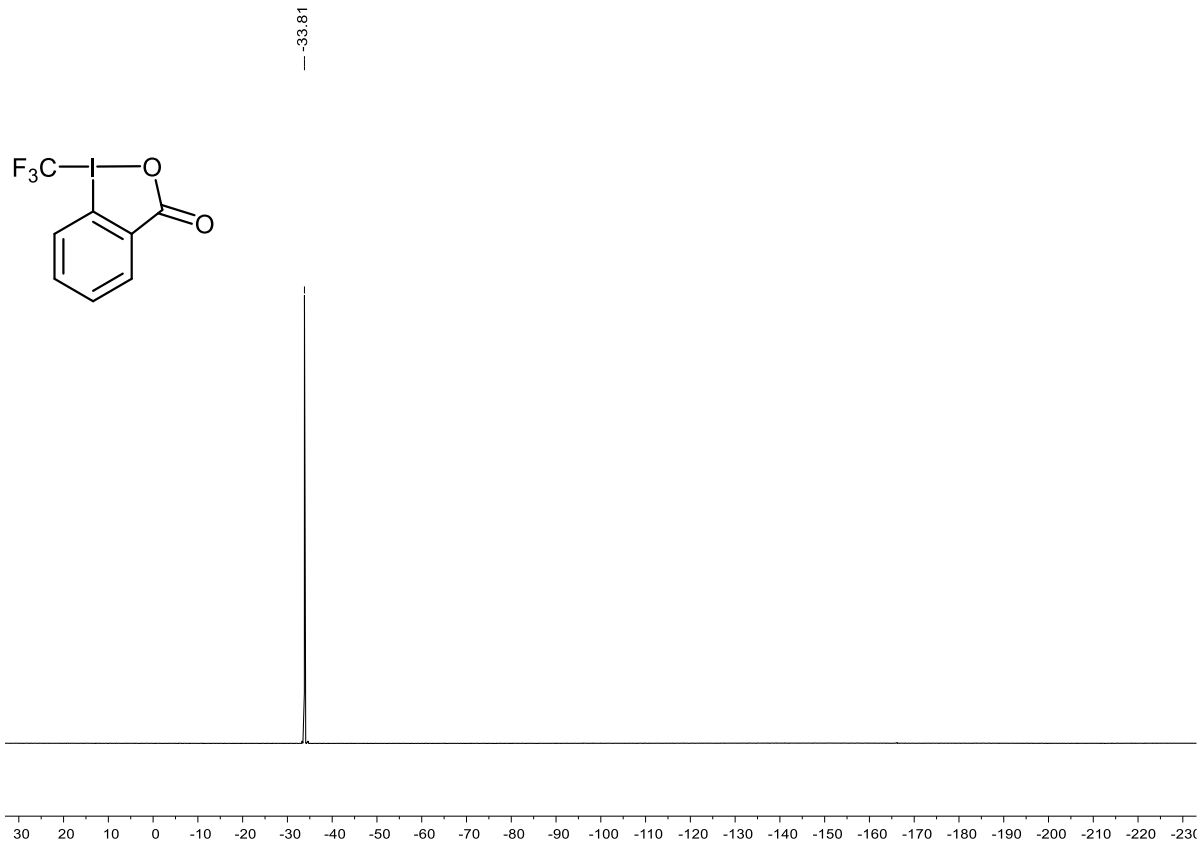
Togni reagent (2)



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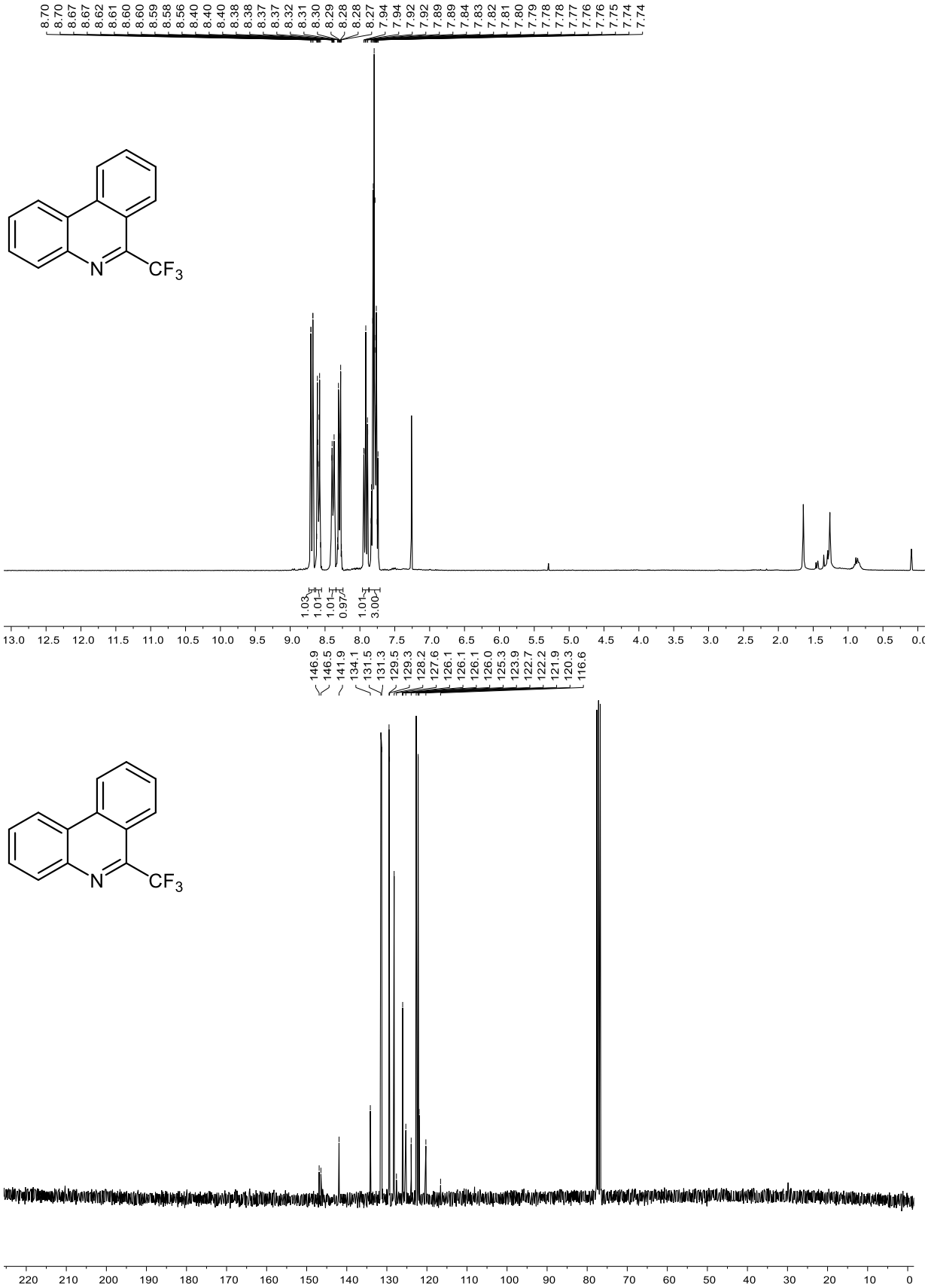
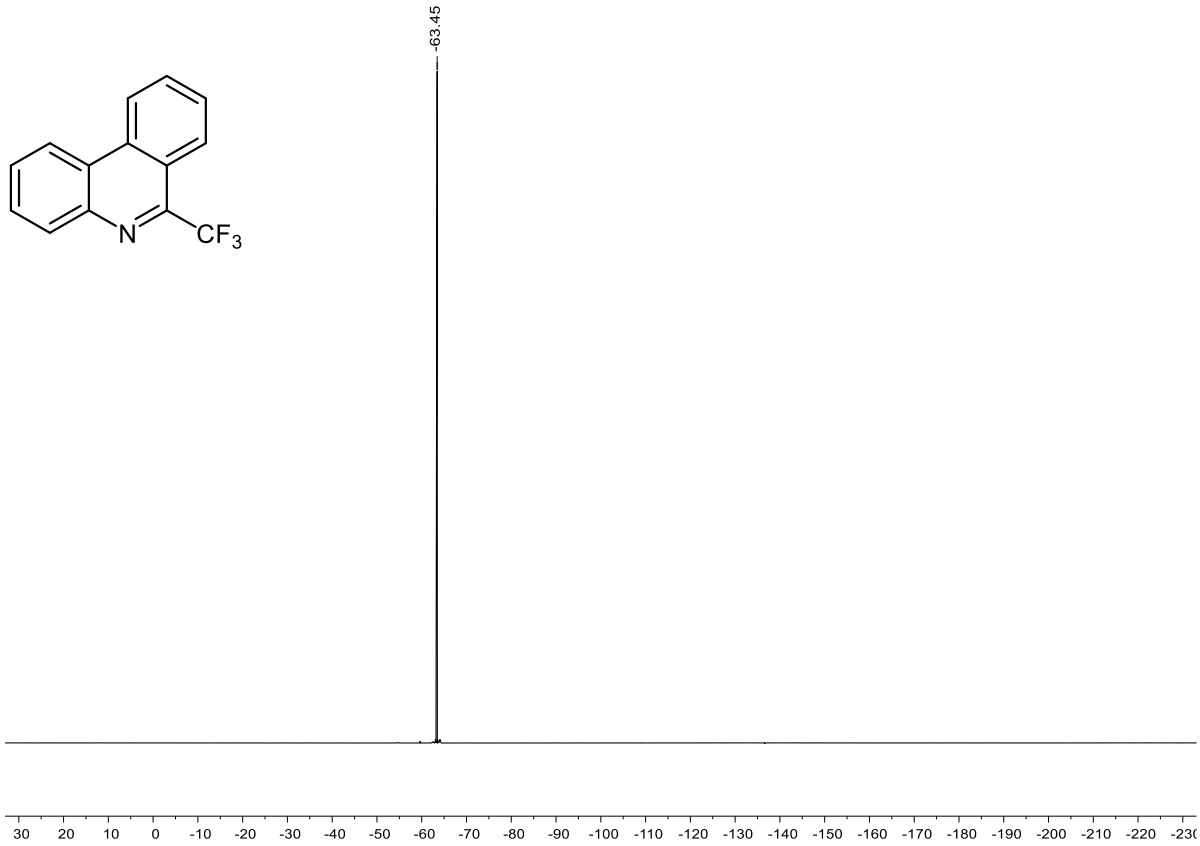
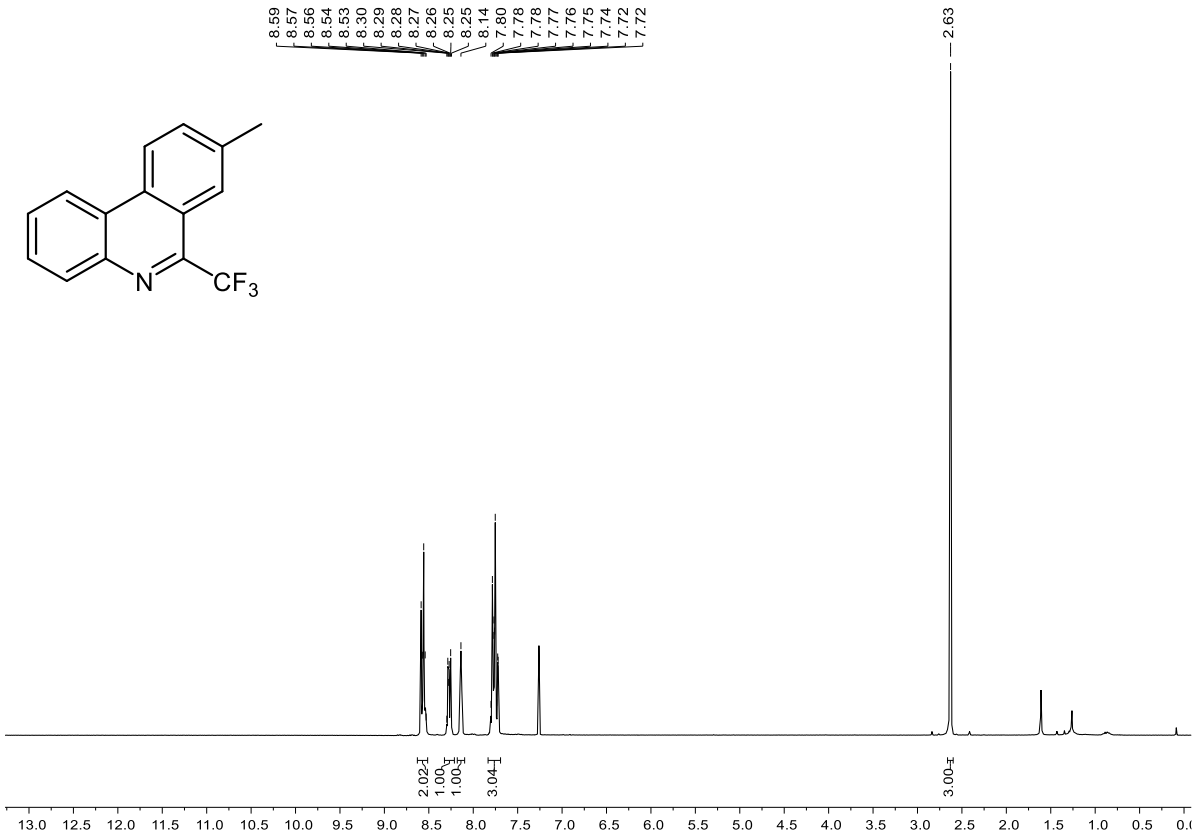
F3C
I
O
O
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

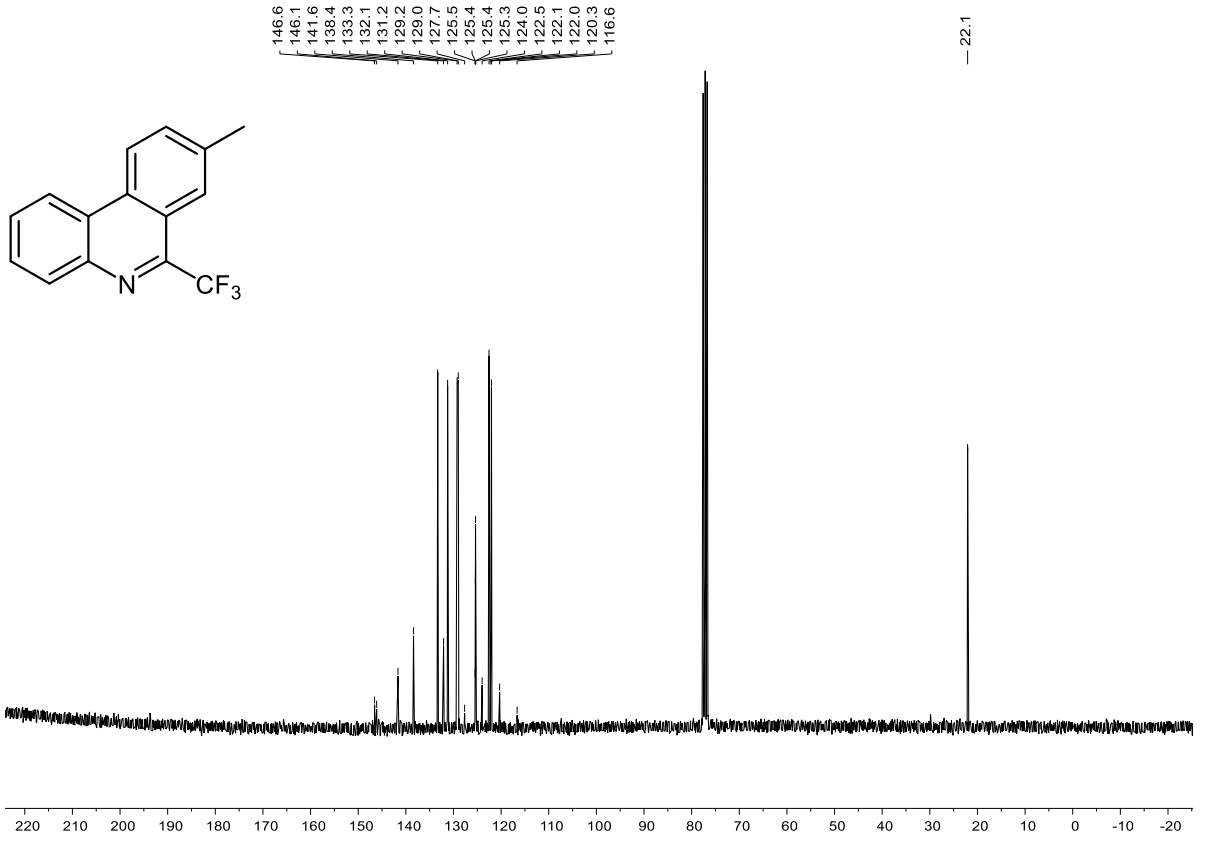
6-(Trifluoromethyl)phenanthridine (3a)





8-Methyl-6-(trifluoromethyl)phenanthridine (3b)

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141.6
138.4
133.3
132.1
131.2
129.2
129.0
127.7
125.5
125.4
125.4
125.3
124.0
122.5
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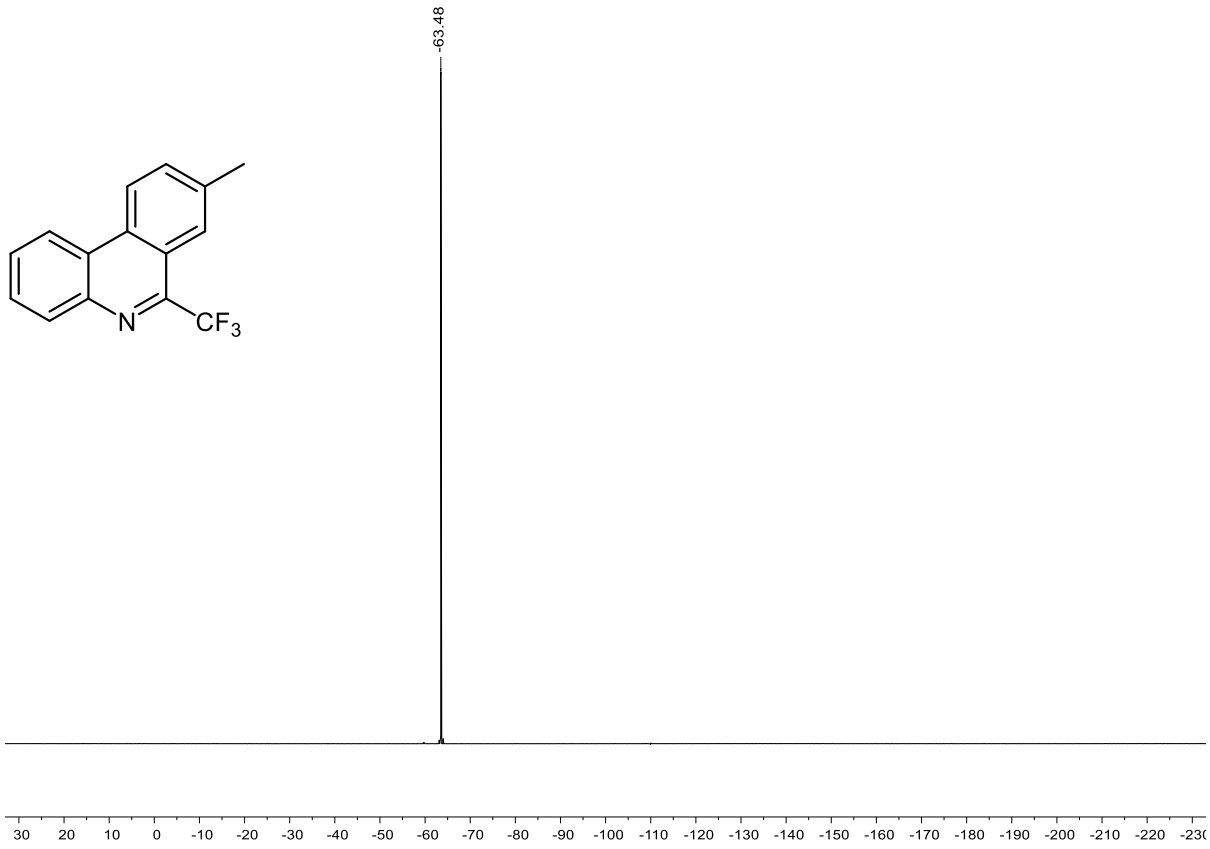
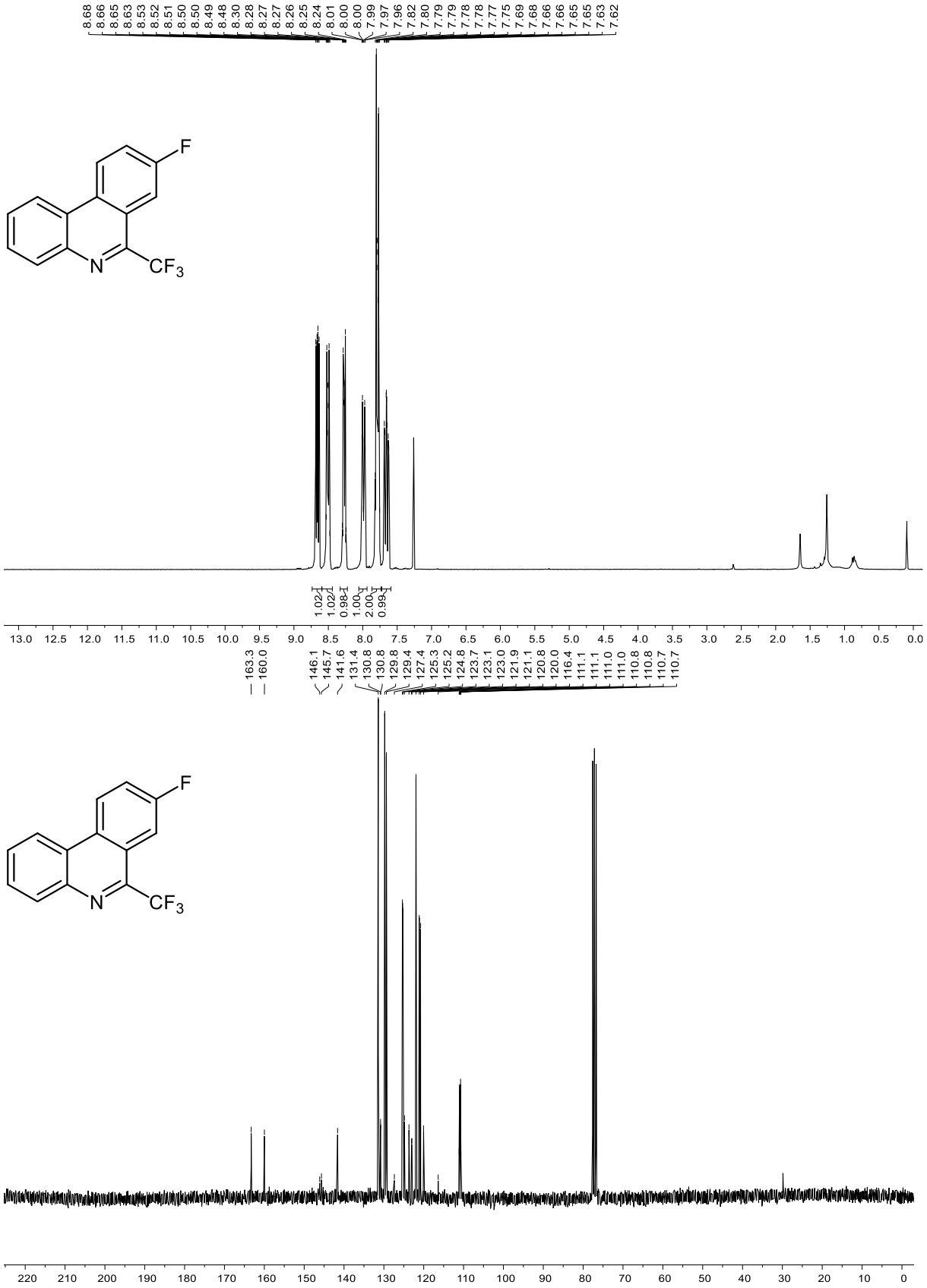
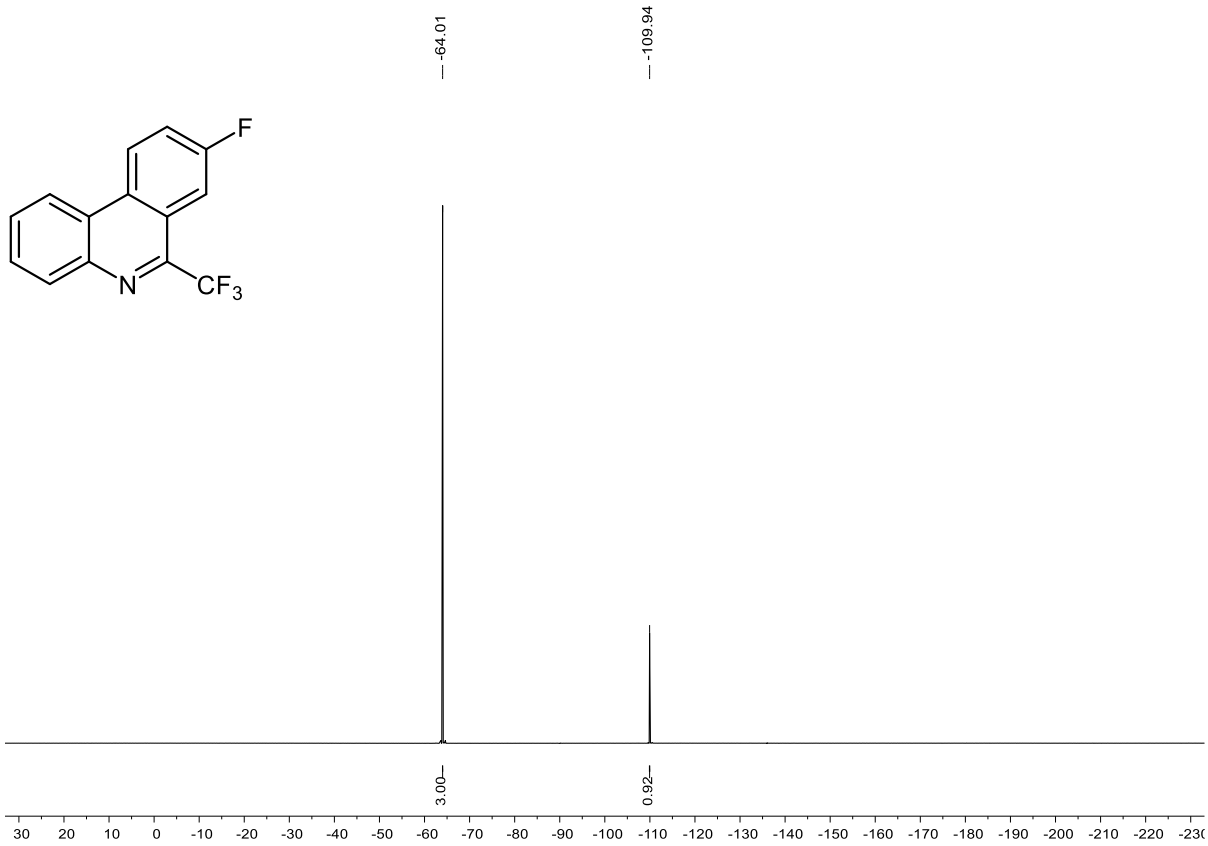
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

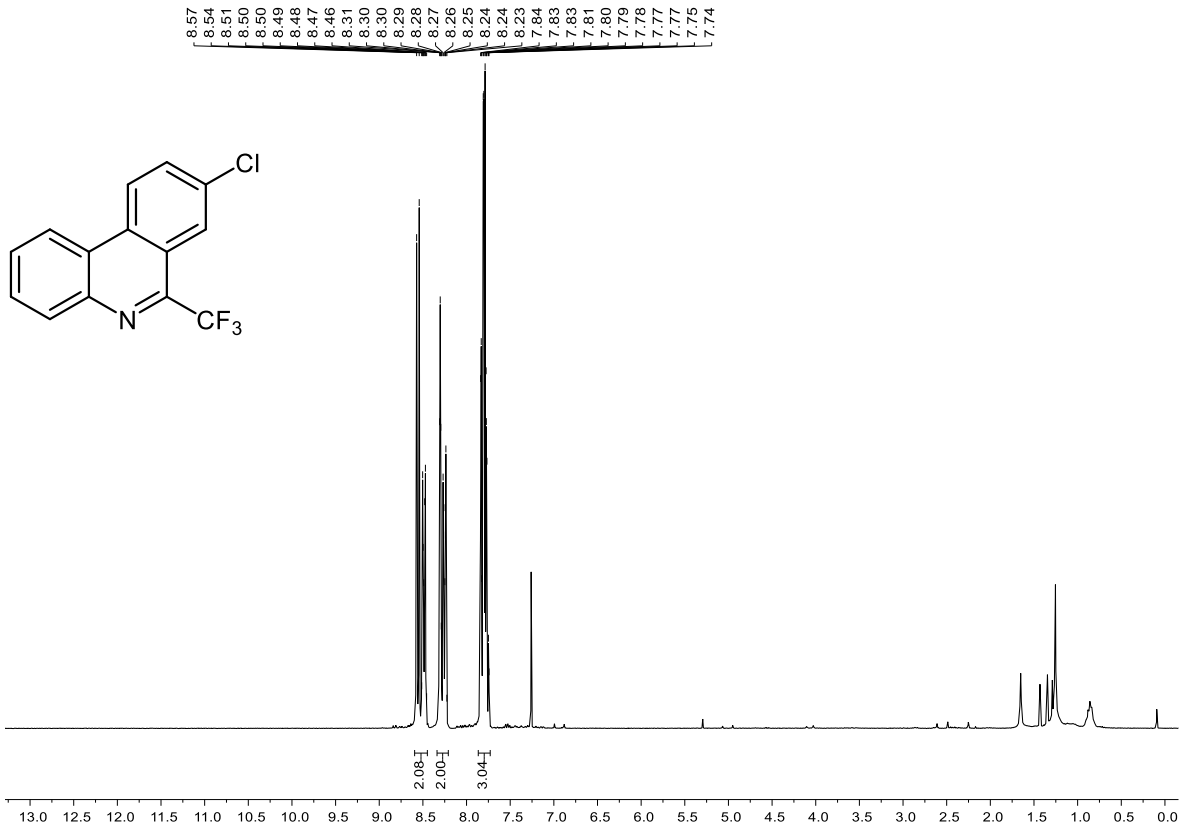

-63.48
N
CF3
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230

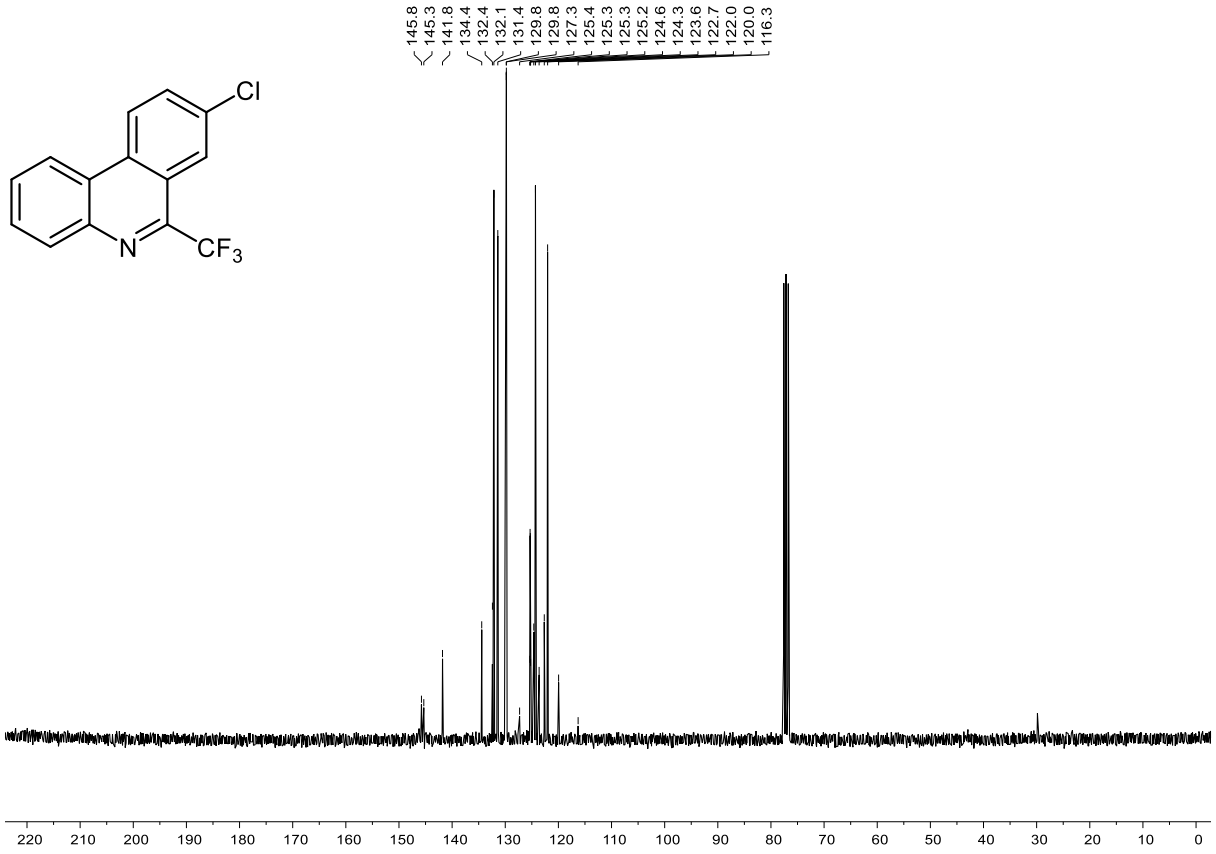
8-Fluoro-6-(trifluoromethyl)phenanthridine (3c)

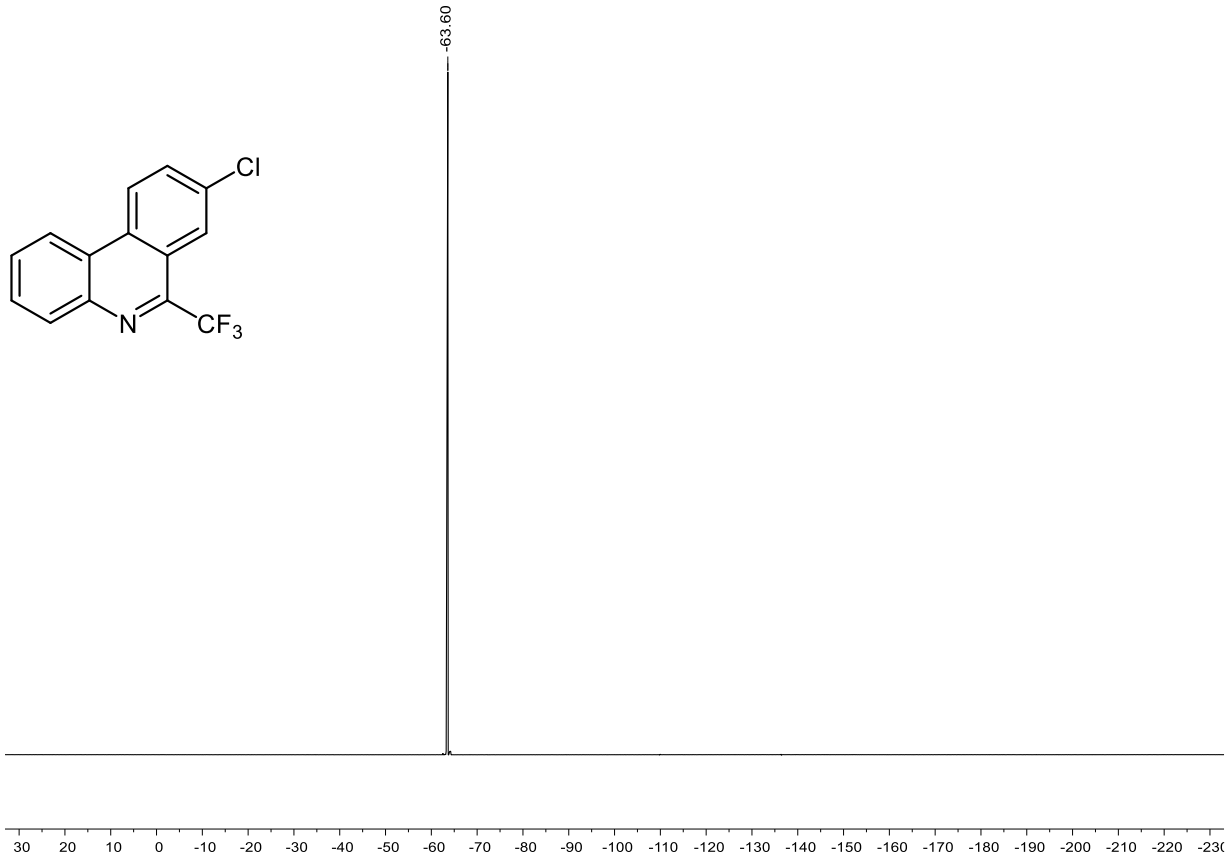




8-Chloro-6-(trifluoromethyl)phenanthridine (3d)




145.8
145.3
141.8
134.4
132.4
132.1
131.4
129.8
129.8
127.3
125.4
125.3
125.3
125.2
124.6
124.3
123.6
122.7
122.0
120.0
116.3
Cl
N
CF3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


-63.60
Cl
N
CF3
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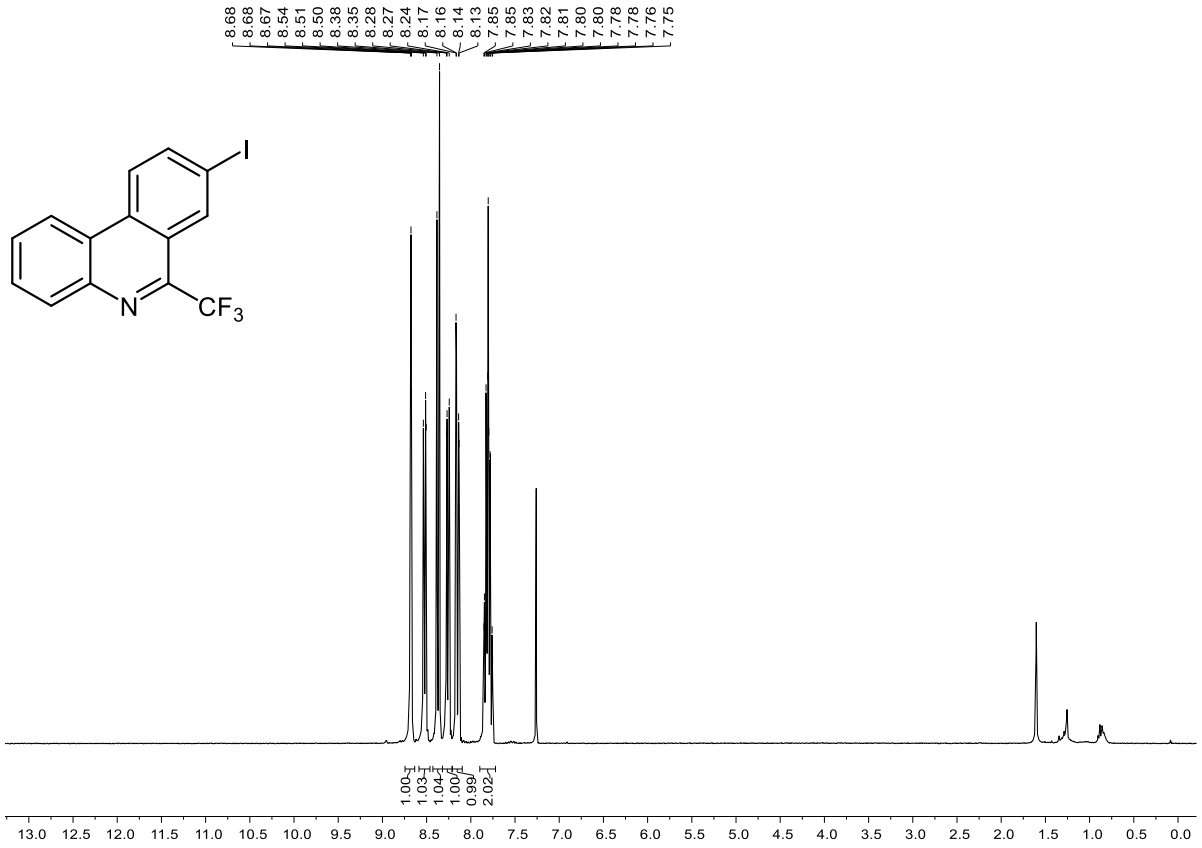
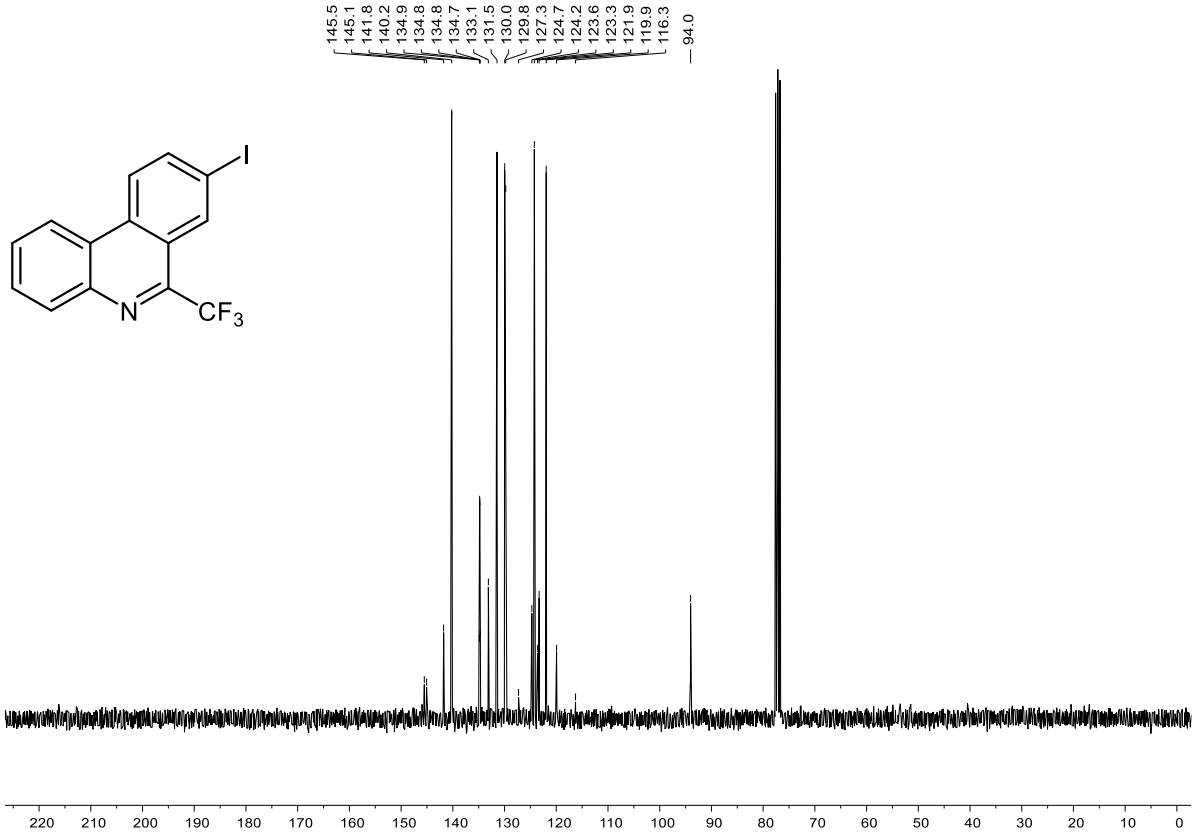
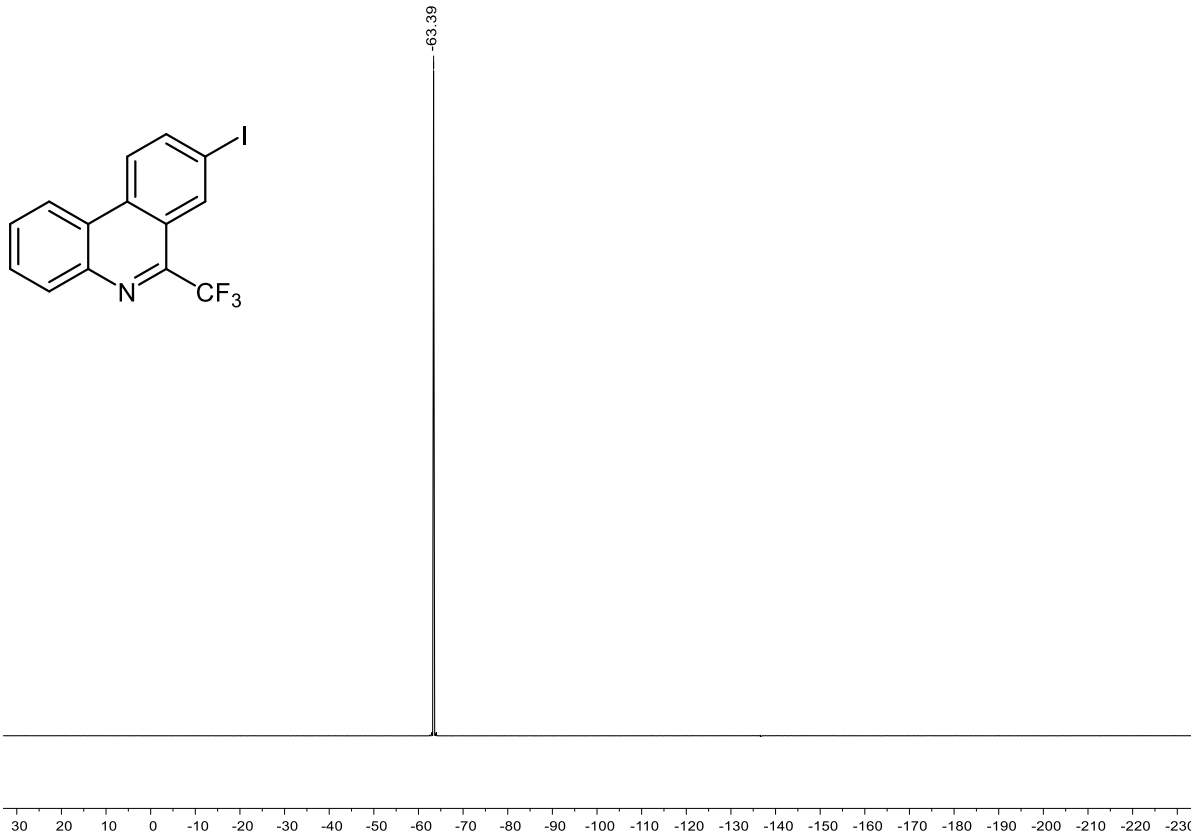
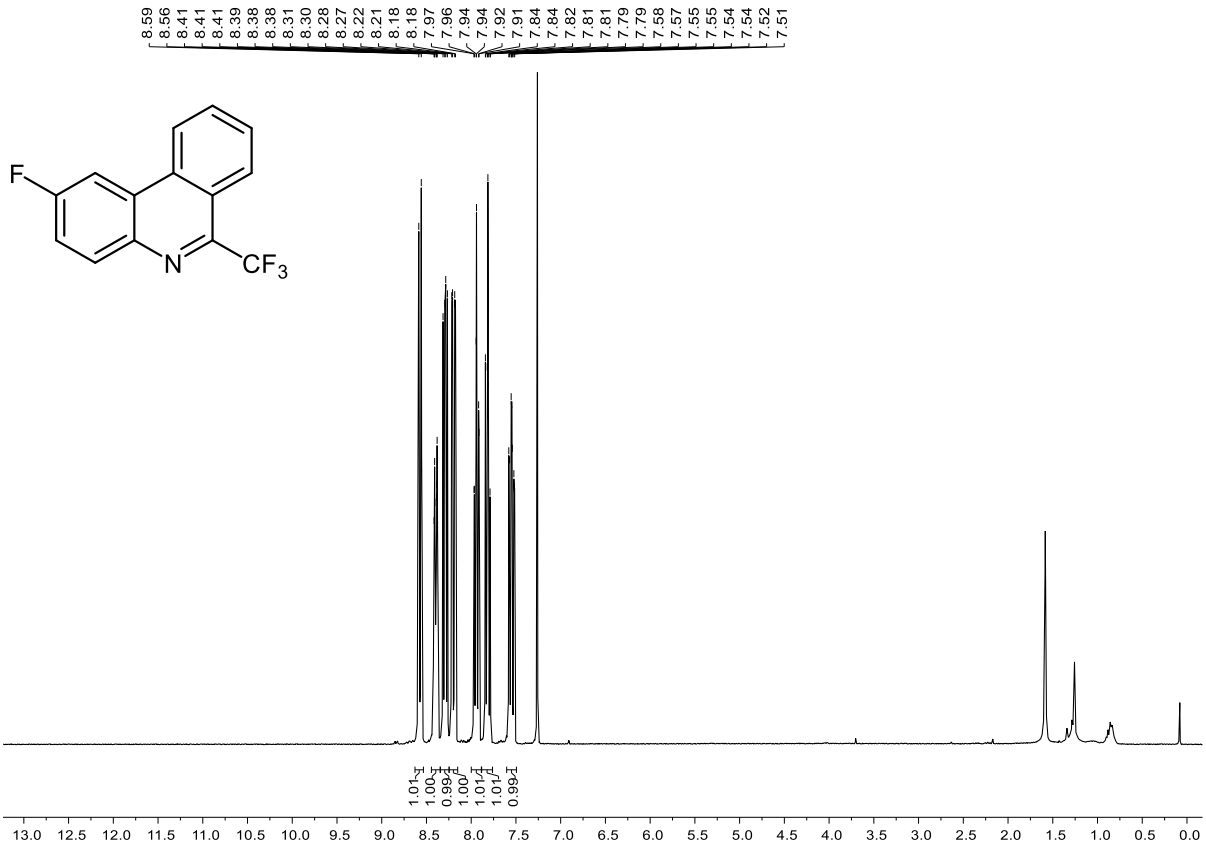
8-Iodo-6-(trifluoromethyl)phenanthridine (3e)

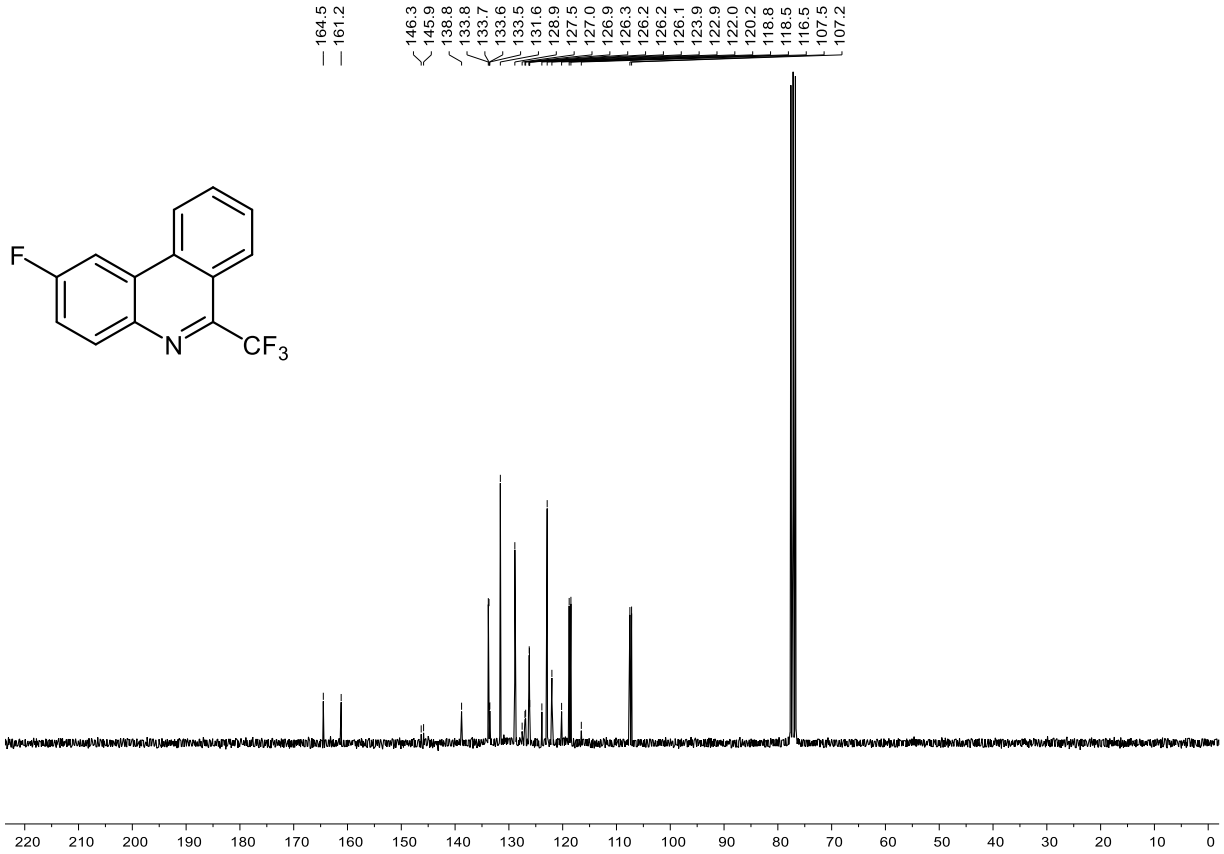






2-Fluoro-6-(trifluoromethyl)phenanthridine (3f)

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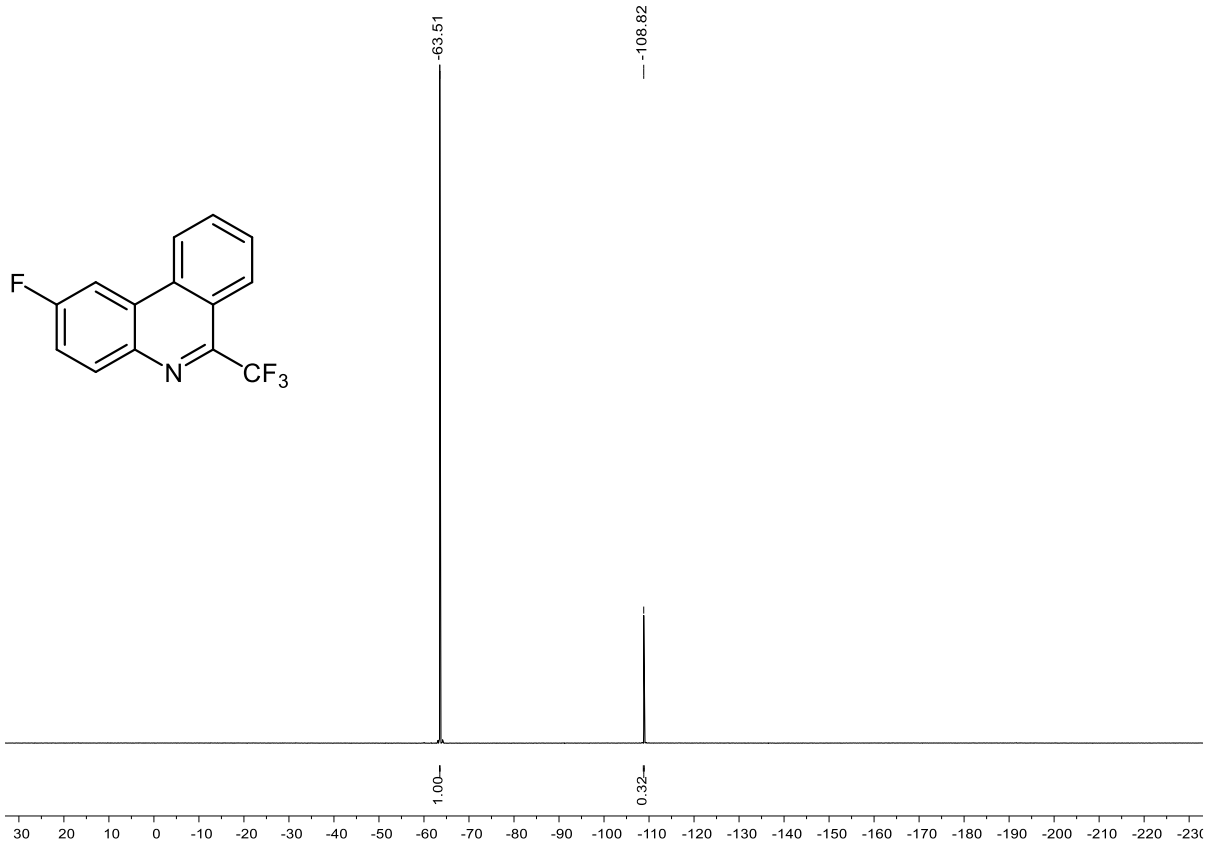
146.3
145.9
138.8
133.8
133.7
133.6
133.5
131.6
128.9
127.5
127.0
126.9
126.3
126.2
126.2
126.1
123.9
122.9
122.0
120.2
118.8
118.5
116.5
107.5
107.2
F
N
CF3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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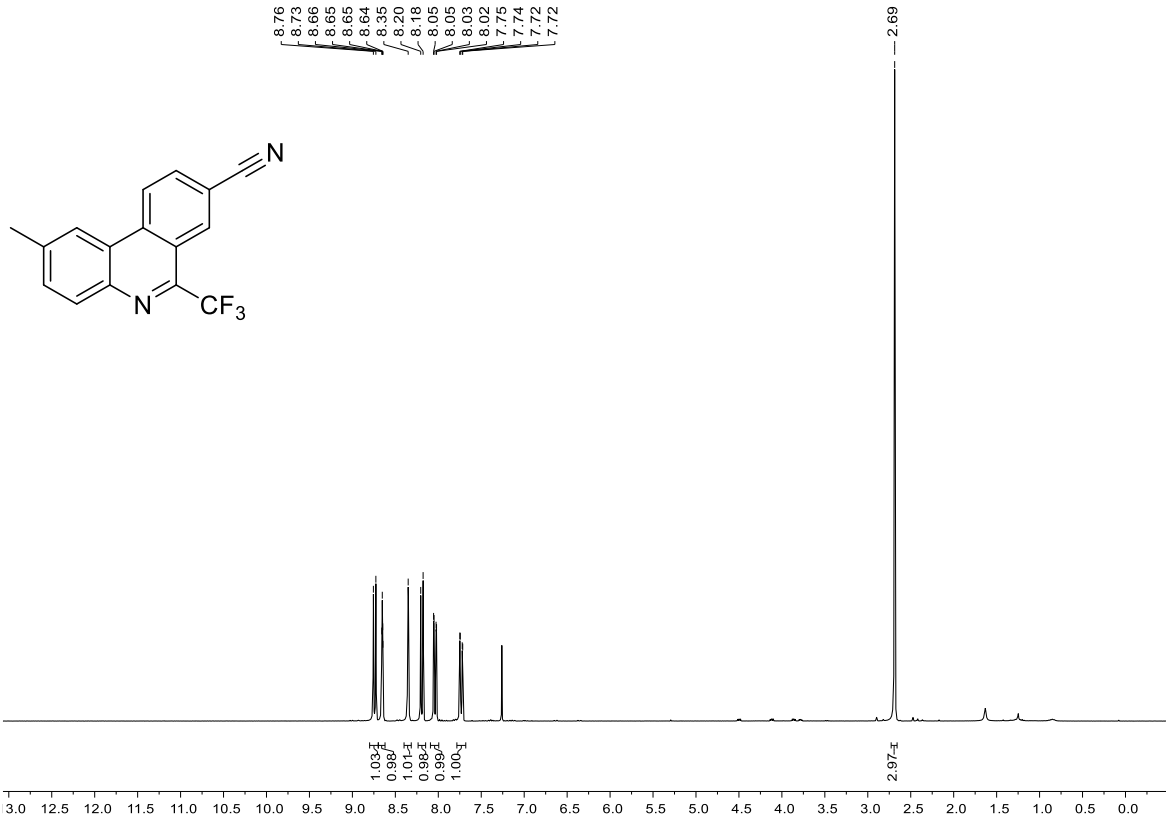
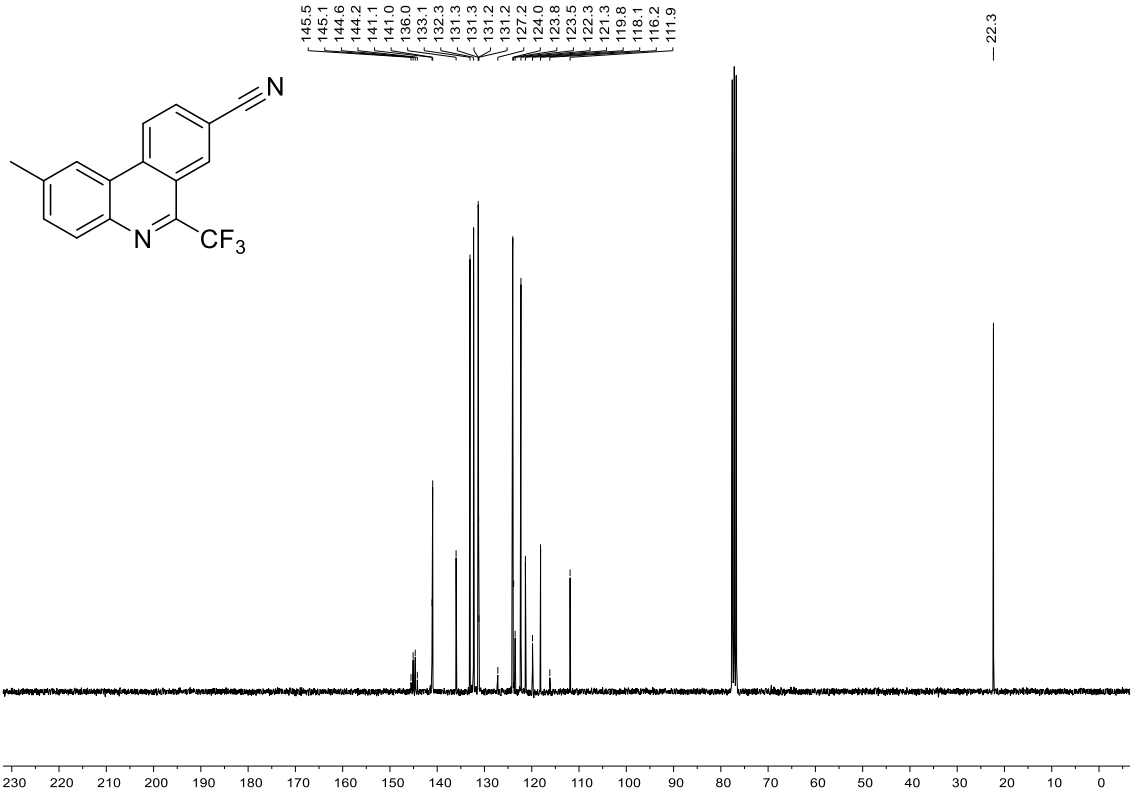
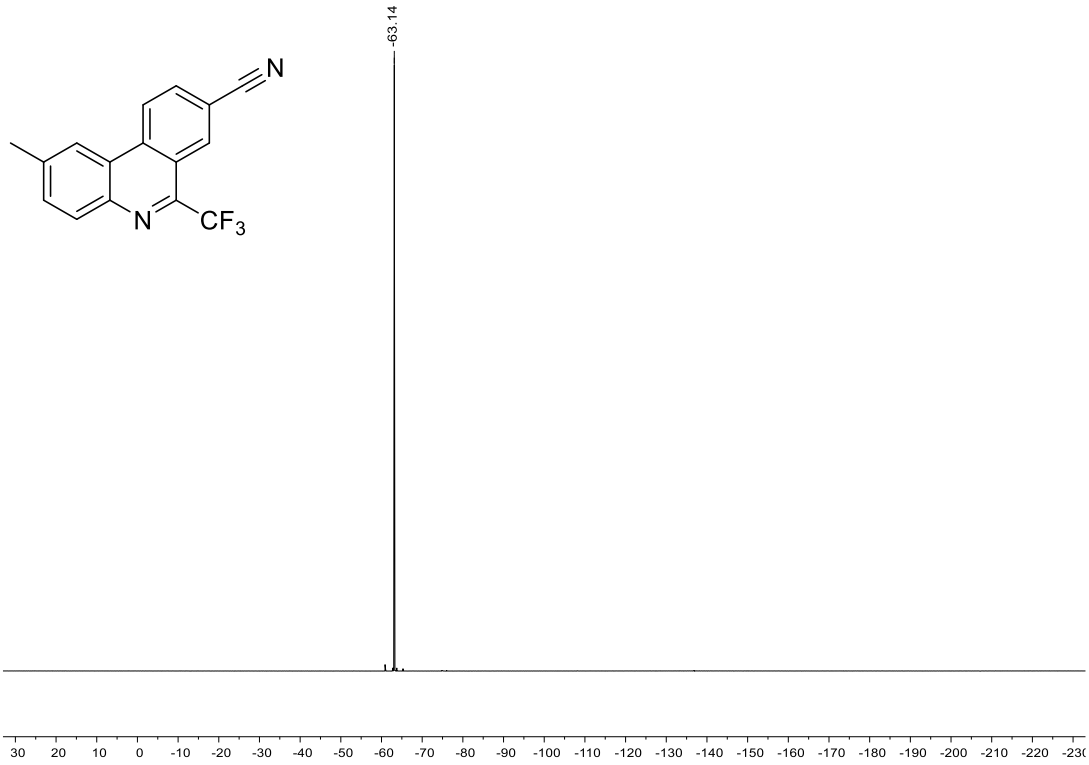
-108.82
F
N
CF3
1.00
0.32
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23

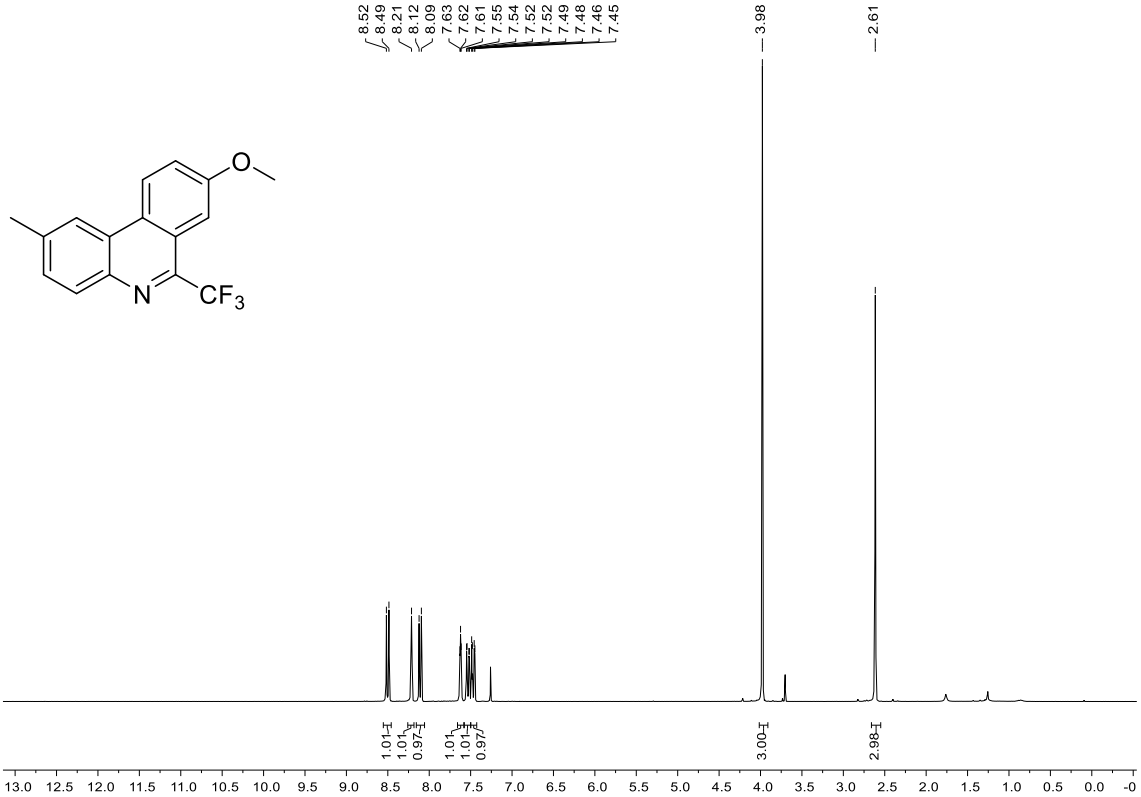
2-Methyl-6-(trifluoromethyl)phenanthridine-8-carbonitrile (3g)

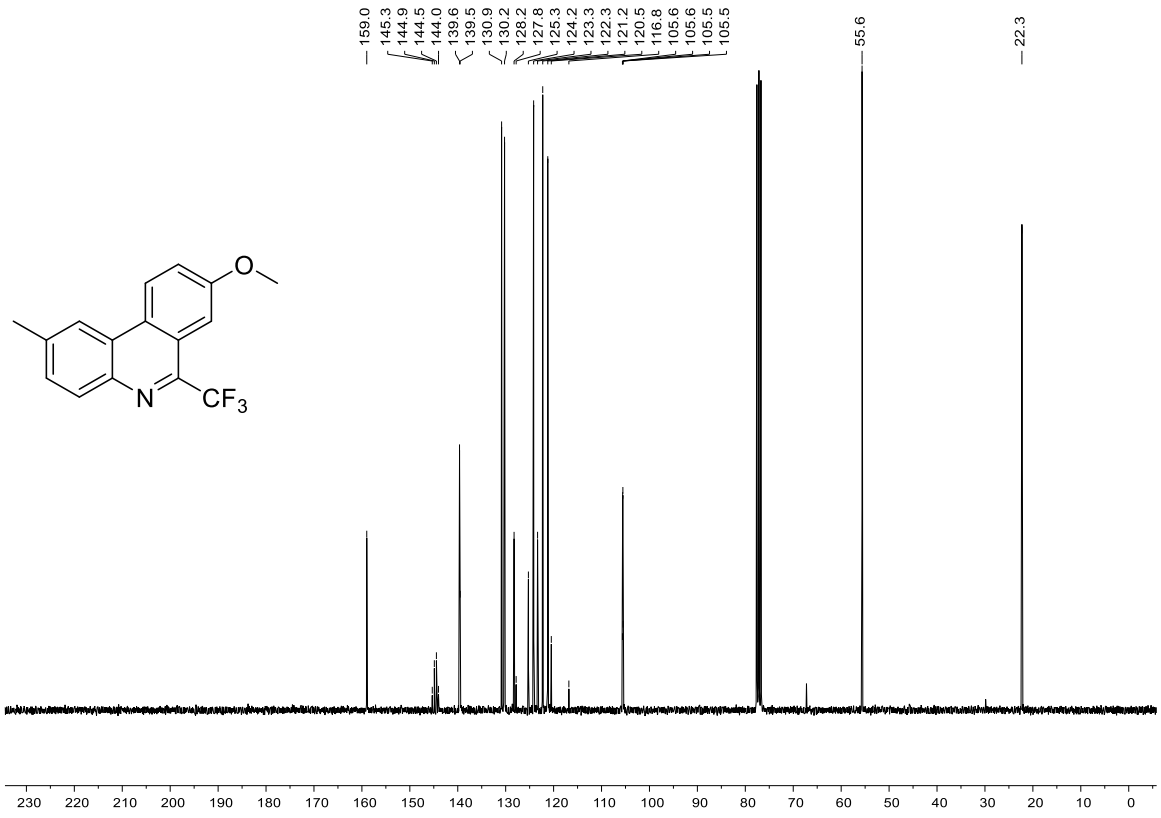






8-Methoxy-2-methyl-6-(trifluoromethyl)phenanthridine (3h)

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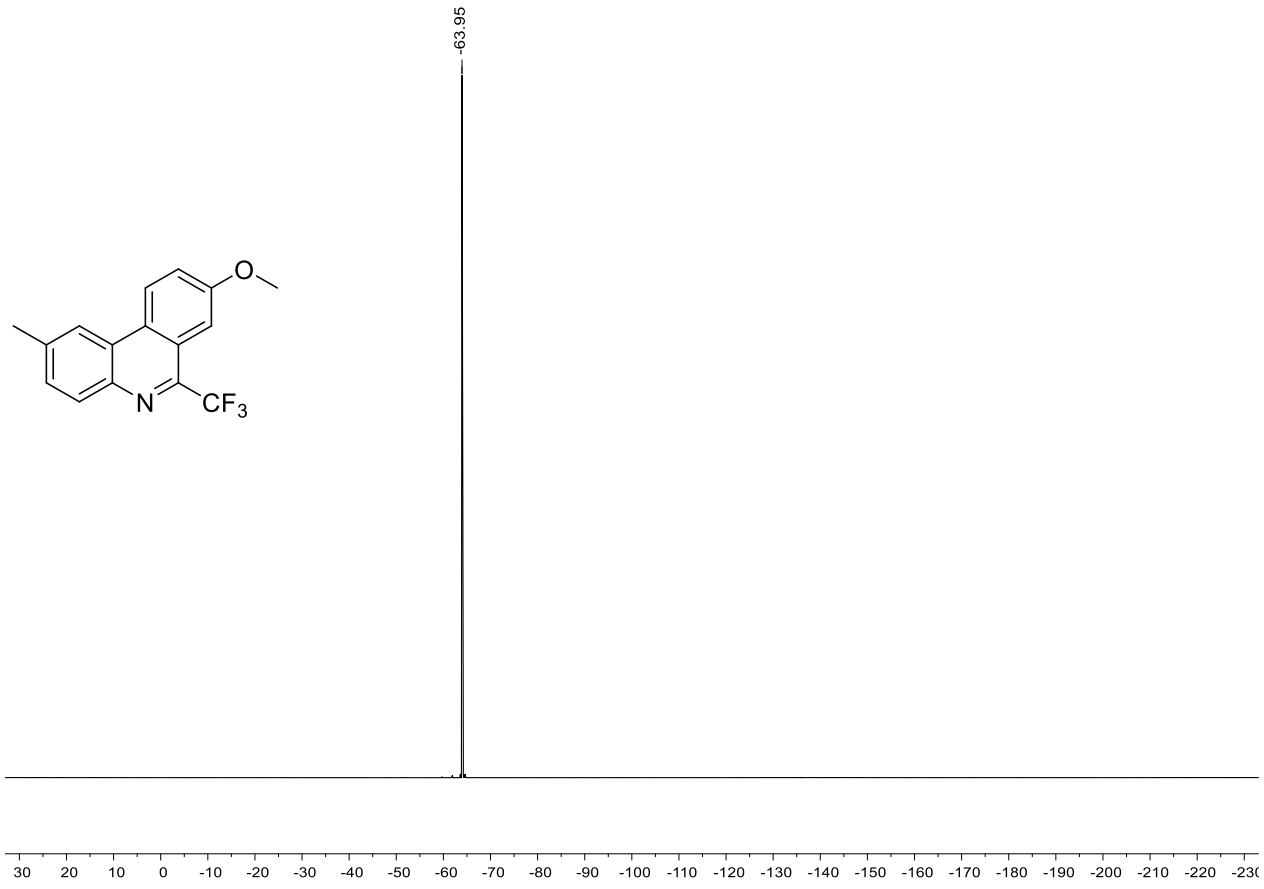
139.6
139.5
130.9
130.2
128.2
127.8
125.3
124.2
123.3
122.3
121.2
120.5
116.8
105.6
105.6
105.5
105.5
55.6
22.3
O
N
CF3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


-63.95
O
N
CF3
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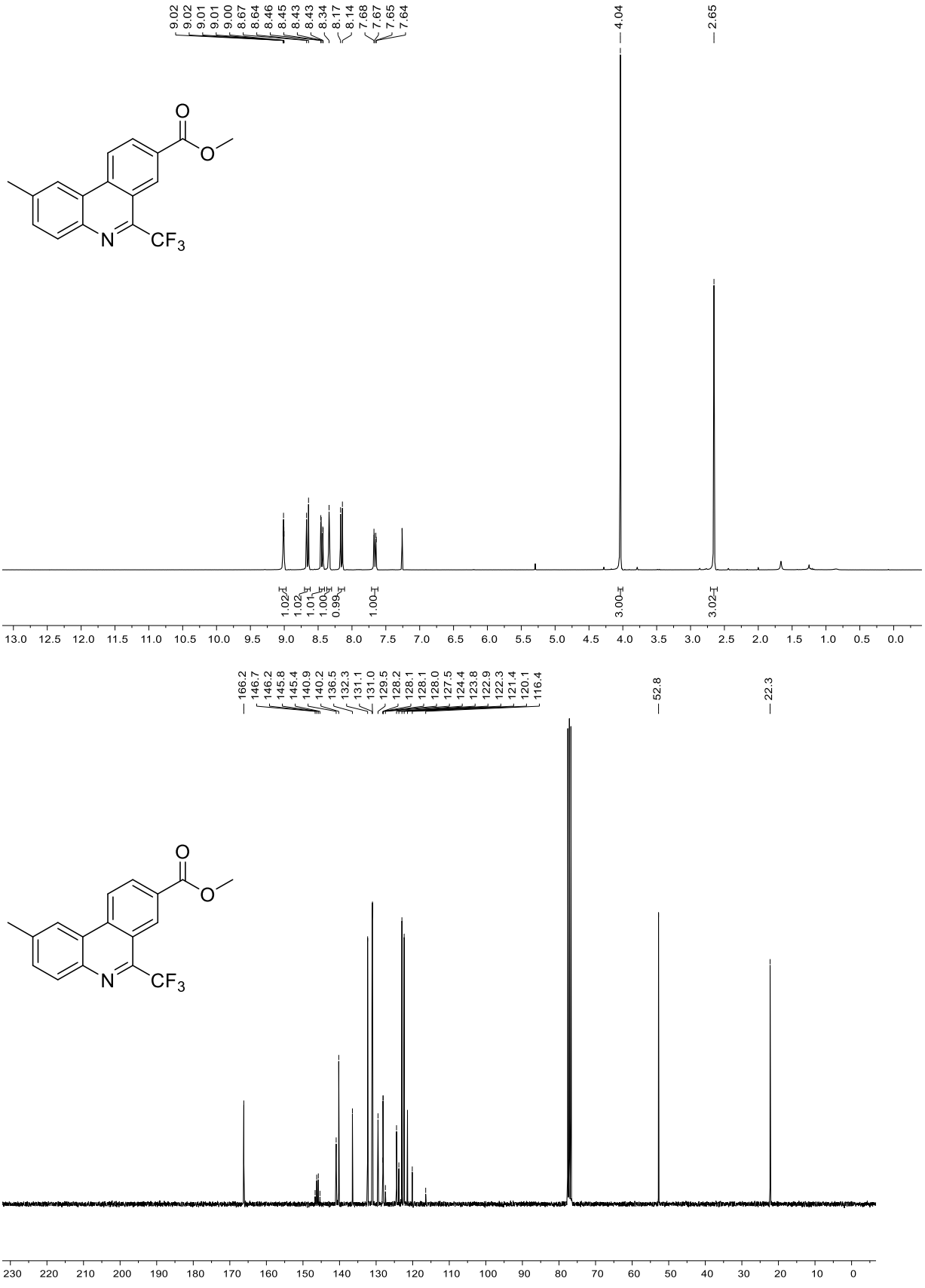
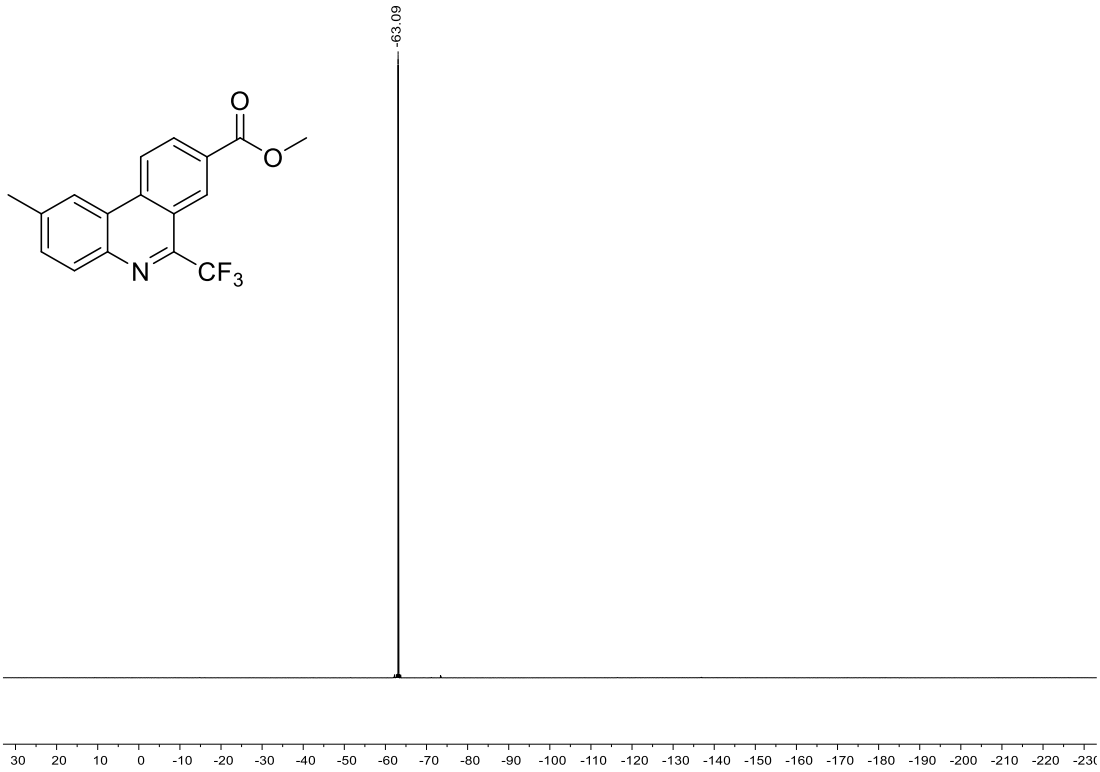
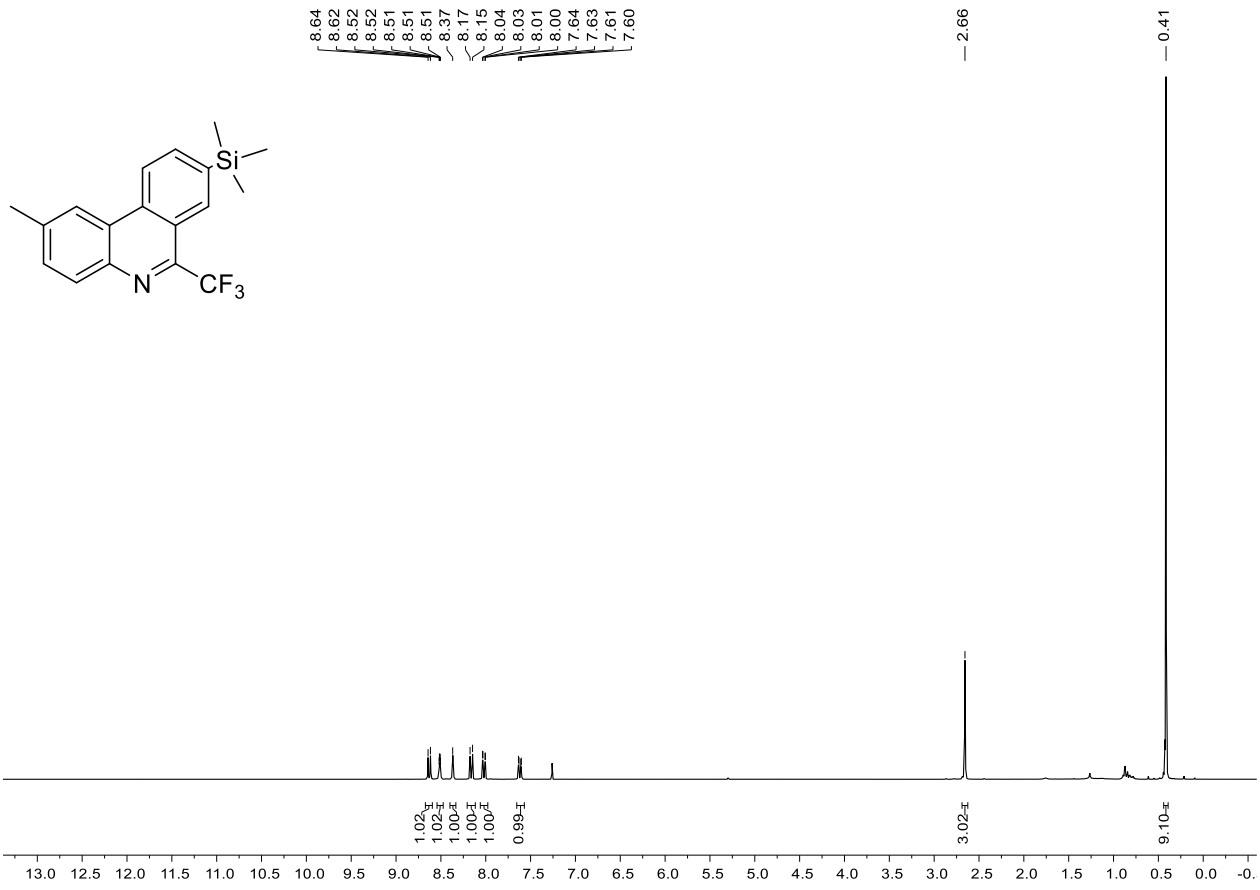
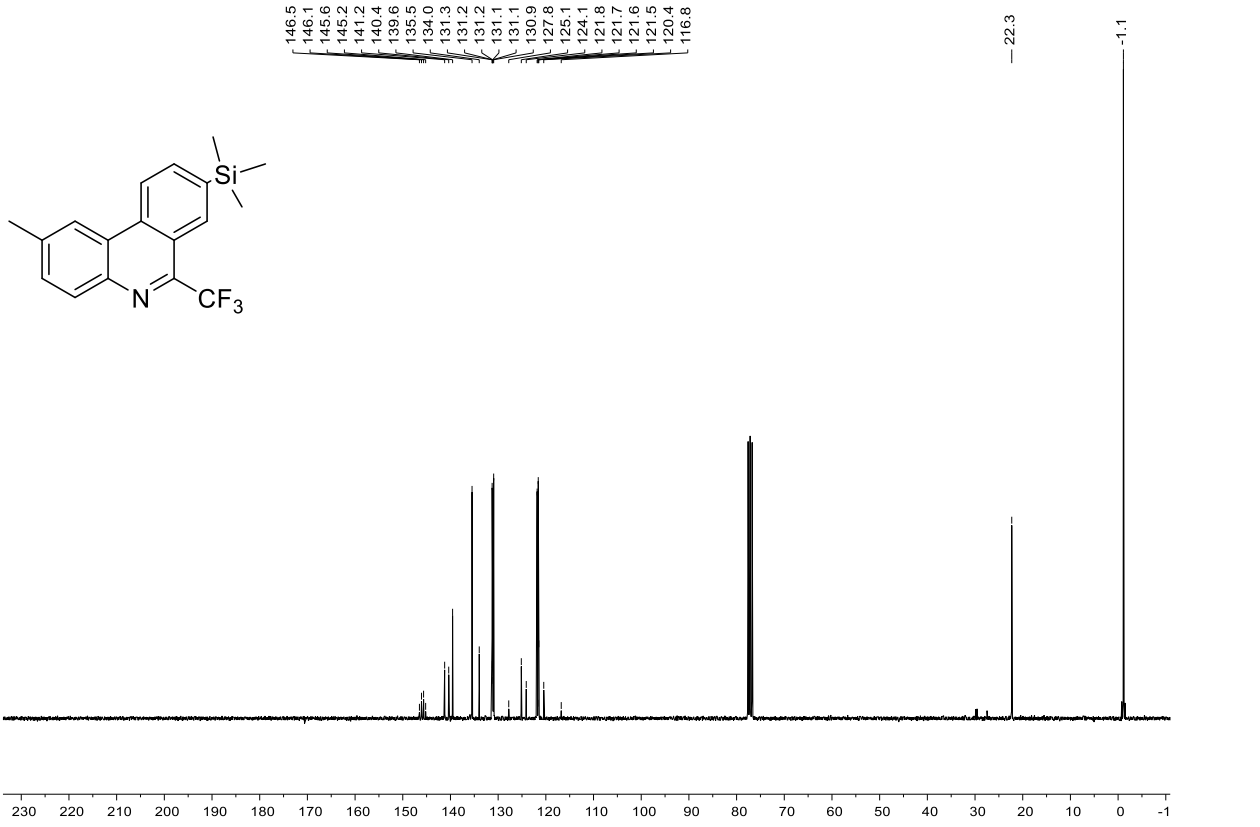
Methyl 2-methyl-6-(trifluoromethyl)phenanthridine-8-carboxylate (3i)





2-Methyl-6-(trifluoromethyl)-8-(trimethylsilyl)phenanthridine (3j)

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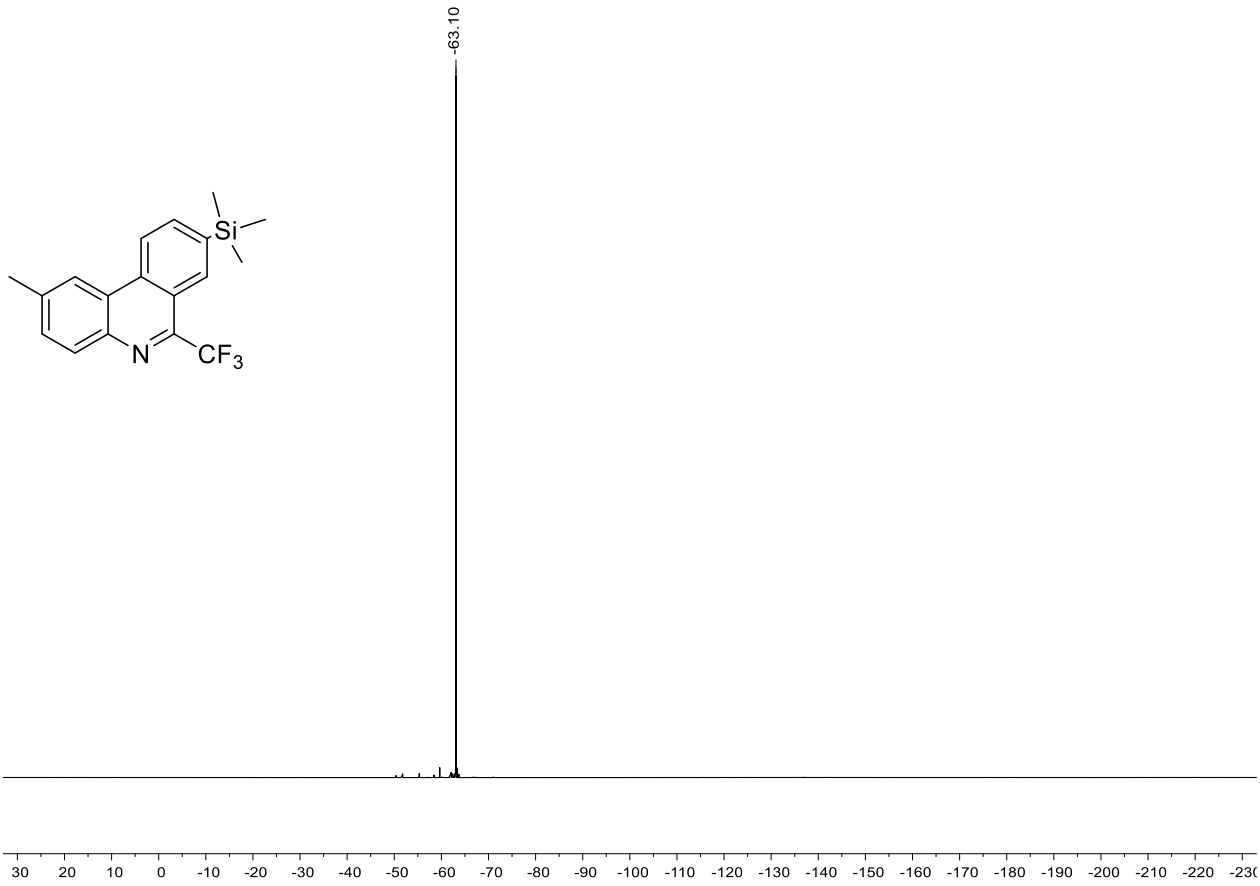
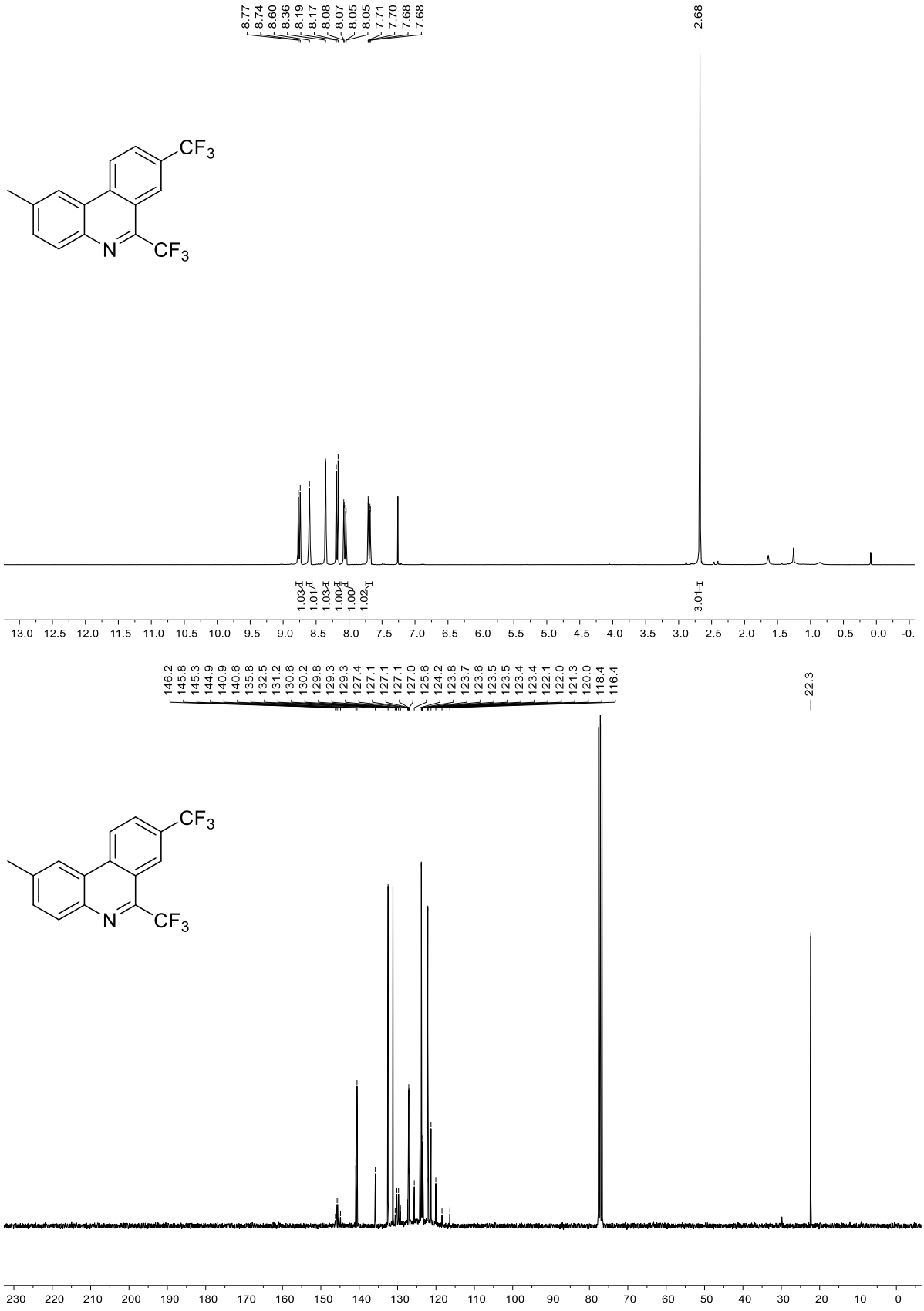
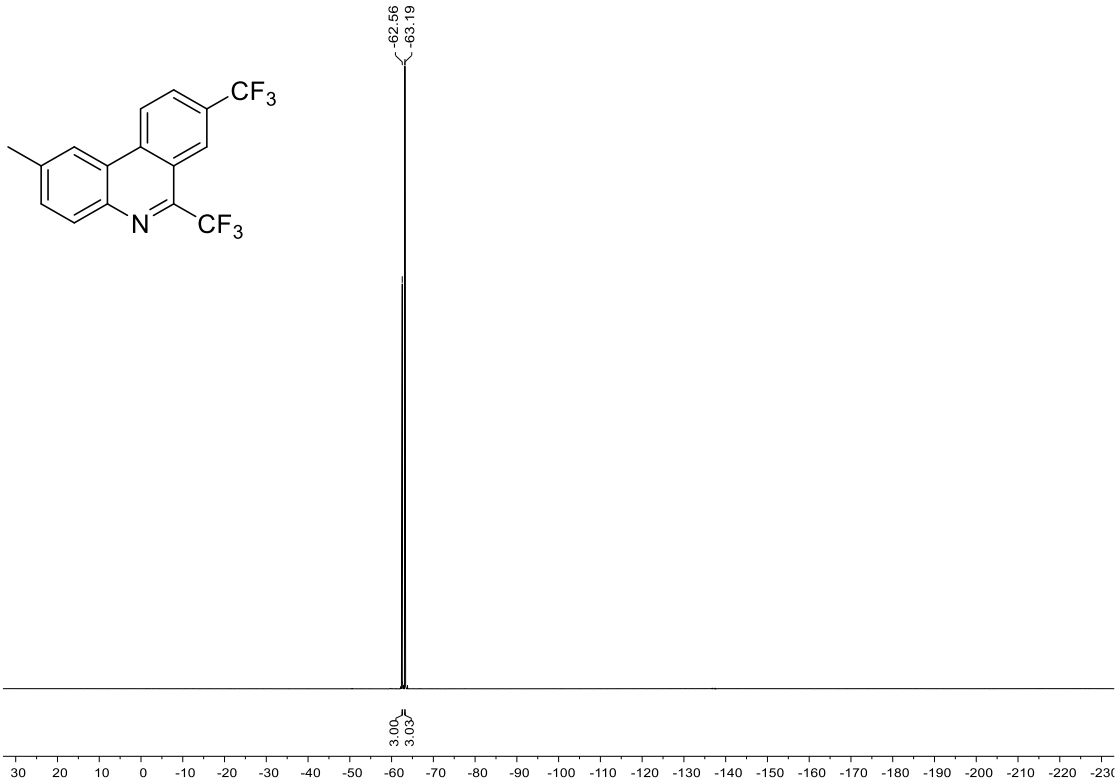
145.6
145.2
141.2
140.4
139.6
135.5
134.0
131.3
131.2
131.2
131.1
131.1
130.9
127.8
125.1
124.1
121.8
121.7
121.6
121.5
120.4
116.8
22.3
-1.1
Si
N
CF3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

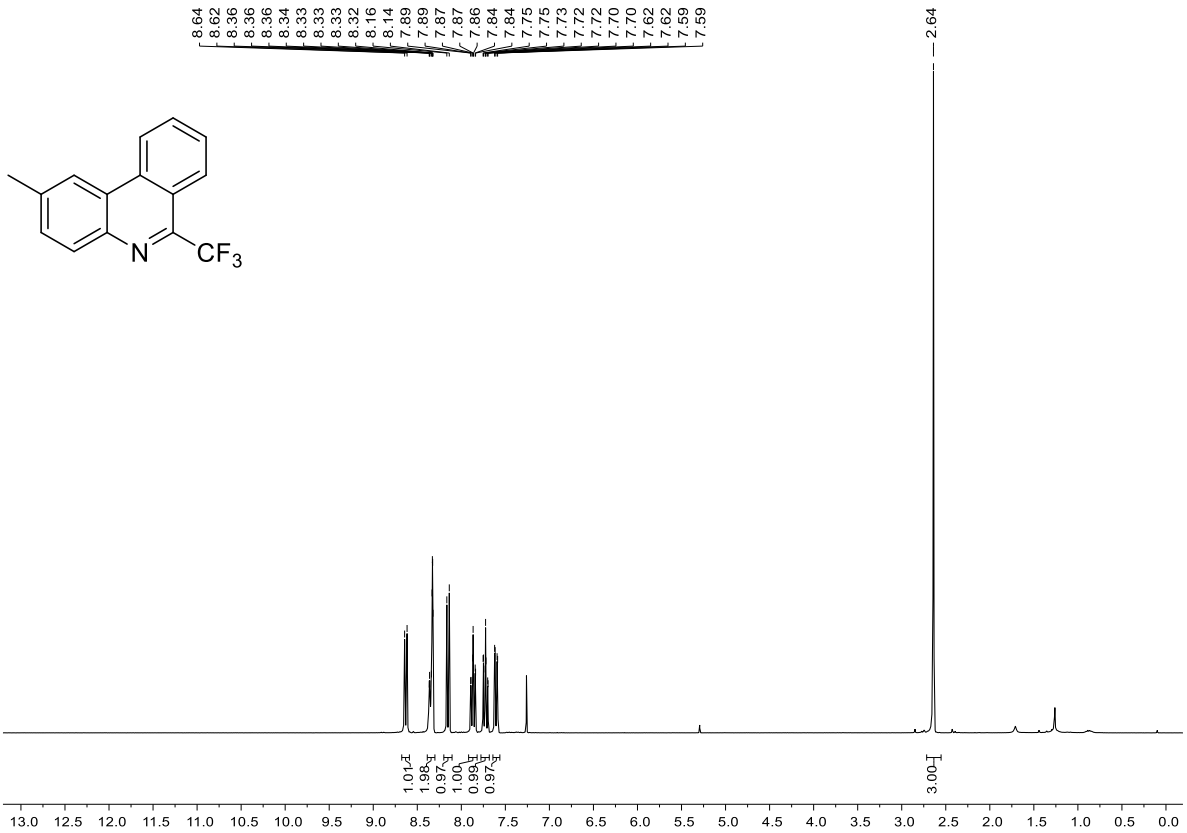

-63.10
Si
N
CF3
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23

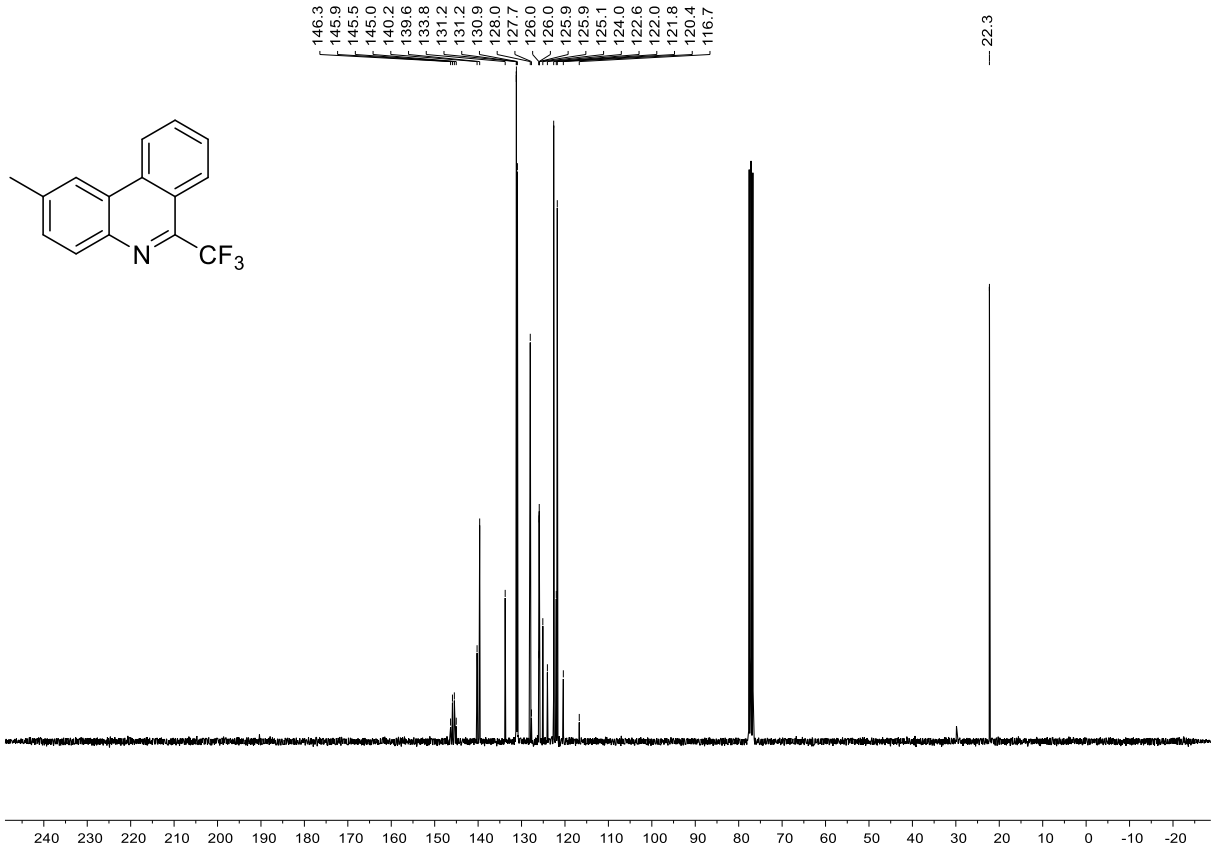
2-Methyl-6,8-bis(trifluoromethyl)phenanthridine (3k)





2-Methyl-6-(trifluoromethyl)phenanthridine (3l)

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145.0
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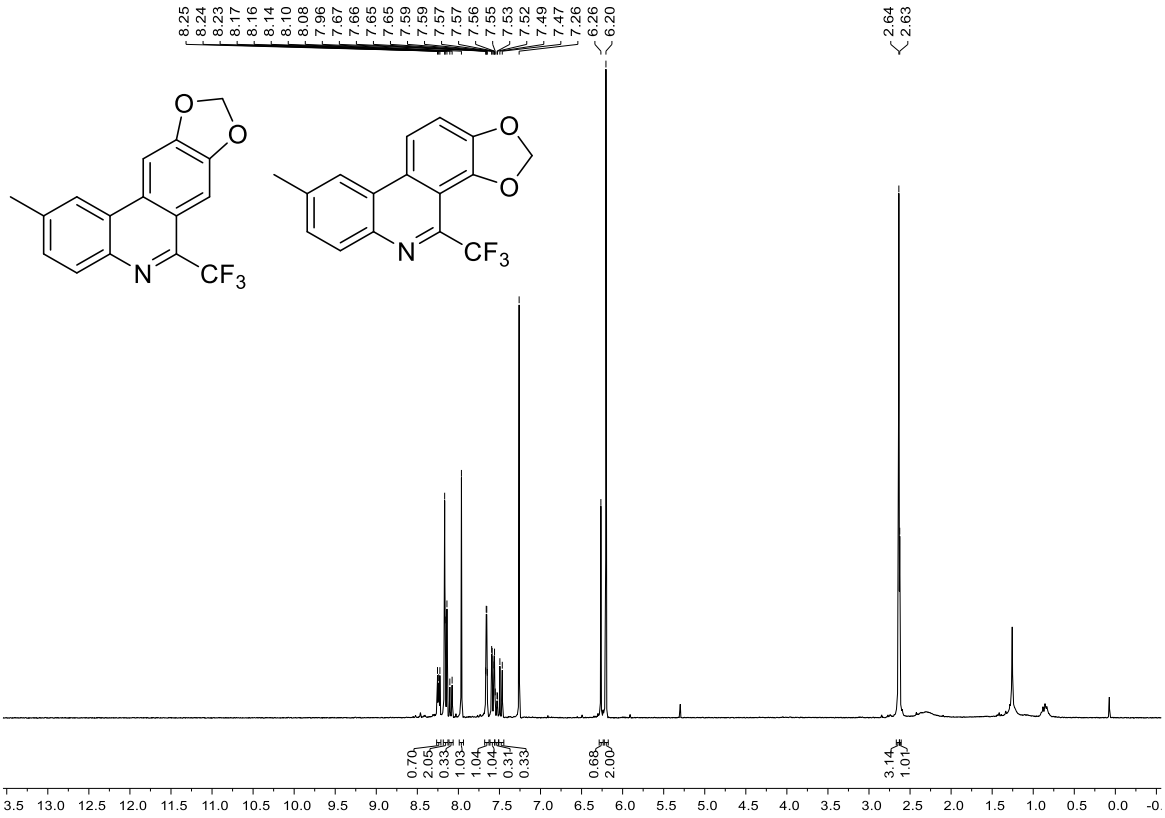
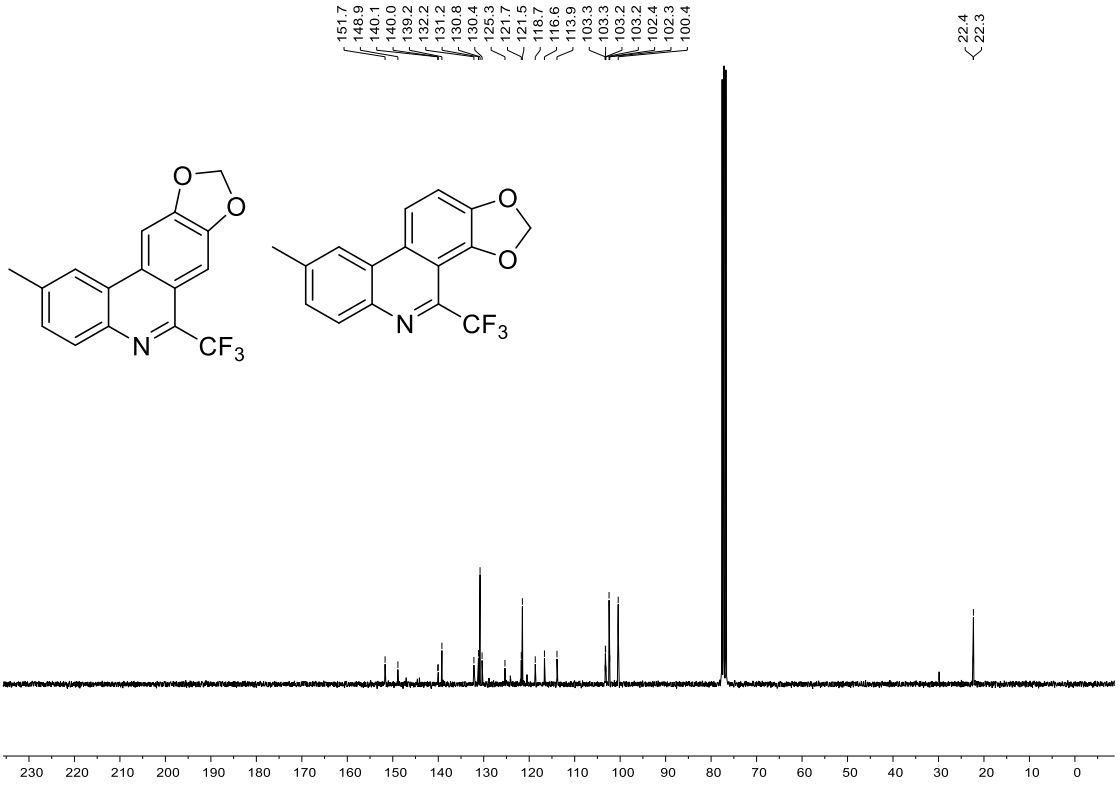
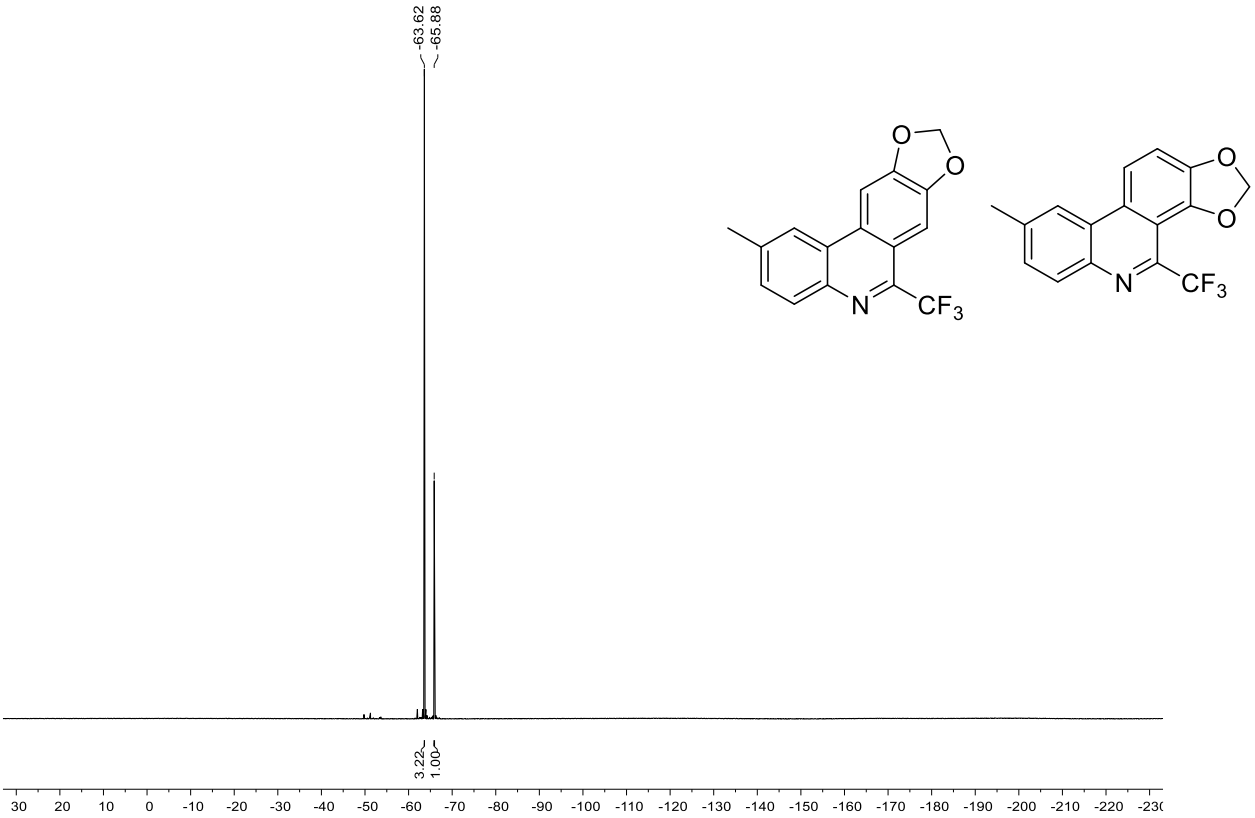
139.6
133.8
131.2
131.2
130.9
128.0
127.7
126.0
126.0
125.9
125.9
125.1
124.0
122.6
122.0
121.8
120.4
116.7
22.3
N
CF3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20


-63.32
N
CF3
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230

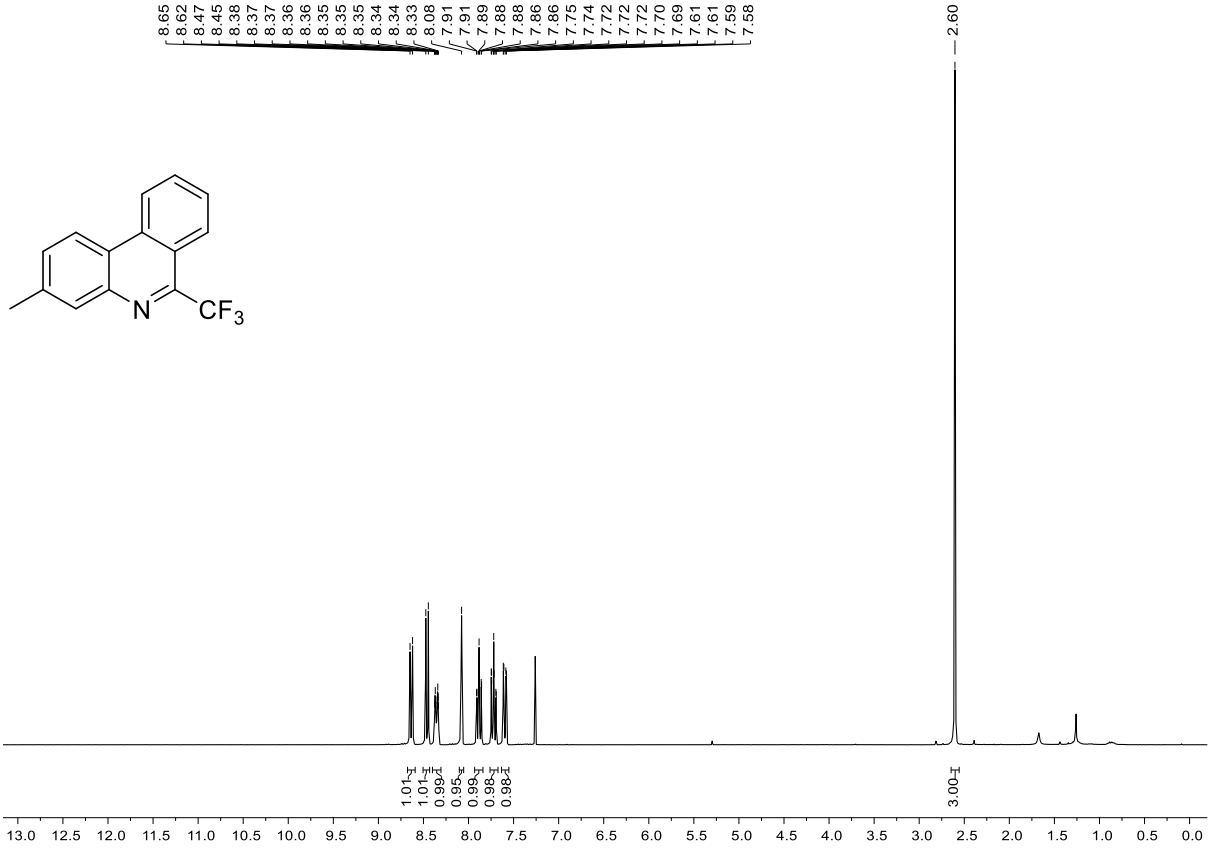
2-Methyl-6-(trifluoromethyl)-[1,3]dioxolo[4,5-j]phenanthridine (3m) and 8-methyl-4-(trifluoromethyl)-[1,3]dioxolo[4,5-i]phenanthridine (3m')

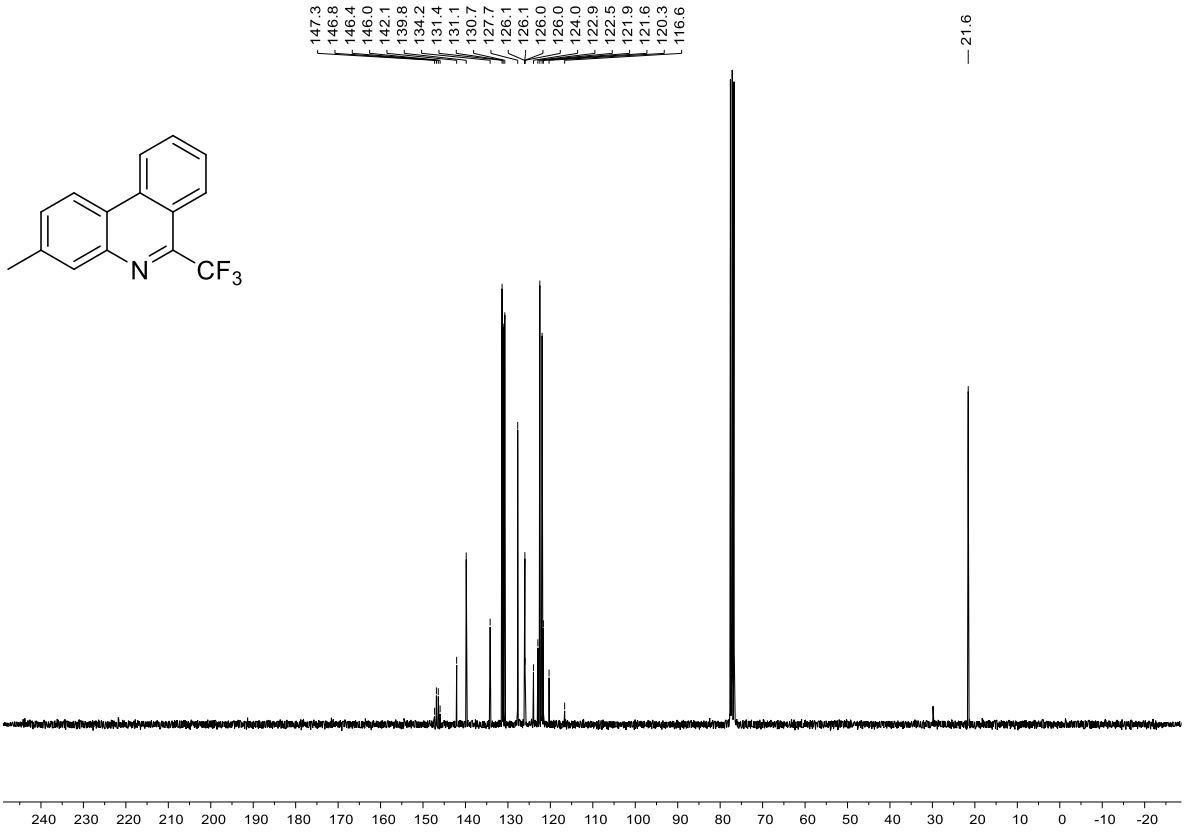






3-Methyl-6-(trifluoromethyl)phenanthridine (3n)

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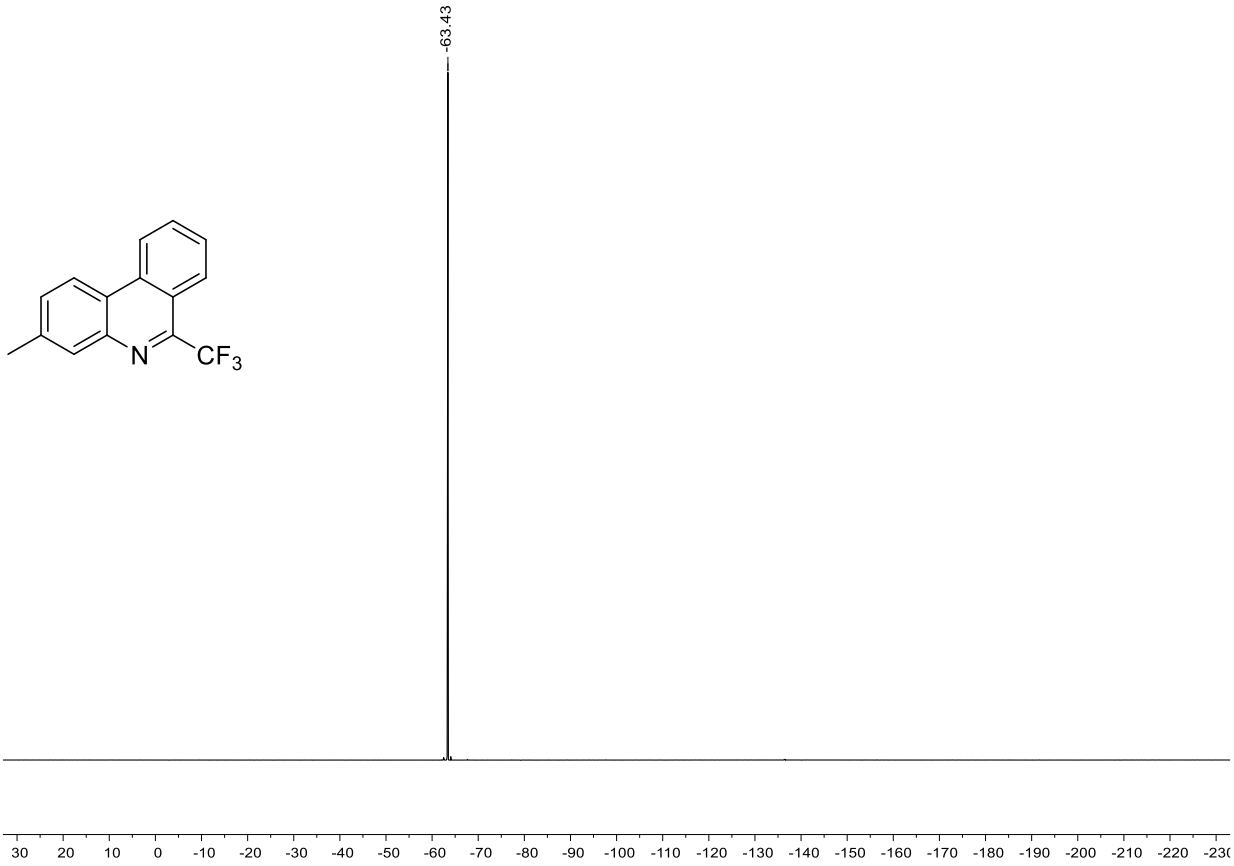
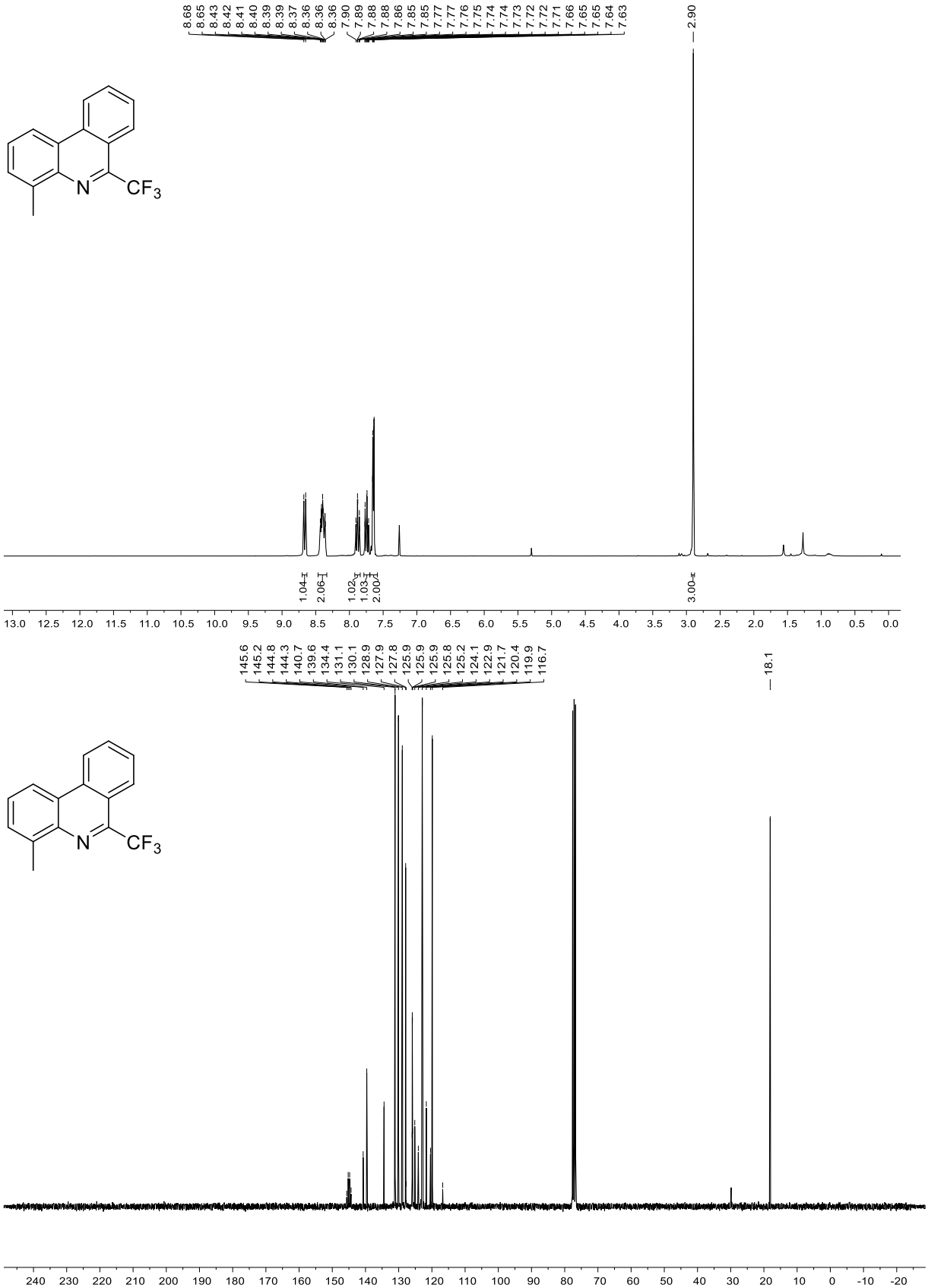
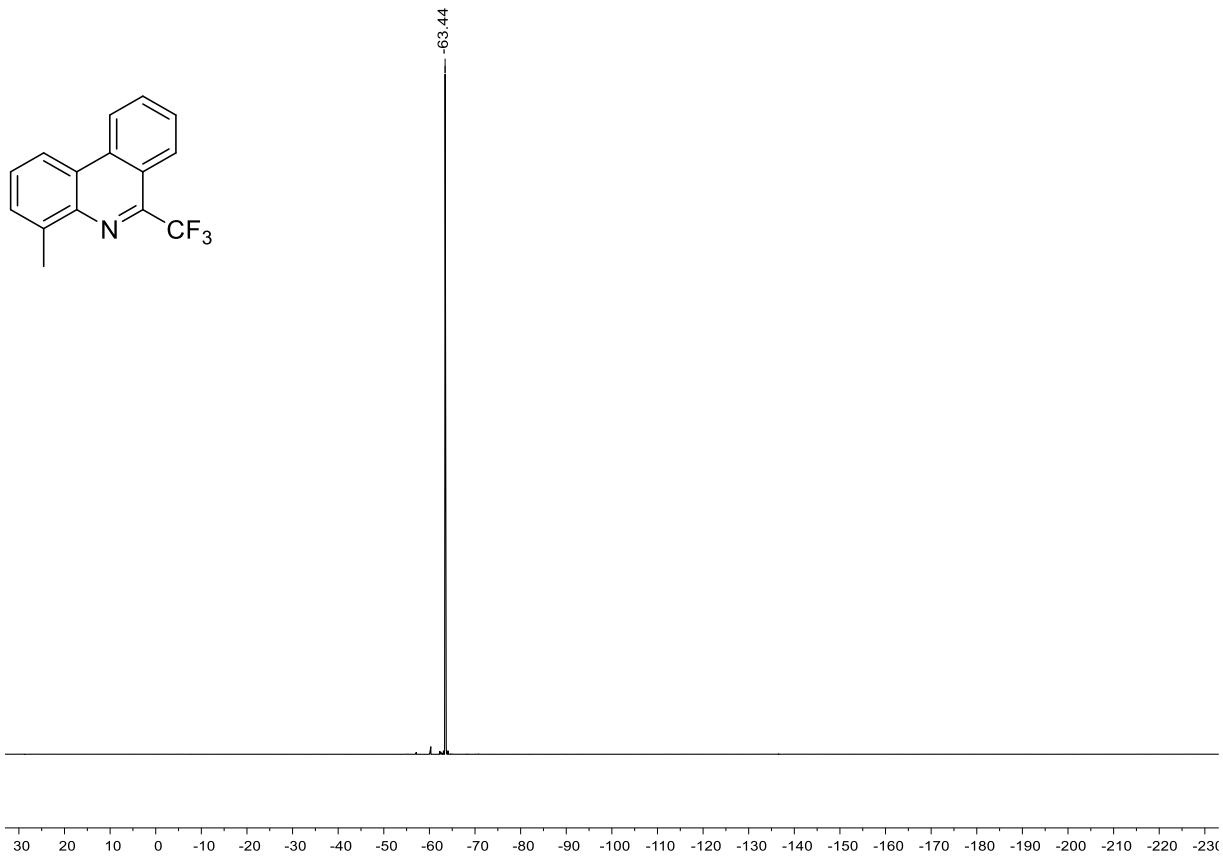
146.8
146.4
146.0
142.1
139.8
134.2
131.4
131.1
130.7
127.7
126.1
126.1
126.0
126.0
124.0
122.9
122.5
121.9
121.6
120.3
116.6
21.6
N
CF3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20


-63.43
N
CF3
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23

4-Methyl-6-(trifluoromethyl)phenanthridine (3o)




-63.44
N
CF3
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230

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