# Supporting Information

## Synthesis of pyrrolo[1,2-*a*]naphthyridines by Lewis acid mediated cycloisomerization

Anika Flader,[a,b] Silvio Parpart,[a] Peter Ehlers,[a,b] and Peter Langer*[a,b]

[a] *Universität Rostock, Institut für Chemie, Albert-Einstein-Str. 3a, 18059 Rostock*

*E-mail: peter.langer@uni-rostock.de*

[b] *Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock*

## Contents

## General Information

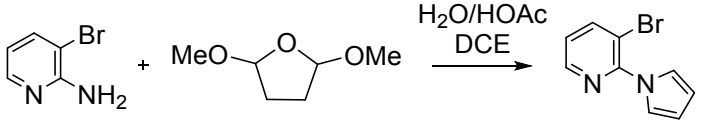
The nuclear magnetic resonance spectra ($^{1}H/^{13}C/^{19}F$ NMR) were recorded on a Bruker AVANCE 300 III, 250 II or 500. The analyzed chemical shifts $\delta$ are referenced to residual solvents signals of the deuterated solvents $CDCl_3$ ($\delta$ = 7.26 ppm/77.2 ppm) DMSO-$d_6$ ($\delta$ = 2.50 ppm/39.5 ppm) or $C_6D_6$ ($\delta$ = 7.16 ppm/128.1 ppm). Multiplicities due to spin-spin correlation are reported as follows: s = singlet, brs = broad singlett, d = doublet, t = triplet, m = multiplet and further described through their coupling constants *J*. Infrared spectra (IR) were measured as attenuated total reflection (ATR) experiments with a Nicolet 6700 FT-IR spectrometer and a Nicolet 550 FT-IR spectrometer. The signals have been characterized through their wave numbers $\tilde{\nu}$ and their corresponding absorption as strong (s), medium (m) or weak (w). Basic and high resolution mass spectra (MS/HRMS) were measured on instruments which are paired with a preceding gas chromatograph (GC) or liquid chromatograph (LC). The samples have been ionized through electron impact ionization (EI) on an Agilent 6890 N/5973 GC-MS equipped with a HP-5 capillary column using helium carrier gas or by applying electron spray ionization (ESI) on an Agilent 1200/6210 Time-of-Flight (TOF) LC-MS. Melting points (mp) were determined by a Micro-Hot-Stage GalenTM III Cambridge Instruments and are not corrected.

## Materials

The applied solvents toluene, xylene, MeCN, DCE, DCM were obtained as dry solvents through commercial sources and employed without further purification. Solvents for extraction and column chromatography were available after previous distillation. Other reagents, catalysts, ligands, Lewis acids and bases have been utilized in purchased purity. Column chromatography was performed using Merck Silica gel 60 (particle size 63–200 µm).

## Preparation of [1,8]naphthyridines

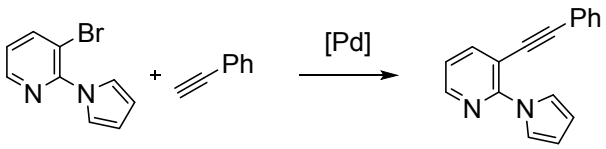
### Starting materials




**1a**

**3-Bromo-2-([1*H*]-pyrrol-1-yl)pyridine 1a.** To a solution of 2-amino-3-bromopyridine (5.8 mmol, 1.0 g) in 1.5 ml DCE at 80 °C 2,5-dimethoxytetrahydrofuran (1.05 eq., 6.1 mmol, 0.79 ml) was added. A mixture of $H_2O$/HOAc (2:1, 2 ml) was poured into the solution. The reaction was stirred at 80 °C for 12 h. Thereafter, the crude product was washed with distilled water and extracted with DCM. Following the evaporation of the organic solvent the product **1a** was obtained after column chromatography (heptane/DCM, 5:1) as a white solid (978.1 mg, 76%); mp 36–39 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.45 (dd, $^3J$ = 4.6 Hz, $^4J$ = 1.6 Hz, 1H, $CH_{pyridine}$), 8.03 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.6 Hz, 1H, $CH_{pyridine}$), 7.41–7.32 (m, 2H, $CH_{pyrrole}$), 7.11 (dd, $^3J$ = 7.9 Hz, $^3J$ = 4.6 Hz, 1H, $CH_{pyridine}$), 6.39–6.32 (m, 2H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 150.1 ($C_{pyridine}$), 147.6, 143.7, 122.7 ($CH_{pyridine}$), 121.5 ($CH_{pyrrole}$), 112.5 ($C_{pyridine}$), 110.2 ($CH_{pyrrole}$) ppm. **MS (EI, 70 eV):** *m/z* (%) = 224 ($[C_9H_7{}^{81}BrN_2]^+$, 98), 222 ($[C_9H_7{}^{79}BrN_2]^+$, 100), 198 (16), 197 (42), 196 (17), 195 (41), 158 (12), 156 (12), 143 (20), 142 (18), 117 (12), 116 (60), 89 (20), 78 (12), 76 (25), 63 (12), 51 (18), 50 (17), 39 (18). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_9H_7{}^{79}BrN_2$ ($[M+H]^+$) 222.98654, found 222.98668. Calcd. for $C_9H_7{}^{81}BrN_2$ ($[M+H]^+$) 224.98453, found 224.98458.

## Optimization of Sonogashira reaction giving 3-alynyl-2-pyrrolopyridines[a]



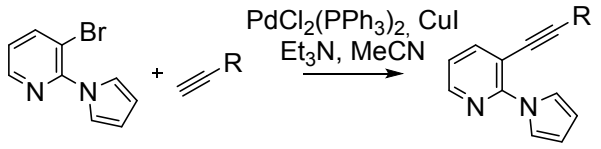

**1a** **2a**

| entry | catalyst (0.03 eq.) | ligand (0.06 eq.) | base | eq. | solvent | temp. [°C] | time [h] | yield [%][c] |
|---|---|---|---|---|---|---|---|---|
| 1 | $PdCl_2(PPh_3)_2$ | – | $NEt_3$ | 3 | DMF | 100 | 24 | 20 |
| 2 | $PdCl_2(PPh_3)_2$ | P(*t*Bu)$_3$ | $NEt_3$ | 3 | DMF | 100 | 24 | – |
| 3 | $PdCl_2(PPh_3)_2$ | – | – | – | $Et_2NH$ | r.t. | 48 | 63 |
| 4 | $PdCl_2(PPh_3)_2$ | – | – | – | $NEt_3$ | r.t. | 48 | – |
| 5[b] | $PdCl_2(PPh_3)_2$ | – | $NEt_3$ | 3 | DMF | 80 | 3 | –[d] |
| 6 | $Pd(OAc)_2$ | $PCy_3$ | $NEt_3$ | 1.5 | THF | 50 | 48 | – |
| 7 | $Pd(OAc)_2$ | XPhos | $NEt_3$ | 1.5 | THF | 50 | 48 | –[d] |
| 8 | $PdCl_2(PPh_3)_2$ | – | $NEt_3$ | 3 | dioxane | 50 | 4 | 45 |
| 9 | $P(PPh_3)_4$ | – | $NEt_3$ | 3 | dioxane | 50 | 4 | – |
| 10 | $PdCl_2(PPh_3)_2$ | – | $NEt_3$ | 3 | MeCN | 50 | 16 | 88 |
| 11 | $Pd(OAc)_2$ | CataCXium A | $NEt_3$ | 3 | MeCN | 50 | 16 | 92 |

[a]reaction condotions: 1a (0.5 mmol, 111.5 mg) and phenylacetylene (1.5 eq., 0.75 mmol, 82 µl) react with CuI (0.02 eq., 0.01 mmol, 1.9 mg) in 2 ml of solvent in a glas tube under argon. [b]reaction with phenylacetylene (3 eq.). [c]isolated yields. [d]occurence of inseparable mixtures.

The following Sonogashira couplings were carried out employing the reaction conditions of **entry 10** sufficiently. These are economically advantageous with regards to **entry 11** which requires a sophisticated ligand.

## Sonogashira reaction giving 2a–m

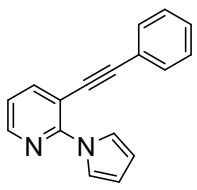



**1a** **2a-m**

### General procedure

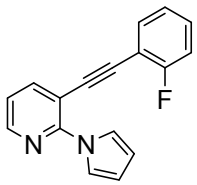
**1a** was dissolved in 3 ml MeCN under an argon atmosphere. After the addition of $PdCl_2(PPh_3)_2$ (0.03 eq.), CuI (0.02 eq.) and $Et_3N$ (3 eq.) in advance of the corresponding acetylene (1.2 eq.) the reaction is stirred at 50 °C for 24 h. The reaction mixture was subsequently cooled to room temperature and washed with distilled water and extracted with DCM. The combined organic layers were collected and the solvent evaporated. The crude product was thereafter purified by column chromatography (heptane/DCM, 5:1) to give the alkynylated products **2a–m**. Thereby, 1–2 ml $Et_3N$ were added to 250 ml eluent mixture to deactivate the acidic silica.

### Substrate characterization

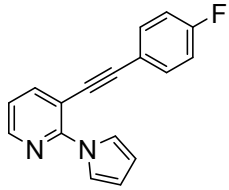



**3-(Phenylethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2a.** The reaction of **1a** (0.9 mmol, 200 mg) with phenylacetylene (1.08 mmol, 118.3 µl) gave **2a** as a pale brown solid (382 mg, 88%); mp 82–84 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.43 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.96 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.85–7.80 (m, 2H, $CH_{pyrrole}$), 7.57–7.50 (m, 2H, $CH_{Ph}$), 7.42–7.34 (m, 3H, $CH_{Ph}$), 7.16 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{pyridine}$), 6.39–6.35 (m, 2H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 151.3 ($C_{pyridine}$), 147.9, 143.4 ($CH_{pyridine}$), 131.6, 129.1, 128.6 ($CH_{Ph}$), 122.6 ($C_{Ph}$), 120.8 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 110.5 ($CH_{pyrrole}$), 110.4 ($C_{pyridine}$), 96.1, 85.7 ($C_{alkyne}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3052 (w), 1562 (w), 1469 (w), 1437 (m), 1336 (w), 1060 (w), 800 (w), 728 (m), 687 (m), 624 (w), 553 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 244 ($[M]^+$, 100), 243 (77), 242 (43), 241 (5), 218 (11), 216 (8), 215 (5),

214 (6), 190 (6), 189 (5), 177 (6), 151 (6), 150 (9), 121 (11), 109 (6), 77 (5), 75 (5), 51 (5), 39 (5). **HRMS (EI):** *m/z* = calcd. for $C_{17}H_{12}N_2$ ($M^+$) 244.09950, found 244.09919.

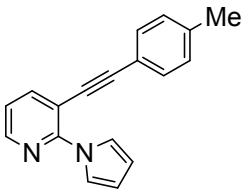


**3-((2-Fluorophenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2b.** 2-ethynyl-1-fluorobenzene (0.6 mmol, 78 µl) reacted with **1a** (0.5 mmol, 111.5 mg) to **2b** as a pale brown oil (106 mg, 81%); $R_f$ 0.39 (heptane/ethyl acetate 5:1). **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.44 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.97 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.88–7.83 (m, 2H, $CH_{pyrrole}$), 7.50 (ddd, $^3J$ = 7.7 Hz, $^3J$ = 7.1 Hz, $^4J$ = 2.0 Hz, 1H, $CH_{Ar}$), 7.39–7.33 (m, 1H, $CH_{Ar}$), 7.15 (dd, $^3J$ = 7.6 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{pyridine}$), 7.21–7.11 (m, 2H, $CH_{Ar}$), 6.40–6.35 (m, 2H, $CH_{pyrrole}$) ppm. **$^{19}$F NMR (235 MHz, $CDCl_3$):** $\delta$ = −109.1 ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 162.92 (d, $^1J_{C,F}$ = 252.7 Hz, C-F), 151.2 ($C_{pyridine}$), 148.4, 143.6 ($CH_{pyridine}$), 133.32 (d, $^4J_{C,F}$ = 1.3 Hz, $CH_{Ar}$), 130.87 (d, $^3J_{C,F}$ = 8.0 Hz, $CH_{Ar}$), 124.24 (d, $^3J_{C,F}$ = 3.7 Hz, $CH_{Ar}$), 120.7 ($CH_{pyrrole}$), 120.1 ($CH_{pyridine}$), 115.80 (d, $^2J_{C,F}$ = 20.6 Hz, $CH_{Ar}$), 111.31 (d, $^2J_{C,F}$ = 15.6 Hz, $C_{Ar}$), 110.5 ($CH_{pyrrole}$), 110.2 ($C_{pyridine}$), 90.54 (d, $^3J_{C,F}$ = 3.2 Hz, $C_{alkyne}$), 89.6 ($C_{alkyne}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3065 (br, w), 2921 (w), 1708 (br, w), 1560 (m), 1472 (m), 1434 (m), 1224 (m), 1095 (m), 1058 (m), 797 (m), 754 (s), 728 (s), 544 (m), 470 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 262 ($[M]^+$, 100), 261 (61), 260 (33), 243 (6), 242 (8), 236 (10), 234 (5), 168 (5), 130 (5), 118 (5). **HRMS (ESI-TOF):** *m/z* = calculated for $C_{17}H_{11}FN_2$ ($[M+H]^+$) 263.09790, found 263.09786.

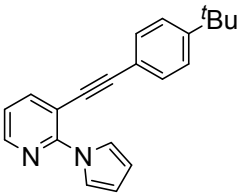


**3-((4-Fluorophenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2c. 1a** (0.5 mmol, 111.5 mg) and 4-ethynyl-1-fluorobenzene (0.6 mmol, 68.8 µl) achieved **2c** as a yellow solid (113 mg, 86%); mp 78–82 °C. **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.43 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.93 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.83–7.72 (m, 2H, $CH_{pyrrole}$), 7.56–7.46 (m, 2H, $CH_{Ar}$), 7.15 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{pyrrole}$), 7.12–7.02 (m, 2H, $CH_{Ar}$), 6.38 (dt, $^3J$ = 3.8 Hz, $^4J$ = 2.3 Hz, 2H, $CH_{pyrrole}$) ppm. **$^{19}$F NMR (235 MHz, $CDCl_3$):** $\delta$ = −109.4 ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 162.98 (d, $^1J_{C,F}$ = 250.9 Hz, C-F), 151.3 ($C_{pyridine}$), 148.0, 143.1 ($CH_{pyridine}$), 133.50 (d, $^3J_{C,F}$ = 8.5 Hz, $CH_{Ar}$), 120.7 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 118.67 (d, $^4J_{C,F}$ = 3.5 Hz, $C_{Ar}$), 115.97 (d, $^2J_{C,F}$ = 22.2 Hz, $CH_{Ar}$), 110.4 ($CH_{pyrrole}$), 110.1 ($C_{pyridine}$), 94.9 ($C_{alkyne}$), 85.40 (d, $^5J_{C,F}$ = 1.6 Hz, $C_{alkyne}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3049 (w), 1600 (w), 1562 (w), 1505 (w), 1472 (w), 1439 (w), 1216 (w), 1056 (w), 833 (w), 806 (w), 728 (m), 640 (w), 620 (w), 532 (w), 522 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 262 ([M]+, 100),

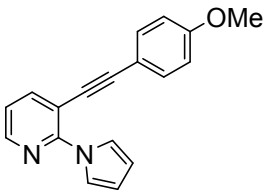
261 (75), 260 (39), 236 (12), 234 (7), 232 (5), 208 (5), 195 (5), 169 (5), 168 (7), 130 (5), 118 (5), 39 (5). **HRMS (EI):** *m/z* = calcd. for $C_{17}H_{11}FN_2$ ($M^+$) 262.09008, found 262.08955.



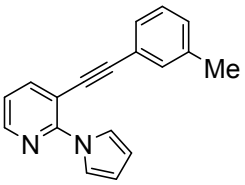

**3-((4-Methylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2d.** 4-Ethynyltoluene (0.6 mmol, 76 µl) and **1a** (0.5 mmol, 111.5 mg) gave **2d** as a yellow solid (101 mg,78%); mp 71–75 °C. **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.42 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.94 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.89–7.79 (m, 2H, $CH_{pyrrole}$), 7.43 (d, $^3J$ = 8.1 Hz, 2H, $CH_{Ar}$), 7.18 (d, $^3J$ = 8.6 Hz, 2H, $CH_{Ar}$), 7.14 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{pyridine}$), 6.43–6.33 (m, 2H, $CH_{pyrrole}$), 2.39 (s, 3H, Me) ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 151.2 ($C_{pyridine}$), 147.7, 143.2 ($CH_{pyridine}$), 139.4 (C-Me), 131.4, 129.4 ($CH_{Ar}$), 120.7 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 119.5 ($C_{Ar}$), 110.5 ($C_{pyridine}$), 110.3 ($CH_{pyrrole}$), 96.3, 85.1 ($C_{alkyne}$), 21.7 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 3030 (w), 2916 (w), 1703 (br, w), 1565 (w), 1474 (w), 1439 (w), 1339 (w), 1311 (w), 1099 (w), 1060 (w), 1017 (w), 818 (w), 733 (m), 529 (w) $cm^{-1}$.**MS (EI, 70 eV):** *m/z* (%) = 258 ($[M]^+$, 100), 257 (47), 256 (12), 255 (17), 243 (15), 242 (36), 232 (7), 231 (6), 128 (6), 39 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2$ ($[M+H]^+$) 259.12297, found 259.12281.



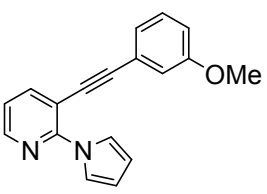

**3-((4-*tert*-Butylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2e.** The reaction of **1a** (0.5 mmol, 111.5 mg) with 4-*tert*-butylphenylacetylene (0.6 mmol, 108 µl) resulted in the product **2e** as a pale brown oil (155 mg, 98%); $R_f$ 0.45 (heptane/ethyl acetate 5:1). **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.42 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.94 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.86–7.79 (m, 2H, $CH_{pyrrole}$), 7.48 (d, $^3J$ = 8.6 Hz, 2H, $CH_{Ar}$), 7.40 (d, $^3J$ = 8.7 Hz, 2H, $CH_{Ar}$), 7.15 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{pyridine}$), 6.43–6.35 (m, 2H, $CH_{pyrrole}$), 1.34 (s, 9H, $CH_{3tBu}$) ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 152.5 ($C_{pyridine}$), 147.8, 143.2 ($CH_{pyridine}$), 131.3, 125.7 ($CH_{Ar}$), 120.7($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 119.6 ($C_{Ar}$), 110.5 ($C_{pyridine}$), 110.3 ($CH_{pyrrole}$), 110.2 (C-*t*Bu), 96.3, 85.1 ($C_{alkyne}$), 35.0 ($C_{tBu}$), 31.3 ($CH_{3tBu}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2953 (w), 1562 (w), 1469 (w), 1437 (w), 1338 (w), 1059 (w), 926 (w), 833 (w), 724 (m), 625 (w), 561 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 300 ($[M]^+$, 67), 286 (23), 285 (100), 284 (8), 283 (8), 270 (23), 269 (18), 268 (10), 267 (5), 258 (6), 257 (27), 255 (18), 244 (13), 243 (20), 242 (21), 241 (5), 128 (26), 121 (6), 115 (6), 41 (7), 39 (5). **HRMS (EI):** *m/z* = calcd. for $C_{21}H_{20}N_2$ ($M^+$) 300.16210, found 300.16165.




**3-((4-Methoxyphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2f. 1a** (0.25 mmol, 56 mg) and 4-ethynylanisole (0.3 mmol, 40 µl) gave **2f** as a solid (61 mg, 89%); mp 61–64 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.40 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.92 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.85–7.79 (m, 2H, $CH_{pyrrole}$), 7.48–7.45 (m, 2H, $CH_{Ar}$), 7.14 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{pyridine}$), 6.94–6.86 (m, 2H, $CH_{Ar}$), 6.42–6.31 (m, 2H, $CH_{pyrrole}$), 3.83 (s, 3H, OMe) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 160.3 (C-OMe), 151.1 ($C_{pyridine}$), 147.6, 143.0 ($CH_{pyridine}$), 133.1 ($CH_{Ar}$), 120.7 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 114.7 ($C_{Ar}$), 114.3 ($CH_{Ar}$), 110.7 ($C_{pyridine}$), 110.3 ($CH_{pyrrole}$), 96.2, 84.5 ($C_{alkyne}$), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 3011 (br, w), 2215 (w), 1604 (w), 1508 (m), 1435 (w), 1245 (m), 1173 (w), 1028 (w), 833 (w), 725 (m), 699 (w), 536 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 274 ([M]$^+$, 100), 260 (6), 259 (33), 258 (7), 242 (5), 232 (7), 231 (41), 230 (25), 229 (29), 205 (13), 203 (11), 177 (5), 176 (5), 164 (7), 137 (6), 115 (7), 39 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2O$ ([M+H]$^+$) 275.11789, found 275.11784.

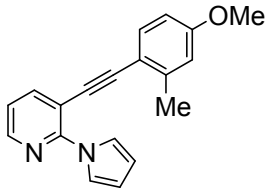



**3-((3-Methylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2g.** 3-ethynyltoluene (0.6 mmol, 77 µl) and **1a** (0.5 mmol, 111.5 mg) gave **2g** as a yellow oil (123 mg, 95%); $R_f$ 0.44 (heptane/ethyl acetate 5:1). **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.43 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.94 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.90–7.86 (m, 2H, $CH_{pyrrole}$), 7.40–7.35 (m, 2H, $CH_{Ar}$), 7.29 (t, $^3J$ = 7.7 Hz, 1H, $CH_{Ar}$), 7.24–7.18 (m, 1H, $CH_{Ar}$), 7.14 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{pyridine}$), 6.45–6.41 (m, 2H, $CH_{pyrrole}$), 2.39 (s, 3H, Me) ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 151.2 ($C_{pyridine}$), 147.8, 143.1 ($CH_{pyridine}$), 138.2 (C-Me), 132.0, 129.9, 128.6, 128.4 ($CH_{Ar}$), 122.3 ($C_{Ar}$), 120.6 ($CH_{pyrrole}$), 120.1 ($CH_{pyridine}$), 110.3 ($CH_{pyrrole}$), 110.2 ($C_{pyridine}$), 96.2, 85.3 ($C_{alkyne}$), 21.3 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2915 (w), 1705 (br, w), 1558 (w), 1474 (w), 1433 (w), 1308 (w), 1165 (w), 1057 (w), 782 (w), 728 (w), 687 (w), 442 (w), 406 (w) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 258 ([M]$^+$, 100), 257 (42), 256 (11), 255 (17), 243 (16), 242 (36), 231 (8), 128 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2$ ([M+H]$^+$) 259.12297, found 259.12289.

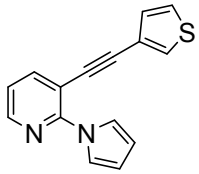



**3-((3-Methoxyphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2h.** Substrate **1a** (0.5 mmol, 111.5 mg) reacted with 3-ethynylanisole (0.6 mmol, 78 µl) to give **2h** as a brown oil (152 mg, 98%); $R_f$ 0.38 (heptane/ethyl acetate 5:1). **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.43 (dd,

$^3J$ = 4.8 Hz, $^4J$ = 1.8 Hz, 1H, $CH_{pyridine}$), 7.95 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.8 Hz, 1H, $CH_{pyridine}$), 7.86–7.78 (m, 2H, $CH_{pyrrole}$), 7.30 (d, $^3J$ = 7.9 Hz, 1H, $CH_{Ar}$), 7.15 (dd, $^3J$ = 7.8 Hz, $^4J$ = 4.8 Hz, 1H, $CH_{pyridine}$), 7.15–7.11 (m, 1H, $CH_{Ar}$), 7.05 (dd, $^4J$ = 2.5 Hz, $^4J$ = 1.4 Hz, 1H, $CH_{Ar}$), 6.94 (ddd, $^3J$ = 8.4 Hz, $^4J$ = 2.7 Hz, $^3J$ = 1.1 Hz, 1H, $CH_{Ar}$), 6.41–6.29 (m, 2H, $CH_{pyrrole}$), 3.83 (s, 3H, OMe) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 159.5 ($C_{Ar}$), 151.3 ($C_{pyridine}$), 148.0, 143.3 ($CH_{pyridine}$), 129.7, 124.1 ($CH_{Ar}$), 123.6 ($C_{Ar}$), 120.8 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 116.4, 115.7 ($CH_{Ar}$), 110.5 ($CH_{pyrrole}$), 110.3 ($C_{pyridine}$), 96.0, 85.5 ($C_{alkyne}$), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 2936 (br, w), 2833 (w), 1710 (br, w), 1573 (m), 1475 (m), 1434 (m), 1235 (m), 1038 (m), 868 (m), 708 (m), 730 (m), 684 (m), 551 (m), 461 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) =274 ($[M]^+$, 100), 273 (23), 244 (12), 243 (17), 242 (19), 241 (7), 231 (24), 230 (18), 229 (23), 205 (8), 204 (7), 203 (10), 164 (8), 115 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2O$ ($[M+H]^+$) 275.11789, found 275.11807.

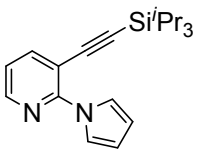



**3-((4-Methoxy-2-methylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)-pyridine 2i.** The reaction of **1a** (0.5 mmol, 111.5 mg) and 1-ethynyl-4-methoxy-2-methylbenzene (0.6 mmol, 87.7 mg) gave **2i** as a yellow oil (141 mg, 98%); $R_f$ 0.50 (heptane/ethyl acetate 5:1). **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.40 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.93 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.82–7.77 (m, 2H, $CH_{pyrrole}$), 7.42 (d, $^3J$ = 8.4 Hz, 1H, $CH_{Ar}$), 7.15 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{pyridine}$), 6.77 (d, $^4J$ = 2.6 Hz, 1H, $CH_{Ar}$), 6.73 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.6 Hz, 1H, $CH_{Ar}$), 6.38–6.31 (m, 2H, $CH_{pyrrole}$)), 3.82 (s, 3H, OMe), 2.45 (s, 3H, Me) ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 160.3 (C-OMe), 151.0 ($C_{pyridine}$), 147.6, 143.2 ($CH_{pyridine}$), 142.4 (C-Me), 133.6 ($CH_{Ar}$), 120.7 ($CH_{pyrrole}$), 120.2 ($CH_{pyridine}$), 115.4 ($CH_{Ar}$), 114.7 ($C_{Ar}$), 111.6 ($CH_{Ar}$), 111.1 ($C_{pyridine}$), 110.3 ($CH_{pyrrole}$), 95.5, 88.0 ($C_{alkyne}$), 55.4 (OMe), 21.2 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2916 (br, w), 2205 (w), 1706 (br, w), 1602 (m), 1560 (m), 1472 (m), 1433 (m), 1294 (m), 1236 (s), 1036 (m), 797 (m), 727 (m), 561 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 288 ($[M]^+$, 58), 287 (100), 273 (19), 272 (17), 271 (8), 261 (8), 256 (7), 255 (10), 245 (14), 244 (21), 243 (42), 242 (18), 230 (7), 229 (8), 218 (10), 205 (9), 151 (6), 128 (6), 122 (7), 39 (7). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{19}H_{16}N_2O$ ($[M+H]^+$) 289.13354, found 289.13364.

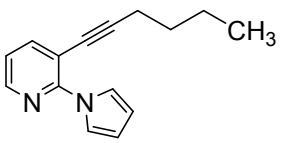



**2-([1*H*]-pyrrol-1-yl)-3-(thiophen-3-ylethynyl)pyridine 2j.** The starting material **1a** (0.5 mmol, 111.5 mg) and 1-ethynyl-4-methoxy-2-methylbenzene (0.6 mmol, 59 µl) delivered **2j** as a yellow oil (117 mg,

94%); $R_f$ 0.48 (heptane/ethyl acetate 5:1). **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.42 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.92 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.87–7.81 (m, 2H, $CH_{pyrrole}$), 7.57 (dd, $^4J$ = 3.0 Hz, $^4J$ = 1.2 Hz, 1H,$CH_{thioph.}$), 7.32 (dd, $^3J$ = 5.0 Hz, $^4J$ = 3.0 Hz, 1H, $CH_{thioph.}$), 7.21 (dd, $^3J$ = 5.0 Hz, $^4J$ = 1.2 Hz, 1H, $CH_{thioph.}$), 7.12 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{pyridine}$), 6.44–6.38 (m, 2H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 151.1 ($C_{pyridine}$), 147.8, 143.0 ($CH_{pyridine}$), 129.5, 129.4, 125.8 ($CH_{thioph.}$), 121.5 ($C_{thioph.}$), 120.6 ($CH_{pyrrole}$), 120.1 ($CH_{pyridine}$), 110.3 ($CH_{pyrrole}$), 110.0 ($C_{pyridine}$), 91.4, 85.2 ($C_{alkyne}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3107 (w), 3050 (w), 1561 (w), 1473 (w), 1438 (w), 1335 (w), 1058 (w), 1017 (w), 869 (w), 781 (w), 726 (m), 625 (w) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 250 ([M]$^+$,100), 249 (62), 248 (24), 224 (11), 223 (5), 222 (6), 205 (18), 140 (5), 113 (5), 45 (5), 39 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{15}H_{10}N_2S$ ([M+H]$^+$) 251.06375, found 251.06395.

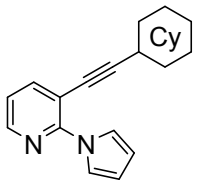



**2-([1*H*]-pyrrol-1-yl)-3-((triisopropylsilyl)ethynyl)pyridine 2k.** The reaction of **1a** (1 mmol, 223 mg) with ethynyltriisopropylsilane (1.2 mmol, 269 µl) achieved product **2k** as a pale yellow oil (295 mg, 94%); $R_f$ 0.60 (heptane/ethyl acetate 5:1). **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.40 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.90 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.88–7.85 (m, 2H, $CH_{pyrrole}$), 7.09 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{pyridine}$), 6.33–6.27 (m, 2H, $CH_{pyrrole}$), 1.16–1.09 (m, 21H, $i$Pr$_3$) ppm. **$^{29}$Si INEPT NMR (60 MHz, $CDCl_3$):** $\delta$ = −1.4 ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 151.2 ($C_{pyridine}$), 148.0, 144.5 ($CH_{pyridine}$), 120.6 ($CH_{pyrrole}$), 119.9 ($CH_{pyridine}$), 110.3 ($CH_{pyrrole}$), 110.0 ($C_{pyridine}$), 102.8, 99.7 ($C_{alkyne}$), 18.8 ($CH_{3i\text{Pr}}$), 11.5 ($CH_{i\text{Pr}}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2942 (w), 2864 (m), 2153 (w), 1720 (br, w), 1531 (m), 1476 (m), 1436 (s), 1070 (m), 881 (m), 727 (m), 674 (m), 629 (m), 557 (w), 412 (w) cm$^{-1}$.**MS (EI, 70 eV):** *m/z* (%) = 324 ([M]$^+$, 12), 282 (32), 281 (100), 253 (23), 240 (12), 239 (30), 225 (14), 223 (10), 211 (18), 209 (11), 195 (35), 181 (15), 169 (12), 168 (12), 43 (10). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{20}H_{28}N_2Si$ ([M+H]$^+$) 325.20945, found 325.20938.



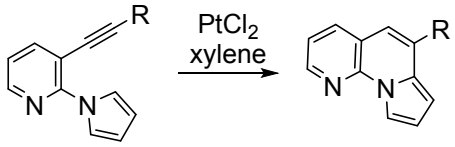

**3-(*n*-Hex-1-yn-1-yl)-2-([1*H*]-pyrrol-1-yl)pyridine 2l.** 1-Hexyne (0.6 mmol, 69 µl) and **1a** (0.5 mmol, 111.5 mg) gave the desired product **2l** as a yellow oil (98 mg,87%); $R_f$ 0.43 (heptane/ethyl acetate 5:1). **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.36 (dd, $^3J$ = 4.8 Hz, $^3J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.81 (dd, $^3J$ = 7.7 Hz, $^3J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.79–7.74 (m, 2H, $CH_{pyrrole}$), 7.08 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{pyridine}$), 6.36–6.32 (m, 2H, $CH_{pyrrole}$), 2.45 (t, $^3J$ = 7.0 Hz, 2H,

$CH_2$), 1.70–1.53 (m, 2H, $CH_2$), 1.54–1.40 (m, 2H, $CH_2$), 0.96 (t, $^3J$ = 7.2 Hz, 3H, $CH_3$) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 151.3 ($C_{pyridine}$), 147.2, 143.6 ($CH_{pyridine}$), 120.6 ($CH_{pyrrole}$), 120.0 ($CH_{pyridine}$), 110.9 ($C_{pyridine}$), 110.0 ($CH_{pyrrole}$), 98.0, 76.9 ($C_{alkyne}$), 30.4, 22.2, 19.5 ($CH_2$), 13.7 ($CH_3$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2930 (w), 2870 (w), 2230 (w), 1530 (m), 1474 (m), 1434 (s), 1336 (m), 1073 (m), 1068 (m), 925 (m), 797 (m), 725 (s), 517 (m), 545 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 224 ($[M]^+$, 5), 223 (8), 209 (5), 196 (5), 195 (22), 194 (6), 193 (7), 183 (13), 182 (100), 181 (67), 179 (14), 169 (5), 168 (14), 155 (12), 154 (9), 153 (6), 128 (5), 127 (7), 63 (5), 51 (5), 43 (7), 41 (14), 39 (12), 29 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{15}H_{16}N_2$ ($[M+H]^+$) 225.13862, found 225.13859. Calcd. for $C_{15}H_{16}N_2$ ($[M+Na]^+$) 247.12057, found 247.12030.




**3-(Cyclohexylethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2m.** The reaction of **1a** (1 mmol, 223 mg) with ethynylcyclohexane (1.2 mmol, 157 µl) provided **2m** as a yellow oil (214 mg, 86%); $R_f$ 0.56 (heptane/ethyl acetate 5:1). **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.35 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.81 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{pyridine}$), 7.81–7.77 (m, 2H, $CH_{pyrrole}$), 7.07 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{pyridine}$), 6.36–6.29 (m, 2H, $CH_{pyrrole}$), 2.64 (tt, $^3J_{a,a}$ = 9.2 Hz, $^3J_{a,e}$ = 3.8 Hz, 1H, $CH_a$), 1.96–1.84 (m, 2H, $CH_2$), 1.81–1.67 (m,2H, $CH_2$), 1.63–1.48 (m, 3H, $CH_2$), 1.45–1.30 (m, 3H, $CH_2$) ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 151.2 ($C_{pyridine}$), 147.2, 143.6 ($CH_{pyridine}$), 120.6 ($CH_{pyrrole}$), 120.0 ($CH_{pyridine}$), 110.9 ($C_{pyridine}$), 109.9 ($CH_{pyrrole}$), 101.7, 76.9 ($C_{alkyne}$), 32.2 ($CH_2$), 30.1 (CH), 25.9, 25.0 ($CH_2$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2926 (m), 2852 (w), 2223 (w), 1717 (br, w), 1451 (m), 1434 (s), 1336 (m), 1074 (m), 926 (m), 796 (m), 726 (s), 617 (w) $cm^{-1}$.**MS (EI, 70 eV):** *m/z* (%) = 250 ($[M]^+$, 28), 249 (20), 221 (18), 209 (13), 207 (23), 206 (13), 205 (17), 196 (17), 195 (100), 193 (20), 192 (12), 182 (24), 181 (16), 169 (17), 168 (22), 155 (14). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{17}H_{18}N_2$ ($[M+H]^+$) 251.15428, found 251.15414.

## Cycloisomerization to give [1,8]naphthyridines 3a–m

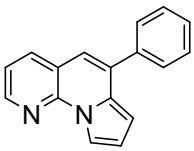



**2a-m** **3a-m**

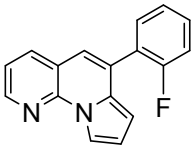
### General procedure

In a glas tube the Sonogashira product **2a-m** was dissolved in xylene (3 ml, isomeric mixture) under an argon atmosphere. The catalyst $PtCl_2$ (0.05 eq.) was added to the mixture. The solution was stirred at 120 °C for 24 h. After cooling to room temperature the crude product was diluted with water and extracted with DCM. For further purification the organic solvent was evaporated and column chromatography (heptane/DCM, 5:1 → 3:1) was performed. Thereby, 1–2 ml $Et_3N$ were added to 250 ml eluent mixture to deactivate the acidic silica.

### Product characterization

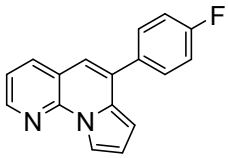


**6-Phenylpyrrolo[1,2-*a*][1,8]naphthyridine 3a. 2a** (0.2 mmol, 50 mg) cyclized in the presence of $PtCl_2$ (0.01 mmol, 2.7 mg) to give **3a** as a pale yellow solid (25 mg, 50%); mp 102–105 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.54 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.46 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.97 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.72 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.6 Hz, 2H, $CH_{Ph}$), 7.55–7.44 (m, 3H, $CH_{Ph}$), 7.30 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{naphtyr.}$), 6.91 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, $^3J$ = 3.8 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.68 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 146.6 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 138.5 ($C_{Ph}$), 136.3 ($CH_{naphtyr.}$), 134.2 ($C_{naphtyr.}$), 131.5 ($C_{pyrrole}$), 128.8, 128.5, 128.5 ($CH_{Ph}$), 120.1 ($CH_{naphtyr.}$), 119.2 ($C_{naphtyr.}$), 116.2 ($CH_{naphtyr.}$), 114.5 ($CH_{naphtyr.}$), 113.3, 105.3 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3119 (w), 3094 (w), 2921 (w), 2851 (w), 1726 (w), 1595 (w), 1531 (w), 1493 (w), 1442 (w), 1370 (w), 1297 (w), 1143 (w), 1074 (w), 958 (w), 848 (w), 761 (m), 740 (m), 701 (m), 663 (w), 583 (w), 446 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 244 ($[M]^+$, 100), 243 (81), 242 (43), 218 (13), 216 (8), 214 (7), 190 (7), 151 (7), 150 (10), 122 (5), 121 (7), 77 (6), 51 (7), 39 (8). **HRMS (EI, 70 eV):** *m/z* = calcd. for $C_{17}H_{12}N_2$ 244.09950, found 244.09919.

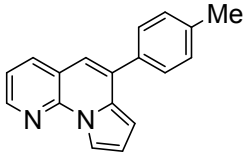


**6-(2-Fluorophenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3b. 2b** (0.36 mmol, 95 mg) gave **3b** under the influence of $PtCl_2$ (0.02 mmol, 5.3 mg) as a pale green solid (58 mg, 61%); mp 96–99 °C. **$^1$H NMR (300 MHz, $CDCl_3$):**

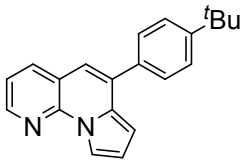
$\delta$ = 8.56 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.8 Hz, 1H, $CH_{naphtyr.}$), 8.43 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.96 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.62 (td, $^3J$ = 7.5 Hz, $^3J$ = 7.5 Hz, $^4J$ = 1.9 Hz, 1H, $CH_{Ar}$), 7.43 (dddd, $^3J$ = 9.2 Hz, $^3J$ = 8.1 Hz, $^4J_{H,F}$ = 5.1 Hz, $^4J$ = 1.8 Hz, 1H, $CH_{Ar}$), 7.31 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{naphtyr.}$), 7.29–7.23 (m, 1H, $CH_{Ar}$), 7.23–7.20 (m, 1H, $CH_{Ar}$) 6.95 (d, $^5J_{H,F}$ = 1.2 Hz, 1H, $CH_{naphtyr.}$), 6.82 (dd, $^3J$ = 3.8 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.47 (dt, $^3J$ = 3.8 Hz, $^3J$ = 1.4 Hz, $^5J_{H,F}$ = 1.4 Hz 1H, $CH_{pyrrole}$) ppm. **$^{19}$F NMR (235 MHz, $CDCl_3$):** $\delta$ = −114.3 ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 160.14 (d, $^1J_{C,F}$ = 248.5 Hz, C-F), 147.1 ($CH_{naphtyr.}$), 144.1 ($C_{naphtyr.}$), 136.4 ($CH_{naphtyr.}$), 131.4 ($C_{Ar}$), 131.22 (d, $^4J_{C,F}$ = 3.3 Hz, $CH_{Ar}$), 130.12 (d, $^3J_{C,F}$ = 8.2 Hz, $CH_{Ar}$), 128.0 ($C_{pyrrole}$), 125.76 (d, $^2J_{C,F}$ = 14.9 Hz, $C_{Ar}$), 124.27 (d, $^3J_{C,F}$ = 3.7 Hz, $CH_{Ar}$), 120.1 ($CH_{naphtyr.}$), 118.8 ($C_{naphtyr.}$), 117.96 (d, $^4J_{C,F}$ = 2.1 Hz, $CH_{naphtyr.}$), 116.30 (d, $^2J_{C,F}$ = 22.3 Hz, $CH_{Ar}$), 114.3, 113.3 ($CH_{pyrrole}$), 105.07 (d, $^5J_{C,F}$ = 1.8 Hz, $CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3033 (w), 2921 (w), 2851 (w), 1724 (br, w), 1571 (m), 1433 (m), 1370 (m), 1259 (m), 1216 (m), 1087 (m), 1037 (m), 863 (m), 781 (m), 757 (m), 720 (s), 651 (m), 525 (m), 434 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 262 ([M]$^+$, 100), 261 (26), 260 (14), 242 (5), 118 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{17}H_{11}FN_2$ ([M+H]$^+$) 263.09790, found 263.09795.



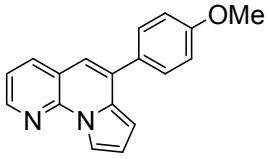

**6-(4-Fluorophenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3c. 2c** (0.2 mmol, 45 mg) reacted with $PtCl_2$ (0.01 mmol, 2.3 mg) to give **3c** as a pale green solid (19 mg, 42%); mp 128–131 °C. **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.55 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.43 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.95 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.73–7.64 (m, 2H, $CH_{Ar}$), 7.30 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{naphtyr.}$), 7.24–7.12 (m, 2H, $CH_{Ar}$), 6.87 (s, 1H, $CH_{naphtyr.}$), 6.83 (dd, $^3J$ = 3.8 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.62 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$) ppm. **$^{19}$F NMR (235 MHz, $CDCl_3$):** $\delta$ = −113.4 ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 162.95 (d, $^1J_{C,F}$ = 247.6 Hz, C-F), 147.0 ($CH_{naphtyr.}$), 144.1 ($C_{naphtyr.}$), 136.1 ($CH_{naphtyr.}$), 134.60 (d, $^4J_{C,F}$ = 3.4 Hz, $C_{Ar}$), 133.1 ($C_{naphtyr.}$), 131.4 ($C_{pyrrole}$), 130.13 (d, $^3J_{C,F}$ = 8.1 Hz, $CH_{Ar}$), 120.2 ($CH_{naphtyr.}$), 119.1 ($C_{naphtyr.}$), 116.3 ($CH_{pyrrole}$), 115.73 (d, $^2J_{C,F}$ = 21.4 Hz, $CH_{Ar}$), 114.5 ($CH_{naphtyr.}$), 113.3, 105.0 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3041 (w), 2921 (w), 1724 (w), 1601 (w), 1508 (m), 1454 (m), 1438 (m), 1368 (w), 1298 (w), 1223 (m), 1160 (m), 1092 (m), 1036 (w), 857 (m), 831 (m), 794 (m), 725 (m), 623 (m), 556 (m), 510 (m), 497 (m), 448 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 262 ([M]$^+$, 100), 261 (36), 260 (19), 118 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{17}H_{11}FN_2$ ([M+H]$^+$) 263.09790, found 263.09759.



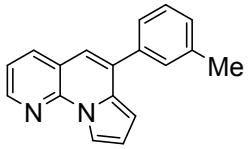

**6-(4-Tolyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3d.** The reaction of **2d** (0.3 mmol, 78 mg) with $PtCl_2$ (0.015 mmol, 4 mg) gave **3d** as a yellow solid (34 mg, 68%); mp 86–91 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.53 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.47 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.96 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.64–7.57 (m, 2H, $CH_{Ar}$), 7.35–7.25 (m, 3H, $CH_{naphtyr./Ar}$), 6.89 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, $^3J$ = 3.8 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.69 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 2.45 (s, 3H, Me) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 146.3 ($CH_{naphtyr.}$), 143.8 ($C_{naphtyr.}$), 138.4 (C-Me), 136.3 ($CH_{naphtyr.}$), 135.6 ($C_{Ar}$), 134.2 ($C_{naphtyr.}$), 131.6 ($C_{pyrrole}$), 129.5, 128.3 ($CH_{Ar}$), 120.0 ($CH_{naphtyr.}$), 119.4 ($C_{naphtyr.}$), 115.8, 114.5 ($CH_{naphtyr.}$), 113.4, 105.3 ($CH_{pyrrole}$), 21.5 (Me) ppm. **IR(ATR):** $\tilde{\nu}$ = 3120 (m), 2917 (m), 2851 (m), 1723 (m), 1665 (w), 1604 (m), 1571 (m), 1510 (m), 1436 (s), 1369 (m), 1299 (m), 1282 (m), 1180 (m), 1145 (m), 1095 (m), 1060 (m), 1033 (m), 927 (m), 850 (m), 816 (s), 761 (s), 735 (vs), 722 (vs), 624 (m), 557 (m), 496 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 258 ($[M]^+$, 100), 257 (21), 256 (6), 255 (10), 243 (6), 242 (14), 128 (8). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2$ ($[M+H]^+$) 259.12297, found 259.12293.



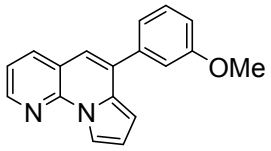

**6-(4-*tert*-Butylphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3e.** Starting material **2e** (0.3 mmol, 90.1 mg) reacted with $PtCl_2$ (0.015 mmol, 4 mg) giving **3e** as a brown oil (59 mg, 66%); $R_f$ 0.58 (heptane/ethyl acetate 5:1). **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.53 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.45 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.94 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.70–7.65 (m, 2H, $CH_{Ar}$), 7.55–7.50 (m, 2H, $CH_{Ar}$), 7.29 (dd, $^3J$ = 7.8 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{naphtyr.}$), 6.90 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, $^3J$ = 3.8 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.73 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 1.41 (s, 9H, $CH_{3tBu}$) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 151.6 (C-*t*Bu), 146.6 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 136.0 ($CH_{naphtyr.}$), 135.6 ($C_{Ar}$), 134.1 ($C_{naphtyr.}$), 131.6 ($C_{pyrrole}$), 128.1, 125.7 ($CH_{Ar}$), 120.0 ($CH_{naphtyr.}$), 119.3 ($C_{naphtyr.}$), 116.0 ($CH_{pyrrole}$), 114.3 ($CH_{naphtyr.}$), 113.2, 105.3 ($CH_{pyrrole}$), 34.9 ($C_{tBu}$), 31.5 ($CH_{3tBu}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2957 (w), 1721 (w), 1589 (w), 1512 (w), 1434 (m), 1362 (m), 1268 (m), 1146 (w), 1092 (m), 1018 (w), 831 (m), 787 (m), 768 (m), 722 (m), 610 (m), 542 (m), 448 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 300 ($[M]^+$, 100), 286 (13), 285 (64), 270 (12), 269 (8), 268 (7), 257 (13), 255 (9), 244 (7), 243 (9), 242 (12), 128 (15). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{21}H_{20}N_2$ ($[M+H]^+$) 301.16993, found 301.16950.



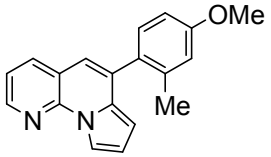

**6-(4-Methoxyphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3f. 2f** (0.15 mmol, 42 mg) cyclized under influence of $PtCl_2$ (0.01 mmol, 2 mg) giving **3f** as a pale yellow solid (17 mg, 40%); mp 123–128 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.53 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.44 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.96 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.69–7.62 (m, 2H, $CH_{Ar}$), 7.30 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{naphtyr.}$), 7.06–7.00 (m, 2H, $CH_{Ar}$), 6.87 (s, 1H, $CH_{naphtyr.}$), 6.83 (dd, $^3J$ = 3.8 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.68 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 3.89 (s, 3H, OMe) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 160.0 (C-OMe), 146.3 ($CH_{naphtyr.}$), 143.7 ($C_{naphtyr.}$), 136.1 ($CH_{naphtyr.}$), 133.9 ($C_{Ar}$), 131.7 ($C_{naphtyr.}$), 131.0 ($C_{pyrrole}$), 129.6 ($CH_{Ar}$), 120.1 ($CH_{naphtyr.}$), 119.4 ($C_{naphtyr.}$), 115.6 ($CH_{pyrrole}$), 114.4 ($CH_{naphtyr.}$), 114.2 ($CH_{Ar}$), 113.3, 105.2 ($CH_{pyrrole}$), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 2919 (w), 2849 (w), 1720 (w), 1601 (w), 1509 (w), 1436 (w), 1367 (w), 1280 (w), 1239 (w), 1175 (w), 1111 (w), 1032 (w), 834 (w), 782 (w), 768 (w), 732 (w), 621 (w), 563 (w), 523 (w), 445 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 274 ($[M]^+$, 100), 259 (18), 242 (5), 231 (21), 230 (13), 229 (19), 205 (15), 204 (7), 203 (6), 115 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2O$ ($[M+H]^+$) 275.11789, found 275.11788. Calcd. for $C_{18}H_{14}N_2O$ ($[M+Na]^+$) 297.09983, found 297.10014.




**6-(3-Tolyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3g. 2g** (0.32 mmol, 82 mg) and $PtCl_2$ (0.016 mmol, 4 mg) gave the product **3g** as a yellow oil (21 mg, 25%); mp 86–89 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.54 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.47 (dd, $^3J$ = 3.0 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.98 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.57–7.47 (m, 2H, $CH_{Ar}$), 7.42–7.36 (m, 1H, $CH_{Ar}$), 7.32 (dd, $^3J$ = 7.8 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{naphtyr.}$), 7.29–7.27 (m, 1H, $CH_{Ar}$), 6.90 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, $^3J$ = 3.8 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.69 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 2.45 (s, 3H, Me) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 146.4 ($CH_{naphtyr.}$), 143.8 ($C_{naphtyr.}$), 138.5 (C-Me), 136.4 ($CH_{naphtyr.}$), 134.5 ($C_{Ar}$), 131.6 ($C_{naphtyr.}$), 129.3, 129.1, 128.7, 125.6 ($CH_{Ar}$), 120.1 ($CH_{naphtyr.}$), 119.4 ($C_{naphtyr.}$), 116.0 ($CH_{pyrrole}$), 114.6 ($CH_{naphtyr.}$), 113.4, 105.4 ($CH_{pyrrole}$), 21.7 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 3142 (w), 2917 (w), 1722 (w), 1603 (w), 1571 (w), 1531 (w), 1436 (m), 1366 (w), 1304 (w), 1283 (w), 1091 (w), 1038 (w), 1019 (w), 860 (m), 782 (m), 728 (m), 708 (m), 665 (w), 589 (w), 447 (w), 436 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 258 ($[M]^+$, 100), 257 (20), 256 (5), 255 (11), 243 (6), 242 (16), 128 (8). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2$ ($[M+H]^+$) 259.12297, found 259.12314.

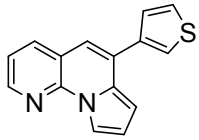



**6-(3-Methoxyphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3h.** Substrate **2h** (0.6 mmol, 166 mg) and $PtCl_2$ (0.03 mmol, 8 mg) reacted to **3h** as a pale brown oil (99 mg, 60%); $R_f$ 0.36 (heptane/ethyl acetate 5:1). **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.54 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.45 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.96 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.41 (dd, $^3J$ = 8.1 Hz, $^3J$ = 7.5 Hz, 1H, $CH_{Ar}$), 7.34–7.26 (m, 3H, $CH_{naphtyr./Ar}$), 7.00 (ddd, $^3J$ = 8.2 Hz, $^4J$ = 2.6 Hz, $^4J$ = 1.1 Hz, 1H, $CH_{Ar}$), 6.92 (s, 1H, $CH_{naphtyr.}$), 6.84 (dd, $^3J$ = 3.8 Hz, $^4J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.71 (dd, $^3J$ = 3.8 Hz, $^3J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 3.88 (s, 3H, OMe) ppm. **$^{13}$C-NMR (75 MHz, $CDCl_3$):** $\delta$ = 159.9 (C-OMe), 146.8 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 139.9 ($C_{Ar}$), 136.2 ($CH_{naphtyr.}$), 134.0 ($C_{naphtyr.}$), 131.4 ($C_{pyrrole}$), 129.8, 120.9 ($CH_{Ar}$), 120.1 ($CH_{naphtyr.}$), 119.1 ($C_{naphtyr.}$), 116.2 ($CH_{pyrrole}$), 114.4 ($CH_{naphtyr.}$), 114.1, 114.0 ($CH_{Ar}$), 113.3, 105.2 ($CH_{pyrrole}$), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 2933 (w), 2832 (w), 1574 (m), 1434 (m), 1239 (m), 1169 (m), 1038 (m), 851 (m), 785 (m), 725 (m), 694 (m), 555 (m), 447 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 274 ($[M]^+$, 100), 259 (9), 258 (9), 242 (6), 231 (9), 230 (7), 229 (13), 205 (5), 203 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{18}H_{14}N_2O$ ($[M+H]^+$) 275.11789, found 275.11795.

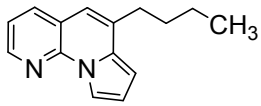



**6-(4-Methoxy-2-methylphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3i.** **2i** (0.5 mmol, 149 mg) and $PtCl_2$ (0.03 mmol, 7 mg) achieved **3i** as a pale brown oil (92 mg, 62%); $R_f$ 0.40 (heptane/ethyl acetate 5:1). **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.57 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.45 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.93 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 7.33 (d, $^3J$ = 8.4 Hz, 1H, $CH_{Ar}$), 7.30 (dd, $^3J$ = 7.8 Hz, $^4J$ = 4.8 Hz, 1H, $CH_{naphtyr.}$), 6.93 (d, $^4J$ = 2.6 Hz, 1H, $CH_{Ar}$), 6.87 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.7 Hz, 1H, $CH_{Ar}$), 6.82 (dd, $^3J$ = 3.7 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.78 (s, 1H, $CH_{naphtyr.}$), 6.29 (dd, $^3J$ = 3.9 Hz, $^4J$ = 1.6 Hz, 1H, $CH_{pyrrole}$), 3.90 (s, 3H, OMe), 2.29 (s, 3H, Me) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 159.4 (C-OMe), 146.6 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 137.9 (C-Me), 135.8 ($CH_{naphtyr.}$), 133.6 ($C_{Ar}$), 132.5 ($C_{naphtyr.}$), 130.7 ($CH_{Ar}$), 130.2 ($C_{pyrrole}$), 119.9 ($CH_{naphtyr.}$), 119.0 ($C_{naphtyr.}$), 117.0 ($CH_{Ar}$), 115.8 ($CH_{pyrrole}$), 113.9 ($CH_{naphtyr.}$), 113.1 ($CH_{pyrrole}$), 111.1 ($CH_{Ar}$), 105.1 ($CH_{pyrrole}$), 55.3 (OMe), 20.2 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2919 (w), 2833 (w), 1722 (w), 1604 (w), 1560 (w), 1499 (w), 1455 (m), 1434 (m), 1368 (w), 1291 (m), 1237 (m), 1161 (w), 1042 (m), 940 (w), 856 (w), 788 (m), 725 (m), 626 (w), 557 (w), 446 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 288 ($[M]^+$, 86), 287 (100), 273 (10), 272 (10), 271 (5), 256 (5), 255 (8), 245 (8), 244 (13), 243

(30), 242 (15), 229 (7), 218 (5), 205 (5), 128 (6), 122 (7), 109 (5). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{19}H_{16}N_2O$ ([M+H]$^+$) 289.13354, found 289.13338.

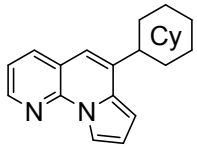


**6-(Thiophen-3-yl)pyrrolo[1,2-*a*][1,8]naphthyridine 3j. 2j** (0.3 mmol, 86 mg) reacted with $PtCl_2$ (0.015 mmol, 4 mg) giving **3j** as a yellow solid (35 mg, 41%); $R_f$ 0.55 (heptane/ethyl acetate 5:1). **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.54 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.47 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.97 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.70 (dd, $^4J$ = 2.9 Hz, $^4J$ = 1.4 Hz, 1H, $CH_{thioph.}$), 7.50 (dd, $^3J$ = 5.0 Hz, $^4J$ = 1.4 Hz, 1H, $CH_{thioph.}$), 7.46 (dd, $^3J$ = 5.0 Hz, $^4J$ = 2.9 Hz, 1H, $CH_{thioph.}$), 7.31 (dd, $^3J$ = 7.8 Hz, $^3J$ = 4.8 Hz, 1H, $CH_{naphtyr.}$), 7.00 (s, 1H. $CH_{naphtyr.}$), 6.85 (dd, $^3J$ = 3.8 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.81 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 146.3 ($CH_{naphtyr.}$), 143.7 ($C_{naphtyr.}$), 138.9 ($C_{thioph.}$), 136.4 ($CH_{naphtyr.}$), 131.2 ($C_{naphtyr.}$), 128.9 ($C_{pyrrole}$), 127.8, 126.1, 123.5 ($CH_{thioph.}$), 120.1 ($CH_{naphtyr.}$), 119.2 ($C_{naphtyr.}$), 115.6 ($CH_{pyrrole}$), 114.7 ($CH_{naphtyr.}$), 113.5, 105.3 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3091 (w), 2921 (w), 1717 (br, w), 1570 (m), 1469 (m), 1435 (s), 1136 (m), 1080 (m), 859 (m), 836 (m), 777 (m), 715 (s), 633 (m), 448 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 250 ([M]$^+$, 100), 249 (22), 248 (9), 205 (10). **HRMS (EI):** *m/z* = calcd. for $C_{15}H_{10}N_2S$ ([M]$^+$) 250.05592, found 250.05591.



**6-(*n*-Butyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3l.** Substrate **2l** (0.2 mmol, 50 mg) and $PtCl_2$ (0.01 mmol, 2.6 mg) resulted in product **3l** as an oil (19 mg, 37%); $R_f$ 0.63 (heptane/ethyl acetate 5:1). **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.48 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.33 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.87 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.25 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{naphtyr.}$), 6.80 (dd, $^3J$ = 3.7 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.73 (s, 1H, $CH_{naphtyr.}$), 6.62 (dd, $^3J$ = 3.7 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 2.79 (t, $^3J$ = 7.7 Hz, 2H, $CH_2$), 1.78 (p, $^3J$ = 7.5 Hz, 2H, $CH_2$), 1.45 (hept, $^3J$ = 7.4 Hz, 2H, $CH_2$), 0.98 (t, $^3J$ = 7.3 Hz, 3H, $CH_3$) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 146.1 ($CH_{naphtyr.}$), 144.0 ($C_{naphtyr.}$), 135.4 ($CH_{naphtyr.}$), 134.0 ($C_{naphtyr.}$), 132.6 ($C_{pyrrole}$), 119.8 ($CH_{naphtyr.}$), 119.3 ($C_{naphtyr.}$), 114.7 ($CH_{pyrrole}$), 113.8 ($CH_{naphtyr.}$), 112.7, 102.7 ($CH_{pyrrole}$), 32.2, 31.1, 22.9 ($CH_2$), 14.1 ($CH_3$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2855 (w), 2927 (w), 2858 (w), 1723 (w), 1612 (w), 1592 (w), 1559 (w), 1537 (w), 1459 (w), 1436 (w), 1377 (w), 1289 (w), 1171 (w), 1090 (w), 1033 (w), 849 (w), 783 (w), 726 (w) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 224 ([M]$^+$, 40), 195 (12), 194 (5), 193 (7), 183 (13), 182

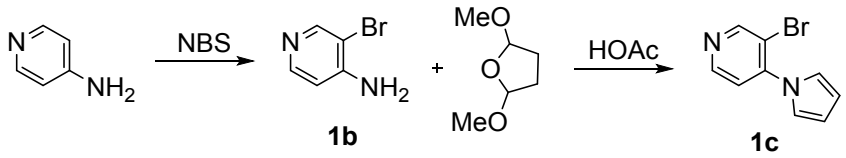
(100), 181 (42), 179 (5), 168 (7), 154 (5), 127 (6). **HRMS (ESI-TOF):** *m/z* = calcd. for $C_{15}H_{16}N_2$ ($[M+H]^+$) 225.13862, found 225.13887.

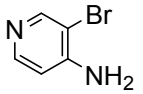



**6-(Cyclohexyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3m.** Starting material **2m** (0.8 mmol, 204 mg) and $PtCl_2$ (0.04 mmol, 10.6 mg) gave **3m** as an oil (127 mg, 62%); $R_f$ 0.58 (heptane/ethyl acetate 5:1). **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.47 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.7 Hz, 1H, $CH_{naphtyr.}$), 8.37 (dd, $^3J$ = 3.0 Hz, $^4J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 7.86 (dd, $^3J$ = 7.8 Hz, $^3J$ = 1.8 Hz, 1H, $CH_{naphtyr.}$), 7.23 (dd, $^3J$ = 7.7 Hz, $^3J$ = 4.7 Hz, 1H, $CH_{naphtyr.}$), 6.82 (dd, $^3J$ = 3.7 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.74 (s, 1H, $CH_{naphtyr.}$), 6.67 (dd, $^3J$ = 3.8 Hz, $^3J$ = 1.5 Hz, 1H, $CH_{pyrrole}$), 2.86 (tt, $^3J_{a,a}$ = 8.2 Hz, $^3J_{a,e}$ = 3.2 Hz, 1H, $CH_a$), 2.22–2.05 (m, 2H, $CH_2$), 1.98–1.79 (m, 3H, $CH_2$), 1.62–1.44 (m, 3H, $CH_2$), 1.47–1.24 (m, 2H, $CH_2$) ppm. **$^{13}$C NMR (63 MHz, $CDCl_3$):** $\delta$ = 146.1 ($CH_{naphtyr.}$), 143.8 ($C_{naphtyr.}$), 139.2 ($C_{naphtyr.}$), 135.5 ($CH_{naphtyr.}$), 132.3 ($C_{pyrrole}$), 119.8 ($CH_{naphtyr.}$), 119.3 ($C_{naphtyr.}$), 113.7 ($CH_{pyrrole}$), 112.6 ($CH_{naphtyr.}$), 112.2, 102.4 ($CH_{pyrrole}$), 40.4 (CH), 33.1, 27.0, 26.5 ($CH_2$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2924 (m), 2850 (m), 1720 (br, w), 1560 (w), 1434 (s), 1336 (m), 1289 (m), 1073 (m), 1059 (m), 845 (m), 783 (m), 721 (s), 615 (m), 554 (m), 448 (m) $cm^{-1}$**. MS (EI, 70 eV):** *m/z* (%) = 250 ($[M]^+$, 100), 249 (23), 235 (6), 221 (18), 219 (6), 209 (12), 207 (23), 206 (13), 205 (22), 196 (13), 195 (70), 194 (19), 193 (27), 192 (11), 182 (26), 181 (17), 169 (6), 168 (22), 140 (6), 56 (6), 41 (13), 39 (8). **HRMS (EI):** *m/z* = calcd. for $C_{17}H_{18}N_2$ ($[M]^+$) 250.14645, found 250.14577.

## Preparation of [1,6]naphthyridines

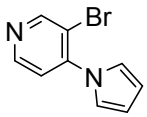
### Starting materials



**4-Amino-3-bromo-pyridine 1b**

*N*-Bromosuccinimide (1.1 eq., 29.2 mmol, 5.2 g) was added slowly to a stirred solution of 4-aminopyridine (26.6 mmol, 2.5 g) in 140 ml acetonitrile. The mixture was stirred for 48 h at room temperature. Afterwards the solvent was removed under reduced pressure and the product was purified by column chromatography (heptane/ethyl acetate, 2:1 → 1:2) to yield 4-amino-3-bromopyridine **1b** as a white solid (86% yield, 3.95 g). **$^1$H NMR (300 MHz, DMSO-*d*$_6$):** $\delta$ = 11.11 (bs, 2H, $NH_2$), 8.23 (s, 1H, $CH_{pyridine}$), 7.96 (d, $^3J$ = 5.5 Hz, 1H, $CH_{pyridine}$), 6.68 (d, $^3J$ = 5.5 Hz, 1H, $CH_{pyridine}$) ppm. **$^{13}$C NMR (75 MHz, DMSO-*d*$_6$):** $\delta$ = 151.4 (C-$NH_2$), 150.8, 148.2, 109.9 ($CH_{pyridine}$), 105.5 (C-Br) ppm. **IR (ATR):** $\tilde{\nu}$ = 3440 (w), 3342 (w), 3217 (w), 2946 (w), 2545 (br, w), 1700 (s), 1632 (s), 1501 (m), 1199 (s), 1074 (w), 1014 (m), 815 (s), 633 (s), 562 (s) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 174 ($[C_9H_7{}^{81}BrN_2]^+$, 100), 172 ($[C_9H_7{}^{79}BrN_2]^+$, 99), 145 (2), 119 (8), 117 (6), 93 (53). **HRMS (EI, 70 eV):** *m/z* = calcd. for $C_5H_5N_2{}^{79}Br$ ($[M]^+$) 171.96306, found 171.96313. Calcd. for $C_5H_5N_2{}^{81}Br$ ($[M]^+$) 173.96102, found 173.96131.

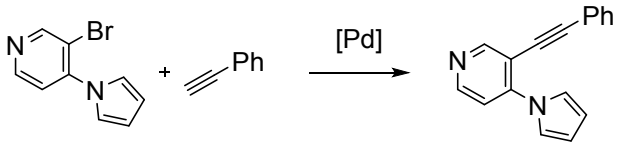


**3-Bromo-4-([1*H*]-pyrrol-1-yl)pyridine 1c**

2,5-dimethoxytetrahydrofuran (2.5 eq., 28.9 mmol, 3.75 ml) was added to a stirred solution of **1b** (17.3 mmol, 3.0 g) in 12 ml HOAc. The mixture was then refluxed (120 °C) for 1 h. Afterwards, the reaction mixture was diluted with DCM and washed with distilled water and $NaHCO_3$ solution subsequently. The aqueous phase was extracted with DCM. The organic fractions were combined and the solvent removed under vacuum. Finally, the crude product was purified from reagent residues through column chromatography (heptane/ethyl acetate, 4:1) to obtain **1c** as a white solid (79% yield, 2.03 g). **$^1$H NMR (300 MHz, DMSO-*d*$_6$):** $\delta$ = 8.87 (s, 1H, $CH_{pyridine}$), 8.60 (d, $^3J$ = 5.2 Hz, 1H, $CH_{pyridine}$), 7.48 (d, $^3J$ = 5.2 Hz, 1H, $CH_{pyridine}$), 7.19 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.33 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (75 MHz, DMSO-*d*$_6$):** $\delta$ = 153.4, 149.8 ($CH_{pyridine}$), 145.7 ($C_{pyridine}$), 121.8 ($CH_{pyridine}$), 121.6 ($CH_{pyrrole}$), 114.5 (C-Br), 110.5 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3118 (br, w), 1737 (w), 1574 (s), 1497 (s), 1339 (s), 1180 (w), 1069 (s), 1017 (s),

834 (s), 726 (s), 667 (s), 619 (s), 570 (s) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 222 ($[C_9H_7N_2{}^{81}Br]^+$, 100), 223 (12), 224 ($[C_9H_7N_2{}^{79}Br]^+$, 98), 225 (10), 196 (7), 183 (3), 156 (4), 143 (27), 142 (18), 116 (67). **HRMS (EI, 70 eV):** *m/z* = calcd. for $C_9H_7N_2{}^{79}Br$ ($[M]^+$) 221.97871, found 221.97828. Calcd. for $C_9H_7N_2{}^{81}Br$ ($[M]^+$) 223.97667, found 223.97663.

## Optimization of Sonogashira reaction giving 3-alynyl-4-pyrrolopyridines[a]



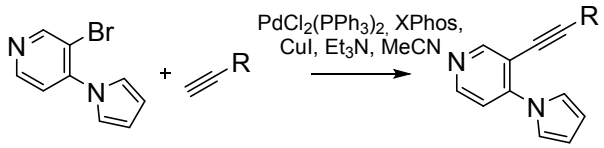

**1c** **4a**

| entry | catalyst (0.05 eq.) | ligand (0.1 eq.) | base | eq. | solvent | temp. [°C] | yield [%][b] |
|---|---|---|---|---|---|---|---|
| 1 | $Pd(PPh_3)_2Cl_2$ | – | $Et_3N$ | 3 | DMF | 140 | 59 |
| 2 | $Pd(PPh_3)_2Cl_2$ | – | $Et_3N$ | 3 | dioxane | 50 | 56 |
| 3 | $Pd(PPh_3)_2Cl_2$, | $P(tBu)_3 \cdot HBF_4$ | $Et_3N$ | 3 | dioxane | 50 | 65 |
| 4 | $Pd(PPh_3)_2Cl_2$, | $P(tBu)_3 \cdot HBF_4$ | $HNiPr_2$ | 3 | dioxane | 50 | 65 |
| 5 | $Pd(MeCN)_2Cl_2$, | $P(tBu)_3 \cdot HBF_4$ | $Et_3N$ | 3 | dioxane | 50 | 69 |
| 6 | $Pd(MeCN)_2Cl_2$, | XPhos | $Et_3N$ | 3 | dioxane | 50 | 73 |
| 7 | $Pd(MeCN)_2Cl_2$, | XPhos | $Et_3N$ | 3 | dioxane | r.t. | 81 |

[a]reaction condotions: **1a** (0.45 mmol, 100 mg) and phenylacetylene (1.5 eq., 0.68 mmol, 73 µl) react with CuI (0.05 eq., 0.01 mmol, 4.3 mg) in 2 ml of solvent in a glas tube under argon for 24 h. [b]isolated yields.

The following Sonogashira couplings were carried out employing the reaction conditions of **entry 7** sufficiently.

## Sonogashira reaction giving 4a-n



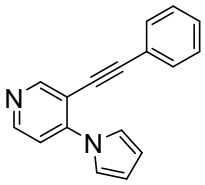

**1c** **4a-n**

### General procedure

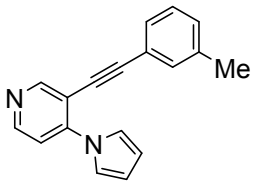
**1c** was dissolved in 2 ml dioxane under an argon atmosphere. After the addition of $Pd(MeCN)_2Cl_2$ (0.05 eq.), CuI (0.05 eq.), XPhos (0.1 eq.) and $Et_3N$ (3 eq.) in advance of the corresponding acetylene (1.5 eq.) the reaction is stirred at room temperature for 24 h. The reaction mixture was subsequently cooled to room temperature and washed with distilled water and ethyl acetate. The organic layers were collected and the solvent evaporated. The

crude product was thereafter purified by column chromatography (heptane/ethyl acetate, 10:1 → 2:1) to give the alkynylated products **4a–n**[1].

**Substrate characterization**



**3-(Phenylethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4a.** Reaction of **1c** (0.45 mmol, 100 mg) and phenylacetylene (0.07 mmol, 73 µl gave **4a** as a white solid (88 mg, 81%); mp 68–69 °C. **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.77 (bs, 1H, $CH_{pyridine}$), 8.51 (bs, 1H, $CH_{pyridine}$), 7.43–7.39 (m, 2H, Ph), 7.31 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.27–7.25 (m, 3H, Ph), 7.18–7.13 (m, 1H, $CH_{pyridine}$), 6.32 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR[2] (62.9 MHz, $CDCl_3$):** $\delta$ = 155.0, 149.5 ($CH_{pyridine}$), 147.2 ($C_{pyridine}$), 131.6, 129.1, 128.6 ($CH_{Ph}$), 122.4 ($C_{Ph}$), 120.8 ($CH_{pyrrole}$), 111.3 ($CH_{pyrrole}$), 96.8, 84.2 ($C_{alkyne}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3130 (w), 3055 (w), 2220 (w), 1562 (m), 1589 (m), 1393 (m), 1344 (m), 1185 (w), 1062 (m), 1018 (m), 920 (w), 836 (s), 749 (s), 722 (s), 685 (s), 621 (m), 562 (s) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 244 ([$M^+$], 100), 243 (69), 242 (36), 218 (8), 216 (7), 215 (5), 214 (5), 189 (6), 150 (8), 122 (5). **HRMS (EI, 70 eV):** calcd. for $C_{17}H_{12}N_2$ ([$M]^+$) 244.09950, found 244.09904.

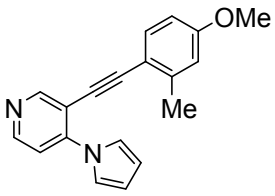


**3-((3-Methylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4b.** Reaction of **1c** (1.35 mmol, 300 mg) and tolylacetylene (2.02 mmol, 234.3 mg) gave **4b** as a white solid (304 mg, 88%); mp 99–100 °C. **$^1$H NMR (250 MHz, $C_6D_6$):** $\delta$ = 8.91 (s, 1H, $CH_{pyridine}$), 8.21 (d, $^3J$ = 5.5 Hz, 1H, $CH_{pyridine}$), 7.27 (d, $^3J$ = 7.6 Hz, 1H, $CH_{Ar}$), 7.22 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.23 (s, 1H, $CH_{Ar}$), 6.94 (t, $^3J$ = 7.6 Hz, 1H, $CH_{Ar}$), 6.82 (d, $^3J$ = 7.6 Hz, 1H, $CH_{Ar}$), 6.52 (d, $^3J$ = 5.5 Hz, 1H, $CH_{pyridine}$), 6.36 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 1.96 (s, 3H, Me) ppm. **$^{13}$C NMR (62.9 MHz, $C_6D_6$):** $\delta$ = 155.5, 150.1 ($CH_{pyridine}$), 147.1 ($C_{pyridine}$), 138.4 ($C_{Ar}$), 132.4, 130.1, 129.1, 128.6 ($CH_{Ar}$), 122.8 ($C_{Ar}$), 121.0 ($CH_{pyrrole}$), 117.1 ($CH_{pyridine}$), 113.0 ($C_{pyridine}$), 111.5 ($CH_{pyrrole}$), 97.2, 84.6 ($C_{alkyne}$), 21.0 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 3034 (w), 2919 (w), 2207 (w), 1720 (w), 1577 (w), 1558 (m), 1498 (s), 1392 (w), 1339 (s), 1180 (w), 1062 (m), 1018 (m), 827 (w), 782 (m), 722 (s), 687 (m), 569 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 258 ([$M^+$], 100), 257 (38), 256 (12), 255 (16), 243 (22), 242 (32), 241 (4), 231 (6), 229 (4), 214 (4),

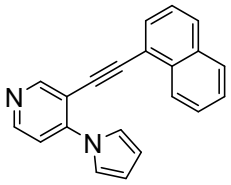
[1] The pyridine fragment provides very broad signals in $^1$H and $^{13}$C NMR spectra. Therefore, it was not possible to detect all pyridine signals of some substrates. Known effects that can lead to broad or undetectable NMR signals are exchange broadening due to changes in the spin and rotational states of the observed atom or aggregation with the solvent. However, all signals reappear in the cyclized products **5a–n**.

[2] *meta*-$C_{pyridine}$ and *meta*-$CH_{pyridine}$ are undetectable.

202 (3), 164 (3), 163 (6). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{14}N_2$ ([M]$^+$) 258.11515, found 258.11562.

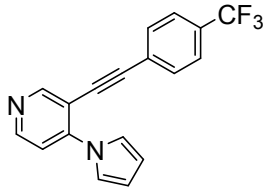



**3-((4-Methoxy-2-methylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4c.** Reaction of **1c** (1.35 mmol, 300 mg) and 4-methoxy-2-methylphenylacetylene (294.9 mg, 2.017 mmol) gave **4c** as a yellow solid (356 mg, 91%); mp 77–78 °C. **$^1$H NMR (250 MHz, $C_6D_6$):** $\delta$ = 8.90 (bs, 1H, $CH_{pyridine}$), 8.20 (bs, 1H, $CH_{pyridine}$), 7.35–7.15 (m, 3H, $CH_{Ar}$), 6.54–6.31 (m, 5H, $CH_{Ar}$), 3.20 (s, 3H, OMe), 2.23 (s, 3H, Me) ppm. **$^{13}$C NMR (62.9 MHz, $C_6D_6$):** δ = 160.7 ($C_{Ar}$), 155.5, 149.7 ($CH_{pyridine}$), 146.6 ($C_{pyridine}$), 142.6 ($C_{Ar}$), 133.9 ($CH_{Ar}$), 121.0 ($CH_{pyrrole}$), 117.3 ($CH_{pyridine}$), 115.7 ($CH_{Ar}$), 115.0 ($C_{Ar}$), 113.8 ($C_{pyridine}$), 111.8 ($CH_{Ar}$), 111.3 ($CH_{pyrrole}$), 96.4, 87.2 ($C_{alkyne}$), 54.8 (OMe), 21.0 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2957 (w), 2202 (w), 1725 (w), 1602 (w), 1560 (m), 1491 (m), 1341 (w), 1276 (w), 1237 (s), 1022 (w), 846 (w), 815 (s), 726 (s), 688 (m), 576 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 288 ([M$^+$], 100), 287 (77), 273 (9), 272 (15), 271 (8), 257 (6), 256 (9), 255 (10), 246 (7), 245 (40), 244 (23), 243 (39), 242 (15), 230 (10), 229 (10), 218 (7), 217 (6), 216 (5), 205 (5), 151 (6). **HRMS (EI, 70 eV):** calcd. for $C_{19}H_{16}ON_2$ ([M]$^+$) 288.12571, found 288.12528.

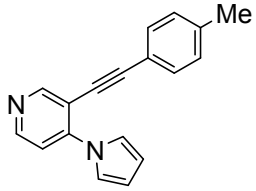



**3-(Naphtalen-1-ylethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4d.** Reaction of **1c** (1.57 mmol, 350 mg) and 1-naphthylacetylene (2.35 mmol, 364 µl) gave **4d** as a white solid (458 mg, 99%); mp 121–122 °C. **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 9.00 (bs, 2H, $CH_{pyridine}$), 8.27–8.23 (m, 1H, $CH_{naphthyl.}$), 7.90–7.85 (m, 2H, $CH_{naphthyl.}$), 7.78–7.74 (m, 1H, $CH_{naphthyl.}$), 7.58–7.50 (m, 2H, $CH_{naphthyl.}$), 7.47–7.44 (m, 1H, $CH_{naphthyl.}$), 7.45 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.18–7.05 (m, 1H, $CH_{pyridine}$), 6.46 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR[3] (62.9 MHz, $CDCl_3$):** $\delta$ = 133.2, 133.2 ($C_{naphthyl.}$), 131.1, 129.8, 128.5, 127.2, 126.8, 126.2, 125.3 ($CH_{naphthyl.}$), 121.0 ($CH_{pyrrole}$), 120.0 ($C_{naphthyl.}$), 111.6 ($CH_{pyrrole}$), 95.6, 88.7 ($C_{alkyne}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3043 (w), 2206 (w), 1556 (w), 1494 (m), 1388 (w), 1340 (m), 1179 (w), 1063 (m), 1019 (w), 832 (m), 803 (s), 777 (s), 728 (s), 672 (m), 620 (m), 560 (s) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 293 ([M$^+$], 100), 292 (50), 291 (11), 266 (6), 265 (8), 264 (7), 238 (3), 200 (6), 174 (2), 146 (6), 132 (5). **HRMS (EI, 70 eV):** calcd. for $C_{21}H_{13}N_2$ ([M]$^+$) 293.10732, found 293.10668.

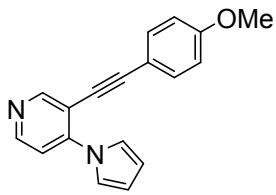
[3] All carbon signals of the pyridine moiety were undetectable.




**3-((4-Trifluoromethylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4e.** Reaction of **1c** (2.02 mmol, 450 mg,) and 4-(trifluoromethyl)-phenylacetylene (2.80 mmol, 494 µl) gave **4e** as a yellow solid (343 mg, 55%); mp 75–76 ˚C. **$^1$H NMR (300 MHz, $C_6D_6$):** $\delta$ = 8.92 (bs, 1H, $CH_{pyridine}$), 8.32 (bs, 1H, $CH_{pyridine}$), 7.22–7.13 (m, 6H, $CH_{Ar}$), 6.58 (bs, 1H, $CH_{pyridine}$), 6.40 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (75 MHz, $C_6D_6$):** $\delta$ = 155.5, 150.7 ($CH_{pyridine}$), 147.3 ($C_{pyridine}$), 131.9 ($CH_{Ar}$), 130.5 (q, $^2J_{C,F}$ = 32.6 Hz, $C_{Ar}$), 126.3 (q, $^4J_{C,F}$ = 1.4 Hz, $C_{Ar}$), 125.5 (q, $^3J_{C,F}$ = 3.8 Hz, $CH_{Ar}$), 124.4 (q, $^1J_{C,F}$ = 272.3 Hz, $CF_3$), 120.9 ($CH_{pyrrole}$), 117.3 ($CH_{pyridine}$), 111.6 ($CH_{pyrrole}$), 105.2($C_{pyridine}$), 95.1, 87.0 ($C_{alkyne}$) ppm. $^{19}$F NMR (282 MHz, $C_6D_6$) $\delta$ = −62.59 ppm. **IR (ATR):** $\tilde{\nu}$ = 2929 (w), 1724 (w), 1613 (w), 1583 (w), 1557 (w), 1496 (m), 1407 (w), 1324 (s), 1163 (m), 1101 (s), 1062 (s), 1016 (m), 834 (s), 729 (s), 675 (m), 577 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 312 ([M$^+$], 100), 311 (37), 310 (8), 293 (5), 291 (5), 286 (7), 243 (9), 242 (20), 214 (4), 199 (4). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{11}F_3N_2$ ([M]$^+$) 312.28855, found 312.28849.



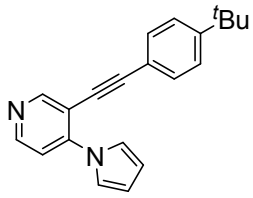

**3-((4-Methylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4f.** Reaction of **1c** (1.57 mmol, 350 mg) and 4-methylphenylacetylene (2.35 mmol, 274 mg) gave **4f** as a white solid (355 mg, 88%); mp 97–98 ˚C. **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.91 (bs, 2H, $CH_{pyridine}$), 7.42 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.40 (d, $^3J$ = 7.9 Hz, 2H, $CH_{Ar}$), 7.18 (d, $^3J$ = 7.9 Hz, 2H, $CH_{Ar}$), 7.19–7.10 (m, 1H, $CH_{pyridine}$), 6.42 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 2,38 (s, 3H, Me) ppm. **$^{13}$C NMR[4] (62.9 MHz, $CDCl_3$):** $\delta$ = 139.6 (C-Me), 131.6, 129.4 ($CH_{Ar}$), 120.8 ($CH_{pyrrole}$), 119.2 ($C_{Ar}$), 111.4 ($CH_{pyrrole}$), 97.6, 83.7 ($C_{alkyne}$), 21.7 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 3128 (w), 2658 (w), 2217 (m), 1560 (m), 1494 (s), 1389 (s), 1313 (w), 1179 (m), 1115 (w), 1068 (s), 1016 (s), 821 (m), 808 (s), 732 (s), 685 (m), 623 (w), 577 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 258 ([M$^+$], 100), 257 (40), 256 (12), 255 (14), 243 (17), 242 (30), 231 (5), 163 (6), 139 (3), 128 (4). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{14}N_2$ ([M]$^+$) 258.11515, found 258.11472.



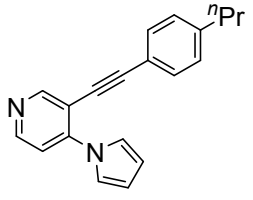

**3-((4-Methoxyphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4g.** Reaction of **1c** (1.57 mmol, 350 mg) and 4-methoxyphenylacetylene (2.35 mmol, 311 mg) gave **4g** as a yellow solid (408 mg, 95%); mp 89–90 ˚C. **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.72 (bs, 2H,

[4] All carbon signals of the pyridine moiety were undetectable.

$CH_{pyridine}$), 7.45 (d, $^3J$ = 8.9 Hz, 2H, $CH_{Ar}$), 7.45 (t, $^3J$ = 2.0 Hz, 2H, $CH_{pyrrole}$), 7.31 (bs, 1H, $CH_{pyridine}$), 6.89 (d, $^3J$ = 8.9 Hz, 2H, $CH_{Ar}$), 6.41 (t, $^3J$ = 2.0 Hz, 2H, $CH_{pyrrole}$), 3.83 (s, 3H, OMe) ppm. **$^{13}$C NMR[5] (62.9 MHz, $CDCl_3$):** $\delta$ = 160.5 (C-OMe), 133.3 ($CH_{Ar}$), 120.9 ($CH_{pyrrole}$), 114.5 ($C_{Ar}$), 114.4 ($CH_{Ar}$), 111.5 ($CH_{pyrrole}$), 97.5, 82.9 ($C_{alkyne}$), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 3035 (w), 2933 (w), 2218 (m), 1559 (m), 1504 (s), 1338 (m), 1290 (m), 1247 (s), 1174 (m), 1067 (m), 1020 (s), 826 (s), 732 (s), 686 (s), 326 (m), 542 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 274 ([$M^+$], 100), 273 (8), 259 (36), 232 (8), 231 (46), 230 (38), 229 (34), 205 (10), 204 (9), 203 (12), 151 (7), 137 (12). **HRMS (EI, 70 eV)**: calcd. for $C_{18}H_{14}N_2O$ ([$M]^+$) 274.11006, found 274.10990.



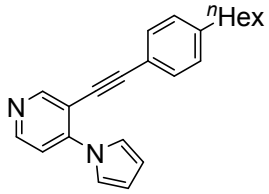

**3-((4-*tert*-Butylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4h.** Reaction of **1c** (1.57 mmol, 350 mg) and 4-*tert*-butylphenylacetylene (2.35 mmol, 425 µl) gave **4h** as a brown oil (463 mg, 98%). **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.99 (bs, 2H, $CH_{pyridine}$), 7.46 (d, $^3J$ = 8.6 Hz, 2H, $CH_{Ar}$), 7.42 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.39 (d, $^3J$ = 8.6 Hz, 2H, $CH_{Ar}$), 7.20–7.09 (m, 1H, $CH_{pyridine}$), 6.41 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 1.33 (s, 9H, $CH_{3tBu}$) ppm. **$^{13}$C[6] NMR (62.9 MHz, $CDCl_3$):** $\delta$ = 152.6 (C-*t*Bu), 131.4, 125.6 ($CH_{Ar}$), 120.8 ($CH_{pyrrole}$), 119.3 ($C_{Ar}$), 111.3 ($CH_{pyrrole}$), 97.3, 83.7 ($C_{alkyne}$), 35.0 ($C_{tBu}$), 31.2 ($CH_{3tBu}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2960 (m), 2866 (w), 2217 (w), 1724 (w), 1559 (m), 1494 (s), 1394 (m), 1340 (s), 1266 (w), 1180 (w), 1063 (m), 1018 (m), 926 (w), 831 (s), 724 (s), 677 (m), 617 (w), 562 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 300 ([$M^+$], 64), 286 (22), 285 (100), 270 (11), 269 (17), 257 (22), 256 (7), 255 (16), 244 (10), 243 (17), 242 (13), 128 (12). **HRMS (EI, 70 eV):** calcd. for $C_{21}H_{20}N_2$ ([$M]^+$) 300.16210, found 300.16172.



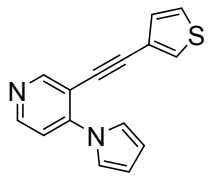

**3-((4-*n*-Propylphenly)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4i.** Reaction of **1c** (1.35 mmol, 300 mg,) and 4-*n*-propylphenylacetylene (2.02 mmol, 291 mg) gave **4i** as a white solid (332 mg, 86%), mp 74–75 °C. **$^1$H NMR (300 MHz, $C_6D_6$):** $\delta$ = 8.93 (bs, 1H, $CH_{pyridine}$), 8.22 (bs, 1H, $CH_{pyridine}$), 7.38 (d, $^3J$ = 8.3 Hz, 2H, $CH_{Ar}$) 7.23 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.85 (d, $^3J$ = 8.3 Hz, 2H, $CH_{Ar}$), 6.52 (d, $^3J$ = 5.0 Hz, 1H, $CH_{pyridine}$), 6.37 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 2.29 (t, $^3J$ = 7.6 Hz, 2H, $CH_2$), 1.40 (tq, $^3J$ = 7.6 Hz, $^3J$ = 7.3 Hz, 2H, $CH_2$), 0.77 (t, $^3J$ = 7.3 Hz, 3H, $CH_3$) ppm. **$^{13}$C NMR (75 MHz, $C_6D_6$):** $\delta$ = 155.5, 150.0 ($CH_{pyridine}$), 147.0

[5] All carbon signals of the pyridine moiety were undetectable.
[6] All carbon signals of the pyridine moiety were undetectable.

($C_{pyridine}$), 144.0 ($C_{Ar}$), 131.9, 129.0 ($CH_{Ar}$), 121.0 ($CH_{pyrrole}$), 120.3 ($C_{Ar}$), 117.2 ($CH_{pyridine}$), 111.4 ($CH_{pyrrole}$), 105.0 ($C_{pyridine}$), 97.3, 84.4 ($C_{alkyne}$), 38.1 ($CH_2$), 24.5 ($CH_2$), 13.8 ($CH_3$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2954 (w), 2926 (w), 2220 (w), 1715 (w), 1560 (m), 1497 (m), 1343 (m), 1182 (w), 1119 (w), 1062 (m), 1018 (m), 835 (s), 812 (s), 727 (s), 672 (m), 622 (w), 563 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 286 ([$M^+$], 68), 258 (20), 257 (100), 256 (19), 255 (37), 243 (12), 242 (16), 230 (4), 229 (6), 163 (9). **HRMS (EI, 70 eV):** calcd. for $C_{20}H_{18}N_2$ ([$M]^+$) 286.14645, found 286.14637.

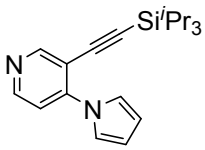



**3-((4-*n*-Hexylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4j.** Reaction of **1c** (1.35 mmol, 300 mg) and 4-*n*-hexylphenylacetylene (2.02 mmol, 424 µl) gave **4j** as a yellow oil (367 mg, 83%). **$^1$H NMR (300 M Hz, $C_6D_6$):** $\delta$ = 8.66 (s, 1H, $CH_{pyridine}$), 8.08 (d, $^3J$ = 5.3 Hz, 1H, $CH_{pyridine}$), 7.40 (d, $^3J$ = 8.3 Hz, 2H, $CH_{Ar}$), 7.23 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.90 (d, $^3J$ = 8.3 Hz, 2H, $CH_{Ar}$), 6.70 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.51 (d, $^3J$ = 5.3 Hz, 1H, $CH_{pyridine}$), 2.36 (t, $^3J$ = 7.3 Hz, 2H, $CH_2$), 1.47–1.40 (m, 2H, $CH_2$), 1.27–1.15 (m, 6H, $CH_2$), 0.87 (t, $^3J$ = 6.8 Hz, 3H, $CH_3$) ppm. **$^{13}$C NMR (75 MHz, $C_6D_6$):** $\delta$ = 154.3, 149.7 ($CH_{pyridine}$), 147.1 ($C_{pyridine}$), 144.3 ($C_{Ar}$), 131.9, 128.9 ($CH_{Ar}$), 121.0 ($CH_{pyrrole}$), 120.3 ($C_{Ar}$), 117.2 ($CH_{pyridine}$), 111.4 ($CH_{pyrrole}$), 105.0 ($C_{pyridine}$), 97.3, 84.4 ($C_{alkyne}$), 36.2, 32.0, 31.4, 29.2, 23.0 ($CH_2$), 14.3 ($CH_3$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2925 (w), 2854 (w), 2217 (w), 1722 (w), 1575 (m), 1495 (s), 1395 (w), 1339 (m), 1180 (w), 1063 (m), 1016 (m), 827 (m), 721 (s), 667 (w), 618 (w), 569 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 328 ([$M^+$], 59), 285 (6), 272 (6), 271 (15), 258 (29), 257 (100), 256 (23), 255 (43), 244 (5), 243 (20), 242 (18), 229 (6), 228 (9), 227 (6), 202 (5). **HRMS (EI, 70 eV):** calcd. for $C_{23}H_{24}N_2$ ([$M]^+$) 328.19340, found 328.19342.

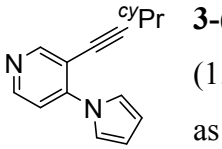



**3-(Thiophen-3-ylethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4k.** Reaction of **1c** (1.35 mmol, 300 mg,) and thiophen-3-ylacetylene (2.02 mmol, 199 µl) gave **4k** as a white solid (254 mg, 76%), mp 80–81 °C. **$^1$H NMR (250 MHz, $C_6D_6$):** $\delta$ = 8.84 (s, 1H, $CH_{pyridine}$), 8.21 (d, $^3J$ = 5.5 Hz, 1H, $CH_{pyridine}$), 7.20 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 7.14 (dd, $^3J$ = 1.2 Hz, $^3J$ = 3.0 Hz, 1H, $CH_{thioph.}$), 6.93 (dd, $^3J$ = 1.2 Hz, $^3J$ = 5.0 Hz, 1H, $CH_{thioph.}$), 6.71 (dd, $^3J$ = 5.0 Hz, $^3J$ = 3.0 Hz, 1H, $CH_{thioph.}$), 6.56 (d, $^3J$ = 5.5 Hz, 1H, $CH_{pyridine}$), 6.34 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (62.9 MHz, $C_6D_6$):** $\delta$ = 155.3, 150.1 ($CH_{pyridine}$), 147.0 ($C_{pyridine}$), 129.9, 129.7, 125.9 ($CH_{thioph.}$), 121.9 ($C_{thioph.}$), 120.9 ($CH_{pyrrole}$), 117.1 ($CH_{pyridine}$), 112.8 ($C_{pyridine}$), 111.5 ($CH_{pyrrole}$), 92.4, 84.4 ($C_{alkyne}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3100 (w), 2928 (w), 2216 (w), 1721 (w), 1558 (m), 1493 (m),

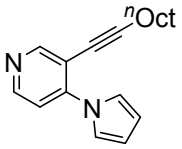
1386 (w), 1335 (m), 1116 (w), 1061 (m), 1013 (w), 827 (m), 791 (m), 731 (s), 676 (s), 621 (s), 571 (s), 483 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 250 ([$M^+$], 100), 249 (55), 248 (22), 224 (5), 223 (6), 222 (5), 216 (3), 205 (16), 179 (3). **HRMS (EI, 70 eV):** calcd. for $C_{15}H_{10}N_2S$ ([$M]^+$) 250.05592., found 250.05594.




**4-([1*H*]-pyrrol-1-yl)-3-((triisopropylsilyl)ethynyl)pyridine 4l.** Reaction of **1c** (1.35 mmol, 300 mg) and ethynyltriisopropylsilane (2.02 mmol, 449 µl) gave **4l** as a yellow oil (339 mg, 78%). **$^1$H NMR (300 MHz, $C_6D_6$):** δ = 8.99 (s, 1H, $CH_{pyridine}$), 8.27 (d, $^3J$ = 5.5 Hz, 1H, $CH_{pyridine}$), 7.30 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.55 (d, $^3J$ = 5.5 Hz, 1H, $CH_{pyridine}$), 6.45 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 1.21 (s, 3H, $CH_{i\mathrm{Pr}}$), 1.20 (s, 18H, $CH_{3i\mathrm{Pr}}$) ppm. **$^{13}$C NMR (75 MHz, $C_6D_6$):** δ = 156.6, 150.3 ($CH_{pyridine}$), 147.3 ($C_{pyridine}$), 120.9 ($CH_{pyrrole}$), 116.9 ($CH_{pyridine}$), 112.9 ($C_{pyridine}$), 111.3 ($CH_{pyridine}$), 102.2, 99.7 ($C_{alkyne}$), 18.8 ($CH_{3i\mathrm{Pr}}$), 11.7 ($CH_{i\mathrm{Pr}}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2941 (m), 2863 (m), 2154 (w), 1724 (w), 1579 (w), 1559 (w), 1497 (s), 1462 (w), 1341 (m), 1063 (m), 1018 (m), 881 (m), 831 (s), 722 (s), 667 (s), 562 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 324 ([$M^+$], 5), 283 (6), 282 (26), 281 (100), 253 (19), 239 (16), 225 (12), 211 (17), 195 (19), 181 (6), 169 (8), 168 (7), 149 (12), 113 (9). **HRMS (EI, 70 eV):** calcd. for $C_{20}H_{28}N_2Si$ ([$M]^+$) 324.20163, found 324.20133.



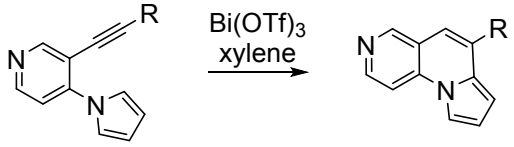

**3-([Cyclopropyl]ethynyl)-4-(1*H*-pyrrol-1-yl)pyridine 4m.** Reaction of **1c** (1.35 mmol, 300 mg) and ethynylcyclopropane (2.02 mmol, 171 µl) gave **4m** as a white solid (155 mg, 56%); mp 120–121 °C. **$^1$H NMR (300 MHz, $C_6D_6$):** δ = 8.82 (bs, 1H, $CH_{pyridine}$), 8.19–8.17 (m, 1H, $CH_{pyridine}$), 7.66–7.62 (m, 1H, $CH_{pyridine}$), 7.16–7.14 (m, 2H, $CH_{pyrrole}$), 7.35–7.33 (m, 2H, $CH_{pyrrole}$), 1.30–1.18 (m, 1H, CH), 0.57–0.53 (m, 2H, $CH_2$), 0.37–0.34 (m, 2H, $CH_2$) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 155.8, 149.5 ($CH_{pyridine}$), 147.2 ($C_{pyridine}$), 120.8 ($CH_{pyrrole}$), 117.1 ($CH_{pyridine}$), 113.6 ($C_{pyridine}$), 111.1 ($CH_{pyrrole}$), 101.4, 71.1 ($C_{alkyne}$), 8.6 ($CH_2$), 0.8 (CH) ppm. **IR (ATR):** $\tilde{\nu}$ = 2926 (w), 2857 (w), 2228 (w), 1721 (m), 1581 (w), 1558 (w), 1498 (s), 1340 (m), 1271 (s), 1121 (m), 1064 (m), 1019 (w), 952 (w), 829 (w), 724 (s), 675 (w), 579 (s) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 208 ([$M^+$], 68), 207 (100), 206 (16), 205 (17), 193 (8), 192 (6), 181 (11), 180 (38), 179 (20), 168 (3), 155 (21), 152 (4), 89 (4). **HRMS (ESI-TOF):** calcd. for $C_{14}H_{11}N_2$ ([M+H]$^+$) 207.09167, found 207.09121.




**3-(Dec-1-yn-1-yl)-4-(1*H*-pyrrol-1-yl)pyridine 4n.** Reaction of **1c** (1.57 mmol, 350 mg) and 1-decyne (2.35 mmol, 424 µl,) gave **4n** as a brown solid (244 mg, 56%), mp 76–77 °C. **$^1$H NMR (250 MHz, $CDCl_3$):** δ = 8.77 (bs, 2H, $CH_{pyridine}$), 7.36–7.23 (m, 1H, $CH_{pyridine}$), 6.97 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 6.31 (t, $^3J$ = 2.2 Hz, 2H, $CH_{pyrrole}$), 2.45 (t, $^3J$ = 7.0 Hz, 2H, $CH_2$), 1.65–1.57 (m, 2H, $CH_2$), 1.47–1.22 (m, 10H, $CH_2$), 0.89 (t, $^3J$ = 6.6 Hz, 3H, $CH_3$) ppm. **$^{13}$C NMR[7] (62.9 MHz, $CDCl_3$):** δ = 154.0, 146.4 ($CH_{pyridine}$), 121.5, 111.0 ($CH_{pyrrole}$), 31.9, 29.3, 29.2, 29.1, 28.3, 22.7, 19.8 ($CH_2$), 14.2 ($CH_3$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2923 (m), 2853 (w), 2230 (w), 1720 (w), 1575 (s), 1496 (s), 1396 (w), 1339 (m), 1180 (w), 1122 (w), 1063 (s), 1016 (s), 925 (w), 828 (m), 720 (s), 667 (m), 617 (m), 570 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 280 ([$M^+$], 7), 279 (8), 209 (8), 195 (27), 193 (9), 183 (16), 182 (100), 181 (48), 169 (14), 168 (11), 167 (4), 155 (11), 154 (5). **HRMS (EI, 70 eV):** calcd. for $C_{19}H_{24}N_2$ ([$M]^+$) 280.19340, found 280.19281.

[7] Carbon signals for the *meta*- and *para*-position of the pyridine moiety were undetectable as well as the alkyne signals.

## Cycloisomerization to give [1,6]naphthyridines 5a–n

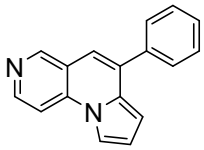



**4a-n** **5a-n**

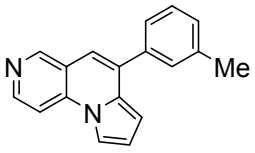
### General procedure

In a pressure tube the Sonogashira product **4a-n** was dissolved in xylene (3 ml, isomeric mixture) under an argon atmosphere. The catalyst $Bi(OTf)_3$ (1 eq.) was added to the mixture. The solution was stirred at 120 °C for 24 h. After cooling to room temperature the crude product was diluted with water and extracted with ethyl acetate. For further purification the organic solvent was evaporated and column chromatography (heptane/acetone, 2:1 → 1:1) was performed.

### Product Characterisation

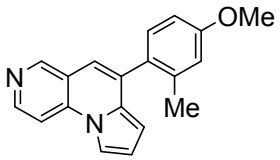



**6-(Phenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5a.** Reaction of **4a** (0.41 mmol, 100 mg) with $Bi(OTf)_3$ (0.41 mmol, 268 mg) gave **5a** as a white solid (55 mg, 55%); mp 217–218 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.99–8.97 (bs, 1H, $CH_{naphthyr.}$), 8.62 (d, $^3J$ = 6.1 Hz, 1H, $CH_{naphthyr.}$), 7.95–7.94 (m, 1H, $CH_{naphthyr.}$), 7.79 (d, $^3J$ = 6.1 Hz, 1H, $CH_{naphthyr.}$), 7.71–7.68 (m, 2H, $CH_{Ph}$), 7.53–7.47 (m, 3H, $CH_{Ph}$), 7.05–7.03 (m, 1H, $CH_{pyrrole}$), 6.93–6.91 (m, 1H, $CH_{pyrrole}$), 6.75–6.72 (m, 1H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (62.9 MHz, $CDCl_3$):** $\delta$ = 149.2, 145.4 ($CH_{naphthyr.}$), 138.2, 138.1, 135.5, 131.6 ($C_{Ar}$), 129.0 ($CH_{Ph}$), 129.0 ($CH_{Ph}$), 128.5 ($CH_{Ph}$), 120.6 ($C_{naphthyr.}$), 115.2, 114.8, 114.0, 109.1 ($CH_{Ar}$), 105.9 ($CH_{pyrrole}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 1673 (w), 1602 (m), 1492 (w), 1258 (s), 1231 (s), 1169 (s), 1035 (s), 816 (w), 766 (m), 697 (m), 631 (s), 573 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 244 ([$M^+$], 100), 243 (33), 242 (17), 216 (5), 215 (4), 189 (4), 163 (2). **HRMS (EI, 70 eV):** calcd. for $C_{17}H_{12}N_2$ ([M]$^+$) 244.09950, found 244.09913.

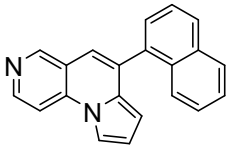



**6-(3-Methylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5b.** Reaction of **4b** (0.58 mmol, 150 mg) with $Bi(OTf)_3$ (0.58 mmol, 381 mg) gave **5b** as a white solid (76 mg, 51%); mp 125–126 °C. **$^1$H NMR (300 MHz, $C_6D_6$):** $\delta$ = 8.80 (s, 1H, $CH_{naphthyr.}$), 8.45 (d, $^3J$ = 5.7 Hz, 1H, $CH_{naphthyr.}$), 7.41 (d, $^3J$ = 7.6 Hz, 1H, $CH_{Ar}$), 7.38–7.36 (m, 2H, $CH_{pyrrole/Ar}$), 7.20 (dd, $^3J$ = 7.6 Hz, $^3J$ = 7.6 Hz, 1H, $CH_{Ar}$), 7.05 (d, $^3J$ = 7.6 Hz, 1H, $CH_{Ar}$), 6.91 (d, $^3J$ = 5.7 Hz, 1H, $CH_{naphthyr.}$), 6.71–6.67 (m, 2H, $CH_{pyrrole}$), 6.58 (s, 1H, $CH_{naphthyr.}$), 2.19 (s, 3H, Me) ppm. **$^{13}$C NMR (75 MHz, $C_6D_6$):** $\delta$ = 151.1, 147.5

($CH_{naphthyr.}$), 139.0, 138.4, 137.1, 134.5, 131.6 ($C_{Ar}$), 129.4, 129.3, 128.8, 125.9 ($CH_{Ar}$), 120.3 ($C_{Ar}$), 115.3, 114.3, 113.5, 108.3, 105.1 ($CH_{Ar}$), 21.4 ($CH_3$) ppm. **IR (ATR):** $\tilde{\nu}$ = 3029 (w), 2919 (w), 1732 (w), 1597 (m), 1484 (m), 1414 (w), 1363 (w), 1302 (w), 1202 (w), 1131 (w), 1037 (w), 851 (w), 810 (m), 787 (s), 709 (s), 645 (w), 569 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 258 ([$M^+$], 100), 257 (16), 256 (5), 255 (9), 243 (6), 242 (13), 229 (2), 214 (2), 202 (2). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{14}N_2$ ([$M]^+$) 258.11515, found 258.11553.

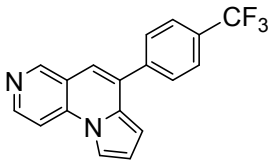



**6-(4-Methoxy-2-methylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5c.** Reaction of **4c** (0.52 mmol, 150 mg) with $Bi(OTf)_3$ (0.52 mmol, 338 mg) gave **5c** as a yellow solid (109 mg, 73%); mp 92–93 °C. **$^1$H NMR (300 MHz, $C_6D_6$):** $\delta$ = 8.80 (s, 1H, $CH_{naphthyr.}$), 8.47 (d, $^3J$ = 5.7 Hz, 1H, $CH_{naphthyr.}$), 7.42 (dd, $^3J$ = 3.0 Hz, $^4J$ = 1.3 Hz, 1H, $CH_{pyrrole}$), 7.22 (d, $^3J$ = 8.4 Hz, 1H, $CH_{Ar}$), 7.01 (d, $^3J$ = 5.7 Hz, 1H, $CH_{naphthyr.}$), 6.87 (d, $^4J$ = 2.6 Hz, 1H, $CH_{Ar}$), 6.75 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.6 Hz, 1H, $CH_{Ar}$), 6.67 (dd, $^3J$ = 3.8 Hz, $^3J$ = 3.0 Hz, 1H, $CH_{pyrrole}$), 6.49 (s, 1H, $CH_{naphthyr.}$), 6.32 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.3 Hz, 1H, $CH_{pyrrole}$), 3.44 (s, 3H, OMe), 2.10 (s, 3H, Me) ppm. **$^{13}$C NMR (75 MHz, $C_6D_6$):** $\delta$ = 160.1 (C), 150.9, 147.4 (CH), 138.1, 137.3, 134.1, 132.5, 131.1 (C), 130.6 (CH), 120.1 (C), 116.3, 116.3, 114.4, 113.4, 111.5, 108.4, 105.2 (CH), 54.9 (OMe), 20.1 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 2951 (w), 2921 (w), 1601 (m), 1491 (m), 1421 (w), 1364 (w), 1250 (s), 1232 (s), 1167 (s), 1113 (w), 1033 (s), 811 (m), 718 (w), 701 (m), 632 (s), 571 (w) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 288 ([$M^+$], 99), 287 (100), 273 (6), 272 (8), 256 (5), 255 (7), 245 (8), 244 (12), 243 (25), 242 (13), 229 (7), 205 (3). **HRMS (EI, 70 eV):** calcd. for $C_{19}H_{16}ON_2$ ([$M]^+$) 288.12511, found 288.12571.

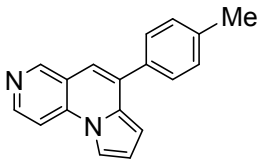



**6-(Naphth-1-yl)pyrrolo[1,2-*a*][1,6]naphthyridine 5d.** Reaction of **4d** (0.68 mmol, 200 mg) with $Bi(OTf)_3$ (0.68 mmol, 446 mg) gave **5d** as a white solid (100 mg, 51%); mp 103–104 °C. **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.96 (s, 1H, $CH_{naphthyr.}$), 8.64–8.66 (m, 1H, $CH_{naphthyr.}$), 7.97–7.90 (m, 3H, $CH_{Ar/pyrrole}$), 7.84 (d, $^3J$ = 8.5 Hz, 1H, $CH_{Ar}$), 7.74 (d, $^3J$ = 5.7 Hz, 1H, $CH_{Ar}$), 7.62–7.47 (m, 3H, $CH_{Ar}$), 7.41–7.34 (m, 1H, $CH_{naphthyl.}$), 7.08 (s, 1H, $CH_{naphthyr.}$), 6.79 (dd, $^3J$ = 3.8 Hz, $^3J$ = 3.0 Hz, 1H, $CH_{pyrrole}$), 6.20 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.2 Hz, 1H, $CH_{pyrrole}$) ppm. **$^{13}$C NMR (62.9 MHz, $CDCl_3$):** $\delta$ = 150.7, 147.2 (CH), 137.6, 135.8, 133.9, 133.2, 132.5, 131.8 (C), 128.8, 128.5, 127.1, 126.3, 126.2, 125.9, 125.5 (CH), 120.0 (C), 116.9, 114.6, 113.3, 108.6, 105.5 (CH) ppm. **IR (ATR):** $\tilde{\nu}$ = 3042 (w), 1598 (w), 1489 (w), 1416 (w), 1364 (w), 1299 (w), 1197 (w), 1030 (m), 906 (m), 854 (w), 800 (m), 774 (s), 712 (s), 664 (m), 569 (m) $cm^{-1}$. **MS**

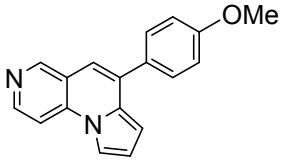
**(EI, 70 eV):** *m/z* (%) = 294 ([M$^+$], 100), 293 (93), 292 (54), 291 (12), 290 (6), 265 (6), 264 (6), 238 (4). **HRMS (ESI-TOF):** calcd. for $C_{21}H_{15}N_2$ ([M+H]$^+$) 295.12352, found 295.12336.



**6-(4-[Trifluoromethyl]phenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5e.** Reaction of **4e** (0.64 mmol, 200 mg) with $Bi(OTf)_3$ (0.64 mmol, 420 mg) gave **5e** as a white solid (49 mg, 35%); mp 110–111 °C. **$^1$H NMR (300 MHz, $C_6D_6$):** $\delta$ = 8.79 (s, 1H, $CH_{naphthyr.}$), 8.46 (d, $^3J$ = 5.8 Hz, 1H, $CH_{naphthyr.}$), 7.44 (d, $^3J$ = 8.1 Hz, 2H, $CH_{Ar}$), 7.35–7.33 (m, 1H, $CH_{pyrrole}$), 7.32 (d, $^3J$ = 8.1 Hz, 2H, $CH_{Ar}$), 6.88 (d, $^3J$ = 5.8 Hz, 1H, $CH_{naphthyr.}$), 6.67 (dd, $^3J$ = 3.8 Hz, $^3J$ = 3.0 Hz, 1H, $CH_{pyrrole}$), 6.46 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.3 Hz, 1H, $CH_{pyrrole}$), 6.39 (s, 1H, $CH_{naphthyr.}$) ppm. **$^{13}$C NMR (75 MHz, $C_6D_6$):** $\delta$ = 151.3, 148.0 ($CH_{naphthyr.}$), 142.3, 137.3, 132.7, 130.7 ($C_{Ar}$), 130.5 (q, $^2J_{C,F}$ = 32.4 Hz, $C_{Ar}$), 128.9 (CH), 125.8 (q, $^3J_{C,F}$ = 3.8 Hz, $CH_{Ar}$), 125.0 (q, $^1J_{C,F}$ = 272.1 Hz, $CF_3$), 119.8 ($C_{naphthyr.}$), 116.0, 114.4, 113.8, 108.3, 104.9 (CH) ppm. **$^{19}$F NMR (282 MHz, $C_6D_6$):** $\delta$ = −62.06 ppm. **IR (ATR):** $\tilde{\nu}$ = 3106 (w), 3026 (w), 1616 (w), 1600 (m), 1500 (w), 1625 (w), 1370 (w), 1322 (s), 1165 (m), 1096 (s), 1066 (s), 1015 (m), 830 (s), 712 (s), 689 (s), 614 (m), 567 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 312 ([M$^+$], 100), 311 (20), 293 (4), 243 (7), 242 (10), 214 (3). **HRMS (EI, 70 eV):** calcd. for $C_{18}H_{11}N_2F_3$ ([M]$^+$) 312.08688, found 312.08676.

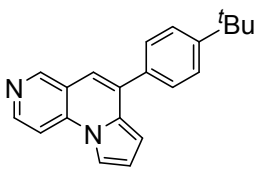


**6-(4-Methylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5f.** Reaction of **4f** (0.58 mmol, 150 mg) with $Bi(OTf)_3$ (0.58 mmol, 381 mg) gave **5f** as a white solid (74 mg, 50%); mp 130–131 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.93 (s, 1H, $CH_{naphthyr.}$), 8.57 (d, $^3J$ = 6.0 Hz, 1H, $CH_{naphthyr.}$) 7.90 (s, 1H, $CH_{naphtyr.}$), 7.83 (d, $^3J$ = 6.0 Hz, 1H, $CH_{naphthyr.}$), 7.52 (d, $^3J$ = 8.0 Hz, 2H, $CH_{Ar}$), 7.26 (d, $^3J$ = 8.0 Hz, 2H, $CH_{Ar}$), 6.97–6.95 (m, 1H, $CH_{pyrrole}$), 6.90–6.88 (m, 1H, $CH_{pyrrole}$), 6.71–6.70 (m, 1H, $CH_{pyrrole}$), 2.38 (s, 3H, Me) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 147.3, 143.3 ($CH_{naphthyr.}$), 139.2, 138.9, 136.3, 134.9, 131.8 ($C_{Ar}$), 129.8, 128.3 ($CH_{Ar}$), 121.0 ($C_{naphthyr.}$), 115.9, 114.4, 114.1, 109.6, 106.6 ($CH_{Ar}$), 21.6 (Me) ppm. **IR (ATR):** $\tilde{\nu}$ = 1600 (m), 1496 (m), 1424 (w), 1367 (w), 1254 (s), 1161 (s), 1133 (m), 1028 (s), 808 (s), 712 (m), 635 (s), 559 (w) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 258 ([M$^+$], 100), 257 (12), 243 (4), 242 (9), 202 (2), 129 (2), 128 (9). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{15}N_2$ ([M+H]$^+$) 259.12352, found 259.12432.

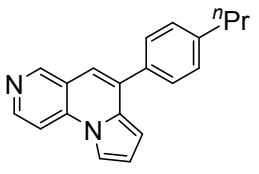


**6-(4-Methoxyphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5g.** Reaction of **4g** (0.64 mmol, 175 mg) with $Bi(OTf)_3$ (0.64 mmol,

419 mg) gave **5g** as a white solid (136 mg, 78%); mp 137–138 °C. **$^1$H NMR (300 MHz, $CDCl_3$):** $\delta$ = 8.97 (s, 1H, $CH_{naphthyr.}$), 8.62 (d, $^3J$ = 6.1 Hz, 1H, $CH_{naphthyr.}$), 7.95 (dd, $^3J$ = 3.1 Hz, $^4J$ = 1.2 Hz, 1H, $CH_{pyrrole}$), 7.83 (d, $^3J$ = 6.1 Hz, 1H, $CH_{naphthyr.}$), 7.64 (d, $^3J$ = 8.9 Hz, 2H, $CH_{Ar}$), 7.04 (d, $^3J$ = 8.9 Hz, 2H, $CH_{Ar}$), 7.00 (s, 1H, $CH_{naphthyr.}$), 6.93 (dd, $^3J$ = 3.1 Hz, $^3J$ = 3.8 Hz, 1H, $CH_{pyrrole}$), 6.74 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.2 Hz, 1H, $CH_{pyrrole}$), 3.90 (s, 3H, OMe) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$):** $\delta$ = 160.1 ($C_{Ar}$), 150.4, 146.6 ($CH_{naphthyr.}$), 137.4, 134.4, 131.7 ($C_{Ar}$), 130.8 ($CH_{Ar}$), 129.6 ($CH_{Ar}$), 120.4 ($C_{naphthyr.}$), 114.6, 114.5 ($CH_{Ar}$), 114.3 ($CH_{Ar}$), 113.6 ($CH_{naphthyr.}$), 108.6 ($C_{naphthyr.}$), 105.2 ($CH_{pyrrole}$), 55.5 (OMe) ppm. **IR (ATR):** $\tilde{\nu}$ = 1599 (w), 1493 (w), 1366 (w), 1249 (s), 1232 (s), 1170 (s), 1109 (w), 1036 (s), 1019 (s), 829 (m), 806 (m), 714 (w), 681 (s), 636 (s), 568 (s) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 274 ([M$^+$], 100), 259 (19), 231 (21), 230 (17), 29 (20), 205 (9), 203 (7), 176 (5). **HRMS (ESI-TOF):** calcd. for $C_{18}H_{15}ON_2$ ([M+H]$^+$) 275.11844, found 275.12061.

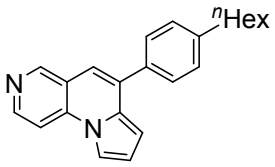



**6-(4-*tert*-Butylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5h.** Reaction of **4h** (0.67 mmol, 200 mg,) with $Bi(OTf)_3$ (0.67 mmol, 437 mg) gave **5h** as a white solid (82 mg, 41%); mp 70–71 °C. **$^1$H NMR (250 MHz, $CDCl_3$):** $\delta$ = 8.94 (s, 1H, $CH_{naphthyr.}$), 8.59 (d, $^3J$ = 6.0 Hz, 1H, $CH_{naphthyr.}$), 7.89 (dd, $^3J$ = 3.0 Hz, $^4J$ = 1.3 Hz, 1H, $CH_{pyrrole}$), 7.89 (d, $^3J$ = 6.0 Hz, 1H, $CH_{naphthyr.}$), 7.66–7.62 (m, 2H, $CH_{Ar}$), 7.55–7.50 (m, 2H, $CH_{Ar}$), 7.00 (s, 1H, $CH_{naphthyr.}$), 6.87 (dd, $^3J$ = 3.0 Hz, $^3J$ = 3.8 Hz, 1H, $CH_{pyrrole}$), 6.73 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.3 Hz, 1H, $CH_{pyrrole}$), 1.40 (s, 9H, $CH_{3tBu}$) ppm. **$^{13}$C NMR (62.9 MHz, $CDCl_3$):** $\delta$ = 151.8 ($C_{Ar}$), 150.5, 146.7 ($CH_{naphthyr.}$), 137.4, 135.4, 134.6, 131.5 ($C_{Ar}$), 128.1, 125.8 ($CH_{Ar}$), 120.4 ($C_{naphthyr.}$), 114.9, 114.6, 113.5, 108.6, 105.3 (CH), 34.9 (C), 31.5 ($CH_{3tBu}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2957 (m), 2865 (w), 1597 (m), 1491 (m), 1421 (w), 1361 (m), 1267 (w), 1178 (w), 1108 (w), 1037 (w), 908 (w), 830 (s), 809 (m), 714 (s), 701 (s), 621 (w), 542 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 300 ([M$^+$], 100), 286 (18), 285 (81), 284 (5), 270 (11), 269 (10), 268 (7), 257 (21), 256 (6), 255 (15), 243 (12), 242 (14), 214 (3), 143 (6), 128 (28). **HRMS (EI, 70 eV):** calcd. for $C_{21}H_{20}N_2$ ([M]$^+$) 300.39690, found 300.39686.

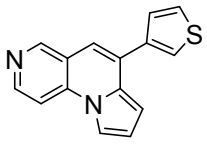



**6-(4-*n*-Propylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5i.** Reaction of **4i** (0.45 mmol, 130 mg) with $Bi(OTf)_3$ (0.45 mmol, 298 mg) gave **5i** as a yellow solid (68 mg, 53%); mp 90–91 °C. **$^1$H NMR (300 MHz, $C_6D_6$):** $\delta$ = 8.79 (s, 1H, $CH_{naphthyr.}$), 8.44 (d, $^3J$ = 5.7 Hz, 1H, $CH_{naphthyr.}$), 7.53 (d, $^3J$ = 8.3 Hz, 1H, $CH_{Ar}$), 7.37 (dd, $^3J$ = 2.9 Hz, $^4J$ = 1.4 Hz, 1H, $CH_{pyrrole}$), 7.13 (d,

$^3J$ = 8.3 Hz, 1H, $CH_{Ar}$), 6.92 (d, $^3J$ = 5.7 Hz, 1H, $CH_{naphthyr.}$), 6.72 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.4 Hz, 1H, $CH_{pyrrole}$), 6.68 (dd, $^3J$ = 3.8 Hz, $^3J$ = 2.9 Hz, 1H, $CH_{pyrrole}$), 6.60 (s, 1H, $CH_{naphthyr.}$), 2.50 (t, $^3J$ = 7.6 Hz, 2H, $CH_2$), 1.59 (tq, $^3J$ = 7.6 Hz, $^3J$ = 7.3 Hz, 2H, $CH_2$), 0.90 (t, $^3J$ = 7.3 Hz, 3H, $CH_3$) ppm. **$^{13}$C NMR (75 MHz, $C_6D_6$):** $\delta$ = 151.1, 147.4 ($CH_{naphthyr.}$), 143.1, 137.1, 136.4, 134.4, 131.6 (C), 129.0, 128.6 ($CH_{Ar}$), 120.3 ($C_{naphthyr.}$), 115.2, 114.3, 113.5, 108.2, 105.1 ($CH_{Ar}$), 38.1, 24.9 ($CH_2$), 14.0 ($CH_3$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2955 (w), 2926 (w), 2868 (w), 1596 (m), 1489 (m), 1422 (m), 1364 (w), 1302 (w), 1177 (w), 829 (m), 808 (s), 713 (s), 700 (s), 568 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 286 ([M$^+$], 100), 258 (13), 257 (66), 256 (11), 255 (25), 243 (6), 242 (8), 229 (3), 228 (3), 202 (2). **HRMS (EI, 70 eV):** calcd. for $C_{20}H_{18}N_2$ ([M]$^+$) 286.14645, found 286.14708.




**6-(4-*n*-Hexylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5j.** Reaction of **4j** (0.46 mmol, 150 mg,) with $Bi(OTf)_3$ (0.46 mmol, 299 mg) gave **5j** as a yellow oil (67 mg, 45%). **$^1$H NMR (300 MHz, $C_6D_6$):** $\delta$ = 8.79 (s, 1H, $CH_{naphthyr.}$), 8.44 (d, $^3J$ = 5.8 Hz, 1H, $CH_{naphthyr.}$), 7.55 (d, $^3J$ = 8.2 Hz, 2H, $CH_{Ar}$), 7.37 (dd, $^3J$ = 3.0 Hz, $^4J$ = 1.3 Hz, 1H, $CH_{pyrrole}$), 7.17 (d, $^3J$ = 8.2 Hz, 2H, $CH_{Ar}$), 6.91 (d, $^3J$ = 5.8 Hz, 1H, $CH_{naphthyr.}$), 6.73 (dd, $^3J$ = 3.8 Hz, $^4J$ = 1.3 Hz, 1H, $CH_{pyrrole}$), 6.69 (dd, $^3J$ = 3.8 Hz, $^3J$ = 3.8 Hz, 1H, $CH_{pyrrole}$), 6.61 (s, 1H, $CH_{naphthyr.}$), 2.57 (t, $^3J$ = 7.7 Hz, 2H, $CH_2$), 1.62–1.58 (m, 2H, $CH_2$), 1.34–1.24 (m, 6H, $CH_2$), 0.90 (t, $^3J$ = 6.8 Hz, 3H, $CH_3$) ppm. **$^{13}$C NMR (75 MHz, $C_6D_6$):** $\delta$ = 151.1, 147.4 ($CH_{naphthyr.}$), 143.4, 137.1, 136.4, 134.4, 131.6 (C), 129.0, 128.7 ($CH_{Ar}$), 120.3 (C), 115.2, 114.3, 113.5, 108.3, 105.1 (CH), 36.2, 32.2, 31.9, 29.4, 23.1 ($CH_2$), 14.4 ($CH_3$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2923 (s), 2853 (m), 1597 (m), 1491 (m), 1422 (m), 1365 (w), 1303 (w), 1176 (w), 1037 (w), 828 (s), 810 (s), 714 (s), 702 (s), 569 (m) cm$^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 328 ([M$^+$], 100), 271 (5), 270 (3), 258 (13), 257 (53), 256 (10), 255 (22), 243 (4), 242 (7), 229 (3), 228 (3). **HRMS (EI, 70 eV):** calcd. for $C_{23}H_{24}N_2$ ([M]$^+$) 328.19340, found 328.19321.



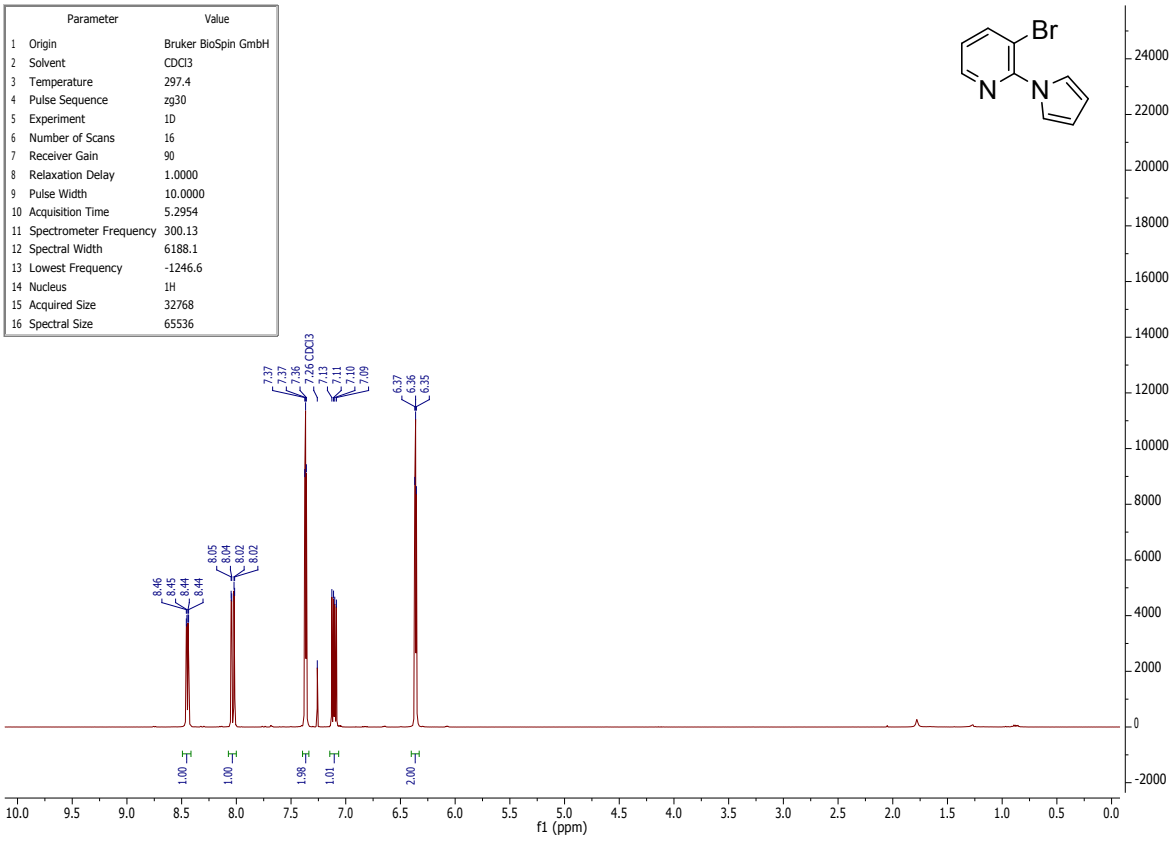

**6-(Thiophen-3-yl)pyrrolo[1,2-*a*][1,6]naphthyridine 5k.** Reaction of **4k** (0.46 mmol, 115 mg,) with $Bi(OTf)_3$ (0.46 mmol, 301 mg) gave **5k** as a white solid (82 mg, 72%); mp 234–235 °C. **$^1$H NMR (300 MHz, $C_6D_6$):** $\delta$ = 8.76 (s, 1H, $CH_{naphthyr.}$), 8.43 (d, $^3J$ = 5.7 Hz, 1H, $CH_{naphthyr.}$), 7.34 (dd, $^3J$ = 2.8 Hz, $^4J$ = 1.6 Hz, 1H, $CH_{pyrrole}$), 7.26 (dd, $^3J$ = 5.0 Hz, $^4J$ = 1.3 Hz, 1H, $CH_{thioph.}$), 7.19 (dd, $^4J$ = 3.0 Hz, $^4J$ = 1.3 Hz, 1H, $CH_{thioph.}$), 6.97 (dd, $^3J$ = 5.0 Hz, $^4J$ = 3.0 Hz, 1H, $CH_{thioph.}$), 6.88 (d, $^3J$ = 5.7 Hz, 1H, $CH_{naphthyr.}$), 6.70–6.66 (m, 2H, $CH_{pyrrole}$), 6.59 (s, 1H, $CH_{naphtyr.}$) ppm.

**$^{13}$C NMR (75 MHz, $C_6D_6$):** $\delta$ = 151.0, 147.5 ($CH_{naphthyr.}$), 139.3, 137.0, 131.1, 128.9 (C), 127.9, 126.0, 123.6 (CH), 120.0 ($C_{naphthyr.}$), 114.9, 114.2, 113.5, 108.2, 105.0 ($CH_{naphthyr.}$) ppm. **IR (ATR):** $\tilde{\nu}$ = 2922 (w), 1599 (w), 1495 (w), 1422 (w), 1357 (w), 1258 (s), 1230 (s), 1171 (s), 1034 (s), 838 (w), 785 (m), 706 (s), 636 (s), 570 (m), 540 (m) $cm^{-1}$. **MS (EI, 70 eV):** *m/z* (%) = 250 ([$M^+$], 100), 249 (18), 248 (9), 223 (3), 222 (2), 205 (10), 204 (2), 203 (3), 178 (3), 151 (2). **HRMS (EI, 70 eV):** calcd. for $C_{15}H_{10}N_2S$ ([$M]^+$) 250.05592, found 250.05610.

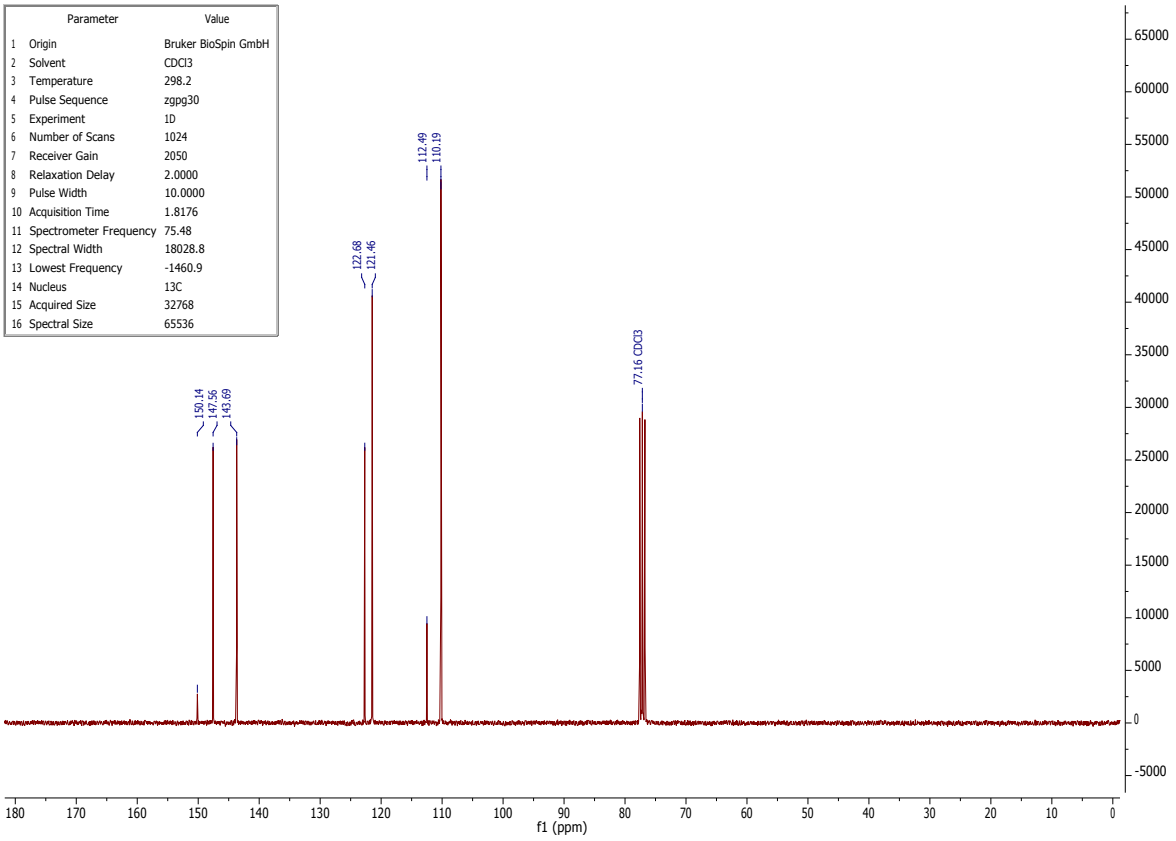
# $^{1}H/^{13}C/^{19}F$ NMR spectra for all substrates

## 3-Bromo-2-([1*H*]-pyrrol-1-yl)pyridine 1a

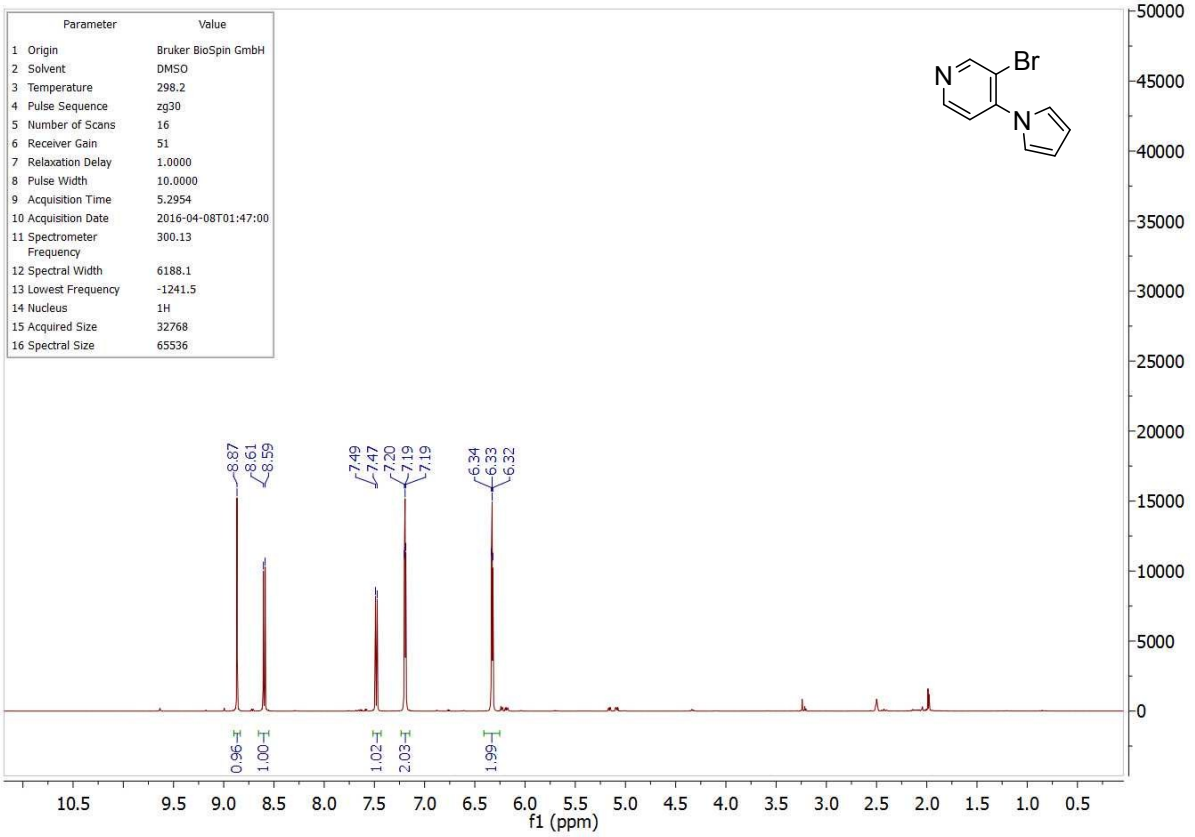
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 297.4 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 90 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.6 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

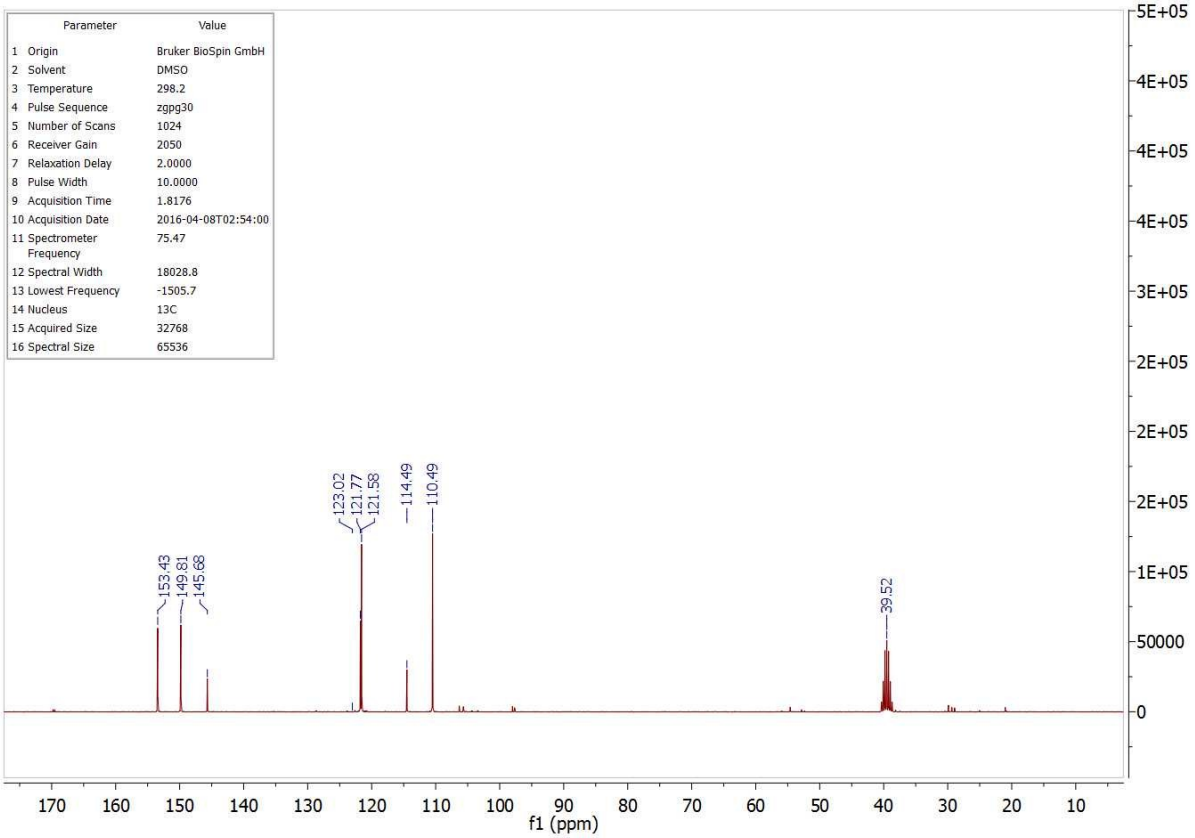



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1460.9 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |



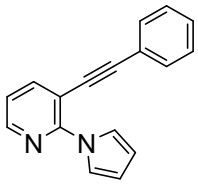
## 3-Bromo-4-([1*H*]-pyrrol-1-yl)pyridine 1c

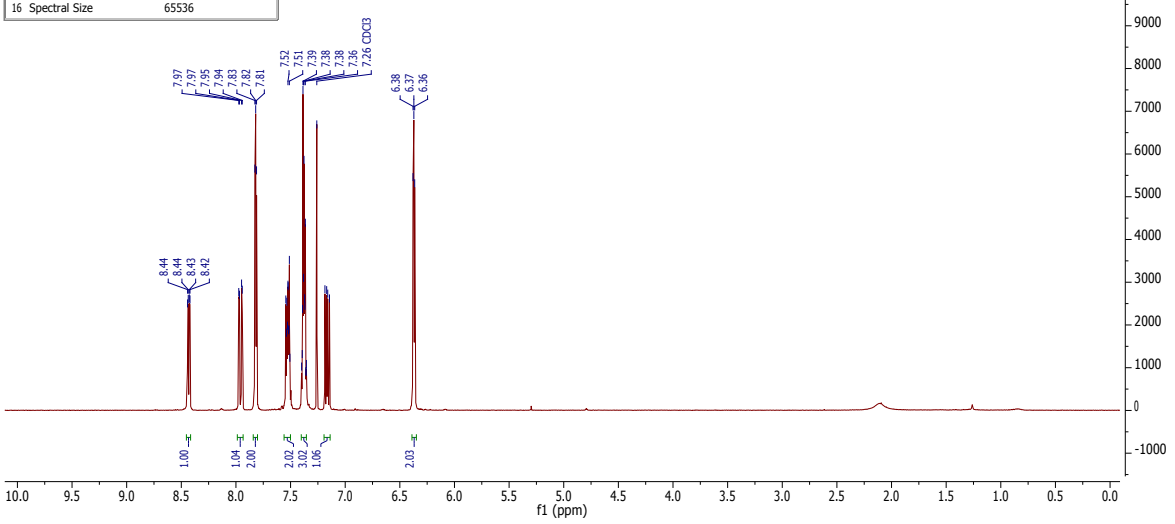


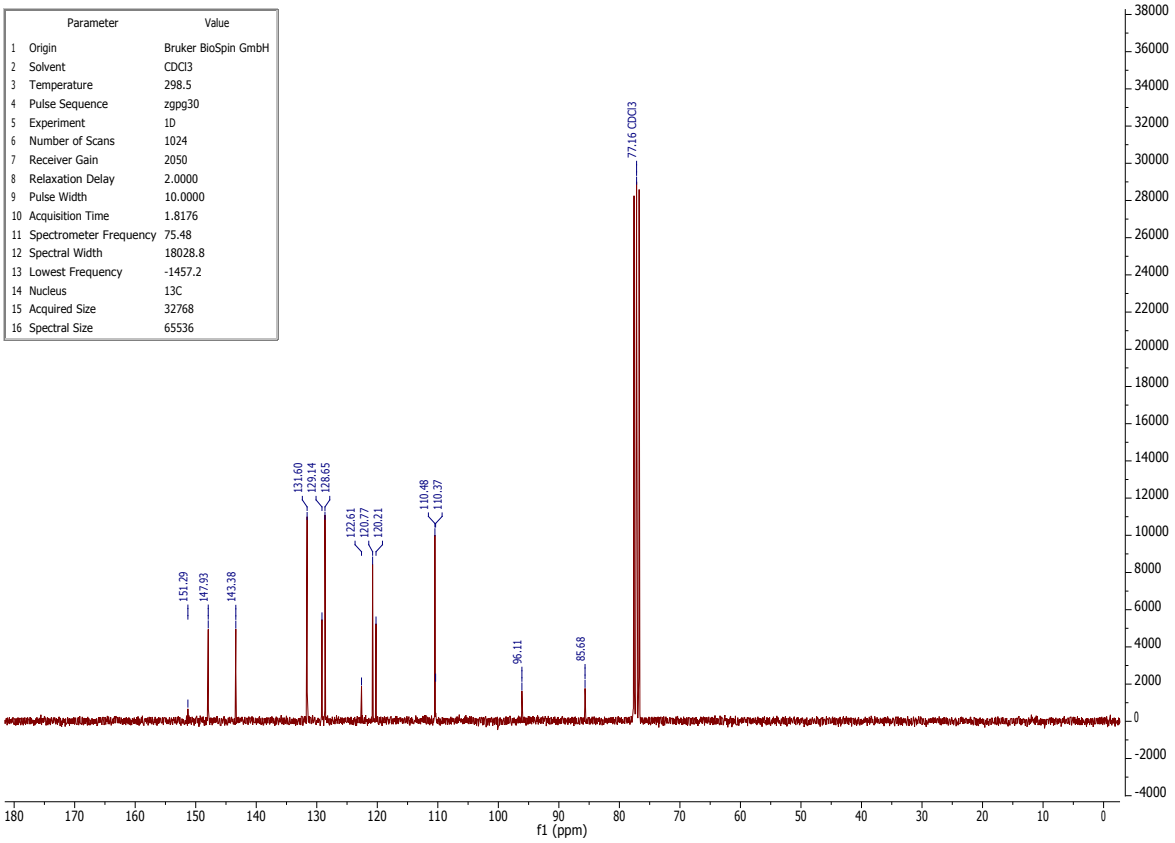
## 3-(Phenylethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2a

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 287 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.9 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |



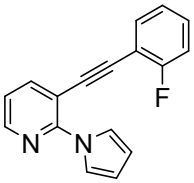



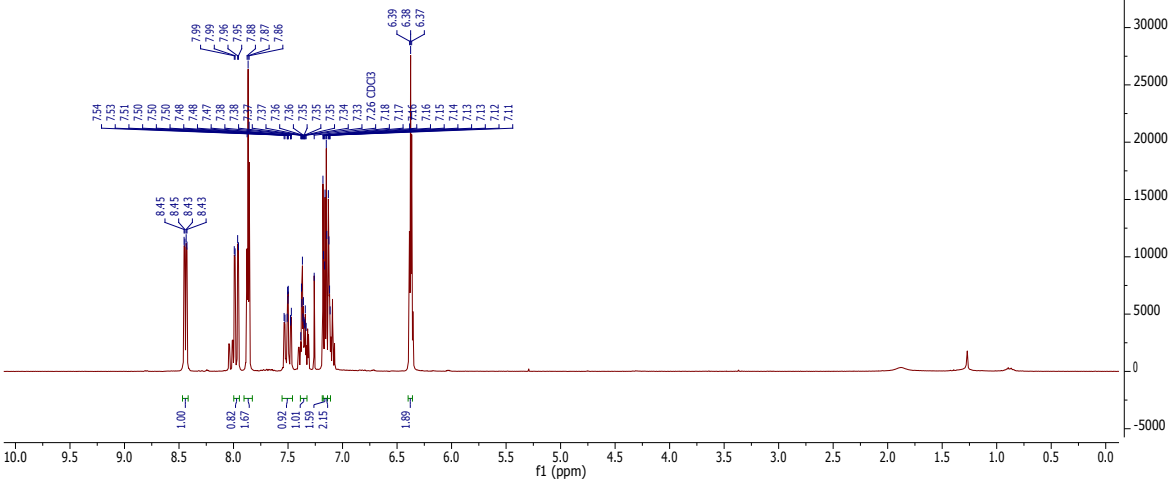

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.5 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1457.2 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |



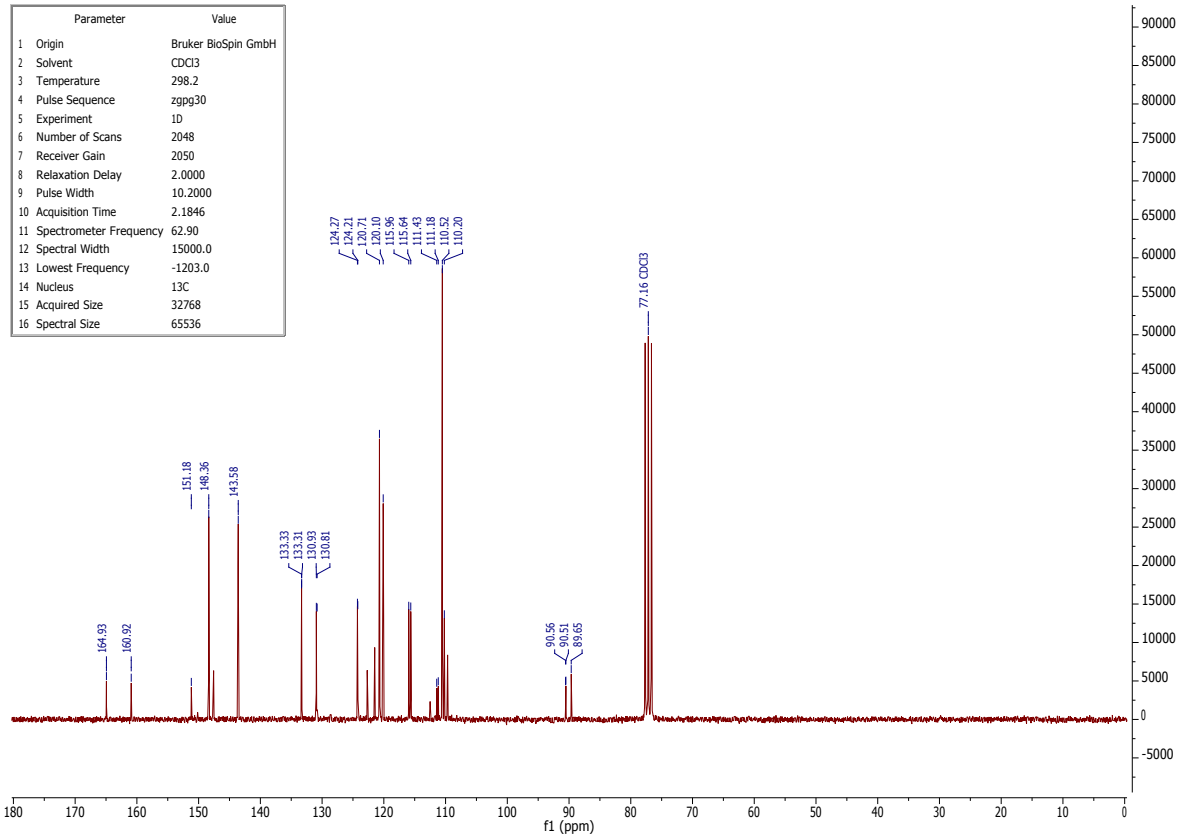
## 3-((2-Fluorophenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2b

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 32 |
| 7 | Receiver Gain | 645 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 11.4000 |
| 10 | Acquisition Time | 6.3439 |
| 11 | Spectrometer Frequency | 250.13 |
| 12 | Spectral Width | 5165.3 |
| 13 | Lowest Frequency | -1038.7 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

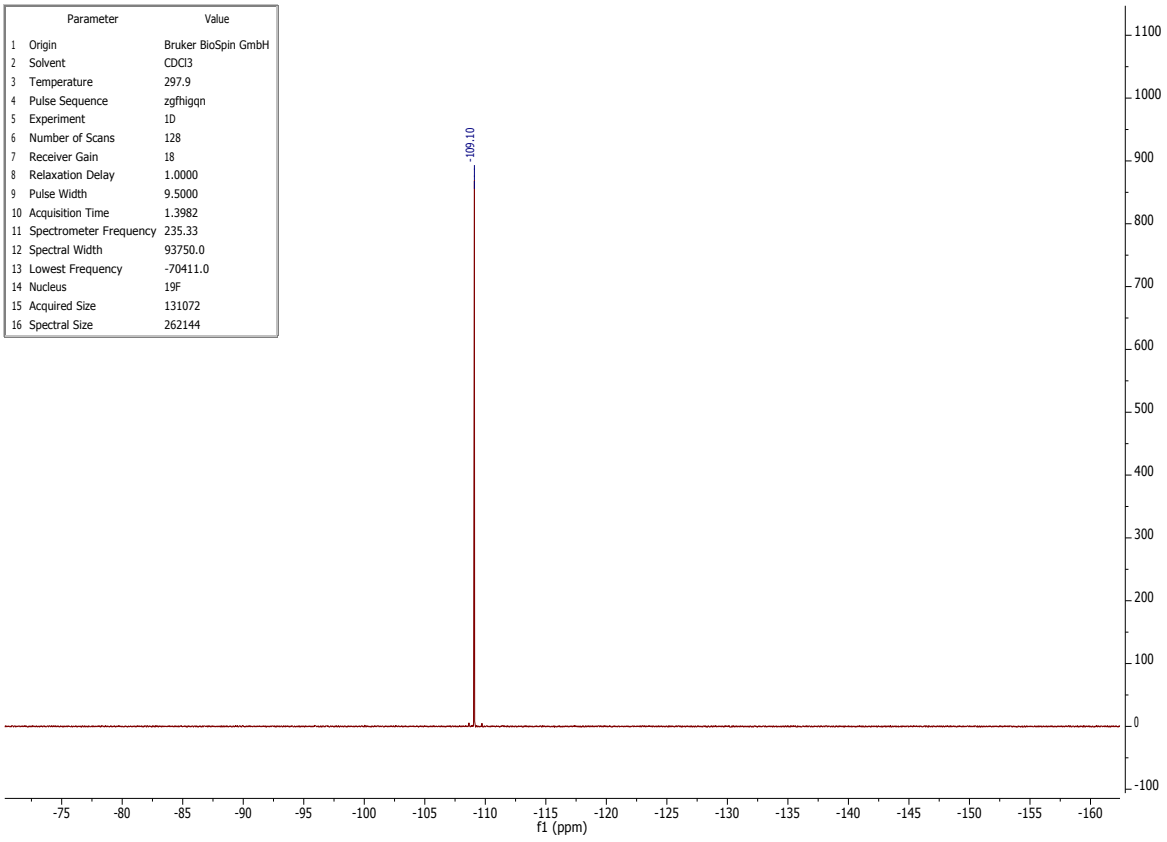



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 2048 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.2000 |
| 10 | Acquisition Time | 2.1846 |
| 11 | Spectrometer Frequency | 62.90 |
| 12 | Spectral Width | 15000.0 |
| 13 | Lowest Frequency | -1203.0 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

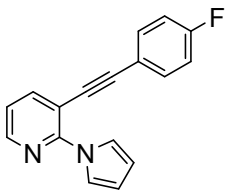


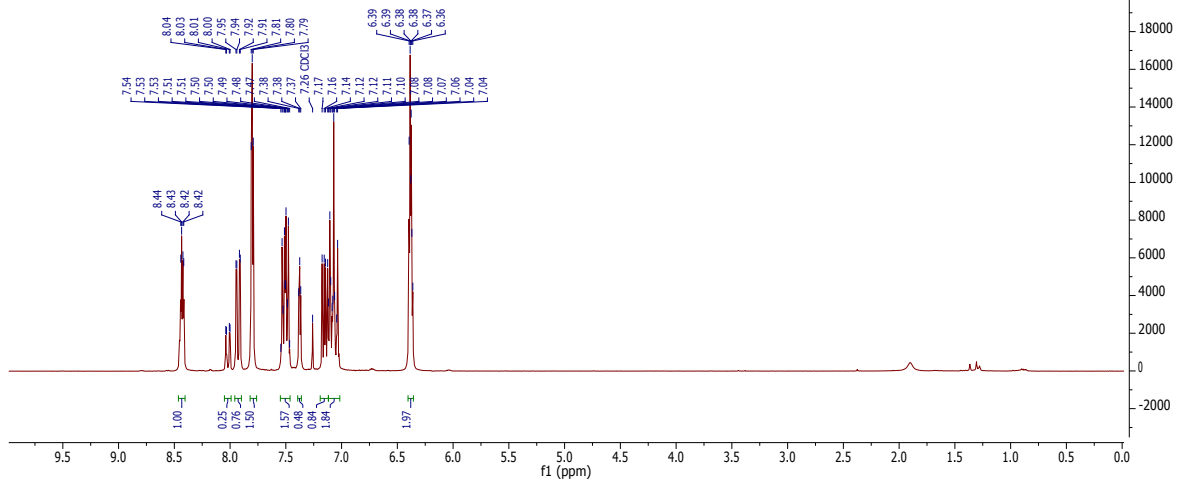
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 297.9 |
| 4 | Pulse Sequence | zgfhigqn |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 128 |
| 7 | Receiver Gain | 18 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 9.5000 |
| 10 | Acquisition Time | 1.3982 |
| 11 | Spectrometer Frequency | 235.33 |
| 12 | Spectral Width | 93750.0 |
| 13 | Lowest Frequency | -70411.0 |
| 14 | Nucleus | 19F |
| 15 | Acquired Size | 131072 |
| 16 | Spectral Size | 262144 |



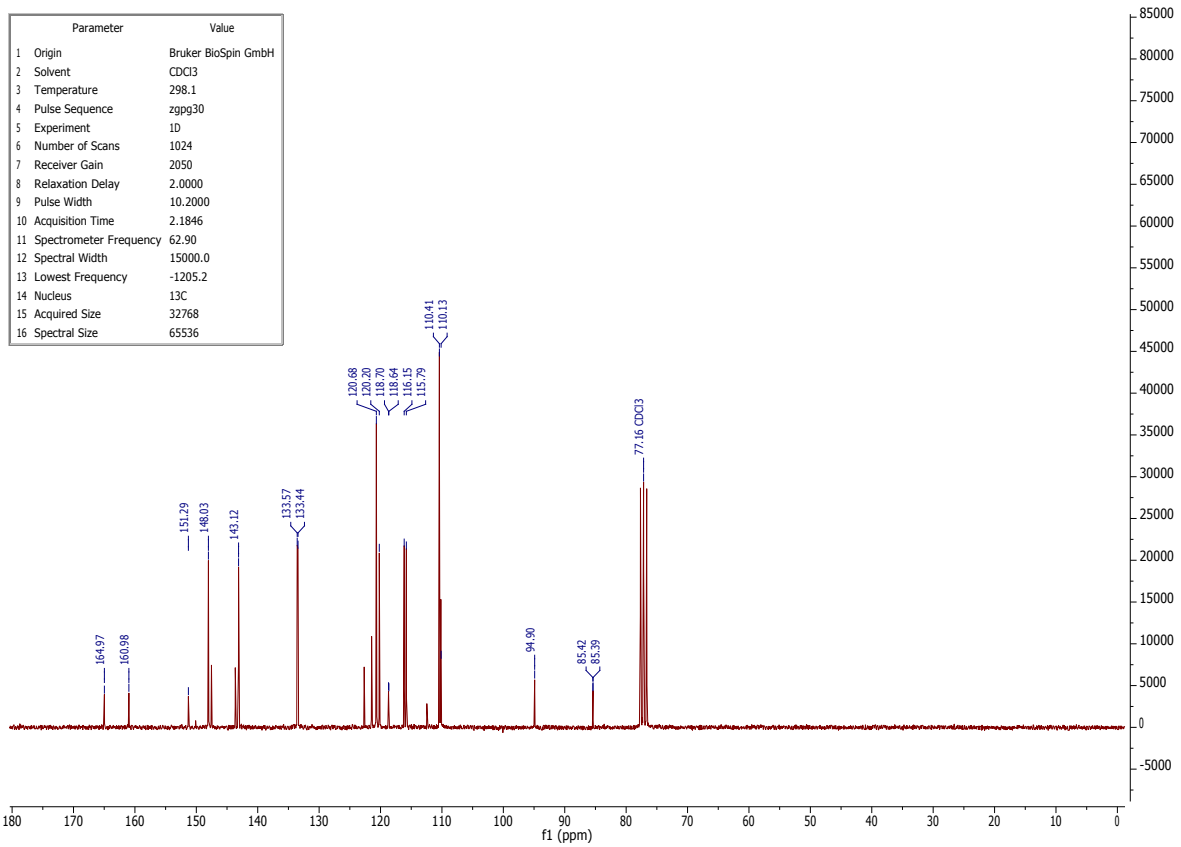
## 3-((4-Fluorophenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2c

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 512 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 11.4000 |
| 10 | Acquisition Time | 6.3439 |
| 11 | Spectrometer Frequency | 250.13 |
| 12 | Spectral Width | 5165.3 |
| 13 | Lowest Frequency | -1038.5 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

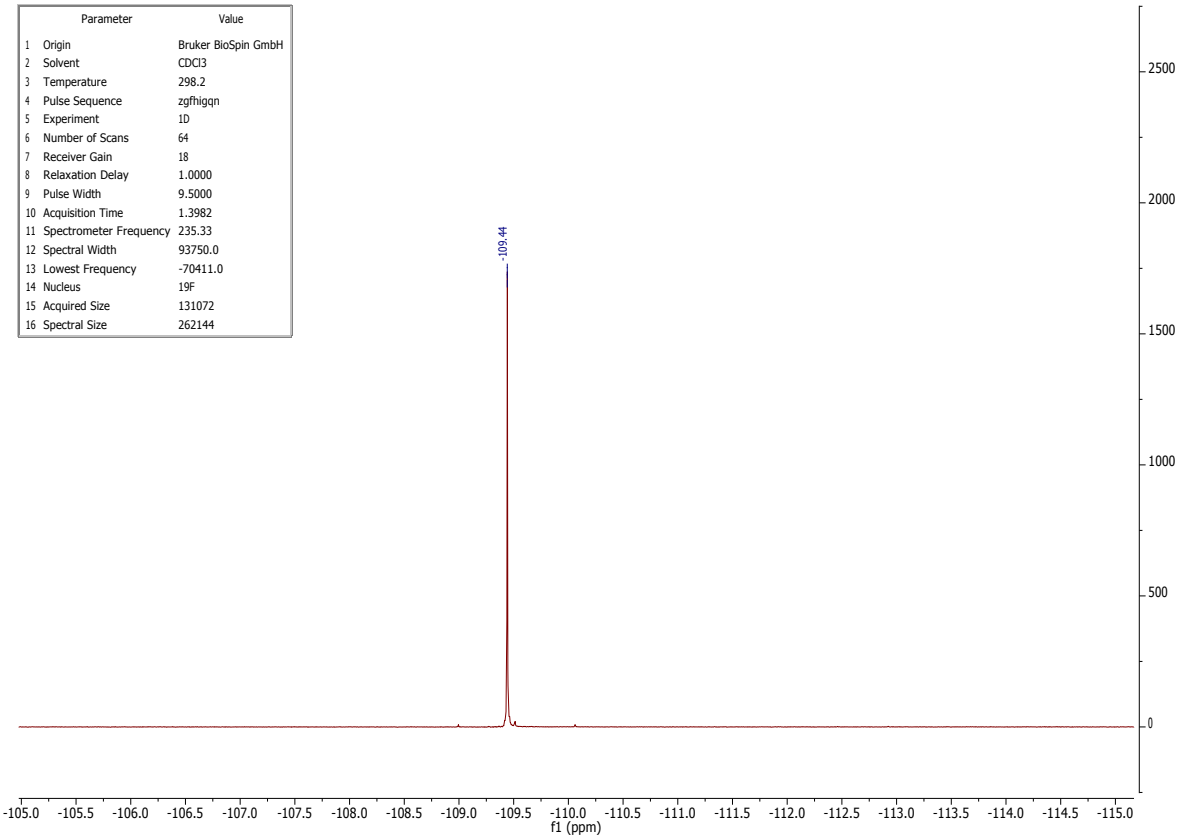



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.1 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.2000 |
| 10 | Acquisition Time | 2.1846 |
| 11 | Spectrometer Frequency | 62.90 |
| 12 | Spectral Width | 15000.0 |
| 13 | Lowest Frequency | -1205.2 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

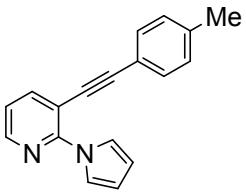


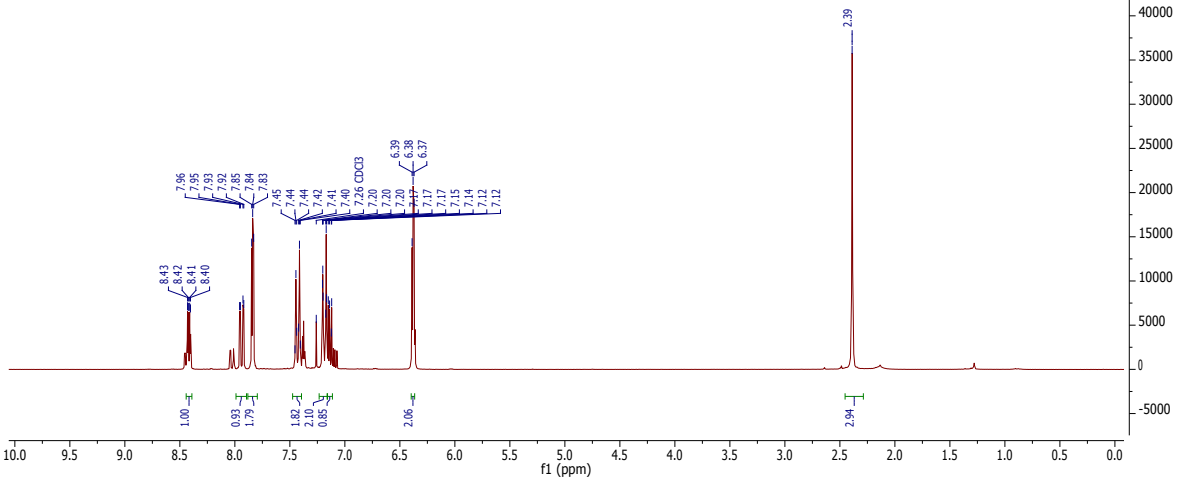
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgfhigqn |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 64 |
| 7 | Receiver Gain | 18 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 9.5000 |
| 10 | Acquisition Time | 1.3982 |
| 11 | Spectrometer Frequency | 235.33 |
| 12 | Spectral Width | 93750.0 |
| 13 | Lowest Frequency | -70411.0 |
| 14 | Nucleus | 19F |
| 15 | Acquired Size | 131072 |
| 16 | Spectral Size | 262144 |



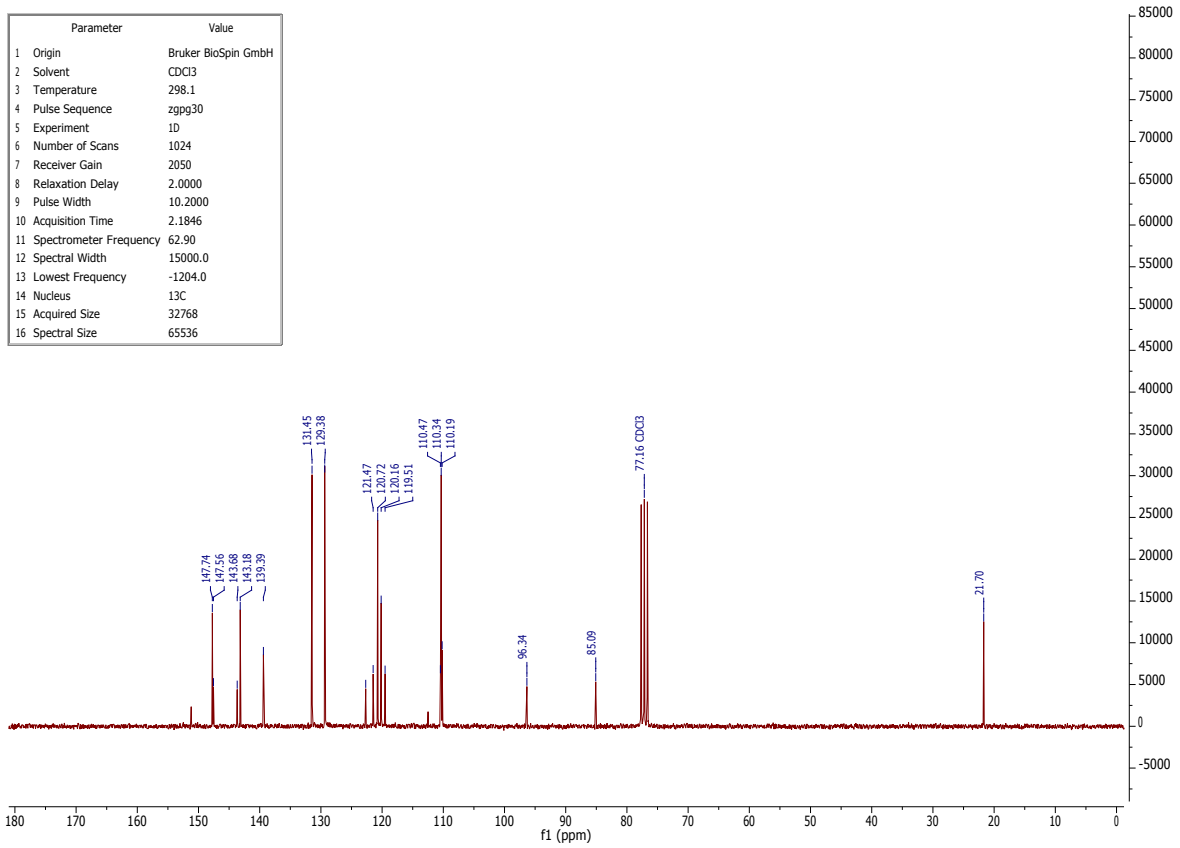
## 3-((4-Methylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2d

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.3 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 645 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 11.4000 |
| 10 | Acquisition Time | 6.3439 |
| 11 | Spectrometer Frequency | 250.13 |
| 12 | Spectral Width | 5165.3 |
| 13 | Lowest Frequency | -1038.7 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |



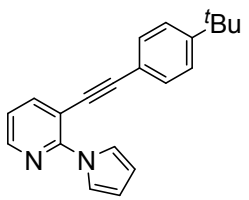




| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.1 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.2000 |
| 10 | Acquisition Time | 2.1846 |
| 11 | Spectrometer Frequency | 62.90 |
| 12 | Spectral Width | 15000.0 |
| 13 | Lowest Frequency | -1204.0 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |



## 3-((4-*tert*-Butylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2e

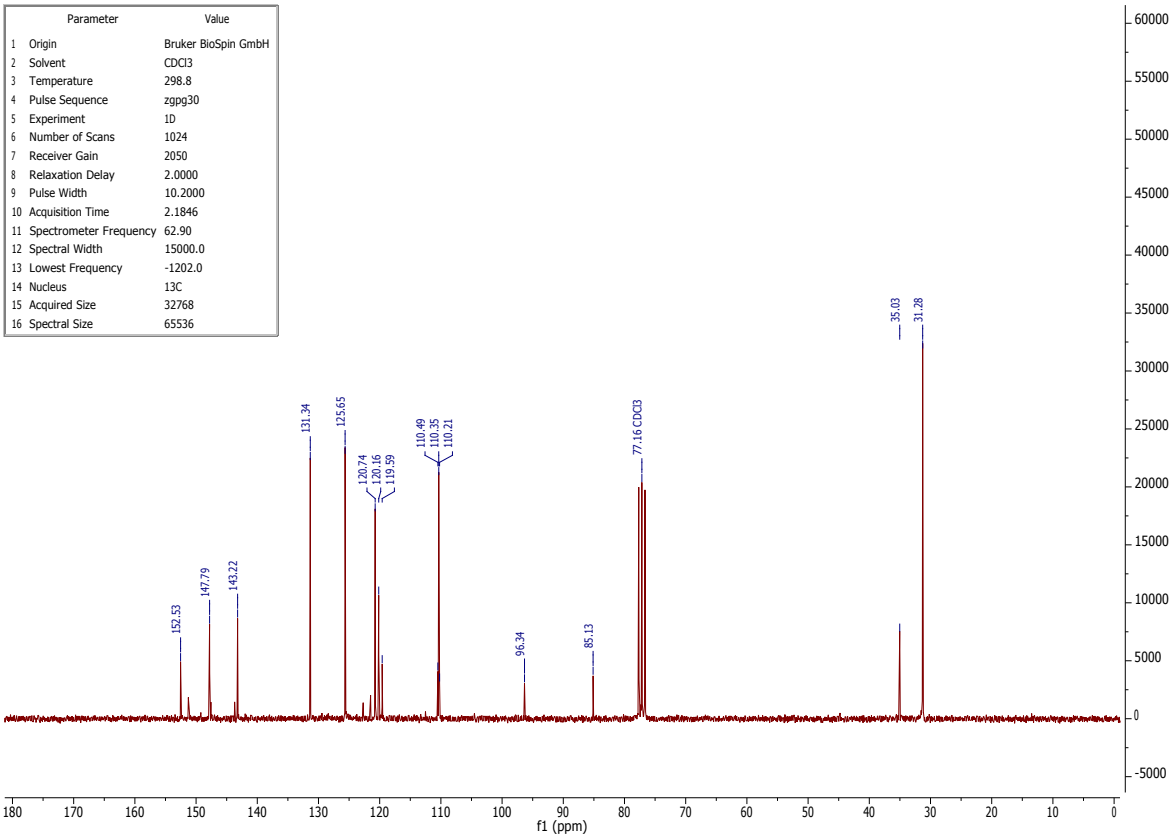
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 51 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1247.0 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |





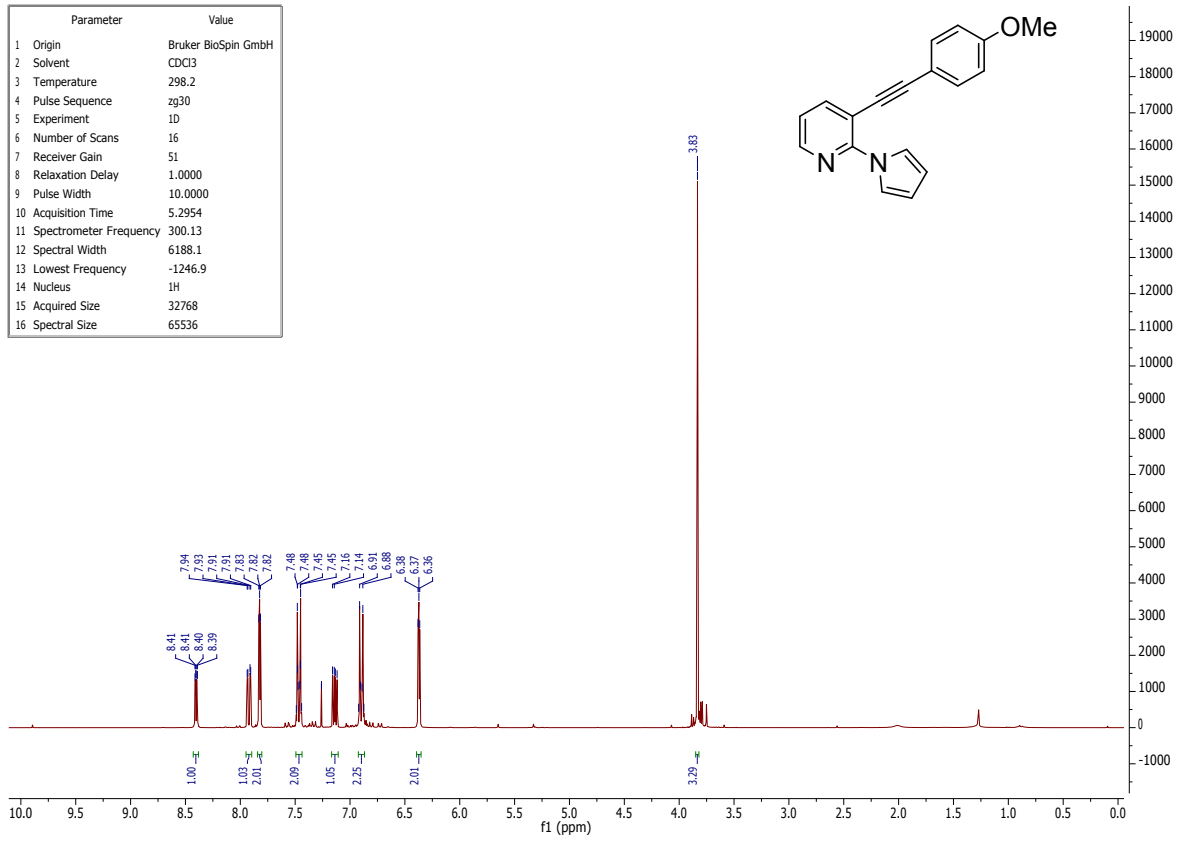


| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.8 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.2000 |
| 10 | Acquisition Time | 2.1846 |
| 11 | Spectrometer Frequency | 62.90 |
| 12 | Spectral Width | 15000.0 |
| 13 | Lowest Frequency | -1202.0 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

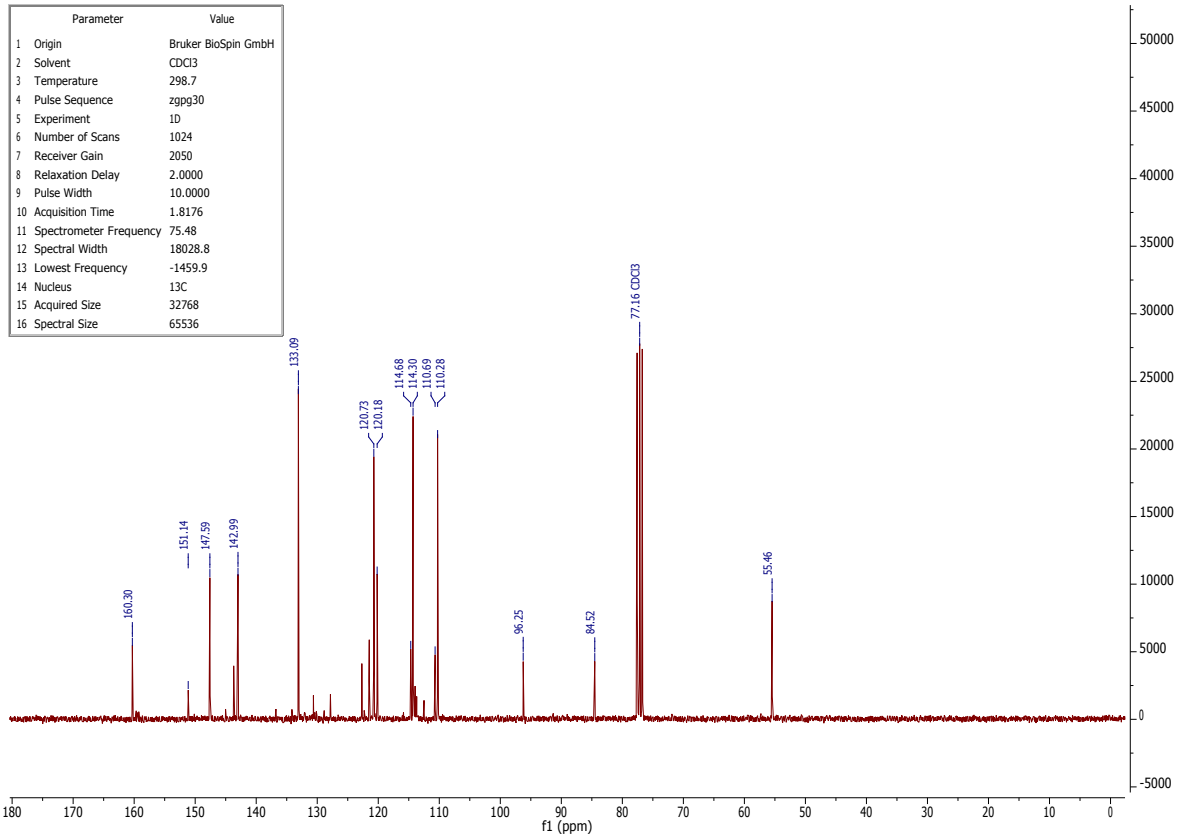


## 3-((4-Methoxyphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2f

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 51 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.9 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

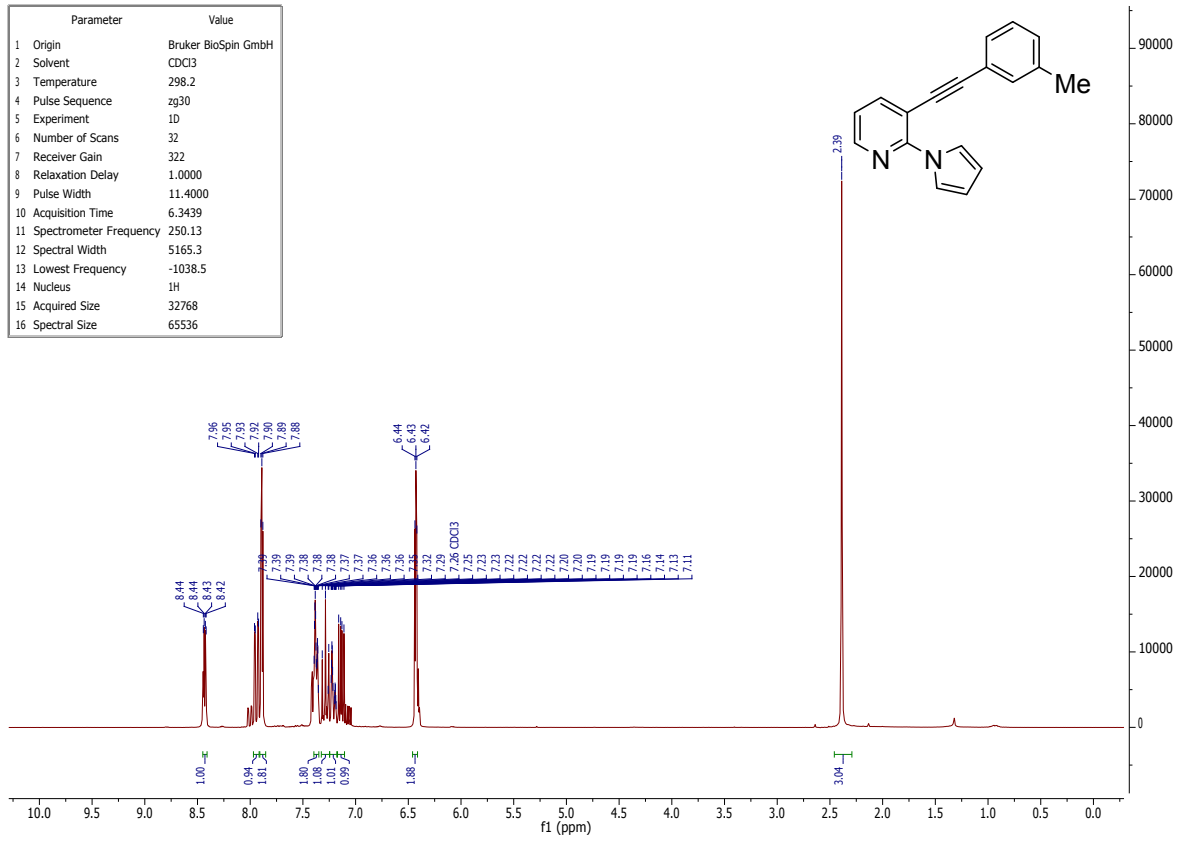



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.7 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1459.9 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

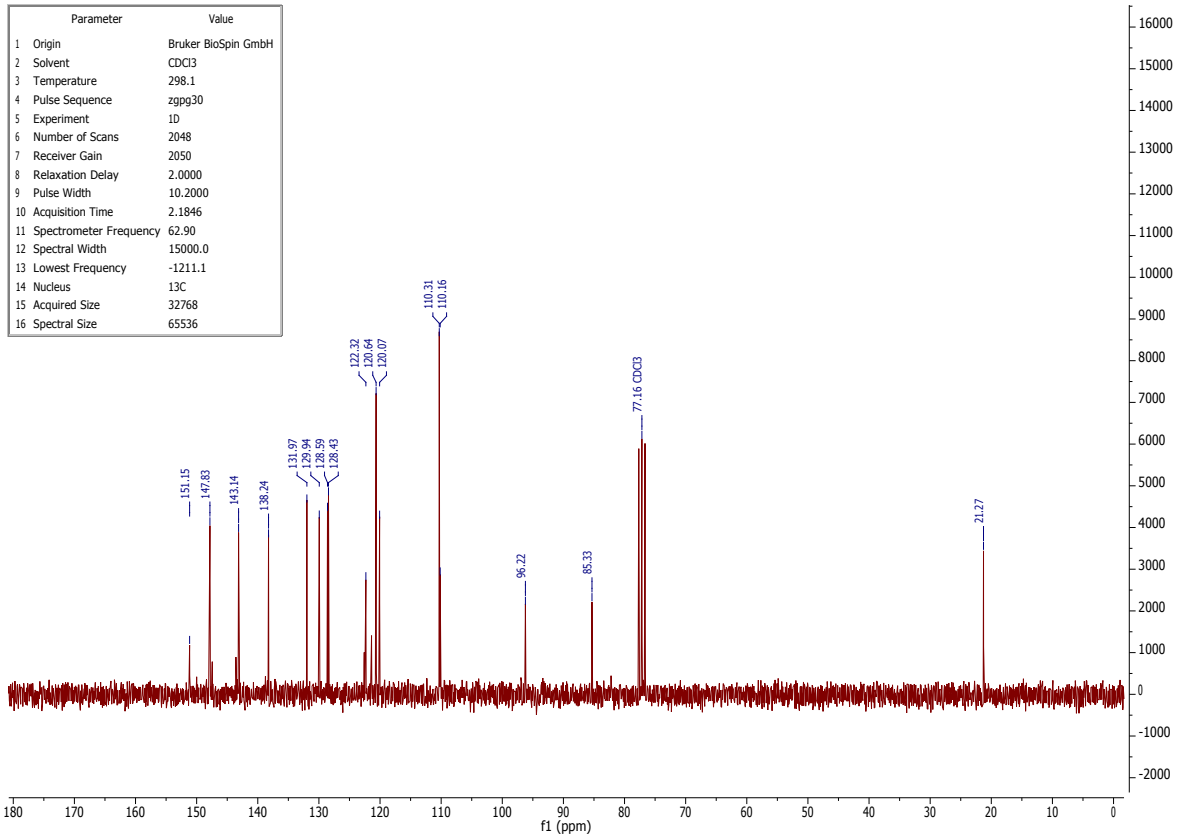


## 3-((3-Methylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2g

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 32 |
| 7 | Receiver Gain | 322 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 11.4000 |
| 10 | Acquisition Time | 6.3439 |
| 11 | Spectrometer Frequency | 250.13 |
| 12 | Spectral Width | 5165.3 |
| 13 | Lowest Frequency | -1038.5 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

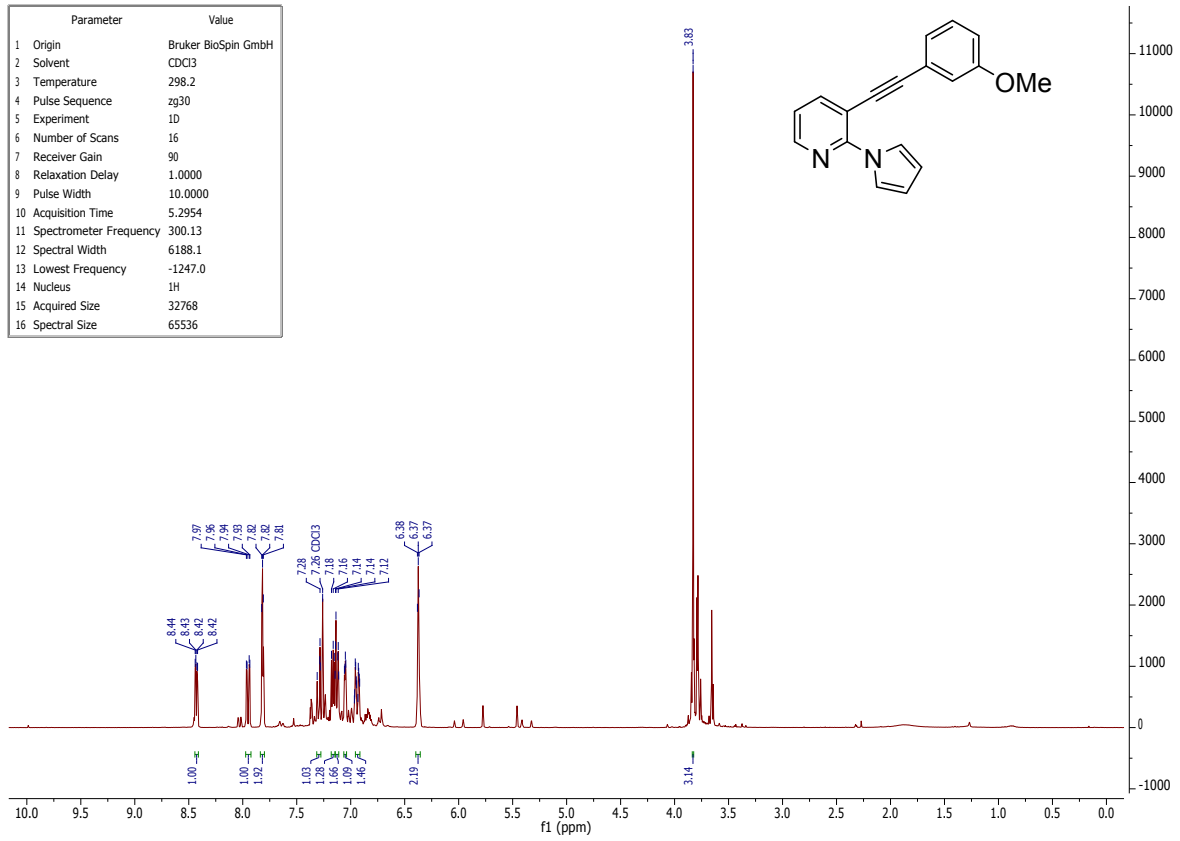



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.1 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 2048 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.2000 |
| 10 | Acquisition Time | 2.1846 |
| 11 | Spectrometer Frequency | 62.90 |
| 12 | Spectral Width | 15000.0 |
| 13 | Lowest Frequency | -1211.1 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

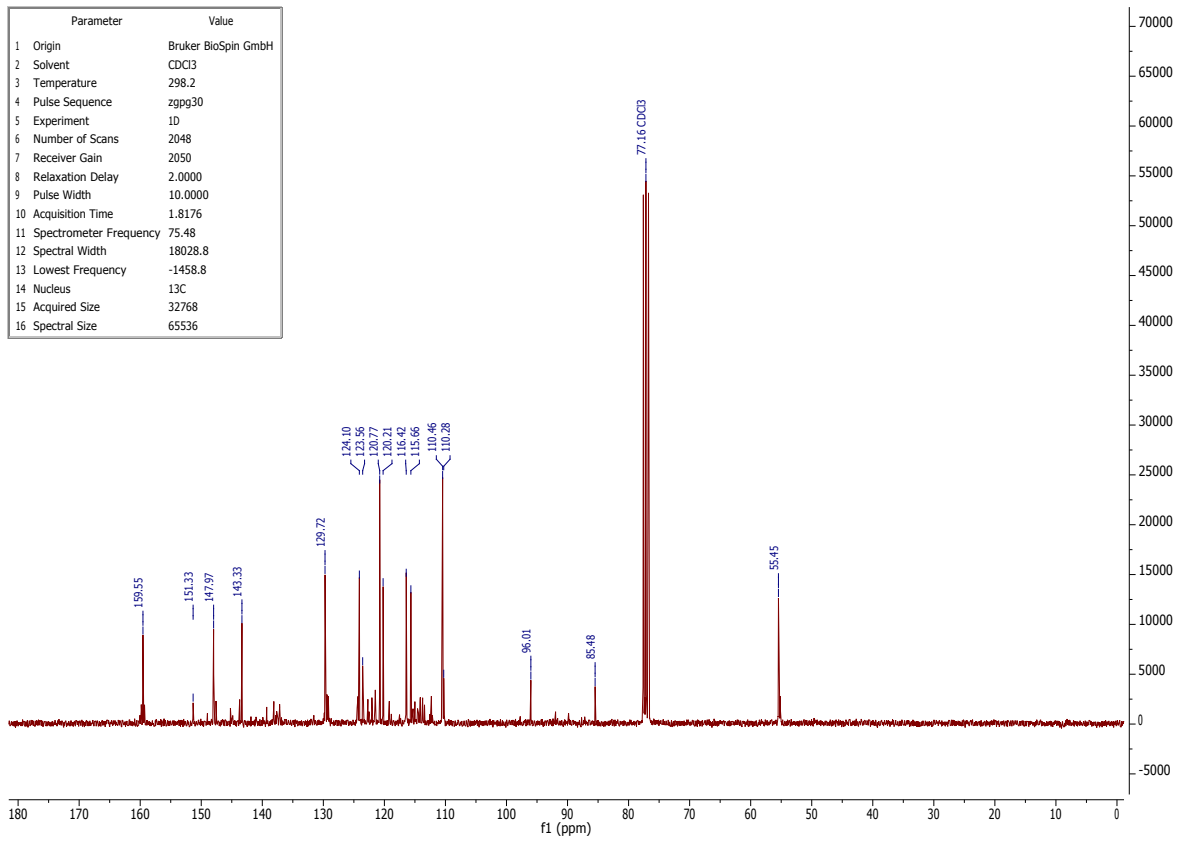


## 3-((3-Methoxyphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2h

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 90 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1247.0 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

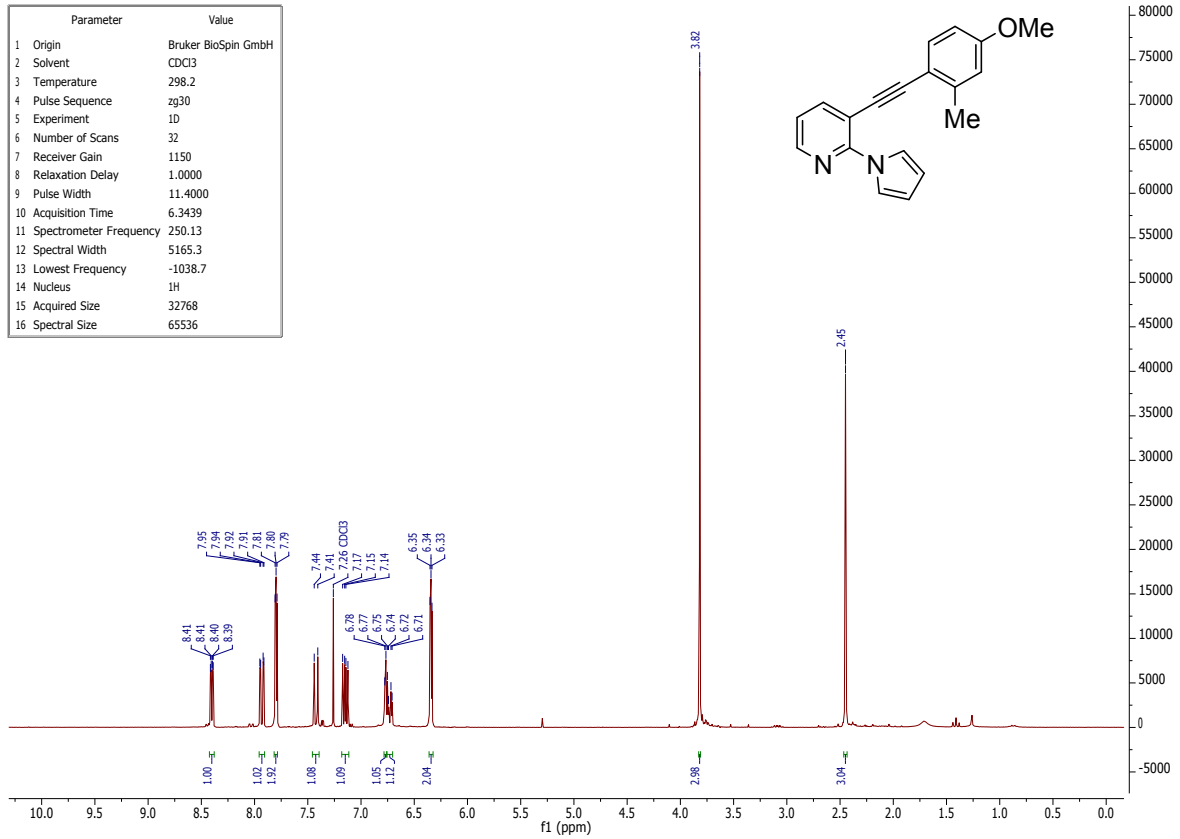



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 2048 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1458.8 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

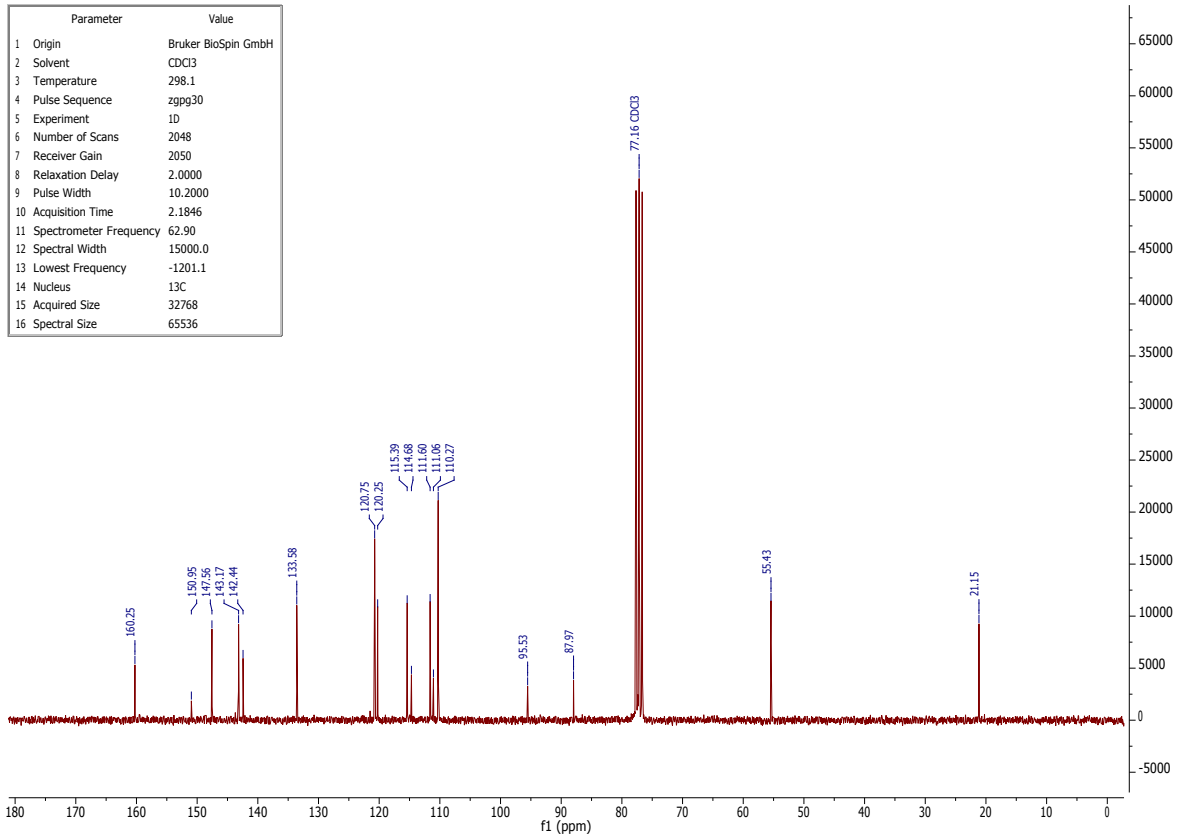


## 3-((4-Methoxy-2-methylphenyl)ethynyl)-2-([1*H*]-pyrrol-1-yl)-pyridine 2i

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 32 |
| 7 | Receiver Gain | 1150 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 11.4000 |
| 10 | Acquisition Time | 6.3439 |
| 11 | Spectrometer Frequency | 250.13 |
| 12 | Spectral Width | 5165.3 |
| 13 | Lowest Frequency | -1038.7 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

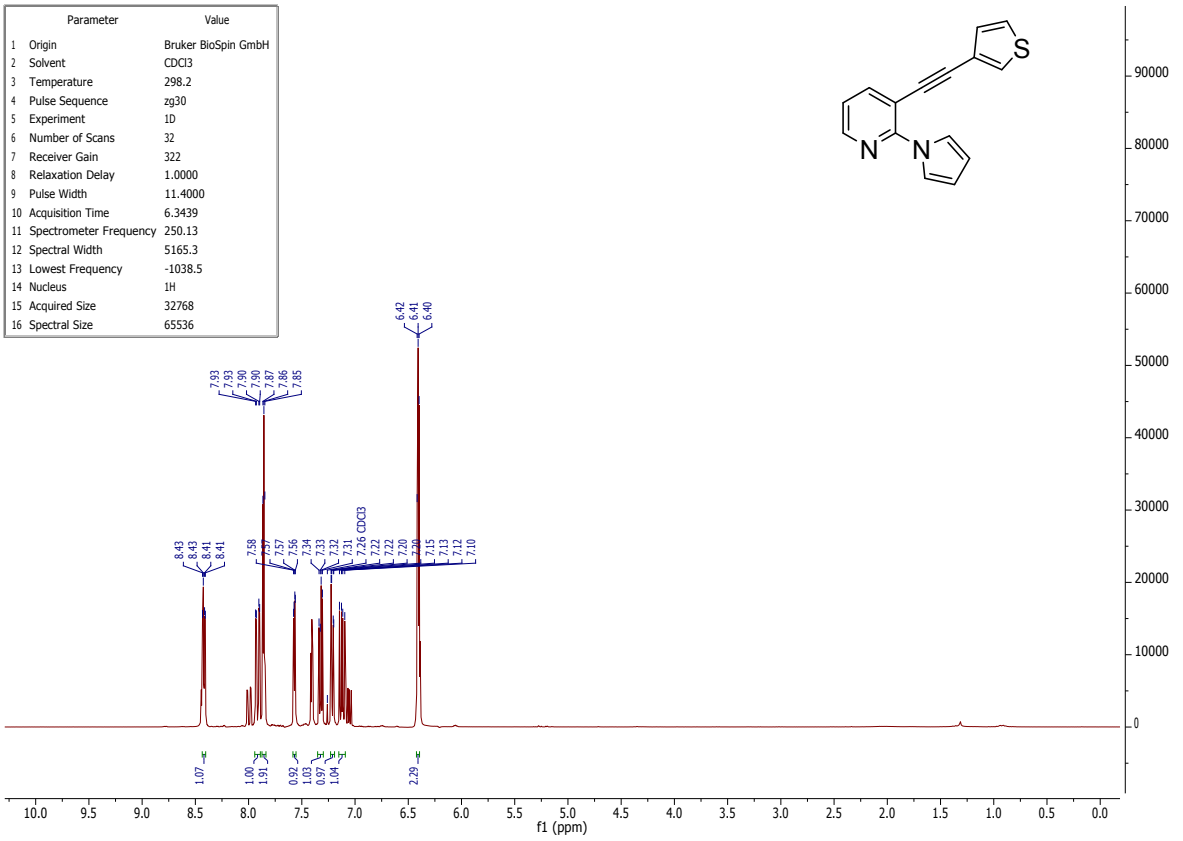



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.1 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 2048 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.2000 |
| 10 | Acquisition Time | 2.1846 |
| 11 | Spectrometer Frequency | 62.90 |
| 12 | Spectral Width | 15000.0 |
| 13 | Lowest Frequency | -1201.1 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

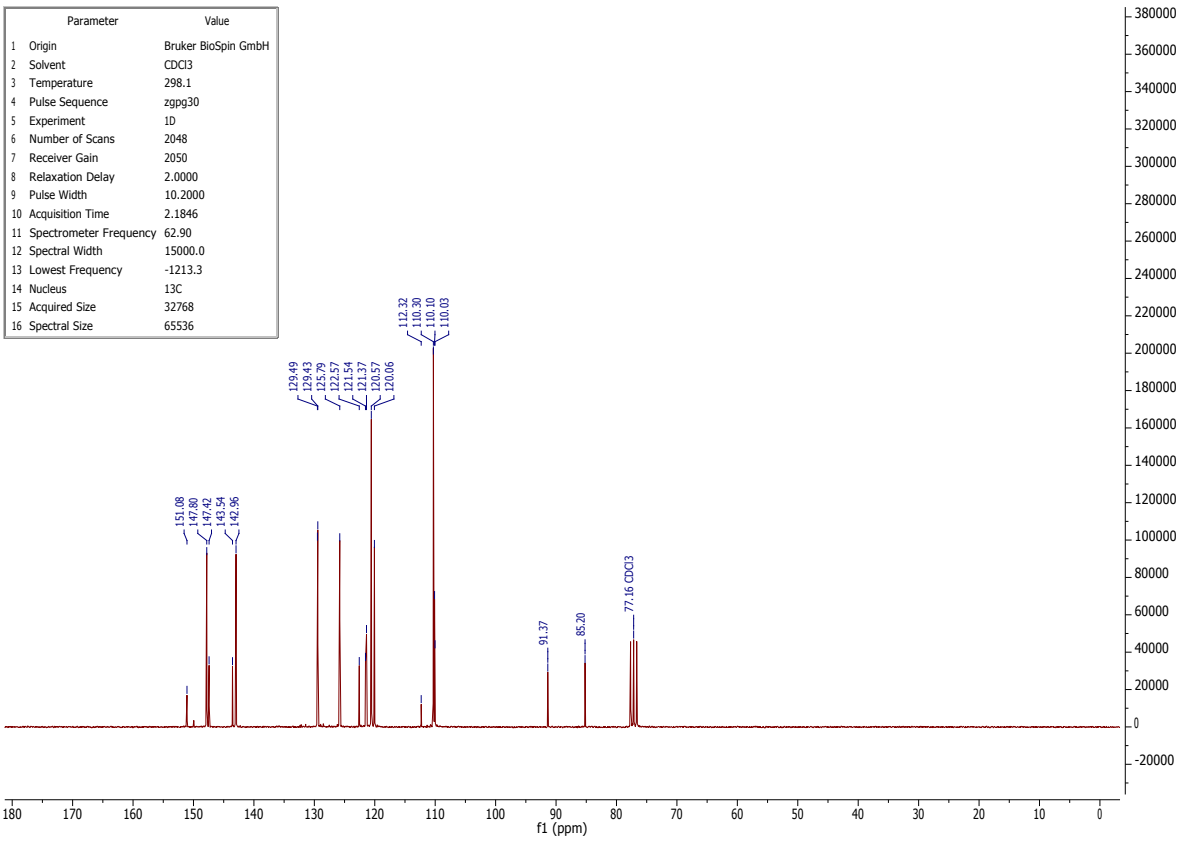


## 2-([1*H*]-pyrrol-1-yl)-3-(thiophen-3-ylethynyl)pyridine 2j

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 32 |
| 7 | Receiver Gain | 322 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 11.4000 |
| 10 | Acquisition Time | 6.3439 |
| 11 | Spectrometer Frequency | 250.13 |
| 12 | Spectral Width | 5165.3 |
| 13 | Lowest Frequency | -1038.5 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

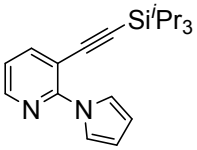



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.1 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 2048 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.2000 |
| 10 | Acquisition Time | 2.1846 |
| 11 | Spectrometer Frequency | 62.90 |
| 12 | Spectral Width | 15000.0 |
| 13 | Lowest Frequency | -1213.3 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |



## 2-([1*H*]-pyrrol-1-yl)-3-((triisopropylsilyl)ethynyl)pyridine 2k

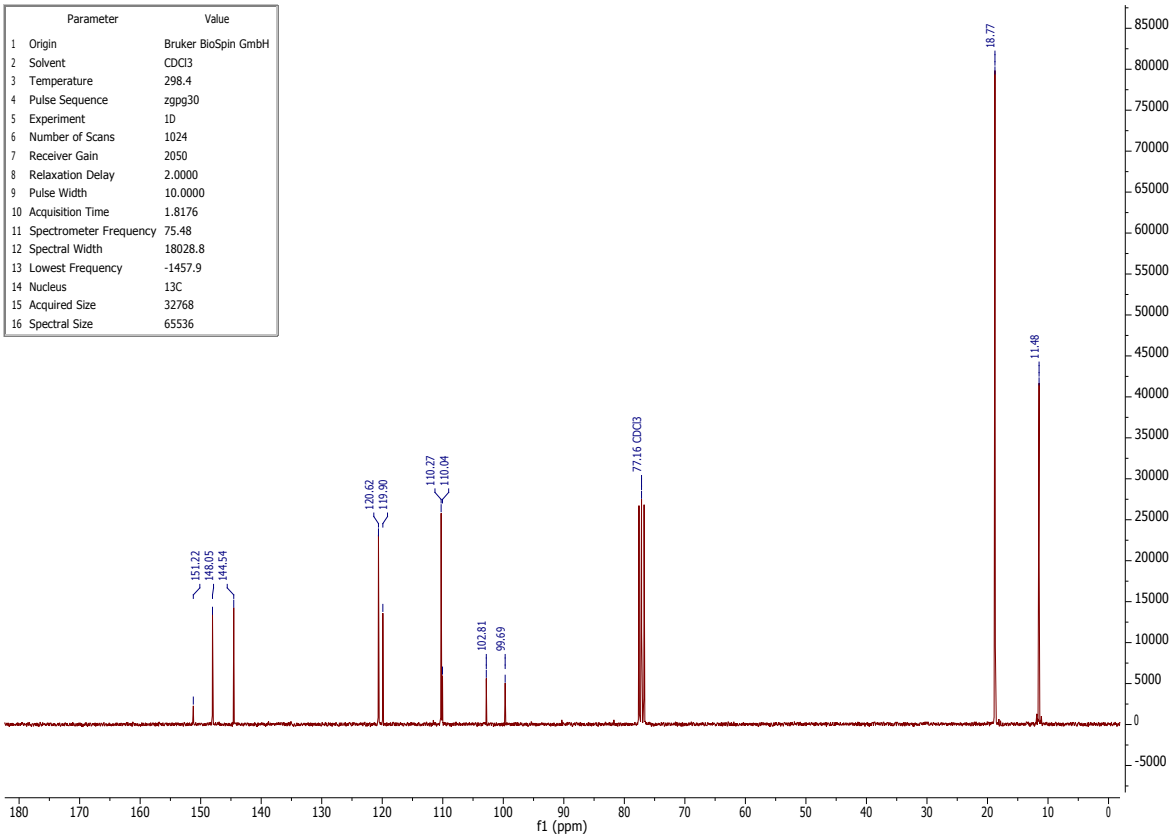
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 51 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.9 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |





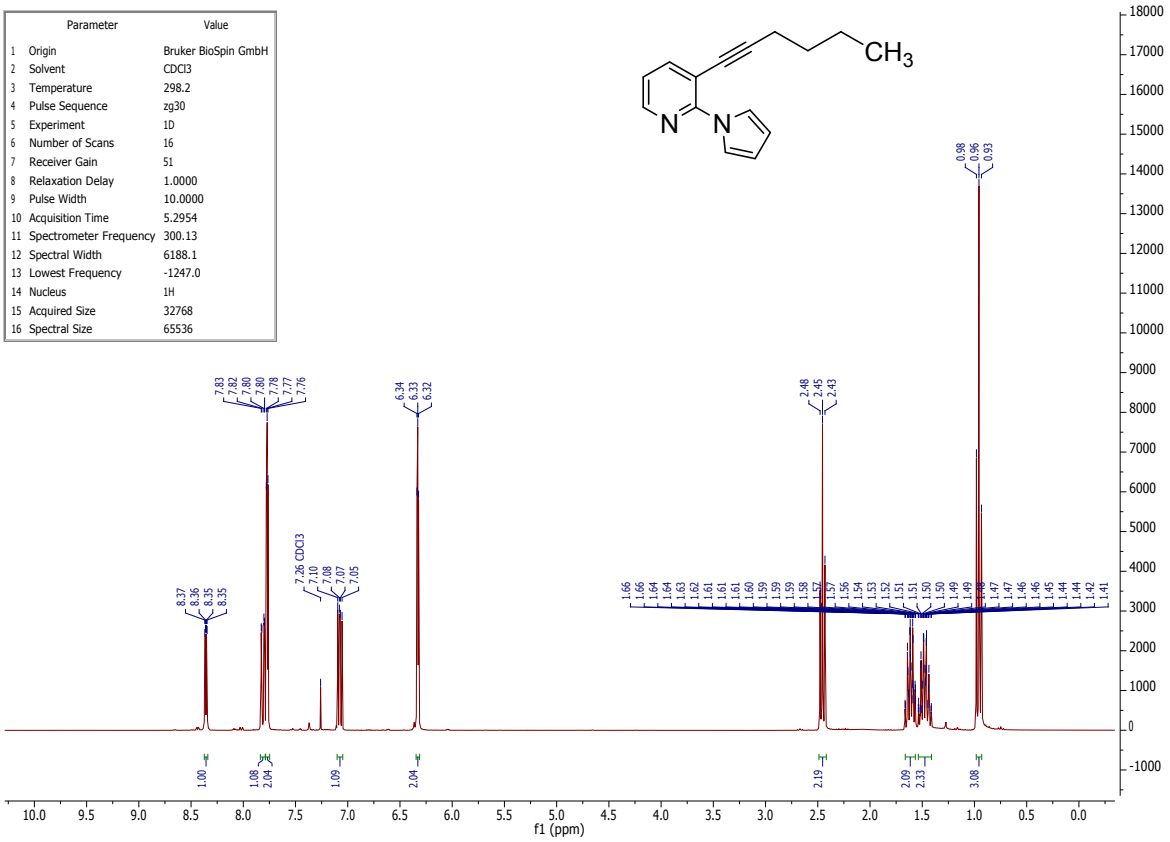


| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.4 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1457.9 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

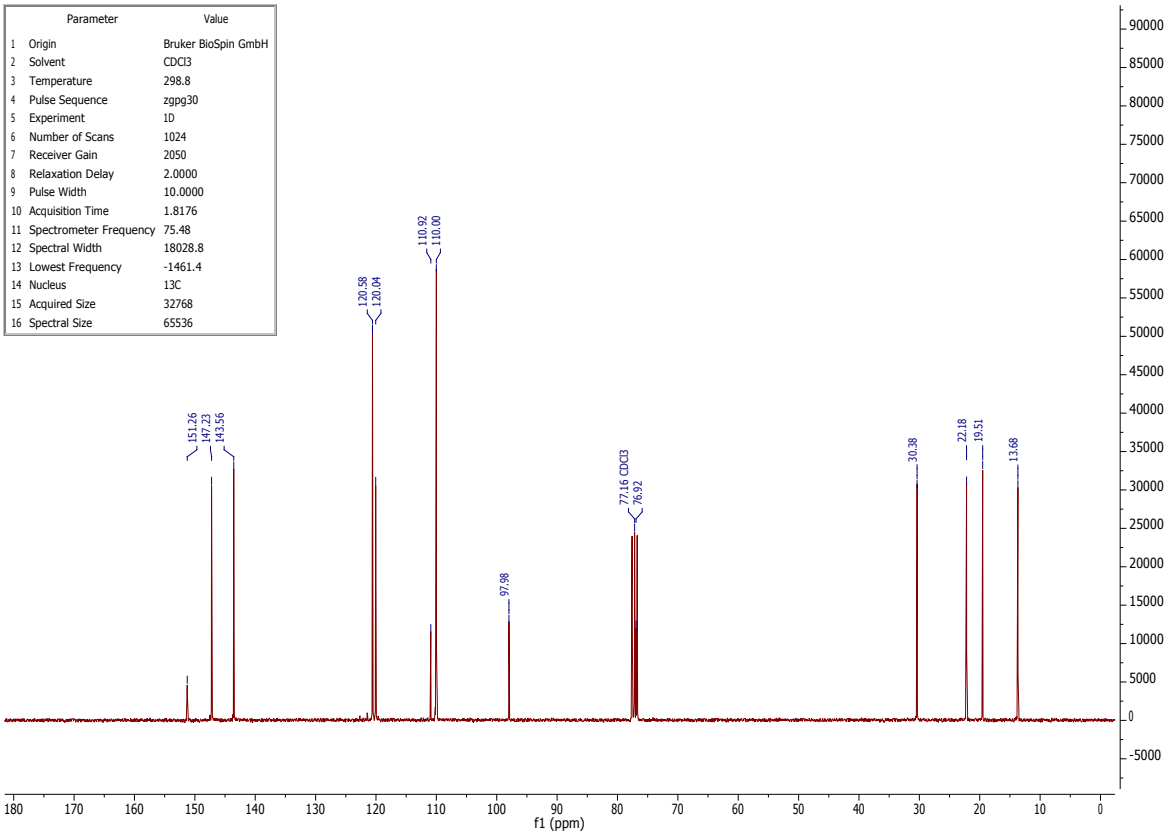


## 3-(*n*-Hex-1-yn-1-yl)-2-([1*H*]-pyrrol-1-yl)pyridine 2l

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 51 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1247.0 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

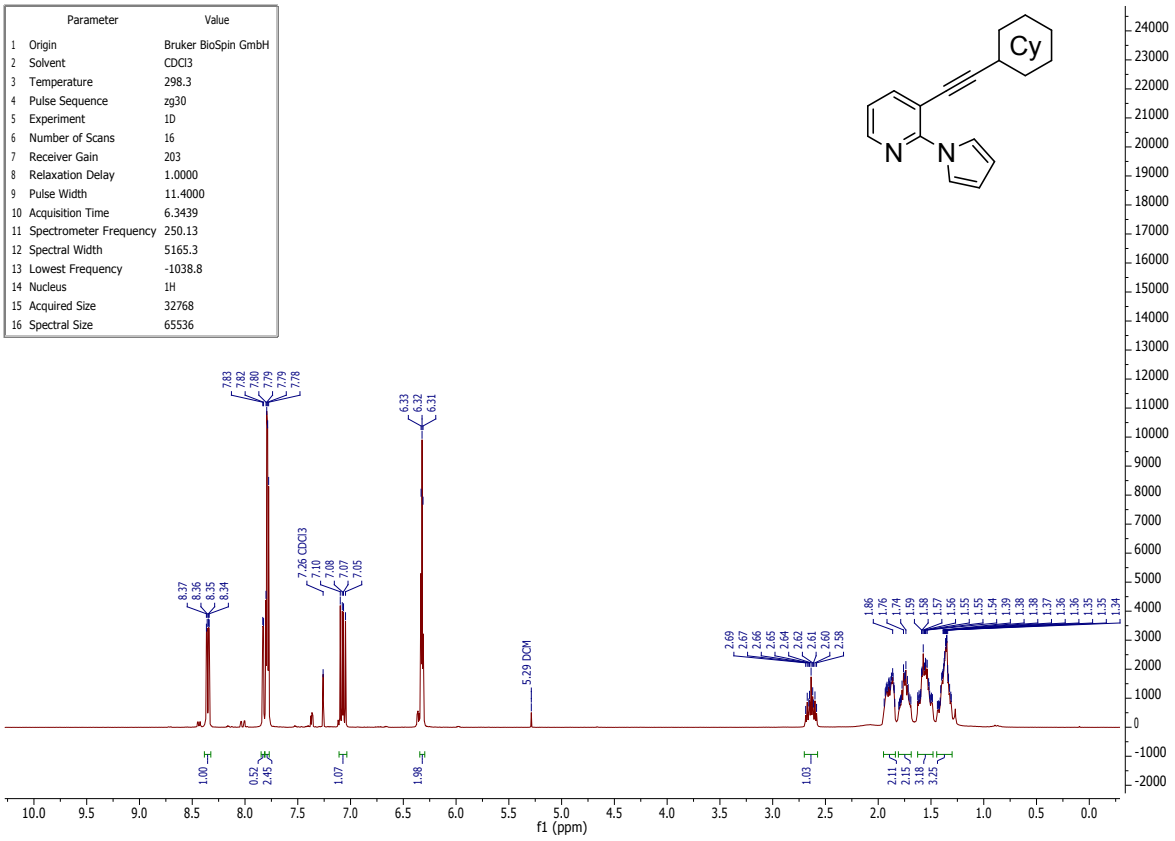



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.8 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1461.4 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

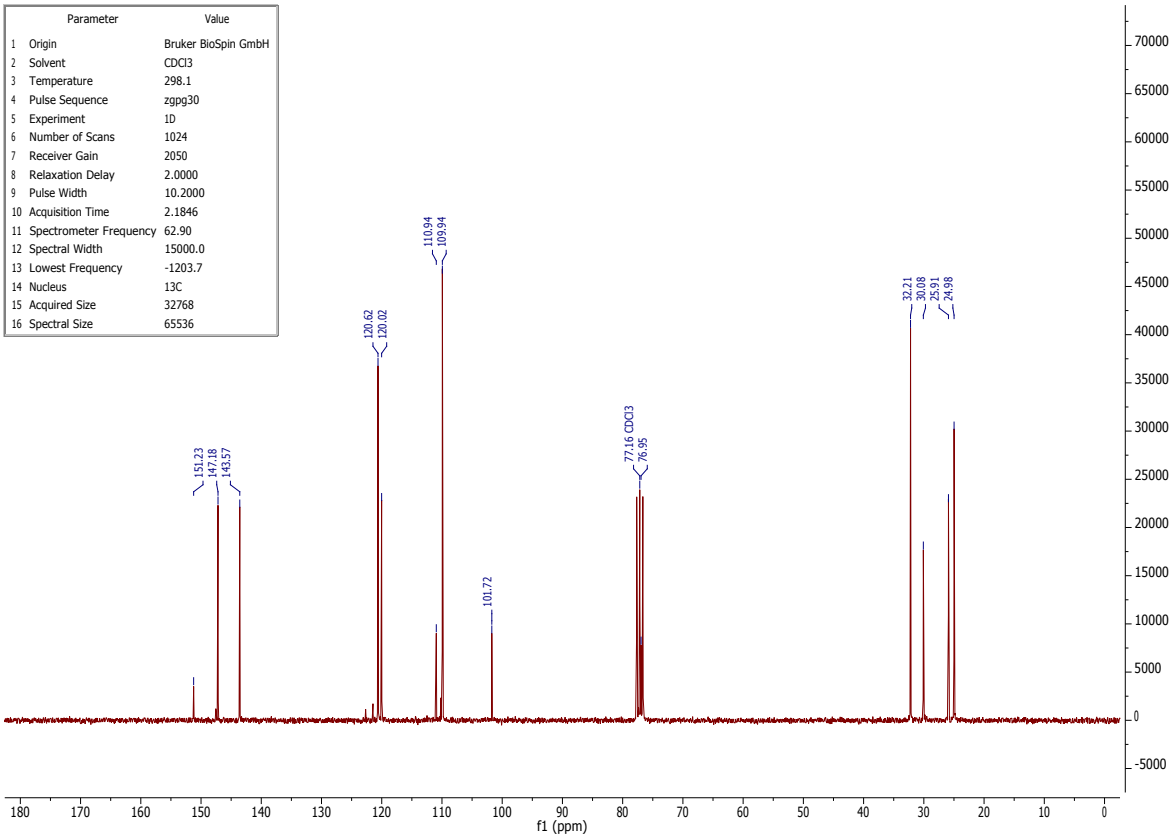


## 3-(Cyclohexylethynyl)-2-([1*H*]-pyrrol-1-yl)pyridine 2m

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.3 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 203 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 11.4000 |
| 10 | Acquisition Time | 6.3439 |
| 11 | Spectrometer Frequency | 250.13 |
| 12 | Spectral Width | 5165.3 |
| 13 | Lowest Frequency | -1038.8 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

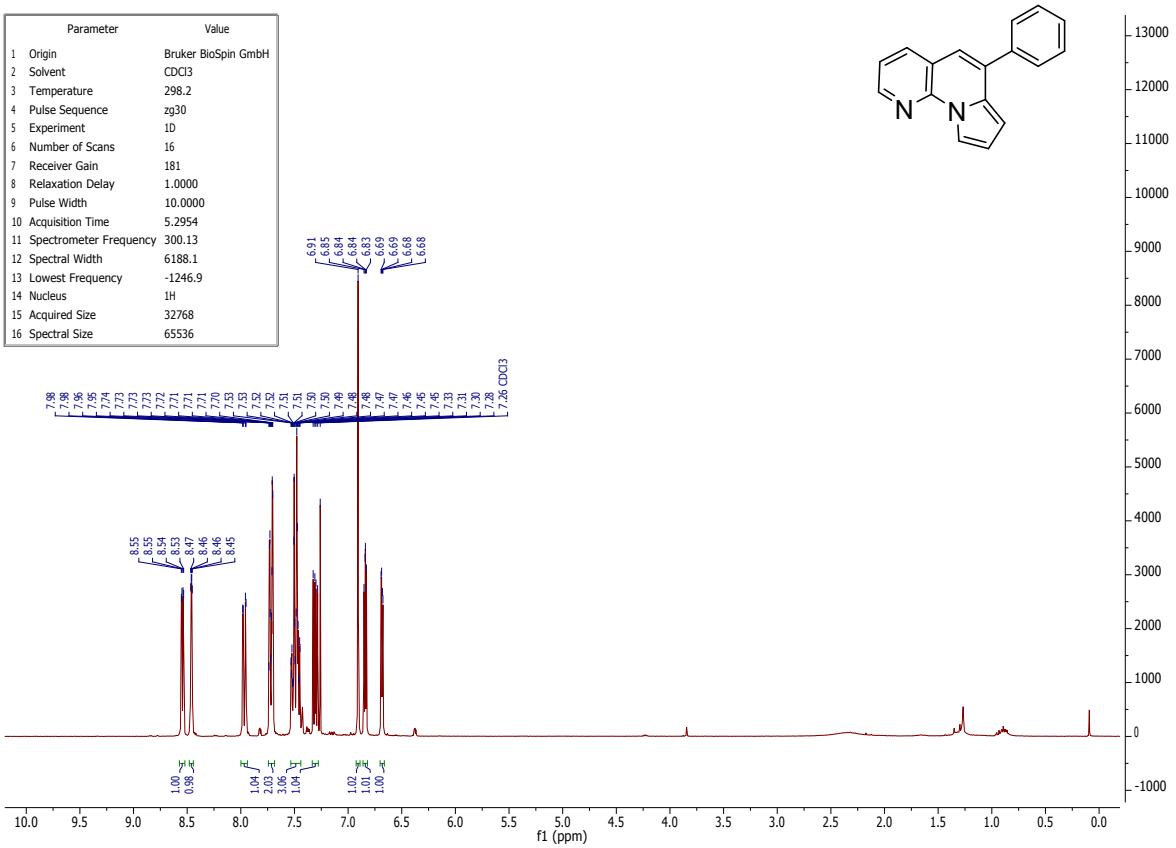



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.1 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.2000 |
| 10 | Acquisition Time | 2.1846 |
| 11 | Spectrometer Frequency | 62.90 |
| 12 | Spectral Width | 15000.0 |
| 13 | Lowest Frequency | -1203.7 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

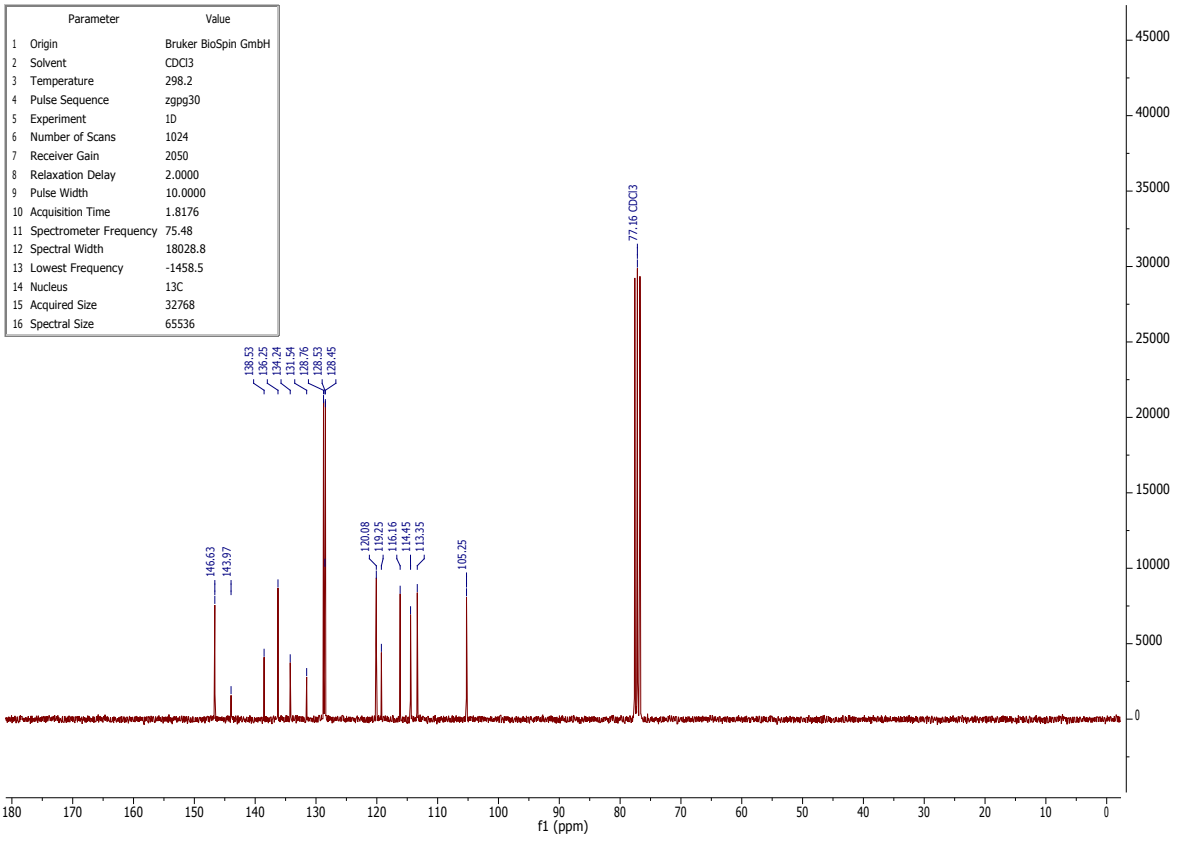


## 6-Phenylpyrrolo[1,2-*a*][1,8]naphthyridine 3a

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 181 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.9 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

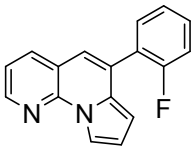


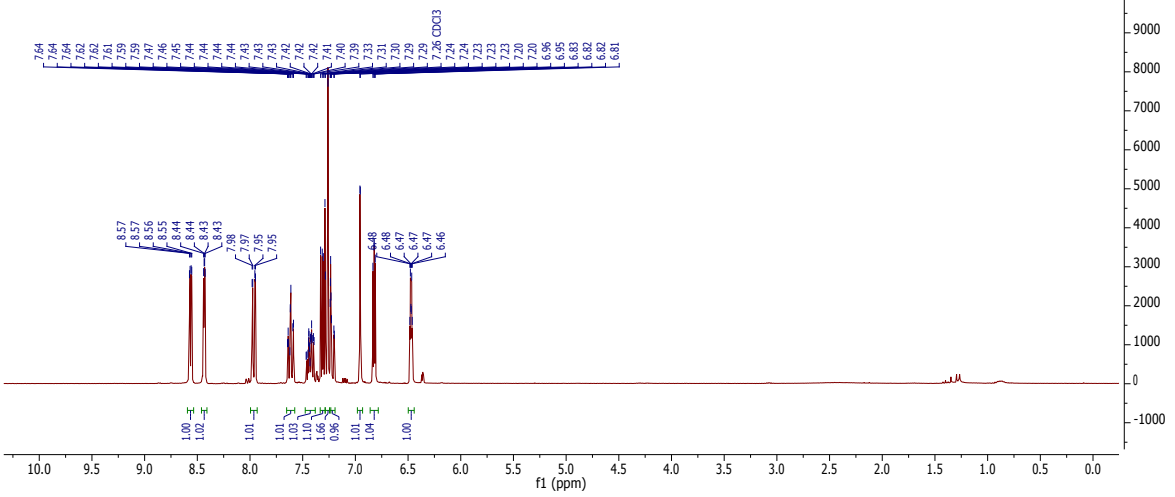

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1458.5 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |



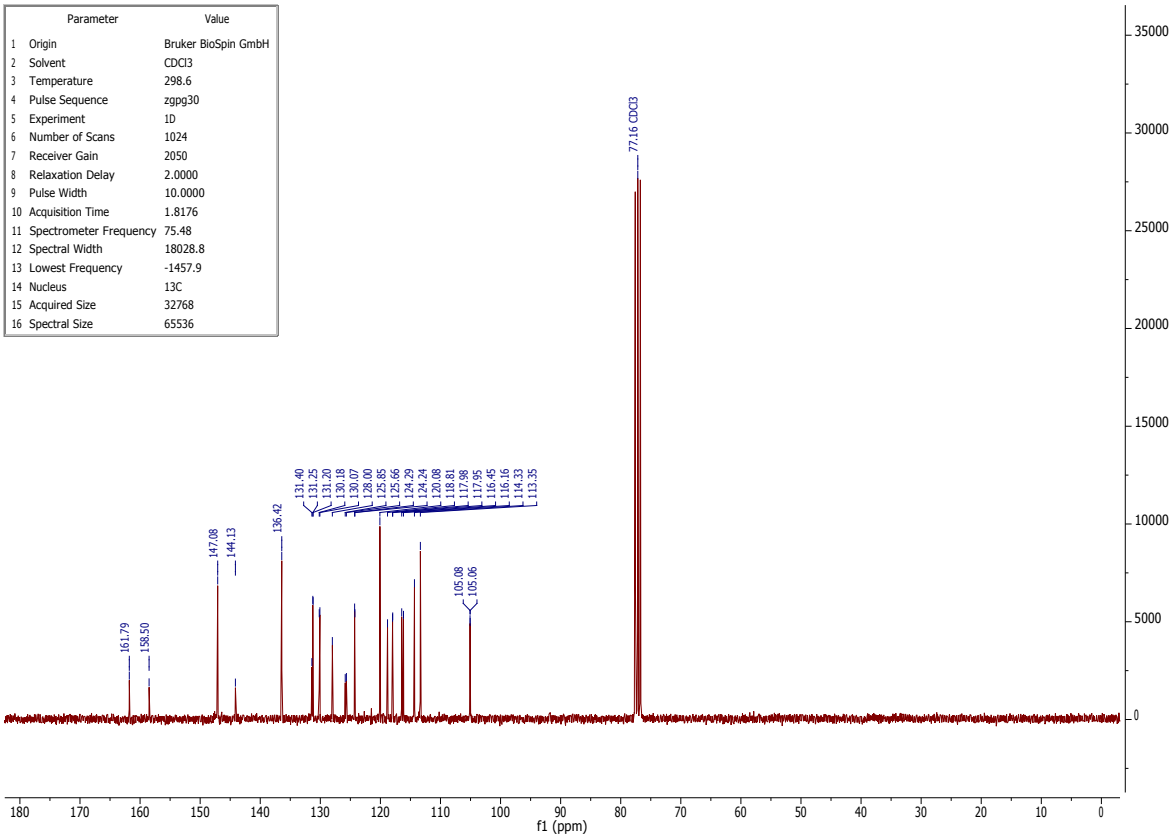
## 6-(2-Fluorophenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3b

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 181 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.9 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

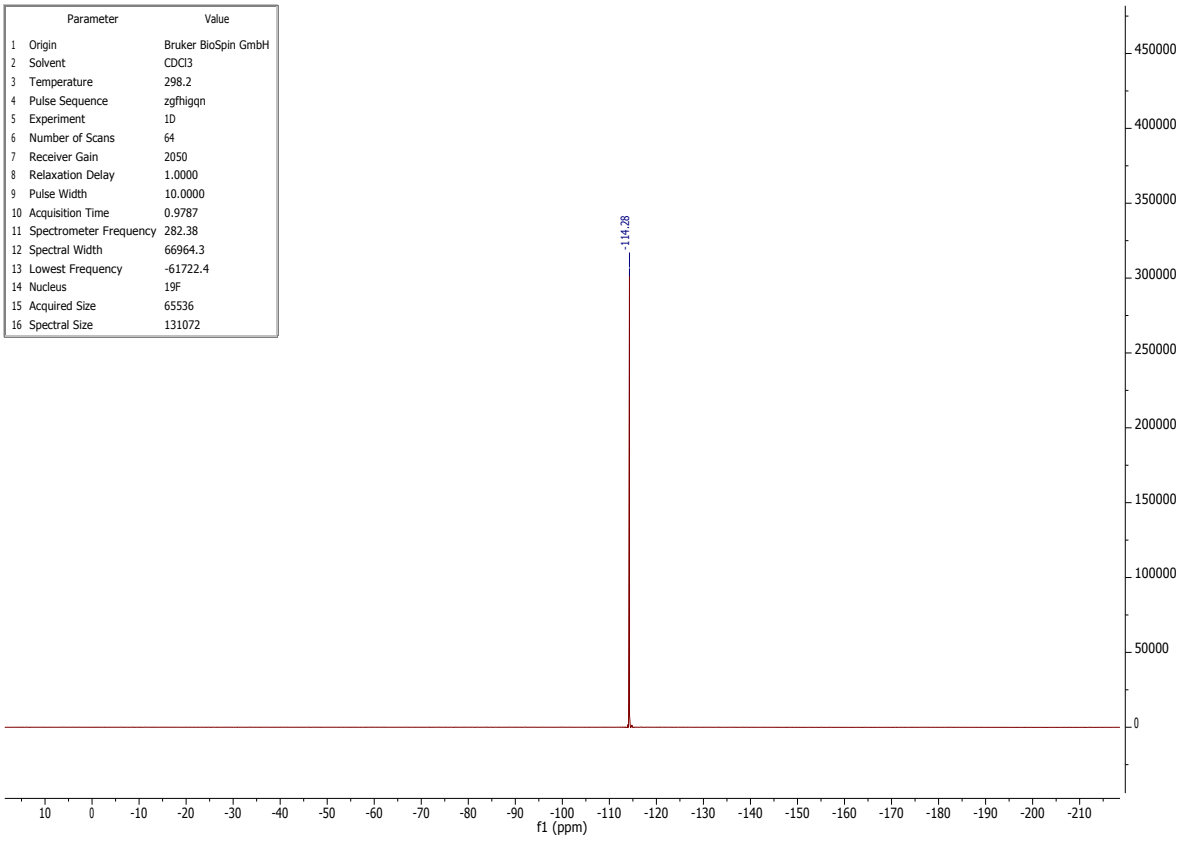



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.6 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1457.9 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

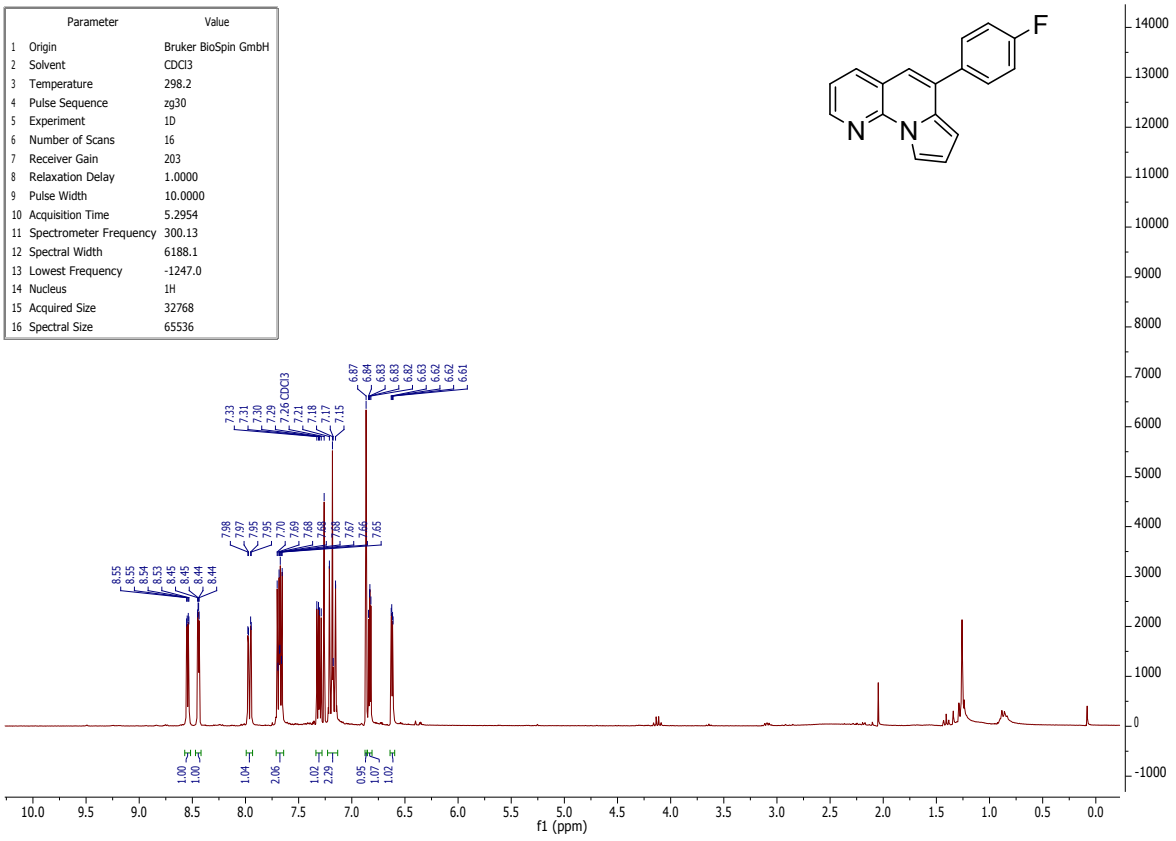


| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgfhigqn |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 64 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 0.9787 |
| 11 | Spectrometer Frequency | 282.38 |
| 12 | Spectral Width | 66964.3 |
| 13 | Lowest Frequency | -61722.4 |
| 14 | Nucleus | 19F |
| 15 | Acquired Size | 65536 |
| 16 | Spectral Size | 131072 |

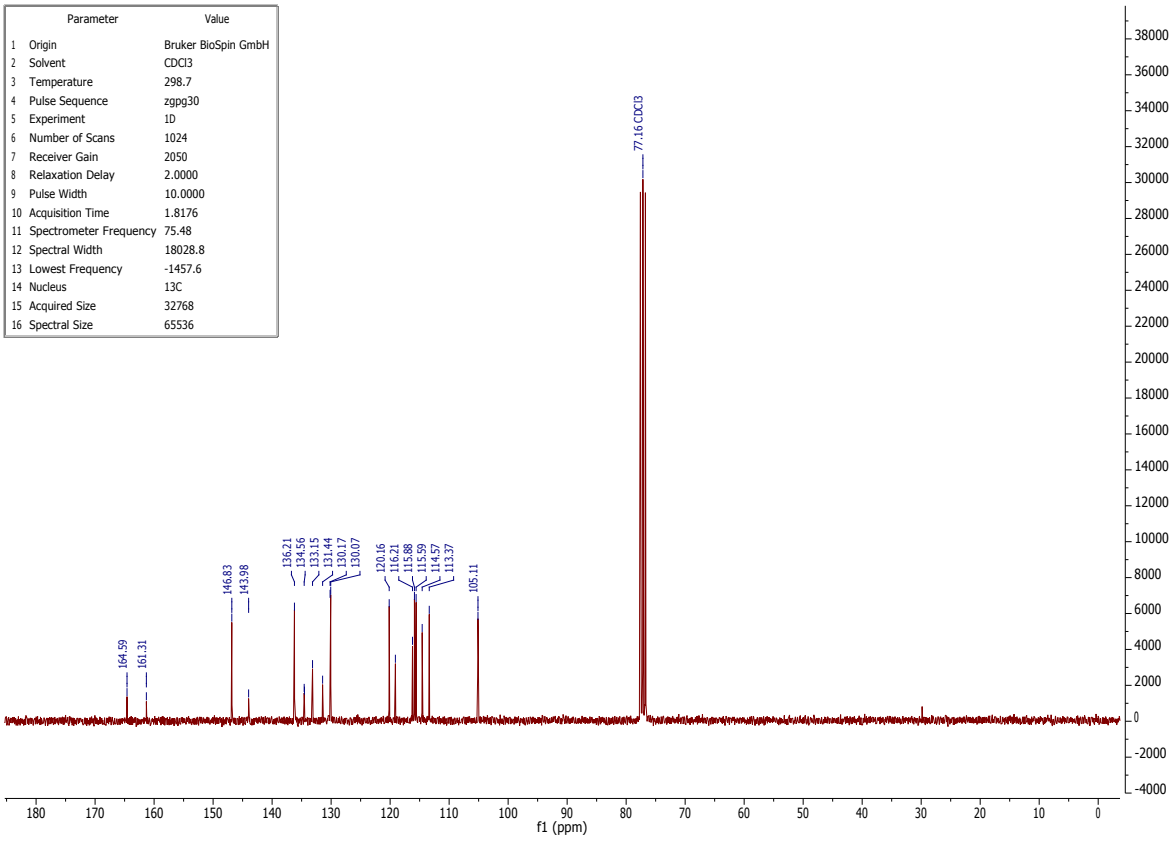


## 6-(4-Fluorophenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3c

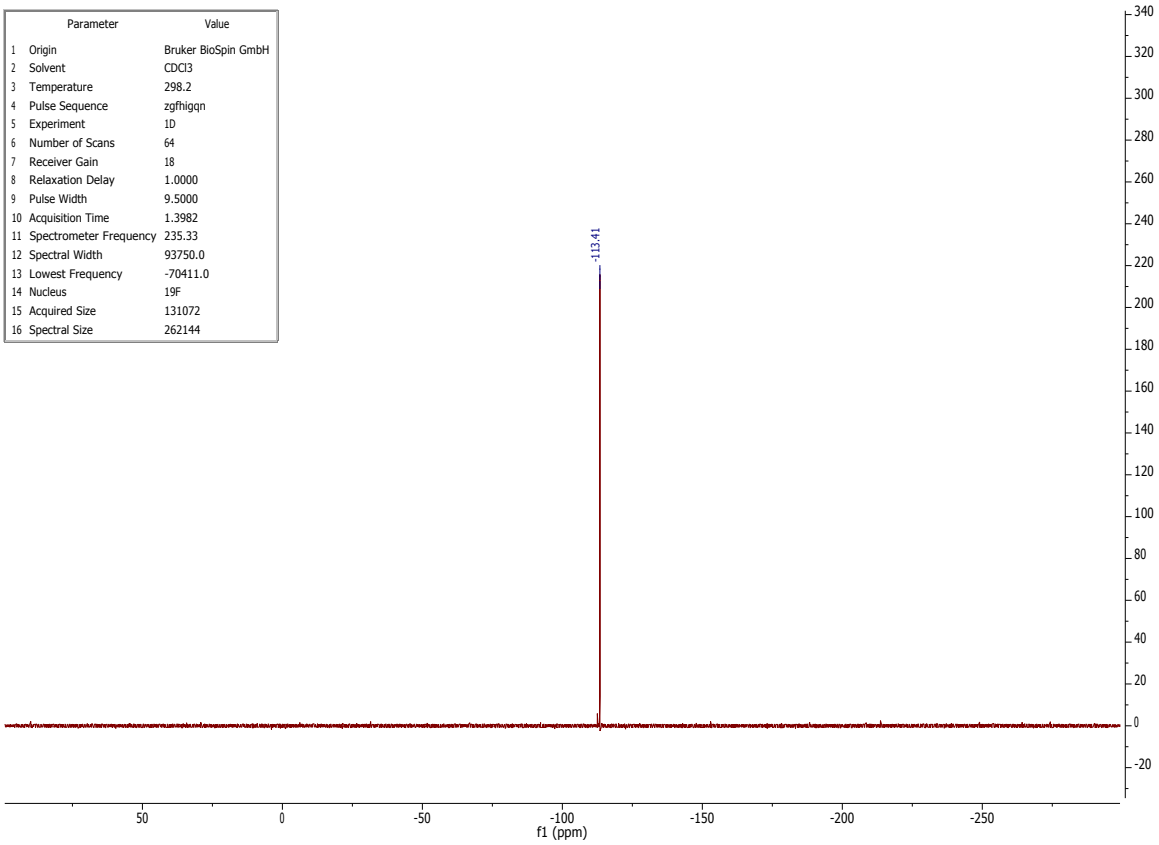
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 203 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1247.0 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |




| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.7 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1457.6 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

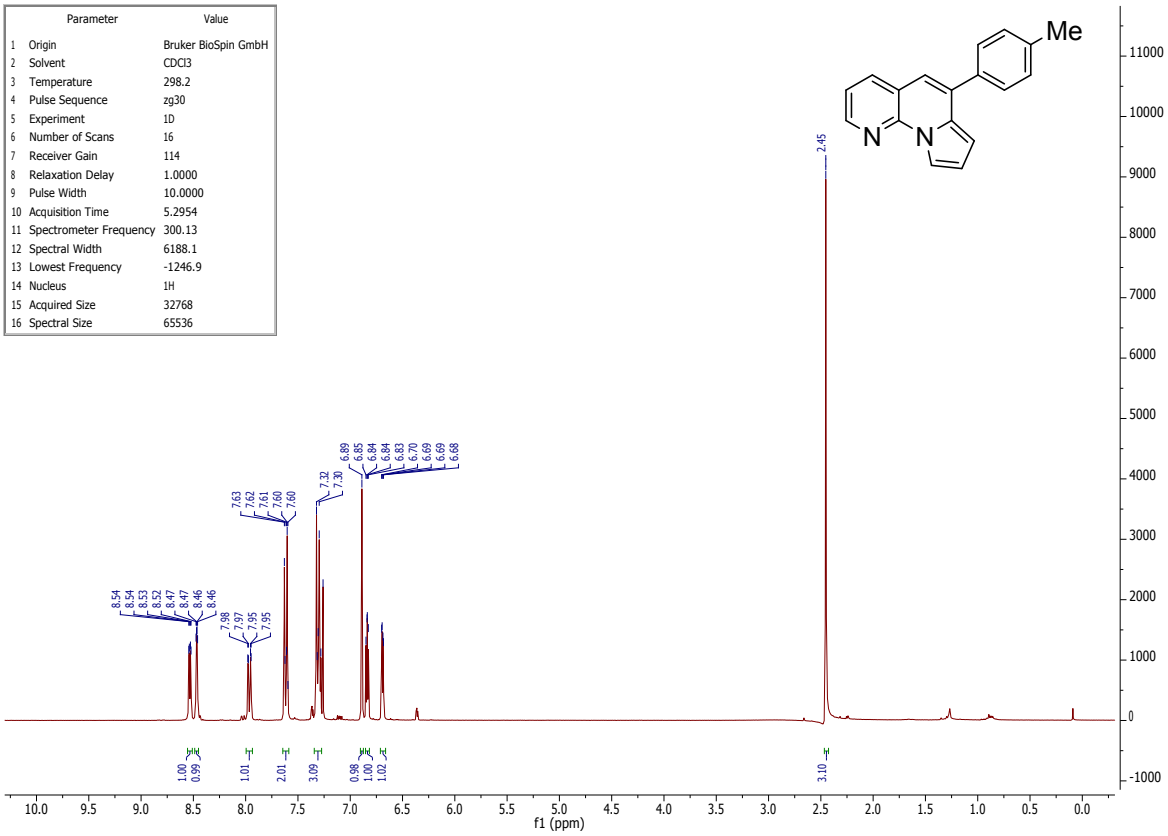


| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgfhigqn |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 64 |
| 7 | Receiver Gain | 18 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 9.5000 |
| 10 | Acquisition Time | 1.3982 |
| 11 | Spectrometer Frequency | 235.33 |
| 12 | Spectral Width | 93750.0 |
| 13 | Lowest Frequency | -70411.0 |
| 14 | Nucleus | 19F |
| 15 | Acquired Size | 131072 |
| 16 | Spectral Size | 262144 |

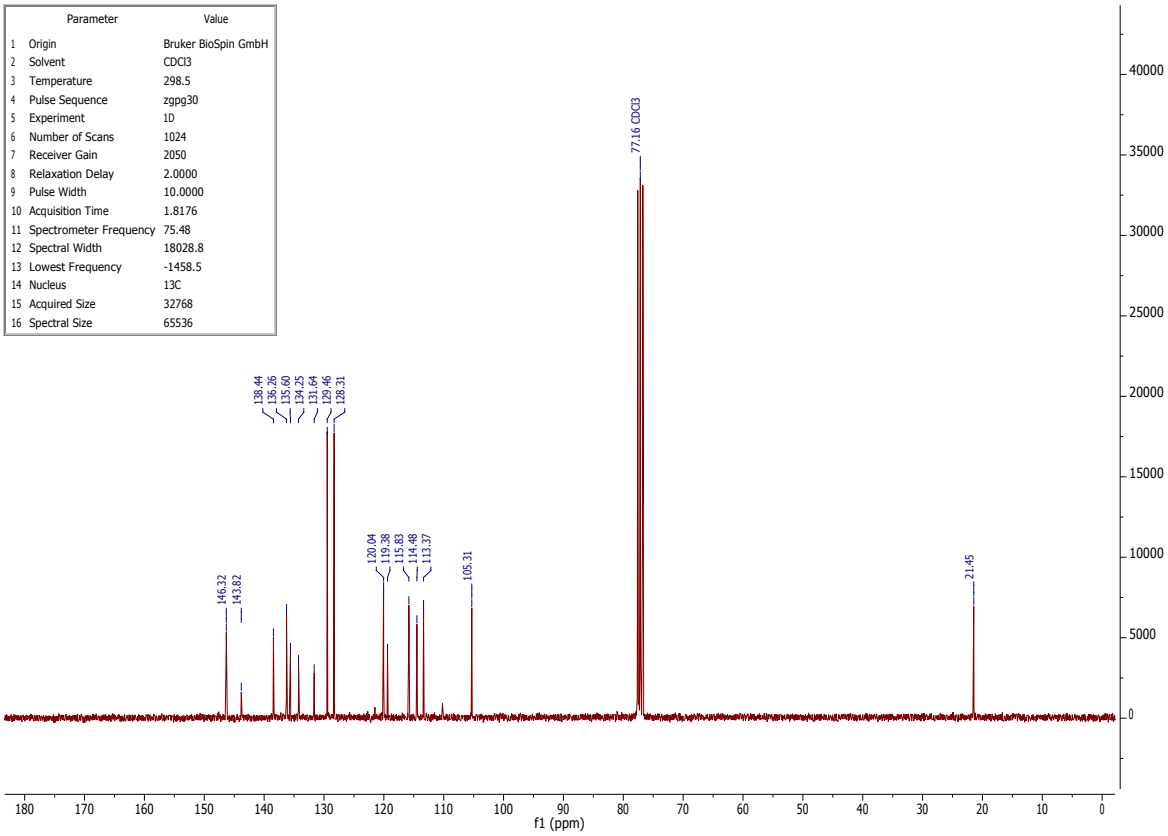


## 6-(4-Tolyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3d

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 114 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.9 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

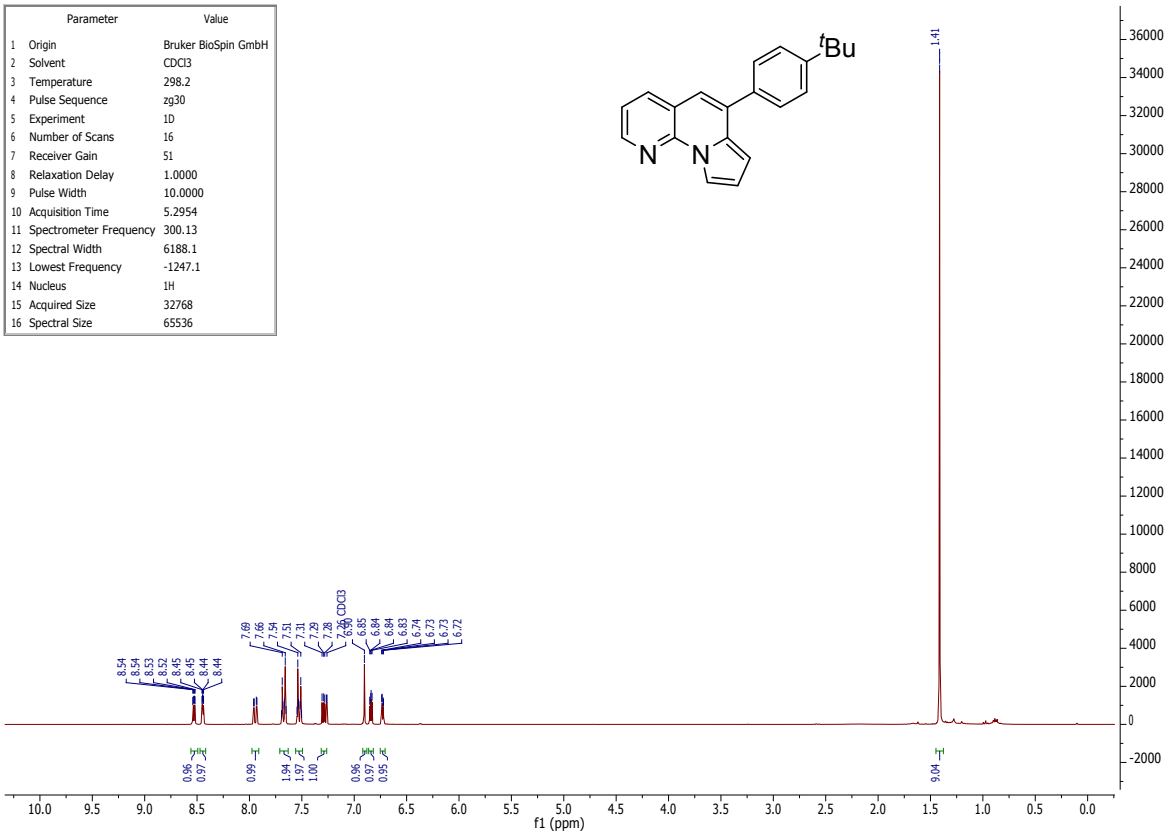



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.5 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1458.5 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

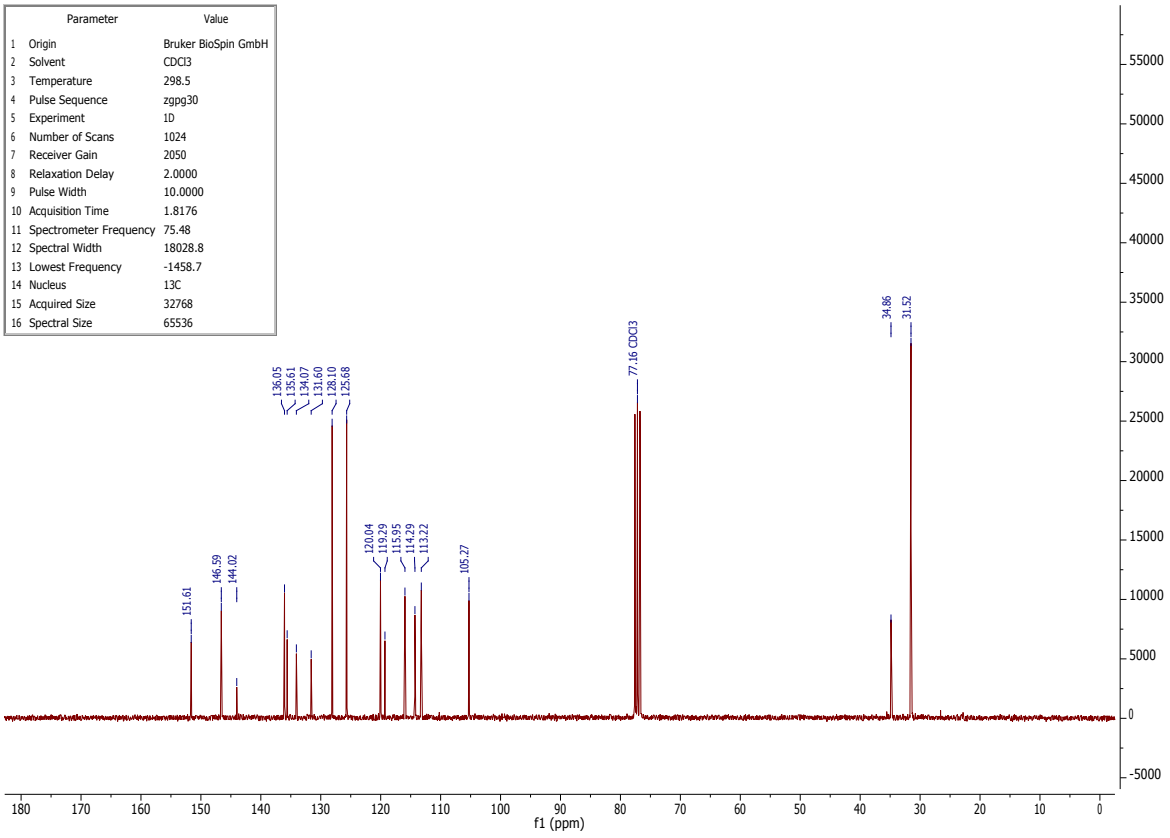


## 6-(4-*tert*-Butylphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3e

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 51 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1247.1 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

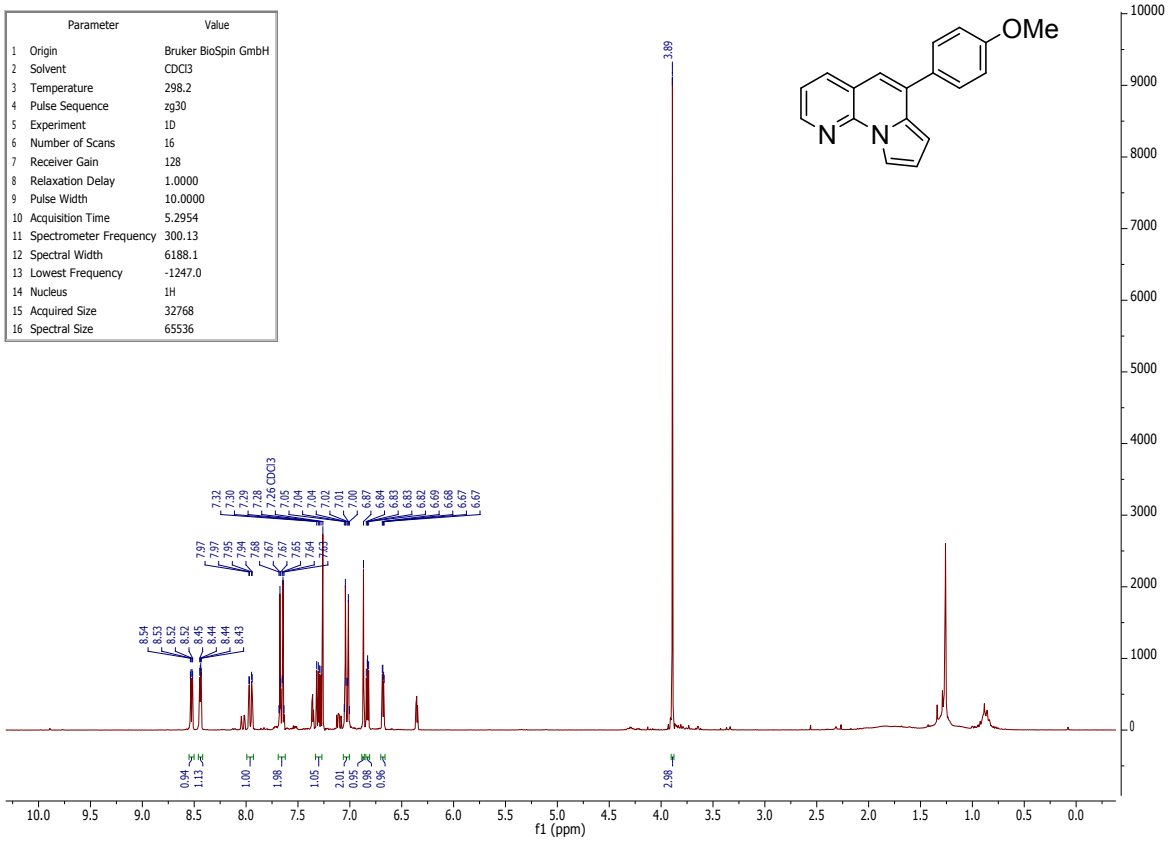



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.5 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1458.7 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

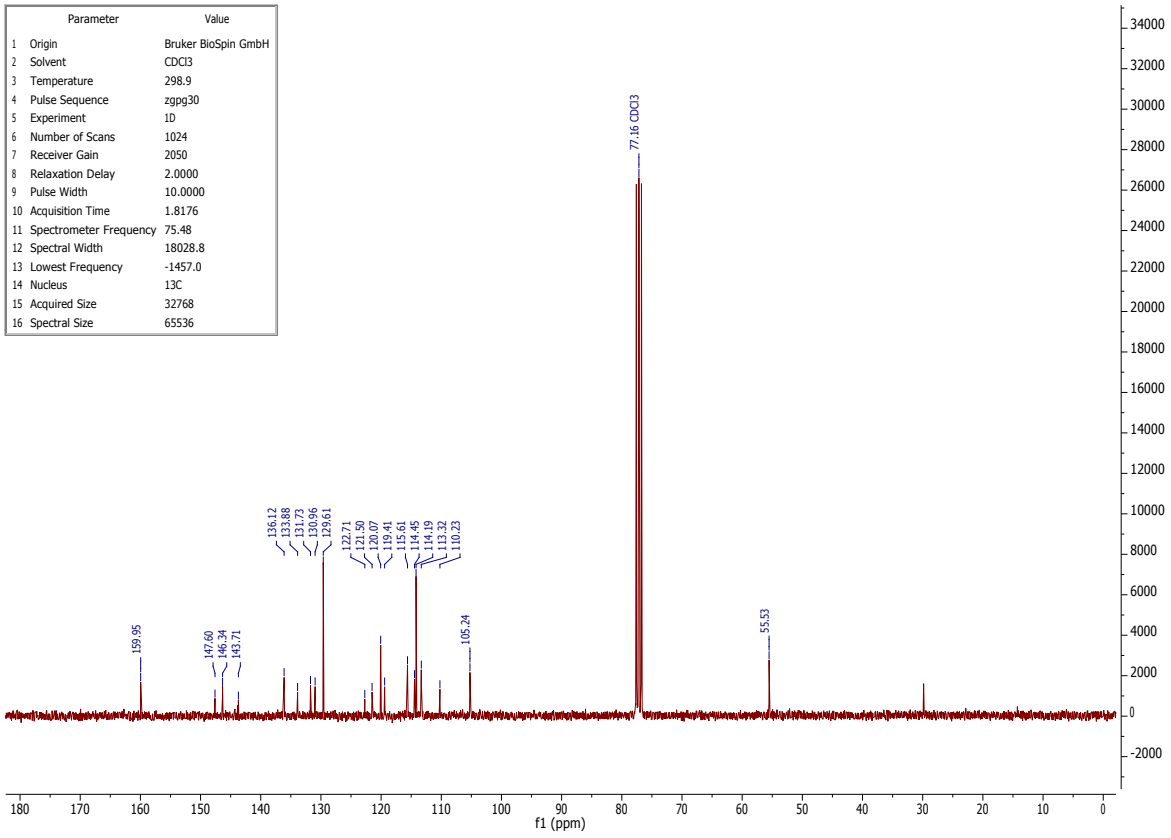


## 6-(4-Methoxyphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3f

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 128 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1247.0 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

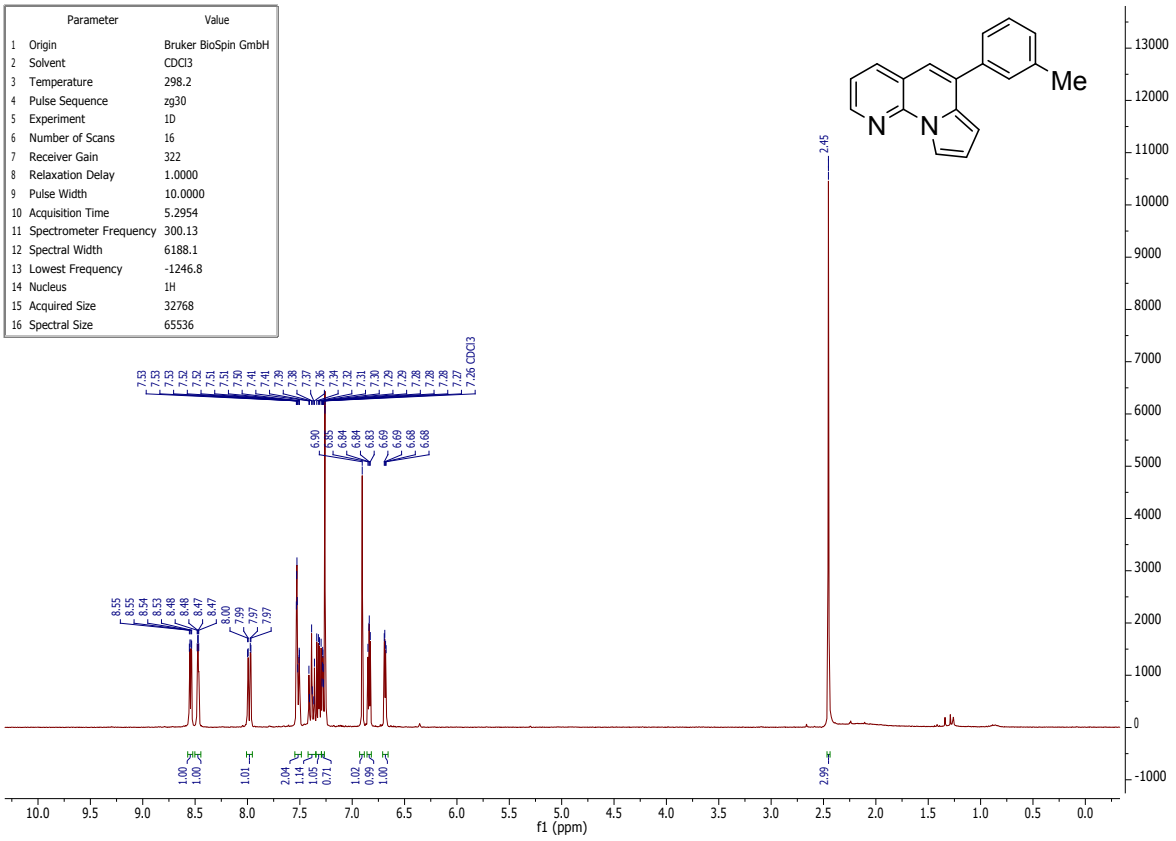



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.9 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1457.0 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

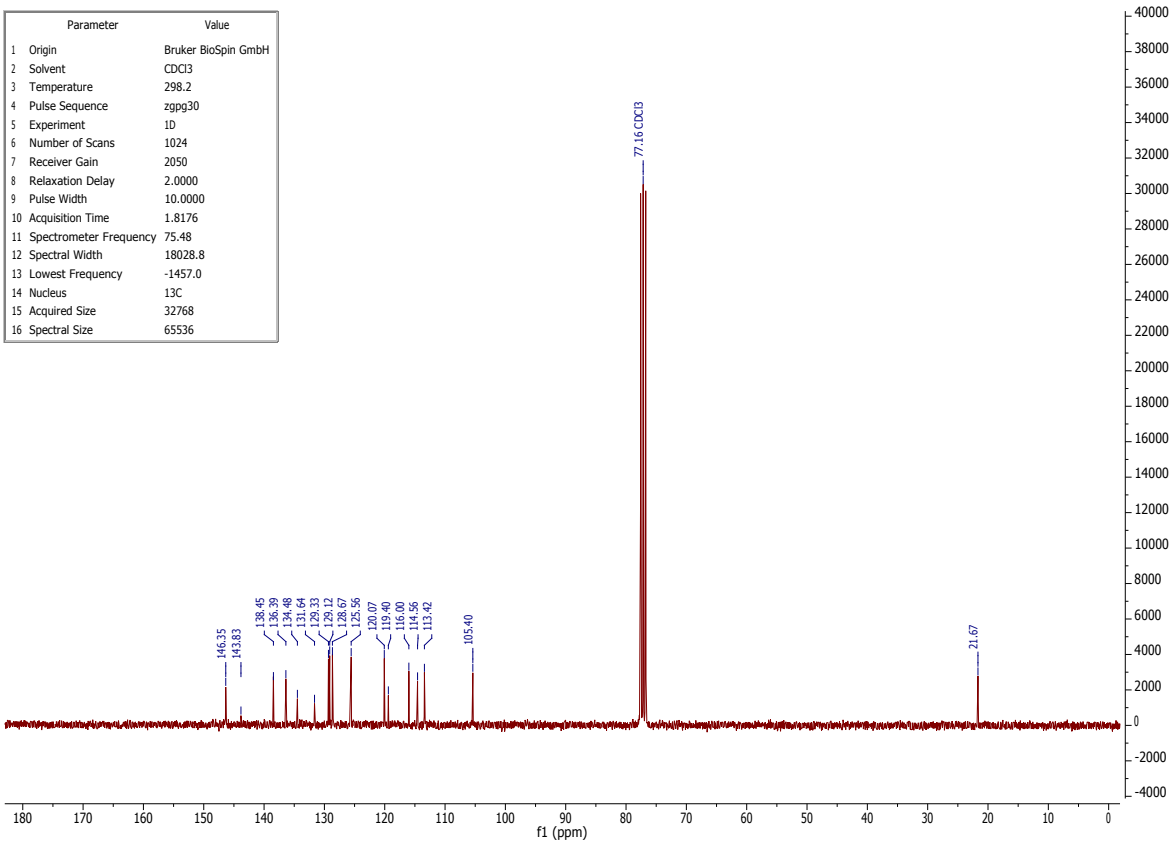


## 6-(3-Tolyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3g

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 322 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.8 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

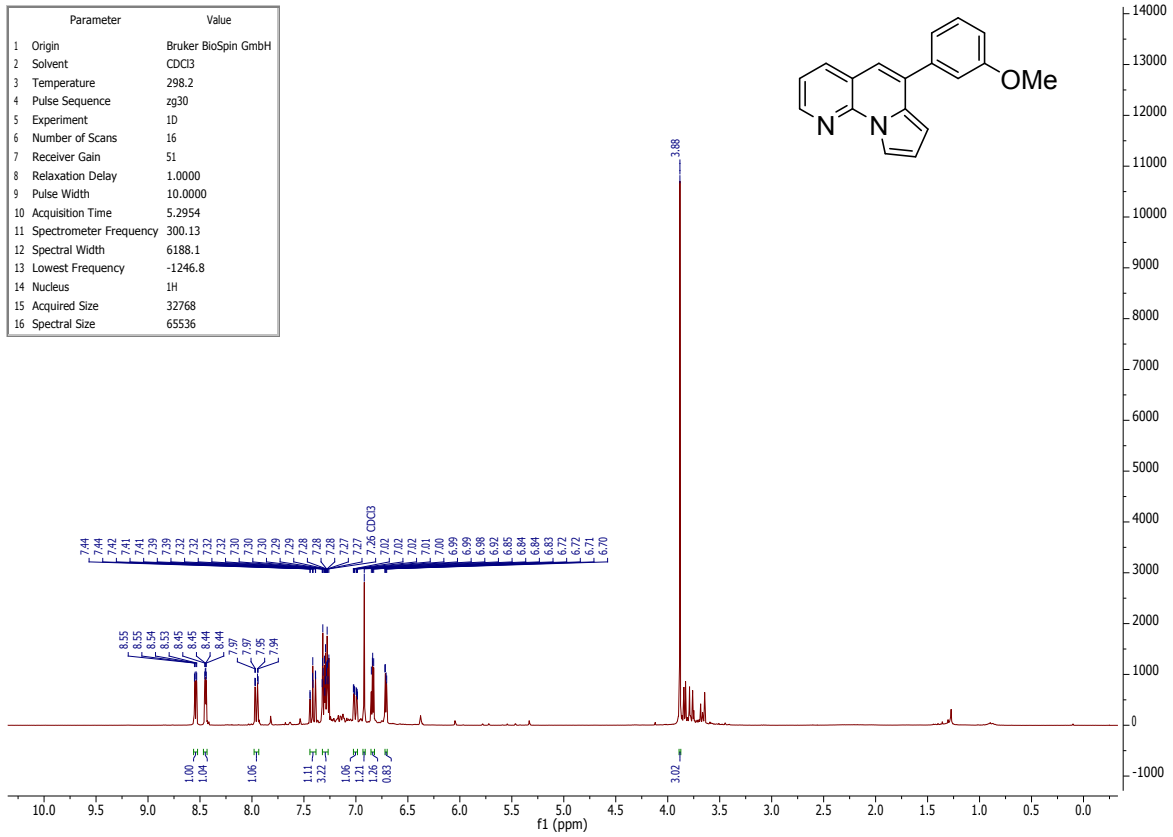



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1457.0 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

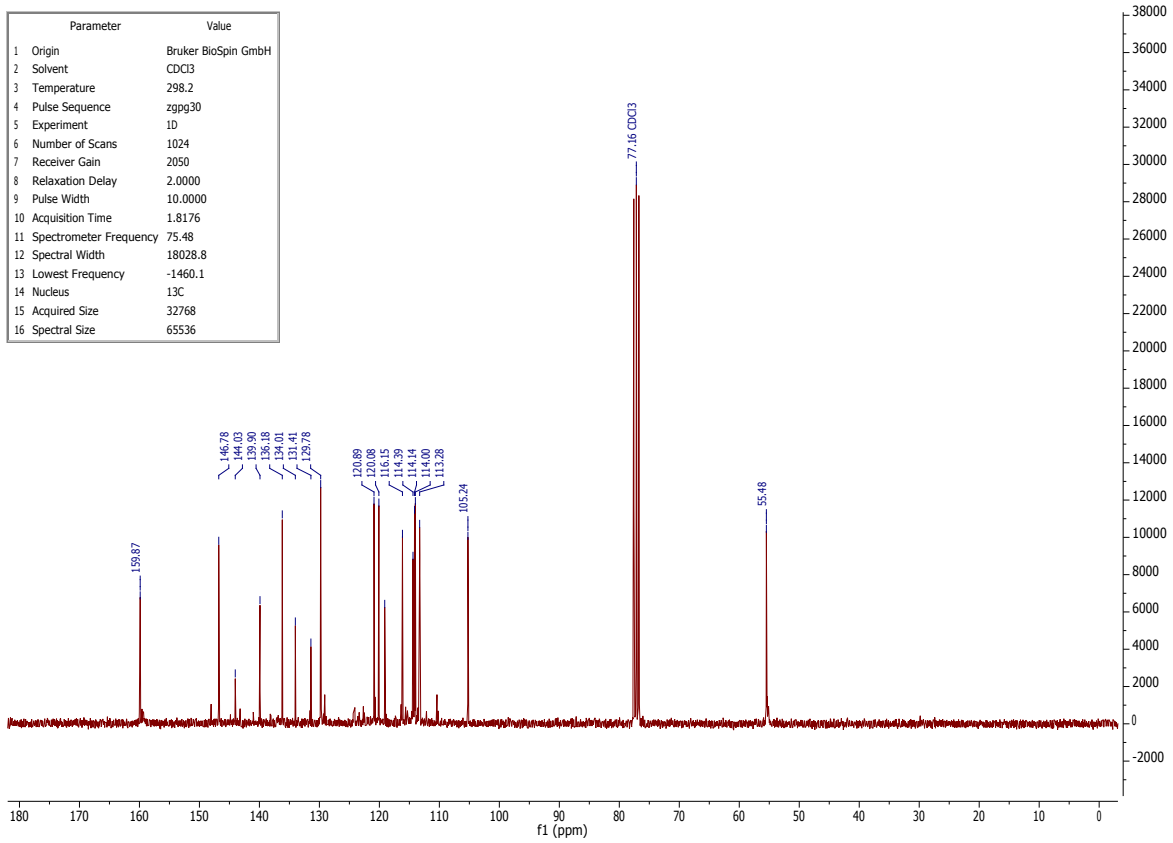


## 6-(3-Methoxyphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3h

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 51 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.8 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

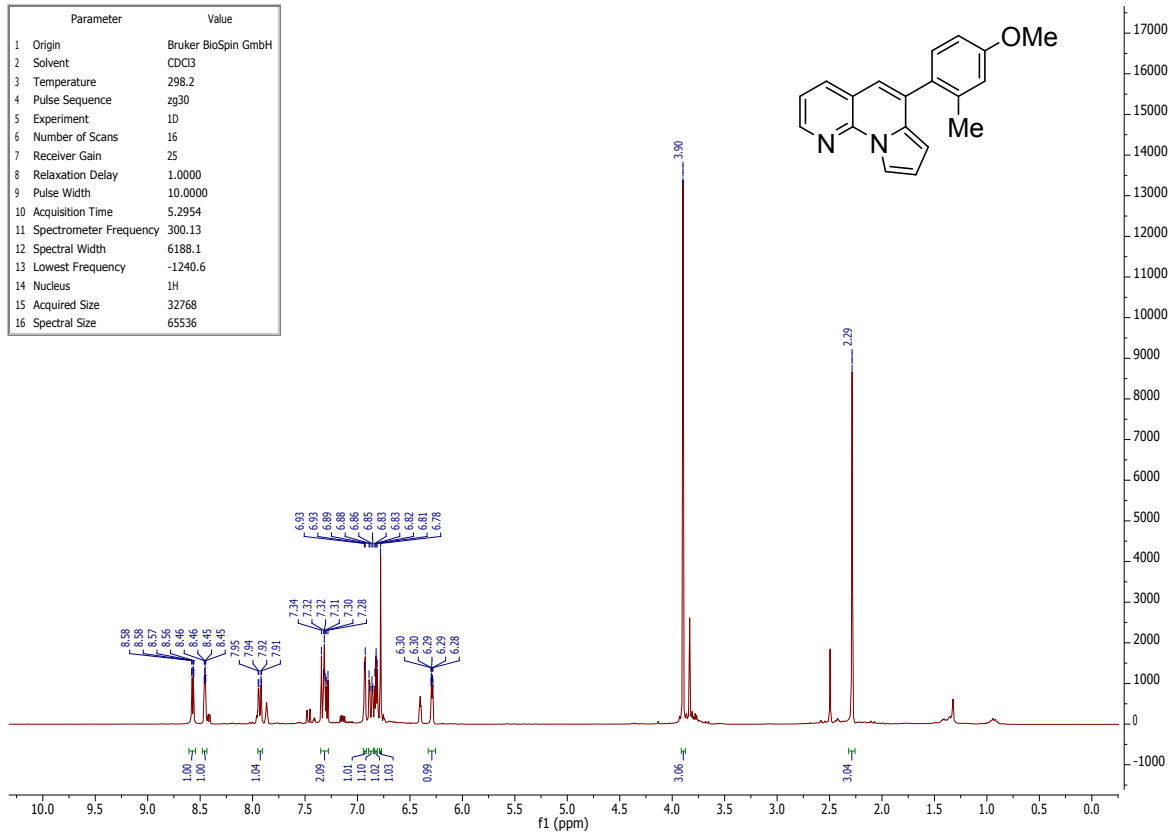



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1460.1 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

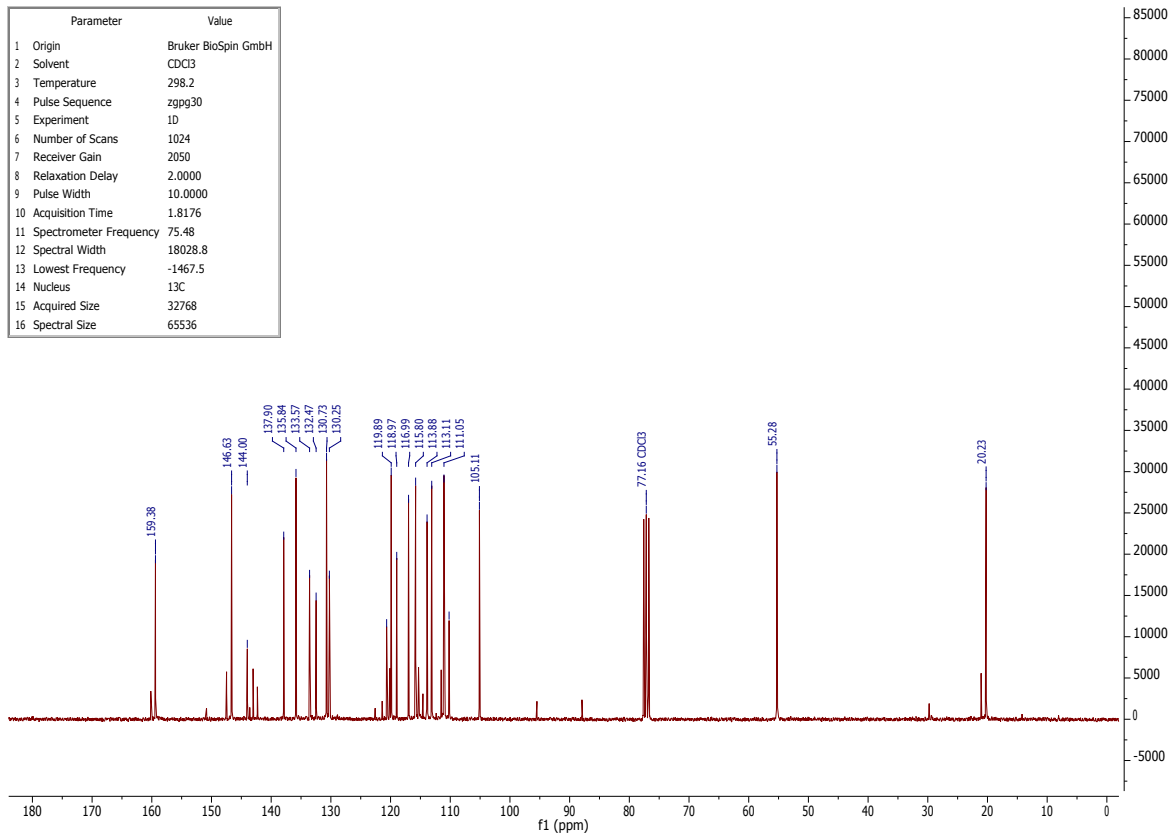


## 6-(4-Methoxy-2-methylphenyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3i

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 25 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1240.6 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

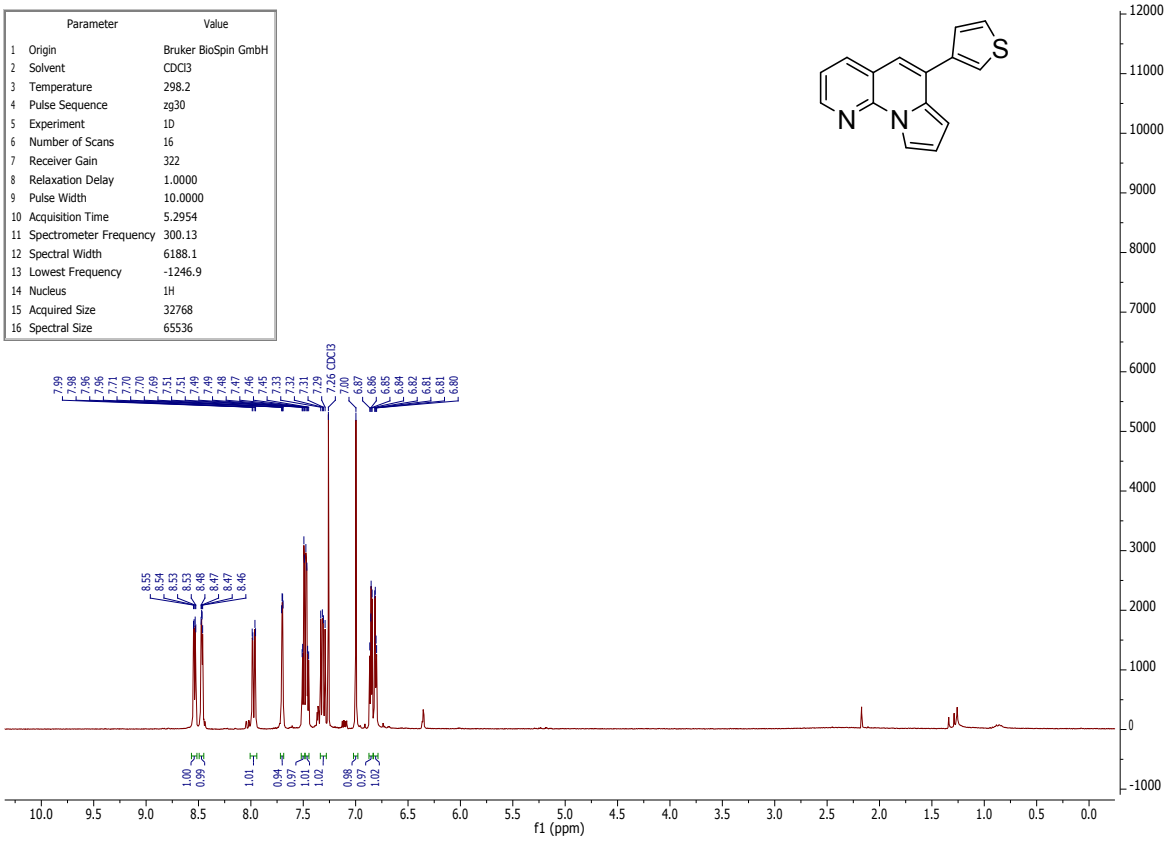



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1467.5 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

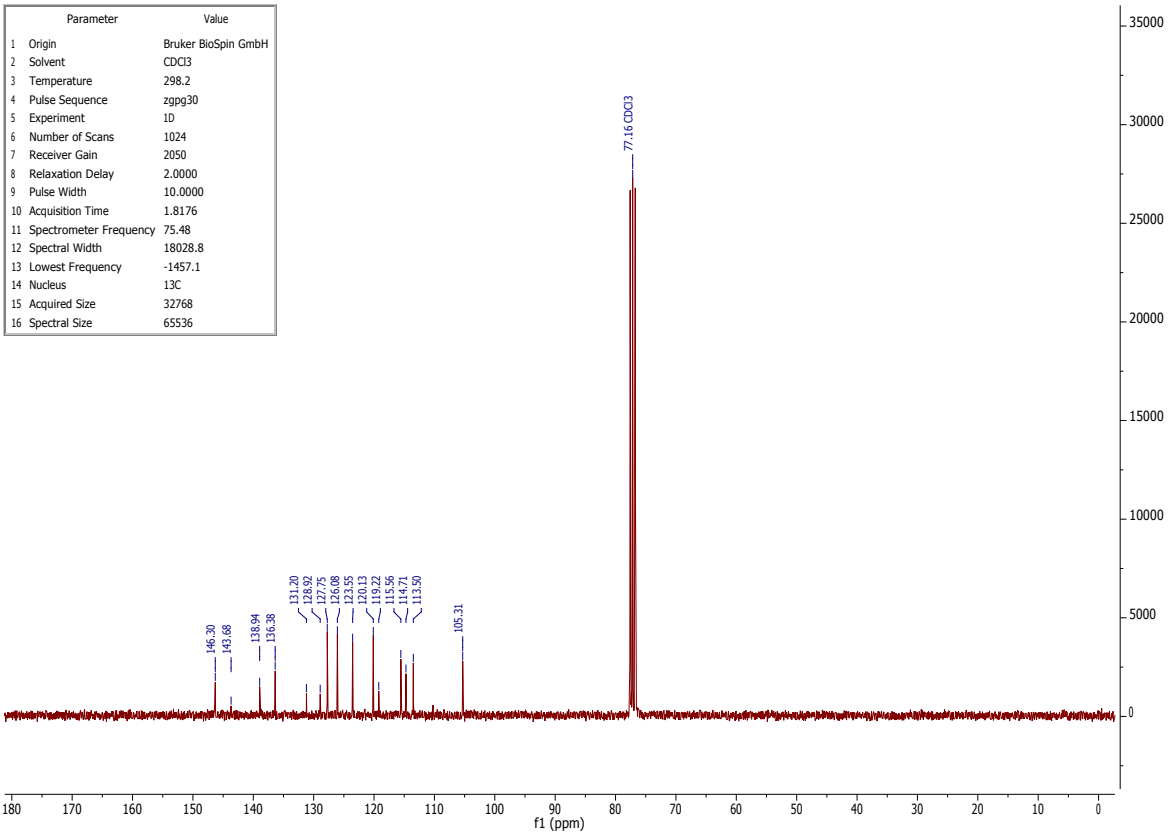


## 6-(Thiophen-3-yl)pyrrolo[1,2-*a*][1,8]naphthyridine 3j

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 322 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.9 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

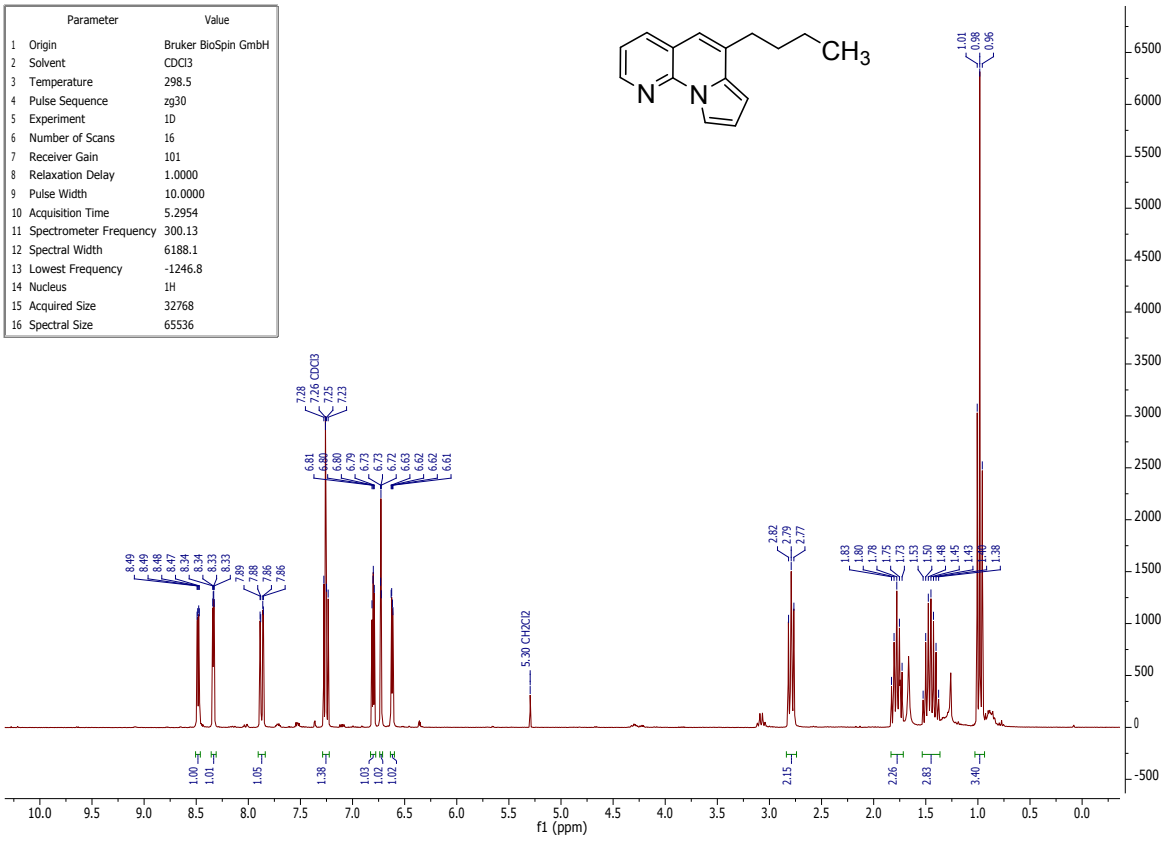



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1457.1 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

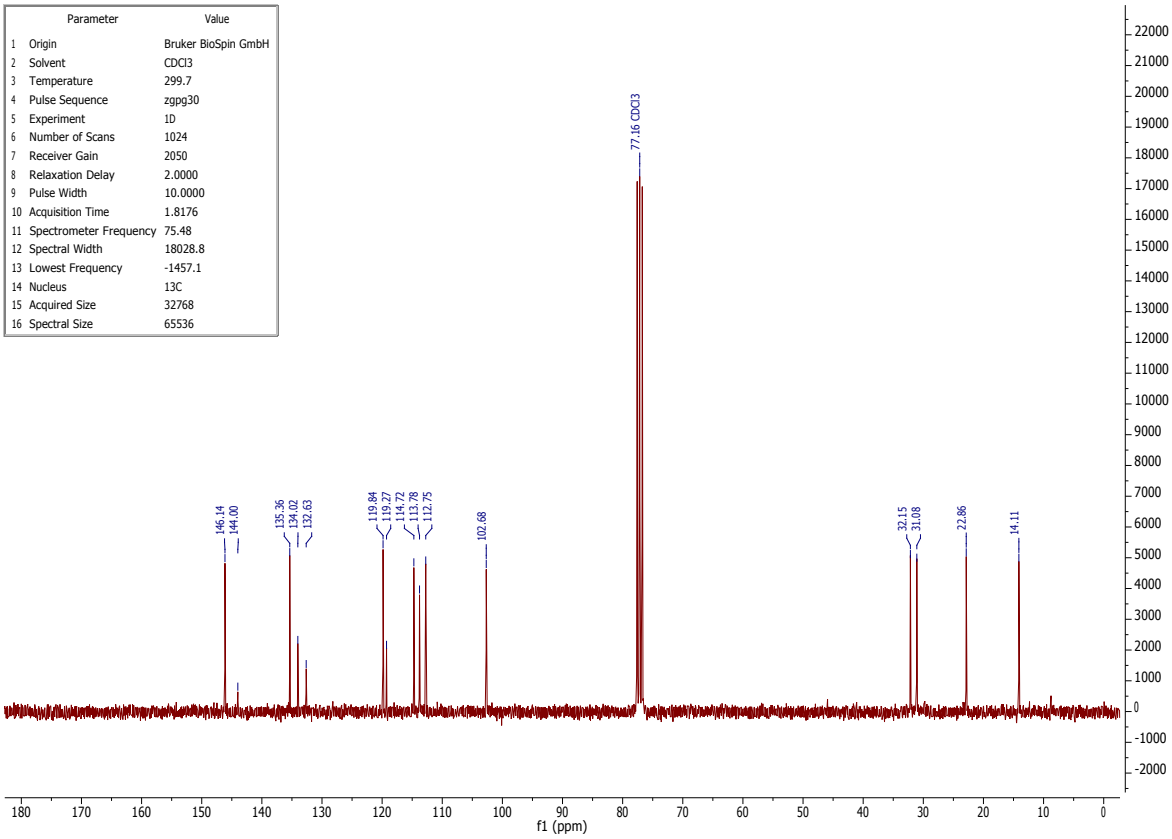


## 6-(*n*-Butyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3l

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.5 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 101 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 5.2954 |
| 11 | Spectrometer Frequency | 300.13 |
| 12 | Spectral Width | 6188.1 |
| 13 | Lowest Frequency | -1246.8 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

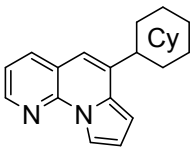


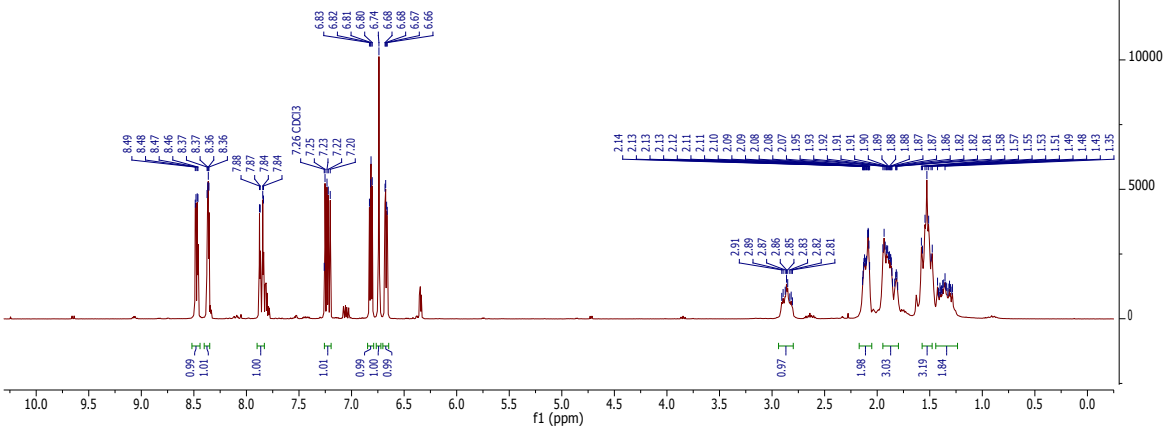

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 299.7 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.0000 |
| 10 | Acquisition Time | 1.8176 |
| 11 | Spectrometer Frequency | 75.48 |
| 12 | Spectral Width | 18028.8 |
| 13 | Lowest Frequency | -1457.1 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |



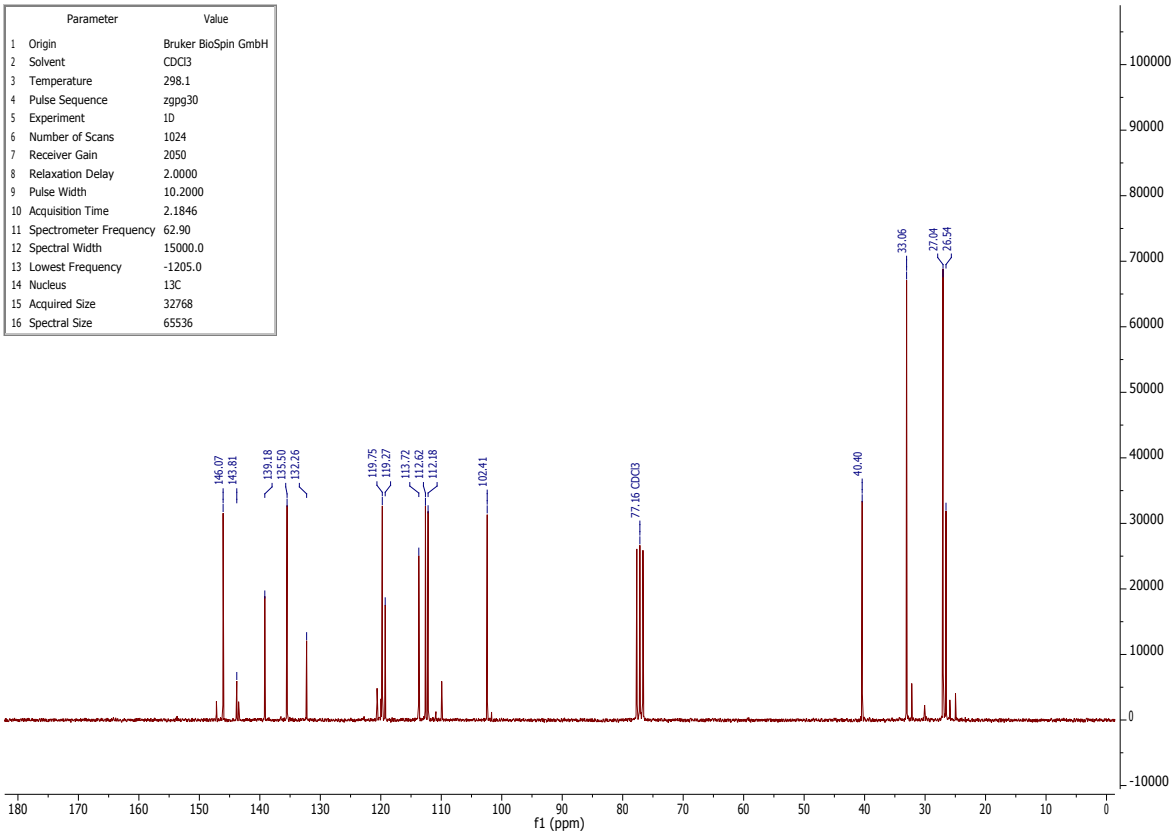
## 6-(Cyclohexyl)pyrrolo[1,2-*a*][1,8]naphthyridine 3m

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 16 |
| 7 | Receiver Gain | 287 |
| 8 | Relaxation Delay | 1.0000 |
| 9 | Pulse Width | 11.4000 |
| 10 | Acquisition Time | 6.3439 |
| 11 | Spectrometer Frequency | 250.13 |
| 12 | Spectral Width | 5165.3 |
| 13 | Lowest Frequency | -1038.7 |
| 14 | Nucleus | 1H |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

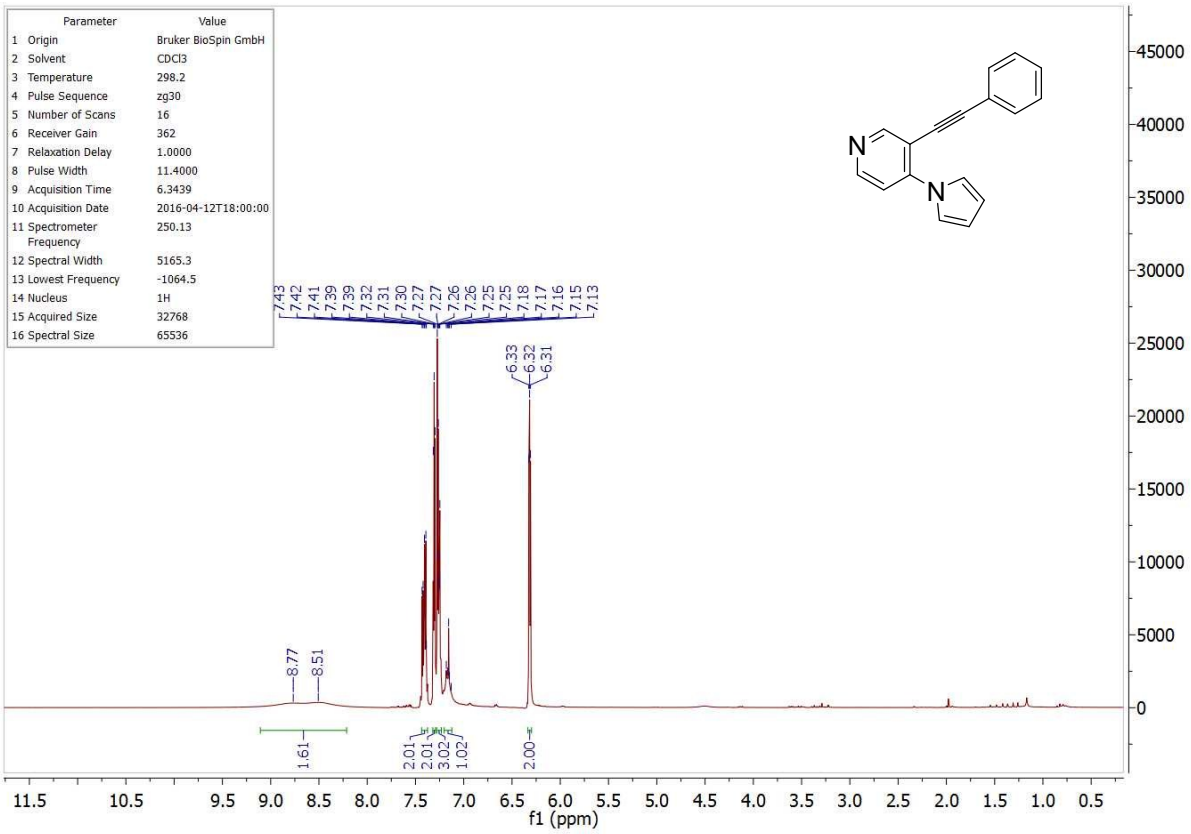


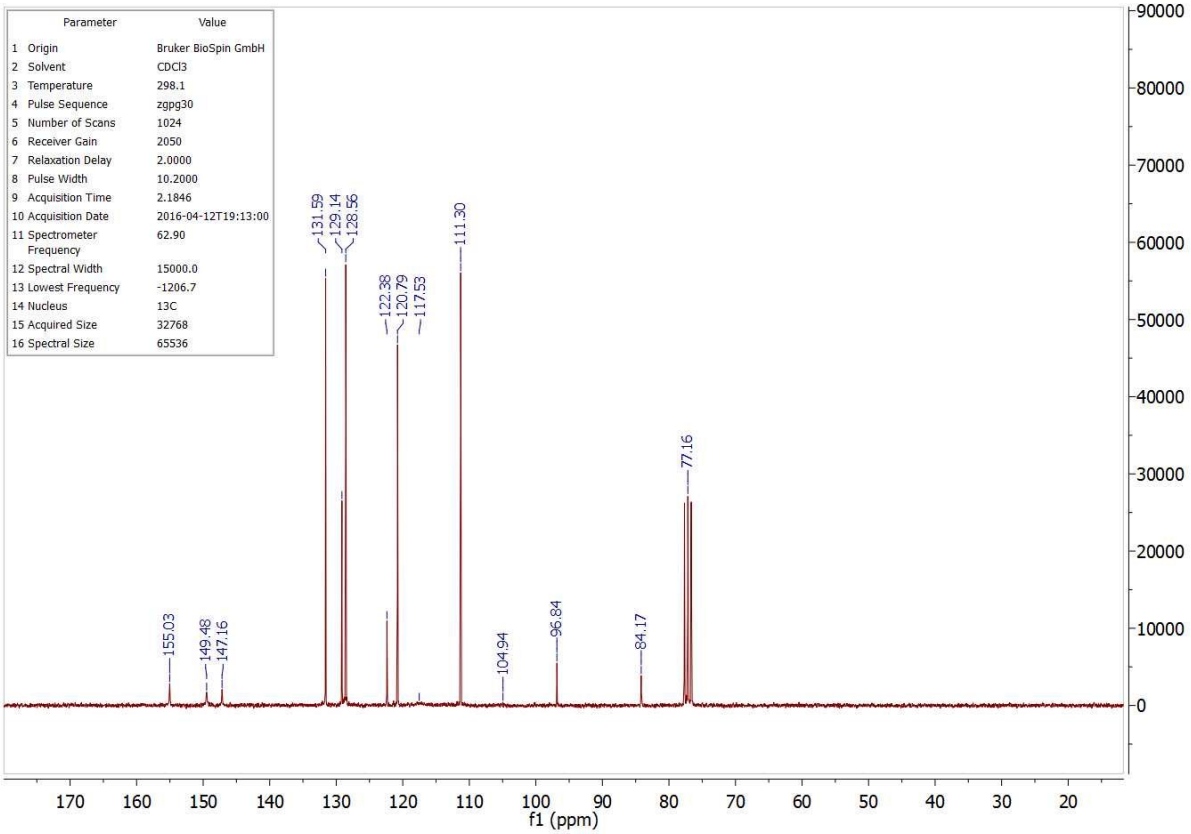




| | Parameter | Value |
|---|---|---|
| 1 | Origin | Bruker BioSpin GmbH |
| 2 | Solvent | CDCl3 |
| 3 | Temperature | 298.1 |
| 4 | Pulse Sequence | zgpg30 |
| 5 | Experiment | 1D |
| 6 | Number of Scans | 1024 |
| 7 | Receiver Gain | 2050 |
| 8 | Relaxation Delay | 2.0000 |
| 9 | Pulse Width | 10.2000 |
| 10 | Acquisition Time | 2.1846 |
| 11 | Spectrometer Frequency | 62.90 |
| 12 | Spectral Width | 15000.0 |
| 13 | Lowest Frequency | -1205.0 |
| 14 | Nucleus | 13C |
| 15 | Acquired Size | 32768 |
| 16 | Spectral Size | 65536 |

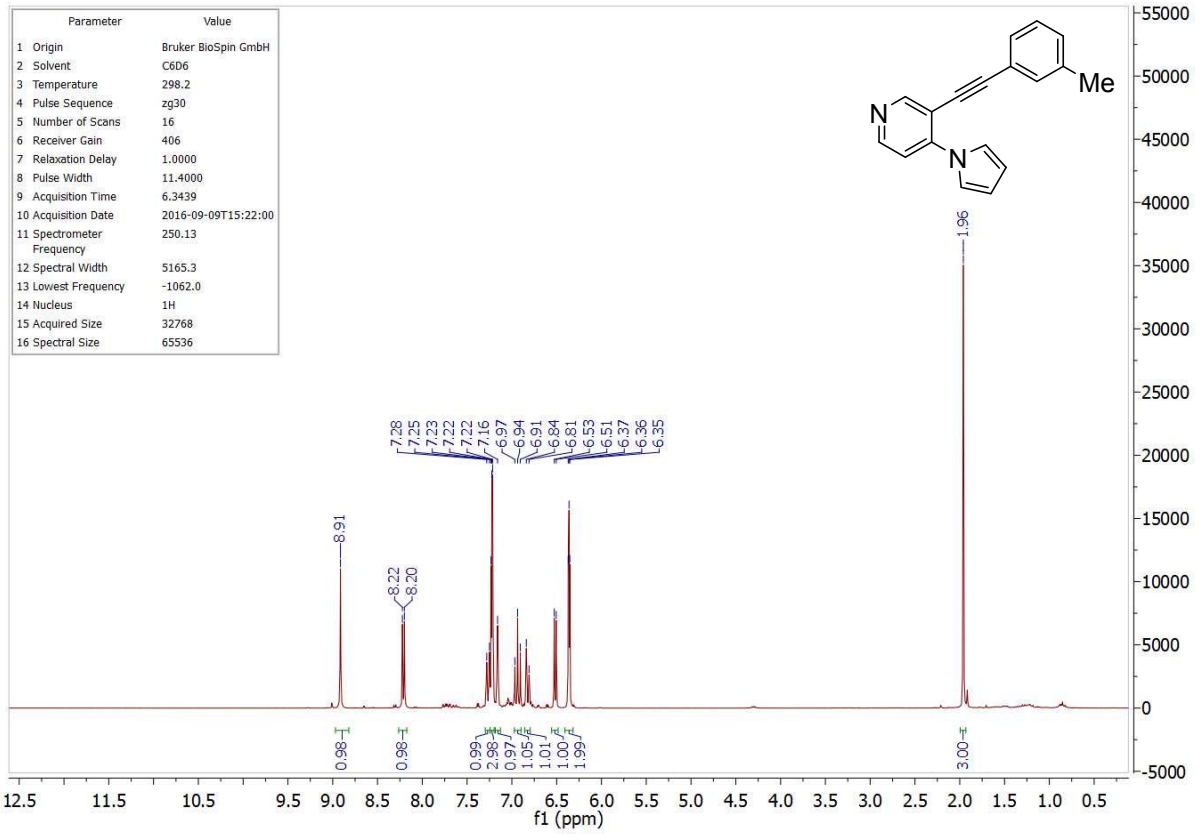


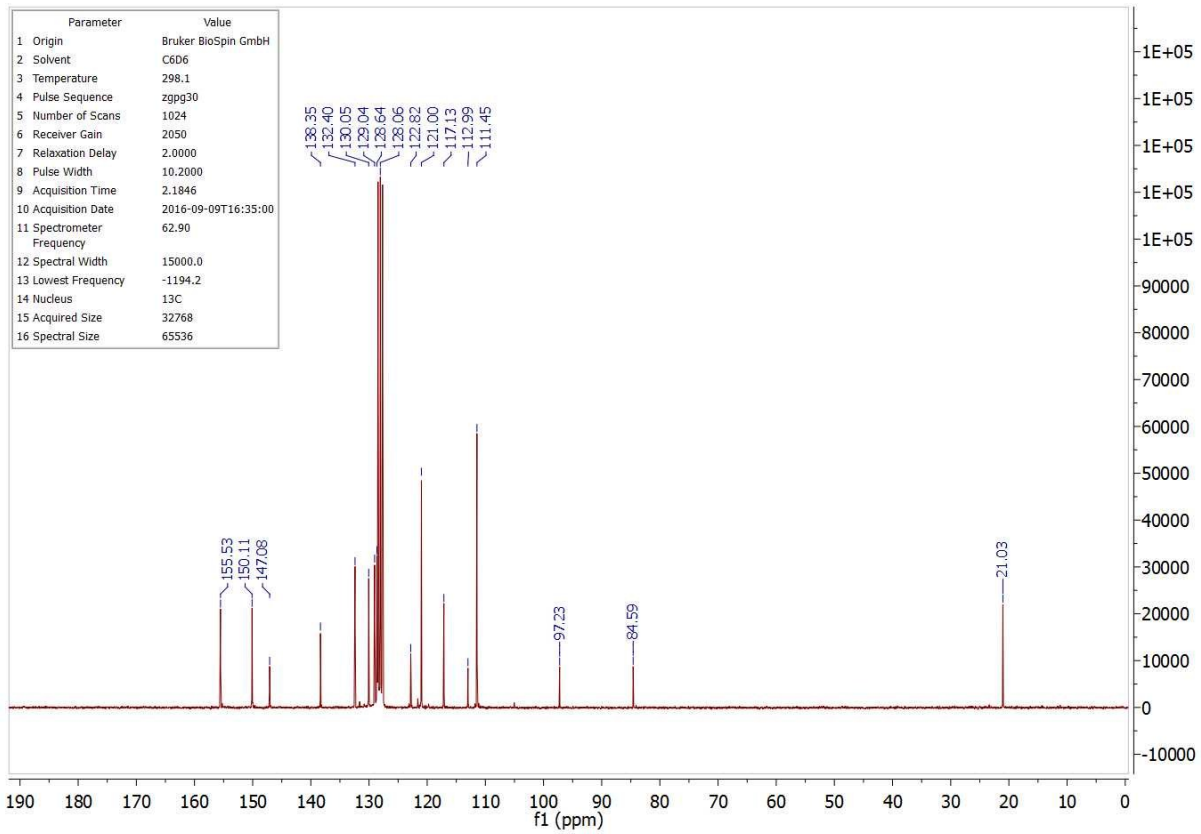
## 3-(Phenylethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4a



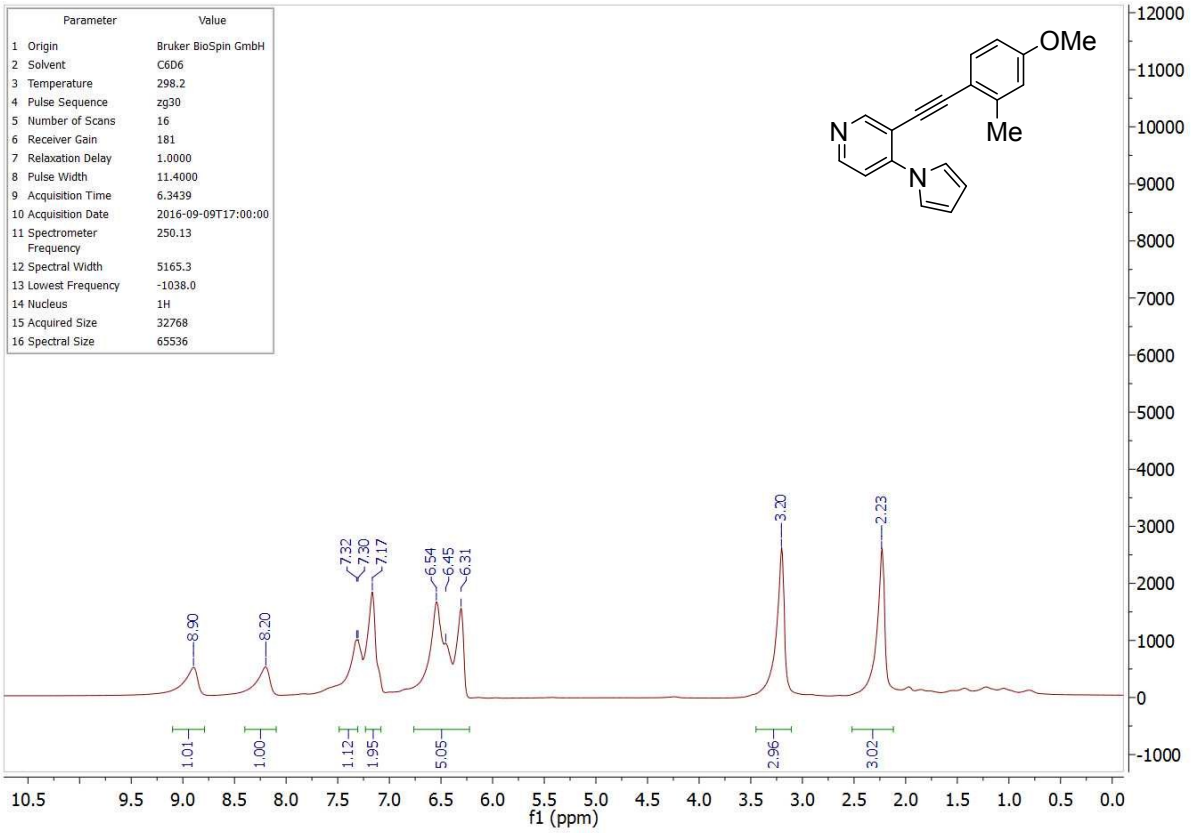



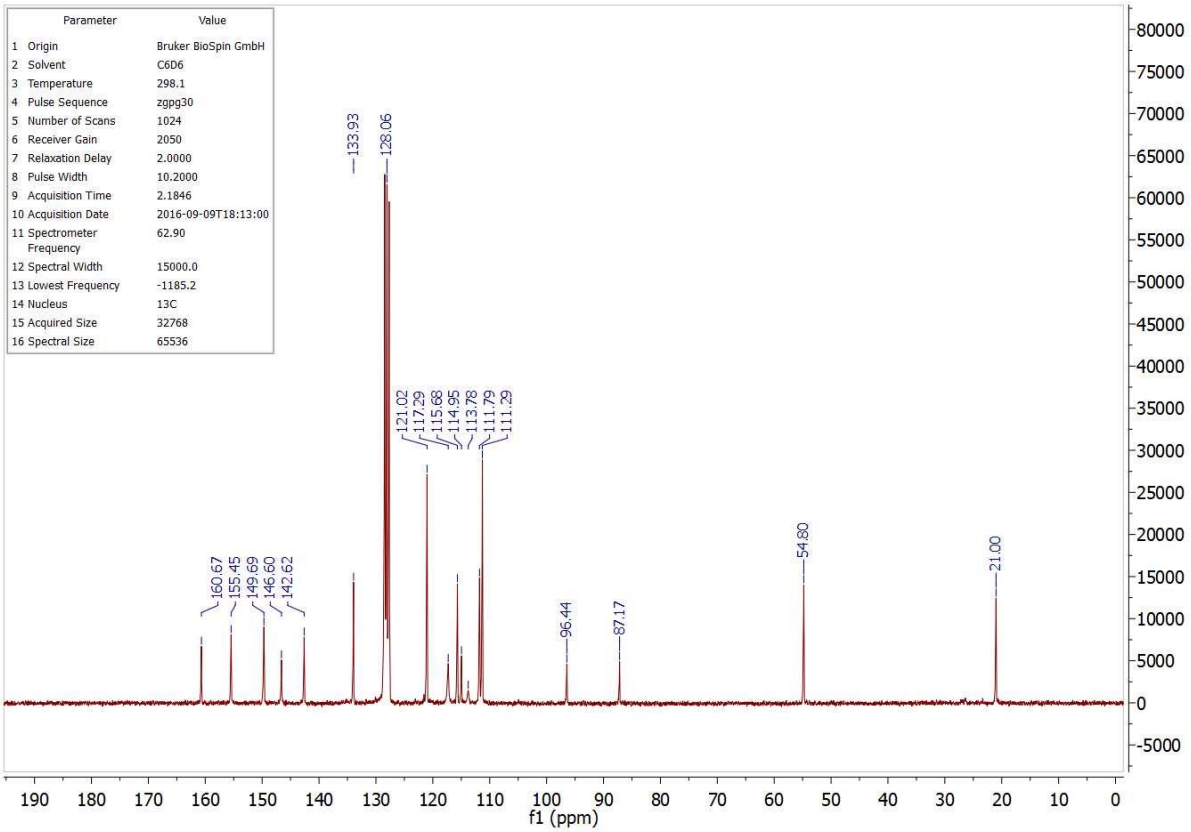
## 3-((3-Methylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4b



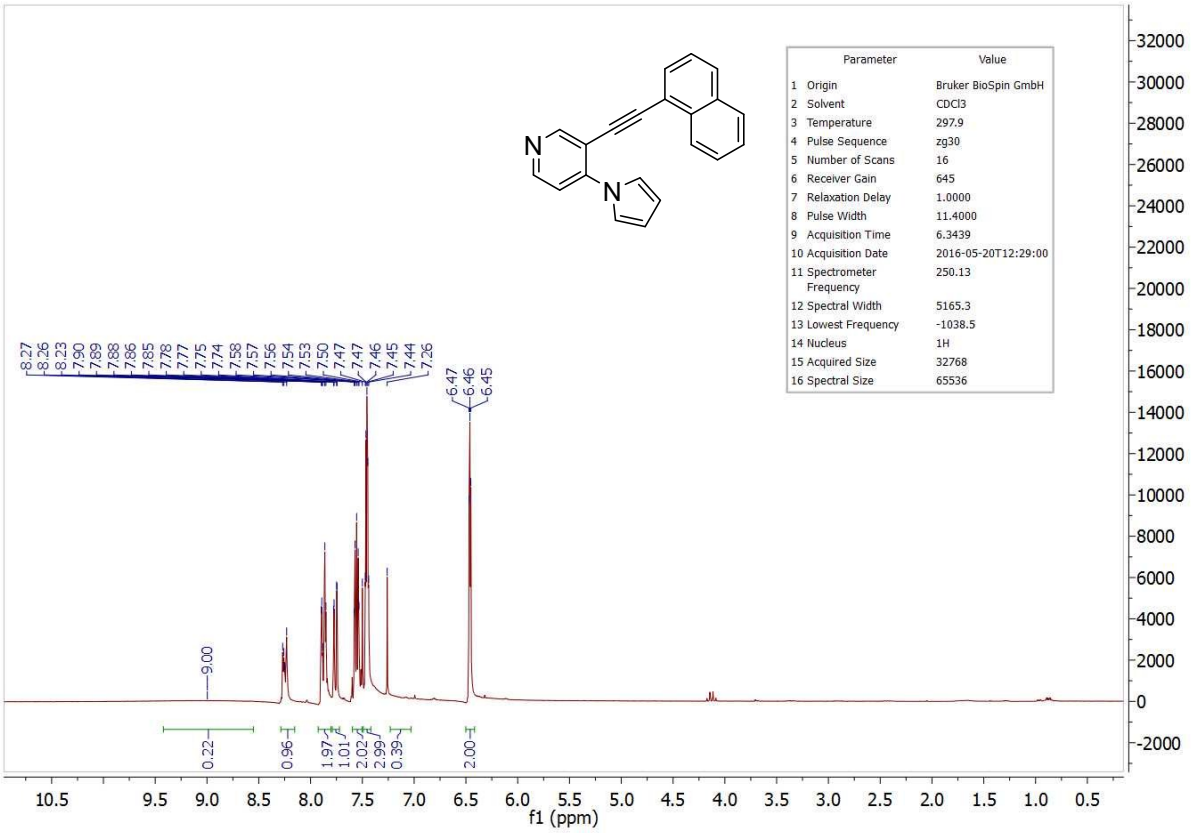



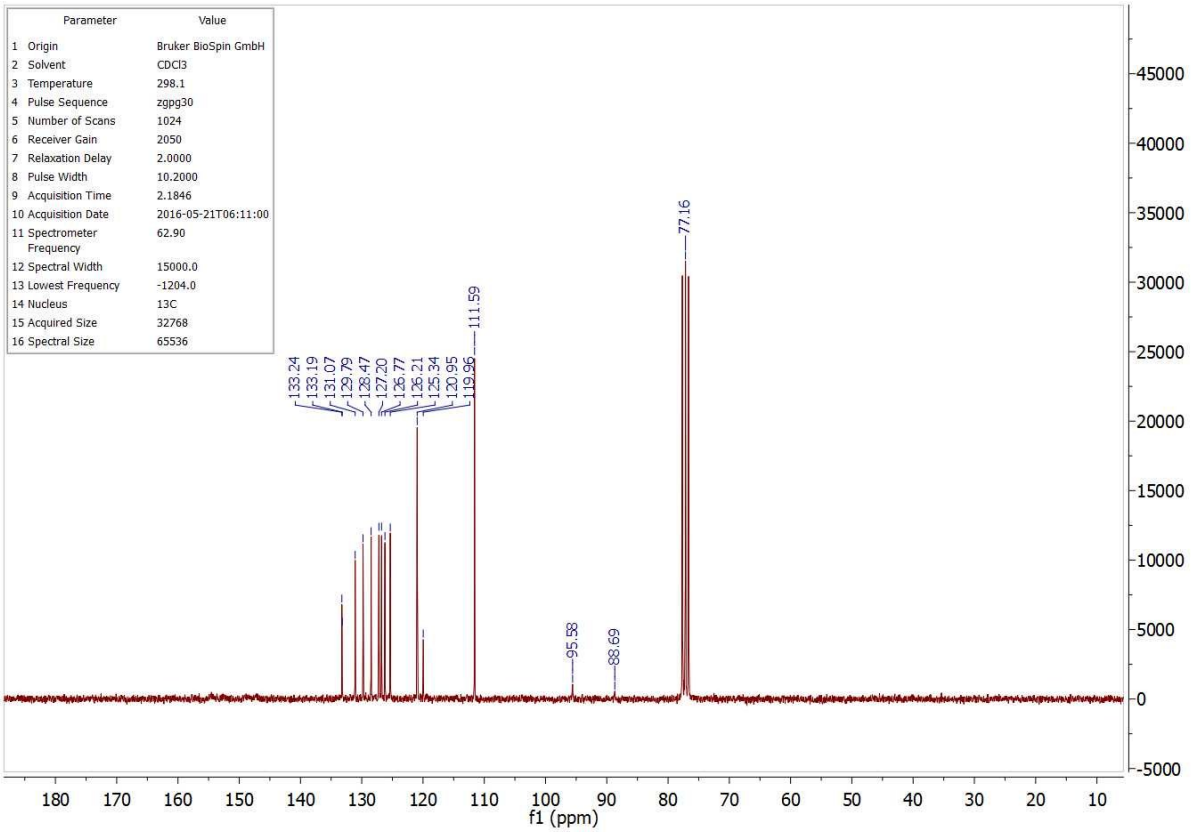
## 3-((4-Methoxy-2-methylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4c



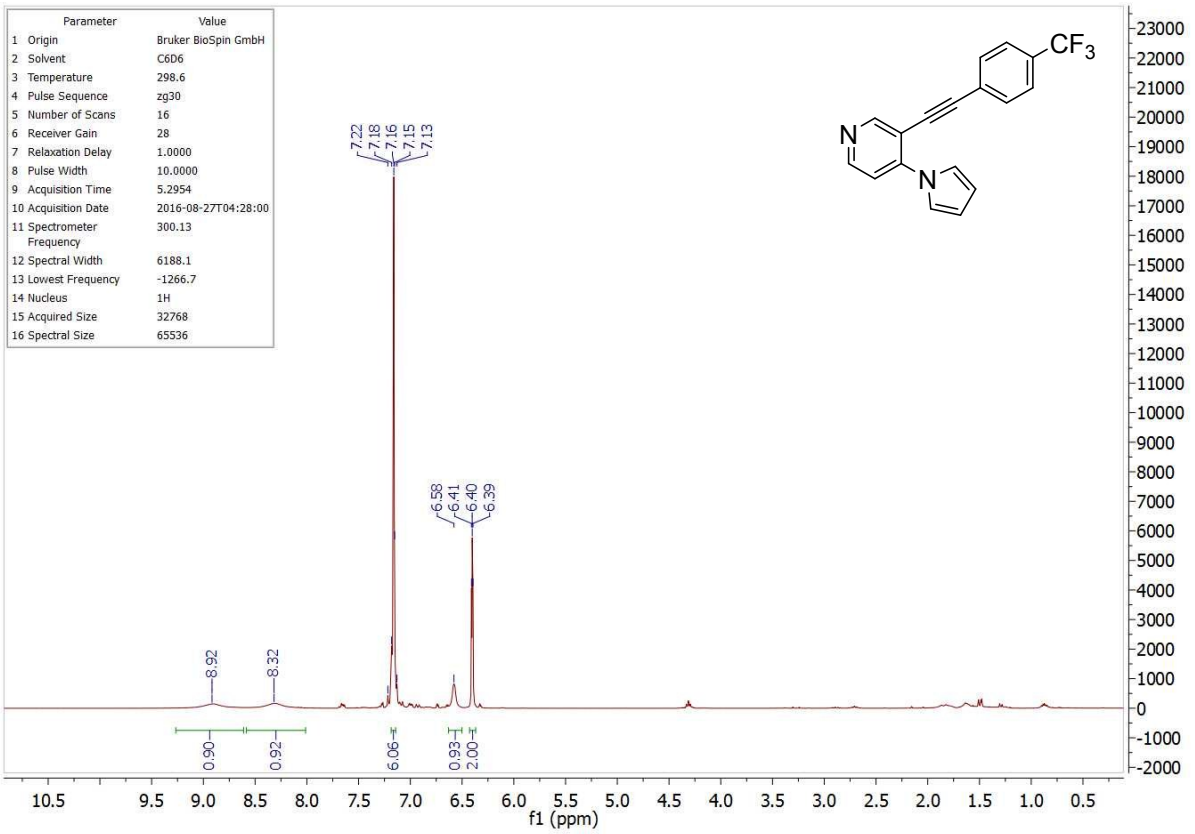



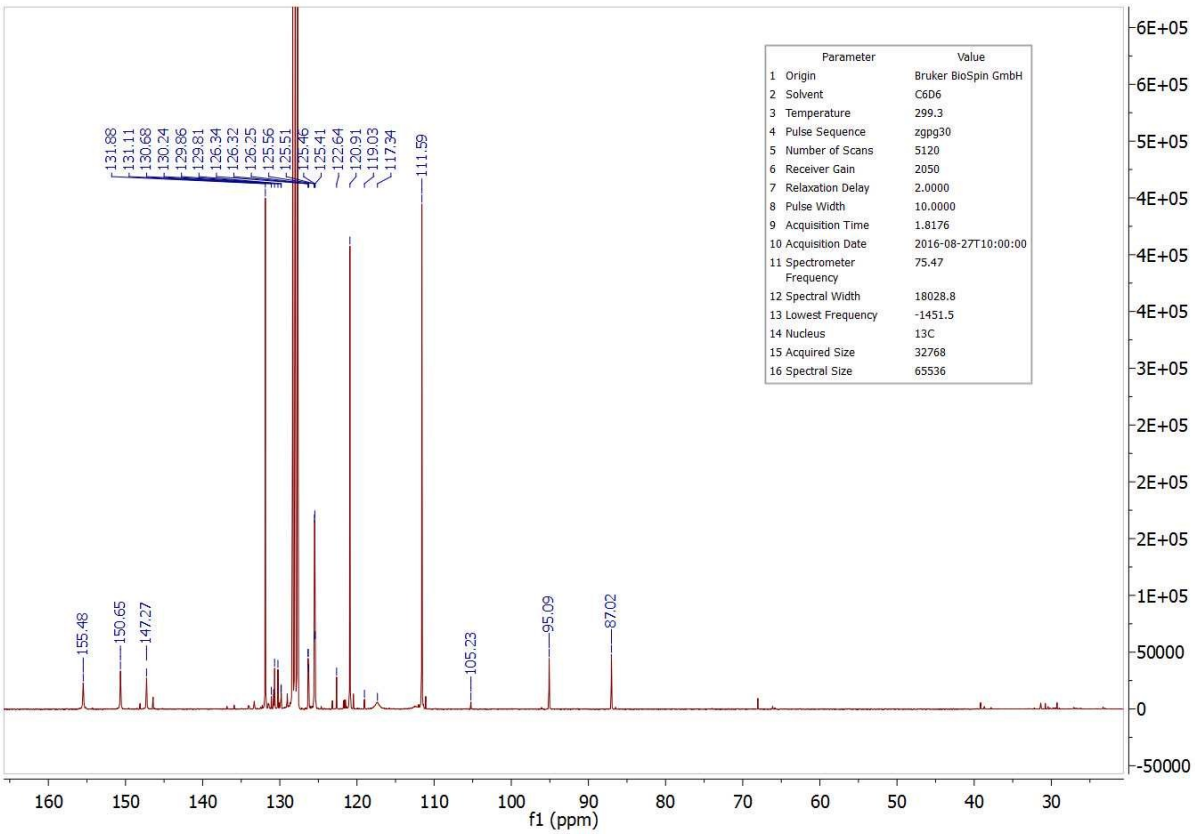
## 3-(Naphtalen-1-ylethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4d

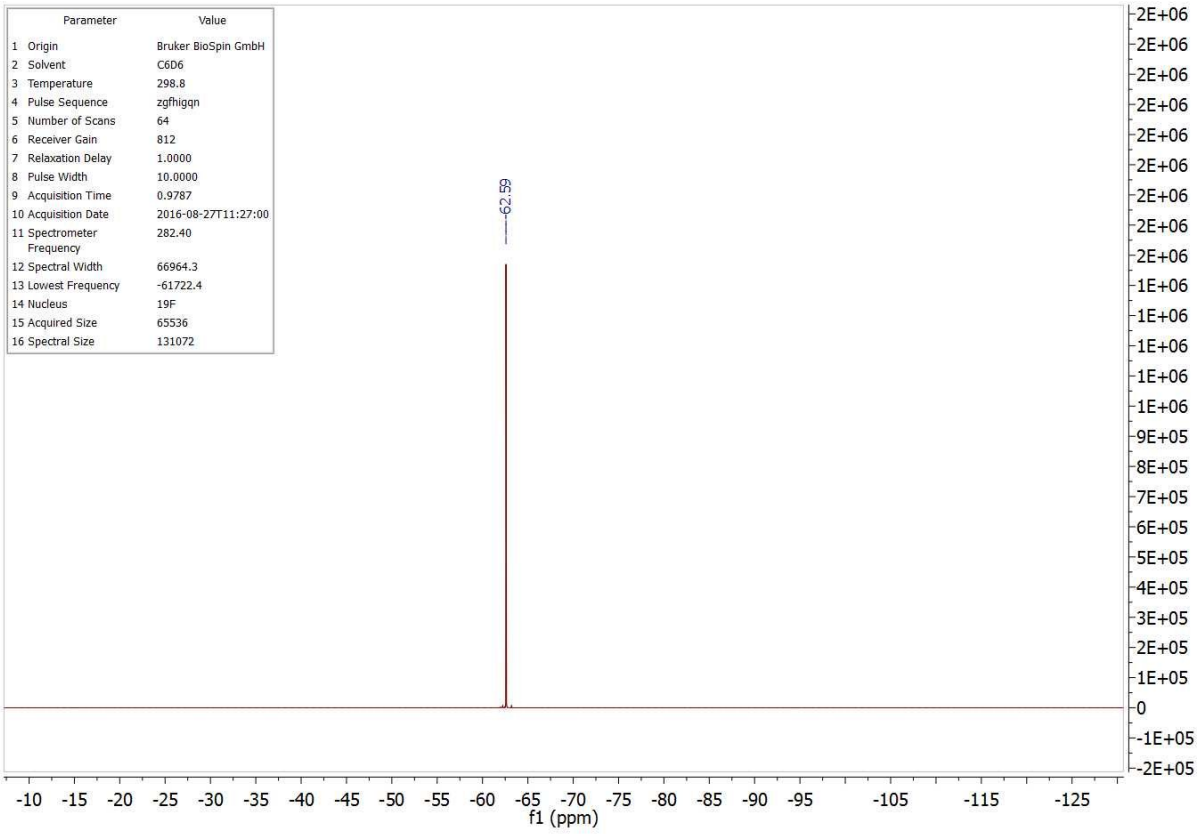


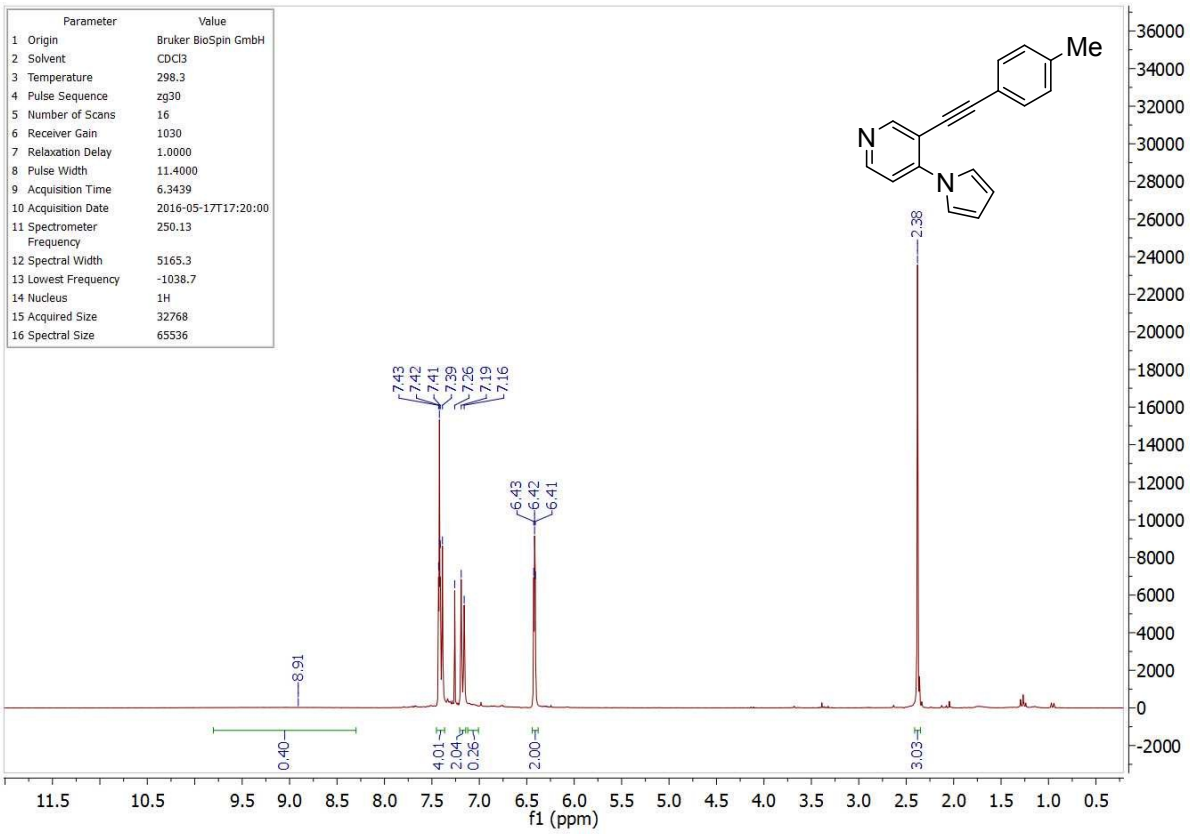
## 3-((4-Trifluoromethylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4e

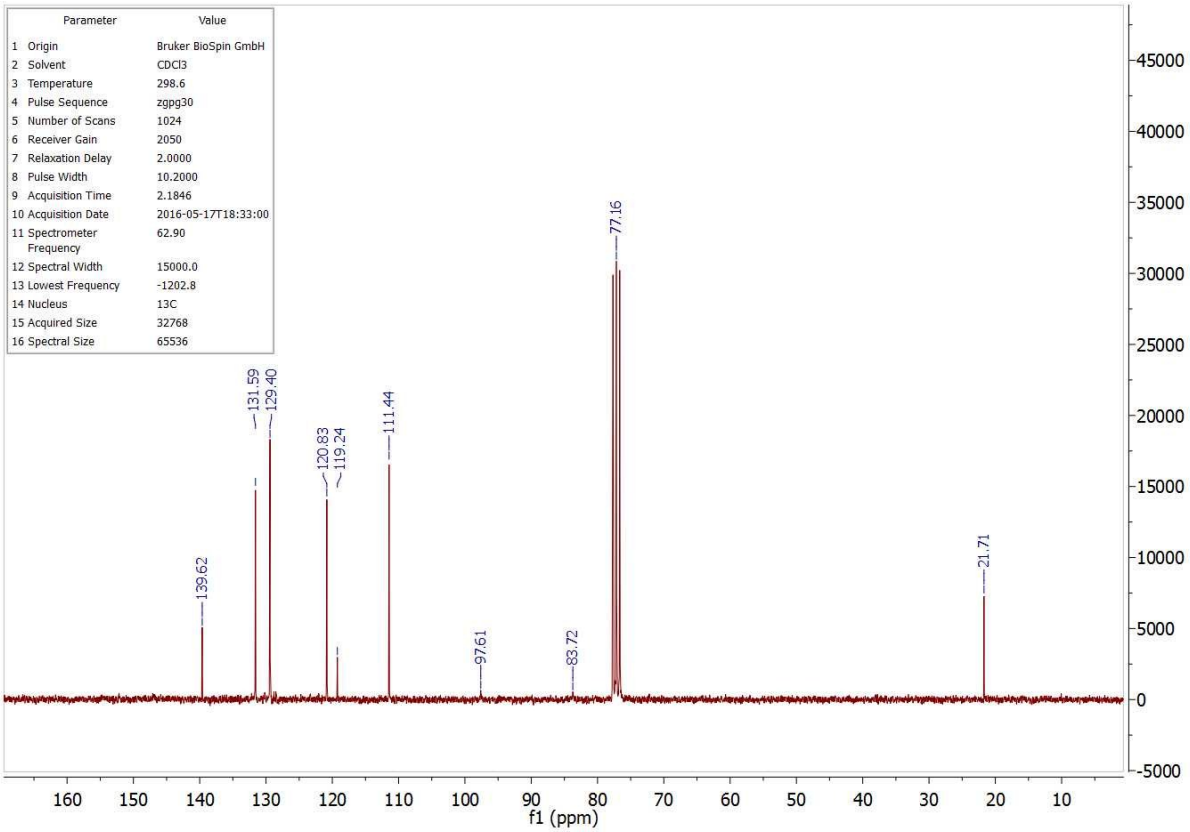


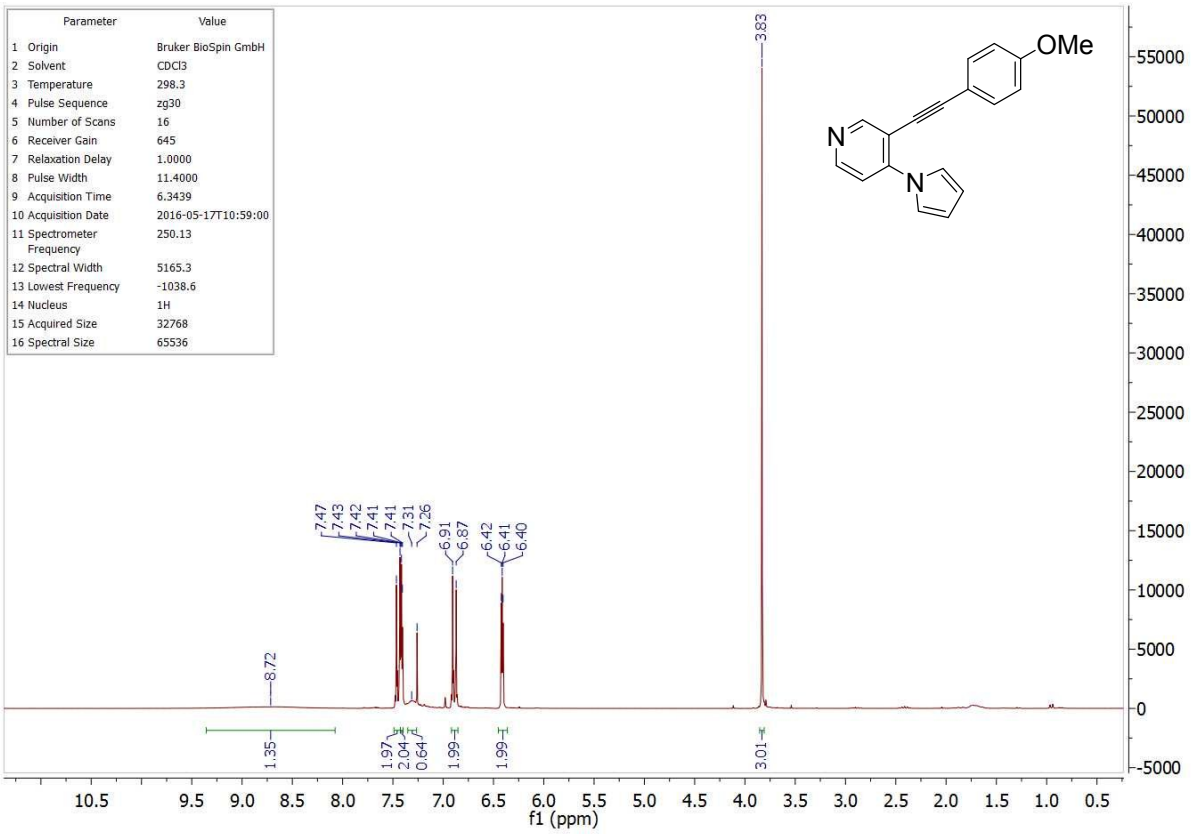

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent C6D6
3 Temperature 298.8
4 Pulse Sequence zgfhigqn
5 Number of Scans 64
6 Receiver Gain 812
7 Relaxation Delay 1.0000
8 Pulse Width 10.0000
9 Acquisition Time 0.9787
10 Acquisition Date 2016-08-27T11:27:00
11 Spectrometer Frequency 282.40
12 Spectral Width 66964.3
13 Lowest Frequency -61722.4
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
-62.59
2E+06
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
-1E+05
-2E+05
-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125
f1 (ppm)

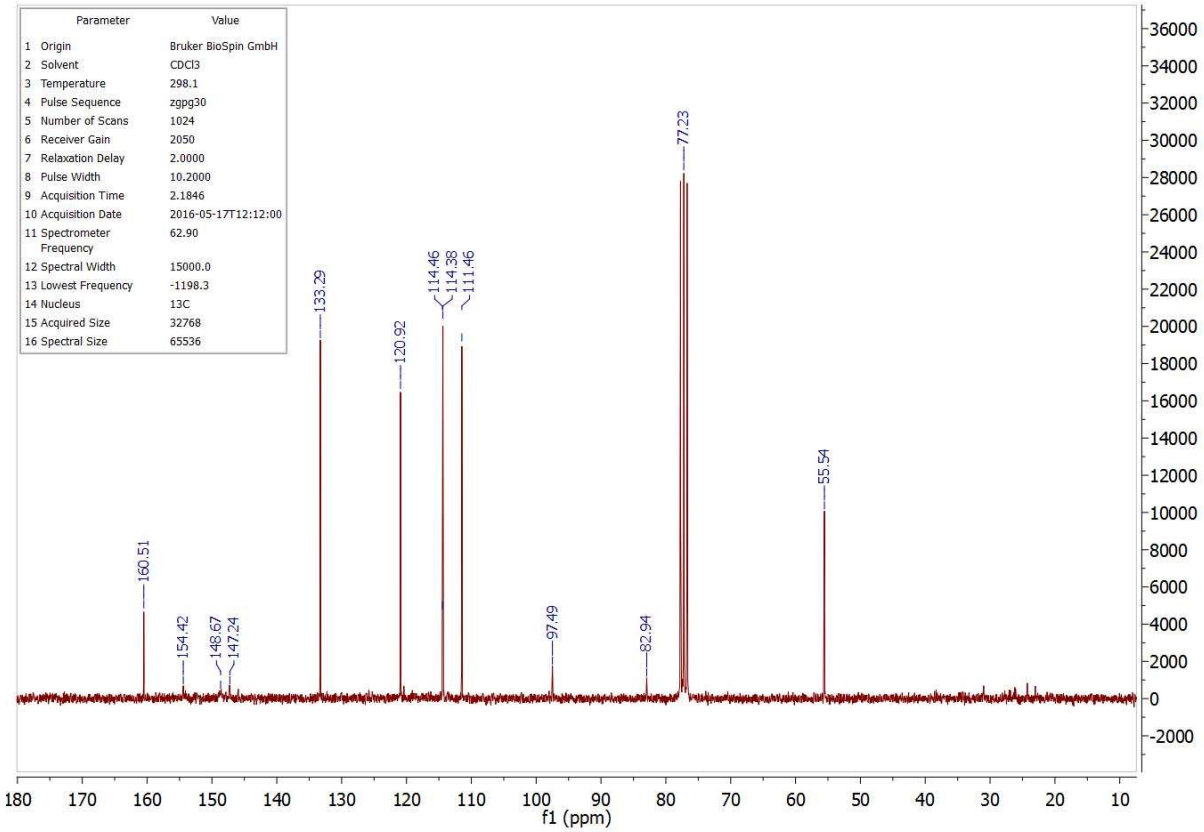
## 3-((4-Methylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4f



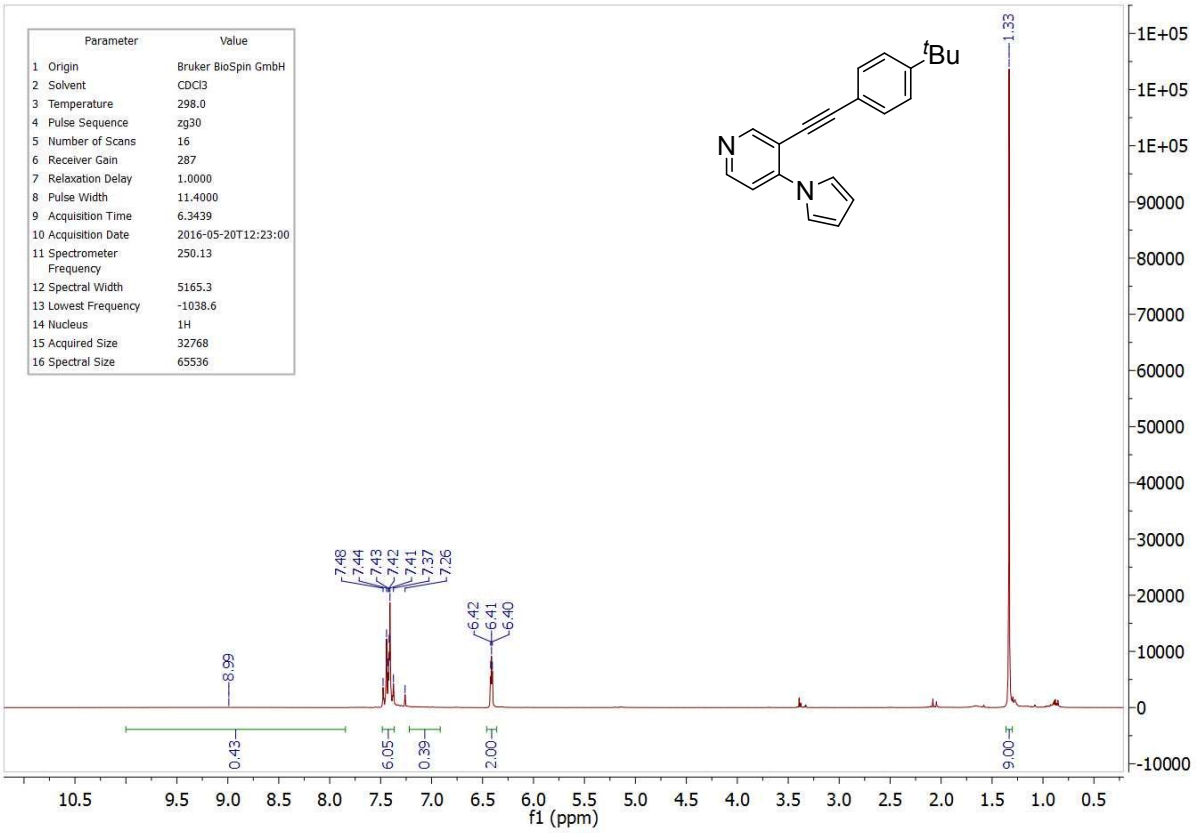



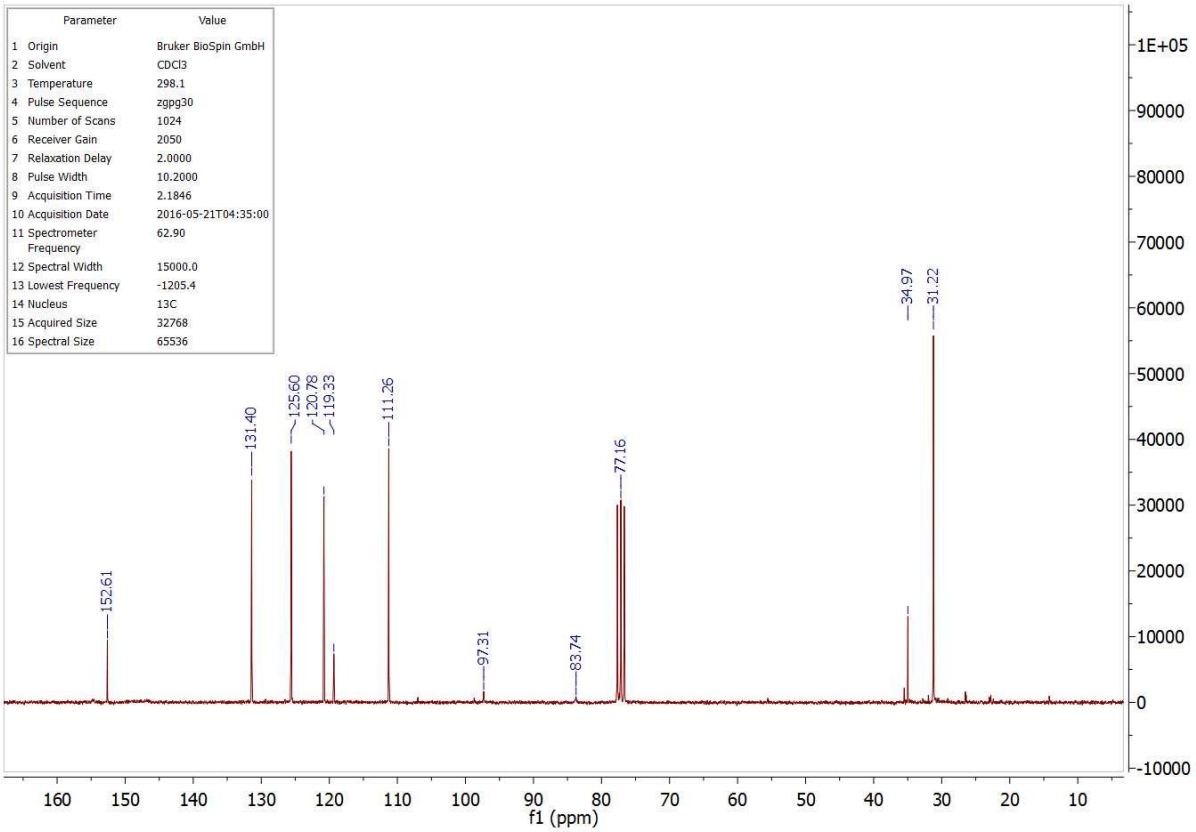
## 3-((4-Methoxyphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4g



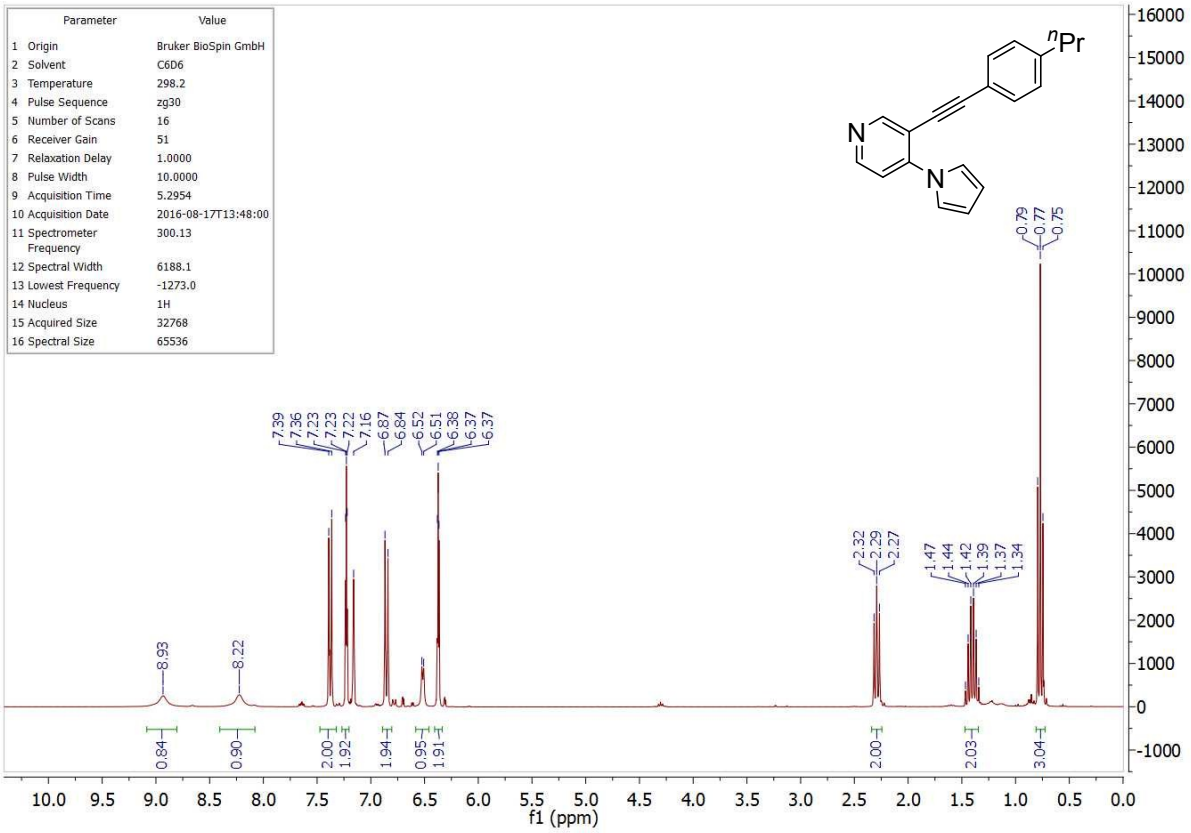



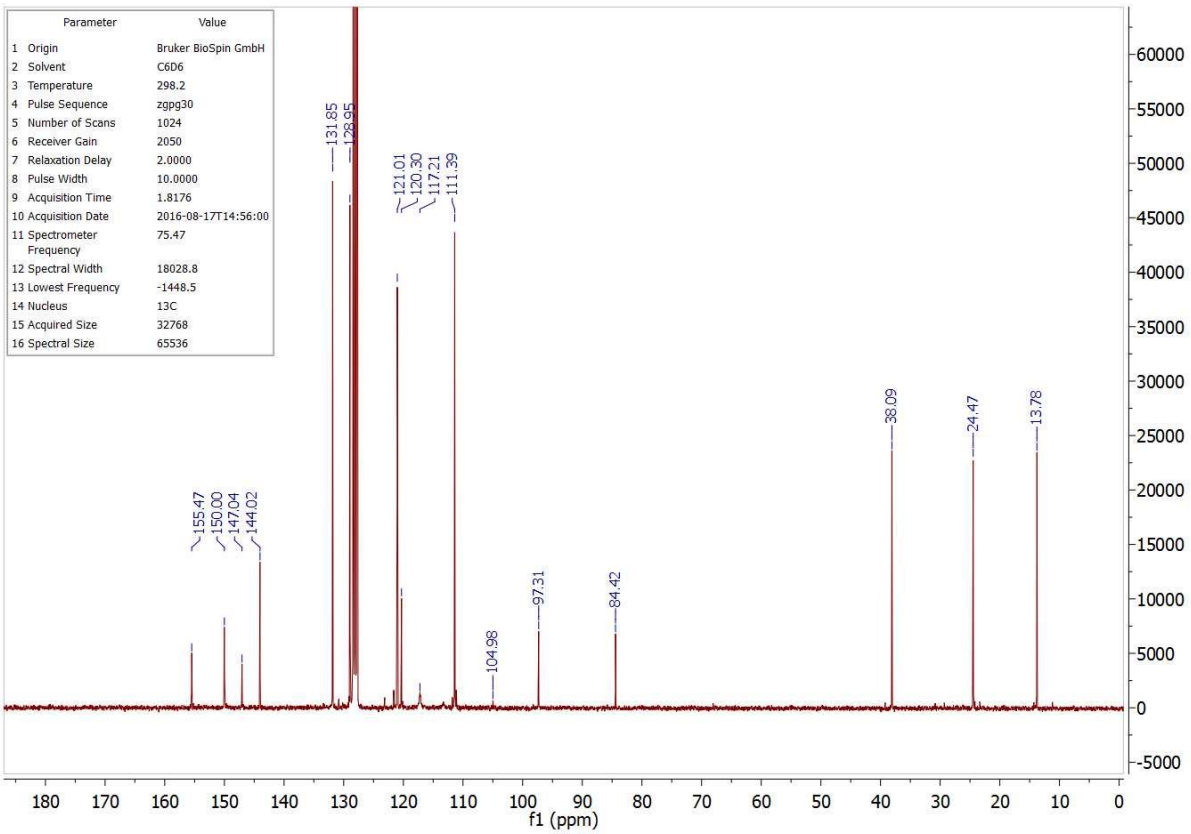
## 3-((4-*tert*-Butylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4h



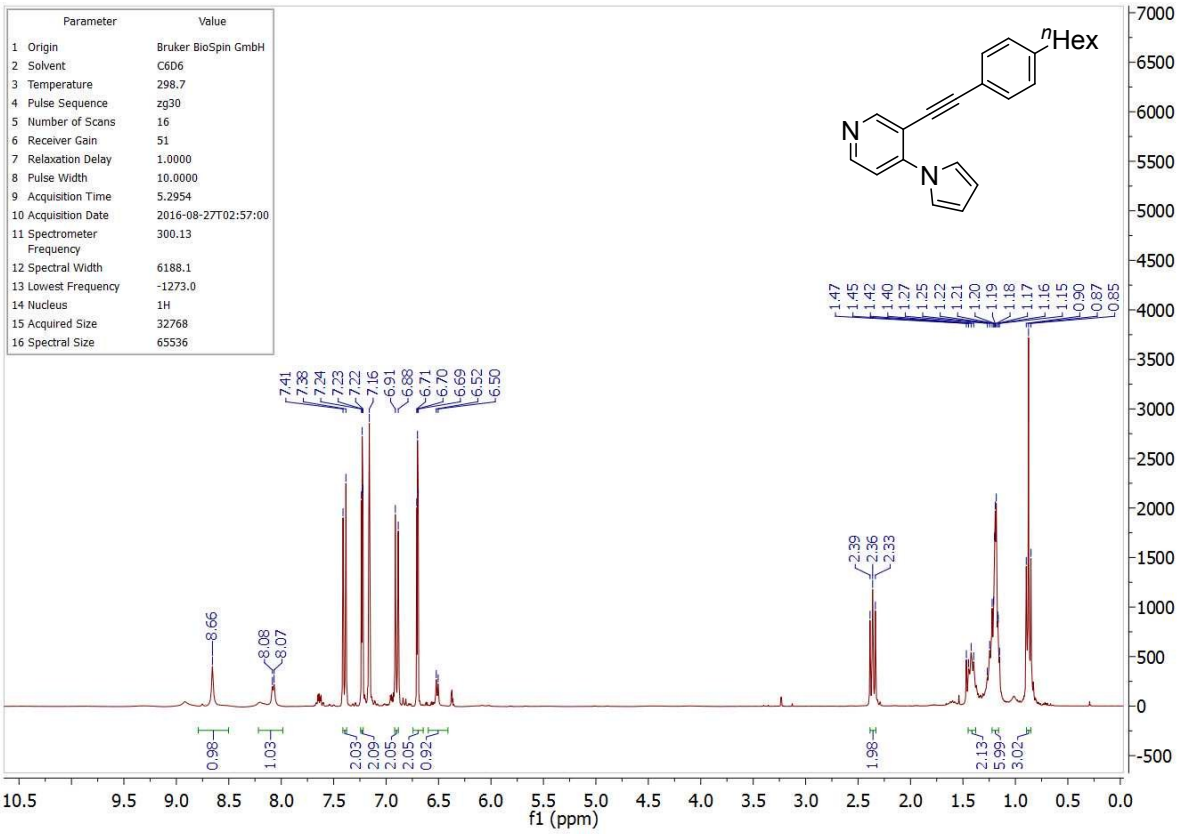



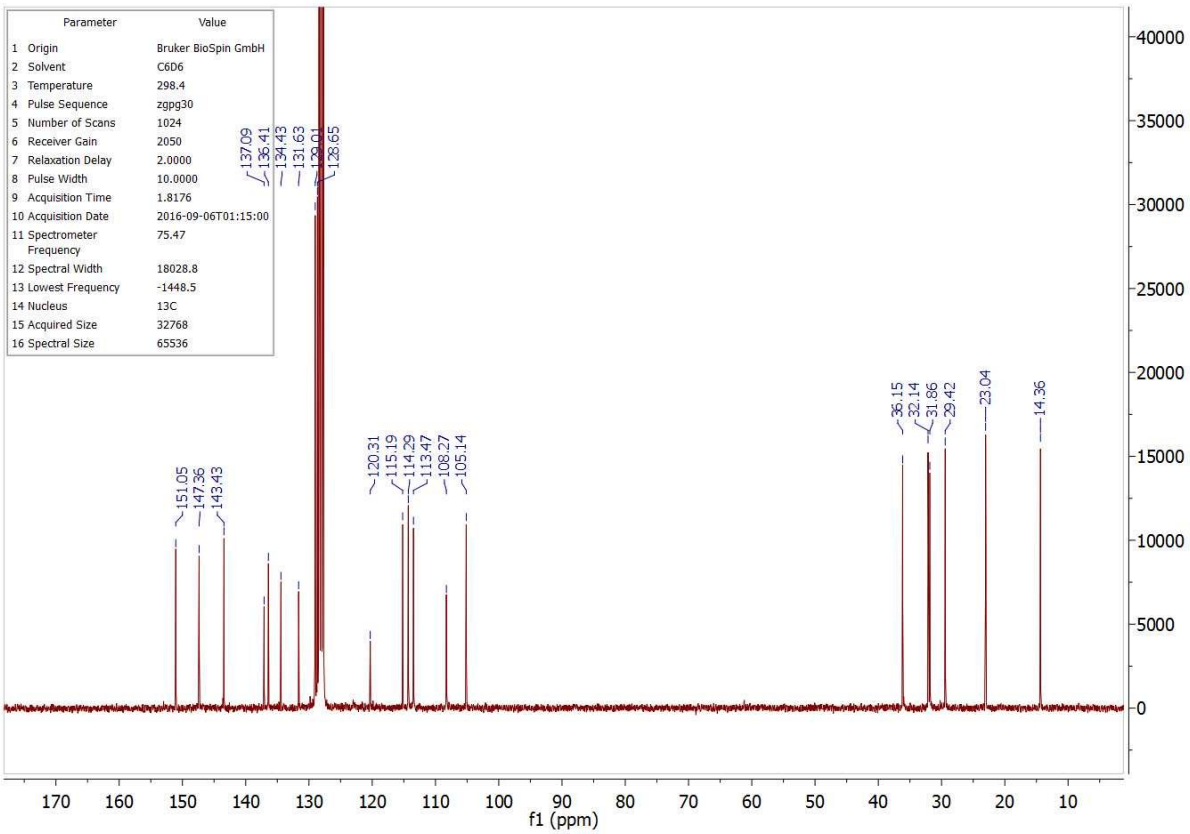
## 3-((4-*n*-Propylphenly)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4i



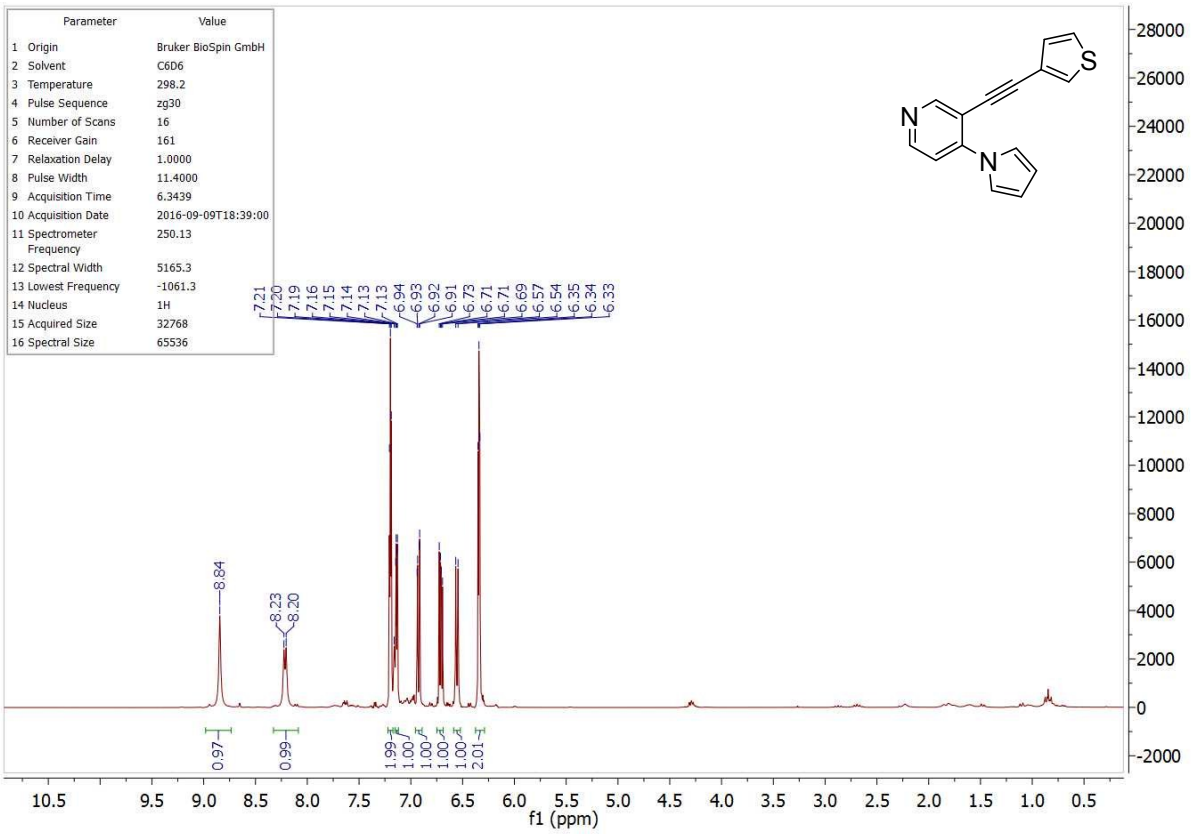



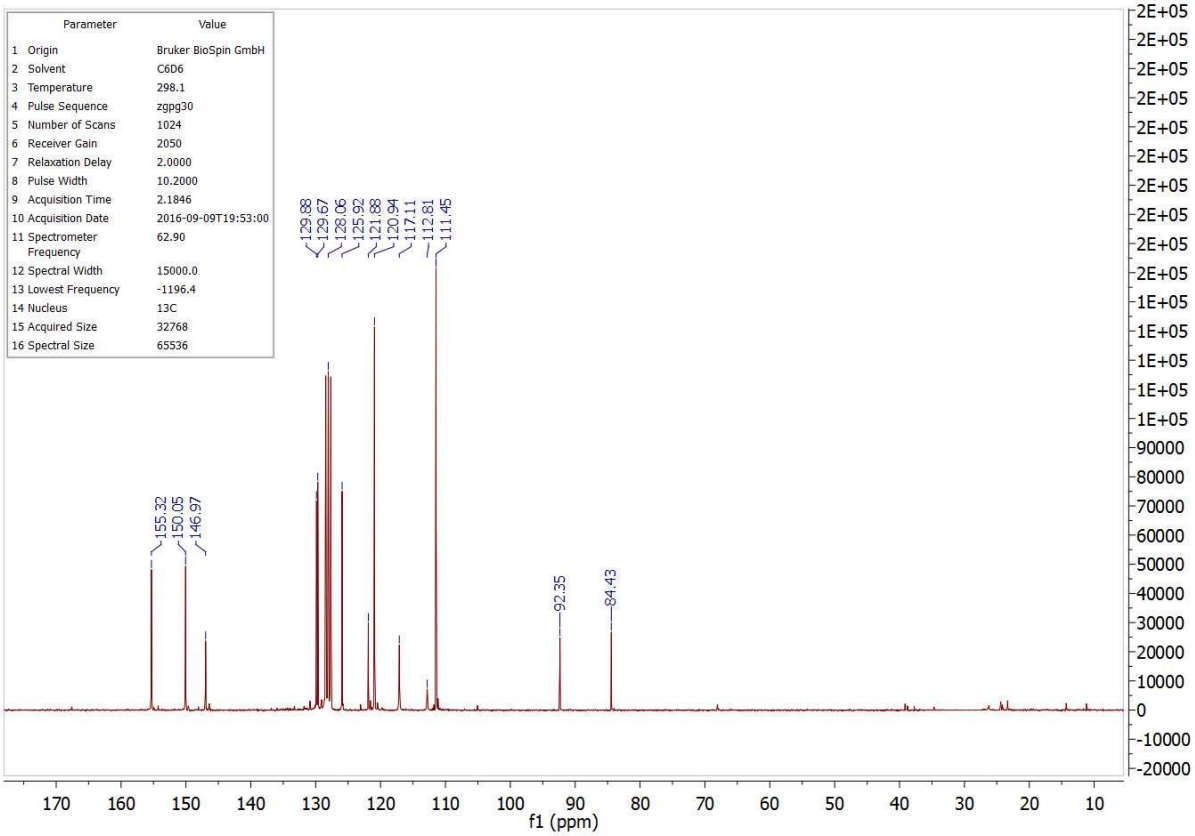
## 3-((4-*n*-Hexylphenyl)ethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4j



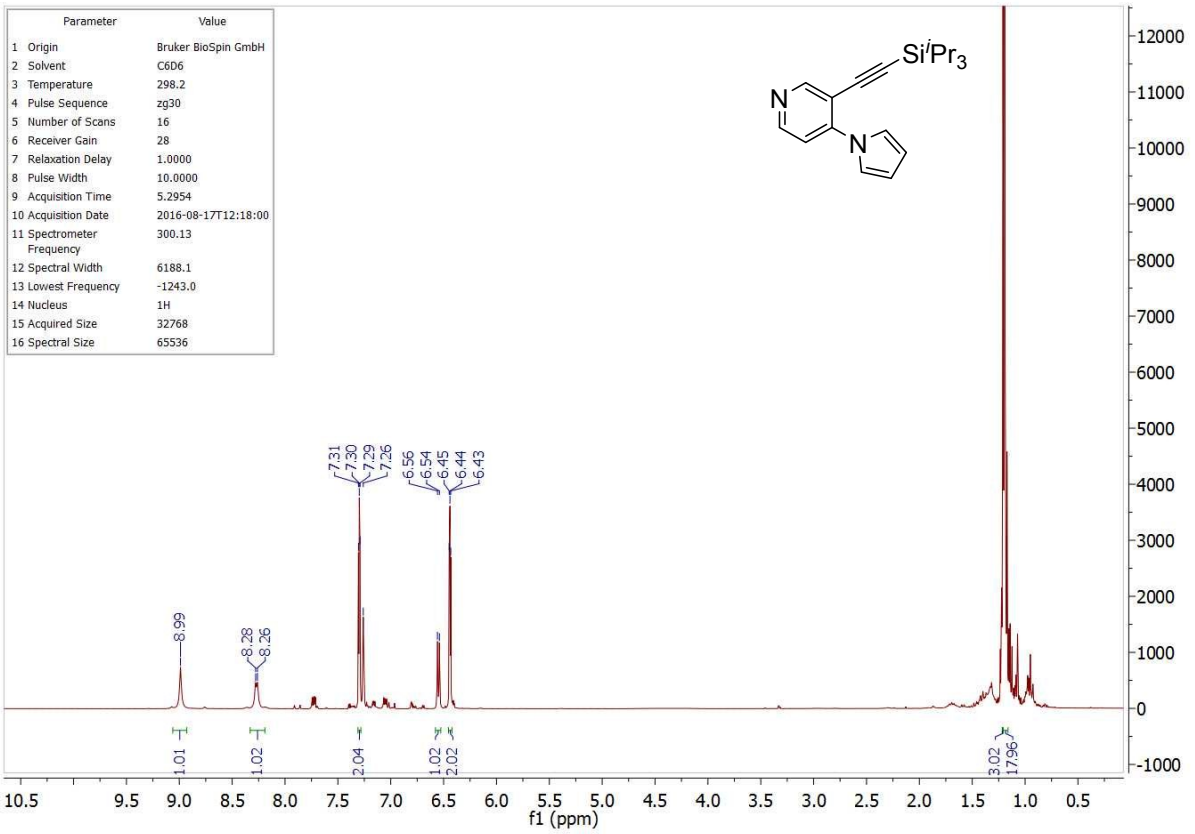



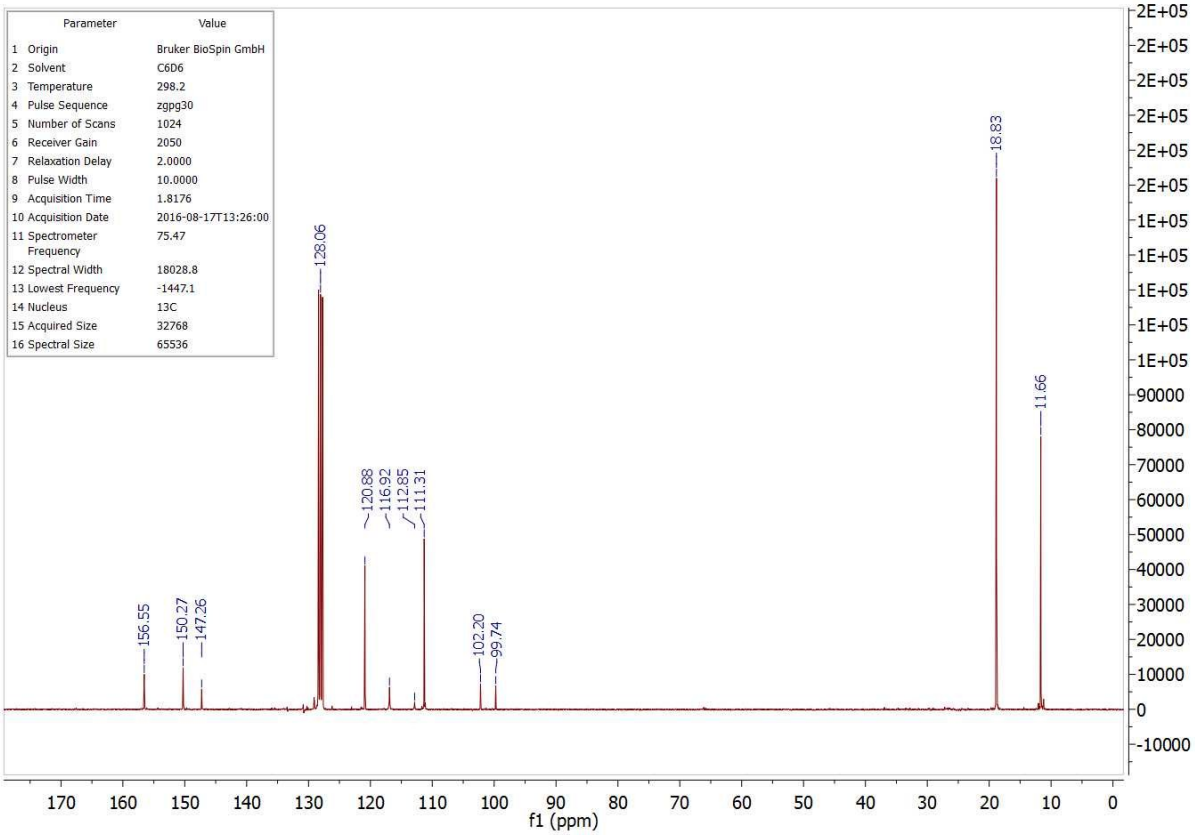
## 3-(Thiophen-3-ylethynyl)-4-([1*H*]-pyrrol-1-yl)pyridine 4k



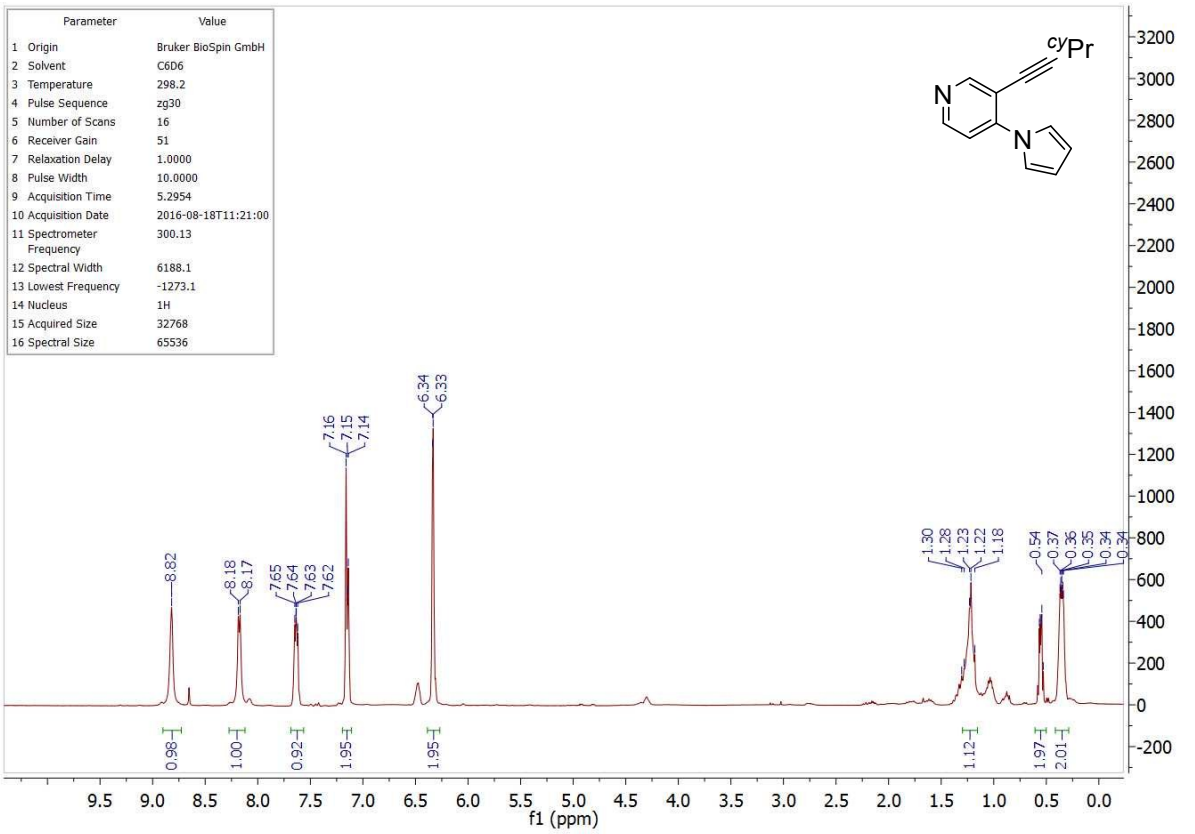



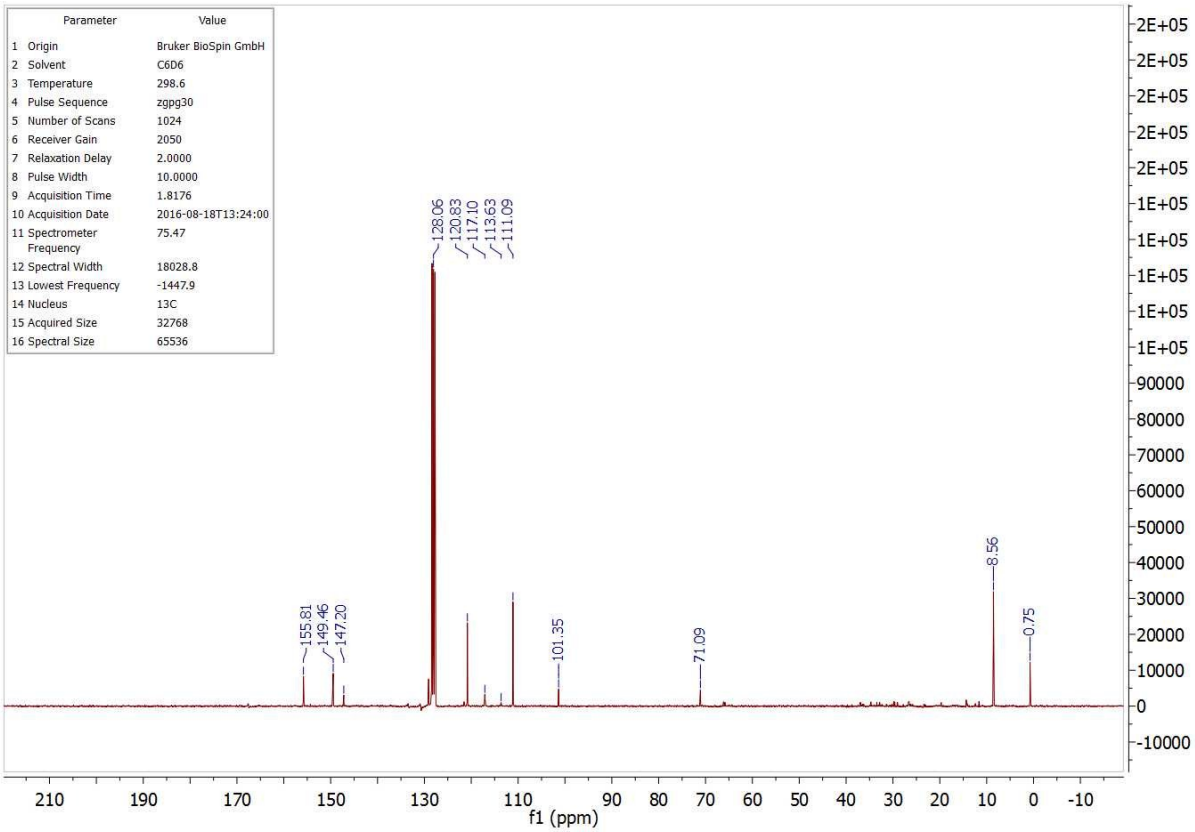
## 4-([1*H*]-pyrrol-1-yl)-3-((triisopropylsilyl)ethynyl)pyridine 4l



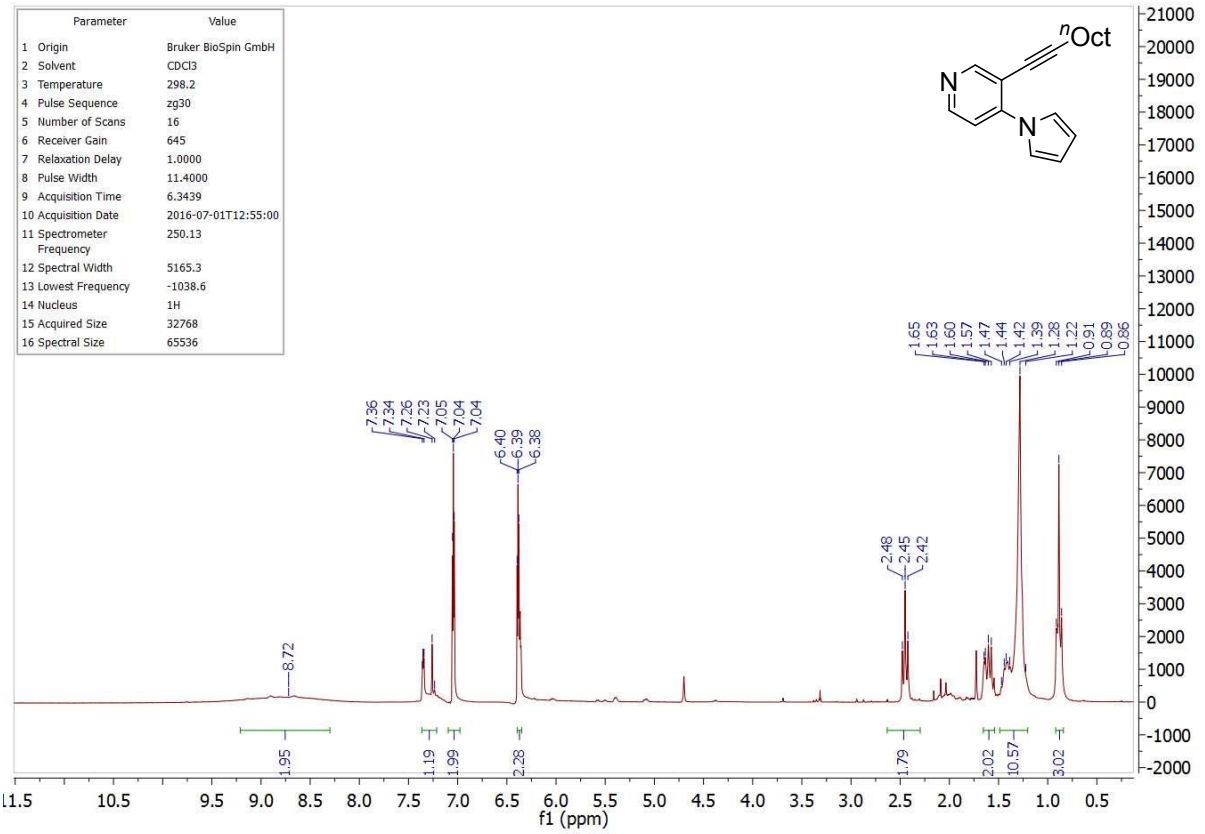



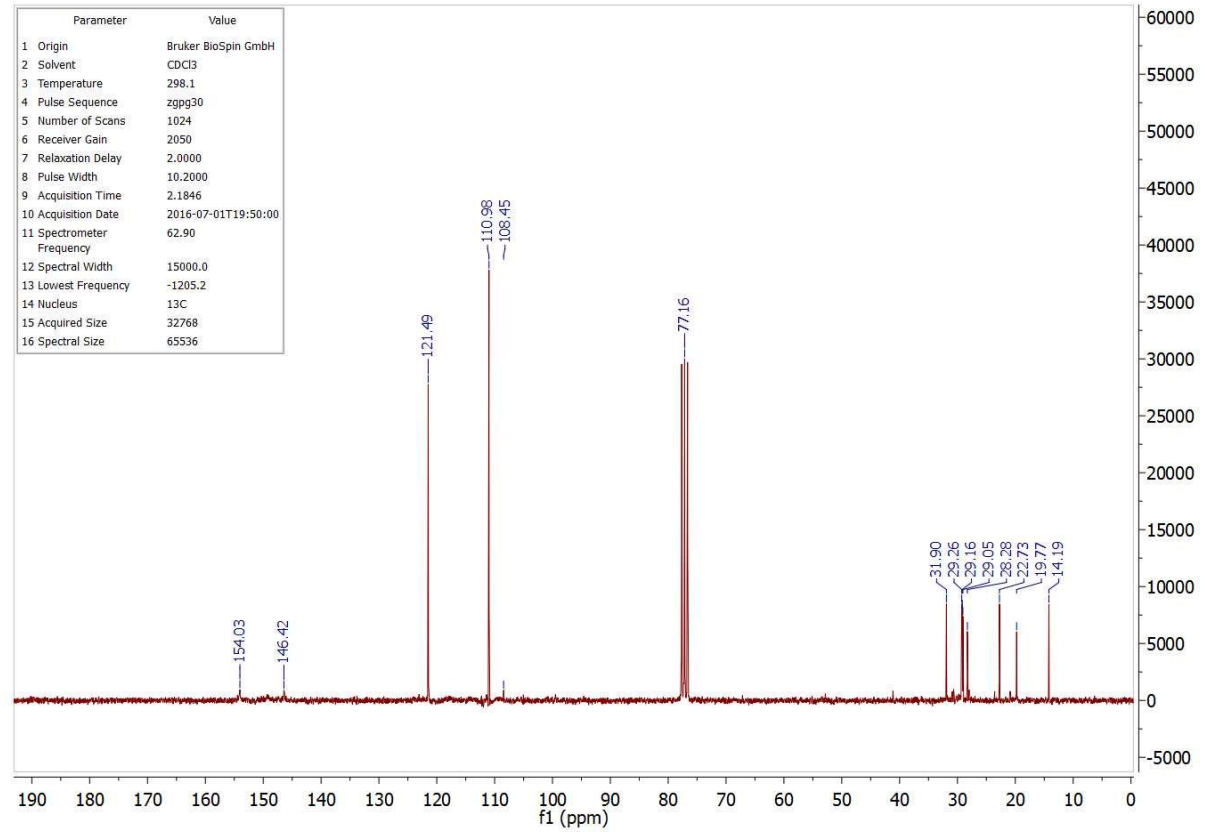
## 3-([Cyclopropyl]ethynyl)-4-(1*H*-pyrrol-1-yl)pyridine 4m



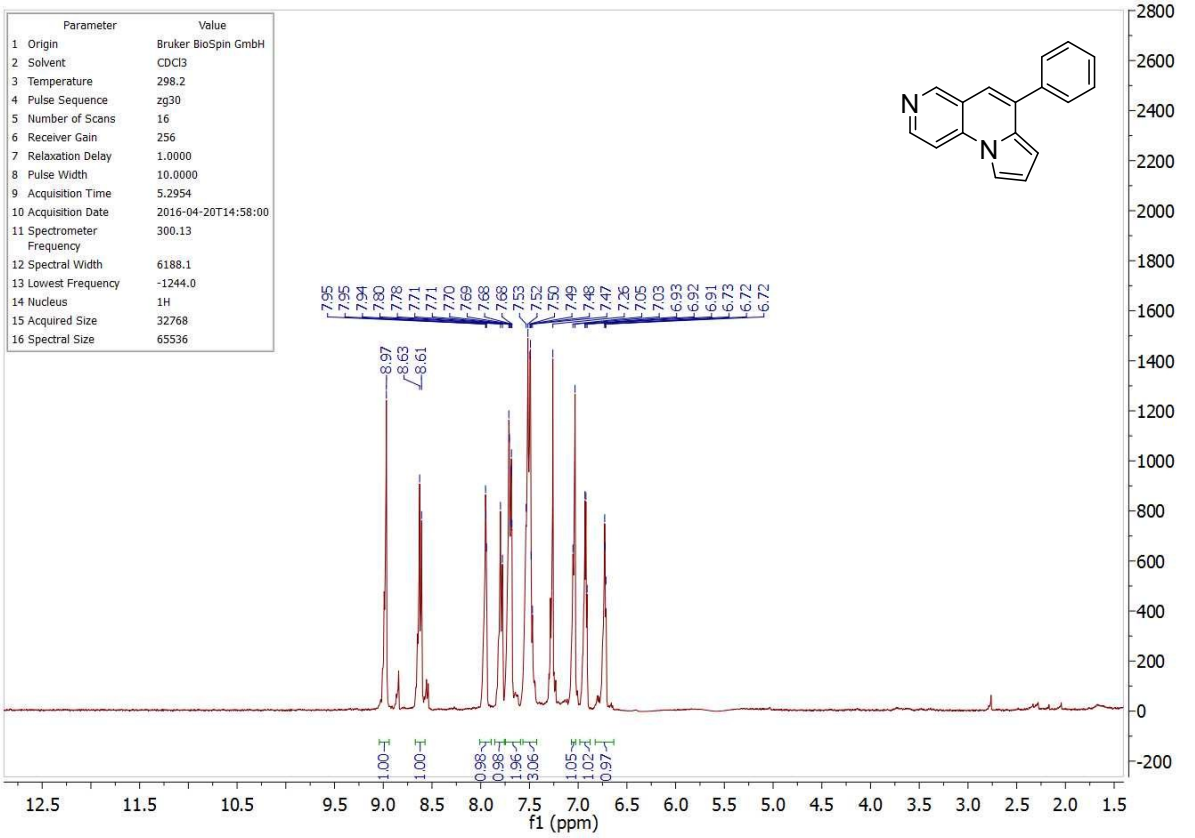



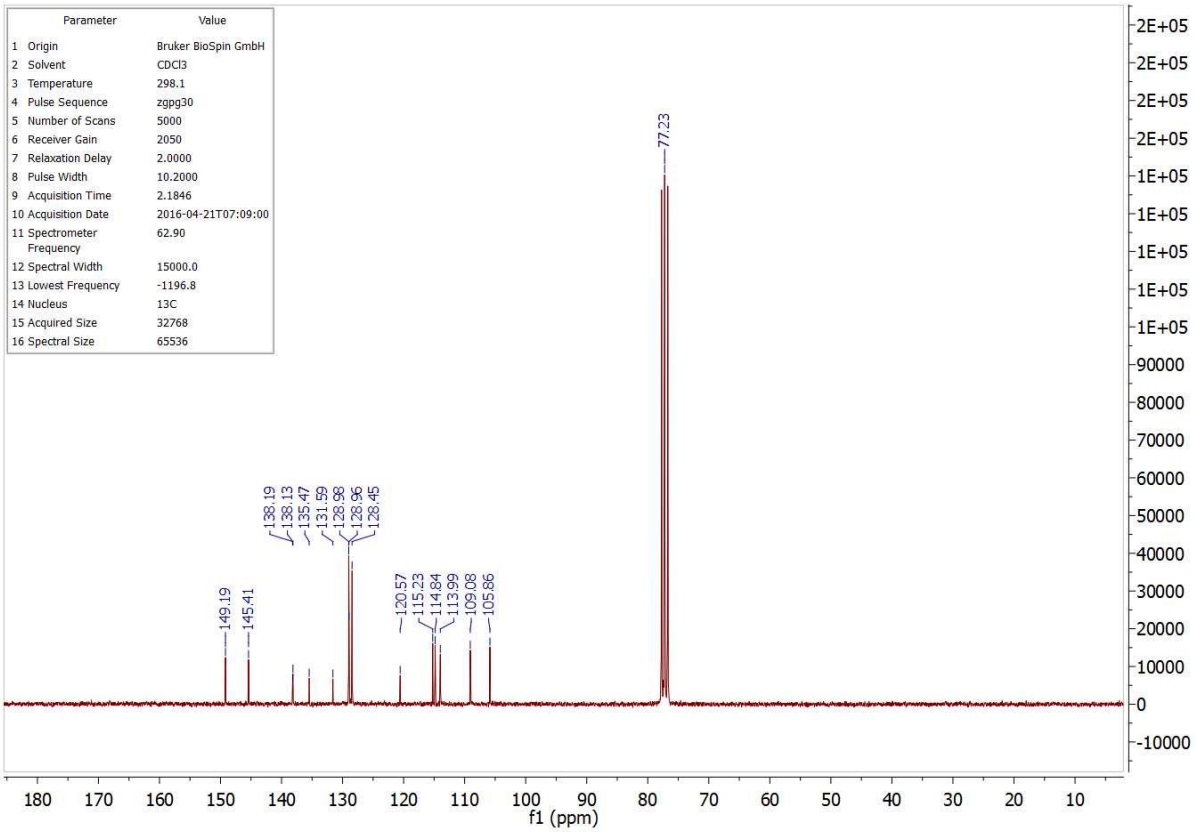
## 3-(Dec-1-yn-1-yl)-4-(1*H*-pyrrol-1-yl)pyridine 4n



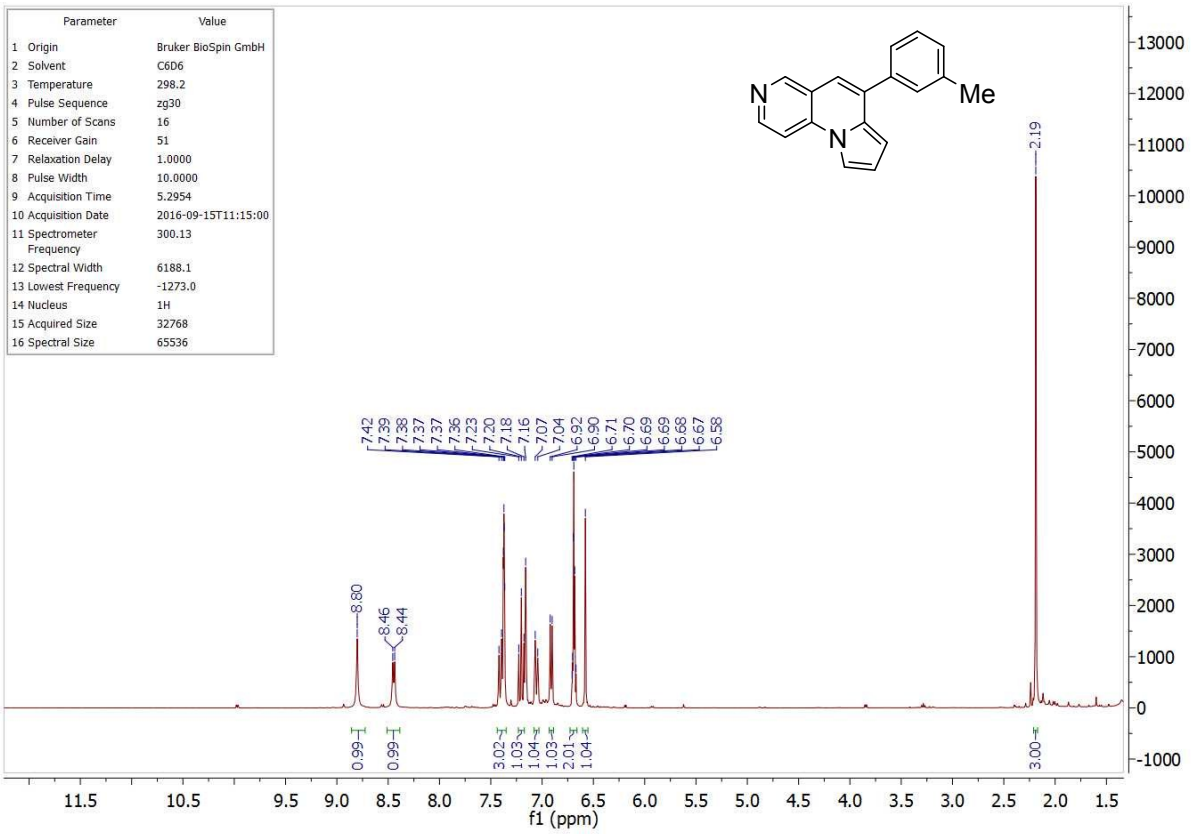



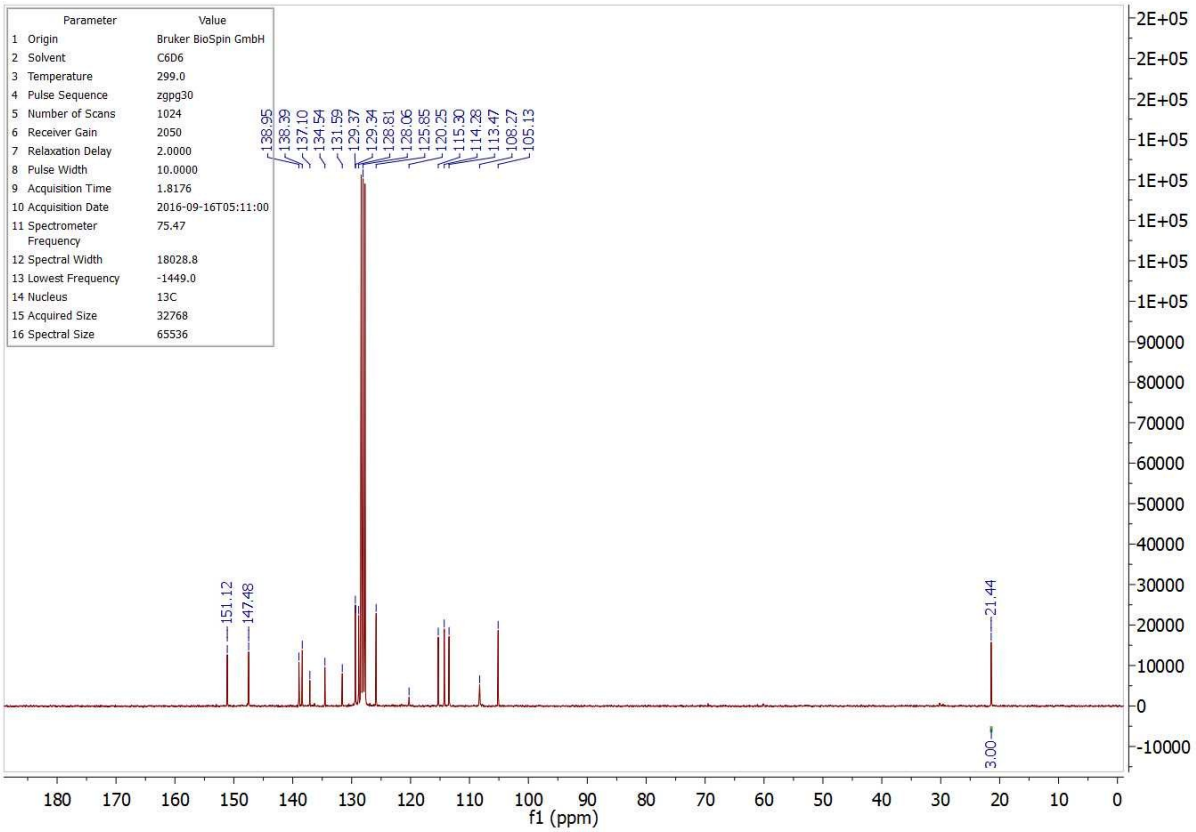
## 6-(Phenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5a



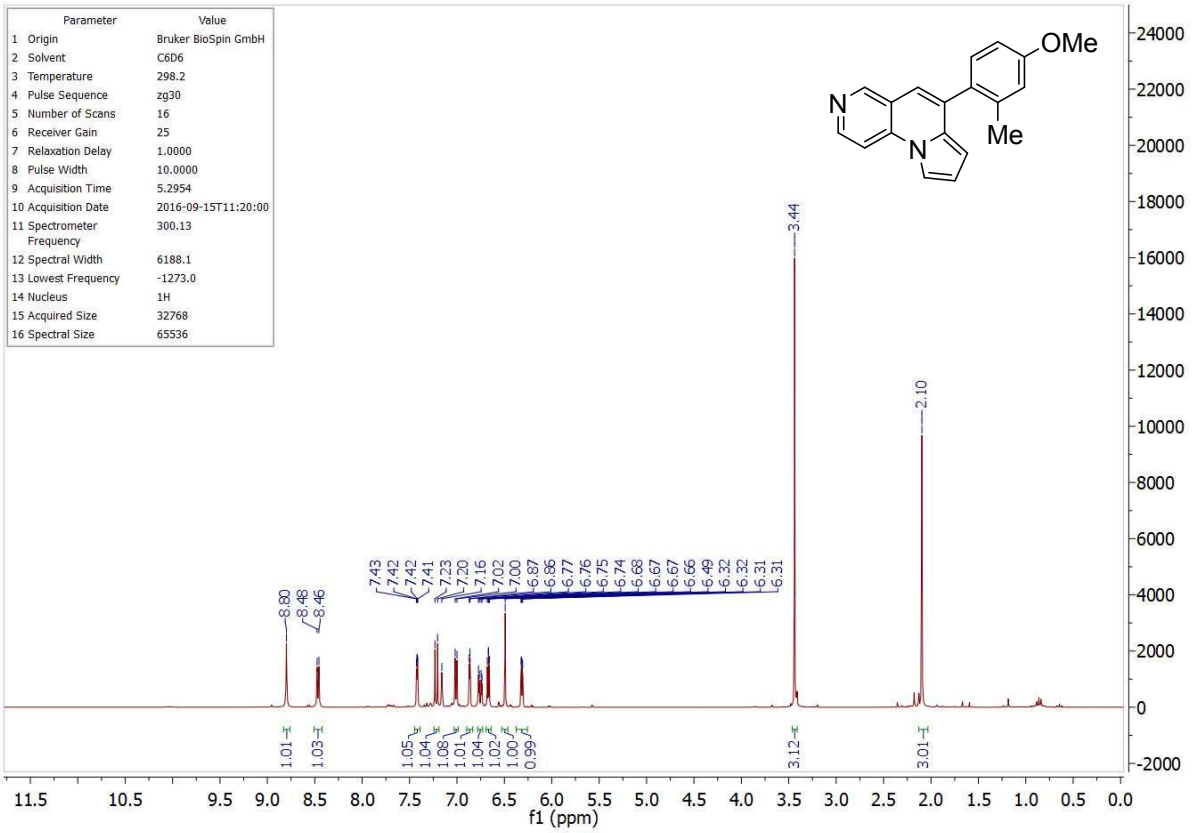



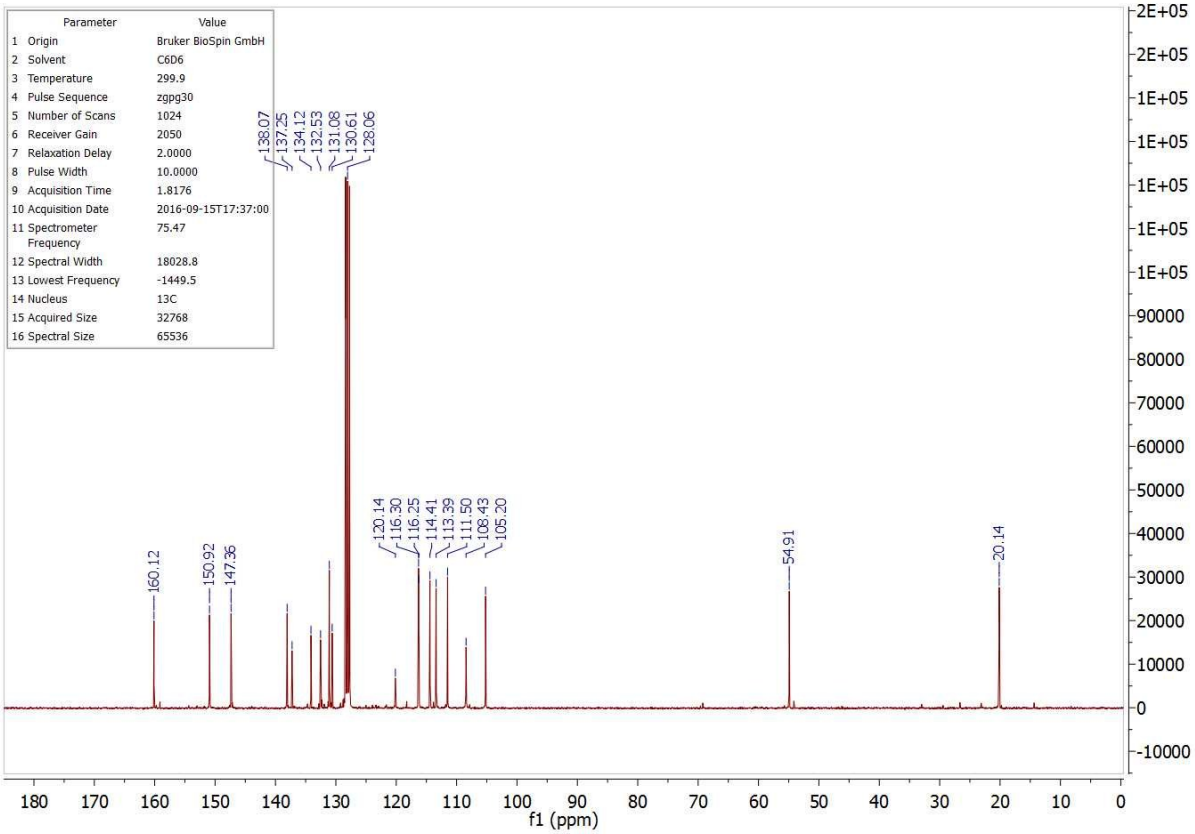
## 6-(3-Methylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5b



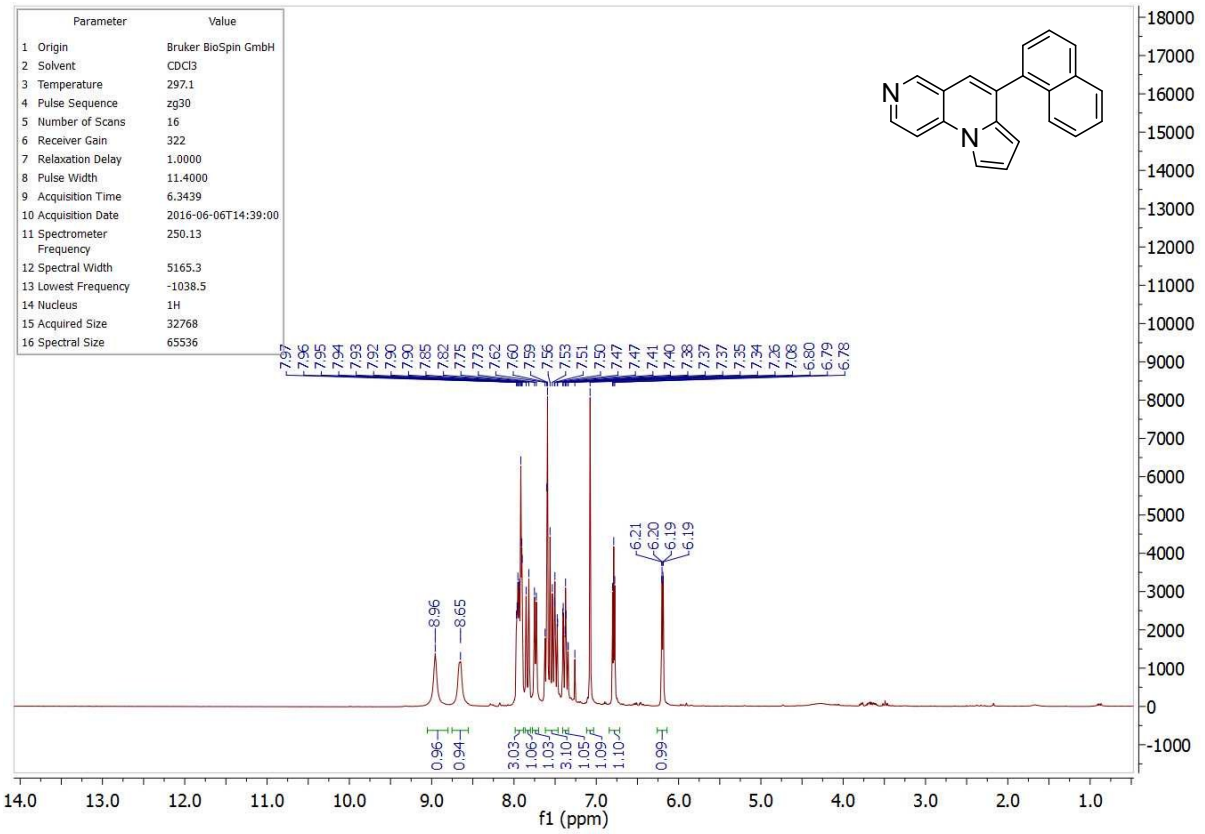



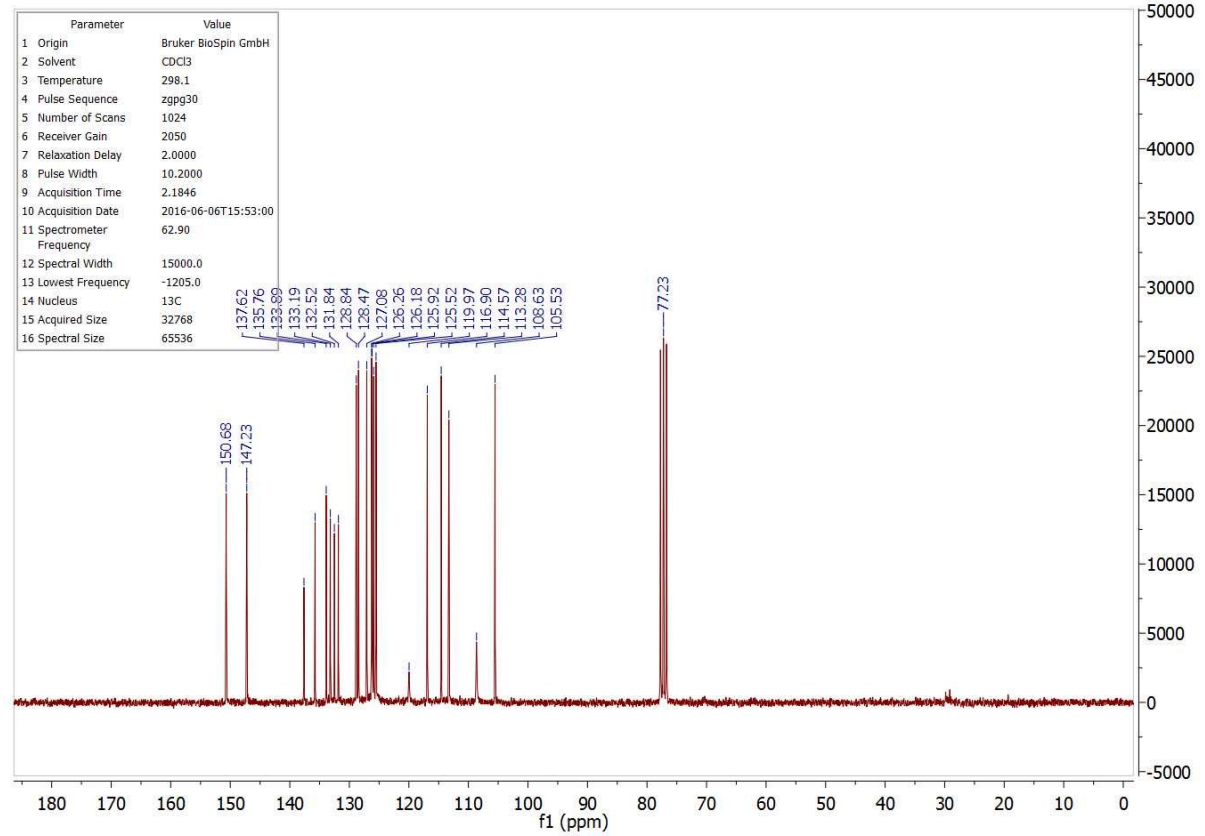
## 6-(4-Methoxy-2-methylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5c



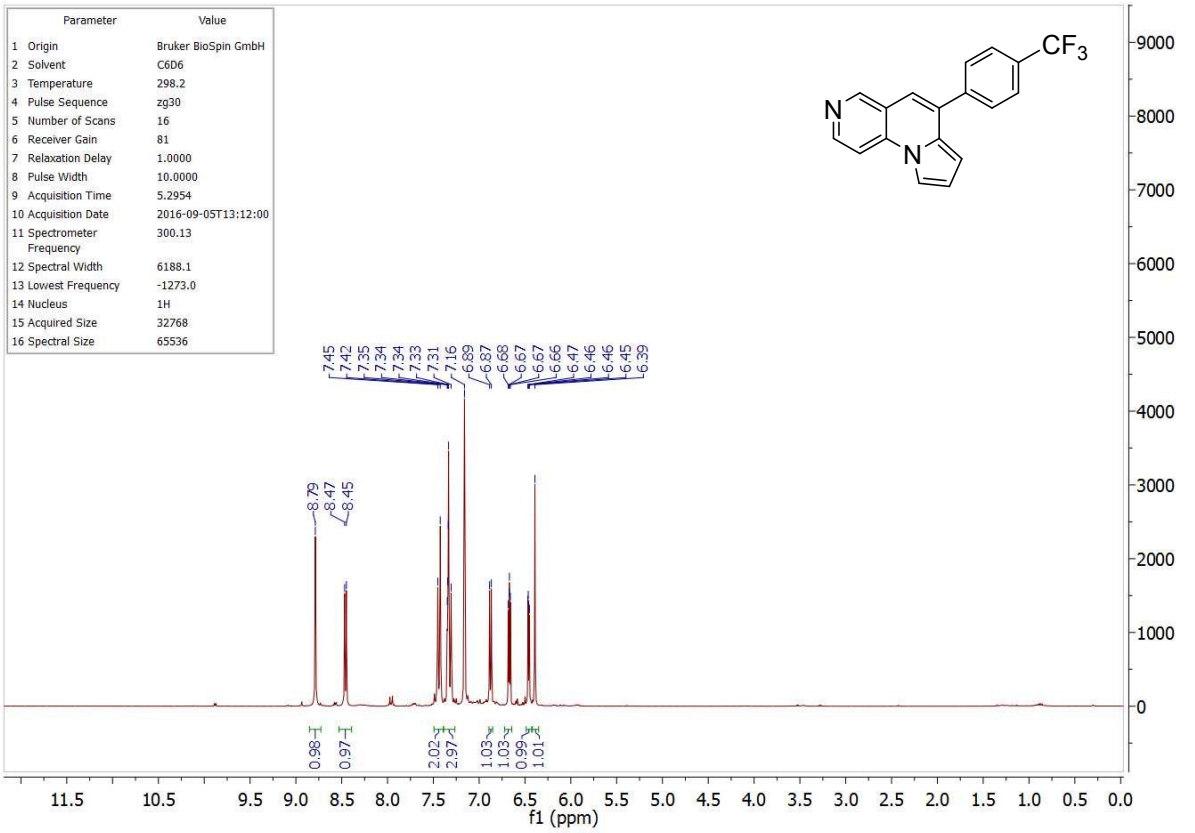



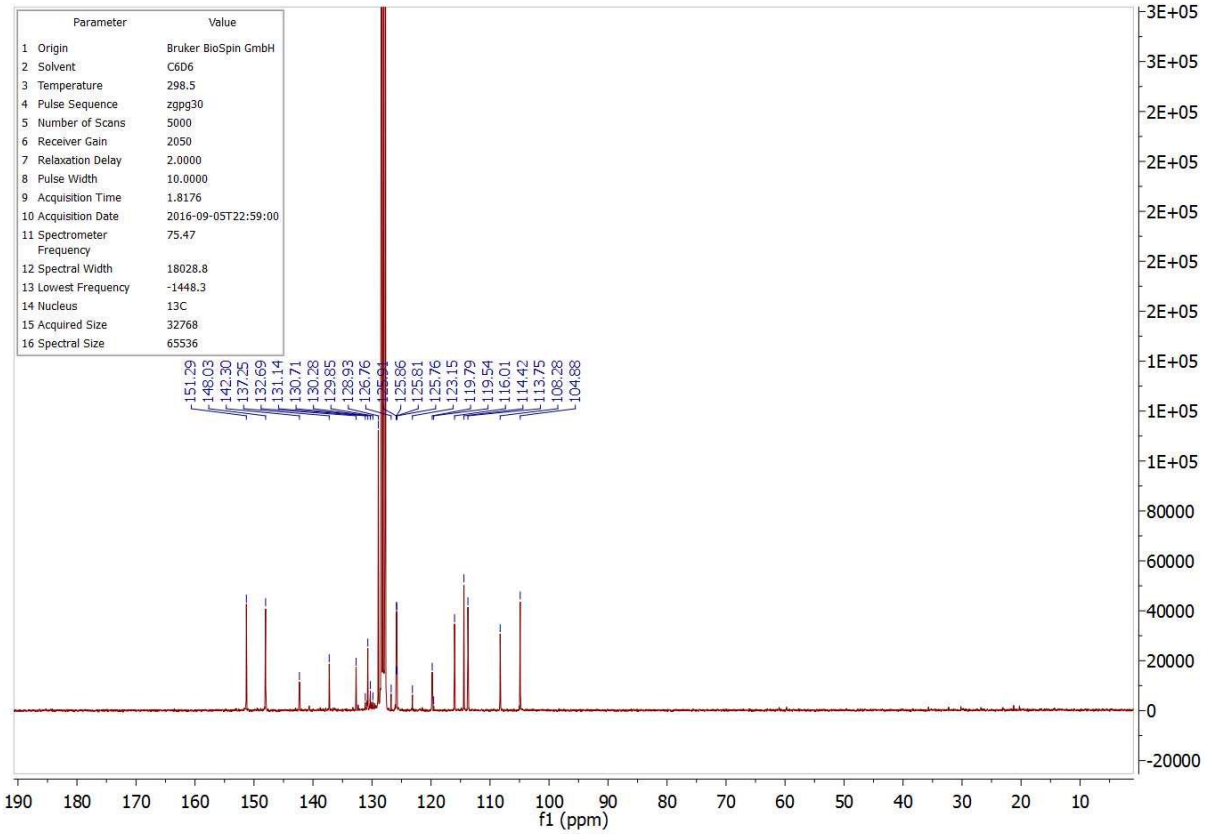
## 6-(Naphth-1-yl)pyrrolo[1,2-*a*][1,6]naphthyridine 5d

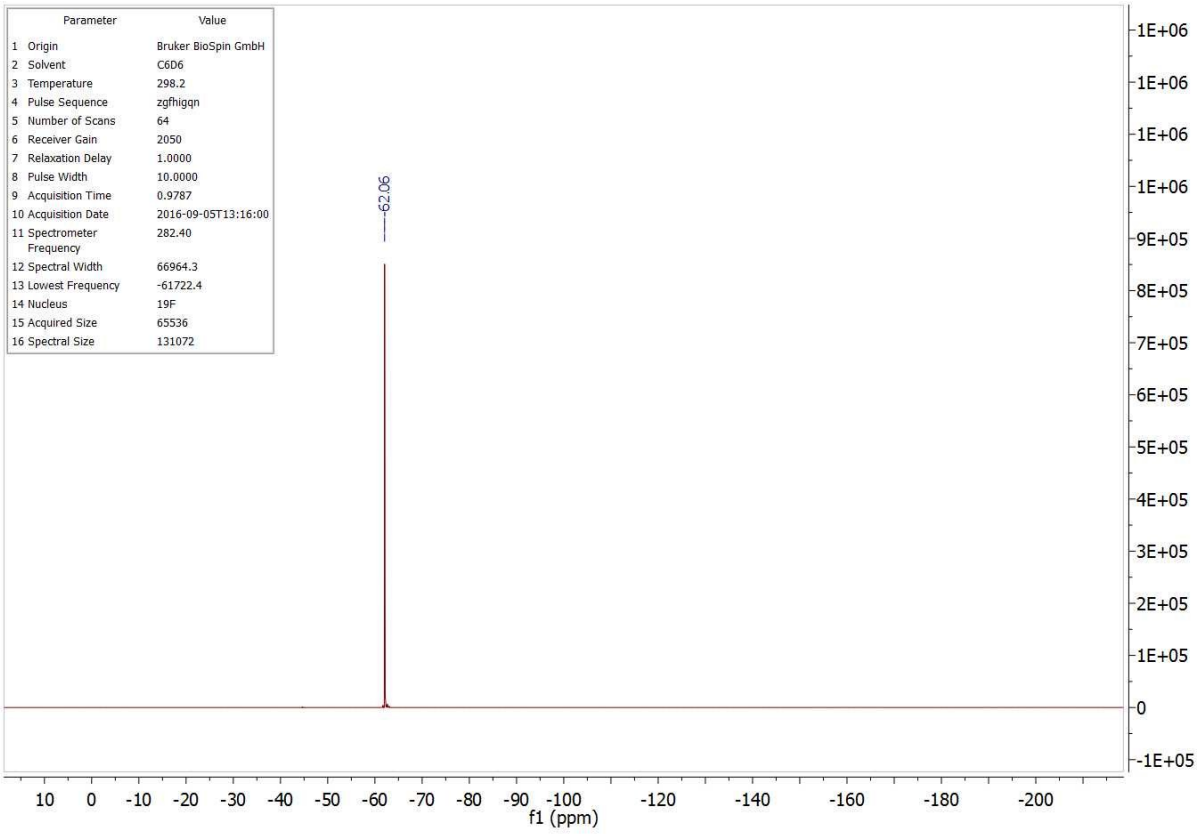


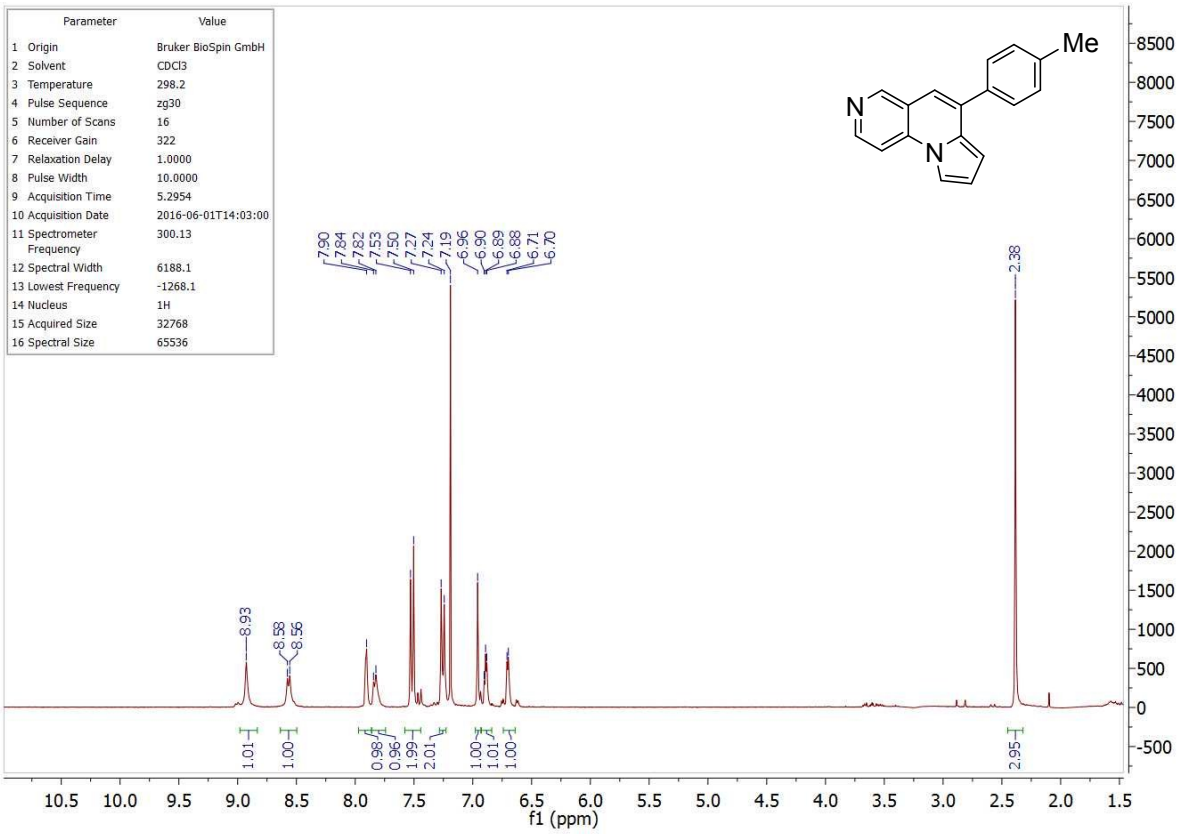
## 6-(4-[Trifluoromethyl]phenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5e

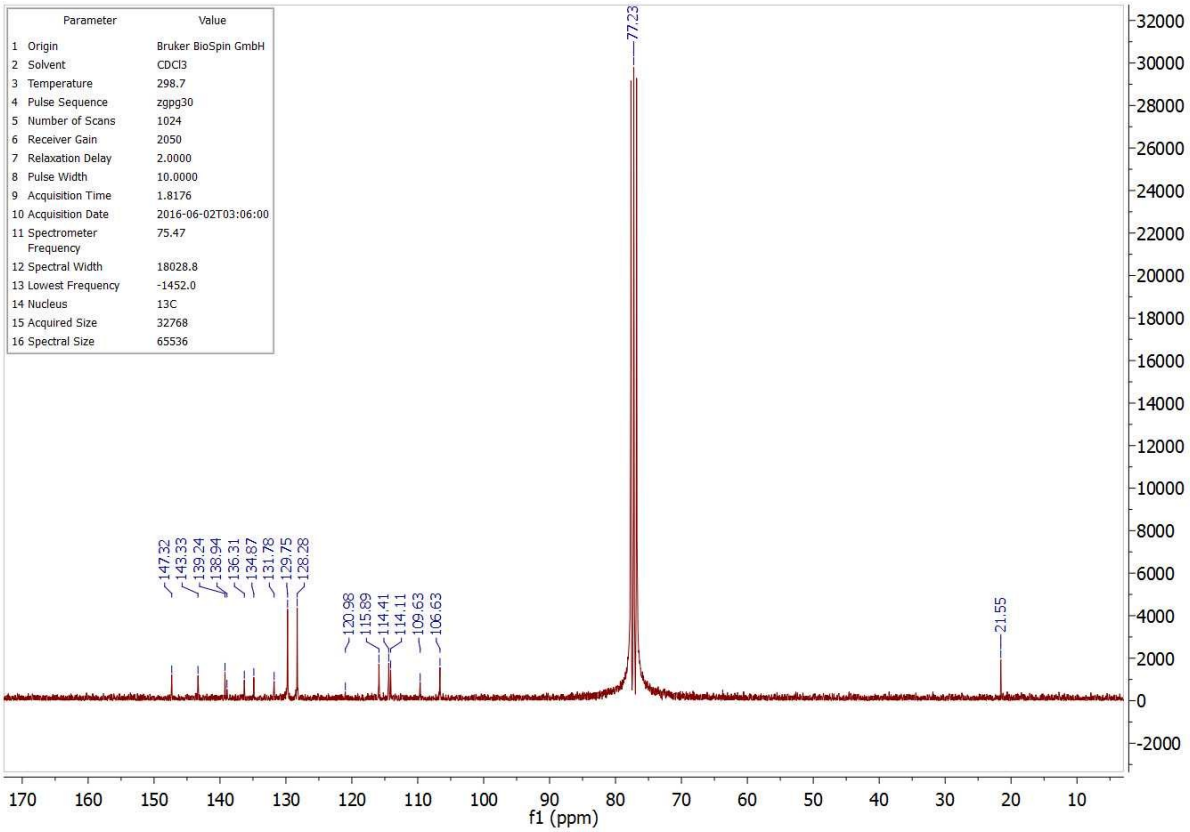


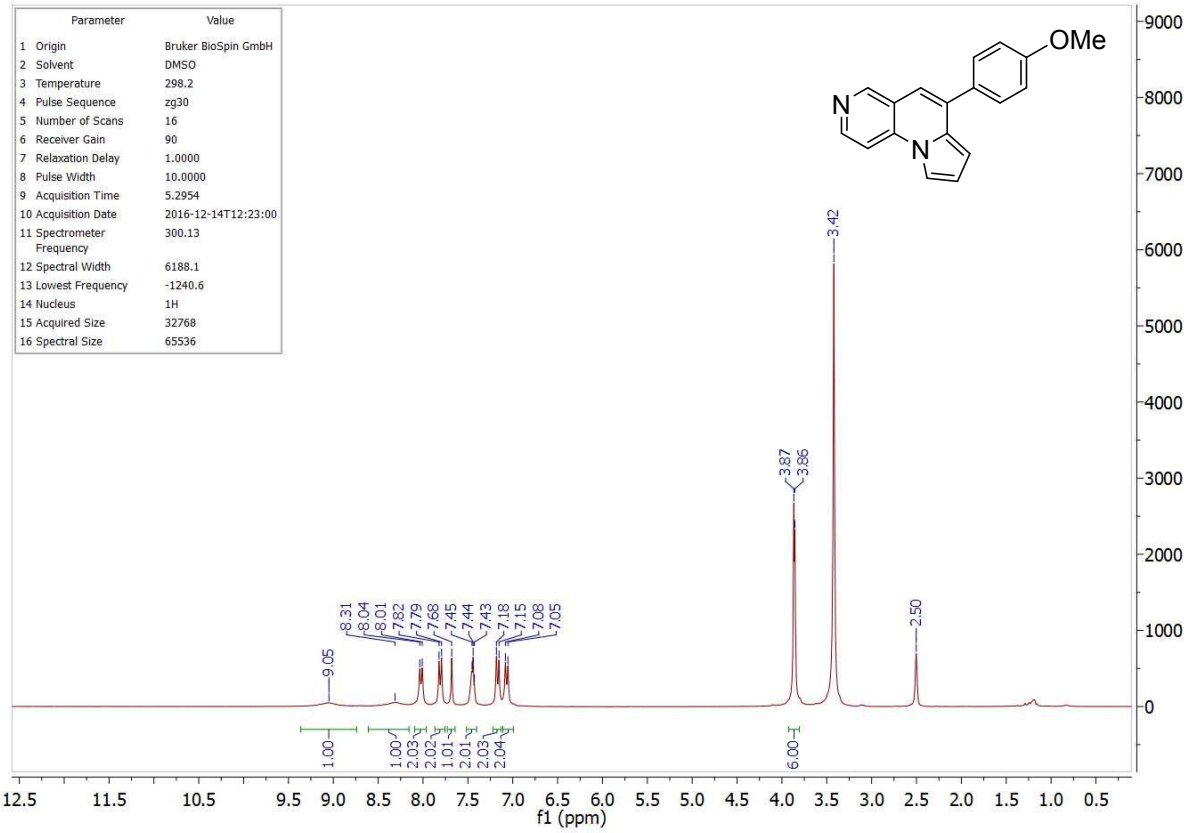

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent C6D6
3 Temperature 298.2
4 Pulse Sequence zgfhigqn
5 Number of Scans 64
6 Receiver Gain 2050
7 Relaxation Delay 1.0000
8 Pulse Width 10.0000
9 Acquisition Time 0.9787
10 Acquisition Date 2016-09-05T13:16:00
11 Spectrometer Frequency 282.40
12 Spectral Width 66964.3
13 Lowest Frequency -61722.4
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
-62.06
1E+06
1E+06
1E+06
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
-1E+05
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

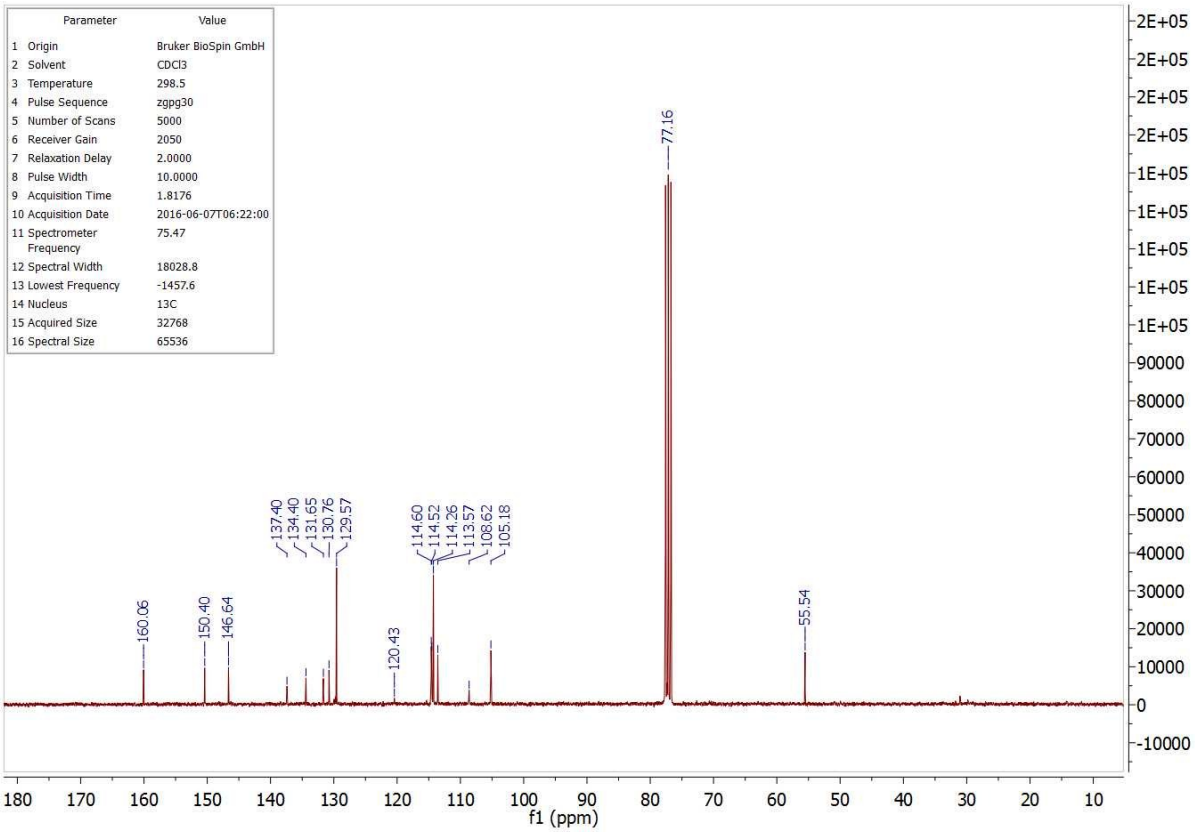
## 6-(4-Methylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5f



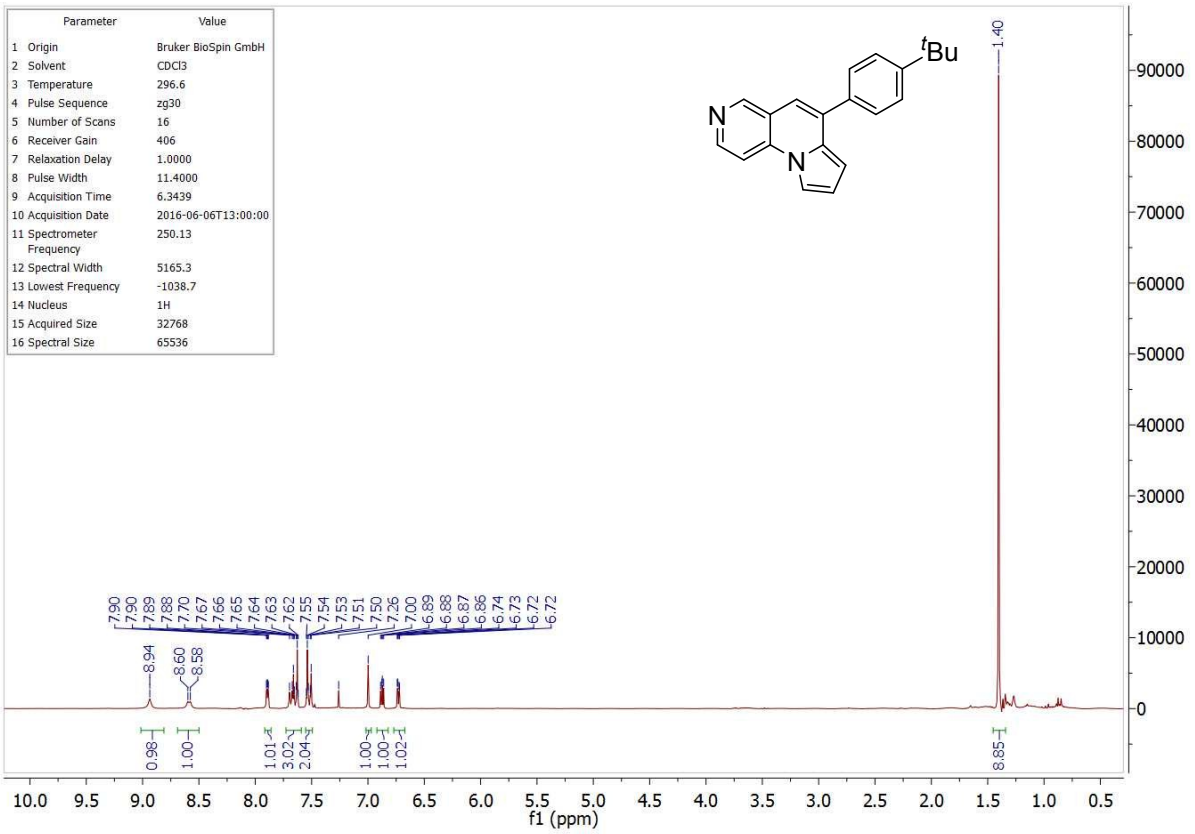



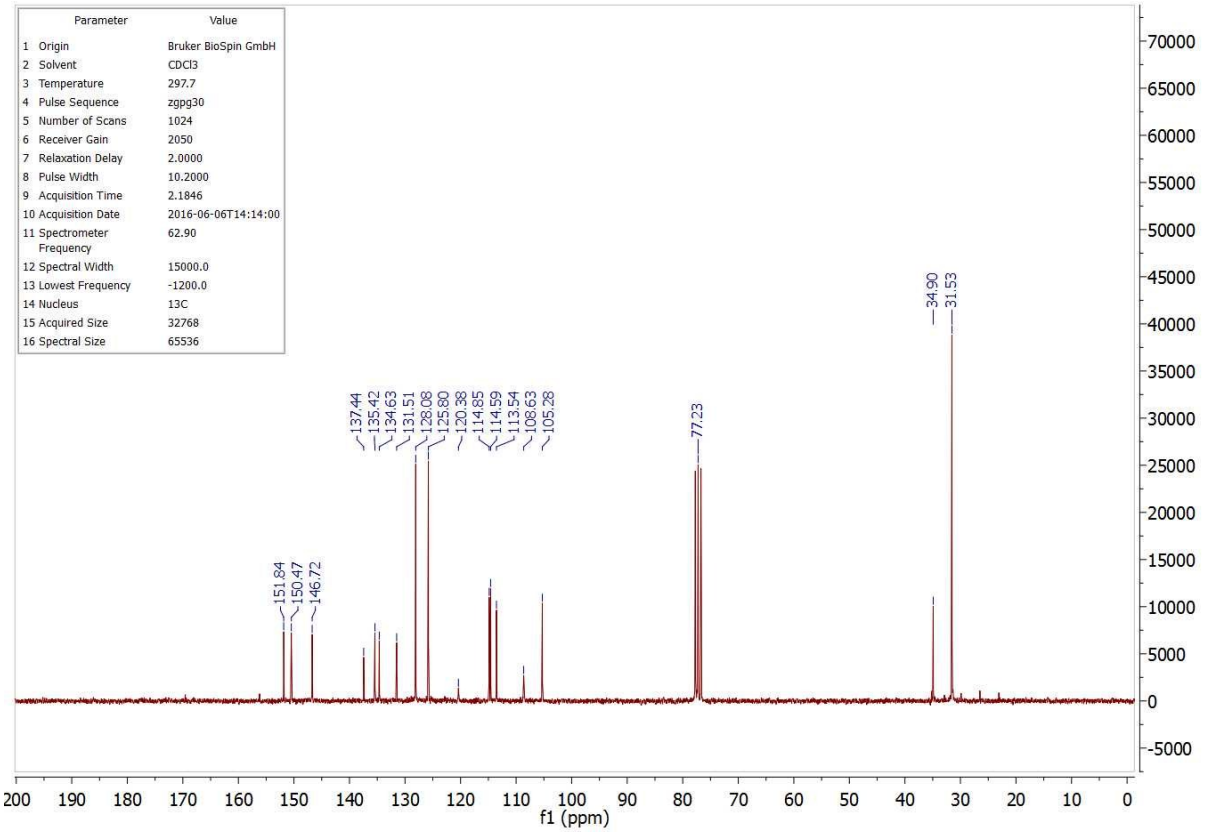
## 6-(4-Methoxyphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5g



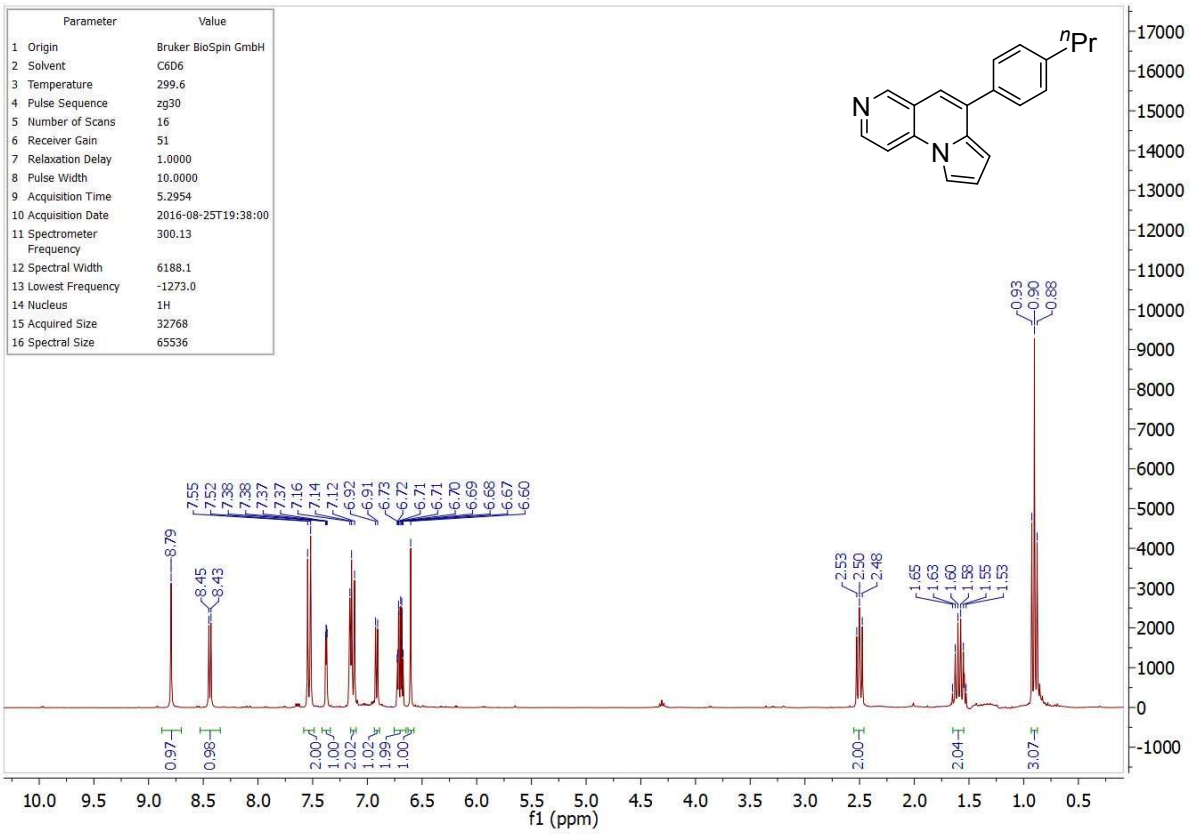



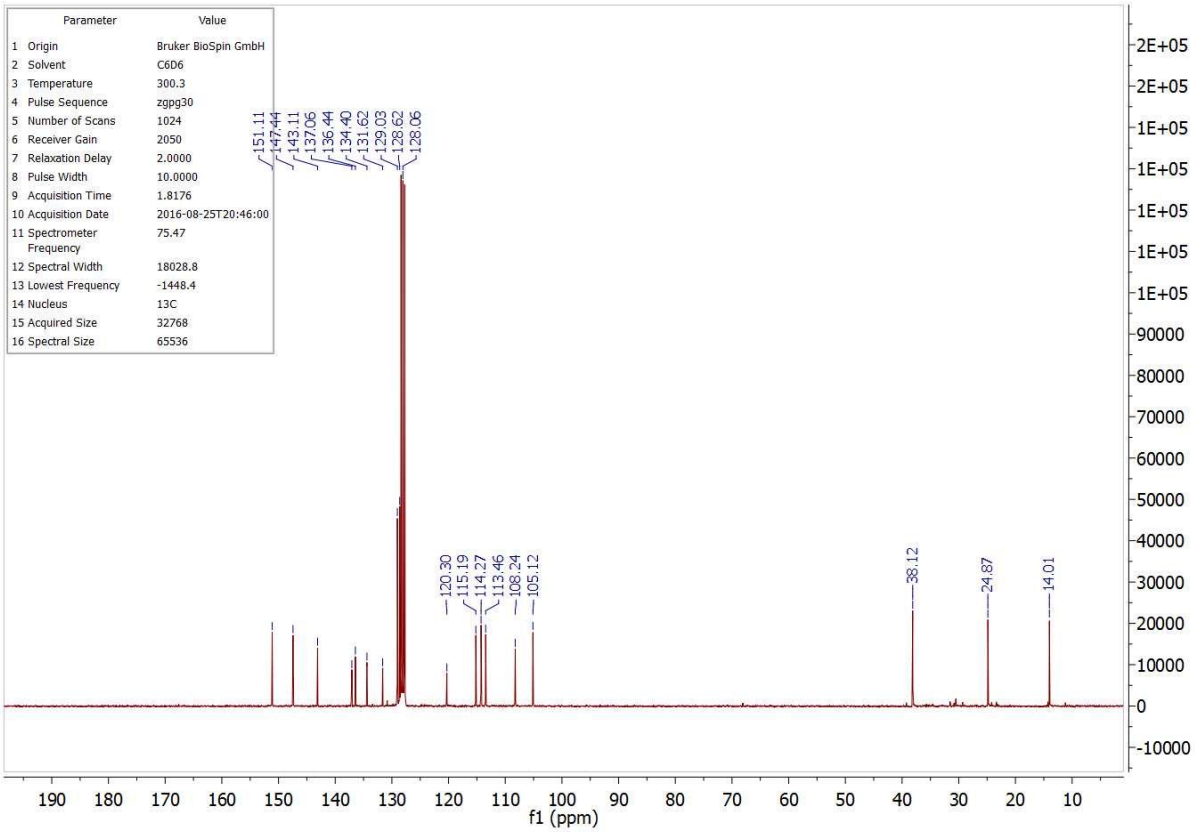
## 6-(4-*tert*-Butylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5h



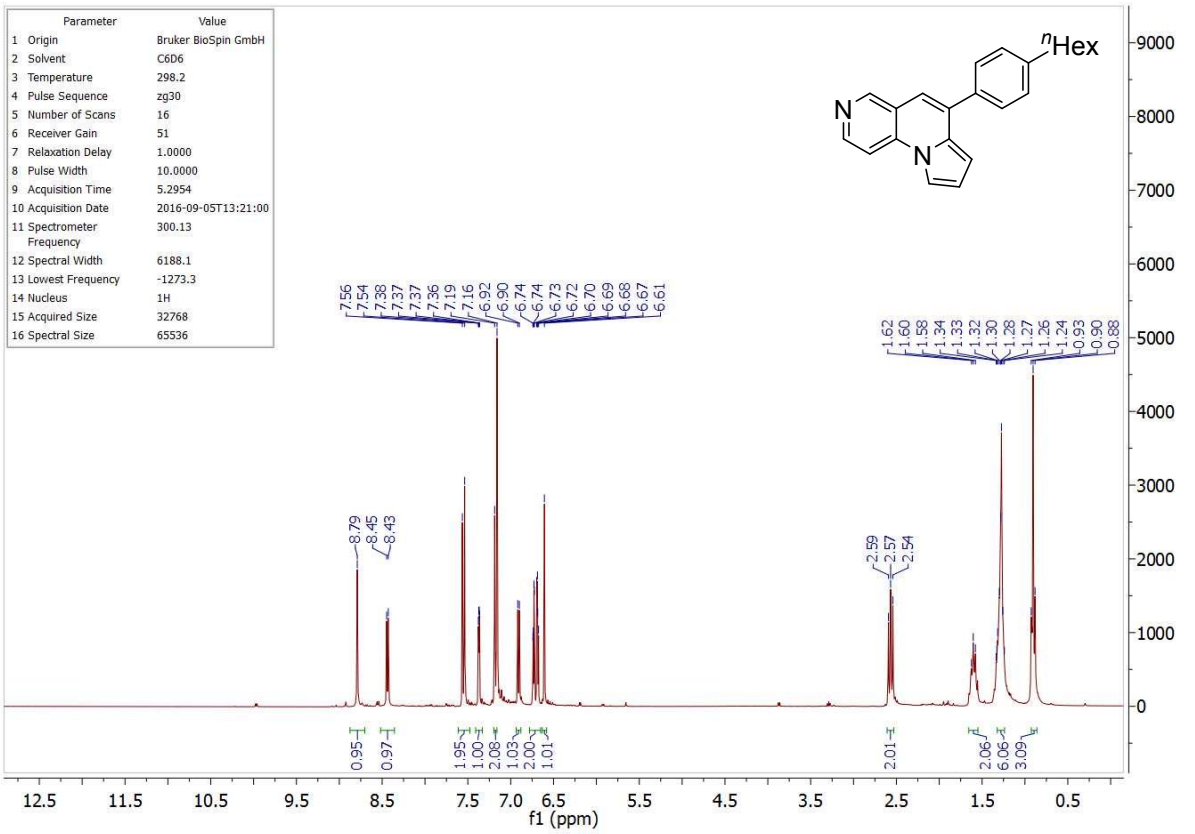



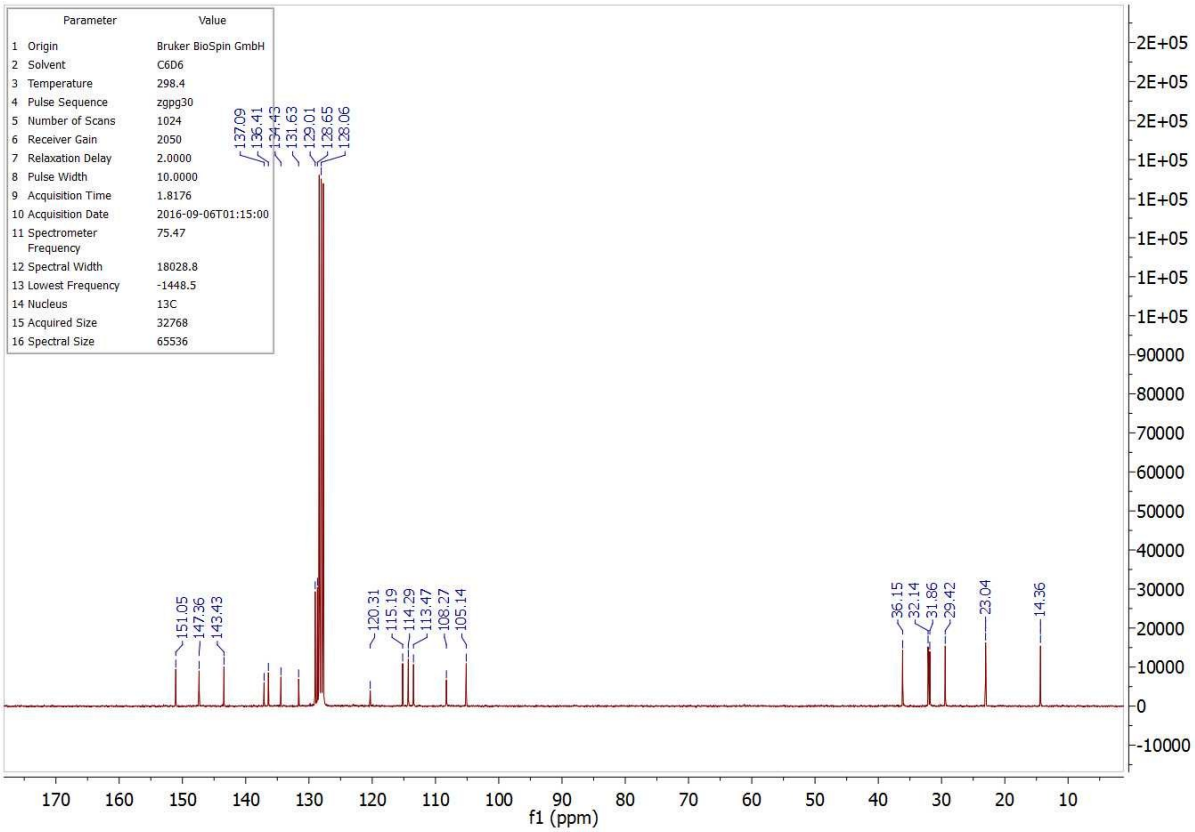
## 6-(4-*n*-Propylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5i



## 6-(4-*n*-Hexylphenyl)pyrrolo[1,2-*a*][1,6]naphthyridine 5j



## 6-(Thiophen-3-yl)pyrrolo[1,2-*a*][1,6]naphthyridine 5k